

---

## Supplementary information

---

# Aromatic ring-opening metathesis

---

In the format provided by the  
authors and unedited

# Supplementary Information

## Aromatic Ring-Opening Metathesis

Valeriia Hutskalova, Christof Sparr\*

Department of Chemistry, University of Basel

Email: christof.sparr@unibas.ch

### Supplementary Methods

#### Table of Contents

|                                                                                              |     |
|----------------------------------------------------------------------------------------------|-----|
| General Information .....                                                                    | 1   |
| Preparation of Substrates .....                                                              | 2   |
| Aromatic Ring-Opening Metathesis .....                                                       | 57  |
| Aromatic Ring Opening (ArROM) – Ring-Closing Metathesis (RCM) Cascade: Tetraphene .....      | 58  |
| ArROM with Twofold RCM: Naphthalene .....                                                    | 59  |
| ArROM with Twofold RCM: Benzofused Five-Membered Heterocycles .....                          | 60  |
| Bidirectional Twofold ArROM – RCM to Polycyclic Aromatic Hydrocarbons (PAHs) .....           | 62  |
| Equilibration of Indoles by ArROM – RCM .....                                                | 65  |
| ArROM – Twofold RCM for <i>N</i> -Aryl Indoles .....                                         | 77  |
| Atroposelective Aromatic Ring-Opening Metathesis – RCM Cascade .....                         | 84  |
| Atroposelective Aromatic Ring-Opening Metathesis – Twofold RCM .....                         | 95  |
| Atroposelective Indole Ring-Opening Metathesis .....                                         | 103 |
| Determination of the Rotational Barriers .....                                               | 108 |
| Computational Studies .....                                                                  | 111 |
| Gibbs Free Energy Differences of the Selected Pairs of Starting Materials and Products ..... | 111 |
| Comparison of Metathesis Catalysts .....                                                     | 113 |
| Visualization of Noncovalent interactions (NCI) in DFT Computed Metallacycles .....          | 115 |
| Cartesian Coordinates for All Optimized Geometries .....                                     | 117 |
| NMR Spectra .....                                                                            | 170 |
| HPLC Data .....                                                                              | 322 |
| X-Ray Data (Dr. Alessandro Prescimone) .....                                                 | 348 |
| Microcrystal Electron Diffraction (Dr. Alessandro Prescimone, Eldico) .....                  | 349 |
| Supplementary References .....                                                               | 350 |



## General Information

All reaction solvents and reagents were obtained from commercial suppliers and used without further purification unless stated otherwise. Solvents for extractions and chromatography were technical grade. Syringes were used to transfer air and moisture sensitive liquids and solutions. Analytical thin layer chromatography (Merck silica gel 60 F254 plates) was utilized for monitoring reactions and visualized by UV light (254 nm and 350 nm). Flash Chromatography was performed with SiliCycle silica gel 60 (230-400 Mesh) or otherwise stated stationary columns. Concentration *in vacuo* was performed by rotary evaporation to ~10 mbar at 40°C and drying at  $\sim 10^{-2}$  mbar at room temperature.

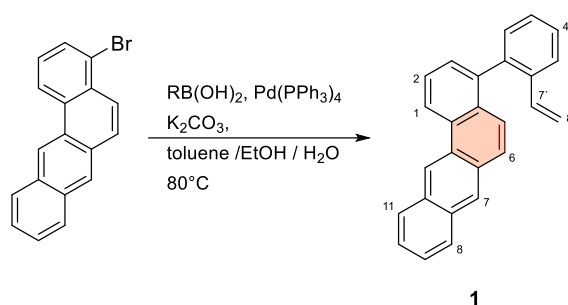
All metathesis reactions were performed using degassed and dried solvents in an argon-filled glovebox. Commercially available dry solvents were charged with molecular sieves (3Å) (predried at 180°C ( $\sim 10^{-2}$  mbar) for 24 h before use) and were degassed using the freeze–pump–thaw method. Solvent flasks were then transferred to an argon-filled glovebox and used within seven days of storage over molecular sieves.<sup>1</sup>

<sup>1</sup>H-NMR spectra were recorded on Bruker DPX 400 MHz or Bruker DRX 500 MHz spectrometers at 298 K in the indicated deuterated solvent supplied by *Cambridge Isotope Laboratories*. Chemical shifts ( $\delta$ ) are quoted in parts per million (ppm) and referenced to the residual solvent peak ( $\delta$  = 7.26 ppm for CDCl<sub>3</sub> and 2.50 ppm for (CD<sub>3</sub>)<sub>2</sub>SO). The multiplicities are reported in Hz as: s = singlet, br = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dm = doublet of multiplets, and ddm = doublet of doublet of multiplets. <sup>13</sup>C- and 2D-NMR spectra were recorded with <sup>1</sup>H-decoupling on Bruker DRX 500 MHz spectrometers at 298 K in the indicated deuterated solvent supplied by *Cambridge Isotope Laboratories*. Chemical shifts ( $\delta$ ) are quoted in parts per million (ppm) and referenced to the residual solvent peak ( $\delta$  = 77.16 ppm for CDCl<sub>3</sub> and 39.52 ppm for (CD<sub>3</sub>)<sub>2</sub>SO).

Melting points were measured on a Büchi B-565 melting point apparatus and are uncorrected. IR spectroscopy was measured on an ATR Varian Scimitar 800 FT-IR spectrometer and reported in cm<sup>-1</sup>. The intensities of the bands are reported as: w = weak, m = medium, s = strong. High-resolution mass spectrometry (HR-ESI) was recorded by Dr. Michael Pfeffer at the University of Basel on a *Bruker MaXis 4G QTOF* ESI mass spectrometer. Optical rotations were measured at 296 K on a Jasco P-2000 digital polarimeter with a path length of 10.0 cm, using the 589.3 nm sodium D-line and concentrations are reported in g/100 mL. UV/Vis spectra were measured in acetonitrile solution on a Jasco V-770 spectrometer with a 10 mm sample cell at 20°C.

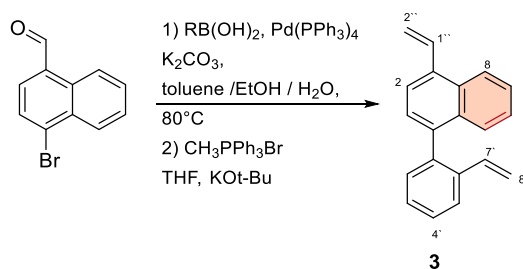
## Preparation of Substrates

### 4-(2-Vinylphenyl)tetraphene (**1**):



4-Bromotetraphene (92.2 mg, 300  $\mu\text{mol}$ , 1.00 eq.), (2-vinylphenyl)boronic acid (49.3 mg, 333  $\mu\text{mol}$ , 1.11 eq.),  $\text{Pd}(\text{PPh}_3)_4$  (17.3 mg, 15.0  $\mu\text{mol}$ , 5 mol%), and  $\text{K}_2\text{CO}_3$  (124 mg, 900  $\mu\text{mol}$ , 3.00 eq.) were weighed into a 10 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before a degassed mixture of toluene,  $\text{H}_2\text{O}$ , ethanol (2 : 2 : 1) (3.3 mL, 0.11  $\text{mol}\cdot\text{L}^{-1}$ ) was added. The resulting mixture was stirred at 80°C for 18 h, then cooled to room temperature, filtered through a thin layer of silica gel and  $\text{Na}_2\text{SO}_4$  using EtOAc (20 mL). The solvents were removed under reduced pressure and the residue was purified by the silica gel chromatography (cyclohexane/EtOAc 100:0 $\rightarrow$ 80:20) to give the desired product 4-(2-vinylphenyl)tetraphene as a white solid (85.5 mg, 259  $\mu\text{mol}$ , 86%, m.p. 169.6 – 170.0°C):  $R_f$  0.24 (cyclohexane/ $\text{CH}_2\text{Cl}_2$  9:1);  $\nu_{\text{max}}$ (neat): 3052w, 3010w, 2916w, 1931w, 1829w, 1624w, 1548w, 1262w, 1210w, 1158w, 1075w, 993m, 913m, 872m, 838w, 755s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.25 (1H, s, C12H), 8.91 (1H, d,  $^3J$  8.4 Hz, C1H), 8.34 (1H, s, C7H), 8.19 – 8.13 (1H, m, C11H), 8.04 (1H, dd,  $^3J$  6.3,  $^4J$  2.6 Hz, C8H), 7.80 – 7.76 (1H, m, C3'H), 7.73 (1H, dd,  $^3J$  8.4,  $^3J$  7.2 Hz, C2H), 7.68 (1H, d,  $^3J$  9.3 Hz, C6H), 7.61 – 7.53 (2H, m, C9H, C10H), 7.50 – 7.44 (2H, m, C3H, C4'H), 7.40 (1H, td,  $^3J$  7.4,  $^4J$  1.4 Hz, C5'H), 7.33 (1H, dd,  $^3J$  7.4,  $^4J$  1.1 Hz, C6'H), 7.31 (1H, d,  $^3J$  9.3 Hz, C5H), 6.39 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7'H), 5.69 (1H, dd,  $^3J$  17.5,  $^2J$  1.2 Hz, C8'H), 5.03 (1H, dd,  $^3J$  11.0,  $^2J$  1.2 Hz, C8'H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 139.71 (C1'), 139.65 (C4), 136.9 (C2'), 135.3 (C7'), 132.21 (C11a), 132.17 (C7a), 131.1 (C6'), 130.8 (C12b), 130.6 (C4a), 130.5 (C6a), 129.1 (C12a), 129.0 (C3), 128.7 (C11), 128.0 (C4'), 127.9 (C8), 127.7 (C5'), 127.5 (C6), 126.9 (C7), 126.3 (C2), 126.0 (C9), 125.9 (C10), 125.0 (C3'), 125.0 (C5), 122.6 (C1), 122.0 (C12), 114.9 (C8'); ESI-MS:  $m/z$  calcd. for  $\text{C}_{26}\text{H}_{18}\text{Ag}$  437.0454 found 437.0450 [ $\text{M}+\text{Ag}^+$ ].

### 1-Vinyl-4-(2-vinylphenyl)naphthalene (3):

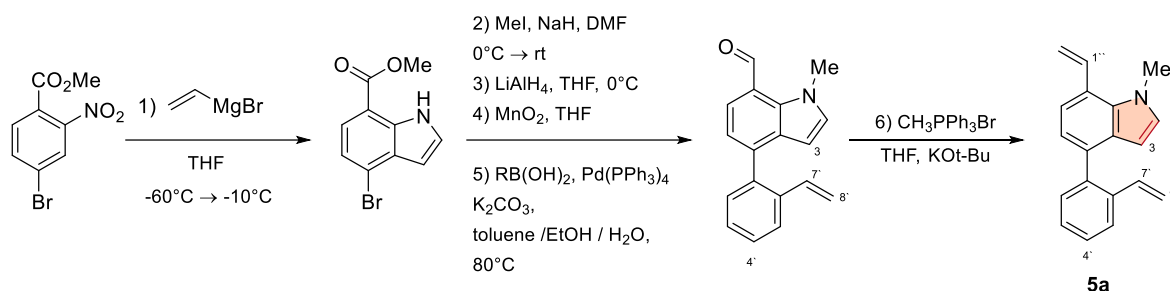


**Step 1:** 4-Bromo-1-naphthaldehyde (188 mg, 800  $\mu\text{mol}$ , 1.00 eq.), (2-vinylphenyl)boronic acid (131 mg, 888  $\mu\text{mol}$ , 1.11 eq.),  $\text{Pd}(\text{PPh}_3)_4$  (46.2 mg, 40.0  $\mu\text{mol}$ , 5 mol%), and  $\text{K}_2\text{CO}_3$  (332 mg, 2.40 mmol, 3.00 eq.) were weighed into a 10 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before a degassed mixture of toluene,  $\text{H}_2\text{O}$ , ethanol (2 : 2 : 1) (6.7 mL, 0.12  $\text{mol}\cdot\text{L}^{-1}$ ) was added. The resulting mixture was stirred at  $80^\circ\text{C}$  for 18 h, then cooled to room temperature, filtered through a thin layer of silica gel and  $\text{Na}_2\text{SO}_4$  using EtOAc (20 mL). The solvents were removed under reduced pressure and the residue was purified by the silica gel chromatography (cyclohexane/EtOAc 100:0 $\rightarrow$ 80:20) to give the desired 4-(2-vinylphenyl)-1-naphthaldehyde as orange oil (160 mg, 619  $\mu\text{mol}$ , 77%):  $R_f$  0.68 (cyclohexane/EtOAc 5:1).

**Step 2:** To a suspension of methyltriphenylphosphonium-bromide (310 mg, 867  $\mu\text{mol}$ , 1.40 eq.) in THF (6.2 mL) at  $0^\circ\text{C}$  was added dry  $\text{KOt-Bu}$  (111 mg, 991  $\mu\text{mol}$ , 1.60 eq.) under argon. After stirring the resulting suspension for 50 min at  $0^\circ\text{C}$ , a solution of 4-(2-vinylphenyl)-1-naphthaldehyde (160 mg, 619  $\mu\text{mol}$ , 1.00 eq.) in THF (6.2 mL) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 18 h. Water was then added and the mixture was extracted with EtOAc (3 $\times$ 30 mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0 $\rightarrow$ 80:20) to give the desired product 1-vinyl-4-(2-vinylphenyl)naphthalene **3** as yellow oil (97.0 mg, 378  $\mu\text{mol}$ , 61%):  $R_f$  0.78 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}(\text{neat})$ : 3061w, 3023w, 2924w, 1829w, 1716w, 1688w, 1626w, 1578w, 1512w, 1424w, 1378w, 1264w, 1056w, 989w, 915m, 847m, 764m;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.18 (1H, d,  $^3J$  8.5 Hz, C8H), 7.79 – 7.73 (1H, m, C3'H), 7.71 – 7.64 (1H, m, C2H), 7.58 – 7.48 (3H, m, C1''H, C5H, 7H), 7.46 – 7.42 (1H, m, C4'H), 7.40 – 7.34 (2H, m, C6H, C5'H), 7.33 (1H, d,  $^3J$  7.3 Hz, C3H), 7.27 (1HM ddd,  $^3J$  7.5,  $^4J$  1.4,  $^5J$  0.4 Hz, C6'H), 6.33 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7'H), 5.85 (1H, dd,  $^3J$  17.3,  $^2J$  1.5 Hz, C2''H), 5.66 (1H, dd,  $^3J$  17.5,  $^2J$  1.2 Hz, C8'H), 5.52 (1H, dd,  $^3J$  10.9,  $^2J$  1.5 Hz, C2''H), 5.00 (1H, dd,  $^3J$  11.0,  $^2J$  1.2 Hz, C8'H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 139.5 (C1'), 138.9 (C4), 136.9 (C2'), 135.42 (C1), 135.37 (C7'), 134.6 (C1''), 132.5 (C4a), 131.2 (C8a), 131.1 (C6'), 128.0 (C4'), 127.6 (C5'), 127.5 (C3), 127.2 (C5), 126.1 (C7), 126.0 (C6), 124.9 (C3'), 124.1 (C8), 123.2 (C2), 117.3 (C2''), 114.6 (C8'); ESI-MS:  $m/z$  calcd. for  $\text{C}_{20}\text{H}_{16}\text{Ag}$  363.0297 found 363.0304 [ $\text{M}+\text{Ag}^+$ ].

**Note:** 1-Vinyl-4-(2-vinylphenyl)naphthalene **3** was used directly in the next step due to its polymerization upon storage at  $4^\circ\text{C}$ .

### 1-Methyl-7-vinyl-4-(2-vinylphenyl)-1H-indole (5a):



**Step 1:** According to a modified literature procedure:<sup>2</sup> Methyl 4-bromo-2-nitrobenzoate (1.66 g, 6.40 mmol, 1.00 eq.) was dissolved in dry THF (9.0 mL) and the resulting solution was cooled to  $-60^\circ\text{C}$  under argon atmosphere. Vinylmagnesium bromide solution in THF (17.9 mmol, 17.9 mL,  $1.0\text{ mol}\cdot\text{L}^{-1}$ , 2.80 eq.) was added dropwise at  $-60^\circ\text{C}$ . The reaction mixture was stirred at  $-60^\circ\text{C}$  for 1 h, then gradually warmed up to  $-10^\circ\text{C}$ . The reaction progress was checked by  $^1\text{H-NMR}$ . Upon the reaction completion, it was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  solution and extracted with EtOAc ( $3\times 50\text{ mL}$ ). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0 $\rightarrow$ 50:50) to give the desired methyl 4-bromo-1H-indole-7-carboxylate as a white solid (550 mg, 2.16 mmol, 34%). The spectral data were in accordance with those previously reported in the literature.<sup>2</sup>

**Step 2:** 4-Bromo-1H-indole-7-carboxylate (550 mg, 2.16 mmol, 1.00 eq.) was dissolved in dry DMF (8.0 mL). NaH (60% dispersion in mineral oil, 173 mg, 4.33 mmol, 2.00 eq.) was added portionwise at  $0^\circ\text{C}$  and the resulting solution was stirred at  $0^\circ\text{C}$  for 5 minutes before methyl iodide MeI (461 mg, 200  $\mu\text{L}$ , 3.25 mmol, 1.50 eq.) was added dropwise at this temperature. The reaction mixture was allowed to warm up to room temperature, then quenched with MeOH, diluted with water and extracted with EtOAc ( $3\times 60\text{ mL}$ ). The combined organic layer was washed with brine ( $3\times 100\text{ mL}$ ), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0 $\rightarrow$ 50:50) to give the desired methyl 4-bromo-1-methyl-1H-indole-7-carboxylate as a white solid (466 mg, 1.74 mmol, 80%).

**Steps 3 and 4:** To a solution of 4-bromo-1-methyl-1H-indole-7-carboxylate (466 mg, 1.74 mmol, 1.00 eq.) in dry THF (9.0 mL) was added  $\text{LiAlH}_4$  (79.2 mg, 2.09 mmol, 1.20 eq.) portionwise at  $0^\circ\text{C}$  under argon. The reaction mixture was stirred for 2 h allowing to warm up to room temperature (the reaction progress was controlled by  $^1\text{H-NMR}$ ), cooled to  $0^\circ\text{C}$ , quenched with  $\text{H}_2\text{O}$  (0.25 mL) and 10% NaOH solution (0.16 mL). The resulting mixture was diluted with EtOAc and filtered through a thin silica gel layer. Solvents were removed under reduced pressure and the crude product was used in the next step without any additional purification. The obtained (4-bromo-1H-indol-7-yl)methanol was dissolved in THF (20 mL) and  $\text{MnO}_2$  (1.81 g, 20.9 mmol, 12.0 eq.) was added portionwise. The reaction mixture was stirred for 18 hours at rt, filtered through celite (rinsing with EtOAc) and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0 $\rightarrow$ 60:40) to give the title compound as a white solid (287 mg, 1.21 mmol, 69% over two steps):  $R_f$  0.32 (cyclohexane/EtOAc 4:1).

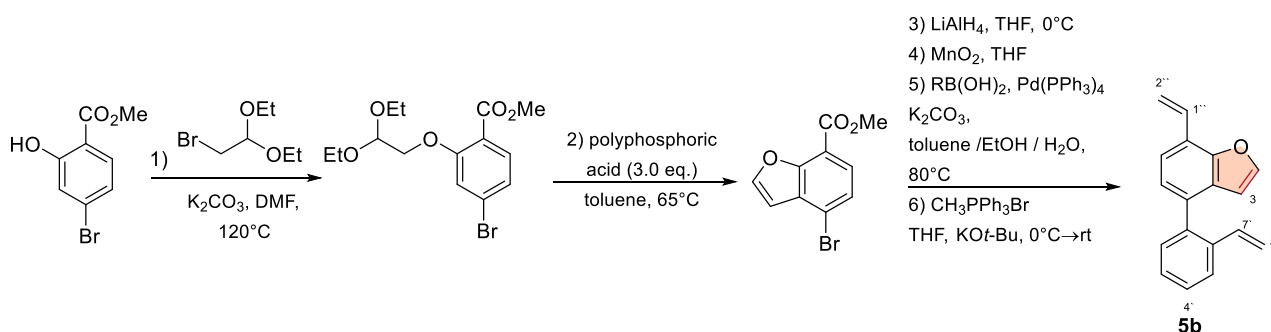
**Step 5:** 4-Bromo-1-methyl-1H-indole-7-carbaldehyde (187 mg, 785  $\mu\text{mol}$ , 1.00 eq.), (2-vinylphenyl)boronic acid (129 mg, 872  $\mu\text{mol}$ , 1.11 eq.),  $\text{Pd(PPh}_3)_4$  (45.4 mg, 39.3  $\mu\text{mol}$ , 5 mol%), and  $\text{K}_2\text{CO}_3$  (326 mg, 2.36 mmol, 3.00 eq.) were weighed into a 20 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before a degassed mixture of toluene,  $\text{H}_2\text{O}$ , ethanol (2 : 2 : 1) (6.5 mL,  $0.12\text{ mol}\cdot\text{L}^{-1}$ ) was added. The resulting mixture was stirred at  $80^\circ\text{C}$  for 18 h, then cooled to room temperature, filtered through a thin layer of silica gel and  $\text{Na}_2\text{SO}_4$  using EtOAc (20 mL). The solvents were removed under reduced pressure and the residue was purified by the silica gel chromatography (cyclohexane/EtOAc 100:0 $\rightarrow$ 60:40) to give the desired product 1-methyl-4-(2-vinylphenyl)-1H-indole-7-carbaldehyde as yellow oil (160 mg, 612  $\mu\text{mol}$ , 78%):  $R_f$  0.40 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$ (neat): 3059w, 2917w, 2850w, 2737w, 1886s, 1579s, 1520m, 1475w, 1394w, 1342w, 1317w, 1220m

1086m, 1032m, 791m;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.26 (1H, s, CHO), 7.76 (1H, d,  $^3J$  7.4 Hz, C6H), 7.75 – 7.70 (1H, m, C3'H), 7.45 – 7.40 (1H, m, C4'H), 7.39 – 7.33 (2H, m, C5'H, C6'H), 7.14 (1H, d,  $^3J$  7.4 Hz, C5H), 7.06 (1H, d,  $^3J$  3.2 Hz, C2H), 6.51 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7'H), 6.28 (1H, d,  $^3J$  3.2 Hz, C3H), 5.71 (1H, dd,  $^3J$  17.5,  $^2J$  1.2 Hz, C8'H), 5.10 (1H, dd,  $^3J$  11.0,  $^2J$  1.2 Hz, C8'H), 4.18 (3H, s, N-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 190.9 (CHO), 141.0 (C4), 138.8 (C1'), 136.1 (C2'), 135.5 (C7'), 133.8 (C7a), 132.6 (C2), 131.3 (C3a), 130.4 (C6), 130.3 (C6'), 128.2 (C4'), 127.6 (C5'), 125.4 (C3'), 122.2 (C7), 120.8 (C5), 114.8 (C8'), 102.7 (C3), 39.3 (N-CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{16}\text{NO}$  262.1126 found 262.1225 [ $\text{M}+\text{H}^+$ ].

**Step 6:** To a suspension of methyltriphenylphosphonium-bromide (329 mg, 920  $\mu\text{mol}$ , 2.00 eq.) in THF (4.6 mL) at 0°C was added dry KOt-Bu (119 mg, 1.06 mmol, 2.30 eq.) under argon. After stirring the resulting suspension for 50 min at 0°C, a solution of 1-methyl-4-(2-vinylphenyl)-1H-indole-7-carbaldehyde (120 mg, 460  $\mu\text{mol}$ , 1.00 eq.) in THF (4.6 mL) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 18 h. Water was then added and the mixture was extracted with EtOAc (3×30 mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by neutral alumina column chromatography (cyclohexane/EtOAc 100:0→70:30) to give the desired product 1-methyl-7-vinyl-4-(2-vinylphenyl)-1H-indole **5a** as yellow oil (80.0 mg, 308  $\mu\text{mol}$ , 67%);  $R_f$  0.70 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$ (neat): 3089w, 3060w, 2974w, 2918w, 1824w, 1702w, 1623w, 1593w, 1520w, 1472m, 1396w, 1290s, 1087m, 988m, 906s, 823s;  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  = 7.72 (1H, d,  $^3J$  7.8 Hz, C3'H), 7.65 – 7.55 (1H, m, C1''H), 7.40 – 7.35 (1H, m, C4'H), 7.35 – 7.31 (2H, m, C5'H, C6'H), 7.27 (1H, d,  $^3J$  7.4 Hz, C6H), 6.98 (1H, d,  $^3J$  3.2 Hz, C2H), 6.92 (1H, d,  $^3J$  7.4 Hz, C5H), 6.56 (1H, dd,  $^3J$  17.6,  $^3J$  11.0 Hz, C7'H), 6.12 (1H, d,  $^3J$  3.2 Hz, C3H), 5.75 – 5.63 (2H, m, C8'H, C2''H), 5.39 (1H, dd,  $^3J$  10.8,  $^2J$  1.6 Hz, C2''H), 5.06 (1H, dd,  $^2J$  11.0,  $^3J$  1.3 Hz, C8'H), 4.04 (3H, s, N-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  = 140.2 (C1'), 136.4 (C2'), 136.3 (C7'), 134.9 (C1''), 134.0 (C7a), 133.5 (C4), 131.4 (C2), 130.9 (C6'), 129.8 (C3a), 127.8 (C4'), 127.7 (C5'), 125.4 (C3'), 121.5 (C5), 120.9 (C6), 116.4 (C2''), 114.0 (C8'), 101.1 (C3), 37.7 (N-CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{17}\text{AgN}$  366.0406 found 366.0408 [ $\text{M}+\text{Ag}^+$ ].

**Note:** Decomposition of 1-methyl-7-vinyl-4-(2-vinylphenyl)-1H-indole **5a** was observed during silica gel chromatography, therefore neutral alumina has to be used for purification.

## 7-Vinyl-4-(2-vinylphenyl)benzofuran (5b):



**Steps 1 and 2:** A mixture of methyl 4-bromo-2-hydroxybenzoate (809 mg, 3.50 mmol, 1.00 eq.), 2-bromo-1,1-diethoxyethane (1.04 g, 5.25 mmol, 1.50 eq.), dry  $\text{K}_2\text{CO}_3$  (1.21 g, 8.75 mmol, 2.50 eq.) in dry DMF (7.0 mL) was stirred at  $120^\circ\text{C}$  for 18 h under argon. The reaction mixture was then cooled down to room temperature, diluted with water, extracted with EtOAc ( $3 \times 50$  mL). The combined organic layer was then washed with brine ( $3 \times 100$  mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The obtained residue (1.57 g) was then introduced to the next step without additional purification. According to a modified literature procedure:<sup>3</sup> Crude methyl 4-bromo-2-(2,2-diethoxyethoxy)benzoate (1.57 g) in 8.8 mL of toluene was added to the mixture of polyphosphoric acid (4.59 g, 13.6 mmol) in 38 mL of toluene that was stirred at  $65^\circ\text{C}$  for 30 min. The obtained reaction mixture was stirred at  $65^\circ\text{C}$  for 4 h, then cooled down to room temperature, diluted with water and extracted with EtOAc ( $3 \times 100$  mL). The combined organic layer was washed with sodium bicarbonate solution, brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0  $\rightarrow$  70:30) to give methyl 4-bromobenzofuran-7-carboxylate as yellow solid (240 mg, 941  $\mu\text{mol}$ , 27% over two steps):  $R_f$  0.40 (cyclohexane/EtOAc 4:1).

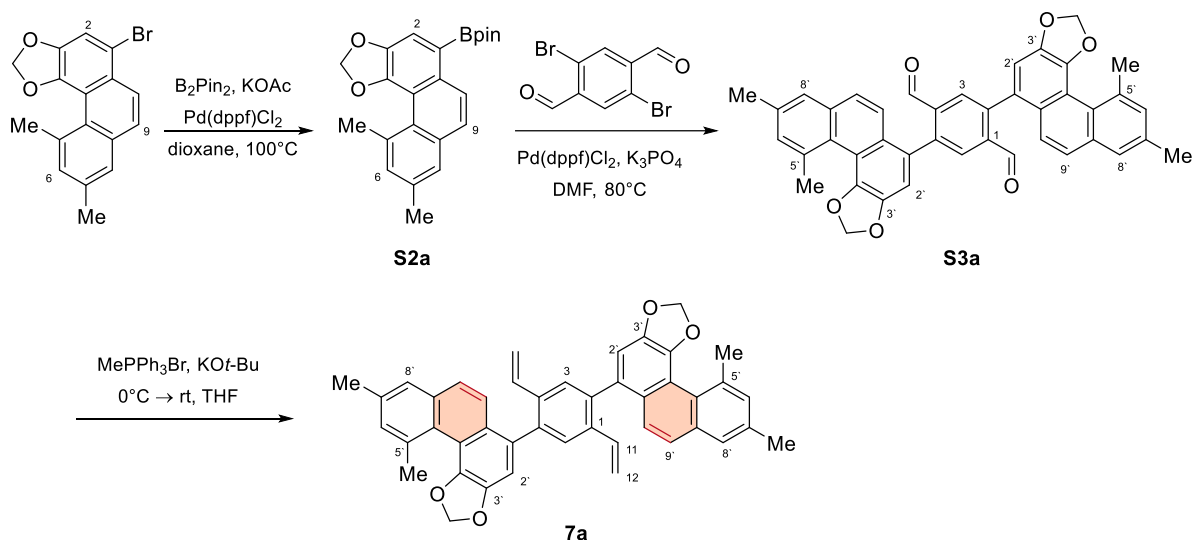
**Steps 3 and 4:** To a solution of 4-bromobenzofuran-7-carboxylate (267 mg, 1.05 mmol, 1.00 eq.) in dry THF (6.6 mL) was added  $\text{LiAlH}_4$  (47.7 mg, 1.26 mmol, 1.20 eq.) portionwise at  $0^\circ\text{C}$  under argon. The reaction mixture was stirred for 2 h allowing to warm up (the reaction progress was controlled by  $^1\text{H-NMR}$ ), cooled to  $0^\circ\text{C}$ , quenched with  $\text{H}_2\text{O}$  (0.10 mL) and 10% NaOH solution (0.15 mL). The resulting mixture was diluted with EtOAc and filtered through a thin silica gel layer. Solvents were removed under reduced pressure and the crude product was used in the next step without any additional purification. The obtained (4-bromobenzofuran-7-yl)methanol was dissolved in THF (12 mL) and  $\text{MnO}_2$  (1.09 g, 12.6 mmol, 12.0 eq.) was added portionwise. The reaction mixture was stirred for 18 h at rt, filtered through celite (rinsing with EtOAc) and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0  $\rightarrow$  60:40) to give the title compound as a white solid (73.0 mg, 324  $\mu\text{mol}$ , 31% over two steps):  $R_f$  0.46 (cyclohexane/EtOAc 4:1).

**Step 5:** 4-Bromobenzofuran-7-carbaldehyde (74.3 mg, 330  $\mu\text{mol}$ , 1.00 eq.), (2-vinylphenyl)boronic acid (54.2 mg, 366  $\mu\text{mol}$ , 1.11 eq.),  $\text{Pd(PPh}_3)_4$  (19.1 mg, 16.5  $\mu\text{mol}$ , 5 mol%), and  $\text{K}_2\text{CO}_3$  (137 mg, 99.0  $\mu\text{mol}$ , 3.00 eq.) were weighed into a 10 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before a degassed mixture of toluene,  $\text{H}_2\text{O}$ , ethanol (2 : 2 : 1) (2.8 mL, 0.12  $\text{mol} \cdot \text{L}^{-1}$ ) was added. The resulting mixture was stirred at  $80^\circ\text{C}$  for 18 h, then cooled to room temperature, filtered through a thin layer of silica gel and  $\text{Na}_2\text{SO}_4$  using EtOAc (20 mL). The solvents were removed under reduced pressure and the residue was purified by the silica gel chromatography (cyclohexane/EtOAc 100:0  $\rightarrow$  60:40) to give the desired product 4-(2-vinylphenyl)benzofuran-7-carbaldehyde **S1** as yellow oil (56.0 mg, 226  $\mu\text{mol}$ , 68%):  $R_f$  0.40 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}(\text{neat})$ : 3149w, 3060w, 2920w, 2850w, 2730w, 1688s, 1608s, 1538m, 1474w, 1410w, 1375m, 1252s, 1204m, 1135m, 1024m, 916w, 828w, 791w, 741w;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.5 (1H, s, CHO), 7.87 (1H, d,  $^3J$  7.7 Hz, C6H), 7.77 (1H, d,  $^3J$  2.2 Hz, C2H), 7.76 – 7.70 (1H, m, C3'H), 7.48 – 7.42 (1H, m, C4'H), 7.39 (1H, td,  $^3J$  7.4,  $^4J$  1.3 Hz, C5'H), 7.36 – 7.31 (2H, m, C6'H, C5H), 6.64 (1H, d,  $^3J$  2.2 Hz, C3H), 6.51 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7'H), 5.74 (1H, dd,  $^3J$  17.5,  $^2J$  1.1 Hz, C8'H), 5.17 (1H, dd,  $^3J$  11.0,  $^2J$  1.1 Hz, C8'H);  $^{13}\text{C NMR}$

(126 MHz, CDCl<sub>3</sub>)  $\delta$  = 188.8 (CHO), 153.8 (C7a), 146.5 (C2), 141.2 (C4), 137.6 (C1'), 136.1 (C2'), 135.2 (C7'), 130.2 (C6'), 129.1 (C3a), 128.7 (C4'), 127.9 (C5'), 126.3 (C6), 125.9 (C3'), 124.8 (C5), 120.4 (C7), 115.6 (C8'), 106.7 (C3); ESI-MS:  $m/z$  calcd. for C<sub>17</sub>H<sub>12</sub>NaO<sub>2</sub> 271.0730 found 271.0734 [M+Na<sup>+</sup>].

**Step 6:** To a suspension of methyltriphenylphosphonium-bromide (161 mg, 451  $\mu$ mol, 2.00 eq.) in THF (2.3 mL) at 0°C was added dry KO<sup>t</sup>-Bu (58.2 mg, 519  $\mu$ mol, 2.30 eq.) under argon. After stirring the resulting suspension for 50 min at 0°C, a solution of 4-(2-vinylphenyl)benzofuran-7-carbaldehyde **S1** (56 mg, 226  $\mu$ mol, 1.00 eq.) in THF (2.3 mL) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 18 h. Water was then added and the mixture was extracted with EtOAc (3×30 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was purified by neutral alumina column chromatography (cyclohexane/EtOAc 100:0→70:30) to give the desired product 7-vinyl-4-(2-vinylphenyl)benzofuran **5b** as yellow oil (44.0 mg, 179  $\mu$ mol, 79%);  $R_f$  0.70 (cyclohexane/EtOAc 5:1); <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 7.78 – 7.71 (1H, m, C3'H), 7.70 (1H, d,  $J$  2.2 Hz, C2H), 7.46 – 7.29 (4H, m, C6H, C4'H, C5'H, C6'H), 7.14 (1H, d, <sup>3</sup> $J$  7.3 Hz, C5H), 7.04 (1H, dd, <sup>3</sup> $J$  17.8, <sup>3</sup> $J$  11.3 Hz, C1''H), 6.68 – 6.52 (2H, m, C3H, C7'H), 6.26 (1H, dd, <sup>3</sup> $J$  17.8, <sup>2</sup> $J$  1.3 Hz, C2''H), 5.73 (1H, dd, <sup>3</sup> $J$  17.5, <sup>2</sup> $J$  1.2 Hz, C8'H), 5.54 (1H, dd, <sup>3</sup> $J$  11.3, <sup>2</sup> $J$  1.3 Hz, C2''H), 5.12 (1H, dd, <sup>3</sup> $J$  11.0, <sup>2</sup> $J$  1.2 Hz, C8'H); <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 152.6 (C7a), 145.5 (C2), 138.9 (C1'), 136.4 (C2'), 136.0 (C7'), 134.0 (C4), 131.8 (C1''), 130.8 (C6'), 128.2 (C3a), 128.0 (C5'), 125.8 (C3'), 124.9 (C5), 123.2 (C6), 121.7 (C7), 117.5 (C2''), 114.8 (C8'), 106.9 (C3); ESI-MS:  $m/z$  calcd. for C<sub>8</sub>H<sub>15</sub>O 247.1117 found 247.1115 [M+H<sup>+</sup>].

### 5,5'-(2,5-Divinyl-1,4-phenylene)bis(9,11-dimethylphenanthro[3,4-d][1,3]dioxole) (7a):



**Step 1:** 5-Bromo-9,11-dimethylphenanthro[3,4-d][1,3]dioxole (180 mg, 547  $\mu$ mol, 1.00 eq.), bis(pinacolato)diboron (153 mg, 600  $\mu$ mol, 1.10 eq.), dry KOAc (161 mg, 1.64 mmol, 3.00 eq.),  $Pd(dppf)_2Cl_2$  (40 mg, 54.7  $\mu$ mol, 10 mol%) were weighed in a 10 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before dioxane (3.4 mL) was added. The reaction mixture was stirred at  $100^\circ C$  for 18 h under argon, cooled down to room temperature, filtered through a thin silica gel layer (using EtOAc to wash the filter bed). The solvents were removed under reduced pressure and crude product was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0 $\rightarrow$ 60:40) to give the desired product **S2a** as a colorless oil (120 mg, 319  $\mu$ mol, 58%):  $R_f$  0.67 (cyclohexane/EtOAc 5:1);  $\nu_{max}$ (neat): 2977w, 2932w, 2874w, 1609w, 1528w, 1477w, 1446w, 1387s, 1343m, 1316w, 1272s, 1141s, 1103w, 1043m, 945w, 859m, 740w, 694w;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 8.50 (1H, d,  $^3J$  9.1 Hz, C10H), 7.75 (1H, s, C2H), 7.45 – 7.34 (3H, m, C8H, C9H), 7.27 (1H, s, C6H), 6.12 (2H, s, OCH<sub>2</sub>O), 2.66 (3H, s, C5-CH<sub>3</sub>), 2.49 (3H, s, C7-CH<sub>3</sub>), 1.42 (12H, s, 4 $\times$ CH<sub>3</sub>, BPin);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 145.8 (C4), 144.6 (C3), 136.33 (C5), 136.26 (C7), 135.4 (C10a), 133.5 (C8a), 131.2 (C6), 126.7 (C10), 125.9 (C9), 125.5 (C4b), 124.9 (C8), 116.5 (C2), 116.4 (C4a), 100.3 (OCH<sub>2</sub>O), 83.9 (–C(CH<sub>3</sub>)<sub>2</sub>–, BPin), 25.1 (–C(CH<sub>3</sub>)<sub>2</sub>–, BPin), 23.8 (C5-CH<sub>3</sub>), 21.3 (C7-CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $C_{23}H_{26}BO_4$  377.1923 found 377.1913 [ $M+H^+$ ].

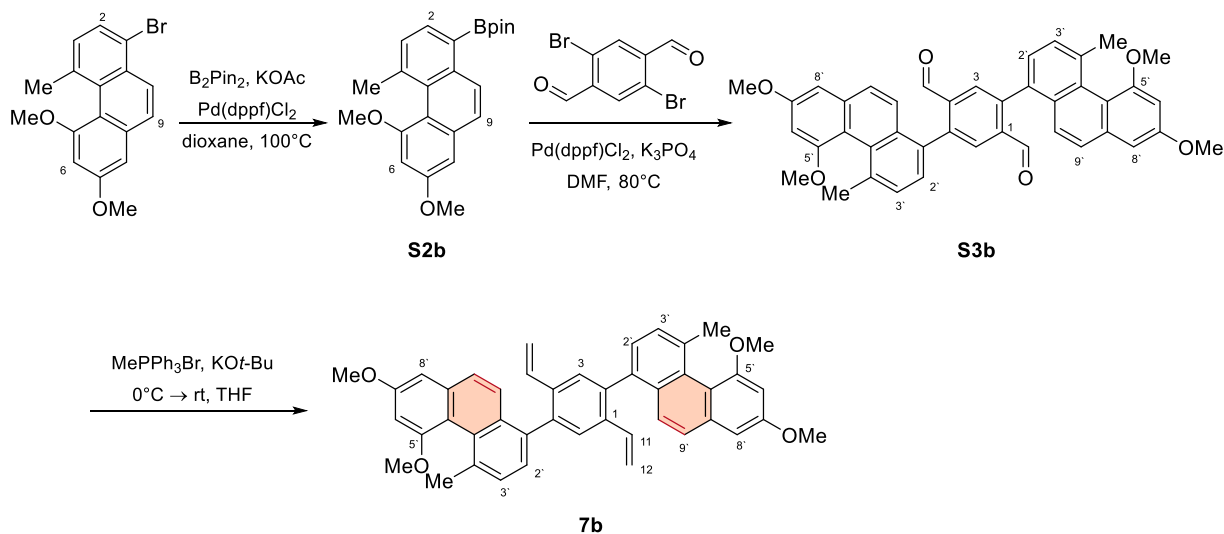
**Step 2:** 2-(9,11-Dimethylphenanthro[3,4-d][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **S2a** (155 mg, 411  $\mu$ mol, 3.00 eq.), 2,5-dibromoterephthalaldehyde (40.0 mg, 137  $\mu$ mol, 1.00 eq.),  $K_3PO_4$  (116 mg, 548  $\mu$ mol, 4.00 eq.),  $Pd(dppf)_2Cl_2$  (15.8 mg, 13.7  $\mu$ mol, 10 mol%) were weighed in a 10 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before dry DMF (2.2 mL) was added. The reaction mixture was stirred at  $100^\circ C$  for 18 h under argon, cooled down to room temperature and diluted with water. Extraction with EtOAc (3 $\times$ 15 mL) was performed and the combined organic layer was washed with brine (3 $\times$ 20 mL), dried over anhydrous  $Na_2SO_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0 $\rightarrow$ 70:30) to give the desired product **S3a** as an orange solid (32.0 mg, 50.7  $\mu$ mol, 37%, m.p.  $250 - 252^\circ C$  (decomposition)):  $R_f$  0.35 (cyclohexane/EtOAc 5:1);  $\nu_{max}$ (neat): 2919m, 2852m, 1690s, 1590m, 1443s, 1392s, 1271s, 1202w, 1150w, 1102m, 1041m, 943w, 857m, 802w, 735w, 619w;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 9.82 (1H, s, CHO), 9.82 (1H, s, CHO), 8.19 (2H, s, C3H, C6H), 7.45 – 7.33 (6H, m, C6'H, C8'H, C9'H), 7.32 (1H, s, C2'), 7.26 (1H, s, C2'H), 7.22 (1H, d,  $^3J$  9.1 Hz, C10'H), 7.14 (1H, d,  $^3J$  9.1 Hz, C10'H), 6.36 – 6.20 (4H, m, OCH<sub>2</sub>O), 2.77 (6H, s, C5'-CH<sub>3</sub>), 2.53 (3H, s, C7'-CH<sub>3</sub>), 2.52 (3H, s, C7'-CH<sub>3</sub>);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 191.6 (CHO), 145.1 (C3'), 143.93 (C4'), 143.91 (C4'), 143.8 (C1, C4), 138.28 (C2, C5), 138.25 (C2, C5), 137.16 (C7'), 137.15 (C7'), 136.82 (C5'), 136.80 (C5'), 133.64 (C8a'), 133.62 (C8a'), 132.17 (C6'), 132.15 (C6'), 131.22 (C3, C6), 131.20 (C3, C6), 128.7 (C10a'), 128.6 (C10a'), 127.6 (C1'), 126.9 (C9'), 126.8 (C9'), 125.30 (C8'), 125.27 (C8'), 125.20 (C4b'), 125.18



(C4b'), 123.5 (C10'), 123.4 (C10'), 116.7 (C4a'), 111.2 (C2'), 111.1 (C2'), 100.8 (OCH<sub>2</sub>O), 24.0 (C5'-CH<sub>3</sub>), 21.3 (C7'-CH<sub>3</sub>).

**Step 3:** To a suspension of methyltriphenylphosphonium-bromide (78.8 mg, 221  $\mu$ mol, 4.50 eq.) in THF (1.0 mL) at 0°C was added dry KOt-Bu (28.6 mg, 255  $\mu$ mol, 5.20 eq.) under argon. The resulting suspension was stirred for 40 min at 0°C and a solution of 2,5-bis(9,11-dimethylphenanthro[3,4-d][1,3]dioxol-5-yl)terephthalaldehyde **S3a** (30.9 mg, 49.0  $\mu$ mol, 1.00 eq.) in THF (1.0 mL) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 18 h. Water was then added and the mixture was extracted with EtOAc (3 $\times$ 15 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0 $\rightarrow$ 70:30) to give the desired product **7a** as a white solid (9.00 mg, 14.4  $\mu$ mol, 29%, m.p. 250 – 253°C (decomposition)): R<sub>f</sub> 0.59 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$ (neat): 3080w, 2924w, 2867w, 1735w, 1694w, 1590m, 1476m, 1449s, 1426s, 1270s, 1205w, 1099m, 1042s, 990w, 945m, 909m, 856m, 804m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.69 (1H, s, C3H, C6H), 7.68 (1H, s, C3H, C6H), 7.41 (2H, d, <sup>3</sup>J 8.6 Hz, C8'H), 7.37 – 7.26 (7H, m, 1 $\times$ C2'H, C6'H, C9'H, C10'H), 7.22 (1H, s, C2'H), 6.45 (2H, dd, <sup>3</sup>J 17.5, <sup>3</sup>J 11.1 Hz, C11H), 6.28 – 6.16 (4H, m, OCH<sub>2</sub>O), 5.64 (2H, d, <sup>3</sup>J 17.5 Hz, C12H), 5.02 (2H, d, <sup>3</sup>J 11.1 Hz, C12H), 2.78 (6H, s, C5'-CH<sub>3</sub>), 2.52 (3H, s, C7'-CH<sub>3</sub>), 2.51 (3H, s, C7'-CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  144.9 (C3'), 142.8 (C4'), 139.4 (C2, C5), 136.7 (C5', C7'), 136.4 (C1, C4), 136.3 (C1, C4), 134.8 (C11), 134.7 (C11), 133.84 (C8a'), 133.8 (C8a'), 132.38 (C1'), 132.36 (C1'), 131.63 (C4b'), 131.6 (C4b'), 128.2 (C10a'), 127.9 (C3, C6), 125.6 (C6'/C9'/C10'), 125.5 (C6'/C9'/C10'), 125.4 (C6'/C9'/C10'), 125.11 (C8'), 125.08 (C8'), 124.89, 124.86, 116.52 (C4a'), 116.50 (C4a'), 115.1 (C12), 115.0 (C12), 110.9 (C2'), 100.4 (OCH<sub>2</sub>O), 24.0 (C5'-CH<sub>3</sub>), 21.3 (C7'-CH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>44</sub>H<sub>35</sub>O<sub>4</sub> 627.2530 found 627.2517 [M+H<sup>+</sup>].

## 8,8'-(2,5-Divinyl-1,4-phenylene)bis(2,4-dimethoxy-5-methylphenanthrene) (7b):



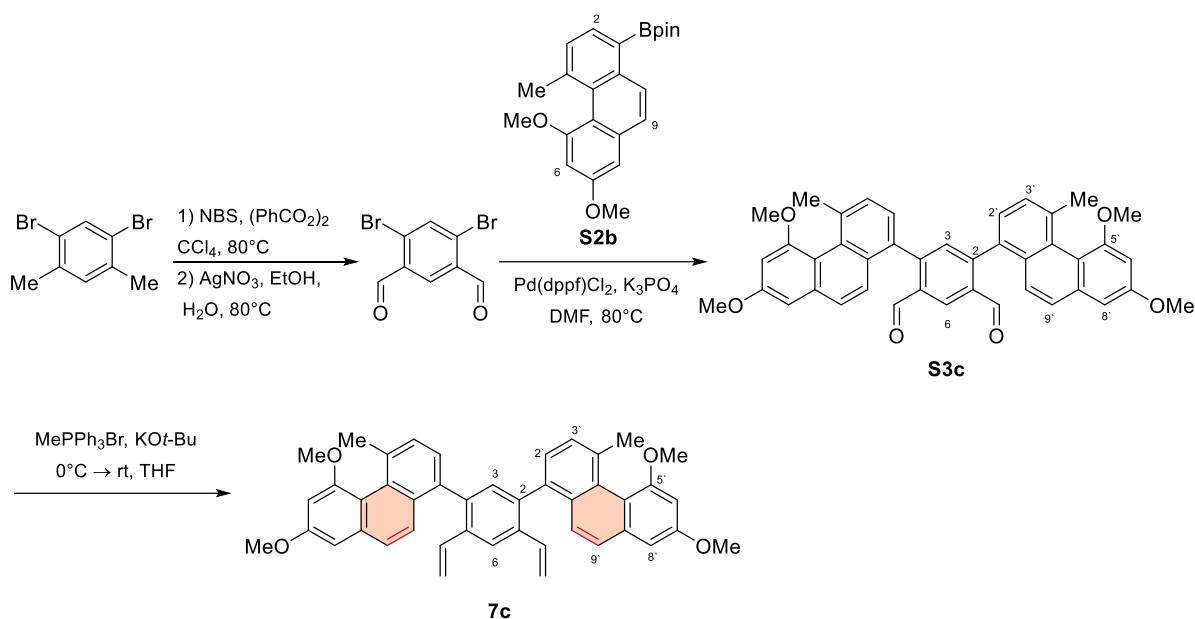
**Step 1:** 1-Bromo-5,7-dimethoxy-4-methylphenanthrene (435 mg, 1.31 mmol, 1.00 eq.), bis(pinacolato)diboron (400 mg, 1.58 mmol, 1.20eq.), dry KOAc (387 mg, 3.94 mmol, 3.00 eq.),  $Pd(dppf)_2Cl_2$  (96.1 mg, 13.1  $\mu mol$ , 10 mol%) were weighed in a 10 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before dry dioxane (7.2 mL) was added. The reaction mixture was stirred at  $100^\circ C$  for 18 h under argon, cooled down to room temperature, filtered through a thin silica gel layer (using EtOAc to wash the filter bed). The solvents were removed under reduced pressure and crude product was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0→60:40) to give the desired product **S2b** as a colorless oil (300 mg, 793  $\mu mol$ , 60%);  $R_f$  0.47 (cyclohexane/EtOAc 5:1);  $\nu_{max}(neat)$ : 2977w, 2933w, 2823w, 1602s, 1526m, 1453m, 1341s, 1286s, 1236w, 1218m, 1146s, 1065s, 1021w, 963w, 908w, 838w, 731w;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 8.54 (1H, d,  $^3J$  8.9 Hz, C10H), 7.97 (1H, d,  $^3J$  7.2 Hz, C2H), 7.50 (1H, d,  $^3J$  8.9 Hz, C9H), 7.40 (1H, d,  $^3J$  7.2 Hz, C3H), 6.86 (1H, d,  $^4J$  2.4 Hz, C8H), 6.64 (1H, d,  $^4J$  2.4 Hz, C6H), 3.97 (3H, s, C7-OCH<sub>3</sub>), 3.90 (3H, s, C5-OCH<sub>3</sub>), 2.54 (3H, s, C4-CH<sub>3</sub>), 1.41 (12H, s, 4×CH<sub>3</sub>, Bpin);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 159.0 (C7), 158.2 (C5), 140.2 (C4), 136.8 (C10a), 135.5 (C8a), 134.0 (C2), 128.9 (C4a), 128.4 (C10), 128.0 (C3), 126.0 (C9), 115.9 (C4b), 99.9 (C8), 98.0 (C6), 83.7 (−C(CH<sub>3</sub>)<sub>2</sub>−, BPin), 55.6 (C7-OCH<sub>3</sub>), 55.1 (C5-OCH<sub>3</sub>), 25.1 (−C(CH<sub>3</sub>)<sub>2</sub>−, BPin), 24.4 (C4-CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $C_{23}H_{28}BO_4$  379.2079 found 379.2080 [ $M+H^+$ ].

**Step 2:** 2-(5,7-Dimethoxy-4-methylphenanthren-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **S2b** (96.0 mg, 254  $\mu mol$ , 3.00 eq.), 2,5-dibromoterephthalaldehyde (24.7 mg, 84.6  $\mu mol$ , 1.00 eq.),  $K_3PO_4$  (71.8 mg, 338  $\mu mol$ , 4.00 eq.),  $Pd(dppf)_2Cl_2$  (9.78 mg, 8.46  $\mu mol$ , 10 mol%) were weighed in a 10 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before dry DMF (1.5 mL) was added. The reaction mixture was stirred at  $100^\circ C$  for 18 h under argon, cooled down to room temperature and diluted with water. Extraction with EtOAc (3×15 mL) was performed and the combined organic layer was washed with brine (3×20 mL), dried over anhydrous  $Na_2SO_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0→70:30) to give the desired product **S3b** as yellow oil (15.0 mg, 23.6  $\mu mol$ , 28%, m.p.  $250 - 252^\circ C$ );  $R_f$  0.38 (cyclohexane/EtOAc 5:1);  $\nu_{max}(neat)$ : 2934w, 2855w, 2746w, 1689s, 1603w, 1527w, 1453m, 1400m, 1359m, 1310m, 1275m, 1160s, 1121m, 1058w, 943w, 832w, 792w;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 9.81 (1H, s, CHO), 9.81 (1H, s, CHO), 8.19 (2H, s, C3H, C6H), 7.61 – 7.53 (2H, m, C3'H), 7.51 – 7.38 (5H, m, C9'H, C10'H, C2'H), 7.31 (1H, d,  $^3J$  8.9 Hz, C10'H), 6.88 (1H, d,  $^4J$  2.4 Hz, C8'H), 6.86 (1H, d,  $^4J$  2.4 Hz, C8'H), 6.78 – 6.72 (2H, m, C6'H), 4.00 (6H, s, C5'-OCH<sub>3</sub>), 3.99 (3H, s, C7'-OCH<sub>3</sub>), 3.98 (3H, s, C7'-OCH<sub>3</sub>), 2.65 (6H, s, C4'-CH<sub>3</sub>);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 192.0 (CHO), 159.6 (C7'), 158.3 (C5'), 144.1 (C2, C5), 138.2 (C1, C4), 138.1 (C1, C4), 137.8 (C4'), 135.6 (C8a'), 131.3 (C10a'), 131.15 (C3, C6), 131.13 (C3, C6), 130.8 (C1'), 129.6 (C4a'), 128.64 (C3'), 128.62 (C3'), 127.6 (C2'), 127.5 (C2'), 127.1 (C9'), 127.0 (C9'), 125.24 (C10'), 125.2 (C10'), 115.60 (C4b), 115.57 (C4b), 100.21 (C8'),

100.18 (C8'), 98.7 (C6'), 55.7 (C7'-OCH<sub>3</sub>), 55.2 (C5'-OCH<sub>3</sub>), 24.3 (C4'-CH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>42</sub>H<sub>35</sub>O<sub>6</sub> 635.2428 found 635.2426 [M+H<sup>+</sup>].

**Step 3:** To a suspension of methyltriphenylphosphonium-bromide (98.0 mg, 274 μmol, 4.50 eq.) in THF (1.0 mL) at 0°C was added dry KOt-Bu (35.6 mg, 317 μmol, 5.20 eq.) under argon. The resulting suspension was stirred for 40 min at 0°C and a solution of 2,5-bis(5,7-dimethoxy-4-methylphenanthren-1-yl)terephthalaldehyde **S3b** (38.7 mg, 61.0 μmol, 1.00 eq.) in THF (1.0 mL) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 18 h. Water was then added and the mixture was extracted with EtOAc (3×20 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0→70:30) to give the desired product **7b** as a white solid (26.0 mg, 41.2 μmol, 68%, m.p. 146.7 – 147°C):  $\nu_{\text{max}}$ (neat): 2952w, 2930w, 2823w, 1603s, 1527w, 1453m, 1358w, 1308w, 1273w, 1160s, 1056w, 987w, 832w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.69 (1H, s, C3H/C6H), 7.68 (1H, s, C3H/C6H), 7.55 – 7.50 (2H, m, C3'H), 7.49 – 7.37 (6H, m, C2'H, C9'H, C10'H), 6.88 (1H, d, <sup>3</sup>J 2.4 Hz, C8'H), 6.86 (1H, d, <sup>3</sup>J 2.4 Hz, C8'H), 6.76 – 6.62 (2H, m, C6'H), 6.45 (2H, dd, <sup>3</sup>J 17.5, <sup>3</sup>J 11.1 Hz, C11H), 5.59 (2H, dd, <sup>3</sup>J 17.5, <sup>2</sup>J 0.9 Hz, C12H), 5.23 – 4.79 (2H, m, C12H), 3.99 (6H, s, C7'-OCH<sub>3</sub>), 3.98 (3H, s, C5'-OCH<sub>3</sub>), 3.97 (3H, s, C5'-OCH<sub>3</sub>), 2.64 (6H, s, C4'-CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 159.2 (C5'), 158.3 (C7'), 139.5 (C2, C5), 136.2 (C1, C4, C4'), 136.1 (C1, C4, C4'), 135.7 (C8a'), 135.22 (C1'), 135.19 (C1'), 135.13 (C11), 135.09 (C11), 131.2 (C10a'), 131.1 (C10a'), 129.2 (C4a'), 128.67 (C3'), 128.65 (C3'), 127.84 (C3/C4), 127.83 (C3/C4), 127.01 (C2'), 126.96 (C2'), 126.64 (C10'), 126.6 (C10'), 125.9 (C9'), 125.8 (C9'), 115.79 (C4b'), 115.76 (C4b'), 114.54 (C12), 114.49 (C12), 100.11 (C8'), 100.07 (C8'), 98.2 (C6'), 55.7 (C5'-OCH<sub>3</sub>), 55.1 (C7'-OCH<sub>3</sub>), 24.3 (C4'-CH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>44</sub>H<sub>39</sub>O<sub>4</sub> 631.2843 found 631.2837 [M+H<sup>+</sup>].

### 8,8'-(4,6-Divinyl-1,3-phenylene)bis(2,4-dimethoxy-5-methylphenanthrene) (7c):

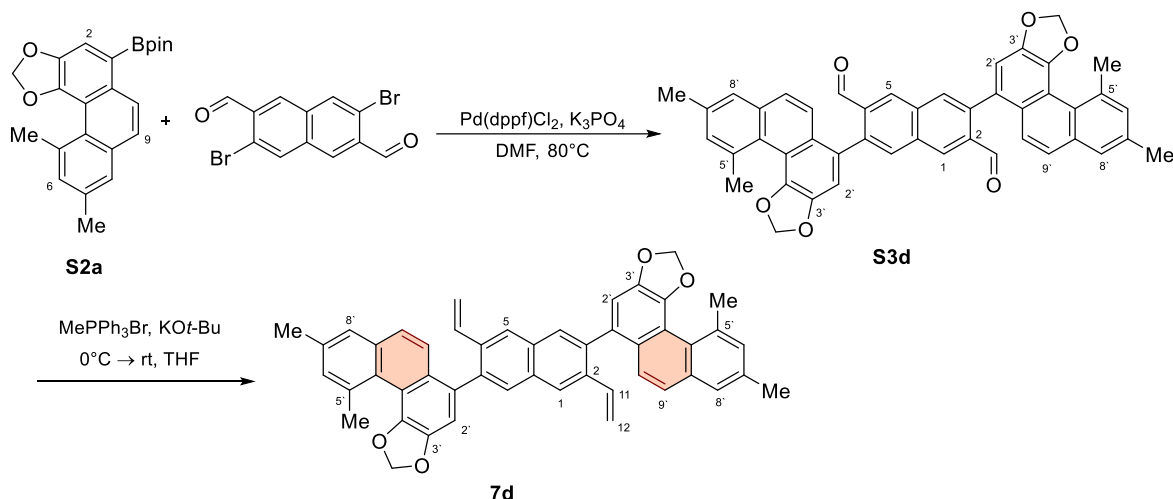


**Step 1:** According to a modified literature procedure:<sup>4</sup> *N*-bromosuccinimide (NBS) (730 mg, 4.10 mmol, 4.10 eq.) and benzoyl peroxide (7.27 mg, 30.0  $\mu$ mol, 3 mol%) were added to a solution of 1,5-dibromo-2,4-dimethylbenzene (264 mg, 1.00 mmol, 1.00 eq.) in 1.0 mL  $\text{CCl}_4$  under argon. The reaction mixture was stirred at reflux for 18 h, cooled down to room temperature, filtered off and rinsed with  $\text{CCl}_4$  (1.0 mL). The solvent was then removed under reduced pressure and the obtained crude product was used for the next step without any additional purification. Crude 1,5-dibromo-2,4-bis(dibromomethyl)benzene was dissolved in EtOH (20 mL) and a solution of  $\text{AgNO}_3$  (713 mg, 4.20 mmol) in water (8.0 mL) was added. The resulting mixture was refluxed under argon for 18 h. EtOH was removed under reduced pressure and extraction with dichloromethane was performed ( $3 \times 20$  mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0  $\rightarrow$  70:30) to give the desired product 4,6-dibromoisophthalaldehyde as a white solid (140 mg, 480  $\mu$ mol, 48% over two steps). The spectral data were in accordance with those previously reported in the literature.<sup>5</sup>

**Step 2:** 2-(5,7-Dimethoxy-4-methylphenanthren-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (136 mg, 360  $\mu$ mol, 3.00 eq.), 4,6-dibromoisophthalaldehyde (35.0 mg, 120  $\mu$ mol, 1.00 eq.),  $\text{K}_3\text{PO}_4$  (102 mg, 338  $\mu$ mol, 4.00 eq.),  $\text{Pd}(\text{dppf})_2\text{Cl}_2$  (8.78 mg, 12.0  $\mu$ mol, 10 mol%) were weighed in a 10 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before dry DMF (2.0 mL) was added. The reaction mixture was stirred at 100°C for 18 h under argon, cooled down to room temperature and diluted with water. Extraction with EtOAc ( $3 \times 15$  mL) was performed and the combined organic layer was washed with brine ( $3 \times 120$  mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0  $\rightarrow$  70:30) to give the desired product **S3c** as a yellow solid (60.0 mg, 94.5  $\mu$ mol, 79%, m.p. 174.8 – 176.0°C);  $R_f$  0.15 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$ (neat): 2992w, 2941w, 2833w, 1696m, 1603m, 1527w, 1454w, 1426w, 1359w, 1307w, 1220w, 1161w, 1116w, 1054w, 906m, 730m;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.83 (1H, s, CHO), 9.81 (1H, s, CHO), 8.86 – 8.79 (1H, m, C6H), 7.68 – 7.67 (1H, m, C3H), 7.51 (2H, d,  $^3J$  7.6 Hz, C3'H), 7.48 – 7.38 (5H, m, C2'H, C9'H, 1xC10'H), 7.35 – 7.31 (1H, m, C10'H), 6.91 – 6.78 (2H, m, C8'H), 6.76 – 6.68 (2H, m, C6'H), 3.97 (12H, s, 4 $\times$ OCH<sub>3</sub>), 2.61 (6H, s, C4'–CH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 191.4 (CHO), 159.6 (C7'), 158.3 (C5'), 149.1 (C2, C4), 149.0 (C2, C4), 138.0 (C4'), 136.7 (C3), 136.5 (C3), 135.6 (C8a'), 135.5 (C8a'), 134.81 (C1, C5), 134.8 (C1, C5), 130.91 (C10a'), 130.86 (C10a'), 130.81 (C1'), 130.77 (C1'), 129.60 (C4a'), 129.56 (C4a'), 128.53 (C3'), 128.50, (C3') 127.2 (C9'), 127.1 (C2'), 126.9 (C6), 126.8 (C6), 125.0 (C10'), 115.47 (C4b'), 100.2 (C8'), 98.7 (C6'), 55.7 (C5'–OCH<sub>3</sub>/C7'–OCH<sub>3</sub>), 55.2 (C5'–OCH<sub>3</sub>/C7'–OCH<sub>3</sub>), 24.3 (C4'–CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{42}\text{H}_{35}\text{O}_6$  635.2428 found 635.2424 [ $\text{M}+\text{H}^+$ ].

**Step 3:** To a suspension of methyltriphenylphosphonium-bromide (135 mg, 378  $\mu\text{mol}$ , 4.50 eq.) in THF (1.0 mL) at 0°C was added dry KOt-Bu (49.0 mg, 437  $\mu\text{mol}$ , 5.20 eq.) under argon. The resulting suspension was stirred for 40 min at 0°C and a solution of 4,6-bis(5,7-dimethoxy-4-methylphenanthren-1-yl)isophthalaldehyde **S3c** (53.3 mg, 84.0  $\mu\text{mol}$ , 1.00 eq.) in THF (1.0 mL) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 18 h. Water was then added and the mixture was extracted with EtOAc (3×20 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0→70:30) to give the desired product **7c** as a beige solid (41.0 mg, 65.0  $\mu\text{mol}$ , 77%, m.p. 166 – 167°C): *R<sub>f</sub>* 0.61 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}(\text{neat})$ : 3085w, 3005w, 2932w, 2855w, 1735w, 1602m, 1526m, 1453m, 1423m, 1357m, 1308m, 1274m, 1216m, 1159s, 1117m, 1058w, 986w, 911w, 832w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.12 – 8.05 (1H, m, C6H), 7.49 – 7.33 (8H, m, C2'H, C3'H, C9'H, C10'H), 7.32 – 7.28 (1H, m, C3H), 6.84 (<sup>3</sup>J 2.4 Hz), 6.82 (<sup>3</sup>J 2.4 Hz) (1H, C8'H), 6.70 – 6.64 (2H, m, C6'H), 6.59 – 6.45 (2H, m, C11H), 5.83 – 5.74 (2H, m, C12H), 5.24 – 4.96 (2H, m, C12H), 3.962 (3H, s, C7'-OCH<sub>3</sub>), 3.956 (3H, s, C7'-OCH<sub>3</sub>), 3.950 (6H, s, C5'-OCH<sub>3</sub>), 2.58 (6H, s, C4'-CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 159.2 (C7'), 158.3 (C5'), 139.5 (C2, C4), 139.3 (C2, C4), 136.5 (C1, C5), 136.4 (C1, C5), 136.2 (C4'), 136.1 (C4'), 135.7 (C8a'), 135.6 (C11), 134.94 (C1'), 134.88 (C1'), 134.79 (C3'), 131.0 (C10a'), 129.22 (C4a'), 129.19 (C4a'), 128.64 (C3'), 128.58 (C3'), 127.0 (C2'), 126.6 (C2'), 126.5 (C10'), 125.7 (C9'), 115.8 (C4b'), 114.7 (C12), 100.0 (C8'), 98.2 (C6'), 55.7 (C7'-OCH<sub>3</sub>), 55.1 (C5'-OCH<sub>3</sub>), 24.2 (C4'-CH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>44</sub>H<sub>39</sub>O<sub>4</sub> 631.2843 found 631.2836 [M+H<sup>+</sup>].

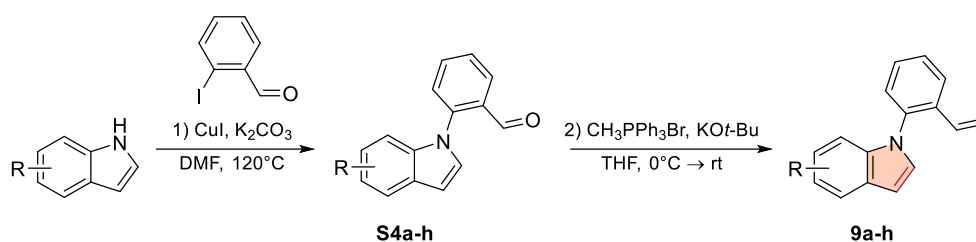
### 5,5'-(3,7-Divinylphenanthro-2,6-diyl)bis(9,11-dimethylphenanthro[3,4-*d*][1,3]dioxole) (7d):



**Step 1:** 2-(9,11-Dimethylphenanthro[3,4-*d*][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **S2a** (69.0 mg, 183  $\mu\text{mol}$ , 2.80 eq.), 3,7-dibromonaphthalene-2,6-dicarbaldehyde (22.0 mg, 65.5  $\mu\text{mol}$ , 1.00 eq.),  $\text{K}_3\text{PO}_4$  (55.6 mg, 262  $\mu\text{mol}$ , 4.00 eq.),  $\text{Pd(dppf)Cl}_2$  (4.79 mg, 6.55  $\mu\text{mol}$ , 10 mol%) were weighed in a 10 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before dry DMF (2.2 mL) was added. The reaction mixture was stirred at  $100^\circ\text{C}$  for 18 h under argon, cooled down to room temperature and diluted with water. Extraction with EtOAc ( $3 \times 15$  mL) was performed and the combined organic layer was washed with brine ( $3 \times 20$  mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0  $\rightarrow$  70:30) to give the desired product **S3d** as an orange solid (8.00 mg, 11.8  $\mu\text{mol}$ , 18%, m.p.  $185.5 - 190.0^\circ\text{C}$ ):  $R_f$  0.32 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}(\text{neat})$ : 2967w, 2920w, 2860w, 1691m, 1588m, 1447m, 1397w, 1269m, 1226w, 1068m, 1042m, 943w, 904w, 857w, 755s;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.84 (2H, s, CHO), 8.67 (2H, s, C1H, C5H), 8.19 (2H, s, C4H, C8H), 7.39 (2H, s, C8'H), 7.36 (2H, s, C6'H), 7.30 (2H, s, C2'H), 7.30 – 7.26 (2H, m, C9'H), 7.13 (d,  $^3J$  9.1 Hz), 7.11 (d,  $^3J$  9.1 Hz) (C10'H), 6.33 – 6.19 (4H, m,  $\text{OCH}_2\text{O}$ ), 2.78 (6H, s, C5'–CH<sub>3</sub>), 2.51 (6H, s, C7'–CH<sub>3</sub>);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 192.0 (CHO), 145.0 (C3'), 143.6 (C4'), 140.6 (C3, C7), 137.1 (C7'), 136.8 (C5'), 135.5 (C2, C6), 134.5 (C4a, C8a), 133.7 (C8a'), 133.2 (C4, C8), 132.1 (C6'), 129.0 (C1, C5), 128.8 (C10a), 128.6 (C1'), 126.6 (C9'), 125.3 (C8'), 125.2 (C4b') 123.63 (C10'), 123.6 (C10'), 116.6 (C4a'), 111.2 (C2'), 100.7 ( $\text{OCH}_2\text{O}$ ), 24.0 (C5'–CH<sub>3</sub>), 21.3 (C7'–CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{46}\text{H}_{33}\text{O}_6$  681.2272 found 681.2262 [ $\text{M}+\text{H}^+$ ].

**Step 2:** To a suspension of methyltriphenylphosphonium-bromide (36.7 mg, 103  $\mu\text{mol}$ , 4.50 eq.) in THF (1.0 mL) at  $0^\circ\text{C}$  was added dry KOt-Bu (13.3 mg, 119  $\mu\text{mol}$ , 5.20 eq.) under argon. The resulting suspension was stirred for 40 min at  $0^\circ\text{C}$  and a solution of 3,7-bis(9,11-dimethylphenanthro[3,4-*d*][1,3]dioxol-5-yl)naphthalene-2,6-dicarbaldehyde **S3d** (14.4 mg, 21.2  $\mu\text{mol}$ , 1.00 eq.) in THF (1.0 mL) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 18 h. Water was then added and the mixture was extracted with EtOAc ( $3 \times 20$  mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0  $\rightarrow$  70:30) to give the desired product **7d** as yellow oil (11.0 mg, 16.3  $\mu\text{mol}$ , 77%):  $R_f$  0.50 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}(\text{neat})$ : 3085w, 3005w, 2932w, 2855w, 1735w, 1602s, 1526w, 1453m, 1423m, 1357m, 1308m, 1216s, 1159s, 1058m, 986w, 911w, 832m;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.15 – 8.08 (2H, s, C1H, C5H), 7.88 (2H, s, C4H, C8H), 7.37 (2H, s, C8'H), 7.33 (2H, s, C6'H), 7.25 – 7.20 (4H, m, C2'H, C9'H), 7.20 – 7.12 (2H, m, C10'H), 6.51 (2H, dd,  $^3J$  17.3,  $^3J$  11.0 Hz, C11H), 6.28 – 6.15 (4H, m,  $\text{OCH}_2\text{O}$ ), 5.76 (2H, dd,  $^3J$  17.3,  $^2J$  1.0 Hz, C12H), 5.08 (2H, dd,  $^3J$  11.1,  $^2J$  1.0 Hz, C12H), 2.78 (6H, s, C5'–CH<sub>3</sub>), 2.50 (6H, s, C7'–CH<sub>3</sub>);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 144.8 (C3'), 142.8 (C4'), 138.9 (C3, C7), 136.7 (C5'/C7'), 136.50 (C5'/C7'), 136.46 (C2, C6), 135.6 (C11), 133.8 (C8a'), 132.51 (C4a, C8a), 132.48 (C4a, C8a), 131.6 (C6'), 130.2 (C4, C8), 128.3 (C10a'), 125.5 (C9'), 125.4 (C4b'), 125.1 (C8'), 124.9 (C10'), 124.8 (C10'), 123.84 (C1'), 123.83 (C1, C5), 116.5 (C4a'), 115.7 (C12), 115.6 (C12), 111.02 (C2'), 110.99 (C2'), 100.4 ( $\text{OCH}_2\text{O}$ ), 24.0 (C5'–CH<sub>3</sub>), 21.3 (C7'–CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{48}\text{H}_{37}\text{O}_4$  677.2686 found 677.2671 [ $\text{M}+\text{H}^+$ ].

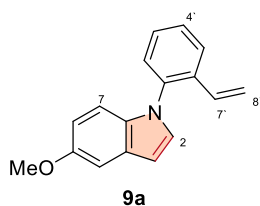
## General Procedure A for the synthesis of 1-(2-vinylphenyl)-indoles 9a-i:



**Step 1:** A crimp cap vial was charged with the corresponding indole (1.00 eq.), 2-iodobenzaldehyde (1.00 eq.),  $K_2CO_3$  (2.00 eq.) and CuI (0.10 eq.). The vial was sealed, evacuated and backfilled with argon before DMF ( $0.50 \text{ mol} \cdot \text{L}^{-1}$ ) was added. The resulting mixture was stirred at  $120^\circ\text{C}$  for 18 h, then cooled to room temperature, diluted with water, and extracted with EtOAc ( $\times 3$ ). The combined organic layer was washed with brine ( $\times 3$ ), dried over anhydrous  $Na_2SO_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0 $\rightarrow$ 70:30) to give the desired aldehyde **S4a-h**.

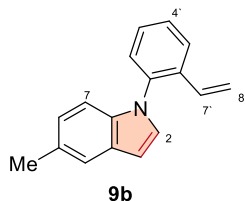
**Step 2:** To a suspension of methyltriphenylphosphonium-bromide (1.50 eq. or 2.00 eq.) in THF ( $0.10 \text{ mol} \cdot \text{L}^{-1}$ ) with regard to aldehyde **S4a-h** at  $0^\circ\text{C}$  was added dry KOt-Bu (1.70 eq. or 2.30 eq.) under argon. After stirring the resulting suspension for 50 min at  $0^\circ\text{C}$ , a solution of the corresponding aldehyde **S2a-h** (1.00 eq.) in THF ( $0.10 \text{ mol} \cdot \text{L}^{-1}$ ) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 18 h. Water was then added and the mixture was extracted with EtOAc ( $\times 3$ ). The combined organic layer was dried over anhydrous  $Na_2SO_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0 $\rightarrow$ 70:30) to give the desired product **9a-h**.

### 5-Methoxy-1-(2-vinylphenyl)-1H-indole (9a):



Step 1 of the general procedure **A** was performed with 5-methoxy-1H-indole (125 mg, 850  $\mu\text{mol}$ ), 2-iodobenzaldehyde (197 mg, 850  $\mu\text{mol}$ ),  $K_2CO_3$  (235 mg, 1.70 mmol) and CuI (16.2 mg, 85.0  $\mu\text{mol}$ ) to give 2-(5-methoxy-1H-indol-1-yl)benzaldehyde **S4a** as yellow oil (110 mg, 438  $\mu\text{mol}$ , 52%);  $R_f$  0.50 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S4a** (106 mg, 420  $\mu\text{mol}$ ) was subjected to the step 2 utilizing methyltriphenylphosphonium-bromide (300 mg, 0.84 mmol, 2.00 eq.) and KOt-Bu (108 mg, 966  $\mu\text{mol}$ , 2.30 eq.) to give **9a** as a yellow oil (70.0 mg, 281  $\mu\text{mol}$ , 67%);  $R_f$  0.55 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}(\text{neat})$ : 3067w, 2994w, 2945w, 2830w, 1701w, 1623w, 1576w, 1489s, 1487s, 1444m, 1344w, 1253s, 1220m, 1159s, 1116w, 1032m, 992w, 918w, 834w, 804m, 753m, 718m;  $^1\text{H}$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 7.74 (1H, dd,  $^3J$  7.7,  $^4J$  1.7 Hz, C3'H), 7.46 – 7.41 (1H, m, C4'H), 7.39 (1H, td,  $^3J$  7.5,  $^4J$  1.7 Hz, C5'H), 7.35 – 7.30 (1H, m, C6'H), 7.16 (1H, d,  $^3J$  3.1 Hz, C2'H), 7.15 (1H, d,  $^4J$  2.3 Hz, C4'H), 7.02 – 6.95 (1H, m, C7'H), 6.83 (1H, dd,  $^3J$  8.9,  $^4J$  2.3 Hz, C6'H), 6.60 (1H, dd,  $^3J$  3.1,  $^4J$  0.8 Hz, C3'H), 6.32 (1H, dd,  $^3J$  17.6,  $^3J$  11.0 Hz, C7'H), 5.72 (1H, dd,  $^3J$  17.6,  $^2J$  1.1 Hz, C8'H), 5.18 (1H, dd,  $^3J$  11.0,  $^2J$  1.1 Hz, C8'H), 3.87 (3H, s,  $OCH_3$ );  $^{13}\text{C}$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 154.6 (C5), 137.4 (C1'), 135.2 (C2'), 132.9 (C7a), 132.4 (C7'), 130.0 (C2), 129.0 (C3a), 128.7 (C5'), 128.2 (C4', C6'), 126.4 (C3'), 116.3 (C8'), 112.5 (C6), 111.8 (C7), 102.6 (C3), 102.5 (C4), 56.0 ( $OCH_3$ ); ESI-MS:  $m/z$  calcd. for  $C_{17}H_{16}NO$  250.1226 found 250.1217 [ $M+H^+$ ].

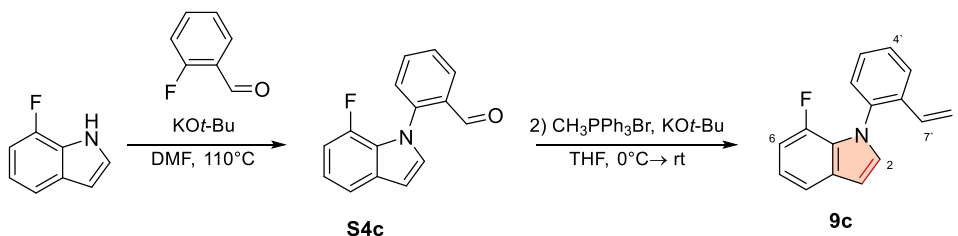
### 5-Methyl-1-(2-vinylphenyl)-1H-indole (9b):



9b

Step 1 of the general procedure **A** was performed with 5-methyl-1H-indole (111 mg, 850  $\mu$ mol), 2-iodobenzaldehyde (197 mg, 850  $\mu$ mol),  $K_2CO_3$  (235 mg, 1.70 mmol) and CuI (16.2 mg, 85.0  $\mu$ mol) to give 2-(5-methyl-1H-indol-1-yl)benzaldehyde **S4b** as yellow oil (115 mg, 489  $\mu$ mol, 58%);  $R_f$  0.59 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S4b** (113 mg, 480  $\mu$ mol) was subjected to the step 2 utilizing methyltriphenylphosphonium-bromide (343 mg, 960  $\mu$ mol, 2.00 eq.) and KOt-Bu (124 mg, 1.10 mmol, 2.30 eq.) to give **9b** as yellow oil (80.0 mg, 343  $\mu$ mol, 71%);  $R_f$  0.60 (cyclohexane/EtOAc 6:1);  $\nu_{max}(neat)$ : 3093w, 3015w, 2916w, 2855w, 1490s, 1469m, 1366w, 1332m, 1295w, 1222m, 1160m, 1118w, 1061w, 992w, 916w, 795w, 760m, 718m;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 7.78 – 7.69 (1H, m, C3'H), 7.51 – 7.47 (1H, m, C4H), 7.45 – 7.41 (1H, m, C4'H), 7.39 (td,  $^3J$  7.5,  $^4J$  1.7 Hz, C5'H), 7.35 – 7.30 (1H, m, C6'H), 7.15 (1H, d,  $^3J$  3.2 Hz, C2H), 7.01 – 6.97 (2H, m, C6H, C7H), 6.60 (1H, d,  $^3J$  3.2 Hz, C3H), 6.32 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7'H), 5.73 (1H, dd,  $^3J$  17.5,  $^2J$  1.1 Hz, C8'H), 5.18 (1H, dd,  $^3J$  11.0,  $^2J$  1.1 Hz, C8'H), 2.47 (3H, d,  $^4J$  0.8 Hz, C5-CH<sub>3</sub>);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 137.4 (C1'), 136.0 (C7a), 135.2 (C2'), 132.4 (C7'), 129.6 (C2), 129.5 (C5), 128.8 (C3a), 128.7 (C5'), 128.3 (C6'), 128.2 (C4'), 126.4 (C3'), 123.9 (C6), 120.6 (C4), 116.2 (C8'), 110.7 (C7), 102.5 (C3), 21.5 (C5-CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $C_{17}H_{16}N$  234.1277 found 234.1277 [ $M+H^+$ ].

### 7-Fluoro-1-(2-vinylphenyl)-1H-indole (9c):



S4c

9c

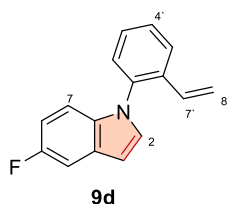
**Step 1:** A crimp cap vial was charged with 7-fluoro-1H-indole (115 mg, 850  $\mu$ mol, 1.00 eq.), KOt-Bu (143 mg, 1.28 mmol, 1.50 eq.), and 3.7 mL of dry DMF under argon. The obtained mixture was stirred at 110°C while 2-fluorobenzaldehyde (160 mg, 1.29 mmol, 1.52 eq.) was added dropwise over 10 minutes. The reaction mixture was stirred at 110°C for 16 h, then cooled to room temperature, diluted with water, and extracted with EtOAc (3×20 mL). The combined organic layer was washed with brine (3×80 mL), dried over anhydrous  $Na_2SO_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0→70:30) to give the desired aldehyde **S4c** as a yellow oil (68.2 mg, 285  $\mu$ mol, 34%);  $R_f$  0.66 (cyclohexane/EtOAc 5:1).

**Step 2:** 2-(7-Fluoro-1H-indol-1-yl)benzaldehyde (66.0 mg, 276  $\mu$ mol) **S4c** was subjected to the step 2 according of the general procedure **A** utilizing methyltriphenylphosphonium-bromide (138 mg, 386  $\mu$ mol, 1.40 eq.) and KOt-Bu (49.5 mg, 441  $\mu$ mol, 1.60 eq.) to give **9c** as a transparent oil (32.0 mg, 135  $\mu$ mol, 49%);  $R_f$  0.69 (cyclohexane/EtOAc 9:1);  $\nu_{max}(neat)$ : 3109w, 3074w, 2858w, 2758w, 1696s, 1599m, 1595m, 1491s, 1459w, 1398w, 1340w, 1277w, 1241m, 1160w, 1048w, 955w, 824w, 768m, 719m;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 7.72 – 7.67 (1H, m, C3'H), 7.48 – 7.40 (2H, m, C4'H, C4H), 7.39 – 7.33 (2H, m, C5'H, C6'H), 7.11 (1H, d,  $^3J$  3.1 Hz, C2H), 7.05 (1H, td,  $^3J$  7.9,  $^4J$  4.4 Hz, C5H), 6.85 (1H, ddd,  $^3J$  12.2,  $^3J$  7.8,  $^4J$  0.7 Hz, C6H), 6.70 – 6.63 (1H, m,



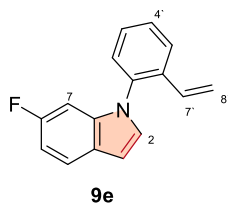
C3H), 6.31 (1H, dd,  $^3J$  17.5,  $^3J$  11.1 Hz, C7'H), 5.69 (1H, dd,  $^3J$  17.5,  $^2J$  1.1 Hz, C8'H), 5.18 (1H, dd,  $^3J$  11.1,  $^2J$  1.1 Hz, C8'H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 150.2 (d,  $^1J_{\text{CF}}$  246.8 Hz, C7), 138.2 (C1'), 135.5 (C2'), 132.61 (d,  $^2J_{\text{CF}}$  4.7 Hz, C7a), 131.9 (C7'), 131.0 (C2), 128.6 (C4'), 128.3 (C6'), 128.1 (C5'), 125.4 (C3a), 125.8 (C3'), 120.5 (d,  $^3J_{\text{CF}}$  6.4 Hz, C5), 116.8 (d,  $^4J_{\text{CF}}$  28.6 Hz, C4), 116.6 (C8'), 108.1 (d,  $^2J_{\text{CF}}$  18.9 Hz, C6), 103.6 (C3);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -132.28; ESI-MS:  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{13}\text{FN}$  238.1027 found 238.1023  $[\text{M}+\text{H}^+]$ .

### 5-Fluoro-1-(2-vinylphenyl)-1H-indole (9d):



Step 1 of the general procedure **A** was performed with 5-fluoro-1H-indole (176 mg, 1.30 mmol), 2-iodobenzaldehyde (302 mg, 1.30 mmol),  $\text{K}_2\text{CO}_3$  (359 mg, 2.60 mmol) and  $\text{CuI}$  (24.8 mg, 130  $\mu\text{mol}$ ) to give 2-(5-fluoro-1H-indol-1-yl)benzaldehyde **S4d** as yellow oil (165 mg, 690  $\mu\text{mol}$ , 53%):  $R_f$  0.45 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S4d** (165 mg, 690  $\mu\text{mol}$ ) was subjected to the step 2 utilizing methyltriphenylphosphonium-bromide (370 mg, 1.03 mmol, 1.50 eq.) and  $\text{KOt-Bu}$  (132 mg, 1.17 mmol, 1.70 eq.) to give **9d** as a transparent oil (100 mg, 421  $\mu\text{mol}$ , 61%):  $R_f$  0.63 (cyclohexane/EtOAc 9:1);  $\nu_{\text{max}}$ (neat): 3068w, 2963w, 1624w, 1578w, 1490s, 1473s, 1448w, 1335w, 1260s, 1136m, 1093s, 1018s, 960w, 917w, 860s, 799s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.75 (1H, dd,  $^3J$  7.8,  $^4J$  1.6 Hz, C3'H), 7.49 – 7.43 (1H, m, C4'H), 7.40 (1H, td,  $^3J$  7.6,  $^4J$  1.6 Hz, C5'H), 7.35 – 7.29 (2H, m, C6'H, C4H), 7.22 (1H, d,  $^3J$  3.2 Hz, C2H), 6.99 (1H, dd,  $^3J$  8.9,  $^3J_{\text{HF}}$  4.5 Hz, C7H), 6.91 (1H, td,  $^3J$  9.1,  $^4J$  2.5 Hz, C6H), 6.63 (1H, dd,  $^3J$  3.2,  $^4J$  0.7 Hz, C3H), 6.26 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7'H), 5.73 (1H, dd,  $^3J$  17.5,  $^2J$  1.0 Hz, C8'H), 5.19 (1H, dd,  $^3J$  11.0,  $^2J$  1.0 Hz, C8'H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 158.3 (d,  $^1J_{\text{CF}}$  234.8 Hz, C5), 137.0 (C1'), 135.3 (C2'), 134.2 (C7a), 132.1 (C7'), 131.0 (C2), 128.8 (C5', C3a), 128.5 (C4'), 128.3 (C6'), 126.5 (C3'), 116.6 (C8'), 111.7 (d,  $^3J_{\text{CF}}$  9.7 Hz, C7), 110.7 (d,  $^2J_{\text{CF}}$  26.3 Hz, C6), 105.7 (d,  $^2J_{\text{CF}}$  23.5 Hz, C4), 102.9 (d,  $^4J_{\text{CF}}$  4.7 Hz, C3);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -124.69; ESI-MS:  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{12}\text{AgFN}$  343.9999 found 343.9993  $[\text{M}+\text{Ag}^+]$ .

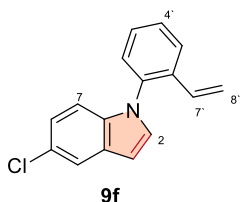
### 6-Fluoro-1-(2-vinylphenyl)-1H-indole (9e):



Step 1 of the general procedure **A** was performed with 6-fluoro-1H-indole (176 mg, 1.30 mmol), 2-iodobenzaldehyde (302 mg, 1.30 mmol),  $\text{K}_2\text{CO}_3$  (359 mg, 2.60 mmol) and  $\text{CuI}$  (24.8 mg, 130  $\mu\text{mol}$ ) to give 2-(6-fluoro-1H-indol-1-yl)benzaldehyde **S4e** as yellow oil (197 mg, 823  $\mu\text{mol}$ , 63%):  $R_f$  0.59 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S4e** (196 mg, 820  $\mu\text{mol}$ ) was subjected to the step 2 utilizing methyltriphenylphosphonium-bromide (586 mg, 1.64 mmol, 2.00 eq.) and  $\text{KOt-Bu}$  (212 mg, 1.89 mmol, 2.30 eq.) to give **9e** as a white solid (155 mg, 653  $\mu\text{mol}$ , 80%, m.p. 62.5 – 63.1  $^{\circ}\text{C}$ ):  $R_f$  0.81 (cyclohexane/EtOAc 9:1);  $\nu_{\text{max}}$ (neat): 3067w, 2921w, 1619m, 1485s, 1465m, 1342m, 1290w, 1214s, 1177m, 1119w, 991w, 933m, 834w, 768m, 716m, 630s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.76 (1H, dd,  $^3J$  7.8,  $^4J$  1.6 Hz, C3'H), 7.59 (1H, dd,  $^3J$  8.6,  $^4J$  5.3 Hz, C4H), 7.49 – 7.43 (1H, m, C4'H), 7.41 (1H, td,  $^3J$  7.6,  $^4J$  1.6 Hz, C5'H), 7.34 – 7.30 (1H,

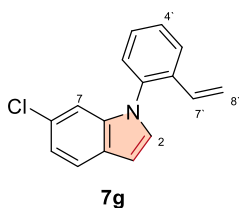
m, C6`H), 7.17 (1H, d,  $^3J$  3.2 Hz, C2H), 6.92 (1H, ddd,  $^3J$  9.5,  $^3J$  8.7,  $^4J$  2.3 Hz, C5H), 6.76 (1H, dd,  $^3J$  9.8,  $^4J$  2.3 Hz, C7H), 6.65 (1H, dd,  $^3J$  3.2,  $^4J$  0.9 Hz, C3H), 6.28 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7`H), 5.74 (1H, dd,  $^3J$  17.5,  $^2J$  1.0 Hz, C8`H), 5.21 (1H, dd,  $^3J$  11.0,  $^2J$  1.0 Hz, C8`H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 160.3 (d,  $^1J_{\text{CF}}$  238.0 Hz, C6), 137.6 (d,  $^3J_{\text{CF}}$  12.1 Hz, C7a), 136.8 (C1`), 135.2 (C2`), 132.1 (C7`), 129.9 (d,  $^5J_{\text{CF}}$  3.7 Hz, C2), 128.8 (C5`), 128.6 (C4`), 128.1 (C6`), 126.5 (C3`), 124.9 (C3a), 121.7 (d,  $^3J_{\text{CF}}$  10.0 Hz, C4), 116.7 (C8`), 109.0 (d,  $^2J_{\text{CF}}$  24.6 Hz, C5), 103.0 (C3), 97.4 (d,  $^2J_{\text{CF}}$  26.7 Hz, C7);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -120.42; ESI-MS: m/z calcd. for  $\text{C}_{16}\text{H}_{13}\text{FN}$  238.1027 found 237.1021  $[\text{M}+\text{H}^+]$ .

### 5-Chloro-1-(2-vinylphenyl)-1H-indole (9f):



Step 1 of the general procedure **A** was performed with 5-chloro-1H-indole (129 mg, 850  $\mu\text{mol}$ ), 2-iodobenzaldehyde (197 mg, 850  $\mu\text{mol}$ ),  $\text{K}_2\text{CO}_3$  (235 mg, 1.70 mmol) and  $\text{CuI}$  (16.2 mg, 85.0  $\mu\text{mol}$ ) to give 2-(5-chloro-1H-indol-1-yl)benzaldehyde **S4f** as yellow oil (170 mg, 665  $\mu\text{mol}$ , 78%):  $R_f$  0.48 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S4f** (161 mg, 630  $\mu\text{mol}$ ) was subjected to the step 2 utilizing methyltriphenylphosphonium-bromide (450 mg, 1.26 mmol, 2.00 eq.) and  $\text{KOt-Bu}$  (163 mg, 1.45 mmol, 2.30 eq.) to give **9f** as yellow oil (90.0 mg, 355  $\mu\text{mol}$ , 56%):  $R_f$  0.67 (cyclohexane/EtOAc 6:1);  $\nu_{\text{max}}(\text{neat})$ : 3066w, 2968w, 2929w, 2855w, 1600w, 1570w, 1487s, 1462s, 1368w, 1327w, 1286w, 1229w, 1149w, 1064m, 1019w, 955w, 916w, 869w, 797m, 753s, 719s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.75 (1H, dd,  $^3J$  7.8,  $^4J$  1.6 Hz, C3`H), 7.69 – 7.58 (1H, m, C4H), 7.49 – 7.44 (1H, m, C4`H), 7.40 (1H, td,  $^3J$  7.6,  $^4J$  1.6 Hz, C5`H), 7.31 (1H, dd,  $^3J$  7.6,  $^4J$  1.3 Hz, C6`H), 7.21 (1H, d,  $^3J$  3.2 Hz, C2H), 7.16 – 7.05 (1H, m, C6H), 7.02 – 6.95 (1H, m, C7H), 6.62 (1H, dd,  $^3J$  3.2,  $^5J$  0.8 Hz, C3H), 6.24 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7`H), 5.73 (1H, dd,  $^3J$  17.5,  $^2J$  1.0 Hz, C8`H), 5.19 (1H, dd,  $^3J$  11.0,  $^2J$  1.0 Hz, C8`H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 136.8 (C1`), 136.0 (C7a), 135.3 (C2`), 132.0 (C7`), 130.7 (C2), 129.5 (C3a), 128.8 (C5`), 128.7 (C4`), 128.2 (C6`), 126.5 (C3`), 126.0 (C5), 122.6 (C6), 120.3 (C4), 116.7 (C8`), 112.0 (C7), 102.6 (C3); ESI-MS: m/z calcd. for  $\text{C}_{16}\text{H}_{12}\text{ClN}$  254.0731 found 254.0727  $[\text{M}+\text{Ag}^+]$ .

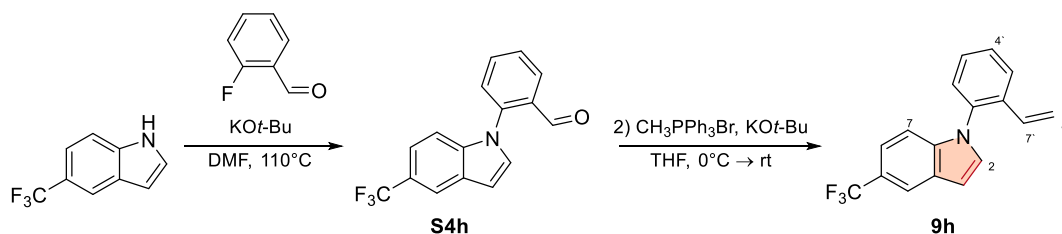
### 6-Chloro-1-(2-vinylphenyl)-1H-indole (9g):



Step 1 of the general procedure **A** was performed with 6-chloro-1H-indole (129 mg, 850  $\mu\text{mol}$ ), 2-iodobenzaldehyde (197 mg, 850  $\mu\text{mol}$ ),  $\text{K}_2\text{CO}_3$  (235 mg, 1.70 mmol) and  $\text{CuI}$  (16.2 mg, 85.0  $\mu\text{mol}$ ) to give 2-(6-chloro-1H-indol-1-yl)benzaldehyde **S4g** as yellow oil (122 mg, 477  $\mu\text{mol}$ , 56%):  $R_f$  0.36 (cyclohexane/EtOAc 9:1). The obtained aldehyde **S4g** (120 mg, 470  $\mu\text{mol}$ ) was subjected to the step 2 utilizing methyltriphenylphosphonium-bromide (336 mg, 940  $\mu\text{mol}$ , 2.00 eq.) and  $\text{KOt-Bu}$  (121 mg, 1.08 mmol, 2.30 eq.) to give **9g** as a transparent oil (55.0 mg, 217  $\mu\text{mol}$ , 46%):  $R_f$  0.71 (cyclohexane/EtOAc 5:1);

$\nu_{\max}(\text{neat})$ : 3067w, 2986w, 2921w, 2851w, 1844w, 1701w, 1600w, 1566w, 1506m, 1462s, 1336m, 1234w, 1142w, 1060w, 991w, 918w, 849w, 807w, 768w, 718w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.76 (1H, dd,  $^3J$  7.8,  $^4J$  1.5 Hz, C3'H), 7.59 (1H, d,  $^3J$  8.4 Hz, C4H), 7.47 (1H, td,  $^3J$  7.8,  $^4J$  1.2 Hz, C4'H), 7.41 (1H, td,  $^3J$  7.8,  $^4J$  1.5 Hz, C5'H), 7.32 (1H, dd,  $^3J$  7.7,  $^4J$  1.2 Hz, C6'H), 7.17 (1H, d,  $^3J$  3.2 Hz, C2H), 7.12 (1H, dd,  $^3J$  8.4,  $^4J$  1.9 Hz, C5H), 7.09 – 7.05 (1H, m, C7H), 6.65 (1H, dd,  $^3J$  3.2,  $^4J$  0.8 Hz, C3H), 6.26 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7'H), 5.73 (1H, dd,  $^3J$  17.5,  $^2J$  1.0 Hz, C8'H), 5.21 (1H, dd,  $^3J$  11.0,  $^2J$  1.0 Hz, C8'H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 137.9 (C7a), 136.6 (C1'), 135.3 (C2'), 131.9 (C7'), 130.2 (C2), 128.8 (C5'), 128.7 (C4'), 128.4 (C6), 128.2 (C6'), 127.0 (C3a), 126.6 (C3'), 121.8 (C4), 121.0 (C5), 116.9 (C8'), 110.9 (C7), 103.1 (C3); ESI-MS:  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{12}\text{ClN}$  253.0653 found 253.0653 [ $\text{M}^+$ ].

### 5-(Trifluoromethyl)-1-(2-vinylphenyl)-1H-indole (9h):

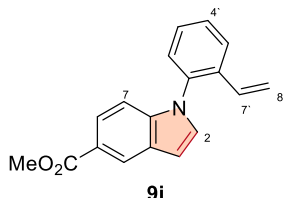


**Step 1:** A crimp cap vial was charged with 5-trifluoromethyl-1H-indole (174 mg, 940  $\mu\text{mol}$ , 1.00 eq.), KOt-Bu (158 mg, 1.41 mmol, 1.50 eq.), and 4.7 mL of dry DMF under argon. The obtained mixture was stirred at 110°C while 2-fluorobenzaldehyde (177 mg, 1.43 mmol, 1.52 eq.) was added dropwise over 10 minutes. The reaction mixture was stirred at 110°C for 16 h, then cooled to room temperature, diluted with water, and extracted with EtOAc (3×20 mL). The combined organic layer was washed with brine (3×80 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0→70:30) to give the desired aldehyde **S4h** as a yellow oil (155 mg, 536  $\mu\text{mol}$ , 57%);  $R_f$  0.33 (cyclohexane/EtOAc 5:1).

### Step 2:

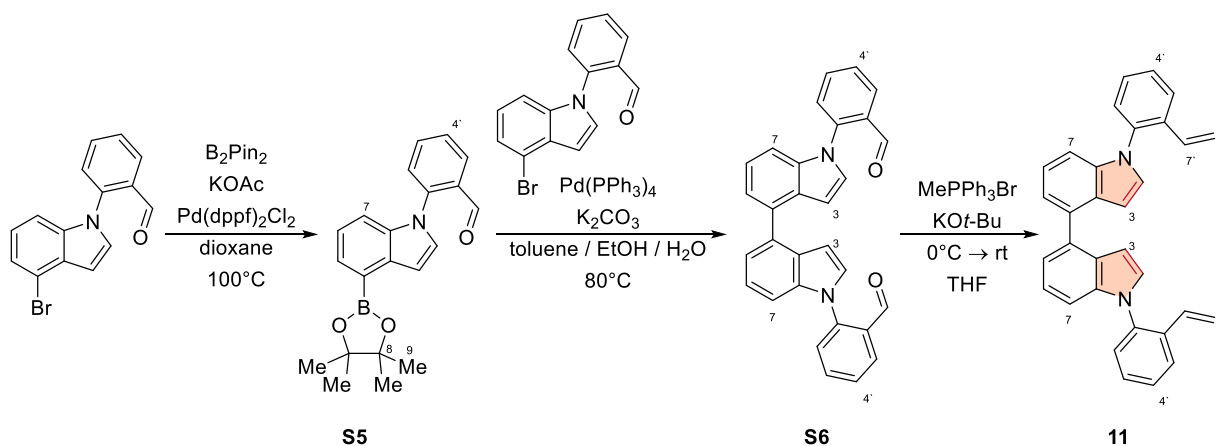
2-(5-(Trifluoromethyl)-1H-indol-1-yl)benzaldehyde **S4h** (153 mg, 530  $\mu\text{mol}$ ) was subjected to the step 2 according of the general procedure **A** utilizing methyltriphenylphosphonium-bromide (379 mg, 1.06 mmol, 2.00 eq.) and KOt-Bu (137 mg, 2.20 mmol, 2.30 eq.) to give **9h** as a transparent oil (87.0 mg, 303  $\mu\text{mol}$ , 57%);  $R_f$  0.65 (cyclohexane/EtOAc 6:1);  $\nu_{\max}(\text{neat})$ : 3093w, 2988w, 2901w, 1627w, 1495m, 1456w, 1341s, 1318m, 1235wm 1165w, 1115s, 1054m, 918w, 810w, 767w, 729w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.07 – 7.89 (1H, m, C4H), 7.85 – 7.68 (1H, m, C3'H), 7.51 – 7.45 (1H, m, C4'H), 7.45 – 7.36 (2H, m, C5'H, C6H), 7.35 – 7.31 (1H, m, C6'H), 7.29 (1H, d,  $^3J$  3.2 Hz, C2H), 7.14 (1H, d,  $^3J$  8.7 Hz, C7H), 6.77 (1H, d,  $^3J$  3.2 Hz, C3H), 6.22 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7'H), 5.74 (1H, d,  $^3J$  17.5 Hz, C8'H), 5.20 (d,  $^3J$  11.0 Hz, C8'H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 138.8 (C7a), 136.5 (C1'), 135.3 (C2'), 131.8 (C7'), 131.2 (C2), 128.90 (C4'), 128.86 (C5'), 128.2 (C6'), 127.8 (C3a), 126.6 (C3'), 125.5 (q,  $^1J_{\text{CF}}$  271.5 Hz,  $\text{CF}_3$ ), 122.7 (q,  $^2J_{\text{CF}}$  32.0 Hz, C5), 119.1 (q,  $^3J_{\text{CF}}$  2.6 Hz, C6), 118.79 (q,  $^3J_{\text{CF}}$  4.3 Hz, C4), 117.0 (C8'), 111.3 (C7), 103.8 (C3);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = –60.31; ESI-MS:  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{N}$  288.0994 found 288.0987 [ $\text{M}+\text{H}^+$ ].

### Methyl 1-(2-vinylphenyl)-1*H*-indole-5-carboxylate (**9i**):



Step 1 of the general procedure **A** was performed with methyl 1*H*-indole-5-carboxylate (149 mg, 850  $\mu$ mol), 2-iodobenzaldehyde (197 mg, 850  $\mu$ mol),  $K_2CO_3$  (235 mg, 1.70 mmol) and CuI (16.2 mg, 85.0  $\mu$ mol) to give methyl 1-(2-formylphenyl)-1*H*-indole-5-carboxylate **S4i** as yellow oil (200 mg, 716  $\mu$ mol, 84%);  $R_f$  0.33 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S4i** (185 mg, 662  $\mu$ mol) was subjected to the step 2 utilizing methyltriphenylphosphonium-bromide (331 mg, 927  $\mu$ mol, 1.40 eq.) and KO*t*-Bu (119 mg, 1.06 mmol, 1.60 eq.) to give **9i** as yellow oil (150 mg, 541  $\mu$ mol, 82%);  $R_f$  0.61 (cyclohexane/EtOAc 5:1);  $\nu_{max}(neat)$ : 3382w, 2949w, 1709s, 1612m, 1492m, 1445m, 1333m, 1267s, 1229m, 1195m, 1123w, 1086w, 987w, 912w, 753s;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 8.46 (1H, d,  $^4J$  1.3 Hz, C4*H*), 7.87 (1H, dd,  $^3J$  8.7,  $^4J$  1.6 Hz, C6*H*), 7.76 (1H, dd,  $^3J$  7.8,  $^4J$  1.3 Hz, C3'*H*), 7.55 – 7.45 (1H, m, C4'*H*), 7.42 (1H, td,  $^3J$  7.6,  $^4J$  1.3 Hz, C5'*H*), 7.33 (1H, dd,  $^3J$  7.8,  $^4J$  1.3 Hz, C6'*H*), 7.25 (1H, d,  $^3J$  3.2 Hz, C2*H*), 7.08 (1H, d,  $^3J$  8.7 Hz, C7*H*), 6.77 (1H, d,  $^3J$  3.2 Hz, C3*H*), 6.23 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7'*H*), 5.83 – 5.65 (1H, m, C8'*H*), 5.19 (1H, dd,  $^3J$  11.0,  $^2J$  0.8 Hz, C8'*H*), 3.94 (3H, s,  $CO_2CH_3$ );  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 168.2 ( $CO_2CH_3$ ), 139.9 (C7*a*), 136.6 (C1'), 135.3 (C2'), 131.9 (C7'), 130.9 (C2), 128.9 (C5'), 128.8 (C4'), 128.2 (C6'), 128.1 (C3*a*), 126.6 (C3'), 124.1 (C4), 123.7 (C6), 122.4 (C5), 117.0 (C8'), 110.7 (C7), 104.3 (C3), 52.0 ( $OCH_3$ ); ESI-MS:  $m/z$  calcd. for  $C_{88}H_{77}O_8$  1261.5613 found 1261.5632 [ $2M+H^+$ ]; ESI-MS:  $m/z$  calcd. for  $C_{18}H_{16}NO_2$  278.1176 found 278.1177 [ $M+H^+$ ].

### 1,1'-Bis(2-vinylphenyl)-1*H*,1'*H*-4,4'-biindole (**11**):



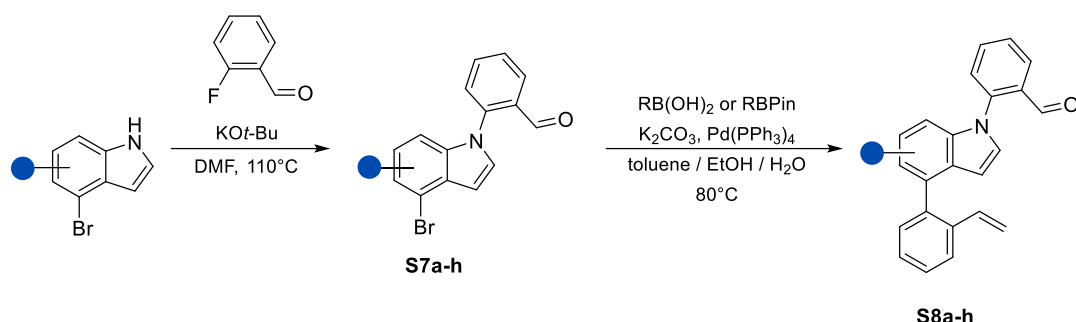
**Step 1:** According to the modified literature procedure:<sup>6</sup> 2-(4-Bromo-1*H*-indol-1-yl)benzaldehyde (540 mg, 1.80 mmol, 1.00 eq.), bis(pinacolato)diboron (549 mg, 2.16 mmol, 1.20eq.), dry KOAc (530 mg, 5.40 mmol, 3.00 eq.), Pd(dppf) $_2$ Cl $_2$ ·CH $_2$ Cl $_2$  (132 mg, 180  $\mu$ mol, 10 mol%) were weighed in a 20 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before dioxane (10 mL) was added. The reaction mixture was stirred at 100°C for 18 h under argon, cooled down to room temperature, filtered through a thin silica gel layer (using EtOAc to wash the filter bed). The solvents were removed under reduced pressure and crude product was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0→60:40) to give the desired product **S5** as yellow oil (420 mg, 1.21 mmol, 67%);  $R_f$  0.58 (cyclohexane/EtOAc 5:1);  $\nu_{max}(neat)$ : 3081w, 3058w, 2922w, 2851w, 2751w, 1696s, 1598m, 1513m, 1489m, 1420m, 1268w, 1194w, 994w, 912w, 754s;  $^1H$  NMR (500 MHz,

CDCl<sub>3</sub>)  $\delta$  = 9.65 (1H, s, CHO), 8.10 (1H, dd, <sup>3</sup>J 7.8, <sup>4</sup>J 1.6 Hz, C3'H), 7.75 (1H, td, <sup>3</sup>J 7.7, <sup>4</sup>J 1.6 Hz, C5'H), 7.71 (1H, dd, <sup>3</sup>J 6.9, <sup>4</sup>J 0.9 Hz, C5H), 7.57 (1H, t, <sup>3</sup>J 7.6 Hz, C4'H), 7.48 (1H, dd, <sup>3</sup>J 7.7, <sup>4</sup>J 1.0 Hz, C6'H), 7.34 (1H, d, <sup>3</sup>J 3.2 Hz, C2H), 7.32 – 7.27 (2H, m, C3H, C7H), 7.25 – 7.20 (1H, m, C6H), 1.42 (12H, s, 4×CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 189.9 (CHO), 142.3 (C1'), 137.9 (C7a), 135.2 (C5'), 133.6 (C3a), 132.3 (C2'), 130.3 (C2), 129.0 (C5, C4), 128.7 (C3'), 128.4 (C4'), 128.3 (C6'), 122.7 (C6), 113.1 (C7), 106.5 (C3), 83.8 (C8), 25.2 (C9); ESI-MS: m/z calcd. for C<sub>21</sub>H<sub>22</sub>BNNaO<sub>3</sub> 370.1589 found 370.1591 [M+Na<sup>+</sup>].

**Step 2:** 2-(4-Bromo-1H-indol-1-yl)benzaldehyde (66.0 mg, 220  $\mu$ mol, 1.00 eq.), 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indol-1-yl)benzaldehyde (**S5**) (84.8 mg, 244  $\mu$ mol, 1.11 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub> (12.7 mg, 11.0  $\mu$ mol, 5 mol%), and K<sub>2</sub>CO<sub>3</sub> (91.2 mg, 660  $\mu$ mol, 3.00 eq.) were weighed in a 10 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before a degassed mixture of toluene, H<sub>2</sub>O, ethanol (2 : 2 : 1) (2 mL, 0.11 mol·L<sup>-1</sup>) was added. The resulting mixture was stirred at 80°C for 18 h, then cooled to room temperature, filtered through a thin layer of silica gel and Na<sub>2</sub>SO<sub>4</sub> using EtOAc (15-20 mL). The solvents were removed under reduced pressure and the residue was purified by the silica gel chromatography (cyclohexane/EtOAc 100:0→70:30) to give the desired product 2,2'-(1H,1'H-[4,4'-biindole]-1,1'-diyl)dibenzaldehyde **S6** as yellow oil (82.0 mg, 186  $\mu$ mol, 85%): R<sub>f</sub> 0.42 (cyclohexane/EtOAc 5:1);  $\nu_{\max}$ (neat): 3061w, 2919w, 2857w, 2755w, 1693s, 1598m, 1487m, 1411m, 1295w, 1184w, 884w, 755; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.77 (2H, d, <sup>4</sup>J 0.8 Hz, CHO), 8.15 (2H, dd, <sup>3</sup>J 7.8, <sup>4</sup>J 1.4 Hz, C3'H), 7.80 (2H, td, <sup>3</sup>J 7.6, <sup>4</sup>J 1.4 Hz, C5'H), 7.66 – 7.55 (4H, m, C4'H, C6'H), 7.48 (2H, dd, <sup>3</sup>J 7.3, <sup>4</sup>J 0.9 Hz, C5H), 7.37 (2H, dd, <sup>3</sup>J 8.2, <sup>3</sup>J 7.3 Hz, C6H), 7.33 (2H, d, <sup>3</sup>J 3.3 Hz, C2H), 7.27 – 7.22 (2H, m, C7H), 6.83 (2H, dd, <sup>3</sup>J 3.3, <sup>5</sup>J 0.9 Hz, C3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 190.0 (CHO), 142.3 (C1'), 139.0 (C7a), 135.3 (C5'), 134.0 (C4), 132.3 (C2'), 129.8 (C2), 128.7 (C3'), 128.5 (C4'/C6'), 128.4 (C4'/C6'), 127.8 (C3a), 123.4 (C6), 122.0 (C5), 109.4 (C7), 104.9 (C3); ESI-MS: m/z calcd. for C<sub>30</sub>H<sub>20</sub>KN<sub>2</sub>O<sub>2</sub> 479.1156 found 479.1155 [M+K<sup>+</sup>].

**Step 3:** To a suspension of methyltriphenylphosphonium-bromide (264 mg, 740  $\mu$ mol, 4.00 eq.) in THF (1.9 mL) at 0°C was added dry KOt-Bu (95.5 mg, 851  $\mu$ mol, 4.60 eq.) under argon. After stirring the resulting suspension for 50 min at 0°C, a solution of 2,2'-(1H,1'H-[4,4'-biindole]-1,1'-diyl)dibenzaldehyde **S6** (81.5 mg, 185  $\mu$ mol, 1.00 eq.) in THF (1.9 mL) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 18 h. Water was then added and the mixture was extracted with EtOAc (3×30 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0→70:30) to give the desired product 1,1'-bis(2-vinylphenyl)-1H,1'H-4,4'-biindole **11** as yellow oil (66.0 mg, 151  $\mu$ mol, 82%): R<sub>f</sub> 0.57 (cyclohexane/EtOAc 5:1);  $\nu_{\max}$ (neat): 3062w, 2924w, 2837w, 1836w, 1709w, 1627w, 1597w, 1508w, 1488m, 1293m, 1181m, 1052w, 992w, 909m, 751s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.82 – 7.76 (2H, m, C3'H), 7.49 – 7.39 (8H, m, C5H, C4'H, C5'H, C6'H), 7.30 (2H, dd, <sup>3</sup>J 8.2, <sup>3</sup>J 7.3 Hz, C6H), 7.22 (2H, d, <sup>3</sup>J 3.2 Hz, C2H), 7.16 – 7.10 (2H, m, C7H), 6.79 (2H, dd, <sup>3</sup>J 3.2, <sup>5</sup>J 0.8 Hz, C3H), 6.42 (2H, dd, <sup>3</sup>J 17.5, <sup>3</sup>J 11.0 Hz, C7'H), 5.77 (2H, dd, <sup>3</sup>J 17.5, <sup>2</sup>J 1.0 Hz, C8'H), 5.23 (2H, dd, <sup>3</sup>J 11.0, <sup>2</sup>J 1.0 Hz, C8'H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 138.1 (C7a), 137.5 (C1'), 135.3 (C2'), 133.9 (C4), 132.5 (C7'), 129.3 (C2), 128.7 (C5'), 128.5 (C4'), 128.3 (C6'), 127.6 (C3a), 126.4 (C3'), 122.4 (C6), 121.2 (C5), 116.3 (C8'), 110.0 (C7), 103.5 (C3); ESI-MS: m/z calcd. for C<sub>32</sub>H<sub>25</sub>N<sub>2</sub> 437.2012 found 437.2000 [M+H<sup>+</sup>].

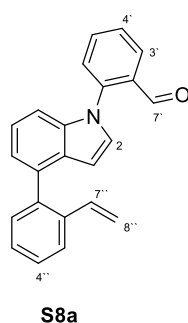
## General Procedure B for the Synthesis of S8a-h:



**Step 1:** A crimp cap vial was charged with the corresponding indole (1.00 eq.), KOt-Bu (1.50 eq.), and dry DMF (0.23 mol·L<sup>-1</sup>) under argon. The obtained mixture was heated to 110°C and 2-fluorobenzaldehyde (1.52 eq.) was added dropwise over 10 minutes. The resulting solution was stirred at 110°C until the reaction was completed (the progress was monitored by <sup>1</sup>H-NMR). The mixture was cooled to room temperature, diluted with water, and extracted with EtOAc (×3). The combined organic layer was washed with brine (×3), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0→70:30) to give the desired aldehyde **S7a-h**.

**Step 2:** Aldehyde **S7a-h** (1.00 eq.), the corresponding boronic acid or ester (1.11 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol%), and K<sub>2</sub>CO<sub>3</sub> (3.00 eq.) were weighed into a 10 or 20 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before a degassed mixture of toluene, H<sub>2</sub>O, ethanol (2 : 2 : 1) (0.12 mol·L<sup>-1</sup>) was added. The resulting mixture was stirred at 80°C for 18 h, then cooled to room temperature, filtered through a thin layer of silica gel and Na<sub>2</sub>SO<sub>4</sub> using EtOAc (15-20 mL). The solvents were removed under reduced pressure and the residue was purified by the silica gel chromatography (cyclohexane/EtOAc 100:0→80:20) to give the desired product **S8a-h**.

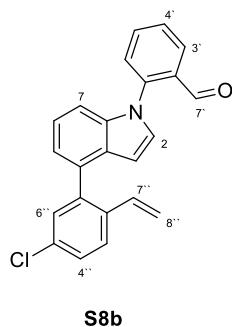
### 2-(4-(2-Vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8a):



Step 1 of the general procedure **B** was performed with 4-bromo-1H-indole (471 mg, 2.40 mmol), 2-fluorobenzaldehyde (453 mg, 3.65 mmol), KOt-Bu (404 mg, 3.60 mmol) over 2 h to give 2-(4-bromo-1H-indol-1-yl)benzaldehyde **S7a** as yellow oil (630 mg, 2.10 mmol, 88%); *R*<sub>f</sub> 0.50 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S7a** (163 mg, 543 μmol) was subjected to the step 2 utilizing (2-vinylphenyl)boronic acid (89.2 mg, 603 μmol) to give **S8a** as yellow oil (160 mg, 495 μmol, 91%); *R*<sub>f</sub> 0.57 (cyclohexane/EtOAc 5:1); *v*<sub>max</sub>(neat): 3055w, 2966w, 2851w, 2752w, 1688s, 1595s, 1485s, 1418s, 1262s, 1169s, 1101m, 1020m, 904w, 822w, 751s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 9.72 (1H, s, CHO), 8.13 (1H, dd, <sup>3</sup>*J* 7.8, <sup>4</sup>*J* 1.4 Hz, C3'*H*), 7.84 – 7.75 (2H, m, C5'*H*, C3''*H*), 7.63 – 7.59 (1H, m, C4'*H*), 7.56 (1H, d, <sup>3</sup>*J* 7.9 Hz, C6'*H*), 7.46 – 7.36 (3H, m, C4''*H*, C5''*H*, C6''*H*), 7.31 – 7.27 (2H, m, C2*H*, C6*H*), 7.20 (1H, dt, <sup>3</sup>*J* 8.4, <sup>4</sup>*J* 0.9 Hz, C7*H*), 7.11 (1H, dd, <sup>3</sup>*J* 7.1, <sup>4</sup>*J* 0.9 Hz, C5*H*), 6.67 (1H, dd, <sup>3</sup>*J* 17.5, <sup>3</sup>*J* 11.0 Hz, C7''*H*), 6.51 (1H, d, <sup>3</sup>*J* 3.2, C3*H*), 5.75 (1H, dd, <sup>3</sup>*J* 17.5, <sup>2</sup>*J* 1.2 Hz, C8''*H*), 5.13 (1H, dd, <sup>3</sup>*J* 11.0, <sup>2</sup>*J* 1.2 Hz, C8''*H*); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 189.9 (C7'), 142.3 (C2'), 139.5 (C1'), 138.4 (C7*a*), 136.2 (C2''), 136.0 (C7'), 135.3 (C5'), 134.1 (C4), 132.2 (C1'), 130.8 (C6''), 129.9 (C2), 128.7 (C3'), 128.49 (C4'), 128.47 (C3*a*), 128.35 (C6'), 127.7 (C4''), 127.6 (C5''), 125.4 (C3''), 123.1

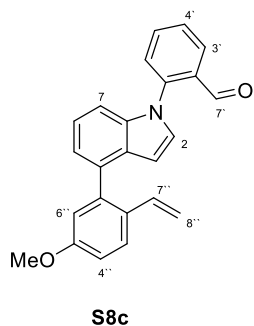
(C6), 122.7 (C5), 114.3 (C8''), 109.3 (C7), 104.5 (C3); ESI-MS:  $m/z$  calcd. for  $C_{23}H_{17}AgNO$  430.0356 found 430.0348  $[M+Ag^+]$ .

### 2-(4-(5-Chloro-2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8b):



Step 1 of the general procedure **B** was performed with 4-bromo-1H-indole (471 mg, 2.40 mmol), 2-fluorobenzaldehyde (453 mg, 3.65 mmol), KOT-Bu (404 mg, 3.60 mmol) over 2 h to give 2-(4-bromo-1H-indol-1-yl)benzaldehyde **S7b** as yellow oil (630 mg, 2.10 mmol, 88%):  $R_f$  0.50 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S7b** (137 mg, 455  $\mu$ mol) was subjected to the step 2 utilizing 2-(5-chloro-2-vinylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (134 mg, 505  $\mu$ mol) to give **S8b** as yellow oil (150 mg, 419  $\mu$ mol, 92%):  $R_f$  0.48 (cyclohexane/EtOAc 5:1);  $\nu_{max}(\text{neat})$ : 3064w, 2855w, 2760w, 1695s, 1598s, 1512m, 1489s, 1395m, 1299w, 1193w, 1109w, 1058w, 913m, 825m, 757s;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 9.70 (1H, s, CHO), 8.13 (1H, dd,  $^3J$  7.8,  $^4J$  1.4 Hz, C3'H), 7.86 – 7.74 (1H, m, C5'H), 7.68 (1H, d,  $^3J$  8.5 Hz, C3''H), 7.61 (1H, tt,  $^3J$  7.8,  $^4J$  1.0 Hz, C4'H), 7.55 (1H, d,  $^3J$  7.8 Hz, C6'H), 7.44 (1H, d,  $^4J$  2.2 Hz, C6''H), 7.38 (1H, ddd,  $^3J$  8.4,  $^4J$  2.3,  $^5J$  0.6 Hz, C4''H), 7.30 (1H, d,  $^3J$  2.9 Hz, C2H), 7.27 (1H, dd,  $^3J$  8.3,  $^3J$  7.1 Hz, C6H), 7.20 (1H, dt,  $^3J$  8.3,  $^4J$  0.9 Hz, C7H), 7.08 (1H, dd,  $^3J$  7.1,  $^4J$  0.9 Hz, C5H), 6.59 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7''H), 6.50 (1H, dd,  $^3J$  2.9,  $^5J$  0.9 Hz, C3H), 5.72 (1H, dd,  $^3J$  17.5,  $^2J$  1.1 Hz, C8''H), 5.15 (1H, dd,  $^3J$  11.0,  $^2J$  1.1 Hz, C8''H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 189.8 (CHO), 142.1 (C1'), 141.0 (C1''), 138.4 (C7a), 135.3 (C5'), 134.9 (C7''), 134.8 (C2''), 133.2 (C5''), 132.6 (C4), 132.3 (C2'), 130.6 (C6''), 130.2 (C2), 128.8 (C3'), 128.6 (C4'), 128.4 (C6'), 128.2 (C7a), 127.8 (C4''), 126.8 (C3''), 123.1 (C6), 122.5 (C5), 114.8 (C8''), 109.8 (C7), 104.2 (C3); ESI-MS:  $m/z$  calcd. for  $C_{23}H_{16}AgClNO$  463.9966 found 463.9965  $[M+Ag^+]$ .

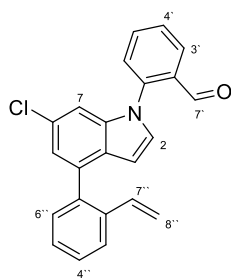
### 2-(4-(5-Methoxy-2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8c):



Step 1 of the general procedure **B** was performed with 4-bromo-1H-indole (471 mg, 2.40 mmol), 2-fluorobenzaldehyde (453 mg, 3.65 mmol), KOT-Bu (404 mg, 3.60 mmol) over 2 h to give 2-(4-bromo-1H-indol-1-yl)benzaldehyde **S7c** as yellow oil (630 mg, 2.10 mmol, 88%):  $R_f$  0.50 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S7c** (100 mg, 334  $\mu$ mol) was subjected to the step 2 utilizing 2-(5-methoxy-2-vinylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (96.4 mg, 371  $\mu$ mol) to give **S8c** as yellow oil (100 mg, 283  $\mu$ mol, 85%):  $R_f$  0.28 (cyclohexane/EtOAc 5:1);  $\nu_{max}(\text{neat})$ : 3060w, 2958w, 2853w, 2758w, 1695s, 1600s, 1516m, 1487s, 1423m, 1296m, 1229m, 1166m, 1043w, 908m, 758m, 732m;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 9.72 (1H, s, CHO), 8.13 (1H, dd,  $^3J$  7.8,  $^4J$  1.5 Hz, C3'H), 7.78 (1H, td,  $^3J$  7.7,  $^4J$  1.5 Hz, C5'H), 7.75 – 7.68 (1H, m, C3''H), 7.60 (1H, t,  $^3J$  7.6 Hz, C4'H), 7.55 (1H, d,  $^3J$  7.9 Hz, C6'H), 7.31 – 7.26 (2H, m, C2H, C6H), 7.20 (1H, d,  $^3J$  8.3 Hz, C7H), 7.17 – 7.07 (1H, m, C5H), 7.00 – 6.94 (2H, m, C4''H, C6''H), 6.58 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7''H),

6.53 (1H, d,  $^3J$  3.2 Hz, C3H), 5.62 (1H, dd,  $^3J$  17.5,  $^2J$  1.1 Hz, C8''H), 5.01 (1H, dd,  $^3J$  11.0,  $^2J$  1.1 Hz, C8''H), 3.85 (3H, s, OCH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 189.9 (CHO), 159.1 (C5''), 142.2 (C1'), 140.8 (C1''), 138.4 (C7a), 135.32 (C5'), 135.29 (C7''), 134.1 (C4), 132.2 (C2'), 130.0 (C2), 129.1 (C2''), 128.7 (C3'), 128.5 (C4'), 128.38 (C3a), 128.35 (C6'), 126.6 (C3''), 123.1 (C6), 122.5 (C5), 115.2 (C6''), 114.2 (C4''), 112.2 (C8''), 109.4 (C7), 104.5 (C3), 55.6 (OCH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>24</sub>H<sub>19</sub>KNO<sub>2</sub> 392.1047 found 392.1048 [M+K<sup>+</sup>].

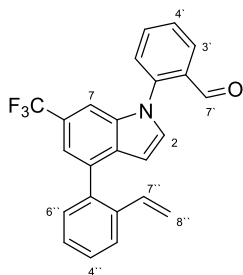
### 2-(6-Chloro-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8d):



**S8d**

Step 1 of the general procedure **B** was performed with 4-bromo-6-chloro-1H-indole (237 mg, 1.03 mmol), 2-fluorobenzaldehyde (194 mg, 1.56 mmol), KO<sup>t</sup>-Bu (173 mg, 1.54 mmol) over 18 h to give 2-(4-bromo-6-chloro-1H-indol-1-yl)benzaldehyde **S7d** as yellow oil (182 mg, 544  $\mu$ mol, 53%): *R<sub>f</sub>* 0.38 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S7d** (182 mg, 544  $\mu$ mol) was subjected to the step 2 utilizing (2-vinylphenyl)boronic acid (89.3 mg, 604  $\mu$ mol) to give **S8d** as yellow oil (192 mg, 537  $\mu$ mol, 99%): *R<sub>f</sub>* 0.39 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$ (neat): 3066w, 2843w, 2752w, 1691s, 1597s, 1507m, 1460m, 1412s, 1126w, 992w, 911s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.69 (1H, s, CHO), 8.13 (1H, dd,  $^3J$  7.8,  $^4J$  1.4 Hz, C3'H), 7.82 – 7.78 (1H, m, C5'H), 7.77 – 7.74 (1H, m, C3''H), 7.67 – 7.60 (1H, m, C4'H), 7.54 (1H, d,  $^3J$  7.8 Hz, C6'H), 7.45 – 7.35 (3H, m C4''H, C5''H, C6''H), 7.25 (1H, d,  $^3J$  3.3 Hz, C2H), 7.17 (1H, dd,  $^4J$  1.7,  $^5J$  0.9 Hz, C7H), 7.11 (1H, d,  $^4J$  1.7 Hz, C5H), 6.63 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7''H), 6.46 (1H, dd,  $^4J$  3.3,  $^5J$  0.9 Hz, C3H), 5.77 (1H, dd,  $^3J$  17.5,  $^2J$  1.2 Hz, C8''H), 5.17 (1H, dd,  $^3J$  11.0,  $^2J$  1.2 Hz, C8''H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 189.5 (CHO), 141.5 (C1'), 138.6 (C7a), 138.2 (C1''), 136.2 (C2''), 135.5 (C7''), 135.4 (C5'), 135.3 (C6), 132.3 (C2'), 130.62 (C6''), 130.60 (C2), 129.03 (C3'), 129.01 (C4), 128.99 (C4'), 128.4 (C6'), 128.2 (C4''), 127.8 (C5''), 127.1 (C3a), 125.5 (C3''), 123.0 (C6), 114.9 (C8''), 109.3 (C7), 104.6 (C3); ESI-MS: *m/z* calcd. for C<sub>23</sub>H<sub>16</sub>AgClNO 463.9966 found 463.9966 [M+Ag<sup>+</sup>].

### 2-(6-(Trifluoromethyl)-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8e):



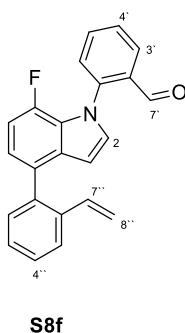
**S8e**

Step 1 of the general procedure **B** was performed with 4-bromo-6-(trifluoromethyl)-1H-indole (248 mg, 940  $\mu$ mol), 2-fluorobenzaldehyde (177 mg, 1.43 mmol), KO<sup>t</sup>-Bu (158 mg, 1.41 mmol) over 18 h to give 2-(4-bromo-6-(trifluoromethyl)-1H-indol-1-yl)benzaldehyde **S7e** as yellow oil (176 mg, 478  $\mu$ mol, 51%): *R<sub>f</sub>* 0.30 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S7e** (176 mg, 478  $\mu$ mol) was subjected to the step 2 utilizing (2-vinylphenyl)boronic acid (78.5 mg, 531  $\mu$ mol) to give **S8e** as yellow oil (156 mg, 399  $\mu$ mol, 83%): *R<sub>f</sub>* 0.36 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$ (neat): 3061w, 2927w, 2852w, 2756w, 1696m, 1598m, 1505m, 1420m, 1368m, 1306m, 1253m, 1174s, 1114s,



992w, 917m, 865w, 765s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.67 (1H, s, CHO), 8.16 (1H, dd,  $^3J$  7.8,  $^4J$  1.4 Hz, C3'H), 7.83 (1H, td,  $^3J$  7.7,  $^4J$  1.4 Hz, C5'H), 7.80 – 7.76 (1H, m, C3''H), 7.71 – 7.63 (1H, m, C4'H), 7.57 (1H, d,  $^3J$  7.9 Hz, C6'H), 7.49 – 7.32 (6H, m, C2H, C4''H, C5''H, C6''H, C5H, C7H), 6.59 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7''H), 6.55 (1H, dd,  $^3J$  3.2,  $^5J$  0.8 Hz, C3H), 5.76 (1H, dd,  $^3J$  17.5,  $^2J$  1.1 Hz, C8''H), 5.16 (1H, dd,  $^3J$  11.0,  $^2J$  1.1 Hz, C8'H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 189.2 (CHO), 141.2 (C1'), 138.2 (C1''), 137.4 (C7a), 136.3 (C2''), 135.5 (C5'), 135.4 (C7''), 134.9 (C4), 132.6 (C2'), 132.4 (C2), 130.8 (C7a), 130.7 (C6''), 129.3 (C4', C3'), 128.5 (C6'), 128.3 (C4''), 127.8 (C5''), 125.6 (C3''), 119.1 (q,  $^3J_{\text{CF}}$  3.2 Hz, C5), 115.1 (C8''), 106.7 (q,  $^3J_{\text{CF}}$  3.9 Hz, C7), 104.6 (C3);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  –60.63; ESI-MS:  $m/z$  calcd. for  $\text{C}_{24}\text{H}_{16}\text{AgF}_3\text{NO}$  498.0229 found 498.0224 [ $\text{M}+\text{Ag}^+$ ].

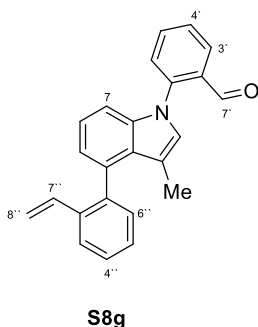
### 2-(7-Fluoro-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8f):



Step 1 of the general procedure **B** was performed with 4-bromo-7-fluoro-1H-indole (161 mg, 750  $\mu\text{mol}$ ), 2-fluorobenzaldehyde (141 mg, 1.14 mmol),  $\text{KOt-Bu}$  (126 mg, 1.13 mmol) over 3 h to give 2-(4-bromo-7-fluoro-1H-indol-1-yl)benzaldehyde **S7f** as yellow solid (143 mg, 449  $\mu\text{mol}$ , 60%):  $R_f$  0.45 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S7f** (127 mg, 400  $\mu\text{mol}$ ) was subjected to the step 2 utilizing (2-vinylphenyl)boronic acid (65.7 mg, 444  $\mu\text{mol}$ ) to give **S8f** as yellow oil (130 mg, 381  $\mu\text{mol}$ , 95%):  $R_f$  0.45 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}(\text{neat})$ : 3046w, 2851w, 1691m, 1597m, 1500m, 1404w, 1239w, 1191w, 1105w, 994w, 905w, 821w, 769w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.82 (1H, s, CHO), 8.08 (1H, dd,  $^3J$  7.8,  $^4J$  1.5 Hz, C3'H), 7.79 – 7.67 (2H, m, C5'H, C3''H), 7.65 – 7.58 (1H, m, C4'H), 7.53 (1H, d,  $^3J$  7.6 Hz, C6'H), 7.49 – 7.32 (3H, m, C4''H, C5''H, C6''H), 7.19 (1H, d,  $^3J$  3.2 Hz, C2H), 7.03 – 6.91 (2H, m, C5H, C6H), 6.63 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7''H), 6.49 (1H, d,  $^3J$  3.2, C3H), 5.74 (1H, dd,  $^3J$  17.5,  $^2J$  1.2 Hz, C8''H), 5.14 (1H, dd,  $^3J$  11.0,  $^2J$  1.2 Hz, C8'H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 189.5 (CHO), 149.41 (d,  $^1J_{\text{CF}}$  246.6 Hz, C7), 142.8 (C1'), 136.4 (C2''), 135.8 (C7''), 134.5 (C5'), 132.5 (C2'), 132.2 ( $^3J_{\text{CF}}$  3.8 Hz, C3a), 138.8 (C1''), 131.5 (C2), 130.9 (C6''), 130.1 (C4), 128.7 (C4', C6'), 128.3 (C3'), 127.8 (C4''), 127.7 (C5''), 125.6 (d,  $^2J_{\text{CF}}$  7.7 Hz, C7a), 125.4 (C3''), 122.7 (d,  $^3J_{\text{CF}}$  6.3 Hz, C5), 114.5 (C8''), 108.6 (d,  $^2J_{\text{CF}}$  17.9 Hz, C6), 105.3 (C3); ESI-MS:  $m/z$  calcd. for  $\text{C}_{23}\text{H}_{17}\text{FNO}$  342.1289 found 342.1286 [ $\text{M}+\text{H}^+$ ].

### 2-(3-Methyl-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8g):

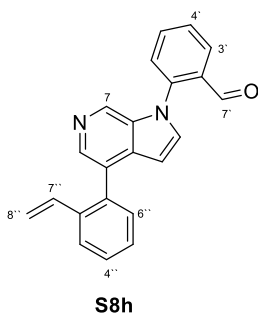
Step 1 of the general procedure **B** was performed with 4-bromo-3-methyl-1H-indole (237 mg, 1.13 mmol), 2-fluorobenzaldehyde (213 mg, 1.71 mmol),  $\text{KOt-Bu}$  (190 mg, 1.69 mmol) over 18 h to give 2-(4-bromo-3-methyl-1H-indol-1-yl)benzaldehyde **S7g** as yellow oil (223 mg, 710  $\mu\text{mol}$ , 63%):  $R_f$  0.48 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S7g** (360 mg, 1.15 mmol) was subjected to the step



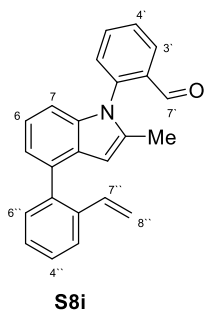
2 utilizing (2-vinylphenyl)boronic acid (188 mg, 1.27 mmol) to give **S8g** as yellow solid (95.0 mg, 282  $\mu\text{mol}$ , 25%, m.p. 70.0 – 70.6°C) after NP-prep-HPLC (from hexane/EtOAc 98:2 to 80:20, 18 mL/min, 40°C):  $R_f$  0.60 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}(\text{neat})$ : 3058w, 2943w, 2922w, 2857w, 2750w, 1829w, 1692s, 1598s, 1488s, 1457m, 1422s, 1300w, 1263w, 1160w, 1096w, 1049w, 1019w, 909m, 752s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.74 (1H, s, CHO), 8.11 (1H, dd,  $^3J$  7.8,  $^4J$  1.5 Hz, C3'H), 7.75 (1H, td,  $^3J$  7.7,  $^4J$  1.5 Hz, C5'H), 7.71 (1H, d,  $^3J$  7.7 Hz, C3''H), 7.60 – 7.54 (1H, m, C4'H), 7.53 (1H, d,  $^3J$  7.7 Hz, C6'H), 7.44 – 7.38 (1H, m, C4''H), 7.36 – 7.32 (2H, m, C5''H, C6''H), 7.22 (1H, dd,  $^3J$  8.3,  $^3J$  6.9 Hz, C6H), 7.17 (1H, dd,  $^3J$  8.3,  $^4J$  1.2 Hz, C7H), 7.02 (1H, q,  $^4J$  1.1 Hz, C2H), 6.97 (1H, dd,  $^3J$  6.9,  $^4J$  1.2 Hz, C5H), 6.51 (1H, dd,  $^3J$  17.4,  $^3J$  11.0 Hz, C7''H), 5.70 (1H, dd,  $^3J$  17.6,  $^2J$  1.2 Hz, C8''H), 5.08 (1H, dd,  $^3J$  11.0,  $^2J$  1.2 Hz, C8''H), 1.74 (3H, d,  $^4J$  1.1 Hz, C3-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 190.2 (CHO), 142.5 (C1'), 140.0 (C1''), 139.0 (C7a), 136.8 (C2''), 135.6 (C7''), 135.2 (C5'), 134.7 (C4), 132.1 (C2'), 130.8 (C6''), 128.6 (C3'), 128.4 (C2), 128.2 (C6'), 128.1 (C4'), 127.8 (C4''), 127.3 (C3a), 127.0 (C5''), 124.3 (C3''), 122.8 (C6), 122.2 (C5), 114.6 (C8''), 114.3 (C3), 109.3 (C7), 11.4 (C3-CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{24}\text{H}_{19}\text{AgNO}$  444.0512 found 444.0507 [ $\text{M}+\text{Ag}^+$ ].

## 2-(4-(2-Vinylphenyl)-1H-pyrrolo[2,3-c]pyridin-1-yl)benzaldehyde (S8h):

Step 1 of the general procedure **B** was performed with 4-bromo-1H-pyrrolo[2,3-c]pyridine (256 mg, 1.30 mmol), 2-fluorobenzaldehyde (245 mg, 1.98 mmol),  $\text{KOt-Bu}$  (219 mg, 1.95 mmol) over 18 h to give 2-(4-bromo-1H-pyrrolo[2,3-c]pyridin-1-yl)benzaldehyde **S7h** as yellow oil (260 mg, 863  $\mu\text{mol}$ , 66%). The obtained aldehyde **S7h** (102 mg, 340  $\mu\text{mol}$ ) was subjected to the step 2 utilizing (2-vinylphenyl)boronic acid (55.8 mg, 377  $\mu\text{mol}$ ) to give **S8h** as yellow oil (96.0 mg, 296  $\mu\text{mol}$ , 87%):  $R_f$  0.41 (cyclohexane/EtOAc 1:1);  $\nu_{\text{max}}(\text{neat})$ : 3012w, 2853w, 2751w, 1696m, 1598m, 1500m, 1425m, 1308w, 1262w, 1218w, 1172w, 1080w, 995w, 877w, 751s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.75 (1H, s, CHO), 8.61 (1H, s, C7H), 8.29 (1H, s, C5H), 8.16 (1H, dd,  $^3J$  7.8,  $^4J$  1.6 Hz, C3'H), 7.83 (1H, td,  $^3J$  7.7,  $^4J$  1.6 Hz, C5'H), 7.78 (1H, d,  $^3J$  7.8 Hz, C3''H), 7.68 (1H, t,  $^3J$  7.8 Hz, C4'H), 7.60 (1H, d,  $^3J$  7.7 Hz, C6'H), 7.49 – 7.38 (4H, m, C2H, C4''H, C5''H, C6''H), 6.64 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7''H), 6.58 – 6.56 (1H, m, C3H), 5.77 (1H, dd,  $^3J$  17.5,  $^2J$  1.0 Hz, C8''H), 5.18 (1H, dd,  $^3J$  11.0,  $^2J$  1.0 Hz, C8''H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 189.0 (CHO), 140.8 (C1'), 136.7 (C2''), 136.1 (C1''), 135.48 (C7''), 135.45 (C5'), 135.0 (C7a), 133.6 (C3a), 133.4 (C2), 132.6 (C7), 132.2 (C2'), 130.9 (C6''), 129.5 (C3'), 129.3 (C4'), 128.8 (C4), 128.4 (C6'), 128.3 (C4''), 127.9 (C5''), 125.7 (C3''), 115.2 (C8''), 103.9 (C3); ESI-MS:  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{17}\text{N}_2\text{O}$  325.1335 found 325.1341 [ $\text{M}+\text{H}^+$ ].

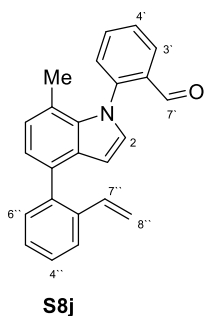


### 2-(2-Methyl-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (**S8i**):



Step 1 of the general procedure **B** was performed with 4-bromo-2-methyl-1H-indole (290 mg, 1.38 mmol), 2-fluorobenzaldehyde (260 mg, 2.10 mmol), KOt-Bu (232 mg, 2.07 mmol) over 18 h to give 2-(4-bromo-2-methyl-1H-indol-1-yl)benzaldehyde **S7i** as yellow oil (230 mg, 732  $\mu$ mol, 53%);  $R_f$  0.50 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S7i** (229 mg, 730  $\mu$ mol) was subjected to the step 2 utilizing (2-vinylphenyl)boronic acid (120 mg, 810  $\mu$ mol) to give **S8i** as yellow oil (211 mg, 625  $\mu$ mol, 86%);  $R_f$  0.50 (cyclohexane/EtOAc 5:1);  $\nu_{\max}$ (neat): 3058w, 2920w, 2852w, 2752w, 1695s, 1598m, 1555w, 1488m, 1422m, 1321w, 1266m, 1233w, 1193w, 1162w, 1085w, 1054w, 998<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.47 (1H, s, CHO), 8.15 (1H, dd, <sup>3</sup>J 7.8, <sup>4</sup>J 1.4 Hz, C3'H), 7.81 (1H, td, <sup>3</sup>J 7.6, <sup>4</sup>J 1.7 Hz, C5'H), 7.76 (1H, dd, <sup>3</sup>J 7.6, <sup>4</sup>J 1.6 Hz, C3''H), 7.70 – 7.61 (1H, m, C4'H), 7.46 (1H, d, <sup>3</sup>J 7.8 Hz, C6'H), 7.45 – 7.34 (3H, m, C4''H, C5''H, C6''H), 7.14 (1H, dd, <sup>3</sup>J 8.1, <sup>3</sup>J 7.3 Hz, C6H), 7.04 (1H, dd, <sup>3</sup>J 7.3, <sup>4</sup>J 0.9 Hz, C5H), 6.89 (1H, dt, <sup>3</sup>J 8.1, <sup>4</sup>J 0.9 Hz, C7H), 6.69 (1H, dd, <sup>3</sup>J 17.5, <sup>3</sup>J 11.0 Hz, C7''H), 6.30 – 6.23 (1H, m, C3H), 5.74 (1H, dd, <sup>3</sup>J 17.5, <sup>2</sup>J 1.3 Hz, C8''H), 5.13 (1H, dd, <sup>3</sup>J 11.0, <sup>2</sup>J 1.3 Hz, C8''H), 2.20 (3H, d, <sup>4</sup>J 1.0 Hz, C2-CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 190.0 (CHO), 140.9 (C1'), 139.9 (C7a), 139.8 (C1''), 138.0 (C2), 136.2 (C2''), 136.0 (C7''), 135.4 (C5'), 134.0 (C2'), 132.7 (C4), 130.8 (C6''), 130.2 (C6'), 129.3 (C4'), 128.6 (C3'), 127.9 (C3a), 127.58 (C5''), 127.55 (C4''), 125.3 (C3''), 122.5 (C5), 121.8 (C6), 114.1 (C8''), 109.0 (C7), 102.3 (C3); 13.3 (CH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>24</sub>H<sub>20</sub>NO 338.1539 found 338.1538 [M+H<sup>+</sup>].

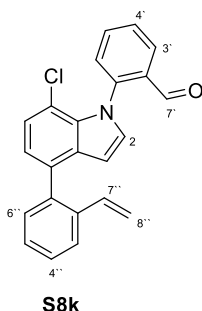
### 2-(7-Methyl-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (**S8j**):



Step 1 of the general procedure **B** was performed with 4-bromo-7-methyl-1H-indole (158 mg, 750  $\mu$ mol), 2-fluorobenzaldehyde (141 mg, 1.14 mmol), KOt-Bu (126 mg, 1.13 mmol) over 18 h to give 2-(4-bromo-7-methyl-1H-indol-1-yl)benzaldehyde **S7j** as yellow oil (75.0 mg, 239  $\mu$ mol, 32%);  $R_f$  0.40 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S7j** (67.5 mg, 215  $\mu$ mol) was subjected to the step 2 utilizing (2-vinylphenyl)boronic acid (35.3 mg, 239  $\mu$ mol) to give **S8j** as yellow oil (68.0 mg, 202  $\mu$ mol, 94%);  $R_f$  0.51 (cyclohexane/EtOAc 5:1);  $\nu_{\max}$ (neat): 3059w, 3021w, 2974w, 2922w, 2858w, 2752w, 1696s, 1597s, 1486m, 1457m, 1401m, 1268w, 1191w, 1151w, 1110w, 1039w, 994w, 903w, 821m, 772s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.52 (1H, s, CHO), 8.06 (1H, dd, <sup>3</sup>J 7.8, <sup>4</sup>J 1.5 Hz, C3'H), 7.79 – 7.70 (2H, m, C3''H, C5'H), 7.62 (1H, t, <sup>3</sup>J 7.6 Hz, C4'H), 7.54 (1H, d, <sup>3</sup>J 7.9 Hz, C6'H), 7.46 – 7.34 (3H, m, C4''H, C5''H, C6''H), 7.13 (1H, d, <sup>3</sup>J 3.3 Hz, C2H), 7.00 (2H, s, C5H, C6H), 6.67 (1H, dd, <sup>3</sup>J 17.5, <sup>3</sup>J 11.0 Hz, C7''H), 6.45 (1H, d, <sup>3</sup>J 3.3 Hz, C3H), 5.73 (1H, dd, <sup>3</sup>J 17.5, <sup>2</sup>J 1.2 Hz, C8''H), 5.12 (1H, dd, <sup>3</sup>J 11.0, <sup>2</sup>J 1.2 Hz, C8''H), 1.96 (3H, s, C7-CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 189.9 (CHO), 144.3 (C1'), 139.7 (C1''), 137.2 (C7a), 136.3 (C2''), 136.1 (C7''), 134.4 (C5'), 134.2 (C2'), 132.2 (C4), 131.3 (C2), 130.9 (C6''), 130.0 (C6'), 129.2 (C4'), 128.9 (C3a), 127.60 (C3'/C4'), 127.56 (C3'/C4''),

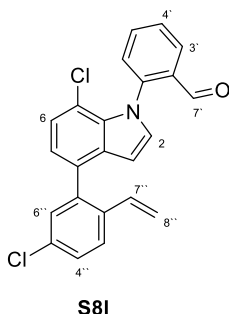
127.54 (C5''), 125.4 (C6), 125.3 (C3''), 122.6 (C5), 120.5 (C7), 114.1 (C8''), 104.2 (C3), 19.2 (C7-CH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>24</sub>H<sub>20</sub>NO 338.1539 found 338.1531 [M+H<sup>+</sup>].

## 2-(7-Chloro-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8k):



Step 1 of the general procedure **B** was performed with 4-bromo-7-chloro-1H-indole (254 mg, 1.10 mmol), 2-fluorobenzaldehyde (208 mg, 1.67 mmol), KOt-Bu (185 mg, 1.65 mmol) over 18 h to give 2-(4-bromo-7-chloro-1H-indol-1-yl)benzaldehyde **S7k** (110 mg, 329 μmol, 30%): R<sub>f</sub> 0.57 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S7k** (136 mg, 406 μmol) was subjected to the step 2 utilizing (2-vinylphenyl)boronic acid (66.8 mg, 451 μmol) to give **S8k** as yellow oil (120 mg, 335 μmol, 83%): R<sub>f</sub> 0.44 (cyclohexane/EtOAc 5:1); ν<sub>max</sub>(neat): 2964w, 2924w, 2855w, 2753w, 1696s, 1598m, 1492m, 1399m, 1336w, 1261w, 1193w, 1164m, 1101m, 1038w, 822w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 9.60 (1H, s, CHO), 8.05 (1H, dd, <sup>3</sup>J 7.7, <sup>4</sup>J 1.5 Hz, C3'H), 7.85 – 7.67 (2H, m, C5'H, C3''H), 7.63 (1H, t, <sup>3</sup>J 7.7 Hz, C4'H), 7.52 (1H, d, <sup>3</sup>J 7.1 Hz, C6'H), 7.22 (1H, d, <sup>3</sup>J 7.8 Hz, C6H), 7.17 (1H, d, <sup>3</sup>J 3.2 Hz, C2H), 7.01 (1H, d, <sup>3</sup>J 7.8 Hz, C5H), 6.62 (1H, dd, <sup>3</sup>J 17.5, <sup>3</sup>J 11.0 Hz, C7''H), 6.47 (1H, d, <sup>3</sup>J 3.2 Hz, C3H), 5.74 (1H, dd, <sup>3</sup>J 17.5, <sup>2</sup>J 1.1 Hz, C8''H), 5.15 (1H, d, <sup>3</sup>J 11.0 Hz, C8''H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 189.5 (CHO), 142.8 (C1'), 138.6 (C1''), 136.1 (C2''), 135.7 (C7''), 134.2 (C5'), 134.0 (C2'), 133.1 (C7a), 132.2 (C2), 130.8 (C4, C6''), 130.1 (C6'), 129.3 (C4'), 128.0 (C4''), 127.7 (C5''), 127.6 (C3'), 125.5 (C3''), 124.1 (C6), 123.2 (C5), 116.3 (C7), 114.6 (C8''), 104.5 (C3); ESI-MS: m/z calcd. for C<sub>23</sub>H<sub>16</sub>ClNO 358.0993 found 358.0988 [M+H<sup>+</sup>].

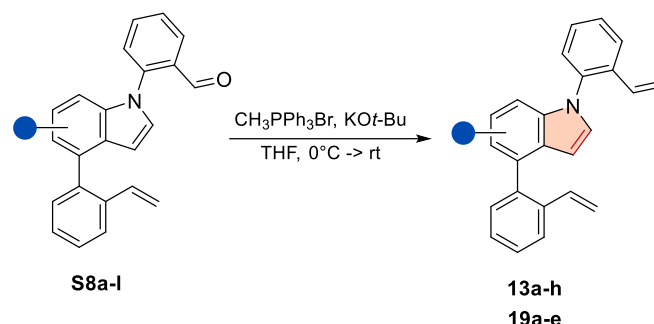
## 2-(7-Chloro-4-(5-chloro-2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8l):



Step 1 of the general procedure **B** was performed with 4-bromo-7-chloro-1H-indole (254 mg, 1.10 mmol), 2-fluorobenzaldehyde (208 mg, 1.67 mmol), KOt-Bu (185 mg, 1.65 mmol) over 18 h to give 2-(4-bromo-7-chloro-1H-indol-1-yl)benzaldehyde **S7k** (110 mg, 329 μmol, 30%): R<sub>f</sub> 0.57 (cyclohexane/EtOAc 5:1). The obtained aldehyde **S7k** (145 mg, 433 μmol) was subjected to the step 2 utilizing 2-(5-chloro-2-vinylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (127 mg, 481 μmol) to give **S8l** as yellow oil (80.0 mg, 204 μmol, 47%) after NP-prep-HPLC (from hexane/EtOAc 98:2 to 80:20, 18 mL/min, 40°C): R<sub>f</sub> 0.57 (cyclohexane/EtOAc 5:1); ν<sub>max</sub>(neat): 3067w, 2848w, 2754w, 1696w, 1597w, 1492w, 1403w, 1264w, 1194w, 1166w, 1101w, 990w, 912w, 823w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 9.60 (1H, s, CHO), 8.06 (1H, dd, <sup>3</sup>J 7.8, <sup>4</sup>J 1.5 Hz, C3'H), 7.72 (1H, td, <sup>3</sup>J 7.6, <sup>4</sup>J 1.5 Hz, C5'H), 7.67 (1H, d, <sup>3</sup>J 8.3 Hz, C3''H), 7.66 – 7.61 (1H, m, C4'H), 7.52 (1H, d, <sup>3</sup>J 7.6 Hz, C6'H), 7.42 – 7.37 (2H, m, C4''H, C6''H), 7.23 (1H, d, <sup>3</sup>J 7.8 Hz, C6H), 7.20 (1H, d, <sup>3</sup>J 3.3 Hz, C2H), 6.99 (1H, d, <sup>3</sup>J 7.8 Hz, C5H), 6.54 (1H, dd, <sup>3</sup>J 17.5, <sup>3</sup>J 11.0 Hz, C7''H), 6.46 (1H, d, <sup>3</sup>J 3.3 Hz, C3H), 5.72 (1H, dd, <sup>3</sup>J 17.5, <sup>2</sup>J 1.0 Hz, C8''H), 5.16 (1H, dd, <sup>3</sup>J 11.0, <sup>2</sup>J 1.0 Hz, C8''H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

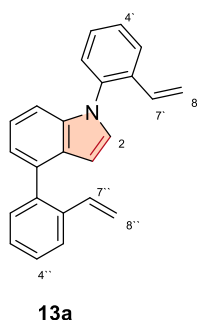
$\delta$  = 189.4 (CHO), 142.6 ( $C1'$ ), 140.1 ( $C1''$ ), 134.9 ( $C2''$ ), 134.7 ( $C7''$ ), 134.2 ( $C5'$ ), 134.1 ( $C2'$ ), 133.6 ( $C7a$ ), 133.3 ( $C5''$ ), 132.4 ( $C2$ ), 131.6 ( $C4$ ), 130.6 ( $C6''$ ), 130.5 ( $C3a$ ), 130.1 ( $C6'$ ), 129.4 ( $C4'$ ), 128.1 ( $C4''$ ), 127.8 ( $C3'$ ), 126.8 ( $C3''$ ), 124.2 ( $C6$ ), 123.0 ( $C5$ ), 116.8 ( $C7$ ), 115.2 ( $C8''$ ), 104.2 ( $C3$ ); ESI-MS:  $m/z$  calcd. for  $C_{23}H_{16}Cl_2NO$  392.0603 found 392.0600  $[M+H]^+$ .

### General Procedure C for the synthesis of 13a-i, 19a-e:



To a suspension of methyltriphenylphosphonium-bromide (1.40 eq. or 2.00 eq.) in THF (0.10 mol·L<sup>-1</sup> with regard to aldehyde **S8a-l**) at 0°C was added dry KOt-Bu (1.60 eq. or 2.30 eq.) under argon. After stirring the resulting suspension for 50 min at 0°C, a solution of the corresponding aldehyde **S8a-l** (1.00 eq.) in THF (0.10 mol·L<sup>-1</sup>) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 18 h. Water was then added and the mixture was extracted with EtOAc (×3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0→70:30) to give the desired product.

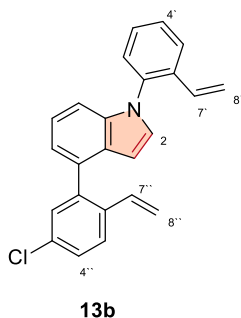
### 1,4-Bis(2-vinylphenyl)-1H-indole (13a):



Prepared according to the general procedure **C** using 2-(4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde **S8a** (158 mg, 490  $\mu$ mol, 1.00 eq.), methyltriphenylphosphonium-bromide (245 mg, 686  $\mu$ mol, 1.40 eq.) and KOt-Bu (88.0 mg, 784  $\mu$ mol, 1.60 eq.) to give **13a** as colorless oil (70.0 mg, 218  $\mu$ mol, 44%):  $R_f$  0.71 (cyclohexane/EtOAc 5:1);  $\nu_{max}$  (neat): 3058w, 3024w, 2925w, 1830w, 1709w, 1597m, 1512m, 1490s, 1473m, 1421s, 1299m, 1170m, 1056w, 922m, 907m, 752s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.80 – 7.73 (2H, m, C3'H, C3''H), 7.49 – 7.34 (6H, m, C4'H, C5'H, C6'H, C4''H, C5''H, C6''H), 7.22 (1H, dd, <sup>3</sup>J 8.3, <sup>3</sup>J 7.1 Hz, C6H), 7.17 (1H, d, <sup>3</sup>J 3.2 Hz, C2H), 7.10 (1H, dd, <sup>3</sup>J 8.3, <sup>4</sup>J 0.9 Hz, C7H), 7.06 (1H, dd, <sup>3</sup>J 7.1, <sup>4</sup>J 0.9 Hz, C5H), 6.72 (1H, dd, <sup>3</sup>J 17.5, <sup>3</sup>J 11.0 Hz, C7''H), 6.43 (1H, dd, <sup>3</sup>J 3.2, <sup>5</sup>J 0.8 Hz, C3H), 6.37 (1H, dd, <sup>3</sup>J 17.5, <sup>3</sup>J 11.0 Hz, C7'H), 5.75 (1H, dd, <sup>3</sup>J 17.5, <sup>2</sup>J 1.0 Hz, C8'H), 5.74 (1H, dd, <sup>3</sup>J 17.5, <sup>2</sup>J 1.3 Hz, C8''H), 5.22 (1H, dd, <sup>3</sup>J 11.0, <sup>2</sup>J 1.0 Hz, C8'H), 5.12 (1H, dd, <sup>3</sup>J 11.0, <sup>2</sup>J 1.3 Hz, C8''H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 140.0 ( $C1'$ ), 137.5 ( $C7a$ ), 137.3 ( $C1'$ ), 136.20 ( $C2''$ ), 136.18 ( $C7''$ ), 135.2 ( $C2'$ ), 133.5 ( $C4$ ), 132.4 ( $C7'$ ), 130.9 ( $C6''$ ), 129.6 ( $C2$ ), 128.7 ( $C5'$ ), 128.38 ( $C4'/C4''$ ), 128.36 ( $C4'/C4''$ ), 128.2 ( $C3a$ ), 127.6 ( $C5''$ ), 127.5 ( $C6'$ ), 126.4 ( $C3'$ ), 125.3 ( $C3''$ ), 122.1 ( $C6$ ), 121.9 ( $C5$ ), 116.4 ( $C8'$ ), 114.0

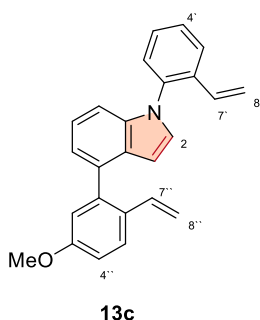
(C8''), 110.1 (C7), 103.0 (C3); ESI-MS:  $m/z$  calcd. for  $C_{24}H_{20}N$  322.1590 found 322.1586  $[M+H^+]$ .

#### 4-(5-Chloro-2-vinylphenyl)-1-(2-vinylphenyl)-1H-indole (13b):



Prepared according to the general procedure C using 2-(4-(5-chloro-2-vinylphenyl)-1H-indol-1-yl)benzaldehyde **S8b** (147 mg, 410  $\mu$ mol, 1.00 eq.), methyltriphenylphosphonium-bromide (205 mg, 574  $\mu$ mol, 1.40 eq.) and KOt-Bu (73.6 mg, 656  $\mu$ mol, 1.60 eq.) to give **13b** as yellow oil (77.0 mg, 216  $\mu$ mol, 53%);  $R_f$  0.64 (cyclohexane/EtOAc 5:1);  $\nu_{max}$  (neat): 3086w, 3062w, 2986w, 1898w, 1836w, 1702w, 1630m, 1590m, 1512s, 1491s, 1425s, 1298m, 1267w, 1171m, 1100w, 991w, 913s, 825m, 755s;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 7.78 (1H, dd,  $^3J$  7.7,  $^4J$  1.6 Hz, C3'H), 7.68 (1H, d,  $^3J$  8.5 Hz, C3''H), 7.50 – 7.33 (5H, m, C4'H, C5'H, C6'H, C4''H, C6''H), 7.21 (1H, dd,  $^3J$  8.2,  $^3J$  7.1 Hz, C6H), 7.19 (1H, d,  $^3J$  3.2 Hz, C2H), 7.11 (1H, dt,  $^3J$  8.2,  $^4J$  0.9 Hz, C7H), 7.03 (1H, dd,  $^3J$  7.1,  $^4J$  0.9 Hz, C5H), 6.64 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7''H), 6.42 (1H, dd,  $^3J$  3.2,  $^5J$  0.9 Hz, C3H), 6.34 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7'H), 5.75 (1H, dd,  $^3J$  17.5,  $^2J$  1.0 Hz, C8'H), 5.22 (1H, dd,  $^3J$  11.0,  $^2J$  1.0 Hz, C8'H), 5.72 (1H, dd,  $^3J$  17.5,  $^2J$  1.1 Hz, C8''H), 5.14 (1H, dd,  $^3J$  11.0,  $^2J$  1.1 Hz, C8''H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 141.5 (C1'), 137.5 (C7a), 137.1 (C1'), 135.3 (C2'), 135.1 (C7''), 134.8 (C2''), 133.1 (C5'), 132.3 (C7'), 132.1 (C4), 130.7 (C6''), 129.9 (C2), 128.7 (C5'), 128.5 (C4'), 128.4 (C6'), 127.9 (C3a), 127.6 (C4''), 126.7 (C3''), 126.4 (C3'), 122.1 (C6), 121.8 (C5), 116.5 (C8'), 114.5 (C8''), 110.6 (C7), 102.7 (C3); ESI-MS:  $m/z$  calcd. for  $C_{24}H_{18}AgClN$  462.0173 found 462.0177  $[M+Ag^+]$ .

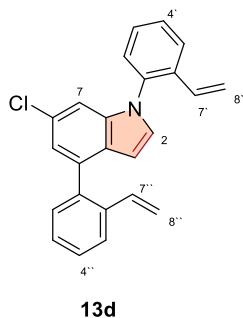
#### 4-(5-Methoxy-2-vinylphenyl)-1-(2-vinylphenyl)-1H-indole (13c):



Prepared according to the general procedure C using 2-(4-(5-methoxy-2-vinylphenyl)-1H-indol-1-yl)benzaldehyde **S8c** (110 mg, 311  $\mu$ mol, 1.00 eq.), methyltriphenylphosphonium-bromide (167 mg, 467  $\mu$ mol, 1.50 eq.) and KOt-Bu (59.4 mg, 529  $\mu$ mol, 1.70 eq.) to give **13c** as colorless oil (60.0 mg, 171  $\mu$ mol, 55%);  $R_f$  0.57 (cyclohexane/EtOAc 6:1);  $\nu_{max}$  (neat): 3074w, 2960w, 2832w, 1601m, 1566w, 1488s, 1426m, 1296m, 1229m, 1166m, 1045w, 994w, 920w;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 7.78 (1H, dd,  $^3J$  7.7,  $^4J$  1.6 Hz, C3'H), 7.70 (1H, d,  $^3J$  8.7 Hz, C3''H), 7.49 – 7.36 (3H, m, C4'H, C5'H, C6'H), 7.22 (1H, dd,  $^3J$  8.2,  $^3J$  7.2 Hz, C6H), 7.18 (1H, d,  $^3J$  3.2 Hz, C2H), 7.10 (1H, dt,  $^3J$  8.2,  $^4J$  0.9 Hz, C7H), 7.06 (1H, dd,  $^3J$  7.2,  $^4J$  0.9 Hz, C5H), 7.01 (1H, d,  $^4J$  2.7 Hz, C6''H), 6.97 (1H, dd,  $^3J$  8.7,  $^4J$  2.7 Hz, C4''H), 6.63 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7''H), 6.45 (1H, dd,  $^3J$  3.2,  $^5J$  0.8 Hz, C3H), 6.37 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7'H), 5.76 (1H, dd,  $^3J$  17.5,  $^2J$  1.0 Hz, C8'H), 5.61 (1H, dd,  $^3J$  17.5, 1.3 Hz, C8''H), 5.22 (1H, dd,  $^3J$  11.0,  $^2J$  1.0 Hz, C8'H), 5.01 (1H, dd,  $^3J$  11.0,  $^2J$  1.3 Hz, C8''H), 3.85 (3H, s, OCH<sub>3</sub>);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 158.9 (C5'), 141.1 (C1'), 137.3 (C7a), 137.1 (C1'), 135.4 (C7''), 135.1 (C2'), 133.4

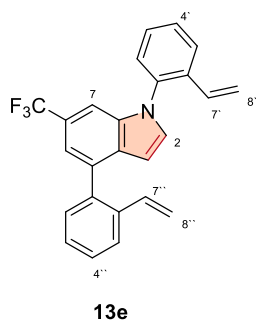
(C4), 132.2 (C7'), 129.5 (C2), 129.0 (C2''), 128.6 (C5'), 128.2 (C4'/C6'), 127.9 (C3a), 126.4 (C3''/C3'), 126.3 (C3''/C3'), 121.9 (C6), 121.6 (C5), 116.3 (C8'), 115.1 (C6''), 113.9 (C4''), 111.7 (C8''), 110.0 (C7), 102.8 (C3), 55.4 (OCH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>25</sub>H<sub>21</sub>AgNO 458.0669 found 458.0674 [M+Ag<sup>+</sup>].

### 6-Chloro-1,4-bis(2-vinylphenyl)-1H-indole (13d):



Prepared according to the general procedure **C** using 2-(6-chloro-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde **S8d** (190 mg, 531 μmol, 1.00 eq.), methyltriphenylphosphonium-bromide (379 mg, 1.06 mmol, 2.00 eq.) and KO<sup>t</sup>-Bu (137 mg, 1.22 mmol, 2.30 eq.) to give **13d** as yellow oil (120 mg, 337 μmol, 64%): R<sub>f</sub> 0.75 (cyclohexane/EtOAc 5:1); ν<sub>max</sub> (neat): 3063w, 3019w, 2925w, 1832w, 1722w, 1592w, 1505m, 1458m, 1415m, 1322m, 1215w, 1166m, 1076w, 991w, 912s, 855w, 755s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.81 – 7.73 (2H, m, C3'H, C3''H), 7.51 – 7.46 (1H, m, C4'H), 7.45 – 7.35 (5H, m, C5'H, C6'H, C4''H, C5''H, C6''H), 7.15 (1H, d, <sup>3</sup>J 3.2 Hz, C2H), 7.08 (1H, dd, <sup>3</sup>J 1.8, <sup>5</sup>J 0.9 Hz, C7H), 7.05 (1H, d, <sup>3</sup>J 1.8 Hz, C5H), 6.68 (1H, dd, <sup>3</sup>J 17.5, <sup>3</sup>J 11.0 Hz, C7''H), 6.38 (1H, dd, <sup>3</sup>J 3.2, <sup>5</sup>J 0.9 Hz, C3H), 6.32 (1H, dd, <sup>3</sup>J 17.5, <sup>3</sup>J 11.0 Hz, C7'H), 5.76 (1H, dd, <sup>3</sup>J 17.5, <sup>2</sup>J 1.0 Hz, C8'H), 5.75 (1H, dd, <sup>3</sup>J 17.5, <sup>2</sup>J 1.2 Hz, C8''H), 5.25 (1H, dd, <sup>3</sup>J 11.1, <sup>2</sup>J 1.0 Hz, C8'H) 5.16 (1H, dd, <sup>3</sup>J 11.0, <sup>2</sup>J 1.2 Hz, C8''H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 138.6 (C1''), 137.7 (C7a), 136.7 (C1'), 136.2 (C2''), 135.7 (C7'), 135.3 (C2'), 134.7 (C4), 132.0 (C7'), 130.7 (C6''), 130.2 (C2), 128.84 (C4'/C5'), 128.77 (C4'/C5'), 128.3 (C6'), 128.1 (C6), 128.0 (C4''), 127.7 (C5''), 126.8 (C3a), 126.6 (C3'), 125.4 (C3''), 122.3 (C5), 116.9 (C8''), 114.6 (C8'), 110.0 (C7), 103.1 (C3); ESI-MS: m/z calcd. for C<sub>24</sub>H<sub>18</sub>AgClN 462.0173 found 462.0165 [M+Ag<sup>+</sup>].

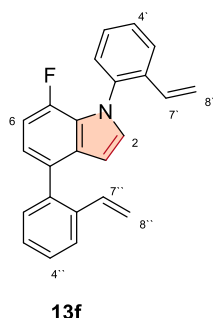
### 6-(Trifluoromethyl)-1,4-bis(2-vinylphenyl)-1H-indole (13e):



Prepared according to the general procedure **C** using 2-(6-(trifluoromethyl)-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde **S8e** (150 mg, 383 μmol, 1.00 eq.), methyltriphenylphosphonium-bromide (274 mg, 766 μmol, 2.00 eq.) and KO<sup>t</sup>-Bu (98.9 mg, 881 μmol, 2.30 eq.) to give **13e** as a white solid (130 mg, 334 μmol, 87%, m.p. 85.2 – 86.2°C): R<sub>f</sub> 0.69 (cyclohexane/EtOAc 5:1); ν<sub>max</sub> (neat): 3065w, 3017w, 2926w, 1826w, 1734w, 1627w, 1599w, 1503m, 1422s, 1369s, 1335m, 1305m, 1225s, 1175s, 1113s, 991m, 917s, 867m, 759s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.83 – 7.72 (2H, m, C3'H, C3''H), 7.51 (1H, td, <sup>3</sup>J 7.4, <sup>4</sup>J 0.9 Hz, C4'H), 7.47 – 7.40 (3H, m, C5'H, C4''H, C6''H), 7.40 – 7.28 (5H, m, C2H, C5H, C7H, C6'H, C5''H), 6.64 (1H, dd, <sup>3</sup>J 17.5, <sup>3</sup>J 11.0 Hz, C7''H), 6.47 (1H, d, <sup>3</sup>J 3.2, C3H), 6.29 (1H, dd, <sup>3</sup>J 17.4, <sup>3</sup>J 11.0 Hz, C7'H), 5.77 (1H, dd, <sup>3</sup>J 17.4, <sup>4</sup>J 1.0 Hz, C8'H), 5.76 (1H, dd, <sup>3</sup>J 17.5, <sup>4</sup>J 1.2 Hz, C8''H), 5.24 (1H, d, <sup>3</sup>J 11.0 Hz, C8'H), 5.16 (1H, dd, <sup>3</sup>J 11.0, <sup>4</sup>J 1.2 Hz, C8''H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 138.6 (C1''), 136.5 (C1'), 136.4 (C7a), 136.3 (C2''), 135.6 (C7'),

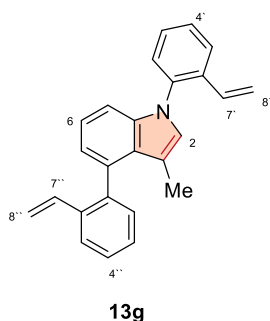
135.3 (C2'), 134.3 (C4), 132.1 (C2), 131.9 (C7'), 130.8 (C4''), 130.5 (C3a), 128.98 (C6''/C6'), 128.94 (C5'), 128.3 (C4'), 128.1 (C6''/C6'), 127.7 (C5''), 126.7 (C3'), 125.5 (C3''), 125.2 (q,  $^1J_{CF}$  271.8 Hz, CF<sub>3</sub>), 124.4 (q,  $^2J_{CF}$  32.1 Hz, C6) 118.4 (q,  $^3J_{CF}$  3.4 Hz, C5), 117.1 (C8'), 114.7 (C8''), 107.7 (q,  $^3J_{CF}$  4.3 Hz, C7), 103.3 (C3);  $^{19}F$  NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -60.45; ESI-MS: m/z calcd. for C<sub>25</sub>H<sub>18</sub>AgF<sub>3</sub>N 496.0437 found 496.0437 [M+Ag<sup>+</sup>].

### 7-Fluoro-1,4-bis(2-vinylphenyl)-1H-indole (13f):



Prepared according to the general procedure C using 2-(7-fluoro-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde **S8f** (119 mg, 350  $\mu$ mol, 1.00 eq.), methyltriphenylphosphonium-bromide (175 mg, 490  $\mu$ mol, 1.40 eq.) and KOt-Bu (62.8 mg, 560  $\mu$ mol, 1.60 eq.) to give **13f** as yellow oil (50.0 mg, 147  $\mu$ mol, 42%):  $R_f$  0.75 (cyclohexane/EtOAc 5:1);  $\nu_{max}$  (neat): 3062w, 3017w, 1831w, 1717w, 1625w, 1580w, 1500s, 1402m, 1296m, 1240s, 1185m, 1110w, 991w, 907s  $^1H$  NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.78 – 7.74 (1H, m, C3'H), 7.72 (1H, d,  $^3J$  7.7 Hz, C3'H), 7.49 – 7.34 (6H, m, C4'H, C5'H, C6'H, C4''H, C5''H, C6''H), 7.09 (1H, d,  $^3J$  3.2 Hz, C2H), 7.00 – 6.86 (2H, m, C5H, C6H), 6.67 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7''H), 6.41 (1H, d,  $^3J$  3.0 Hz, C3H), 6.40 – 6.33 (1H, m, C7'H), 5.73 (1H, dd,  $^3J$  17.5,  $^2J$  1.1 Hz, C8''H), 5.72 (1H, dd,  $^3J$  17.5,  $^3J$  1.0 Hz, C8'H), 5.22 (1H, d,  $^3J$  11.1 Hz, C8'H), 5.14 (1H, dd,  $^3J$  11.0,  $^2J$  1.1 Hz, C8''H);  $^{13}C$  NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 149.6 (d,  $^1J_{CF}$  247.0 Hz, C7), 139.2 (C1''), 138.2 (C1'), 136.3 (C2''), 136.0 (C7''), 135.4 (C2'), 132.00 (d,  $^3J_{CF}$  4.3 Hz, C3a), 132.0 (C7'), 131.1 (C2), 131.0 (C6''), 129.5 (d,  $^4J_{CF}$  Hz, C4), 128.6 (C4'), 128.4 (C4''), 128.3 (C6'), 128.2 (C5'), 127.6 (C5''), 125.8 (C3'), 125.4 (C3''), 124.8 (C7a), 122.0 (d,  $^3J_{CF}$  6.4 Hz, C5), 116.6 (C8'), 114.2 (C8''), 107.9 (d,  $^2J_{CF}$  17.8 Hz, C6), 103.8 (C3); ESI-MS: m/z calcd. for C<sub>24</sub>H<sub>19</sub>FN 340.1496 found 340.1498 [M+H<sup>+</sup>].

### 3-Methyl-1,4-bis(2-vinylphenyl)-1H-indole (13g):

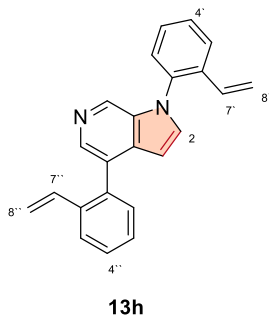


Prepared according to the general procedure C using 2-(3-methyl-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde **S8g** (87.7 mg, 260  $\mu$ mol, 1.00 eq.), methyltriphenylphosphonium-bromide (186 mg, 520  $\mu$ mol, 2.00 eq.) and KOt-Bu (67.1 mg, 598  $\mu$ mol, 2.30 eq.) to give **13g** as a white solid (60.0 mg, 179  $\mu$ mol, 69%, m.p. 119.4 – 120.9°C):  $R_f$  0.77 (cyclohexane/EtOAc 6:1);  $\nu_{max}$  (neat): 3068w, 2945w, 1628w, 1595w, 1573w, 1489s, 1453m, 1429s, 1307m, 1172w, 1049w, 993m, 914s;  $^1H$  NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.76 (1H, dd,  $^3J$  7.6,  $^4J$  1.7 Hz, C3'H), 7.73 – 7.67 (1H, m, C3''H), 7.47 – 7.28 (6H, m, C4'H, C5'H, C6'H, C4''H, C5''H, C6''H), 7.16 (1H, dd,  $^3J$  8.2,  $^3J$  7.1 Hz, C6H), 7.06 (1H, dd,  $^3J$  8.2,  $^4J$  1.0 Hz, C7H), 6.93 – 6.87 (2H, m, C2H, C5H), 6.55 (1H, d,  $^3J$  17.6,  $^3J$  11.0 Hz, C7''H), 6.41 (1H, dd,  $^3J$  17.1,  $^3J$  11.1 Hz, C7'H), 5.76 (1H, dd,  $^3J$  17.1,  $^2J$  1.1 Hz, C8'H), 5.70 (1H, dd,  $^3J$  17.6,  $^2J$  1.3 Hz, C8''H), 5.22 (1H, d,  $^3J$  11.1 Hz, C8'H), 5.07 (1H, dd,  $^3J$  11.0,  $^2J$  1.3 Hz, C8''H), 1.74 (3H, d,  $^4J$  1.1 Hz, CH<sub>3</sub>);  $^{13}C$  NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 140.5 (C1''), 138.0 (C7a), 137.4 (C1'), 136.8 (C2''), 135.8 (C7'), 135.1 (C2'), 134.2 (C4), 132.6 (C7'), 131.0 (C6''), 128.7 (C5'),



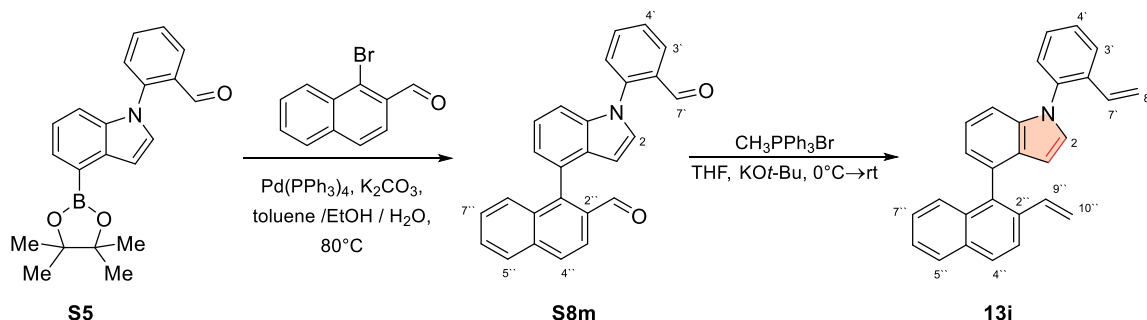
128.4 ( $C4'/C6'$ ), 128.1 ( $C4'/C6'$ ), 128.0 ( $C2$ ), 127.5 ( $C4''$ ), 126.9 ( $C5''/C3a$ ), 126.3 ( $C3'$ ), 124.2 ( $C3''$ ), 121.8 ( $C6$ ), 121.4 ( $C5$ ), 116.1 ( $C8'$ ), 114.0 ( $C8''$ ), 112.9 ( $C3$ ), 110.1 ( $C7$ ), 11.5 ( $CH_3$ ); ESI-MS:  $m/z$  calcd. for  $C_{25}H_{21}N$  335.1669 found 335.1662 [ $M^+$ ].

#### 1,4-Bis(2-vinylphenyl)-1H-pyrrolo[2,3-c]pyridine (13h):



Prepared according to the general procedure **C** using 2-(4-(2-vinylphenyl)-1H-pyrrolo[2,3-c]pyridin-1-yl)benzaldehyde **S8h** (90.8 mg, 280  $\mu$ mol, 1.00 eq.), methyltriphenylphosphonium-bromide (200 mg, 560  $\mu$ mol, 2.00 eq.) and KO $t$ -Bu (72.3 mg, 644  $\mu$ mol, 2.30 eq.) to give **13h** as a transparent oil (65.0 mg, 202  $\mu$ mol, 72%);  $R_f$  0.47 (cyclohexane/EtOAc 1:1);  $\nu_{max}$  (neat): 3060w, 3013w, 1832w, 1694w, 1598w, 1499m, 1451w, 1424s, 1303w, 1172m, 1118w, 1082w, 991w, 914w, 879w;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 8.49 (1H, d,  $^4J$  0.7 Hz, C7H), 8.23 (1H, s, C5H), 7.81 – 7.75 (2H, m, C3'H, C3''H), 7.55 – 7.47 (1H, m, C4'H), 7.47 – 7.38 (5H, m, C5'H, C6'H, C4''H, C5''H, C6''H), 7.32 (1H, d,  $^3J$  3.1 Hz, C2H), 6.68 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7''H), 6.48 (1H, dd,  $^3J$  3.1,  $^5J$  0.8 Hz, C3H), 6.33 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7'H), 5.89 – 5.69 (2H, m, C8'H, C8''H), 5.27 (1H, dd,  $^3J$  11.0,  $^5J$  0.9 Hz, C8'H), 5.17 (1H, dd,  $^3J$  11.0,  $^2J$  1.2 Hz, C8''H);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 140.1 (C5), 136.6 (C2''), 136.5 (C1''), 136.2 (C1'), 135.7 (C7''), 135.2 (C2'), 134.1 (C7a), 133.4 (C7), 133.2 (C3a), 133.1 (C2), 131.8 (C7'), 131.0 (C6''), 129.0 (C4'), 128.9 (C5'), 128.4 (C4), 128.2 (C4''), 128.1 (C6'), 127.8 (C5''), 126.8 (C3'/C3''), 125.6 (C3'/C3''), 117.4 (C8'), 114.9 (C8''), 102.5 (C3); ESI-MS:  $m/z$  calcd. for  $C_{23}H_{19}N_2$  323.1543 found 323.1549 [ $M+H^+$ ].

#### 4-(2-Vinylnaphthalen-1-yl)-1-(2-vinylphenyl)-1H-indole (13i):

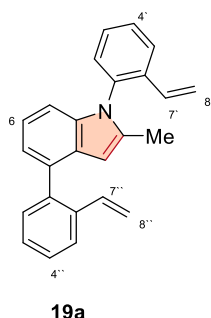


**Step 1:** 1-Bromo-2-naphthaldehyde (63.5 mg, 270  $\mu$ mol, 1.00 eq.), 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indol-1-yl)benzaldehyde (**S5**) (105 mg, 302  $\mu$ mol, 1.12 eq.),  $Pd(PPh_3)_4$  (15.6 mg, 13.5  $\mu$ mol, 5 mol%), and  $K_2CO_3$  (112 mg, 810  $\mu$ mol, 3.00 eq.) were weighed in a 10 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before a degassed mixture of toluene,  $H_2O$ , ethanol (2 : 2 : 1) (2.5 mL, 0.11 mol·L $^{-1}$ ) was added. The resulting mixture was stirred at 80°C for 18 h, then cooled to room temperature, filtered through a thin layer of silica gel and  $Na_2SO_4$  using EtOAc (15-20 mL). The solvents were removed under reduced pressure

and the residue was purified by the silica gel chromatography (cyclohexane/EtOAc 100:0→60:40) to give the desired product 1-(1-(2-formylphenyl)-1*H*-indol-4-yl)-2-naphthaldehyde **S8m** as yellow oil (97.0 mg, 258 μmol, 96%); *R*<sub>f</sub> 0.29 (cyclohexane/EtOAc 5:1); *v*<sub>max</sub> (neat): 3057w, 2853w, 2753w, 1691s, 1597m, 1488m, 1424w, 1248w, 1219w, 958w, 760w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 9.84 (1H, s, C2''-CHO), 9.74 (1H, s, C2'-CHO), 8.18 – 8.12 (2H, m, C3''H, C3'H), 8.01 (1H, d, <sup>3</sup>*J* 8.4 Hz, C4''H), 7.97 (1H, d, <sup>3</sup>*J* 8.2 Hz, C5''H), 7.82 (1H, td, <sup>3</sup>*J* 7.7, <sup>4</sup>*J* 1.6 Hz, C5'H), 7.72 – 7.53 (4H, m, C4'H, C6'H, C6''H, C8''H), 7.48 – 7.41 (2H, m, C7''H), 7.41 – 7.30 (2H, m, C6H), 7.31 – 7.19 (3H, m, C2H, C5H, C7H), 6.29 – 6.12 (1H, m, C3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 193.1 (C2''-CHO), 189.6 (C2'-CHO), 145.2 (C1''), 141.8 (C1'), 138.2 (C7a), 136.4 (C4a''), 135.4 (C5'), 132.6 (C2''), 132.3 (C2'), 131.7 (C8a''), 130.7 (C2), 130.2 (C3a), 129.0 (C3'), 128.9 (C6''), 128.8 (C4'), 128.7 (C4''), 128.4 (C6'), 128.2 (C4/C5''), 128.0 (C8''), 127.0 (C7''), 124.2 (C5), 123.0 (C6), 122.3 (C3''), 110.5 (C7), 103.9 (C3); ESI-MS: *m/z* calcd. for C<sub>28</sub>H<sub>18</sub>NO<sub>2</sub> 376.1332 found 376.1337 [M+H<sup>+</sup>].

**Step 2:** To a suspension of methyltriphenylphosphonium-bromide (372 mg, 1.04 mmol, 4.00 eq.) in THF (2.6 mL) at 0°C was added dry KOt-Bu (134 mg, 1.20 mmol, 4.60 eq.) under argon. The resulting suspension was stirred for 40 min at 0°C and a solution of 1-(1-(2-formylphenyl)-1*H*-indol-4-yl)-2-naphthaldehyde **S8m** (97.6 mg, 260 μmol, 1.00 eq.) in THF (2.6 mL) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 18 h. Water was then added and the mixture was extracted with EtOAc (3×30 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0→70:30) to give the desired product **13i** as a white solid (80.0 mg, 215 μmol, 83%, m.p. 75.0 – 76.0°C); *R*<sub>f</sub> 0.71 (cyclohexane/EtOAc 5:1); *v*<sub>max</sub> (neat): 3082w, 3061w, 1631w, 1598w, 1512m, 1490s, 1422s, 14294w, 1214w, 1171w, 1028w, 992w, 914w, 823; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.90 – 7.84 (2H, m, C3''H, C4''H), 7.79 (1H, d, <sup>3</sup>*J* 7.4 Hz, C3'H), 7.49 – 7.40 (5H, m, C4'H, C5'H, C6'H, C5''H, C7''H), 7.34 – 7.27 (3H, m, C6H, C6''H, C8''H), 7.20 (1H, dt, <sup>3</sup>*J* 8.3, <sup>4</sup>*J* 0.9 Hz, C7H), 7.11 (1H, d, <sup>3</sup>*J* 3.2 Hz, C2H), 7.07 (1H, dd, <sup>3</sup>*J* 7.1, <sup>4</sup>*J* 0.9 Hz, C5H), 6.63 (1H, dd, <sup>3</sup>*J* 17.6, <sup>3</sup>*J* 11.0 Hz, C9''H), 6.41 (1H, dd, <sup>3</sup>*J* 17.5, <sup>3</sup>*J* 11.0 Hz, C7'H), 6.09 (1H, dd, <sup>3</sup>*J* 3.2, <sup>5</sup>*J* 0.8 Hz, C3H), 5.82 (1H, dd, <sup>3</sup>*J* 17.6, <sup>2</sup>*J* 1.0 Hz, C10''H), 5.76 (1H, dd, <sup>3</sup>*J* 17.5, <sup>2</sup>*J* 1.0 Hz, C8'H), 5.24 (1H, dd, <sup>3</sup>*J* 11.0, <sup>2</sup>*J* 1.0 Hz, C8'H), 5.15 (1H, dd, <sup>3</sup>*J* 11.0, <sup>2</sup>*J* 1.0 Hz, C10''H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 137.4 (C7a), 137.3 (C1'), 136.9 (C1''), 136.0 (C9''), 135.2 (C2'), 133.3 (C2''/C4a''), 133.2 (C2''/C4a''), 132.4 (C7'), 131.1 (C4), 129.7 (C2), 129.3 (C3a), 128.7 (C5'), 128.4 (C8a''), 128.3 (C4'/C6'), 127.9 (C3''), 127.8 (C8''), 127.5 (C5''), 126.5 (C3'), 126.1 (C6''), 125.8 (C7''), 122.72 (C5), 122.65 (C4''), 122.2 (C6), 116.4 (C8'), 114.2 (C10''), 110.3 (C7), 102.9 (C3); ESI-MS: *m/z* calcd. for C<sub>28</sub>H<sub>22</sub>N 372.1747 found 372.1741 [M+H<sup>+</sup>].

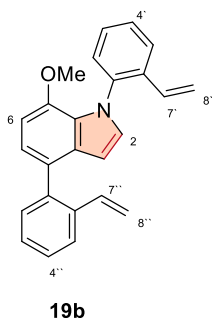
## 2-Methyl-1,4-bis(2-vinylphenyl)-1*H*-indole (19a):



Prepared according to the general procedure **C** using 2-(2-methyl-4-(2-vinylphenyl)-1*H*-indol-1-yl)benzaldehyde **S8i** (58.0 mg, 172 μmol, 1.00 eq.), methyltriphenylphosphonium-bromide (123 mg, 344 μmol, 2.00 eq.) and KOt-Bu (44.4 mg, 396 mmol, 2.30 eq.) to give **19a** as yellow oil (40.4 mg, 120 μmol, 70%, m.p. 150.8 – 152.4°C); *R*<sub>f</sub> 0.71 (cyclohexane/EtOAc 5:1); *v*<sub>max</sub> (neat): 3058w, 3018w, 2918w, 2846w, 1826w, 1624w, 1602w, 1553m, 1488m, 1455m, 1422m, 1385m, 1323m, 1261w, 1162w, 1084w, 994w, 910w, 768s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.79 (1H, dd, <sup>3</sup>*J* 7.8, <sup>4</sup>*J* 1.3 Hz, C3'H), 7.78 – 7.73 (1H, m, C3''H), 7.53 – 7.46 (2H, m, C4'H, C6''H), 7.43 (1H, td, <sup>3</sup>*J* 7.6, <sup>4</sup>*J* 1.3 Hz, C5'H), 7.41 – 7.33 (2H, m, C4''H, C5''H), 7.30 (1H, d, <sup>3</sup>*J* 7.6 Hz, C6'H), 7.15 – 7.07 (1H, m, C6H), 7.00 (1H, dd, <sup>3</sup>*J* 7.2, <sup>4</sup>*J* 0.7 Hz, C5H), 6.84 (1H, d, <sup>3</sup>*J* 8.1 Hz, C7H), 6.75 (1H, dd, <sup>3</sup>*J* 17.6, <sup>3</sup>*J* 11.0 Hz, C7''H), 6.18 (1H, s, C3H), 6.14 (1H, dd, <sup>3</sup>*J* 17.6, <sup>3</sup>*J* 11.1 Hz, C7'H), 5.73 (1H, dd, <sup>3</sup>*J* 17.6, <sup>2</sup>*J* 1.2 Hz, C8''H), 5.69 (1H, d, <sup>3</sup>*J* 17.6 Hz, C8'H), 5.16 (1H, d, <sup>3</sup>*J* 11.1 Hz, C8'H), 5.12 (1H, dd, <sup>3</sup>*J* 11.0, <sup>2</sup>*J* 1.2 Hz, C8''H), 2.12 (3H, s, C2-CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ =

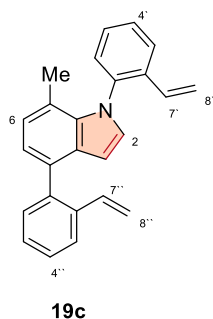
140.3 ( $C1''$ ), 138.5 ( $C7a$ ), 138.1 ( $C2$ ), 136.8 ( $C2''$ ), 136.3 ( $C7''$ ), 136.1 ( $C2''$ ), 135.8 ( $C1'$ ), 132.2 ( $C4$ ), 131.9 ( $C7'$ ), 130.9 ( $C6''$ ), 129.8 ( $C6'$ ), 129.0 ( $C4'$ ), 128.8 ( $C5'$ ), 127.8 ( $C3a$ ), 127.5 ( $C5''$ ), 127.3 ( $C4''$ ), 126.2 ( $C3'$ ), 125.2 ( $C3''$ ), 121.8 ( $C5$ ), 120.9 ( $C6$ ), 116.5 ( $C8'$ ), 113.8 ( $C8''$ ), 109.4 ( $C7$ ), 100.9 ( $C3$ ), 13.2 ( $C2-CH_3$ ); ESI-MS:  $m/z$  calcd. for  $C_{25}H_{22}N$  336.1747 found 336.1745 [ $M+H^+$ ].

### 7-Methoxy-1,4-bis(2-vinylphenyl)-1H-indole (19b):



Prepared according to the general procedure **C** using 2-(7-methoxy-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (42.4 mg, 120  $\mu$ mol, 1.00 eq.), methyltriphenylphosphonium-bromide (85.7 mg, 240  $\mu$ mol, 2.00 eq.) and  $KOt-Bu$  (31.0 mg, 276  $\mu$ mol, 2.30 eq.) to give **19b** as colorless oil (32.0 mg, 91.1  $\mu$ mol, 76%);  $R_f$  0.75 (cyclohexane/EtOAc 6:1);  $\nu_{max}$  (neat): 3069w, 3031w, 1624w, 1600w, 1574w, 1528w, 1495s, 1457m, 1428m, 1297m, 1251s, 1176w, 1094m, 1051w, 993w, 914m;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 7.74 (1H, dd,  $^3J$  7.4,  $^4J$  1.7 Hz,  $C6''H$ ), 7.69 – 7.65 (1H, m,  $C3'H$ ), 7.46 (1H, dd,  $^3J$  7.1,  $^4J$  1.8 Hz,  $C3''H$ ), 7.42 – 7.29 (5H, m,  $C4'H$ ,  $C5'H$ ,  $C6'H$ ,  $C4''H$ ,  $C5''H$ ), 7.00 (1H, d,  $^3J$  3.1 Hz,  $C2H$ ), 6.95 (1H, d,  $^3J$  7.9 Hz,  $C5H$ ), 6.74 (1H, dd,  $^3J$  17.6,  $^3J$  11.0 Hz,  $C7''H$ ), 6.67 (1H, d,  $^3J$  7.9 Hz,  $C6H$ ), 6.40 – 6.29 (2H, m,  $C3H$ ,  $C7'H$ ), 5.72 (1H, dd,  $3J$  17.6,  $2J$  1.3 Hz,  $C8''H$ ), 5.67 (1H, dd,  $3J$  17.6,  $2J$  1.1 Hz,  $C8'H$ ), 5.19 – 5.06 (2H, m,  $C8'H$ ,  $C8''H$ ), 3.61 (3H, s,  $OCH_3$ );  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 147.0 ( $C7$ ), 139.9 ( $C4$ ), 139.6 ( $C1'$ ), 136.40 ( $C7''$ ), 136.37 ( $C2''$ ), 135.6 ( $C2'$ ), 132.6 ( $C7'$ ), 131.1 ( $C3''$ ), 130.5 ( $C2$ ), 130.3 ( $C3a$ ), 128.6 ( $C6'$ ), 127.9 ( $C4'$ ), 127.52 ( $C4''$ ), 127.48 ( $C5'$ ), 127.2 ( $C5''$ ), 126.8 ( $C7a$ ), 126.4 ( $C1''$ ), 125.3 ( $C6''$ ), 125.0 ( $C3'$ ), 122.3 ( $C5$ ), 115.5 ( $C8'$ ), 113.7 ( $C8''$ ), 103.5 ( $C6$ ), 103.2 ( $C3$ ), 55.8 ( $OCH_3$ ); ESI-MS:  $m/z$  calcd. for  $C_{25}H_{22}NO$  352.1696 found 352.1698 [ $M+H^+$ ].

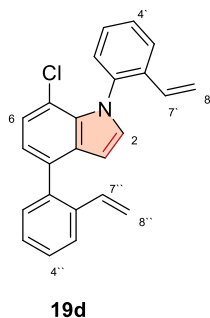
### 7-Methyl-1,4-bis(2-vinylphenyl)-1H-indole (19c):



Prepared according to the general procedure **C** using 2-(7-methyl-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde **S8j** (59.0 mg, 175  $\mu$ mol, 1.00 eq.), methyltriphenylphosphonium-bromide (87.4 mg, 245  $\mu$ mol, 1.40 eq.) and  $KOt-Bu$  (31.4 mg, 280  $\mu$ mol, 1.60 eq.) to give **19c** as colorless oil (34.0 mg, 101  $\mu$ mol, 58%);  $R_f$  0.68 (cyclohexane/EtOAc 5:1);  $\nu_{max}$  (neat): 3060w, 3021w, 2924m, 2850w, 1813w, 1703w, 1627w, 1598w, 1487s, 1453s, 1412w, 1380w, 1317m, 1266m, 1185w, 1150w, 1114w, 1039w, 991m, 903s, 871m, 760s;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 7.78 – 7.74 (1H, m,  $C3''H$ ), 7.71 (1H, d,  $^3J$  7.8 Hz,  $C3'H$ ), 7.50 – 7.43 (2H, m,  $C4'H$ ,  $C6''H$ ), 7.41 – 7.31 (4H, m,  $C5'H$ ,  $C6'H$ ,  $C4''H$ ,  $C5''H$ ), 7.02 (1H, d,  $^3J$  3.2 Hz,  $C2H$ ), 6.95 (2H, s,  $C5H$ ,  $C6H$ ), 6.72 (1H, dd,  $^3J$  17.6,  $^3J$  11.0 Hz,  $C7''H$ ), 6.38 (1H, d,  $^3J$  3.2 Hz,  $C3H$ ), 6.23 (1H, dd,  $^3J$  17.5,  $^3J$  11.1 Hz,  $C7'H$ ), 5.73 (1H, dd,  $^3J$  17.6,  $^2J$  1.2 Hz,  $C8''H$ ), 5.71 (1H, dd,  $^3J$  17.5,  $^2J$  1.0 Hz,  $C8'H$ ), 5.18 (1H, d,  $^3J$  11.1 Hz,  $C8'H$ ), 5.11 (1H, dd,  $^3J$  11.0,  $^2J$  1.2 Hz,  $C8''H$ ), 1.96 (3H, s,  $C7-CH_3$ );  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 140.1 ( $C1''$ ), 139.3 ( $C1'$ ),

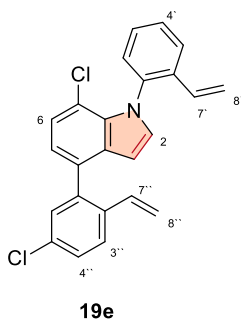
136.9 (C2'), 136.28 (C7''), 136.25 (C2''), 136.1 (C7a), 131.8 (C7'), 131.6 (C4), 131.0 (C6''), 130.4 (C2), 129.8 (C4''), 128.9 (C4'), 128.6 (C3a), 127.9 (C5'), 127.5 (C5''), 127.3 (C6'), 125.27 (C3'), 125.2 (C3''), 124.4 (C6), 121.9 (C5), 121.1 (C7), 116.7 (C8'), 113.8 (C8''), 102.9 (C3), 18.6 (C7-CH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>25</sub>H<sub>21</sub>AgN 442.0719 found 442.0714 [M+Ag<sup>+</sup>].

### 7-Chloro-1,4-bis(2-vinylphenyl)-1H-indole (19d):



Prepared according to the general procedure C using 2-(7-chloro-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde **S8k** (119 mg, 333 μmol, 1.00 eq.), methyltriphenylphosphonium-bromide (238 mg, 665 μmol, 2.00 eq.) and KOt-Bu (85.8 mg, 765 μmol, 2.30 eq.) to give **19d** as yellow oil (36.0 mg, 101 μmol, 30%): R<sub>f</sub> 0.83 (cyclohexane/EtOAc 6:1); ν<sub>max</sub> (neat): 3064w, 3026w, 2983w, 1844w, 1736w, 1627w, 1594w, 1492s, 1476s, 1413w, 1335w, 1262m, 1165s, 1107w, 991w, 914m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.79 – 7.73 (1H, m, C3''H), 7.69 (1H, d, <sup>3</sup>J 8.0 Hz, C3'H), 7.49 – 7.33 (6H, m, C4'H, C5'H, C6'H, C4''H, C5''H, C6''H), 7.18 (1H, d, <sup>3</sup>J 7.7 Hz, C6H), 7.06 (1H, d, <sup>3</sup>J 3.2 Hz, C2H), 6.96 (1H, d, <sup>3</sup>J 7.7 Hz, C5H), 6.66 (1H, dd, <sup>3</sup>J 17.5, <sup>3</sup>J 11.0 Hz, C7''H), 6.40 (1H, d, <sup>3</sup>J 3.2 Hz, C3H), 6.28 – 6.14 (1H, dd, m, C7'H), 5.73 (1H, dd, <sup>3</sup>J 17.5, <sup>2</sup>J 1.2 Hz, C8''H), 5.69 (1H, dd, <sup>3</sup>J 17.5, <sup>2</sup>J 1.0 Hz, C8'H), 5.18 (1H, d, <sup>3</sup>J 11.1 Hz, C8'H), 5.14 (1H, dd, <sup>3</sup>J 11.0, <sup>2</sup>J 1.2 Hz, C8''H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 139.0 (C1'), 138.1 (C1'), 136.9 (C2'), 136.3 (C2''), 135.9 (C7'), 132.7 (C4), 132.6 (C7a), 131.8 (C7'), 131.7 (C2), 130.8 (C6''/C4''), 130.6 (C3a), 129.7 (C4'), 129.0 (C6'), 127.81 (C5'), 127.76 (C6''/C4''), 127.6 (C5''), 125.38 (C3''), 125.32 (C3'), 123.5 (C6), 122.5 (C5), 116.7 (C8'), 116.6 (C7), 114.4 (C8''), 103.3 (C3); ESI-MS: m/z calcd. for C<sub>24</sub>H<sub>18</sub>AgClN 462.0173 found 462.0174 [M+Ag<sup>+</sup>].

### 7-Chloro-4-(5-chloro-2-vinylphenyl)-1-(2-vinylphenyl)-1H-indole (19e):

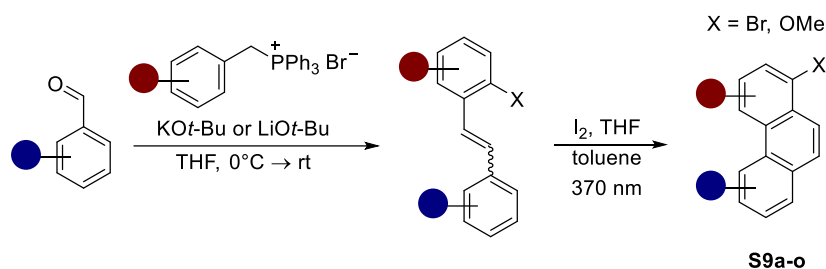


Prepared according to the general procedure C using 2-(7-chloro-4-(5-chloro-2-vinylphenyl)-1H-indol-1-yl)benzaldehyde **S8l** (75.0 mg, 191 μmol, 1.00 eq.), methyltriphenylphosphonium-bromide (137 mg, 382 μmol, 2.00 eq.) and KOt-Bu (49.3 mg, 440 μmol, 2.30 eq.) to give **19e** as a colorless oil (62.0 mg, 159 μmol, 83%): R<sub>f</sub> 0.60 (cyclohexane/EtOAc 5:1); ν<sub>max</sub> (neat): 3085w, 3013w, 2925w, 2855w, 1842w, 1716w, 1591w, 1492s, 1411m, 1333w, 1262m, 1218w, 1165m, 1098m, 988m, 911s, 824s, 763s, 727s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.69 (1H, d, <sup>3</sup>J 7.9 Hz, C3'H), 7.67 (1H, d, <sup>3</sup>J 8.6 Hz, C3''H), 7.51 – 7.45 (1H, m, C4'H), 7.42 (1H, d, <sup>3</sup>J 2.1 Hz, C6''H), 7.40 – 7.33 (3H, m, C5'H, C6'H, C4''H), 7.18 (1H, d, <sup>3</sup>J 7.8 Hz, C6H), 7.08 (1H, d, <sup>3</sup>J 3.2 Hz, C2H), 6.94 (1H, d, <sup>3</sup>J 7.8 Hz, C5H), 6.58 (1H, dd, <sup>3</sup>J 17.5, <sup>3</sup>J 11.0 Hz, C7''H), 6.39 (1H, d, <sup>3</sup>J 3.2 Hz, C3H), 6.30 – 6.05 (1H, m, C7'H), 5.71 (1H, dd, <sup>3</sup>J 17.5, <sup>2</sup>J 0.9 Hz, C8''H), 5.69 (1H, dd, <sup>3</sup>J 17.5, <sup>2</sup>J 1.1 Hz, C8'H), 5.18 (1H, d, <sup>3</sup>J 11.1 Hz, C8'H), 5.15 (1H, dd, <sup>3</sup>J 11.0, <sup>2</sup>J 0.9 Hz, C8''H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 140.5 (C1'), 137.9

(C1'), 136.9 (C2'), 134.86 (C2''), 134.85 (C7''), 133.2 (C5''), 132.7 (C7a), 131.9 (C2), 131.7 (C7'), 131.1 (C4), 130.6 (C6''), 130.4 (C3a), 129.6 (C6'), 129.1 (C4'), 127.9 (C4''), 127.8 (C5'), 126.8 (C3''), 125.4 (C3'), 123.5 (C6), 122.4 (C5), 117.1 (C7), 116.8 (C8'), 114.9 (C8''), 103.0 (C3); ESI-MS: m/z calcd. for C<sub>24</sub>H<sub>17</sub>AgCl<sub>2</sub>N 495.9783 found 495.9779 [M<sup>+</sup>].

## Synthesis of S9a-o

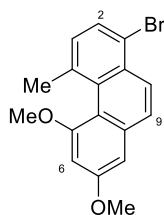
### General Procedure D:



**Step 1:** According to the modified literature procedure<sup>7</sup>: A mixture of the corresponding phosphorous ylide (1.20 eq.) in THF (0.10 mol·L<sup>-1</sup> with regard to aldehyde) was cooled to 0°C under argon and dry KOt-Bu or LiOt-Bu (2.00 eq.) was added portionwise. After stirring the resulting suspension for 60 min at 0°C, a solution of the corresponding aldehyde (1.00 eq.) in THF (0.10 mol·L<sup>-1</sup>) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred for 18 h. Water was then added and the mixture was extracted with EtOAc (×3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0→70:30) to give the desired alkene.

**Step 2:** According to the modified literature procedure<sup>8</sup>: The corresponding alkene (a mixture of *E* and *Z*-isomers) (1.00 eq.) and I<sub>2</sub> (1.50 eq.) were weighed in the flask which was sealed, evacuated and backfilled with argon before toluene (7.0 mmol·L<sup>-1</sup>) and THF (30 eq.) were added. The flask was then transferred to the photoreactor utilizing Kessil 370 nm lamp (unless otherwise noted) as a light source and water for cooling. (The set-up was wrapped with aluminium foil for safety reasons.) The resulting solution was stirred upon irradiation (100% intensity) under argon and the reaction progress was monitored via <sup>1</sup>H-NMR. Upon the reaction completion, an aqueous saturated solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was added (1:1 volume) and the obtained mixture was stirred for 15 minutes and extracted with EtOAc (×3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was purified by flash silica gel column chromatography (cyclohexane/EtOAc 100:0→70:30) to give the desired phenanthrene derivative.

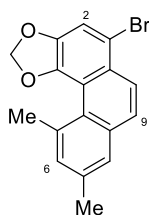
### 1-Bromo-5,7-dimethoxy-4-methylphenanthrene (S9a):



**S9a**

Step 1 of the general procedure **D** was performed using (2-bromo-5-methylbenzyl)triphenylphosphonium bromide (1.39 g, 2.64 mmol, 1.20 eq.), 3,5-dimethoxybenzaldehyde (366 mg, 2.20 mmol, 1.00 eq.), and KO<sup>t</sup>-Bu (444 mg, 3.96 mmol, 1.80 eq.) to give (*E, Z*)-1-bromo-2-(3,5-dimethoxystyryl)-4-methylbenzene as a transparent oil (450 mg, 1.35 mmol, 61%). The obtained alkene (500 mg, 1.50 mmol) was subjected to the step 2 according to the general procedure **D** over 72 h utilizing Kessil-370-Gen2 as a light source to obtain the product **S9a** as white solid (370 mg, 1.12 mmol, 75%) after NP-prep-HPLC (from hexane/EtOAc 98:2 to 80:20, 18 mL/min, 40°C): *R<sub>f</sub>* 0.49 (cyclohexane/EtOAc 6:1); *v*<sub>max</sub> (neat): 299w, 2931w, 2853w, 1601s, 1564s, 1519w, 1452s, 1356s, 1308m, 1282w, 1234w, 1219m, 1160s, 1110m, 1060s, 1024w, 936w, 833m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 8.04 (1H, d, <sup>3</sup>*J* 9.0 Hz, C10*H*), 7.66 (1H, d, <sup>3</sup>*J* 7.9 Hz, C2*H*), 7.55 (1H, d, <sup>3</sup>*J* 9.0 Hz, C9*H*), 7.27 – 7.22 (1H, m, C3*H*), 6.87 (1H, d, <sup>4</sup>*J* 2.4 Hz, C8*H*), 6.68 (1H, d, <sup>4</sup>*J* 2.4 Hz, C6*H*), 3.97 (3H, s, C7–OCH<sub>3</sub>), 3.92 (3H, s, C5–OCH<sub>3</sub>), 2.49 (3H, s, C4–CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 159.6 (C7), 158.2 (C5), 136.3 (C4), 135.9 (C8*a*), 131.1 (C4*a*), 130.7 (C10*a*), 129.5 (C3), 128.9 (C2), 127.3 (C9), 126.8 (C10), 119.4 (C1), 115.4 (C4*b*), 100.1 (C8), 98.6 (C6), 55.7 (C7–OCH<sub>3</sub>), 55.2 (C5–OCH<sub>3</sub>), 23.9 (C4–CH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>17</sub>H<sub>16</sub>BrO<sub>2</sub> 331.0328 found 331.0328 [M+H<sup>+</sup>].

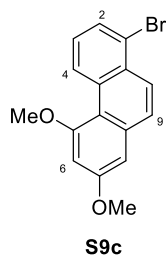
### 5-Bromo-9,11-dimethylphenanthro[3,4-d][1,3]dioxole (S9b):



**S9b**

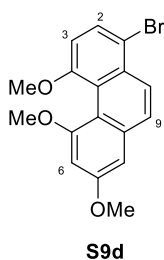
Step 1 of the general procedure **D** was performed using ((6-bromobenzo[d][1,3]dioxol-5-yl)methyl)triphenylphosphonium bromide (2.20 g, 3.96 mmol, 1.20 eq.), 3,5-dimethylbenzaldehyde (443 mg, 3.30 mmol, 1.00 eq.), and LiO<sup>t</sup>-Bu (528 mg, 6.60 mmol, 2.00 eq.) to give (*E, Z*)-5-bromo-6-(3,5-dimethylstyryl)benzo[d][1,3]dioxol as a beige solid (912 mg, 2.75 mmol, 83%). The obtained alkene (795 mg, 2.40 mmol) was subjected to the step 2 according to the general procedure **D** over 72 h to obtain the product **S9b** as a beige solid (500 mg, 1.52 mmol, 63%, m.p. 109.2 – 109.7°C): *R<sub>f</sub>* 0.40 (cyclohexane/CH<sub>2</sub>Cl<sub>2</sub> 5:1); *v*<sub>max</sub> (neat): 3070w, 3010w, 2958w, 2895m, 2784w, 1721w, 1680w, 1592m, 1434s, 1361m, 1265s, 1149m, 1098s, 1040s, 941s, 897m, 846s, 752w, 708m, 648m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.91 (1H, d, <sup>3</sup>*J* 9.1 Hz, C10*H*), 7.49 (1H, s, C2*H*), 7.44 (d, <sup>3</sup>*J* 9.2 Hz, C9*H*), 7.41 (1H, s, C8*H*), 7.30 (1H, s, C6*H*), 6.13 (2H, s, OCH<sub>2</sub>O), 2.65 (3H, s, C5–CH<sub>3</sub>), 2.50 (3H, s, C7–CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 145.4 (C3), 143.0 (C4), 137.1 (C7), 136.6 (C5), 133.8 (C8*a*), 132.0 (C6), 127.5 (C10*a*), 127.0 (C9), 125.2 (C8), 125.14 (C10), 125.06 (C4*b*), 117.6 (C4*a*), 114.2 (C1), 113.2 (C2), 100.8 (OCH<sub>2</sub>O), 23.8 (C5–CH<sub>3</sub>), 21.2 (C7–CH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>34</sub>H<sub>26</sub>AgBr<sub>2</sub>O<sub>4</sub> 762.9243 found 762.9257 [2M+Ag<sup>+</sup>].

### 1-Bromo-5,7-dimethoxyphenanthrene (S9c):



Step 1 of the general procedure **D** was performed using (2-bromobenzyl)triphenylphosphonium bromide (1.35 g, 2.64 mmol, 1.20 eq.), 3,5-dimethoxybenzaldehyde (366 mg, 2.20 mmol, 1.00 eq.), and KOt-Bu (444 mg, 3.96 mmol, 1.80 eq.) to give (*E, Z*)-1-(2-bromostyryl)-3,5-dimethoxybenzene as a beige solid (350 mg, 1.10 mmol, 50%, m.p. 121.4 – 122.0°C). The obtained alkene (112 mg, 350 μmol) was subjected to the step 2 according to the general procedure **D** over 48 h utilizing SOLIS-365C as a light source to obtain the product **S9c** as a beige solid (95.0 mg, 300 μmol, 86%): *R*<sub>f</sub> 0.53 (cyclohexane/CH<sub>2</sub>Cl<sub>2</sub> 5:1); *v*<sub>max</sub>(neat): 3137w, 2996w, 2963w, 2931m, 2851w, 1728w, 1678w, 1612s, 1568s, 1454s, 1358s, 1302s, 1266m, 1199m, 1160s, 1067s, 1024m, 944m, 908w, 838m, 756w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 9.58 (1H, dt, <sup>3</sup>*J* 8.7, <sup>4</sup>*J* 0.9 Hz, C4H), 8.24 (1H, dd, <sup>3</sup>*J* 9.1, <sup>5</sup>*J* 0.6 Hz, C10H), 7.81 (1H, dd, <sup>3</sup>*J* 7.6, <sup>4</sup>*J* 0.9 Hz, C2H), 7.73 (1H, d, <sup>3</sup>*J* 9.1 Hz, C9H), 7.42 (1H, dd, <sup>3</sup>*J* 8.7, <sup>3</sup>*J* 7.6 Hz, C3H), 6.93 (1H, d, <sup>4</sup>*J* 2.5 Hz, C8H), 6.81 (1H, d, <sup>4</sup>*J* 2.5 Hz, C6H), 4.10 (3H, s, C5–OCH<sub>3</sub>), 3.97 (3H, s, C7–OCH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 160.0 (C5), 158.8 (C7), 135.7 (C8a), 132.5 (C4a), 130.1 (C10a), 129.5 (C2), 128.6 (C9), 127.5 (C4), 126.9 (C10, C3), 123.2 (C1), 115.5 (C4b), 101.5 (C8), 100.1 (C6), 56.0 (C5–OCH<sub>3</sub>), 55.6 (C7–OCH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>16</sub>H<sub>14</sub>BrO<sub>2</sub> 317.0172 found 317.0169 [M+H<sup>+</sup>].

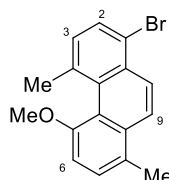
### 1-Bromo-4,5,7-trimethoxyphenanthrene (S9d):



Step 1 of the general procedure **D** was performed using (2-bromo-5-methoxybenzyl)triphenylphosphonium bromide (700 mg, 1.29 mmol, 1.20 eq.), 3,5-dimethoxybenzaldehyde (179 mg, 1.08 mmol, 1.00 eq.), and LiOt-Bu (172 mg, 2.15 mmol, 2.00 eq.) to give (*E, Z*)-1-bromo-2-(3,5-dimethoxystyryl)-4-methoxybenzene as a transparent oil (350 mg, 1.00 mmol, 93%). The obtained alkene (279 mg, 800 μmol) was subjected to the step 2 according to the general procedure **D** over 24 h to obtain the product **S9d** as yellow oil (255 mg, 734 μmol, 92%): *R*<sub>f</sub> 0.26 (cyclohexane/EtOAc 5:1); *v*<sub>max</sub>(neat): 3068w, 2934w, 2832w, 1601s, 1519m, 1460m, 1423m, 1356m, 1323s, 1250s, 1218m, 1159s, 1071s, 1005w, 939w, 834m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.99 (1H, d, <sup>3</sup>*J* 9.0 Hz, C10H), 7.68 (1H, d, <sup>3</sup>*J* 8.5 Hz, C2H), 7.60 (1H, d, <sup>3</sup>*J* 9.0 Hz, C9H), 6.93 (1H, d, <sup>3</sup>*J* 8.5 Hz, C3H), 6.86 (1H, d, <sup>4</sup>*J* 2.4 Hz, C8H), 6.74 (1H, d, <sup>4</sup>*J* 2.4 Hz, C6H), 3.99 (3H, s, C4–OCH<sub>3</sub>), 3.98 (3H, s, C5–OCH<sub>3</sub>), 3.96 (3H, s, C7–OCH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 159.4 (C7), 159.1 (C5), 156.9 (C4), 135.4 (C8a), 131.6 (C10a), 129.3 (C2), 128.3 (C9), 126.1 (C10), 121.7 (C4a), 113.9 (C4b), 113.1 (C1), 108.9 (C3), 100.1 (C8), 99.6 (C6), 56.0 (C4–OCH<sub>3</sub>/C5–OCH<sub>3</sub>), 55.99 (C4–OCH<sub>3</sub>/C5–OCH<sub>3</sub>), 55.7 (C7–OCH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>34</sub>H<sub>30</sub>AgBr<sub>2</sub>O<sub>6</sub> 798.9455 found 798.9458 [2M+Ag<sup>+</sup>].



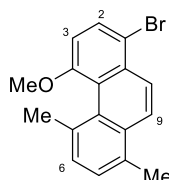
### 1-Bromo-5-methoxy-4,8-dimethylphenanthrene (S9e):



**S9e**

Step 1 of the general procedure **D** was performed using (2-bromo-5-methylbenzyl)triphenylphosphonium bromide (1.10 g, 2.10 mmol, 1.20 eq.), 5-methoxy-2-methylbenzaldehyde (263 mg, 1.75 mmol, 1.00 eq.), and KOt-Bu (353 mg, 3.15 mmol, 1.80 eq.) to give (*E*, *Z*)-1-bromo-2-(5-methoxy-2-methylstyryl)-4-methylbenzene as a transparent oil (350 mg, 1.10 mmol, 63%). The obtained alkene (251 mg, 790  $\mu$ mol) was subjected to the step 2 according to general procedure **D** over 192 h to obtain the product **S9e** as yellow oil (115 mg, 365  $\mu$ mol, 46%);  $R_f$  0.67 (cyclohexane/CH<sub>2</sub>Cl<sub>2</sub> 5:1);  $\nu_{\max}(\text{neat})$ : 3081w, 2981w, 2953w, 2927m, 2828w, 1591w, 1563m, 1448s, 1377w, 1299w, 1260s, 1223m, 1167w, 1101s, 1025w, 940w, 867w, 811s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.09 (1H, d, <sup>3</sup>*J* 9.2 Hz, C10H), 7.82 (1H, d, <sup>3</sup>*J* 9.2 Hz, C9H), 7.72 (1H, d, <sup>3</sup>*J* 7.9 Hz, C2H), 7.40 (1H, dd, <sup>3</sup>*J* 8.0, <sup>5</sup>*J* 0.8 Hz, C7H), 7.27 (d, <sup>3</sup>*J* 7.9 Hz, C3H), 6.95 (1H, d, <sup>3</sup>*J* 8.0 Hz, C6H), 3.91 (3H, s, OCH<sub>3</sub>), 2.68 (3H, s, C8-CH<sub>3</sub>), 2.50 (3H, s, C4-CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.5 (C5), 137.2 (C4), 133.4 (C8a), 131.3 (C10a), 131.0 (C4a), 129.6 (C2), 129.2 (C3), 128.7 (C7), 126.1 (C10), 125.7 (C8), 123.6 (C9), 120.6 (C4b), 119.2 (C1), 107.2 (C6), 55.1 (OCH<sub>3</sub>), 23.8 (C4-CH<sub>3</sub>), 19.2 (C8-CH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>17</sub>H<sub>15</sub>BrO 314.0301 found 314.0301 [M<sup>+</sup>].

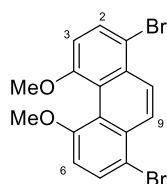
### 1-Bromo-4-methoxy-5,8-dimethylphenanthrene (S9f):



**S9f**

Step 1 of the general procedure **D** was performed using (2-bromo-5-methoxybenzyl)triphenylphosphonium bromide (1.30 g, 2.40 mmol, 1.20 eq.), 2,5-dimethylbenzaldehyde (268 mg, 2.00 mmol, 1.00 eq.), and LiOt-Bu (320 mg, 4.00 mmol, 2.00 eq.) to give (*E*, *Z*)-1-bromo-2-(2,5-dimethylstyryl)-4-methoxybenzene as a transparent oil (600 mg, 1.89 mmol, 95%). The obtained alkene (381 mg, 1.20 mmol) was subjected to the step 2 according to the general procedure **D** over 192 h to obtain the product **S9f** as a beige solid (75.0 mg, 238  $\mu$ mol, 20%, m.p. 94.1 – 94.5°C) after NP-prep-HPLC (from hexane/EtOAc 98:2 to 80:20, 18 mL/min, 40°C):  $R_f$  0.57 (cyclohexane/EtOAc 5:1);  $\nu_{\max}(\text{neat})$ : 2964w, 2928w, 2862w, 2830w, 1581m, 1520m, 1450s, 1416s, 1378w, 1307s, 1257s, 1098s, 1028m, 975w, 939w, 817s, 712w, 644m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.00 (1H, d, <sup>3</sup>*J* 9.2 Hz, C10H), 7.92 (1H, d, <sup>3</sup>*J* 9.2 Hz, C9H), 7.77 (1H, d, <sup>3</sup>*J* 8.5 Hz, C2H), 7.36 (2H, s, C6H, C7H), 6.89 (1H, d, <sup>3</sup>*J* 8.5 Hz, C3H), 3.92 (3H, s, OCH<sub>3</sub>), 2.72 (3H, s, C8-CH<sub>3</sub>), 2.51 (3H, s, C5-CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 156.5 (C4), 135.4 (C5), 132.7 (C10a), 131.9 (C8a), 130.7 (C8), 130.4 (C2), 128.9 (C6), 128.4 (C4b), 127.8 (C7), 125.2 (C9), 124.2 (C10), 123.0 (C4a), 113.0 (C1), 107.7 (C3), 55.3 (C4-OCH<sub>3</sub>), 23.6 (C5-CH<sub>3</sub>), 19.6 (C8-CH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>17</sub>H<sub>15</sub>BrO 314.0301 found 314.0297 [M<sup>+</sup>].

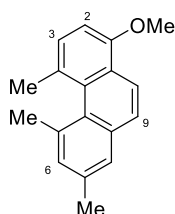
### 1,8-Dibromo-4,5-dimethoxyphenanthrene (S9g):



**S9g**

Step 1 of the general procedure **D** was performed using (2-bromo-5-methoxybenzyl)triphenylphosphonium bromide (1.30 g, 2.40 mmol, 1.20 eq.), 2-bromo-5-methoxybenzaldehyde (430 mg, 2.00 mmol, 1.00 eq.), and LiOt-Bu (320 mg, 4.00 mmol, 2.00 eq.) to give (*E, Z*)-1,2-bis(2-bromo-5-methoxyphenyl)ethene as a white solid (754 mg, 1.89 mmol, 95%). The obtained alkene (450 mg, 1.13 mmol) was subjected to the step 2 according to the general procedure **D** over 24 h to obtain the product **S9g** as a white solid (440 mg, 1.11 mmol, 98%, m.p. 90.9 – 88.6°C):  $R_f$  0.28 (cyclohexane/EtOAc 5:1);  $\nu_{\max}(\text{neat})$ : 2992w, 2931w, 2832w, 1588wm 1514m, 1443w, 1416m, 1311s, 1240s, 1108w, 1081s, 977w, 907m;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.09 (2H, s, C9H, C10H), 7.78 (2H, d,  $^3J$  8.5 Hz, C2H, C7H), 6.97 (2H, d,  $^3J$  8.5 Hz, C3H, C6H), 4.00 (6H, s,  $\text{OCH}_3$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 157.5 (C4, C5), 132.5 (C8a, C10a), 130.9 (C2, C7), 127.1 (C9, C10), 120.9 (C4a, C4b), 112.8 (C1, C8), 109.1 (C3, C6), 56.1 (C4– $\text{OCH}_3$ , C5– $\text{OCH}_3$ ); ESI-MS:  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{13}\text{Br}_2\text{O}_2$  394.9277 found 394.9720 [ $\text{M}+\text{H}^+$ ].

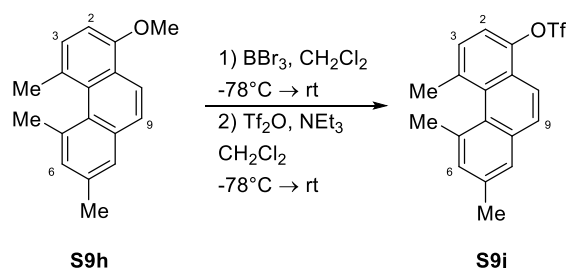
### 1-Methoxy-4,5,7-trimethylphenanthrene (S9h):



**S9h**

Step 1 of the general procedure **D** was performed using (3,5-dimethylbenzyl)triphenylphosphonium bromide (997 mg, 2.16 mmol, 1.20 eq.), 2-bromo-5-methoxybenzaldehyde (270 mg, 1.80 mmol, 1.00 eq.), and KOt-Bu (364 mg, 3.24 mmol, 1.80 eq.) to give (*E, Z*)-2-(3,5-dimethylstyryl)-1-methoxy-4-methylbenzen as a beige solid (380 mg, 1.51 mmol, 84%, m.p. 88.6 – 89.5°C). The obtained alkene (177 mg, 700  $\mu\text{mol}$ ) was subjected to the step 2 according to the general procedure **D** over 48 h to obtain the product **S9h** as a white solid (140 mg, 559  $\mu\text{mol}$ , 80%):  $R_f$  0.69 (cyclohexane/EtOAc 5:1);  $\nu_{\max}(\text{neat})$ : 2995w, 2949w, 2829w, 1828w, 1588m, 1524w, 1453s, 1376w, 1289s, 1256s, 1165w, 1024s, 907w, 854w, 802w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.04 (1H, d,  $^3J$  8.9 Hz, C10H), 7.49 (1H, d,  $^3J$  8.9 Hz, C9H), 7.47 (1H, s, C8H), 7.35 (1H, d,  $^3J$  8.1 Hz, C3H), 7.26 (1H, s, C6H), 6.99 (1H, d,  $^3J$  8.1 Hz, C2H), 4.04 (3H, s,  $\text{OCH}_3$ ), 2.60 (3H, s, C5– $\text{CH}_3$ ), 2.56 (3H, s, C4– $\text{CH}_3$ ), 2.55 (3H, s, C7– $\text{CH}_3$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 153.2 (C1), 135.9 (C5), 135.6 (C7), 134.4 (C8a), 131.7 (C4a), 130.1 (C6), 128.5 (C4b), 128.4 (C3), 127.6 (C4), 125.7 (C9), 124.6 (C8), 124.3 (C10a), 119.9 (C10), 106.2 (C2), 56.1 ( $\text{OCH}_3$ ), 22.7 (C5– $\text{CH}_3$ ), 22.2 (C4– $\text{CH}_3$ ), 21.3 (C7– $\text{CH}_3$ ); ESI-MS:  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{18}\text{AgO}$  357.0403 found 357.0395 [ $\text{M}+\text{Ag}^+$ ].

