

Supplementary Information

Enantioselective Homologation of Helical Architectures From Fluorenones to Phenanthrenones with Enhanced Circular Dichroism

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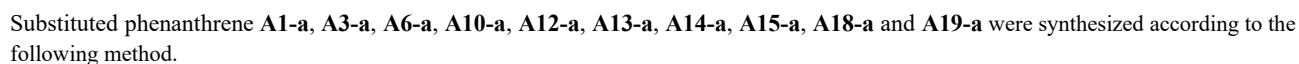
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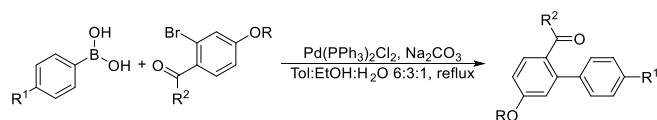
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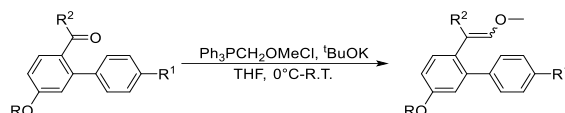
1. General information.

^1H NMR spectra were recorded at Bruker ASCENDTM 600M (600MHz). The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, m = multiple, br. = broad), coupling constants (Hz), integration. $^{13}\text{C}\{^1\text{H}\}$ NMR data were collected at 151 MHz with complete proton decoupling. $^{19}\text{F}\{^1\text{H}\}$ NMR data were collected at 564 MHz with complete proton decoupling. Diastereomeric ratio (d.r.) were determined by ^1H NMR. Enantiomeric excesses (e.e.) were determined by chiral HPLC analysis on Daicel chiralcel **IA**, chiralcel **IA-3**, chiralcel **IC**, chiralcel **ID**, chiralcel **IE**, chiralcel **IK** and chiralcel **AD-H** columns or UPC² analysis on Daicel Chiralcel **IC-3**, Chiralcel **OZ-3**, Chiralcel **OJ-3** and Chiralcel **AD-3** in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^{25}$ (c: g/100 mL, in DCM). High resolution mass spectra (HRMS) analyses were recorded on a Thermo Scientific LTQ Orbitrap XL with positive ion mode or negative ion mode and MeOH were used to dissolve the sample. IR spectra were recorded on Pierkin Elmer 100 FT/IR spectrometer, and the wave numbers of the absorption peaks are given in cm^{-1} . Circularly Polarized Luminescence (CPL) spectra were recorded on JASCO CPL-300 spectrometer. UV absorption and Circular Dichroism (CD) spectra were recorded on Chirascan V100 spectrometer. Fluorescence spectra and fluorescence lifetime were recorded on FlouoroMax⁺ spectrometer. THF and toluene was distilled from sodium benzophenone ketyl. CH_2Cl_2 , CHCl_3 , $\text{ClCH}_2\text{CH}_2\text{Cl}$, $\text{Cl}_2\text{CHCH}_2\text{Cl}$, $\text{Cl}_2\text{CHCHCl}_2$ were distilled over CaH_2 . All commercially available reagents were purchased from Bide Pharmatech Ltd. (Shanghai) and used as received without additional purification.

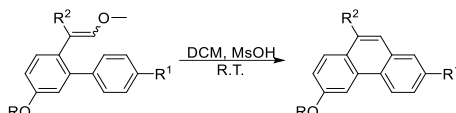




Under N₂ atmosphere, at room temperature, a 100 mL three-necked bottle was charged with the corresponding boric acid (15 mmol, 1.5 equiv.), aryl bromide (10 mmol, 1.0 equiv.) Na₂CO₃ (20 mmol, 2 equiv.), Pd(PPh₃)₂Cl₂ (0.5 mmol, 0.05 equiv.) and toluene: ethanol: water 6:3:1 (0.25 M in relation to the aryl bromide). The resulting reaction mixture was heated to reflux and react for 2 hours. Upon reaction completion, after removal of solvent under reduced pressure, the mixture was diluted with water (40 mL) and DCM (40 mL), and the aqueous layer was extracted with DCM (2×10 mL). The combined organic phases were washed with saturated aq. NaCl (2×20 mL), dried over Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (50:1 to 20:1 Pet:Et₂O as the eluent) to afford the corresponding biphenyl compound as a colorless oil.

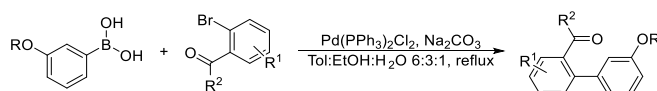
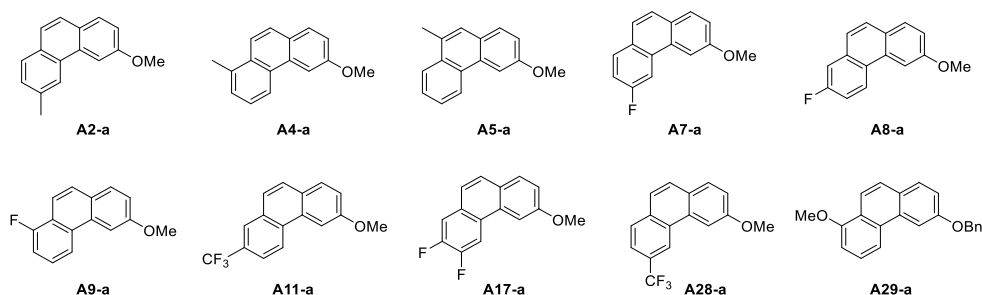


Under N₂ atmosphere, at room temperature, a 100 mL round bottom flask was charged with the (methoxymethyl)triphenylphosphonium chloride (20 mmol, 2.0 equiv.), t-BuOK (22 mmol, 2.2 equiv.) and anhydrous THF (0.5 M in relation to the phosphonium chloride). The mixture was stirred for 40 min under 0 °C, then the corresponding biphenyl compound (10 mmol, 1.0 equiv.) was added. After addition, the reaction mixture was stay at 0 °C to stir for 30 min, than the reaction mixture was warmed up to room temperature and further allowed to stir for 3 h. Upon reaction completion, the reaction was quenched with 20 mL of saturated NH₄Cl, and the aqueous layer was extracted with EtOAc (2×10 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (20:1 EtOAc : Pet as the eluent) to afford the enol ether (*Z/E* mixture) as a colorless oil.



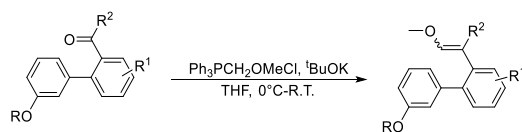
Under air atmosphere, at room temperature, a 100 mL round bottom flask was charged with the corresponding enol ether (10 mmol, 1.0 equiv.) and DCM (1.0 M in relation to the enol ether). MsOH (10 mmol, 1.0 equiv. 1.0 M in DCM) was added dropwise. The resulting reaction mixture was stirred for 3 h. Upon reaction completion, the mixture was diluted with water (20 mL) and the aqueous layer was extracted with DCM (3×10 mL). The combined organic phases were washed with saturated aq. NaHCO₃ (2×20 mL), dried over Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue (**A1-a**, **A3-a**, **A6-a**, **A10-a**, **A12-a**, **A13-a**, **A14-a**, **A15-a**, **A18-a** and **A19-a**) was used without further purification.

Substituted phenanthrene **A2-a**, **A4-a**, **A5-a**, **A7-a**, **A8-a**, **A9-a**, **A11-a**, **A17-a**, **A28-a** and **A29-a** were synthesized according to the following method.

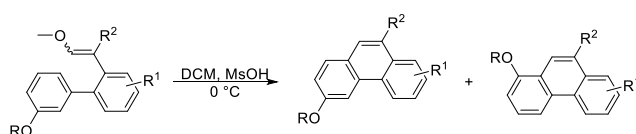


Under N₂ atmosphere, at room temperature, a 100 mL three-necked bottle was charged with the corresponding boric acid (15 mmol, 1.5 equiv.), the corresponding aryl bromide (10 mmol, 1.0 equiv.) Na₂CO₃ (20 mmol, 2 equiv.), Pd(PPh₃)₂Cl₂ (0.5 mmol, 0.05 equiv.) and toluene:ethanol:water 6:3:1 (0.25 M in relation to the aryl bromide). The resulting reaction mixture was heated to reflux and react for 2 hours. Upon reaction completion, after removal of solvent under reduced pressure the mixture was diluted with water (40 mL) and DCM (40 mL), and the aqueous layer was extracted with DCM (2×10 mL). The combined organic phases were washed with saturated aq. NaCl (2×20 mL), dried

over Na₂SO₄. Then, the solution was concentrated under reduced pressure, and the crude residue was subjected to column chromatography on silica gel (50:1 to 20:1 Pet:Et₂O as the eluent) to afford the corresponding biphenyl compound as a colorless oil.

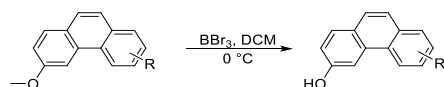
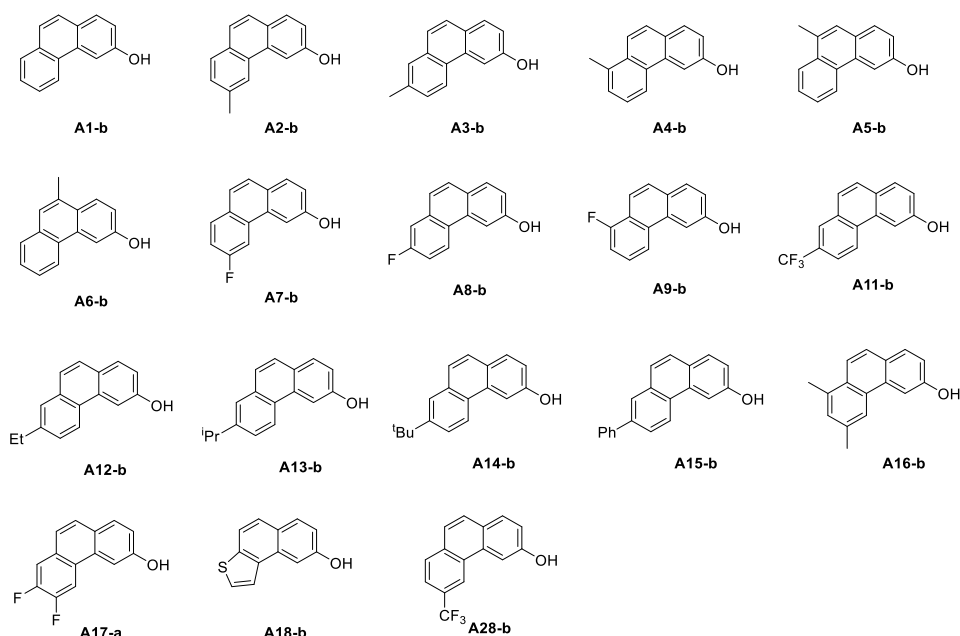


Under N₂ atmosphere, at room temperature, a 100 mL round bottom flask was charged with the (methoxymethyl)triphenylphosphonium chloride (20 mmol, 2.0 equiv.) ^tBuOK (22 mmol, 2.2 equiv.) and anhydrous THF (0.5 M in relation to the phosphonium chloride). The mixture was stirred for 40 min under 0 °C., then the corresponding biphenyl compound (10 mmol, 1.0 equiv.) was added. After addition, the reaction mixture was stay at 0 °C to stir for 30 min, than the reaction mixture was warmed up to room temperature and further allowed to stir for 3 h. Upon reaction completion, the reaction was quenched with 20 mL saturated NH₄Cl, and the aqueous layer was extracted with EtOAc (2×10 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (20:1 EtOAc : Pet as the eluent) to afford the enol ether (*Z/E* mixture) as a colorless oil.



Under air atmosphere, at room temperature, a 100 mL round bottom flask was charged with the corresponding enol ether (10 mmol, 1.0 equiv.) and DCM (1.0 M in relation to the **S3**). MsOH (10 mmol, 1.0 equiv 1.0 M in DCM) was added dropwise after the reaction was cooled to 0 °C. The resulting reaction mixture was stirred for 12 h. Upon reaction completion, the mixture was diluted with water (20 mL) and the aqueous layer was extracted with DCM (3×10 mL). The combined organic phases were washed with saturated aq. NaHCO₃ (2×20 mL), dried over Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue (**A2-a**, **A4-a**, **A5-a**, **A7-a**, **A8-a**, **A9-a**, **A11-a**, **A17-a**, **A28-a** and **A29-a**) was used without further purification.

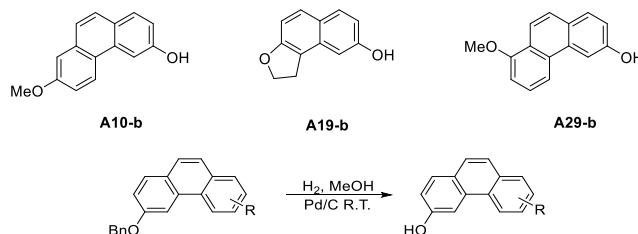
Substituted phenanthrene-3-ols **A2-b**, **A3-b**, **A4-b**, **A5-b**, **A6-b**, **A7-b**, **A8-b**, **A9-b**, **A11-b**, **A12-b**, **A13-b**, **A14-b**, **A15-b**, **A16-b**, **A17-b**, **A18-b** and **A28-b** were synthesized according to the following method, and **A1-b** is a commercially available reagent.



Under air atmosphere, at room temperature, a 100 mL round bottom flask was charged with the corresponding phenanthrene (10 mmol, 1.0 equiv.) and DCM (1.0 M in relation to the phenanthrene). BBr₃ (20 mmol, 2.0 equiv., 1.0 M in DCM) was added dropwise after the reaction was cooled to 0 °C. The resulting reaction mixture was stirred for 1 h. Upon reaction completion, the mixture was poured into ice and the

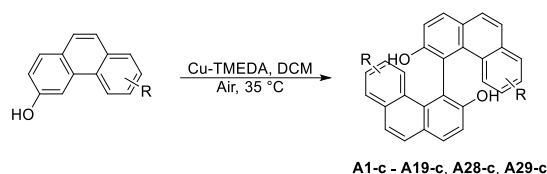
aqueous layer was extracted with DCM (3×10 mL). The combined organic phases were washed with saturated aq. NaHCO₃ (2×20 mL), dried over Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (8:2:1 – 5:2:1 Pet:DCM:Et₂O) to afford the phenanthrene-3-ol derivative (**A2-b**, **A3-b**, **A4-b**, **A5-b**, **A6-b**, **A7-b**, **A8-b**, **A9-b**, **A11-b**, **A12-b**, **A13-b**, **A14-b**, **A15-b**, **A16-b**, **A17-b**, **A18-b** and **A28-b**) as a white solid.

Substituted phenanthrene-3-ols **A10-b**, **A29-b** and analogue **A19-b** were synthesized according to the following method.



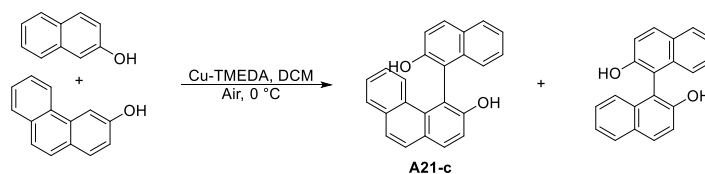
Under H₂ atmosphere, at room temperature, a 250 mL round bottom flask was charged with the corresponding phenanthrene (10 mmol, 1.0 equiv.), Pd/C (m/m 0.1) and MeOH (0.1 M in relation to the phenanthrene). The resulting reaction mixture was stirred for 2 h. Upon reaction completion, the mixture was filtered through a pad of celite. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (8:2:1 – 5:2:1 Pet:DCM:Et₂O as the eluent) to afford the (**A10-b**, **A19-b** and **A29-b**) as a white solid. **Hydrogenation of the double bond of furan unit of A19-b also occurs under these conditions.**

Substituted bi-3-phenanthrenols **A1-c–A19-c**, **A26-c** and **A27-c** were synthesized according to the following method. **A26-c** and **A27-c** are commercially available reagents.

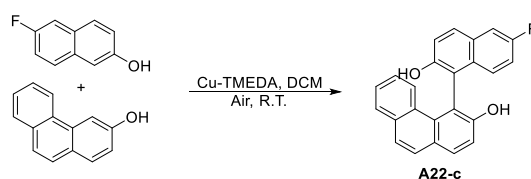


Under air atmosphere, at room temperature, a 250 mL round bottom flask was charged with the phenanthrenol (**A1-b–A19-b**, **A28-b** or **A29-b**; 20 mmol, 1.0 equiv.) and DCM (0.1 M in relation to the substituted phenanthren-3-ol). Cu-TMEDA (20 mmol, 1.0 equiv.) was added. After addition, the reaction mixture was allowed to stir 2-8 h at 35 °C. Upon reaction completion, the reaction was quenched with 100 mL saturated NH₄Cl, and the aqueous layer was extracted with DCM (2×10 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was used without further purification.

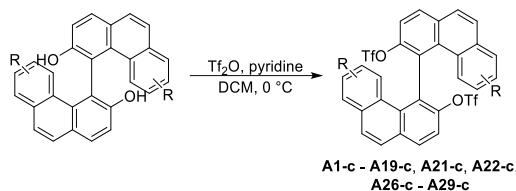
A21-c and **A22-c** were synthesized according to the following method.



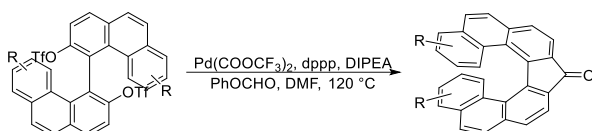
Under air atmosphere, at room temperature, a 250 mL round bottom flask was charged with the **A1-b** (10 mmol, 1.0 equiv.), naphthalen-2-ol (20 mmol, 2.0 equiv.) and DCM (0.1 M in relation to the naphthalen-2-ol). Cu-TMEDA (3 mmol, 0.3 equiv.) was added. After addition, the reaction mixture was allowed to stir 4 h at 0 °C. Upon reaction completion, the reaction was quenched with 100 mL saturated NH₄Cl, and the aqueous layer was extracted with DCM (2×10 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue (mixture of **A21-c** and binaphthol) was used without further purification.



Under air atmosphere, at room temperature, a 250 mL round bottom flask was charged with the **A1-b** (10 mmol, 1.0 equiv.), 6-fluoronaphthalen-2-ol (15 mmol, 1.5 equiv.) and DCM (0.1 M in relation to the naphthalen-2-ol). Cu-TMEDA (3 mmol, 0.3 equiv.) was added. After addition, the reaction mixture was allowed to stir 2 h at 35 °C. Upon reaction completion, the reaction was quenched with 100 mL saturated NH₄Cl, and the aqueous layer was extracted with DCM (2×10 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue (mixture of **A22-c** and 6-fluoronaphthalen-2-ol) was used without further purification.

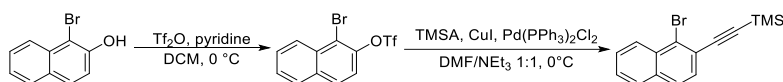


Under air atmosphere, at room temperature, a 100 mL round bottom flask was charged with the diphenol (**A1-c–A19-c, A21-c, A22-c** or **A26-c–A29-c**; 10 mmol, 1.0 equiv.), pyridine (30 mmol, 3.0 equiv.) and DCM (0.1 M in relation to the diphenol). Tf₂O (25 mmol, 2.5 equiv.) was added after the reaction was cooled to 0 °C. After addition, the reaction mixture was stay at 0 °C for 20 min. Upon reaction completion, the reaction was quenched with 20 mL saturated KHSO₄, and the aqueous layer was extracted with DCM (2×10 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (Pet:EtOAc = 15:1 to 9:1 as the eluent) to afford the crude product. Pure products were obtained by recrystallization from MeOH and DCM as a white crystal.



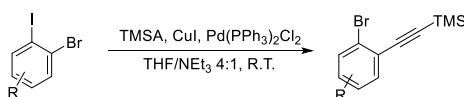
Under N₂ atmosphere, at room temperature, a 100 mL seal tube was charged with the OTf-diphenol derivative (**A1-c–A19-c, A21-c, A22-c** or **A26-c–A29-c**; 5 mmol, 1.0 equiv.), Pd(COOCF₃)₂ (1 mmol, 0.2 equiv.), dppp (1.5 mmol, 0.3 equiv.), DIPEA (60 mmol, 12 equiv.), phenyl formate (6 mmol, 1.2 equiv.) and anhydrous DMF (0.2 M in relation to the substrate). The resulting reaction mixture was sealed and heated to 130 °C for 36 hours. Upon reaction completion, the mixture was diluted with water (50 mL) and EtOAc (100 mL), and the organic phase layer was washed by water (3×30 mL). The organic phases were washed with 2 M HCl (50 mL) and saturated aq. NaCl (2×20 mL), dried over Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (4:1 to 1:1 Pet:DCM as the eluent) to afford the crude racemic helical fluorenones. Pure products were obtained by recrystallization from DCM and MeOH or hot PhMe and MeOH or hot 1,1,2,2-TCE and MeOH as dark red to orange crystal.

2.1.2 Racemic helical fluorenones A20, A23-A25 and A30 were synthesized according to the following method.^[2,3]

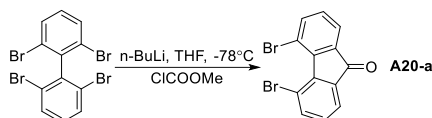


Under air atmosphere, at room temperature, a 100 mL round bottom flask was charged with 1-bromonaphthalen-2-ol (10 mmol, 1.0 equiv.), pyridine (15 mmol, 1.5 equiv.) and DCM (0.5 M in relation to the 1-bromonaphthalen-2-ol). Tf₂O (12.5 mmol, 1.25 equiv.) was added after the reaction was cooled to 0 °C. After addition, the reaction mixture was stay at 0 °C for 20 min. Upon reaction completion, the reaction was quenched with 20 mL saturated KHSO₄, and the aqueous layer was extracted with DCM (2×10 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was used without further purification.

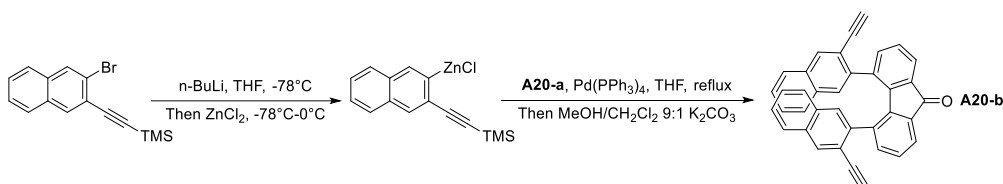
Under air atmosphere, at room temperature, a 100 mL round bottom flask was charged with the 1-bromonaphthalen-2-yl trifluoromethanesulfonate (10 mmol, 1.0 equiv.), CuI (1 mmol, 0.1 equiv.), Pd(PPh₃)Cl₂ (1 mmol, 0.1 equiv.) and DMF/NEt₃ (1/1 v/v, 0.5 M in relation to the substrate). TMSA (11 mmol, 1.1 equiv.) was added after the reaction was cooled to 0 °C. After addition, the reaction mixture was stay at 0 °C for 2 h. Upon reaction completion, the reaction was quenched with 50 mL saturated KHSO₄, and the aqueous layer was extracted with EtOAc (2×30 mL). The combined organic phases were washed with water (3×30 mL) and saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (Pet as the eluent) to afford the product as a colorless oil (9.3 mmol, 93% yield).



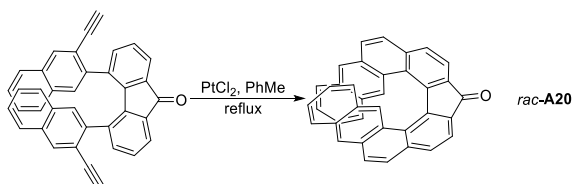
Under air atmosphere, at room temperature, a 100 mL round bottom flask was charged with the corresponding *o*-bromoiodobenzene (10 mmol, 1.0 equiv.), CuI (1 mmol, 0.1 equiv.), Pd(PPh₃)Cl₂ (1 mmol, 0.1 equiv.) and THF/NEt₃ (4/1 v/v, 0.5 M in relation to the *o*-bromoiodobenzene). TMSA (10.5 mmol, 1.05 equiv.) was added. After addition, the reaction mixture was allowed to stir 4 h at room temperature. Upon reaction completion, the reaction was quenched with 50 mL saturated KHSO₄, and the aqueous layer was extracted with EtOAc (2×30 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (Pet as the eluent) to afford the product as a colorless oil.



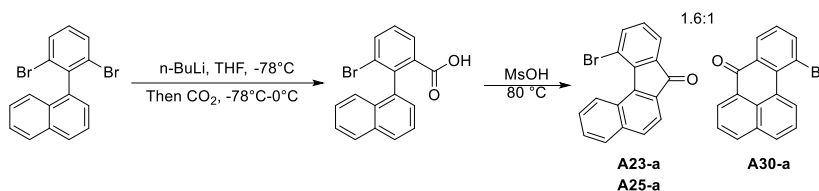
Under N₂ atmosphere, at room temperature, a 100 mL round bottom flask was charged with the 2,2',6,6'-tetrabromo-1,1'-biphenyl (10 mmol, 1.0 equiv.) and anhydrous THF (0.1 M in relation to the 2,2',6,6'-tetrabromo-1,1'-biphenyl). *n*-BuLi (21 mmol, 2.1 equiv.) was added dropwise after the reaction was cooled to -78 °C. The solution was stirred for another 40 min under such conditions, then CICOOMe (50 mmol, 5 equiv.) was added. After addition, the reaction mixture was stay at -78 °C and further allowed to stir overnight. Upon reaction completion, the reaction was quenched with 50 mL saturated NH₄Cl, and the aqueous layer was extracted with EtOAc (2×10 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (4:1 Pet:DCM as the eluent) to afford the crude fluorenone. Pure **A20-a** was obtained by recrystallization from MeOH and DCM as a bright yellow crystal.



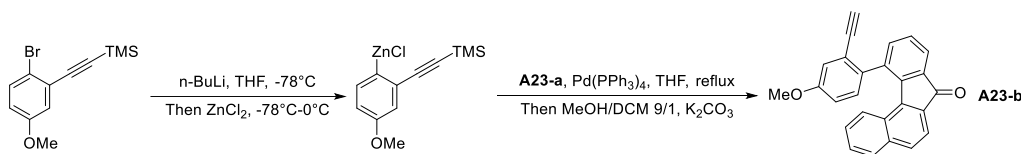
Under N₂ atmosphere, at room temperature, a 100 mL round bottom flask was charged with the ((3-bromonaphthalen-2-yl)ethynyl)trimethylsilane (15 mmol, 3.0 equiv.) and anhydrous THF (1 M in relation to the ((3-bromonaphthalen-2-yl)ethynyl)trimethylsilane). *n*-BuLi (16.5 mmol, 3.3 equiv.) was added dropwise after the reaction was cooled to -78 °C. The solution was stirred for another 30 min under such conditions, then ZnCl₂ (16.5 mmol, 3.3 equiv. in 15 mL THF) was added. After addition, the reaction mixture was stay at -78 °C and further allowed to stir for 30 min then the reaction mixture was warming up to 0 °C and stirred for 30 min. After that **A20-a** (5 mmol, 1 equiv.) and Pd(PPh₃)₄ (1 mmol, 0.2 equiv.) was added, the resulting reaction mixture was heated to reflux and react for 48 hours. Upon reaction completion, the reaction was quenched with 50 mL saturated NH₄Cl, and the aqueous layer was extracted with EtOAc (2×10 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. The solution was concentrated under reduced pressure, the crude residue was dissolved in MeOH/DCM 9/1 20 mL then K₂CO₃ (50 mmol, 10 equiv.) was added. After addition, the reaction mixture was allowed to stir 4 h. Upon reaction completion the mixture was diluted with water (50 mL), and the aqueous layer was extracted with DCM (2×20 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (Pet:DCM = 2:1 as the eluent) to afford the **A20-b** (a mixture of diastereomers) as a yellow solid.



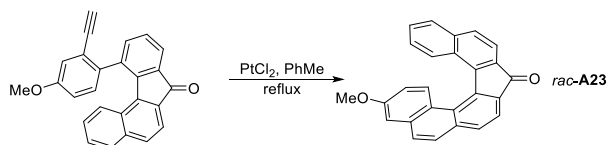
Under N₂ atmosphere, at room temperature, a 250 mL seal tube was charged with the **A20-b** (2 mmol, 1.0 equiv.), PtCl₂ (0.4 mmol, 0.2 equiv.) and anhydrous toluene (0.025 M in relation to **A20-b**). The resulting reaction mixture was heated to reflux and react for 17 hours. Upon reaction completion, Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (1:1 to 1:2 Pet:DCM as the eluent) to afford the crude *rac*-**A20**. Pure *rac*-**A20** was obtained by recrystallization from DCM and MeOH as dark red crystal.



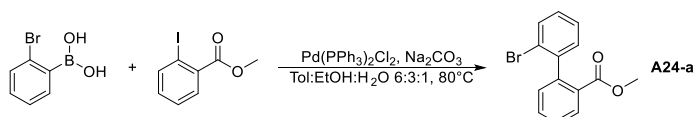
Under N₂ atmosphere, at room temperature, a 100 mL round bottom flask was charged with the 1-(2,6-dibromophenyl)naphthalene (15 mmol, 1.0 equiv.) and anhydrous THF (0.5 M in relation to the 1-(2,6-dibromophenyl)naphthalene). n-BuLi (16.5 mmol, 1.1 equiv.) was added dropwise after the reaction was cooled to -78 °C. The solution was stirred for another 30 min under such conditions, then continuously bubble dry carbon dioxide gas through the mixture for 3 hours while slowly raising the temperature of the mixture to 0 °C. Upon reaction completion, the reaction was quenched with 50 mL 2 M HCl, and the aqueous layer was extracted with DCM (2×40 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. The solution was concentrated under reduced pressure, then the crude residue was dispersed in 60 mL MsOH. The resulting reaction mixture was heated to 80 °C and react for 6 hours. Upon reaction completion, the mixture was poured into ice and the aqueous layer was extracted with DCM (2×50 mL). The combined organic phases were washed with saturated aq. NaHCO₃ (2×20 mL), dried over Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (4:1 – 1:1 Pet:DCM) to afford the crude fluorenone **A23-a** orange solid and crude anthrone **A23-a'** as yellow solid. Pure **A23-a** was obtained by recrystallization from MeOH and DCM as an orange crystal.



Under N₂ atmosphere, at room temperature, a 100 mL round bottom flask was charged with the ((2-bromo-5-methoxyphenyl)ethynyl)trimethylsilane (3 mmol, 1.5 equiv.) and anhydrous THF (1 M in relation to the ((2-bromo-5-methoxyphenyl)ethynyl)trimethylsilane)). n-BuLi (3.2 mmol, 1.6 equiv.) was added dropwise after the reaction was cooled to -78 °C. The solution was stirred for another 30 min under such conditions, then ZnCl₂ (3.2 mmol, 1.6 equiv. in 10 mL THF) was added. After addition, the reaction mixture was stay at -78 °C and further allowed to stir for 30 min then the reaction mixture was warming up to 0 °C and stirred for 30 min. **A23-a** (2 mmol, 1 equiv.) and Pd(PPh₃)₄ (0.2 mmol, 0.1 equiv) were added, the resulting reaction mixture was heated to reflux and react for 6 hours. Upon reaction completion, the reaction was quenched with 50 mL saturated NH₄Cl, and the aqueous layer was extracted with EtOAc (2×10 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. The solution was concentrated under reduced pressure, the crude residue was dissolved in MeOH/DCM (9/1, 20 mL), then K₂CO₃ (4 mmol, 2 equiv.) was added. After addition, the reaction mixture was allowed to stir for 1 h. Upon reaction completion the mixture was diluted with water 50 mL and the aqueous layer was extracted with DCM (2×20 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (9:1 Pet:EtOAc as the eluent) to afford the **A23-b** as an orange solid.

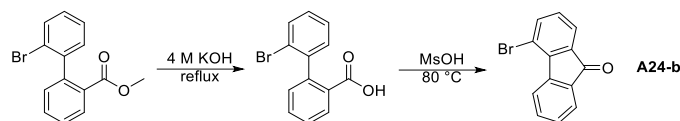


Under N₂ atmosphere, at room temperature, a 250 mL seal tube was charged with **A23-b** (1 mmol, 1.0 equiv.), PtCl₂ (0.1 mmol, 0.1 equiv.) and anhydrous toluene (0.01 M in relation to **A23-b**). The resulting reaction mixture was heated to reflux and react for 8 hours. Upon reaction completion, Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (4:1 to 2:1 Pet:DCM as the eluent) to afford the crude *rac*-**A23**. Pure *rac*-**A23** was obtained by recrystallization from DCM and MeOH as deep red crystal.

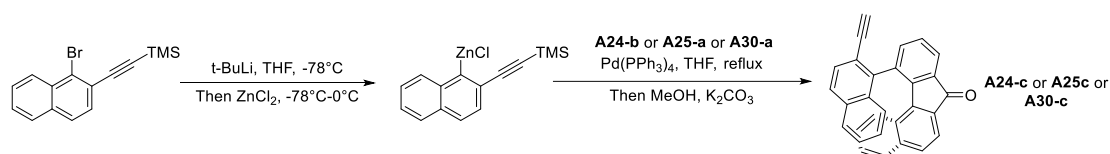


Under N₂ atmosphere, at room temperature, a 100 mL three-necked bottle was charged with the (2-bromophenyl)boronic acid (13 mmol, 1.3 equiv.), methyl 2-iodobenzoate (10 mmol, 1.0 equiv.) Na₂CO₃ (20 mmol, 2 equiv.), Pd₂(PPh₃)Cl₂ (0.5 mmol, 0.05 equiv.) and toluene:ethanol:water 6:3:1 (0.25 M in relation to the methyl 2-iodobenzoate). The resulting reaction mixture was heated to 80 °C and react for 2 hours. Upon reaction completion, after removal of solvent under reduced pressure the mixture was diluted with water (40 mL) and DCM (40

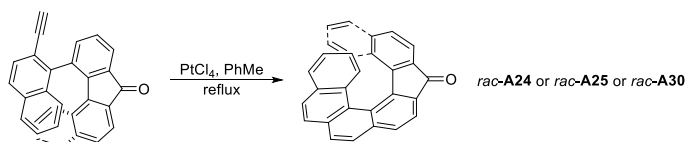
mL) and the aqueous layer was extracted with DCM (2×10 mL). The combined organic phases were washed with saturated aq. NaCl (2×20 mL), dried over Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was used without further purification.



Under air atmosphere, at room temperature, a 250 mL round bottom flask was charged with the crude **A24-a** and 100 mL 4 M KOH solution. The resulting reaction mixture was heated to reflux and react for 12 hours. After the reaction was complete, add 100 mL of water to dilute the reaction mixture, wash the mixture with DCM (50 mL), 6 M HCl was added to adjust the pH to 1-2 and the aqueous layer was extracted with DCM (3×20 mL). The combined organic phases were washed with saturated aq. NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was dispersed in 60 mL MeOH. The resulting reaction mixture was heated to 80 °C and react for 6 hours. Upon reaction completion, the mixture was poured into ice and the aqueous layer was extracted with DCM (3×20 mL). The combined organic phases were washed with saturated aq. NaHCO₃ (2×20 mL), dried over Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (6:1–2:1 Pet:DCM) to afford the crude fluorenone. Pure **A24-b** was obtained by recrystallization from MeOH and DCM as a yellow crystal.

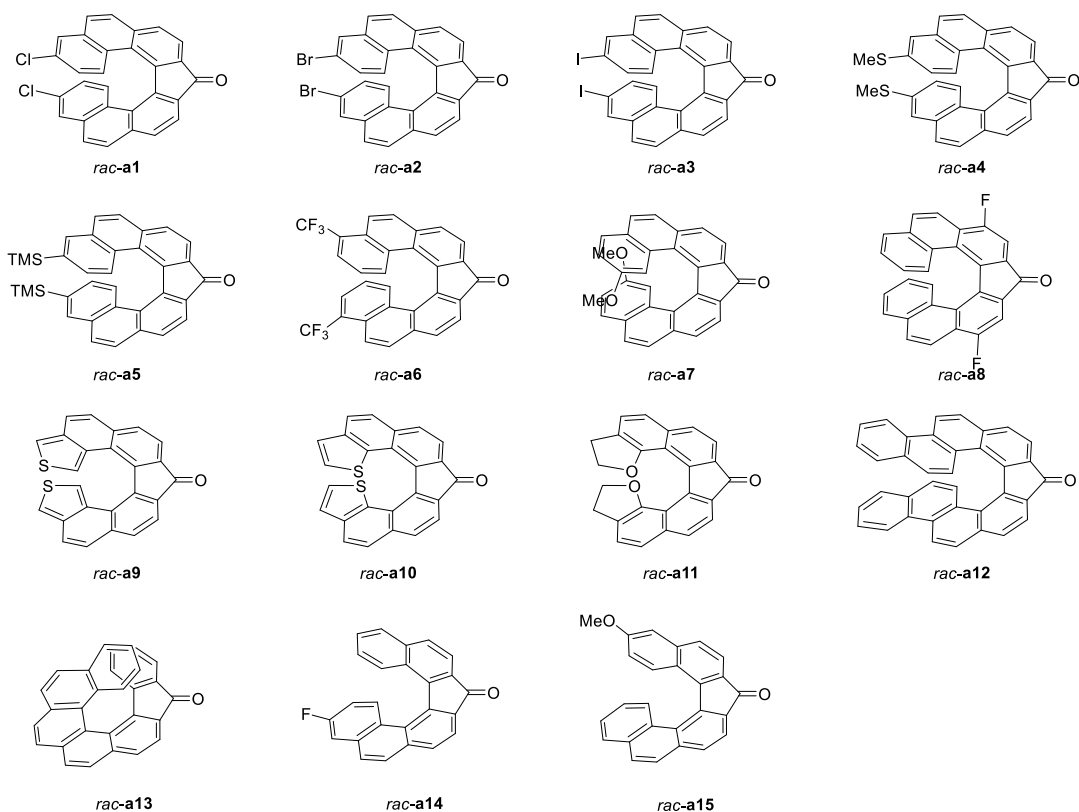


Under N₂ atmosphere, at room temperature, a 100 mL round bottom flask was charged with the ((1-bromonaphthalen-2-yl)ethynyl)trimethylsilane (7.5 mmol, 1.5 equiv.) and anhydrous THF (1 M in relation to the ((1-bromonaphthalen-2-yl)ethynyl)trimethylsilane). t-BuLi (15.5 mmol, 3.1 equiv.) was added dropwise after the reaction was cooled to -78 °C. The solution was stirred for another 30 min under such conditions, then ZnCl₂ (8 mmol, 1.6 equiv. in 15 mL THF) was added. After addition, the reaction mixture was stay at -78 °C and further allowed to stir for 30 min then the reaction mixture was warming up to 0 °C and stirred for 30 min. Then remove n-pentane from the mixture using an oil pump under reduced pressure. After that **A24-b** or **A25-5** or **A30-5** (5 mmol, 1 equiv.) and Pd(PPh₃)₄ (0.5 mmol, 0.1 equiv.) were added, the resulting reaction mixture was heated to reflux and react for 6 hours. Upon reaction completion, the reaction was quenched with 50 mL saturated NH₄Cl, and the aqueous layer was extracted with EtOAc (2×10 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. The solution was concentrated under reduced pressure, the crude residue was dissolved in MeOH 20 mL then K₂CO₃ (10 mmol, 2 equiv.) was added. After addition, the reaction mixture was allowed to stir 4 h. Upon reaction completion the mixture was diluted with water 50 mL and the aqueous layer was extracted with DCM (2×20 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (2:1 Pet:DCM as the eluent) to afford the **A24-c** and **A30-c** as a yellow solid or **A25-c** as an orange solid.

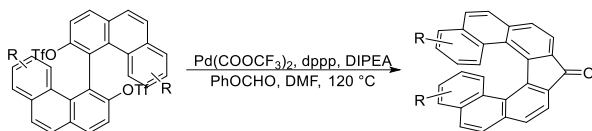


Under N₂ atmosphere, at room temperature, a 250 mL seal tube was charged with **A24-c** or **A25-c** or **A30-c** (1 mmol, 1.0 equiv.), PtCl₄ (0.1 mmol, 0.1 equiv.) and anhydrous toluene (0.01 M in relation to **A24-c** or **A25-c** or **A30-c**). The resulting reaction mixture was heated to reflux and react for 12 hours. Upon reaction completion, Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (4:1 to 2:1 Pet:DCM as the eluent) to afford the crude *rac*-**A24** or *rac*-**A25**. Pure *rac*-**A24** and *rac*-**A30** was obtained by recrystallization from DCM and PE as an orange crystal. Pure *rac*-**A25** was obtained by recrystallization from DCM and MeOH as a dark red crystal.

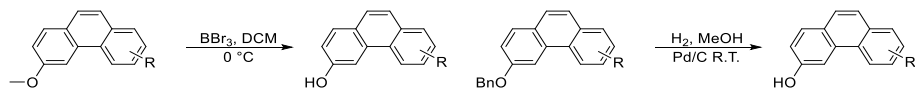
2.2 Unavailable substrates from the current methods



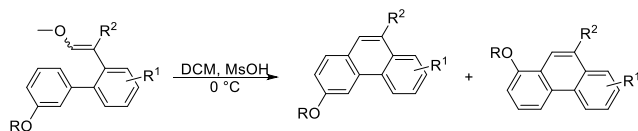
rac-a1, *rac-a2*, *rac-a3*, *rac-a7*, *rac-a8*, *rac-a10* and *rac-a12* were failed in the palladium-catalyzed ring-closing step, and the reaction systems were complex and no target product was detected.



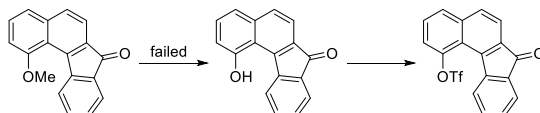
rac-a4 and *rac-a5* were failed in the deprotection step. The Pd/C catalysts can't remove the protective group and boron tribromide causes substrate decomposition



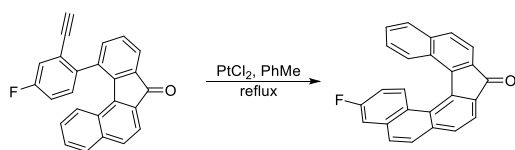
rac-a6 and *rac-a9* were failed in the MsOH-catalyzed ring-closing step, and the reaction systems were complex and no target product was detected.



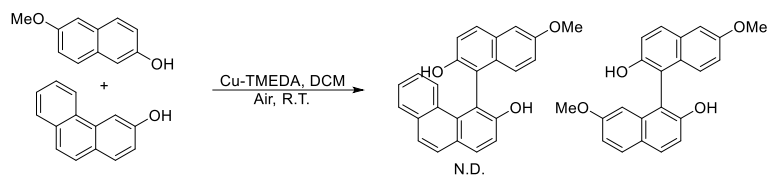
The synthesis of compound *rac-a13* failed due to the unsuccessful acquisition of its synthetic precursor.



rac-**a14** was failed in the platinum-catalyzed ring-closing step, and the reaction systems was complex and only trace product was detected.

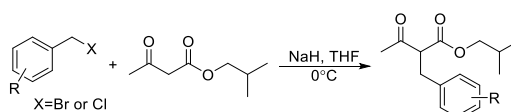
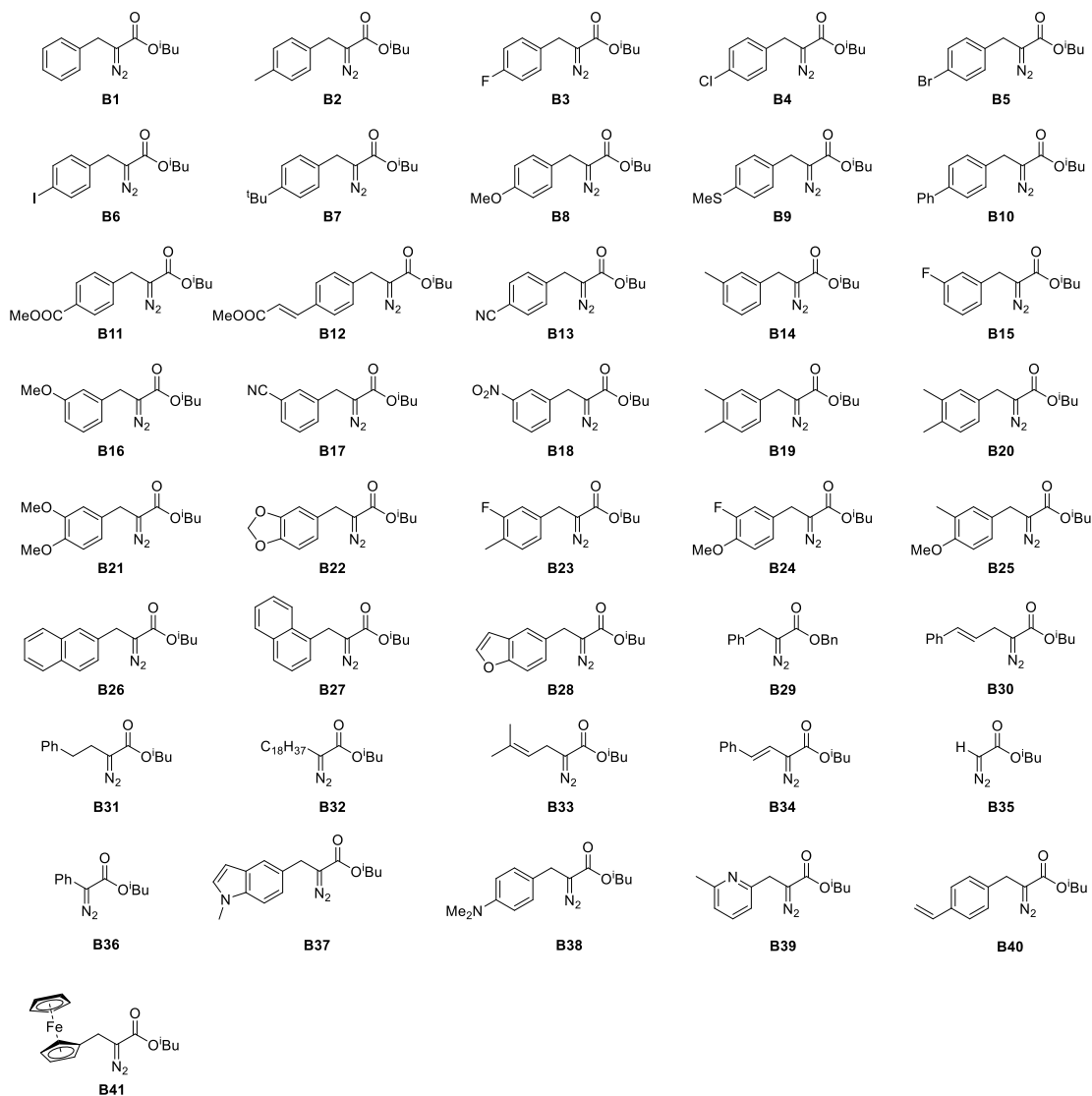


rac-**a15** was failed in the oxidative coupling step, and only the binaphthol was detected.

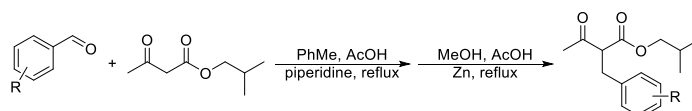


2.3 General procedure for the synthesis of α -diazo compound (B1-B34).

α -Diazo compounds **B1-B34** were synthesized according to the following method.

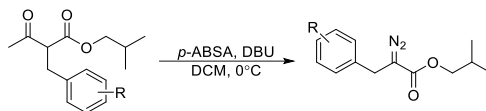


Under air atmosphere, at room temperature, a 100 mL round bottom flask were charged with NaH (22.5 mmol, 1.5 equiv.) and THF (0.5 M in relation to NaH). The reaction was cooled with an ice bath, after full cooling isobutyl acetoacetate (22.5 mmol, 1.5 equiv.) was added. The resulting reaction mixture was stirred for 10 min then corresponding benzyl bromide or benzyl chloride (15 mmol, 1.0 equiv.) was added. After addition, the reaction mixture was warming up to room temperature (65°C when benzyl chloride was used) and stirred for 8 h. Upon reaction completion, the mixture was diluted with water (20 mL) and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue (**B1-a** – **B33-a**, **B39-a** and **B40-a**) was used without further purification.



Under air atmosphere, at room temperature, a 100 mL round bottom flask was charged with the isobutyl acetoacetate (11 mmol, 1.1 equiv.), the corresponding benzaldehyde (10 mmol, 1.0 equiv.), piperidine (0.5 mmol, 0.05 equiv.), AcOH (2 mmol, 0.2 equiv.) and toluene (0.5 M in

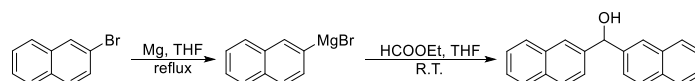
relation to the benzaldehyde). The resulting reaction mixture was heated to reflux with a Dean-Stark apparatus and react for 6 hours. Upon reaction completion, the solution was concentrated under reduced pressure. Then zinc powder (30 mmol, 3.0 equiv.), AcOH (20 mmol, 2.0 equiv.) and MeOH (0.5 M in relation to the benzaldehyde) was added. After addition, the reaction mixture was heated to reflux for 1 h. Upon reaction completion, the reaction was quenched with 50 mL of water, and the aqueous layer was extracted with EtOAc (2×20 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue (**B37-a**, **B38-a** and **B41-a**) was used without further purification.



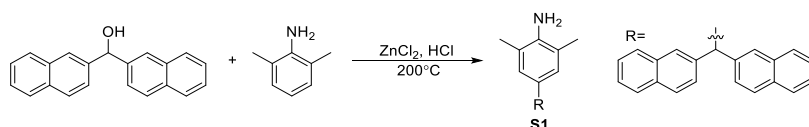
Under air atmosphere, at room temperature, a 250 mL round bottom flask was charged with the **B1-a – B34-a** and **B36-a –B41-a** (15 mmol, 1.0 equiv.), *p*-ABSA (30 mmol, 2.0 equiv.) and DCM (0.1 M in relation to the **S5**). DBU (30 mmol, 2.0 equiv.) was added dropwise after the reaction was cooled to 0 °C the solution was stirred for another 8 hours under such conditions. Upon reaction completion, after removal of solvent under reduced pressure the mixture was diluted with saturated NH₄Cl (20 mL) and Et₂O (30 mL) and the aqueous layer was extracted with Et₂O (2×10 mL). The combined organic phases were washed with saturated aq. NaCl (2×20 mL), dried over Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (Pet:Et₂O = 30:1 to 10:1 as the eluent) to afford the corresponding α -diazo ester (**B1–B34** and **B36–B41**).

2.4 General procedure for the synthesis of chiral *N, N'*-dioxides.

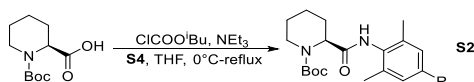
Chiral *N, N'*-dioxide **L3-PiMe₂CH(2-Nap)₂** was synthesized according to the following method.



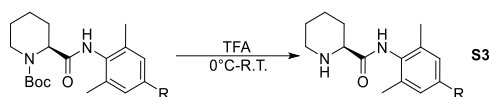
Under N₂ atmosphere, at room temperature, a 100 mL round bottom flask was charged with the 2-bromonaphthalene (22 mmol, 2.2 equiv.), magnesium chips (24 mmol, 2.4 equiv.) and anhydrous THF (1 M in relation to the 2-bromonaphthalene). The resulting reaction mixture was stirred for 1 h, after the reaction was cooled to room temperature ethyl formate (10 mmol, 1.0 equiv.) was added. After addition, resulting reaction mixture was stirred for 1 h. Upon reaction completion, the reaction was quenched with 20 mL of saturated NH₄Cl, and the aqueous layer was extracted with EtOAc (2×20 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude product was washed with petroleum ether to obtain the di(naphthalen-2-yl)methanol as a white solid which was used without further purification.



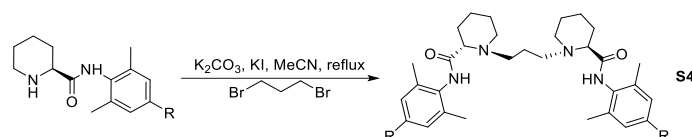
Under air atmosphere, at room temperature, a 100 mL round bottom flask was charged with the di(naphthalen-2-yl)methanol (10 mmol, 1.0 equiv.), 2,6-dimethylaniline (15 mmol, 1.5 equiv.). Heating the mixture to 200 °C until melted and stir well. Next, ZnCl₂ (5 mmol, 0.5 equiv.) was added after stir for two minutes and immediately concentrated hydrochloric acid (2 mL) was added. The resulting reaction mixture was stirred for 10 min. Upon reaction completion, the mixture was cooled down to room temperature and the reaction was quenched with 10 mL water, 6 M NaOH was added to adjust the pH to 10-11, and the aqueous layer was extracted with DCM (3×10 mL). The combined organic phases were washed with saturated aq. NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was washed with petroleum ether. Pure **S1** was obtained by recrystallization from MeOH and DCM as a light pink crystal powder.



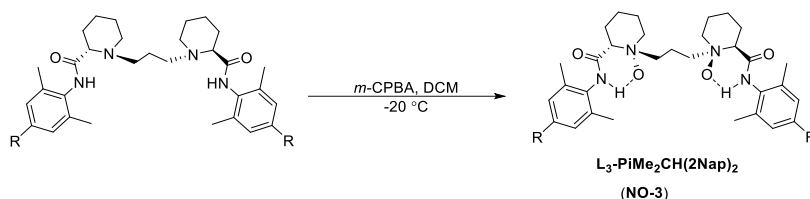
Under air atmosphere, at room temperature, a 100 mL round bottom flask was charged with the (*S*)-1-(tert-butoxycarbonyl)piperidine-2-carboxylic acid (10 mmol, 1.0 equiv.), triethylamine (15 mmol, 1.5 equiv.) and anhydrous THF (0.5 M in relation to the proline). Isobutyl chloroformate (12 mmol, 1.2 equiv.) was added dropwise after the reaction was cooled to 0 °C and the solution was stirred for another 30 min under such conditions, then the amine **S1** (15 mmol, 1.5 equiv.) was added. After addition, the reaction mixture was heated to reflux for 24h. Upon reaction completion, the mixture was washed with saturated aq. KHSO₄, saturated aq. NaHCO₃ and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic phases were washed with saturated aq. NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure affording the **S2** as a maroon solid which was used without further purification.



Under air atmosphere, at room temperature, a 100 mL round bottom flask was charged with the **S2**, TFA (20 mL) was added dropwise after the solution was cooled to 0 °C and stirred for another 1 h under such conditions. Upon reaction completion, saturated aq. Na₂CO₃ was added dropwise until no more gas was emitted, 6 M NaOH was added to adjust the pH to 10-11 and the aqueous layer was extracted with DCM (3×10 mL). The combined organic phases were washed with saturated aq. NaCl (2×20 mL), dried over anhydrous Na₂SO₄. Then, the solution was concentrated under reduced pressure. The crude residue was subjected to column chromatography on silica gel (9:1 to 1:1 Pet:EtOAc as the eluent) to afford the **S3** as a white solid. (4.9 g, 86.8 % yield, R_f = 0.2 EtOAc).



Under air atmosphere, at room temperature, a 100 mL round bottom flask was charged with the **S3** (5 mmol, 1.0 equiv.), K₂CO₃ (15 mmol, 3.0 equiv.), KI (5 mmol, 1.0 equiv.), 1,3-dibromopropane (2.5 mmol, 0.5 equiv.) and MeCN (0.25 M in relation to the **S9**). The reaction mixture was heated to reflux for 24 h. Upon reaction completion, the mixture was diluted with water (20 mL) and EtOAc (20 mL) and the aqueous layer was extracted with EtOAc (2×10 mL). The combined organic phases were washed with saturated aq. NaCl (2×20 mL), dried over Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (5:1 to 1:1 Pet:EtOAc as the eluent) to afford the **S4** as a white solid. (2.36g, 91.2 % yield, R_f = 0.4 EtOAc).



Under air atmosphere, at room temperature, a 100 mL round bottom flask was charged with the **S4** (1 mmol, 1.0 equiv.) and DCM (0.25 M in relation to the **S7**). *m*-CPBA (11 mmol, 2.2 equiv.) was added after the reaction was cooled to -20 °C. The solution was stirred for another 40 min under such conditions. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (15:1 to 1:1 EtOAc:MeOH as the eluent) to afford the **L₃-PiMe₂CH(2Nap)₂** as a colorless foam solid. (839 mg, 78.5 % yield, R_f = 0.34 EtOAc:MeOH = 1/1). Other *N,N'*-dioxide ligands were prepared by the similar procedure.

3. Optimization of the reaction conditions.

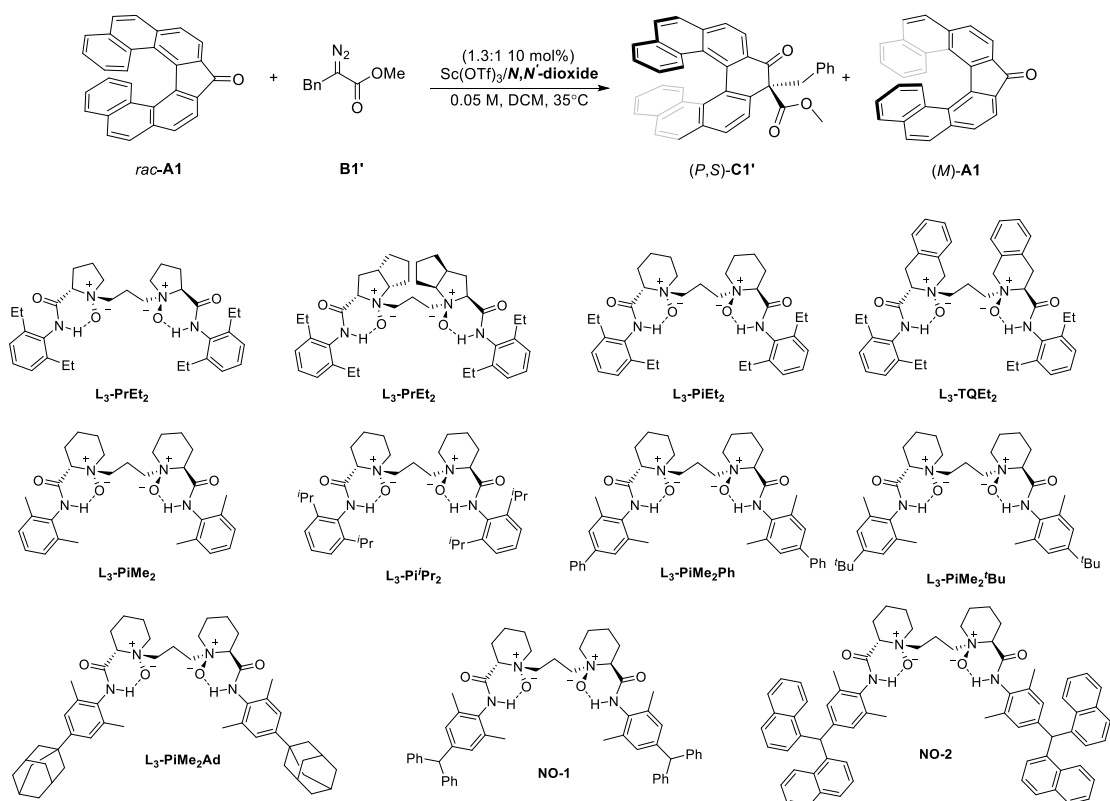
Table S1. Screening of the metal salt.

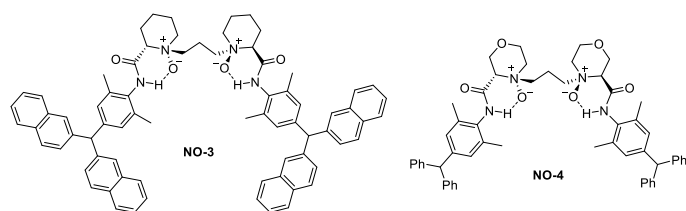
$\text{rac-A1} + \text{B1'} \xrightarrow[0.05 \text{ M, DCM, } 35^\circ\text{C}]{(1.3:1 \text{ } 10 \text{ mol}\%)\text{ M(OTf)}_3/\text{rac-L}_3\text{-PiEt}_2} \text{C1'} + \text{rac-A1}$

entry ^a	Metal salt	yield of C1' (%) ^b	d.r. of C1' ^c	ee of C1' (%) ^d	yield of A1 (%) ^b	ee of A1 (%) ^e
1	Sc(OTf) ₃	37	4/1	0/0	63	0
2	Y(OTf) ₃	N.R.	-	-	100	0
3	La(OTf) ₃	N.R.	-	-	100	0
4	Yb(OTf) ₃	N.R.	-	-	100	0
5	In(OTf) ₃	N.R.	-	-	100	0
6	Mg(OTf) ₂	N.R.	-	-	100	0
7	Al(OTf) ₃	N.R.	-	-	100	0

^aUnless otherwise noted, the reactions were carried out with helical fluorenone **A1** (0.05 mmol), diazo compound **B1'** (0.025 mmol), M(OTf)₃/rac-L₃-PiEt₂ (1.3:1, 10 mol%) in DCM (0.05 M) under air atmosphere at 35 °C for 12 h. ^bDetermined by ¹H NMR, the reaction mixture was filtered through 100-200 mesh silica gel, dried by rotary evaporation, then 0.05 mmol 1,1,2,2-tetrachloroethane was added as an internal standard to determine the ¹H NMR yield. ^cDetermined by ¹H NMR. ^dDetermined by UPCC on a chiral stationary phase. ^eDetermined by HPLC on a chiral stationary phase.

Table S2. Screening of the ligands.





entry ^a	Ligand	yield of C1' (%) ^b	d.r. of C1' ^c	ee of C1' (%) ^d	yield of A1 (%) ^b	ee of A1 (%) ^e
1	L ₃ -PrEt ₂	N.R.	-	-	100	0
2	L ₃ -RaEt ₂	N.R.	-	-	100	0
3	L ₃ -TQEt ₂	14	2.4/1	36/84	86	3
4	L ₃ -PiEt ₂	45	3.6/1	77/66	55	35
5	L ₃ -PiMe ₂	31	4.8/1	80/76	69	22
6	L ₃ -Pi ⁱ Pr ₂	N.R.	-	-	100	0
7	L ₃ -PiMe ₂ ⁱ Bu	25	4.0/1	77/75	75	17
8	L ₃ -PiMe ₂ Ad	37	3.1/1	70/77	63	21
9	L ₃ -PiMe ₂ Ph	46	2.8/1	80/84	54	31
10	NO-1	20	5.0/1	80/73	80	15
11	NO-4	18	5.2/1	83/71	82	14
12	NO-3	31	7.0/1	91/70	69	32
13	NO-2	27	6.8/1	83/45	73	24

^aUnless otherwise noted, the reactions were carried out with helical fluorenones **A1** (0.05 mmol), diazo compound **B1'** (0.025 mmol), Sc(OTf)₃/N,N'-dioxide (1.3:1, 10 mol%) in DCM (0.05 M) under air atmosphere at 35 °C for 24 h. ^bDetermined by ¹H NMR, the reaction mixture was filtered through 100-200 mesh silica gel, dried by rotary evaporation, then 0.05 mmol 1,1,2,2-tetrachloroethane was added as an internal standard to determine the ¹H NMR yield. ^cDetermined by ¹H NMR. ^dDetermined by UPCC on a chiral stationary phase. ^eDetermined by HPLC on a chiral stationary phase.

Table S3. Screening of the substrate ratio.

entry ^a	A1:B35	yield of C1' (%) ^b	d.r. of C1' ^c	ee of C1' (%) ^d	yield of A1 (%) ^b	ee of A1 (%) ^e
1	1:0.5	31	7.0/1	91/70	69	32
2	1:0.75	47	5.1/1	85/77	53	51
3	1:1	52	4.0/1	82/85	48	52
4	1:1.25	57	3.6/1	80/86	43	58

^aUnless otherwise noted, the reactions were carried out with helical fluorenones **A1** (0.05 mmol), diazo compound **B1'** (X mmol), Sc(OTf)₃/NO-3 (1.3:1, 10 mol%) in DCM (0.05 M) under air atmosphere at 35 °C for 12 h. ^bDetermined by ¹H NMR, the reaction mixture was filtered through 100-200 mesh silica gel, dried by rotary evaporation, then 0.05 mmol 1,1,2,2-tetrachloroethane was added as an internal standard to determine the ¹H NMR yield. ^cDetermined by ¹H NMR. ^dDetermined by UPCC on a chiral stationary phase. ^eDetermined by HPLC on a chiral stationary phase.

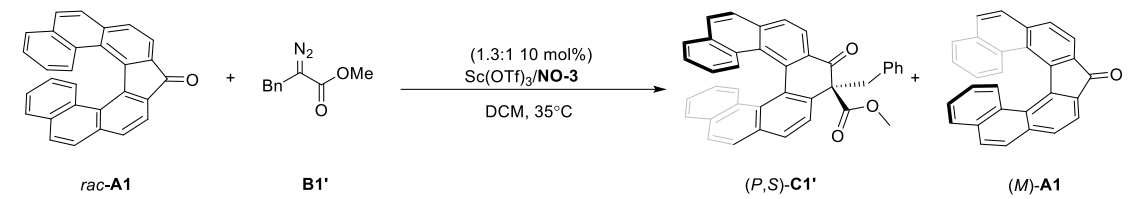
Table S4. Screening of the reaction temperature.

entry ^a	temperature	yield of C1' (%) ^b	d.r. of C1' ^c	ee of C1' (%) ^d	yield of A1 (%) ^b	ee of A1 (%) ^e
1	0 °C	31	6.9/1	93/70	69	31
2	10 °C	46	5.9/1	90/83	54	55
3	20 °C	46	5.9/1	90/83	54	53
4	35 °C	57	3.6/1	80/86	43	58

^aUnless otherwise noted, the reactions were carried out with helical fluorenones **A1** (0.05 mmol), diazo compound **B1'** (0.0625 mmol), Sc(OTf)₃/NO-3 (1.3:1, 10 mol%) in solvent (0.05 M) under air atmosphere at indicated temperature for 12 h. ^bDetermined by ¹H NMR, the reaction mixture was filtered through 100-200 mesh silica gel, dried by rotary evaporation, then 0.05 mmol 1,1,2,2-tetrachloroethane was added as an internal standard to determine the ¹H NMR yield. ^cDetermined by ¹H NMR. ^dDetermined by UPCC on a chiral stationary phase. ^eDetermined by HPLC on a chiral stationary phase.

by UPCC on a chiral stationary phase. ^aDetermined by HPLC on a chiral stationary phase.

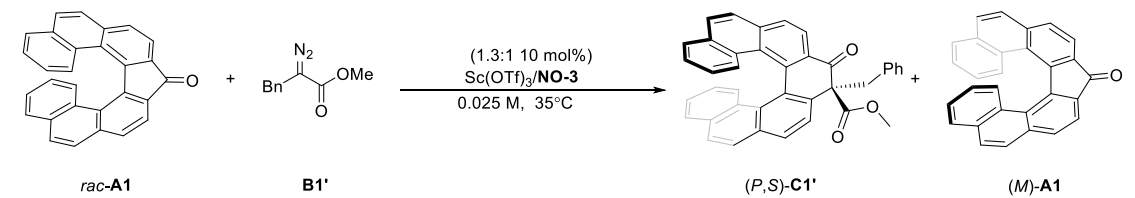
Table S5. Screening of the reactant concentration.



entry ^a	A1:B35 / M	yield of C1' (%) ^b	d.r. of C1' ^c	ee of C1' (%) ^d	yield of A1 (%) ^b	ee of A1 (%) ^e
1	1:1 / 2 mL DCM	39	5.8/1	90/76	61	40
2	1:1 / 3 mL DCM	47 (24 h)	5.3/1	87/80	53	53
3	1:1.25 / 2 mL DCM	48	5.3/1	90/80	52	57
4	1:1.25 / 3 mL DCM	57 (24 h)	4.3/1	86/80	43	70

^aUnless otherwise noted, the reactions were carried out with helical fluorenones **A1** (0.05 mmol), diazo compound **B1'** (X mmol), Sc(OTf)₃/NO-3 (1.3:1, 10 mol%) in DCM under air atmosphere at 35 °C for 12 h. ^bIsolated yield of **A1** and **C1'**. ^cDetermined by ¹H NMR, the reaction mixture was filtered through 100-200 mesh silica gel, dried by rotary evaporation, then 0.05 mmol 1,1,2,2-tetrachloroethane was added as an internal standard to determine the ¹H NMR yield. ^dDetermined by ¹H NMR. ^eDetermined by UPCC on a chiral stationary phase. ^fDetermined by HPLC on a chiral stationary phase.

Table S6. Screening of the solvent.



entry ^a	solvent	yield of C1' (%) ^b	d.r. of C1' ^c	ee of C1' (%) ^d	yield of A1 (%) ^b	ee of A1 (%) ^e
1	CH ₂ Cl ₂	48	5.3/1	90/80	52	57
2	CHCl ₃	73	3.0/1	80/91	27	>99
3	ClCH ₂ CH ₂ Cl	90	2.2/1	74/89	10	>99
4	ClCH ₂ CHCl ₂	75	2.9/1	73/91	25	96
5	Cl ₂ CHCHCl ₂	79	2.3/1	72/92	21	>99

^aUnless otherwise noted, the reactions were carried out with helical fluorenones **A1** (0.05 mmol), diazo compound **B1'** (0.0625 mmol), Sc(OTf)₃/NO-3 (1.3:1, 10 mol%) in solvent (0.025 M) under air atmosphere at 35 °C for 12 h. ^bDetermined by ¹H NMR, the reaction mixture was filtered through 100-200 mesh silica gel, dried by rotary evaporation, then 0.05 mmol 1,1,2,2-tetrachloroethane was added as an internal standard to determine the ¹H NMR yield. ^cDetermined by ¹H NMR. ^dDetermined by UPCC on a chiral stationary phase. ^eDetermined by HPLC on a chiral stationary phase.

Table S7. Screening of the ester group of the diazo compound.



entry ^a	R	yield of C (%) ^b	d.r. of C ^c	ee of C (%) ^d	yield of A1 (%) ^b	ee of A1 (%) ^e
1	Me	48 (C1')	5.3:1	90/80	52	57
2	Et	50	5.2:1	92/81	50	67
3	ⁱ Pr	57	5.0:1	92/91	43	83
4	^t Bu	43	2.2:1	94/74	57	33
5	ⁱ Bu	57 (C1)	5.2:1	95/91	43	87
6	Bn	46	5.3:1	93/90	54	57
7		58	3.6:1	92/76	42	78
8		62	4.0:1	93/91	38	94
9		54	4.6:1	91/78	46	75
10		49	5.7:1	91/81	51	70
11		57	4.9:1	93/82	43	86
12		55	4.5:1	93/81	45	82

^aUnless otherwise noted, the reactions were carried out with helical fluorenones **A1** (0.05 mmol), diazo compound **B** (0.0625 mmol), Sc(OTf)₃/**NO-3** (1.3:1, 10 mol%) in DCM (0.025 M) under air atmosphere at 35 °C for 12 h. ^bDetermined by ¹H NMR, the reaction mixture was filtered through 100-200 mesh silica gel, dried by rotary evaporation, then 0.05 mmol 1,1,2,2-tetrachloroethane was added as an internal standard to determine the ¹H NMR yield. ^cDetermined by ¹H NMR. ^dDetermined by UPCC on a chiral stationary phase. ^eDetermined by HPLC on a chiral stationary phase.

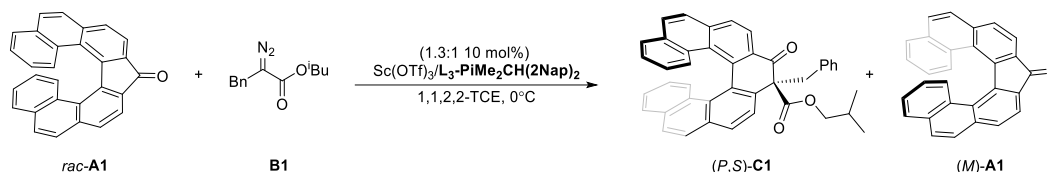
Table S8. Rescreening of the solvent and reaction temperature.

entry ^a	solvent / T	yield of C1 (%) ^b	d.r. of C1 ^c	ee of C1 (%) ^d	yield of A1 (%) ^b	ee of A1 (%) ^e
1	CH ₂ Cl ₂ 35 °C	57	5.2 : 1	95 / 91	43	87
2	CH ₂ Cl ₂ 0 °C	29	12 : 1	95 / 91	71	33
3	CHCl ₃ 0 °C	47	2.9 : 1	89 / 78	53	42
4	ClCH ₂ CHCl ₂ 0 °C	61	3.9 : 1	95 / 93	39	88
5	Cl ₂ CHCHCl ₂ 0 °C	49	8.7 : 1	98 / 93	51	80
6 ^f	Cl ₂ CHCHCl ₂ 0 °C	55 (8 h)	6.8 : 1	98 / 92	45	90
7 ^g	Cl ₂ CHCHCl ₂ 0 °C	55 (8 h)	7.8 : 1	98 / 93	45	94
8 ^g	Cl ₂ CHCHCl ₂ 0 °C	51 (6 h)	8.3 : 1	98 / 91	49	82

^aUnless otherwise noted, the reactions were carried out with helical fluorenones **A1** (0.05 mmol), diazo compound **B1** (0.0625 mmol), Sc(OTf)₃/**NO-3** (1.3:1, 10 mol%) in solvent (0.025 M) under air atmosphere for 12 h. ^bDetermined by ¹H NMR, the reaction mixture was filtered through 100-200 mesh silica gel, dried by rotary evaporation, then 0.05 mmol 1,1,2,2-tetrachloroethane was added as an internal standard to determine the ¹H NMR yield. ^cDetermined by ¹H NMR. ^dDetermined by HPLC on a chiral stationary phase. ^eSc(OTf)₃/**NO-3** (1.3:1, 20 mol%) was used. ^fSc(OTf)₃/**NO-3** (1.3:1, 10 mol%) was activated in THF for 30 minutes under 35 °C and the catalyst was used after THF was evaporated.

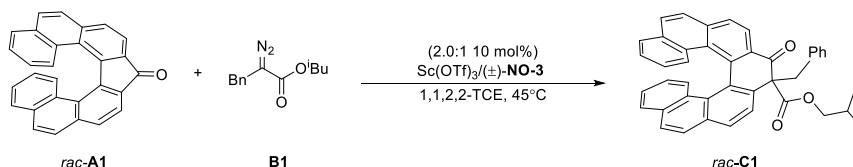
4. Typical procedure for the kinetic resolution of helical fluorenones.

4.1 Typical procedure for the kinetic resolution.



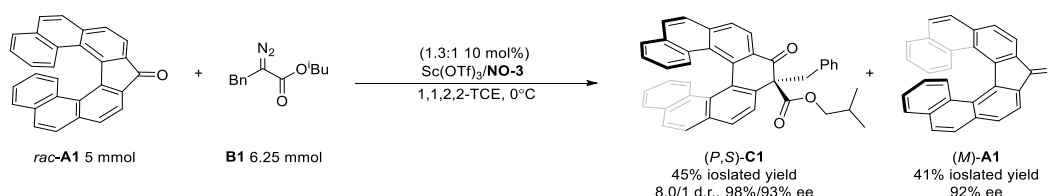
Procedure for the synthesis of the product C1: To a dry test tube under nitrogen atmosphere was added Sc(OTf)_3 (3.2 mg, 0.0065 mmol, 13 mol%), **NO-3** (5.4 mg, 0.005 mmol, 10 mol%) in THF (1.0 mL), and the mixture was stirred at 35 °C for 20 minutes. Substrate **A1** (19 mg, 0.05 mmol, 1.0 equiv.) was added to the test tube after THF was evaporated. Then the resulting mixture was stirred at 35 °C for 20 minutes. Substrate **B1** (18 μL , 0.0625 mmol, 1.5 equiv.) was added after the reaction was cooled to 0 °C the solution was stirred for another 8 h under such conditions. After the ee value of spiral fluorenone **A1** was increased to more than 90% (detected by chiral HPLC), the reaction solution was filtered by a short silica gel column to quench the reaction, and the solution was concentrated under reduced pressure. The crude residue was subjected to column chromatography on silica gel (25:1 Pet:Acetone as the eluent) to afford the product (*P, S*)-**C1** and (*M*)-**A1**. The enantiomeric excess (ee) of product (*P, S*)-**C** and (*M*)-**A1** was determined by HPLC with Daicel chiralcel **IA**, chiralcel **IC**, chiralcel **ID**, chiralcel **IK** or UPC² with Daicel Chiralcel **OZ-3**, Chiralcel **OJ-3**, chiralcel **AD-3**, chiralcel **IC** in comparison with the authentic racemates.

4.2 Typical procedure for the synthesis of racemic product C

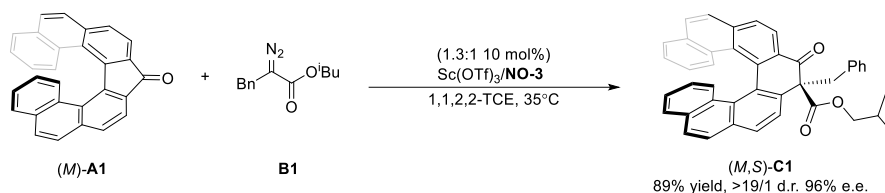


Procedure for the synthesis of the product C1: To a dry test tube under nitrogen atmosphere was added Sc(OTf)_3 (4.9 mg, 0.01 mmol, 20 mol%), ($\pm$)-**NO-3** (5.4 mg, 0.005 mmol, 10 mol%) and Substrate **A1** (19 mg, 0.05 mmol, 1.0 equiv.). Then the resulting mixture was stirred at 35 °C for 20 minutes after that substrate **B1** (29 μL , 0.1 mmol, 2.0 equiv) was added and the solution was stirred for another 8 h under such conditions. After the substrate **A1** was fully consumed (detected by TLC). Upon reaction completion, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (15:1 Pet:EtOAc as the eluent) to afford the racemic product **C1**.

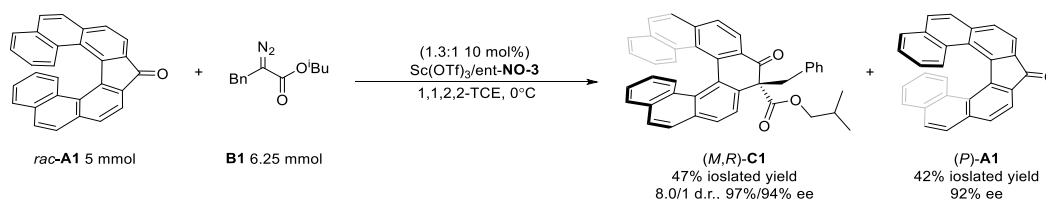
4.3 Gram-scale synthesis and stereo-divergent synthesis of the A1 and C1.



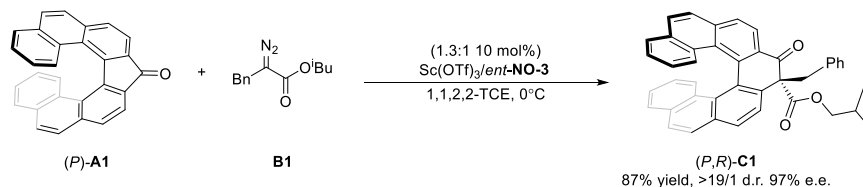
Procedure for the synthesis of the product (*P, S*)-C1: To a dry test tube under nitrogen atmosphere was added Sc(OTf)_3 (319.9 mg, 0.65 mmol, 13 mol%), **NO-3** (534.7 mg, 0.5 mmol, 10 mol%) in THF (20.0 mL), and the mixture was stirred at 35 °C for 20 minutes. Substrate **A1** (1.9 g, 5.0 mmol, 1.0 equiv.) was added to the test tube after THF was evaporated. Then the resulting mixture was stirred at 35 °C for 20 minutes. substrate **B1** (1.8 mL, 6.25 mmol, 1.5 equiv) was added after the reaction was cooled to 0 °C the solution was stirred for another 180 min under such conditions. After the ee value of spiral fluorenone **A1** was increased to more than 90% (detected by chiral HPLC), the reaction solution was filtered by a short silica gel column to quench the reaction, and the solution was concentrated under reduced pressure. The crude residue was subjected to column chromatography on silica gel (25:1 Pet:Acetone as the eluent) to afford the product (*P, S*)-**C1** and (*M*)-**A1**.



Procedure for the synthesis of the product (*M*, *S*)-C1: To a dry test tube under nitrogen atmosphere was added Sc(OTf)_3 (3.2 mg, 0.0065 mmol, 13 mol%), **NO-3** (5.4 mg, 0.005 mmol, 10 mol%) in THF (1.0 mL), and the mixture was stirred at 35 °C for 20 minutes. Substrate (*M*)-**A1** (19 mg, 0.05 mmol, 1.0 equiv.) was added to the test tube after THF was evaporated. Then the resulting mixture was stirred at 35 °C for 20 minutes. Substrate **B1** (18 μL , 0.0625 mmol, 1.5 equiv) was added and the solution was stirred under such conditions. After the substrate (*M*)-**A1** was fully consumed (detected by chiral TLC), the reaction solution was filtered by a short silica gel column to quench the reaction, and the solution was concentrated under reduced pressure. The crude residue was subjected to column chromatography on silica gel (2:1 Pet:DCM as the eluent) to afford the product (*M*, *S*)-**C1**.



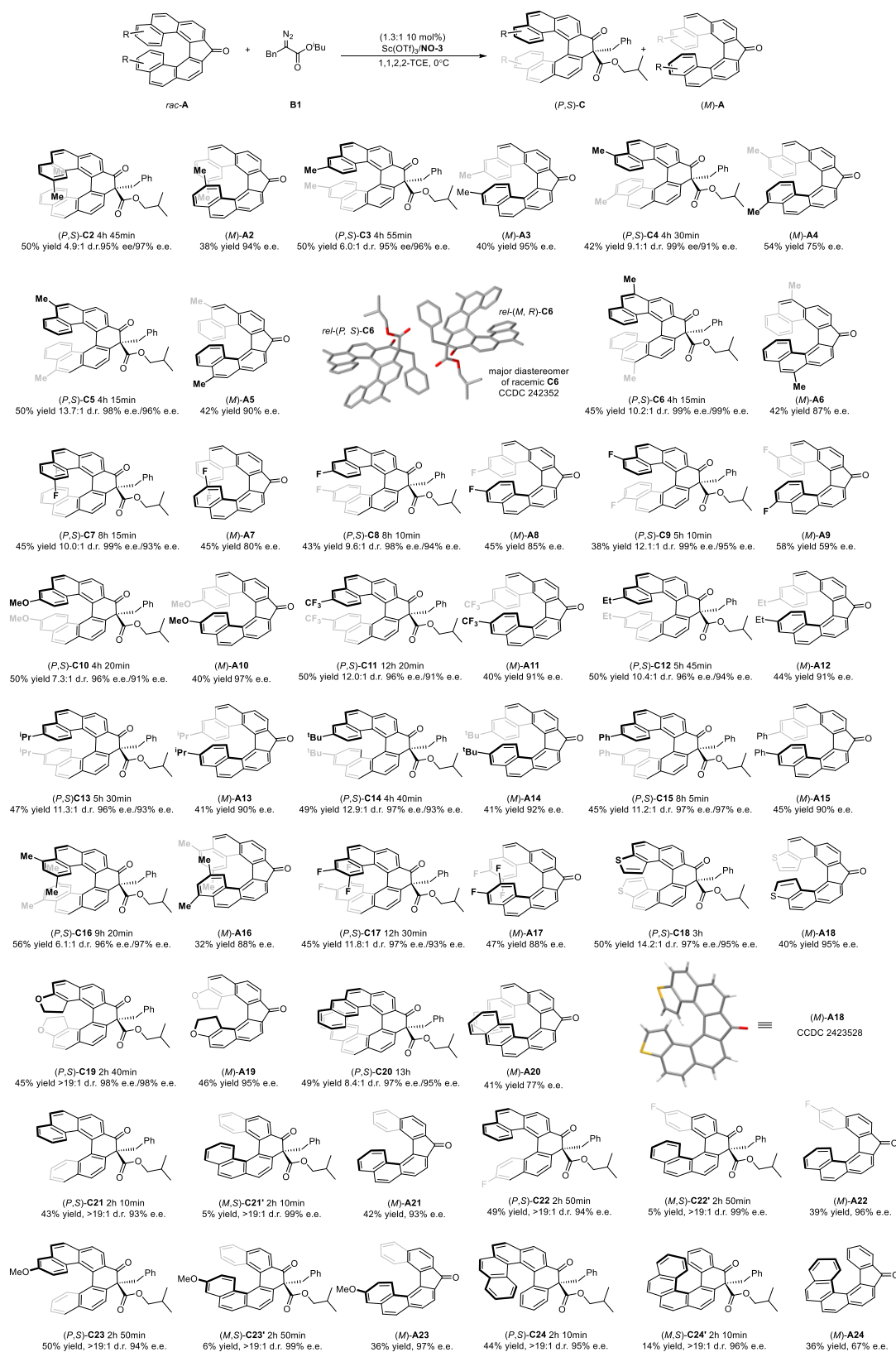
Procedure for the synthesis of the product (*M*, *R*)-C1: To a dry test tube under nitrogen atmosphere was added Sc(OTf)_3 (319.9 mg, 0.65 mmol, 13 mol%), *ent*-**NO-3** (534.7 mg, 0.5 mmol, 10 mol%) in THF (20.0 mL), and the mixture was stirred at 35 °C for 20 minutes. Substrate **A1** (1.9 g, 5.0 mmol, 1.0 equiv.) was added to the test tube after THF was evaporated. Then the resulting mixture was stirred at 35 °C for 20 minutes. Substrate **B1** (1.8 mL, 6.25 mmol, 1.5 equiv) was added after the reaction was cooled to 0 °C the solution was stirred for another 180 min under such conditions. After the ee value of spiral fluorenone **A1** was increased to more than 90% (detected by chiral HPLC), the reaction solution was filtered by a short silica gel column to quench the reaction, and the solution was concentrated under reduced pressure. The crude residue was subjected to column chromatography on silica gel (25:1 Pet:Acetone as the eluent) to afford the product (*M*, *R*)-**C1** and *P*-**A1**.

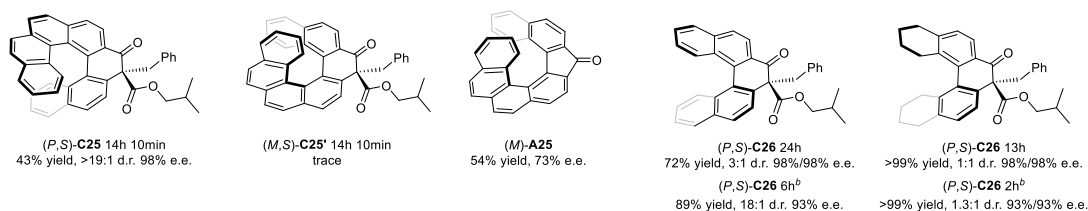


Procedure for the synthesis of the product (*P*, *R*)-C1: To a dry test tube under nitrogen atmosphere was added Sc(OTf)_3 (3.2 mg, 0.0065 mmol, 13 mol%), *ent*-**NO-3** (5.4 mg, 0.005 mmol, 10 mol%) in THF (1.0 mL), and the mixture was stirred at 35 °C for 20 minutes. Substrate (*P*)-**A1** (19 mg, 0.05 mmol, 1.0 equiv.) was added to the test tube after THF was evaporated. Then the resulting mixture was stirred at 35 °C for 20 minutes. Substrate **B1** (18 μL , 0.0625 mmol, 1.5 equiv) was added and the solution was stirred under such conditions. After the substrate (*P*)-**A1** was fully consumed (detected by chiral TLC), the reaction solution was filtered by a short silica gel column to quench the reaction, and the solution was concentrated under reduced pressure. The crude residue was subjected to column chromatography on silica gel (2:1 Pet:DCM as the eluent) to afford the product (*P*, *R*)-**C1**.

5. The list of substrate scope.

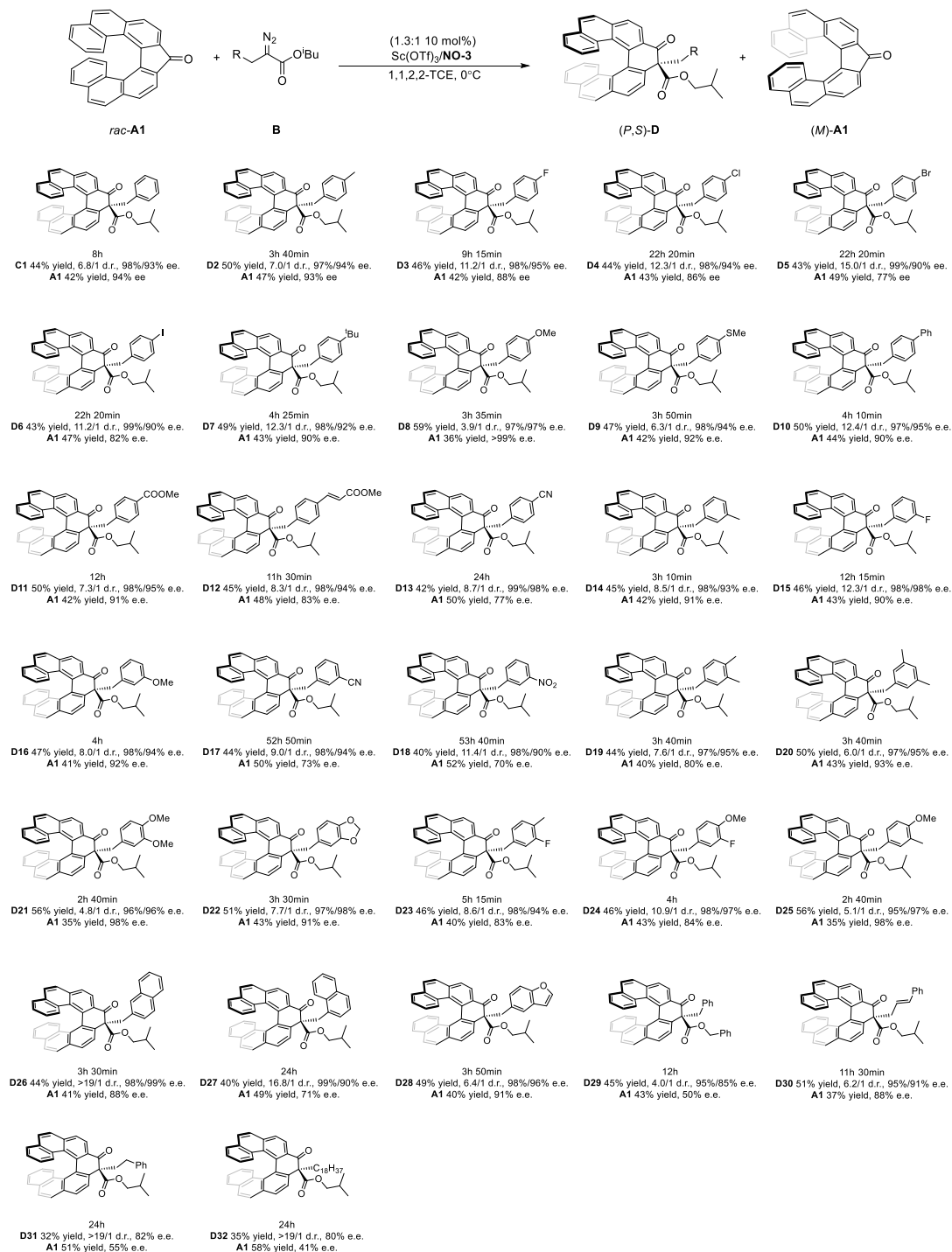
Table S9. Substrate scope of helical fluorenones ^a





^a Unless otherwise noted, the reactions were carried out with helical fluorenones **A** (0.05 mmol), diazo compound **B1** (0.0625 mmol), Sc(OTf)₃/NO-3 (1.3:1, 10 mol%) in 1,1,2,2-TCE (0.025 M) under air atmosphere at 0°C. ^b The reaction was carried out at 35°C. The reported yields were all isolated yields obtained through column chromatography. The d.r. value was determined by ¹H NMR spectroscopy and the e.e. value was determined by HPLC and UPCC analysis on a chiral stationary phase.

Table S10. Substrate scope of α-diazo esters ^a

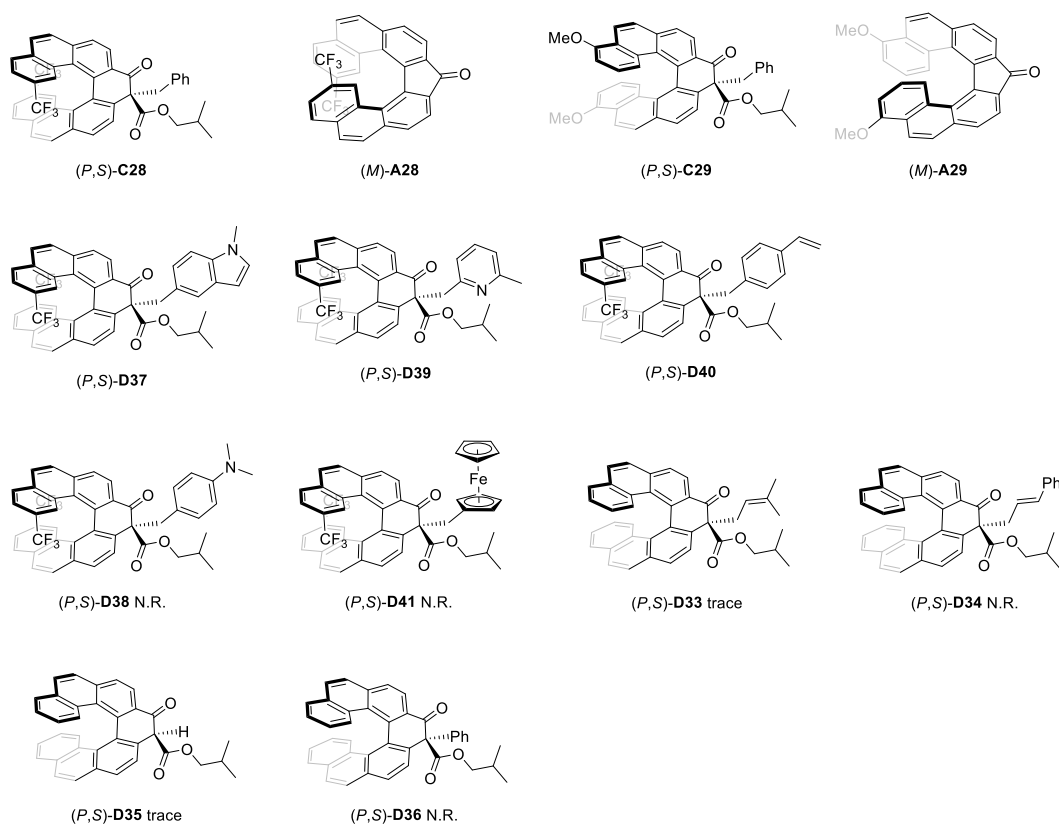


^a Unless otherwise noted, the reactions were carried out with helical fluorenones **A1** (0.05 mmol), diazo compound **B** (0.0625 mmol), Sc(OTf)₃/NO-3 (1.3:1, 10 mol%) in 1,1,2,2-TCE (0.025 M) under air atmosphere at 0°C. The reported yields were all isolated yields obtained through column chromatography. The d.r. value was determined by ¹H NMR spectroscopy and the e.e. value was determined by HPLC and UPCC analysis on a

chiral stationary phase.

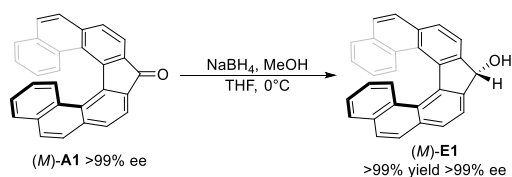
Table S11. Failed substrate scopes. ^a

Chiral HPLC cannot separate the enantiomeric and diastereoisomers of the product

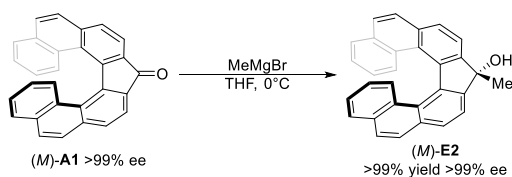


^a Unless otherwise noted, the reactions were carried out with helical fluorenones **A** (0.05 mmol), diazo compound **B** (0.0625 mmol), Sc(OTf)₃/NO-3 (1.3:1, 10 mol%) in 1,1,2,2-TCE (0.025 M) under air atmosphere at 0°C. The reported yields were all isolated yields obtained through column chromatography. The d.r. value was determined by ¹H NMR spectroscopy and the e.e. value was determined by HPLC and UPCC analysis on a chiral stationary phase.

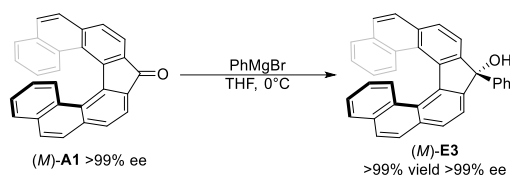
6. Synthetic transformation.



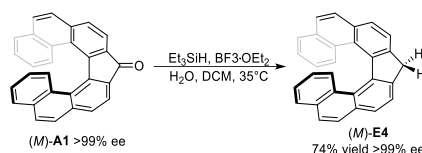
Under air atmosphere, at room temperature, a test tube was charged with the (M)-A1 (0.1 mmol, 1.0 equiv.), MeOH (0.1 mmol, 1.0 equiv.) and THF (2.0 mL). NaBH₄ (0.5 mmol, 5.0 equiv.) was added after the reaction was cooled to 0 °C. The solution was stirred for 20 min under such conditions. Then, the mixture was diluted with water (1.0 mL) and the aqueous layer was extracted with EtOAc (3×5 mL). Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (9:1 to 4:1 Pet:EtOAc as the eluent) to afford the (M)-E1 as a white solid.



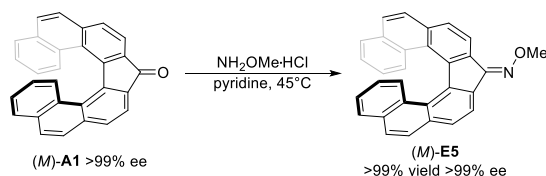
Under N₂ atmosphere, at room temperature, a test tube was charged with the (*M*)-**A1** (0.1 mmol, 1.0 equiv.) and THF (2 mL). MeMgBr (0.2 mmol, 2.0 equiv. 1 M in THF) was added after the reaction was cooled to 0 °C. The solution was stirred for 5 min under such conditions. Then, the mixture was diluted with water (1.0 mL) and the aqueous layer was extracted with EtOAc (3×5 mL). Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (9:1 to 4:1 Pet:EtOAc as the eluent) to afford the (*M*)-**E2** as a white solid.



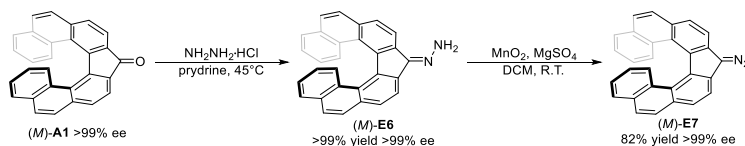
Under N₂ atmosphere, at room temperature, a test tube was charged with the (*M*)-**A1** (0.1 mmol, 1.0 equiv.) and THF (2.0 mL). PhMgBr (0.2 mmol, 2 equiv. 1 M in THF) was added after the reaction was cooled to 0 °C. The solution was stirred for 5 min under such conditions. Then, the mixture was diluted with water (1.0 mL) and the aqueous layer was extracted with EtOAc (3×5 mL). Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (9:1 Pet:EtOAc as the eluent) to afford the (*M*)-**E3** as a white solid.



Under N₂ atmosphere, at room temperature, a test tube was charged with the (*M*)-**A1** (0.1 mmol, 1.0 equiv.), H₂O (0.2 mmol, 2 equiv.), Et₃SiH (0.5 mmol, 5 equiv.) and DCM (2.0 mL). BF₃·OEt₂ (0.4 mmol, 4 equiv.) was added after the reaction was cooled to 0 °C. The resulting reaction mixture was stirred 8 h while slowly heat up to 35 °C. Upon reaction completion, the mixture was diluted with water (1 mL) and the aqueous layer was extracted with DCM (3×5 mL). Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (9:1 Pet:EtOAc as the eluent) to afford the (*M*)-**E4** as a white solid.

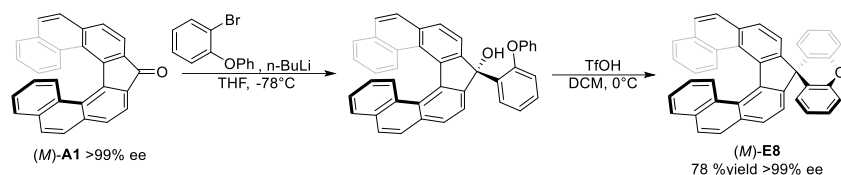


Under air atmosphere, at room temperature, a test tube was charged with the (*M*)-**A1** (0.1 mmol, 1.0 equiv.), NH₂OMe·HCl (0.5 mmol, 5.0 equiv.) and pyridine (2.0 mL). The resulting reaction mixture was heated to 45 °C and react for 8 hours. Upon reaction completion, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (9:1 to 4:1 Pet:EtOAc as the eluent) to afford the (*M*)-**E5** as a bright orange solid.

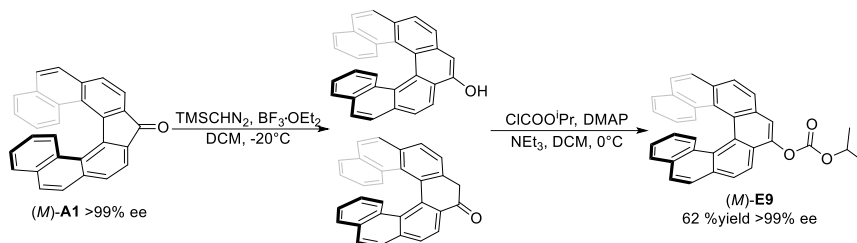


Under air atmosphere, at room temperature, a test tube was charged with the (*M*)-**A1** (0.3 mmol, 1.0 equiv.), NH₂NH₂·HCl (3 mmol, 10.0 equiv.) and pyridine (2.0 mL). The resulting reaction mixture was heated to 45 °C and react for 20 hours. Upon reaction completion, Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (4:1 to 1:1 Pet:EtOAc as the eluent) to afford the (*M*)-**E6** as an orange solid.

Under air atmosphere, at room temperature, a test tube was charged with the (*M*)-**E6** (0.1 mmol, 1.0 equiv.), MgSO₄ (0.2 mmol, 2.0 equiv.) and DCM (5.0 mL). MnO₂ (0.35 mmol, 3.5 equiv.) was added after the reaction was cooled to 0 °C. The resulting reaction mixture was warmed to room temperature and react for 1 hour. Upon reaction completion, the mixture was filtered through a pad of celite. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (4:1 to 2:1 Pet:DCM as the eluent) to afford the (*M*)-**E7** as a brownish red solid.

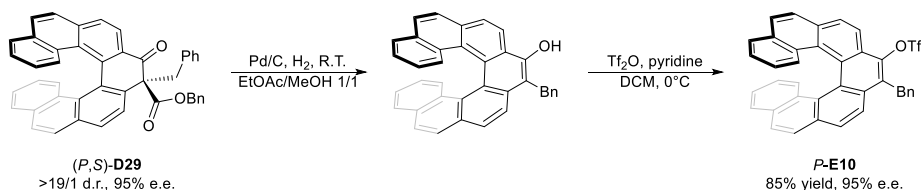


Under air atmosphere, at room temperature, a test tube was charged with the 1-bromo-2-phenoxybenzene (0.2 mmol, 2.0 equiv.) and anhydrous THF (2.0 mL). *n*-BuLi (0.22 mmol, 2.2 equiv.) was added dropwise after the reaction was cooled to -78 °C. The solution was stirred for another 30 min under such conditions, then *(M)*-A1 (0.1 mmol, 1.0 equiv. in 2.0 mL THF) was added. After addition, the reaction mixture was stay at -78 °C and further allowed to stir for 30 min then the reaction mixture was warming up to 0 °C and stirred for 30 min. After that, the reaction was quenched by 5 mL water, and the aqueous layer was extracted with EtOAc (2×5 mL). The combined organic phases were washed with saturated NaCl (2×20 mL), dried over anhydrous Na₂SO₄. The solution was concentrated under reduced pressure, and the crude residue was dissolved in DCM (5.0 mL) then TfOH (0.01 mmol, 0.1 equiv.) was added. After addition, the reaction mixture was allowed to stir 10 min. Upon reaction completion the mixture was diluted with saturated NaHCO₃ 10 mL and the aqueous layer was extracted with DCM (2×5 mL). The combined organic phases were washed with saturated NaCl (10 mL), dried over Na₂SO₄. Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (4:1 Pet:DCM as the eluent) to afford the *(M)*-E8 as a white solid.



Under N₂ atmosphere, at room temperature, a test tube was charged with the *(M)*-A1 (0.2 mmol, 1.0 equiv.), BF₃•OEt₂ (0.4 mmol, 2 equiv.) and DCM (2.0 mL). TMSCHN₂ (0.8 mmol, 4 equiv.) was added after the reaction was cooled to -40 °C. The solution was stirred for 2 mins under such conditions. Then, the mixture was diluted with water (1 mL) and the aqueous layer was extracted with DCM (3×5 mL). The combined organic phases were washed with saturated aq. NaCl (2×20 mL), dried over anhydrous Na₂SO₄ and the solution was concentrated under reduced pressure affording the product as a light yellow solid (mixture of ketone and enol) which was used without further purification.

Under air atmosphere, at room temperature, a test tube was charged with the mixture of ketone and enol (0.2 mmol, 1.0 equiv.), DMAP (0.02 mmol, 0.1 equiv.), NEt₃ (0.4 mmol, 2 equiv.) and DCM (5 mL). ClCOOPr (0.3 mmol, 1.5 equiv.) was added after the reaction was cooled to 0 °C. The solution was stirred for 20 mins under such conditions. Then, the mixture was diluted with water (1 mL) and the aqueous layer was extracted with DCM (3×5 mL). Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (9:1 to 4:1 Pet:EtOAc as the eluent) to afford the *(M)*-E9 as a light yellow solid.



Under H₂ atmosphere, at room temperature, a test tube was charged with the *(P,S)*-D29 (0.2 mmol, 1.0 equiv.), Pd/C (13 mg) and MeOH/EtOAc 1:1 2 mL. The solution was stirred for 30 mins under such conditions. Upon reaction completion, the mixture was filtered through a pad of celite. Then, the solution was concentrated under reduced pressure affording the product as a light-yellow solid which was used without further purification.

Under air atmosphere, at room temperature, a test tube was charged with the phenol (0.2 mmol, 1.0 equiv.), pyridine (0.3 mmol, 1.5 equiv.) and DCM (5 mL). Tf₂O (0.3 mmol, 1.5 equiv.) was added after the reaction was cooled to 0 °C. The solution was stirred for 5 mins under such conditions. Then, the mixture was diluted with water (1 mL) and the aqueous layer was extracted with DCM (3×5 mL). Then, the solution was concentrated under reduced pressure, the crude residue was subjected to column chromatography on silica gel (15:1 to 9:1 Pet:Et₂O as the eluent) to afford the *(P)*-E10 as a light-yellow solid.

7. UV Absorption and Circular Dichroism.

isobutyl (*P, S*)-9-benzyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate

1×10^{-3} mmol/mL in DCM, 349 nm, $|g_{\text{abs}}| = 1.33 \times 10^{-2}$.

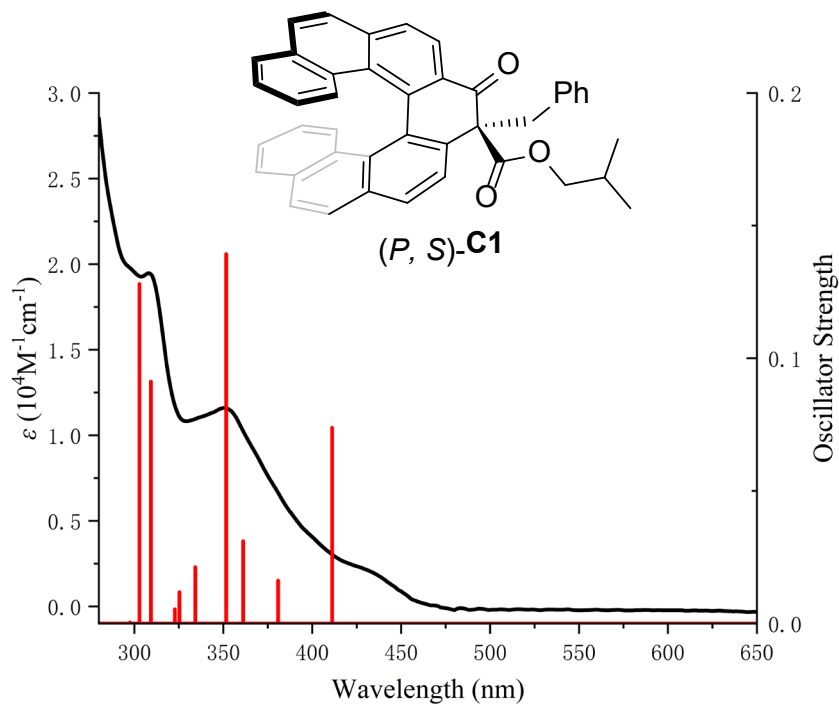


Figure S1 Experimental UV/vis spectrum of (*P, S*)-C1 (black line) and Oscillator strength f of (*P, S*)-C1 (red bar) calculated by the TD-DFT method at the PBE0/def2-TZVP level of theory.