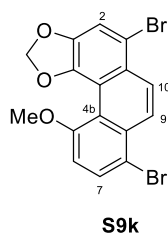
### 4,5,7-Trimethylphenanthren-1-yl trifluoromethanesulfonate (S9j):



**Step 1:** According to a modified literature procedure<sup>9</sup>: 1-Methoxy-4,5,7-trimethylphenanthrene **S9h** (125 mg, 500  $\mu\text{mol}$ , 1.00 eq.) was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (13 mL) and the resulting solution was cooled to  $-78^\circ\text{C}$  under argon. A solution of  $\text{BBr}_3$  in  $\text{CH}_2\text{Cl}_2$  (1.0 mL, 1.00 mmol, 2.00 eq.,  $1.0 \text{ mol}\cdot\text{L}^{-1}$ ) and a reaction mixture was left stirring for 18 h. Then water was added and the resulting mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3\times 20 \text{ mL}$ ). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0 $\rightarrow$ 60:40) to give the desired product 4,5,7-trimethylphenanthren-1-ol **S7i** as yellow oil (58.0 mg, 245  $\mu\text{mol}$ , 49%):  $R_f$  0.47 (cyclohexane/EtOAc 3:1);  $\nu_{\text{max}}(\text{neat})$ : 3501w, 3394w, 2995w, 2924w, 1596m, 1528w, 1450s, 1387w, 1331w, 1291s, 1215w, 1151w, 1079w, 871w, 803w, 710w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.92 (1H, d,  $^3J$  8.9 Hz, C10H), 7.48 (1H, d,  $^3J$  8.9 Hz, C9H), 7.46 (1H, s, C8H), 7.27 – 7.24 (2H, m, C3H, C6H), 6.93 (1H, d,  $^3J$  7.9 Hz, C2H), 5.09 (1H, s, OH), 2.58 (3H, s, C5-CH<sub>3</sub>), 2.54 (6H, s, C4-CH<sub>3</sub>, C7-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 149.0 (C1), 136.0 (C5), 135.8 (C7), 134.3 (C8a), 131.9 (C4a), 130.2 (C6), 128.6 (C4b), 128.5 (C3), 128.1 (C4), 125.9 (C9), 124.7 (C8), 122.9 (C10a), 119.4 (C10), 110.9 (C2), 22.7 (C5-CH<sub>3</sub>), 22.3 (C4-CH<sub>3</sub>), 21.3 (C7-CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{16}\text{NaO}$  259.1093 found 259.1088 [ $\text{M}+\text{Na}^+$ ].

**Step 2:** According to a modified literature procedure<sup>10</sup>: A solution of 4,5,7-trimethylphenanthren-1-ol (78.0 mg, 330  $\mu\text{mol}$ , 1.00 eq.) and  $\text{NEt}_3$  (67.0 mg, 660  $\mu\text{mol}$ , 2.00 eq.) in dry  $\text{CH}_2\text{Cl}_2$  (3.0 mL) was cooled to  $-78^\circ\text{C}$ . Trifluoromethanesulfonic anhydride (158 mg, 561  $\mu\text{mol}$ , 1.70 eq.) was added dropwise and the reaction mixture for stirred for 18 h. A saturated aqueous solution of  $\text{NH}_4\text{Cl}$  was then added and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3\times 20 \text{ mL}$ ). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0 $\rightarrow$ 80:20) to give the desired product 4,5,7-trimethylphenanthren-1-yl trifluoromethanesulfonate **S9j** as yellow oil (106 mg, 289  $\mu\text{mol}$ , 87%):  $R_f$  0.75 (cyclohexane/EtOAc 6:1);  $\nu_{\text{max}}(\text{neat})$ : 2992w, 2923w, 1861w, 1738w, 1657w, 1612w, 1418s, 1208s, 1139s, 1052m, 960w, 890s, 828s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.72 (1H, d,  $^3J$  8.9 Hz, C10H), 7.60 (1H, d,  $^3J$  8.9 Hz, C9H), 7.48 (1H, s, C8H), 7.43 – 7.40 (2H, m, C2H, C3H), 7.31 (1H, s, C6H), 2.60 (3H, s, C4-CH<sub>3</sub>), 2.55 (3H, s, C7-CH<sub>3</sub>), 2.53 (3H, s, C5-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 143.4 (C1), 136.9 (C5), 136.1 (C4), 136.0 (C7), 133.9 (C8a), 132.6 (C4a), 131.3 (C6), 129.0 (C9), 128.0 (C3), 127.9 (C4b), 126.2 (C10a), 125.2 (C8), 118.0 (C10), 117.7 (C2), 22.9 (C4-CH<sub>3</sub>), 22.7 (C7-CH<sub>3</sub>), 21.3 (C5-CH<sub>3</sub>);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -73.34; ESI-MS:  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{15}\text{F}_3\text{NaO}_3\text{S}$  391.0586 found 391.0580 [ $\text{M}+\text{Na}^+$ ].

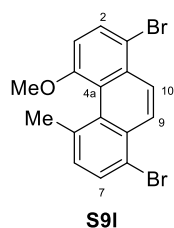
### 5,8-Dibromo-11-methoxyphenanthro[3,4-d][1,3]dioxole (S9k):



Step 1 of the general procedure **D** was performed using ((6-bromobenzo[d][1,3]dioxol-5-yl)methyl)triphenylphosphonium bromide (1.00 g, 1.80 mmol, 1.20 eq.), 2-bromo-5-methoxybenzaldehyde (323 mg, 1.50 mmol, 1.00 eq.), and  $\text{LiOt-Bu}$  (240 mg, 3.00 mmol, 2.00 eq.) to give (*E*, *Z*)-5-bromo-6-(2-bromo-5-methoxystyryl)benzo[d][1,3]dioxole as a transparent oil (465 mg, 1.13 mmol, 75%). The obtained alkene (350 mg, 850  $\mu\text{mol}$ ) was subjected to the step 2 according to the general procedure **D** over 200 h to obtain the

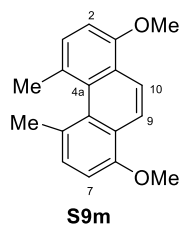
product **S9k** as a white solid (130 mg, 317  $\mu$ mol, 37%, m.p. 125.3 – 126.0°C):  $R_f$  0.50 (cyclohexane/EtOAc 4:1);  $\nu_{\max}$  (neat): 2999w, 2962w, 2902w, 2837w, 1863w, 1721w, 1676w, 1573m, 1430s, 1350w, 1273s, 1165w, 1105m, 1049s, 997w, 940m, 845m, 792m;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.10 (1H, d,  $^3J$  9.5 Hz, C10H), 7.92 (1H, d,  $^3J$  9.5 Hz, C9H), 7.80 (1H, d,  $^3J$  8.5 Hz, C7H), 7.53 (1H, s, C2H), 6.97 (1H, d,  $^3J$  8.5 Hz, C6H), 6.16 (2H, s,  $\text{OCH}_2\text{O}$ ), 4.01 (3H, s,  $\text{OCH}_3$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 157.1 (C5), 146.3 (C3), 144.3 (C4), 132.8 (C8a), 132.0 (C7), 128.0 (C10), 126.9 (C10a), 124.7 (C9), 119.6 (C4b), 115.4 (C4a), 114.3 (C1), 114.0 (C2), 113.0 (C8), 109.5 (C6), 101.2 ( $\text{OCH}_2\text{O}$ ), 56.1 ( $\text{OCH}_3$ ); ESI-MS:  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{10}\text{Br}_2\text{NaO}_3$  430.8889 found 430.8887 [ $\text{M}+\text{Na}^+$ ].

### 1,8-Dibromo-4-methoxy-5-methylphenanthrene (**S9l**):



Step 1 of the general procedure **D** was performed using (2-bromo-5-methylbenzyl)triphenylphosphonium bromide (947 mg, 1.80 mmol, 1.20 eq.), 2-bromo-5-methoxybenzaldehyde (323 mg, 1.50 mmol, 1.00 eq.), and  $\text{LiOt-Bu}$  (240 mg, 3.00 mmol, 2.00 eq.) to give (*E, Z*)-1-bromo-2-(2-bromo-5-methoxystyryl)-4-methylbenzene as a transparent oil (435 mg, 1.14 mmol, 76%). The obtained alkene (275 mg, 720  $\mu$ mol) was subjected to the step 2 according to the general procedure **D** over 48 h utilizing Kessil-370-Gen2 as a light source to obtain the product **S9l** as a beige solid (150 mg, 395  $\mu$ mol, 55%, m.p. 94.3 – 95.6°C):  $R_f$  0.63 (cyclohexane/EtOAc 5:1);  $\nu_{\max}$  (neat): 2967w, 2929w, 2851w, 1587w, 1558w, 1446m, 1417s, 1300s, 1259s, 1231s, 1098s, 1022m, 980w, 934w, 811m;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.15 (1H, d,  $^3J$  9.3 Hz, C9H), 8.05 (1H, d,  $^3J$  9.3 Hz, C10H), 7.80 (1H, d,  $^3J$  8.5 Hz, C2H), 7.75 (1H, d,  $^3J$  7.9 Hz, C7H), 7.29 (1H, d,  $^3J$  7.9 Hz, C6H), 6.92 (1H, d,  $^3J$  8.5 Hz, C3H), 3.93 (3H, s,  $\text{OCH}_3$ ), 2.48 (3H, s,  $\text{C5-CH}_3$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 156.4 (C4), 137.3 (C5), 133.0 (C10a), 131.5 (C8a), 131.3 (C2), 130.4 (C4b), 130.3 (C7), 129.7 (C6), 127.8 (C9), 126.0 (C10), 122.4 (C4a), 119.3 (C8), 113.1 (C1), 108.3 (C3), 55.4 ( $\text{OCH}_3$ ), 23.7 (C7- $\text{CH}_3$ ); ESI-MS:  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{13}\text{Br}_2\text{O}$  378.9328 found 378.9318 [ $\text{M}+\text{H}^+$ ].

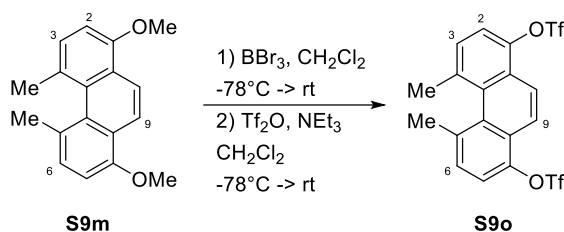
### 1,8-Dimethoxy-4,5-dimethylphenanthrene (**S9m**):



Step 1 of the general procedure **D** was performed using (2-methoxy-5-methylbenzyl)triphenylphosphonium bromide (1.72 g, 3.60 mmol, 1.20 eq.), 2-methoxy-5-methylbenzaldehyde (451 mg, 3.00 mmol, 1.00 eq.), and  $\text{KOt-Bu}$  (606 mg, 5.40 mmol, 1.80 eq.) to give (*E, Z*)-1,2-bis(5-methoxy-2-methylphenyl)ethene as a transparent oil (760 mg, 2.83 mmol, 94%). The obtained alkene (322 mg, 120 mmol) was subjected to the step 2 according to the general procedure **D** over 72 h to obtain the product **S9m** as a white solid (110 mg, 413  $\mu$ mol, 34%, m.p. 155.2 – 157.3°C):  $R_f$  0.54 (cyclohexane/EtOAc 5:1);  $\nu_{\max}$  (neat): 3006w, 2935w, 2842w, 1580s, 1526w, 1493m, 1451m, 1427s, 1378w, 1326w, 1291m, 1245s, 1214m, 1142s, 1079w, 1028s, 911w, 801s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.03 (2H, s, C9H, C10H), 7.30

(2H, d,  $^3J$  8.1 Hz, C3H, C6H), 6.95 (2H, d,  $^3J$  8.1 Hz, C2H, C7H), 4.01 (6H, s,  $2 \times \text{OCH}_3$ ), 2.52 (6H, s,  $2 \times \text{CH}_3$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 153.1 (C1, C8), 131.5 (C4a, C4b), 128.2 (C3, C6), 127.9 (C4, C5), 124.9 (C8a, C10a), 119.2 (C9, C10), 106.4 (C2, C7), 56.0 ( $\text{OCH}_3$ ), 22.1 ( $\text{CH}_3$ ); ESI-MS:  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{18}\text{AgO}_2$  373.0352 found 3763.0348 [ $\text{M}+\text{Ag}^+$ ].

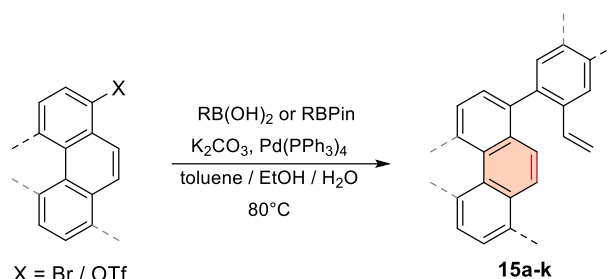
#### 4,5-Dimethylphenanthrene-1,8-diyl bis(trifluoromethanesulfonate) (S9o):



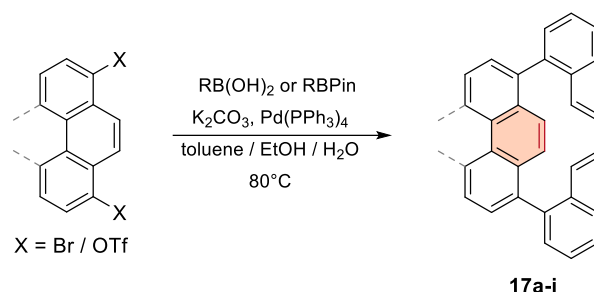
**Step 1:** According to a modified literature procedure<sup>9</sup>: 1,8-Dimethoxy-4,5-dimethylphenanthrene (394 mg, 1.48 mmol, 1.00 eq.) was dissolved in dry  $\text{CH}_2\text{Cl}_2$  (37 mL) and the resulting solution was cooled to  $-78^\circ\text{C}$  under argon. A solution of  $\text{BBr}_3$  in  $\text{CH}_2\text{Cl}_2$  (5.9 mL, 5.92 mmol, 4.00 eq.,  $1.0 \text{ mol} \cdot \text{L}^{-1}$ ) and a reaction mixture was left stirring for 18 h. Then water was added and the resulting mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 20 \text{ mL}$ ). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0  $\rightarrow$  60:40) to give the desired product 4,5-dimethylphenanthrene-1,8-diol **S9n** as a white solid (112 mg, 470  $\mu\text{mol}$ , 32%, m.p.  $205.5 - 206.0^\circ\text{C}$  (decomposition)):  $R_f$  0.33 (cyclohexane/EtOAc 5:2);  $\nu_{\text{max}}$  (neat): 3216w, 2929w, 1847w, 1707w, 1590m, 1498w, 1446w, 1400m, 1337m, 1291m, 1243s, 1155m, 1121s, 972m, 854s, 806s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.94 (2H, s, C9H, C10H), 7.24 (2H, d,  $^3J$  7.8 Hz, C3H, C6H), 6.93 (1H, d,  $^3J$  7.8 Hz, C2H, C7H), 5.12 (2H, s, OH), 2.51 (6H, s,  $\text{OCH}_2$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 148.9 (C1, C8), 131.7 (C4a, C4b), 128.6 (C4, C5), 128.5 (C3, C6), 123.4 (C8a, C10a), 118.9 (C9, C10), 111.3 (C2, C7), 22.2 ( $\text{CH}_3$ ); ESI-MS:  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{13}\text{O}_2$  237.0921 found 237.0925 [ $\text{M}-\text{H}^+$ ].

**Step 2:** According to a modified literature procedure<sup>10</sup>: A solution of 4,5-dimethylphenanthrene-1,8-diol (62.0 mg, 260  $\mu\text{mol}$ , 1.00 eq.) and  $\text{NEt}_3$  (78.9 mg, 780  $\mu\text{mol}$ , 3.00 eq.) in dry  $\text{CH}_2\text{Cl}_2$  (2.0 mL) was cooled to  $-78^\circ\text{C}$ . Trifluoromethanesulfonic anhydride (183 mg, 650  $\mu\text{mol}$ , 2.50 eq.) was added dropwise and the reaction mixture for stirred for 18 h. A saturated aqueous solution of  $\text{NH}_4\text{Cl}$  was then added and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 20 \text{ mL}$ ). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0  $\rightarrow$  80:20) to give the desired product 4,5-dimethylphenanthrene-1,8-diyl bis(trifluoromethanesulfonate) **S9o** as a white solid (91.0 mg, 181  $\mu\text{mol}$ , 70%, m.p.  $98.3 - 99.0^\circ\text{C}$ ):  $R_f$  0.45 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$  (neat): 2973m, 2920w, 1593w, 1420s, 1210s, 1137s, 1086s, 966m, 883m, 813m, 652w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.93 (2H, s, C9H, C10H), 7.60 – 7.46 (4H, m, C2H, C3H, C6H, C7H), 2.61 (6H, s, C4- $\text{CH}_3$ , C5- $\text{CH}_3$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 143.3 (C1, C8), 136.8 (C4, C5), 131.7 (C4a, C4b), 129.3 (C3, C6), 126.5 (C10a, C8a), 120.7 (C9, C10), 119.3 (C2, C7), 22.8 (C4- $\text{CH}_3$ , C5- $\text{CH}_3$ );  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -73.19; ESI-MS:  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{12}\text{F}_6\text{KO}_6\text{S}_2$  540.9611 found 540.9609 [ $\text{M}+\text{K}^+$ ].

## General Procedure E for the Synthesis of 15a-k, 17a-i:

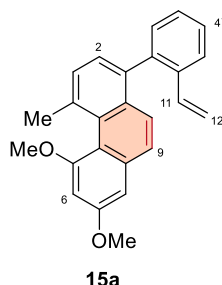


The bromide/triflate **S9** (1.00 eq.), the corresponding boronic acid or ester (1.11 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol%), and K<sub>2</sub>CO<sub>3</sub> (3.00 eq.) were weighed into a 10 or 20 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before a degassed mixture of toluene, H<sub>2</sub>O, ethanol (2 : 2 : 1) (0.12 mol·L<sup>-1</sup>) was added. The resulting mixture was stirred at 80°C for 18 h, then cooled to room temperature, filtered through a thin layer of silica gel and Na<sub>2</sub>SO<sub>4</sub> using EtOAc (15-20 mL). The solvents were removed under reduced pressure and the residue was purified by the silica gel chromatography (cyclohexane/EtOAc 100:0→80:20) to give the desired product.



The bromide/triflate **S9** (1.00 eq.), the corresponding boronic acid or ester (2.80 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol%), and K<sub>2</sub>CO<sub>3</sub> (4.00 eq.) were weighed into a 10 or 20 mL crimp cap vial. The vial was sealed, evacuated and backfilled with argon before a degassed mixture of toluene, H<sub>2</sub>O, ethanol (2 : 2 : 1) (0.12 mol·L<sup>-1</sup>) was added. The resulting mixture was stirred at 80°C for 18 h, then cooled to room temperature, filtered through a thin layer of silica gel and Na<sub>2</sub>SO<sub>4</sub> using EtOAc (15-20 mL). The solvents were removed under reduced pressure and the residue was purified by the silica gel chromatography (cyclohexane/EtOAc 100:0→80:20) to give the desired product.

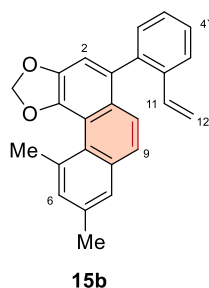
### 5,7-Dimethoxy-4-methyl-1-(2-vinylphenyl)phenanthrene (**15a**):



Prepared according to the general procedure **E** using 1-bromo-5,7-dimethoxy-4-methylphenanthrene **S9a** (66.2 mg, 200 μmol, 1.00 eq.) and (2-vinylphenyl)boronic acid (32.8 mg, 222 μmol, 1.11 eq.) to give **15a** as yellow oil (56.0 mg, 158 μmol, 79%): *R*<sub>f</sub> 0.63 (cyclohexane/EtOAc 6:1); *v*<sub>max</sub> (neat): 3049w, 2996w, 2960w, 2856w, 1603s, 1526m, 1453m, 1424m, 1356m, 1274m, 1216m, 1159s, 1109m, 1057m, 988w, 908m, 832m, 730m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.74 (1H, dd, <sup>3</sup>*J* 7.9, <sup>4</sup>*J* 1.2 Hz, C3'*H*), 7.46 (1H, <sup>3</sup>*J* 7.0 Hz, C3*H*), 7.44 – 7.39 (1H, m, C4'*H*), 7.38 – 7.31 (2H, m, C5'*H*, C9*H*), 7.31 – 7.26 (2H, m, C6'*H*, C2*H*), 7.23 (1H, d, <sup>3</sup>*J* 8.9 Hz, C10*H*), 6.83 (1H, d, <sup>4</sup>*J* 2.4 Hz, C8*H*), 6.70 (1H, d, <sup>4</sup>*J* 2.4 Hz, C6*H*), 6.41 (1H, dd, <sup>3</sup>*J* 17.5, <sup>3</sup>*J* 11.0 Hz, C11*H*), 5.66 (1H, dd, <sup>3</sup>*J* 17.5, <sup>2</sup>*J* 1.2 Hz, C12*H*), 4.98 (1H, dd, <sup>3</sup>*J* 11.0, <sup>2</sup>*J* 1.2 Hz, C12*H*), 3.97 (3H, s, C5–OCH<sub>3</sub>), 3.96 (3H, s, C7–OCH<sub>3</sub>), 2.60 (3H, s, C4–CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 159.2 (C7), 158.2 (C5), 140.2 (C1'), 137.2 (C2'), 136.0 (C4), 135.7 (C8*a*, C11), 135.4 (C1), 131.7 (C6'), 131.0 (C10*a*), 129.2 (C4*a*), 128.6 (C3), 127.7 (C4'), 127.6 (C5'), 126.9 (C2), 126.5 (C10), 125.7 (C9), 124.8

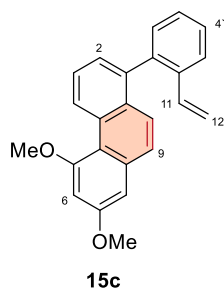
(C3'), 115.7 (C4b), 114.4 (C12), 100.0 (C8), 98.1 (C6), 55.6 (C7–OCH<sub>3</sub>), 55.1 (C5–OCH<sub>3</sub>), 24.2 (C4–CH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>25</sub>H<sub>22</sub>AgO<sub>2</sub> 461.0665 found 461.0673 [M+Ag<sup>+</sup>].

### 9,11-Dimethyl-5-(2-vinylphenyl)phenanthro[3,4-d][1,3]dioxole (15b):



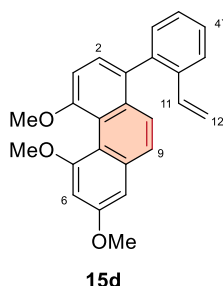
Prepared according to the general procedure **E** using 5-bromo-9,11-dimethylphenanthro[3,4-d][1,3]dioxole **S9b** (165 mg, 500 μmol, 1.00 eq.) and (2-vinylphenyl)boronic acid (82.1 mg, 555 μmol, 1.11 eq.) to give **15b** as a beige solid (150 mg, 426 μmol, 85%, m.p. 140.7 – 142.0°C): *R<sub>f</sub>* 0.64 (cyclohexane/EtOAc 7:1); *v*<sub>max</sub> (neat): 3055w, 2975w, 2872w, 2769w, 1747w, 1622w, 1588m, 1435s, 1382s, 1263s, 1103s, 1038s, 998m, 942m, 866m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.73 (1H, d, <sup>3</sup>*J* 7.8 Hz, C3'*H*), 7.43 (1H, t, <sup>3</sup>*J* 7.6 Hz, C4'*H*), 7.39 – 7.33 (2H, m, C5'*H*, C8*H*), 7.32 – 7.27 (2H, m, C6'*H*, C6*H*), 7.22 (1H, d, <sup>3</sup>*J* 9.1 Hz, C9*H*), 7.12 – 7.06 (2H, m, C10*H*, C2*H*), 6.41 (1H, dd, <sup>3</sup>*J* 17.5, <sup>3</sup>*J* 11.0 Hz, C11*H*), 6.17 (2H, dd, <sup>2</sup>*J* 9.5, <sup>5</sup>*J* 1.4 Hz, OCH<sub>2</sub>O), 5.67 (1H, d, <sup>3</sup>*J* 17.5 Hz, C12*H*), 5.03 (1H, d, <sup>3</sup>*J* 11.0 Hz, C12*H*), 2.74 (3H, s, C5–CH<sub>3</sub>), 2.49 (3H, s, C7–CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 144.8 (C3), 142.6 (C4), 139.8 (C1'), 137.2 (C2'), 136.61 (C7), 136.58 (C5), 135.4 (C11), 133.7 (C10*a*), 132.7 (C1), 131.55 (C6), 131.53 (C6'), 128.01 (C4*b*), 127.96 (C4'), 127.7 (C5'), 125.38 (C8*a*), 125.32 (C9), 125.0 (C8, C3'), 124.8 (C10), 116.4 (C4*a*), 114.8 (C12), 110.8 (C2), 100.3 (OCH<sub>2</sub>O), 24.0 (C5–CH<sub>3</sub>), 21.2 (C7–CH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>25</sub>H<sub>20</sub>AgO<sub>2</sub> 459.0509 found 459.0507 [M+Ag<sup>+</sup>].

### 5,7-Dimethoxy-1-(2-vinylphenyl)phenanthrene (15c):



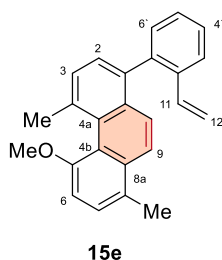
Prepared according to the general procedure **E** using 1-bromo-5,7-dimethoxyphenanthrene **S9c** (79.3 mg, 250 μmol, 1.00 eq.) and (2-vinylphenyl)boronic acid (41.1 mg, 278 μmol, 1.11 eq.) to give **15c** as a beige solid (70.0 mg, 206 μmol, 82%, m.p. 180.0 – 181.0°C): *R<sub>f</sub>* 0.51 (cyclohexane/EtOAc 5:1); *v*<sub>max</sub> (neat): 3054w, 3003w, 2938w, 2835w, 1834w, 1735w, 1609s, 1528m, 1453s, 1311s, 1199s, 1157s, 1103m, 1060m, 954m, 914m, 864m, 807m, 764m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 9.63 (1H, d, <sup>3</sup>*J* 8.7 Hz, C4*H*), 7.76 (1H, d, <sup>3</sup>*J* 7.8 Hz, C3'*H*), 7.64 (1H, dd, <sup>3</sup>*J* 8.7, <sup>3</sup>*J* 7.1 Hz, C3*H*), 7.50 (1H, d, <sup>3</sup>*J* 9.1 Hz, C9*H*), 7.47 – 7.42 (1H, m, C4'*H*), 7.41 – 7.35 (3H, m, C2*H*, C10*H*, C5'*H*), 7.31 (1H, dd, <sup>3</sup>*J* 7.5, <sup>4</sup>*J* 1.4 Hz, C6'*H*), 6.87 (1H, d, <sup>4</sup>*J* 2.5 Hz, C8*H*), 6.81 (1H, d, <sup>4</sup>*J* 2.5 Hz, C6*H*), 6.32 (1H, dd, <sup>3</sup>*J* 17.5, <sup>3</sup>*J* 11.0 Hz, C11*H*), 5.65 (1H, dd, <sup>3</sup>*J* 17.5, <sup>2</sup>*J* 1.1 Hz, C12*H*), 4.97 (1H, dd, <sup>3</sup>*J* 11.0, <sup>2</sup>*J* 1.1 Hz, C12*H*), 4.14 (3H, s, C5–OCH<sub>3</sub>), 3.95 (3H, s, C7–OCH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 160.2 (C5), 158.5 (C7), 140.5 (C1'), 138.8 (C1), 137.0 (C2'), 135.4 (C11), 131.2 (C6'), 130.7 (C4*a*), 130.4 (C10*a*), 127.8 (C4'), 127.4 (C5'), 127.3 (C4), 127.0 (C9), 126.9 (C2), 126.3 (C10), 125.8 (C3), 124.8 (C3'), 115.9 (C4*b*), 114.5 (C12), 101.4 (C8), 99.7 (C6), 56.0 (C5–OCH<sub>3</sub>), 55.6 (C7–OCH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>24</sub>H<sub>20</sub>AgO<sub>2</sub> 447.0509 found 447.0503 [M+Ag<sup>+</sup>].

#### 4,5,7-Trimethoxy-1-(2-vinylphenyl)phenanthrene (15d):



Prepared according to the general procedure E using 1-bromo-4,5,7-trimethoxyphenanthrene **S9d** (86.8 mg, 250  $\mu$ mol, 1.00 eq.) and (2-vinylphenyl)boronic acid (41.1 mg, 278  $\mu$ mol, 1.11 eq.) to give **15d** as yellow solid (65.6 mg, 177  $\mu$ mol, 71%, m.p. 86.0 – 86.5°C):  $R_f$  0.55 (cyclohexane/EtOAc 5:1);  $\nu_{\max}$  (neat): 3085w, 2988w, 2933w, 2830w, 1600m, 1525m, 1452m, 1424m, 1353w, 1320w, 1243m, 1215m, 1156s, 1064s, 986w, 912w, 835w, 758w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.77 – 7.70 (1H, m, C3'H), 7.44 – 7.40 (1H, m, C4'H), 7.38 (1H, d,  $^3J$  9.1 Hz, C9H), 7.37 – 7.33 (1H, m, C5'H), 7.32 – 7.28 (2H, m, C2H, C6'H), 7.20 (1H, d,  $^3J$  9.1 Hz, C10H), 7.12 (1H, d,  $^3J$  8.1 Hz, C3H), 6.81 (1H, d,  $^4J$  2.4 Hz, C8H), 6.75 (1H, d,  $^4J$  2.4 Hz, C6H), 6.42 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C11H), 5.67 (1H, d,  $^2J$  1.3 Hz, C12H), 4.99 (1H, dd,  $^3J$  11.0,  $^2J$  1.2 Hz, C12H), 4.07 (3H, s, C4–OCH<sub>3</sub>), 4.04 (3H, s, C5–OCH<sub>3</sub>), 3.94 (3H, s, C7–OCH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 159.13 (C5), 159.05 (C7), 156.8 (C4), 139.9 (C1'), 137.4 (C2'), 135.7 (C11), 135.1 (C8a), 132.1 (C10a), 131.8 (C6'), 130.4 (C1), 127.7 (C2), 127.60 (C4'), 127.57 (C5'), 126.8 (C9), 125.8 (C10), 124.8 (C3'), 119.6 (C4a), 114.3 (C12), 114.2 (C4b), 107.7 (C3), 100.0 (C8), 99.1 (C6), 55.96 (C5–OCH<sub>3</sub>), 55.91 (C4–OCH<sub>3</sub>), 55.7 (C7–OCH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{25}\text{H}_{22}\text{AgO}_3$  477.0614 found 477.0608 [ $\text{M}+\text{Ag}^+$ ].

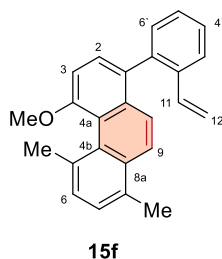
#### 4-Methoxy-1,5-dimethyl-8-(2-vinylphenyl)phenanthrene (15e):



Prepared according to the general procedure E using 1-bromo-5-methoxy-4,8-dimethylphenanthrene **S9e** (107 mg, 340  $\mu$ mol, 1.00 eq.) and (2-vinylphenyl)boronic acid (55.8 mg, 278  $\mu$ mol, 1.11 eq.) to give **15e** as a white solid (88.0 mg, 260  $\mu$ mol, 77%, m.p. 80.5 – 81.5°C):  $R_f$  0.64 (cyclohexane/EtOAc 7:1);  $\nu_{\max}$  (neat): 3057w, 2949w, 2929w, 2831w, 2730w, 1577m, 1527m, 1450m, 1427s, 1376w, 1327m, 1258s, 1219m, 1164w, 1098s, 1021w, 980w, 912w, 815s, 759s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.75 (1H, d,  $^3J$  6.8 Hz, C3'H), 7.59 (1H, d,  $^3J$  9.2 Hz, C9H), 7.48 (1H, d,  $^3J$  7.4 Hz, C3H), 7.42 (1H, dd,  $^3J$  7.6,  $^4J$  1.3 Hz, C4'H), 7.39 – 7.32 (3H, m, C2H, C7H, C5'H), 7.32 – 7.27 (2H, m, C10H, C6'H), 6.96 (1H, d,  $^3J$  8.0 Hz, C6H), 6.42 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C11H), 5.67 (1H, dd,  $^3J$  17.5,  $^2J$  1.2 Hz, C12H), 4.99 (1H, dd,  $^3J$  11.0,  $^2J$  1.1 Hz, C12H), 3.97 (3H, s, C5–OCH<sub>3</sub>), 2.62 (3H, s, C8–CH<sub>3</sub>), 2.61 (3H, s, C4–CH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 155.5 (C5), 140.0 (C1'), 137.2 (C2'), 137.0 (C4), 135.6 (C11), 135.1 (C1), 133.2 (C8a), 131.7 (C6'), 131.6 (C10a), 129.1 (C4a), 128.3 (C3), 128.1 (C7), 127.8 (C4'), 127.6 (C5'), 127.5 (C2), 125.7 (C10), 125.5 (C8), 124.8 (C3'), 121.9 (C9), 120.9 (C4b), 114.4 (C12), 106.6 (C6), 55.0 (OCH<sub>3</sub>), 24.0 (C4–CH<sub>3</sub>), 19.2 (C8–CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{25}\text{H}_{22}\text{O}$  338.1665 found 338.1659 [ $\text{M}^+$ ].

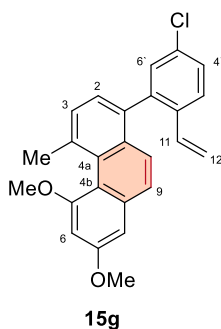


#### 4-Methoxy-5,8-dimethyl-1-(2-vinylphenyl)phenanthrene (**15f**):



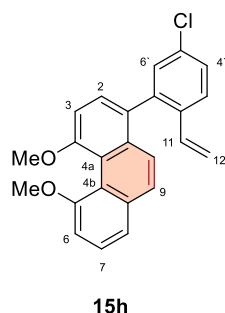
Prepared according to the general procedure **E** using 1-bromo-4-methoxy-5,8-dimethylphenanthrene **S9f** (59.9 mg, 190  $\mu$ mol, 1.00 eq.) and (2-vinylphenyl)boronic acid (31.2 mg, 211  $\mu$ mol, 1.11 eq.) to give **15f** as a transparent oil (52.0 mg, 154  $\mu$ mol, 81%):  $R_f$  0.77 (cyclohexane/EtOAc 5:1);  $\nu_{\max}$  (neat): 3060w, 3017w, 2956w, 2928w, 2863w, 2831w, 1681w, 1578m, 1526m, 1453s, 1381w, 1305s, 1252s, 1219m, 1099s, 1026w, 993w, 908m, 820m, 761m, 729s, 630s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.78 – 7.73 (1H, m, C3'H), 7.69 (1H, d,  $^3J$  9.2 Hz, C9H), 7.48 – 7.41 (1H, m, C4'H), 7.39 (1H, d,  $^3J$  8.0 Hz, C2H), 7.37 – 7.29 (4H, m, C6H, C7H, C5'H, C6'H), 7.21 (1H, d,  $^3J$  9.2 Hz, C10H), 7.07 (1H, d,  $^3J$  8.0 Hz, C3H), 6.43 (1H, dd,  $^3J$  17.6,  $^3J$  11.0 Hz, C11H), 5.67 (1H, dd,  $^3J$  17.6,  $^2J$  1.2 Hz, C12H), 5.01 (1H, dd,  $^3J$  11.0,  $^2J$  1.2 Hz, C12H), 3.99 (3H, s,  $\text{OCH}_3$ ), 2.65 (3H, s, C8-CH<sub>3</sub>), 2.59 (3H, s, C5-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 156.5 (C4), 139.8 (C1'), 137.4 (C2'), 135.6 (C11), 135.4 (C5), 133.1 (C10a), 131.9 (C6'), 131.7 (C8a), 130.5 (C8), 130.2 (C1), 128.8 (C4b), 128.59 (C2/C6), 128.52 (C2/C6), 127.8 (C4'), 127.6 (C5'), 127.3 (C7), 124.9 (C3'), 123.9 (C10), 123.6 (C9), 121.0 (C4a), 114.5 (C12), 106.4 (C3), 55.0 ( $\text{OCH}_3$ ), 23.8 (C5-CH<sub>3</sub>), 19.6 (C8-CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{25}\text{H}_{22}\text{AgO}$  445.0716 found 445.0720 [ $\text{M}+\text{Ag}^+$ ].

#### 1-(5-Chloro-2-vinylphenyl)-5,7-dimethoxy-4-methylphenanthrene (**15g**):



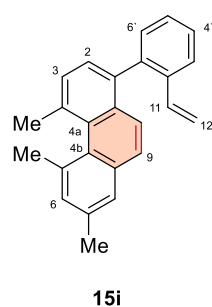
Prepared according to the general procedure **E** using 1-bromo-5,7-dimethoxy-4-methylphenanthrene **S9a** (77.8 mg, 235  $\mu$ mol, 1.00 eq.) and 2-(5-chloro-2-vinylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (71.5 mg, 270  $\mu$ mol, 1.11 eq.) to give **15g** as a beige solid (70.0 mg, 180  $\mu$ mol, 77%):  $R_f$  0.52. (cyclohexane/EtOAc 6:1);  $\nu_{\max}$  (neat): 3007w, 2948w, 1600s, 1527w, 1453m, 1424w, 1358w, 1310w, 1272w, 1218m, 1162s, 1116m, 1058w, 1024w, 988w, 914w, 829m, 736w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.66 (1H, d,  $^3J$  8.5 Hz, C3'H), 7.46 (1H, d,  $^3J$  7.4 Hz, C3H), 7.38 (1H, dd,  $^3J$  8.5,  $^4J$  2.3 Hz, C4'H), 7.36 (1H, d,  $^3J$  9.0 Hz, C9H), 7.30 (1H, d,  $^4J$  2.3 Hz, C6'H), 7.26 – 7.24 (1H, m, C2H), 7.19 (1H, d,  $^3J$  9.0 Hz, C10H), 6.83 (1H, d,  $^4J$  2.4 Hz, C8H), 6.70 (1H, d,  $^4J$  2.4 Hz, C6H), 6.33 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C11H), 5.63 (1H, dd,  $^3J$  17.5,  $^2J$  1.1 Hz, C12H), 5.00 (1H, dd,  $^3J$  11.0,  $^2J$  1.1 Hz, C12H), 3.98 (3H, s, C5-OCH<sub>3</sub>), 3.96 (3H, s, C7-OCH<sub>3</sub>), 2.60 (3H, s, C4-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 159.3 (C7), 158.2 (C5), 141.7 (C1'), 136.6 (C4), 135.8 (C2'), 135.6 (C8a), 134.6 (C11), 133.9 (C1), 133.1 (C5'), 131.4 (C6'), 130.7 (C10a), 129.2 (C4a), 128.6 (C3), 127.9 (C4'), 126.6 (C2), 126.2 (C3'), 126.03 (C9/C10), 126.01 (C9/C10), 115.7 (C4b), 115.0 (C12), 100.1 (C8), 98.3 (C6), 55.7 (C7-OCH<sub>3</sub>), 55.1 (C5-OCH<sub>3</sub>), 24.2 (C4-CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{25}\text{H}_{21}\text{AgClO}_2$  495.0276 found 495.0276 [ $\text{M}+\text{Ag}^+$ ].

### 1-(5-Chloro-2-vinylphenyl)-4,5-dimethoxyphenanthrene (**15h**):



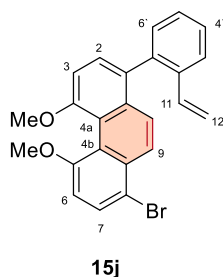
Prepared according to the general procedure **E** using 1,8-dibromo-4,5-dimethoxyphenanthrene **S9g** (110 mg, 278  $\mu$ mol, 1.00 eq.) and 2-(5-chloro-2-vinylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (69.9 mg, 264  $\mu$ mol, 0.95 eq.) but at 120°C over 18 h to give **15h** as a transparent oil (36.0 mg, 96.0  $\mu$ mol, 36%) after NP-prep-HPLC (from hexane/EtOAc 98:2 to 80:20, 18 mL/min, 35°C):  $R_f$  0.48 (cyclohexane/EtOAc 5:1);  $\nu_{\max}$ (neat): 3054w, 2994w, 2933w, 2832w, 1590w, 1524s, 1453s, 1433m, 1314s, 1249s, 1108m, 1064s, 983w, 908m, 862w, 818s, 731s, 632s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.66 (1H, d,  $^3J$  8.5 Hz, C3'H), 7.52 (1H, t,  $^3J$  7.8 Hz, C7H), 7.47 (1H, d,  $^3J$  9.0 Hz, C9H), 7.42 – 7.36 (2H, m, C8H, C4'H), 7.34 (1H, d,  $^3J$  8.1 Hz, C2H), 7.30 (1H, d,  $^3J$  2.2 Hz, C6'H), 7.17 (1H, d,  $^3J$  9.0 Hz, C10H), 7.15 – 7.11 (2H, m, C3H, C6H), 6.34 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C11H), 5.63 (1H, dd,  $^3J$  17.5,  $^2J$  1.1 Hz, C12H), 5.00 (1H, dd,  $^3J$  11.0,  $^2J$  1.1 Hz, C12H), 4.09 (3H, s, C4–OCH<sub>3</sub>), 4.08 (3H, s, C5–OCH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 158.0 (C5), 157.6 (C4), 141.4 (C1'), 136.0 (C2'), 134.6 (C11), 134.4 (C8a), 133.2 (C5'), 132.8 (C10a), 131.6 (C6'), 128.8 (C1), 128.4 (C2), 127.9 (C4'), 127.3 (C9), 127.0 (C7), 126.2 (C3'), 124.7 (C10), 119.6 (C8), 119.3 (C4a/C4b), 119.2 (C4a/C4b), 115.0 (C12), 108.4 (C6), 107.5 (C3), 55.96 (C4–OCH<sub>3</sub>/C5–OCH<sub>3</sub>), 55.94 (C4–OCH<sub>3</sub>/C5–OCH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{24}\text{H}_{19}\text{ClNaO}_2$  397.0966 found 397.0959 [ $\text{M}+\text{Na}^+$ ].

### 4,5,7-Trimethyl-1-(2-vinylphenyl)phenanthrene (**15i**):



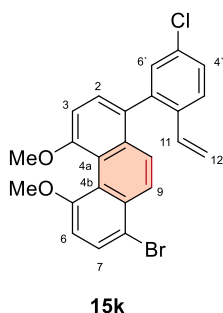
Prepared according to the general procedure **E** using 4,5,7-trimethylphenanthren-1-yl trifluoromethanesulfonate **S9j** (99.5 mg, 270  $\mu$ mol, 1.00 eq.) and (2-vinylphenyl)boronic acid (47.9 mg, 324  $\mu$ mol, 1.20 eq.) **15i** as a white solid (70.0 mg, 217  $\mu$ mol, 80%, m.p. 73.3 – 74.2°C);  $R_f$  0.77 (cyclohexane/EtOAc 5:1);  $\nu_{\max}$ (neat): 3055w, 3017w, 2922w, 2850w, 1604w, 1445m, 1375w, 1304w, 1173w, 1028w, 990w, 909m, 855m, 829m, 756s, 720s, 646w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.84 – 7.67 (1H, m, C3'H), 7.49 – 7.26 (8H, m, C2H, C3H, C6H, C8H, C9H, C4'H, C5'H, C6'H), 7.20 – 7.05 (1H, m, C10H), 6.54 – 6.31 (1H, m, C11H), 5.71 (d,  $^3J$  17.5 Hz, C12H), 5.64 (d,  $^3J$  17.5 Hz, C12H), 5.09 (d,  $^3J$  11.0 Hz, C12H), 4.93 (d,  $^3J$  11.1 Hz, C12H), 2.67 – 2.60 (6H, m, C4–CH<sub>3</sub>, C5–CH<sub>3</sub>), 2.52 (3H, s, C7–CH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 140.1 (C1'), 140.0 (C1'), 137.1 (C2'), 136.0 (C5), 135.8 (C7), 135.7 (C11), 135.5 (C11), 135.35 (C1), 135.26 (C1), 135.2 (C4), 133.9 (C8a), 133.86 (C8a), 132.3 (C10a), 131.8 (C6'), 131.7 (C6'), 130.9 (C4a), 130.7 (C4a), 130.3 (C6), 128.8 (C4b), 128.5 (C4a), 127.9 (C3), 127.8 (C5'), 127.7 (C4'), 127.65 (C3), 127.4 (C5'), 127.3 (C2), 126.3 (C9), 125.1 (C3'), 124.7 (C11), 124.6 (C10, C8), 114.5 (C12), 22.9 (C4–CH<sub>3</sub>), 22.8 (C5–CH<sub>3</sub>), 22.7 (C7–CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{25}\text{H}_{22}\text{Ag}$  429.0767 found 429.0768 [ $\text{M}+\text{Ag}^+$ ].

### 1-Bromo-4,5-dimethoxy-8-(2-vinylphenyl)phenanthrene (**15j**):



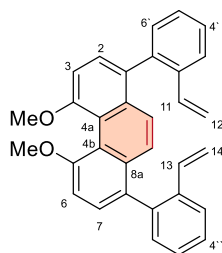
Prepared according to the general procedure **E** using 1,8-dibromo-4,5-dimethoxyphenanthrene **S9g** (131 mg, 330  $\mu$ mol, 1.00 eq.) and (2-vinylphenyl)boronic acid (44.9 mg, 304  $\mu$ mol, 0.92 eq.) over 7 h to give **15j** as a white solid (48.0 mg, 114  $\mu$ mol, 38%, m.p. 84.1 – 85.2°C): after NP-prep-HPLC (from hexane/EtOAc 98:2 to 80:20, 18 mL/min, 40°C) after NP-prep-HPLC (from hexane/EtOAc 98:2 to 80:20, 18 mL/min, 40°C):  $R_f$  0.33 (cyclohexane/EtOAc 5:1);  $v_{max}$  (neat): 3004w, 2932w, 2839w, 2753w, 2721w, 2668w, 2622w, 1582w, 1580w, 1522m, 1451w, 1421m, 1313s, 1265m, 1238m, 1109w, 1068s, 983w, 908m, 809m, 731s, 663w;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 7.87 (1H, d,  $^3J$  9.2 Hz, C9H), 7.81 – 7.74 (2H, m, C3'H, C7H), 7.46 – 7.40 (2H, m, C2H, C4'H), 7.36 (1H, td,  $^3J$  7.4,  $^4J$  1.2 Hz, C5'H), 7.32 (1H, d,  $^3J$  9.2 Hz, C10H), 7.28 (1H, dd,  $^3J$  7.4,  $^4J$  1.4 Hz, C6'H), 7.16 (1H, d,  $^3J$  8.1 Hz, C3H), 6.98 (1H, d,  $^3J$  8.5 Hz, C6H), 6.40 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C11H), 5.67 (1H, dd,  $^3J$  17.5,  $^2J$  1.1 Hz, C12H), 5.00 (1H, dd,  $^3J$  11.0,  $^2J$  1.1 Hz, C12H), 4.08 (3H, s, C4–OCH<sub>3</sub>), 4.06 (3H, s, C5–OCH<sub>3</sub>);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 157.5 (C5), 157.4 (C4), 139.4 (C1'), 137.4 (C2'), 135.6 (C11), 132.9 (C10a), 132.3 (C8a), 131.8 (C6'), 130.4 (C7), 130.3 (C1), 129.1 (C2), 127.9 (C4'), 127.7 (C5'), 126.8 (C10), 125.6 (C9), 125.0 (C3'), 121.2 (C4b), 118.9 (C4a), 114.6 (C12), 112.8 (C8), 108.7 (C6), 107.8 (C3), 56.1 (C5–OCH<sub>3</sub>), 56.0 (C4–OCH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $C_{24}H_{19}BrAgO_2$  524.9614 found 524.9608 [M+Ag<sup>+</sup>].

### 1-Bromo-8-(5-chloro-2-vinylphenyl)-4,5-dimethoxyphenanthrene (**15k**):



Prepared according to the general procedure **E** using 1,8-dibromo-4,5-dimethoxyphenanthrene **S9g** (102 mg, 258  $\mu$ mol, 1.00 eq.) and 2-(5-chloro-2-vinylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (64.8 mg, 245  $\mu$ mol, 0.95 eq.) but at 75°C over 7 h to give **15k** as a transparent oil (37.0 mg, 81.5  $\mu$ mol, 32%) after NP-prep-HPLC (from hexane/EtOAc 98:2 to 80:20, 18 mL/min, 40°C):  $R_f$  0.43 (cyclohexane/EtOAc 5:1);  $v_{max}$  (neat): 3063w, 2949w, 2932w, 2836w, 1742w, 1721w, 1669w, 1585w, 1522m, 1461w, 1428m, 1313s, 1249s, 1235s, 1106m, 1067s, 1018m, 985w, 907m, 807s, 729s;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  = 7.90 (1H, d,  $^3J$  9.2 Hz, C9H), 7.76 (1H, d,  $^3J$  8.5 Hz, C7H), 7.66 (1H, d,  $^3J$  8.5 Hz, C3'H), 7.42 – 7.36 (2H, m, C2H, C4'H), 7.29 (1H, s, C6'H), 7.29–7.27 (1H, m, C10H), 7.15 (1H, d,  $^3J$  8.1 Hz, C3H), 6.98 (1H, d,  $^3J$  8.5 Hz, C6H), 6.32 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C11H), 5.64 (1H, dd,  $^3J$  17.5,  $^2J$  1.0 Hz, C12H), 5.02 (1H, dd,  $^3J$  11.0,  $^2J$  1.0 Hz, C12H), 4.07 (3H, s, C4–OCH<sub>3</sub>), 4.06 (3H, s, C5–OCH<sub>3</sub>);  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  = 157.7 (C4), 157.5 (C5), 140.9 (C1'), 136.0 (C2'), 134.5 (C11), 133.2 (C5'), 132.7 (C10a), 132.3 (C8a), 131.5 (C6'), 130.5 (C7), 129.0 (C2), 128.8 (C1), 128.1 (C4'), 126.34 (C3'), 126.31 (C10), 125.9 (C9), 121.2 (C4b), 119.0 (C4a), 115.2 (C12), 112.9 (C4), 108.8 (C6), 107.8 (C3), 56.1 (C5–OCH<sub>3</sub>), 56.0 (C4–OCH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $C_{24}H_{19}BrClO_2$  453.0251 found 453.0240 [M+H<sup>+</sup>].

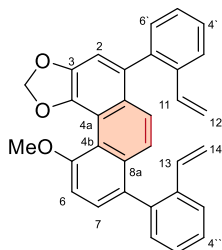
#### 4,5-Dimethoxy-1,8-bis(2-vinylphenyl)phenanthrene (17a):



**17a**

Prepared according to the general procedure **E** using 1,8-dibromo-4,5-dimethoxyphenanthrene **S9g** (131 mg, 330  $\mu\text{mol}$ , 1.00 eq.) and (2-vinylphenyl)boronic acid (137 mg, 924  $\mu\text{mol}$ , 2.80 eq.) to give **17a** as a white solid (120 mg, 271  $\mu\text{mol}$ , 82%, m.p. 95.0 – 95.7°C):  $R_f$  0.61 (cyclohexane/EtOAc 6:1);  $\nu_{\text{max}}$ (neat): 3057w, 3006w, 2930w, 2830w, 1624w, 1571m, 1524m, 1425m, 1310s, 1258s, 1076s, 982m, 910m, 810s, 758s, 702w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.74 – 7.63 (2H, m, C3'H, C3''H), 7.42 – 7.34 (4H, m, C2H, C7H, C4'H, C4''H), 7.34 – 7.22 (4H, m, C5'H, C6'H, C5''H, C6''H), 7.17 (2H, dd,  $^3J$  8.1,  $^4J$  1.3 Hz, C3H, C6H), 7.14 – 7.06 (2H, m, C9H, C10H), 6.53 – 6.30 (2H, m, C11H, C13H), 5.74 – 5.55 (2H, m, C12H, C14H), 5.14 – 4.91 (2H, m, C12H, C14H), 4.13 (6H, s, C4–OCH<sub>3</sub>, C5–OCH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 157.43 (C4, C5), 157.39 (C4, C5), 139.7 (C1', C1''), 139.6 (C1', C1''), 137.29 (C2', C2''), 137.28 (C2', C2''), 135.7 (C11, C13), 135.6 (C11, C13), 132.8 (C8a, C10a), 131.9 (C6', C6''), 131.8 (C6', C6''), 130.2 (C1, C8), 130.1 (C1, C8), 128.7 (C2, C7), (C2, C7), 127.70 (C4', C4''), 127.67 (C4', C4''), 127.54 (C5', C5''), 127.47 (C5', C5''), 125.18 (C9, C10), 125.15 (C9, C10), 124.9 (C3', C3''), 124.8 (C3', C3''), 119.2 (C4a, C4b), 119.1 (C4a, C4b), 114.4 (C12, C14), 114.3 (C12, C14), 107.41 (C3, C6), 107.37 (C3, C6), 55.9 (C4–OCH<sub>3</sub>, C5–OCH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for C<sub>32</sub>H<sub>26</sub>Ag 517.1080 found 517.1084 [M+Ag<sup>+</sup>].

#### 11-Methoxy-5,8-bis(2-vinylphenyl)phenanthro[3,4-d][1,3]dioxole (17b):

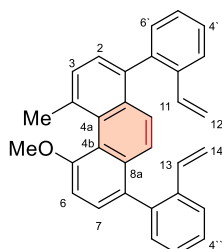


**17b**

Prepared according to the general procedure **E** using 5,8-dibromo-11-methoxyphenanthro[3,4-d][1,3]dioxole **S9k** (80.0 mg, 195  $\mu\text{mol}$ , 1.00 eq.) and (2-vinylphenyl)boronic acid (80.8 mg, 546  $\mu\text{mol}$ , 2.80 eq.) to give **17b** as a yellow oil (75.5 mg, 165  $\mu\text{mol}$ , 85%):  $R_f$  0.61 (cyclohexane/EtOAc 6:1);  $\nu_{\text{max}}$ (neat): 3061w, 3012w, 2932w, 2876w, 1582m, 1538m, 1434s, 1366m, 1291s, 1219w, 1160w, 1071s, 995w, 949w, 908s, 864w, 813m, 633s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.72 – 7.63 (2H, m, C3'H, C3''H), 7.47 – 7.34 (3H, m, C7H, C4'H, C4''H), 7.33 – 7.27 (2H, m, C5'H, C5''H), 7.25 – 7.18 (2H, m, C6'H, C6''H), 7.18 – 7.14 (1H, m, C6H), 7.13 – 7.11 (1H, m, C2H), 7.09 – 7.03 (1H, m, C10H), 6.98 – 6.88 (1H, m, C9H), 6.50 – 6.29 (2H, m, C11H, C13H), 6.27 – 6.14 (2H, m, OCH<sub>2</sub>O), 5.73 – 5.52 (2H, m, C12H, C14H), 5.05 – 4.91 (2H, m, C12H, C14H), 4.13 (3H, s, OCH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 157.12 (C5), 157.08 (C5), 145.32 (C3), 145.28 (C3), 143.81 (C4), 143.78 (C4), 139.6 (C1'/C1''), 137.23 (C2'/C2''), 137.20 (C2'/C2''), 137.16 (C2'/C2''), 137.15 (C2'/C2''), 135.60 (C11/C13), 135.5 (C11/C13), 135.4 (C11/C13), 135.3 (C11/C13), 133.09 (C8a), 133.07 (C8a), 132.61 (C1), 132.59 (C1), 131.7 (C6'/C6''), 131.6 (C6'/C6''), 131.53 (C6'/C6''), 131.48 (C6'/C6''), 130.5 (C8), 130.4 (C8), 129.6 (C7), 127.9 (C4'/C5'), 127.74 (C4'/C5'), 127.71(C4'/C5'), 127.6, 127.5 (C4'/C5'), 127.4 (C10a), 126.10 (C10), 126.06 (C10), 124.93 (C3'/C3''), 124.92 (C3'/C3''), 124.86 (C3'/C3''), 124.80 (C3'/C3''), 122.6 (C9), 117.92 (C4b), 117.87 (C4b), 114.7 (C12, C14), 114.5 (C4a), 111.3 (C2), 111.2

(C2), 107.8 (C6), 100.6 (OCH<sub>2</sub>O), 56.0 (OCH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>32</sub>H<sub>24</sub>AgO<sub>3</sub> 563.0771 found 563.0771 [M+Ag<sup>+</sup>].

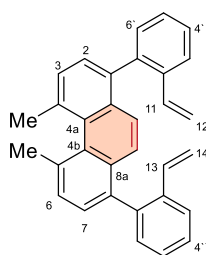
#### 4-Methoxy-5-methyl-1,8-bis(2-vinylphenyl)phenanthrene (17c):



**17c**

Prepared according to the general procedure **E** using 1,8-dibromo-4-methoxy-5-methylphenanthrene **S9I** (76.0 mg, 200 μmol, 1.00 eq.) and (2-vinylphenyl)boronic acid (82.9 mg, 560 μmol, 2.80 eq.) to give **17c** as a white solid (65.2 mg, 153 μmol, 76%, m.p. 89.9 – 90.7°C); R<sub>f</sub> 0.69 (cyclohexane/EtOAc 13:2); ν<sub>max</sub>(neat): 3060w, 3006w, 2953w, 2929w, 2834w, 1630w, 1576w, 1527w, 1448m, 1426m, 1298m, 1259m, 1225m, 1165w, 1098s, 1022w, 989w, 910s, 820s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.73 – 7.67 (2H, m, C3'H, C3''H), 7.51 (1H, dd, <sup>3</sup>J 7.5, <sup>4</sup>J 2.3 Hz, C3H), 7.43 – 7.25 (8H, m, C2H, C7H, C4'H, C5'H, C6'H, C4''H, C5''H, C6''H), 7.18 – 7.09 (2H, m, C9H, C6H), 7.08 – 7.02 (1H, m, C10H), 6.53 – 6.33 (2H, m, C11H, C13H), 5.70 – 5.58 (2H, m, C12H, C14H), 5.07 – 4.92 (2H, m, C12H, C14H), 4.05 (3H, s, OCH<sub>3</sub>), 2.68 (3H, s, C4-CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 156.5 (C5), 156.4 (C5), 139.90 (C1'), 139.87 (C1'), 139.65 (C1''), 139.6 (C1''), 137.3 (C2''), 137.1 (C4), 137.0 (C2'), 135.7 (C11/C13), 135.6 (C11/C13), 135.1 (C1), 133.2 (C8a), 131.9 (C10a), 131.8 (C10a), 131.7 (C6'/C6''), 131.6 (C6'/C6''), 130.4 (C8), 130.3 (C8), 128.9 (C4a), 128.8 (C7), 128.4 (C3), 128.3 (C3), 127.8 (C2/C4'/C5'/C4''/C5''), 127.7 (C2/C4'/C5'/C4''/C5''), 127.6 (C2/C4'/C5'/C4''/C5''), 127.5 (C2/C4'/C5'/C4''/C5''), 125.8 (C10), 124.9 (C3'/C3''), 124.84, 124.7 (C3'/C3''), 124.06 (C9), 124.01 (C9), 120.8 (C4b), 120.7 (C4b), 114.5 (C12/C14), 114.4 (C12/C14), 106.5 (C6), 106.4 (C6), 55.1 (OCH<sub>3</sub>), 24.2 (C4-CH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>32</sub>H<sub>26</sub>AgO 533.1029 found 533.1033 [M+Ag<sup>+</sup>].

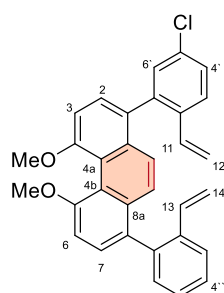
#### 4,5-Dimethyl-1,8-bis(2-vinylphenyl)phenanthrene (17d):



**17d**

Prepared according to the general procedure **E** using 4,5-dimethylphenanthrene-1,8-diyl bis(trifluoromethanesulfonate) **S9o** (60.3 mg, 120 μmol, 1.00 eq.) and (2-vinylphenyl)boronic acid (49.7 mg, 336 μmol, 2.80 eq.) to give **17d** as a white solid (39.0 mg, 95.0 μmol, 72%, m.p. 154.5 – 156.0°C); R<sub>f</sub> 0.79 (cyclohexane/EtOAc 5:1); ν<sub>max</sub>(neat): 3017w, 2955w, 2903w, 1431w, 1260w, 1182w, 1072w, 991m, 909s, 819s, 756s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.81 – 7.57 (2H, m, C3'H, C3''H), 7.53 – 7.42 (2H, m, C3H, C6H), 7.40 – 7.15 (m, 8H), 7.11 – 6.95 (2H, m, C9H, C10H), 6.55 – 6.22 (2H, m, C11H, C13H), 5.78 – 5.51 (2H, m, C12H, C14H), 5.19 – 4.81 (2H, m, C12H, C14H), 2.74 – 2.66 (m, 6H, s, C4-CH<sub>3</sub>, C5-CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 139.9, 139.7, 139.6, 137.1, 137.0, 135.8, 135.64, 135.60, 135.5, 135.4, 135.3, 135.23, 135.20, 135.1, 132.3, 131.9, 131.9, 131.8, 131.64, 131.62, 131.60, 131.1, 130.8, 130.7, 130.6, 128.2, 128.0, 128.0, 127.8, 127.8, 127.8, 127.75, 127.70, 127.6, 127.5, 127.4, 127.3, 125.1, 125.0, 124.72, 124.66, 124.62, 124.5, 124.4, 114.51, 114.49, 22.98, 22.95, 22.91, 22.86; ESI-MS: m/z calcd. for C<sub>32</sub>H<sub>26</sub>Ag 517.1080 found 517.1084 [M+Ag<sup>+</sup>].

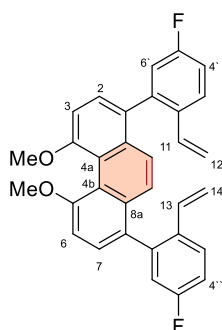
### 1-(5-Chloro-2-vinylphenyl)-4,5-dimethoxy-8-(2-vinylphenyl)phenanthrene (17e):



**17e**

Prepared according to the general procedure E using 1-bromo-4,5-dimethoxy-8-(2-vinylphenyl)phenanthrene **15j** (39.5 mg, 95.0  $\mu\text{mol}$ , 1.00 eq.) and 2-(5-chloro-2-vinylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27.4 mg, 104  $\mu\text{mol}$ , 1.09 eq.) to give **17e** as a transparent oil (23.9 mg, 50.1  $\mu\text{mol}$ , 53%):  $R_f$  0.56 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$ (neat): 3090w, 2932w, 2829w, 1587w, 1527w, 1453w, 1431w, 1314m, 1261m, 1078m, 968w, 909w, 811w, 733w, 632w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.73 – 7.67 (1H, m, C3''H), 7.64 – 7.58 (1H, m, C3'H), 7.43 – 7.22 (7H, m, C2H, C7H, C4'H, C6'H, C4''H, C5''H, C6''H), 7.21 – 7.15 (2H, m, C3H, C6H), 7.14 – 7.03 (2H, m, C9H, C10H), 6.52 – 6.23 (2H, m, C11H, C13H), 5.71 – 5.52 (2H, m, C12H, C14H), 5.05 – 4.93 (2H, m, C12H, C14H), 4.13 (6H, s, C4–OCH<sub>3</sub>, C5–OCH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 157.73 (C4), 157.70 (C4), 157.42 (C5), 157.37 (C5), 141.3 (C1'), 141.2 (C1'), 139.6 (C1''), 139.5 (C1''), 137.30 (C2''), 137.26 (C1''), 135.9 (C2'), 135.7 (C13), 135.5 (C13), 134.7 (C11), 134.5 (C11), 133.1 (C5'), 133.0 (C5'), 132.8 (C8a), 132.6 (C10a), 131.9 (C6''), 131.8 (C6''), 131.6 (C6'), 131.5 (C6'), 130.23 (C8), 130.16 (C8), 128.8 (C2/C7), 128.7 (C2/C7), 128.64 (C2/C7), 128.55 (C1), 128.4 (C1), 127.9 (C4''/C5''), 127.8 (C4''/C5''), 127.75 (C4'), 127.73 (C4'), 127.6 (C4''/C5''), 127.5 (C4''/C5''), 126.2 (C3'), 126.1 (C3'), 125.53 (C9), 125.51 (C9), 124.9 (C3''), 124.8 (C3''), 124.75 (C10), 124.70 (C10), 119.3 (C4a/C4b), 119.2 (C4a/C4b), 119.13 (C4a/C4b), 119.09 (C4a/C4b), 114.9 (C12/C14), 114.5 (C12/C14), 114.4 (C12/C14), 107.6 (C6), 107.5 (C6), 107.40 (C3), 107.36 (C3), 55.9 (C4–OCH<sub>3</sub>, C5–OCH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{32}\text{H}_{25}\text{AgClO}_2$  583.0589 found 583.0590 [ $\text{M}+\text{Ag}^+$ ].

### 1,8-Bis(5-fluoro-2-vinylphenyl)-4,5-dimethoxyphenanthrene (17f):



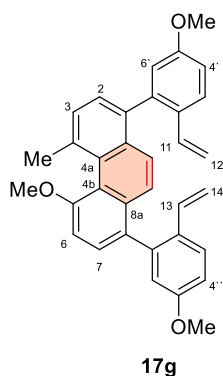
**17f**

Prepared according to the general procedure E using 1,8-dibromo-4,5-dimethoxyphenanthrene **S9g** (69.3 mg, 175  $\mu\text{mol}$ , 1.00 eq.) and 2-(5-fluoro-2-vinylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (122 mg, 480  $\mu\text{mol}$ , 2.80 eq.) to give **17f** as yellow solid (73.0 mg, 153  $\mu\text{mol}$ , 87%, m.p. 64.5 – 66.0°C):  $R_f$  0.54 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$ (neat): 3059w, 2981w, 2938w, 2835w, 1573m, 1527m, 1483s, 1431m, 1314s, 1262s, 1214m, 1143m, 1076s, 984w, 909w, 814m, 775m, 700w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.69 – 7.59 (2H, m, C3'H, C3''H), 7.39 – 7.34 (2H, m, C2H, C7H), 7.20 – 7.15 (2H, m, C3H, C6H), 7.12 – 7.04 (4H, m, C9H, C10H, C4'H, C4''H), 7.02 – 6.93 (2H, m, C6'H, C6''H), 6.42 – 6.17 (2H, m, C11H, C13H), 5.62 – 5.46 (2H, m, C12H, C14H), 5.02 – 4.85 (2H, m, C12H, C14H), 4.13 (6H, s, C4–OCH<sub>3</sub>, C5–OCH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 162.05 (d,  $^1J_{\text{CF}}$  248.0 Hz, C5', C5''), 157.68 (C4, C5), 157.65 (C4, C5), 141.5 (C1', C1''), 134.7 (C11, C13), 134.5 (C11, C13), 133.66 (C2', C2''), 133.63 (C2', C2''), 132.50 (C8a, C10a), 132.49 (C8a, C10a), 129.0 (C1, C8), 128.6 (C2, C7), 128.5 (C2, C7), 126.7 (C3', C3''), 126.6 (C3', C3''), 126.5 (C3', C3''), 125.1 (C9, C10), 125.0 (C9, C10), 119.21 (C4a, C4b), 119.17 (C4a, C4b), 118.4 (C12, C14), 118.3 (C12, C14),



118.21 (C6', C6''), 118.16 (C6', C6''), 114.9 (C4', C4''), 114.8 (C4', C4''), 114.2 (C4', C4''), 114.1 (C4', C4''), 107.51 (C3, C6), 107.47 (C3, C6), 56.0 (C4–OCH<sub>3</sub>, C5–OCH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>32</sub>H<sub>24</sub>AgF<sub>2</sub>O<sub>2</sub> 585.0790 found 585.0797 [M+Ag<sup>+</sup>].

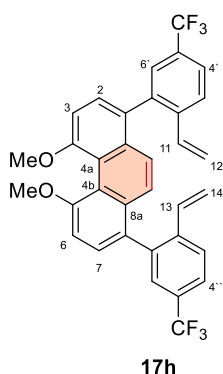
#### 4-Methoxy-1,8-bis(5-methoxy-2-vinylphenyl)-5-methylphenanthrene (17g):



Prepared according to the general procedure E using 1,8-dibromo-4-methoxy-5-methylphenanthrene **S9i** (41.8 mg, 110 μmol, 1.00 eq.) and 2-(5-methoxy-2-vinylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (80.1 mg, 308 μmol, 2.80 eq.) to give **17g** as a white solid (45.0 mg, 92.5 μmol, 84%, m.p. 89.2 – 90.5°C): R<sub>f</sub> 0.50 (cyclohexane/EtOAc 5:1); ν<sub>max</sub>(neat): 3081w, 2963w, 2930w, 2833w, 2729w, 1686w, 1602m, 1576m, 1527m, 1456m, 1326m, 1257m, 1219m, 1166w, 1098s, 1053w, 1021w, 980w, 907w, 816s, 757s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.70 – 7.59 (2H, m, C3'H, C3''H), 7.55 – 7.48 (1H, m, C3H), 7.44 – 7.39 (1H, m, C7H), 7.38 – 7.31 (1H, m, C2H), 7.22 – 7.14 (1H, m, C10H), 7.13 – 7.05 (2H, m, C9H, C6H), 6.99 – 6.90 (2H, m, C4'H, C4''H), 6.86 – 6.75 (2H, m, C6'H, C6''H), 6.44 – 6.33 (1H, m, C13H), 6.29 (1H, dd, <sup>3</sup>J 17.5, <sup>3</sup>J 11.0 Hz, C11H), 5.59 – 5.42 (2H, m, C12H, C14H), 4.94 – 4.73 (2H, m, C12H, C14H), 4.05 (3H, s, C5–OCH<sub>3</sub>), 3.80 (3H, s, C5'–OCH<sub>3</sub>, C5''–OCH<sub>3</sub>), 3.78 (3H, s, C5'–OCH<sub>3</sub>, C5''–OCH<sub>3</sub>), 3.78 (3H, s, C4'–OCH<sub>3</sub>, C4''–OCH<sub>3</sub>), 3.77 (3H, s, C5'–OCH<sub>3</sub>, C5''–OCH<sub>3</sub>), 2.67 (3H, s, C4–CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 159.0 (C5'/C5''), 158.92 (C5'/C5''), 158.86 (C5'/C5''), 156.5 (C5), 156.4 (C5), 141.2 (C1'), 140.95 (C1''), 140.92 (C1''), 137.11 (C4), 137.07 (C4), 135.14 (C1), 135.07 (C1), 135.0 (C13), 134.9 (C11), 133.18 (C8a), 133.16 (C8a), 131.6 (C10a), 130.33 (C8), 130.26 (C8), 130.18 (C2''), 130.00 (C2'), 129.97 (C2'), 128.9 (C4a), 128.80 (C4a), 128.76 (C7), 128.6 (C7), 128.4 (C3), 128.3 (C3), 127.6 (C2), 127.5 (C2), 126.1 (C3'/C3''), 126.0 (C3'/C3''), 125.9 (C3'/C3''), 125.91 (C10), 125.88 (C10), 124.13 (C9), 124.08 (C9), 120.7 (C4b), 116.3 (C6'/C6''), 116.2 (C6'/C6''), 116.1 (C6'/C6''), 116.0 (C6'/C6''), 114.23 (C4'/C4''), 114.19 (C4'/C4''), 112.31 (C12/C14), 112.29 (C12/C14), 112.28 (C12/C14), 112.26 (C12/C14), 55.5 (C4'–OCH<sub>3</sub>, C4''–OCH<sub>3</sub>), 55.1 (C5–OCH<sub>3</sub>), 24.2 (C4–CH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>34</sub>H<sub>30</sub>AgO<sub>3</sub> 593.1240 found 593.1231 [M+Ag<sup>+</sup>].

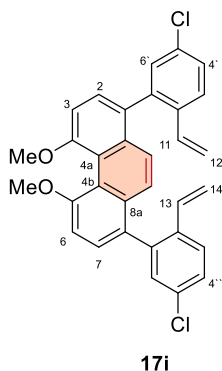
#### 4,5-Dimethoxy-1,8-bis(5-(trifluoromethyl)-2-vinylphenyl)phenanthrene (17h):

Prepared according to the general procedure E using 1,8-dibromo-4,5-dimethoxyphenanthrene **S9g** (35.6 mg, 90.0 μmol, 1.00 eq.) and 4,4,5,5-tetramethyl-2-(5-(trifluoromethyl)-2-vinylphenyl)-1,3,2-dioxaborolane (72.4 mg, 243 μmol, 2.70 eq.) to give **17h** as a transparent oil (36.9 mg, 63.8 μmol, 71%): R<sub>f</sub> 0.59 (cyclohexane/EtOAc 5:1); ν<sub>max</sub>(neat): 2935w, 2852w, 1614w, 1571w, 1527m, 1456w, 1408w, 1335s, 1257s, 1166ss, 1119s, 1077s, 1020w, 985w, 909w, 811w, 734w, 653w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.81



– 7.75 (2H, m, C3'H, C3''H), 7.65 – 7.59 (2H, m, C4'H, C4''H), 7.56 – 7.49 (2H, m, C6'H, C6''H), 7.41 – 7.35 (2H, m, C2H, C7H), 7.22 – 7.15 (2H, m, C3H, C6H), 7.10 – 7.01 (2H, m, C9H, C10H), 6.57 – 6.28 (2H, m, C11H, C13H), 5.76 – 5.66 (2H, m, C12H, C14H), 5.15 – 5.05 (2H, m, C12H, C14H), 4.14 (3H, s, C4–OCH<sub>3</sub>/C5–OCH<sub>3</sub>), 4.14 (3H, s, C4–OCH<sub>3</sub>/C5–OCH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 157.89 (C4, C5), 157.85 (C4, C5), 140.8 (C2', C2''), 140.0 (C1', C1''), 134.7 (C11, C13), 134.5 (C11, C13), 132.51 (C8a, C10a), 132.48 (C8a, C10a), 128.8 (C2, C7), 128.72 (C2, C7), 128.66 (C6', C6''), 128.59 (C6', C6''), 129.53 (q, <sup>2</sup>J<sub>CF</sub> 31.6 Hz, C5', C5''), 125.4 (C3', C3''), 125.3 (C3', C3''), 125.04 (C9, C10), 125.02 (C9, C10), 124.6 (C4', C4''), 124.5 (C4', C4''), 119.30 (C4a, C4b), 119.28 (C4a, C4b), 117.0 (C12, C14), 116.9 (C12, C14), 107.7 (C3, C6), 107.6 (C3, C6), 56.0 (C4–OCH<sub>3</sub>, C5–OCH<sub>3</sub>); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ = –62.39, –62.42; ESI-MS: m/z calcd. for C<sub>34</sub>H<sub>24</sub>AgF<sub>6</sub>O<sub>2</sub> 685.0726 found 685.0719 [M+Ag<sup>+</sup>].

### 1,8-Bis(5-chloro-2-vinylphenyl)-4,5-dimethoxyphenanthrene (17i):



Prepared according to the general procedure **E** using 1,8-dibromo-4,5-dimethoxyphenanthrene **S9g** (71.3 mg, 180.0 μmol, 1.00 eq.) and 2-(5-chloro-2-vinylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (129 mg, 486 μmol, 2.70 eq.) to give **17i** as a white solid (40.0 mg, 78.2 μmol, 78%, m.p. 116.7 – 117.5°C): R<sub>f</sub> 0.67 (cyclohexane/EtOAc 5:1); ν<sub>max</sub>(neat): 2992w, 2929w, 1587w, 1527m, 1470w, 1431w, 1314w, 1262w, 1235w, 1078s, 985w, 907s, 812m, 713s, 632s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.64 – 7.59 (2H, m, C3'H, C3''H), 7.39 – 7.32 (4H, m, C2H, C7H, C4'H, C4''H), 7.29 – 7.24 (2H, m, C6'H, C6''H), 7.19 – 7.14 (2H, m, C3H, C6H), 7.12 – 7.07 (2H, m, C9H, C10H), 6.49 – 6.14 (2H, m, C11H, C13H), 5.76 – 5.52 (2H, m, C12H, C14H), 5.08 – 4.89 (2H, m, C12H, C14H), 4.13 (6H, s, C4–OCH<sub>3</sub>, C5–OCH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 157.74 (C4, C5), 157.70 (C4, C5), 141.2 (C1', C1''), 141.1 (C1', C1''), 135.95 (C2', C2''), 135.89 (C2', C2''), 134.7 (C11, C13), 134.5 (C11, C13), 133.1 (C5', C5''), 132.5 (C10a), 131.6 (C6', C6''), 131.5 (C6', C6''), 128.8 (C1, C8), 128.7 (C1, C8), 128.5 (C2, C7), 127.9 (C4', C4''), 126.3 (C3', C3''), 126.2 (C3', C3''), 125.10 (C9, C10), 125.07 (C9, C10), 119.22 (C4a, C4b), 119.18 (C4a, C4b), 115.1 (C12, C14), 114.9 (C12, C14), 107.6 (C3, C6), 107.5 (C3, C6), 56.0 (C4–OCH<sub>3</sub>, C5–OCH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>32</sub>H<sub>24</sub>AgCl<sub>2</sub>O<sub>2</sub> 617.0199 found 617.0197 [M+Ag<sup>+</sup>].



# Aromatic Ring-Opening Metathesis

## Optimization Studies

Technique for inert conditions: All reactions involving Mo- and Ru-catalysts were performed using degassed and dried solvents in an argon-filled glovebox. Commercially available dry solvents were loaded with molecular sieves and were degassed using the freeze–pump–thaw method. Solvent flasks were then transferred to a nitrogen-filled glovebox and used within seven days of storage over molecular sieves.<sup>1</sup> Optimization studies were performed in 1 or 10 mL crimp cap vials closed in a glovebox. If temperature alteration was necessary, the vials were taken out of the glovebox and heated.

### General procedure F for method optimization (7.50 $\mu\text{mol}$ scale):

The catalyst was weighed into a 2 mL crimp cap vial. A solution of the corresponding substrate (7.50  $\mu\text{mol}$ , 1.00 eq.) in the indicated solvent was then added. The reaction was stirred for the specified time at the indicated temperature, cooled down to room temperature, diluted with EtOAc and filtered through a thin layer of silica gel. Solvents were then removed under reduced pressure and the residue was analyzed by  $^1\text{H}$ -NMR using durene (1,2,4,5-tetramethylbenzene) as an internal standard.

### General procedure G for method optimization (70.0 $\mu\text{mol}$ scale):

The catalyst was weighed into a 10 mL crimp cap vial. A solution of the corresponding substrate (70.0  $\mu\text{mol}$ ) in the indicated solvent was then added. The reaction was stirred for the specified time at the indicated temperature, cooled down to room temperature, diluted with EtOAc and filtered through a thin layer of silica gel. Solvents were then removed under reduced pressure and the residue was analyzed by  $^1\text{H}$ -NMR. The obtained crude product was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0→80:20) to give the desired product. The isolated yield was reported.

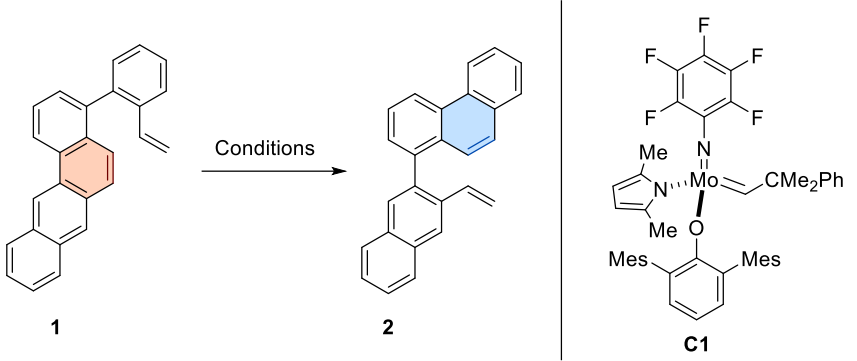
### General optimization procedure H for atroposelective aromatic ring-opening metathesis with *in situ* catalyst formation:

The Mo-precatalyst and the indicated ligand were weighed into a 2 mL crimp cap vial before the specified solvent was added to reach the desired concentration. The obtained solution was stirred at room temperature for 1 h (in an argon-filled glovebox) and then transferred to the corresponding substrate. The resulting reaction mixture was stirred at the specified temperature for a period as stated. The solution was then diluted with EtOAc and filtered through a thin layer of silica gel. Solvents were removed and the obtained crude was analyzed by  $^1\text{H}$ -NMR using durene (1,2,4,5-tetramethylbenzene) as an internal standard. The e.r. of the product was determined by HPLC on a chiral stationary phase (as specified).

## Aromatic Ring Opening (ArROM) – Ring-Closing Metathesis (RCM) Cascade: Tetraphene

**Optimization Studies (15.0  $\mu\text{mol}$  scale):** Performed according to the general procedure **F** utilizing 4-(2-vinylphenyl)tetraphene (4.96 mg, 15.0  $\mu\text{mol}$ ) and toluene (0.50 mL, 0.03  $\text{mol}\cdot\text{L}^{-1}$ ) with the reaction time of 18 h.

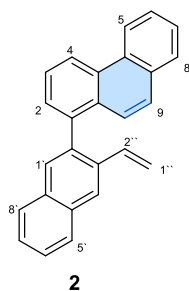
**Supplementary Table 1.** Reaction conditions optimization for tetraphene ring-opening metathesis



| Entry <sup>a</sup> | Catalyst (mol%) | Solvent | Temp. [°C] | Conversion <sup>b</sup> [%] | Yield <sup>b</sup> [%] |
|--------------------|-----------------|---------|------------|-----------------------------|------------------------|
| 1                  | <b>C1</b> (10)  | Toluene | 50         | >95                         | 73                     |
| 2                  | <b>C1</b> (10)  | Toluene | 65         | >95                         | 80                     |
| 3                  | <b>C1</b> (20)  | Toluene | 65         | >95                         | 49                     |
| 4                  | <b>C1</b> (20)  | Toluene | 85         | >95                         | 41                     |

<sup>a</sup>Reactions were performed on 15.0  $\mu\text{mol}$  scale of **1** for 18 h. <sup>b</sup>Conversion and yield were determined by <sup>1</sup>H-NMR with durene as an internal standard.

### 1-(3-Vinylnaphthalen-2-yl)phenanthrene (**2**):



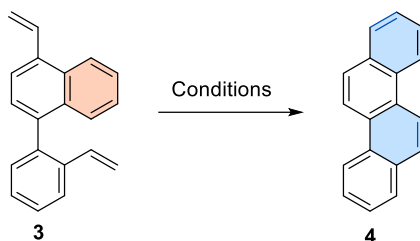
Prepared according to the general procedure **G** using 4-(2-vinylphenyl)tetraphene (23.1 mg, 70.0  $\mu\text{mol}$ ) and **C1** (5.83 mg, 7.00  $\mu\text{mol}$ , 10 mol%) to give the title compound as a white solid (18.9 mg, 57.2  $\mu\text{mol}$ , 82%, m.p. 92.8 – 94.0°C):  $R_f$  0.77 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$  (neat): 3052w, 3010w, 2923w, 2860w, 1931w, 1798w, 1692w, 1591w, 1492w, 1450w, 1413w, 1262m, 1160w, 1090w, 1033w, 988w, 906s, 807s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.80 (1H, d, <sup>3</sup>J 7.2 Hz, C4H), 8.78 (1H, d, <sup>3</sup>J 6.0 Hz, C5H), 8.19 (1H, s, C4'H), 7.99 – 7.93 (1H, m, C5'H), 7.86 (1H, dd, <sup>3</sup>J 7.8, <sup>4</sup>J 1.3 Hz, C8H), 7.83 (1H, d, <sup>3</sup>J 7.9 Hz, C8'H), 7.81 (1H, s, C1'H), 7.73 (1H, dd, <sup>3</sup>J 8.4, <sup>3</sup>J 7.2 Hz, C3H), 7.69 (1H, ddd, <sup>3</sup>J 8.4, <sup>3</sup>J 7.0, <sup>4</sup>J 1.3 Hz, C6H), 7.64 – 7.58 (2H, m, C7H, C9H), 7.57 – 7.48 (3H, m, C2H, C6'H, C7'H), 7.40 (1H, d, <sup>3</sup>J 9.1 Hz, C10H), 6.49 – 6.37 (1H, m, C2''H), 5.77 (1H, dd, <sup>3</sup>J 17.4, <sup>2</sup>J 1.2 Hz, C1''H), 5.04 (dd, <sup>3</sup>J 11.0, <sup>2</sup>J 1.2 Hz, C1''H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 139.5 (C1), 138.3 (C2'), 135.8 (C3'), 135.6 (C2''), 133.2 (C4'a), 132.9 (C8a'), 131.9 (C8a), 131.0 (C10a), 130.48 (C4b), 130.45 (C4a), 129.7 (C1'), 128.7 (C8), 128.6 (C2), 128.0 (C5'), 127.8 (C8'), 127.1 (C9), 126.88 (C6), 126.84 (C7), 126.4 (C7' / C6'), 126.0 (C3), 125.1 (C10), 124.0 (C4'), 123.0 (C5), 122.5 (C4), 115.5 (C1''); ESI-MS: m/z calcd. for C<sub>26</sub>H<sub>18</sub>Ag 437.0454 found 437.0453 [M+Ag<sup>+</sup>].

## ArROM with Twofold RCM: Naphthalene

**Optimization Studies (7.50  $\mu\text{mol}$  scale):** Performed according to the general procedure **F** utilizing 1-vinyl-4-(2-vinylphenyl)naphthalene (1.92 mg, 7.50  $\mu\text{mol}$ ) and toluene (0.25 mL, 0.03 mol·L<sup>-1</sup>) with 18 h reaction time.

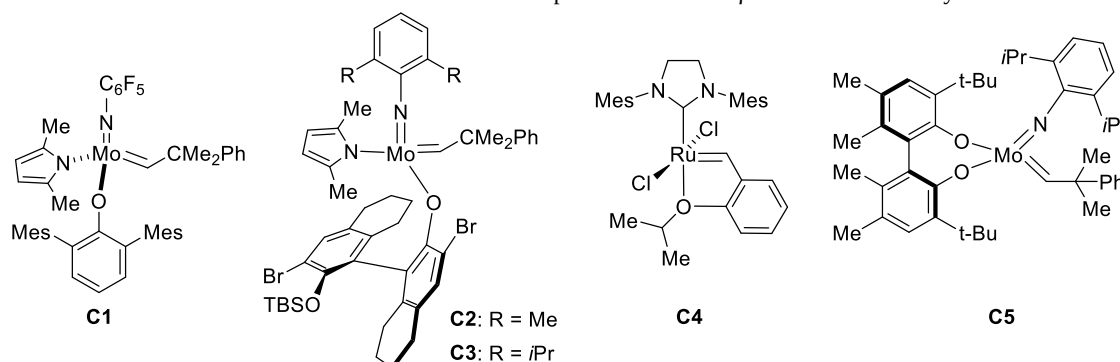
**Optimization Studies (70.0  $\mu\text{mol}$  scale):** Performed according to the general procedure **G** utilizing 1-vinyl-4-(2-vinylphenyl)naphthalene (17.9 mg, 70.0  $\mu\text{mol}$ ) and toluene (2.3 mL, 0.03 mol·L<sup>-1</sup>) with the reaction time of 18 h.

**Supplementary Table 2.** Reaction conditions optimization for naphthalene ring-opening metathesis

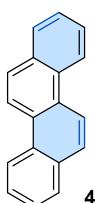


| Entry           | Catalyst (mol%) | Solvent | Temp. [°C] | Conversion <sup>b</sup> [%] | Yield <sup>b</sup> [%] |
|-----------------|-----------------|---------|------------|-----------------------------|------------------------|
| 1 <sup>a</sup>  | <b>C1</b> (20)  | Toluene | 65         | 5                           | 3                      |
| 2 <sup>a</sup>  | <b>C1</b> (20)  | Toluene | 85         | 32                          | 25                     |
| 3 <sup>a</sup>  | <b>C1</b> (10)  | Toluene | 120        | 30                          | 25                     |
| 4 <sup>a</sup>  | <b>C1</b> (20)  | Toluene | 120        | 63                          | 48                     |
| 5 <sup>a</sup>  | <b>C4</b> (20)  | Toluene | 65         | No conv.                    | –                      |
| 6 <sup>a</sup>  | <b>C4</b> (20)  | Toluene | 85         | No conv.                    | –                      |
| 7 <sup>a</sup>  | <b>C3</b> (20)  | Toluene | 85         | 9                           | 4                      |
| 8 <sup>a</sup>  | <b>C5</b> (20)  | Toluene | 85         | No conv.                    | –                      |
| 9 <sup>a</sup>  | <b>C2</b> (20)  | Toluene | 85         | 53                          | 46                     |
| 10 <sup>a</sup> | <b>C2</b> (30)  | Toluene | 85         | 69                          | 41                     |
| 11 <sup>a</sup> | <b>C2</b> (20)  | Toluene | 120        | 85                          | 70                     |
| 12 <sup>c</sup> | <b>C1</b> (20)  | Toluene | 120        | 71                          | 51 <sup>d</sup>        |
| 13 <sup>c</sup> | <b>C2</b> (10)  | Toluene | 120        | 83                          | 74 <sup>d</sup>        |
| 14 <sup>c</sup> | <b>C2</b> (20)  | Toluene | 120        | 92                          | 64 <sup>d</sup>        |

<sup>a</sup>Reactions were performed on 7.50  $\mu\text{mol}$  scale of **3** for 18 h. <sup>b</sup>Conversion and yield were determined by <sup>1</sup>H-NMR with durene as an internal standard. <sup>c</sup>Reactions were performed on 70.0  $\mu\text{mol}$  scale. <sup>d</sup>Isolated yield.



### Chrysene (**4**):

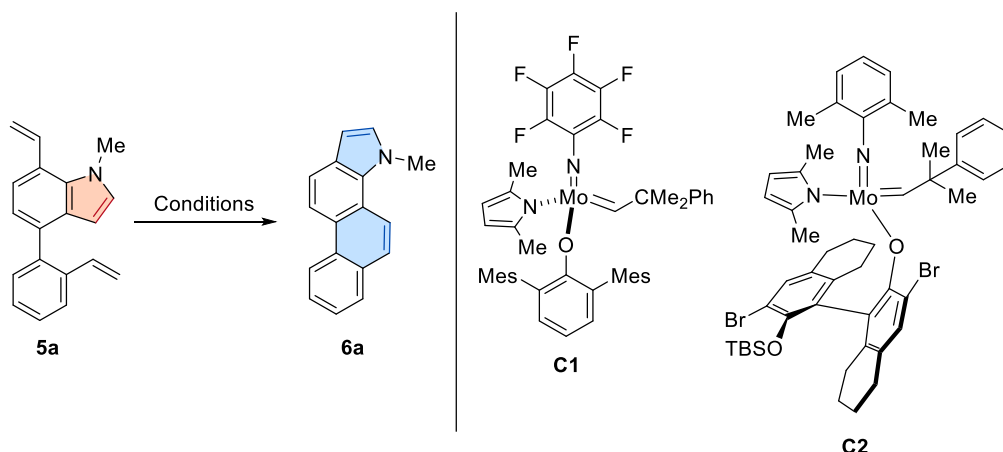


Prepared according to the general procedure **G** using 1-vinyl-4-(2-vinylphenyl)naphthalene (17.9 mg, 70.0  $\mu\text{mol}$ ) and **C2** (7.05 mg, 7.00  $\mu\text{mol}$ , 10 mol%) to give the title compound as a white solid (11.8 mg, 51.7  $\mu\text{mol}$ , 74%). The spectral data were in accordance with those previously reported in the literature.<sup>11</sup>

## ArROM with Twofold RCM: Benzofused Five-Membered Heterocycles

**Optimization Studies:** Performed according to the general procedure **F** utilizing 1-methyl-7-vinyl-4-(2-vinylphenyl)-1*H*-indole **5a** (1.95 mg, 7.50  $\mu\text{mol}$ ) and toluene (0.25 mL, 0.03  $\text{mol}\cdot\text{L}^{-1}$ ) with the reaction time of 18 h.

**Supplementary Table 3.** Reaction conditions optimization for ArROM with twofold RCM of indole



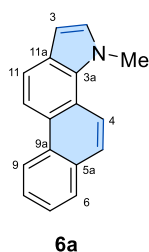
| Entry <sup>a</sup> | Catalyst (mol%) | Solvent | Temp. [°C] | Conversion <sup>b</sup> [%] | Yield <sup>b</sup> [%] |
|--------------------|-----------------|---------|------------|-----------------------------|------------------------|
| 1                  | <b>C1</b> (10)  | Toluene | 65         | >95                         | 92                     |
| 2                  | <b>C1</b> (20)  | Toluene | 85         | >95                         | 98                     |
| 3                  | <b>C2</b> (10)  | Toluene | 65         | >95                         | 98                     |

<sup>a</sup>Reactions were performed on 7.50  $\mu\text{mol}$  scale of **5a** for 18 h. <sup>b</sup>Conversion and yield were determined by <sup>1</sup>H-NMR with durene as an internal standard.

### General procedure I for ArROM with twofold RCM for benzofused five-membered heterocycles:

The catalyst **C2** (7.05 mg, 7.00  $\mu\text{mol}$ , 10 mol%) was weighed into a 10 mL crimp cap vial. A solution of the indole/benzofuran derivative (70.0  $\mu\text{mol}$ , 1.00 eq.) in toluene (2.3 mL, 0.03  $\text{mol}\cdot\text{L}^{-1}$ ) was then added. The reaction was stirred for 18 h at the indicated temperature, cooled down to room temperature, diluted with EtOAc and filtered through a thin layer of silica gel. Solvents were then removed under reduced pressure. The obtained crude product was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0→80:20) to give the desired product.

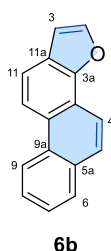
### 3-Methyl-3*H*-naphtho[1,2-*g*]indole (**6a**):



Prepared according to the general procedure **I** using 1-methyl-7-vinyl-4-(2-vinylphenyl)-1*H*-indole **5a** (18.2 mg, 70.0  $\mu\text{mol}$ ) to give the title compound **6a** as a white solid (15.9 mg, 68.7  $\mu\text{mol}$ , 98%, m.p. 140.1 – 140.8°C): *R*<sub>f</sub> 0.44 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$  (neat): 3054w, 2924w, 2855w, 1928w, 1755w, 1689w, 1524w, 1487w, 1426w, 1306m, 1266w, 1220w, 1123m, 1036w, 898w, 861w, 810m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.70 (1H, d, <sup>3</sup>*J* 8.4 Hz, C9H), 8.50 (1H, d, <sup>3</sup>*J* 9.2 Hz, C4H), 8.40 (1H, d, <sup>3</sup>*J* 8.8 Hz, C10H), 7.85 (1H, d, <sup>3</sup>*J* 6.9 Hz,

C6H), 7.82 (1H, d,  $^3J$  8.8 Hz, C11H), 7.77 (1H, d,  $^3J$  9.2 Hz, C5H), 7.59 (1H, ddd,  $^3J$  8.4,  $^3J$  6.9,  $^4J$  1.4 Hz, C8H), 7.53–7.44 (1H, m, C7H), 7.06 (1H, d,  $^3J$  3.0 Hz, C2H), 6.59 (1H, d,  $^3J$  3.0 Hz, C3H), 4.30 (3H, s, N–CH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 131.7 (C3a), 131.5 (C9a), 130.6 (C5a, C2), 128.5 (C6), 127.3 (C11a), 126.8 (C9b), 126.6 (C8), 126.0 (C5), 125.5 (C7), 123.3 (C9), 121.0 (C11), 120.8 (C9b), 120.3 (C4), 115.4 (C10), 101.8 (C3), 39.0 (N–CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for C<sub>17</sub>H<sub>13</sub>AgN 338.0093 found 338.0087 [M+Ag<sup>+</sup>].

### Phenanthro[1,2-b]furan (6b):

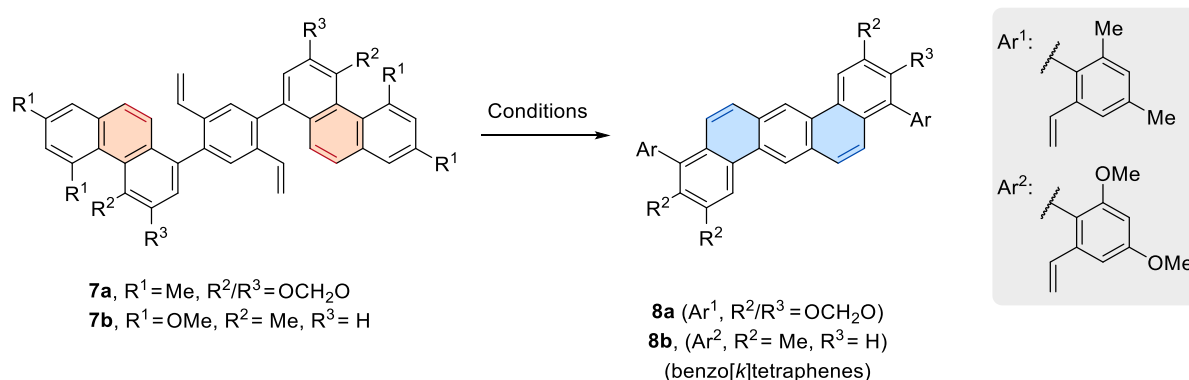


Prepared according to the general procedure **I** using 7-vinyl-4-(2-vinylphenyl)benzofuran **5b** (17.2 mg, 70.0  $\mu\text{mol}$ ) to give the title compound **6b** as a white solid (14.1 mg, 64.6  $\mu\text{mol}$ , 92%, m.p. 112.0 – 112.5°C):  $R_f$  0.47 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$  (neat): 3055w, 2923w, 2848w, 1920w, 1690w, 1599m, 1524w, 1489w, 1375w, 1307m, 1124m, 1037m, 941w, 862m, 811s;  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.73 (1H, d,  $^3J$  8.3 Hz, C9H), 8.56 (1H, d,  $^3J$  8.6 Hz, C10H), 8.31 (1H, d,  $^3J$  8.9 Hz, C4H), 7.95 (1H, d,  $^3J$  7.9 Hz, C6H), 7.90 (1H, d,  $^3J$  8.9 Hz, C5H), 7.85 (1H, d,  $^3J$  8.6 Hz, C11H), 7.82 (1H, d,  $^3J$  2.1 Hz, C2H), 7.68 (1H, ddd,  $^3J$  8.3,  $^3J$  7.0,  $^4J$  1.4 Hz, C8H), 7.60 (1H, ddd,  $^3J$  8.0,  $^3J$  7.0,  $^4J$  1.1 Hz, C7H), 6.97 (1H, d,  $^3J$  2.1 Hz, C3H);  $^{13}\text{C}$  NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 151.7 (C3a), 144.9 (C2), 131.8 (C5a), 130.8 (C9a), 129.1 (C6), 127.7 (C5), 127.6 (C9b), 127.1 (C8), 126.3 (C7), 124.3 (C11a), 123.1 (C9), 119.9 (C11), 119.2 (C3b), 119.1 (C4), 118.1 (C10), 107.5 (C3); ESI-MS:  $m/z$  calcd. for C<sub>32</sub>H<sub>20</sub>AgO<sub>2</sub> 543.0509 found 543.0515 [2M+Ag<sup>+</sup>].

## Bidirectional Twofold ArROM – RCM to Polycyclic Aromatic Hydrocarbons (PAHs)

**Optimization Studies (3.00  $\mu$ mol scale):** Performed according to the general procedure **F** utilizing 5,5'-(2,5-divinyl-1,4-phenylene)bis(9,11-dimethylphenanthro[3,4-d][1,3]dioxole) **7a** (1.88 mg, 3.00  $\mu$ mol) or 8,8'-(2,5-divinyl-1,4-phenylene)bis(2,4-dimethoxy-5-methylphenanthrene) **7b** (1.89 mg, 3.00  $\mu$ mol) and toluene (0.15 mL).

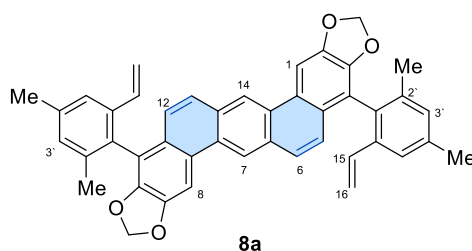
**Supplementary Table 4.** Reaction conditions optimization: bidirectional twofold ArROM – RCM to PAHs



| Entry <sup>a</sup> | Substrate | Catalyst (mol%) | Temp. [°C] | Conversion <sup>b</sup> [%] | Yield <sup>b</sup> [%] |
|--------------------|-----------|-----------------|------------|-----------------------------|------------------------|
| 1                  | <b>7a</b> | <b>C1</b> (20)  | 65         | NR                          | –                      |
| 2                  | <b>7a</b> | <b>C1</b> (20)  | 85         | >95                         | –                      |
| 3                  | <b>7b</b> | <b>C1</b> (20)  | 85         | >95                         | 65                     |
| 4                  | <b>7b</b> | <b>C1</b> (10)  | 85         | 9                           | 5                      |

<sup>a</sup>Reactions were performed on 3.00  $\mu$ mol scale of **7a/7b** for 18 h. <sup>b</sup>Conversion and yield were determined by <sup>1</sup>H-NMR with durene as an internal standard.

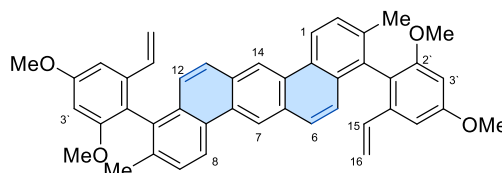
### Benzo[*k*]tetraphene (**8a**):



Prepared according to the general procedure **G** using 5,5'-(2,5-divinyl-1,4-phenylene)bis(9,11-dimethylphenanthro[3,4-d][1,3]dioxole) **7a** (13.8 mg, 22.0  $\mu$ mol) and **C1** (3.66 mg, 4.40  $\mu$ mol, 20 mol%) in toluene (1.2 mL) to give the title compound as a white solid (9.20 mg, 14.7  $\mu$ mol, 67%, decomposition without melting at 293 – 295°C):  $R_f$  0.54 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$ (neat): 3003w, 2949w, 2916w, 2851w, 1728w, 1604w, 1453s, 1411m, 1244s, 1164m, 1101w, 1045s, 945w, 851w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.96 (2H, s, C7H, C14H), 8.28 (2H, s, C1H, C8H), 7.75 (2H, d, <sup>3</sup>J 9.2 Hz, C6H, C13H), 7.47 (2H, s, C5'H), 7.20 (2H, d, <sup>3</sup>J 9.2 Hz, C5H, C12H), 7.17 (2H, s, C3'H), 6.47 – 6.24 (2H, m, C15H), 6.13 – 5.97 (4H, m, OCH<sub>2</sub>O), 5.67 (2H, d, <sup>3</sup>J 17.4 Hz, C16H), 5.09 – 4.93 (2H, m, C16H), 2.46 (6H, s, C4'-CH<sub>3</sub>), 2.03 (6H, s, C2'-CH<sub>3</sub>); <sup>13</sup>C NMR (126

MHz, CDCl<sub>3</sub>)  $\delta$  = 147.6 (C2, C9), 145.4 (C3, C10), 138.2 (C4'), 137.9 (C2'), 135.3 (C1'), 130.7 (C3'), 130.3 (C6a, C13a), 129.5 (C6'), 128.9 (C7a, C14a), 127.2 (C4a, C11a), 126.7 (C4b, C7b), 126.1 (C6, C13), 124.0 (C5, C12), 123.5 (C5'), 121.9 (C7, C14), 117.3 (C4, C11), 114.9 (C16), 101.6 (OCH<sub>2</sub>O), 101.1 (C1, C8), 21.6 (C4'-CH<sub>3</sub>), 20.3 (C2'-CH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>44</sub>H<sub>34</sub>O<sub>4</sub> 626.2452 found 626.2457 [M<sup>+</sup>].

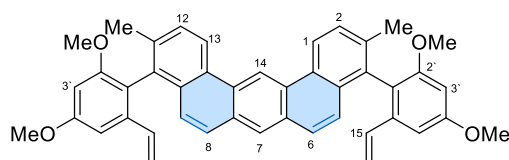
#### 4,11-Bis(2,4-dimethoxy-6-vinylphenyl)-3,10-dimethylbenzo[k]tetraphene (8b):



**8b**

Prepared according to the general procedure **G** using 8,8'-(2,5-divinyl-1,4-phenylene)bis(2,4-dimethoxy-5-methylphenanthrene) **7b** (18.9 mg, 30.0  $\mu$ mol) and **C1** (5.00 mg, 6.00  $\mu$ mol, 20 mol%) in toluene (1.5 mL) to give the title compound as a beige solid (10.6 mg, 16.8  $\mu$ mol, 56%, decomposition without melting at 290 – 293°C): R<sub>f</sub> 0.36 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$ (neat): 3055w, 3003w, 2935m, 2849w, 1600s, 1570s, 1457m, 1421m, 1277w, 1201s, 1155s, 1083w, 1034w, 913w, 828w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.10 (2H, s, C14H, C7H), 8.80 (2H, d, <sup>3</sup>J 8.5 Hz, C1H, C8H), 7.79 (2H, d, <sup>3</sup>J 9.3 Hz, C6H, C13H), 7.63 (2H, d, <sup>3</sup>J 8.5 Hz, C8H, C9H), 7.26 (2H, d, <sup>3</sup>J 9.3 Hz, C5H, C12H), 6.93 (2H, d, <sup>4</sup>J 2.3 Hz, C5'H), 6.61 (2H, d, <sup>4</sup>J 2.3 Hz, C3'H), 6.23 – 6.00 (2H, m, C15H), 5.64 (2H, d, <sup>3</sup>J 17.4 Hz, C16H), 4.97 (2H, d, <sup>3</sup>J 10.9 Hz, C16H), 3.97 (6H, s, C4'-OCH<sub>3</sub>), 3.65 (3H, s, C2'-OCH<sub>3</sub>), 3.65 (3H, s, C3'-CH<sub>3</sub>, C10'-CH<sub>3</sub>), 2.19 (3H, s, C3'-CH<sub>3</sub>, C10'-CH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>44</sub>H<sub>39</sub>O<sub>4</sub> 631.2843 found 631.2841 [M+H<sup>+</sup>].

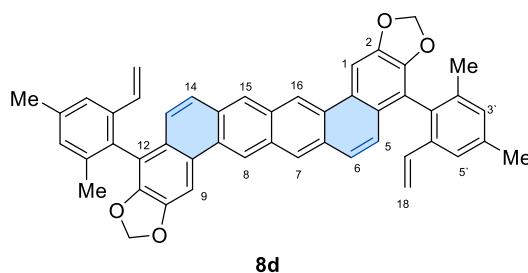
#### 4,10-Bis(2,4-dimethoxy-6-vinylphenyl)-3,11-dimethylbenzo[m]tetraphene (8c):



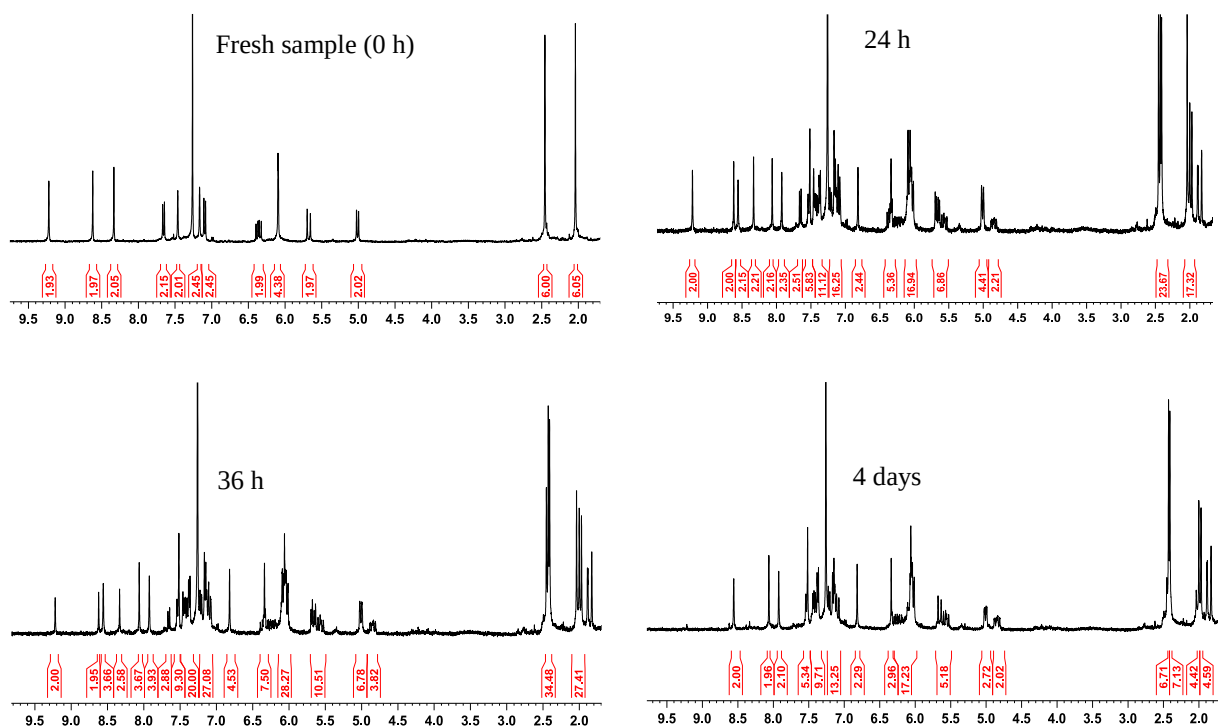
**8c**

Prepared according to the general procedure **G** 8,8'-(4,6-divinyl-1,3-phenylene)bis(2,4-dimethoxy-5-methylphenanthrene) **7c** (17.7 mg, 28.0  $\mu$ mol) and **C1** (4.66 mg, 5.60  $\mu$ mol, 20 mol%) in toluene (1.4 mL) to give the title compound as a white solid (11.1 mg, 17.6  $\mu$ mol, 63%, m.p. 168 – 169°C): R<sub>f</sub> 0.32 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$ (neat): 2992w, 2930w, 2850w, 1735w, 1599m, 1570m, 1455m, 1420m, 1315m, 1276w, 1201s, 1154s, 1080m, 1033w, 917w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 10.09 (1H, s, C14H), 8.99 (2H, d, <sup>3</sup>J 8.4 Hz, C1H, C13H), 8.23 (1H, s, C7H), 7.86 – 7.62 (4H, m, C2H, C13H), 7.24 (2H, d, <sup>3</sup>J 9.2 Hz, C5H, C9H), 6.93 (2H, d, <sup>4</sup>J 2.2 Hz, C5'H), 6.61 (2H, d, <sup>4</sup>J 2.0 Hz, C3'H), 6.40 – 6.03 (2H, m, C15H), 5.64 (2H, d, <sup>3</sup>J 17.4, C16H), 4.97 (2H, d, <sup>3</sup>J 11.1 Hz, C16H), 3.97 (6H, s, C4'-OCH<sub>3</sub>), 3.66 (3H, s, C2'-OCH<sub>3</sub>), 3.65 (3H, s, C2'-OCH<sub>3</sub>), 2.21 (6H, s, C3'-CH<sub>3</sub>, C11-CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 160.4 (C4'), 158.6 (C2'), 138.6 (C6'), 136.5 (C3, C11), 135.0 (C15), 134.2 (C4, C10), 131.7 (C4a, C9a), 130.2 (C6a, C7a), 129.4 (C13b, C14a), 129.0 (C13a, C14b), 128.8 (C2, C12), 127.0 (C7), 126.9 (C6, C8), 125.1 (C5, C9), 122.2 (C1, C13), 120.6 (C1'), 116.2 (C14), 115.1 (C16), 100.9 (C5'), 98.7 (C3'), 56.0 (C2'-OCH<sub>3</sub>), 55.6 (C4'-OCH<sub>3</sub>), 20.6 (C3-CH<sub>3</sub>, C11-CH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>88</sub>H<sub>77</sub>O<sub>8</sub> 1261.5613 found 1261.5632 [2M+H<sup>+</sup>].

## Dibenzo[*a,j*]tetracene (**8d**):



Prepared according to the general procedure **G** using 5,5'-(3,7-divinylnaphthalene-2,6-diyl)bis(9,11-dimethylphenanthro[3,4-*d*][1,3]dioxole) **7d** (6.77 mg, 10.0  $\mu\text{mol}$ ) and **C1** (1.67 mg, 2.00  $\mu\text{mol}$ , 20 mol%) in toluene (0.5 mL) to give the title compound as a yellow solid (2.10 mg, 3.1  $\mu\text{mol}$ , 31%):  $R_f$  0.57 (cyclohexane/EtOAc 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.22 (2H, s, C8H, C16H), 8.62 (2H, s, C1H, C9H), 8.33 (2H, s, C7H, C15H), 7.65 (2H, d,  $^3J$  9.3 Hz, C6H, C14H), 7.46 (2H, s, C5'H), 7.16 (2H, s, C3'H), 7.09 (2H, d,  $^3J$  9.3 Hz, C5H, C13H), 6.36 (2H, dd,  $^3J$  17.5,  $^3J$  11.1 Hz, C17H), 6.15 – 5.98 (4H, m,  $\text{OCH}_2\text{O}$ ), 5.76 – 5.47 (2H, m, C18H), 5.01 (2H, d,  $^3J$  11.1 Hz, C18H), 2.45 (6H, s, C2'- $\text{CH}_3$ ), 2.04 (6H, s, C4'- $\text{CH}_3$ ); ESI-MS:  $m/z$  calcd. for  $\text{C}_{48}\text{H}_{36}\text{O}_4$  676.2608 found 676.2596 [ $\text{M}^+$ ]. Rapid decomposition of **8d** at room temperature in  $\text{CDCl}_3$  solution was observed (see the  $^1\text{H}$ -NMR spectra below):





## Equilibration of Indoles by ArROM – RCM

**Optimization Studies:** Performed according to the general procedure **F** utilizing 5-fluoro-1-(2-vinylphenyl)-1*H*-indole **9d** (1.78 mg, 7.50  $\mu\text{mol}$ ) and toluene (0.25 mL, 0.03 mol·L<sup>-1</sup>) with the reaction time of 18 h.

**Optimization Studies (70.0  $\mu\text{mol}$  scale):** Performed according to the general procedure **G** utilizing 5-fluoro-1-(2-vinylphenyl)-1*H*-indole **9d** (16.6 mg, 70.0  $\mu\text{mol}$ ) and toluene (2.3 mL, 0.03 mol·L<sup>-1</sup>) with 18h reaction time.

**Supplementary Table 5.** Reaction conditions optimization equilibration of indoles by ArROM – RCM

**9b:** R = Me  
**9d:** R = F  
**9f:** R = Cl

**10b:** R = Me  
**10d:** R = F  
**10f:** R = Cl

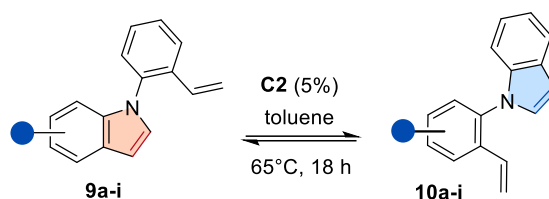
**C1**

**C2**

| Entry           | Substrate | Catalyst (mol%) | Solvent | Temp. [°C] | ( <b>9</b> : <b>10</b> ) <sup>b</sup> | Yield <sup>b</sup> [%] |
|-----------------|-----------|-----------------|---------|------------|---------------------------------------|------------------------|
| 1 <sup>a</sup>  | <b>9b</b> | <b>C1</b> (20)  | Toluene | 65         | 1 : 2.4                               | — <sup>d</sup>         |
| 2 <sup>a</sup>  | <b>9b</b> | <b>C2</b> (5)   | Toluene | 65         | 1 : 2.4                               | — <sup>d</sup>         |
| 3 <sup>a</sup>  | <b>9b</b> | <b>C2</b> (20)  | Toluene | 65         | 1 : 2.3                               | — <sup>d</sup>         |
| 4 <sup>a</sup>  | <b>9f</b> | <b>C1</b> (20)  | Toluene | 65         | 1 : 0.4                               | — <sup>d</sup>         |
| 5 <sup>a</sup>  | <b>9f</b> | <b>C2</b> (5)   | Toluene | 65         | 1 : 0.4                               | — <sup>d</sup>         |
| 6 <sup>a</sup>  | <b>9f</b> | <b>C2</b> (20)  | Toluene | 65         | 1 : 0.4                               | — <sup>d</sup>         |
| 7 <sup>a</sup>  | <b>9d</b> | <b>C1</b> (5)   | Toluene | 65         | 1 : 0.9                               | 44 ( <b>10d</b> )      |
| 8 <sup>a</sup>  | <b>9d</b> | <b>C1</b> (10)  | Toluene | 65         | 1 : 1                                 | 50 ( <b>10d</b> )      |
| 9 <sup>a</sup>  | <b>9d</b> | <b>C1</b> (20)  | Toluene | 65         | 1 : 1                                 | 45 ( <b>10d</b> )      |
| 10 <sup>a</sup> | <b>9d</b> | <b>C1</b> (20)  | Toluene | 85         | 1 : 1                                 | 43 ( <b>10d</b> )      |
| 11 <sup>a</sup> | <b>9d</b> | <b>C2</b> (20)  | Toluene | 65         | 1 : 0.9                               | 41 ( <b>10d</b> )      |
| 12 <sup>c</sup> | <b>9d</b> | <b>C1</b> (5)   | Toluene | 65         | 1 : 1                                 | 87 <sup>e</sup>        |
| 13 <sup>c</sup> | <b>9d</b> | <b>C2</b> (5)   | Toluene | 65         | 1 : 1                                 | 90 <sup>e</sup>        |

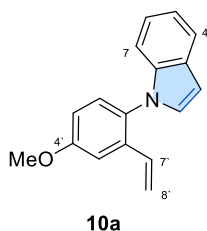
<sup>a</sup>Reactions were performed on 7.50  $\mu\text{mol}$  scale of **9b**, **9d**, **9f** for 18 h. <sup>b</sup>Conversion and yield were determined by <sup>1</sup>H-NMR with durene as an internal standard. <sup>c</sup>Reactions were performed on 70.0  $\mu\text{mol}$  scale of **9d**. <sup>d</sup>Only a mixture of **9b/10b** or **9f/10f** was observed by <sup>1</sup>H-NMR, no internal standard was added <sup>e</sup>Isolated yield of the mixture.

## General procedure J for the equilibration of indoles by ArROM – RCM:



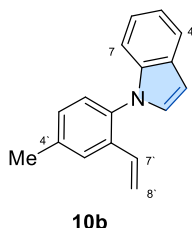
Catalyst **C2** (3.52 mg, 3.50  $\mu\text{mol}$ , 5 mol%) was weighed into a 10 mL crimp cap vial (dried at 130°C overnight) in an argon-filled glovebox. A solution of the corresponding indole **9a-i** (70.0  $\mu\text{mol}$ , 1.00 eq.) in dry and degassed toluene (2.3 mL, 0.03  $\text{mol}\cdot\text{L}^{-1}$ ) was added. The vial was capped in the glovebox, subsequently taken out and stirred at 65°C for 18 h. The reaction mixture was then filtered through a thin layer of silica gel using EtOAc (10–15 mL). The solvents were removed under reduced pressure and the residue was purified by the silica gel chromatography (cyclohexane/EtOAc 100:0→80:20) to give the inseparable mixture of the starting material **9a-i** and the corresponding product **10a-i**. The yield was reported for the obtained mixture, while the ratio of **9a-i** and **10a-i** was analyzed by  $^1\text{H}$ -NMR of the crude and after the purification of silica gel chromatography.

### 1-(4-Methoxy-2-vinylphenyl)-1H-indole (10a):



Prepared according to the general procedure **J** using 5-methoxy-1-(2-vinylphenyl)-1H-indole **9a** (17.5 mg, 70.0  $\mu\text{mol}$ ) to obtain the mixture of **9a** and **10a** (1:5.3) as yellow oil (17.1 mg, 68.6  $\mu\text{mol}$ , 98%).  $^1\text{H}$ -NMR of both crude and purified mixture show the ratio **9a** : **10a** = 1 : 5.3.  $R_f$  (mixture, 1 spot) 0.31 (cyclohexane/EtOAc 9:1);  $\nu_{\text{max}}$ (neat) (mixture): 3052w, 2992w, 2934w, 2835w, 1610w, 1571wm 1496s, 1458m, 1291m, 1223s, 1161w, 1098w, 1029w, 918w, 853w, 818w, 743m;  $^1\text{H}$  NMR (**10a**) (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.71 – 7.65 (1H, m, C4H), 7.27 – 7.22 (2H, m, C3'H, C6'H), 7.17 – 7.11 (3H, m, C2H, C5H, C6H), 7.07 – 7.02 (1H, m, C7H), 6.93 (1H, dd,  $^3J$  8.6,  $^4J$  2.9 Hz, C5'H), 6.66 (1H, d,  $^3J$  2.1 Hz, C3H), 6.22 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7'H), 5.72 – 5.67 (1H, m, C8'H), 5.16 (1H, dd,  $^3J$  11.0,  $^2J$  0.7 Hz, C8'H), 3.91 (3H, s,  $\text{OCH}_3$ );  $^{13}\text{C}$  NMR (**10a**) (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 159.5 (C4'), 137.9 (C7a), 136.6 (C2'), 132.2 (C7'), 130.4 (C1'), 129.8 (C2), 129.6 (C6'), 128.4 (C3a), 122.2 (C6), 120.9 (C4), 120.1 (C5), 116.5 (C8'), 114.4 (C5'), 110.9 (C7), 110.8 (C3'), 102.6 (C3), 55.7 ( $\text{OCH}_3$ ); ESI-MS (mixture):  $m/z$  calcd. for  $\text{C}_{17}\text{H}_{15}\text{O}$  249.1148 found 249.1138 [ $\text{M}^+$ ].

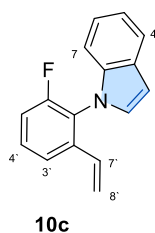
### 1-(4-Methyl-2-vinylphenyl)-1H-indole (10b):



Prepared according to the general procedure **J** using 5-methyl-1-(2-vinylphenyl)-1H-indole **7c** (16.3 mg, 70.0  $\mu\text{mol}$ ) to obtain the mixture of **9b** and **10b** (1:2.4) as yellow oil (15.9 mg, 68.1  $\mu\text{mol}$ , 97%).  $^1\text{H}$ -NMR of both crude and purified mixture show the ratio **9b** : **10b** = 1 : 2.4.  $R_f$  (mixture, 1 spot) 0.31 (cyclohexane/EtOAc 9:1);  $\nu_{\text{max}}$ (neat) (mixture): 3078w, 3027w, 2923w, 2857w, 1611w, 1494s, 1457s, 1336m, 1310m, 1222m, 1158w, 1058w, 991w, 915m, 822m, 741s;  $^1\text{H}$  NMR (**10b**) (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.72 – 7.67 (1H, m, C4H), 7.56 (1H, s, C3'H), 7.22 – 7.20 (2H, m, C5'H, C6'H), 7.18 – 7.14 (3H, m, C5H, C6H, C2H), 6.67 (1H, dd,  $^3J$  3.2,  $^4J$  0.8 Hz, C3H), 6.27 (1H, dd,

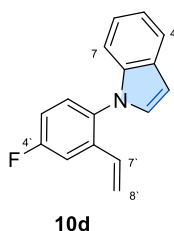
$^3J$  17.5,  $^3J$  11.0 Hz, C7'H), 5.71 (1H, dd,  $^3J$  17.5,  $^2J$  1.1 Hz, C8'H), 5.15 (1H, dd,  $^3J$  11.0,  $^2J$  1.1 Hz, C8'H), 2.47 (3H, s, C4'-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (**10b**) (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 138.2 (C4'), 137.7 (C7a), 134.9 (C2'), 134.8 (C1'), 132.3 (C7'), 129.6 (C2), 129.5 (C5'), 128.5 (C3a), 128.2 (C6'), 126.8 (C3'), 122.2 (C6), 120.9 (C4), 120.1 (C5), 116.0 (C8'), 111.0 (C7), 102.7 (C3), 21.4 (C4'-CH<sub>3</sub>); ESI-MS (of the mixture):  $m/z$  calcd. for C<sub>17</sub>H<sub>15</sub>AgN 340.0250 found 340.0245 [M+Ag<sup>+</sup>].

### 1-(2-Fluoro-6-vinylphenyl)-1H-indole (10c):



Prepared according to the general procedure **J** using 7-fluoro-1-(2-vinylphenyl)-1H-indole **9c** (16.6 mg, 70.0  $\mu\text{mol}$ ) to obtain the mixture of **9c** and **10c** (1:2.2) as yellow oil (14.5 mg, 61.1  $\mu\text{mol}$ , 87%).  $^1\text{H}$ -NMR of both crude and purified mixture show the ratio **9c** : **10c** = 1 : 2.2.  $R_f$  (**10c**) 0.64 (cyclohexane/EtOAc 9:1);  $\nu_{\text{max}}$ (neat) (mixture): 3070w, 2962w, 2906w, 1701w, 1576m, 1487s, 1452m, 1328m, 1261s, 1135m, 1105w, 1013w, 949m, 921m, 802s, 741s;  $^1\text{H}$  NMR (**10c**) (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 – 7.68 (1H, m, C4H), 7.54 (1H, d,  $^3J$  8.0 Hz, C3'H), 7.38 – 7.33 (1H, m, C4'H), 7.22 – 7.16 (3H, m, C4H, C5H, C5'H), 7.14 (1H, dd,  $^3J$  3.2,  $^5J$  0.7 Hz, C2H), 7.01 – 6.96 (1H, m, C7H), 6.73 (1H, dd,  $^3J$  3.2,  $^4J$  0.9 Hz, C3H), 6.21 (1H, dd,  $^3J$  17.5,  $^3J$  11.1 Hz, C7'H), 5.74 (1H, dd,  $^3J$  17.5,  $^2J$  0.9 Hz, C8'H), 5.22 (1H, d,  $^3J$  11.1 Hz, C8'H);  $^{13}\text{C}$  NMR (**10c**) (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 159.0 (d,  $^1J_{\text{CF}}$  251.0 Hz, C6'), 138.4 (C2'), 137.5 (C7a), 131.9 (C7'), 131.3 (d,  $^2J_{\text{CF}}$  3.3 Hz, C1'), 129.4 (C2), 128.29 (d,  $^3J_{\text{CF}}$  2.0 Hz, C4'), 128.4 (C3a), 122.5 (C6), 121.4 (d,  $^3J_{\text{CF}}$  3.6 Hz, C3'H), 121.0 (C4), 120.4 (C5), 117.8 (C8'), 115.5 (d,  $^2J_{\text{CF}}$  20.5 Hz, C5'H), 110.7 (C7), 103.6 (C3);  $^{19}\text{F}$  NMR (**10c**) (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -121.39; ESI-MS (of the mixture):  $m/z$  calcd. for C<sub>16</sub>H<sub>13</sub>FN 238.1027 found 238.1022 [M+H<sup>+</sup>].

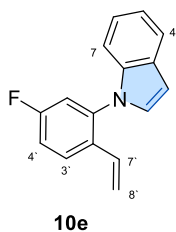
### 1-(4-Fluoro-2-vinylphenyl)-1H-indole (10d):



Prepared according to the general procedure **J** using 5-fluoro-1-(2-vinylphenyl)-1H-indole **9d** (16.6 mg, 70.0  $\mu\text{mol}$ ) to obtain the mixture of **9d** and **10d** (1:1) as a transparent oil (14.9 mg, 62.8  $\mu\text{mol}$ , 90%).  $^1\text{H}$ -NMR of both crude and purified mixture show the ratio **9d** : **10d** = 1 : 1.  $R_f$  (**10d**) 0.66 (cyclohexane/EtOAc 9:1);  $\nu_{\text{max}}$ (neat) (mixture): 3062w, 2962w, 2905w, 1511m, 1493s, 1474m, 1334w, 1268w, 1214w, 1145w, 1066w, 920w, 860w, 804w, 745w;  $^1\text{H}$  NMR (**10d**) (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.71 – 7.68 (1H, m, C4H), 7.44 – 7.41 (1H, m, C3'H), 7.32 – 7.29 (1H, m, C6'H), 7.21 – 7.16 (2H, m, C5H, C6H), 7.15 (1H, d,  $^3J$  3.1 Hz, C2H), 7.10 (1H, ddd,  $^3J$  8.6,  $^3J$  7.8,  $^4J$  2.9 Hz, C5'H), 7.07 – 7.03 (1H, m, C7H), 6.69 (1H, dd,  $^3J$  3.2,  $^4J$  0.8 Hz, C3H), 6.22 (1H, dd,  $^3J$  17.5,  $^3J$  11.1, C7'H), 5.73 (1H, dd,  $^3J$  17.5,  $^2J$  1.1 Hz, C8'H), 5.23 (1H, d,  $^3J$  11.1 Hz, C8'H);  $^{13}\text{C}$  NMR (**10d**) (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 162.41 (d,  $^1J_{\text{CF}}$  247.3 Hz, C4'), 137.7 (C7a), 137.5 (d,  $^3J_{\text{CF}}$  8.2 Hz, C2'), 133.3 (d,  $^4J_{\text{CF}}$  2.8 Hz, C1'), 131.4 (d,  $^4J_{\text{CF}}$  2.1 Hz, C7'), 130.2 (d,  $^3J_{\text{CF}}$  8.9 Hz, C6'), 129.5 (C2), 128.5 (C3a), 122.5 (C6), 121.0 (C4), 120.3 (C5), 117.6 (C8'), 115.7 (d,  $^2J_{\text{CF}}$  23.0 Hz, C5'), 112.6 (d,  $^2J_{\text{CF}}$  23.3 Hz,

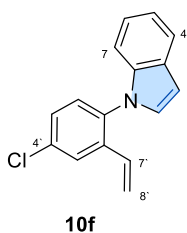
C3'), 110.8 (C7), 103.2 (C3);  $^{19}\text{F}$  NMR (**10d**) (376 MHz,  $\text{CDCl}_3$ )  $\delta = -113.20$ ; ESI-MS (of the mixture):  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{12}\text{FN}$  237.0948 found 237.0944 [ $\text{M}^+$ ].

### 1-(5-Fluoro-2-vinylphenyl)-1H-indole (10e):



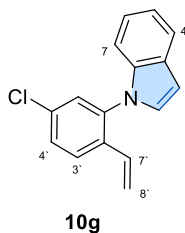
Prepared according to the general procedure **J** using 6-fluoro-1-(2-vinylphenyl)-1H-indole **9e** (16.6 mg, 70.0  $\mu\text{mol}$ ) to obtain the mixture of **9e** and **10e** (1:0.5) as yellow oil (16.0 mg, 67.4  $\mu\text{mol}$ , 96%).  $^1\text{H}$ -NMR of both crude and purified mixture show the ratio **9e** : **10e** = 1 : 0.5.  $R_f$  (mixture, 1 spot) 0.70 (cyclohexane/EtOAc 9:1);  $\nu_{\text{max}}$ (neat) (mixture): 3065w, 3013w, 1619m, 1606w, 1486s, 1462s, 1342w, 1214s, 1177w, 1118w, 992w, 933w, 827w, 766w, 716w, 676w;  $^1\text{H}$  NMR (**10e**) (500 MHz,  $\text{CDCl}_3$ )  $\delta = 7.74 - 7.67$  (2H, m, C4H, C3'H), 7.22 – 7.16 (4H, m, C2H, C5H, C6H, C4'H), 7.15 – 7.11 (1H, m, C7H), 7.09 (1H, dd,  $^3J_{\text{HF}}$  9.0,  $^4J$  2.7 Hz, C6'H), 6.69 (1H, dd,  $^3J$  3.2,  $^4J$  0.8 Hz, C3H), 6.28 (1H, dd,  $^3J$  17.5,  $^3J$  11.1 Hz, C7'H), 5.67 (1H, d,  $^3J$  17.5 Hz, C8'H), 5.17 (1H, d,  $^3J$  11.1 Hz, C8'H);  $^{13}\text{C}$  NMR (**10e**) (126 MHz,  $\text{CDCl}_3$ )  $\delta = 162.4$  (d,  $^1J_{\text{CF}}$  249.8 Hz, C5'), 138.4 (d,  $^3J_{\text{CF}}$  9.5 Hz, C1'), 137.3 (C7a), 136.8 (C2'), 131.6 (C7'), 129.2 (C2), 128.7 (C3a), 128.0 (d,  $^3J_{\text{CF}}$  9.1 Hz, C3'), 122.6 (C6), 121.1 (C4), 120.5 (C5), 116.1 (C8'), 115.6 (d,  $^2J_{\text{CF}}$  21.3 Hz, C4'), 115.2 (d,  $^2J_{\text{CF}}$  22.5 Hz, C6'), 110.9 (C7), 103.6 (C3);  $^{19}\text{F}$  NMR (**10e**) (376 MHz,  $\text{CDCl}_3$ )  $\delta = -112.6$ ; ESI-MS (of the mixture):  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{13}\text{FN}$  238.1027 found 238.1017 [ $\text{M}+\text{H}^+$ ].

### 1-(4-Chloro-2-vinylphenyl)-1H-indole (10f):



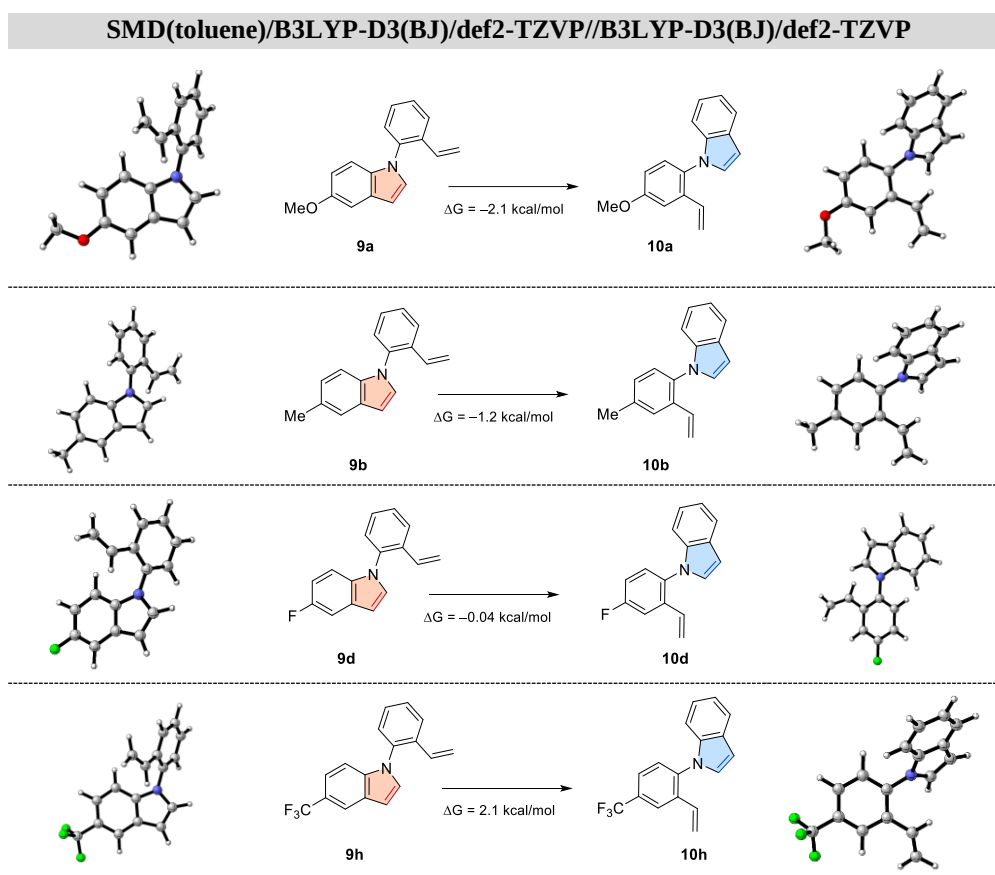
Prepared according to the general procedure **J** using 5-chloro-1-(2-vinylphenyl)-1H-indole **9f** (17.8 mg, 70.0  $\mu\text{mol}$ ) to obtain the mixture of **9f** and **10f** (1:0.4) as a transparent oil (17.0 mg, 67.0  $\mu\text{mol}$ , 96%).  $^1\text{H}$ -NMR of both crude and purified mixture show the ratio **9f** : **10f** = 1 : 0.4.  $R_f$  (mixture, 1 spot) 0.74 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$ (neat) (mixture): 3060w, 2926w, 2851w, 1850w, 1600w, 1569w, 1487s, 1461s, 1329m, 1286w, 1230w, 1203w, 1149w, 1121w, 1064w, 990w, 955w, 917w, 754s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta = 7.72$  (d,  $^4J$  2.4 Hz, C3'H), 7.71 – 7.68 (1H, m, C4H), 7.37 (1H, dd,  $^4J$  8.4,  $^3J$  2.4 Hz, C5'H), 7.28 (1H, d,  $^3J$  8.4 Hz, C6'H), 7.20 – 7.16 (2H, m, C5H, C6H), 7.15 (1H, d,  $^3J$  3.2 Hz, C2H), 7.09 – 7.05 (1H, m, C7H), 6.69 (1H, dd,  $^3J$  3.2,  $^5J$  0.8 Hz, C3H), 6.25 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C7'H), 5.75 (1H, dd,  $^3J$  17.5,  $^2J$  0.9 Hz, C8'H), 5.24 (1H, dd,  $^3J$  11.0,  $^2J$  0.9 Hz, C8'H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta = 137.5$  (C7a), 136.8 (C2'), 135.8 (C1'), 134.2 (C4'), 131.3 (C7'), 129.6 (C6'), 129.3 (C2), 128.7 (C5'), 128.6 (C3a), 126.4 (C3'), 122.5 (C6), 121.1 (C4), 120.4 (C5), 117.7 (C8'), 110.8 (C7), 103.5 (C3); ESI-MS (of the mixture):  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{12}\text{ClN}$  253.0653 found 253.0650 [ $\text{M}^+$ ].

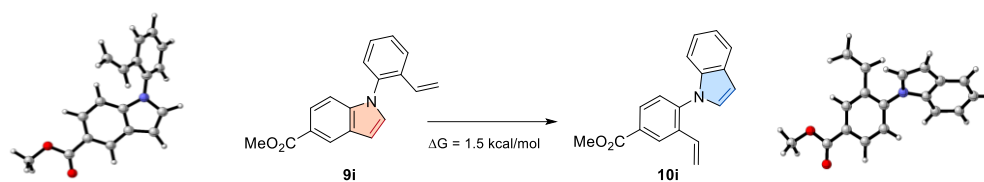
## 1-(5-Chloro-2-vinylphenyl)-1H-indole (10g):



Prepared according to the general procedure **J** using 6-chloro-1-(2-vinylphenyl)-1H-indole **9g** (17.8 mg, 70.0  $\mu\text{mol}$ ) to obtain the mixture of **9g** and **10g** (1:0.3) as yellow oil (16.0 mg, 67.4  $\mu\text{mol}$ , 96%).  $^1\text{H}$ -NMR of both crude and purified mixture show the ratio **9g** : **10g** = 1 : 0.3.  $R_f$  (**mixture**, **1 spot**) 0.36 (cyclohexane/EtOAc 9:1);  $\nu_{\text{max}}$ (neat) (mixture): 3063w, 3021w, 2926w, 2841w, 1713w, 1597m, 1507m, 1487s, 1335m, 1141m, 1108w, 1080w, 991w, 846w, 906w, 767w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.72 – 7.66 (2H, m, C4H, C3'H), 7.43 – 7.40 (1H, m, C4'H), 7.36 (1H, d,  $^4J$  2.2 Hz, C6'H), 7.23 – 7.17 (2H, m, C5H, C6H), 7.16 (1H, d,  $^3J$  3.2 Hz, C2H), 7.12 – 7.09 (1H, m, C7H), 6.70 (1H, dd,  $^3J$  3.2,  $^5J$  0.8 Hz, C3H), 6.28 (1H, dd,  $^3J$  17.4,  $^3J$  11.0 Hz, C7'H), 5.72 (1H, dd,  $^3J$  17.4,  $^2J$  0.9 Hz, C8'H), 5.23 – 5.19 (1H, m, C8'H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 138.1 (C1'), 137.3 (C7a), 133.9 (C5'), 133.8 (C2'), 131.4 (C7'), 129.2 (C2), 128.63 (C3a), 128.55 (C4'), 128.3 (C6'), 127.5 (C3'), 122.6 (C6), 121.1 (C4), 120.5 (C5), 116.9 (C8'), 110.9 (C7), 103.7 (C3); ESI-MS (of the mixture):  $m/z$  calcd. for  $\text{C}_{16}\text{H}_{13}\text{ClN}$  254.0731 found 254.0720  $[\text{M}+\text{H}^+]$ .

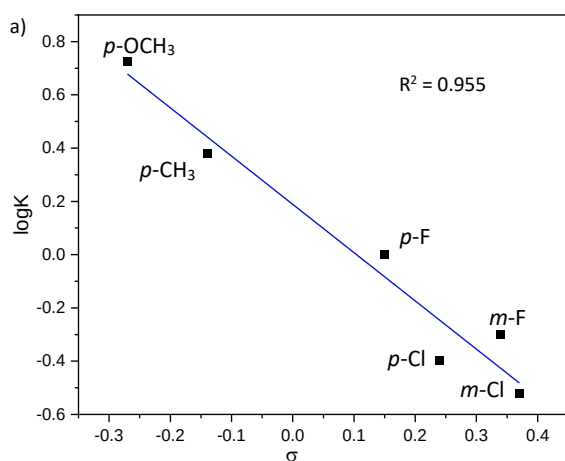
**Supplementary Table 6.** Gibbs free energies for selected pairs of idoles **9** and **10** obtained by density functional theory (DFT) calculations



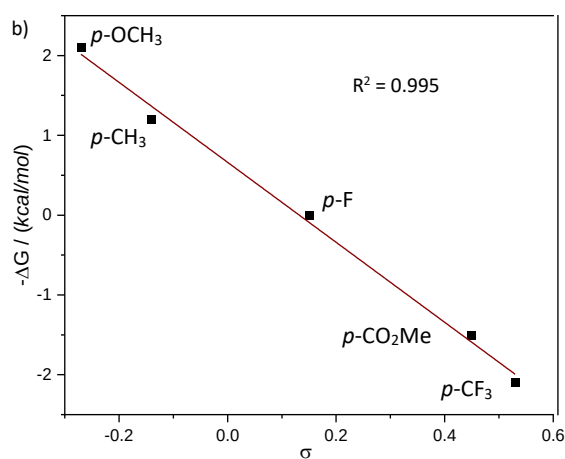


Density functional theory (DFT) calculations were performed using the Gaussian 16 (revision C.01) program. Geometry optimizations were performed at the B3LYP-D3(BJ) level of theory with the def2-TZVP basis set in the gas phase.<sup>12</sup> Harmonic vibrational frequencies were evaluated for the optimized geometries, with minima characterized by the absence of imaginary frequencies. Quasiharmonic corrections to the entropy for frequencies below 100 cm<sup>-1</sup> were calculated with the Goodvibes program by employing the method of Grimme. Single point energies were calculated at B3LYP-D3(BJ) level of theory with the def2-TZVP basis set with implicit solvation model SMD for toluene. The optimized structures were visualized in CYLView<sup>13</sup>.

**Supplementary Table 7.** Hammett plots for experimental and DFT calculated data of indoles equilibration



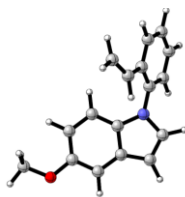
Hammett plot for experimental equilibrium constants



Hammett plot for DFT calculated Gibbs free energies

## Cartesian Coordinates for Optimized Geometries

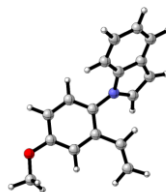
9a:



**G<sub>sol</sub>** = -786.925232

C -2.28315700 0.95764900 -0.68909600  
C -3.24804100 0.05734700 -0.20184800  
C -2.87111700 -1.13770800 0.39408700  
C -1.51335000 -1.43685600 0.51166300  
C -0.55329600 -0.51081700 0.03061300  
C -0.92832400 0.67764900 -0.57750000  
C -0.78435800 -2.55725200 1.03248400  
C 0.54252600 -2.29150500 0.85692200  
N 0.70714200 -1.04998000 0.26613900  
O -4.59618600 0.28392700 -0.28097200  
C -5.04457600 1.47987800 -0.88615900  
C 1.94763500 -0.49549000 -0.13266600  
C 2.37588900 0.74106000 0.38031300  
C 3.60491400 1.23901600 -0.06936200  
C 4.38272900 0.54050300 -0.97710500  
C 3.95023000 -0.68994600 -1.46199200  
C 2.73157900 -1.19965900 -1.04310300  
C 1.57942600 1.44645800 1.39049800  
C 1.63849200 2.74858800 1.66153200  
H -2.58530900 1.88185800 -1.15701200  
H -3.63617200 -1.81520300 0.74885000  
H -0.19318100 1.37586800 -0.95151000  
H -1.19551200 -3.44228400 1.48803900  
H 1.40986600 -2.87142700 1.12403100  
H -6.13105700 1.45048400 -0.84177400  
H -4.72897400 1.54571800 -1.93229200  
H -4.68639600 2.36337100 -0.34808700  
H 3.96911500 2.17359500 0.33526300  
H 5.33345800 0.94706400 -1.29621100  
H 4.55416600 -1.24397000 -2.16831200  
H 2.36239300 -2.14083800 -1.42819800  
H 0.87823000 0.83172200 1.94190200  
H 2.28244800 3.42740100 1.11622500  
H 1.02321000 3.18160300 2.43820000

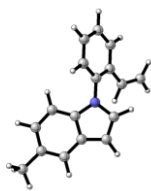
10a:



**G<sub>sol</sub>** = -786.92865

C -2.11098600 -1.65828800 0.88839900  
C -3.04784200 -0.84175000 0.24625500  
C -2.64932300 0.37042600 -0.29976000  
C -1.31542900 0.79578900 -0.21682500  
C -0.39314900 -0.02529400 0.44173800  
C -0.79943500 -1.24345000 0.98562200  
C -0.87917000 2.05508900 -0.83198100  
C 1.42271300 1.45413400 1.30593400  
N 0.96284100 0.37010900 0.57491500  
O -4.31671400 -1.32549000 0.19486600  
C -5.31057600 -0.54372700 -0.44596500  
C 2.05272800 -0.27603700 0.01699900  
C 3.21808400 0.42948700 0.41245700  
C 4.46516500 -0.02259000 -0.03468200  
C 4.52230200 -1.13926000 -0.84914400  
C 3.35387300 -1.81755600 -1.23414700  
C 2.10515000 -1.39615100 -0.80896600  
C 2.78319600 1.52335800 1.23098200  
C -1.65608100 3.10040600 -1.10969600  
H -2.43609600 -2.60212900 1.30366000  
H -3.35438500 0.98836800 -0.83302600  
H -0.06795100 -1.85732900 1.49364400  
H 0.17793000 2.11640000 -1.06196800  
H 0.71853600 2.08219000 1.82437000  
H -6.23607000 -1.10756900 -0.36103800  
H -5.07555000 -0.38889000 -1.50292200  
H -5.43004400 0.42701300 0.04391200  
H 5.37082900 0.49703100 0.25208800  
H 5.48110100 -1.49810000 -1.20024700  
H 3.43074500 -2.68494000 -1.87673700  
H 1.20417600 -1.91423500 -1.10820500  
H 3.40442100 2.26238200 1.70850300  
H -2.71094100 3.12180400 -0.86503600  
H -1.25019900 3.98364600 -1.58364600

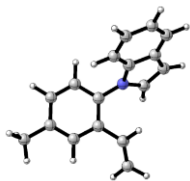
**9b:**



**G<sub>sol</sub>** = -711.691284

C -2.70285900 -2.33639100 0.70125700  
C -3.77699800 -1.75916400 0.03047400  
C -3.66241600 -0.48047900 -0.48761100  
C -2.48226200 0.26128200 -0.35339500  
C -1.41432300 -0.33184500 0.34001400  
C -1.52776800 -1.61935200 0.85820600  
C -2.33861000 1.59316400 -0.95380600  
C -0.07719800 1.58642000 1.20544800  
N -0.20482200 0.37859500 0.53578500  
C 1.05974100 -0.04137400 0.14921600  
C 1.98788300 0.93386000 0.58532100  
C 3.34732600 0.75385900 0.30065600  
C 3.76649800 -0.36455900 -0.40090100  
C 2.81146800 -1.31031600 -0.82886900  
C 1.46124100 -1.16638500 -0.56675100  
C 1.23534900 1.95402300 1.25523700  
C -3.33222600 2.44213300 -1.20885100  
C 5.22273700 -0.58386700 -0.71532000  
H -2.78336400 -3.33640400 1.10637200  
H -4.69754200 -2.31274400 -0.10031700  
H -4.48586000 -0.05375300 -1.04414300  
H -0.68920300 -2.04033200 1.39592000  
H -1.32442800 1.88944700 -1.19547500  
H -0.95339600 2.07220400 1.59888200  
H 4.07124200 1.49140600 0.62657400  
H 3.14886300 -2.17747100 -1.38397100  
H 0.74506100 -1.89986500 -0.91103400  
H 1.62258400 2.84440300 1.72154700  
H -4.36088800 2.22436200 -0.94925400  
H -3.14078900 3.39684800 -1.67946900  
H 5.83429800 0.23975300 -0.34669200  
H 5.38848200 -0.66855300 -1.79224500  
H 5.59318700 -1.50553000 -0.25913200

**10b:**

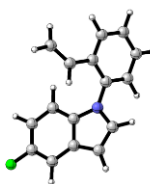


**G<sub>sol</sub>** = -711.693176

C -2.38698100 -1.77833400 0.72597000  
C -3.36581300 -0.99193100 0.11116200

C -2.99509500 0.25058100 -0.38220300  
C -1.68611900 0.74004100 -0.28409500  
C -0.73259800 -0.06769300 0.35096400  
C -1.08842100 -1.31859200 0.84863800  
C -1.30428300 2.03449900 -0.86146700  
C 1.00038900 1.50148400 1.22088100  
N 0.60327400 0.37988700 0.50833200  
C 1.73566000 -0.25266400 0.02091700  
C 2.86116400 0.50161500 0.44044200  
C 4.13963900 0.07643600 0.06137500  
C 4.26664600 -1.06308300 -0.71244900  
C 3.13720900 -1.78947500 -1.12416900  
C 1.85886600 -1.39515400 -0.76606200  
C 2.35966300 1.60824400 1.20193100  
C -2.12096300 3.06484900 -1.07299200  
C -4.77851500 -1.49211900 -0.01807600  
H -2.64823300 -2.75447600 1.11630000  
H -3.73378700 0.85137000 -0.89695300  
H -0.33489000 -1.91763000 1.34192200  
H -0.25753700 2.13741800 -1.12317500  
H 0.25760600 2.12411400 1.68920100  
H 5.01523400 0.63465700 0.36818500  
H 5.25026400 -1.40180300 -1.01085900  
H 3.26778700 -2.67322300 -1.73499200  
H 0.98902900 -1.95076200 -1.08859000  
H 2.93811400 2.38062700 1.68036100  
H -3.16687700 3.04217700 -0.79293200  
H -1.75866200 3.97704500 -1.52715400  
H -4.81099200 -2.45375500 -0.53481600  
H -5.39865700 -0.78940300 -0.57386800  
H -5.23401100 -1.63778700 0.96443300

**9d:**



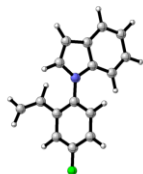
**G<sub>sol</sub>** = -771.670593

C -2.42486200 1.24003600 -1.05366400  
C -3.48776100 0.51039600 -0.51484200  
C -3.32342900 -0.62559700 0.24223900  
C -2.01203500 -1.05802700 0.48073700  
C -0.92981300 -0.31235700 -0.05196700  
C -1.12302000 0.82832400 -0.82508900  
C -1.44647700 -2.17186400 1.18067400  
C -0.08990400 -2.07729300 1.05648200  
N 0.24321000 -0.95090300 0.32501300  
F -4.74537800 0.95389800 -0.76249500  
C 1.55994500 -0.58133800 -0.05088500  
C 2.10056800 0.64740600 0.36330700  
C 3.40005100 0.95689900 -0.05659400



C 4.13497900 0.08568100 -0.84265400  
 C 3.58755100 -1.13310600 -1.23103700  
 C 2.29899400 -1.45929200 -0.83858100  
 C 1.33886200 1.54080000 1.24333400  
 C 1.52810400 2.85194200 1.37479700  
 H -2.63872300 2.12035100 -1.64307700  
 H -4.18426600 -1.15551300 0.62589400  
 H -0.28844000 1.38153500 -1.23099100  
 H -1.97946400 -2.94000200 1.71500700  
 H 0.69088400 -2.70828100 1.44620100  
 H 3.84947000 1.88294700 0.27527100  
 H 5.14098300 0.34938200 -1.14158100  
 H 4.15737800 -1.82058600 -1.84181300  
 H 1.84270200 -2.38939400 -1.15024200  
 H 0.54859800 1.06947800 1.81529600  
 H 2.26860000 3.39275000 0.79866000  
 H 0.92769700 3.43292800 2.06120300

**10d:**

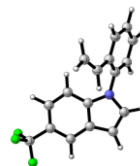


**G<sub>sol</sub>** = -771.670654

C -2.40367000 -1.82174500 0.73617800  
 C -3.33531100 -1.01426900 0.10490400  
 C -3.01554700 0.22568300 -0.40326100  
 C -1.70831100 0.71247900 -0.28809900  
 C -0.76000800 -0.09151600 0.36616200  
 C -1.11070300 -1.34202200 0.86756200  
 C -1.32014600 2.00548200 -0.86375300  
 C 0.95916300 1.47154000 1.27477300  
 N 0.57110000 0.36375000 0.53505500  
 F -4.59935900 -1.46584000 -0.03242700  
 C 1.70758800 -0.24226200 0.02359000  
 C 2.82634400 0.51386400 0.45643800  
 C 4.10725700 0.11298400 0.05957300  
 C 4.24213300 -1.00494600 -0.74382900  
 C 3.11872100 -1.73374300 -1.16745900  
 C 1.83812200 -1.36322400 -0.79237000  
 C 2.31674100 1.59440000 1.24977100  
 C -2.14182900 3.02267200 -1.11373900  
 H -2.69390200 -2.79073600 1.11659900  
 H -3.77395700 0.79340800 -0.92280700  
 H -0.35771800 -1.93180100 1.37185800  
 H -0.26573200 2.11692800 -1.08641000  
 H 0.21207200 2.07312700 1.76353400  
 H 4.97842200 0.67272000 0.37585800  
 H 5.22762500 -1.32478300 -1.05634000  
 H 3.25575600 -2.60022300 -1.80106300  
 H 0.97279400 -1.92069500 -1.12407500

H 2.88940400 2.36056400 1.74482200  
 H -3.19732000 2.98941700 -0.87343700  
 H -1.77418500 3.93612100 -1.56072600

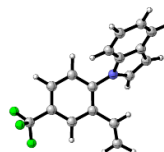
**9h:**



**G<sub>sol</sub>** = -1009.585083

C -1.68414100 0.94270200 -0.73562500  
 C -2.65149800 0.08747700 -0.18354800  
 C -2.29212800 -1.07470900 0.48151800  
 C -0.93899100 -1.38799100 0.60502800  
 C 0.02497800 -0.50350400 0.05318200  
 C -0.33552600 0.65670900 -0.62443100  
 C -0.21750700 -2.47909100 1.19183600  
 C 1.10807100 -2.23719500 0.98606100  
 N 1.27380300 -1.03752800 0.30842900  
 C 2.51979700 -0.50815500 -0.12045900  
 C 2.96475100 0.73658300 0.35427300  
 C 4.19508900 1.20722500 -0.12118800  
 C 4.95311000 0.47488200 -1.01871300  
 C 4.50100000 -0.76245700 -1.46712100  
 C 3.28175800 -1.24719600 -1.01996200  
 C 2.18305900 1.48231100 1.34455000  
 C 2.24387000 2.78060000 1.55057500  
 C -4.11110800 0.40252800 -0.32540400  
 F -4.75009300 -0.49199000 -1.11911500  
 F -4.75614000 0.37121500 0.86486600  
 F -4.33389900 1.62015600 -0.85882200  
 H -2.00042000 1.83746100 -1.25061400  
 H -3.05027600 -1.72639100 0.89536000  
 H 0.40894300 1.31752200 -1.04410800  
 H -0.63331300 -3.32869800 1.70636400  
 H 1.97503100 -2.80460400 1.27925800  
 H 4.57421100 2.14825500 0.25342100  
 H 5.90475700 0.86127700 -1.35919100  
 H 5.09025200 -1.34166100 -2.16534800  
 H 2.89766400 -2.19463500 -1.37391100  
 H 1.49171100 0.89456500 1.93586200  
 H 2.87870200 3.43178200 0.96333100  
 H 1.63981000 3.24907400 2.31477800

**10h:**

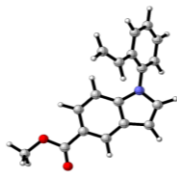


**G<sub>sol</sub>** = -1009.581787

C -1.70341200 -1.29020700 0.71509600

C -2.56677100 -0.35178900 0.15327700  
 C -2.07342200 0.84637300 -0.33320100  
 C -0.70996600 1.15106800 -0.26858800  
 C 0.14649700 0.20342600 0.31621100  
 C -0.35372600 -1.00516600 0.79838800  
 C -0.18187500 2.39664000 -0.83890600  
 C -0.85824600 3.53569800 -0.96902400  
 N 1.52764700 0.46855800 0.44353200  
 C 2.08104600 1.55787700 1.10708600  
 C 3.43891600 1.45982600 1.10673200  
 C 3.77967800 0.25264500 0.41010000  
 C 2.56178000 -0.35156900 0.01038300  
 C 4.98720000 -0.36879100 0.07395400  
 C 4.95644700 -1.55253700 -0.64112500  
 C 3.73866200 -2.12771000 -1.03715700  
 C 2.52677000 -1.53622300 -0.72062400  
 C -4.02659900 -0.68121500 0.01986100  
 F -4.26349400 -1.47848400 -1.04807100  
 F -4.49401900 -1.33973900 1.10105600  
 F -4.78938400 0.41765600 -0.13899000  
 H -2.08813000 -2.22508000 1.09768000  
 H -2.74707400 1.54764200 -0.80311900  
 H 0.32776300 -1.70702300 1.25799500  
 H 0.84958500 2.35826600 -1.16904100  
 H -1.87597900 3.64907400 -0.61640500  
 H -0.40292800 4.40283900 -1.42737200  
 H 1.43543600 2.30420700 1.53638900  
 H 4.12070800 2.16119300 1.55755000  
 H 5.93048100 0.07422000 0.36723500  
 H 5.88365200 -2.04354600 -0.90601900  
 H 3.74563500 -3.04963900 -1.60358200  
 H 1.59150700 -1.97703900 -1.03675500

**9i:**

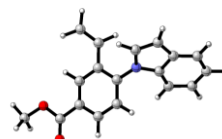


**G<sub>sol</sub>** = -900.331177

C 1.73366700 -0.81491100 -0.54835800  
 C 2.63730500 0.16598300 -0.08733700  
 C 2.17493600 1.37444100 0.41980400  
 C 0.80270200 1.60792500 0.47439500  
 C -0.08594400 0.59963400 0.01742700  
 C 0.36923800 -0.61052000 -0.50318000  
 C -0.00555700 2.71300700 0.90413500  
 C -1.30561100 2.35968400 0.70250700  
 N -1.37227100 1.07498000 0.17627100  
 C 4.10357100 -0.04362900 -0.12740800  
 O 4.92746700 0.75708000 0.24995300  
 O 4.44333300 -1.24800300 -0.63961400

C 5.84837900 -1.51525900 -0.70774000  
 C -2.56839500 0.41315100 -0.20632200  
 C -2.94493000 -0.79005400 0.41273200  
 C -4.12851700 -1.39805300 -0.02367900  
 C -4.90752200 -0.83594600 -1.02068600  
 C -4.52442200 0.36387900 -1.61205800  
 C -3.35216100 0.98160700 -1.20592000  
 C -2.14365000 -1.35250600 1.50558400  
 C -2.13441100 -2.62756500 1.88781700  
 H 2.12440100 -1.74104200 -0.94165100  
 H 2.88998000 2.11149600 0.75846100  
 H -0.32009800 -1.36521900 -0.85363700  
 H 0.34043900 3.64547600 1.31689300  
 H -2.21638100 2.89761900 0.90388500  
 H 5.93689500 -2.51014000 -1.13590000  
 H 6.29287500 -1.48517300 0.28664300  
 H 6.34796700 -0.78086800 -1.33891700  
 H -4.45636800 -2.30890400 0.45849000  
 H -5.82235600 -1.32524400 -1.32824600  
 H -5.13051300 0.81080200 -2.38871900  
 H -3.02071100 1.90188800 -1.66817500  
 H -1.49994600 -0.65068800 2.02223600  
 H -2.71769700 -3.38910600 1.38530900  
 H -1.52105100 -2.95357900 2.71645500

**10i:**

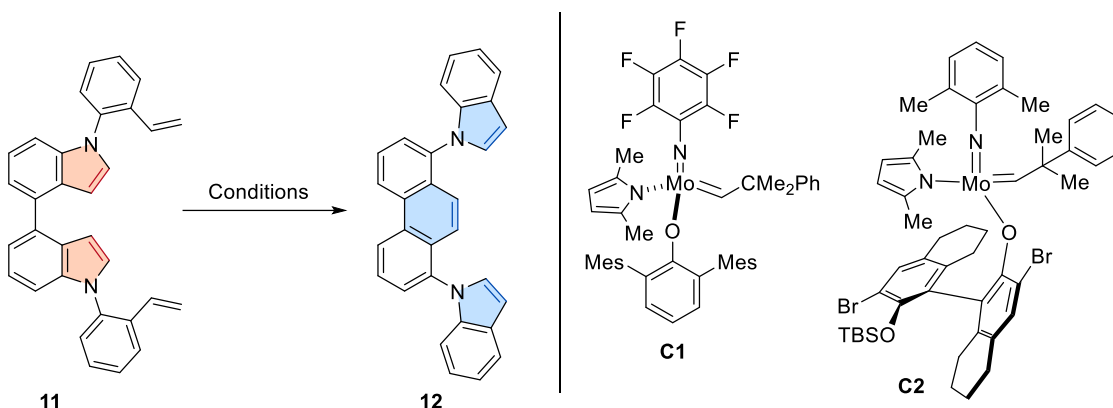


**G<sub>sol</sub>** = -900.328796

C -1.58533000 -1.42982900 0.72649700  
 C -2.49751700 -0.50559600 0.21329100  
 C -2.04460700 0.72647700 -0.24217000  
 C -0.69189000 1.07201100 -0.19595700  
 C 0.20702200 0.13296000 0.33988600  
 C -0.24432300 -1.10709800 0.79138500  
 C -0.21439100 2.34957900 -0.74098500  
 C 2.11272600 1.53376500 1.11790200  
 N 1.58158200 0.43844500 0.44663000  
 C -3.93114300 -0.89332000 0.15980300  
 O -4.36225100 -1.96029700 0.52598400  
 O -4.71239100 0.08217500 -0.34418900  
 C -6.11084100 -0.22545600 -0.42885800  
 C 2.63327000 -0.34052900 -0.01946600  
 C 3.83882600 0.29605100 0.36790600  
 C 5.05917400 -0.27966300 -0.00163100  
 C 5.05318600 -1.45113500 -0.73725700  
 C 3.84716900 -2.05848200 -1.12104200  
 C 2.62309500 -1.51255900 -0.77137700  
 C 3.47287500 1.47971000 1.09145400  
 C -0.92548900 3.47223400 -0.81875300

H -1.94786100 -2.38547200 1.07751900  
H -2.75014000 1.41677400 -0.67870100  
H 0.46938400 -1.80146100 1.21208400  
H 0.80802900 2.35196300 -1.10068800  
H 1.45197200 2.25136800 1.57219800  
H -6.57918400 0.65883200 -0.85158200  
H -6.51421500 -0.43862100 0.56028700  
H -6.27219100 -1.09015000 -1.07138900  
H 5.99304500 0.18890100 0.28202800  
H 5.99058700 -1.90703300 -1.02793500  
H 3.87291200 -2.96984400 -1.70385000  
H 1.69672600 -1.97830800 -1.07740100  
H 4.14018700 2.19471500 1.54255000  
H -1.93616300 3.54429200 -0.43622000  
H -0.50788300 4.36518700 -1.26342600

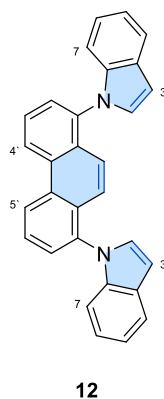
**Supplementary Table 8.** Reaction conditions optimization for metathesis involving twofold ArROM and threefold RCM



| Entry          | Catalyst (mol%) | Solvent | Temp. [°C] | Conversion <sup>b</sup> [%] | Yield <sup>b</sup> [%] |
|----------------|-----------------|---------|------------|-----------------------------|------------------------|
| 1 <sup>a</sup> | <b>C2</b> (20)  | Toluene | 65         | NR                          | —                      |
| 2 <sup>a</sup> | <b>C2</b> (20)  | Toluene | 85         | 9                           | 6                      |
| 3 <sup>a</sup> | <b>C2</b> (20)  | Toluene | 120        | 32                          | 27                     |
| 4 <sup>a</sup> | <b>C2</b> (30)  | Toluene | 120        | 34                          | 16                     |
| 5 <sup>a</sup> | <b>C1</b> (20)  | Toluene | 120        | 50                          | 49                     |
| 6 <sup>c</sup> | <b>C1</b> (10)  | Toluene | 120        | 77                          | 41 <sup>d</sup>        |

<sup>a</sup>Reactions were performed on 7.50  $\mu\text{mol}$  scale of **11** for 18 h. <sup>b</sup>Conversion and yield were determined by <sup>1</sup>H-NMR with durene as an internal standard. <sup>c</sup>on 70.0  $\mu\text{mol}$  scale. <sup>d</sup> Isolated yield.

### 1,8-Di(1-*H*-indol-1-yl)phenanthrene (**12**):



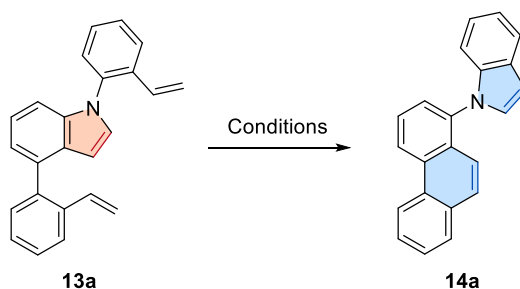
The catalyst **C1** (5.83 mg, 7.00  $\mu\text{mol}$ , 10 mol%) was weighed into a 10 mL crimp cap vial. A solution of the **11** (30.6 mg, 70.0  $\mu\text{mol}$ , 1.00 eq.) in toluene (2.3 mL, 0.03 mol·L<sup>-1</sup>) was then added. The reaction was stirred for 18 h at the indicated temperature, cooled down to room temperature, diluted with EtOAc and filtered through a thin layer of silica gel. Solvents were then removed under reduced pressure. The obtained crude product was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0→80:20) to give the desired product **12** as a beige solid (11.8 mg, 28.9  $\mu\text{mol}$ , 41%); *R*<sub>f</sub> 0.67 (cyclohexane/EtOAc 3:1);  $\nu_{\text{max}}$  (neat): 3054w, 2926w, 2854w, 1674w, 1599m, 1512m, 1464s, 1329m, 1260m, 1082m, 1013w, 883w, 788w, 741s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.84 (2H, d, <sup>3</sup>*J* 8.4 Hz, C4'*H*, C5'*H*), 7.76 (2H, dd, <sup>3</sup>*J* 8.4, <sup>3</sup>*J* 7.5 Hz, C3'*H*, C6'*H*), 7.66 – 7.60 (4H, m, C2'*H*, C7'*H*, C4*H*), 7.28 – 7.22 (2H, m, C2*H*), 7.17 (s, 1H, C9'*H*/C10'*H*), 7.14 (1H, s, C9'*H*/C10'*H*), 7.11 – 6.99 (4H, m, C5*H*, C6*H*), 7.04 – 6.95 (2H, m, C7*H*), 6.70 – 6.64 (2H, m, C3*H*); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 138.24, 138.21 (C7*a*), 137.0 (C1'), 131.63 (C10*a*'/C8*a*'), 131.61 (C10*a*'/C8*a*'), 129.87, 129.84 (C2), 129.4 (C4*a*'/C4*b*'), 128.59, 128.56 (C3*a*), 126.98 (C3'/C6'), 126.97 (C3'/C6'), 126.7 (C2'), 123.47, 123.45 (C4'/C5'), 122.98, 122.96 (C9'/C10'), 122.5, 122.4 (C6), 121.14, 121.10 (C4), 120.37, 120.34 (C5), 110.8 (C7), 103.4 (C3); ESI-MS: *m/z* calcd. for C<sub>30</sub>H<sub>21</sub>N<sub>2</sub> 409.1699 found 409.1691 [M+H<sup>+</sup>].

## ArROM – Twofold RCM for *N*-Aryl Indoles

**Optimization Studies (7.50  $\mu\text{mol}$  scale):** Performed according to the general procedure **F** utilizing 1,4-bis(2-vinylphenyl)-1*H*-indole **13a** (2.41 mg, 7.50  $\mu\text{mol}$ ) and toluene (0.25 mL, 0.03 mol·L<sup>-1</sup>) with the reaction time of 18 h.

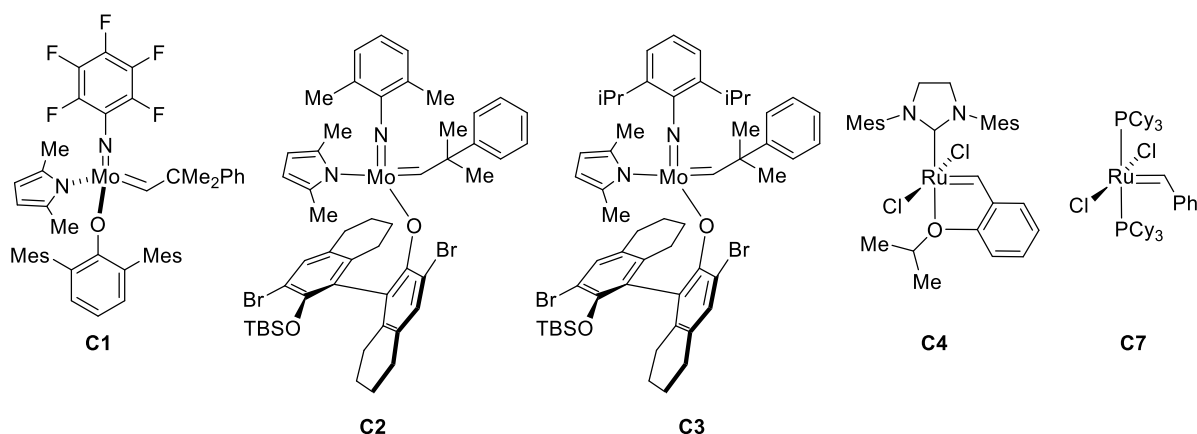
**Optimization Studies (70.0  $\mu\text{mol}$  scale):** Performed according to the general procedure **G** utilizing 1,4-bis(2-vinylphenyl)-1*H*-indole **13a** (22.5 mg, 70.0  $\mu\text{mol}$ ) and toluene (2.3 mL, 0.03 mol·L<sup>-1</sup>) with the reaction time of 18 h.

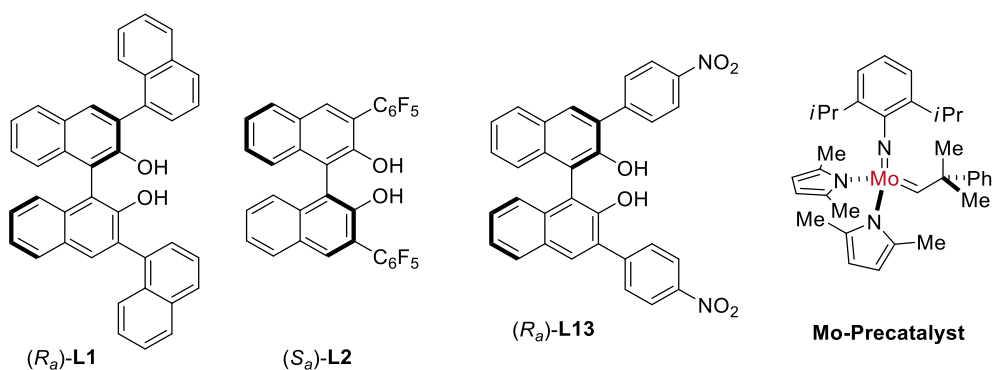
**Supplementary Table 9.** Reaction conditions optimization for ArROM – twofold RCM for *N*-aryl indoles



| Entry           | Catalyst (mol%)       | Ligand (mol%)                        | Solvent | Temp. [°C] | Conversion <sup>b</sup> [%] | Yield <sup>b</sup> [%] |
|-----------------|-----------------------|--------------------------------------|---------|------------|-----------------------------|------------------------|
| 1 <sup>a</sup>  | <b>C1</b> (10)        | –                                    | Toluene | 65         | >95                         | 76                     |
| 2 <sup>a</sup>  | <b>C1</b> (20)        | –                                    | Toluene | 65         | >95                         | 93                     |
| 3 <sup>a</sup>  | <b>C4</b> (10)        | –                                    | Toluene | 65         | 63                          | 47                     |
| 4 <sup>a</sup>  | <b>C7</b> (10)        | –                                    | Toluene | 65         | 15                          | 9                      |
| 5 <sup>a</sup>  | <b>C3</b> (10)        | –                                    | Toluene | 65         | 53                          | 45                     |
| 6 <sup>a</sup>  | <b>C2</b> (10)        | –                                    | Toluene | rt         | 67                          | 47                     |
| 7 <sup>a</sup>  | <b>C2</b> (10)        | –                                    | Toluene | <b>65</b>  | >95                         | 95                     |
| 8 <sup>a</sup>  | <b>C2</b> (10)        | –                                    | Toluene | <b>85</b>  | >95                         | 83                     |
| 9 <sup>a</sup>  | <b>C2</b> (10)        | –                                    | Toluene | <b>110</b> | >95                         | 48                     |
| 10 <sup>a</sup> | <b>Precat. 1</b> (10) | ( <i>R<sub>a</sub></i> )- <b>L1</b>  | Toluene | 65         | 67                          | 67                     |
| 11 <sup>a</sup> | <b>Precat. 1</b> (10) | ( <i>S<sub>a</sub></i> )- <b>L2</b>  | Toluene | 65         | >95                         | 96                     |
| 12 <sup>a</sup> | <b>Precat. 1</b> (10) | ( <i>R<sub>a</sub></i> )- <b>L13</b> | Toluene | 65         | NR                          | –                      |
| 13 <sup>c</sup> | <b>C1</b> (10)        | –                                    | Toluene | 65         | 42                          | 42 <sup>d</sup>        |
| 14 <sup>c</sup> | <b>C1</b> (15)        | –                                    | Toluene | 65         | >95                         | 90 <sup>d</sup>        |
| 15 <sup>c</sup> | <b>C2</b> (10)        | –                                    | Toluene | 65         | >95                         | 96 <sup>d</sup>        |

<sup>a</sup>Reactions were performed on 7.50  $\mu\text{mol}$  scale of **13a** for 18 h. <sup>b</sup>Conversion and yield were determined by <sup>1</sup>H-NMR with durene as an internal standard. <sup>c</sup>Reactions were performed on 70.0  $\mu\text{mol}$  scale. <sup>d</sup>Isolated yield.

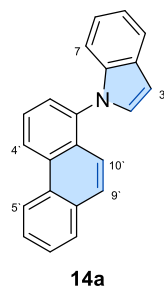




### General Procedure K for indole ring-opening metathesis:

The catalyst **C2** (7.05 mg, 7.00  $\mu\text{mol}$ , 10 mol%) was weighed into a 10 mL crimp cap vial. A solution of the indole derivative **13a-i** (70.0  $\mu\text{mol}$ , 1.00 eq.) in toluene (2.3 mL, 0.03 mol·L<sup>-1</sup>) was then added. The reaction was stirred for 18 h at the indicated temperature, cooled down to room temperature, diluted with EtOAc and filtered through a thin layer of silica gel. Solvents were then removed under reduced pressure. The obtained crude product was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0→80:20) to give the desired product.

### 1-(Phenanthren-1-yl)-1H-indole (**14a**):



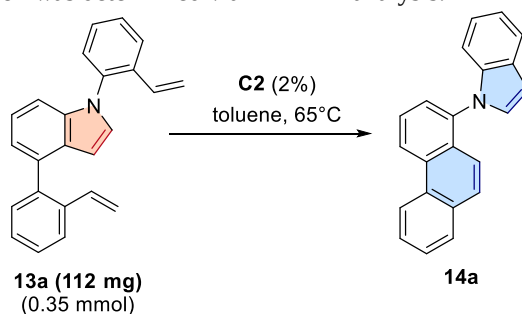
Prepared according to the general procedure **K** using 1,4-bis(2-vinylphenyl)-1H-indole **13a** (22.5 mg, 70.0  $\mu\text{mol}$ ) to give the title compound **14a** as a white solid (19.8 mg, 67.5  $\mu\text{mol}$ , 96%, m.p. 150.5 – 151°C): *R<sub>f</sub>* 0.74 (cyclohexane/EtOAc 8:1);  $\nu_{\text{max}}$  (neat): 3052w, 2923w, 2844w, 1730w, 1599m, 1511m, 1465s, 1328s, 1215m, 1167w, 1078w, 1011w, 907w, 807m, 741s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.83 (1H, d, <sup>3</sup>*J* 8.5 Hz, C4'*H*), 8.78 (1H, d, <sup>3</sup>*J* 8.3 Hz, C5'*H*), 7.88 (1H, dd, <sup>3</sup>*J* 7.9, <sup>4</sup>*J* 1.3 Hz, C8'*H*), 7.80 – 7.74 (2H, m, C3'*H*, C4*H*), 7.72 (1H, ddd, <sup>3</sup>*J* 8.3, <sup>3</sup>*J* 7.0, <sup>4</sup>*J* 1.4 Hz, C6'*H*), 7.68 – 7.61 (3H, m, C2'*H*, C7'*H*, C9'*H*), 7.39 (1H, d, <sup>3</sup>*J* 3.2 Hz, C2*H*), 7.31 (1H, d, <sup>3</sup>*J* 9.1 Hz, C10*H*), 7.19 (1H, ddd, <sup>3</sup>*J* 8.0, <sup>3</sup>*J* 7.0, <sup>4</sup>*J* 1.1 Hz, C5*H*), 7.13 (1H, ddd, <sup>3</sup>*J* 8.2, <sup>3</sup>*J* 7.0, <sup>4</sup>*J* 1.3 Hz, C6*H*), 7.02 (1H, dt, <sup>3</sup>*J* 8.2, <sup>4</sup>*J* 1.1 Hz, C7*H*), 6.80 (1H, dd, <sup>3</sup>*J* 3.2, <sup>4</sup>*J* 0.9 Hz, C3*H*); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 138.2 (C7*a*), 136.6 (C1'), 132.0 (C8*a*'), 131.7 (C4*a*'), 130.1 (C4*b*'), 129.9 (C2), 129.3 (C10*a*'), 128.7 (C8'), 128.5 (C3*a*'), 128.2 (C9'), 127.2 (C7'), 127.1 (C6'), 126.3 (C3'), 126.0 (C2'), 123.04 (C4'), 122.98 (C5'), 122.2 (C6), 121.6 (C10'), 120.9 (C4), 120.2 (C5), 110.9 (C7), 103.0 (C3); ESI-MS: *m/z* calcd. for C<sub>22</sub>H<sub>15</sub>NAg 400.0250 found 400.0248 [M+Ag<sup>+</sup>].

**Scale-up (C2 (5 mol%))**: Performed according to the modified general procedure **K** using 1,4-bis(2-vinylphenyl)-1H-indole **13a** (112 mg, 350  $\mu\text{mol}$ ) and **C2** (17.6 mg, 17.5  $\mu\text{mol}$ , 5 mol%) with the reaction time of 18 h to give the title compound **14a** as a white solid (101 mg, 344  $\mu\text{mol}$ , 98%).

**Scale-up (C2 (2 mol%))**: Performed according to the modified general procedure **K** using 1,4-bis(2-vinylphenyl)-1H-indole **13a** (112 mg, 350  $\mu\text{mol}$ ) and **C2** (7.05 mg, 7.00  $\mu\text{mol}$ , 2 mol%) with the reaction time of 18 h to give the title compound **14a** as a white solid (99.5 mg, 339  $\mu\text{mol}$ , 97%).

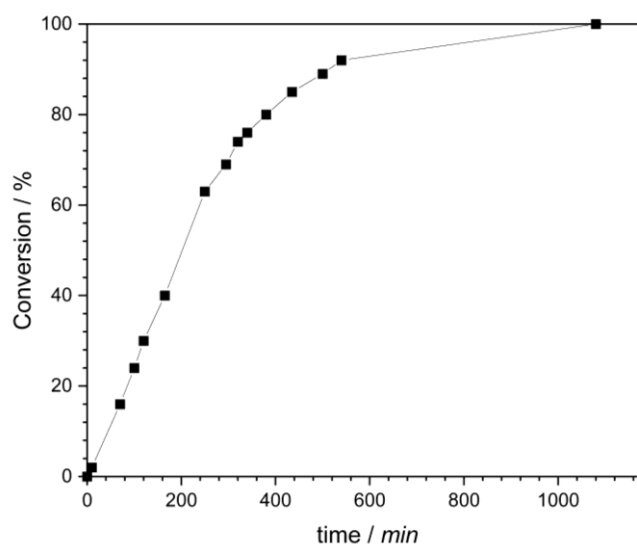
### Reaction monitoring versus time:

The reaction of **13a** on 350  $\mu\text{mol}$  scale with 2 mol% loading of **C2** performed according to the procedure described above was monitored versus time over 18 hours. The reaction was placed in the glovebox and aliquots were taken after the indicated time. Conversion was determined via  $^1\text{H}$ -NMR analysis.



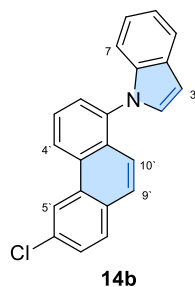
**Supplementary Table 10.** Reaction progress

| Reaction time | Conversion |
|---------------|------------|
| min           | %          |
| 0             | 0          |
| 10            | 2          |
| 70            | 16         |
| 100           | 24         |
| 120           | 30         |
| 165           | 40         |
| 250           | 63         |
| 295           | 69         |
| 320           | 74         |
| 340           | 76         |
| 380           | 80         |
| 435           | 85         |
| 500           | 89         |
| 540           | 92         |
| 1080          | 100        |



Reaction conditions: **13a** (112 mg, 350  $\mu\text{mol}$ ), **C2** (7.05 mg, 7.00  $\mu\text{mol}$ , 2 mol%), toluene, Ar.

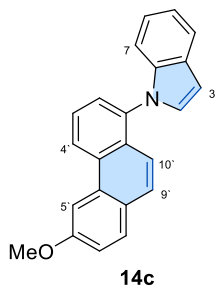
### 1-(6-Chlorophenanthren-1-yl)-1H-indole (**14b**):



Prepared according to the general procedure **K** using 4-(5-chloro-2-vinylphenyl)-1-(2-vinylphenyl)-1H-indole **13b** (24.9 mg, 70.0  $\mu\text{mol}$ ) to give the title compound as a beige solid (22.0 mg, 67.1  $\mu\text{mol}$ , 96%):  $R_f$  0.74 (cyclohexane/EtOAc 6:1);  $\nu_{\text{max}}$  (neat): 3060w, 2930w, 2855w, 1793w, 1593w, 1513w, 1463m, 1401w, 1327w, 1212w, 1149w, 1094w, 1012w, 978w, 840m, 747m;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.80 – 8.66 (2H, m, C4'H, C5'H), 7.82 (1H, d,  $^3J$  8.5 Hz, C8'H), 7.80 – 7.74 (2H, m, C4H, C3'H), 7.71 – 7.66 (1H, m, C2'H), 7.64 – 7.57 (2H, m, C7'H, C9'H), 7.37 (1H, d,  $^3J$  3.2 Hz, C2H), 7.31 (1H, d,  $^3J$  9.1 Hz, C10'H), 7.24 – 7.17 (1H, m, C5H), 7.14 (1H, td,  $^3J$  7.6,  $^4J$  1.1 Hz, C6H), 7.01 (1H, d,  $^3J$  8.2 Hz, C7H), 6.80 (1H, dd,  $^3J$  3.2,  $^4J$  0.7 Hz, C3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 138.1 (C7a), 136.7 (C1'), 133.1 (C8a'), 131.2 (C4b'), 130.7 (C4a'), 130.3 (C6'), 130.1 (C8'),

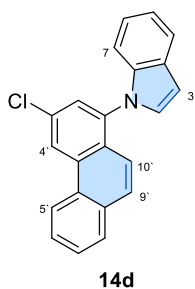
129.8 (C2), 129.6 (C10a'), 128.5 (C3a), 127.7 (C7'), 127.5 (C9'), 126.65 (C2'), 126.63 (C3'), 123.1 (C4'), 122.8 (C5'), 122.3 (C6), 122.0 (C10'), 121.0 (C4), 120.3 (C5), 110.8 (C7), 103.2 (C3); ESI-MS: m/z calcd. for C<sub>22</sub>H<sub>14</sub>ClNNa 350.0707 found 350.0701 [M+Na<sup>+</sup>].

### 1-(6-Methoxyphenanthren-1-yl)-1H-indole (14c):



Prepared according to the modified general procedure **K** using 4-(5-methoxy-2-vinylphenyl)-1-(2-vinylphenyl)-1H-indole **13c** (24.6 mg, 70.0 μmol) and the catalyst **C2** (14.1 mg, 14.0 μmol, 20 mol%) to give the title compound **14c** as a beige solid (22.0 mg, 68.0 μmol, 97%, m.p. 165.0 – 166.7°C): R<sub>f</sub> 0.50 (cyclohexane/EtOAc 6:1); ν<sub>max</sub> (neat): 3054w, 2934w, 2835w, 1609m, 1602m, 1512m, 1469s, 1399w, 1329w, 1291w, 1234s, 1145w, 1036w, 908w, 837w, 736m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 8.74 (1H, d, <sup>3</sup>J 8.5 Hz, C4'H), 8.12 (1H, d, <sup>4</sup>J 2.4 Hz, C5'H), 7.79 (1H, d, <sup>3</sup>J 8.7 Hz, C8'H), 7.78 – 7.71 (2H, m, C4H, C3'H), 7.64 (1H, dd, <sup>3</sup>J 7.4, <sup>4</sup>J 1.0 Hz, C2'H), 7.59 (1H, d, <sup>3</sup>J 9.1 Hz, C9'H), 7.38 (1H, d, <sup>3</sup>J 3.2 Hz, C2H), 7.29 (1H, dd, <sup>3</sup>J 8.7, <sup>4</sup>J 2.4 Hz, C7'H), 7.21 – 7.15 (2H, m, C5H, C10'H), 7.13 (1H, td, <sup>3</sup>J 7.6, <sup>4</sup>J 1.2 Hz, C6H), 7.04 – 6.99 (1H, m, C7H), 6.79 (1H, dd, <sup>3</sup>J 3.2, <sup>4</sup>J 0.8 Hz, C3H), 4.05 (3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 159.0 (C6'), 138.3 (C7a), 136.7 (C1'), 131.6 (C4b'), 131.2 (C4a'), 130.3 (C8'), 130.0 (C2), 129.9 (C10a'), 128.6 (C3a), 127.9 (C9'), 126.8 (C8a'), 126.2 (C2'), 125.9 (C3'), 123.2 (C4'), 122.3 (C6), 121.1 (C4), 120.3 (C5), 119.3 (C10'), 117.4 (C7'), 111.0 (C7), 104.5 (C5'), 103.1 (C3), 55.7 (OCH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>23</sub>H<sub>17</sub>NOAg 430.0356 found 430.0349 [M+Ag<sup>+</sup>].

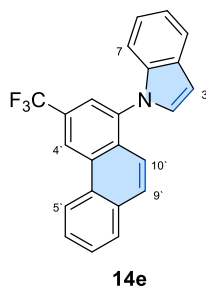
### 1-(3-Chlorophenanthren-1-yl)-1H-indole (14d):



Prepared according to the general procedure **K** using 6-chloro-1,4-bis(2-vinylphenyl)-1H-indole **13d** (24.9 mg, 70.0 μmol) to give the title compound **14d** as a beige oil (22.5 mg, 68.6 μmol, 98%); R<sub>f</sub> 0.76 (cyclohexane/EtOAc 5:1); ν<sub>max</sub> (neat): 3055w, 2926w, 2855w, 1719w, 1684w, 1593m, 1515m, 1459s, 1326m, 1214m, 1134w, 1083w, 1034w, 966w, 906m, 823m, 639w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 8.78 (1H, d, <sup>4</sup>J 1.9 Hz, C4'H), 8.68 (1H, d, <sup>3</sup>J 8.3 Hz, C5'H), 7.89 (1H, dd, <sup>3</sup>J 7.8, <sup>4</sup>J 1.4 Hz, C8'H), 7.81 – 7.70 (2H, m, C4H, C6'H), 7.70 – 7.60 (3H, m, C7'H, C9'H, C2'H), 7.36 (1H, d, <sup>3</sup>J 3.2 Hz, C2H), 7.31 – 7.28 (1H, m, C10'H), 7.20 (1H, ddd, <sup>3</sup>J 7.9, <sup>3</sup>J 7.0, <sup>4</sup>J 1.2 Hz, C5H), 7.16 (ddd, <sup>3</sup>J 8.2, <sup>3</sup>J 7.0, <sup>4</sup>J 1.3 Hz, C6H), 7.07 – 7.01 (1H, m, C7H), 6.81 (1H, dd, <sup>3</sup>J 3.2, <sup>4</sup>J 0.8 Hz, C3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 138.1 (C7a), 137.9 (C1'), 132.7 (C4a'), 132.5 (C8a'), 132.2 (C3), 129.7 (C2), 129.3 (C4b'), 128.9 (C8), 128.7 (C3a), 128.5 (C9'), 128.0 (C7'), 127.8 (C10a'), 127.6 (C6'), 126.6 (C2'), 123.2 (C5'), 122.8 (C4'), 122.7 (C6), 121.4 (C10') 121.2 (C4), 120.6 (C5), 110.9 (C7), 103.8 (C3); ESI-MS: m/z calcd. for C<sub>22</sub>H<sub>15</sub>ClN 328.0888 found 328.0883 [M+H<sup>+</sup>].

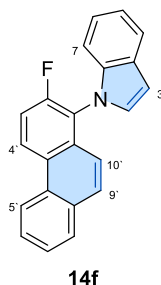


### 1-(3-(Trifluoromethyl)phenanthren-1-yl)-1*H*-indole (**14e**):



Prepared according to the general procedure **K** using 6-(trifluoromethyl)-1,4-bis(2-vinylphenyl)-1*H*-indole **13e** (27.3 mg, 70.0  $\mu\text{mol}$ ) to give the title compound **14e** as a beige oil (25.0 mg, 69.2  $\mu\text{mol}$ , 99%):  $R_f$  0.73 (cyclohexane/EtOAc 6:1);  $\nu_{\text{max}}$  (neat): 3059w, 2932w, 862w, 1607w, 1516m, 1461s, 1383w, 1334m, 1287s, 1235m, 1164s, 1125s, 990w, 888w, 827m, 744s, 668m, 618m;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.09 (1H, s, C4'*H*), 8.80 (1H, d,  $^3J$  8.1 Hz, C5'*H*), 7.93 (1H, dd,  $^3J$  7.9,  $^4J$  1.2 Hz, C8'*H*), 7.87 (1H, d,  $^3J$  1.4 Hz, C2'*H*), 7.84 – 7.76 (3H, m, C4*H*, C6'*H*, C9'*H*), 7.72 (1H, ddd,  $^3J$  7.9,  $^3J$  7.1,  $^4J$  1.1 Hz, C7'*H*), 7.44 – 7.35 (2H, m, C2*H*, C10'*H*), 7.22 (1H, ddd,  $^3J$  8.0,  $^3J$  7.0,  $^4J$  1.1 Hz, C5*H*), 7.16 (1H, ddd,  $^3J$  8.2,  $^3J$  7.0,  $^4J$  1.2 Hz, C6*H*), 7.00 (1H, dd,  $^3J$  8.2,  $^4J$  0.9 Hz, C7*H*), 6.83 (1H, dd,  $^3J$  3.2,  $^4J$  0.8 Hz, C3*H*);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 138.2 (C7*a*), 137.7 (C1'), 132.3 (C8*a*'), 131.6 (C4*a*'), 131.3 (C10*a*'), 130.6 (C6'), 130.1 (C4*b*'), 129.7 (C2), 129.1 (C8'), 128.8 (C3*a*), 128.2 (C7'), 128.0 (C9'), 123.2 (C5'), 122.8 (C6), 122.1 (q,  $^3J_{\text{CF}}$  3.1 Hz, C2'), 121.31 (C4), 121.27 (C10'), 120.7 (C5), 120.41 (q,  $J_{\text{CF}}$  3.7 Hz, C4'), 110.8 (C7), 104.0 (C3);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -61.8; ESI-MS:  $m/z$  calcd. for  $\text{C}_{23}\text{H}_{14}\text{F}_3\text{NAg}$  468.0124 found 468.0116 [ $\text{M}^+\text{Ag}^+$ ].

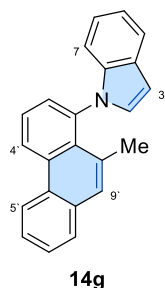
### 1-(2-Fluorophenanthren-1-yl)-1*H*-indole (**14f**):



Prepared according to the general procedure **K** using 7-fluoro-1,4-bis(2-vinylphenyl)-1*H*-indole **13f** (23.8 mg, 70.0  $\mu\text{mol}$ ) to give the title compound **14f** as a white solid (21.6 mg, 69.4  $\mu\text{mol}$ , 99%, m.p. 119.5 – 120.1°C):  $R_f$  0.55 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$  (neat): 3054w, 2927w, 2854w, 1731w, 1615m, 1515m, 1480s, 1299m, 1259m, 1139m, 1090w, 1012w, 908w, 816s, 741s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.83 (1H, dd,  $^3J$  9.2,  $^4J_{\text{HF}}$  4.9 Hz, C4'*H*), 8.70 (1H, d,  $^3J$  8.4 Hz, C5'*H*), 7.88 (1H, d,  $^3J$  7.7 Hz, C8'*H*), 7.77 (1H, d,  $^3J$  7.8 Hz, C4*H*), 7.75 – 7.71 (1H, m, C6'*H*), 7.69 (1H, d,  $^3J$  9.2 Hz, C9'*H*), 7.67 – 7.57 (2H, m, C7'*H*, C3'*H*), 7.32 (1H, d,  $^3J$  3.2 Hz, C2*H*), 7.23 – 7.19 (2H, m, C5*H*, C10'*H*), 7.18 – 7.11 (1H, m, C6*H*), 6.93 (1H, d,  $^3J$  8.1 Hz, C7*H*), 6.85 (1H, d,  $^3J$  3.2 Hz, C3*H*);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 157.3 (d,  $^1J_{\text{CF}}$  251.8 Hz, C2'), 138.0 (C7*a*), 131.6 (C8*a*'), 131.5 (C10*a*'), 130.0 (C4*b*'), 129.8 (C2), 129.6 (C9'), 129.0 (C8'), 128.6 (C3*a*), 127.8 (d,  $^4J_{\text{CF}}$  2.2 Hz, C4*a*'), 127.6 (C6'), 127.2 (C7'), 125.0 (d,  $^3J_{\text{CF}}$  8.8 Hz, C4'), 122.8 (C5'), 122.6 (C6), 122.2 (d,  $^2J_{\text{CF}}$  12.7 Hz, C1'), 121.3 (d,  $^4J_{\text{CF}}$  4.8 Hz, C10'), 121.2 (C4), 120.5 (C5), 115.8 (d,  $^2J_{\text{CF}}$  22.5 Hz, C3'), 110.7 (C7), 103.9 (C3);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -121.43; ESI-MS:  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{14}\text{AgFN}$  418.0156 found 418.0151 [ $\text{M}^+\text{Ag}^+$ ].

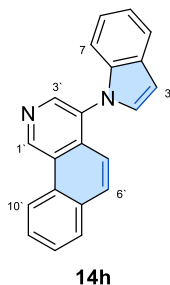
### 1-(10-Methylphenanthren-1-yl)-1*H*-indole (**14g**):

Prepared according to the modified general procedure **K** using 3-methyl-1,4-bis(2-vinylphenyl)-1*H*-indole **13g** (23.5 mg, 70.0  $\mu\text{mol}$ ) and **C2** (14.1 mg, 14.0  $\mu\text{mol}$ , 20 mol%) give the title compound **14g** as a white solid (11.2 mg, 36.4  $\mu\text{mol}$ , 52%, m.p. 119.1 – 120.0°C) after preparative thin layer chromatography (pTLC, cyclohexane/EtOAc



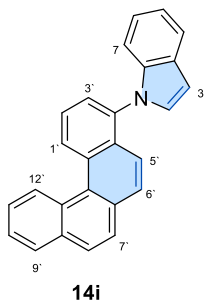
8:1);  $R_f$  0.69 (cyclohexane/EtOAc 8:1);  $\nu_{\max}$  (neat): 3057w, 2967w, 2932w, 1597w, 1509m, 1464s, 1369w, 1329m, 1214m, 1147w, 1094w, 1049w, 1031w, 887w, 821w, 743s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.92 (1H, dd,  $^3J$  8.5,  $^4J$  1.0 Hz, C4'H), 8.72 (1H, d,  $^3J$  8.2 Hz, C5'H), 7.83 – 7.77 (1H, m, C8'H), 7.76 – 7.68 (2H, m, C4H, C3'H), 7.68 – 7.58 (2H, m, C6'H, C7'H), 7.53 – 7.47 (2H, m, C2'H, C9'H), 7.26 (1H, d,  $^3J$  3.1 Hz, C2H), 7.19 – 7.08 (2H, m, C5H, C6H), 6.88 (1H, d,  $^3J$  8.2 Hz, C7H), 6.74 (1H, dd,  $^3J$  3.1,  $^4J$  0.8 Hz, C3H), 1.84 (3H, d,  $^4J$  0.9 Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 139.6 (C7a), 136.5 (C1'), 133.0 (C4a'), 132.0 (C8a'), 131.7 (C10'), 130.8 (C9'), 130.5 (C2), 130.2 (C10a'), 129.6 (C4b'), 129.3 (C2'), 128.3 (C3a), 127.8 (C8'), 127.4 (C7'), 126.6 (C6'), 126.0 (C3'), 124.3 (C4'), 123.0 (C5'), 122.6 (C6), 121.0 (C4), 120.1 (C5), 110.8 (C7), 102.9 (C3), 20.7 ( $\text{CH}_3$ ); ESI-MS:  $m/z$  calcd. for  $\text{C}_{23}\text{H}_{17}\text{AgN}$  414.0406 found 414.0412 [ $\text{M}+\text{Ag}^+$ ].

#### 4-(1H-Indol-1-yl)benzo[h]isoquinoline (14h):



Prepared according to the modified general procedure **K** 1,4-bis(2-vinylphenyl)-1H-pyrrolo[2,3-c]pyridine **13h** (22.6 mg, 70.0  $\mu\text{mol}$ ) and **C2** (14.1 mg, 14.0  $\mu\text{mol}$ , 20 mol%) give the title compound **14h** as a white solid (9.50 mg, 32.3  $\mu\text{mol}$ , 46%, m.p. 119.1 – 120.0°C):  $R_f$  0.64 (cyclohexane/EtOAc 3:2);  $\nu_{\max}$  (neat): 3123w, 3051w, 2930w, 1706w, 1595w, 1512m, 1334m, 1081w, 1005w, 968w, 906w,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.17 (1H, s, C3'H), 8.91 (1H, d,  $^3J$  8.1 Hz, C10'H), 8.81 (1H, s, C1'H), 7.95 (1H, d,  $^3J$  7.9 Hz, C7'H), 7.90 (1H, d,  $^3J$  9.1 Hz, C6'H), 7.83 (1H, ddd,  $^3J$  8.1,  $^3J$  7.1,  $^4J$  1.4 Hz, C9'H), 7.78 (1H, dt,  $^3J$  7.9,  $^4J$  1.2 Hz, C4H), 7.73 (1H, ddd,  $^3J$  7.9,  $^3J$  7.1,  $^4J$  1.1 Hz, C8'H), 7.38 (1H, d,  $^3J$  3.2 Hz, C2H), 7.36 (1H, d,  $^3J$  9.1 Hz, C5'H), 7.22 (1H, ddd,  $^3J$  7.9,  $^3J$  7.1,  $^4J$  1.1 Hz, C5H), 7.20 – 7.14 (1H, m, C6H), 7.04 (1H, dd,  $^3J$  8.1,  $^5J$  0.8 Hz, C7H), 6.84 (1H, dd,  $^3J$  3.2,  $^5J$  0.8 Hz, C3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 146.8 (C3'), 144.0 (C1'), 138.3 (C7a), 133.4 (C4a'), 133.0 (C6'), 132.3 (C6a'), 129.7 (C2), 129.3 (C7'/C10a'), 128.9 (C3a), 128.6 (C9'), 128.2 (C8'), 126.0 (C10b'), 122.8 (C6), 122.6 (C10'), 121.3 (C4), 120.7 (C5), 120.1 (C5'), 110.7 (C7), 104.1 (C3); ESI-MS:  $m/z$  calcd. for  $\text{C}_{21}\text{H}_{15}\text{N}_2$  295.1230 found 295.1235 [ $\text{M}+\text{H}^+$ ].

#### 1-(Benzo[c]phenanthren-4-yl)-1H-indole (14i):



Prepared according to the general procedure **K** using 4-(2-vinylnaphthalen-1-yl)-1-(2-vinylphenyl)-1H-indole **13i** (26.0 mg, 70.0  $\mu\text{mol}$ ) to give the title compound as a white solid (23.5 mg, 68.4  $\mu\text{mol}$ , 98%, m.p. 166.2 – 167.0°C):  $R_f$  0.68 (cyclohexane/EtOAc 5:1);  $\nu_{\max}$  (neat): 3053w, 2927w, 2854w, 1735w, 1602m, 1566w, 1463s, 1328m, 1237m, 1142w, 1036w, 837s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 9.33 – 9.21 (1H, m, C1'H), 9.14 (1H, d,  $^3J$  8.4 Hz, C12'H), 8.06 (1H, dd,  $^3J$  8.0,  $^4J$  1.5 Hz, C9'H), 7.95 (1H, d,  $^3J$  8.5 Hz, C8'H), 7.84 – 7.62 (7H, m, C2'H, C3'H, C7'H, C10'H, C11'H, C4H, C6'H), 7.46 (1H, d,  $^3J$  8.8, C5'H), 7.44 (1H, d,  $^3J$  3.2 Hz, C2H), 7.20 (1H, ddd,  $^3J$  8.0,  $^3J$  6.9,  $^4J$  1.2 Hz, C5H), 7.15 (1H, ddd,  $^3J$  8.0,  $^3J$  6.9,  $^4J$  1.2 Hz,

C6H), 7.12 – 7.06 (1H, m, C7H), 6.83 (1H, dd,  $^3J$  3.2,  $^5J$  0.8 Hz, C3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 138.2 (C7a), 136.5 (C4'), 133.8 (C12'b), 131.8 (C12c'), 131.3 (C6a'), 130.8 (C4a'), 130.3 (C12a'), 130.2 (C2), 128.8 (C9'), 128.7 (C3a), 128.5 (C1'), 128.3 (C8'), 128.2 (C12'/C6'), 127.6 (C8a'), 126.8 (C4), 126.6 (C11'), 126.3 (C10'), 125.8 (C2'), 125.0 (C3'), 122.5 (C6), 122.4 (C5'), 121.1 (C7'), 120.4 (C5), 111.1 (C7), 103.3 (C3); ESI-MS:  $m/z$  calcd. for  $\text{C}_{26}\text{H}_{18}\text{N}$  344.1434 found 344.1427  $[\text{M}+\text{H}^+]$ .

## Atroposelective Aromatic Ring-Opening Metathesis – RCM Cascade

**Optimization Studies (15.0  $\mu\text{mol}$  scale) of **15a**:** Performed according to the general procedure **H** utilizing 5,7-dimethoxy-4-methyl-1-(2-vinylphenyl)phenanthrene **15a** (5.32 mg, 15.0  $\mu\text{mol}$ ) and the corresponding solvent (0.50 mL, 0.03  $\text{mol}\cdot\text{L}^{-1}$ ) with the reaction time of 18 h.

**Supplementary Table 11.** Reaction conditions optimization for atroposelective aromatic ring-opening metathesis – RCM cascade

**15a**

formed in situ

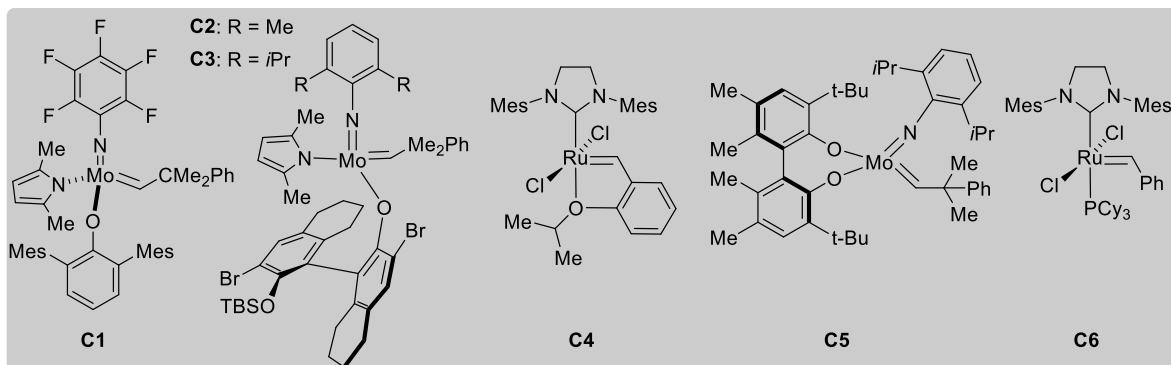
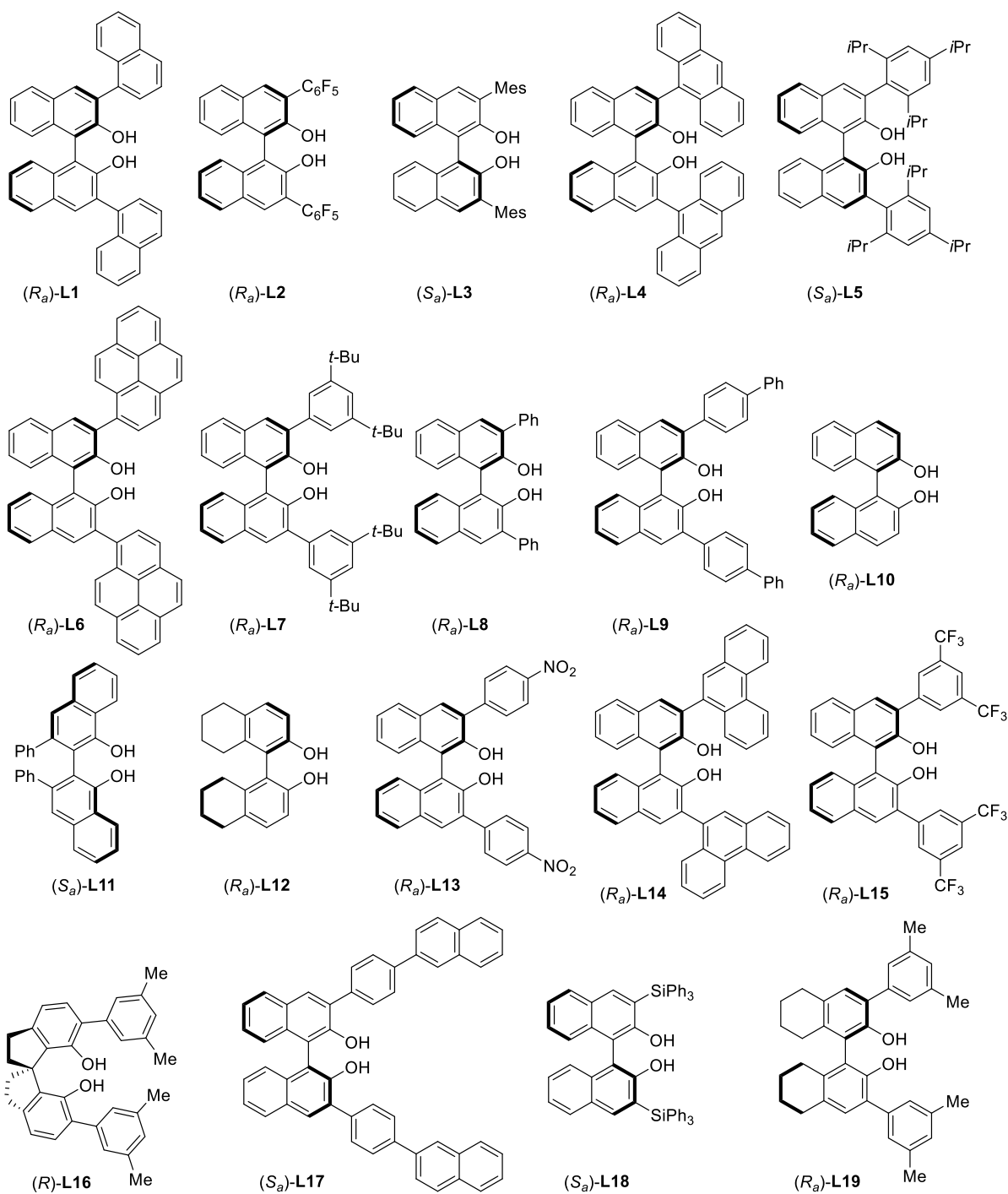
**(*S<sub>a</sub>*) or (*R<sub>a</sub>*)-16a**

**Mo-Precatalyst**

**Mo-Precatalyst 2**

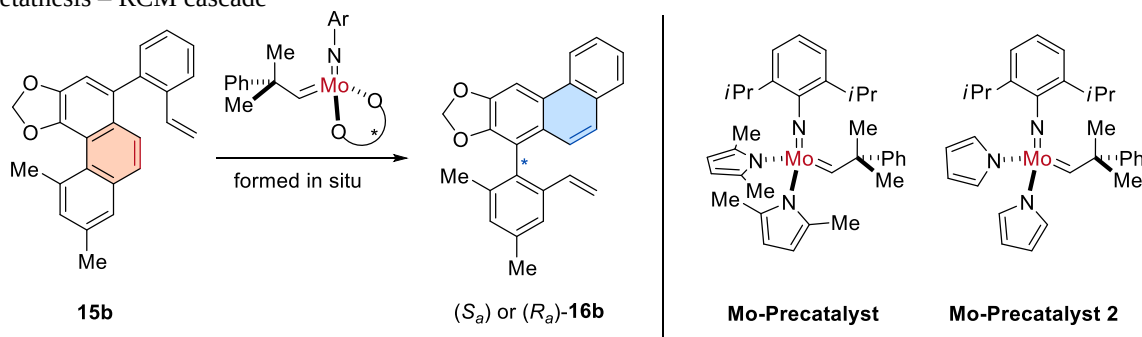
| Entry <sup>a</sup> | Catalyst (mol%)          | Ligand (mol%)                            | Solvent                                        | Temp. [°C] | Conversion <sup>b</sup> [%] | Yield <sup>b</sup> [%] | e. r. <sup>c</sup> |
|--------------------|--------------------------|------------------------------------------|------------------------------------------------|------------|-----------------------------|------------------------|--------------------|
| 1                  | <b>C1</b> (10)           | –                                        | Toluene                                        | 65         | >95                         | –                      | 50 : 50            |
| 2                  | <b>Mo-Precat.</b> (20)   | ( <i>R<sub>a</sub></i> )- <b>L4</b> (60) | Toluene                                        | 65         | >95                         | 48                     | 14 : 86            |
| 3                  | <b>Mo-Precat.</b> (10)   | ( <i>R<sub>a</sub></i> )- <b>L4</b> (30) | Toluene                                        | 50         | NR                          | 0                      | –                  |
| 4                  | <b>Mo-Precat.</b> (20)   | ( <i>R<sub>a</sub></i> )- <b>L4</b> (60) | Toluene                                        | 50         | >95                         | 75                     | 13 : 87            |
| 5                  | <b>Mo-Precat.</b> (30)   | ( <i>R<sub>a</sub></i> )- <b>L4</b> (90) | Toluene                                        | 50         | >95                         | 60                     | 15 : 85            |
| 6                  | <b>Mo-Precat.</b> (10)   | ( <i>S<sub>a</sub></i> )- <b>L3</b> (30) | Toluene                                        | 65         | NR                          | –                      | –                  |
| 7                  | <b>Mo-Precat. 2</b> (10) | ( <i>S<sub>a</sub></i> )- <b>L3</b> (30) | Toluene                                        | 65         | NR                          | –                      | –                  |
| 8                  | <b>Mo-Precat.</b> (20)   | ( <i>S<sub>a</sub></i> )- <b>L3</b> (60) | Toluene                                        | 65         | 75                          | 57                     | 97 : 3             |
| 9                  | <b>Mo-Precat. 2</b> (20) | ( <i>S<sub>a</sub></i> )- <b>L3</b> (60) | Toluene                                        | 65         | NR                          | –                      | –                  |
| 10                 | <b>Mo-Precat.</b> (20)   | ( <i>S<sub>a</sub></i> )- <b>L3</b> (60) | Toluene                                        | 50         | NR                          | –                      | –                  |
| 11                 | <b>Mo-Precat.</b> (30)   | ( <i>S<sub>a</sub></i> )- <b>L3</b> (90) | Toluene                                        | 65         | >95                         | 54                     | 95 : 5             |
| 12                 | <b>Mo-Precat.</b> (10)   | ( <i>S<sub>a</sub></i> )- <b>L5</b> (30) | Toluene                                        | 65         | NR                          | –                      | –                  |
| 13                 | <b>Mo-Precat.</b> (10)   | ( <i>R<sub>a</sub></i> )- <b>L6</b> (30) | Toluene                                        | 65         | >95                         | 51                     | 4 : 96             |
| 14                 | <b>Mo-Precat.</b> (10)   | ( <i>R<sub>a</sub></i> )- <b>L7</b> (30) | Toluene                                        | 65         | >95                         | 67                     | 19 : 81            |
| 15                 | <b>Mo-Precat.</b> (10)   | ( <i>R<sub>a</sub></i> )- <b>L8</b> (30) | Toluene                                        | 65         | >95                         | 61                     | 10 : 90            |
| 16                 | <b>Mo-Precat.</b> (10)   | ( <i>R<sub>a</sub></i> )- <b>L2</b> (30) | Toluene                                        | 65         | >95                         | 66                     | 33 : 67            |
| 17                 | <b>Mo-Precat.</b> (10)   | ( <i>R<sub>a</sub></i> )- <b>L9</b> (30) | Toluene                                        | 65         | >95                         | 68                     | 15 : 85            |
| 18                 | <b>Mo-Precat.</b> (10)   | ( <i>R<sub>a</sub></i> )- <b>L1</b> (30) | Toluene                                        | 65         | >95                         | 80                     | 6 : 94             |
| 19                 | <b>Mo-Precat.</b> (10)   | ( <i>S<sub>a</sub></i> )- <b>L1</b> (30) | Toluene                                        | 65         | >95                         | 76                     | 95 : 5             |
| 20                 | <b>Mo-Precat.</b> (10)   | ( <i>R<sub>a</sub></i> )- <b>L1</b> (30) | Toluene                                        | 50         | 16                          | 14                     | –                  |
| 21                 | <b>Mo-Precat.</b> (20)   | ( <i>R<sub>a</sub></i> )- <b>L1</b> (60) | Toluene                                        | 50         | >95                         | 88                     | 6 : 94             |
| 22                 | <b>Mo-Precat.</b> (10)   | ( <i>R<sub>a</sub></i> )- <b>L1</b> (30) | C <sub>6</sub> F <sub>6</sub>                  | 65         | 13                          | 4                      | –                  |
| 23                 | <b>Mo-Precat.</b> (10)   | ( <i>R<sub>a</sub></i> )- <b>L1</b> (30) | CF <sub>3</sub> -C <sub>6</sub> H <sub>5</sub> | 65         | NR                          | –                      | –                  |
| 24                 | <b>Mo-Precat.</b> (10)   | ( <i>R<sub>a</sub></i> )- <b>L1</b> (30) | DCE                                            | 65         | >95                         | 70                     | 2 : 98             |
| 25                 | <b>C5</b> (20)           | –                                        | Toluene                                        | 65         | 4                           | 3                      | –                  |

<sup>a</sup>Reactions were performed on 15.0  $\mu\text{mol}$  scale of **15a** for 18 h. <sup>b</sup>Conversion and yield were determined by <sup>1</sup>H-NMR with durene as an internal standard. <sup>c</sup>Determined by HPLC on a chiral stationary phase of the crude product (Chiralpak IC-N3 column (3  $\mu\text{m}$ , 250x4.6 mm, heptane/*i*PrOH 97.5:2.5, 1.0 mL/min, 20°C).



**Optimization Studies (15.0  $\mu\text{mol}$  scale) of 15b:** Performed according to the general procedure **H** utilizing 9,11-dimethyl-5-(2-vinylphenyl)phenanthro[3,4-d][1,3]dioxole **15b** (5.29 mg, 15.0  $\mu\text{mol}$ ) with the reaction time of 18 h.

**Supplementary Table 12.** Reaction conditions optimization for atroposelective aromatic ring-opening metathesis – RCM cascade



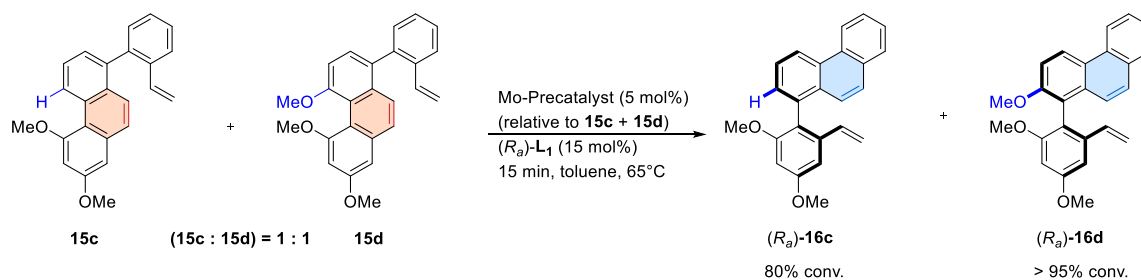
| Entry <sup>a</sup> | Catalyst (mol%)        | Ligand (mol%)                      | Conc. mol·L <sup>-1</sup> | Solvent                                         | Temp. [°C] | Conversion <sup>b</sup> [%] | Yield <sup>b</sup> [%] | e. r. <sup>c</sup> |
|--------------------|------------------------|------------------------------------|---------------------------|-------------------------------------------------|------------|-----------------------------|------------------------|--------------------|
| 1                  | <b>C6</b> (10)         | —                                  | 0.03                      | Toluene                                         | Rt         | 9                           | —                      | 50 : 50            |
| 2                  | <b>C6</b> (10)         | —                                  | 0.03                      | Toluene                                         | 65         | 35                          | —                      | 50 : 50            |
| 3                  | <b>C4</b> (10)         | —                                  | 0.03                      | Toluene                                         | Rt         | 5                           | —                      | 50 : 50            |
| 4                  | <b>C4</b> (10)         | —                                  | 0.03                      | Toluene                                         | 65         | 56                          | —                      | 50 : 50            |
| 5                  | <b>C4</b> (10)         | —                                  | 0.03                      | Toluene                                         | 80         | 92                          | 50                     | 50 : 50            |
| 6                  | <b>C1</b> (10)         | —                                  | 0.03                      | Toluene                                         | 40         | >95                         | 84                     | 50 : 50            |
| 7                  | <b>C1</b> (10)         | —                                  | 0.03                      | Toluene                                         | 65         | >95                         | 84                     | 50 : 50            |
| 8                  | <b>C5</b> (10)         | —                                  | 0.03                      | Toluene                                         | 40         | NR                          | —                      | —                  |
| 9                  | <b>C5</b> (10)         | —                                  | 0.03                      | Toluene                                         | 65         | 5                           | 4                      | 51 : 49            |
| 10                 | <b>C5</b> (30)         | —                                  | 0.03                      | Toluene                                         | 65         | 31                          | 17                     | 51 : 49            |
| 11                 | <b>C5</b> (30)         | —                                  | 0.03                      | Toluene                                         | 80         | 47                          | 22                     | 52 : 48            |
| 12                 | <b>C2</b> (10)         | —                                  | 0.03                      | Toluene                                         | 65         | >95                         | 67                     | 41 : 59            |
| 13                 | <b>Mo-Precat.</b> (10) | (R <sub>a</sub> )- <b>L10</b> (10) | 0.03                      | Toluene                                         | 65         | NR                          | —                      | —                  |
| 14                 | <b>Mo-Precat.</b> (10) | (S <sub>a</sub> )- <b>L11</b> (10) | 0.03                      | Toluene                                         | 65         | NR                          | —                      | —                  |
| 15                 | <b>Mo-Precat.</b> (10) | (S <sub>a</sub> )- <b>L12</b> (10) | 0.03                      | Toluene                                         | 65         | NR                          | —                      | —                  |
| 16                 | <b>Mo-Precat.</b> (10) | (R <sub>a</sub> )- <b>L10</b> (10) | 0.03                      | Toluene                                         | 65         | >95                         | 86                     | 41 : 59            |
| 17                 | <b>Mo-Precat.</b> (10) | (R <sub>a</sub> )- <b>L10</b> (30) | 0.03                      | Toluene                                         | 65         | >95                         | 89                     | 44 : 56            |
| 18                 | <b>Mo-Precat.</b> (10) | (R <sub>a</sub> )- <b>L10</b> (30) | 0.03                      | Toluene                                         | 40         | >95                         | 88                     | 40 : 60            |
| 19                 | <b>Mo-Precat.</b> (10) | (R <sub>a</sub> )- <b>L4</b> (30)  | 0.03                      | Toluene                                         | 65         | >95                         | 89                     | 22 : 78            |
| 20                 | <b>Mo-Precat.</b> (10) | (R <sub>a</sub> )- <b>L4</b> (30)  | 0.03                      | Toluene                                         | 40         | 91                          | 88                     | 30 : 70            |
| 21                 | <b>Mo-Precat.</b> (10) | (R <sub>a</sub> )- <b>L4</b> (30)  | 0.03                      | Toluene                                         | Rt         | 47                          | 45                     | 20 : 80            |
| 22                 | <b>Mo-Precat.</b> (10) | (R <sub>a</sub> )- <b>L13</b> (30) | 0.03                      | Toluene                                         | 65         | 0                           | —                      | —                  |
| 23                 | <b>Mo-Precat.</b> (10) | (S <sub>a</sub> )- <b>L3</b> (30)  | 0.03                      | Toluene                                         | 65         | 25                          | 24                     | 87 : 13            |
| 24                 | <b>Mo-Precat.</b> (10) | (S <sub>a</sub> )- <b>L3</b> (30)  | 0.03                      | Toluene                                         | 80         | 18                          | 18                     | 87 : 13            |
| 25                 | <b>Mo-Precat.</b> (20) | (S <sub>a</sub> )- <b>L3</b> (60)  | 0.03                      | Toluene                                         | 65         | >95                         | 74                     | 87 : 13            |
| 26                 | <b>Mo-Precat.</b> (20) | (S <sub>a</sub> )- <b>L3</b> (60)  | <b>0.06</b>               | Toluene                                         | 65         | >95                         | 67                     | 87 : 13            |
| 27                 | <b>Mo-Precat.</b> (20) | (S <sub>a</sub> )- <b>L3</b> (60)  | <b>0.015</b>              | Toluene                                         | 65         | >95                         | 64                     | 84 : 16            |
| 28                 | <b>Mo-Precat.</b> (20) | (S <sub>a</sub> )- <b>L3</b> (60)  | 0.03                      | Toluene:CH <sub>2</sub> Cl <sub>2</sub> (3 : 2) | 50         | >95                         | 85                     | 84 : 16            |
| 29 <sup>d</sup>    | <b>Mo-Precat.</b> (20) | (S <sub>a</sub> )- <b>L3</b> (60)  | 0.03                      | Toluene                                         | 50         | >95                         | 77                     | 86 : 14            |
|                    | <b>Mo-Precat.</b> (10) | (S <sub>a</sub> )- <b>L3</b> (30)  | 0.03                      | Toluene                                         | 50         | 8                           | 7                      | 90 : 10            |
|                    | <b>Mo-Precat.</b> (30) | (S <sub>a</sub> )- <b>L3</b> (90)  | 0.03                      | Toluene                                         | 50         | >95                         | 76                     | 87 : 13            |
|                    | <b>Mo-Precat.</b> (20) | (S <sub>a</sub> )- <b>L3</b> (60)  | 0.03                      | Toluene                                         | 40         | 5                           | 5                      | 84 : 16            |

| Entry | Catalyst (mol%)        | Ligand (mol%)                      | Concen. mol·L <sup>-1</sup> | Solvent                         | Temp. [°C] | Conversion [%] | Yield [%] | e. r.   |
|-------|------------------------|------------------------------------|-----------------------------|---------------------------------|------------|----------------|-----------|---------|
| 33    | <b>Mo-Precat.</b> (20) | (S <sub>a</sub> )- <b>L3</b> (60)  | 0.03                        | CH <sub>2</sub> Cl <sub>2</sub> | 40         | 58             | 57        | 80 : 20 |
| 34    | <b>Mo-Precat.</b> (10) | (R <sub>a</sub> )- <b>L1</b> (30)  | 0.03                        | Toluene                         | 65         | 83             | 77        | 29 : 71 |
| 35    | <b>Mo-Precat.</b> (10) | (R <sub>a</sub> )- <b>L6</b> (30)  | 0.03                        | Toluene                         | 65         | >95            | 98        | 40 : 60 |
| 36    | <b>Mo-Precat.</b> (10) | (R <sub>a</sub> )- <b>L7</b> (30)  | 0.03                        | Toluene                         | 65         | >95            | 83        | 35 : 65 |
| 37    | <b>Mo-Precat.</b> (10) | (R <sub>a</sub> )- <b>L14</b> (30) | 0.03                        | Toluene                         | 65         | 0              | –         | –       |
| 38    | <b>Mo-Precat.</b> (10) | (R <sub>a</sub> )- <b>L15</b> (30) | 0.03                        | Toluene                         | 65         | >95            | 95        | 44 : 56 |
| 39    | <b>Mo-Precat.</b> (10) | (R <sub>a</sub> )- <b>L9</b> (30)  | 0.03                        | Toluene                         | 65         | >95            | 90        | 41 : 59 |
| 40    | <b>Mo-Precat.</b> (10) | (S <sub>a</sub> )- <b>L5</b> (30)  | 0.03                        | Toluene                         | 65         | NR             | –         | –       |
| 41    | <b>Mo-Precat.</b> (10) | (R)- <b>L16</b> (30)               | 0.03                        | Toluene                         | 65         | 5              | 5         | 58 : 42 |
| 42    | <b>Mo-Precat.</b> (10) | (S <sub>a</sub> )- <b>L17</b> (30) | 0.03                        | Toluene                         | 65         | >95            | 84        | 63 : 37 |
| 43    | <b>Mo-Precat.</b> (10) | (S <sub>a</sub> )- <b>L18</b> (30) | 0.03                        | Toluene                         | 65         | <5%            | –         | 56 : 44 |
| 44    | <b>Mo-Precat.</b> (10) | (R <sub>a</sub> )- <b>L19</b> (30) | 0.03                        | Toluene                         | 65         | NR             | –         | –       |
| 45    | <b>Mo-Precat.</b> (20) | (S <sub>a</sub> )- <b>L3</b> (60)  | 0.03                        | Benzene                         | 50         | >95            | 74        | 87 : 13 |
| 46    | <b>Mo-Precat.</b> (20) | (S <sub>a</sub> )- <b>L3</b> (60)  | 0.03                        | Benzene                         | 40         | >95            | 81        | 86 : 14 |
| 47    | <b>Mo-Precat.</b> (20) | (S <sub>a</sub> )- <b>L3</b> (60)  | 0.03                        | m-Xylene                        | 50         | >95            | 79        | 87 : 13 |
| 48    | <b>Mo-Precat.</b> (20) | (S <sub>a</sub> )- <b>L3</b> (60)  | 0.03                        | DCE                             | 50         | 25             | 24        | 69 : 31 |
| 49    | <b>Mo-Precat.</b> (20) | (S <sub>a</sub> )- <b>L3</b> (60)  | 0.03                        | CF <sub>3</sub> -toluene        | 50         | >95            | 81        | 86 : 14 |
| 50    | <b>Mo-Precat.</b> (20) | (S <sub>a</sub> )- <b>L3</b> (60)  | 0.03                        | C <sub>6</sub> F <sub>6</sub>   | 50         | 31             | 25        | 72 : 28 |
| 51    | <b>Mo-Precat.</b> (20) | (S <sub>a</sub> )- <b>L3</b> (60)  | 0.03                        | Mesitylene                      | 50         | >95            | 74        | 86 : 14 |
| 53    | <b>Mo-Precat.</b> (20) | (S <sub>a</sub> )- <b>L3</b> (60)  | 0.03                        | 1,2-Dichloro-<br>benzene        | 50         | >95            | –         | 85 : 15 |

<sup>a</sup>Reactions were performed on 15.0 μmol scale of **15b** for 18 h. <sup>b</sup>Conversion and yield were determined by <sup>1</sup>H-NMR with durenene as an internal standard. <sup>c</sup>Determined by HPLC on a chiral stationary phase of the crude product (Chiralpak IG-N3 column (3 μm, 250x4.6 mm, heptane/*i*PrOH 96:4, 1.0 mL/min, 20°C). <sup>d</sup>Mo-Precatalyst and the ligand were stirred at 55°C for 1 h before the substrate was added

### Competition experiment: Investigation of the effect of substituent's size on the reaction rate

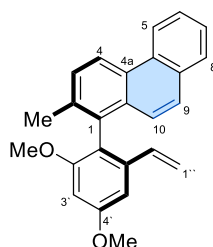
Control experiment was performed according to the general procedure **H** using **15c** (2.55 mg, 7.50 μmol), **15d** (2.78 mg, 7.50 μmol) in toluene (0.5 mL) at 65°C for 15 minutes. After the indicated time, <sup>1</sup>H-NMR analysis of the crude reaction mixture revealed that full conversion was achieved for the transformation of **15d** to **16d**, while 80% conversion was observed for the substrate **15c**.



## General procedure L for atroposelective aromatic ring-opening metathesis – RCM cascade:

Mo-precursor (2.07 mg, 3.50  $\mu\text{mol}$ , 5 mol%), (*R<sub>a</sub>*)-[1,2':4,1'':3'',1''':-quaternaphthalene]-2'',3'-diol (*R<sub>a</sub>*)-**L1** (5.66 mg, 10.5  $\mu\text{mol}$ , 15 mol%) were weighed in 10mL crimp cap vial and toluene (1.5 mL) was added. The obtained solution was stirred for 1 h at room temperature in an argon-filled glovebox before a solution of the corresponding substrate (70.0  $\mu\text{mol}$ , 1.00 eq.) in toluene (0.83 mL) was added. The capped vial was then taken out of the glovebox and stirred at 65°C for 18 h. The reaction mixture was diluted with EtOAc and filtered through a thin layer of silica gel. The solvents were removed under reduced pressure and the residue was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0→80:20) to give the desired product. The e.r. of the isolated products were determined by HPLC on a chiral stationary phase.

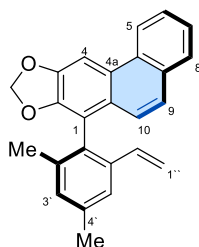
### (*R<sub>a</sub>*)-1-(2,4-Dimethoxy-6-vinylphenyl)-2-methylphenanthrene ((*R<sub>a</sub>*)-**16a**):



(*R<sub>a</sub>*)-**16a**

Prepared according to the general procedure **L** using 5,7-dimethoxy-4-methyl-1-(2-vinylphenyl)phenanthrene **15a** (24.8 mg, 70.0  $\mu\text{mol}$ ) to give the title compound (*R<sub>a</sub>*)-**16a** as a beige solid (20.6 mg, 58.1  $\mu\text{mol}$ , 83%, 2:98 e.r., m.p. 136.1 – 137.0°C): *R<sub>f</sub>* 0.36 (cyclohexane/EtOAc 5:1);  $[\alpha]_D^{20} = +29$ . (c 0.18,  $\text{CHCl}_3$ );  $\nu_{\text{max}}$  (neat): 3062w, 2921m, 2850w, 1729w, 1600s, 1594s, 1458s, 1422m, 1316s, 1276w, 1201s, 1156s, 1083m, 1033w, 915w, 816s, 754s;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.71 (1H, d,  $^3J$  8.2 Hz, C5H), 8.65 (1H, d,  $^3J$  8.5 Hz, C4H), 7.82 (1H, d,  $^3J$  6.7 Hz, C8H), 7.63 (1H, ddd,  $^3J$  8.3,  $^3J$  7.0,  $^4J$  1.4 Hz, C6H), 7.59 (1H, d,  $^3J$  8.5 Hz, C3H), 7.57 – 7.52 (2H, m, C7H, C9H), 7.24 (1H, d,  $^3J$  8.8 Hz, C10H), 6.91 (1H, d,  $^4J$  2.3 Hz, C5'H), 6.59 (1H, d,  $^4J$  2.3 Hz, C3'H), 6.06 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C2''H), 5.61 (1H, dd,  $^3J$  17.5,  $^2J$  1.2 Hz, C1''H), 4.93 (1H, dd,  $^3J$  11.0,  $^2J$  1.1 Hz, C1''H), 3.95 (3H, s, C4'-OCH<sub>3</sub>), 3.61 (3H, s, C2'-OCH<sub>3</sub>), 2.17 (3H, s, C2-CH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 160.4 (C4'), 158.6 (C2'), 138.6 (C6'), 136.1 (C2), 135.0 (C2''), 133.9 (C1), 131.7 (C10a), 131.6 (C8a), 130.7 (C4b), 128.8 (C3), 128.6 (C4a), 128.5 (C8), 126.9 (C9), 126.5 (C6), 126.2 (C7), 125.0 (C10), 122.7 (C5), 122.0 (C4), 120.5 (C1'), 115.1 (C1''), 100.8 (C5'), 98.7 (C3'), 56.0 (C2'-OCH<sub>3</sub>), 55.6 (C4'-OCH<sub>3</sub>), 20.5 (C2-CH<sub>3</sub>); ESI-MS: *m/z* calcd. for  $\text{C}_{25}\text{H}_{22}\text{AgO}_2$  461.0665 found 461.0658 [*M*+*Ag*<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IC 3  $\mu\text{m}$ , 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 97.5 : 2.5, 20°C): *t*<sub>major</sub> = 5.7 min and *t*<sub>minor</sub> = 5.1 min.

### (*S<sub>a</sub>*)-7-(2,4-Dimethyl-6-vinylphenyl)phenanthro[2,3-d][1,3]dioxole ((*S<sub>a</sub>*)-**16b**):



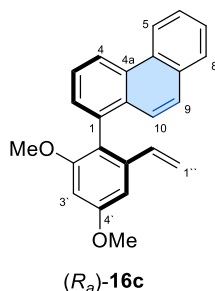
(*S<sub>a</sub>*)-**16b**

Prepared according to the modified general procedure **L** using 9,11-dimethyl-5-(2-vinylphenyl)phenanthro[3,4-d][1,3]dioxole **15b** (24.7 mg, 70.0  $\mu\text{mol}$ ), Mo-precursor (4.14 mg, 7.00  $\mu\text{mol}$ , 10 mol%), (*S<sub>a</sub>*)-[3-(2,4-dimethylphenyl)-3'-mesityl-[1,1'-binaphthalene]-2,2'-diol ((*S<sub>a</sub>*)-**L3**) (11.0 mg, 21.0  $\mu\text{mol}$ , 30 mol%) to give the title compound (*S<sub>a</sub>*)-**16b** as a white solid (20.4 mg, 57.9  $\mu\text{mol}$ , 83%, 86:14 e.r., m.p. 146.6 – 147.0°C): *R<sub>f</sub>* 0.78 (cyclohexane/EtOAc 8:1);  $[\alpha]_D^{20} = -10$  (c 0.56,  $\text{CHCl}_3$ );  $\nu_{\text{max}}$  (neat): 3043w, 2985w, 2956w, 2917w, 2855w, 1607w, 1563w, 1452s, 1391m, 1265m, 1233s, 1161w, 1104m, 1042s,



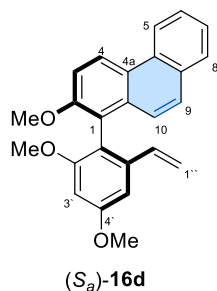
941m, 908m, 857m, 816s, 748s, 667w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.54 (1H, d,  $^3J$  8.3 Hz, C5H), 8.11 (1H, s, C4H), 7.87 – 7.78 (1H, m, C8H), 7.62 (1H, ddd,  $^3J$  8.3,  $^3J$  7.0,  $^4J$  1.4 Hz, C6H), 7.56 – 7.50 (2H, m, C7H, C9H), 7.44 (1H, s, C5'H), 7.19 (1H, d,  $^3J$  9.0 Hz, C10H), 7.14 (1H, s, C3'H), 6.27 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C2''H), 6.11 – 5.95 (2H, m,  $\text{OCH}_2\text{O}$ ), 5.64 (1H, dd,  $J$   $^3J$  17.5,  $^2J$  1.2 Hz, C1''H), 4.96 (1H, dd,  $^3J$  11.0,  $^2J$  1.2 Hz, C1''H), 2.44 (3H, s, C4'–CH<sub>3</sub>), 1.98 (3H, s, C2'–CH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 147.6 (C2/C3), 145.2 (C2/C3), 138.2 (C4'), 137.8 (C2'), 137.3 (C6'), 135.3 (C2''), 131.5 (C8a), 130.7 (C3'), 130.4 (C4b), 129.5 (C1'), 128.7 (C8), 127.6 (C10a), 126.9 (C4a), 126.4 (C6), 125.9 (C7), 125.5 (C9), 123.8 (C10), 123.5 (C5'), 122.7 (C5), 116.7 (C1), 114.9 (C1''), 101.5 ( $\text{OCH}_2\text{O}$ ), 100.4 (C4), 21.5 (C2'–CH<sub>3</sub>), 20.2 (C4'–CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for  $\text{C}_{25}\text{H}_{20}\text{AgO}_2$  459.0509 found 459.0503 [ $\text{M}+\text{Ag}^+$ ]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu\text{m}$ , 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 96 : 4, 20°C):  $t_{\text{major}}$  = 8.1 min and  $t_{\text{minor}}$  = 9.1 min.

**(*R*<sub>a</sub>)-1-(2,4-Dimethoxy-6-vinylphenyl)phenanthrene ((*R*<sub>a</sub>)-16c):**



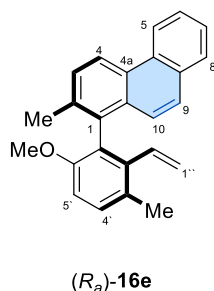
Prepared according to the general procedure **L** using 5,7-dimethoxy-1-(2-vinylphenyl)phenanthrene **15c** (23.8 mg, 70.0  $\mu\text{mol}$ ) to give the title compound (*R*<sub>a</sub>)-**16c** as a beige oil (19.0 mg, 55.8  $\mu\text{mol}$ , 80%, 30:70 e.r.):  $R_f$  0.41 (cyclohexane/EtOAc 5:1);  $[\alpha]_D^{20}$  = +7.0 (c 0.18,  $\text{CHCl}_3$ );  $\nu_{\text{max}}$  (neat): 3054w, 2999w, 2959w, 2874w, 2834w, 1600s, 1454m, 1420m, 1318s, 1277w, 1201s, 1156s, 1088w, 1033w, 990w, 914w, 832w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.81 – 8.63 (2H, m, C4H, C5H), 7.88 – 7.82 (1H, m, C8H), 7.70 (1H, dd,  $^3J$  8.3,  $^3J$  7.2 Hz, C3H), 7.66 (1H, ddd,  $^3J$  8.4,  $^3J$  7.0,  $^4J$  1.4 Hz, C6H), 7.62 – 7.55 (2H, m, C7H, C9H), 7.41 (1H, dd,  $^3J$  7.2,  $^4J$  1.0 Hz, C2H), 7.36 (1H, d,  $^3J$  9.1 Hz, C10H), 6.90 (1H, d,  $^4J$  2.3 Hz, C5'H), 6.58 (1H, d,  $^4J$  2.3 Hz, C3'H), 6.20 (1H, dd,  $^3J$  17.5,  $^3J$  11.0 Hz, C2''H), 5.63 (1H, dd,  $^3J$  17.5,  $^2J$  1.1 Hz, C1''H), 4.97 (1H, dd,  $^3J$  11.0,  $^2J$  1.1 Hz, C1''H), 3.95 (3H, s, C4'– $\text{OCH}_3$ ), 3.62 (3H, s, C2'– $\text{OCH}_3$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 160.4 (C4'), 158.9 (C2'), 138.9 (C6'), 135.4 (C1), 135.4 (C2''), 132.0 (C8a), 131.6 (C10a), 130.7 (C4b), 130.5 (C4a), 129.6 (C2), 128.6 (C8), 126.9 (C9), 126.62 (C6/C7), 126.61 (C6/C7), 126.1 (C3), 125.0 (C10), 123.0 (C5), 122.2 (C4), 121.7 (C1'), 115.0 (C1''), 100.8 (C5'), 98.5 (C3'), 56.0 (C2'– $\text{OCH}_3$ ), 55.6 (C4'– $\text{OCH}_3$ ); ESI-MS:  $m/z$  calcd. for  $\text{C}_{24}\text{H}_{20}\text{AgO}$  447.0509 found 447.0506 [ $\text{M}+\text{Ag}^+$ ]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IB 3  $\mu\text{m}$ , 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 97.5 : 2.5, 20°C):  $t_{\text{major}}$  = 7.1 min and  $t_{\text{minor}}$  = 6.6 min.

**(*S<sub>a</sub>*)-1-(2,4-Dimethoxy-6-vinylphenyl)-2-methoxyphenanthrene ((*S<sub>a</sub>*)-16d):**



Prepared according to the modified general procedure **L** using 4,5,7-trimethoxy-1-(2-vinylphenyl)phenanthrene **15d** (25.9 mg, 70.0  $\mu$ mol), Mo-precursor (4.14 mg, 7.00  $\mu$ mol, 10 mol%), and (*R<sub>a</sub>*)-[1,2':4',1'':3'',1'''-quaternaphthalene]-2'',3'-diol (11.3 mg, 21.0  $\mu$ mol, 30 mol%) to give the title compound (*R<sub>a</sub>*)-**16d** as a white solid (25.4 mg, 68.6  $\mu$ mol, 98%, 94:6 e.r., m.p. 157.0 – 158.0°C): *R<sub>f</sub>* 0.33 (cyclohexane/EtOAc 5:1);  $[\alpha]_D^{20} = -5.1$  (c 0.44, CHCl<sub>3</sub>);  $\nu_{\max}$  (neat): 3058w, 3005w, 2934w, 2836w, 1732w, 1599s, 1571s, 1528w, 1460s, 1418m, 1316s, 1274s, 1200s, 1155s, 1068s, 1032m, 911w, 815m, 752m, 632s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.74 (d, <sup>3</sup>*J* 9.1 Hz, C4*H*), 8.66 (1H, d, <sup>3</sup>*J* 8.3 Hz, C5*H*), 7.80 (1H, d, <sup>3</sup>*J* 7.9 Hz, C8*H*), 7.62 (1H, ddd, <sup>3</sup>*J* 8.3, <sup>3</sup>*J* 7.1, <sup>4</sup>*J* 1.3 Hz, C6*H*), 7.56 (1H, d, <sup>3</sup>*J* 9.1 Hz, C9*H*), 7.52 (1H, td, <sup>3</sup>*J* 7.5, <sup>4</sup>*J* 1.0 Hz, C7*H*), 7.45 (1H, d, <sup>3</sup>*J* 9.1 Hz, C3*H*), 7.21 (1H, d, <sup>3</sup>*J* 9.1 Hz, C10*H*), 6.92 (1H, d, <sup>4</sup>*J* 2.3 Hz, C5''*H*), 6.60 (1H, d, <sup>4</sup>*J* 2.3 Hz, C3''*H*), 6.18 (1H, dd, <sup>3</sup>*J* 17.5, <sup>3</sup>*J* 11.0 Hz, C2''*H*), 5.63 (1H, dd, <sup>3</sup>*J* 17.5, <sup>2</sup>*J* 1.1 Hz, C1''*H*), 4.95 (1H, dd, <sup>3</sup>*J* 11.0, <sup>2</sup>*J* 1.1 Hz, C1''*H*), 3.94 (3H, s, C4'-OCH<sub>3</sub>), 3.86 (3H, s, C2-OCH<sub>3</sub>), 3.62 (3H, s, 3H, s, C2'-OCH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 160.4 (C4'), 159.0 (C2'), 156.0 (C2), 139.0 (C6'), 135.3 (C2''), 133.0 (C4*b*), 131.0 (C8*a*), 130.8 (C10*a*), 128.6 (C8), 127.5 (C9), 126.7 (C6), 125.8 (C7), 124.9 (C4*a*), 124.6 (C10), 123.8 (C4), 122.4 (C5), 121.4 (C1), 117.6 (C1'), 114.8 (C1''), 112.6 (C3), 100.9 (C5'), 98.8 (C3'), 56.8 (C2-OCH<sub>3</sub>), 56.1 (C2'-OCH<sub>3</sub>), 55.5 (C4'-OCH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>25</sub>H<sub>22</sub>AgO<sub>3</sub> 477.0614 found 447.0620 [M+Ag<sup>+</sup>]. The e.r. of the isolateGd product was determined by HPLC on a chiral stationary phase (Chiralcel I 3  $\mu$ m, 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 90 : 10, 20°C): *t*<sub>major</sub> = 7.0 min and *t*<sub>minor</sub> = 7.7 min.

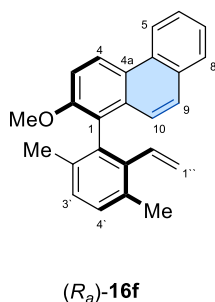
**(*R<sub>a</sub>*)-1-(6-Methoxy-3-methyl-2-vinylphenyl)-2-methylphenanthrene ((*R<sub>a</sub>*)-16e):**



Prepared according to the general procedure **L** using 4-methoxy-1,5-dimethyl-8-(2-vinylphenyl)phenanthrene **15e** (23.7 mg, 70.0  $\mu$ mol) to give the title compound (*R<sub>a</sub>*)-**16e** as a yellow oil (20.6 mg, 60.9  $\mu$ mol, 87%, >99:1 e.r.): *R<sub>f</sub>* 0.85 (cyclohexane/EtOAc 5:1);  $[\alpha]_D^{20} = +55$  (c 0.15, CHCl<sub>3</sub>);  $\nu_{\max}$  (neat): 3008w, 2925w, 2855w, 1579m, 1463s, 1378w, 1257s, 1088m, 1056m, 922w, 867w, 813s, 750s, 683w, 637w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.70 (1H, d, <sup>3</sup>*J* 8.3 Hz, C5*H*), 8.62 (1H, d, <sup>3</sup>*J* 8.5 Hz, C4*H*), 7.82 (1H, dd, <sup>3</sup>*J* 7.9, <sup>4</sup>*J* 1.3 Hz, C8*H*), 7.63 (1H, ddd, <sup>3</sup>*J* 8.5, <sup>3</sup>*J* 7.0, <sup>4</sup>*J* 1.4 Hz, C6*H*), 7.59 – 7.50 (3H, m, C3*H*, C7*H*, C9*H*), 7.29 (1H, d, <sup>3</sup>*J* 8.5 Hz, C4''*H*), 7.26 – 7.22 (1H, m, C10*H*), 6.90 (1H, d, <sup>3</sup>*J* 8.5 Hz, C5''*H*), 6.18 (1H, dd, <sup>3</sup>*J* 17.9, <sup>3</sup>*J* 11.7 Hz, C2''*H*), 5.01 – 4.82 (2H, m, C1''*H*), 3.60 (3H, s, OCH<sub>3</sub>), 2.40 (3H, s, C3'-CH<sub>3</sub>), 2.16 (3H, s, C2-CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 155.5 (C6'), 138.5 (C2'), 135.3 (C3), 135.1 (C2), 134.3 (C2''), 131.6 (C8*a*), 131.2 (C10*a*), 130.8 (C4*b*), 130.6 (C4'), 128.8 (C3), 128.5 (C8), 128.4 (C3'), 128.3 (C4*a*), 127.5 (C1'), 126.7 (C9), 126.5 (C6), 126.1 (C7), 125.0 (C10), 122.8 (C5), 121.8 (C4), 119.0 (C1''), 110 (C5'), 56.1 (OCH<sub>3</sub>), 20.8 (C3'-CH<sub>3</sub>), 20.5 (C2-CH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>25</sub>H<sub>23</sub>O 339.1743 found 339.1742 [M+H<sup>+</sup>]. The e.r. of the isolated

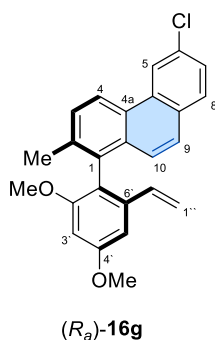
product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu$ m, 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 97.5 : 2.5, 20°C):  $t_{\text{major}} = 4.4$  min and  $t_{\text{minor}} = 4.7$  min.

**(*R<sub>a</sub>*)-1-(3,6-Dimethyl-2-vinylphenyl)-2-methoxyphenanthrene ((*R<sub>a</sub>*)-16f):**



Prepared according to the general procedure **L** using 4-methoxy-5,8-dimethyl-1-(2-vinylphenyl)phenanthrene **15f** (23.7 mg, 70.0  $\mu$ mol) to give the title compound (*R<sub>a</sub>*)-**16f** as a beige solid (5.30 mg, 15.7  $\mu$ mol, 22%, >99:1 e.r., m.p. 127.5 – 129.0°C):  $R_f$  0.44 (cyclohexane/EtOAc 5:1);  $[\alpha]_D^{20} = +25$  (c 0.55, CHCl<sub>3</sub>);  $\nu_{\text{max}}$  (neat): 3060w, 3003w, 2959w, 2916w, 2837w, 1731w, 1592w, 1527w, 1461m, 1257m, 1169w, 1082m, 921w, 795s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.72 (1H, d, <sup>3</sup>*J* 9.0 Hz, C4H), 8.66 (1H, d, <sup>3</sup>*J* 7.9 Hz, C5H), 7.81 (1H, dd, <sup>3</sup>*J* 7.9, <sup>4</sup>*J* 1.3 Hz, C8H), 7.63 (1H, ddd, <sup>3</sup>*J* 7.9, <sup>3</sup>*J* 7.0, <sup>4</sup>*J* 1.4 Hz, C6H), 7.58 – 7.49 (2H, m, C7H, C10H), 7.42 (1H, d, <sup>3</sup>*J* 9.0 Hz, C3H), 7.22 (1H, d, <sup>3</sup>*J* 7.7 Hz, C4'H), 7.18 (1H, d, <sup>3</sup>*J* 7.8 Hz, C3'H), 7.10 (1H, d, <sup>3</sup>*J* 9.1 Hz, C9H), 6.32 – 6.23 (1H, m, C2''H), 4.95 – 4.87 (2H, m, C1''H), 3.88 (3H, s, OCH<sub>3</sub>), 2.41 (3H, s, C5'-CH<sub>3</sub>), 1.85 (3H, s, C2'-CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 154.9 (C2), 138.2 (C6'), 135.2 (C1'/C2''), 135.1 (C2'), 133.2 (C5'), 131.8 (C10a), 131.0 (C8a), 130.8 (C4b), 129.8 (C4'), 128.6 (C8), 128.5 (C3'), 127.7 (C10), 126.8 (C6), 125.8 (C7), 125.6 (C1), 124.8 (C4a), 124.2 (C9), 123.4 (C4), 122.4 (C5), 118.4 (C1''), 112.0 (C3), 56.3 (OCH<sub>3</sub>), 21.1 (C5'-CH<sub>3</sub>), 20.1 (C2'-CH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>25</sub>H<sub>22</sub>AgO 445.0716 found 445.0713 [M+Ag<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu$ m, 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 99 : 1, 20°C):  $t_{\text{major}} = 5.1$  min and  $t_{\text{minor}} = 5.4$  min.

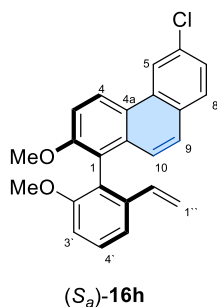
**(*R<sub>a</sub>*)-6-Chloro-1-(2,4-dimethoxy-6-vinylphenyl)-2-methylphenanthrene ((*R<sub>a</sub>*)-16g):**



Prepared according to the general procedure **L** using 1-(5-chloro-2-vinylphenyl)-5,7-dimethoxy-4-methylphenanthrene **15g** (27.2 mg, 70.0  $\mu$ mol) to give the title compound (*R<sub>a</sub>*)-**16g** as a transparent oil (17.6 mg, 45.3  $\mu$ mol, 65%, 95:5 e.r.):  $R_f$  0.40 (cyclohexane/EtOAc 5:1);  $[\alpha]_D^{20} = +10$  (c 0.14, CHCl<sub>3</sub>);  $\nu_{\text{max}}$  (neat): 2995w, 2936w, 2834w, 1600m, 1570m, 1454m, 1421w, 1316w, 1278w, 1201m, 1156s, 1082w, 1011w, 910w, 836w, 732w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.66 (1H, d, <sup>3</sup>*J* 1.9 Hz, C5H), 8.55 (1H, d, <sup>3</sup>*J* 8.5 Hz, C4H), 7.75 (1H, d, <sup>3</sup>*J* 8.5 Hz, C8H), 7.60 (1H, d, <sup>3</sup>*J* 8.5 Hz, C3H), 7.54 – 7.46 (2H, m, C7H, C9H), 7.25 (1H, d, <sup>3</sup>*J* 9.2 Hz, C10H), 6.90 (1H, d, <sup>3</sup>*J* 2.3 Hz, C5'H), 6.59 (1H, d, <sup>3</sup>*J* 2.3 Hz, C3'H), 6.04 (1H, dd, <sup>3</sup>*J* 17.5, <sup>3</sup>*J* 11.0 Hz, C2''H), 5.62 (1H, dd, <sup>3</sup>*J* 17.5, <sup>2</sup>*J* 1.1 Hz, C1''H), 4.94 (1H, dd, <sup>3</sup>*J* 11.0, <sup>2</sup>*J* 1.1 Hz, C1'H), 3.95 (3H, s, C4'-OCH<sub>3</sub>), 3.62 (3H, s, C2'-OCH<sub>3</sub>), 2.17 (3H, s, C2-CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 160.5 (C4'), 158.5 (C2'), 138.6 (C6'), 136.9 (C2), 134.8 (C2''), 134.0 (C1), 132.5 (C8a), 132.0 (C10a/C6), 131.9 (C4b), 129.9 (C8), 129.1 (C3), 127.7 (C4a), 126.7 (C7), 126.2 (C9), 125.3 (C10), 122.5 (C5), 122.0 (C4), 120.2 (C1'), 115.2 (C1''), 100.9 (C5'), 98.6 (C3'), 56.0 (C2'-OCH<sub>3</sub>),

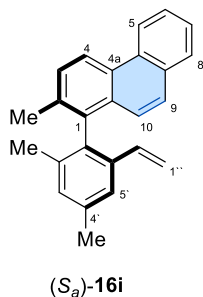
55.6 (C4'-OCH<sub>3</sub>), 20.5 (C2-CH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>25</sub>H<sub>21</sub>AgClO<sub>2</sub> 495.0276 found 495.0273 [M+Ag<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu$ m, 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 97.5 : 2.5, 20°C): *t*<sub>major</sub> = 5.7 min and *t*<sub>minor</sub> = 6.0 min.

**(S<sub>a</sub>)-6-Chloro-2-methoxy-1-(2-methoxy-6-vinylphenyl)phenanthrene ((S<sub>a</sub>)-16h):**



Prepared according to the general procedure **L** using 1-(5-chloro-2-vinylphenyl)-4,5-dimethoxyphenanthrene **15h** (26.2 mg, 70.0  $\mu$ mol) to give the title compound (S<sub>a</sub>)-**16h** as a beige solid (18.0 mg, 48.0  $\mu$ mol, 69%, 89:11 e.r., m.p. 182.3 – 183.3°C): *R*<sub>f</sub> 0.28 (cyclohexane/EtOAc 5:1);  $\nu_{\text{max}}$  (neat): 3062w, 2934w, 2837w, 1833w, 1736w, 1570m, 1515m, 1468s, 1400w, 1254s, 1198w, 1062s, 1010s, 911m, 871m, 838s, 775w, 743m; [ $\alpha$ ]<sub>D</sub><sup>21</sup> = -27 (c 0.16, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.65 (1H, d, <sup>3</sup>*J* 9.1 Hz, C4H), 8.61 (1H, d, <sup>4</sup>*J* 1.8 Hz, C5H), 7.72 (1H, d, <sup>3</sup>*J* 8.4 Hz, C8H), 7.50 (1H, d, <sup>3</sup>*J* 9.1 Hz, C9H), 7.48 – 7.45 (2H, m, C3H, C7H), 7.44 – 7.38 (2H, m, C4'H, C5'H), 7.15 (1H, d, <sup>3</sup>*J* 9.1 Hz, C10H), 6.99 (1H, dd, <sup>3</sup>*J* 7.9, <sup>4</sup>*J* 1.3 Hz, C3'H), 6.15 (1H, dd, <sup>3</sup>*J* 17.5, <sup>3</sup>*J* 11.0 Hz, C2''H), 5.63 (1H, dd, <sup>3</sup>*J* 17.5, <sup>2</sup>*J* 1.2 Hz, C1''H), 4.95 (1H, dd, <sup>3</sup>*J* 11.0, <sup>2</sup>*J* 1.2 Hz, C1'H), 3.86 (3H, s, C2-OCH<sub>3</sub>), 3.64 (3H, s, C2'-OCH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 158.0 (C2'), 156.2 (C2), 138.8 (C6'), 135.0 (C2''), 132.8 (C4b), 132.7 (C6), 132.0 (C10a), 129.9 (C8), 129.3 (C8a), 128.9 (C4'), 126.9 (C9), 126.3 (C7), 124.8 (C10), 124.4 (C1'), 123.98 (C4), 123.91 (C4a), 122.1 (C5), 121.7 (C1), 117.5 (C5'), 115.0 (C1''), 112.8 (C3), 110.4 (C3'), 56.7 (C2-OCH<sub>3</sub>), 56.1 (C2'-OCH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>24</sub>H<sub>20</sub>ClO<sub>2</sub> 375.1146 found 375.1151 [M+H<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu$ m, 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 90 : 10, 20°C): *t*<sub>major</sub> = 5.4 min and *t*<sub>minor</sub> = 6.5 min.

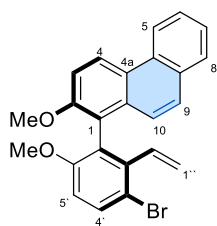
**(S<sub>a</sub>)-1-(2,4-Dimethyl-6-vinylphenyl)-2-methylphenanthrene ((S<sub>a</sub>)-16i):**



Prepared according to the general procedure **L** using 4,5,7-trimethyl-1-(2-vinylphenyl)phenanthrene **15i** (22.6 mg, 70.0  $\mu$ mol) to give the title compound (S<sub>a</sub>)-**16i** as a transparent oil (21.0 mg, 65.1  $\mu$ mol, 93%, 11:89 e.r.): *R*<sub>f</sub> 0.67 (cyclohexane/EtOAc 5:1); [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +45 (c 0.10, CHCl<sub>3</sub>);  $\nu_{\text{max}}$  (neat): 3042w, 2949w, 2917m, 2857w, 1606w, 1559w, 1459m, 1378w, 1304w, 1261w, 1220w, 1035w, 990w, 910w, 856w, 816s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.73 (1H, d, <sup>3</sup>*J* 8.2 Hz, C5H), 8.66 (1H, d, <sup>3</sup>*J* 8.5 Hz, C4H), 7.83 (1H, dd, <sup>3</sup>*J* 7.9, <sup>4</sup>*J* 1.2 Hz, C8H), 7.65 (1H, ddd, <sup>3</sup>*J* 8.2, <sup>3</sup>*J* 7.0, <sup>4</sup>*J* 1.2 Hz, C6H), 7.60 (1H, d, <sup>3</sup>*J* 8.5 Hz, C3H), 7.58 – 7.53 (2H, m, C7H, C9H), 7.43 (1H, s, C5'H), 7.17 (1H, d, <sup>3</sup>*J* 9.1 Hz, C10H), 7.13 (1H, s, C3'H), 6.08 (1H, dd, <sup>3</sup>*J* 17.5, <sup>3</sup>*J* 11.0 Hz, C2''H), 5.58 (1H, dd, <sup>3</sup>*J* 17.5, <sup>2</sup>*J* 1.3 Hz, C1'H), 4.88 (1H, dd, <sup>3</sup>*J* 11.0, <sup>2</sup>*J* 1.3 Hz, C1''H), 2.46 (3H, s, C4'-CH<sub>3</sub>), 2.12 (3H, s, C2-CH<sub>3</sub>), 1.80 (3H, s, C2'-CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 137.1 (C4'), 137.0 (C2'), 136.9 (C1), 136.7 (C6'), 135.3 (C1'), 135.0 (C2), 131.6 (C8a), 130.9 (C10a), 130.7 (C4b), 130.6 (C3'), 129.0 (C3),

128.7 (C4a), 128.6 (C8), 127.1 (C9), 126.6 (C6), 126.4 (C7), 124.6 (C10), 123.3 (C5'), 122.7 (C5), 121.9 (C4), 114.3 (C1''), 21.5 (C4'-CH<sub>3</sub>), 20.3 (C2-CH<sub>3</sub>), 20.0 (C2'-CH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>25</sub>H<sub>22</sub>Ag 429.0767 found 429.0763 [M+Ag<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3 μm, 250x 4.6 mm, 1.0 mL/min, heptane/iPrOH 99.5 : 0.5, 40°C): t<sub>major</sub> = 9.8 min and t<sub>minor</sub> = 9.4 min.

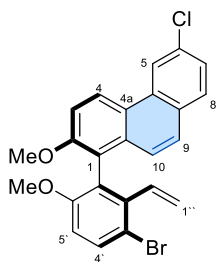
**(S<sub>a</sub>)-1-(3-Bromo-6-methoxy-2-vinylphenyl)-2-methoxyphenanthrene ((S<sub>a</sub>)-16j):**



**(S<sub>a</sub>)-16j**

Prepared according to the modified general procedure **L** using 1-bromo-4,5-dimethoxy-8-(2-vinylphenyl)phenanthrene **15j** (29.4 mg, 70.0 μmol), Mo-precursor (4.14 mg, 7.00 μmol, 10 mol%), and (*R<sub>a</sub>*)-[1,2':4,1'':3'',1'''-quaternaphthalene]-2'',3'-diol (11.3 mg, 21.0 μmol, 30 mol%) to give the title compound (*S<sub>a</sub>*)-**16j** as a white solid (28.0 mg, 66.8 μmol, 95%, >99:1 e.r., m.p. 80.0 – 82.0°C): R<sub>f</sub> 0.37 (cyclohexane/EtOAc 5:1); [α]<sub>D</sub><sup>20</sup> = -2.4 (c 0.20, CHCl<sub>3</sub>); ν<sub>max</sub> (neat): 3049w, 3003w, 2934w, 2836w, 170w, 1578w, 1528w, 1454s, 1429m, 1254s, 1065s, 906m, 866w, 807s, 838s, 648w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 8.72 (1H, d, <sup>3</sup>J 9.1 Hz, C4H), 8.64 (1H, d, <sup>3</sup>J 8.3 Hz, C5H), 7.81 (1H, dd, <sup>3</sup>J 7.9, <sup>4</sup>J 1.1 Hz, C8H), 7.66 (1H, d, <sup>3</sup>J 8.8 Hz, C4'H), 7.63 (1H, ddd, <sup>3</sup>J 8.3, <sup>3</sup>J 7.0, <sup>4</sup>J 1.4 Hz, C6H), 7.58 (1H, d, <sup>3</sup>J 9.1 Hz, C9H), 7.52 (1H, ddd, <sup>3</sup>J 7.9, <sup>3</sup>J 7.0, <sup>4</sup>J 1.1 Hz, C7H), 7.40 (1H, d, <sup>3</sup>J 9.1 Hz, C3H), 7.17 (1H, d, <sup>3</sup>J 9.1 Hz, C10H), 6.87 (1H, d, <sup>3</sup>J 8.8 Hz, C5'H), 6.38 (1H, dd, <sup>3</sup>J 17.7, <sup>3</sup>J 11.6 Hz, C2''H), 5.01 – 4.75 (2H, m, C1''H), 3.87 (3H, s, C2-OCH<sub>3</sub>), 3.61 (3H, s, C6'-OCH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 157.3 (C6'), 155.2 (C2), 139.8 (C2'), 134.8 (C2''), 132.8 (C4'), 132.2 (C10a), 131.0 (C8a), 130.8 (C4b), 128.6 (C8), 127.7 (C9), 126.8 (C6), 126.4 (C1'), 125.8 (C7), 124.7 (C4a), 124.1 (C10), 123.9 (C4), 122.4 (C5), 122.0 (C1), 120.1 (C1''), 114.7 (C3'), 112.2 (C3), 111.7 (C5'), 56.5 (C2-OCH<sub>3</sub>), 56.3 (C6'-OCH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>24</sub>H<sub>30</sub>BrO<sub>2</sub> 419.0641 found 419.0641 [M+H<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3 μm, 250x 4.6 mm, 1.0 mL/min, heptane/iPrOH 97.5 : 2.5, 20°C): t<sub>major</sub> = 7.3 min and t<sub>minor</sub> = 8.2 min.

**(S<sub>a</sub>)-1-(3-Bromo-6-methoxy-2-vinylphenyl)-6-chloro-2-methoxyphenanthrene ((S<sub>a</sub>)-16k):**



**(S<sub>a</sub>)-16k**

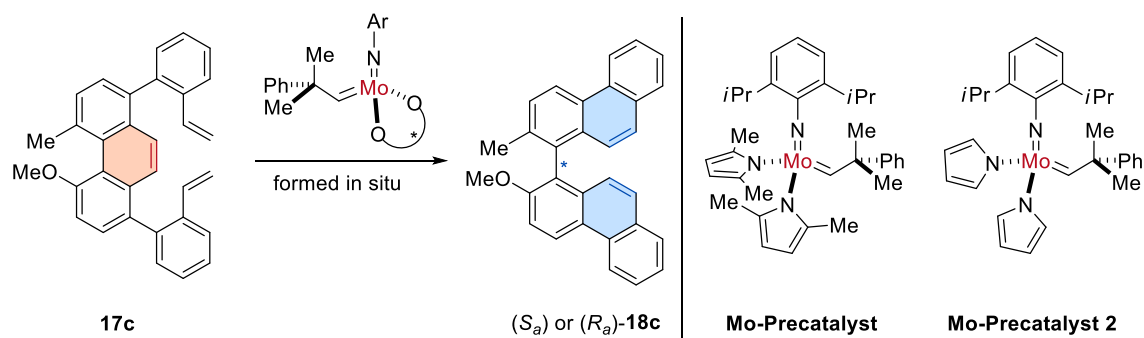
Prepared according to the general procedure **L** using 1-bromo-8-(5-chloro-2-vinylphenyl)-4,5-dimethoxyphenanthrene **15k** (31.8 mg, 70.0 μmol) to give the title compound (*S<sub>a</sub>*)-**16k** as a beige solid (28.5 mg, 62.8 μmol, 90%, >99:1 e.r., m.p. 90.9 – 92.0°C): R<sub>f</sub> 0.36 (cyclohexane/EtOAc 5:1); [α]<sub>D</sub><sup>20</sup> = -11 (c 0.10, CHCl<sub>3</sub>); ν<sub>max</sub> (neat): 3005w, 2933w, 2837w, 1578w, 1254m, 1447m, 1274s, 1254s, 1203w, 1093m, 1065m, 1034m, 930m, 867w, 808m, 694w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 8.62 (1H, d, <sup>3</sup>J 9.0 Hz, C4H), 8.58 (1H, d, <sup>4</sup>J 1.9 Hz, C5H), 7.73 (1H, d, <sup>3</sup>J 8.5 Hz, C8H), 7.66 (1H, d, <sup>3</sup>J 8.8 Hz, C4'H), 7.53 (1H, d, <sup>3</sup>J 9.1 Hz, C9H), 7.47 (1H, dd, <sup>3</sup>J 8.5, 1.9 Hz, C7H), 7.40 (1H, d, <sup>3</sup>J 9.0 Hz, C3H), 7.17 (1H, dd, <sup>3</sup>J 9.1, <sup>5</sup>J 0.6 Hz, C10H), 6.87 (1H, d,

$^3J$  8.8 Hz, C5`H), 6.37 (1H, dd,  $^3J$  17.7,  $^3J$  11.6 Hz, C2``H), 4.91 (1H, dd,  $^3J$  11.6,  $^2J$  1.6 Hz, C1``H), 4.85 (1H, dd,  $^3J$  17.7,  $^2J$  1.6 Hz, C1``H), 3.88 (3H, s, C2–OCH<sub>3</sub>), 3.62 (3H, s, C6`–OCH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 157.3 (C6`), 155.7 (C2), 139.8 (C2`), 134.8 (C2``), 132.9 (C4`), 132.8 (C6), 132.4 (C10a), 132.0 (C4b), 130.0 (C8), 129.2 (C8a), 127.0 (C9), 126.3 (C7), 126.1 (C1`), 124.5 (C10), 124.0 (C4), 123.7 (C4a), 122.14 (C1), 122.11 (C5), 120.1 (C1``), 114.7 (C3`), 112.4 (C3), 111.7 (C5`), 56.4 (C2–OCH<sub>3</sub>), 56.3 (C6`–OCH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for C<sub>24</sub>H<sub>19</sub>BrClO<sub>2</sub> 453.0251 found 453.0232 [M+H<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu\text{m}$ , 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 90 : 10, 20°C):  $t_{\text{major}}$  = 5.8 min and  $t_{\text{minor}}$  = 6.0 min.

## Atroposelective Aromatic Ring-Opening Metathesis – Twofold RCM

**Optimization Studies (15.0  $\mu\text{mol}$  scale) of **17c**:** Performed according to the general procedure **H** utilizing 4-methoxy-5-methyl-1,8-bis(2-vinylphenyl)phenanthrene **17c** (3.20 mg, 7.50  $\mu\text{mol}$ ) and the corresponding solvent (0.25 mL, 0.03  $\text{mol}\cdot\text{L}^{-1}$ ) with the reaction time of 18 h.

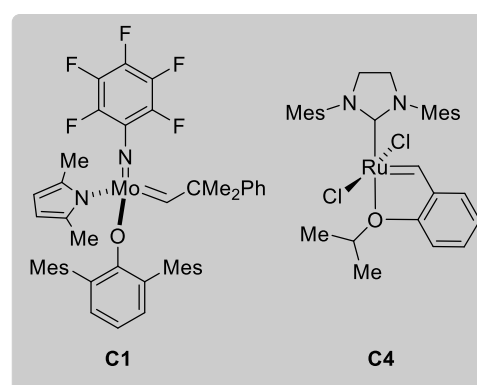
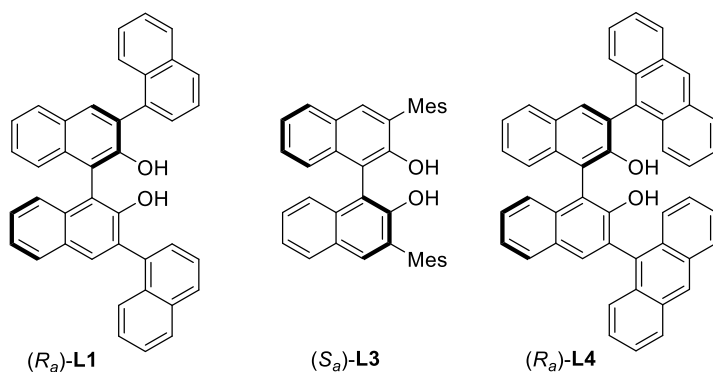
**Supplementary Table 13.** Reaction conditions optimization for atroposelective phenanthrene ring-opening metathesis and RCM



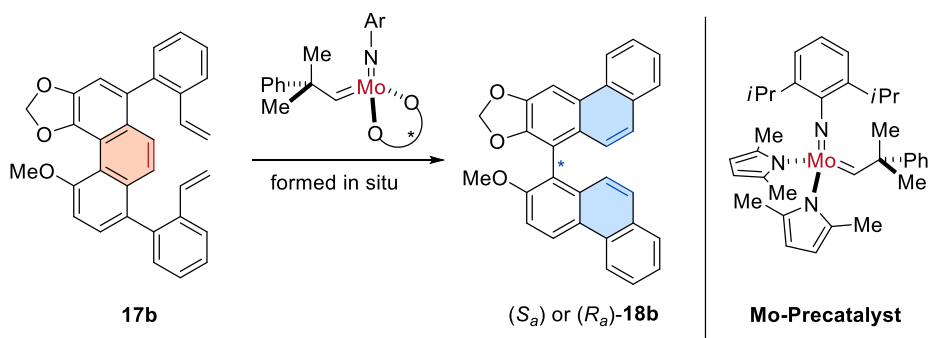
| Entry <sup>a</sup> | Catalyst (mol%)          | Ligand (mol%)                     | Solvent | Temp. [°C] | Conversion <sup>b</sup> [%] | Yield <sup>b</sup> [%] | e. r. <sup>c</sup> |
|--------------------|--------------------------|-----------------------------------|---------|------------|-----------------------------|------------------------|--------------------|
| 1                  | <b>C1</b> (20)           | —                                 | Toluene | 85         | 44                          | 37                     | 50 : 50            |
| 2                  | <b>Mo-Precat.</b> (20)   | (S <sub>a</sub> )- <b>L3</b> (60) | Toluene | 85         | 54                          | 42                     | > 1 : 99           |
| 3                  | <b>Mo-Precat.</b> (30)   | (R <sub>a</sub> )- <b>L4</b> (90) | Toluene | 85         | 76                          | 45                     | > 99 : 1           |
| 4                  | <b>Mo-Precat.</b> (20)   | (R <sub>a</sub> )- <b>L4</b> (60) | Toluene | 85         | 78                          | 68                     | > 99 : 1           |
| 5                  | <b>Mo-Precat.</b> (10)   | (R <sub>a</sub> )- <b>L4</b> (30) | Toluene | 85         | NR                          | —                      | —                  |
| 6 <sup>d</sup>     | <b>Mo-Precat.</b> (20)   | (R <sub>a</sub> )- <b>L4</b> (60) | Toluene | 85         | 52                          | 47                     | > 99 : 1           |
| 7                  | <b>Mo-Precat. 2</b> (20) | (R <sub>a</sub> )- <b>L4</b> (60) | Toluene | 85         | 69                          | 59                     | > 99 : 1           |
| 8 <sup>e</sup>     | <b>Mo-Precat.</b> (20)   | (R <sub>a</sub> )- <b>L4</b> (60) | Toluene | 85         | 30                          | 24                     | > 99 : 1           |
| 9                  | <b>Mo-Precat.</b> (20)   | (R <sub>a</sub> )- <b>L4</b> (60) | Toluene | 100        | 56                          | 53                     | > 99 : 1           |
| 10                 | <b>Mo-Precat.</b> (20)   | (R <sub>a</sub> )- <b>L1</b> (60) | Toluene | 85         | 75                          | 66                     | > 99 : 1           |

<sup>a</sup>Reactions were performed on 7.50  $\mu\text{mol}$  scale of **17c** for 18 h with the solvent concentration of 0.03  $\text{mol}\cdot\text{L}^{-1}$ .

<sup>b</sup>Conversion and yield were determined by <sup>1</sup>H-NMR with durene as an internal standard. <sup>c</sup>Determined by HPLC on a chiral stationary phase of the crude product (Chiralpak IG-N3 column (3  $\mu\text{m}$ , 250x4.6 mm, heptane/iPrOH 85:15, 1.0 mL/min, 20°C). <sup>d</sup>48 h reaction time. <sup>e</sup>Concentration = 0.015  $\text{mol}\cdot\text{L}^{-1}$ .



**Supplementary Table 14.** Reaction conditions optimization for atroposelective phenanthrene ring-opening metathesis and RCM



| Entry <sup>a</sup> | Catalyst (mol%)        | Ligand (mol%)                  | Solvent | Temp. [°C] | Conversion <sup>b</sup> [%] | Yield <sup>b</sup> [%] | e. r. <sup>c</sup> |
|--------------------|------------------------|--------------------------------|---------|------------|-----------------------------|------------------------|--------------------|
| 1                  | <b>C4</b> (10)         | —                              | Toluene | 65         | NR                          | —                      | —                  |
| 2                  | <b>C4</b> (20)         | —                              | Toluene | 85         | NR                          | —                      | —                  |
| 3                  | <b>C1</b> (10)         | —                              | Toluene | 65         | NR                          | —                      | —                  |
| 4                  | <b>C1</b> (20)         | —                              | Toluene | 85         | 53                          | —                      | 50 : 50            |
| 5                  | <b>Mo-Precat.</b> (20) | <b>(S<sub>a</sub>)-L3</b> (60) | Toluene | 85         | 13                          | 11                     | > 99 : 1           |
| 6                  | <b>Mo-Precat.</b> (20) | <b>(R<sub>a</sub>)-L4</b> (60) | Toluene | 85         | 54                          | 45                     | > 1 : 99           |
| 7 <sup>d</sup>     | <b>Mo-Precat.</b> (20) | <b>(R<sub>a</sub>)-L4</b> (60) | Toluene | 85         | 52                          | 48                     | > 1 : 99           |
| 8                  | <b>Mo-Precat.</b> (30) | <b>(R<sub>a</sub>)-L4</b> (90) | Toluene | 85         | 88                          | 79                     | 2 : 98             |
| 9                  | <b>Mo-Precat.</b> (20) | <b>(R<sub>a</sub>)-L1</b> (60) | Toluene | 85         | >95                         | 80                     | > 1 : 99           |

<sup>a</sup>Reactions were performed on 7.50 μmol scale of **17b** for 18 h with the solvent concentration of 0.03 mol·L<sup>-1</sup>.

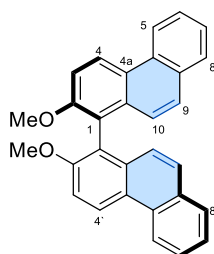
<sup>b</sup>Conversion and yield were determined by <sup>1</sup>H-NMR with durene as an internal standard. <sup>c</sup>Determined by HPLC on a chiral stationary phase of the crude product (Chiralpak IC-N3 column (3 μm, 250x4.6 mm, heptane/iPrOH 80:20, 1.0 mL/min, 20°C). <sup>d</sup>48 h reaction time.



### General procedure M for atroposelective aromatic ring-opening metathesis – twofold RCM cascade:

Mo-precursor (4.14 mg, 7.00  $\mu\text{mol}$ , 10 mol%), (*R<sub>a</sub>*)-[1,2':4',1'':3'',1'''-quaternaphthalene]-2'',3'-diol (11.3 mg, 21.0  $\mu\text{mol}$ , 30 mol%) were weighed in 10 mL crimp cap vial and toluene (1.5 mL) was added. The obtained solution was stirred for 1 h at room temperature in an argon-filled glovebox before a solution of the corresponding substrate (70.0  $\mu\text{mol}$ , 1.00 eq.) in toluene (0.83 mL) was added. The capped vial was then taken out of the glovebox and stirred at 85°C for 18 h. The reaction mixture was diluted with EtOAc and filtered through a thin layer of silica gel. The solvents were removed under reduced pressure and the residue was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0→80:20) to give the desired product. The e.r. of the isolated products were determined by HPLC on a chiral stationary phase.

#### (*S<sub>a</sub>*)-2,2'-Dimethoxy-1,1'-biphenanthrene ((*S<sub>a</sub>*)-18a):



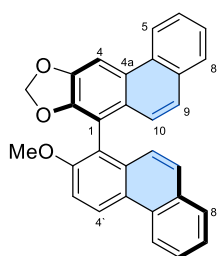
(*S<sub>a</sub>*)-18a

Prepared according to the general procedure **M** using 4,5-dimethoxy-1,8-bis(2-vinylphenyl)phenanthrene **17a** (31.0 mg, 70.0  $\mu\text{mol}$ ) to give the title compound (*S<sub>a</sub>*)-**18a** as a white solid (26.0 mg, 62.7  $\mu\text{mol}$ , 90%, >99:1 e.r., m.p. 210.0 – 212.0°C (decomposition)): *R<sub>f</sub>* 0.36 (cyclohexane/EtOAc 5:1);  $[\alpha]_D^{20} = -77$  (c 0.19,  $\text{CHCl}_3$ );  $\nu_{\text{max}}$  (neat): 3058w, 2995w, 2934w, 2837w, 1590w, 1527w, 1461m, 1377w, 1274s, 1256s, 1201w, 1086w, 945w, 865w, 787m, 752m;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.89 – 8.82 (2H, m, C4H, C4'H), 8.71 (2H, d,  $^3J$  8.4 Hz, C5H, C5'H), 7.78 (2H,  $^3J$  7.9,  $^4J$  1.4 Hz, C8H, C8'H), 7.65 (2H, ddd,  $^3J$  8.4,  $^3J$  7.0,  $^4J$  1.4 Hz, C6H, C6'H), 7.55 (2H, d,  $^3J$  9.2 Hz, C3H, C3'H), 7.52 (2H, ddd,  $^3J$  8.0,  $^3J$  7.0,  $^4J$  1.1 Hz, C7H, C7'H), 7.46 (2H, d,  $^3J$  9.2 Hz, C9H, C9'H), 7.07 (2H, dd,  $^3J$  9.2,  $^5J$  0.7 Hz, C10H, C10'H), 3.82 (6H, s, 2  $\times$  OCH<sub>3</sub>);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 156.2 (C2, C2'), 133.0 (C10a, C10a'), 131.0 (C8a, C8a'), 130.8 (C4b, C4b'), 128.6 (C8, C8'), 127.7 (C9, C9'), 126.8 (C6, C6'), 125.9 (C7, C7'), 125.1 (C1, C1'), 124.6 (C10, C10'), 124.1 (C4, C4'), 122.4 (C5, C5'), 121.5 (C4a, C4a'), 112.8 (C3, C3'), 56.8 (OCH<sub>3</sub>); ESI-MS: *m/z* calcd. for  $\text{C}_{30}\text{H}_{22}\text{AgO}_2$  521.0665 found 521.0659 [*M*+*Ag*<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu\text{m}$ , 250  $\times$  4.6 mm, 1.0 mL/min, heptane/*i*PrOH 90 : 10, 20°C): *t*<sub>major</sub> = 12.6 min and *t*<sub>minor</sub> = 14.8 min.

**Scale-up (5 mol% catalyst loading):** Performed according to the modified general procedure **M** using 4,5-dimethoxy-1,8-bis(2-vinylphenyl)phenanthrene **17a** (111 mg, 250  $\mu\text{mol}$ ), Mo-precursor (7.40 mg, 12.5  $\mu\text{mol}$ , 5.0 mol%), and (*R<sub>a</sub>*)-[1,2':4',1'':3'',1'''-quaternaphthalene]-2'',3'-diol (13.5 mg, 25.0  $\mu\text{mol}$ , 10 mol%) with the reaction time of 18 h to give the title compound **18a** as a beige solid (100 mg, 241  $\mu\text{mol}$ , 97%).

#### (*S<sub>a</sub>*)-7-(2-Methoxyphenanthren-1-yl)phenanthro[2,3-d][1,3]dioxole ((*S<sub>a</sub>*)-18b):

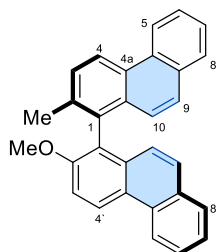
Prepared according to the general procedure **M** using 11-methoxy-5,8-bis(2-vinylphenyl)phenanthro[3,4-d][1,3]dioxole **17b** (32.0 mg, 70.0  $\mu\text{mol}$ ) to give the title compound (*S<sub>a</sub>*)-**18b** as a beige solid (24.2 mg, 56.5  $\mu\text{mol}$ , 81%, >99:1 e.r., m.p. 266.0 – 267.0°C (decomposition)): *R<sub>f</sub>* 0.36 (cyclohexane/EtOAc 6:1);  $[\alpha]_D^{20} = -82$  (c



(*S<sub>a</sub>*)-**18b**

0.18, CHCl<sub>3</sub>);  $\nu_{\max}$ (neat): 3063w, 3010w, 2928w, 2852w, 1592w, 1454s, 1393m, 1258s, 1233s, 1059m, 952m, 815m, 750s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.88 (1H, d, <sup>3</sup>J 9.1 Hz, C4'*H*), 8.70 (1H, d, <sup>3</sup>J 8.1 Hz, C5'*H*), 8.59 (1H, d, <sup>3</sup>J 8.2 Hz, C5*H*), 8.21 (1H, s, C4*H*), 7.84 – 7.77 (2H, m, C8*H*, C8'*H*), 7.72 – 7.60 (2H, m, C6*H*, C6'*H*), 7.58 – 7.50 (4H, m, C7*H*, C3'*H*, C7'*H*, C9'*H*), 7.45 (1H, d, <sup>3</sup>J 9.0 Hz, C9*H*), 7.21 (1H, d, <sup>3</sup>J 9.2 Hz, C10'*H*), 7.16 (1H, d, <sup>3</sup>J 9.0 Hz, C10*H*), 6.07 (2H, dd, <sup>2</sup>J 17.7, <sup>5</sup>J 1.3 Hz, OCH<sub>2</sub>O), 3.87 (3H, s, OCH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 156.3 (C2'), 147.8 (C3), 146.2 (C2), 132.7 (C10*a*'), 131.5 (C8*a*), 131.0 (C8*a*'), 130.8 (C4*b*'), 130.5 (C4*b*'), 128.7 (C8'), 128.6 (C8), 128.29 (C10*a*'), 128.25 (C10'), 126.98 (C6'), 126.96 (C4*a*'), 126.4 (C6), 126.1 (C7'), 125.9 (C7), 125.4 (C9), 125.2 (C4*a*'), 125.0 (C4'), 124.3 (C10), 124.2 (C10'), 122.8 (C5), 122.4 (C5'), 118.4 (C1'), 113.7 (C1), 112.5 (C3'), 101.6 (OCH<sub>2</sub>O), 100.7 (C4), 56.7 (OCH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>30</sub>H<sub>20</sub>AgO<sub>3</sub> 535.0458 found 535.0453 [M+Ag<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IC 3  $\mu$ m, 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 80 : 20, 20°C): *t*<sub>major</sub> = 26.2 min and *t*<sub>minor</sub> = 12.9 min.

#### (*R<sub>a</sub>*)-2-Methoxy-2'-methyl-1,1'-biphenanthrene ((*R<sub>a</sub>*)-**18c**):

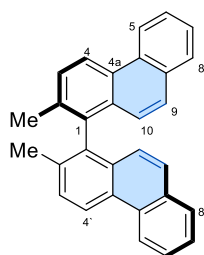


(*R<sub>a</sub>*)-**18c**

Prepared according to the general procedure **M** using 4-methoxy-5-methyl-1,8-bis(2-vinylphenyl)phenanthrene **17c** (29.9 mg, 70.0  $\mu$ mol) to give (*S<sub>a</sub>*)-**18c** the title compound as a white solid (27.3 mg, 68.5  $\mu$ mol, 98%, >99:1 e.r., m.p. 209.0 – 210.5°C): *R<sub>f</sub>* 0.57 (cyclohexane/EtOAc 13:2); [ $\alpha$ ]<sub>D</sub><sup>20</sup> = –25 (c 0.09, CHCl<sub>3</sub>);  $\nu_{\max}$ (neat): 3039w, 2924w, 2848w, 1589w, 1527w, 1459m, 1377w, 1273m, 1260m, 1200w, 1081m, 947w, 865w, 814s, 749s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.86 (1H, d, <sup>3</sup>J 9.2 Hz, C4'*H*), 8.82 – 8.68 (3H, m, C4*H*, C5*H*, C5'*H*), 7.82 – 7.76 (2H, m, C8*H*, C8'*H*), 7.70 (1H, d, <sup>3</sup>J 8.5 Hz, C3*H*), 7.69 – 7.64 (2H, m, C6*H*, C6'*H*), 7.59 – 7.50 (3H, m, C7*H*, C3'*H*, C7'*H*), 7.48 – 7.43 (2H, m, C9*H*, C9'*H*), 7.10 (1H, d, <sup>3</sup>J 9.2 Hz, C10*H*), 6.96 (1H, d, <sup>3</sup>J 9.2 Hz, C10'*H*), 3.82 (3H, s, OCH<sub>3</sub>), 2.14 (3H, s, C2–CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 155.6 (C2'), 136.2 (C2), 133.9 (C1), 132.5 (C10*a*'), 131.8 (C10*a*'), 131.6 (C8*a*'), 131.0 (C8*a*'), 130.8 (C4*b*'), 129.0 (C3), 128.8 (C4*a*'), 128.7 (C8), 128.5 (C8'), 128.0 (C9), 127.0 (C9'), 126.9 (C6'), 126.6 (C6/C7), 126.3 (C6/C7), 126.0 (C7'), 125.1 (C4*a*'), 125.0 (C10), 124.3 (C10'), 124.1 (C4'), 124.0 (C1'), 122.8 (C5), 122.4 (C4), 122.3 (C5'), 112.4 (C3'), 56.5 (OCH<sub>3</sub>), 20.5 (C2–CH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>30</sub>H<sub>22</sub>AgO 505.0716 found 505.0709 [M+Ag<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu$ m, 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 85 : 15, 20°C): *t*<sub>major</sub> = 6.0 min and *t*<sub>minor</sub> = 7.3 min.

#### (*S<sub>a</sub>*)-2,2'-Dimethyl-1,1'-biphenanthrene ((*S<sub>a</sub>*)-**18d**):

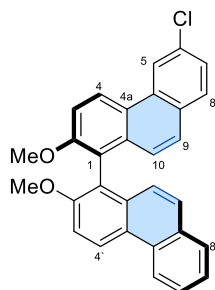
Prepared according to the general procedure **M** using 4,5-dimethyl-1,8-bis(2-vinylphenyl)phenanthrene **17d** (28.7 mg, 70.0  $\mu$ mol) to give the title compound (*S<sub>a</sub>*)-**18d** as a white solid (22.2 mg, 58.0  $\mu$ mol, 83%,



(*S<sub>a</sub>*)-**18d**

>99:1 e.r., m.p. 89.0 – 89.8°C);  $R_f$  0.79 (cyclohexane/EtOAc 5:1);  $[\alpha]_D^{20} = -26$  (c 0.11, CHCl<sub>3</sub>);  $\nu_{\max}(\text{neat})$ : 3054w, 3003w, 2941w, 2915w, 2859w, 1618w, 1523w, 1458w, 1303w, 1260w, 1229w, 1101w, 1038w, 968w, 864w, 816m, 752s;  $^1\text{H NMR}$  (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.79 (2H, d,  $^3J$  8.3 Hz, C5H, C5'H), 8.77 (2H, d,  $^3J$  8.5 Hz, C4H, C4'H), 7.81 (2H, dd,  $^3J$  7.9,  $^4J$  1.2 Hz, C8H, C8'H), 7.73 – 7.65 (4H, m, C3H, C3'H, C6H, C6'H), 7.57 (2H, ddd,  $^3J$  7.9,  $^3J$  7.1,  $^4J$  1.1 Hz, C7H, C7'H), 7.47 (2H, d,  $^3J$  9.1 Hz, C9H, C9'H), 7.03 (2H, d,  $^3J$  9.1 Hz, C10H, C10'H), 2.09 (6H, s, C2–CH<sub>3</sub>, C2'–CH<sub>3</sub>);  $^{13}\text{C NMR}$  (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 136.7 (C1, C1'), 135.4 (C2, C2'), 131.6 (C8a, C8a'), 131.3 (C10a, C10a'), 130.7 (C4b, C4b'), 129.1 (C3, C3'), 128.9 (C4a, C4a'), 128.6 (C8, C8'), 127.3 (C9, C9'), 126.7 (C6, C6'), 126.5 (C7, C7'), 124.7 (C10, C10'), 122.8 (C5, C5'), 122.3 (C4, C4'), 20.3 (C2–CH<sub>3</sub>, C2'–CH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for C<sub>30</sub>H<sub>22</sub>Ag 489.0772 found 489.0767 [M+Ag<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu\text{m}$ , 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 99 : 1, 20°C):  $t_{\text{major}}$  = 7.3 min and  $t_{\text{minor}}$  = 8.7 min.

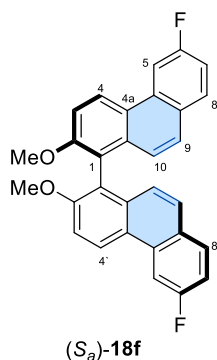
**(*S<sub>a</sub>*)-6-Chloro-2,2'-dimethoxy-1,1'-biphenanthrene ((*S<sub>a</sub>*)-18e):**



(*S<sub>a</sub>*)-**18e**

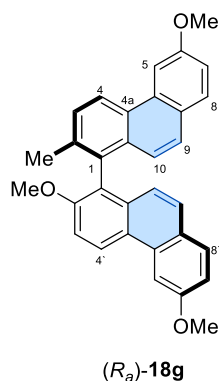
Prepared according to the general procedure **M** using 1-(5-chloro-2-vinylphenyl)-4,5-dimethoxy-8-(2-vinylphenyl)phenanthrene **17e** (33.4 mg, 70.0  $\mu\text{mol}$ ) to give the title (*S<sub>a</sub>*)-**18e** compound as a beige solid (20.0 mg, 44.5  $\mu\text{mol}$ , 64%, >99:1 e.r., m.p. 227.0 – 228.4°C);  $R_f$  0.41 (cyclohexane/EtOAc 5:1);  $[\alpha]_D^{19} = -93$  (c 0.417, CHCl<sub>3</sub>);  $\nu_{\max}(\text{neat})$ : 3061w, 3004w, 2952w, 2838w, 1616w, 1589m, 1517m, 1459m, 1271s, 1254s, 1199w, 1086s, 1011m, 906m, 868m, 815m, 729s;  $^1\text{H NMR}$  (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.85 (1H, d,  $^3J$  9.0 Hz, C4'H), 8.75 (1H, d,  $^3J$  9.0 Hz, C4H), 8.71 (1H, d,  $^3J$  8.0 Hz, C5'H), 8.66 (1H, d,  $^4J$  2.0 Hz, C5H), 7.78 (1H, dd,  $^3J$  7.9,  $^4J$  1.2 Hz, C8'H), 7.70 (1H, d,  $^3J$  8.4 Hz, C8H), 7.66 (1H, ddd,  $^3J$  8.0,  $^3J$  7.0,  $^4J$  1.4 Hz, C6'H), 7.57 – 7.50 (3H, m, C3H, C3'H, C7'H), 7.49 – 7.45 (2H, m, C7H, C9'H), 7.41 (1H, d,  $^3J$  9.1 Hz, C9H), 7.10 – 7.02 (2H, m, C10H, C10'H), 3.82 (6H, s, C2–OCH<sub>3</sub>, C2'–OCH<sub>3</sub>);  $^{13}\text{C NMR}$  (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 156.6 (C2), 156.1 (C2'), 133.2 (C10a), 132.9 (C10a'), 132.7 (C6), 132.0 (C4b), 131.0 (C8a'), 130.8 (C4b'), 130.0 (C8), 129.3 (C8a), 128.6 (C8'), 127.8 (C9'), 127.0 (C9), 126.8 (C6'), 126.3 (C7), 125.9 (C7'), 125.1 (C4a'), 124.9 (C10), 124.4 (C10'), 124.2 (C4/C4'), 124.1 (C4a), 122.4 (C5'), 122.1 (C5), 121.5 (C1), 121.1 (C1'), 112.9 (C3/C3'), 112.7 (C3/C3'), 56.72 (C2–OCH<sub>3</sub>/C2'–OCH<sub>3</sub>), 56.69 (C2–OCH<sub>3</sub>/C2'–OCH<sub>3</sub>); ESI-MS:  $m/z$  calcd. for C<sub>30</sub>H<sub>22</sub>ClO<sub>2</sub> 449.1303 found 449.1306 [M+H<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu\text{m}$ , 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 90 : 10, 20°C):  $t_{\text{major}}$  = 11.4 min and  $t_{\text{minor}}$  = 14.1 min.

**(S<sub>a</sub>)-6,6'-Difluoro-2,2'-dimethoxy-1,1'-biphenanthrene ((S<sub>a</sub>)-18f):**



Prepared according to the general procedure **M** using 1,8-bis(5-fluoro-2-vinylphenyl)-4,5-dimethoxyphenanthrene **17f** (33.5 mg, 70.0 μmol) to give the title compound (S<sub>a</sub>)-**18f** as a beige solid (28.6 mg, 63.5 μmol, 91%, >99:1 e.r., m.p. 235.0 – 237.0°C): R<sub>f</sub> 0.45 (cyclohexane/EtOAc 3:1); [α]<sub>D</sub><sup>19</sup> = –73 (c 0.10, CHCl<sub>3</sub>); ν<sub>max</sub> (neat): 2968w, 2964w, 2838w, 1627m, 1591m, 1529m, 1497s, 1459m, 1379w, 1268s, 1199s, 1082s, 905m, 835s, 730m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 8.70 (2H, d, <sup>3</sup>J 9.2 Hz, C4H, C4'H), 8.30 (2H, dd, <sup>3</sup>J<sub>HF</sub> 11.4, <sup>4</sup>J<sub>HH</sub> 2.4 Hz, C5H, C5'H), 7.75 (2H, dd, <sup>3</sup>J<sub>HH</sub> 8.7, <sup>3</sup>J<sub>HF</sub> 6.0 Hz, C8H, C8'H), 7.54 (2H, d, <sup>3</sup>J 9.2 Hz, C3H, C3'H), 7.44 (d, <sup>3</sup>J 9.2 Hz, C9H, C9'H), 7.31 – 7.25 (2H, m, C7H, C7'H), 7.01 (2H, d, <sup>3</sup>J 9.2 Hz, C10H, C10'H), 3.82 (6H, s, 2 × OCH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 161.9 (d, <sup>1</sup>J<sub>CF</sub> 245.0 Hz, C6, C6'), 156.6 (C2, C2'), 133.2 (C10a, C10a'), 132.4 (d, <sup>3</sup>J<sub>CF</sub> 8.6 Hz, C4b, C4'b), 130.6 (d, <sup>3</sup>J<sub>CF</sub> 9.1 Hz, C8, C8'), 127.7 (d, <sup>4</sup>J<sub>CF</sub> 1.4 Hz, C8a, C8a'), 127.1 (C9, C9'), 124.5 (C4a, C4a'), 124.31 (C4, C4'), 123.7 (C10, C10'), 121.3 (C1, C1'), 114.8 (d, <sup>2</sup>J<sub>CF</sub> 23.9 Hz, C7, C7'), 112.7 (C3, C3'), 107.5 (d, J = 22.3 Hz, C5, C5'), 56.7 (OCH<sub>3</sub>); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ = –113.59; ESI-MS: m/z calcd. for C<sub>30</sub>H<sub>20</sub>AgF<sub>2</sub>O<sub>2</sub> 557.0477 found 557.0469 [M+Ag<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3 μm, 250x 4.6 mm, 1.0 mL/min, heptane/iPrOH 90 : 10, 20°C): t<sub>major</sub> = 9.6 min and t<sub>minor</sub> = 13.7 min.

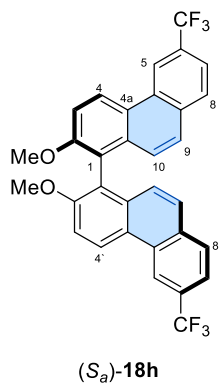
**(R<sub>a</sub>)-2,6,6'-Trimethoxy-2'-methyl-1,1'-biphenanthrene ((S<sub>a</sub>)-18g):**



Prepared according to the general procedure **M** using 4-methoxy-1,8-bis(5-methoxy-2-vinylphenyl)-5-methylphenanthrene **17g** (34.1 mg, 70.0 μmol) to give the title compound (S<sub>a</sub>)-**18g** as a beige solid (30.5 mg, 66.5 μmol, 95%, >99:1 e.r., 99.5 – 101.0°C): R<sub>f</sub> 0.40 (cyclohexane/EtOAc 3:1); [α]<sub>D</sub><sup>19</sup> = –149 (c 0.17, CHCl<sub>3</sub>); ν<sub>max</sub> (neat): 2992w, 2931w, 2837w, 1617s, 1500s, 1458m, 1374w, 1260s, 1230s, 1175w, 1079m, 1036m, 959w, 907m, 834s, 730s, 651w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 8.76 (1H, d, <sup>3</sup>J 9.2 Hz, C4'H), 8.66 (1H, d, <sup>3</sup>J 8.6 Hz, C4H), 8.14 (1H, d, <sup>4</sup>J 2.4 Hz, C5H), 8.09 (1H, d, <sup>4</sup>J 2.3 Hz, C5'H), 7.73 – 7.68 (2H, m, C8H, C8'H), 7.67 (1H, d, <sup>3</sup>J 8.5 Hz, C3H), 7.52 (1H, d, <sup>3</sup>J 9.2 Hz, C3'H), 7.43 – 7.36 (2H, m, C9H, C9'H), 7.22 – 7.15 (2H, m, C7H, C7'H), 6.97 (1H, d, <sup>3</sup>J 9.1 Hz, C10H), 6.82 (1H, d, <sup>3</sup>J 9.1 Hz, C10'H), 4.06 (3H, s, C6'–OCH<sub>3</sub>), 4.05 (3H, s, C6–OCH<sub>3</sub>), 3.81 (3H, s, C2'–OCH<sub>3</sub>), 2.14 (3H, s, C2–CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ = 158.8 (C6), 158.6 (C6'), 155.7 (C2'), 136.2 (C2), 134.0 (C1), 132.9 (C10a'), 132.12 (C4b/C10a/C4b'), 132.08 (C4b/C10a/C4b'), 132.05 (C4b/C10a/C4b'), 130.1 (C8'), 129.9 (C8), 128.6 (C3), 128.2 (C8a), 127.6 (C9'), 126.6 (C9), 126.4 (C4a), 125.8 (C8a'), 124.6 (C4a'), 124.10 (C1'), 124.06 (C4'), 122.7 (C10), 122.3 (C4), 122.0 (C10'), 116.4 (C7), 115.9 (C7'), 112.1 (C3'), 104.14 (C5), 104.06 (C5'), 56.5 (C2'–OCH<sub>3</sub>), 55.72 (C6–OCH<sub>3</sub>/C6'–OCH<sub>3</sub>), 55.70 (C6–OCH<sub>3</sub>/C6'–OCH<sub>3</sub>), 20.5 (C2–CH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>32</sub>H<sub>26</sub>AgO<sub>3</sub> 565.0927 found 565.0924 [M+Ag<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase

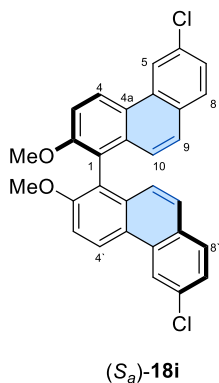
(Chiralcel IG 3  $\mu\text{m}$ , 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 90 : 10, 20°C):  $t_{\text{major}} = 13.5$  min and  $t_{\text{minor}} = 16.2$  min.

**(*S<sub>a</sub>*)-2,2'-Dimethoxy-6,6'-bis(trifluoromethyl)-1,1'-biphenanthrene ((*S<sub>a</sub>*)-18h):**



Prepared according to the general procedure **M** using 4,5-dimethoxy-1,8-bis(5-(trifluoromethyl)-2-vinylphenyl)phenanthrene **17h** (31.8 mg, 55.0  $\mu\text{mol}$ ), Mo-precursor (3.25 mg, 5.50  $\mu\text{mol}$ , 10 mol%), (*R<sub>a</sub>*)-[1,2':4',1'':3'',1'''-quaternaphthalene]-2'',3'-diol (8.90 mg, 16.5  $\mu\text{mol}$ , 30 mol%) to give the title compound (*S<sub>a</sub>*)-**18h** as a white solid (14.5 mg, 26.3  $\mu\text{mol}$ , 48%, >99:1 e.r., m.p. 250 – 253°C (decomposition)):  $R_f$  0.43 (cyclohexane/EtOAc 5:1);  $[\alpha]_D^{20} = -82$  (c 0.47,  $\text{CHCl}_3$ );  $\nu_{\text{max}}(\text{neat})$ : 3002w, 2962w, 2918w, 2848w, 1733w, 1620w, 1598w, 1527w, 1462w, 1413m, 1376w, 1320s, 1284s, 1262s, 1162s, 1115s, 1071s, 1020m, 907m, 844s, 731s, 647w, 615w;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta = 8.97$  (2H, s, C5H, C5'H), 8.87 (2H, d,  $^3J$  9.0 Hz, C4H, C4'H), 7.89 (2H, d,  $^3J$  8.3 Hz, C8H, C8'H), 7.73 (2H, dd,  $^3J$  8.3,  $^4J$  1.4 Hz, C7H, C7'H), 7.61 (2H, d,  $^3J$  9.0 Hz, C3H, C3'H), 7.51 (2H, d,  $^3J$  9.2 Hz, C9H, C9'H), 7.17 (2H, d,  $^3J$  9.2 Hz, C10H, C10'H), 3.84 (6H, s,  $\text{OCH}_3$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta = 156.7$  (C2, C2'), 133.2 (C10a, C10a'), 132.8 (C8a, C8a'), 130.3 (C4b, C4b'), 129.3 (C8, C8'), 128.6 (q,  $^2J_{\text{CF}}$  32.0 Hz, C6, C6'), 127.1 (C9, C9'), 126.7 (C10, C10'), 124.9 (q,  $^1J_{\text{CF}}$  271.2 Hz,  $\text{CF}_3$ ), 124.8 (C4a, C4a'), 124.4 (C4, C4'), 121.8 (q,  $^3J_{\text{CF}}$  3.4 Hz, C7, C7'), 121.2 (C1, C1'), 120.0 (q,  $^3J_{\text{CF}}$  4.5 Hz, C5, C5'), 113.2 (C3, C3'), 56.7 ( $\text{OCH}_3$ );  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta -61.69$ ; ESI-MS:  $m/z$  calcd. for  $\text{C}_{32}\text{H}_{20}\text{AgF}_3\text{O}_2$  657.0413 found 657.0408 [ $\text{M} + \text{Ag}^+$ ]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu\text{m}$ , 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 90 : 10, 20°C):  $t_{\text{major}} = 6.0$  min and  $t_{\text{minor}} = 6.9$  min.

**(*S<sub>a</sub>*)-6,6'-Dichloro-2,2'-dimethoxy-1,1'-biphenanthrene ((*S<sub>a</sub>*)-18i):**

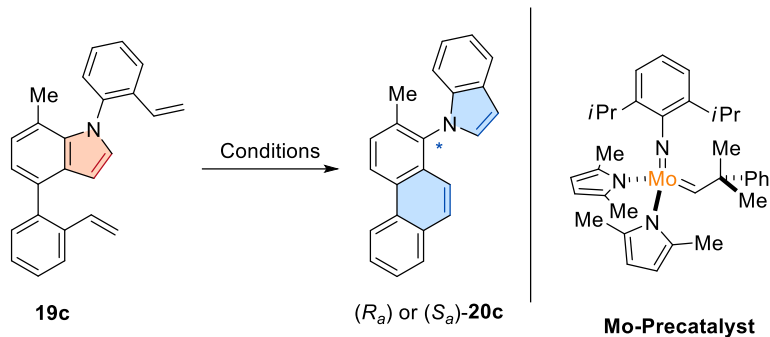


Prepared according to the general procedure **M** using 1,8-bis(5-chloro-2-vinylphenyl)-4,5-dimethoxyphenanthrene **17i** (35.8 mg, 70.0  $\mu\text{mol}$ ) to give the title compound (*S<sub>a</sub>*)-**18i** as a beige solid (31.0 mg, 64.1  $\mu\text{mol}$ , 92%, >99:1 e.r., m.p. 280.0 – 282.0°C (decomposition)):  $R_f$  0.39 (cyclohexane/EtOAc 5:1);  $[\alpha]_D^{19} = -182$  (c 0.20,  $\text{CHCl}_3$ );  $\nu_{\text{max}}(\text{neat})$ : 3081w, 2958w, 2837w, 1730w, 1617w, 1589w, 1490m, 1468m, 1399w, 1285s, 1253s, 1181m, 1086s, 1019m, 907s, 870s, 837s, 729s, 649m;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta = 8.75$  (2H, d,  $^3J$  9.1 Hz, C4H, C4'H), 8.66 (2H, d,  $^4J$  1.7 Hz, C5H, C5'H), 7.70 (2H, d,  $^3J$  8.4 Hz, C8H, C8'H), 7.55 (2H, d,  $^3J$  9.1 Hz, C3H, C3'H), 7.47 (2H, dd,  $^3J$  8.4,  $^4J$  1.7 Hz, C7H, C7'H), 7.42 (2H, d,  $^3J$  9.2 Hz, C9H, C9'H), 7.05 (2H, d,  $^3J$  9.2 Hz, C10H, C10'H), 3.82 (6H, s,  $\text{OCH}_3$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta = 156.6$  (C2, C2'), 133.2 (C10a, C10a'), 132.8 (C6, C6'), 132.0 (C4b, C4b'), 130.0 (C8, C8'), 129.3 (C8a, C8a'), 127.1 (C9, C9'), 126.4 (C7, C7'), 124.8 (C10, C10'), 124.3 (C4, C4'), 124.1 (C4, C4a'), 122.1 (C5, C5'), 121.2 (C1, C1'), 112.9 (C3, C3'), 56.7 ( $\text{OCH}_3$ ); ESI-MS:  $m/z$  calcd. for  $\text{C}_{30}\text{H}_{20}\text{AgCl}_2\text{O}_2$  588.9886 found 588.9897

[M+Ag<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu$ m, 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 90 : 10, 20°C):  $t_{\text{major}}$  = 10.6 min and  $t_{\text{minor}}$  = 14.7 min.

## Atroposelective Indole Ring-Opening Metathesis

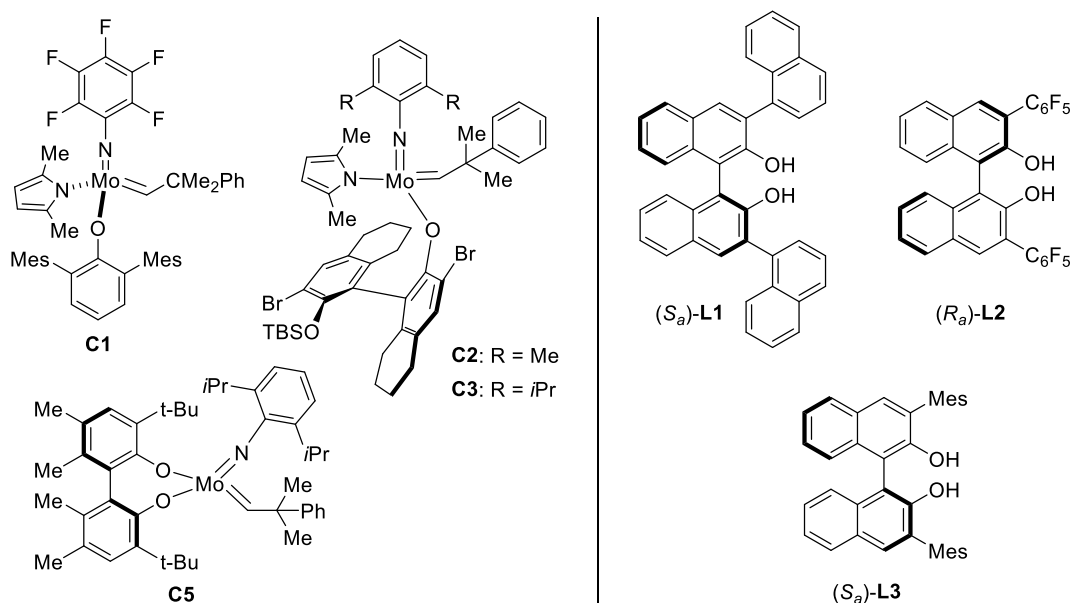
**Optimization Studies (7.50  $\mu\text{mol}$  scale):** Performed according to the general procedure **H** utilizing 7-methyl-1,4-bis(2-vinylphenyl)-1*H*-indole **19c** (2.52 mg, 7.50  $\mu\text{mol}$ ) and toluene (0.25 mL, 0.03  $\text{mol}\cdot\text{L}^{-1}$ ) with the reaction time of 18 h.



**Supplementary Table 15.** Reaction conditions optimization for atroposelective indole ring-opening metathesis and twofold RCM

| Entry <sup>a</sup> | Catalyst (mol%)        | Ligand (mol%)            | Solvent | Temp. [°C] | Conversion <sup>b</sup> [%] | Yield <sup>b</sup> [%] | e.r. <sup>c</sup> |
|--------------------|------------------------|--------------------------|---------|------------|-----------------------------|------------------------|-------------------|
| 1                  | <b>C1</b> (20)         | —                        | Toluene | 65         | 56                          | 46                     | 50:50             |
| 2                  | <b>C2</b> (10)         | —                        | Toluene | 65         | >95                         | 68                     | 50:50             |
| 3                  | <b>C3</b> (10)         | —                        | Toluene | 65         | 65                          | 64                     | 50:50             |
| 4                  | <b>C5</b> (10)         | —                        | Toluene | 65         | 13                          | 11                     | 93:7              |
| 5                  | <b>C5</b> (20)         | —                        | Toluene | 65         | 21                          | 20                     | 93:7              |
| 6                  | <b>Mo-Precat.</b> (10) | $(S_a)$ - <b>L1</b> (30) | Toluene | 65         | >95                         | 84                     | 75:25             |
| 7                  | <b>Mo-Precat.</b> (20) | $(S_a)$ - <b>L1</b> (60) | Toluene | 65         | >95                         | 87                     | 74:26             |
| 8                  | <b>Mo-Precat.</b> (20) | $(S_a)$ - <b>L1</b> (60) | Toluene | 50         | >95                         | 61                     | 70:30             |
| 9                  | <b>Mo-Precat.</b> (20) | $(R_a)$ - <b>L2</b> (60) | Toluene | 65         | >95                         | 83                     | 6:94              |
| 10                 | <b>Mo-Precat.</b> (20) | $(S_a)$ - <b>L2</b> (60) | Toluene | rt         | 75                          | —                      | 95:5              |
| 11                 | <b>Mo-Precat.</b> (20) | $(S_a)$ - <b>L3</b> (60) | Toluene | 65         | >95                         | 41                     | 91:9              |

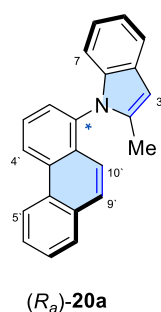
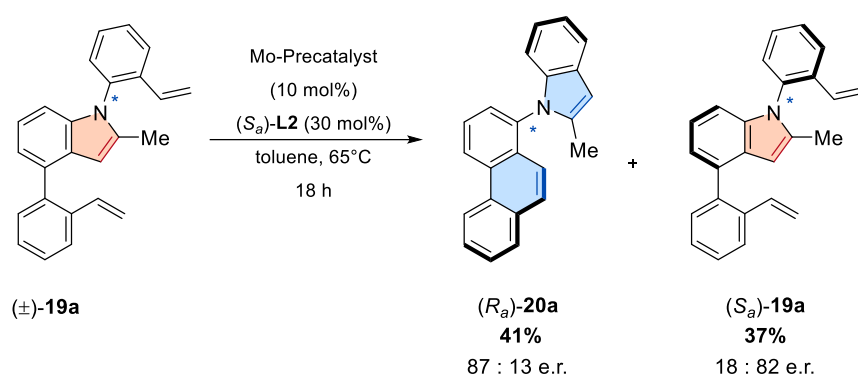
<sup>a</sup>Reactions were performed on 7.50  $\mu\text{mol}$  scale of **19c** for 18 h. <sup>b</sup>Conversion and yield were determined by <sup>1</sup>H-NMR with durene as an internal standard. <sup>c</sup>Determined by HPLC on a chiral stationary phase of the crude product (Chiralpak IG-N3 column (3  $\mu\text{m}$ , 250x4.6 mm, heptane/*i*-PrOH 96:4, 1.0 mL/min, 20°C).



## General Procedure N for atroposelective indole ring-opening metathesis:

Mo-precursor (4.14 mg, 7.00  $\mu$ mol, 10%), (*S<sub>a</sub>*)-3,3'-bis(perfluorophenyl)-[1,1'-binaphthalene]-2,2'-diol (*S<sub>a</sub>*)-**L2** (13.0 mg, 21.0  $\mu$ mol, 30 mol%) were weighed in 10mL crimp cap vial and toluene (1.5 mL) was added. The obtained solution was stirred for 1 h at room temperature in an argon-filled glovebox before a solution of the corresponding substrate (70.0  $\mu$ mol, 1.00 eq.) in toluene (0.83 mL) was added. The capped vial was then taken out of the glovebox and stirred at 65°C for 18 h. The reaction mixture was diluted with EtOAc and filtered through a thin layer of silica gel. The solvents were removed under reduced pressure and the residue was purified by silica gel column chromatography (cyclohexane/EtOAc 100:0→80:20) to give the desired product. The e.r. of the isolated products were determined by HPLC on a chiral stationary phase.

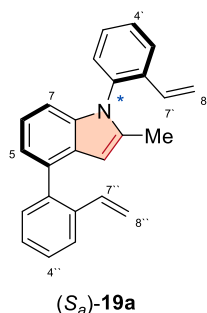
### (*R<sub>a</sub>*)-2-Methyl-1-(phenanthren-1-yl)-1*H*-indole ((*R<sub>a</sub>*)-**20a**):



Prepared according to the general procedure **N** using 2-methyl-1,4-bis(2-vinylphenyl)-1*H*-indole ( $\pm$ )-**19a** (23.5 mg, 70.0  $\mu$ mol) to give the title compound (*R<sub>a</sub>*)-**20a** as yellow oil (8.90 mg, 29.0  $\mu$ mol, 41%, 87 : 13 e.r.) after preparative thin layer chromatography (pTLC, cyclohexane/EtOAc 5:1): *R<sub>f</sub>* 0.55 (cyclohexane/EtOAc 5:1);  $[\alpha]_D^{22} = -86$  (c 0.47, CHCl<sub>3</sub>);  $\nu_{\text{max}}$  (neat): 3052w, 2981w, 2917w, 2844w, 1599w, 1554w, 1467s, 1385m, 1321w, 1218w, 1159w; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.87 (1H, d, <sup>3</sup>*J* 8.6 Hz, C4'*H*), 8.78 (1H, d, <sup>3</sup>*J* 8.0 Hz, C5'*H*), 7.92 – 7.84 (1H, m, C8'*H*), 7.80 (1H, dd, <sup>3</sup>*J* 8.6, <sup>3</sup>*J* 7.4 Hz, C3'*H*), 7.72 (1H, ddd, <sup>3</sup>*J* 8.0, <sup>3</sup>*J* 7.0, <sup>4</sup>*J* 1.4 Hz, C6'*H*), 7.67 – 7.57 (4H, m, C4*H*, C2'*H*, C7'*H*, C9'*H*), 7.13 (1H, ddd, <sup>3</sup>*J* 8.0, <sup>3</sup>*J* 7.1, <sup>4</sup>*J* 1.0 Hz, C5*H*), 7.05 – 6.94 (2H, m, C6*H*, C10'*H*), 6.78 (1H, dd, <sup>3</sup>*J* 8.2, <sup>4</sup>*J* 1.0 Hz, C7*H*), 6.56 – 6.46 (1H, m, C3*H*), 2.17 (3H, d, <sup>4</sup>*J* 0.9 Hz, C2–CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 139.4 (C7*a*), 138.5 (C2), 135.2 (C1'), 132.1 (C8*a*'), 131.9 (C4*a*'), 130.6 (C10*a*'), 130.3 (C4*b*'), 128.9 (C8'), 128.6 (C9'), 128.4 (C3*a*), 127.6 (C2'), 127.31 (C6'/C7'), 127.26 (C6'/C7'), 126.5 (C3'), 123.6 (C4'), 123.1 (C5'), 121.5 (C10'), 121.2 (C6), 120.1 (C5), 119.7 (C4), 110.4 (C7), 101.1 (C3), 13.1 (C2–CH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>23</sub>H<sub>18</sub>N 308.1434 found 308.1436 [M+H<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu$ m, 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 97.5 : 2.5, 20°C): *t*<sub>major</sub> = 5.8 min and *t*<sub>minor</sub> = 6.1 min.

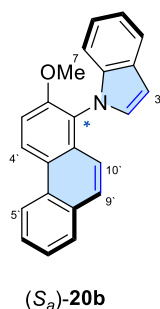


**(*S<sub>a</sub>*)-2-Methyl-1,4-bis(2-vinylphenyl)-1*H*-indole ((*S<sub>a</sub>*)-**19a**):**



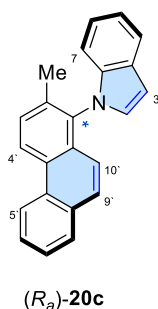
Prepared according to the general procedure **N** using 2-methyl-1,4-bis(2-vinylphenyl)-1*H*-indole ( $\pm$ )-**19a** (23.5 mg, 70.0  $\mu$ mol) to give (*R<sub>a</sub>*)-2-methyl-1,4-bis(2-vinylphenyl)-1*H*-indole (*S<sub>a</sub>*)-**19a** as yellow solid (8.70 mg, 26.0  $\mu$ mol, 37% recovered, 18 : 82 e.r., m.p. 150.4 – 151.5°C) after preparative thin layer chromatography (pTLC, cyclohexane/EtOAc 5:1);  $R_f$  0.71 (cyclohexane/EtOAc 5:1);  $[\alpha]_D^{22} = -8.0$  (c 1.1, CHCl<sub>3</sub>). The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu$ m, 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 97.5 : 2.5, 20°C):  $t_{major} = 4.1$  min and  $t_{minor} = 3.9$  min.

**(*S<sub>a</sub>*)-1-(2-Methoxyphenanthren-1-yl)-1*H*-indole ((*S<sub>a</sub>*)-**20b**):**



Prepared according to the general procedure **N** using 7-methoxy-1,4-bis(2-vinylphenyl)-1*H*-indole **19b** (24.6 mg, 70.0  $\mu$ mol) to give the title compound (*S<sub>a</sub>*)-**20b** as a beige oil (9.0 mg, 27.8  $\mu$ mol, 40%, 75 : 25 e.r.) after preparative thin layer chromatography (pTLC, cyclohexane/EtOAc 4:1);  $R_f$  0.29 (cyclohexane/EtOAc 5:1);  $[\alpha]_D^{22} = -61$  (c 0.11, CHCl<sub>3</sub>);  $\nu_{max}$  (neat): 3051w, 2962w, 2842w, 1692w, 1611m, 1528w, 1480s, 1454s, 1356w, 1274m, 1068m, 969w, 907m, 816w, 734s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.81 (1H, d, <sup>3</sup>*J* 9.1 Hz, C4'*H*), 8.67 (1H, d, <sup>3</sup>*J* 8.3 Hz, C5'*H*), 7.85 – 7.80 (1H, m, C8'*H*), 7.76 (1H, dt, <sup>3</sup>*J* 7.9, <sup>4</sup>*J* 0.9 Hz, C4*H*), 7.68 (1H, ddd, <sup>3</sup>*J* 8.3, <sup>3</sup>*J* 7.0, <sup>4</sup>*J* 1.4 Hz, C6'*H*), 7.61 – 7.54 (2H, m, C7'*H*, C9'*H*), 7.51 (1H, d, <sup>3</sup>*J* 9.1 Hz, C3'*H*), 7.27 (1H, d, <sup>3</sup>*J* 3.2 Hz, C2*H*), 7.19 – 7.14 (1H, m, C5*H*), 7.10 (1H, ddd, <sup>3</sup>*J* 8.1, <sup>3</sup>*J* 7.1, <sup>4</sup>*J* 1.2 Hz, C6*H*), 7.04 (1H, d, <sup>3</sup>*J* 9.2 Hz, C10'*H*), 6.87 – 6.83 (1H, m, C7*H*), 6.81 (1H, dd, <sup>3</sup>*J* 3.1, <sup>4</sup>*J* 0.9 Hz, C3*H*), 3.85 (3H, s, OCH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 154.7 (C2'), 138.0 (C7*a*), 131.7 (C10*a*'), 131.0 (C8*a*'), 130.29 (C4*b*'), 130.23 (C2), 129.0 (C9'), 128.9 (C8'), 128.4 (C3*a*), 127.3 (C6'), 126.4 (C7'), 125.2 (C4*a*'), 124.6 (C4'), 122.6 (C1'), 122.4 (C5'), 122.1 (C6), 121.4 (C10'), 121.0 (C4), 120.0 (C5), 112.7 (C3'), 110.9 (C7), 102.8 (C3), 56.6 (OCH<sub>3</sub>); ESI-MS: *m/z* calcd. for C<sub>23</sub>H<sub>18</sub>O 324.1383 found 324.1381 [M+H<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IB 3  $\mu$ m, 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 97.5 : 2.5, 20°C):  $t_{major} = 9.1$  min and  $t_{minor} = 9.5$  min.

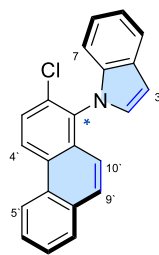
**(*R<sub>a</sub>*)-1-(2-Methylphenanthren-1-yl)-1*H*-indole ((*R<sub>a</sub>*)-**20c**):**



Prepared according to the general procedure **N** using 7-methyl-1,4-bis(2-vinylphenyl)-1*H*-indole **19c** (23.5 mg, 70.0  $\mu$ mol) to give the title compound (*R<sub>a</sub>*)-**20c** as a beige oil (20.1 mg, 65.4  $\mu$ mol, 93%, 97 : 3 e.r.);  $R_f$  0.72 (cyclohexane/EtOAc 5:1);  $[\alpha]_D^{22} = -121$  (c 0.09, CHCl<sub>3</sub>);  $\nu_{max}$  (neat): 3053w, 3017w, 2922w, 2848w, 1600w, 1474s, 1391w, 1320m, 1218m, 1010w, 968w, 816m, 741s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.87 – 8.69 (2H, m, C4'*H*, C5'*H*), 7.85 (1H, d, <sup>3</sup>*J* 7.8 Hz, C8'*H*), 7.78 (1H, d, <sup>3</sup>*J* 8.0 Hz, C4*H*), 7.73 – 7.64 (2H, m, C3'*H*,

C6`H), 7.63 – 7.54 (2H, m, C7`H, C9`H), 7.24 (1H, d,  $^3J$  3.0 Hz, C2H), 7.21 – 7.16 (1H, m, C5H), 7.11 (1H, t,  $^3J$  7.5 Hz, C6H), 6.97 (1H, d,  $^3J$  9.1 Hz, C10`H), 6.86 – 6.76 (2H, m, C3H, C7H), 2.17 (3H, s, C2`–CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 137.7 (C7a), 135.6 (C2`), 134.4 (C1`), 131.7 (C8a`), 130.8 (C10a`), 130.2 (C4b`), 129.7 (C4a`), 129.4 (C2), 129.0 (C3`), 128.8 (C8`), 128.5 (C9`), 128.3 (C3a), 127.1 (C6`), 126.9 (C7`), 123.3 (C4`), 122.8 (C5`), 122.4 (C6), 121.7 (C10`), 121.1 (C4), 120.1 (C5), 110.7 (C7), 103.0 (C3), 17.8 (CH<sub>3</sub>); ESI-MS: m/z calcd. for C<sub>23</sub>H<sub>18</sub>N 308.1434 found 308.1431 [M+H<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu$ m, 250x 4.6 mm, 1.0 mL/min, heptane/iPrOH 96 : 4, 20°C): t<sub>major</sub> = 5.3 min and t<sub>minor</sub> = 5.5 min.

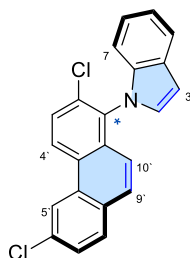
**(S<sub>a</sub>)-1-(2-Chlorophenanthren-1-yl)-1H-indole ((S<sub>a</sub>)-20d):**



(S<sub>a</sub>)-20d

Prepared according to the general procedure **N** using 7-chloro-1,4-bis(2-vinylphenyl)-1H-indole **19d** (24.9 mg, 70.0  $\mu$ mol) to give the title compound (S<sub>a</sub>)-**20d** as a beige solid (20.9 mg, 63.8  $\mu$ mol, 91%, 96:4 e.r., m.p. 115.7 – 117.0°C): R<sub>f</sub> 0.42 (cyclohexane/EtOAc 5:1); [ $\alpha$ ]<sub>D</sub><sup>22</sup> = –82 (c 0.11, CHCl<sub>3</sub>);  $\nu_{\max}$  (neat): 3058w, 2922w, 2855w, 1588w, 1512m, 1469s, 1391w, 1317w, 1227w, 1144w, 1078w, 1034w, 897w, 859w, 817m, 745s; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.79 (1H, d,  $^3J$  9.0 Hz, C4`H), 8.72 (1H, d,  $^3J$  8.3 Hz, C5`H), 7.90 – 7.85 (1H, m, C8`H), 7.83 (1H, d,  $^3J$  9.0 Hz, C3`H), 7.78 (1H, dt,  $^3J$  7.9,  $^4J$  0.9 Hz, C4H), 7.73 (1H, ddd,  $^3J$  8.3,  $^3J$  7.0,  $^4J$  1.4 Hz, C6`H), 7.68 – 7.62 (2H, m, C7`H, C9`H), 7.27 (1H, d,  $^3J$  3.2 Hz, C2H), 7.20 (1H, ddd,  $^3J$  7.9,  $^3J$  7.1,  $^4J$  1.0 Hz, C5H), 7.14 (1H, td,  $^3J$  7.9,  $^4J$  1.2 Hz, C6H), 7.02 (1H, d,  $^3J$  9.1 Hz, C10`H), 6.85 (1H, dd,  $^3J$  3.2,  $^4J$  0.9 Hz, C3H), 6.85 – 6.81 (1H, m, C7H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 137.6 (C7a), 133.4 (C1`), 132.4 (C2`), 131.92 (C10a`), 131.90 (C8a`), 130.1 (C4a`), 129.8 (C4b`), 129.7 (C9`), 129.4 (C2), 129.0 (C8`), 128.4 (C3a), 127.64 (C3`/C6`), 127.63 (C3`/C6`), 127.59 (C7`), 124.7 (C4`), 122.9 (C5`), 122.6 (C6), 121.4 (C10`), 121.2 (C4), 120.5 (C5), 110.7 (C7), 103.7 (C3); ESI-MS: m/z calcd. for C<sub>22</sub>H<sub>14</sub>AgClN 433.9860 found 433.9860 [M+Ag<sup>+</sup>]. The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IG 3  $\mu$ m, 250x 4.6 mm, 1.0 mL/min, heptane/iPrOH 99 : 1, 20°C): t<sub>major</sub> = 7.8 min and t<sub>minor</sub> = 8.4 min.

**(S<sub>a</sub>)-1-(2,6-Dichlorophenanthren-1-yl)-1H-indole ((S<sub>a</sub>)-20e):**



(S<sub>a</sub>)-20e

Prepared according to the general procedure **N** using 7-chloro-4-(5-chloro-2-vinylphenyl)-1-(2-vinylphenyl)-1H-indole **19e** (27.3 mg, 70.0  $\mu$ mol) to give the title compound (S<sub>a</sub>)-**20e** as a white solid (17.0 mg, 46.9  $\mu$ mol, 67%, 96:4 e.r., m.p. 67.0 – 68.0°C) after preparative thin layer chromatography (pTLC, cyclohexane/EtOAc 5:1): R<sub>f</sub> 0.61 (cyclohexane/EtOAc 5:1); [ $\alpha$ ]<sub>D</sub><sup>22</sup> = –56 (c 0.11, CHCl<sub>3</sub>);  $\nu_{\max}$  (neat): 2973w, 2902w, 1697w, 1587w, 1511w, 1467s, 1383w, 1317w, 1225w, 1153w, 1076m, 904w, 868w, 839w, 790m; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.70 (d,  $^3J$  8.8 Hz, C4`H), 8.68 (1H, d,  $^4J$  1.9 Hz, C5`H), 7.85 (1H, d,  $^3J$  8.8 Hz, C3`H), 7.81 (1H, d,  $^3J$  8.5 Hz, C8`H),

7.78 (1H, dt,  $^3J$  7.9,  $^4J$  1.1 Hz, C4H), 7.65 – 7.58 (2H, m, C7'H, C9'H), 7.26 (1H, d,  $^3J$  2.9 Hz, C2H), 7.24 – 7.18 (1H, m, C5H), 7.14 (1H, ddd,  $^3J$  8.2,  $^3J$  7.1,  $^4J$  1.1 Hz, C6H), 7.03 (1H, dd,  $^3J$  9.2,  $^5J$  0.6 Hz, C10'H), 6.86 (1H, dd,  $^3J$  3.2,  $^5J$  0.9 Hz, C3H), 6.82 (1H, dd,  $^3J$  8.2,  $^6J$  0.9 Hz, C7H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 137.6 (C7a), 133.7 (C6'), 133.5 (C1'), 133.2 (C2'), 132.2 (C10a'), 130.9 (C4b'), 130.3 (C8'), 130.2 (C8a'), 129.3 (C2), 129.0 (C4a'), 128.4 (C3a), 128.2 (C7'), 128.0 (C3'), 124.7 (C4'), 122.70 (C5'), 122.68 (C6), 121.8 (C10'), 121.2 (C4), 120.6 (C5), 110.7 (C7), 103.8 (C3); ESI-MS:  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{13}\text{Cl}_2\text{NNa}$  384.0317 found 384.0311  $[\text{M}+\text{Na}^+]$ . The e.r. of the isolated product was determined by HPLC on a chiral stationary phase (Chiralcel IB 3  $\mu\text{m}$ , 250x 4.6 mm, 1.0 mL/min, heptane/*i*PrOH 97.5 : 2.5, 20°C):  $t_{\text{major}}$  = 6.7 min and  $t_{\text{minor}}$  = 7.3 min.

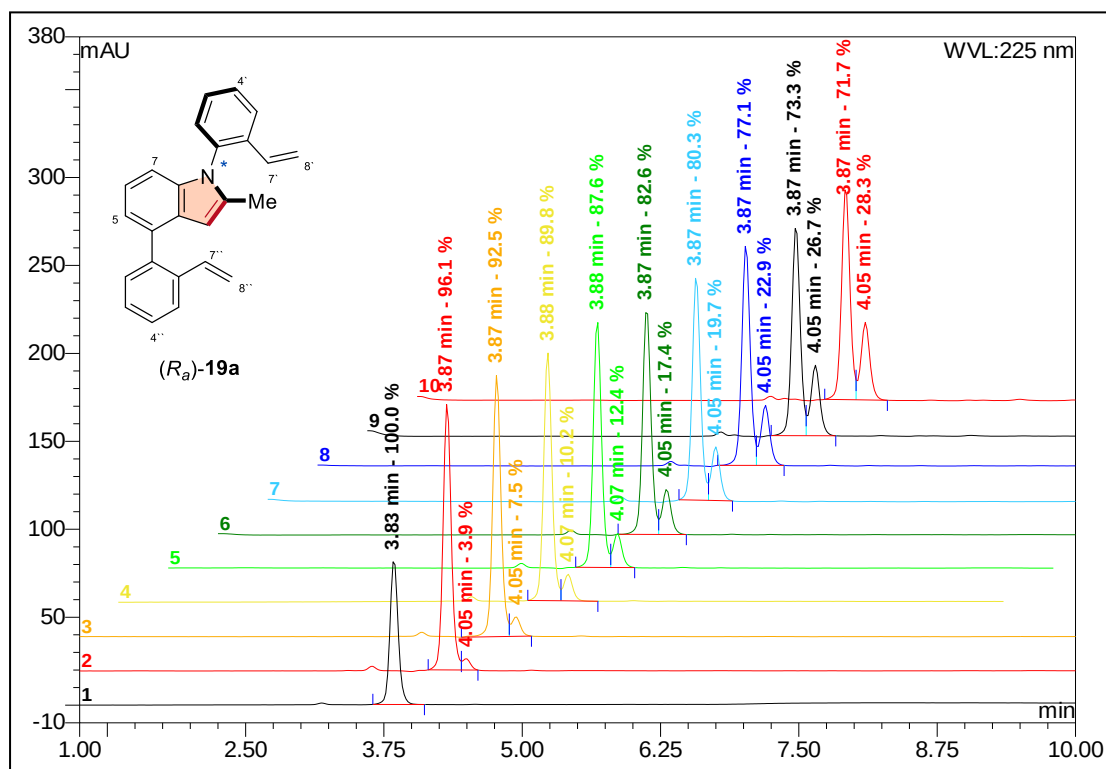
## Determination of the Rotational Barriers

Separation of atropisomers (**(R<sub>a</sub>)-19a** and (**(S<sub>a</sub>)-19a**) was performed on a chiral stationary phase (Chiralpak IG (3 μm, 250×4.6 mm), heptane/*i*PrOH 97.5 : 2.5, 1.0 mL/min, 20°C), Separation of atropisomers (**(R<sub>a</sub>)-20a** and (**(S<sub>a</sub>)-20a**) was performed on a chiral stationary phase (Chiralpak IG (3 μm, 250×4.6 mm), heptane/*i*PrOH 97.5 : 2.5, 1.0 mL/min, 20°C).

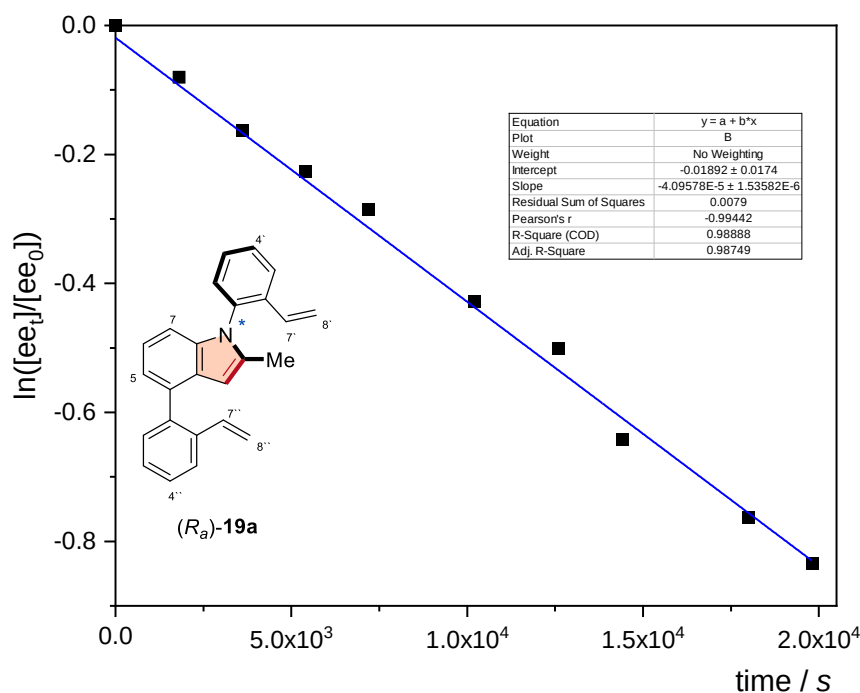
### Determination of the Rotational Barrier of 19a:

A stirred solution of (**(R<sub>a</sub>)-19a**) (*t* = 3.9 min) in heptane was heated to 115°C for 5.5 h. Aliquots were withdrawn in regular time intervals and analyzed by NP-HPLC (Chiralpak IG (3 μm, 250×4.6 mm), heptane/*i*PrOH 97.5 : 2.5, 1.0 mL/min, 20°C) (Figure S1). The rate constant was obtained from the slope of the plot ln([*ee*<sub>t</sub>]/[*ee*<sub>0</sub>]) against *t* (Figure S2) to give *k<sub>r</sub>* = 4.10•10<sup>-5</sup> s<sup>-1</sup>. With *k<sub>r</sub>* and Eyring equation, the Gibbs free energy energy Δ*G*<sup>‡</sup> of the rotational barrier was calculated:

$$\Delta G^\ddagger = -RT \ln \left( \frac{k_r h}{2k_B T} \right) = 130 \text{ kJ} \cdot \text{mol}^{-1}$$



**Figure S1.** Overlay of the HPLC traces of the thermal isomerization of (**(R<sub>a</sub>)-19a**) after 0, 0.5, 1, 1.5, 2, 2.8, 3.5, 4, 5, 5.5 h

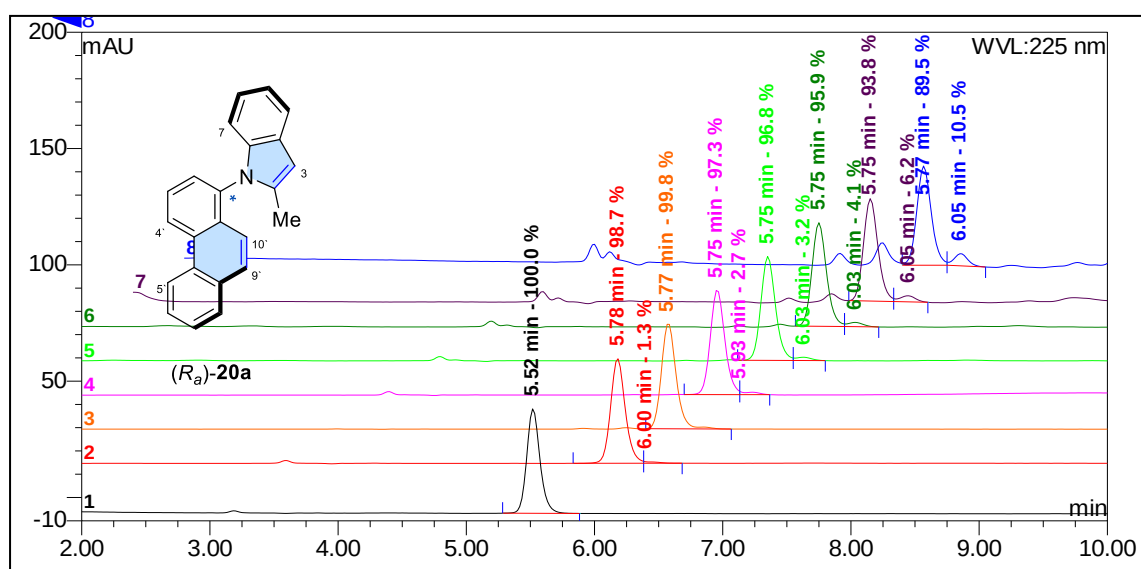


**Figure S2.** Plot for the racemization of **(R<sub>a</sub>)-19a** in heptane at 115°C

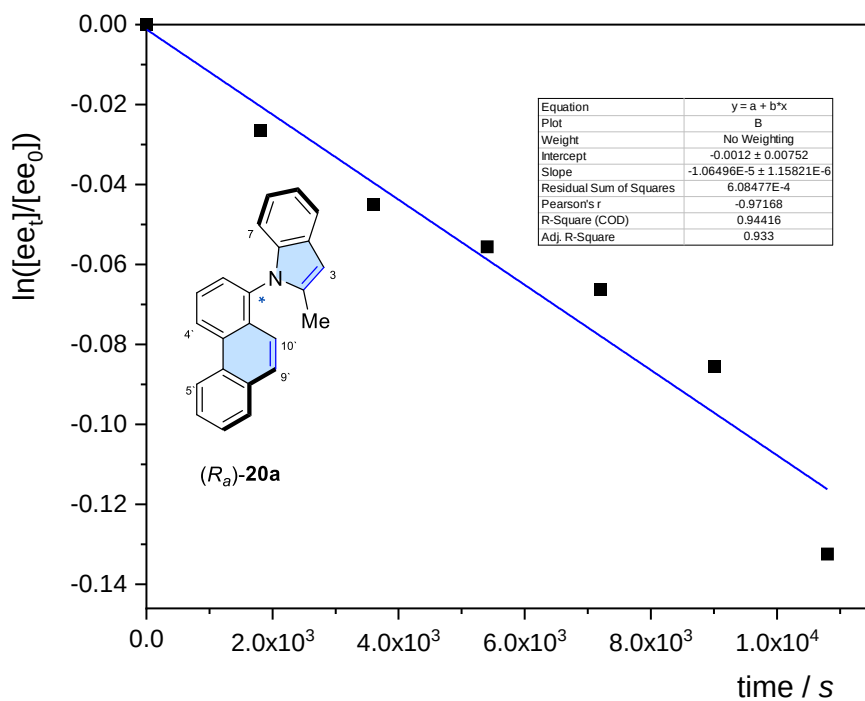
#### Determination of the Rotational Barrier of **20a**:

A stirred solution of **(R<sub>a</sub>)-20a** (*t* = 5.8 min) in heptane was heated to 140°C for 3.5 h. Aliquots were withdrawn in regular time intervals and analyzed by NP-HPLC (Chiralpak IG (3 μm, 250×4.6 mm), heptane/*i*PrOH 97.5 : 2.5, 1.0 mL/min, 20°C) (Figure S3). The rate constant was obtained from the slope of the plot  $\ln([ee_t]/[ee_0])$  against *t* (Figure S4) to give  $k_r = 1.06 \cdot 10^{-5} \text{ s}^{-1}$ . With  $k_r$  and Eyring equation, the Gibbs free energy  $\Delta G^\ddagger$  of the rotational barrier was calculated:

$$\Delta G^\ddagger = -RT \ln \left( \frac{k_r h}{2k_B T} \right) = 144 \text{ kJ} \cdot \text{mol}^{-1}$$



**Figure S3.** Overlay of the HPLC traces of the thermal isomerization of **(R<sub>a</sub>)-20a** after 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5 h



**Figure S4.** Plot for the racemization of **(*R<sub>a</sub>*)-20a** in heptane at **140°C**

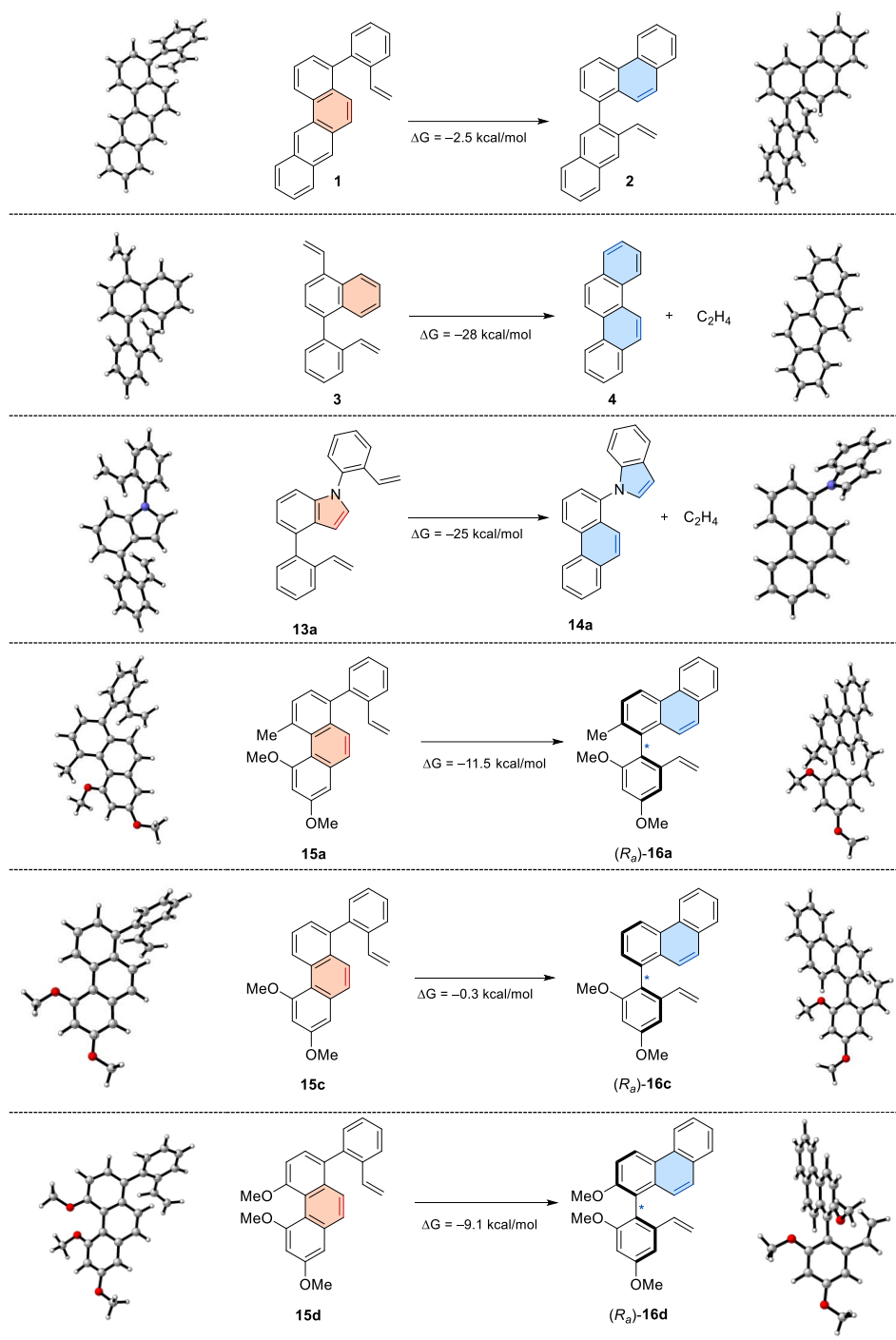
**Note:** Deviation from linearity may arise from the particularly slow racemization of **(*R<sub>a</sub>*)-20a** along with the decomposition of the product as indicated by the appearance of new signals in addition to ones for **20a**.

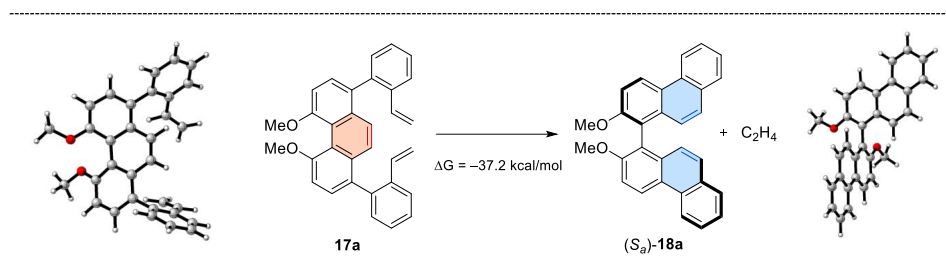
## Computational Studies

### Gibbs Free Energy Differences of the Selected Pairs of Starting Materials and Products

Density functional theory (DFT) calculations were performed using the Gaussian 16 (revision C.01) program<sup>14</sup>. Geometry optimizations were performed at the B3LYP-D3(BJ) level of theory with the def2-TZVP basis set in the gas phase<sup>12</sup>. Harmonic vibrational frequencies were evaluated for the optimized geometries, with minima characterized by the absence of imaginary frequencies. Quasiharmonic corrections to the entropy for frequencies below 100 cm<sup>-1</sup> were calculated with the Goodvibes program by employing the method of Grimme. Single point energies were calculated at B3LYP-D3(BJ) level of theory with the def2-TZVP basis set with implicit solvation model SMD for toluene. The optimized structures were visualized in CYLView<sup>13</sup>.

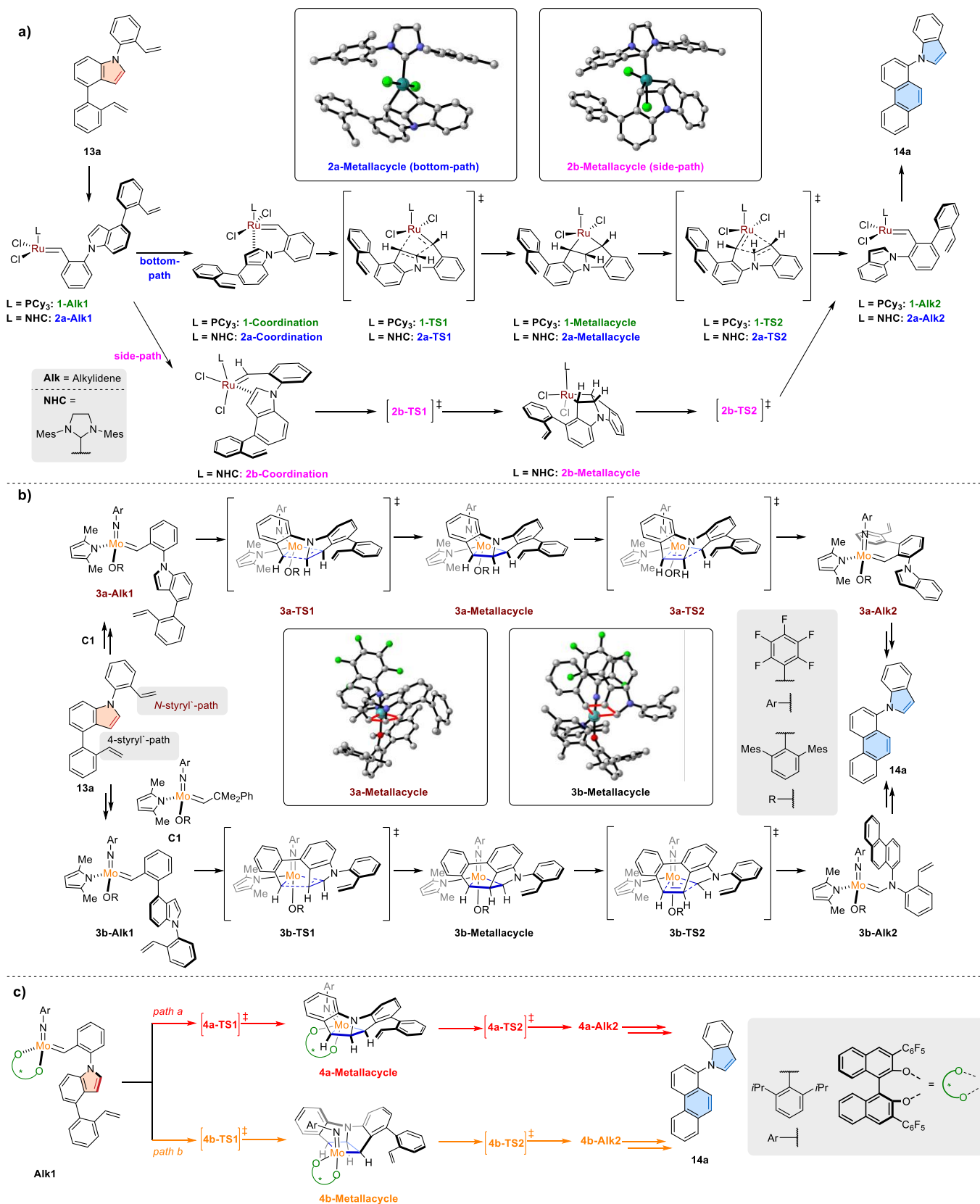
**Supplementary Table 16.** DFT computed Gibbs free energies for selected substrates and the corresponding products (SMD(toluene)/B3LYP-D3(BJ)/def2-TZVP//B3LYP-D3(BJ)/def2-TZVP)



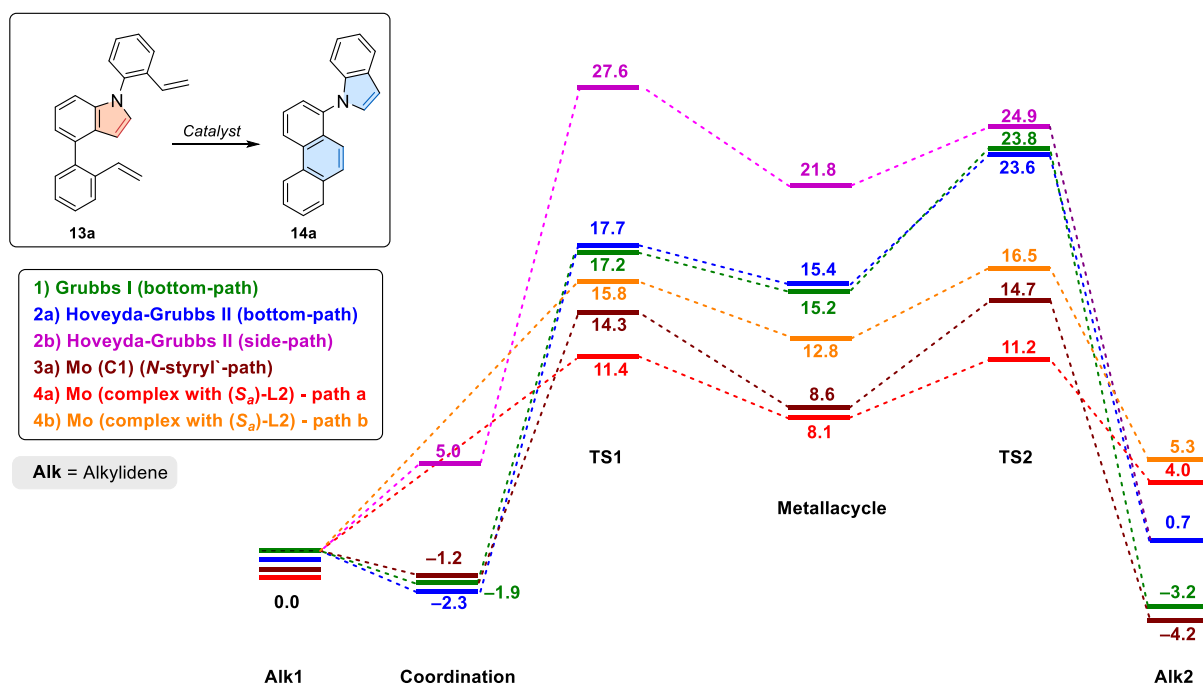




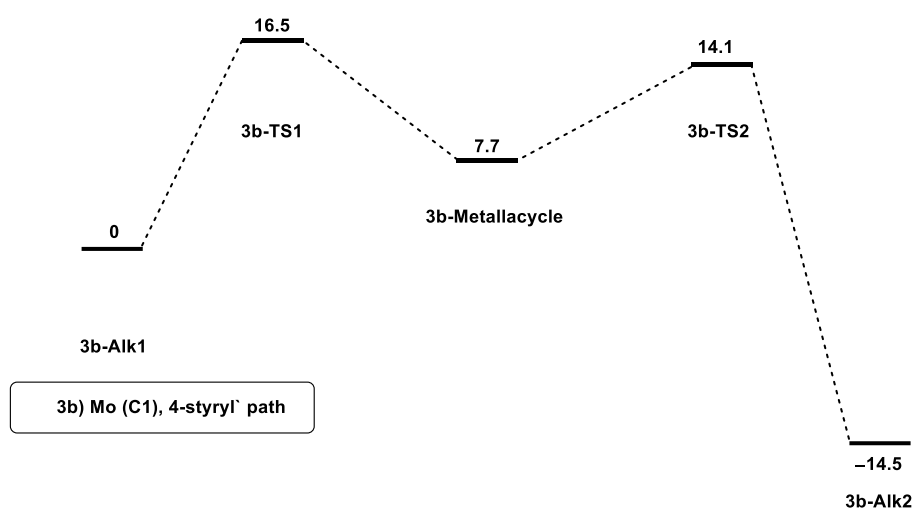
## Comparison of Metathesis Catalysts



Density functional theory (DFT) calculations were performed using the Gaussian 16 (revision C.01) program.<sup>14</sup> Geometries of intermediates and transition states were optimized using the dispersion-corrected B3LYP-D3 functional. The SDD basis set was used for Mo/Ru atoms, while the 6-31G(d) basis set was applied for other atoms. Vibrational frequency calculations were performed at the same level of theory of the optimization to confirm if each structure is a local minimum (zero imaginary frequencies) or a transition state (one imaginary frequency). Single-point energy calculations were carried out using the M06 functional with the SDD basis set for Mo/Ru atoms and 6-311+G(d,p) basis set for other atoms<sup>15</sup>. Solvent effects were accounted for with the SMD model of toluene, which was the solvent of choice in experiments. Quasiharmonic corrections to the entropy for frequencies below 100 cm<sup>-1</sup> were calculated with the Goodvibes program by employing the method of Grimme<sup>16</sup>.



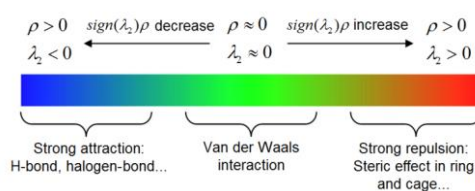
**Figure S6.** DFT-calculated Gibbs free energies (kcal/mol) of the reaction profiles of **13a** with different Mo- and Ru-based catalysts. SMD(toluene)/M06/SDD(Mo/Ru)-6-311+G(d,p)//B3LYP-D3(BJ)/SDD(Mo/Ru)-6-31G(d)



**Figure S7.** DFT-calculated Gibbs free energies (kcal/mol) of the reaction profile of **13a** with **C1** as a catalyst, 4-styryl' path.

## Visualization of Noncovalent interactions (NCI) in DFT Computed Metallacycles

The Multiwgn software<sup>17</sup>, version 3.8, and .fchk files from the single-point DFT-calculations were used for the noncovalent interactions (NCI) analysis<sup>18</sup>, and VMD<sup>19</sup>, version 1.9.4, for the visualization. An isovalue of 0.5 and grid spacing of 0.116 Bohr was used for the isosurfaces in the 3D representations.



The colour code used for NCI plots

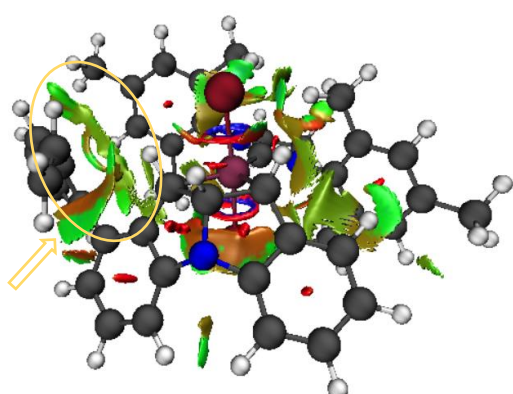


Figure S8. NCI plot for 2a-Metallacycle

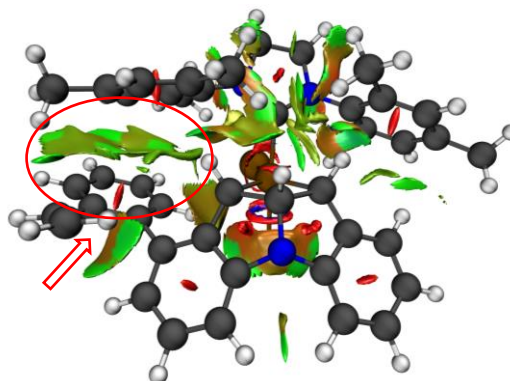


Figure S9. NCI plot for 2b-Metallacycle

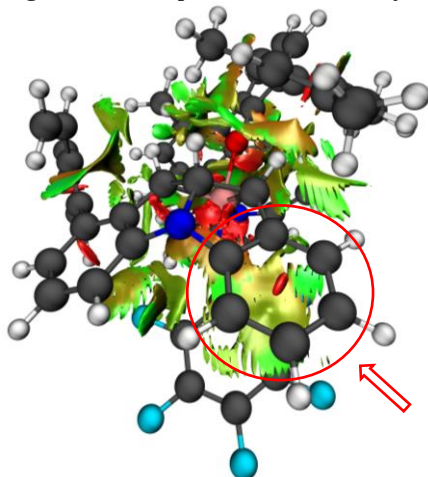


Figure S10. NCI plot for 3a-Metallacycle

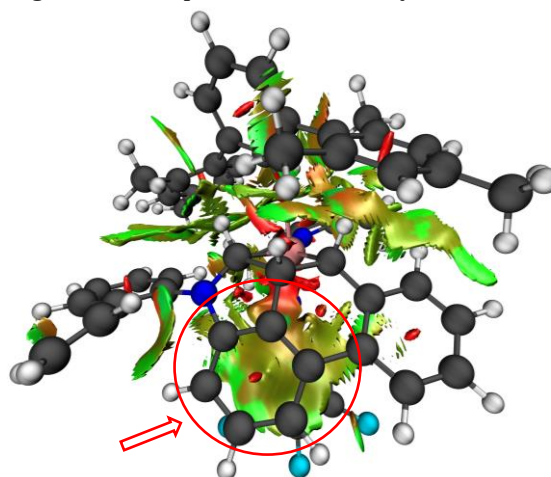


Figure S11. NCI plot for 3b-Metallacycle

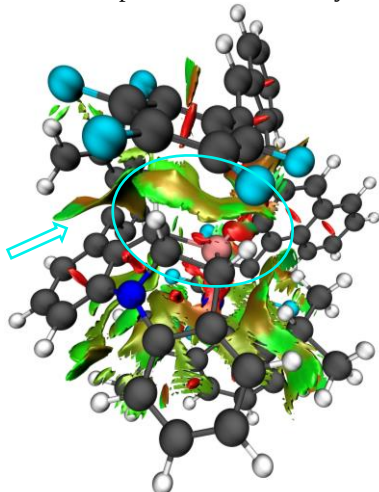


Figure S11. NCI plot for 4a-Metallacycle

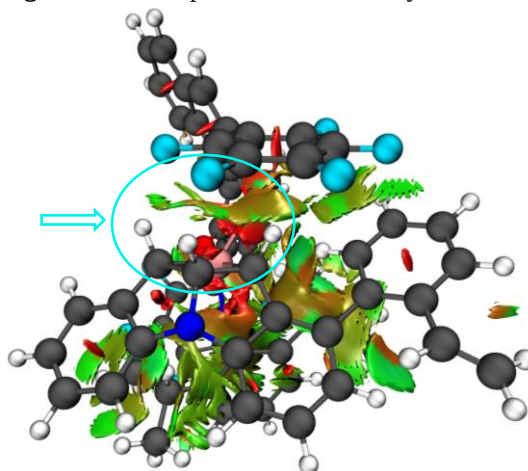
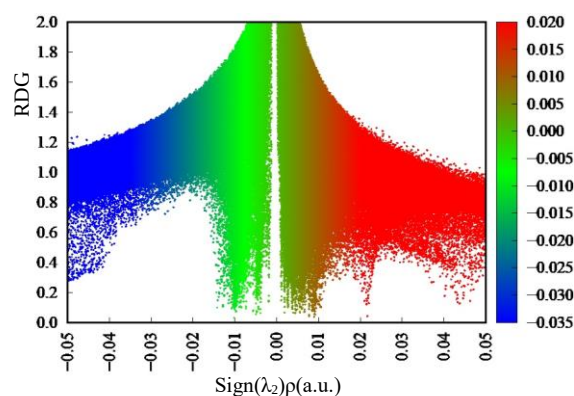
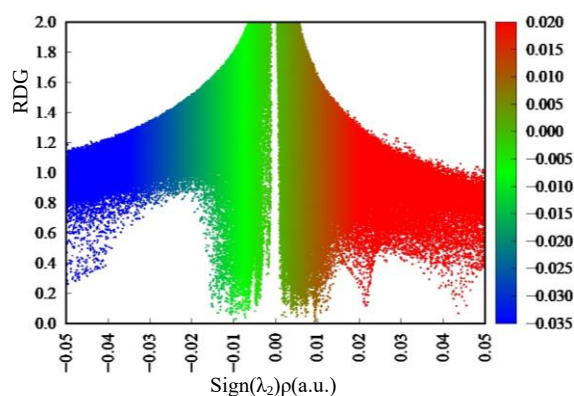


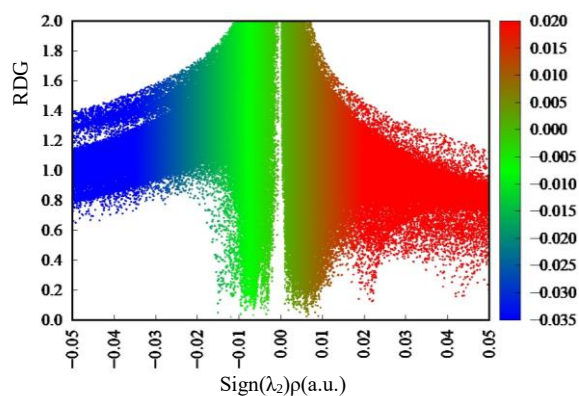
Figure S12. NCI plot for 4b-Metallacycle



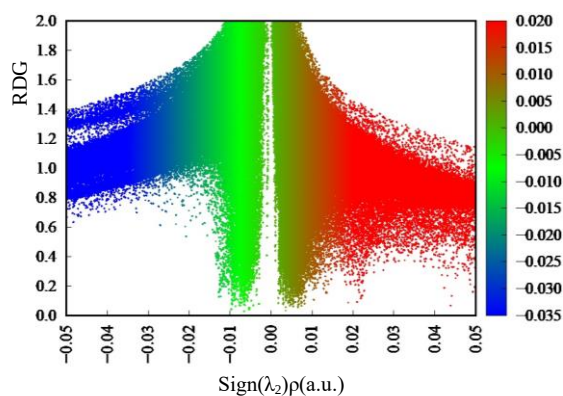
**Figure S13.** RDG scatter plot for **2a**-Metallacycle



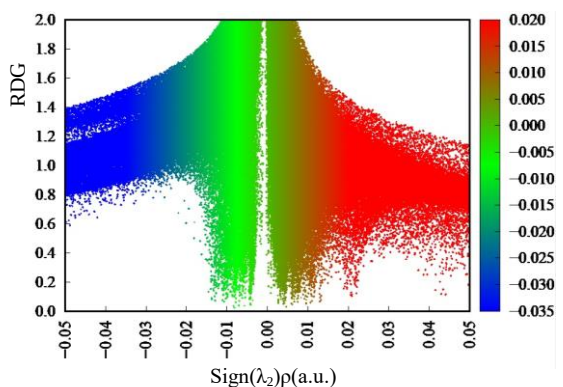
**Figure S14.** RDG scatter plot for **2b**-Metallacycle



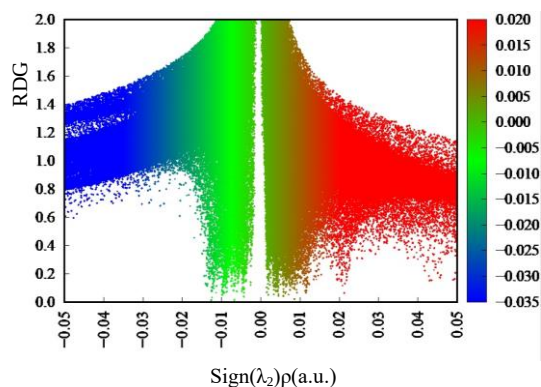
**Figure S15.** RDG scatter plot for **3a**-Metallacycle



**Figure S16.** RDG scatter plot for **3b**-Metallacycle



**Figure S17.** RDG scatter plot for **4a**-Metallacycle



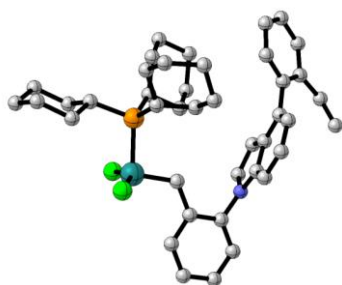
**Figure S18.** RDG scatter plot for **4b**-Metallacycle

**Note:** NCI analysis of a selection of metallacycles (**2a/b**, **3a/b**, **4a/b**) was performed to determine the major NCIs that could contribute to the energy differences between these reaction intermediates. The commonly observed NCIs included C–H $\cdots\pi$  and  $\pi$ – $\pi$  interactions. For example, stronger  $\pi$ – $\pi$  interactions observed for the metallacycle **3b** (Figure S11) in comparison to the metallacycle **3a** (Figure S10) could partially explain its higher stability. On the other hand, metallacycle-**4a** possesses more C–H $\cdots\pi$  interactions (Figure S11) than metallacycle **4b** (Figure S12), which might be among the factors causing its lower Gibbs free energy.



## Cartesian Coordinates for All Optimized Geometries

### 1-Alk1:



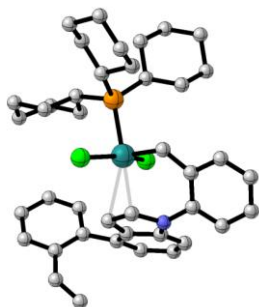
**G<sub>sol</sub>** = -3003.519161

P 1.90460800 -0.82185100 -0.01971800  
Ru 2.23636600 1.38719800 -0.28482900  
Cl 3.23068400 1.81524000 1.78574400  
Cl 2.46978800 1.31570900 -2.60268900  
C 0.51856700 1.95169600 -0.02219900  
H -0.32800500 1.27605300 0.06995700  
H -0.37486100 0.08145600 1.68214500  
C 0.81504000 -1.60907800 -1.31606300  
C 1.33639700 -1.27197000 1.70912500  
C 3.52473000 -1.74251400 -0.21365800  
C 5.37384200 -2.58139300 -1.72027700  
C 5.85088600 -2.11199600 0.71555300  
C 6.42821700 -2.12675200 -0.70450100  
C 4.58542100 -1.24812400 0.78857200  
C 4.09935600 -1.72687200 -1.64233900  
H 5.11521500 -3.63326500 -1.52717300  
H 5.60894000 -3.14053100 1.02289000  
H 6.76555200 -1.11313900 -0.96451400  
H 4.84260600 -0.20833300 0.55681000  
H 4.32189400 -0.69644300 -1.93991800  
H 3.28339300 -2.78580300 0.03054000  
H 5.77905200 -2.53940200 -2.73846700  
H 6.59400800 -1.73626100 1.42906500  
H 7.31069400 -2.77627100 -0.75380800  
H 4.19180800 -1.23410900 1.80939600  
H 3.36842200 -2.10363700 -2.36421300  
C -0.19827400 -3.72156500 -2.28055500  
C -1.17789000 -1.46863700 -2.85045600  
C -1.47901800 -2.95370800 -2.62637000  
C -0.47465900 -0.83812300 -1.64084700  
C 0.51519600 -3.10060400 -1.06972000  
H 0.48290500 -3.70746000 -3.14362500  
H -0.53327200 -1.35283600 -3.73388700  
H -2.19911000 -3.05673400 -1.80409600  
H -1.15641700 -0.84216200 -0.78319900  
H -0.13370100 -3.19949500 -0.19108800  
H 1.44651600 -1.52673300 -2.20921000  
H -0.42300600 -4.77527100 -2.07257500

H -2.10124400 -0.91904500 -3.05895800  
H -1.95185500 -3.38747200 -3.51617900  
H -0.23606800 0.20257900 -1.86384200  
H 1.43388200 -3.65780800 -0.85442600  
C -0.53272200 -1.17907200 3.42005200  
C 1.28009400 -2.91291400 3.64213500  
C -0.19961400 -2.60028400 3.88191200  
C 1.66639500 -2.70876000 2.16972300  
C -0.15169300 -0.95275500 1.95072100  
H 0.01176600 -0.45533400 4.04304300  
H 1.89660100 -2.25338100 4.26940500  
H -0.81687700 -3.31913200 3.32162000  
H 1.12486900 -3.43614600 1.55530900  
H -0.77718800 -1.59038800 1.31421200  
H 1.92207800 -0.57799800 2.32498300  
H -1.59818800 -0.96813700 3.55010400  
H 1.51322500 -3.94234600 3.94138400  
H -0.45177600 -2.72858800 4.94161000  
H 2.73185500 -2.92165500 2.04980000  
C 0.19056000 3.37476900 -0.04295200  
C -1.14100200 3.80102200 -0.28320800  
C 1.17184400 4.37249500 0.13764000  
N -2.16810700 2.82369800 -0.44083800  
C -1.46112400 5.15176000 -0.36754200  
C 0.84972800 5.72338400 0.04830800  
H 2.18847500 4.07699800 0.38068800  
C -2.65959900 2.04029500 0.59698800  
C -2.51937200 2.22211800 -1.64675100  
C -0.46460900 6.11775000 -0.21120000  
H -2.49318500 5.43355100 -0.55052700  
H 1.62474600 6.47019900 0.19100800  
C -3.33644300 0.93299100 0.01968300  
C -2.53502200 2.22067000 1.97752500  
C -3.24755700 1.08830800 -1.40584000  
H -2.20396400 2.67388300 -2.57619500  
H -0.71753600 7.17147800 -0.27794600  
C -3.87500300 -0.06201600 0.86808100  
C -3.11579400 1.25742900 2.79297300  
H -2.00845900 3.07639000 2.38743500  
H -3.68683400 0.44309600 -2.15010600  
C -3.76094400 0.13041900 2.24571800  
C -4.39169000 -1.34321000 0.31788500  
H -3.05466500 1.36152700 3.87200100  
H -4.17701000 -0.61955600 2.91217800  
C -3.72932100 -2.51261200 0.72251500  
C -5.44265700 -1.44555300 -0.62796200  
C -4.04999800 -3.76223500 0.19533600  
H -2.92720900 -2.42218600 1.44885700  
C -5.72420900 -2.71081400 -1.17474400  
C -6.30896100 -0.33352700 -1.05780800  
C -5.04575900 -3.85849300 -0.77611800

H -3.51137700 -4.64603500 0.52526400  
H -6.51758500 -2.78894200 -1.91393900  
C -6.57607200 0.80615700 -0.40925900  
H -6.82841800 -0.51779500 -1.99841500  
H -5.29648000 -4.81903900 -1.21671900  
H -6.12802200 1.05707400 0.54509700  
H -7.27027400 1.52754500 -0.83007400

### 1-Coordination:



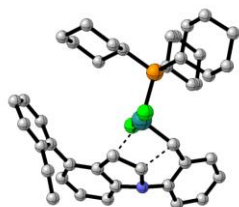
$G_{sol} = -3003.522163$

P 2.00792900 -0.63408800 0.07670900  
Ru 0.05783700 0.41718000 -0.62788700  
Cl 0.33806100 -0.38071000 -2.85432400  
Cl -0.71530800 0.43387100 1.61423000  
C 0.76560000 2.12154700 -0.65024900  
H 1.85113700 2.23144600 -0.60356200  
H 3.31048500 1.46452000 -1.54799700  
C 2.66680500 -0.07624400 1.73553700  
C 3.38044700 -0.67989000 -1.19810200  
C 1.63991100 -2.45359200 0.36046300  
C 0.45469400 -4.23482200 1.70953100  
C 1.04676400 -4.67134500 -0.70721800  
C 0.05576500 -4.96850600 0.42375800  
C 1.19410100 -3.16112500 -0.93457000  
C 0.61046300 -2.72549400 1.47364900  
H 1.40336000 -4.64598200 2.08593200  
H 2.02930400 -5.09904000 -0.45645900  
H -0.94549600 -4.63532800 0.11920400  
H 0.23334800 -2.74529400 -1.25815000  
H -0.35765000 -2.29959300 1.19129800  
H 2.59477600 -2.89431800 0.67889100  
H -0.29326000 -4.40490700 2.49426100  
H 0.72192700 -5.15287200 -1.63766500  
H -0.00839500 -6.04906400 0.60408300  
H 1.89016100 -2.96995800 -1.75606200  
H 0.89739000 -2.23314800 2.40770400  
C 4.30962100 -0.36833300 3.63764100  
C 3.07708000 1.81916000 3.35825800  
C 4.37524900 1.15179000 3.82701000  
C 2.73168900 1.45266200 1.90795600

C 3.98575200 -0.73208500 2.18086300  
H 3.53160900 -0.78452200 4.29355500  
H 2.24812700 1.49926700 4.00515400  
H 5.21927300 1.54976400 3.24407800  
H 3.48755600 1.87855100 1.23430700  
H 4.80457400 -0.38047200 1.54068500  
H 1.87093800 -0.41564700 2.40912300  
H 5.25711600 -0.83469800 3.93525900  
H 3.14917900 2.90949200 3.45621500  
H 4.57487800 1.39726100 4.87731200  
H 1.76605100 1.88934600 1.64705000  
H 3.94078000 -1.82120500 2.07012500  
C 5.01722200 0.66558800 -2.59303800  
C 5.37717000 -1.81000600 -2.26565700  
C 6.05815400 -0.45202700 -2.46866800  
C 4.43878400 -1.79226800 -1.04909100  
C 4.06258300 0.68771800 -1.39012600  
H 4.42708000 0.51386800 -3.50747100  
H 4.79557200 -2.06299300 -3.16358400  
H 6.71305900 -0.24445300 -1.60930300  
H 5.03383000 -1.63235900 -0.14379700  
H 4.62547500 0.95550000 -0.48584600  
H 2.81200000 -0.87883500 -2.11498200  
H 5.51012700 1.64083100 -2.69202300  
H 6.12701600 -2.60118600 -2.14126500  
H 6.70162300 -0.47531800 -3.35664000  
H 3.96545200 -2.77254900 -0.94681200  
C 0.13504000 3.44148300 -0.62375400  
C -1.26294400 3.69347200 -0.59501700  
C 0.99040200 4.55904600 -0.49765300  
N -2.15626700 2.61984700 -0.77839400  
C -1.75673200 4.98291400 -0.40122600  
C 0.50017200 5.84542300 -0.30889600  
H 2.06364600 4.38857700 -0.52398200  
C -3.07166600 2.13791500 0.16075200  
C -1.82497200 1.57496200 -1.65093900  
C -0.88004900 6.05583500 -0.24714900  
H -2.83044800 5.13862200 -0.40208600  
H 1.18694300 6.67986000 -0.20564500  
C -3.32992200 0.77936800 -0.15003400  
C -3.61180700 2.75210300 1.29336000  
C -2.53966000 0.44286800 -1.29954300  
H -1.30991400 1.79768800 -2.57261700  
H -1.27573000 7.05627700 -0.10005000  
C -4.11547800 -0.00799800 0.71194100  
C -4.43366800 1.97544400 2.10149100  
H -3.38295900 3.78100100 1.54633700  
H -2.56435800 -0.47986100 -1.85978900  
C -4.67270500 0.61478500 1.82618500  
C -4.16603900 -1.48127700 0.51622300  
H -4.87988900 2.42024100 2.98621400  
H -5.28302400 0.02962400 2.50751400

C -3.49465200 -2.25771700 1.47130800  
 C -4.74647000 -2.11469000 -0.60961200  
 C -3.37642700 -3.64004000 1.33464300  
 H -3.02591200 -1.74784200 2.30681400  
 C -4.59015700 -3.50685000 -0.74041300  
 C -5.52322100 -1.43115900 -1.65892700  
 C -3.92089100 -4.26740100 0.21397300  
 H -2.84616100 -4.21658300 2.08692700  
 H -5.02268300 -3.99732100 -1.60892000  
 C -6.15222400 -0.25058500 -1.59823700  
 H -5.61824900 -2.00843200 -2.57882900  
 H -3.82436500 -5.34137700 0.08261500  
 H -6.13984300 0.37844600 -0.71612400  
 H -6.71484600 0.11393600 -2.45275000

### 1-TS1:



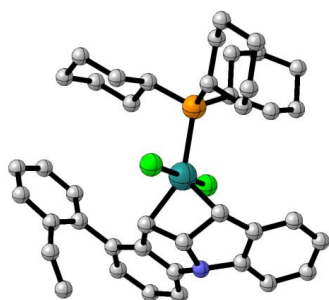
**G<sub>sol</sub>** = -3003.491686

P 1.91001600 -0.79854500 0.17280300  
 Ru -0.03160000 0.30509000 -0.63335100  
 Cl 0.22923600 -0.77914500 -2.79514400  
 Cl -0.46375000 1.13874000 1.59318400  
 C 0.37824300 1.95833500 -1.44149700  
 H 0.85992300 1.89771700 -2.42536600  
 H 2.81304800 0.88386800 -2.06785900  
 C 2.62649500 -0.01125700 1.69829900  
 C 3.19183600 -1.04570400 -1.15102300  
 C 1.43240900 -2.52020500 0.70790900  
 C -0.13701000 -3.86913300 2.16544700  
 C 0.78603700 -4.86910400 0.03415800  
 C -0.40120900 -4.83273000 1.00294200  
 C 1.14475900 -3.46528700 -0.47398300  
 C 0.21740000 -2.46698000 1.65644200  
 H 0.69191400 -4.25161000 2.77953400  
 H 1.66002100 -5.30323300 0.54263800  
 H -1.29621400 -4.49917200 0.46261300  
 H 0.32257800 -3.05944500 -1.07466500  
 H -0.64677400 -2.05024700 1.11969900  
 H 2.28771500 -2.92532900 1.26615300  
 H -1.01352000 -3.80948300 2.82077900  
 H 0.56304100 -5.52102100 -0.81930400  
 H -0.61550800 -5.83991500 1.38255100  
 H 2.00924400 -3.52926100 -1.14196000  
 H 0.40136400 -1.78871100 2.49526600  
 C 4.02806300 -0.07302500 3.78605300

C 3.30699200 2.14932900 2.80152700  
 C 4.38896900 1.40668900 3.59660200  
 C 3.02187100 1.45792600 1.46253300  
 C 3.74531900 -0.76153000 2.44039000  
 H 3.13381500 -0.15078900 4.42060500  
 H 2.37429600 2.18166400 3.38038800  
 H 5.34481600 1.47468700 3.05573400  
 H 3.92017900 1.50484500 0.83300200  
 H 4.66329600 -0.76089900 1.84105300  
 H 1.74626400 0.01646800 2.35123500  
 H 4.83542200 -0.59944100 4.31049600  
 H 3.60748000 3.19006500 2.62699000  
 H 4.54531000 1.88528300 4.57124900  
 H 2.21735200 1.97986400 0.94042000  
 H 3.47744200 -1.81015800 2.61131500  
 C 4.49998200 -0.04942700 -3.05806900  
 C 5.22077700 -2.25179300 -2.02849200  
 C 5.68390700 -0.97089700 -2.73543200  
 C 4.39460200 -1.92899200 -0.77347100  
 C 3.67185200 0.26212200 -1.80366800  
 H 3.84675000 -0.53214600 -3.79763500  
 H 4.60569400 -2.84740000 -2.71794900  
 H 6.38845100 -0.43638800 -2.08094800  
 H 5.03185500 -1.40090400 -0.05473300  
 H 4.28636200 0.83183400 -1.09540900  
 H 2.60478300 -1.56706100 -1.91623000  
 H 4.85735300 0.88382700 -3.51099200  
 H 6.08401200 -2.87223000 -1.75720200  
 H 6.23370900 -1.22054200 -3.65111600  
 H 4.07096600 -2.85608300 -0.28766300  
 C 0.29706900 3.31951000 -0.86787100  
 C -1.00484500 3.78414200 -0.61004500  
 C 1.38848800 4.15330500 -0.62402700  
 N -2.01238400 2.83862500 -0.94096200  
 C -1.22391400 5.05945700 -0.10216800  
 C 1.17849700 5.42269900 -0.07998500  
 H 2.39446300 3.80218700 -0.83486800  
 C -2.93979300 2.33310200 -0.00229500  
 C -1.52003900 1.73953400 -1.71256400  
 C -0.11900700 5.86979000 0.17708600  
 H -2.23115000 5.43049300 0.04687300  
 H 2.02677700 6.06653100 0.13119300  
 C -3.08536700 0.94436100 -0.19305200  
 C -3.63608400 3.01289400 0.99414200  
 C -2.15131900 0.52328000 -1.22202700  
 H -1.40613400 1.88150500 -2.78484000  
 H -0.27887000 6.86614300 0.57803500  
 C -3.96459500 0.19997100 0.60824400  
 C -4.50903500 2.26807200 1.78391200  
 H -3.50429600 4.07401900 1.16268400  
 H -2.33223000 -0.31320800 -1.88368000  
 C -4.67415800 0.88780800 1.59650800

C -4.05165000 -1.27903100 0.49489600  
 H -5.07627800 2.76862600 2.56315700  
 H -5.36500900 0.33746300 2.22784000  
 C -3.69581900 -2.02566100 1.62769500  
 C -4.43421100 -1.95910400 -0.68785700  
 C -3.70447800 -3.41910400 1.61570300  
 H -3.38581400 -1.48885900 2.51905600  
 C -4.38880000 -3.36462800 -0.69134400  
 C -4.92311700 -1.31044900 -1.91921900  
 C -4.04156600 -4.09332000 0.44227000  
 H -3.43076500 -3.97194000 2.50915500  
 H -4.66457400 -3.88947600 -1.60242400  
 C -5.55685800 -0.13708900 -2.03801600  
 H -4.79171500 -1.91240100 -2.81848900  
 H -4.03412900 -5.17890100 0.40934600  
 H -5.76190400 0.50732500 -1.19077600  
 H -5.90135300 0.20529500 -3.00941200

### 1-Metallacycle:



$G_{\text{sol}} = -3003.494994$

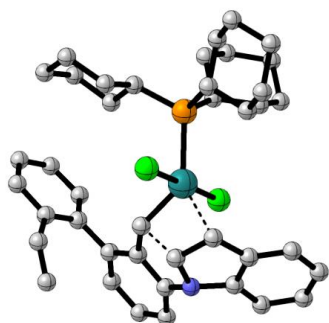
P 1.87200700 -0.84623200 0.17057300  
 Ru 0.00714800 0.38485500 -0.66633100  
 Cl 0.23061800 -0.70711300 -2.82318600  
 Cl -0.35483200 1.26018200 1.56433300  
 C 0.15521300 2.11001200 -1.60918800  
 H 0.63908100 2.02254200 -2.58331500  
 H 2.64796600 0.87007500 -2.11144000  
 C 2.57549500 -0.15470800 1.74702900  
 C 3.17068700 -1.00206400 -1.15040000  
 C 1.36191100 -2.58393500 0.59185000  
 C -0.24838200 -3.97448600 1.95793400  
 C 0.70746000 -4.89036800 -0.19758900  
 C -0.50006700 -4.87912700 0.74626200  
 C 1.09477700 -3.47097900 -0.63704600  
 C 0.13129100 -2.55465800 1.52158200  
 H 0.56457900 -4.39494700 2.56864900  
 H 1.56416400 -5.35836100 0.31023300  
 H -1.37817500 -4.50719300 0.20356600  
 H 0.29587900 -3.02913200 -1.24271200  
 H -0.71534900 -2.09879100 0.98941300  
 H 2.20209000 -3.02369000 1.14621600

H -1.13720800 -3.93530900 2.59685000  
 H 0.49503200 -5.50149600 -1.08327800  
 H -0.73761500 -5.89905800 1.07448100  
 H 1.98012400 -3.51758400 -1.27962500  
 H 0.31489000 -1.92010200 2.39504900  
 C 3.83927500 -0.37530800 3.91101300  
 C 3.46421800 1.91095100 2.88503800  
 C 4.40067700 1.04171300 3.73424200  
 C 3.16940900 1.25022900 1.53304600  
 C 3.53528000 -1.04217700 2.55866600  
 H 2.91114500 -0.32578500 4.49783400  
 H 2.51366300 2.06380700 3.41306100  
 H 5.38222600 0.98005200 3.24069700  
 H 4.10334800 1.17300700 0.96097500  
 H 4.47333700 -1.19635100 2.01298400  
 H 1.66642400 -0.01175300 2.34158900  
 H 4.54117600 -0.99733100 4.48052600  
 H 3.90318900 2.90380500 2.72669500  
 H 4.57068500 1.50479300 4.71402600  
 H 2.47287200 1.86885400 0.95883900  
 H 3.10229800 -2.03300600 2.73383200  
 C 4.43379800 0.07308800 -3.04467700  
 C 5.30788100 -2.05187100 -1.97372900  
 C 5.68182200 -0.74291500 -2.68180100  
 C 4.42806500 -1.78784200 -0.74189800  
 C 3.55277700 0.33401700 -1.81501600  
 H 3.84062100 -0.47173200 -3.79176200  
 H 4.75989100 -2.70068300 -2.67168100  
 H 6.32201900 -0.14597300 -2.01534700  
 H 5.00321000 -1.20683000 -0.01062600  
 H 4.09633200 0.96881400 -1.10577400  
 H 2.63195400 -1.57300700 -1.91540600  
 H 4.72315900 1.02651800 -3.50380200  
 H 6.21136500 -2.59834100 -1.67591700  
 H 6.27437200 -0.95416700 -3.58026600  
 H 4.16222500 -2.73490800 -0.25786600  
 C 0.25403300 3.41230600 -0.92013500  
 C -1.00868500 3.83653400 -0.47029400  
 C 1.38240100 4.19247600 -0.68831900  
 N -2.01218200 2.91213900 -0.85514500  
 C -1.15645600 5.02428000 0.23629500  
 C 1.24667400 5.38230200 0.03260500  
 H 2.35555300 3.86283000 -1.04186500  
 C -2.96740400 2.36452600 0.02272300  
 C -1.42429900 1.84238700 -1.65752600  
 C -0.01053000 5.78645700 0.49028500  
 H -2.12681600 5.36905600 0.57124900  
 H 2.11936600 5.99526300 0.23631400  
 C -3.02390400 0.96470200 -0.12431000  
 C -3.79415100 3.03696700 0.91952000  
 C -2.00843300 0.52101800 -1.07422800  
 H -1.68998400 1.87024700 -2.71892700



H -0.10839900 6.71733200 1.04112500  
 C -3.94930200 0.20624700 0.60809900  
 C -4.69106800 2.27430800 1.66638600  
 H -3.75929900 4.11311900 1.03011600  
 H -2.26222300 -0.25345600 -1.79129000  
 C -4.77185600 0.88470400 1.51476500  
 C -4.00726800 -1.27614000 0.51102200  
 H -5.35305800 2.77169600 2.36925600  
 H -5.49227200 0.31840500 2.09678200  
 C -3.74887900 -2.00563100 1.68044000  
 C -4.30501800 -1.97356200 -0.68570700  
 C -3.77556200 -3.39880100 1.69270900  
 H -3.50819500 -1.45647700 2.58563000  
 C -4.27621200 -3.37917000 -0.66176800  
 C -4.69344600 -1.34129500 -1.96106400  
 C -4.03022200 -4.09061700 0.50883100  
 H -3.58432700 -3.93783500 2.61565400  
 H -4.48722100 -3.91735300 -1.58228100  
 C -5.33102900 -0.17775000 -2.14170700  
 H -4.47692100 -1.94718900 -2.84092200  
 H -4.03695900 -5.17654300 0.49616900  
 H -5.61810700 0.46787000 -1.31944200  
 H -5.59563200 0.15408700 -3.14142600

#### 1-TS2:



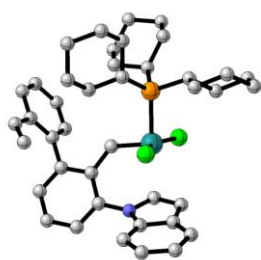
**G<sub>sol</sub>** = -3003.481276

P -1.87991600 0.52230700 0.07874300  
 Ru 0.01339900 -0.70128800 -0.68420800  
 Cl -0.42819500 0.00817400 -3.03162700  
 Cl 0.46595400 -1.50254000 1.58974900  
 C 0.75872400 -2.63756400 -1.72942000  
 H 0.19065400 -2.65157200 -2.65130700  
 H -2.25651100 -1.95288700 -1.48114000  
 C -2.33284900 0.28783200 1.87675800  
 C -3.25708800 -0.07326700 -1.02592300  
 C -1.85373300 2.36698700 -0.14557600  
 C -0.91370800 4.54807100 0.67032400  
 C -1.88816100 4.38030600 -1.65876000  
 C -0.85044400 5.07415000 -0.76797400  
 C -1.75772400 2.85069900 -1.60142700

C -0.75068100 3.02269500 0.70529200  
 H -1.88320300 4.81629800 1.11687600  
 H -2.89809800 4.66998100 -1.33161700  
 H 0.15380500 4.88151300 -1.16791300  
 H -0.80371700 2.52999400 -2.03018400  
 H 0.22958400 2.74101500 0.30263300  
 H -2.82597700 2.69550400 0.24781200  
 H -0.14109200 5.01852100 1.28528800  
 H -1.78648000 4.71692000 -2.69769600  
 H -0.99847600 6.16140500 -0.78539300  
 H -2.53656900 2.39373700 -2.21928500  
 H -0.77481400 2.66307500 1.73956300  
 C -3.40707200 1.10027700 4.01235800  
 C -2.97612900 -1.36794800 3.67119100  
 C -3.88270100 -0.32209300 4.33086500  
 C -2.86333400 -1.13162300 2.16032100  
 C -3.27360100 1.33861500 2.49902500  
 H -2.42722200 1.26735000 4.48224700  
 H -1.96985700 -1.32236100 4.10867500  
 H -4.91043800 -0.44927200 3.95903700  
 H -3.85641100 -1.24837900 1.70736100  
 H -4.26465300 1.28062600 2.03148700  
 H -1.35578300 0.35944500 2.37094200  
 H -4.09341800 1.84065400 4.44230400  
 H -3.35805500 -2.37879100 3.86021400  
 H -3.92053300 -0.47399500 5.41667900  
 H -2.19700700 -1.87590400 1.71899000  
 H -2.90420400 2.35454700 2.33268900  
 C -4.25946800 -2.00874200 -2.29760600  
 C -5.65903900 0.04075400 -1.78460900  
 C -5.66682400 -1.48007500 -1.98896300  
 C -4.66111800 0.45560700 -0.69201900  
 C -3.26073600 -1.60599100 -1.20445500  
 H -3.91527200 -1.60209300 -3.25836000  
 H -5.38006800 0.53214700 -2.72747400  
 H -6.04165300 -1.96388500 -1.07486300  
 H -4.99325600 0.05053700 0.27186700  
 H -3.52460300 -2.10205900 -0.26525200  
 H -2.94899300 0.33874400 -1.99433000  
 H -4.27701800 -3.10071000 -2.40152800  
 H -6.66361000 0.39802300 -1.52632600  
 H -6.36025600 -1.74996900 -2.79472100  
 H -4.65037600 1.54724800 -0.59148800  
 C 0.93734700 -3.78509000 -0.86867900  
 C 2.16678000 -3.64084300 -0.18451100  
 C 0.10782300 -4.88015200 -0.60514400  
 N 2.83831200 -2.50201800 -0.66315600  
 C 2.55667900 -4.54547400 0.79999700  
 C 0.50249600 -5.79860300 0.36118100  
 H -0.83483400 -4.99097200 -1.13344600  
 C 3.53599200 -1.57932100 0.15454900  
 C 1.99904600 -1.83353300 -1.61754600

C 1.70923600 -5.62110400 1.06028800  
 H 3.47739700 -4.41905800 1.35572700  
 H -0.12600300 -6.65470900 0.58598400  
 C 3.02718800 -0.27423700 0.03257000  
 C 4.62355900 -1.88342900 0.96363600  
 C 1.87442700 -0.16951100 -0.90131500  
 H 2.46386400 -1.52264300 -2.55307700  
 H 1.99409100 -6.34291900 1.82021300  
 C 3.66297300 0.77319900 0.71426400  
 C 5.20877700 -0.84560200 1.69097200  
 H 5.02356900 -2.88978400 1.00482100  
 H 2.00705600 0.55247400 -1.70965100  
 C 4.73686000 0.46032800 1.56383200  
 C 3.23937700 2.19455400 0.60205000  
 H 6.05757300 -1.05223300 2.33582200  
 H 5.22371000 1.26681500 2.10348700  
 C 2.81714400 2.84032500 1.77268700  
 C 3.30418700 2.92921500 -0.60675400  
 C 2.46570500 4.18818100 1.77631400  
 H 2.76301800 2.25995900 2.68881700  
 C 2.90046600 4.27605700 -0.58980900  
 C 3.81545800 2.40839200 -1.89002800  
 C 2.50571900 4.91027300 0.58386400  
 H 2.14944900 4.66471000 2.69962500  
 H 2.93864000 4.84065000 -1.51792600  
 C 4.77824300 1.49766900 -2.08200800  
 H 3.38306200 2.88770100 -2.76845400  
 H 2.22279000 5.95854800 0.56403200  
 H 5.28979800 1.00257500 -1.26434100  
 H 5.09073400 1.23400000 -3.08826100

### 1-Alk2:



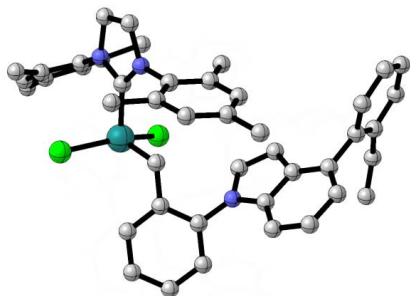
**G<sub>sol</sub>** = -3003.524311

P 1.41036300 -1.17673800 0.13432600  
 Ru -0.70328800 -0.78969300 -0.71682800  
 Cl -0.00877600 -1.20882200 -2.95833200  
 Cl -1.65510400 -1.32466300 1.37391000  
 C -0.62429300 1.04560900 -0.56714800  
 H 2.18679600 1.47677100 -0.94755500  
 C 1.71573600 -0.58087400 1.87688100  
 C 2.80121700 -0.61603300 -0.99686000  
 C 1.68429400 -3.02935900 0.28565400

C 1.28615100 -5.19779400 1.52598000  
 C 1.68319800 -5.23536700 -0.96621100  
 C 0.96935300 -5.91390100 0.20824400  
 C 1.33867300 -3.74274200 -1.03515700  
 C 0.94745100 -3.70060000 1.45923300  
 H 2.35625900 -5.31745500 1.75294000  
 H 2.77107600 -5.35212900 -0.84856800  
 H -0.11606200 -5.88374800 0.03400900  
 H 0.26458300 -3.62984300 -1.23179800  
 H -0.13268300 -3.56447500 1.34466000  
 H 2.75927000 -3.15189000 0.46768400  
 H 0.73594300 -5.65951200 2.35502900  
 H 1.41512100 -5.71994300 -1.91296600  
 H 1.25075800 -6.97243400 0.27046400  
 H 1.84204600 -3.27056000 -1.88378000  
 H 1.21900600 -3.23106500 2.40978200  
 C 3.24799500 -0.53023300 3.89521400  
 C 1.40921400 1.18292800 3.65630700  
 C 2.82446000 0.91518300 4.17962100  
 C 1.28173800 0.86822100 2.15936400  
 C 3.13866500 -0.85601500 2.39856400  
 H 2.60030300 -1.21602600 4.46016000  
 H 0.69337900 0.55871300 4.21043300  
 H 3.52952200 1.60093500 3.68607300  
 H 1.88722900 1.58052400 1.58667100  
 H 3.85888300 -0.23814200 1.84840300  
 H 1.01578700 -1.20679500 2.44260700  
 H 4.27439000 -0.70858400 4.23985300  
 H 1.12357600 2.22531700 3.83138100  
 H 2.88213600 1.12457200 5.25501600  
 H 0.24317400 0.99938900 1.84981500  
 H 3.42193500 -1.90027500 2.22522400  
 C 4.10170400 1.35523800 -1.92642600  
 C 5.09735400 -0.95780100 -2.01574000  
 C 5.39638300 0.53826800 -1.88155100  
 C 4.10569800 -1.43787200 -0.94490700  
 C 3.10279800 0.88897100 -0.85875100  
 H 3.63789200 1.25270500 -2.91783600  
 H 4.66973100 -1.15340100 -3.00941500  
 H 5.90679200 0.72145200 -0.92416800  
 H 4.57211900 -1.35209100 0.04401300  
 H 3.52228700 1.09854500 0.13281400  
 H 2.35570500 -0.76662500 -1.98739000  
 H 4.31321700 2.42067800 -1.78428600  
 H 6.02234100 -1.54415700 -1.94890600  
 H 6.08357500 0.86359700 -2.67241700  
 H 3.90047300 -2.49911900 -1.10954400  
 H 0.33651600 1.50543600 -0.34609400  
 C -1.67557400 2.06242100 -0.62580100  
 C -1.30279100 3.43080000 -0.49694100  
 C -3.06753600 1.77129600 -0.65711800  
 C -2.27498600 4.42025400 -0.33743300

C 0.12728500 3.84637900 -0.56119100  
 C -4.02631900 2.76792700 -0.48269600  
 N -3.48457300 0.45237000 -0.90278300  
 C -3.62863200 4.09161500 -0.30923900  
 H -1.95853800 5.45226100 -0.22699400  
 C 0.76760300 3.77075000 -1.80567300  
 C 0.82623200 4.37105500 0.55235300  
 H -5.07674100 2.50159300 -0.52586700  
 C -2.84341700 -0.35564900 -1.84795000  
 C -4.34368300 -0.33334000 -0.15050600  
 H -4.37642200 4.86911200 -0.18601900  
 C 2.07480100 4.21873200 -1.98009900  
 H 0.21680400 3.35934400 -2.64650300  
 C 2.14437200 4.82159200 0.35054100  
 C 0.28853200 4.48133300 1.92025700  
 C -3.31601800 -1.65074000 -1.72560000  
 H -2.32484700 0.10239600 -2.67574300  
 C -4.26613600 -1.66232500 -0.65735800  
 C -5.12638300 -0.01029300 0.96320900  
 C 2.76686300 4.74985100 -0.89139300  
 H 2.54593900 4.15170700 -2.95571200  
 H 2.68747000 5.22961200 1.19919700  
 C -0.72701000 3.81892000 2.49006800  
 H 0.84358200 5.17995000 2.54644100  
 H -3.03096700 -2.47401400 -2.36563800  
 C -5.02471500 -2.67579800 -0.04744300  
 C -5.87106800 -1.03176200 1.53596300  
 H -5.14099300 0.99415500 1.37084700  
 H 3.78600400 5.10667000 -1.00862600  
 H -1.32187300 3.07518700 1.97513600  
 H -0.97820900 4.00243200 3.53059600  
 C -5.82808700 -2.35085700 1.03406700  
 H -4.97341000 -3.69541700 -0.41837000  
 H -6.49563500 -0.81238700 2.39706000  
 H -6.42475200 -3.12068800 1.51412100

## 2a-Alk1:



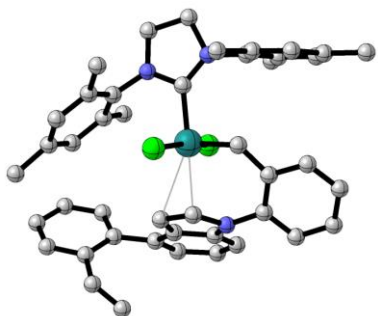
$G_{\text{sol}} = -2881.811972$

C 2.33838500 -0.82351000 0.92006500  
 Ru 2.22727400 0.76156200 -0.19963000  
 Cl 3.59835200 2.05018900 1.20169500

Cl 1.75330300 -0.16334200 -2.30354200  
 C 0.56185800 1.40939100 0.17783100  
 H -0.21130800 0.83410600 0.68165300  
 N 1.52104200 -1.32192600 1.87402500  
 N 3.44688000 -1.61090800 0.87249100  
 H 8.42762900 -0.76929100 -2.78841100  
 C 0.21538400 -0.86884900 2.23232500  
 C 2.10150400 -2.47706900 2.58085300  
 C 3.37676500 -2.76711600 1.77401300  
 C 4.47247900 -1.50255000 -0.12136600  
 H 1.39506100 -3.31198900 2.58220600  
 H 2.31427800 -2.20768900 3.62142200  
 H 4.27412800 -2.81745000 2.39770500  
 H 3.30582300 -3.69496400 1.19483300  
 C -2.35357400 -0.04170000 2.93773900  
 C -0.88807000 -1.42105800 1.56107200  
 C 0.06814800 0.08737100 3.24592000  
 C -1.22957000 0.48813500 3.57837400  
 C -2.16486000 -0.99663800 1.93157200  
 C -0.68696900 -2.39943200 0.43164800  
 C 1.27068600 0.69444600 3.92189200  
 H -1.36414500 1.23338400 4.35865300  
 H -3.02786600 -1.40670100 1.41589700  
 C -3.74290900 0.41226900 3.30739400  
 C 6.42994800 -1.23993000 -2.10103300  
 C 4.29828300 -2.16398200 -1.35377100  
 C 5.65025000 -0.79440700 0.17105300  
 C 6.60578000 -0.66285900 -0.84274400  
 C 5.28209000 -2.00757100 -2.32851000  
 C 3.12188900 -3.07378100 -1.60488700  
 C 5.94457300 -0.25539100 1.54770100  
 H 7.51260400 -0.09933800 -0.63521500  
 H 5.14671400 -2.49303100 -3.29202600  
 C 7.44836200 -1.03952700 -3.19609900  
 H -0.17468500 -1.91964600 -0.41026700  
 H -1.64772100 -2.77526900 0.07195300  
 H -0.07702500 -3.25856300 0.73576900  
 H 1.89749200 -0.06790900 4.40087000  
 H 0.96128200 1.40356300 4.69503300  
 H 1.90383700 1.22402600 3.20206500  
 H -3.73856200 0.99405700 4.23451900  
 H -4.41401100 -0.44325500 3.44689400  
 H -4.17432900 1.03573100 2.51774700  
 H 5.05319400 -0.22366100 2.17340400  
 H 6.34134300 0.76177400 1.49450300  
 H 6.69878200 -0.88477000 2.03962000  
 H 2.90004200 -3.13136600 -2.67300800  
 H 2.21842900 -2.72787600 -1.10183300  
 H 3.34404600 -4.09161400 -1.25400200  
 H 7.13860200 -0.23245200 -3.87239300  
 H 7.56691700 -1.94356000 -3.80321700  
 C 0.14255400 2.70109200 -0.36627600

C -1.17396900 2.86409700 -0.86814100  
 C 1.00606800 3.81638000 -0.39579200  
 N -2.05017300 1.75585700 -0.91454400  
 C -1.60335100 4.10245900 -1.34773300  
 C 0.56784500 5.05085300 -0.86552400  
 H 2.00716100 3.70912500 0.00749800  
 C -3.36332200 1.72331100 -0.45143700  
 C -1.74831100 0.51495000 -1.48104500  
 C -0.73847100 5.19589400 -1.33731500  
 H -2.60613800 4.19185500 -1.75170600  
 H 1.24454300 5.89981900 -0.85818200  
 C -3.87550900 0.42561400 -0.72314100  
 C -4.11514200 2.70042300 0.20855500  
 C -2.83364100 -0.30996100 -1.38199500  
 H -0.77599100 0.34978500 -1.92605800  
 H -1.08172500 6.15453100 -1.71499100  
 C -5.18315200 0.09393200 -0.30936100  
 C -5.41049900 2.36097200 0.58639100  
 H -3.70388200 3.68058000 0.42346400  
 H -2.89614700 -1.32250900 -1.75021400  
 C -5.93230000 1.07620100 0.33928300  
 C -5.69481300 -1.29403100 -0.46282400  
 H -6.02752000 3.09590000 1.09491100  
 H -6.94223400 0.83802100 0.66007200  
 C -5.96074300 -2.01024200 0.71307700  
 C -5.86161100 -1.93964200 -1.71394000  
 C -6.35563500 -3.34696200 0.68710600  
 H -5.82889800 -1.50109400 1.66346700  
 C -6.23278900 -3.29642200 -1.71543600  
 C -5.71168900 -1.29449900 -3.03081500  
 C -6.48054900 -3.99803500 -0.53925900  
 H -6.54723700 -3.87587600 1.61633600  
 H -6.34863300 -3.79938600 -2.67237400  
 C -5.80327500 0.00476500 -3.33851100  
 H -5.55952900 -1.99919600 -3.84857800  
 H -6.77200200 -5.04362700 -0.58172300  
 H -5.98144000 0.77425400 -2.59693800  
 H -5.70205800 0.33093700 -4.36948000

## 2a-Coordination:

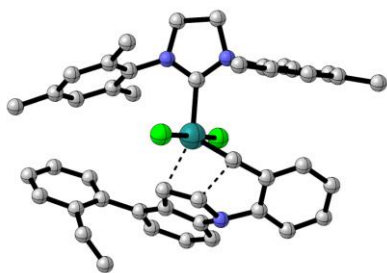


$G_{\text{sol}} = -2881.815616$

C 1.37523800 -1.77164800 0.48207300  
 Ru 0.49668600 -0.21300300 -0.39284900  
 Cl 0.29588700 -1.24880500 -2.55384700  
 Cl 0.14433100 0.76363600 1.75495400  
 C 1.99907800 0.77862200 -0.76902800  
 H 2.93916900 0.25153600 -0.92534500  
 N 2.59808200 -2.00360700 1.01278400  
 N 0.58063300 -2.82033400 0.81636700  
 H -4.73275100 -4.04486400 -2.20968000  
 C 3.79498100 -1.27647700 0.73114300  
 C 2.69377100 -3.31893500 1.67453000  
 C 1.22759300 -3.77589700 1.72326000  
 C -0.74903700 -2.98791000 0.30501000  
 H 3.14182300 -3.21434200 2.66597900  
 H 3.32511700 -3.99160200 1.08096400  
 H 1.08675800 -4.80205100 1.37396800  
 H 0.79683300 -3.68955700 2.72828200  
 C 6.13721100 0.14124800 0.17253100  
 C 4.27256300 -0.35303800 1.67311200  
 C 4.46368900 -1.51284200 -0.48146000  
 C 5.63304000 -0.79144000 -0.73995400  
 C 5.44310400 0.34763300 1.36912000  
 C 3.52112700 -0.09702600 2.95275600  
 C 3.88699000 -2.44557200 -1.51687500  
 H 6.15334900 -0.95367100 -1.68097900  
 H 5.81555000 1.07928300 2.08218600  
 C 7.41065700 0.89814200 -0.11842300  
 C -3.27086700 -3.14386000 -0.89191500  
 C -1.85006600 -2.40463400 0.95324300  
 C -0.90774800 -3.74418500 -0.87360000  
 C -2.17293100 -3.81003000 -1.44988200  
 C -3.09717500 -2.46865800 0.31522700  
 C -1.76410300 -1.81280800 2.33685600  
 C 0.26249000 -4.45526300 -1.50214800  
 H -2.30040300 -4.36937800 -2.37336900  
 H -3.94879600 -1.99282200 0.79013000  
 C -4.61063400 -3.15314300 -1.58595800  
 H 2.50262300 0.24762100 2.74390800  
 H 4.03180100 0.65940100 3.55580600  
 H 3.43689700 -1.00766100 3.55915700  
 H 3.64018000 -3.42681900 -1.09642200  
 H 4.59561100 -2.59946300 -2.33565500  
 H 2.95972200 -2.03914100 -1.94063800  
 H 7.59957800 0.96475600 -1.19464900  
 H 8.27840500 0.40271500 0.33651500  
 H 7.37057700 1.91551100 0.28542900  
 H 1.06516000 -3.75183100 -1.73333000  
 H -0.03901500 -4.93657000 -2.43642600  
 H 0.66619900 -5.23367600 -0.84131800  
 H -2.19462800 -0.80990300 2.36504000  
 H -0.73670000 -1.72833100 2.68838900  
 H -2.32890400 -2.44361700 3.03618200

H -4.71381900 -2.27727200 -2.23950600  
 H -5.43407500 -3.11418000 -0.86663400  
 C 2.19132300 2.22226200 -0.88008000  
 C 1.16328700 3.20284400 -0.87248600  
 C 3.52625300 2.68171700 -0.91782200  
 N -0.18683200 2.79863200 -0.89961000  
 C 1.47653000 4.56204000 -0.87096700  
 C 3.83750800 4.03618200 -0.89694100  
 H 4.31944300 1.94041700 -0.92811000  
 C -1.16579800 3.10620900 0.03953400  
 C -0.58951700 1.65281000 -1.59799500  
 C 2.80738700 4.97907500 -0.86658300  
 H 0.67078100 5.28740900 -0.90246600  
 H 4.87484600 4.35691200 -0.90926400  
 C -2.21244700 2.15248400 -0.09265900  
 C -1.18405000 4.10462700 1.01811000  
 C -1.82044900 1.23858900 -1.12568700  
 H -0.08492100 1.37659500 -2.51079800  
 H 3.03567500 6.04088600 -0.86362100  
 C -3.33523400 2.22299700 0.76168200  
 C -2.30044400 4.16501800 1.83883800  
 H -0.35550500 4.79156400 1.14237900  
 H -2.39665800 0.41904600 -1.52796800  
 C -3.35826200 3.24509800 1.71054200  
 C -4.42631900 1.21308700 0.73974600  
 H -2.35950100 4.93444400 2.60311000  
 H -4.21910000 3.32989600 2.36688500  
 C -4.70357400 0.55426300 1.94810800  
 C -5.18913700 0.88029800 -0.40847000  
 C -5.69113200 -0.42383200 2.04643000  
 H -4.10730900 0.81077900 2.81823000  
 C -6.15248200 -0.13843500 -0.29669300  
 C -5.10505400 1.55885500 -1.71570400  
 C -6.41560700 -0.78093400 0.90947500  
 H -5.87596100 -0.91501800 2.99737900  
 H -6.72776600 -0.40368100 -1.18000400  
 C -4.75164400 2.82502700 -1.96452300  
 H -5.44166900 0.94849900 -2.55406600  
 H -7.17899200 -1.55217400 0.95970600  
 H -4.43599600 3.50816000 -1.18432200  
 H -4.77536000 3.21399500 -2.97815400

## 2a-TS1:



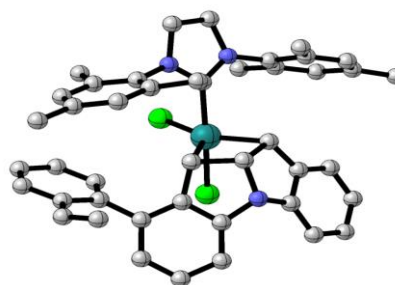
**G<sub>sol</sub>** = -2881.783817

Ru 0.33098800 -0.12584900 -0.42132500  
 Cl -0.13800200 -1.22226700 -2.54110000  
 Cl 0.63113300 0.96081100 1.71827400  
 C 1.66136600 0.87402500 -1.30645000  
 H 1.98218500 0.44938800 -2.26472500  
 C 2.44839900 2.03967400 -0.85134000  
 C 1.71755700 3.22664400 -0.67988000  
 C 3.82876300 2.04749700 -0.66571100  
 N 0.33250600 3.06870400 -0.94825800  
 C 2.34505900 4.41198900 -0.31423200  
 C 4.46205200 3.22382200 -0.25825300  
 H 4.39394100 1.13720900 -0.81503100  
 C -0.68018400 3.32724300 -0.00715500  
 C 0.01657500 1.84780400 -1.62173400  
 C 3.72507000 4.39665300 -0.08558000  
 H 1.78386000 5.33615200 -0.23966900  
 H 5.53473600 3.22497800 -0.08772200  
 C -1.68693400 2.34122900 -0.11223400  
 C -0.75793000 4.38099000 0.89976200  
 C -1.22490300 1.33298200 -1.05934700  
 H 0.16499900 1.80703300 -2.69820100  
 H 4.22564900 5.31537000 0.20574100  
 C -2.87459100 2.47375900 0.63277500  
 C -1.91368500 4.47539700 1.66772700  
 H 0.04306800 5.10101500 1.00559500  
 H -1.89622900 0.73634600 -1.66143700  
 C -2.95852000 3.55532200 1.52057900  
 C -4.03978200 1.55258200 0.54822800  
 H -2.02010200 5.29292800 2.37476200  
 H -3.87210900 3.69103200 2.09043300  
 C -4.55399100 1.05794800 1.75814000  
 C -4.70735400 1.22292100 -0.65778600  
 C -5.69763800 0.26487200 1.80479000  
 H -4.03068700 1.30602300 2.67610600  
 C -5.82492200 0.37190500 -0.59386100  
 C -4.38029500 1.76839000 -1.99139300  
 C -6.33500100 -0.08850200 0.61558600  
 H -6.07393500 -0.08932200 2.76039400  
 H -6.32875000 0.11174100 -1.52129100  
 C -3.94812200 3.00141700 -2.27836200  
 H -4.59886000 1.09327400 -2.81900000  
 H -7.21887700 -0.71959000 0.62776800  
 H -3.74386700 3.74064500 -1.51150300  
 H -3.79046300 3.30583400 -3.30889100  
 C 0.97722600 -1.81039700 0.51165500  
 N 2.21616800 -2.13590300 0.93399000  
 N 0.11867600 -2.75751600 0.93280700  
 C 3.46178600 -1.54140300 0.55182700  
 C 2.24421300 -3.46212800 1.58806800  
 C 0.75581200 -3.74502800 1.82033800  
 C -1.24417800 -2.87644700 0.50306200



C 4.20332400 -0.83975600 1.51660500  
 C 3.97960400 -1.80403700 -0.72942200  
 H 2.82144000 -3.41848500 2.51365600  
 H 2.71406100 -4.19375500 0.91888800  
 H 0.45850900 -4.75903600 1.54467900  
 H 0.45304200 -3.56175500 2.85802500  
 C -2.26586100 -2.21670100 1.20207100  
 C -1.51350900 -3.70648200 -0.60023300  
 C 5.47977700 -0.38921100 1.16624800  
 C 3.64858900 -0.58101000 2.89222400  
 C 5.25747200 -1.32435800 -1.03419500  
 C 3.20136300 -2.60325400 -1.74308200  
 C -3.57450600 -2.35980400 0.72953400  
 C -1.98514600 -1.40316200 2.44096800  
 C -2.83489100 -3.81989500 -1.02913900  
 C -0.40989400 -4.44596700 -1.31122100  
 C 6.02313000 -0.61895400 -0.10015300  
 H 6.05935800 0.16067300 1.90369600  
 H 2.66476200 -0.10697200 2.82478200  
 H 4.31782500 0.07287000 3.45877400  
 H 3.53371800 -1.51075700 3.46491000  
 H 5.66859800 -1.52216100 -2.02143400  
 H 2.87840400 -3.56762200 -1.33291800  
 H 3.81576600 -2.80603100 -2.62506200  
 H 2.29471500 -2.08370000 -2.07017000  
 C -3.87507900 -3.14067600 -0.38794700  
 H -4.37430900 -1.85090800 1.25342000  
 H -2.91913300 -1.17272100 2.95986300  
 H -1.47952700 -0.45940800 2.21312700  
 H -1.33182400 -1.94285500 3.13593400  
 H -3.05520000 -4.44708500 -1.88955600  
 H 0.29995800 -3.73949900 -1.74912300  
 H -0.81930600 -5.05613700 -2.12114300  
 H 0.14095000 -5.11467100 -0.63781700  
 C 7.38289200 -0.07746800 -0.46817600  
 C -5.29059300 -3.24503700 -0.89983900  
 H 7.29919800 0.92129500 -0.91768500  
 H 7.88653600 -0.71951000 -1.19835900  
 H 8.02886500 0.01399600 0.41094500  
 H -5.50092800 -2.44830200 -1.62415500  
 H -6.01829200 -3.14231900 -0.08876700  
 H -5.46505000 -4.20240900 -1.40204200

## 2a-Metallacycle:



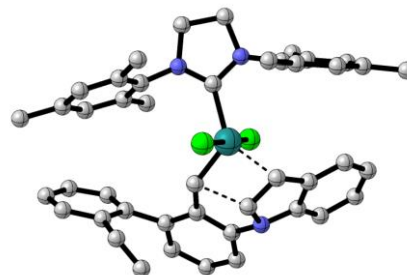
**G<sub>sol</sub>** = -2881.787365

Ru 0.40479700 -0.09919400 -0.45479500  
 Cl -0.14739100 -1.18449500 -2.55111600  
 Cl 0.78563300 0.95193100 1.69343300  
 C 1.60961400 1.07198300 -1.49625500  
 H 1.90171000 0.60513000 -2.43708900  
 C 2.54474400 2.05316500 -0.91385200  
 C 1.86430200 3.21779300 -0.52088400  
 C 3.91998400 1.95027200 -0.74617800  
 N 0.49191400 3.11808200 -0.84977200  
 C 2.53997600 4.27772500 0.07308900  
 C 4.60732600 3.00258000 -0.13582000  
 H 4.43535000 1.04984700 -1.05556000  
 C -0.57516200 3.38809600 0.01798100  
 C 0.23255900 1.87598800 -1.57318500  
 C 3.91997100 4.14898200 0.27137100  
 H 2.03120400 5.18990000 0.35870200  
 H 5.67911800 2.92761500 0.02324500  
 C -1.55236900 2.37117100 -0.06448900  
 C -0.73702100 4.51162600 0.82416100  
 C -1.05989300 1.28567000 -0.92288300  
 H 0.02127500 2.00920700 -2.63893500  
 H 4.46345000 4.96732600 0.73502200  
 C -2.79011100 2.54395700 0.58290800  
 C -1.93303600 4.63343200 1.52633900  
 H 0.02247400 5.27979700 0.88603100  
 H -1.75737000 0.80644800 -1.60129700  
 C -2.94649500 3.68156300 1.39098600  
 C -3.95762200 1.62770500 0.46852900  
 H -2.09776300 5.50328500 2.15555000  
 H -3.89662700 3.83739100 1.89133500  
 C -4.56378000 1.20509100 1.66284500  
 C -4.55646100 1.26340100 -0.76260600  
 C -5.73457000 0.45168200 1.66869300  
 H -4.09558100 1.48392900 2.60165700  
 C -5.70271600 0.44972200 -0.73565900  
 C -4.12645500 1.74153200 -2.09344500  
 C -6.30588000 0.06428500 0.45680300  
 H -6.18490500 0.15561100 2.61201700  
 H -6.15356000 0.16238700 -1.68215600

C -3.67125100 2.96093200 -2.40297700  
 H -4.28032200 1.02640400 -2.90166100  
 H -7.21032400 -0.53652700 0.43884800  
 H -3.52821800 3.73601400 -1.65771800  
 H -3.43290700 3.21745800 -3.43112600  
 C 0.86702100 -1.82229300 0.51806500  
 N 2.09535200 -2.20203000 0.92305000  
 N -0.03209300 -2.71901600 0.95102300  
 C 3.35971500 -1.65293300 0.52635300  
 C 2.06820500 -3.52410000 1.58473900  
 C 0.57175600 -3.72618900 1.84375900  
 C -1.40465500 -2.80613400 0.54685600  
 C 4.14097300 -0.98359200 1.48413000  
 C 3.85291100 -1.93376700 -0.76103900  
 H 2.66285700 -3.50288300 2.49969900  
 H 2.48814100 -4.28232000 0.91203500  
 H 0.21635800 -4.72594900 1.58664600  
 H 0.29439200 -3.51158600 2.88233800  
 C -2.39302200 -2.12573800 1.27085600  
 C -1.71769600 -3.65244100 -0.53123100  
 C 5.41945800 -0.56066600 1.11070900  
 C 3.63546700 -0.74205500 2.88156300  
 C 5.13865200 -1.48850500 -1.08497700  
 C 3.04790800 -2.71892100 -1.76472400  
 C -3.72145400 -2.28917500 0.86802500  
 C -2.04661100 -1.26155600 2.45700600  
 C -3.05736900 -3.77660400 -0.89817400  
 C -0.64466900 -4.40244800 -1.27746500  
 C 5.93413500 -0.79813800 -0.16597600  
 H 6.02623300 -0.02997600 1.84014500  
 H 2.64456500 -0.28117000 2.85718300  
 H 4.31624600 -0.08112300 3.42553000  
 H 3.56290100 -1.67851500 3.45101800  
 H 5.53055800 -1.70138200 -2.07688900  
 H 2.62987200 -3.63133600 -1.32424100  
 H 3.67586800 -3.01350400 -2.61059900  
 H 2.20055600 -2.14492900 -2.15385800  
 C -4.07075700 -3.09751200 -0.21578400  
 H -4.49819600 -1.77154100 1.41707700  
 H -2.95598200 -0.93894800 2.97013200  
 H -1.48292300 -0.36920900 2.16554700  
 H -1.42060900 -1.79965300 3.17863400  
 H -3.31432400 -4.42057600 -1.73584000  
 H 0.03260500 -3.70165800 -1.77340200  
 H -1.08916400 -5.04282600 -2.04454600  
 H -0.04914300 -5.04317600 -0.61507900  
 C 7.29778000 -0.28413400 -0.55703200  
 C -5.50951200 -3.23217500 -0.64995700  
 H 7.76409400 -0.91957300 -1.31707700  
 H 7.96933600 -0.23218300 0.30607900  
 H 7.22835300 0.72822600 -0.97779300  
 H -5.70416500 -4.21659800 -1.08863600

H -5.76001900 -2.47823500 -1.40649000  
 H -6.19613500 -3.08740100 0.18994900

## 2a-TS2:



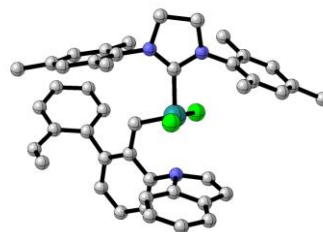
**G<sub>sol</sub>** = -2881.774347

Ru -0.59242700 -0.05432400 0.56144600  
 Cl -0.03591000 -1.06326000 2.71161400  
 Cl -1.07092000 0.91917600 -1.60323900  
 C -1.92453400 1.26132100 1.75619500  
 H -2.22952500 0.62583400 2.57885600  
 C -2.84247100 2.05067200 0.94460900  
 C -2.11043200 3.12239000 0.39267300  
 C -4.18799200 1.87766600 0.62709000  
 N -0.79939300 3.09716700 0.92067300  
 C -2.68639000 3.99812600 -0.52151000  
 C -4.78121200 2.76555700 -0.26715400  
 H -4.74232000 1.04949500 1.05070100  
 C 0.36468700 3.38412300 0.16782800  
 C -0.68438700 1.96897100 1.76582000  
 C -4.03140500 3.80334500 -0.84077100  
 H -2.11671600 4.79361500 -0.98618000  
 H -5.82800900 2.64854900 -0.53214400  
 C 1.30178800 2.32688100 0.06297900  
 C 0.59057300 4.64432500 -0.36851900  
 C 0.93891600 1.03431800 0.70857900  
 H -0.01719800 2.01397800 2.61853700  
 H -4.50662800 4.47805700 -1.54722800  
 C 2.55095800 2.62023300 -0.52311900  
 C 1.78022800 4.87980800 -1.05527600  
 H -0.13454700 5.43487700 -0.21423500  
 H 1.67200900 0.66159700 1.42897400  
 C 2.74708400 3.88369800 -1.11326100  
 C 3.75029200 1.73322400 -0.52475700  
 H 1.97498200 5.85514400 -1.49078400  
 H 3.70875300 4.09300900 -1.57006900  
 C 4.36672500 1.47512300 -1.75910800  
 C 4.40006900 1.31804600 0.66227900  
 C 5.60665600 0.84764400 -1.84334100  
 H 3.85994400 1.79795200 -2.66351800  
 C 5.62373200 0.63564900 0.55237700  
 C 3.93303300 1.61491000 2.03383200  
 C 6.24202300 0.42646200 -0.67540900

H 6.06661100 0.68185600 -2.81349400  
 H 6.11815100 0.31304600 1.46496300  
 C 3.39868900 2.76043900 2.47333600  
 H 4.12178800 0.82157900 2.75714100  
 H 7.20652000 -0.07029300 -0.71992100  
 H 3.21715800 3.60858500 1.82185800  
 H 3.13534300 2.87942900 3.52042000  
 C -0.63803900 -1.86679000 -0.41251900  
 N -1.81409100 -2.39011000 -0.82818200  
 N 0.34116000 -2.71689200 -0.74785500  
 C -3.12671100 -1.89019600 -0.54134700  
 C -1.66138200 -3.73362300 -1.41743900  
 C -0.14238100 -3.84190100 -1.57459000  
 C 1.73313600 -2.64770900 -0.42857500  
 C -3.87676100 -1.30977600 -1.58053800  
 C -3.68949500 -2.12716000 0.72743400  
 H -2.19683900 -3.79403700 -2.36749300  
 H -2.07242900 -4.48960200 -0.73721100  
 H 0.26645900 -4.78559400 -1.20751200  
 H 0.18500000 -3.70164900 -2.61126000  
 C 2.59998900 -1.96179400 -1.28862200  
 C 2.20130900 -3.41008800 0.65485600  
 C -5.17835800 -0.89198900 -1.29819000  
 C -3.33204700 -1.19535300 -2.97992700  
 C -5.00011900 -1.69376700 0.95703900  
 C -2.94591800 -2.88035900 1.80226100  
 C 3.97229100 -2.06709000 -1.04867200  
 C 2.06695200 -1.15998800 -2.44914200  
 C 3.57970700 -3.46450700 0.86665600  
 C 1.25250200 -4.16161800 1.55253900  
 C -5.75424300 -1.06585900 -0.03705000  
 H -5.75810600 -0.42221100 -2.08888100  
 H -2.27320400 -0.93552500 -2.97161200  
 H -3.86506000 -0.41924300 -3.53608200  
 H -3.46396900 -2.14035800 -3.52631500  
 H -5.44608400 -1.87364000 1.93259600  
 H -2.46006000 -3.77749500 1.40254700  
 H -3.63744000 -3.19622600 2.58900500  
 H -2.15592300 -2.28116500 2.26567000  
 C 4.47915500 -2.81011600 0.01991100  
 H 4.65768900 -1.55975200 -1.71616900  
 H 2.88809300 -0.71077500 -3.01295800  
 H 1.39767000 -0.35949300 -2.11619000  
 H 1.48584800 -1.78470800 -3.13924100  
 H 3.95927800 -4.05138400 1.70006800  
 H 0.57274900 -3.46770000 2.05600300  
 H 1.80605400 -4.71646700 2.31564000  
 H 0.64346200 -4.88435200 0.99450900  
 C -7.14792600 -0.56358700 0.24862100  
 C 5.96513500 -2.91365200 0.26246500  
 H -7.78674300 -0.62801700 -0.63835600  
 H -7.12921000 0.49019600 0.55863000

H -7.62237300 -1.13136500 1.05554100  
 H 6.24687500 -3.92416200 0.57866000  
 H 6.28561200 -2.22354400 1.05276600  
 H 6.53490000 -2.66555700 -0.63792900

## 2a-Alk2:



**G<sub>sol</sub>** = -2881.810857

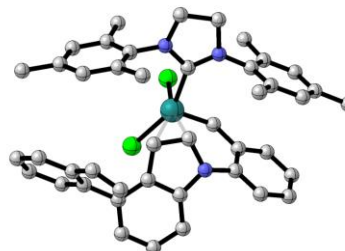
C -0.94439900 -1.74072700 0.72454400  
 Ru -0.84380300 0.12165700 0.04257900  
 Cl -1.10890300 -0.40983600 -2.28714900  
 Cl -1.35384800 0.77732100 2.25455100  
 C 0.95254400 0.38982900 -0.17574900  
 H 1.73373900 -0.29336700 0.15333800  
 N -0.08802300 -2.45938600 1.48718400  
 N -2.12189400 -2.41749100 0.68829200  
 H -7.00900400 -1.82092300 -3.14206900  
 C 1.32229900 -2.25466300 1.59334600  
 C -0.65571600 -3.74501200 1.93189700  
 C -2.13716900 -3.59819800 1.56302400  
 C -3.26493800 -2.06160800 -0.09963900  
 H -0.49351000 -3.88263100 3.00364700  
 H -0.16846700 -4.57216500 1.40077000  
 H -2.53848800 -4.46648900 1.03360600  
 H -2.76888100 -3.40517700 2.43846500  
 C 4.08701100 -1.89579300 1.78327000  
 C 1.86027000 -1.72959200 2.77861700  
 C 2.13825600 -2.63710600 0.51700600  
 C 3.51811500 -2.45057000 0.63396300  
 C 3.24433300 -1.54842300 2.84383400  
 C 0.97889500 -1.37318900 3.94683500  
 C 1.53468400 -3.18207700 -0.75328100  
 H 4.15746200 -2.72538500 -0.19751800  
 H 3.67428600 -1.12965200 3.75095200  
 C 5.57389000 -1.65913500 1.87766300  
 C -5.42832800 -1.36847000 -1.73345200  
 C -4.26511200 -1.22397200 0.41311200  
 C -3.36780000 -2.62527700 -1.38857300  
 C -4.45044900 -2.26598200 -2.18375300  
 C -5.32713400 -0.87586000 -0.43524600  
 C -4.28207100 -0.73923400 1.84089500  
 C -2.32334400 -3.58483200 -1.89708200  
 H -4.52777300 -2.68092300 -3.18591400  
 H -6.10044200 -0.21281400 -0.05306700



C -6.56160000 -0.95522600 -2.64005800  
 H 0.18166800 -0.68925800 3.64301700  
 H 1.56500400 -0.90097500 4.74082400  
 H 0.50232300 -2.26500400 4.37520600  
 H 0.83996400 -4.00646900 -0.55724300  
 H 2.31565400 -3.54774400 -1.42374400  
 H 0.96809400 -2.40731500 -1.28270300  
 H 6.11837700 -2.24323800 1.12997200  
 H 5.95836500 -1.92423700 2.86898800  
 H 5.80513700 -0.60107100 1.70536300  
 H -1.35126300 -3.09034300 -1.96644800  
 H -2.58981100 -3.94861700 -2.89352800  
 H -2.21429100 -4.45690100 -1.24025800  
 H -4.24497100 0.35320600 1.88933800  
 H -3.42872700 -1.10160500 2.41228800  
 H -5.20649800 -1.06724400 2.33261700  
 H -6.20646900 -0.27536000 -3.42491500  
 H -7.35065600 -0.43835100 -2.08500200  
 C 1.39457000 1.54647900 -0.94708100  
 C 2.67476700 1.62898800 -1.54566100  
 C 0.49985000 2.61619500 -1.14136500  
 C 3.03765000 2.79751900 -2.22679200  
 C 3.57758800 0.44821800 -1.65226400  
 C 0.86088800 3.76604700 -1.82732600  
 N -0.80917300 2.51393100 -0.52996200  
 C 2.14778900 3.86088300 -2.36164400  
 H 4.02201400 2.85040000 -2.68112500  
 C 3.13556500 -0.60503600 -2.46557800  
 C 4.89556200 0.42573800 -1.13996200  
 H 0.14442000 4.57502900 -1.92925700  
 C -1.98987000 2.58006800 -1.34053800  
 C -1.05111100 3.38923200 0.57419000  
 H 2.44695900 4.75441300 -2.90126900  
 C 3.99168400 -1.64284800 -2.83000500  
 H 2.11649500 -0.57685400 -2.84208500  
 C 5.74872100 -0.61667100 -1.54014300  
 C 5.42704900 1.41872300 -0.19064700  
 C -2.94588000 3.31297900 -0.71923500  
 H -2.00644100 2.01749400 -2.26036600  
 C -2.38016700 3.84950400 0.50339900  
 C -0.17531800 3.76913200 1.58070700  
 C 5.31273800 -1.63731500 -2.38070200  
 H 3.63284000 -2.43621000 -3.47899300  
 H 6.76943800 -0.62586800 -1.16660500  
 C 4.73322600 2.12630000 0.70988300  
 H 6.51205600 1.52374100 -0.20462800  
 H -3.95871100 3.45276700 -1.07295600  
 C -2.86596900 4.68646200 1.51536000  
 C -0.66933900 4.62040100 2.56793600  
 H 0.84265300 3.39584500 1.60813400  
 H 5.99803700 -2.42672200 -2.67632400  
 H 3.65638300 2.04608400 0.81004800

H 5.23782800 2.80932900 1.38668300  
 C -2.00180600 5.06501200 2.54029900  
 H -3.89182700 5.04344300 1.49336900  
 H -0.01701900 4.93283000 3.37792400  
 H -2.36076200 5.71946700 3.32954200

## 2b-Coordination:



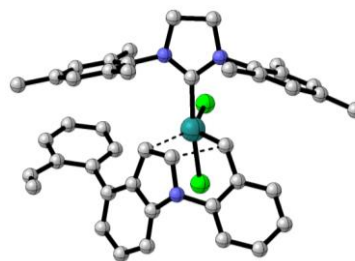
**G<sub>sol</sub>** = -2881.804022

C -0.94139700 -1.82441000 0.33502300  
 Ru -0.30683500 -0.38020900 -0.95958200  
 Cl -0.84663400 -1.87227400 -2.77364200  
 Cl 1.25194900 0.62921300 -2.44817000  
 C -1.94337500 0.43667000 -1.22618800  
 H -2.50682800 -0.01530900 -2.04888100  
 N -2.15497900 -2.08954400 0.88080600  
 N -0.08772400 -2.78387500 0.76693000  
 H 6.13045800 -2.41623800 1.00952700  
 C -3.38086800 -1.36470100 0.74296900  
 C -2.17868100 -3.34152800 1.66266000  
 C -0.70489100 -3.76864700 1.66785300  
 C 1.33442600 -2.77235800 0.58793500  
 H -2.82786800 -4.07440300 1.17291800  
 H -2.57512200 -3.15105500 2.66478900  
 H -0.24969900 -3.70741900 2.66254200  
 H -0.55037600 -4.78111900 1.28296200  
 C -5.84636200 -0.04295400 0.55380100  
 C -4.26125300 -1.69489700 -0.30438200  
 C -3.74506800 -0.43137500 1.73013700  
 C -4.97168400 0.22409800 1.60789900  
 C -5.47746100 -1.01158600 -0.38320800  
 C -3.92466900 -2.77172300 -1.30056200  
 C -2.88201100 -0.12889900 2.93168000  
 H -5.24714500 0.96419600 2.35605200  
 H -6.15740900 -1.25085400 -1.19723400  
 C -7.15447000 0.69813300 0.43970200  
 C 4.12099300 -2.79144100 0.30274800  
 C 1.90894100 -3.47518900 -0.48628200  
 C 2.13556900 -2.14371800 1.56256400  
 C 3.52087700 -2.14718600 1.38859300  
 C 3.30079200 -3.45594300 -0.61011500  
 C 1.09054800 -4.27020000 -1.46786200  
 C 1.54432500 -1.53131200 2.81161500

H 4.14527400 -1.64496700 2.12241500  
 H 3.75457100 -3.99113700 -1.44110300  
 C 5.61767100 -2.80127100 0.12358700  
 H -2.96323900 -2.58961500 -1.79067000  
 H -4.69817100 -2.83582200 -2.07128500  
 H -3.86393300 -3.75475000 -0.81504300  
 H -1.99546200 -0.76504300 2.97784900  
 H -3.44940600 -0.27751500 3.85764400  
 H -2.55053600 0.91587500 2.92456900  
 H -6.98014400 1.77455100 0.32539400  
 H -7.77015900 0.56323200 1.33702900  
 H -7.73516400 0.35611300 -0.42222000  
 H 0.52263900 -1.17797100 2.65707000  
 H 2.14317300 -0.68200200 3.15364300  
 H 1.51959600 -2.26504300 3.62848700  
 H 0.93352300 -3.70330800 -2.38962000  
 H 0.09583400 -4.50118600 -1.08114200  
 H 1.60363200 -5.20657400 -1.71246800  
 H 5.90870600 -2.17245700 -0.72433200  
 H 5.98417600 -3.81548100 -0.07302000  
 C -2.62645200 1.61584300 -0.70644100  
 C -2.07033200 2.51914800 0.22874900  
 C -3.90992700 1.91180100 -1.20673400  
 N -0.73934900 2.31753500 0.66534900  
 C -2.77969000 3.63559700 0.66414100  
 C -4.6166300 3.03520700 -0.78779400  
 H -4.34295900 1.23920500 -1.93972900  
 C 0.33294600 3.07611000 0.17576200  
 C -0.26593700 1.01826500 0.93947500  
 C -4.05475000 3.89542200 0.15718300  
 H -2.32119000 4.29742600 1.39202500  
 H -5.59945900 3.24204800 -1.20027400  
 C 1.49812500 2.27991100 0.22775400  
 C 0.34527500 4.37739100 -0.32669400  
 C 1.10670100 0.97896100 0.70053600  
 H -0.83775700 0.42238300 1.62650500  
 H -4.60049100 4.77157900 0.49483200  
 C 2.73878700 2.81051300 -0.16190600  
 C 1.57820100 4.88750900 -0.72334600  
 H -0.56297800 4.96455200 -0.40412400  
 H 1.79071000 0.19733800 0.98205300  
 C 2.75552300 4.12505000 -0.63169000  
 C 3.98530100 2.00186100 -0.13821700  
 H 1.63386600 5.90127800 -1.10930400  
 H 3.70183600 4.56058400 -0.93721800  
 C 4.58973500 1.73594000 -1.37385900  
 C 4.58091200 1.50180100 1.04666100  
 C 5.77486600 1.00935200 -1.46641700  
 H 4.09358300 2.08978100 -2.27096300  
 C 5.76601800 0.75290700 0.92552600  
 C 4.09115200 1.71794000 2.42055100  
 C 6.37131200 0.52063600 -0.30497400

H 6.22027100 0.82071100 -2.43876100  
 H 6.23150800 0.37051800 1.83100800  
 C 3.27469700 2.66562300 2.90129900  
 H 4.51619000 1.01725900 3.14087300  
 H 7.29776500 -0.04399800 -0.35539900  
 H 2.82916900 3.43374800 2.28193700  
 H 3.04707400 2.69920700 3.96308500

## 2b-TS1:



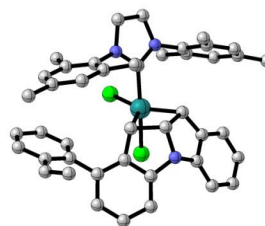
**G<sub>sol</sub>** = -2881.767913

C 2.08032700 0.84834500 -0.12070000  
 H 2.82965000 0.17737500 -0.53575300  
 C 2.50430900 2.25075200 -0.23748100  
 C 1.66668700 3.15523700 -0.91842500  
 C 3.76605000 2.67932200 0.18887600  
 N 0.40531500 2.63234500 -1.32679200  
 C 2.07527300 4.46056800 -1.16435300  
 C 4.16013100 4.00256500 -0.01092200  
 H 4.41918100 1.97541200 0.69721000  
 C -0.80516800 3.11251600 -0.75016100  
 C 0.32126700 1.22325000 -1.38595100  
 C 3.31929600 4.88673200 -0.68920200  
 H 1.44275200 5.12960000 -1.73692500  
 H 5.12993700 4.33789200 0.34413500  
 C -1.62700900 2.01711700 -0.42608400  
 C -1.19108900 4.42124900 -0.50333200  
 C -0.90905300 0.79349100 -0.79487600  
 H 0.83087200 0.72988500 -2.20282200  
 H 3.63879800 5.90816700 -0.87309900  
 C -2.86809400 2.21479700 0.18485300  
 C -2.45359500 4.61538000 0.06486500  
 H -0.54381500 5.26133000 -0.72239400  
 H -1.43922300 -0.09062400 -1.11722600  
 C -3.27685400 3.53875400 0.40056300  
 C -3.65447000 1.09061500 0.76225600  
 H -2.79366200 5.62730700 0.26516100  
 H -4.23943700 3.71851800 0.86796200  
 C -3.06608600 0.40901300 1.83705700  
 C -4.98651800 0.79070200 0.39010200  
 C -3.78520700 -0.52984300 2.57526000  
 H -2.05245900 0.66885900 2.12810000  
 C -5.69894200 -0.14093700 1.16561000

C -5.68587700 1.37567000 -0.76687500  
 C -5.11501500 -0.79371200 2.24820100  
 H -3.30756600 -1.02753900 3.41354800  
 H -6.73031600 -0.35889800 0.89830900  
 C -5.15298800 1.90076400 -1.87838900  
 H -6.77287900 1.31093900 -0.70662900  
 H -5.69600500 -1.50445900 2.83008800  
 H -4.08317100 1.98275900 -2.03195100  
 H -5.79299000 2.27262200 -2.67345300  
 Ru 0.57488700 0.03139600 0.64610000  
 C 0.91357400 -1.86694800 -0.15307500  
 N 2.10581700 -2.52712100 -0.15240400  
 N -0.03777900 -2.79689100 -0.42268600  
 C 1.98444400 -3.98387900 -0.33333000  
 C 3.41882500 -1.95817000 -0.13643000  
 C -1.41014800 -2.57064400 -0.76365900  
 C 0.48727700 -4.16317300 -0.60040700  
 H 2.31674000 -4.49849400 0.57463200  
 H 2.61432300 -4.31976400 -1.16330000  
 C 3.97559000 -1.56277700 -1.37247600  
 C 4.13647800 -1.81804900 1.05770200  
 C -2.42124300 -2.85703300 0.16410000  
 C -1.71806200 -2.18535500 -2.08364500  
 H 0.00977500 -4.84598800 0.10720900  
 H 0.27119600 -4.51713800 -1.61488300  
 C 5.22846800 -0.95426100 -1.38070200  
 C 3.19704400 -1.71524700 -2.65524100  
 C 3.61783600 -2.30016700 2.38635600  
 C 5.39014700 -1.18948600 1.00075400  
 C -3.75051500 -2.68437200 -0.23825900  
 C -2.10340600 -3.37708900 1.54083700  
 C -3.05675400 -2.00991400 -2.43279300  
 C -0.62807300 -1.96185600 -3.10193600  
 C 5.94296000 -0.73549900 -0.19491100  
 H 5.65049700 -0.62608200 -2.32774900  
 H 2.82068700 -2.73405600 -2.79658400  
 H 3.81902300 -1.46145100 -3.51801000  
 H 2.32227100 -1.05514400 -2.66662500  
 H 2.73544400 -2.93056300 2.28182100  
 H 4.39988200 -2.85660800 2.91575600  
 H 3.31541600 -1.45701100 3.01490900  
 H 5.94339600 -1.05518200 1.92749700  
 C -4.08985000 -2.24846400 -1.51801400  
 H -4.53896800 -2.88391200 0.47902200  
 H -2.98942000 -3.33391800 2.17860700  
 H -1.77773600 -4.42560200 1.49947800  
 H -1.30449800 -2.80062500 2.01343700  
 H -3.30088600 -1.69139400 -3.44369400  
 H -0.00161500 -2.85244100 -3.23087600  
 H 0.04166900 -1.15001200 -2.80650000  
 H -1.05516900 -1.70805900 -4.07603600  
 C 7.26773100 -0.01385700 -0.22183300

C -5.52854900 -2.04608500 -1.91962000  
 H 7.91819900 -0.39923200 -1.01511800  
 H 7.79651700 -0.11216900 0.73085800  
 H 7.12373400 1.05720900 -0.41379500  
 H -5.76771800 -2.60081800 -2.83496200  
 H -5.72823300 -0.98612500 -2.11191500  
 H -6.21011800 -2.37790900 -1.13134100  
 Cl 0.49578700 -1.13643300 2.68504300  
 Cl 0.28659700 2.03310500 2.03159300

## 2b-Metallacycle:



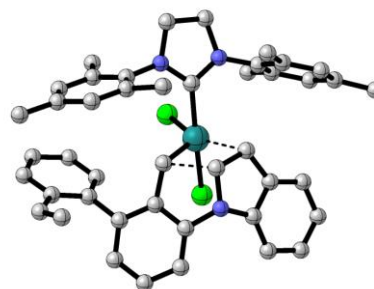
$G_{sol} = -2881.777161$

C 1.95493600 0.82904600 -0.64974500  
 H 2.51571600 0.07419500 -1.18380000  
 C 2.64370300 2.11506100 -0.48279100  
 C 1.78774400 3.17776800 -0.82092800  
 C 3.94851900 2.36173400 -0.06217900  
 N 0.55036200 2.68107200 -1.28940100  
 C 2.20206100 4.50042700 -0.70036400  
 C 4.37274100 3.68483800 0.06275400  
 H 4.59787200 1.53248100 0.19996100  
 C -0.71025100 3.14063600 -0.84113100  
 C 0.57228100 1.22397700 -1.29290500  
 C 3.50265900 4.73761000 -0.24784400  
 H 1.54790300 5.32653700 -0.94958700  
 H 5.37891800 3.90182000 0.40870900  
 C -1.50049600 2.06292000 -0.40233500  
 C -1.17843800 4.44667200 -0.81917100  
 C -0.78528400 0.78027300 -0.58438600  
 H 0.54837100 0.80203000 -2.30020200  
 H 3.84587500 5.76330300 -0.14771700  
 C -2.78817400 2.28207200 0.09401400  
 C -2.47059500 4.66224800 -0.32674600  
 H -0.57831500 5.27253900 -1.18054900  
 H -1.35339700 0.00972200 -1.09605200  
 C -3.25865100 3.60559700 0.12431400  
 C -3.57404900 1.19418800 0.73500700  
 H -2.86367800 5.67419900 -0.29364500  
 H -4.24952700 3.79838400 0.52137700  
 C -2.98791000 0.55999000 1.83920700  
 C -4.90702800 0.87864500 0.37636100  
 C -3.70659400 -0.34819600 2.61481200

H -1.97291400 0.82453800 2.11801800  
 C -5.62319900 -0.01069000 1.19546100  
 C -5.59816900 1.39874400 -0.81652800  
 C -5.03832700 -0.61982300 2.30286300  
 H -3.22648900 -0.81572500 3.46882100  
 H -6.65504400 -0.23798500 0.93817400  
 C -5.05236200 1.80191100 -1.97143900  
 H -6.68621300 1.38573200 -0.74382300  
 H -5.61968300 -1.30465300 2.91461800  
 H -3.98064700 1.81908000 -2.13466500  
 H -5.67942200 2.13538500 -2.79334200  
 Ru 0.60495700 0.04728000 0.65315700  
 C 0.80433700 -1.87085400 -0.10182800  
 N 1.98840500 -2.54775600 -0.09549900  
 N -0.16475900 -2.78726600 -0.33925700  
 C 1.82421500 -4.01027500 -0.16799800  
 C 3.31123400 -1.99577100 -0.12021400  
 C -1.53415400 -2.53540900 -0.67599500  
 C 0.35069400 -4.15281500 -0.55458500  
 H 2.04545100 -4.45368300 0.80999700  
 H 2.50969000 -4.44168700 -0.90212400  
 C 3.89608100 -1.77164900 -1.38652100  
 C 4.02465500 -1.74061800 1.05782300  
 C -2.54422500 -2.83344900 0.24850900  
 C -1.84303700 -2.11386500 -1.98393500  
 H -0.18793500 -4.86644300 0.07293300  
 H 0.21100800 -4.44288800 -1.60342300  
 C 5.16998700 -1.21239600 -1.44919900  
 C 3.14598500 -2.08919500 -2.65759800  
 C 3.48849000 -2.06088500 2.42777800  
 C 5.30224800 -1.17051900 0.94386500  
 C -3.87369000 -2.65963000 -0.15037100  
 C -2.22449500 -3.36470800 1.62043900  
 C -3.18270000 -1.93288900 -2.32846900  
 C -0.75673500 -1.88415500 -3.00595400  
 C 5.88340700 -0.88309000 -0.28901200  
 H 5.61455000 -1.01890700 -2.42258200  
 H 2.83663800 -3.13956700 -2.70451300  
 H 3.76887900 -1.88535700 -3.53281900  
 H 2.23299700 -1.49089500 -2.74945300  
 H 2.63037500 -2.73162900 2.38898800  
 H 4.27395700 -2.51848500 3.03946800  
 H 3.14750600 -1.15513300 2.93907100  
 H 5.85288600 -0.95170100 1.85586300  
 C -4.21509200 -2.20442700 -1.42277700  
 H -4.66148400 -2.87571100 0.56350900  
 H -3.10407500 -3.30634400 2.26651000  
 H -1.91806700 -4.41908500 1.57545600  
 H -1.41228600 -2.80117800 2.08452000  
 H -3.42804700 -1.58981400 -3.33102700  
 H 0.01225900 -1.20016200 -2.63799000  
 H -1.17269000 -1.46584100 -3.92684000

H -0.24310300 -2.81791700 -3.26741400  
 C 7.23427700 -0.21790600 -0.38207600  
 C -5.65587400 -2.02314500 -1.82693100  
 H 7.85230500 -0.67181300 -1.16458900  
 H 7.77862300 -0.28258500 0.56481300  
 H 7.12684800 0.84604900 -0.63061000  
 H -5.90145500 -2.63344700 -2.70478200  
 H -5.85569300 -0.97740800 -2.08292200  
 H -6.33281300 -2.30788000 -1.01639500  
 Cl 0.32653900 -1.04849600 2.68117400  
 Cl 0.55898200 2.09010100 1.98781200

## 2b-TS2:



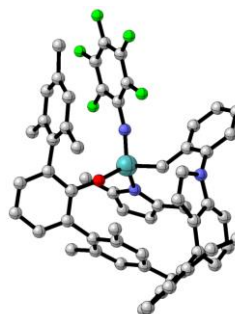
**G<sub>sol</sub>** = -2881.77235

C 2.04436700 0.85519100 -0.89163900  
 H 2.60622900 0.03473800 -1.30747000  
 C 2.71296600 2.11732300 -0.57209500  
 C 1.80628800 3.16773200 -0.80889400  
 C 3.98589200 2.38263300 -0.07249600  
 N 0.61072800 2.63639900 -1.36181600  
 C 2.13118200 4.48712000 -0.51830600  
 C 4.32961400 3.70549100 0.20428900  
 H 4.67366300 1.56631200 0.12352200  
 C -0.68283000 3.05825800 -0.95662300  
 C 0.75075900 1.22416100 -1.43489400  
 C 3.40724700 4.73928800 -0.00940000  
 H 1.42321300 5.29399900 -0.66295200  
 H 5.31433800 3.93798200 0.59877200  
 C -1.45944700 2.03374800 -0.37952700  
 C -1.17712600 4.34562200 -1.10362000  
 C -0.85782100 0.68129100 -0.36669900  
 H 0.34216400 0.74216200 -2.31708800  
 H 3.68846000 5.76258400 0.22216500  
 C -2.75608200 2.31229600 0.07390400  
 C -2.46247600 4.62436100 -0.62443300  
 H -0.58664100 5.11099500 -1.59374800  
 H -1.45921100 -0.06312100 -0.89224700  
 C -3.23674600 3.62688300 -0.04175000  
 C -3.54481900 1.27058800 0.78283300  
 H -2.86063600 5.63034300 -0.71773200  
 H -4.23065800 3.85389700 0.32829200

C -2.95389600 0.67661400 1.90723300  
 C -4.87435700 0.92957000 0.43075600  
 C -3.66144800 -0.22415400 2.70227400  
 H -1.94129000 0.95495500 2.18069100  
 C -5.58027200 0.05397300 1.27195200  
 C -5.56860000 1.39998600 -0.78162700  
 C -4.98770300 -0.52228300 2.39356100  
 H -3.17376900 -0.66719300 3.56470100  
 H -6.60789700 -0.19511700 1.01805100  
 C -5.02713800 1.73276100 -1.96059100  
 H -6.65601900 1.40688800 -0.69998100  
 H -5.56019600 -1.20216400 3.01898000  
 H -3.95704000 1.72085500 -2.13485600  
 H -5.65606700 2.03272300 -2.79391900  
 Ru 0.65135100 0.06246700 0.59595800  
 C 0.77977600 -1.87409600 -0.09768800  
 N 1.95557700 -2.56669100 -0.04317300  
 N -0.19720800 -2.79053500 -0.30680100  
 C 1.76957500 -4.02733400 -0.03063700  
 C 3.28041200 -2.02298600 -0.08906600  
 C -1.56534200 -2.54287700 -0.64746400  
 C 0.30845000 -4.16773100 -0.46066500  
 H 1.94569700 -4.41248800 0.98091500  
 H 2.47188200 -4.51516800 -0.71132300  
 C 3.88224000 -1.89371200 -1.36069600  
 C 3.97679600 -1.67645500 1.07661500  
 C -2.57739400 -2.82410900 0.28096400  
 C -1.87373400 -2.13033800 -1.95881200  
 H -0.25803100 -4.85459500 0.17185000  
 H 0.20059700 -4.49020000 -1.50435500  
 C 5.15857100 -1.34311100 -1.44766600  
 C 3.14401800 -2.29860400 -2.61370100  
 C 3.41904600 -1.88748700 2.45950000  
 C 5.25685200 -1.11777300 0.93709800  
 C -3.90597500 -2.63976800 -0.11747200  
 C -2.26712600 -3.35565000 1.65498700  
 C -3.21239600 -1.94286400 -2.30414400  
 C -0.78591100 -1.91998300 -2.98324700  
 C 5.85664000 -0.92789000 -0.30574600  
 H 5.61686400 -1.22373900 -2.42658600  
 H 2.85420700 -3.35563300 -2.59988800  
 H 3.76736900 -2.13579900 -3.49719600  
 H 2.22108800 -1.72283500 -2.74216100  
 H 2.57957600 -2.58252500 2.46471200  
 H 4.20274900 -2.26645700 3.12461200  
 H 3.04341600 -0.95036700 2.88329000  
 H 5.79453700 -0.82924600 1.83731500  
 C -4.24607000 -2.19703900 -1.39434500  
 H -4.69441600 -2.84071200 0.60068700  
 H -3.11625200 -3.19687400 2.32482300  
 H -2.07230000 -4.43707500 1.62265400  
 H -1.39203000 -2.86316200 2.08307800

H -3.45615700 -1.60948200 -3.31039200  
 H 0.00201400 -1.26054400 -2.61149600  
 H -1.19394600 -1.48626900 -3.90069800  
 H -0.29817000 -2.86577900 -3.25166400  
 C 7.21071000 -0.27409300 -0.42871600  
 C -5.68677200 -2.01447100 -1.79853700  
 H 7.82593200 -0.76493500 -1.19068100  
 H 7.75512300 -0.29953600 0.52007000  
 H 7.10839200 0.77869000 -0.72293600  
 H -6.36302100 -2.27558200 -0.97931400  
 H -5.93956800 -2.64451600 -2.66027800  
 H -5.88095400 -0.97412800 -2.07853100  
 Cl 0.19767100 -0.99964900 2.64301900  
 Cl 0.69139400 2.10876000 1.92816100