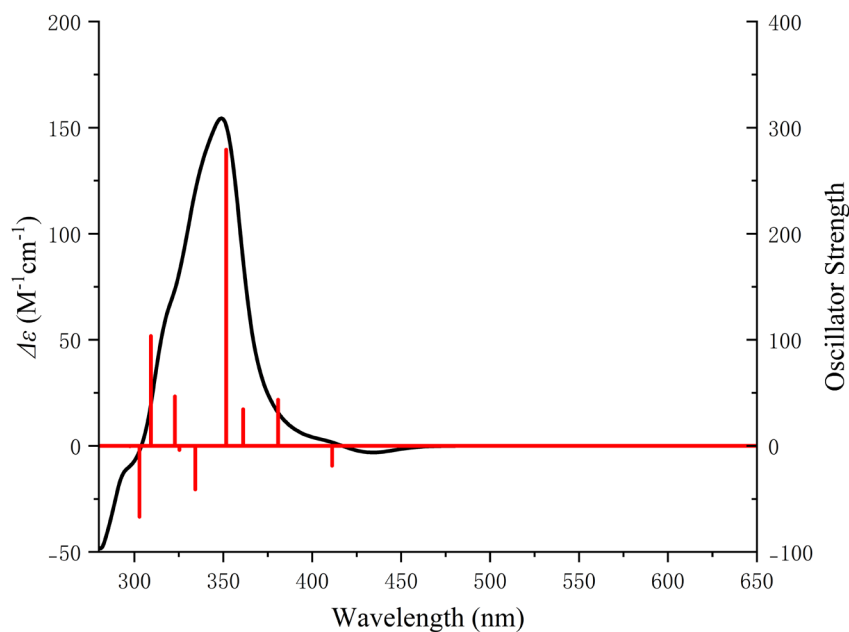


Figure S2. Experimental ECD spectrum of (*P, S*)-C1 (black line) and rotatory strength R of (*P, S*)-C1 (red bar) calculated by the TD-DFT method at the PBE0/def2-TZVP level of theory.

isobutyl (*M, R*)-9-benzyl-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate

1×10^{-3} mmol/mL in DCM, 349 nm, $|g_{\text{abs}}| = 1.33 \times 10^{-2}$.

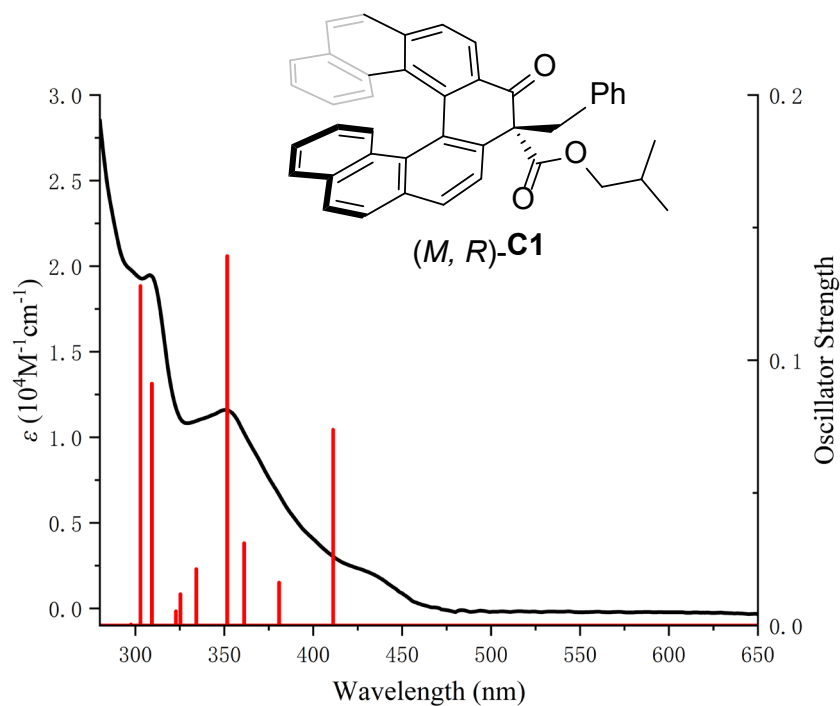


Figure S3. Experimental UV/vis spectrum of (*M, R*)-C1 (black line) and Oscillator strength f of (*M, R*)-C1 (red bar) calculated by the TD-DFT method at the PBE0/def2-TZVP level of theory.

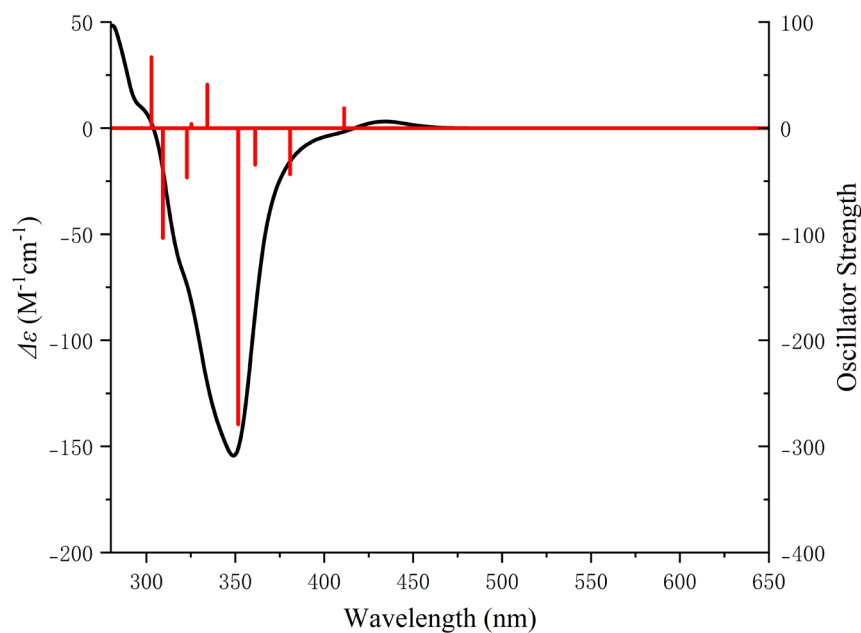


Figure S4. Experimental ECD spectrum of (*M, R*)-C1 (black line) and rotatory strength R of (*M, R*)-C1 (red bar) calculated by the TD-DFT method at the PBE0/def2-TZVP level of theory.

isobutyl (*M, S*)-9-benzyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate

1×10^{-3} mmol/mL in DCM, 349 nm, $|g_{\text{abs}}| = 1.40 \times 10^{-2}$.

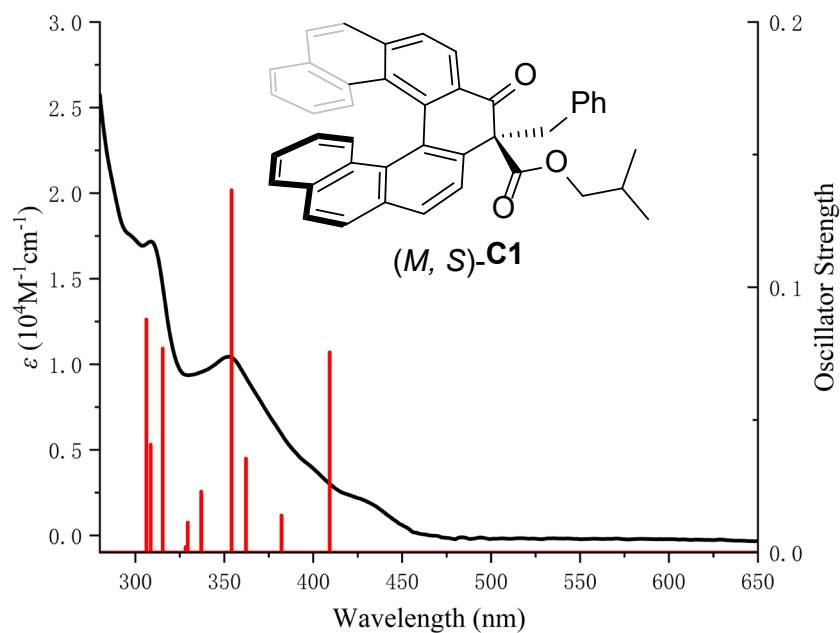


Figure S5. Experimental UV/vis spectrum of (*M, S*)-C1 (black line) and Oscillator strength f of (*M, S*)-C1 (red bar) calculated by the TD-DFT method at the PBE0/def2-TZVP level of theory.

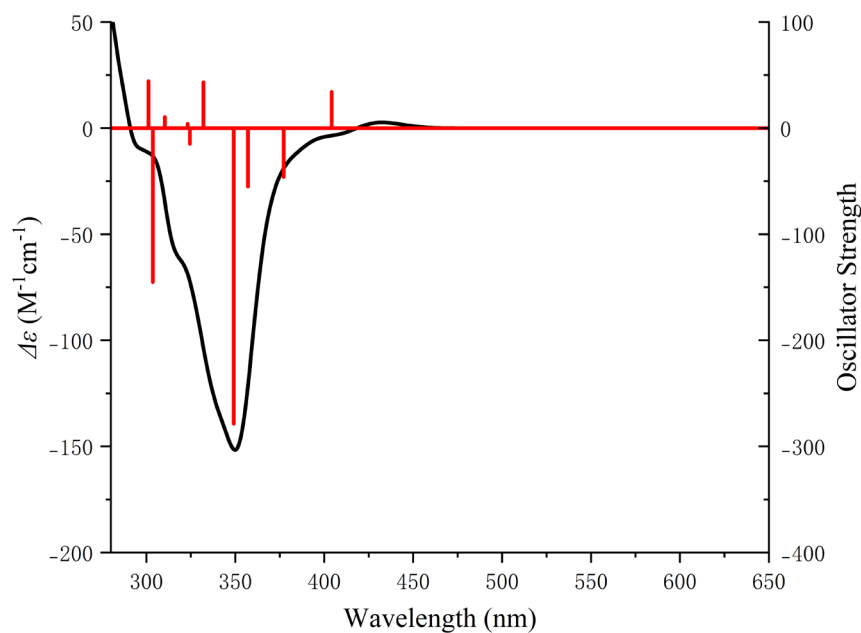


Figure S6. Experimental ECD spectrum of (*M, S*)-C1 (black line) and rotatory strength R of (*M, S*)-C1 (red bar) calculated by the TD-DFT method at the PBE0/def2-TZVP level of theory.

isobutyl (*P, R*)-9-benzyl-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate

1×10^{-3} mmol/mL in DCM, 349 nm, $|g_{\text{abs}}| = 1.40 \times 10^{-2}$.

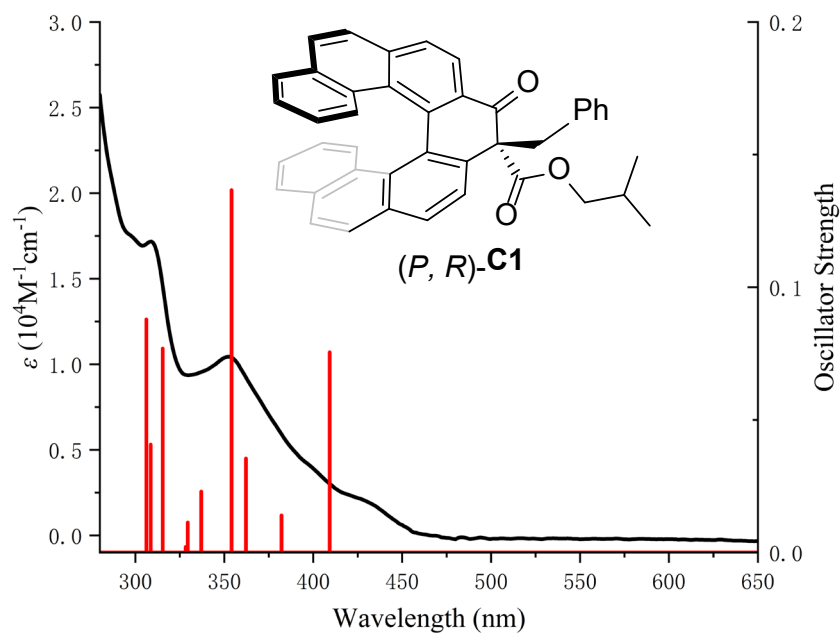


Figure S7. Experimental UV/vis spectrum of (*P, R*)-C1 (black line) and Oscillator strength f of (*P, R*)-C1 (red bar) calculated by the TD-DFT method at the PBE0/def2-TZVP level of theory.

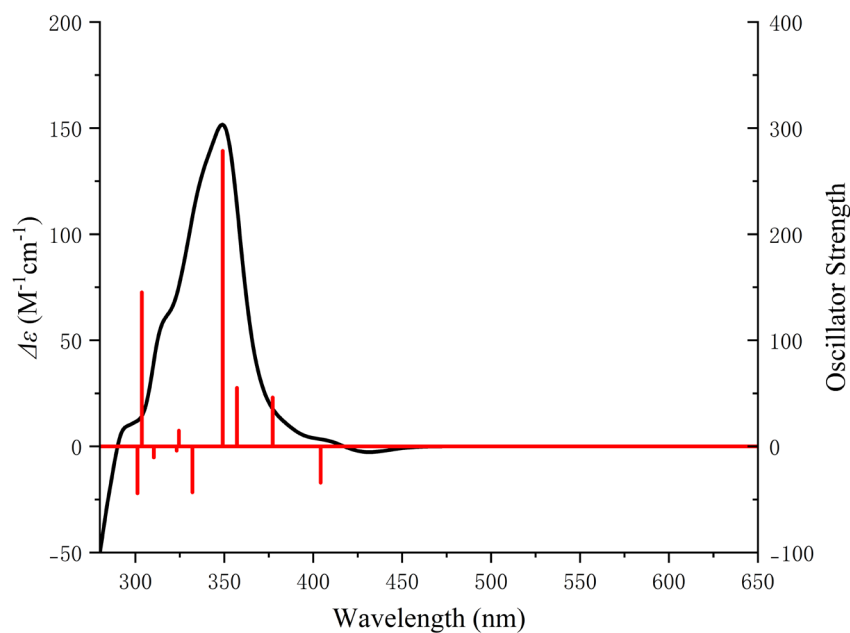


Figure S8. Experimental ECD spectrum of (*P, R*)-C1 (black line) and rotatory strength R of (*P, R*)-C1 (red bar) calculated by the TD-DFT method at the PBE0/def2-TZVP level of theory.

(P)-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A1)

1×10^{-3} mmol/mL in DCM, 362 nm, $|g_{\text{abs}}| = 7.66 \times 10^{-3}$.

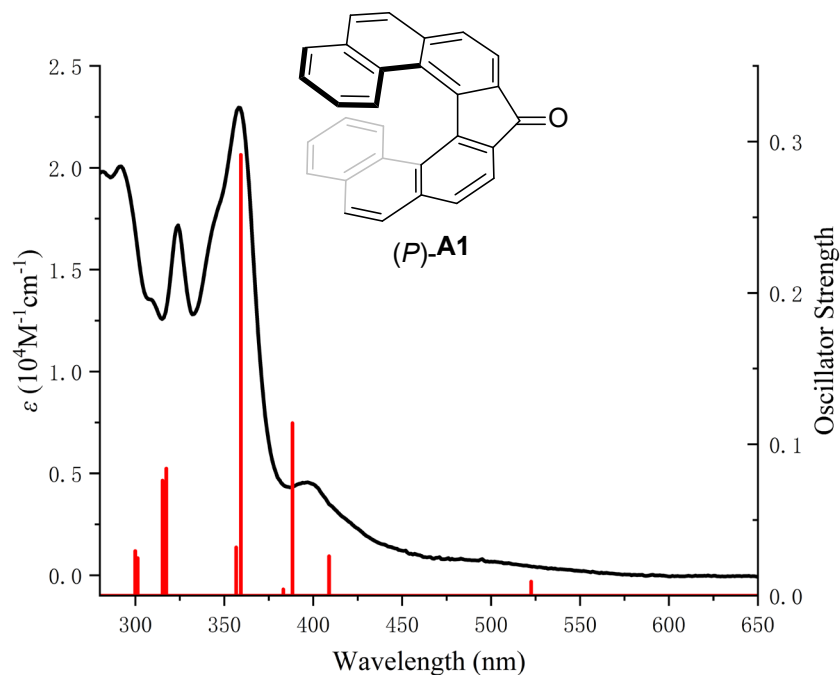


Figure S9. Experimental UV/vis spectrum of (M)-A1 (black line) and Oscillator strength f of (M)-A1 (red bar) calculated by the TD-DFT method at the PBE0/def2-TZVP level of theory.

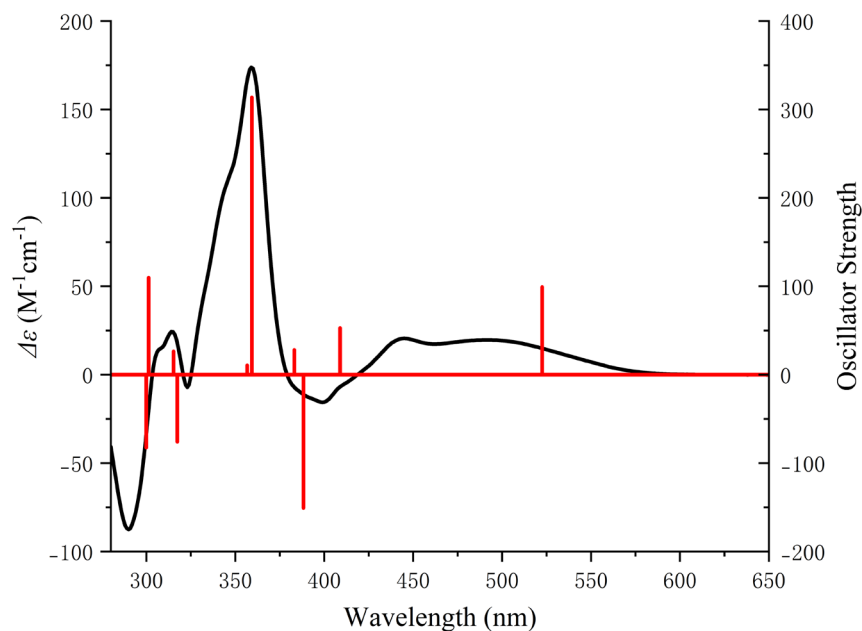


Figure S10. Experimental ECD spectrum of (M)-A1 (black line) and rotatory strength R of (M)-A1 (red bar) calculated by the TD-DFT method at the PBE0/def2-TZVP level of theory.

(*M*)-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A1)

1×10^{-3} mmol/mL in DCM, 362 nm, $|g_{\text{abs}}| = 7.66 \times 10^{-3}$.

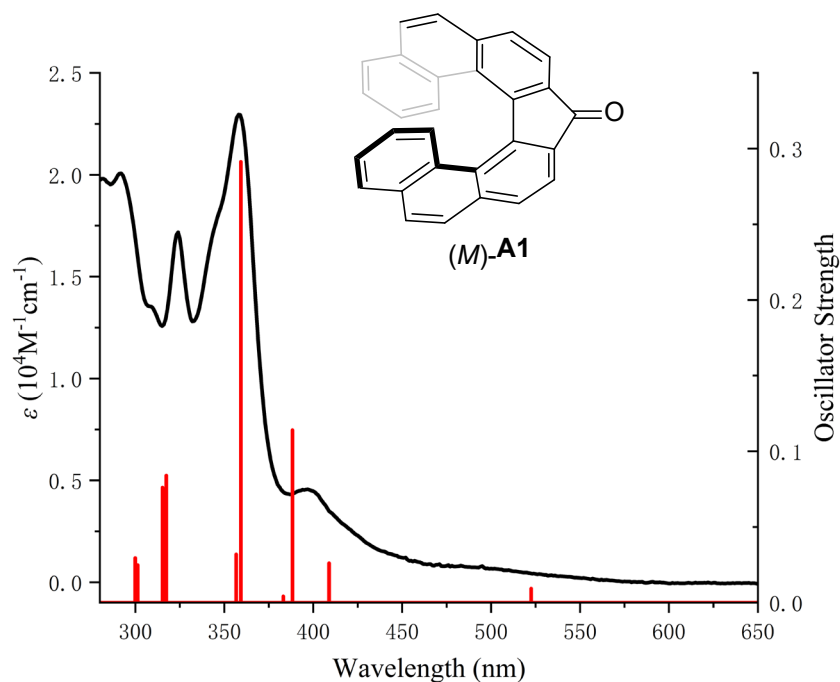


Figure S11. Experimental UV/vis spectrum of (*M*)-A1 (black line) and Oscillator strength f of (*M*)-A1 (red bar) calculated by the TD-DFT method at the PBE0/def2-TZVP level of theory.

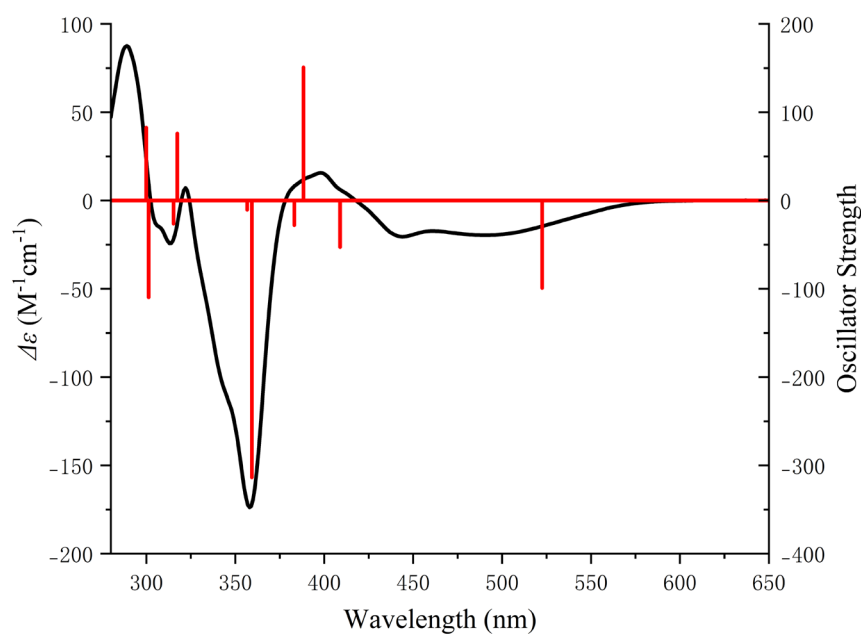


Figure S12. Experimental ECD spectrum of (*M*)-A1 (black line) and rotatory strength R of (*M*)-A1 (red bar) calculated by the TD-DFT method at the PBE0/def2-TZVP level of theory.

(*M*)-2,16-dimethyl-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A2)

1×10^{-3} mmol/mL in DCM, 366 nm, $|g_{\text{abs}}| = 8.27 \times 10^{-3}$.

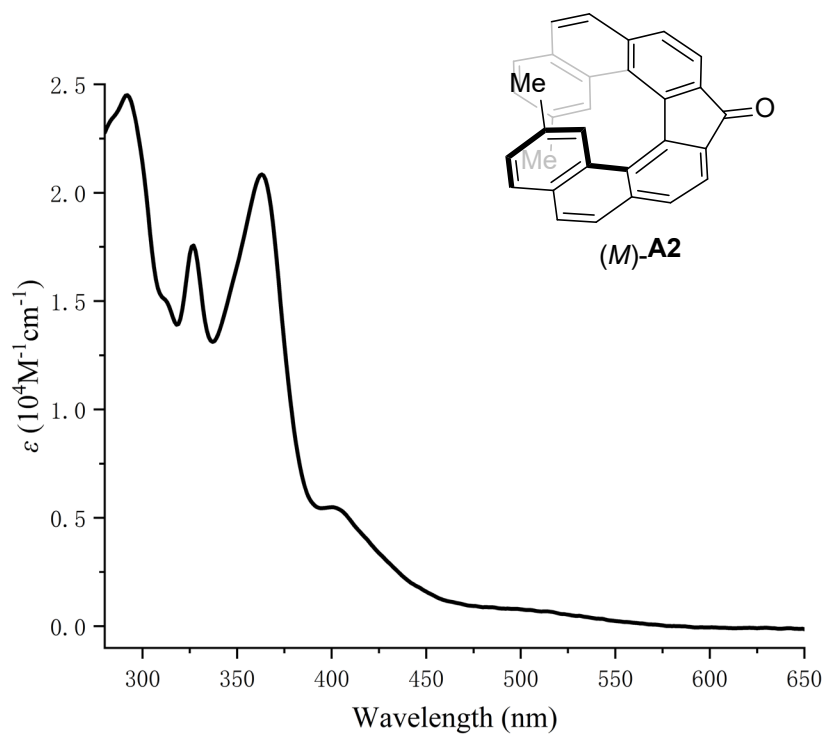


Figure S13. Experimental UV/vis absorption spectrum of (*M*)-A2.

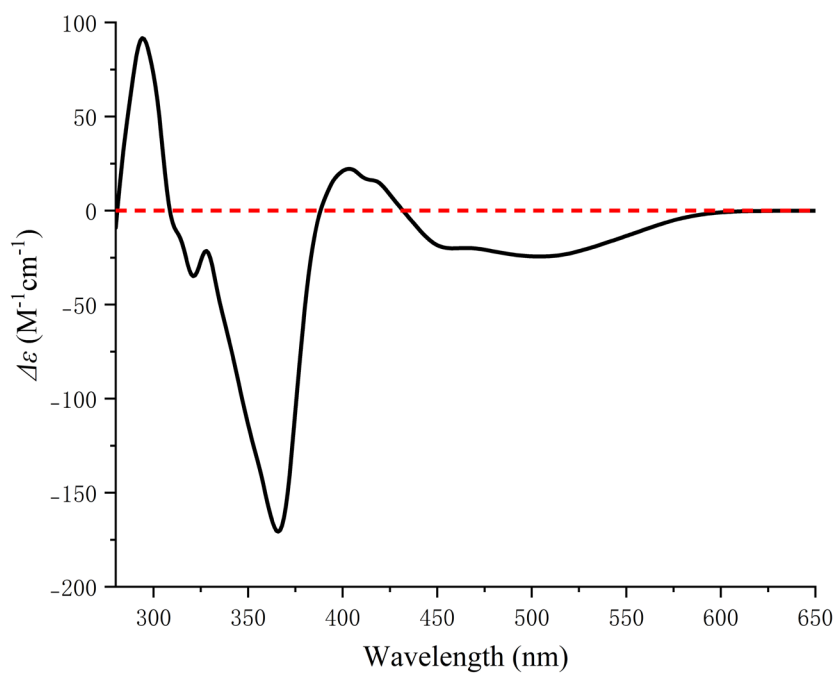


Figure S14. Experimental ECD spectrum of (*M*)-A2.

(M)-3,15-dimethyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A3)

1×10^{-3} mmol/mL in DCM, 363 nm, $|g_{\text{abs}}| = 7.83 \times 10^{-3}$.

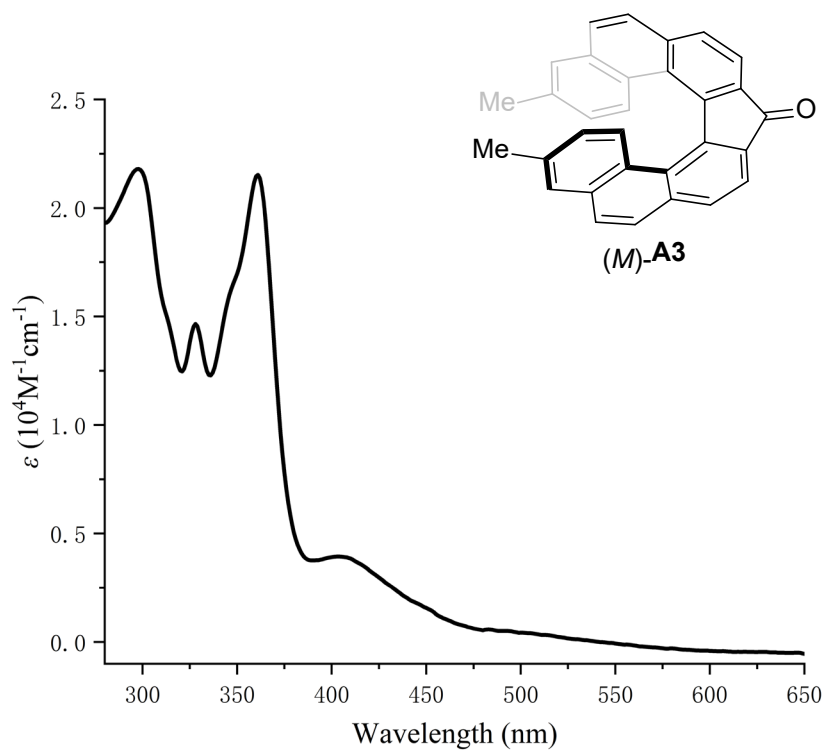


Figure S15. Experimental UV/vis absorption spectrum of (M)-A3.

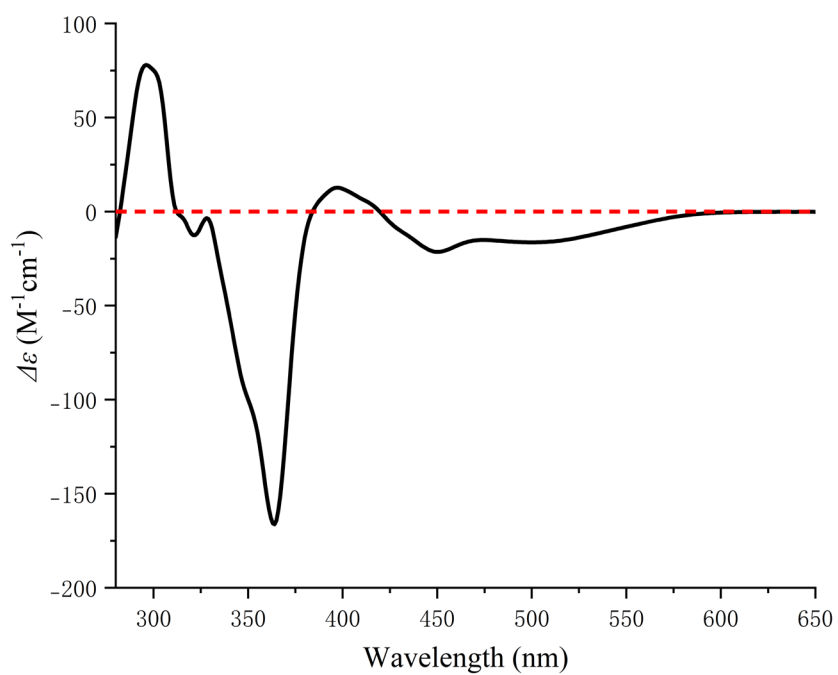


Figure S16. Experimental ECD spectrum of (M)-A3.

(*M*)-4,14-dimethyl-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A4)

1×10^{-3} mmol/mL in DCM, 367 nm, $|g_{\text{abs}}| = 6.86 \times 10^{-3}$.

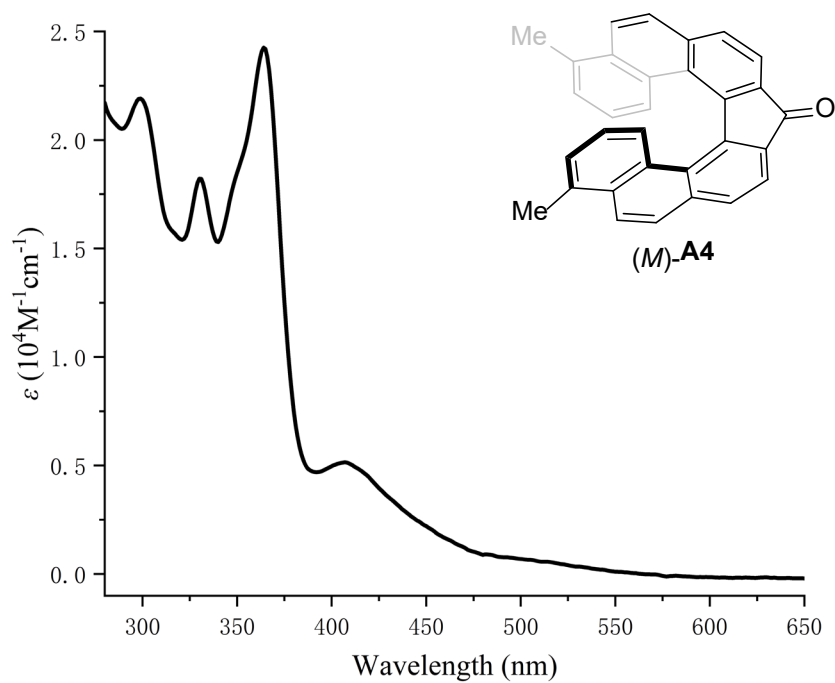


Figure S17. Experimental UV/vis absorption spectrum of (*M*)-A4.

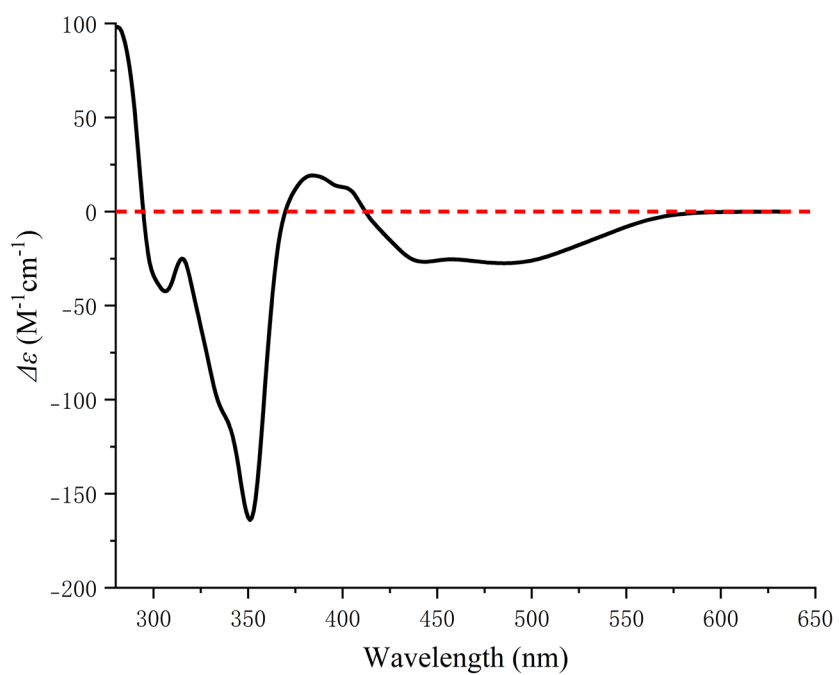


Figure S18. Experimental ECD spectrum of (*M*)-A4.

(*M*)-5,13-dimethyl-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A5)

1×10^{-3} mmol/mL in DCM, 367 nm, $|g_{\text{abs}}| = 5.84 \times 10^{-3}$.

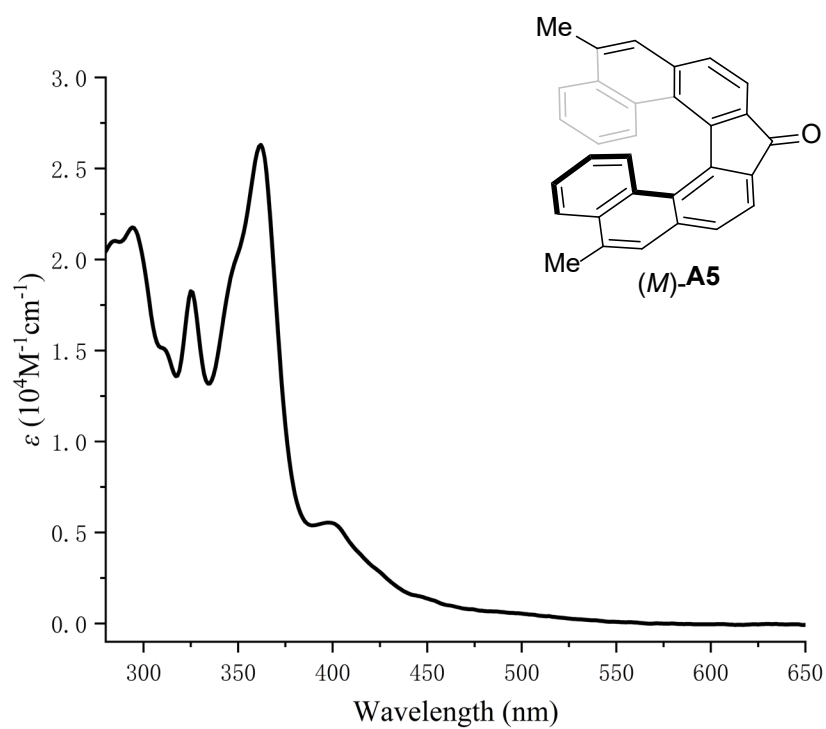


Figure S19. Experimental UV/vis absorption spectrum of (*M*)-A5.

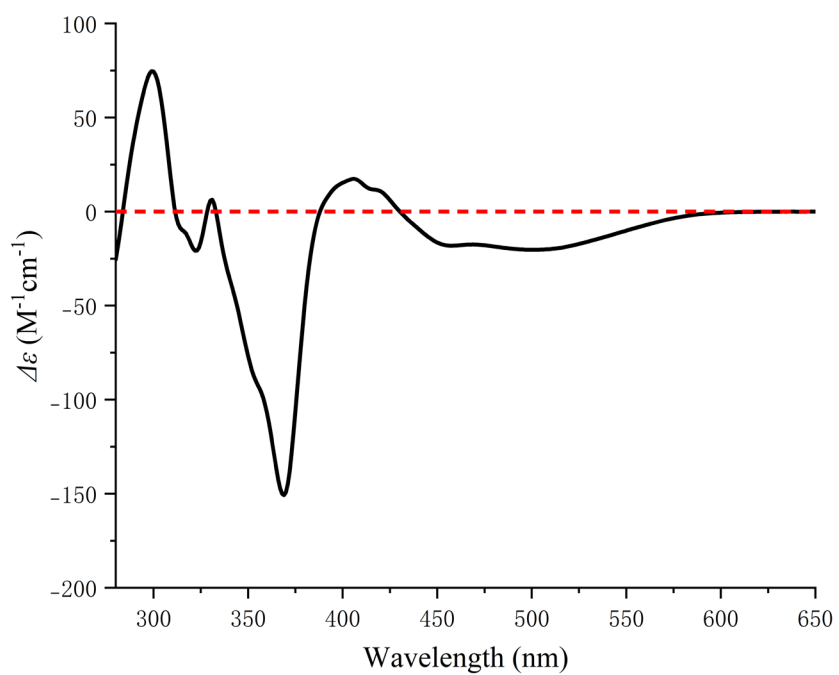


Figure S20. Experimental ECD spectrum of (*M*)-A5.

(M)-5,13-dimethyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A6)

1×10^{-3} mmol/mL in DCM, 366 nm, $|g_{\text{abs}}| = 5.20 \times 10^{-3}$.

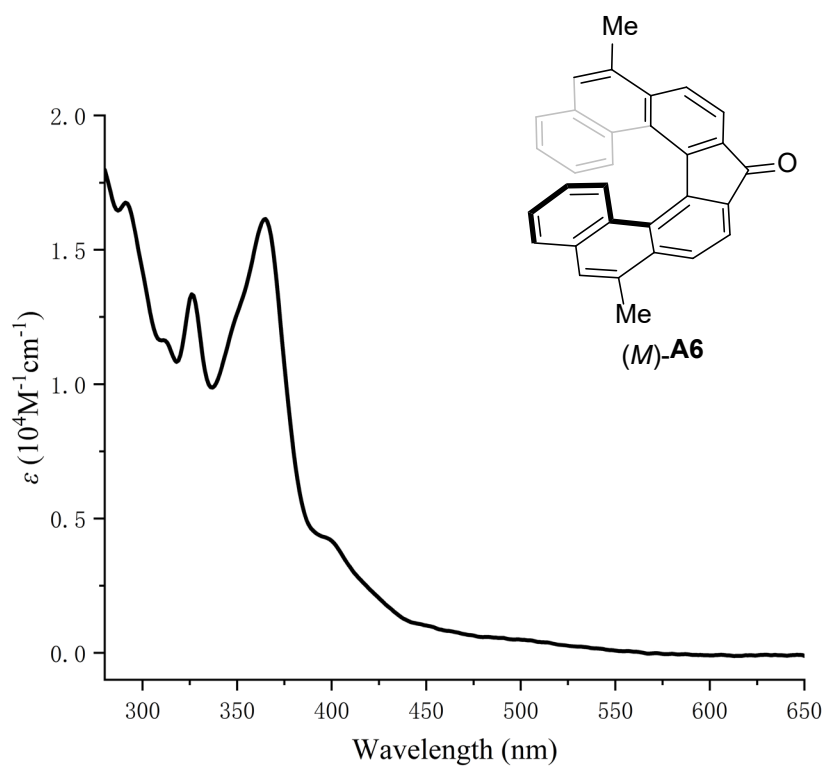


Figure S21. Experimental UV/vis absorption spectrum of (M)-A6.

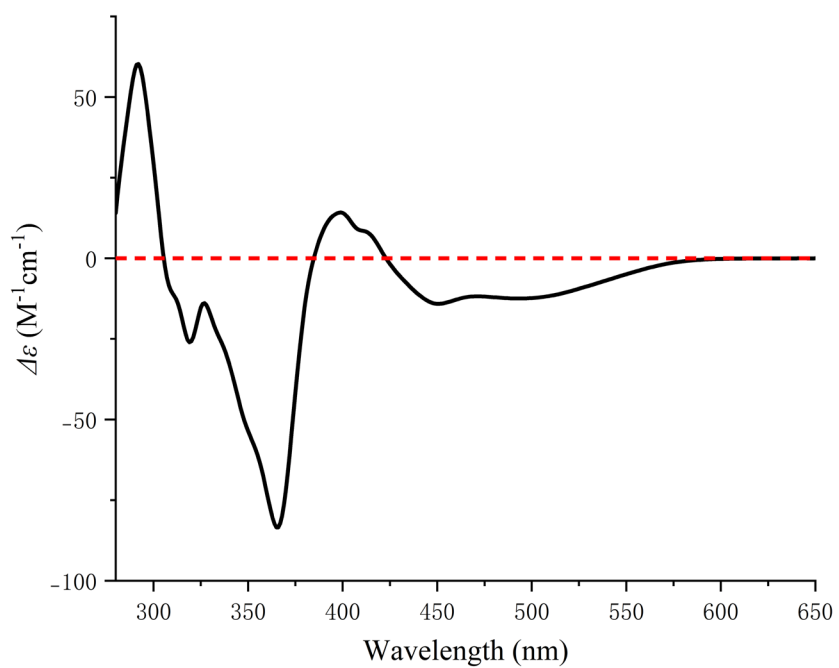


Figure S22. Experimental ECD spectrum of (M)-A6.

(M)-2,16-difluoro-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A7)

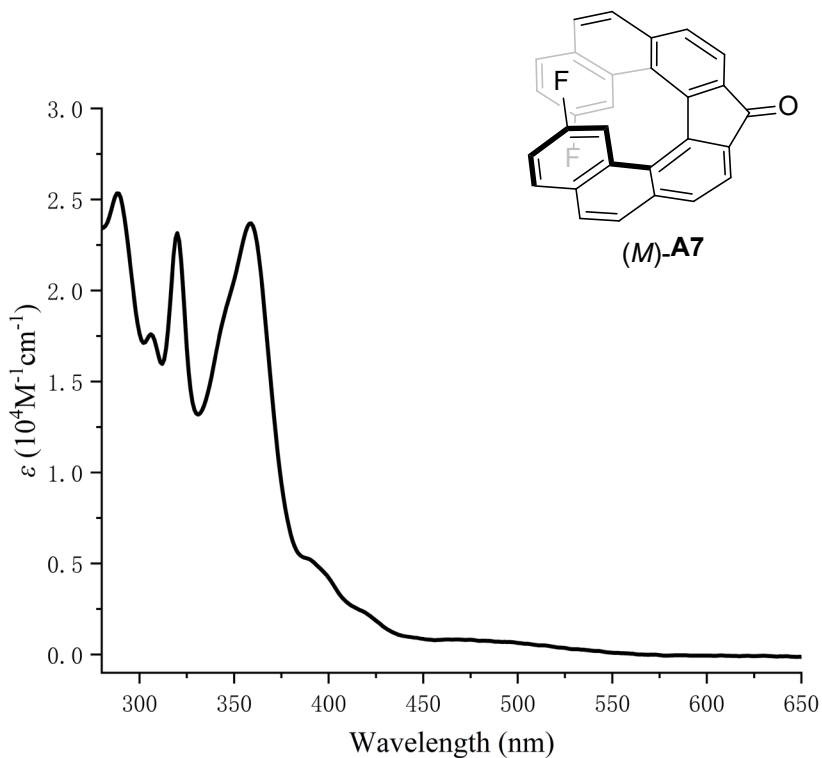
 1×10^{-3} mmol/mL in DCM, 361 nm, $|g_{\text{abs}}| = 6.59 \times 10^{-3}$.

Figure S23. Experimental UV/vis absorption spectrum of (*M*)-A7.

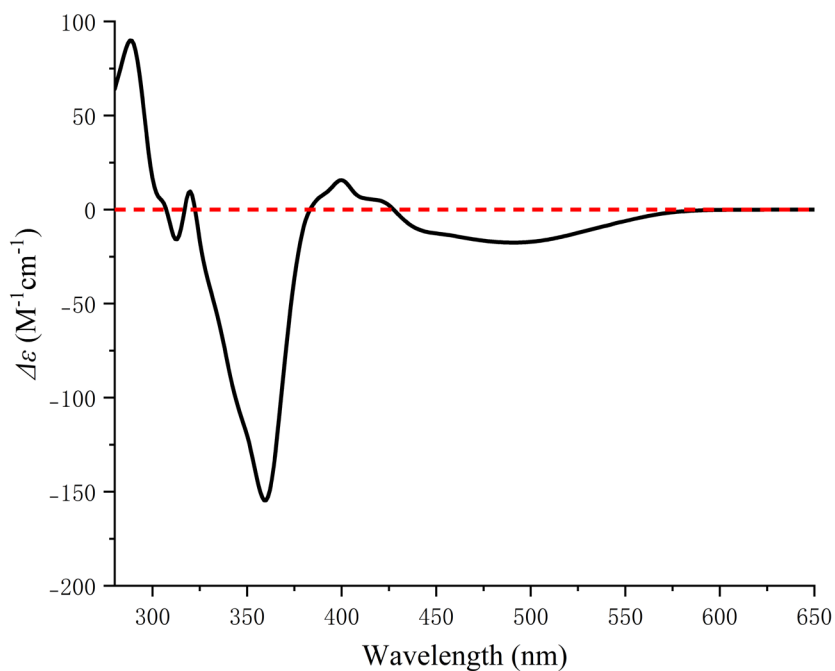


Figure S24. Experimental ECD spectrum of (*M*)-A6.

(*M*)-3,15-difluoro-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A8**)**

1×10^{-3} mmol/mL in DCM, 358 nm, $|g_{\text{abs}}| = 7.78 \times 10^{-3}$.

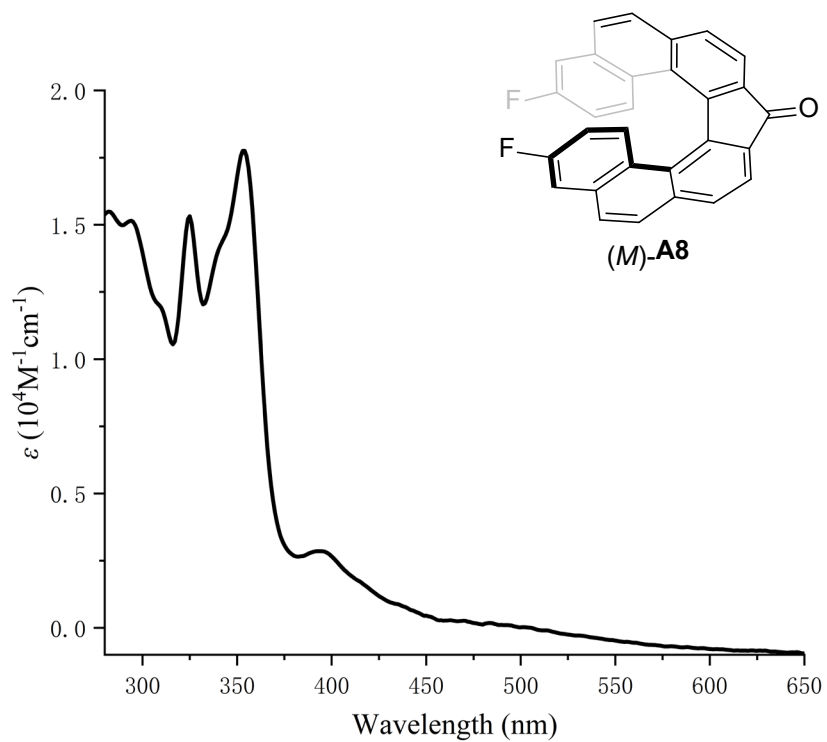


Figure S25. Experimental UV/vis absorption spectrum of (*M*)-**A8**

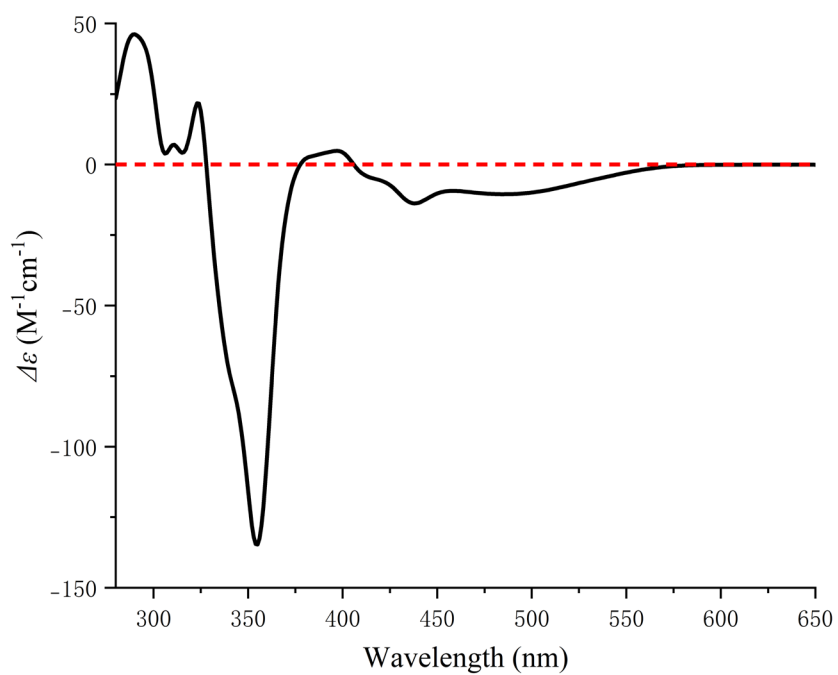


Figure S26. Experimental ECD spectrum of (*M*)-**A8**

(*M*)-4,14-difluoro-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A9**)**

1×10^{-3} mmol/mL in DCM, 362 nm, $|g_{\text{abs}}| = 0.79 \times 10^{-3}$.

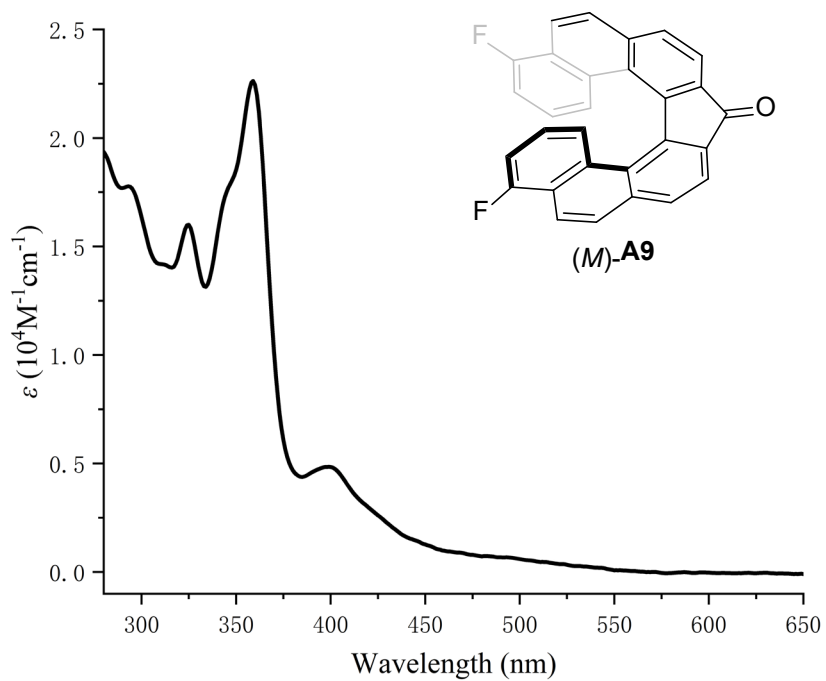


Figure S27. Experimental UV/vis absorption spectrum of (*M*)-**A8**

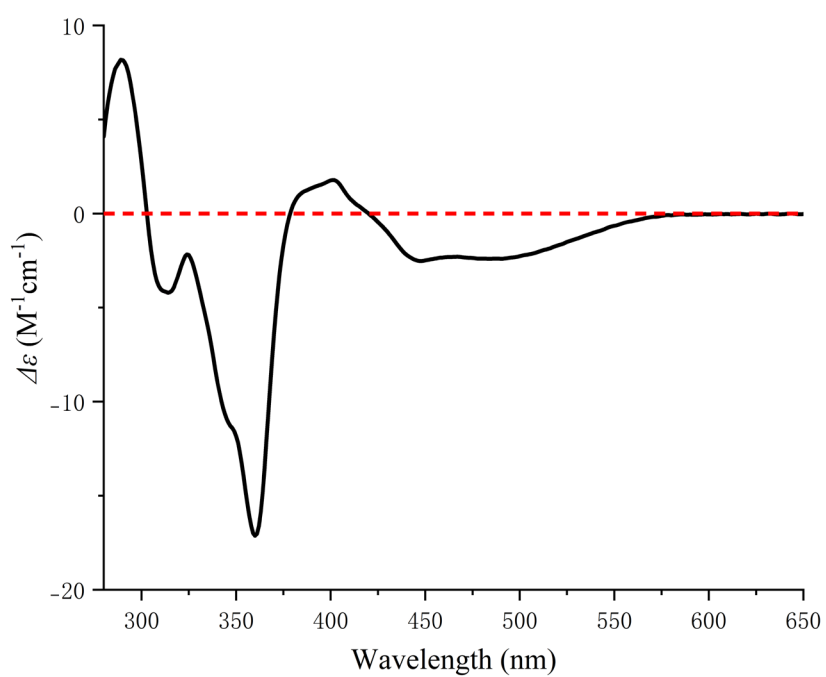


Figure S28. Experimental ECD spectrum of (*M*)-**A9**.

(*M*)-3,15-dimethoxy-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A10)

1×10^{-3} mmol/mL in DCM, 365 nm, $|g_{\text{abs}}| = 7.09 \times 10^{-3}$.

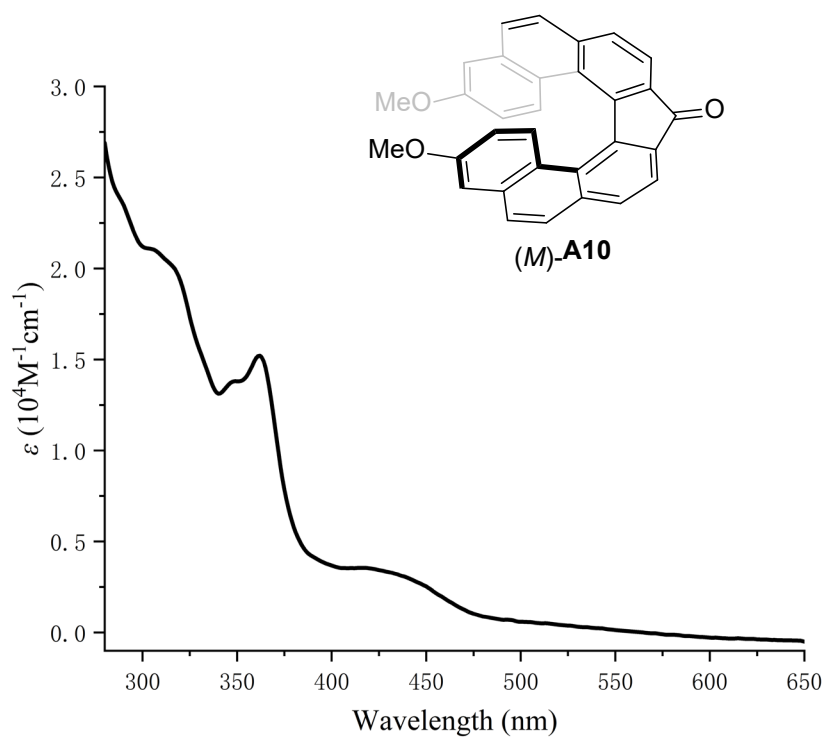


Figure S29. Experimental UV/vis absorption spectrum of (*M*)-A10.

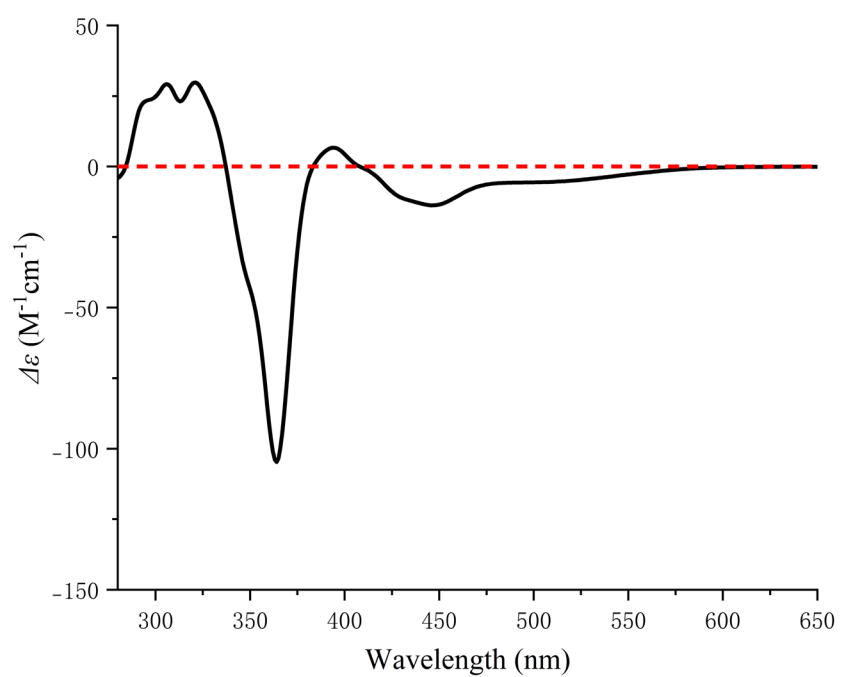


Figure S30. Experimental ECD spectrum of (*M*)-A10.

(*M*)-3,15-bis(trifluoromethyl)-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A11)

1×10^{-3} mmol/mL in DCM, 361 nm, $|g_{\text{abs}}| = 8.39 \times 10^{-3}$.

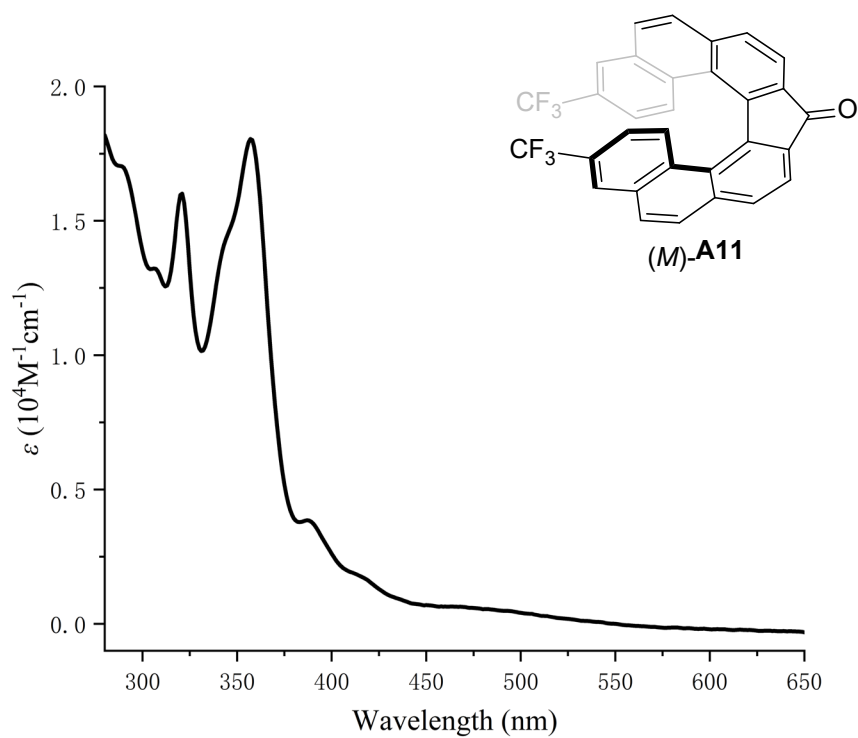


Figure S31. Experimental UV/vis absorption spectrum of (*M*)-A11.

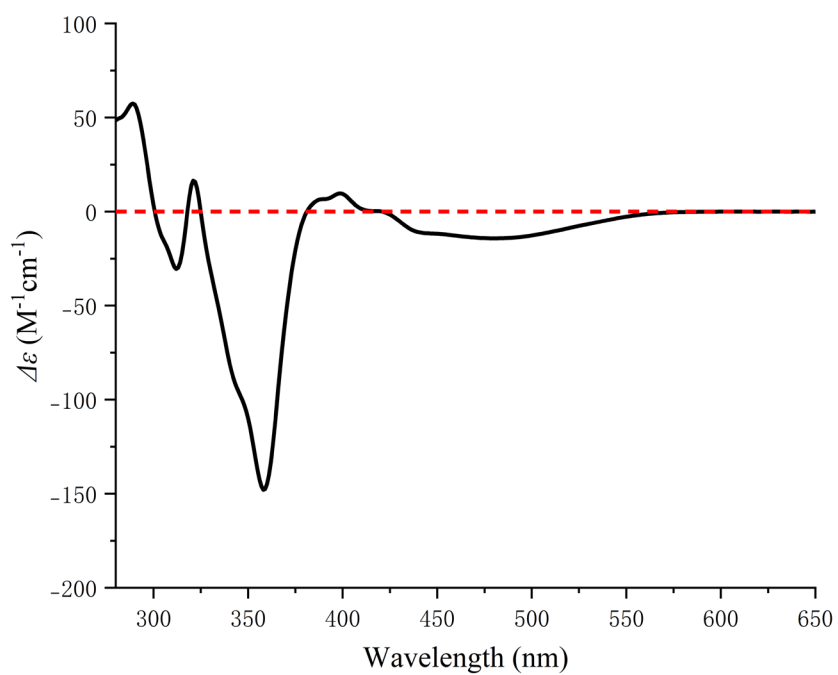


Figure S32. Experimental ECD spectrum of (*M*)-A11.

(*M*)-3,15-diethyl-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A12)

1×10^{-3} mmol/mL in DCM, 364 nm, $|g_{\text{abs}}| = 7.76 \times 10^{-3}$.

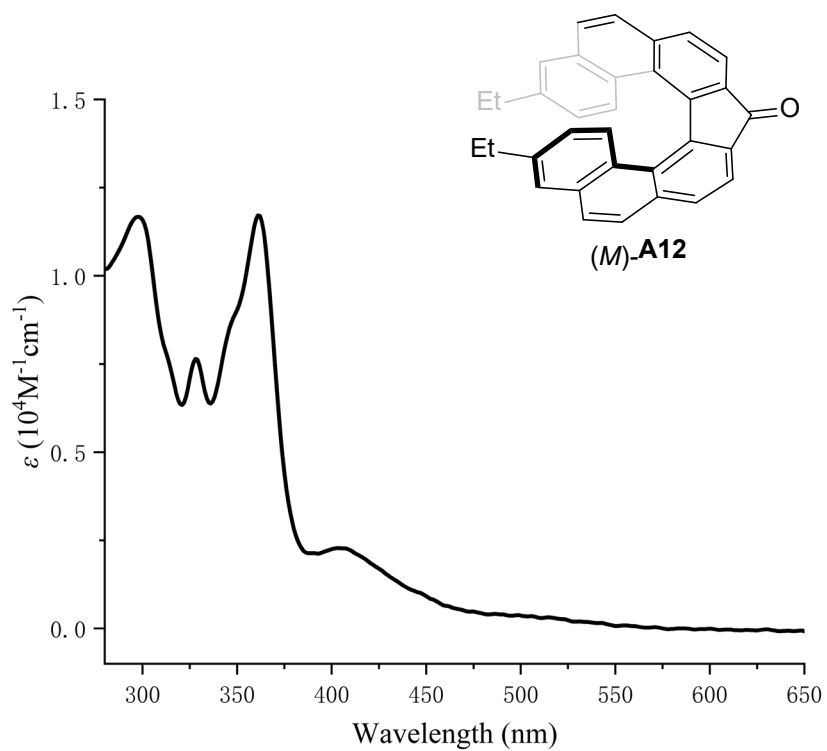


Figure S33. Experimental UV/vis absorption spectrum of (*M*)-A12.

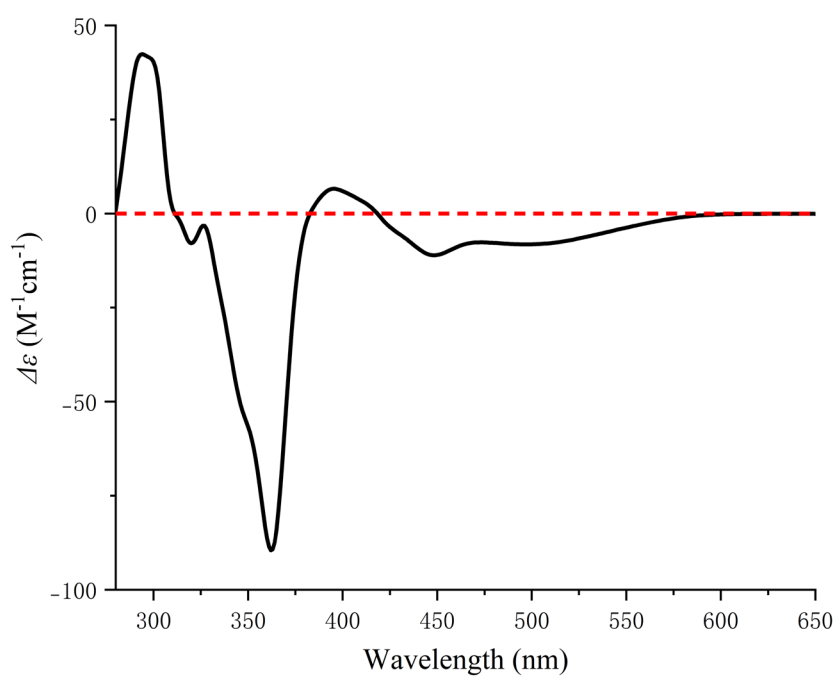


Figure S34. Experimental ECD spectrum of (*M*)-A12.

(*M*)-3,15-diisopropyl-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A13)

1×10^{-3} mmol/mL in DCM, 364 nm, $|g_{\text{abs}}| = 8.39 \times 10^{-3}$.

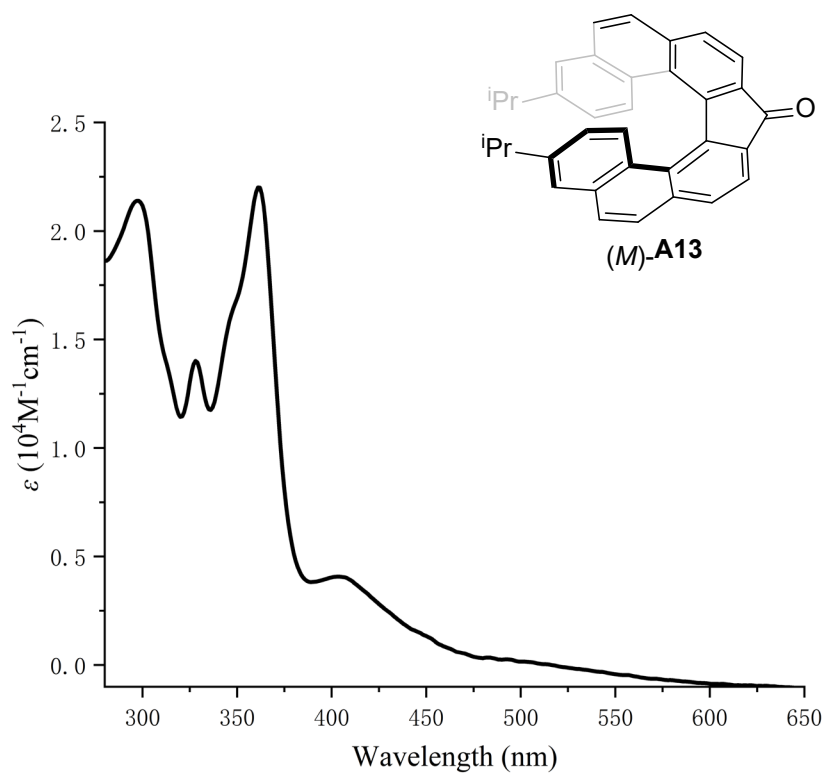


Figure S35. Experimental UV/vis absorption spectrum of (*M*)-A13.

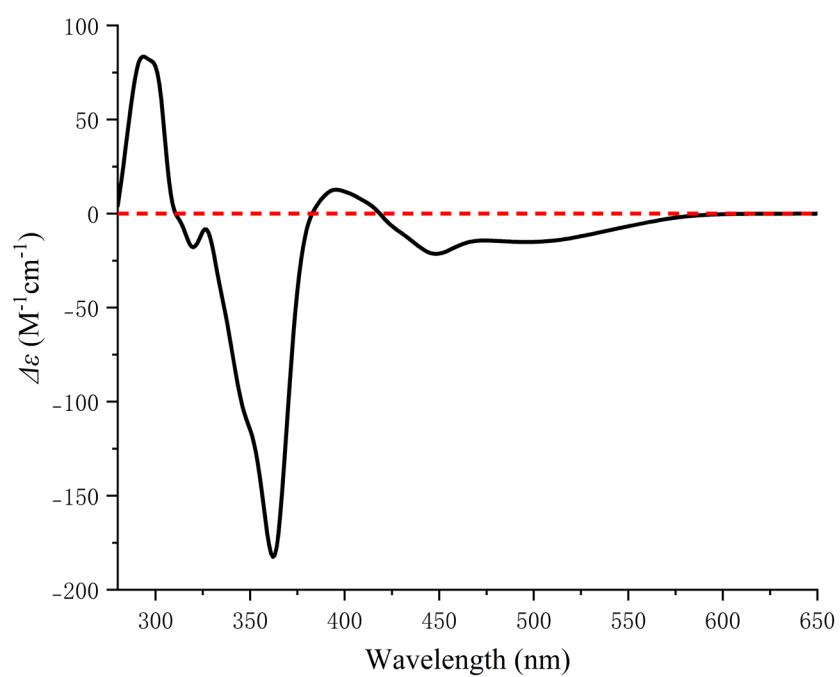


Figure S36. Experimental ECD spectrum of (*M*)-A13.

(*M*)-3,15-di-*tert*-butyl-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A14)

1×10^{-3} mmol/mL in DCM, 364 nm, $|g_{\text{abs}}| = 8.98 \times 10^{-3}$.

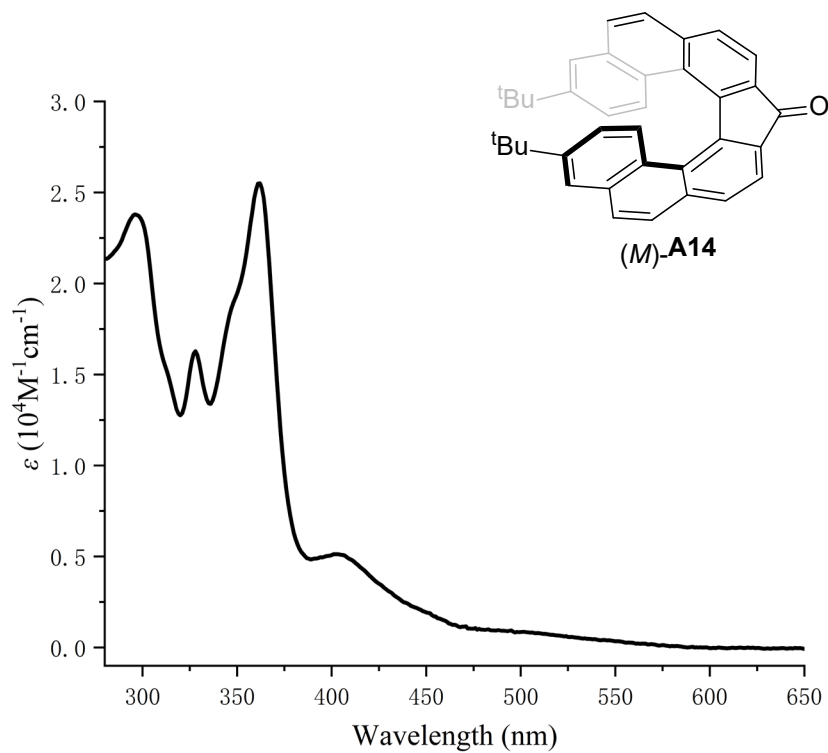


Figure S37. Experimental UV/vis absorption spectrum of (*M*)-A14.

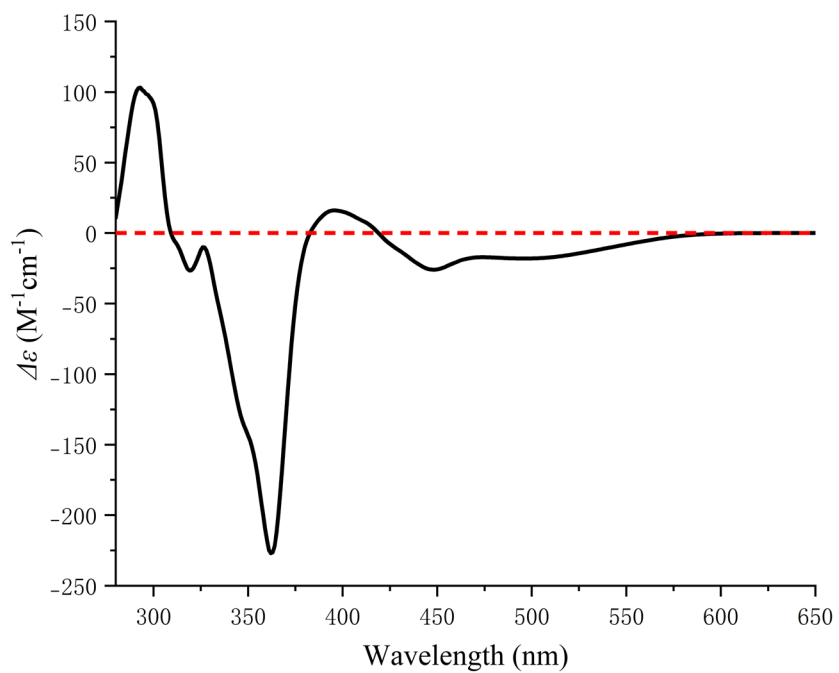


Figure S38. Experimental ECD spectrum of (*M*)-A14.

(M)-3,15-diphenyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A15)

1×10^{-3} mmol/mL in DCM, 375 nm, $|g_{\text{abs}}| = 1.13 \times 10^{-2}$.

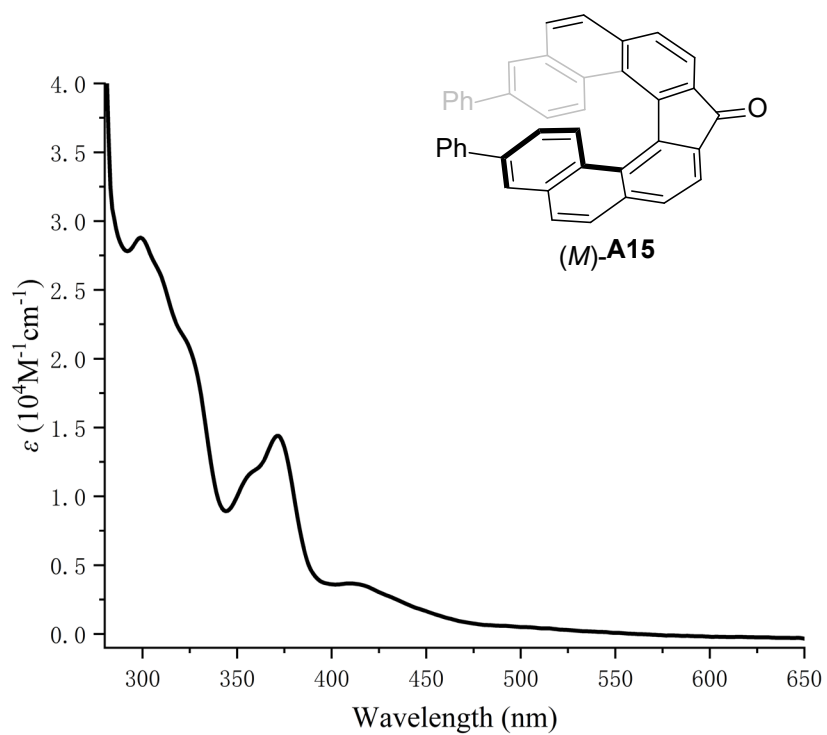


Figure S39 Experimental UV/vis absorption spectrum of (M)-A15.

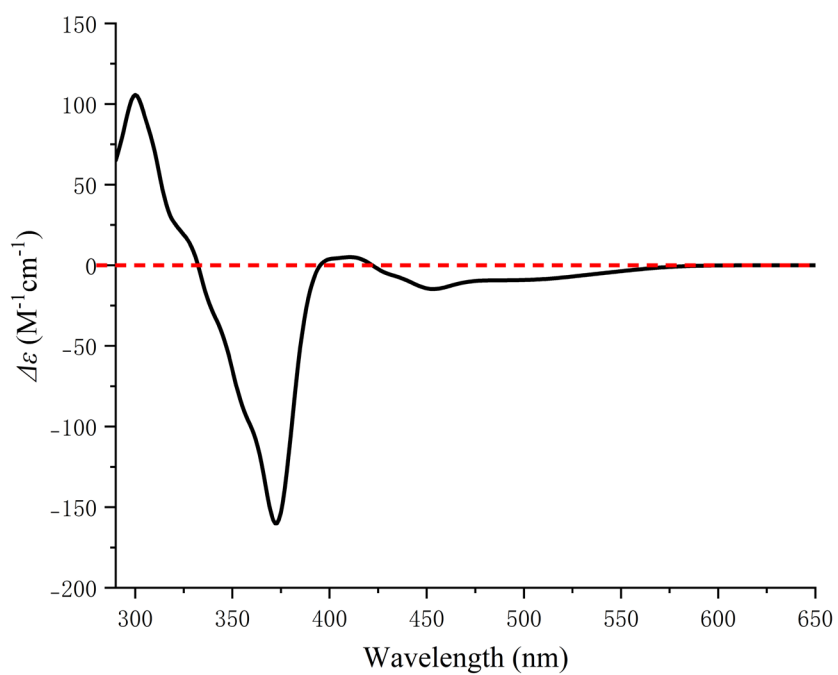


Figure S40. Experimental ECD spectrum of (M)-A15.

(*M*)-2,4,14,16-tetramethyl-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A16)

1×10^{-3} mmol/mL in DCM, 379 nm, $|g_{\text{abs}}| = 5.67 \times 10^{-3}$.

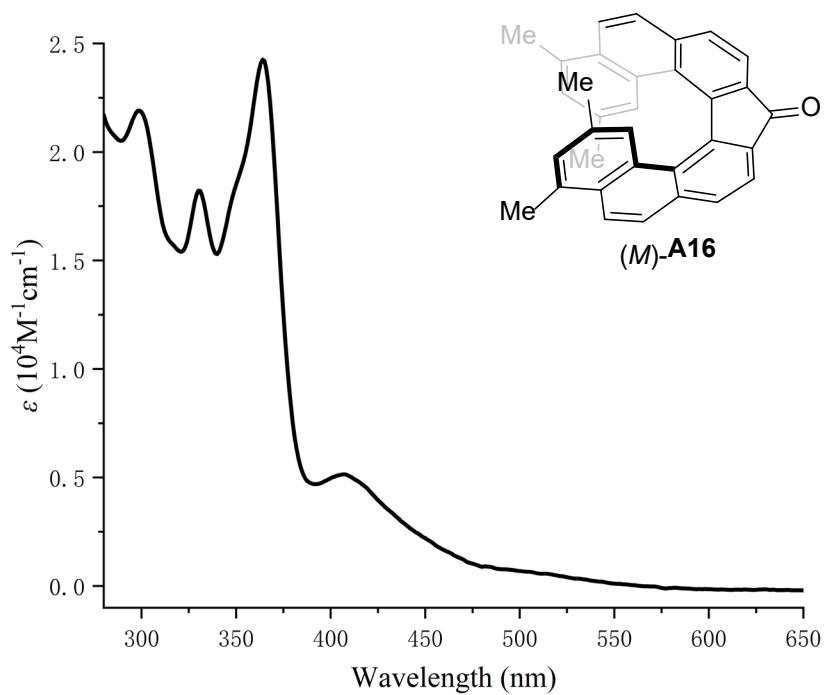


Figure S41. Experimental UV/vis absorption spectrum of (*M*)-A16.

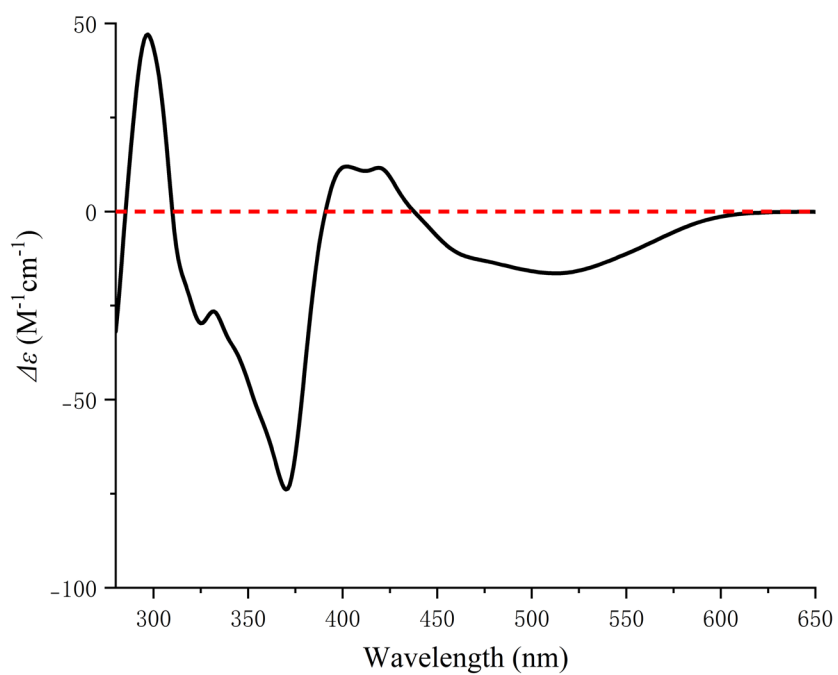


Figure S42. Experimental ECD spectrum of (*M*)-A16.

(*M*)-2,3,15,16-tetrafluoro-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A17)

1×10^{-3} mmol/mL in DCM, 363 nm, $|g_{\text{abs}}| = 8.8 \times 10^{-3}$.

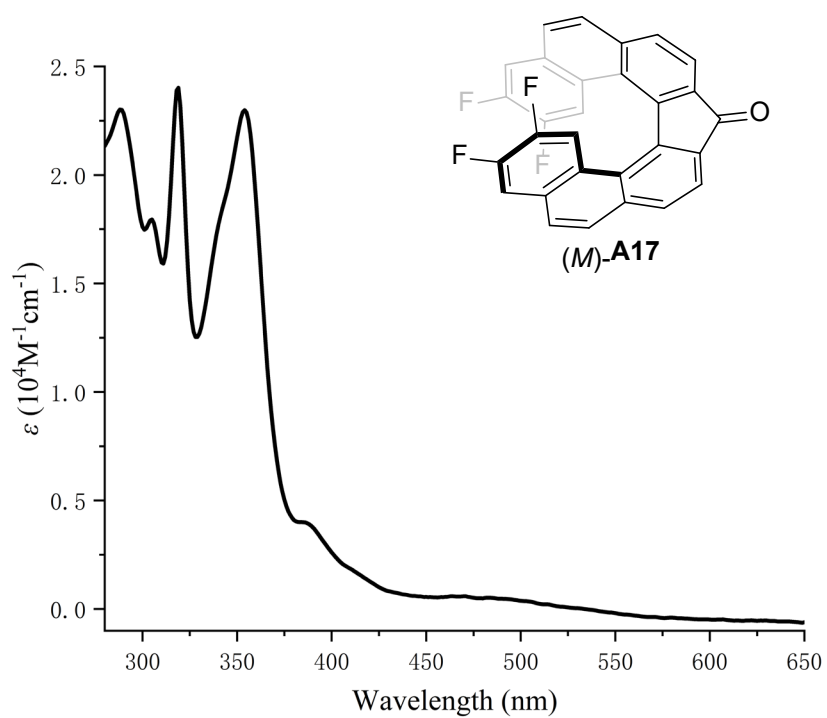


Figure S43. Experimental UV/vis absorption spectrum of (*M*)-A17.

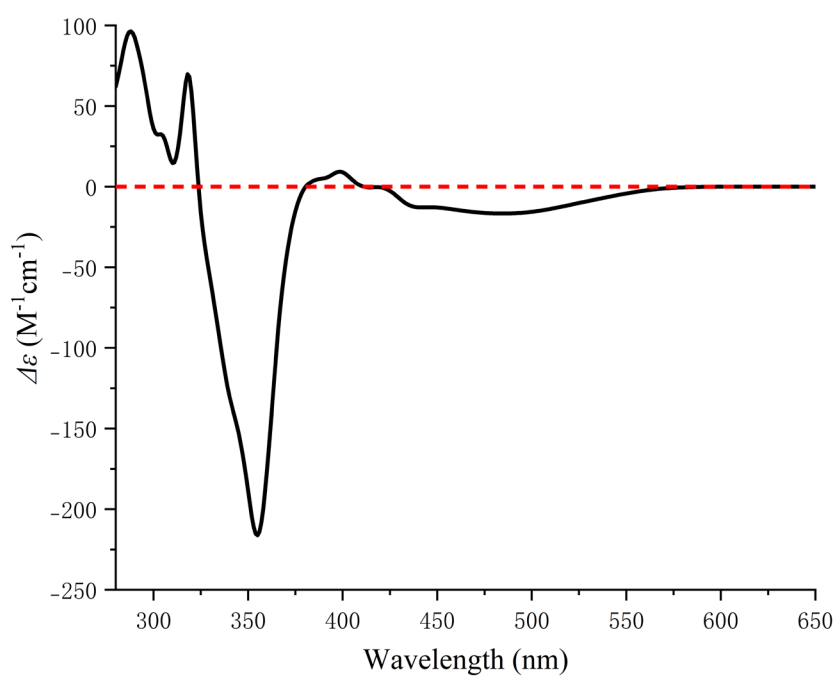


Figure S44. Experimental ECD spectrum of (*M*)-A17.

(*M*)-8*H*-dibenzo[*b*]thieno[5,4-*c*:4',5'-*g*]fluoren-8-one (A18)

1×10^{-3} mmol/mL in DCM, 288 nm, $|g_{\text{abs}}| = 4.66 \times 10^{-3}$, 345 nm, $|g_{\text{abs}}| = 3.96 \times 10^{-3}$.

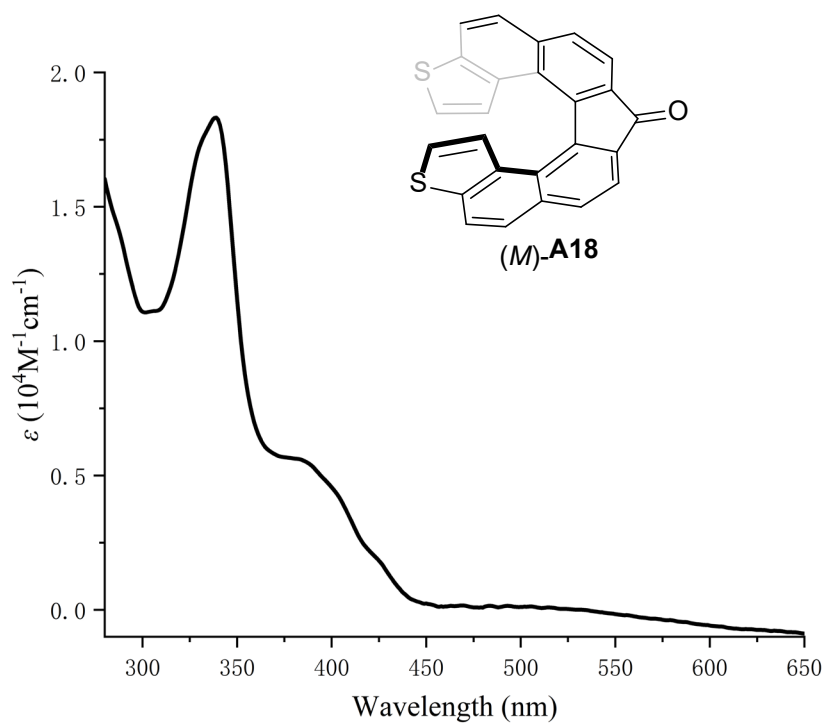


Figure S45. Experimental UV/vis absorption spectrum of (*M*)-A18.

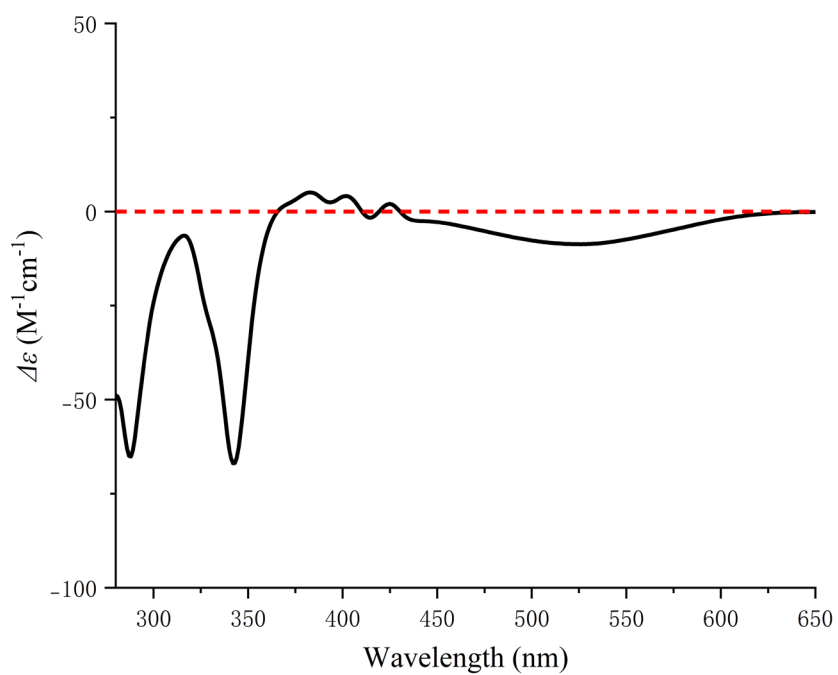


Figure S46. Experimental ECD spectrum of (*M*)-A18.

(*M*)-1,2,14,15-tetrahydro-8*H*-dibenzo[*b*]furan[5,4-*c*:4',5'-*g*]fluoren-8-one (A19)

1×10^{-3} mmol/mL in DCM, 348 nm, $|g_{\text{abs}}| = 7.92 \times 10^{-3}$.

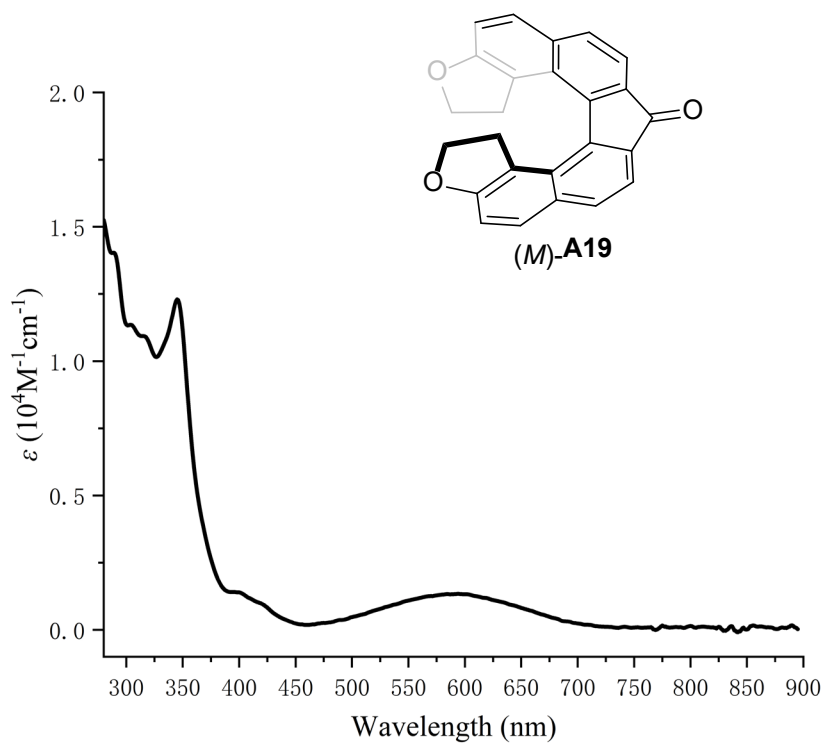


Figure S47. Experimental UV/vis absorption spectrum of (*M*)-A19.

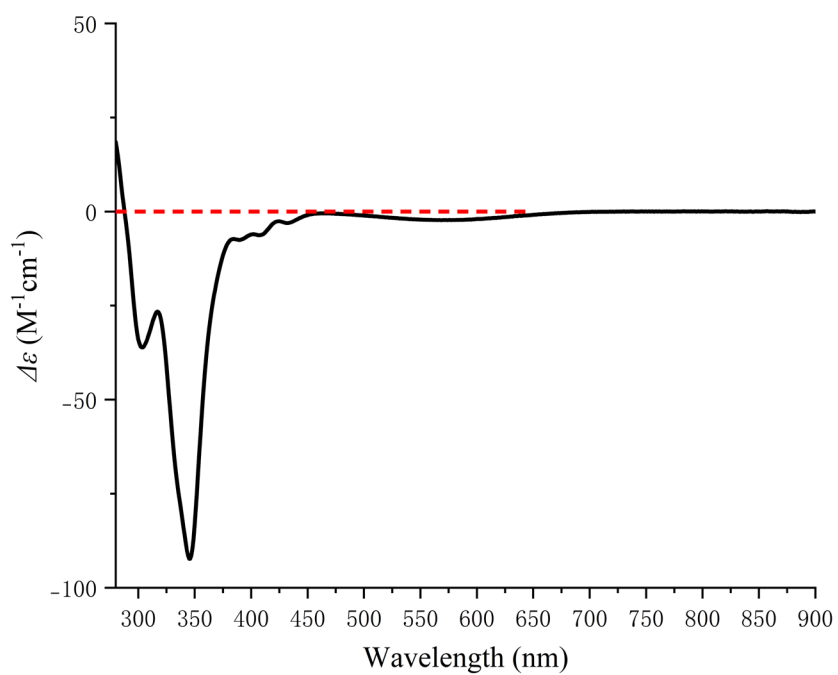


Figure S48. Experimental ECD spectrum of (*M*)-A19.

(M)-3H-cyclopenta[2,1-a:3,4-a']ditetraphen-3-one (A20)

1×10^{-3} mmol/mL in DCM, 366 nm, $|g_{\text{abs}}| = 9.94 \times 10^{-3}$.

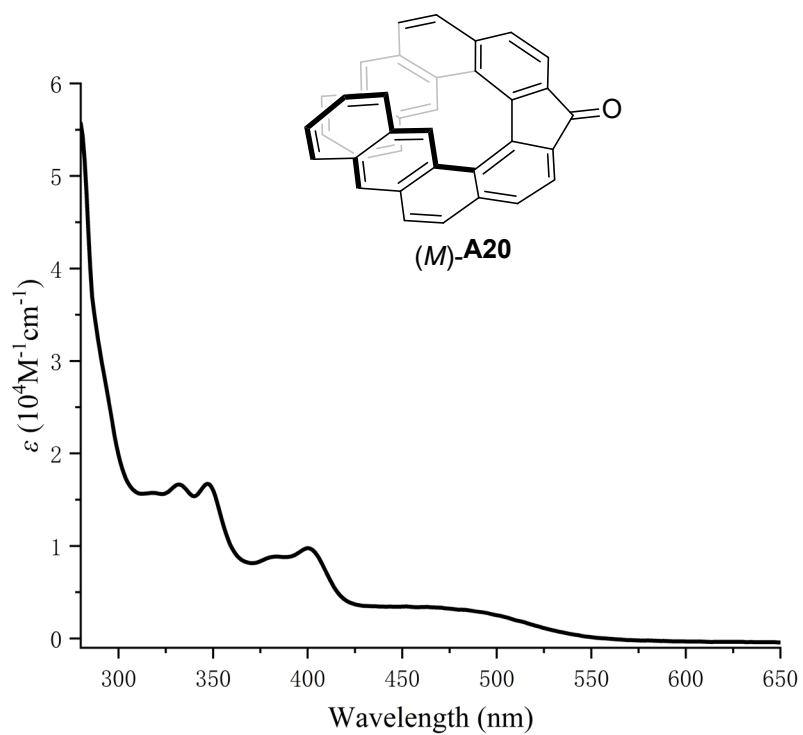


Figure S49. Experimental UV/vis absorption spectrum of (M)-A20.

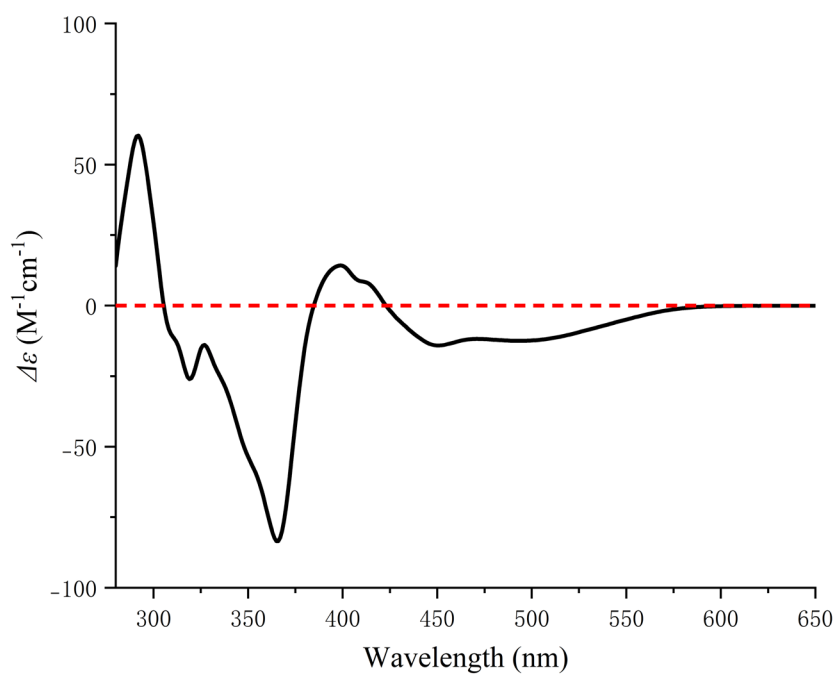


Figure S50. Experimental ECD spectrum of (M)-A20.

(*M*)-9H-benzo[6,7]indeno[2,1-c]phenanthren-9-one (A21)

1×10^{-3} mmol/mL in DCM, 359 nm, $|g_{\text{abs}}| = 1.96 \times 10^{-3}$.

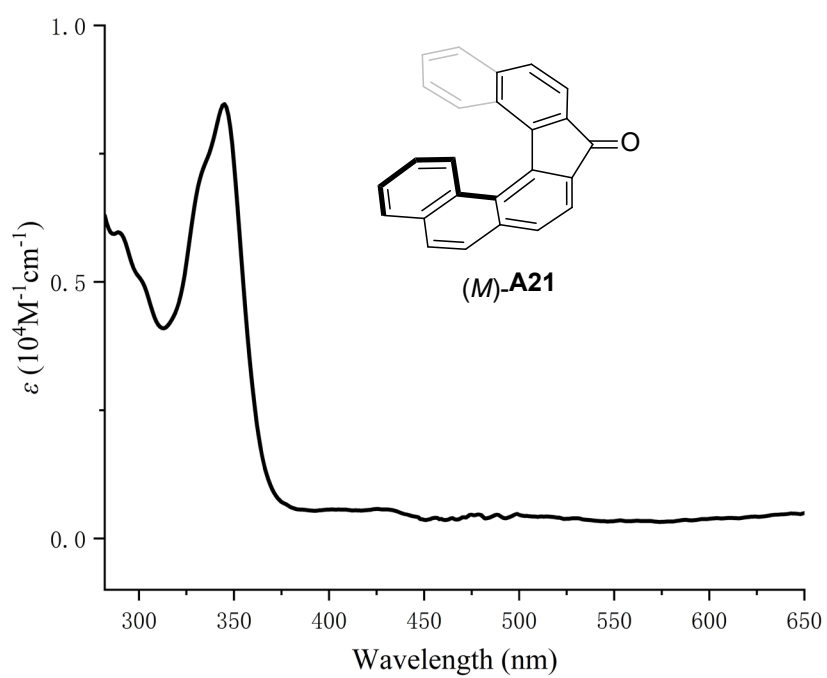


Figure S51. Experimental UV/vis absorption spectrum of (*M*)-A21.

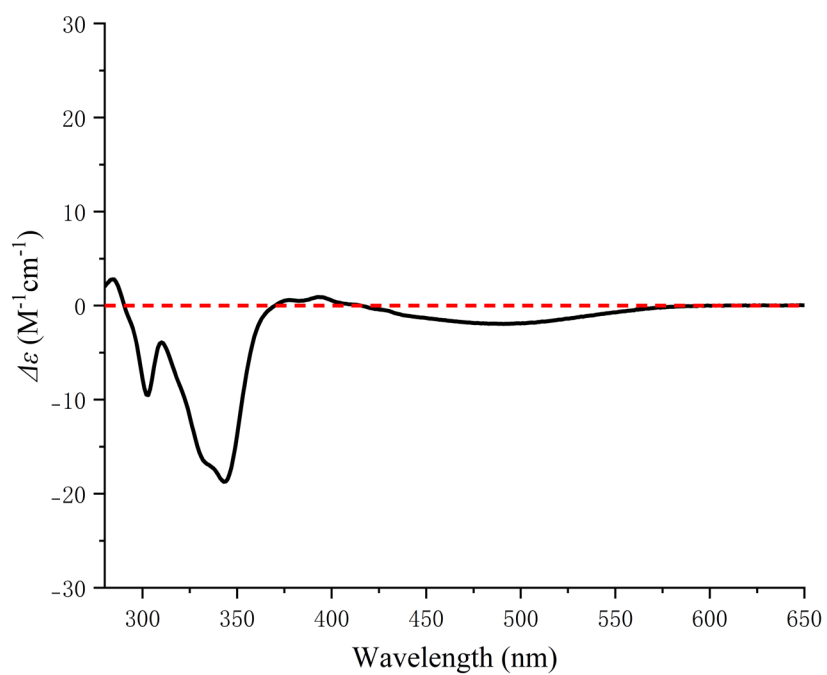


Figure S52. Experimental ECD spectrum of (*M*)-A21.

(*M*)-13-fluoro-9H-benzo[6,7]indeno[2,1-*c*]phenanthren-9-one (A22)

1×10^{-3} mmol/mL in DCM, 336 nm, $|g_{\text{abs}}| = 2.67 \times 10^{-3}$.

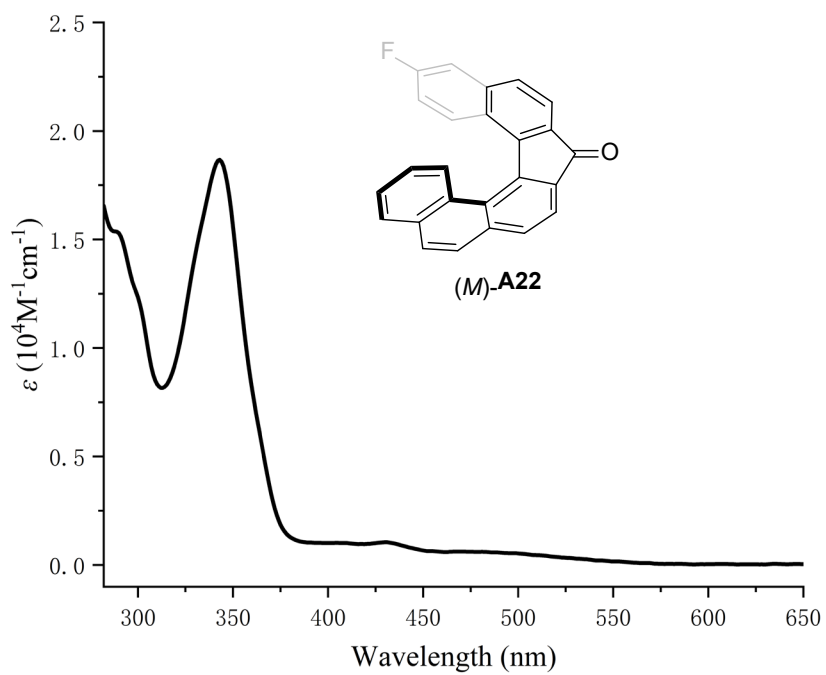


Figure S53. Experimental UV/vis absorption spectrum of (*M*)-A22.

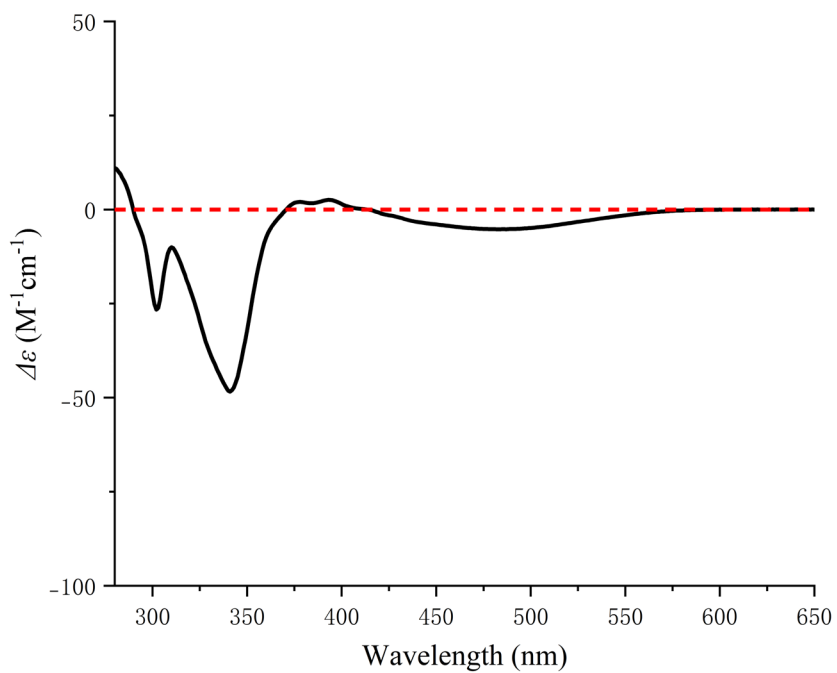


Figure S54. Experimental ECD spectrum of (*M*)-A22.

(*M*)-3-methoxy-9H-benzo[6,7]indeno[2,1-c]phenanthren-9-one (A23)

1×10^{-3} mmol/mL in DCM, 345 nm, $|g_{\text{abs}}| = 1.21 \times 10^{-3}$.