### 3a-Alk1:



**G<sub>sol</sub>** = -3084.794048

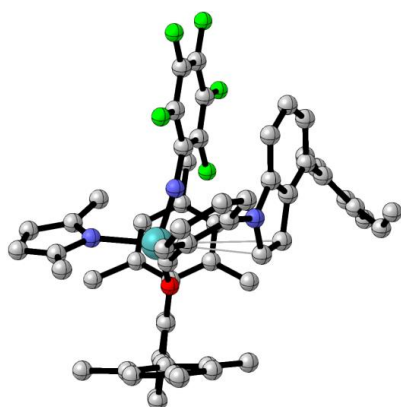
Mo 0.90198000 0.37512600 -0.88166600  
 N 2.49798200 -0.34534400 -1.02177500  
 C 3.68628200 -0.91386900 -0.68181000  
 C 3.71715500 -2.12542500 0.03293300  
 C 4.91563700 -2.72607600 0.38675500  
 C 6.12300900 -2.10833900 0.06962700  
 C 6.12210200 -0.89580400 -0.61532300  
 C 4.91826800 -0.31754400 -0.99527400  
 F 2.56507500 -2.70002600 0.39994500  
 F 4.91725000 -3.87127500 1.08226800  
 F 7.27875800 -2.65470500 0.46364400  
 F 7.28067600 -0.28484600 -0.88963200  
 F 4.94030800 0.85978200 -1.64012200  
 N 0.52273700 1.45099100 -2.53912400  
 C 1.24557700 2.64537000 -2.74391600  
 C 0.80015300 3.22619400 -3.90160300  
 C -0.21597100 2.37435500 -4.45027200  
 C -0.37266500 1.29993300 -3.60947500  
 C 2.29170500 3.10155400 -1.77681300  
 H 2.68547300 4.07283600 -2.09036700  
 H 3.13623600 2.40628000 -1.71369800  
 H 1.89470700 3.23663700 -0.76087300  
 C -1.30514300 0.14321900 -3.74685000  
 H -1.87614000 0.25333400 -4.67401200

H -2.02319300 0.08764100 -2.92177400  
 H -0.77714800 -0.81634200 -3.78781800  
 H -0.77303300 2.53788900 -5.36421000  
 H 1.15667900 4.16213500 -4.31292200  
 O 0.37267200 1.17336000 0.75925200  
 C 0.50559000 2.31021100 1.48624500  
 C -0.45991500 3.32186700 1.30630600  
 C -0.34173200 4.47641500 2.08506900  
 C 0.70765400 4.62427500 2.99438600  
 C 1.66289300 3.61739900 3.12967500  
 C 1.58203200 2.43800700 2.37695800  
 C 2.25691300 0.13782100 3.14001900  
 C 2.60374600 1.35915100 2.51581400  
 C 3.92450600 1.56480300 2.07423500  
 C 4.89088900 0.57989000 2.32387900  
 C 4.58205500 -0.60250700 2.99281100  
 C -3.21842000 1.77714700 -0.77693400  
 C -2.39376200 2.05339900 0.31978000  
 C -1.48737400 3.13162600 0.24433600  
 C -1.46142500 3.94871600 -0.90857400  
 C -2.31171900 3.64562700 -1.97287700  
 C -3.18642500 2.55794200 -1.93373800  
 C 3.24872800 -0.81660100 3.36506900  
 H 2.48620700 3.73214000 3.82887300  
 H 0.78223300 5.52631000 3.59438600  
 H -1.07967600 5.26439800 1.96855100  
 C -0.22890800 -1.11675000 -1.11862800  
 H -1.21824400 -0.78645600 -0.76720700  
 H 5.91385000 0.75607700 1.99709500  
 H 2.98100600 -1.74293900 3.86901100  
 H -3.88970500 0.92502600 -0.72850100  
 H -2.26217200 4.25488600 -2.87139200  
 C 4.34690600 2.81536900 1.33564900  
 H 3.49094900 3.38698800 0.97377700  
 H 4.93718100 3.48062200 1.97870900  
 H 4.97181300 2.55471100 0.47448800  
 C 5.65078300 -1.60601000 3.35354600  
 H 5.32168800 -2.63309500 3.16906000  
 H 6.57084200 -1.44073800 2.78501300  
 H 5.90586600 -1.53374200 4.41874000  
 C 0.84066200 -0.13520200 3.58626800  
 H 0.80013100 -1.01502600 4.23550100  
 H 0.42071100 0.71603300 4.13291600  
 H 0.18572800 -0.31543300 2.72674100  
 C -2.50050900 1.18178700 1.54918200  
 H -3.54652900 0.93929400 1.75774300  
 H -1.97329300 0.23093400 1.41718100  
 H -2.07850700 1.67182300 2.43036300  
 C -4.07479400 2.24649100 -3.11225400  
 H -4.90152000 2.96485000 -3.18976000  
 H -3.50871800 2.29985600 -4.04897100  
 H -4.50732600 1.24568700 -3.02786100

C -0.54060200 5.14104000 -1.03199000  
 H -0.97016100 6.02878400 -0.54939400  
 H 0.42945800 4.96526500 -0.56168400  
 H -0.37112900 5.38092200 -2.08474700  
 C -0.11576200 -2.50675900 -1.50706000  
 C -1.10880900 -3.43823400 -1.12210900  
 C 0.96206000 -2.97795400 -2.28132200  
 N -2.20942400 -2.99642200 -0.33225300  
 C -1.01844500 -4.77872900 -1.48733300  
 C 1.05303800 -4.31809200 -2.64132600  
 H 1.71967800 -2.26829800 -2.59534500  
 C -3.34613900 -2.36590200 -0.82041000  
 C -2.22289400 -2.91525500 1.05722100  
 C 0.06486100 -5.22416700 -2.24610300  
 H -1.80039000 -5.46087800 -1.16917300  
 H 1.89396900 -4.65796100 -3.23870900  
 C -4.09710800 -1.90923600 0.29702700  
 C -3.75124200 -2.15759800 -2.14195000  
 C -3.35923400 -2.27362800 1.47399300  
 H -1.40260300 -3.33735100 1.61990500  
 H 0.13344500 -6.26950000 -2.53115200  
 C -5.31693100 -1.22985500 0.07760300  
 C -4.94944200 -1.47970500 -2.33490800  
 H -3.15397000 -2.51273000 -2.97536400  
 H -3.64884700 -2.08565100 2.49686200  
 C -5.71595000 -1.02214500 -1.24354200  
 C -6.10178800 -0.67595200 1.21302100  
 H -5.30545700 -1.30026500 -3.34500800  
 H -6.64879500 -0.49847300 -1.43032700  
 C -6.26285400 0.71632800 1.26888800  
 C -6.64237300 -1.47322200 2.25352400  
 C -6.90863700 1.33795600 2.33653500  
 H -5.83952700 1.31869300 0.47099800  
 C -7.26396000 -0.82207600 3.33422400  
 C -6.64721100 -2.94729300 2.28222600  
 C -7.40217700 0.56176600 3.38397500  
 H -7.00651900 2.41948000 2.35508300  
 H -7.66713100 -1.42931500 4.14099700  
 C -6.57239000 -3.80163300 1.25475400  
 H -6.78960000 -3.36535200 3.27905400  
 H -7.89386000 1.02849700 4.23271400  
 H -6.46210600 -3.47771000 0.22664100  
 H -6.62772400 -4.87244500 1.42810000



### 3a-Coordination:



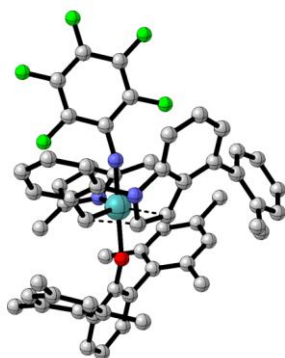
**G<sub>sol</sub>** = -3084.796028

C 2.22575000 -1.66150600 -0.07448600  
H 3.20563100 -1.25235700 0.19916900  
C 2.05353100 -3.08593800 0.20560200  
C 0.92308200 -3.59955000 0.88162600  
C 3.04336800 -4.00013800 -0.20207100  
N -0.03013200 -2.71282600 1.43770800  
C 0.76989300 -4.97538900 1.06945500  
C 2.88019900 -5.37188500 -0.02999600  
H 3.93442400 -3.61657700 -0.68782600  
C -1.40260100 -2.70515600 1.20846300  
C 0.30170600 -1.56727800 2.15559500  
C 1.73177300 -5.86390900 0.59444400  
H -0.09526800 -5.33481300 1.61685900  
H 3.64946800 -6.05446100 -0.37863300  
C -1.93064200 -1.52986600 1.81211000  
C -2.20314800 -3.60604500 0.50097700  
C -0.82613700 -0.83098700 2.40520600  
H 1.32412600 -1.41046600 2.45868100  
H 1.59998800 -6.93152500 0.74119500  
C -3.31573600 -1.26309000 1.73445400  
C -3.55949100 -3.31376500 0.41297500  
H -1.78001200 -4.47808700 0.01523100  
H -0.87849100 0.07720000 2.98300300  
C -4.10514500 -2.16477400 1.01792200  
C -3.90474100 -0.03477500 2.33075700  
H -4.21430300 -3.98551200 -0.13414400  
H -5.17274100 -1.98024600 0.94280700  
C -4.62144800 0.82251700 1.48400400  
C -3.74672300 0.32755500 3.69389600  
C -5.14332300 2.03373300 1.93430200  
H -4.74485500 0.54699600 0.44436000  
C -4.23758400 1.57706300 4.11375800  
C -3.15968000 -0.52871000 4.74150700  
C -4.92996000 2.42587400 3.25506500  
H -5.68957200 2.67452600 1.24797500  
H -4.09703900 1.86491200 5.15269600

C -3.11815000 -1.86530700 4.78583800  
H -2.78416300 0.02196900 5.60433000  
H -5.30565800 3.37855300 3.61688700  
H -3.49894900 -2.48967900 3.98557100  
H -2.69498700 -2.37457800 5.64667200  
Mo 1.19464100 -0.22748900 -0.75000500  
N 2.05540500 0.12280200 -2.54658400  
C 1.48682000 1.11343900 -3.37454400  
C 3.29129000 -0.24018300 -3.10285800  
C 2.37315400 1.39644700 -4.38249000  
C 0.09064100 1.61050700 -3.17549200  
C 3.50959800 0.54163300 -4.21234300  
C 4.13892300 -1.35546700 -2.58856100  
H 2.21008600 2.11175900 -5.17861000  
H -0.11300000 1.96041200 -2.15897100  
H -0.64686600 0.83300100 -3.41400200  
H -0.09561600 2.45845200 -3.83967500  
H 4.38225700 0.48795800 -4.85105800  
H 4.54577200 -1.17105600 -1.58931800  
H 3.57533600 -2.29459100 -2.54520300  
H 4.98468600 -1.50003300 -3.26833000  
N -0.33511200 -0.97213400 -1.17509800  
C -1.58314700 -1.17921300 -1.66820900  
C -2.60712600 -0.23065900 -1.50623400  
C -1.88549200 -2.34083100 -2.40049700  
C -3.86042300 -0.41658200 -2.06933800  
F -2.35919400 0.88065700 -0.80665700  
C -3.14406100 -2.54344600 -2.94992300  
F -0.94908100 -3.28412300 -2.54736700  
C -4.13635000 -1.57744700 -2.78809700  
F -4.82209200 0.50925100 -1.90483400  
F -3.41727800 -3.66939200 -3.62058200  
F -5.35155100 -1.76985200 -3.31040400  
O 1.39671900 1.44662800 0.17680400  
C 2.04195100 2.53899200 0.63970200  
C 1.41369100 3.79574700 0.52043700  
C 3.30742000 2.41508500 1.24505200  
C 0.04844700 3.91839100 -0.06381700  
C 2.09261200 4.92571700 0.98759800  
C 3.95157500 3.57062600 1.69957700  
C 3.92957000 1.07780400 1.45586200  
C -1.07026100 3.51723800 0.69465400  
C -0.12683200 4.43782400 -1.35828600  
H 1.60631500 5.89309300 0.89881800  
C 3.35632200 4.82392200 1.56758200  
H 4.92594600 3.47081500 2.17016500  
C 3.52435400 0.30253700 2.56330000  
C 4.93803400 0.60820500 0.59592400  
C -2.34297900 3.62823700 0.13890800  
C -0.90308700 2.94682200 2.08113900  
C -1.42189700 4.52399500 -1.88473200  
C 1.06068700 4.82858000 -2.20706400

H 3.86665800 5.71225800 1.92751100  
 C 4.11946200 -0.94160900 2.77948900  
 C 2.46530500 0.82122200 3.50546500  
 C 5.52302100 -0.63956600 0.85718000  
 C 5.36607900 1.41166600 -0.60899800  
 C -2.53830700 4.10630600 -1.16004200  
 H -3.19712600 3.29810400 0.72179000  
 H -1.87346800 2.77557000 2.55600300  
 H -0.37967100 1.98675000 2.03275100  
 H -0.30939500 3.60736700 2.72368500  
 H -1.55338600 4.90232700 -2.89642100  
 H 0.73315300 5.22579700 -3.17280800  
 H 1.68312500 5.58774300 -1.72200200  
 H 1.70757000 3.96401000 -2.40237900  
 C 5.11982800 -1.43455900 1.93265900  
 H 3.80330800 -1.53851600 3.63266900  
 H 1.52179300 1.00107800 2.98008900  
 H 2.27606100 0.11157600 4.31650600  
 H 2.76395600 1.77819500 3.94777100  
 H 6.30824100 -0.99924400 0.19598600  
 H 6.24987900 0.96967100 -1.07835600  
 H 4.57276600 1.44458300 -1.36587700  
 H 5.59696600 2.44733000 -0.34214100  
 C -3.92165000 4.10971700 -1.76333000  
 C 5.71440700 -2.80240300 2.16017000  
 H -4.64517400 4.61361900 -1.11092300  
 H -3.93725800 4.61141100 -2.73613800  
 H -4.27808700 3.08186300 -1.90758100  
 H 5.02536500 -3.58646200 1.82072000  
 H 6.65407000 -2.92591100 1.61249400  
 H 5.91287400 -2.98126600 3.22269700

### 3a-TS1:



$G_{\text{sol}} = -3084.771209$

C 0.43957200 2.08369700 0.21466000  
 H -0.40940900 2.76107700 0.25630000  
 C 1.74905600 2.68954200 0.49259500  
 C 2.43126500 2.19667900 1.62527700  
 C 2.30847300 3.74408300 -0.23118100

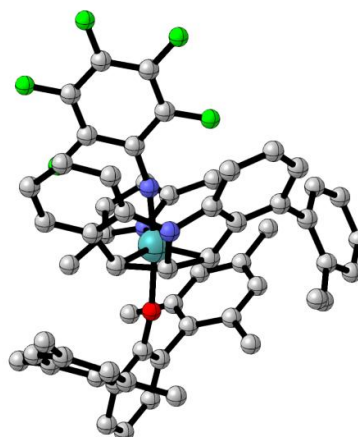
N 1.75811500 1.14379800 2.30340900  
 C 3.64676400 2.74151700 2.02620800  
 C 3.54323100 4.27511000 0.14946200  
 H 1.78342000 4.13414200 -1.09682700  
 C 2.28023600 -0.16679600 2.42476300  
 C 0.37507200 1.03801600 1.99317700  
 C 4.20789500 3.77662700 1.27136900  
 H 4.13020100 2.38982400 2.93083300  
 H 3.97873300 5.08764100 -0.42383800  
 C 1.23390600 -1.09974200 2.27660100  
 C 3.59158400 -0.56275700 2.66742600  
 C 0.01792500 -0.36362000 1.90378000  
 H -0.28958700 1.79146100 2.39197300  
 H 5.15647500 4.20707200 1.57751800  
 C 1.47246900 -2.46477100 2.46522900  
 C 3.82753300 -1.92992800 2.83401000  
 H 4.39867300 0.15616200 2.74176400  
 H -0.96762200 -0.70559900 2.19185200  
 C 2.78687200 -2.85985400 2.75574600  
 C 0.40992500 -3.49412000 2.30819400  
 H 4.83633200 -2.27362900 3.04259800  
 H 2.99244300 -3.91464700 2.90846400  
 C 0.57099100 -4.42882500 1.27554700  
 C -0.72079900 -3.58869300 3.15660400  
 C -0.34780000 -5.45597600 1.06967700  
 H 1.43123800 -4.33014300 0.62234600  
 C -1.64260100 -4.62419400 2.91972100  
 C -1.00532800 -2.70628900 4.30447000  
 C -1.45920700 -5.55799400 1.90435300  
 H -0.19754600 -6.16492100 0.26122500  
 H -2.51105400 -4.70294500 3.56907400  
 C -0.14683900 -2.01968400 5.06961900  
 H -2.06062200 -2.67320000 4.57672700  
 H -2.18649700 -6.35140300 1.75850200  
 H 0.92392200 -2.02307400 4.90475700  
 H -0.51095100 -1.43886800 5.91222000  
 Mo -0.10094700 0.26351300 -0.30401300  
 N -0.62694400 -0.21532300 -2.24814500  
 C -0.42751700 -1.47125000 -2.81232000  
 C -0.83554100 0.69831200 -3.27837000  
 C -0.53159000 -1.35578900 -4.18316400  
 C -0.15663800 -2.67786100 -1.96916500  
 C -0.78039900 0.02118000 -4.47911600  
 C -1.08479800 2.14712700 -3.01401600  
 H -0.45917500 -2.17254400 -4.89096300  
 H -0.86013300 -2.75830000 -1.13210600  
 H 0.85598000 -2.68528100 -1.54799800  
 H -0.27248800 -3.58531300 -2.56999600  
 H -0.94006300 0.46000900 -5.45631700  
 H -1.89860400 2.28766200 -2.29600100  
 H -0.20237900 2.66220400 -2.60825700  
 H -1.36572600 2.65354700 -3.94282500



N 1.56483100 -0.23917800 -0.62525500  
 C 2.79606200 -0.43375200 -1.14930900  
 C 3.53311100 -1.61167300 -0.92148000  
 C 3.38560900 0.54071500 -1.98284300  
 C 4.80712400 -1.78708800 -1.44254000  
 F 2.98940800 -2.60011800 -0.20162500  
 C 4.66062100 0.37598100 -2.50514400  
 F 2.69938500 1.64532200 -2.29367100  
 C 5.37811900 -0.78805600 -2.23007600  
 F 5.48863600 -2.91235400 -1.19739900  
 F 5.20266700 1.32173200 -3.28029100  
 F 6.60678800 -0.95001700 -2.72855700  
 O -1.99406700 0.77805400 0.05899600  
 C -3.25157000 1.17027600 -0.18595100  
 C -4.19674200 0.25165000 -0.69659200  
 C -3.64091000 2.50540600 0.09577200  
 C -3.84795000 -1.17452800 -0.95119200  
 C -5.50287300 0.69306400 -0.93685600  
 C -4.95536600 2.90265400 -0.16600400  
 C -2.66558800 3.46276000 0.69283900  
 C -3.65557800 -2.05238400 0.13480800  
 C -3.78905000 -1.66549600 -2.26848500  
 H -6.22398500 -0.02237900 -1.32200300  
 C -5.88881200 2.00764700 -0.68490700  
 H -5.24102300 3.92787100 0.05389700  
 C -2.27560400 3.29236100 2.04107600  
 C -2.11702500 4.52284900 -0.05629500  
 C -3.39895900 -3.40131100 -0.11421800  
 C -3.77305500 -1.56354600 1.55811200  
 C -3.52025200 -3.02210700 -2.47639600  
 C -4.01357300 -0.76008800 -3.45403600  
 H -6.90846000 2.32746800 -0.87757100  
 C -1.28177300 4.11242300 2.57874300  
 C -2.91609500 2.22476900 2.89493700  
 C -1.10786000 5.31173000 0.51544500  
 C -2.58176700 4.85331100 -1.45564300  
 C -3.31846600 -3.90460100 -1.41570100  
 H -3.25487000 -4.07140200 0.72603300  
 H -3.62003300 -2.38365600 2.26528700  
 H -3.03255700 -0.78750000 1.77260200  
 H -4.75667200 -1.11819500 1.74993400  
 H -3.45237700 -3.38964300 -3.49765800  
 H -3.69219900 -1.24946600 -4.37652700  
 H -5.07089500 -0.48713100 -3.55950500  
 H -3.44098600 0.16488700 -3.35787200  
 C -0.65276700 5.10485500 1.81704000  
 H -0.98118000 3.96841100 3.61498400  
 H -2.63877600 1.22249400 2.55255500  
 H -2.61024000 2.32429300 3.94114300  
 H -4.00854000 2.27959500 2.84577800  
 H -0.66118300 6.10311900 -0.08323700  
 H -1.73193600 5.06962800 -2.11181000

H -3.16305000 4.04591900 -1.90056800  
 H -3.21789800 5.74799800 -1.44333900  
 C -2.97203200 -5.35206900 -1.66192800  
 C 0.50391200 5.89485500 2.37625300  
 H -3.38603500 -6.00285500 -0.88388500  
 H -3.34785000 -5.69621400 -2.63116500  
 H -1.88366100 -5.49810800 -1.65992500  
 H 1.45294600 5.37823500 2.18202100  
 H 0.57209900 6.88635500 1.91673200  
 H 0.41456000 6.02506800 3.45996500

### 3a-Metallacycle



**G<sub>sol</sub>** = -3084.780385

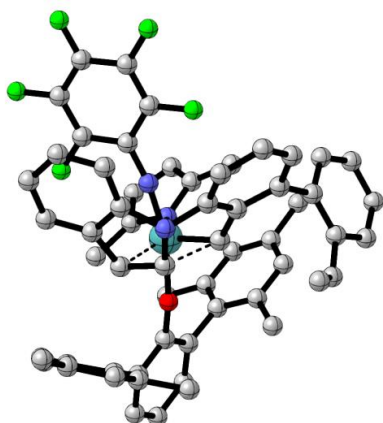
C 0.84711900 1.80704900 0.52871500  
 H 0.17137000 2.64873200 0.56030300  
 C 2.28468600 2.10497500 0.42287100  
 C 3.02164100 1.27067400 1.28686300  
 C 2.93995200 3.02821500 -0.38601400  
 N 2.14719500 0.49906300 2.07771400  
 C 4.41427200 1.28917200 1.28988100  
 C 4.33805300 3.06342800 -0.38214900  
 H 2.36726800 3.67995700 -1.03800600  
 C 2.25843300 -0.88333500 2.32470900  
 C 0.75451700 0.84368200 1.77415600  
 C 5.06161300 2.18994200 0.43591900  
 H 4.99016700 0.64727200 1.94462300  
 H 4.86351500 3.76225700 -1.02523200  
 C 1.02570400 -1.52775600 2.10355500  
 C 3.38291300 -1.57751100 2.76107900  
 C 0.01851700 -0.55718200 1.61702900  
 H 0.26404000 1.39534100 2.57746600  
 H 6.14717200 2.22077900 0.42747100  
 C 0.89468900 -2.89513000 2.36359600  
 C 3.25634800 -2.95182500 2.97806900  
 H 4.31909600 -1.07113400 2.95991800  
 H -0.95441900 -0.59728400 2.10057900  
 C 2.03519900 -3.59794600 2.78817700

C -0.37825300 -3.64110900 2.17070400  
 H 4.11677800 -3.51925200 3.31981900  
 H 1.94695000 -4.66147900 2.98635800  
 C -0.39699300 -4.63415200 1.18241100  
 C -1.53361700 -3.43095900 2.96245900  
 C -1.52488600 -5.42071200 0.95602200  
 H 0.49351800 -4.77203100 0.57693900  
 C -2.66478500 -4.22728200 2.70806500  
 C -1.64813000 -2.45727500 4.06487900  
 C -2.66650700 -5.21772600 1.73019700  
 H -1.51135800 -6.17865000 0.17857100  
 H -3.55456100 -4.07170400 3.31287100  
 C -0.68358100 -1.95088800 4.84486400  
 H -2.67604900 -2.16964200 4.28586800  
 H -3.55615100 -5.81974500 1.56945100  
 H 0.36315500 -2.20718300 4.73436900  
 H -0.93747400 -1.26457400 5.64771500  
 Mo -0.14543200 0.15069200 -0.37026800  
 N -0.93158200 -0.43511200 -2.17583000  
 C -0.85552500 -1.73111500 -2.68968600  
 C -1.17642500 0.44080300 -3.23472400  
 C -1.08809300 -1.67282300 -4.04617700  
 C -0.57268000 -2.91407600 -1.82163700  
 C -1.28371000 -0.29854800 -4.39243600  
 C -1.23903600 1.92423500 -3.05078100  
 H -1.13520400 -2.52603900 -4.71161500  
 H -1.27397100 -2.97951600 -0.98301600  
 H 0.43979700 -2.89285000 -1.39889500  
 H -0.67205800 -3.83421600 -2.40616300  
 H -1.49326200 0.10427800 -5.37568500  
 H -2.02915000 2.22163100 -2.35366200  
 H -0.29406700 2.34075800 -2.67262200  
 H -1.44214100 2.40495500 -4.01269800  
 N 1.43358600 -0.49724400 -0.83103700  
 C 2.68786200 -0.69536400 -1.29271400  
 C 3.45925800 -1.80515600 -0.89783200  
 C 3.28543000 0.23708200 -2.16559000  
 C 4.79210300 -1.92169900 -1.26603800  
 F 2.90135500 -2.76018400 -0.14661600  
 C 4.61857400 0.13284000 -2.53002300  
 F 2.55667100 1.25442100 -2.63698800  
 C 5.37661200 -0.94590900 -2.07389600  
 F 5.51958700 -2.96809300 -0.85746000  
 F 5.18170700 1.05466300 -3.31808200  
 F 6.66215800 -1.05184600 -2.42190200  
 O -1.81326300 1.14450900 0.08126100  
 C -2.96030500 1.84112500 0.03717900  
 C -4.13449400 1.23712000 -0.47654000  
 C -3.00683900 3.17351800 0.51530800  
 C -4.12089600 -0.17376800 -0.94760900  
 C -5.31694400 1.98277200 -0.51706800  
 C -4.21064000 3.88212400 0.45325000

C -1.79821700 3.81896200 1.10089000  
 C -3.96736700 -1.21073000 -0.00875700  
 C -4.27426200 -0.47720600 -2.31405900  
 H -6.21110700 1.50687600 -0.90946200  
 C -5.36558100 3.29906200 -0.06293200  
 H -4.23059700 4.90216900 0.82775200  
 C -1.39720900 3.48828800 2.40956800  
 C -1.04876900 4.74866200 0.35099800  
 C -3.90892900 -2.53277700 -0.45441600  
 C -3.90641000 -0.91287800 1.46989000  
 C -4.20031500 -1.81120200 -2.72075300  
 C -4.53971000 0.59253700 -3.34720300  
 H -6.29472800 3.85982700 -0.10087600  
 C -0.21895200 4.03966800 2.92358500  
 C -2.20909900 2.51998200 3.23605400  
 C 0.12827200 5.27052400 0.89621300  
 C -1.48481000 5.16053500 -1.03448100  
 C -4.00488700 -2.85041200 -1.81052000  
 H -3.77586200 -3.32793100 0.27199600  
 H -3.95077500 -1.83622300 2.05171300  
 H -2.98188000 -0.39174200 1.73662300  
 H -4.73351900 -0.26463900 1.78130500  
 H -4.27190700 -2.03882200 -3.78129800  
 H -4.19661700 0.26538800 -4.33170000  
 H -5.61333900 0.81396300 -3.41958800  
 H -4.03758600 1.53133400 -3.10620100  
 C 0.57584900 4.90772500 2.17014900  
 H 0.09617200 3.76929400 3.92953300  
 H -2.21387000 1.52067600 2.78595600  
 H -1.80728600 2.43530100 4.25067600  
 H -3.25644200 2.83326500 3.30398600  
 H 0.72115500 5.96342500 0.30292800  
 H -0.71337400 5.76342400 -1.52316200  
 H -1.69415000 4.29137700 -1.66402600  
 H -2.40659900 5.75313400 -1.00431300  
 C -3.89072200 -4.27779000 -2.28573500  
 C 1.90366200 5.40062900 2.68875900  
 H -3.17279900 -4.35557000 -3.11064100  
 H -3.55247800 -4.93708600 -1.48008500  
 H -4.85094600 -4.66194600 -2.65392300  
 H 2.72437700 4.81343600 2.25600300  
 H 2.07689400 6.44880500 2.42129400  
 H 1.96863600 5.31034000 3.77771600

### 3a-TS2:

**G<sub>sol</sub>** = -3084.77064

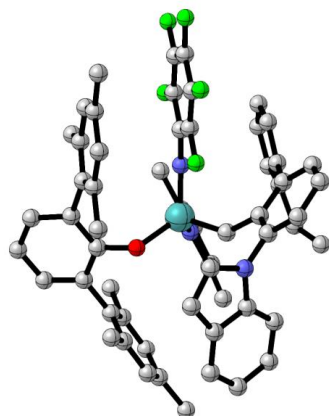


C 0.76156100 2.05091300 0.87088400  
 H 0.03717200 2.82885100 0.69818800  
 C 2.20057900 2.24383800 0.67846800  
 C 2.87500800 1.33861500 1.52512100  
 C 2.92064300 3.06559700 -0.18470100  
 N 1.92352100 0.68061600 2.34381300  
 C 4.25540300 1.17677800 1.46247400  
 C 4.31192300 2.94021200 -0.22542500  
 H 2.40248100 3.76489700 -0.83331400  
 C 2.00498800 -0.69646800 2.67883600  
 C 0.63199100 1.12720600 1.96252800  
 C 4.96428000 1.99386400 0.57484600  
 H 4.77189900 0.44695600 2.07414500  
 H 4.89044500 3.56624400 -0.89770800  
 C 0.93306200 -1.49416700 2.21878900  
 C 3.05397600 -1.23442100 3.41570300  
 C -0.13371600 -0.80275700 1.46894900  
 H -0.12907900 1.21243900 2.72655900  
 H 6.04407500 1.89470900 0.51542700  
 C 0.91755800 -2.85841400 2.55146200  
 C 3.06570500 -2.60645400 3.67229400  
 H 3.83105700 -0.58730000 3.80603900  
 H -1.12680800 -0.83968000 1.92205200  
 C 2.00772000 -3.40489800 3.24644600  
 C -0.22310200 -3.74947700 2.20257900  
 H 3.88420300 -3.04334600 4.23594800  
 H 1.99117700 -4.46335300 3.48666000  
 C -0.00109000 -4.76632700 1.26752500  
 C -1.49396500 -3.63588700 2.81907100  
 C -1.00822200 -5.66075300 0.90887800  
 H 0.97733100 -4.83318000 0.80187500  
 C -2.49944500 -4.53889700 2.42987300  
 C -1.85424400 -2.66299500 3.86765900  
 C -2.26738500 -5.54402400 1.49520700  
 H -0.81151500 -6.43273700 0.17124200  
 H -3.47957600 -4.45476400 2.89234900  
 C -1.06632500 -2.01303500 4.73610900  
 H -2.92877300 -2.50903700 3.96196000  
 H -3.06679200 -6.22765900 1.22483300  
 H 0.01045400 -2.12485400 4.76569400

H -1.50874000 -1.35394900 5.47773200  
 Mo -0.09611600 0.19024500 -0.22800600  
 N -0.73059900 -0.58597100 -2.04535300  
 C -0.50200200 -1.88310700 -2.48855600  
 C -0.89609800 0.23022800 -3.16242800  
 C -0.56304500 -1.89456100 -3.86766800  
 C -0.22096500 -2.99929000 -1.53886200  
 C -0.80760500 -0.55302600 -4.29524500  
 C -1.05732500 1.71465700 -3.05518400  
 H -0.46165200 -2.77172500 -4.49514800  
 H -0.99190200 -3.07446200 -0.76631100  
 H 0.74176400 -2.87649200 -1.02522500  
 H -0.19354800 -3.95267500 -2.07623600  
 H -0.91609500 -0.19956300 -5.31346700  
 H -1.94519400 2.00277300 -2.48338900  
 H -0.18912700 2.19929900 -2.58266200  
 H -1.15086900 2.14615700 -4.05667300  
 N 1.55755100 -0.24100200 -0.65604900  
 C 2.77873000 -0.39409700 -1.20903200  
 C 3.65707800 -1.40622300 -0.77887100  
 C 3.22900400 0.47433400 -2.22151300  
 C 4.93901400 -1.51616900 -1.29647100  
 F 3.25358700 -2.26656300 0.16508200  
 C 4.51062800 0.37435100 -2.74104500  
 F 2.41192700 1.43268900 -2.67374400  
 C 5.36945200 -0.62137600 -2.27662900  
 F 5.76805300 -2.47275100 -0.86034200  
 F 4.93272400 1.23187500 -3.67698700  
 F 6.60741400 -0.71922100 -2.77080200  
 O -1.84295200 1.10762000 0.02763200  
 C -3.02498100 1.71136800 -0.18203700  
 C -4.09615800 1.01043100 -0.79013600  
 C -3.21005900 3.05131700 0.23460900  
 C -3.95751800 -0.41275800 -1.20102600  
 C -5.31180000 1.67507900 -0.98573600  
 C -4.44133100 3.67676300 0.01553300  
 C -2.12445400 3.79545100 0.93296400  
 C -3.83790600 -1.40735900 -0.21308700  
 C -3.97378400 -0.77224500 -2.56267700  
 H -6.12647100 1.12611800 -1.44922000  
 C -5.49333500 3.00025000 -0.59686400  
 H -4.56629700 4.70457800 0.34592500  
 C -1.86577900 3.53644200 2.29298300  
 C -1.36177100 4.76033600 0.24450000  
 C -3.66875400 -2.73837600 -0.59911700  
 C -3.94137200 -1.05906700 1.25182100  
 C -3.79193600 -2.11292300 -2.90793300  
 C -4.20607900 0.23936600 -3.66052500  
 H -6.44661800 3.49495200 -0.75740300  
 C -0.82458400 4.21547900 2.93231300  
 C -2.68123400 2.51280200 3.04533300  
 C -0.32281100 5.41253800 0.91662800

C -1.63373700 5.07064600 -1.20809400  
 C -3.62130500 -3.10706100 -1.94452900  
 H -3.55943200 -3.50011000 0.16643500  
 H -3.92902800 -1.96379700 1.86438200  
 H -3.11615200 -0.41790100 1.57633500  
 H -4.86544400 -0.50962500 1.46766200  
 H -3.75372100 -2.38043500 -3.96080500  
 H -3.73074000 -0.09047200 -4.58747000  
 H -5.27928500 0.36784800 -3.85798000  
 H -3.81005900 1.22402900 -3.40639500  
 C -0.02605200 5.14128200 2.25551900  
 H -0.62074400 4.00381200 3.98003800  
 H -2.52407500 1.50669400 2.63904600  
 H -2.41409200 2.49952700 4.10679100  
 H -3.75454900 2.71422700 2.96145300  
 H 0.27856100 6.14043700 0.37602400  
 H -0.87979400 5.75520800 -1.60849700  
 H -1.63181500 4.16169200 -1.81726100  
 H -2.61756900 5.53401400 -1.34338000  
 C -3.37569600 -4.53815900 -2.35322600  
 C 1.15499600 5.79297400 2.93141300  
 H -2.56065600 -4.59448600 -3.08440800  
 H -3.09925600 -5.15418800 -1.49188300  
 H -4.26252300 -4.98687100 -2.81940900  
 H 2.08092400 5.25092000 2.69759900  
 H 1.29011700 6.82714900 2.59674800  
 H 1.04219500 5.79807400 4.02033800

### 3a-Alk2:



**G<sub>sol</sub>** = -3084.800721

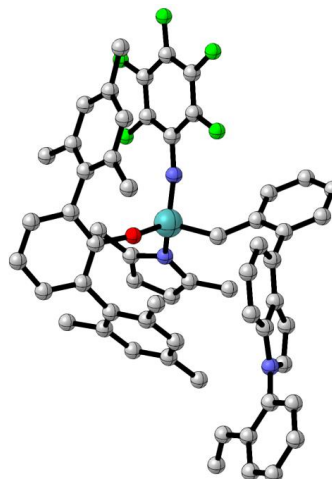
Mo 0.25594200 0.11784400 0.59708500  
 N -1.48357100 0.10906900 0.78445800  
 C -2.79216300 0.05186300 0.42301400  
 C -3.16330700 -0.42837500 -0.84635700  
 C -4.49374400 -0.57155000 -1.20731900  
 C -5.49935800 -0.19729500 -0.32002900  
 C -5.16102500 0.30220000 0.93596900  
 C -3.82641100 0.42077700 1.29696800

F -2.21915500 -0.76024000 -1.73480800  
 F -4.81637600 -1.01323700 -2.43048600  
 F -6.78213400 -0.28048300 -0.68683500  
 F -6.12537700 0.66985300 1.78884100  
 F -3.53010800 0.89714400 2.51359800  
 N 1.25938000 0.02203100 2.35219500  
 C 0.80331300 0.52169400 3.58644700  
 C 1.73711400 0.21833600 4.54412000  
 C 2.81398400 -0.48049900 3.90210300  
 C 2.50784000 -0.59546700 2.56948400  
 C -0.48955900 1.25379500 3.73005900  
 H -0.60500600 1.58384700 4.76706400  
 H -1.34921400 0.62981900 3.47151600  
 H -0.53490300 2.14841100 3.09444800  
 C 3.30681200 -1.22146700 1.47432100  
 H 4.31297000 -1.43911600 1.84185500  
 H 3.42562700 -0.56015900 0.60908300  
 H 2.86758400 -2.16084200 1.12392400  
 H 3.72741500 -0.83191800 4.36540000  
 H 1.67380400 0.49426900 5.58919700  
 O 1.02202600 1.38779600 -0.64350100  
 C 1.11176000 2.74235600 -0.47605900  
 C 2.36157300 3.27814900 -0.10290900  
 C 2.47491500 4.66322000 0.04934800  
 C 1.38197500 5.50275500 -0.16090000  
 C 0.15959500 4.95398300 -0.53498200  
 C -0.00465500 3.57011900 -0.70335300  
 C -1.50295200 2.49390500 -2.42580800  
 C -1.33849000 3.06755100 -1.14435300  
 C -2.46927900 3.29485100 -0.33328100  
 C -3.74391600 3.01202800 -0.83716000  
 C -3.92998900 2.49241700 -2.11763100  
 C 5.31248000 1.01987400 -0.81586200  
 C 4.16588700 1.78999900 -1.01459800  
 C 3.55089100 2.40229300 0.09822000  
 C 4.09031200 2.23060800 1.38699900  
 C 5.24213400 1.45154900 1.54121800  
 C 5.86294500 0.83389900 0.45559600  
 C -2.79243600 2.21475200 -2.88372000  
 H -0.69400300 5.59872100 -0.72208000  
 H 1.48686200 6.57767500 -0.04798800  
 H 3.44105400 5.07656100 0.32381900  
 C 0.50700500 -1.56191800 -0.19934900  
 H 1.56272200 -1.50356300 -0.50438400  
 H -4.61097200 3.20363800 -0.20861400  
 H -2.91356200 1.78842800 -3.87737500  
 H 5.77801100 0.54220000 -1.67329600  
 H 5.64416300 1.30488700 2.54097100  
 C -2.34563800 3.82998500 1.07574100  
 H -1.39263100 3.54909900 1.53077600  
 H -2.40381000 4.92514400 1.10621200  
 H -3.15076800 3.43875600 1.70513500

C -5.31267300 2.24822500 -2.67289200  
 H -5.37790500 1.27845000 -3.17613500  
 H -6.07159800 2.26928600 -1.88443400  
 H -5.58144600 3.01575500 -3.40994100  
 C -0.31919500 2.20546700 -3.31534800  
 H -0.64312400 2.01630800 -4.34359000  
 H 0.38742900 3.04224900 -3.32549000  
 H 0.23327100 1.32780000 -2.96472500  
 C 3.60459400 1.95873100 -2.40509600  
 H 4.33812600 1.65956100 -3.15915000  
 H 2.71209700 1.33921400 -2.54194000  
 H 3.31450900 2.99716600 -2.59775100  
 C 7.06420100 -0.05957100 0.64310300  
 H 7.85227000 0.16627700 -0.08479800  
 H 7.48952700 0.04371400 1.64646200  
 H 6.79031500 -1.11395800 0.50306100  
 C 3.43546100 2.84591300 2.60072200  
 H 3.53915400 3.93717600 2.61491100  
 H 2.36467800 2.62217300 2.62870100  
 H 3.87541500 2.44793100 3.51823900  
 C -0.23859000 -2.71826400 -0.66687900  
 C -1.20539600 -3.39984100 0.11538500  
 C -0.01949700 -3.15427800 -1.99257000  
 C -1.95246300 -4.42783600 -0.47309200  
 C -1.47190300 -3.03418400 1.53233400  
 C -0.76781800 -4.18325700 -2.55774400  
 N 0.96407100 -2.49199200 -2.78158800  
 C -1.75122500 -4.81346800 -1.79801700  
 H -2.68780800 -4.94540500 0.13561900  
 C -2.77939200 -2.67446200 1.88224900  
 C -0.46265800 -3.00317300 2.52591100  
 H -0.56849300 -4.47666000 -3.58333000  
 C 0.70813200 -1.50896200 -3.73173100  
 C 2.33506500 -2.54650800 -2.56340100  
 H -2.34213700 -5.61645800 -2.22766200  
 C -3.09130500 -2.20506000 3.15700200  
 H -3.55075600 -2.71477800 1.11875400  
 C -0.78410600 -2.47918200 3.78841600  
 C 0.90138200 -3.53306200 2.36067800  
 C 1.88633500 -0.95095100 -4.15386100  
 H -0.31417400 -1.29401800 -4.00731400  
 C 2.94694200 -1.59301700 -3.42384000  
 C 3.06619700 -3.33603800 -1.67080500  
 C -2.07868100 -2.07741000 4.10631100  
 H -4.10939000 -1.90963000 3.39288300  
 H 0.00459000 -2.39447800 4.52951600  
 C 1.30008400 -4.53307000 1.56373300  
 H 1.63145100 -3.07983000 3.02761400  
 H 1.98908300 -0.17195400 -4.89606700  
 C 4.34514800 -1.45888700 -3.39083600  
 C 4.44630000 -3.16373300 -1.64934100  
 H 2.57013400 -4.04431000 -1.01475100

H -2.29554600 -1.67731100 5.09232300  
 H 0.62802400 -5.05620800 0.89184600  
 H 2.33315000 -4.86849300 1.58044700  
 C 5.07890400 -2.23898700 -2.50508200  
 H 4.84279300 -0.74765300 -4.04383800  
 H 5.04626700 -3.75505500 -0.96379700  
 H 6.15946200 -2.13478400 -2.46660100

### 3b-Alk1:



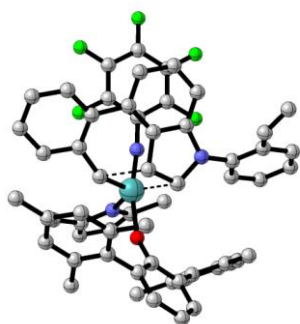
$G_{\text{sol}} = -3084.795006$

Mo 0.98206000 0.34699000 -0.81836200  
 N 2.55473200 -0.36541100 -1.14333000  
 C 3.79684200 -0.87836600 -0.93080700  
 C 3.95764500 -2.12189800 -0.29310700  
 C 5.21598700 -2.65457400 -0.05586700  
 C 6.35431700 -1.94095800 -0.42285200  
 C 6.22470900 -0.69635200 -1.03326900  
 C 4.96149500 -0.18181500 -1.29165500  
 F 2.87495500 -2.79131600 0.12041100  
 F 5.34408500 -3.82768700 0.57938900  
 F 7.56941400 -2.42576500 -0.14060500  
 F 7.31844400 0.00944000 -1.34625300  
 F 4.85973800 1.03111000 -1.85885300  
 N 0.43358200 1.44253300 -2.42125200  
 C 1.06018300 2.68806700 -2.62319700  
 C 0.50788400 3.27612800 -3.73151900  
 C -0.47662100 2.37279000 -4.25362500  
 C -0.50772500 1.26270100 -3.44376300  
 C 2.13351500 3.17964400 -1.70368200  
 H 2.46729400 4.17170100 -2.02193600  
 H 3.01130500 2.52299300 -1.69840300  
 H 1.78663700 3.28166300 -0.66614700  
 C -1.34548400 0.03526300 -3.58132200  
 H -1.97976200 0.13208900 -4.46809300  
 H -2.00075900 -0.11807200 -2.71661700  
 H -0.74107600 -0.87139600 -3.69577700  
 H -1.08955900 2.52164600 -5.13383300

H 0.77728800 4.24658500 -4.12911300  
O 0.61477800 1.11576400 0.87897300  
C 0.71954500 2.21234800 1.66018300  
C -0.32065000 3.16260000 1.60334500  
C -0.21989800 4.28261500 2.43309800  
C 0.88142100 4.45317900 3.27531600  
C 1.90551100 3.50559800 3.29234500  
C 1.84511000 2.36357800 2.48347300  
C 2.69200700 0.06984800 3.06989000  
C 2.92748500 1.33570900 2.48446400  
C 4.18834400 1.62207600 1.92875400  
C 5.21276500 0.66960100 2.02857300  
C 5.01867700 -0.55750000 2.65992600  
C -3.06663300 1.48640800 -0.38724600  
C -2.21271200 1.79237100 0.67816000  
C -1.40149400 2.94336000 0.60113000  
C -1.50808400 3.80158200 -0.51714900  
C -2.39071400 3.46996100 -1.54580600  
C -3.16527000 2.30860600 -1.51071100  
C 3.73850300 -0.84893400 3.14761800  
H 2.76651700 3.63998700 3.94090300  
H 0.94226800 5.32752400 3.91646200  
H -1.01151600 5.02569600 2.41097600  
C -0.18620400 -1.12563900 -0.95713800  
H -1.11914500 -0.77601100 -0.48794700  
H 6.18976000 0.90624000 1.61169800  
H 3.55814600 -1.81103800 3.62265200  
H -3.64616900 0.56908800 -0.34315100  
H -2.43984900 4.11329100 -2.42009700  
C 4.48116500 2.92815700 1.22480500  
H 3.56754100 3.44444400 0.92479800  
H 5.04706100 3.61386300 1.86858700  
H 5.08316400 2.74902800 0.32747300  
C 6.15623800 -1.52925000 2.86269500  
H 5.85472500 -2.55909400 2.64769300  
H 7.01284500 -1.29038000 2.22568100  
H 6.50437700 -1.50488600 3.90351300  
C 1.33448800 -0.29467200 3.62115900  
H 1.39438600 -1.19590300 4.23879000  
H 0.91610200 0.51404300 4.22977400  
H 0.62221400 -0.48647200 2.81085300  
C -2.18325300 0.86356300 1.86911200  
H -3.19411900 0.52684700 2.11596500  
H -1.59154800 -0.03667200 1.66905900  
H -1.75438400 1.34659900 2.75057000  
C -4.07493400 1.96390900 -2.66319400  
H -4.92126900 2.65939200 -2.72773600  
H -3.53127000 2.02668700 -3.61199000  
H -4.48013100 0.95320400 -2.56331700  
C -0.68900800 5.06537100 -0.64326200  
H -1.15862500 5.90085200 -0.10768700  
H 0.31481400 4.94947300 -0.22855000

H -0.59414100 5.35128400 -1.69405600  
C -0.16290600 -2.51587900 -1.35653500  
C -1.11430000 -3.42054600 -0.82264300  
C 0.78853400 -2.98895600 -2.28127400  
C -1.08737600 -4.75801100 -1.22730500  
C 0.80164900 -4.32242200 -2.67185100  
H 1.50876000 -2.28559900 -2.68627700  
C -0.14020100 -5.21125400 -2.14639600  
H -1.81581500 -5.44609200 -0.80832500  
H 1.54040500 -4.66934600 -3.38859400  
H -0.13751000 -6.25394500 -2.45084400  
C -2.10246700 -2.98090400 0.20432600  
C -3.34709600 -2.42535500 -0.16087500  
C -1.82868300 -3.13785300 1.56243200  
C -4.28103000 -2.07862300 0.85475000  
C -2.76037500 -2.76792500 2.55192000  
H -0.87276700 -3.56092400 1.85693300  
C -4.00098600 -2.23967300 2.21504400  
H -2.50350600 -2.90122400 3.59848600  
H -4.72048200 -1.95546200 2.97524600  
N -5.41377100 -1.56318400 0.22858700  
C -3.95863900 -2.10121400 -1.42199900  
C -5.20099600 -1.59328600 -1.14994500  
C -6.66491600 -1.31353400 0.86072500  
C -7.21279100 -2.31285100 1.67227400  
C -7.35320500 -0.10250600 0.64312800  
C -8.44832500 -2.12385300 2.28409100  
H -6.66693200 -3.24146200 1.80078700  
C -8.60478500 0.05627500 1.26310500  
C -9.15040500 -0.93504500 2.07168300  
H -8.86394000 -2.90421100 2.91442700  
H -9.13077500 0.99642700 1.13154500  
H -10.11367900 -0.77580300 2.54709600  
C -6.76653500 0.97700800 -0.16760100  
C -7.46448200 1.85647500 -0.89538500  
H -5.68353300 1.05250100 -0.15055500  
H -6.96491300 2.65255100 -1.43772900  
H -8.54695400 1.80845400 -0.98338400  
H -5.98200800 -1.25151600 -1.81265000  
H -3.52476300 -2.23879400 -2.40182600



**3b-TS1:**

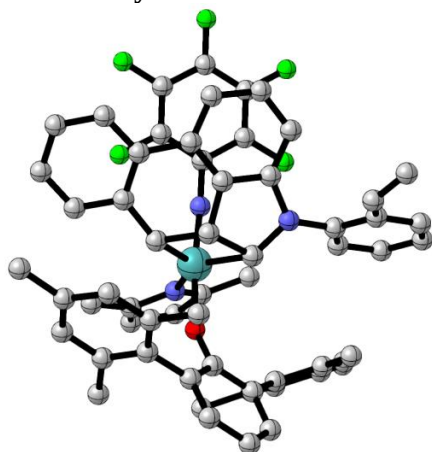
**G<sub>sol</sub>** = -3084.768776

C 0.60452200 2.02752300 -0.06590800  
H -0.23573700 2.70986000 0.08985300  
C 1.88932300 2.73882300 0.08038900  
C 2.99987600 2.32991300 0.86749100  
C 1.96457200 3.96043500 -0.61178300  
C 4.11257700 3.18064400 0.94744200  
C 3.09907900 4.76272700 -0.55675100  
H 1.10849500 4.27693500 -1.19741300  
C 1.81112300 -1.04450000 2.04310000  
C 0.45977100 0.79957200 1.60021100  
C 4.17615500 4.37799200 0.24233500  
H 4.94228200 2.89408300 1.58570300  
H 3.12793400 5.69544500 -1.11190500  
C -0.31993500 -0.41581800 1.51003800  
H 0.05047000 1.68433900 2.06795800  
H 5.05636500 5.00870500 0.32305700  
H -1.37278900 -0.47718600 1.75481000  
Mo -0.20751500 0.37330200 -0.72680500  
N -0.82864200 0.31037900 -2.69484600  
C -1.15292200 -0.85435100 -3.38565000  
C -1.06357100 1.39433900 -3.53740000  
C -1.61403700 -0.50783200 -4.63846700  
C -0.96016100 -2.20916700 -2.78423100  
C -1.55572200 0.91634500 -4.73523200  
C -0.68228500 2.79436100 -3.17324800  
H -1.94635300 -1.20179200 -5.40067100  
H -1.56716300 -2.35512900 -1.88288100  
H 0.08834200 -2.40010900 -2.52085500  
H -1.27227200 -2.97815500 -3.49726000  
H -1.81850500 1.52297900 -5.59311400  
H -1.10724700 3.12112500 -2.21914100  
H 0.40821300 2.90705700 -3.09699800  
H -1.03566000 3.48507200 -3.94577000  
N 1.32713200 -0.44550100 -1.03912000  
C 2.57804800 -0.91823700 -1.23400100  
C 2.95337900 -2.24116200 -0.93719700  
C 3.58368500 -0.06557700 -1.74047600  
C 4.26228800 -2.67781900 -1.07746900

F 2.03450400 -3.09840100 -0.47576600  
C 4.89641000 -0.49116300 -1.87753500  
F 3.27353500 1.18965100 -2.07748500  
C 5.24010400 -1.80067500 -1.54192100  
F 4.59440300 -3.93198300 -0.74712300  
F 5.83690900 0.34556000 -2.33198100  
F 6.50520800 -2.21313700 -1.66652100  
O -2.06545800 0.91564300 -0.18719800  
C -3.13534200 0.99124300 0.61098700  
C -4.09310700 -0.05081800 0.62673300  
C -3.32579300 2.13098600 1.43309600  
C -3.99885500 -1.24036000 -0.26525900  
C -5.20151400 0.06438900 1.47614500  
C -4.44614000 2.20127800 2.26479100  
C -2.36244100 3.26466700 1.39007600  
C -3.86805500 -2.52932100 0.29351700  
C -4.17434100 -1.09199300 -1.65895600  
H -5.93978500 -0.73217700 1.46562200  
C -5.38562800 1.17297700 2.29704100  
H -4.58035800 3.08679200 2.88024700  
C -1.50738000 3.52328100 2.48108700  
C -2.32470400 4.10005100 0.25494800  
C -3.90895500 -3.64412900 -0.55010800  
C -3.71176700 -2.74002100 1.78310000  
C -4.21773700 -2.23371100 -2.46197200  
C -4.33141700 0.26562500 -2.29395800  
H -6.25824800 1.24353200 2.93929200  
C -0.58554300 4.57153000 2.39194000  
C -1.57954800 2.69919500 3.74837600  
C -1.39610400 5.14582800 0.21017000  
C -3.29421000 3.88887600 -0.88225800  
C -4.08112900 -3.51750300 -1.92995900  
H -3.81083600 -4.63512900 -0.11330700  
H -3.30247900 -3.73158700 1.99245800  
H -3.04432500 -1.99898700 2.23303700  
H -4.67128700 -2.65469000 2.30723200  
H -4.34377900 -2.10984900 -3.53464500  
H -4.75999700 0.17776400 -3.29583200  
H -4.97400100 0.91782100 -1.69311200  
H -3.35973400 0.75707800 -2.39765300  
C -0.51151700 5.39345300 1.26393800  
H 0.08907200 4.75255300 3.22632900  
H -1.76577100 1.64136900 3.54123700  
H -0.65288800 2.78607300 4.32506900  
H -2.40021100 3.03785600 4.39255800  
H -1.36919500 5.78701000 -0.66829000  
H -3.17500000 4.66133800 -1.64758500  
H -3.15097900 2.91388000 -1.35625700  
H -4.32858700 3.91806400 -0.52100300  
C -4.07337400 -4.72927700 -2.82886500  
C 0.48311400 6.52642400 1.20385100  
H -4.34481700 -5.63813300 -2.28139300

H -4.77163900 -4.61316200 -3.66479200  
H -3.07675700 -4.89179600 -3.26185200  
H 1.49644400 6.17598000 1.42640500  
H 0.49971400 6.98863300 0.21192600  
H 0.23576600 7.30901700 1.93217500  
C 1.83685600 0.34329400 1.81212500  
N 0.49334600 -1.48728500 1.94105800  
C 3.03234500 1.00630900 1.52367300  
C 2.99169700 -1.77539000 2.20469000  
C 4.22005000 0.27553400 1.69124500  
C 4.18974800 -1.07603500 2.06264000  
H 5.17371500 0.73277400 1.45152300  
H 5.12764100 -1.61290200 2.17085200  
H 2.97576100 -2.84356400 2.38005600  
C 0.07883600 -2.84439500 1.93985400  
C 0.30206900 -3.64938000 3.07780700  
C -0.53843700 -3.36485500 0.80229300  
C -0.08628800 -4.99793500 3.00669400  
C -0.90906700 -4.70393800 0.75658500  
H -0.69694700 -2.72247900 -0.05236700  
C -0.67442200 -5.52606000 1.86152700  
H 0.04690800 -5.62532100 3.88229600  
H -1.38102700 -5.09564300 -0.13788700  
H -0.96613600 -6.57186700 1.83740600  
C 0.87726100 -3.07445400 4.30330100  
C 1.54971400 -3.74992900 5.24273100  
H 0.73742200 -2.00281200 4.42712000  
H 1.92067100 -3.25190300 6.13294000  
H 1.76380300 -4.81183300 5.15426900

### 3b-Metallacycle:



**G<sub>sol</sub>** = -3084.78279

C 0.74112100 1.83627800 0.37173500  
H -0.00730200 2.61658500 0.47711900  
C 2.09835400 2.42530900 0.27114200  
C 3.23859800 1.87970300 0.91416400  
C 2.23554000 3.60920300 -0.46711600  
C 4.46624600 2.54927200 0.80004600  
C 3.46597600 4.24514200 -0.59114300

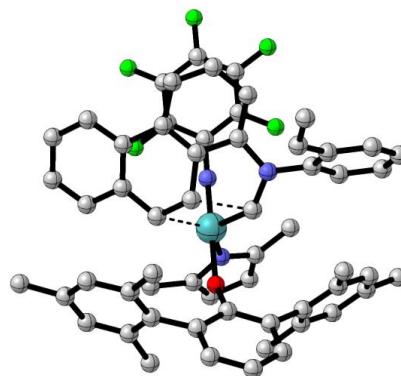
H 1.35474700 4.02831100 -0.94229700  
C 1.64071300 -1.31230700 2.01277100  
C 0.56026400 0.73775300 1.47294500  
C 4.58754300 3.71617800 0.05372700  
H 5.33903400 2.15082400 1.30719900  
H 3.54860700 5.15484400 -1.17879300  
C -0.38211100 -0.52146700 1.17977000  
H 0.09520900 1.24764900 2.32146300  
H 5.55030900 4.21248200 -0.02285500  
H -1.41320300 -0.44324500 1.51639100  
Mo -0.20684500 0.36488400 -0.78591800  
N -0.83367000 0.29514200 -2.73080700  
C -1.16638600 -0.82893900 -3.47937900  
C -0.96920000 1.42393400 -3.54133500  
C -1.54813100 -0.41183900 -4.73706300  
C -1.04857800 -2.21014900 -2.92175100  
C -1.41968700 1.01185800 -4.77735900  
C -0.53243600 2.78179200 -3.08480500  
H -1.87461600 -1.06006400 -5.54072400  
H -1.69321500 -2.35938100 -2.04879800  
H -0.01764500 -2.44581800 -2.62598800  
H -1.35686000 -2.94114400 -3.67551300  
H -1.61600900 1.66061900 -5.62198000  
H -0.92132100 3.04226400 -2.09513500  
H 0.56307300 2.85985900 -3.03385700  
H -0.88615100 3.54386400 -3.78673700  
N 1.33065400 -0.44738200 -1.11997100  
C 2.57579900 -0.95744000 -1.25485400  
C 2.88857600 -2.28715700 -0.91817600  
C 3.63041000 -0.14459400 -1.72420600  
C 4.19075400 -2.76098700 -0.96375600  
F 1.91280700 -3.10935100 -0.51196100  
C 4.93609200 -0.61017600 -1.77032500  
F 3.37336200 1.10488200 -2.11948000  
C 5.21959500 -1.92029000 -1.38432000  
F 4.46704500 -4.01528800 -0.58776500  
F 5.92618400 0.18760000 -2.18671900  
F 6.47789500 -2.36924400 -1.41791200  
O -1.96755300 1.14833500 -0.22860000  
C -3.03971900 1.28476500 0.56151500  
C -4.06294500 0.30593400 0.55410200  
C -3.16197800 2.41939500 1.40392000  
C -4.03355700 -0.88812400 -0.33633300  
C -5.17490400 0.48546800 1.38778400  
C -4.28864300 2.55472700 2.21853000  
C -2.10932100 3.47072800 1.41915300  
C -3.98299100 -2.18073000 0.22653700  
C -4.19876000 -0.73291800 -1.73013500  
H -5.96191200 -0.26247900 1.35890600  
C -5.29824200 1.59471700 2.21856400  
H -4.36831300 3.43550300 2.84995500  
C -1.25936200 3.61325100 2.53382900



C -1.97559700 4.33930400 0.31669200  
 C -4.09309400 -3.29313600 -0.61402100  
 C -3.84618900 -2.39862200 1.71693000  
 C -4.31216800 -1.87144000 -2.53039500  
 C -4.28154000 0.63201700 -2.36366300  
 H -6.17455800 1.71626700 2.84808400  
 C -0.25215700 4.58341000 2.50349600  
 C -1.42136500 2.74648500 3.76314300  
 C -0.95811700 5.29765400 0.32623400  
 C -2.94979100 4.26670800 -0.83429100  
 C -4.25772500 -3.15994500 -1.99388100  
 H -4.05294700 -4.28655600 -0.17432400  
 H -3.46845400 -3.40225300 1.92807300  
 H -3.16503800 -1.67667500 2.17633500  
 H -4.80917100 -2.28794000 2.23052100  
 H -4.43042600 -1.74334700 -3.60343000  
 H -4.68130900 0.56506000 -3.37897700  
 H -4.91727000 1.30661000 -1.77996300  
 H -3.28914900 1.08605300 -2.43366800  
 C -0.07785700 5.42927100 1.40556300  
 H 0.41457600 4.67837800 3.35807100  
 H -1.72117300 1.72494400 3.50932900  
 H -0.49223400 2.70998300 4.34151000  
 H -2.20322100 3.13824700 4.42579700  
 H -0.85722000 5.96629600 -0.52612800  
 H -2.70385700 5.00459600 -1.60357500  
 H -2.95482000 3.27715500 -1.29890300  
 H -3.97218900 4.46014100 -0.48830100  
 C -4.32777000 -4.37282500 -2.88859900  
 C 1.04076200 6.44091900 1.38198200  
 H -3.34307900 -4.60227800 -3.31834000  
 H -4.66006800 -5.25955400 -2.33840100  
 H -5.01496800 -4.21415600 -3.72671000  
 H 1.99373000 5.95976000 1.12981800  
 H 0.85635800 7.22204000 0.63731900  
 H 1.16421200 6.92328000 2.35784500  
 C 1.85021700 0.04905700 1.77955700  
 N 0.29452000 -1.61314800 1.78716100  
 C 3.12474800 0.57176400 1.58679500  
 C 2.70791000 -2.16376100 2.29780400  
 C 4.21099800 -0.27868000 1.87673000  
 C 3.99056700 -1.60407000 2.25952300  
 H 5.22927700 0.06786900 1.74085900  
 H 4.84528800 -2.24246500 2.46393700  
 H 2.55659000 -3.22006400 2.48108500  
 C -0.25602500 -2.91917100 1.82852700  
 C -0.25462400 -3.64920900 3.03700300  
 C -0.77741000 -3.46980400 0.65668000  
 C -0.77208200 -4.95507100 3.00914000  
 C -1.27893600 -4.76679800 0.65551900  
 H -0.76148900 -2.88170200 -0.25005300  
 C -1.27069400 -5.51435000 1.83602200

H -0.81166000 -5.52073600 3.93467900  
 H -1.67687800 -5.18593100 -0.26276400  
 H -1.66775500 -6.52514600 1.84641100  
 C 0.23412100 -3.03467600 4.28008500  
 C 0.71419200 -3.69271900 5.34182100  
 H 0.20081900 -1.94772400 4.30735000  
 H 1.03407600 -3.16134800 6.23256700  
 H 0.81733800 -4.77457600 5.35735900

### 3b-TS2:

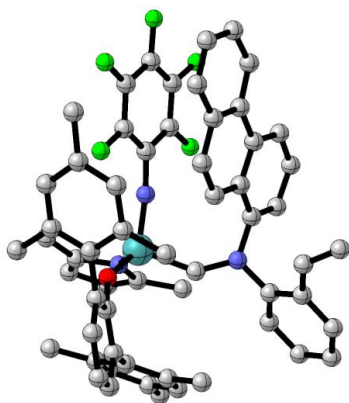


$G_{\text{sol}} = -3084.772545$

C -0.63617700 1.89751300 -0.69316400  
 H 0.16833800 2.62121000 -0.71522700  
 C -1.97815700 2.50190400 -0.59599700  
 C -3.09960000 1.91371900 -1.23542100  
 C -2.12204600 3.73167200 0.05946600  
 C -4.32211400 2.60329800 -1.21734500  
 C -3.34799900 4.38648600 0.08790800  
 H -1.25140400 4.17001000 0.53664900  
 C -1.56009200 -1.43052900 -1.84035700  
 C -0.46727700 0.73509900 -1.52515400  
 C -4.45029800 3.82384900 -0.56388300  
 H -5.18607800 2.17981200 -1.71900600  
 H -3.44451700 5.33522500 0.60776300  
 C 0.48588200 -0.94587900 -0.71986900  
 H 0.31067700 0.75866400 -2.28599900  
 H -5.40818700 4.33534000 -0.55957300  
 H 1.54941600 -1.04567700 -0.93938800  
 Mo 0.13867400 0.38680900 0.77097800  
 N 0.72723500 0.35725200 2.75852500  
 C 0.98588400 -0.75622700 3.54717200  
 C 0.94535600 1.50004900 3.52499900  
 C 1.40035300 -0.32175500 4.79051600  
 C 0.76193700 -2.14424900 3.03775700  
 C 1.36923300 1.10788100 4.77839300  
 C 0.58036600 2.85913600 3.01027300

|                                      |                                       |
|--------------------------------------|---------------------------------------|
| H 1.68345500 -0.95999300 5.61853200  | H 3.21925400 0.88060400 2.50947200    |
| H 1.33528700 -2.34527800 2.12559400  | C 0.56837900 5.62676100 -1.13838900   |
| H -0.29612300 -2.33023300 2.81105900 | H 0.03120900 5.05614900 -3.13997700   |
| H 1.07891400 -2.87404800 3.78928400  | H 2.38563500 3.32127300 -4.31908300   |
| H 1.60767100 1.77187900 5.60023300   | H 1.87254600 1.89789500 -3.43250700   |
| H 0.91387200 3.02336100 1.97948700   | H 0.65977200 2.97640800 -4.16355300   |
| H -0.50756400 3.02240900 3.02795700  | H 1.35828200 5.94573400 0.83655400    |
| H 1.04033000 3.63885500 3.62601800   | H 3.10559100 4.76412000 1.84467100    |
| N -1.48433400 -0.22514200 1.11887200 | H 3.09531700 3.02773900 1.49879500    |
| C -2.74022400 -0.70881800 1.23724900 | H 4.29234600 4.06019900 0.72765700    |
| C -3.02576800 -2.07568700 1.05765300 | C 3.80454400 -4.62369200 2.91615800   |
| C -3.82578100 0.14603200 1.52131800  | C -0.43075100 6.75539500 -1.06835000  |
| C -4.32637500 -2.55446100 1.07262600 | H 2.78626500 -4.77121700 3.30118100   |
| F -2.02069800 -2.93352600 0.82890300 | H 4.08594100 -5.53314900 2.37454200   |
| C -5.13065300 -0.32554400 1.53902000 | H 4.46508900 -4.52605600 3.78451400   |
| F -3.59879800 1.43787200 1.76967400  | H -1.45713500 6.36799700 -1.07097700  |
| C -5.38428700 -1.67735800 1.30764700 | H -0.29867100 7.34955700 -0.15859200  |
| F -4.57295700 -3.85051700 0.84669300 | H -0.33557600 7.42842500 -1.92845800  |
| F -6.14871000 0.50869400 1.77960000  | C -1.70144800 -0.03696000 -1.80648600 |
| F -6.64082700 -2.13263000 1.31382400 | N -0.26727400 -1.84809700 -1.45977900 |
| O 1.97665100 1.07250100 0.28490000   | C -2.97319200 0.54442700 -1.76853700  |
| C 3.06712700 1.14538700 -0.48472000  | C -2.63934100 -2.25693300 -2.12186000 |
| C 4.01326500 0.08738200 -0.49609900  | C -4.07603800 -0.29252900 -2.05275800 |
| C 3.30063300 2.29510200 -1.28555700  | C -3.89667900 -1.65358200 -2.27468800 |
| C 3.89442800 -1.11390100 0.37880800  | H -5.08239000 0.10997800 -2.03713300  |
| C 5.13955600 0.19520100 -1.32339400  | H -4.75970000 -2.27857200 -2.48381700 |
| C 4.43848500 2.35474700 -2.09379300  | H -2.52287800 -3.33384000 -2.15246100 |
| C 2.36827200 3.45492200 -1.25107300  | C 0.22647100 -3.16094100 -1.71149900  |
| C 3.78349700 -2.39920200 -0.19468500 | C 0.32925000 -3.64492700 -3.03329700  |
| C 4.01671300 -0.98022400 1.78004400  | C 0.59599100 -3.94856500 -0.61977700  |
| H 5.86405900 -0.61377700 -1.30829000 | C 0.80439700 -4.95420200 -3.20814500  |
| C 5.35949700 1.30998000 -2.12552300  | C 1.06937300 -5.24224300 -0.82300500  |
| H 4.60018900 3.24694200 -2.69280600  | H 0.49723700 -3.54056300 0.37874800   |
| C 1.55935400 3.76146200 -2.36425400  | C 1.16642200 -5.74720400 -2.12134900  |
| C 2.31147000 4.26483200 -0.09828900  | H 0.92686300 -5.33498000 -4.21710400  |
| C 3.76730300 -3.52025400 0.64149100  | H 1.36045000 -5.84870900 0.02878300   |
| C 3.71102200 -2.61199300 -1.69136200 | H 1.53922500 -6.75317500 -2.28971100  |
| C 4.00908200 -2.12809100 2.57486100  | C -0.00835200 -2.78211300 -4.17512900 |
| C 4.18172900 0.36783600 2.43225900   | C -0.41233200 -3.20556000 -5.37810000 |
| H 6.24543600 1.37369400 -2.75006100  | H 0.07981400 -1.71250800 -3.99866700  |
| C 0.67085500 4.83854000 -2.28706100  | H -0.62102600 -2.50286200 -6.17848300 |
| C 1.61713500 2.94202000 -3.63336900  | H -0.56295800 -4.25823700 -5.60240200 |
| C 1.40404600 5.32795800 -0.05772400  |                                       |
| C 3.24824200 4.01650200 1.05895200   |                                       |
| C 3.87471300 -3.40600700 2.02812700  |                                       |
| H 3.67116700 -4.50555500 0.19257600  |                                       |
| H 3.24231300 -3.57194900 -1.92285200 |                                       |
| H 3.14675000 -1.82346300 -2.19853800 |                                       |
| H 4.71008600 -2.61366000 -2.14465800 |                                       |
| H 4.09105800 -2.01311600 3.65277300  |                                       |
| H 4.57533400 0.26129400 3.44662400   |                                       |
| H 4.85832500 1.00998700 1.85858600   |                                       |

### 3b-Alk2:



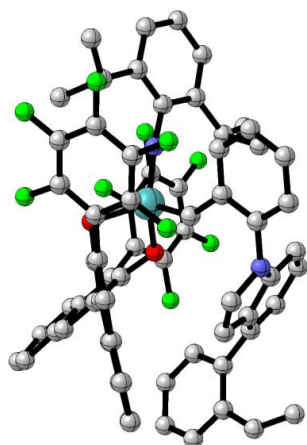
G<sub>sol</sub> = -3084.818185

C -2.61099300 -0.00919700 -1.77189200  
H -2.54033200 0.99486100 -2.17001500  
C -3.90677200 -0.52398600 -1.44690200  
C -4.02774200 -1.83453300 -0.90408500  
C -5.05903300 0.27527200 -1.62085900  
C -5.32071100 -2.29143100 -0.56146100  
C -6.30797000 -0.19459200 -1.26577100  
H -4.93817800 1.27869200 -2.01958900  
C -0.37861300 -2.77518200 -0.63680200  
C -1.48352600 -0.72530000 -1.52765900  
C -6.43595500 -1.49093800 -0.73401600  
H -5.45130400 -3.27440100 -0.12418400  
H -7.18492100 0.43426100 -1.38571300  
C 1.38609300 -1.14755900 -0.15228500  
H -0.51500000 -0.29235200 -1.74399500  
H -7.41340600 -1.86228600 -0.44167700  
H 2.42752800 -0.91876500 -0.41724200  
Mo 0.87256400 0.30039200 1.00798100  
N 1.88724300 -0.09112900 2.73141100  
C 2.65698800 -1.14888500 3.20897400  
C 1.87226500 0.90710000 3.72248100  
C 3.14749600 -0.81149700 4.45105100  
C 2.84377800 -2.41617300 2.44866100  
C 2.65705800 0.49497600 4.77244100  
C 1.03093500 2.13921300 3.59217400  
H 3.76891100 -1.44312800 5.07385300  
H 3.49242200 -2.26334000 1.57999300  
H 1.89037300 -2.82193900 2.09160800  
H 3.31872900 -3.16561200 3.08977500  
H 2.83121000 1.05049400 5.68558500  
H 1.29292900 2.75455100 2.72249400  
H -0.03987200 1.90025400 3.51441800  
H 1.16038100 2.76820800 4.47810900  
N -0.79493800 -0.07048000 1.38758000  
C -2.11933000 -0.15456600 1.66138100  
C -2.67399700 -1.32341900 2.21645900  
C -2.99752200 0.90273000 1.36042700

C -4.04206300 -1.44400800 2.41604600  
F -1.87865300 -2.35540500 2.50830600  
C -4.36241200 0.79887300 1.58315800  
F -2.50344800 2.02493400 0.82830700  
C -4.88793200 -0.38103600 2.10494100  
F -4.56165700 -2.59178600 2.87091900  
F -5.18447100 1.81101100 1.26859600  
F -6.20585800 -0.50349400 2.28251000  
O 1.35151500 1.94029900 0.08643400  
C 2.03403000 2.53770800 -0.91836000  
C 3.41163100 2.29102400 -1.09942400  
C 1.34771400 3.44229900 -1.75415600  
C 4.13711600 1.28985600 -0.26823500  
C 4.09176800 2.99102100 -2.10212600  
C 2.06647600 4.11454100 -2.74921400  
C -0.11726700 3.67695100 -1.61021600  
C 4.56440000 0.08053400 -0.85592900  
C 4.42235600 1.55391900 1.08775100  
H 5.15564900 2.80997800 -2.22758900  
C 3.43254500 3.90336600 -2.92280800  
H 1.53536600 4.81869400 -3.38366700  
C -0.99923800 3.17668900 -2.58567400  
C -0.61769800 4.43454500 -0.53287900  
C 5.25932500 -0.84670600 -0.07107100  
C 4.26633600 -0.24010900 -2.30420200  
C 5.10255900 0.59464700 1.83985400  
C 4.05640500 2.87494100 1.71901300  
H 3.97801600 4.44362300 -3.69077700  
C -2.36898600 3.43704600 -2.46247300  
C -0.49499400 2.34300700 -3.74211000  
C -1.99159300 4.66147000 -0.43955700  
C 0.31427500 4.99269500 0.51353400  
C 5.53502900 -0.60860400 1.27769500  
H 5.57736100 -1.78255600 -0.52461000  
H 4.45276900 -1.29652400 -2.51460800  
H 3.22334800 -0.02067100 -2.55879400  
H 4.88294000 0.35599300 -2.98679800  
H 5.27798900 0.78330200 2.89503400  
H 4.11028000 2.80799700 2.80866900  
H 4.74096200 3.66607700 1.38599600  
H 3.04864700 3.19256100 1.44554600  
C -2.88793000 4.15526400 -1.38443200  
H -3.04811200 3.05340800 -3.22210500  
H 0.18924800 1.55873900 -3.39869700  
H -1.32616600 1.86461300 -4.26944100  
H 0.06198700 2.94316000 -4.47074400  
H -2.37438800 5.23366900 0.40289900  
H -0.20864100 5.69005200 1.17494800  
H 0.72863000 4.18664500 1.12859400  
H 1.16243200 5.51650200 0.05895900  
C 6.26847600 -1.62074800 2.12167300  
C -4.37610900 4.31905000 -1.20203100

H 5.75576700 -1.76542200 3.07880900  
 H 6.33804200 -2.59001400 1.61732900  
 H 7.29028900 -1.28824500 2.34486200  
 H -4.75713700 3.56154200 -0.50547000  
 H -4.62812800 5.30049700 -0.78549600  
 H -4.91395700 4.20357100 -2.14936500  
 C -1.54847100 -2.03507100 -0.94729900  
 N 0.92616300 -2.21667100 -0.86395300  
 C -2.82178200 -2.61750300 -0.66839300  
 C -0.45818800 -4.05758200 -0.12540400  
 C -2.86818300 -3.92733600 -0.14289600  
 C -1.71154100 -4.63803000 0.11377800  
 H -3.82368500 -4.39233400 0.06732500  
 H -1.77017700 -5.64315900 0.51969700  
 H 0.45530300 -4.60189900 0.08980100  
 C 1.84249100 -2.98443800 -1.66516300  
 C 1.54532800 -3.26630800 -3.01592400  
 C 3.02348400 -3.45514500 -1.08678400  
 C 2.47882700 -4.01762500 -3.74817800  
 C 3.93633200 -4.19387000 -1.83634800  
 H 3.21486200 -3.24427700 -0.04383200  
 C 3.66061900 -4.47887200 -3.17423500  
 H 2.27985800 -4.20353500 -4.79885200  
 H 4.85203800 -4.54856400 -1.37245800  
 H 4.36663200 -5.04789200 -3.77170700  
 C 0.32159500 -2.75898800 -3.65576100  
 C -0.36129700 -3.39262100 -4.61518100  
 H -0.04148800 -1.79866100 -3.30473600  
 H -1.24717600 -2.94758100 -5.05742200  
 H -0.07643300 -4.37828200 -4.97419300

#### 4a-Alk1:



$G_{\text{sol}} = -3905.714963$

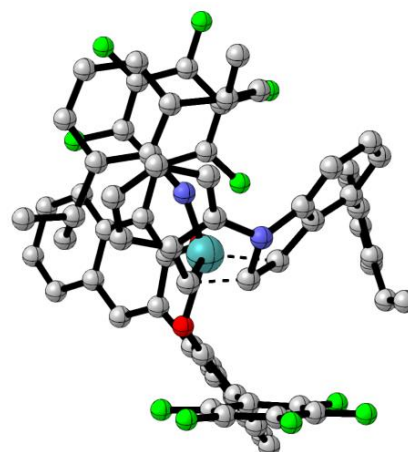
Mo -0.81540100 0.50912200 -0.22498400  
 O 1.14733000 0.59266300 -0.10302200  
 O -0.92050600 -0.36803500 -1.97533400  
 N -2.07064500 1.69612900 0.04213400  
 C -1.30480300 -0.83930100 1.00053500

C -2.83371400 2.79208600 0.37407400  
 C -2.40991700 3.66906800 1.40710300  
 C -3.20977900 4.77781700 1.68379500  
 C -4.38822200 5.00996400 0.97508600  
 C -4.80224800 4.12429400 -0.01923300  
 C -4.04362100 2.99772100 -0.33800400  
 C 1.95393500 0.49909200 -1.18357400  
 C 1.94426000 -0.68415200 -1.99714000  
 C 2.87686100 -0.76964300 -3.01243300  
 C 3.82112200 0.25070700 -3.27768800  
 C 3.77989300 1.45465600 -2.50514400  
 C 2.81173900 1.55482100 -1.46526300  
 C -0.38625200 -1.62329600 -1.88761700  
 C 0.99230800 -1.81303900 -1.80279800  
 C 1.49438100 -3.14340900 -1.58775200  
 C 0.57680700 -4.24219400 -1.53201500  
 C -0.81246800 -3.99676400 -1.66145600  
 C -1.30089300 -2.72285700 -1.81915800  
 C -1.17015600 3.34609000 2.21984000  
 C -1.49148700 2.25980300 3.26476500  
 C -0.53722500 4.55999200 2.91086900  
 C -4.45265000 2.01309200 -1.42006700  
 C -3.67170700 2.27588100 -2.72319500  
 C -5.96385300 1.98890700 -1.68186800  
 H -0.48538000 -1.56328800 0.90659000  
 H -2.91187100 5.47116000 2.46262700  
 H -4.99256100 5.88270500 1.20595300  
 H -5.72984400 4.31314300 -0.54832100  
 H -0.42156100 2.92838200 1.53034200  
 H -0.58105700 1.96162000 3.79318700  
 H -1.91936700 1.36746900 2.80446300  
 H -2.21143300 2.64523800 3.99653700  
 H 0.42327800 4.27324700 3.35277100  
 H -1.17005900 4.92747000 3.72695600  
 H -0.36353000 5.38520600 2.21748800  
 H -4.15769000 1.01606600 -1.06875200  
 H -3.91065900 1.51306700 -3.47070900  
 H -2.59221400 2.25539000 -2.54921600  
 H -3.93430500 3.25807600 -3.13378400  
 H -6.52994100 1.83955700 -0.75568700  
 H -6.21209600 1.17590500 -2.36763900  
 H -6.30838600 2.92114500 -2.14419500  
 C -2.75225300 -2.43749100 -1.80859200  
 C -3.36847700 -1.67704300 -2.80813100  
 C -3.55899100 -2.85824000 -0.74617500  
 C -4.71286100 -1.33075500 -2.73977700  
 C -4.90114500 -2.50506200 -0.64683200  
 C -5.47884200 -1.73014500 -1.64825900  
 C 2.62783200 2.79964400 -0.68531100  
 C 3.59035000 3.30279300 0.18951000  
 C 1.42958400 3.51241400 -0.78059700  
 C 3.38515200 4.46998000 0.92274000

C 1.19623400 4.67841600 -0.06568400  
 C 2.18368600 5.16156300 0.79044800  
 F -3.03779300 -3.59963000 0.24551300  
 F -5.63320200 -2.89558900 0.40253500  
 F -6.76458100 -1.37430100 -1.56725300  
 F -5.27467900 -0.60296600 -3.71652200  
 F -2.67356100 -1.26958600 -3.87457200  
 F 0.44035500 3.05814100 -1.57897600  
 F 0.03100000 5.32776800 -0.18152000  
 F 1.97113400 6.27883100 1.49189000  
 F 4.75135800 2.64786100 0.35056000  
 F 4.32786400 4.92585700 1.75446400  
 C 2.86985100 -3.41285600 -1.35963700  
 C 1.06411800 -5.55346700 -1.30125500  
 C 3.31144200 -4.69757400 -1.12598000  
 C 2.40768500 -5.78317700 -1.10634800  
 H 2.77082600 -6.78983300 -0.92160700  
 H 4.36593000 -4.86701800 -0.93536700  
 H 0.35086800 -6.37305200 -1.26700200  
 H 3.57591500 -2.59345400 -1.32861500  
 H -1.50080000 -4.83447400 -1.60179300  
 C 4.70447300 2.48746000 -2.81422600  
 C 4.79039200 0.11515300 -4.30500800  
 C 5.68635600 1.12581700 -4.56772400  
 C 5.63516600 2.32389900 -3.81615100  
 H 4.80944400 -0.80635900 -4.88116700  
 H 2.89001100 -1.65866700 -3.63626400  
 H 6.42732700 1.01174200 -5.35321900  
 H 6.33691500 3.12402400 -4.03350600  
 H 4.67181200 3.41553900 -2.25426700  
 C -2.02631800 -2.19685100 2.92691800  
 C -3.62758900 -0.67422300 1.92857400  
 N -0.68375300 -2.70035100 2.97756900  
 C -2.98844300 -2.62832900 3.82978600  
 C -4.59368300 -1.11631400 2.82937900  
 H -3.86364800 0.07984900 1.18512900  
 C 0.37284900 -1.84420400 3.30856800  
 C -0.19123200 -3.62657200 2.04655000  
 C -4.28009900 -2.09444700 3.77580500  
 H -2.71913700 -3.37579400 4.56919800  
 H -5.59663700 -0.70245400 2.78801400  
 C 1.52590100 -2.25789300 2.59359700  
 C 0.35518500 -0.72777100 4.14530000  
 C 1.13966500 -3.40984500 1.81841900  
 H -0.86595500 -4.35099400 1.61582100  
 H -5.03614800 -2.43958500 4.47439600  
 C 2.70595700 -1.48432700 2.68667600  
 C 1.53580500 -0.00316900 4.25656200  
 H 1.77955300 -4.00073500 1.18287800  
 C 2.68240100 -0.36849000 3.52731700  
 C 3.88208100 -1.71456200 1.80461300  
 H 1.57374300 0.86756700 4.90503200

H 3.58046300 0.23639900 3.61130900  
 C 4.23946900 -0.64837500 0.96411300  
 C 4.62432700 -2.91860200 1.73404200  
 C 5.27912500 -0.74745700 0.04258200  
 H 3.66111800 0.26539700 1.02538600  
 C 5.66039400 -3.00492600 0.78547500  
 C 4.42633400 -4.09180700 2.60276700  
 C 5.99018800 -1.94407900 -0.05366300  
 H 5.51440400 0.09737000 -0.59611700  
 H 6.23078200 -3.92925900 0.72834200  
 C 3.88932600 -4.13618000 3.82766500  
 H 4.82440200 -5.01839400 2.18810700  
 H 6.79816300 -2.04933200 -0.77222300  
 H 3.49602800 -3.25862700 4.32713900  
 H 3.83518500 -5.07529700 4.37055000  
 C -2.33078900 -1.21331100 1.95060200  
 H -0.54740900 -0.43776500 4.67251600

**4a-TS1:**



**G<sub>sol</sub>** = -3905.696718

C 1.50452900 -1.51911000 -1.86298400  
 H 2.02591200 -0.88975000 -2.57450600  
 C 1.05157000 -2.85119000 -2.29877700  
 C 1.25904300 -3.79790700 -1.27283800  
 C 0.45356500 -3.24967800 -3.49161100  
 N 2.00479500 -3.22008100 -0.22624700  
 C 0.77502000 -5.09874300 -1.37667300  
 C -0.02020300 -4.55858700 -3.61506000  
 H 0.33618900 -2.54171300 -4.30451100  
 C 1.74686800 -3.39440700 1.15432300  
 C 2.24058800 -1.80414400 -0.52198300  
 C 0.11910400 -5.46266500 -2.55754600  
 H 0.91100000 -5.81844400 -0.57885500  
 H -0.50356300 -4.87264800 -4.53504700  
 C 1.59669300 -2.15223200 1.79081100

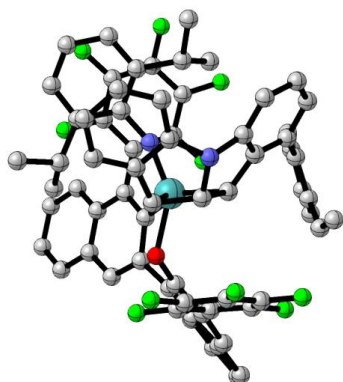
C 1.64781200 -4.58599700 1.86714900  
C 1.73357500 -1.05428200 0.81626400  
H 3.29884200 -1.55412000 -0.61368900  
H -0.26233400 -6.47431100 -2.65947900  
C 1.34073800 -2.06542600 3.16181000  
C 1.37460500 -4.50322800 3.23786100  
H 2.39378800 -0.23306000 1.10432700  
C 1.22080900 -3.26961000 3.87491700  
C 1.09660100 -0.74435700 3.80175800  
H 1.29557600 -5.41780300 3.81798900  
H 1.01544100 -3.22948300 4.94012600  
C -0.18156600 -0.50679800 4.32330600  
C 2.05735600 0.29754400 3.82534500  
C -0.54159000 0.73791700 4.83622000  
H -0.91707800 -1.30215000 4.28637000  
C 1.66312700 1.55227400 4.32271000  
C 3.45154000 0.18265100 3.36515500  
C 0.38542000 1.77768700 4.82576400  
H -1.55086700 0.89700300 5.19920600  
H 2.38988100 2.36057000 4.32144300  
C 4.21566400 -0.91165200 3.23961200  
H 3.90783600 1.14044000 3.12557200  
H 0.11521500 2.76111500 5.19891200  
H 3.86730600 -1.90800600 3.48675900  
H 5.23399600 -0.82260100 2.87393900  
Mo 0.32964200 -0.30834600 -0.45603600  
N -0.94375000 -1.51240400 -0.51906500  
O 1.28729000 1.15888600 -1.49019500  
C 1.73322700 2.31284400 -0.96326100  
C 0.88690100 3.37001200 -0.62869200  
C 3.15418900 2.44132400 -0.78303400  
C -0.58047700 3.28839600 -0.84757500  
C 1.43343600 4.55409300 -0.02340600  
C 3.68061600 3.60175500 -0.26128600  
C 4.04867600 1.30478200 -1.10692200  
C -1.35899500 2.24444900 -0.25253100  
C -1.24922900 4.28177500 -1.53106800  
C 2.85285000 4.67416500 0.13683400  
C 0.62980400 5.61815500 0.47795900  
H 4.75483700 3.69611500 -0.13396800  
C 4.05487700 0.66829500 -2.35338300  
C 4.95013600 0.80719200 -0.15628000  
O -0.74763900 1.17268700 0.26391200  
C -2.75155100 2.32548500 -0.18715800  
C -2.66407800 4.36781700 -1.55315900  
H -0.67548300 5.06063400 -2.02570600  
C 3.40760100 5.84631000 0.71475500  
C 1.19596000 6.73594300 1.04966700  
H -0.44838900 5.53793100 0.42448800  
C 4.85217400 -0.44257600 -2.61616600  
F 3.26774000 1.10103000 -3.34472900  
C 5.76104800 -0.29809100 -0.39533900

F 5.04447000 1.38450600 1.05293000  
C -3.43440700 3.41266700 -0.81380600  
C -3.47963200 1.25640600 0.53943400  
C -3.32626300 5.42221900 -2.23297900  
C 2.60012600 6.86634700 1.15828200  
H 4.48866300 5.91264400 0.80963700  
H 0.55252000 7.52481000 1.42928300  
C 5.71018900 -0.93221800 -1.63449900  
F 4.78502800 -1.05075300 -3.80600300  
F 6.58339300 -0.75370000 0.55883600  
C -4.84127500 3.59477700 -0.74823600  
C -3.16027000 0.96445100 1.87333500  
C -4.49393200 0.48370300 -0.03740900  
C -4.69501900 5.55275500 -2.17352300  
H -2.72558200 6.13356500 -2.79411400  
H 3.03178900 7.75788500 1.60342100  
F 6.47792300 -1.99619500 -1.87947200  
C -5.45432700 4.63443900 -1.41168100  
H -5.43835700 2.91085800 -0.15636400  
C -3.78606500 -0.05680700 2.57715000  
F -2.23494400 1.68553100 2.51602300  
C -5.14873800 -0.53052400 0.65503100  
F -4.87926400 0.69869700 -1.30683600  
H -5.19216500 6.36440800 -2.69641800  
H -6.53216600 4.75244500 -1.34585600  
C -4.78449200 -0.80820200 1.96590000  
F -3.43262600 -0.33606100 3.84224000  
F -6.12101000 -1.23682100 0.06677600  
F -5.37502700 -1.80722600 2.63229800  
C -2.07119300 -2.13954400 -0.99080000  
C -2.63970300 -3.15785400 -0.17972800  
C -2.67613800 -1.73331100 -2.21402800  
C -3.90348100 -3.63500700 -0.51995700  
C -1.84979500 -3.70425400 0.99628700  
C -3.94800600 -2.23565600 -2.49334900  
C -1.92967100 -0.86567600 -3.22078100  
C -4.57026400 -3.15077000 -1.64569900  
H -4.37305900 -4.39548500 0.09527100  
C -2.05586200 -5.20995100 1.20212700  
C -2.12894400 -2.92448600 2.28835800  
H -0.79424200 -3.55481000 0.75946000  
H -4.45638300 -1.91971700 -3.39808000  
C -2.22625200 0.65697000 -3.13647000  
C -2.15655900 -1.36712100 -4.65783300  
H -0.86862400 -1.00378700 -3.00331100  
H -5.56695700 -3.51187200 -1.88053800  
H -1.34800800 -5.57389700 1.95461200  
H -1.88537000 -5.76254100 0.27202300  
H -3.06540600 -5.44319100 1.55993000  
H -1.53452000 -3.33674600 3.10988500  
H -3.18666200 -2.97956300 2.56495800  
H -1.85216600 -1.87506400 2.16500300



H -2.95402900 0.89302600 -2.36630900  
H -2.63299100 1.02533800 -4.08468300  
H -1.31771700 1.22957200 -2.92790800  
H -1.99711600 -2.44611900 -4.74148500  
H -1.46624600 -0.85650500 -5.33939500  
H -3.17261300 -1.14597500 -5.00277700  
H 1.80033500 -5.54596500 1.38908600

#### 4a-Metallacycle:



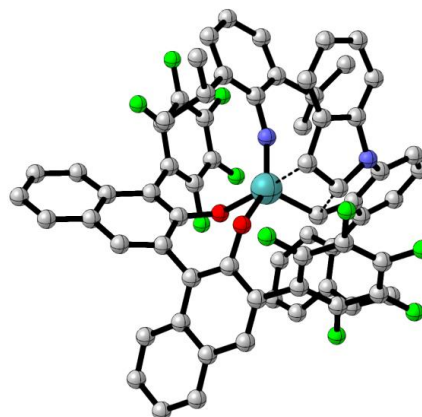
**G<sub>sol</sub>** = -3905.702039

C 1.44210700 -1.55626800 -1.85170200  
H 1.96234800 -0.94495200 -2.57960400  
C 0.97427000 -2.89285300 -2.25658700  
C 1.18976200 -3.82285800 -1.21697700  
C 0.35910500 -3.30899800 -3.43442600  
N 1.95348500 -3.23177500 -0.19088300  
C 0.69719500 -5.12246300 -1.29149600  
C -0.12339500 -4.61710400 -3.52875500  
H 0.23530200 -2.61451200 -4.25780300  
C 1.71438200 -3.38214700 1.19618800  
C 2.19051900 -1.82219700 -0.51330100  
C 0.02422600 -5.50328700 -2.45727400  
H 0.83960500 -5.82858300 -0.48268500  
H -0.62019700 -4.94458900 -4.43683900  
C 1.57233900 -2.12895400 1.81244200  
C 1.62388600 -4.56064700 1.93144100  
C 1.70070200 -1.04975700 0.81750900  
H 3.24830200 -1.57728700 -0.61990400  
H -0.36430900 -6.51425900 -2.53649500  
C 1.32941900 -2.01656200 3.18413700  
C 1.36516400 -4.45268900 3.30327700  
H 2.36480700 -0.22432800 1.08311100  
C 1.21646300 -3.20784700 3.91965600  
C 1.08962900 -0.68288700 3.79957500  
H 1.29256400 -5.35659800 3.90072400  
H 1.02126300 -3.14902100 4.98592600  
C -0.18148600 -0.43677200 4.33460900  
C 2.04555700 0.36340600 3.78145200  
C -0.53993200 0.82030200 4.81737900

H -0.91390600 -1.23565600 4.33078800  
C 1.65287900 1.63017200 4.24816400  
C 3.43346000 0.23848700 3.30492500  
C 0.38130100 1.86395900 4.76287600  
H -1.54484600 0.98519500 5.19012300  
H 2.37558700 2.44131500 4.21275600  
C 4.20119600 -0.85718500 3.22138500  
H 3.87938700 1.18656200 3.01255000  
H 0.11118000 2.85659900 5.11081500  
H 3.85998500 -1.84130300 3.52231000  
H 5.21371900 -0.78320700 2.83677100  
Mo 0.29472800 -0.31122200 -0.45329400  
N -0.99464100 -1.50181600 -0.48759900  
O 1.30435900 1.12339200 -1.48678700  
C 1.78162900 2.26993400 -0.97377200  
C 0.96552700 3.35088100 -0.63788700  
C 3.20783400 2.36687100 -0.81054200  
C -0.50380400 3.31135600 -0.85433800  
C 1.54613600 4.52182100 -0.03916000  
C 3.76684700 3.51540400 -0.29606600  
C 4.07249500 1.21066500 -1.14500000  
C -1.31213800 2.29179200 -0.25888900  
C -1.14449300 4.32045700 -1.54214900  
C 2.96910800 4.60728300 0.10992300  
C 0.77266100 5.60586900 0.46696900  
H 4.84429400 3.58510400 -0.18136800  
C 4.04015700 0.56576600 -2.38700400  
C 4.98209300 0.69903400 -0.20955500  
O -0.73427500 1.20370500 0.26334400  
C -2.70304500 2.40506500 -0.20584900  
C -2.55684300 4.44037100 -1.57497000  
H -0.54878200 5.08330300 -2.03574600  
C 3.55692400 5.76561200 0.68303900  
C 1.37037900 6.70949200 1.03403200  
H -0.30758400 5.55213700 0.42131600  
C 4.80387500 -0.56702100 -2.65605600  
F 3.24708700 1.01145800 -3.36776900  
C 5.75872800 -0.42918900 -0.45457400  
F 5.12000300 1.28514000 0.99148900  
C -3.35608500 3.50271300 -0.84414000  
C -3.45665700 1.34874200 0.51248600  
C -3.18930000 5.50808200 -2.26236800  
C 2.77813900 6.80523900 1.13236400  
H 4.64000000 5.80543100 0.76950200  
H 0.74940900 7.51413700 1.41794600  
C 5.66708700 -1.07200400 -1.68685800  
F 4.69868900 -1.18158600 -3.83987500  
F 6.58648700 -0.89791700 0.48836700  
C -4.76001700 3.71022000 -0.79833500  
C -3.15879500 1.05533500 1.85057000  
C -4.46273200 0.58060400 -0.08342200  
C -4.55589400 5.66557200 -2.21997700

H -2.56790200 6.20700000 -2.81649500  
 H 3.23491100 7.68595600 1.57396500  
 F 6.40155300 -2.15789300 -1.93747100  
 C -5.34368000 4.76154100 -1.46980600  
 H -5.37738800 3.03580200 -0.21627900  
 C -3.79998300 0.03732000 2.54479600  
 F -2.23779700 1.77103600 2.50576300  
 C -5.13349400 -0.42989400 0.59982700  
 F -4.82504400 0.79892200 -1.35710900  
 H -5.03004300 6.48709400 -2.74880100  
 H -6.41993400 4.89998100 -1.41988700  
 C -4.79071600 -0.71045600 1.91615200  
 F -3.46699200 -0.24183200 3.81546400  
 F -6.10103400 -1.13019800 -0.00331200  
 F -5.39838200 -1.70542500 2.57316000  
 C -2.12019800 -2.15656500 -0.92758400  
 C -2.66827300 -3.15719500 -0.08053200  
 C -2.74445500 -1.80123800 -2.15713100  
 C -3.92722300 -3.66481000 -0.39446900  
 C -1.86667400 -3.65693000 1.10768400  
 C -4.00914600 -2.33407400 -2.41097200  
 C -2.03708800 -0.94352400 -3.19733300  
 C -4.61044500 -3.23106300 -1.53015600  
 H -4.37896700 -4.41172600 0.24988400  
 C -2.05327400 -5.15811800 1.36068500  
 C -2.15381700 -2.84141200 2.37536400  
 H -0.81410200 -3.50138000 0.86292200  
 H -4.52804300 -2.05616000 -3.32226500  
 C -2.41043200 0.54469100 -3.14805100  
 C -2.26055000 -1.48169200 -4.62136400  
 H -0.96641000 -1.01347400 -2.98466900  
 H -5.60239300 -3.61659900 -1.74553400  
 H -1.33586100 -5.49034300 2.11852400  
 H -1.88271800 -5.73682000 0.44661800  
 H -3.05738500 -5.39224700 1.73283200  
 H -1.56279900 -3.22897400 3.21120500  
 H -3.21287500 -2.89056600 2.64779900  
 H -1.87888900 -1.79542700 2.22328800  
 H -1.80254400 1.10500900 -3.86762800  
 H -2.23811400 0.97378000 -2.16277100  
 H -3.46514100 0.69558000 -3.39344900  
 H -2.09460200 -2.56109700 -4.67779700  
 H -1.57548300 -0.98474500 -5.31793400  
 H -3.27883700 -1.27697300 -4.97029900  
 H 1.77043500 -5.52920300 1.46904600

#### 4a-TS2:

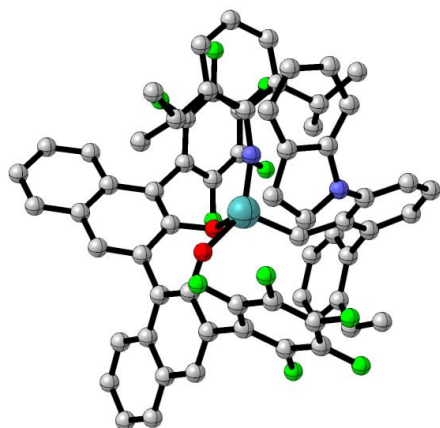


**G<sub>sol</sub>** = -3905.697097

C 1.50397500 -1.57883500 -1.98375600  
 H 1.93034000 -0.89828500 -2.70757900  
 C 0.88358700 -2.85161300 -2.37403800  
 C 1.06059900 -3.77863300 -1.32556600  
 C 0.18061000 -3.22940100 -3.51533100  
 N 1.90734700 -3.21062900 -0.34297300  
 C 0.46060500 -5.03274200 -1.34878100  
 C -0.40633400 -4.49573800 -3.56207300  
 H 0.07851200 -2.54151900 -4.34685300  
 C 1.73008700 -3.38630700 1.05543800  
 C 2.18572300 -1.86203800 -0.72586100  
 C -0.28601900 -5.37533500 -2.48036300  
 H 0.56577400 -5.72766200 -0.52466200  
 H -0.96710700 -4.79689100 -4.44155000  
 C 1.51279200 -2.18138900 1.74535800  
 C 1.75375400 -4.60345900 1.73045700  
 C 1.49903600 -0.98186400 0.90567500  
 H 3.18914000 -1.49809700 -0.53881200  
 H -0.76101500 -6.35079400 -2.52430300  
 C 1.33305400 -2.17445300 3.13597800  
 C 1.52662700 -4.60123100 3.11064300  
 H 2.23803600 -0.20982700 1.15012200  
 C 1.31975300 -3.40653400 3.80419300  
 C 1.09532700 -0.88394100 3.84117500  
 H 1.53705600 -5.54193700 3.65269900  
 H 1.16866100 -3.41875800 4.87915100  
 C -0.16565800 -0.66356700 4.40768100  
 C 2.06060900 0.15410600 3.87217000  
 C -0.50500500 0.56399300 4.97423600  
 H -0.90599200 -1.45389500 4.36349400  
 C 1.68811300 1.38991000 4.42854100  
 C 3.43383400 0.05374800 3.34780400  
 C 0.42644600 1.59966700 4.97660200  
 H -1.50286000 0.71495400 5.37033400  
 H 2.41727500 2.19595500 4.43377100



|               |             |             |               |             |             |
|---------------|-------------|-------------|---------------|-------------|-------------|
| C 4.19220200  | -1.03660800 | 3.16360000  | F -2.15858000 | 1.74358500  | 2.63243100  |
| H 3.87860200  | 1.01743900  | 3.10820500  | C -5.07412300 | -0.42612100 | 0.71474900  |
| H 0.17053100  | 2.56948200  | 5.39278900  | F -4.76049100 | 0.81291000  | -1.23347800 |
| H 3.85758800  | -2.03842300 | 3.40766800  | H -5.08780500 | 6.45235300  | -2.60408600 |
| H 5.19373300  | -0.93860100 | 2.75704800  | H -6.42450300 | 4.86859600  | -1.21676200 |
| Mo 0.30852100 | -0.27849900 | -0.47187600 | C -4.73315400 | -0.71331400 | 2.02952300  |
| N -1.01100000 | -1.42518900 | -0.59270300 | F -3.39699000 | -0.28024000 | 3.92431200  |
| O 1.29692100  | 1.15804800  | -1.50225500 | F -6.04129100 | -1.12292800 | 0.10643700  |
| C 1.79392400  | 2.29655900  | -0.98313000 | F -5.33998900 | -1.71356900 | 2.68097200  |
| C 0.98910800  | 3.37953300  | -0.63131000 | C -2.14407400 | -2.05608600 | -1.04544100 |
| C 3.21975600  | 2.37520800  | -0.82326600 | C -2.69141600 | -3.08501700 | -0.23137000 |
| C -0.48590100 | 3.33331300  | -0.80292400 | C -2.76703100 | -1.65793300 | -2.26090200 |
| C 1.58651600  | 4.54895000  | -0.04792000 | C -3.94721700 | -3.58553800 | -0.56746200 |
| C 3.79525900  | 3.51987400  | -0.31754300 | C -1.88752200 | -3.62838000 | 0.93730600  |
| C 4.06917900  | 1.20428500  | -1.14441700 | C -4.02875700 | -2.18683200 | -2.53776000 |
| C -1.26318700 | 2.31324800  | -0.16351000 | C -2.06064600 | -0.75239700 | -3.26050600 |
| C -1.15190500 | 4.32789600  | -1.48609200 | C -4.62839100 | -3.11600900 | -1.69048400 |
| C 3.01212500  | 4.62387000  | 0.08320000  | H -4.39895800 | -4.35578200 | 0.04872600  |
| C 0.82735700  | 5.64359900  | 0.45717500  | C -2.12692500 | -5.12322000 | 1.18390500  |
| H 4.87402300  | 3.57626100  | -0.20649100 | C -2.10835500 | -2.82402100 | 2.22508500  |
| C 4.04977100  | 0.56328300  | -2.38799500 | H -0.83567300 | -3.51025900 | 0.66969700  |
| C 4.95134700  | 0.67629200  | -0.19170700 | H -4.54697600 | -1.87830800 | -3.43951100 |
| O -0.64995500 | 1.25079100  | 0.36730900  | C -2.40791400 | 0.73609700  | -3.11673200 |
| C -2.65357900 | 2.41527100  | -0.08151300 | C -2.31044500 | -1.19827200 | -4.71153100 |
| C -2.56535000 | 4.43834100  | -1.47807700 | H -0.98763700 | -0.85171300 | -3.06711100 |
| H -0.57596900 | 5.08630800  | -2.00953900 | H -5.61807800 | -3.49827600 | -1.92194000 |
| C 3.61591300  | 5.78319900  | 0.63785600  | H -1.39427700 | -5.49376000 | 1.90938600  |
| C 1.44067700  | 6.74811900  | 1.00507200  | H -2.02146400 | -5.70112500 | 0.26003200  |
| H -0.25364300 | 5.59741300  | 0.42395500  | H -3.12384700 | -5.31674500 | 1.59670300  |
| C 4.80517200  | -0.57677400 | -2.64857300 | H -1.49853600 | -3.24366700 | 3.03159800  |
| F 3.27192100  | 1.01801000  | -3.37755200 | H -3.15699200 | -2.85520400 | 2.53628800  |
| C 5.72256500  | -0.45757800 | -0.42986200 | H -1.81223200 | -1.78248500 | 2.08294600  |
| F 5.06469100  | 1.25183700  | 1.01695800  | H -1.79981000 | 1.32940900  | -3.80900600 |
| C -3.33333800 | 3.50200600  | -0.71379300 | H -2.21722500 | 1.10109200  | -2.10961600 |
| C -3.39046000 | 1.34907600  | 0.63896500  | H -3.46313100 | 0.91830000  | -3.33795700 |
| C -3.22568100 | 5.49306400  | -2.15909200 | H -2.17124800 | -2.27574400 | -4.83741000 |
| C 2.85049400  | 6.83330400  | 1.08537300  | H -1.62198800 | -0.67479400 | -5.38478600 |
| H 4.70021600  | 5.81545800  | 0.71123300  | H -3.32753800 | -0.95009200 | -5.03488400 |
| H 0.83111500  | 7.56201700  | 1.38773000  | H 1.96702000  | -5.52573800 | 1.20288300  |
| C 5.64601200  | -1.09366600 | -1.66674000 |               |             |             |
| F 4.70901500  | -1.18937100 | -3.83382300 |               |             |             |
| F 6.53226200  | -0.93932600 | 0.52283900  |               |             |             |
| C -4.73701500 | 3.69969200  | -0.63113000 |               |             |             |
| C -3.08705300 | 1.04179200  | 1.97293300  |               |             |             |
| C -4.39939500 | 0.58644900  | 0.03921000  |               |             |             |
| C -4.59176200 | 5.64076200  | -2.07998500 |               |             |             |
| H -2.62554200 | 6.19024600  | -2.73850800 |               |             |             |
| H 3.31942800  | 7.71493700  | 1.51223500  |               |             |             |
| F 6.37010100  | -2.18889200 | -1.90681400 |               |             |             |
| C -5.34892300 | 4.73868200  | -1.29712100 |               |             |             |
| H -5.33232200 | 3.02825000  | -0.02294200 |               |             |             |
| C -3.73413300 | 0.02145000  | 2.65928200  |               |             |             |

**4a-Alk2:**

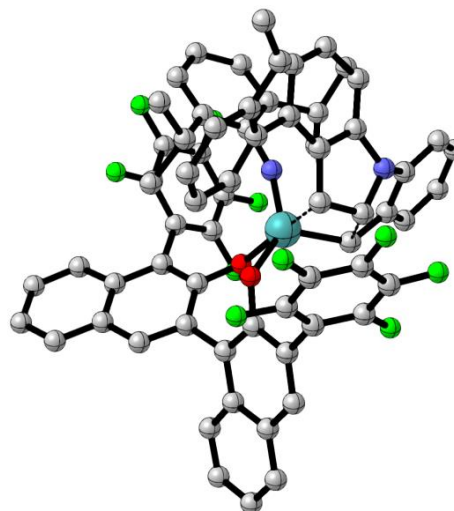
**G<sub>sol</sub>** = -3905.708656

C 1.76854900 -2.01582100 -2.24719400  
H 2.09240400 -1.29662400 -2.98437800  
C 0.90252300 -3.14913800 -2.46576900  
C 0.86181700 -3.88475600 -1.25326500  
C 0.15611300 -3.58692600 -3.56672500  
N 1.71007600 -3.24883300 -0.33054000  
C 0.06432600 -5.01973100 -1.11202900  
C -0.64338400 -4.71473100 -3.42893900  
H 0.19767000 -3.04395300 -4.50490600  
C 1.56822600 -3.31778700 1.08621300  
C 2.24964900 -2.12251500 -0.95562300  
C -0.69345700 -5.41562300 -2.21058200  
H 0.01979400 -5.56724300 -0.17911900  
H -1.24043300 -5.05863900 -4.26771500  
C 1.32499200 -2.12737900 1.80720900  
C 1.65993200 -4.54078500 1.75219600  
C 1.20748900 -0.84980900 1.12001200  
H 3.04596100 -1.57863000 -0.47587300  
H -1.33220900 -6.28932600 -2.12383100  
C 1.21364600 -2.18088300 3.21351600  
C 1.46784000 -4.59160500 3.13302600  
H 1.90038200 -0.06021900 1.44660300  
C 1.24928200 -3.41838000 3.85973200  
C 1.02150800 -0.89914200 3.95404500  
H 1.52046300 -5.54641000 3.64706300  
H 1.13568400 -3.45436600 4.93890900  
C -0.24910200 -0.59402400 4.45370800  
C 2.05909300 0.06216400 4.05877700  
C -0.52744200 0.64329300 5.03365000  
H -1.04254300 -1.32566100 4.34989500  
C 1.75290700 1.30499500 4.64010500  
C 3.43235200 -0.10831300 3.55128700  
C 0.48183400 1.59935700 5.12342500  
H -1.53203700 0.86395900 5.37522300  
H 2.53890900 2.05289800 4.70627500  
C 4.11116600 -1.22975900 3.26833300  
H 3.95516100 0.83509800 3.40369700

H 0.27850100 2.57463700 5.55562100  
H 3.70649800 -2.22463600 3.40980900  
H 5.12317900 -1.16363300 2.88228500  
Mo 0.27826500 -0.15781000 -0.37162700  
N -0.99160400 -1.31758200 -0.69558500  
O 1.30241900 1.11928300 -1.50003400  
C 1.84587600 2.26763300 -1.03670500  
C 1.04784100 3.36656500 -0.73037400  
C 3.26432000 2.31882000 -0.85823800  
C -0.42925400 3.29687400 -0.88727400  
C 1.65531000 4.55872200 -0.21603600  
C 3.85135000 3.47754600 -0.39763000  
C 4.08640200 1.11006600 -1.09785400  
C -1.19744400 2.34464400 -0.13778900  
C -1.09963300 4.19028100 -1.69362400  
C 3.08114100 4.61646500 -0.07321300  
C 0.90459700 5.69480700 0.19955700  
H 4.92838700 3.51805200 -0.26418400  
C 4.09729800 0.42844600 -2.31874100  
C 4.90750200 0.59196900 -0.08792600  
O -0.55961700 1.38708900 0.56692200  
C -2.58767900 2.40056400 -0.12289600  
C -2.51516300 4.24427000 -1.75063600  
H -0.52765200 4.89797500 -2.28787000  
C 3.69444000 5.79917500 0.41825200  
C 1.52837800 6.82290600 0.68329000  
H -0.17638500 5.66158500 0.14330200  
C 4.85482400 -0.72143200 -2.52006200  
F 3.34965400 0.85755600 -3.34385100  
C 5.67596800 -0.55512200 -0.26599100  
F 4.96085200 1.19331300 1.11140900  
C -3.28006100 3.36522100 -0.91869700  
C -3.32520900 1.42425100 0.71461100  
C -3.18532600 5.17714800 -2.58301200  
C 2.93837900 6.88708800 0.78461100  
H 4.77774600 5.82100100 0.50737000  
H 0.92876500 7.67268800 0.99731300  
C 5.64857100 -1.21816200 -1.49030500  
F 4.79988500 -1.36533800 -3.69134400  
F 6.43865200 -1.02472100 0.73074300  
C -4.69448500 3.48802900 -0.93745300  
C -3.15651000 1.39107000 2.10453700  
C -4.23238900 0.51186100 0.16773200  
C -4.55920400 5.25635600 -2.59343300  
H -2.58761200 5.83338300 -3.21066200  
H 3.41546200 7.78654000 1.16242100  
F 6.36806200 -2.32783700 -1.67018100  
C -5.31640900 4.40677000 -1.75375400  
H -5.29059200 2.85455900 -0.29034500  
C -3.86818200 0.50741900 2.90818100  
F -2.30294900 2.23035500 2.70134500  
C -4.95704800 -0.37876200 0.95281800

F -4.43081100 0.47209400 -1.15792500  
 H -5.06297400 5.97322400 -3.23505500  
 H -6.40016400 4.48137600 -1.75048000  
 C -4.78079200 -0.36894900 2.33077400  
 F -3.67744600 0.47796400 4.23731300  
 F -5.79709500 -1.25719600 0.39358700  
 F -5.43294000 -1.25458300 3.09416600  
 C -2.07399700 -1.99016300 -1.21838300  
 C -2.70582000 -2.96976400 -0.40472200  
 C -2.55445300 -1.68199800 -2.51884200  
 C -3.89530400 -3.53155400 -0.86504400  
 C -2.05378200 -3.41193100 0.89427500  
 C -3.74746400 -2.28025800 -2.92648500  
 C -1.78166000 -0.74887900 -3.43794900  
 C -4.42804100 -3.17351100 -2.10264600  
 H -4.40928200 -4.26718900 -0.25578800  
 C -2.40646300 -4.85128400 1.29185600  
 C -2.34078300 -2.46872400 2.06926500  
 H -0.97665600 -3.37058900 0.72285500  
 H -4.15068300 -2.04914800 -3.90657700  
 C -2.12600900 0.73068400 -3.20199900  
 C -1.96197800 -1.08804200 -4.92509900  
 H -0.71976800 -0.88084000 -3.19861300  
 H -5.36315700 -3.61359600 -2.43714200  
 H -1.75077000 -5.17600000 2.10765000  
 H -2.28671800 -5.54552700 0.45477100  
 H -3.43926400 -4.93063900 1.65112500  
 H -1.75524000 -2.78813600 2.93739100  
 H -3.39806700 -2.50295500 2.34716100  
 H -2.06246900 -1.43981100 1.83222100  
 H -1.48466700 1.37372800 -3.81468300  
 H -1.98939400 1.01716200 -2.16081500  
 H -3.17082400 0.93290600 -3.45836000  
 H -1.82031300 -2.15499900 -5.12082700  
 H -1.23705600 -0.52517300 -5.52368800  
 H -2.96011400 -0.80930400 -5.28185100  
 H 1.89138800 -5.43892000 1.19024500

#### 4b-TS1:



**G<sub>sol</sub>** = -3905.689731

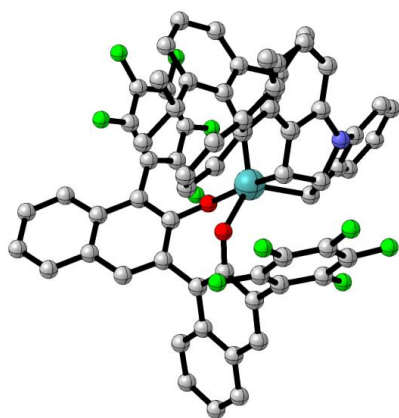
C 2.31617100 -0.65253900 0.48283000  
 H 2.87555200 0.16967400 0.07098600  
 C 2.42152100 -2.01412400 -0.03439900  
 C 2.11700300 -2.90360100 1.02214600  
 C 2.71824800 -2.49316800 -1.32107500  
 N 2.06453300 -2.17027000 2.23229900  
 C 1.91626400 -4.25925800 0.80302200  
 C 2.50453000 -3.87019600 -1.53437300  
 C 1.21272200 -2.42426500 3.33424500  
 C 2.15933900 -0.78747300 1.92009800  
 C 2.08798400 -4.72047900 -0.50720200  
 H 2.66371400 -4.27912900 -2.52489700  
 C 0.34446200 -1.34714600 3.62083000  
 C 1.21562700 -3.57823300 4.10769600  
 C 0.45652500 -0.19813900 2.70290800  
 H 2.72118400 -0.16971300 2.61110300  
 H 1.91931700 -5.77053900 -0.72561600  
 C -0.51932900 -1.44174600 4.71124100  
 C 0.32466300 -3.66650500 5.18305500  
 H 0.65738200 0.77622800 3.16929700  
 C -0.53164400 -2.60639000 5.48540400  
 H 0.31789800 -4.56144500 5.79765100  
 H -1.21143200 -2.68225500 6.32833700  
 Mo 0.10973400 0.05232300 0.77240000  
 N -0.53637900 -1.49098300 0.26786100  
 O 0.90033700 1.67141500 -0.20562600  
 C 0.82929700 2.90831500 0.32733900  
 C -0.33126700 3.67643300 0.29517500  
 C 2.02676400 3.44645100 0.90212600  
 C -1.51080600 3.21235900 -0.47259200  
 C -0.36381300 4.93892200 0.97785100  
 C 2.01687800 4.67590300 1.51634300  
 C 3.28092800 2.66735000 0.76484800

C -2.13133700 1.95171400 -0.19879300  
 C -2.05641200 4.02060700 -1.44753600  
 C 0.82835000 5.44030000 1.59772400  
 C -1.55071100 5.71406000 1.10991000  
 H 2.93425400 5.07619100 1.93973600  
 C 3.89923900 2.51231400 -0.47994000  
 C 3.86707300 2.01463800 1.84512200  
 O -1.57483600 1.10967400 0.67854600  
 C -3.33820800 1.60819500 -0.81331000  
 C -3.25219900 3.68726800 -2.12732200  
 H -1.57031500 4.96340000 -1.68304800  
 C 0.80261200 6.68930900 2.27071200  
 C -1.54690800 6.91634300 1.78162600  
 H -2.47440000 5.33759800 0.68759300  
 C 5.03654900 1.72794300 -0.64664700  
 F 3.37908700 3.11318700 -1.55754000  
 C 4.99500200 1.21158800 1.70713900  
 F 3.27392800 2.05682700 3.05765500  
 C -3.93651700 2.48047500 -1.77473300  
 C -3.99874800 0.33895400 -0.42807300  
 C -3.80729000 4.54792900 -3.10927400  
 C -0.35853600 7.42084700 2.35962000  
 H 1.72252900 7.05259600 2.72221400  
 H -2.47068900 7.48050800 1.87437300  
 C 5.58280600 1.06859400 0.45432900  
 F 5.61006400 1.60098900 -1.84483300  
 F 5.47440700 0.53575200 2.75946000  
 C -5.18630100 2.21821000 -2.39808900  
 C -4.36772900 0.10144600 0.90116300  
 C -4.32406700 -0.65984900 -1.35243000  
 C -5.00658800 4.24970700 -3.71386100  
 H -3.26656700 5.45521100 -3.36680400  
 H -0.36947900 8.37396800 2.88006800  
 F 6.65652600 0.29072800 0.30269900  
 C -5.70451100 3.07702000 -3.34167500  
 H -5.74748600 1.33548000 -2.11503300  
 C -5.02128600 -1.06093100 1.29100300  
 F -4.10931200 1.01218400 1.84896000  
 C -4.98661200 -1.82711300 -0.98663100  
 F -4.01999200 -0.50930700 -2.65125000  
 H -5.42471500 4.91481300 -4.46366500  
 H -6.66245600 2.85283000 -3.80238600  
 C -5.31652500 -2.03744200 0.34628400  
 F -5.34041100 -1.26200800 2.57694200  
 F -5.30208100 -2.74675500 -1.90708500  
 F -5.89616100 -3.18273500 0.72630300  
 C -1.18767100 -2.46458800 -0.45973100  
 C -1.85850700 -3.49614400 0.25134300  
 C -1.22980400 -2.40226600 -1.88080000  
 C -2.67718900 -4.36486700 -0.46976900  
 C -1.66366700 -3.66331500 1.74612800  
 C -2.07067100 -3.29365800 -2.54626000

C -0.33505000 -1.44438100 -2.64277000  
 C -2.80600000 -4.25201800 -1.85216900  
 H -3.22007200 -5.14336300 0.05597000  
 C -1.53609800 -5.13756000 2.15696600  
 C -2.77066000 -2.96615400 2.54802200  
 H -0.72342600 -3.17381300 1.99913700  
 H -2.14186600 -3.24731200 -3.62727600  
 C -0.98937000 -0.08843400 -2.94524100  
 C 0.22224500 -2.06417200 -3.93215600  
 H 0.51362800 -1.25535900 -1.98592300  
 H -3.46557300 -4.92424200 -2.39197900  
 H -1.23180300 -5.19984700 3.20667700  
 H -0.78829800 -5.65665600 1.54799200  
 H -2.48583800 -5.67503900 2.05696000  
 H -2.62531300 -3.13060100 3.61962600  
 H -3.75705900 -3.35240500 2.27314500  
 H -2.75386300 -1.88861800 2.36729100  
 H -0.24586100 0.59287500 -3.37392800  
 H -1.39393600 0.38022500 -2.04794700  
 H -1.81171700 -0.19828000 -3.65726600  
 H 0.68349900 -3.03750000 -3.73909800  
 H 0.98236100 -1.40392600 -4.35925700  
 H -0.56125100 -2.19763800 -4.68661100  
 H 1.91473800 -4.37917500 3.89413400  
 H -1.19538800 -0.62274900 4.93698400  
 C 3.25069400 -1.59754600 -2.38250200  
 C 4.25966000 -2.04079900 -3.27918400  
 C 2.76870700 -0.28187100 -2.52196600  
 C 4.69491500 -1.17352800 -4.29571300  
 C 3.21152600 0.55864700 -3.53803600  
 H 2.00714100 0.09600500 -1.85431500  
 C 4.17269000 0.10612400 -4.44139400  
 H 5.49240600 -1.50771700 -4.95179100  
 H 2.81589800 1.56644700 -3.60481200  
 H 4.53625100 0.75574500 -5.23222000  
 C 4.92630700 -3.34943000 -3.13195700  
 C 5.39393300 -4.09717200 -4.13890000  
 H 5.04656700 -3.71166600 -2.11327600  
 H 5.91629100 -5.03026700 -3.95060400  
 H 5.26072700 -3.81332300 -5.17964800  
 H 1.63784100 -4.93325100 1.60457400

#### 4b-Metallacycle:

G<sub>sol</sub> = -3905.694549

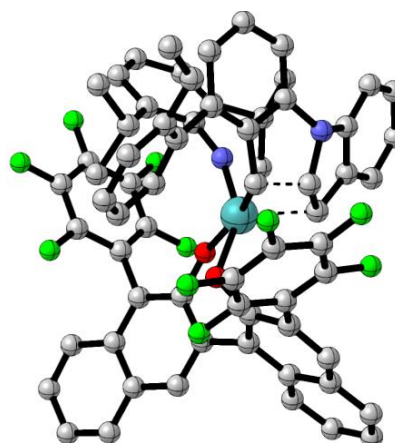


C 2.18773600 -0.61939700 0.41676100  
H 2.79506300 0.19894900 0.05993300  
C 2.47243400 -1.97504900 -0.05300000  
C 2.22897200 -2.89443200 0.99624000  
C 2.88035600 -2.41776300 -1.32221900  
N 2.07578000 -2.19397900 2.20564900  
C 2.18404900 -4.26364900 0.76569300  
C 2.82180000 -3.80938700 -1.54659900  
C 1.22233100 -2.48214500 3.28787300  
C 2.07320200 -0.75917500 1.94582000  
C 2.45340600 -4.70012200 -0.53727200  
H 3.06228900 -4.19412500 -2.53034600  
C 0.44281800 -1.35157400 3.61522900  
C 1.13424500 -3.65975000 4.02068000  
C 0.73779000 -0.23334100 2.68663800  
H 2.89561700 -0.24336700 2.44445300  
H 2.40593800 -5.76184700 -0.75999600  
C -0.43526400 -1.40126200 4.69072400  
C 0.23645100 -3.70008100 5.09500400  
H 0.88411500 0.75120900 3.14352300  
C -0.53897600 -2.58748800 5.42847300  
H 0.15610400 -4.60889100 5.68386300  
H -1.22606100 -2.63961100 6.26726400  
Mo 0.10524200 0.02672300 0.74281900  
N -0.55366100 -1.54100200 0.32670900  
O 0.86981400 1.68557000 -0.21474700  
C 0.77653100 2.89877700 0.36144700  
C -0.39676400 3.64885700 0.35711800  
C 1.96665800 3.44124500 0.95085000  
C -1.56098100 3.19640000 -0.43897000  
C -0.45307700 4.88460700 1.08571100  
C 1.93377300 4.64655200 1.60988700  
C 3.23295700 2.68848100 0.78410900  
C -2.15710900 1.91148300 -0.23713100  
C -2.11863200 4.03902000 -1.37784200  
C 0.73058100 5.38418400 1.72292900

C -1.65370000 5.63210800 1.24785900  
H 2.84423000 5.04926000 2.04571100  
C 3.83272600 2.55356000 -0.47239600  
C 3.84390400 2.03229700 1.84863400  
O -1.59064600 1.02778400 0.59412500  
C -3.35491400 1.57350100 -0.87161900  
C -3.29985100 3.71201100 -2.08540500  
H -1.65268300 5.00288700 -1.56242900  
C 0.68264200 6.60567600 2.44313300  
C -1.67120400 6.80797100 1.96495000  
H -2.57137300 5.25512600 0.81284500  
C 4.97410300 1.78155300 -0.66563100  
F 3.29028900 3.16075200 -1.53466400  
C 4.97459300 1.23826900 1.68194200  
F 3.27503200 2.06275900 3.07170100  
C -3.96241500 2.47589200 -1.79776000  
C -4.01153300 0.29062000 -0.52493400  
C -3.86404900 4.60577800 -3.03197800  
C -0.49172600 7.31189900 2.56093200  
H 1.59633500 6.96836300 2.90753400  
H -2.60519700 7.35085100 2.07987300  
C 5.54074000 1.11066800 0.41780000  
F 5.53329600 1.67522700 -1.87235800  
F 5.47387500 0.55127000 2.71853300  
C -5.20006800 2.21576500 -2.44598900  
C -4.40945700 0.03291300 0.79184400  
C -4.31976400 -0.69005200 -1.47301000  
C -5.05061700 4.31021100 -3.66239500  
H -3.34104200 5.53543100 -3.24134800  
H -0.51946800 8.24399400 3.11752600  
F 6.61636300 0.34105400 0.23933100  
C -5.72708300 3.10664900 -3.35399400  
H -5.74374900 1.30829200 -2.21173300  
C -5.08186000 -1.12960000 1.14753000  
F -4.16429400 0.92677300 1.75927100  
C -4.99033600 -1.86238600 -1.13985800  
F -3.99318500 -0.51338700 -2.76292700  
H -5.47560600 5.00079300 -4.38477900  
H -6.67472600 2.88420700 -3.83613200  
C -5.35080800 -2.09347500 0.18199500  
F -5.44862000 -1.33973100 2.41861200  
F -5.28495900 -2.76685800 -2.08174600  
F -5.94284200 -3.24176900 0.52981500  
C -1.20667200 -2.52176200 -0.38939600  
C -1.91661700 -3.51755200 0.33465300  
C -1.21850200 -2.49885900 -1.81317300  
C -2.74417200 -4.38394200 -0.38011000  
C -1.75024500 -3.65841300 1.83582400  
C -2.06546400 -3.38863000 -2.47202400  
C -0.29096500 -1.57902200 -2.58224700  
C -2.83972100 -4.30855300 -1.76734400  
H -3.31946700 -5.13206800 0.15507800

C -1.59738500 -5.12743500 2.25800400  
 C -2.88842300 -2.97682000 2.60615000  
 H -0.82726700 -3.14561000 2.10534800  
 H -2.11203300 -3.37213300 -3.55525700  
 C -0.92669600 -0.22698900 -2.94012800  
 C 0.28590900 -2.24619900 -3.83891900  
 H 0.54656300 -1.38249600 -1.91317800  
 H -3.50416900 -4.97951400 -2.30254700  
 H -1.35475800 -5.17966500 3.32333200  
 H -0.79415000 -5.61774300 1.69690100  
 H -2.51903900 -5.69857100 2.10001100  
 H -2.76118400 -3.12816600 3.68232900  
 H -3.86286600 -3.38163800 2.31448600  
 H -2.88781500 -1.90034200 2.41741700  
 H -0.17276100 0.43161100 -3.38521900  
 H -1.33759300 0.27821600 -2.06467000  
 H -1.74168600 -0.35574300 -3.65722500  
 H 0.73406800 -3.21609700 -3.60206400  
 H 1.06097500 -1.60697100 -4.27105700  
 H -0.48219300 -2.39815400 -4.60553400  
 H 1.75972200 -4.51336900 3.78601200  
 H -1.04378100 -0.53754100 4.94181000  
 C 3.35524800 -1.47184600 -2.36741200  
 C 4.44116100 -1.80761000 -3.22066200  
 C 2.73918700 -0.21760900 -2.53901500  
 C 4.81386700 -0.90706700 -4.23286400  
 C 3.12068200 0.65603800 -3.55205500  
 H 1.92471600 0.08287300 -1.89600900  
 C 4.15579000 0.30319000 -4.41696500  
 H 5.66839600 -1.15518600 -4.85440800  
 H 2.61897300 1.61346200 -3.64532300  
 H 4.47270100 0.98075300 -5.20442100  
 C 5.24515700 -3.03048800 -3.02902800  
 C 5.84065800 -3.72686700 -4.00486700  
 H 5.35953400 -3.36960200 -2.00178400  
 H 6.45688700 -4.59255600 -3.78171300  
 H 5.72401500 -3.46786800 -5.05404500  
 H 1.95707800 -4.96882900 1.55660600

#### 4b-TS2:



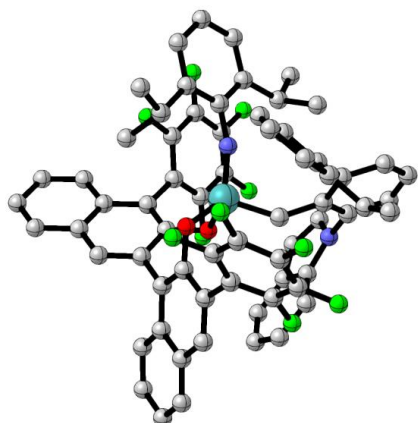
G<sub>sol</sub> = -3905.688699

C 2.12932500 -0.36052900 0.43873100  
 H 2.61894600 0.38843100 -0.16785000  
 C 2.66814500 -1.72384100 0.40275000  
 C 2.57342600 -2.31446400 1.68477500  
 C 3.23116400 -2.42767800 -0.67311600  
 N 2.23024800 -1.33158800 2.62745300  
 C 2.85289200 -3.66138100 1.88426500  
 C 3.51629600 -3.79150400 -0.45986600  
 C 1.39733500 -1.41430800 3.75398900  
 C 2.04920000 -0.04307700 1.96195800  
 C 3.30078100 -4.39537100 0.77882900  
 H 3.90081400 -4.38281700 -1.28254300  
 C 0.53630900 -0.29611500 3.80731200  
 C 1.37908400 -2.38426700 4.75193700  
 C 0.70503200 0.54018700 2.59721200  
 H 2.82781600 0.67694900 2.21889900  
 H 3.51854800 -5.45236600 0.89925700  
 C -0.31284800 -0.11875000 4.89297000  
 C 0.49994700 -2.20593500 5.82661300  
 H 0.73607400 1.62295000 2.74699800  
 C -0.32916500 -1.08417500 5.90649100  
 H 0.47713500 -2.94875000 6.61823100  
 H -0.99498500 -0.96311600 6.75518100  
 Mo 0.01651800 0.12124400 0.68725800  
 N -0.50641600 -1.53984100 0.87129300  
 O 0.55122800 1.64290200 -0.65286800  
 C 0.49045800 2.79498100 0.03468700  
 C -0.73305000 3.41756600 0.30786500  
 C 1.71510900 3.40180100 0.49276700  
 C -1.92929100 3.00872600 -0.46568000  
 C -0.78431200 4.51150200 1.23196200  
 C 1.66995800 4.47930800 1.34870400  
 C 3.00271100 2.87275600 -0.01153700  
 C -2.39587700 1.65535000 -0.50900300

C -2.59576200 3.96011900 -1.21319100  
 C 0.43657700 5.03052400 1.77671400  
 C -2.00804800 5.08490600 1.67585700  
 H 2.59467500 4.93059900 1.69658000  
 C 3.23451300 2.71995900 -1.38499200  
 C 4.03416400 2.47388300 0.84100800  
 O -1.82293400 0.70201300 0.23434200  
 C -3.51865200 1.31930000 -1.26680800  
 C -3.72447900 3.65119300 -2.00771200  
 H -2.23575500 4.98506800 -1.20019200  
 C 0.39080700 6.10289500 2.70425500  
 C -2.01949200 6.11754400 2.58799500  
 H -2.94146700 4.68401500 1.29809600  
 C 4.40851200 2.15886300 -1.87686000  
 F 2.31878900 3.12148600 -2.27114600  
 C 5.19865400 1.87070600 0.37783400  
 F 3.87897900 2.57927900 2.17966700  
 C -4.20573400 2.30360400 -2.03224800  
 C -3.99313700 -0.08638300 -1.24104800  
 C -4.39082100 4.64347800 -2.77272900  
 C -0.81102100 6.64151900 3.10358500  
 H 1.32822700 6.48815000 3.09761800  
 H -2.96824900 6.53017000 2.91918400  
 C 5.38553500 1.70858800 -0.99225500  
 F 4.61543900 2.07149900 -3.19282400  
 F 6.12781600 1.43943900 1.23914900  
 C -5.35450200 2.01204600 -2.81638500  
 C -4.56836700 -0.63693900 -0.09351600  
 C -3.87577100 -0.91934100 -2.35318100  
 C -5.49558800 4.32729900 -3.52938300  
 H -4.00957000 5.66118900 -2.74657300  
 H -0.83539400 7.45956400 3.81737300  
 F 6.50034000 1.14127200 -1.45586700  
 C -5.98115300 2.99758700 -3.54511700  
 H -5.74189700 0.99906800 -2.83034800  
 C -4.97130600 -1.96716400 -0.03783900  
 F -4.75003800 0.12936300 0.99056600  
 C -4.26262300 -2.25494600 -2.31963900  
 F -3.34038800 -0.44450900 -3.48796400  
 H -5.99892000 5.09344900 -4.11168000  
 H -6.85776300 2.75341000 -4.13841500  
 C -4.81857500 -2.77851400 -1.15821000  
 F -5.51861600 -2.47581000 1.07587300  
 F -4.07253100 -3.04491200 -3.38654700  
 F -5.20852900 -4.05649200 -1.11851700  
 C -1.15180400 -2.73035500 0.62801800  
 C -1.99088000 -3.25337200 1.65492700  
 C -1.03335300 -3.37855200 -0.63262700  
 C -2.75619100 -4.38048100 1.35866000  
 C -2.04374000 -2.59018000 3.01924000  
 C -1.82628400 -4.50131800 -0.86871500  
 C -0.07740800 -2.85936800 -1.68697300

C -2.68676300 -4.99466400 0.10917400  
 H -3.41642400 -4.78907800 2.11478000  
 C -2.40721800 -3.56230900 4.14892100  
 C -3.00115100 -1.38608300 3.01960900  
 H -1.04133400 -2.21045100 3.22501400  
 H -1.76821500 -4.99971200 -1.83025500  
 C -0.77459200 -1.86500400 -2.62861800  
 C 0.60138100 -3.97729800 -2.48920500  
 H 0.70926400 -2.32631000 -1.15348400  
 H -3.30322100 -5.86291100 -0.10113000  
 H -2.28811200 -3.05824000 5.11219000  
 H -1.75969800 -4.44607700 4.14594400  
 H -3.44831200 -3.89865600 4.08034400  
 H -2.98279900 -0.89708000 3.99988600  
 H -4.02590500 -1.70816500 2.81630600  
 H -2.72005900 -0.64995100 2.26453900  
 H -0.06838900 -1.48329000 -3.37290700  
 H -1.18300200 -1.01135000 -2.07970700  
 H -1.59602400 -2.35071000 -3.16292000  
 H 1.05513200 -4.72110400 -1.82731500  
 H 1.39156800 -3.54797200 -3.11315100  
 H -0.10332700 -4.48807400 -3.15521900  
 H 2.04992600 -3.23449900 4.72394100  
 H -0.97231300 0.74288600 4.93572200  
 C 3.50522700 -1.76416400 -1.97373600  
 C 4.70428500 -2.01261500 -2.69193600  
 C 2.56923000 -0.86851600 -2.52053400  
 C 4.88384700 -1.39487700 -3.94155800  
 C 2.76189000 -0.27549300 -3.76359800  
 H 1.66420300 -0.64121000 -1.97534400  
 C 3.92218000 -0.55260200 -4.48689100  
 H 5.82022100 -1.55352000 -4.46696900  
 H 2.01721200 0.41431800 -4.14881300  
 H 4.09596000 -0.08128800 -5.44959000  
 C 5.79427500 -2.83340300 -2.13107100  
 C 6.65145800 -3.57490400 -2.84319300  
 H 5.89564400 -2.81441600 -1.04826400  
 H 7.45712500 -4.12021200 -2.36111400  
 H 6.57274200 -3.67399500 -3.92273000  
 H 2.75710900 -4.12768600 2.85721000



**4b-Alk2:**

**G<sub>sol</sub>** = -3905.706586

```

C 1.22913100 -0.56885200 1.06249300
H 1.75852500 0.38891500 1.20225100
C 1.65015700 -1.66374300 1.93793000
C 1.19579200 -1.67501400 3.27734400
C 2.49145000 -2.70731900 1.49317300
N 0.30296300 -0.66619900 3.72322500
C 1.55104200 -2.70658400 4.14475200
C 2.84737100 -3.72754000 2.38625600
C 0.48719200 0.70825200 3.59470500
C -1.05074500 -0.89979500 3.98234500
C 2.37590400 -3.73675800 3.69661000
H 3.49455900 -4.52402500 2.03287600
C -0.77507600 1.33333400 3.77829900
C 1.65193600 1.43918200 3.33743300
C -1.72655000 0.28624200 4.04191300
H -1.39954300 -1.91737900 4.08545200
H 2.65620400 -4.54067200 4.37035000
C -0.86618700 2.72816500 3.64519200
C 1.52706100 2.81728700 3.19985300
H -2.78008300 0.40532100 4.23972800
C 0.27846700 3.45546100 3.34256200
H 2.40705000 3.40806700 2.96854900
H 0.21625700 4.53069200 3.20754300
Mo -0.00331900 -0.14859600 -0.28781500
N -0.87266400 -1.63017300 -0.61189600
O 0.88316500 1.08062100 -1.54685800
C 1.16613800 2.29889300 -0.99282600
C 0.12534400 3.18727900 -0.72741800
C 2.51392600 2.62663900 -0.65346100
C -1.27429700 2.82129700 -1.06793900
C 0.39702800 4.43492900 -0.08751900
C 2.77567100 3.84832100 -0.06570300
C 3.62997800 1.68035000 -0.87602000
C -1.94727100 1.77911300 -0.34676400
C -1.95380400 3.48472000 -2.06494600

```

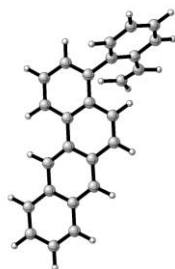
```

C 1.74922700 4.76852300 0.23998800
C -0.62849200 5.34722300 0.28304500
H 3.79740400 4.10519900 0.19556700
C 3.89767700 1.09858200 -2.12032200
C 4.54346900 1.41056500 0.15187700
O -1.25878600 1.09398800 0.60639200
C -3.27094600 1.45991600 -0.62992000
C -3.29877200 3.17988100 -2.39047200
H -1.44454400 4.26702500 -2.62138200
C 2.02895700 5.99512700 0.89762800
C -0.32673500 6.52531300 0.92854300
H -1.65985100 5.09582200 0.06598000
C 5.02564500 0.31266600 -2.33494800
F 3.08745500 1.32343600 -3.16139000
C 5.69467400 0.65850200 -0.04930300
F 4.32754300 1.88525500 1.39404100
C -3.98235500 2.16306200 -1.64920800
C -3.92017000 0.37879300 0.14589400
C -3.98376500 3.86831600 -3.42482800
C 1.01407800 6.85914700 1.23757600
H 3.06242400 6.23185000 1.13745200
H -1.12681700 7.20374200 1.21054700
C 5.94202600 0.11890000 -1.30662500
F 5.24768400 -0.24181600 -3.53262000
F 6.55388300 0.45697000 0.95565800
C -5.34077700 1.89694700 -1.96836200
C -4.12639100 0.50959100 1.52142200
C -4.37534000 -0.79470000 -0.45933200
C -5.29558400 3.57612700 -3.71892700
H -3.44860800 4.63448600 -3.97984000
H 1.23596300 7.79204300 1.74719000
F 7.03996200 -0.61382200 -1.52058300
C -5.97865800 2.58402400 -2.97644000
H -5.88245000 1.14962800 -1.39950000
C -4.75980400 -0.48101500 2.26409600
F -3.74362900 1.62597300 2.15139800
C -5.03670000 -1.78544500 0.25749100
F -4.19190200 -0.98551100 -1.77414600
H -5.81091100 4.10772300 -4.51329900
H -7.01800300 2.36431800 -3.20286800
C -5.22410900 -1.62849300 1.62760100
F -4.95252900 -0.33087000 3.58287500
F -5.47481600 -2.89378800 -0.35440200
F -5.84630000 -2.57888500 2.33266300
C -1.50906500 -2.64824800 -1.28677300
C -2.19440600 -3.64733500 -0.54524200
C -1.46578400 -2.66378600 -2.70812900
C -2.85477600 -4.64590900 -1.26238900
C -2.16144600 -3.63613500 0.97574500
C -2.14542900 -3.68708700 -3.36817700
C -0.72813500 -1.56966100 -3.46187500
C -2.83732100 -4.66584200 -2.65592400

```

H -3.39679000 -5.41745600 -0.72748500  
 C -0.80478300 -4.15472200 1.48490500  
 C -3.28638900 -4.45152700 1.62829600  
 H -2.25375700 -2.59011400 1.29502300  
 H -2.13817400 -3.72265300 -4.45225100  
 C -1.58459400 -0.29253500 -3.57556900  
 C -0.23628900 -1.99677200 -4.85041700  
 H 0.16737800 -1.31928600 -2.87653200  
 H -3.36430000 -5.45098700 -3.19061100  
 H -0.76785800 -4.13439500 2.57979600  
 H 0.01949000 -3.54663100 1.11870300  
 H -0.64478400 -5.18893400 1.15783600  
 H -3.31132600 -4.24982000 2.70460700  
 H -3.11511900 -5.52760000 1.50516600  
 H -4.27047600 -4.22120600 1.21848600  
 H -0.99467700 0.52582100 -4.00061100  
 H -1.96698500 0.03533400 -2.60745000  
 H -2.45222100 -0.47479700 -4.21958300  
 H 0.33205700 -2.93247600 -4.81351300  
 H 0.41281300 -1.21883100 -5.26575100  
 H -1.06901100 -2.13590800 -5.54935700  
 H 2.61616000 0.95146800 3.23321500  
 H -1.82578200 3.22465400 3.75675000  
 C 2.97404100 -2.77962000 0.08291400  
 C 4.34985800 -2.68762900 -0.22405500  
 C 2.05640800 -3.02346800 -0.94929200  
 C 4.74976300 -2.81435700 -1.56705600  
 C 2.47081400 -3.14559000 -2.27311700  
 H 1.01120600 -3.14842400 -0.70607100  
 C 3.82699700 -3.03236000 -2.58360800  
 H 5.79775900 -2.69432300 -1.81651700  
 H 1.73777300 -3.33849900 -3.04948500  
 H 4.16488400 -3.10412400 -3.61295200  
 C 5.33666100 -2.42139900 0.83606700  
 C 6.63724700 -2.73304200 0.78925900  
 H 4.95330800 -1.92652700 1.72515100  
 H 7.30511700 -2.46543000 1.60155300  
 H 7.07906900 -3.26212100 -0.05038700  
 H 1.18165600 -2.68353500 5.16508900

1:

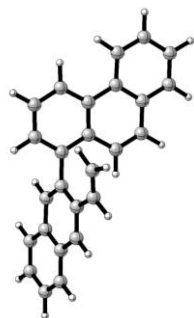


**G<sub>sol</sub>** = -1001.792236

C -1.05764200 3.07482100 -0.05322000  
 C -2.22509900 2.31436800 -0.14710800

C -2.16157300 0.93530400 -0.22045100  
 C -0.90078400 0.28921500 -0.23432300  
 C 0.28629900 1.05918500 -0.13478100  
 C 0.17303200 2.45629300 -0.03903800  
 C -0.80732100 -1.13991400 -0.34587200  
 C 0.38496300 -1.77107100 -0.34951800  
 C 1.61710500 -1.04741100 -0.24094300  
 C 1.58062000 0.38367800 -0.13474500  
 C 2.83581400 -1.71115900 -0.24056100  
 C 4.05086300 -1.02669200 -0.13773800  
 C 4.02177800 0.40089700 -0.03165200  
 C 2.78621600 1.06212100 -0.03427300  
 C 5.30753200 -1.68907900 -0.13454300  
 C 6.47115300 -0.98090300 -0.03206000  
 C 6.44351300 0.43221100 0.07308600  
 C 5.25279400 1.10207000 0.07315600  
 C -3.42601000 0.15612800 -0.31213100  
 C -4.11384000 0.18715000 -1.52447400  
 C -5.29091800 -0.52386400 -1.71616500  
 C -5.79642200 -1.29441300 -0.67839200  
 C -5.12497600 -1.33139500 0.53271200  
 C -3.94564500 -0.60649400 0.75551600  
 C -3.36166900 -0.70823900 2.10058100  
 C -2.46377500 0.06891000 2.70592700  
 H -1.12112500 4.15308700 0.01458900  
 H -3.19240300 2.79956700 -0.13986300  
 H 1.06023900 3.06659200 0.04160600  
 H -1.72196600 -1.70834100 -0.43041700  
 H 0.43310200 -2.84970400 -0.43603200  
 H 2.84477100 -2.79207500 -0.32209100  
 H 2.80142900 2.13990200 0.04712100  
 H 5.32542700 -2.76917900 -0.21501100  
 H 7.42285800 -1.49638900 -0.03062100  
 H 7.37435000 0.97855000 0.15348600  
 H 5.22989000 2.18220100 0.15339600  
 H -3.69980100 0.77313700 -2.33510100  
 H -5.79965500 -0.48274800 -2.67041100  
 H -6.70734400 -1.86376500 -0.81002600  
 H -5.52363400 -1.92735100 1.34468500  
 H -3.76889900 -1.53333600 2.67825500  
 H -2.00888000 0.92859600 2.23974600  
 H -2.16441300 -0.14904400 3.72274300

2:

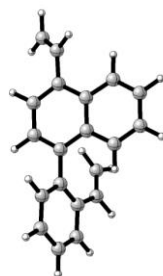


**G<sub>sol</sub>** = -1001.796143

C 1.40491700 3.04743600 -0.51710100  
 C 2.51530000 2.23689200 -0.52160600  
 C 2.40272100 0.84564800 -0.33255700  
 C 1.11042000 0.29407900 -0.12170700  
 C -0.02357600 1.14826300 -0.09151200  
 C 0.13344400 2.50207000 -0.30485500  
 C 0.97222000 -1.11793600 0.05683900  
 C -1.05801500 0.20223000 2.66595500  
 C -1.83295900 0.13294300 1.42074500  
 C -1.38717000 0.59923300 0.13884100  
 C -3.09896700 -0.41338700 1.51100000  
 C -3.97967700 -0.50005200 0.41437100  
 C -3.54129400 -0.00669200 -0.84623000  
 C -2.23643100 0.52798500 -0.93760600  
 C -5.27861800 -1.05200500 0.52056200  
 C -6.10344800 -1.11193100 -0.57234400  
 C -5.66711600 -0.62327500 -1.82238400  
 C -4.41363200 -0.08341000 -1.95560200  
 C 3.55721200 -0.03454500 -0.34888000  
 C 4.87262400 0.43073200 -0.54498900  
 C 5.94581600 -0.43146000 -0.55218100  
 C 5.75183800 -1.80714900 -0.36402600  
 C 4.48051800 -2.29195000 -0.17166200  
 C 3.36758900 -1.42826900 -0.15923000  
 C 2.04848900 -1.93765600 0.03836400  
 C 0.03308800 0.90893500 2.96225400  
 H 1.51314600 4.11316300 -0.67159000  
 H 3.48544500 2.68369500 -0.67988700  
 H -0.73639100 3.14543100 -0.28223500  
 H -0.01709700 -1.52553000 0.20572800  
 H -1.48580900 -0.40012500 3.46240000  
 H -3.44227800 -0.77717500 2.47272600  
 H -1.88569400 0.87589200 -1.90182700  
 H -5.61106400 -1.42557800 1.48148400  
 H -7.09532700 -1.53535300 -0.48108700  
 H -6.32831900 -0.67750700 -2.67752500  
 H -4.07510200 0.29090100 -2.91406100  
 H 5.05592900 1.48477300 -0.69290800  
 H 6.94469000 -0.04340500 -0.70424400  
 H 6.59894400 -2.48062300 -0.37095000

H 4.31449300 -3.35239800 -0.02554300  
 H 1.92521800 -3.00521700 0.17414700  
 H 0.53307100 1.55807200 2.26133000  
 H 0.45438500 0.85060600 3.95729400

3:

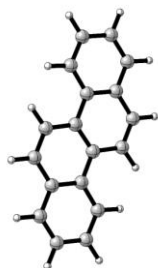


**G<sub>sol</sub>** = -771.85614

C 1.73945700 -1.95109800 -0.16506000  
 C 0.34195100 -1.82588300 -0.18498200  
 C -0.26488900 -0.59490200 -0.25599900  
 C 0.54652500 0.57417000 -0.33819100  
 C 1.97024100 0.45036000 -0.30026500  
 C 2.56507700 -0.84819700 -0.20675800  
 C -0.02476300 1.86436600 -0.44866400  
 C 0.75932600 2.98565200 -0.50130700  
 C 2.16054800 2.86915900 -0.43775100  
 C 2.74688400 1.63448400 -0.33813800  
 C 4.02518600 -1.01262800 -0.18678800  
 C 4.68465700 -1.94087900 0.50352100  
 C -1.74849100 -0.50487200 -0.28765100  
 C -2.38976000 -0.89466400 -1.46303500  
 C -3.76942600 -0.82503400 -1.60206200  
 C -4.53557200 -0.34689500 -0.54825900  
 C -3.91214100 0.04007000 0.62669100  
 C -2.52271100 -0.03985700 0.79720300  
 C -2.00397300 0.36196800 2.11226300  
 C -0.82142800 0.11922200 2.67694000  
 H 2.17917500 -2.93924100 -0.13929600  
 H -0.27236100 -2.71582400 -0.13602600  
 H -1.10093000 1.95337200 -0.48768800  
 H 0.30275800 3.96331200 -0.58568500  
 H 2.77683400 3.75858700 -0.46588000  
 H 3.82305000 1.56436300 -0.27520700  
 H 4.59946700 -0.32019600 -0.79260100  
 H 4.17497700 -2.63767600 1.15763900  
 H 5.76164000 -2.02353300 0.44341100  
 H -1.78177800 -1.24442700 -2.28756500  
 H -4.23686000 -1.13151900 -2.52871000  
 H -5.61161000 -0.27526600 -0.63928800  
 H -4.51125900 0.40521900 1.45198700

H -2.73048900 0.91057300 2.70515700  
H -0.03280700 -0.43438400 2.19220500  
H -0.61998800 0.47939100 3.67729200

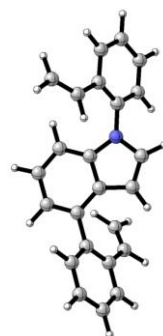
**4:**



**G<sub>sol</sub>** = – –693.301514

C -3.66822200 -1.47954300 0.00000000  
C -2.45599100 -0.75875500 0.00000000  
C -1.21802500 -1.45676300 0.00000000  
C -1.26162300 -2.86820600 -0.00000100  
C -2.45599100 -3.54926300 -0.00000100  
C -3.67453900 -2.85183600 -0.00000100  
C -2.44777600 0.66249800 0.00000100  
C -1.28340900 1.35999800 0.00000100  
C -0.01740400 0.70512700 0.00000000  
C 0.01740400 -0.70512700 0.00000000  
C 1.21802500 1.45676300 0.00000000  
C 2.45599100 0.75875500 0.00000000  
C 2.44777600 -0.66249800 0.00000100  
C 1.28340900 -1.35999800 0.00000100  
C 1.26162300 2.86820600 -0.00000100  
C 2.45599100 3.54926300 -0.00000100  
C 3.67453900 2.85183600 -0.00000100  
C 3.66822200 1.47954300 0.00000000  
H -4.59930800 -0.92581600 0.00000000  
H -0.34448800 -3.43776200 -0.00000200  
H -2.4551000 -4.63159300 -0.00000200  
H -4.61038700 -3.39526800 -0.00000100  
H -3.39639900 1.18533900 0.00000200  
H -1.32535400 2.43848400 0.00000200  
H 3.39639900 -1.18533900 0.00000200  
H 1.32535400 -2.43848400 0.00000200  
H 0.34448800 3.43776200 -0.00000200  
H 2.4551000 4.63159300 -0.00000200  
H 4.61038700 3.39526800 -0.00000100  
H 4.59930800 0.92581600 0.00000000

**13a:**

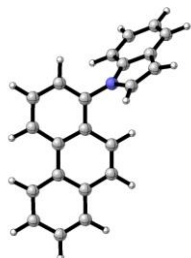


**G<sub>sol</sub>** = – –980.876099

C 0.16582600 1.58281300 2.09579400  
C 1.47570000 1.39899300 1.62620600  
C 1.75212700 0.59648800 0.52788700  
C 0.66839400 -0.00925800 -0.13133500  
C -0.64674100 0.20425600 0.34920600  
C -0.91454100 0.98547100 1.47040100  
C 0.56508100 -0.88035300 -1.26359000  
C -0.75775700 -1.16466300 -1.43220800  
N -1.51042200 -0.50472900 -0.47097200  
C -2.91401000 -0.62403000 -0.31235000  
C 3.14128700 0.41336600 0.03934300  
C 3.79288300 1.52879600 -0.48824900  
C 5.07095700 1.44550900 -1.02333000  
C 5.71972700 0.21854000 -1.04902700  
C 5.08881700 -0.89624600 -0.52150300  
C 3.81028700 -0.82975300 0.04945300  
C 3.29736500 -2.07106400 0.64772000  
C 2.36413700 -2.23110500 1.58461000  
C -3.74348000 0.50457200 -0.42317600  
C -5.11909800 0.31759500 -0.23975200  
C -5.65161100 -0.93143800 0.03075400  
C -4.81575200 -2.04016900 0.12195700  
C -3.44914300 -1.88087700 -0.04405400  
C -3.17994100 1.81449200 -0.76799400  
C -3.74328600 2.99515900 -0.52119300  
H -0.00025600 2.20261900 2.96711400  
H 2.29740300 1.87290100 2.14751600  
H -1.92337200 1.12726500 1.83062700  
H 1.37506000 -1.24588600 -1.87044900  
H -1.25414700 -1.76929100 -2.17218000  
H 3.26645200 2.47463000 -0.49337800  
H 5.54694100 2.32854300 -1.42959700  
H 6.71080900 0.12954100 -1.47478000  
H 5.60092300 -1.85094000 -0.52718900  
H 3.80583500 -2.96294900 0.29181800  
H 1.81974900 -1.40742500 2.02111400  
H 2.12677700 -3.22275600 1.94715000  
H -5.78092600 1.16579400 -0.35063200  
H -6.72042700 -1.04478500 0.15645000

H -5.22510000 -3.02003700 0.32878200  
H -2.77673200 -2.72342900 0.04778500  
H -2.21148100 1.79158500 -1.25306200  
H -4.68668200 3.09116700 0.00181800  
H -3.26124700 3.91398700 -0.82552200

**14a:**

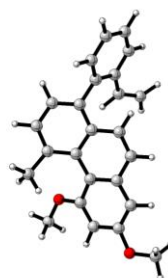


**G<sub>sol</sub>** = -902.316956

C 0.53911300 2.93017700 -0.48960000  
C 1.73681700 2.29449900 -0.25534800  
C 1.81752900 0.89200900 -0.16585500  
C 0.62401700 0.13384900 -0.31591000  
C -0.58803300 0.81308900 -0.58944700  
C -0.63177300 2.18670000 -0.66722800  
C 3.06672900 0.19832900 0.08964200  
C 3.05919700 -1.21532900 0.21558700  
C 1.82728900 -1.92744700 0.09283100  
C 0.66283700 -1.28768100 -0.16484600  
C 4.30030200 0.86606400 0.21921300  
C 5.46669800 0.17659600 0.46244400  
C 5.45258900 -1.21950400 0.58910300  
C 4.26477200 -1.89945300 0.46646900  
N -1.78503100 0.07207000 -0.77085000  
C -2.06850900 -0.75782200 -1.84389600  
C -3.30576600 -1.31177900 -1.68888100  
C -3.84124300 -0.81390700 -0.45548500  
C -2.86351000 0.05243200 0.09678800  
C -5.03813900 -1.01285600 0.24290800  
C -5.22779400 -0.36271500 1.44893900  
C -4.24132500 0.48522500 1.97969300  
C -3.04723800 0.70386900 1.31364500  
H 0.50289400 4.00976200 -0.55057800  
H 2.62642300 2.89366700 -0.13165700  
H -1.57508400 2.67414600 -0.87246100  
H 1.84245900 -3.00354500 0.21479700  
H -0.25915100 -1.84427900 -0.24813700  
H 4.34555200 1.94085700 0.12299900  
H 6.39967500 0.71708500 0.55573600  
H 6.37246100 -1.75605000 0.78135800  
H 4.23821600 -2.97812400 0.56124900  
H -1.34720600 -0.86922400 -2.63562800  
H -3.78472000 -1.98727400 -2.37766100  
H -5.80212300 -1.66841000 -0.15584800  
H -6.14934300 -0.50852900 1.99735900

H -4.41737500 0.97599500 2.92800700  
H -2.28481000 1.35336600 1.72181700

**15a:**

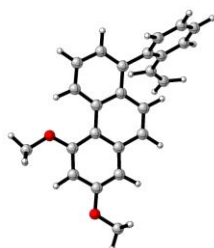


**G<sub>sol</sub>** = -1116.516113

C -0.97095200 3.00629700 -0.41378300  
C 0.27663600 2.40652900 -0.45650600  
C 0.35744200 0.99400400 -0.30604300  
C -0.85700900 0.24455000 -0.37678900  
C -2.11340600 0.89451200 -0.28840500  
C -2.14741500 2.27472300 -0.27119400  
C 1.59950600 0.24361800 -0.19812900  
C 1.62698500 -1.11631300 -0.59603400  
C 0.39026800 -1.78114500 -0.85924400  
C -0.79153000 -1.15654700 -0.66025300  
C 2.79704900 0.73934700 0.39616600  
C 3.97761700 0.02707500 0.33386600  
C 4.00459700 -1.25519200 -0.23616600  
C 2.83308000 -1.84438400 -0.65383300  
C -3.38904600 0.13407200 -0.26286000  
C -3.71230400 -0.74411300 0.79187200  
C -4.94072000 -1.41423000 0.75297300  
C -5.82634900 -1.24188600 -0.29750000  
C -5.50543200 -0.37459700 -1.33598000  
C -4.29785700 0.30667900 -1.30879000  
C -2.79255300 -0.92195100 1.92340800  
C -2.72767300 -1.98850500 2.71807000  
C 1.44190600 3.28774300 -0.83180700  
O 2.68884200 1.88951800 1.10624700  
C 3.84591500 2.43701400 1.70919500  
O 5.22966500 -1.84505400 -0.26633900  
C 5.31970400 -3.16062400 -0.78577000  
H -1.03261900 4.08218000 -0.52874800  
H -3.09927800 2.78517500 -0.20098900  
H 0.41874400 -2.82325600 -1.15215500  
H -1.71780500 -1.69939800 -0.77873900  
H 4.89189000 0.40287600 0.76456300  
H 2.80091100 -2.86677800 -0.99825200  
H -5.21326000 -2.05722500 1.57926400  
H -6.77116400 -1.77009300 -0.29939900  
H -6.19248400 -0.22759800 -2.15925400  
H -4.03543900 0.97644800 -2.11757000  
H -2.09995400 -0.10644700 2.09530700

H -3.35523000 -2.85920100 2.57276300  
H -2.02282600 -2.02902000 3.53741100  
H 1.10775100 4.01382300 -1.57492500  
H 2.26143200 2.71843000 -1.26564000  
H 1.83627900 3.84024900 0.01994800  
H 3.52020300 3.34812700 2.20549100  
H 4.60788000 2.68052300 0.96320900  
H 4.27061700 1.75315100 2.44921800  
H 6.37202900 -3.43042400 -0.74140000  
H 4.97559300 -3.20159500 -1.82309800  
H 4.73793300 -3.86570500 -0.18504200

**15c:**

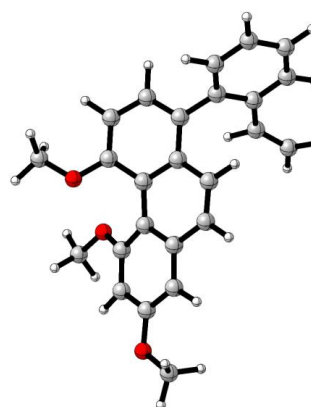


**G<sub>sol</sub>** = -1077.219238

C -0.94075700 3.11719800 0.08260000  
C 0.28933100 2.50107800 0.08122400  
C 0.41668500 1.10172900 -0.08006700  
C -0.79186200 0.35500300 -0.24537200  
C -2.05345400 1.00679300 -0.21365100  
C -2.11517700 2.37623400 -0.06144900  
C 1.69104900 0.39465200 -0.09879000  
C 1.69476000 -1.00963400 -0.31777700  
C 0.45955500 -1.69759600 -0.50666500  
C -0.72550400 -1.05227600 -0.46715400  
C 2.98039400 0.99137000 0.09130800  
C 4.13633900 0.24130700 0.05005900  
C 4.09530700 -1.14153100 -0.17754500  
C 2.88579600 -1.76462500 -0.35817300  
C -3.32390700 0.24461500 -0.35819000  
C -3.79822100 -0.60727600 0.65882700  
C -5.01279600 -1.27442500 0.46057300  
C -5.73740700 -1.12381900 -0.70984300  
C -5.26500900 -0.28354400 -1.71198800  
C -4.06917800 0.39510500 -1.52793000  
C -3.03901600 -0.76501200 1.90622300  
C -3.11230400 -1.79775100 2.74386200  
O 3.03388100 2.32985700 0.32293400  
C 4.28958900 2.95221900 0.52933200  
O 5.30699700 -1.75785900 -0.19540300  
C 5.33468500 -3.15721500 -0.41970300  
H -0.99592800 4.19156700 0.20488800  
H 1.16929900 3.10238100 0.19999500  
H -3.07969000 2.86686000 -0.04026000  
H 0.49439000 -2.76563800 -0.68211800

H -1.64499400 -1.59953400 -0.61241400  
H 5.10529600 0.69106400 0.19309300  
H 2.81181900 -2.82731800 -0.53117800  
H -5.40461800 -1.89889600 1.25241300  
H -6.67580000 -1.64861300 -0.83504500  
H -5.82653100 -0.15385200 -2.62809500  
H -3.69059800 1.04792000 -2.30395500  
H -2.34609900 0.03649600 2.13424900  
H -3.74831600 -2.65402000 2.55620200  
H -2.51753200 -1.82370500 3.64681200  
H 4.07294700 4.00471600 0.69633400  
H 4.93506600 2.84837800 -0.34683700  
H 4.79813700 2.54198300 1.40578000  
H 6.38283800 -3.44513100 -0.39661600  
H 4.90825400 -3.41110400 -1.39433700  
H 4.79163000 -3.69513800 0.36257500

**15d:**

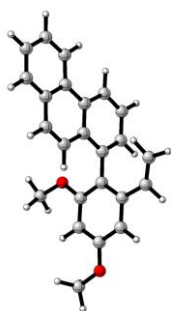


**G<sub>sol</sub>** = -1191.753662

C -0.91402400 2.87459800 -0.22785000  
C 0.29162500 2.20235500 -0.31974200  
C 0.33201000 0.78182900 -0.22466700  
C -0.90741600 0.09193500 -0.33762400  
C -2.14036700 0.79082600 -0.23381700  
C -2.11506700 2.16594700 -0.14353800  
C 1.55405300 0.00651500 -0.14274500  
C 1.53885800 -1.33997400 -0.58401300  
C 0.28156300 -1.95583100 -0.86641300  
C -0.88390900 -1.30111800 -0.66015300  
C 2.76903800 0.45614300 0.45793800  
C 3.92848500 -0.28439700 0.34988100  
C 3.91484600 -1.54928900 -0.25951500  
C 2.72433400 -2.09848200 -0.67677300  
C -3.44577500 0.08296000 -0.25433000  
C -3.81720700 -0.82735000 0.75678600  
C -5.07033400 -1.44587900 0.67540400  
C -5.93662000 -1.19095200 -0.37446900  
C -5.56941400 -0.29148500 -1.36928000  
C -4.33524800 0.33738400 -1.30037800  
C -2.91950100 -1.08960500 1.88948500

C -2.90773300 -2.18887800 2.64101400  
 O 2.69742100 1.56940000 1.22414900  
 C 3.88586000 2.10381000 1.77119400  
 O 5.12527100 -2.16761000 -0.32466300  
 C 5.17491700 -3.46932300 -0.88169000  
 H -0.94346400 3.95285900 -0.26002300  
 H -3.04578900 2.71020700 -0.04856400  
 H 0.27839100 -2.98997700 -1.18803000  
 H -1.82532400 -1.81163900 -0.80039900  
 H 4.85846200 0.05214900 0.77975600  
 H 2.66202500 -3.10841600 -1.05232000  
 H -5.37775100 -2.11379900 1.46908100  
 H -6.90159900 -1.68015100 -0.40942000  
 H -6.24060700 -0.08004600 -2.19166800  
 H -4.03630100 1.03013700 -2.07650400  
 H -2.19615200 -0.31088200 2.10103000  
 H -3.56868900 -3.02637100 2.45436000  
 H -2.21468100 -2.29134400 3.46500500  
 H 3.59100500 3.00764800 2.29932400  
 H 4.60591100 2.35696300 0.98760900  
 H 4.35178800 1.40976600 2.47709600  
 H 6.22051800 -3.76690000 -0.85971800  
 H 4.81606000 -3.47259400 -1.91491600  
 H 4.58332900 -4.17660400 -0.29306800  
 O 1.45616200 2.83053300 -0.61188000  
 C 1.49565900 4.24223800 -0.59427200  
 H 2.52843700 4.51517400 -0.79880800  
 H 0.85104800 4.67429500 -1.36587800  
 H 1.20074400 4.63706900 0.38260000

**16c:**

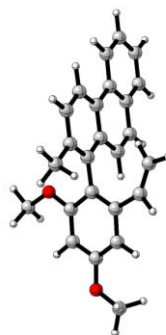


**G<sub>sol</sub>** = -1077.219727

C 1.29373900 2.25637400 2.04113000  
 C 0.02015200 1.89886200 1.58718400  
 C -0.13608300 0.91307000 0.63664000  
 C 1.00583100 0.24676200 0.12240800  
 C 2.30164600 0.60150100 0.58563400  
 C 2.41057900 1.62125000 1.55010500  
 C 0.87320200 -0.76765000 -0.87681100  
 C 1.95457500 -1.40575200 -1.38106300  
 C 3.27519400 -1.09464300 -0.93463900  
 C 3.46116500 -0.08963100 0.05039800

C 4.39348000 -1.77004600 -1.46182400  
 C 5.66653700 -1.47367700 -1.03721700  
 C 5.85679000 -0.48330400 -0.06339800  
 C 4.77840200 0.19018400 0.46488000  
 C -1.50413400 0.55557400 0.17221200  
 C -2.10883800 -0.58376300 0.71862300  
 C -3.40555900 -0.96968700 0.37830900  
 C -4.12210900 -0.18836500 -0.52435300  
 C -3.54361500 0.94585400 -1.07481200  
 C -2.23723500 1.32353100 -0.75138500  
 O -1.34774700 -1.28156600 1.60456300  
 O -5.39496000 -0.46632500 -0.91977600  
 C -6.03262300 -1.61253500 -0.38692300  
 C -1.86381000 -2.47082400 2.16997700  
 C -1.73401400 2.52265500 -1.44190000  
 C -0.48266400 2.94086900 -1.62823000  
 H 1.39976600 3.03672000 2.78373900  
 H -0.85543700 2.40420700 1.97279900  
 H 3.38215700 1.91696200 1.91720200  
 H -0.11894100 -1.01191400 -1.22950300  
 H 1.83586200 -2.16938100 -2.14027600  
 H 4.23033200 -2.53276400 -2.21371100  
 H 6.51746500 -1.99983200 -1.45001300  
 H 6.85667400 -0.24555800 0.27616500  
 H 4.95816500 0.94656300 1.21467600  
 H -3.84453200 -1.84901200 0.81695000  
 H -4.12126300 1.53045200 -1.77753800  
 H -7.02339000 -1.64017000 -0.83391700  
 H -6.12899600 -1.54746900 0.70110100  
 H -5.49319200 -2.52814600 -0.64768200  
 H -2.09574800 -3.21229900 1.39957600  
 H -2.76010900 -2.27579900 2.76654500  
 H -1.07949700 -2.85728100 2.81605600  
 H -2.52566300 3.11370600 -1.89296700  
 H 0.38309300 2.42258800 -1.24809800  
 H -0.29874200 3.84191400 -2.19907200

**16a:**

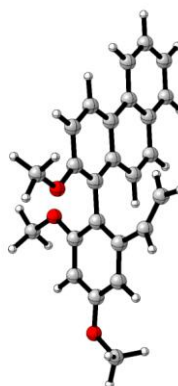


**G<sub>sol</sub>** = -1116.534424



C -1.28175600 2.79952800 0.81624000  
 C -0.00177300 2.24737300 0.65123200  
 C 0.10403800 0.92829200 0.23806400  
 C -1.05736200 0.14854000 0.00911800  
 C -2.34616700 0.71834700 0.18528000  
 C -2.41953700 2.06284400 0.58879700  
 C 1.45177500 0.32426700 0.04849800  
 C 2.21463800 0.47542700 -1.11494600  
 C 1.78990300 1.21350600 -2.31503000  
 C -0.95154900 -1.21266000 -0.42006700  
 C 1.99883800 -0.41155700 1.11694800  
 C 3.25677600 -0.98876400 1.03793100  
 C 4.00843300 -0.82655300 -0.12588000  
 C 3.49809700 -0.09820000 -1.18676400  
 C -3.52577400 -0.09191000 -0.05548200  
 C -3.36635400 -1.43857100 -0.47428600  
 C -4.50395800 -2.23444400 -0.71238900  
 C -5.77113400 -1.72902900 -0.54475100  
 C -5.93517800 -0.39996200 -0.12986700  
 C -4.83725600 0.39622700 0.10788300  
 C -2.05109700 -1.96712700 -0.65028400  
 C 0.58422500 1.64900800 -2.68205100  
 C 1.22037600 3.08552100 0.90137500  
 O 1.20925100 -0.50555600 2.21933100  
 C 1.66870100 -1.26215300 3.32435400  
 O 5.23303600 -1.42108500 -0.11653600  
 C 6.04895900 -1.29197600 -1.26786500  
 H -1.37013200 3.83180800 1.13260200  
 H -3.38040200 2.53566400 0.72962900  
 H 2.60731100 1.39723000 -3.00667700  
 H 0.03483100 -1.63061100 -0.56325100  
 H 3.68398900 -1.55599500 1.84977500  
 H 4.06963200 0.03570800 -2.09224500  
 H -4.36089300 -3.25961600 -1.03225300  
 H -6.63732900 -2.35069600 -0.73065900  
 H -6.93028800 0.00407800 0.00499400  
 H -4.99662400 1.41555600 0.42797400  
 H -1.95059500 -2.99535100 -0.97641500  
 H -0.30824400 1.50791100 -2.09457500  
 H 0.46994300 2.16660400 -3.62583100  
 H 0.94766600 4.05662300 1.31388200  
 H 1.77656900 3.25293600 -0.02387600  
 H 1.90144000 2.59425500 1.59849000  
 H 2.58799200 -0.84156200 3.74215800  
 H 1.84256300 -2.30578800 3.04722400  
 H 0.87743800 -1.21247300 4.06813800  
 H 6.96511500 -1.83487600 -1.04850800  
 H 6.28772800 -0.24416300 -1.47164400  
 H 5.56880900 -1.72995100 -2.14763600

16d:

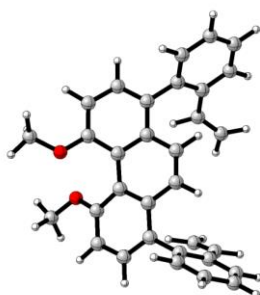


G<sub>sol</sub> = -1191.768188

C -1.23423700 2.71687400 0.55565900  
 C 0.01368800 2.08895500 0.43199300  
 C 0.08892800 0.73651500 0.12723100  
 C -1.10060000 -0.00663000 -0.03735000  
 C -2.37019900 0.62031800 0.09514200  
 C -2.39243200 1.99192300 0.38897300  
 C 1.42308800 0.09528000 -0.00830000  
 C 2.23523100 0.24168300 -1.13686000  
 C 1.85983300 0.99600000 -2.34380400  
 C -1.04658400 -1.39969800 -0.36620600  
 C 1.91294900 -0.65556800 1.07685000  
 C 3.16182400 -1.25643100 1.04124400  
 C 3.96364400 -1.09598300 -0.08868600  
 C 3.51137900 -0.34811100 -1.16258200  
 C -3.57943700 -0.16248100 -0.08015800  
 C -3.47013000 -1.54134000 -0.39740200  
 C -4.63517100 -2.31255200 -0.57220900  
 C -5.88394500 -1.75272800 -0.43946200  
 C -5.99875800 -0.39184200 -0.12452000  
 C -4.87241500 0.38135100 0.05003700  
 C -2.17400800 -2.12694400 -0.53808400  
 C 0.64974700 1.28339100 -2.82110100  
 O 1.08055000 -0.74184700 2.14789100  
 C 1.48877200 -1.50485700 3.26766800  
 O 5.17721400 -1.71223300 -0.03454200  
 C 6.04273000 -1.58349100 -1.14847800  
 H -1.29923800 3.76974900 0.78491400  
 H -3.33505900 2.50911200 0.49147700  
 H 2.71522900 1.31677000 -2.93191800  
 H -0.07646800 -1.86188200 -0.48128800  
 H 3.54720800 -1.83589100 1.86526900  
 H 4.12175200 -0.21410800 -2.04247000  
 H -4.52886000 -3.36308200 -0.81502000  
 H -6.77205000 -2.35591900 -0.57602900  
 H -6.97835300 0.05609100 -0.01699400  
 H -4.99569900 1.42650600 0.29431900  
 H -2.11172900 -3.17908600 -0.78909600  
 H -0.26580400 0.98461400 -2.33508100

H 0.55351500 1.83146600 -3.74956500  
H 2.39852200 -1.09769100 3.71839900  
H 1.65752200 -2.55120600 2.99699100  
H 0.67209500 -1.44414200 3.98277000  
H 6.93984600 -2.14462800 -0.89801800  
H 6.30739400 -0.53756800 -1.32914600  
H 5.59307500 -2.00233200 -2.05342900  
O 1.19616000 2.74175300 0.58947800  
C 1.17874500 4.13609300 0.82862900  
H 2.22085000 4.44001300 0.89222700  
H 0.69385500 4.67615400 0.01017600  
H 0.67516000 4.37730800 1.76955400

**17a:**

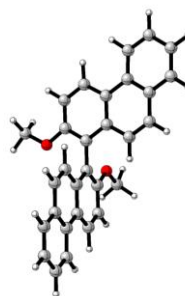


**G<sub>sol</sub>** = -1385.699341

C -2.86061900 2.60544000 -0.62237000  
C -1.47757400 2.63816100 -0.57993300  
C -0.74155400 1.45412100 -0.29317000  
C -1.44562000 0.22141700 -0.35962900  
C -2.86581600 0.19770400 -0.38588500  
C -3.54306600 1.39521000 -0.48096900  
C 0.68955000 1.42466200 -0.05064500  
C 1.40277800 0.22499800 -0.31801400  
C 0.65931500 -0.96546600 -0.58575900  
C -0.69006200 -0.98353700 -0.50819000  
C 1.41516800 2.49216000 0.55048500  
C 2.79829800 2.46209300 0.58362500  
C 3.49079300 1.32941100 0.14720900  
C 2.81837700 0.19121000 -0.23799300  
C -3.62777300 -1.07551700 -0.34313600  
C 3.58354700 -1.04372700 -0.55675300  
C -3.54949600 -1.95367500 0.75799800  
C -4.30516400 -3.13146100 0.73182000  
C -5.11091100 -3.45074900 -0.34841500  
C -5.18901800 -2.58242000 -1.43155600  
C -4.45344400 -1.40677800 -1.41955100  
C -2.71887800 -1.61925900 1.92270100  
C -2.17525800 -2.49053900 2.77002700  
C 4.22300000 -1.10418800 -1.79412800  
C 4.95868000 -2.21463000 -2.18658200  
C 5.05621100 -3.30228900 -1.33016200  
C 4.42749700 -3.25604500 -0.09677300

C 3.69332400 -2.13887800 0.32811900  
C 3.10945200 -2.22157600 1.67397700  
C 2.53875400 -1.28454000 2.43195200  
O -0.76335100 3.74067900 -0.90992200  
C -1.43948400 4.97039900 -1.07483000  
O 0.69125900 3.45762400 1.16687900  
C 1.35859800 4.59707000 1.66946500  
H -3.42515600 3.50782900 -0.79957200  
H -4.62545200 1.39438100 -0.48763100  
H 1.20270500 -1.87694500 -0.78675600  
H -1.22590500 -1.91360400 -0.62713800  
H 3.35505600 3.28829800 0.99796400  
H 4.57187100 1.31789300 0.19697400  
H -4.27989300 -3.78875200 1.59082300  
H -5.68799100 -4.36649100 -0.33970100  
H -5.81917900 -2.81906500 -2.27912400  
H -4.49768900 -0.73203200 -2.26479700  
H -2.52626700 -0.56327000 2.07199900  
H -2.28316600 -3.56133300 2.64834300  
H -1.58056000 -2.15402900 3.60832100  
H 4.12461800 -0.25841500 -2.46267200  
H 5.44089600 -2.23100500 -3.15534900  
H 5.61710300 -4.18152700 -1.61954300  
H 4.50871500 -4.10313700 0.57358300  
H 3.18825000 -3.21616300 2.10421100  
H 2.41425800 -0.25897000 2.12420600  
H 2.17625400 -1.54491200 3.41791800  
H -0.66844600 5.71107800 -1.27422600  
H -1.98689700 5.24798300 -0.16922400  
H -2.13384000 4.93920900 -1.91988000  
H 0.58220000 5.24818400 2.06459700  
H 1.90534100 5.11943900 0.87884600  
H 2.05227700 4.33624000 2.47455000

**18a:**



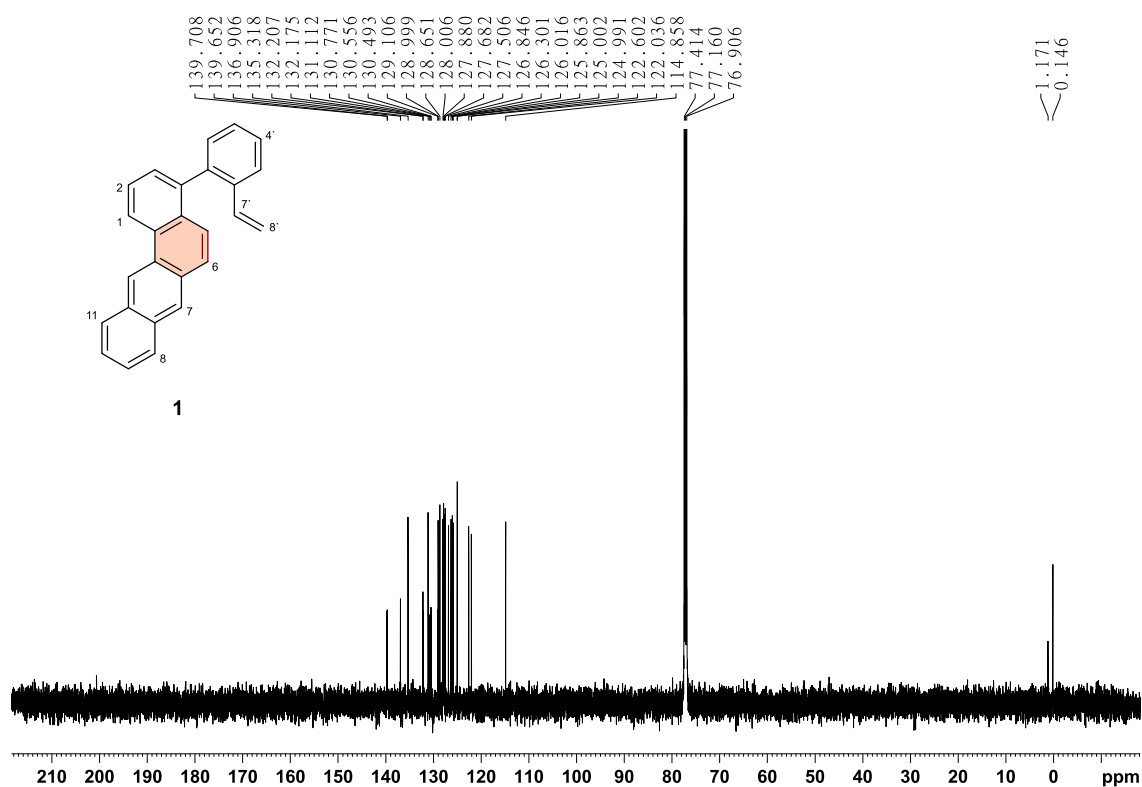
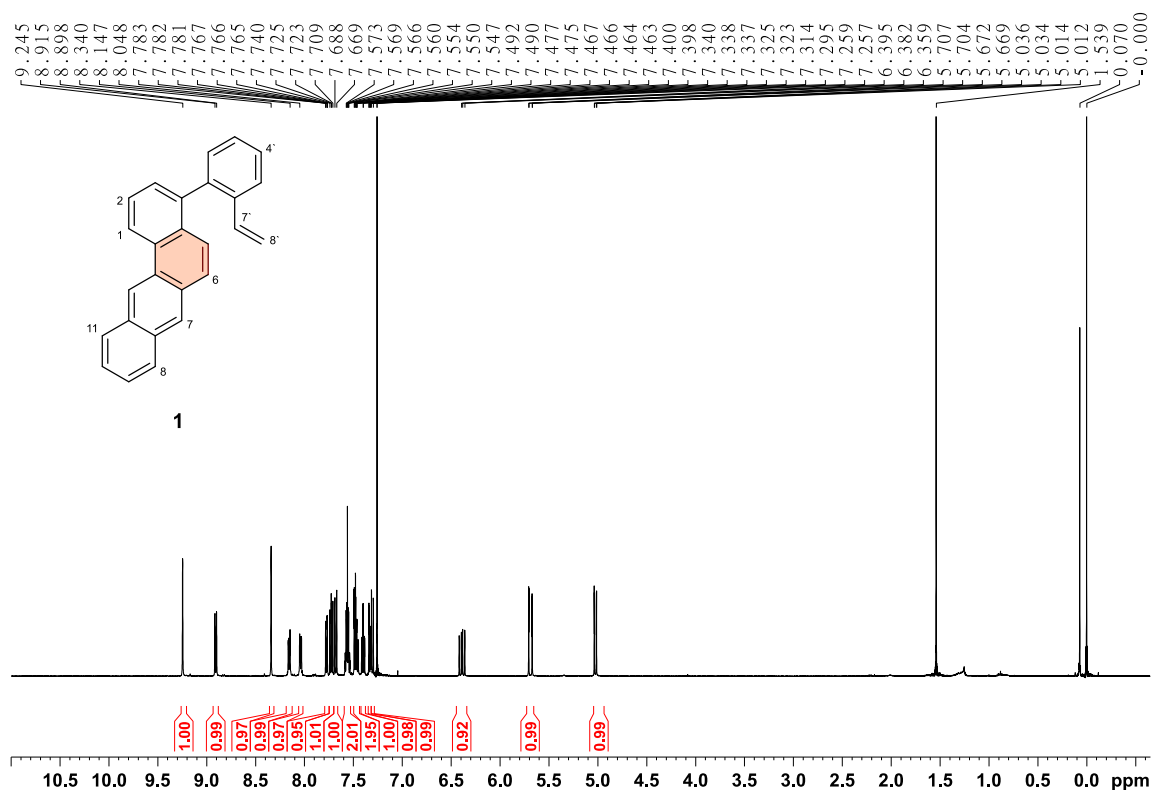
**G<sub>sol</sub>** = -1307.158936

C -2.18562200 1.87843500 -1.96919000  
C -0.93065400 1.86269500 -1.34248800  
C -0.66914000 0.95565200 -0.32465100  
C -1.67599300 0.05269200 0.08135400  
C -2.95060500 0.06070700 -0.55054300  
C -3.16447500 0.99416600 -1.57553700  
C 0.66914000 0.95565200 0.32465000  
C 1.67599300 0.05269200 -0.08135400

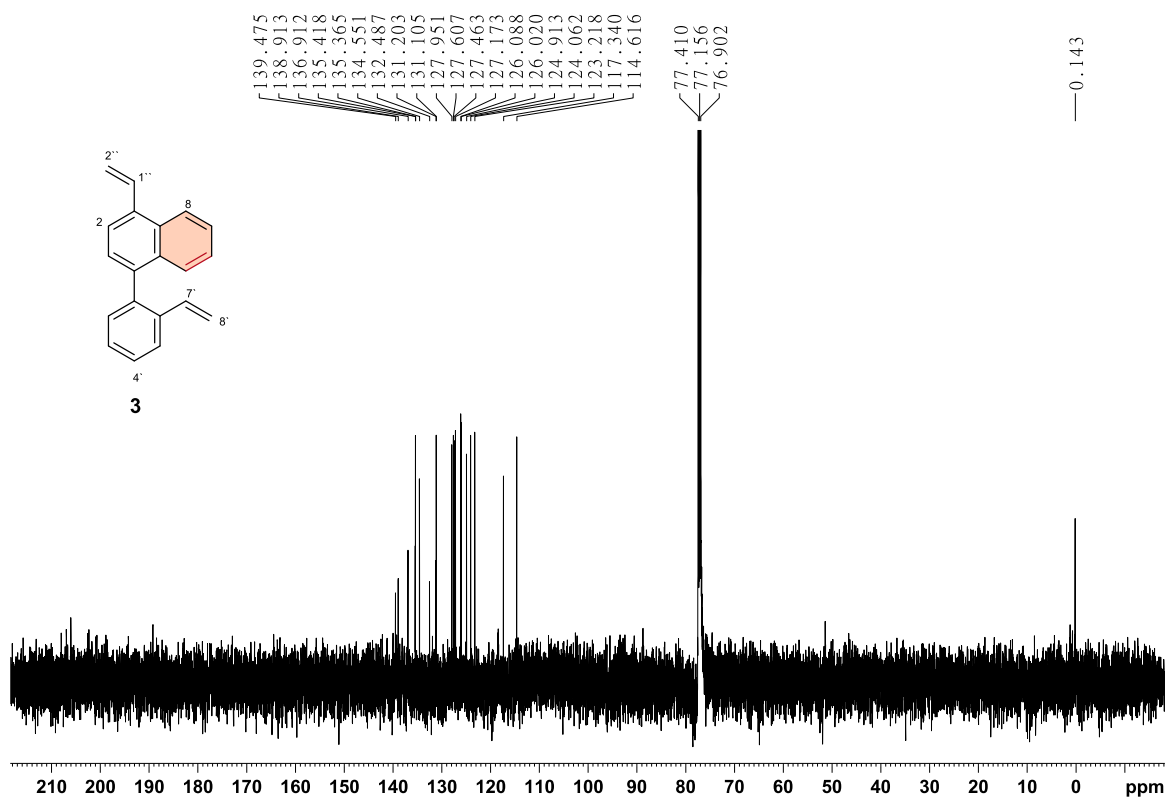
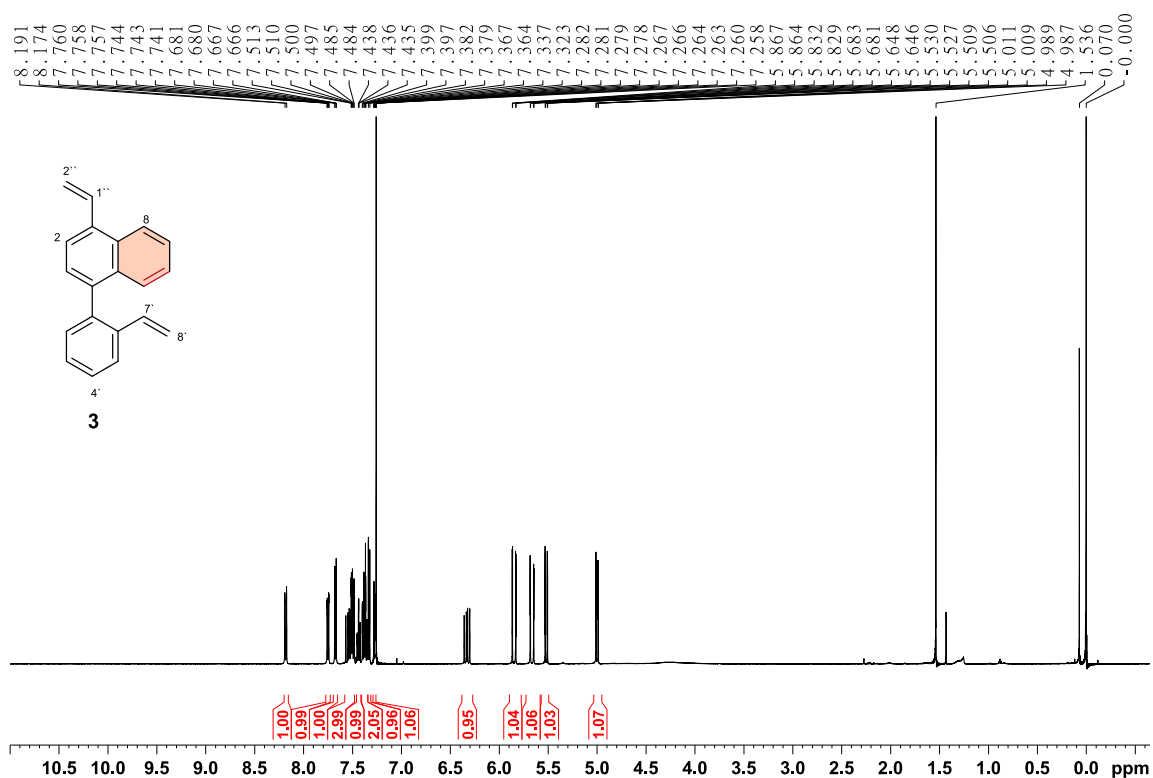
C 1.42860600 -0.88720500 -1.13410000  
 C -1.42860600 -0.88720500 1.13410000  
 C 0.93065400 1.86269500 1.34248800  
 C 2.18562200 1.87843500 1.96919000  
 C 3.16447500 0.99416600 1.57553700  
 C 2.95060500 0.06070700 0.55054300  
 C -3.96946200 -0.87955200 -0.12254700  
 C 3.96946200 -0.87955200 0.12254700  
 C -3.67208000 -1.79203200 0.92286200  
 C -4.65064600 -2.71123200 1.34744900  
 C -5.89603100 -2.74157600 0.76581900  
 C -6.19626100 -1.84252100 -0.26669400  
 C -5.25415000 -0.93518300 -0.69785800  
 C -2.37943100 -1.76341900 1.53154500  
 C 5.25415000 -0.93518300 0.69785800  
 C 6.19626100 -1.84252000 0.26669400  
 C 5.89603100 -2.74157600 -0.76581900  
 C 4.65064700 -2.71123100 -1.34744900  
 C 3.67208000 -1.79203100 -0.92286200  
 C 2.37943200 -1.76341900 -1.53154500  
 O 0.08549400 2.70093100 -1.68046900  
 C -0.12465300 3.64786000 -2.71120800  
 O -0.08549400 2.70093100 1.68046800  
 C 0.12465300 3.64785900 2.71120900  
 H -2.39507700 2.57959800 -2.76280100  
 H -4.11798500 1.03414900 -2.08126900  
 H 0.45782300 -0.88398800 -1.60867200  
 H -0.45782300 -0.88398800 1.60867100  
 H 2.39507700 2.57959800 2.76280100  
 H 4.11798500 1.03414900 2.08126900  
 H -4.40239500 -3.39919200 2.14672900  
 H -6.63985400 -3.45271800 1.10072700  
 H -7.17464200 -1.86009000 -0.72954100  
 H -5.51779200 -0.25632600 -1.49587200  
 H -2.17296300 -2.46724000 2.32888100  
 H 5.51779200 -0.25632600 1.49587200  
 H 7.17464200 -1.86009000 0.72954100  
 H 6.63985400 -3.45271700 -1.10072700  
 H 4.40239500 -3.39919200 -2.14673000  
 H 2.17296300 -2.46724000 -2.32888100  
 H 0.80889700 4.19731800 -2.80500400  
 H -0.93022300 4.34345600 -2.45828200  
 H -0.35339700 3.16065000 -3.66359500  
 H -0.80889800 4.19731600 2.80500600  
 H 0.93022200 4.34345500 2.45828400  
 H 0.35339600 3.16064800 3.66359500

# NMR Spectra

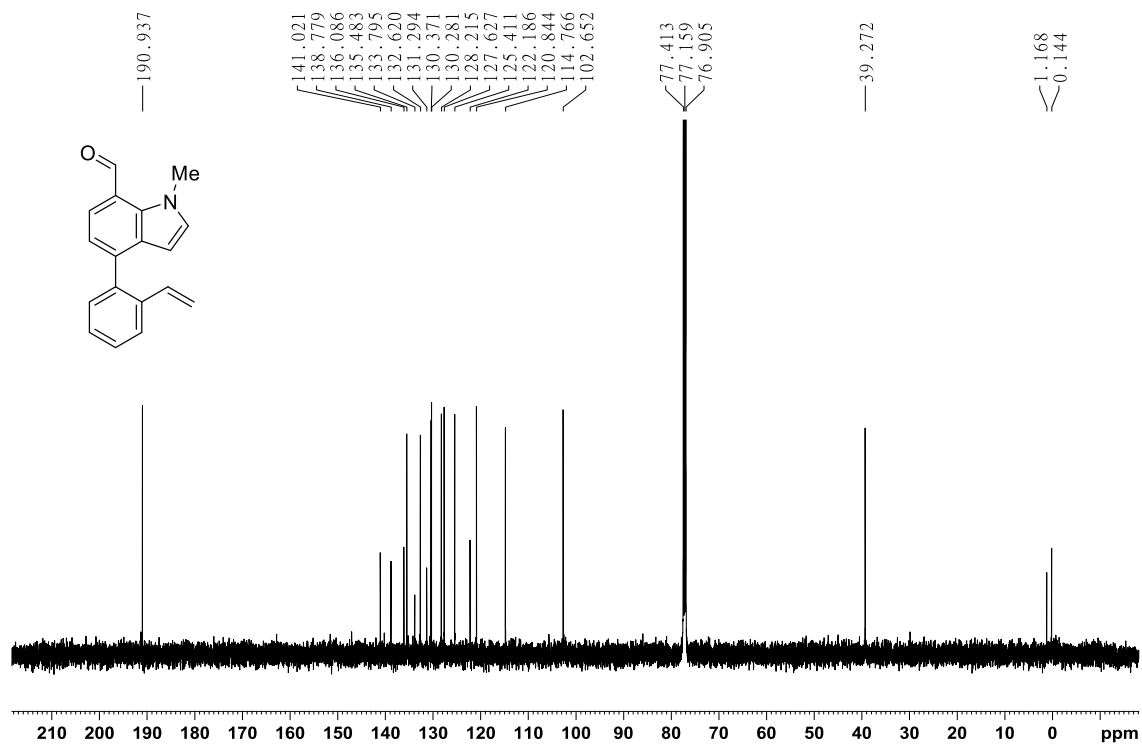
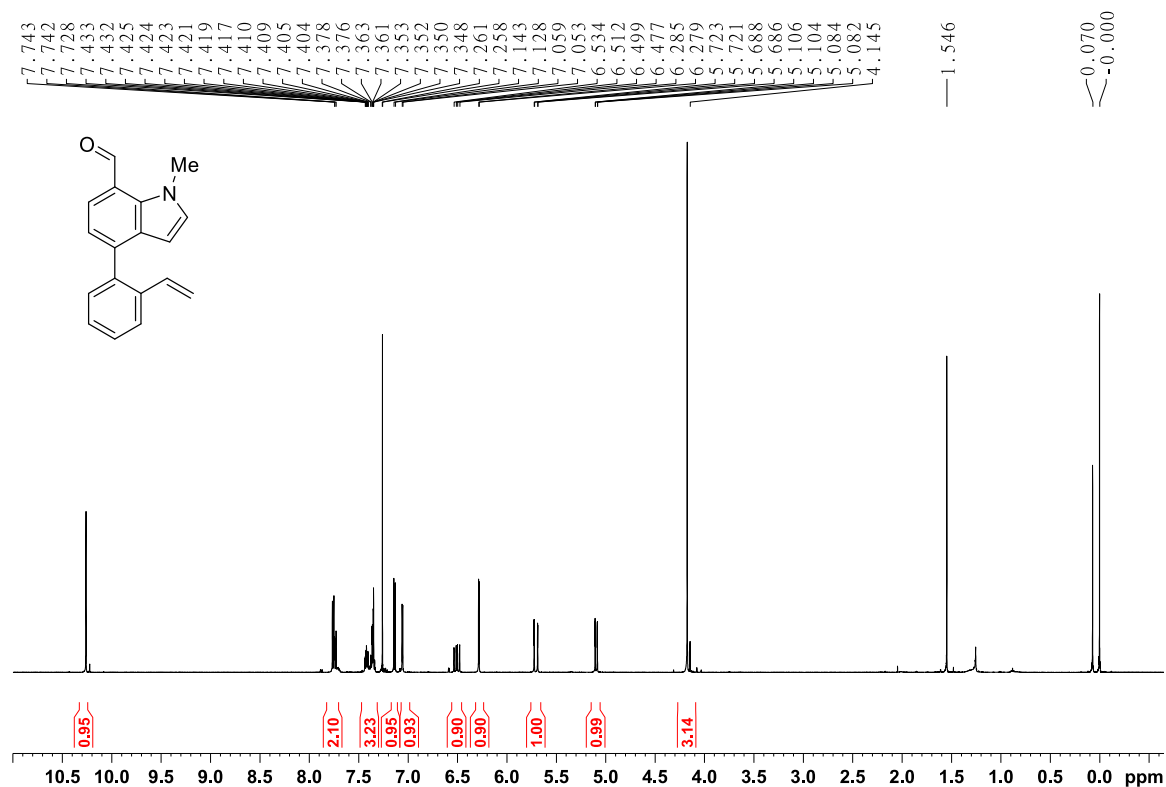
## 4-(2-Vinylphenyl)tetraphene (1):



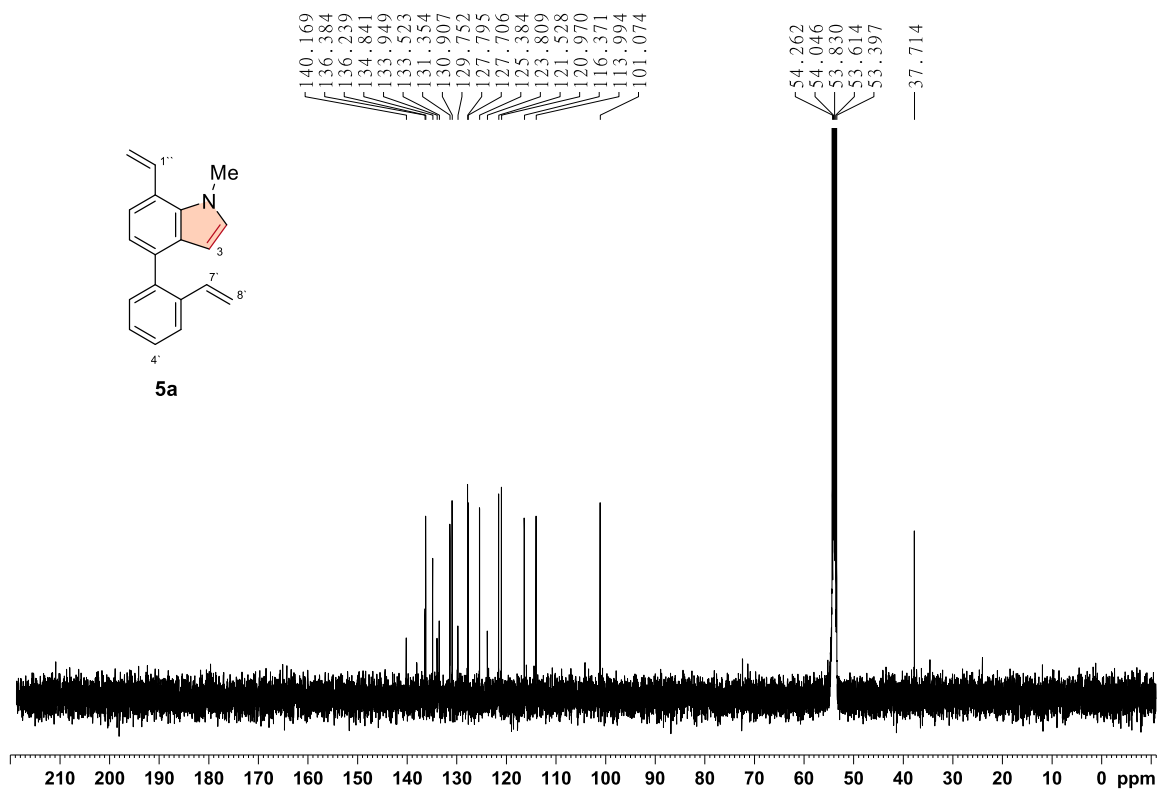
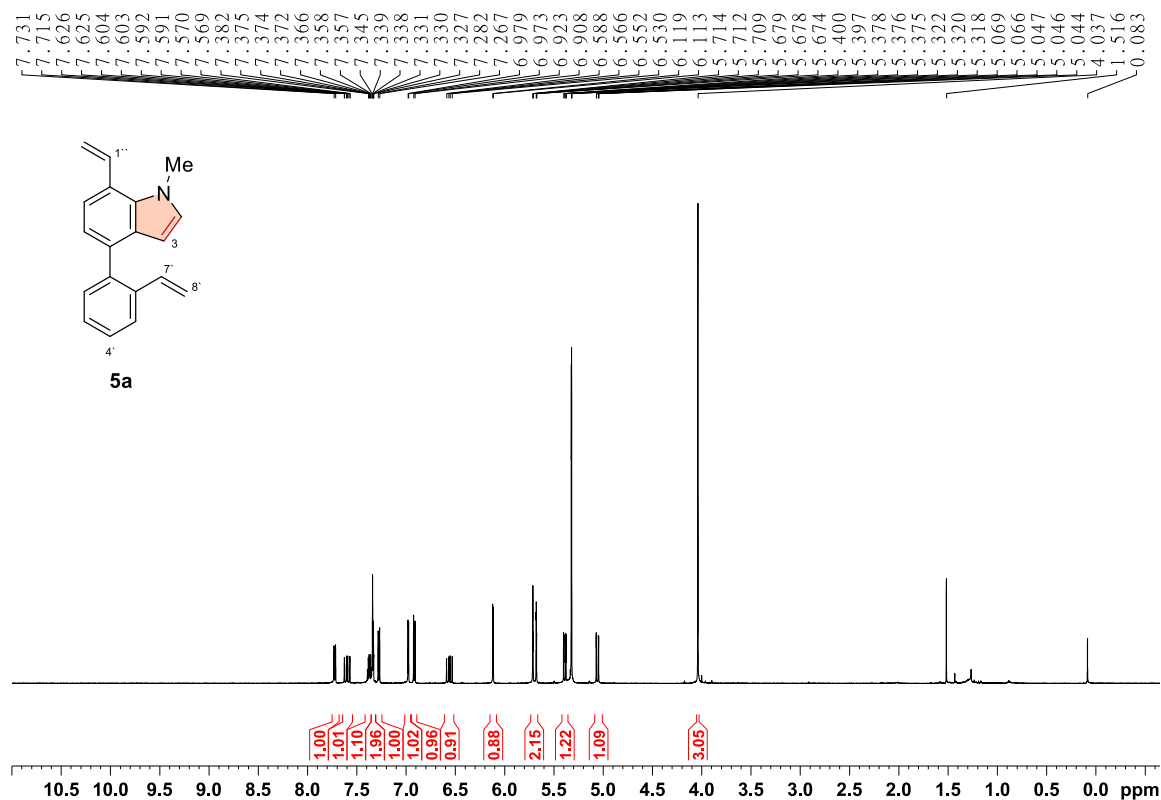
**1-Vinyl-4-(2-vinylphenyl)naphthalene (3):**



**1-Methyl-4-(2-vinylphenyl)-1H-indole-7-carbaldehyde**

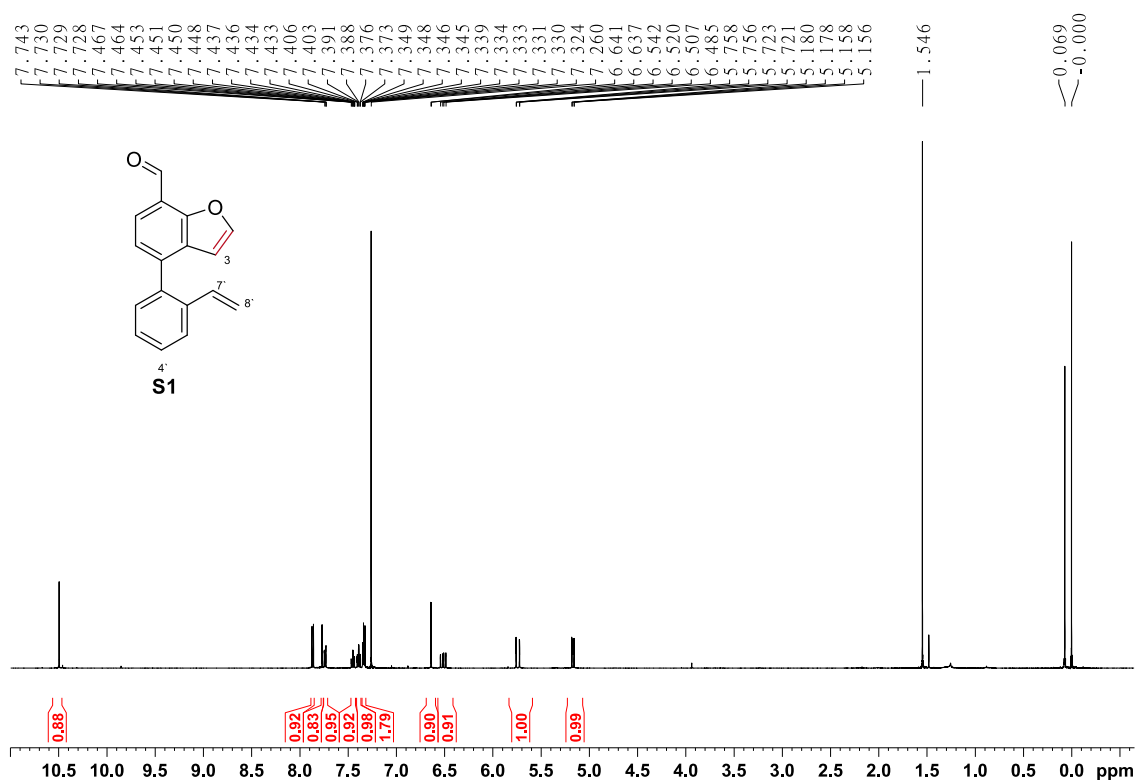


**1-Methyl-7-vinyl-4-(2-vinylphenyl)-1H-indole (5a):**

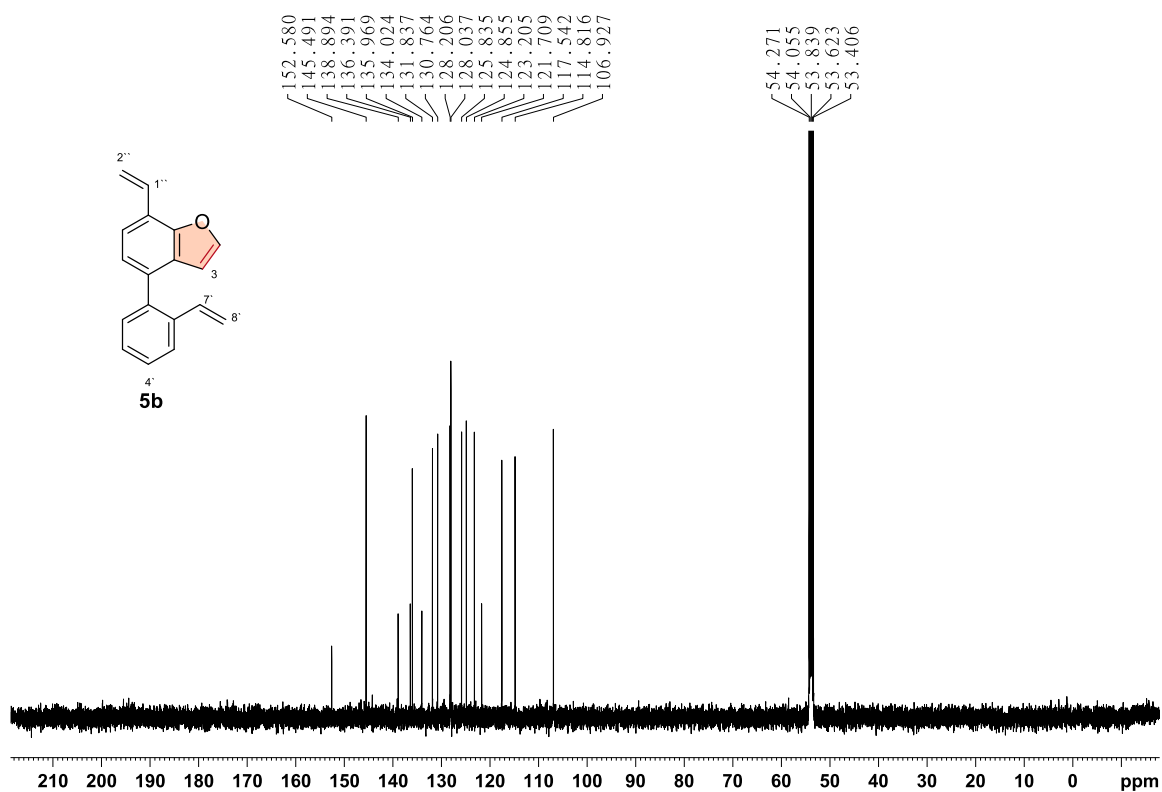
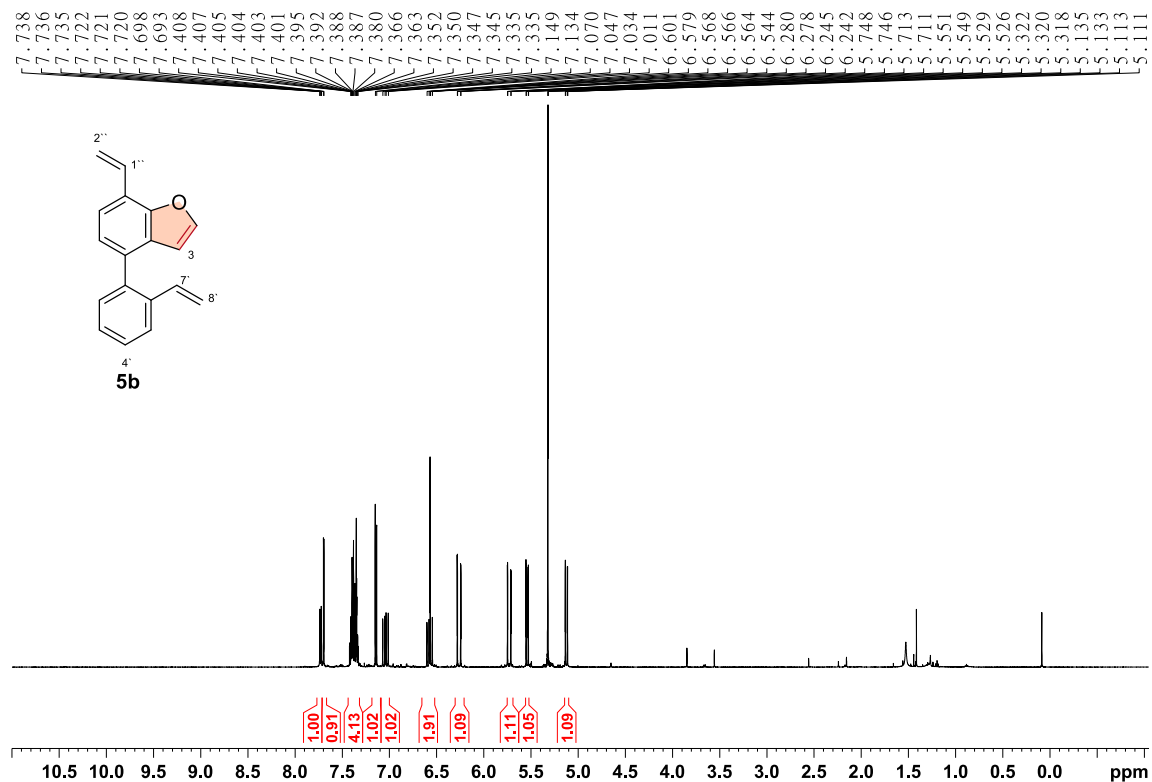




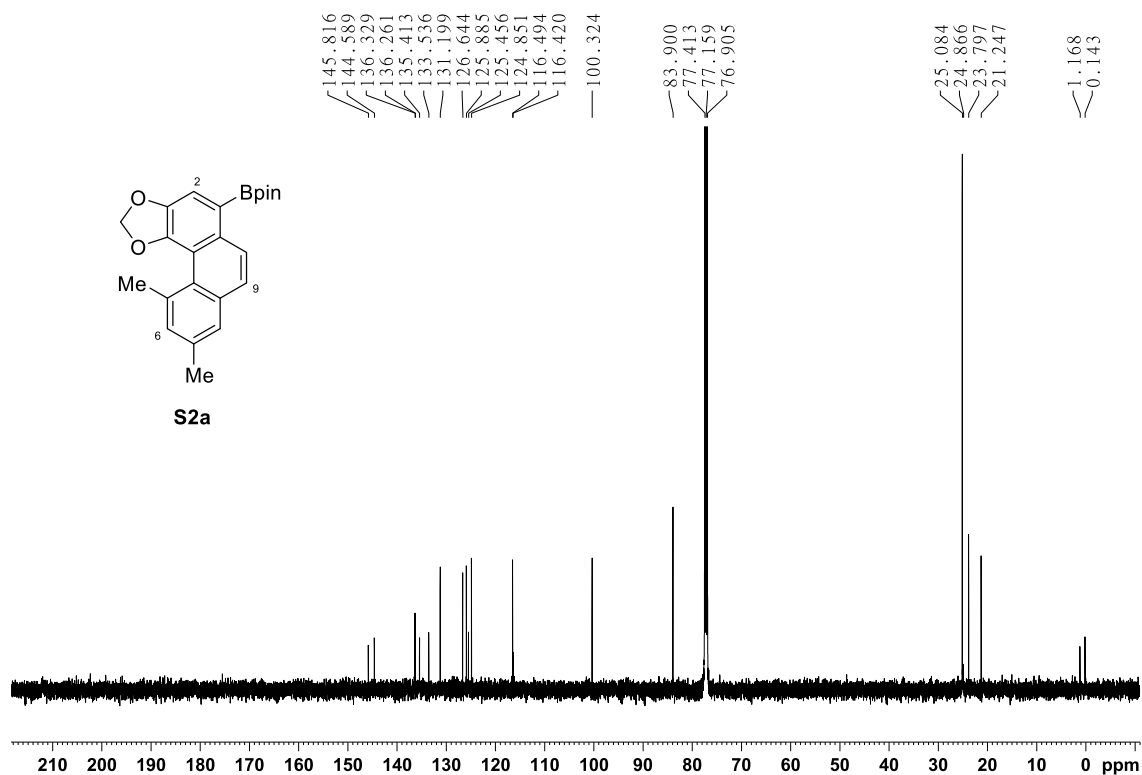
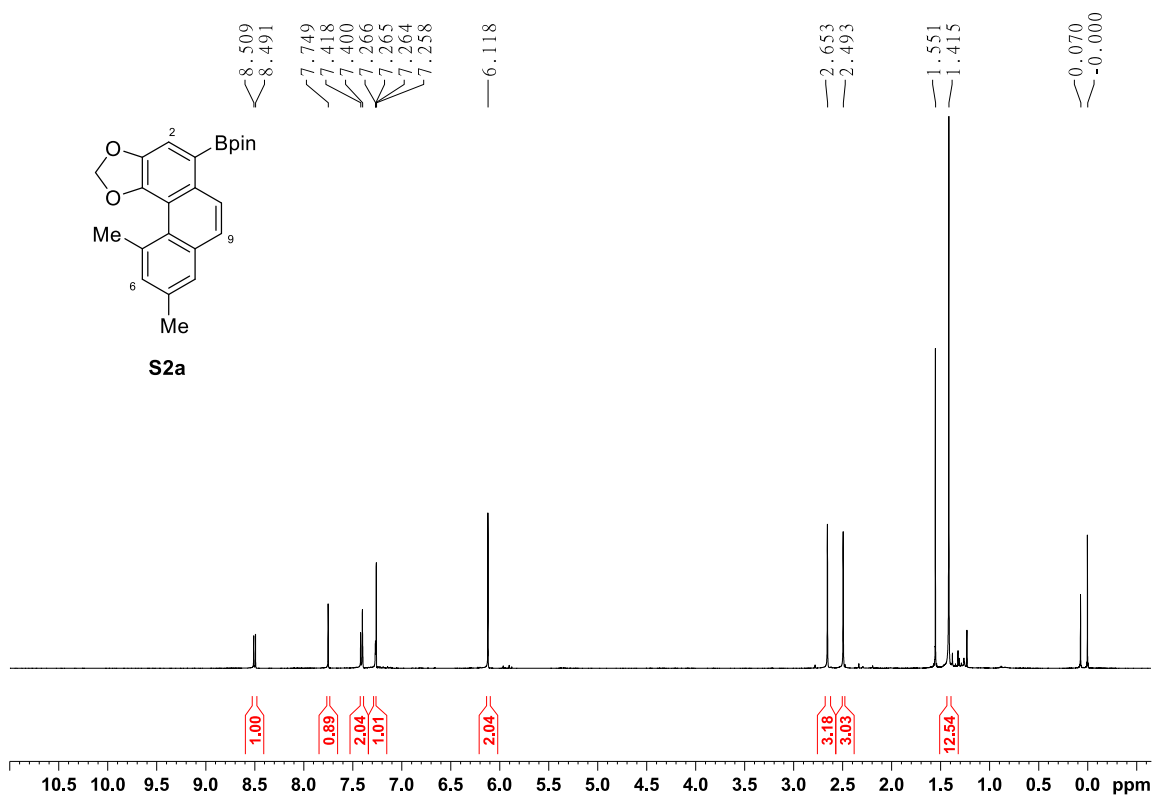
**4-(2-Vinylphenyl)benzofuran-7-carbaldehyde (S1):**



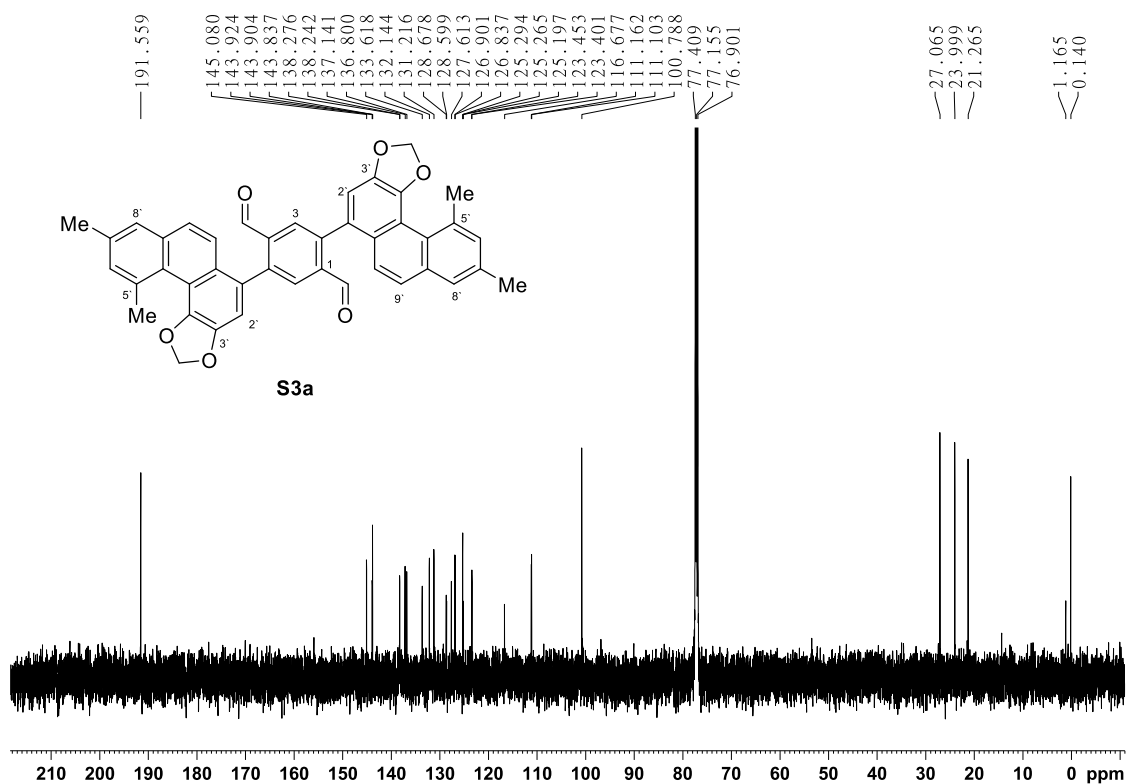
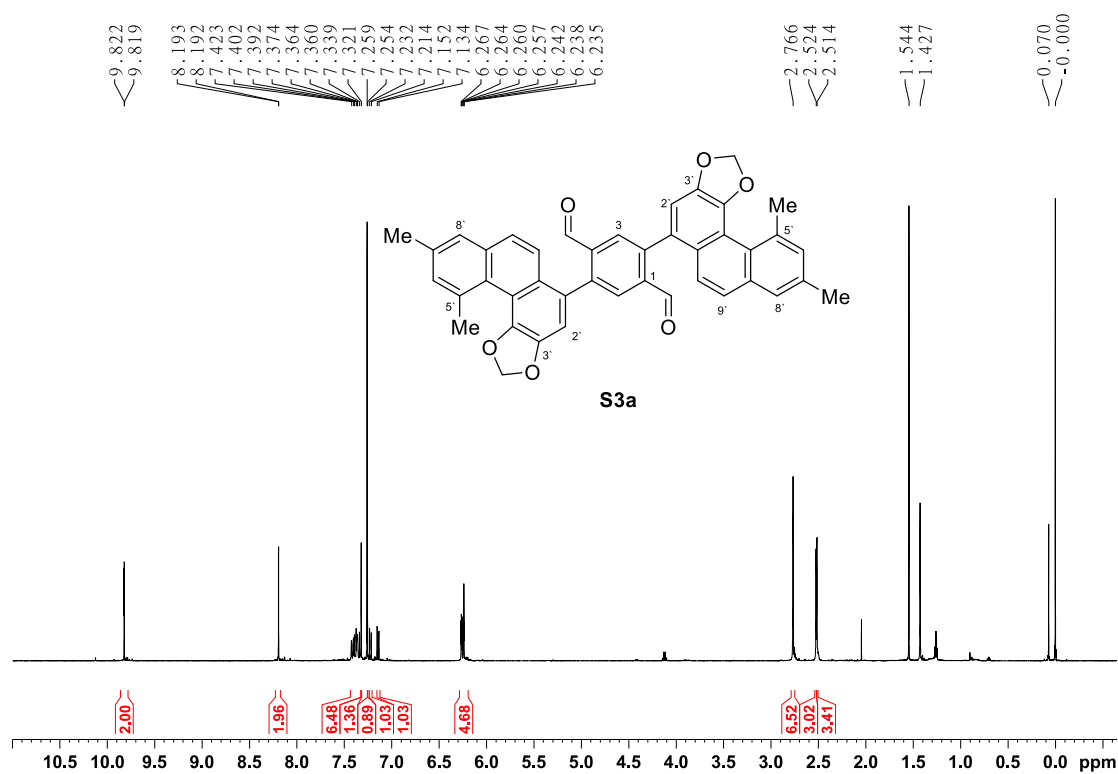
**7-Vinyl-4-(2-vinylphenyl)benzofuran (5b):**



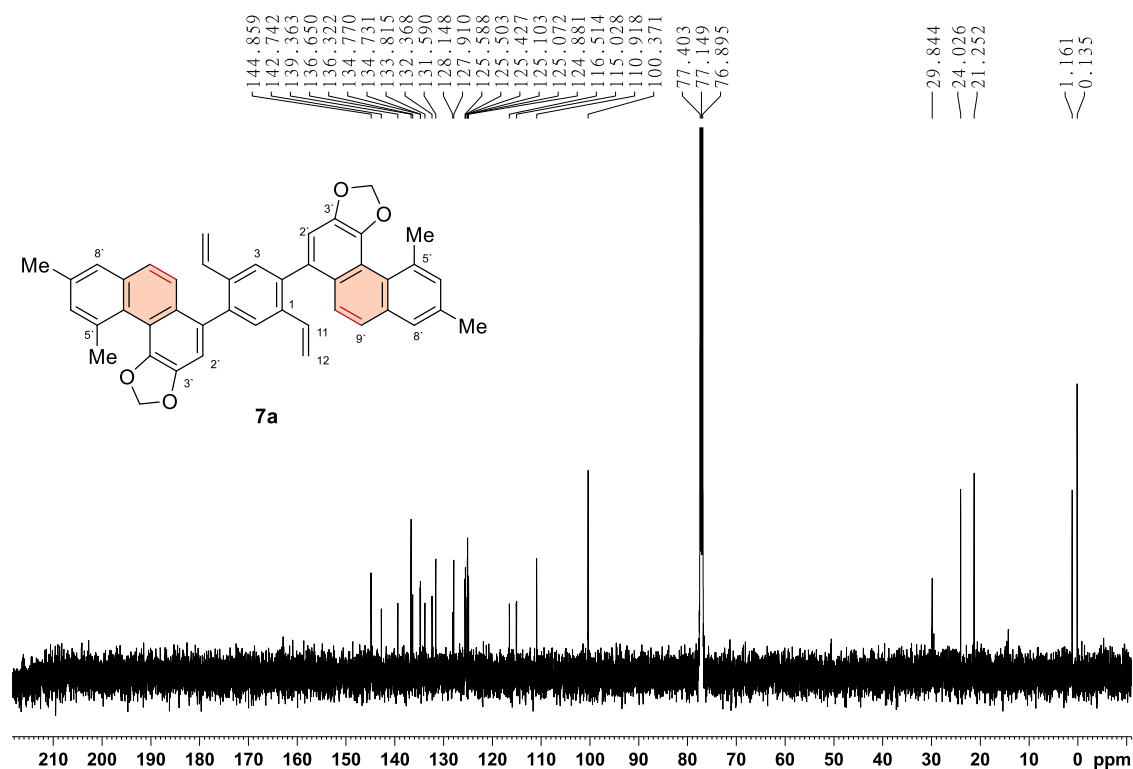
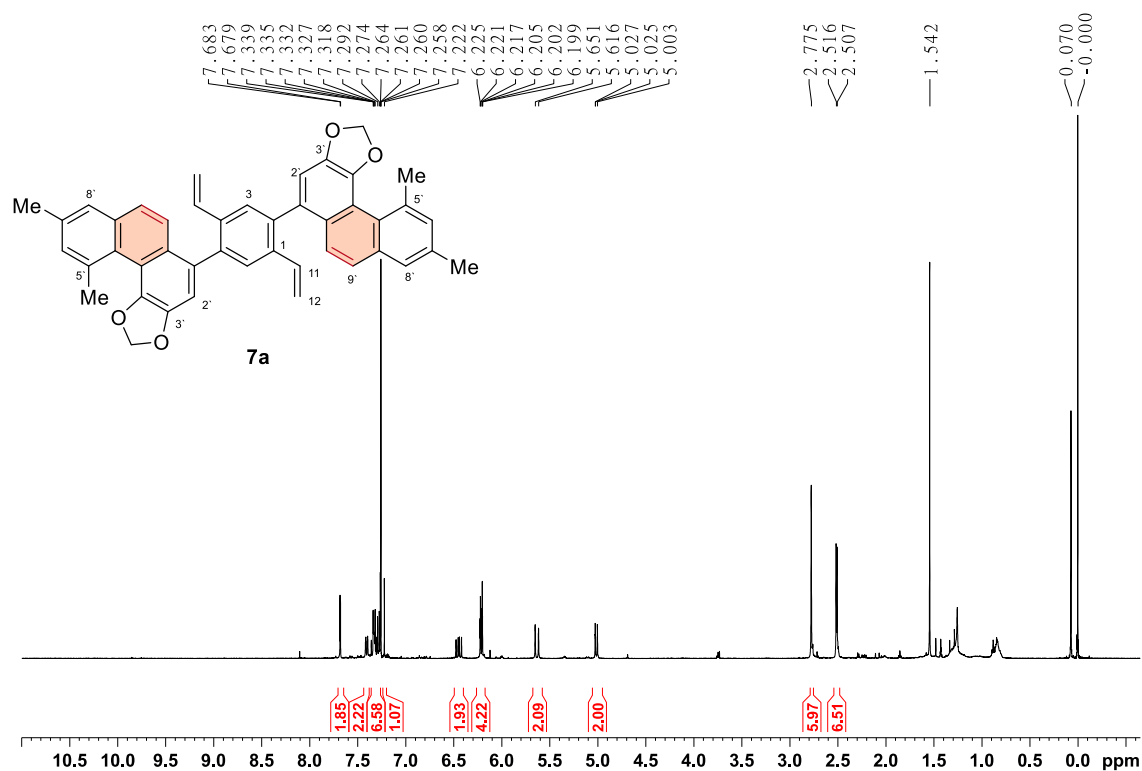
**2-(9,11-Dimethylphenanthro[3,4-d][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S2a):**