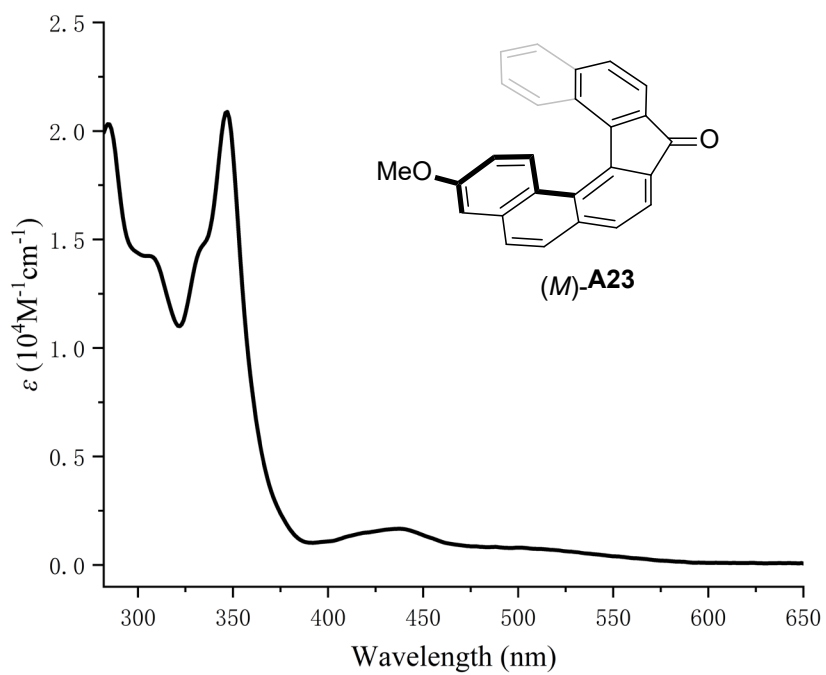


Figure S55. Experimental UV/vis absorption spectrum of (*M*)-A23.

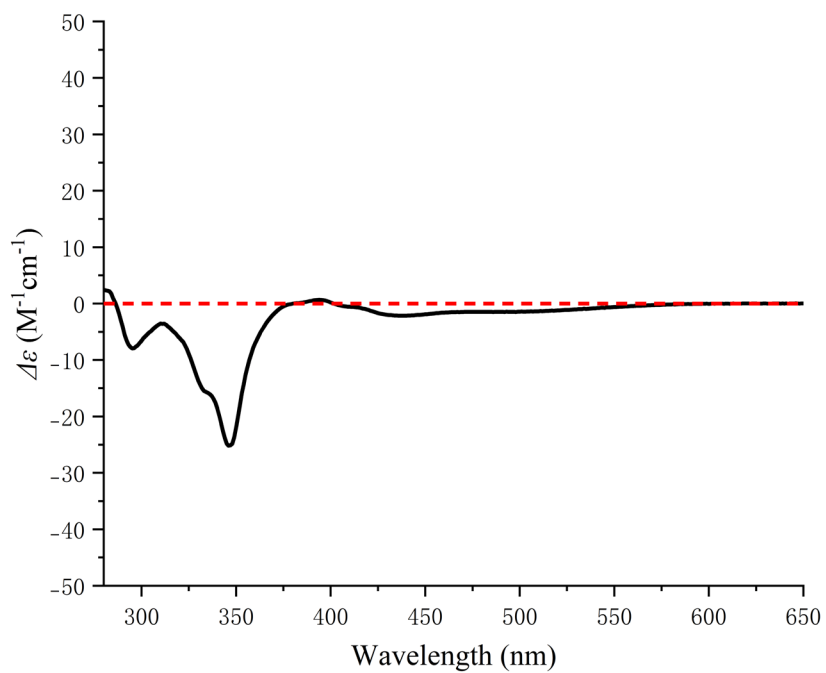


Figure S56. Experimental ECD spectrum of (*M*)-A23.

(M)-7H-benzo[c]indeno[1,2-g]phenanthren-7-one (A24)

1×10^{-3} mmol/mL in DCM, 292 nm, $|g_{\text{abs}}| = 3.23 \times 10^{-3}$.

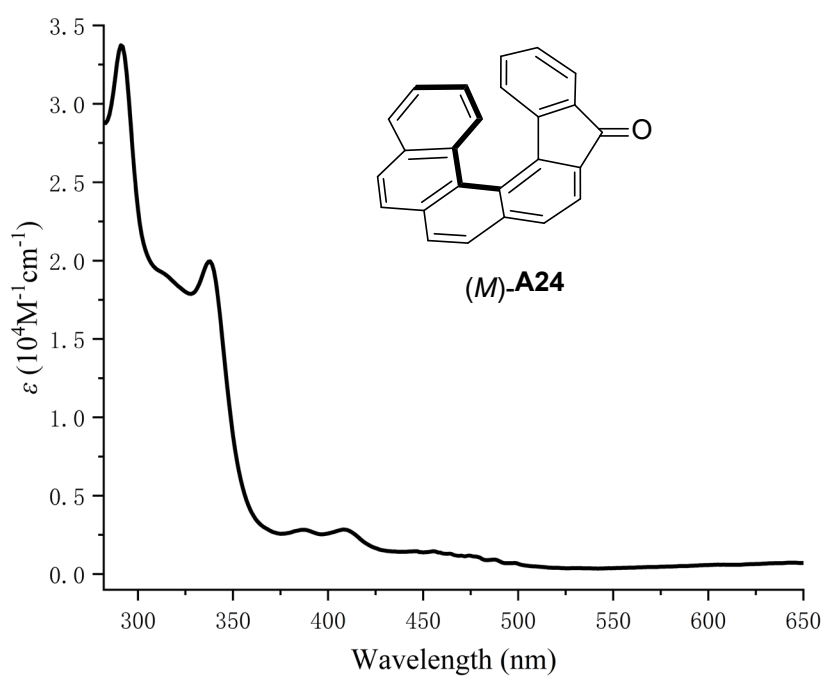


Figure S57. Experimental UV/vis absorption spectrum of (M)-A24.

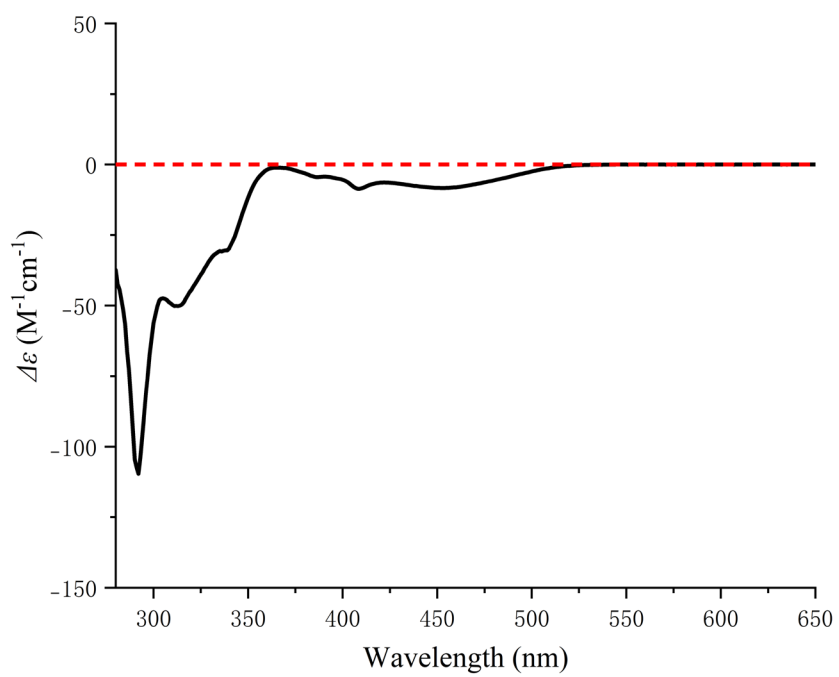


Figure S58. Experimental ECD spectrum of (M)-A24.

(*M*)-7H-benzo[*c*]benzo[6,7]indeno[1,2-*g*]phenanthren-7-one (A25)

1×10^{-3} mmol/mL in DCM, 352 nm, $|g_{\text{abs}}| = 5.39 \times 10^{-3}$.

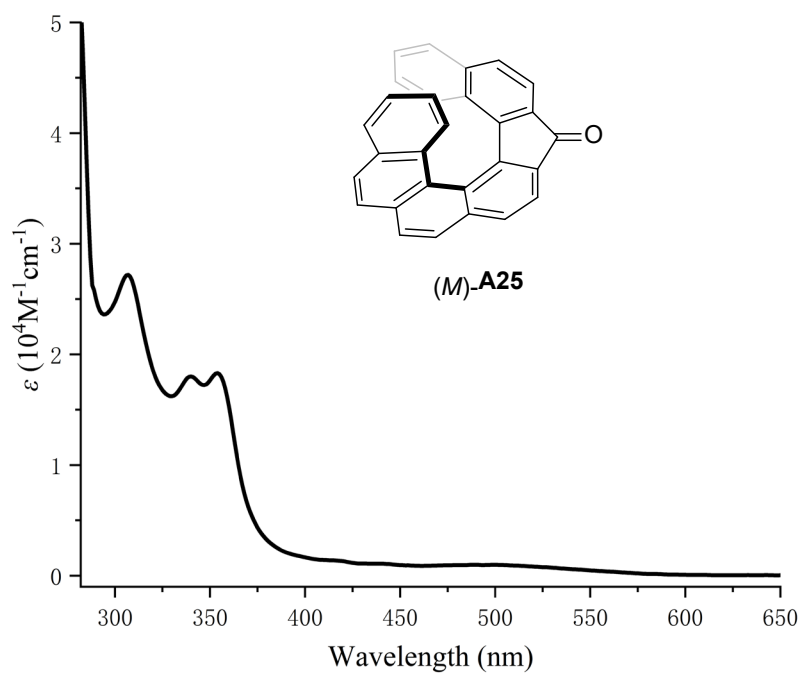


Figure S59. Experimental UV/vis absorption spectrum of (*M*)-A25.

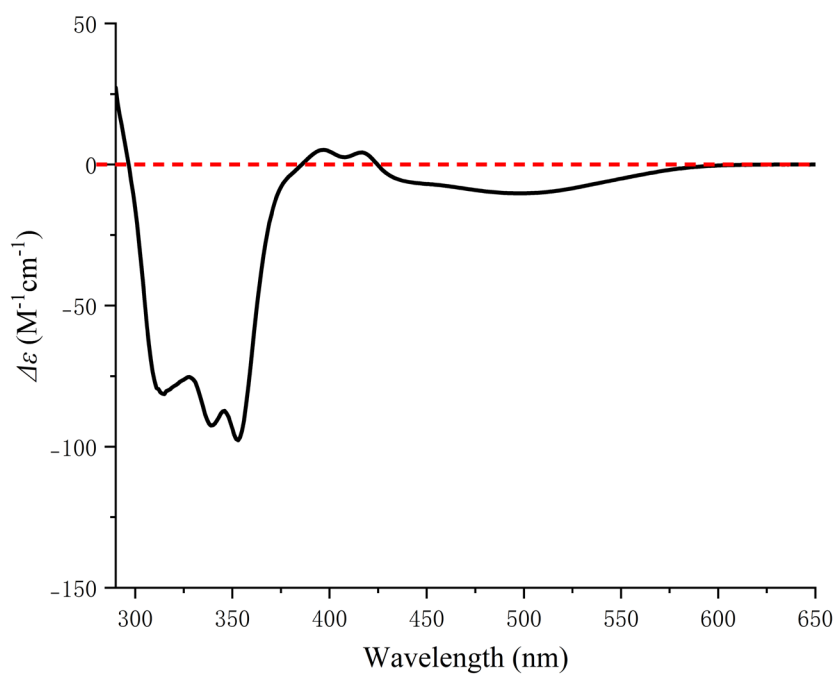


Figure S60. Experimental ECD spectrum of (*M*)-A25.

(*M*)-9H-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one-*O*-methyl oxime (E5)

1×10^{-3} mmol/mL in DCM, 358 nm, $|g_{\text{abs}}| = 1.14 \times 10^{-2}$.

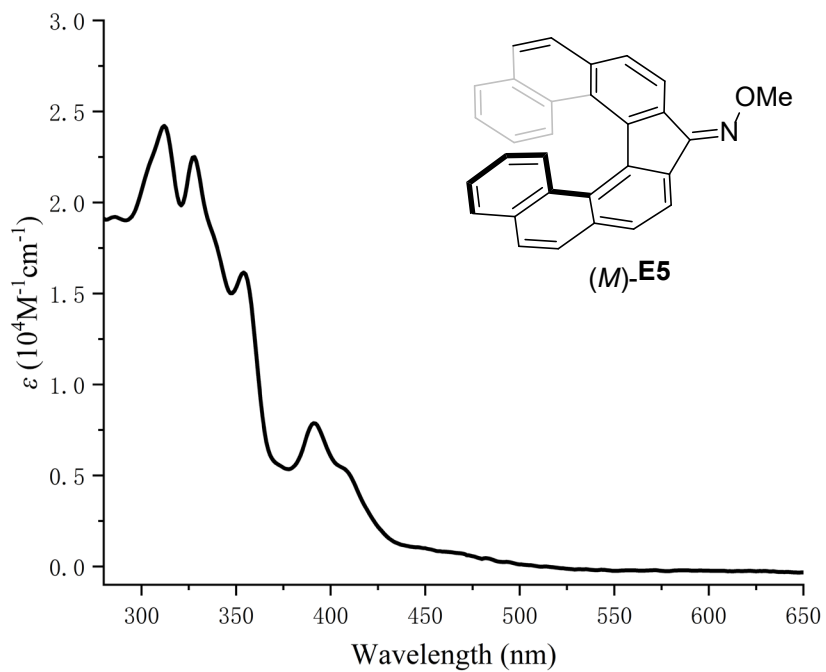


Figure S61. Experimental UV/vis absorption spectrum of (*M*)-E5.

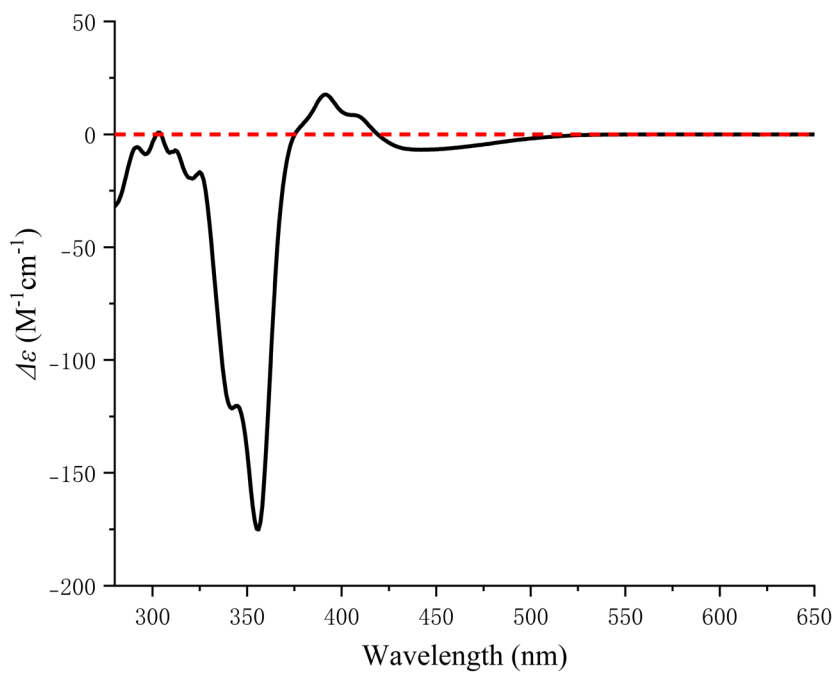


Figure S62. Experimental ECD spectrum of (*M*)-E5.

(*M*)-(9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-ylidene)hydrazine (E6)

1×10^{-3} mmol/mL in DCM, 359 nm, $|g_{\text{abs}}| = 9.32 \times 10^{-3}$.

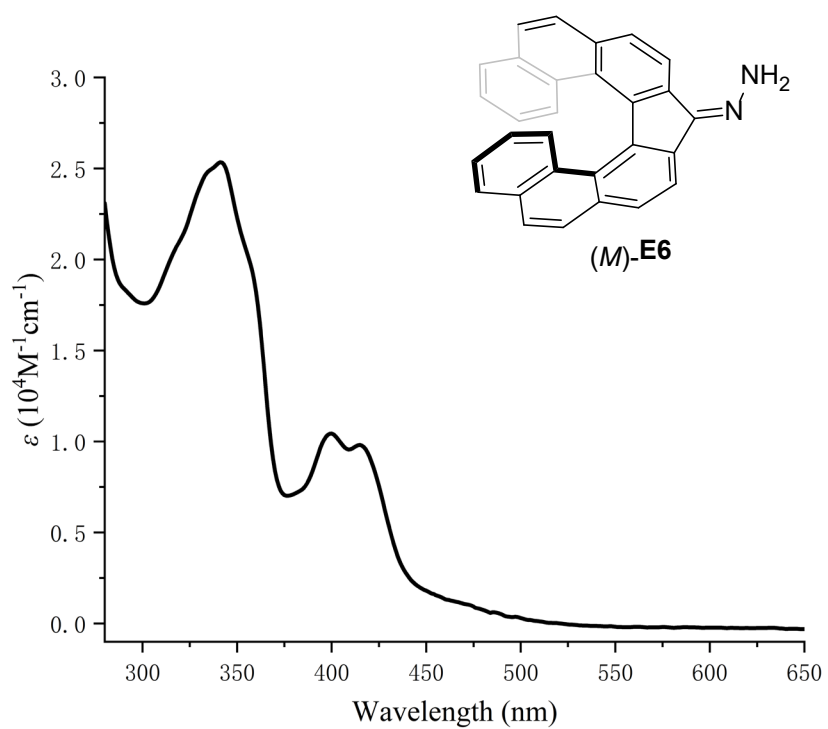


Figure S63. Experimental UV/vis absorption spectrum of (*M*)-E6.

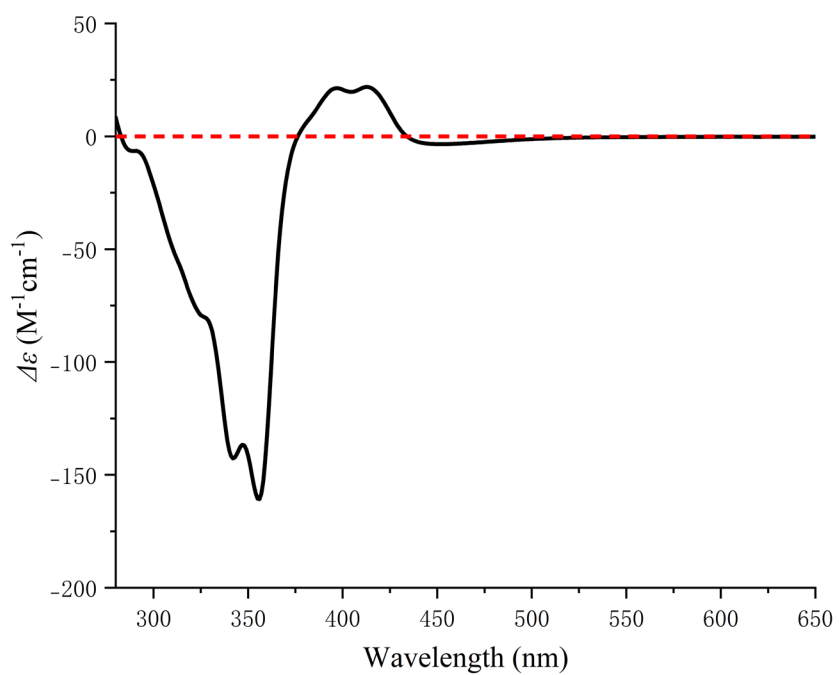


Figure S64. Experimental ECD spectrum of (*M*)-E6.

(*M*)-9-diazo-9H-cyclopenta[1,2-c:4,3-c']diphenanthrene (E7)

1×10^{-3} mmol/mL in DCM, 359 nm, $|g_{\text{abs}}| = 9.1 \times 10^{-3}$.

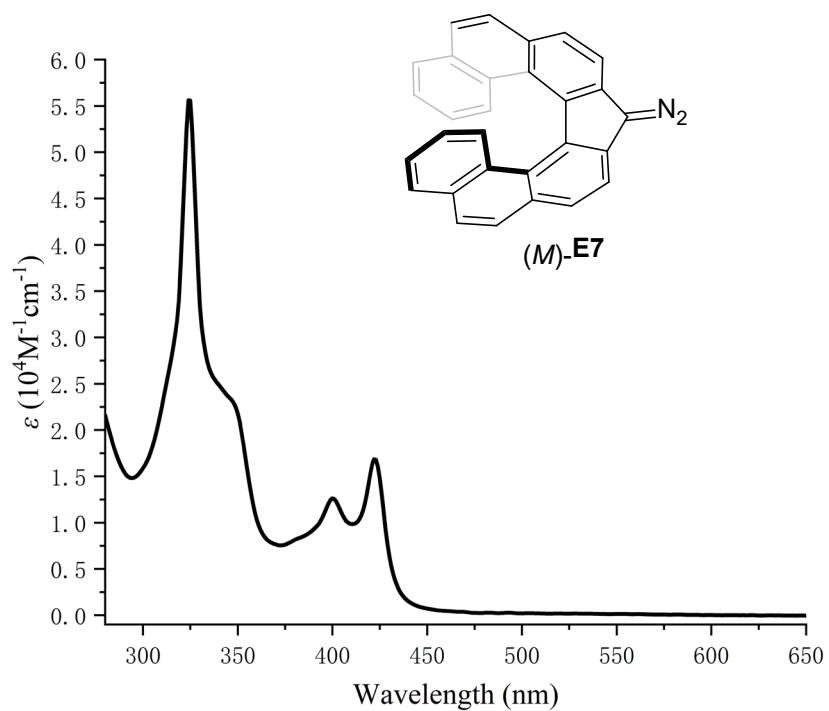


Figure S65. Experimental UV/vis absorption spectrum of (*M*)-E7.

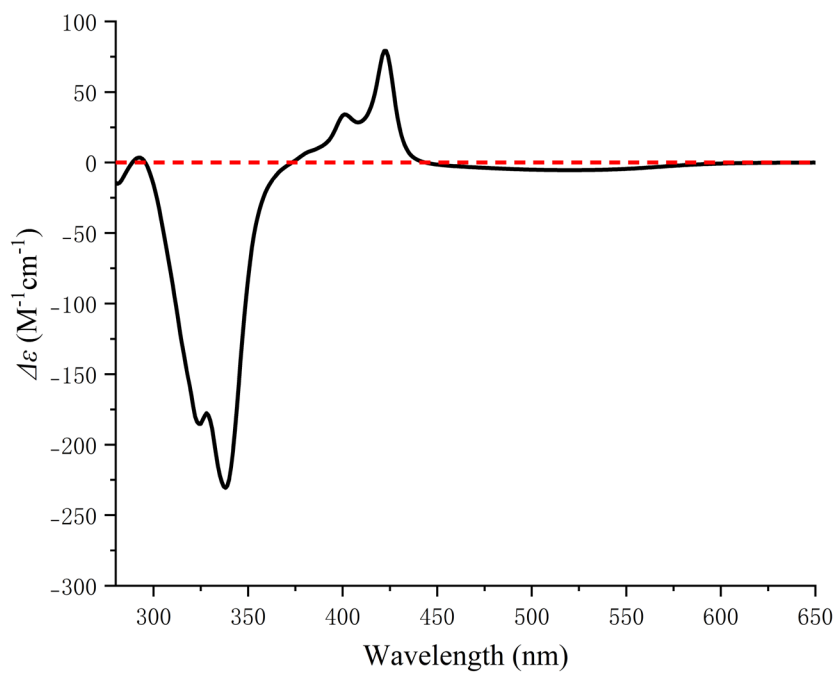


Figure S66. Experimental ECD spectrum of (*M*)-E7.

(*M*)-spiro[cyclopenta[1,2-c:4,3-c']diphenanthrene-9,9'-xanthene] (E8)

1×10^{-3} mmol/mL in DCM, 325 nm, $|g_{\text{abs}}| = 1.36 \times 10^{-2}$.

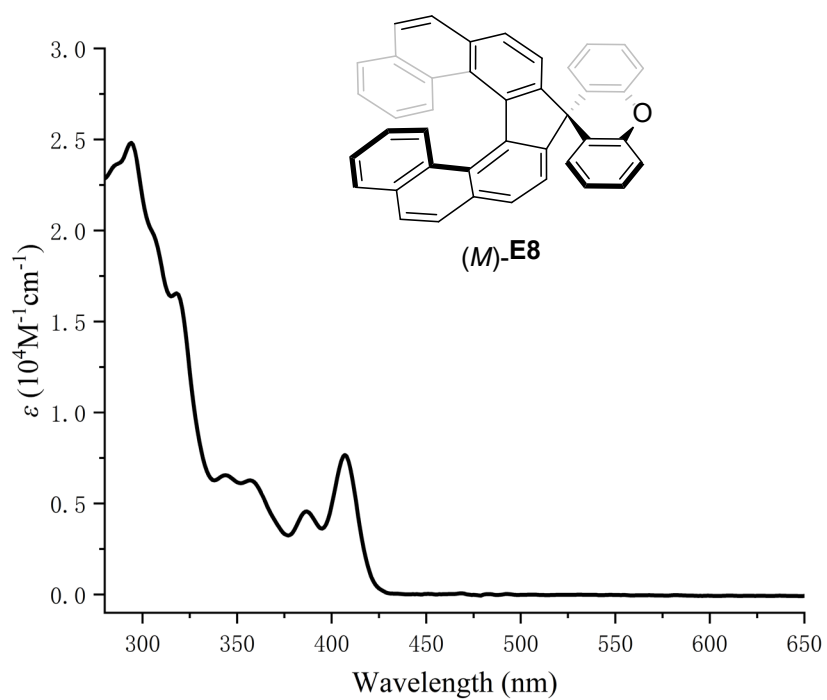


Figure S67. Experimental UV/vis absorption spectrum of (*M*)-E8.

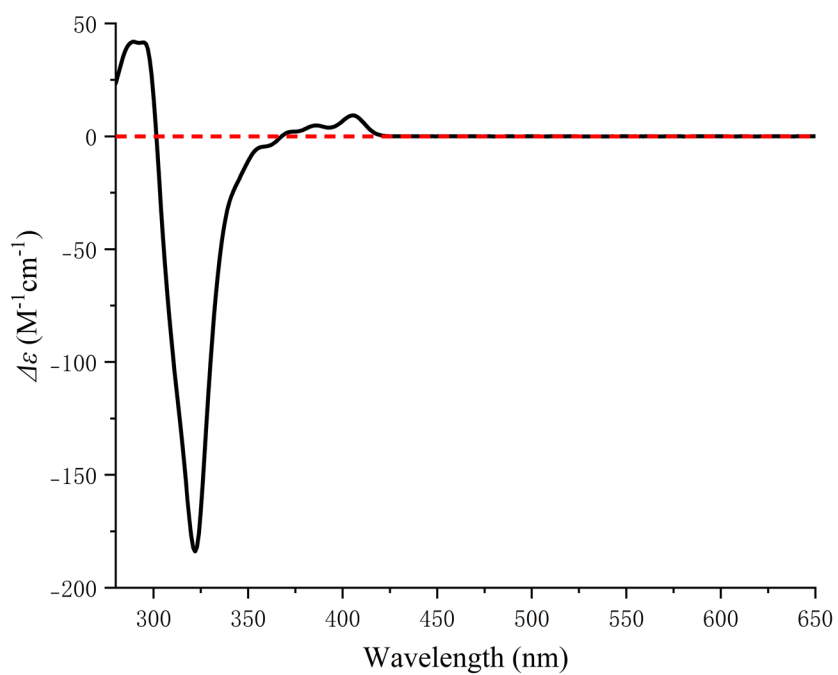


Figure S68. Experimental ECD spectrum of (*M*)-E8.

isobutyl (*P, S*)-3-benzyl-4-oxo-3,4-dihydrohexahelicene-3-carboxylate (C21)

1×10^{-3} mmol/mL in DCM, 327 nm, $|g_{\text{abs}}| = 5.27 \times 10^{-3}$.

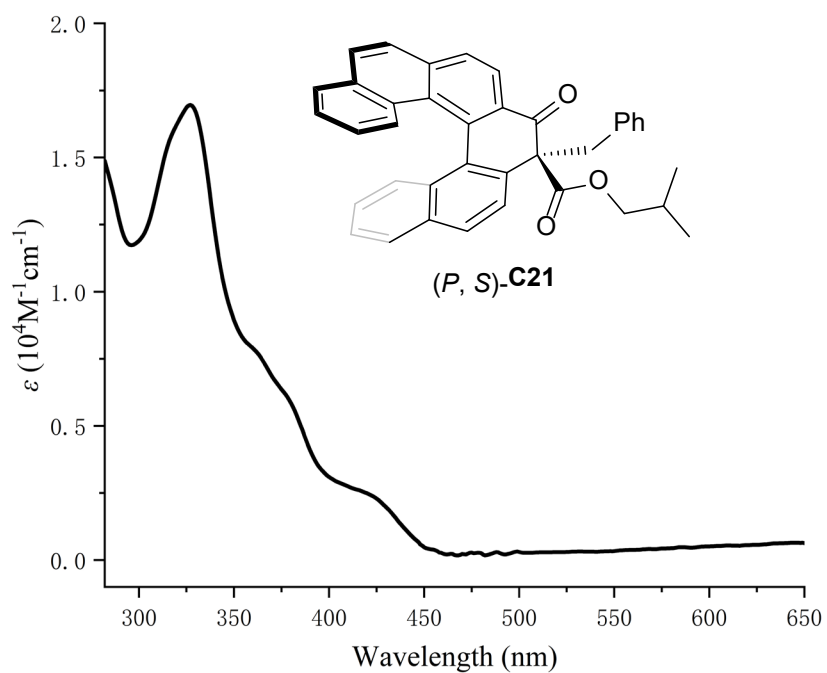


Figure S69. Experimental UV/vis absorption spectrum of (*P, S*)-C21.

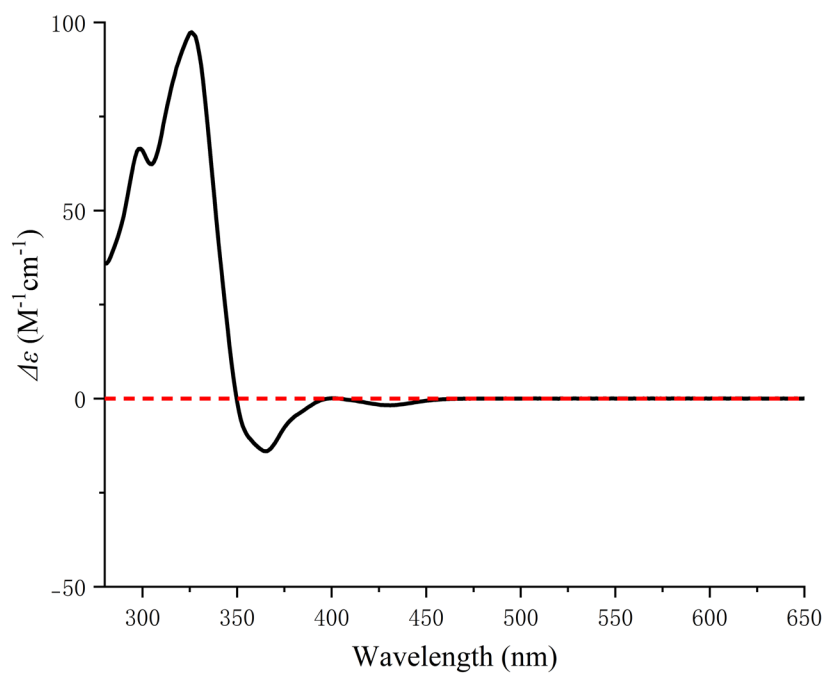


Figure S70. Experimental ECD spectrum of (*P, S*)-C21.

isobutyl (*M, S*)-4-benzyl-3-oxo-3,4-dihydrohexahelicene-4-carboxylate (C21)

1×10^{-3} mmol/mL in DCM, 324 nm, $|g_{\text{abs}}| = 1.10 \times 10^{-3}$.

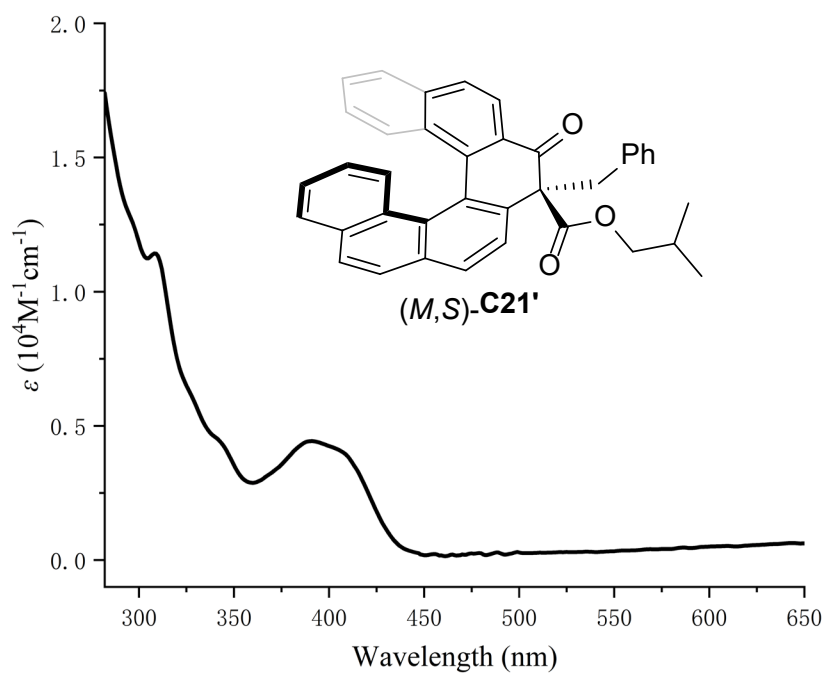


Figure S71. Experimental UV/vis absorption spectrum of (*M, S*)-C21.

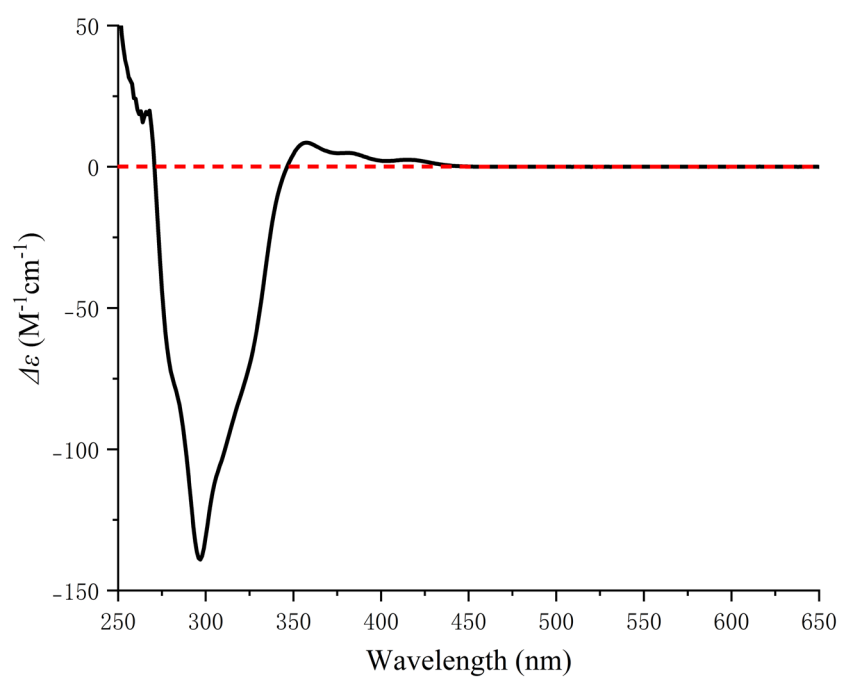


Figure S72 Experimental ECD spectrum of (*M, S*)-C21.

isobutyl (*P, S*)-3-benzyl-14-fluoro-4-oxo-3,4-dihydrohexahelicene-3-carboxylate (C22)

1×10^{-3} mmol/mL in DCM, 321 nm, $|g_{\text{abs}}| = 5.82 \times 10^{-3}$.

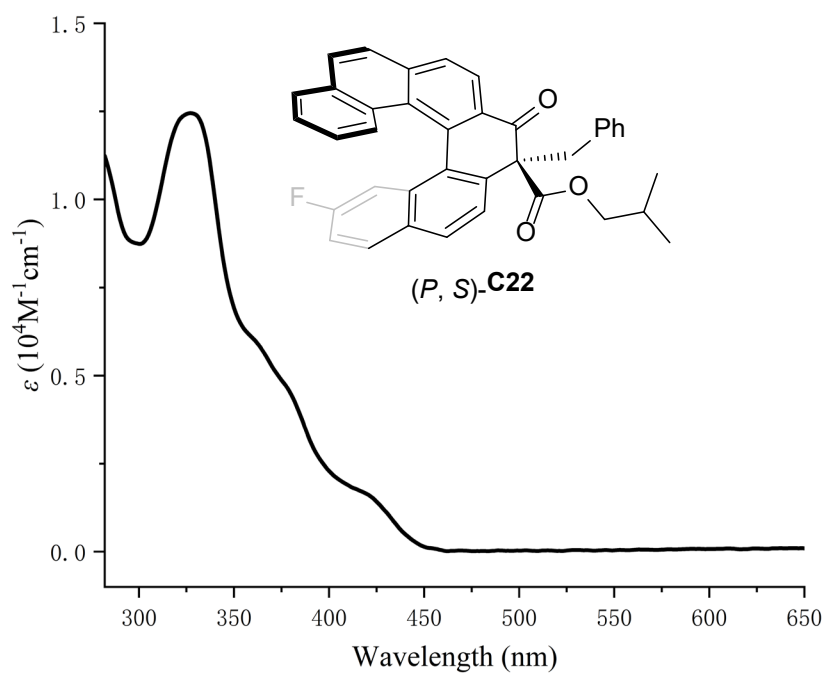


Figure S73. Experimental UV/vis absorption spectrum of (*P, S*)-C22.

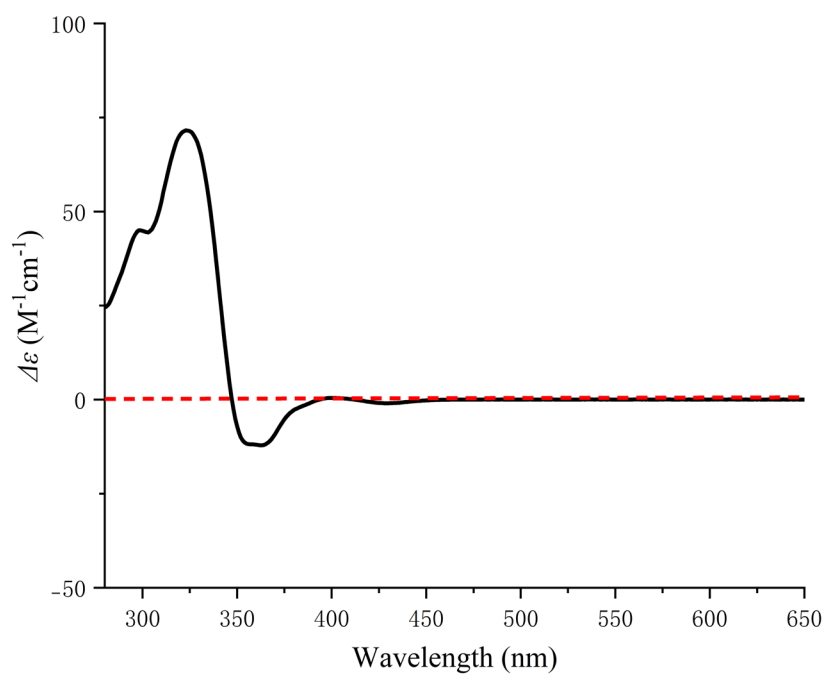


Figure S74. Experimental ECD spectrum of (*P, S*)-C22.

isobutyl (*M,S*)-4-benzyl-15-fluoro-3-oxo-3,4-dihydrohexahelicene-4-carboxylate (C22)

1×10^{-3} mmol/mL in DCM, 324 nm, $|g_{\text{abs}}| = 1.08 \times 10^{-2}$.

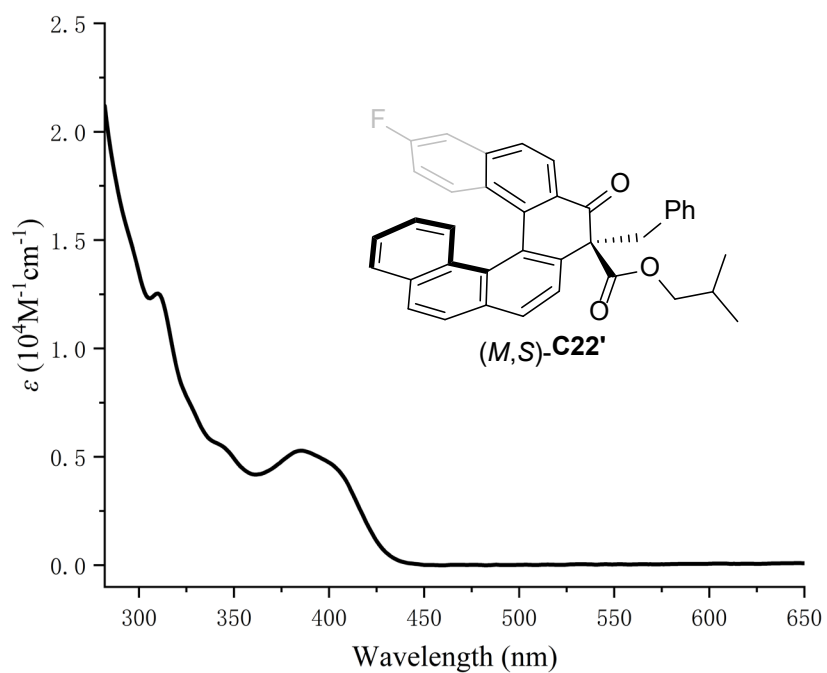


Figure S75. Experimental UV/vis absorption spectrum of (*M,S*)-**C22**.

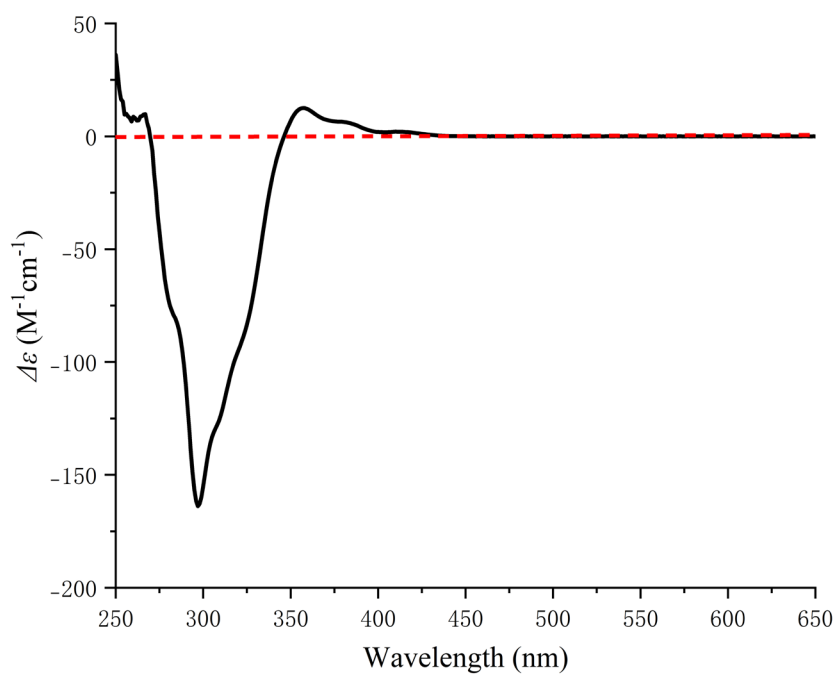


Figure S76. Experimental ECD spectrum of (*M,S*)-**C22**.

isobutyl (*P, S*)-3-benzyl-10-methoxy-4-oxo-3,4-dihydrohexahelicene-3-carboxylate (C23)

1×10^{-3} mmol/mL in DCM, 330 nm, $|g_{\text{abs}}| = 5.01 \times 10^{-3}$.

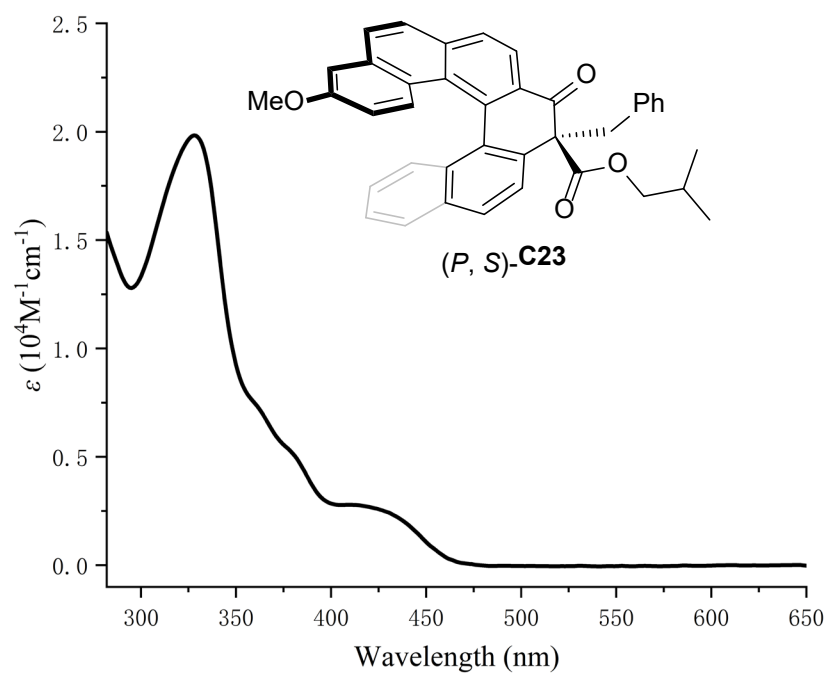


Figure S77. Experimental UV/vis absorption spectrum of (*P, S*)-**C23**.

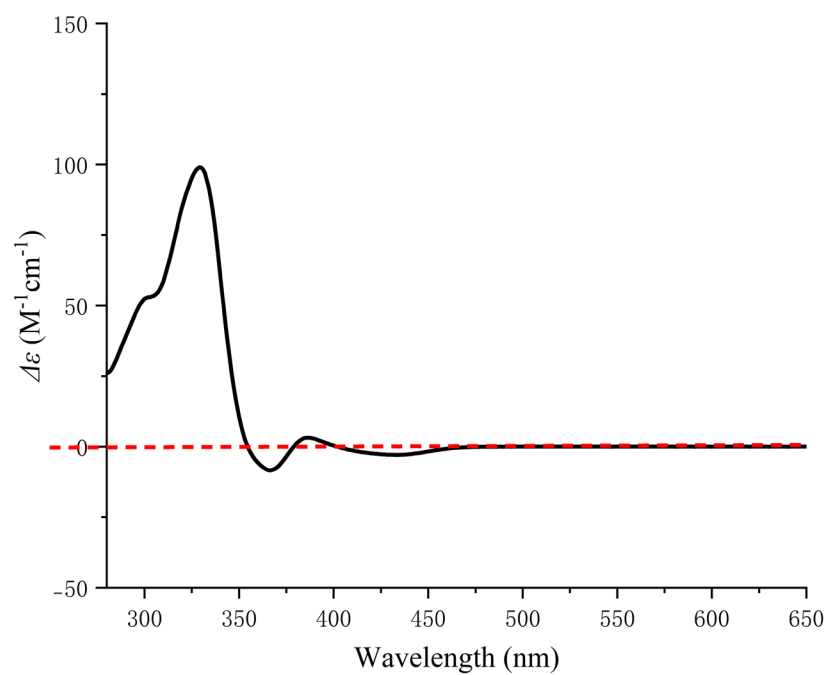


Figure S78. Experimental ECD spectrum of (*P, S*)-**C23**.

isobutyl (*M, S*)-4-benzyl-10-methoxy-3-oxo-3,4-dihydrohexahelicene-4-carboxylate (**C23**)

1×10^{-3} mmol/mL in DCM, 307 nm, $|g_{\text{abs}}| = 9.28 \times 10^{-3}$.

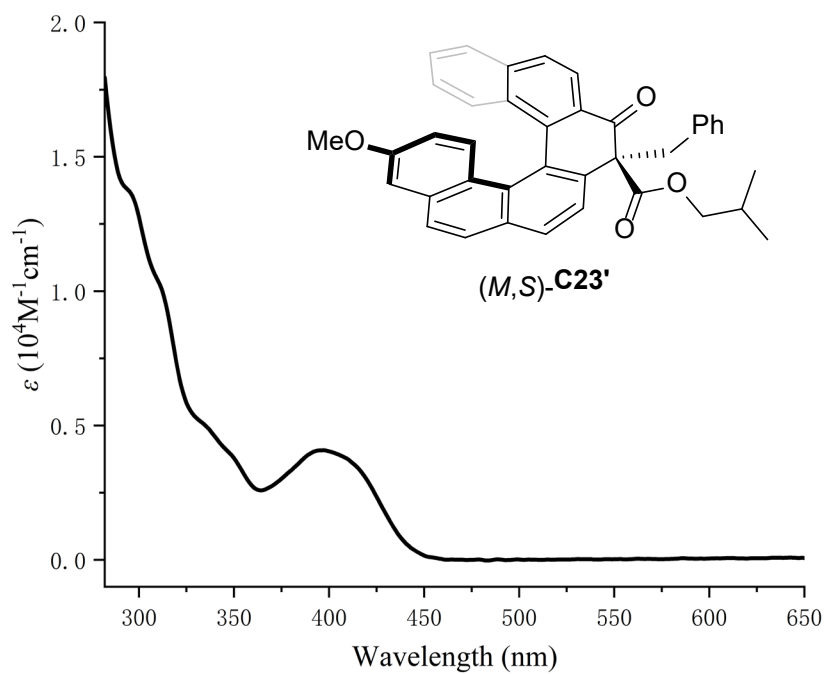


Figure S79. Experimental UV/vis absorption spectrum of (*M, S*)-**A23**.

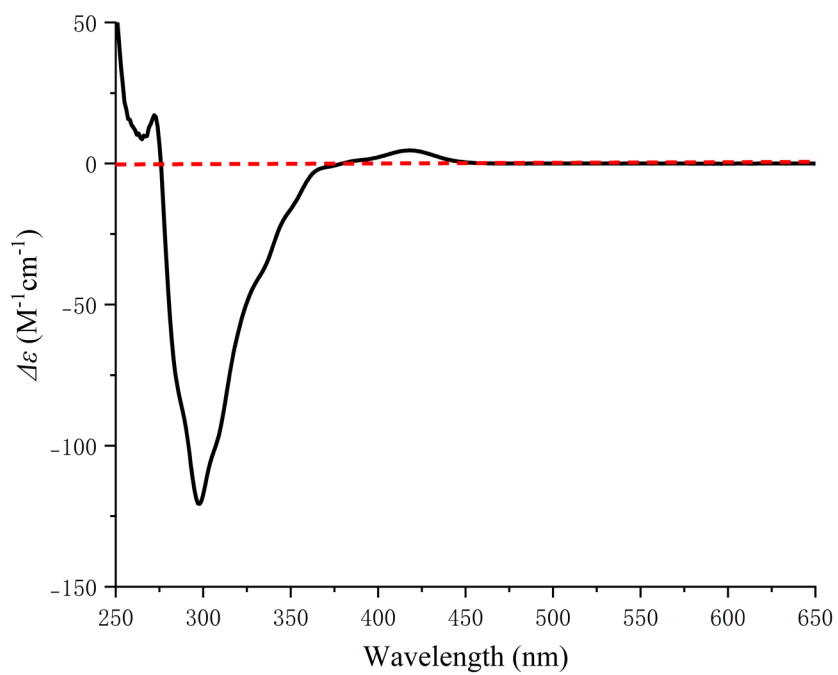


Figure S80. Experimental ECD spectrum of (*M, S*)-**A23**.

isobutyl (*P, S*)-1-benzyl-2-oxo-1,2-dihydrohexahelicene-1-carboxylate (C24)

1×10^{-3} mmol/mL in DCM, 333 nm, $|g_{\text{abs}}| = 5.19 \times 10^{-3}$.

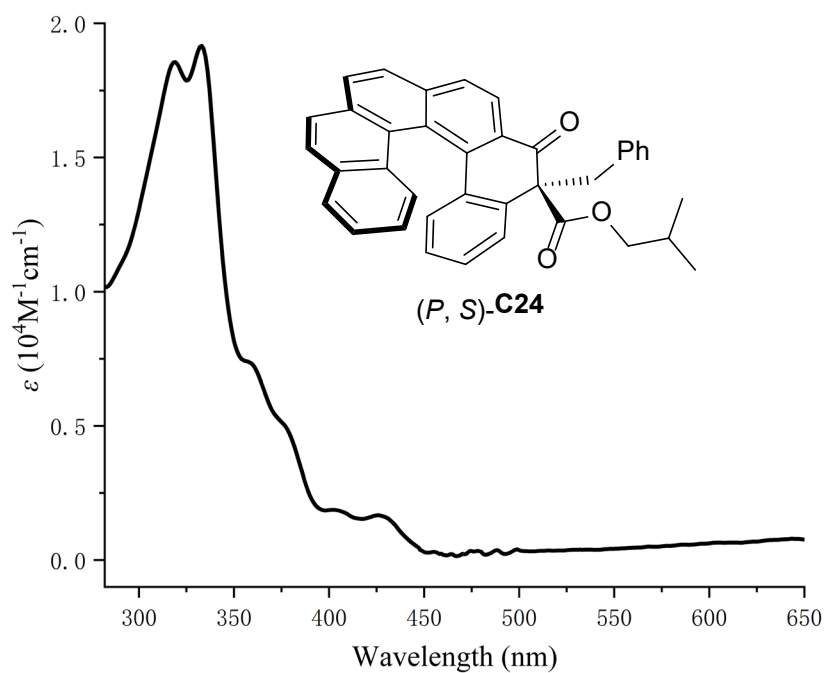


Figure S81. Experimental UV/vis absorption spectrum of (*P, S*)-C24.

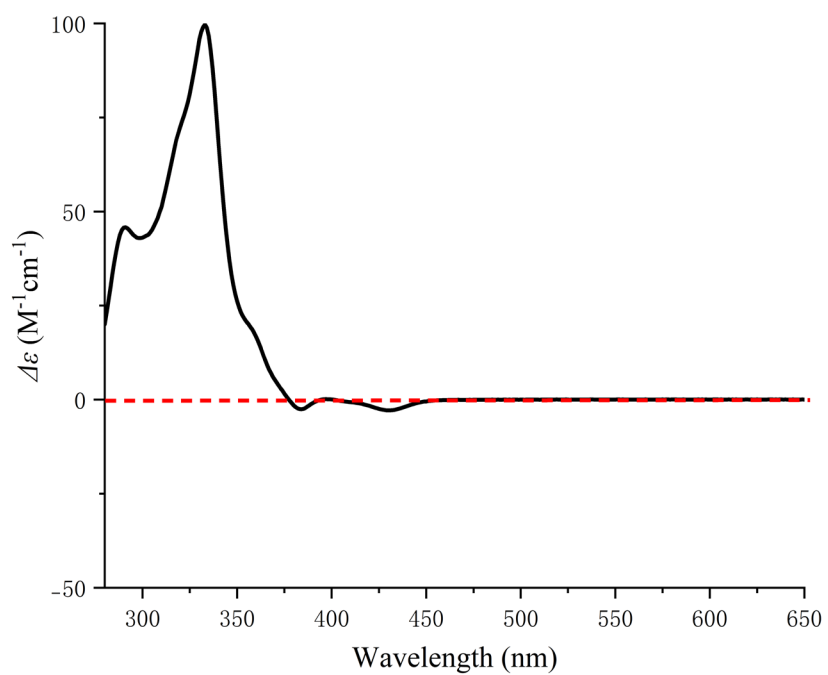


Figure S82. Experimental ECD spectrum of (*P, S*)-C24.

isobutyl (*M, S*)-2-benzyl-1-oxo-1,2-dihydrohexahelicene-2-carboxylate (C24)

1×10^{-3} mmol/mL in DCM, 316 nm, $|g_{\text{abs}}| = 7.73 \times 10^{-3}$.

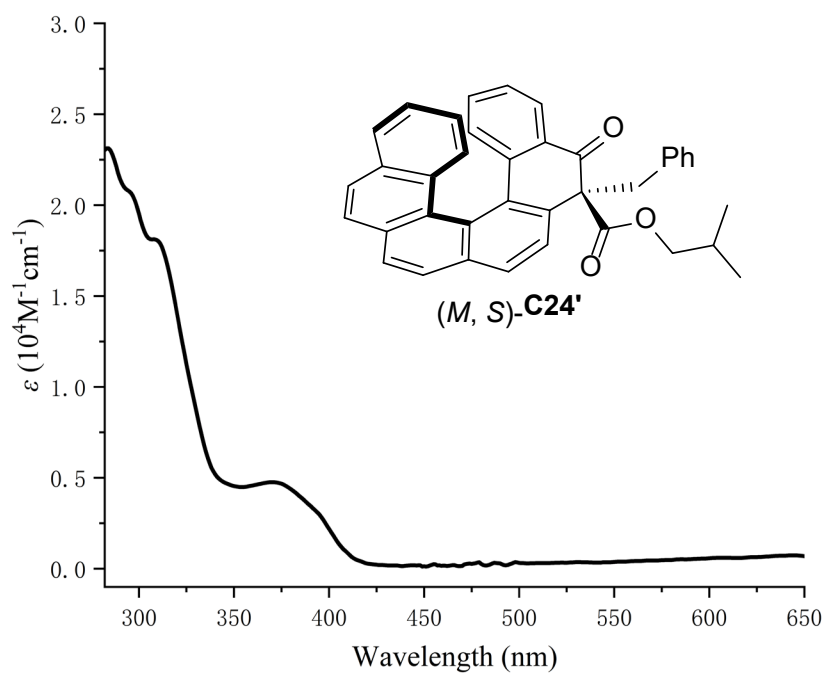


Figure S83. Experimental UV/vis absorption spectrum of (*M, S*)-**C24**.

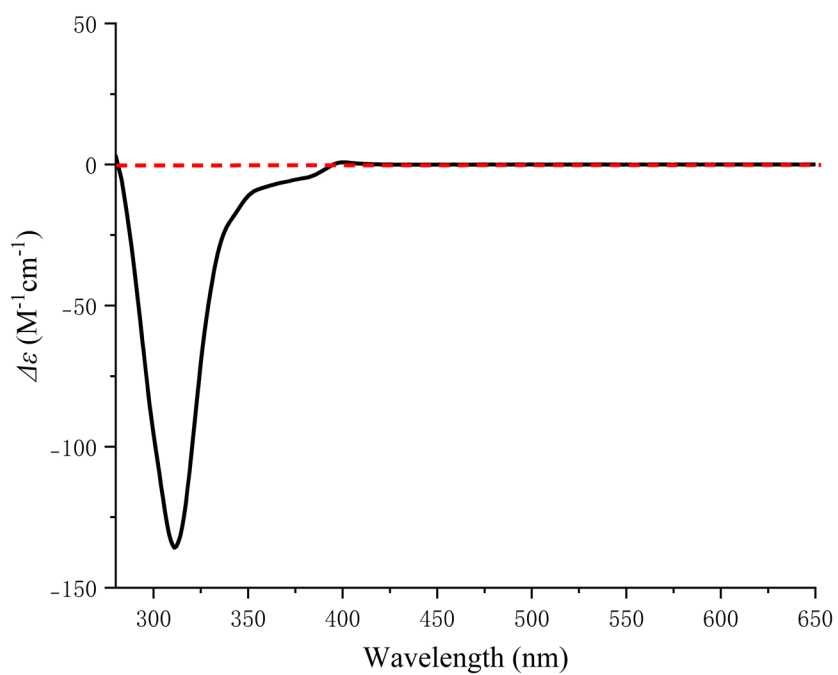


Figure S84. Experimental ECD spectrum of (*M, S*)-**C24**.

isobutyl (*P, S*)-7-benzyl-8-oxo-7,8-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-7-carboxylate (**C25**)

1×10^{-3} mmol/mL in DCM, 345 nm, $|g_{\text{abs}}| = 6.26 \times 10^{-3}$.

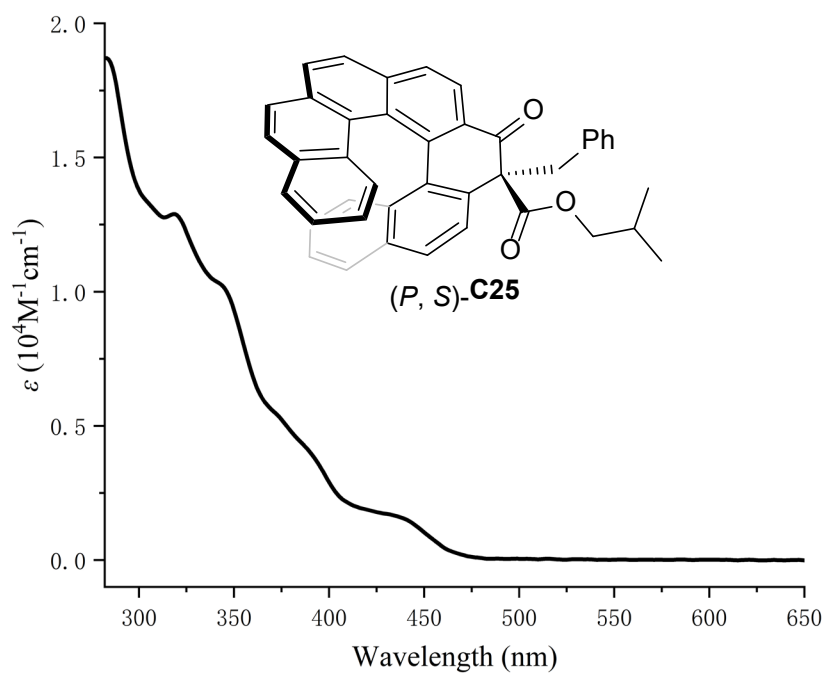


Figure S85. Experimental UV/vis absorption spectrum of (*P, S*)-**C25**.

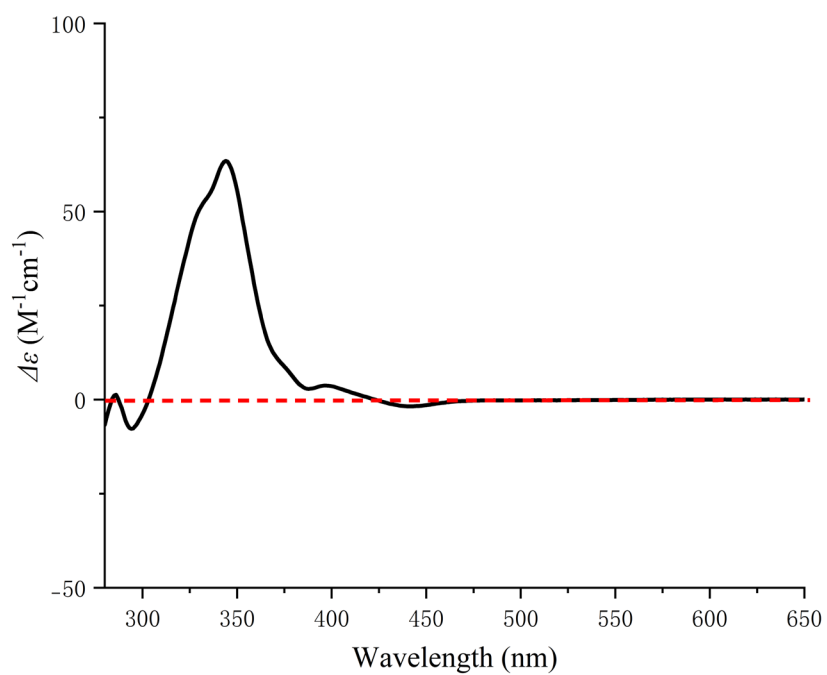


Figure S86. Experimental ECD spectrum of (*P, S*)-**C25**.

isobutyl (*P, S*)-3-benzyl-4-oxo-3,4-dihydrodibenzo[*c,g*]phenanthrene-3-carboxylate (**C26**)

1×10^{-3} mmol/mL in DCM, 277 nm, $|g_{\text{abs}}| = 3.45 \times 10^{-3}$.

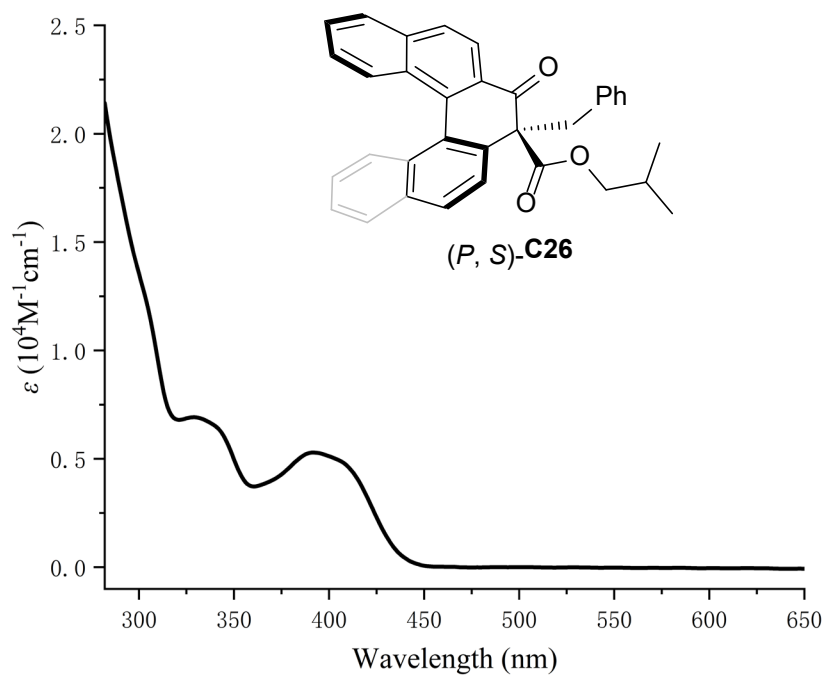


Figure S87. Experimental UV/vis absorption spectrum of (*P, S*)-**C26**.

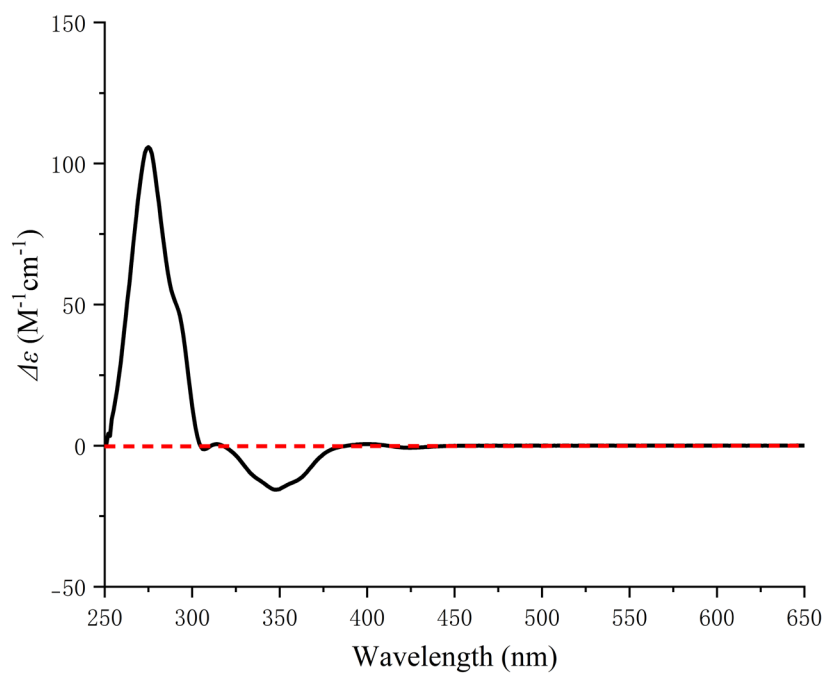


Figure S88. Experimental UV/vis absorption spectrum of (*P, S*)-**C26**.

Table S12. Experimental chiroptical properties of [7]helical compounds.

compound	$\lambda_{\max}$ (nm)	ϵ ($M^{-1}cm^{-1}$)	$\Delta\epsilon$ ($M^{-1}cm^{-1}$)	g_{abs}
(<i>P,S</i>)-C1	349	11572.2	154.4	0.0133
(<i>M,R</i>)-C1	349	11572.2	-154.4	-0.0133
(<i>P,R</i>)-C1	349	10768.8	151.3	0.0140
(<i>M,S</i>)-C1	349	10768.8	-151.3	-0.0140
(<i>P,S</i>)-C21	327	16945.6	96.9	0.0057
(<i>M,S</i>)-C21'	324	7001.1	-76.8	-0.0110
(<i>P,S</i>)-C22	321	12214.6	71.1	0.0059
(<i>M,S</i>)-C22'	324	9032.1	-95.1	-0.0108
(<i>P,S</i>)-C23	330	19747.8	98.9	0.0050
(<i>M,S</i>)-C23'	307	10810.9	-100.3	-0.0093
(<i>P,S</i>)-C24	333	19178.7	99.7	0.0052
(<i>M,S</i>)-C24'	316	16217.1	-124.9	-0.0077
(<i>P,S</i>)-C25	345	10107.6	63.2	0.0063
(<i>P,S</i>)-C26	277	23775.3	103.4	0.0035
(<i>P</i>)-A1	362	21253.8	162.7	0.0077
(<i>M</i>)-A1	362	21253.8	-162.7	-0.0077
(<i>M</i>)-A2	366	20312.7	-167.5	-0.0083
(<i>M</i>)-A3	363	20969.9	-164.2	-0.0078
(<i>M</i>)-A4	367	23210.3	-159.2	-0.0069
(<i>M</i>)-A5	367	22341.8	-128.7	-0.0058
(<i>M</i>)-A6	366	16062.2	-83.5	-0.0052
(<i>M</i>)-A7	361	23196.9	-152.8	-0.0066
(<i>M</i>)-A8	358	15615.7	-121.5	-0.0078
(<i>M</i>)-A9	362	21207.2	-16.6	-0.0008
(<i>M</i>)-A10	365	14568.6	-103.4	-0.0071
(<i>M</i>)-A11	361	16686.1	-140.1	-0.0084
(<i>M</i>)-A12	364	11270.4	-87.5	-0.0078
(<i>M</i>)-A13	364	21177.3	-177.6	-0.0084
(<i>M</i>)-A14	374	24725.3	-221.9	-0.0090
(<i>M</i>)-A15	375	13569.4	-153.3	-0.0113
(<i>M</i>)-A16	379	8247.9	-46.8	-0.0057
(<i>M</i>)-A17	363	14927.1	-131.5	-0.0088
(<i>M</i>)-A18	288	13979.5	-65.1	-0.0047
	345	15854.4	-62.7	-0.0040
(<i>M</i>)-A19	348	11321.7	-89.7	-0.0079
(<i>M</i>)-A20	366	8396.5	-83.5	-0.0099
(<i>M</i>)-A21	313	4095.2	-4.8	-0.0019
(<i>M</i>)-A22	336	16692.7	-44.6	-0.0027
(<i>M</i>)-A23	345	20457.1	-81.8	-0.0012
(<i>M</i>)-A24	352	18050.6	-97.3	-0.0054
(<i>M</i>)-A25	292	33940.7	-109.6	-0.0032
(<i>M</i>)-E5	358	14402.3	-164.8	-0.0114
(<i>M</i>)-E6	359	15448.4	-143.9	-0.0093
(<i>M</i>)-E7	339	25140.2	-228.6	-0.0091
(<i>M</i>)-E8	325	12232.1	-165.8	-0.0136

8. Fluorescence Properties and Circularly Polarized Luminescence.

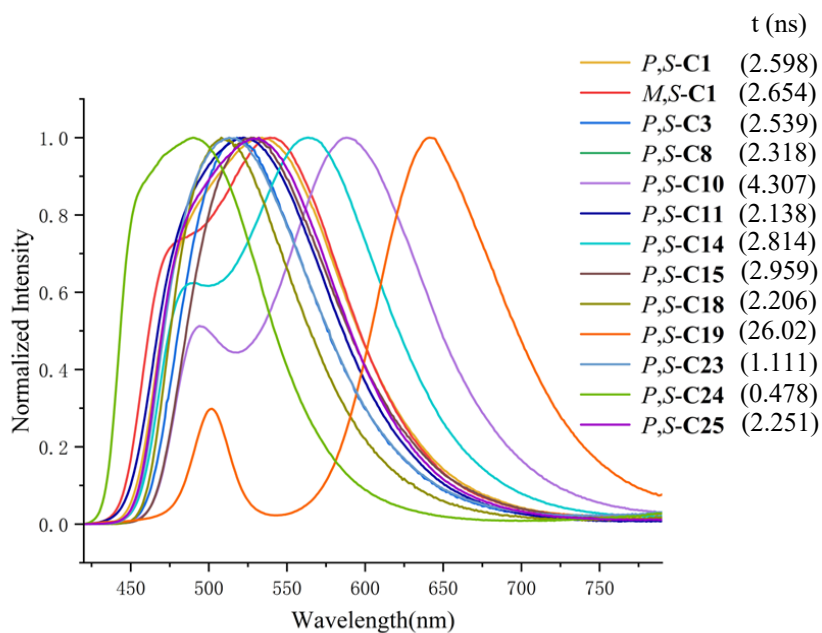


Figure S89. Experimental fluorescence of helical phenanthrene.

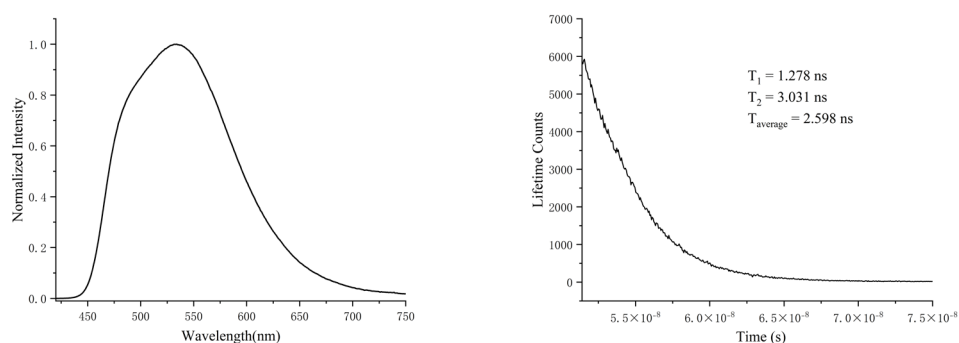


Figure S90. Experimental fluorescence spectra and fluorescence lifetime of *P, S*-C1 and *M, R*-C1 was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL C1 in DCM. The fluorescence lifetime was measured with a SpectraLED (407 nm) as the excitation source and a picosecond photon detection module as the detector ($\lambda_{\text{em}} = 530 \text{ nm}$).

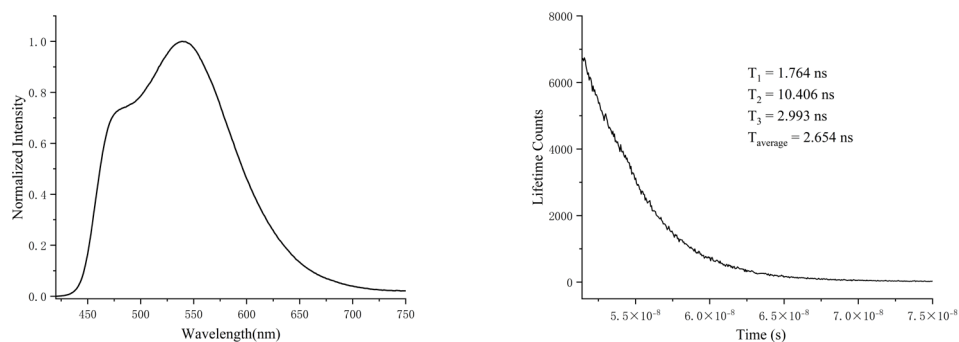


Figure S91. Experimental fluorescence and fluorescence lifetime of *P*, *R*-**C1** and *M*, *S*-**C1** was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL **C1** in DCM. The fluorescence lifetime was measured with a SpectraLED (407 nm) as the excitation source and a picosecond photon detection module as the detector ($\lambda_{em} = 540$ nm).

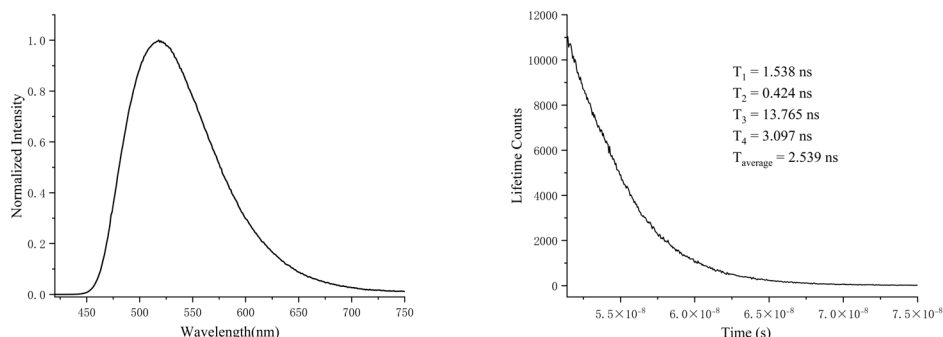


Figure S92. Experimental fluorescence and fluorescence lifetime of *P*, *S*-**C3** was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *P*, *S*-**C3** in DCM. The fluorescence lifetime was measured with a SpectraLED (407 nm) as the excitation source and a picosecond photon detection module as the detector ($\lambda_{em} = 517$ nm).

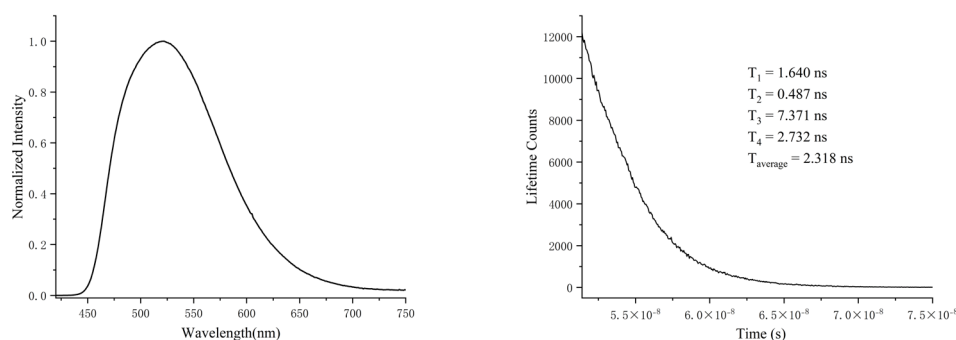


Figure S93. Experimental fluorescence and fluorescence lifetime of *P*, *S*-**C8** was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *P*, *S*-**C8** in DCM. The fluorescence lifetime was measured with a SpectraLED (407 nm) as the excitation source and a picosecond photon detection module as the detector ($\lambda_{em} = 510$ nm).

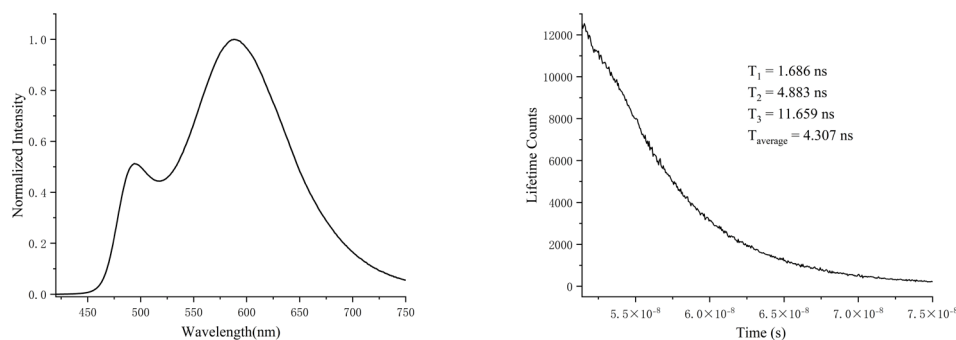


Figure S94. Experimental fluorescence and fluorescence lifetime of *P*, *S*-**C10** was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *P*, *S*-**C10** in DCM. The fluorescence lifetime was measured with a SpectraLED (407 nm) as the excitation source and a picosecond

photon detection module as the detector ($\lambda_{em} = 588$ nm).

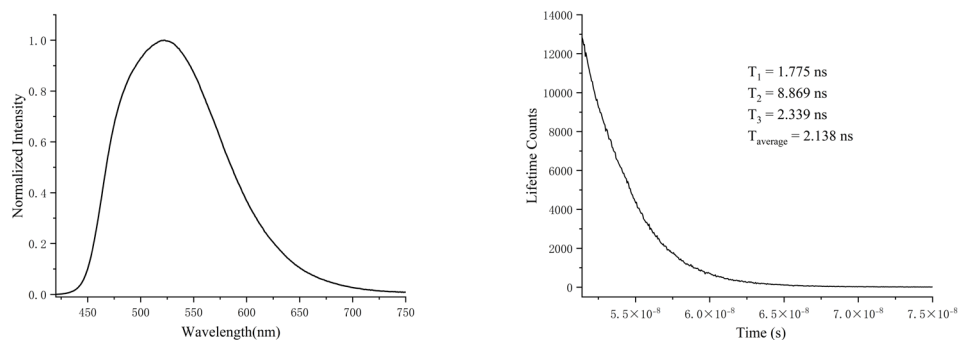


Figure S95. Experimental fluorescence and fluorescence lifetime of *P, S-C11* was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *P, S-C11* in DCM. The fluorescence lifetime was measured with a SpectraLED (407 nm) as the excitation source and a picosecond photon detection module as the detector ($\lambda_{em} = 520$ nm).

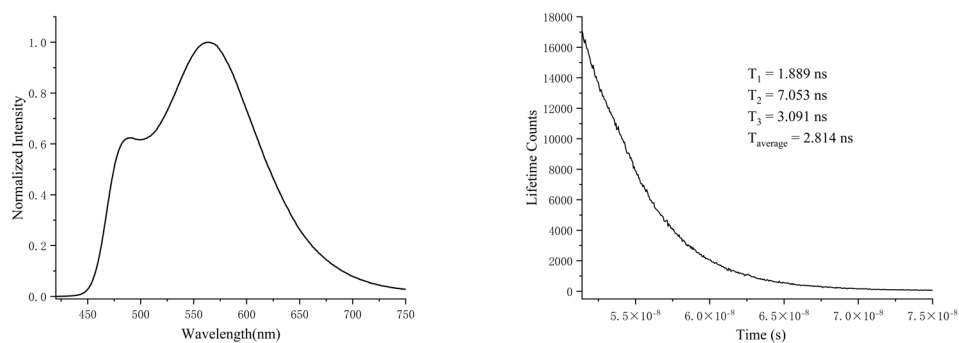


Figure S96. Experimental fluorescence and fluorescence lifetime of *P, S-C14* was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *P, S-C14* in DCM. The fluorescence lifetime was measured with a SpectraLED (407 nm) as the excitation source and a picosecond photon detection module as the detector ($\lambda_{em} = 560$ nm).

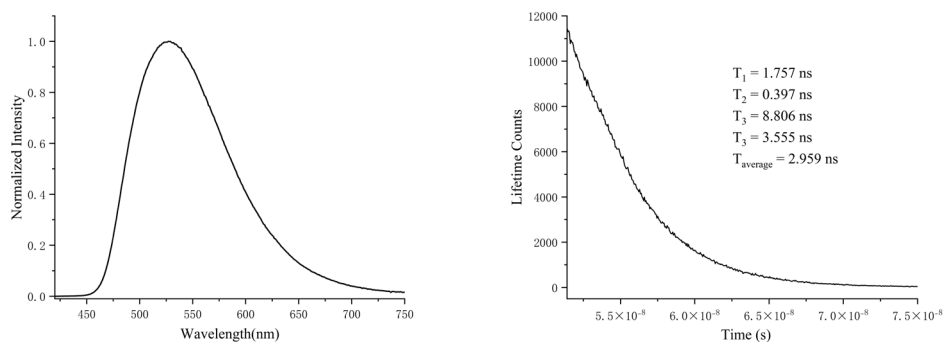


Figure S97. Experimental fluorescence and fluorescence lifetime of *P, S-C15* was carried out at 300 K at a concentration of 1×10^{-3}

mmol/mL *P*, *S*-**C15** in DCM. The fluorescence lifetime was measured with a SpectraLED (407 nm) as the excitation source and a picosecond photon detection module as the detector ($\lambda_{\text{em}} = 525$ nm).

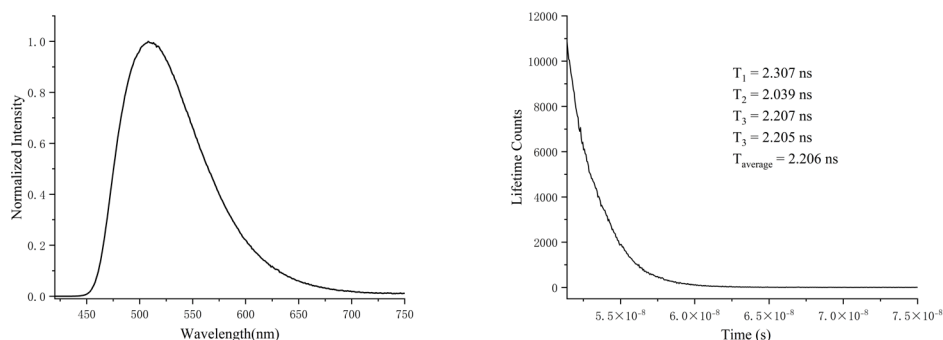


Figure S98. Experimental fluorescence and fluorescence lifetime of *P*, *S*-**C18** was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *P*, *S*-**C18** in DCM. The fluorescence lifetime was measured with a SpectraLED (407 nm) as the excitation source and a picosecond photon detection module as the detector ($\lambda_{\text{em}} = 510$ nm).

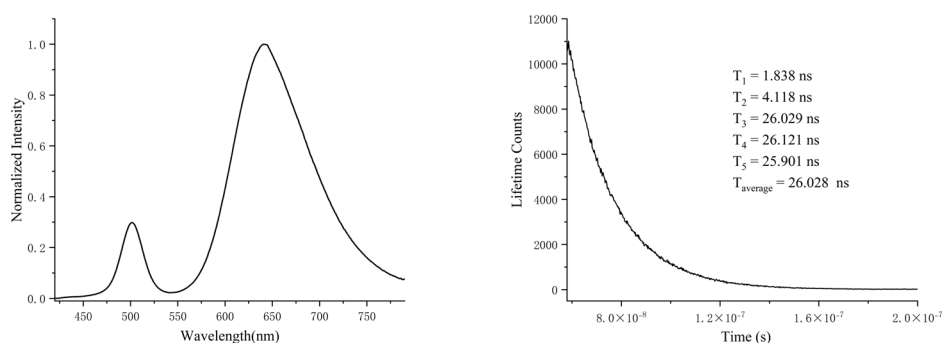


Figure S99. Experimental fluorescence and fluorescence lifetime of *P*, *S*-**C19** was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *P*, *S*-**C19** in DCM. The fluorescence lifetime was measured with a SpectraLED (407 nm) as the excitation source and a picosecond photon detection module as the detector ($\lambda_{\text{em}} = 660$ nm).

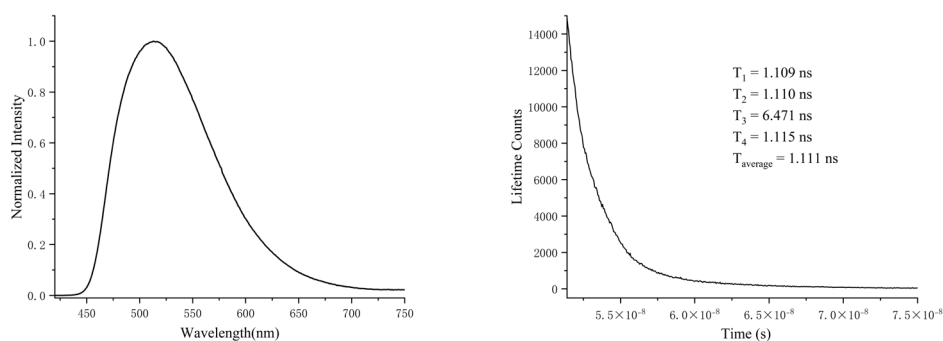


Figure S100. Experimental fluorescence and fluorescence lifetime of *P*, *S*-**C23** was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *P*, *S*-**C23** in DCM. The fluorescence lifetime was measured with a SpectraLED (407 nm) as the excitation source and a picosecond photon detection module as the detector ($\lambda_{em} = 490$ nm).

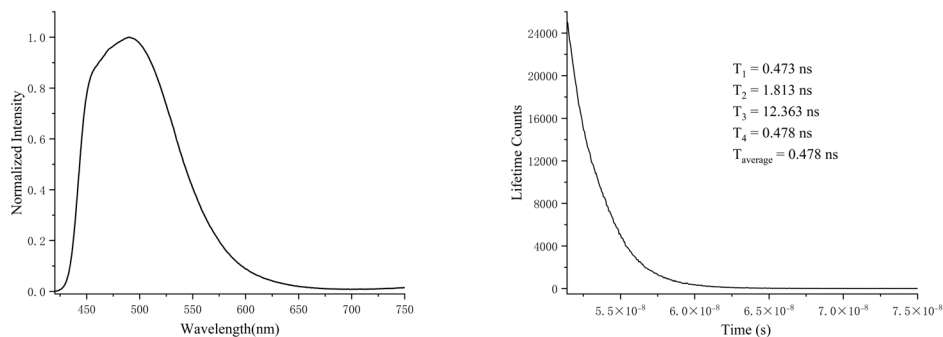


Figure S101. Experimental fluorescence and fluorescence lifetime of *P*, *S*-**C24** was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *P*, *S*-**C24** in DCM. The fluorescence lifetime was measured with a SpectraLED (407 nm) as the excitation source and a picosecond photon detection module as the detector ($\lambda_{em} = 530$ nm).

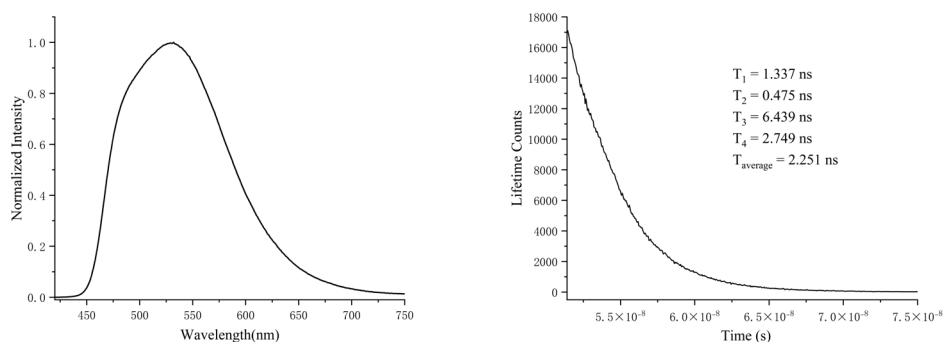


Figure S102. Experimental fluorescence and fluorescence lifetime of *P*, *S*-**C25** was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *P*, *S*-**C25** in DCM. The fluorescence lifetime was measured with a SpectraLED (407 nm) as the excitation source and a picosecond photon detection module as the detector ($\lambda_{em} = 530$ nm).

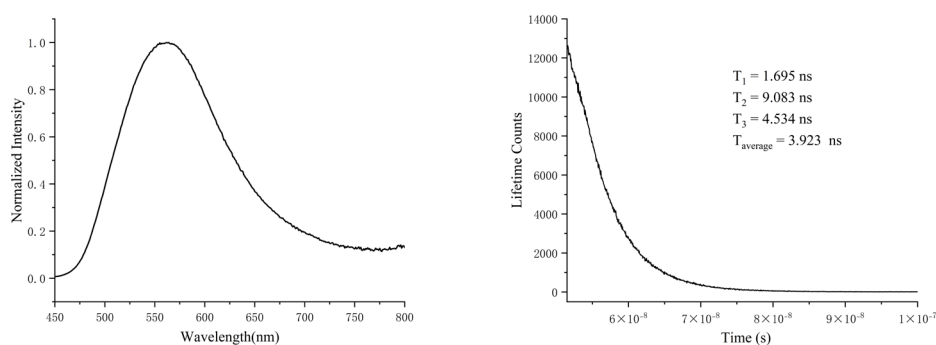


Figure S103. Experimental fluorescence and fluorescence lifetime of *M-A10* was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *M-A10* in DCM. The fluorescence lifetime was measured with a SpectraLED (407 nm) as the excitation source and a picosecond photon detection module as the detector ($\lambda_{em} = 560$ nm).

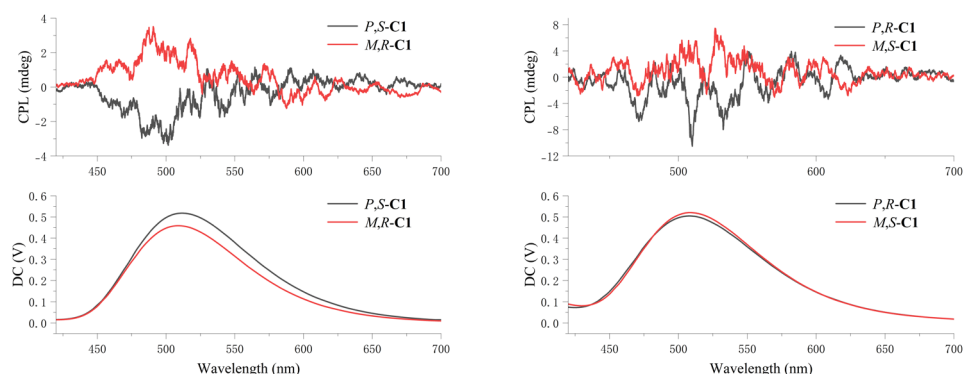


Figure S104. Experimental CPL of *P, S-C1*, *M, R-C1*, *P, R-C1* and *M, S-C1* were carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *C1* in DCM. *P, S-C1* -3.6×10^{-4} , *M, R-C1* $+3.4 \times 10^{-4}$ wavelength 500 nm, excitation wavelength 340 nm. *P, R-C1* -3.8×10^{-4} , *M, S-C1* $+2.2 \times 10^{-4}$ wavelength 500 nm, excitation wavelength 340 nm.

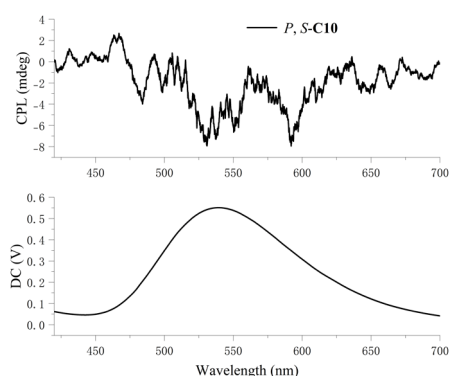


Figure S105. Experimental CPL of *P, S-C10* was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *P, S-C10* in DCM. *P, S-C10* -6.1×10^{-4} wavelength 540 nm, excitation wavelength 340 nm.

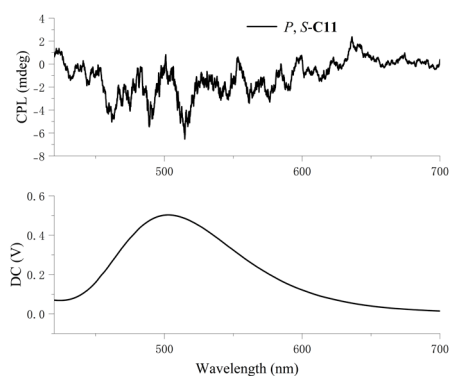


Figure S106. Experimental CPL of *P, S-C11* was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *P, S-C11* in DCM. *P, S-C11* - 3.9×10^{-4} wavelength 510 nm, excitation wavelength 340 nm.

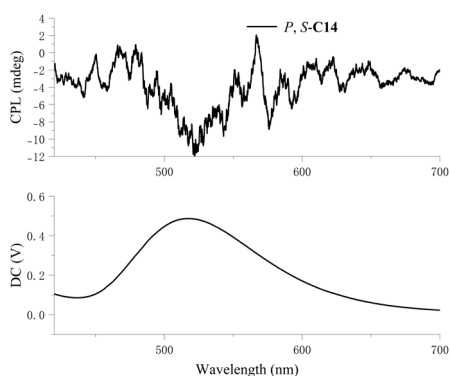


Figure S107. Experimental CPL of *P, S-C14* was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *P, S-C14* in DCM. *P, S-C14* - 9.3×10^{-4} wavelength 520 nm, excitation wavelength 340 nm.

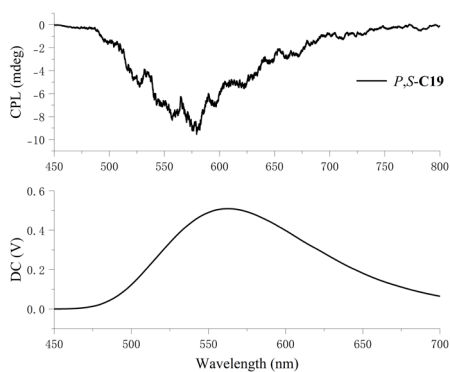


Figure S108. Experimental CPL and g_{lum} of *M-A19* was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *P, S-C19* in DCM. *P, S-C19* - 1.1×10^{-3} wavelength 560 nm, excitation wavelength 340 nm.

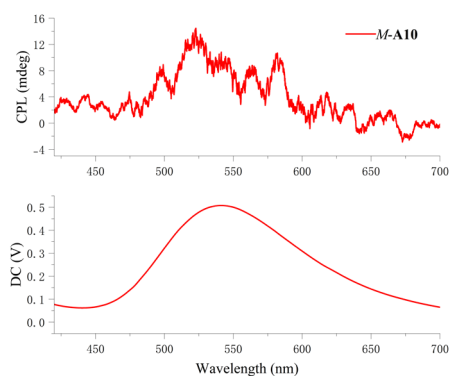


Figure S109. Experimental CPL and g_{lum} of *M*-**A10** was carried out at 300 K at a concentration of 1×10^{-3} mmol/mL *M*-**A10** in DCM. *M*-**A10** $+1.2 \times 10^{-3}$ wavelength 540 nm, excitation wavelength 340 nm.

9 DFT Analysis.

Computational details

All calculations were performed using Gaussian 09 program package^[4], employing the PBE0 hybrid functional^[5] with usage of empirical Grimme's dispersion correction (GD3-BJ)^[6,7] and def2-TZVP^[8] basis set. Geometries were optimized in dichloromethane solvent and characterized by frequency analysis at 300 K, and the relative Gibbs free energy (kcal/mol) was calculated at the PBE0/def2TZVP level. The simulated g_{abs} were performed by time-dependent DFT (TD-DFT) calculations at the PBE0/6-311G(d) level. The electric and magnetic transition dipole moments of all structures were calculated by Multiwfn^[9,10]. The isosurface plots of frontier molecular orbitals were generated by VMD 1.9.3^[11]. The three-dimensional structures were generated using CYLView20^[12].

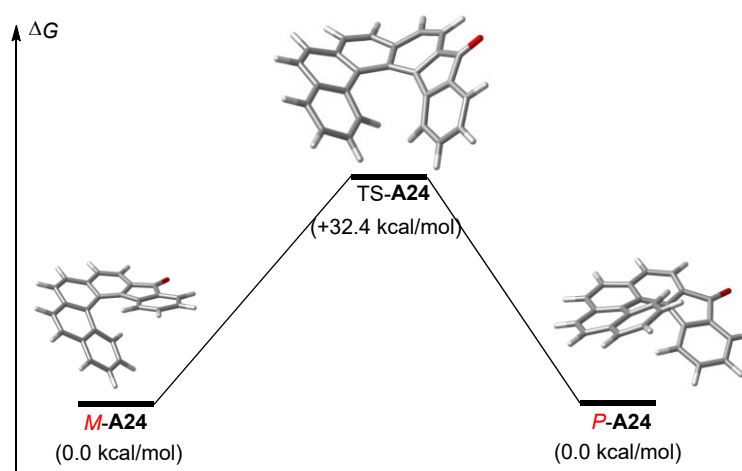


Figure 110. Computed diastereomerization of **A24**. Optimized geometries were at the PBE0-D3BJ/def2TZVP//PBE0-D3BJ/def2SVP level of theory.

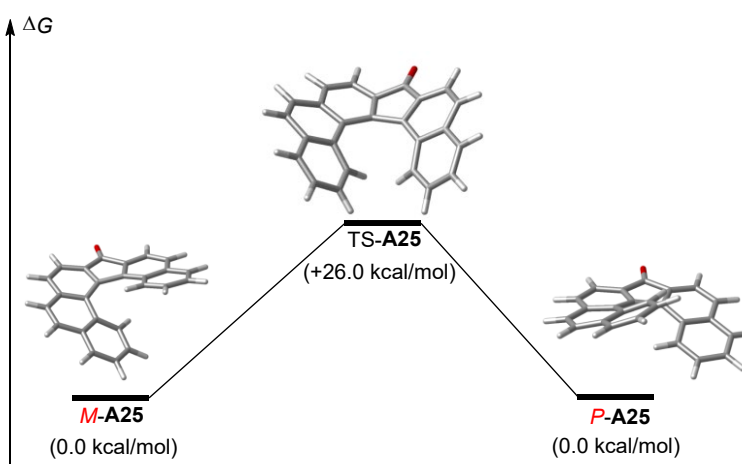


Figure 111. Computed diastereomerization of **A25**. Optimized geometries were at the PBE0-D3BJ/def2TZVP//PBE0-D3BJ/def2SVP level of theory.

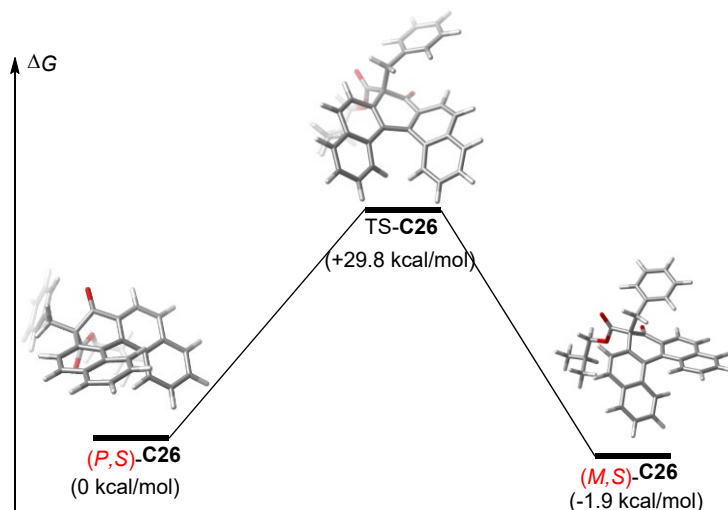


Figure 112. Computed diastereomerization of C26. Optimized geometries were at the PBE0-D3BJ/def2TZVP//PBE0-D3BJ/def2SVP level of theory.

Table S13. Calculated chiroptical properties of [7]helical compounds.

compound	state	$ \mu $ (10^{-18} esu·cm) ^a	$ m $ (10^{-20} erg·G ⁻¹) ^b	θ (degree) ^c	g_{cal} ^d	g_{abs}
(<i>P,S</i>)-C1	S ₀ -S ₄	3.29	4.97	70.1	0.0206	0.0133
(<i>M,R</i>)-C1	S ₀ -S ₄	3.30	4.97	70.1	-0.0205	-0.0133
(<i>P,R</i>)-C1	S ₀ -S ₄	3.24	4.84	69.2	0.0211	0.0140
(<i>M,S</i>)-C1	S ₀ -S ₄	3.24	4.83	69.2	-0.0211	-0.0140
(<i>P</i>)-A1	S ₀ -S ₅	4.76	5.11	75.1	0.0110	0.0077
(<i>M</i>)-A1	S ₀ -S ₅	4.76	5.11	75.1	-0.0110	-0.0077
(<i>M</i>)-A2	S ₀ -S ₆	4.42	5.19	73.5	-0.0133	-0.0083
(<i>M</i>)-A3	S ₀ -S ₆	4.30	5.40	77.8	-0.0106	-0.0078
(<i>M</i>)-A4	S ₀ -S ₅	4.31	5.14	78.7	-0.0097	-0.0069
(<i>M</i>)-A5	S ₀ -S ₅	5.25	5.45	78.2	-0.0085	-0.0058
(<i>M</i>)-A6	S ₀ -S ₆	4.76	4.54	77.8	-0.0080	-0.0052
(<i>M</i>)-A8	S ₀ -S ₅	4.58	5.57	75.3	-0.0123	-0.0078
(<i>M</i>)-A10	S ₀ -S ₆	3.81	5.66	79	-0.0113	-0.0071
(<i>M</i>)-A11	S ₀ -S ₅	4.62	6.53	79.2	-0.0105	-0.0084
(<i>M</i>)-A12	S ₀ -S ₆	4.30	5.61	77	-0.0117	-0.0078
(<i>M</i>)-A13	S ₀ -S ₅	4.33	6.07	75.4	-0.0141	-0.0084
(<i>M</i>)-A14	S ₀ -S ₆	4.41	6.34	74.8	-0.0151	-0.0090
(<i>M</i>)-A15	S ₀ -S ₅	3.75	6.92	75.7	-0.0182	-0.0113

^a μ : Transition electric dipole moment. ^b m : Transition magnetic dipole moment. ^c θ : Angle between μ and m . ^d $g_{\text{cal}} = 4\cos\theta|m||\mu|/(|m|^2+|\mu|^2)$.

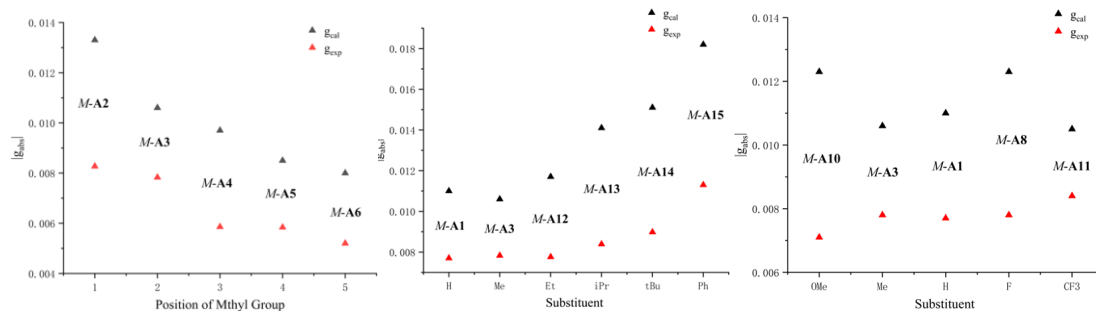


Figure S113. Comparison between experimental and calculated dissymmetric absorption factors g_{exp} vs g_{cal} .

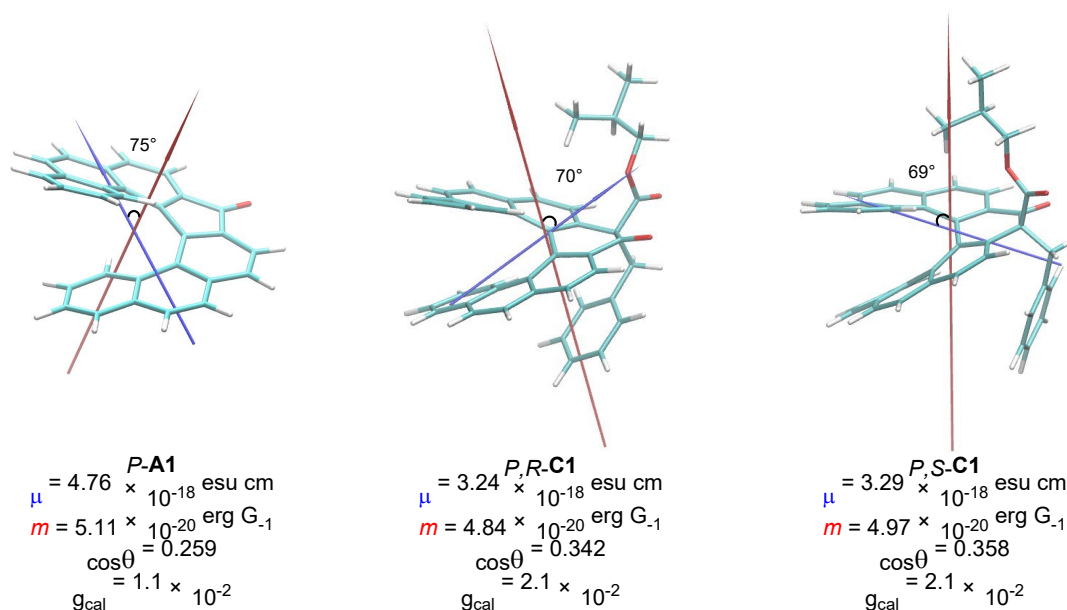


Figure S114. The transition electric dipole moment μ (blue arrow) and the transition magnetic dipole moment m (red arrow) of (*P,S*)-C1, (*P,R*)-C1 from $S_0 \rightarrow S_4$ transition and (*P*)-A1 from $S_0 \rightarrow S_5$ transition, calculated by the TD-DFT method at the PBE0/def2-TZVP level of theory.

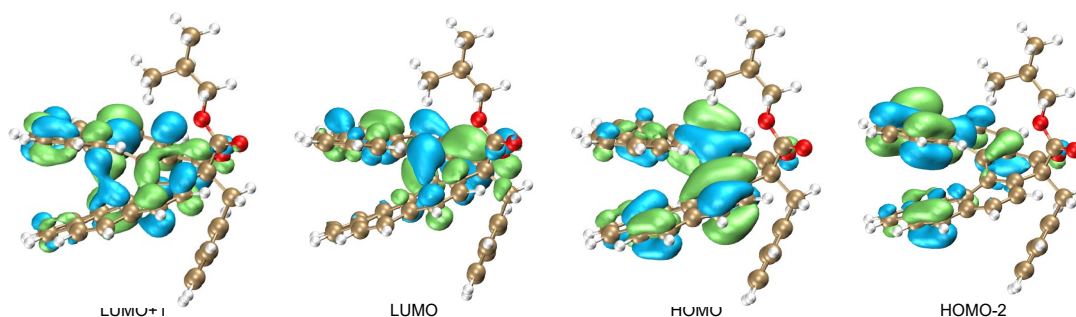


Figure S115. Frontier molecular orbitals of (*P,S*)-C1 calculated by the DFT method at the PBE0/def2-TZVP level of theory.

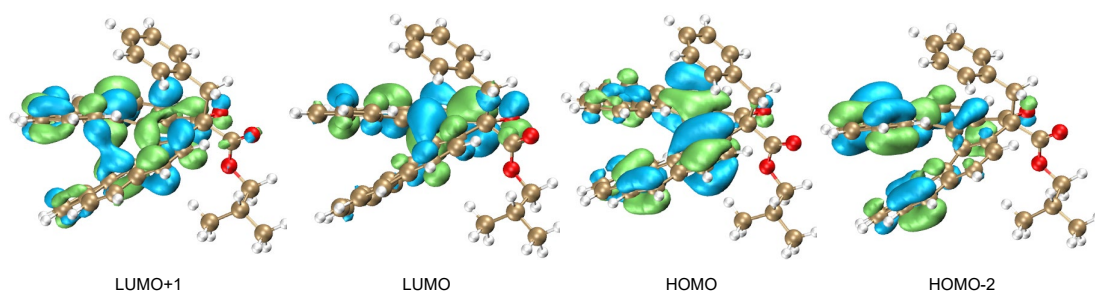


Figure S116. Frontier molecular orbitals of (*P,R*)-C1 calculated by the DFT method at the PBE0/def2-TZVP level of theory.

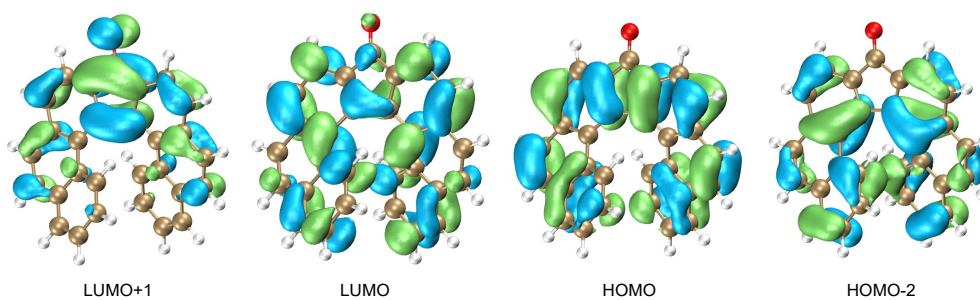


Figure S117. Frontier molecular orbitals of (*P*)-**A1** calculated by the DFT method at the PBE0/def2-TZVP level of theory.

Table S14. TD-DFT vertical one-electron excitations calculated for (*P,S*)-**C1** at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.9162	425.16	0.0738	HOMO > LUMO 85.4% HOMO-1 > LUMO 9.3%
S ₂	3.1406	394.78	0.0162	HOMO-1 > LUMO 81.5% HOMO > LUMO 9.1%
S ₃	3.0352	375.12	0.0310	HOMO > LUMO+1 50.1% HOMO-2 > LUMO 38.5% HOMO-1 > LUMO+1 5.0%
S ₄	3.3912	365.61	0.1393	HOMO-2 > LUMO 49.9% HOMO > LUMO+1 36.8% HOMO-1 > LUMO+1 65.0%
S ₅	3.5606	348.22	0.0213	HOMO-2 > LUMO+1 8.5% HOMO > LUMO+2 8.4%
S ₆	3.6541	339.30	0.0118	HOMO-3 > LUMO 45.0% HOMO-2 > LUMO+1 25.7% HOMO-1 > LUMO+1 16.1%
S ₇	3.6818	336.75	0.0054	HOMO-7 > LUMO 47.3% HOMO-4 > LUMO 15.3% HOMO-8 > LUMO 10.0% HOMO-3 > LUMO 6.5%
S ₈	3.8352	323.28	0.0912	HOMO-2 > LUMO+1 47.7%, HOMO-3 > LUMO 32.6% HOMO-1 > LUMO+2 6.7%
S ₉	3.9126	316.88	0.1280	HOMO > LUMO+2 70.4% HOMO-1 > LUMO+1 7.2% HOMO-3 > LUMO 5.8%
S ₁₀	3.9811	311.43	0.0004	HOMO-4 > LUMO 80.4% HOMO-7 > LUMO 12.4%

^aExcitation energies with oscillator strength larger than 0.01 were listed. ^bRelative contribution larger than 5% was listed.

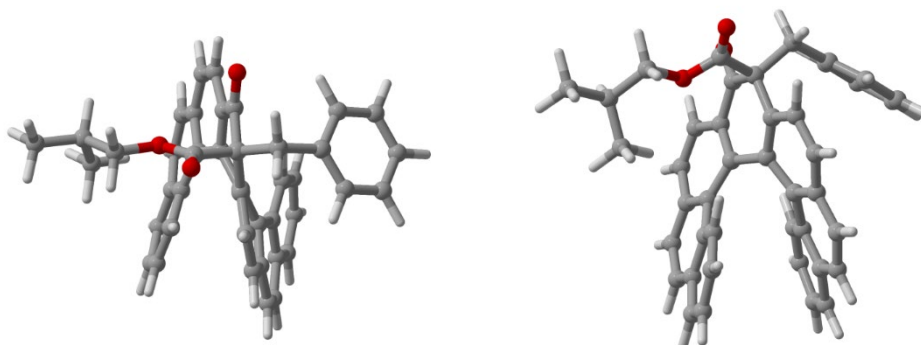
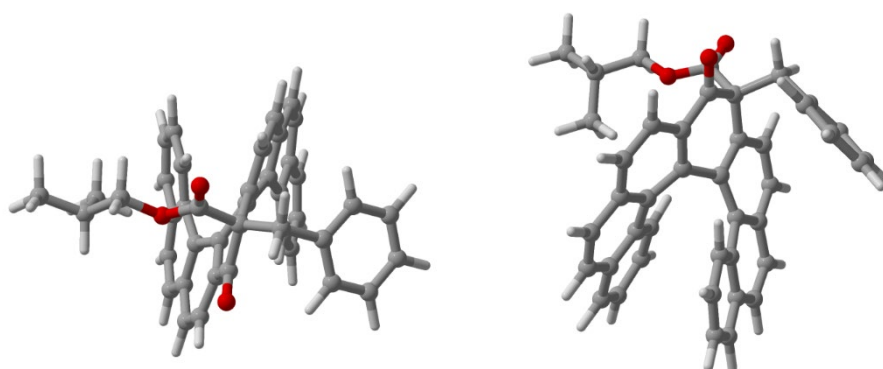


Figure S118. DFT optimized structures of (*P,S*)-**C1** at the PBE0/def2-TZVP level of theory.

Table S15. Summary of the TD-DFT calculation results of (*M,R*)-C1 at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.9162	425.16	0.0738	HOMO > LUMO 85.3%
				HOMO-1 > LUMO 9.4%
S ₂	3.1406	394.78	0.0162	HOMO-1 > LUMO 81.4%
				HOMO > LUMO 9.2%
S ₃	3.3052	375.12	0.0210	HOMO > LUMO+1 50.1%
				HOMO-2 > LUMO 38.4%
				HOMO-1 > LUMO+1 5.0%
S ₄	3.3912	365.61	0.1393	HOMO-2 > LUMO 50.0%
				HOMO > LUMO+1 36.8%
S ₅	3.5605	348.22	0.0213	HOMO-1 > LUMO+1 65.2%
				HOMO-2 > LUMO+1 8.4%
				HOMO > LUMO+2 8.3%
S ₆	3.6541	339.30	0.0118	HOMO-3 > LUMO 45.9%
				HOMO-2 > LUMO+1 26.2%
				HOMO-1 > LUMO+1 15.7%
S ₇	3.6818	336.75	0.0054	HOMO-7 > LUMO 47.4%
				HOMO-4 > LUMO 15.6%
				HOMO-8 > LUMO 10.3%
				HOMO-3 > LUMO 6.0%
S ₈	3.8352	323.28	0.0912	HOMO-2 > LUMO+1 47.8%
				HOMO-3 > LUMO 32.5%
				HOMO-1 > LUMO+2 6.7%
S ₉	3.9126	316.88	0.1280	HOMO > LUMO+2 70.7%
				HOMO-1 > LUMO+1 7.1%
				HOMO-3 > LUMO 5.6%
S ₁₀	3.9811	311.43	0.0004	HOMO-4 > LUMO 80.1%
				HOMO-7 > LUMO 12.5%

**Figure S119.** DFT optimized structures of (*M,R*)-C1 at the PBE0/def2-TZVP level of theory.**Table S16.** Summary of the TD-DFT calculation results of (*M,S*)-C1 at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.9718	417.20	0.0754	HOMO > LUMO 85.3%
				HOMO-1 > LUMO 9.4%
S ₂	3.1777	390.17	0.0140	HOMO-1 > LUMO 81.4%
				HOMO > LUMO 9.2%
S ₃	3.3497	370.13	0.0353	HOMO > LUMO+1 50.1%
				HOMO-2 > LUMO 38.4%
				HOMO-1 > LUMO+1 5.0%
S ₄	3.4244	362.06	0.1366	HOMO-2 > LUMO 50.0%
				HOMO > LUMO+1 36.8%
S ₅	3.5936	345.01	0.0230	HOMO-1 > LUMO+1 65.2%
				HOMO-2 > LUMO+1 8.4%
				HOMO > LUMO+2 8.3%
S ₆	3.6744	337.42	0.0113	HOMO-3 > LUMO 45.9%

S ₇	3.6875	336.23	0.0021	HOMO-2 > LUMO+1 26.2%
				HOMO-1 > LUMO+1 15.7%
				HOMO-7 > LUMO 47.4%
				HOMO-4 > LUMO 15.6%
				HOMO-8 > LUMO 10.3%
S ₈	3.8342	323.36	0.0769	HOMO-3 > LUMO 6.0%
				HOMO-2 > LUMO+1 47.8%
				HOMO-3 > LUMO 32.5%
S ₉	3.9163	316.58	0.0407	HOMO-1 > LUMO+2 6.7%
				HOMO > LUMO+2 70.7%
				HOMO-1 > LUMO+1 7.1%
S ₁₀	3.9465	314.16	0.0879	HOMO-3 > LUMO 5.6%
				HOMO-4 > LUMO 80.1%
				HOMO-7 > LUMO 12.5%

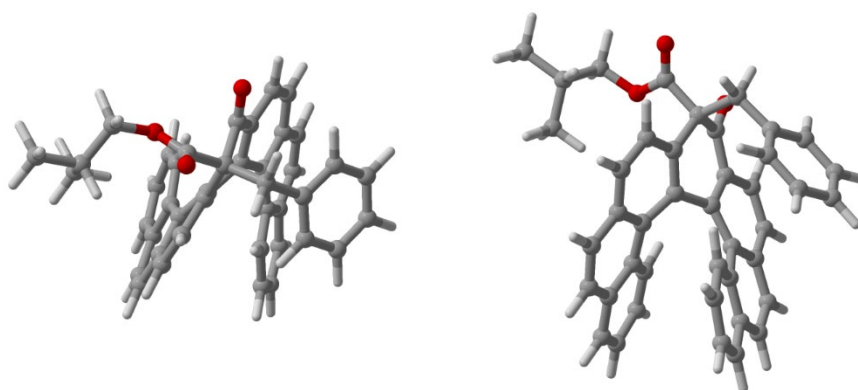


Figure S120. DFT optimized structures of (*M,S*)-C1 at the PBE0/def2-TZVP level of theory.

Table S17. Summary of the TD-DFT calculation results of (*P,R*)-C1 at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.9716	417.23	0.0755	HOMO > LUMO 85.3%
				HOMO-1 > LUMO 9.4%
S ₂	3.1776	390.19	0.0140	HOMO-1 > LUMO 81.4%
				HOMO > LUMO 9.2%
S ₃	3.3496	370.14	0.0354	HOMO > LUMO+1 50.1%
				HOMO-2 > LUMO 38.4%
				HOMO-1 > LUMO+1 5.0%
S ₄	3.4244	362.07	0.1366	HOMO-2 > LUMO 50.0%
				HOMO > LUMO+1 36.8%
S ₅	3.5936	345.01	0.0230	HOMO-1 > LUMO+1 65.2%
				HOMO-2 > LUMO+1 8.4%
				HOMO > LUMO+2 8.3%
S ₆	3.6744	337.43	0.0113	HOMO-3 > LUMO 45.9%
				HOMO-2 > LUMO+1 26.2%
				HOMO-1 > LUMO+1 15.7%
S ₇	3.6874	336.24	0.0021	HOMO-7 > LUMO 47.4%
				HOMO-4 > LUMO 15.6%
				HOMO-8 > LUMO 10.3%
				HOMO-3 > LUMO 6.0%
S ₈	3.8342	323.37	0.0769	HOMO-2 > LUMO+1 47.8%
				HOMO-3 > LUMO 32.5%
				HOMO-1 > LUMO+2 6.7%
S ₉	3.9161	316.60	0.0407	HOMO > LUMO+2 70.7%
				HOMO-1 > LUMO+1 7.1%
				HOMO-3 > LUMO 5.6%
S ₁₀	3.9464	314.17	0.0879	HOMO-4 > LUMO 80.1%
				HOMO-7 > LUMO 12.5%

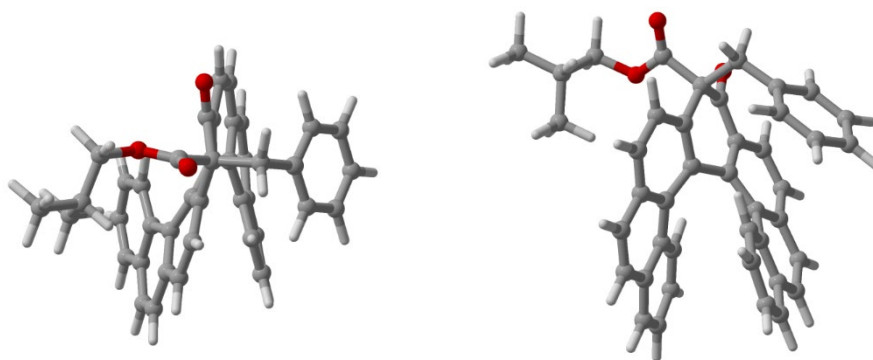


Figure S121. DFT optimized structures of (*P,R*)-C1 at the PBE0/def2-TZVP level of theory.

Table S18. Summary of the TD-DFT calculation results of (*P*)-A1 at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.3414	529.52	0.0093	HOMO > LUMO 97.8%
S ₂	2.9812	415.89	0.0260	HOMO-2 > LUMO 84.9%
				HOMO > LUMO+1 13.2%
S ₃	3.1363	395.31	0.1140	HOMO-1 > LUMO 83.1%
				HOMO-5 > LUMO 10.8%
S ₄	3.1778	390.15	0.0042	HOMO-5 > LUMO 65.2%
				HOMO-3 > LUMO 20.5%
				HOMO-1 > LUMO 8.2%
S ₅	3.3850	366.28	0.2913	HOMO > LUMO+1 82.2%
				HOMO-2 > LUMO 13.1%
S ₆	3.4089	363.71	0.0319	HOMO-3 > LUMO 75.6%
				HOMO-5 > LUMO 17.3%
S ₇	3.8222	324.38	0.0840	HOMO > LUMO+2 66.7%
				HOMO-1 > LUMO+1 25.7%
S ₈	3.8472	322.27	0.0761	HOMO-4 > LUMO 94.0%
S ₉	4.0224	308.24	0.0249	HOMO-2 > LUMO+1 94.1%
S ₁₀	4.0397	306.92	0.0294	HOMO-1 > LUMO+1 46.5%
				HOMO > LUMO+2 22.7%
				HOMO-3 > LUMO+1 10.5%
				HOMO-2 > LUMO+2 7.5%
				HOMO > LUMO+3 6.4%

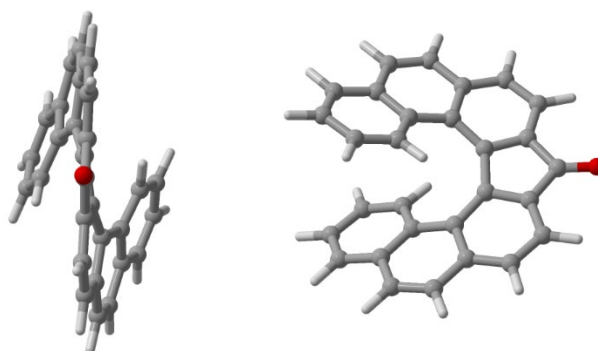


Figure S122. DFT optimized structures of (*P*)-A1 at the PBE0/def2-TZVP level of theory.

Table S19. Summary of the TD-DFT calculation results of (*M*)-A1 at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.3415	529.51	0.0093	HOMO > LUMO 97.8%
S ₂	2.9812	415.89	0.0260	HOMO-2 > LUMO 84.9%
				HOMO > LUMO+1 13.2%

S ₃	3.1363	395.32	0.1140	HOMO-1 > LUMO 83.1% HOMO-5 > LUMO 10.8%
S ₄	3.1779	390.15	0.0042	HOMO-5 > LUMO 65.2% HOMO-3 > LUMO 20.5% HOMO-1 > LUMO 8.2%
S ₅	3.3850	366.28	0.2913	HOMO > LUMO+1 82.2% HOMO-2 > LUMO 13.1%
S ₆	3.4089	363.70	0.0319	HOMO-3 > LUMO 75.6% HOMO-5 > LUMO 17.3%
S ₇	3.8221	324.38	0.0840	HOMO > LUMO+2 66.7% HOMO-1 > LUMO+1 25.7%
S ₈	3.8473	322.27	0.0761	HOMO-4 > LUMO 94.0%
S ₉	4.0223	308.24	0.0249	HOMO-2 > LUMO+1 94.1% HOMO-1 > LUMO+1 46.5% HOMO > LUMO+2 22.7%
S ₁₀	4.0396	306.92	0.0295	HOMO-3 > LUMO+1 10.5% HOMO-2 > LUMO+2 7.5% HOMO > LUMO+3 6.4%

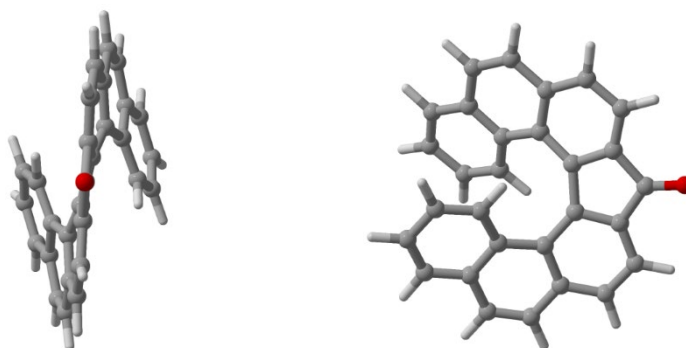


Figure S123. DFT optimized structures of (*M*)-**A1** at the PBE0/def2-TZVP level of theory.

Table S20. Summary of the TD-DFT calculation results of (*M*)-**A2** at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength	Description ^b
S ₁	2.2864	542.27	0.0109	HOMO > LUMO 98.0%
S ₂	2.9557	419.47	0.0208	HOMO-2 > LUMO 85.3% HOMO -> LUMO+1 12.8%
S ₃	3.0316	408.97	0.1300	HOMO-1 > LUMO 93.1%
S ₄	3.1609	392.24	0.0005	HOMO-5 > LUMO 48.3% HOMO-3 > LUMO 40.1% HOMO-6 > LUMO 5.3%
S ₅	3.2881	377.07	0.0050	HOMO-3 > LUMO 55.3% HOMO-5 > LUMO 34.2%
S ₆	3.3572	369.31	0.2483	HOMO > LUMO+1 81.8% HOMO-2 > LUMO 12.4%
S ₇	3.7545	330.23	0.0943	HOMO-4 > LUMO 93.6%
S ₈	3.8111	325.33	0.0705	HOMO > LUMO+2 47.1% HOMO-1 > LUMO+1 42.3% HOMO-1 > LUMO+1 41.2%
S ₉	3.9602	313.08	0.0339	HOMO > LUMO+2 40.7% HOMO-3 > LUMO+1 10.1%
S ₁₀	4.0229	308.20	0.0183	HOMO-2 > LUMO+1 94.8%

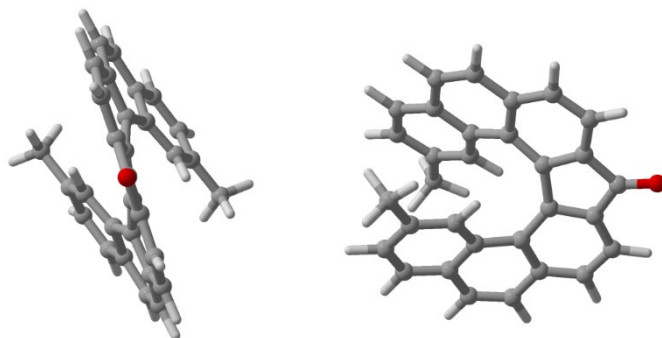


Figure S124. DFT optimized structures of (*M*)-**A2** at the PBE0/def2-TZVP level of theory.

Table S21. Summary of the TD-DFT calculation results of (*M*)-**A3** at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength	Description ^b
S ₁	2.2922	540.91	0.0098	HOMO > LUMO 98.0%
S ₂	2.9244	423.97	0.0360	HOMO-2 > LUMO 89.8% HOMO > LUMO+1 8.3%
S ₃	3.0135	411.42	0.0721	HOMO-1 > LUMO 89.8% HOMO-3 > LUMO 5.3%
S ₄	3.1610	392.23	0.0254	HOMO-5 > LUMO 67.3% HOMO-3 > LUMO 23.0%
S ₅	3.3547	369.58	0.0597	HOMO-3 > LUMO 68.7% HOMO-5 > LUMO 24.7%
S ₆	3.3906	365.67	0.2379	HOMO > LUMO+1 86.5% HOMO-2 > LUMO 8.1%
S ₇	3.7555	330.14	0.0565	HOMO-4 > LUMO 94.5%
S ₈	3.7794	328.05	0.0437	HOMO > LUMO+2 66.3% HOMO-1 > LUMO+1 29.2%
S ₉	4.0268	307.90	0.0264	HOMO-2 > LUMO+1 93.2% HOMO-1 > LUMO+1 37.8% HOMO - LUMO+2 22.9%
S ₁₀	4.0536	305.86	0.0948	HOMO-3 > LUMO+1 12.7% HOMO > LUMO+3 11.3% HOMO-2 > LUMO+2 7.7%

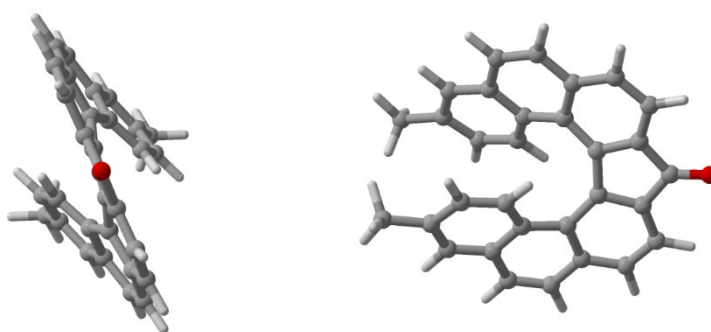


Figure S124. DFT optimized structures of (*M*)-**A3** at the PBE0/def2-TZVP level of theory.

Table S22. Summary of the TD-DFT calculation results of (*M*)-**A4** at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.3010	538.82	0.0085	HOMO > LUMO 97.5%
S ₂	2.8930	428.56	0.0359	HOMO-2 > LUMO 89.4% HOMO > LUMO+1 8.3%
S ₃	3.0036	412.79	0.1199	HOMO-1 > LUMO 94.8%
S ₄	3.1666	391.54	0.0032	HOMO-5 > LUMO 65.6%

					HOMO-3 > LUMO 23.1%
					HOMO-6 > LUMO 7.0%
S ₅	3.3495	370.16	0.2544		HOMO > LUMO+1 85.5%
					HOMO-2 > LUMO 8.1%
S ₆	3.3744	367.43	0.0291		HOMO-3 > LUMO 72.2%
					HOMO-5 > LUMO 21.0%
S ₇	3.7363	331.83	0.0867		HOMO > LUMO+2 65.5%
					HOMO-1 > LUMO+1 27.5%
S ₈	3.7889	327.23	0.1127		HOMO-4 > LUMO 93.1%
					HOMO-1 > LUMO+1 47.8%
S ₉	3.9411	314.59	0.0693		HOMO > LUMO+2 26.9%
					HOMO-3 > LUMO+1 7.1%
					HOMO-2 > LUMO+2 6.7%
S ₁₀	3.9484	314.01	0.0194		HOMO-2 > LUMO+1 95.3%

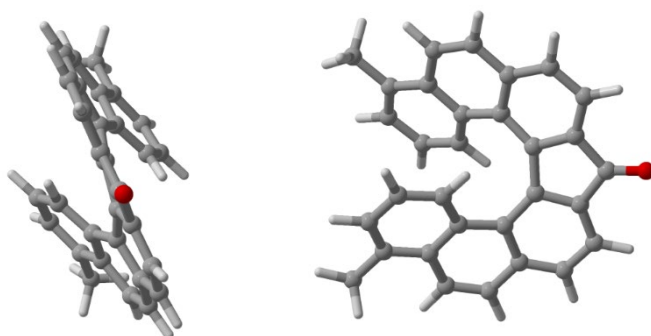


Figure S126. DFT optimized structures of (*M*)-**A4** at the PBE0/def2-TZVP level of theory.

Table S23. Summary of the TD-DFT calculation results of (*M*)-**A5** at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.3401	529.83	0.0046	HOMO > LUMO 97.8%
S ₂	2.9716	417.23	0.0277	HOMO-2 > LUMO 81.7%
				HOMO > LUMO+1 16.3%
S ₃	3.1395	394.91	0.1385	HOMO-1 > LUMO 82.7%
				HOMO-5 > LUMO 10.4%
S ₄	3.1991	387.56	0.0054	HOMO-5 > LUMO 61.5%
				HOMO-3 > LUMO 23.4%
				HOMO-1 > LUMO 7.7%
S ₅	3.3483	370.29	0.3501	HOMO > LUMO+1 79.7%
				HOMO-2 > LUMO 16.0%
S ₆	3.4102	363.57	0.0363	HOMO-3 > LUMO 72.1%
				HOMO-5 > LUMO 19.9%
S ₇	3.8116	325.28	0.0891	HOMO > LUMO+2 56.2%
				HOMO-1 > LUMO+1 34.2%
S ₈	3.8504	322.00	0.0710	HOMO-4 > LUMO 93.5%
S ₉	3.9781	311.67	0.0326	HOMO-2 > LUMO+1 93.8%
				HOMO-1 > LUMO+1 40.9%
S ₁₀	3.9934	310.48	0.0330	HOMO > LUMO+2 31.8%
				HOMO-3 > LUMO+1 9.9%
				HOMO > LUMO+3 6.1%
				HOMO-2 > LUMO+2 5.3%

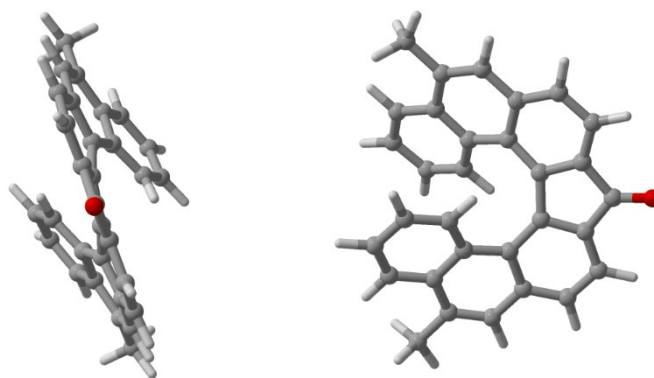


Figure S127. DFT optimized structures of (*M*)-**A5** at the PBE0/def2-TZVP level of theory.

Table S24. Summary of the TD-DFT calculation results of (*M*)-**A6** at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.3363	530.69	0.0108	HOMO > LUMO 97.3%
S ₂	2.9318	422.90	0.0224	HOMO-2 > LUMO 84.5%
				HOMO > LUMO+1 13.2%
S ₃	3.1210	397.26	0.1154	HOMO-1 > LUMO 78.5%
				HOMO-5 > LUMO 14.5%
S ₄	3.1762	390.35	0.0133	HOMO-3 > LUMO 44.4%,
				HOMO-5 > LUMO 37.1%
				HOMO-1 > LUMO 12.3%
S ₅	3.3049	375.15	0.0109	HOMO-3 > LUMO 50.1%
				HOMO-5 > LUMO 41.1%
S ₆	3.3223	373.19	0.2856	HOMO > LUMO+1 82.1%
				HOMO-2 > LUMO 13.0%
S ₇	3.7321	332.21	0.0994	HOMO-4 > LUMO 94.6%
S ₈	3.8192	324.64	0.0699	HOMO > LUMO+2 53.4%
				HOMO-1 > LUMO+1 37.0%
S ₉	3.9217	316.15	0.0176	HOMO-2 > LUMO+1 95.7%
				HOMO-1 > LUMO+1 37.4%
S ₁₀	3.9559	313.42	0.0039	HOMO > LUMO+2 30.2%
				HOMO-3 > LUMO+1 16.5%
				HOMO-2 > LUMO+2 5.8%

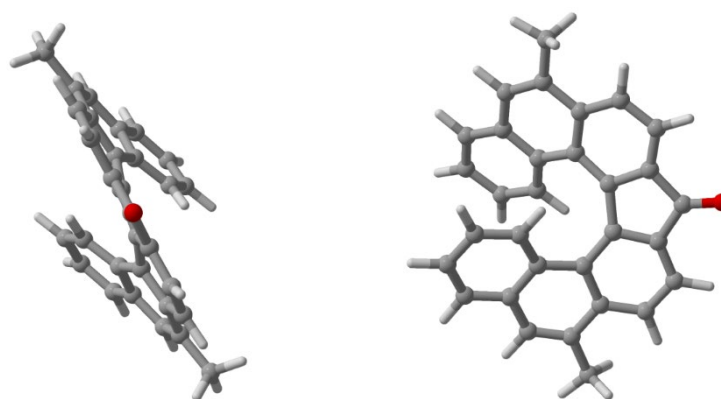


Figure S128. DFT optimized structures of (*M*)-**A5** at the PBE0/def2-TZVP level of theory.

Table S25. Summary of the TD-DFT calculation results of (*M*)-**A8** at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.3553	526.40	0.0111	HOMO > LUMO 97.9%
S ₂	2.9982	413.53	0.0367	HOMO-2 > LUMO 87.5%

				HOMO > LUMO+1 10.6%
				HOMO-1 > LUMO 82.5%
				HOMO-3 > LUMO 8.3%
				HOMO-5 > LUMO 75.4%
S ₄	3.1618	392.13	0.0232	HOMO-3 > LUMO 10.6%
				HOMO-1 > LUMO 8.6%
S ₅	3.4338	361.07	0.2734	HOMO > LUMO+1 85.0%
				HOMO-2 > LUMO 10.7%
S ₆	3.4438	360.02	0.0690	HOMO-3 > LUMO 77.5%
				HOMO-5 > LUMO 14.7%
S ₇	3.7621	329.56	0.0865	HOMO > LUMO+2 76.6%
				HOMO-1 > LUMO+1 18.4%
S ₈	3.8693	320.43	0.0404	HOMO-4 > LUMO 94.8%
S ₉	4.0727	304.42	0.0238	HOMO-2 > LUMO+1 91.2%
				HOMO-1 > LUMO+1 43.5%
				HOMO > LUMO+2 14.4%
S ₁₀	4.1068	301.90	0.0750	HOMO-3 > LUMO+1 13.2%
				HOMO-2 > LUMO+2 12.8%
				HOMO > LUMO+4 8.9%

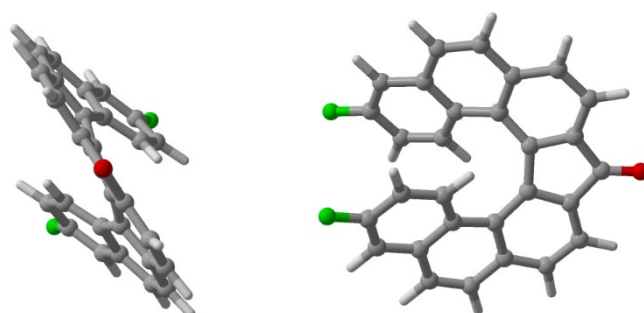


Figure S129. DFT optimized structures of (*M*)-**A8** at the PBE0/def2-TZVP level of theory.

Table S26. Summary of the TD-DFT calculation results of (*M*)-**A10** at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.2428	552.82	0.0148	HOMO > LUMO 98.1%
S ₂	2.7691	447.74	0.0372	HOMO-1 > LUMO 95.4%
S ₃	2.8423	436.22	0.0494	HOMO-2 > LUMO 94.3%
				HOMO-5 > LUMO 74.4%
S ₄	3.1669	391.50	0.0225	HOMO-3 > LUMO 17.9%
				HOMO-3 > LUMO 74.0%
S ₅	3.779	367.05	0.0812	HOMO-5 > LUMO 18.3%
S ₆	3.4066	363.96	0.1879	HOMO > LUMO+1 90.8%
S ₇	3.6368	340.91	0.0082	HOMO-4 > LUMO 96.5%
				HOMO > LUMO+2 63.6%
S ₈	3.6824	336.69	0.0058	HOMO-1 > LUMO+1 33.6%
				HOMO-1 > LUMO+1 52.3%
S ₉	3.9403	314.65	0.3478	HOMO > LUMO+2 22.0%
				HOMO-2 > LUMO+2 12.8%
				HOMO-2 > LUMO+1 65.6%
S ₁₀	3.9840	311.20	0.0230	HOMO-1 > LUMO+2 27.7%

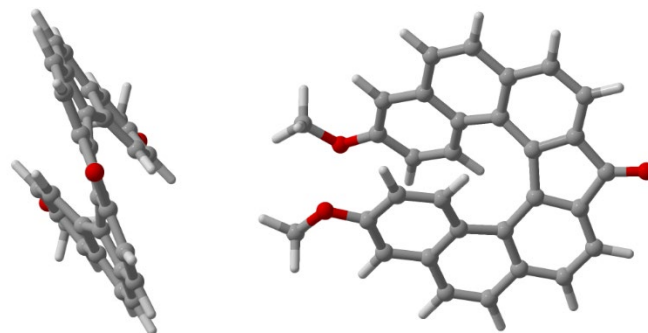


Figure S130. DFT optimized structures of (*M*)-**A10** (left: top view, right: side view). at the PBE0/def2-TZVP level of theory.

Table S27. Summary of the TD-DFT calculation results of (*M*)-**A11** at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.3540	526.69	0.0109	HOMO > LUMO 98.0%
S ₂	3.0310	409.05	0.0014	HOMO-2 > LUMO 67.4% HOMO > LUMO+1 30.5%
S ₃	3.1441	394.34	0.0096	HOMO-5 > LUMO 79.0% HOMO-3 > LUMO 10.0% HOMO-1 > LUMO 5.3%
S ₄	3.2739	378.71	0.0939	HOMO-1 > LUMO 78.8% HOMO-3 > LUMO 9.4%
S ₅	3.3172	373.76	0.2682	HOMO > LUMO +1 65.7% HOMO-2 > LUMO 30.8%
S ₆	3.4776	356.52	0.0383	HOMO-3 > LUMO 75.5% HOMO-5 > LUMO 13.3% HOMO-1 > LUMO 6.9%
S ₇	3.7826	327.77	0.0893	HOMO > LUMO+2 82.1% HOMO-1 > LUMO+1 10.9%
S ₈	3.8987	318.01	0.0715	HOMO-4 > LUMO 93.4% HOMO > LUMO+3 33.6% HOMO-1 > LUMO+1 30.6%
S ₉	4.0042	309.63	0.0169	HOMO-2 > LUMO+2 12.7% HOMO-6 > LUMO 5.7% HOMO-3 > LUMO+1 5.3%
S ₁₀	4.0079	309.35	0.0251	HOMO-2 > LUMO+1 92.5%

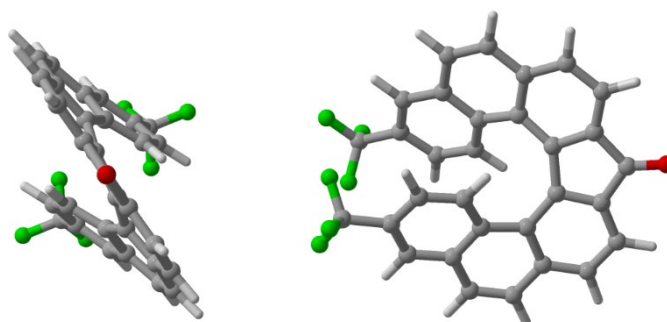


Figure S131. DFT optimized structures of (*M*)-**A11** at the PBE0/def2-TZVP level of theory.

Table S28. Summary of the TD-DFT calculation results of (*M*)-**A12** at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.2926	540.81	0.0093	HOMO > LUMO 98.0%
S ₂	2.9278	423.47	0.0359	HOMO-2 > LUMO 89.6%, HOMO > LUMO+1 8.5%

S ₃	3.0068	412.35	0.0749	HOMO-1 > LUMO 90.0% HOMO-3 -> LUMO 5.1%
S ₄	3.1610	392.23	0.0257	HOMO-5 > LUMO 67.0% HOMO-3 > LUMO 23.4%
S ₅	3.3535	369.71	0.0599	HOMO-3 > LUMO 68.6% HOMO-5 > LUMO 24.9%
S ₆	3.3883	365.92	0.2383	HOMO > LUMO+1 86.3% HOMO-2 > LUMO 8.2%
S ₇	3.7598	329.76	0.0610	HOMO-4 > LUMO 94.4%
S ₈	3.7816	327.86	0.0405	HOMO > LUMO+2 63.8% HOMO-1 > LUMO+1 31.6%
S ₉	4.0298	307.67	0.0295	HOMO-2 > LUMO+1 93.5%
S ₁₀	4.0500	306.14	0.1221	HOMO-1 > LUMO+1 40.5%
				HOMO > LUMO+2 26.2%
				HOMO-3 > LUMO+1 10.9%
				HOMO > LUMO+3 9.7%
				HOMO-2 > LUMO+2 5.8%

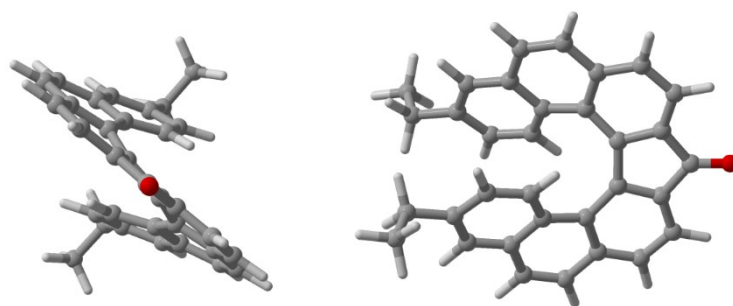


Figure S132. DFT optimized structures of (*M*)-**A12** at the PBE0/def2-TZVP level of theory.

Table S29. Summary of the TD-DFT calculation results of (*M*)-**A13** at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.3077	537.25	0.0107	HOMO > LUMO 97.8%
S ₂	2.9105	425.95	0.0352	HOMO-2 > LUMO 74.5%
				HOMO-1 > LUMO 14.5%
				HOMO > LUMO+1 8.9%
S ₃	3.0497	406.55	0.0864	HOMO-1 > LUMO 75.6%
				HOMO-2 > LUMO 14.3%
S ₄	3.1712	390.97	0.0250	HOMO-5 > LUMO 63.9%
				HOMO-3 > LUMO 27.0%
S ₅	3.3571	369.31	0.2393	HOMO > LUMO+1 86.6%
				HOMO-2 > LUMO 8.2%
S ₆	3.3655	368.40	0.0513	HOMO-3 > LUMO 65.0%
				HOMO-5 > LUMO 28.3%
S ₇	3.7481	330.79	0.0459	HOMO-4 > LUMO 94.3%
S ₈	3.7651	329.30	0.0443	HOMO > LUMO+2 65.5%
				HOMO-1 > LUMO+1 27.6%
S ₉	3.9532	313.63	0.0372	HOMO-2 > LUMO+1 78.9%
				HOMO-1 > LUMO+1 13.6%
				HOMO-1 > LUMO+1 33.0%
S ₁₀	4.0230	308.19	0.0812	HOMO > LUMO+2 24.3%
				HOMO-3 > LUMO+1 12.7%
				HOMO-2 > LUMO+1 7.9%
				HOMO > LUMO+3 7.7%
				HOMO-2 > LUMO+2 7.0%

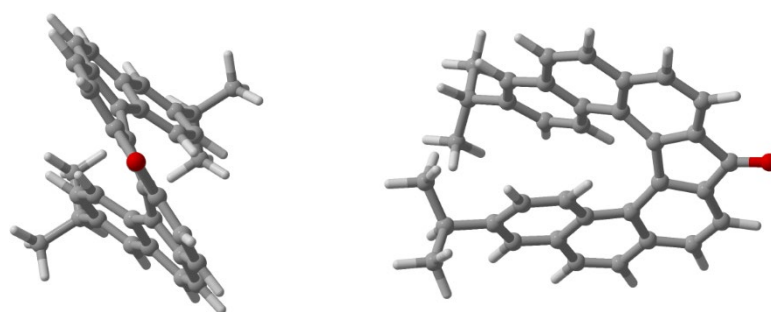


Figure S133. DFT optimized structures of (*M*)-**A13** at the PBE0/def2-TZVP level of theory.

Table S30. Summary of the TD-DFT calculation results of (*M*)-**A14** at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.3066	5.3751	0.0109	HOMO > LUMO 97.8%
S ₂	2.9235	424.09	0.0341	HOMO-2 > LUMO 88.8%
				HOMO > LUMO+1 9.2%
S ₃	3.0718	403.62	0.0934	HOMO-1 > LUMO 89.7%
				HOMO-3 > LUMO 5.2%
S ₄	3.1678	391.39	0.0283	HOMO-5 > LUMO 62.6%
				HOMO-3 > LUMO 28.6%
S ₅	3.3550	369.55	0.0475	HOMO-3 > LUMO 63.4%
				HOMO-5 > LUMO 29.8%
S ₆	3.3688	368.03	0.2482	HOMO > LUMO+1 86.4%
				HOMO-2 > LUMO 9.1%
S ₇	3.7441	331.15	0.0458	H-OMO4 > LUMO 94.6%
S ₈	3.7778	328.19	0.0583	HOMO > LUMO+2 69.6%
				HOMO-1 > LUMO+1 25.5%
S ₉	3.9786	311.63	0.0342	HOMO-2 > LUMO+1 93.2%
				HOMO-1 > LUMO+1 36.6%
				HOMO > LUMO+2 19.6%
S ₁₀	4.0322	307.49	0.0478	HOMO-3 > LUMO+1 15.8%
				HOMO-2 > LUMO+2 10.9%
				HOMO > LUMO+3 9.4%

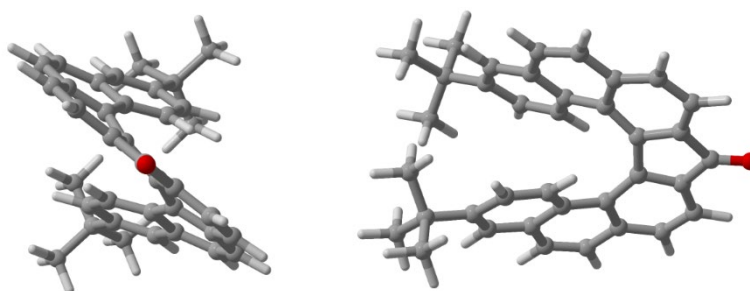


Figure S134. DFT optimized structures of (*M*)-**A13** at the PBE0/def2-TZVP level of theory.

Table S31. Summary of the TD-DFT calculation results of (*M*)-**A15** at the PBE0/def2-TZVP level of theory.

Excited States	Energy (eV)	Wavelength (nm)	Oscillator Strength ^a	Description ^b
S ₁	2.3064	537.56	0.0106	HOMO > LUMO 98.0%
S ₂	2.8449	435.81	0.0897	HOMO-1 > LUMO 94.7%
S ₃	2.8619	433.22	0.0263	HOMO-2 > LUMO 88.6%
				HOMO > LUMO+1 7.3%

S ₄	3.1521	393.34	0.0252	HOMO-8 > LUMO 67.1% HOMO-3 > LUMO 22.2%
S ₅	3.2524	381.20	0.1736	HOMO > LUMO+1 87.9% HOMO-2 > LUMO 7.6%
S ₆	3.3371	371.53	0.0509	HOMO-3 > LUMO 71.4% HOMO-8 > LUMO 22.3%
S ₇	3.6253	342.00	0.0971	HOMO-1 > LUMO+1 78.1% HOMO > LUMO+2 17.5
S ₈	3.6661	338.19	0.0007	HOMO-4 > LUMO 76.0% HOMO-5 > LUMO 14.1%
S ₉	3.8105	325.38	0.0067	HOMO-2 > LUMO+1 90.8% HOMO > LUMO+2 31.4% HOMO > LUMO+3 14.3%
S ₁₀	3.8444	322.50	0.5412	HOMO-1 > LUMO+1 11.6% HOMO-3 > LUMO+1 8.9% HOMO-2 > LUMO+2 7.2% HOMO-2 > LUMO+3 6.6%

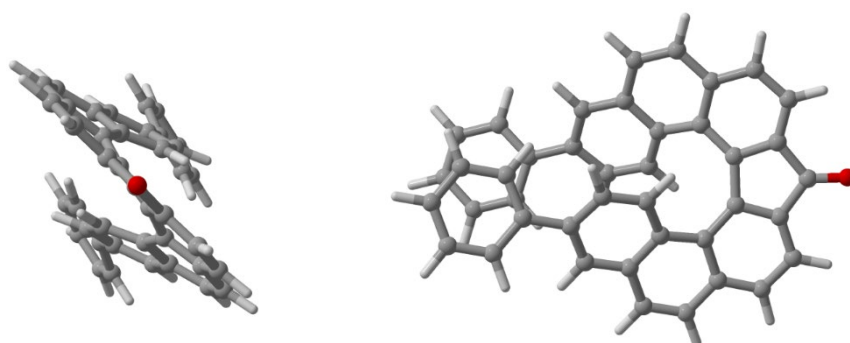
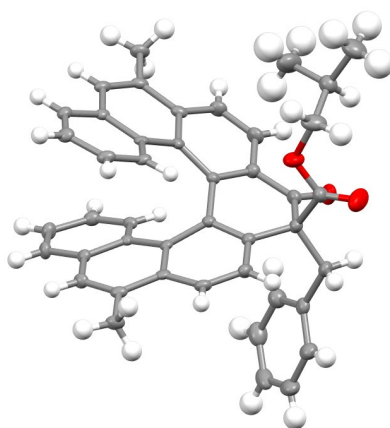


Figure S135. DFT optimized structures of (*M*)-**A15** at the PBE0/def2-TZVP level of theory.

10 X-ray crystal structure.

The crystal of racemic product *rac*-C6 was obtained in the n-hexane at room temperature. CCDC 2423527 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

The yellow crystal in block-shape, with approximate dimensions of 0.164×0.191× 0.296 mm³, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source ($K_{\alpha} = 1.54178\text{\AA}$). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package^[13-15]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested^[16].



Crystallographic Data for C₄₄H₃₆O₃.

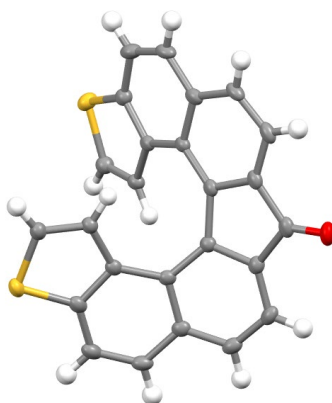
Formula	C ₄₄ H ₃₆ O ₃
Formula mass (amu)	612.73
Space group	<i>Pbca</i> (No.61)
<i>a</i> (Å)	17.3273(4)
<i>b</i> (Å)	16.1076(4)
<i>c</i> (Å)	23.2632(6)
α (deg)	90
β (deg)	90
γ (deg)	90
<i>V</i> (Å ³)	6492.8(3)
<i>Z</i>	8
λ (Å)	1.54178
<i>T</i> (K)	143(2)
ρ_{calc} (g cm ⁻³)	1.254
μ (mm ⁻¹)	0.603
Transmission factors	0.822, 1.000
$2\theta_{\text{max}}$ (deg)	68.269
No. of unique data, including $F_o^2 < 0$	5891
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	5010
No. of variables	429
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ ^a	0.0717
$R_w(F_o^2)$ ^b	0.1706
Goodness of fit	1.045

^a $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $R_w(F_o^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2]/3$.

The crystal of (*M*)-**A18** was obtained in the DCM at room temperature. CCDC 2423528 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

The red crystal in block-shape, with approximate dimensions of 0.270×0.325×0.402 mm³, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 143(2)K equipped with micro-focus Cu radiation source (K_{α} = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package^[13-15]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested^[16].



Crystallographic Data for C₂₅H₁₂OS₂.

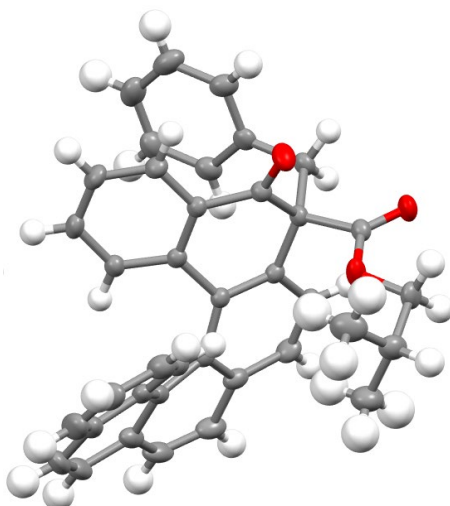
Formula	C ₂₅ H ₁₂ OS ₂
Formula mass (amu)	392.47
Space group	P2 ₁ (No.5)
<i>a</i> (Å)	10.6348(4)
<i>b</i> (Å)	7.4184(3)
<i>c</i> (Å)	11.7184(4)
α (deg)	90
β (deg)	106.881(1)
γ (deg)	90
<i>V</i> (Å ³)	884.67(6)
<i>Z</i>	2
λ (Å)	1.54178
<i>T</i> (K)	143(2)
ρ_{calcd} (g cm ⁻³)	1.473
μ (mm ⁻¹)	2.826
Transmission factors	0.421–0.649
$2\theta_{\text{max}}$ (deg)	68.231
No. of unique data, including $F_o^2 < 0$	3151
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	3141
No. of variables	253
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ ^a	0.0215
$R_w(F_o^2)$ ^b	0.0541
Goodness of fit	1.039
Flack Parameter	0.052(4)

^a $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $R_w(F_o^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2] / 3$.

The crystal of product *M*, **S-C24'** was obtained in the n-hexane at room temperature. CCDC 2472266 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

The yellow crystal in block-shape, with approximate dimensions of 0.096×0.134×0.192 mm³, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source (K_{α} = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package^[13-15]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested^[16].



Crystallographic Data for C₃₈H₃₀O₃.

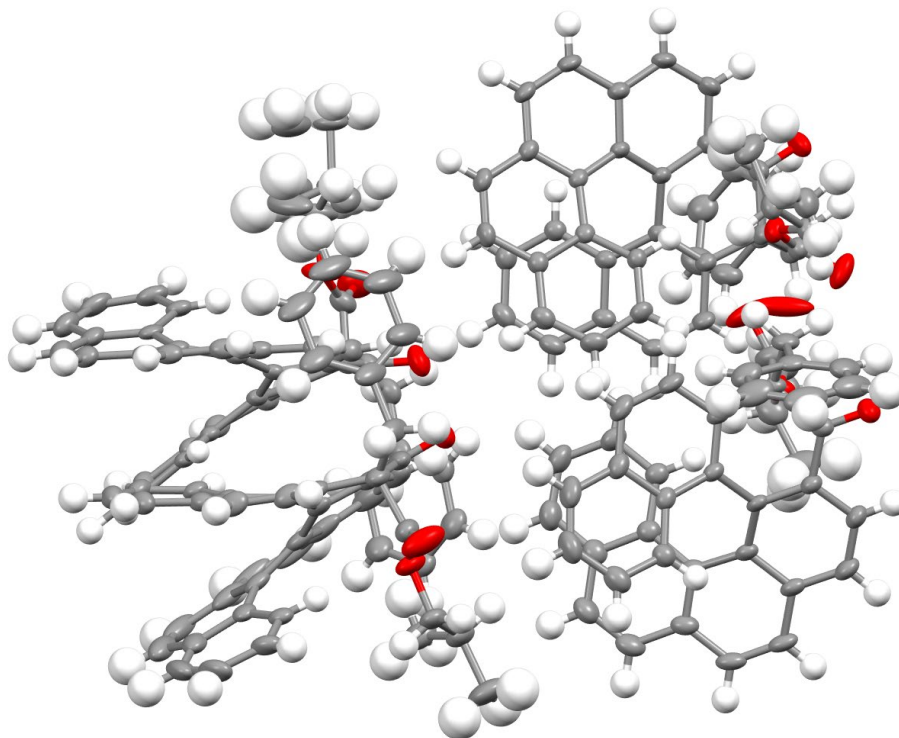
Formula	C ₃₈ H ₃₀ O ₃
Formula mass (amu)	534.62
Space group	P21 (No. 4)
<i>a</i> (Å)	11.2696(2)
<i>b</i> (Å)	13.6820(3)
<i>c</i> (Å)	18.7988(4)
α (deg)	90
β (deg)	98.113(1)
γ (deg)	90
<i>V</i> (Å ³)	2869.59(10)
<i>Z</i>	2
λ (Å)	1.54178
<i>T</i> (K)	173(2)
ρ_{calcd} (g cm ⁻³)	1.237
μ (mm ⁻¹)	0.606
Transmission factors	0.914-1.000
$2\theta_{\text{max}}$ (deg)	68.345
No. of unique data, including $F_o^2 < 0$	10388
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	10047
No. of variables	743
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ ^a	0.0285
$R_w(F_o^2)$ ^b	0.0725
Goodness of fit	1.040

^a $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $R_w(F_o^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2] / 3$.

The crystal of racemic product *rac*-C25 was obtained in the n-hexane at room temperature. CCDC 2475114 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

The yellow crystal in block-shape, with approximate dimensions of 0.104×0.119×0.634 mm³, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source (K_{α} = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package^[13-15]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested^[16].



Crystallographic Data for 4(C₄₂H₃₂O₃).

Formula	4(C ₄₂ H ₃₂ O ₃)
Formula mass (amu)	12240.4(4)
Space group	P2(1)/c (No. 14)
<i>a</i> (Å)	18.3831(4)
<i>b</i> (Å)	41.2872(9)
<i>c</i> (Å)	16.1280(3)
α (deg)	90
β (deg)	90.533(1)
γ (deg)	90
<i>V</i> (Å ³)	12240.4(4)
<i>Z</i>	4
λ (Å)	1.54178
<i>T</i> (K)	173(2)
ρ_{calcd} (g cm ⁻³)	1.269
μ (mm ⁻¹)	0.616
Transmission factors	0.645–1.000
$2\theta_{\text{max}}$ (deg)	68.343
No. of unique data, including $F_o^2 < 0$	22402
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	17251
No. of variables	1669
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ ^a	0.0745
$R_w(F_o^2)$ ^b	0.2021
Goodness of fit	1.040

^a $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $R_w(F_o^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum w F_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2] / 3$.

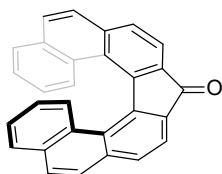
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12 The analytical and spectral characterization data.

12.1 Analytical and spectral characterization data of the helical fluorenones.

(*M*)-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (*M*-A1)



Following the typical procedure for gram scale synthesis, after recrystallization.

ee = >99%, dark red solid; R_f = 0.35 (PE/DCM = 1/1). $[\alpha]_D^{25} = -10242$ ($c = 3.8 \times 10^{-2}$, in CH_2Cl_2).

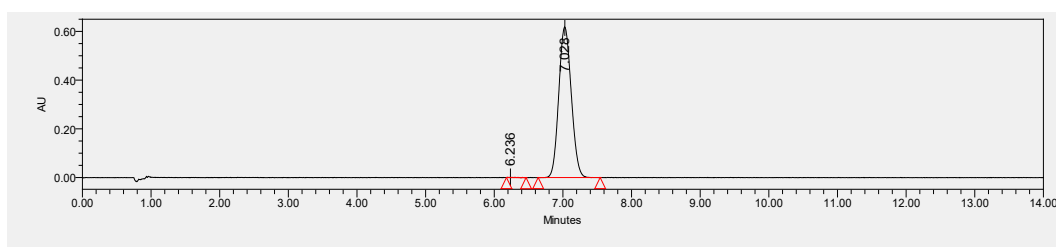
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **OZ-3** column), $\text{CO}_2/\text{MeOH} = 70/30$, flow rate 1.5 mL/min, $\lambda = 243$ nm, retention time: t (major) = 7.028 min, t (minor) = 6.236 min.

^1H NMR (600 MHz, CDCl_3) δ 7.87 (d, $J = 7.2$ Hz, 2H), 7.72 (d, $J = 7.8$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.52 – 7.50 (m, 4H), 7.08 (t, $J = 7.8$ Hz, 2H), 6.26 (t, $J = 7.8$ Hz, 2H).

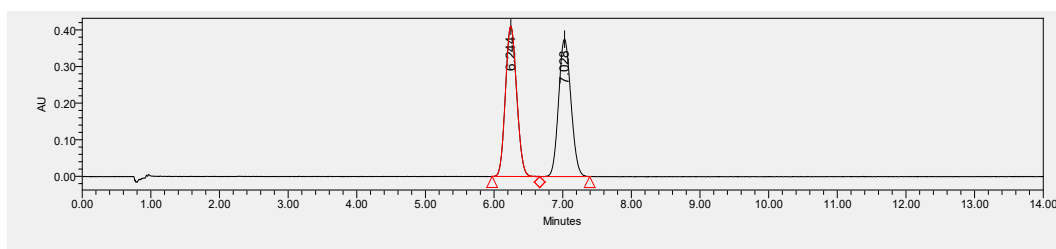
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.16, 147.03, 138.00, 135.06, 131.94, 130.53, 129.58, 128.35, 127.87, 127.53, 126.90, 126.56, 123.69, 120.65.

ESI-HRMS: calcd for $\text{C}_{29}\text{H}_{17}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 381.1274, found 381.1274.

IR (neat): 1702, 1611, 1529, 1306, 851, 736, 701 cm^{-1} .

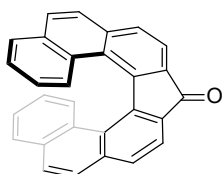


Retention Time	Area	% Area	Height
6.236	6083	0.08	871
7.028	7805583	99.92	617793



Retention Time	Area	% Area	Height
6.244	4667408	49.95	410517
7.028	4676773	50.05	375181

(*P*)-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (*P*-A1)



Following the typical procedure for gram scale synthesis, after recrystallization.

ee = >99%, dark red solid; R_f = 0.35 (PE/DCM = 1/1). $[\alpha]_D^{25} = 10912$ ($c = 3.8 \times 10^{-2}$, in CH_2Cl_2).

Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **OZ-3** column), $\text{CO}_2/\text{MeOH} = 70/30$, flow rate 1.5 mL/min, $\lambda = 243$ nm, retention time: t (major) = 6.254 min, t (minor) = 7.018 min.

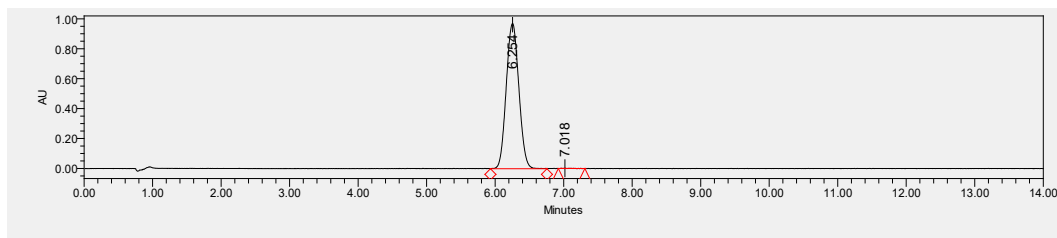
^1H NMR (600 MHz, CDCl_3) δ 7.87 (d, $J = 7.2$ Hz, 2H), 7.72 (d, $J = 7.8$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.52 – 7.50 (m, 4H), 7.08 (t, $J = 7.8$ Hz, 2H), 6.26 (t, $J = 7.8$ Hz, 2H).

$J = 8.4$ Hz, 2H), 7.52 – 7.50 (m, 4H), 7.08 (t, $J = 7.8$ Hz, 2H), 6.26 (t, $J = 7.8$ Hz, 2H).

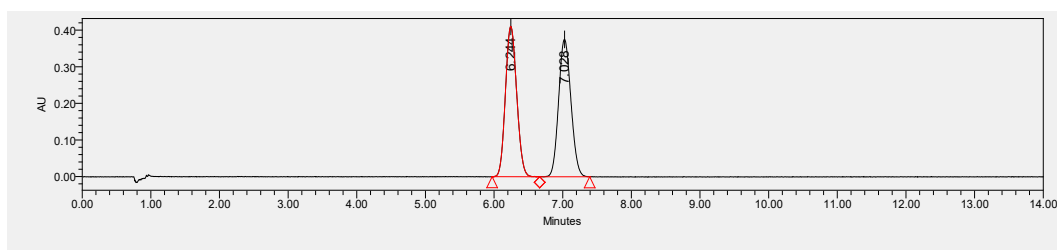
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.16, 147.03, 138.00, 135.06, 131.94, 130.53, 129.58, 128.35, 127.87, 127.53, 126.90, 126.56, 123.69, 120.65.

ESI-HRMS: calcd for $\text{C}_{29}\text{H}_{17}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 381.1274, found 381.1274.

IR (neat): 1702, 1611, 1529, 1306, 851, 736, 701 cm^{-1} .

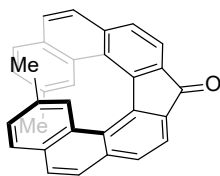


Retention Time	Area	% Area	Height
6.254	12412579	99.91	970853
7.018	10925	0.09	1570



Retention Time	Area	% Area	Height
6.244	4667408	49.95	410517
7.028	4676773	50.05	375181

(*M*)-2,16-dimethyl-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A2)



Following the typical procedure for the kinetic resolution.

(4 h 45 min) 15.5 mg, 38% yield; ee = 95%, dark red solid; R_f = 0.35 (PE/DCM = 1/1). $[\alpha]_D^{25} = -11708$ ($c = 4.0 \times 10^{-2}$, in CH_2Cl_2).

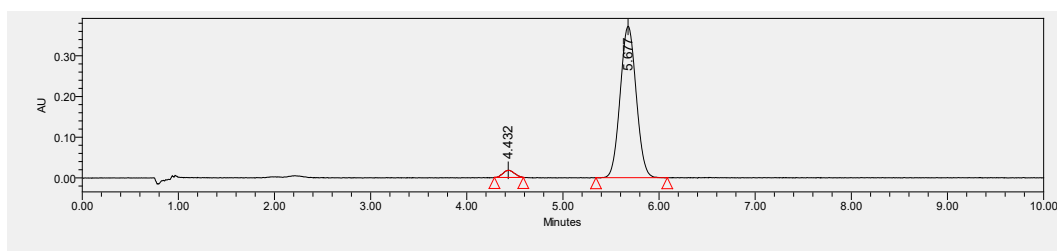
Dissolved in MeOH for UPCC; HPLC (Chiralcel **OZ-3** column), $\text{CO}_2/\text{MeOH} = 70/30$, flow rate 1.5 mL/min, $\lambda = 243$ nm, retention time: t (major) = 5.677 min, t (minor) = 4.432 min.

^1H NMR (600 MHz, CDCl_3) δ 7.87 (d, $J = 7.6$ Hz, 2H), 7.72 (d, $J = 7.6$ Hz, 2H), 7.60 (d, $J = 8.6$ Hz, 2H), 7.53 (d, $J = 8.6$ Hz, 2H), 7.43 (d, $J = 7.8$ Hz, 2H), 7.35 (s, 2H), 6.94 (d, $J = 7.8$ Hz, 2H), 1.53 (s, 6H).

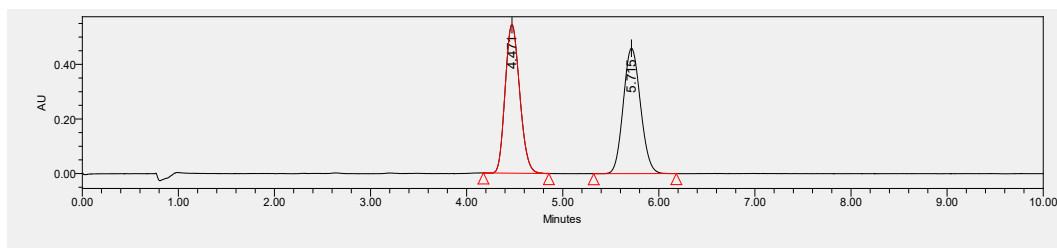
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.39, 147.26, 138.10, 134.90, 133.65, 130.30, 130.20, 129.34, 129.27, 129.19, 128.23, 128.02, 126.18, 126.03, 120.47, 20.90.

ESI-HRMS: calcd for $\text{C}_{31}\text{H}_{21}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 409.1587, found 409.1592.

IR (neat): 1703, 1530, 1304, 1270, 837, 740, 700 cm^{-1} .

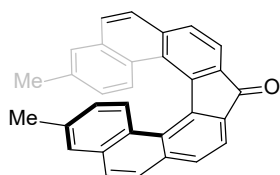


Retention Time	Area	% Area	Height
4.432	144984	3.27	17465
5.677	4290871	96.73	371984



Retention Time	Area	% Area	Height
4.471	5699028	49.89	544271
5.715	5724831	50.11	459552

(*M*)-3,15-dimethyl-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A3)



Following the typical procedure for the kinetic resolution.

(4h 55min) 16.3 mg, 40% yield; ee = 97%, dark red solid; $R_f = 0.35$ (PE/DCM = 1/1). $[\alpha]_D^{25} = -9000$ ($c = 4.0 \times 10^{-2}$, in CH_2Cl_2).

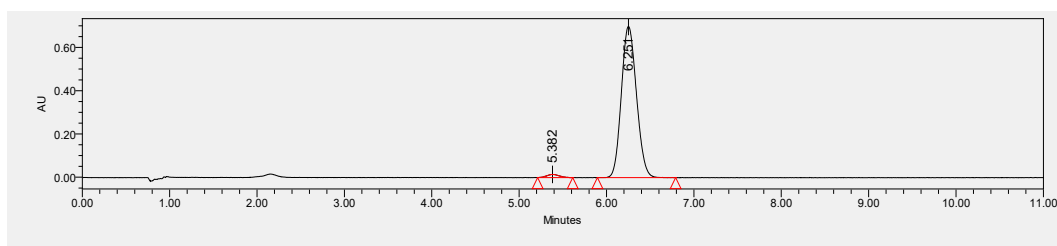
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **OZ-3** column), $\text{CO}_2/\text{MeOH} = 70/30$, flow rate 1.5 mL/min, $\lambda = 243$ nm, retention time: t (major) = 6.261 min, t (minor) = 5.382 min.

^1H NMR (600 MHz, CDCl_3) δ 7.86 (d, $J = 7.6$ Hz, 2H), 7.72 (d, $J = 7.6$ Hz, 2H), 7.58 – 7.54 (m, 4H), 7.33 – 7.31 (d, $J = 8.8$ Hz, 4H), 6.05 (d, $J = 8.4$ Hz, 2H), 2.22 (s, 6H).

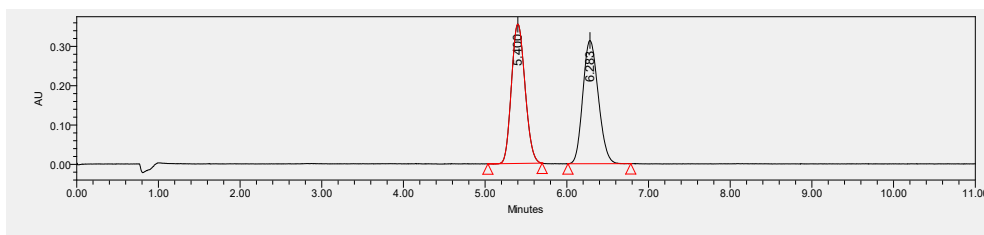
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.48, 146.84, 137.82, 137.43, 135.00, 132.09, 129.37, 129.34, 128.43, 128.35, 128.23, 126.90, 125.84, 125.05, 120.27, 21.02.

ESI-HRMS: calcd for $\text{C}_{31}\text{H}_{21}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 409.1587, found 409.1591.

IR (neat): 1701, 1530, 1307, 1268, 837, 741, 701 cm^{-1} .



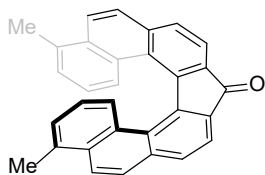
Retention Time	Area	% Area	Height
5.382	141879	1.66	14389
6.251	8387200	98.34	699071



Retention Time	Area	% Area	Height
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5.400	4090184	49.86	354379
6.283	4112988	50.14	313503

(M)-4,14-dimethyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A4)



Following the typical procedure for the kinetic resolution.

(4 h 30 min) 22.0 mg, 54% yield; ee = 77%, dark red solid; R_f = 0.35 (PE/DCM = 1/1). $[\alpha]^{25}_D$ = -6607 (c = 4.0×10^{-2} , in CH_2Cl_2).

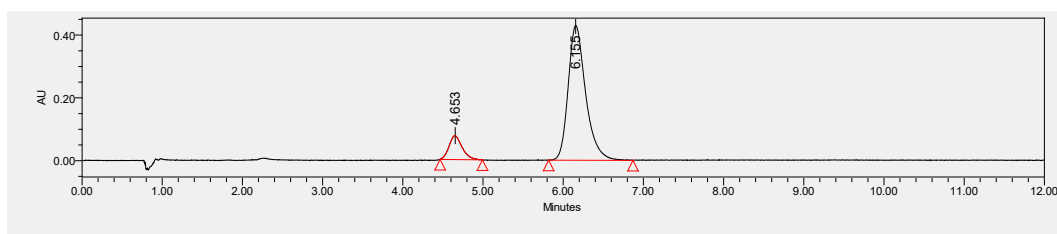
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **OZ-3** column), CO_2/MeOH = 80/20, flow rate 1.5 mL/min, λ = 243 nm, retention time: t (major) = 6.155 min, t (minor) = 4.635 min.

^1H NMR (600 MHz, CDCl_3) δ 7.88 – 7.85 (m, 4H), 7.73 (d, J = 7.8 Hz, 2H), 7.61 (d, J = 9.0 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 7.2 Hz, 2H), 6.15 (t, J = 7.8 Hz, 2H), 2.60 (s, 6H).

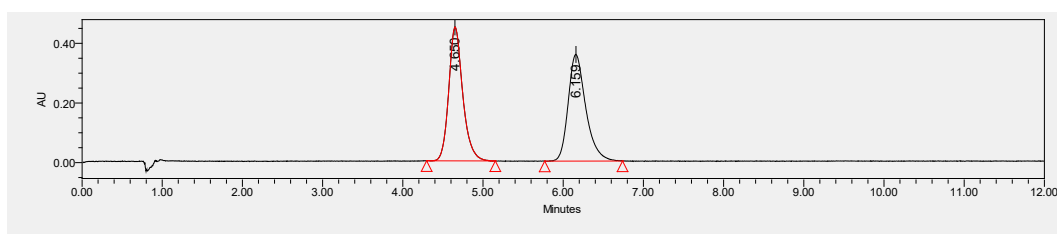
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.36, 147.48, 137.63, 134.99, 132.59, 130.85, 130.64, 129.38, 128.95, 128.69, 126.58, 126.25, 125.57, 123.19, 120.46, 19.65.

ESI-HRMS: calcd for $\text{C}_{31}\text{H}_{21}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 409.1587, found 409.1590.

IR (neat): 1701, 1569, 1300, 1000, 847, 739 cm^{-1} .

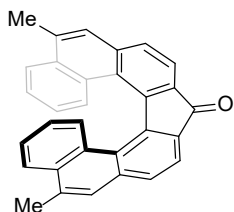


Retention Time	Area	% Area	Height
4.653	861451	11.71	76238
6.155	6497522	88.29	429487



Retention Time	Area	% Area	Height
4.650	5418847	49.86	449320
6.159	5448486	50.14	357901

(M)-5,13-dimethyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A5)



Following the typical procedure for the kinetic resolution.

(4 h 15 min) 17.2 mg, 42% yield; ee = 98%, orange solid; R_f = 0.4 (PE/DCM = 1/1). $[\alpha]^{25}_D$ = -8525 (c = 4.0×10^{-2} , in CH_2Cl_2).

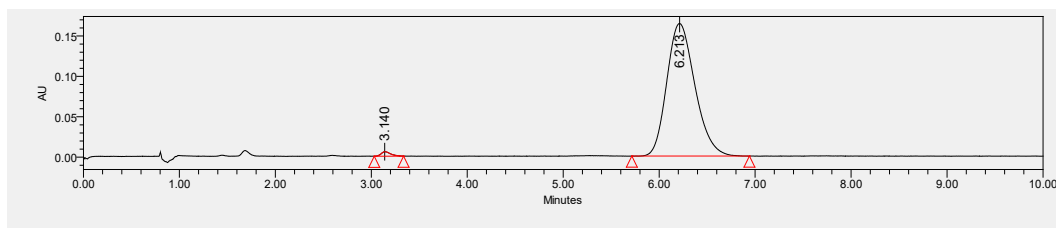
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **OJ-3** column), CO_2/MeOH = 50/50, flow rate 1.5 mL/min, λ = 243 nm, retention time: t (major) = 6.213 min, t (minor) = 3.140 min.

^1H NMR (600 MHz, CDCl_3) δ 7.88 (d, J = 7.2 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 7.2 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.46 (s, 2H), 7.15 (t, J = 7.8 Hz, 2H), 6.27 (t, J = 7.8 Hz, 2H), 2.70 – 2.68 (m, 6H).

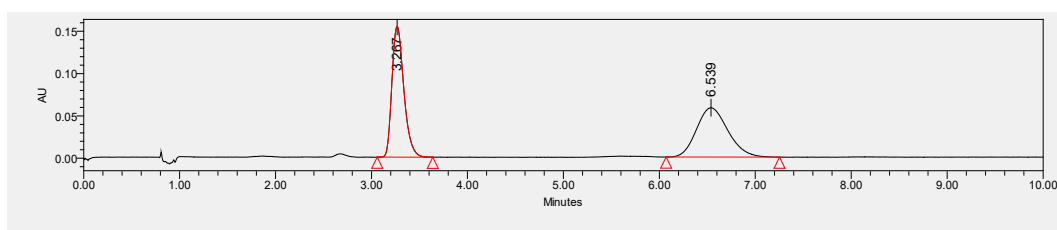
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.23, 146.82, 138.03, 135.56, 134.65, 131.97, 130.74, 128.63, 128.22, 127.94, 127.47, 126.77, 123.39, 122.57, 120.81, 19.76.

ESI-HRMS: calcd for $\text{C}_{31}\text{H}_{21}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 409.1587, found 409.1593.

IR (neat): 1700, 1559, 1300, 879, 760, 706 cm^{-1} .

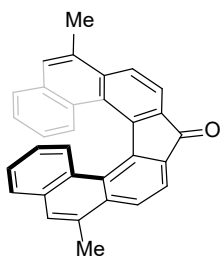


Retention Time	Area	% Area	Height
3.140	38476	1.14	5560
6.213	3338712	98.86	164089



Retention Time	Area	% Area	Height
3.267	1333244	50.18	154517
6.539	1323847	49.82	58264

(M)-6,12-dimethyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A6)



Following the typical procedure for the kinetic resolution.

(4 h 15 min) 17.2 mg, 42% yield; ee = 89%, orange solid; R_f = 0.35 (PE/DCM = 1/1). $[\alpha]^{25}_D = -5425$ ($c = 4.0 \times 10^{-2}$, in CH_2Cl_2).

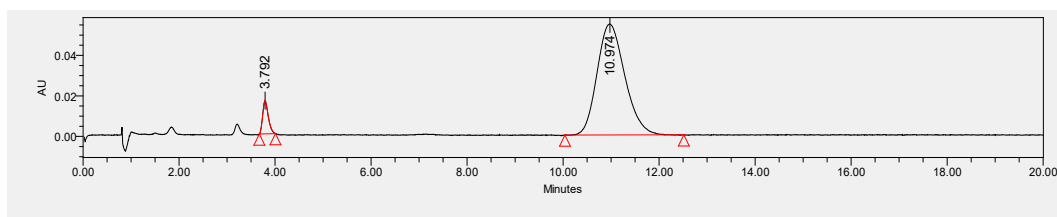
Dissolved in MeOH for UPCC; HPLC (Chiralcel **OJ-3** column), $\text{CO}_2/\text{MeOH} = 50/50$, flow rate 1.5 mL/min, $\lambda = 243$ nm, retention time: t (major) = 10.974 min, t (minor) = 3.792 min.

^1H NMR (600 MHz, CDCl_3) δ 7.95 – 7.92 (m, 4H), 7.52 (d, $J = 8.2$ Hz, 2H), 7.48 (s, 2H), 7.41 (d, $J = 7.8$ Hz, 2H), 7.05 (t, $J = 7.4$ Hz, 2H), 6.26 (t, $J = 7.6$ Hz, 2H), 2.72 (s, 6H).

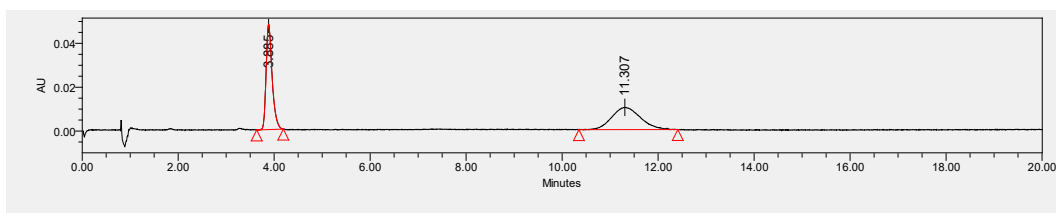
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.45, 147.24, 138.25, 134.63, 132.20, 131.78, 129.96, 129.52, 128.93, 127.58, 127.47, 125.79, 125.49, 123.09, 120.41, 20.60.

ESI-HRMS: calcd for $\text{C}_{31}\text{H}_{21}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 409.1587, found 409.1593.

IR (neat): 1704, 1559, 1300, 879, 760, 701 cm^{-1} .

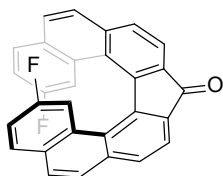


Retention Time	Area	% Area	Height
3.792	132364	5.69	16401
10.974	2194450	94.31	54768



Retention Time	Area	% Area	Height
3.885	417513	49.84	48046
11.307	420216	50.16	10115

(M)-2,16-difluoro-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A7)



Following the typical procedure A.

(8 h 15 min) 18.7 mg, 45% yield; ee = 80%, red solid; R_f = 0.42 (PE/DCM = 1/1). $[\alpha]^{25}_D$ = -6798 (c = 4.2×10^{-2} , in CH_2Cl_2).

Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **OJ-3** column), CO_2/MeOH = 70/30, flow rate 1.5 mL/min, λ = 243 nm, retention time: t (major) = 5.701 min, t (minor) = 4.035 min.

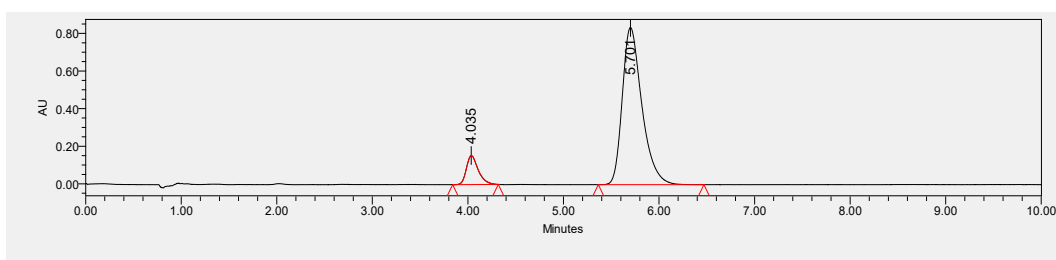
^1H NMR (600 MHz, CDCl_3) δ 7.90 (d, J = 7.6 Hz, 2H), 7.76 (d, J = 7.6 Hz, 2H), 7.66 (d, J = 8.8 Hz, 2H), 7.58 (dt, J = 8.8, 2.4 Hz, 4H), 7.11 (dd, J = 11.0, 2.4 Hz, 2H), 6.89 (td, J = 8.4, 2.4 Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 192.68, 158.68 (d, J = 246.1 Hz), 146.53, 138.19, 134.94, 131.54 (d, J = 9.1 Hz), 129.81, 129.09, 129.00, 128.77 (d, J = 7.5 Hz), 127.41 (d, J = 4.5 Hz), 126.36 (d, J = 1.5 Hz), 121.28, 116.21 (d, J = 22.7 Hz), 112.74 (d, J = 24.2 Hz).

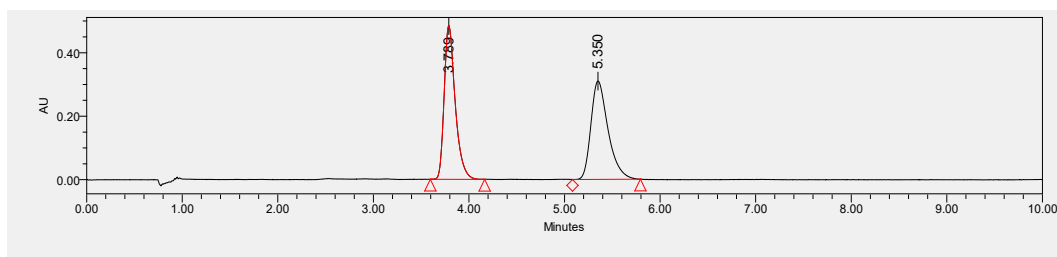
$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3) δ -114.76.

ESI-HRMS: calcd for $\text{C}_{29}\text{H}_{15}\text{F}_2\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 417.1085, found 417.1087.

IR (neat): 1703, 1572, 1503, 1185, 849, 733, 700 cm^{-1} .

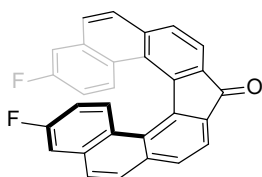


Retention Time	Area	% Area	Height
4.035	1322629	10.01	154331
5.701	11885715	89.99	835765



Retention Time	Area	% Area	Height
3.789	3869774	50.06	484546
5.350	3860507	49.94	309862

(*M*)-3,15-difluoro-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A8**)**



Following the typical procedure for the kinetic resolution.

(8 h 10 min) 18.7 mg, 45% yield; ee = 86%, red solid; R_f = 0.4 (PE/DCM = 1/1). $[\alpha]_D^{25}$ = -5141 (c = 4.2×10^{-2} , in CH_2Cl_2).

Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **AD-3** column), CO_2/MeOH = 80/20, flow rate 1.5 mL/min, λ = 243 nm, retention time: t (major) = 8.105 min, t (minor) = 6.901 min.

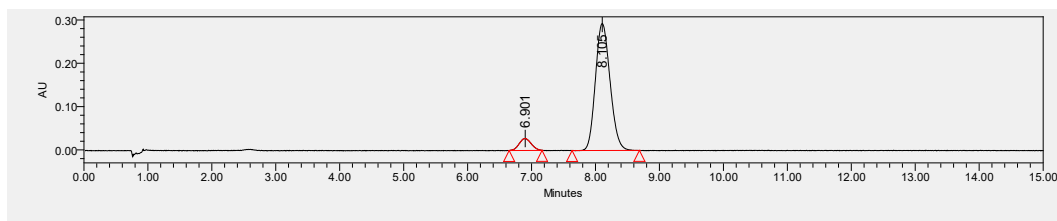
^1H NMR (600 MHz, CDCl_3) δ 7.90 (d, J = 7.6 Hz, 2H), 7.76 (d, J = 7.6 Hz, 2H), 7.66 (d, J = 8.8 Hz, 2H), 7.58 (dt, J = 8.8, 2.4 Hz, 4H), 7.11 (dd, J = 11.0, 2.4 Hz, 2H), 6.89 (td, J = 8.4, 2.4 Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 192.68, 158.68 (d, J = 246.1 Hz), 146.53, 138.19, 134.94, 131.54 (d, J = 9.1 Hz), 129.81, 129.09, 129.00, 128.77 (d, J = 7.5 Hz), 127.41 (d, J = 4.5 Hz), 126.36 (d, J = 1.5 Hz), 121.28, 116.21 (d, J = 22.7 Hz), 112.74 (d, J = 24.2 Hz).

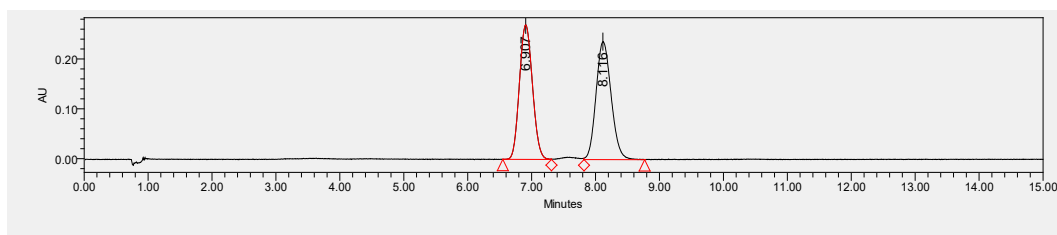
$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3) δ -114.76.

ESI-HRMS: calcd for $\text{C}_{29}\text{H}_{15}\text{F}_2\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 417.1085, found 417.1089.

IR (neat): 1704, 1615, 1532, 1458, 1302, 1260, 1146, 870, 731 cm^{-1} .



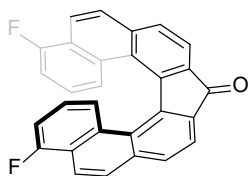
Retention Time	Area	% Area	Height
6.901	363358	7.24	27662
8.105	4658024	92.76	293088



Retention Time	Area	% Area	Height
6.907	3816783	49.58	270237

8.116	3882099	50.42	236775
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(M)-4,14-difluoro-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A9)



Following the typical procedure for the kinetic resolution.

(5 h 10 min) 24.1 mg, 58% yield; ee = 59%, dark red solid; R_f = 0.4 (PE/DCM = 1/1). $[\alpha]^{25}_D$ = -971 (c = 4.2×10^{-2} , in CH_2Cl_2).

Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **AD-3** column), CO_2/MeOH = 70/30, flow rate 1.5 mL/min, λ = 243 nm, retention time: t (major) = 4.584 min, t (minor) = 5.377 min.

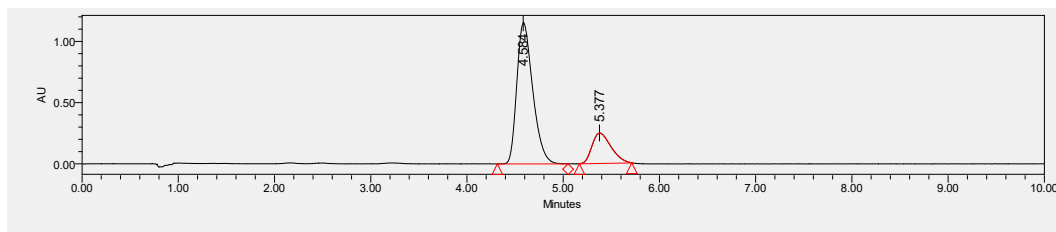
^1H NMR (600 MHz, CDCl_3) δ 7.95 (d, J = 7.2 Hz, 2H), 7.92 (d, J = 7.8 Hz, 2H), 7.79 (d, J = 7.2 Hz, 2H), 7.67 (d, J = 9.0 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.85 (dd, J = 9.8, 7.8 Hz, 2H), 6.31 (td, J = 8.0, 5.8 Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 192.63, 157.59 (d, J = 250.7 Hz), 146.97, 137.92, 135.34, 131.98 (d, J = 3.0 Hz), 130.07, 127.59 (d, J = 3.0 Hz), 127.56, 123.96 (d, J = 7.6 Hz), 123.56 (d, J = 4.3 Hz), 121.43 (d, J = 15.1 Hz), 121.25 (d, J = 6.0 Hz), 121.24, 112.29 (d, J = 19.6 Hz).

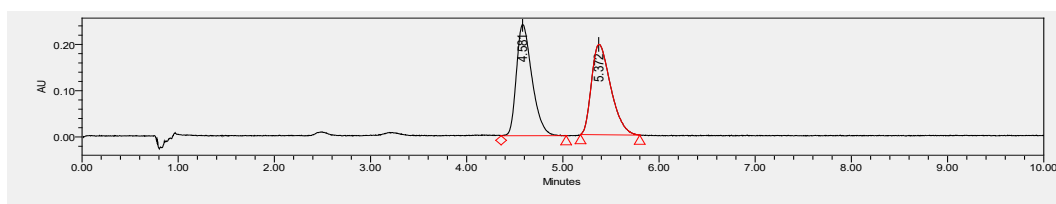
$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3) δ -123.17.

ESI-HRMS: calcd for $\text{C}_{29}\text{H}_{15}\text{F}_2\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 417.1085, found 417.1086.

IR (neat): 1707, 1570, 1458, 1303, 1246, 999, 849, 742 cm^{-1} .

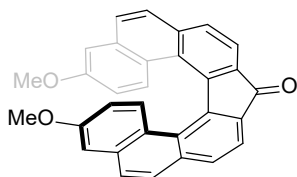


Retention Time	Area	% Area	Height
4.584	13253513	79.50	1153543
5.377	3417889	20.50	249640



Retention Time	Area	% Area	Height
4.581	2696541	49.87	240516
5.372	2710810	50.13	195125

(M)-3,15-dimethoxy-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A10)



Following the typical procedure for the kinetic resolution.

(4 h 20 min) 17.6 mg, 40% yield; ee = 97%, dark red solid; R_f = 0.2 (PE/DCM = 1/1). $[\alpha]^{25}_D$ = -3541 (c = 4.4×10^{-2} , in CH_2Cl_2).

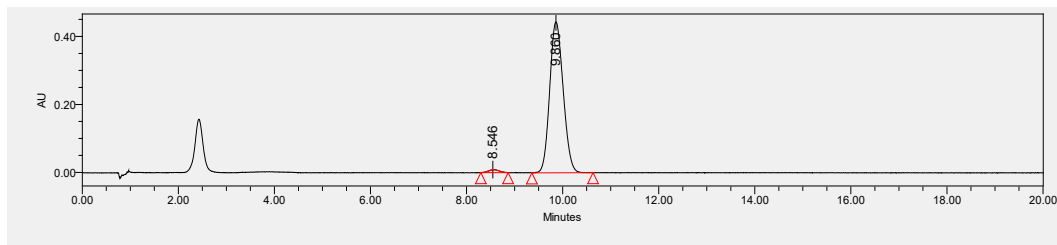
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **OZ-3** column), CO_2/MeOH = 70/30, flow rate 1.5 mL/min, λ = 243 nm, retention time: t (major) = 9.860 min, t (minor) = 8.546 min.

^1H NMR (600 MHz, CDCl_3) δ 7.84 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 7.2 Hz, 2H), 7.56 (dd, J = 9.0, 3.0 Hz, 2H), 7.35 (d, J = 9.0 Hz, 2H), 6.97 (d, J = 2.4 Hz, 2H), 5.92 (dd, J = 9.0, 2.4 Hz, 2H), 3.78 (s, 6H).

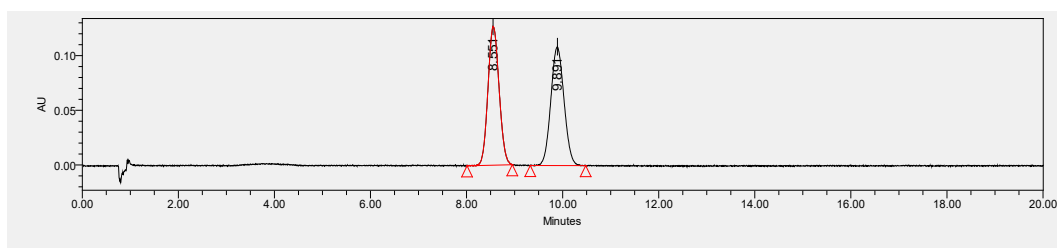
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.53, 159.16, 146.31, 137.15, 135.12, 133.60, 129.71, 129.32, 129.17, 128.26, 127.58, 124.77, 119.85, 113.14, 107.36, 77.03, 55.29.

ESI-HRMS: calcd for $\text{C}_{31}\text{H}_{21}\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) = 441.1485, found 441.1489.

IR (neat): 1702, 1612, 1530, 1464, 1273, 1030, 860, 700 cm^{-1} .

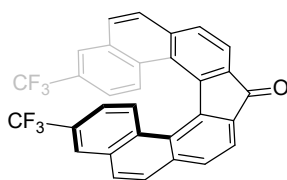


Retention Time	Area	% Area	Height
8.546	134631	1.54	8969
9.860	8612504	98.46	443760



Retention Time	Area	% Area	Height
8.551	2038947	49.63	127011
9.891	2069385	50.37	108730

(*M*)-3,15-bis(trifluoromethyl)-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A11)



Following the typical procedure for the kinetic resolution.

(12 h 20 min) 20.7 mg, 40% yield; ee = 91%, orange solid; R_f = 0.45 (PE/DCM = 1/1). $[\alpha]^{25}_D$ = -4717 (c = 5.2×10^{-2} , in CH_2Cl_2).

Dissolved in MeOH for UPCC; HPLC (Chiralcel IC-3 column), CO_2/MeOH = 80/20, flow rate 1.5 mL/min, λ = 243 nm, retention time: t (major) = 8.144 min, t (minor) = 5.410 min.

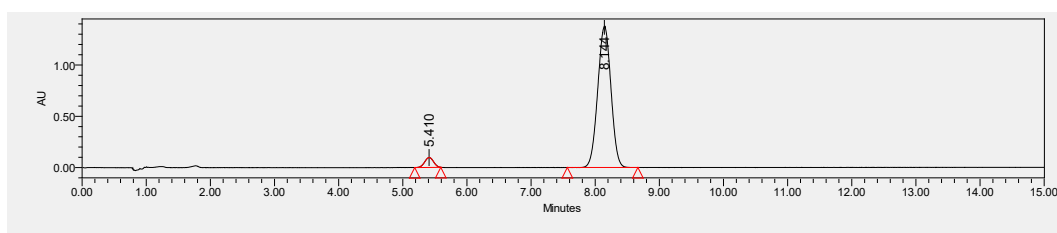
^1H NMR (600 MHz, CDCl_3) δ 7.91 (d, J = 7.8 Hz, 2H), 7.82 (s, 2H), 7.77 (d, J = 7.7 Hz, 2H), 7.69 (dd, J = 9.0, 1.8 Hz, 4H), 7.44 (d, J = 8.4 Hz, 2H), 6.37 (d, J = 8.4 Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 192.30, 146.52, 138.33, 135.14, 132.19, 131.41, 130.19, 129.48 (d, J = 33.2 Hz), 129.21, 128.49, 128.27, 127.18, 123.77, 123.58 (d, J = 273.3 Hz), 121.77, 119.38.

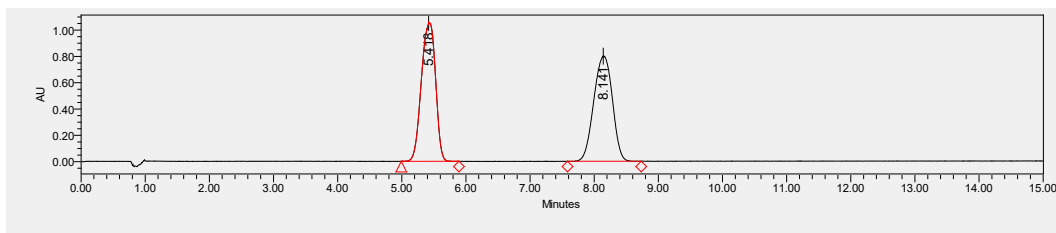
$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3) δ -62.92.

ESI-HRMS: calcd for $\text{C}_{31}\text{H}_{15}\text{F}_6\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 517.1022, found 517.1025.

IR (neat): 1707, 1319, 1120, 1082, 903, 837, 726 cm^{-1} .

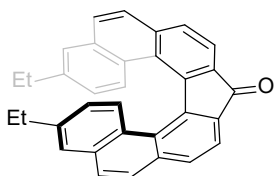


Retention Time	Area	% Area	Height
5.410	922503	4.48	96806
8.144	19684743	95.52	1376565



Retention Time	Area	% Area	Height
5.418	16144559	50.09	1056025
8.141	16086855	49.91	799039

(M)-3,15-diethyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A12)



Following the typical procedure for the kinetic resolution.

(5 h 45 min) 19.2 mg, 44% yield; ee = 91%, dark red solid; R_f = 0.4 (PE/DCM = 1/1). $[\alpha]_D^{25} = -4991$ ($c = 4.4 \times 10^{-2}$, in CH_2Cl_2).

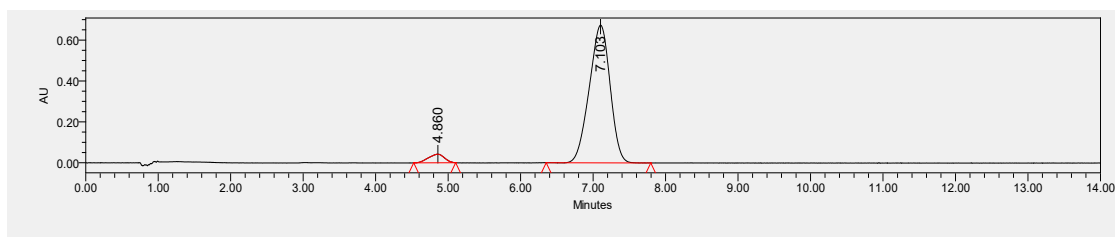
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **AD-3** column), $\text{CO}_2/\text{MeOH} = 70/30$, flow rate 1.5 mL/min, $\lambda = 243$ nm, retention time: t (major) = 7.103 min, t (minor) = 4.860 min.

^1H NMR (600 MHz, CDCl_3) δ 7.84 (d, $J = 7.6$ Hz, 2H), 7.69 (d, $J = 7.6$ Hz, 2H), 7.57 (d, $J = 8.8$ Hz, 2H), 7.53 (d, $J = 8.6$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 2.0$ Hz, 2H), 6.10 (d, $J = 8.4$ Hz, 2H), 2.48 (q, $J = 7.6$ Hz, 4H), 1.08 (t, $J = 7.6$ Hz, 6H).

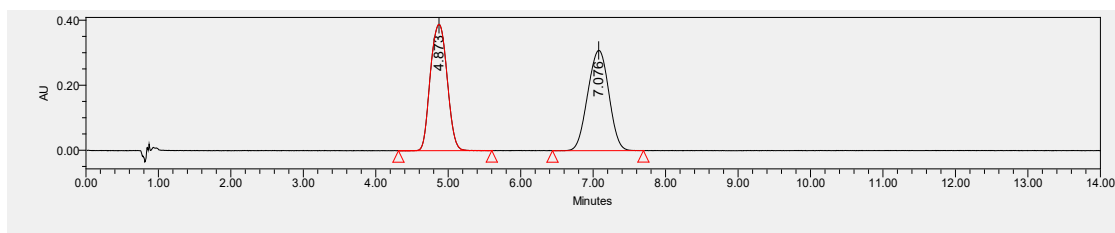
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.41, 146.87, 143.80, 137.79, 134.98, 132.15, 129.55, 129.33, 128.64, 128.39, 128.11, 126.79, 124.73, 124.06, 120.21, 28.50, 15.30.

ESI-HRMS: calcd for $\text{C}_{33}\text{H}_{25}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 437.1900, found 437.1905.

IR (neat): 2995, 1701, 1204, 1306, 840, 739, 704 cm^{-1} .



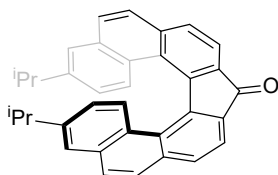
Retention Time	Area	% Area	Height
4.860	642387	4.56	41949
7.103	13434352	95.44	673759



Retention Time	Area	% Area	Height
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4.873	6233611	49.97	388321
7.076	6240265	50.03	308389

(M)-3,15-diisopropyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A13)



Following the typical procedure A.

(5 h 30 min) 19.0 mg, 41% yield; ee = 91%, dark red solid; R_f = 0.5 (PE/DCM = 1/1). $[\alpha]_D^{25} = -7985$ ($c = 4.6 \times 10^{-2}$, in CH_2Cl_2).

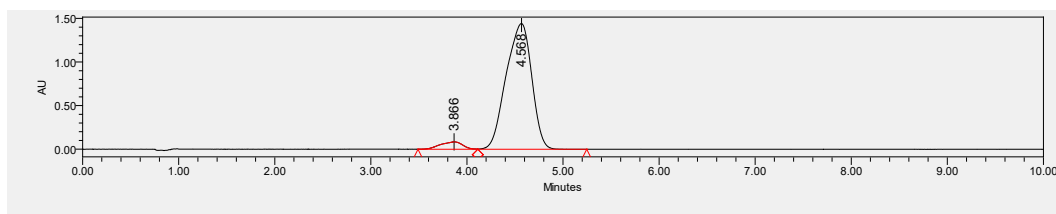
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **AD-3** column), $\text{CO}_2/\text{MeOH} = 70/30$, flow rate 1.5 mL/min, $\lambda = 243$ nm, retention time: t (major) = 3.866 min, t (minor) = 4.566 min.

^1H NMR (600 MHz, CDCl_3) δ 7.85 (d, $J = 7.8$ Hz, 2H), 7.70 (d, $J = 7.2$ Hz, 2H), 7.60 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 9.0$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.32 (s, 2H), 6.21 (dd, $J = 8.4, 1.2$ Hz, 2H), 2.73 (p, $J = 6.6$ Hz, 2H), 1.08 (dd, $J = 9.0, 7.2$ Hz, 12H).

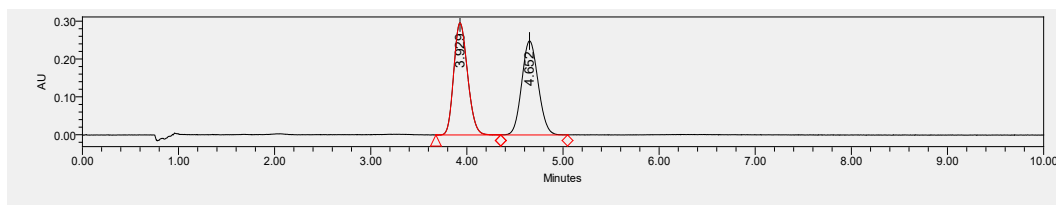
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.38, 148.24, 146.95, 137.78, 135.02, 132.15, 129.74, 129.35, 128.75, 128.42, 127.86, 126.70, 123.36, 122.93, 120.20, 33.48, 23.78, 23.45.

ESI-HRMS: calcd for $\text{C}_{17}\text{H}_{20}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 465.2113, found 465.2118.

IR (neat): 2996, 1736, 1679, 1449, 1349, 1266, 1221, 1170, 1003, 743, 692 cm^{-1} .

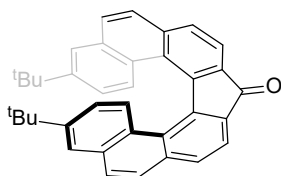


Retention Time	Area	% Area	Height
3.866	320976	4.70	20261
4.566	6505267	95.30	353032



Retention Time	Area	% Area	Height
3.929	2946804	50.01	295893
4.652	2946191	49.99	248314

(M)-3,15-di-tert-butyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A14)



Following the typical procedure for the kinetic resolution.

(5 h 40 min) 20.2 mg, 41% yield; ee = 93%, dark red solid; R_f = 0.5 (PE/DCM = 1/1). $[\alpha]_D^{25} = -8868$ ($c = 4.9 \times 10^{-2}$, in CH_2Cl_2).

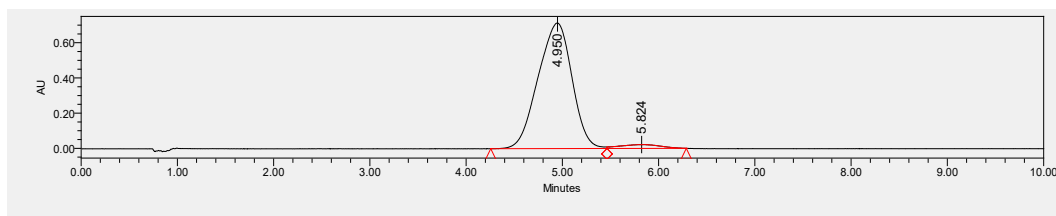
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **AD-3** column), $\text{CO}_2/\text{MeOH} = 90/10$, flow rate 1.5 mL/min, $\lambda = 243$ nm, retention time: t (major) = 4.950 min, t (minor) = 5.824 min.

^1H NMR (600 MHz, CDCl_3) δ 7.85 (d, $J = 7.8$ Hz, 2H), 7.71 (d, $J = 7.2$ Hz, 2H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.55 (d, $J = 9.0$ Hz, 2H), 7.43 (d, $J = 1.2$ Hz, 2H), 6.43 (dd, $J = 9.0, 1.8$ Hz, 2H), 1.14 (s, 18H).

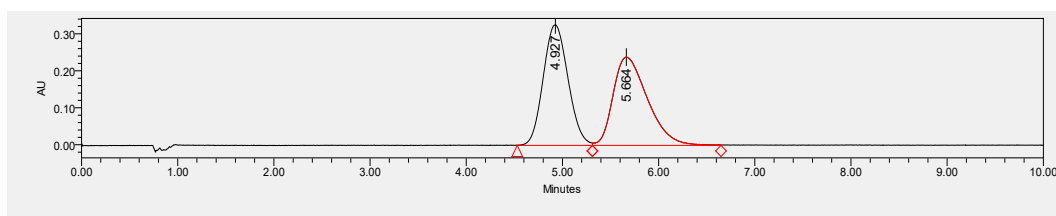
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.37, 150.56, 147.02, 137.78, 135.01, 131.97, 130.05, 129.32, 128.44, 128.31, 127.41, 126.56, 122.28, 122.05, 120.21, 34.47, 31.08.

ESI-HRMS: calcd for $\text{C}_{37}\text{H}_{33}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 493.2526, found 493.2030.

IR (neat): 2958, 1700, 1528, 1307, 912, 842, 731, 481 cm^{-1} .

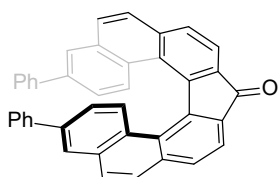


Retention Time	Area	% Area	Height
4.950	17461166	96.47	714177
5.824	639181	3.53	21940



Retention Time	Area	% Area	Height
4.927	5832795	49.66	325998
5.664	5912452	50.34	238772

(*M*)-3,15-diphenyl-9*H*-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A15)



Following the typical procedure for the kinetic resolution.

(8 h 5 min) 23.9 mg, 45% yield; ee = 90%, dark red solid; R_f = 0.3 (PE/DCM = 1/1). $[\alpha]_D^{25} = -4637$ ($c = 5.4 \times 10^{-2}$, in CH_2Cl_2).