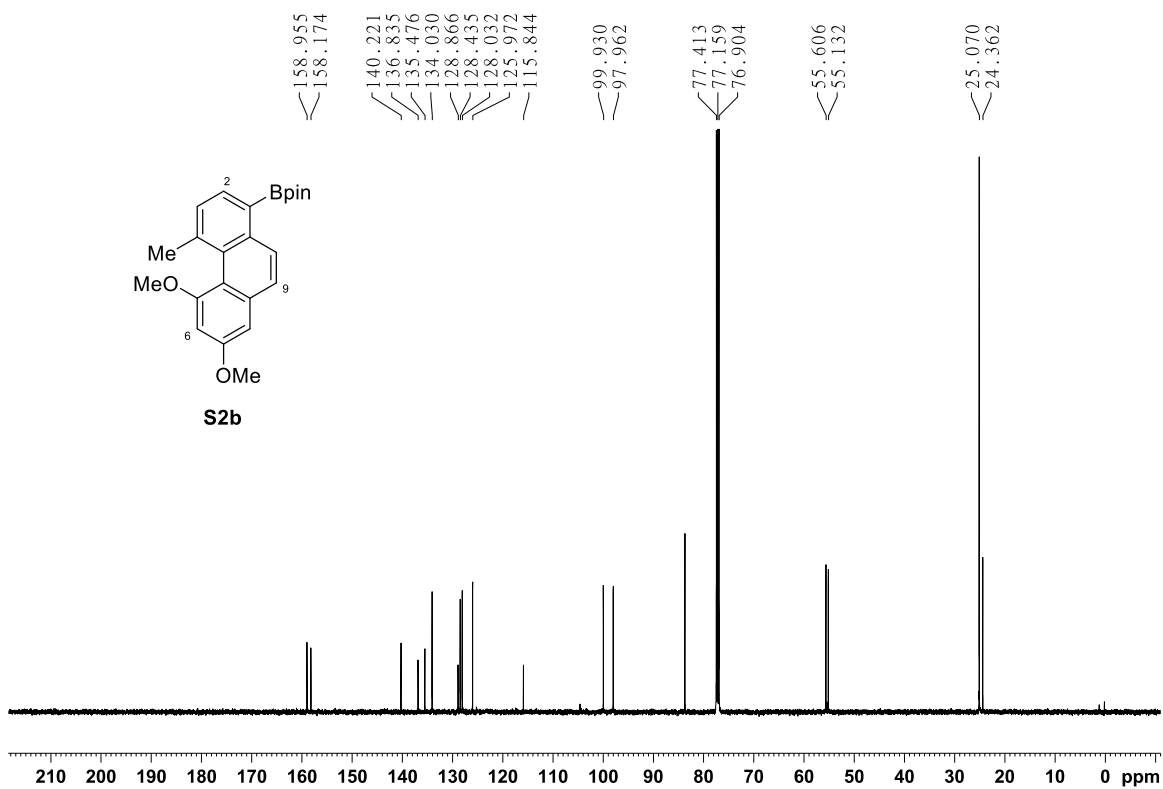
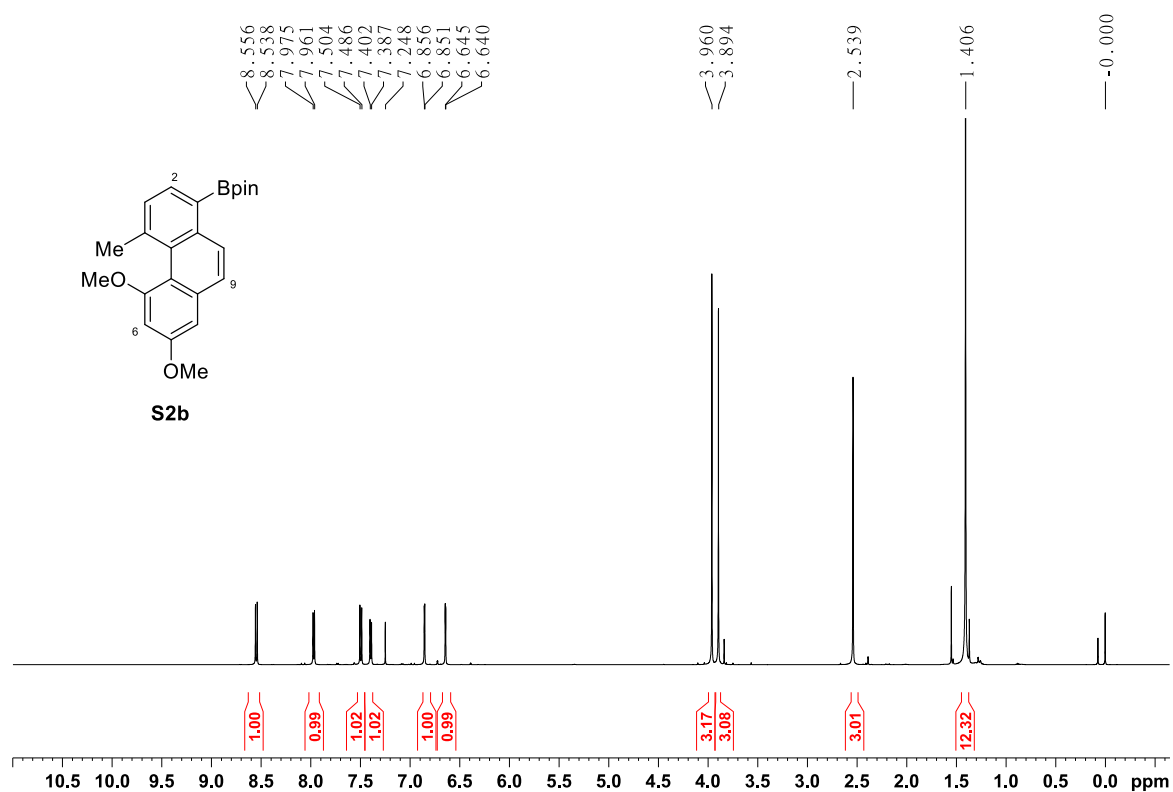
**2,5-Bis(9,11-dimethylphenanthro[3,4-d][1,3]dioxol-5-yl)terephthalaldehyde (S3a):**



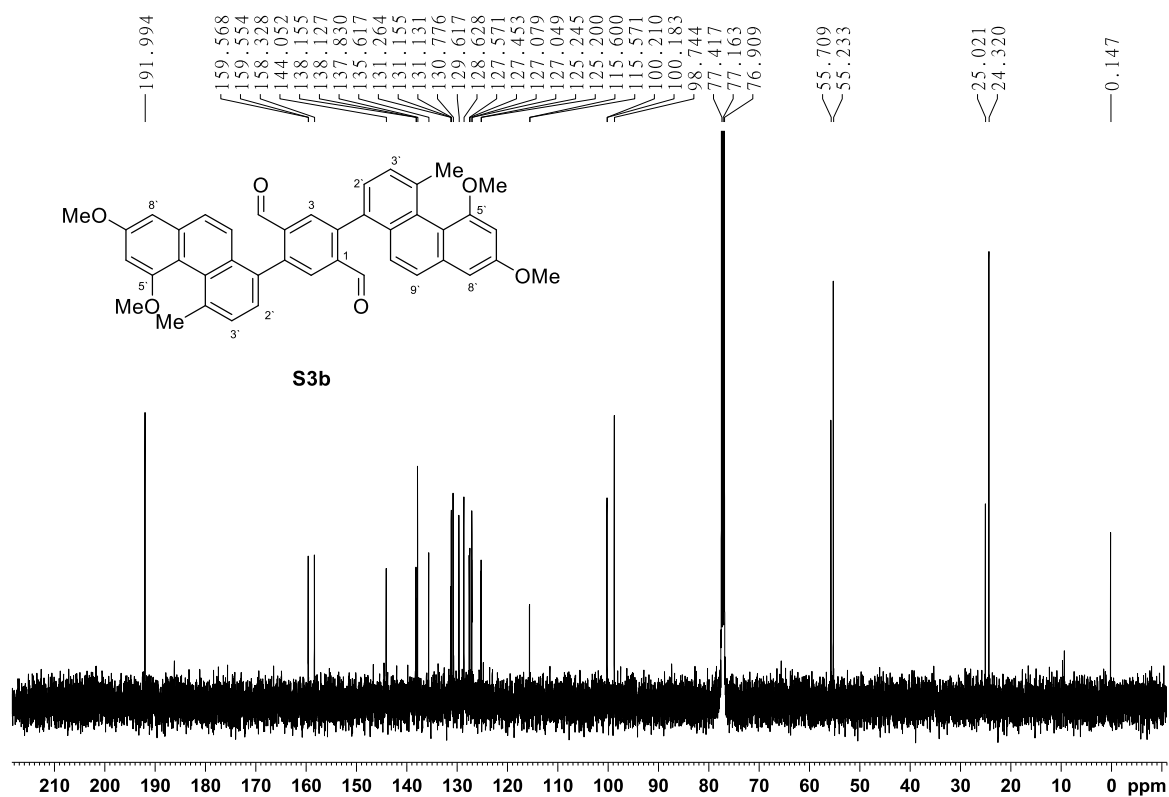
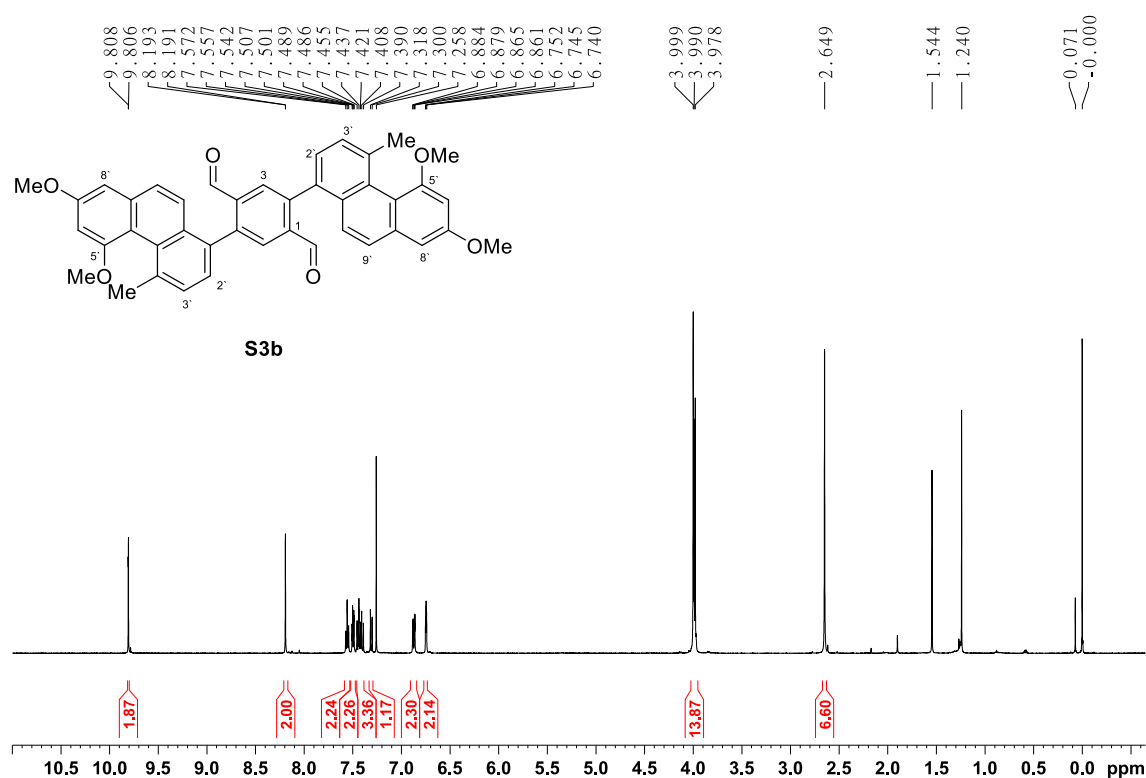
5,5'-(2,5-Divinyl-1,4-phenylene)bis(9,11-dimethylphenanthro[3,4-*d*][1,3]dioxole) (7a):



**2-(5,7-Dimethoxy-4-methylphenanthren-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S2b):**

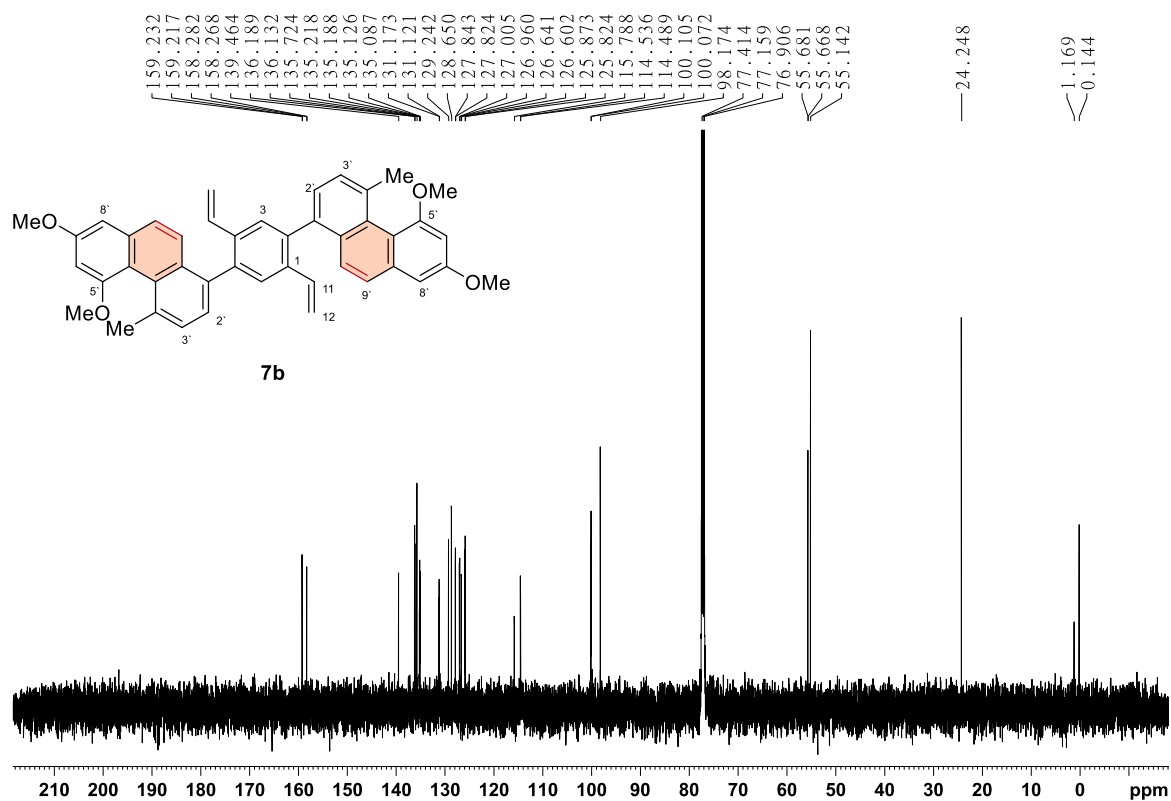
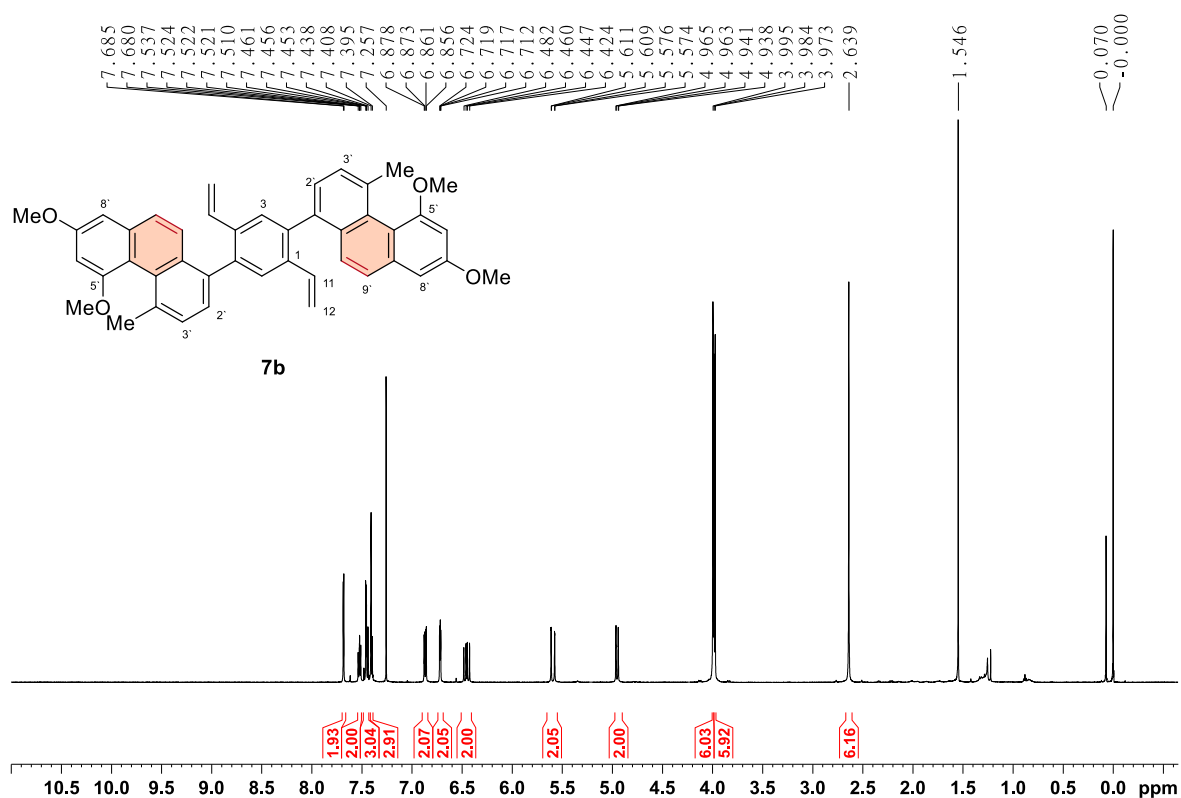


# 2,5-Bis(5,7-dimethoxy-4-methylphenanthren-1-yl)terephthalaldehyde (S3b):

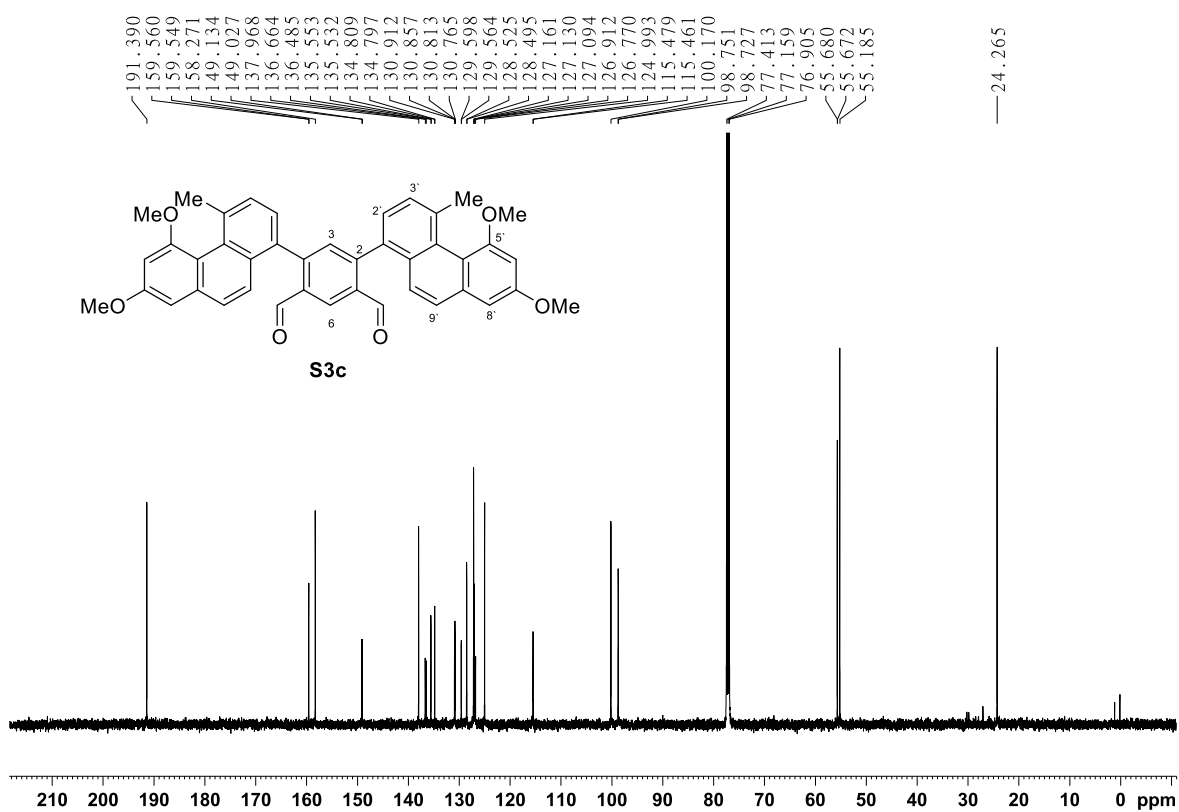
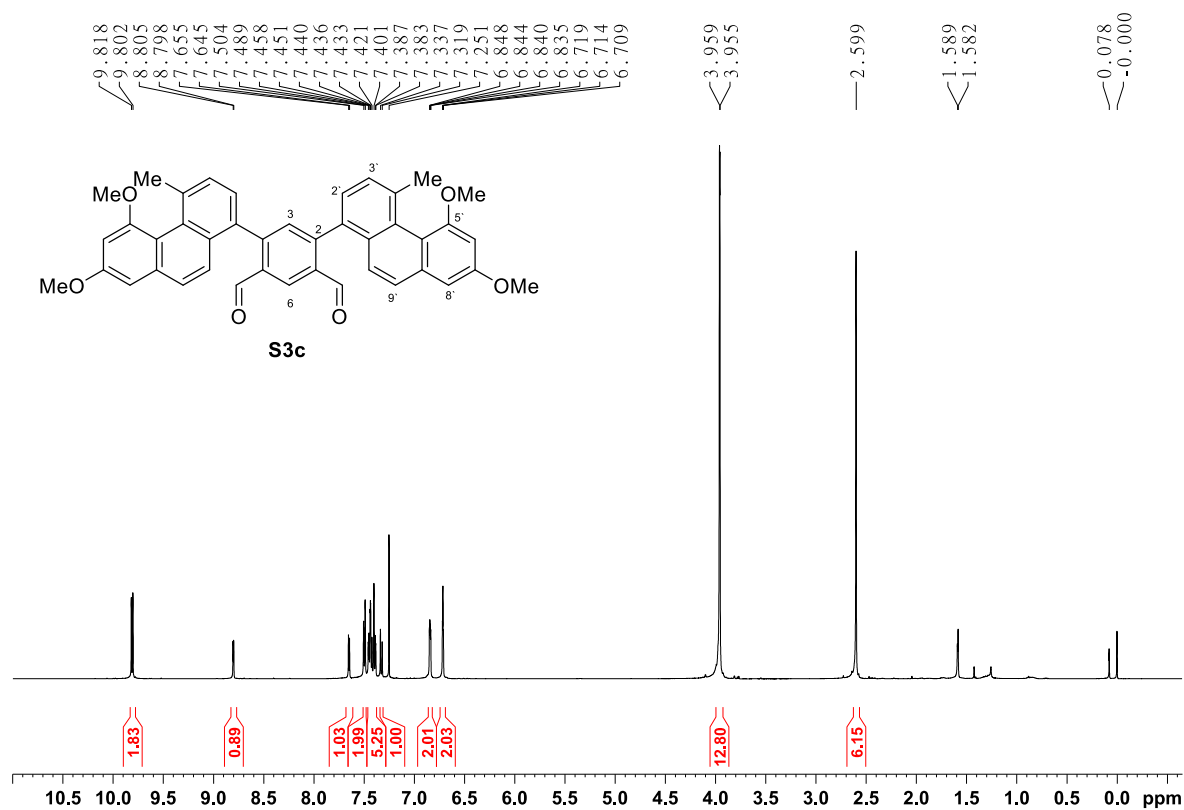




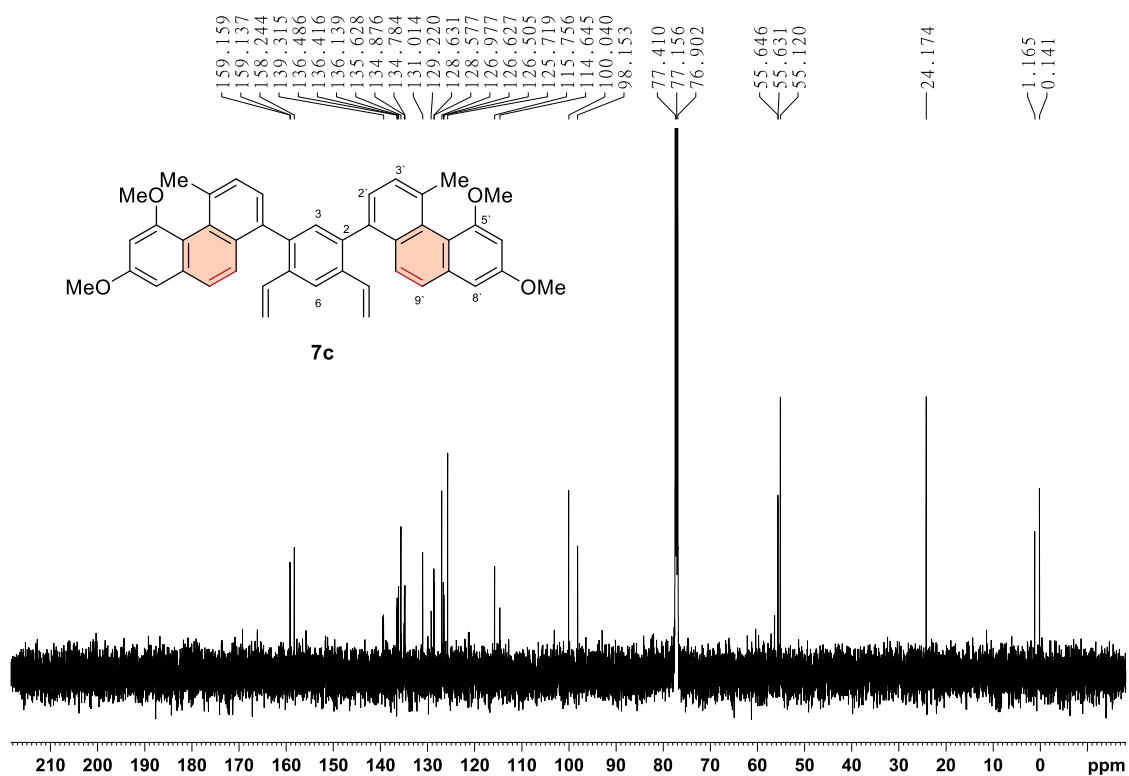
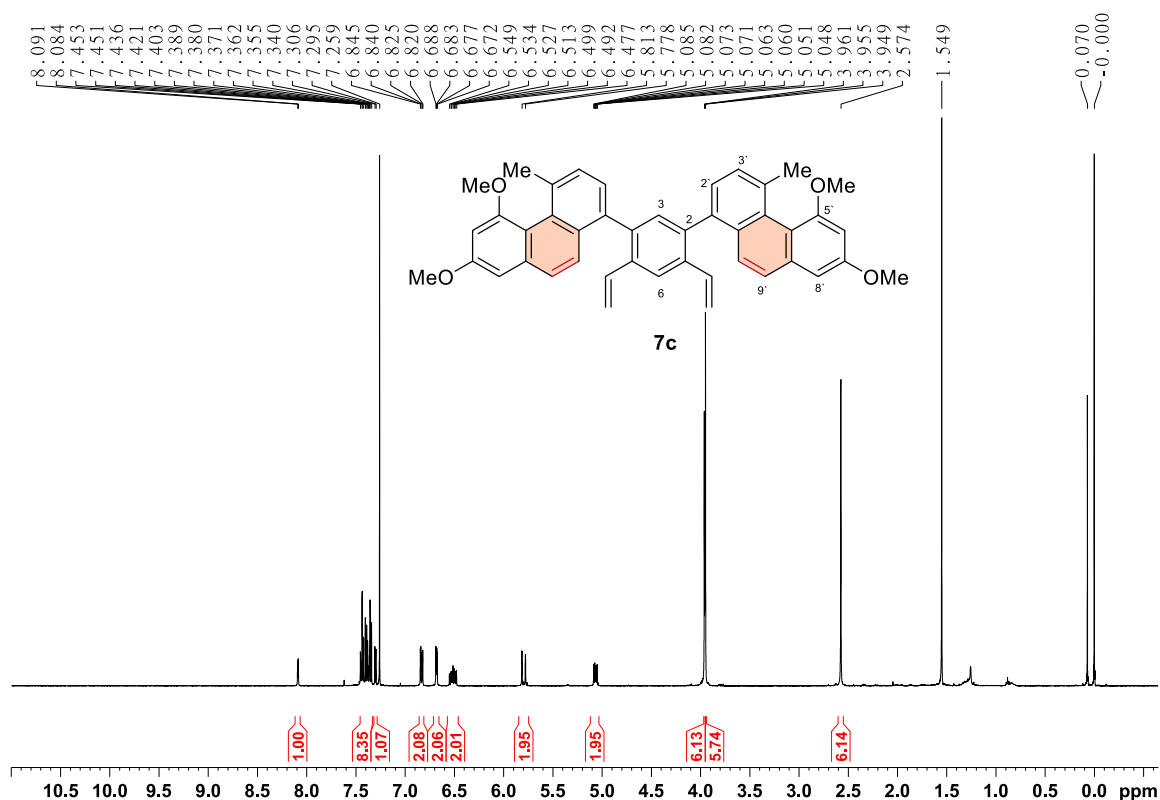
**8,8'-(2,5-Divinyl-1,4-phenylene)bis(2,4-dimethoxy-5-methylphenanthrene) (7b):**



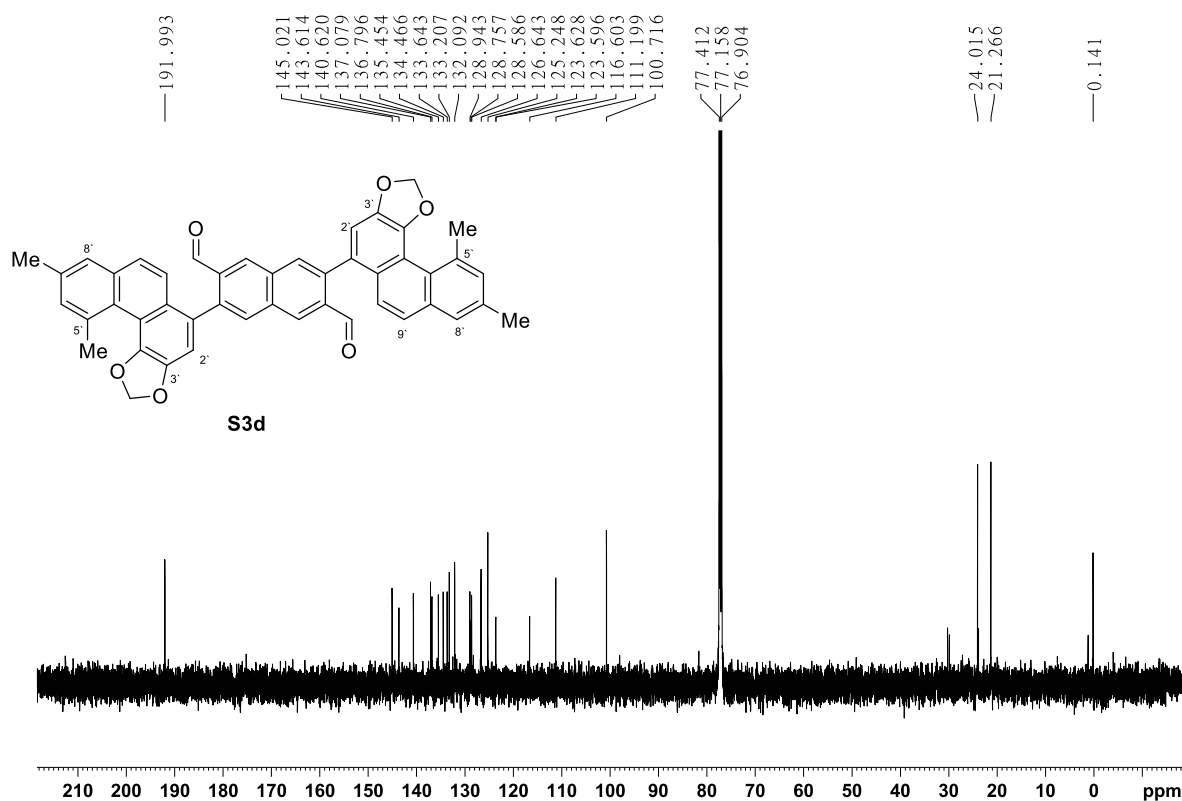
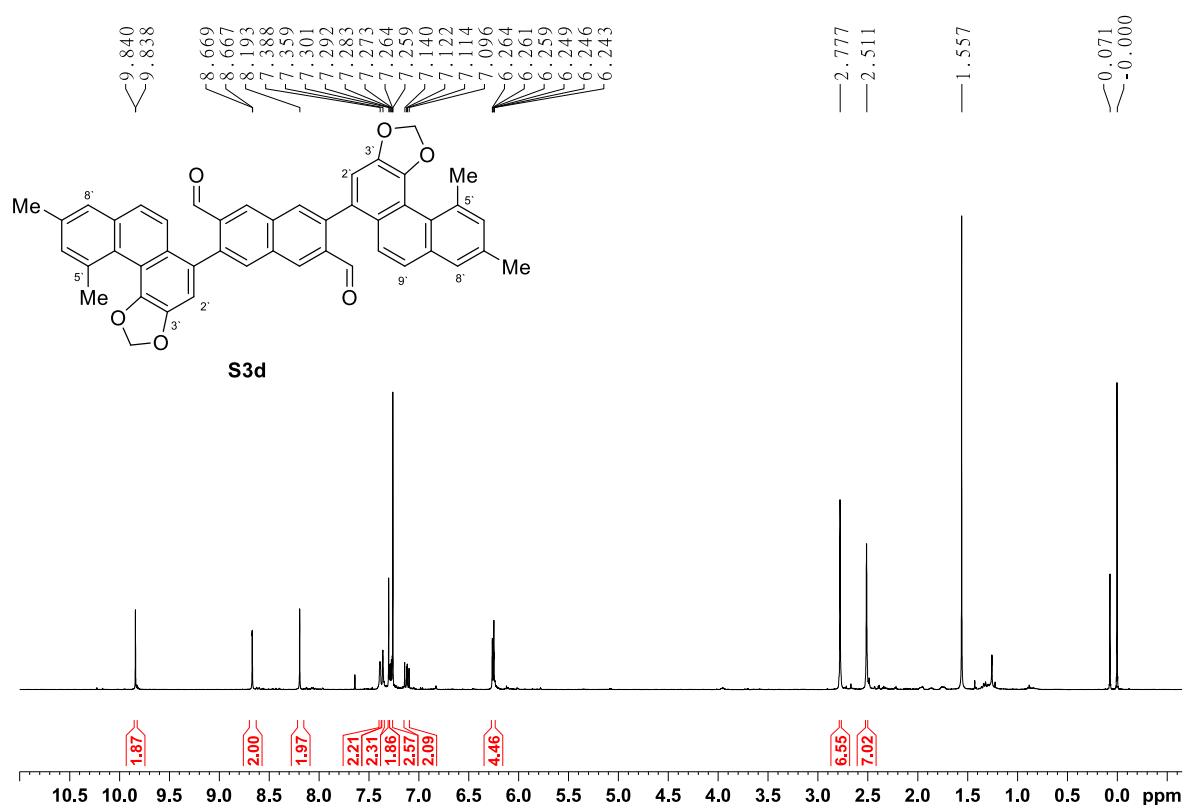
**4,6-Bis(5,7-dimethoxy-4-methylphenanthren-1-yl)isophthalaldehyde (S3c):**



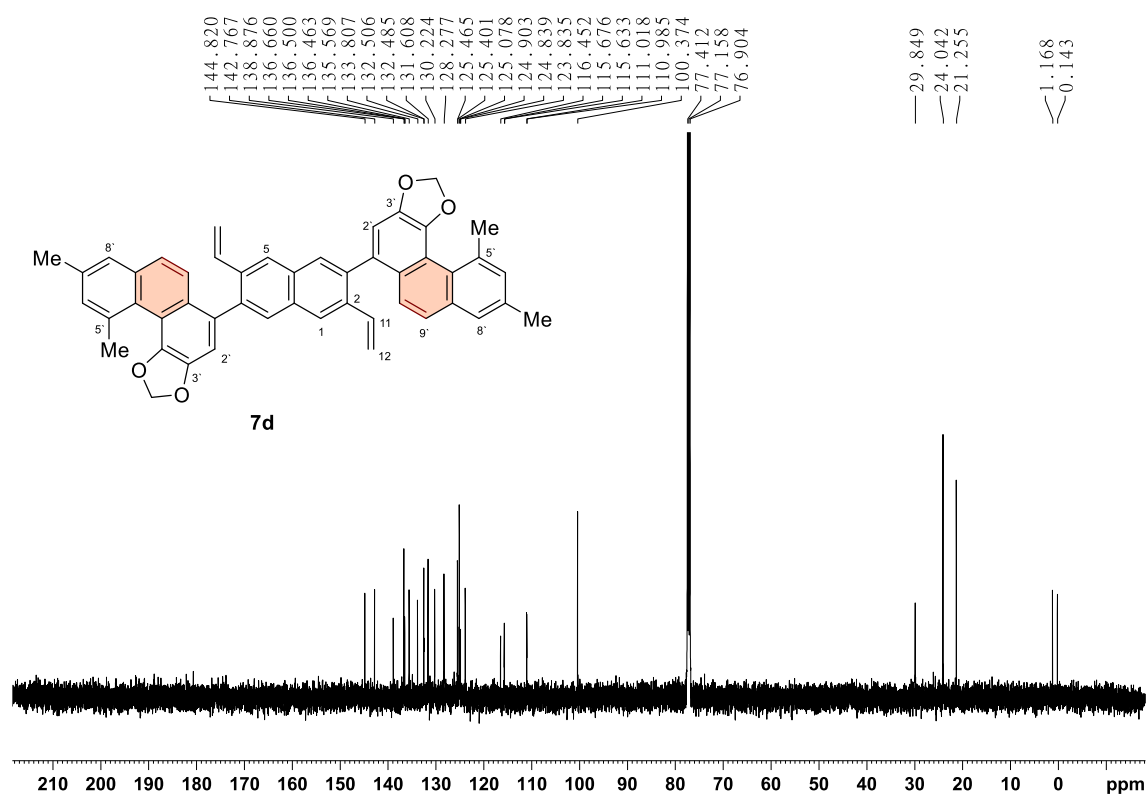
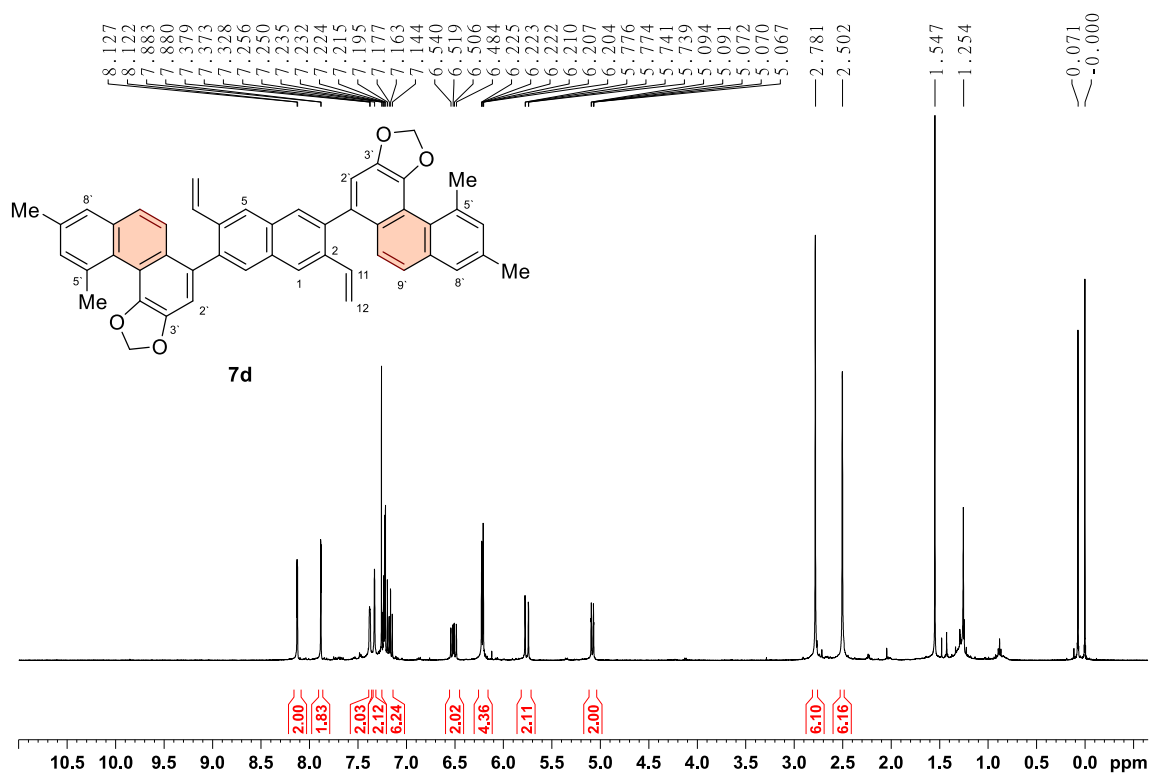
**8,8'-(4,6-Divinyl-1,3-phenylene)bis(2,4-dimethoxy-5-methylphenanthrene) (7c):**



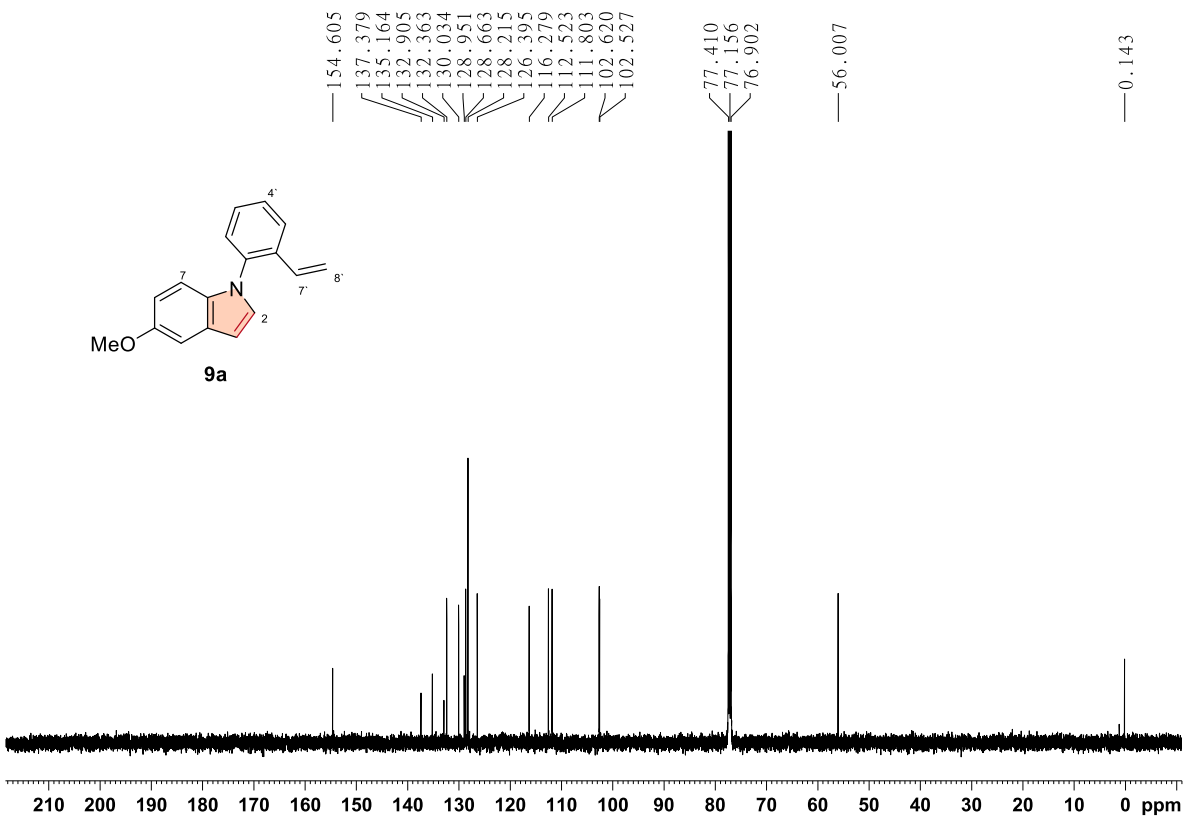
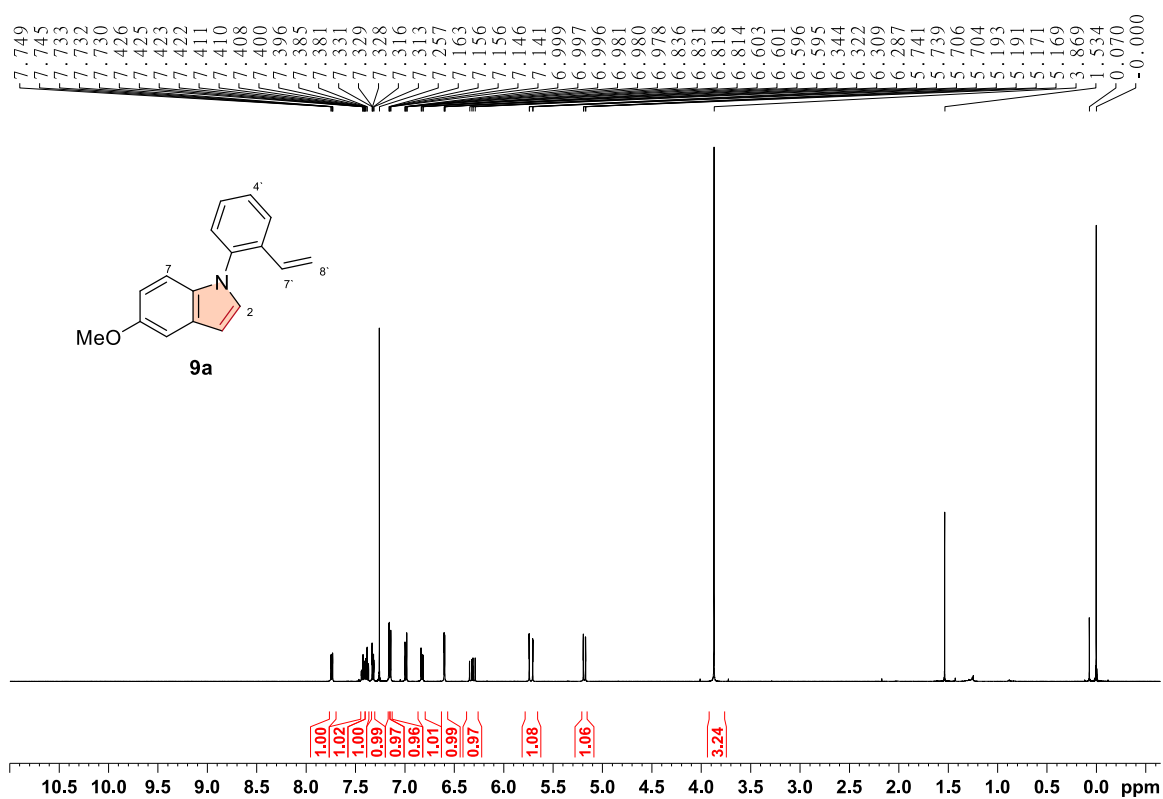
**3,7-Bis(9,11-dimethylphenanthro[3,4-d][1,3]dioxol-5-yl)naphthalene-2,6-dicarbaldehyde (S3d):**



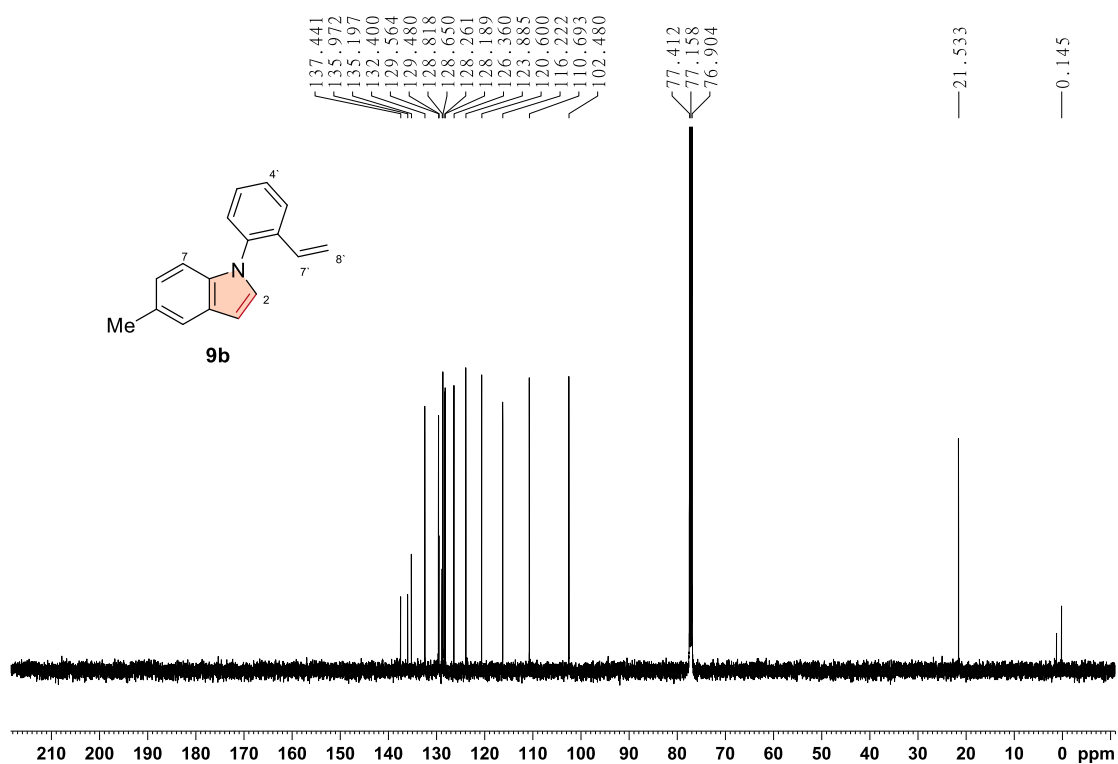
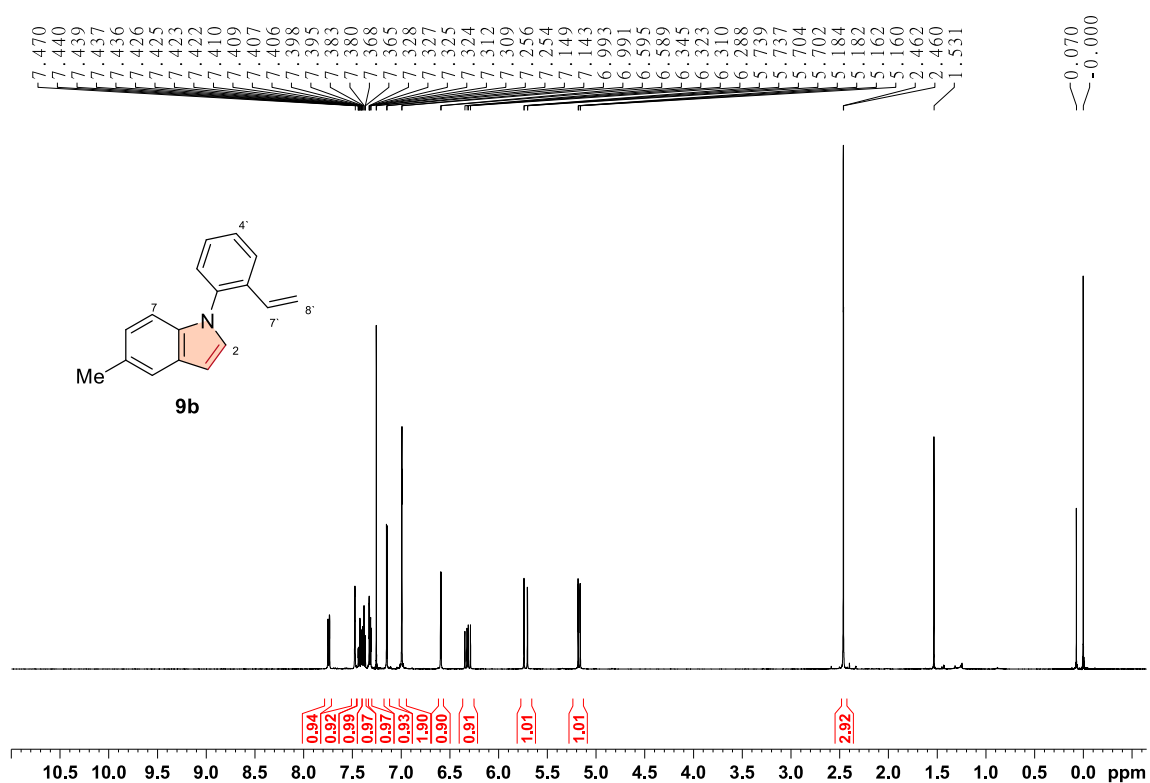
5,5'-(3,7-Divinyl-naphthalene-2,6-diyl)bis(9,11-dimethylphenanthro[3,4-d][1,3]dioxole) (7d):



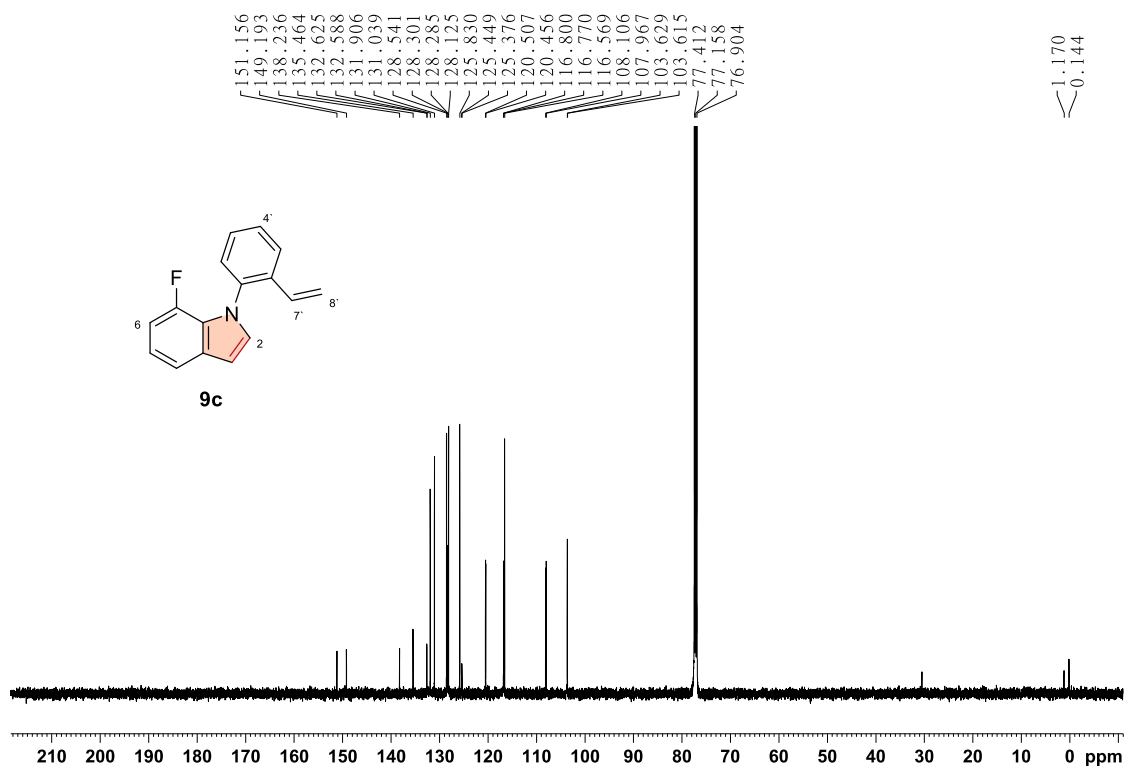
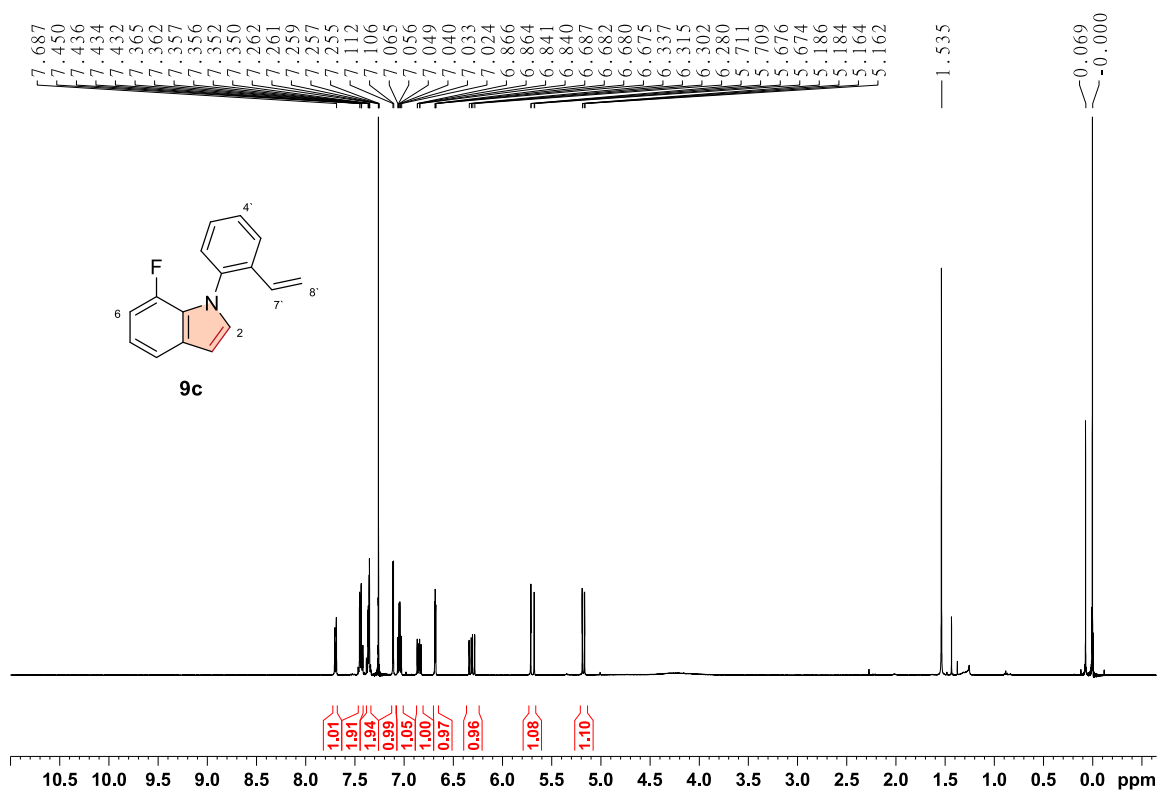
**5-Methoxy-1-(2-vinylphenyl)-1H-indole (9a):**



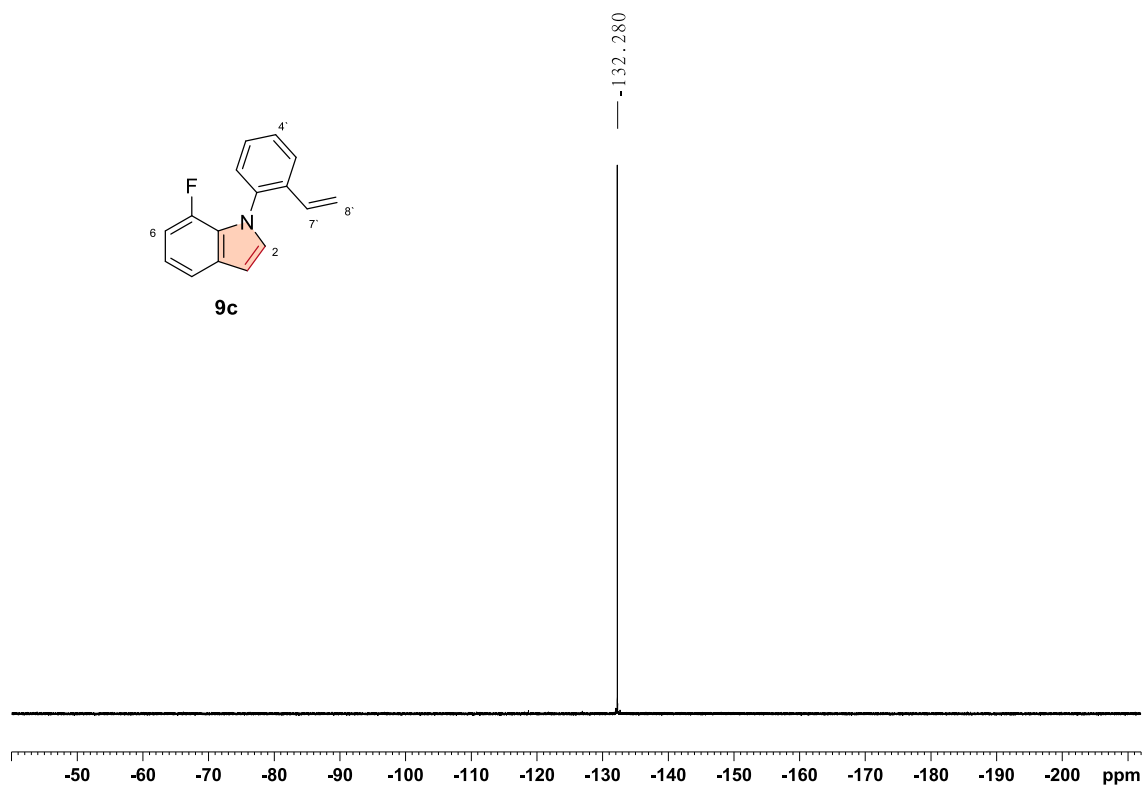
**5-Methyl-1-(2-vinylphenyl)-1H-indole (9b):**



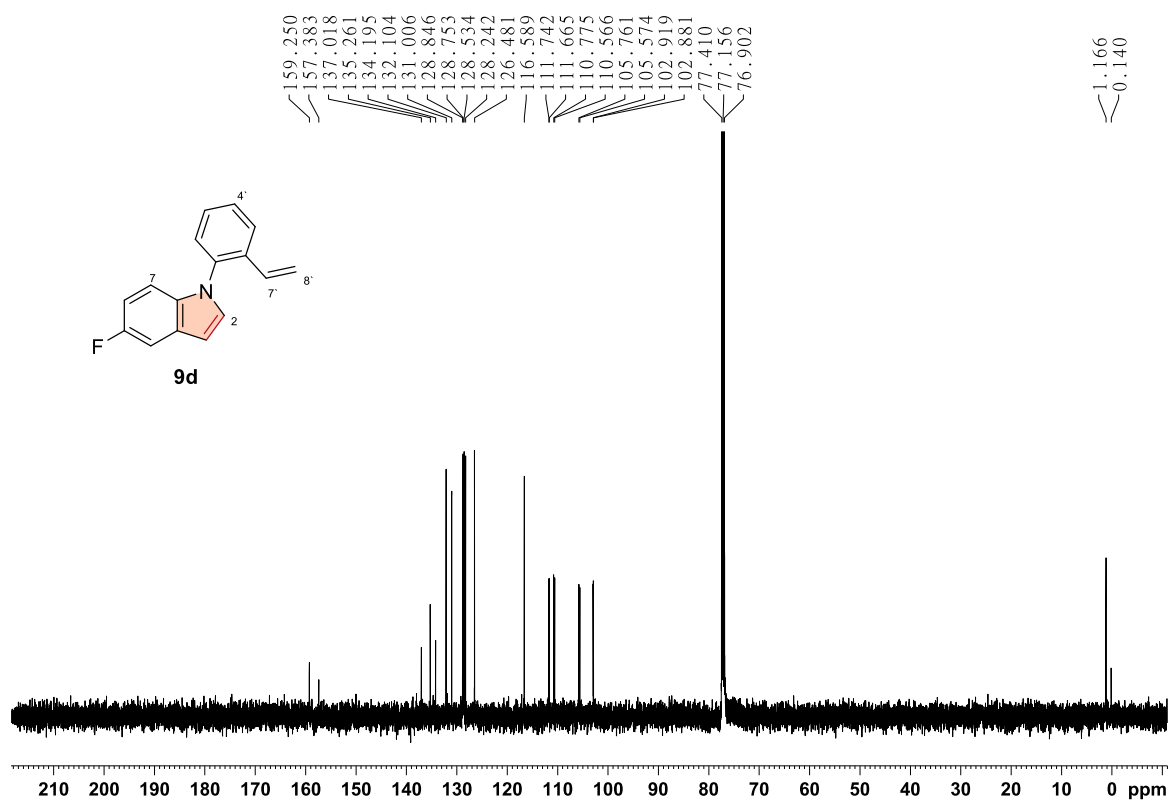
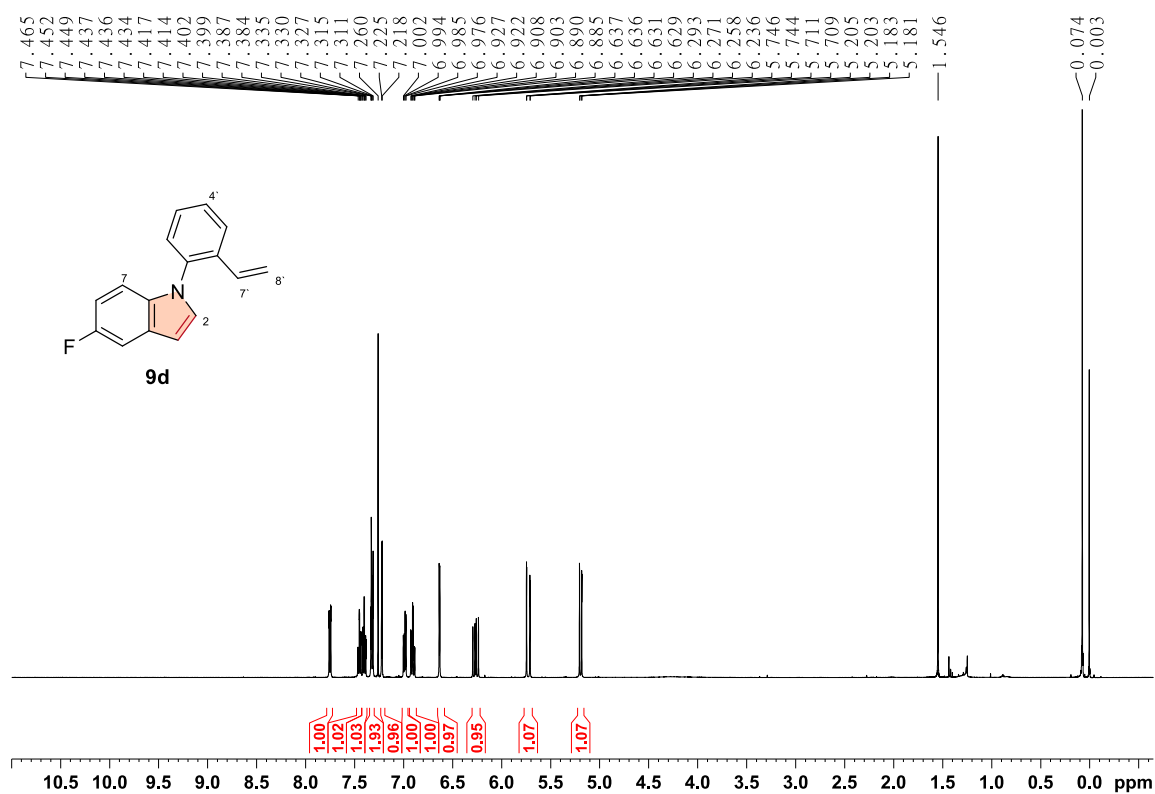
**7-Fluoro-1-(2-vinylphenyl)-1H-indole (9c):**

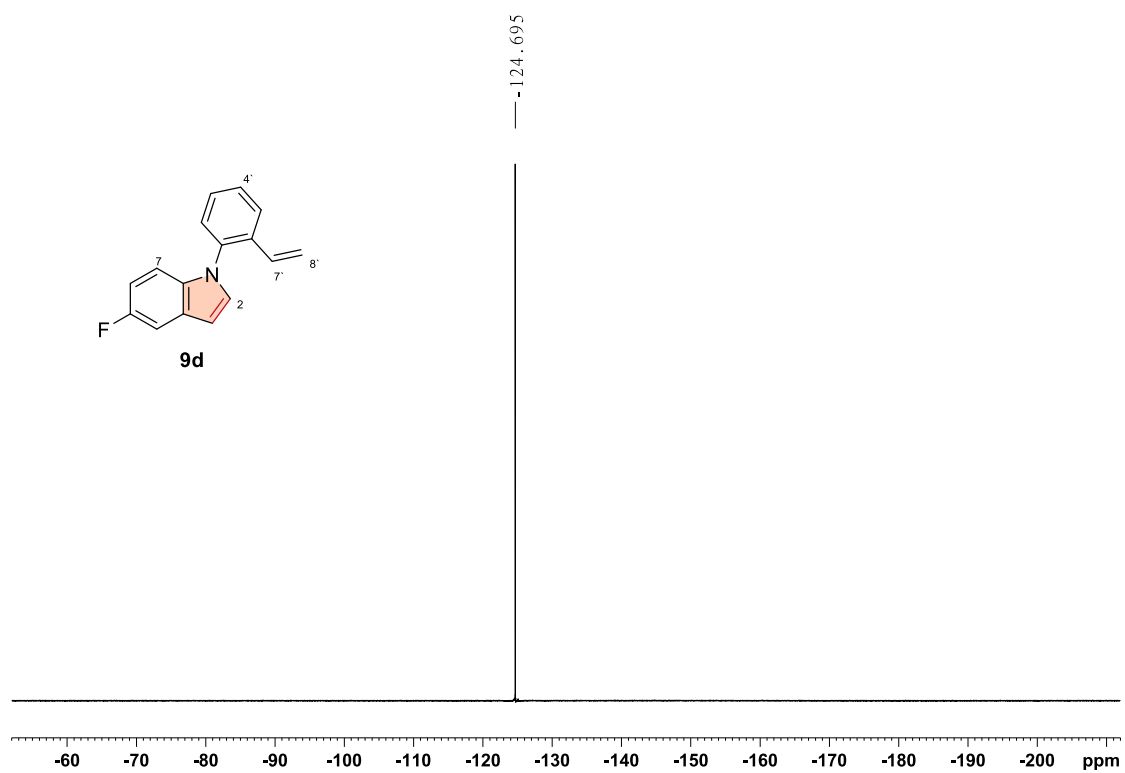




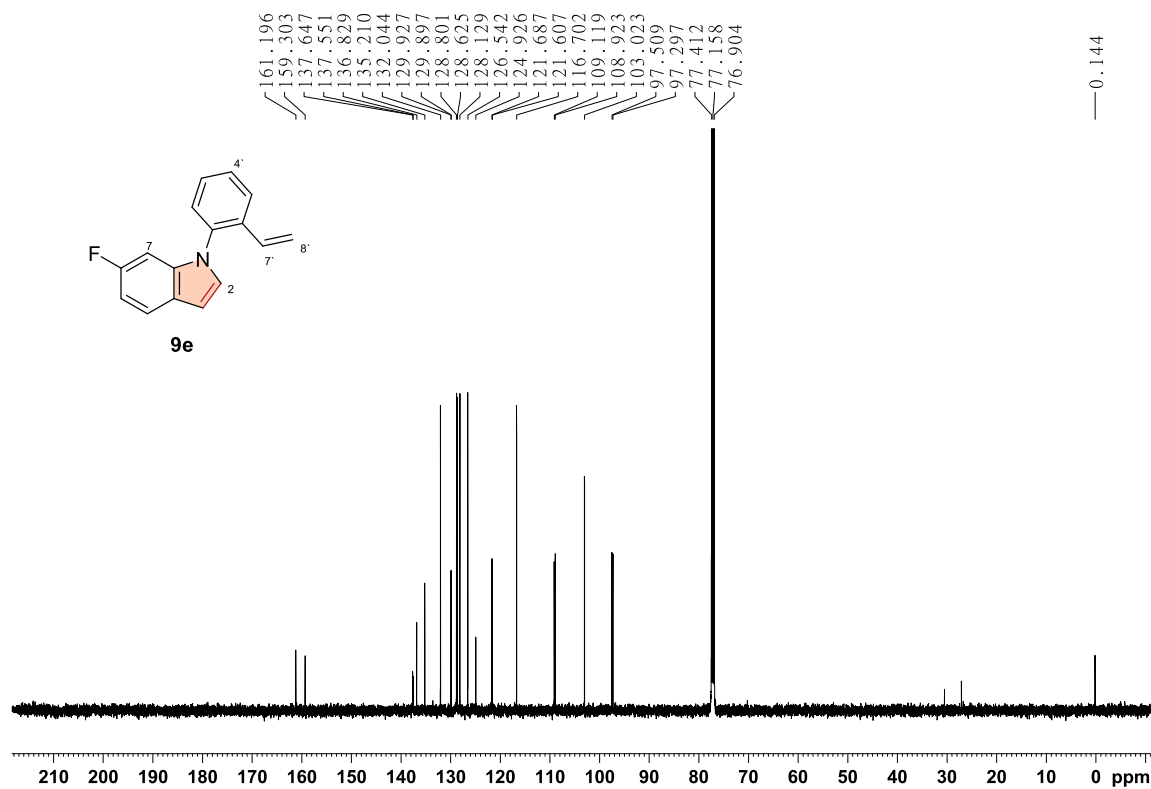
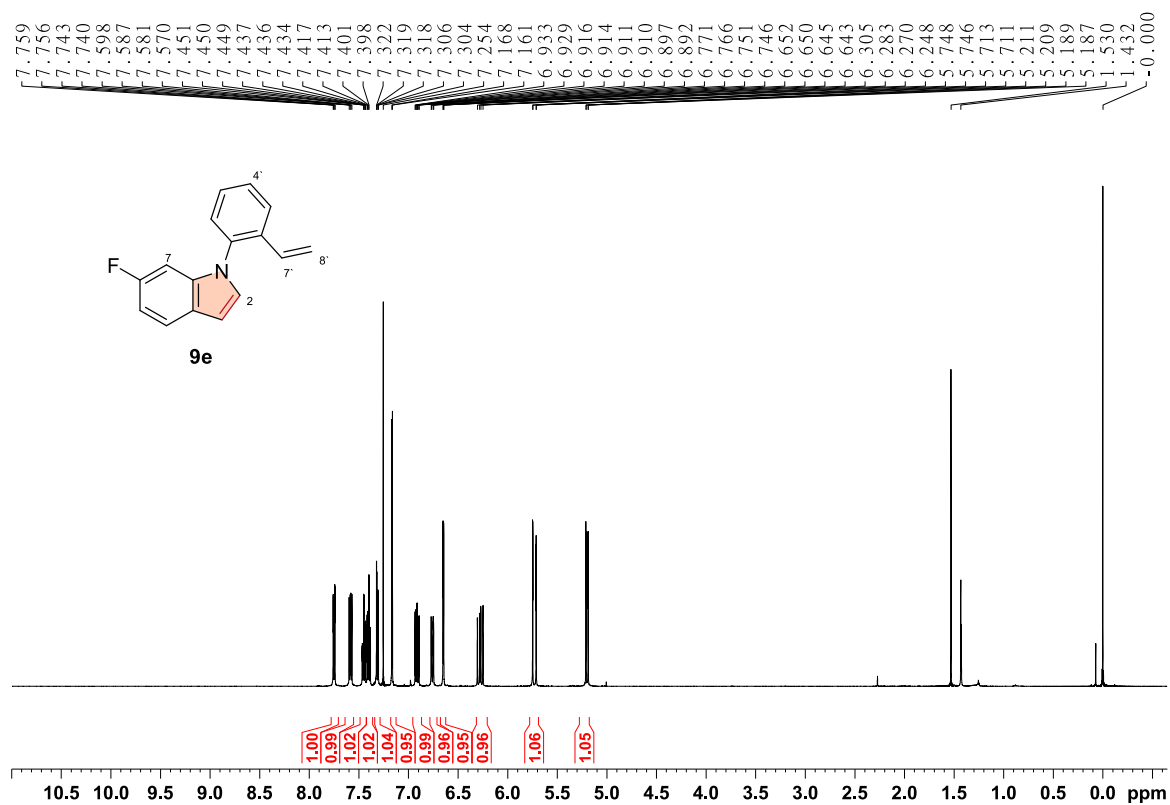


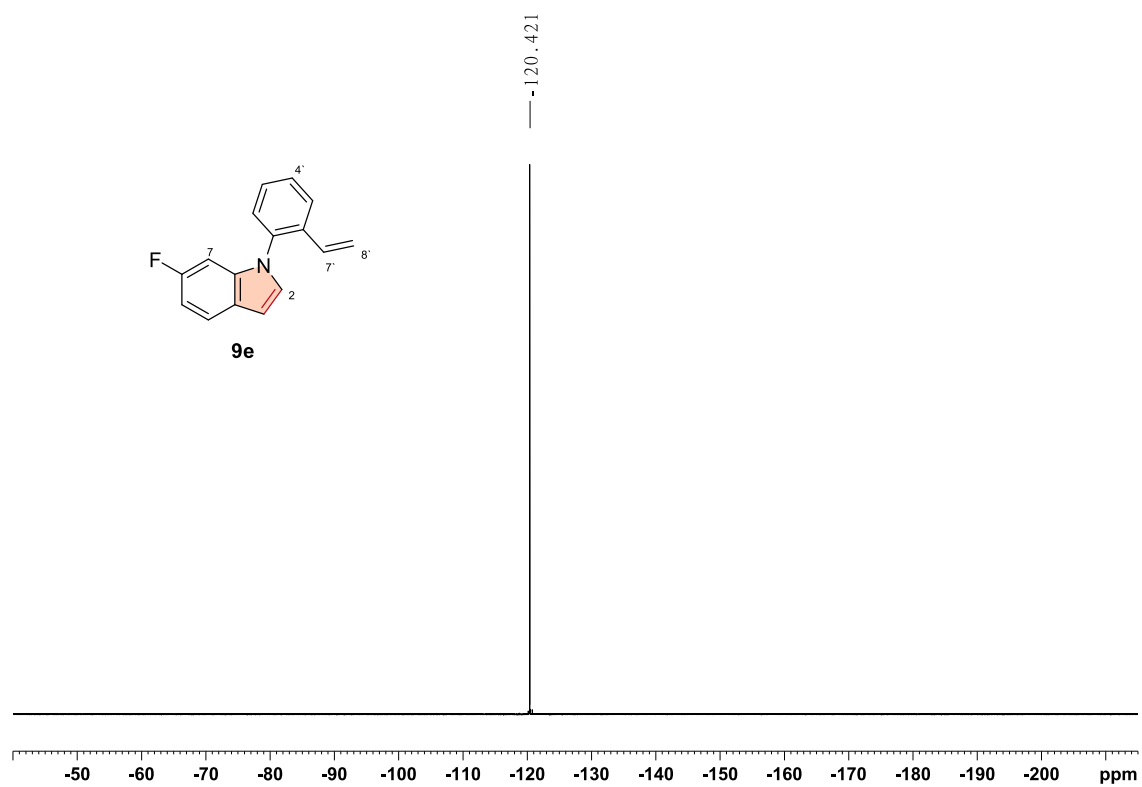
**5-Fluoro-1-(2-vinylphenyl)-1H-indole (9d):**



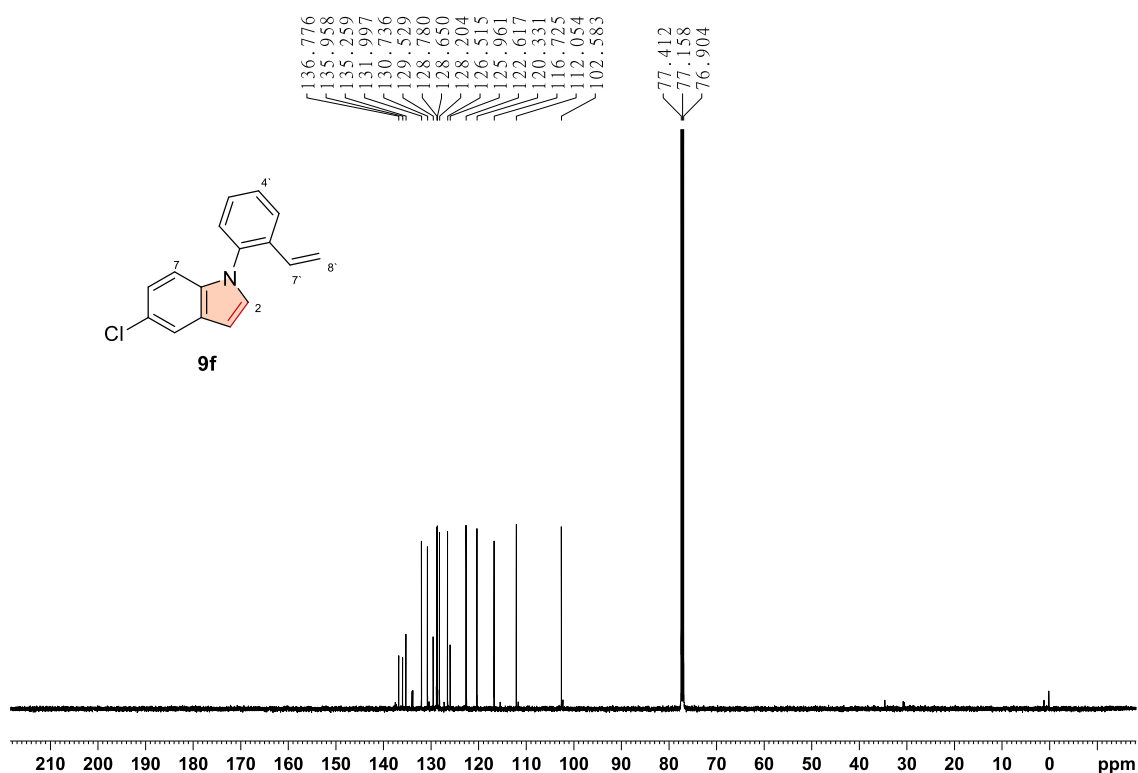
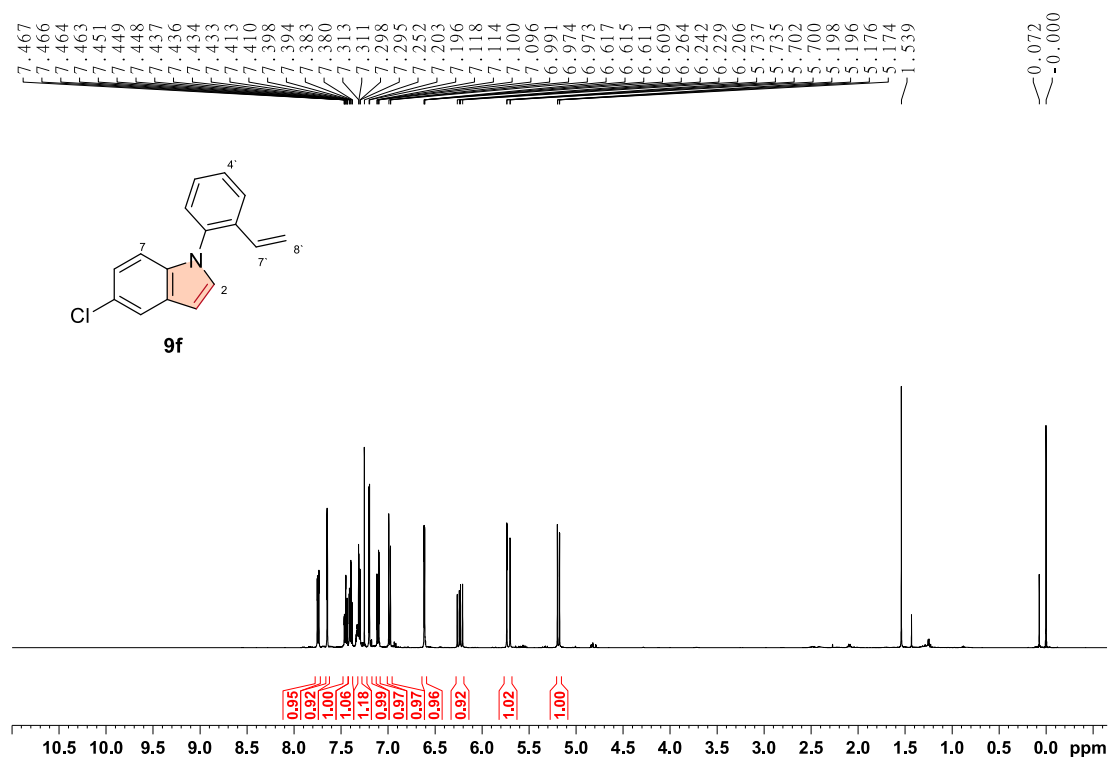


**6-Fluoro-1-(2-vinylphenyl)-1H-indole (9e):**

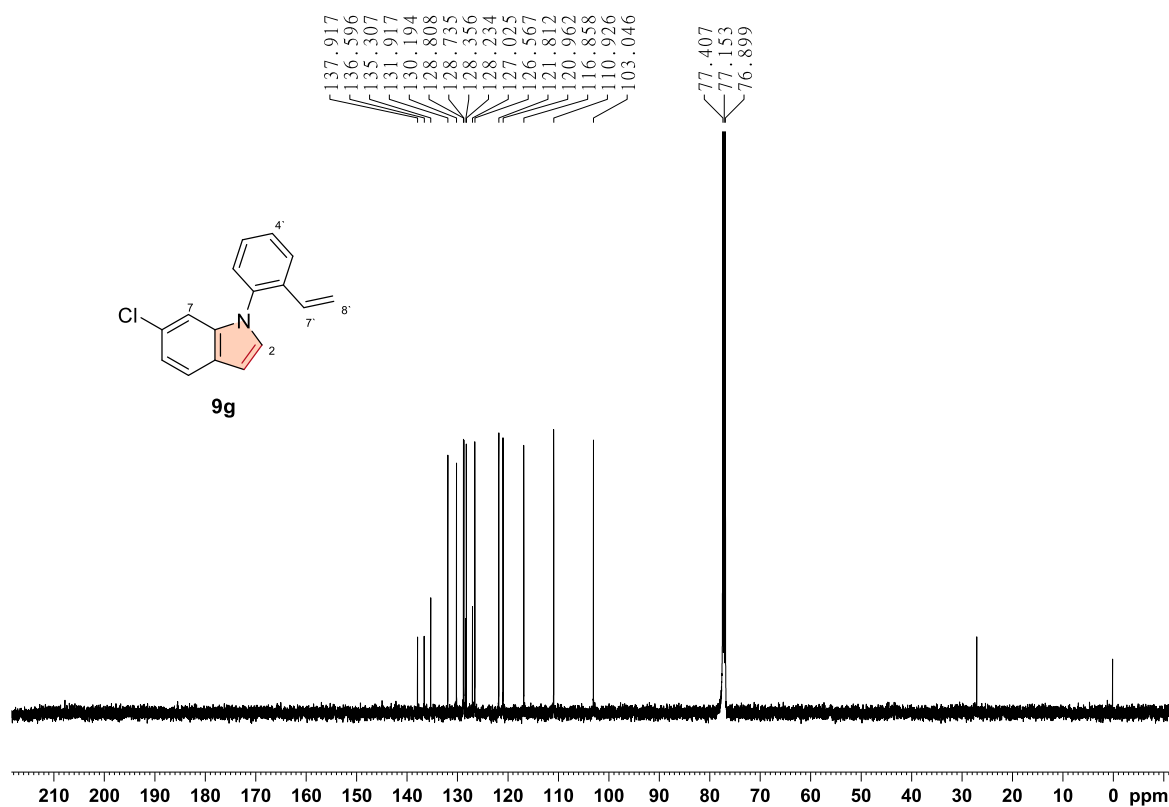
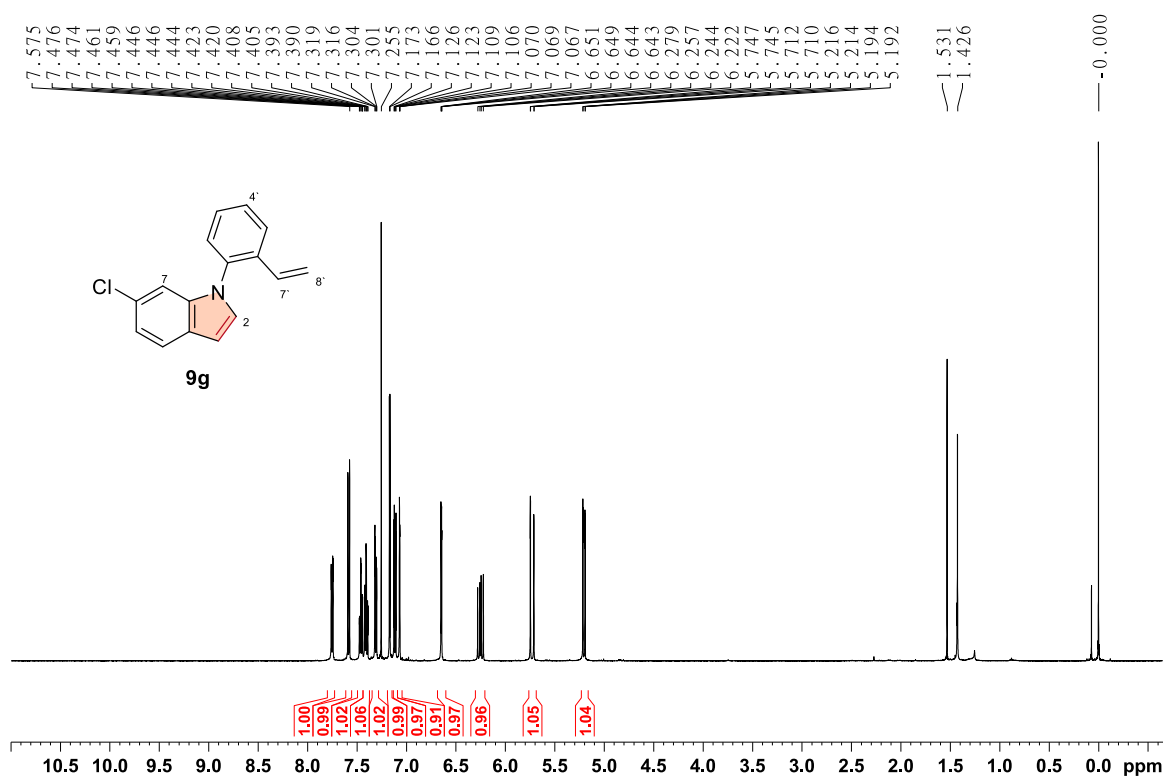




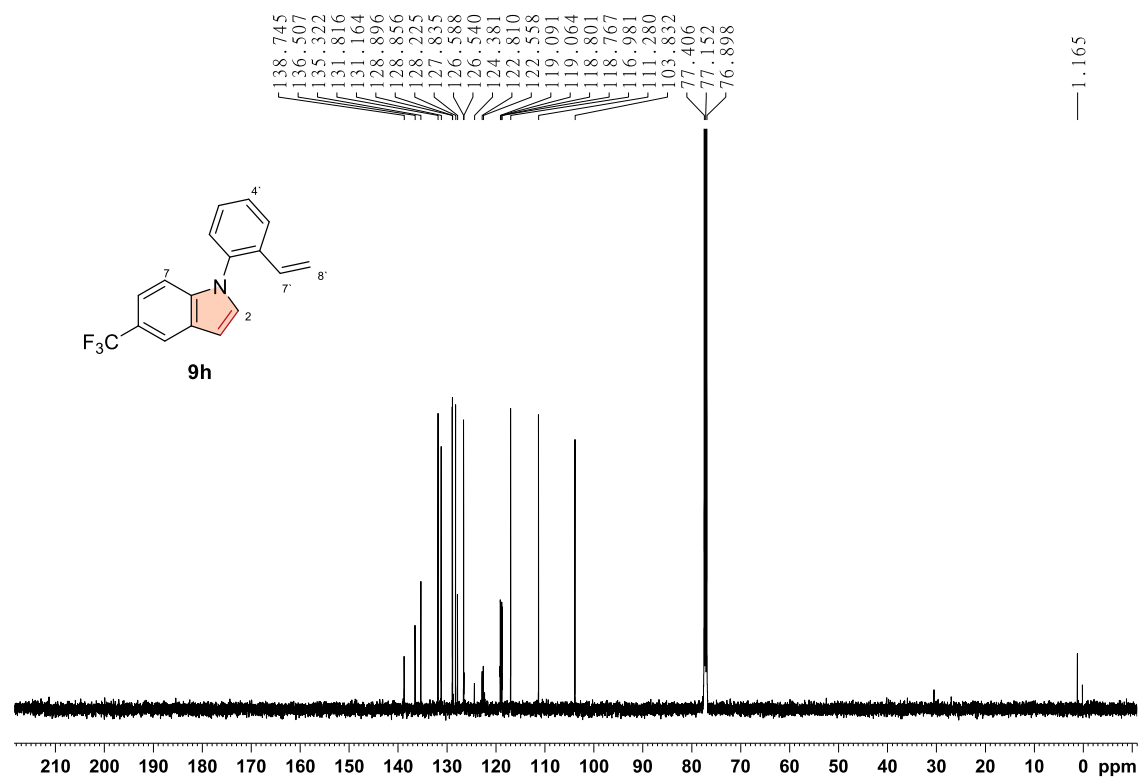
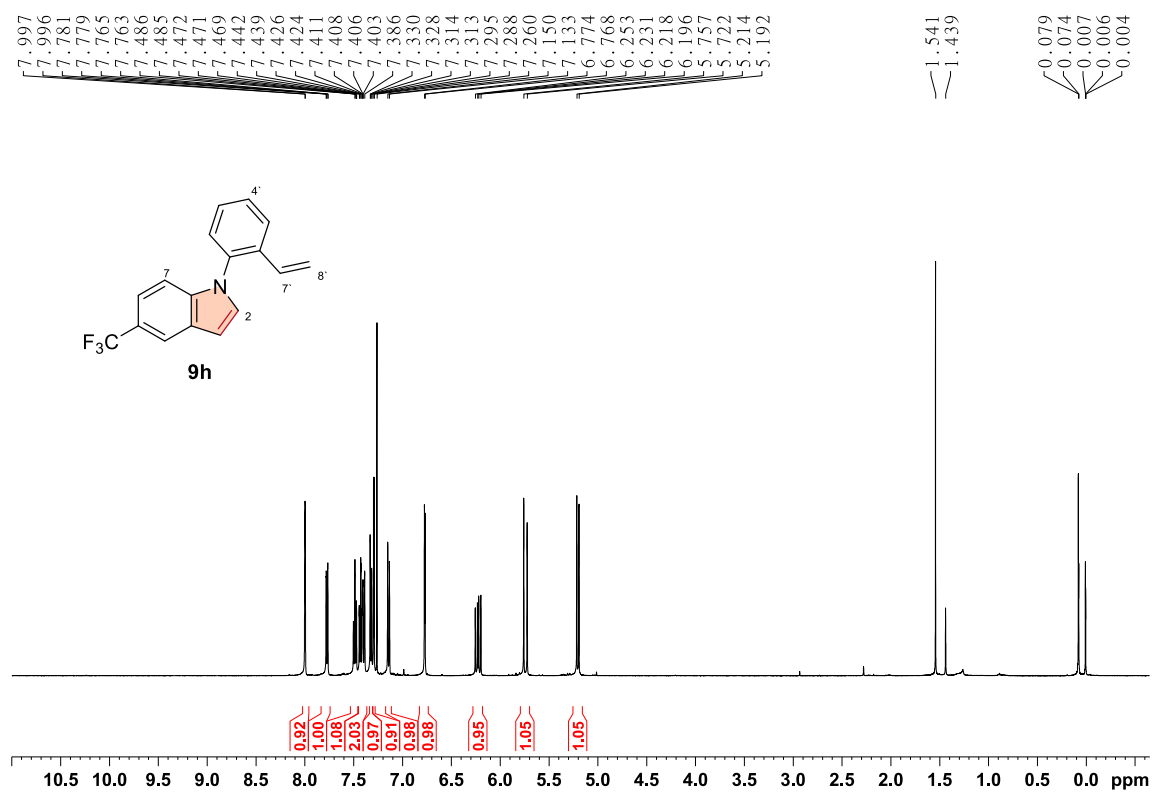
**5-Chloro-1-(2-vinylphenyl)-1H-indole (9f):**



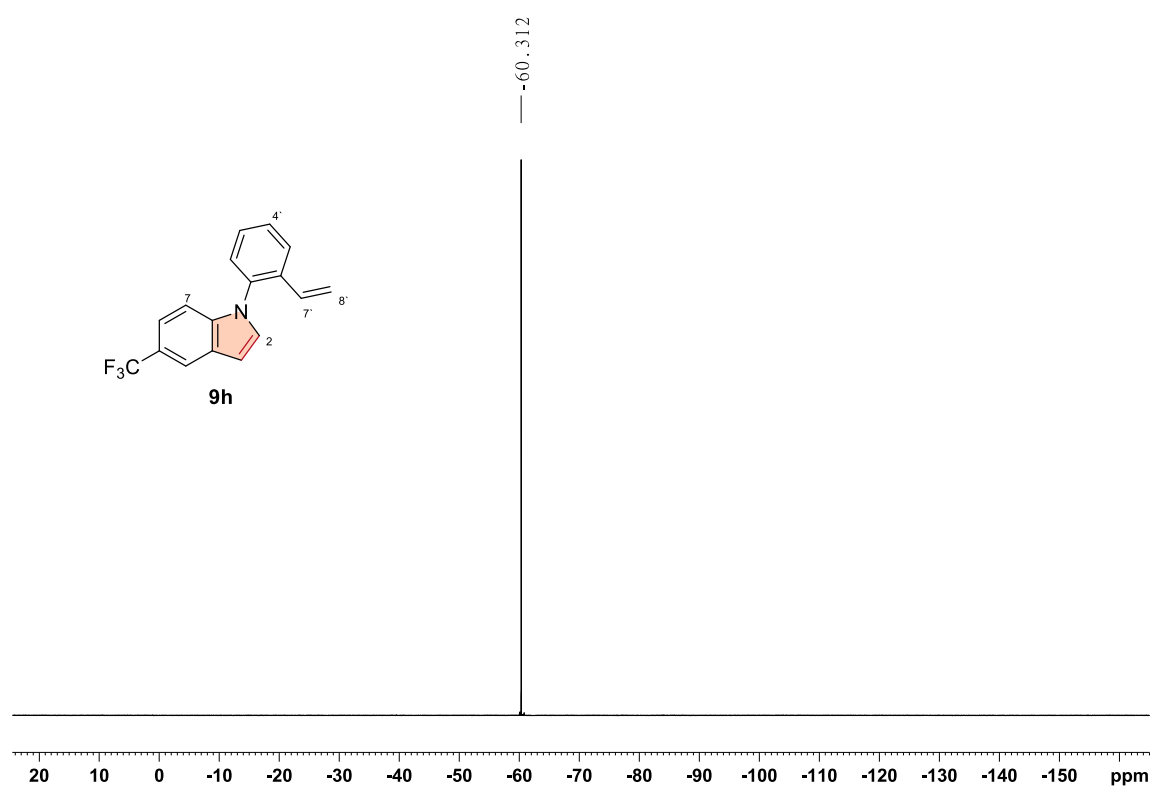
**6-Chloro-1-(2-vinylphenyl)-1H-indole (9g):**



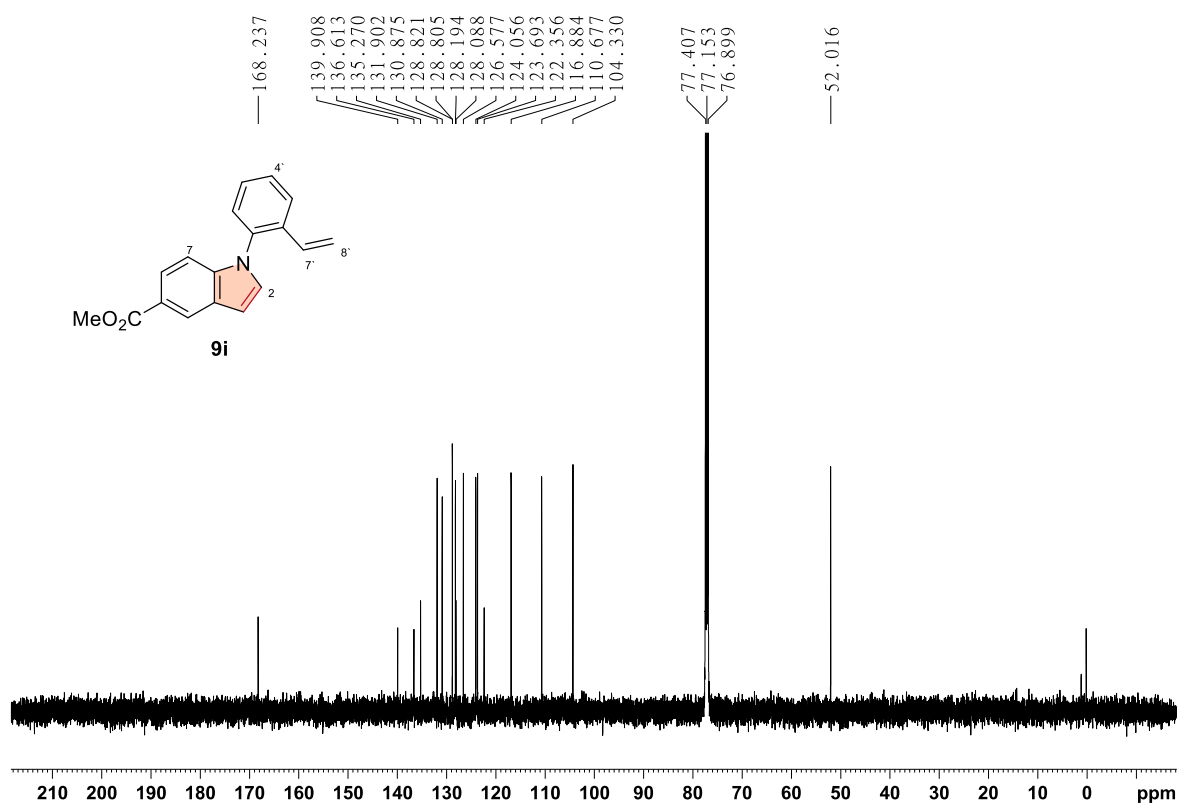
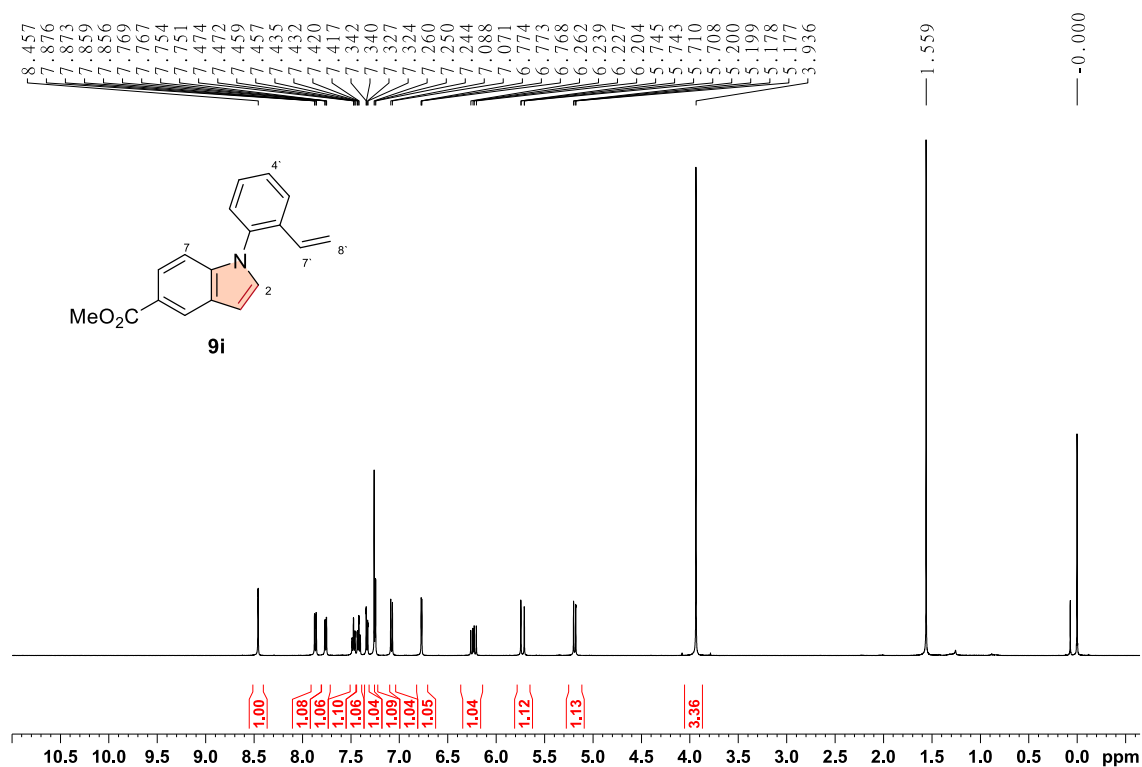
**5-(Trifluoromethyl)-1-(2-vinylphenyl)-1H-indole (9h):**



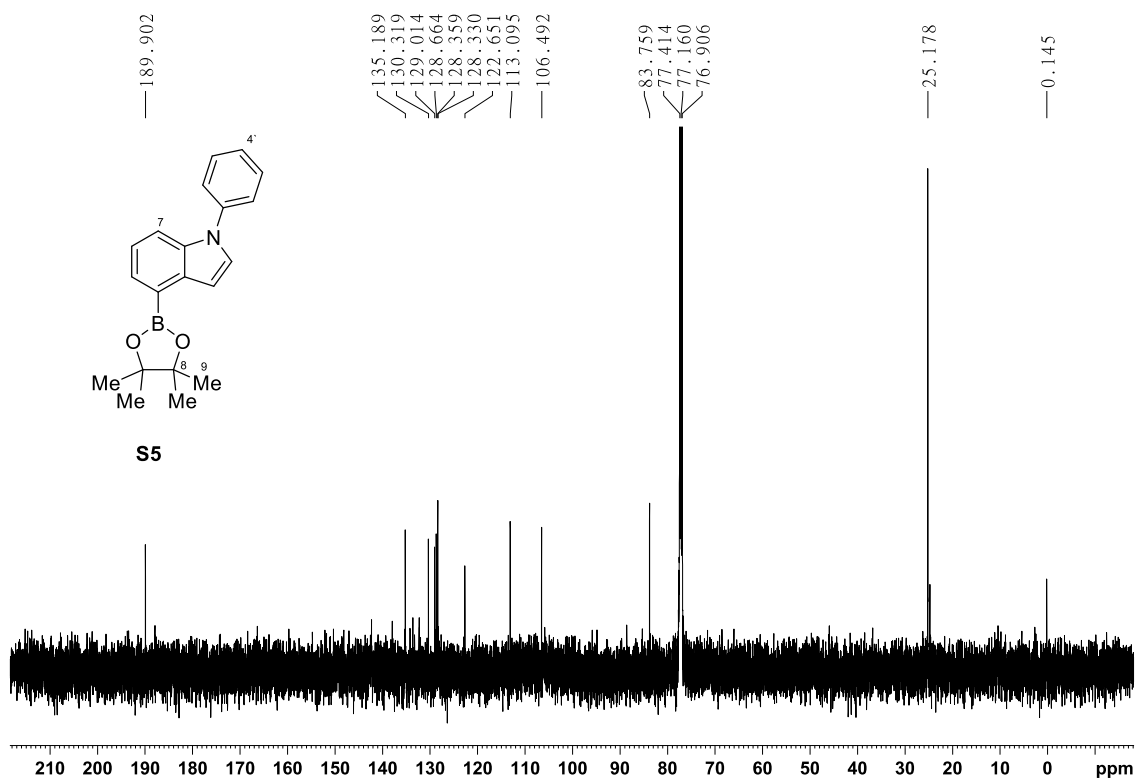
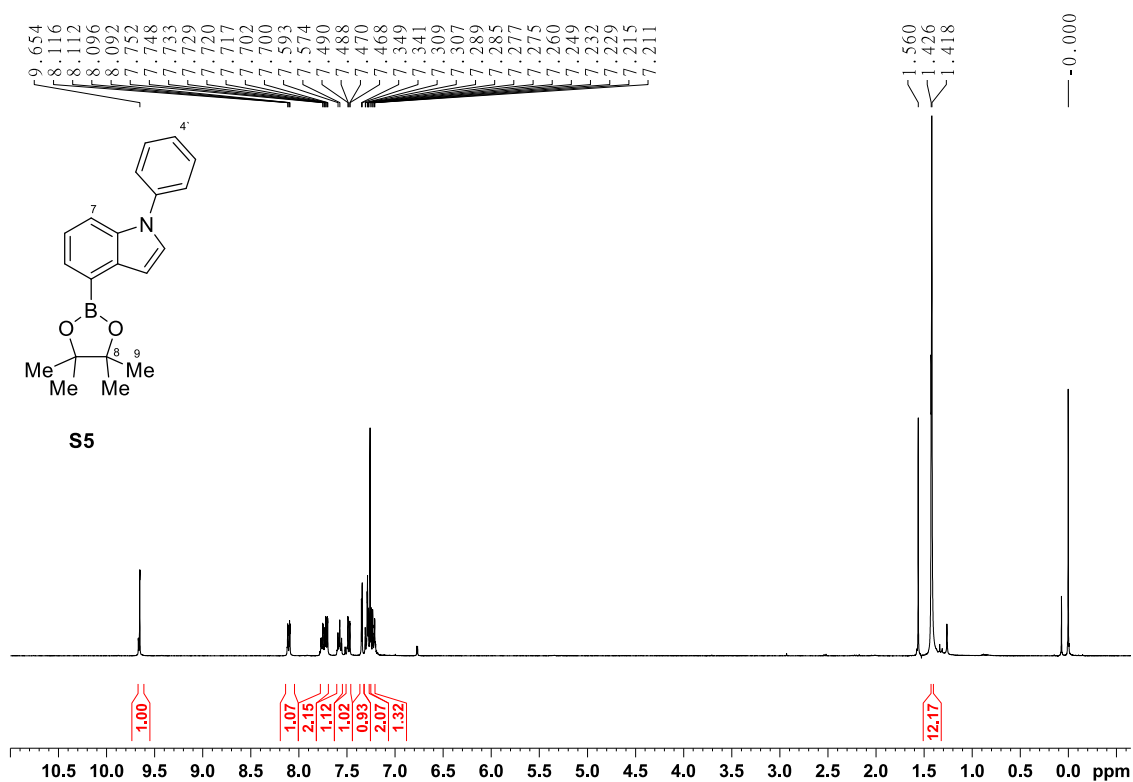




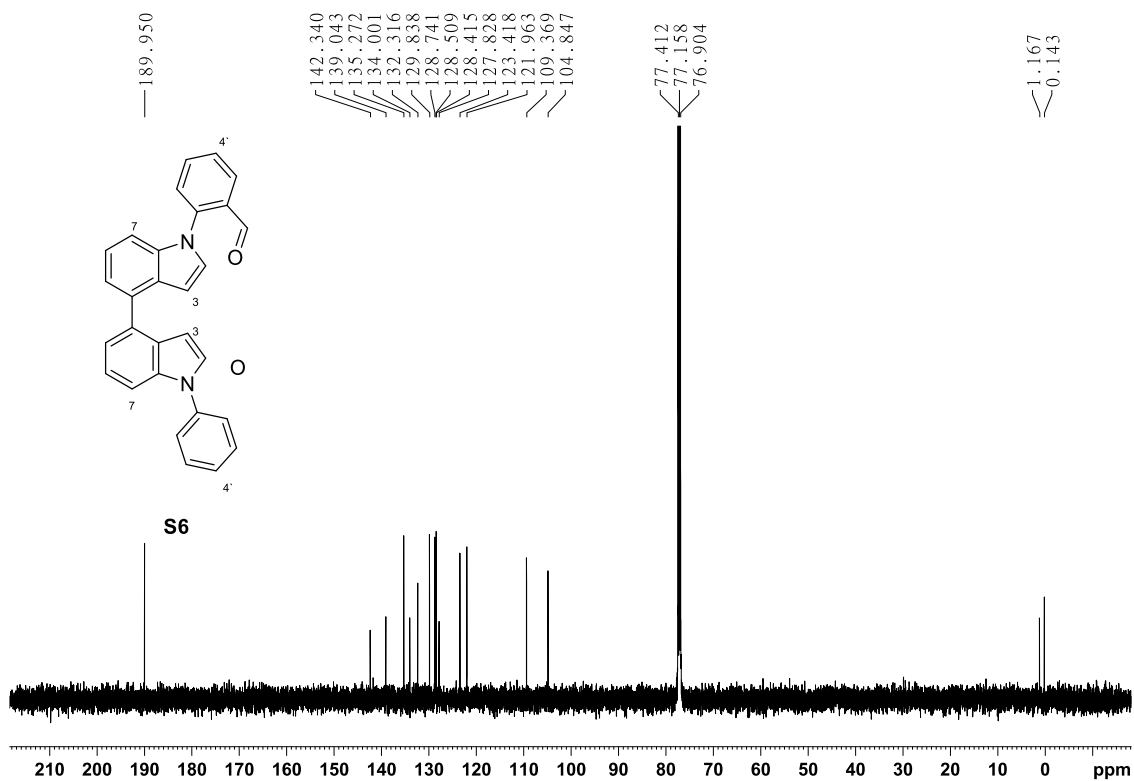
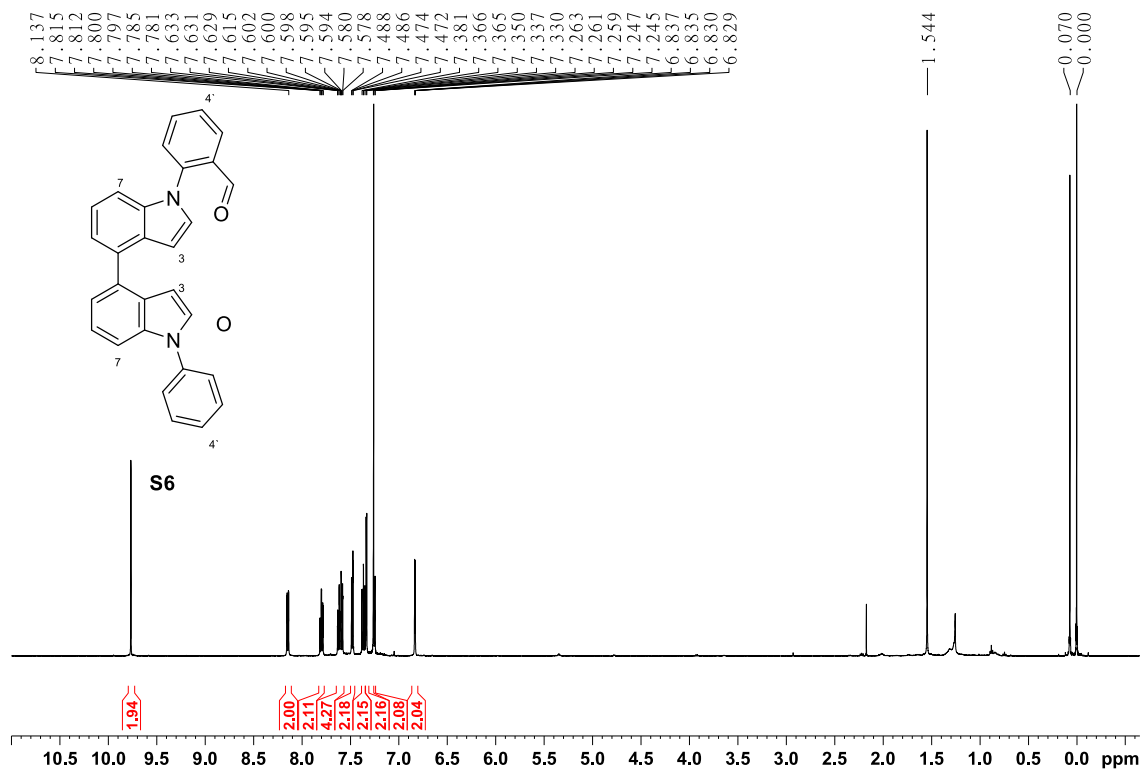
**Methyl 1-(2-vinylphenyl)-1*H*-indole-5-carboxylate (9i):**



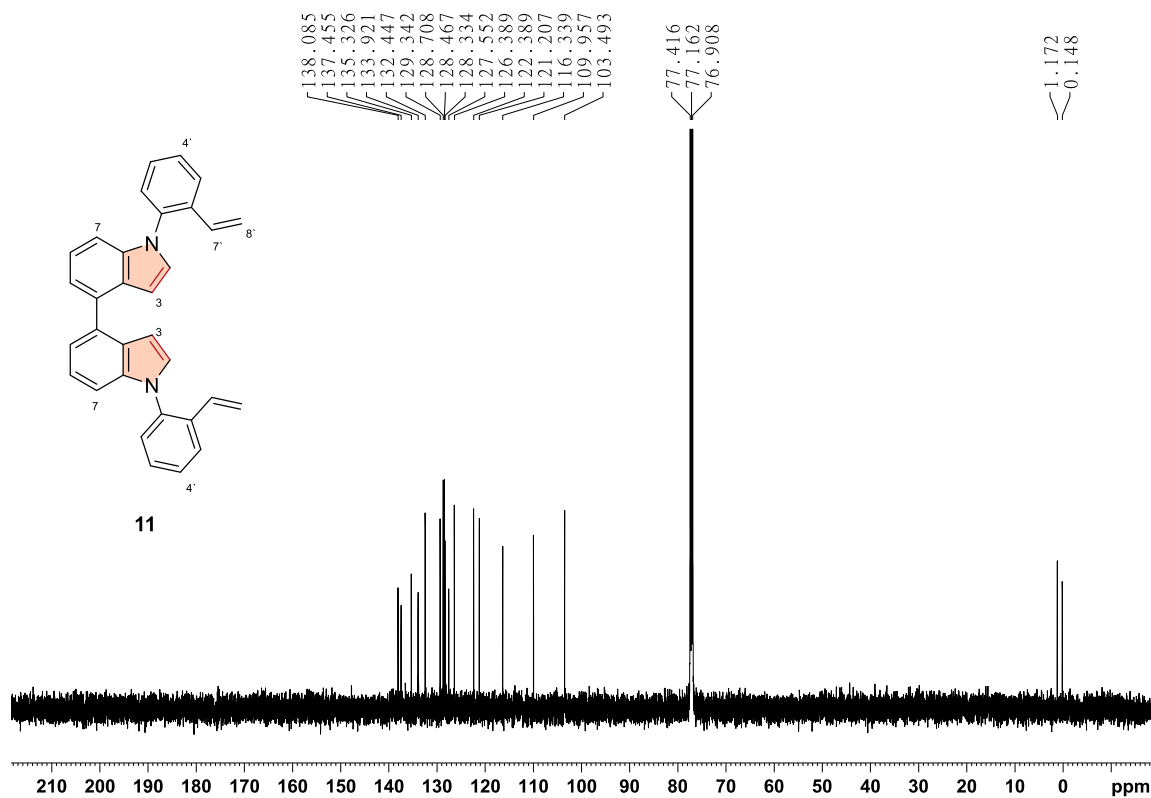
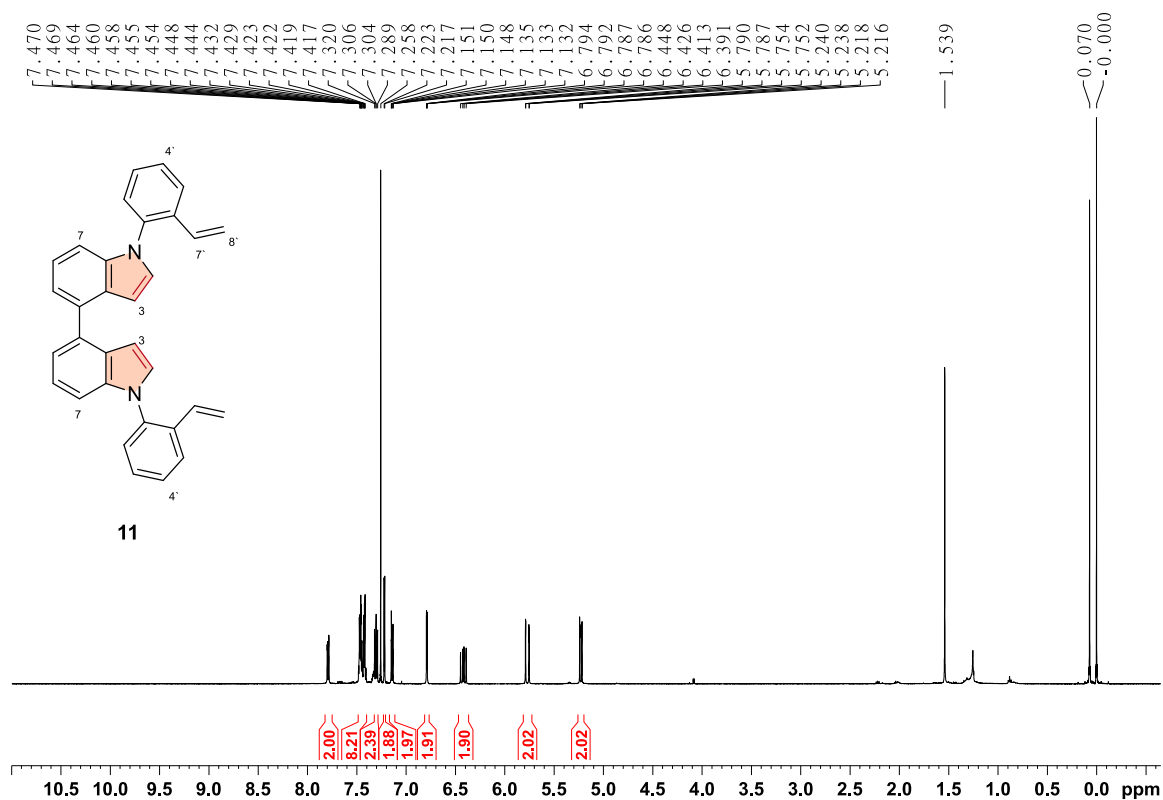
**2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-1-yl)benzaldehyde (S5):**



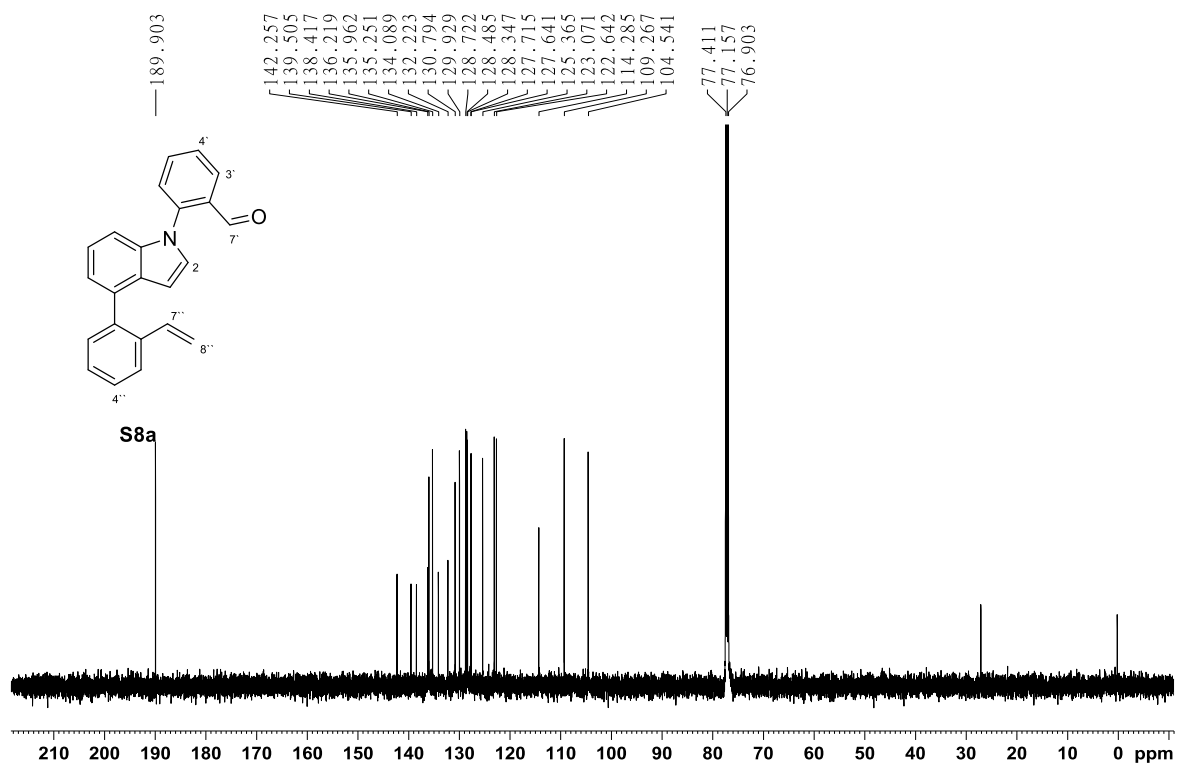
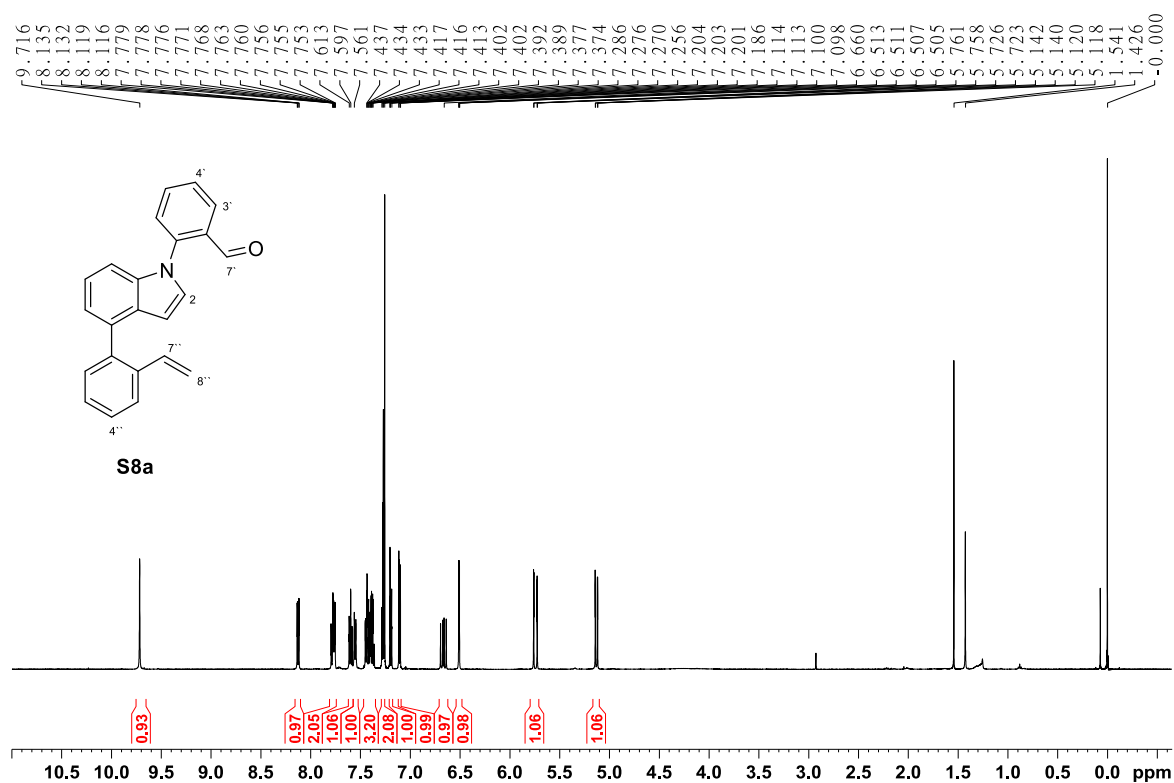
**2,2'-(1*H*,1'*H*-[4,4'-biindole]-1,1'-diyl)dibenzaldehyde (S6):**



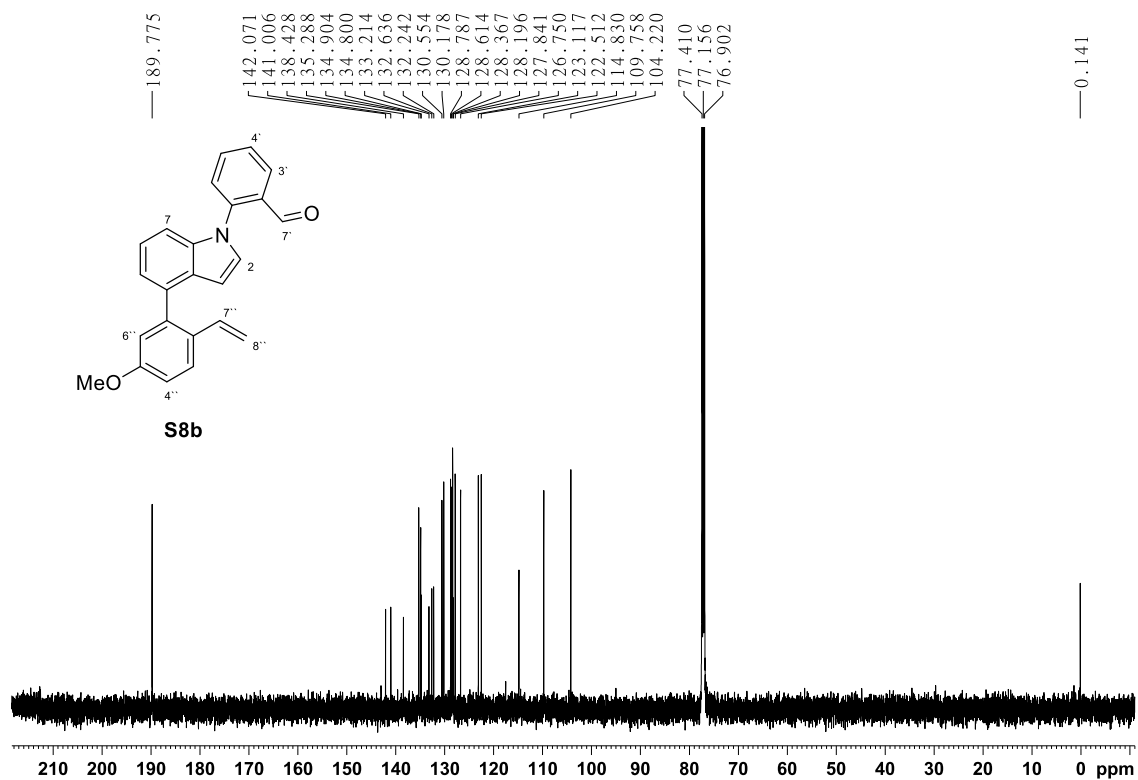
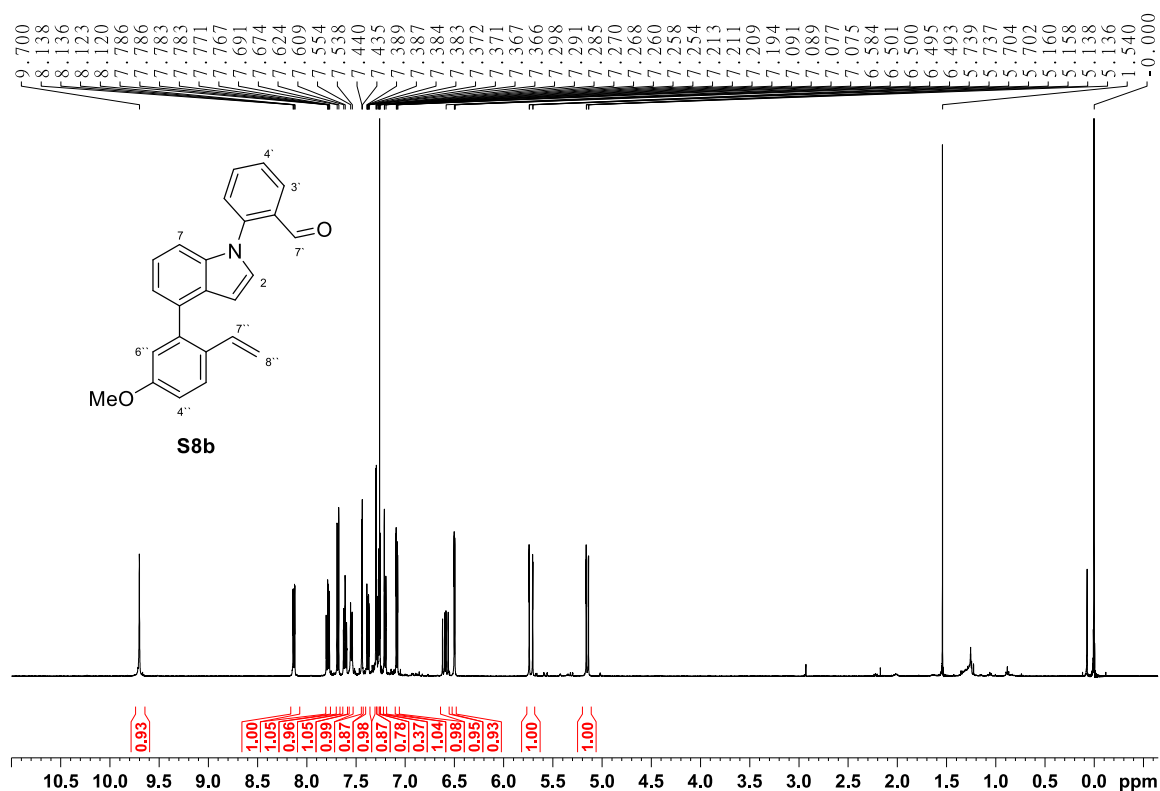
**1,1'-Bis(2-vinylphenyl)-1*H*,1'*H*-4,4'-biindole (11):**



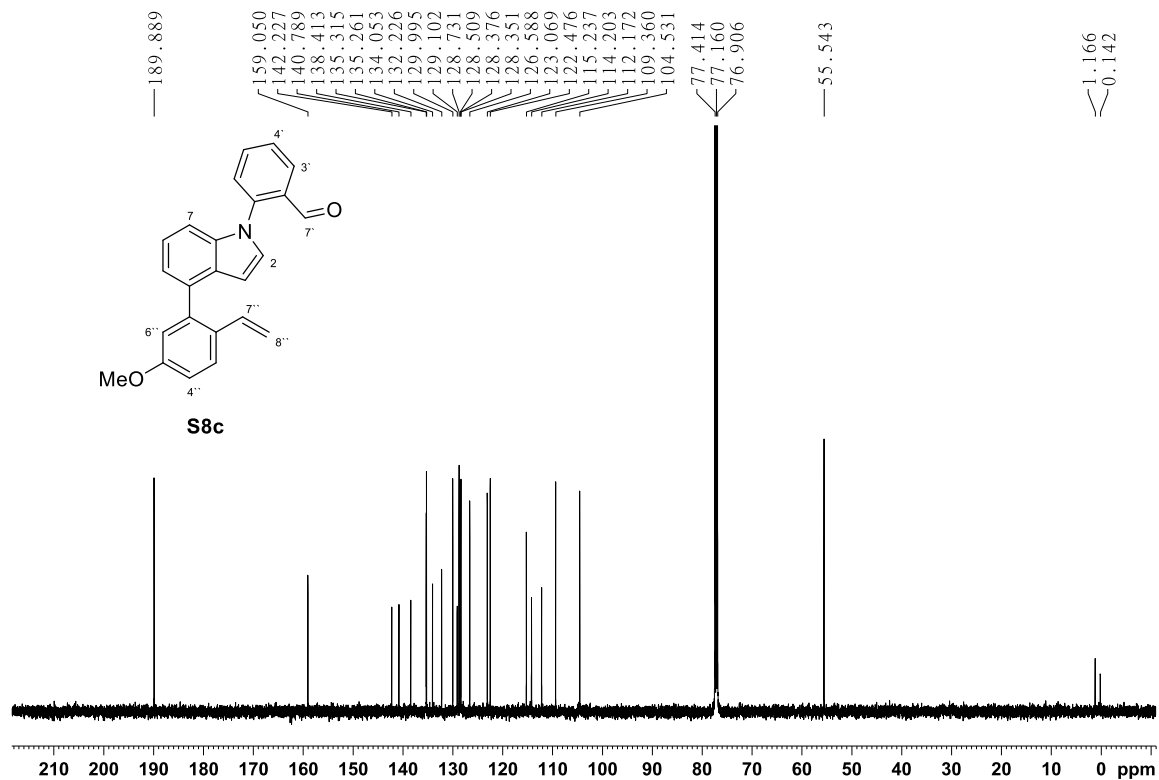
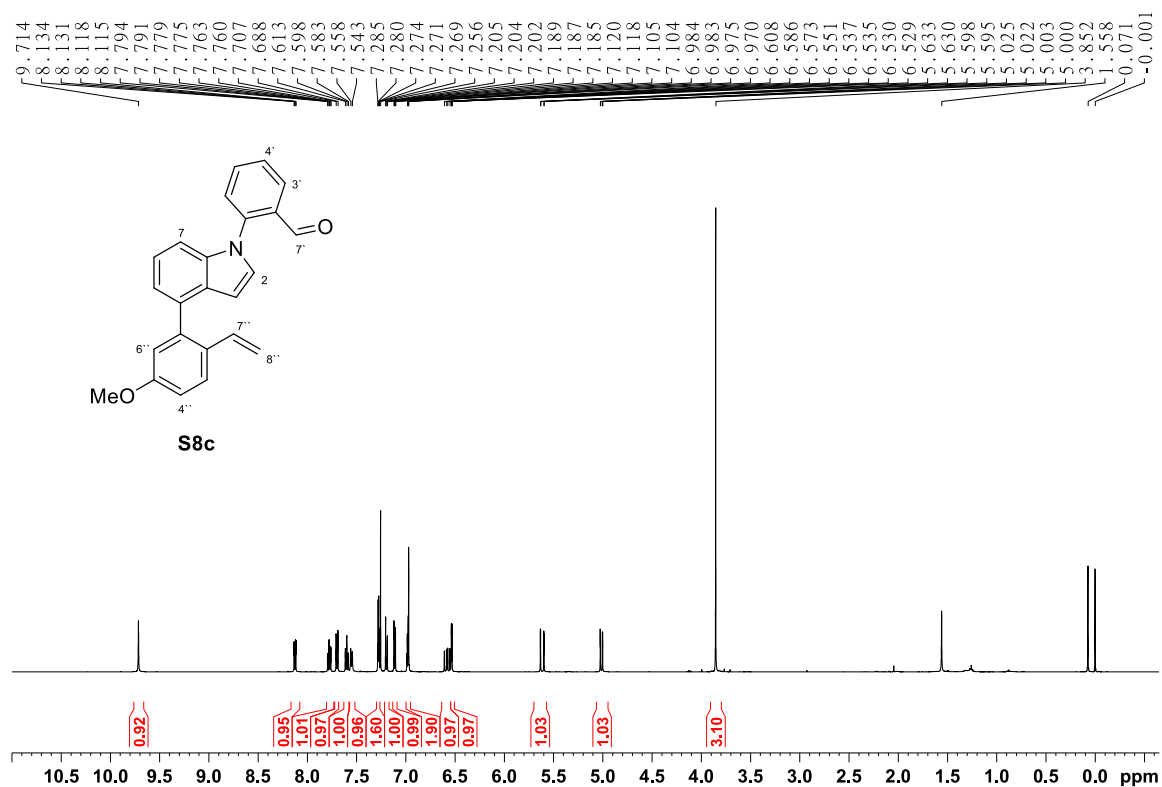
**2-(4-(2-Vinylphenyl)-1*H*-indol-1-yl)benzaldehyde (S8a):**



**2-(4-(5-Chloro-2-vinylphenyl)-1*H*-indol-1-yl)benzaldehyde (S8b):**

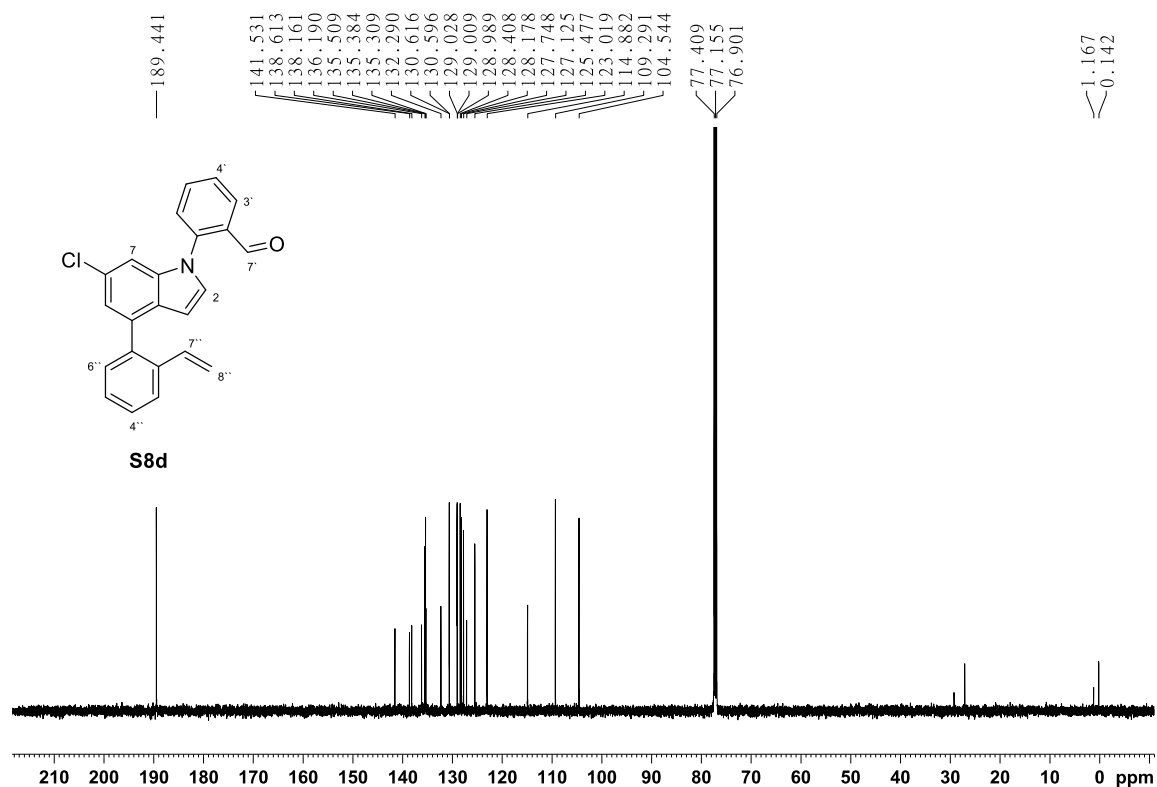
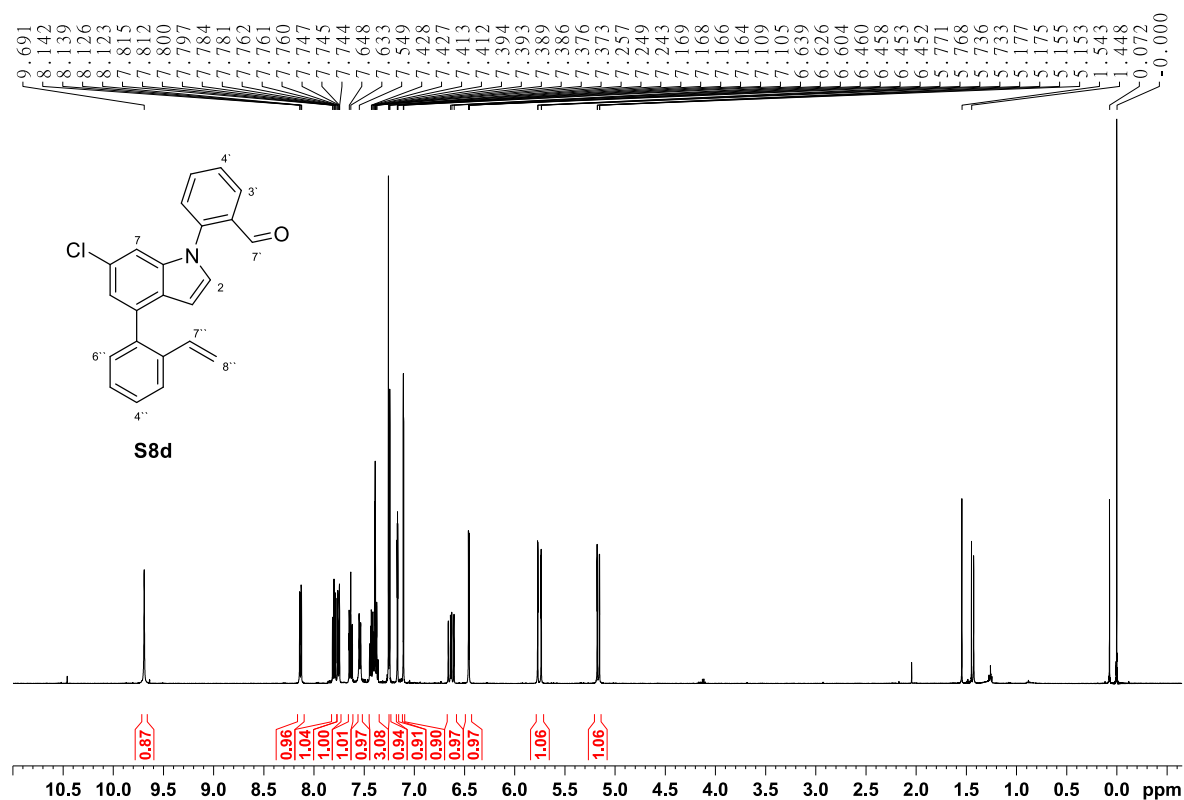


**2-(4-(5-Methoxy-2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8c):**

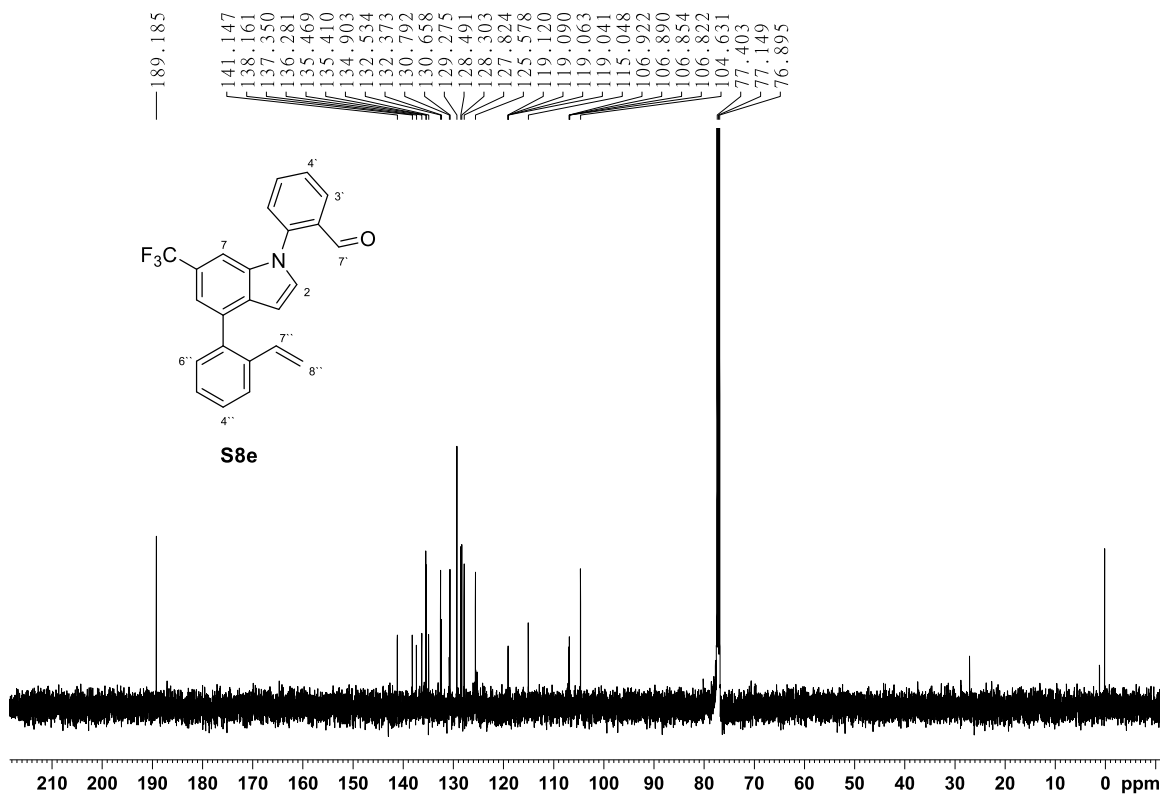
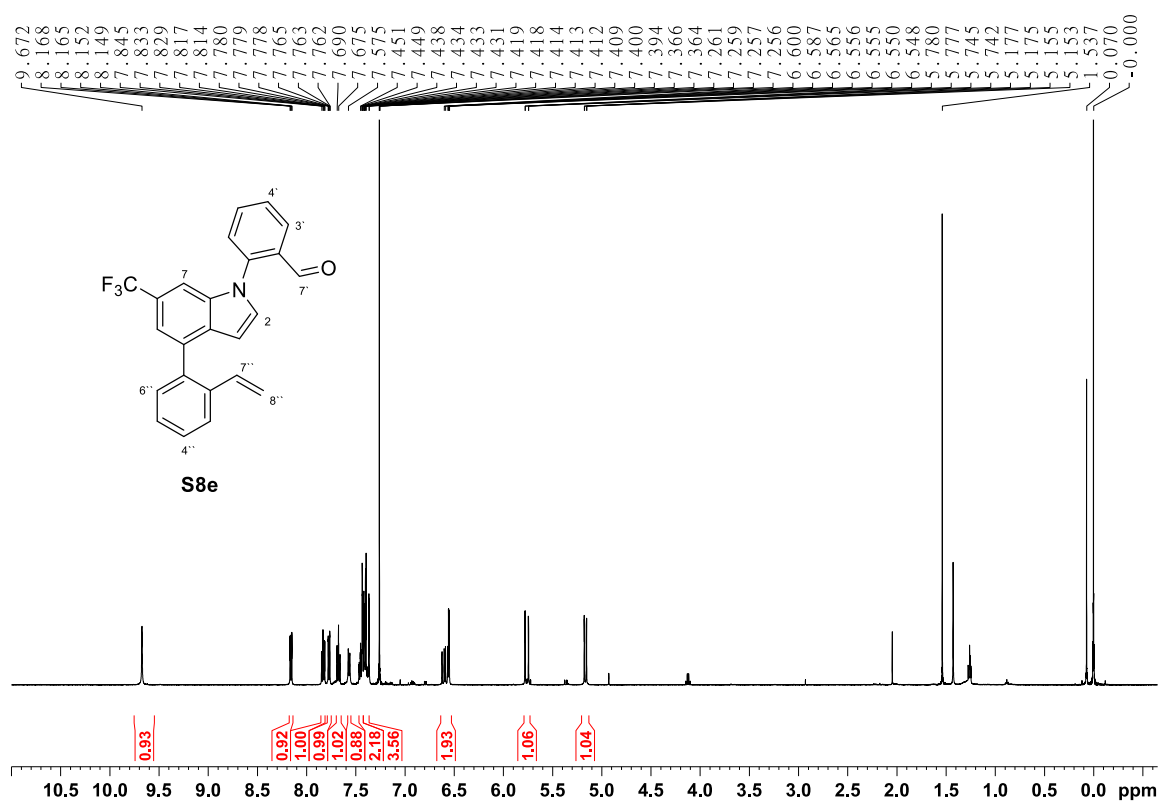




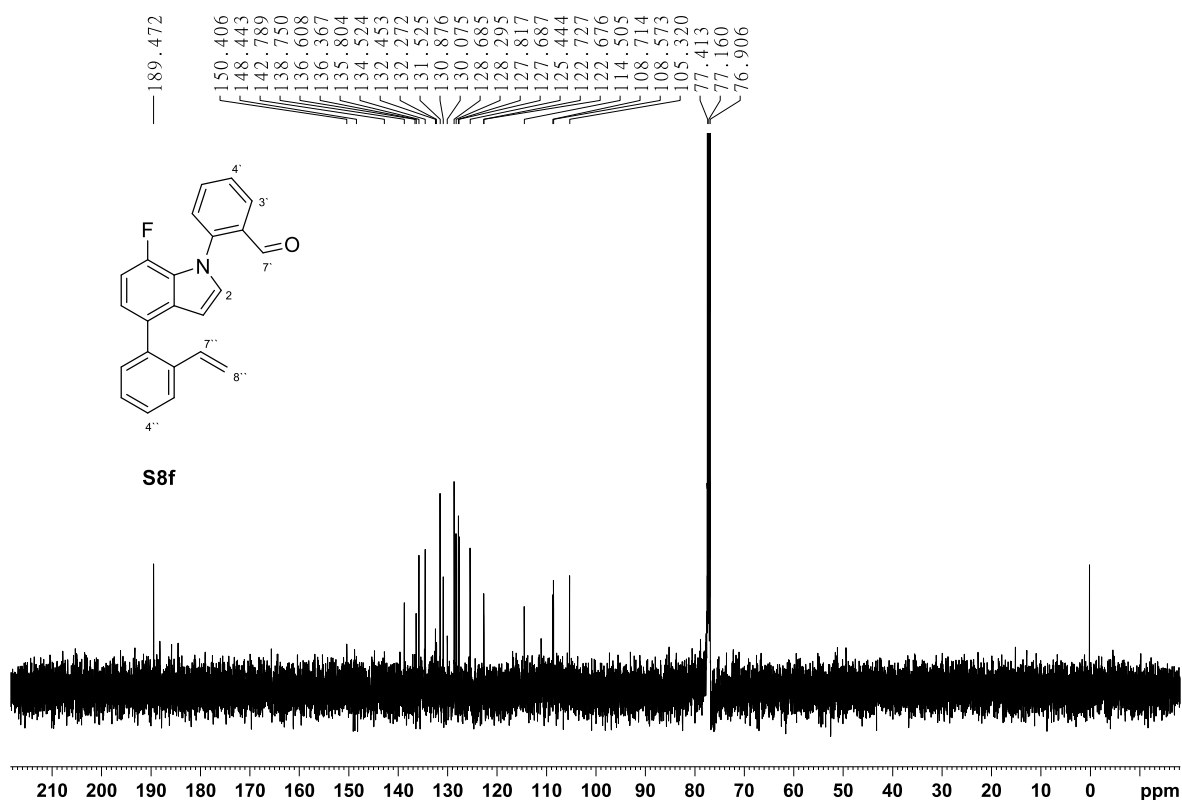
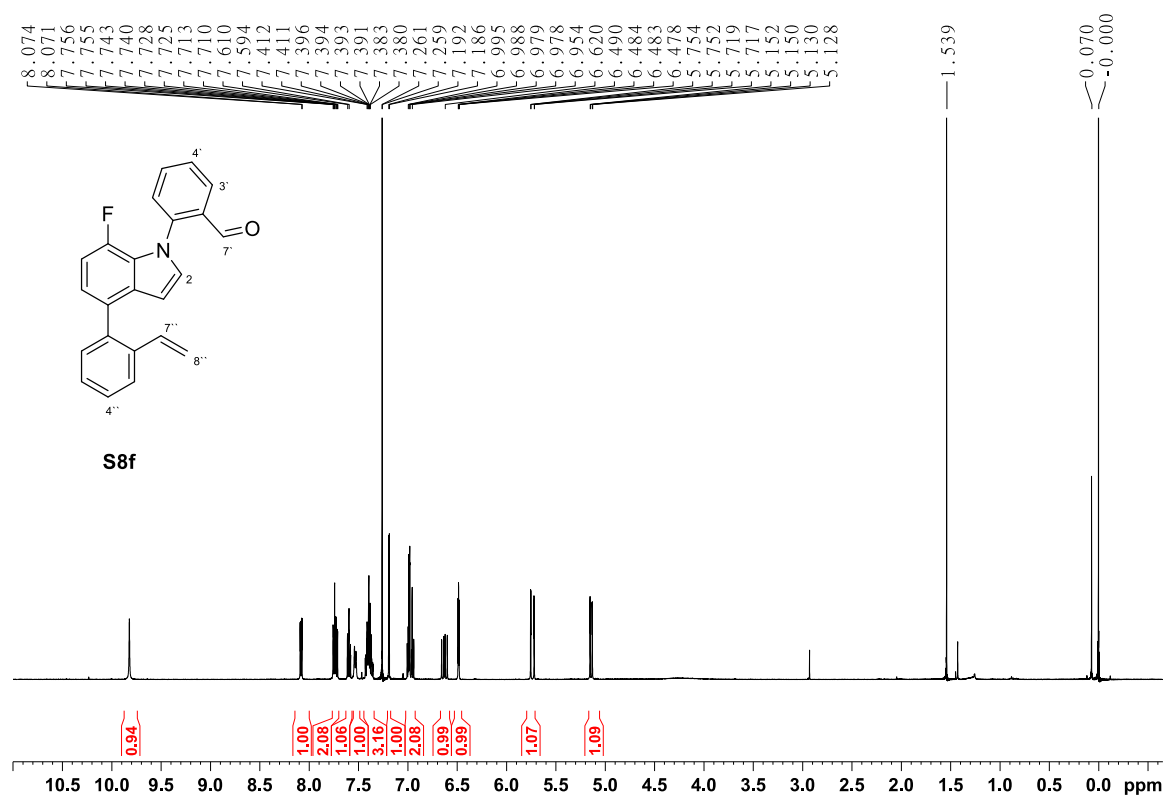
**2-(6-Chloro-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8d):**



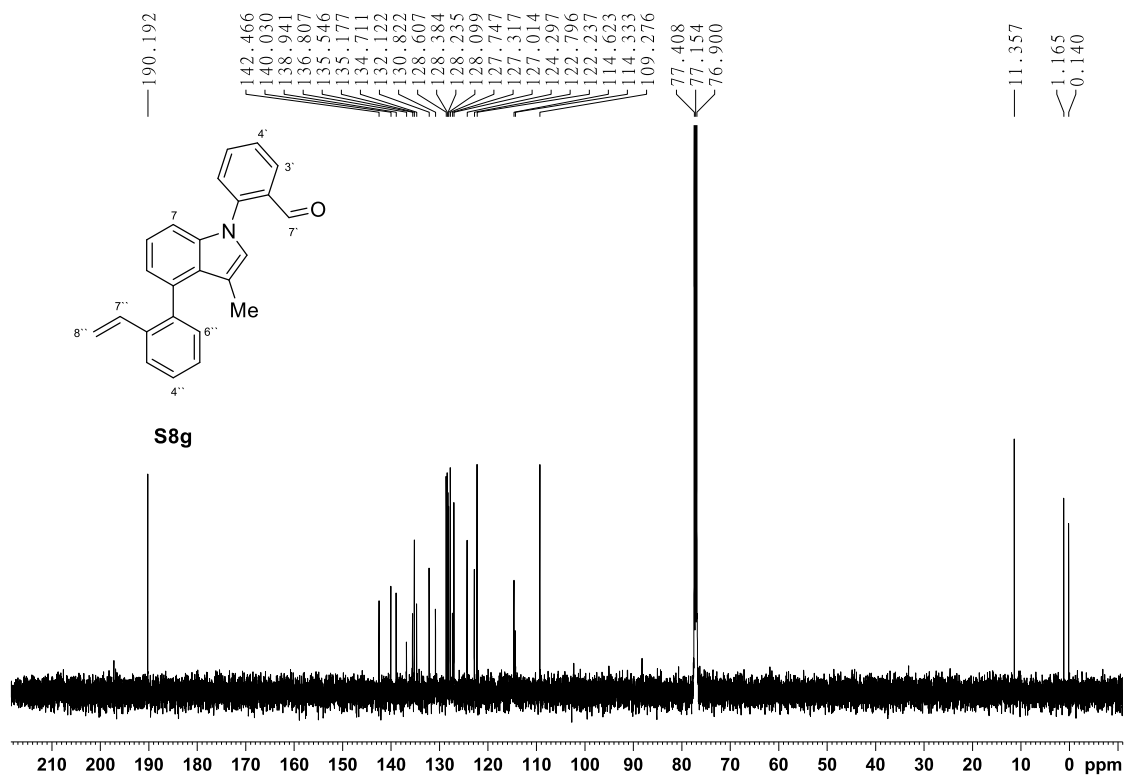
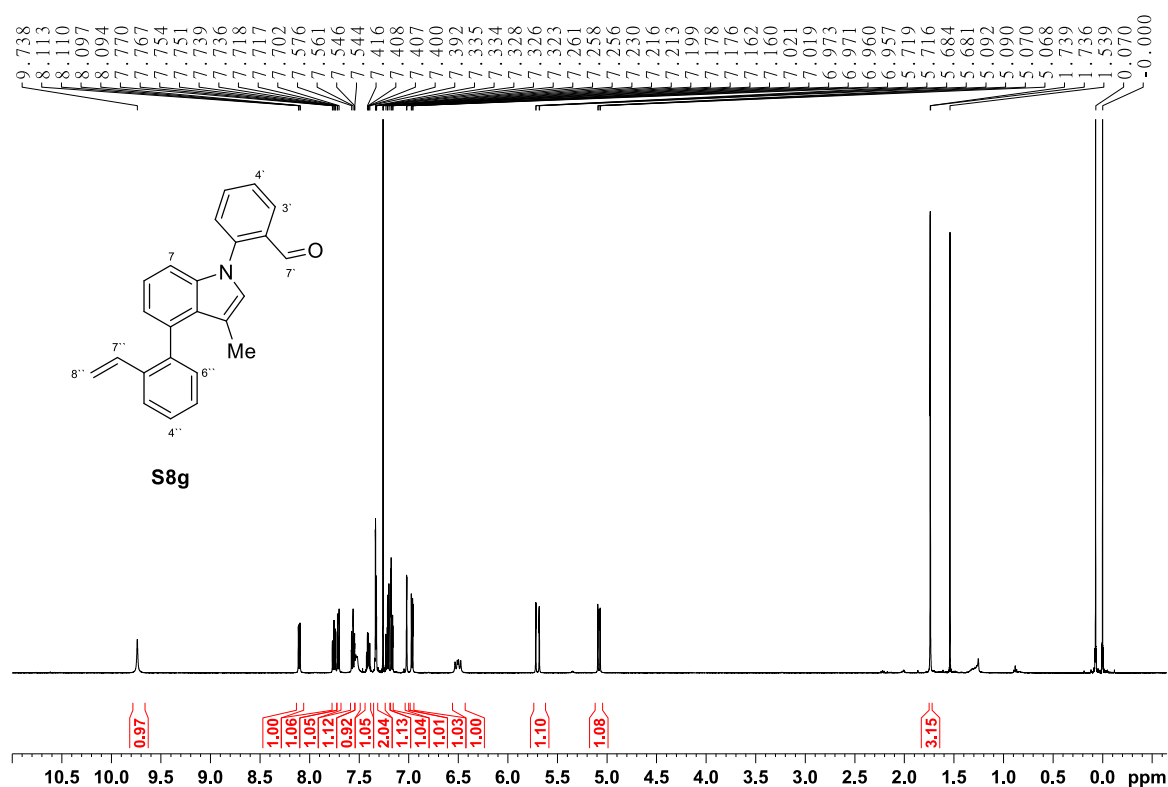
**2-(6-(Trifluoromethyl)-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8e):**



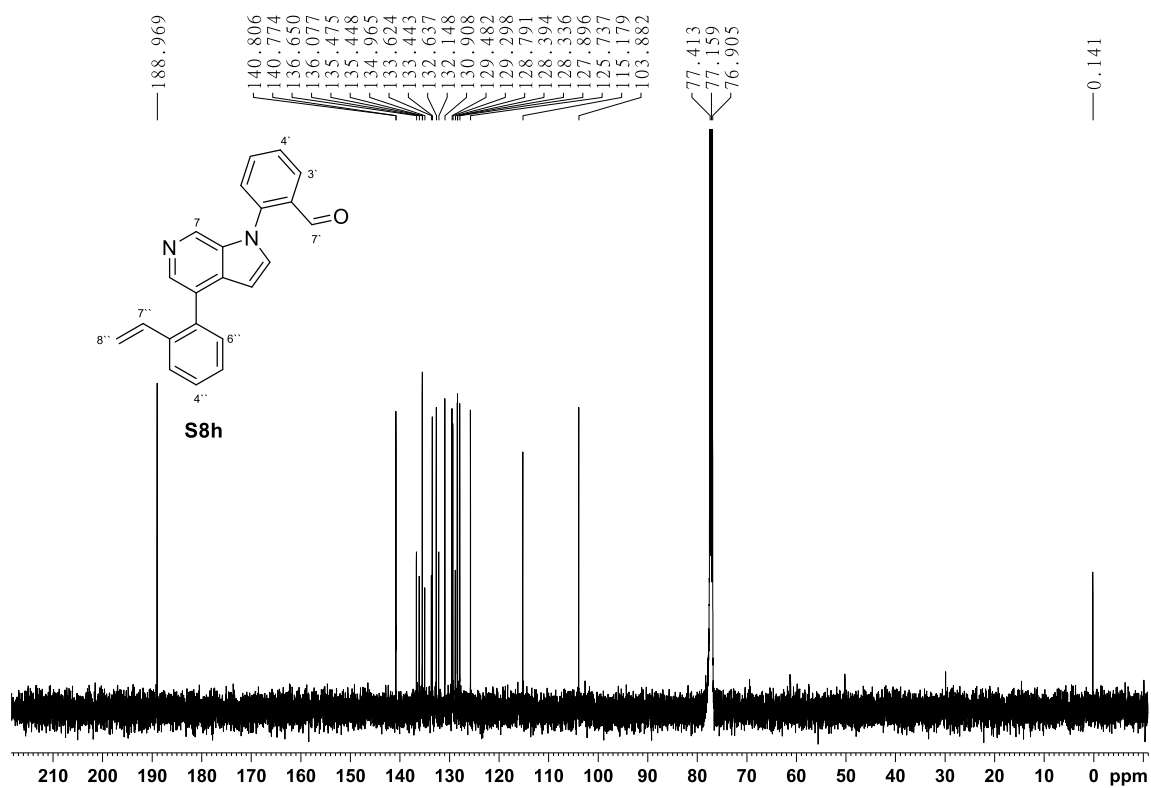
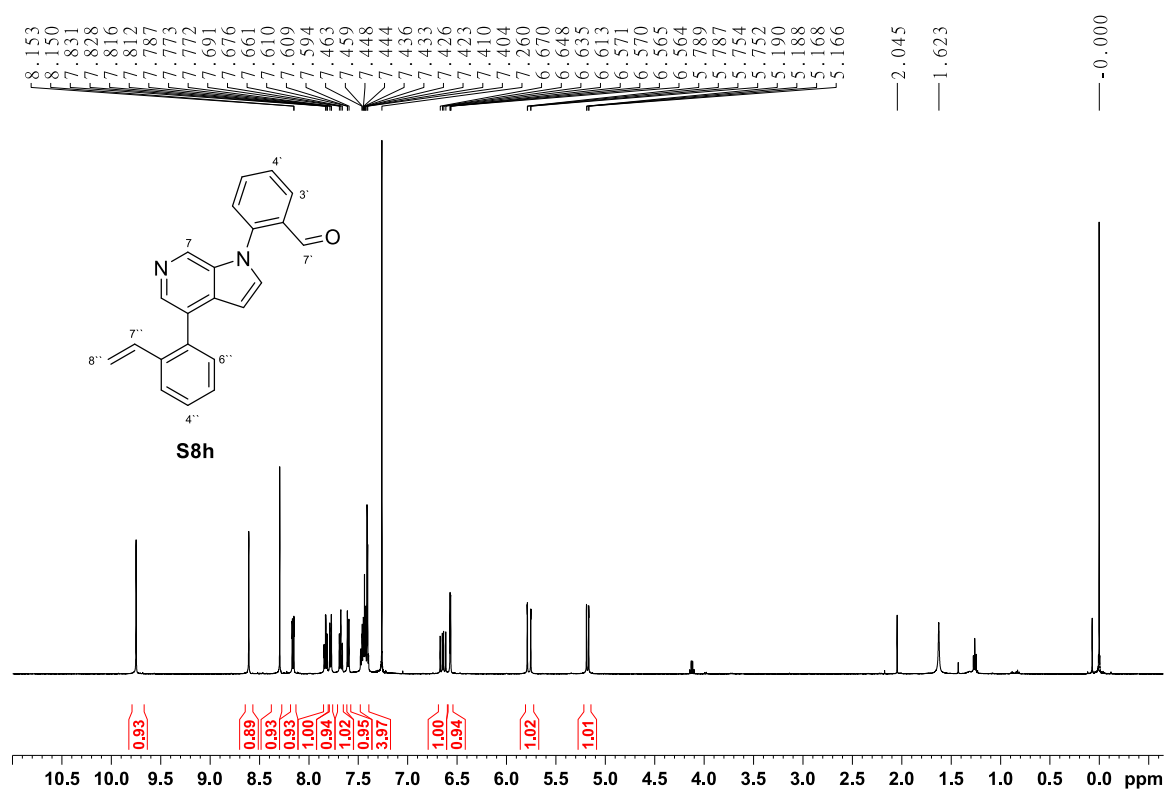
**2-(7-Fluoro-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8f):**



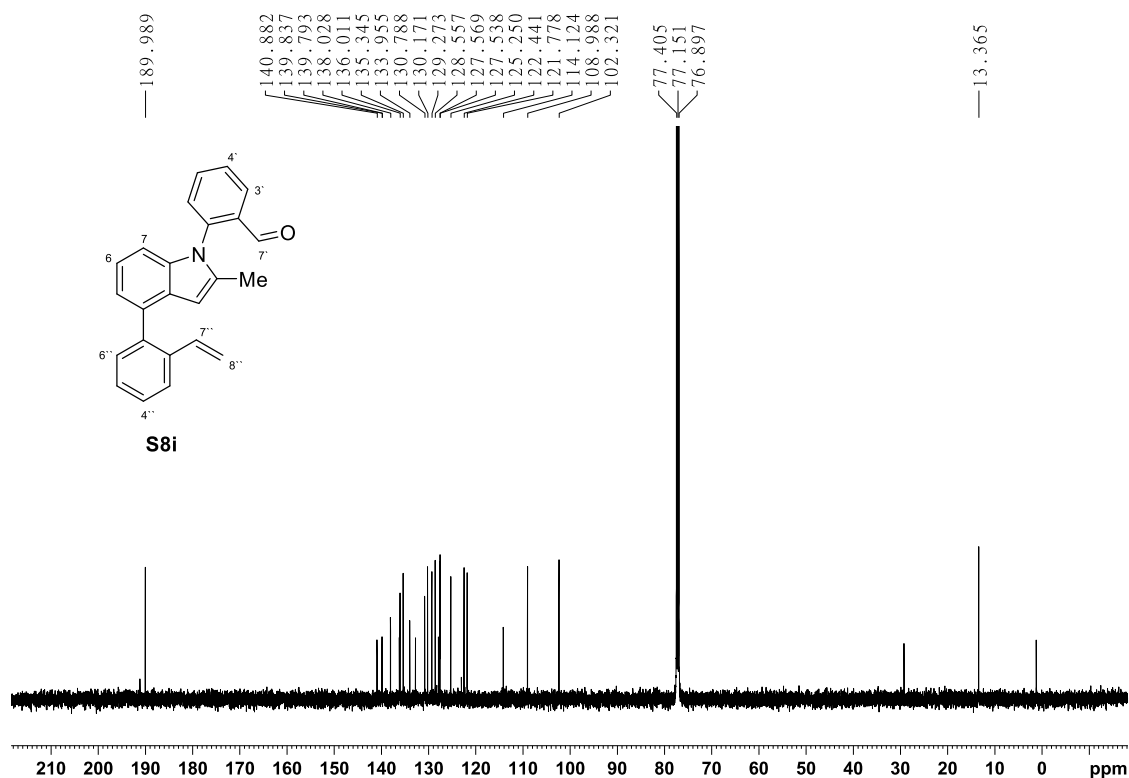
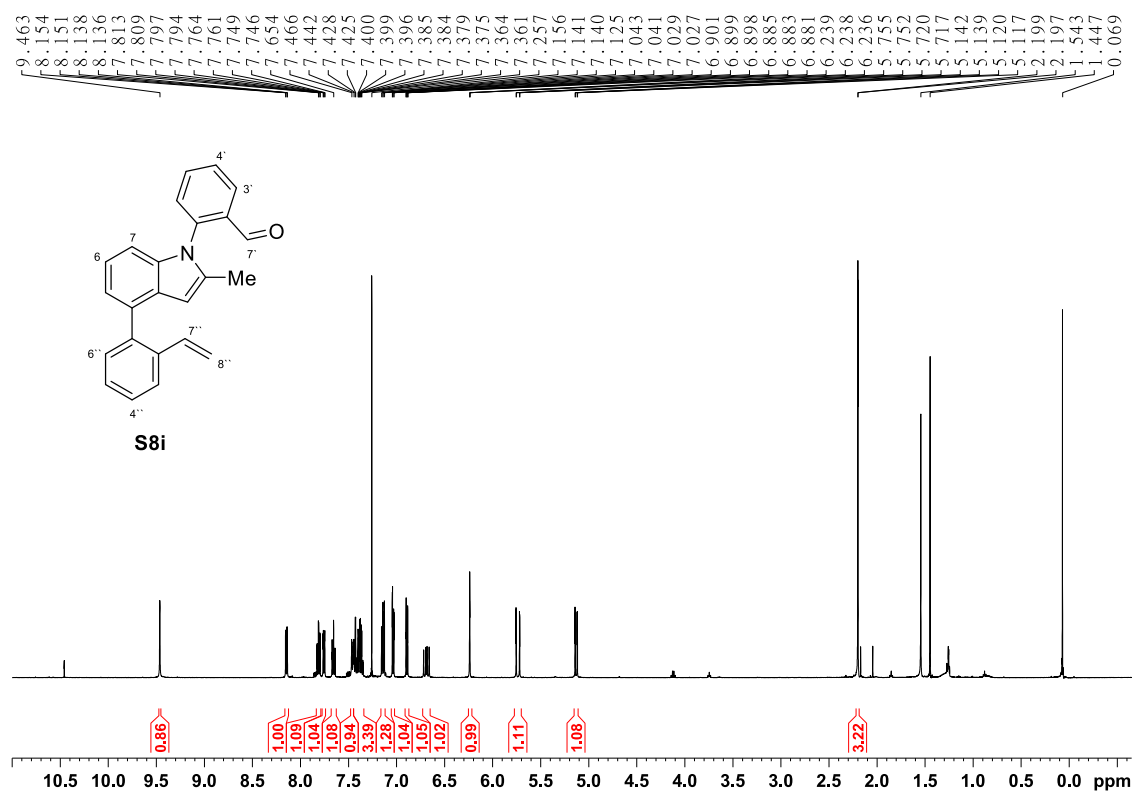
**2-(3-Methyl-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8g):**



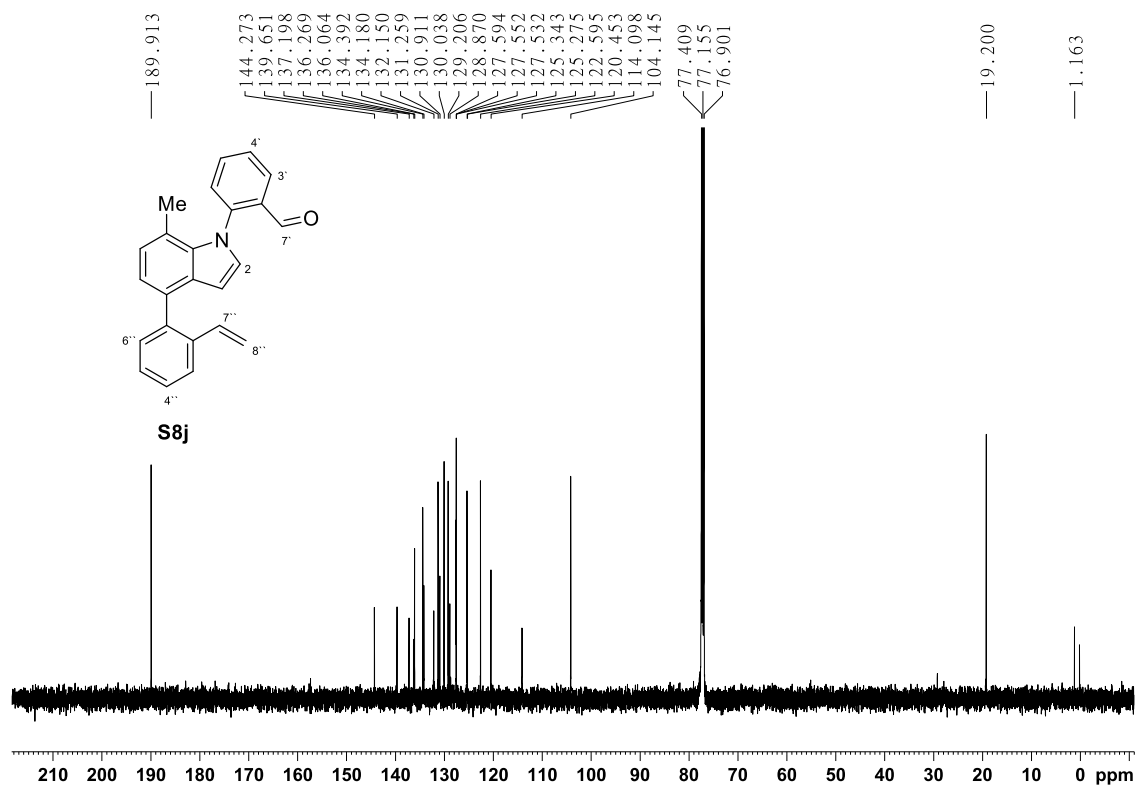
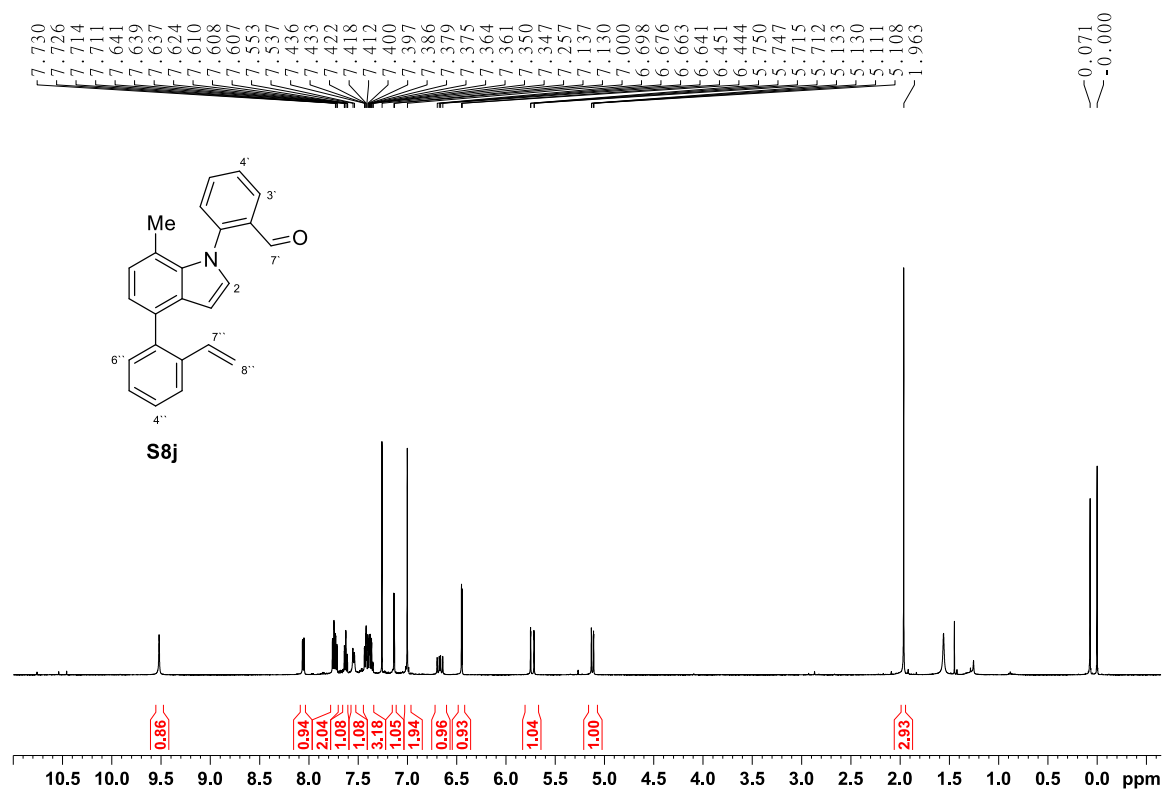
**2-(4-(2-Vinylphenyl)-1H-pyrrolo[2,3-c]pyridin-1-yl)benzaldehyde (S8h):**



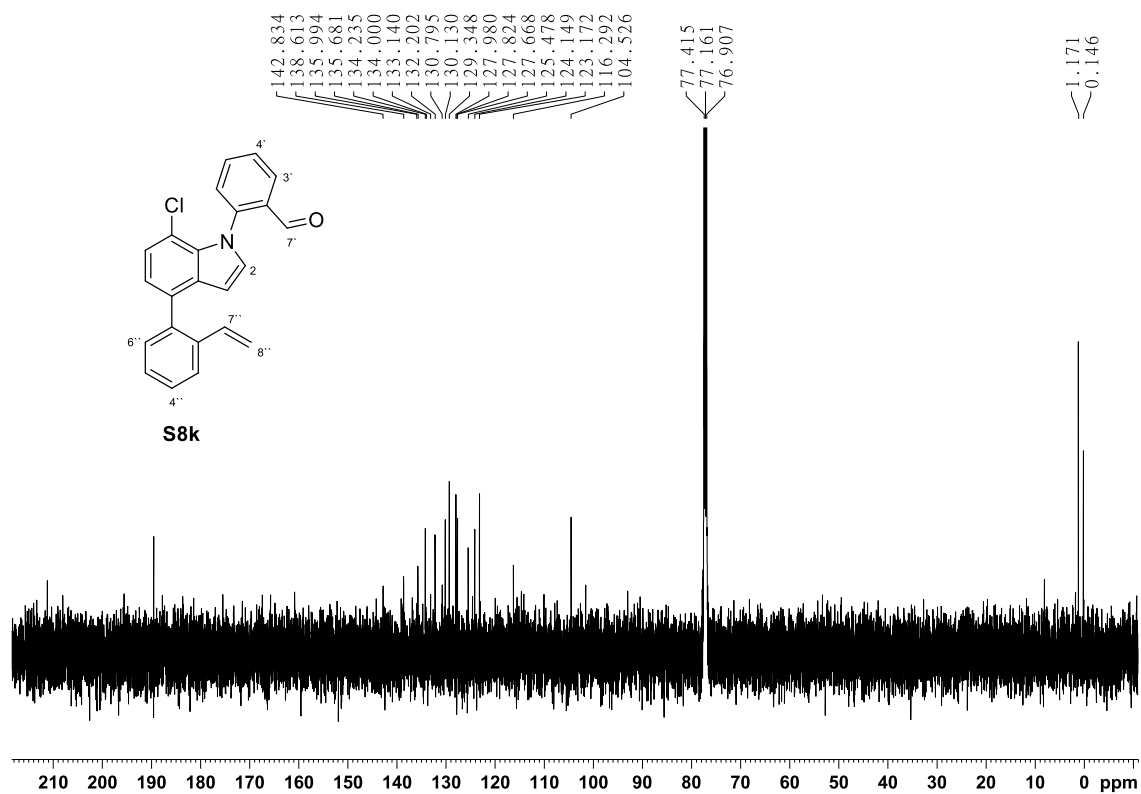
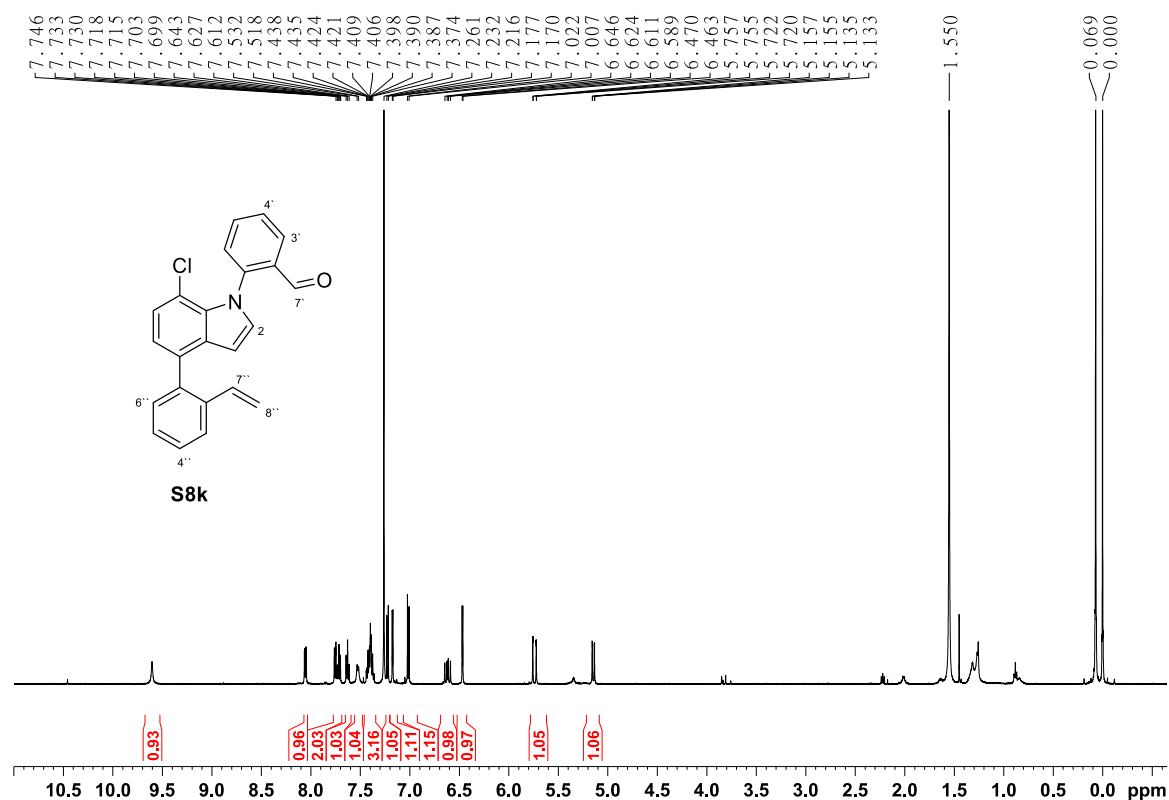
**2-(2-Methyl-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8i):**



**2-(7-Methyl-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8j):**

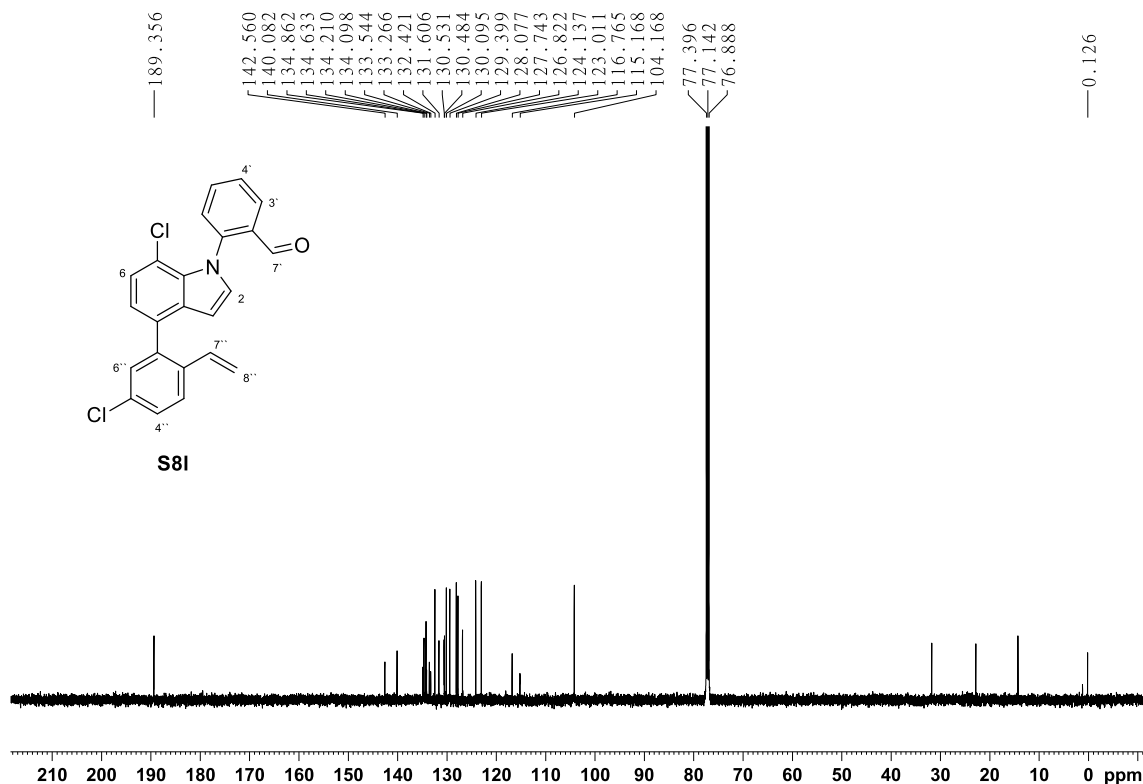
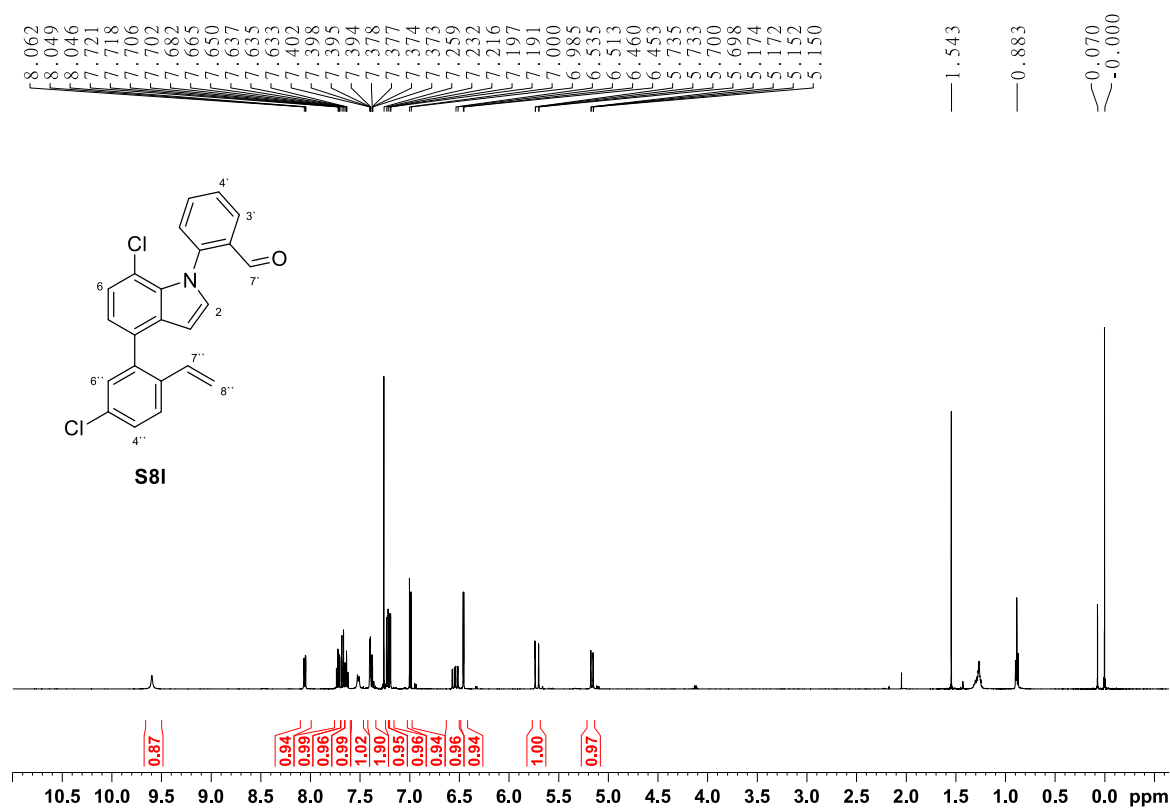


**2-(7-Chloro-4-(2-vinylphenyl)-1H-indol-1-yl)benzaldehyde (S8k):**

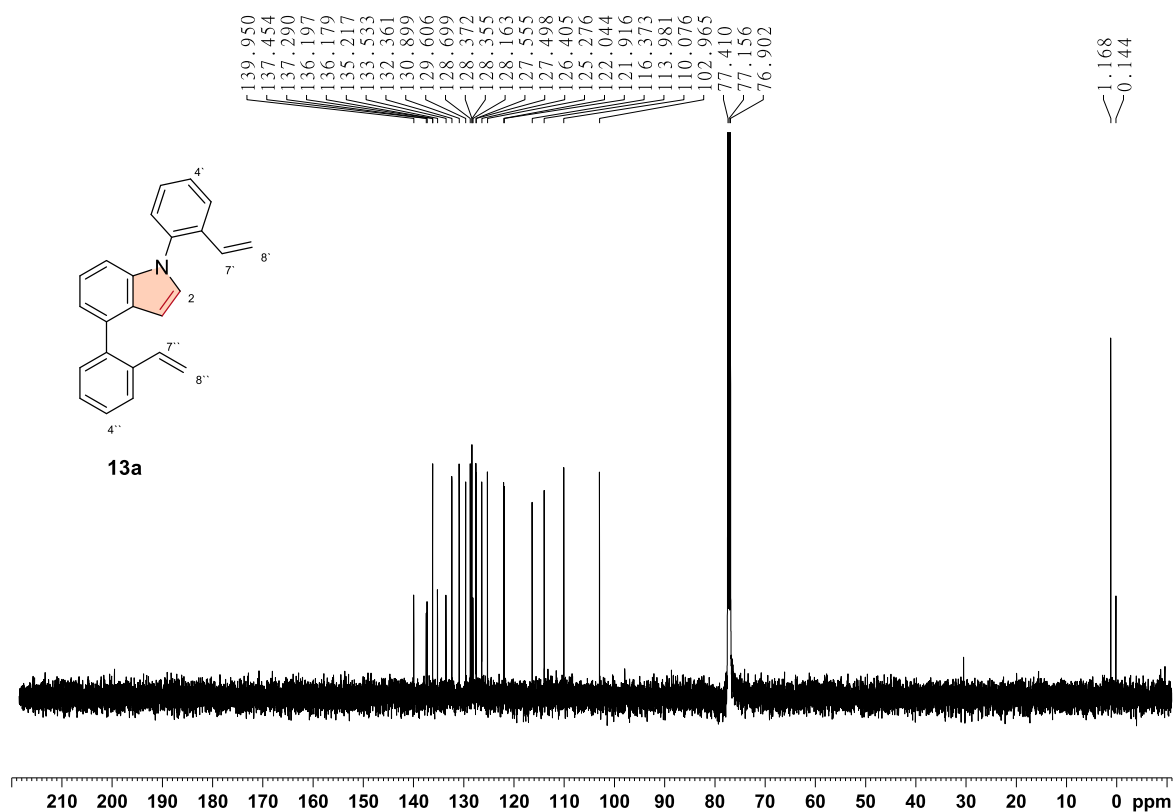
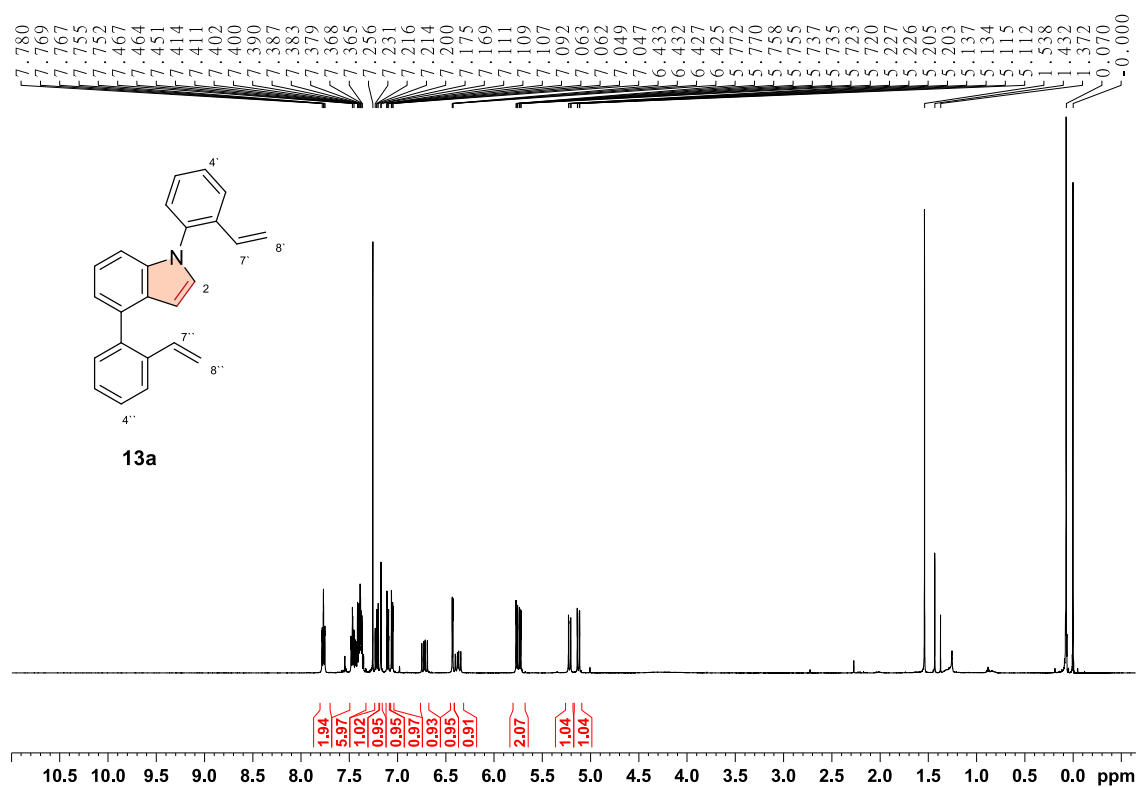




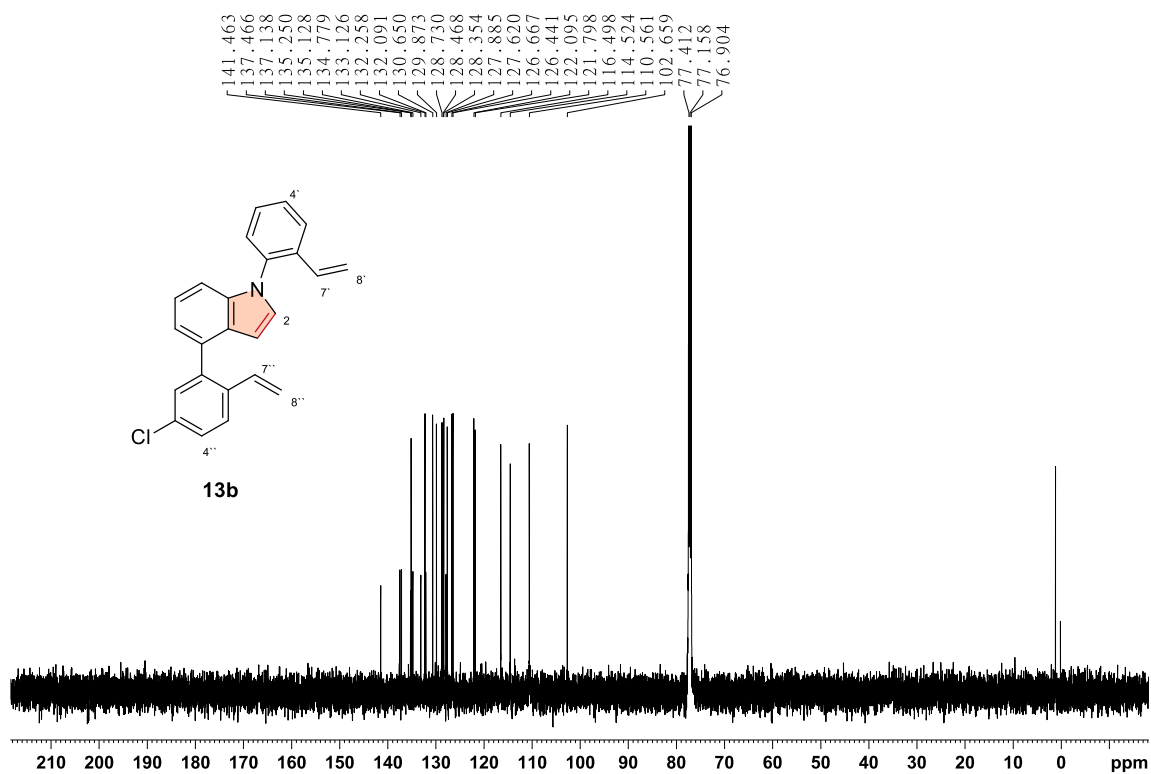
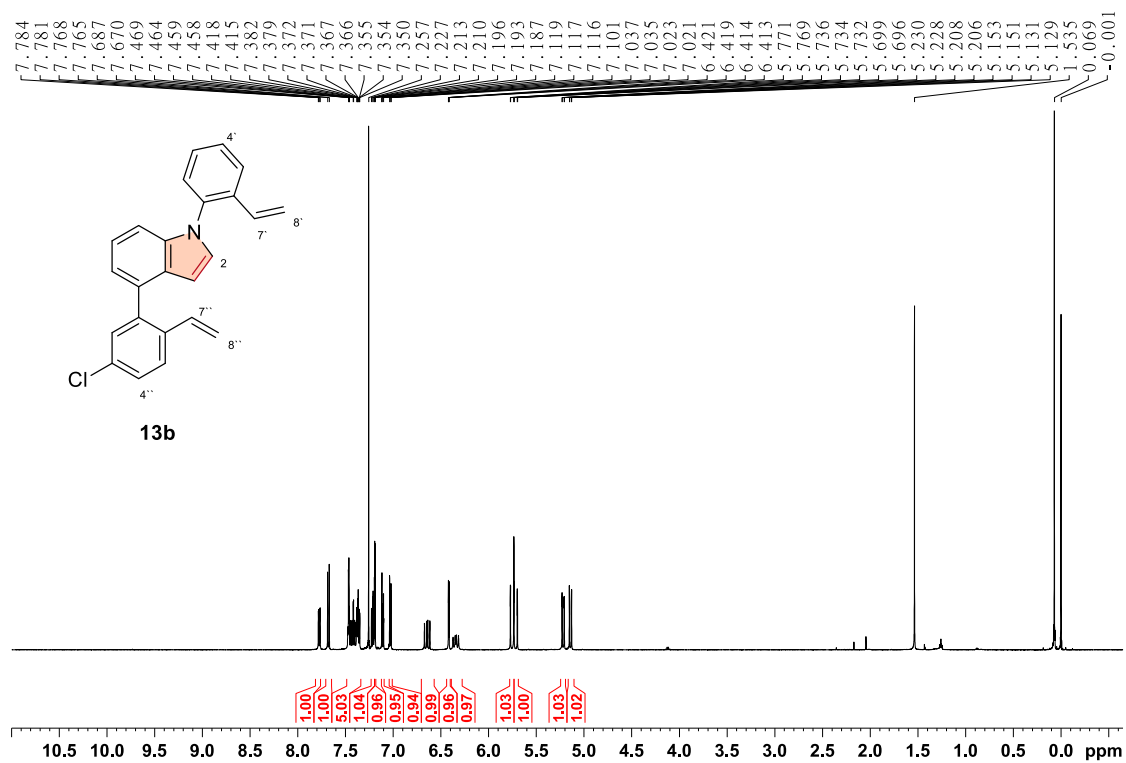
**2-(7-Chloro-4-(5-chloro-2-vinylphenyl)-1*H*-indol-1-yl)benzaldehyde (S8l):**



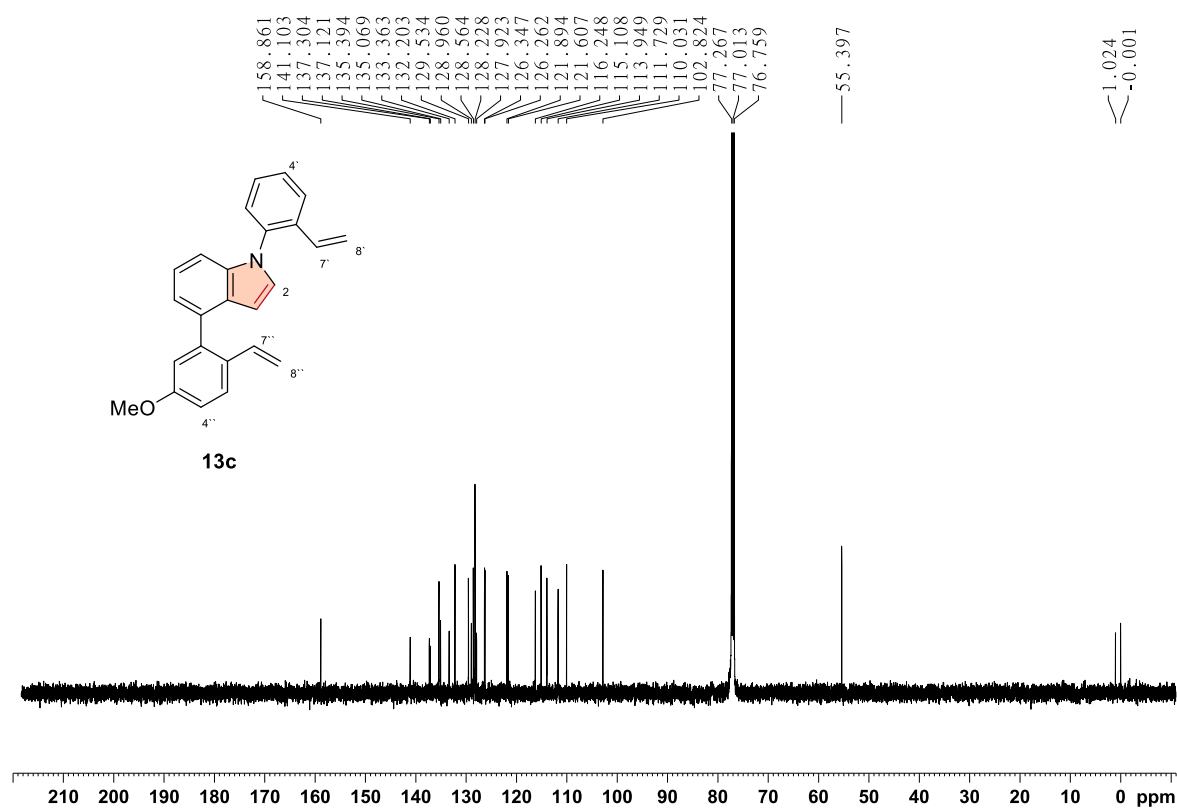
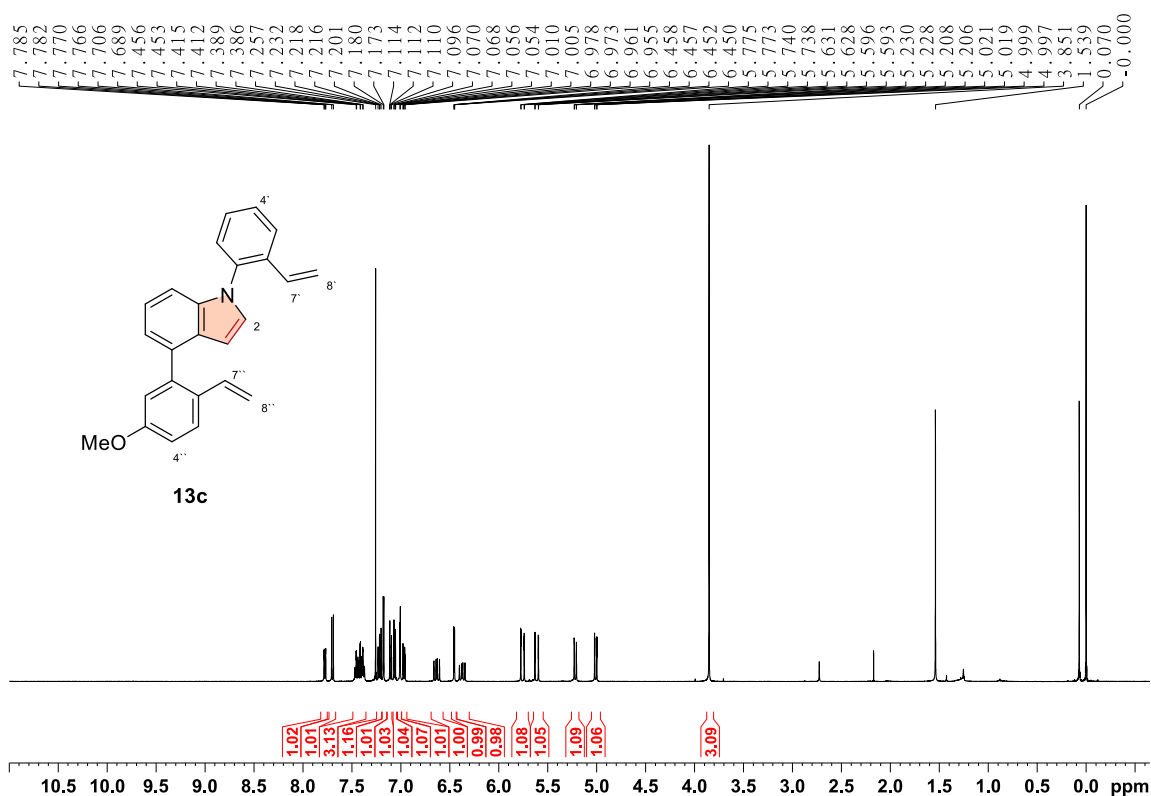
**1,4-Bis(2-vinylphenyl)-1H-indole (13a):**



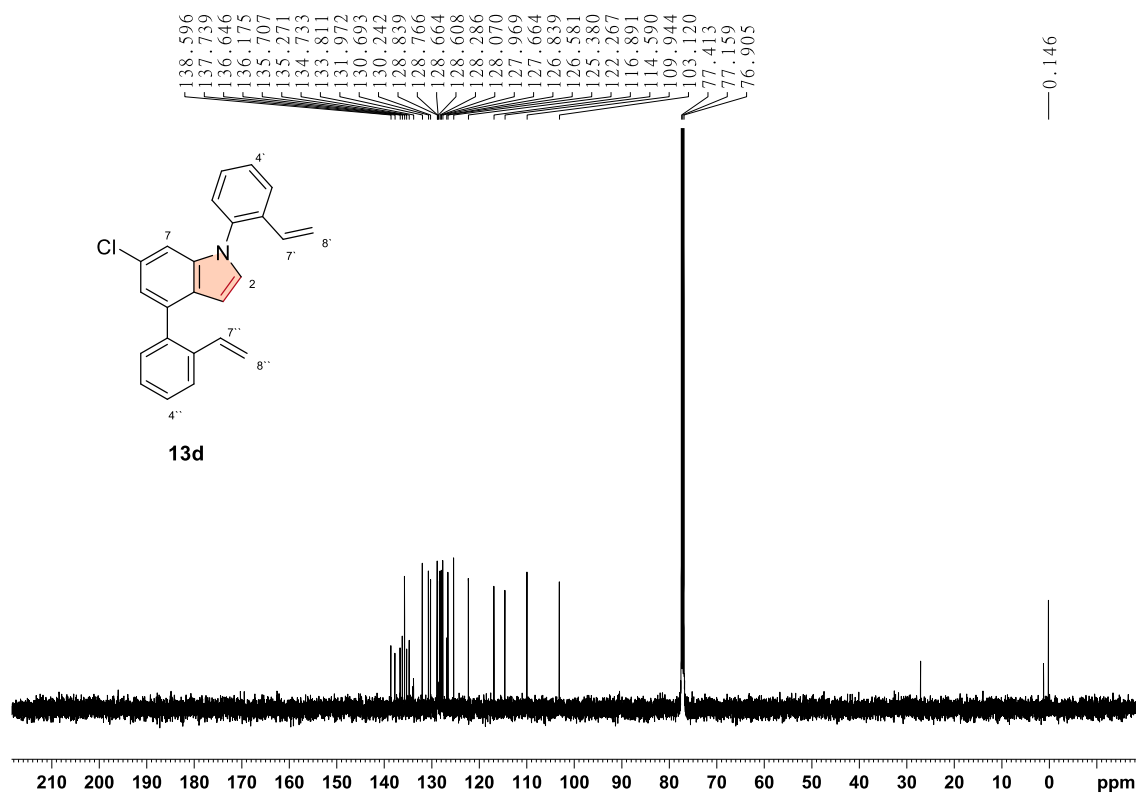
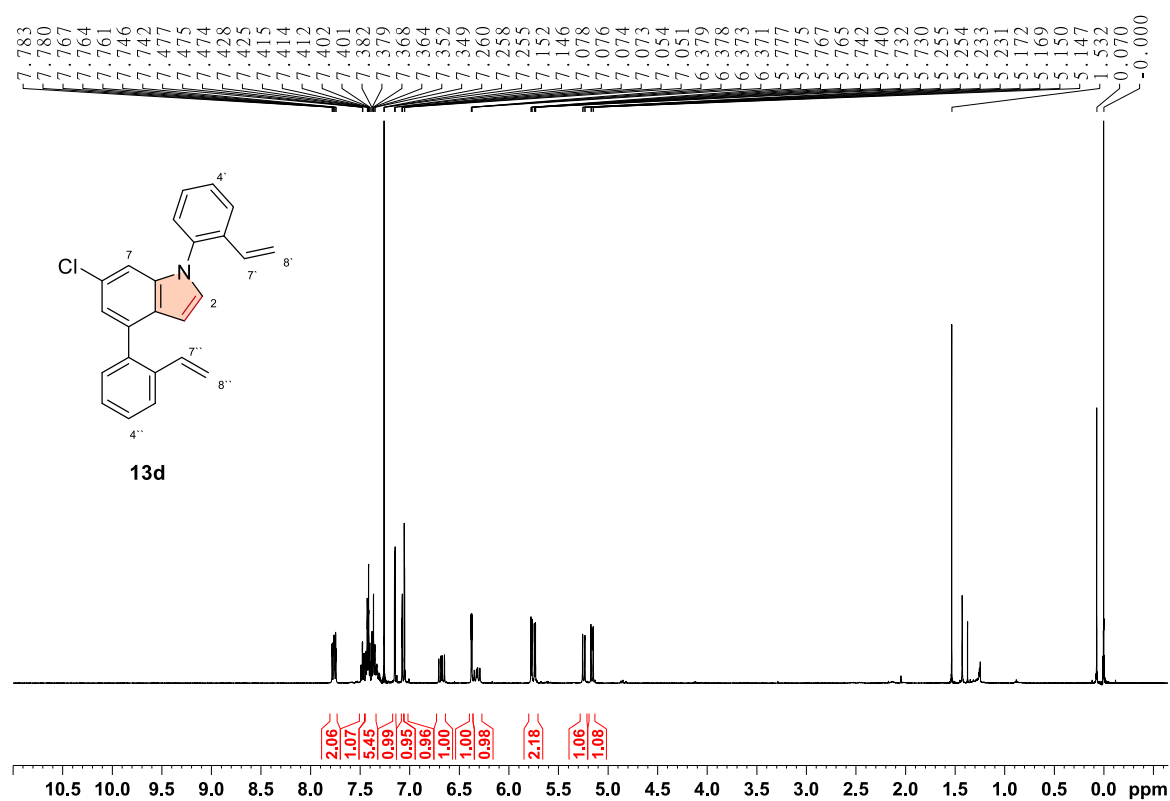
**4-(5-Chloro-2-vinylphenyl)-1-(2-vinylphenyl)-1H-indole (13b):**



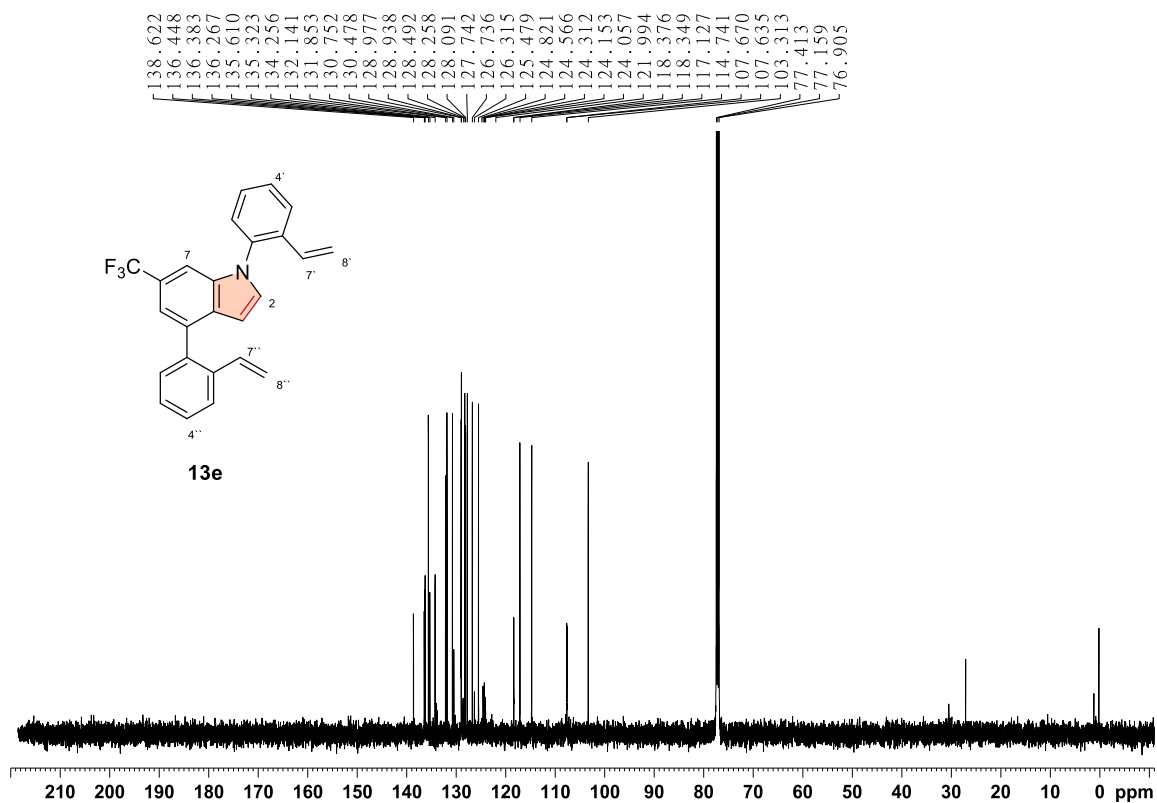
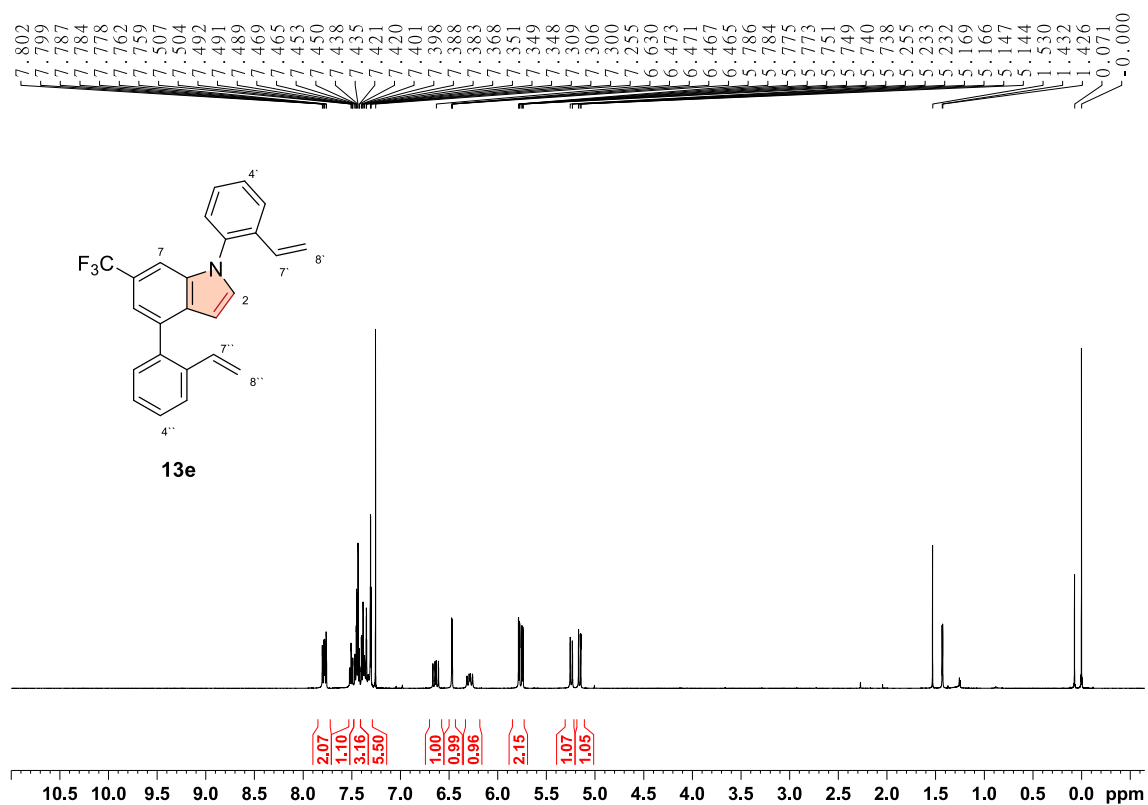
**4-(5-Methoxy-2-vinylphenyl)-1-(2-vinylphenyl)-1H-indole (13c):**

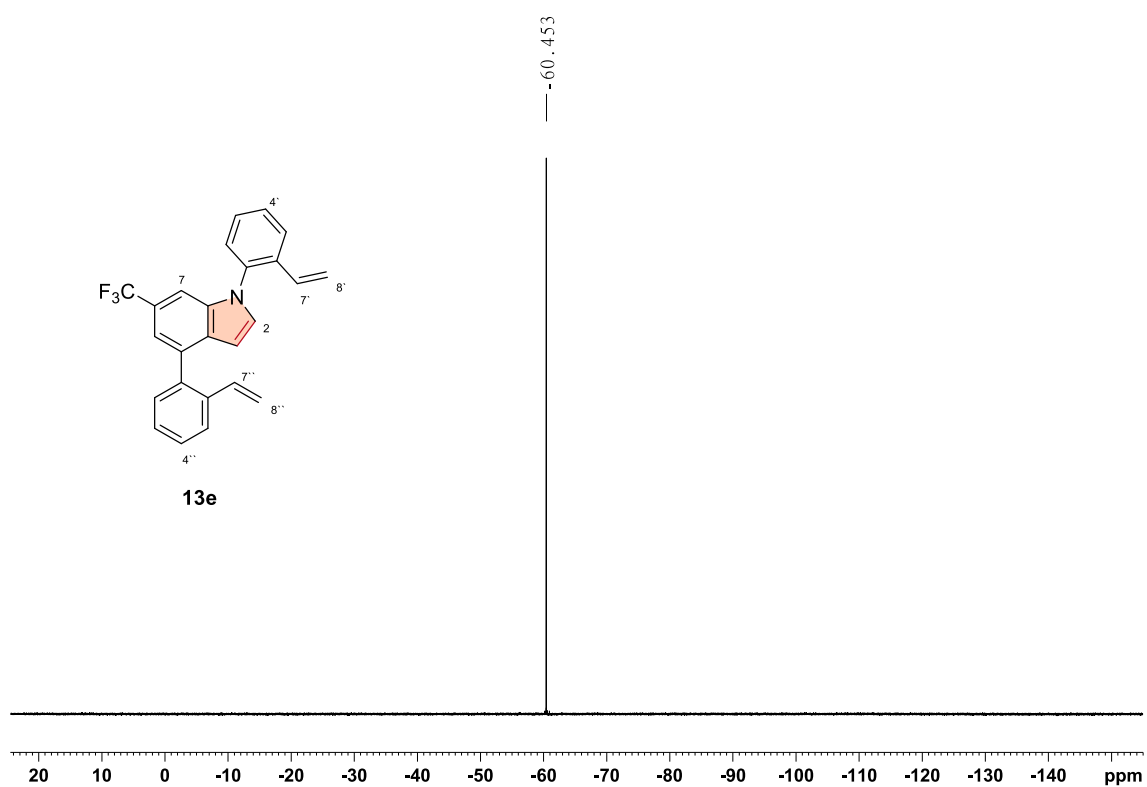


**6-Chloro-1,4-bis(2-vinylphenyl)-1H-indole (13d):**

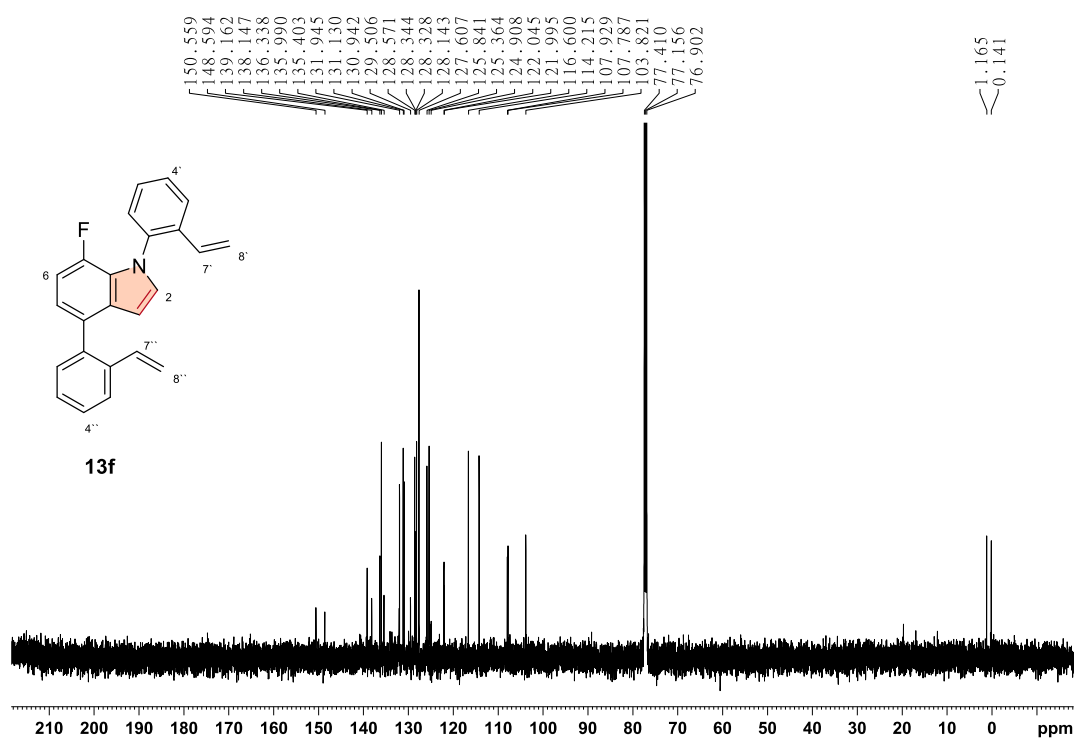
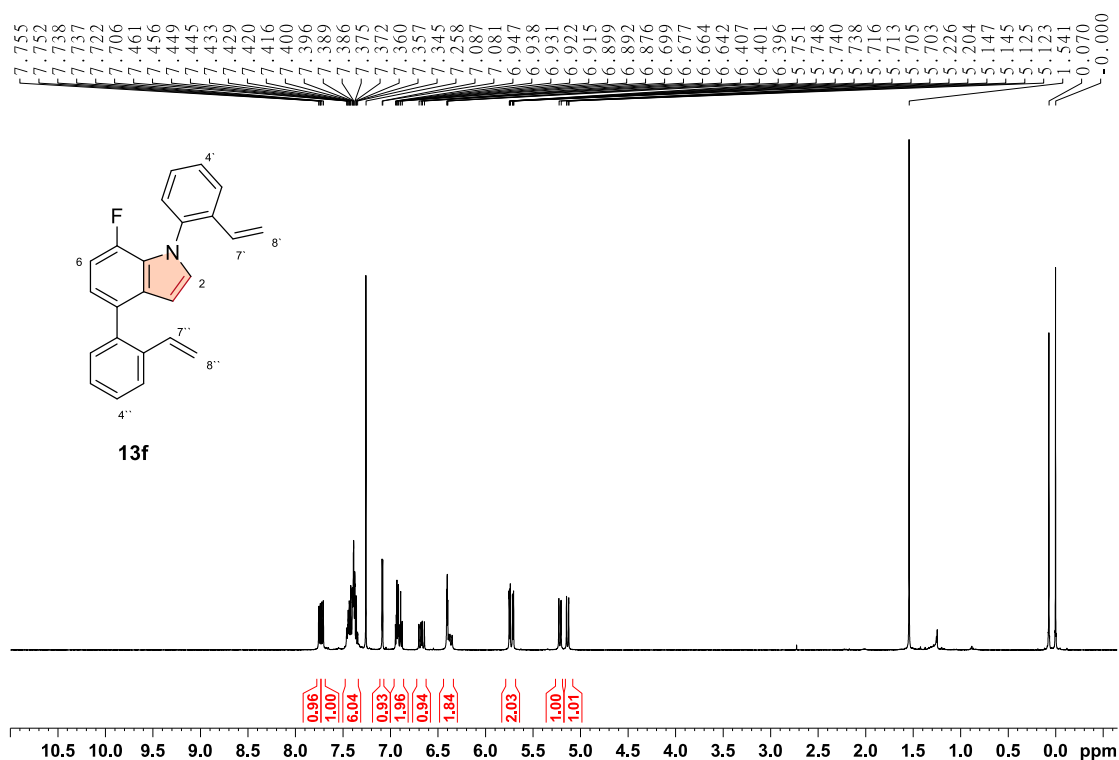