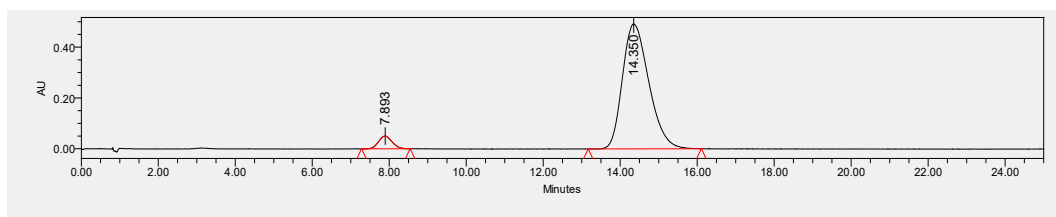
Dissolved in MeOH for UPCC; HPLC (Chiralcel AD-3 column), $\text{CO}_2/\text{MeOH} = 50/50$, flow rate 1.5 mL/min, $\lambda = 243$ nm, retention time: t (major) = 14.350 min, t (minor) = 7.893 min.

^1H NMR (600 MHz, CDCl_3) δ 7.91 (d, $J = 8.4$ Hz, 2H), 7.76 (d, $J = 7.8$ Hz, 2H), 7.70 – 7.67 (m, 4H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.55 (d, $J = 8.4$ Hz, 2H), 7.28 – 7.25 (m, 6H), 7.24 – 7.22 (m, 4H), 6.49 (dd, $J = 8.4, 1.8$ Hz, 2H).

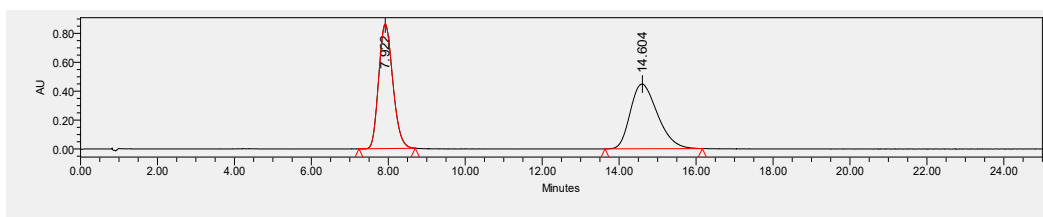
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.24, 146.84, 140.55, 140.26, 138.07, 135.14, 132.36, 129.77, 129.59, 128.70, 128.48, 128.14, 127.39, 127.32, 127.16, 124.51, 122.74, 120.74.

ESI-HRMS: calcd for $\text{C}_{41}\text{H}_{25}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 533.1900, found 533.1902.

IR (neat): 1703, 1311, 910, 847, 753, 699 cm^{-1} .

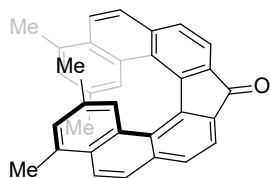


Retention Time	Area	% Area	Height
7.893	1234124	5.01	50093
14.350	23392683	94.99	491549



Retention Time	Area	% Area	Height
7.922	21945272	49.98	861940
14.604	21961482	50.02	447992

(M)-2,4,14,16-tetramethyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A16)



Following the typical procedure for the kinetic resolution.

(9 h 20 min) 14.0 mg, 32% yield; ee = 87%, orange solid; R_f = 0.35 (PE/DCM = 1/1). $[\alpha]_D^{25} = -4991$ ($c = 4.4 \times 10^{-2}$, in CH_2Cl_2).

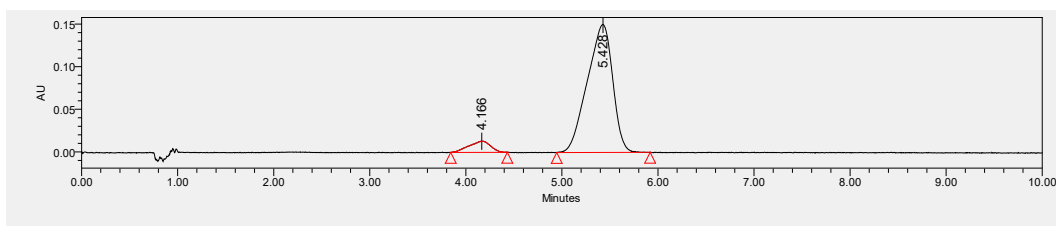
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **AD-3** column), $\text{CO}_2/\text{MeOH} = 70/30$, flow rate 1.5 mL/min, $\lambda = 243$ nm, retention time: t (major) = 5.428 min, t (minor) = 4.166 min.

^1H NMR (600 MHz, CDCl_3) δ 7.82 (d, $J = 7.2$ Hz, 1H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.68 (d, $J = 7.4$ Hz, 1H), 7.52 (d, $J = 9.0$ Hz, 1H), 7.16 (s, 1H), 6.77 (s, 1H), 2.56 (s, 3H), 1.43 (s, 3H).

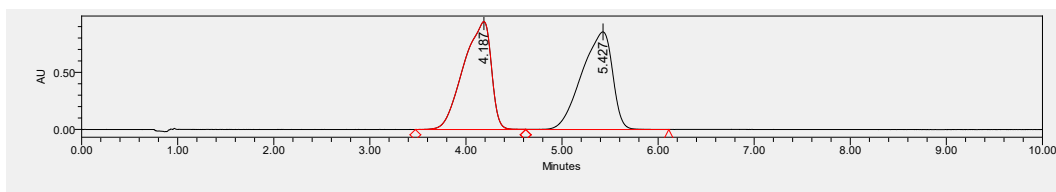
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.50, 147.60, 137.74, 134.77, 132.85, 132.09, 130.59, 130.35, 129.10, 128.85, 128.71, 126.69, 125.73, 125.31, 120.26, 20.68, 19.51.

ESI-HRMS: calcd for $\text{C}_{33}\text{H}_{25}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 437.1900, found 437.1902.

IR (neat): 1700, 1596, 1303, 854, 741, 700 cm^{-1} .



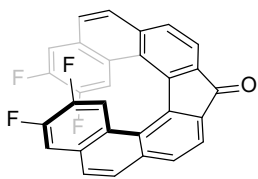
Retention Time	Area	% Area	Height
4.166	206257	6.96	13132
5.428	2758657	93.04	150289



Retention Time	Area	% Area	Height
4.187	18932927	49.94	944915

5.427	18977498	50.06	854696
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(M)-2,3,15,16-tetrafluoro-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A17)



Following the typical procedure for the kinetic resolution.

(12 h 30 min) 21.3 mg, 47% yield; ee = 85%, red solid; R_f = 0.35 (PE/DCM = 1/1). $[\alpha]^{25}_D$ = -7212 (c = 4.6×10^{-2} , in CH_2Cl_2).

Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **IC-3** column), CO_2/MeOH = 80/20, flow rate 1.5 mL/min, λ = 243 nm, retention time: t (major) = 9.828 min, t (minor) = 9.222 min.

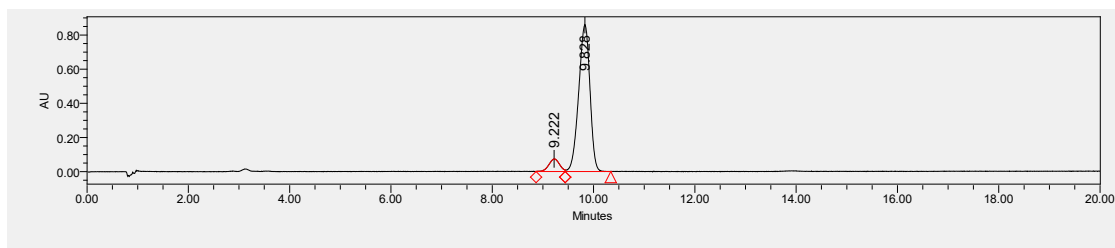
^1H NMR (600 MHz, CDCl_3) δ 7.86 (d, J = 7.6 Hz, 2H), 7.74 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.12 (dd, J = 12.0, 7.8 Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 192.27, 149.82 (dd, J = 253.7, 13.6 Hz), 146.83 (dd, J = 249.2, 13.6 Hz), 145.67, 137.53, 135.10, 130.08, 129.76 (dd, J = 6.6, 1.2 Hz), 128.20, 127.75 (d, J = 1.5 Hz), 126.78 (d, J = 1.5 Hz), 126.72, 121.22, 115.01 (d, J = 19.6 Hz), 113.66 (d, J = 16.6 Hz).

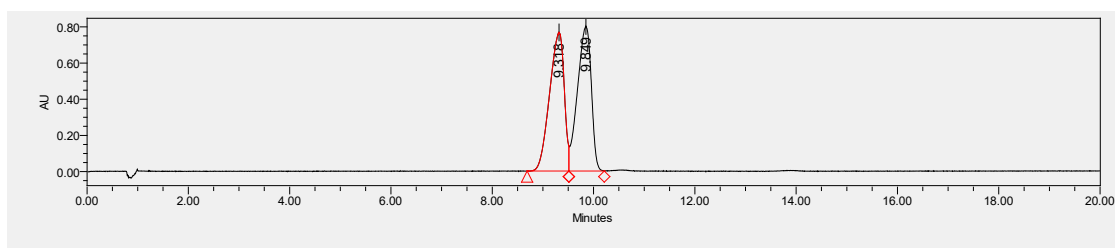
$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3) δ -135.43 (d, J = 22.6 Hz), -138.12 (d, J = 22.6 Hz).

ESI-HRMS: calcd for $\text{C}_{29}\text{H}_{13}\text{F}_4\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 453.0897, found 453.0899.

IR (neat): 1707, 1537, 1506, 1459, 1289, 1188, 1136, 889, 741 cm^{-1} .

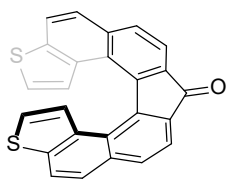


Retention Time	Area	% Area	Height
9.222	1077960	7.52	74192
9.828	13266029	92.48	861430



Retention Time	Area	% Area	Height
9.318	15306619	50.16	766656
9.849	15208278	49.84	801844

(M)-8H-dibenzo[b]thieno[5,4-c:4',5'-g]fluoren-8-one (A18)



Following the typical procedure for the kinetic resolution.

(3 h) 15.7 mg, 40% yield; ee = 96%, dark purple red solid; R_f = 0.42 (PE/DCM = 1/1). $[\alpha]^{25}_D$ = -7075 (c = 4.0×10^{-2} , in CH_2Cl_2).

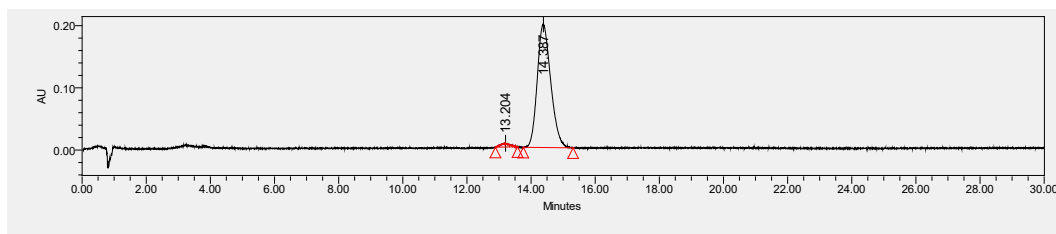
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **AD-3** column), CO_2/MeOH = 70/30, flow rate 1.5 mL/min, λ = 243 nm, retention time: t (major) = 14.387 min, t (minor) = 13.204 min.

¹H NMR (600 MHz, CDCl₃) δ 7.87 – 7.83 (m, 4H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 5.4 Hz, 2H), 6.70 (d, *J* = 5.4 Hz, 2H).

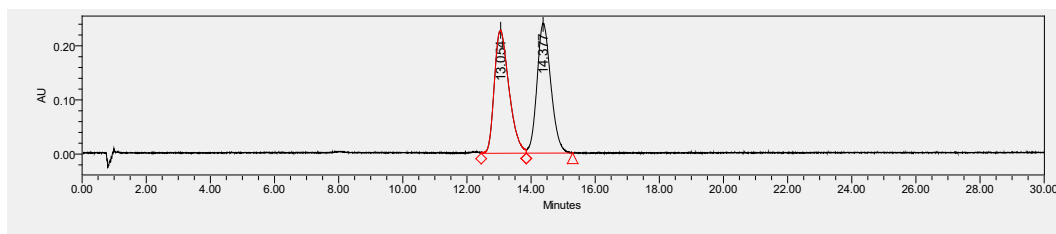
¹³C{¹H} NMR (151 MHz, CDCl₃) δ 193.30, 146.36, 138.86, 137.13, 135.04, 134.67, 130.07, 126.58, 125.81, 125.45, 123.47, 122.58, 119.40.

ESI-HRMS: calcd for C₂₅H₁₂S₂ONa⁺ ([M + Na]⁺) = 415.0222, found 415.0221.

IR (neat): 1703, 1330, 1293, 847, 709 cm⁻¹.

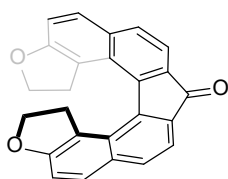


Retention Time	Area	% Area	Height
13.204	116682	1.98	6003
14.387	5780317	98.02	198752



Retention Time	Area	% Area	Height
13.054	7192103	50.02	227392
14.377	7186723	49.98	239844

(*M*)-1,2,14,15-tetrahydro-8*H*-dibenzo[*b*]furan[5,4-*c*:4',5'-*g*]fluoren-8-one (A19)



Following the typical procedure for the kinetic resolution.

(2h 40 min) 16.8 mg, 46% yield; ee = 94%, dark blue solid; *R*_f = 0.55 (PE/DCM = 1/1). [*α*]_D²⁵ = -2036 (*c* = 7.2 × 10⁻³, in CH₂Cl₂).

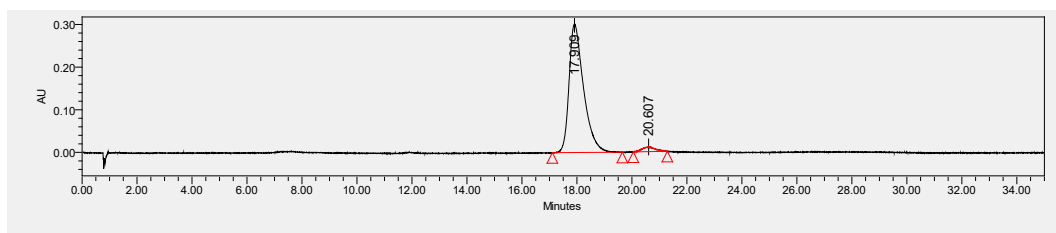
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **IA-3** column), CO₂/MeOH = 90/10, flow rate 1.5 mL/min, λ = 243 nm, retention time: *t* (major) = 17.909 min, *t* (minor) = 20.607 min.

¹H NMR (600 MHz, CDCl₃) δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 4.53 (q, *J* = 9.6 Hz, 2H), 4.42 (td, *J* = 9.6, 6.6 Hz, 2H), 3.55 (ddd, *J* = 18.6, 9.6, 6.6 Hz, 2H), 2.93 (dt, *J* = 19.2, 9.6 Hz, 2H).

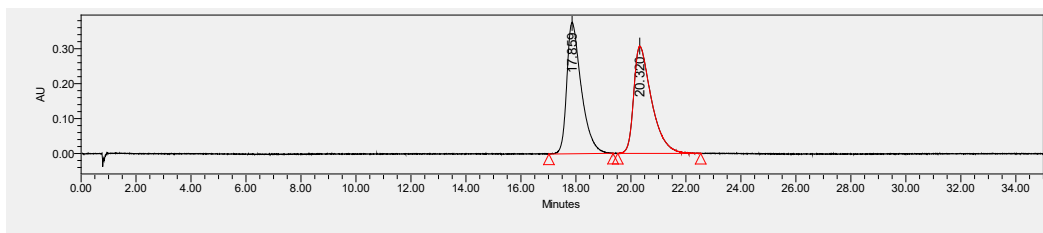
¹³C{¹H} NMR (151 MHz, CDCl₃) δ 193.34, 158.81, 146.93, 135.65, 134.72, 130.42, 130.27, 129.18, 118.69, 117.00, 115.25, 71.69, 31.38.

ESI-HRMS: calcd for C₂₅H₁₇O₃⁺ ([M + H]⁺) = 365.1172, found 365.1171.

IR (neat): 1705, 1607, 1569, 1445, 1345, 1248, 910, 844, 732 cm⁻¹.



Retention Time	Area	% Area	Height
17.909	11014462	96.88	300914
20.607	355210	3.12	10994



Retention Time	Area	% Area	Height
17.859	13760604	50.03	376024
20.320	13745409	49.97	307203

(*M*)-3H-cyclopenta[2,1-a:3,4-a']ditetraphen-3-one (A20)



Following the typical procedure for the kinetic resolution.

(13 h) 19.7 mg, 41 % yield; ee = 77 %, dark red solid; R_f = 0.26 (PE/DCM = 1/1). $[\alpha]_D^{25} = -7223$ ($c = 4.8 \times 10^{-2}$, in CH_2Cl_2).

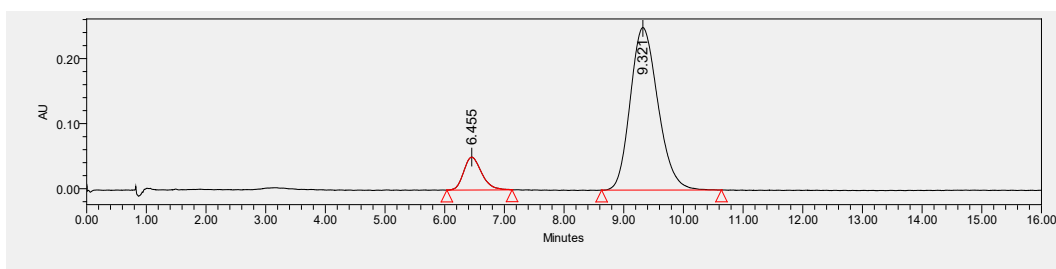
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **OZ-3** column), $\text{CO}_2/\text{MeOH} = 50/50$, flow rate 1.5 mL/min, $\lambda = 243$ nm, retention time: t (major) = 6.455 min, t (minor) = 9.321 min.

^1H NMR (600 MHz, CDCl_3) δ 7.95 (s, 2H), 7.88 (d, $J = 7.4$ Hz, 2H), 7.65 (d, $J = 7.4$ Hz, 2H), 7.52 (d, $J = 8.8$ Hz, 2H), 7.46 – 7.42 (m, 4H), 7.31 (d, $J = 8.2$ Hz, 2H), 7.17 (t, $J = 7.4$ Hz, 2H), 7.04 (t, $J = 7.4$ Hz, 2H), 6.73 (d, $J = 8.2$ Hz, 2H).

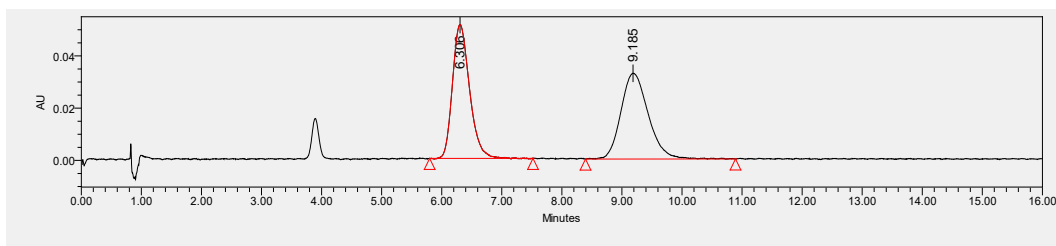
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 192.77, 146.26, 138.29, 135.44, 131.92, 130.43, 129.98, 128.97, 128.93, 128.46, 127.82, 127.37, 127.29, 126.82, 126.76, 125.76, 124.88, 124.55, 121.45.

ESI-HRMS: calcd for $\text{C}_{37}\text{H}_{21}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 481.1587, found 481.1590.

IR (neat): 2922, 1692, 1554, 1295, 950, 909, 733 cm^{-1} .

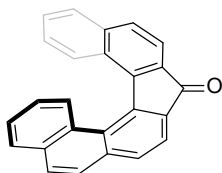


Retention Time	Area	% Area	Height
6.455	1060313	11.66	50632
9.321	8030806	88.34	250013



Retention Time	Area	% Area	Height
6.306	1012969	49.92	51233
9.185	1016226	50.08	32683

(M)-9H-benzo[6,7]indeno[2,1-c]phenanthren-9-one (M-A21)



Following the typical procedure for the kinetic resolution.

(2 h 10 min) 13.9 mg, 42% yield; ee = 93%, red solid; R_f = 0.39 (PE/DCM = 1/1). $[\alpha]^{25}_D$ = -1061 (c = 3.3×10^{-2} , in CH_2Cl_2).

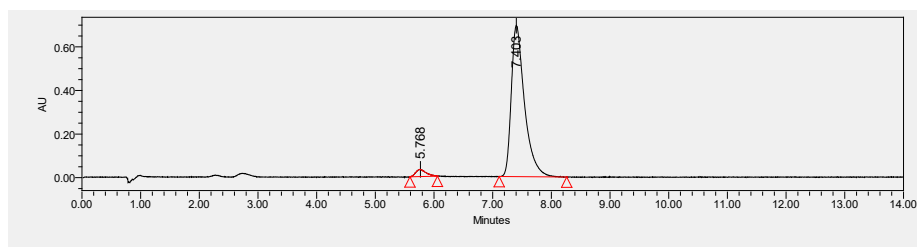
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **OZ-3** column), CO_2/MeOH = 70/30, flow rate 1.5 mL/min, λ = 243 nm, retention time: t (major) = 7.403 min, t (minor) = 5.768 min.

^1H NMR (600 MHz, CDCl_3) δ 8.09 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 5.2 Hz, 5H), 7.74 (d, J = 8.8 Hz, 1H), 7.71 (d, J = 7.4 Hz, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.43 – 7.38 (m, 2H), 7.09 (t, J = 7.6 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H).

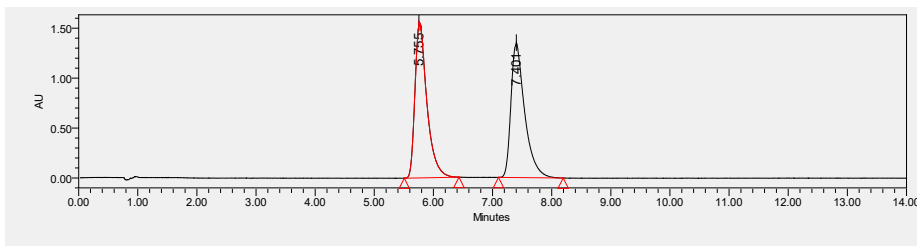
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.87, 148.53, 144.24, 138.62, 138.28, 135.65, 133.03, 132.92, 130.33, 130.30, 130.19, 129.39, 129.23, 129.19, 128.92, 128.48, 128.04, 127.65, 127.63, 127.45, 126.95, 125.73, 124.55, 120.41, 120.08.

ESI-HRMS: calcd for $\text{C}_{25}\text{H}_{15}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 311.1117, found 311.1115.

IR (neat): 2921, 1652, 849, 747 cm^{-1} .

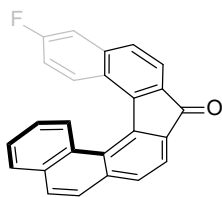


Retention Time	Area	% Area	Height
5.768	400936	3.57	32914
7.403	10839632	96.43	694668



Retention Time	Area	% Area	Height
5.755	21756834	50.09	1555282
7.401	21680499	49.91	1350914

(M)-13-fluoro-9H-benzo[6,7]indeno[2,1-c]phenanthren-9-one (M-A22)



Following the typical procedure for the kinetic resolution.

(2 h 50 min) 13.6 mg, 39% yield; ee = 96%, orange solid; R_f = 0.45 (PE/DCM = 1/1). $[\alpha]^{25}_D$ = -650 (c = 3.4×10^{-2} , in CH_2Cl_2).

Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **OZ-3** column), CO_2/MeOH = 70/30, flow rate 1.5 mL/min, λ = 243 nm, retention time: t (major) = 5.652 min, t (minor) = 4.660 min.

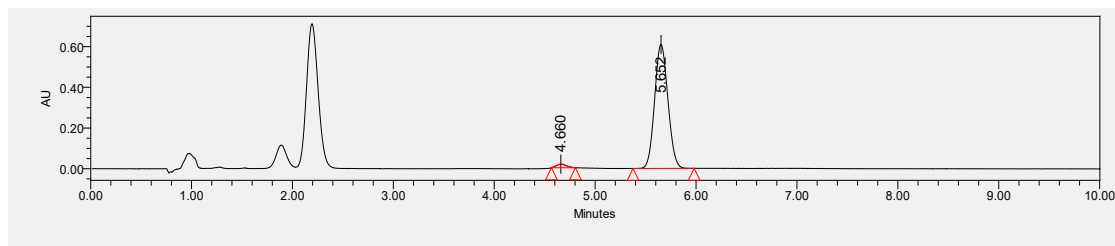
^1H NMR (600 MHz, CDCl_3) δ (d, J = 8.2 Hz, 1H), 7.87 – 7.77 (m, 3H), 7.72 (dd, J = 13.6, 7.8 Hz, 3H), 7.62 (d, J = 8.8 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.45 – 7.38 (m, 2H), 7.13 – 7.09 (m, 1H), 6.80 – 6.75 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.41, 161.64 (d, $J = 250.7$ Hz), 148.77, 143.62, 139.50 (d, $J = 9.1$ Hz), 138.57, 135.59, 133.09, 132.25, 132.23, 131.76 (d, $J = 9.1$ Hz), 130.04, 129.94, 129.50, 129.45, 129.42, 128.33, 127.79, 127.62, 126.95, 124.69, 124.65, 121.16, 120.46, 116.25 (d, $J = 25.7$ Hz), 111.87 (d, $J = 21.1$ Hz).

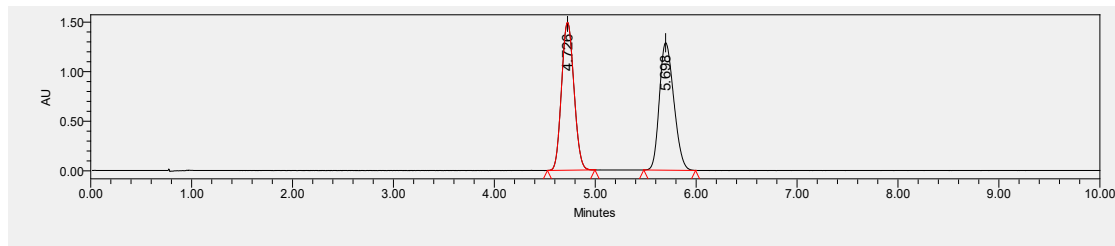
$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3) δ -110.91.

ESI-HRMS: calcd for $\text{C}_{25}\text{H}_{14}\text{FO}^+$ ($[\text{M} + \text{H}]^+$) = 349.1023, found 349.1027.

IR (neat): 2924, 2085, 1628, 1571, 871, 718 cm^{-1} .

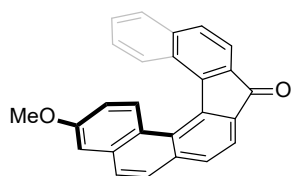


Retention Time	Area	% Area	Height
4.660	123063	2.16	17760
5.652	5574237	97.84	608637



Retention Time	Area	% Area	Height
4.726	12713255	49.98	1492200
5.698	12722517	50.02	1285123

(*M*)-13-methoxy-9H-benzo[6,7]indeno[2,1-c]phenanthren-9-one (*M*-A23)



Following the typical procedure for the kinetic resolution.

(2 h 50 min) 13.0 mg, 36% yield; ee = 97%, red solid; $R_f = 0.31$ (PE/DCM = 1/1). $[\alpha]_D^{25} = -1139$ ($c = 3.6 \times 10^{-2}$, in CH_2Cl_2).

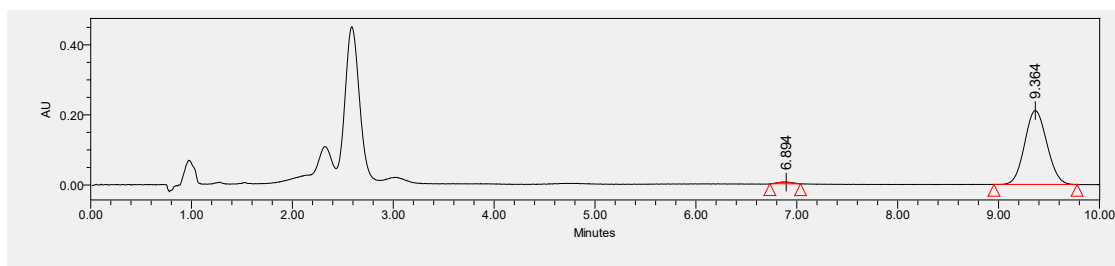
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **OZ-3** column), $\text{CO}_2/\text{MeOH} = 70/30$, flow rate 1.5 mL/min, $\lambda = 243$ nm, retention time: t (major) = 9.364 min, t (minor) = 6.896 min.

^1H NMR (600 MHz, CDCl_3) δ 7.99 (d, $J = 9.0$ Hz, 1H), 7.78 (d, $J = 5.2$ Hz, 3H), 7.74 (d, $J = 7.6$ Hz, 1H), 7.68 – 7.64 (m, 2H), 7.60 (d, $J = 8.8$ Hz, 1H), 7.46 (d, $J = 8.6$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 1H), 7.19 (d, $J = 2.8$ Hz, 1H), 7.04 (t, $J = 8.2$ Hz, 1H), 6.70 (dd, $J = 9.0, 2.8$ Hz, 1H), 3.92 (s, 3H).

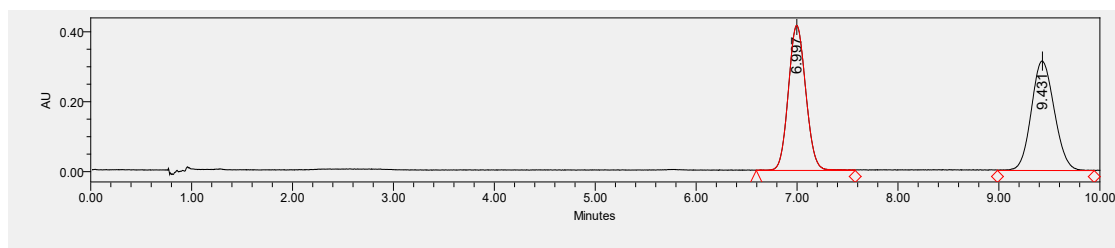
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.94, 158.82, 148.65, 143.38, 138.26, 137.71, 135.73, 134.64, 132.81, 131.68, 130.07, 129.25, 129.03, 129.00, 128.87, 128.55, 127.98, 127.61, 127.54, 125.77, 124.42, 120.03, 119.52, 114.39, 107.96, 55.38.

ESI-HRMS: calcd for $\text{C}_{26}\text{H}_{17}\text{O}_2^+$ ($[\text{M} + \text{H}]^+$) = 361.1223, found 361.1222.

IR (neat): 2923, 1611, 1532, 1272, 856, 760 cm^{-1} .

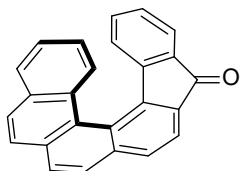


Retention Time	Area	% Area	Height
6.894	48716	1.49	5086
9.364	3230404	98.51	210983



Retention Time	Area	% Area	Height
6.997	4973488	50.09	414675
9.431	4955064	49.91	313069

(M)-7H-benzo[c]indeno[1,2-g]phenanthren-7-one (M-A24)



Following the typical procedure for the kinetic resolution.

(14 h 10 min) 11.9 mg, 36% yield; ee = 67%, yellow solid; R_f = 0.4 (PE/EtOAc = 9/1). $[\alpha]^{25}_D$ = -2209 (c = 3.3 $\times 10^{-2}$, in CH_2Cl_2).

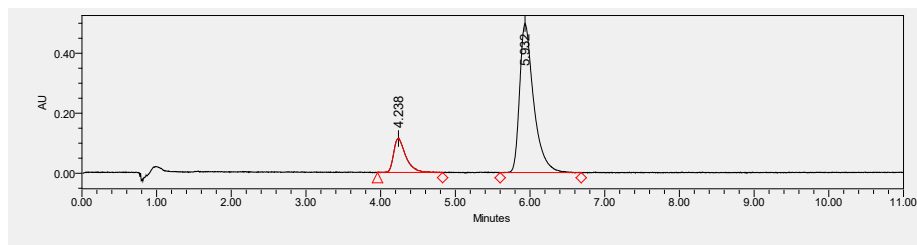
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **OZ-3** column), CO_2/MeOH = 70/30, flow rate 1.5 mL/min, λ = 243 nm, retention time: t (major) = 5.932 min, t (minor) = 4.238 min.

^1H NMR (600 MHz, CDCl_3) δ 8.04 (t, J = 8.6 Hz, 3H), 7.98 (d, J = 7.8 Hz, 1H), 7.94 – 7.87 (m, 4H), 7.66 (d, J = 7.2 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.10 (t, J = 7.2 Hz, 1H), 6.83 (t, J = 7.6 Hz, 1H), 5.93 (d, J = 7.8 Hz, 1H).

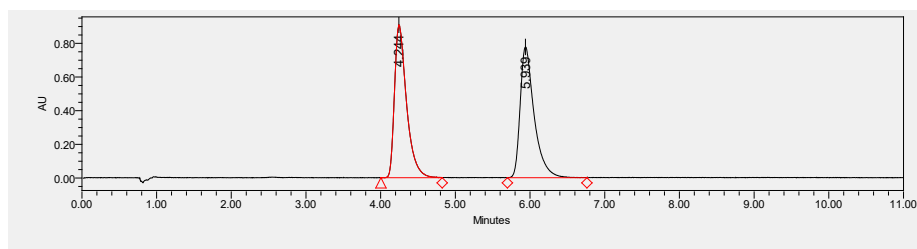
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.54, 145.95, 144.04, 138.50, 133.81, 133.20, 132.74, 132.33, 132.21, 131.17, 129.88, 129.21, 128.99, 128.70, 128.20, 127.80, 127.70, 126.66, 126.41, 126.19, 125.98, 125.44, 124.30, 123.15, 120.71.

ESI-HRMS: calcd for $\text{C}_{25}\text{H}_{15}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 331.1117, found 311.1116.

IR (neat): 2924, 1567, 1362, 848, 747 cm^{-1} .

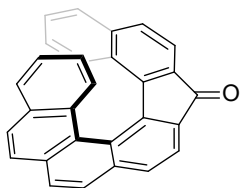


Retention Time	Area	% Area	Height
4.238	1278590	16.55	113005
5.932	6446696	83.45	497056



Retention Time	Area	% Area	Height
4.244	10124361	50.07	908079
5.939	10096377	49.93	776690

(M)-7H-benzo[c]benzo[6,7]indeno[1,2-g]phenanthren-7-one (M-A25)



Following the typical procedure for the kinetic resolution.

(21 h) 20.5 mg, 54% yield; ee = 73%, dark red solid; R_f = 0.42 (PE/EtOAc = 9/1). $[\alpha]_D^{25} = -3955$ ($c = 3.8 \times 10^{-2}$, in CH_2Cl_2).

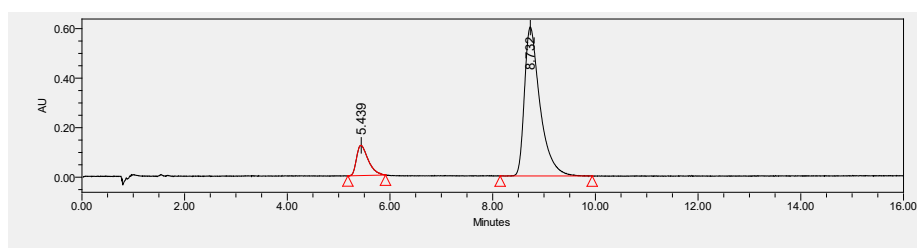
Dissolved in MeOH for UPCC; **HPLC** (Chiralcel **OZ-3** column), $\text{CO}_2/\text{MeOH} = 70/30$, flow rate 1.5 mL/min, $\lambda = 243$ nm, retention time: t (major) = 8.740 min, t (minor) = 5.435 min.

^1H NMR (600 MHz, CDCl_3) δ 7.97 (dd, $J = 8.0, 2.4$ Hz, 2H), 7.93 – 7.90 (m, 3H), 7.86 (d, $J = 8.4$ Hz, 1H), 7.81 (dd, $J = 8.2, 3.4$ Hz, 2H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.47 (d, $J = 8.2$ Hz, 1H), 7.10 – 7.07 (m, 1H), 6.97 (ddd, $J = 8.0, 6.6, 1.2$ Hz, 1H), 6.76 (ddd, $J = 8.4, 6.6, 1.4$ Hz, 1H), 6.29 (ddd, $J = 8.4, 6.6, 1.4$ Hz, 1H), 6.20 (d, $J = 8.6$ Hz, 1H).

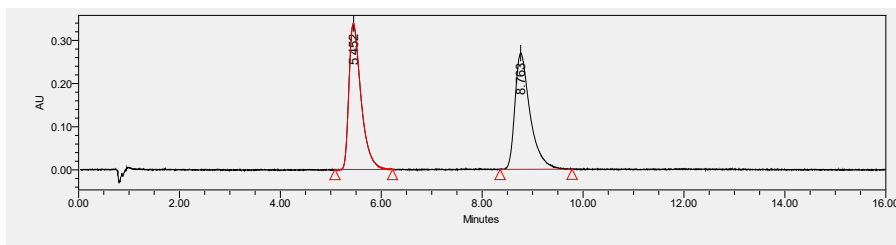
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.61, 148.63, 146.20, 138.68, 137.10, 134.25, 132.14, 131.60, 131.03, 130.72, 129.97, 129.94, 129.14, 128.85, 128.69, 128.06, 127.88, 127.53, 127.39, 127.06, 126.35, 125.67, 125.65, 125.50, 125.21, 119.94, 119.36.

ESI-HRMS: calcd for $\text{C}_{29}\text{H}_{17}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 381.1274, found 381.1274.

IR (neat): 2924, 1609, 1567, 1362, 848, 747 cm^{-1} .



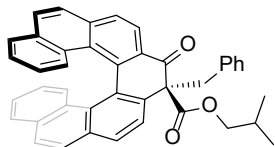
Retention Time	Area	% Area	Height
5.435	1776485	13.36	111706
8.740	11519480	86.64	544979



Retention Time	Area	% Area	Height
5.452	5589395	49.90	338345
8.763	5612055	50.10	269423

12.2 Analytical and spectral characterization data of helical phenanthrenones.

isobutyl (*P, S*)-9-benzyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (*P, S*-C1)



Following the typical procedure for the stereo-divergent synthesis.

>19:1 dr., ee = 98% ee, bright yellow oil; R_f = 0.38 (PE/EA = 9/1). $[\alpha]_D^{25} = 1436$ ($c = 5.8 \times 10^{-2}$, in CH_2Cl_2).

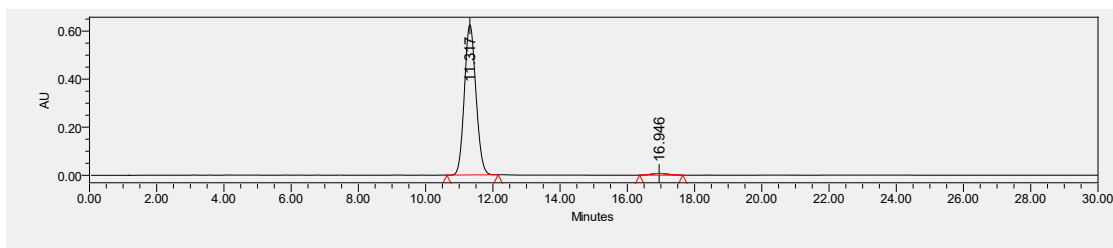
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major) = 11.175 min, t (minor) = 16.761 min.

^1H NMR (600 MHz, CDCl_3) δ 8.24 (d, $J = 7.8$ Hz, 1H), 7.89 (d, $J = 8.2$ Hz, 1H), 7.81 (dd, $J = 8.0, 5.4$ Hz, 2H), 7.49 (t, $J = 8.8$ Hz, 2H), 7.39 (d, $J = 8.6$ Hz, 1H), 7.30 (d, $J = 8.6$ Hz, 1H), 7.21 (t, $J = 9.4$ Hz, 2H), 6.94 – 6.87 (m, 7H), 6.63 (d, $J = 8.4$ Hz, 1H), 6.43 (d, $J = 8.4$ Hz, 1H), 6.37 (t, $J = 7.8$ Hz, 1H), 6.31 (t, $J = 7.8$ Hz, 1H), 4.41 (d, $J = 15.6$ Hz, 1H), 3.97 (d, $J = 15.6$ Hz, 1H), 3.74 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.65 (dd, $J = 10.8, 6.6$ Hz, 1H), 1.48 (septet, $J = 6.6$ Hz, 1H), 0.49 (d, $J = 6.6$ Hz, 3H), 0.43 (d, $J = 6.6$ Hz, 3H).

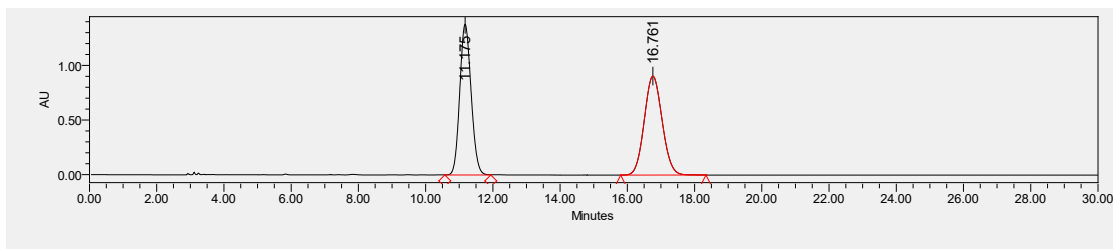
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.25, 170.26, 137.92, 136.91, 136.35, 132.65, 132.51, 131.85, 131.70, 130.79, 129.90, 129.80, 129.67, 129.65, 129.49, 128.96, 128.58, 128.31, 127.89, 127.17, 126.61, 126.08, 125.89, 125.76, 125.63, 125.57, 125.49, 125.46, 124.04, 123.81, 123.29, 72.10, 63.34, 39.52, 29.74, 27.46, 18.56, 18.51.

ESI-HRMS: calcd for $\text{C}_{42}\text{H}_{32}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 607.2244, found 607.2248.

IR (neat): 1736, 1679, 1449, 1349, 1266, 1221, 1170, 1003, 743, 692 cm^{-1} .

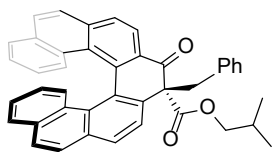


Retention Time	Area	% Area	Height
11.175	32413635	49.20	1379873
16.761	33474096	50.80	905877



Retention Time	Area	% Area	Height
11.317	14905680	98.71	624999
16.946	195051	1.29	6266

isobutyl (*M, R*)-9-benzyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (*M, R*-C1)



Following the typical procedure for the stereo-divergent synthesis.

>19:1 dr., ee = 97% ee, bright yellow oil; R_f = 0.38 (PE/EA = 9/1). $[\alpha]^{25}_D$ = -1417 (c = 5.8×10^{-2} , in CH_2Cl_2).

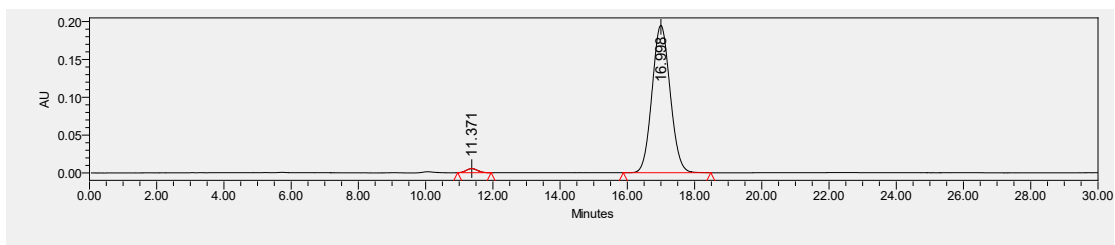
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major) = 16.998 min, t (minor) = 11.371 min.

^1H NMR (600 MHz, CDCl_3) δ 8.24 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.81 (dd, J = 8.0, 5.4 Hz, 2H), 7.49 (t, J = 8.8 Hz, 2H), 7.39 (d, J = 8.6 Hz, 1H), 7.30 (d, J = 8.6 Hz, 1H), 7.21 (t, J = 9.4 Hz, 2H), 6.94 – 6.87 (m, 7H), 6.63 (d, J = 8.4 Hz, 1H), 6.43 (d, J = 8.4 Hz, 1H), 6.37 (t, J = 7.8 Hz, 1H), 6.31 (t, J = 7.8 Hz, 1H), 4.41 (d, J = 15.6 Hz, 1H), 3.97 (d, J = 15.6 Hz, 1H), 3.74 (dd, J = 10.8, 6.6 Hz, 1H), 3.65 (dd, J = 10.8, 6.6 Hz, 1H), 1.48 (septet, J = 6.6 Hz, 1H), 0.49 (d, J = 6.6 Hz, 3H), 0.43 (d, J = 6.6 Hz, 3H).

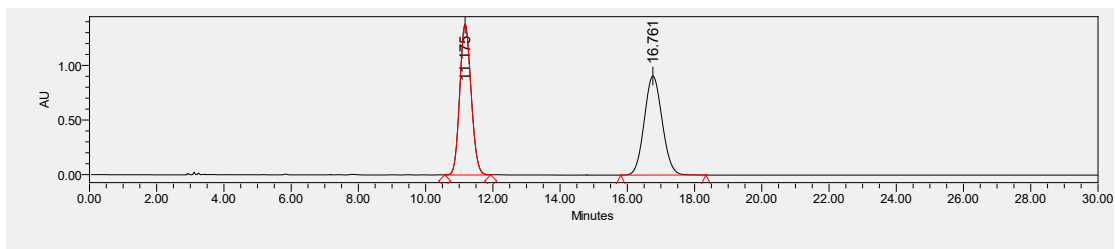
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.25, 170.26, 137.92, 136.91, 136.35, 132.65, 132.51, 131.85, 131.70, 130.79, 129.90, 129.80, 129.67, 129.65, 129.49, 128.96, 128.58, 128.31, 127.89, 127.17, 126.61, 126.08, 125.89, 125.76, 125.63, 125.57, 125.49, 125.46, 124.04, 123.81, 123.29, 72.10, 63.34, 39.52, 29.74, 27.46, 18.56, 18.51.

ESI-HRMS: calcd for $\text{C}_{42}\text{H}_{32}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 607.2244, found 607.2248.

IR (neat): 1736, 1679, 1449, 1349, 1266, 1221, 1170, 1003, 743, 692 cm^{-1} .

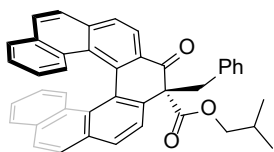


Retention Time	Area	% Area	Height
11.371	127285	1.72	5454
16.998	7270425	98.28	194696



Retention Time	Area	% Area	Height
11.317	14905680	98.71	624999
16.946	195051	1.29	6266

isobutyl (*P, R*)-9-benzyl-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (*P, R*-C1)



Following the typical procedure for the stereo-divergent synthesis.

>19:1 dr., ee = 97% ee, bright yellow oil; R_f = 0.38 (PE/Ea = 9/1). $[\alpha]_D^{25} = 1350$ ($c = 5.8 \times 10^{-2}$, in CH_2Cl_2).

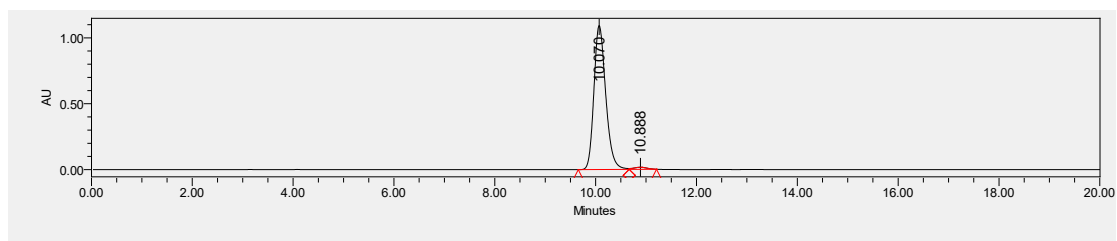
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **ID** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major) = 10.070 min, t (minor) = 10.888 min.

^1H NMR (600 MHz, CDCl_3) δ 8.18 (d, $J = 7.8$ Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 7.8$ Hz, 1H), 7.52 – 7.44 (m, 3H), 7.36 (d, $J = 8.6$ Hz, 1H), 7.32 (d, $J = 8.6$ Hz, 1H), 7.18 (dd, $J = 7.8, 5.4$ Hz, 2H), 6.92 (t, $J = 7.4$ Hz, 1H), 6.86 (t, $J = 7.4$ Hz, 1H), 6.79 (d, $J = 7.4$ Hz, 2H), 6.56 (t, $J = 7.0$ Hz, 3H), 6.40 (t, $J = 7.4$ Hz, 1H), 6.33 (t, $J = 7.8$ Hz, 1H), 6.29 – 6.25 (m, 2H), 4.00 – 3.92 (m, 2H), 3.86 (d, $J = 13.6$ Hz, 1H), 3.77 (d, $J = 13.6$ Hz, 1H), 1.79 (septet, $J = 6.6$ Hz, 1H), 0.67 (dd, $J = 6.6, 4.0$ Hz, 6H).

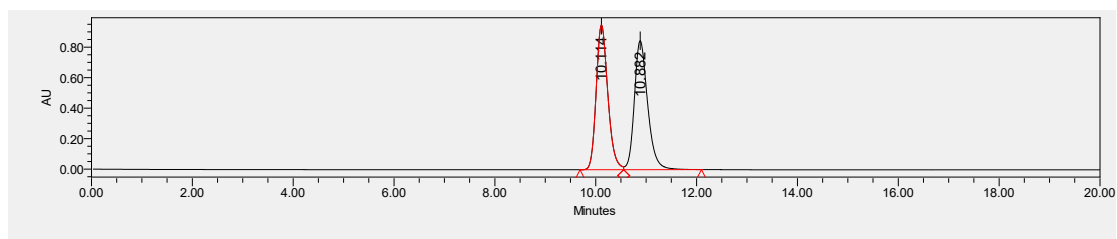
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 196.65, 172.02, 137.76, 136.86, 135.03, 132.78, 132.39, 131.89, 131.63, 130.33, 130.01, 129.76, 129.72, 129.16, 129.08, 128.89, 128.64, 128.32, 127.31, 127.13, 126.62, 126.50, 126.42, 125.89, 125.77, 125.64, 125.51, 125.49, 125.40, 125.00, 123.62, 123.16, 123.13, 71.96, 65.71, 45.37, 27.60, 18.91.

ESI-HRMS: calcd for $\text{C}_{42}\text{H}_{32}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 607.2244, found 607.2248.

IR (neat): 1736, 1679, 1449, 1349, 1266, 1221, 1170, 1003, 743, 692 cm^{-1} .

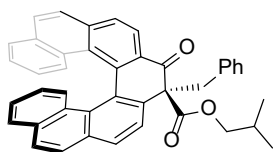


Retention Time	Area	% Area	Height
10.070	17777623	98.15	1092879
10.888	335515	1.85	17203



Retention Time	Area	% Area	Height
10.114	3154393	49.71	197282
10.882	3191186	50.29	175563

isobutyl (*M, S*)-9-benzyl-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (*M, S*-C1)



Following the typical procedure for the stereo-divergent synthesis.

>19:1 dr., ee = 96% ee, bright yellow oil; R_f = 0.38 (PE/EA = 9/1). $[\alpha]^{25}_D$ = -1276 (c = 5.8×10^{-2} , in CH_2Cl_2).

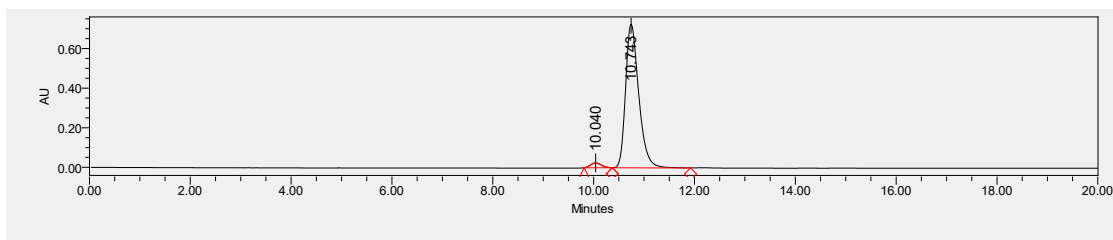
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **ID** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major) = 10.743 min, t (minor) = 10.040 min.

^1H NMR (600 MHz, CDCl_3) δ 8.18 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.36 (d, J = 8.6 Hz, 1H), 7.32 (d, J = 8.6 Hz, 1H), 7.18 (dd, J = 7.8, 5.4 Hz, 2H), 6.92 (t, J = 7.4 Hz, 1H), 6.86 (t, J = 7.4 Hz, 1H), 6.79 (d, J = 7.4 Hz, 2H), 6.56 (t, J = 7.0 Hz, 3H), 6.40 (t, J = 7.4 Hz, 1H), 6.33 (t, J = 7.8 Hz, 1H), 6.29 – 6.25 (m, 2H), 4.00 – 3.92 (m, 2H), 3.86 (d, J = 13.6 Hz, 1H), 3.77 (d, J = 13.6 Hz, 1H), 1.79 (septet, J = 6.6 Hz, 1H), 0.67 (dd, J = 6.6, 4.0 Hz, 6H).

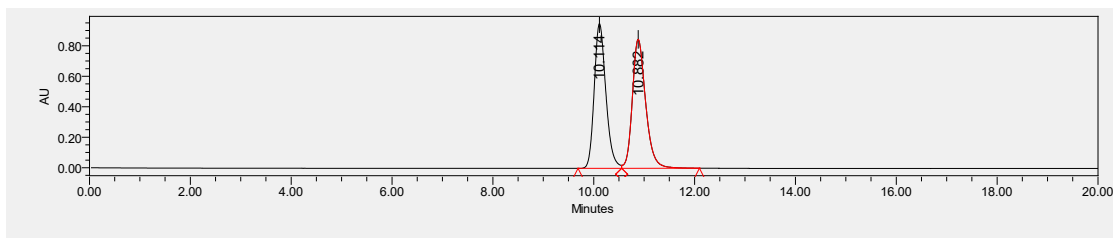
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 196.65, 172.02, 137.76, 136.86, 135.03, 132.78, 132.39, 131.89, 131.63, 130.33, 130.01, 129.76, 129.72, 129.16, 129.08, 128.89, 128.64, 128.32, 127.31, 127.13, 126.62, 126.50, 126.42, 125.89, 125.77, 125.64, 125.51, 125.49, 125.40, 125.00, 123.62, 123.16, 123.13, 71.96, 65.71, 45.37, 27.60, 18.91.

ESI-HRMS: calcd for $\text{C}_{42}\text{H}_{32}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 607.2244, found 607.2248.

IR (neat): 1736, 1679, 1449, 1349, 1266, 1221, 1170, 1003, 743, 692 cm^{-1} .

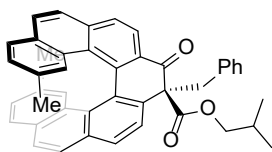


Retention Time	Area	% Area	Height
10.040	281141	2.12	21071
10.743	12982552	97.88	722931



Retention Time	Area	% Area	Height
10.114	3154393	49.71	197282
10.882	3191186	50.29	175563

isobutyl (*P*, *S*)-9-benzyl-2,17-dimethyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C2)



Following the typical procedure for the kinetic resolution.

(4 h 45 min) 30.6 mg, 50% yield; 4.9:1 dr., ee = 97%/97% ee, bright yellow oil; R_f = 0.38 (PE/EA = 9/1).

$[\alpha]_D^{25} = 1040$ ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

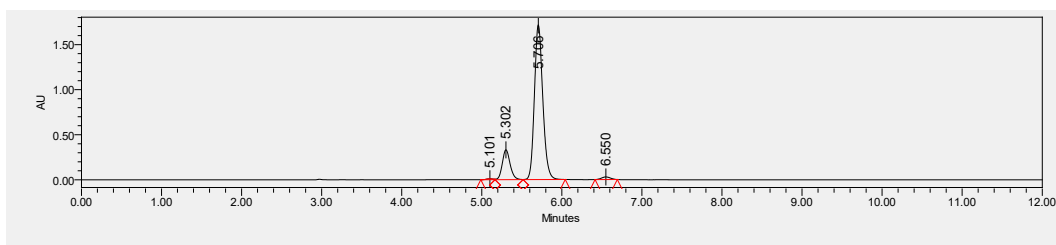
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major₁) = 5.706 min, t (minor₁) = 6.550 min, t (major₂) = 5.302 min, t (minor₂) = 5.101 min.

^1H NMR (600 MHz, CDCl_3) δ 8.23 (d, $J = 7.8$ Hz, 1H), 7.87 (d, $J = 8.4$ Hz, 1H), 7.84 – 7.82 (m, 2H), 7.43 (t, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 9.0$ Hz, 1H), 7.25 (d, $J = 6.0$ Hz, 1H), 7.12 (dd, $J = 9.6, 8.4$ Hz, 2H), 6.95 – 6.89 (m, 5H), 6.78 (d, $J = 7.8$ Hz, 1H), 6.74 (d, $J = 7.8$ Hz, 1H), 6.39 (s, 1H), 6.19 (s, 1H), 4.42 (d, $J = 15.6$ Hz, 1H), 3.97 (d, $J = 15.6$ Hz, 1H), 3.79 (dd, $J = 10.2, 6.0$ Hz, 1H), 3.62 (dd, $J = 10.2, 6.0$ Hz, 1H), 1.75 (s, 3H), 1.71 (s, 3H), 1.50 (septet, $J = 7.2$ Hz, 1H), 0.52 (d, $J = 6.7$ Hz, 3H), 0.46 (d, $J = 6.7$ Hz, 3H).

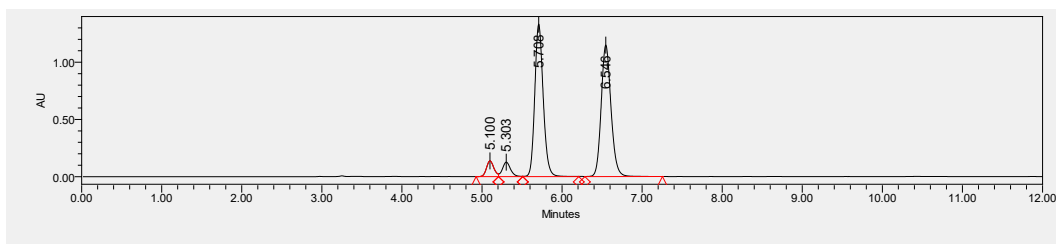
$^{13}\text{C}\{^1\text{H}\}$ NMR (15 MHz, CDCl_3) δ 194.23, 170.29, 138.31, 137.03, 136.43, 133.65, 132.99, 131.01, 130.06, 129.97, 129.92, 129.87, 129.80, 129.56, 129.41, 129.12, 128.58, 128.19, 127.94, 127.88, 127.71, 127.38, 127.28, 126.87, 126.77, 126.66, 126.26, 126.01, 125.50, 124.46, 123.93, 72.06, 63.34, 39.44, 27.48, 21.17, 21.09, 18.66, 18.57.

ESI-HRMS: calcd for $\text{C}_{44}\text{H}_{37}\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) = 613.2737, found 613.2736.

IR (neat): 1736, 1679, 1449, 1349, 1266, 1221, 1170, 1003, 743, 692 cm^{-1} .

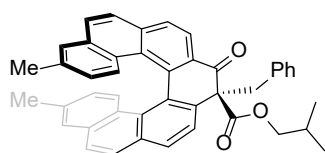


Retention Time	Area	% Area	Height
5.101	61486	0.41	10472
5.302	2244682	14.95	331150
5.706	12489845	83.16	1715798
6.550	222762	1.48	28927



Retention Time	Area	% Area	Height
5.100	885901	4.15	137192
5.303	890015	4.16	126599
5.708	9784024	45.78	1331335
6.546	9809880	45.91	1148778

isobutyl (*P,S*)-9-benzyl-3,16-dimethyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C3)



Following the typical procedure for the kinetic resolution.

(4 h 55 min) 30.6 mg, 50 % yield; 6.0:1 dr., ee = 97%/96% ee, bright yellow oil solid; R_f = 0.38 (PE/EA = 9/1). $[\alpha]_D^{25}$ = 1281 ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/PrOH = 90/10, flow rate

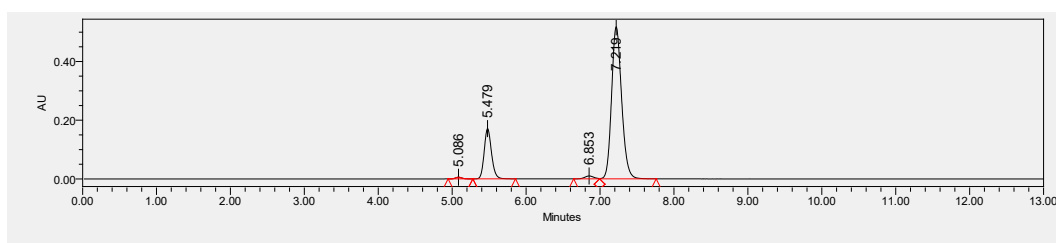
1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 7.219 min, t (minor₁) = 6.853 min, t (major₂) = 5.479 min, t (minor₂) = 5.086 min.

^1H NMR (600 MHz, CDCl_3) δ 8.19 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.78 (t, J = 7.2 Hz, 2H), 7.45 (t, J = 9.0 Hz, 2H), 7.32 (d, J = 9.0 Hz, 1H), 7.23 (d, J = 9.6 Hz, 1H), 6.97 (d, J = 10.2 Hz, 2H), 6.93 – 6.87 (m, 5H), 6.50 (d, J = 8.4 Hz, 1H), 6.30 (d, J = 8.4 Hz, 1H), 6.18 (d, J = 8.4 Hz, 1H), 6.12 (d, J = 8.4 Hz, 1H), 4.39 (d, J = 15.6 Hz, 1H), 3.96 (d, J = 15.6 Hz, 1H), 3.74 (dd, J = 10.8, 6.6 Hz, 1H), 3.64 (dd, J = 10.7, 6.5 Hz, 1H), 2.15 (s, 3H), 2.13 (s, 3H), 1.47 (septet, J = 6.6 Hz, 1H), 0.48 (d, J = 6.6 Hz, 3H), 0.42 (d, J = 6.6 Hz, 3H).

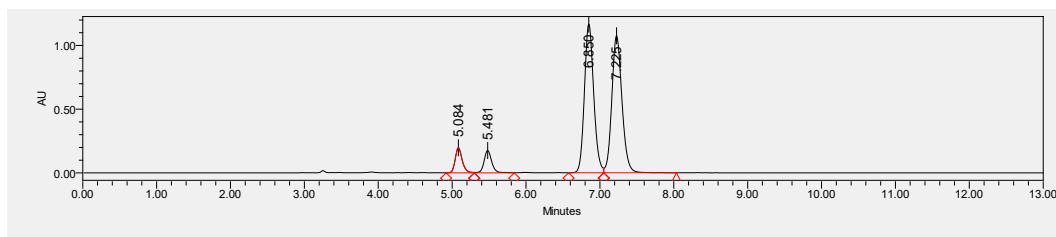
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.37, 170.36, 137.90, 136.59, 136.41, 135.56, 135.20, 132.33, 132.29, 132.02, 131.86, 130.67, 129.90, 129.79, 129.70, 129.27, 128.43, 128.13, 127.84, 127.50, 127.29, 126.97, 126.77, 126.02, 125.96, 125.57, 125.47, 125.41, 125.29, 125.05, 125.00, 123.51, 72.03, 63.28, 39.57, 27.44, 21.09, 21.05, 18.56, 18.50.

ESI-HRMS: calcd for $\text{C}_{44}\text{H}_{37}\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) = 613.2737, found 613.2736.

IR (neat): 1736, 1679, 1449, 1349, 1266, 1221, 1170, 1003, 743, 692 cm^{-1} .

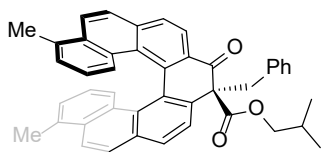


Retention Time	Area	% Area	Height
5.086	34714	0.56	5606
5.479	1178631	19.02	171405
6.853	84531	1.36	9851
7.219	4899352	79.06	517776



Retention Time	Area	% Area	Height
5.084	1295459	5.62	196450
5.481	1259165	5.46	175131
6.850	10198379	44.24	1167452
7.225	10300677	44.68	1075443

isobutyl (*P,S*)-9-benzyl-4,15-dimethyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C4)



Following the typical procedure for the kinetic resolution.

(4 h 30 min) 25.7 mg, 42% yield; 9.7:1 dr., ee = 99%/91% ee, bright yellow oil; R_f = 0.38 (PE/EA = 9/1). $[\alpha]_D^{25} = 1147$ ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

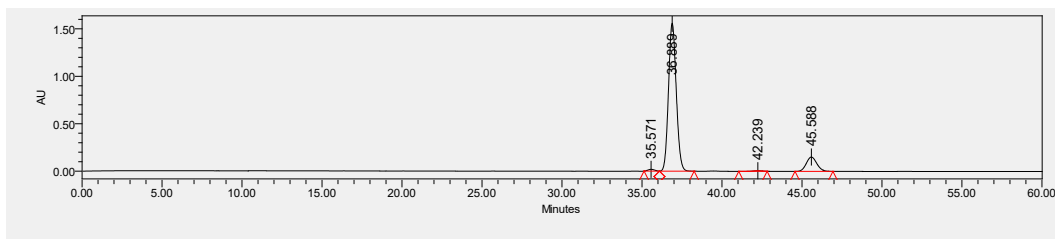
Dissolved in n-hexane for HPLC; **HPLC** (The Chiralcel **IK** columns and Chiralcel **IE** columns are connected in series, with the sample first passing through the Chiralcel **IK** column.), n-hexane/ i PrOH = 70/30, flow rate 0.5 mL/min, $\lambda = 243$ nm, retention time: $t(\text{major}_1) = 36.889$ min, $t(\text{minor}_1) = 35.571$ min, $t(\text{major}_2) = 45.588$ min, $t(\text{minor}_2) = 42.239$ min.

^1H NMR (600 MHz, CDCl_3) δ 8.23 (d, $J = 7.8$ Hz, 1H), 7.85 (d, $J = 7.8$ Hz, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.76 (d, $J = 8.4$ Hz, 1H), 7.57 (d, $J = 9.0$ Hz, 1H), 7.49 – 7.48 (m, 3H), 6.91 – 6.85 (m, 5H), 6.74 (d, $J = 7.2$ Hz, 1H), 6.70 (d, $J = 7.2$ Hz, 1H), 6.38 (d, $J = 8.4$ Hz, 1H), 6.20 – 6.16 (m, 2H), 6.13 (d, $J = 6.6$ Hz, 1H), 4.41 (d, $J = 15.0$ Hz, 1H), 3.96 (d, $J = 15.0$ Hz, 1H), 3.78 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.69 (dd, $J = 10.6, 6.8$ Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H), 1.50 (septet, $J = 6.6$ Hz, 1H), 0.49 (d, $J = 6.6$ Hz, 3H), 0.43 (d, $J = 6.6$ Hz, 3H).

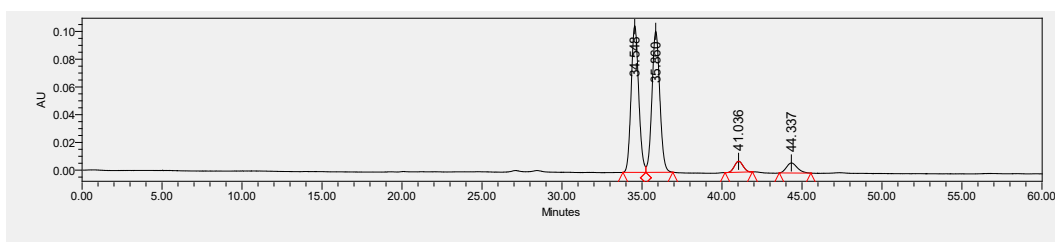
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.31, 170.37, 138.28, 136.43, 136.24, 132.89, 132.69, 132.65, 132.21, 130.75, 130.32, 130.25, 129.90, 129.80, 129.38, 129.34, 128.73, 128.17, 127.82, 127.79, 126.23, 126.07, 125.95, 125.55, 125.26, 125.16, 124.32, 124.13, 123.85, 123.22, 122.97, 122.76, 72.04, 63.13, 40.22, 27.48, 19.31, 19.23, 18.56, 18.52.

ESI-HRMS: calcd for $\text{C}_{44}\text{H}_{36}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 635.2557, found 635.2554.

IR (neat): 2961, 1734, 1666, 1592, 1502, 1451, 1286, 1208, 910, 836, 769, 732, 701 cm^{-1} .

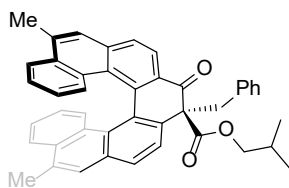


Retention Time	Area	% Area	Height
35.571	548494	0.91	18916
36.889	52474301	87.21	1558041
42.239	220378	0.37	6085
45.588	6926329	11.51	151126



Retention Time	Area	% Area	Height
34.548	3470034	46.16	105754
35.860	3462323	46.06	101621
41.036	296316	3.94	7910
44.337	288476	3.84	6766

isobutyl (*P*, *S*)-9-benzyl-5,14-dimethyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C5)



Following the typical procedure for the kinetic resolution.

(4 h 15 min) 30.6 mg, 50% yield; 13.7:1 dr., ee = 98%/96% ee, bright yellow oil; R_f = 0.38 (PE/EA = 9/1).

$[\alpha]_D^{25} = 1124$ ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/ PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major₁) = 11.041 min, t (minor₁) = 10.232 min, t (major₂) = 12.836

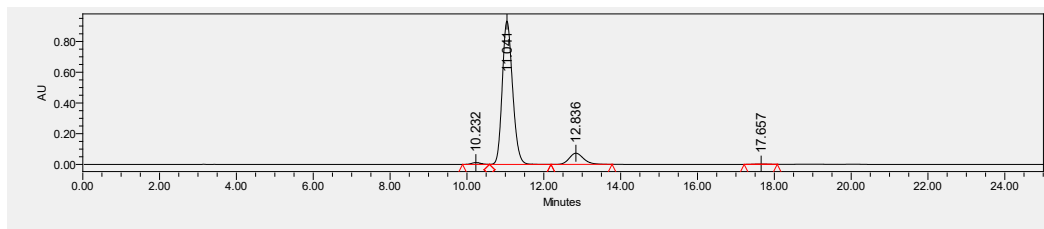
min, t (minor₂) = 17.657 min.

^1H NMR (600 MHz, CDCl_3) δ 8.20 (d, $J = 7.8$ Hz, 1H), 7.83 (d, $J = 7.8$ Hz, 1H), 7.71 (d, $J = 7.8$ Hz, 1H), 7.67 (d, $J = 7.8$ Hz, 1H), 7.32 (t, $J = 7.2$ Hz, 2H), 7.29 (d, $J = 4.2$ Hz, 2H), 6.94 (d, $J = 7.2$ Hz, 1H), 6.89 – 6.86 (m, 5H), 6.66 (d, $J = 8.4$ Hz, 1H), 6.46 (d, $J = 8.4$ Hz, 1H), 6.31 (d, $J = 7.2$ Hz, 1H), 6.26 (d, $J = 7.2$ Hz, 1H), 4.39 (d, $J = 15.6$ Hz, 1H), 3.95 (d, $J = 15.6$ Hz, 1H), 3.78 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.68 (dd, $J = 10.8, 6.6$ Hz, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 1.50 (septet, $J = 6.6$ Hz, 1H), 0.49 (d, $J = 6.6$ Hz, 3H), 0.43 (d, $J = 6.6$ Hz, 3H).

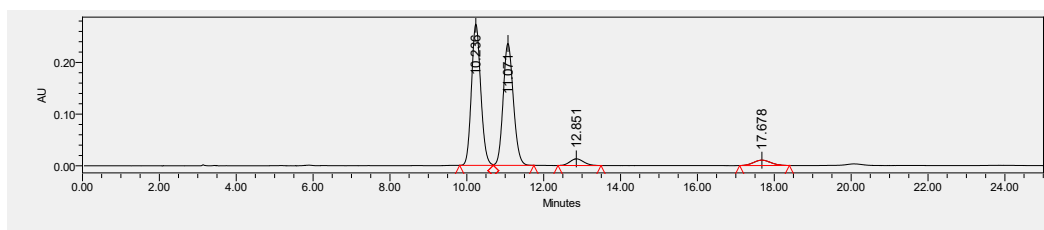
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.21, 170.47, 137.98, 136.91, 136.36, 135.84, 132.78, 132.54, 132.08, 131.54, 131.42, 130.43, 129.92, 129.67, 129.47, 129.16, 129.00, 128.92, 127.81, 127.66, 127.24, 126.02, 125.88, 125.73, 125.45, 125.38, 125.16, 125.07, 125.00, 124.17, 123.19, 122.72, 122.58, 122.55, 72.00, 63.09, 40.08, 27.48, 19.53, 19.33, 18.57, 18.52.

ESI-HRMS: calcd for $\text{C}_{44}\text{H}_{36}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 635.2557, found 635.2558.

IR (neat): 2961, 1733, 1665, 1585, 1448, 1278, 1208, 1036, 910, 760, 731 cm^{-1} .

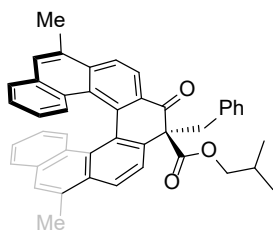


Retention Time	Area	% Area	Height
10.232	200485	1.03	11848
11.041	17385941	89.08	931917
12.836	1879735	9.63	72573
17.657	51733	0.27	1926



Retention Time	Area	% Area	Height
10.236	4179511	46.49	261720
11.071	4160622	46.27	230662
12.851	323327	3.60	12874
17.678	327625	3.64	10436

isobutyl (*P*, *S*)-9-benzyl-6,13-dimethyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C6)



Following the typical procedure for the kinetic resolution.

(4 h 15 min) 27.6 mg, 45% yield; 10.2:1 dr., ee = 99%/99% ee, bright yellow oil; R_f = 0.38 (PE/EA = 9/1).

$[\alpha]_D^{25} = 1017$ ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

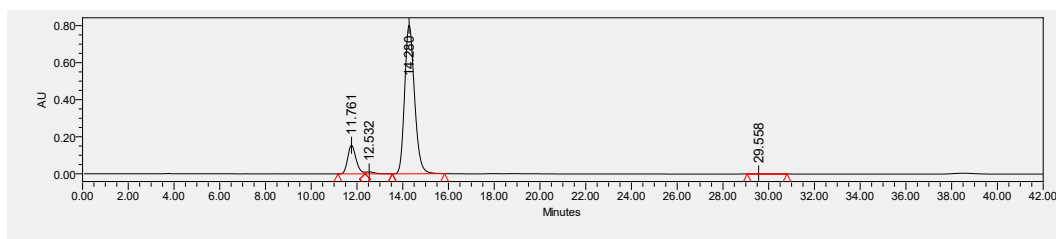
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major₁) = 14.280 min, t (minor₁) = 12.532 min, t (major₂) = 11.176 min, t (minor₂) = 29.558 min.

^1H NMR (600 MHz, CDCl_3) δ 8.25 (d, $J = 8.4$ Hz, 1H), 7.97 (dd, $J = 8.4, 3.6$ Hz, 2H), 7.90 (d, $J = 8.4$ Hz, 1H), 7.19 (s, 1H), 7.12 – 7.09 (m, 3H), 6.93 – 6.87 (m, 6H), 6.85 (t, $J = 7.2$ Hz, 1H), 6.56 (d, $J = 8.4$ Hz, 1H), 6.34 (d, $J = 8.4$ Hz, 1H), 6.29 (t, $J = 7.2$ Hz, 1H), 6.22 (t, $J = 7.2$ Hz, 1H), 4.40 (d, $J = 15.0$ Hz, 1H), 3.98 (d, $J = 15.0$ Hz, 1H), 3.74 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.67 (dd, $J = 10.8, 6.6$ Hz, 1H), 2.65 – 2.64 (m, 6H), 1.49 (septet, $J = 6.6$ Hz, 1H), 0.50 (d, $J = 6.6$ Hz, 3H), 0.43 (d, $J = 6.6$ Hz, 3H).

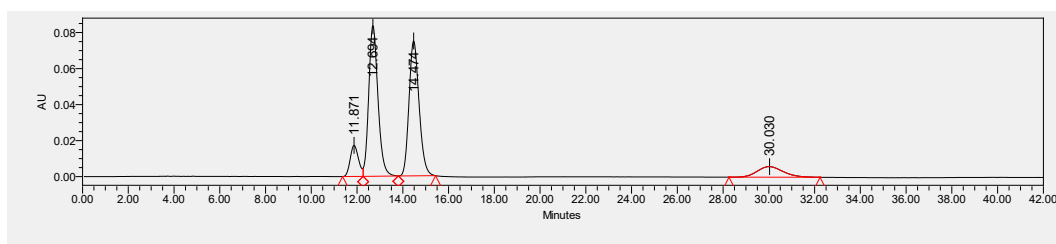
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) 194.36, 170.34, 138.22, 137.12, 136.38, 132.90, 132.07, 131.64, 131.45, 131.26, 130.78, 130.76, 130.61, 130.36, 129.89, 129.37, 128.82, 128.32, 127.88, 126.88, 126.05, 125.95, 125.83, 125.77, 125.74, 125.51, 125.31, 124.58, 124.22, 123.85, 123.00, 122.49, 72.08, 63.12, 39.57, 27.45, 19.86, 19.72, 18.58, 18.54.

ESI-HRMS: calcd for $\text{C}_{44}\text{H}_{37}\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) = 613.2737, found 613.2737.

IR (neat): 3058, 1733, 1668, 1446, 1324, 1274, 1208, 910, 731 cm^{-1} .

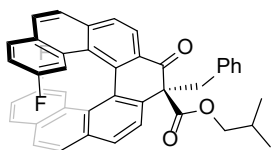


Retention Time	Area	% Area	Height
11.761	3853682	13.75	153425
12.532	172668	0.62	8066
14.280	23977779	85.57	801959
29.558	17735	0.06	350



Retention Time	Area	% Area	Height
11.871	460626	8.41	16755
12.694	2269569	41.44	83204
14.474	2281815	41.67	74781
30.030	464201	8.48	5885

isobutyl (*P*, *S*)-9-benzyl-2,17-difluoro-10-oxo-9,10-dihydrobenzo [1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C7)



Following the typical procedure for the kinetic resolution.

(8 h 15 min) 27.9 mg, 45% yield; 12.5:1 dr., ee = 99%/93% ee, bright yellow oil; R_f = 0.4 (PE/EA = 9/1).

$[\alpha]_D^{25} = 1241$ ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major₁) = 11.774 min, t (minor₁) = 8.490 min, t (major₂) = 7.363 min, t (minor₂) = 8.168 min.

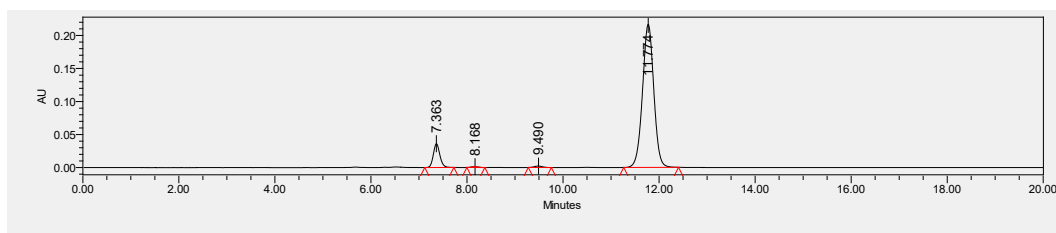
^1H NMR (600 MHz, CDCl_3) δ 8.20 (d, $J = 8.4$ Hz, 1H), 7.85 (d, $J = 8.4$ Hz, 1H), 7.80 (dd, $J = 8.4, 2.4$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 1H), 7.43 (d, $J = 8.4$ Hz, 1H), 7.35 (d, $J = 8.4$ Hz, 1H), 7.26 (d, $J = 8.4$ Hz, 1H), 7.19 – 7.15 (m, 2H), 6.87 – 6.82 (m, 5H), 6.67 – 6.63 (dt, $J = 7.8, 3.0$ Hz, 1H), 6.61 (dt, $J = 7.8, 3.0$ Hz, 1H), 6.12 (dd, $J = 12.0, 1.8$ Hz, 1H), 5.91 (dd, $J = 12.0, 1.8$ Hz, 1H), 4.35 (d, $J = 15.6$ Hz, 1H), 3.88 (d, $J = 15.6$ Hz, 1H), 3.69 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.58 (dd, $J = 10.8, 6.6$ Hz, 1H), 1.42 (septet, $J = 6.6$ Hz, 1H), 0.43 (d, $J = 6.6$ Hz, 3H), 0.37 (d, $J = 6.6$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.81, 169.96, 159.26 (d, $J = 246.1$ Hz), 158.95 (d, $J = 244.62$ Hz), 137.32, 137.16, 136.16, 132.98, 132.92, 129.87, 128.94, 128.74, 128.71, 128.69, 128.66, 128.63, 128.60, 127.93, 126.49, 126.27, 126.19, 125.10 (d, $J = 3.2$ Hz), 125.09 (d, $J = 3.3$ Hz), 124.71, 115.13 (d, $J = 22.7$ Hz), 114.81 (d, $J = 24.2$ Hz), 111.49 (d, $J = 3.0$ Hz), 111.34 (d, $J = 4.5$ Hz), 72.20, 63.44, 39.53, 27.47, 18.58, 18.51.

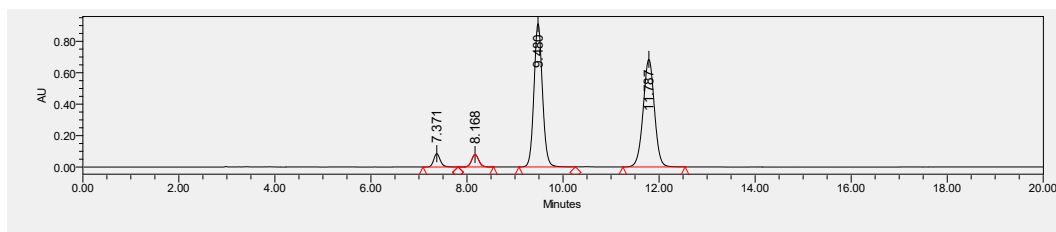
$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3) δ -123.09, -123.19.

ESI-HRMS: calcd for $\text{C}_{42}\text{H}_{30}\text{F}_2\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 643.2055, found 643.2057.

IR (neat): 1736, 1679, 1449, 1349, 1266, 1221, 1170, 1003, 743, 692 cm^{-1} .

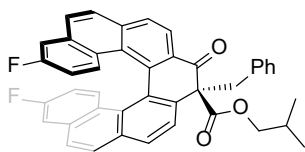


Retention Time	Area	% Area	Height
7.363	341038	8.71	36054
8.168	12946	0.33	1300
9.490	26206	0.67	2250
11.774	3537183	90.29	216602



Retention Time	Area	% Area	Height
7.371	811734	3.38	84891
8.168	832354	3.47	79669
9.480	11192077	46.66	910975
11.787	11152848	46.49	684306

isobutyl (*P*, *S*)-9-benzyl-3,16-difluoro-10-oxo-9,10-dihydrobenzo [1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C8)



Following the typical procedure for the kinetic resolution.

(8 h 10 min) 26.7 mg, 43% yield; 14.2:1 dr., ee = 98%/94% ee, bright yellow oil; R_f = 0.4 (PE/EA = 9/1).

$[\alpha]_D^{25} = 1383$ ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

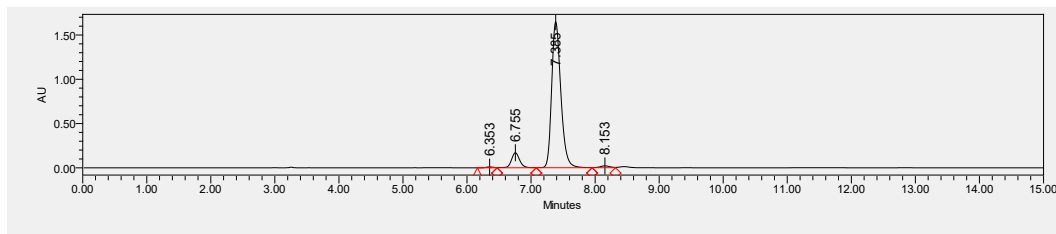
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/ PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major₁) = 7.385 min, t (minor₁) = 8.153 min, t (major₂) = 6.755 min, t (minor₂) = 6.353 min.

^1H NMR (600 MHz, CDCl_3) δ 8.23 (d, $J = 8.0$ Hz, 1H), 7.88 (d, $J = 8.4$ Hz, 1H), 7.82 (dd, $J = 8.4, 1.8$ Hz, 2H), 7.54 (dd, $J = 11.6, 8.8$ Hz, 2H), 7.39 (d, $J = 8.8$ Hz, 1H), 7.30 (d, $J = 8.8$ Hz, 1H), 6.93 – 6.91 (d, $J = 5.2$ Hz, 6H), 6.61 (dd, $J = 9.0, 5.4$ Hz, 1H), 6.39 (dd, $J = 9.0, 5.4$ Hz, 1H), 6.13 (td, $J = 9.0, 2.4$ Hz, 1H), 6.06 (td, $J = 9.0, 2.4$ Hz, 1H), 4.40 (d, $J = 15.0$ Hz, 1H), 3.96 (d, $J = 15.0$ Hz, 1H), 3.74 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.66 (dd, $J = 10.8, 6.6$ Hz, 1H), 1.49 (septet, $J = 6.6$ Hz, 1H), 0.49 (d, $J = 6.6$ Hz, 3H), 0.44 (d, $J = 6.6$ Hz, 3H).

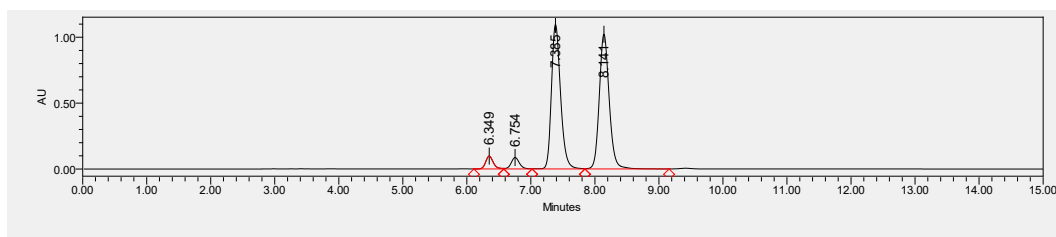
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.03, 170.07, 160.30 (d, $J = 247.9$ Hz), 160.15 (d, $J = 247.9$ Hz), 137.24, 136.38, 136.20, 133.32 (d, $J = 9.1$ Hz), 133.18 (d, $J = 9.1$ Hz), 133.08, 132.20, 130.33, 130.10, 129.89, 129.39, 129.14, 128.91, 128.88, 128.75, 128.54, 127.91, 127.61 (d, $J = 7.6$ Hz), 127.52 (d, $J = 9.1$ Hz), 126.86, 126.52, 126.49, 126.16, 126.12, 125.65, 125.60, 124.06, 112.91 (d, $J = 22.7$ Hz), 112.38 (d, $J = 24.2$ Hz), 110.83 (d, $J = 7.6$ Hz), 110.69 (d, $J = 7.6$ Hz), 72.17, 63.49, 39.45, 27.46, 18.55, 18.50..

ESI-HRMS: calcd for $\text{C}_{42}\text{H}_{30}\text{F}_2\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 643.2055, found 643.2053.

IR (neat): 2926, 1734, 1671, 1605, 1497, 1452, 1287, 1208, 910, 841, 768, 732, 701 cm^{-1} .

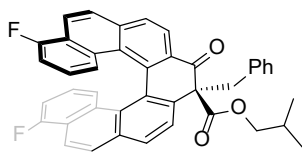


Retention Time	Area	% Area	Height
6.353	66832	0.37	8123
6.755	1508061	8.29	169893
7.385	16383202	90.04	1649517
8.153	237402	1.30	21579



Retention Time	Area	% Area	Height
6.349	807201	3.45	97979
6.754	775873	3.32	87177
7.385	10843295	46.35	1096896
8.141	10967522	46.88	1022591

isobutyl (*P*, *S*)-9-benzyl-4,15-difluoro-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C9)



Following the typical procedure for the kinetic resolution.

(5 h 10 min) 23.6 mg, 38% yield; 12.1:1 dr., ee = 99%/95% ee, bright yellow oil; R_f = 0.4 (PE/EA = 9/1).

$[\alpha]_D^{25} = 1401$ ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major₁) = 9.087 min, t (minor₁) = 8.595 min, t (major₂) = 10.337 min, t (minor₂) = 16.133 min.

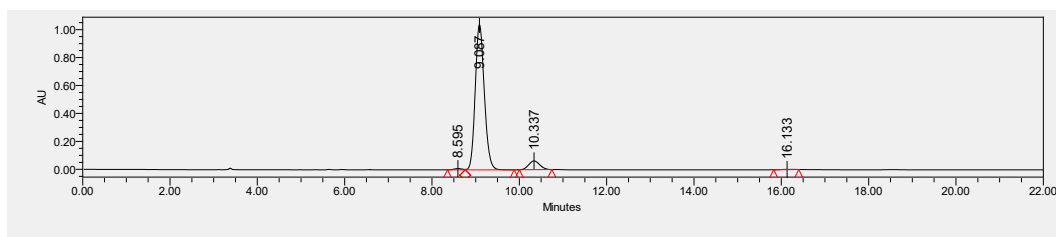
^1H NMR (600 MHz, CDCl_3) δ 8.27 (d, $J = 7.8$ Hz, 1H), 7.92 (d, $J = 7.8$ Hz, 1H), 7.85 (d, $J = 8.4$ Hz, 2H), 7.74 (d, $J = 9.0$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 1H), 7.57 (t, $J = 9.0$ Hz, 2H), 6.95 – 6.89 (m, 5H), 6.67 (t, $J = 8.4$ Hz, 2H), 6.63 (t, $J = 8.4$ Hz, 2H), 6.37 – 6.31 (m, 2H), 6.28 – 6.24 (m, 1H), 6.14 (d, $J = 8.4$ Hz, 1H), 4.41 (d, $J = 15.6$ Hz, 1H), 3.96 (d, $J = 15.6$ Hz, 1H), 3.75 (dd, $J = 10.8$, 6.6 Hz, 1H), 3.66 (dd, $J = 10.8$, 6.6 Hz, 1H), 1.48 (septet, $J = 6.6$ Hz, 1H), 0.49 (d, $J = 6.6$ Hz, 3H), 0.43 (d, $J = 6.6$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.94, 170.01, 157.79 (d, $J = 249.2$ Hz), 157.69 (d, $J = 250.7$ Hz), 137.72, 136.83, 136.14, 133.20, 132.67, 130.88 (d, $J = 3.0$ Hz), 130.74, 130.43 (d, $J = 4.5$ Hz), 130.13, 129.86, 129.19 (d, $J = 2.0$ Hz), 128.95 (d, $J = 1.8$ Hz), 128.85, 128.64, 127.92, 126.20, 126.18, 124.60, 123.97 (d, $J = 9.1$ Hz), 123.37 (d, $J = 7.6$ Hz), 121.84 (d, $J = 4.5$ Hz), 121.70 (d, $J = 3.0$ Hz), 121.45, 121.41, 121.26 (d, $J = 15.1$ Hz), 118.95 (d, $J = 7.6$ Hz), 110.36 (d, $J = 19.6$ Hz), 109.99 (d, $J = 19.6$ Hz), 72.19, 63.41, 39.48, 29.74, 27.45, 18.54, 18.48.

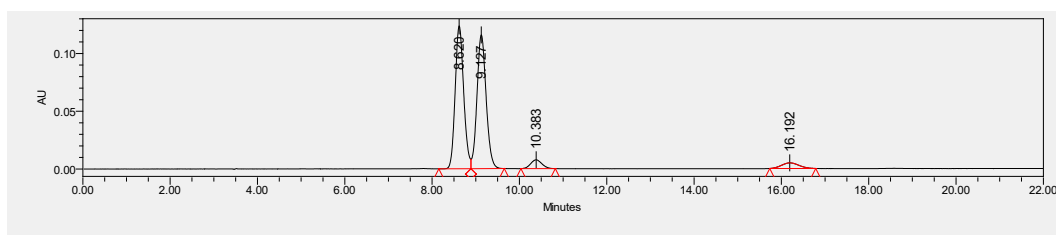
$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3) δ -123.09, -123.19.

ESI-HRMS: calcd for $\text{C}_{42}\text{H}_{30}\text{F}_2\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 643.2055, found 643.2053.

IR (neat): 1736, 1679, 1449, 1349, 1266, 1221, 1170, 1003, 743, 692 cm^{-1} .

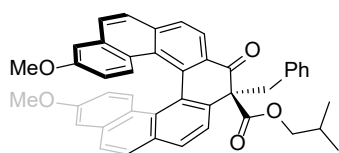


Retention Time	Area	% Area	Height
8.595	114884	0.71	9132
9.087	15036645	92.35	1040063
10.337	1100304	6.76	62568
16.133	30730	0.19	1565



Retention Time	Area	% Area	Height
8.620	1672333	46.07	123650
9.127	1686449	46.46	115767
10.383	137166	3.78	7639
16.192	134326	3.70	4847

isobutyl (*P,S*)-9-benzyl-3,16-dimethoxy-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C10)



Following the typical procedure for the kinetic resolution.

(4 h 20 min) 32.2 mg, 50% yield; 7.3:1 dr., ee = 96%/91% ee, bright orange oil; R_f = 0.29 (PE/EA = 9/1). $[\alpha]_D^{25}$ = 1169 ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

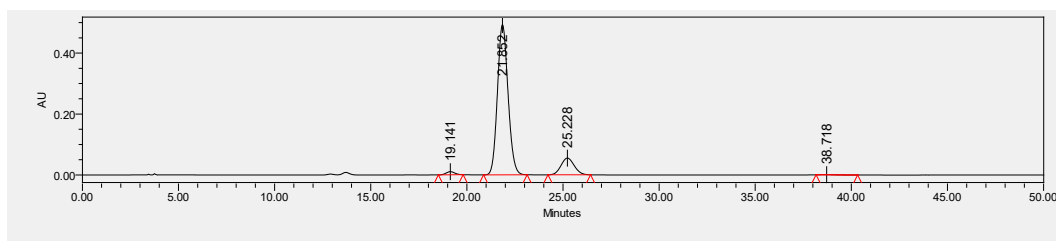
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 21.852 min, t (minor₁) = 19.141 min, t (major₂) = 25.228 min, t (minor₂) = 38.718 min.

^1H NMR (600 MHz, CDCl_3) δ 8.16 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.79 – 7.77 (m, 2H), 7.49 (t, J = 9.0 Hz, 2H), 7.38 (d, J = 9.0 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 6.94 – 6.86 (s, 5H), 6.63 (dd, J = 9.0, 2.4 Hz, 2H), 6.57 (d, J = 9.6 Hz, 1H), 6.36 (d, J = 9.0 Hz, 1H), 6.02 (dd, J = 9.0, 2.4 Hz, 1H), 5.96 (dd, J = 9.0, 2.4 Hz, 1H), 4.38 (d, J = 15.0 Hz, 1H), 3.95 (d, J = 15.0 Hz, 1H), 3.73 (dd, J = 10.8, 6.6 Hz, 1H), 3.69 (s, 3H), 3.68 (s, 3H), 3.63 (dd, J = 10.8, 6.6 Hz, 1H), 1.46 (septet, J = 6.6 Hz, 1H), 0.48 (d, J = 6.6 Hz, 3H), 0.42 (d, J = 6.6 Hz, 3H).

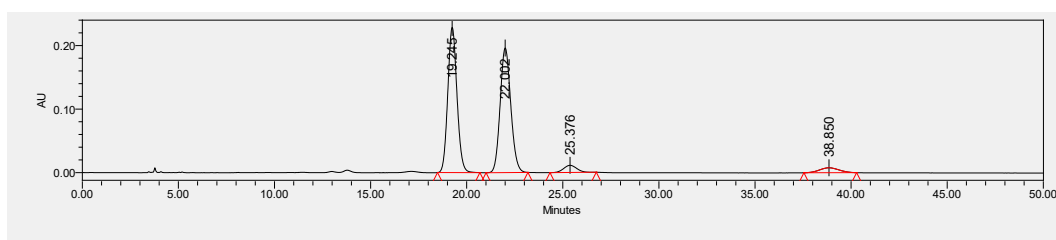
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.38, 170.31, 157.39, 157.18, 137.48, 136.42, 135.94, 133.47, 133.33, 132.43, 131.72, 130.38, 129.90, 129.82, 129.57, 129.23, 128.51, 128.23, 127.85, 126.87, 126.77, 126.17, 126.02, 124.62, 124.24, 123.73, 123.08, 114.19, 113.65, 106.90, 106.85, 72.04, 63.38, 55.23, 39.45, 27.43, 18.55, 18.50.

ESI-HRMS: calcd for $\text{C}_{44}\text{H}_{36}\text{O}_5\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 667.2455, found 667.2455.

IR (neat): 2921, 1733, 1618, 1512, 1464, 1352, 1232, 1035, 854, 781, 700 cm^{-1} .

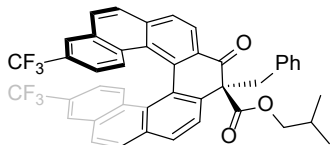


Retention Time	Area	% Area	Height
19.141	325559	1.49	10304
21.852	18882139	86.33	492845
25.228	2633258	12.04	54942
38.718	30189	0.14	606



Retention Time	Area	% Area	Height
19.245	7600030	46.82	228479
22.002	7548393	46.50	196027
25.376	535358	3.30	11244
38.850	549330	3.38	7801

isobutyl (*P*, *S*)-9-benzyl-3,16-bis(trifluoromethyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C11)



Following the typical procedure for the kinetic resolution.

(12 h 20 min) 36.0 mg, 50% yield; 12.0:1 dr., ee = 96%/91% ee, bright yellow oil; $R_f = 0.42$ (PE/EA = 9/1). $[\alpha]_D^{25} = 1116$ ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/ $\text{PrOH} = 90/10$, flow rate

1.0 mL/min, $\lambda = 243$ nm, retention time: $t(\text{major}_1) = 6.775$ min, $t(\text{minor}_1) = 6.349$ min, $t(\text{major}_2) = 8.037$ min, $t(\text{minor}_2) = 7.442$ min.

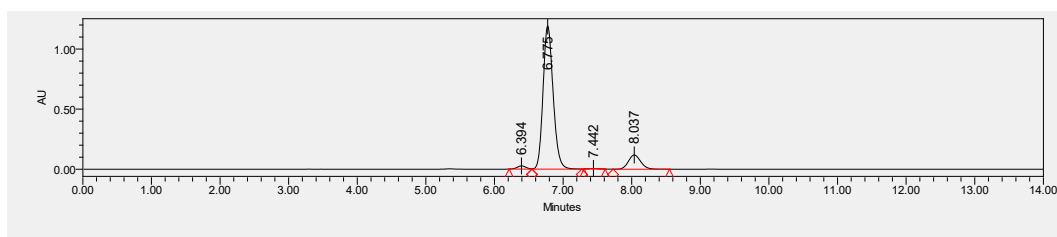
^1H NMR (600 MHz, CDCl_3) δ 8.34 (d, $J = 8.4$ Hz, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.89 – 7.86 (m, 2H), 7.62 – 7.59 (m, 2H), 7.47 (s, 1H), 7.45 (s, 1H), 7.43 (d, $J = 8.4$ Hz, 1H), 7.34 (d, $J = 8.4$ Hz, 1H), 6.94 – 6.86 (m, 5H), 6.60 (d, $J = 8.4$ Hz, 1H), 6.48 (d, $J = 8.4$ Hz, 1H), 6.42 (d, $J = 9.0$ Hz, 1H), 6.38 (d, $J = 8.4$ Hz, 1H), 4.43 (d, $J = 15.0$ Hz, 1H), 3.95 (d, $J = 15.0$ Hz, 1H), 3.80 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.72 (dd, $J = 10.8, 6.6$ Hz, 1H), 1.53 (septet, $J = 6.6$ Hz, 1H), 0.52 (d, $J = 6.6$ Hz, 3H), 0.47 (d, $J = 6.6$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.76, 169.89, 137.47, 137.27, 135.85, 134.09, 133.35, 131.14, 130.95, 130.81, 130.55, 130.16, 129.86, 129.19, 128.82, 128.79, 128.58, 128.38, 127.91, 127.12, 127.08, 126.84, 126.82, 126.30, 125.70, 125.52, 125.31, 123.82 (q, $J = 271.9$ Hz), 123.75 (q, $J = 3.0$ Hz), 123.76 (q, $J = 271.9$ Hz), 119.37 (q, $J = 3.0$ Hz), 118.89 (q, $J = 3.0$ Hz), 72.25, 63.38, 40.12, 27.50, 18.54, 18.49.

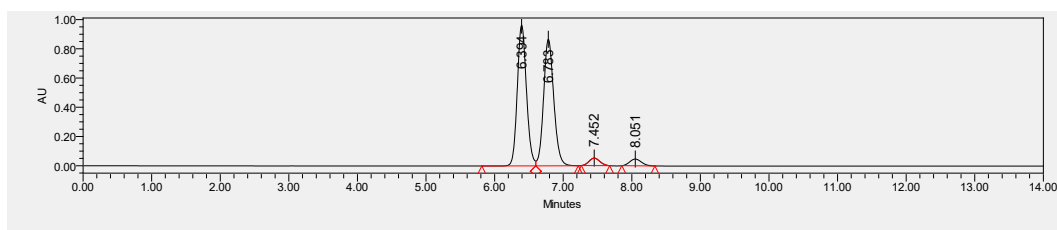
$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3) δ -62.96, -62.98.

ESI-HRMS: calcd for $\text{C}_{44}\text{H}_{30}\text{F}_6\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 743.1991, found 743.1995.

IR (neat): 2964, 1735, 1673, 1349, 1321, 1175, 1123, 1084, 901, 841, 729 cm^{-1} .

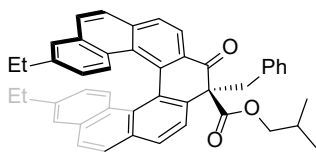


Retention Time	Area	% Area	Height
6.394	237302	1.70	26510
6.775	12176304	87.41	1191016
7.442	39964	0.29	4149
8.037	1476648	10.60	118471



Retention Time	Area	% Area	Height
6.394	8935666	47.07	963667
6.783	8932833	47.06	866535
7.452	562924	2.97	51395
8.051	550964	2.90	46274

isobutyl (*P*, *S*)-9-benzyl-3,16-diethyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C12)



Following the typical procedure for the kinetic resolution.

(5 h 45 min) 32 mg, 50% yield; 10.4:1 dr., ee = 96%/94% ee, bright yellow oil; R_f = 0.45 (PE/EA = 9/1).

$[\alpha]_D^{25} = 1344$ ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA-3** column), n-hexane/ i PrOH = 95/5, flow rate

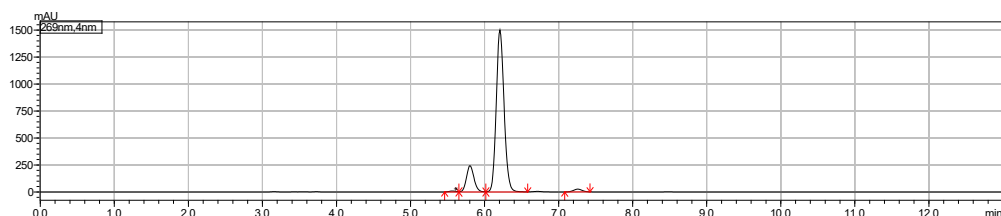
1.0 mL/min, $\lambda = 243$ nm, retention time: t (major₁) = 6.207 min, t (minor₁) = 7.257 min, t (major₂) = 5.803 min, t (minor₂) = 5.563 min.

^1H NMR (600 MHz, CDCl_3) δ 8.20 (d, $J = 7.8$ Hz, 1H), 7.84 (d, $J = 8.4$ Hz, 1H), 7.79 – 7.76 (m, 2H), 7.47 – 7.44 (m, 2H), 7.31 (d, $J = 8.4$ Hz, 1H), 7.22 (d, $J = 8.6$ Hz, 1H), 6.95 (s, 1H), 6.93 (s, 1H), 6.92 – 6.87 (m, 5H), 6.50 (d, $J = 8.4$ Hz, 1H), 6.31 (d, $J = 8.4$ Hz, 1H), 6.18 – 6.15 (m, 1H), 6.12 – 6.09 (m, 1H), 4.40 (d, $J = 15.6$ Hz, 1H), 3.96 (d, $J = 15.6$ Hz, 1H), 3.76 (dd, $J = 10.6, 6.6$ Hz, 1H), 3.66 (dd, $J = 10.6, 6.6$ Hz, 1H), 2.49 – 2.37 (m, 4H), 1.48 (septet, $J = 6.6$ Hz, 1H), 1.10 (t, $J = 7.8$ Hz, 3H), 1.08 (t, $J = 7.8$ Hz, 3H), 0.48 (d, $J = 6.6$ Hz, 3H), 0.43 (d, $J = 6.6$ Hz, 3H).

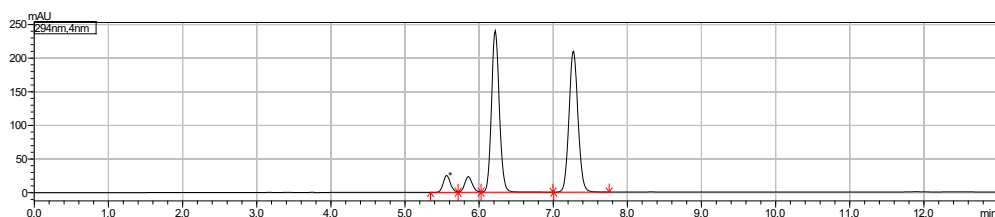
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.40, 170.39, 141.94, 141.60, 137.83, 136.64, 136.37, 132.56, 132.37, 132.02, 131.87, 130.53, 129.91, 129.58, 129.53, 129.46, 128.36, 128.03, 127.83, 127.27, 126.94, 126.03, 125.43, 125.41, 125.26, 125.12, 125.06, 124.71, 124.26, 123.75, 123.61, 72.03, 63.20, 39.83, 28.67, 28.65, 27.47, 18.56, 18.51, 15.71.

ESI-HRMS: calcd for $\text{C}_{46}\text{H}_{40}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 663.2869, found 663.2867.

IR (neat): 2952, 2927, 1735, 1667, 1456, 1272, 1208, 883, 838, 701 cm^{-1} .

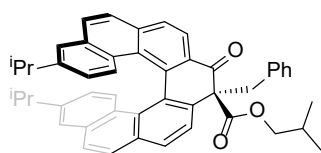


Retention Time	Area	% Area	Height
5.563	50472	0.47	74964
5.803	1416052	13.28	200708
6.207	9014037	84.52	1223627
7.257	184507	1.73	21656



Retention Time	Area	% Area	Height
5.561	169908	4.39	24892
5.854	166100	4.29	23313
6.217	1766630	45.62	240147
7.271	1769451	45.70	209428

isobutyl (*P, S*)-9-benzyl-3,16-diisopropyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C13)



Following the typical procedure for the kinetic resolution.

(5 h 30 min) 31.4 mg, 47% yield; 11.3:1 dr., ee = 96%/93% ee, bright yellow oil; R_f = 0.45 (PE/EA = 9/1). $[\alpha]_D^{25} = 1221$ ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

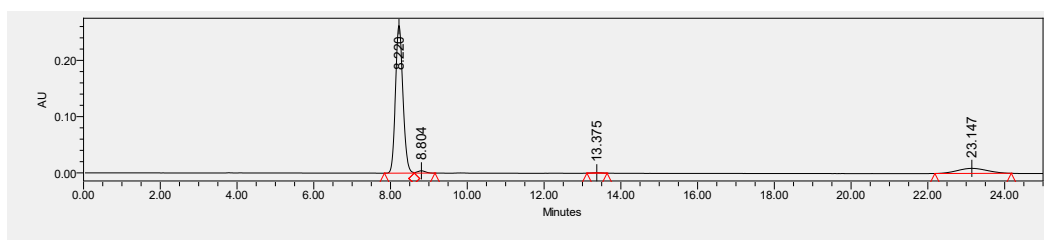
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major₁) = 8.220 min, t (minor₁) = 8.804 min, t (major₂) = 23.147 min, t (minor₂) = 13.375 min.

^1H NMR (600 MHz, CDCl_3) δ 8.21 (d, $J = 8.4$ Hz, 1H), 7.84 (d, $J = 7.8$ Hz, 1H), 7.79 – 7.75 (m, 2H), 7.47 – 7.45 (m, 2H), 7.31 (d, $J = 8.4$ Hz, 1H), 7.22 (d, $J = 9.0$ Hz, 1H), 6.94 (s, 1H), 6.93 (s, 1H), 6.91 – 6.86 (m, 5H), 6.50 (d, $J = 8.4$ Hz, 1H), 6.31 (d, $J = 9.0$ Hz, 1H), 6.18 (d, $J = 8.4$ Hz, 1H), 6.12 (d, $J = 9.0$ Hz, 1H), 4.40 (d, $J = 15.6$ Hz, 1H), 3.96 (d, $J = 15.6$ Hz, 1H), 3.77 (dd, $J = 10.2, 6.0$ Hz, 1H), 3.67 (dd, $J = 10.2, 6.0$ Hz, 1H), 2.74 – 2.64 (m, 2H), 1.49 (septet, $J = 6.6$ Hz, 1H), 1.16 – 1.07 (m, 12H), 0.48 (d, $J = 6.6$ Hz, 3H), 0.43 (d, $J = 6.6$ Hz, 3H).

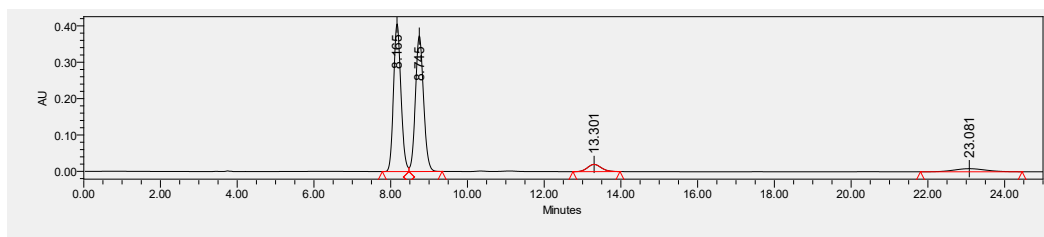
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.44, 170.39, 146.27, 145.93, 137.78, 136.65, 136.35, 132.70, 132.38, 131.89, 131.75, 130.45, 129.89, 129.80, 129.61, 129.55, 129.44, 128.36, 128.01, 127.83, 127.47, 127.09, 126.03, 125.41, 125.39, 125.08, 124.97, 123.66, 123.08, 123.06, 122.71, 122.17, 72.02, 63.13, 39.94, 33.74, 33.72, 27.47, 23.76, 23.74, 23.42, 18.57, 18.52.

ESI-HRMS: calcd for $\text{C}_{48}\text{H}_{44}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 691.3183, found 691.3182.

IR (neat): 2959, 1736, 1667, 1459, 1271, 1209, 883, 839, 755, 700 cm^{-1} .

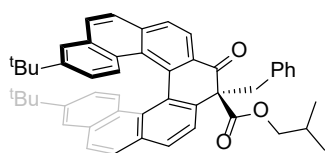


Retention Time	Area	% Area	Height
8.220	3521143	86.84	261948
8.804	42155	1.04	3418
13.375	11474	0.28	635
23.147	479965	11.84	8910



Retention Time	Area	% Area	Height
8.165	5470943	45.95	405292
8.745	5467532	45.92	372498
13.301	482674	4.05	19608
23.081	485951	4.08	8494

isobutyl (*P,S*)-9-benzyl-3,16-di-*tert*-butyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C14)



Following the typical procedure for the kinetic resolution.

(5 h 40 min) 34.2 mg, 49% yield; 12.9:1 dr., ee = 97%/93% ee, bright yellow oil; R_f = 0.49 (PE/EA = 9/1). $[\alpha]^{25}_D$ = 1373 ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

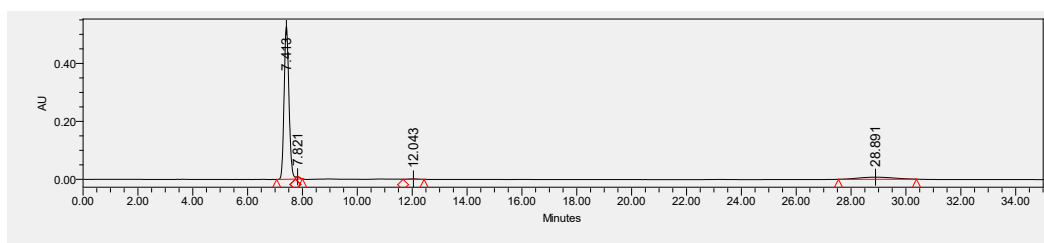
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/ PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 7.413 min, t (minor₁) = 7.821 min, t (major₂) = 28.891 min, t (minor₂) = 12.043 min.

^1H NMR (600 MHz, CDCl_3) δ 8.22 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.79 – 7.76 (m, 2H), 7.48 – 7.46 (m, 2H), 7.31 (d, J = 9.0 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.06 (d, J = 1.2 Hz, 1H), 7.04 (d, J = 1.2 Hz, 1H), 6.92 – 6.86 (m, 5H), 6.51 (d, J = 9.0 Hz, 1H), 6.35 – 6.31 (m, 2H), 6.28 (dd, J = 8.4, 1.2 Hz, 1H), 4.41 (d, J = 15.0 Hz, 1H), 3.97 (d, J = 15.0 Hz, 1H), 3.77 (dd, J = 10.8, 6.6 Hz, 1H), 3.68 (dd, J = 10.8, 6.6 Hz, 1H), 1.49 (septet, J = 6.6 Hz, 1H), 1.19 (s, 9H), 1.18 (s, 9H), 0.48 (d, J = 6.6 Hz, 3H), 0.43 (d, J = 6.6 Hz, 3H).

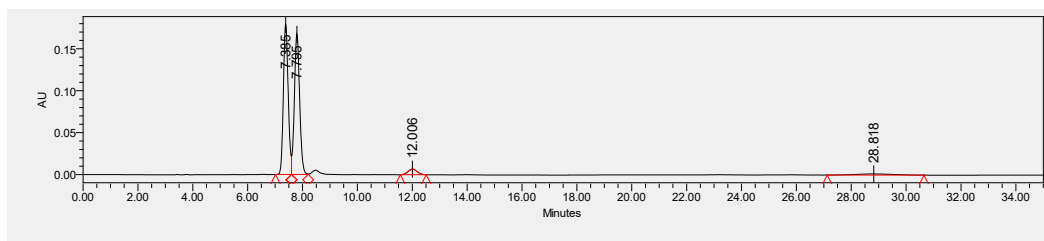
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.48, 170.39, 148.38, 148.03, 137.75, 136.74, 136.33, 132.80, 132.46, 131.59, 131.45, 130.40, 129.91, 129.89, 129.65, 129.55, 129.28, 128.38, 128.02, 127.82, 127.58, 127.40, 127.02, 126.04, 125.36, 125.34, 125.13, 124.69, 124.57, 123.72, 121.90, 121.69, 121.18, 72.01, 63.09, 40.03, 34.28, 34.23, 30.94, 30.92, 30.88, 27.48, 18.57, 18.53.

ESI-HRMS: calcd for $\text{C}_{50}\text{H}_{48}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 719.3496, found 719.3495.

IR (neat): 2985, 1734, 1667, 1594, 1459, 1272, 1207, 911, 838, 731, 700 cm^{-1} .

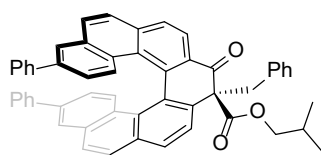


Retention Time	Area	% Area	Height
7.413	6466012	89.54	526647
7.821	78899	1.09	7715
12.043	40047	0.55	1634
28.891	636713	8.82	7212



Retention Time	Area	% Area	Height
7.385	2254295	48.19	179243
7.795	2165428	46.29	167448
12.006	128383	2.74	6157
28.818	129824	2.78	1345

isobutyl (*P,S*)-9-benzyl-10-oxo-3,16-diphenyl-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C15)



Following the typical procedure for the kinetic resolution.

(8 h 5 min) 33.2 mg, 45% yield; 11.2:1 dr., ee = 97%/97% ee, bright yellow oil; R_f = 0.38 (PE/EA = 9/1). $[\alpha]_D^{25} = 1133$ ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/PrOH = 90/10, flow rate

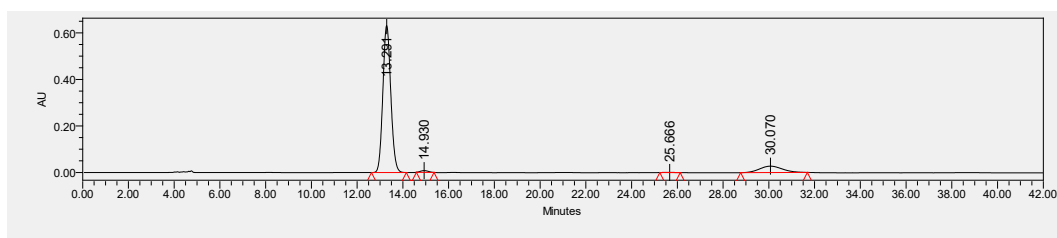
1.0 mL/min, $\lambda = 243$ nm, retention time: $t(\text{major}_1) = 13.291$ min, $t(\text{minor}_1) = 14.930$ min, $t(\text{major}_2) = 25.666$ min, $t(\text{minor}_2) = 30.070$ min.

^1H NMR (600 MHz, CDCl_3) δ 8.27 (d, $J = 8.4$ Hz, 1H), 7.91 (d, $J = 8.4$ Hz, 1H), 7.85 – 7.82 (m, 2H), 7.55 – 7.53 (m, 2H), 7.44 – 7.35 (m, 10H), 7.34 – 7.31 (m, 4H), 6.95 – 6.87 (m, 5H), 6.68 (d, $J = 8.4$ Hz, 1H), 6.59 (d, $J = 8.4$ Hz, 1H), 6.53 (dd, $J = 9.0, 0.6$ Hz, 1H), 6.47 (d, $J = 8.4$ Hz, 1H), 4.43 (d, $J = 15.0$ Hz, 1H), 3.99 (d, $J = 15.0$ Hz, 1H), 3.79 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.69 (dd, $J = 10.8, 6.6$ Hz, 1H), 1.52 (septet, $J = 6.6$ Hz, 1H), 0.51 (d, $J = 6.6$ Hz, 3H), 0.45 (d, $J = 6.6$ Hz, 3H).

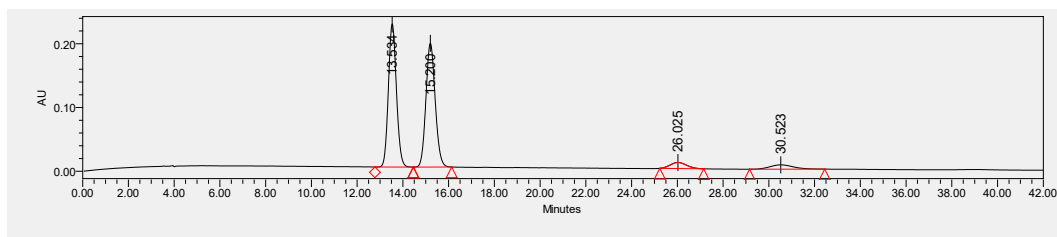
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.24, 170.29, 140.73, 140.62, 138.48, 138.16, 137.84, 136.99, 136.28, 133.04, 132.75, 132.11, 131.96, 130.59, 129.94, 129.76, 129.68, 129.42, 128.79, 128.75, 128.72, 128.57, 128.27, 128.25, 128.19, 127.90, 127.37, 127.28, 127.22, 127.08, 127.05, 126.14, 125.98, 125.94, 125.78, 125.60, 124.40, 124.37, 124.12, 123.08, 122.58, 72.13, 63.33, 39.90, 27.51, 18.60, 18.55.

ESI-HRMS: calcd for $\text{C}_{34}\text{H}_{40}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 759.2870, found 759.2867.

IR (neat): 2961, 1734, 1668, 1594, 1492, 1450, 1275, 1209, 909, 839, 757, 732, 697 cm^{-1} .

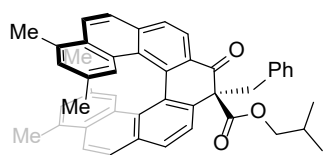


Retention Time	Area	% Area	Height
13.291	15218251	87.76	631559
14.930	181570	1.05	7622
25.666	23547	0.14	724
30.070	1917703	11.06	27555



Retention Time	Area	% Area	Height
13.534	5483295	46.03	224316
15.200	5474998	45.96	194095
26.025	473368	3.97	9498
30.523	480853	4.04	6732

isobutyl (*P,S*)-9-benzyl-2,4,15,17-tetramethyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C16)



Following the typical procedure for the kinetic resolution.

(9 h 20 min) 35.9 mg, 56% yield; 6.1:1 dr., ee = 96%/97% ee, bright yellow oil; R_f = 0.42 (PE/EA = 9/1). $[\alpha]_D^{25} = 851$ ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/PrOH = 90/10, flow rate

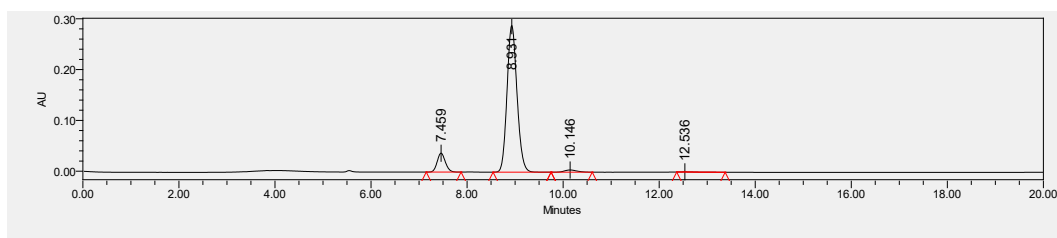
1.0 mL/min, $\lambda = 243$ nm, retention time: t (major₁) = 8.931 min, t (minor₁) = 7.459 min, t (major₂) = 10.146 min, t (minor₂) = 12.536 min.

^1H NMR (600 MHz, CDCl_3) δ 8.21 (d, $J = 8.4$ Hz, 1H), 7.84 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.77 (d, $J = 8.4$ Hz, 1H), 7.50 (d, $J = 8.4$ Hz, 1H), 7.42 – 7.40 (m, 3H), 6.91 – 6.84 (m, 5H), 6.60 (s, 1H), 6.56 (s, 1H), 6.15 (s, 1H), 5.92 (s, 1H), 4.42 (d, $J = 15.0$ Hz, 1H), 3.95 (d, $J = 15.0$ Hz, 1H), 3.85 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.65 (dd, $J = 10.8, 6.6$ Hz, 1H), 2.32 (s, 3H), 2.31 (s, 3H), 1.69 (s, 3H), 1.65 (s, 3H), 1.53 (septet, $J = 6.6$ Hz, 1H), 0.52 (d, $J = 6.6$ Hz, 3H), 0.47 (d, $J = 6.6$ Hz, 3H).

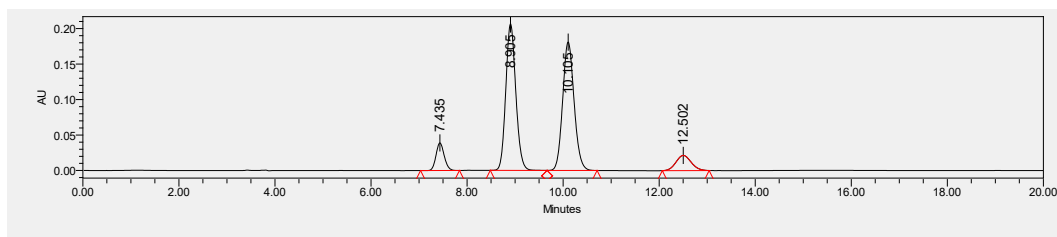
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.29, 170.42, 138.67, 136.54, 136.33, 132.90, 132.45, 132.30, 130.95, 130.17, 130.11, 129.93, 129.75, 129.12, 128.97, 128.60, 128.56, 128.33, 128.27, 127.96, 127.81, 127.77, 127.39, 127.31, 126.01, 125.50, 125.37, 125.34, 125.15, 124.19, 124.15, 123.72, 122.72, 72.00, 63.17, 40.17, 27.51, 21.09, 21.00, 19.20, 19.12, 18.67, 18.58.

ESI-HRMS: calcd for $\text{C}_{46}\text{H}_{40}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 663.2869, found 663.2866.

IR (neat): 2924, 1735, 1666, 1457, 1379, 1285, 1208, 1038. 862, 700 cm^{-1} .

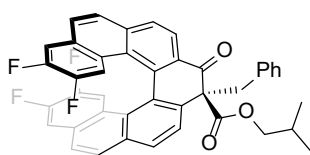


Retention Time	Area	% Area	Height
7.459	439746	9.38	37181
8.931	4162809	88.83	288314
10.146	77506	1.65	4354
12.536	6171	0.13	343



Retention Time	Area	% Area	Height
7.435	464372	6.71	38920
8.905	2994831	43.24	206329
10.105	2996518	43.27	180942
12.502	469749	6.78	21367

isobutyl (*P,S*)-9-benzyl-2,3,16,17-tetrafluoro-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (C17)



Following the typical procedure for the kinetic resolution.

(12 h 30 min) 29.6 mg, 45% yield; 11.8:1 dr., ee = 97%/95% ee, bright yellow oil; R_f = 0.4 (PE/EA = 9/1). $[\alpha]_D^{25} = 937$ ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

Dissolved in n-Hexane for HPLC; **HPLC** (Chiralcel **IK** column), Dissolved in n-hexane for HPLC;

HPLC (Chiralcel **IA** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major₁) = 9.418 min, t (minor₁) = 8.771 min, t (major₂) = 7.633 min, t (minor₂) = 7.269 min.

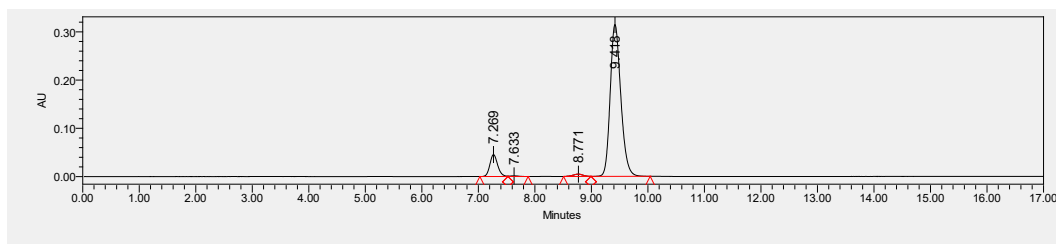
^1H NMR (600 MHz, CDCl_3) δ 8.28 (d, $J = 7.8$ Hz, 1H), 7.93 (d, $J = 7.8$ Hz, 1H), 7.90 (d, $J = 7.8$ Hz, 2H), 7.61 – 7.57 (m, 2H), 7.42 (d, $J = 8.4$ Hz, 1H), 7.32 (d, $J = 9.0$ Hz, 1H), 7.10 – 7.04 (m, 2H), 6.95 – 6.92 (m, 5H), 6.31 (dd, $J = 12.6$, 7.8 Hz, 1H), 6.08 (dd, $J = 13.2$, 8.4 Hz, 1H), 4.42 (d, $J = 15.0$ Hz, 1H), 3.95 (d, $J = 15.0$ Hz, 1H), 3.76 (dd, $J = 10.2$, 6.0 Hz, 1H), 3.67 (dd, $J = 10.2$, 6.0 Hz, 1H), 1.50 (septet, $J = 6.6$ Hz, 1H), 0.52 (d, $J = 6.6$ Hz, 3H), 0.47 (d, $J = 6.6$ Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.60, 169.77, 149.14 (dd, $J = 246.1$, 14.7 Hz), 149.14 (dd, $J = 251.7$, 14.9 Hz), 149.14 (dd, $J = 249.6$, 14.4 Hz), 149.14 (dd, $J = 248.4$, 14.5 Hz), 136.64, 136.58, 136.02, 133.48, 132.43, 130.07, 129.87, 129.68, 129.19, 129.14, 129.07, 129.03, 128.96, 128.49 (dd, $J = 40.5$, 2.9 Hz), 128.18, 127.95, 127.31, 126.45, 126.32, 126.26, 126.06 (dd, $J = 7.1$, 1.7 Hz), 125.81 (d, $J = 2.3$ Hz), 125.43 (dd, $J = 6.9$, 1.7 Hz), 124.66, 113.63 (dd, $J = 19.6$, 4.5 Hz), 113.23 (dd, $J = 16.8$, 8.9 Hz), 72.26, 63.61, 39.40, 29.73, 27.48, 18.56, 18.50.

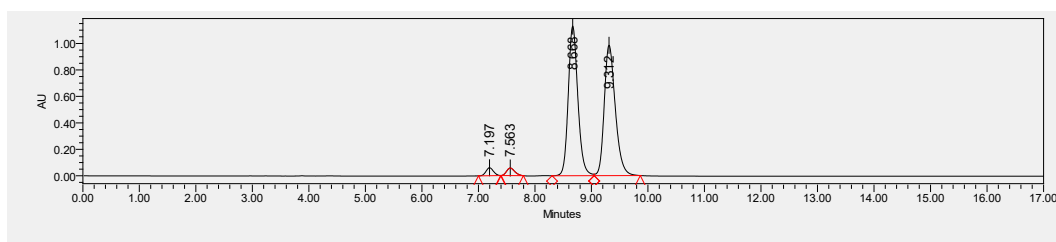
$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3) δ -136.81 (d, $J = 22.6$ Hz), -137.44 (d, $J = 22.6$ Hz), -138.56 (d, $J = 22.6$ Hz), -139.57 (d, $J = 22.6$ Hz).

ESI-HRMS: calcd for $\text{C}_{42}\text{H}_{28}\text{F}_4\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 679.1867, found 679.1865.

IR (neat): 2962, 1734, 1675, 1522, 1457, 1271, 1209, 1192, 895, 734 cm^{-1} .

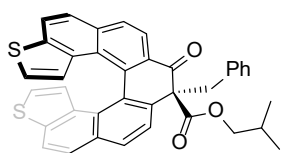


Retention Time	Area	% Area	Height
7.269	437050	9.54	45562
7.633	15883	0.35	1479
8.771	40154	0.88	3904
9.418	4089922	89.24	314383



Retention Time	Area	% Area	Height
7.197	548620	1.97	60062
7.563	574275	2.06	57182
8.668	13345492	47.95	1130418
9.312	13366180	48.02	984835

isobutyl (*P,S*)-8-benzyl-9-oxo-8,9-dihydrobenzo[*b*]thieno[5,4-*c*:4,5-*c'*]phenanthrene-8-carboxylate (C18)



Following the typical procedure for the kinetic resolution.

(3 h) 29.8 mg, 50% yield; 14.2:1 dr., ee = 97%/95% ee, bright yellow oil; R_f = 0.4 (PE/EA = 9/1). $[\alpha]_D^{25}$ = 803 ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

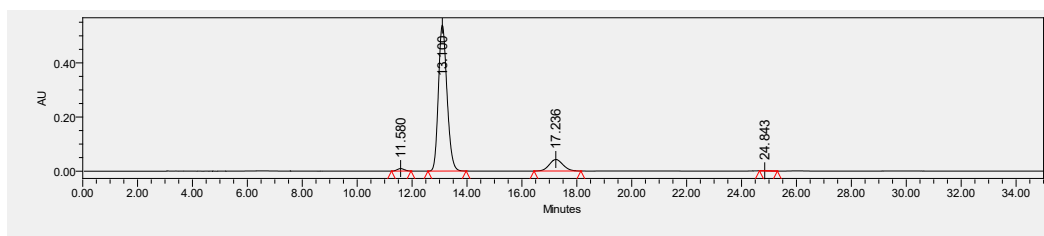
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 11.041 min, t (minor₁) = 10.232 min, t (major₂) = 12.836 min, t (minor₂) = 17.657 min.

^1H NMR (600 MHz, CDCl_3) δ 8.15 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.70 – 7.67 (m, 2H), 7.65 (d, J = 8.4 Hz, 1H), 6.97 – 6.92 (m, 5H), 6.59 (d, J = 5.4 Hz, 1H), 6.52 (d, J = 6.0 Hz, 1H), 5.84 (d, J = 5.4 Hz, 1H), 5.70 (d, J = 6.0 Hz, 1H), 4.36 (d, J = 15.6 Hz, 1H), 3.98 (d, J = 15.6 Hz, 1H), 3.63 (dd, J = 10.8, 6.6 Hz, 1H), 3.55 (dd, J = 10.8, 6.6 Hz, 1H), 1.38 (septet, J = 6.6 Hz, 1H), 0.41 (d, J = 6.6 Hz, 3H), 0.37 (d, J = 6.6 Hz, 3H).

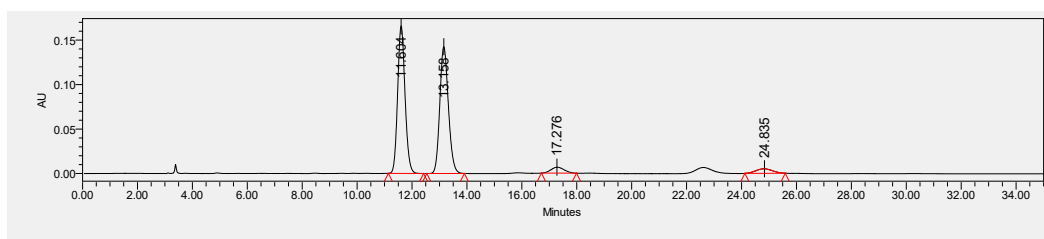
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.56, 170.01, 138.98, 136.55, 136.49, 135.32, 134.90, 133.92, 132.38, 131.39, 130.16, 129.83, 129.60, 129.26, 129.08, 128.48, 128.28, 127.93, 126.01, 124.62, 124.60, 124.32, 124.20, 123.52, 123.38, 122.54, 122.16, 121.32, 72.06, 63.75, 38.55, 27.37, 18.50, 18.44.

ESI-HRMS: calcd for $\text{C}_{38}\text{H}_{28}\text{O}_3\text{S}_2\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 619.1372, found 619.1377.

IR (neat): 2962, 1734, 1675, 1522, 1457, 1271, 1209, 1192, 895, 734 cm^{-1} .

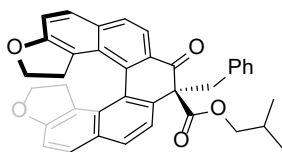


Retention Time	Area	% Area	Height
11.580	166573	1.24	9262
13.100	11730025	87.63	539107
17.236	1483684	11.08	42564
24.843	5251	0.04	272



Retention Time	Area	% Area	Height
11.604	3101228	46.75	165650
13.158	3095732	46.66	142480
17.276	224201	3.38	6664
24.835	213027	3.21	5137

isobutyl (*P,S*)-8-benzyl-9-oxo-1,2,8,9,15,16-hexahydrobenzo[*b*]furo[5,4-*c*:4,5-*c'*]phenanthrene-8-carboxylate (C19)



Following the typical procedure for the kinetic resolution.

(2 h 40 min) 25.6 mg, 45% yield; 21:1 dr., ee = 98%/98% ee, bright orange oil; R_f = 0.55 (PE/EA = 9/1).

$[\alpha]_D^{25} = 523$ ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

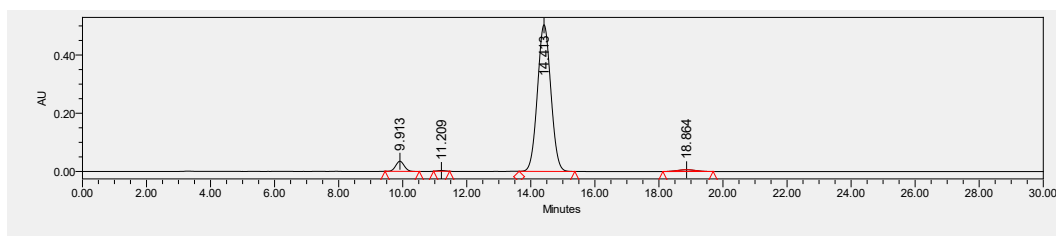
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **AD-H** column), n-hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major₁) = 14.413 min, t (minor₁) = 18.864 min, t (major₂) = 9.913 min, t (minor₂) = 11.233 min.

^1H NMR (600 MHz, CDCl_3) δ 7.83 – 7.78 (m, 3H), 7.73 (d, $J = 9.0$ Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.59 (d, $J = 8.4$ Hz, 1H), 7.19 (d, $J = 8.4$ Hz, 1H), 7.11 (d, $J = 9.0$ Hz, 1H), 6.97 – 6.96 (m, 3H), 6.89 – 6.88 (m, 2H), 4.22 – 4.14 (m, 3H), 3.97 – 3.90 (m, 2H), 3.88 (d, $J = 15.6$ Hz, 1H), 3.62 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.52 (dd, $J = 10.8, 6.6$ Hz, 1H), 1.83 (ddd, $J = 15.6, 9.6, 5.4$ Hz, 1H), 1.69 – 1.62 (m, 2H), 1.59 – 1.54 (m, 1H), 1.40 (septet, $J = 6.6$ Hz, 1H), 0.43 (d, $J = 6.6$ Hz, 3H), 0.41 (d, $J = 6.6$ Hz, 3H).

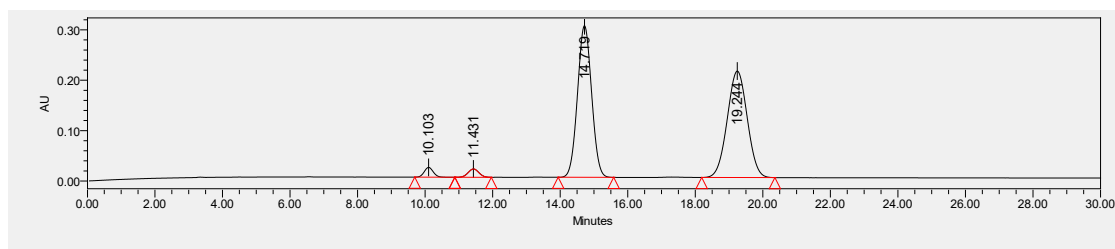
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 195.12, 169.96, 159.38, 159.29, 136.58, 132.92, 132.80, 131.30, 131.22, 130.62, 129.87, 129.83, 129.77, 129.35, 129.05, 128.95, 128.83, 127.79, 125.97, 121.31, 119.57, 118.99, 117.80, 114.78, 112.83, 71.90, 71.82, 71.72, 64.10, 38.45, 31.25, 31.15, 27.43, 18.45, 18.41.

ESI-HRMS: calcd for $\text{C}_{38}\text{H}_{32}\text{O}_5\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 591.2142, found 591.2144.

IR (neat): 2962, 1734, 1675, 1522, 1457, 1271, 1209, 1192, 895, 734 cm^{-1} .

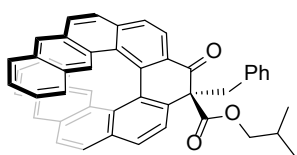


Retention Time	Area	% Area	Height
9.913	644857	4.16	34853
11.233	18428	0.12	1451
14.413	14595722	94.19	503990
18.864	236589	1.53	6034



Retention Time	Area	% Area	Height
10.103	359249	1.98	19364
11.431	365921	2.02	16501
14.719	8726810	48.12	300891
19.244	8682691	47.88	211243

isobutyl (*P, S*)-1-benzyl-2-oxo-1,2-dihydrobenzo[2,1-*a*:3,4-*a'*]ditetraphene-1-carboxylate (C20)



Following the typical procedure for the kinetic resolution.

(13 h) 33.5 mg, 49% yield; 8.4:1 dr., ee = 97%/95% ee, bright yellow oil; R_f = 0.38 (PE/EA = 9/1). $[\alpha]^{25}_D$ = 751 ($c = 7.0 \times 10^{-2}$, in CH_2Cl_2).

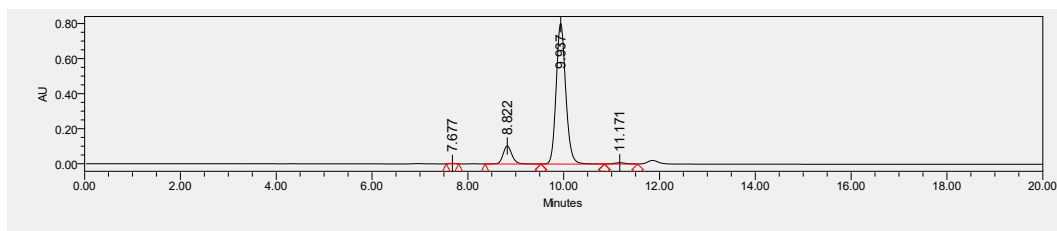
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 9.937 min, t (minor₁) = 11.171 min, t (major₂) = 8.822 min, t (minor₂) = 7.677 min.

^1H NMR (600 MHz, CDCl_3) δ 8.31 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 7.8 Hz, 2H), 7.60 (d, J = 8.2 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.41 (d, J = 6.2 Hz, 2H), 7.38 (s, 1H), 7.31 (t, J = 7.4 Hz, 1H), 7.27 (d, J = 7.4 Hz, 1H), 7.22 (t, J = 7.4 Hz, 1H), 7.17 (dd, J = 9.2, 5.8 Hz, 4H), 7.08 (d, J = 8.4 Hz, 1H), 7.03 – 6.99 (m, 3H), 6.97 (t, J = 7.6 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.8 Hz, 1H), 4.45 (d, J = 15.6 Hz, 1H), 4.01 (d, J = 15.6 Hz, 1H), 3.83 (dd, J = 10.8, 6.6 Hz, 1H), 3.66 (dd, J = 10.8, 6.6 Hz, 1H), 1.53 (septet, J = 6.6 Hz, 1H), 0.54 (d, J = 6.6 Hz, 3H), 0.48 (d, J = 6.6 Hz, 3H).

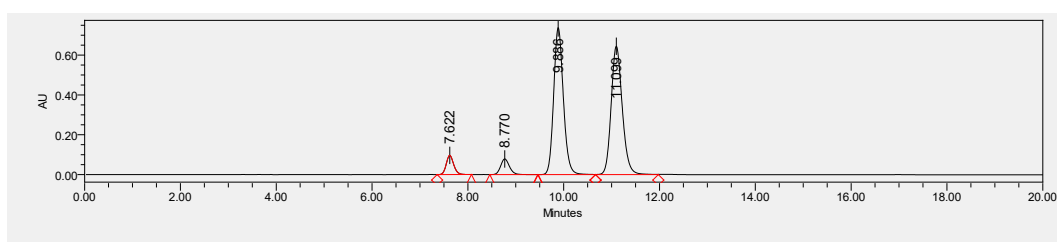
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.13, 170.33, 137.76, 137.43, 136.44, 132.84, 132.58, 131.30, 131.20, 131.15, 130.28, 129.99, 129.93, 129.89, 129.73, 129.68, 129.58, 129.39, 128.41, 128.25, 128.09, 127.94, 127.03, 126.94, 126.91, 126.83, 126.41, 126.09, 126.01, 125.70, 125.53, 125.41, 125.37, 125.22, 125.03, 124.76, 124.66, 124.38, 72.13, 63.40, 39.49, 27.51, 18.67, 18.58.

ESI-HRMS: calcd for $\text{C}_{50}\text{H}_{36}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 707.2557, found 707.2554.

IR (neat): 3051, 2961, 1730, 1667, 1507, 1266, 1205, 839, 737 cm^{-1} .

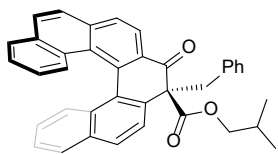


Retention Time	Area	% Area	Height
7.677	23814	0.19	2804
8.822	1333140	10.56	102895
9.937	11137590	88.25	801729
11.171	126515	1.00	7506



Retention Time	Area	% Area	Height
7.622	1041021	4.56	96396
8.770	1008361	4.41	78655
9.886	10389454	45.47	737877
11.099	10411672	45.56	644901

isobutyl (*P,S*)-3-benzyl-4-oxo-3,4-dihydrohexahelicene-3-carboxylate (C21)



Following the typical procedure for the kinetic resolution.

(2 h 10 min) 23 mg, 43% yield; >19:1 dr., ee = 93% ee, bright yellow oil; R_f = 0.54 (PE/DCM = 1/1). $[\alpha]^{25}_D$ = 654 ($c = 5.3 \times 10^{-2}$, in CH_2Cl_2).

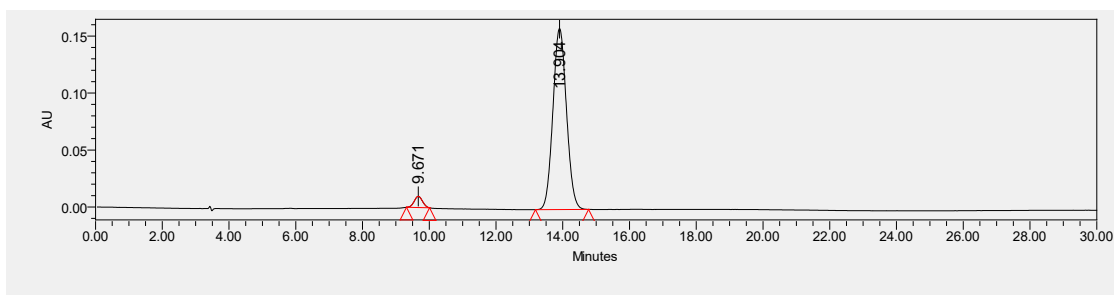
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major) = 13.904 min, t (minor) = 9.671 min.

^1H NMR (600 MHz, CDCl_3) δ 8.15 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.85 – 7.81 (m, 3H), 7.76 (d, J = 8.8 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.16 (t, J = 7.4 Hz, 1H), 7.08 – 7.01 (m, 5H), 6.85 (d, J = 8.8 Hz, 1H), 6.67 (t, J = 7.8 Hz, 2H), 4.26 (d, J = 15.8 Hz, 1H), 4.07 (d, J = 15.8 Hz, 1H), 3.61 (dd, J = 10.8, 6.6 Hz, 1H), 3.51 (dd, J = 10.8, 6.6 Hz, 1H), 1.45 – 1.39 (m, 1H), 0.46 (d, J = 6.8 Hz, 3H), 0.41 (d, J = 6.8 Hz, 3H).

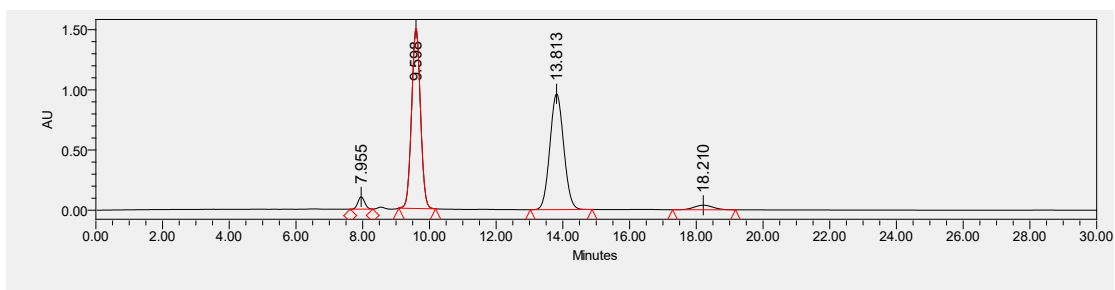
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.31, 170.23, 136.83, 136.52, 135.44, 133.25, 132.90, 132.28, 131.24, 130.47, 130.03, 129.86, 129.78, 129.55, 129.09, 129.02, 128.64, 128.30, 128.01, 127.83, 127.62, 126.66, 126.30, 126.04, 126.02, 125.63, 125.49, 124.86, 124.69, 123.89, 72.09, 63.93, 37.34, 27.35, 18.55, 18.48.

ESI-HRMS: calcd for $\text{C}_{38}\text{H}_{31}\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) = 535.2268, found 535.2269.

IR (neat): 2961, 1731, 1704, 1508, 1206, 854, 819 cm^{-1} .

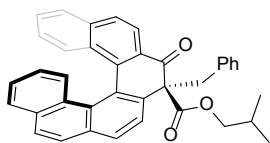


Retention Time	Area	% Area	Height
9.671	170518	3.67	9835
13.904	4477853	96.33	158885



Retention Time	Area	% Area	Height
7.955	1448335	2.49	102221
9.598	27598220	47.43	1493856
13.813	27636961	47.49	961047
18.210	1508004	2.59	37993

isobutyl (*M,S*)-4-benzyl-3-oxo-3,4-dihydrohexahelicene-4-carboxylate (C21')



Following the typical procedure for the kinetic resolution.

(2 h 10 min) 2.7 mg, 5% yield; >19:1 dr., ee = 99% ee, light yellow oil; R_f = 0.44 (PE/DCM = 1/1). $[\alpha]_D^{25} = -663$ ($c = 5.3 \times 10^{-2}$, in CH_2Cl_2).

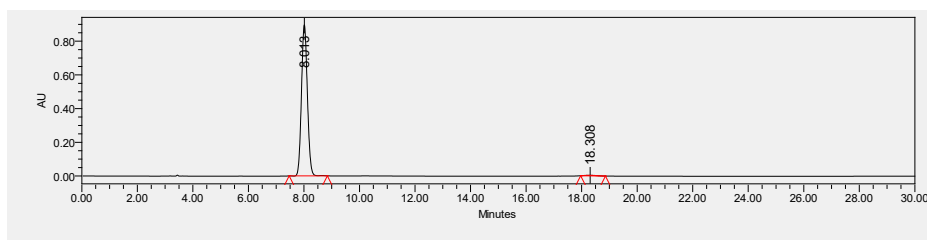
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major) = 18.308 min, t (minor) = 8.013 min.

^1H NMR (600 MHz, CDCl_3) δ 7.97 – 7.93 (m, 2H), 7.79 – 7.72 (m, 3H), 7.70 (s, 1H), 7.60 (d, $J = 8.2$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.19 – 7.13 (m, 2H), 7.01 (d, $J = 8.6$ Hz, 1H), 6.62 (d, $J = 8.6$ Hz, 1H), 6.58 – 6.52 (m, 2H), 6.35 – 6.28 (m, 4H), 6.17 (t, $J = 7.0$ Hz, 1H), 4.02 (dd, $J = 10.6, 6.8$ Hz, 1H), 3.93 (dd, $J = 10.6, 6.9$ Hz, 1H), 3.64 (d, $J = 13.6$ Hz, 1H), 3.50 (d, $J = 13.6$ Hz, 1H), 1.84 (sept, $J = 6.8$ Hz, 1H), 0.71 (dd, $J = 8.8, 6.8$ Hz, 6H).

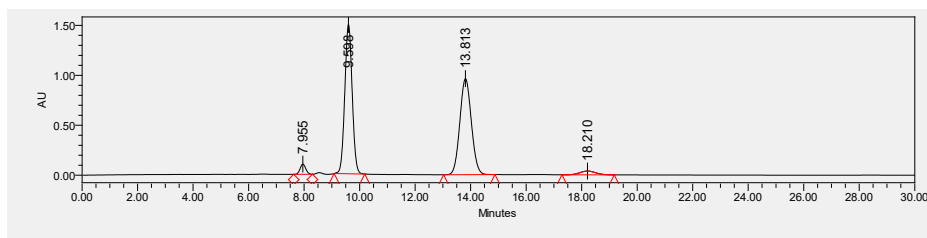
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 197.23, 172.12, 139.79, 136.25, 134.47, 132.44, 132.09, 129.92, 129.63, 129.26, 128.98, 128.96, 128.87, 128.79, 128.43, 127.96, 127.74, 127.66, 127.59, 127.47, 126.66, 126.28, 126.22, 125.67, 125.07, 124.66, 124.01, 121.96, 72.00, 66.04, 45.76, 27.61, 18.95.

ESI-HRMS: calcd for $\text{C}_{38}\text{H}_{31}\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) = 535.2268, found 535.2271.

IR (neat): 2925, 1739, 1673, 1495, 1225, 1039, 836 cm^{-1} .

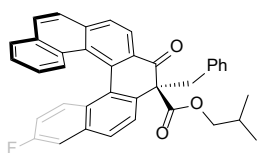


Retention Time	Area	% Area	Height
8.013	13226398	99.30	895823
18.308	92952	0.70	3209



Retention Time	Area	% Area	Height
7.955	1448335	2.49	102221
9.598	27598220	47.43	1493856
13.813	27636961	47.49	961047
18.210	1508004	2.59	37993

isobutyl (*P,S*)-3-benzyl-15-fluoro-4-oxo-3,4-dihydrohexahelicene-3-carboxylate (C22)



Following the typical procedure for the kinetic resolution.

(2 h 50 min) 27 mg, 49% yield; >19:1 dr., ee = 94% ee, light yellow oil; R_f = 0.60 (PE/DCM = 1/1). $[\alpha]_D^{25}$ = 513 ($c = 5.5 \times 10^{-2}$, in CH_2Cl_2).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/ PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major) = 18.308 min, t (minor) = 8.013 min.

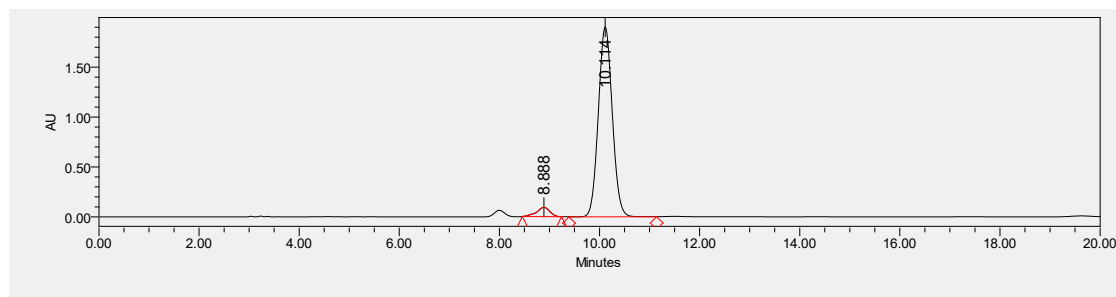
^1H NMR (600 MHz, CDCl_3) δ 8.16 (d, J = 7.8 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 8.6 Hz, 2H), 7.75 (t, J = 8.4 Hz, 3H), 7.31 – 7.27 (m, 2H), 7.27 – 7.25 (m, 1H), 7.09 – 7.00 (m, 5H), 6.84 (dd, J = 9.4, 5.4 Hz, 1H), 6.72 (t, J = 7.8 Hz, 1H), 6.44 (ddd, J = 9.4, 8.2, 2.6 Hz, 1H), 4.26 (d, J = 15.8 Hz, 1H), 4.06 (d, J = 15.8 Hz, 1H), 3.61 (dd, J = 10.8, 6.6 Hz, 1H), 3.51 (dd, J = 10.8, 6.6 Hz, 1H), 1.42 (sept, 6.6 Hz, 1H), 0.46 (d, J = 6.6 Hz, 3H), 0.41 (d, J = 6.6 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.09, 170.13, 160.18, 159.36 (d, J = 262.7 Hz), 136.64 (d, J = 21.1 Hz), 135.06, 134.26 (d, J = 9.1 Hz), 133.18, 132.37, 131.27, 130.16, 130.13, 129.75, 129.42, 129.26, 128.87, 128.79, 128.73, 128.34, 128.23, 128.20, 128.04, 127.75, 126.86, 126.29, 126.15, 126.09, 125.96, 125.05, 123.96, 115.64 (d, J = 24.2 Hz), 110.77 (d, J = 19.6 Hz), 72.14, 63.81, 37.34, 27.35, 18.54, 18.48.

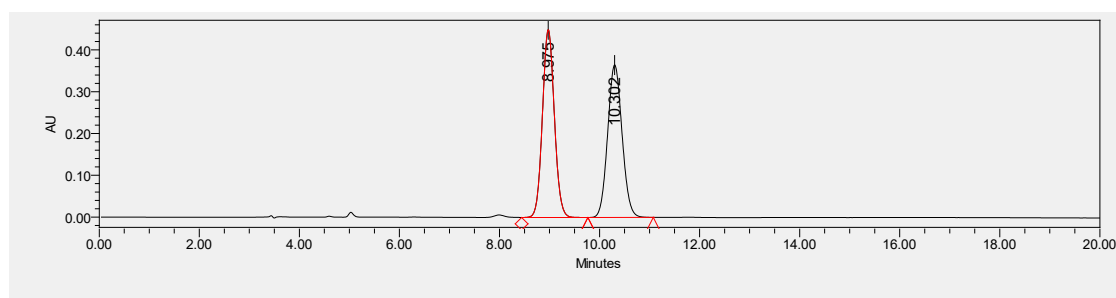
$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3) δ -115.16.

ESI-HRMS: calcd for $\text{C}_{38}\text{H}_{30}\text{FO}_3$ ($[\text{M} + \text{H}]^+$) = 553.2173, found 553.2177.

IR (neat): 2925, 1732, 1705, 1509, 1206, 1205, 962, 803 cm^{-1} .

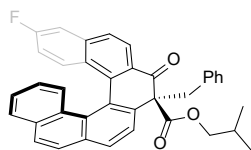


Retention Time	Area	% Area	Height
8.889	772760	2.99	54016
10.114	25091580	97.01	1306441



Retention Time	Area	% Area	Height
8.975	7431235	50.42	449161
10.302	7306594	49.58	364897

isobutyl (*M,S*)-4-benzyl-15-fluoro-3-oxo-3,4-dihydrohexahelicene-4-carboxylate (C22')



Following the typical procedure for the kinetic resolution.

(2 h 50 min) 2.8 mg, 5% yield; >19:1 dr., ee = 99% ee, light yellow oil; R_f = 0.50 (PE/DCM = 1/1). $[\alpha]_D^{25}$ = -690 ($c = 5.5 \times 10^{-2}$, in CH_2Cl_2).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major) = 7.853 min, t (minor) = 16.816 min.

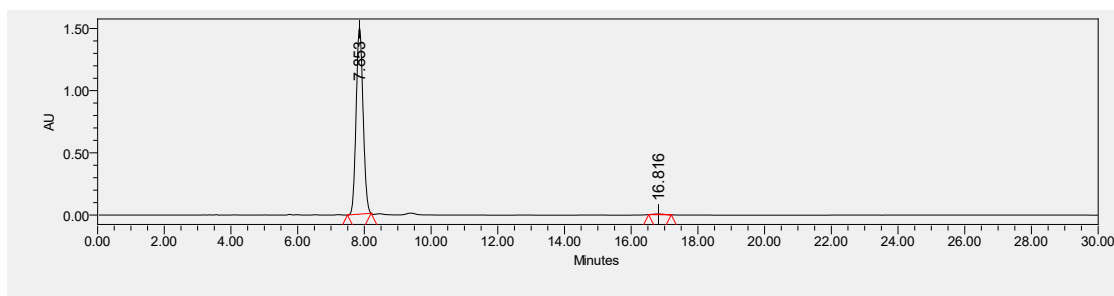
^1H NMR (600 MHz, CDCl_3) δ 7.99 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 2.0 Hz, 2H), 7.71 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.21 – 7.16 (m, 2H), 6.96 (d, J = 8.4 Hz, 1H), 6.60 – 6.56 (m, 2H), 6.35 – 6.31 (m, 1H), 6.30 – 6.28 (m, 4H), 6.18 (dt, J = 8.6, 4.8 Hz, 1H), 4.03 (dd, J = 10.6, 6.8 Hz, 1H), 3.93 (dd, J = 10.6, 6.8 Hz, 1H), 3.66 (d, J = 13.6 Hz, 1H), 3.51 (d, J = 13.6 Hz, 1H), 1.85 – 1.81 (m, 1H), 0.71 (dd, J = 8.4, 6.6 Hz, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 196.84, 171.98, 139.99, 137.61, 134.68, 134.32, 132.54, 132.16, 131.08, 131.06, 130.52, 130.46, 129.78, 129.26, 128.91, 128.47, 127.96, 127.76, 127.71, 126.64, 126.42, 126.27, 125.85, 125.68, 124.64, 124.20, 123.27, 115.10 (d, J = 24.2 Hz), 110.67 (d, J = 21.1 Hz), 72.04, 65.90, 45.95, 27.61, 18.93.

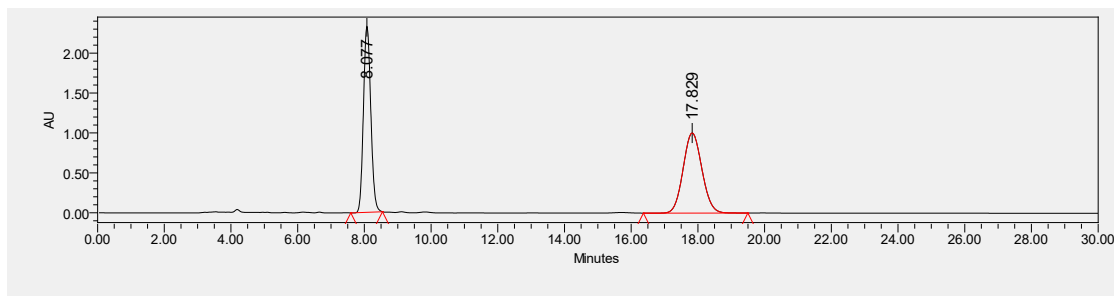
$^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CDCl_3) δ -111.57.

ESI-HRMS: calcd for $\text{C}_{38}\text{H}_{30}\text{FO}_3^+$ ($[\text{M} + \text{H}]^+$) = 553.2173, found 553.2174.

IR (neat): 2926, 1739, 1674, 1625, 1498, 1206, 838 cm^{-1} .

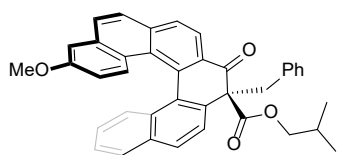


Retention Time	Area	% Area	Height
7.853	21597586	99.51	1493725
16.816	106655	0.49	4476



Retention Time	Area	% Area	Height
8.077	35725825	49.73	2328555
17.829	36113823	50.27	970176

isobutyl (*P,S*)-3-benzyl-10-methoxy-4-oxo-3,4-dihydrohexahelicene-3-carboxylate (C23)



Following the typical procedure for the kinetic resolution.

(2 h 50 min) 28 mg, 50% yield; >19:1 dr., ee = 94% ee, light yellow oil; R_f = 0.43 (PE/DCM = 1/1).

$[\alpha]_D^{25} = 218$ ($c = 5.6 \times 10^{-2}$, in CH_2Cl_2).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/ i PrOH = 90/10, flow rate

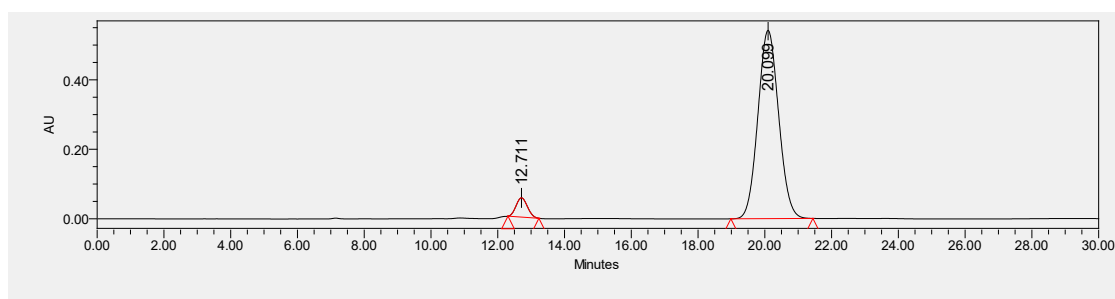
1.0 mL/min, $\lambda = 243$ nm, retention time: t (major) = 20.099 min, t (minor) = 12.711 min.

^1H NMR (600 MHz, CDCl_3) δ 8.08 (d, $J = 7.8$ Hz, 1H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.80 (s, 2H), 7.76 (d, $J = 8.8$ Hz, 1H), 7.74 (d, $J = 8.8$ Hz, 1H), 7.68 (d, $J = 8.2$ Hz, 1H), 7.25 (s, 1H), 7.17 (t, $J = 7.4$ Hz, 1H), 7.06 (ddd, $J = 17.2, 13.8, 5.4$ Hz, 6H), 6.88 (d, $J = 8.6$ Hz, 1H), 6.71 (t, $J = 7.8$ Hz, 1H), 6.32 (dd, $J = 9.2, 2.6$ Hz, 1H), 4.24 (d, $J = 15.89$ Hz, 1H), 4.07 (d, $J = 15.8$ Hz, 1H), 3.79 (s, 3H), 3.59 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.49 (dd, $J = 10.8, 6.6$ Hz, 1H), 1.43 – 1.38 (m, 1H), 0.45 (d, $J = 6.6$ Hz, 3H), 0.40 (d, $J = 6.6$ Hz, 3H).

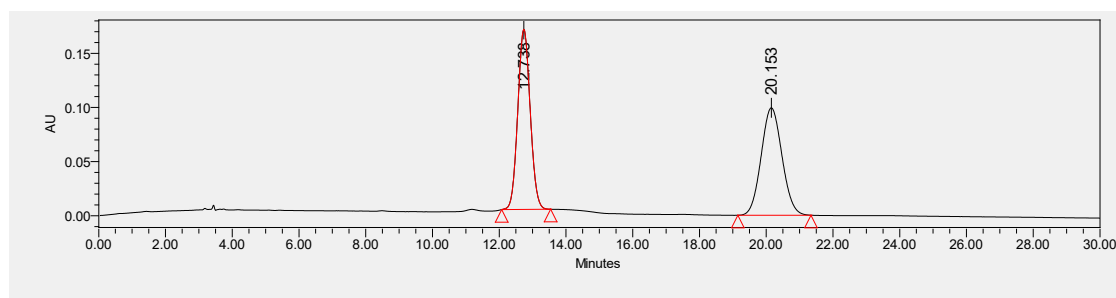
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.42, 170.28, 157.91, 136.90, 135.55, 134.77, 133.93, 133.27, 133.11, 131.35, 129.79, 129.73, 129.70, 129.58, 129.00, 128.90, 128.69, 128.01, 127.87, 126.91, 126.09, 126.01, 125.71, 125.60, 124.91, 124.66, 122.94, 115.29, 107.70, 72.05, 63.99, 55.20, 37.24, 27.34, 18.56, 18.49.

ESI-HRMS: calcd for $\text{C}_{39}\text{H}_{33}\text{O}_4^+$ ($[\text{M} + \text{H}]^+$) = 565.2373, found 565.2371.

IR (neat): 2925, 1731, 1704, 1613, 1515, 1274, 962 cm^{-1} .

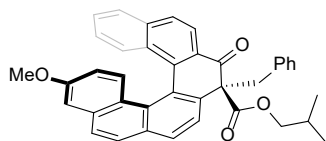


Retention Time	Area	% Area	Height
12.711	258024	3.26	13865
20.099	7662650	96.74	177937



Retention Time	Area	% Area	Height
12.738	4293746	49.96	166180
20.153	4301288	50.04	99166

isobutyl (*M*, *S*)-4-benzyl-10-methoxy-3-oxo-3,4-dihydrohexahelicene-4-carboxylate (C23')



Following the typical procedure for the kinetic resolution.

(2 h 50 min) 3.4 mg, 6% yield; >19:1 dr., ee = 99% ee, light yellow oil; R_f = 0.38 (PE/DCM = 1/1).

$[\alpha]^{25}_D = -557$ ($c = 5.6 \times 10^{-2}$, in CH_2Cl_2).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/PrOH = 90/10, flow rate

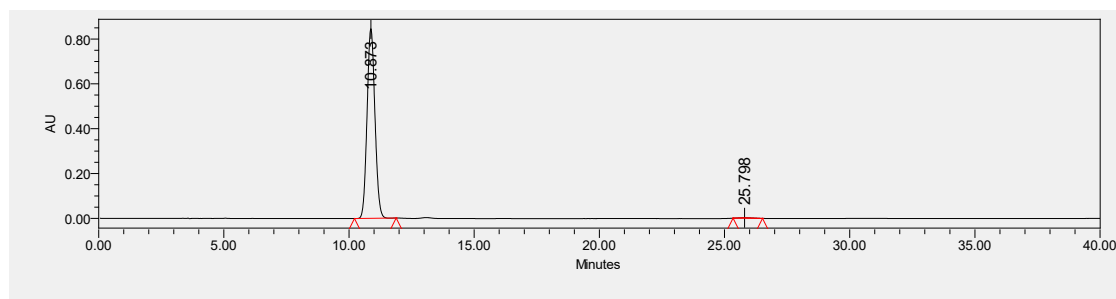
1.0 mL/min, $\lambda = 243$ nm, retention time: t (major) = 10.873 min, t (minor) = 25.798 min.

^1H NMR (600 MHz, CDCl_3) δ 7.94 (d, $J = 8.4$ Hz, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 8.6$ Hz, 1H), 7.72 (d, $J = 8.6$ Hz, 1H), 7.68 (d, $J = 8.6$ Hz, 1H), 7.59 (d, $J = 8.2$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.06 (d, $J = 2.6$ Hz, 1H), 6.91 (d, $J = 9.4$ Hz, 1H), 6.66 – 6.60 (m, 2H), 6.38 – 6.26 (m, 4H), 6.17 (q, $J = 7.6, 5.4$ Hz, 2H), 4.02 (dd, $J = 10.6, 6.8$ Hz, 1H), 3.92 (dd, $J = 10.6, 6.8$ Hz, 1H), 3.77 (s, 3H), 3.63 (d, $J = 13.6$ Hz, 1H), 3.49 (d, $J = 13.6$ Hz, 1H), 1.86 – 1.81 (m, 1H), 0.71 (t, $J = 7.6$ Hz, 6H).

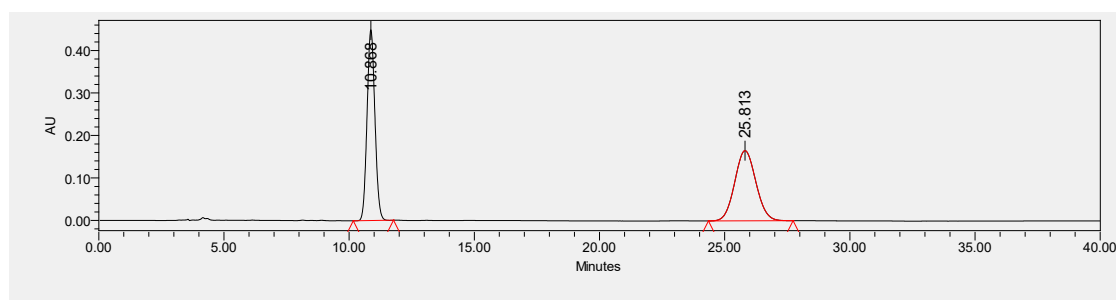
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 197.28, 172.16, 157.56, 139.92, 136.26, 134.54, 134.42, 134.06, 131.15, 129.84, 129.25, 129.03, 128.95, 128.66, 127.80, 127.70, 127.48, 127.33, 127.21, 126.89, 126.64, 125.63, 125.15, 123.70, 121.94, 114.47, 107.59, 71.96, 66.09, 55.16, 45.75, 27.60, 18.94..

ESI-HRMS: calcd for $\text{C}_{39}\text{H}_{33}\text{O}_4^+$ ($[\text{M} + \text{H}]^+$) = 565.2373, found 565.2371.

IR (neat): 2924, 1739, 1672, 1641, 1464, 1239, 1038, 655 cm^{-1} .

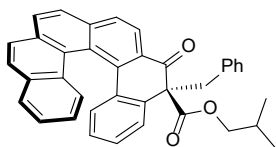


Retention Time	Area	% Area	Height
10.873	18472310	99.52	845572
25.798	88416	0.48	2188



Retention Time	Area	% Area	Height
10.868	9786889	50.22	448529
25.813	9700886	49.78	165200

isobutyl (*P,S*)-1-benzyl-2-oxo-1,2-dihydrohexahelicene-1-carboxylate (C24)



Following the typical procedure for the kinetic resolution.

(14 h 10 min) 23.5 mg, 44% yield; >19:1 dr., ee = 95% ee, light yellow oil; R_f = 0.65 (PE/DCM = 1/1).

$[\alpha]^{25}_D$ = 854 (c = 5.3×10^{-2} , in CH_2Cl_2).

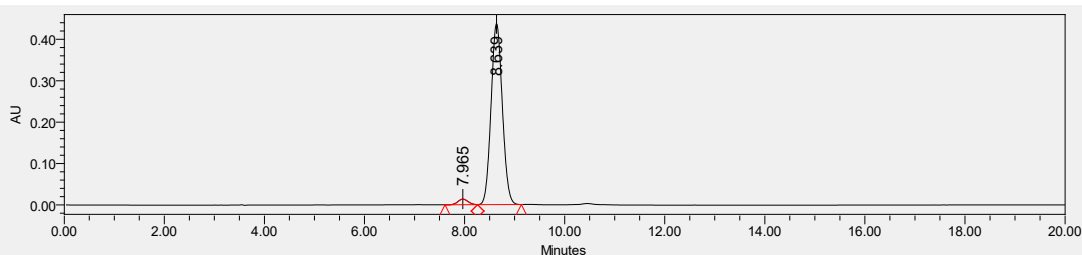
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major) = 8.639 min, t (minor) = 7.965 min.

^1H NMR (600 MHz, CDCl_3) δ 8.30 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.93 – 7.90 (m, 2H), 7.86 (t, J = 7.6 Hz, 2H), 7.80 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.29 (t, J = 7.2 Hz, 1H), 6.95 (q, J = 8.8, 8.6 Hz, 2H), 6.92 – 6.87 (m, 3H), 6.77 – 6.73 (m, 2H), 6.54 (d, J = 8.0 Hz, 1H), 6.31 (t, J = 7.6 Hz, 1H), 4.25 (d, J = 14.6 Hz, 1H), 4.16 (dd, J = 10.8, 6.8 Hz, 1H), 3.95 (d, J = 14.6 Hz, 1H), 3.83 (dd, J = 10.8, 6.8 Hz, 1H), 1.81 (spetet, J = 6.6 Hz, 1H), 0.69 (d, J = 6.6 Hz, 3H), 0.65 (d, J = 6.6 Hz, 3H).

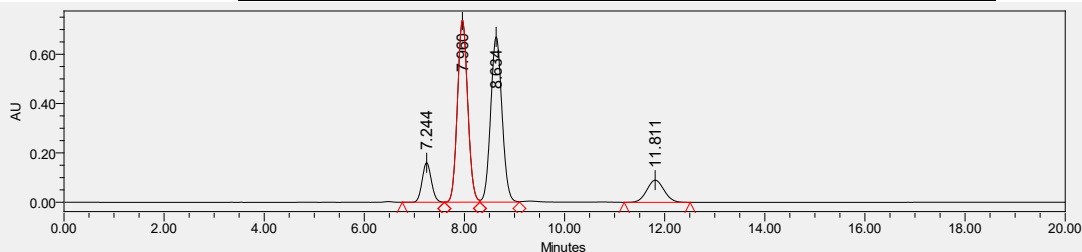
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 195.45, 170.70, 138.86, 137.76, 135.94, 133.00, 132.48, 132.04, 131.57, 129.84, 129.73, 129.54, 129.24, 129.18, 128.68, 128.59, 128.33, 128.04, 127.77, 127.73, 127.60, 127.27, 126.95, 126.08, 126.00, 125.94, 125.84, 125.07, 124.70, 123.61, 72.19, 61.93, 40.95, 27.77, 18.79, 18.77.

ESI-HRMS: calcd for $\text{C}_{38}\text{H}_{31}\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) = 535.2268, found 535.2269.

IR (neat): 2925, 1738, 1665, 1460, 1208, 847, 751 cm^{-1} .

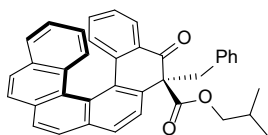


Retention Time	Area	% Area	Height
7.965	160088	2.30	12462
8.639	6806931	97.70	436449



Retention Time	Area	% Area	Height
7.244	2057119	8.14	160391
7.960	10524044	41.64	737967
8.634	10542892	41.72	670119
11.811	2148874	8.50	89812

isobutyl (*M*, *S*)-2-benzyl-1-oxo-1,2-dihydrohexahelicene-2-carboxylate (C24⁺)



Following the typical procedure for the kinetic resolution.

(14 h 10 min) 7.5 mg, 14% yield; >19:1 dr., ee = 96% ee, colorless oil; R_f = 0.56 (PE/DCM = 1/1). $[\alpha]_D^{25}$ = -860 (c = 5.3×10^{-2} , in CH_2Cl_2).

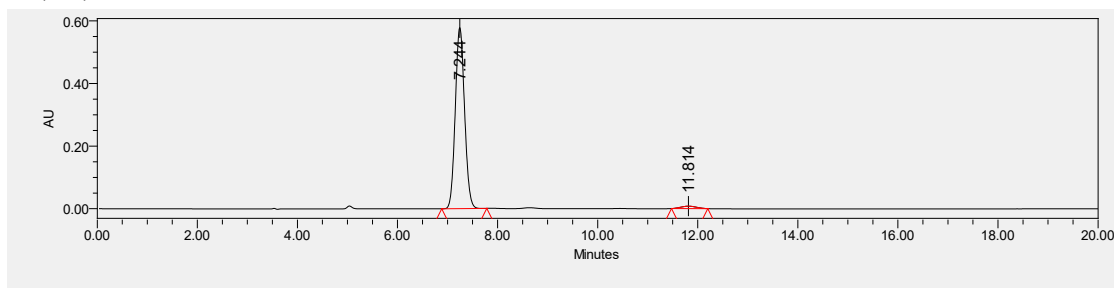
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major) = 11.814 min, t (minor) = 7.244 min.

¹H NMR (600 MHz, CDCl_3) δ 8.03 (dd, J = 12.4, 8.2 Hz, 2H), 7.91 (q, J = 8.4 Hz, 2H), 7.87 – 7.82 (m, 2H), 7.73 (dd, J = 14.0, 8.4 Hz, 2H), 7.66 (d, J = 8.2 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 6.88 (t, J = 8.4 Hz, 1H), 6.83 (t, J = 7.4 Hz, 1H), 6.67 – 6.61 (m, 1H), 6.57 (t, J = 7.4 Hz, 2H), 6.46 (d, J = 7.4 Hz, 2H), 6.38 (t, J = 8.4 Hz, 1H), 6.19 (d, J = 7.8 Hz, 1H), 4.01 (qd, J = 10.6, 6.6 Hz, 2H), 3.76 (d, J = 13.6 Hz, 1H), 3.69 (d, J = 13.6 Hz, 1H), 1.81 (septet, J = 6.6 Hz, 1H), 0.70 (d, J = 6.6 Hz, 6H).

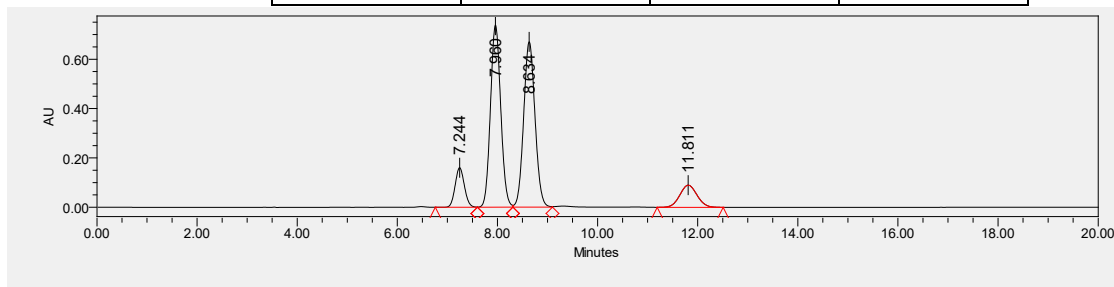
¹³C{¹H} NMR (151 MHz, CDCl_3) δ 197.21, 138.75, 134.29, 134.11, 133.58, 132.16, 131.73, 130.31, 129.94, 129.52, 129.44, 128.85, 128.48, 128.36, 128.17, 127.30, 127.15, 127.10, 126.95, 126.87, 126.64, 126.24, 125.96, 125.51, 125.35, 125.09, 124.36, 71.85, 64.65, 45.50, 27.72, 18.77.

ESI-HRMS: calcd for $\text{C}_{38}\text{H}_{31}\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) = 535.2268, found 535.2271.

IR (neat): 2924, 1732, 1678, 1597, 1457, 1221, 844, 751 cm^{-1} .

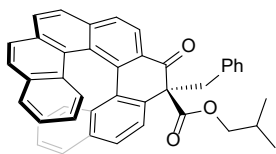


Retention Time	Area	% Area	Height
7.244	7442478	97.80	578161
11.814	167105	2.20	7746



Retention Time	Area	% Area	Height
7.244	2057119	8.14	160391
7.960	10524044	41.64	737967
8.634	10542892	41.72	670119
11.811	2148874	8.50	89812

isobutyl (*P,S*)-7-benzyl-8-oxo-7,8-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-7-carboxylate (C25)



Following the typical procedure for the kinetic resolution.

(21 h) 25.2 mg, 43% yield; >19:1 dr., ee = 98% ee, yellow oil; R_f = 0.33 (PE/EA = 9/1). $[\alpha]_D^{25}$ = 580 (c = 5.8×10^{-2} , in CH_2Cl_2).

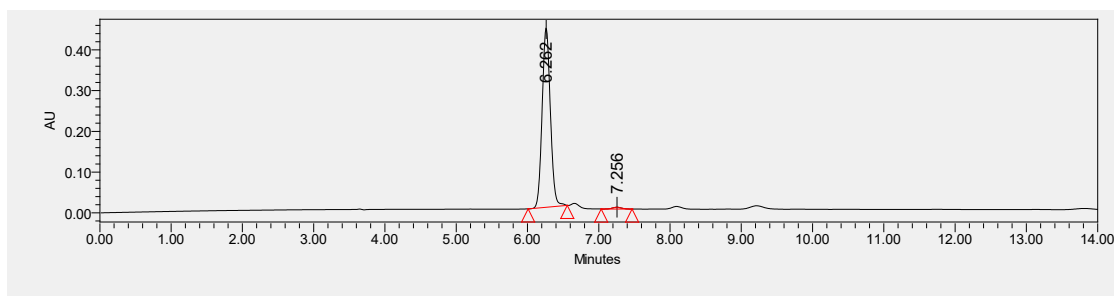
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major) = 6.262 min, t (minor) = 7.256 min.

^1H NMR (600 MHz, CDCl_3) δ 8.42 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 1.6 Hz, 2H), 7.78 (d, J = 8.6 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 7.8 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.00 (t, J = 7.2 Hz, 1H), 6.83 – 6.78 (m, 4H), 6.72 (d, J = 6.4 Hz, 2H), 6.66 (t, J = 7.4 Hz, 1H), 6.26 (t, J = 7.6 Hz, 1H), 5.92 (d, J = 8.6 Hz, 1H), 4.36 (d, J = 15.2 Hz, 1H), 4.09 (dd, J = 10.8, 6.8 Hz, 1H), 4.01 (d, J = 15.2 Hz, 1H), 3.81 (dd, J = 10.8, 6.8 Hz, 1H), 1.70 (septet, J = 6.8 Hz, 1H), 0.60 (d, J = 6.8 Hz, 3H), 0.55 (d, J = 6.8 Hz, 3H).

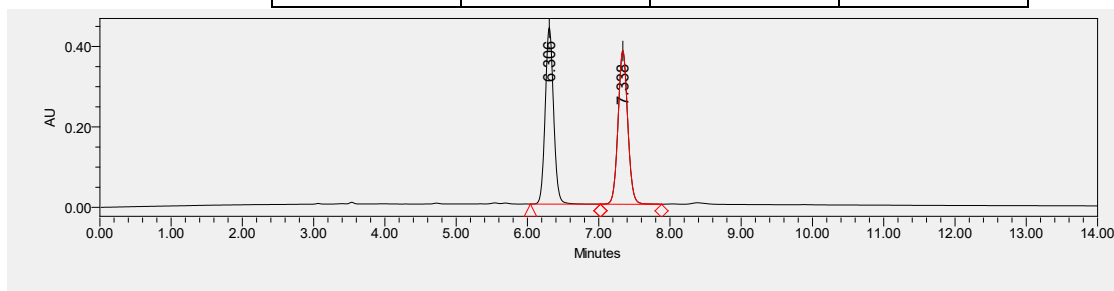
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.72, 170.42, 136.74, 136.66, 136.07, 132.27, 131.21, 131.04, 130.93, 130.86, 130.20, 129.88, 129.47, 128.90, 128.61, 128.58, 128.30, 128.09, 128.04, 127.68, 126.84, 126.82, 126.50, 126.04, 125.92, 125.47, 124.93, 124.80, 124.65, 124.29, 123.96, 123.79, 123.33, 72.25, 62.60, 40.20, 27.61, 18.65.

ESI-HRMS: calcd for $\text{C}_{42}\text{H}_{33}\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) = 585.2424, found 585.2426.

IR (neat): 2924, 1736, 1667, 1461, 1288, 1206, 848 cm^{-1} .

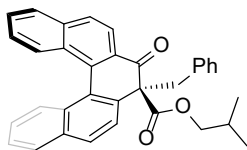


Retention Time	Area	% Area	Height
6.262	3527478	98.92	439578
7.256	38616	1.08	4323



Retention Time	Area	% Area	Height
6.306	3579800	49.85	439104
7.338	3601017	50.15	381672

isobutyl (*P*, *S*)-3-benzyl-4-oxo-3,4-dihydrodibenzo[*c,g*]phenanthrene-3-carboxylate (C26)



Following the typical procedure for the kinetic resolution.

(6 h) 43.2 mg, 89% yield; 18:1 dr., 93% ee, bright yellow oil; $R_f = 0.42$ (PE/EA = 9/1). $[\alpha]_D^{25} = 271$ ($c = 4.8 \times 10^{-2}$, in CH_2Cl_2).

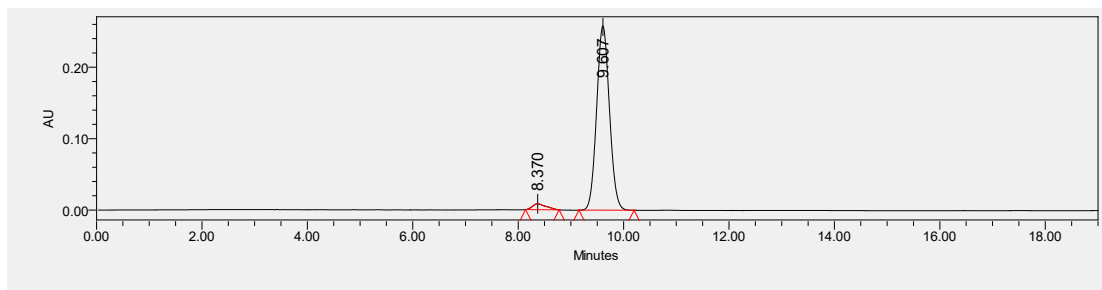
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major) = 9.607 min, t (minor) = 8.369 min.

^1H NMR (600 MHz, CDCl_3) δ 8.14 (d, $J = 8.4$ Hz, 1H), 7.94 – 7.92 (m, 1H), 7.90 (dd, $J = 8.4, 3.6$ Hz, 2H), 7.85 (dd, $J = 8.2, 3.0$ Hz, 2H), 7.55 (t, $J = 7.6$ Hz, 1H), 7.50 (d, $J = 8.6$ Hz, 1H), 7.45 (t, $J = 7.2$ Hz, 1H), 7.37 (d, $J = 8.6$ Hz, 1H), 7.24 (d, $J = 2.8$ Hz, 1H), 7.21 – 7.18 (m, 1H), 6.93 – 6.90 (m, 3H), 6.83 – 6.80 (m, 2H), 4.31 (d, $J = 15.6$ Hz, 1H), 3.96 (d, $J = 15.6$ Hz, 1H), 3.61 – 3.54 (m, 2H), 1.34 (dt, $J = 13.2, 6.6$ Hz, 1H), 0.32 (dd, $J = 6.8, 4.8$ Hz, 6H).

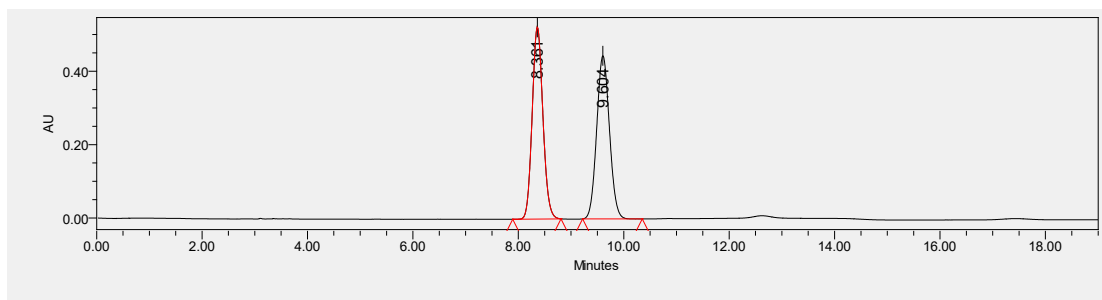
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 195.01, 169.87, 137.16, 136.88, 136.41, 133.25, 132.90, 130.61, 130.23, 129.85, 129.75, 129.21, 129.02, 128.88, 128.30, 128.23, 127.93, 127.85, 127.79, 126.04, 125.96, 125.38, 125.16, 124.98, 122.84, 71.93, 63.23, 38.87, 27.34, 18.33, 18.30.

ESI-HRMS: calcd for $\text{C}_{34}\text{H}_{29}\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) = 485.2111, found 485.2114.

IR (neat): 2924, 1734, 1673, 1460, 1209, 818, 750 cm^{-1} .

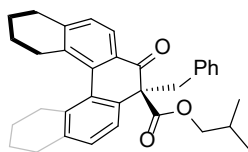


Retention Time	Area	% Area	Height
8.369	647787	3.48	35214
9.607	17983438	96.52	1062804



Retention Time	Area	% Area	Height
8.361	7381614	49.65	522818
9.604	7486419	50.35	444643

isobutyl (*P*, *S*)-3-benzyl-4-oxo-3,4,7,8,9,10,11,12,13,14-decahydrodibenzo[*c,g*]phenanthrene-3-carboxylate (C27)



Following the typical procedure for the kinetic resolution.

(2 h) 49.2 mg, >99% yield; 1.3:1 dr., 93%/93% ee, colorless oil; R_f = 0.66 (PE/EA = 9/1).

Dissolved in *n*-hexane for HPLC; **HPLC** (Chiralcel **IK** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 7.895 min, t (minor₁) = 8.630 min, t (major₂) = 6.417 min, t

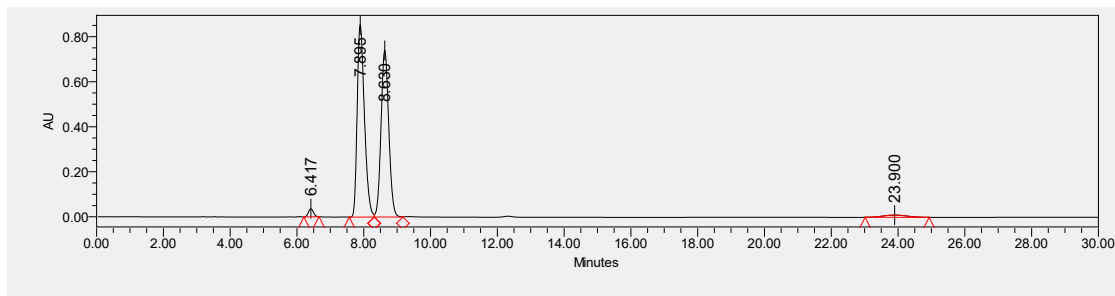
(minor₂) = 23.900 min.

¹H NMR (600 MHz, CDCl₃) δ 7.72 – 6.49 (m, 9H), 3.96 – 3.80 (m, 2H), 3.53 – 3.31 (m, 2H), 2.91 – 2.58 (m, 6H), 2.32 – 2.22 (m, 1H), 1.88 – 1.63 (m, 7H), 1.43 – 1.07 (m, 3H), 0.76 – 0.41 (m, 6H).

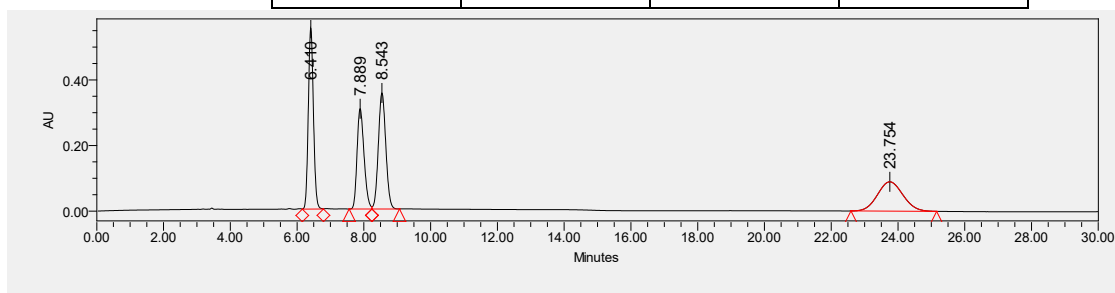
¹³C{¹H} NMR (151 MHz, CDCl₃) δ 197.36, 195.90, 172.69, 170.49, 145.42, 144.81, 138.54, 138.11, 137.97, 137.87, 137.70, 137.44, 137.35, 137.26, 136.60, 135.35, 132.46, 131.94, 131.52, 130.85, 130.74, 130.67, 129.97, 129.74, 128.02, 127.88, 127.76, 126.95, 126.04, 125.89, 124.48, 124.45, 124.31, 124.15, 71.48, 71.46, 65.89, 63.67, 44.83, 37.49, 29.75, 29.44, 28.65, 28.58, 28.36, 28.02, 27.63, 27.53, 27.38, 22.25, 22.10, 22.03, 21.87, 21.73, 21.65, 18.88, 18.67.

ESI-HRMS: calcd for C₃₄H₃₇O₃⁺ ($[M + H]^+$) = 493.2737, found 493.2739.

IR (neat): 2923, 2855, 1734, 1666, 1490, 1199, 820, 7480 cm⁻¹.

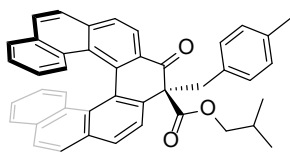


Retention Time	Area	% Area	Height
6.417	370964	1.45	35625
7.895	12831752	50.13	853225
8.630	11890836	46.46	739838
23.900	501382	1.96	9855



Retention Time	Area	% Area	Height
6.410	5556581	27.98	541031
7.889	4436014	22.34	305623
8.543	5494017	27.67	353854
23.754	4371856	22.02	86451

isobutyl (*P*, *S*)-9-(4-methylbenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D2)



Following the typical procedure for the kinetic resolution.

(2 h 40 min) 29.9 mg, 50% yield; 7.0:1 dr., 97%/94 % ee, bright yellow oil; R_f = 0.42 (PE/EA = 9/1).

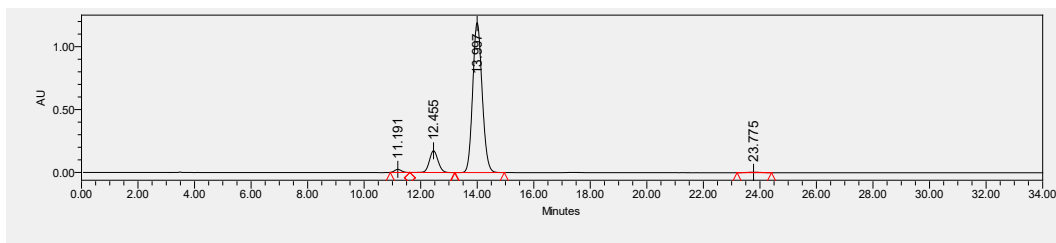
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 13.997 min, t (minor₁) = 11.191 min, t (major₂) = 12.455 min, t (minor₂) = 23.775 min.

¹H NMR (600 MHz, CDCl₃) δ 8.24 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.82 (t, J = 7.8 Hz, 2H), 7.50 (d, J = 7.8 Hz, 2H), 7.40 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 8.4 Hz, 2H), 6.93 (t, J = 7.8 Hz, 1H), 6.89 (t, J = 7.2 Hz, 1H), 6.81 (d, J = 7.8 Hz, 2H), 6.72 (d, J = 7.8 Hz, 2H), 6.62 (d, J = 8.4 Hz, 1H), 6.43 (d, J = 8.4 Hz, 1H), 6.37 (t, J = 7.8 Hz, 1H), 6.31 (t, J = 7.8 Hz, 1H), 4.37 (d, J = 15.6 Hz, 1H), 3.93 (d, J = 15.6 Hz, 1H), 3.74 (dd, J = 10.8, 6.6 Hz, 1H), 3.66 (dd, J = 10.8, 6.6 Hz, 1H), 2.03 (s, 3H), 1.48 (septet, J = 6.6 Hz, 1H), 0.49 (d, J = 6.6 Hz, 3H), 0.43 (d, J = 6.6 Hz, 3H).

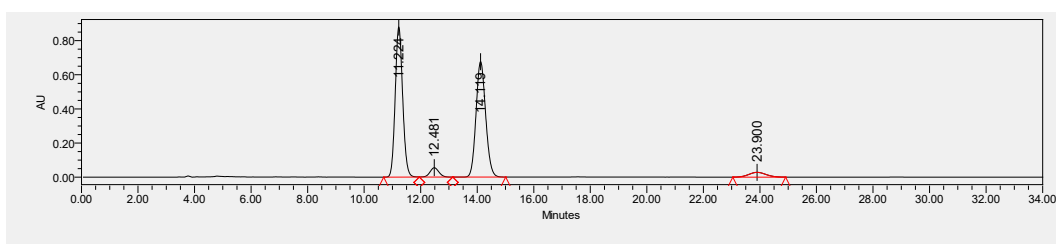
¹³C{¹H} NMR (151 MHz, CDCl₃) δ 194.27, 170.31, 137.90, 136.87, 135.49, 133.17, 132.63, 132.59, 131.83, 131.69, 130.78, 129.91, 129.84, 129.76, 129.63, 129.49, 128.97, 128.61, 128.55, 128.28, 127.12, 126.60, 126.58, 125.86, 125.79, 125.64, 125.54, 125.48, 124.04, 123.78, 123.24, 72.07, 63.37, 39.09, 27.45, 20.79, 18.56, 18.51.

ESI-HRMS: calcd for C₄₃H₃₄O₃Na⁺ ($[M + Na]^+$) = 621.2400, found 621.2402.

IR (neat): 2960, 1733, 1669, 1510, 1269, 1207, 839, 748 cm⁻¹.

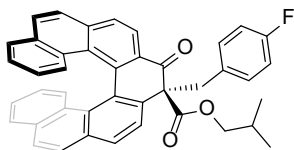


Retention Time	Area	% Area	Height
11.191	410298	1.28	24516
12.455	3684682	11.53	173219
13.997	27760440	86.84	1192423
23.775	110606	0.35	2959



Retention Time	Area	% Area	Height
11.224	16102629	46.66	879326
12.481	1212157	3.51	54921
14.119	16015452	46.40	676334
23.900	1182387	3.43	27930

isobutyl (*P,S*)-9-(4-fluorobenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D3)



Following the typical procedure for the kinetic resolution.

(9 h 15 min) 27.7 mg, 46% yield; 11.2:1 dr., ee = 98%/95% ee, bright yellow oil; R_f = 0.42 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 7.804 min, t (minor₁) = 7.283 min, t (major₂) = 6.562 min, t (minor₂) = 6.217 min.

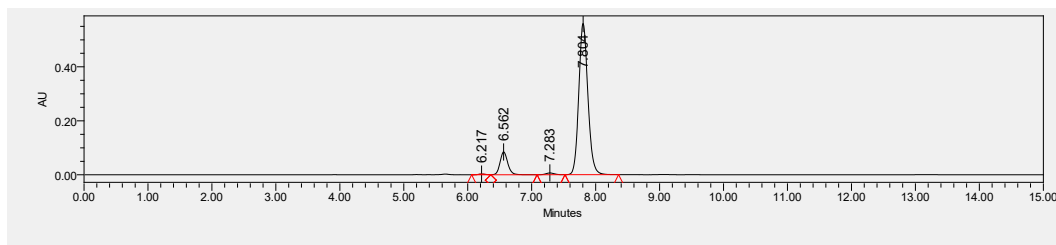
¹H NMR (600 MHz, CDCl₃) δ 8.23 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.23 – 7.20 (m, 2H), 6.95 – 6.86 (m, 4H), 6.62 – 6.58 (m, 3H), 6.41 (d, J = 8.4 Hz, 1H), 6.37 (ddd, J = 8.4, 7.2 1.2 Hz, 1H), 6.33 – 6.30 (m, 1H), 4.36 (d, J = 15.0 Hz, 1H), 3.91 (d, J = 15.0 Hz, 1H), 3.75 (dd, J = 10.8, 6.6 Hz, 1H), 3.66 (dd, J = 10.8, 6.6 Hz, 1H), 1.48 (septet, J = 6.6 Hz, 1H), 0.48 (d, J = 6.6 Hz, 3H), 0.42 (d, J = 6.6 Hz, 3H).

¹³C{¹H} NMR (151 MHz, CDCl₃) δ 194.21, 170.13, 161.25 (d, J = 244.5 Hz), 137.89, 136.95, 132.67, 132.38, 131.93 (d, J = 2.9 Hz), 131.86, 131.69, 131.53, 131.47, 130.81, 129.97, 129.73, 129.64, 129.63, 129.43, 128.89, 128.61, 128.35, 127.31, 126.63 (d, J = 5.6 Hz), 125.90, 125.67, 125.65, 125.57, 125.45, 125.38, 123.97, 123.80, 123.38, 114.65 (d, J = 20.9 Hz), 72.12, 63.35, 38.98, 27.44, 18.53, 18.47.

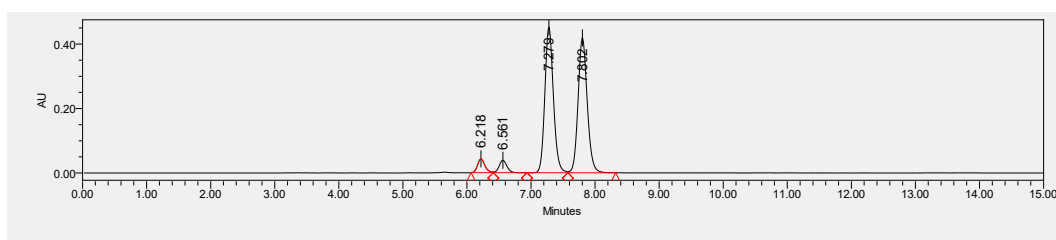
¹⁹F{¹H} NMR (564 MHz, CDCl₃) δ -116.94.

ESI-HRMS: calcd for C₄₂H₃₁FO₃Na⁺ ([M + Na]⁺) = 625.2149, found 625.2148.

IR (neat): 2926, 1731, 1668, 1508, 1270, 1213, 837, 746 cm⁻¹.

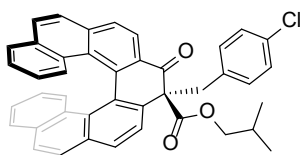


Retention Time	Area	% Area	Height
6.217	19375	0.31	2513
6.562	706326	11.16	84536
7.283	59468	0.94	6589
7.804	5544141	87.59	560033



Retention Time	Area	% Area	Height
6.218	340627	3.78	42776
6.561	323052	3.58	38595
7.279	4173960	46.28	451667
7.802	4181407	46.36	418384

isobutyl (*P,S*)-9-(4-chlorobenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D4)



Following the typical procedure for the kinetic resolution.

(21 h 20 min) 27.2 mg, 44% yield; 12.3:1 dr., 98%/94% ee, bright yellow oil; R_f = 0.42 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 8.845 min, t (minor₁) = 7.810 min, t (major₂) = 6.971

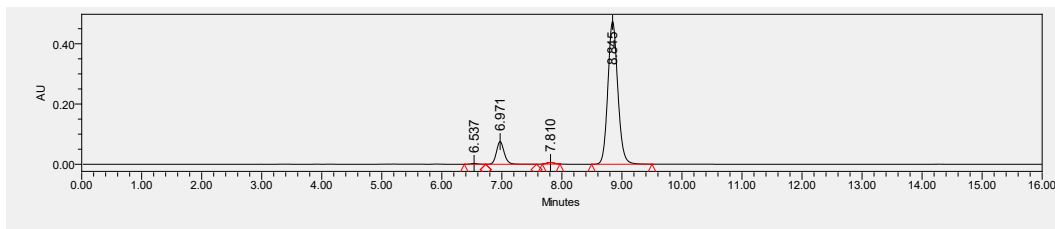
min, t (minor₂) = 6.537 min.

^1H NMR (600 MHz, CDCl_3) δ 8.23 (d, J = 7.8 Hz, 1H), 7.88 – 7.81 (m, 3H), 7.50 (dd, J = 9.0, 3.6 Hz, 2H), 7.40 (d, J = 8.4 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.23 – 7.20 (m, 2H), 6.95 – 6.92 (m, 1H), 6.92 – 6.88 (m, 3H), 6.85 (d, J = 8.4 Hz, 2H), 6.60 (d, J = 8.4 Hz, 1H), 6.42 (d, J = 8.4 Hz, 1H), 6.39 – 6.36 (m, 1H), 6.34 – 6.31 (m, 1H), 4.36 (d, J = 15.0 Hz, 1H), 3.91 (d, J = 15.0 Hz, 1H), 3.75 (dd, J = 10.8, 6.6 Hz, 1H), 3.66 (dd, J = 10.8, 6.6 Hz, 1H), 1.47 (septet, J = 6. Hz, 1H), 0.48 (d, J = 6.6 Hz, 3H), 0.41 (d, J = 6.6 Hz, 3H).

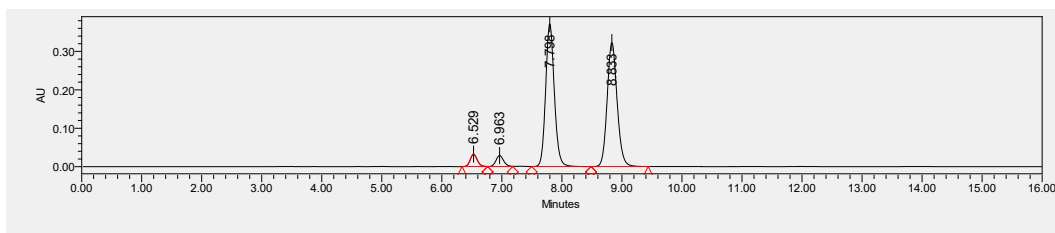
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.07, 170.05, 137.90, 136.98, 134.86, 132.71, 132.10, 131.98, 131.88, 131.70, 131.35, 130.86, 129.98, 129.76, 129.63, 129.42, 128.89, 128.67, 128.39, 127.99, 127.35, 126.66, 126.62, 125.92, 125.70, 125.68, 125.57, 125.46, 125.38, 125.31, 123.98, 123.81, 123.40, 72.18, 63.25, 38.93, 27.44, 18.52, 18.47.

ESI-HRMS: calcd for $\text{C}_{42}\text{H}_{31}^{35}\text{ClO}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 641.1854, found 641.1854, $\text{C}_{42}\text{H}_{31}^{37}\text{ClO}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 643.1824, found 643.1823.

IR (neat): 2959, 1731, 1667, 1495, 1264, 1206, 838, 797, 741 cm^{-1} .

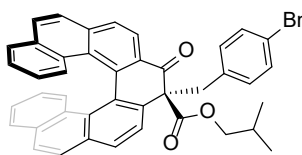


Retention Time	Area	% Area	Height
6.537	20703	0.33	2514
6.971	677820	10.97	75276
7.810	46202	0.75	5279
8.845	5435983	87.95	473747



Retention Time	Area	% Area	Height
6.529	266415	3.34	32375
6.963	259708	3.26	28836
7.798	3732584	46.80	371429
8.833	3716568	46.60	322761

isobutyl (*P*, *S*)-9-(4-bromobenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D5)



Following the typical procedure for the kinetic resolution.

(21 h 20 min) 28.5 mg, 43% yield; 15.0:1 dr., 99%/80% ee, bright yellow oil; R_f = 0.42 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 9.453 min, t (minor₁) = 8.144 min, t (major₂) = 7.285

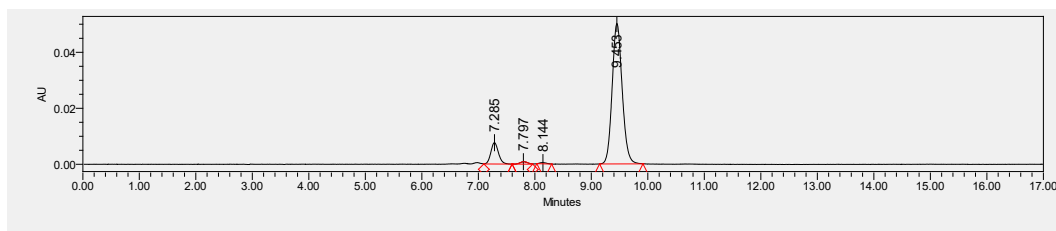
min, t (minor₂) = 7.797 min.

^1H NMR (600 MHz, CDCl_3) δ 8.22 (d, J = 8.4 Hz, 1H), 7.87 – 7.81 (m, 3H), 7.51 (dd, J = 8.4, 4.2 Hz, 2H), 7.41 (d, J = 8.4 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.23 – 7.20 (m, 2H), 7.06 – 7.02 (m, 2H), 6.95 – 6.92 (m, 1H), 6.92 – 6.89 (m, 1H), 6.79 (d, J = 8.4 Hz, 2H), 6.60 (d, J = 8.4 Hz, 1H), 6.43 (d, J = 8.4 Hz, 1H), 6.37 (ddd, J = 7.8, 6.6, 0.6 Hz, 1H), 6.33 (ddd, J = 7.8, 6.6, 0.6 Hz, 1H), 4.34 (d, J = 15.0 Hz, 1H), 3.90 (d, J = 15.0 Hz, 1H), 3.75 (dd, J = 10.8, 6.6 Hz, 1H), 3.66 (dd, J = 10.8, 6.6 Hz, 1H), 1.47 (septet, J = 6.6 Hz, 1H), 0.48 (d, J = 6.6 Hz, 3H), 0.41 (d, J = 6.6 Hz, 3H).

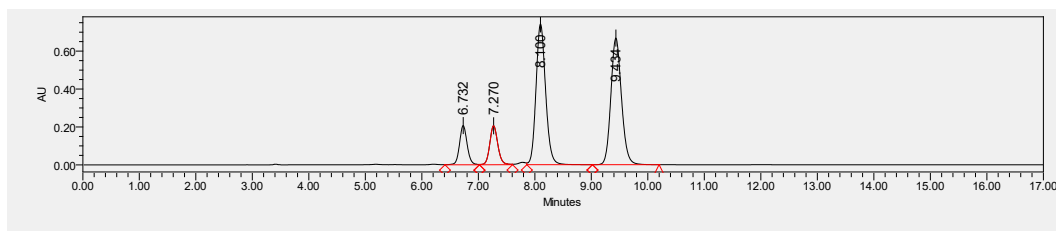
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.04, 170.03, 137.90, 136.98, 135.40, 132.72, 132.04, 131.88, 131.73, 131.70, 130.93, 130.87, 129.98, 129.76, 129.64, 129.62, 129.42, 128.89, 128.68, 128.40, 127.36, 126.66, 126.62, 125.93, 125.72, 125.69, 125.57, 125.46, 125.37, 125.28, 123.99, 123.82, 123.41, 120.17, 72.19, 63.20, 38.97, 27.44, 18.52, 18.46.

ESI-HRMS: calcd for $\text{C}_{42}\text{H}_{31}^{79}\text{BrO}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 685.1349, found 685.1348, $\text{C}_{42}\text{H}_{31}^{81}\text{BrO}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 687.1328, found 687.1330.

IR (neat): 2959, 1732, 1668, 1588, 1268, 1207, 839, 748 cm^{-1} .

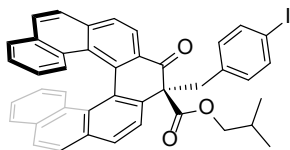


Retention Time	Area	% Area	Height
7.285	71081	10.13	7607
7.797	8132	1.16	870
8.144	3623	0.52	437
9.453	618718	88.19	50141



Retention Time	Area	% Area	Height
6.732	1934161	9.00	206789
7.270	2035648	9.48	205599
8.100	8772356	40.84	742734
9.434	8739470	40.68	667765

isobutyl (*P*, *S*)-9-(4-iodobenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D6)



Following the typical procedure for the kinetic resolution.

(21 h 20 min) 30.5 mg, 43% yield; 11.2:1 dr., 99%/90% ee, bright yellow oil; R_f = 0.44 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 10.248 min, t (minor₁) = 8.446min, t (major₂) = 7.686

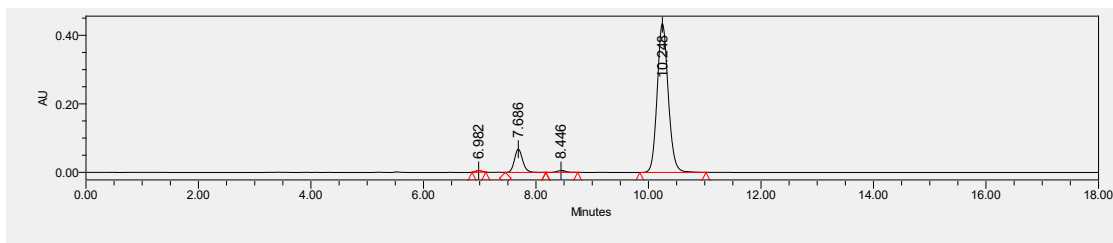
min, t (minor₂) = 6.982min.

^1H NMR (600 MHz, CDCl_3) δ 8.22 (d, J = 7.8 Hz, 1H), 7.87 – 7.81 (m, 3H), 7.51 (dd, J = 8.4, 5.4 Hz, 2H), 7.41 (d, J = 9.0 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.25 – 7.21 (m, 4H), 6.95 – 6.92 (m, 1H), 6.92 – 6.89 (m, 1H), 6.66 (d, J = 8.4 Hz, 2H), 6.60 (d, J = 8.4 Hz, 1H), 6.43 (d, J = 8.4 Hz, 1H), 6.37 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 6.33 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 4.33 (d, J = 15.6 Hz, 1H), 3.89 (d, J = 15.6 Hz, 1H), 3.74 (dd, J = 10.8, 6.6 Hz, 1H), 3.66 (dd, J = 10.8, 6.6 Hz, 1H), 1.47 (septet, J = 6.6 Hz, 1H), 0.48 (d, J = 6.6 Hz, 3H), 0.41 (d, J = 6.6 Hz, 3H).

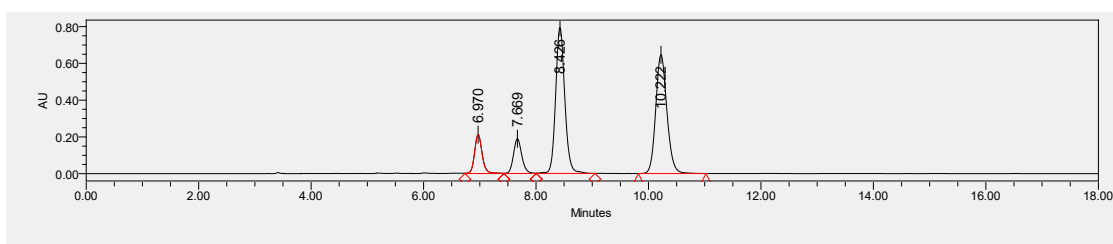
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.01, 170.03, 137.89, 136.98, 136.90, 136.10, 132.72, 132.02, 132.00, 131.89, 131.71, 130.87, 129.98, 129.76, 129.64, 129.43, 128.89, 128.69, 128.40, 127.37, 126.66, 126.63, 125.93, 125.73, 125.69, 125.58, 125.47, 125.38, 125.27, 123.99, 123.82, 123.43, 91.75, 72.20, 63.16, 39.02, 27.44, 18.53, 18.47.

ESI-HRMS: calcd for $\text{C}_{42}\text{H}_{31}\text{IO}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 733.1210, found 733.1209.

IR (neat): 2958, 1732, 1668, 1587, 1267, 1208, 947, 839, 795, 742 cm^{-1} .

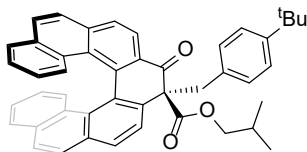


Retention Time	Area	% Area	Height
6.982	37679	0.56	5135
7.686	689455	10.30	68030
8.446	38914	0.58	4423
10.248	5929548	88.56	434154



Retention Time	Area	% Area	Height
6.970	1979293	9.06	211927
7.669	1943330	8.90	189223
8.426	9008550	41.24	794296
10.222	8911723	40.80	646077

isobutyl (*P, S*)-9-(4-(*tert*-butyl)benzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D7)



Following the typical procedure for the kinetic resolution.

(5 h 45 min) 31.4 mg, 49% yield; 12.3:1 dr., 98%/92% ee, bright yellow oil; R_f = 0.44 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 8.916 min, t (minor₁) = 11.171 min, t (major₂) = 9.427

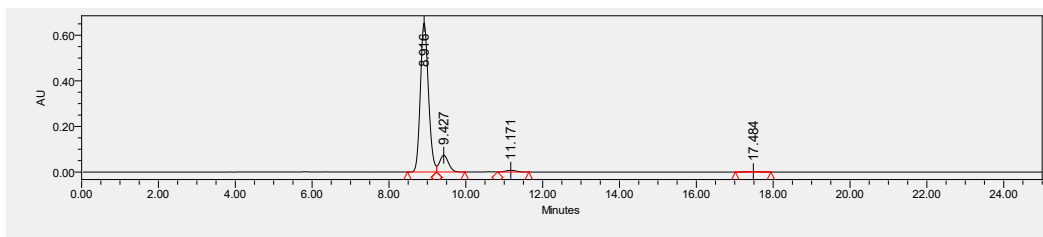
min, t (minor₂) = 17.484 min.