**6-(Trifluoromethyl)-1,4-bis(2-vinylphenyl)-1H-indole (13e):**



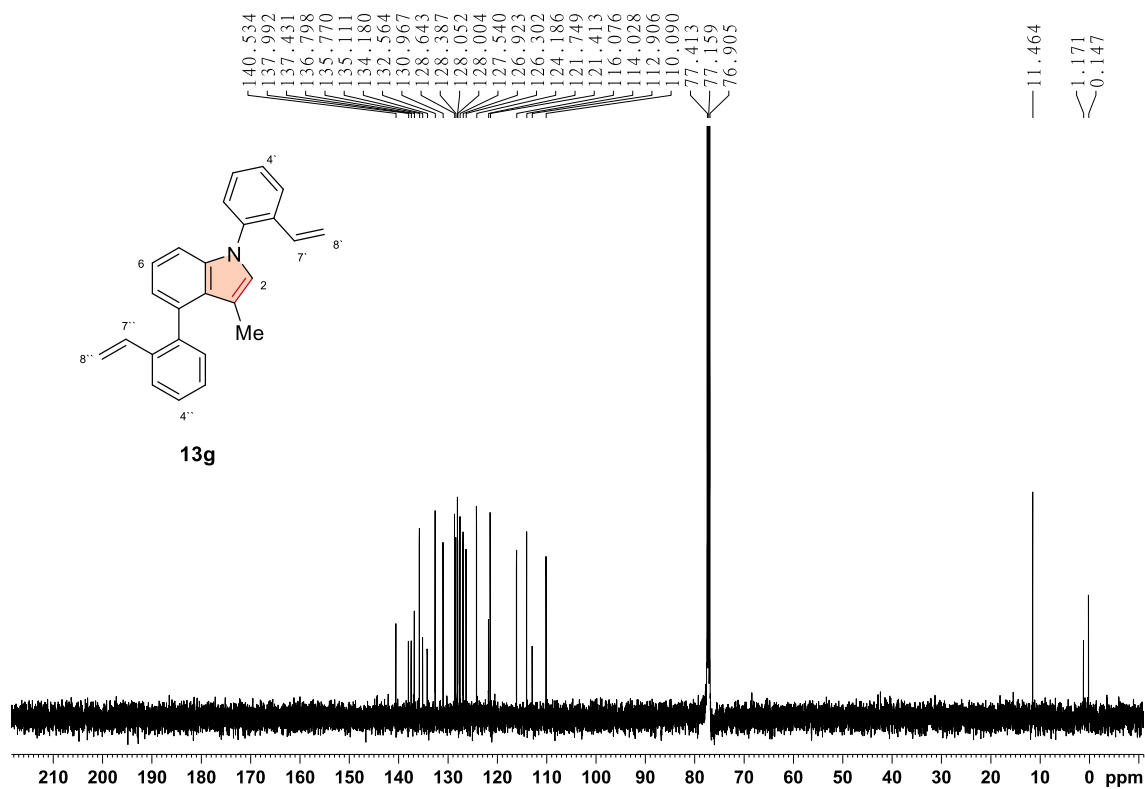
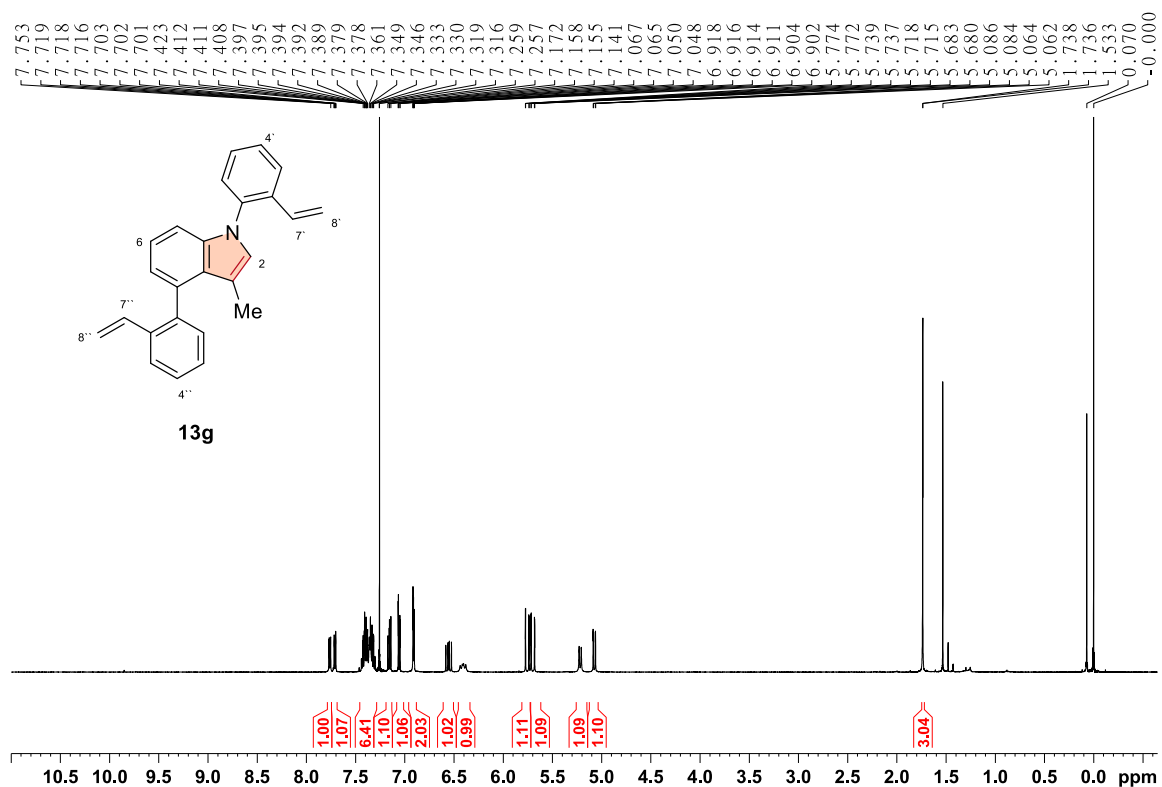


**7-Fluoro-1,4-bis(2-vinylphenyl)-1*H*-indole (13f):**

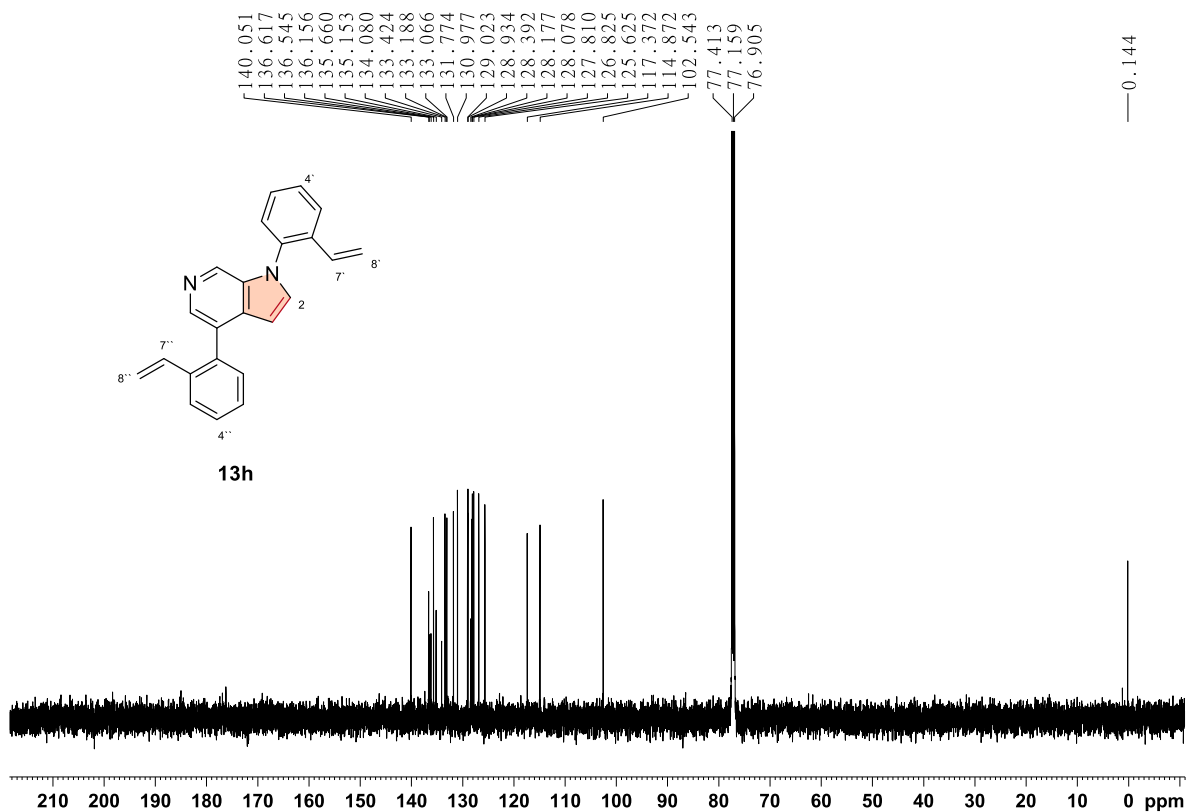
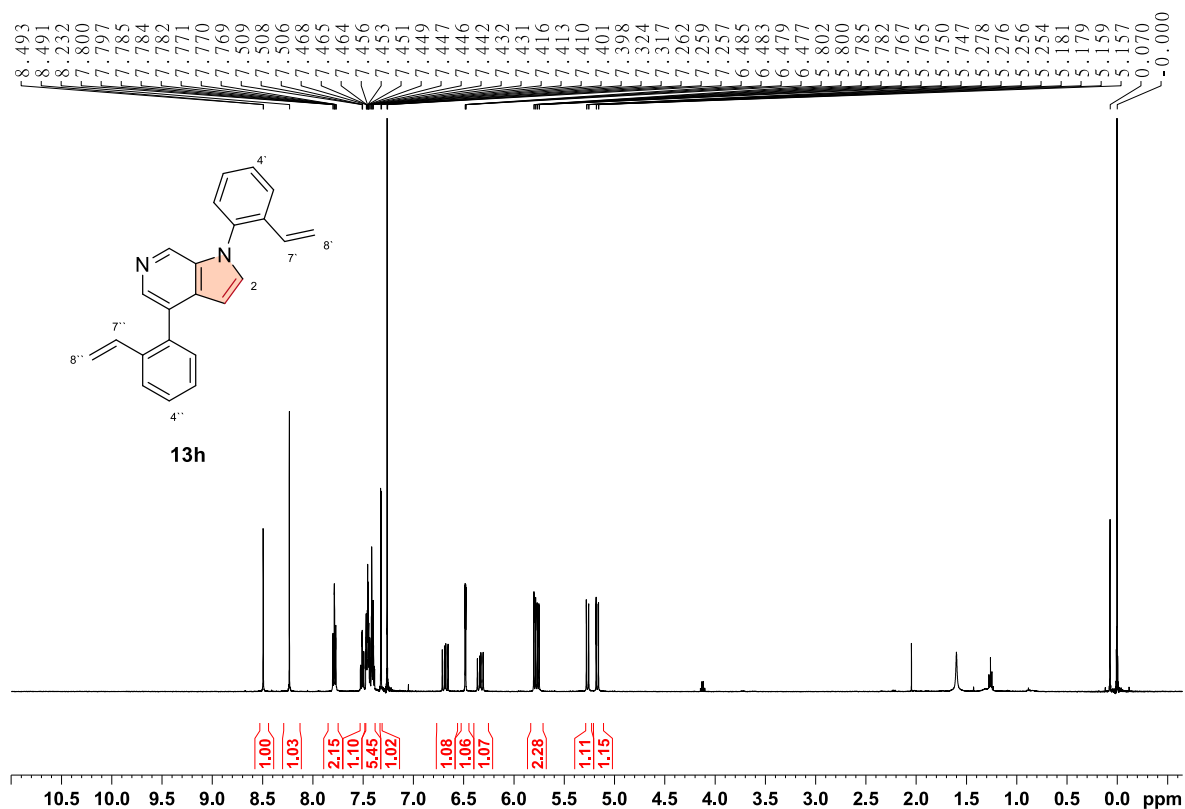




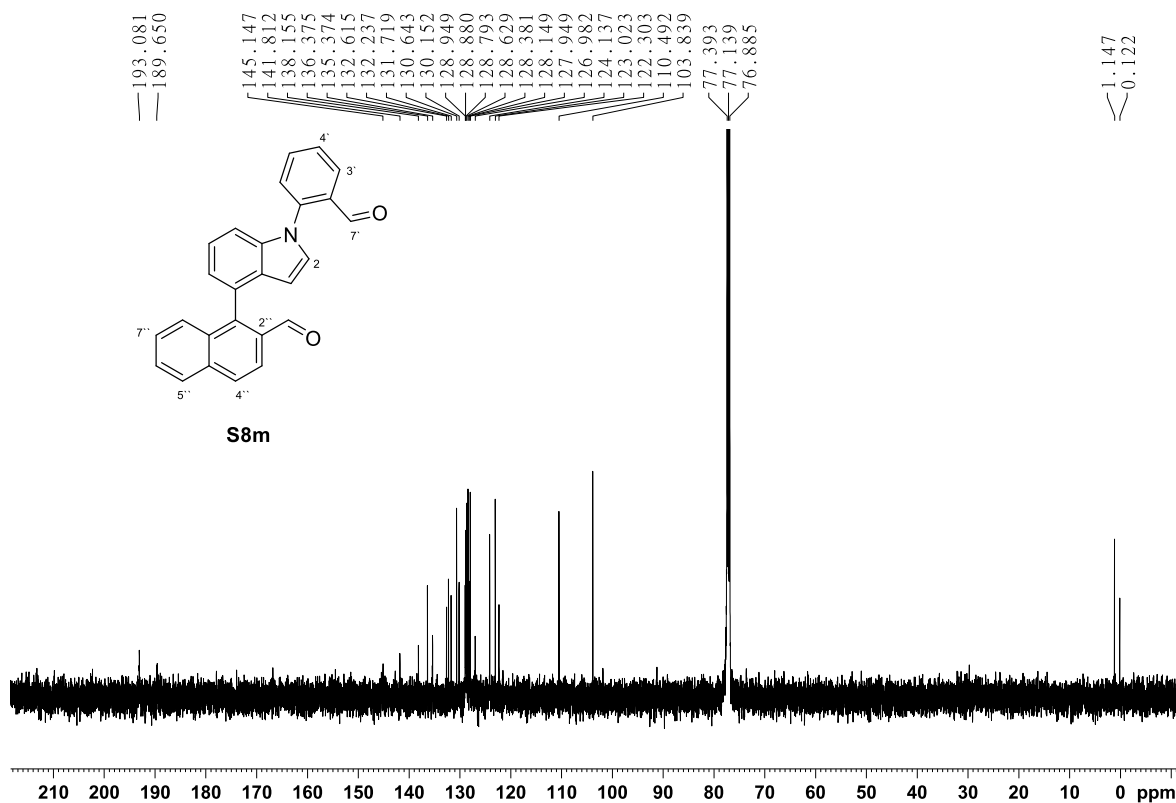
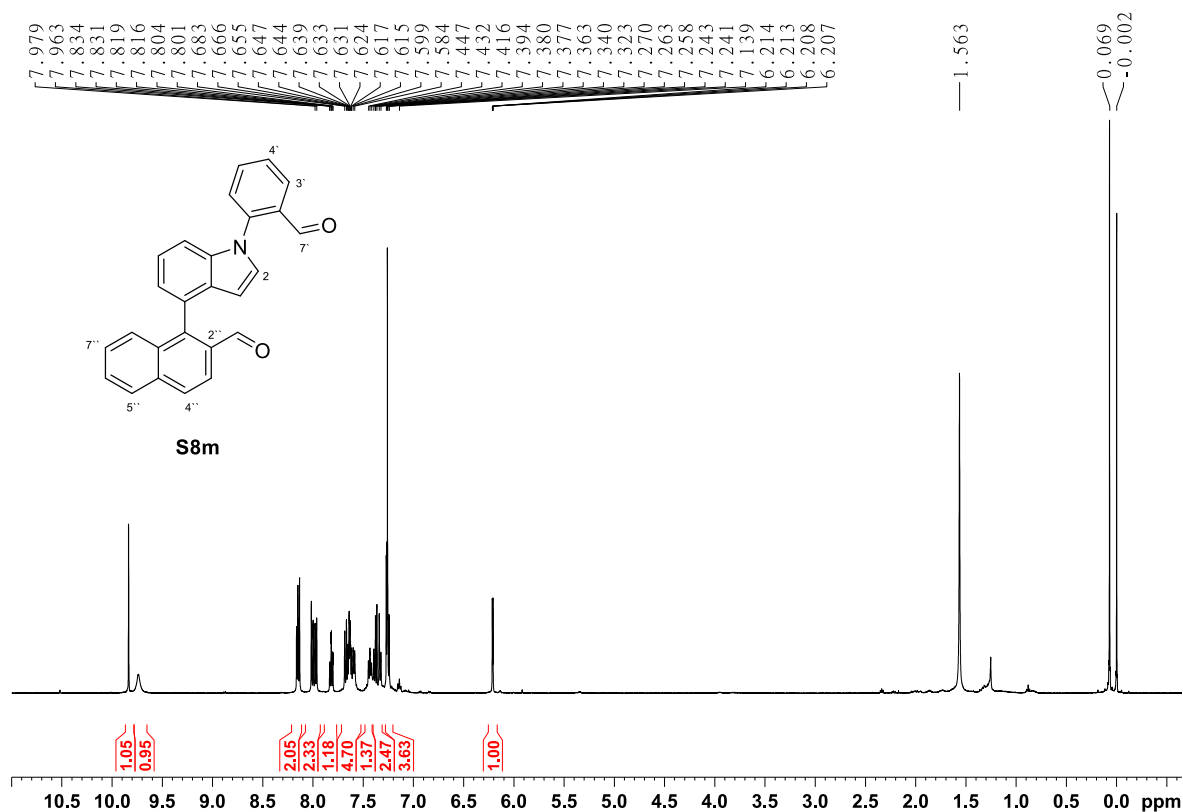
### 3-Methyl-1,4-bis(2-vinylphenyl)-1H-indole (13g):



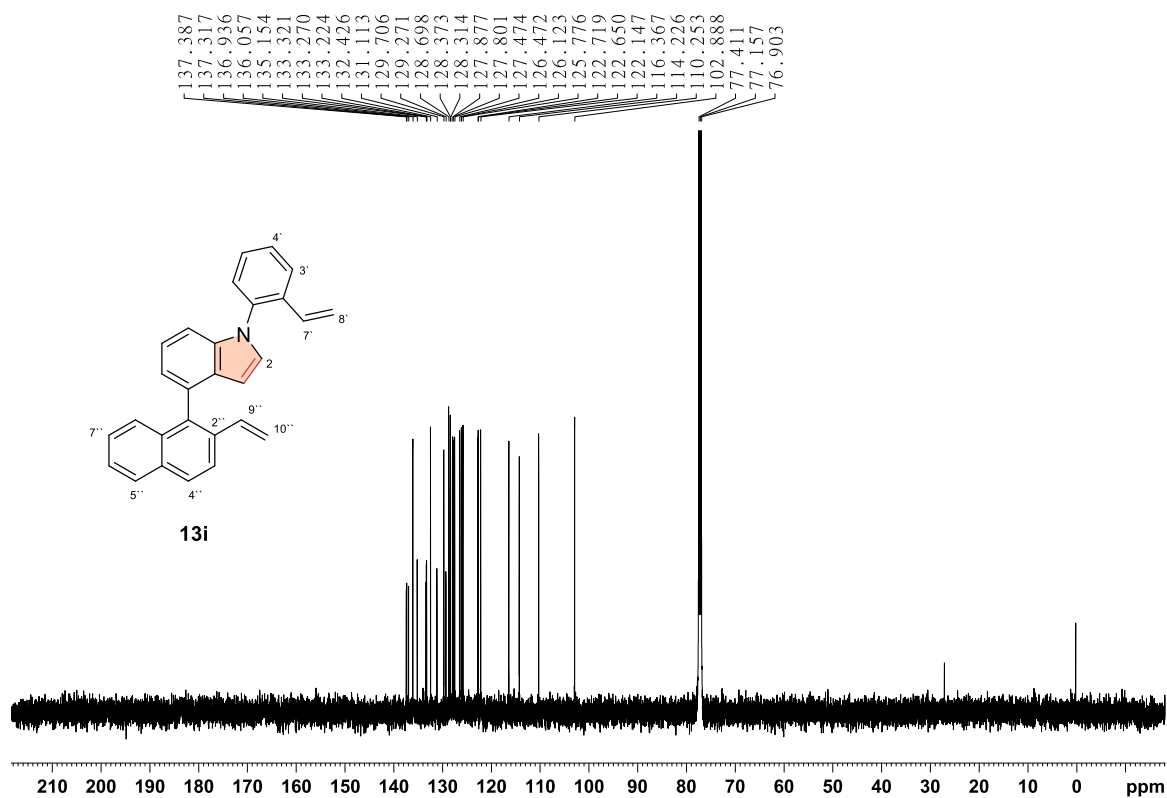
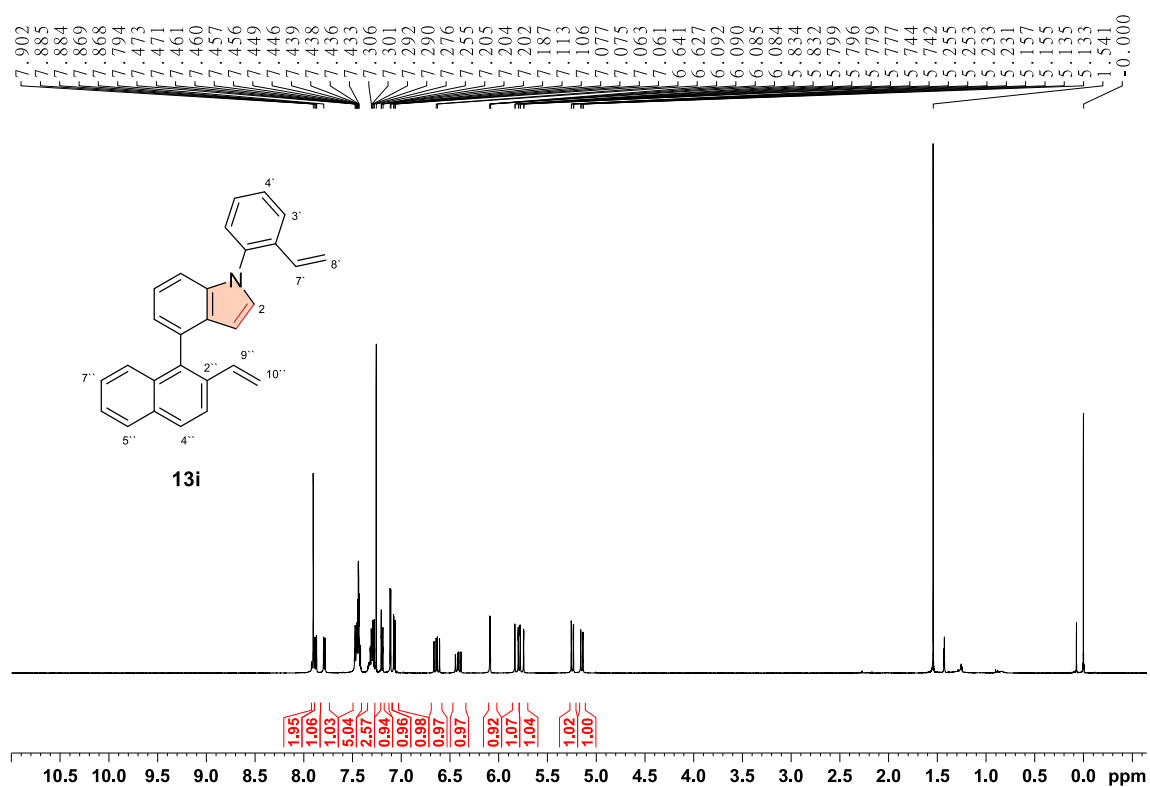
**1,4-Bis(2-vinylphenyl)-1H-pyrrolo[2,3-c]pyridine (13h):**



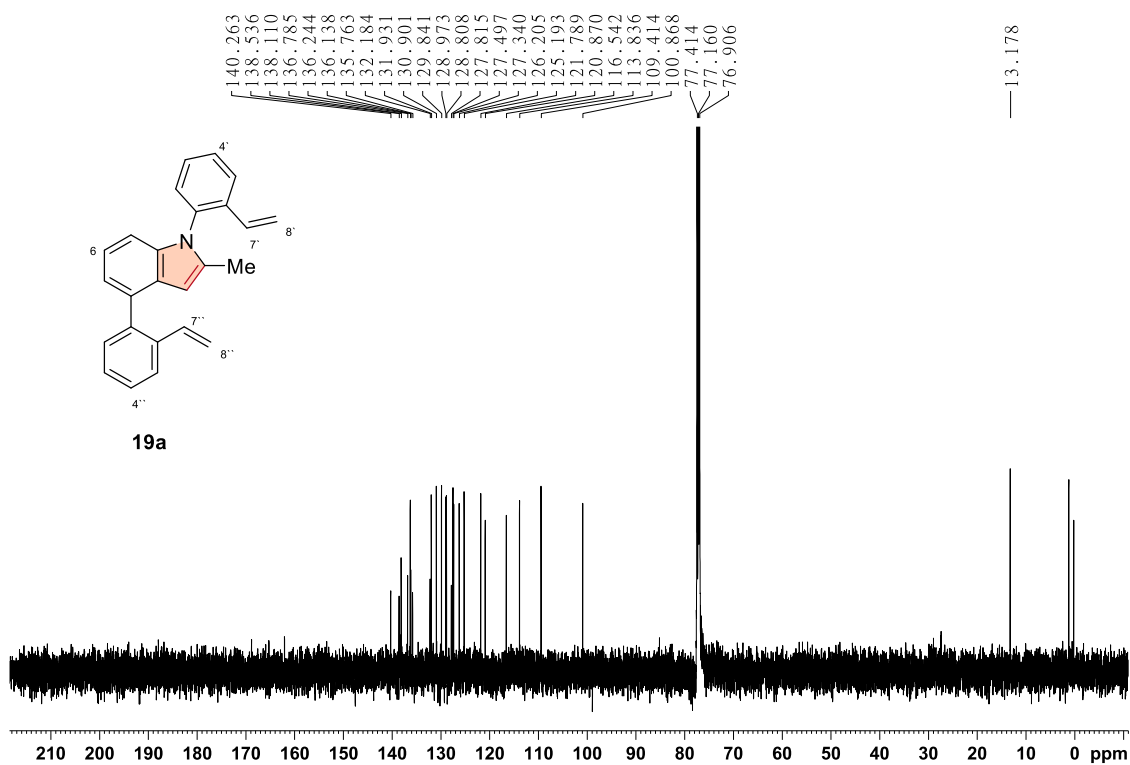
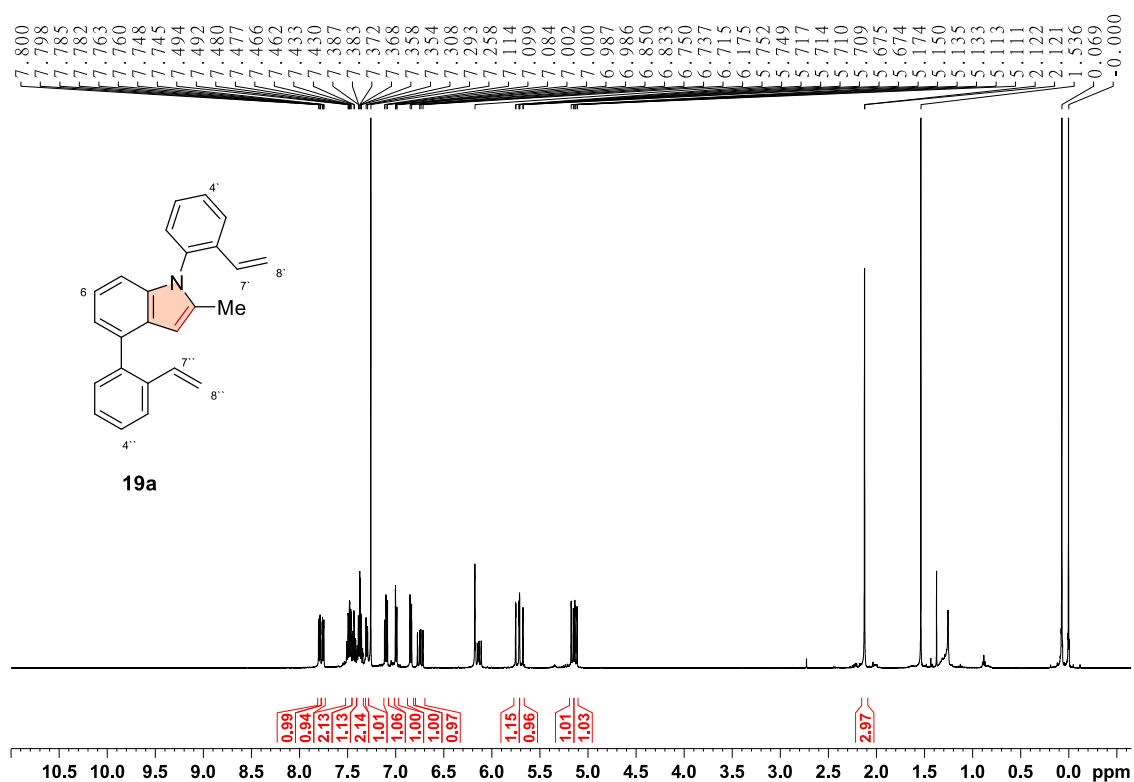
**1-(1-(2-Formylphenyl)-1H-indol-4-yl)-2-naphthaldehyde (S8m):**



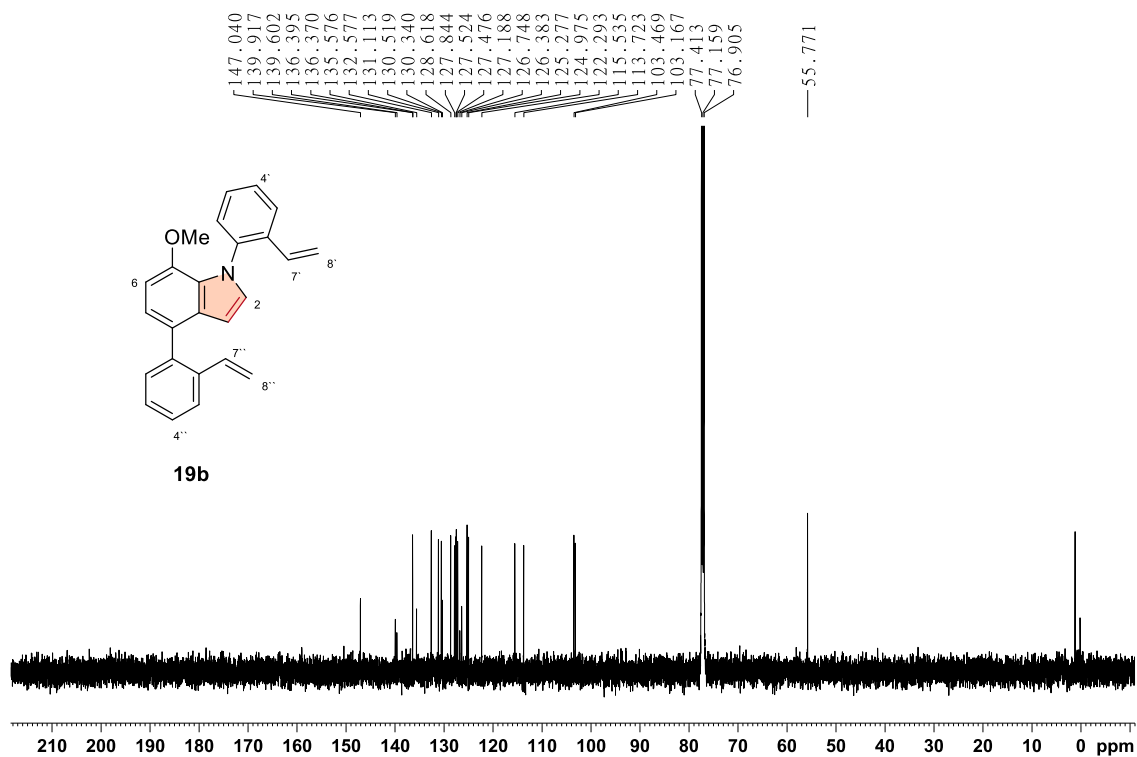
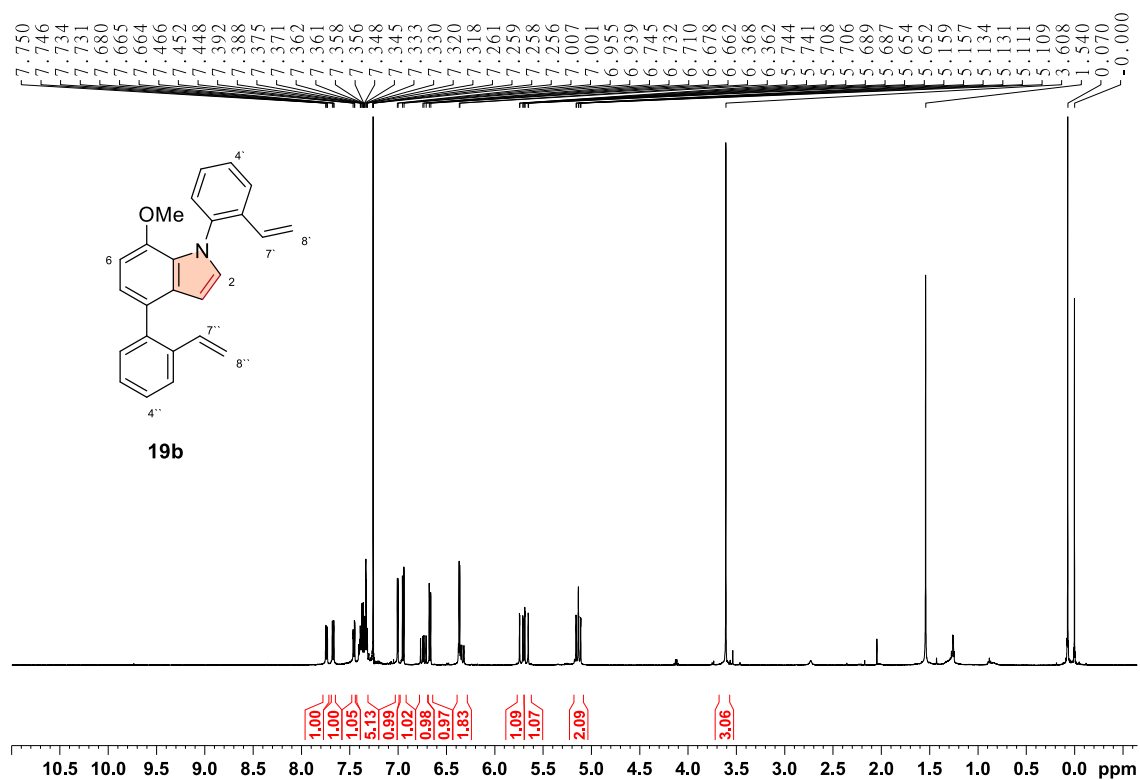
**4-(2-Vinylnaphthalen-1-yl)-1-(2-vinylphenyl)-1H-indole (13i):**



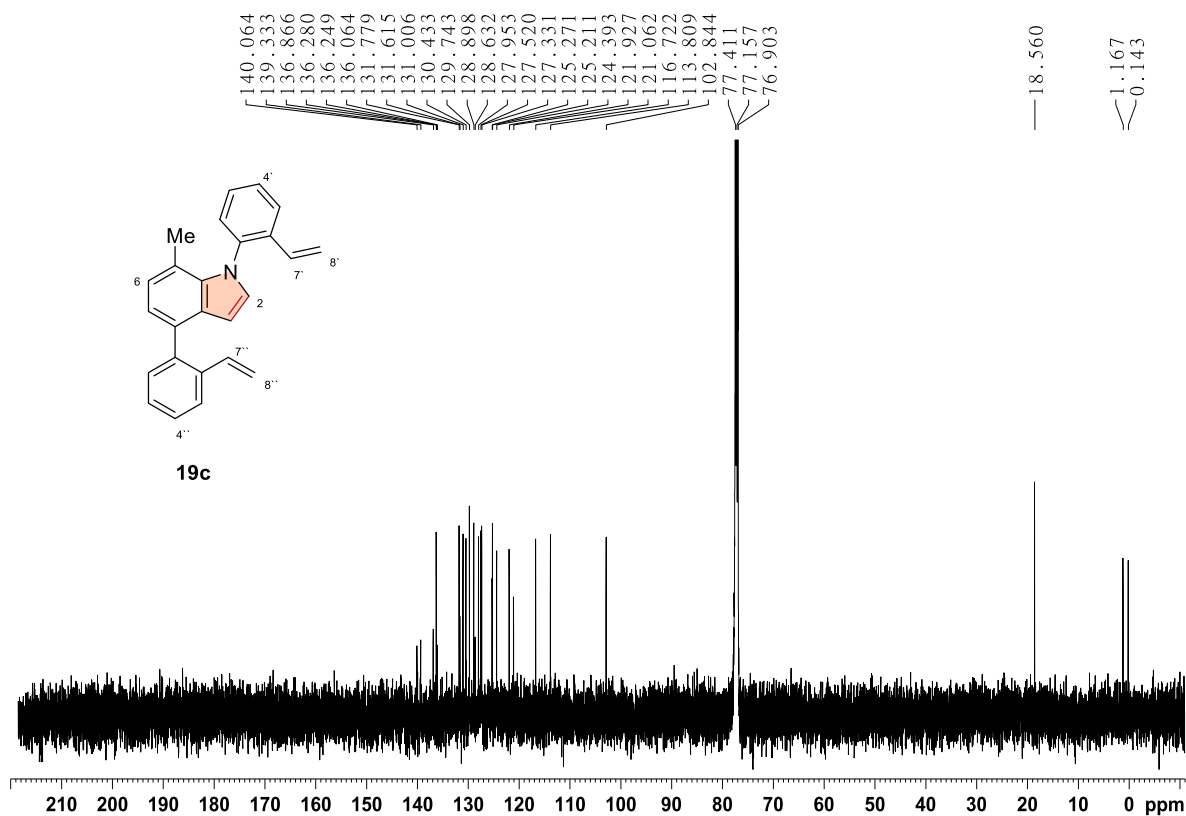
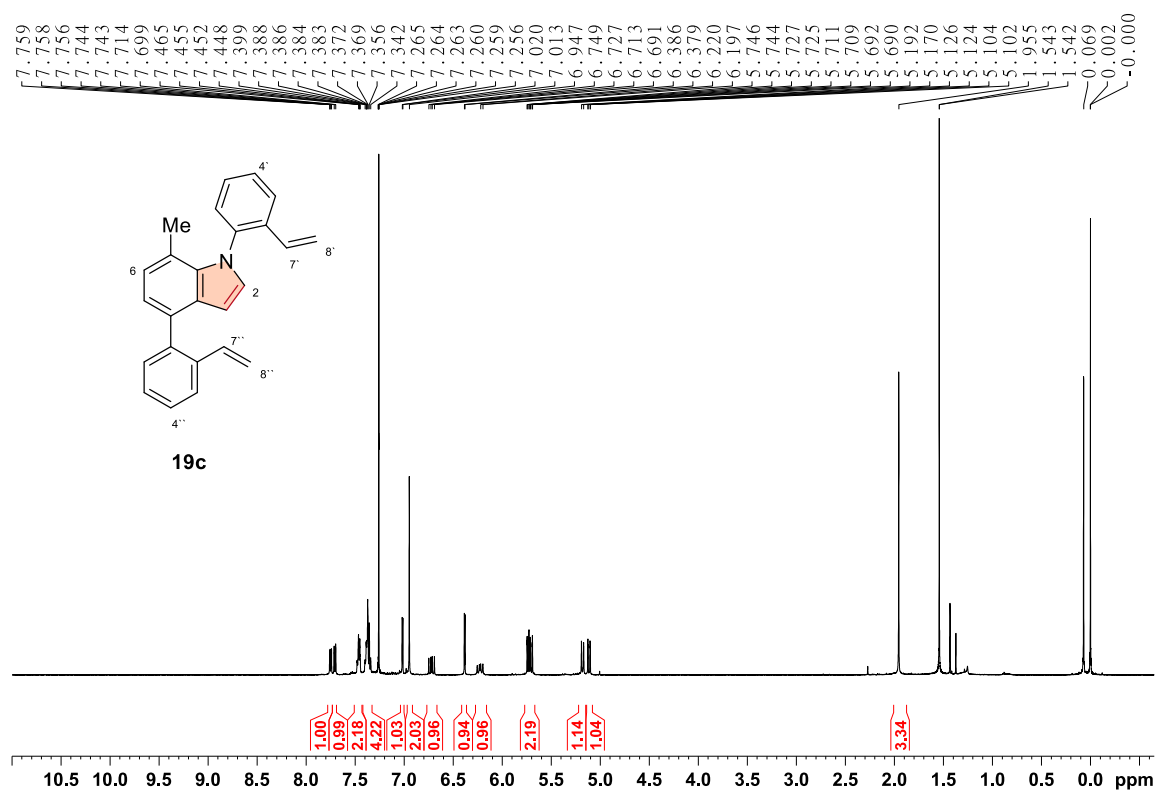
**2-Methyl-1,4-bis(2-vinylphenyl)-1H-indole (19a):**



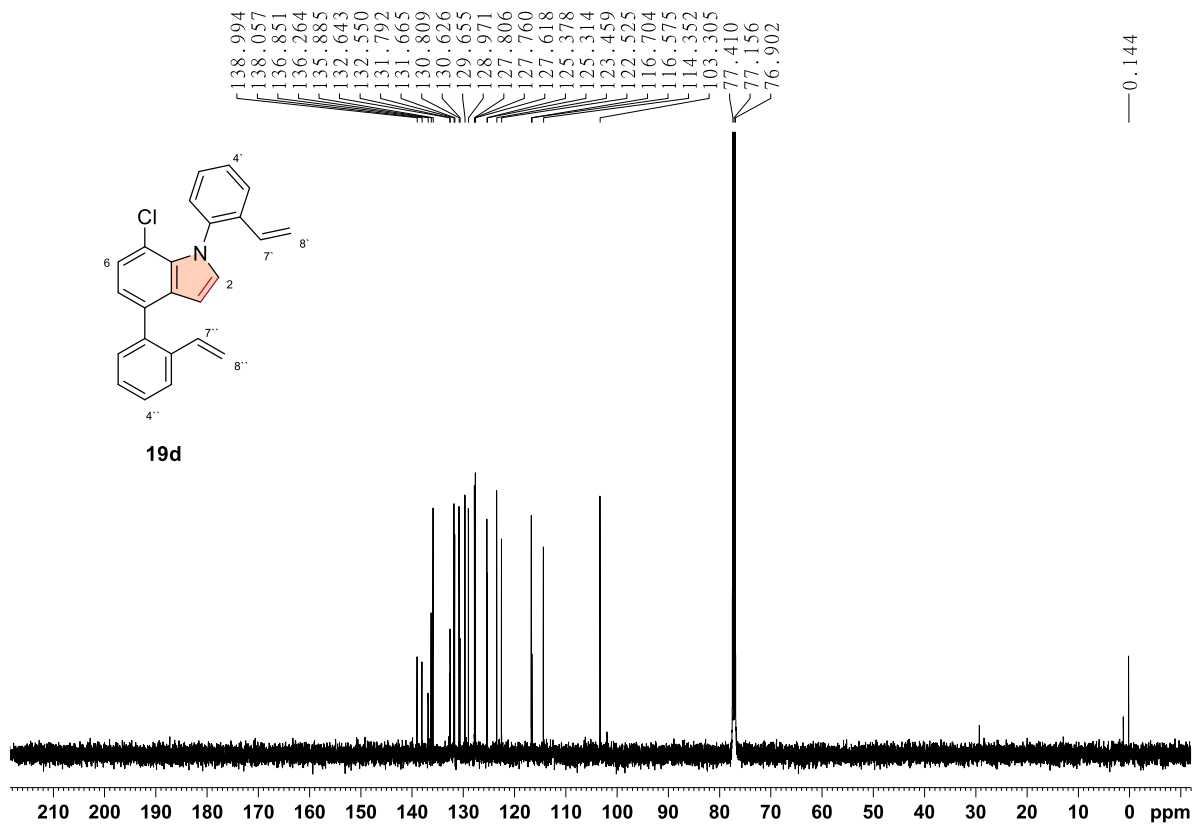
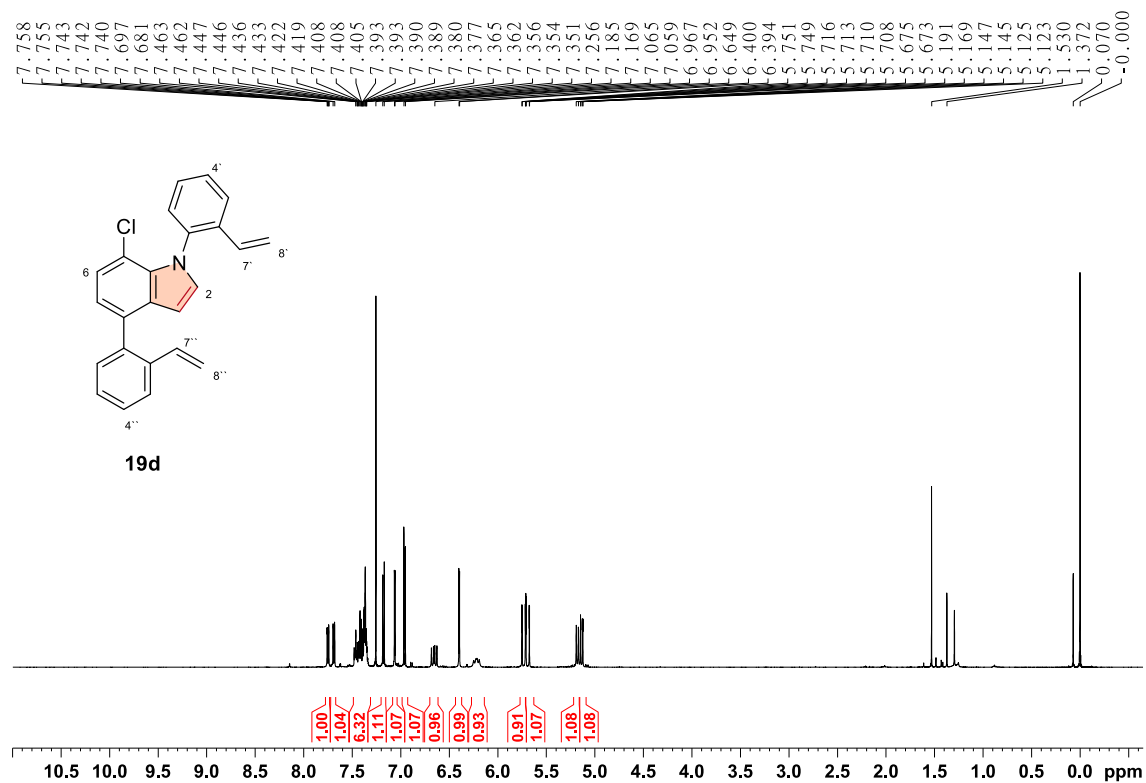
**7-Methoxy-1,4-bis(2-vinylphenyl)-1*H*-indole (19b):**



**7-Methyl-1,4-bis(2-vinylphenyl)-1H-indole (19c):**

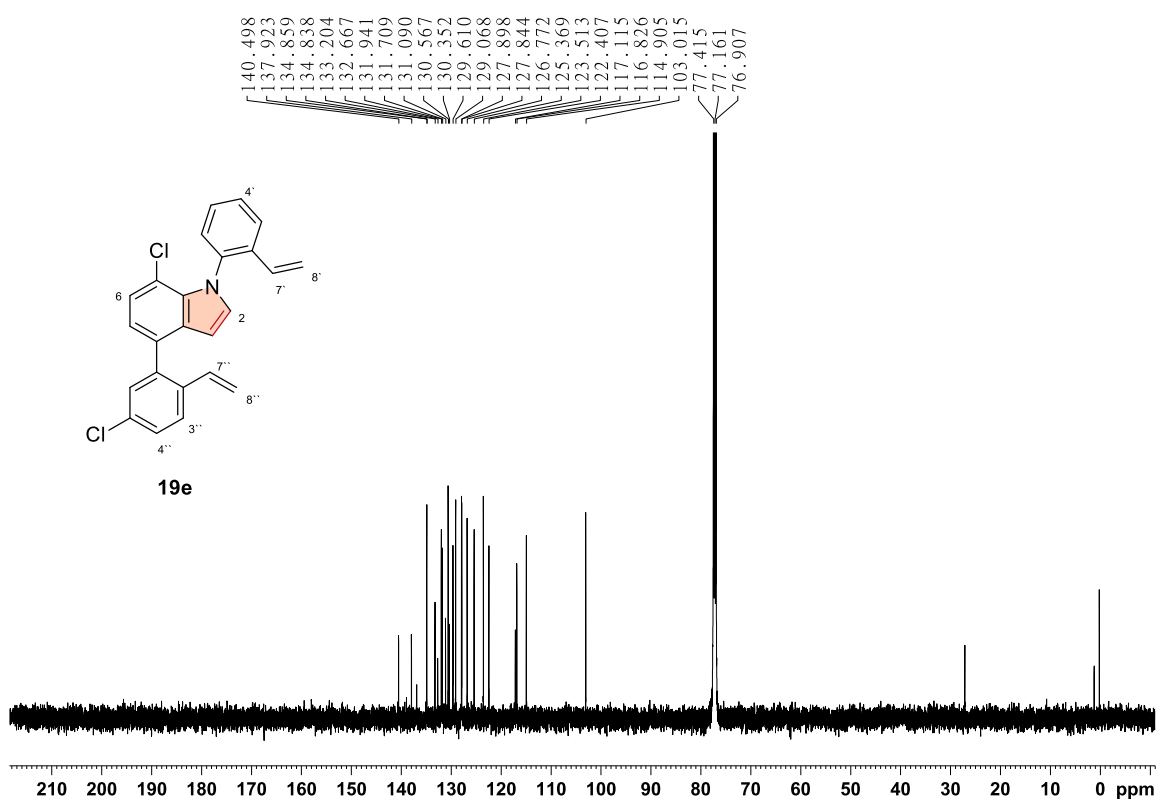
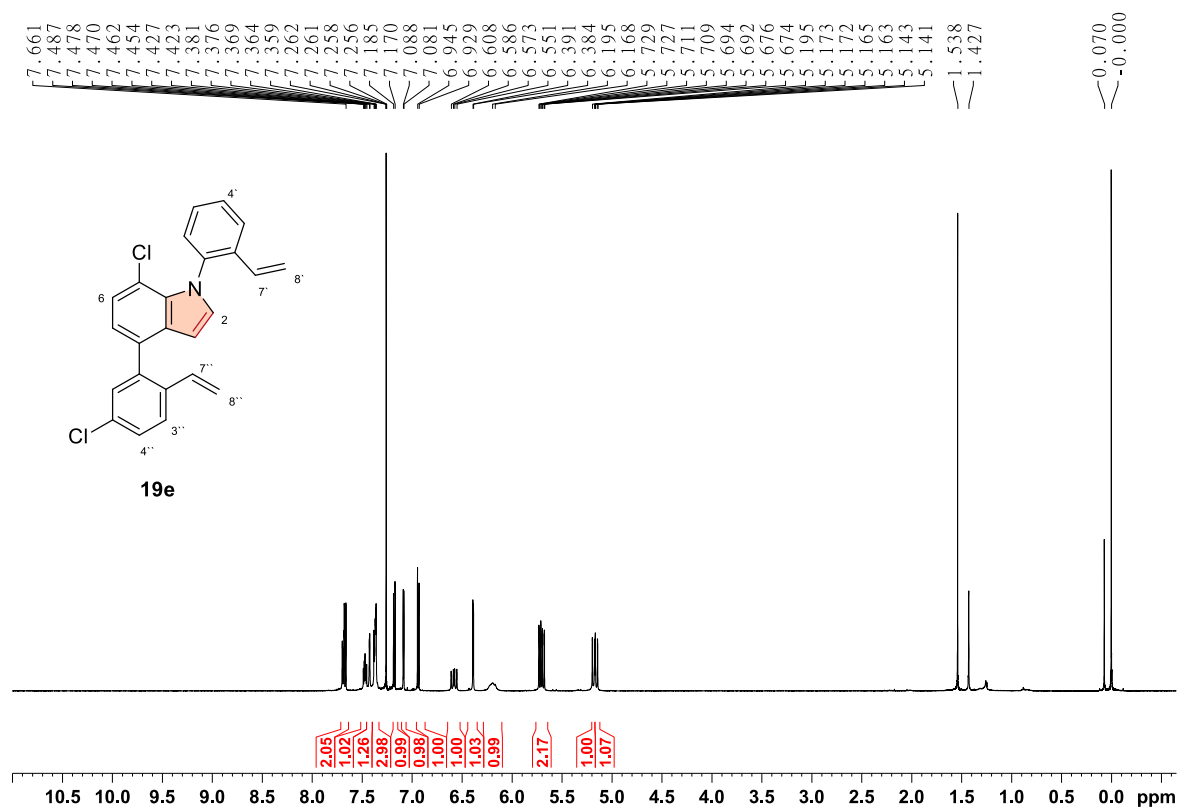


**7-Chloro-1,4-bis(2-vinylphenyl)-1H-indole (19d):**

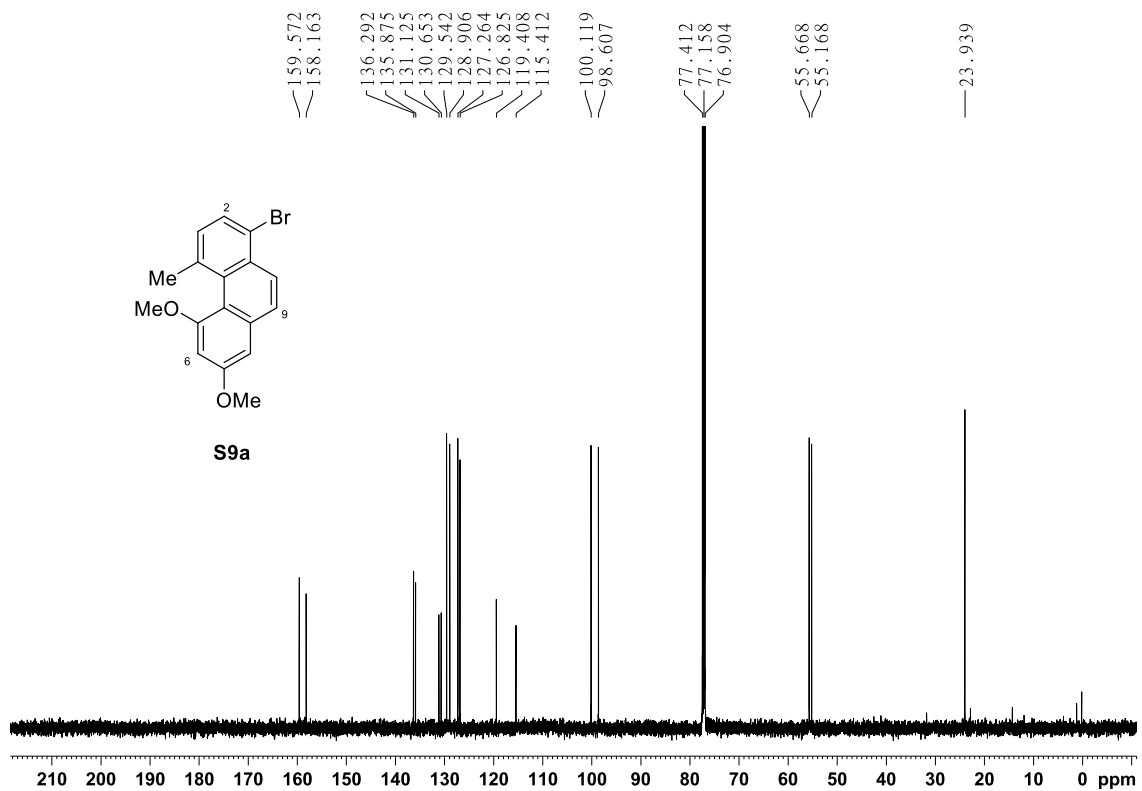
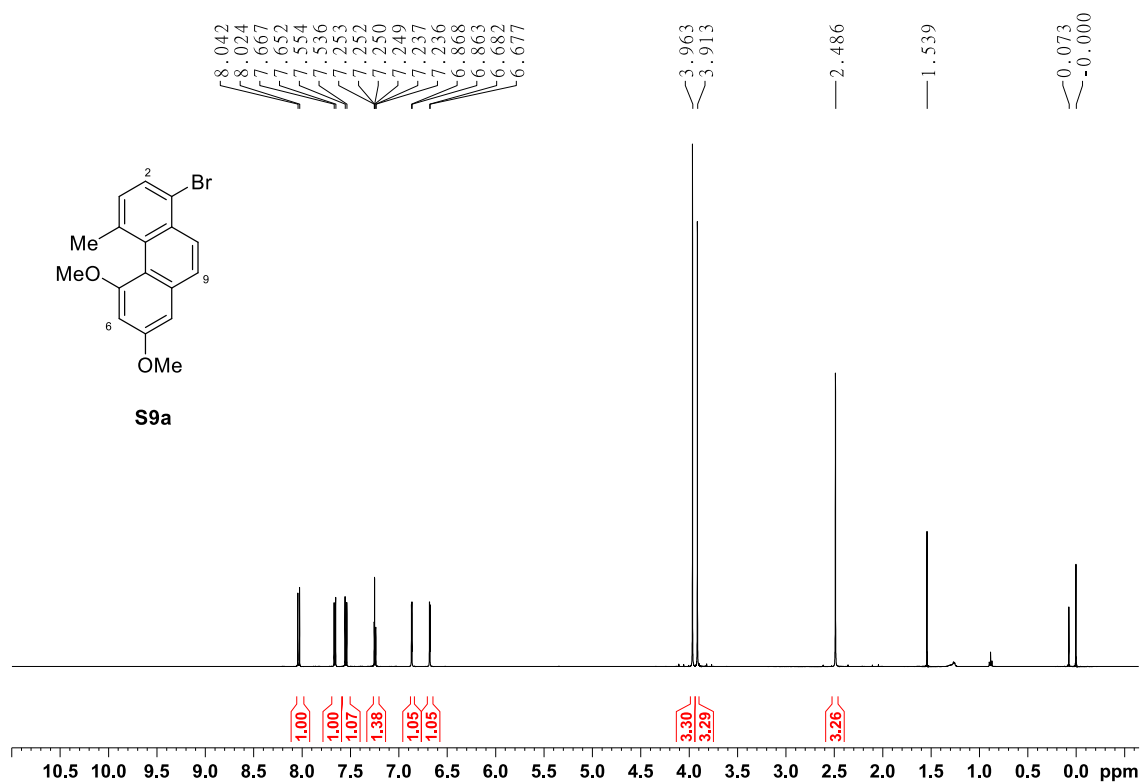




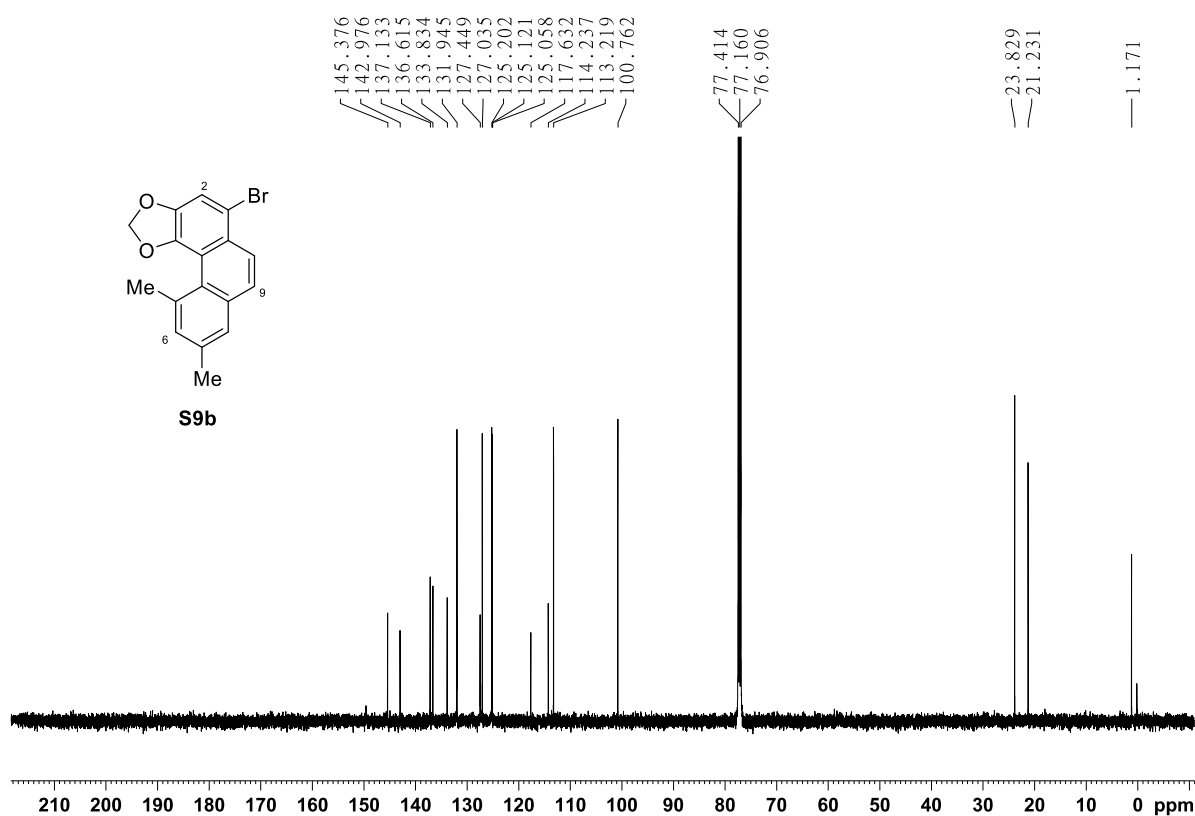
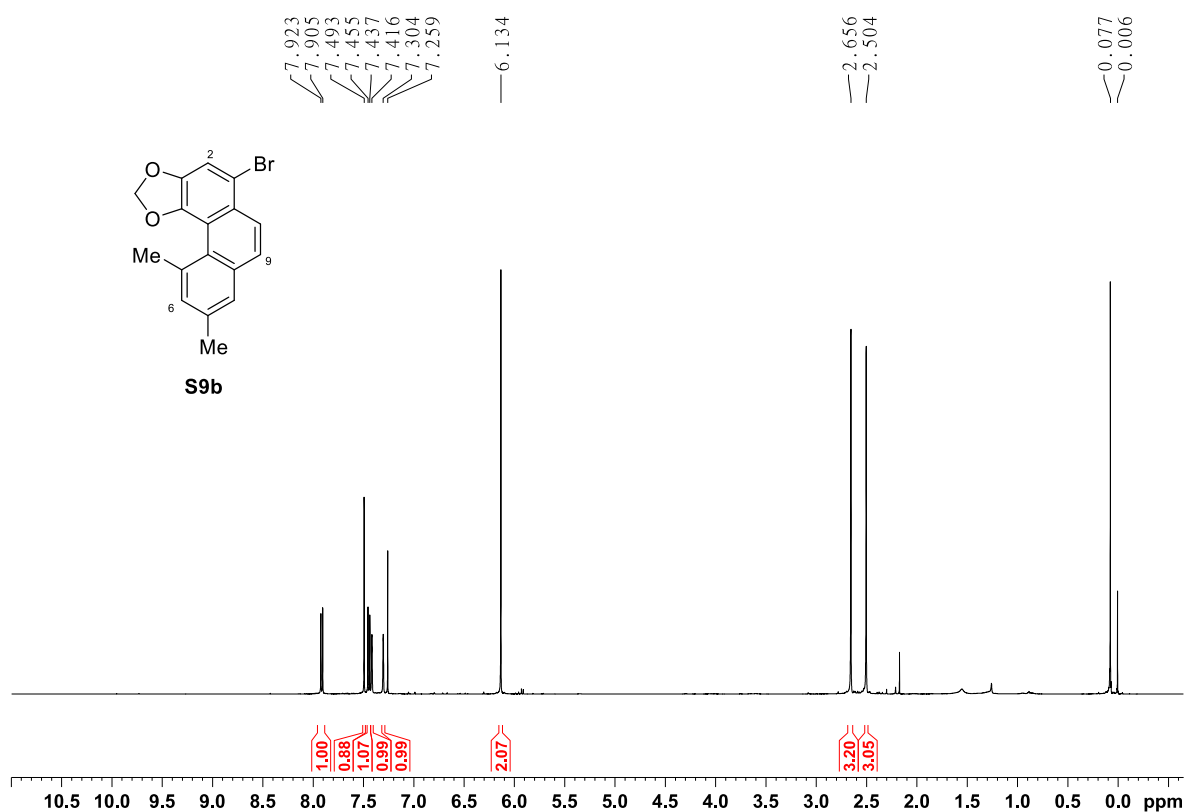
**7-Chloro-4-(5-chloro-2-vinylphenyl)-1-(2-vinylphenyl)-1H-indole (19e):**



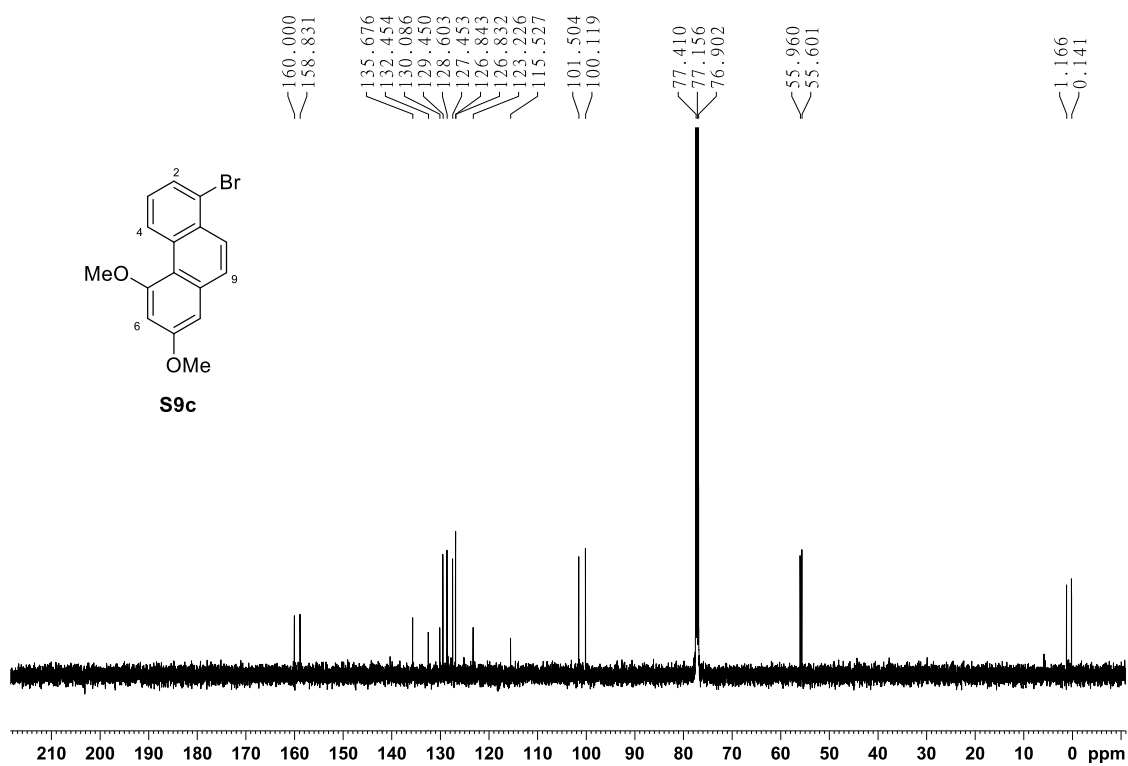
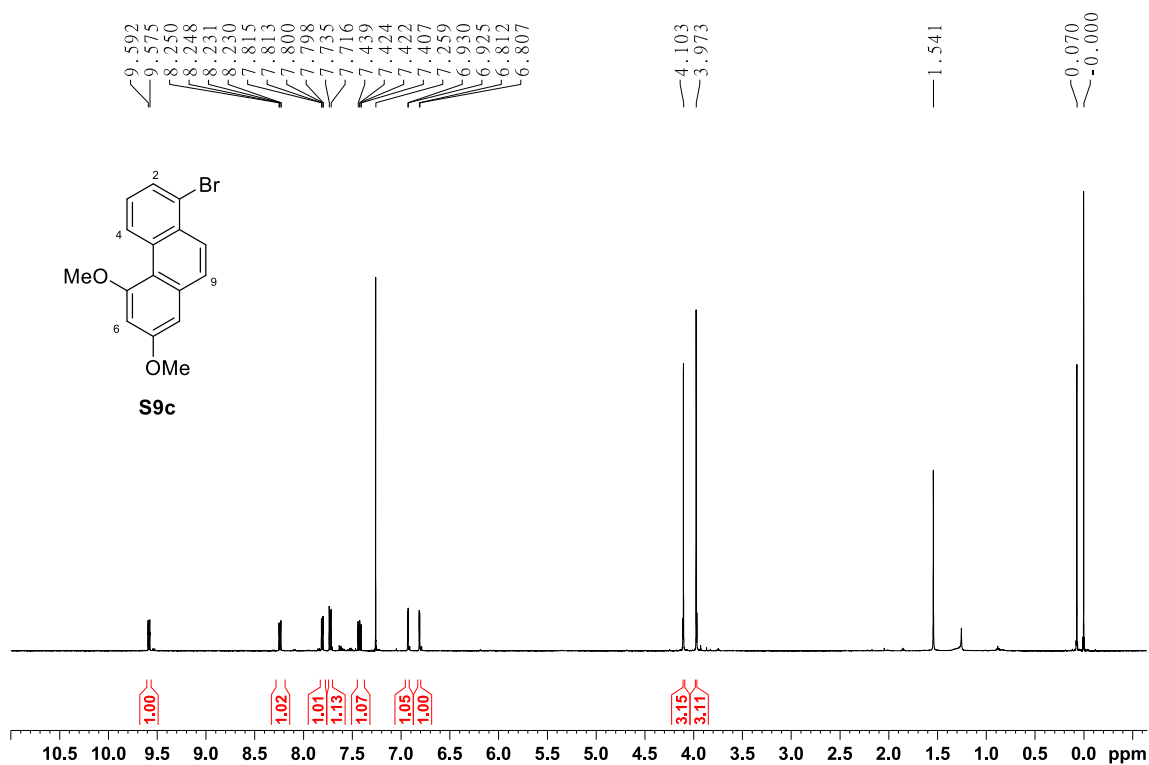
**1-Bromo-5,7-dimethoxy-4-methylphenanthrene (S9a):**



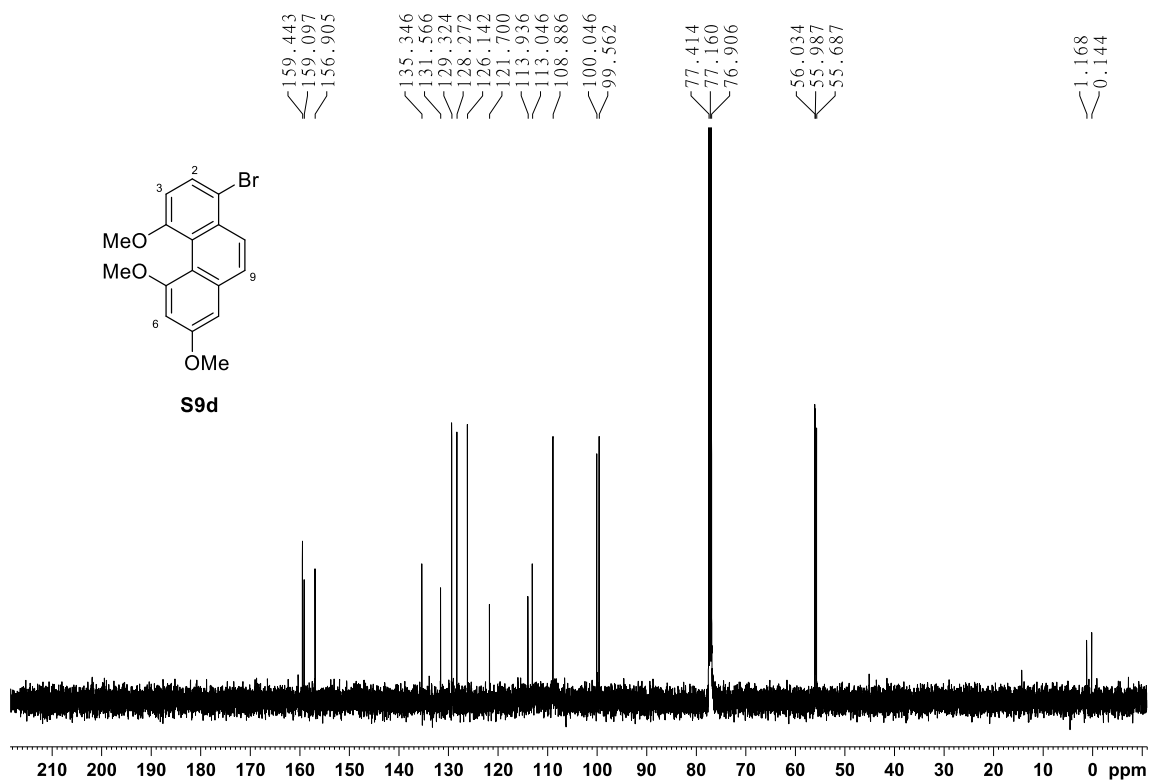
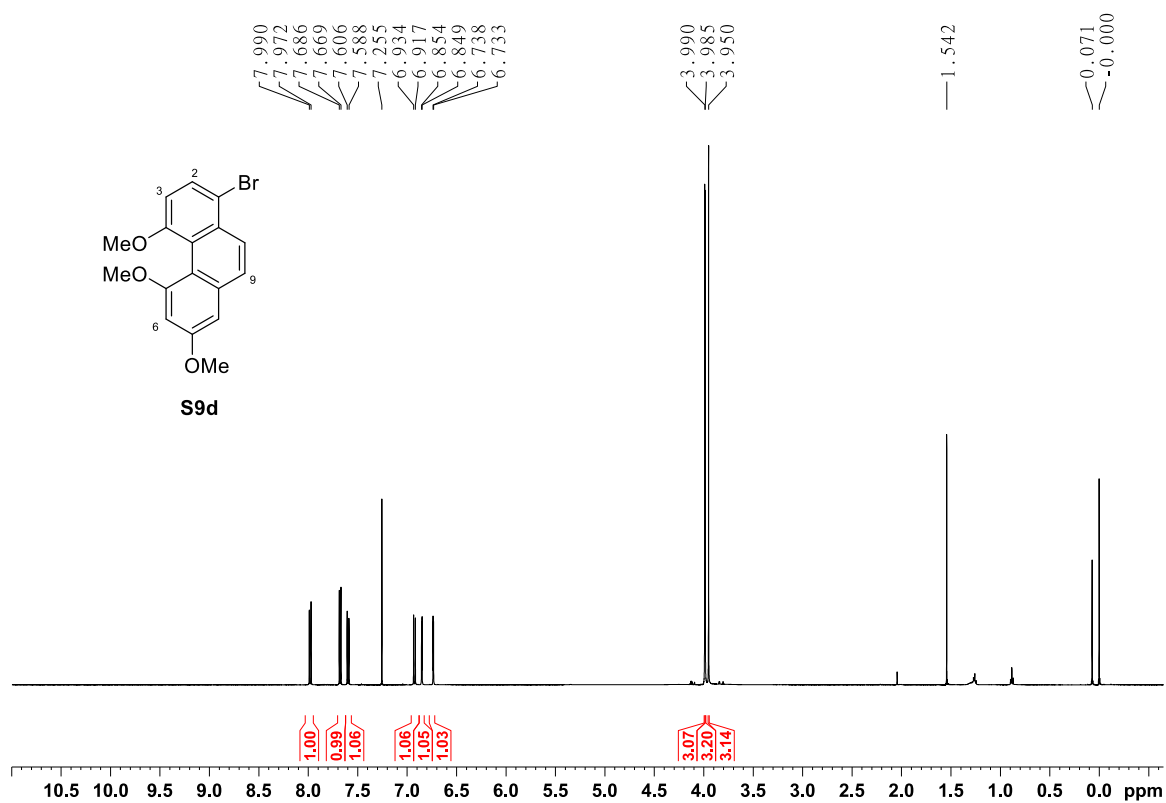
**5-Bromo-9,11-dimethylphenanthro[3,4-d][1,3]dioxole (S9b):**



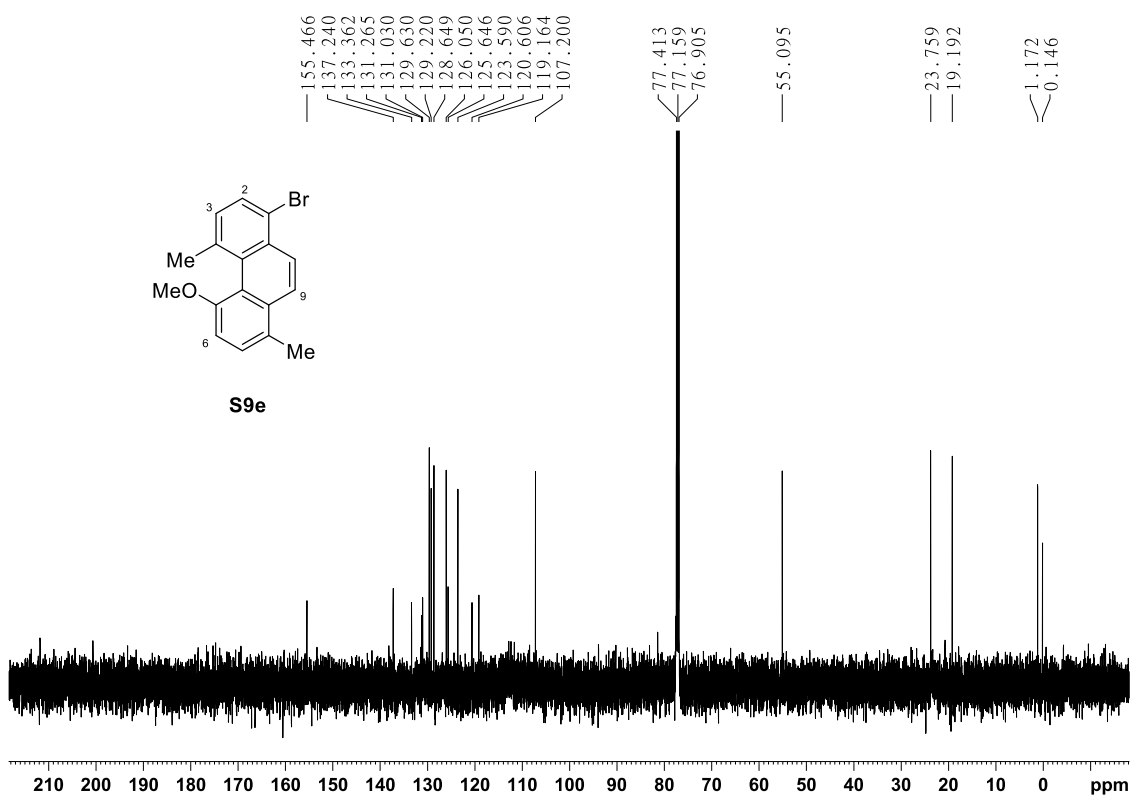
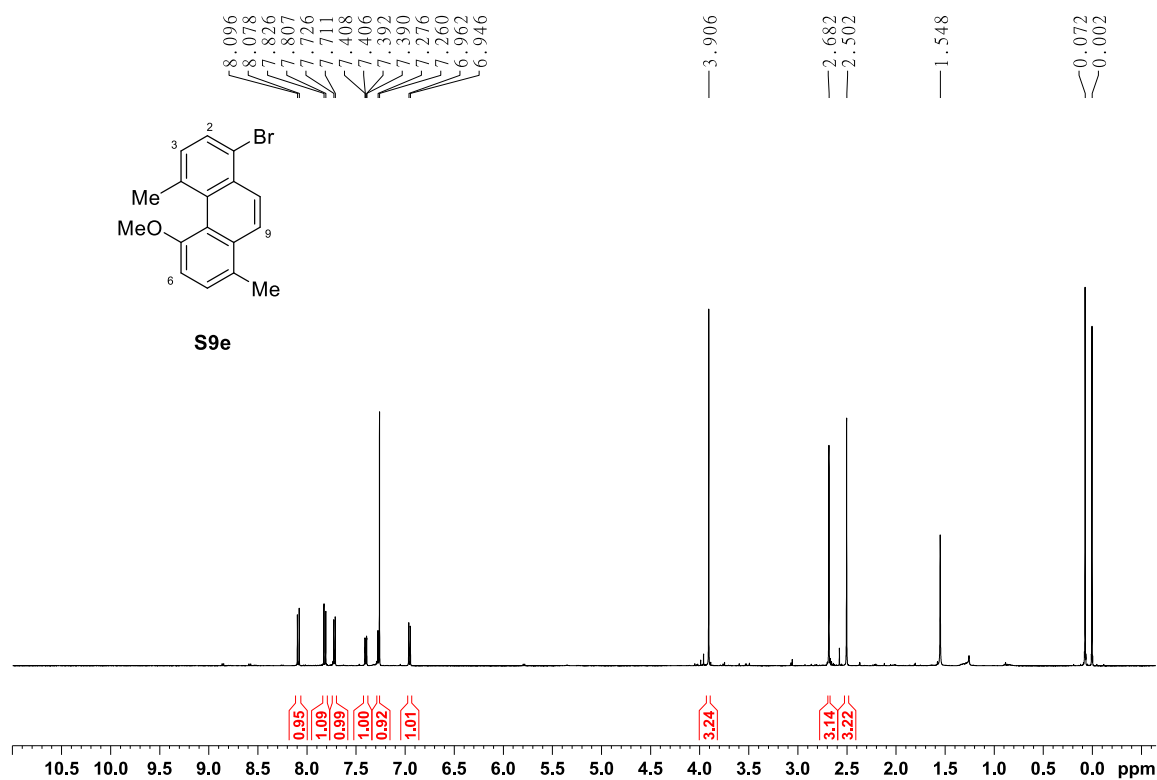
**1-Bromo-5,7-dimethoxyphenanthrene (S9c):**



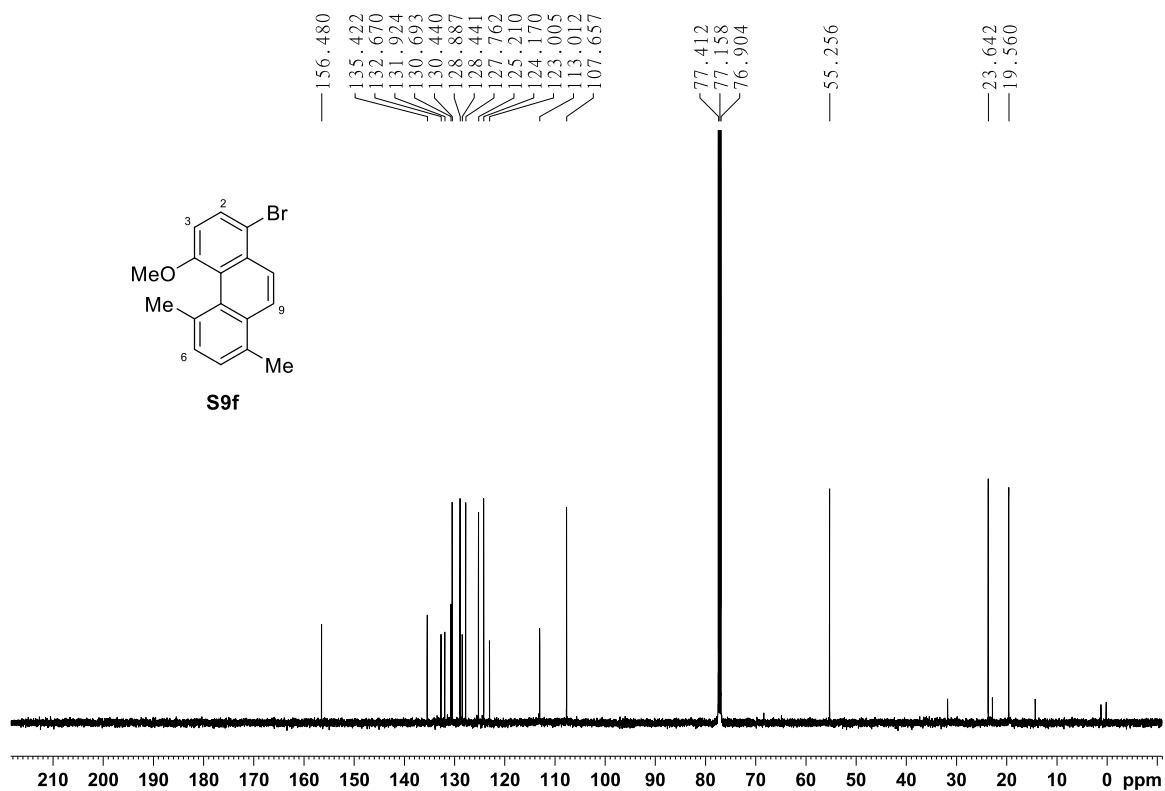
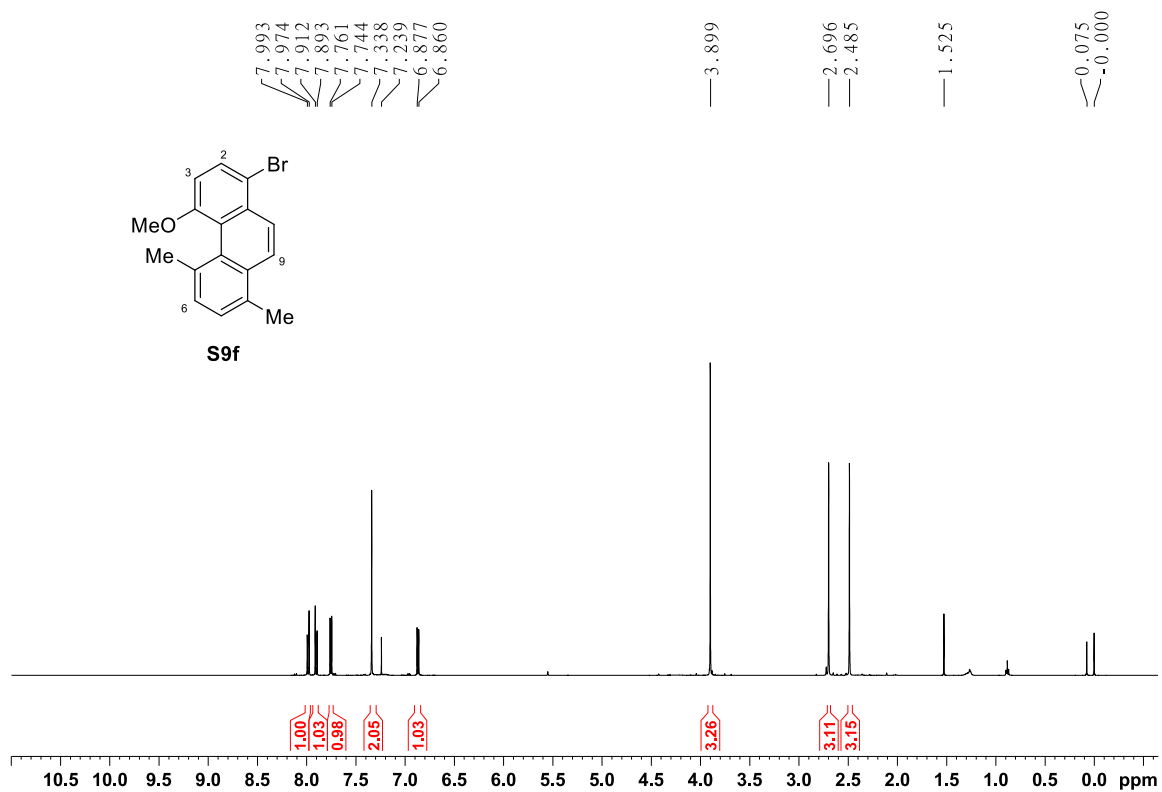
**1-Bromo-4,5,7-trimethoxyphenanthrene (S9d):**



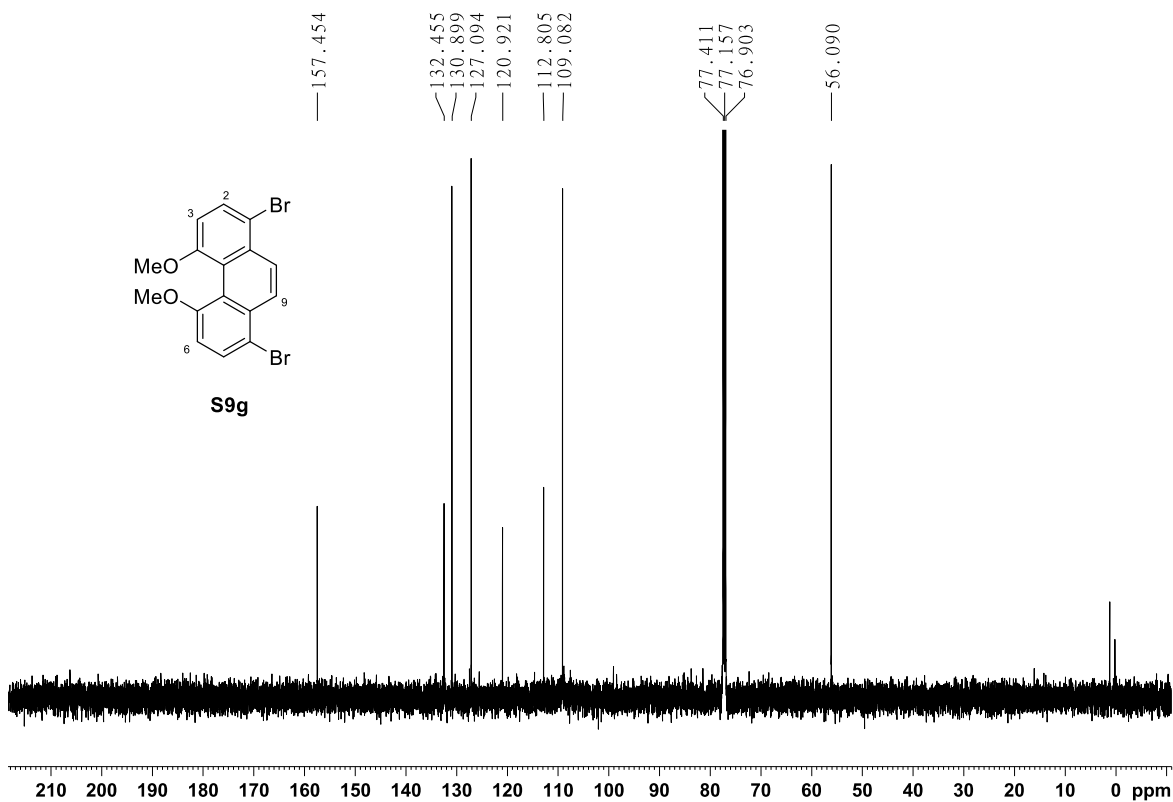
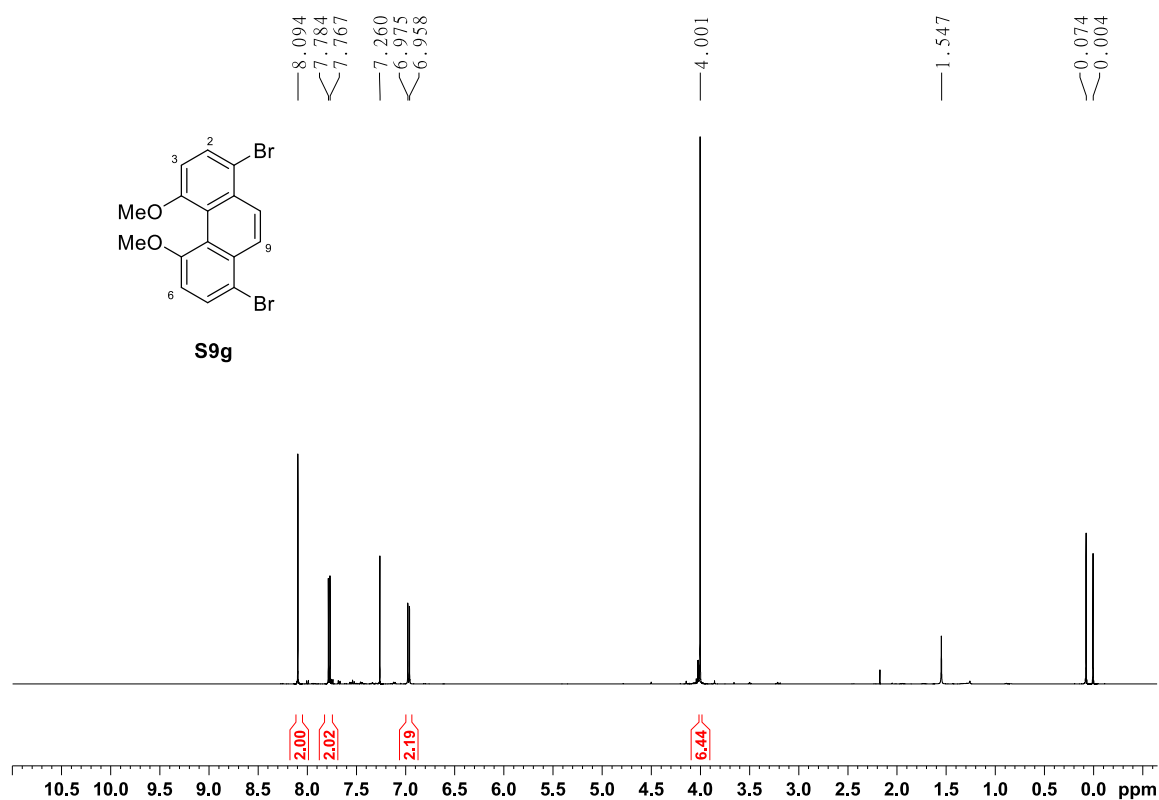
**1-Bromo-5-methoxy-4,8-dimethylphenanthrene (S9e):**



**1-Bromo-4-methoxy-5,8-dimethylphenanthrene (S9f):**

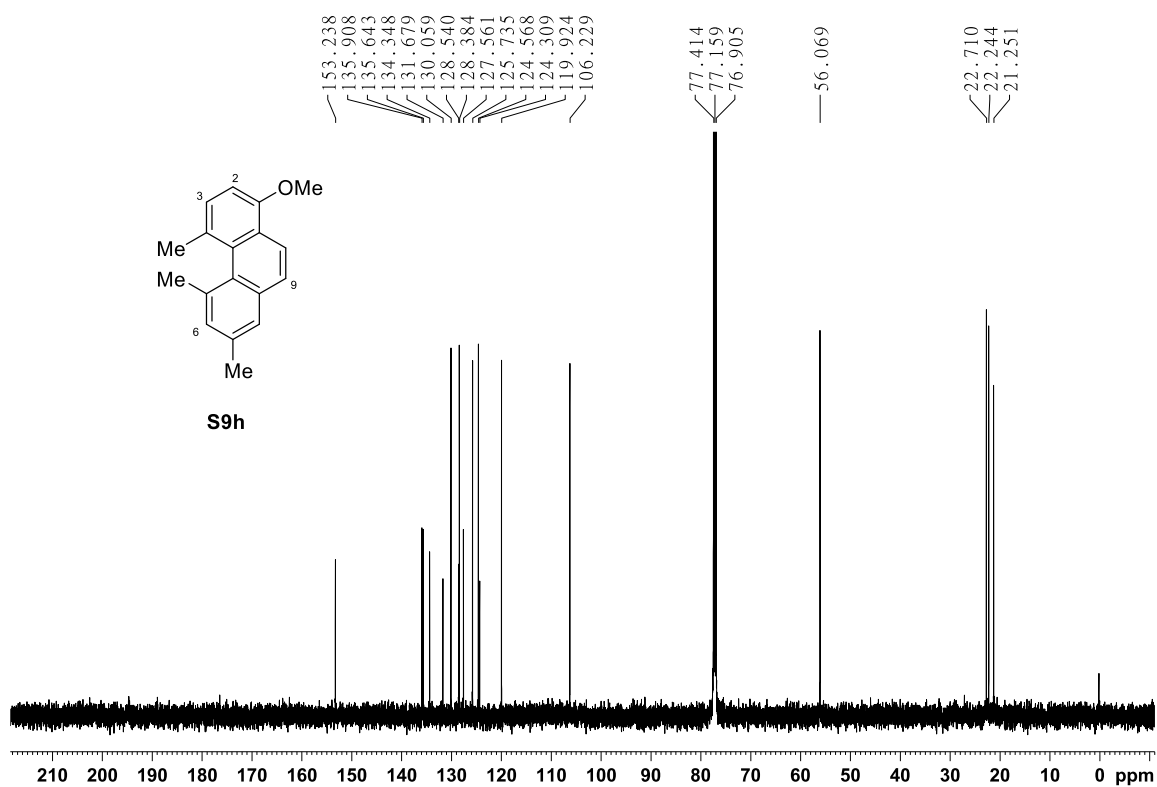
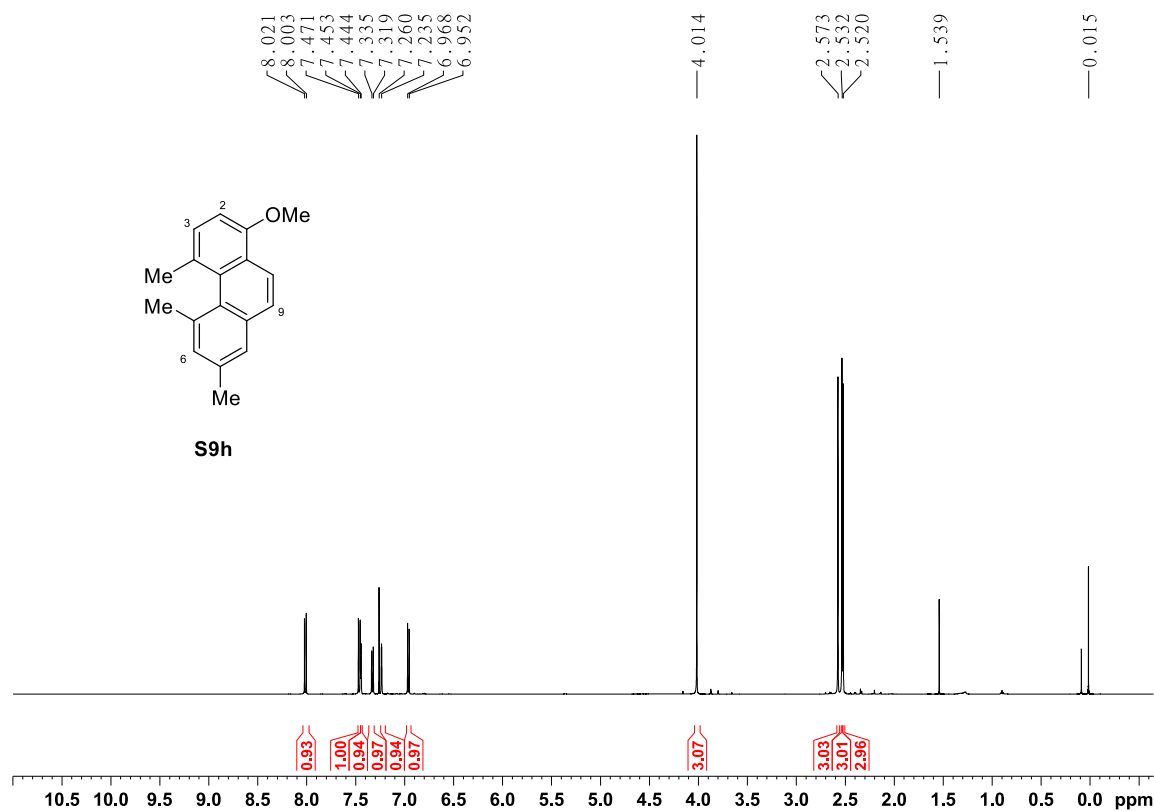


# 1,8-Dibromo-4,5-dimethoxyphenanthrene (S9g):

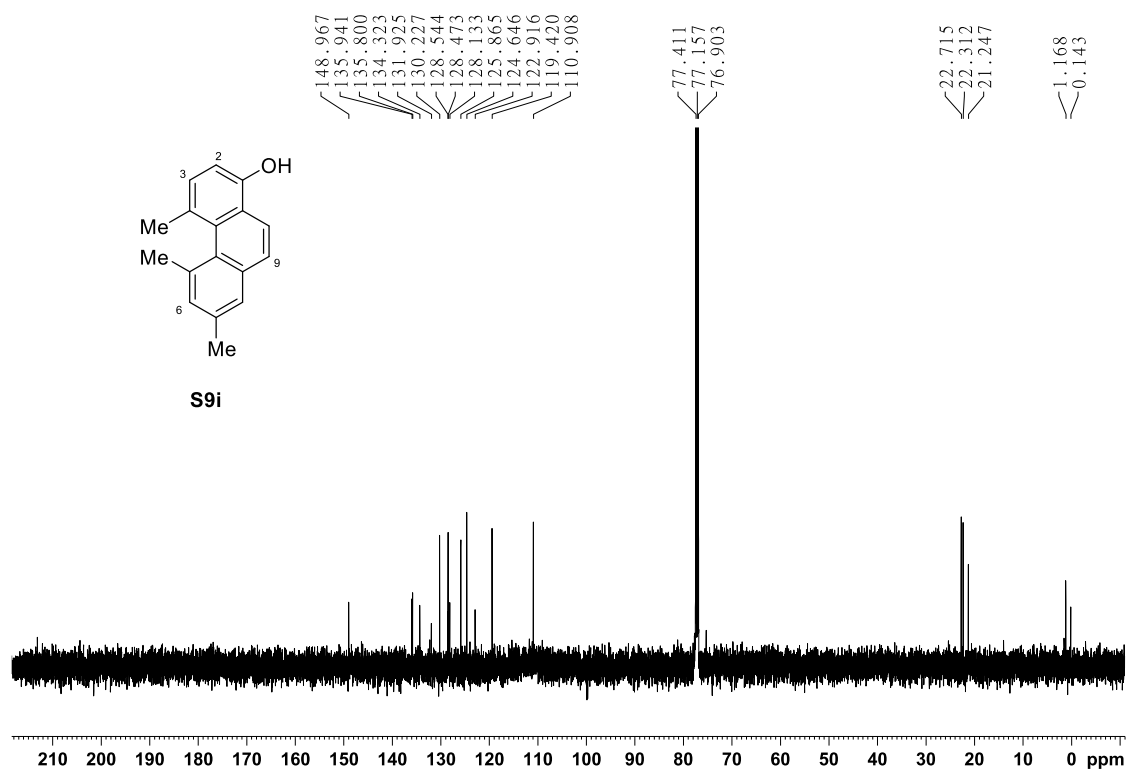
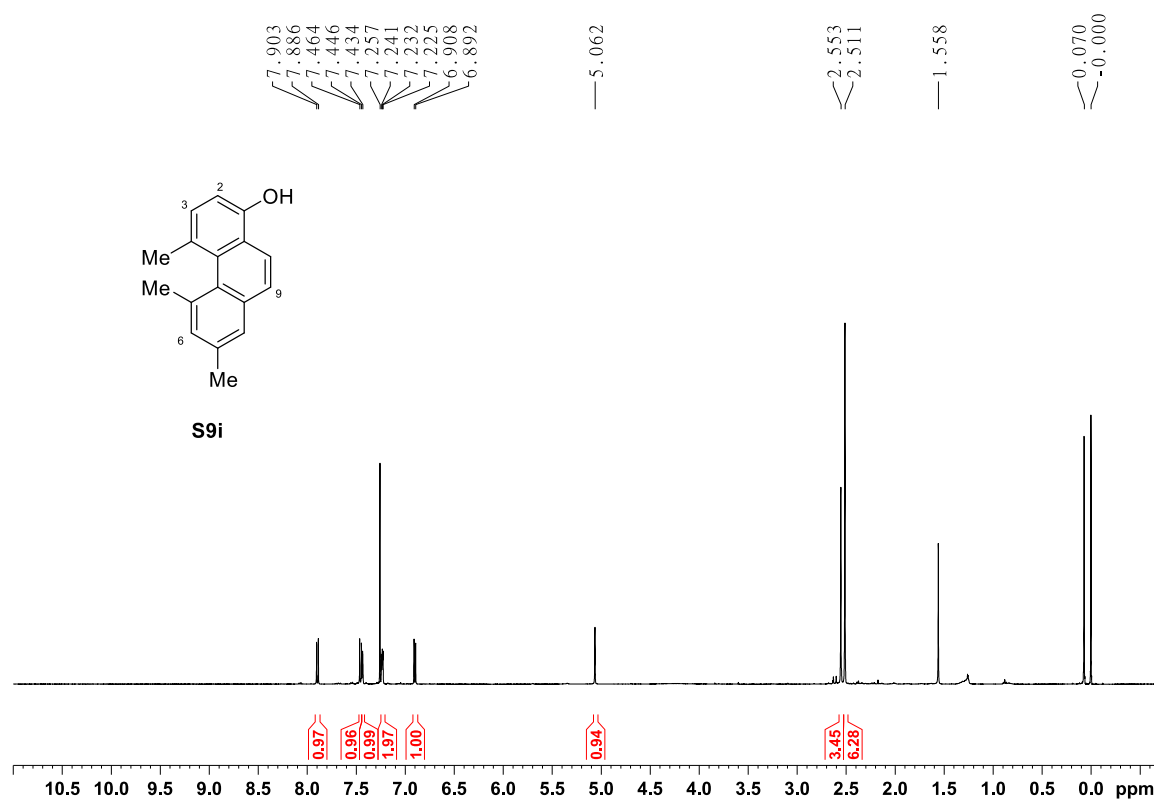




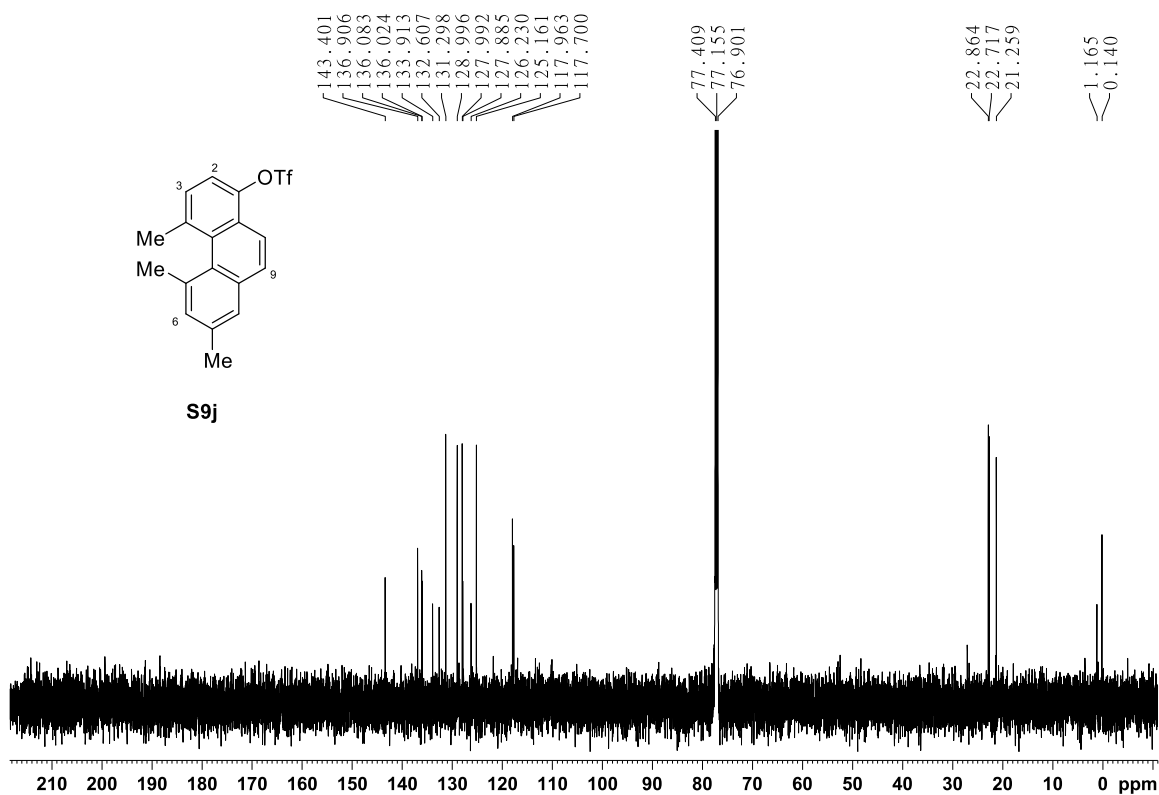
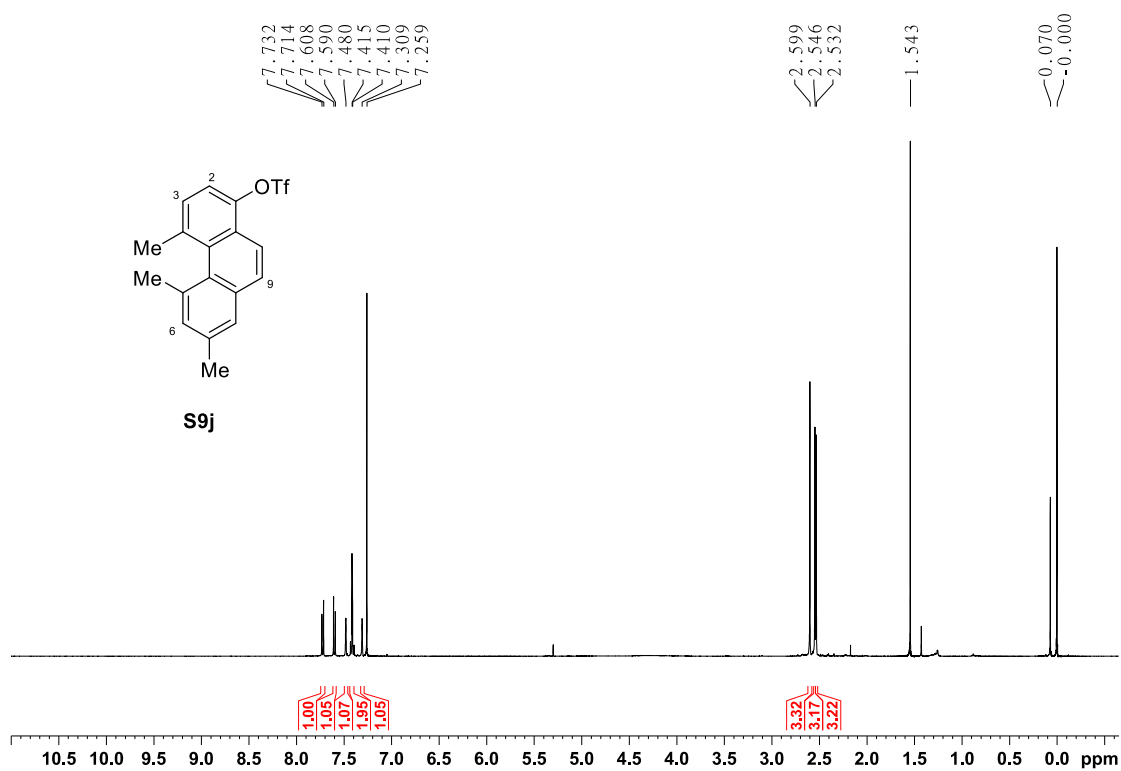
# 1-Methoxy-4,5,7-trimethylphenanthrene (S9h):

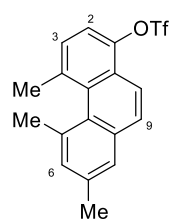


# 4,5,7-Trimethylphenanthren-1-ol (S9i):

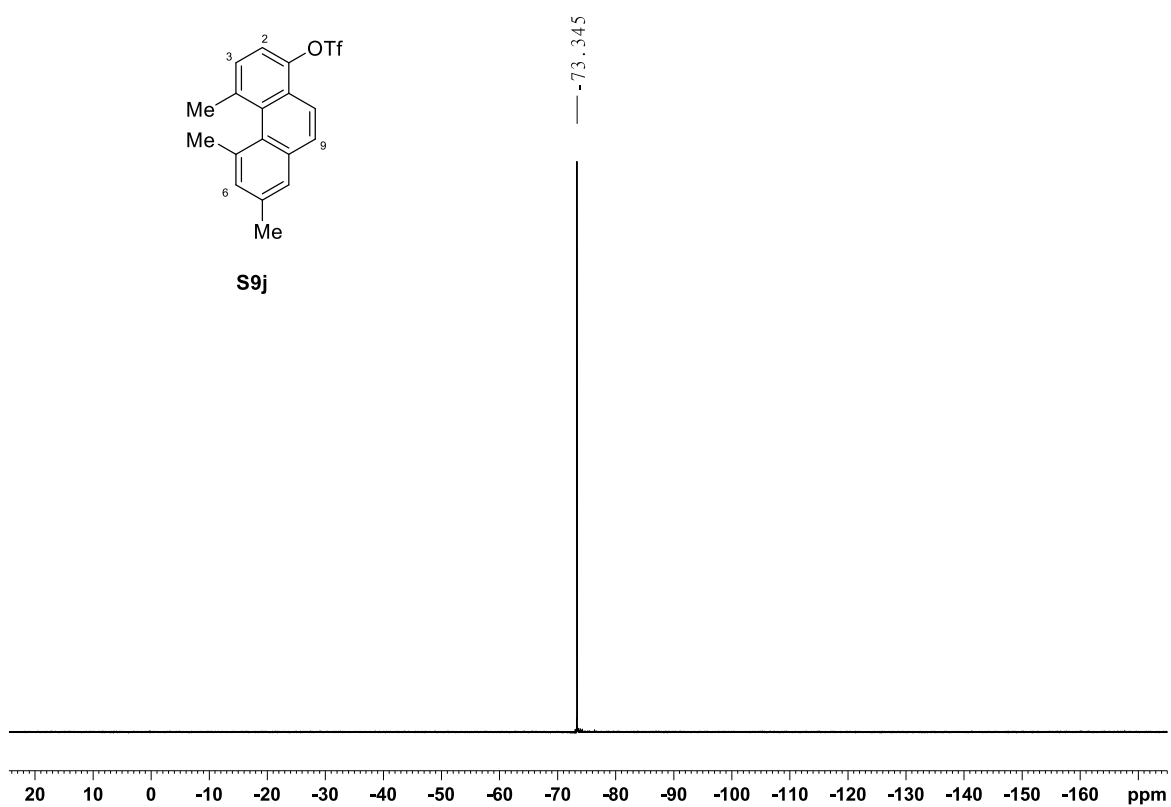


**4,5,7-Trimethylphenanthren-1-yl trifluoromethanesulfonate (S9j):**

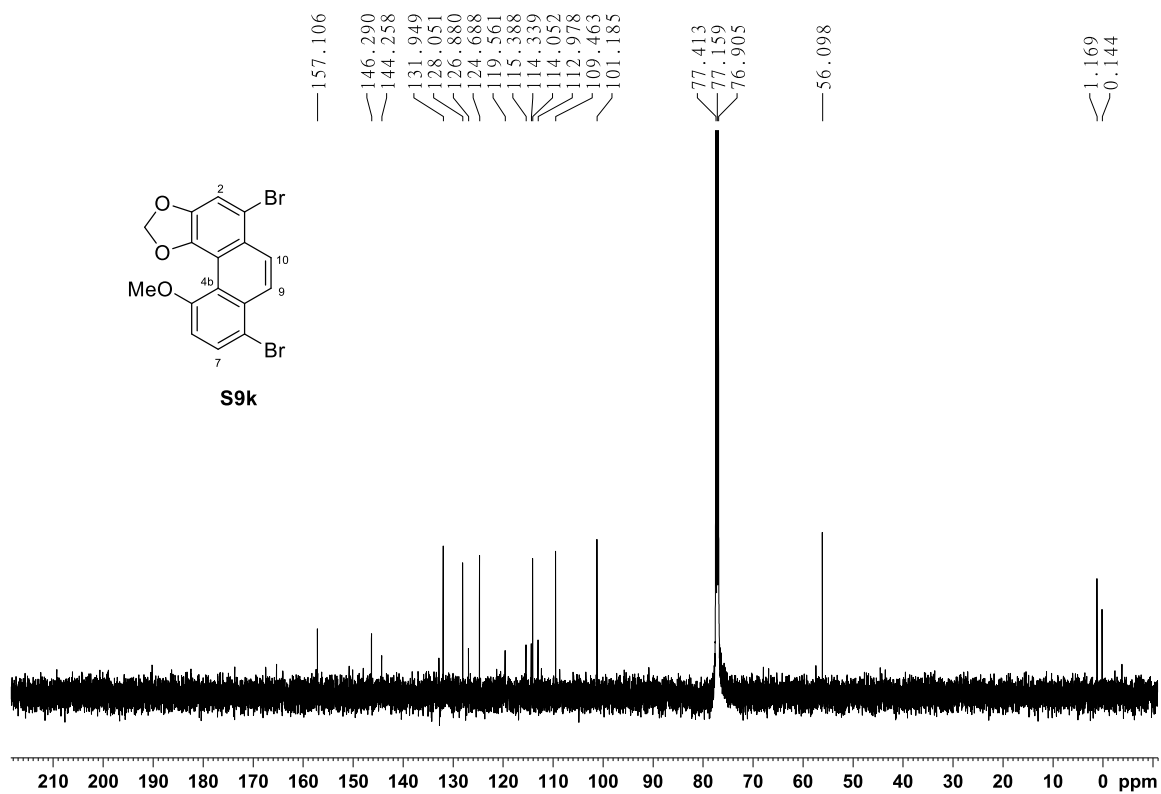
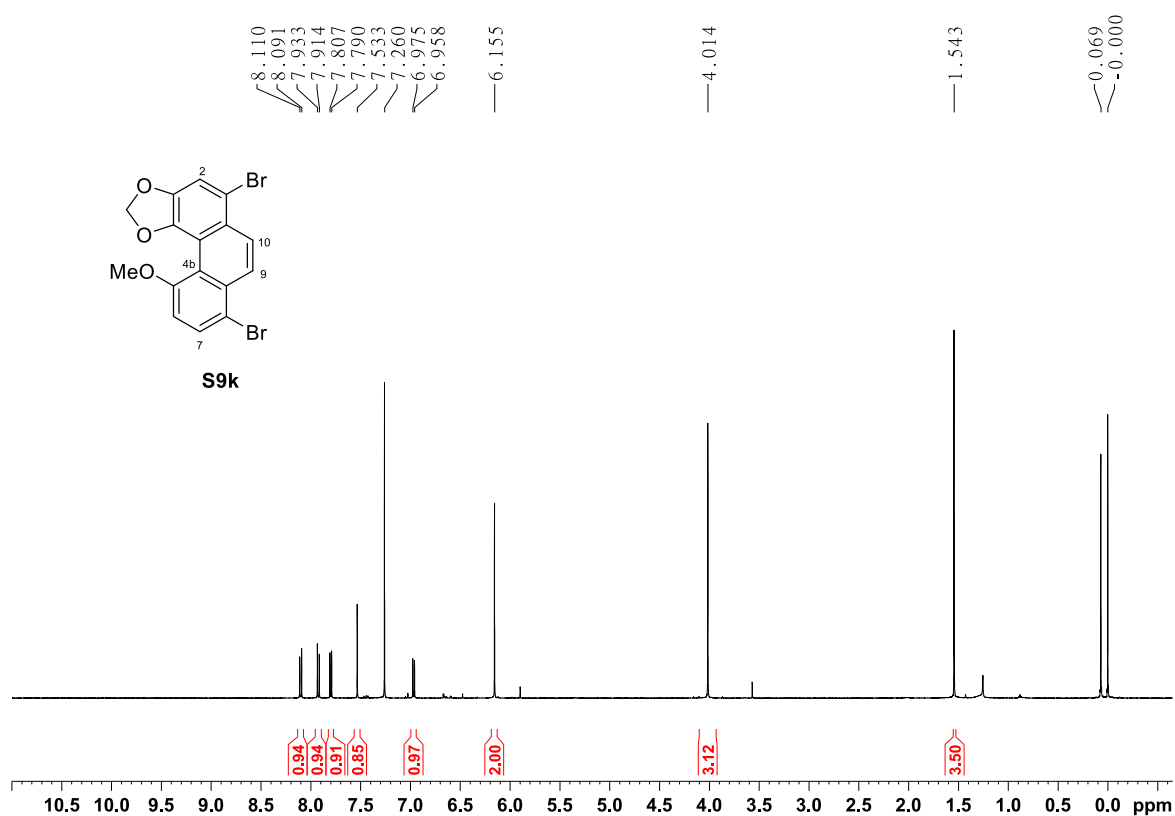




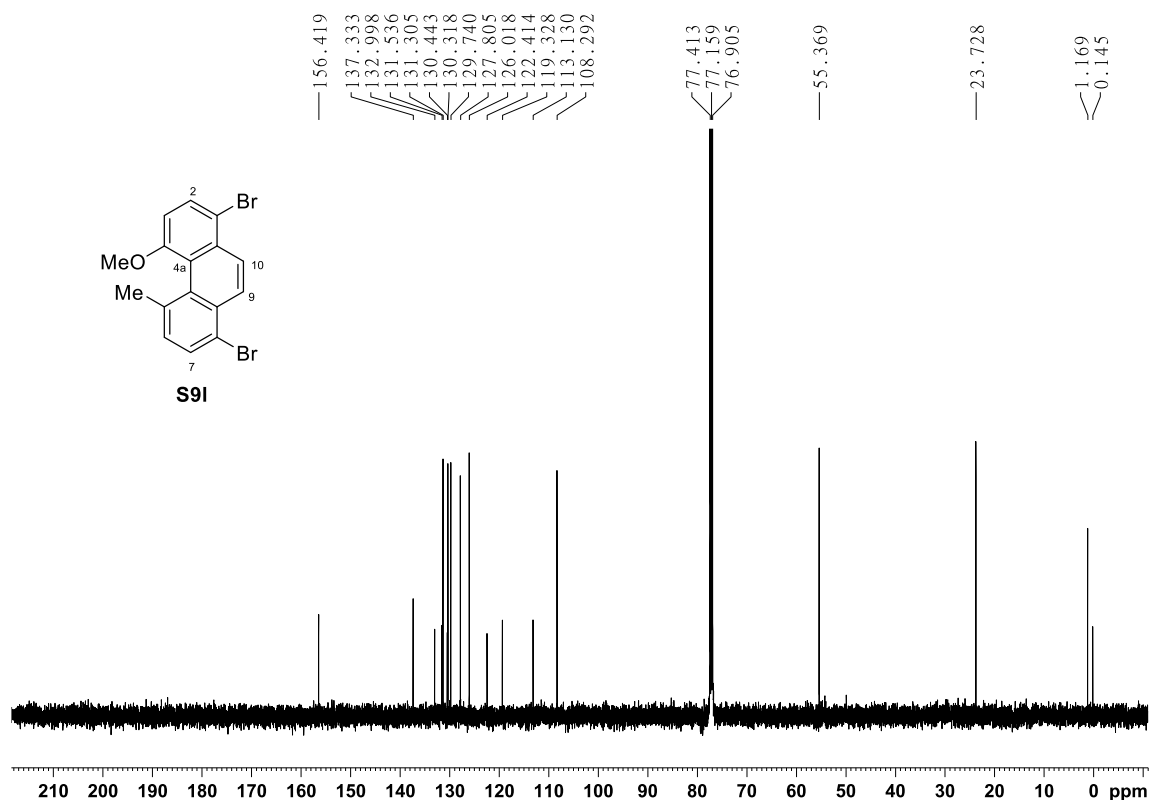
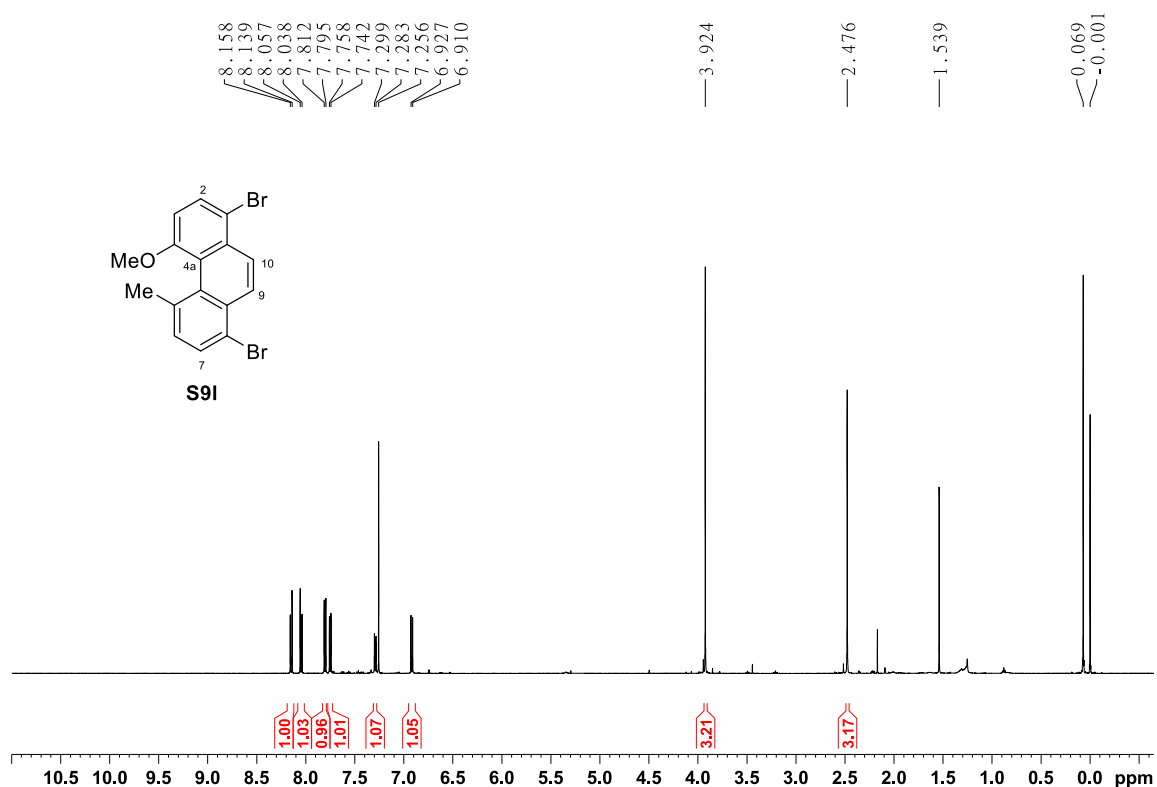
S9j



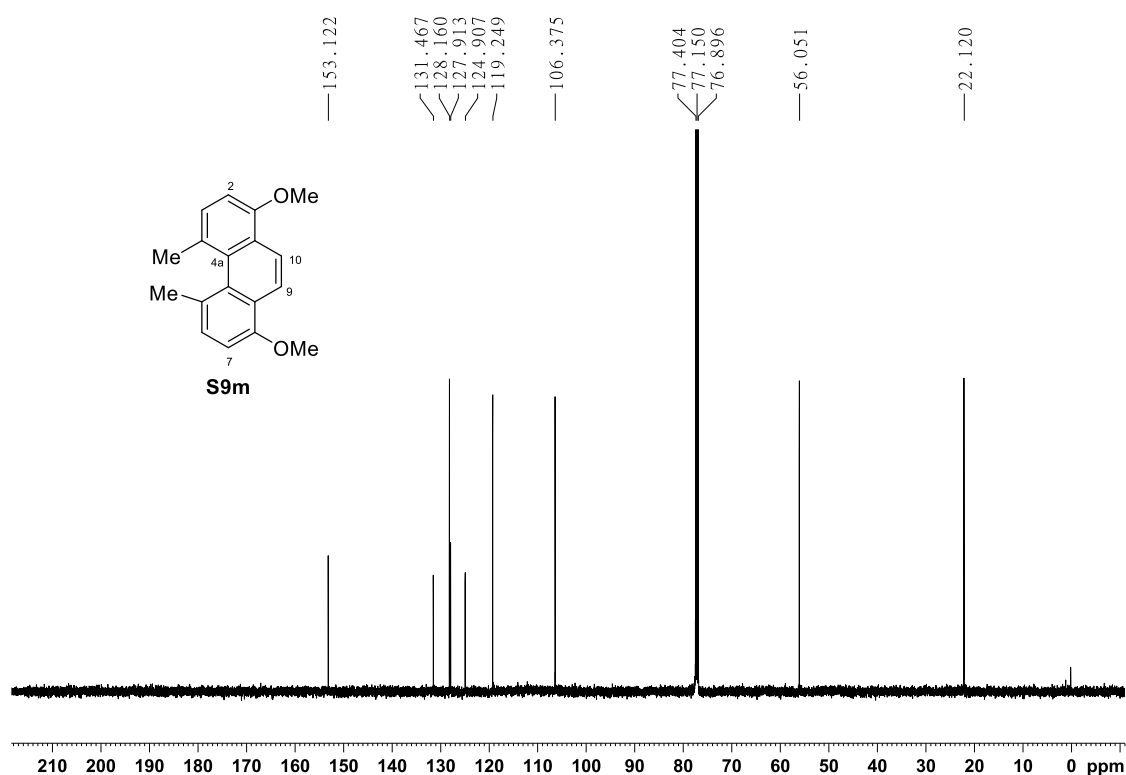
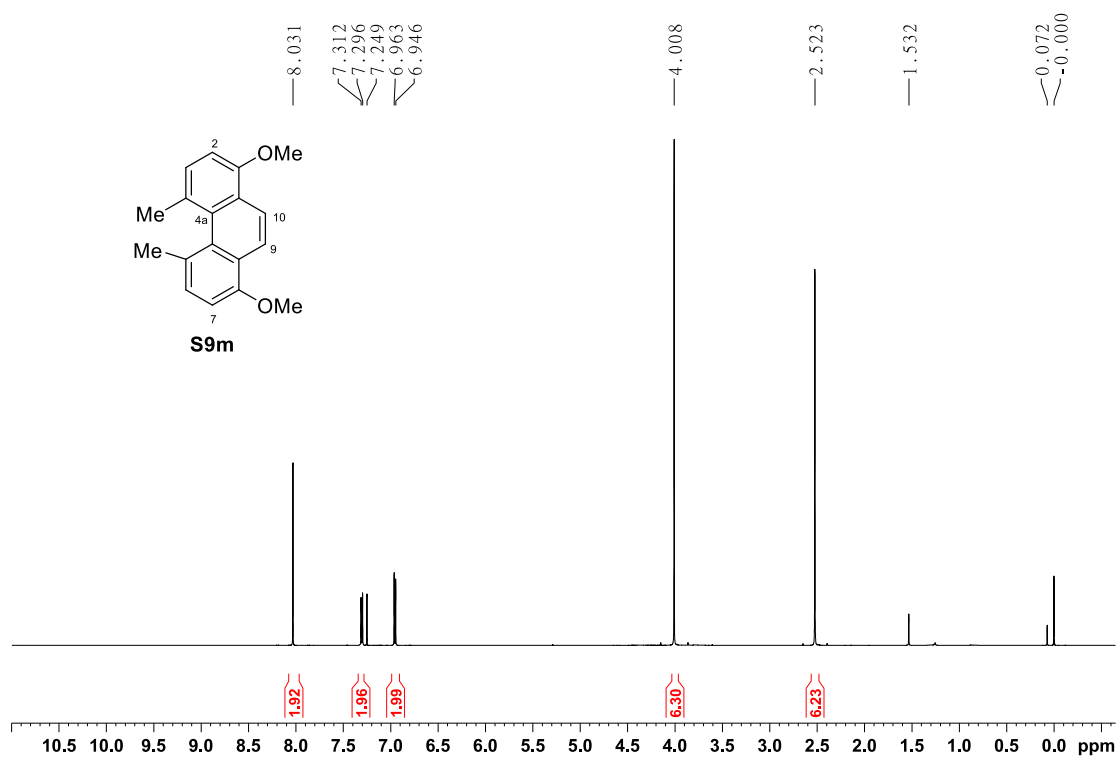
**5,8-Dibromo-11-methoxyphenanthro[3,4-d][1,3]dioxole (S9k):**



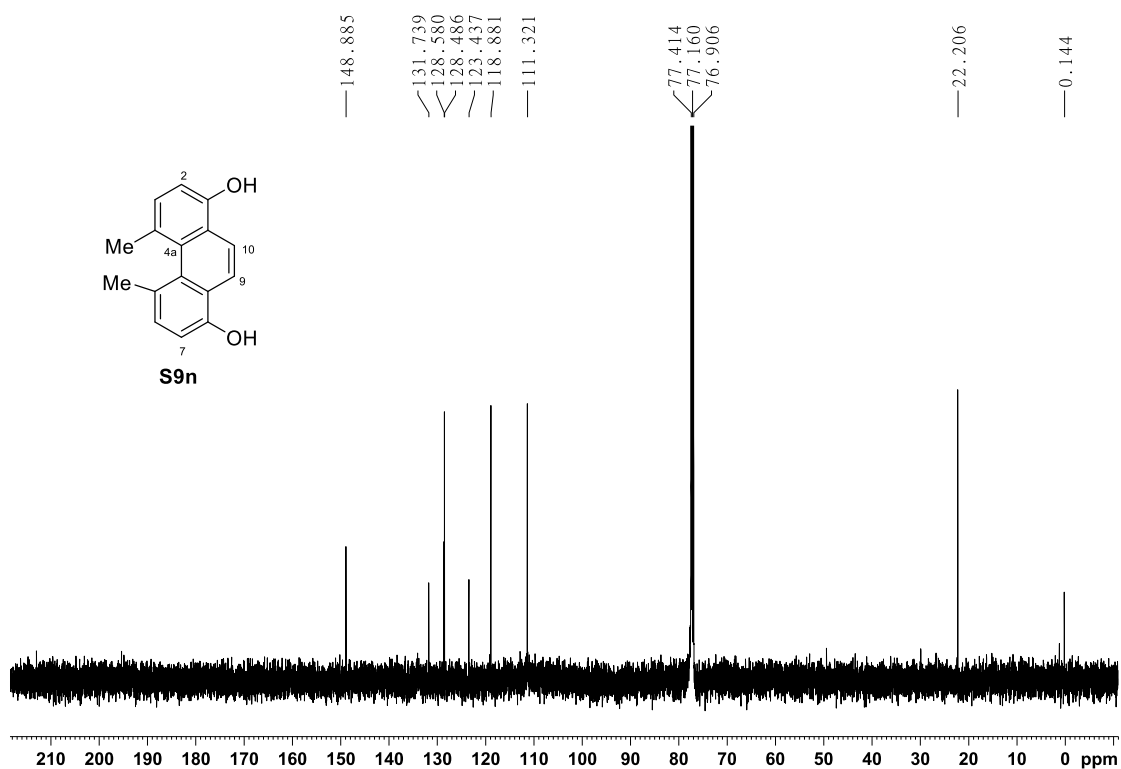
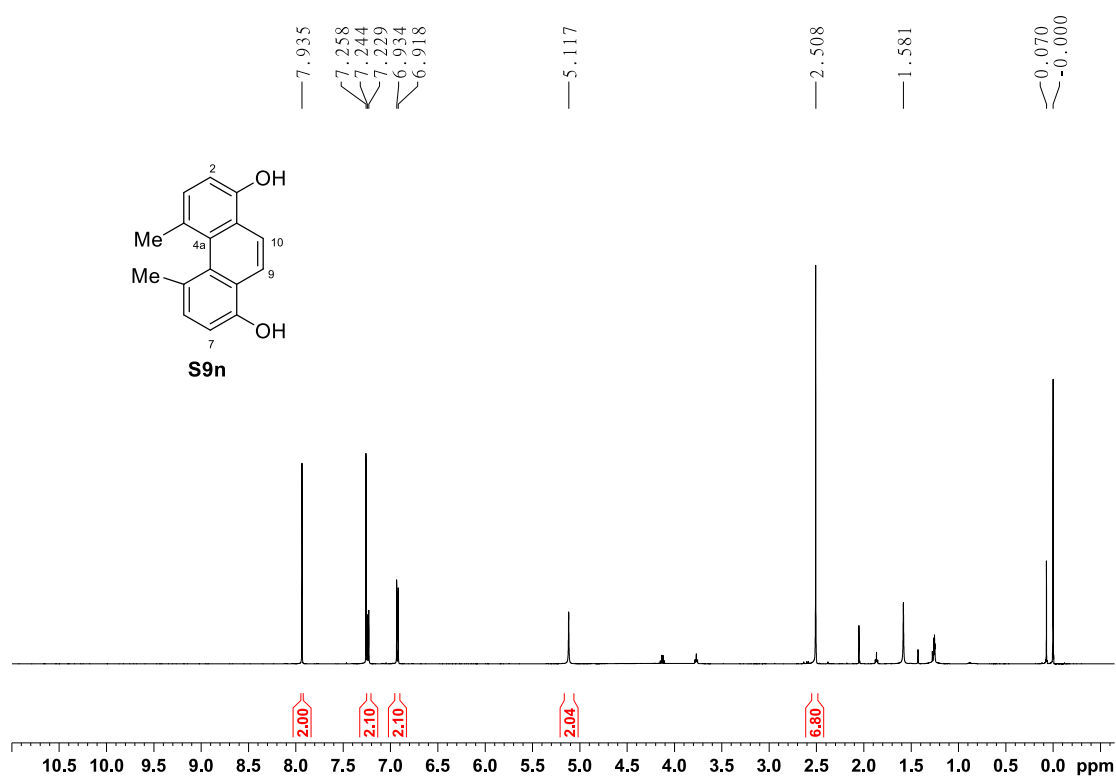
**1,8-Dibromo-4-methoxy-5-methylphenanthrene (S9I):**



# **1,8-Dimethoxy-4,5-dimethylphenanthrene (S9m):**

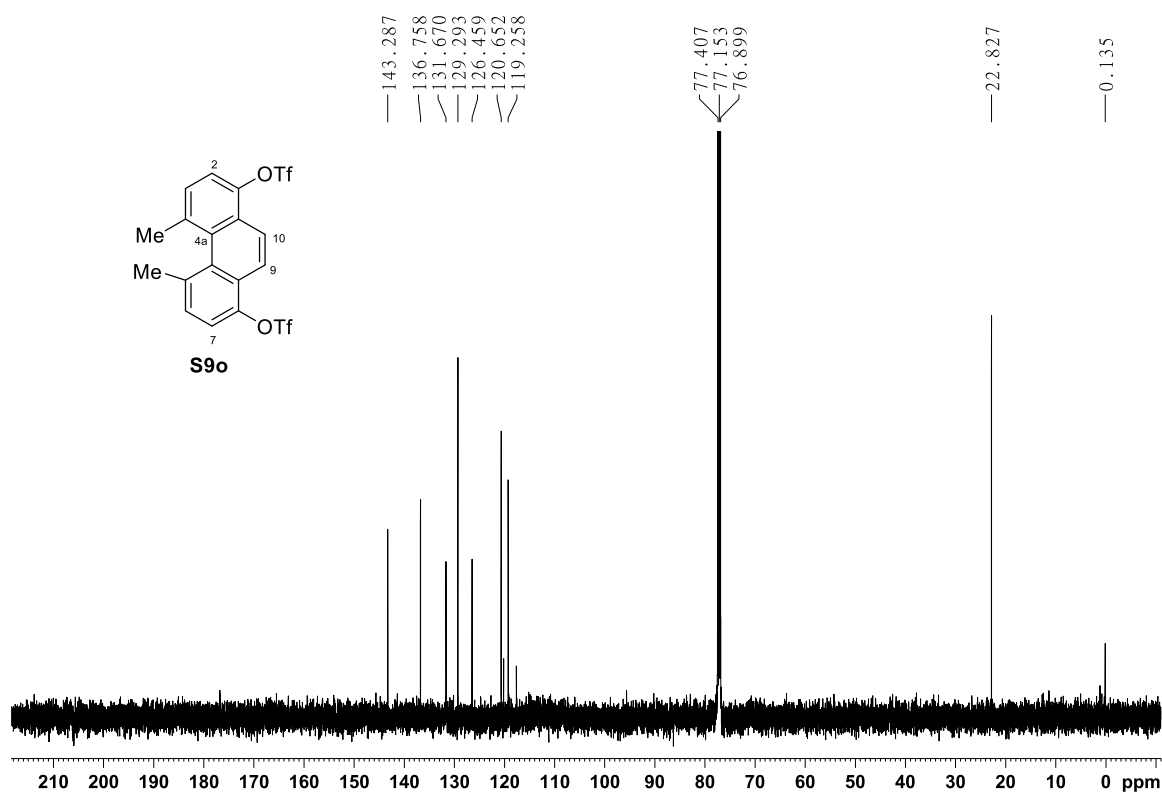
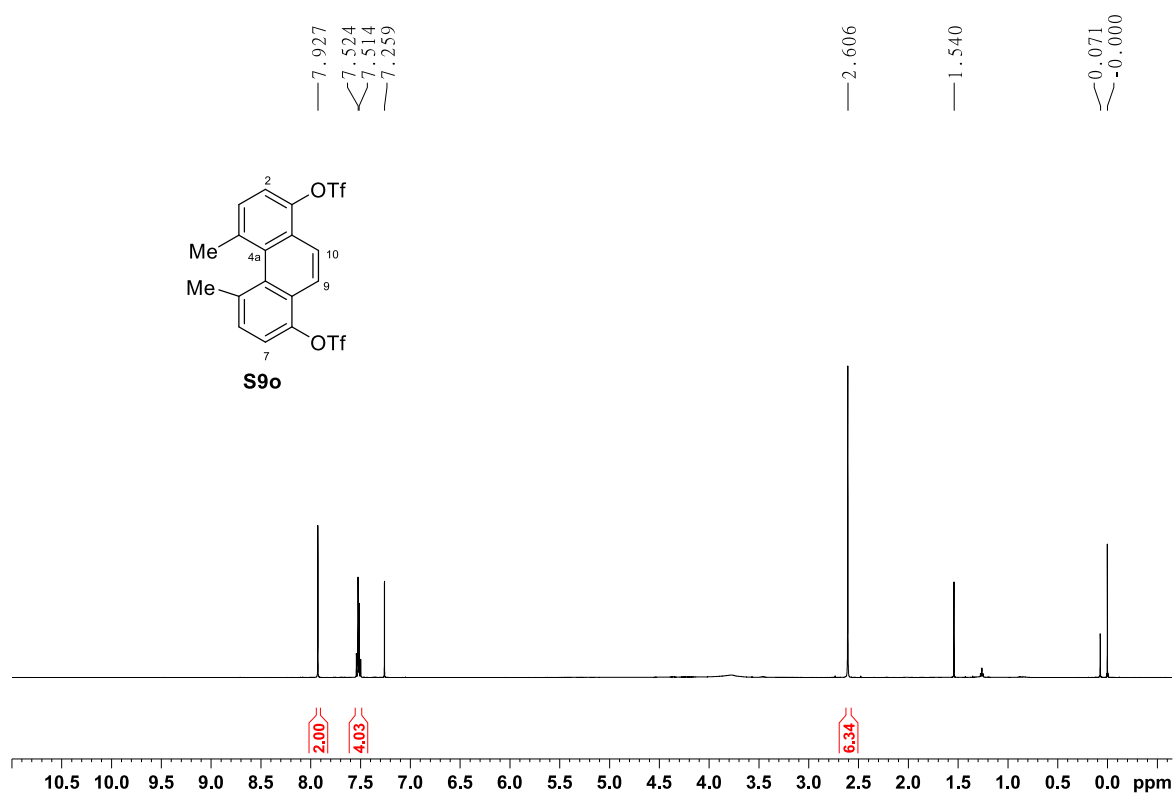


# 4,5-Dimethylphenanthrene-1,8-diol (S9n):

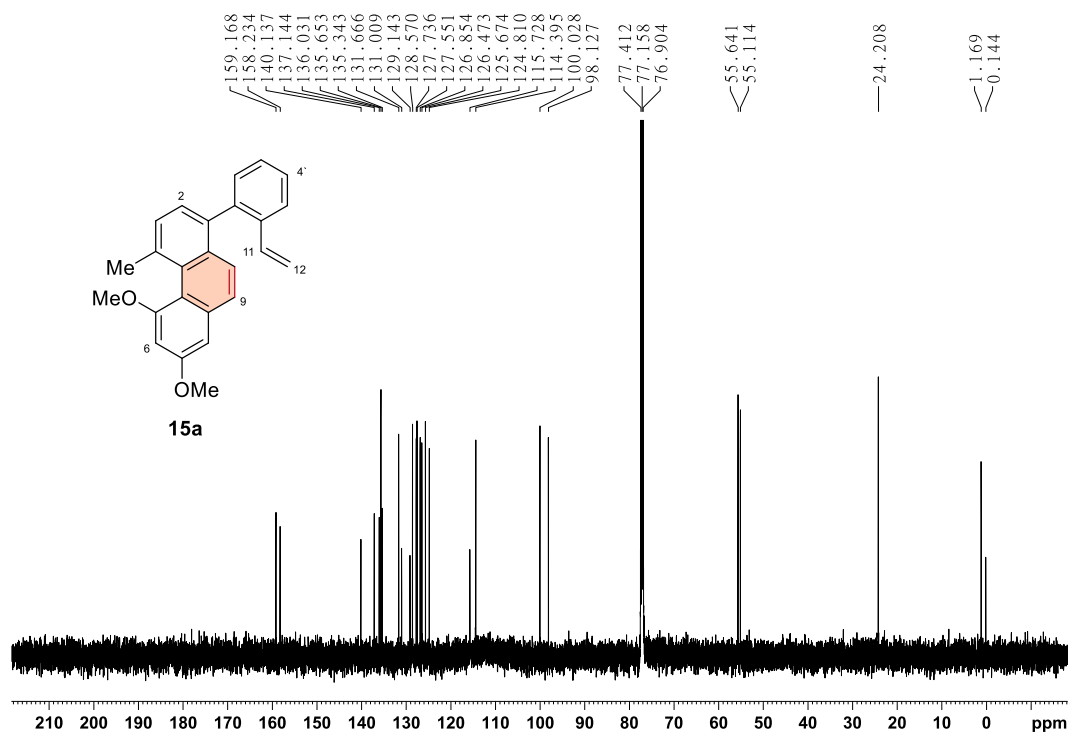
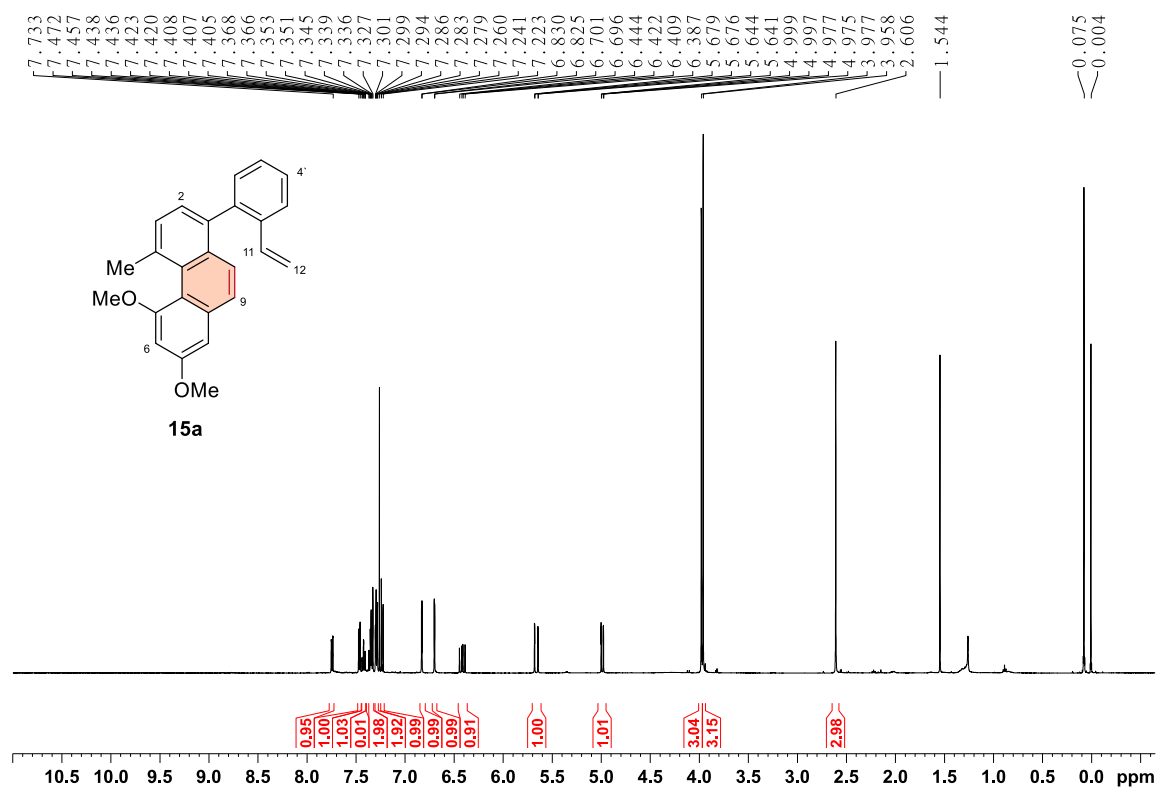




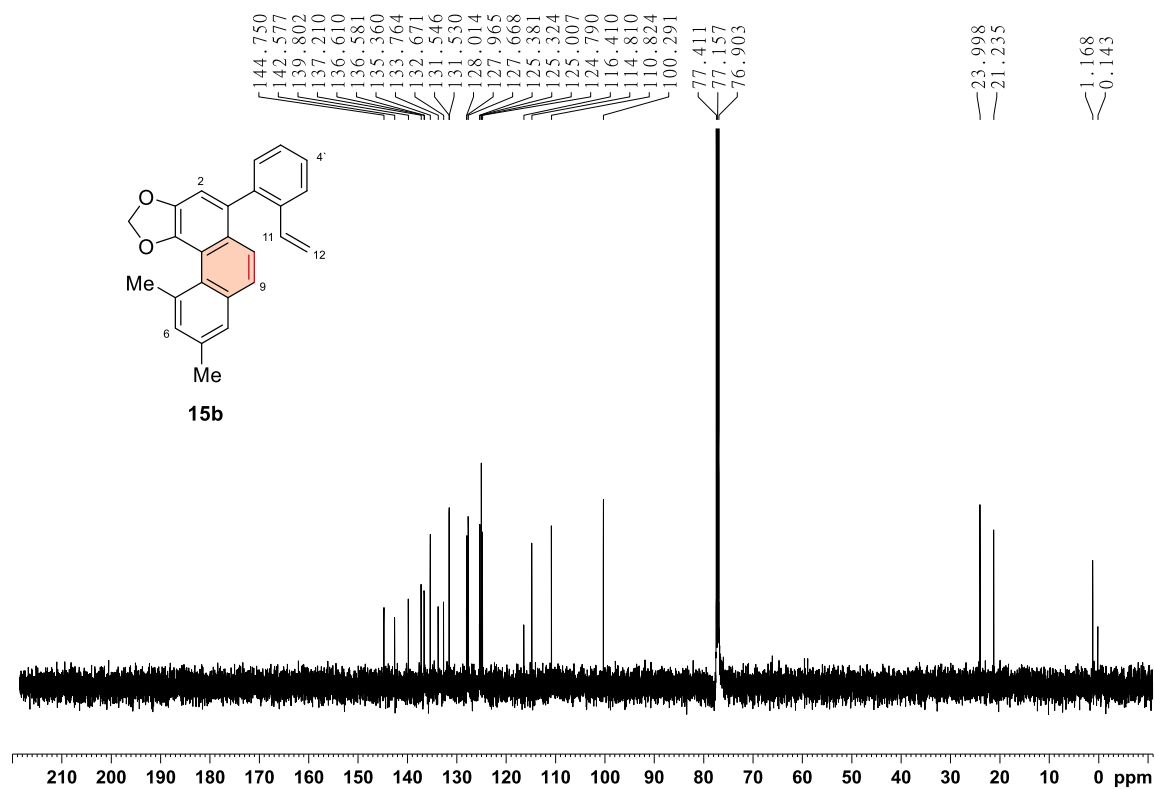
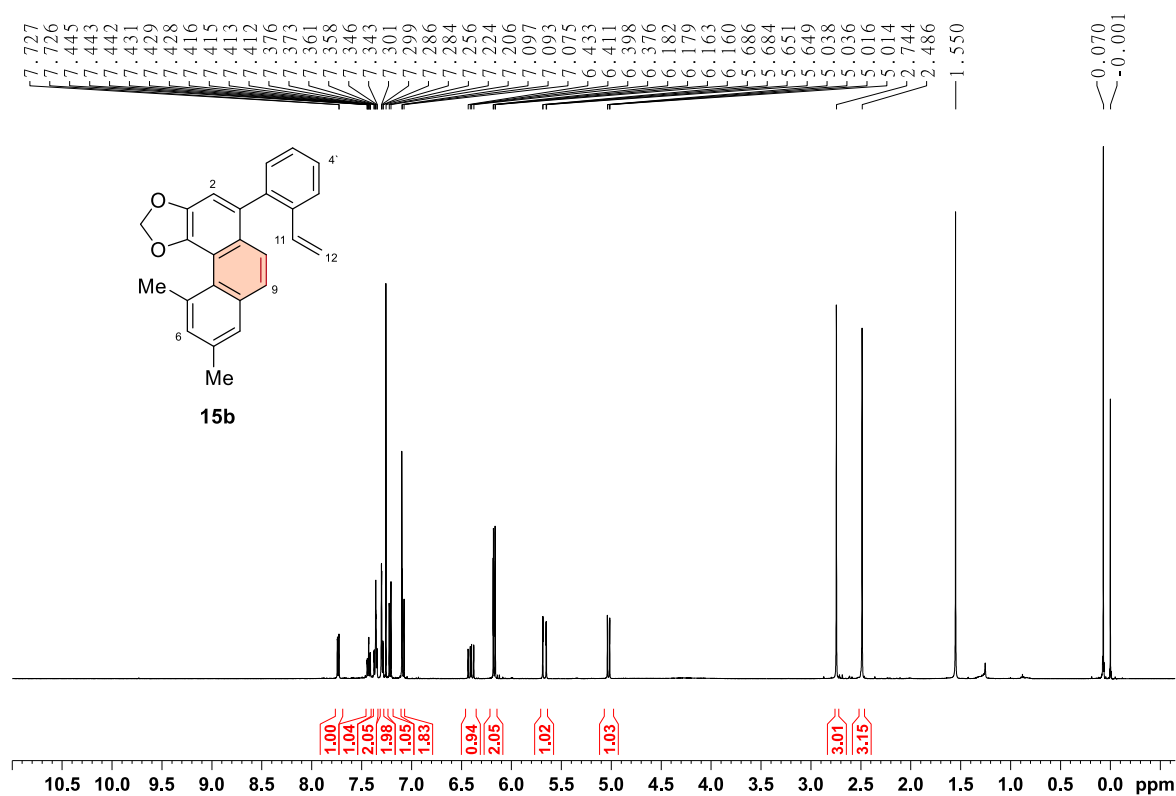
**4,5-Dimethylphenanthrene-1,8-diyl bis(trifluoromethanesulfonate) (S9o):**



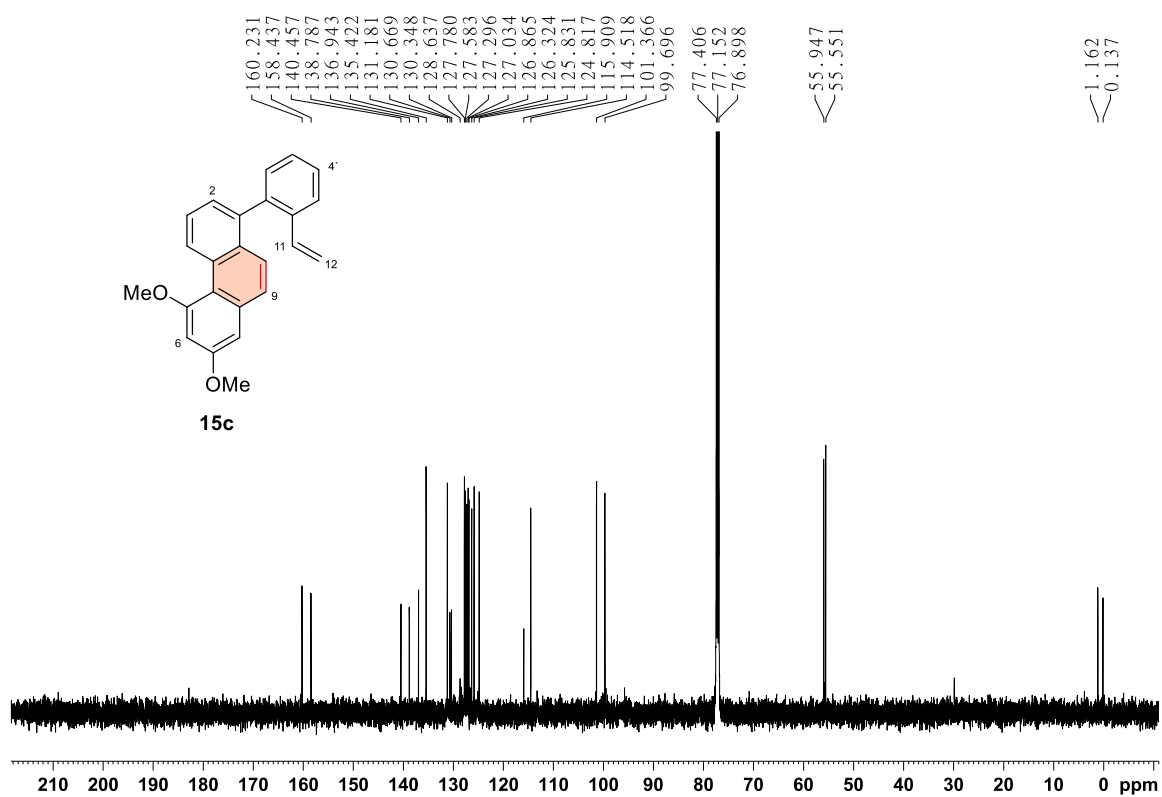
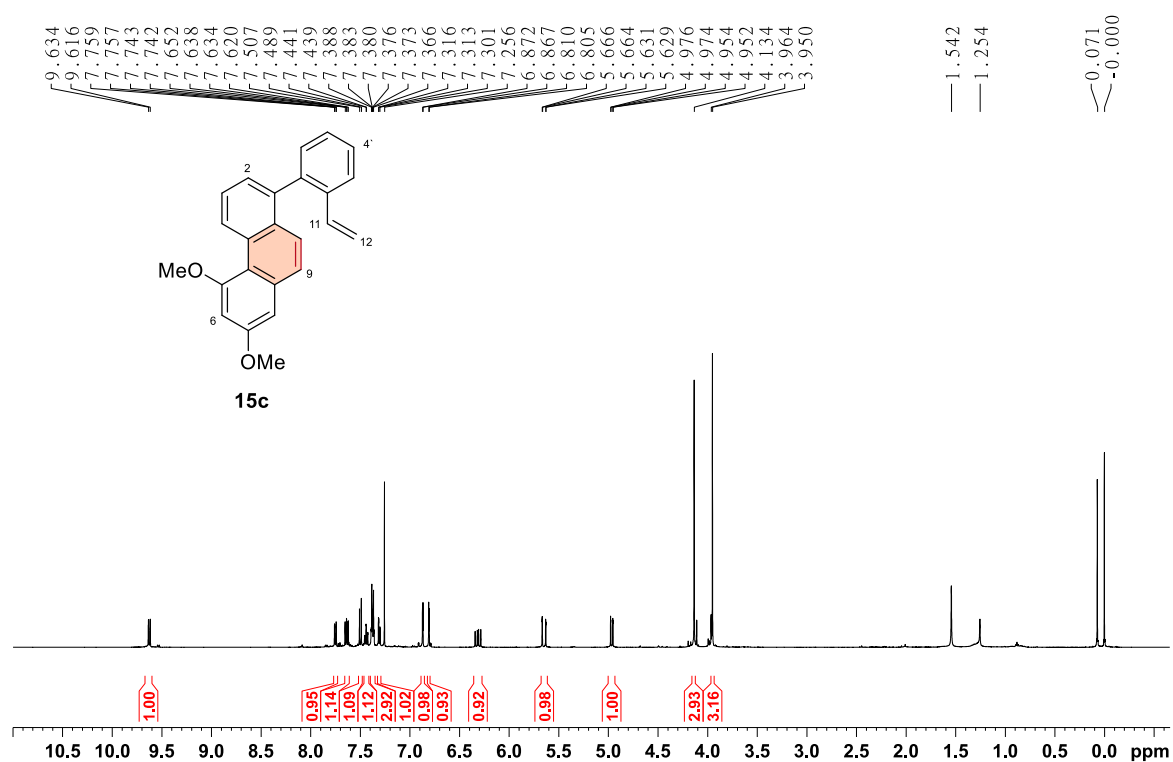
**5,7-Dimethoxy-4-methyl-1-(2-vinylphenyl)phenanthrene (15a):**



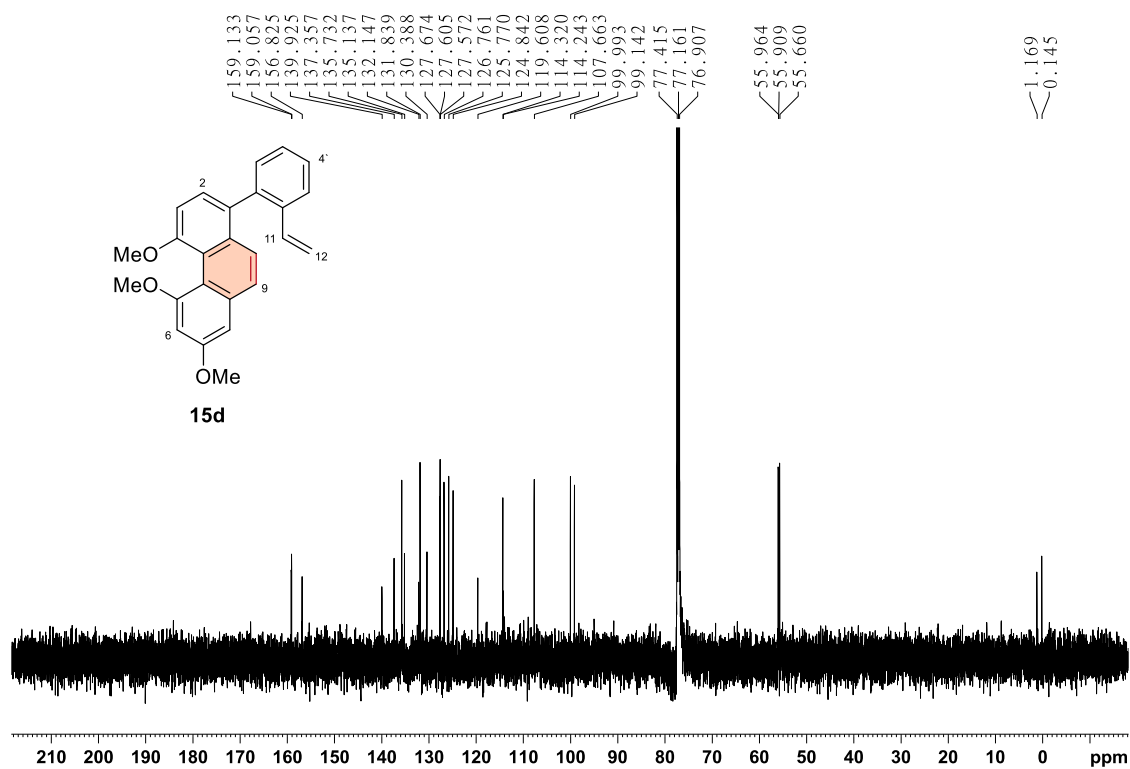
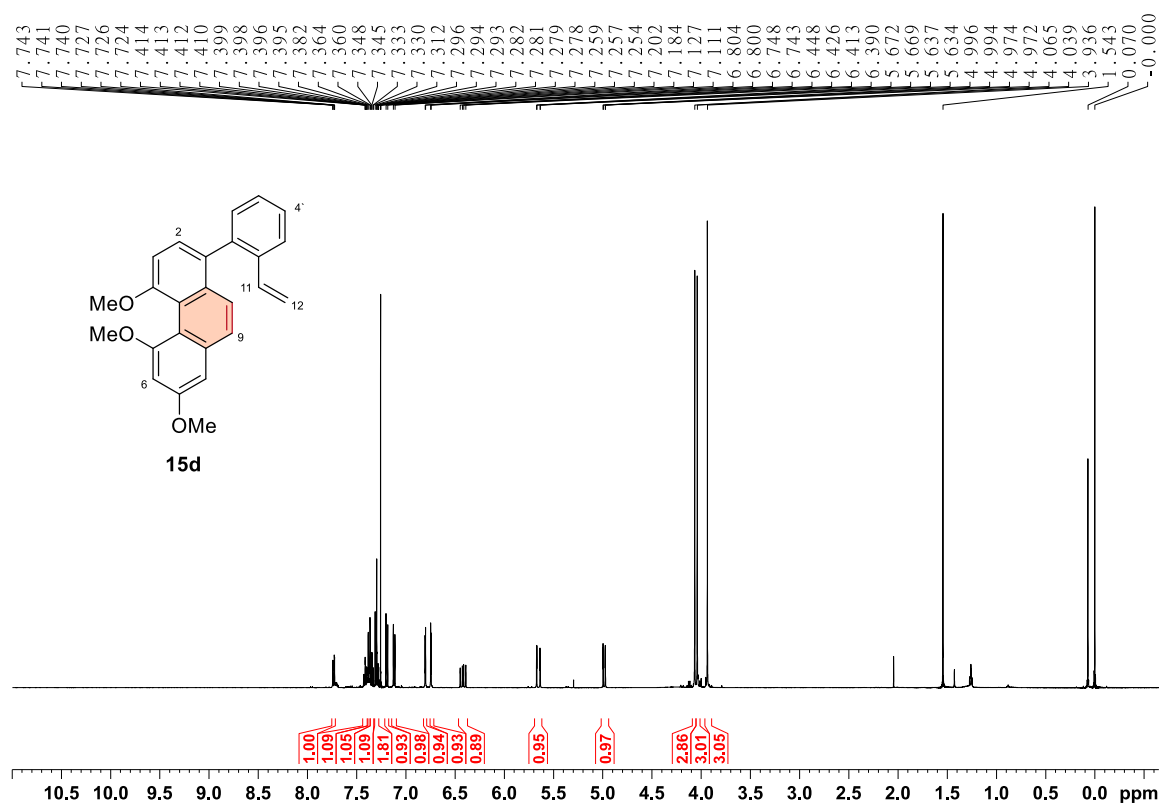
**9,11-Dimethyl-5-(2-vinylphenyl)phenanthro[3,4-d][1,3]dioxole (15b):**



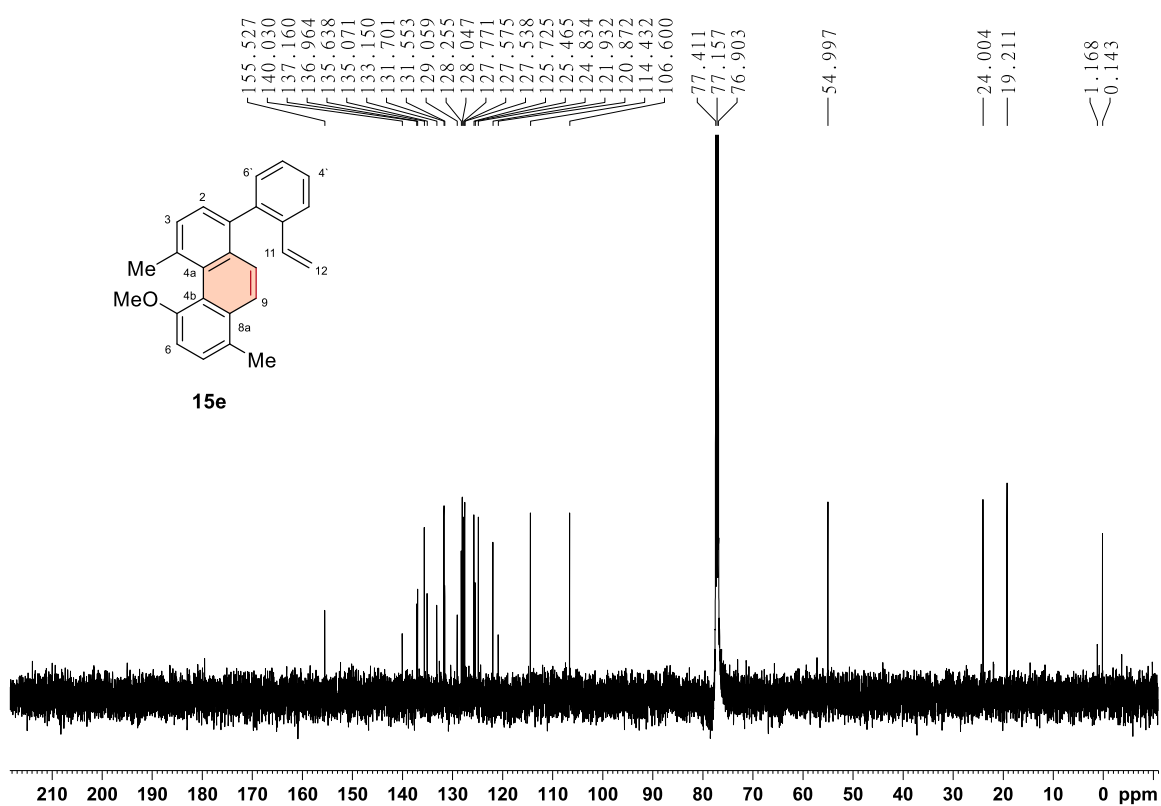
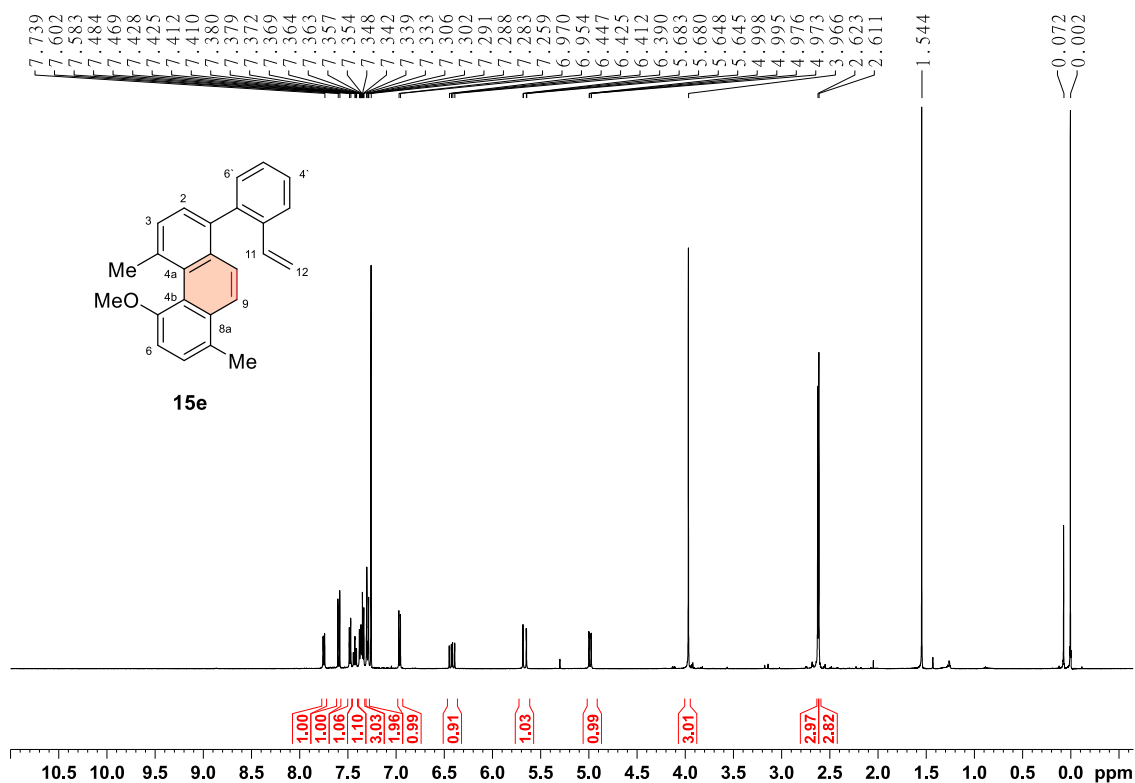
**5,7-Dimethoxy-1-(2-vinylphenyl)phenanthrene (15c):**



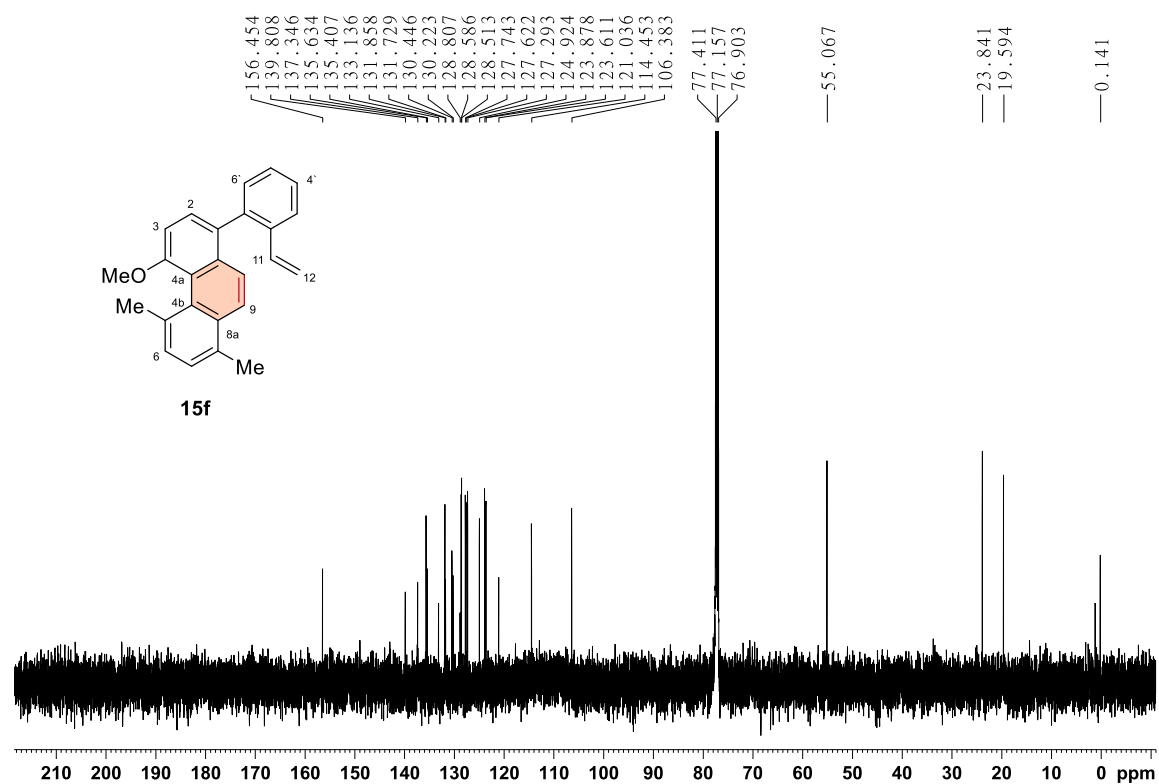
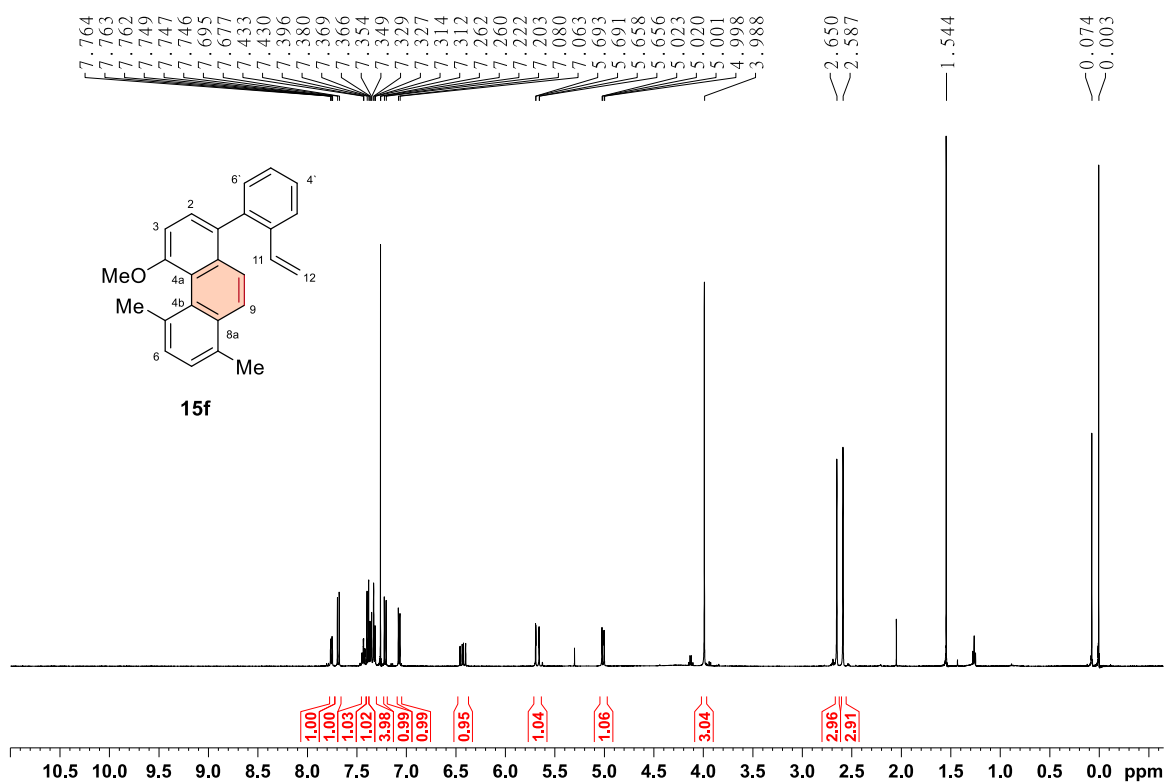
**4,5,7-Trimethoxy-1-(2-vinylphenyl)phenanthrene (15d):**



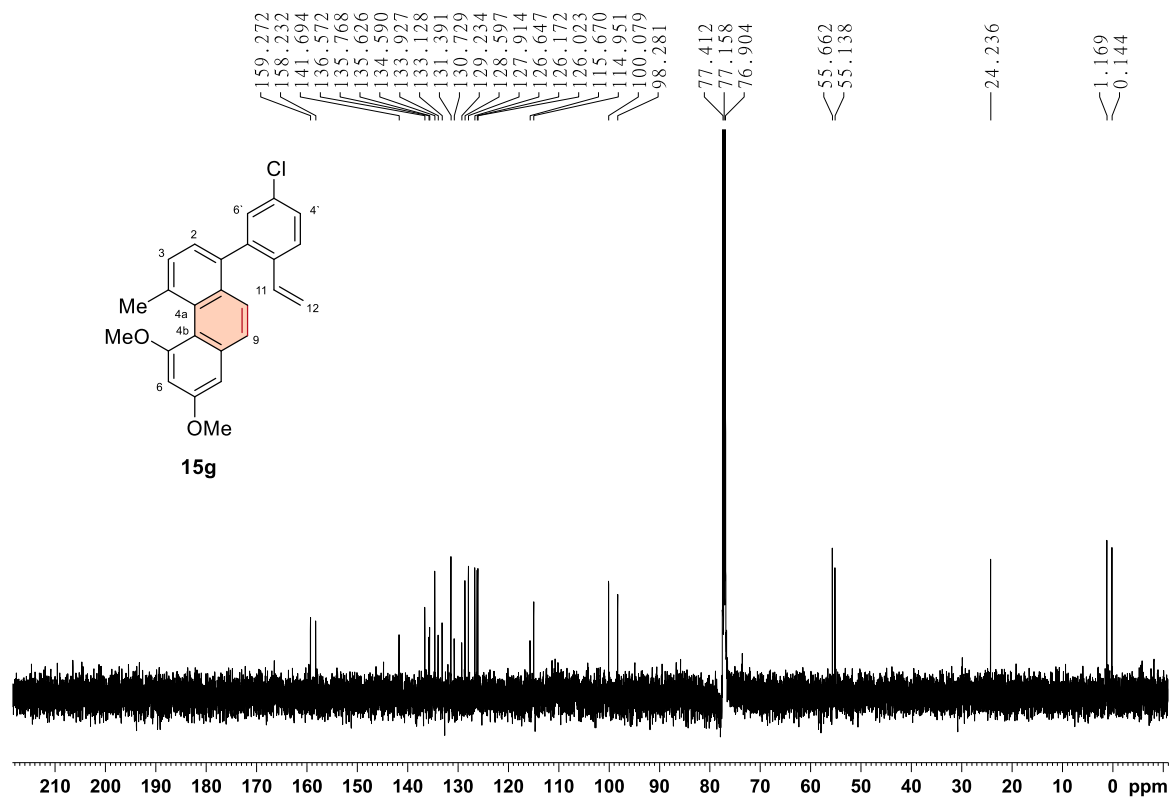
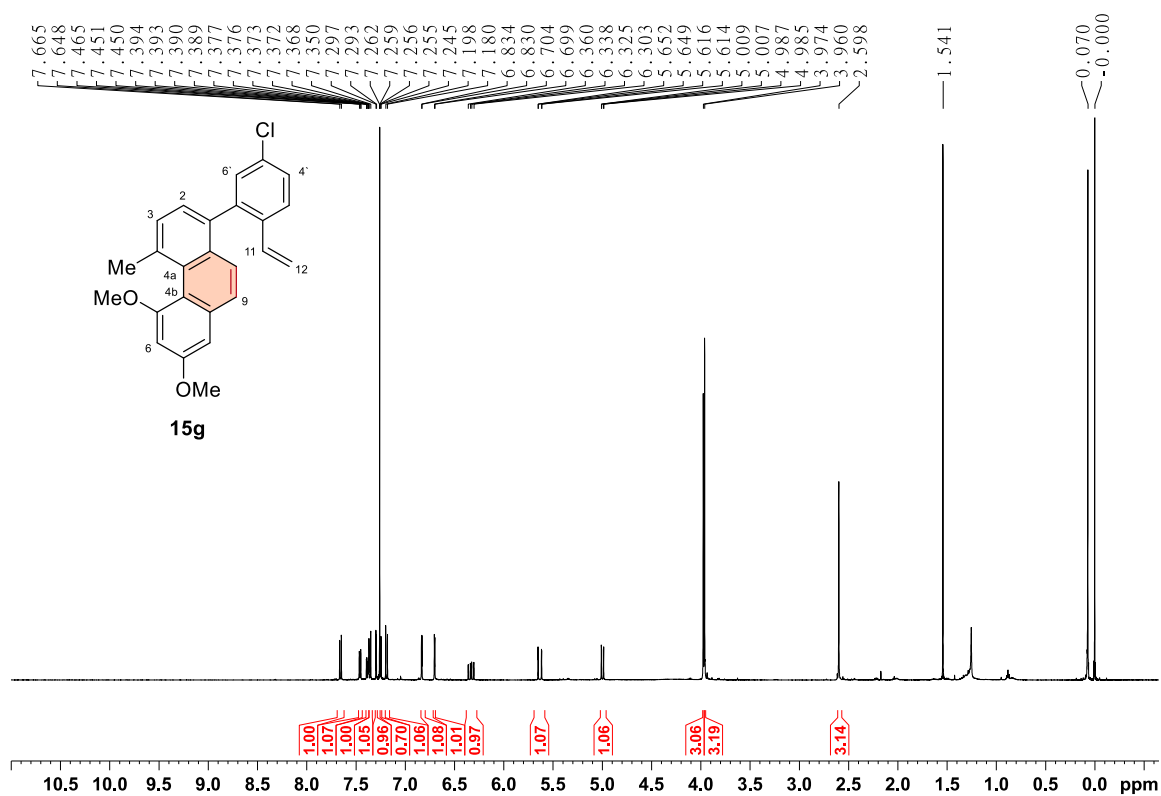
**4-Methoxy-1,5-dimethyl-8-(2-vinylphenyl)phenanthrene (15e):**



**4-Methoxy-5,8-dimethyl-1-(2-vinylphenyl)phenanthrene (15f):**

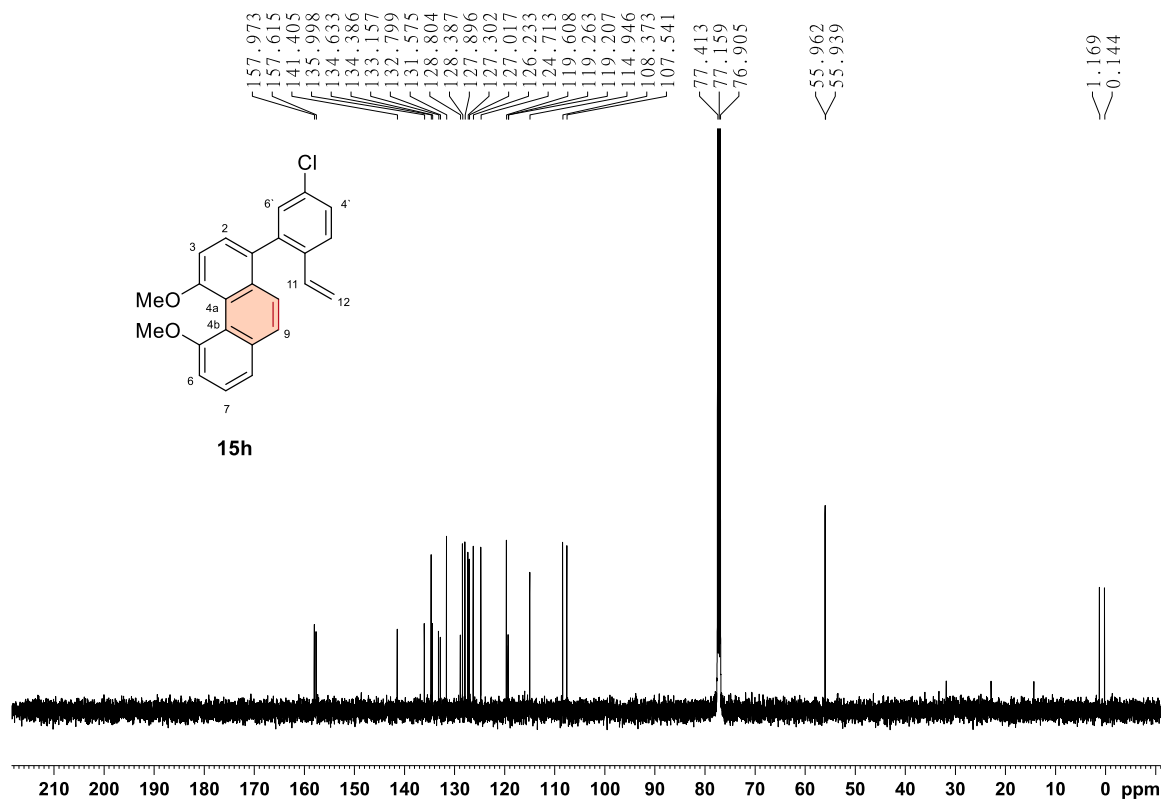
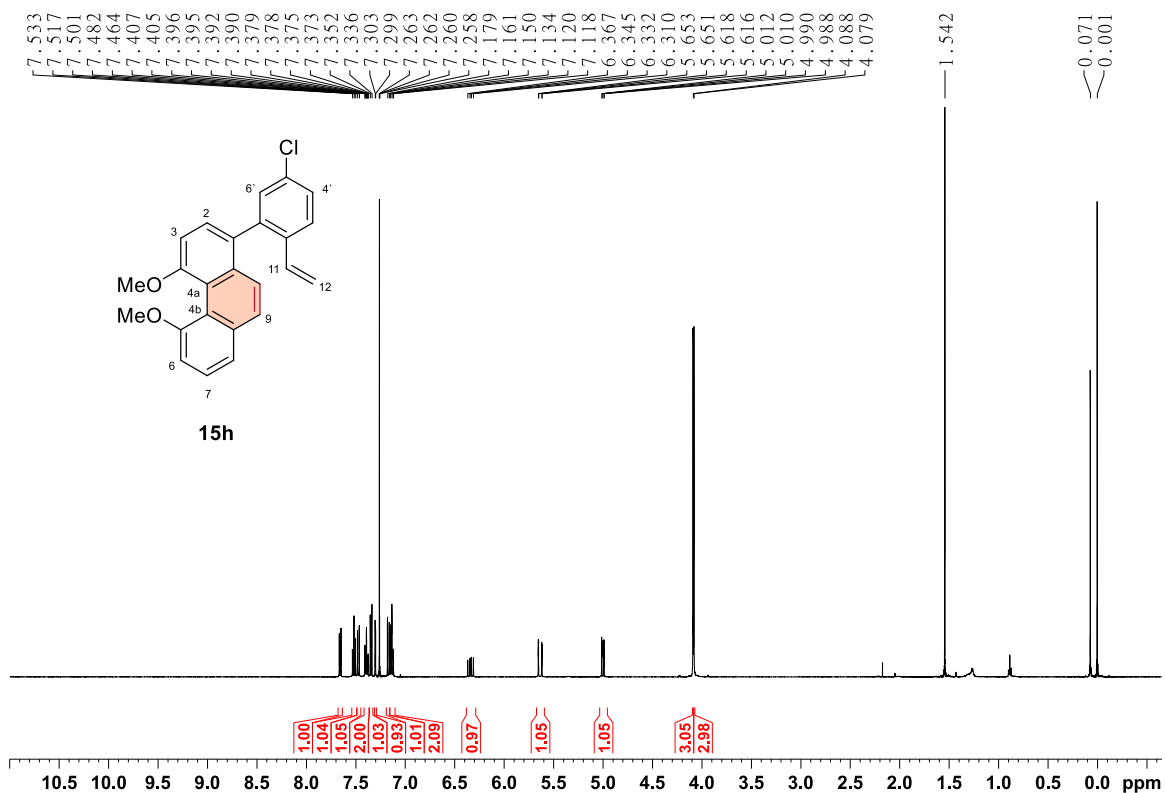


**1-(5-Chloro-2-vinylphenyl)-5,7-dimethoxy-4-methylphenanthrene (15g):**

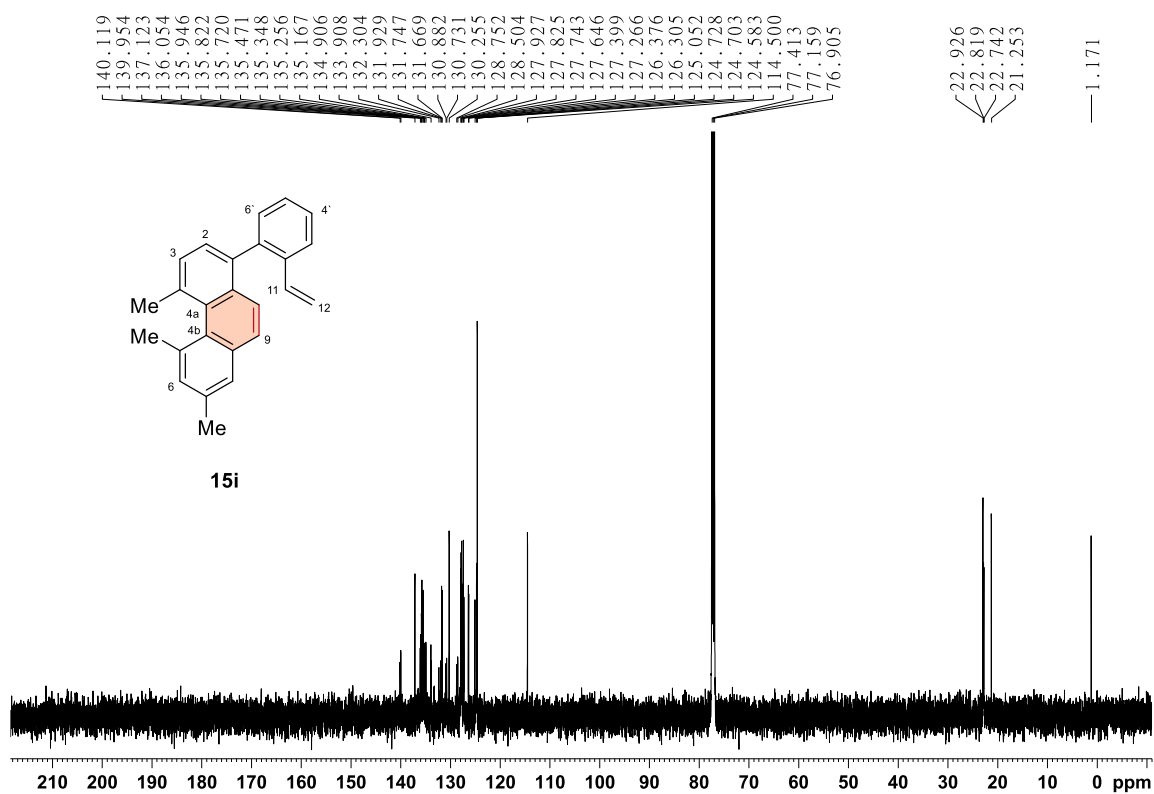
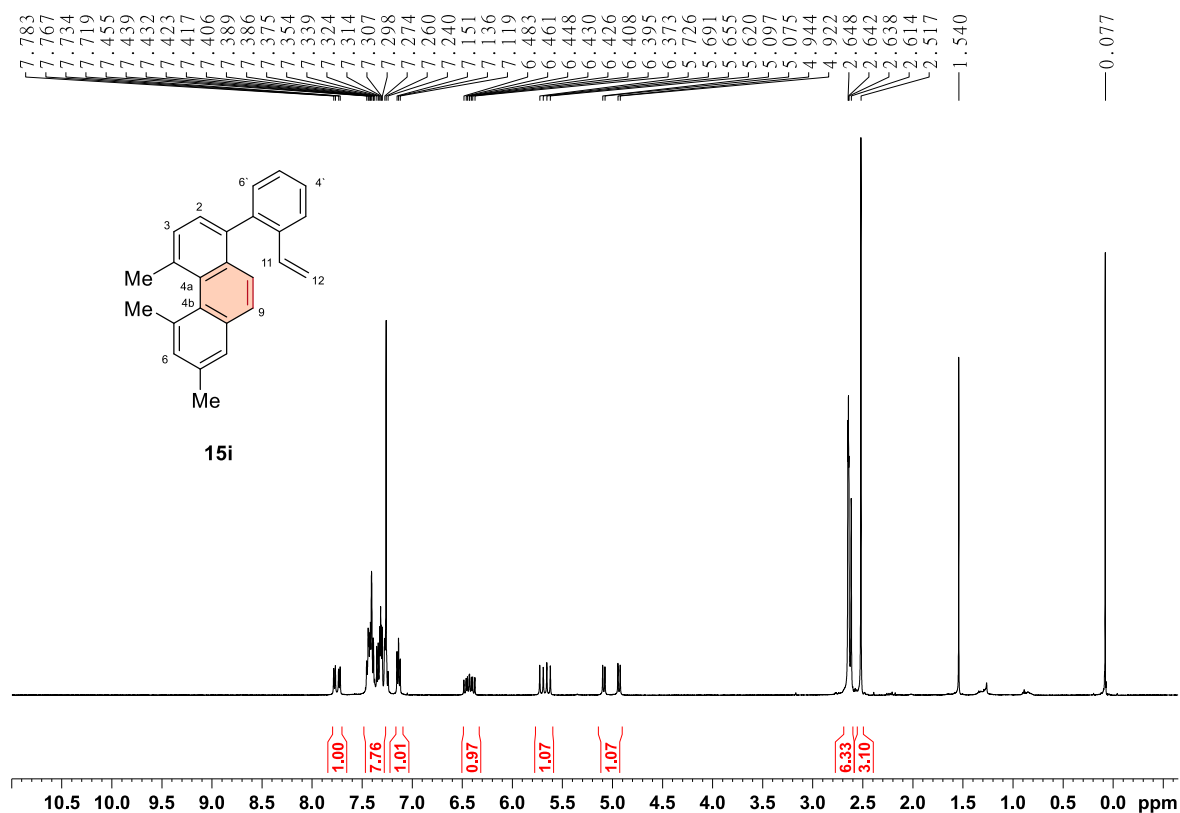




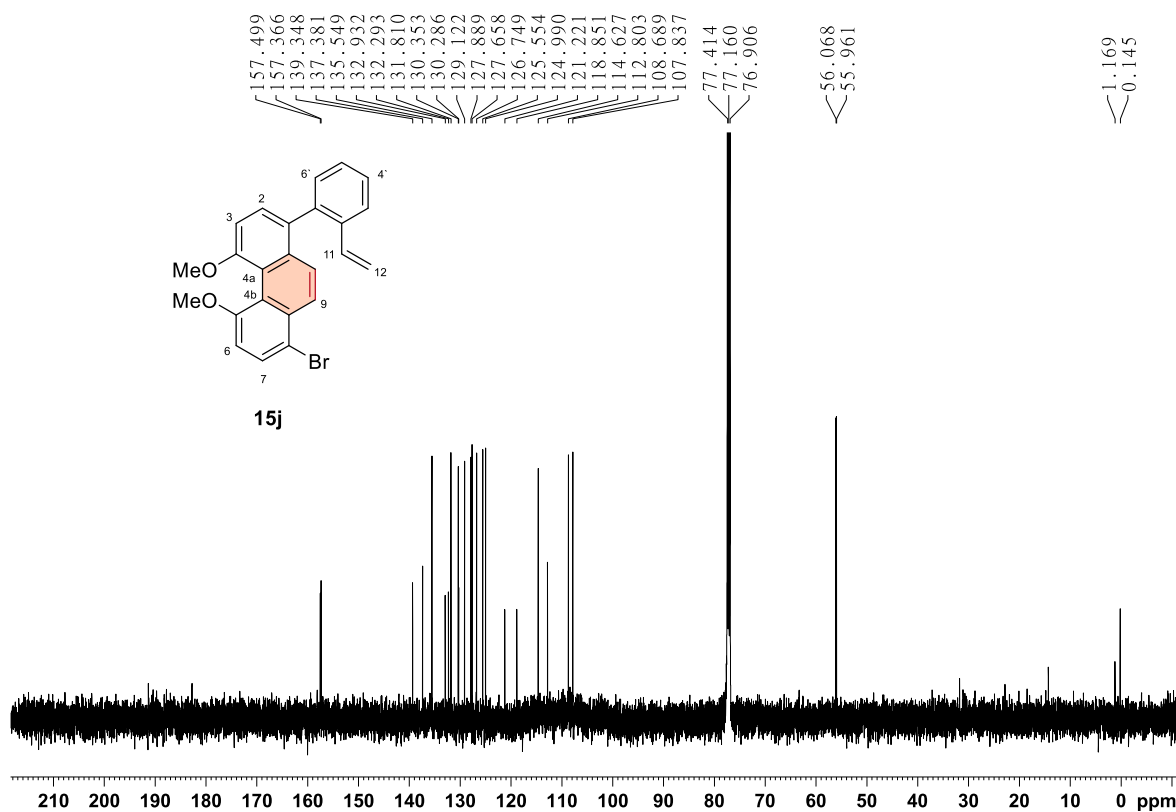
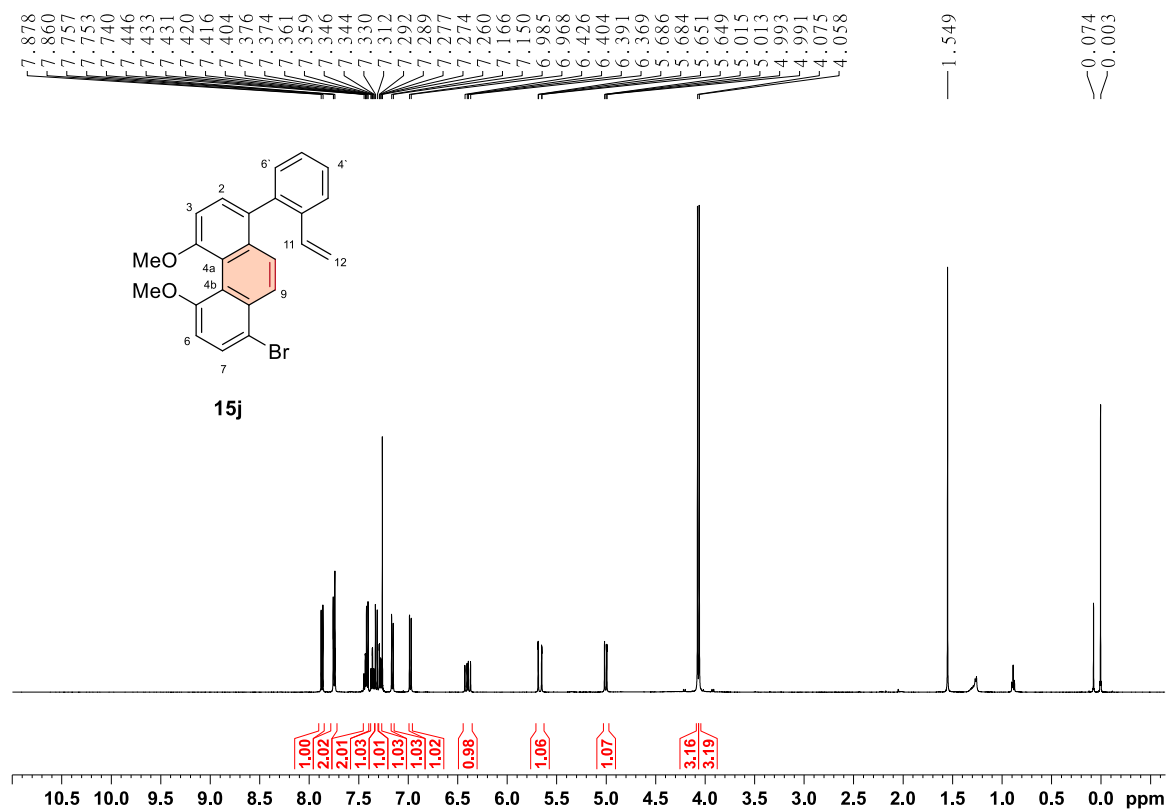
**1-(5-Chloro-2-vinylphenyl)-4,5-dimethoxyphenanthrene (15h):**



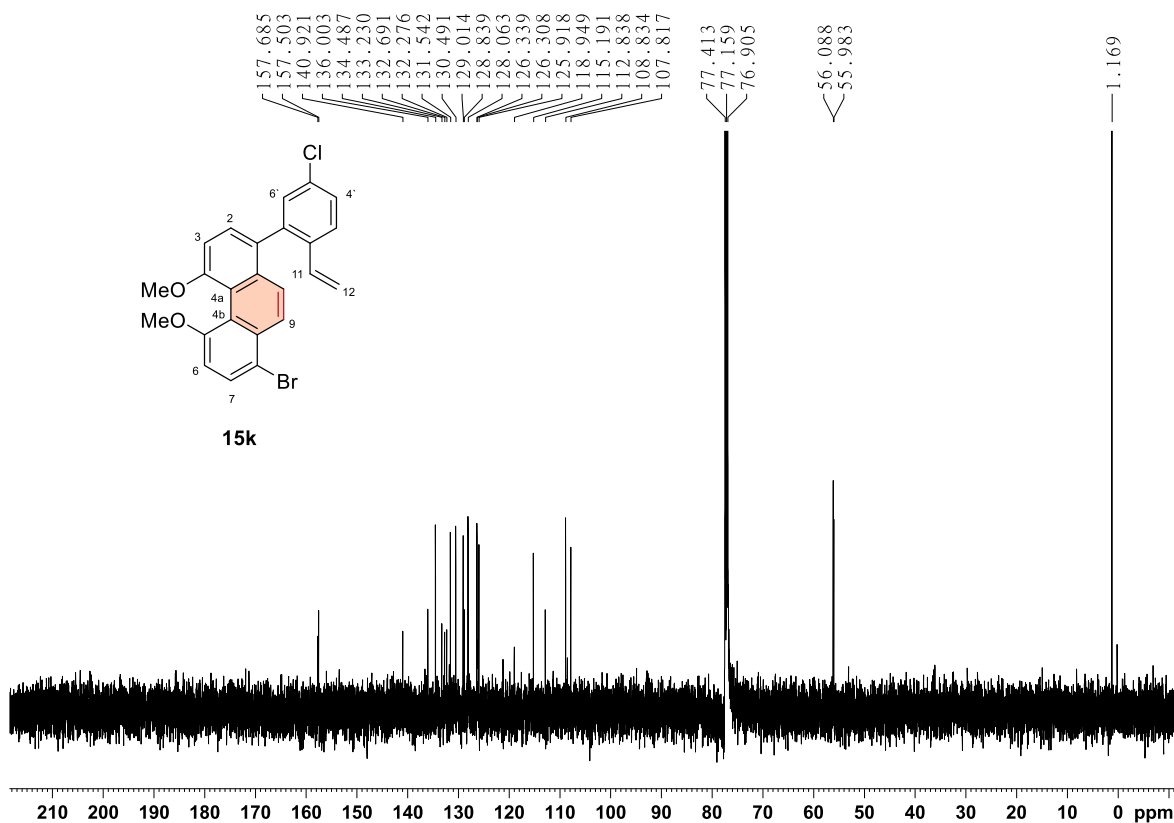
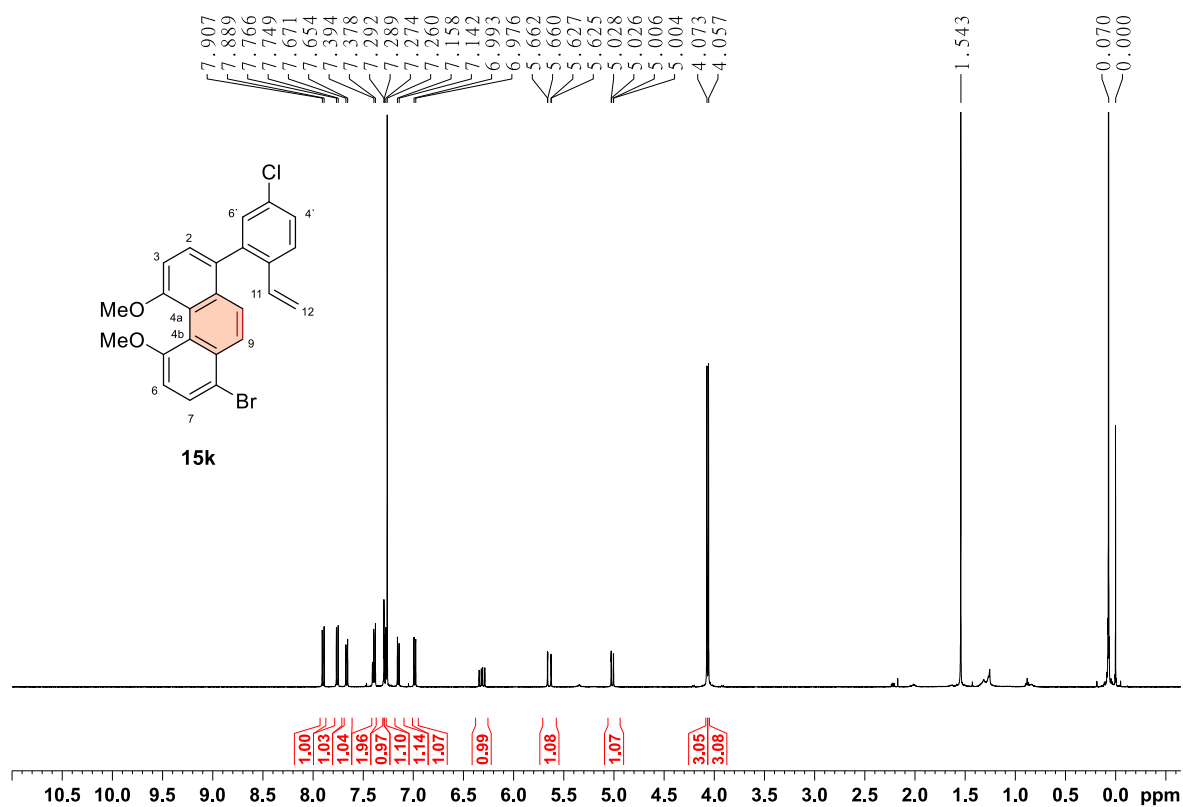
**4,5,7-Trimethyl-1-(2-vinylphenyl)phenanthrene (15i):**



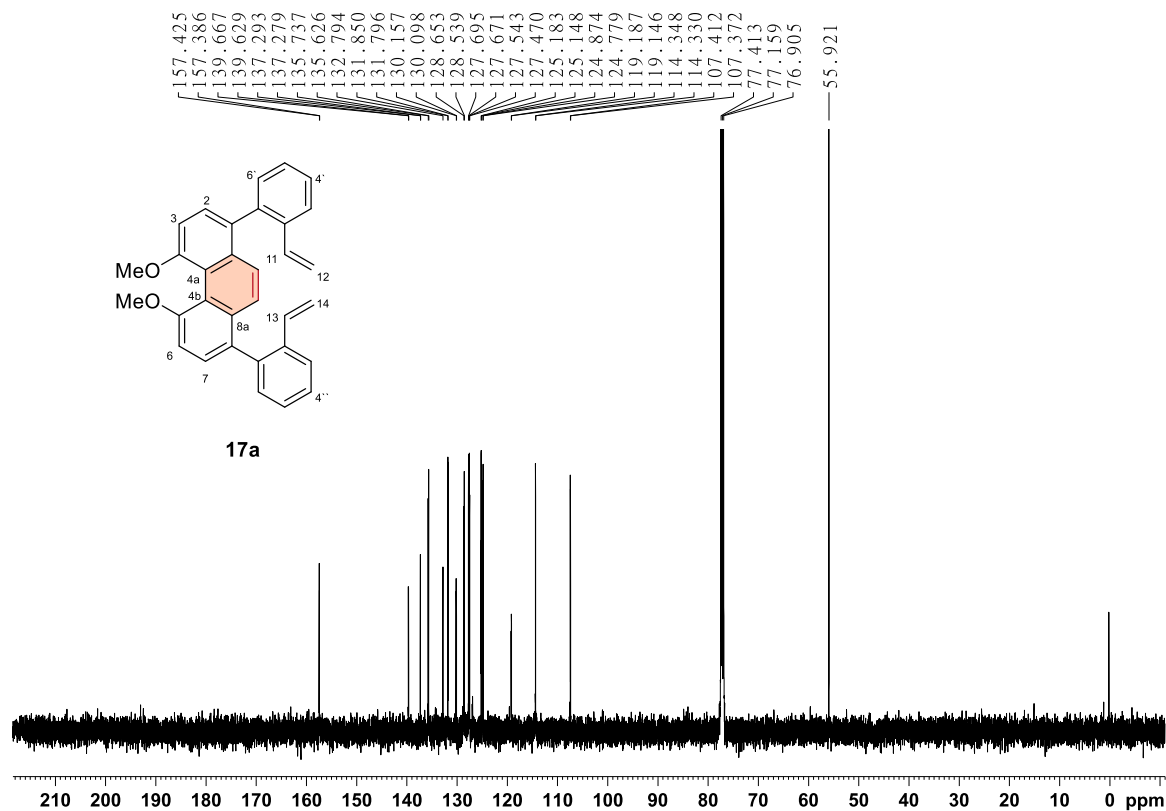
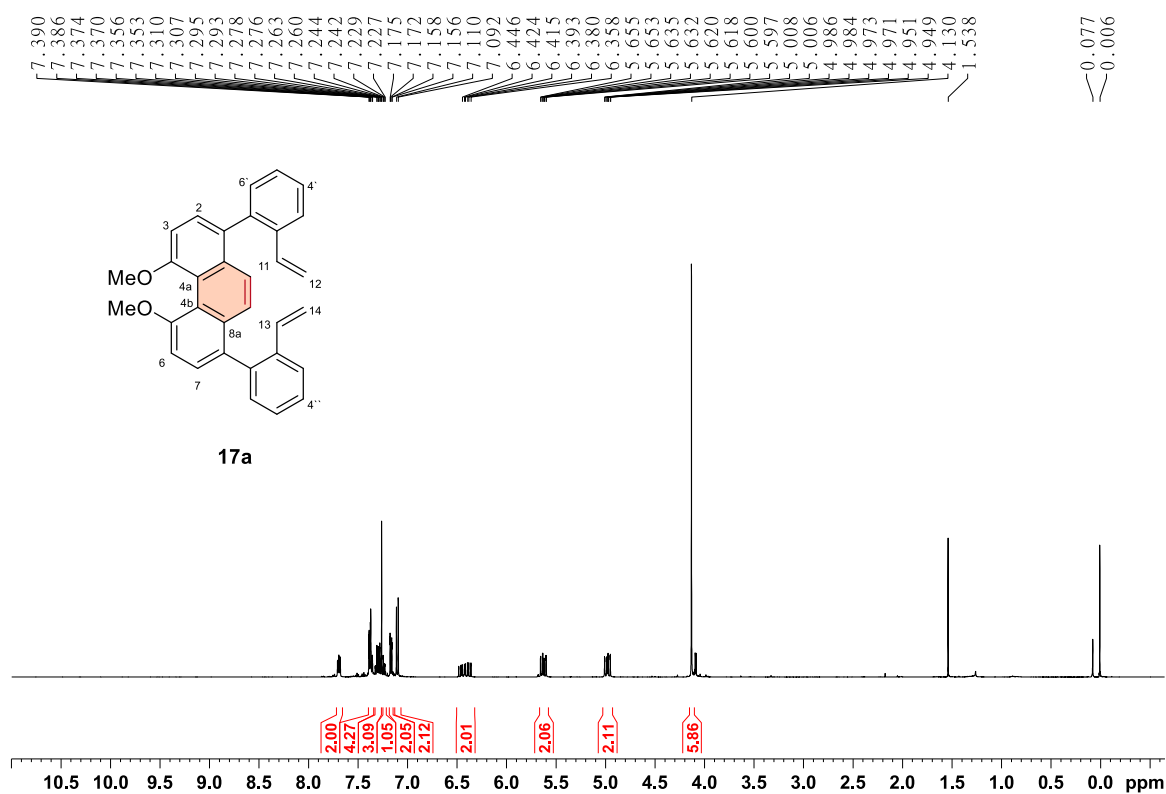
**1-Bromo-4,5-dimethoxy-8-(2-vinylphenyl)phenanthrene (15j):**



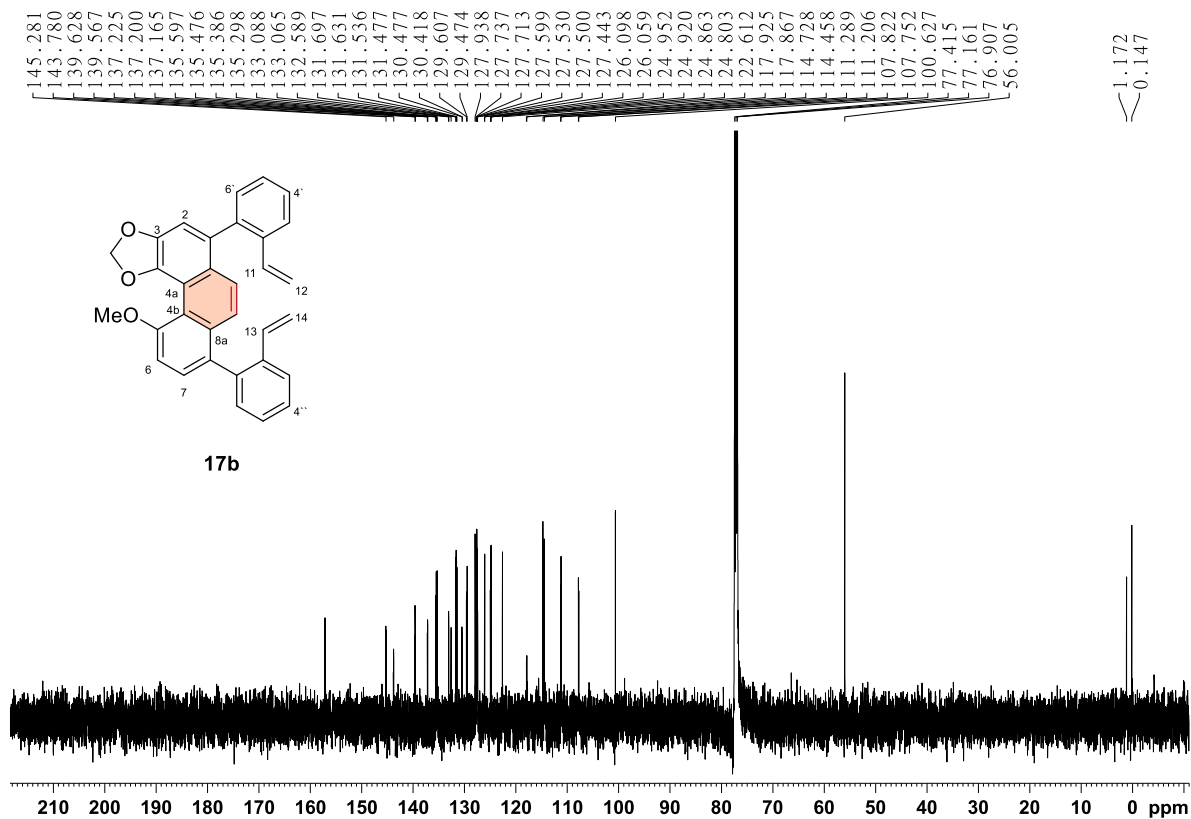
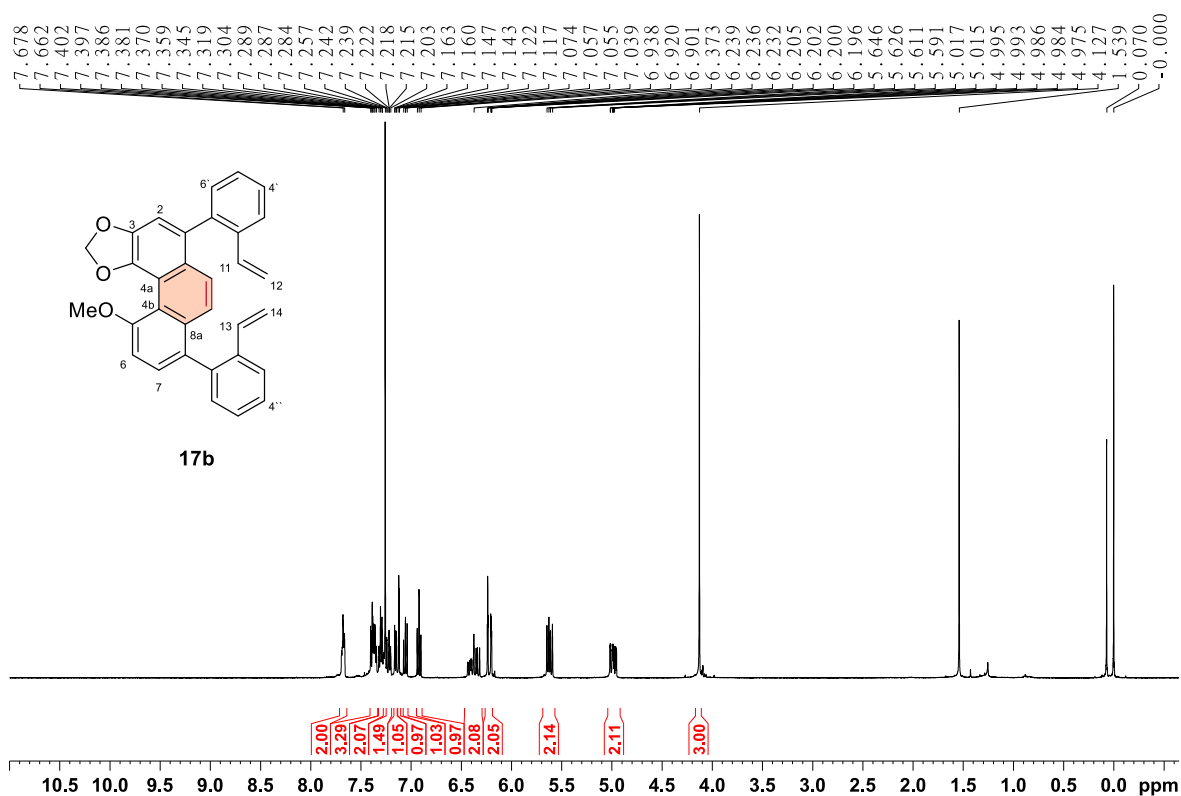
**1-Bromo-8-(5-chloro-2-vinylphenyl)-4,5-dimethoxyphenanthrene (15k):**



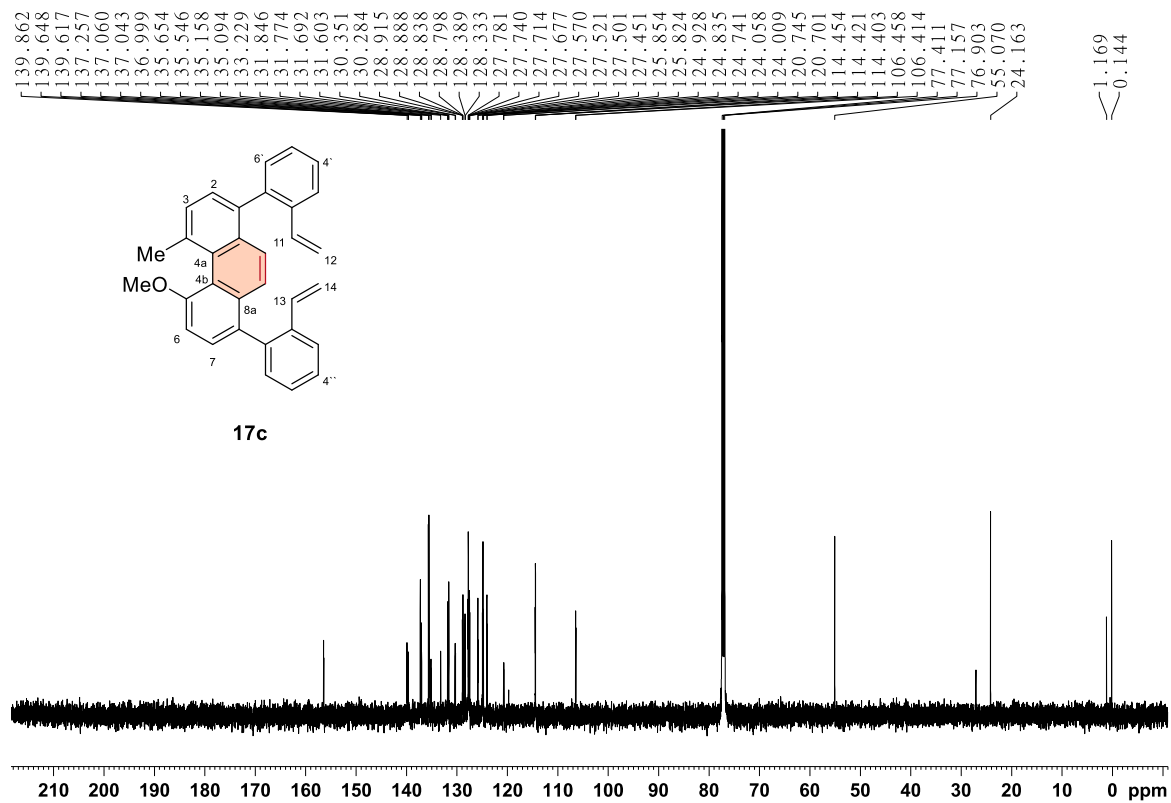
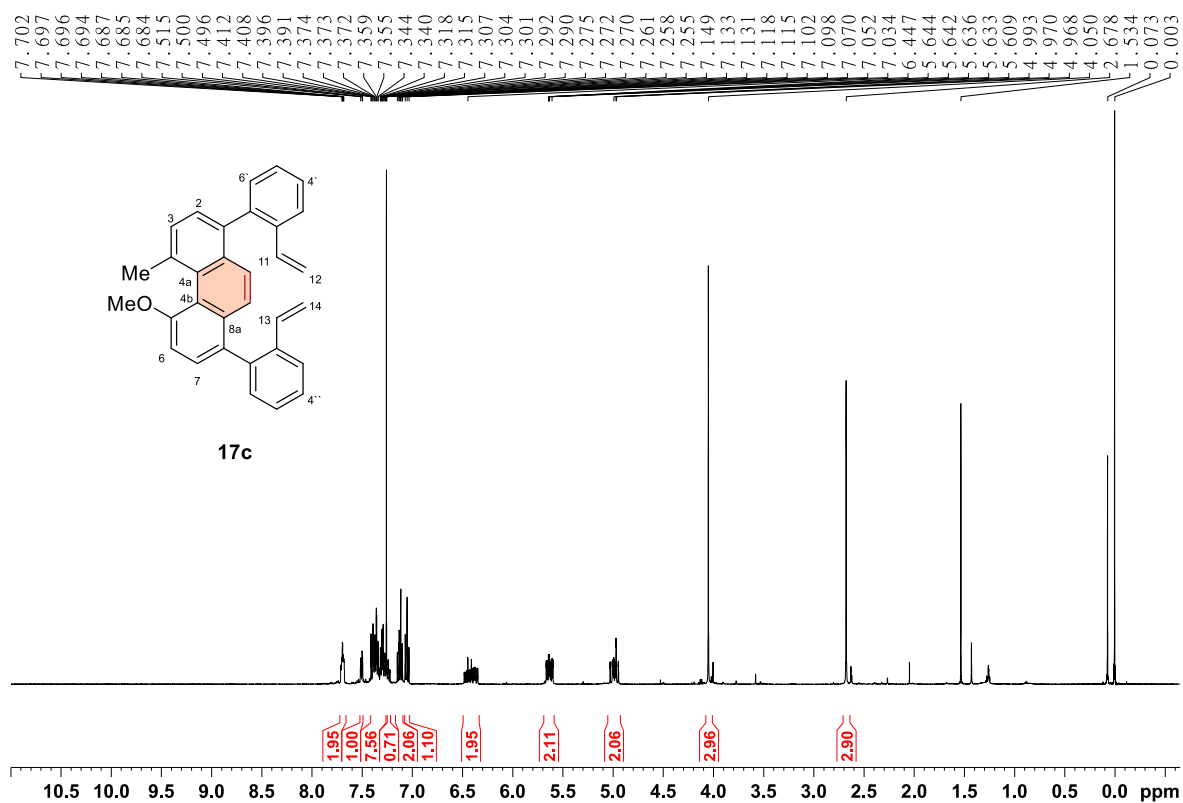
**4,5-Dimethoxy-1,8-bis(2-vinylphenyl)phenanthrene (17a):**



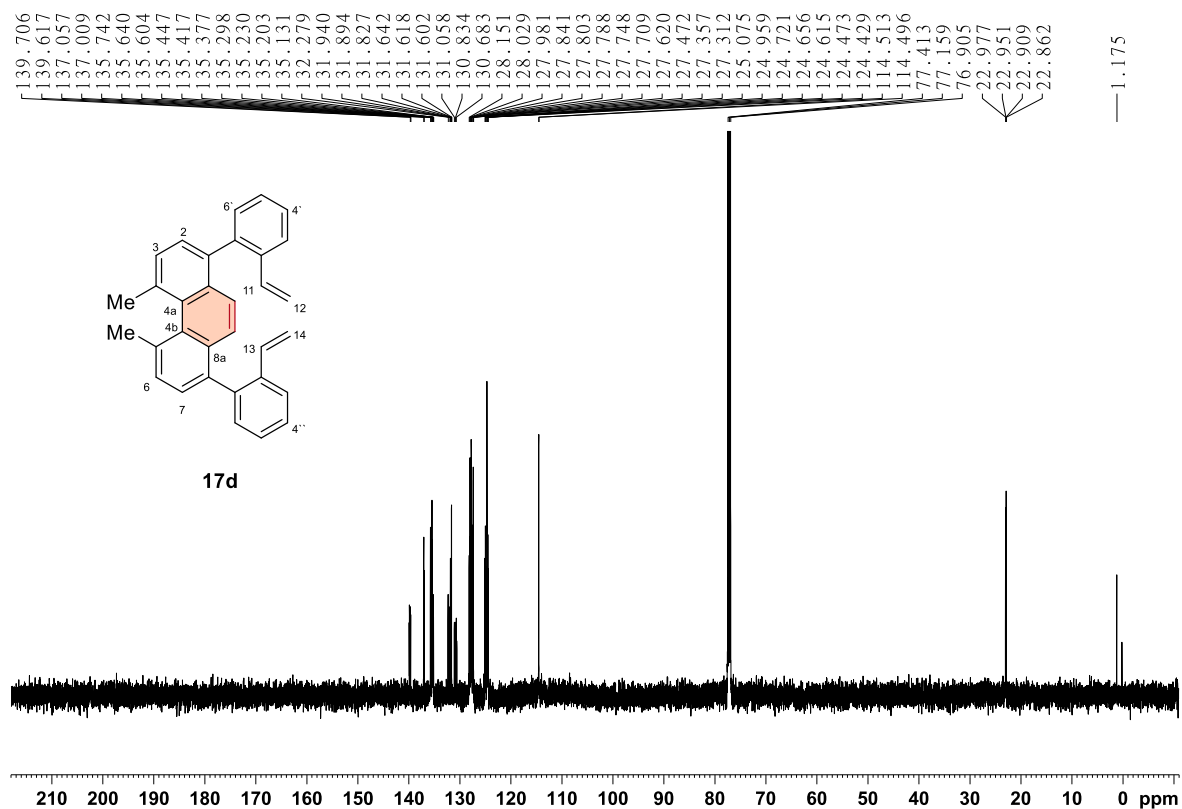
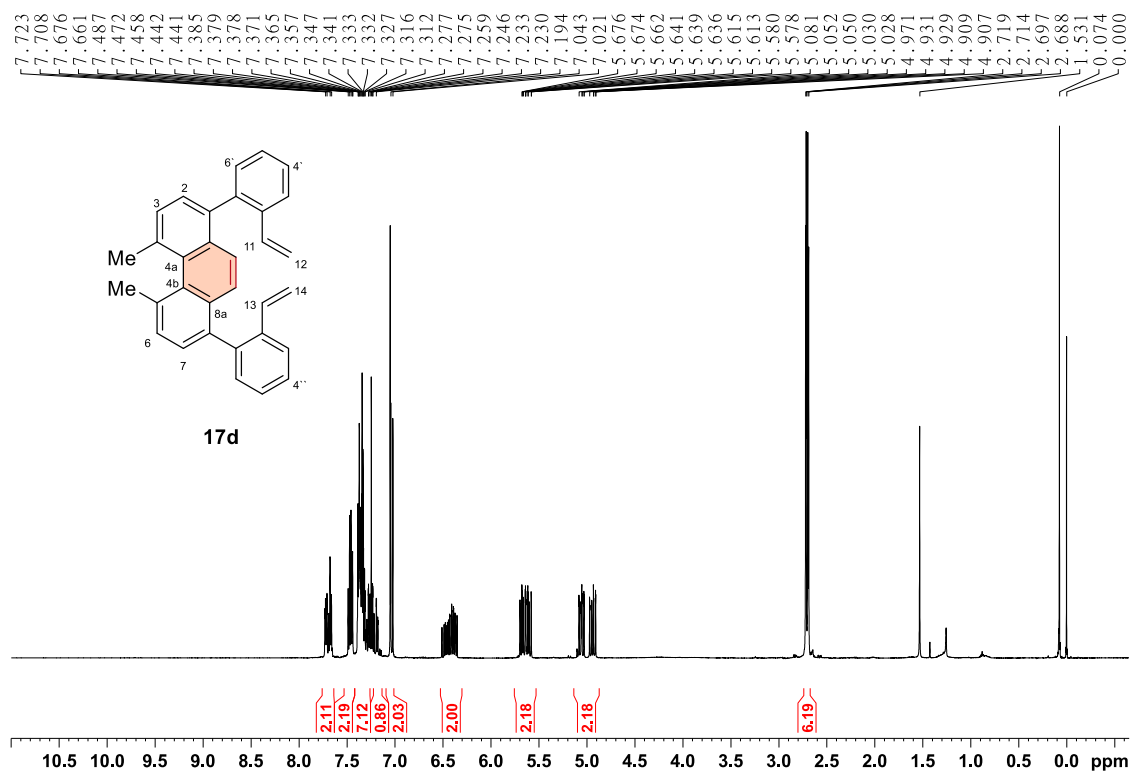
**11-Methoxy-5,8-bis(2-vinylphenyl)phenanthro[3,4-d][1,3]dioxole (17b):**