^1H NMR (600 MHz, CDCl_3) δ 8.23 (d, J = 7.8 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.50 (dd, J = 9.0, 1.2 Hz, 2H), 7.40 (d, J = 9.0 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.23 – 7.20 (m, 2H), 6.95 – 6.93 (m, 2H), 6.91 – 6.88 (m, 1H), 6.84 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 8.4 Hz, 1H), 6.42 (d, J = 8.4 Hz, 1H), 6.38 (ddd, J = 8.4, 7.2, 1.8 Hz, 1H), 6.30 (ddd, J = 8.4, 7.2, 1.8 Hz, 1H), 4.33 (d, J = 15.6 Hz, 1H), 3.95 (d, J = 15.6 Hz, 1H), 3.73 (dd, J = 10.8, 6.6 Hz, 1H), 3.65 (dd, J = 10.8, 6.6 Hz, 1H), 1.48 (septet, J = 6.6 Hz, 1H), 1.04 (s, 9H), 0.50 (d, J = 6.6 Hz, 3H), 0.44 (d, J = 6.6 Hz, 3H).

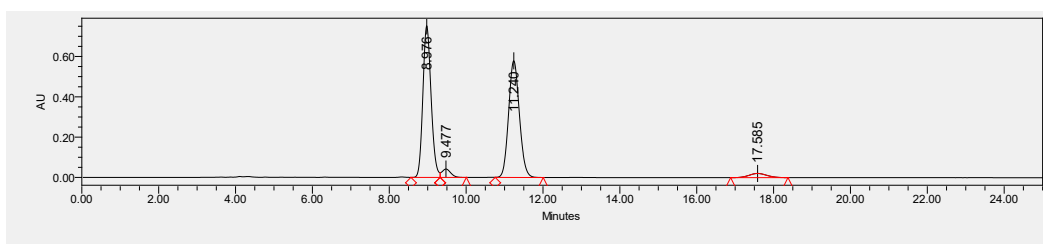
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.40, 170.34, 148.68, 137.84, 136.85, 133.16, 132.69, 132.64, 131.84, 131.70, 130.78, 129.94, 129.90, 129.64, 129.60, 129.47, 128.97, 128.61, 128.27, 127.11, 126.58, 125.88, 125.79, 125.67, 125.54, 125.49, 125.46, 124.80, 124.01, 123.80, 123.27, 72.05, 63.40, 39.07, 34.13, 31.13, 27.45, 18.58, 18.53.

ESI-HRMS: calcd for $\text{C}_{46}\text{H}_{40}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 663.2870, found 663.2870.

IR (neat): 2959, 1734, 1669, 1509, 1270, 1207, 838, 746 cm^{-1} .

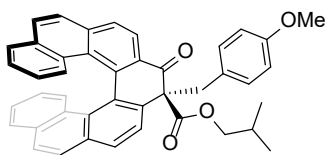


Retention Time	Area	% Area	Height
8.916	9627397	87.67	652464
9.427	1192645	10.86	74061
11.171	110203	1.00	6672
17.484	50933	0.46	1793



Retention Time	Area	% Area	Height
8.976	11218885	47.11	751783
9.477	665261	2.79	41756
11.240	11258240	47.28	578686
17.585	671882	2.82	20734

isobutyl (*P,S*)-9-(4-methoxybenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D8)



Following the typical procedure for the kinetic resolution.

(3 h 35 min) 36.2 mg, 59% yield; 3.9:1 dr., 97%/97% ee, bright yellow oil; R_f = 0.35 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 10.328min, t (minor₁) = 8.711 min, t (major₂) =

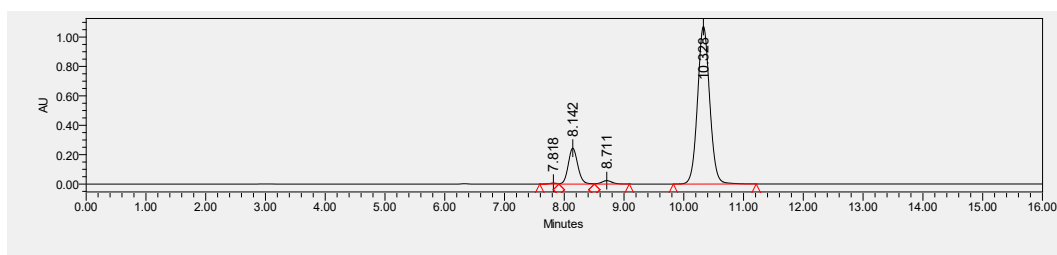
7.148 min, t (minor₂) = 7.818min.

^1H NMR (600 MHz, CDCl_3) δ 8.23 (d, J = 7.8 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.50 (dd, J = 9.0, 3.0 Hz, 2H), 7.39 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 9.0 Hz, 1H), 7.21 (t, J = 7.2 Hz, 2H), 6.94 (d, J = 7.2 Hz, 1H), 6.89 (t, J = 7.2 Hz, 1H), 6.82 (d, J = 8.4 Hz, 2H), 6.61 (d, J = 8.4 Hz, 1H), 6.45 (d, J = 8.4 Hz, 2H), 6.42 (d, J = 8.4 Hz, 1H), 6.36 (t, J = 7.2 Hz, 1H), 6.30 (t, J = 7.2 Hz, 1H), 4.33 (d, J = 15.0 Hz, 1H), 3.89 (d, J = 15.0 Hz, 1H), 3.75 (dd, J = 10.8, 6.6 Hz, 1H), 3.66 (dd, J = 10.8, 6.6 Hz, 1H), 3.50 (s, 3H), 1.49 (septet, J = 6.6 Hz, 1H), 0.49 (d, J = 6.6 Hz, 3H), 0.43 (d, J = 6.6 Hz, 3H).

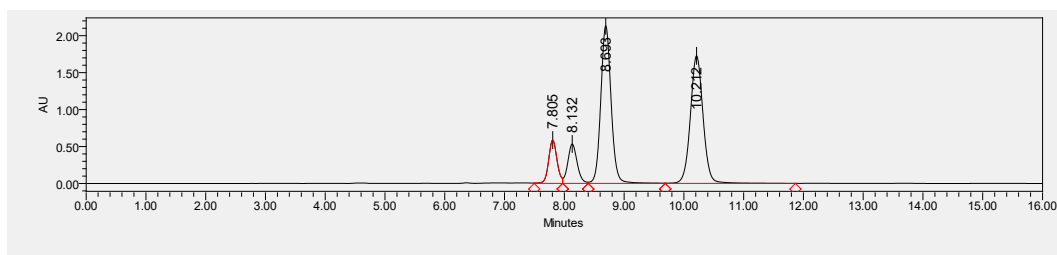
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.37, 170.32, 157.75, 137.90, 136.87, 132.79, 132.62, 131.83, 131.68, 131.00, 130.77, 130.56, 129.96, 129.76, 129.65, 129.62, 129.48, 128.95, 128.55, 128.28, 128.20, 127.16, 126.60, 126.58, 125.86, 125.79, 125.62, 125.57, 125.46, 124.01, 123.78, 123.28, 113.27, 63.47, 54.94, 39.03, 27.46, 18.57, 18.51.

ESI-HRMS: calcd for $\text{C}_{43}\text{H}_{34}\text{O}_4\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 637.2349, found 637.2350.

IR (neat): 2959, 1732, 1669, 1510, 1462, 1248, 1207, 1053, 836, 747 cm^{-1} .

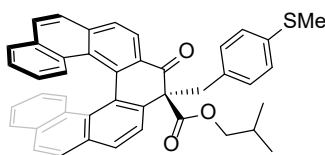


Retention Time	Area	% Area	Height
7.818	36920	0.20	4617
8.142	2652848	14.72	242829
8.711	228707	1.27	21100
10.328	15101989	83.80	1072058



Retention Time	Area	% Area	Height
7.805	5729839	9.14	585800
8.132	5777029	9.22	532853
8.693	25606176	40.86	2131675
10.212	25562676	40.79	1726121

isobutyl (*P,S*)-9-(4-methylthiobenzyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D9)



Following the typical procedure for the kinetic resolution.

(3 h 50 min) 29.6 mg, 47% yield; 6.3:1 dr., 98%/93% ee, bright yellow oil; R_f = 0.44 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/ i PrOH = 90/10, flow rate

1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 10.590 min, t (minor₁) = 8.872 min, t (major₂) =

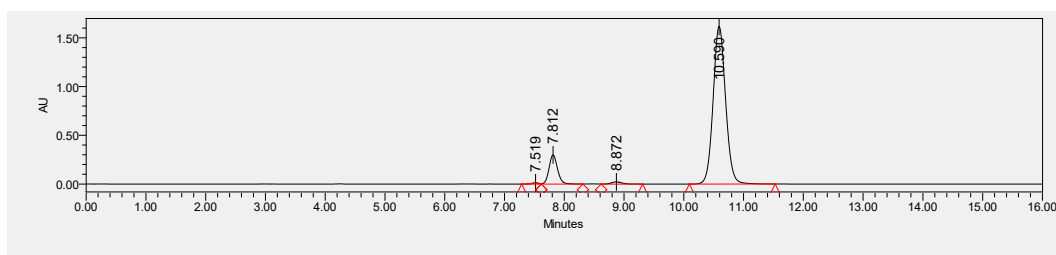
7.812 min, t (minor₂) = 7.519 min.

^1H NMR (600 MHz, CDCl_3) δ 8.23 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 7.8 Hz, 2H), 7.40 (d, J = 9.0 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 7.2 Hz, 2H), 6.93 (t, J = 7.8 Hz, 1H), 6.90 (t, J = 7.2 Hz, 1H), 6.84 – 6.80 (m, 4H), 6.61 (d, J = 8.4 Hz, 1H), 6.43 (d, J = 8.4 Hz, 1H), 6.37 (d, J = 7.8 Hz, 1H), 6.32 (t, J = 7.8 Hz, 1H), 4.35 (d, J = 15.0 Hz, 1H), 3.92 (d, J = 15.0 Hz, 1H), 3.75 (dd, J = 10.8, 6.6 Hz, 1H), 3.66 (dd, J = 10.8, 6.6 Hz, 1H), 2.18 (s, 3H), 1.48 (septet, J = 6.6 Hz, 1H), 0.49 (d, J = 6.6 Hz, 3H), 0.42 (d, J = 6.6 Hz, 3H).

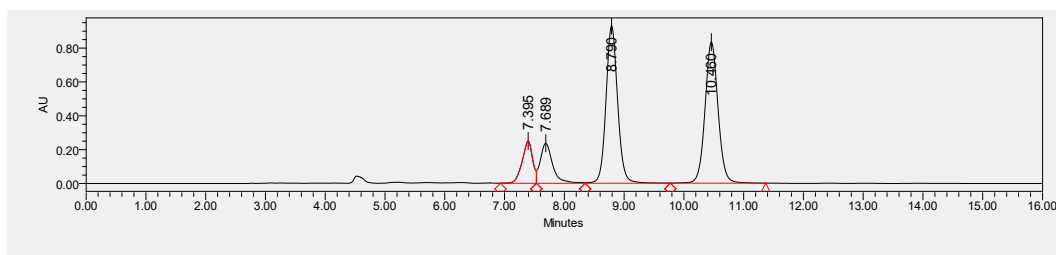
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.18, 170.19, 137.91, 136.92, 135.79, 133.21, 132.67, 132.43, 131.85, 131.69, 130.80, 130.43, 129.96, 129.70, 129.63, 129.45, 128.92, 128.63, 128.34, 127.24, 126.63, 126.60, 126.23, 125.90, 125.77, 125.62, 125.47, 125.43, 124.01, 123.80, 123.33, 72.12, 63.30, 39.15, 27.45, 18.56, 18.50, 15.70.

ESI-HRMS: calcd for $\text{C}_{43}\text{H}_{34}\text{O}_3\text{SNa}^+$ ($[\text{M} + \text{Na}]^+$) = 653.2121, found 653.2121.

IR (neat): 2958, 1731, 1668, 1589, 1500, 1266, 1205, 839, 740 cm^{-1} .

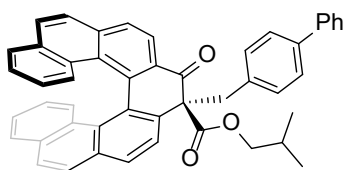


Retention Time	Area	% Area	Height
7.519	102928	0.38	12641
7.812	2953615	11.05	299571
8.872	275584	1.03	22655
10.590	23403951	87.54	1616792



Retention Time	Area	% Area	Height
7.395	3201982	10.14	249281
7.689	3221160	10.20	236208
8.790	12532847	39.70	929962
10.460	12612410	39.95	832848

isobutyl (*P,S*)-9-(4-phenylbenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D10)



Following the typical procedure for the kinetic resolution.

(4 h 10 min) 33.0 mg, 50% yield; 12.4:1 dr., 97%/95% ee, bright yellow oil; R_f = 0.44 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 10.308 min, t (minor₁) = 8.068 min, t (major₂)

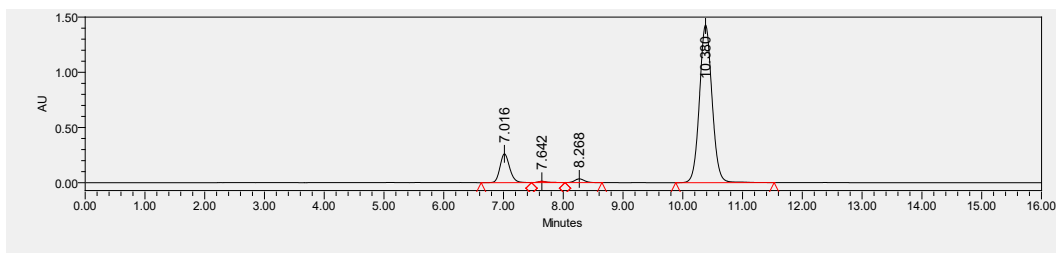
= 7.016 min, t (minor₂) = 7.642min.

¹H NMR (600 MHz, CDCl₃) δ 8.25 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.50 (dd, J = 8.4, 6.6 Hz, 2H), 7.40 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 9.0 Hz, 1H), 7.29 (d, J = 7.0 Hz, 2H), 7.26 – 7.18 (m, 2H), 7.15 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 6.94 (t, J = 7.2 Hz, 1H), 6.89 (t, J = 7.8 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 6.42 (d, J = 8.4 Hz, 1H), 6.38 (t, J = 7.8 Hz, 1H), 6.29 (t, J = 7.8 Hz, 1H), 4.43 (d, J = 15.0 Hz, 1H), 4.00 (d, J = 15.0 Hz, 1H), 3.77 (dd, J = 10.8, 6.6 Hz, 1H), 3.68 (dd, J = 10.8, 6.6 Hz, 1H), 1.50 (septet, J = 6.6 Hz, 1H), 0.50 (d, J = 6.6 Hz, 3H), 0.44 (d, J = 6.6 Hz, 3H).

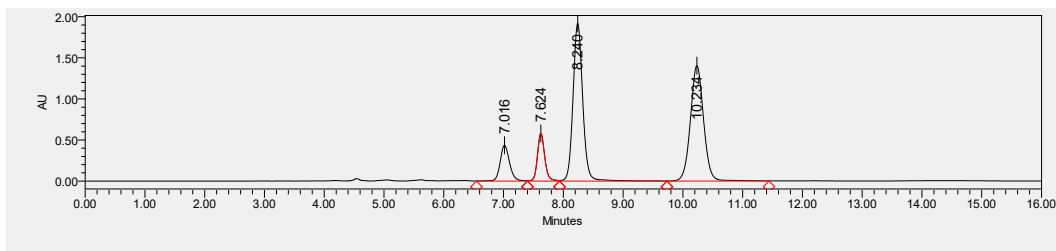
¹³C{¹H} NMR (151 MHz, CDCl₃) δ 194.30, 170.27, 140.70, 138.82, 137.93, 136.92, 135.44, 132.70, 132.59, 131.88, 131.71, 130.82, 130.32, 129.99, 129.79, 129.68, 129.66, 129.49, 128.96, 128.68, 128.50, 128.35, 127.24, 126.90, 126.83, 126.63, 126.61, 126.56, 125.90, 125.75, 125.65, 125.59, 125.49, 125.44, 124.03, 123.82, 123.35, 72.14, 63.38, 39.42, 27.48, 18.58, 18.53.

ESI-HRMS: calcd for C₄₈H₃₆O₃Na⁺ ($[M + Na]^+$) = 683.2557, found 683.2556.

IR (neat): 2959, 1731, 1667, 1508, 1203, 834, 748, 689, 520 cm⁻¹.

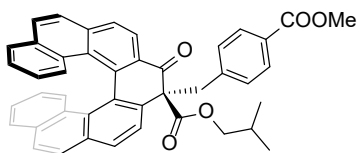


Retention Time	Area	% Area	Height
7.016	2885851	11.96	259976
7.642	68666	0.28	9794
8.268	342950	1.42	32502
10.380	20830356	86.33	1428030



Retention Time	Area	% Area	Height
7.016	4809352	9.07	435589
7.624	4929540	9.29	580834
8.240	21707793	40.93	1918788
10.234	21592009	40.71	1404708

isobutyl (*P,S*)-9-(4-methoxycarbonylbenzyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D11)



Following the typical procedure for the kinetic resolution.

(12 h) 32.1 mg, 50% yield; 7.3:1 dr., 98%/95% ee, bright yellow oil; $R_f = 0.35$ (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major₁) = 13.143 min, t (minor₁) = 10.918 min, t

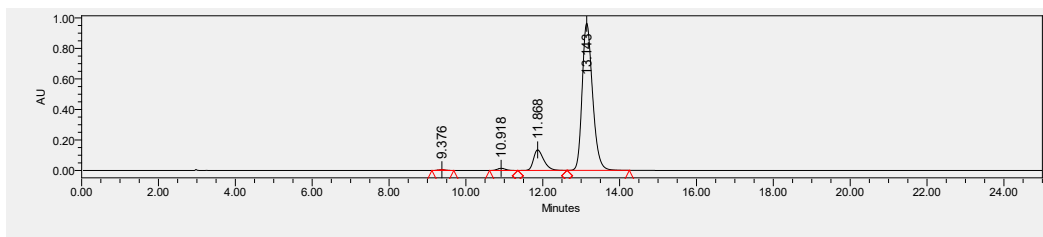
(major₂) = 11.868 min, t (minor₂) = 9.376 min.

¹H NMR (600 MHz, CDCl₃) δ 8.24 (d, $J = 7.8$ Hz, 1H), 7.86 – 7.81 (m, 3H), 7.60 (d, $J = 8.4$ Hz, 2H), 7.51 (d, $J = 8.4$ Hz, 1H), 7.48 (d, $J = 8.4$ Hz, 1H), 7.41 (d, $J = 8.4$ Hz, 1H), 7.22 (d, $J = 8.4$ Hz, 1H), 7.20 (d, $J = 8.4$ Hz, 1H), 7.20 (d, $J = 8.4$ Hz, 1H), 7.01 (d, $J = 8.4$ Hz, 2H), 6.94 (t, $J = 7.2$ Hz, 1H), 6.90 (t, $J = 7.2$ Hz, 1H), 6.61 (d, $J = 8.4$ Hz, 1H), 6.42 (d, $J = 8.4$ Hz, 1H), 6.37 (t, $J = 7.8$ Hz, 1H), 6.31 (t, $J = 7.8$ Hz, 1H), 4.49 (d, $J = 15.6$ Hz, 1H), 4.02 (d, $J = 15.6$ Hz, 1H), 3.75 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.70 (s, 3H), 3.67 (dd, $J = 10.8, 6.6$ Hz, 1H), 1.47 (septet, $J = 6.6$ Hz, 1H), 0.48 (d, $J = 6.6$ Hz, 3H), 0.41 (d, $J = 6.6$ Hz, 3H).

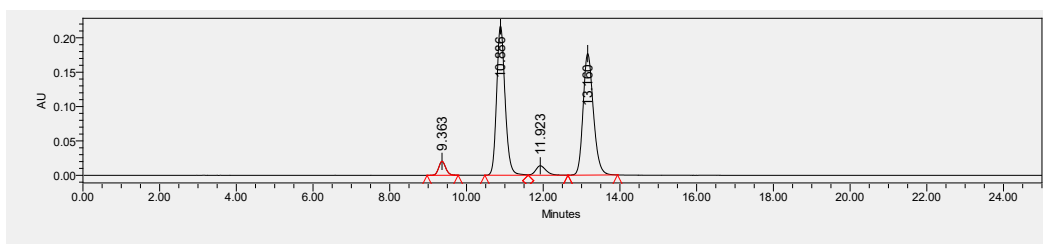
¹³C{¹H} NMR (151 MHz, CDCl₃) δ 193.99, 169.97, 166.86, 142.06, 137.98, 137.02, 132.72, 131.88, 131.71, 130.82, 129.93, 129.80, 129.65, 129.59, 129.42, 129.16, 128.87, 128.71, 128.42, 127.93, 127.36, 126.66, 126.63, 125.95, 125.71, 125.67, 125.58, 125.48, 125.38, 125.26, 124.04, 123.83, 123.38, 72.25, 63.18, 51.82, 39.37, 27.43, 18.52, 18.46.

ESI-HRMS: calcd for C₄₄H₃₄O₅Na⁺ ($[M + Na]^+$) = 665.2298, found 665.2297.

IR (neat): 2957, 1723, 1607, 1279, 1206, 1110, 841, 747 cm⁻¹.

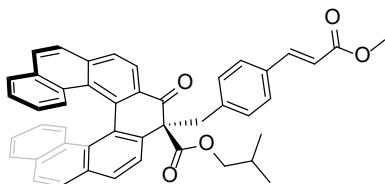


Retention Time	Area	% Area	Height
9.376	58280	0.28	4679
10.918	211426	1.01	14098
11.868	2485812	11.89	134455
13.143	18146902	86.82	964480



Retention Time	Area	% Area	Height
9.363	260379	3.65	20314
10.886	3318286	46.52	217285
11.923	258439	3.62	13746
13.160	3295458	46.20	176687

isobutyl (*P*, *S*, *E*)-9-(4- (3-methoxy-3-oxoprop-1-en-1-yl)benzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D12)



Following the typical procedure for the kinetic resolution.

(10 h 40 min) 30.1 mg, 45% yield; 8.3:1 dr., 99%/94% ee, bright yellow oil; R_f = 0.35 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 26.192 min, t (minor₁) = 17.695min, t

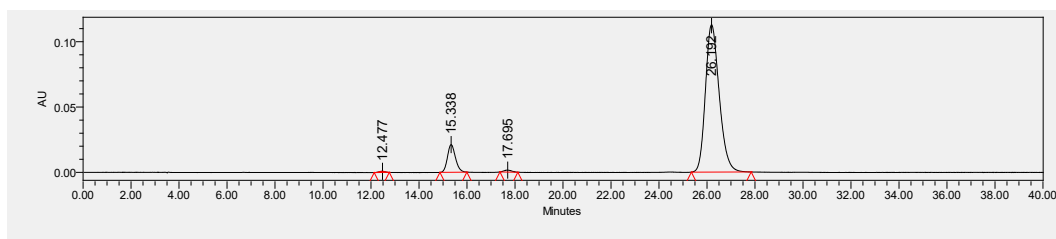
(major₂) = 15.338 min, t (minor₂) = 12.477 min.

¹H NMR (600 MHz, CDCl₃) δ 8.23 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.84 – 7.81 (m, 2H), 7.50 (t, J = 8.4 Hz, 2H), 7.42 (d, J = 1.8 Hz, 1H), 7.40 (d, J = 4.8 Hz, 1H), 7.32 (d, J = 8.6 Hz, 1H), 7.21 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 6.96 – 6.93 (m, 3H), 6.90 (t, J = 7.8 Hz, 1H), 6.62 (d, J = 8.4 Hz, 1H), 6.42 (d, J = 8.4 Hz, 1H), 6.37 (t, J = 7.2 Hz, 1H), 6.33 – 6.29 (m, 1H), 6.14 (d, J = 16.2 Hz, 1H), 4.43 (d, J = 15.6 Hz, 1H), 3.98 (d, J = 15.6 Hz, 1H), 3.75 (dd, J = 10.8, 6.6 Hz, 1H), 3.69 – 3.65 (m, 4H), 1.47 (septet, J = 6.6 Hz, 1H), 0.48 (d, J = 6.6 Hz, 3H), 0.42 (d, J = 6.6 Hz, 3H).

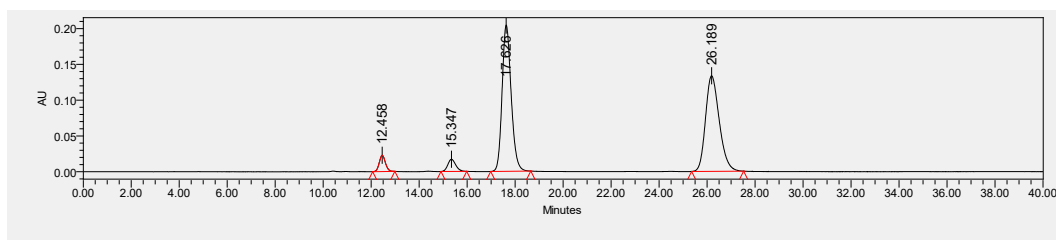
¹³C{¹H} NMR (151 MHz, CDCl₃) δ 194.07, 170.04, 167.44, 144.50, 139.19, 137.91, 136.98, 132.72, 132.20, 132.03, 131.88, 131.71, 130.87, 130.43, 129.99, 129.94, 129.76, 129.65, 129.42, 128.89, 128.70, 128.41, 127.68, 127.34, 126.67, 126.63, 125.94, 125.68, 125.60, 125.47, 125.40, 125.32, 124.01, 123.83, 123.38, 117.03, 72.22, 63.26, 51.56, 39.31, 29.74, 27.44, 18.53, 18.48.

ESI-HRMS: calcd for C₄₆H₃₆O₅Na⁺ ([M + Na]⁺) = 691.2455, found 691.2454.

IR (neat): 2956, 1716, 1506, 1265, 1201, 1168, 1033, 836, 736 cm⁻¹.

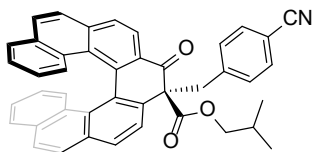


Retention Time	Area	% Area	Height
12.477	15668	0.31	911
15.338	488738	9.69	21213
17.695	33428	0.66	1503
26.192	4503928	89.33	112761



Retention Time	Area	% Area	Height
12.458	406723	3.55	22766
15.347	391189	3.41	17002
17.626	5363628	46.78	204351
26.189	5304328	46.26	133502

isobutyl (*P,S*)-9-(4-cyanobenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D13)



Following the typical procedure for the kinetic resolution.

(24 h) 25.6 mg, 42% yield; 8.7:1 dr., 99%/98% ee, bright yellow oil; R_f = 0.3 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/ i PrOH = 80/20, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 16.868 min, t (minor₁) = 13.509 min, t (major₂) =

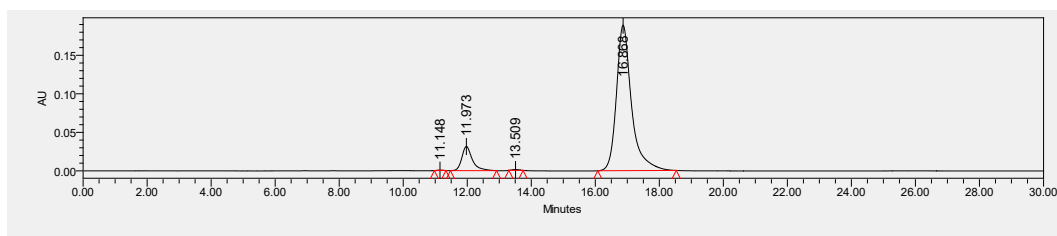
11.973 min, t (minor₂) = 11.148 min.

^1H NMR (600 MHz, CDCl_3) δ 8.22 (d, J = 7.8 Hz, 1H), 7.86 – 7.82 (m, 3H), 7.51 (t, J = 8.4 Hz, 2H), 7.42 (d, J = 9.0 Hz, 1H), 7.34 (d, J = 9.0 Hz, 1H), 7.24 – 7.20 (m, 4H), 7.01 (d, J = 8.4 Hz, 2H), 6.96 – 6.91 (m, 2H), 6.59 (d, J = 8.4 Hz, 1H), 6.41 (d, J = 8.4 Hz, 1H), 6.39 – 6.36 (m, 1H), 6.35 – 6.31 (m, 1H), 4.46 (d, J = 15.6 Hz, 1H), 3.99 (d, J = 15.6 Hz, 1H), 3.76 (dd, J = 10.8, 6.6 Hz, 1H), 3.67 (dd, J = 10.8, 6.6 Hz, 1H), 1.47 (septet, J = 6.6 Hz, 1H), 0.47 (d, J = 6.6 Hz, 3H), 0.41 (d, J = 6.6 Hz, 3H).

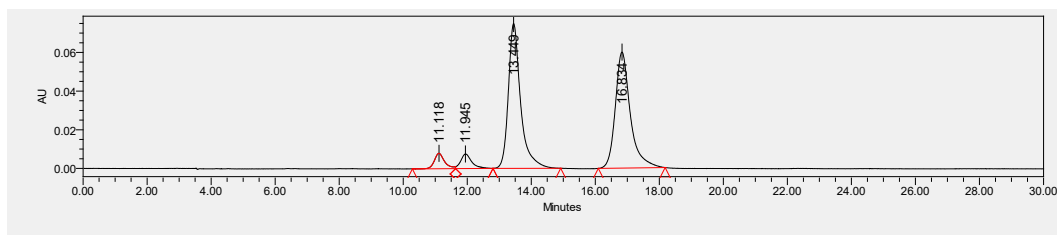
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.85, 169.75, 142.27, 137.91, 137.11, 132.80, 131.92, 131.73, 131.63, 131.50, 130.90, 130.71, 130.00, 129.93, 129.65, 129.42, 129.35, 128.83, 128.79, 128.53, 127.57, 126.76, 126.69, 126.02, 125.85, 125.54, 125.46, 125.32, 124.97, 123.96, 123.87, 123.52, 118.74, 110.02, 72.35, 63.12, 39.55, 27.43, 18.50, 18.44.

ESI-HRMS: calcd for $\text{C}_{43}\text{H}_{31}\text{NO}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 632.2196, found 632.2199.

IR (neat): 2961, 2229, 1726, 1267, 1202, 836, 743, 551 cm^{-1} .

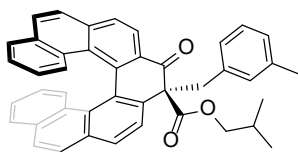


Retention Time	Area	% Area	Height
11.148	6643	0.10	532
11.973	716050	10.36	31415
13.509	16810	0.24	1085
16.868	6170943	89.30	188854



Retention Time	Area	% Area	Height
11.118	177582	4.13	7979
11.945	178562	4.15	7527
13.449	1991214	46.31	74897
16.834	1952173	45.40	59995

isobutyl (*P,S*)-9-(3-methylbenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D14)



Following the typical procedure for the kinetic resolution.

(3 h 10 min) 26.9 mg, 45% yield; 8.5:1 dr., 98%/92% ee, bright yellow oil; R_f = 0.42 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/ i PrOH = 95/5, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 8.740 min, t (minor₁) = 9.750 min, t (major₂) = 7.084

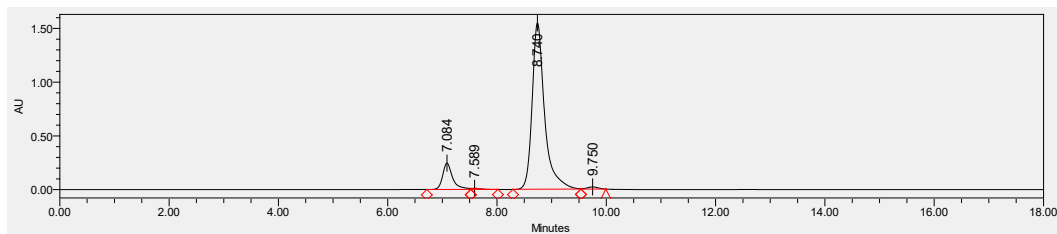
min, t (minor₂) = 7.589 min.

^1H NMR (600 MHz, CDCl_3) δ 8.24 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.83 – 7.81 (m, 2H), 7.50 (dd, J = 8.4, 6.0 Hz, 2H), 7.40 (d, J = 9.0 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.23 – 7.19 (m, 2H), 6.93 (t, J = 7.4 Hz, 1H), 6.89 (t, J = 9.0 Hz, 1H), 6.79 (t, J = 7.8 Hz, 1H), 6.69 (d, J = 7.2 Hz, 3H), 6.63 (d, J = 7.8 Hz, 1H), 6.41 (d, J = 8.4 Hz, 1H), 6.37 (t, J = 7.8 Hz, 1H), 6.31 (t, J = 7.2 Hz, 1H), 4.35 (d, J = 15.6 Hz, 1H), 3.92 (d, J = 15.6 Hz, 1H), 3.75 (dd, J = 10.8, 6.6 Hz, 1H), 3.67 (dd, J = 10.8, 6.6 Hz, 1H), 1.90 (s, 3H), 1.50 (septet, J = 6.6 Hz, 1H), 0.50 (d, J = 6.6 Hz, 3H), 0.45 (d, J = 6.6 Hz, 3H).

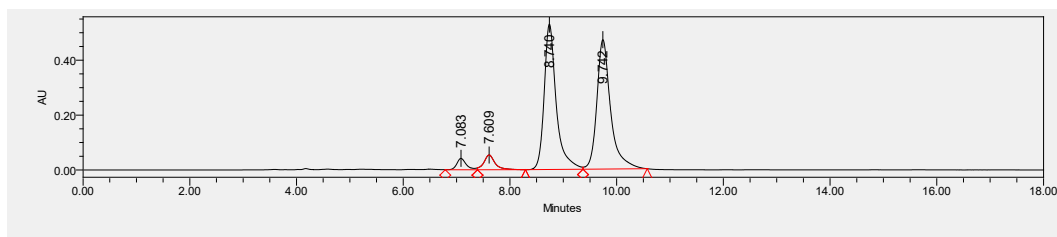
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.31, 170.32, 137.94, 137.24, 136.87, 136.11, 132.98, 132.60, 131.81, 131.69, 130.72, 130.67, 129.91, 129.75, 129.64, 129.49, 128.94, 128.57, 128.28, 127.71, 127.12, 126.82, 126.77, 126.58, 125.86, 125.72, 125.64, 125.53, 125.47, 125.41, 124.03, 123.78, 123.26, 72.04, 63.28, 39.90, 29.74, 27.47, 21.16, 18.58, 18.52.

ESI-HRMS: calcd for $\text{C}_{43}\text{H}_{34}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 621.2400, found 621.2400.

IR (neat): 2923, 1731, 1667, 1590, 1204, 838, 737, 701 cm^{-1} .

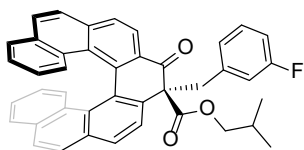


Retention Time	Area	% Area	Height
7.084	3108869	11.08	245642
7.589	119041	0.42	9716
8.740	24550497	87.48	1548594
9.750	287089	1.02	19855



Retention Time	Area	% Area	Height
7.083	513513	2.84	41379
7.609	778586	4.30	53645
8.740	8329420	46.00	529665
9.742	8484924	46.86	471480

isobutyl (*P,S*)-9-(3-fluorobenzyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D15)



Following the typical procedure for the kinetic resolution.

(12 h 15 min) 27.7 mg, 46% yield; 12.3:1 dr., 98%/99% ee, bright yellow oil; R_f = 0.42 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 9.194 min, t (minor₁) = 8.556 min, t (major₂) = 11.115 min, t (minor₂) = 12.842 min.

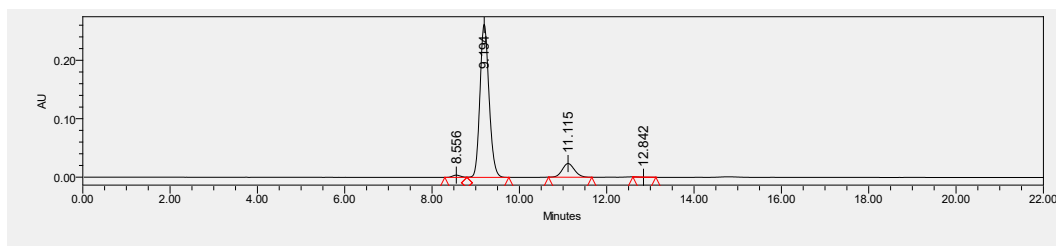
¹H NMR (600 MHz, CDCl₃) δ 8.25 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.84 – 7.82 (m, 2H), 7.50 (dd, J = 13.2, 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 9.0 Hz, 1H), 7.21 (dd, J = 12.0, 7.2 Hz, 2H), 6.94 (t, J = 7.2 Hz, 1H), 6.89 (t, J = 7.2 Hz, 1H), 6.86 (q, J = 7.8 Hz, 1H), 6.74 (dt, J = 10.2, 2.4 Hz, 1H), 6.67 (d, J = 7.8 Hz, 1H), 6.52 – 6.59 (m, 2H), 6.44 (d, J = 8.4 Hz, 1H), 6.37 (ddd, J = 8.4, 6.6, 1.2 Hz, 1H), 6.32 (ddd, J = 8.4, 6.6, 1.2 Hz, 1H), 4.41 (d, J = 15.0 Hz, 1H), 3.95 (d, J = 15.0 Hz, 1H), 3.74 (dd, J = 10.8, 6.6 Hz, 1H), 3.65 (dd, J = 10.8, 6.6 Hz, 1H), 1.47 (septet, J = 6.6 Hz, 1H), 0.48 (d, J = 6.6 Hz, 3H), 0.41 (d, J = 6.6 Hz, 3H).

¹³C{¹H} NMR (151 MHz, CDCl₃) δ 194.06, 170.00, 162.28 (d, J = 244.9 Hz), 138.98 (d, J = 7.6 Hz), 137.92, 136.98, 132.72, 131.96, 131.87, 131.71, 130.85, 129.94, 129.74, 129.67 (d, J = 5.7 Hz), 129.44, 129.23, 129.18, 128.90, 128.66, 128.39, 127.29, 126.62, 125.92, 125.73, 125.64, 125.59, 125.54, 125.52, 125.48, 125.41, 125.29, 124.04, 123.82, 123.35, 117.00 (d, J = 21.9 Hz), 113.07 (d, J = 21.1 Hz), 72.20, 63.26, 39.04, 27.43, 18.52, 18.47.

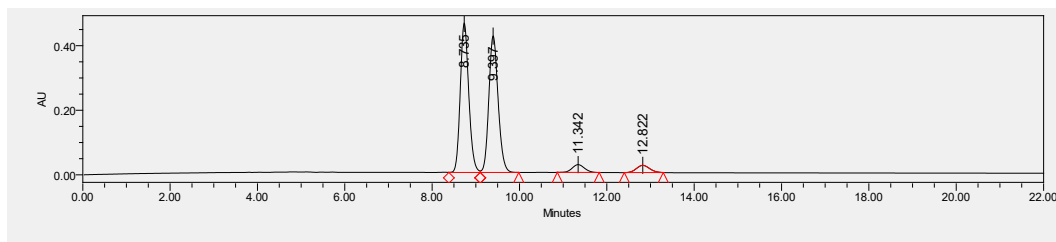
¹⁹F{¹H} NMR (564 MHz, CDCl₃) δ -113.72.

ESI-HRMS: calcd for C₄₂H₃₁FO₃Na⁺ ($[M + Na]^+$) = 625.2149, found 625.2152.

IR (neat): 2959, 1733, 1669, 1578, 1495, 1208, 840, 787, 689 cm⁻¹.

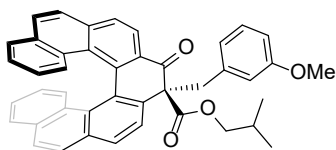


Retention Time	Area	% Area	Height
8.556	48741	1.14	3804
9.194	3783328	88.22	261800
11.115	452686	10.56	23381
12.842	3748	0.09	232



Retention Time	Area	% Area	Height
8.735	6239867	46.52	461876
9.397	6227533	46.43	422549
11.342	474289	3.54	24185
12.822	470837	3.51	22315

isobutyl (*P*, *S*)-9-(3-methoxybenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D16)



Following the typical procedure for the kinetic resolution.

(4 h) 28.9 mg, 47% yield; 8.0:1 dr., 99%/94% ee, bright yellow oil; $R_f = 0.33$ (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: $t(\text{major}_1) = 9.134$ min, $t(\text{minor}_1) = 10.751$ min, $t(\text{major}_2) =$

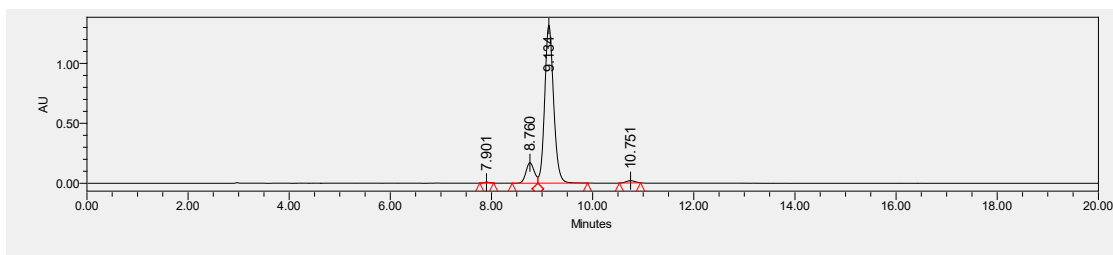
8.760 min, $t(\text{minor}_2) = 7.901$ min.

^1H NMR (600 MHz, CDCl_3) δ 8.25 (d, $J = 7.8$ Hz, 1H), 7.89 (d, $J = 7.8$ Hz, 1H), 7.83 (d, $J = 7.8$ Hz, 1H), 7.82 (d, $J = 8.4$ Hz, 1H), 7.51 (d, $J = 8.4$ Hz, 1H), 7.49 (d, $J = 8.4$ Hz, 1H), 7.40 (d, $J = 9.0$ Hz, 1H), 7.31 (d, $J = 9.0$ Hz, 1H), 7.22 (d, $J = 8.4$ Hz, 1H), 7.20 (d, $J = 7.8$ Hz, 1H), 6.93 (t, $J = 7.2$ Hz, 1H), 6.89 (t, $J = 7.8$ Hz, 1H), 6.84 (t, $J = 7.8$ Hz, 1H), 6.62 (d, $J = 8.4$ Hz, 1H), 6.52 (d, $J = 7.8$ Hz, 1H), 6.45 – 6.40 (m, 3H), 6.37 (t, $J = 7.8$ Hz, 1H), 6.31 (t, $J = 7.8$ Hz, 1H), 4.39 (d, $J = 15.6$ Hz, 1H), 3.95 (d, $J = 15.6$ Hz, 1H), 3.76 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.67 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.31 (s, 3H), 1.48 (septet, $J = 6.6$ Hz, 1H), 0.49 (d, $J = 6.6$ Hz, 3H), 0.42 (d, $J = 6.6$ Hz, 3H).

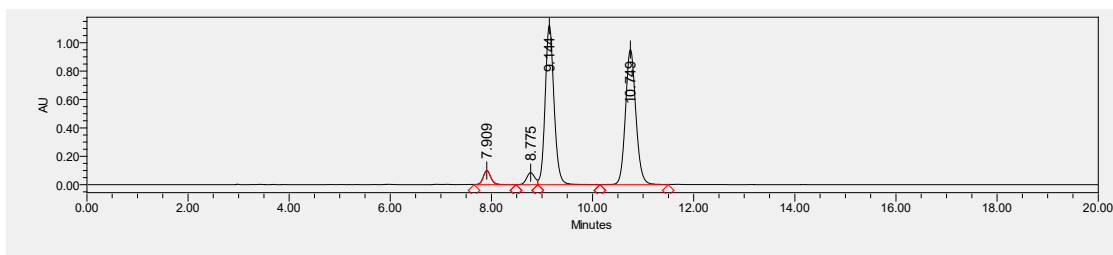
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.08, 170.20, 158.94, 137.97, 137.83, 136.91, 132.75, 132.64, 131.83, 131.70, 130.67, 129.94, 129.68, 129.64, 129.47, 128.88, 128.80, 128.61, 128.31, 127.21, 126.61, 126.59, 125.88, 125.70, 125.63, 125.59, 125.48, 125.39, 124.07, 123.79, 123.32, 122.34, 114.91, 112.22, 72.12, 63.18, 54.70, 39.75, 27.45, 18.55, 18.49.

ESI-HRMS: calcd for $\text{C}_{43}\text{H}_{34}\text{O}_4\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 637.2349, found 637.2351.

IR (neat): 2958, 1732, 1668, 1591, 1496, 1263, 1207, 1041, 840, 745 cm^{-1} .

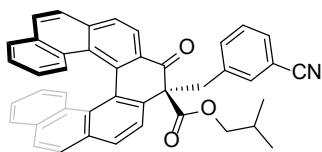


Retention Time	Area	% Area	Height
7.901	57812	0.32	6717
8.760	1946840	10.64	170605
9.134	16061897	87.79	1318135
10.751	229978	1.26	18564



Retention Time	Area	% Area	Height
7.909	1055549	3.61	99729
8.775	955426	3.27	84395
9.144	13619256	46.61	1122387
10.749	13590785	46.51	951314

isobutyl (*P,S*)-9-(3-cyanobenzyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D17)



Following the typical procedure for the kinetic resolution.

(53 h 50 min) 26.8 mg, 44% yield; 9.0:1 dr., 98%/94% ee, bright yellow oil; R_f = 0.31 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **ID** column), n-hexane/PrOH = 80/20, flow rate

1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 19.380 min, t (minor₁) = 15.957 min, t (major₂) =

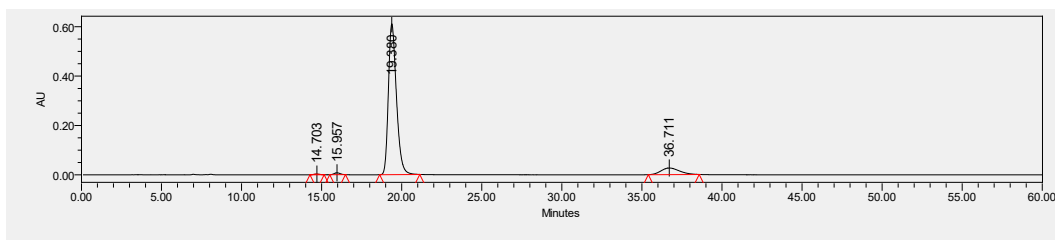
36.711 min, t (minor₂) = 14.703 min.

¹H NMR (600 MHz, CDCl₃) δ 8.24 (d, J = 7.8 Hz, 1H), 7.87 – 7.83 (m, 3H), 7.52 – 7.50 (m, 2H), 7.41 (d, J = 8.4 Hz, 1H), 7.37 (s, 1H), 7.33 (d, J = 9.0 Hz, 1H), 7.23 – 7.18 (m, 3H), 7.07 (d, J = 7.8 Hz, 1H), 6.97 – 6.90 (m, 3H), 6.57 (d, J = 7.8 Hz, 1H), 6.40 – 6.35 (m, 2H), 6.32 (t, J = 7.2 Hz, 1H), 4.43 (d, J = 15.0 Hz, 1H), 3.94 (d, J = 15.0 Hz, 1H), 3.76 (dd, J = 10.8, 6.6 Hz, 1H), 3.67 (dd, J = 10.8, 6.6 Hz, 1H), 1.47 (septet, J = 6.6 Hz, 1H), 0.48 (d, J = 6.6 Hz, 3H), 0.41 (d, J = 6.6 Hz, 3H).

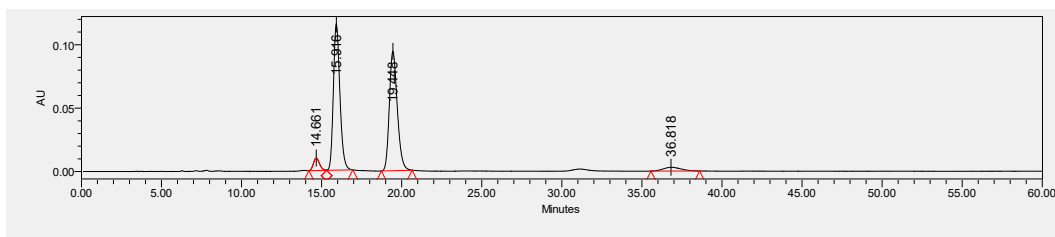
¹³C{¹H} NMR (151 MHz, CDCl₃) δ 193.99, 169.76, 138.00, 137.88, 137.09, 134.33, 133.91, 132.78, 131.91, 131.71, 131.50, 130.91, 130.02, 129.89, 129.63, 129.47, 129.35, 128.80, 128.77, 128.59, 128.53, 127.53, 126.72, 126.66, 125.99, 125.78, 125.60, 125.52, 125.46, 125.33, 124.99, 124.00, 123.85, 123.46, 118.72, 111.92, 72.31, 63.21, 39.13, 29.73, 27.43, 18.50, 18.45.

ESI-HRMS: calcd for C₄₃H₃₁NO₃Na⁺ ($[M + Na]^+$) = 632.2196, found 632.2194.

IR (neat): 2962, 2231, 1731, 1578, 1269, 1208, 841, 750, 690 cm⁻¹.

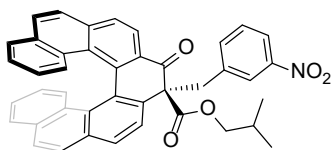


Retention Time	Area	% Area	Height
14.703	68126	0.29	2703
15.957	202649	0.85	7674
19.380	21355113	89.86	611149
36.711	2137676	9.00	26702



Retention Time	Area	% Area	Height
14.661	261449	3.73	9835
15.916	3255006	46.49	115260
19.448	3252978	46.46	94130
36.818	232720	3.32	2988

isobutyl (*P,S*)-9-(3-nitrobenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D18)



Following the typical procedure for the kinetic resolution.

(74 h 40 min) 25.2 mg, 40% yield; 11.4:1 dr., 98%/90% ee, bright yellow oil; R_f = 0.28 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **ID** column), n-hexane/PrOH = 80/20, flow rate

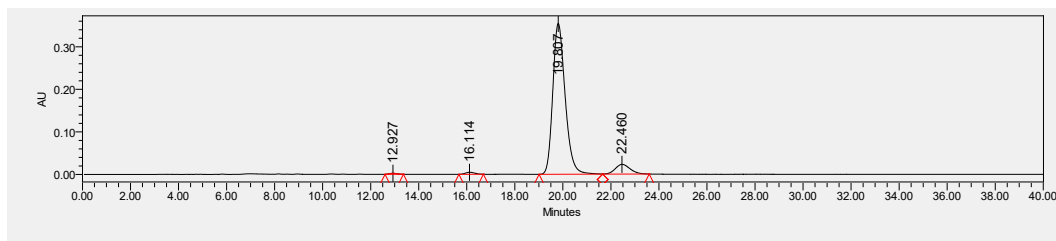
1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 19.807 min, t (minor₁) = 16.114 min, t (major₂) = 22.460 min, t (minor₂) = 12.927 min.

¹H NMR (600 MHz, CDCl₃) δ 8.25 (d, J = 7.8 Hz, 1H), 7.88 – 7.87 (m, 3H), 7.83 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.24 – 7.19 (m, 3H), 7.06 (t, J = 7.8 Hz, 1H), 6.94 (t, J = 7.8 Hz, 1H), 6.90 (t, J = 7.8 Hz, 1H), 6.58 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 8.4 Hz, 1H), 6.37 (t, J = 7.8, 1H), 6.31 (t, J = 7.8, 1H), 4.51 (d, J = 15.6 Hz, 1H), 4.03 (d, J = 15.6 Hz, 1H), 3.78 (dd, J = 10.8, 6.6 Hz, 1H), 3.70 (dd, J = 10.8, 6.6 Hz, 1H), 1.48 (septet, J = 6.6 Hz, 1H), 0.48 (d, J = 6.6 Hz, 3H), 0.42 (d, J = 6.6 Hz, 3H).

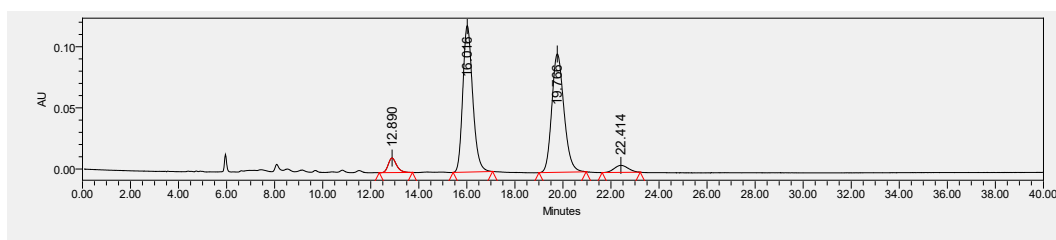
¹³C{¹H} NMR (151 MHz, CDCl₃) δ 193.94, 169.69, 147.69, 138.54, 137.95, 137.11, 136.05, 132.83, 131.90, 131.72, 131.47, 130.90, 130.05, 129.91, 129.64, 129.45, 129.35, 128.90, 128.75, 128.71, 128.52, 127.54, 126.71, 126.67, 125.99, 125.78, 125.58, 125.53, 125.45, 125.31, 125.12, 124.91, 124.01, 123.86, 123.46, 121.34, 72.35, 63.14, 39.23, 27.44, 18.50, 18.45.

ESI-HRMS: calcd for C₄₂H₃₁NO₅Na⁺ ([M + Na]⁺) = 652.2094, found 652.2095.

IR (neat): 2962, 1731, 1529, 1469, 1276, 1207, 840, 736 cm⁻¹.

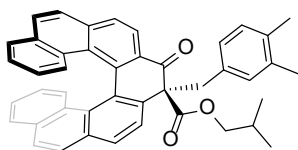


Retention Time	Area	% Area	Height
12.927	50971	0.37	2370
16.114	126272	0.92	4728
19.807	12632173	91.55	354374
22.460	988948	7.17	22852



Retention Time	Area	% Area	Height
12.886	245019	3.36	11194
16.016	3418751	46.84	119779
19.766	3400174	46.58	96755
22.414	235295	3.22	5771

isobutyl (*P,S*)-9-(3,4-dimethylbenzyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D19)



Following the typical procedure for the kinetic resolution.

(2 h 30 min) 27.0 mg, 44% yield; 7.6:1 dr., 97%/95% ee, bright yellow oil; R_f = 0.43 (PE/EA = 9/1).

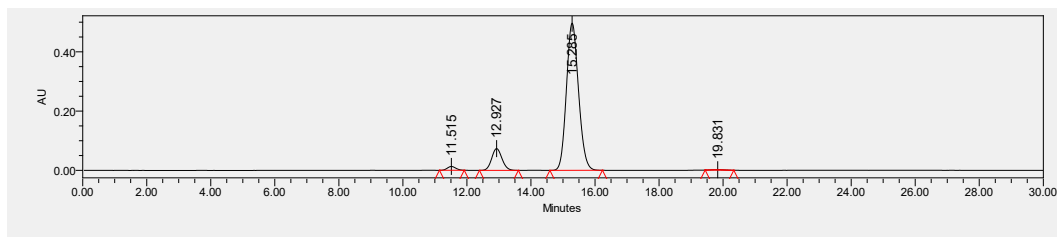
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 15.285 min, t (minor₁) = 11.515 min, t (major₂) =

12.927 min, t (minor₂) = 19.831 min.

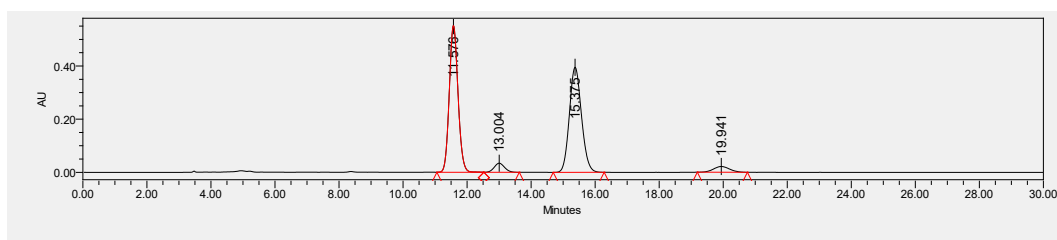
¹H NMR (600 MHz, CDCl₃) δ 8.24 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 9.0 Hz, 2H), 7.39 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 7.8 Hz, 2H), 6.93 (t, J = 7.2 Hz, 1H), 6.89 (t, J = 7.2 Hz, 1H), 6.67 – 6.59 (m, 4H), 6.39 – 6.35 (m, 2H), 6.30 (t, J = 7.8 Hz, 1H), 4.30 (d, J = 15.0 Hz, 1H), 3.88 (d, J = 15.0 Hz, 1H), 3.76 (dd, J = 10.8, 6.6 Hz, 1H), 3.68 (dd, J = 10.8, 6.6 Hz, 1H), 1.90 (s, 3H), 1.76 (s, 3H), 1.51 (septet, J = 6.6 Hz, 1H), 0.51 (d, J = 6.6 Hz, 3H), 0.45 (d, J = 6.6 Hz, 3H).

¹³C{¹H} NMR (151 MHz, CDCl₃) δ 194.38, 170.39, 137.95, 136.84, 135.79, 134.16, 133.42, 133.23, 132.57, 131.81, 131.69, 131.22, 130.63, 129.97, 129.78, 129.61, 129.50, 129.08, 128.95, 128.56, 128.25, 127.10, 126.56, 125.84, 125.73, 125.67, 125.58, 125.56, 125.50, 125.46, 125.41, 124.03, 123.77, 123.22, 72.01, 63.34, 39.75, 27.48, 19.44, 19.06, 18.59, 18.53. **ESI-HRMS**: calcd for C₄₄H₃₆O₃Na⁺ ([M + Na]⁺) = 635.2557, found 635.2560.

IR (neat): 2960, 2928, 1733, 1669, 1588, 1506, 1449, 1269, 1207, 839, 746 cm⁻¹.

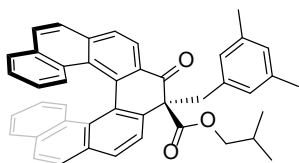


Retention Time	Area	% Area	Height
11.515	236186	1.58	12840
12.927	1636163	10.94	73413
15.285	13034140	87.19	496429
19.831	43092	0.29	1548



Retention Time	Area	% Area	Height
11.576	10435461	46.69	551580
13.004	770057	3.45	34175
15.375	10386018	46.47	395016
19.941	757482	3.39	21571

isobutyl (*P, S*)-9-(3,5-dimethylbenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D20)



Following the typical procedure for the kinetic resolution.

(3 h 30 min) 30.6 mg, 50% yield; 6.0:1 dr., 97%/94% ee, bright yellow oil; $R_f = 0.43$ (PE/EA = 9/1).

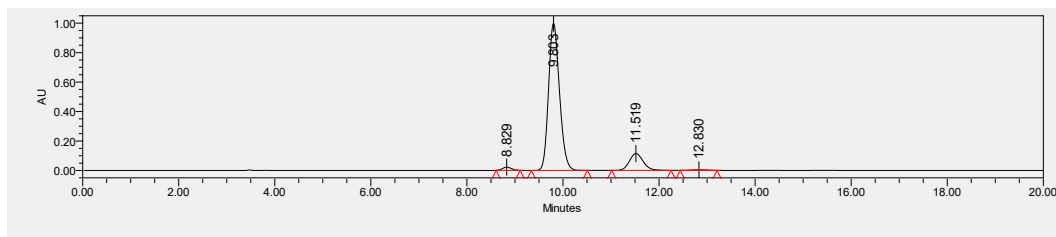
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major₁) = 9.803 min, t (minor₁) = 8.829 min, t (major₂) = 11.519 min, t (minor₂) = 12.830 min.

¹H NMR (600 MHz, CDCl₃) δ 8.25 (d, $J = 8.4$ Hz, 1H), 7.87 (d, $J = 7.8$ Hz, 1H), 7.83 – 7.79 (m, 2H), 7.49 (dd, $J = 8.4, 5.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 1H), 7.31 (d, $J = 9.0$ Hz, 1H), 7.21 (dd, $J = 10.2, 8.4$ Hz, 2H), 6.93 (t, $J = 7.2$ Hz, 1H), 6.88 (d, $J = 7.2$ Hz, 1H), 6.63 (d, $J = 8.4$ Hz, 1H), 6.49 (s, 1H), 6.46 (s, 2H), 6.41 – 6.35 (m, 2H), 6.31 (t, $J = 7.8$ Hz, 1H), 4.28 (d, $J = 15.0$ Hz, 1H), 3.87 (d, $J = 15.0$ Hz, 1H), 3.76 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.67 (dd, $J = 10.8, 6.6$ Hz, 1H), 1.86 (s, 6H), 1.51 (septet, $J = 6.6$ Hz, 1H), 0.51 (d, $J = 6.6$ Hz, 3H), 0.46 (d, $J = 6.6$ Hz, 3H).

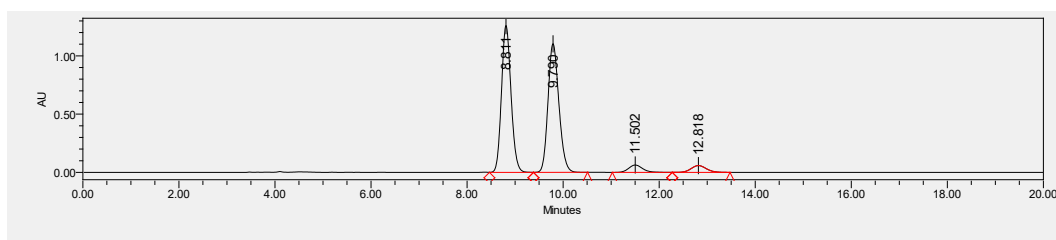
¹³C{¹H} NMR (151 MHz, CDCl₃) δ 194.42, 170.37, 137.97, 137.07, 136.84, 135.94, 133.44, 132.54, 131.79, 131.68, 130.54, 129.91, 129.73, 129.62, 129.50, 128.93, 128.56, 128.24, 127.71, 127.63, 127.07, 126.56, 125.83, 125.68, 125.65, 125.50, 125.48, 125.46, 125.37, 124.01, 123.76, 123.23, 71.98, 63.23, 40.24, 27.48, 21.04, 18.58, 18.53.

ESI-HRMS: calcd for C₄₄H₃₆O₃Na⁺ ($[M + Na]^+$) = 635.2557, found 635.2555.

IR (neat): 2959, 2924, 1734, 1599, 1507, 1462, 1669, 1268, 1208, 841, 748 cm⁻¹.

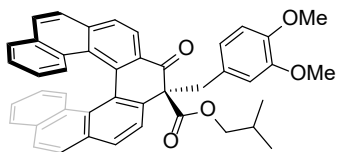


Retention Time	Area	% Area	Height
8.829	279926	1.52	21411
9.803	15768576	85.64	999939
11.519	2291144	12.44	114933
12.830	73570	0.40	3508



Retention Time	Area	% Area	Height
8.811	17380730	46.55	1259571
9.790	17398599	46.60	1102937
11.502	1274109	3.41	62944
12.818	1281439	3.43	58190

isobutyl (*P*, *S*)-9-(3,4-dimethoxybenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D21)



Following the typical procedure for the kinetic resolution.

(2 h 40 min) 36.1 mg, 56% yield; 4.8:1 dr., 96%/96% ee, bright yellow oil; R_f = 0.25 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/ i PrOH = 90/10, flow rate

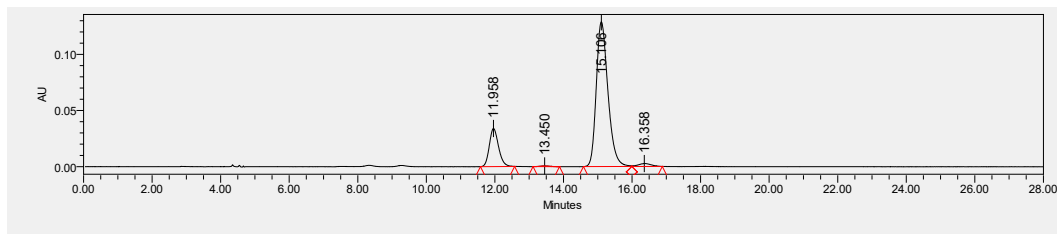
1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 15.106 min, t (minor₁) = 16.358 min, t (major₂)

= 11.958 min, t (minor₂) = 13.450 min.

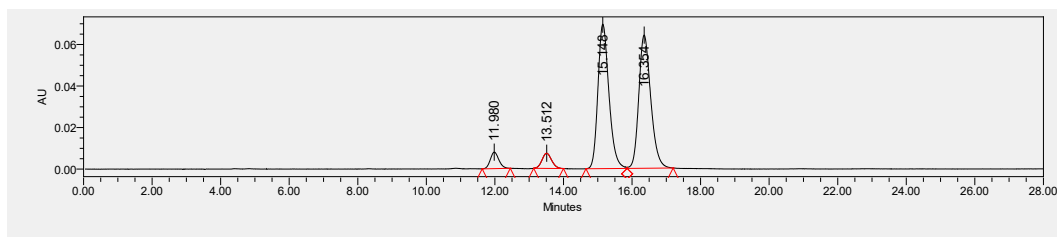
^1H NMR (600 MHz, CDCl_3) δ 8.25 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.50 (dd, J = 8.4, 5.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 7.8 Hz, 2H), 6.93 (t, J = 7.2 Hz, 1H), 6.89 (t, J = 7.2 Hz, 1H), 6.59 (d, J = 8.4 Hz, 1H), 6.41 – 6.35 (m, 4H), 6.33 – 6.27 (m, 2H), 4.30 (d, J = 14.4 Hz, 1H), 3.89 (d, J = 14.4 Hz, 1H), 3.79 (dd, J = 10.8, 6.6 Hz, 1H), 3.71 (dd, J = 10.8, 6.6 Hz, 1H), 3.56 (s, 3H), 3.28 (s, 3H), 1.50 (septet, J = 6.6 Hz, 1H), 0.49 (d, J = 6.6 Hz, 3H), 0.43 (d, J = 6.6 Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.18, 170.25, 147.91, 147.10, 138.00, 136.89, 133.43, 132.61, 131.80, 131.68, 130.57, 130.06, 129.71, 129.60, 129.50, 129.45, 128.80, 128.56, 128.49, 128.29, 127.30, 126.63, 126.59, 125.85, 125.63, 125.60, 125.46, 125.43, 125.24, 123.98, 123.75, 123.42, 122.29, 112.91, 110.51, 72.03, 63.23, 55.53, 55.20, 40.13, 27.47, 18.54, 18.49. **ESI-HRMS**: calcd for $\text{C}_{44}\text{H}_{36}\text{O}_5\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 667.2455, found 667.2454.

IR (neat): 2959, 1733, 1703, 1591, 1513, 1261m 1149, 1028, 843, 753 cm^{-1} .

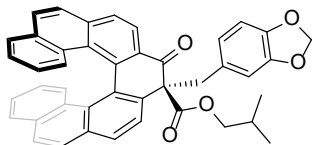


Retention Time	Area	% Area	Height
11.958	632014	16.82	33939
13.450	11725	0.31	631
15.106	3046177	81.05	128957
16.358	68597	1.83	2598



Retention Time	Area	% Area	Height
11.980	136946	4.05	7936
13.512	142888	4.22	7327
15.148	1552592	45.87	69557
16.354	1552550	45.87	64120

isobutyl (*P*, *S*)-9-(benzo[d][1,3]dioxol-5-ylmethyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D22)



Following the typical procedure for the kinetic resolution.

(3 h 30 min) 32.1 mg, 51% yield; 7.7:1 dr., 97%/98% ee, bright yellow oil; R_f = 0.28 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 21.437 min, t (minor₁) = 16.670 min, t (major₂) =

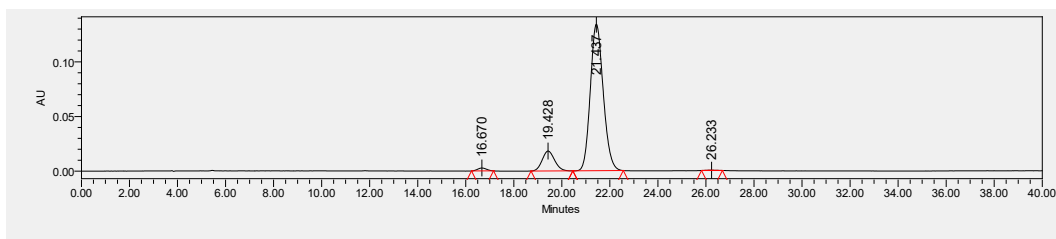
21.437 min, t (minor₂) = 26.233 min.

^1H NMR (600 MHz, CDCl_3) δ 8.25 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.50 (dd, J = 9.0, 3.0 Hz, 2H), 7.40 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 7.8 Hz, 2H), 6.93 (t, J = 7.2 Hz, 1H), 6.89 (t, J = 7.2 Hz, 1H), 6.60 (d, J = 8.4 Hz, 1H), 6.47 – 6.43 (m, 2H), 6.41 (d, J = 8.4 Hz, 1H), 6.37 (d, J = 8.4 Hz, 2H), 6.32 (t, J = 7.8 Hz, 1H), 5.64 (s, 1H), 5.57 (s, 1H), 4.32 (d, J = 15.0 Hz, 1H), 3.85 (d, J = 15.0 Hz, 1H), 3.75 (dd, J = 10.8, 6.6 Hz, 1H), 3.66 (dd, J = 10.8, 6.6 Hz, 1H), 1.48 (septet, J = 6.6 Hz, 1H), 0.49 (d, J = 6.6 Hz, 3H), 0.43 (d, J = 6.6 Hz, 3H).

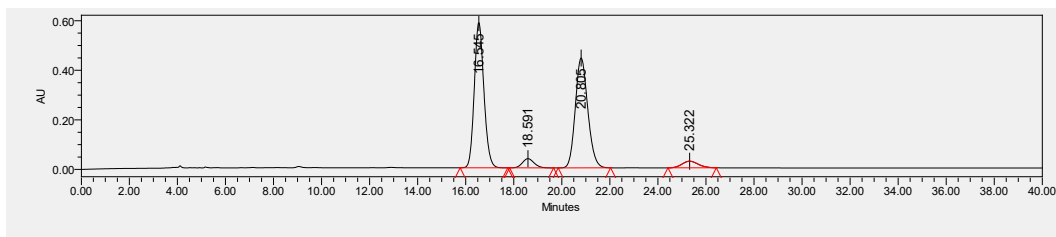
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.32, 170.20, 147.02, 145.74, 137.94, 136.91, 132.64, 132.59, 131.83, 131.68, 130.74, 129.99, 129.88, 129.72, 129.68, 129.63, 129.47, 128.93, 128.57, 128.31, 127.19, 126.62, 126.58, 125.87, 125.77, 125.60, 125.57, 125.51, 125.46, 125.44, 124.03, 123.78, 123.29, 123.23, 110.47, 107.65, 100.52, 72.09, 63.51, 39.49, 27.45, 18.55, 18.50.

ESI-HRMS: calcd for $\text{C}_{43}\text{H}_{32}\text{O}_5\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 651.2142, found 651.2142.

IR (neat): 2924, 1730, 1667, 1491, 1442, 1204, 1037, 933, 839, 737 cm^{-1} .

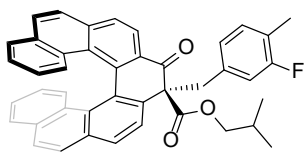


Retention Time	Area	% Area	Height
16.670	69259	1.20	2660
19.428	654386	11.38	18229
21.437	5018700	87.29	134134
26.233	7309	0.13	232



Retention Time	Area	% Area	Height
16.545	16280106	46.84	585848
18.591	1250322	3.60	36994
20.805	15974325	45.96	443034
25.322	1252235	3.60	26703

isobutyl (*P, S*)-9-(3-fluoro-4-methylbenzyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D23)



Following the typical procedure for the kinetic resolution.

(5 h 45 min) 28.4 mg, 46% yield; 8.6:1 dr., 98%/94% ee, bright yellow oil; R_f = 0.41 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 8.907 min, t (minor₁) = 7.110 min, t (major₂) = 6.458 min, t (minor₂) = 6.211 min.

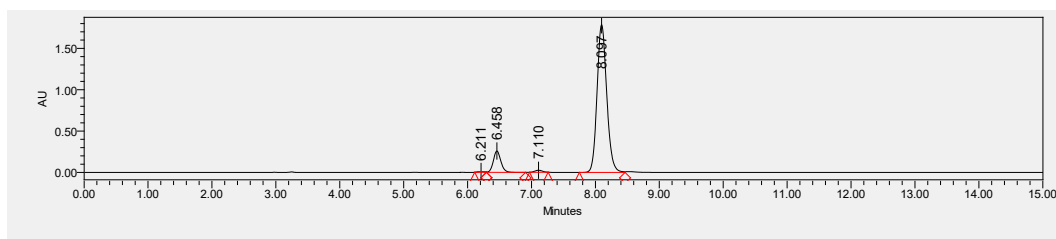
¹H NMR (600 MHz, CDCl₃) δ 8.25 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.84 – 7.82 (m, 2H), 7.50 (dd, J = 10.8, 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.23 – 7.20 (m, 2H), 6.94 (t, J = 7.2 Hz, 1H), 6.90 (t, J = 7.2 Hz, 1H), 6.71 – 6.66 (m, 2H), 6.61 (d, J = 8.4 Hz, 1H), 6.56 (d, J = 7.8 Hz, 1H), 6.45 (d, J = 8.4 Hz, 1H), 6.37 (t, J = 7.2 Hz, 1H), 6.32 (t, J = 7.2 Hz, 1H), 4.37 (d, J = 15.6 Hz, 1H), 3.91 (d, J = 15.6 Hz, 1H), 3.74 (dd, J = 10.8, 6.6 Hz, 1H), 3.65 (dd, J = 10.8, 6.6 Hz, 1H), 1.96 (s 3H), 1.46 (septet, J = 6.6 Hz, 1H), 0.48 (d, J = 6.6 Hz, 3H), 0.41 (d, J = 6.6 Hz, 3H).

¹³C{¹H} NMR (151 MHz, CDCl₃) δ 194.10, 170.06, 160.67 (d, J = 244.3 Hz), 137.92, 136.94, 135.98 (d, J = 7.6 Hz), 132.69, 132.07, 131.85, 131.70, 130.85, 130.71 (d, J = 5.4 Hz), 129.93, 129.74, 129.70, 129.64, 129.44, 128.92, 128.62, 128.35, 127.23, 126.62, 126.59, 125.90, 125.75, 125.60, 125.48, 125.43, 125.40, 125.24 (d, J = 3.0 Hz), 124.05, 123.80, 123.30, 122.38 (d, J = 17.2 Hz), 116.59 (d, J = 22.8 Hz), 72.16, 63.30, 38.70, 29.74, 27.43, 18.53, 18.47, 13.98, 13.96.

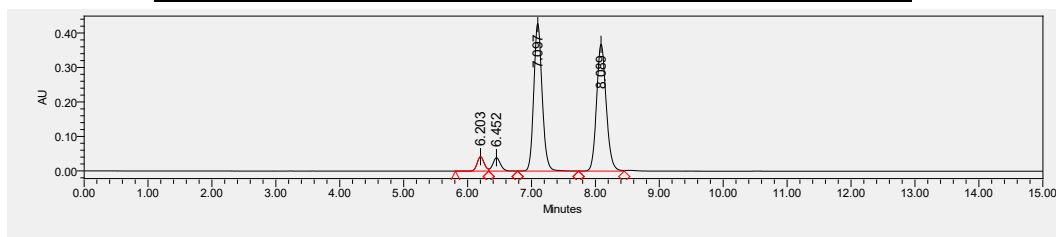
¹⁹F{¹H} NMR (564 MHz, CDCl₃) δ -118.13.

ESI-HRMS: calcd for C₄₃H₃₁FO₃Na⁺ ($[M + Na]^+$) = 639.2306, found 639.2307.

IR (neat): 2960, 1732, 1670, 1509, 1264, 1207, 839, 655 cm⁻¹.

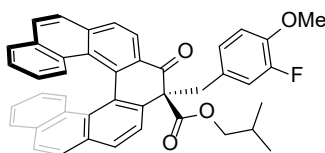


Retention Time	Area	% Area	Height
6.211	68943	0.33	10355
6.458	2104842	9.95	257892
7.110	198194	0.94	24216
8.097	18781442	88.79	1785080



Retention Time	Area	% Area	Height
6.203	324222	3.85	41925
6.452	327025	3.88	38886
7.097	3907567	46.36	428172
8.089	3869655	45.91	367649

isobutyl (*P,S*)-9-(3-fluoro-4-methoxybenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D24)



Following the typical procedure for the kinetic resolution.

(4 h) 29.1 mg, 46% yield; 10.9:1 dr., 98%/97% ee, bright yellow oil; R_f = 0.33 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA-3** column), n-hexane/ i PrOH = 90/10, flow rate

1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 15.064 min, t (minor₁) = 12.377 min, t (major₂)

= 10.112 min, t (minor₂) = 9.872 min.

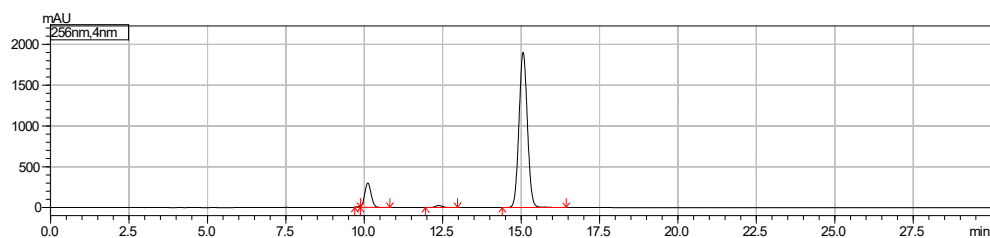
¹H NMR (600 MHz, CDCl₃) δ 8.24 (d, J = 7.8 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.51 (dd, J = 8.4, 1.8 Hz, 2H), 7.40 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 8.4 Hz, 2H), 6.94 (t, J = 7.2 Hz, 1H), 6.90 (t, J = 7.2 Hz, 1H), 6.79 (dd, J = 13.8, 2.4 Hz, 1H), 6.59 (d, J = 8.4 Hz, 1H), 6.53 (d, J = 9.0 Hz, 1H), 6.44 (t, J = 9.0 Hz, 2H), 6.37 (t, J = 7.8 Hz, 1H), 6.32 (t, J = 7.8 Hz, 1H), 4.32 (d, J = 15.0 Hz, 1H), 3.87 (d, J = 15.0 Hz, 1H), 3.75 (dd, J = 10.8, 6.6 Hz, 1H), 3.66 (dd, J = 10.8, 6.6 Hz, 1H), 3.57 (s, 3H), 1.47 (septet, J = 6.6 Hz, 1H), 0.48 (d, J = 6.6 Hz, 3H), 0.42 (d, J = 6.6 Hz, 3H).

¹³C{¹H} NMR (151 MHz, CDCl₃) δ 194.17, 170.07, 151.55 (d, J = 244.8 Hz), 145.77 (d, J = 10.7 Hz), 137.91, 136.95, 132.69, 132.26, 131.86, 131.70, 130.84, 129.98, 129.72, 129.68, 129.63, 129.44, 129.27 (d, J = 6.0 Hz), 128.91, 128.62, 128.36, 127.28, 126.63, 126.61, 125.90, 125.75, 125.63, 125.59, 125.47, 125.41, 125.37, 124.02, 123.80, 123.34, 117.93 (d, J = 18.7 Hz), 112.67, 72.14, 63.38, 55.92, 38.69, 27.44, 18.53, 18.48.

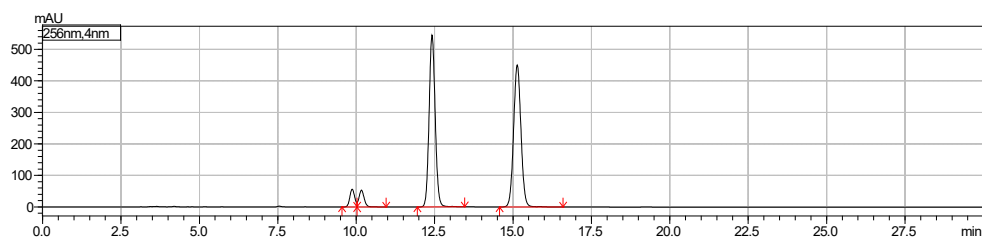
¹⁹F{¹H} NMR (564 MHz, CDCl₃) δ -135.35 (d, J = 5.6 Hz).

ESI-HRMS: calcd for C₄₃H₃₃FO₄Na⁺ ($[M + Na]^+$) = 655.2255, found 655.2256.

IR (neat): 2960, 1731, 1688, 1514, 1443, 1272, 1211, 1126, 1031, 840, 743 cm⁻¹.

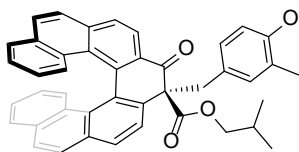


Retention Time	Area	% Area	Height
9.872	73918	0.184	11503
10.112	4237166	10.552	298756
12.377	418679	1.043	25829
15.064	35426609	88.222	11902260



Retention Time	Area	% Area	Height
9.871	614977	3.852	56490
10.167	605941	3.796	53190
12.418	7376809	46.210	545340
15.134	7365834	46.142	450587

isobutyl (*P*, *S*)-9-(3-methyl-4-methoxybenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D25)



Following the typical procedure for the kinetic resolution.

(2 h 40 min) 35.2 mg, 56% yield; 5.1:1 dr., 95%/97% ee, bright yellow oil; R_f = 0.35 (PE/EA = 9/1).

Dissolved in *n*-hexane for HPLC; **HPLC** (Chiralcel **AD-H** column), *n*-hexane/*i*PrOH = 90/10, flow rate 0.5 mL/min, λ = 243 nm, retention time: t (major₁) = 23.805 min, t (minor₁) = 19.076 min, t

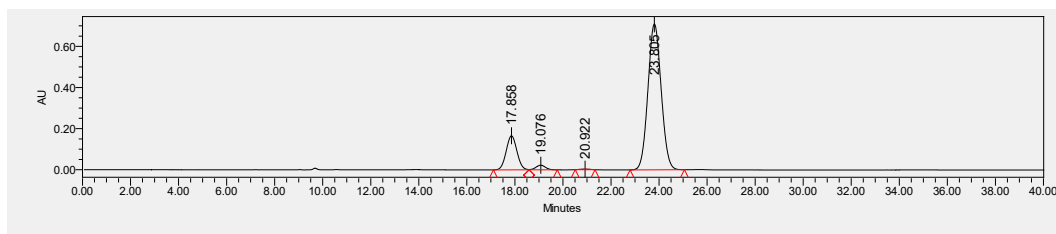
(major₂) = 17.858 min, t (minor₂) = 20.922 min.

¹H NMR (600 MHz, CDCl₃) δ 8.24 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.50 (dd, J = 8.4, 4.2 Hz, 2H), 7.39 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 7.8 Hz, 2H), 6.93 (t, J = 7.8 Hz, 1H), 6.89 (t, J = 7.8 Hz, 1H), 6.68 (s, 1H), 6.62 (d, J = 8.4 Hz, 1H), 6.59 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 8.4 Hz, 1H), 6.38 – 6.35 (m, 1H), 6.32 – 6.29 (m, 2H), 4.27 (d, J = 15.0 Hz, 1H), 3.86 (d, J = 15.0 Hz, 1H), 3.77 – 3.74 (m, 1H), 3.70 – 3.66 (m, 1H), 3.51 (s, 3H), 1.80 (s, 3H), 1.51 (septet, J = 6.6 Hz, 1H), 0.51 (d, J = 6.6 Hz, 3H), 0.45 (d, J = 6.6 Hz, 3H).

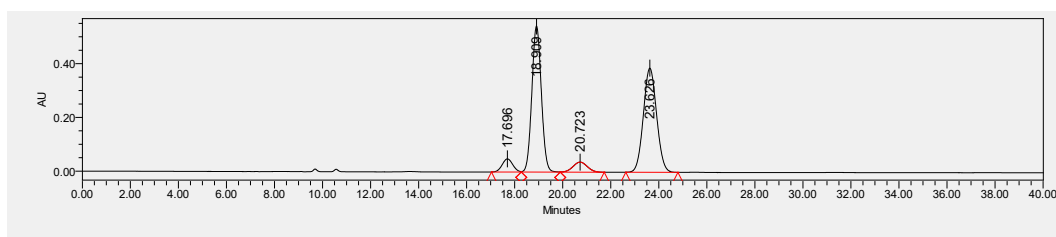
¹³C{¹H} NMR (151 MHz, CDCl₃) δ 194.44, 170.38, 155.95, 137.92, 136.83, 133.22, 132.58, 132.43, 131.81, 131.68, 130.68, 129.96, 129.78, 129.61, 129.49, 128.95, 128.54, 128.24, 127.93, 127.65, 127.10, 126.57, 125.84, 125.75, 125.69, 125.65, 125.60, 125.52, 125.46, 125.41, 124.00, 123.76, 123.25, 123.08, 109.32, 71.99, 63.43, 55.02, 39.35, 27.48, 18.58, 18.53, 15.96.

ESI-HRMS: calcd for C₄₄H₃₆O₄Na⁺ ($[M + Na]^+$) = 651.2506, found 651.2505.

IR (neat): 2924, 1731, 1667, 1503, 1254, 1207, 1033, 838, 736 cm⁻¹.

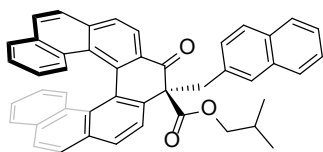


Retention Time	Area	% Area	Height
17.858	5136072	15.59	165675
19.076	628818	1.91	22549
20.922	67890	0.21	2346
23.805	27121200	82.30	709724



Retention Time	Area	% Area	Height
17.696	1506165	4.59	49089
18.909	14917727	45.45	543855
20.723	1564080	4.77	37559
23.626	14835473	45.20	387590

isobutyl (*P,S*)-9-(naphthalen-2-ylmethyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D26)



Following the typical procedure for the kinetic resolution.

(3 h 30 min) 27.9 mg, 44% yield; >19:1 dr., 98%/99% ee, bright yellow oil; $R_f = 0.39$ (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IC** column), n-hexane/PrOH = 90/10, flow rate

1.0 mL/min, $\lambda = 243$ nm, retention time: $t(\text{major}_1) = 15.677$ min, $t(\text{minor}_1) = 13.059$ min, $t(\text{major}_2) =$

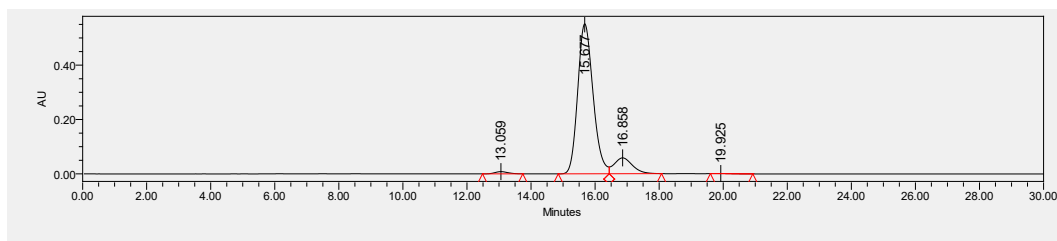
16.858 min, $t(\text{minor}_2) = 19.925$ min.

^1H NMR (600 MHz, CDCl_3) δ 8.24 (d, $J = 7.8$ Hz, 1H), 7.96 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.4$ Hz, 2H), 7.80 (d, $J = 7.8$ Hz, 2H), 7.53 (d, $J = 7.8$ Hz, 1H), 7.48 (t, $J = 9.0$ Hz, 2H), 7.41 – 7.39 (m, 4H), 7.30 (d, $J = 9.0$ Hz, 1H), 7.23 – 7.17 (m, 4H), 7.04 (d, $J = 8.4$ Hz, 1H), 6.93 (t, $J = 7.2$ Hz, 1H), 6.87 (t, $J = 7.2$ Hz, 1H), 6.64 (d, $J = 8.4$ Hz, 1H), 6.39 – 6.36 (m, 2H), 6.26 (t, $J = 7.4$ Hz, 1H), 4.57 (d, $J = 15.6$ Hz, 1H), 4.14 (d, $J = 15.6$ Hz, 1H), 3.76 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.67 (dd, $J = 10.7, 6.6$ Hz, 1H), 1.48 (septet, $J = 6.6$ Hz, 1H), 0.48 (d, $J = 6.6$ Hz, 3H), 0.42 (d, $J = 6.6$ Hz, 3H).

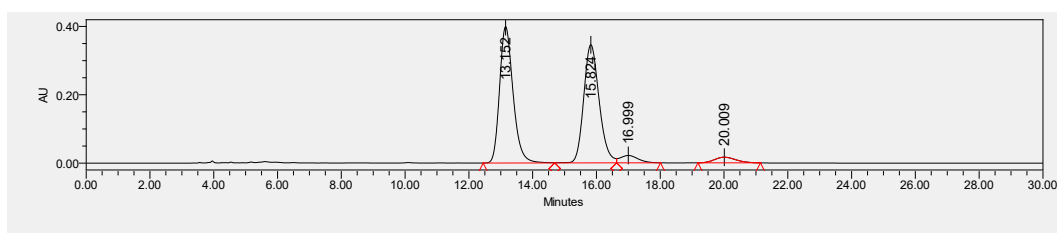
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.17, 170.26, 137.95, 136.91, 134.04, 133.08, 132.70, 132.50, 131.86, 131.71, 130.89, 129.95, 129.78, 129.67, 129.65, 129.49, 128.93, 128.80, 128.67, 128.33, 128.12, 127.62, 127.33, 127.24, 127.22, 126.60, 126.58, 125.89, 125.75, 125.65, 125.56, 125.54, 125.51, 125.49, 125.41, 125.22, 124.08, 123.81, 123.29, 72.16, 63.39, 39.67, 27.46, 18.56, 18.50.

ESI-HRMS: calcd for $\text{C}_{46}\text{H}_{34}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 657.2400, found 657.2400.

IR (neat): 2923, 1731, 1668, 1591, 1205, 839, 739, 474 cm^{-1} .

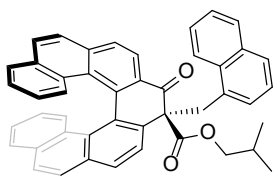


Retention Time	Area	% Area	Height
13.059	188742	0.90	7456
15.677	18344675	87.89	551651
16.858	2321745	11.12	58330
19.925	17906	0.09	589



Retention Time	Area	% Area	Height
13.152	11714639	46.97	398877
15.824	11611025	46.55	345579
16.999	845895	3.39	21576
20.009	770650	3.09	16491

isobutyl (*P,S*)-9-(naphthalen-1-ylmethyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D27)



Following the typical procedure for the kinetic resolution.

(24 h) 25.4 mg, 40% yield; 16.8:1 dr., 99%/90% ee, bright yellow oil; R_f = 0.39 (PE/EA = 9/1).

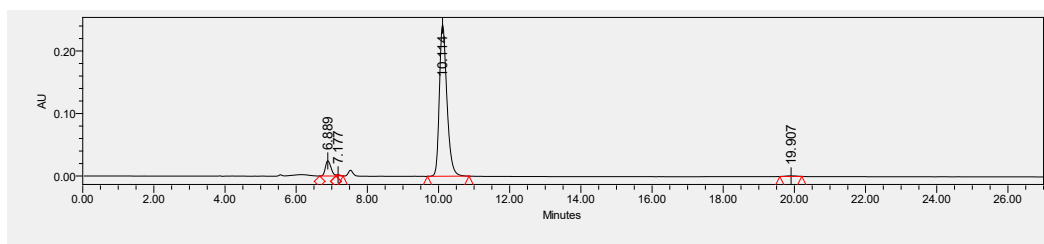
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 10.114 min, t (minor₁) = 19.907 min, t (major₂) = 6.889 min, t (minor₂) = 7.177 min.

^1H NMR (600 MHz, CDCl_3) δ 8.39 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.62 (ddd, J = 8.4, 6.6, 0.6 Hz, 1H), 7.57 (d, J = 9.0 Hz, 1H), 7.50 – 7.43 (m, 4H), 7.32 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 6.97 (t, J = 7.2 Hz, 1H), 6.94 (t, J = 7.2 Hz, 1H), 6.86 (t, J = 7.8 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.61 (d, J = 8.4 Hz, 1H), 6.55 (d, J = 7.4 Hz, 1H), 6.42 (ddd, J = 8.4, 6.6, 0.6 Hz, 1H), 6.39 (ddd, J = 8.4, 6.6, 0.6 Hz, 1H), 4.86 (d, J = 17.4 Hz, 1H), 4.58 (d, J = 17.4 Hz, 1H), 3.72 (dd, J = 10.8, 6.6 Hz, 1H), 3.63 (dd, J = 10.8, 6.6 Hz, 1H), 1.47 (septet, J = 6.6 Hz, 1H), 0.50 (d, J = 6.6 Hz, 3H), 0.44 (d, J = 6.6 Hz, 3H).

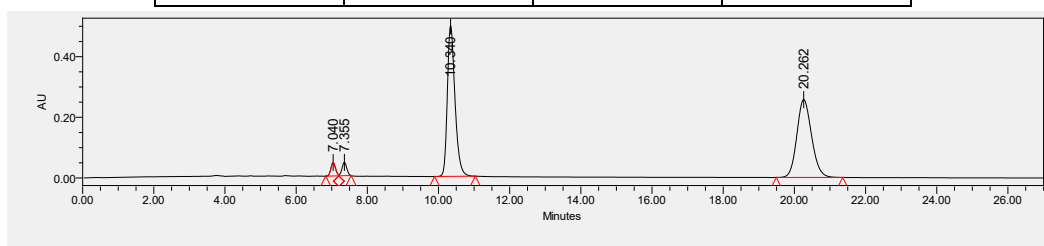
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 193.85, 170.47, 138.03, 137.03, 133.58, 132.80, 132.66, 131.99, 131.96, 131.83, 131.56, 130.94, 130.13, 129.83, 129.74, 129.72, 129.54, 129.04, 128.93, 128.84, 128.48, 127.18, 126.73, 126.70, 126.47, 126.41, 126.06, 126.03, 125.83, 125.77, 125.66, 125.63, 125.60, 125.48, 125.04, 124.98, 124.24, 123.96, 123.39, 123.32, 72.41, 62.75, 34.18, 27.45, 18.58, 18.52.

ESI-HRMS: calcd for $\text{C}_{46}\text{H}_{34}\text{O}_3\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 657.2400, found 657.2401.

IR (neat): 2922, 1730, 1649, 1590, 1507, 1264, 1203, 839, 788, 736, 523 cm^{-1} .

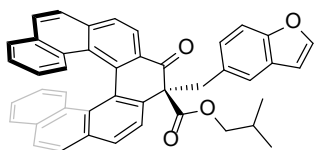


Retention Time	Area	% Area	Height
6.889	264805	6.86	24228
7.177	13531	0.35	1756
10.114	3560474	92.27	241979
19.907	19755	0.51	939



Retention Time	Area	% Area	Height
7.040	407195	2.61	44461
7.355	412552	2.64	43993
10.340	7393840	47.40	496358
20.262	7384236	47.34	256924

isobutyl (*P,S*)-9-(benzofuran-5-ylmethyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D28)



Following the typical procedure for the kinetic resolution.

(3 h 50 min) 30.6 mg, 49% yield; 6.4:1 dr., 98%/96% ee, bright yellow oil; $R_f = 0.33$ (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IC** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major₁) = 15.677 min, t (minor₁) = 14.144 min, t (major₂) =

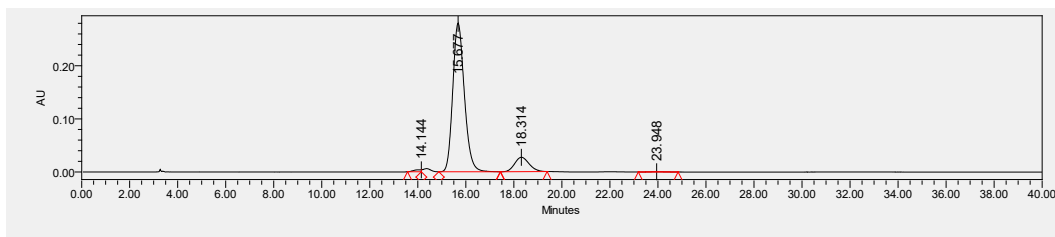
18.314 min, t (minor₂) = 23.948 min.

^1H NMR (600 MHz, CDCl_3) δ 8.23 (d, $J = 7.8$ Hz, 1H), 7.95 (d, $J = 8.4$ Hz, 1H), 7.84 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 7.8$ Hz, 1H), 7.49 (d, $J = 9.0$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 1H), 7.33 (d, $J = 2.4$ Hz, 1H), 7.30 (d, $J = 8.4$ Hz, 1H), 7.22 – 7.18 (m, 3H), 7.04 (d, $J = 9.0$ Hz, 1H), 6.93 (t, $J = 7.2$ Hz, 1H), 6.89 – 6.85 (m, 2H), 6.62 (d, $J = 8.4$ Hz, 1H), 6.37 (d, $J = 9.0$ Hz, 3H), 6.27 (t, $J = 7.6$ Hz, 1H), 4.48 (d, $J = 15.0$ Hz, 1H), 4.05 (d, $J = 15.0$ Hz, 1H), 3.75 (dd, $J = 10.8, 6.6$ Hz, 1H), 3.66 (dd, $J = 10.8, 6.6$ Hz, 1H), 1.48 (septet, $J = 6.6$ Hz, 1H), 0.49 (d, $J = 6.6$ Hz, 3H), 0.42 (d, $J = 6.6$ Hz, 3H).

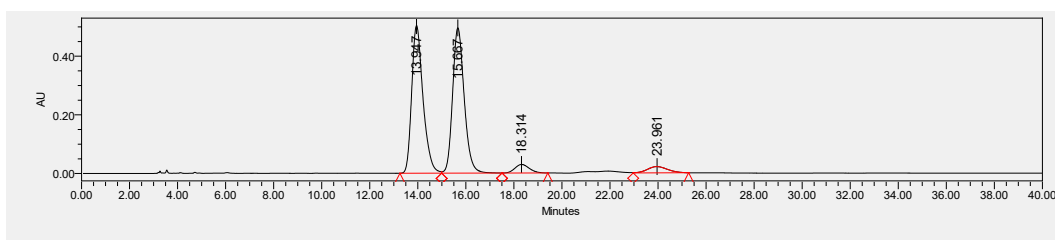
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.41, 170.34, 153.50, 144.68, 137.89, 136.88, 132.69, 132.64, 131.83, 131.69, 130.86, 130.66, 129.96, 129.81, 129.65, 129.63, 129.48, 128.92, 128.59, 128.30, 127.18, 127.09, 126.58, 126.35, 125.88, 125.71, 125.61, 125.55, 125.46, 125.41, 124.01, 123.79, 123.28, 123.10, 122.59, 110.54, 106.46, 72.08, 63.69, 39.58, 27.46, 18.56, 18.51.

ESI-HRMS: calcd for $\text{C}_{44}\text{H}_{32}\text{O}_4\text{Na}^+$ ($[\text{M} + \text{Na}]^+$) = 647.2193, found 647.2192.

IR (neat): 2924, 1731, 1669, 1506, 1264, 1204, 1031, 838, 799, 737 cm^{-1} .

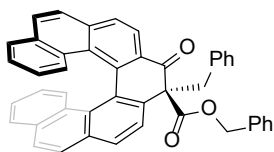


Retention Time	Area	% Area	Height
14.144	80744	0.76	3725
15.677	9389710	88.36	279673
18.314	1133306	10.66	27113
23.948	22648	0.21	461



Retention Time	Area	% Area	Height
13.947	16442297	46.32	503522
15.667	16589940	46.73	495591
18.314	1220485	3.44	29225
23.961	1247013	3.51	21345

benzyl (*P, S*)-9-benzyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D29)



Following the typical procedure for the kinetic resolution.

(12 h) 27.8 mg, 45% yield; 4:1 dr., 95%/85% ee, bright yellow oil; R_f = 0.42 (PE/EA = 9/1).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 10.954 min, t (minor₁) = 12.383 min, t (major₂) = 9.894

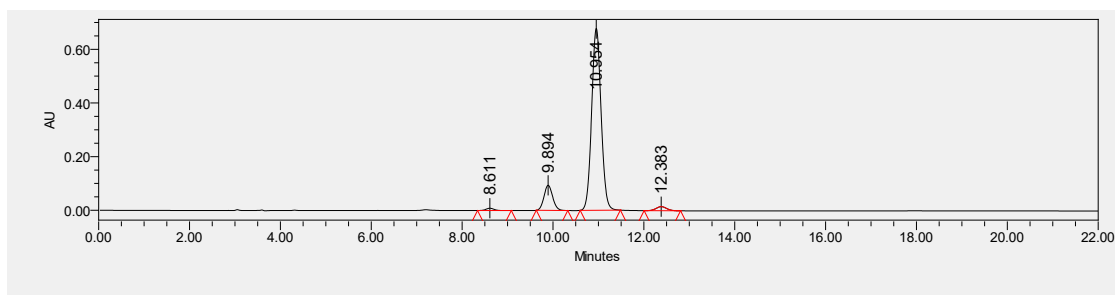
min, t (minor₂) = 8.611 min.

¹H NMR (600 MHz, CDCl₃) δ 8.16 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.77 (dd, J = 8.0, 3.6 Hz, 2H), 7.50 (d, J = 8.8 Hz, 1H), 7.47 (d, J = 8.6 Hz, 1H), 7.40 (d, J = 8.6 Hz, 1H), 7.30 (d, J = 8.6 Hz, 1H), 7.20 (dd, J = 13.4, 7.8 Hz, 2H), 6.95 (d, J = 4.2 Hz, 3H), 6.91 (s, 1H), 6.88 (t, J = 7.4 Hz, 1H), 6.85 – 6.81 (m, 1H), 6.73 – 6.65 (m, 4H), 6.50 (d, J = 8.8 Hz, 1H), 6.42 (d, J = 8.4 Hz, 1H), 6.30 (t, J = 7.6 Hz, 2H), 4.99 (d, J = 12.6 Hz, 1H), 4.81 (d, J = 12.6 Hz, 1H), 4.43 (d, J = 15.4 Hz, 1H), 3.99 (d, J = 15.4 Hz, 1H).

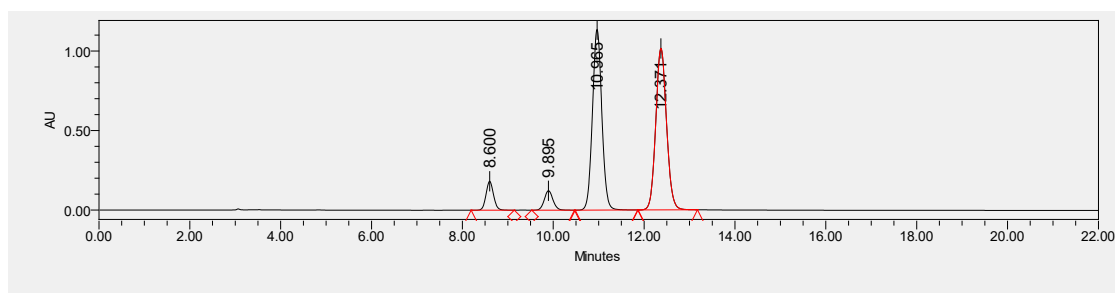
¹³C{¹H} NMR (151 MHz, CDCl₃) δ 194.13, 170.03, 137.83, 136.92, 136.37, 134.63, 132.70, 131.89, 131.79, 131.71, 131.16, 129.91, 129.84, 129.76, 129.72, 129.70, 129.38, 128.93, 128.57, 128.38, 128.26, 127.94, 127.90, 127.71, 127.47, 127.46, 127.33, 127.21, 126.62, 126.51, 126.09, 125.84, 125.79, 125.73, 125.60, 125.51, 125.47, 125.42, 124.00, 123.86, 123.25, 67.61, 63.46, 38.85.

ESI-HRMS: calcd for C₄₄H₃₁O₃⁺ ($[M + H]^+$) = 619.2268, found 619.2267.

IR (neat): 2954, 1735, 1692, 1583, 1506, 1262, 1211, 844, 739 cm⁻¹.

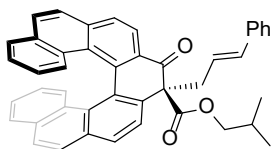


Retention Time	Area	% Area	Height
8.611	102380	0.90	8485
9.894	1242924	10.93	93545
10.954	9777997	85.99	677590
12.383	248325	2.18	15250



Retention Time	Area	% Area	Height
8.600	1614716	4.50	162004
9.895	1627035	4.53	122276
10.965	16336300	45.49	1135510
12.371	16332191	45.48	1008531

isobutyl (*P, S, E*)-9-cinnamyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D30)



Following the typical procedure for the kinetic resolution.

(5 h 50 min) 31.1 mg, 51% yield; 6.2:1 dr., 95%/91% ee, bright yellow oil; R_f = 0.42 (PE/EA = 9/1).

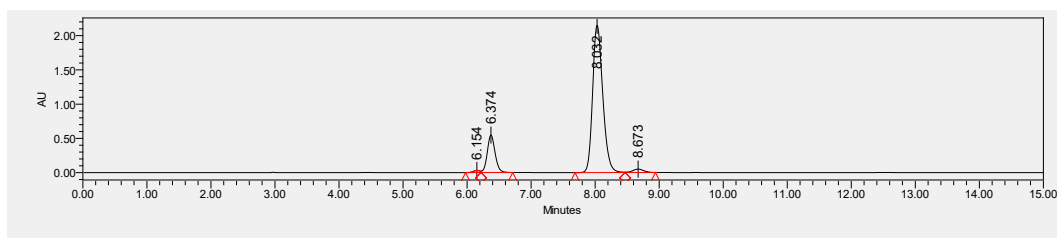
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/*i*PrOH = 90/10, flow rate 1.0 mL/min, λ = 243 nm, retention time: t (major₁) = 8.302 min, t (minor₁) = 8.673 min, t (major₂) = 6.374 min, t (minor₂) = 6.154 min.

¹H NMR (600 MHz, CDCl₃) δ 8.17 (d, J = 7.8 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.25 (d, J = 7.8 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 7.18 (d, J = 7.8 Hz, 2H), 7.14 (t, J = 7.8 Hz, 2H), 7.08 (d, J = 7.2 Hz, 1H), 6.96 (t, J = 7.8 Hz, 1H), 6.89 (t, J = 7.2 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 6.65 (d, J = 15.6 Hz, 1H), 6.48 (d, J = 8.4 Hz, 1H), 6.41 (t, J = 7.8 Hz, 1H), 6.31 (t, J = 7.8 Hz, 1H), 6.04 (dt, J = 14.4 7.2 Hz, 1H), 3.88 (dd, J = 15.0, 6.6 Hz, 1H), 3.67 (dd, J = 10.8, 6.6 Hz, 1H), 3.60 (dd, J = 10.8, 6.6 Hz, 1H), 3.56 (dd, J = 15.0, 6.6 Hz, 1H), 1.50 (septet, J = 6.6 Hz, 1H), 0.53 (d, J = 6.6 Hz, 3H), 0.49 (d, J = 6.6 Hz, 3H).

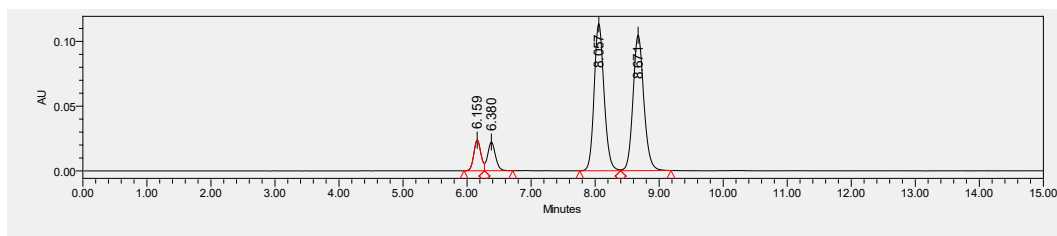
¹³C{¹H} NMR (151 MHz, CDCl₃) δ 194.50, 170.06, 137.50, 137.20, 136.86, 133.94, 132.82, 132.02, 132.00, 131.82, 130.65, 130.42, 129.77, 129.55, 129.44, 128.94, 128.74, 128.50, 128.33, 127.87, 127.28, 127.14, 126.67, 126.19, 126.06, 125.83, 125.63, 125.57, 125.55, 125.24, 123.92, 123.82, 123.24, 72.11, 63.09, 35.76, 27.49, 18.62, 18.57.

ESI-HRMS: calcd for C₄₄H₃₄O₃Na⁺ ($[M + Na]^+$) = 633.2400, found 633.2401.

IR (neat): 3050, 2960, 1728, 1692, 1589, 1505, 1266, 1205, 964, 839, 739 cm⁻¹.