**4-Methoxy-5-methyl-1,8-bis(2-vinylphenyl)phenanthrene (17c):**

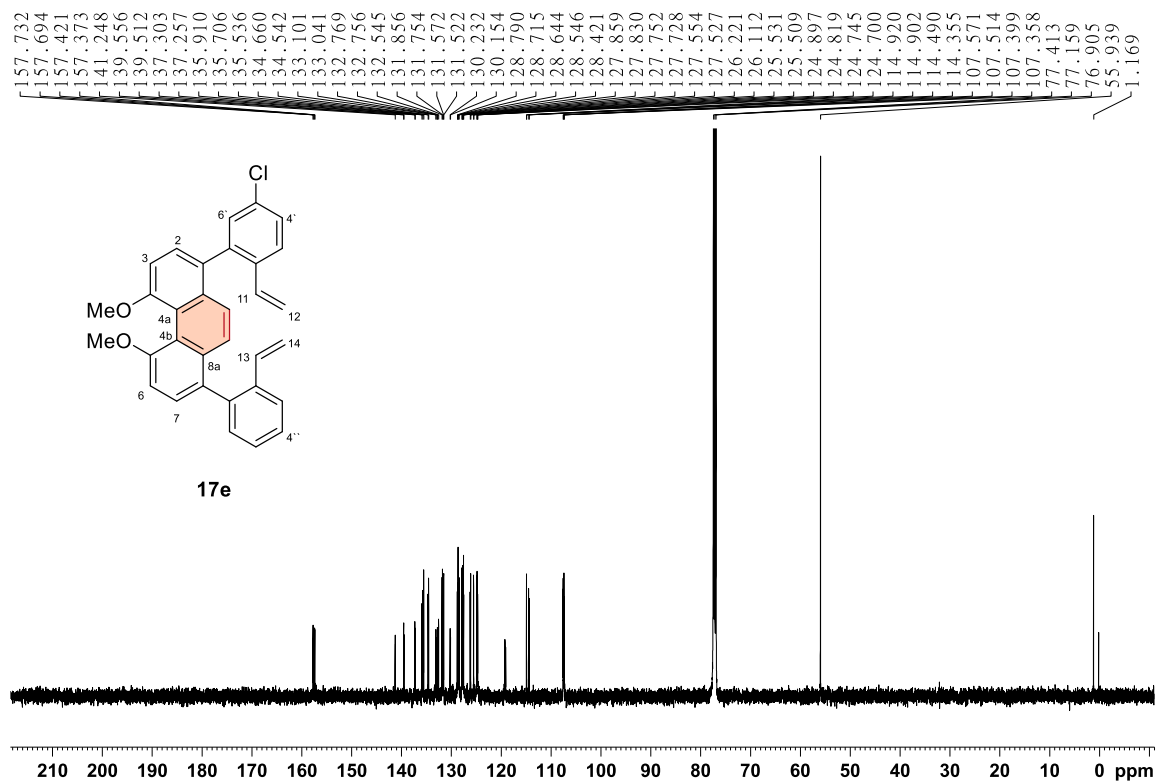
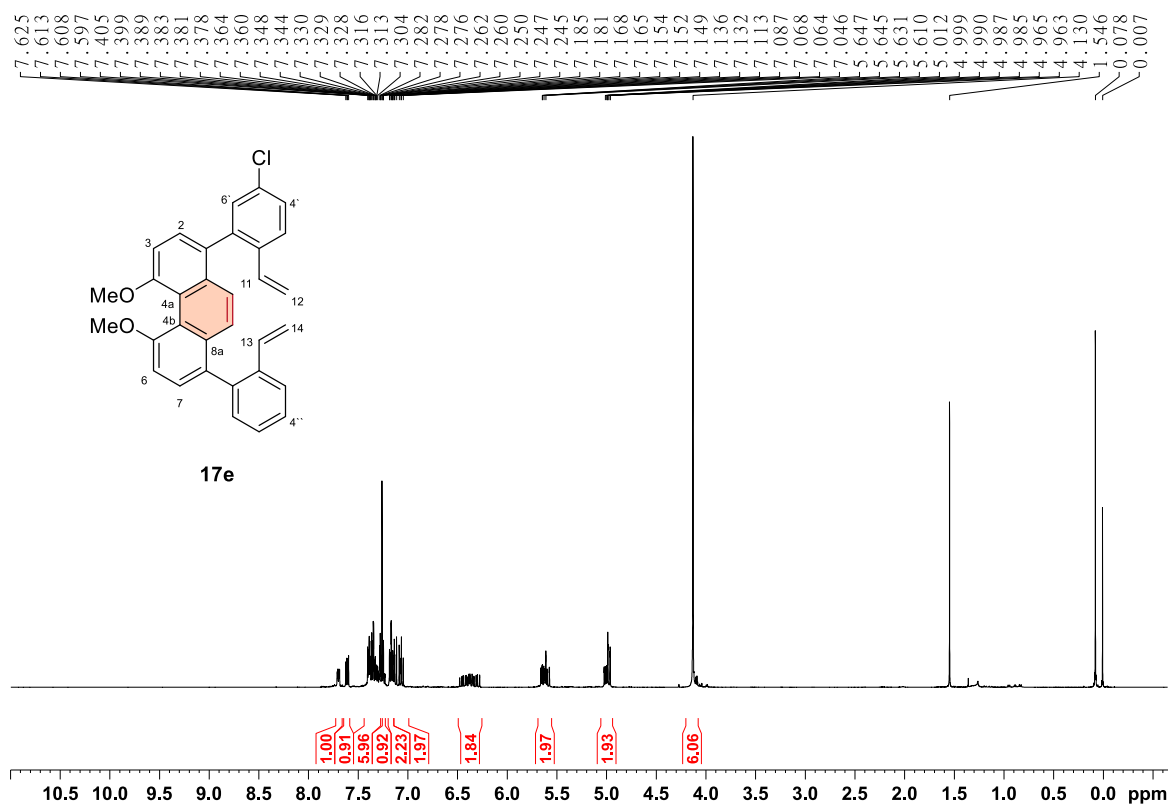


**4,5-Dimethyl-1,8-bis(2-vinylphenyl)phenanthrene (17d):**

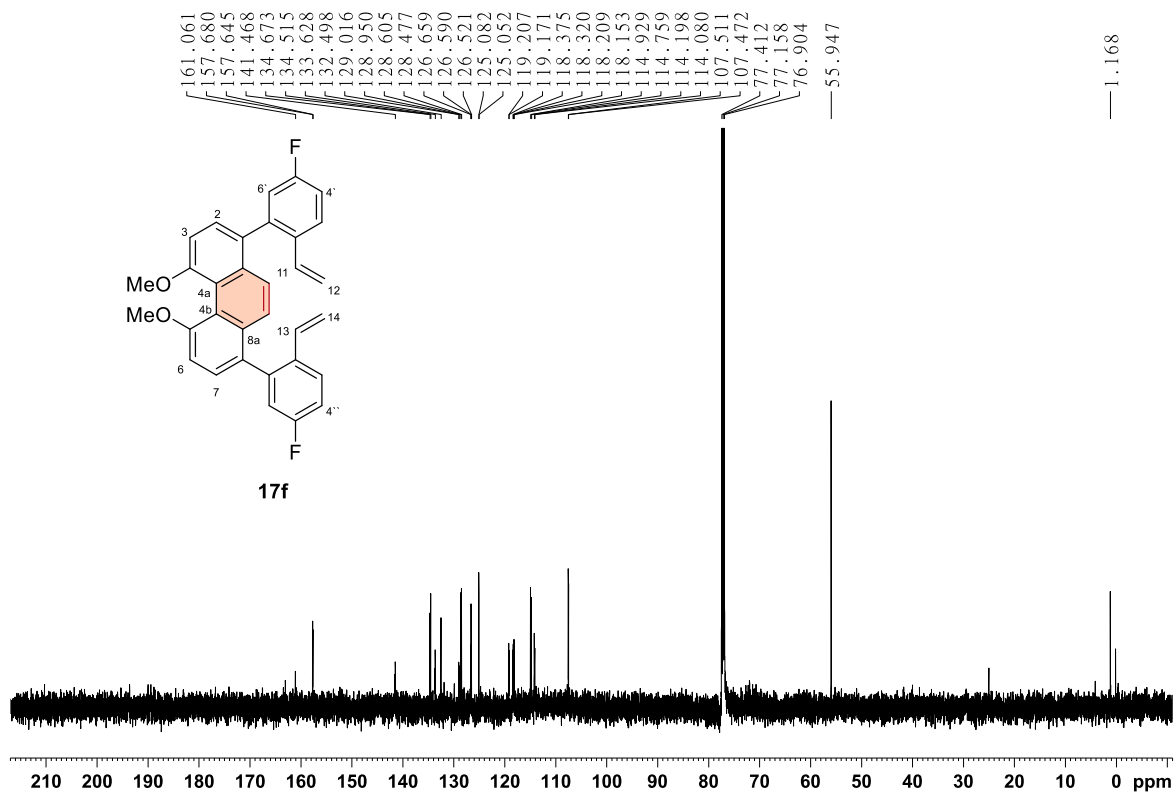
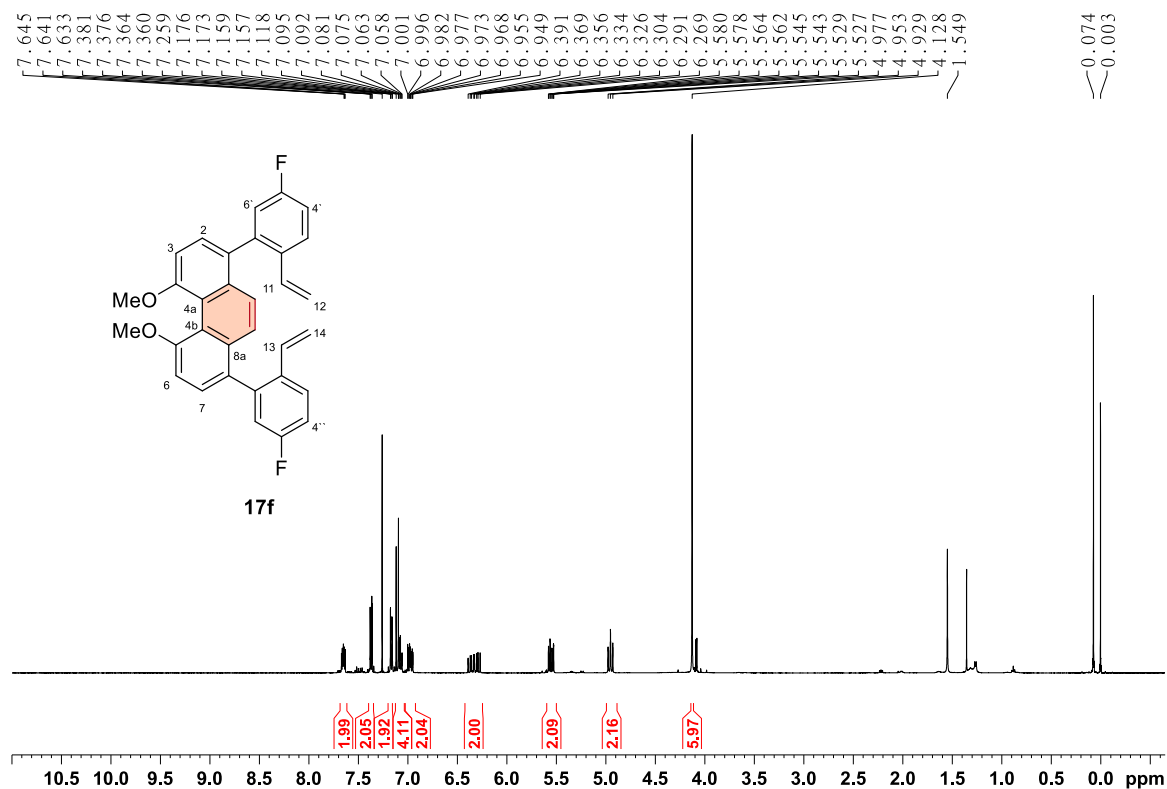




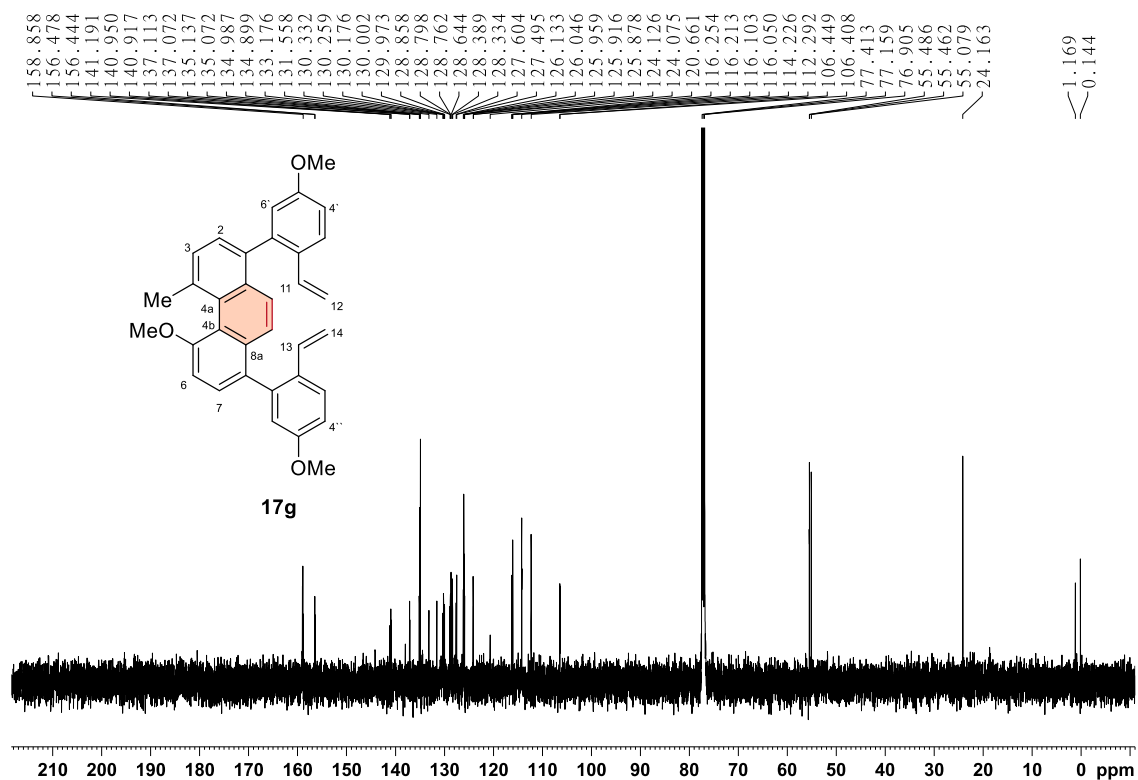
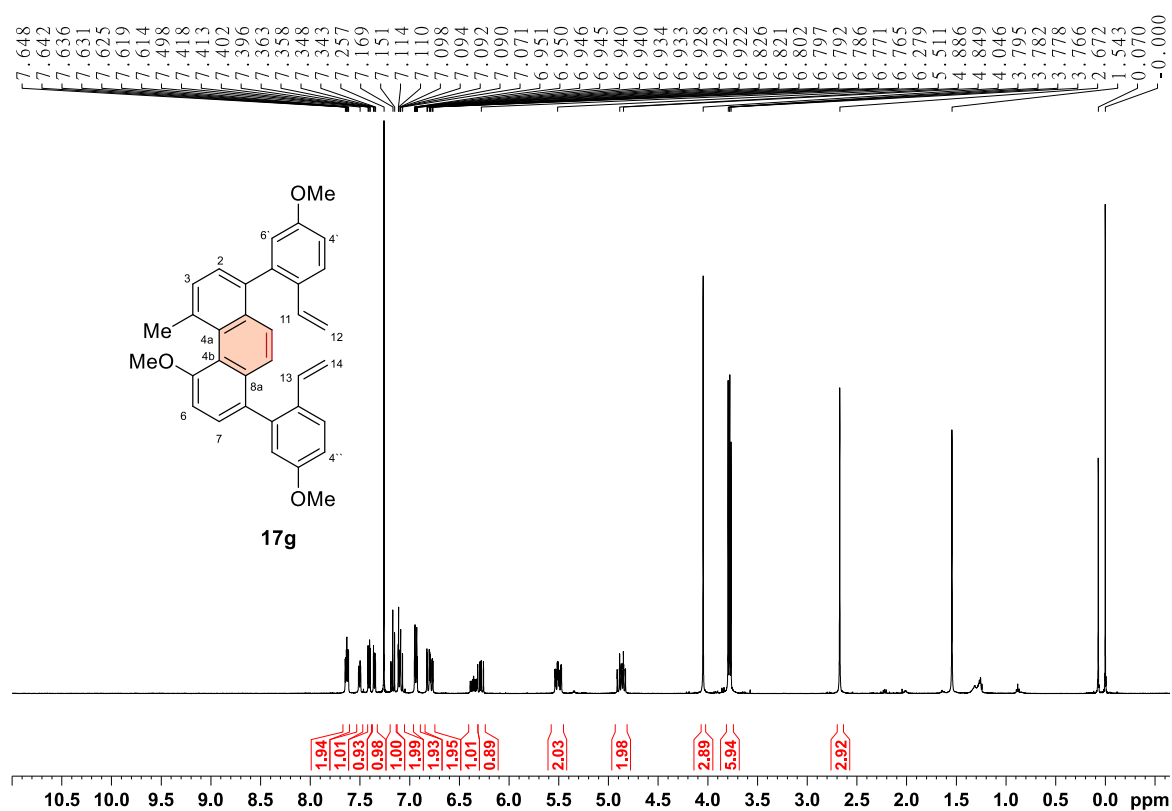
**1-(5-Chloro-2-vinylphenyl)-4,5-dimethoxy-8-(2-vinylphenyl)phenanthrene (17e):**



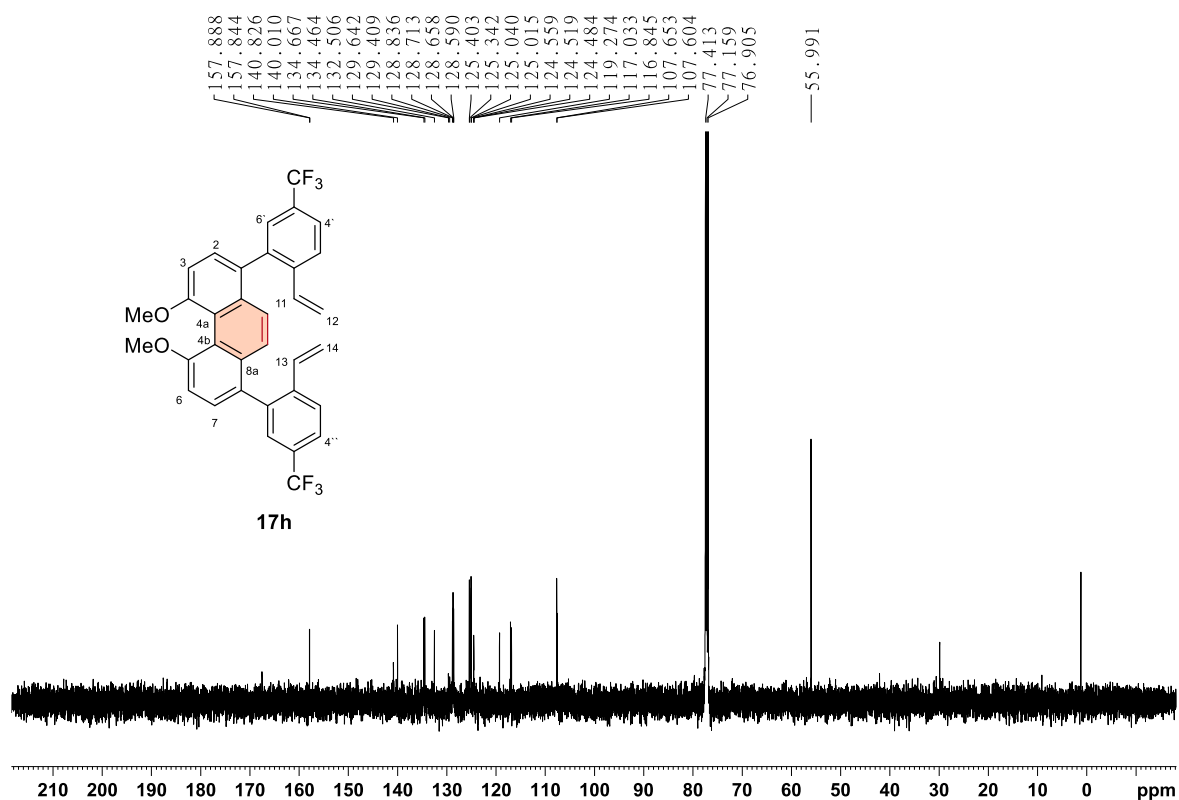
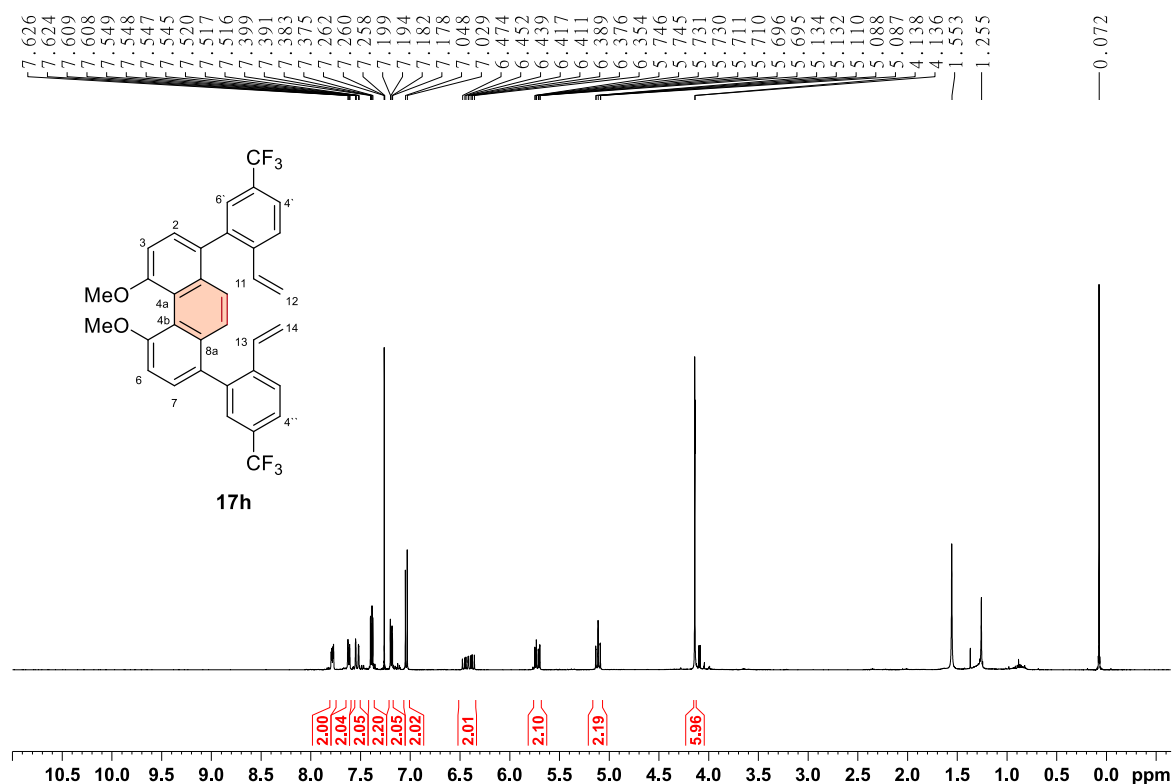
**1,8-Bis(5-fluoro-2-vinylphenyl)-4,5-dimethoxyphenanthrene (17f):**

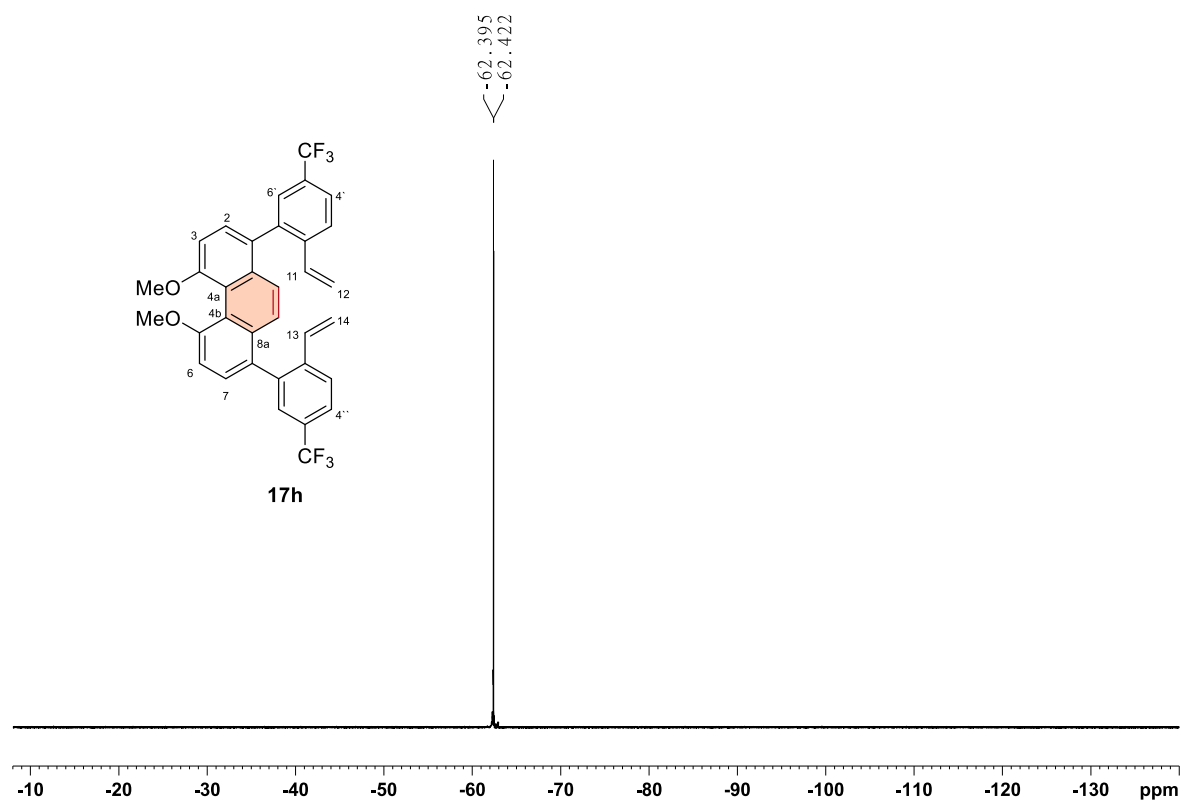


**4-Methoxy-1,8-bis(5-methoxy-2-vinylphenyl)-5-methylphenanthrene (17g):**

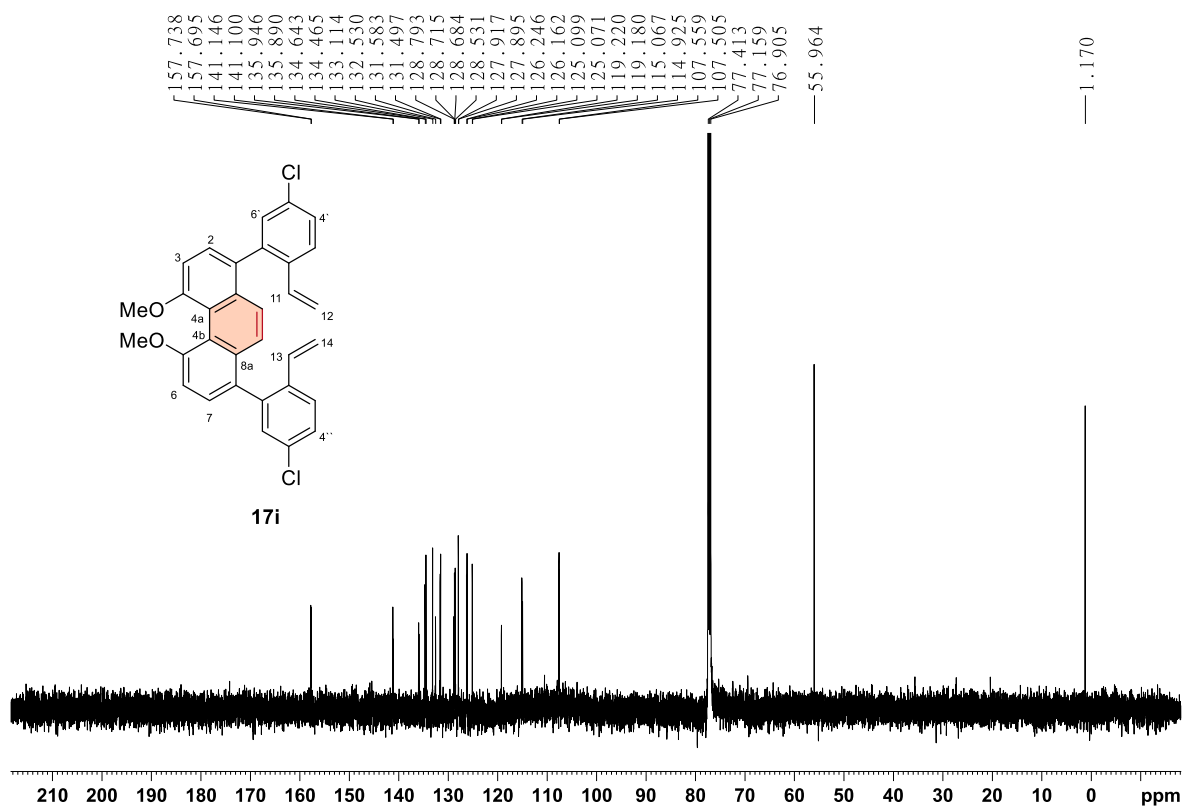
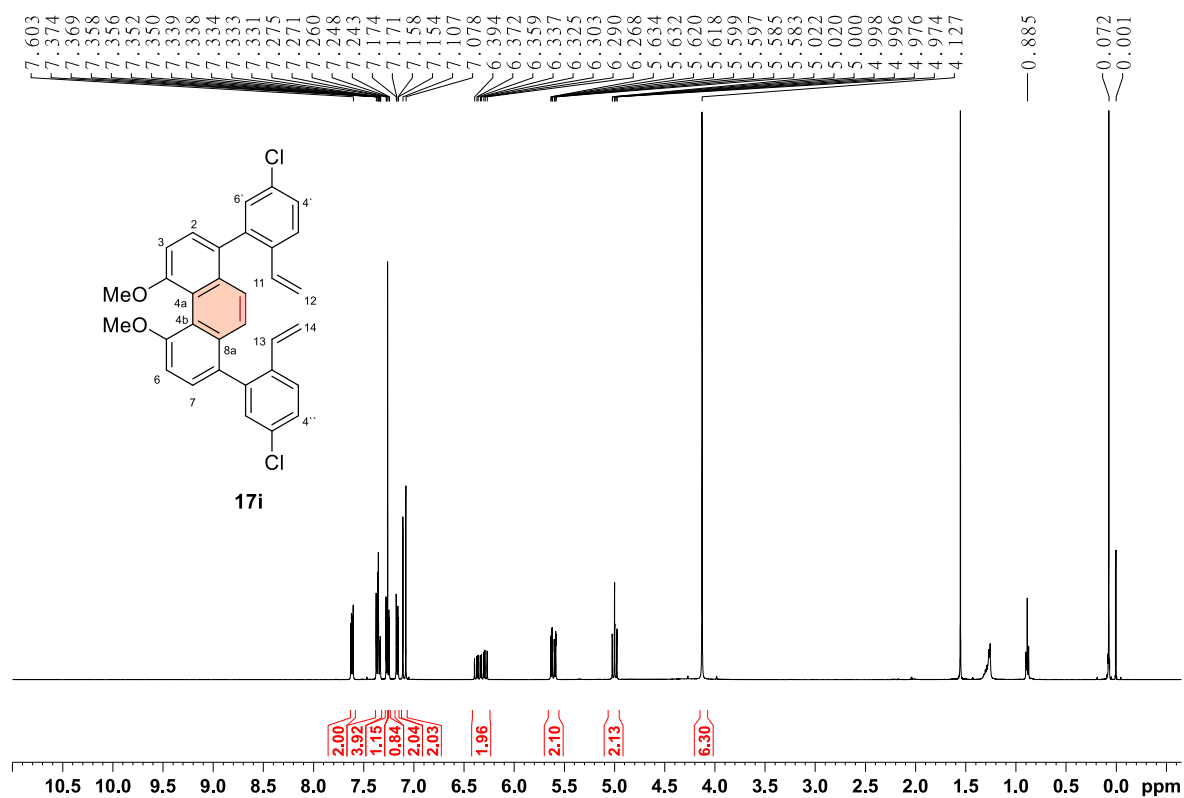


**4,5-Dimethoxy-1,8-bis(5-(trifluoromethyl)-2-vinylphenyl)phenanthrene (17h):**

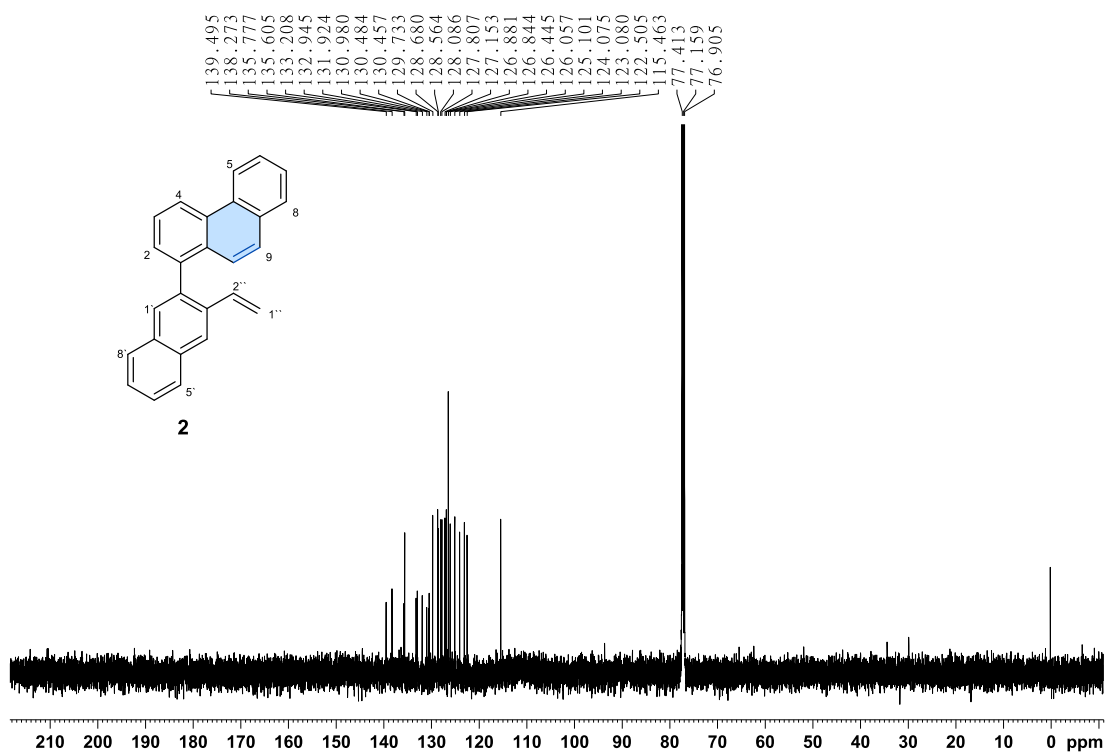
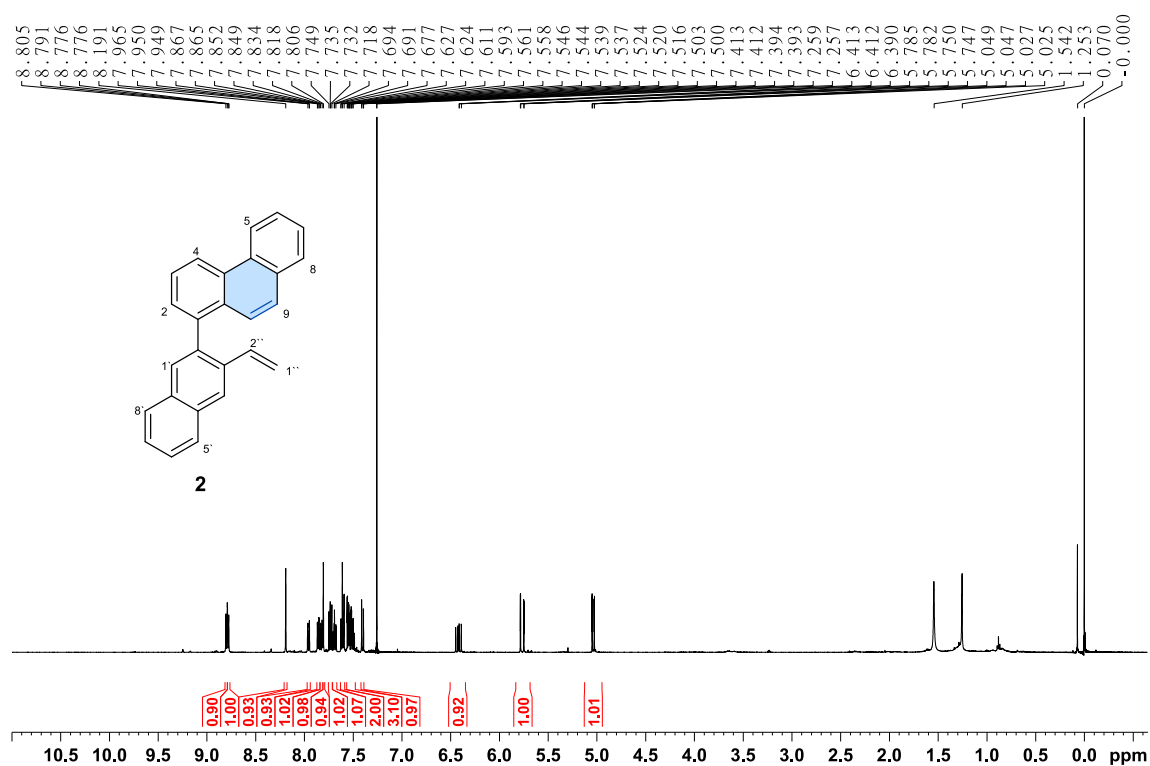




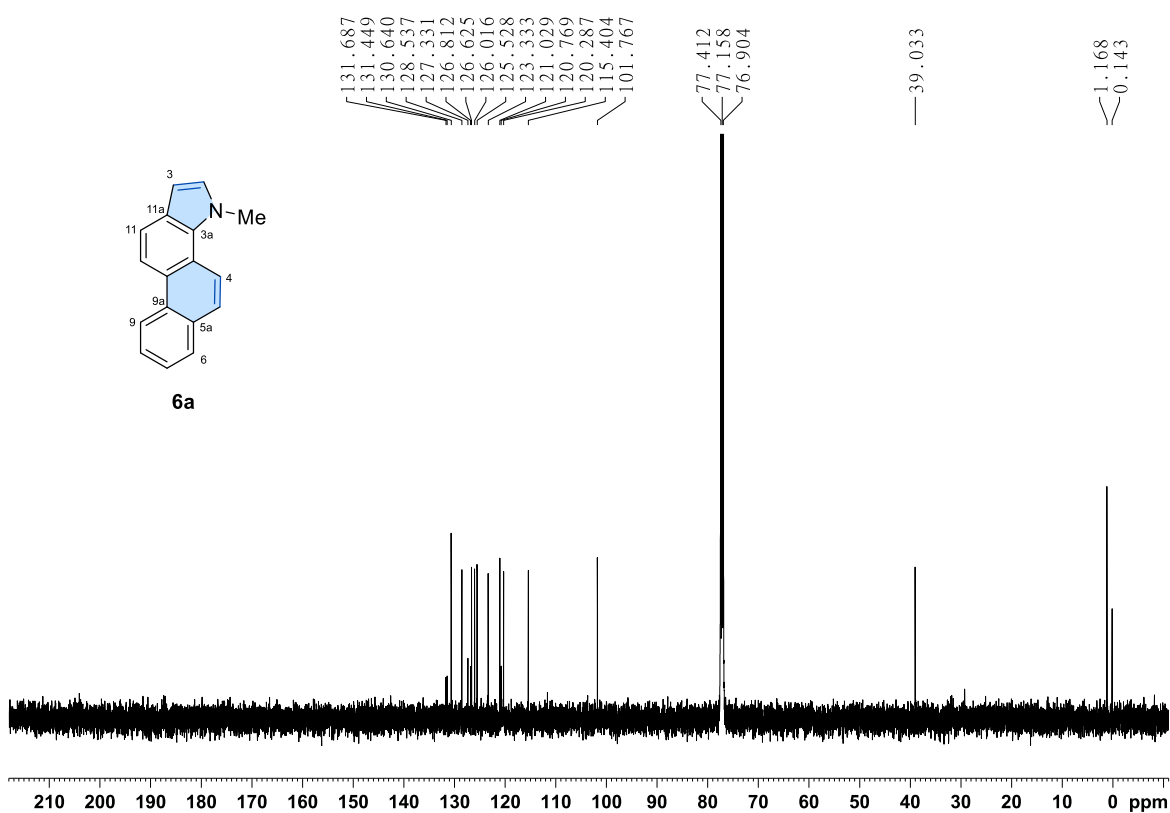
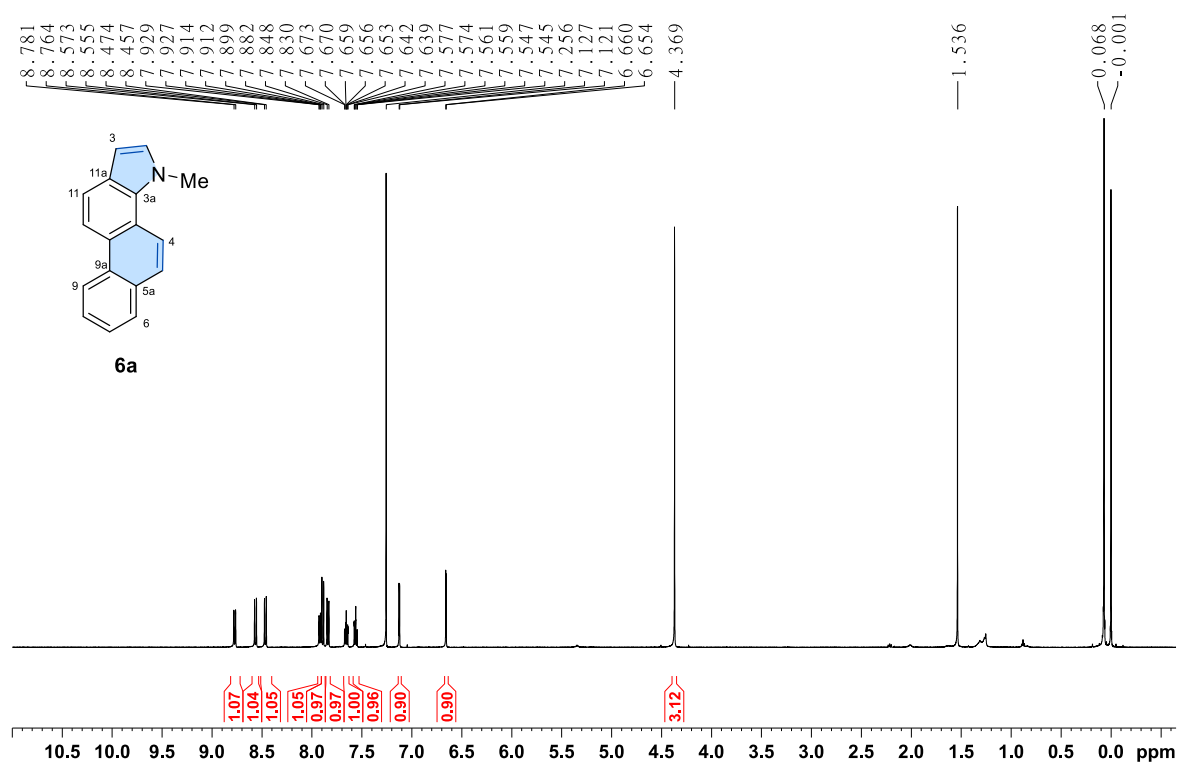
**1,8-Bis(5-chloro-2-vinylphenyl)-4,5-dimethoxyphenanthrene (17i):**



**1-(3-Vinylnaphthalen-2-yl)phenanthrene (2):**

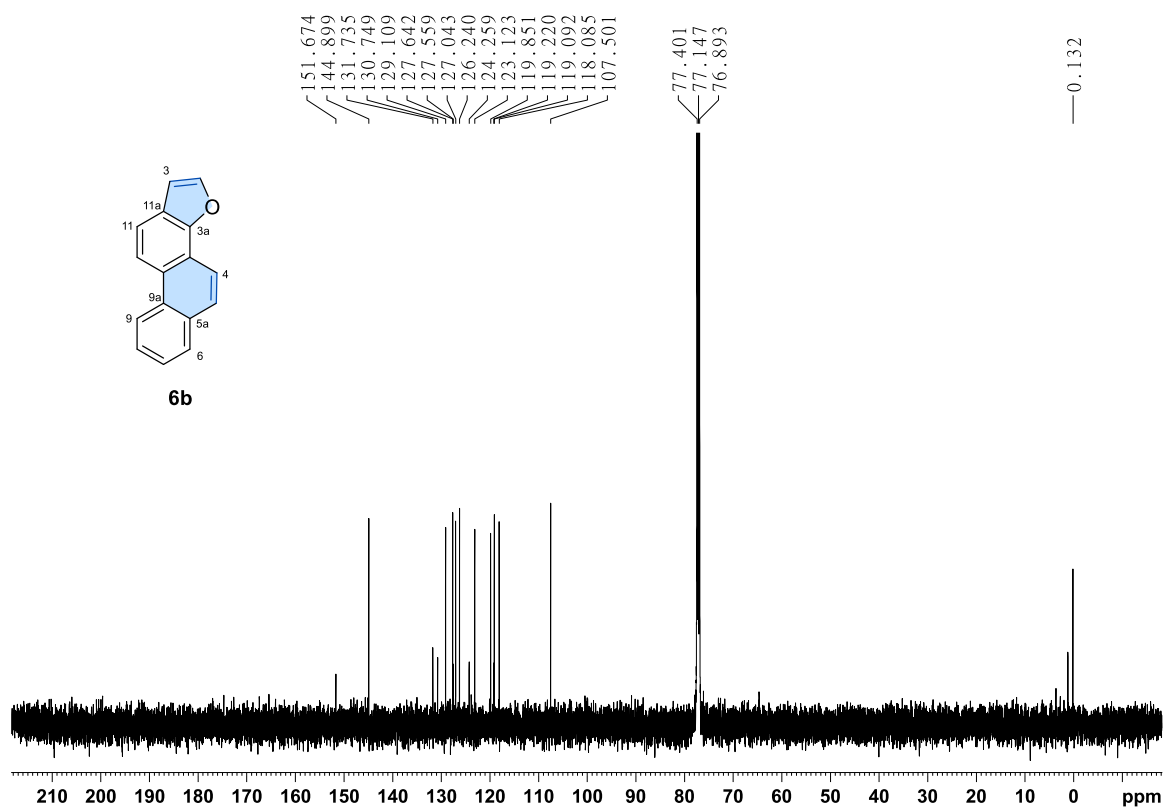
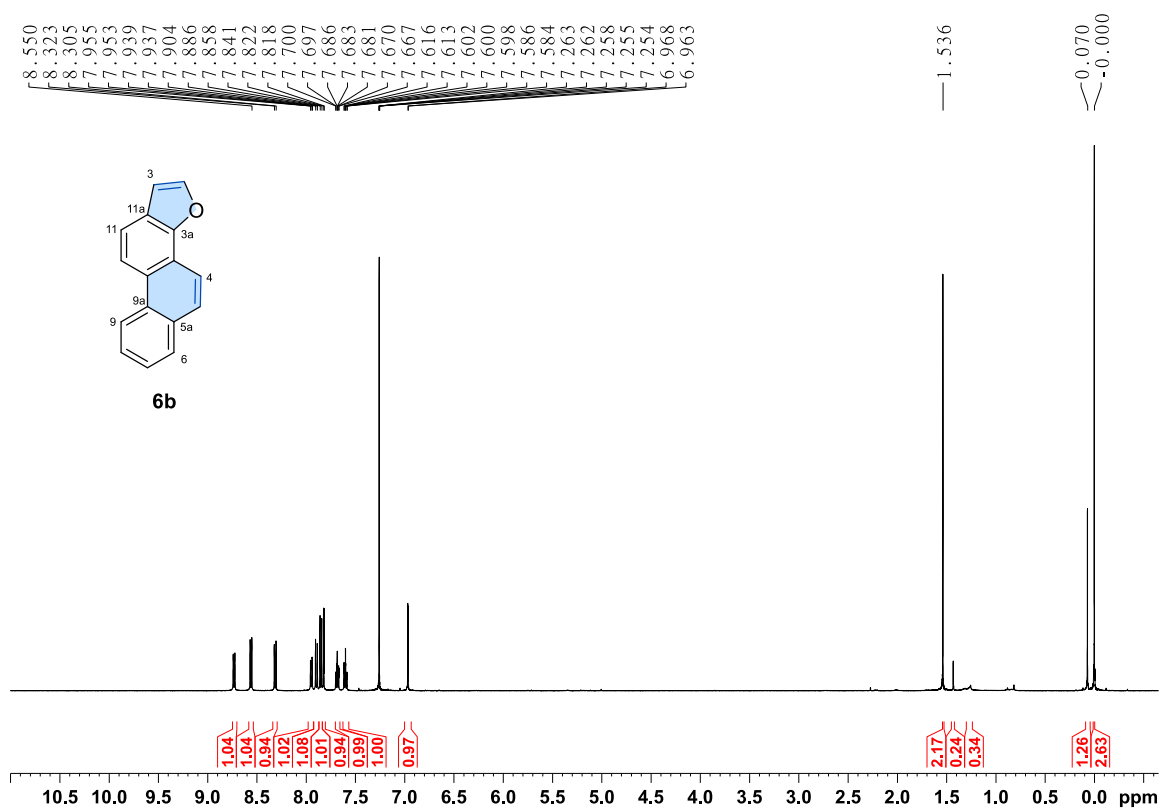


### 3-Methyl-3H-naphtho[1,2-g]indole (6a):

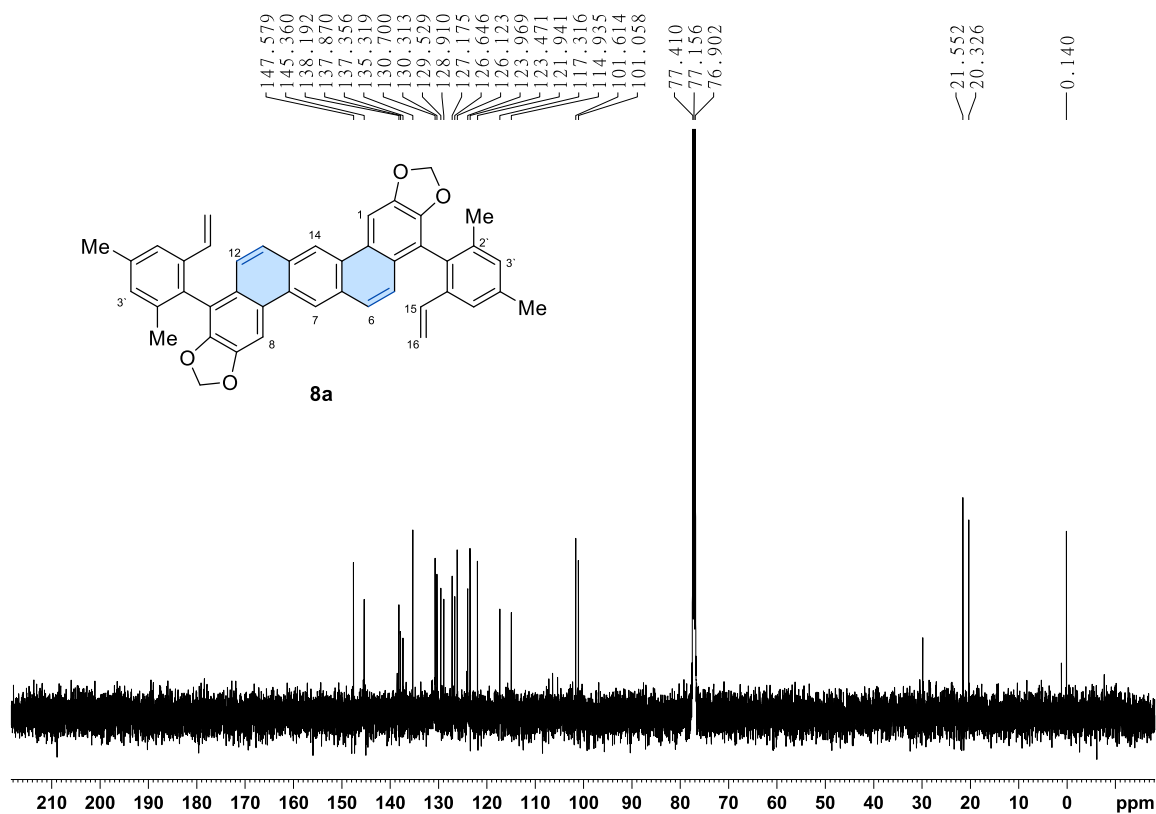
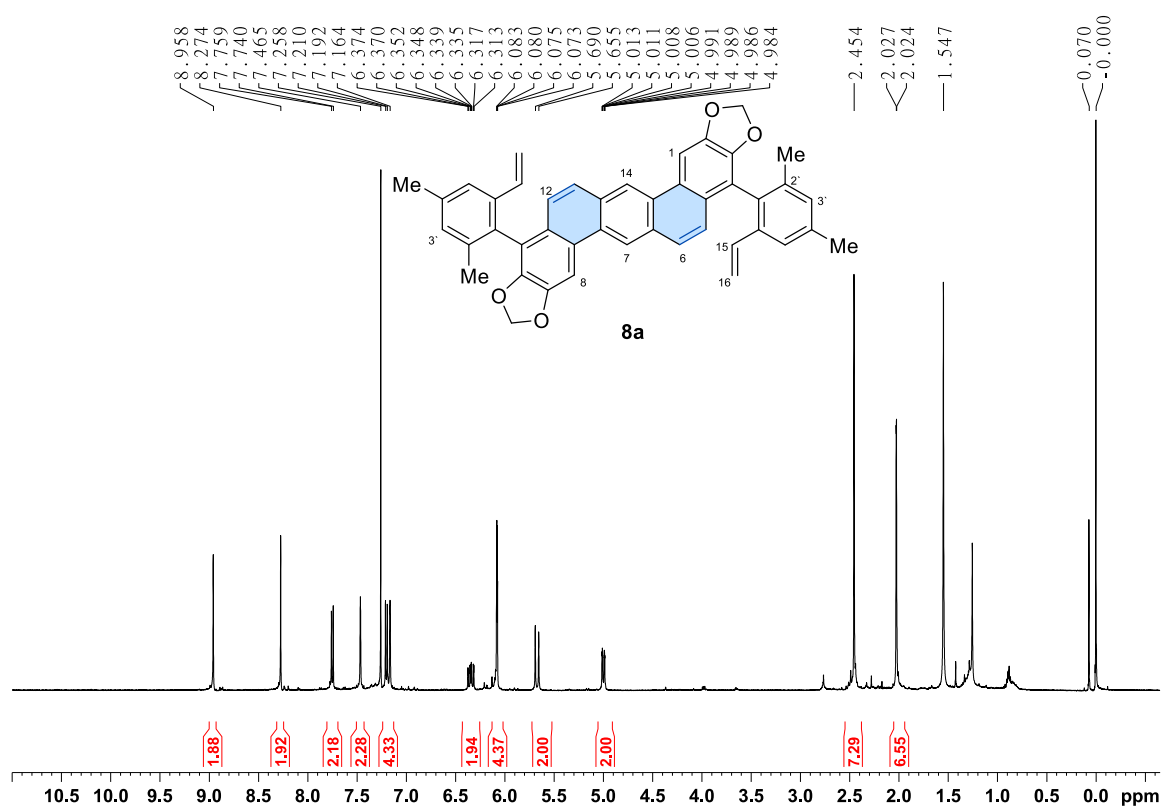




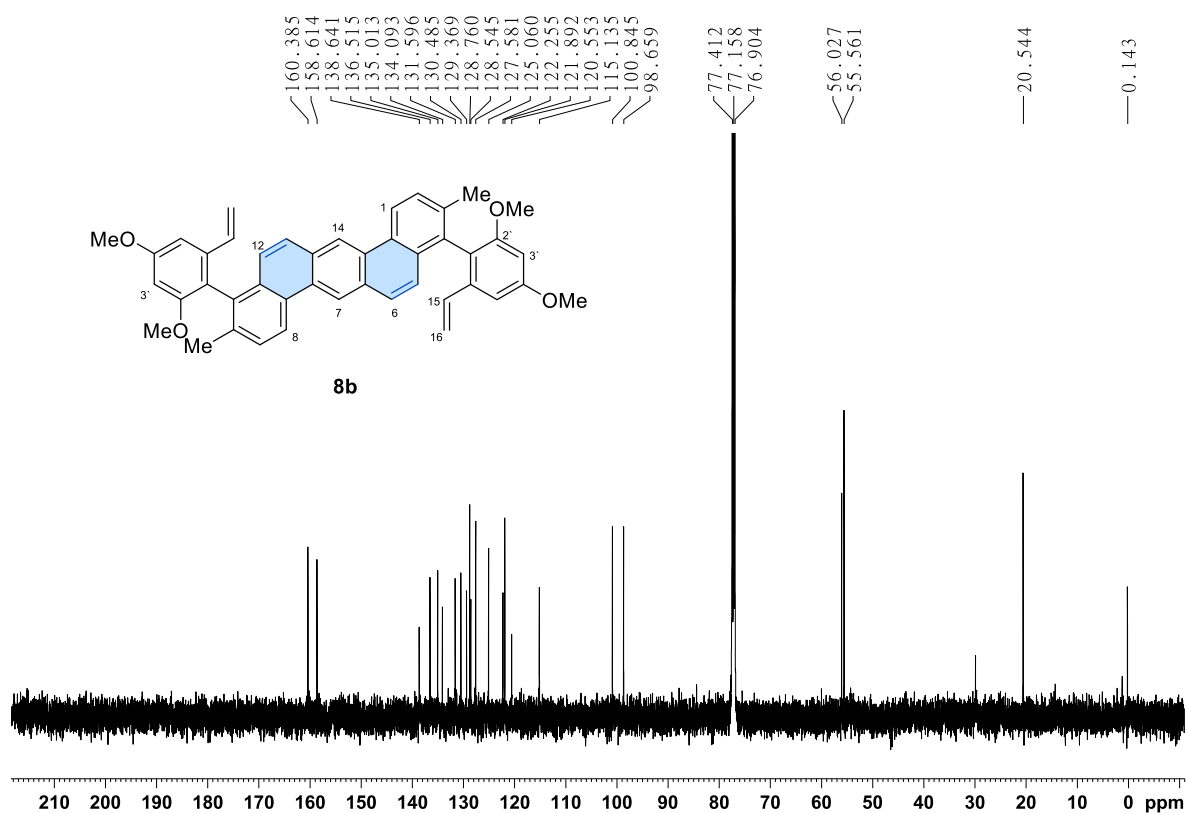
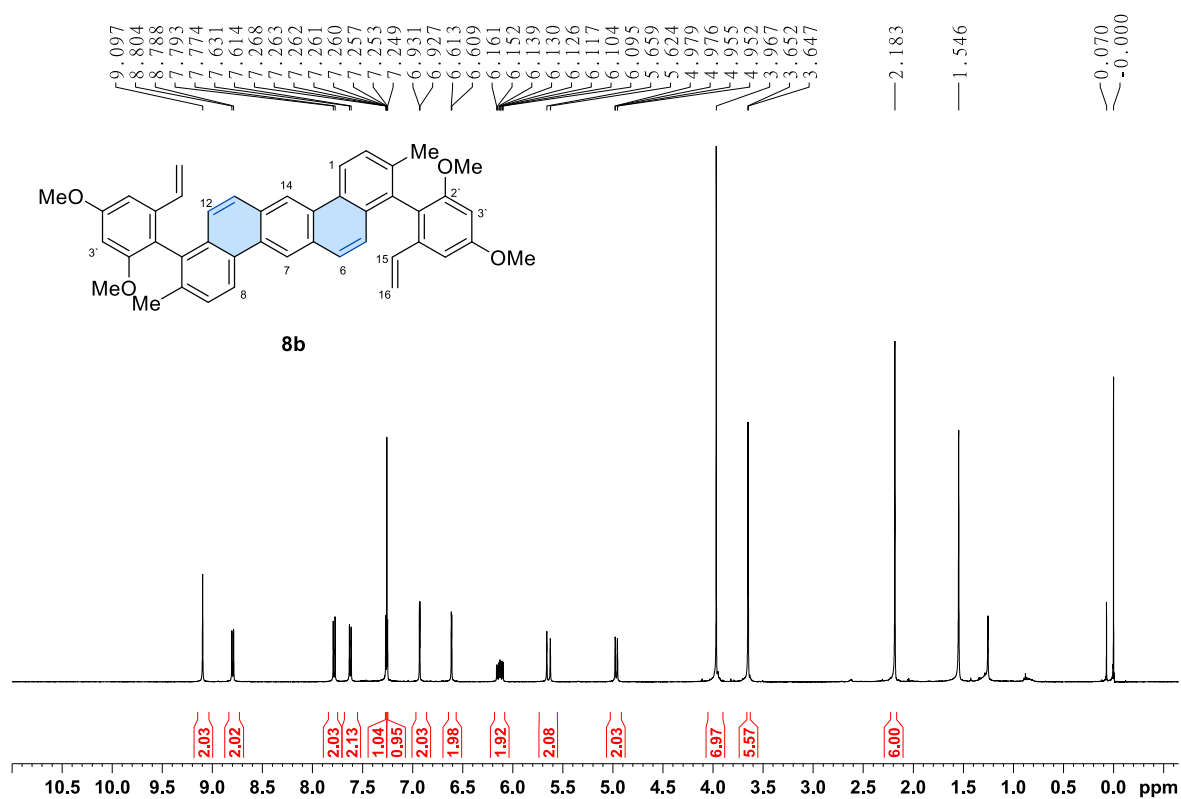
**Phenanthro[1,2-b]furan (6b):**



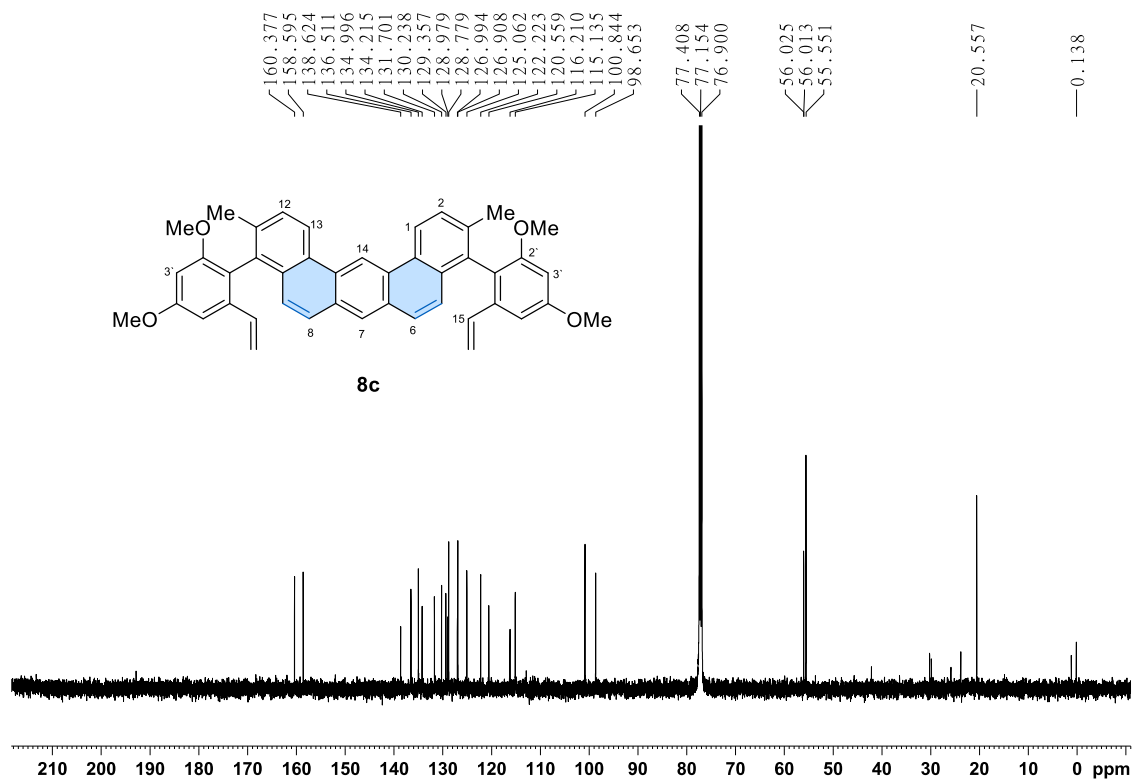
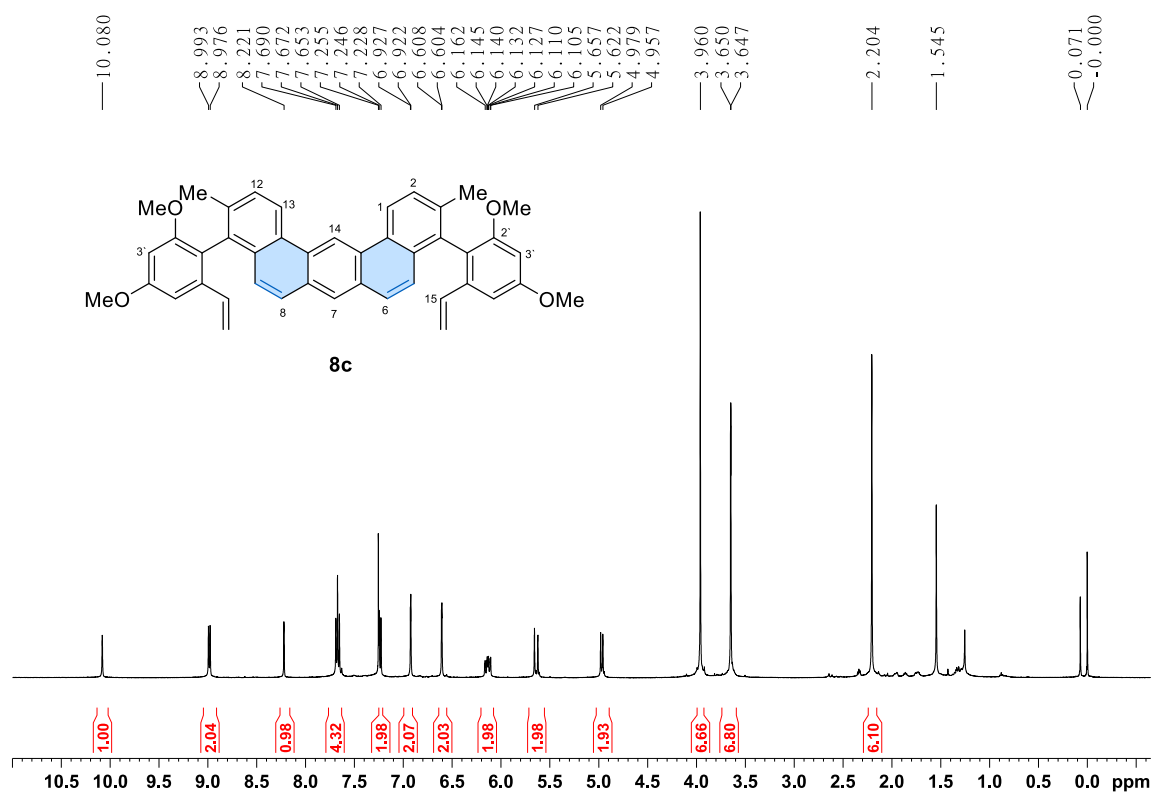
**Benzo[k]tetraphene (8a):**



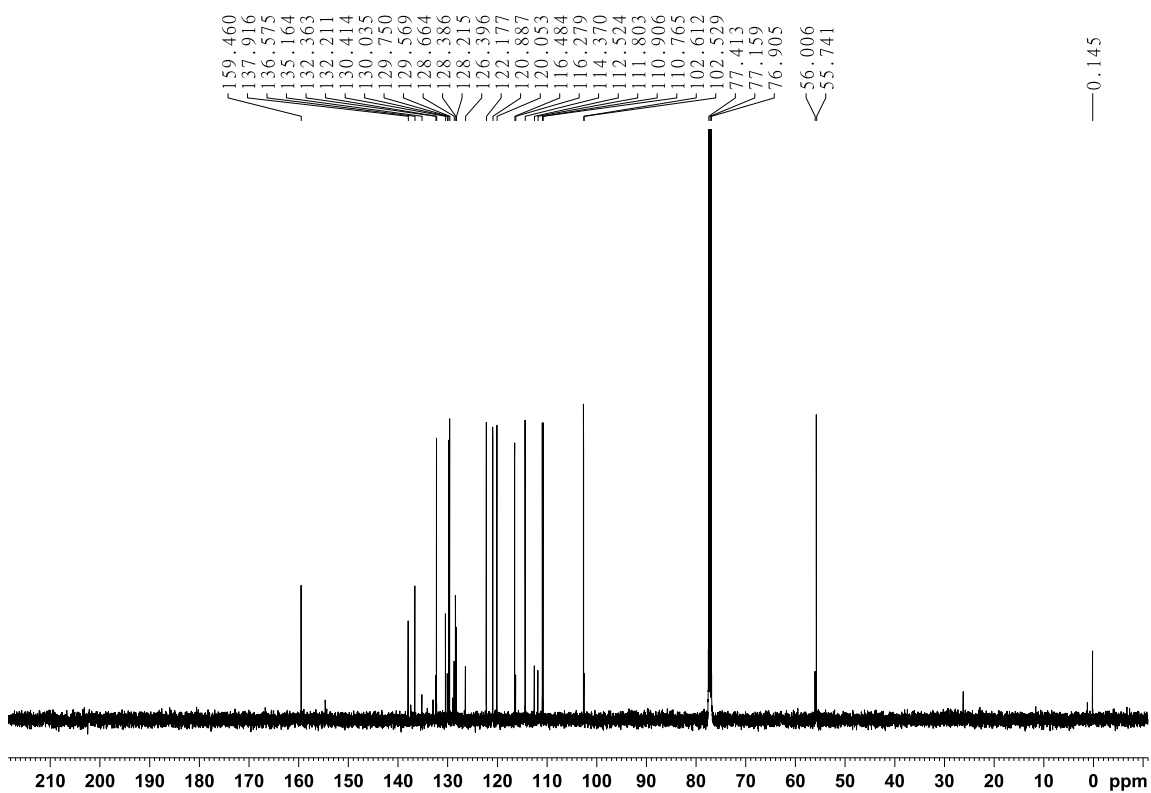
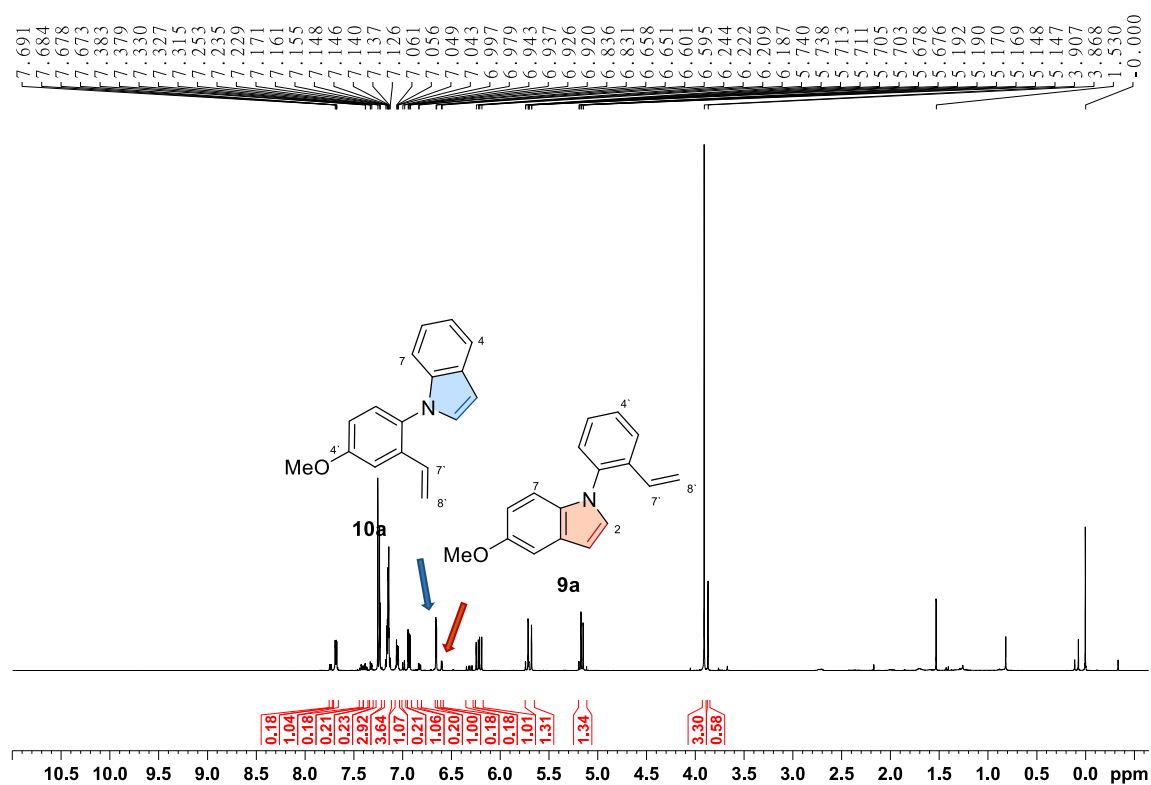
**4,11-Bis(2,4-dimethoxy-6-vinylphenyl)-3,10-dimethylbenzo[k]tetraphene (8b):**



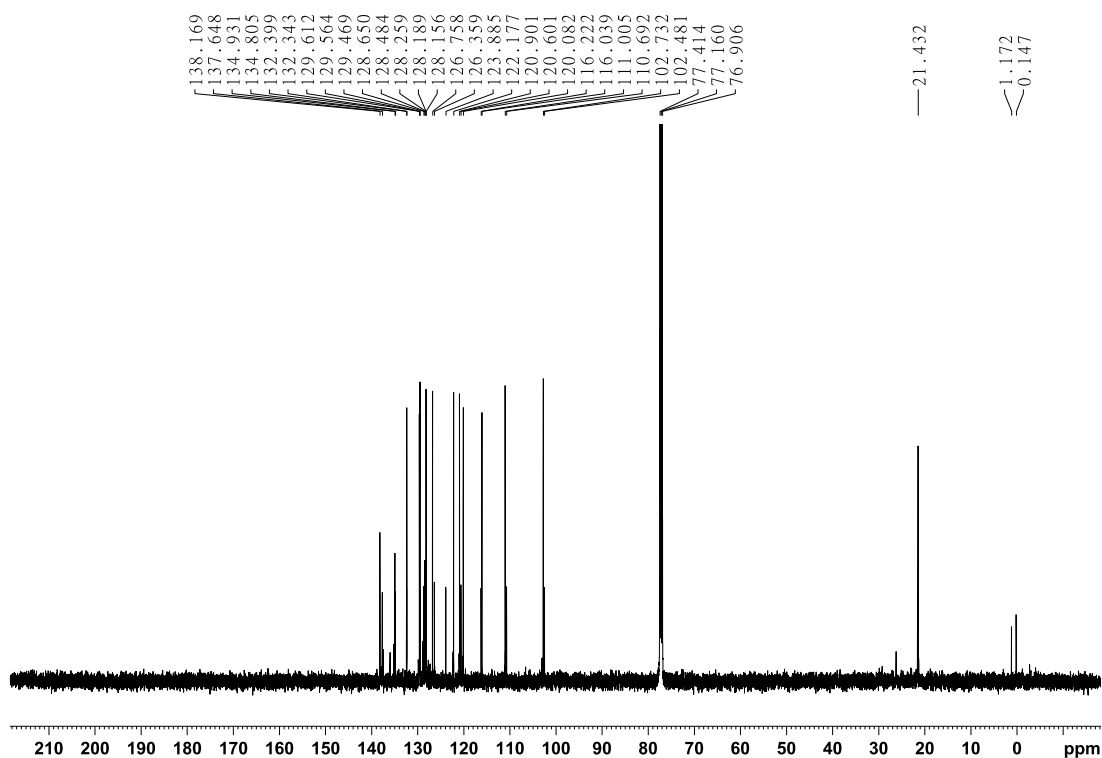
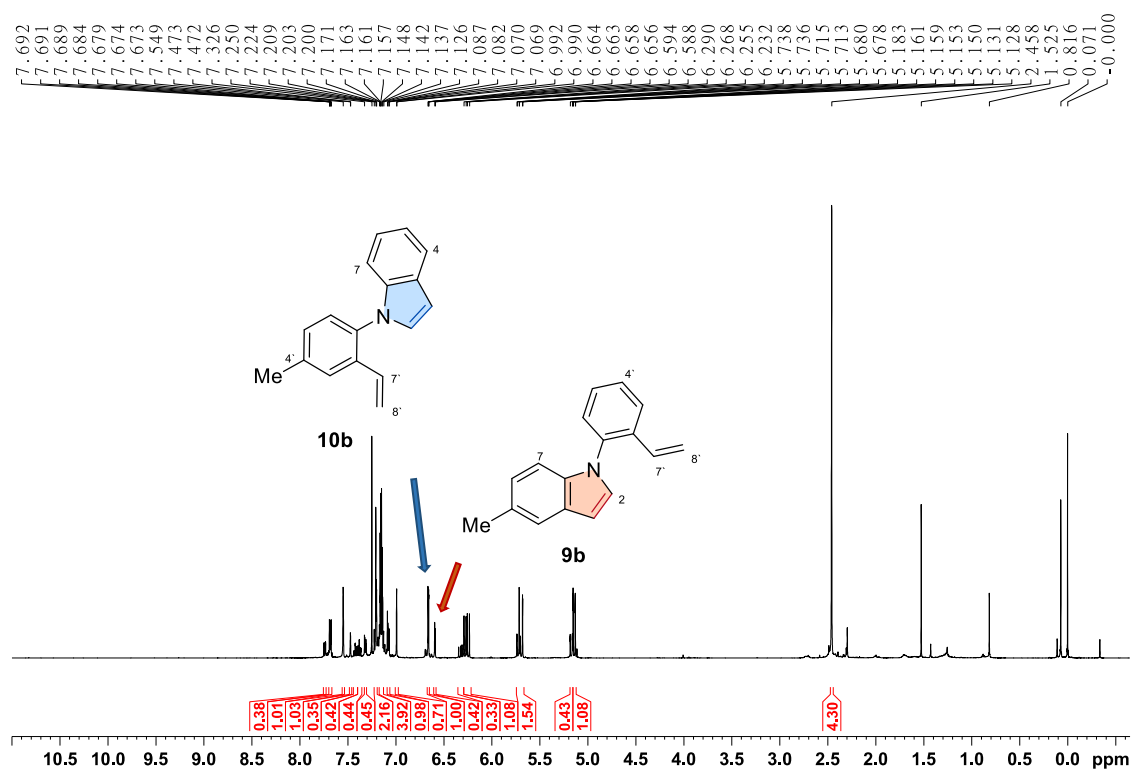
**4,10-Bis(2,4-dimethoxy-6-vinylphenyl)-3,11-dimethylbenzo[*m*]tetraphene (8c):**



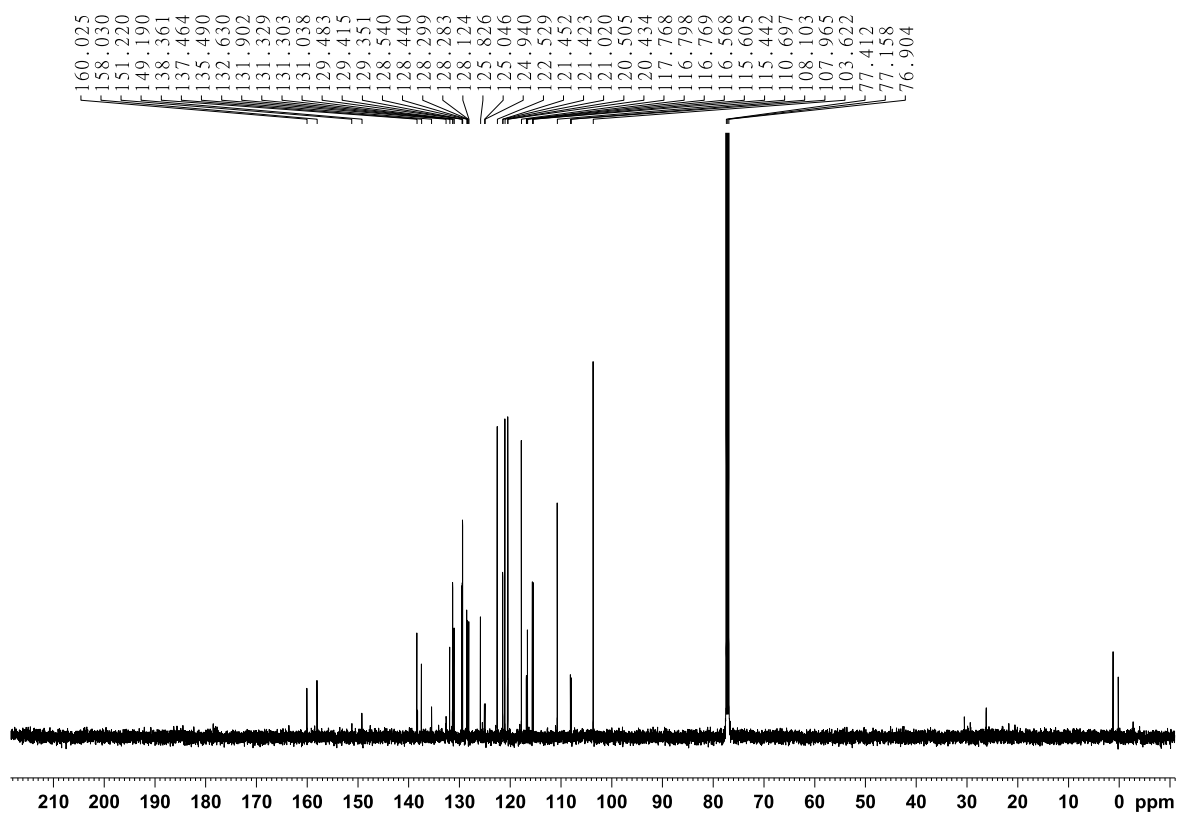
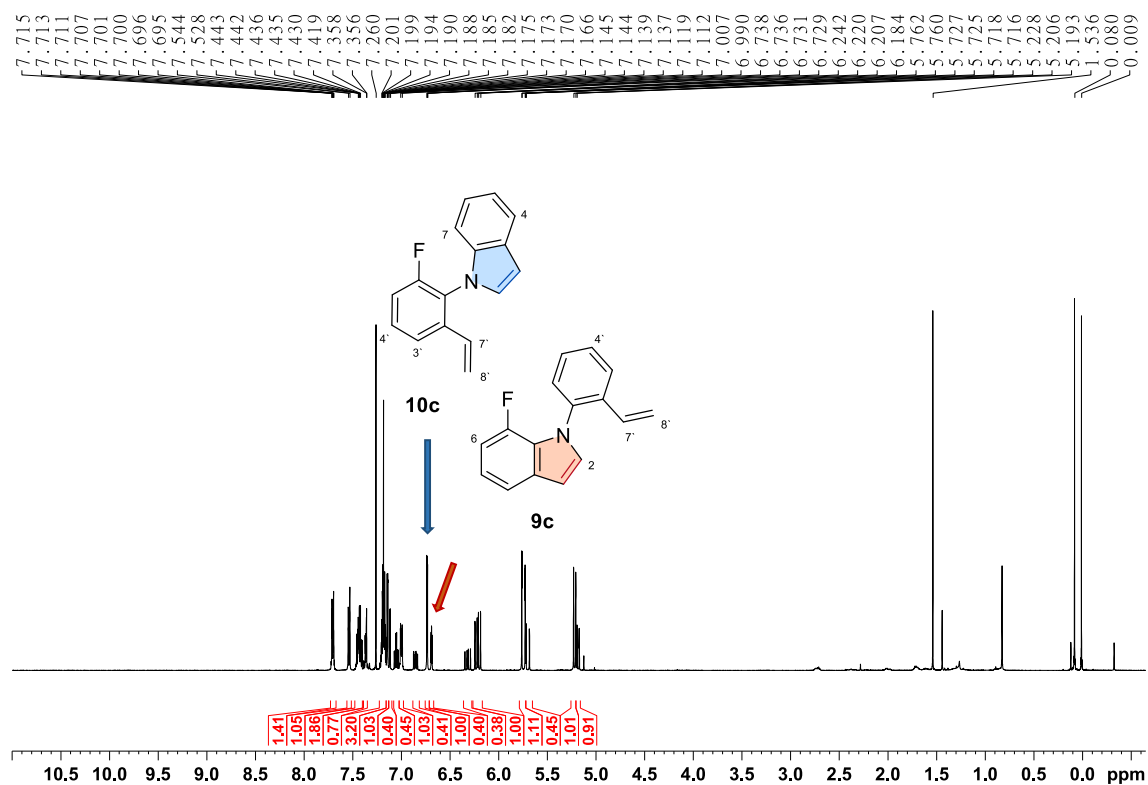
**1-(4-Methoxy-2-vinylphenyl)-1*H*-indole (10a):**

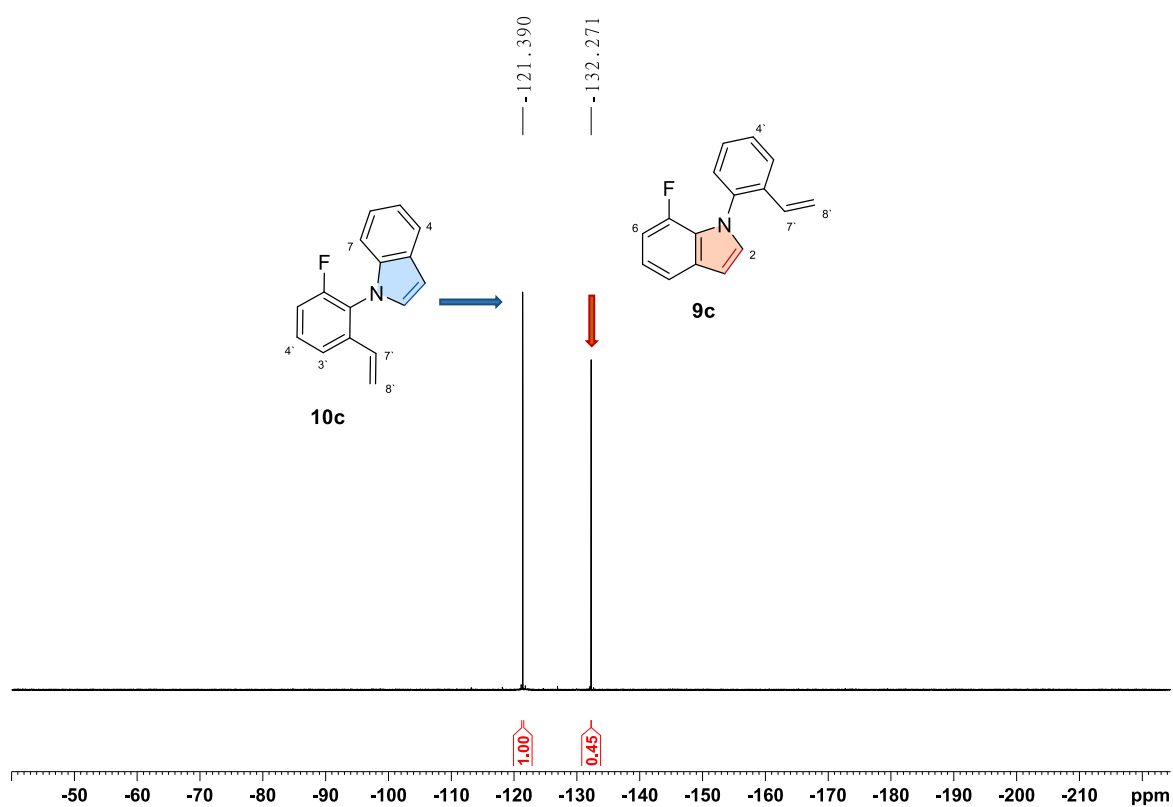


**1-(4-Methyl-2-vinylphenyl)-1H-indole (10b):**



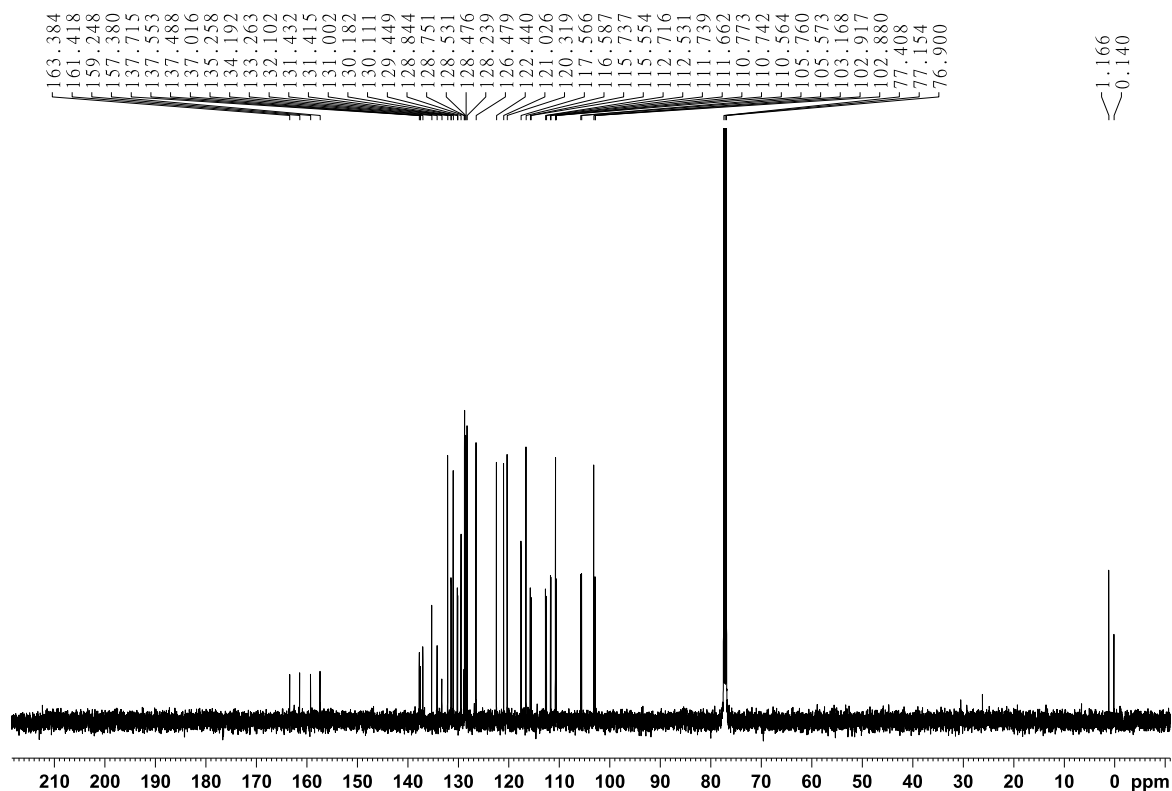
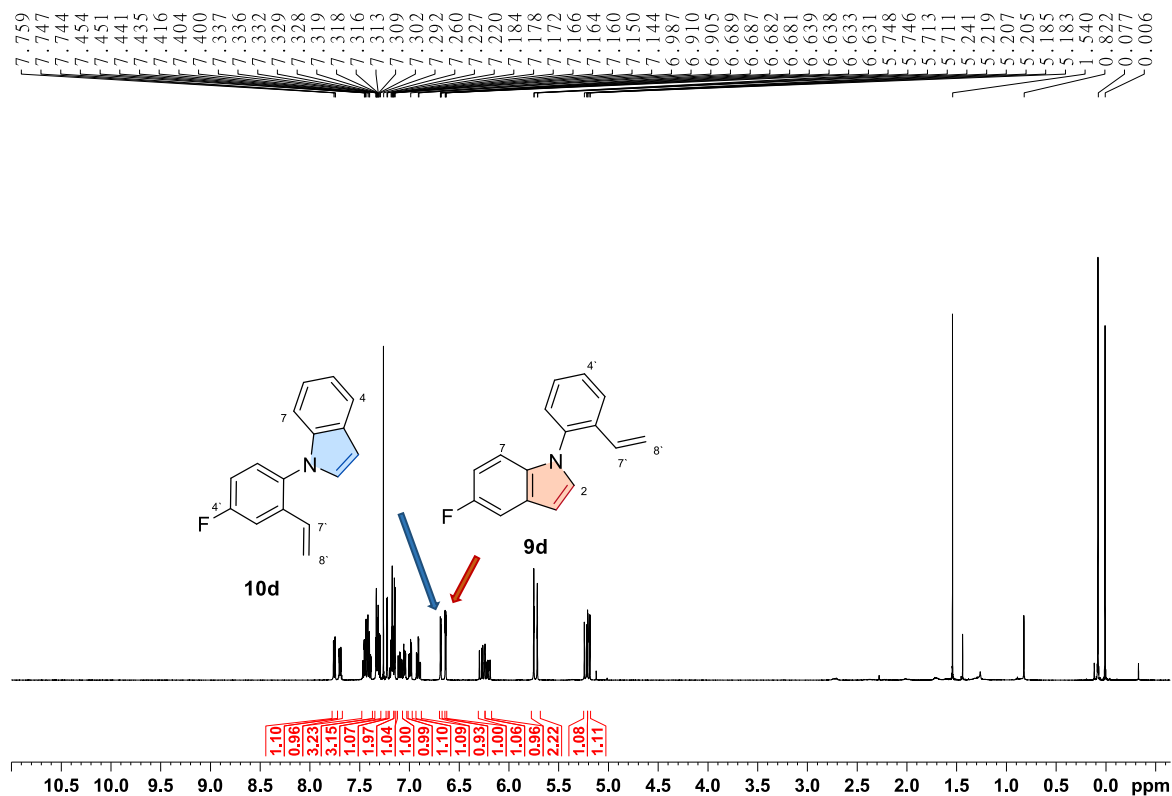
**1-(2-Fluoro-6-vinylphenyl)-1H-indole (10c):**

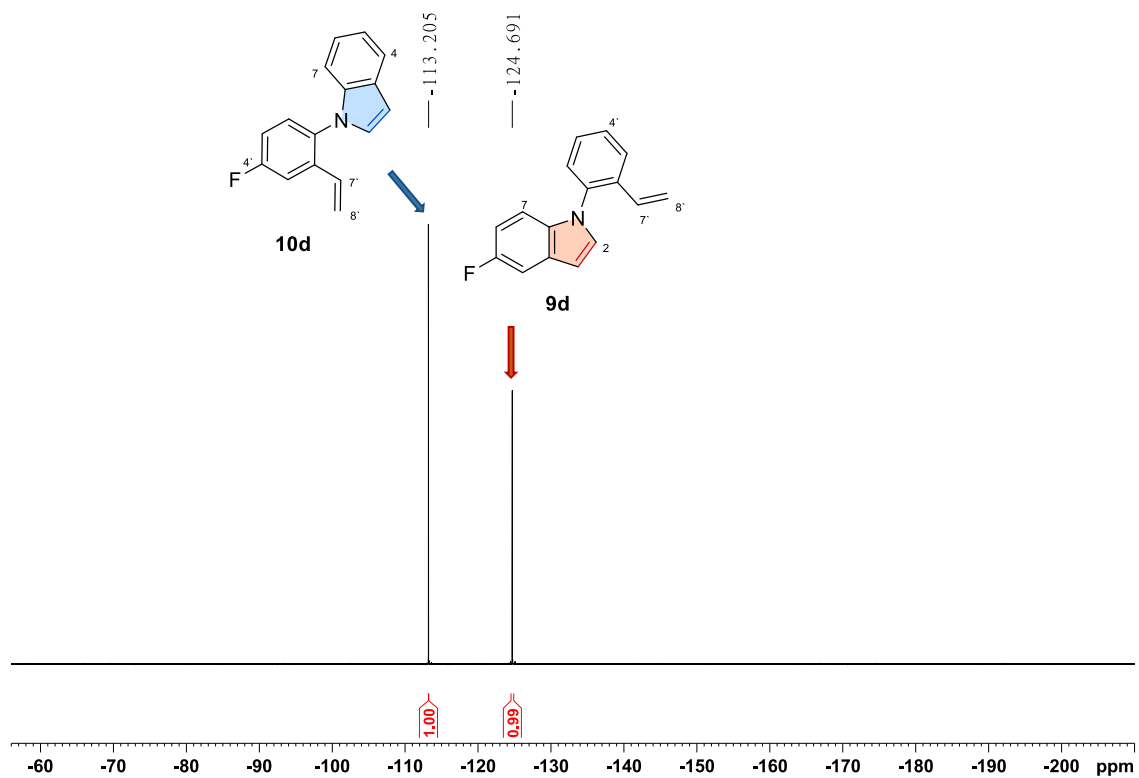




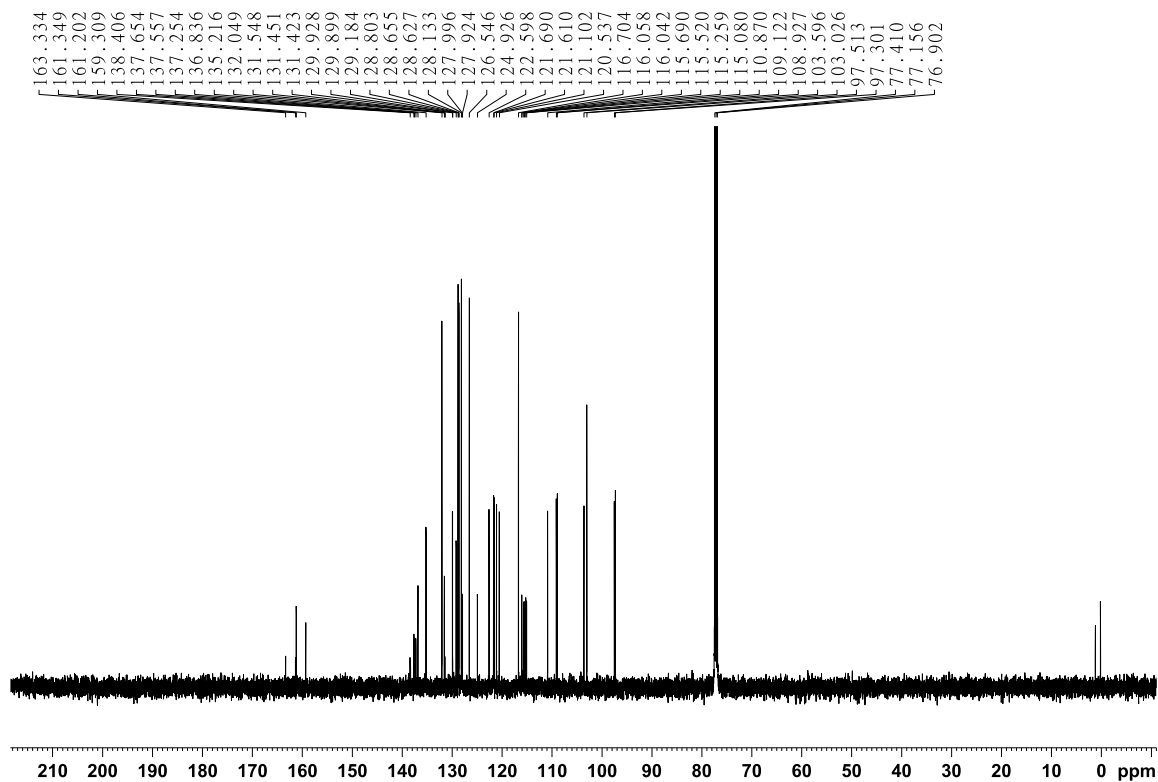
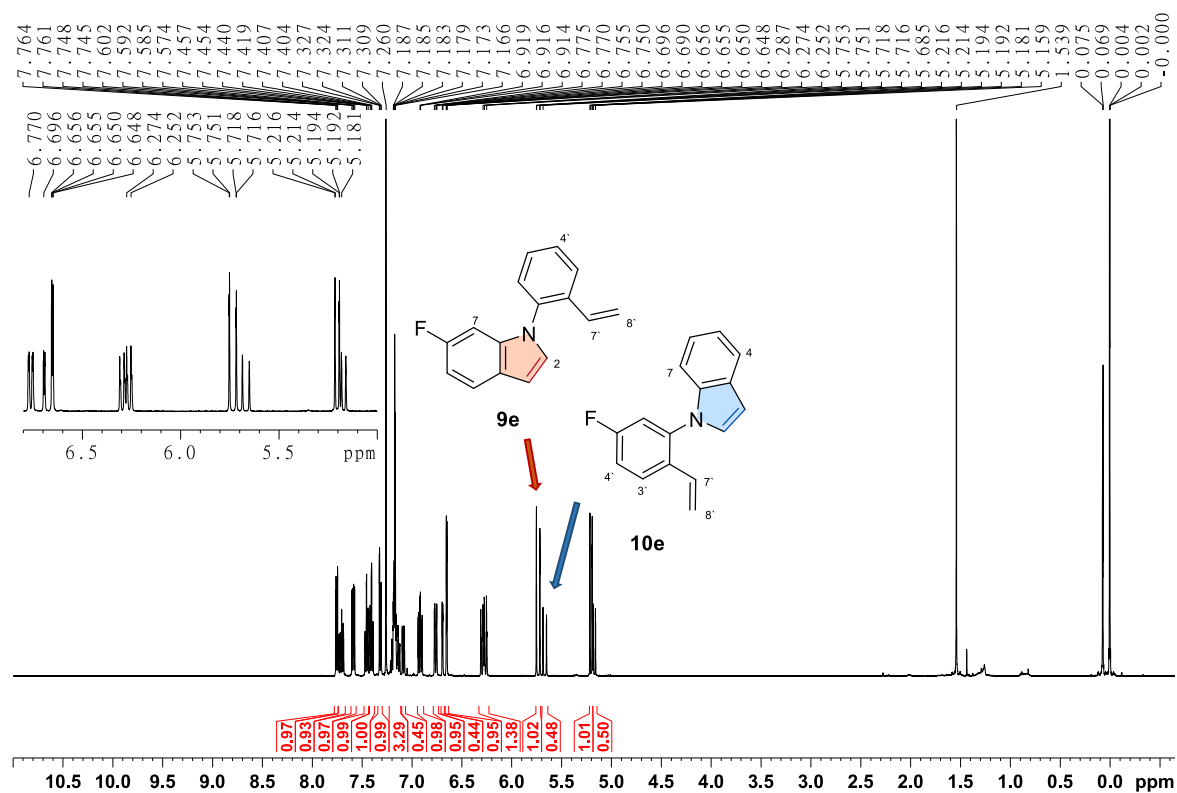


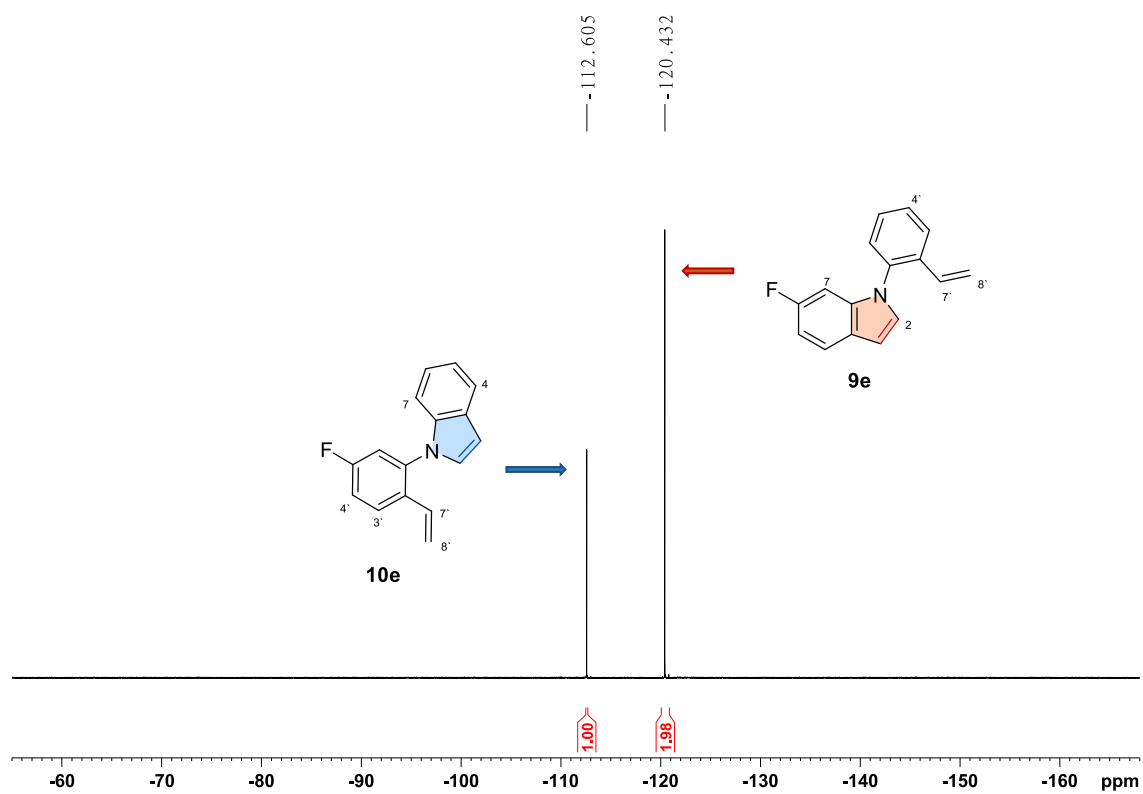
**1-(4-Fluoro-2-vinylphenyl)-1H-indole (10d):**



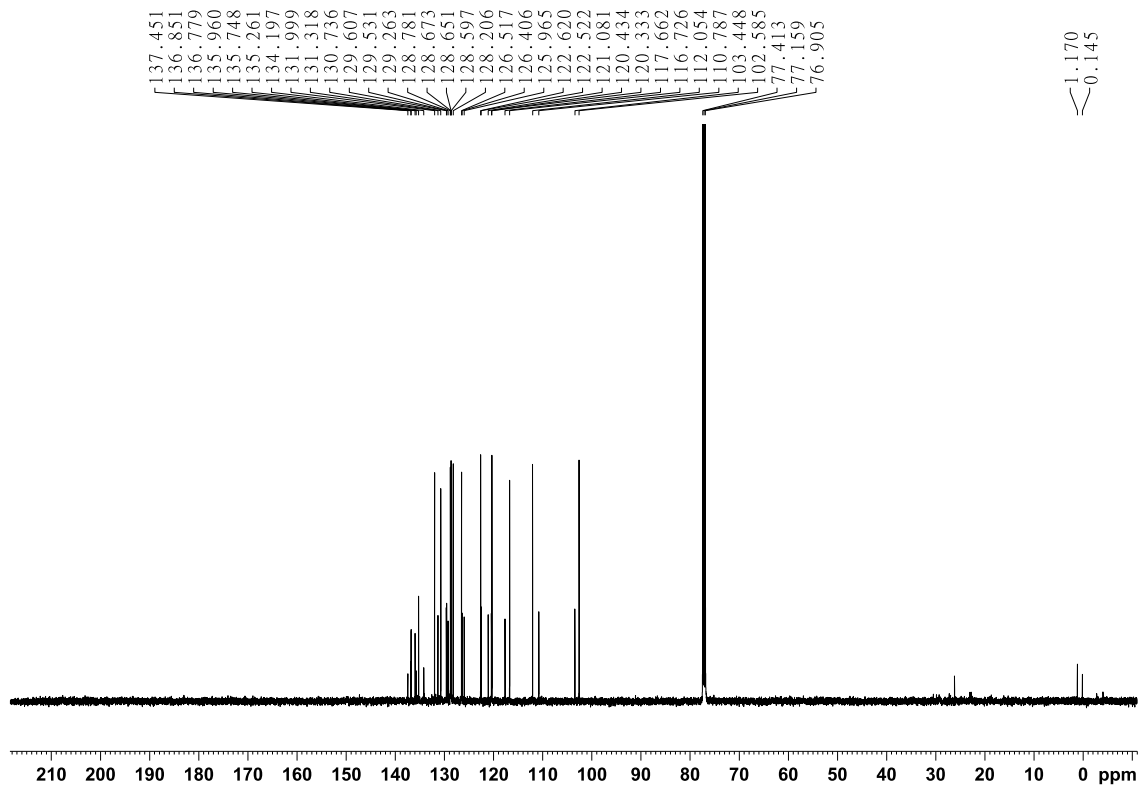
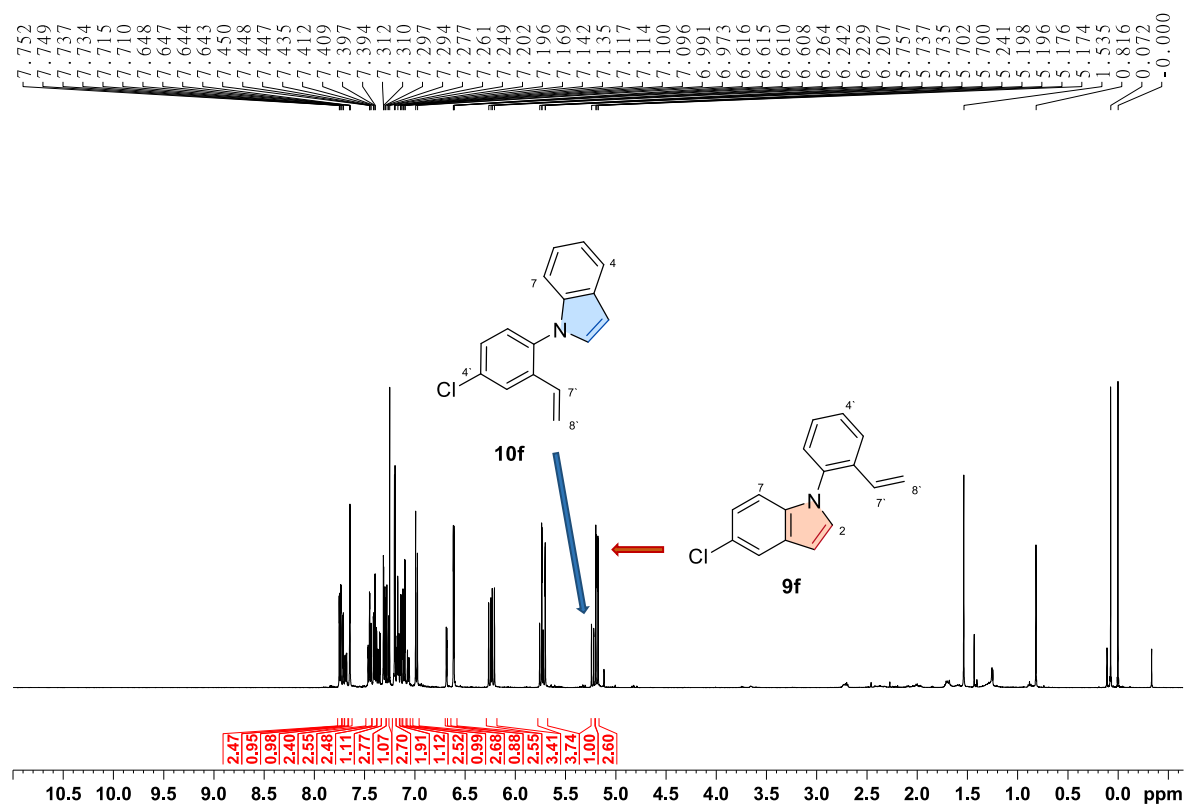


**1-(5-Fluoro-2-vinylphenyl)-1*H*-indole (10e):**

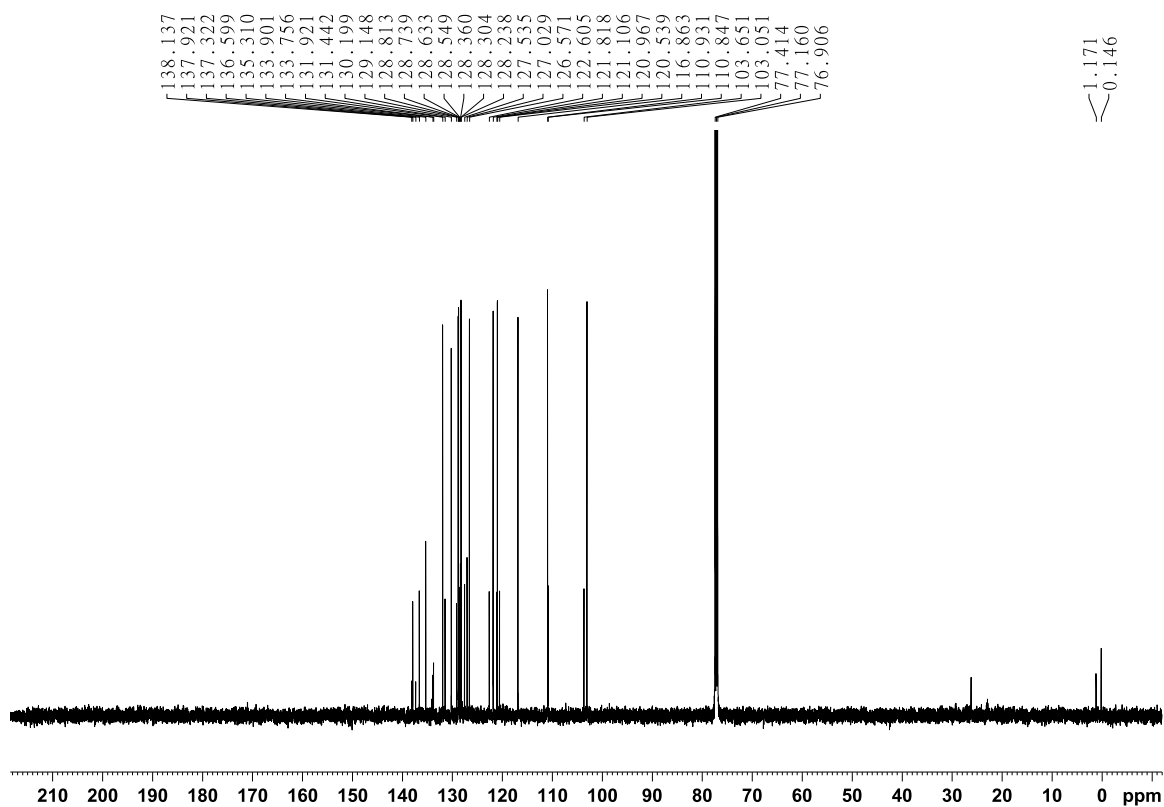
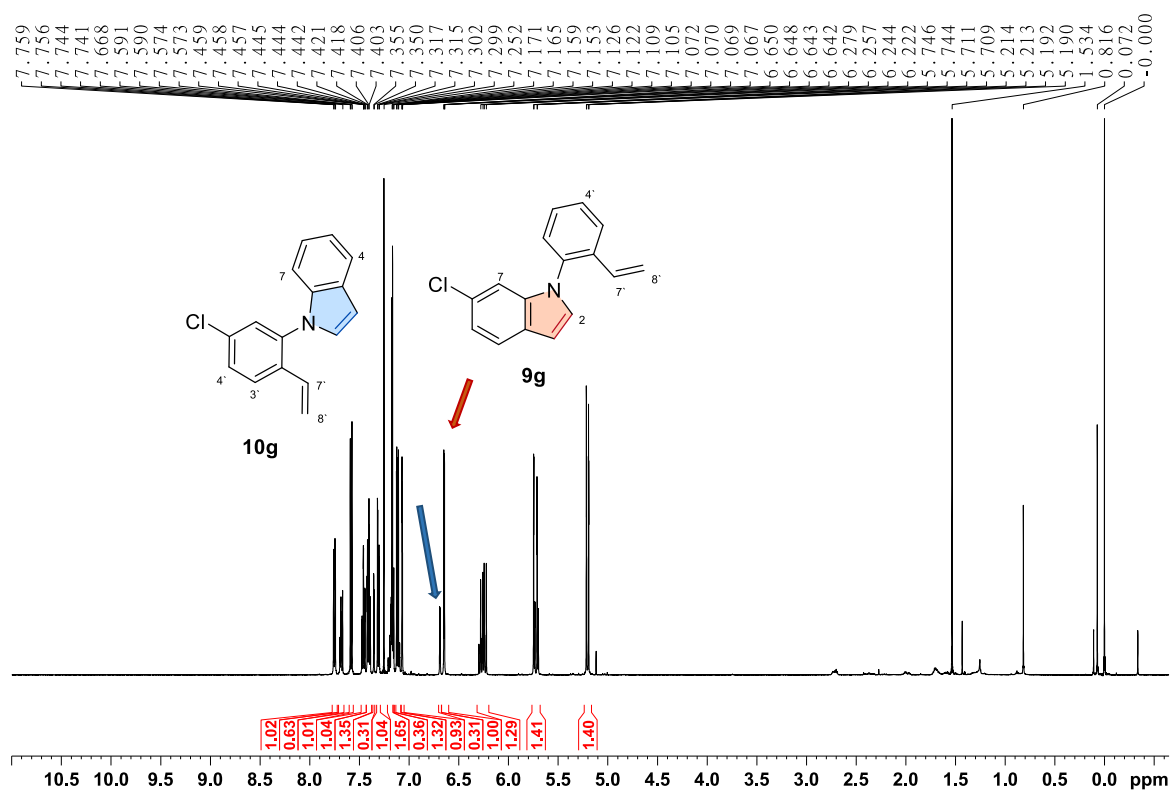




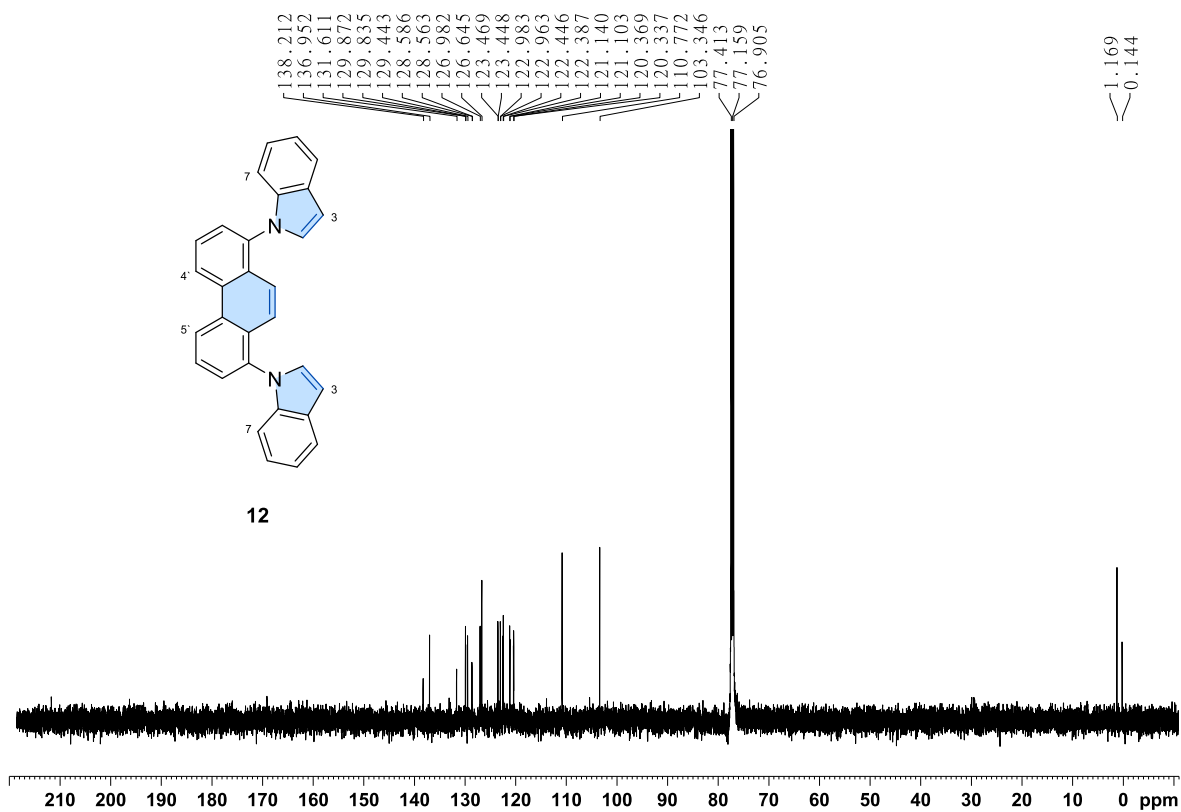
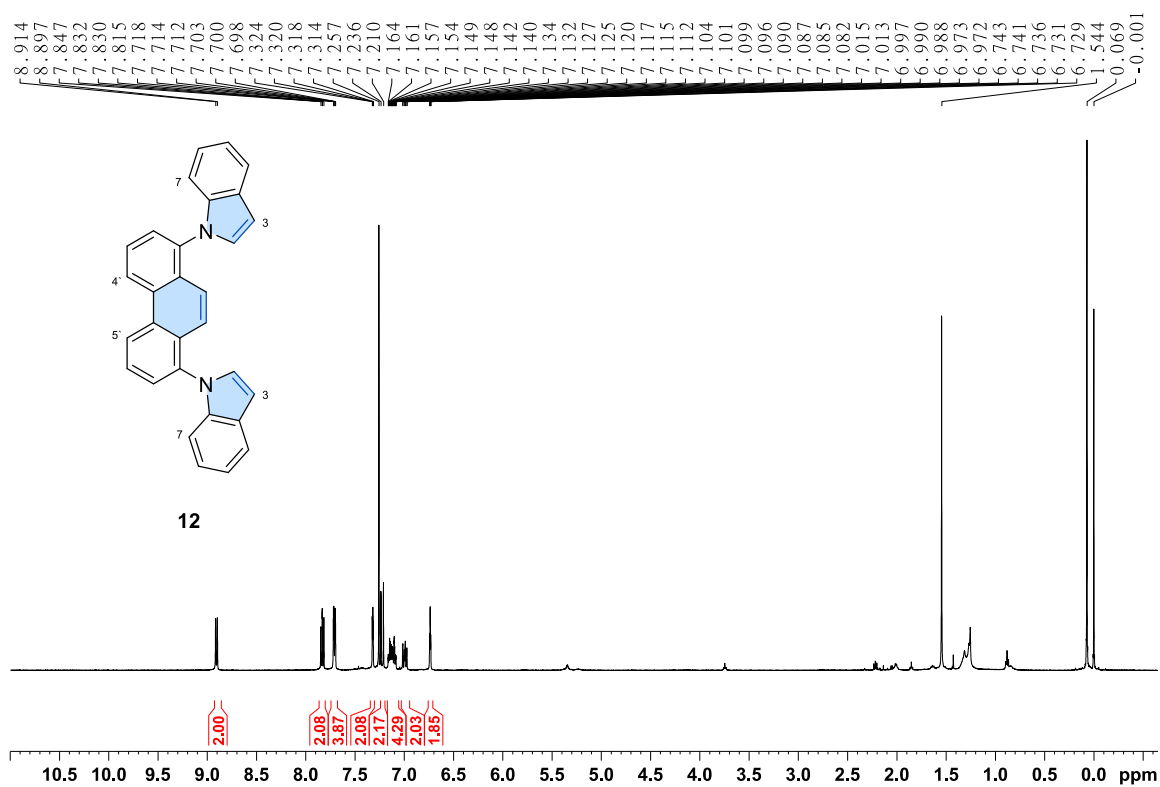
**1-(4-Chloro-2-vinylphenyl)-1H-indole (10f):**



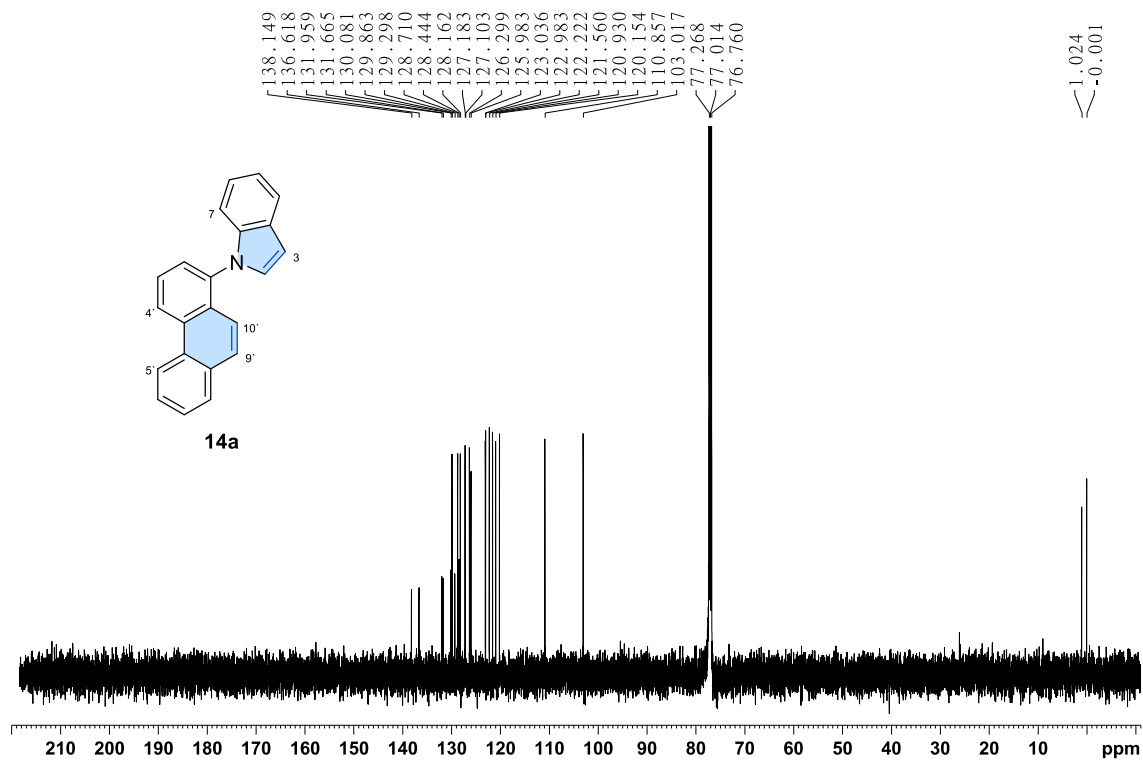
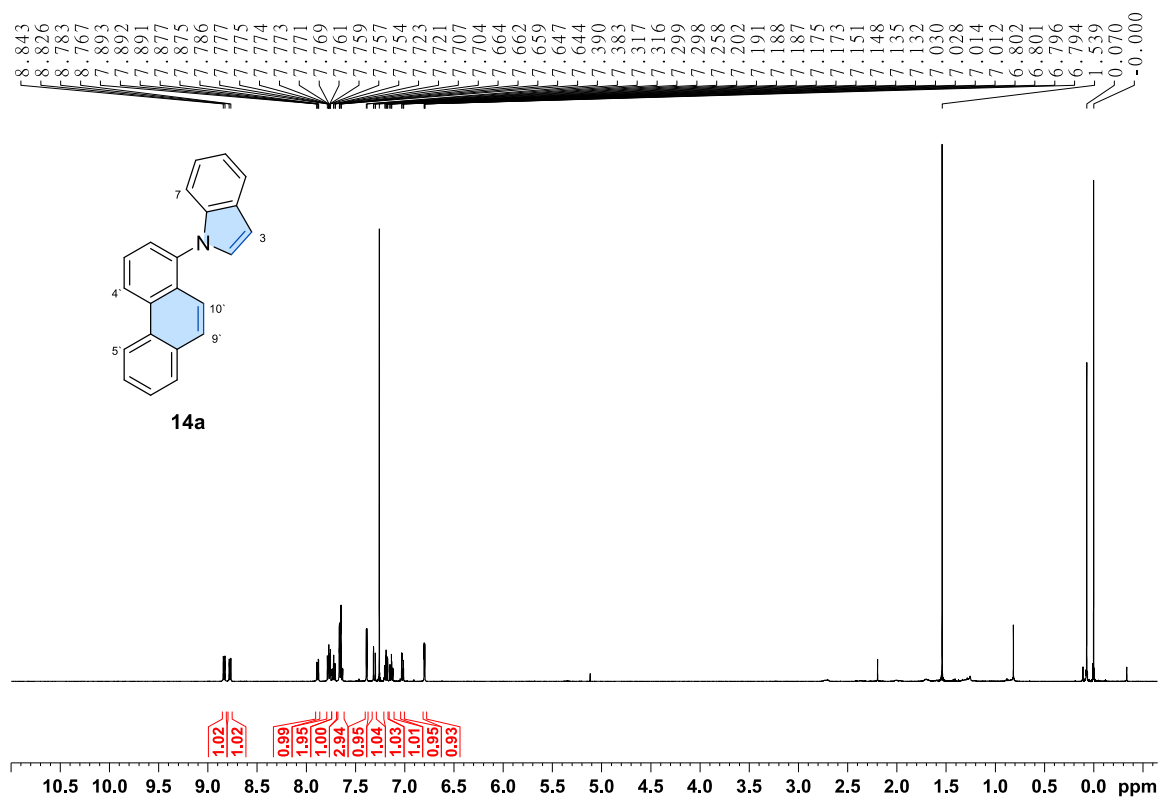
**1-(5-Chloro-2-vinylphenyl)-1H-indole (10g):**



**1,8-Di(1-*H*-indol-1-yl)phenanthrene (12):**

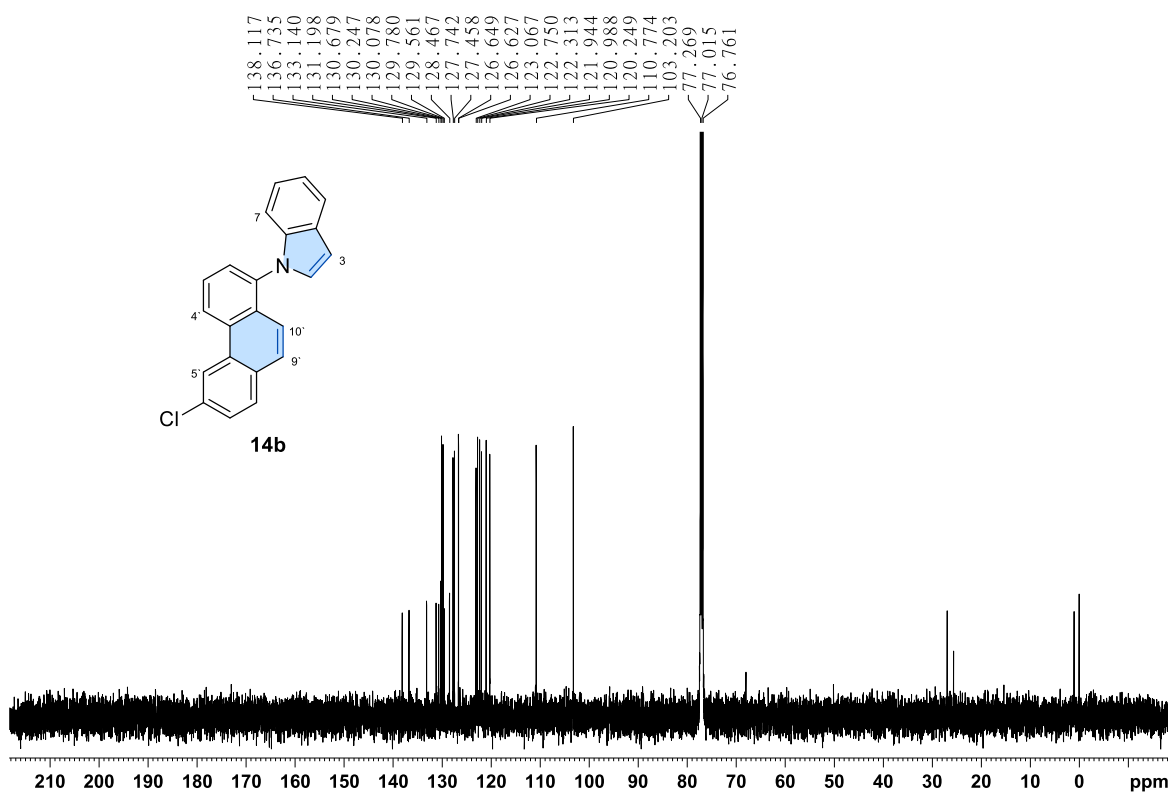
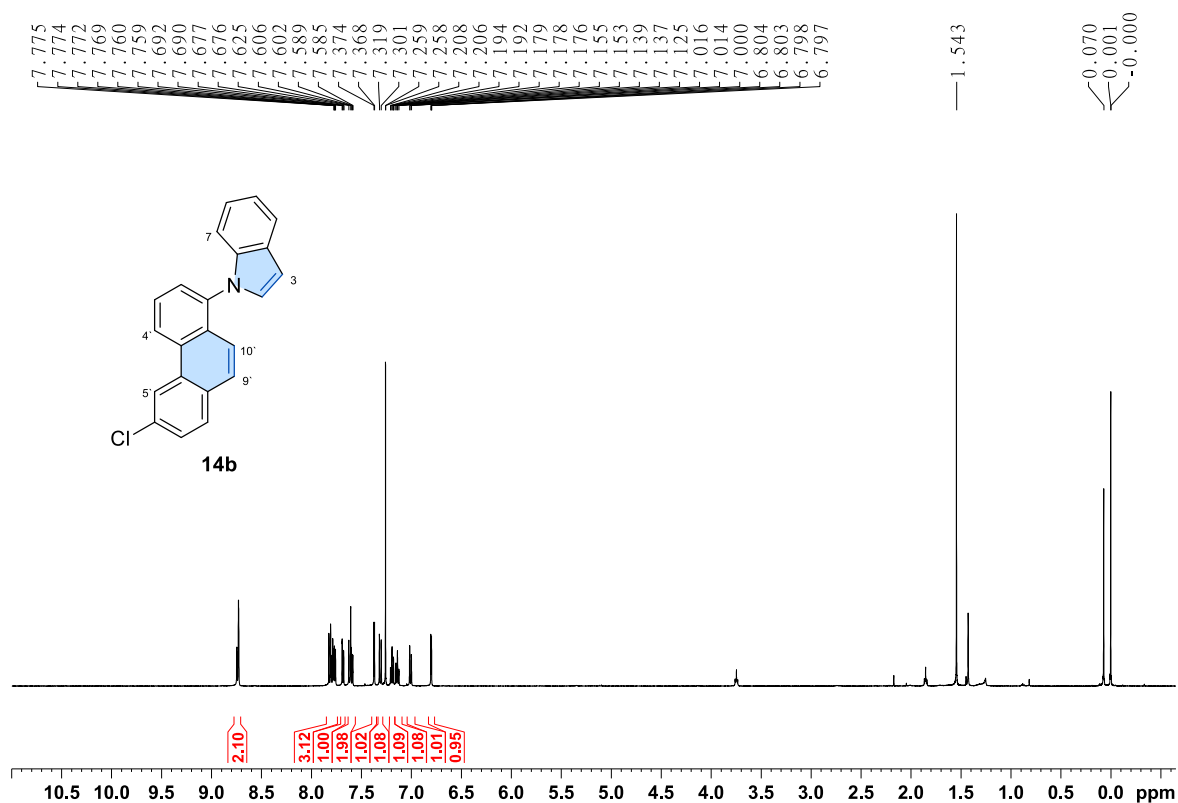


**1-(Phenanthren-1-yl)-1*H*-indole (14a):**

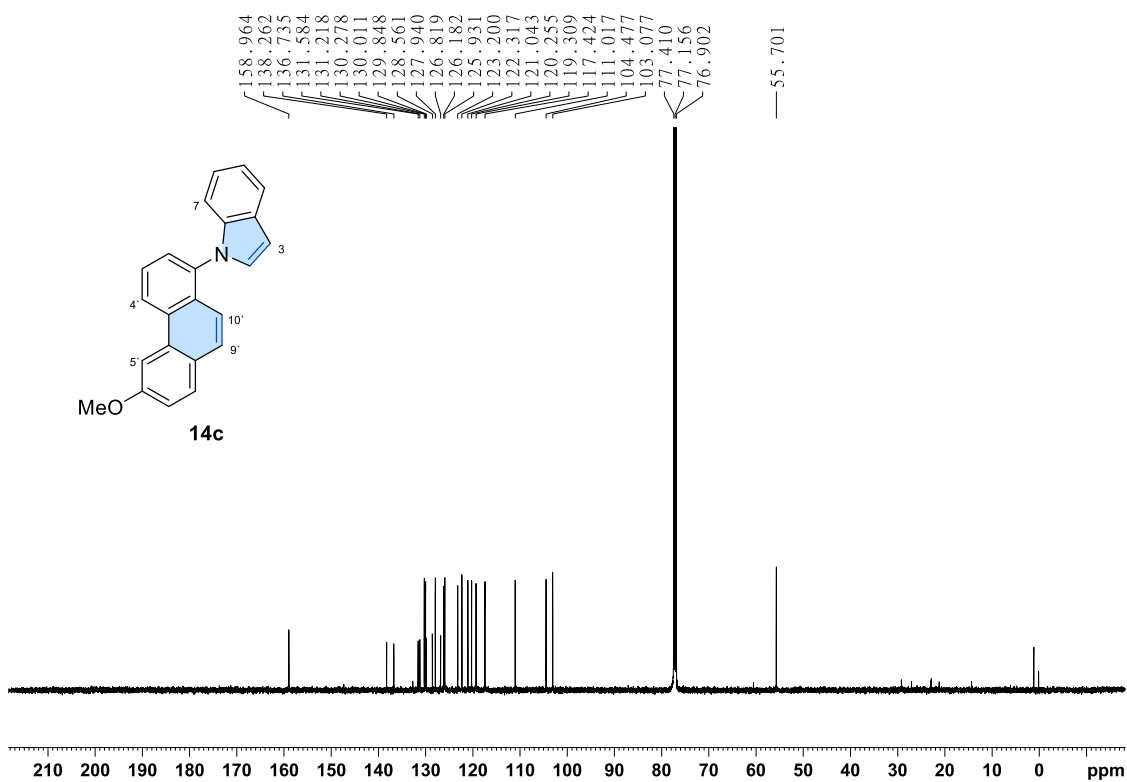
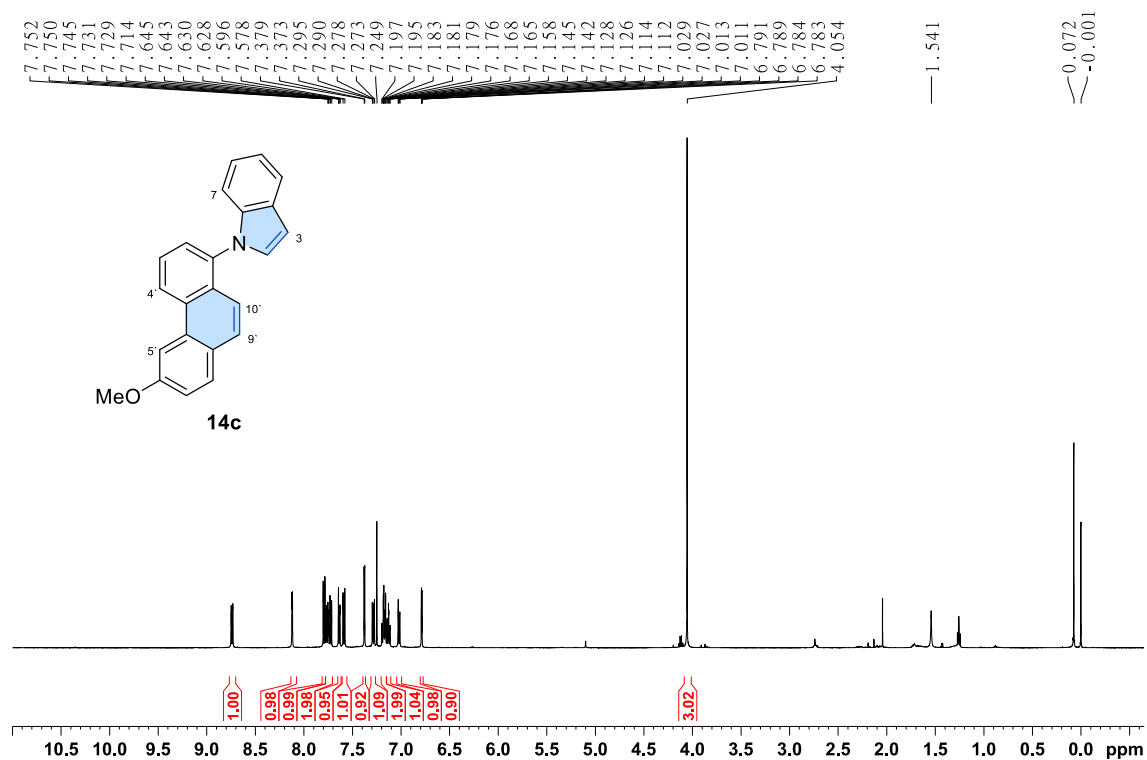




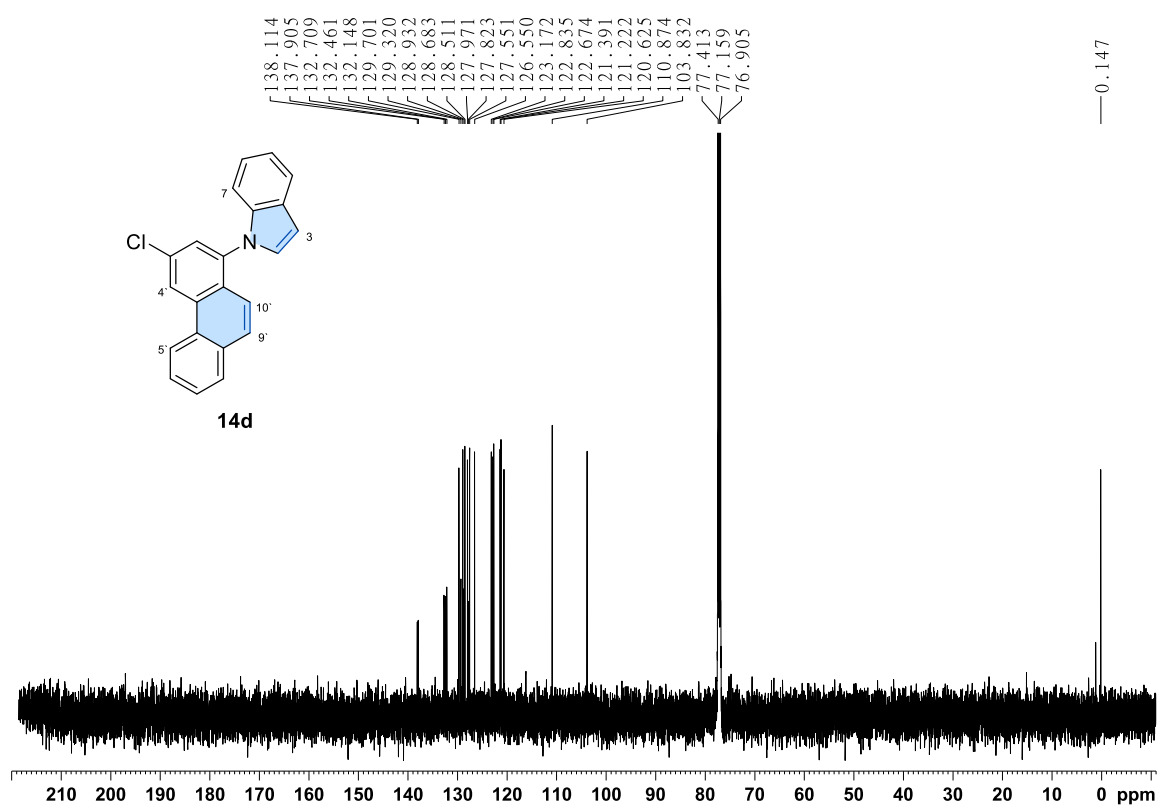
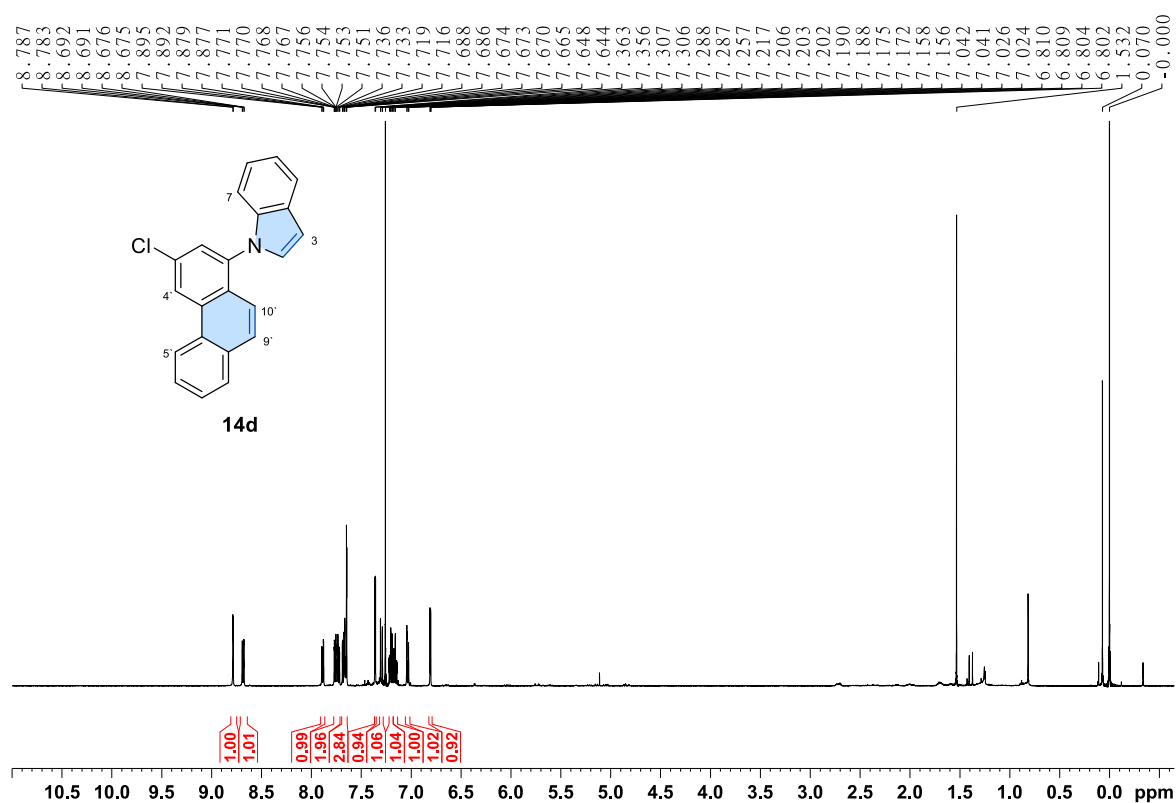
**1-(6-Chlorophenanthren-1-yl)-1H-indole (14b):**



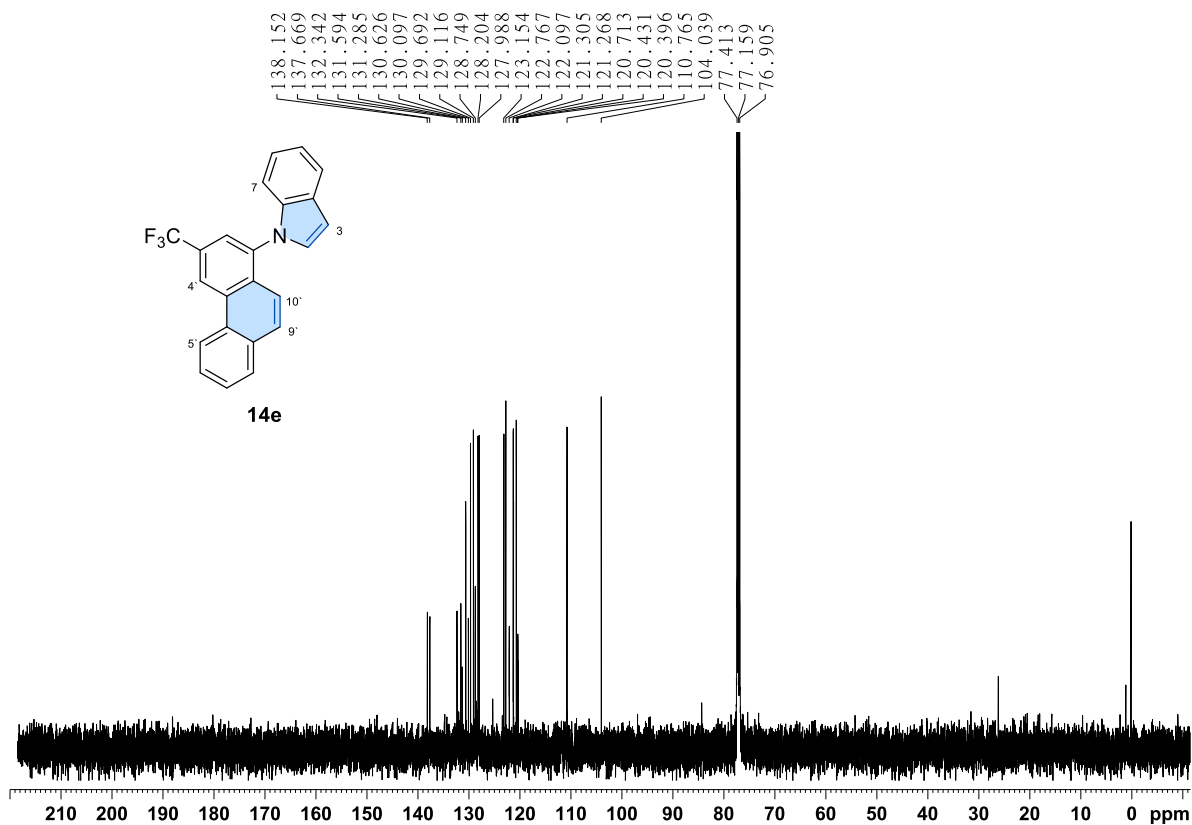
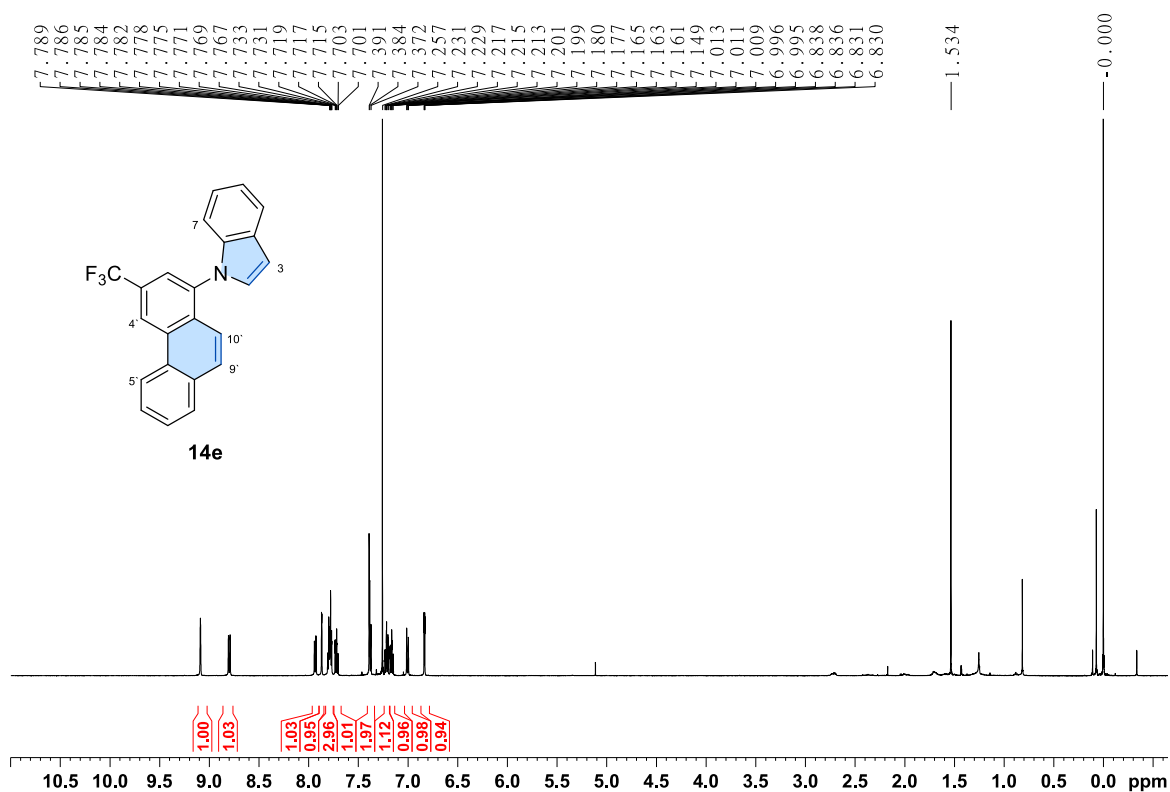
**1-(6-Methoxyphenanthren-1-yl)-1H-indole (14c):**

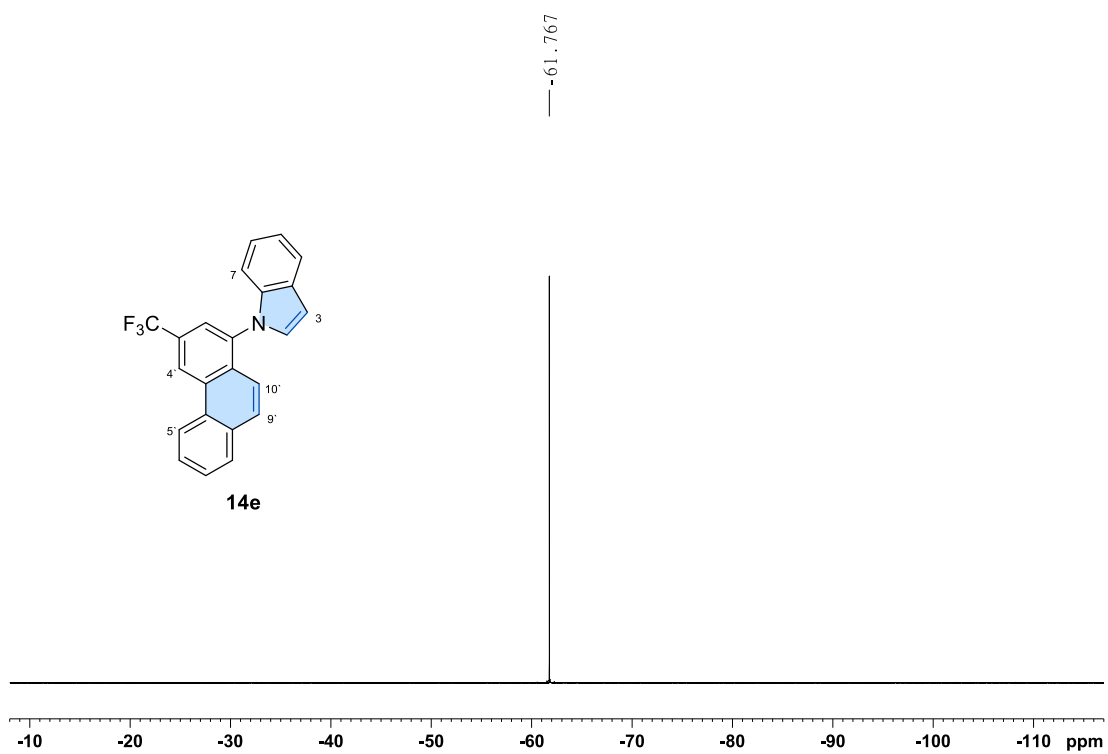


**1-(3-Chlorophenanthren-1-yl)-1H-indole (14d):**

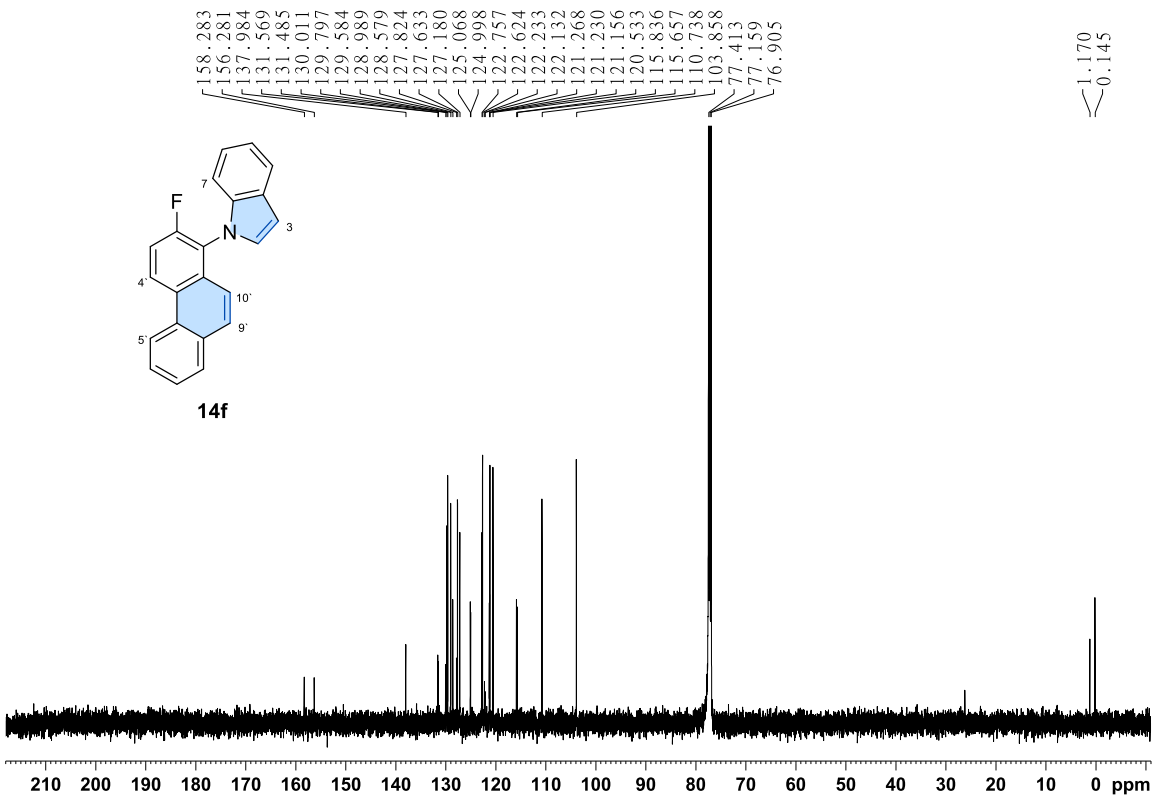
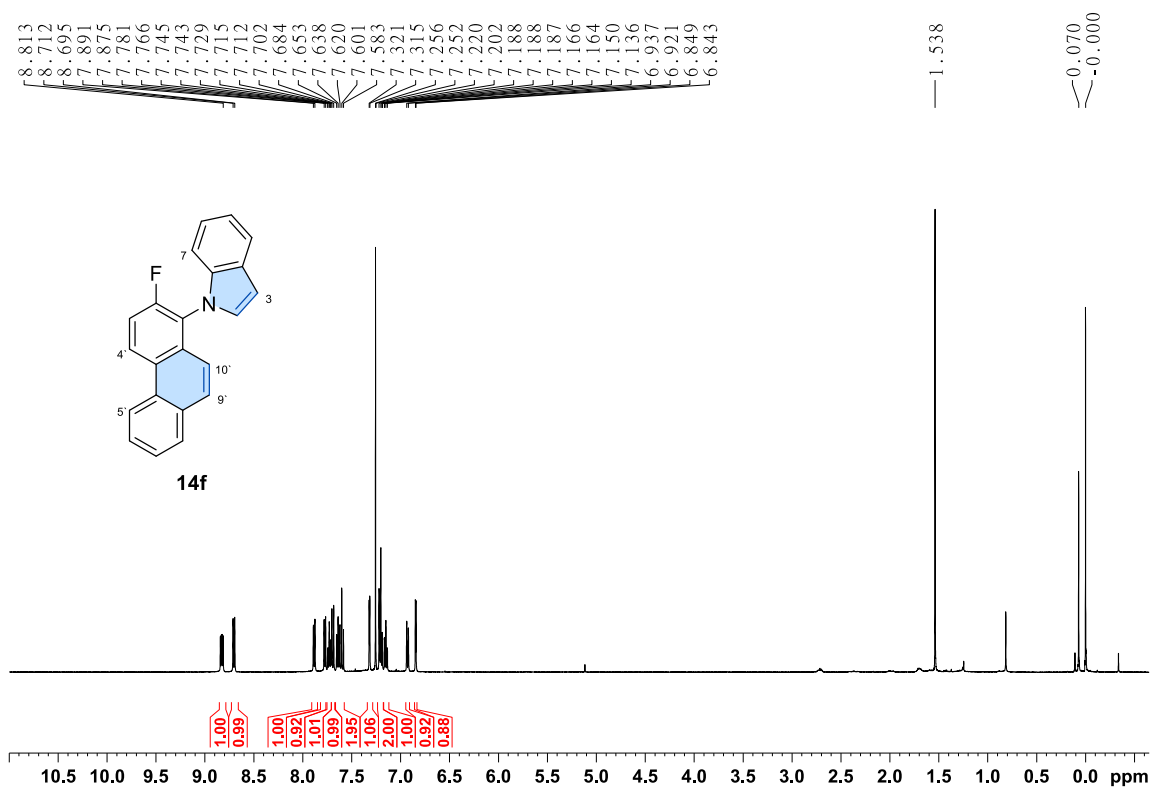


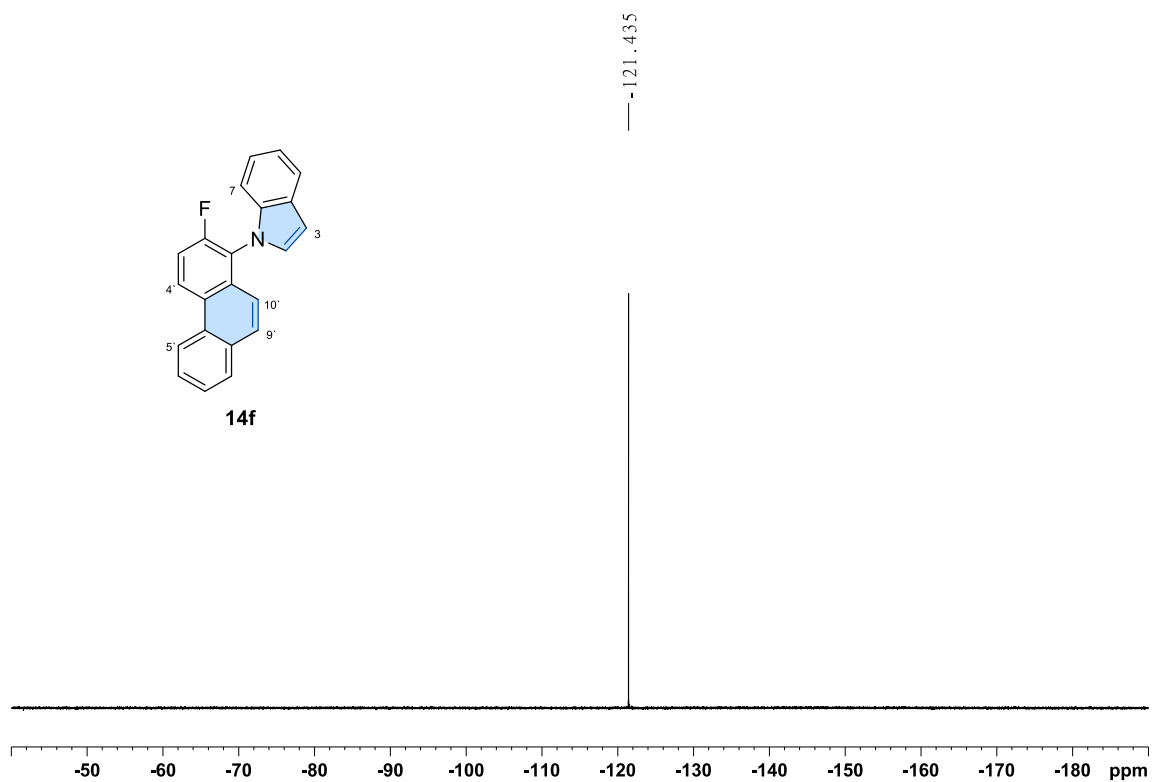
**1-(3-(Trifluoromethyl)phenanthren-1-yl)-1*H*-indole (14e):**



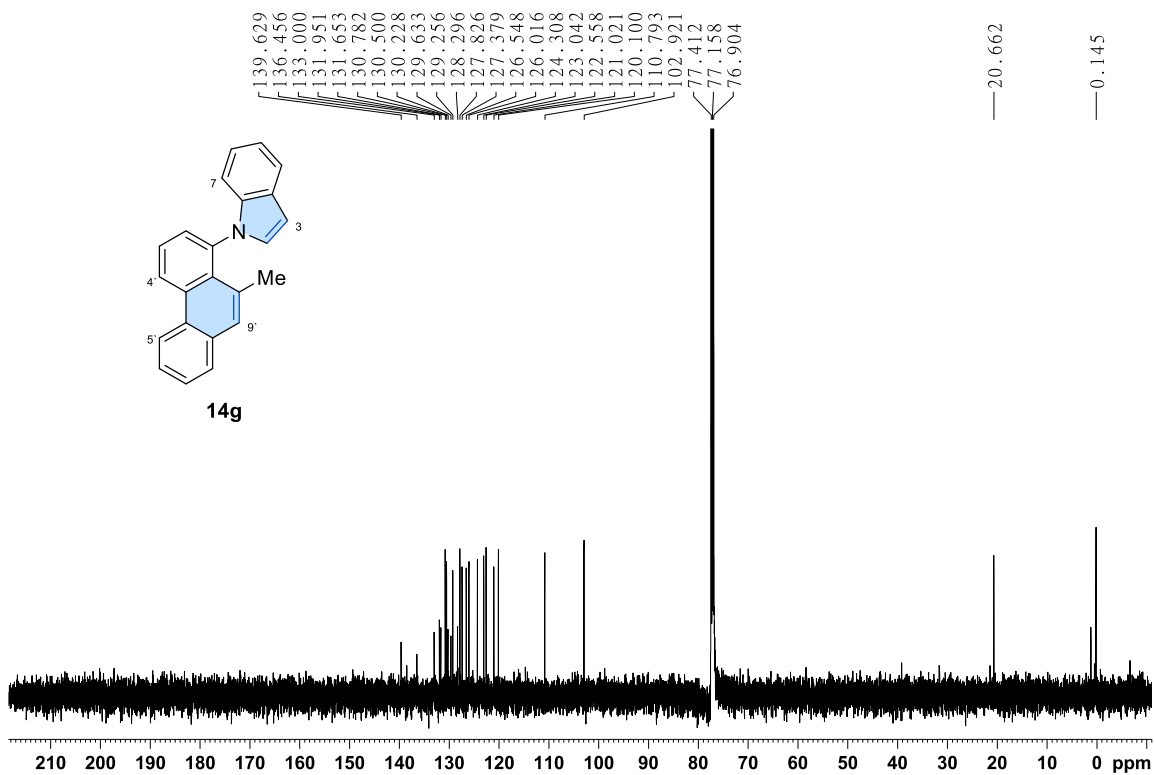
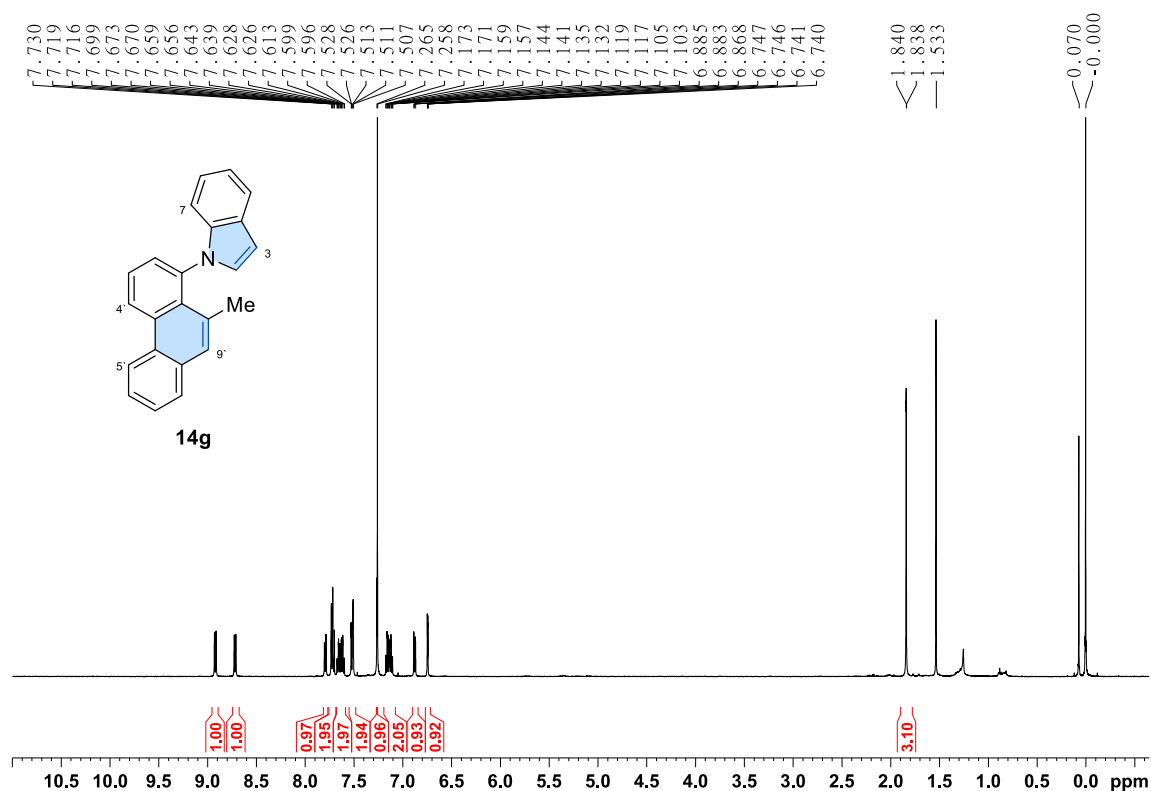


**1-(2-Fluorophenanthren-1-yl)-1*H*-indole (14f):**



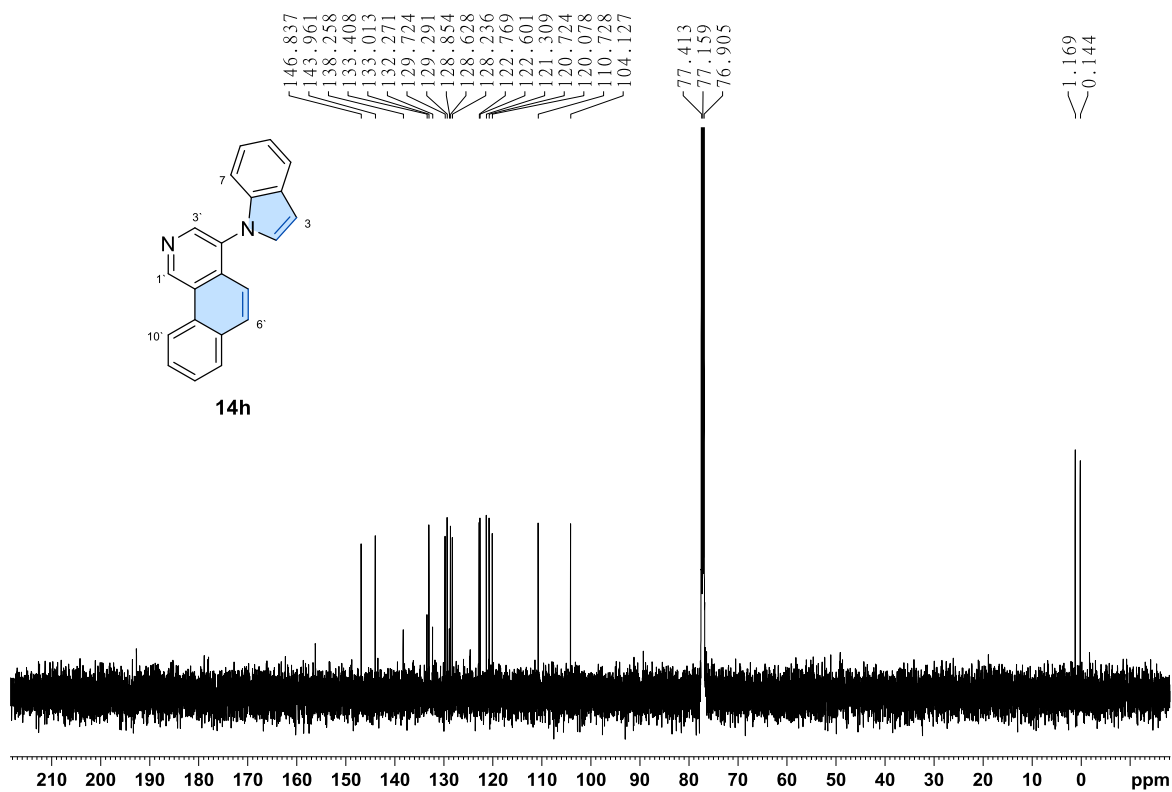
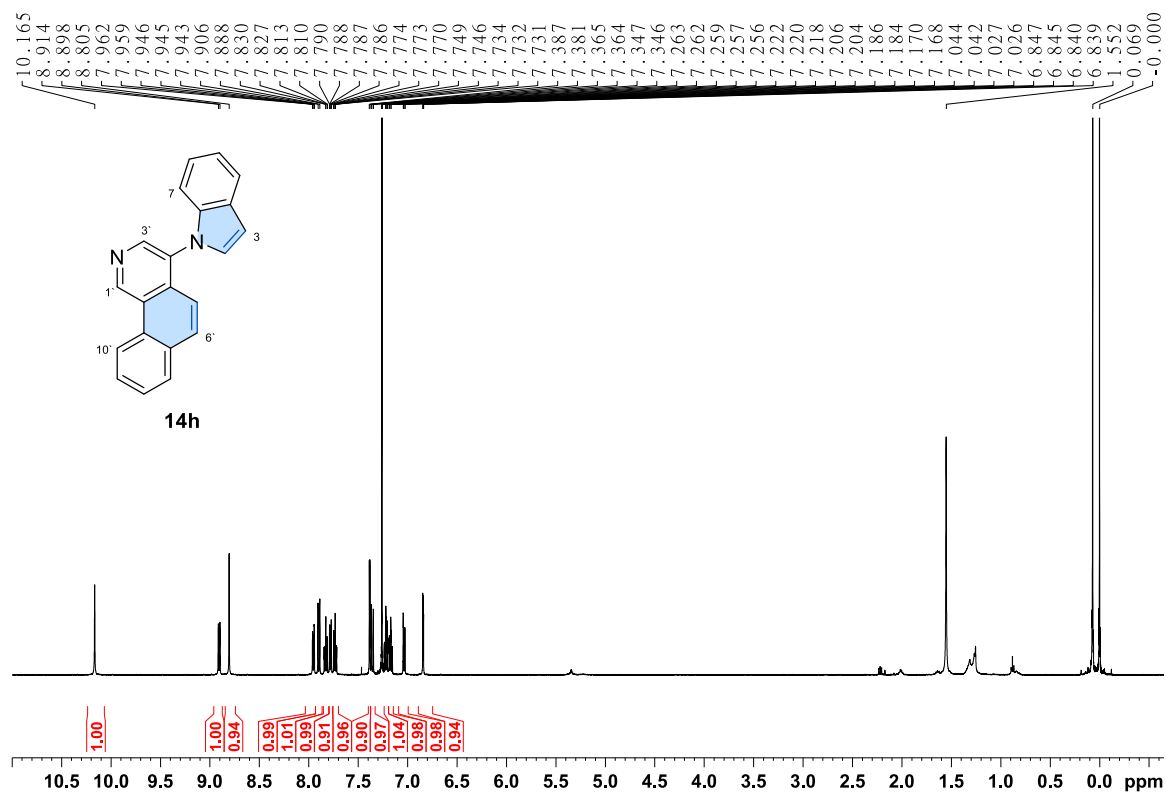


**1-(10-Methylphenanthren-1-yl)-1*H*-indole (14g):**

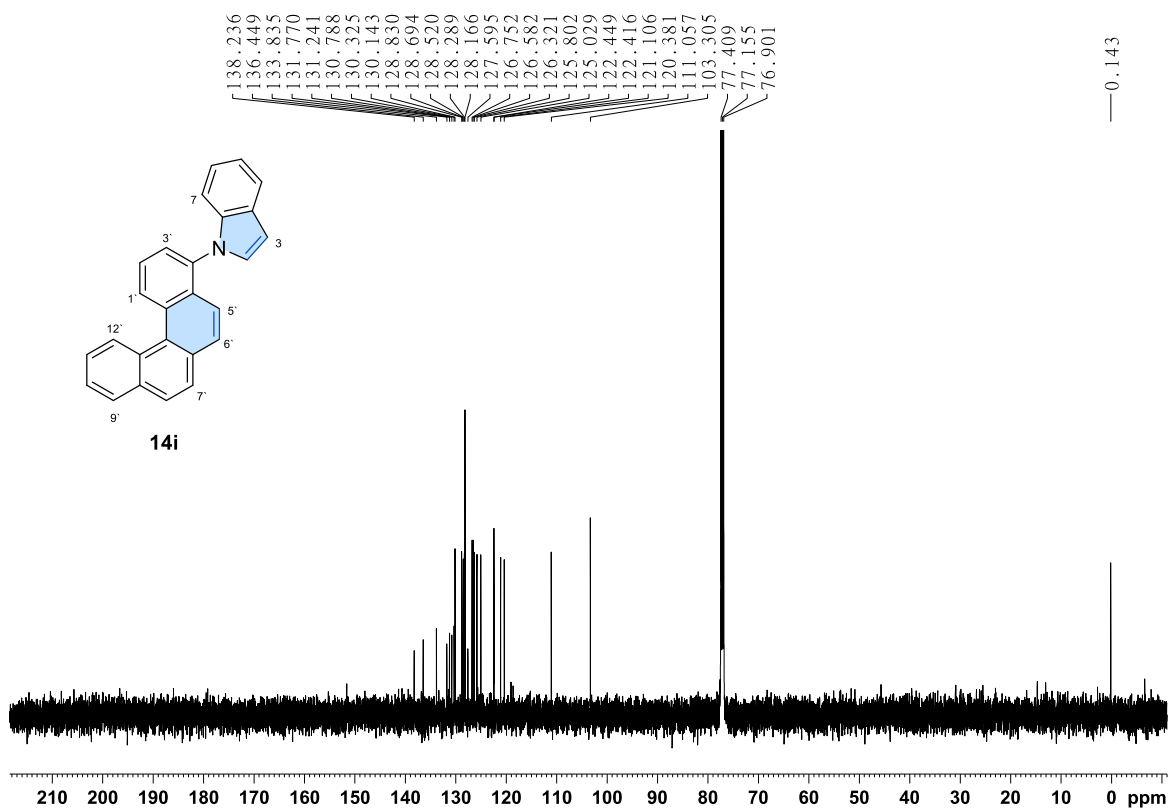
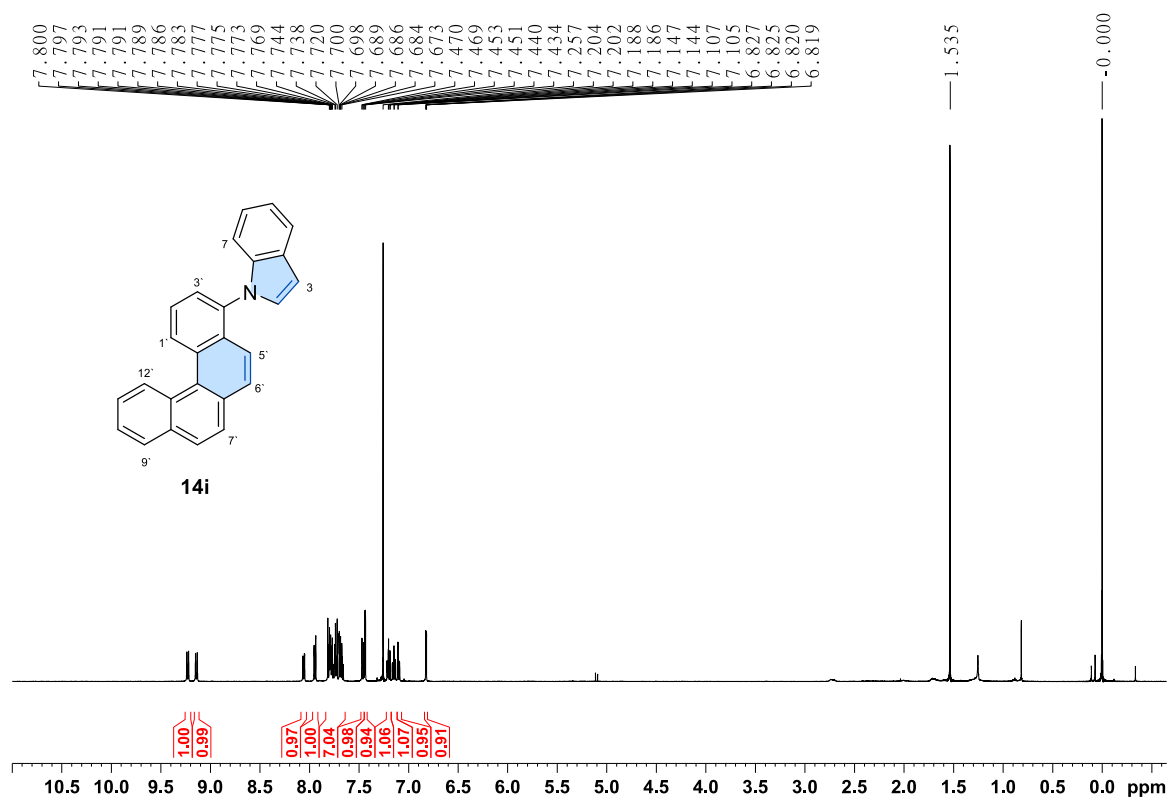




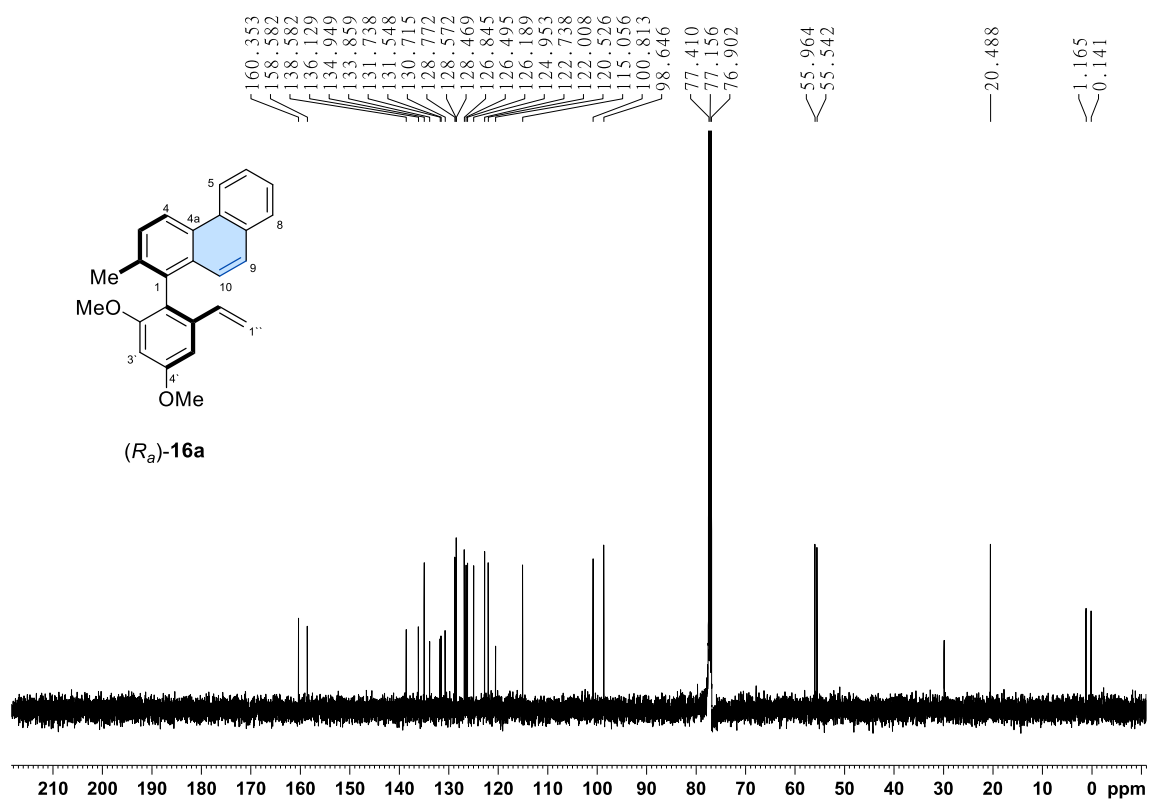
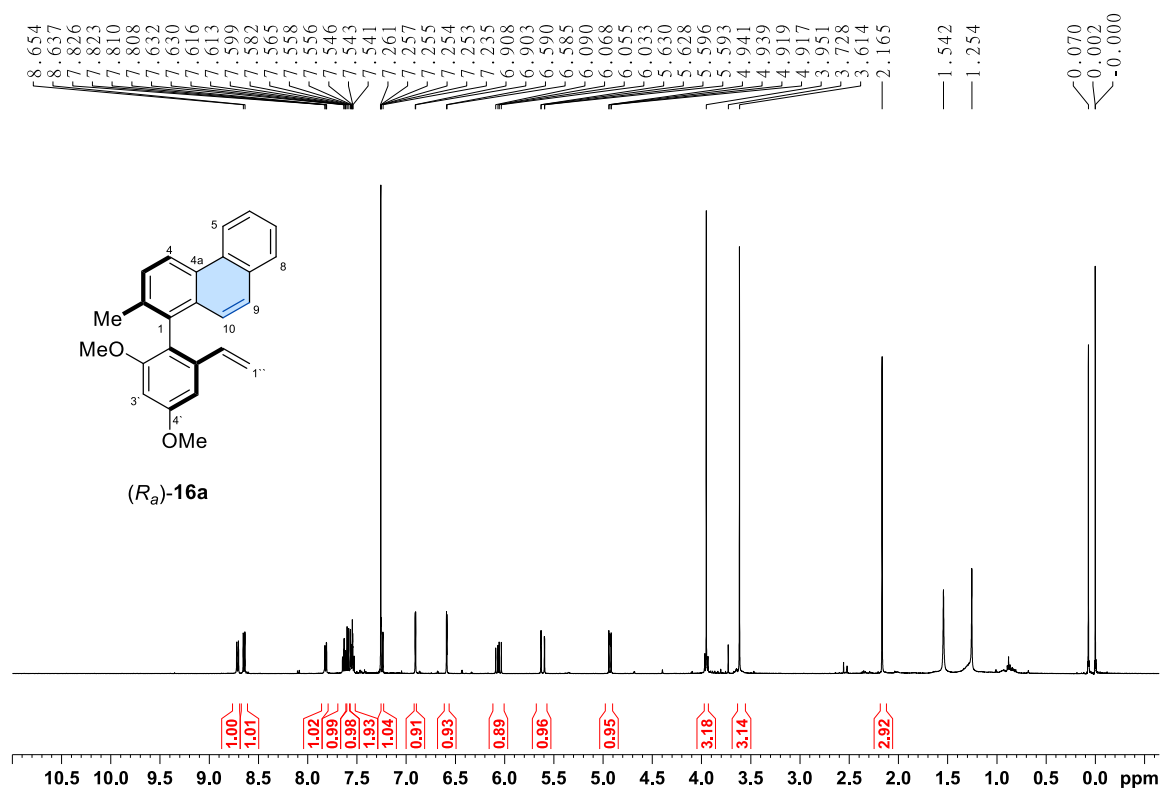
**4-(1*H*-Indol-1-yl)benzo[*h*]isoquinoline (14h):**



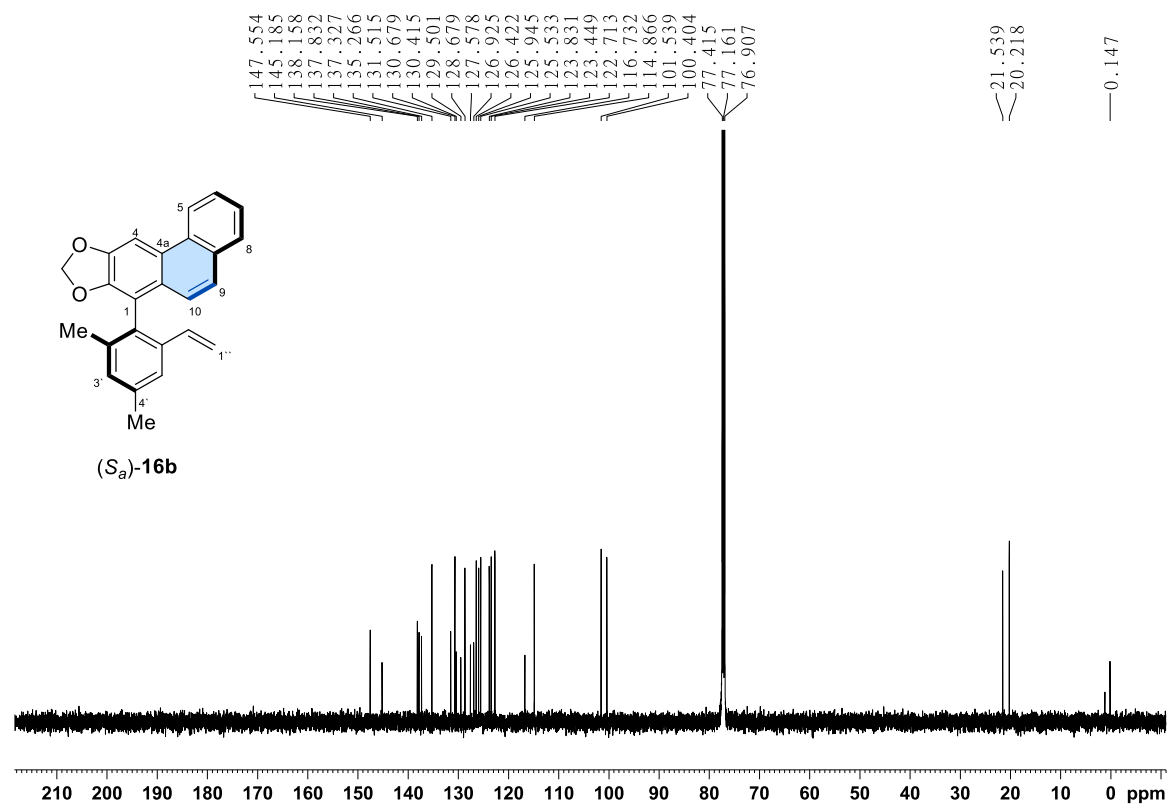
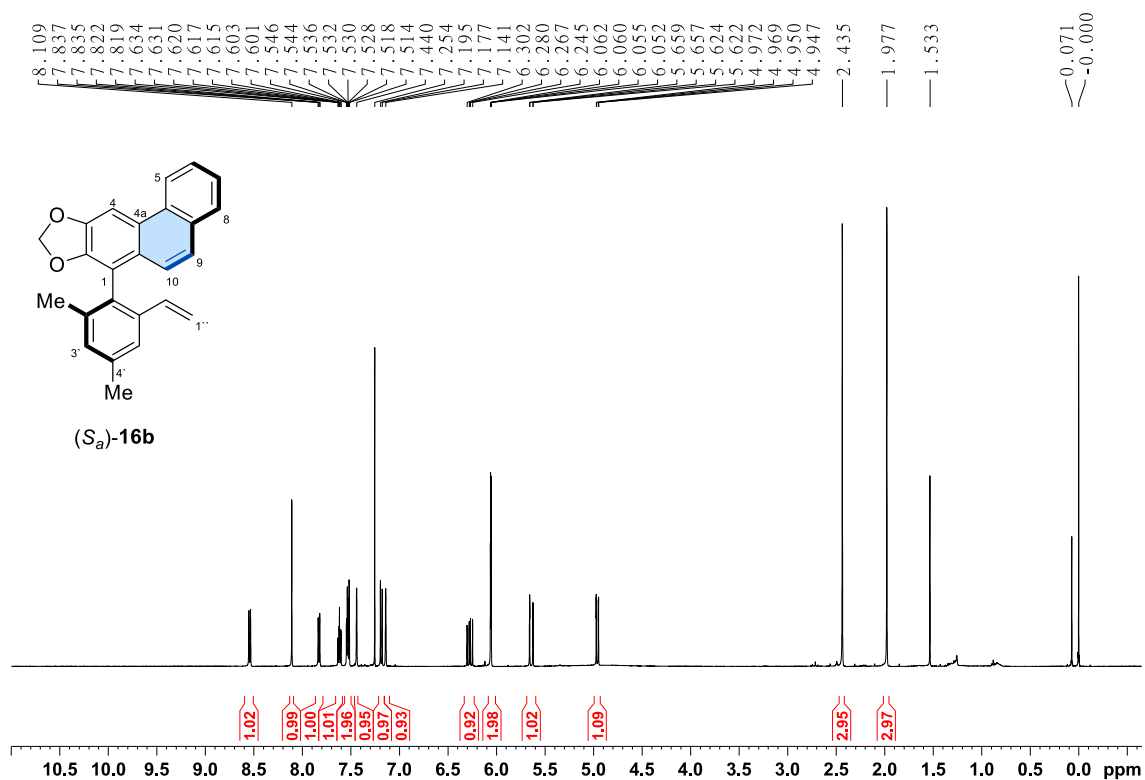
**1-(Benzo[c]phenanthren-4-yl)-1*H*-indole (14i):**



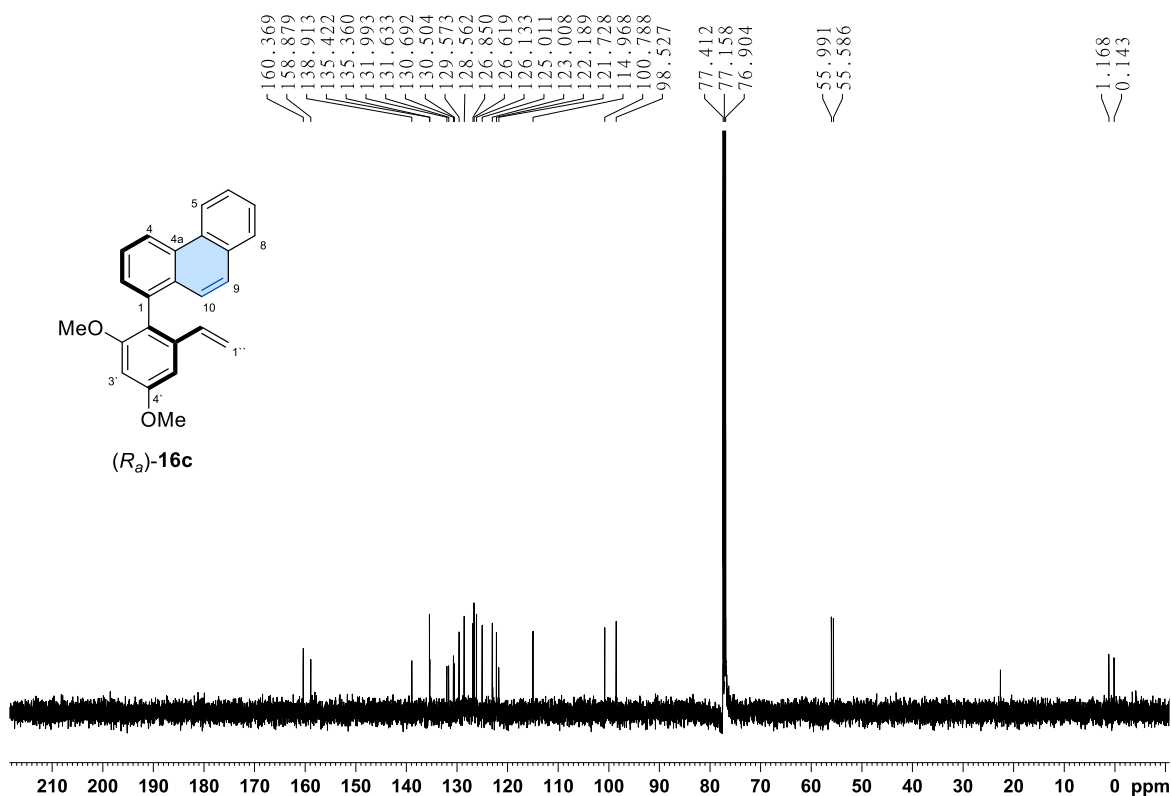
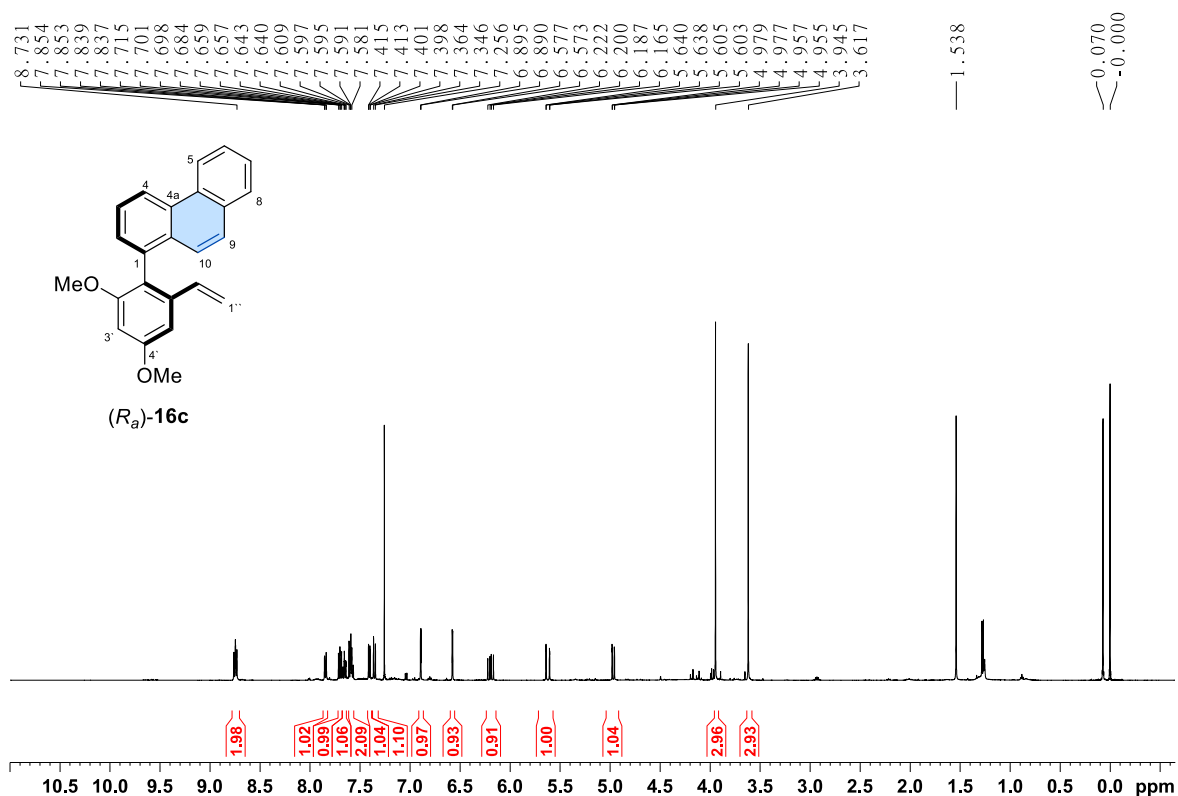
**(*R<sub>a</sub>*)-1-(2,4-Dimethoxy-6-vinylphenyl)-2-methylphenanthrene ((*R<sub>a</sub>*)-16a):**



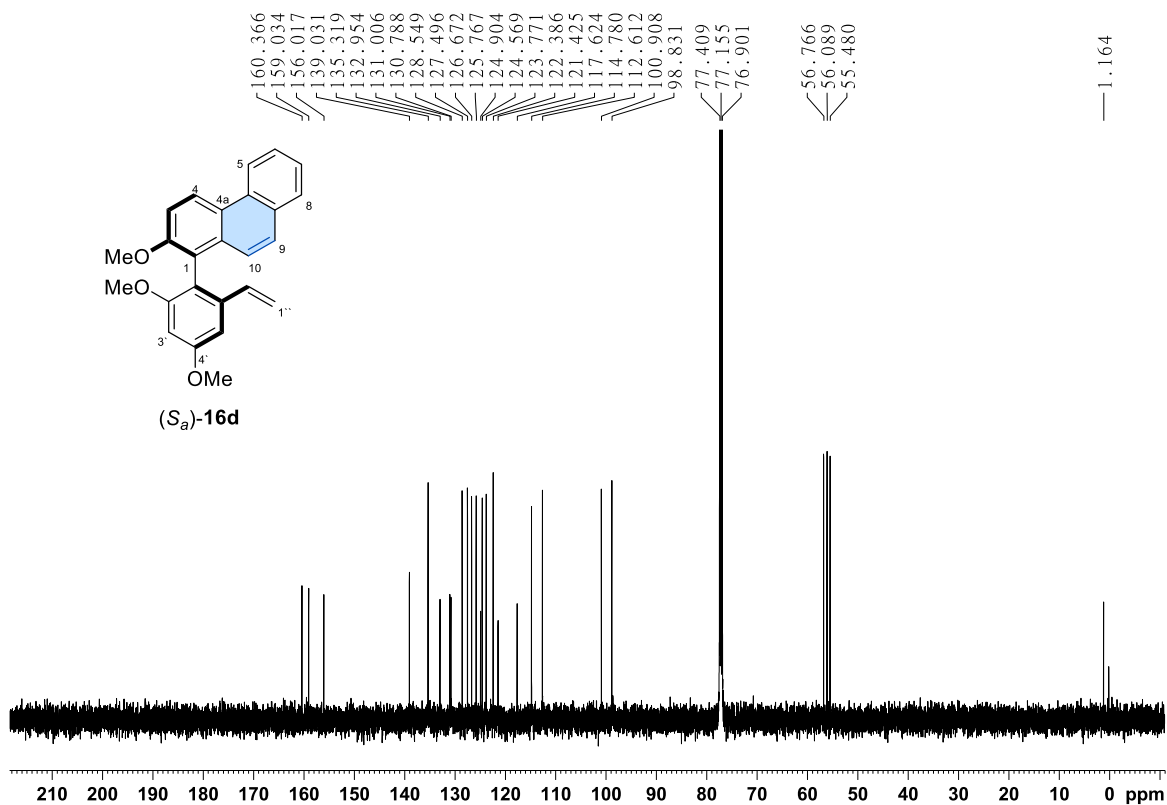
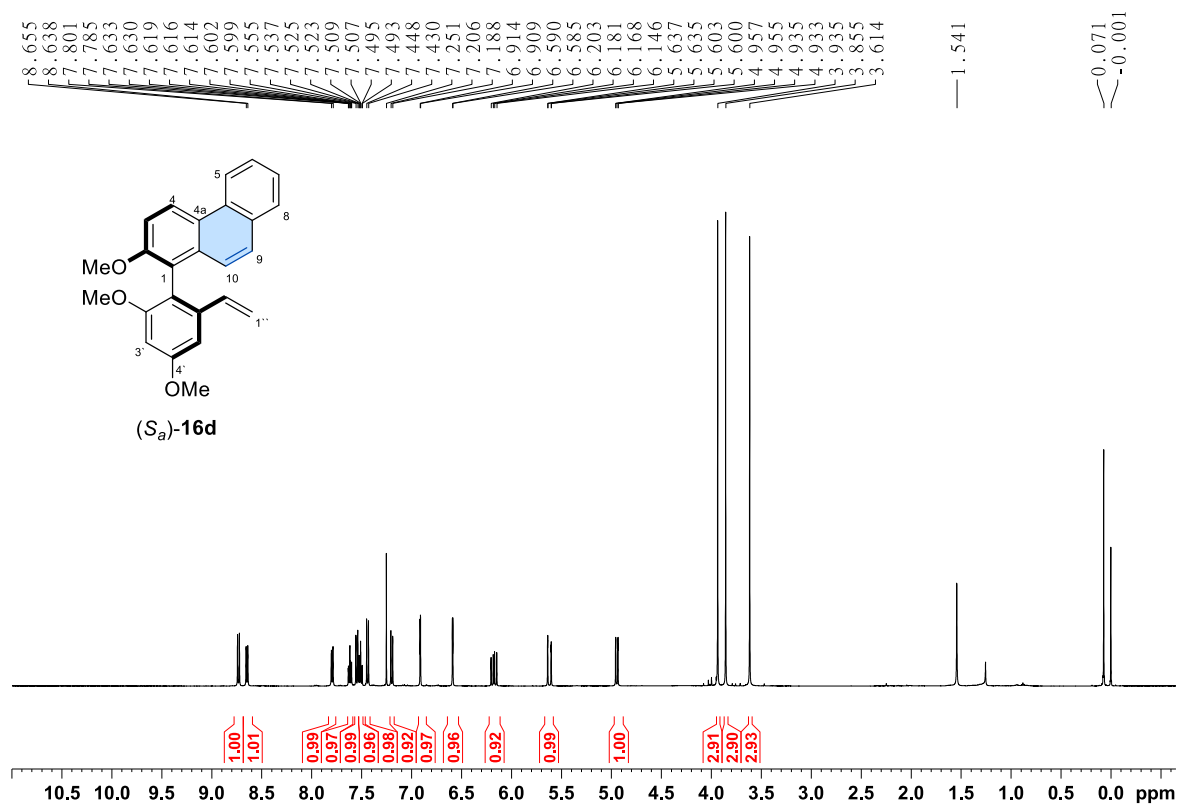
**(S<sub>a</sub>)-7-(2,4-Dimethyl-6-vinylphenyl)phenanthro[2,3-d][1,3]dioxole ((S<sub>a</sub>)-16b):**



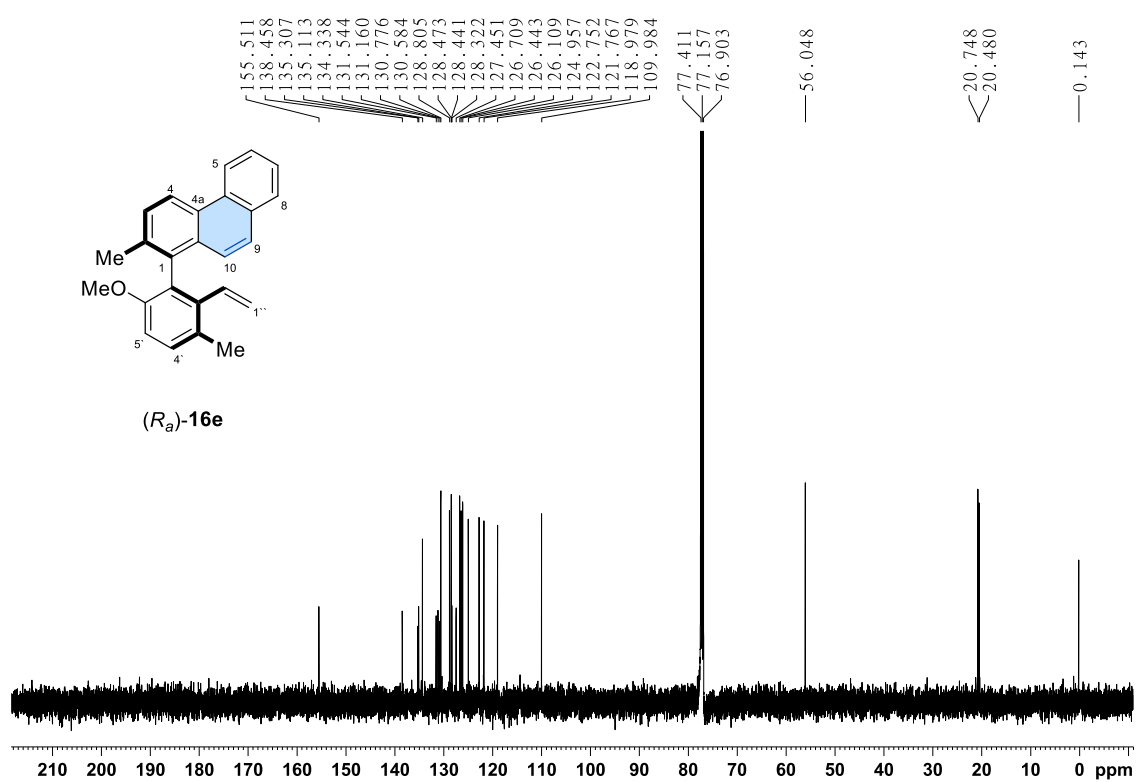
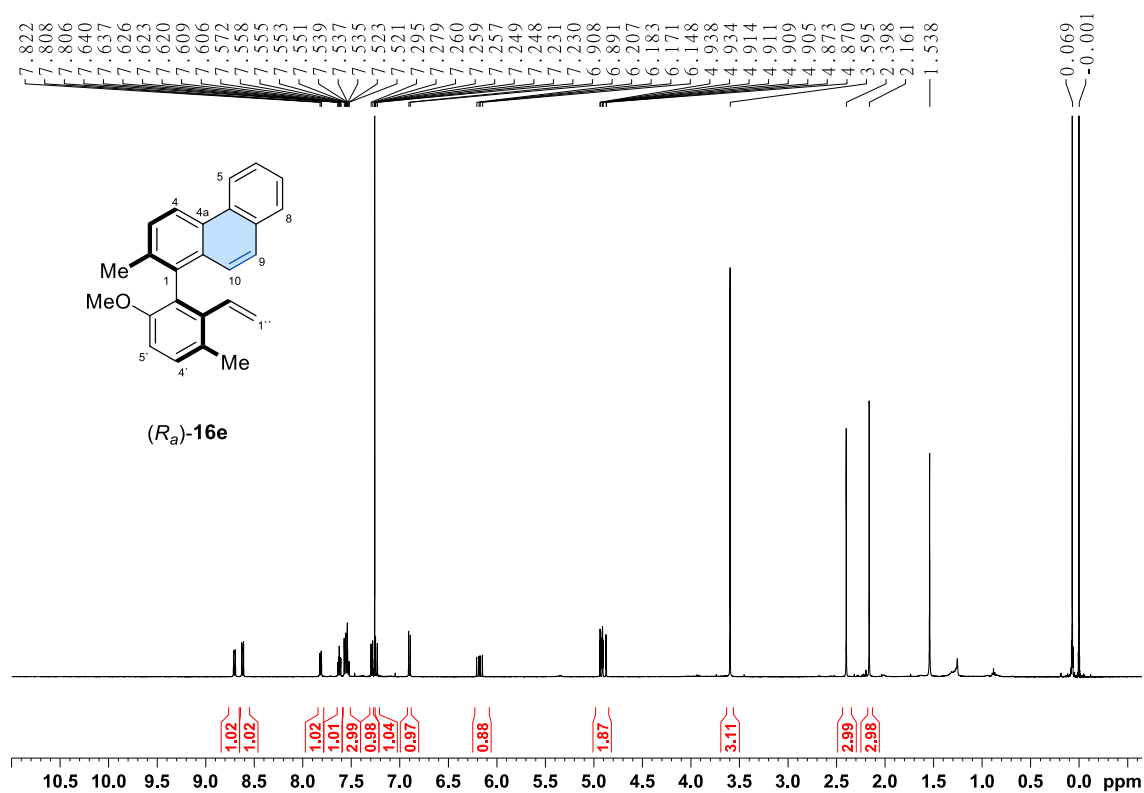
**(*R<sub>a</sub>*)-1-(2,4-Dimethoxy-6-vinylphenyl)phenanthrene ((*R<sub>a</sub>*)-16c):**



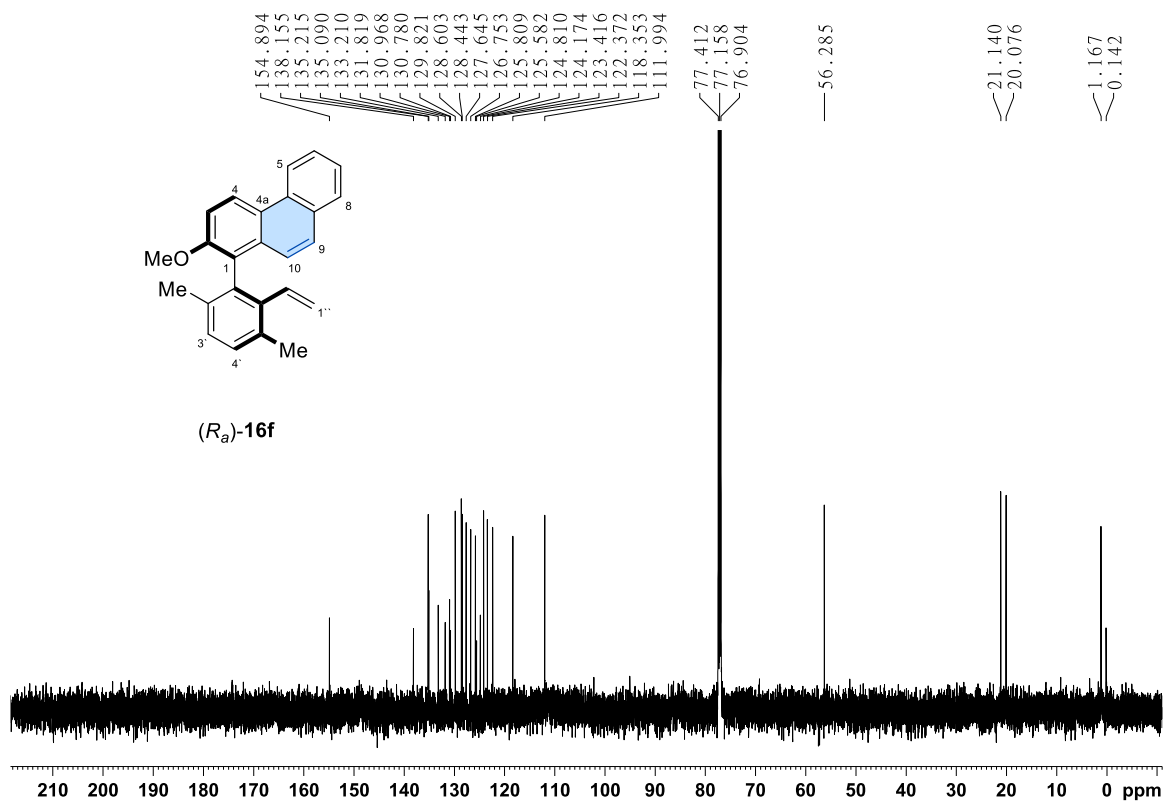
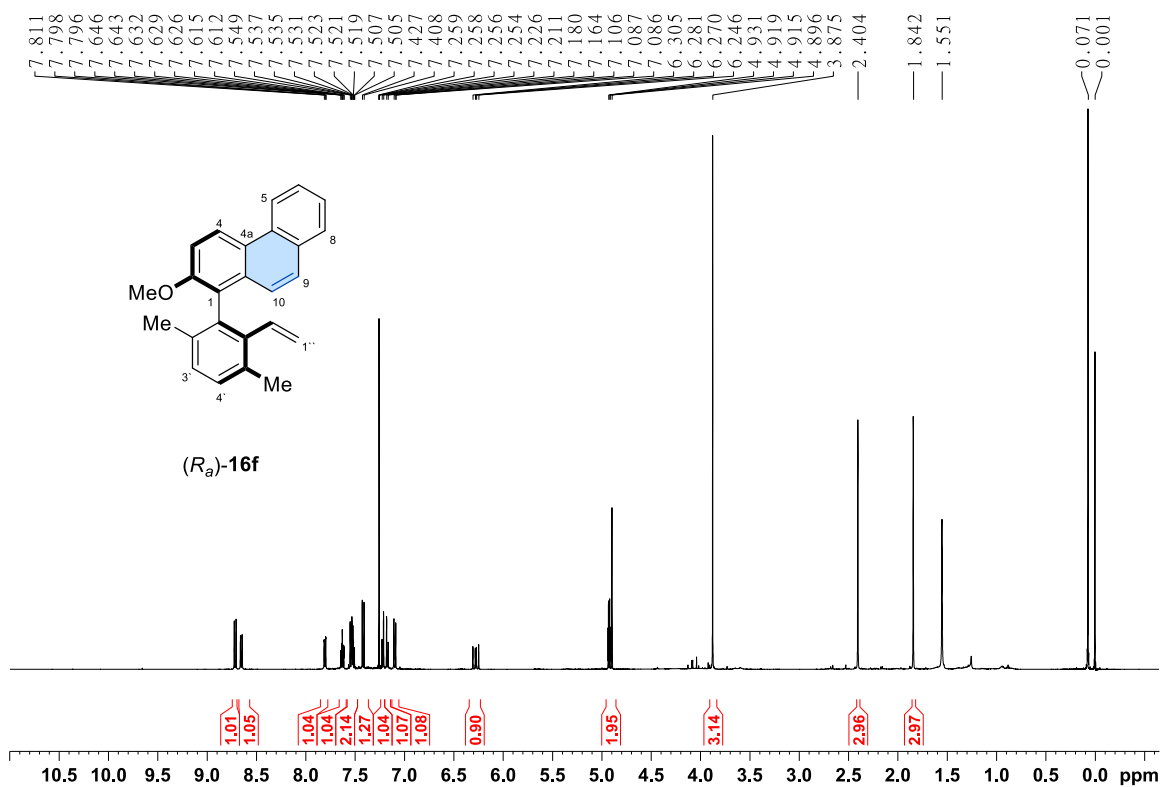
**(*S<sub>a</sub>*)-1-(2,4-Dimethoxy-6-vinylphenyl)-2-methoxyphenanthrene ((*S<sub>a</sub>*)-16d):**



**(*R<sub>a</sub>*)-1-(6-Methoxy-3-methyl-2-vinylphenyl)-2-methylphenanthrene ((*R<sub>a</sub>*)-16e):**

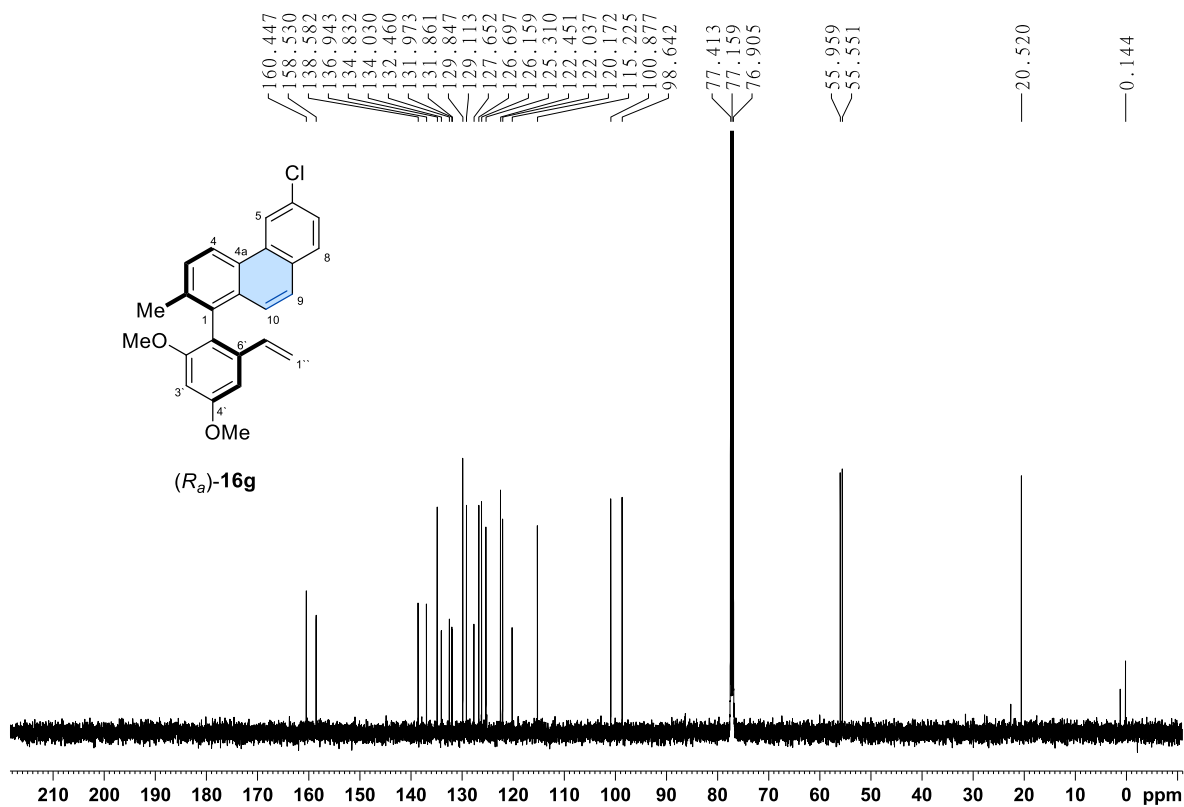
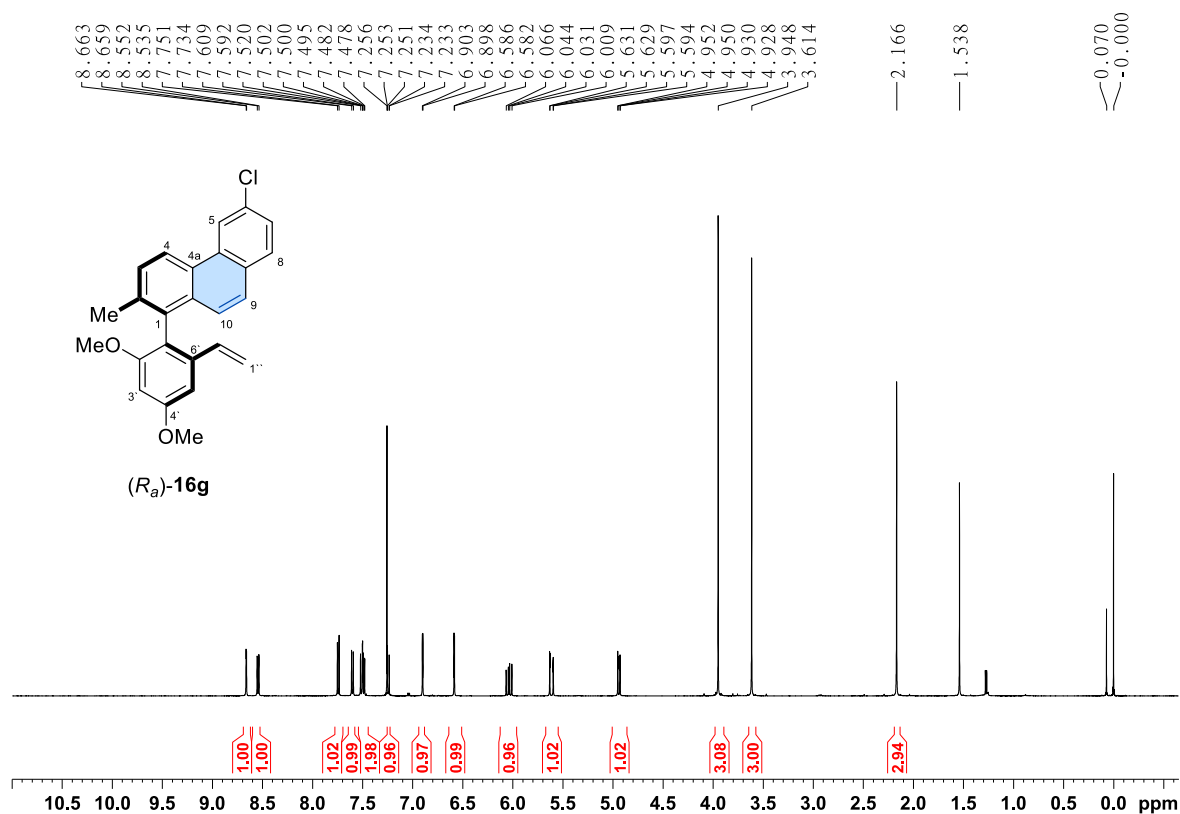


**(*R<sub>a</sub>*)-1-(3,6-Dimethyl-2-vinylphenyl)-2-methoxyphenanthrene ((*R<sub>a</sub>*)-16f):**

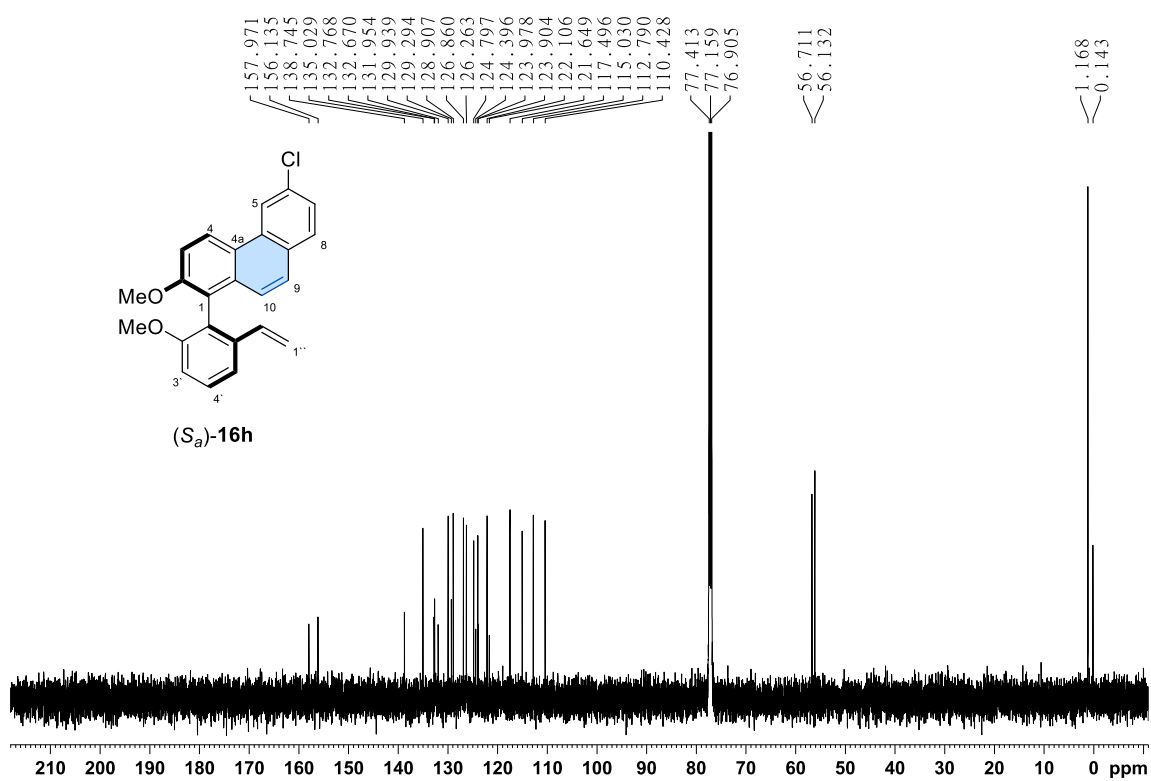
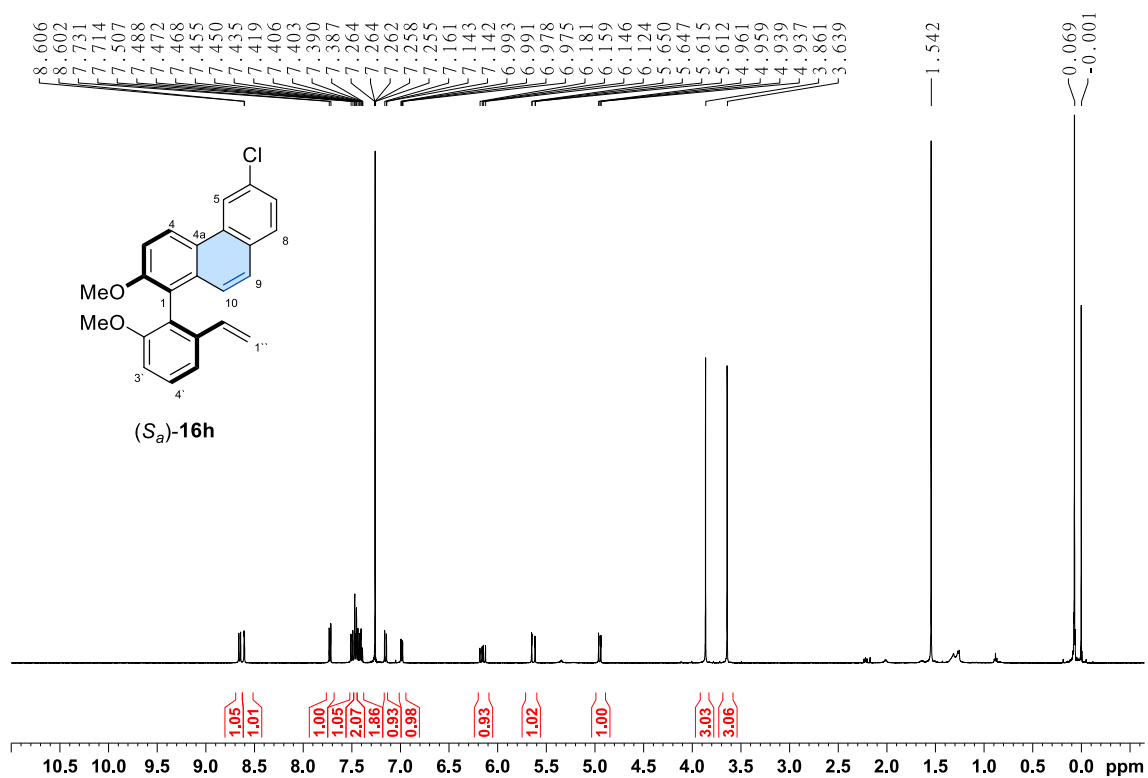




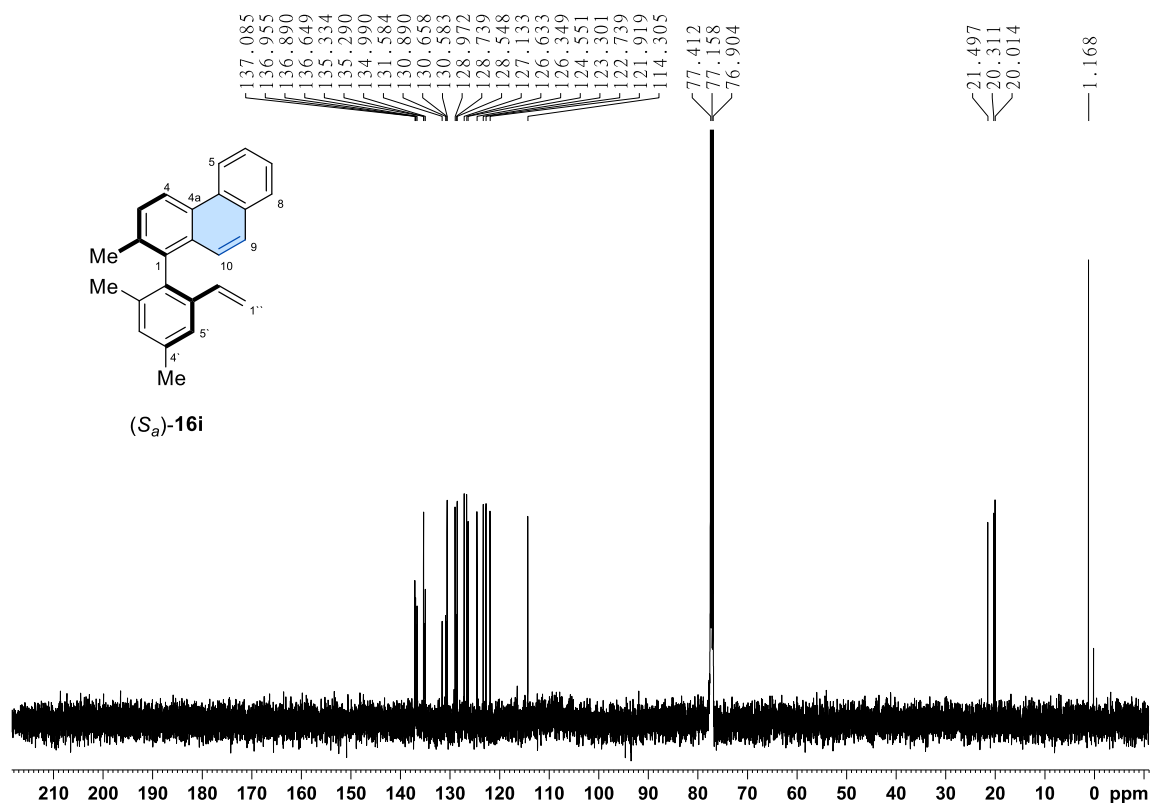
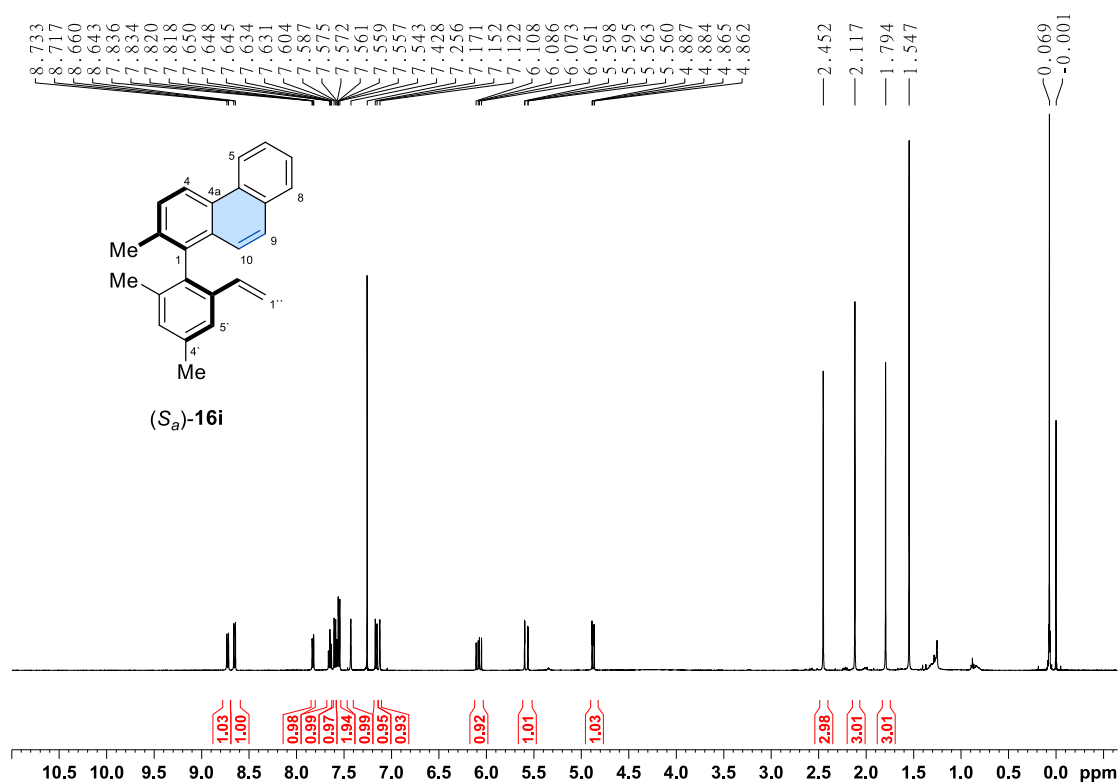
**(*R<sub>a</sub>*)-6-Chloro-1-(2,4-dimethoxy-6-vinylphenyl)-2-methylphenanthrene ((*R<sub>a</sub>*)-16g):**



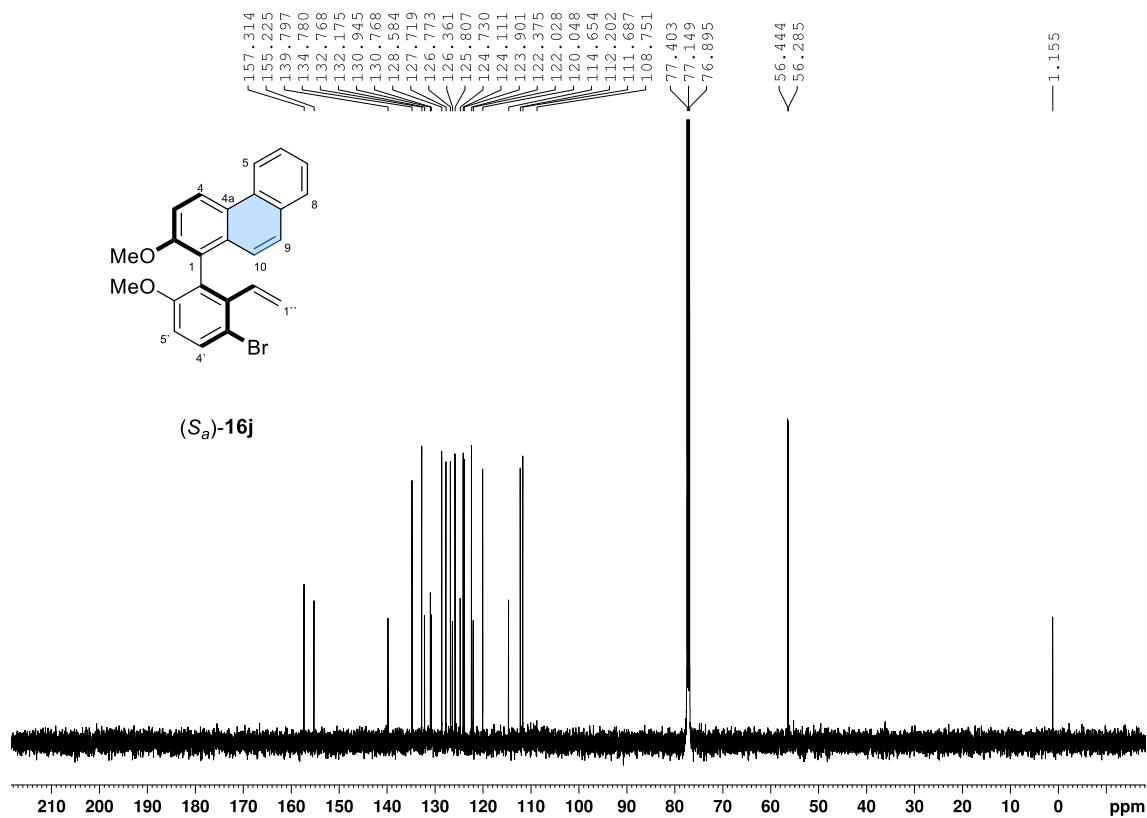
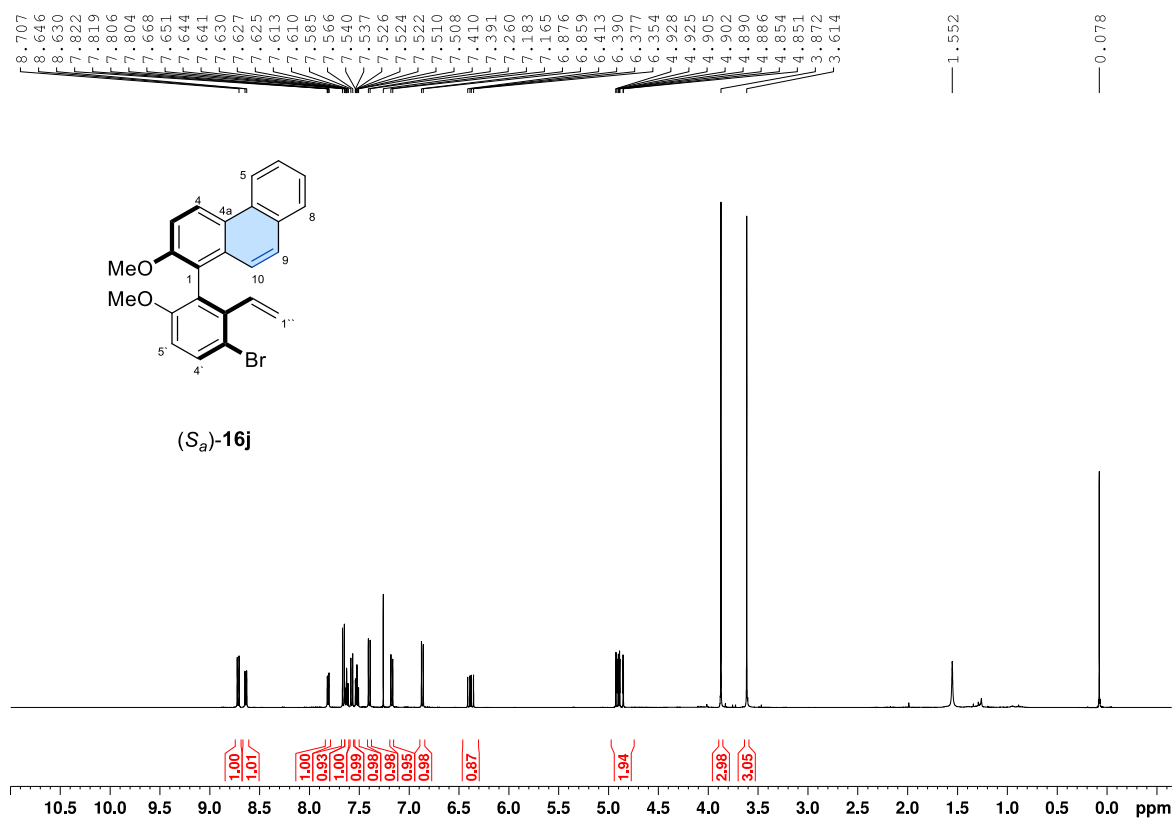
**(S<sub>a</sub>)-6-Chloro-2-methoxy-1-(2-methoxy-6-vinylphenyl)phenanthrene ((S<sub>a</sub>)-16h):**



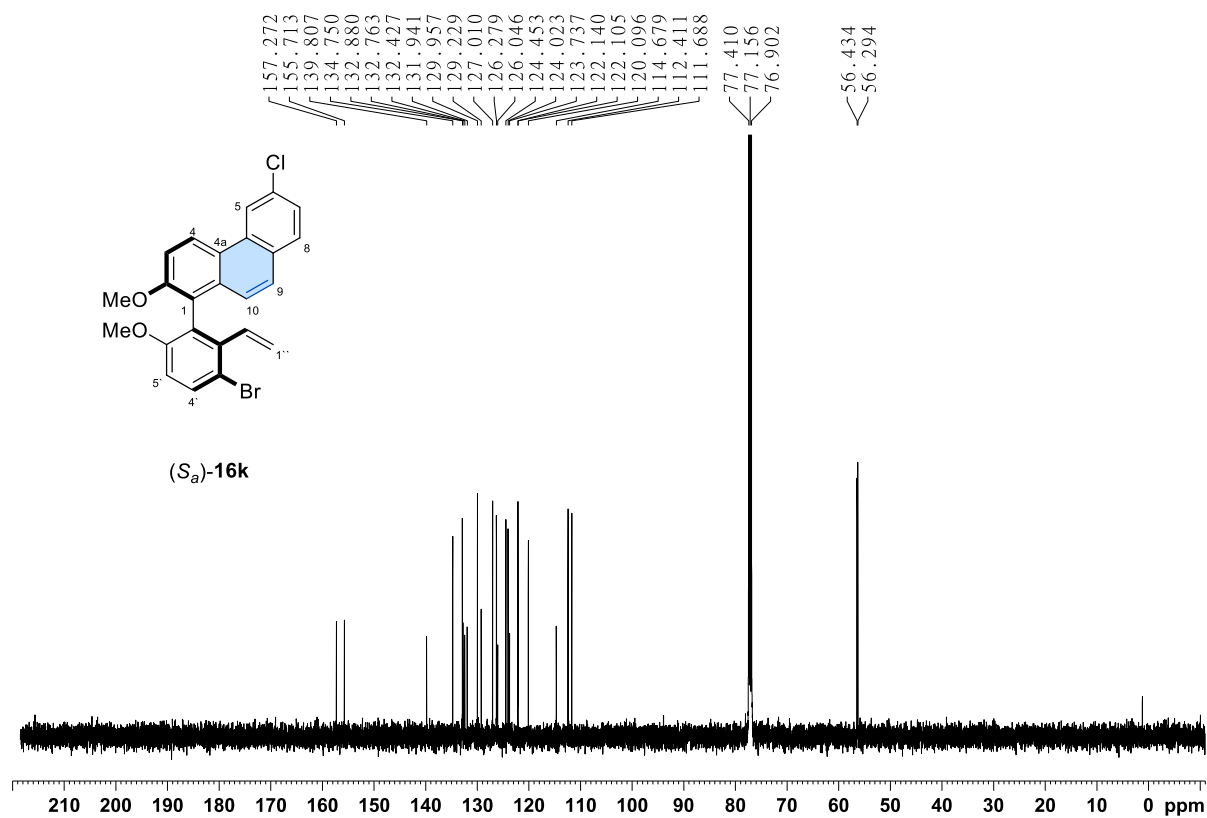
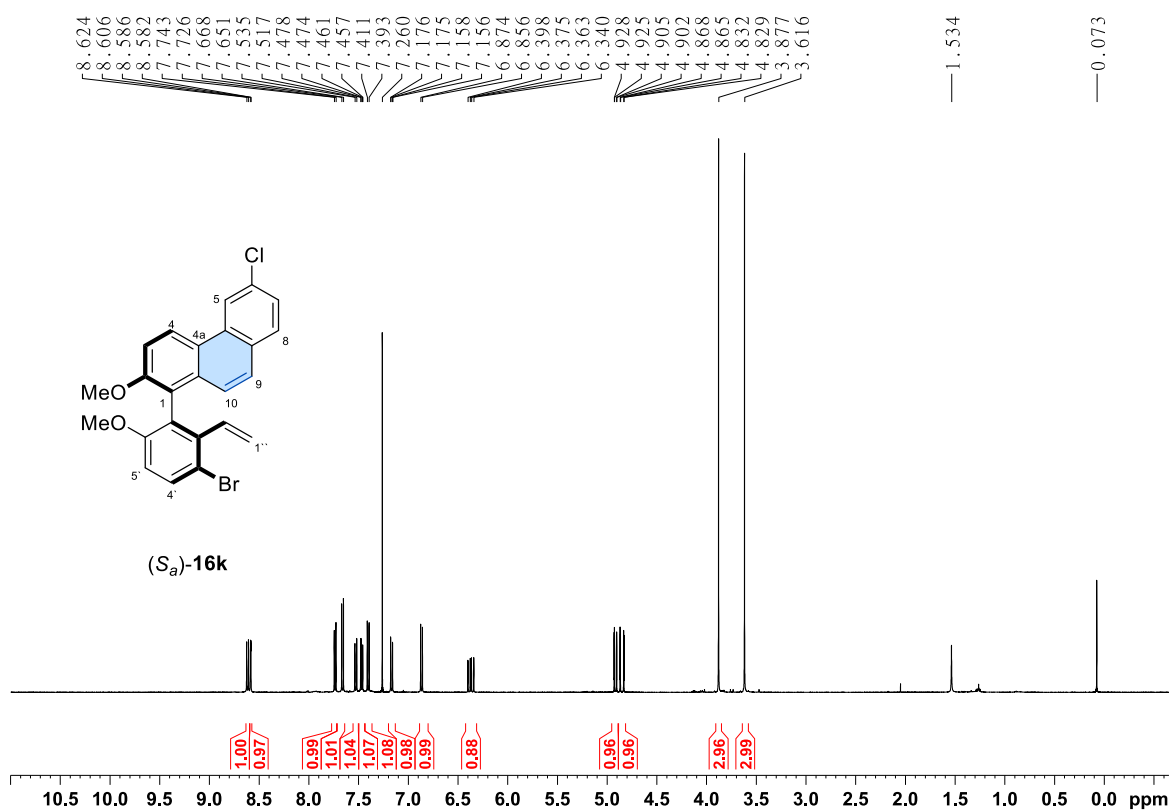
**(S<sub>a</sub>)-1-(2,4-Dimethyl-6-vinylphenyl)-2-methylphenanthrene ((S<sub>a</sub>)-16i):**



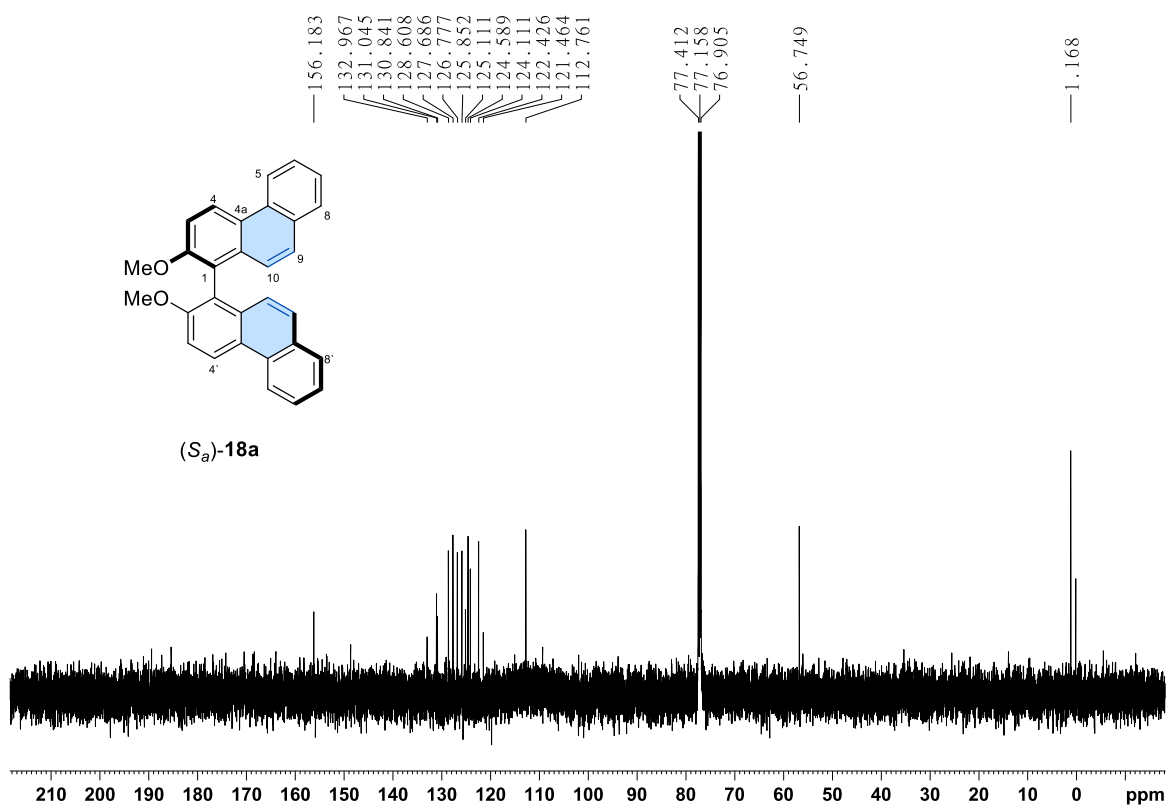
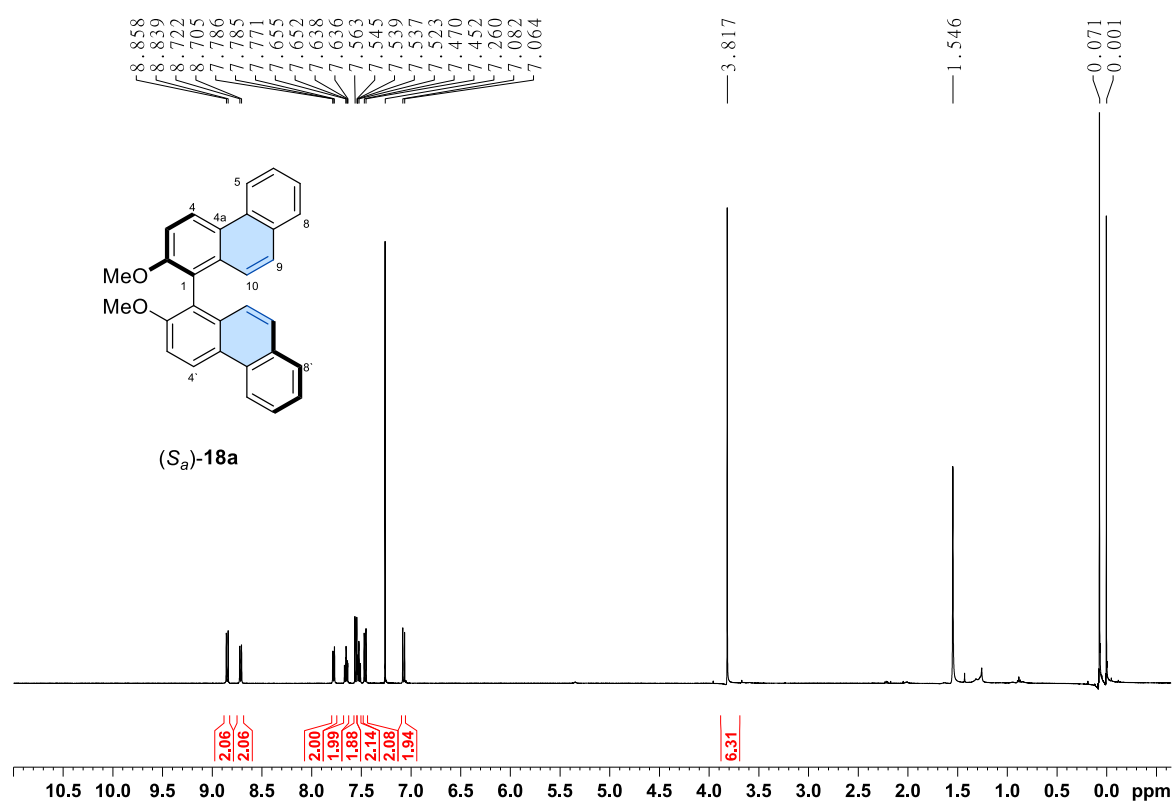
**(S<sub>a</sub>)-1-(3-Bromo-6-methoxy-2-vinylphenyl)-2-methoxyphenanthrene ((S<sub>a</sub>)-16j):**



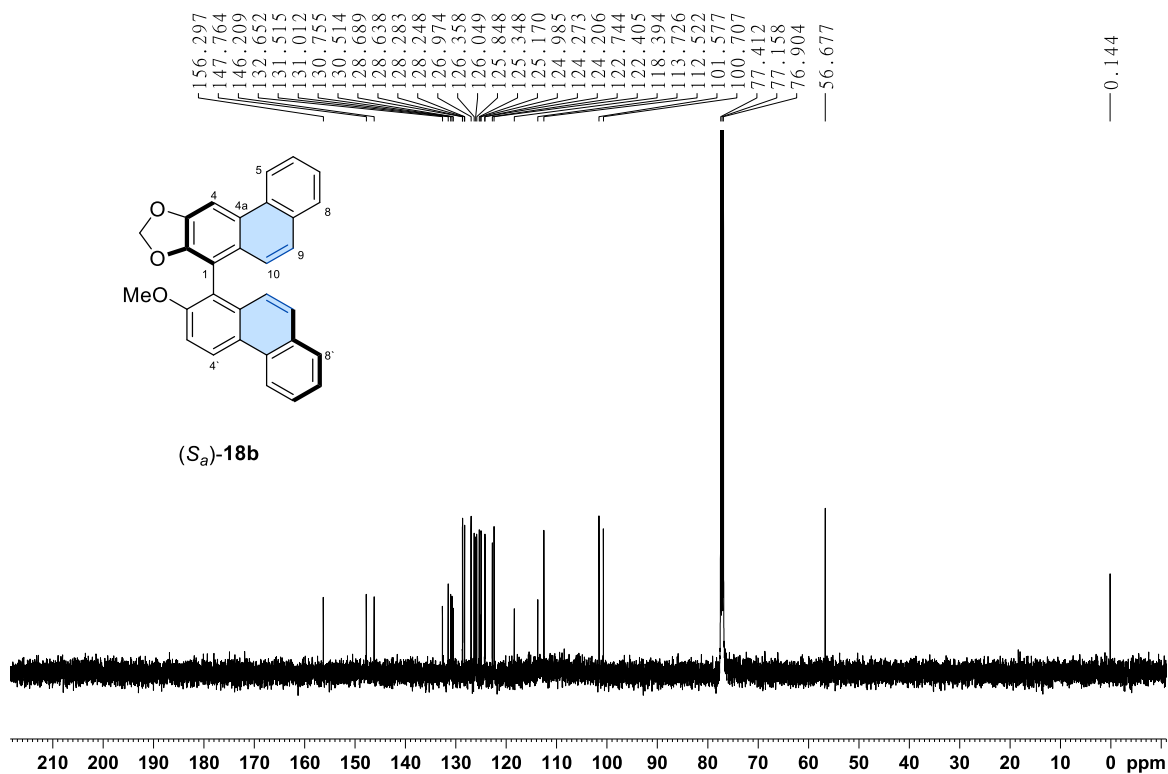
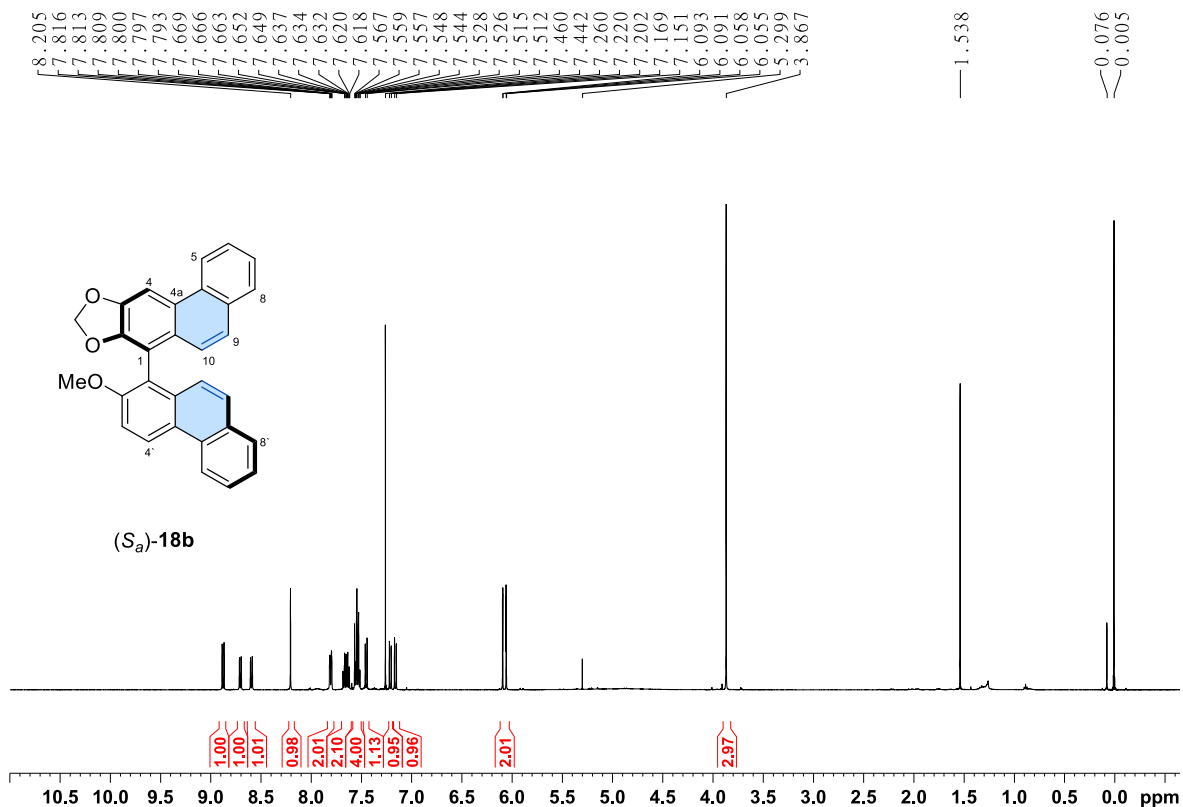
**(S<sub>a</sub>)-1-(3-Bromo-6-methoxy-2-vinylphenyl)-6-chloro-2-methoxyphenanthrene ((S<sub>a</sub>)-16k):**



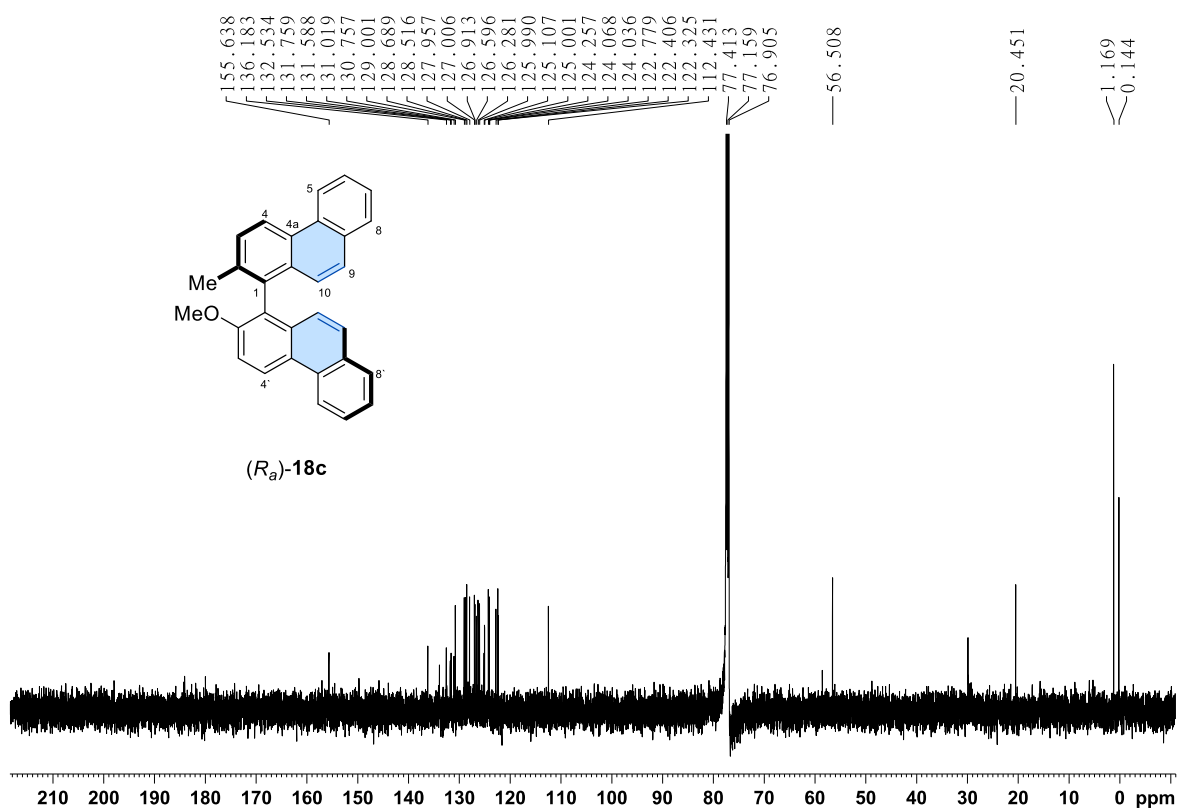
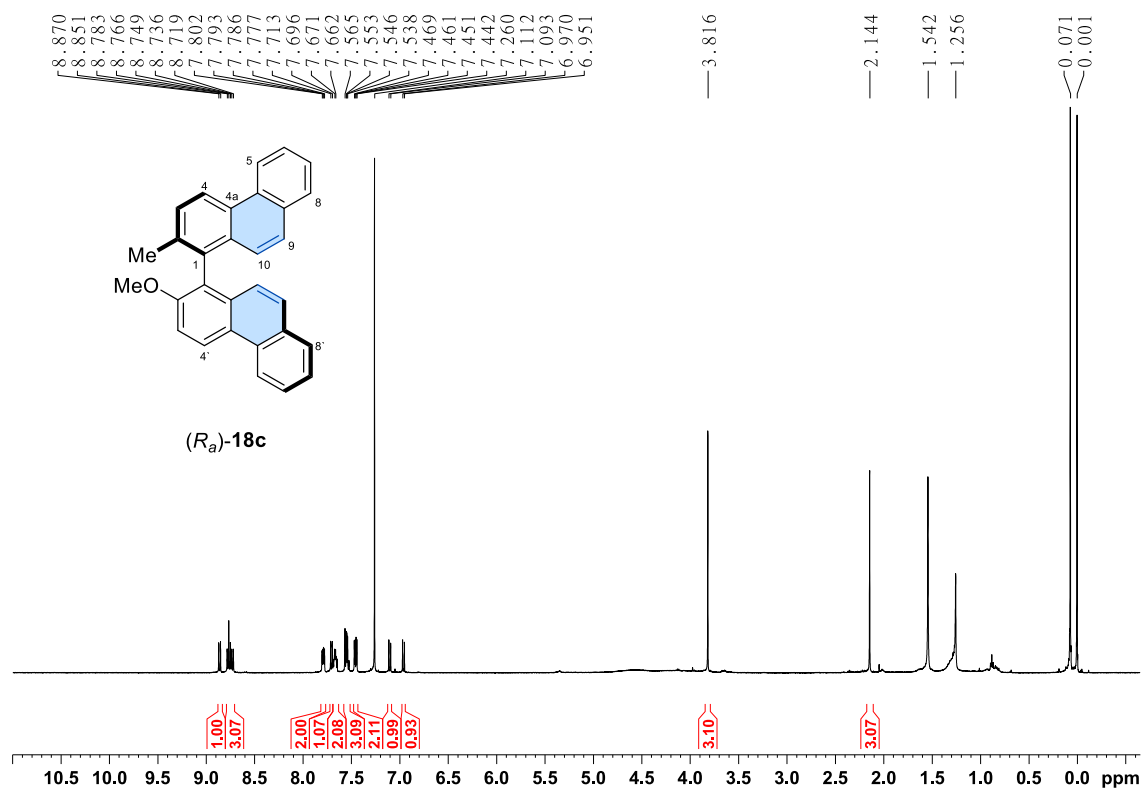
**(S<sub>a</sub>)-2,2'-Dimethoxy-1,1'-biphenanthrene ((S<sub>a</sub>)-18a):**



**(S<sub>a</sub>)-7-(2-Methoxyphenanthren-1-yl)phenanthro[2,3-d][1,3]dioxole ((S<sub>a</sub>)-18b):**

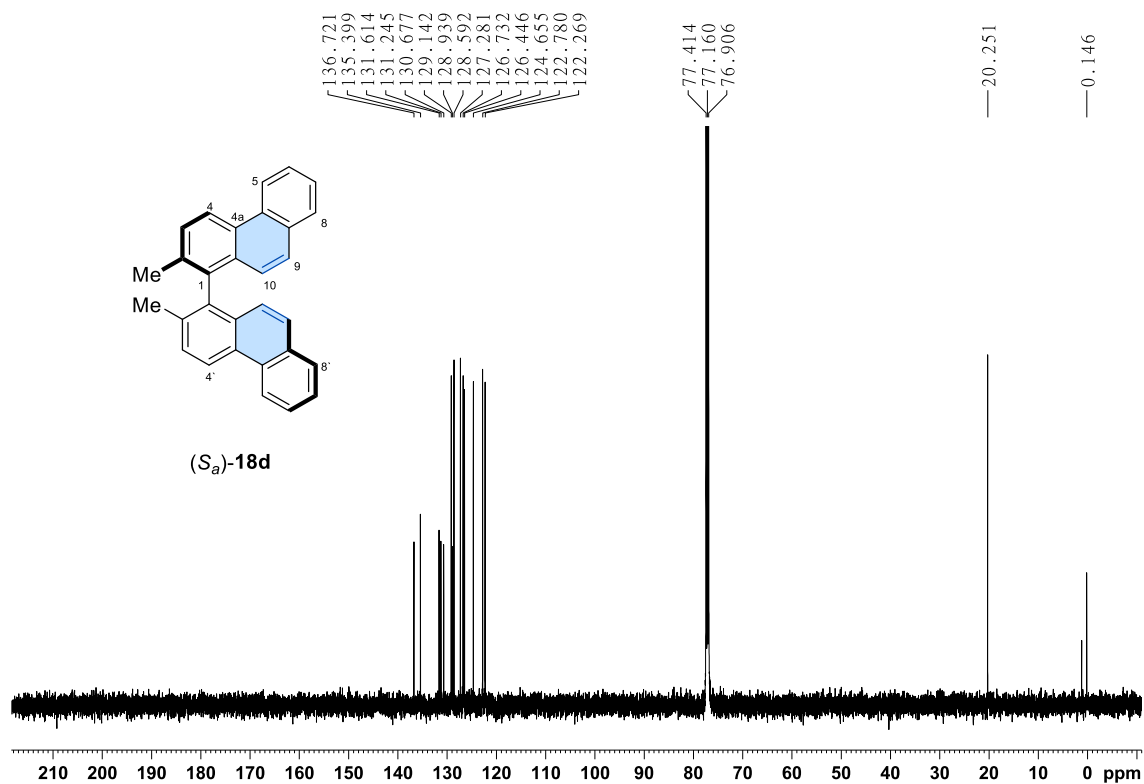
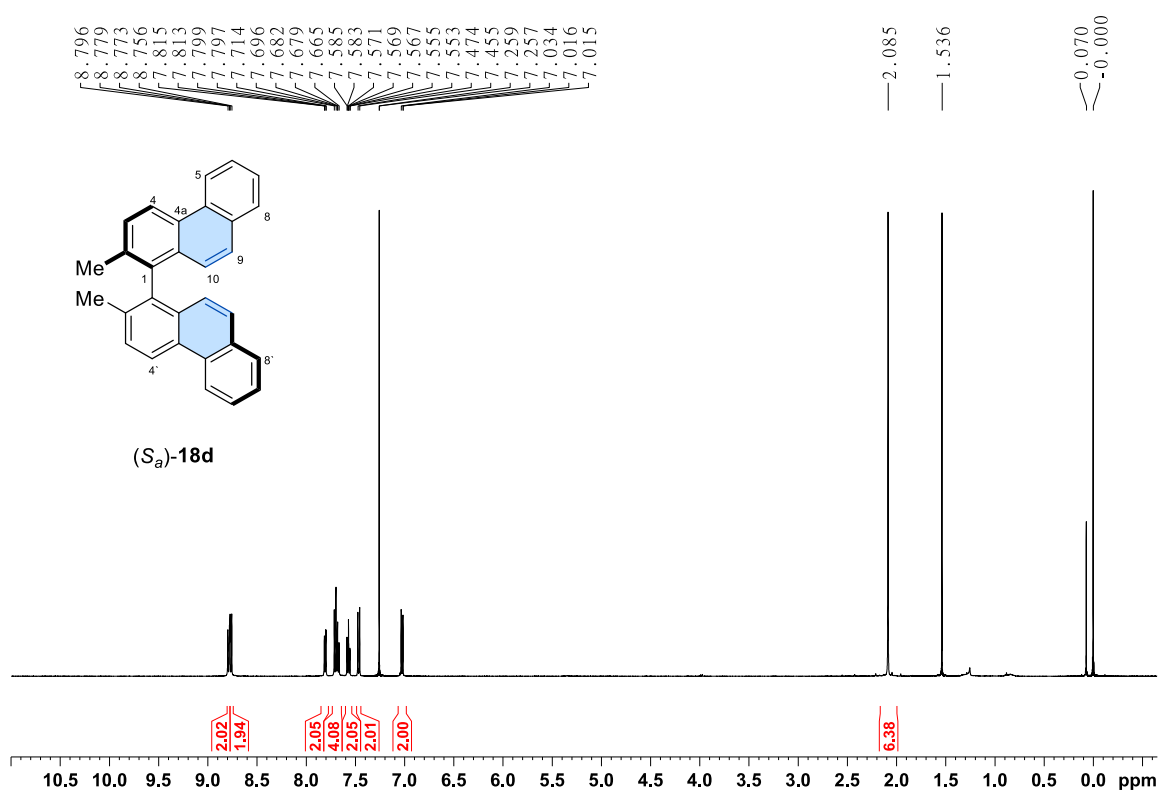


**(*R<sub>a</sub>*)-2-Methoxy-2'-methyl-1,1'-biphenanthrene ((*R<sub>a</sub>*)-18c):**

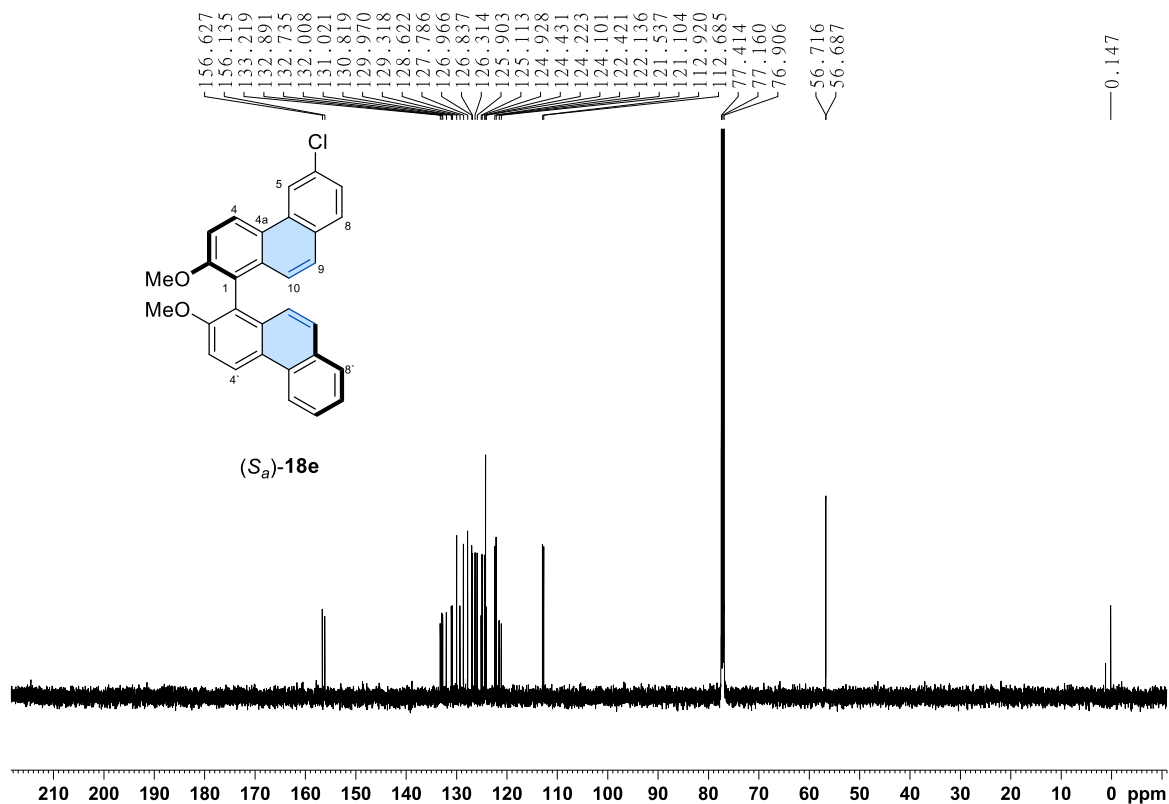
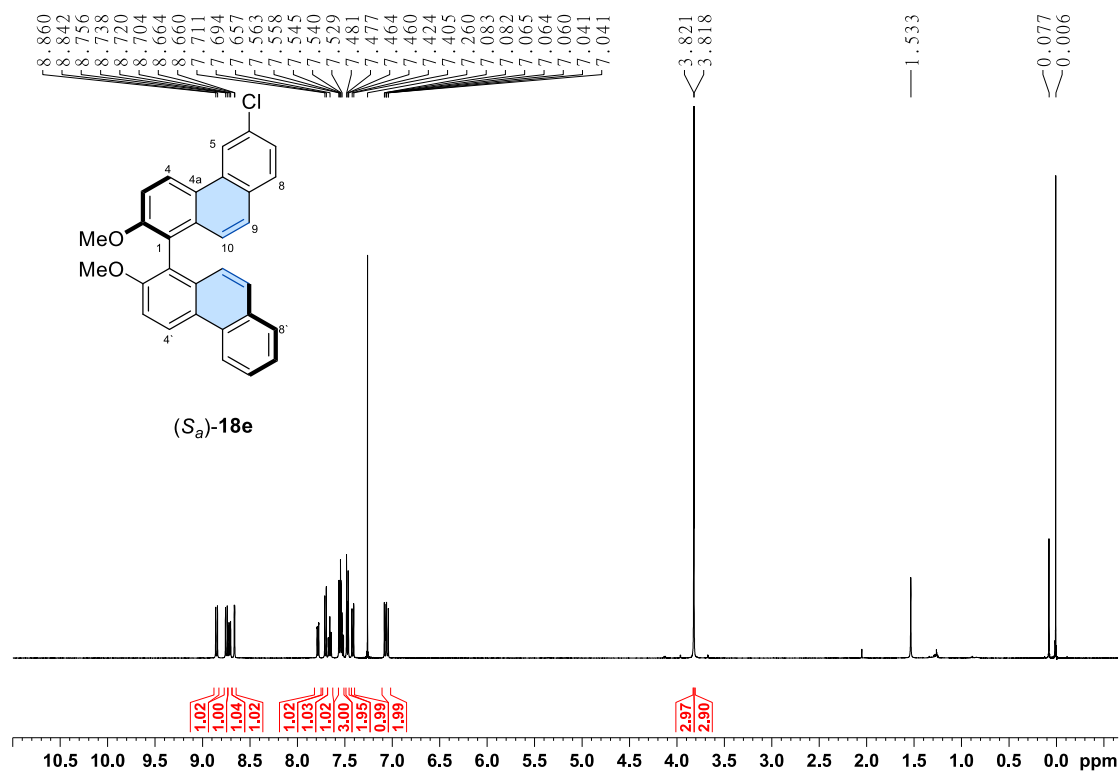




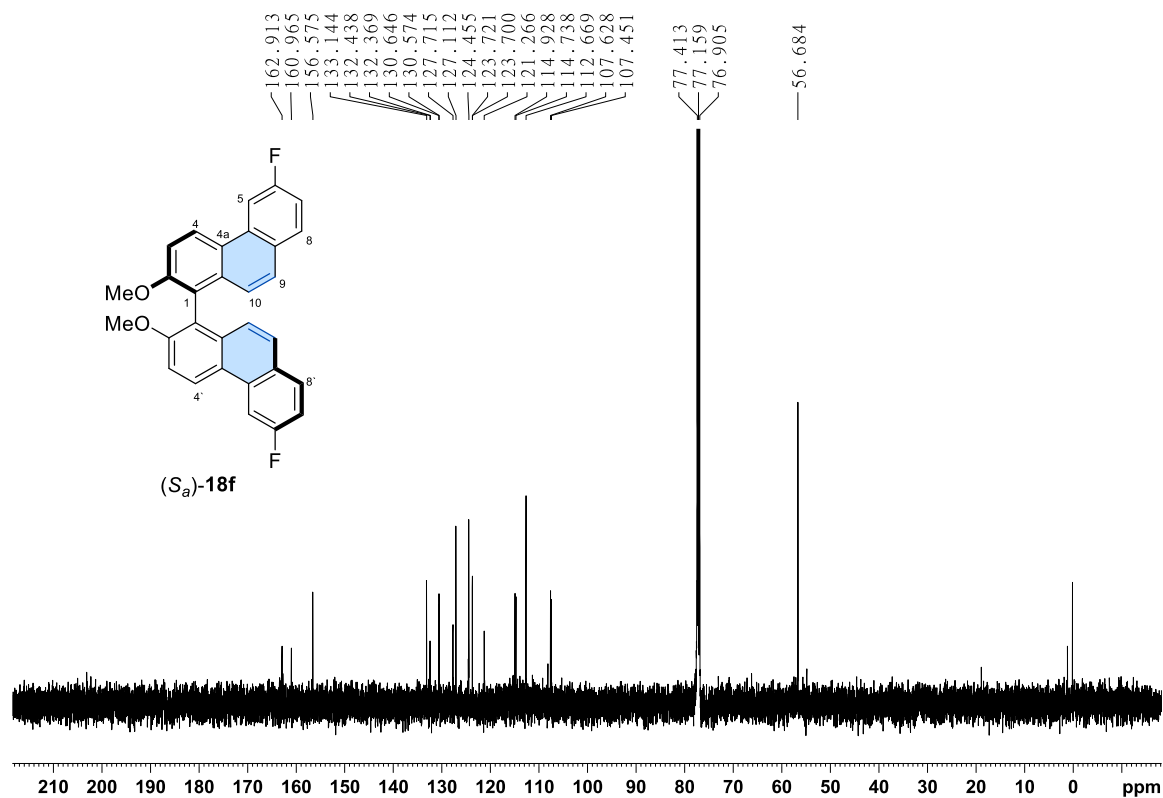
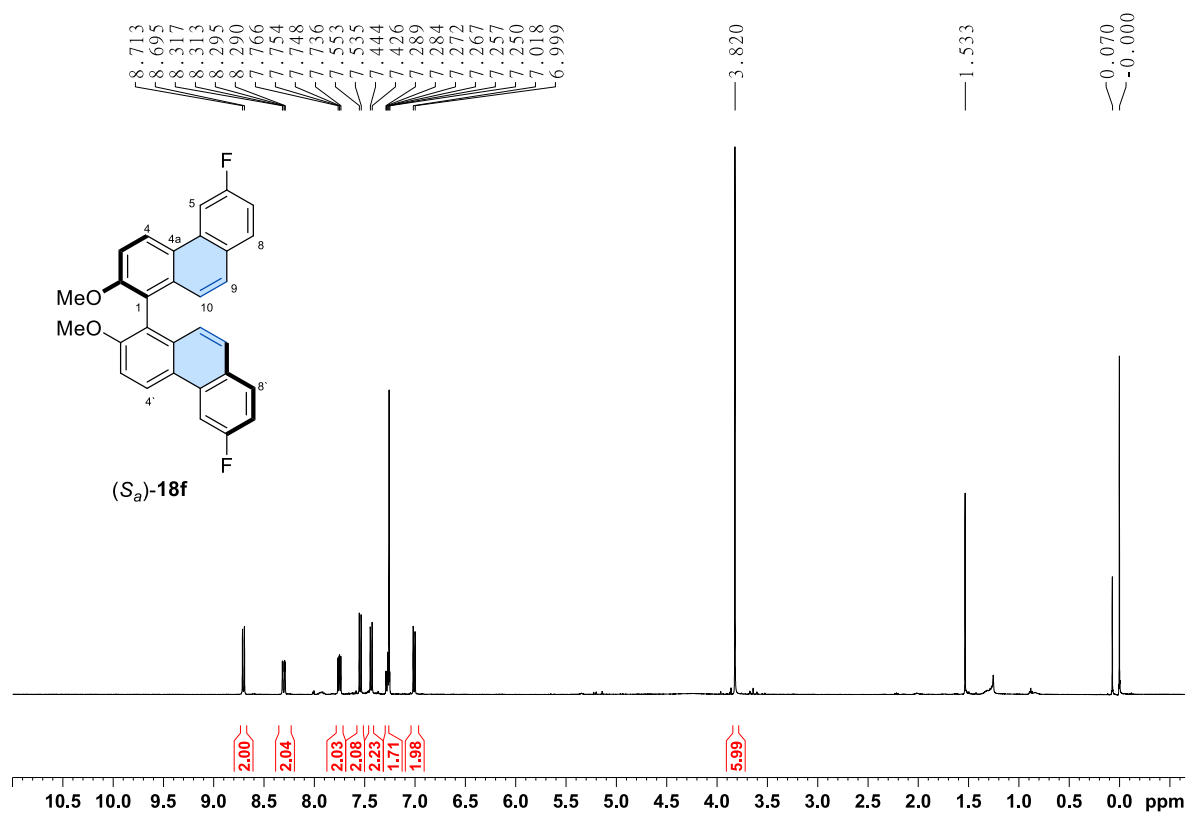
**(S<sub>a</sub>)-2,2'-Dimethyl-1,1'-biphenanthrene ((S<sub>a</sub>)-18d):**

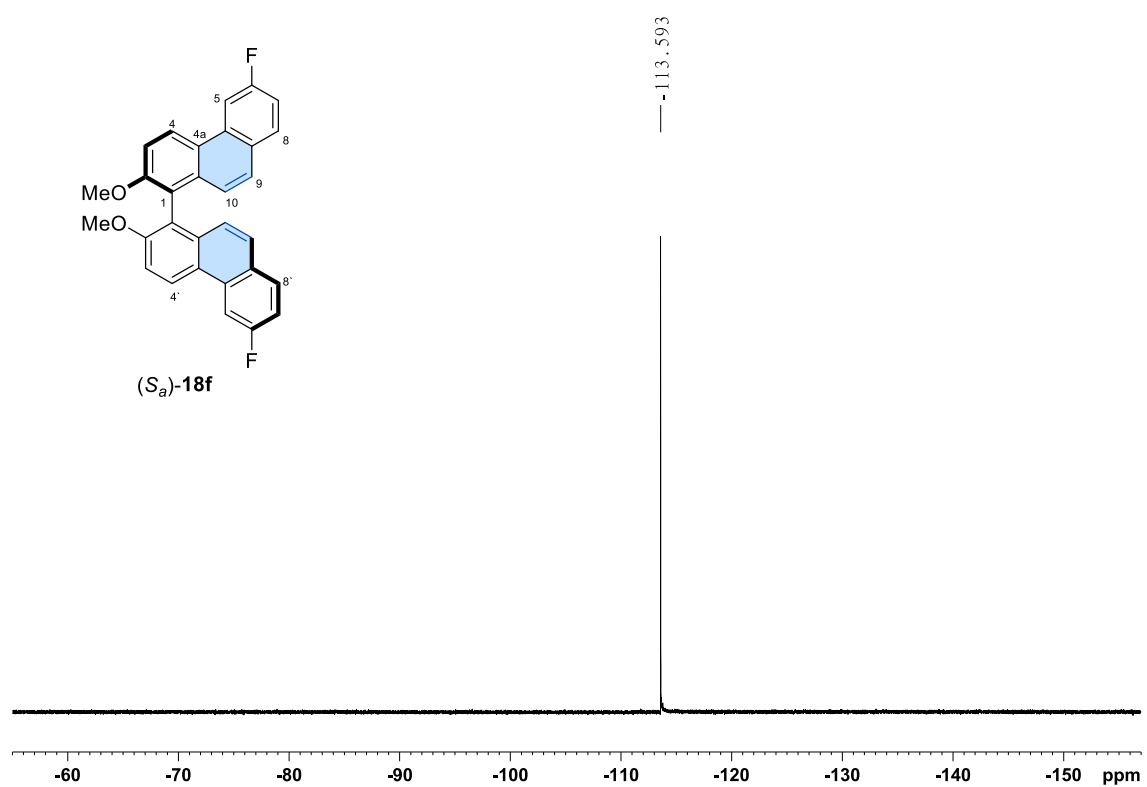


**(S<sub>a</sub>)-6-Chloro-2,2'-dimethoxy-1,1'-biphenanthrene ((S<sub>a</sub>)-18e):**

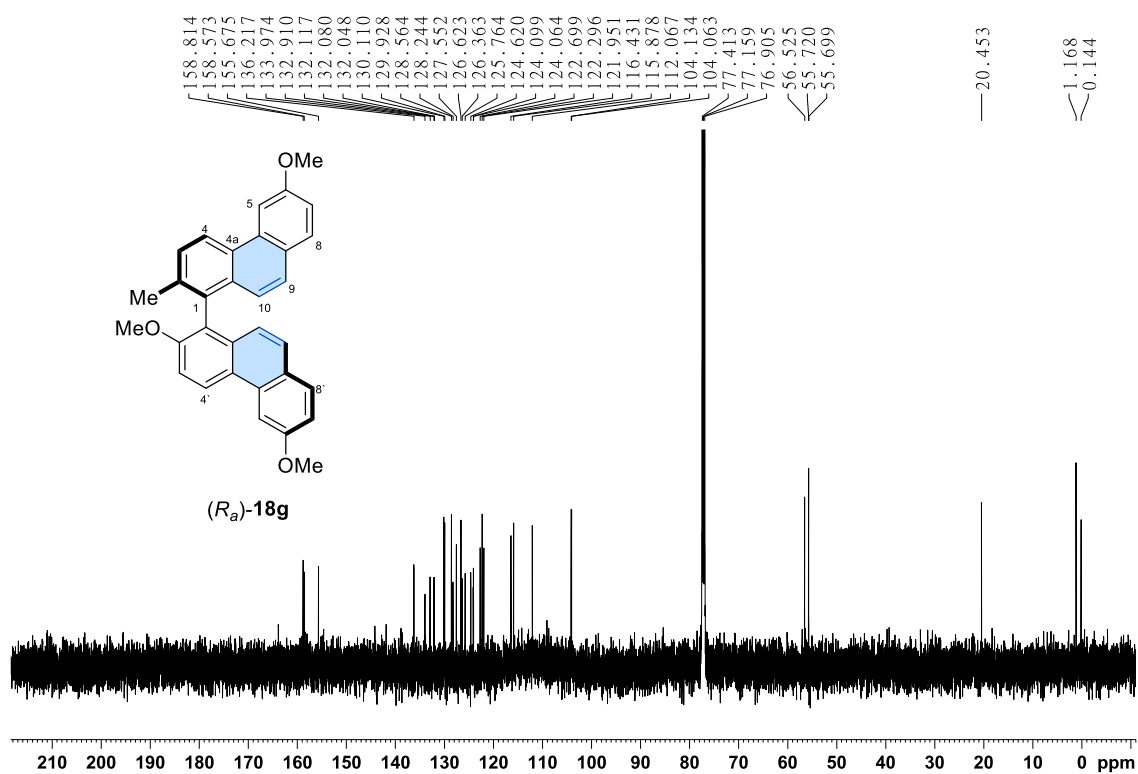
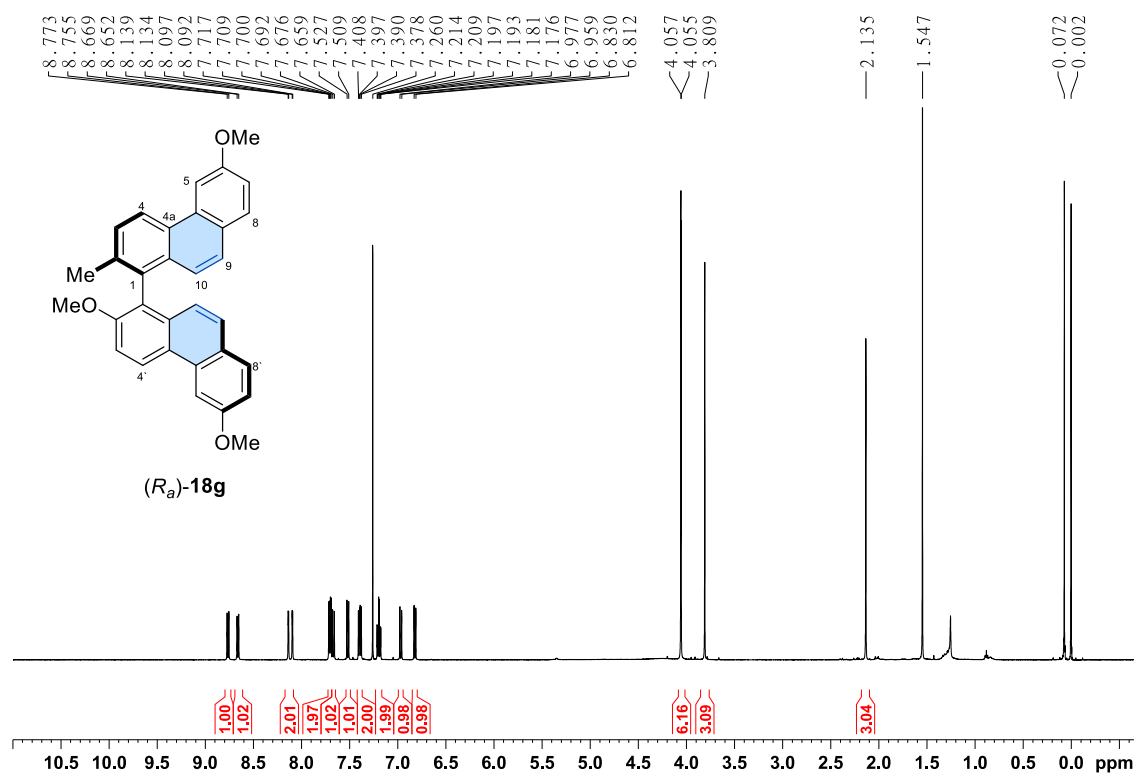


**(S<sub>a</sub>)-6,6'-Difluoro-2,2'-dimethoxy-1,1'-biphenanthrene ((S<sub>a</sub>)-18f):**

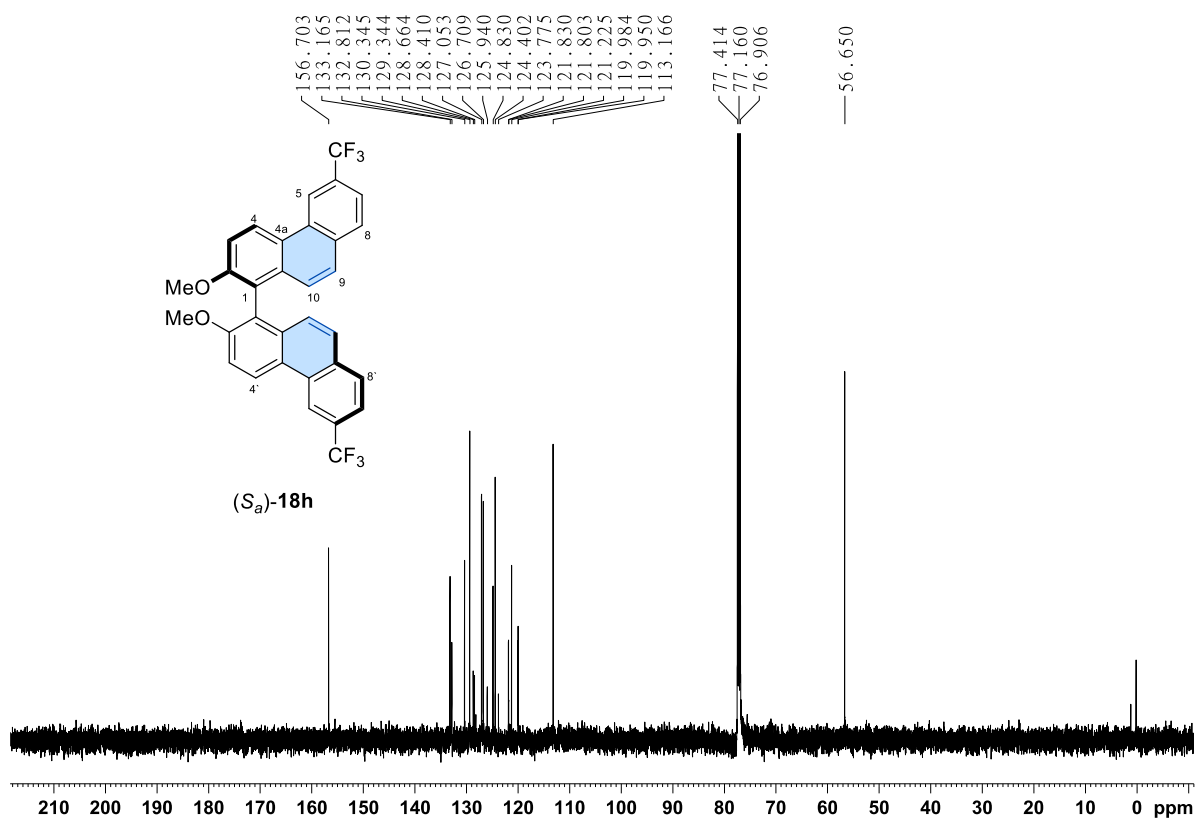
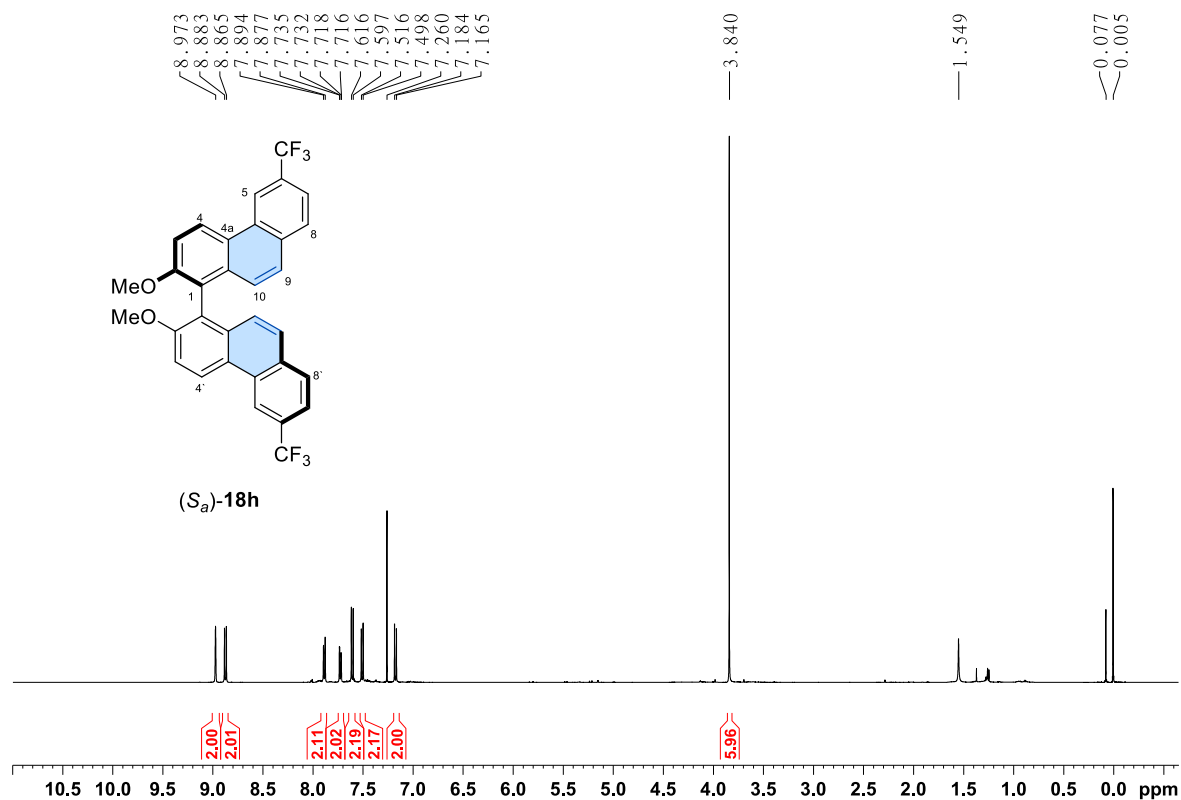


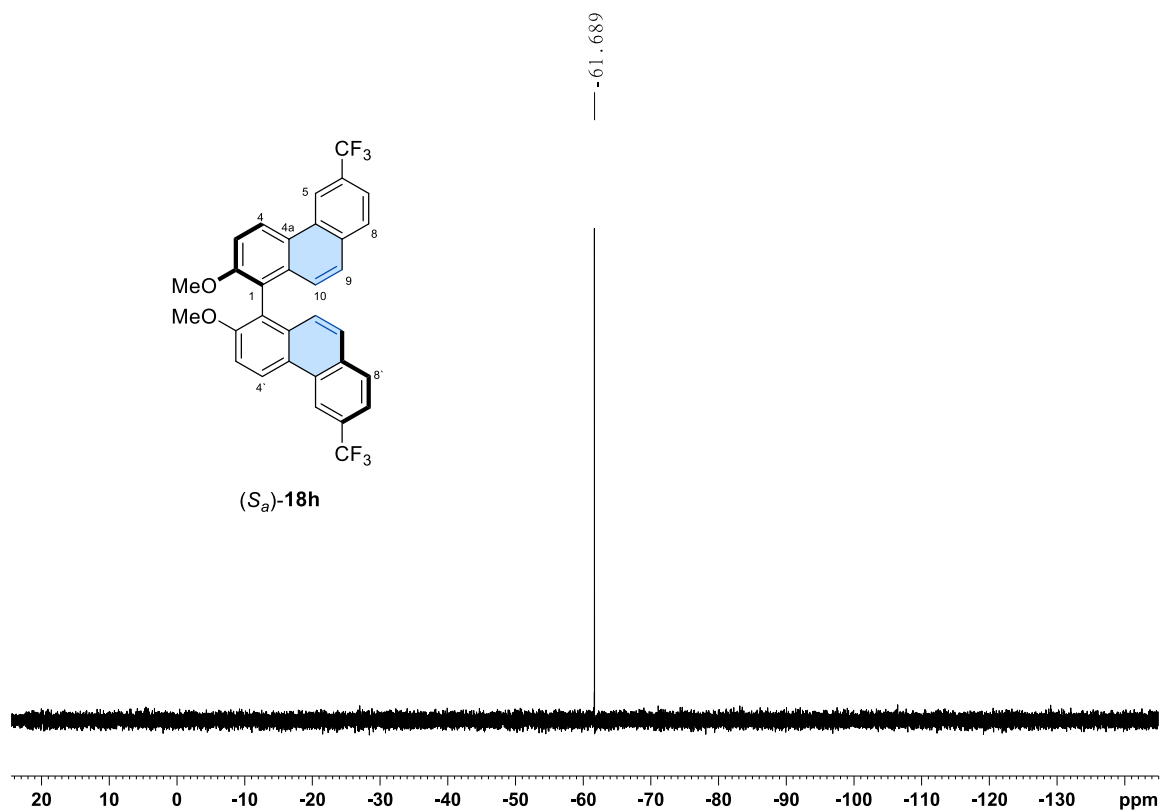


**(*R<sub>a</sub>*)-2,6,6'-Trimethoxy-2'-methyl-1,1'-biphenanthrene ((*S<sub>a</sub>*)-18g):**

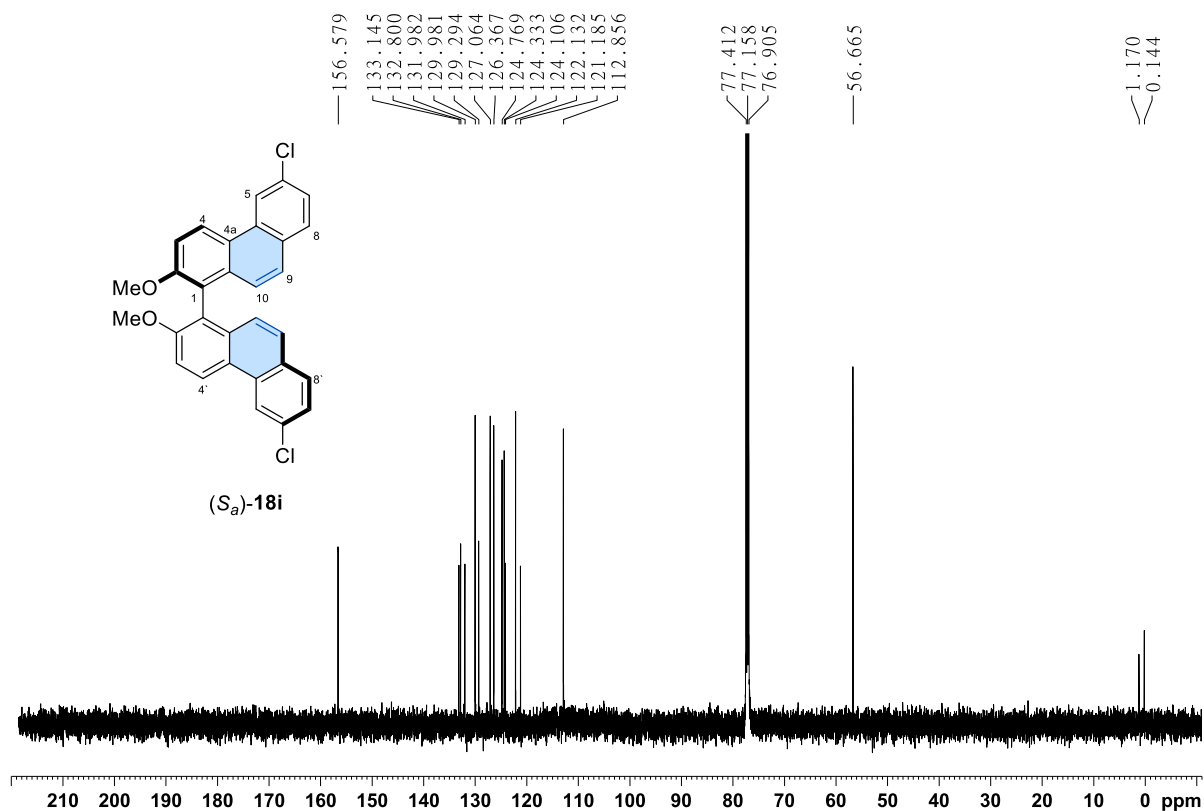
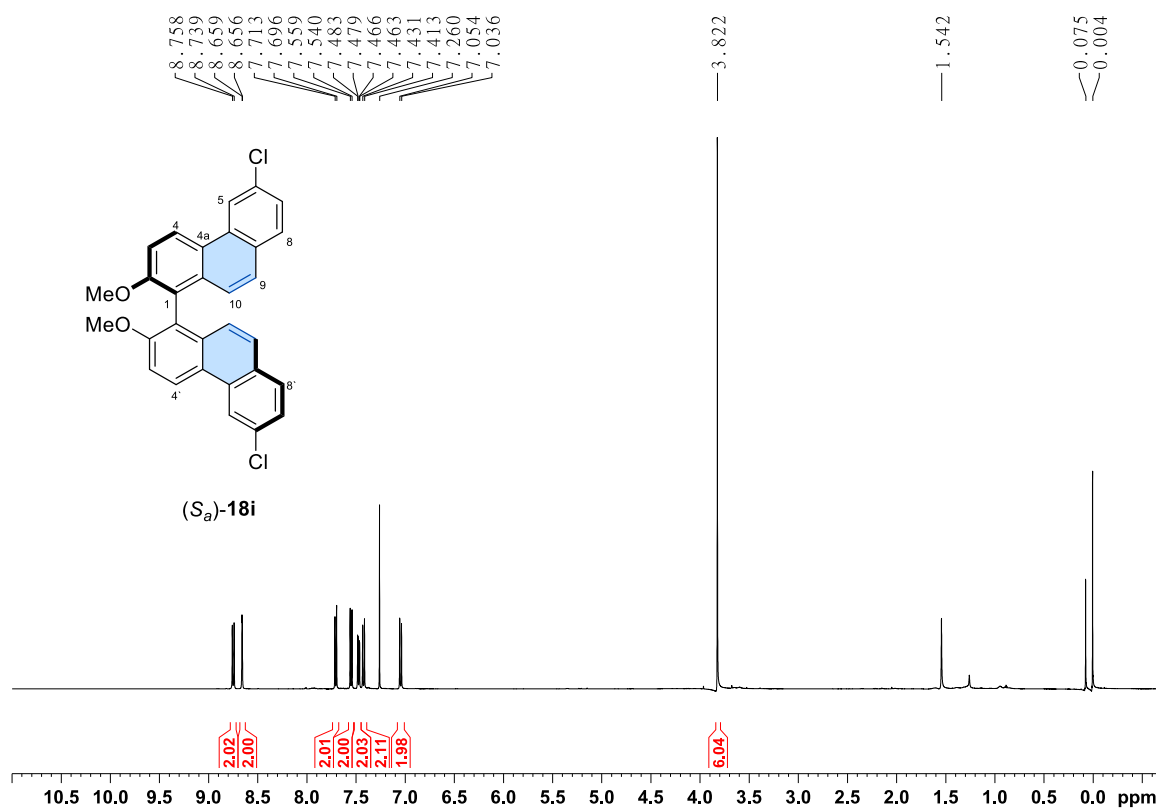


**(S<sub>a</sub>)-2,2'-Dimethoxy-6,6'-bis(trifluoromethyl)-1,1'-biphenanthrene ((S<sub>a</sub>)-18h):**



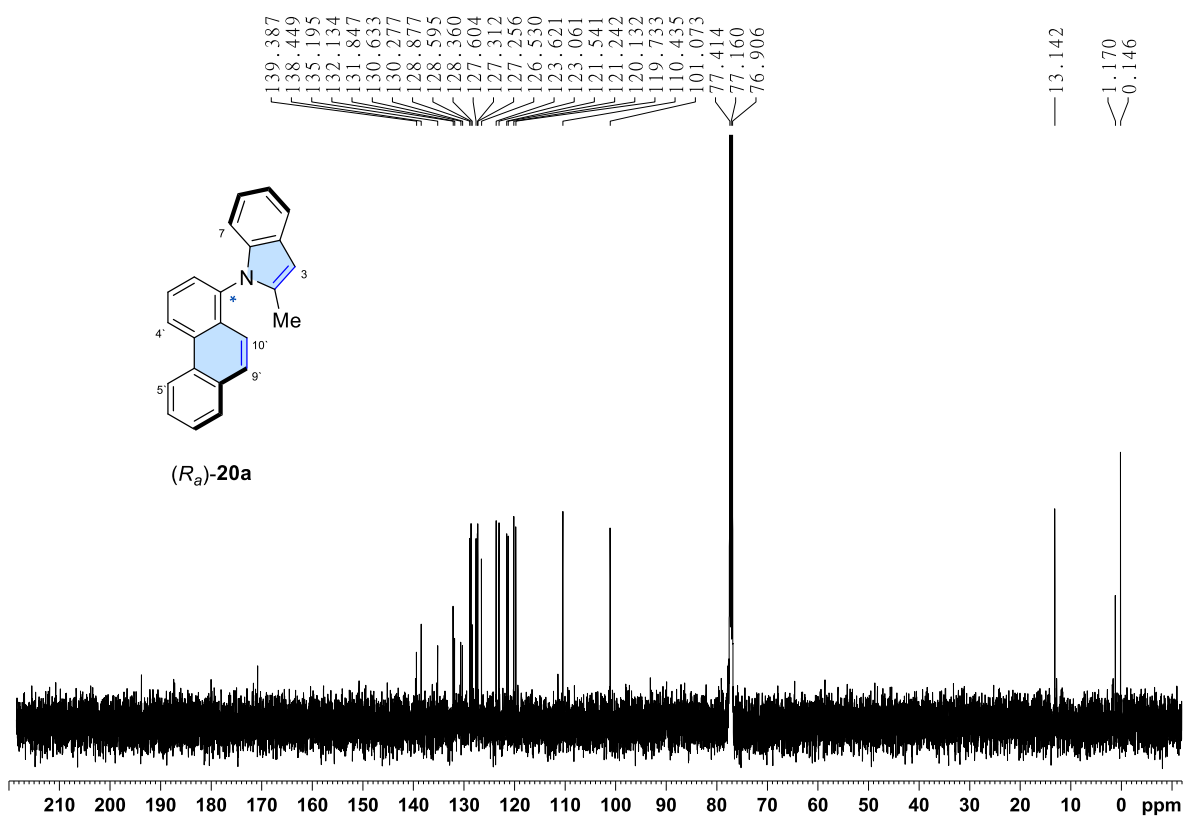
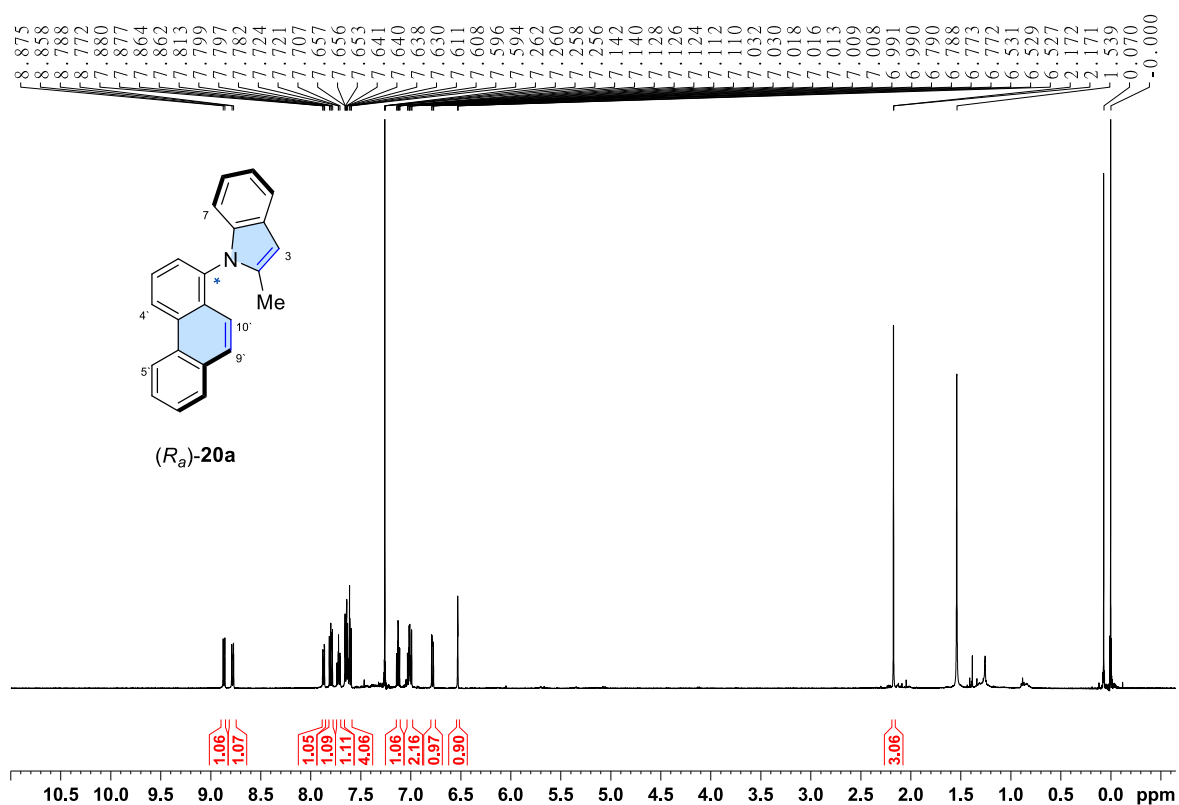


**(S<sub>a</sub>)-6,6'-Dichloro-2,2'-dimethoxy-1,1'-biphenanthrene ((S<sub>a</sub>)-18i):**

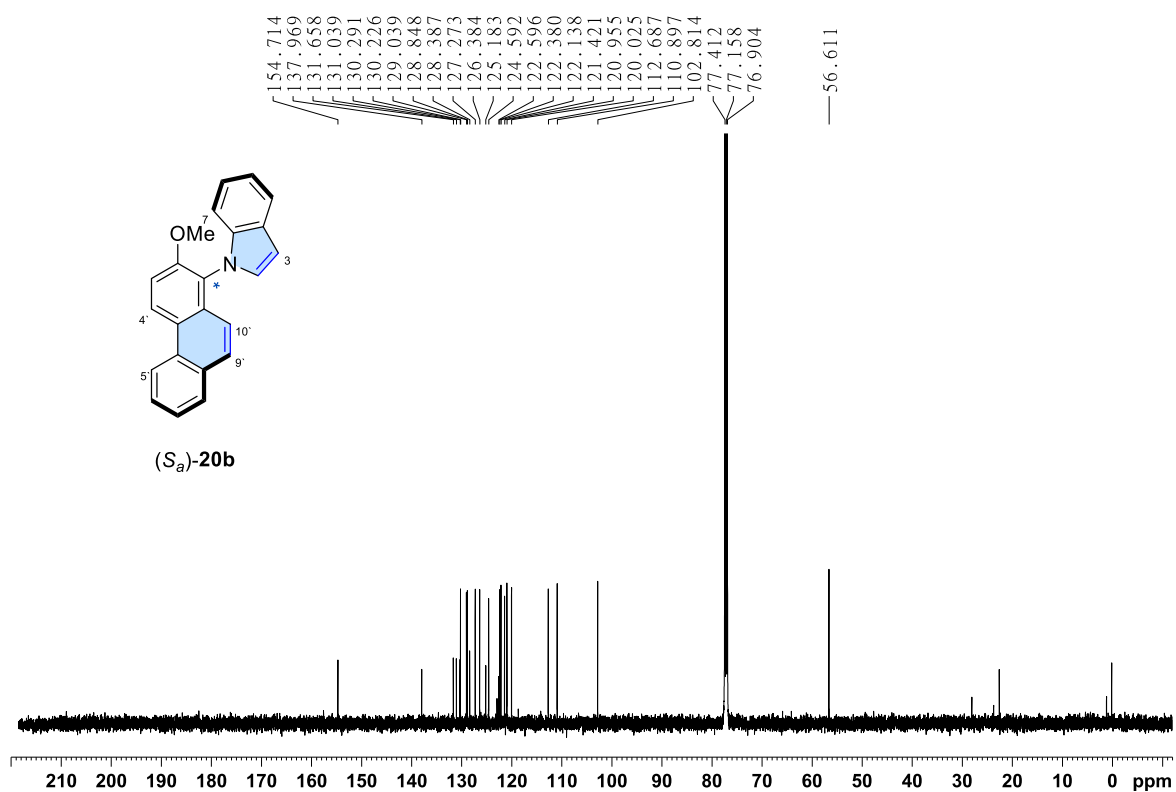
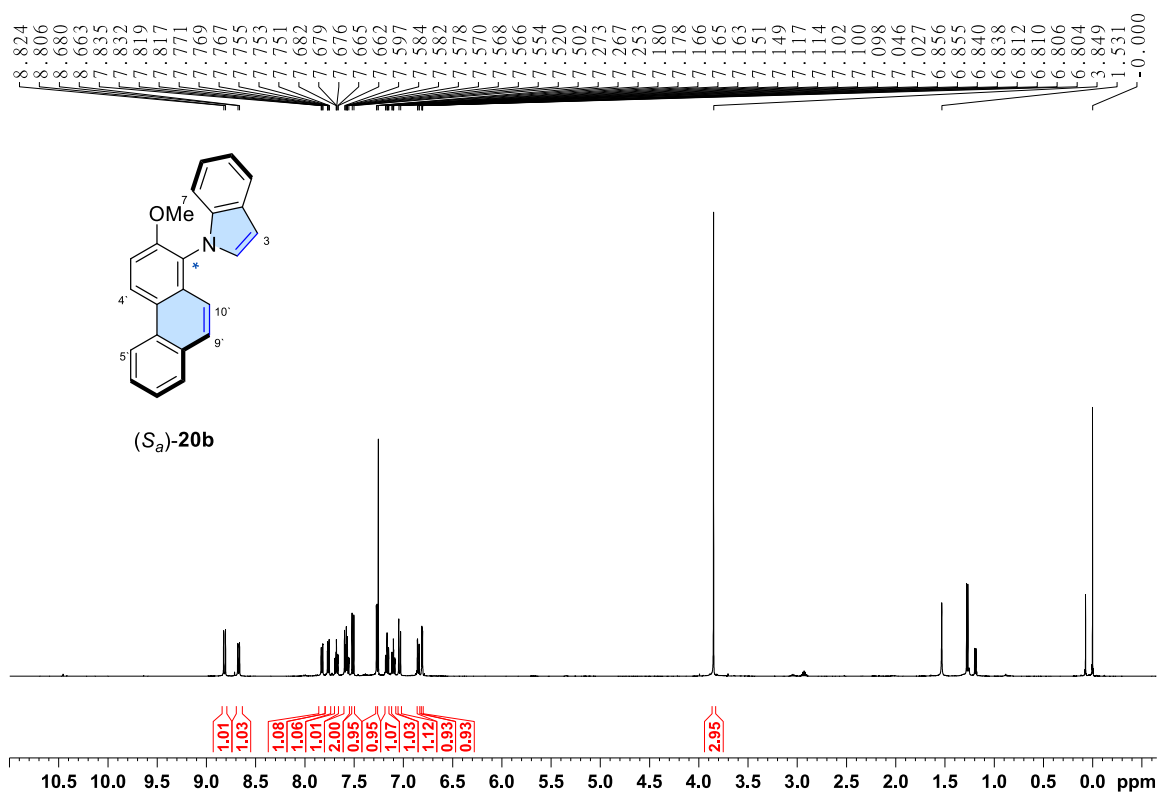




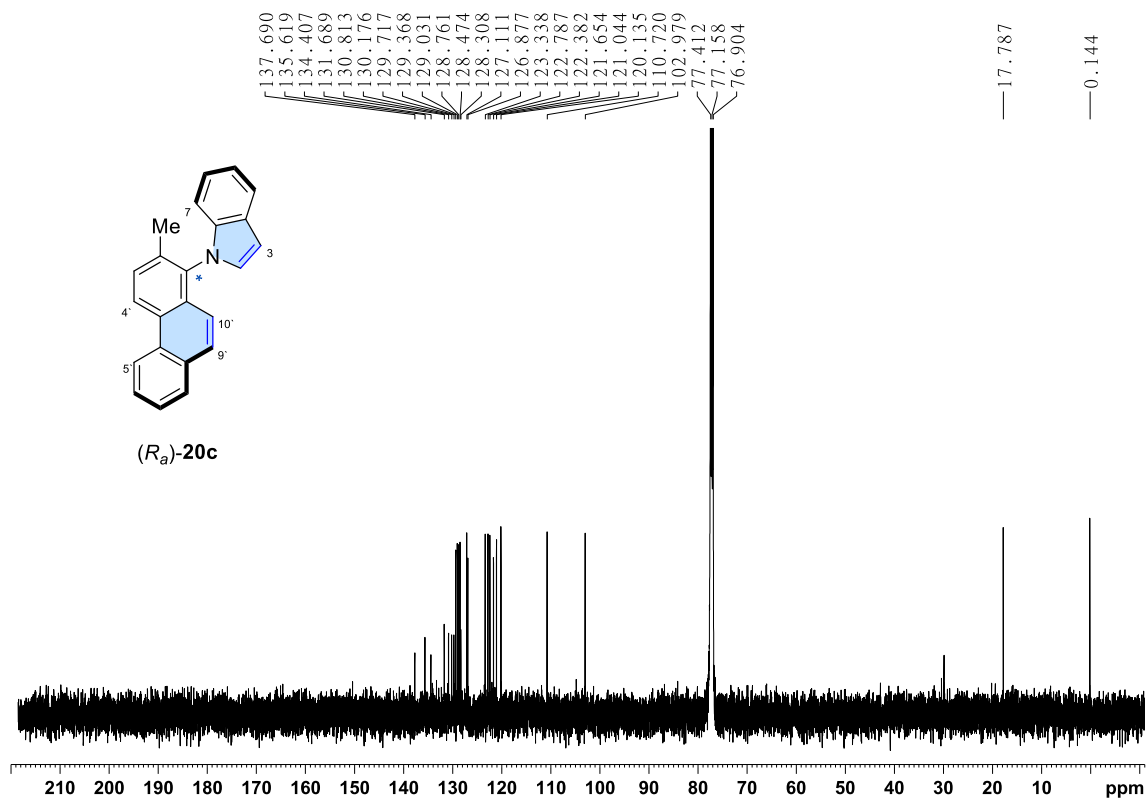
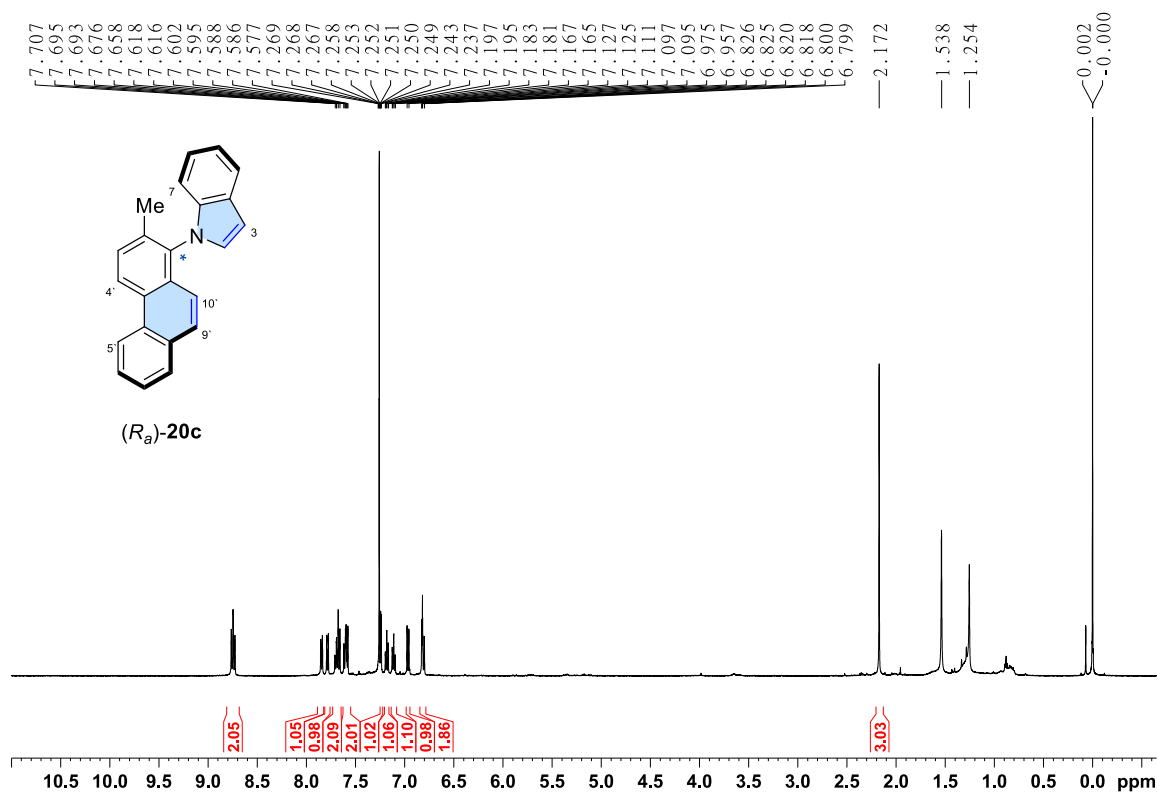
**(*R<sub>a</sub>*)-2-Methyl-1-(phenanthren-1-yl)-1*H*-indole ((*R<sub>a</sub>*)-20a):**



**(S<sub>a</sub>)-1-(2-Methoxyphenanthren-1-yl)-1*H*-indole ((S<sub>a</sub>)-20b):**



**(*R<sub>a</sub>*)-1-(2-Methylphenanthren-1-yl)-1*H*-indole ((*R<sub>a</sub>*)-20c):**

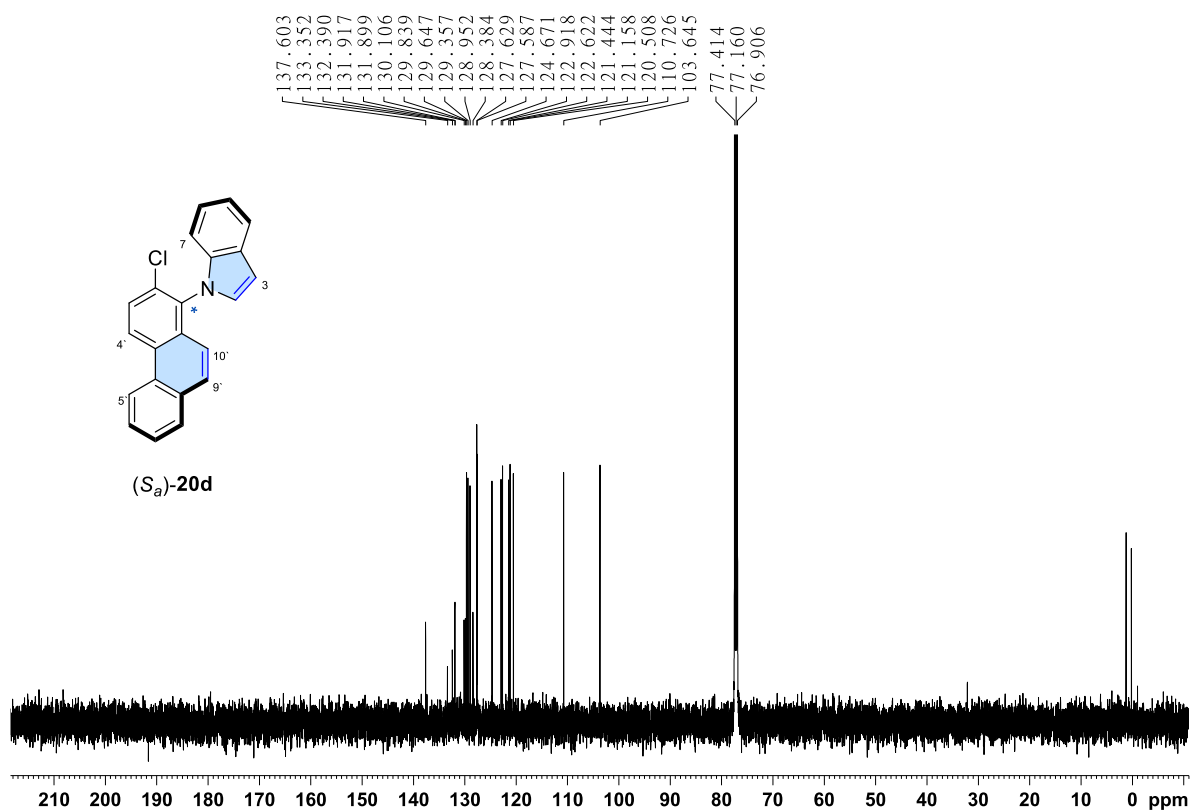


Chemical structure of **(S<sub>a</sub>)-20d** is shown, featuring a fluorene core substituted with a 3,4-dihydro-1H-indole-2-ylidene group and a chlorine atom. The structure is labeled with protons 7, 3, 4', 5, 9', and 10'.

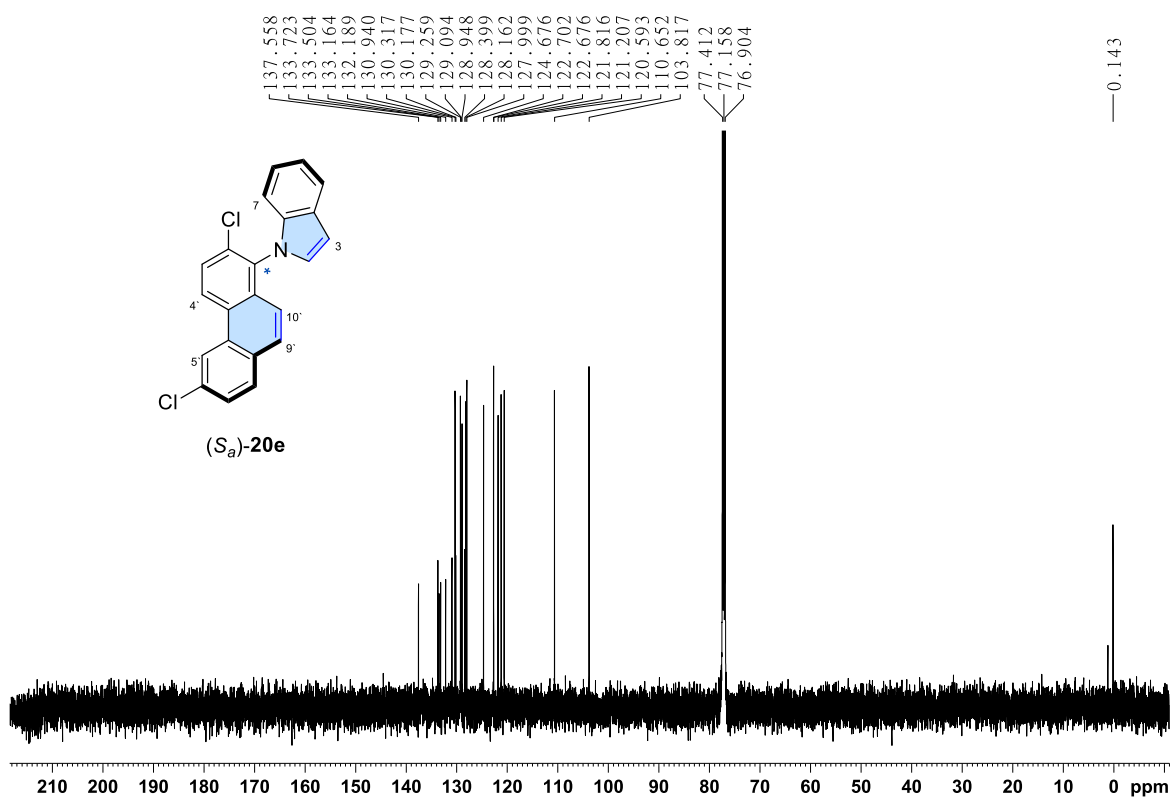
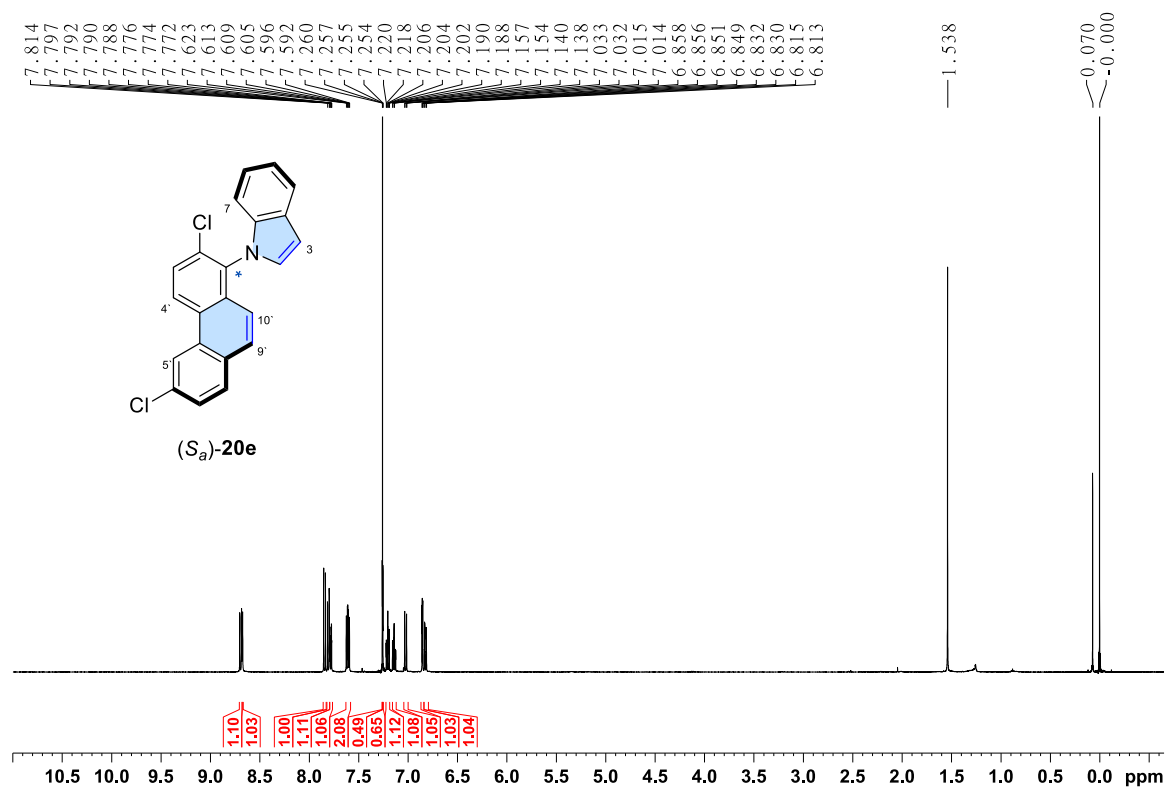
The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) displays peaks corresponding to these protons. The chemical shifts (δ) are listed above the spectrum, and the integration values are shown below the baseline.

Chemical shifts (δ) (ppm): 8.797, 8.779, 8.729, 8.713, 8.882, 7.879, 7.866, 7.864, 7.837, 7.819, 7.793, 7.792, 7.789, 7.777, 7.776, 7.774, 7.734, 7.732, 7.729, 7.718, 7.715, 7.669, 7.667, 7.664, 7.655, 7.653, 7.651, 7.645, 7.639, 7.275, 7.268, 7.260, 7.257, 7.217, 7.215, 7.202, 7.201, 7.199, 7.187, 7.185, 7.153, 7.150, 7.137, 7.134, 7.134, 7.034, 7.016, 6.856, 6.855, 6.850, 6.848, 6.845, 6.843, 6.842, 6.827, 6.825, 1.533, 0.070, -0.000.

Integration values (from left to right): 1.03, 1.01, 1.03, 1.00, 0.98, 1.08, 2.00, 0.96, 1.11, 1.03, 1.07, 0.93, 0.91.



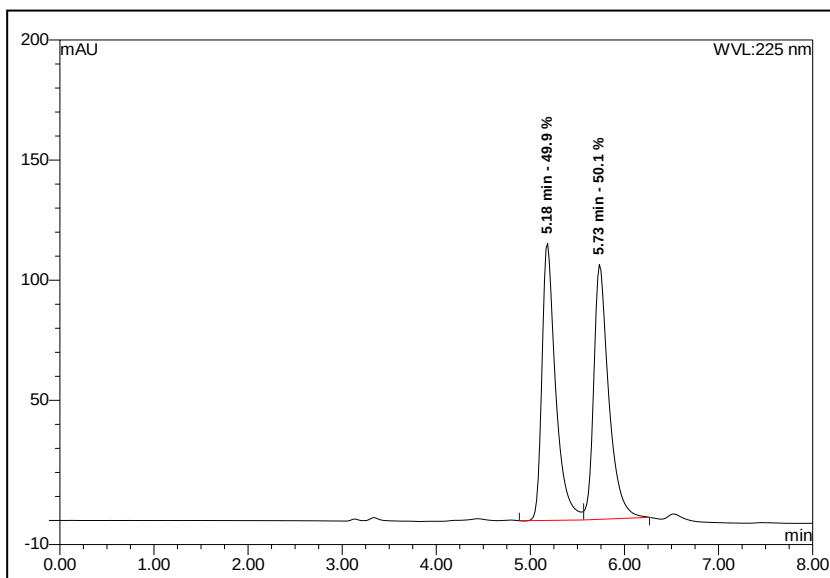
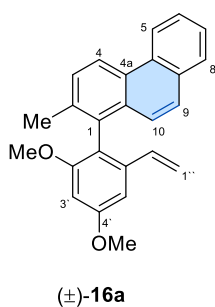
**(S<sub>a</sub>)-1-(2,6-Dichlorophenanthren-1-yl)-1H-indole ((S<sub>a</sub>)-20e):**



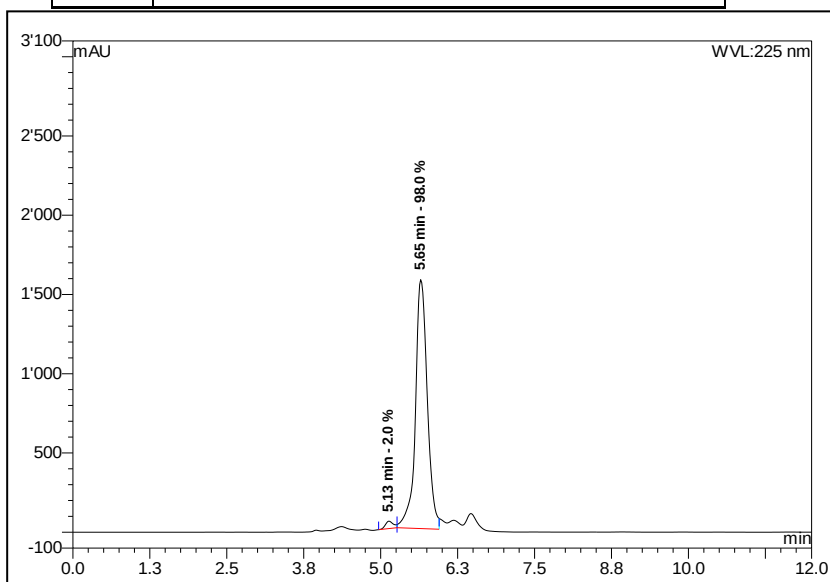
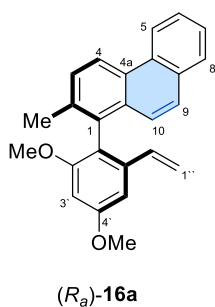
## HPLC Data

### **(*R<sub>a</sub>*)-1-(2,4-Dimethoxy-6-vinylphenyl)-2-methylphenanthrene ((*R<sub>a</sub>*)-16a):**

HPLC conditions: Chiralcel IC (3  $\mu$ m, 250 $\times$ 4.6 mm), heptane/*i*-PrOH 97.5 : 2.5, 1.0 mL/min, 20°C



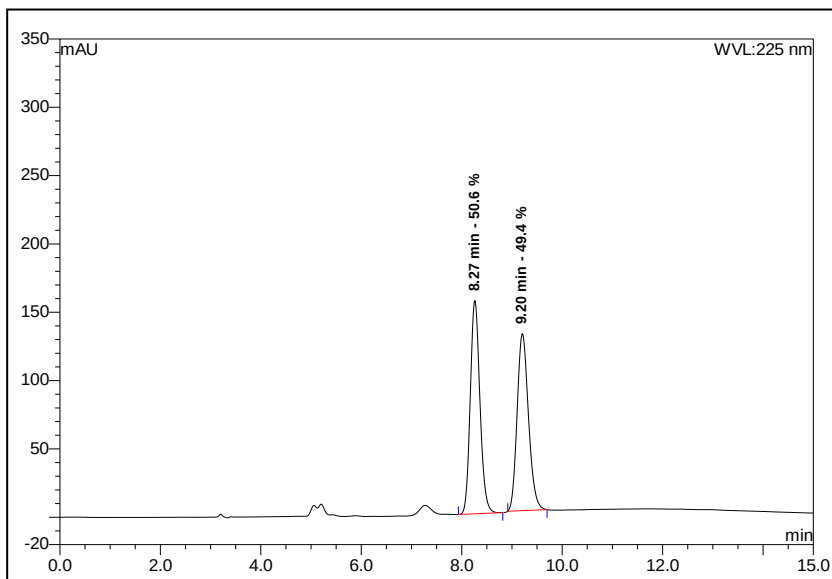
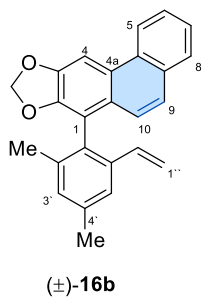
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 5.18            | 115.398       | 19.595          | 49.93         |
| 2      | 5.73            | 106.133       | 19.653          | 50.07         |
| Total: |                 | 221.532       | 39.248          | 100.00        |



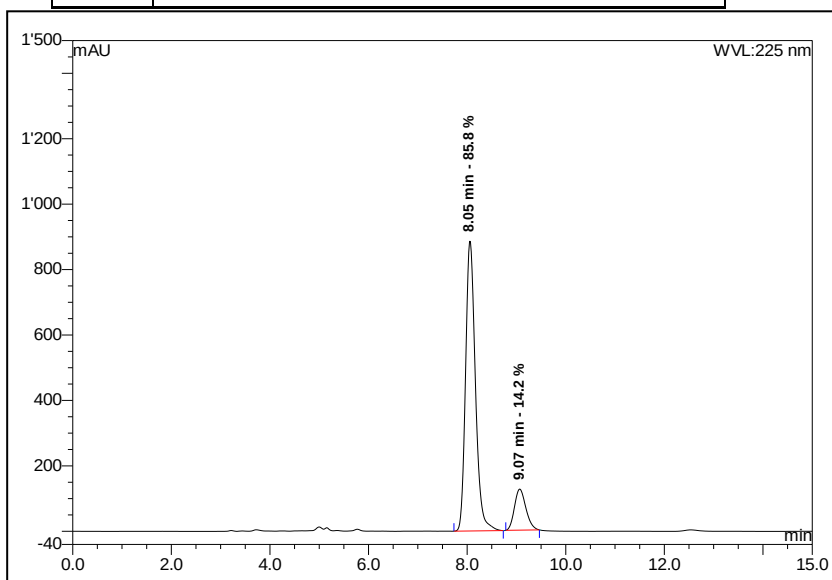
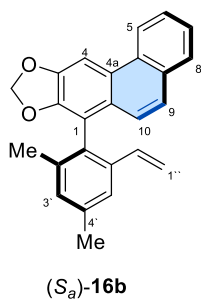
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 5.13            | 46.571        | 7.018           | 1.96          |
| 2      | 5.65            | 1570.519      | 351.729         | 98.04         |
| Total: |                 | 1617.089      | 358.746         | 100.00        |

**(S<sub>a</sub>)-7-(2,4-Dimethyl-6-vinylphenyl)phenanthro[2,3-d][1,3]dioxole ((S<sub>a</sub>)-16b) :**

HPLC conditions: Chiralcel IG (3 μm, 250×4.6 mm), heptane/*i*-PrOH 96 : 4, 1.0 mL/min, 20°C



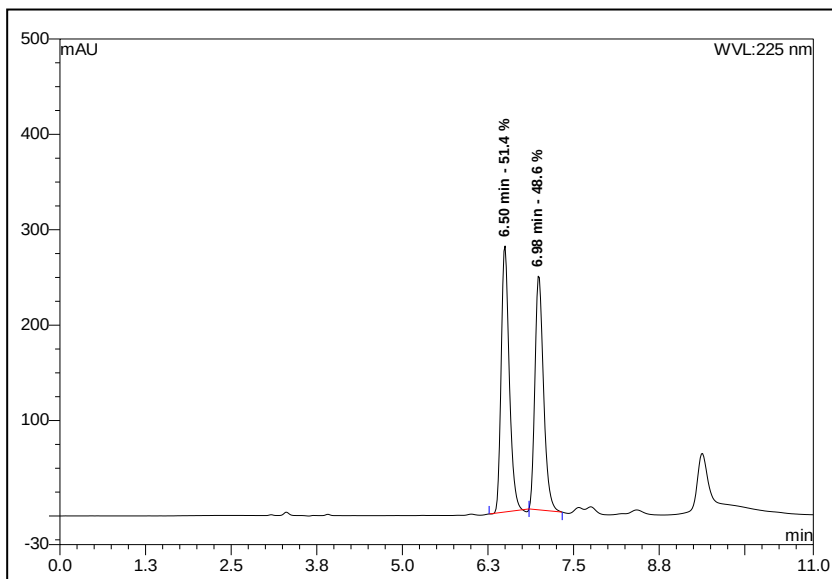
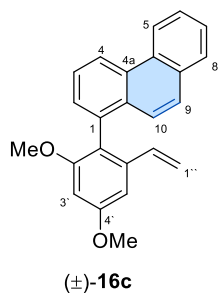
| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 8.27            | 155.997       | 34.686          | 50.57         |
| 2             | 9.20            | 129.497       | 33.906          | 49.43         |
| <b>Total:</b> |                 | 285.494       | 68.592          | 100.00        |



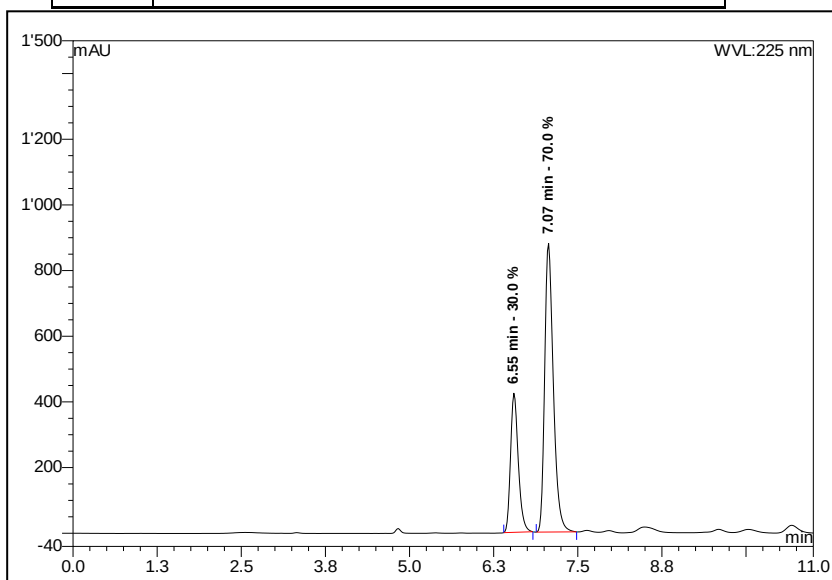
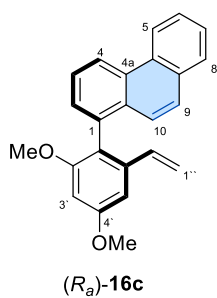
| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 8.05            | 885.442       | 203.904         | 85.80         |
| 2             | 9.07            | 125.794       | 33.754          | 14.20         |
| <b>Total:</b> |                 | 1011.236      | 237.658         | 100.00        |

**(*R<sub>a</sub>*)-1-(2,4-Dimethoxy-6-vinylphenyl)phenanthrene ((*R<sub>a</sub>*)-16c):**

HPLC conditions: Chiralcel IB (3  $\mu$ m, 250 $\times$ 4.6 mm), heptane/*i*-PrOH 97.5 : 2.5, 1.0 mL/min, 20°C



| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 6.50            | 278.786       | 37.982          | 51.41         |
| 2      | 6.98            | 244.889       | 35.904          | 48.59         |
| Total: |                 | 523.674       | 73.886          | 100.00        |

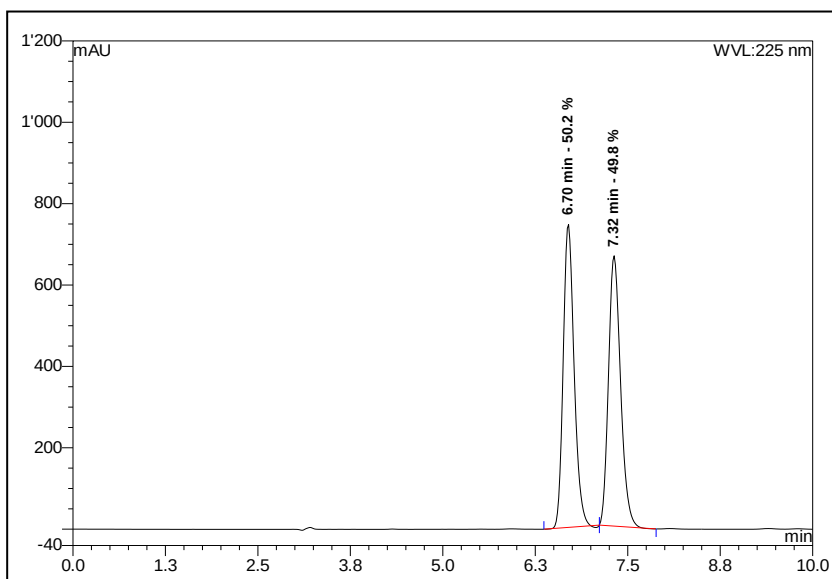
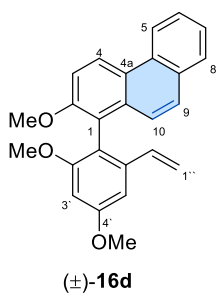


| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 6.55            | 423.759       | 56.370          | 30.02         |
| 2      | 7.07            | 879.139       | 131.389         | 69.98         |
| Total: |                 | 1302.898      | 187.759         | 100.00        |

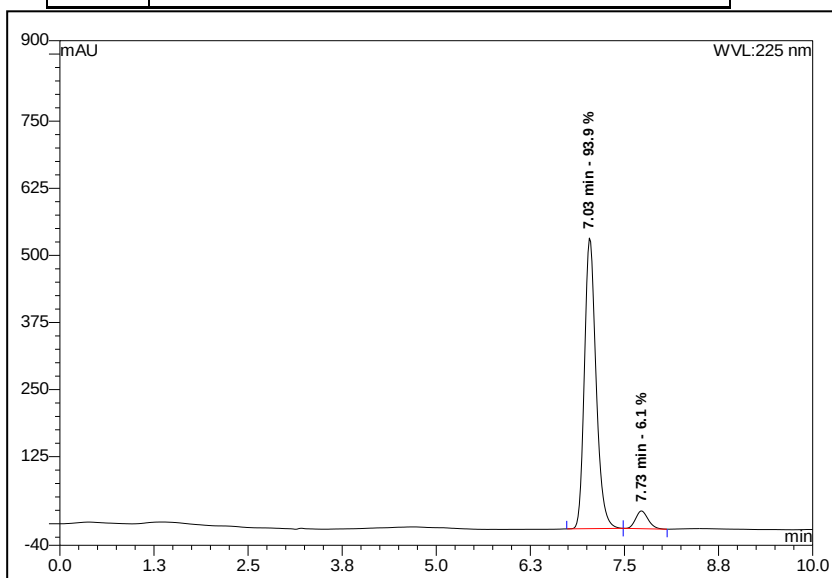
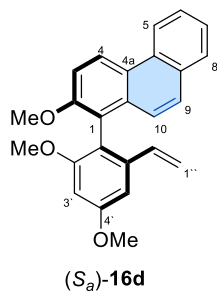


**(S<sub>a</sub>)-1-(2,4-Dimethoxy-6-vinylphenyl)-2-methoxyphenanthrene ((S<sub>a</sub>)-16d):**

HPLC conditions: Chiralcel IG (3 μm, 250×4.6 mm), heptane/*i*-PrOH 90 : 10, 1.0 mL/min, 20°C



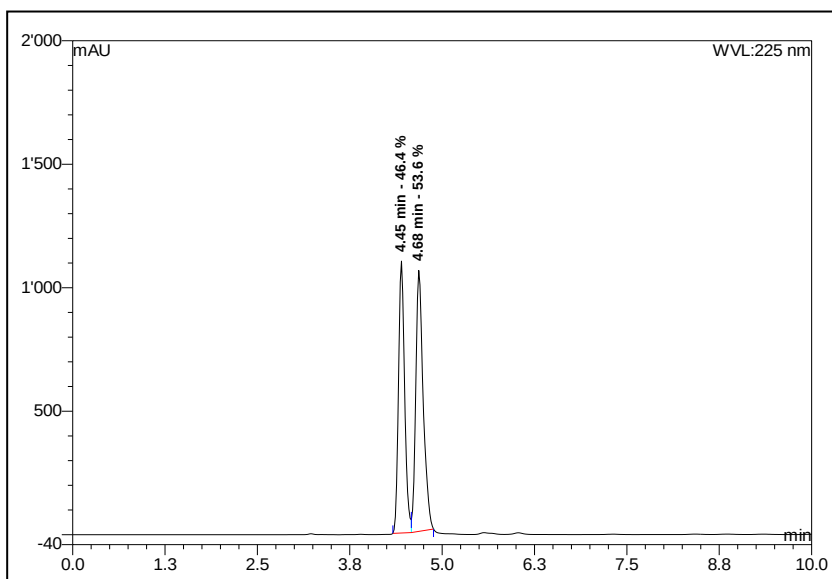
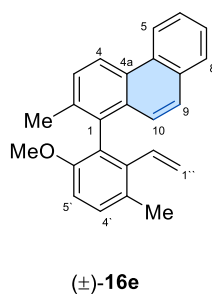
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 6.70            | 744.348       | 126.821         | 50.19         |
| 2      | 7.32            | 664.322       | 125.858         | 49.81         |
| Total: |                 | 1408.670      | 252.678         | 100.00        |



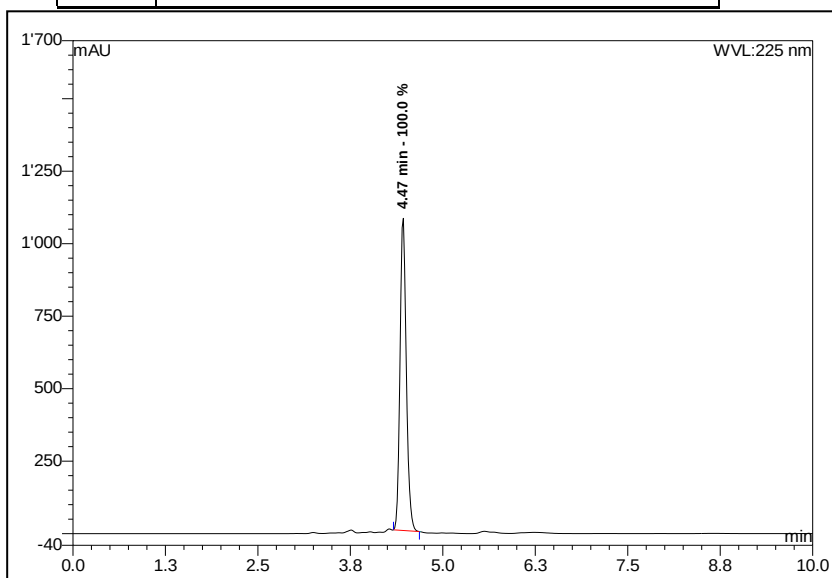
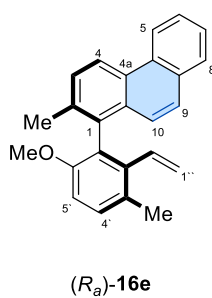
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 7.03            | 541.560       | 96.897          | 93.86         |
| 2      | 7.73            | 32.901        | 6.336           | 6.14          |
| Total: |                 | 574.461       | 103.232         | 100.00        |

**(*R<sub>a</sub>*)-1-(6-Methoxy-3-methyl-2-vinylphenyl)-2-methylphenanthrene ((*R<sub>a</sub>*)-16e):**

HPLC conditions: Chiralcel IG (3  $\mu$ m, 250 $\times$ 4.6 mm), heptane/*i*-PrOH 97.5 : 2.5, 1.0 mL/min, 20°C



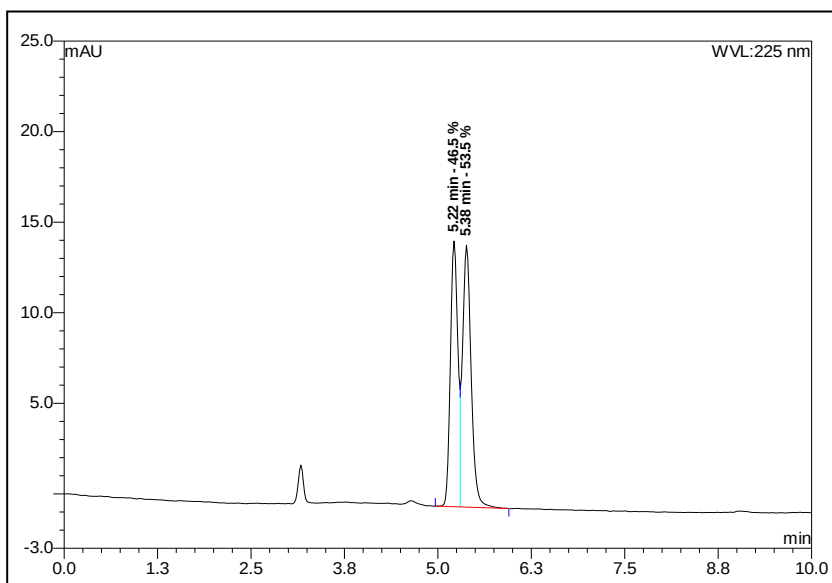
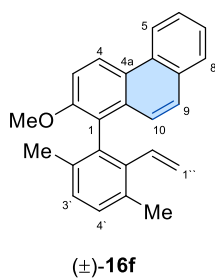
| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 4.45            | 1101.108      | 106.326         | 46.38         |
| 2             | 4.68            | 1056.595      | 122.908         | 53.62         |
| <b>Total:</b> |                 | 1828.666      | 337.446         | 100.00        |



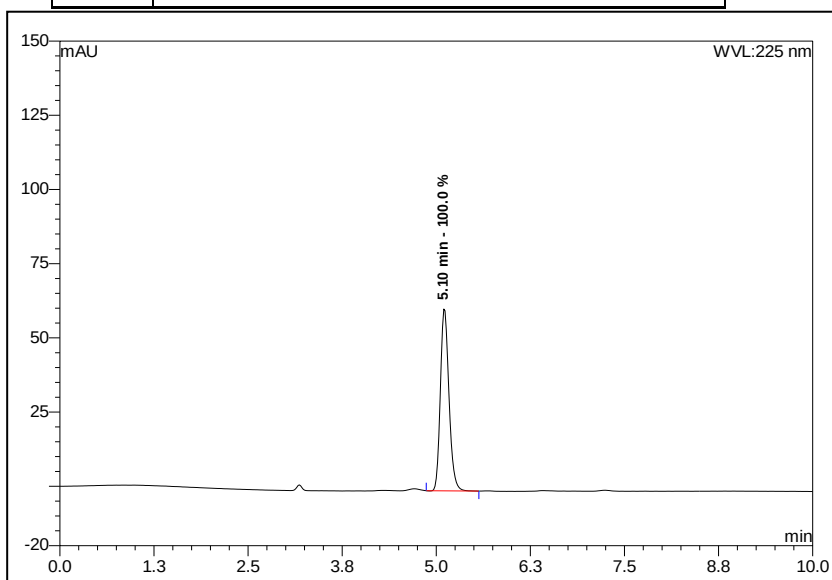
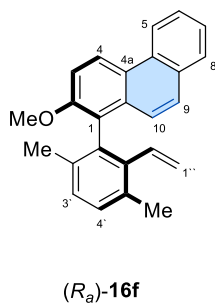
| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 4.47            | 1076.485      | 106.301         | 100.00        |
| <b>Total:</b> |                 | 1076.485      | 106.301         | 100.00        |

**(*R<sub>a</sub>*)-1-(3,6-Dimethyl-2-vinylphenyl)-2-methoxyphenanthrene ((*R<sub>a</sub>*)-16f):**

HPLC conditions: Chiralcel IG (3  $\mu$ m, 250 $\times$ 4.6 mm), heptane/*i*-PrOH 99 : 1, 1.0 mL/min, 20°C



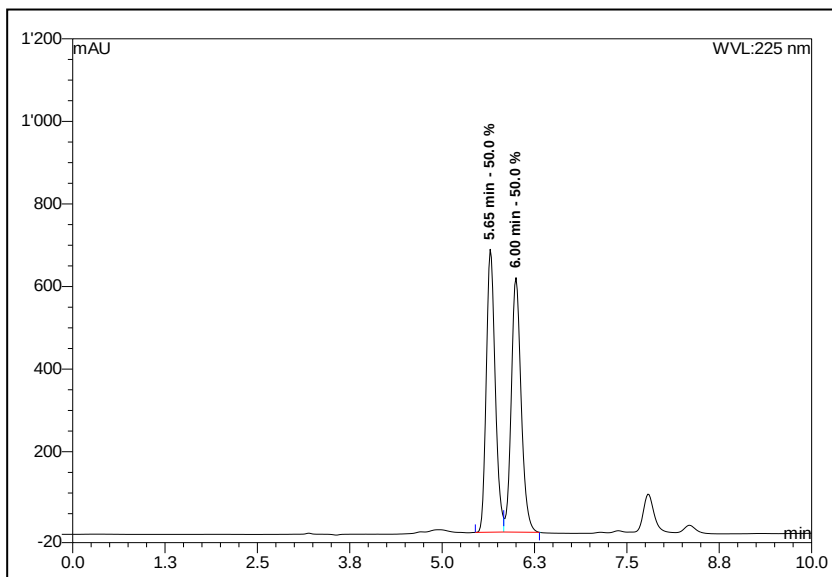
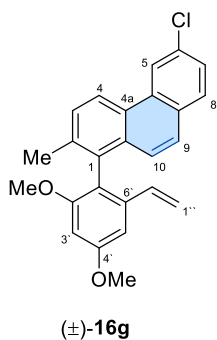
| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 5.22            | 14.668        | 1.688           | 46.50         |
| 2             | 5.38            | 14.463        | 1.942           | 53.50         |
| <b>Total:</b> |                 | 29.131        | 3.630           | 100.00        |



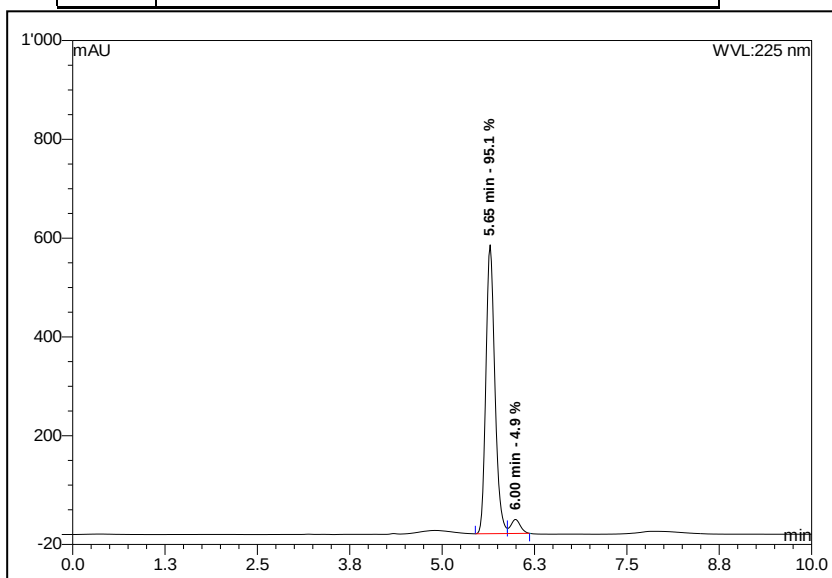
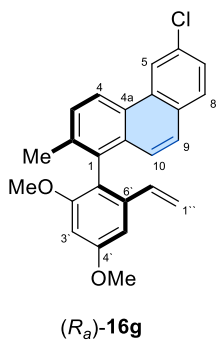
| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 5.10            | 61.268        | 8.126           | 100.00        |
| <b>Total:</b> |                 | 61.268        | 8.126           | 100.00        |

**(*R<sub>a</sub>*)-6-Chloro-1-(2,4-dimethoxy-6-vinylphenyl)-2-methylphenanthrene ((*R<sub>a</sub>*)-16g):**

HPLC conditions: Chiralcel IG (3 μm, 250×4.6 mm), heptane/*i*-PrOH 97.5 : 2.5, 1.0 mL/min, 20°C



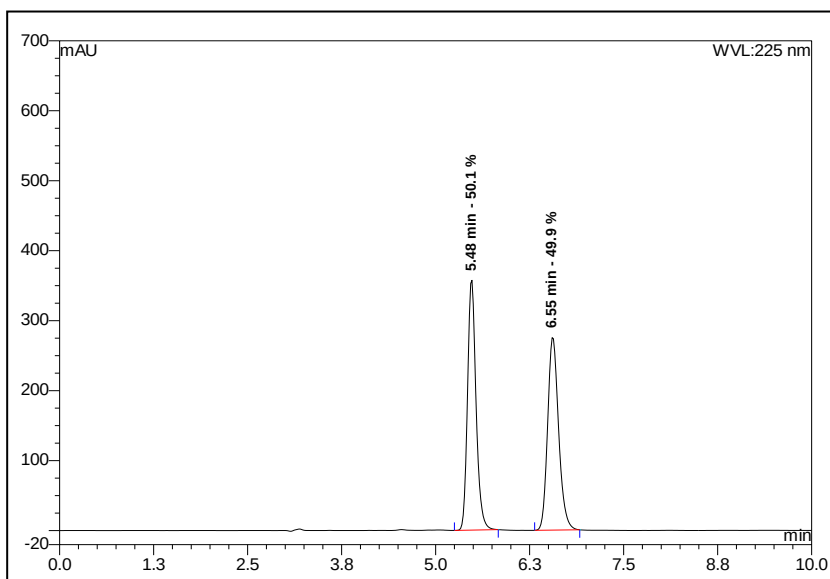
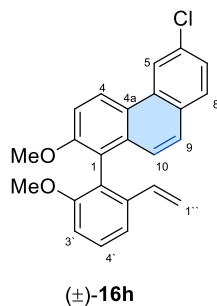
| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 5.65            | 685.091       | 95.527          | 50.05         |
| 2             | 6.00            | 616.242       | 95.349          | 49.95         |
| <b>Total:</b> |                 | 1301.333      | 190.876         | 100.00        |



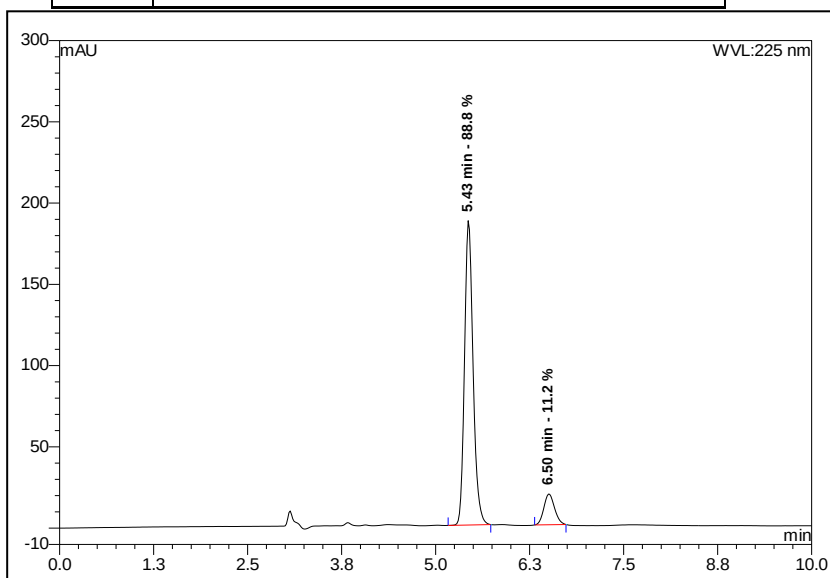
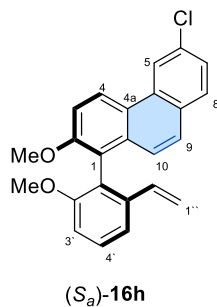
| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 5.65            | 584.750       | 82.191          | 95.06         |
| 2             | 6.00            | 28.279        | 4.275           | 4.94          |
| <b>Total:</b> |                 | 613.029       | 86.465          | 100.00        |

**(*S<sub>a</sub>*)-6-Chloro-2-methoxy-1-(2-methoxy-6-vinylphenyl)phenanthrene ((*S<sub>a</sub>*)-16h):**

HPLC conditions: Chiralcel IG (3  $\mu$ m, 250 $\times$ 4.6 mm), heptane/*i*-PrOH 90 : 10, 1.0 mL/min, 20 $^{\circ}$ C



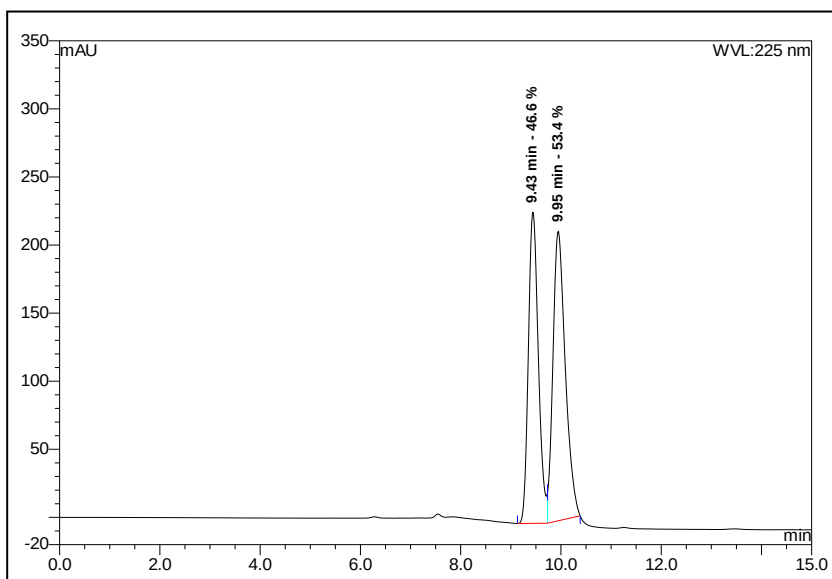
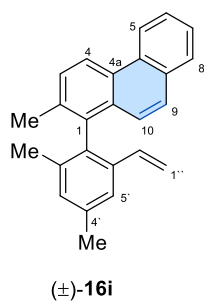
| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 5.48            | 357.042       | 46.935          | 50.15         |
| 2             | 6.55            | 275.174       | 46.657          | 49.85         |
| <b>Total:</b> |                 | 632.216       | 93.593          | 100.00        |



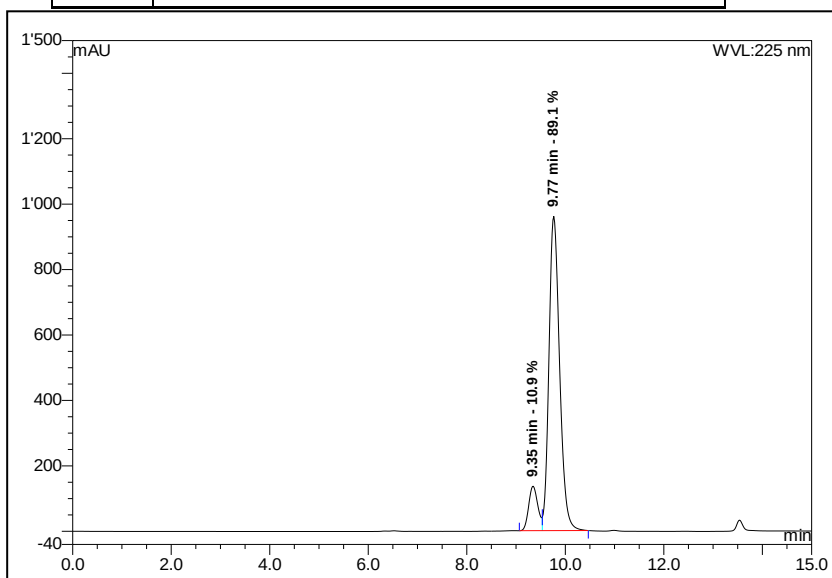
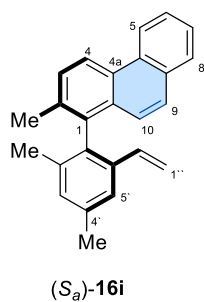
| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 5.43            | 187.261       | 24.695          | 88.83         |
| 2             | 6.50            | 18.878        | 3.106           | 11.17         |
| <b>Total:</b> |                 | 206.139       | 27.801          | 100.00        |

**(S<sub>a</sub>)-1-(2,4-Dimethyl-6-vinylphenyl)-2-methylphenanthrene ((S<sub>a</sub>)-16i):**

HPLC conditions: Chiralcel IG (3 μm, 250×4.6 mm), heptane/*i*-PrOH 99.5 : 0.5, 1.0 mL/min, 40°C



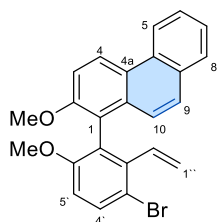
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 9.43            | 228.526       | 52.939          | 46.57         |
| 2      | 9.95            | 212.699       | 60.735          | 53.43         |
| Total: |                 | 441.225       | 113.673         | 100.00        |



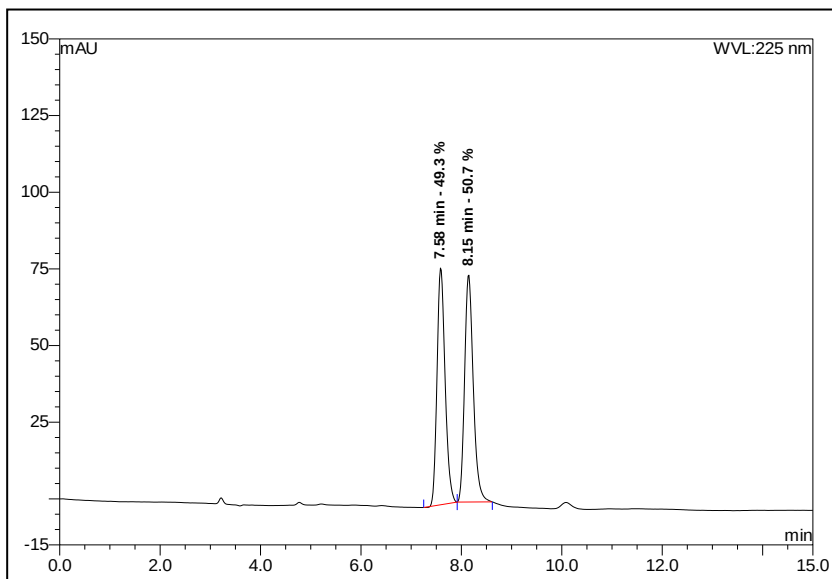
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 9.35            | 135.957       | 29.409          | 10.90         |
| 2      | 9.77            | 960.388       | 240.383         | 89.10         |
| Total: |                 | 1096.345      | 269.792         | 100.00        |

**(*S<sub>a</sub>*)-1-(3-Bromo-6-methoxy-2-vinylphenyl)-2-methoxyphenanthrene ((*S<sub>a</sub>*)-16j):**

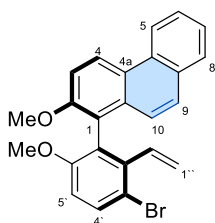
HPLC conditions: Chiralcel IG (3  $\mu$ m, 250 $\times$ 4.6 mm), heptane/*i*-PrOH 97.5 : 2.5, 1.0 mL/min, 20°C



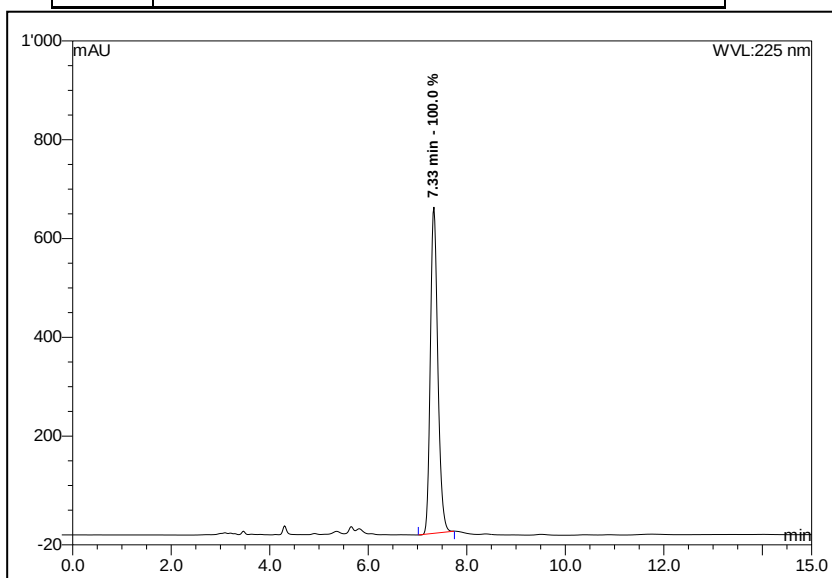
**( $\pm$ )-16j**



| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 7.58            | 77.230        | 14.428          | 49.27         |
| 2             | 8.15            | 73.981        | 14.856          | 50.73         |
| <b>Total:</b> |                 | 151.211       | 29.283          | 100.00        |



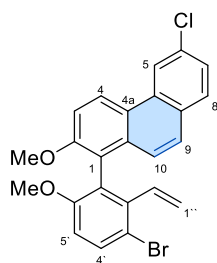
**(*S<sub>a</sub>*)-16j**



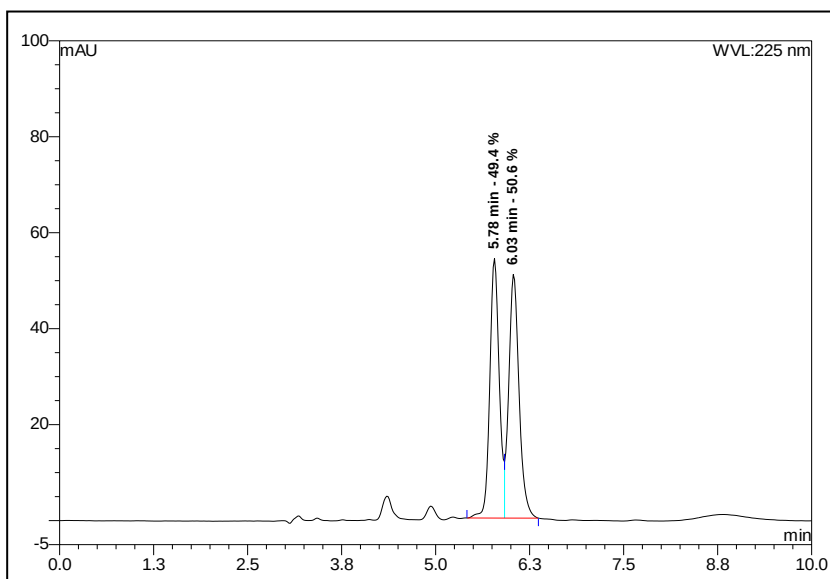
| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 7.33            | 660.290       | 115.707         | 100.00        |
| <b>Total:</b> |                 | 660.290       | 115.707         | 100.00        |

**(S<sub>a</sub>)-1-(3-Bromo-6-methoxy-2-vinylphenyl)-6-chloro-2-methoxyphenanthrene ((S<sub>a</sub>)-16k):**

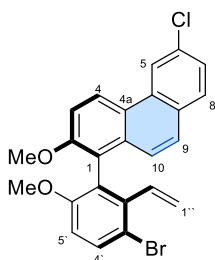
HPLC conditions: Chiralcel IG (3 μm, 250×4.6 mm), heptane/*i*-PrOH 90 : 10, 1.0 mL/min, 20°C



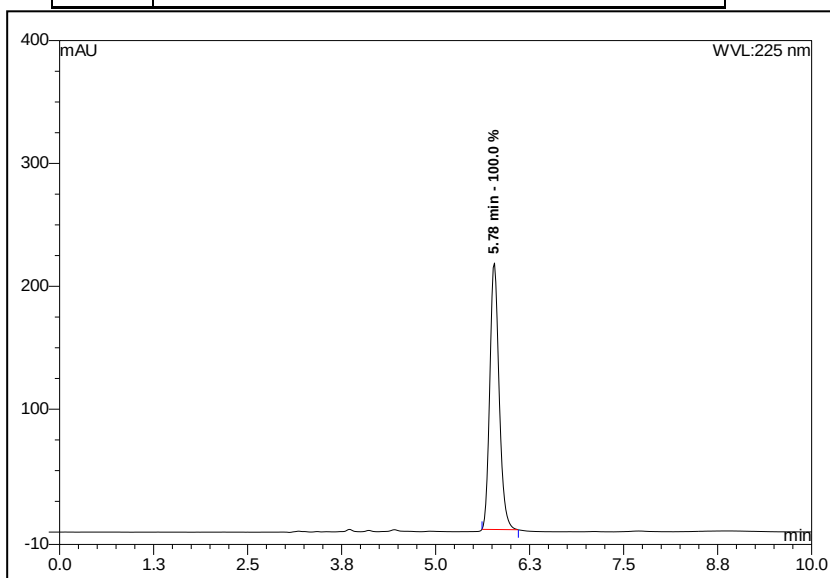
**(±)-16k**



| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 5.78            | 54.104        | 7.903           | 49.45         |
| 2             | 6.03            | 50.771        | 8.080           | 50.55         |
| <b>Total:</b> |                 | 104.875       | 15.983          | 100.00        |



**(S<sub>a</sub>)-16k**

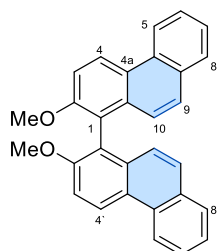


| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 5.78            | 216.893       | 31.186          | 100.00        |
| <b>Total:</b> |                 | 216.893       | 31.186          | 100.00        |

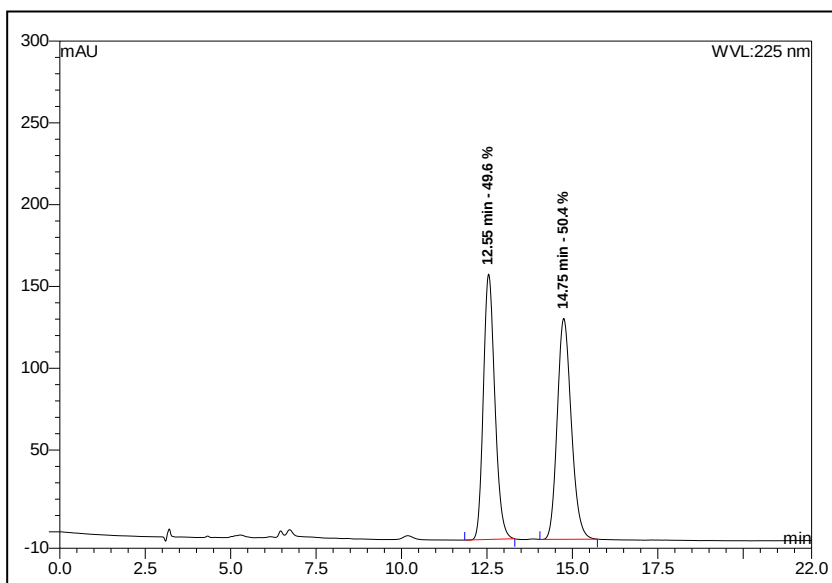


**(*S<sub>a</sub>*)-2,2'-Dimethoxy-1,1'-biphenanthrene ((*S<sub>a</sub>*)-18a):**

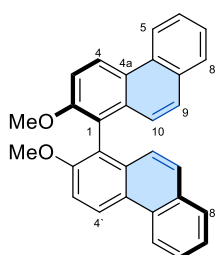
HPLC conditions: Chiralcel IG (3  $\mu$ m, 250 $\times$ 4.6 mm), heptane/*i*-PrOH 90.0 : 10.0, 1.0 mL/min, 20°C



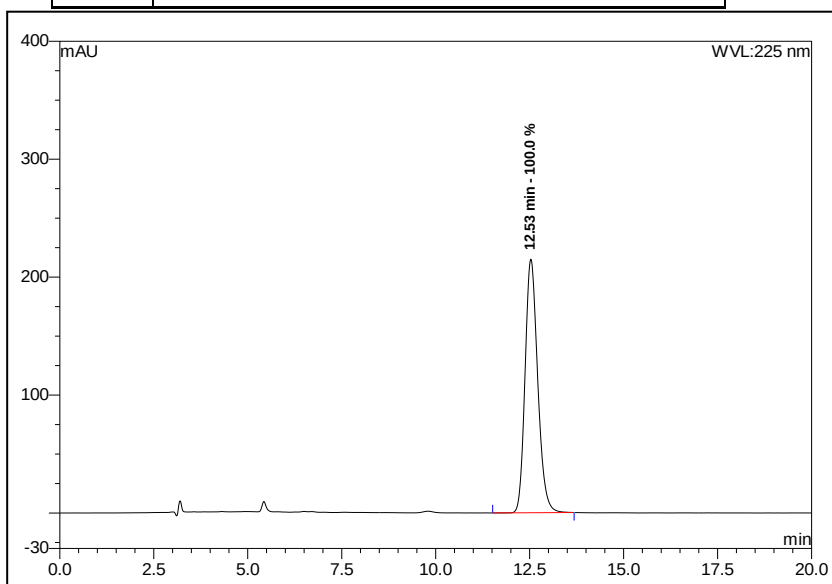
( $\pm$ )-18a



| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 12.55           | 162.269       | 63.215          | 49.57         |
| 2      | 14.75           | 135.020       | 64.323          | 50.43         |
| Total: |                 | 297.288       | 127.537         | 100.00        |



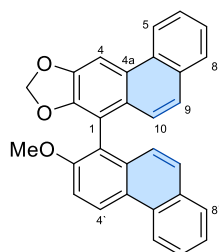
(*S<sub>a</sub>*)-18a



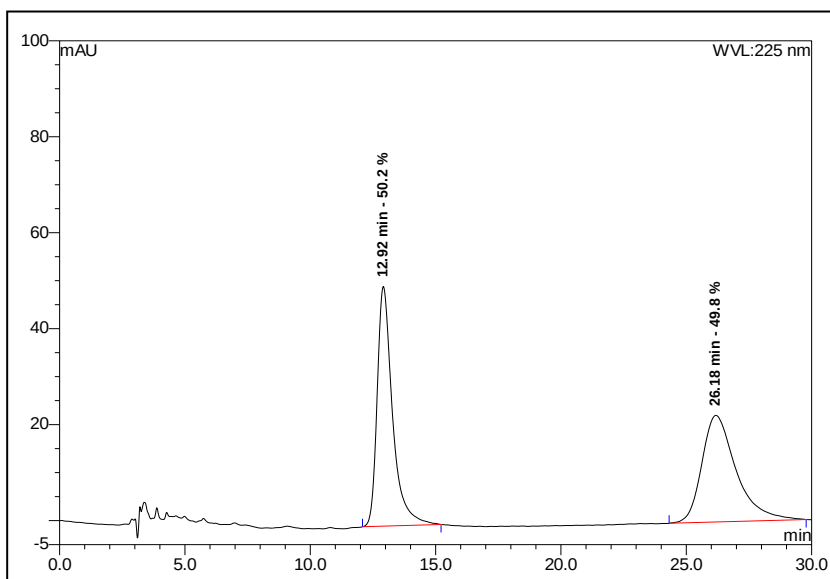
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 12.53           | 215.002       | 83.727          | 100.00        |
| Total: |                 | 215.002       | 83.727          | 100.00        |

**(*S<sub>a</sub>*)-7-(2-Methoxyphenanthren-1-yl)phenanthro[2,3-d][1,3]dioxole ((*S<sub>a</sub>*)-18b):**

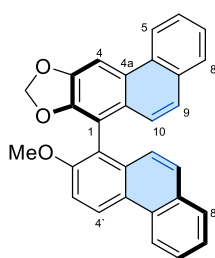
HPLC conditions: Chiralcel IC(3 µm, 250×4.6 mm), heptane/*i*-PrOH 80.0 : 20.0, 1.0 mL/min, 20°C



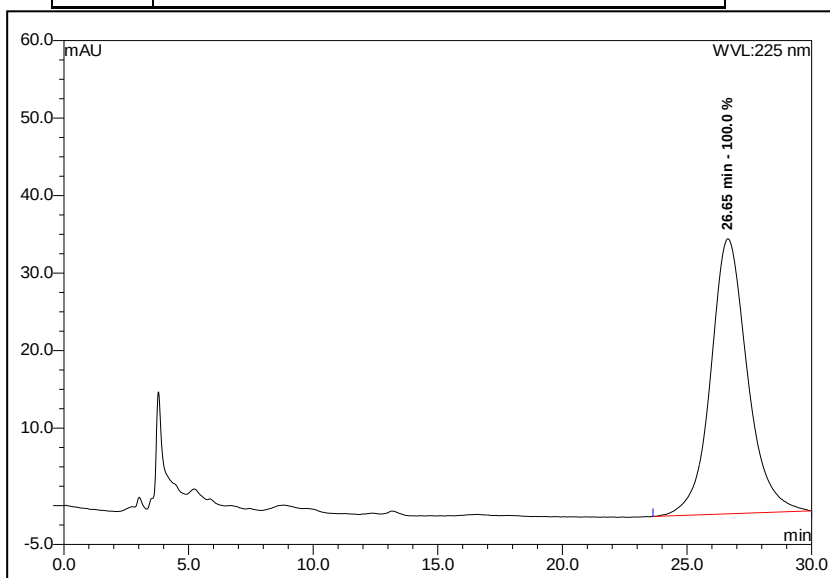
**(±)-18b**



| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 12.92           | 49.950        | 35.429          | 50.16         |
| 2             | 26.18           | 22.209        | 35.199          | 49.84         |
| <b>Total:</b> |                 | 72.159        | 70.629          | 100.00        |



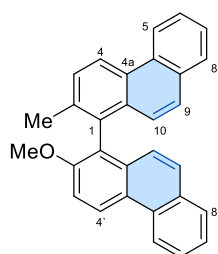
**(*S<sub>a</sub>*)-18b**



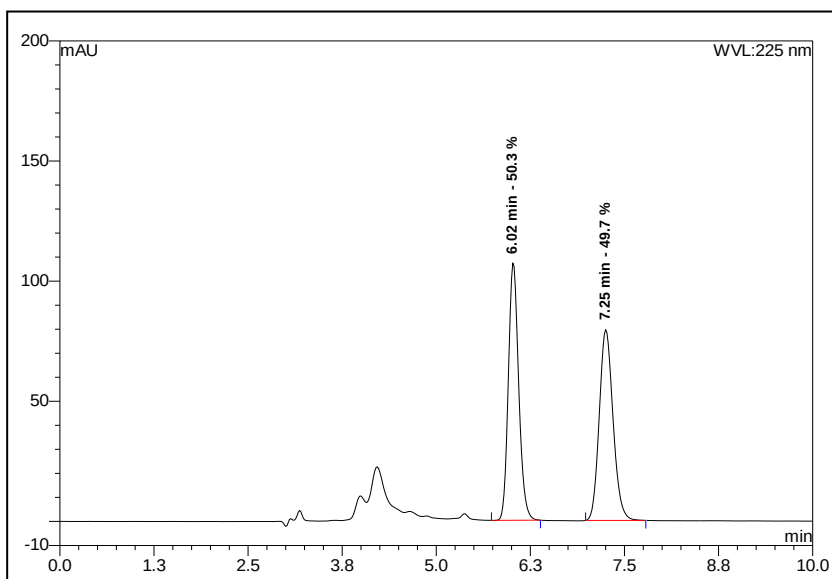
| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 26.65           | 35.473        | 60.640          | 100.00        |
| <b>Total:</b> |                 | 35.473        | 60.640          | 100.00        |

**(*R<sub>a</sub>*)-2-Methoxy-2'-methyl-1,1'-biphenanthrene ((*R<sub>a</sub>*)-18c):**

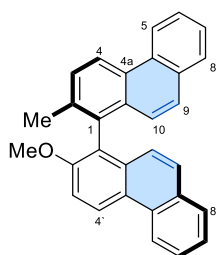
HPLC conditions: Chiralcel IG (3  $\mu$ m, 250 $\times$ 4.6 mm), heptane/*i*-PrOH 85.0 : 15.0, 1.0 mL/min, 20°C



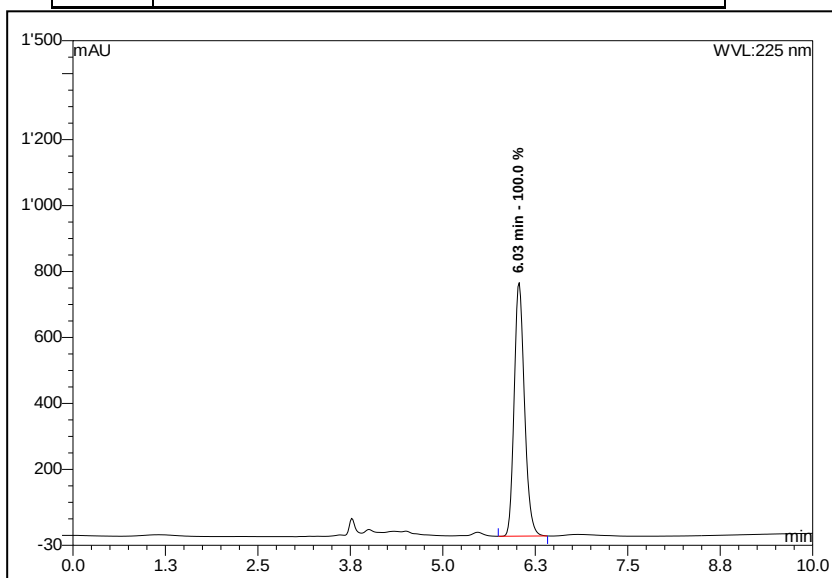
( $\pm$ )-18c



| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 6.02            | 107.163       | 17.032          | 50.26         |
| 2      | 7.25            | 79.422        | 16.855          | 49.74         |
| Total: |                 | 186.585       | 33.887          | 100.00        |



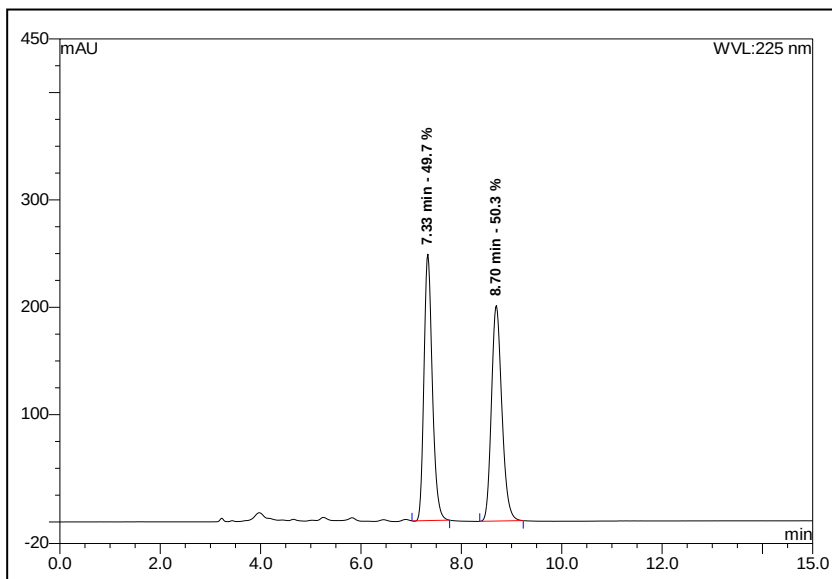
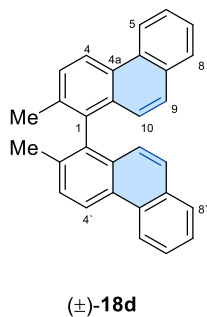
(*R<sub>a</sub>*)-18c



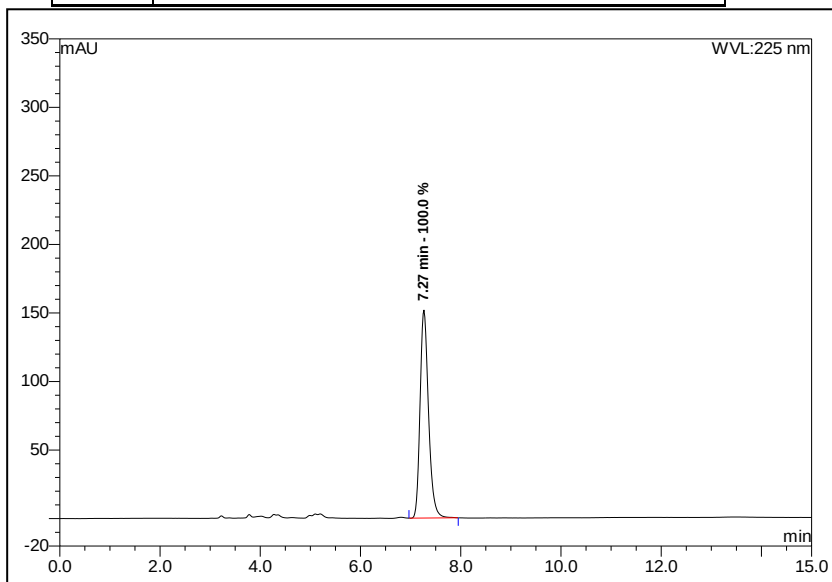
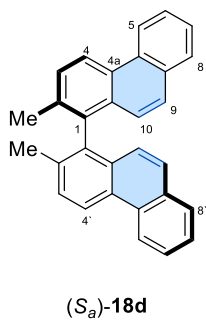
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 6.03            | 768.645       | 124.112         | 100.00        |
| Total: |                 | 768.645       | 124.112         | 100.00        |

**(S<sub>a</sub>)-2,2'-Dimethyl-1,1'-biphenanthrene ((S<sub>a</sub>)-18d):**

HPLC conditions: Chiralcel IG (3 μm, 250×4.6 mm), heptane/*i*-PrOH 99.0 : 1.0, 1.0 mL/min, 20°C



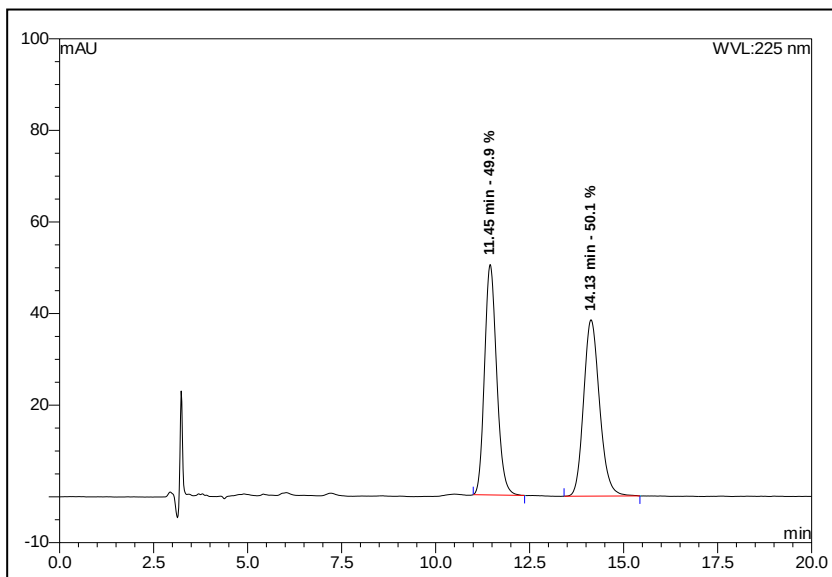
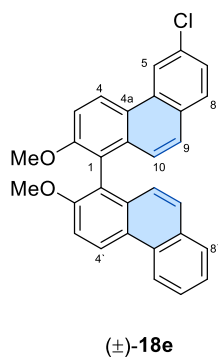
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 7.33            | 248.202       | 47.773          | 49.70         |
| 2      | 8.70            | 200.761       | 48.355          | 50.30         |
| Total: |                 | 448.963       | 96.128          | 100.00        |



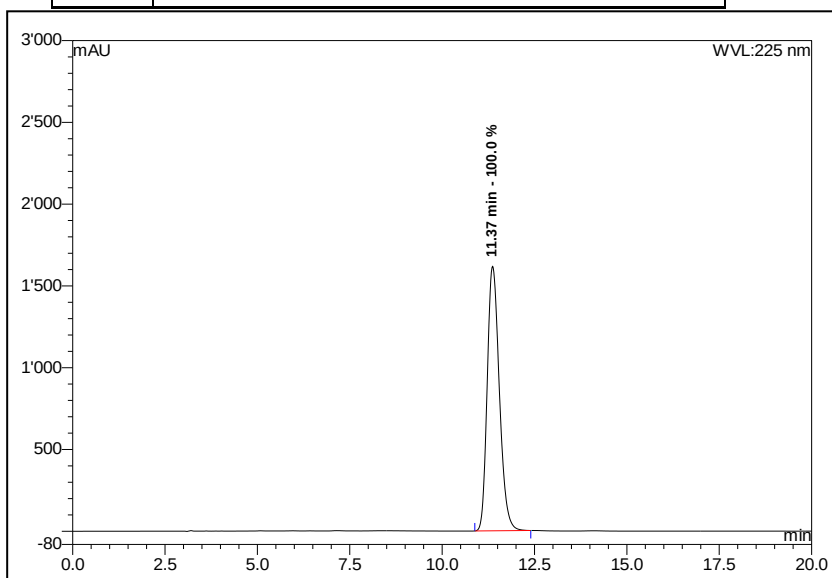
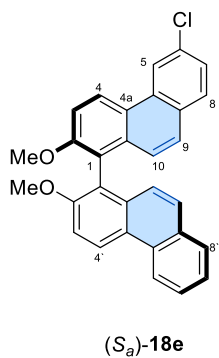
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 7.27            | 151.703       | 29.581          | 100.00        |
| Total: |                 | 151.703       | 29.581          | 100.00        |

**(S<sub>a</sub>)-6-Chloro-2,2'-dimethoxy-1,1'-biphenanthrene ((S<sub>a</sub>)-18e):**

HPLC conditions: Chiralcel IG (3 μm, 250×4.6 mm), heptane/*i*-PrOH 90.0 : 10.0, 1.0 mL/min, 20°C



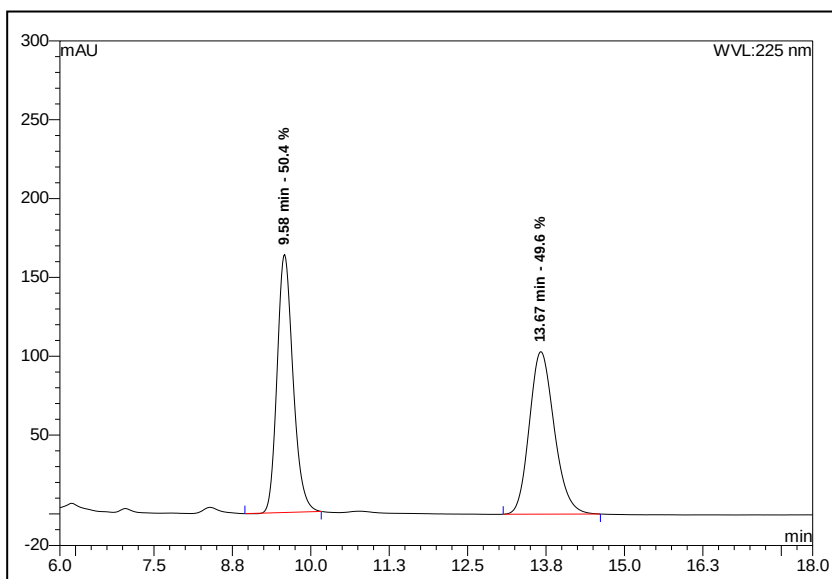
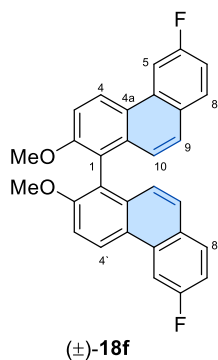
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 11.45           | 50.311        | 18.846          | 49.87         |
| 2      | 14.13           | 38.520        | 18.943          | 50.13         |
| Total: |                 | 88.831        | 37.788          | 100.00        |



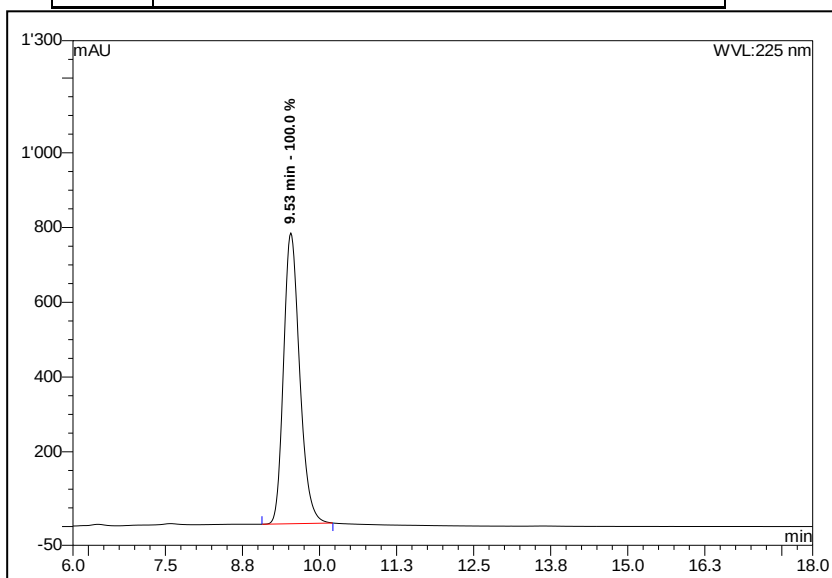
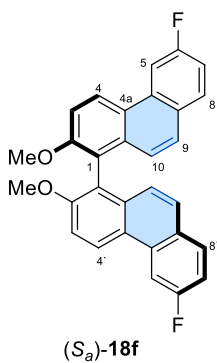
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 11.37           | 1618.303      | 614.977         | 100.00        |
| Total: |                 | 1618.303      | 614.977         | 100.00        |

**(*S<sub>a</sub>*)-6,6'-Difluoro-2,2'-dimethoxy-1,1'-biphenanthrene ((*S<sub>a</sub>*)-18f):**

HPLC conditions: Chiralcel IG (3  $\mu$ m, 250 $\times$ 4.6 mm), heptane/*i*-PrOH 90.0 : 10.0, 1.0 mL/min, 20°C



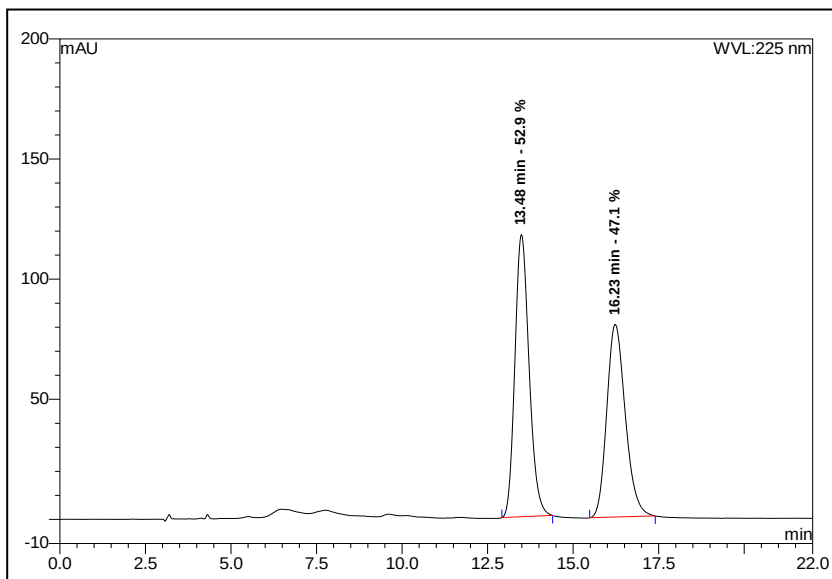
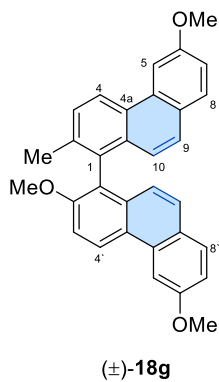
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 9.58            | 163.713       | 48.161          | 50.40         |
| 2      | 13.67           | 103.096       | 47.398          | 49.60         |
| Total: |                 | 266.808       | 95.559          | 100.00        |



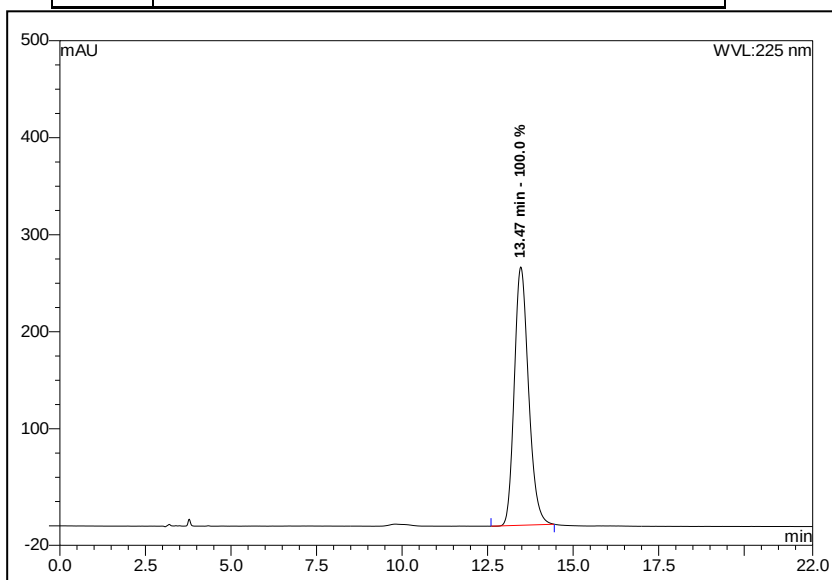
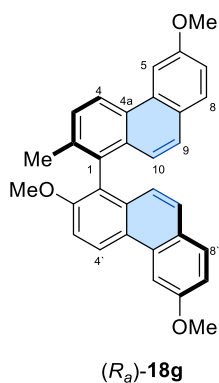
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 9.53            | 778.435       | 235.581         | 100.00        |
| Total: |                 | 778.435       | 235.581         | 100.00        |

**(*R<sub>a</sub>*)-2,6,6'-Trimethoxy-2'-methyl-1,1'-biphenanthrene ((*S<sub>a</sub>*)-18g):**

HPLC conditions: Chiralcel IG (3 µm, 250×4.6 mm), heptane/*i*-PrOH 90.0 : 10.0, 1.0 mL/min, 20°C



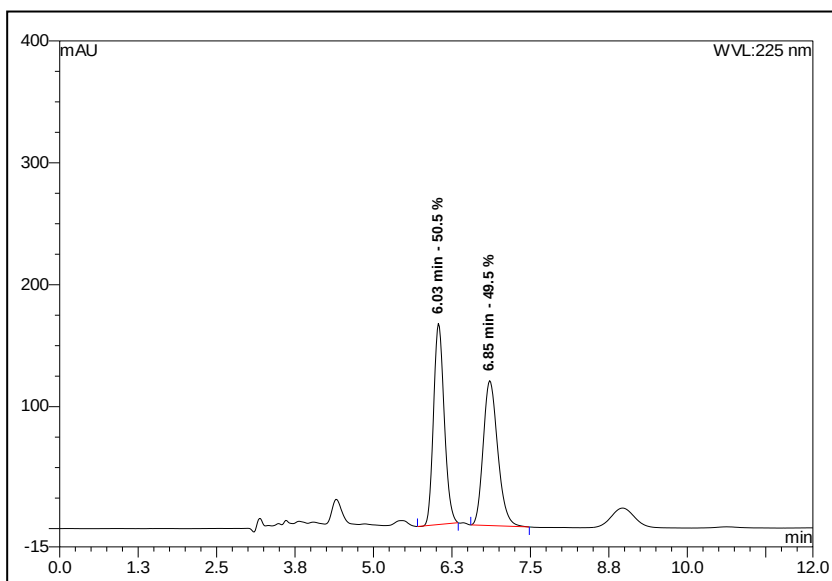
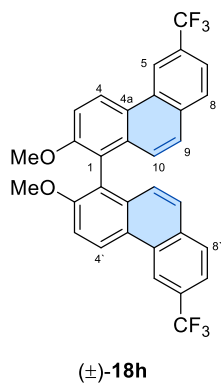
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 13.48           | 117.392       | 56.535          | 52.88         |
| 2      | 16.23           | 80.175        | 50.377          | 47.12         |
| Total: |                 | 197.567       | 106.911         | 100.00        |



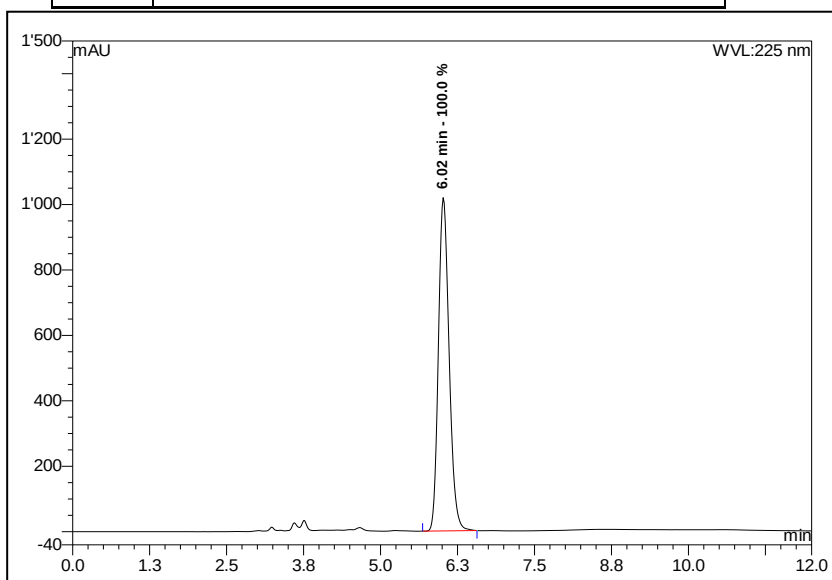
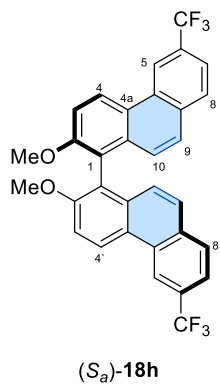
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 13.47           | 266.271       | 128.323         | 100.00        |
| Total: |                 | 266.271       | 128.323         | 100.00        |

**(S<sub>a</sub>)-2,2'-Dimethoxy-6,6'-bis(trifluoromethyl)-1,1'-biphenanthrene ((S<sub>a</sub>)-18h):**

HPLC conditions: Chiralcel IG (3 μm, 250×4.6 mm), heptane/*i*-PrOH 90.0 : 10.0, 1.0 mL/min, 20°C



| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 6.03            | 164.964       | 32.500          | 50.48         |
| 2             | 6.85            | 118.816       | 31.879          | 49.52         |
| <b>Total:</b> |                 | 283.780       | 64.379          | 100.00        |

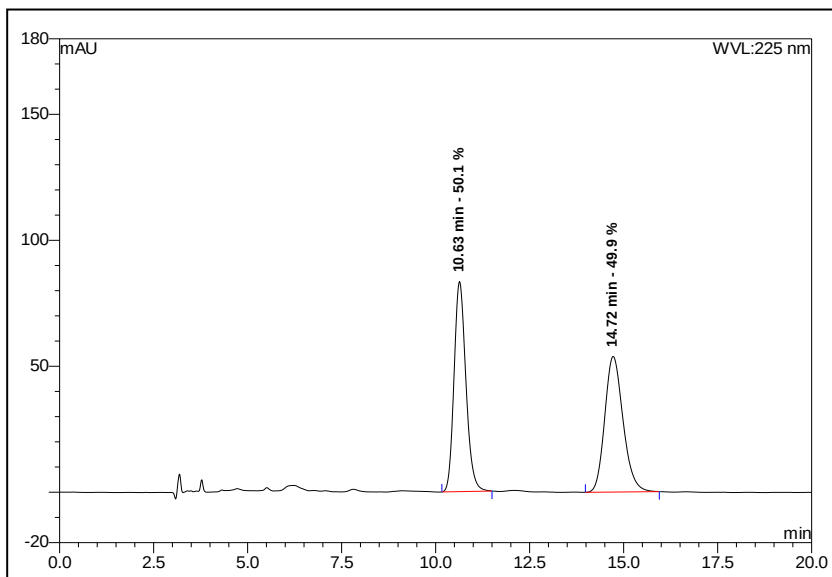
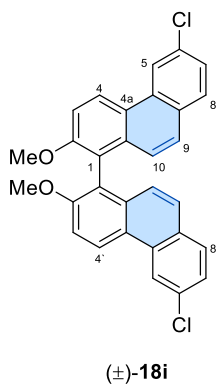


| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 6.02            | 1018.776      | 205.499         | 100.00        |
| <b>Total:</b> |                 | 1018.776      | 205.499         | 100.00        |

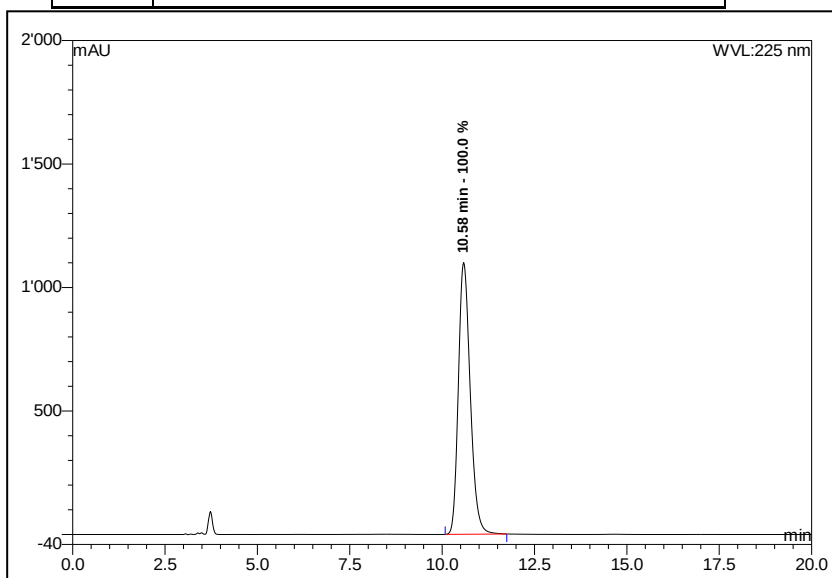
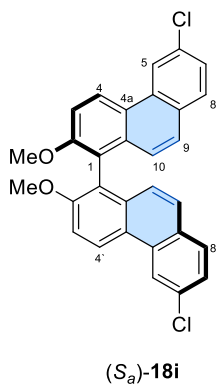


**(S<sub>a</sub>)-6,6'-Dichloro-2,2'-dimethoxy-1,1'-biphenanthrene ((S<sub>a</sub>)-18i):**

HPLC conditions: Chiralcel IG (3 μm, 250×4.6 mm), heptane/*i*-PrOH 90.0 : 10.0, 1.0 mL/min, 20°C



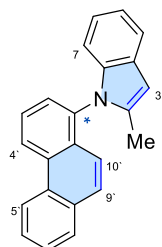
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 10.63           | 83.409        | 30.460          | 50.06         |
| 2      | 14.72           | 53.848        | 30.392          | 49.94         |
| Total: |                 | 137.256       | 60.852          | 100.00        |



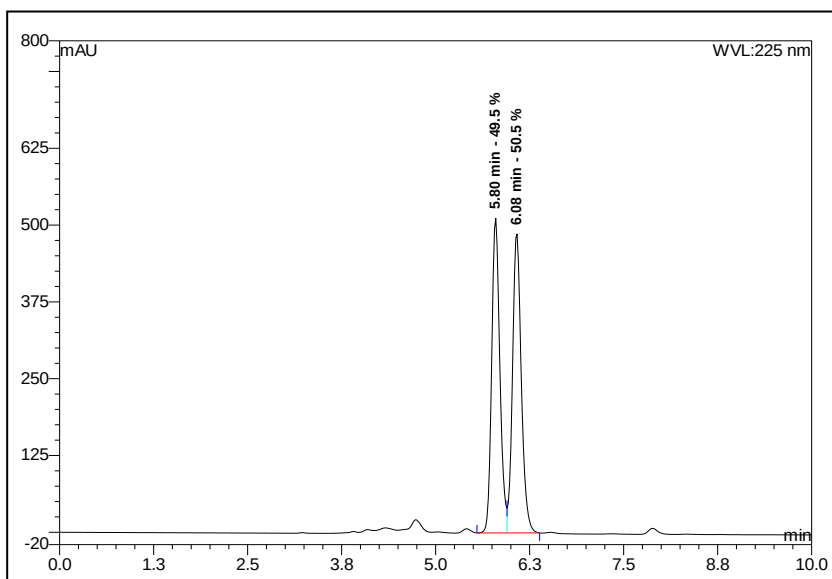
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 10.58           | 1099.953      | 409.374         | 100.00        |
| Total: |                 | 1099.953      | 409.374         | 100.00        |

**(*R<sub>a</sub>*)-2-Methyl-1-(phenanthren-1-yl)-1*H*-indole ((*R<sub>a</sub>*)-20a):**

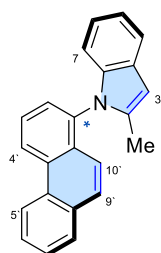
HPLC conditions: Chiralcel IG (3  $\mu$ m, 250 $\times$ 4.6 mm), heptane/*i*-PrOH 97.5 : 2.5, 1.0 mL/min, 20°C



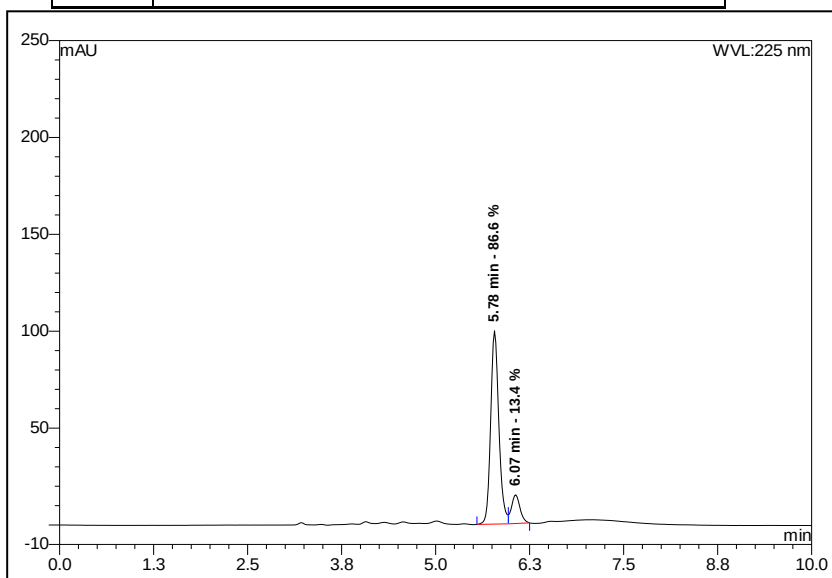
**( $\pm$ )-20a**



| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 5.80            | 512.000       | 64.653          | 49.47         |
| 2      | 6.08            | 486.341       | 66.038          | 50.53         |
| Total: |                 | 998.341       | 130.692         | 100.00        |



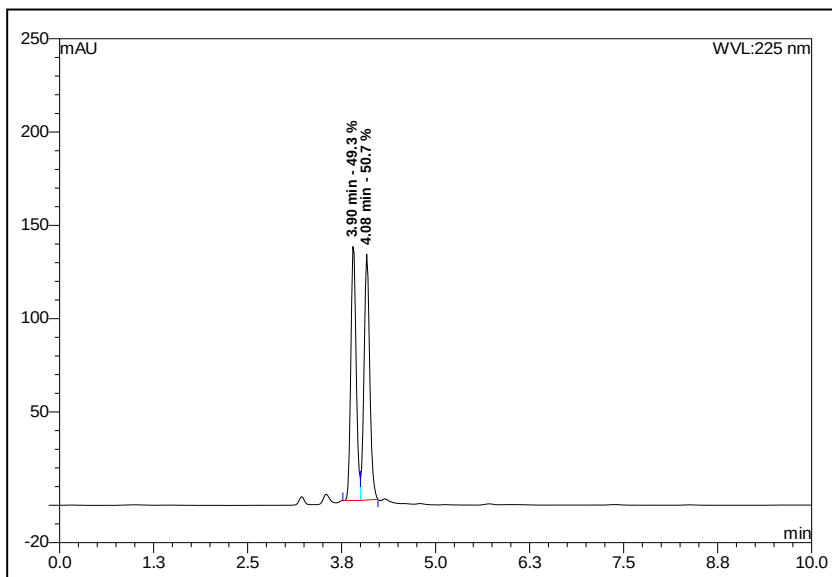
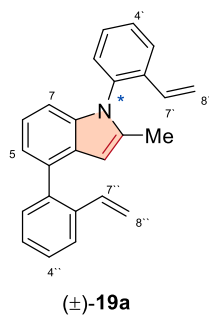
**(*R<sub>a</sub>*)-20a**



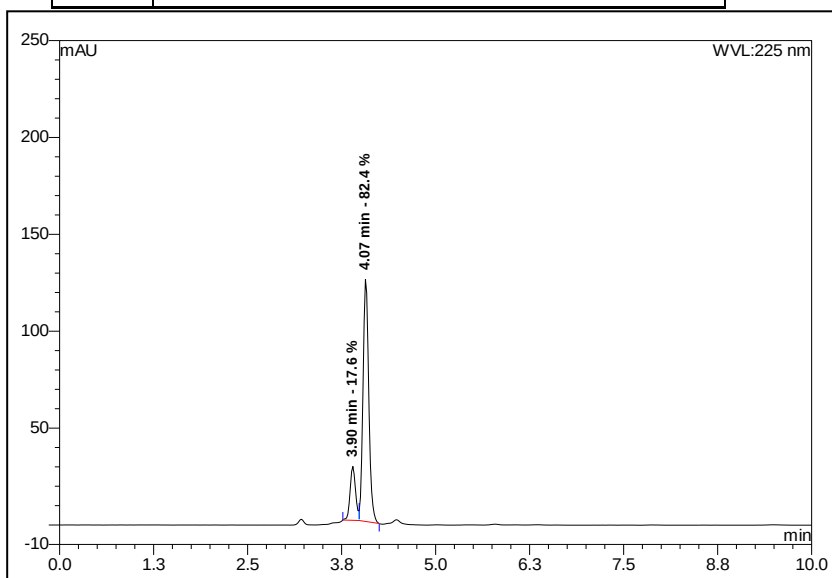
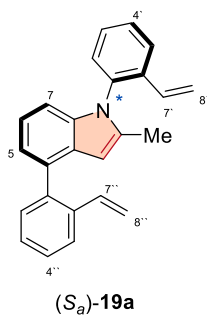
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 5.78            | 99.721        | 12.627          | 86.61         |
| 2      | 6.07            | 14.810        | 1.952           | 13.39         |
| Total: |                 | 114.532       | 14.579          | 100.00        |

**(S<sub>a</sub>)-2-Methyl-1,4-bis(2-vinylphenyl)-1*H*-indole ((S<sub>a</sub>)-19a):**

HPLC conditions: Chiralcel IG (3 μm, 250×4.6 mm), heptane/*i*-PrOH 97.5 : 2.5, 1.0 mL/min, 20°C



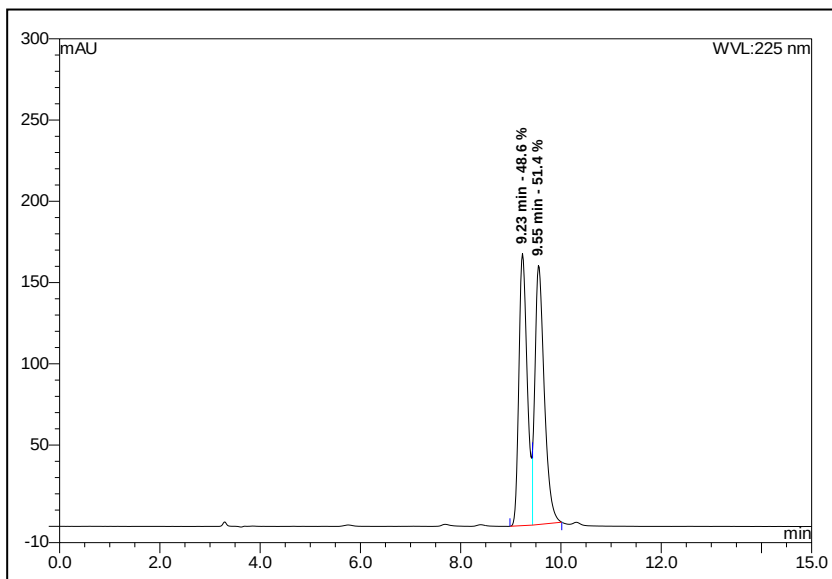
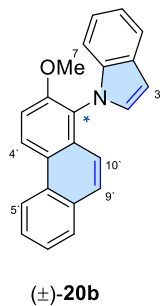
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 3.90            | 136.041       | 11.228          | 49.29         |
| 2      | 4.08            | 131.821       | 11.551          | 50.71         |
| Total: |                 | 267.862       | 22.778          | 100.00        |



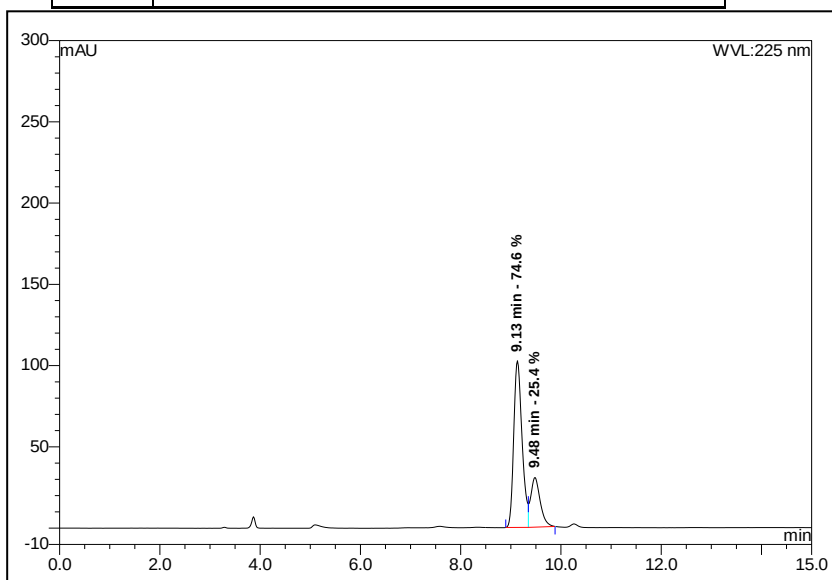
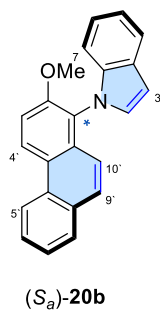
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 3.90            | 27.817        | 2.361           | 17.57         |
| 2      | 4.07            | 124.892       | 11.078          | 82.43         |
| Total: |                 | 152.709       | 13.439          | 100.00        |

**(S<sub>a</sub>)-1-(2-Methoxyphenanthren-1-yl)-1*H*-indole ((S<sub>a</sub>)-20b):**

HPLC conditions: Chiralcel IB (3 μm, 250×4.6 mm), heptane/*i*-PrOH 97.5 : 2.5, 1.0 mL/min, 20°C



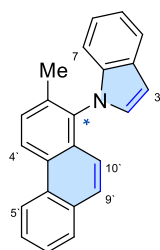
| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 9.23            | 167.459       | 32.482          | 48.59         |
| 2             | 9.55            | 159.365       | 34.369          | 51.41         |
| <b>Total:</b> |                 | 326.824       | 66.851          | 100.00        |



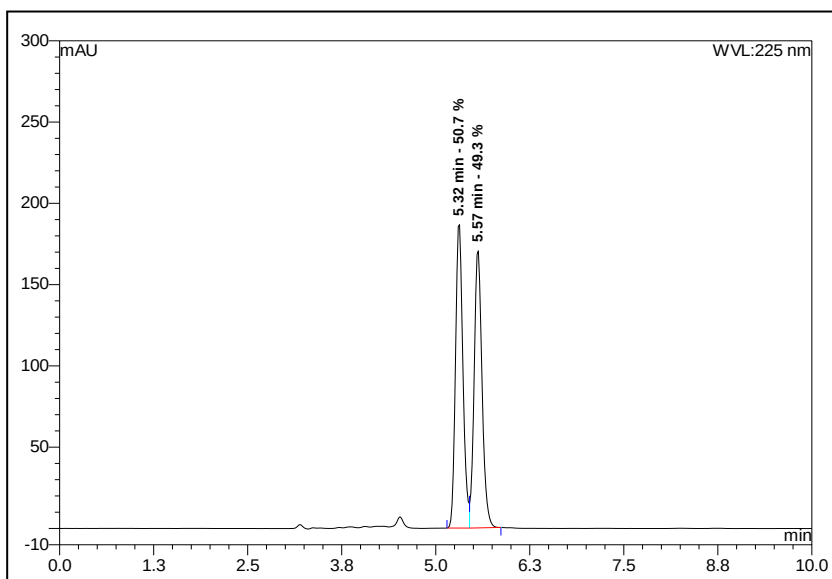
| No.           | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|---------------|-----------------|---------------|-----------------|---------------|
| 1             | 9.13            | 102.544       | 19.732          | 74.61         |
| 2             | 9.48            | 30.523        | 6.716           | 25.39         |
| <b>Total:</b> |                 | 133.067       | 26.448          | 100.00        |

**(*R<sub>a</sub>*)-1-(2-Methylphenanthren-1-yl)-1*H*-indole ((*R<sub>a</sub>*)-20c):**

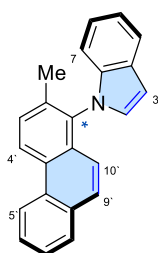
HPLC conditions: Chiralcel IG (3 µm, 250×4.6 mm), heptane/*i*-PrOH 96.0 : 4.0, 1.0 mL/min, 20°C



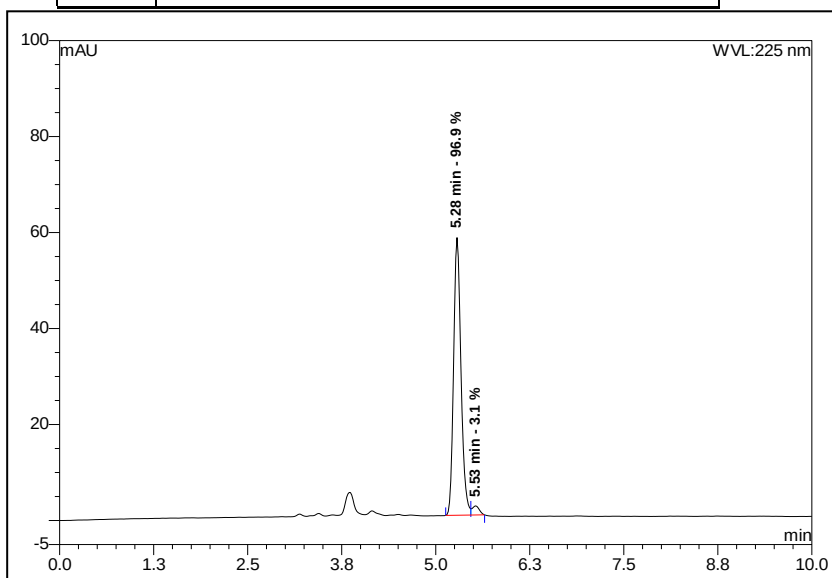
**(±)-20c**



| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 5.32            | 186.610       | 21.401          | 50.73         |
| 2      | 5.57            | 170.463       | 20.786          | 49.27         |
| Total: |                 | 357.073       | 42.186          | 100.00        |



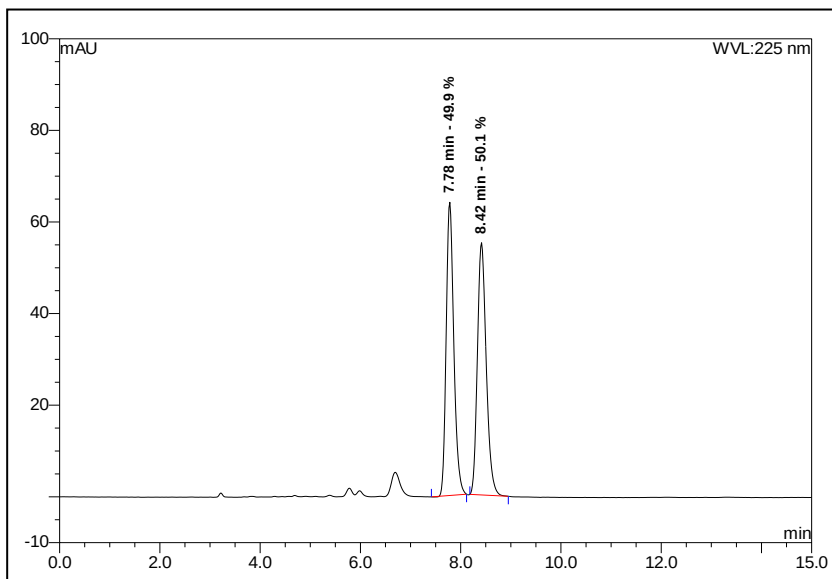
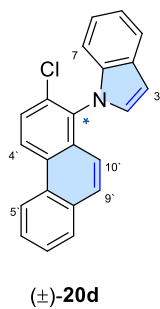
**(*R<sub>a</sub>*)-20c**



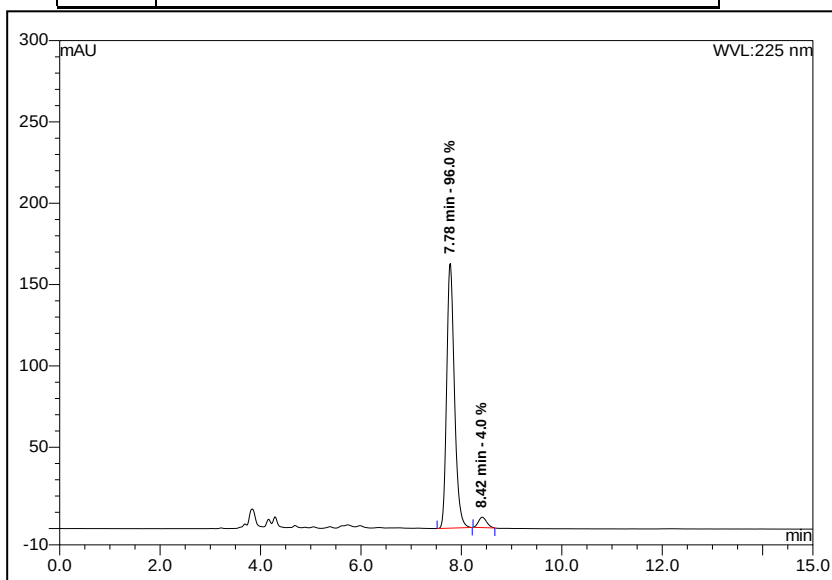
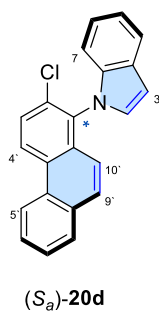
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 5.28            | 57.851        | 6.599           | 96.92         |
| 2      | 5.53            | 1.911         | 0.210           | 3.08          |
| Total: |                 | 59.762        | 6.809           | 100.00        |

**(S<sub>a</sub>)-1-(2-Chlorophenanthren-1-yl)-1H-indole ((S<sub>a</sub>)-20d):**

HPLC conditions: Chiralcel IG (3 μm, 250×4.6 mm), heptane/*i*-PrOH 99.0 : 1.0, 1.0 mL/min, 20°C



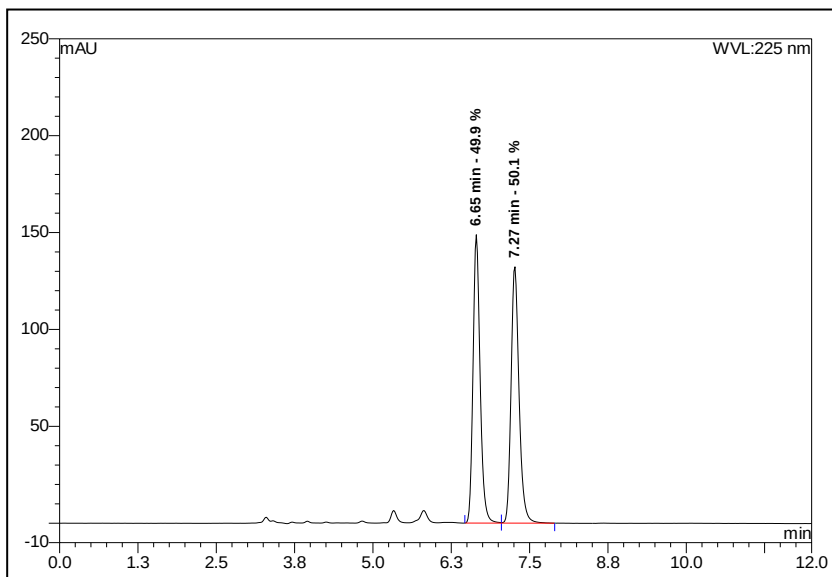
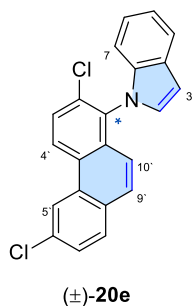
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 7.78            | 64.011        | 11.224          | 49.94         |
| 2      | 8.42            | 55.070        | 11.249          | 50.06         |
| Total: |                 | 119.081       | 22.473          | 100.00        |



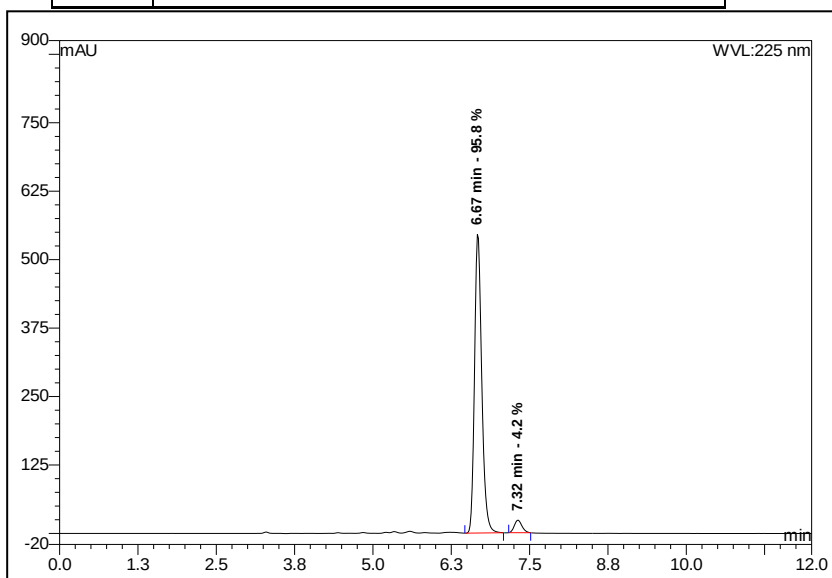
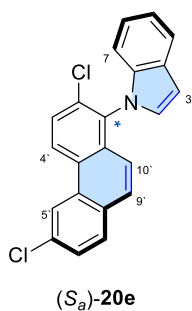
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 7.78            | 162.725       | 29.061          | 96.00         |
| 2      | 8.42            | 6.398         | 1.210           | 4.00          |
| Total: |                 | 169.123       | 30.271          | 100.00        |

**(S<sub>a</sub>)-1-(2,6-Dichlorophenanthren-1-yl)-1H-indole ((S<sub>a</sub>)-20e):**

HPLC conditions: Chiralcel IB (3 μm, 250×4.6 mm), heptane/*i*-PrOH 97.5 : 2.5, 1.0 mL/min, 20°C



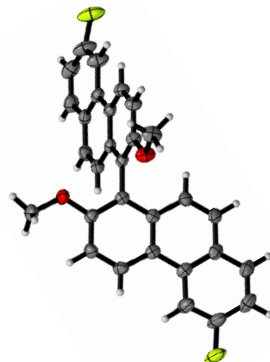
| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 6.65            | 148.800       | 19.449          | 49.89         |
| 2      | 7.27            | 132.282       | 19.535          | 50.11         |
| Total: |                 | 281.081       | 38.983          | 100.00        |



| No.    | Ret.Time<br>min | Height<br>mAU | Area<br>mAU*min | Rel.Area<br>% |
|--------|-----------------|---------------|-----------------|---------------|
| 1      | 6.67            | 545.279       | 72.910          | 95.76         |
| 2      | 7.32            | 22.928        | 3.228           | 4.24          |
| Total: |                 | 568.207       | 76.138          | 100.00        |

## X-Ray Data (Dr. Alessandro Prescimone)

### (*S<sub>a</sub>*)-6,6'-Difluoro-2,2'-dimethoxy-1,1'-biphenanthrene ((*S<sub>a</sub>*)-18f):



CCDC-2358712

Experimental: Single colourless block-shaped crystals of (*S<sub>a</sub>*)-**18f** crystallised from a mixture of dichloromethane and methanol by solvent layering. A suitable crystal with dimensions  $0.2 \times 0.167 \times 0.15 \text{ mm}^3$  was selected and mounted on a mylar loop in perfluoroether oil on a Basel-Cu-Stoe diffractometer. The crystal was kept at a steady  $T = 150 \text{ K}$  during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** (Sheldrick, 2015) using full matrix least squares minimisation on  $F^2$ .

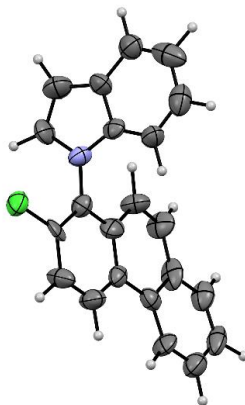
**Crystal Data.**  $\text{C}_{30}\text{H}_{20}\text{F}_2\text{O}_2$  ( $M = 450.46 \text{ g/mol}$ ): tetragonal, space group  $P4_12_12$  (no. 92),  $a = 7.99310(10) \text{ \AA}$ ,  $c = 34.2446(7) \text{ \AA}$ ,  $V = 2187.88(7) \text{ \AA}^3$ ,  $Z = 4$ ,  $T = 150 \text{ K}$ ,  $\mu(\text{Cu K}\alpha) = 0.789 \text{ mm}^{-1}$ ,  $D_{\text{calc}} = 1.368 \text{ g/cm}^3$ , 39624 reflections measured ( $10.332^\circ \leq 2\theta \leq 139.652^\circ$ ), 2058 unique ( $R_{\text{int}} = 0.0461$ ,  $R_{\text{sigma}} = 0.0188$ ) which were used in all calculations. The final  $R_1$  was 0.0349 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0856 (all data).

|                                    |                                                  |                                               |                                                                  |
|------------------------------------|--------------------------------------------------|-----------------------------------------------|------------------------------------------------------------------|
| Empirical formula                  | $\text{C}_{30}\text{H}_{20}\text{F}_2\text{O}_2$ | $2\theta$ range for data collection/ $^\circ$ | 10.332 to 139.652                                                |
| Formula weight                     | 450.46                                           | Index ranges                                  | $-9 \leq h \leq 9$ , $-8 \leq k \leq 9$ , $-40 \leq l \leq 27$   |
| Temperature/K                      | 150                                              | Reflections collected                         | 39624                                                            |
| Crystal system                     | tetragonal                                       | Independent reflections                       | 2058 [ $R_{\text{int}} = 0.0461$ , $R_{\text{sigma}} = 0.0188$ ] |
| Space group                        | $P4_12_12$                                       | Data/restraints/parameters                    | 2058/19/165                                                      |
| $a/\text{\AA}$                     | 7.99310(10)                                      | Goodness-of-fit on $F^2$                      | 1.046                                                            |
| $b/\text{\AA}$                     | 7.99310(10)                                      | Final R indexes [ $I \geq 2\sigma(I)$ ]       | $R_1 = 0.0349$ , $wR_2 = 0.0780$                                 |
| $c/\text{\AA}$                     | 34.2446(7)                                       | Final R indexes [all data]                    | $R_1 = 0.0499$ , $wR_2 = 0.0856$                                 |
| $\alpha/^\circ$                    | 90                                               | Largest diff. peak/hole / $\text{e \AA}^{-3}$ | 0.13/-0.11                                                       |
| $\beta/^\circ$                     | 90                                               | Flack parameter                               | 0.04(7)                                                          |
| $\gamma/^\circ$                    | 90                                               |                                               |                                                                  |
| Volume/ $\text{\AA}^3$             | 2187.88(7)                                       |                                               |                                                                  |
| Z                                  | 4                                                |                                               |                                                                  |
| $\rho_{\text{calc}}/\text{g/cm}^3$ | 1.368                                            |                                               |                                                                  |
| $\mu/\text{mm}^{-1}$               | 0.789                                            |                                               |                                                                  |
| F(000)                             | 936.0                                            |                                               |                                                                  |
| Crystal size/ $\text{mm}^3$        | $0.2 \times 0.167 \times 0.15$                   |                                               |                                                                  |
| Radiation                          | $\text{Cu K}\alpha$ ( $\lambda = 1.54186$ )      |                                               |                                                                  |



## Microcrystal Electron Diffraction (Dr. Alessandro Prescimone, Eldico)

### (*S<sub>a</sub>*)-1-(2-Chlorophenanthren-1-yl)-1*H*-indole ((*S<sub>a</sub>*)-20d):



This structure collected with Electron Diffraction was obtained by kinematical refinement by the merging of 4 datasets collected on 4 different crystals. The absolute configuration has been successfully determined by the means of dynamical refinements<sup>20</sup> according to the following procedure: The structure of both enantiomers obtained by the kinetical refinement of the 4 separate datasets were used for the dynamical refinement keeping the structural parameters fixed, only parameters specific to dynamical refinement were refined. In all four cases the R factors for this enantiomer were consistently 3-4 percent better than those of the other enantiomer.

Experimental: (*S<sub>a</sub>*)-**16d** was crystallised from a mixture of acetone and water by solvent layering. A suitable crystal was selected and **measured** on a **Eldico\_ED** diffractometer. The crystal was kept at 293.15 K during data collection. Using Olex2 (Dolomanov et al., 2009), the structure was solved with the SHELXT (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined with the SHELXL (Sheldrick, 2015) refinement package using Least Squares minimisation.

**Crystal Data** for C<sub>22</sub>H<sub>14</sub>ClN (*M* = 327.79 g/mol): orthorhombic, space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (no. 19), *a* = 5.97(16) Å, *b* = 22.5(6) Å, *c* = 24.2(7) Å, *V* = 3241(153) Å<sup>3</sup>, *Z* = 8, *T* = 293.15 K,  $\mu(\text{electron}) = 0.000 \text{ mm}^{-1}$ , *D*<sub>calc</sub> = 1.344 g/cm<sup>3</sup>, 42897 reflections measured ( $0.136^\circ \leq 2\theta \leq 2.048^\circ$ ), 6616 unique (*R*<sub>int</sub> = 0.2168, *R*<sub>sigma</sub> = 0.2264) which were used in all calculations. The final *R*<sub>1</sub> was 0.1660 (*I* > 2σ(*I*)) and *wR*<sub>2</sub> was 0.3877 (all data).

|                                      |                                               |                                                     |                                                                              |
|--------------------------------------|-----------------------------------------------|-----------------------------------------------------|------------------------------------------------------------------------------|
| Empirical formula                    | C <sub>22</sub> H <sub>14</sub> ClN           | Crystal size/mm <sup>3</sup>                        | 0.02 × 0.002 × 0.001                                                         |
| Formula weight                       | 327.79                                        | Radiation                                           | electron (λ = 0.02851)                                                       |
| Temperature/K                        | 293.15                                        | 2θ range for data collection/°                      | 0.136 to 2.048                                                               |
| Crystal system                       | orthorhombic                                  | Index ranges                                        | -7 ≤ <i>h</i> ≤ 7, -27 ≤ <i>k</i> ≤ 27, -30 ≤ <i>l</i> ≤ 29                  |
| Space group                          | P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> | Reflections collected                               | 42897                                                                        |
| <i>a</i> /Å                          | 5.97(16)                                      | Independent reflections                             | 6616 [ <i>R</i> <sub>int</sub> = 0.2168, <i>R</i> <sub>sigma</sub> = 0.2264] |
| <i>b</i> /Å                          | 22.5(6)                                       | Data/restraints/parameters                          | 6616/0/434                                                                   |
| <i>c</i> /Å                          | 24.2(7)                                       | Goodness-of-fit on <i>F</i> <sup>2</sup>            | 1.044                                                                        |
| α/°                                  | 90                                            | Final <i>R</i> indexes [ <i>I</i> ≥ 2σ( <i>I</i> )] | <i>R</i> <sub>1</sub> = 0.1660, <i>wR</i> <sub>2</sub> = 0.3630              |
| β/°                                  | 90                                            | Final <i>R</i> indexes [all data]                   | <i>R</i> <sub>1</sub> = 0.1893, <i>wR</i> <sub>2</sub> = 0.3877              |
| γ/°                                  | 90                                            | Largest diff. peak/hole / e Å <sup>-3</sup>         | 0.23/-0.1                                                                    |
| Volume/Å <sup>3</sup>                | 3241(153)                                     |                                                     |                                                                              |
| <i>Z</i>                             | 8                                             |                                                     |                                                                              |
| ρ <sub>calc</sub> /g/cm <sup>3</sup> | 1.344                                         |                                                     |                                                                              |
| μ/mm <sup>-1</sup>                   | 0.000                                         |                                                     |                                                                              |
| <i>F</i> (000)                       | 557.0                                         |                                                     |                                                                              |

## Supplementary References

- Williams, D. B. & Lawton, M. Drying of organic solvents: quantitative evaluation of the efficiency of several desiccants. *J. Org. Chem.* **75**, 8351-8354 (2010).
- Luo, H. X. *et al.* Indolo-quinoline boron difluoride dyes: synthesis and spectroscopic properties. *Org. Biomol. Chem.* **14**, 4185-4188 (2016).
- Nishikawa, K. *et al.* Substituent effects of *cis*-cinnamic acid analogues as plant growth inhibitors. *Phytochemistry* **96**, 132-147 (2013).
- Bałczewski, P. *et al.* Efficient Synthesis of Bis(dibromomethyl)arenes as Important Precursors of Synthetically Useful Dialdehydes. *Synthesis* **48**, 3509-3514 (2016).
- Bonifacio, M. C., Robertson, C. R., Jung, J. Y. & T., K. B. Polycyclic Aromatic Hydrocarbons by Ring-Closing Metathesis. *J. Org. Chem.* **70**, 8522-8526 (2005).
- De Lucca, G. V. *et al.* Small Molecule Reversible Inhibitors of Bruton's Tyrosine Kinase (BTK): Structure-Activity Relationships Leading to the Identification of 7-(2-Hydroxypropan-2-yl)-4-[2-methyl-3-(4-oxo-3,4-dihydroquinazolin-3-yl)phenyl]-9H-carbazole-1-carboxamide (BMS-935177). *J. Med. Chem.* **59**, 7915-7935 (2016).
- Chen, P. C. *et al.* Neuroprotective and Antineuroinflammatory Effects of Hydroxyl-Functionalized Stilbenes and 2-Arylbenzo[b]furans. *J. Med. Chem.* **60**, 4062-4073 (2017).
- Ravat, P. *et al.* Configurational Stability of [5]Helicenes. *Org. Lett.* **19**, 3707-3710 (2017).
- Hosokawa, T. *et al.* Synthesis, Structures, and Properties of Hexapole Helicenes: Assembling Six [5]Helicene Substructures into Highly Twisted Aromatic Systems. *J. Am. Chem. Soc.* **139**, 18512-18521 (2017).
- Si, T., Li, B., Xiong, W., Xu, B. & Tang, W. Efficient cross-coupling of aryl/alkenyl triflates with acyclic secondary alkylboronic acids. *Org. Biomol. Chem.* **15**, 9903-9909 (2017).
- Hao, T. *et al.* One-Pot Three-Component Synthesis of Phenanthrenes via Palladium-Catalyzed Catellani and Retro-Diels-Alder Reactions. *J. Org. Chem.* **88**, 10426-10433 (2023).
- Nathusius, M. *et al.* Chrysene-Based Blue Emitters. *Chem. Eur. J.* **26**, 15089-15093 (2020).
- Legault, C. Y.M CTLview20. Université de Sherbrooke (2020). <http://www.cylvview.org>.
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, Jr., J. A., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, Ö., Foresman, J. B., Ortiz, J. V., Cioslowski, J., Fox, D. J. Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT (2009).
- Koengeter, T. *et al.* Catalytic Cross-Metathesis Reactions That Afford *E*- and *Z*-Trisubstituted Alkenyl Bromides: Scope, Applications, and Mechanistic Insights. *J. Am. Chem. Soc.* **145**, 3774-3785 (2023).
- Luchini, G., Alegre-Requena, J. V., Funes-Ardoiz, I., Paton, R. S. GoodVibes: Automated thermochemistry for heterogeneous computational chemistry data. *F1000 Research* **9**, 219 (2020).
- Lu, T. & Chen, F. Multiwfn: a multifunctional wavefunction analyzer. *J. Comput. Chem.* **33**, 580-592 (2012).
- Contreras-Garcia, J. *et al.* NCIPlot: a program for plotting non-covalent interaction regions. *J. Chem. Theory Comput.* **7**, 625-632 (2011).
- William Humphrey, Andrew Dalke & Schulten, K. VMD: Visual molecular dynamics. *J. Mol. Graph.* **14**, 33-38 (1996).
- Klar, P. B. *et al.* Accurate structure models and absolute configuration determination using dynamical effects in continuous-rotation 3D electron diffraction data. *Nat. Chem.* **15**, 848-855 (2023).