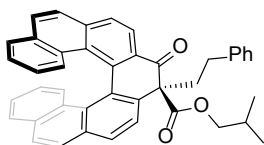


Retention Time	Area	% Area	Height
6.154	219028	0.75	31353
6.374	4607546	15.83	547891
8.032	23697635	81.40	2148642
8.673	589179	2.02	49292



Retention Time	Area	% Area	Height
6.159	182890	6.49	23684
6.380	186526	6.62	22183
8.057	1221120	43.32	113486
8.671	1228410	43.58	104461

isobutyl (*P*, *S*)-10-oxo-9-phenethyl-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D31)



Following the typical procedure for the kinetic resolution.

(24 h) 19.2 mg, 32% yield; >19:1 dr., 82% ee, bright yellow oil; $R_f = 0.42$ (PE/EA = 9/1). $[\alpha]_D^{25} = 984$ ($c = 5.0 \times 10^{-2}$, in CH_2Cl_2).

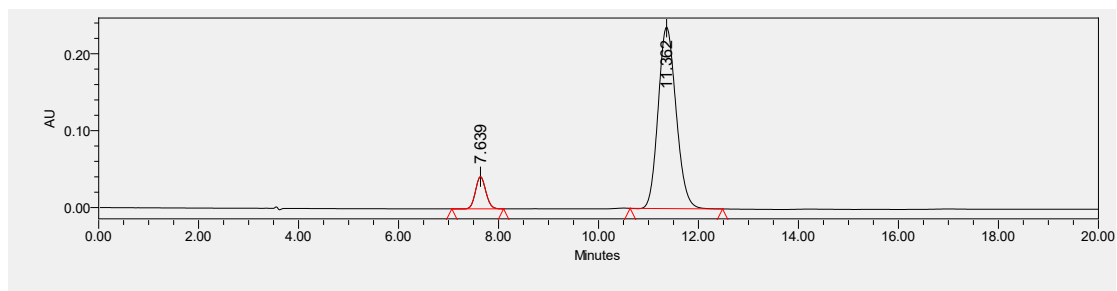
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major) = 11.362 min, t (minor) = 7.639 min.

^1H NMR (600 MHz, CDCl_3) δ 8.22 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.97 (d, $J = 8.2$ Hz, 1H), 7.94 (d, $J = 8.2$ Hz, 1H), 7.88 (d, $J = 7.8$ Hz, 1H), 7.57 (dd, $J = 10.8, 8.6$ Hz, 2H), 7.44 (d, $J = 8.6$ Hz, 1H), 7.38 (d, $J = 8.6$ Hz, 1H), 7.30 – 7.28 (m, 3H), 7.24 (s, 2H), 6.96 (s, 1H), 6.92 (d, $J = 7.8$ Hz, 1H), 6.69 (d, $J = 8.4$ Hz, 1H), 6.56 (d, $J = 8.4$ Hz, 1H), 6.42 (d, $J = 8.2$ Hz, 1H), 6.36 (t, $J = 7.6$ Hz, 1H), 3.68 (dd, $J = 10.8, 6.4$ Hz, 1H), 3.60 (dd, $J = 10.8, 6.4$ Hz, 1H), 3.33 (ddd, $J = 14.2, 12.4, 4.8$ Hz, 1H), 2.83 (ddd, $J = 14.2, 12.4, 4.8$ Hz, 1H), 2.66 (td, $J = 13.2, 4.8$ Hz, 1H), 2.31 (td, $J = 13.2, 4.8$ Hz, 1H), 1.49 (dq, $J = 13.4, 6.6$ Hz, 1H), 0.51 (d, $J = 6.6$ Hz, 3H), 0.46 (d, $J = 6.6$ Hz, 3H).

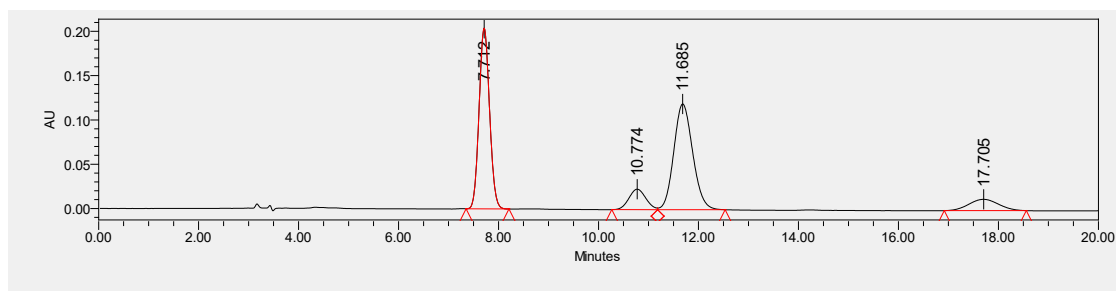
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.42, 170.25, 142.02, 137.54, 136.87, 132.77, 132.01, 131.83, 131.80, 130.79, 130.51, 129.78, 129.75, 129.59, 129.41, 128.98, 128.92, 128.49, 128.45, 128.30, 128.26, 127.36, 126.75, 126.66, 126.01, 125.80, 125.77, 125.70, 125.68, 125.60, 125.51, 125.06, 123.88, 123.83, 123.36, 72.05, 62.89, 34.77, 31.47, 27.47, 18.58, 18.51.

ESI-HRMS: calcd for $\text{C}_{43}\text{H}_{35}\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) = 599.2581, found 599.2584.

IR (neat): 2926, 1730, 1696, 1503, 1455, 1204, 839, 746 cm^{-1} .

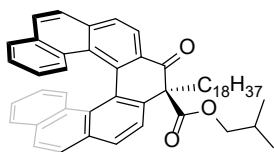


Retention Time	Area	% Area	Height
7.639	581864	9.00	41377
11.362	5882999	91.00	235948



Retention Time	Area	% Area	Height
7.712	2966710	42.69	203999
10.774	502982	7.24	22318
11.685	2978598	42.86	117116
17.705	501712	7.22	12441

isobutyl (*P*, *S*)-9-octadecyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D32)



Following the typical procedure for the kinetic resolution.

(24 h) 26.1 mg, 35% yield; >19:1 dr., 80% ee, bright yellow oil; R_f = 0.65 (PE/EA = 9/1). $[\alpha]_D^{25} = 569$ ($c = 7.5 \times 10^{-2}$, in CH_2Cl_2).

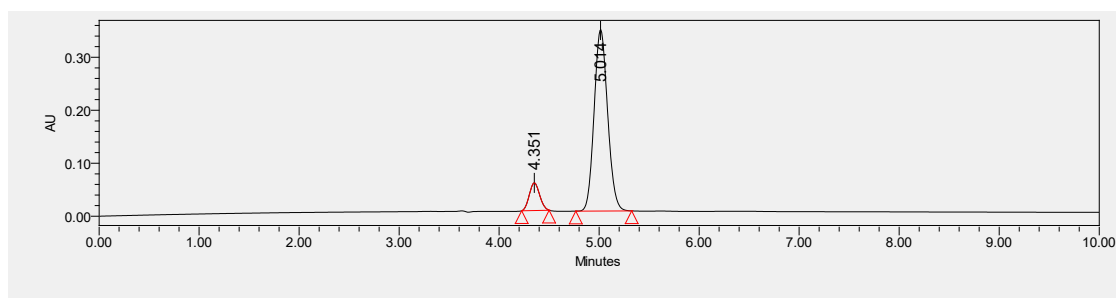
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/*i*PrOH = 90/10, flow rate 0.5 mL/min, $\lambda = 243$ nm, retention time: t (major) = 5.014 min, t (minor) = 4.351 min.

^1H NMR (600 MHz, CDCl_3) δ 8.19 (d, $J = 7.8$ Hz, 1H), 7.91 (d, $J = 8.2$ Hz, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.82 (d, $J = 8.2$ Hz, 1H), 7.56 – 7.53 (m, 2H), 7.43 (d, $J = 8.6$ Hz, 1H), 7.35 (d, $J = 8.6$ Hz, 1H), 7.24 (t, $J = 8.2$ Hz, 2H), 6.95 (t, $J = 7.4$ Hz, 1H), 6.91 (t, $J = 7.4$ Hz, 1H), 6.67 (d, $J = 8.4$ Hz, 1H), 6.53 (d, $J = 8.4$ Hz, 1H), 6.39 (t, $J = 7.6$ Hz, 1H), 6.34 (t, $J = 7.6$ Hz, 1H), 3.67 (dd, $J = 10.8, 6.4$ Hz, 1H), 3.60 (dd, $J = 10.8, 6.4$ Hz, 1H), 2.95 (ddd, $J = 14.2, 12.2, 4.2$ Hz, 1H), 2.54 (ddd, $J = 14.2, 12.2, 4.2$ Hz, 1H), 1.48 (dt, $J = 13.4, 6.6$ Hz, 1H), 1.42 (dd, $J = 8.4, 6.0$ Hz, 1H), 1.39 – 1.34 (m, 1H), 1.24 – 1.21 (m, 29H), 0.99 (dtd, $J = 13.2, 8.2, 4.8$ Hz, 1H), 0.87 (t, $J = 7.0$ Hz, 3H), 0.51 (d, $J = 6.6$ Hz, 3H), 0.46 (d, $J = 6.6$ Hz, 3H).

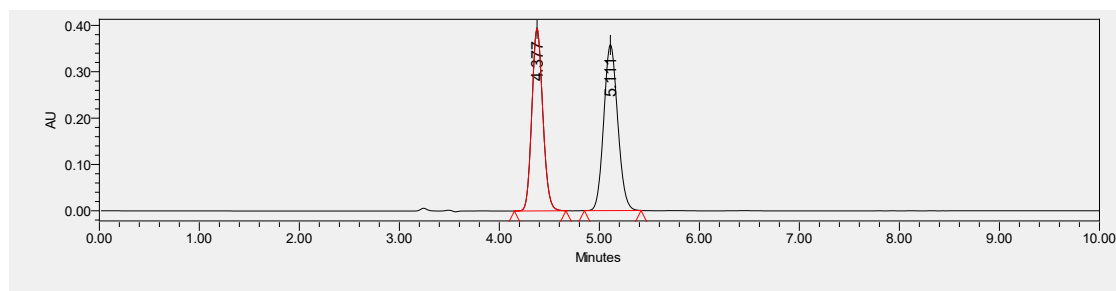
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 194.70, 170.62, 137.55, 136.78, 132.63, 131.96, 131.77, 131.63, 131.36, 130.57, 129.71, 129.63, 129.49, 129.43, 128.94, 128.76, 128.36, 127.18, 126.69, 126.61, 125.95, 125.80, 125.77, 125.58, 125.50, 125.21, 124.00, 123.83, 123.28, 71.90, 62.98, 32.83, 31.95, 30.32, 29.72, 29.68, 29.63, 29.61, 29.38, 29.35, 27.47, 25.19, 22.72, 18.58, 18.52, 14.15.

ESI-HRMS: calcd for $\text{C}_{33}\text{H}_{63}\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) = 747.4772, found 747.4769.

IR (neat): 2923, 2853, 1731, 1688, 1462, 1392, 1205, 964, 840 cm^{-1} .



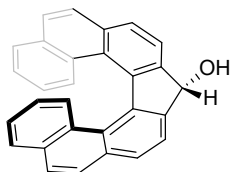
Retention Time	Area	% Area	Height
4.351	359895	10.08	51135
5.014	3208727	89.92	342299



Retention Time	Area	% Area	Height
4.377	2979881	50.08	393571
5.111	2970180	49.92	334451

12.3 Analytical and spectral characterization data of derivative products.

(*M*)-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-ol (E1)



Following the synthetic transformation procedure 1.

38.0 mg, >99% yield; ee >99%, light yellow solid; $R_f = 0.16$ (PE/EA = 9/1). $[\alpha]_D^{16} = -1734.2$ ($c = 3.8 \times 10^{-2}$, in CH_2Cl_2).

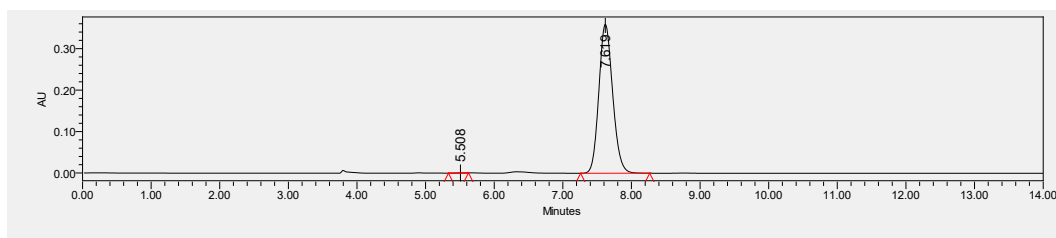
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/ i PrOH = 70/30, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major) = 7.619 min, t (minor) = 5.508 min.

^1H NMR (600 MHz, CDCl_3) δ 7.96 (d, $J = 7.8$ Hz, 1H), 7.89 (s, 2H), 7.86 (d, $J = 7.8$ Hz, 1H), 7.73 (dd, $J = 9.0, 4.8$ Hz, 2H), 7.67 (d, $J = 9.0$ Hz, 2H), 7.58 (t, $J = 7.8$ Hz, 2H), 7.47 (t, $J = 7.8$ Hz, 2H), 7.07 (q, $J = 7.8$ Hz, 2H), 6.25 (t, $J = 7.8$ Hz, 1H), 6.21 (t, $J = 7.8$ Hz, 1H), 5.79 (s, 1H), 2.20 (br., 1H).

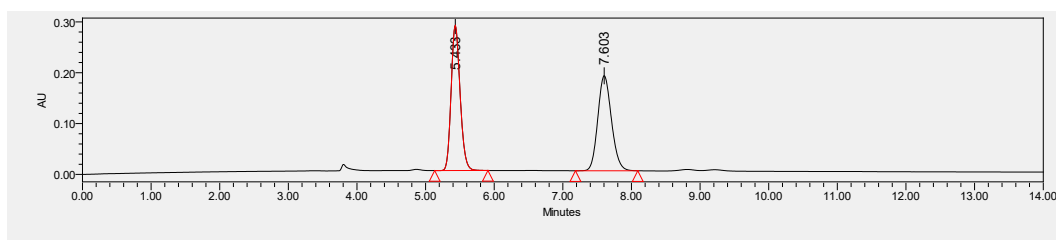
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 147.83, 144.61, 138.38, 136.82, 133.60, 133.44, 131.76, 131.39, 130.69, 130.57, 128.97, 128.46, 128.12, 127.51, 127.37, 127.23, 127.16, 127.05, 126.82, 126.74, 126.71, 126.62, 126.39, 126.27, 123.33, 123.15, 122.62, 121.83, 75.32.

ESI-HRMS: calcd for $\text{C}_{29}\text{H}_{17}^+$ ($[\text{M} - \text{OH}]^+$) = 365.1325, found 365.1324.

IR (neat): 3256, 3045, 2924, 1306, 1263, 1216, 1093, 1017, 834, 741, 704 cm^{-1} .

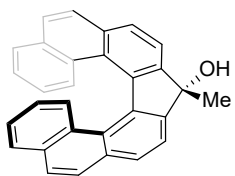


Retention Time	Area	% Area	Height
5.508	812	0.02	103
7.619	5021823	99.98	359052



Retention Time	Area	% Area	Height
5.433	2590622	50.08	284972
7.603	2581976	49.92	186879

(M)-9-methyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-ol (E2)



Following the synthetic transformation procedure 2.

40.0 mg, >99% yield; ee >99%, light yellow solid; $R_f = 0.32$ (PE/EA = 9/1). $[\alpha]_D^{25} = -1947.5$ ($c = 4.0 \times 10^{-2}$, in CH_2Cl_2).

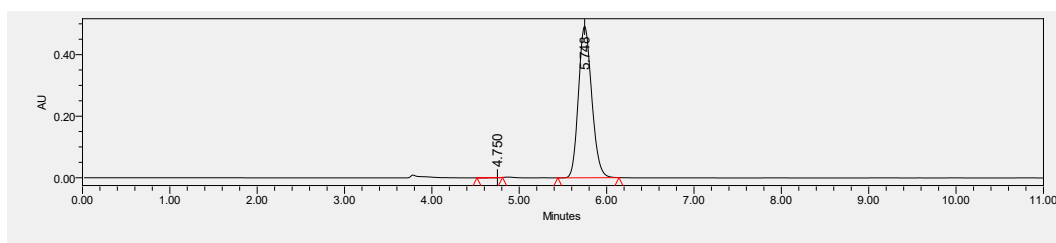
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/ i PrOH = 70/30, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major) = 5.748 min, t (minor) = 4.750 min.

^1H NMR (600 MHz, CDCl_3) δ 7.91 – 7.84 (m, 4H), 7.72 (t, $J = 8.4$ Hz, 2H), 7.65 (dd, $J = 9.0, 3.6$ Hz, 2H), 7.57 (t, $J = 7.2$ Hz, 2H), 7.52 (d, $J = 8.4$ Hz, 1H), 7.49 (d, $J = 8.4$ Hz, 1H), 7.07 (q, $J = 7.8$ Hz, 2H), 6.25 (t, $J = 7.8$ Hz, 1H), 6.22 (t, $J = 7.8$ Hz, 1H), 2.25 (s, 1H), 1.94 (s, 3H).

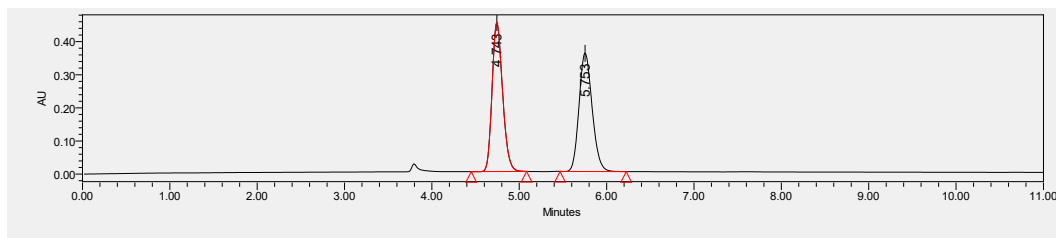
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 151.84, 148.99, 137.02, 135.57, 133.54, 133.49, 131.78, 131.52, 130.71, 130.67, 129.29, 128.87, 128.19, 127.54, 127.47, 127.05, 126.97, 126.82, 126.79, 126.72, 126.64, 126.38, 126.27, 123.28, 123.14, 120.51, 120.46, 79.09, 26.43.

ESI-HRMS: calcd for $\text{C}_{17}\text{H}_{21}^+$ ($[\text{M} - \text{OH}]^+$) = 379.1481, found 379.1480.

IR (neat): 3355, 3045, 1303, 1132, 1023, 838, 798, 743, 655 cm^{-1} .

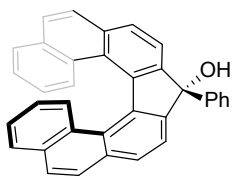


Retention Time	Area	% Area	Height
4.750	6261	0.12	556
5.748	5200400	99.88	492051



Retention Time	Area	% Area	Height
4.743	3757252	50.15	450242
5.753	3734100	49.85	357434

(M)-9-phenyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-ol (E3)



Following the synthetic transformation procedure 3.

46 mg, >99% yield; ee >99%, light yellow solid; $R_f = 0.45$ (PE/EA = 9/1). $[\alpha]^{25}_D = -1241.3$ ($c = 1.0 \times 10^{-2}$, in CH_2Cl_2).

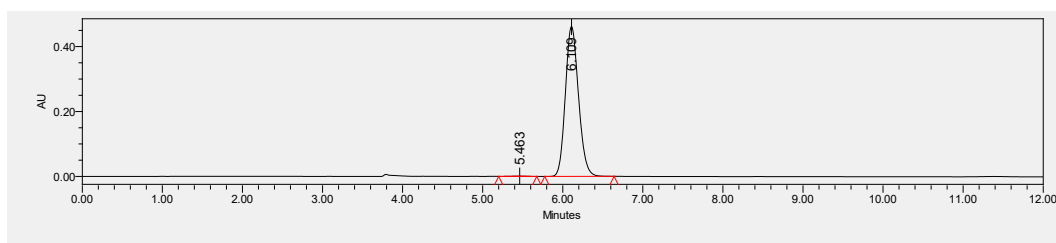
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/ i PrOH = 70/30, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major) = 6.109 min, t (minor) = 5.463 min.

^1H NMR (600 MHz, CDCl_3) δ 7.79 (dd, $J = 14.4, 7.2$ Hz, 2H), 7.67 (q, $J = 8.6$ Hz, 5H), 7.63 (d, $J = 7.8$ Hz, 1H), 7.60 – 7.54 (m, 4H), 7.51 (d, $J = 7.2$ Hz, 2H), 7.12 – 7.07 (m, 2H), 6.31 (t, $J = 7.2$ Hz, 1H), 6.26 (t, $J = 7.2$ Hz, 1H), 2.74 (s, 1H).

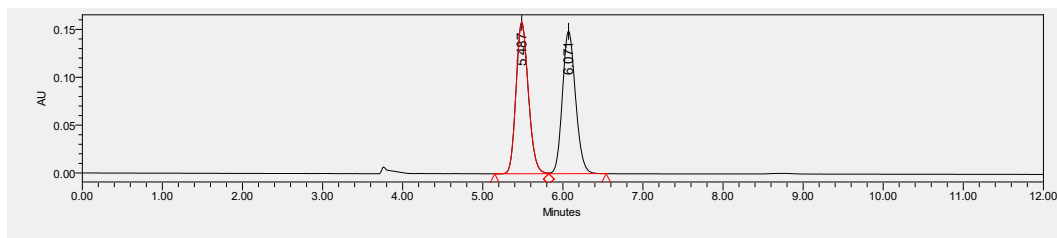
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 151.78, 150.37, 142.60, 137.83, 136.71, 133.60, 133.57, 131.85, 131.60, 130.89, 130.63, 129.60, 129.38, 128.43, 128.11, 127.62, 127.50, 127.40, 127.31, 127.15, 126.84, 126.83, 126.76, 126.48, 126.38, 125.73, 123.40, 123.25, 122.13, 121.88, 83.29.

ESI-HRMS: calcd for $\text{C}_{17}\text{H}_{21}^+$ ($[\text{M} - \text{OH}]^+$) = 441.1638, found 441.1637.

IR (neat): 3552, 3046, 1598, 1495, 1474, 1226, 1013, 837, 804, 748, 695, 660 cm^{-1} .

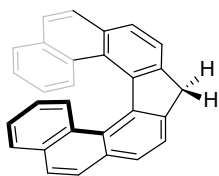


Retention Time	Area	% Area	Height
5.463	9314	0.18	782
6.109	5261784	99.82	462309



Retention Time	Area	% Area	Height
5.487	1692904	50.01	158184
6.071	1692335	49.99	148872

(*M*)-9H-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthrene (E4)



Following the synthetic transformation procedure 4.

27 mg, 74% yield; ee >99%, white solid; R_f = 0.52 (PE/Ea = 9/1). $[\alpha]_D^{25} = -2036.1$ ($c = 3.6 \times 10^{-2}$, in CH_2Cl_2).

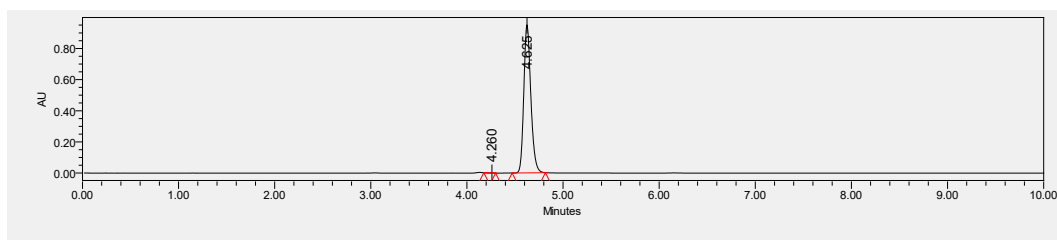
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/ i PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major) = 4.625 min, t (minor) = 4.260 min.

^1H NMR (600 MHz, CDCl_3) δ 8.08 (d, $J = 7.8$ Hz, 2H), 7.88 (d, $J = 7.8$ Hz, 2H), 7.76 (d, $J = 9.0$ Hz, 2H), 7.68 (d, $J = 9.0$ Hz, 2H), 7.59 (d, $J = 7.8$ Hz, 2H), 7.54 (d, $J = 8.3$ Hz, 2H), 7.09 (t, $J = 7.4$ Hz, 2H), 6.39 (s, 2H), 6.26 (t, $J = 7.6$ Hz, 2H).

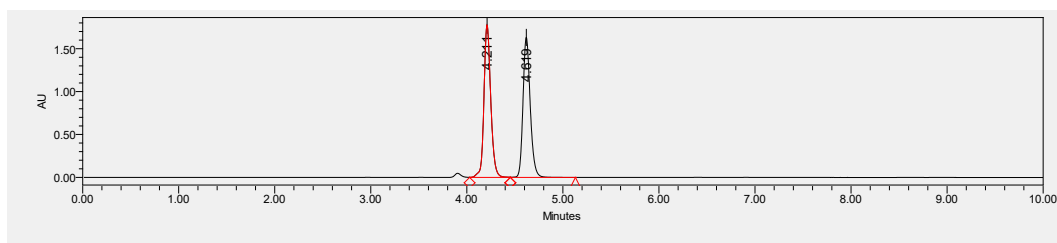
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 143.27, 138.46, 138.17, 133.52, 131.58, 130.80, 127.82, 127.64, 127.58, 126.98, 126.85, 126.53, 126.30, 123.20, 118.50, 109.24, 29.73.

ESI-HRMS: calcd for $\text{C}_{29}\text{H}_{17}^-$ ($[\text{M} - \text{H}]^-$) = 365.1336, found 365.1335.

IR (neat): 3034, 2924, 2854, 1494, 1449, 1315, 1218, 833, 796, 742, 706, 508 cm^{-1} .

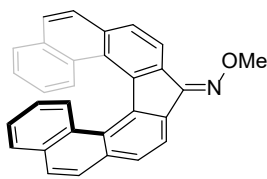


Retention Time	Area	% Area	Height
4.260	1454	0.03	335
4.625	4855519	99.97	949802



Retention Time	Area	% Area	Height
4.211	8464872	50.15	1757383
4.619	8415329	49.85	1622790

(M)-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one-O-methyl oxime (E5)



Following the synthetic transformation procedure 5.

41 mg, >99% yield; ee >99%, bright orange solid; $R_f = 0.4$ (PE/EA = 20/1). $[\alpha]_D^{25} = -3717.5$ ($c = 4.0 \times 10^{-2}$, in CH_2Cl_2).

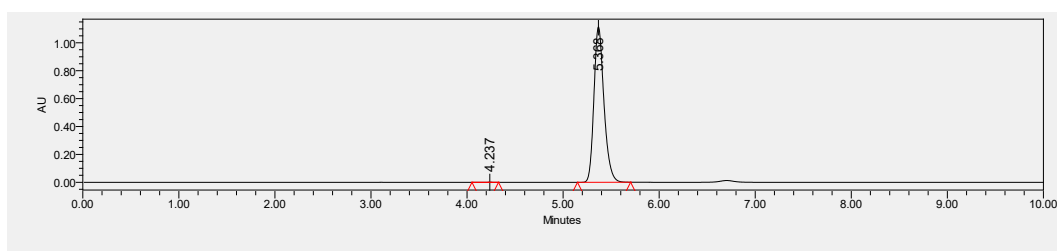
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/*i*PrOH = 70/30, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major) = 5.368 min, t (minor) = 4.237 min.

^1H NMR (600 MHz, CDCl_3) δ 8.61 (d, $J = 8.4$ Hz, 1H), 8.09 (d, $J = 7.8$ Hz, 1H), 7.80 (dd, $J = 7.2, 5.4$ Hz, 2H), 7.70 – 7.65 (m, 3H), 7.62 (d, $J = 8.4$ Hz, 1H), 7.55 – 7.52 (m, 3H), 7.50 (d, $J = 8.4$ Hz, 1H), 7.06 (t, $J = 7.8$ Hz, 2H), 6.26 (t, $J = 7.8$ Hz, 2H), 4.33 (s, 3H).

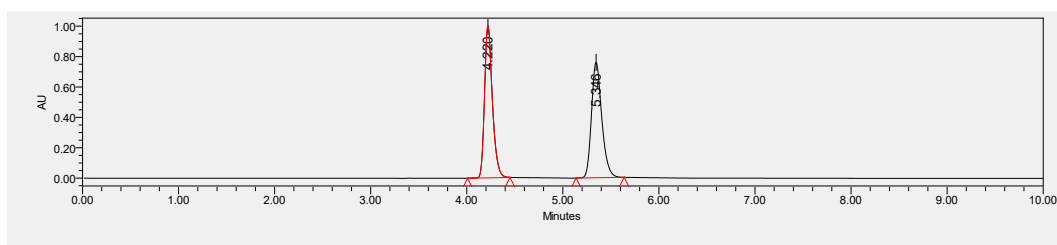
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 151.50, 140.99, 139.04, 136.53, 134.62, 134.19, 131.66, 131.64, 130.75, 130.67, 130.51, 128.66, 128.48, 128.24, 127.89, 127.69, 127.51, 127.44, 127.28, 126.98, 126.92, 126.77, 126.64, 126.46, 126.38, 125.75, 123.54, 123.33, 118.83, 63.88.

ESI-HRMS: calcd for $\text{C}_{30}\text{H}_{19}\text{NO}^+$ ($[\text{M} + \text{H}]^+$) = 410.1539, found 410.1538.

IR (neat): 3044, 2931, 1038, 980, 919, 874, 841, 802, 743, 679 cm^{-1} .

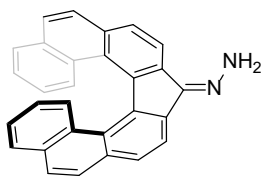


Retention Time	Area	% Area	Height
4.237	1150	0.01	231
5.368	8074177	99.99	1113268



Retention Time	Area	% Area	Height
4.220	5643457	49.94	1000294
5.346	5657915	50.06	758741

(M)-(9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-ylidene)hydrazine (E6)



Following the synthetic transformation procedure 6.

39 mg, >99% yield; ee >99%, orange solid; $R_f = 0.2$ (PE/EA = 4/1). $[\alpha]^{25}_D = -3535.0$ ($c = 3.9 \times 10^{-2}$, in CH_2Cl_2).

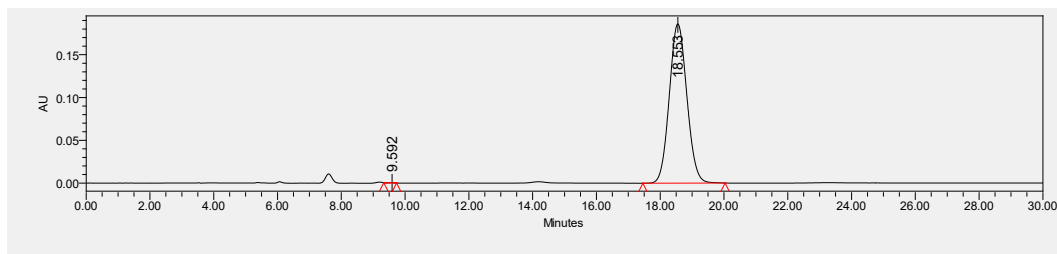
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major) = 18.552 min, t (minor) = 9.582 min.

^1H NMR (600 MHz, CDCl_3) δ 8.12 (d, $J = 7.8$ Hz, 1H), 8.08 (d, $J = 7.8$ Hz, 1H), 7.83 (d, $J = 7.8$ Hz, 1H), 7.78 (d, $J = 7.8$ Hz, 1H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.65 (s, 2H), 7.62 (d, $J = 8.4$ Hz, 1H), 7.55 (t, $J = 7.8$ Hz, 3H), 7.47 (d, $J = 8.4$ Hz, 1H), 7.06 (q, $J = 7.8$ Hz, 2H), 6.68 (s, 2H), 6.28 – 6.23 (m, 2H).

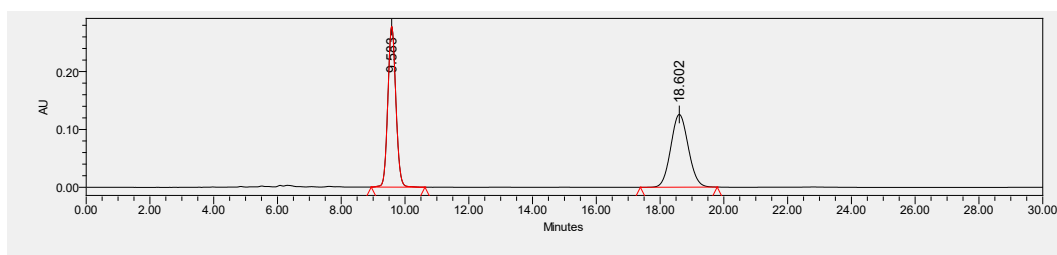
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 144.51, 140.28, 138.69, 136.74, 133.43, 133.26, 133.25, 131.68, 130.68, 130.52, 130.07, 128.75, 128.08, 127.99, 127.78, 127.66, 127.60, 127.32, 127.09, 126.99, 126.71, 126.54, 126.48, 126.39, 123.67, 123.22, 122.03, 118.47.

ESI-HRMS: calcd for $\text{C}_{29}\text{H}_{19}\text{N}_2^+$ ($[\text{M} + \text{H}]^+$) = 395.1543, found 395.1542.

IR (neat): 3404, 3316, 3045, 2855, 2362, 1718, 1579, 1125, 837, 799, 745, 680 cm^{-1} .

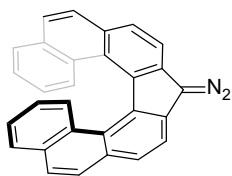


Retention Time	Area	% Area	Height
9.582	2413	0.05	195
18.552	5100076	99.95	133338



Retention Time	Area	% Area	Height
9.583	4859108	50.33	277692
18.602	4794961	49.67	125718

(M)-9-diazo-9H-cyclopenta[1,2-c:4,3-c']diphenanthrene (E7)



Following the synthetic transformation procedure 6.

32 mg, 82% yield; ee >99%, brownish red solid; $R_f = 0.5$ (PE/EA = 9/1). $[\alpha]_D^{25} = -3910.0$ ($c = 3.9 \times 10^{-2}$, in CH_2Cl_2).

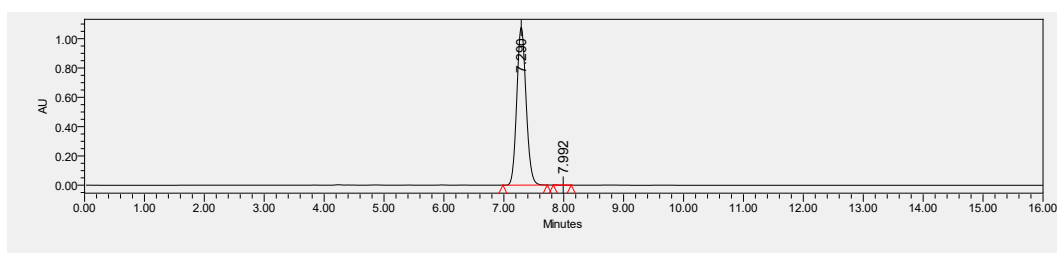
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/PrOH = 90/10, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: retention time: t (major) = 7.290 min, t (minor) = 7.992 min.

^1H NMR (600 MHz, CDCl_3) δ 7.97 (d, $J = 8.0$ Hz, 2H), 7.86 (t, $J = 8.4$ Hz, 4H), 7.74 (d, $J = 8.4$ Hz, 2H), 7.68 (d, $J = 7.8$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 2H), 7.11 (t, $J = 7.4$ Hz, 2H), 6.23 (t, $J = 7.6$ Hz, 2H).

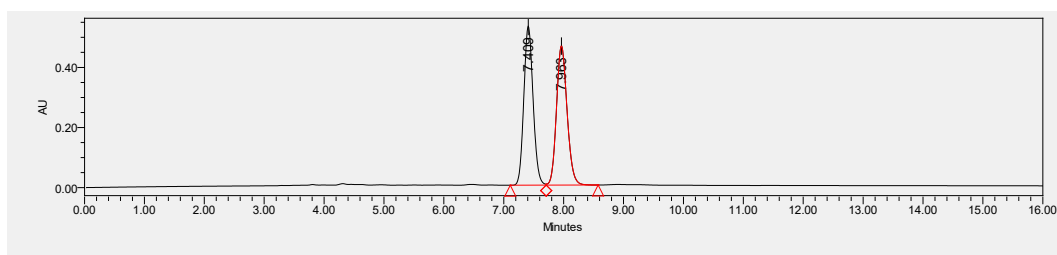
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 133.21, 131.35, 130.51, 130.34, 128.40, 127.68, 127.22, 127.07, 126.81, 126.40, 126.32, 125.76, 123.13, 117.35.

ESI-HRMS: calcd for $\text{C}_{29}\text{H}_{17}\text{N}_2^+$ ($[\text{M} + \text{H}]^+$) = 393.1386, found 393.1390.

IR (neat): 3044, 2924, 2061, 1579, 1441, 1150, 828, 748 cm^{-1} .

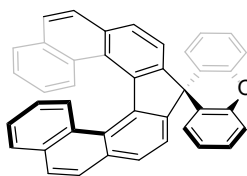


Retention Time	Area	% Area	Height
7.290	11609788	99.98	1077523
7.992	2095	0.02	216



Retention Time	Area	% Area	Height
7.409	5692956	50.03	528510
7.963	5686674	49.97	462989

(*M*)-spiro[cyclopenta[1,2-*c*:4,3-*c'*]diphenanthrene-9,9'-xanthene] (E8**)**



Following the synthetic transformation procedure 8.

41 mg, 78% yield; ee >99%, white solid; R_f = 0.5 (PE/DCM = 4/1). $[\alpha]_D^{25}$ = -784.9 (c = 5.3×10^{-2} , in CH_2Cl_2).

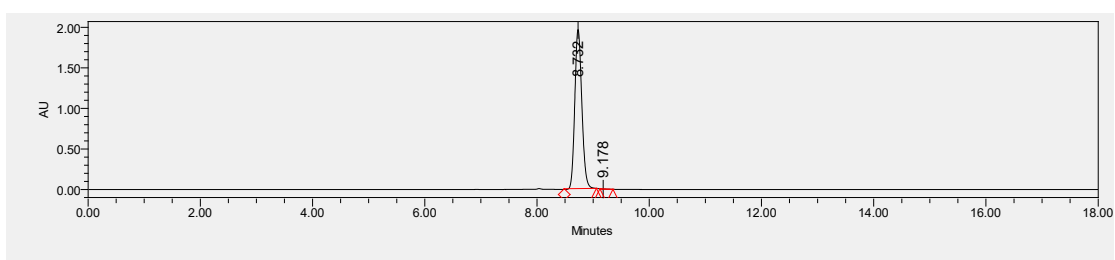
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IE** column), n-hexane/*i*PrOH = 98/2, flow rate 0.5 mL/min, λ = 243 nm, retention time: t (major) = 8.732 min, t (minor) = 9.178 min.

^1H NMR (600 MHz, CDCl_3) δ 7.80 (d, J = 7.8 Hz, 2H), 7.73 (q, J = 8.4 Hz, 6H), 7.65 (d, J = 7.8 Hz, 2H), 7.47 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.21 (t, J = 7.4 Hz, 2H), 7.14 (t, J = 7.4 Hz, 2H), 6.71 (t, J = 7.6 Hz, 2H), 6.52 (d, J = 7.8 Hz, 2H), 6.34 (t, J = 7.6 Hz, 2H).

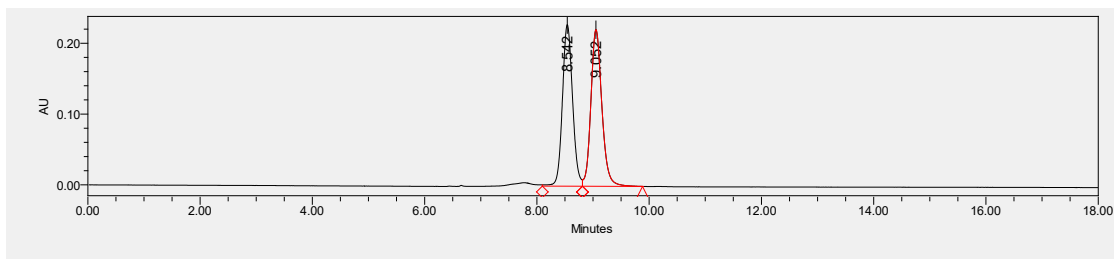
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 156.20, 151.86, 136.56, 132.50, 131.65, 130.92, 129.48, 128.42, 128.17, 127.64, 127.49, 126.93, 126.82, 126.67, 126.48, 123.59, 123.43, 123.33, 123.31, 117.07, 54.39.

ESI-HRMS: calcd for $\text{C}_{41}\text{H}_{25}\text{O}^+$ ($[\text{M} + \text{H}]^+$) = 533.1900, found 533.1902.

IR (neat): 3045, 2924, 1477, 1444, 1289, 1244, 872, 834, 746, 650 cm^{-1} .

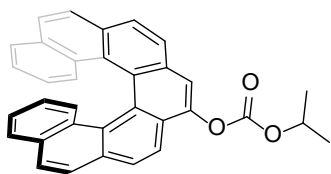


Retention Time	Area	% Area	Height
8.732	17015648	99.94	1960748
9.178	10481	0.06	1381



Retention Time	Area	% Area	Height
8.542	2686178	49.92	222571
9.052	2694512	50.08	213214

(M)-benzo[1,2-c:4,3-c']diphenanthren-9-yl isopropyl carbonate (E9)



Following the synthetic transformation procedure 9.

30 mg, 62% yield; ee >99%, light yellow solid; $R_f = 0.4$ (PE/EA = 9/1). $[\alpha]_D^{25} = -3104.3$ ($c = 4.6 \times 10^{-2}$, in CH_2Cl_2).

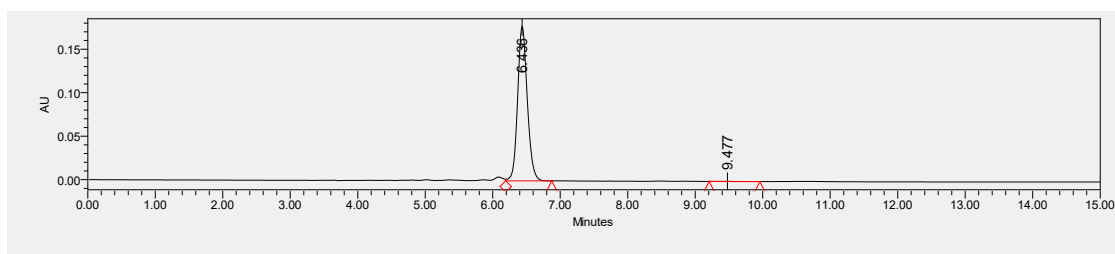
Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IK** column), n-hexane/PrOH = 70/30, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major) = 6.436 min, t (minor) = 6.468 min.

^1H NMR (600 MHz, CDCl_3) δ 8.17 (d, $J = 8.4$ Hz, 1H), 7.97 – 7.90 (m, 4H), 7.71 (t, $J = 9.0$ Hz, 2H), 7.49 (dd, $J = 13.8, 8.4$ Hz, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 7.13 (dd, $J = 13.8, 8.4$ Hz, 2H), 6.90 (t, $J = 7.2$ Hz, 2H), 6.40 (q, $J = 7.2$ Hz, 2H), 5.13 (hept, $J = 6.0$ Hz, 1H), 1.50 (dd, $J = 6.0, 4.8$ Hz, 6H).

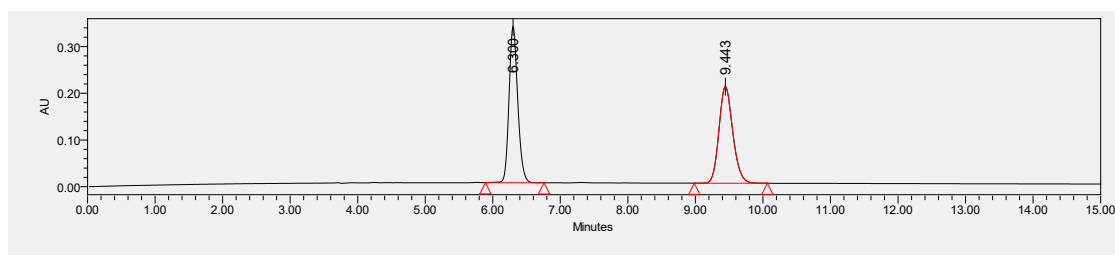
$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3) δ 153.52, 145.35, 131.82, 131.78, 131.32, 130.92, 130.71, 129.41, 129.36, 128.32, 128.29, 128.12, 128.02, 127.84, 127.34, 126.78, 126.67, 126.63, 125.87, 125.68, 125.54, 125.16, 125.08, 124.38, 124.21, 123.76, 123.74, 123.66, 119.54, 117.44, 73.60, 21.90.

ESI-HRMS: calcd for $\text{C}_{34}\text{H}_{25}\text{O}_3^+$ ($[\text{M} + \text{H}]^+$) = 481.1798, found 481.1794.

IR (neat): 3049, 2982, 1757, 1245, 1089, 915, 833, 747 cm^{-1} .

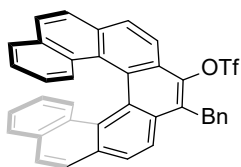


Retention Time	Area	% Area	Height
6.436	11970386	100.00	1211508
9.468	296	0.00	27



Retention Time	Area	% Area	Height
6.300	2995883	50.36	333919
9.443	2952852	49.64	206890

(P)-10-benzylbenzo[1,2-c:4,3-c']diphenanthren-9-yl trifluoromethanesulfonate (E10)



Following the synthetic transformation procedure 10.

105 mg, 85% yield; 95% ee, light yellow solid; $R_f = 0.65$ (PE/Et₂O = 9/1). $[\alpha]^{25}_D = 2972$ ($c = 3.1 \times 10^{-2}$, in CH₂Cl₂).

Dissolved in n-hexane for HPLC; **HPLC** (Chiralcel **IA** column), n-hexane/ⁱPrOH = 98/2, flow rate 1.0 mL/min, $\lambda = 243$ nm, retention time: t (major) = 10.824 min, t (minor) = 12.150 min.

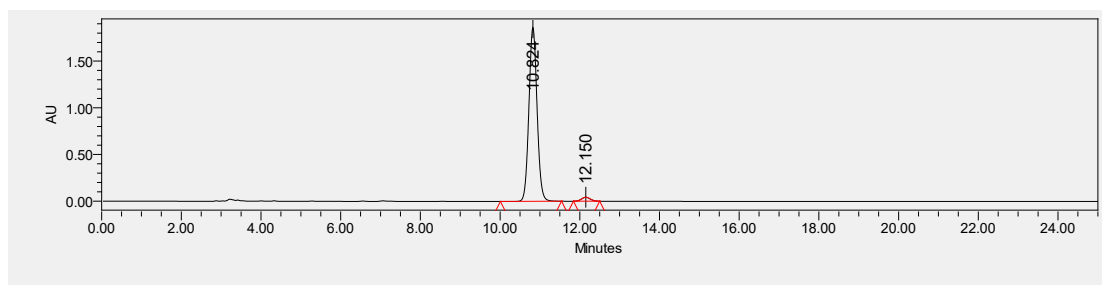
¹H NMR (600 MHz, CDCl₃) δ 8.32 (d, $J = 8.4$ Hz, 1H), 8.08 (d, $J = 8.4$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 7.86 (d, $J = 8.4$ Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.63 (d, $J = 8.4$ Hz, 1H), 7.49 (d, $J = 8.4$ Hz, 1H), 7.47 (d, $J = 8.4$ Hz, 1H), 7.30 – 7.26 (m, 4H), 7.24 (d, $J = 7.4$ Hz, 2H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.06 (d, $J = 8.4$ Hz, 1H), 6.95 – 6.90 (m, 3H), 6.45 (t, $J = 7.8$ Hz, 1H), 6.40 (t, $J = 7.8$ Hz, 1H), 4.93 (d, $J = 16.6$ Hz, 1H), 4.79 (d, $J = 16.6$ Hz, 1H).

¹³C{¹H} NMR (151 MHz, CDCl₃) δ 142.12, 139.30, 131.93, 131.82, 131.08, 130.92, 130.32, 129.27, 129.10, 128.90, 128.74, 128.60, 128.35, 128.30, 128.08, 127.46, 126.77, 126.74, 126.45, 126.41, 125.70, 125.37, 125.32, 125.20, 125.05, 124.60, 124.32, 124.16, 124.04, 123.59, 119.80, 118.89 (q, $J = 320$ Hz), 32.77.

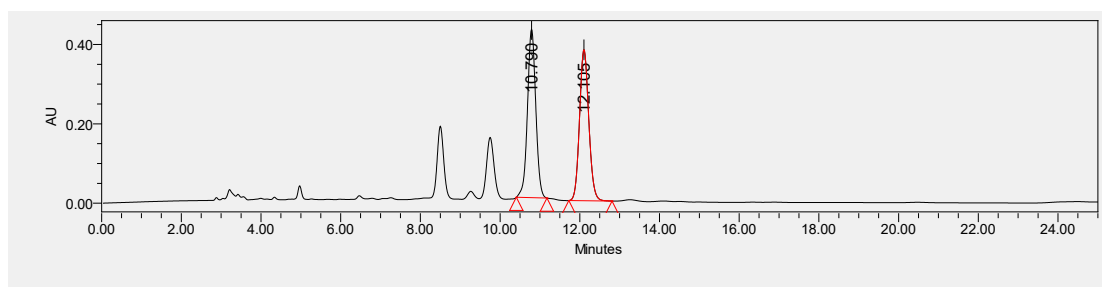
¹⁹F{¹H} NMR (564 MHz, CDCl₃) δ -72.68.

ESI-HRMS: calcd for C₃₈H₂₄F₃O₃S⁺ ($[M + H]^+$) = 617.6617, found 617.6619.

IR (neat): 3052, 2983, 909, 830, 732 cm⁻¹.



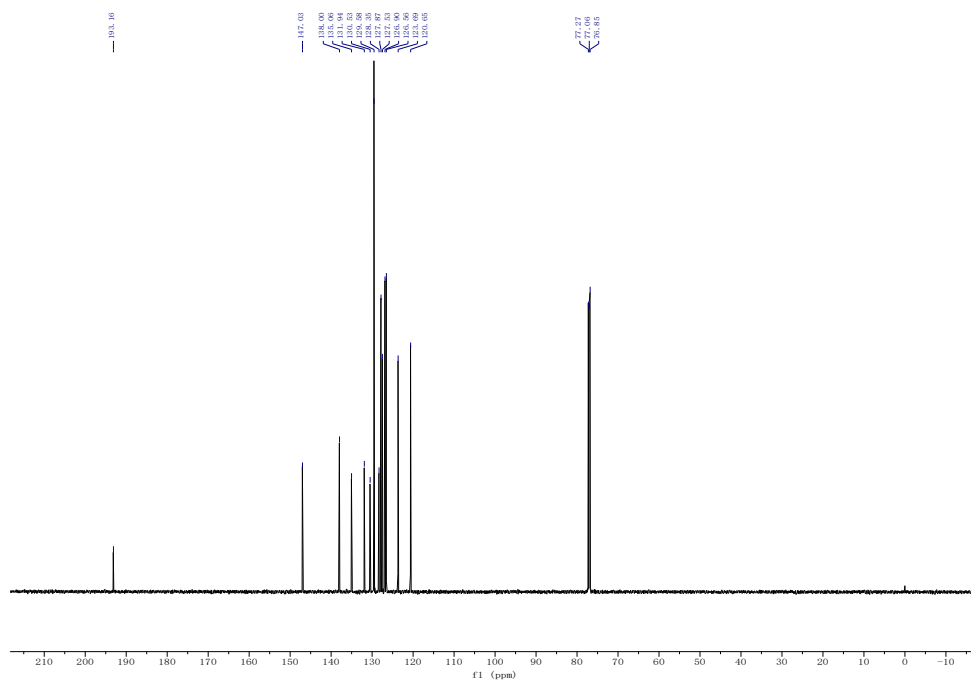
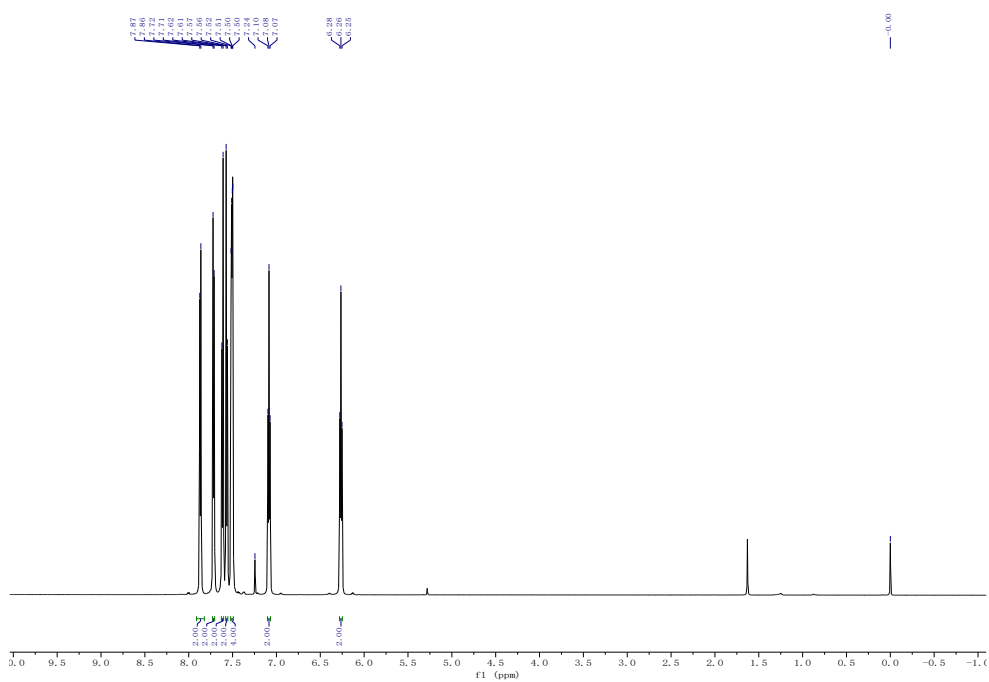
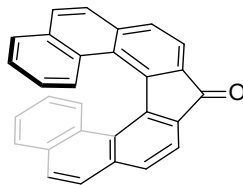
Retention Time	Area	% Area	Height
10.824	26273527	97.54	1859857
12.150	663254	2.46	42809



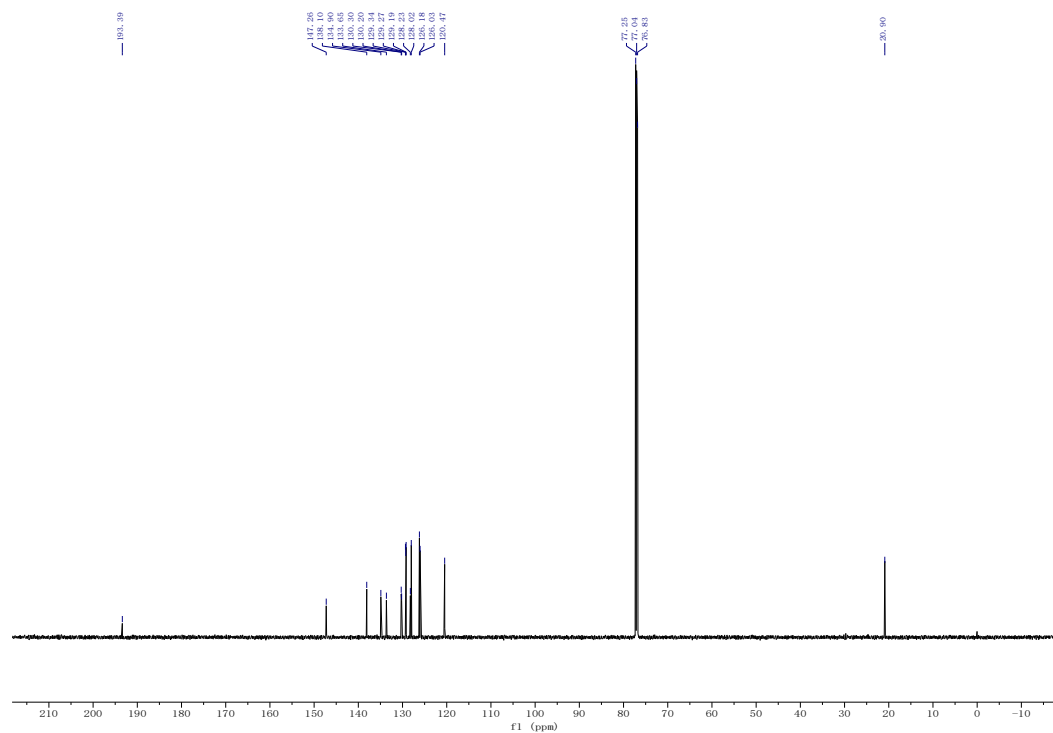
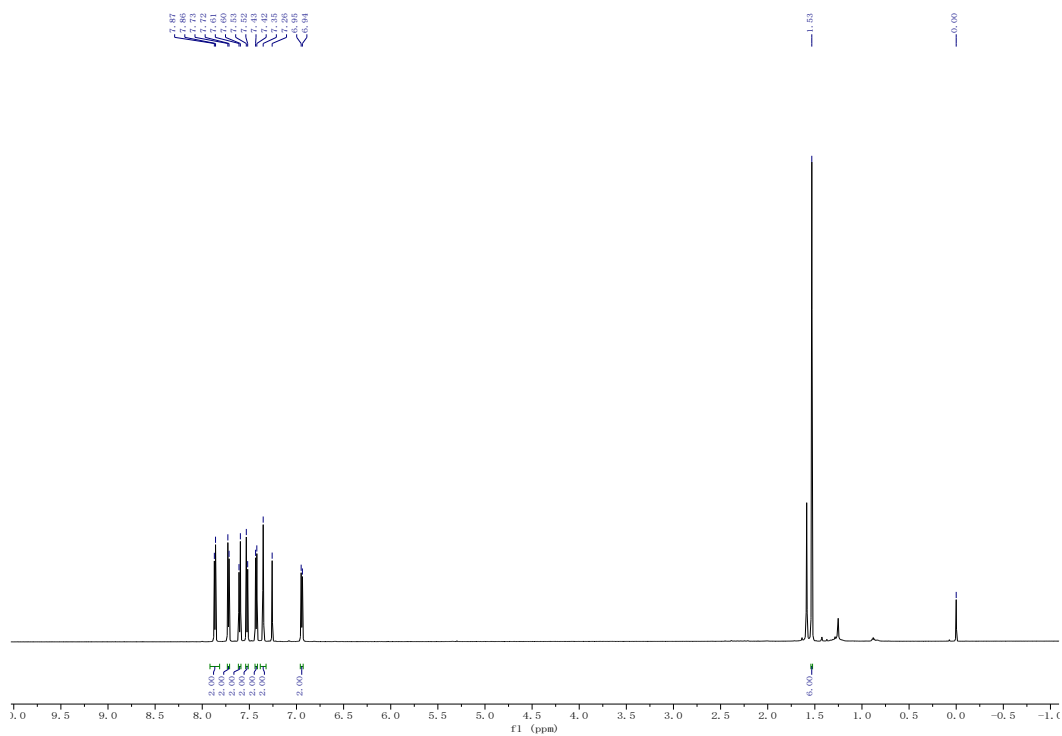
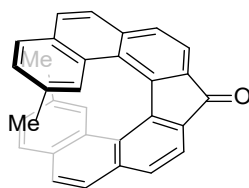
Retention Time	Area	% Area	Height
10.790	6129833	49.99	423995
12.105	6133080	50.01	380369

13. Copies of the NMR spectra for new compounds.

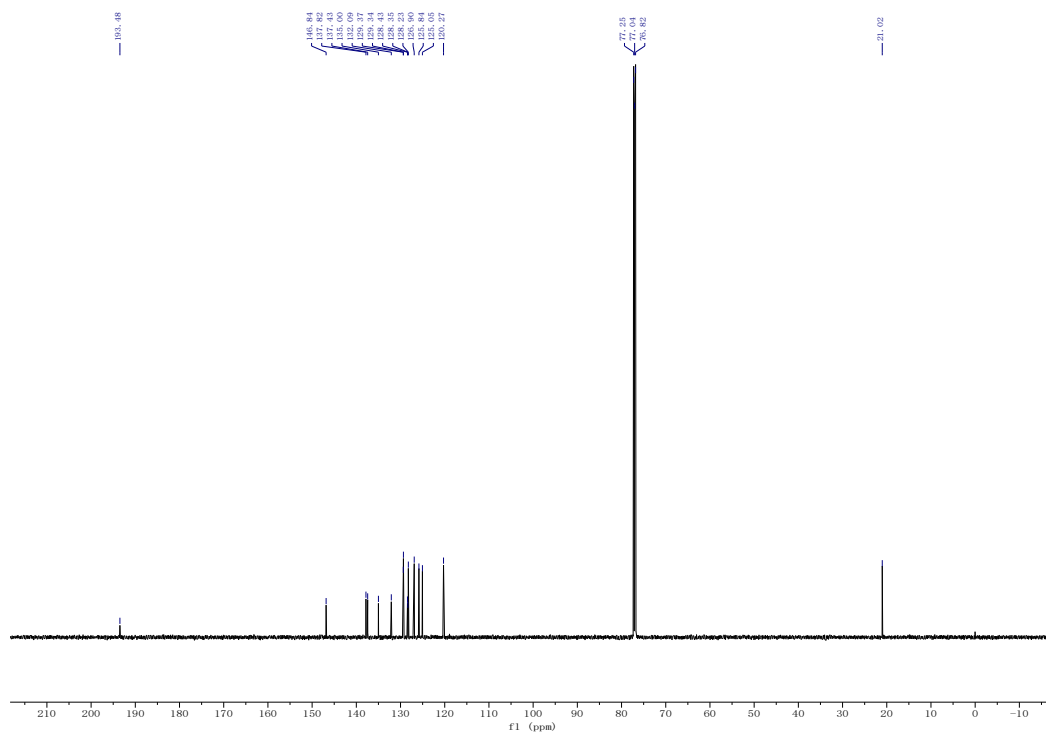
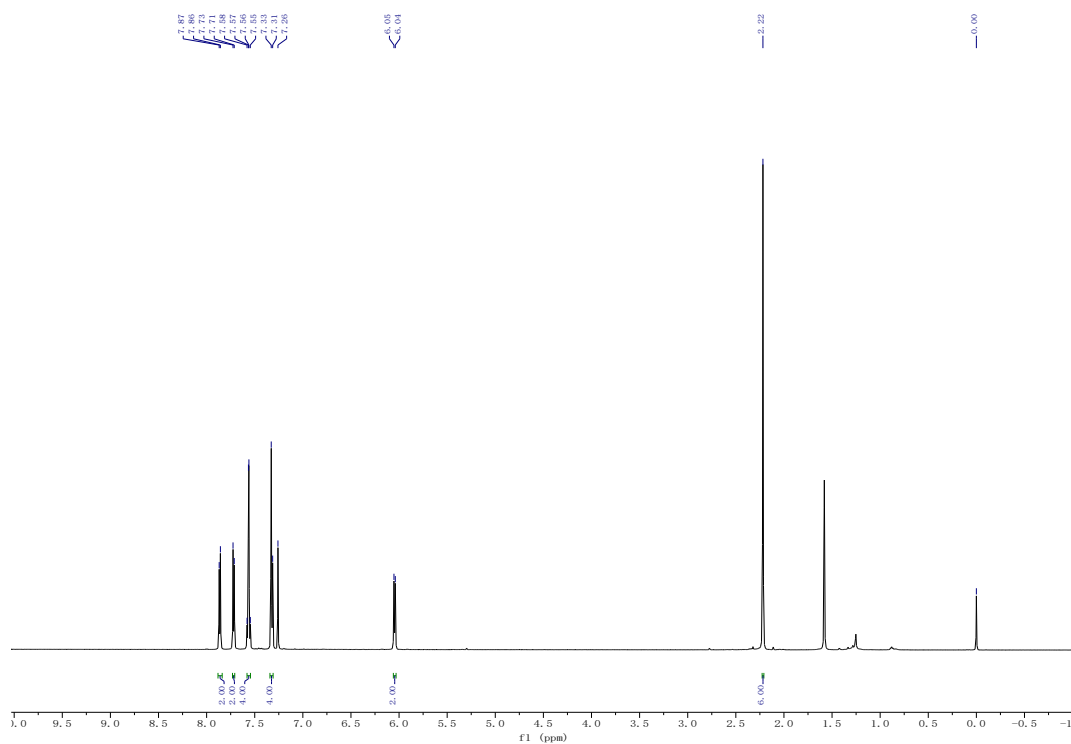
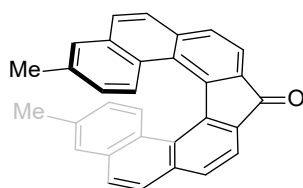
(M)-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A1)



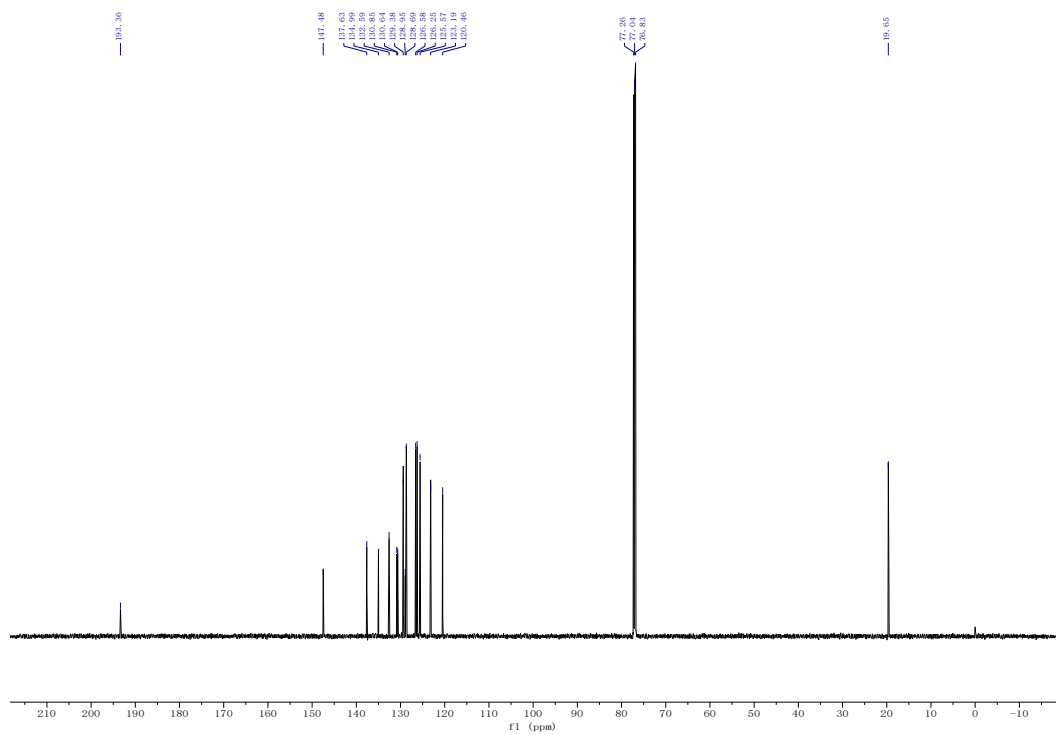
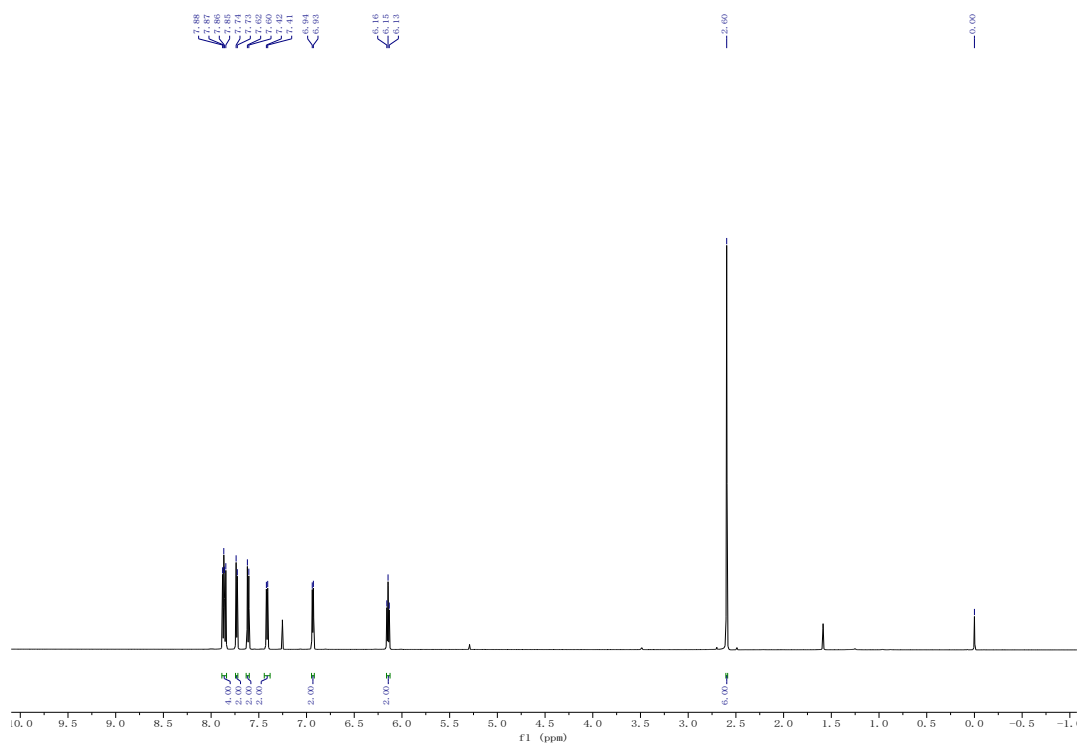
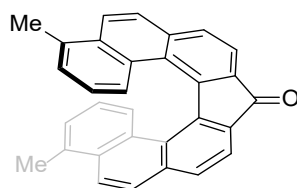
(M)-2,16-dimethyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A2)



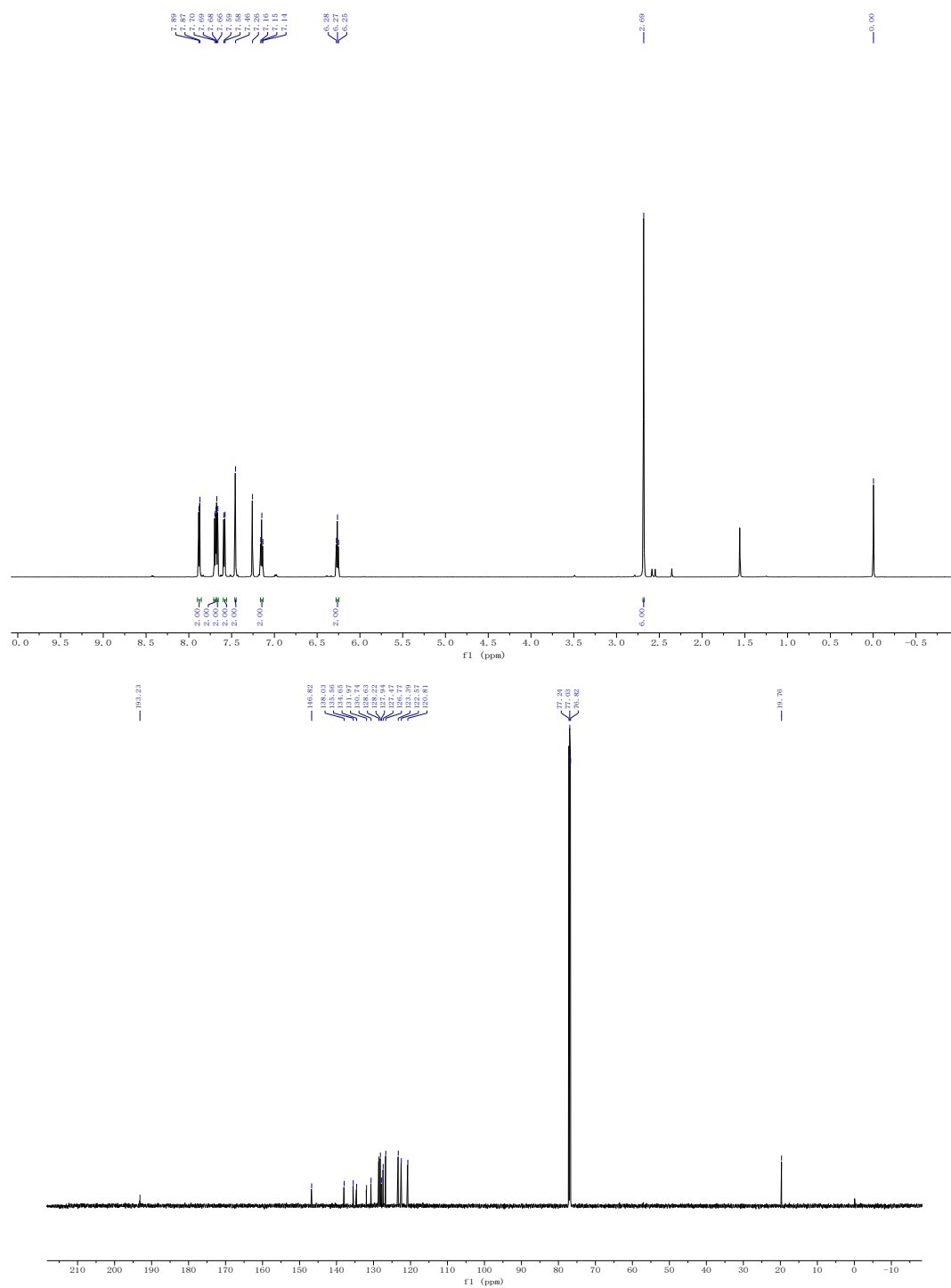
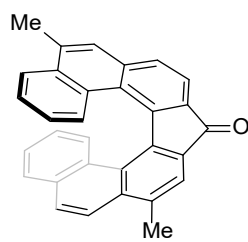
(M)-3,15-dimethyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A3)



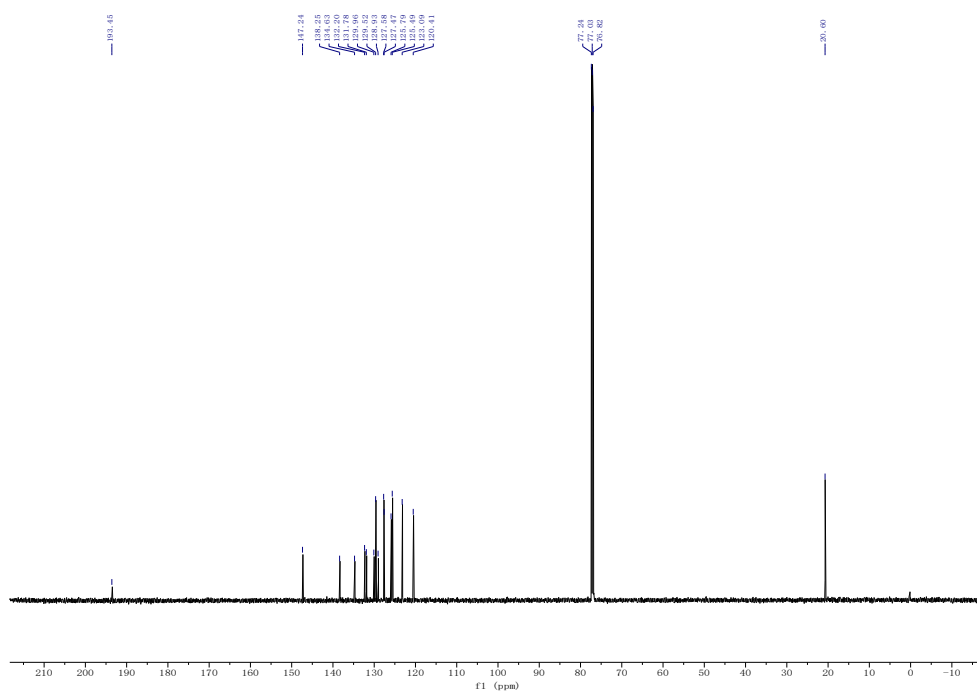
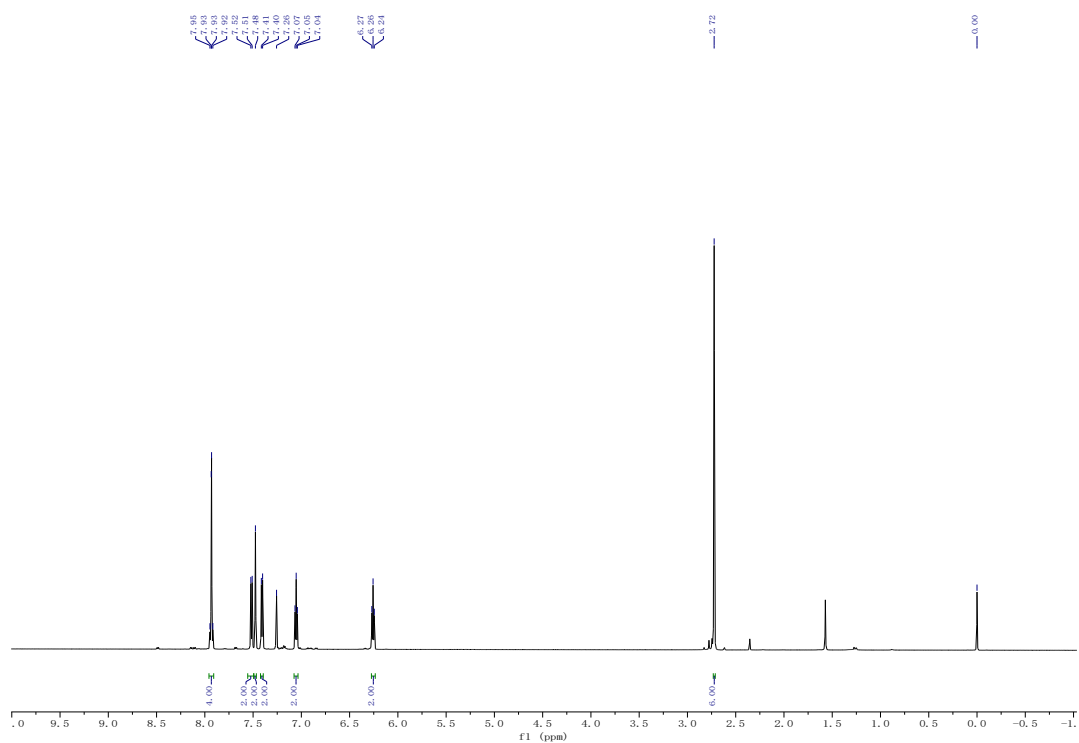
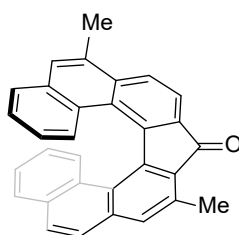
(M)-4,14-dimethyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A4)



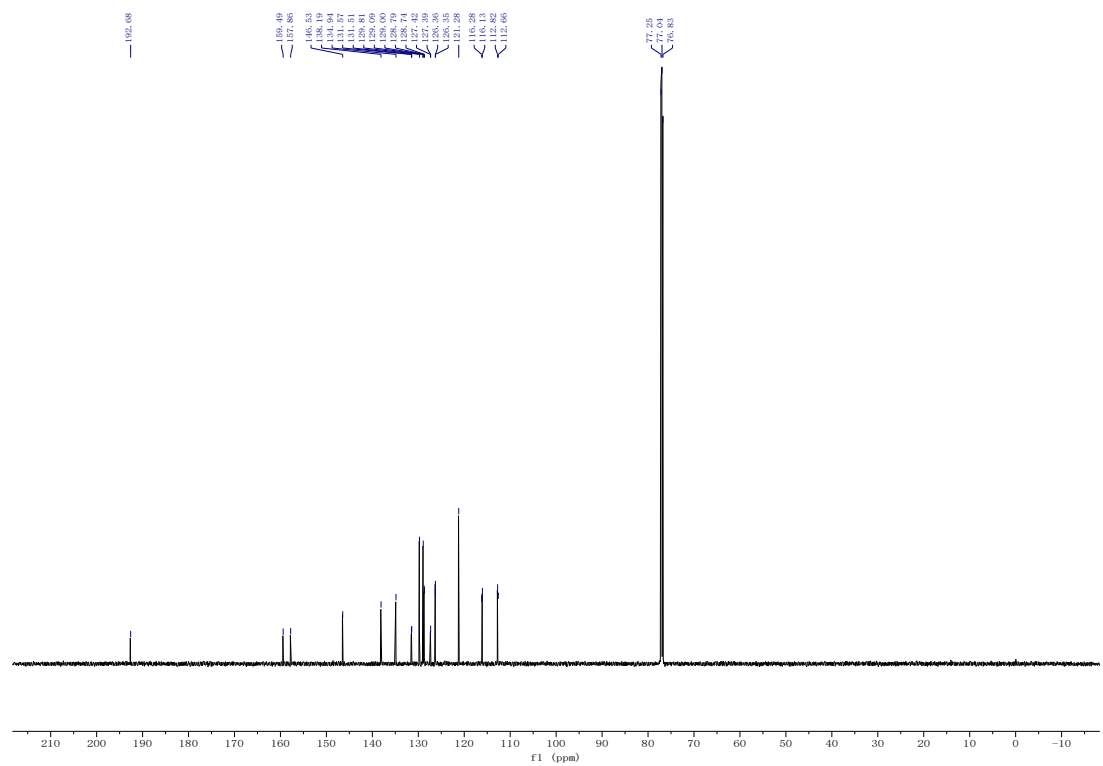
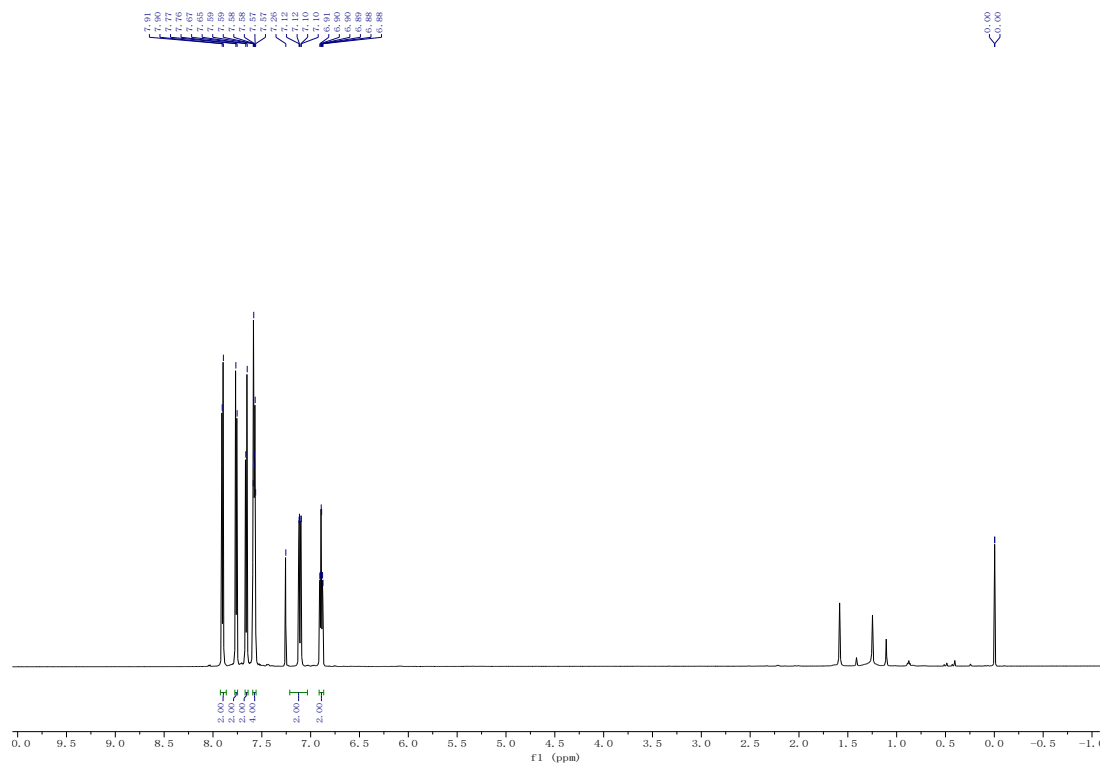
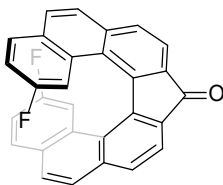
(M)-5,11-dimethyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A5)

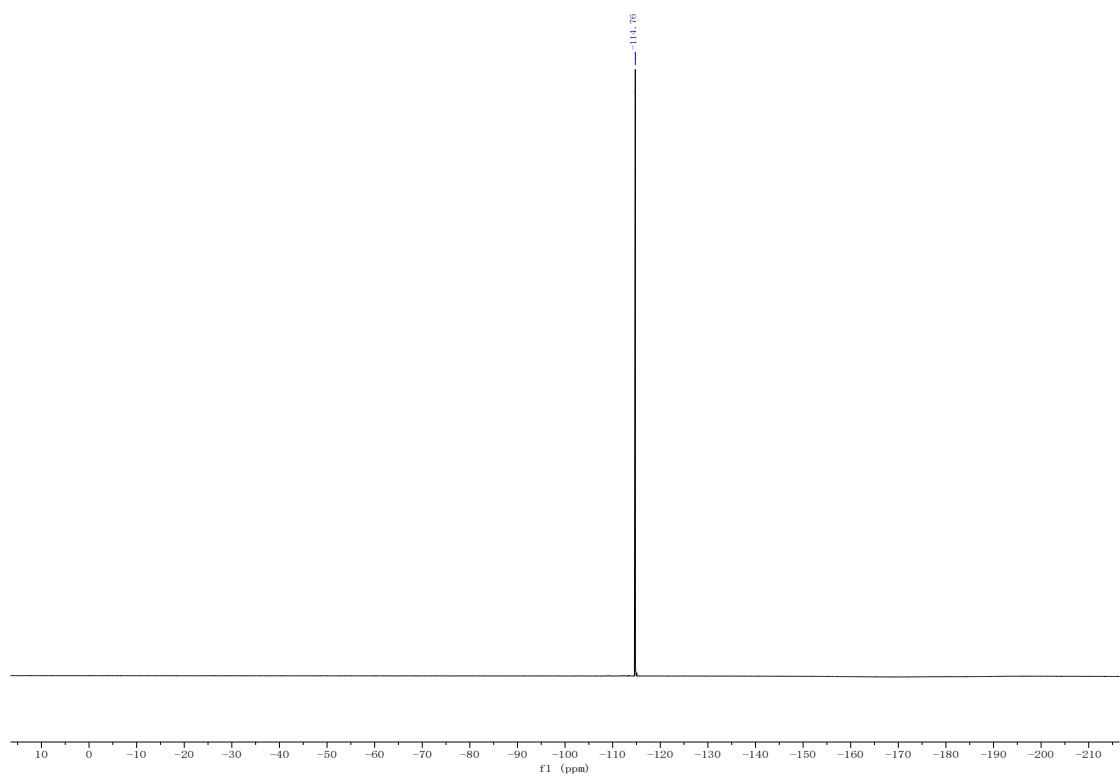


(M)-6,10-dimethyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A6)

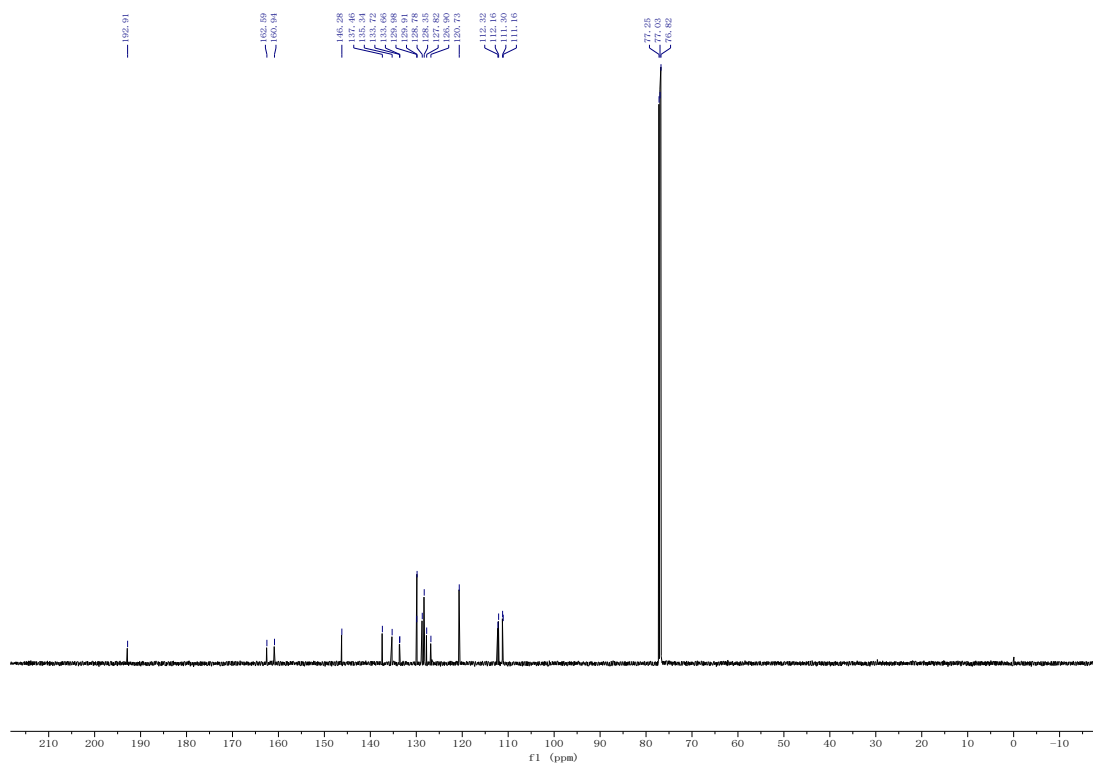
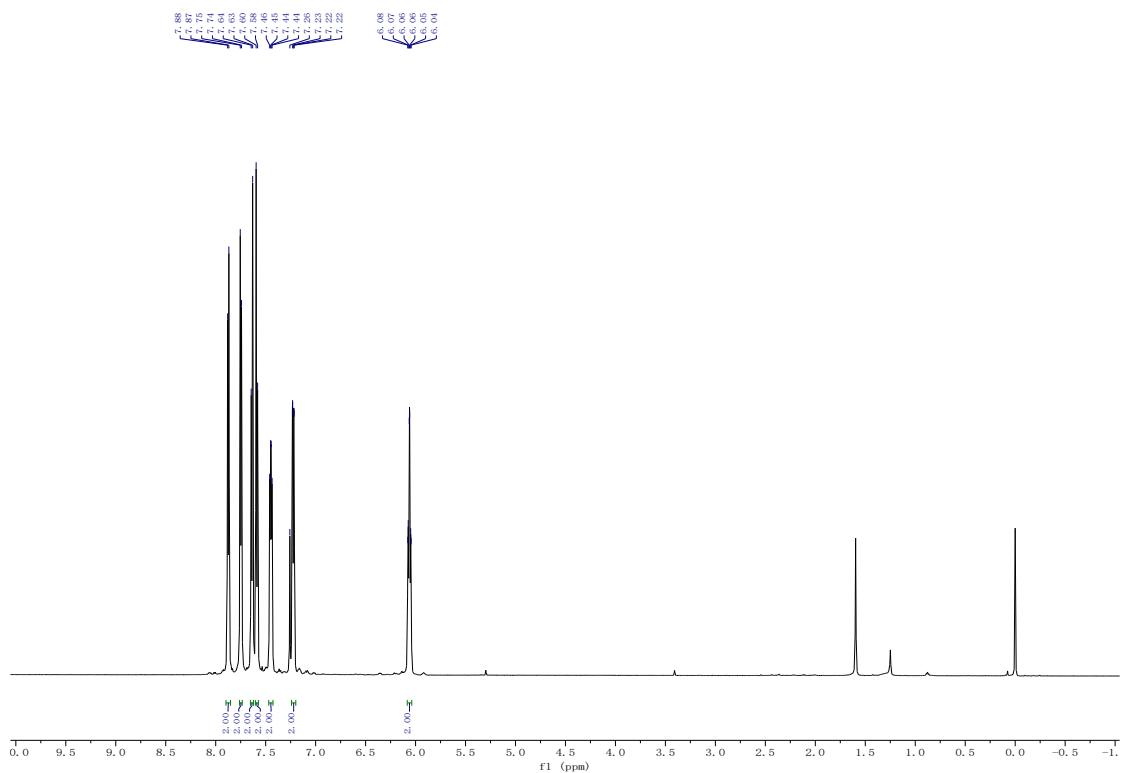
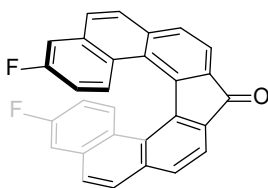


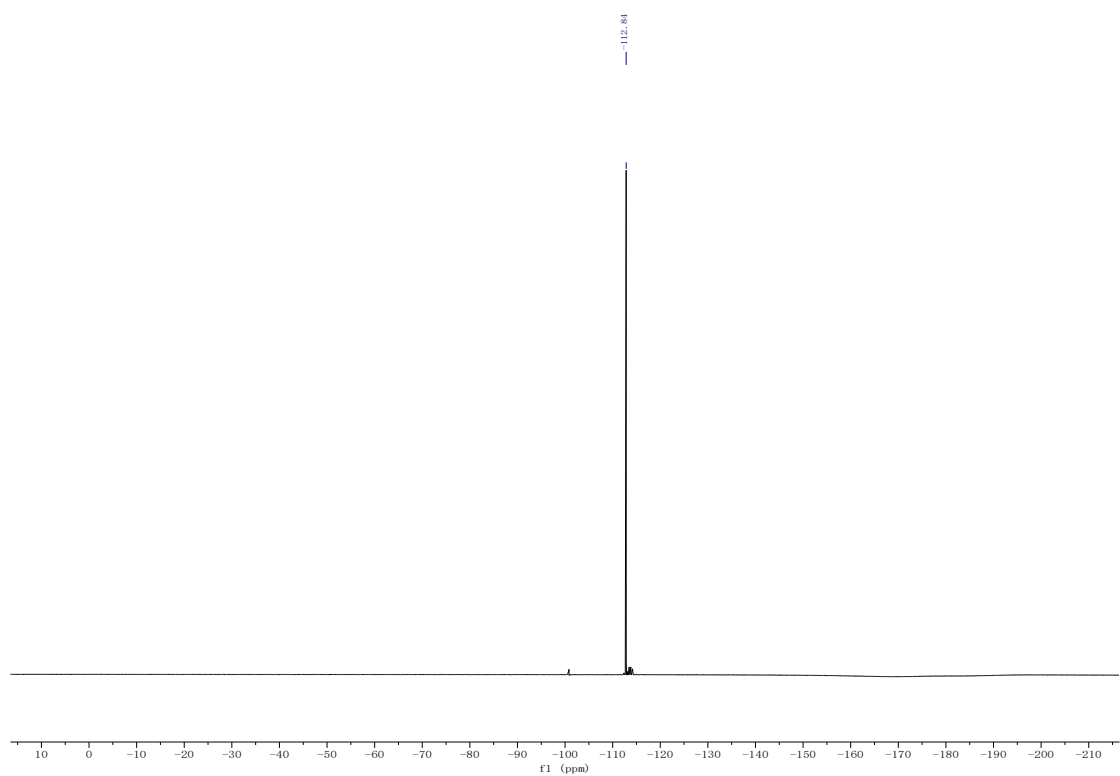
(M)-2,16-difluoro-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A7)



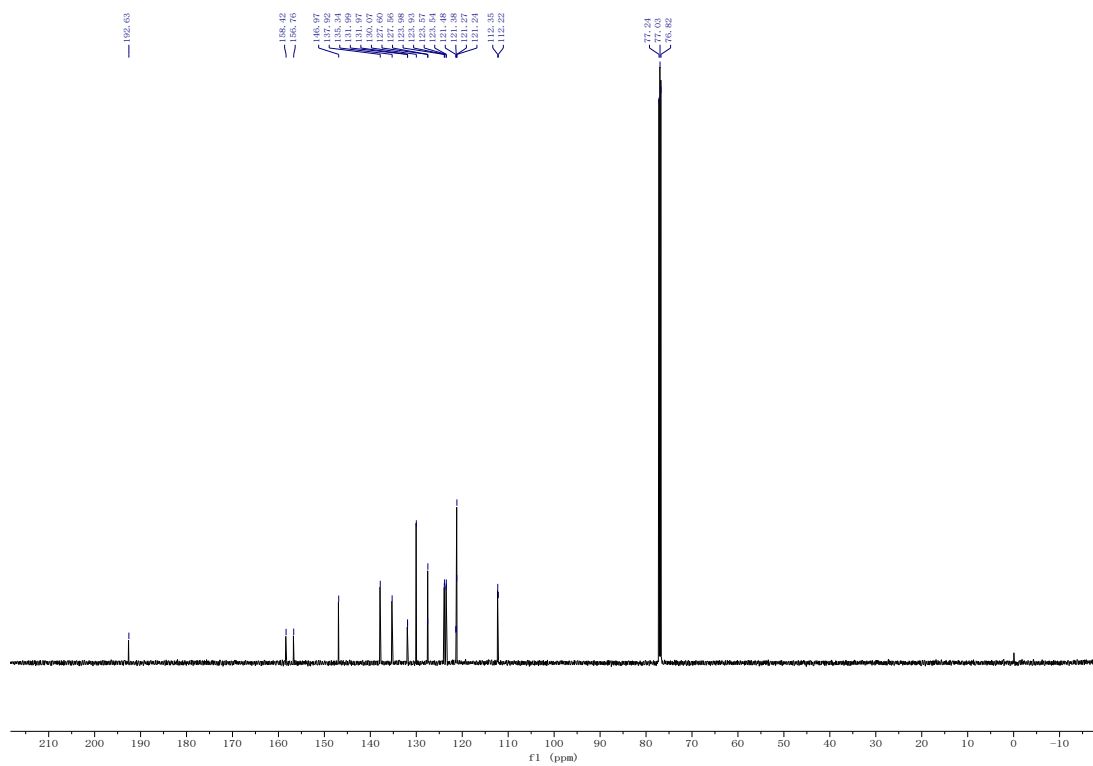
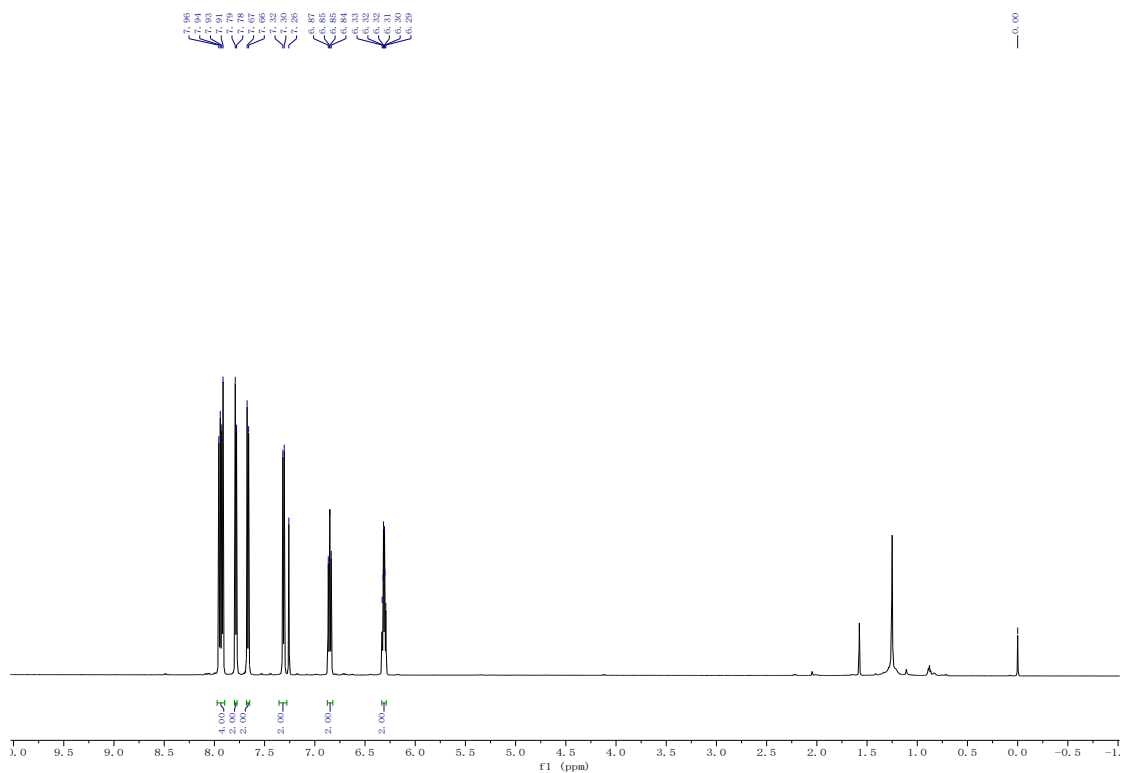
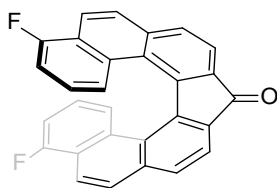


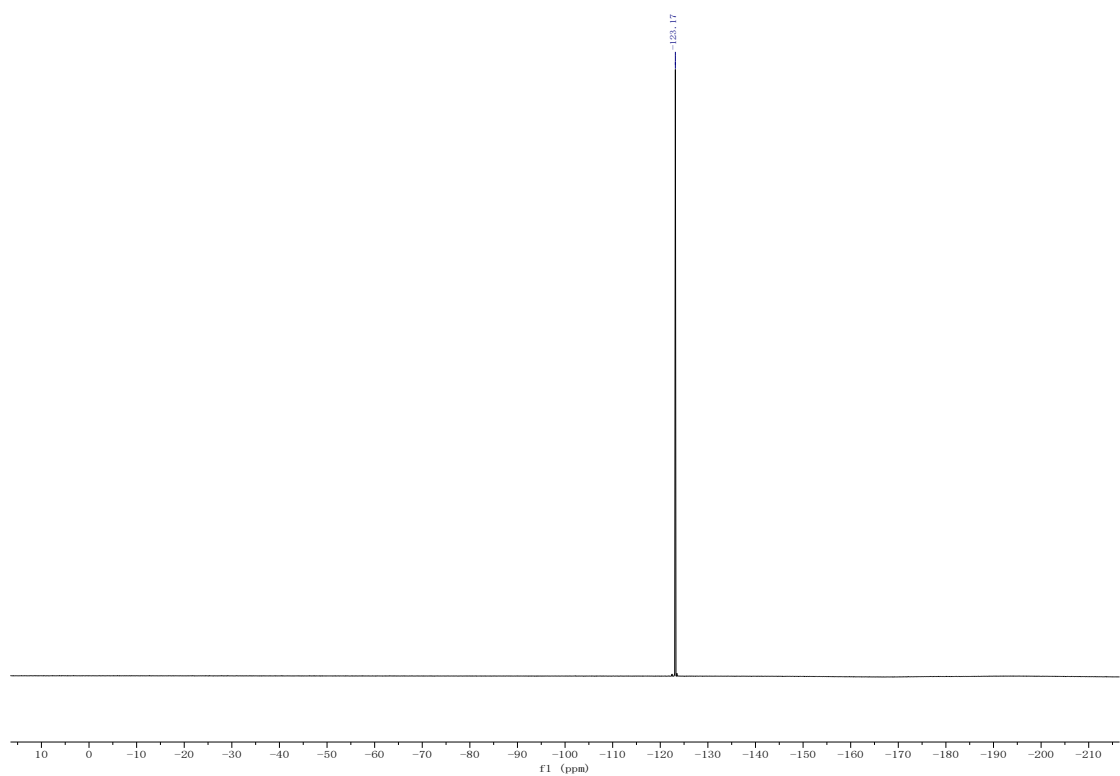
(M)-3,15-difluoro-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A8)



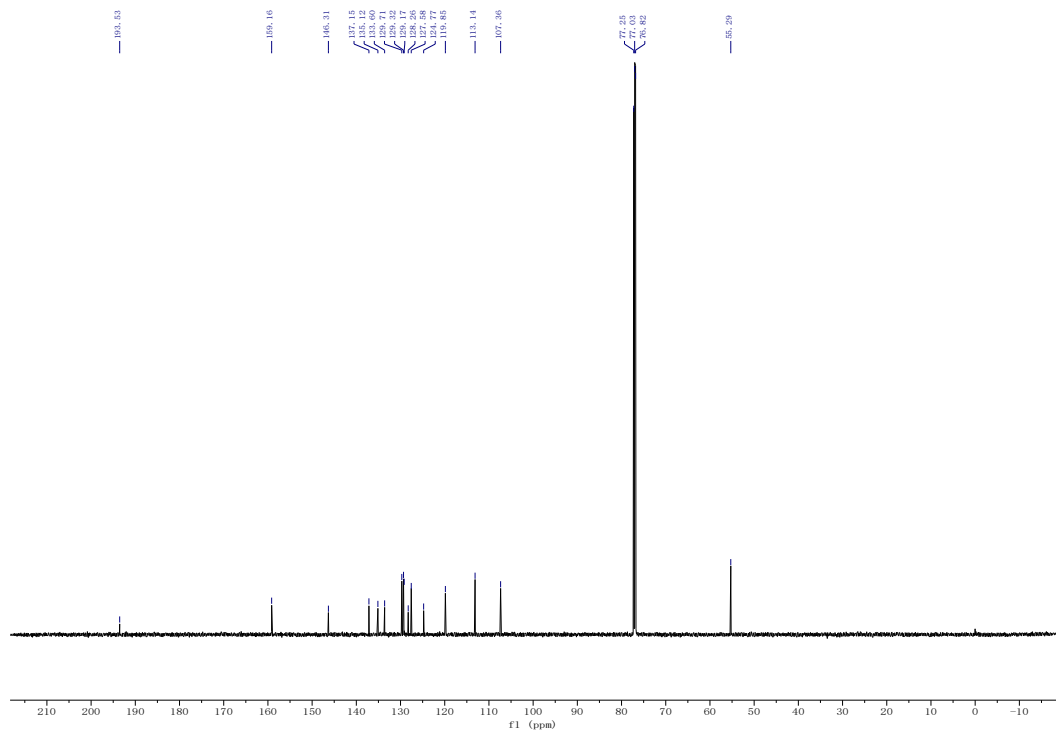
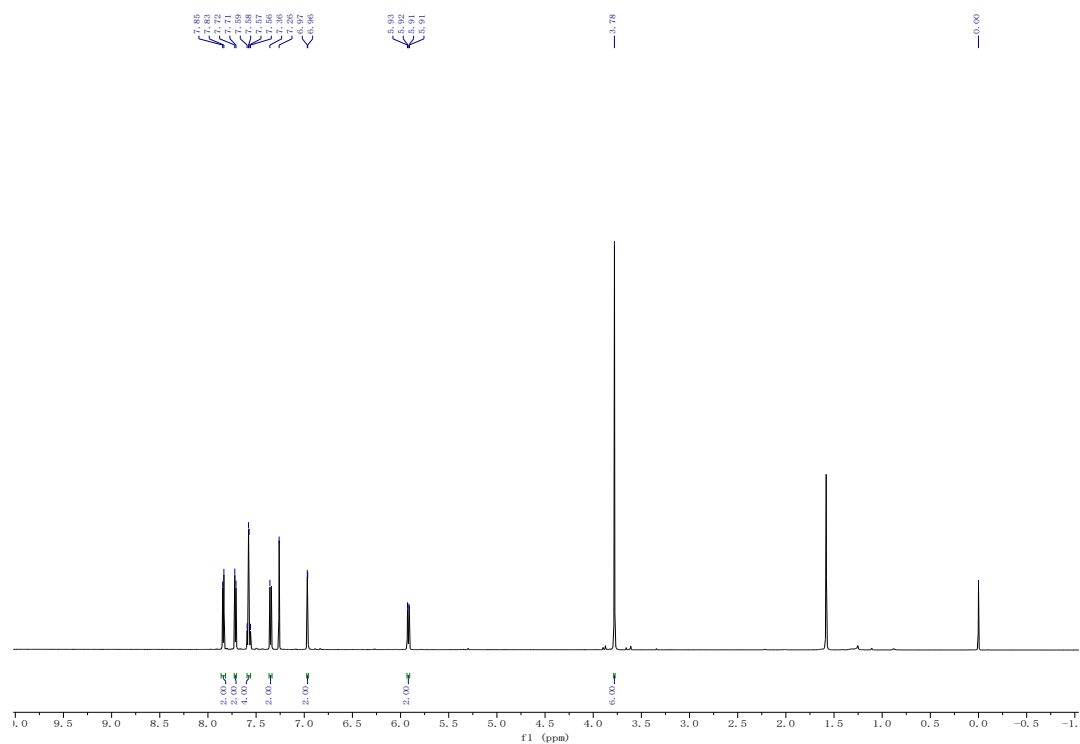
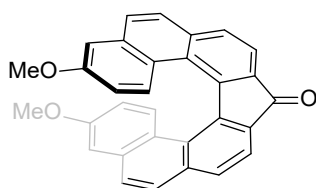


(M)-4,14-difluoro-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A9)

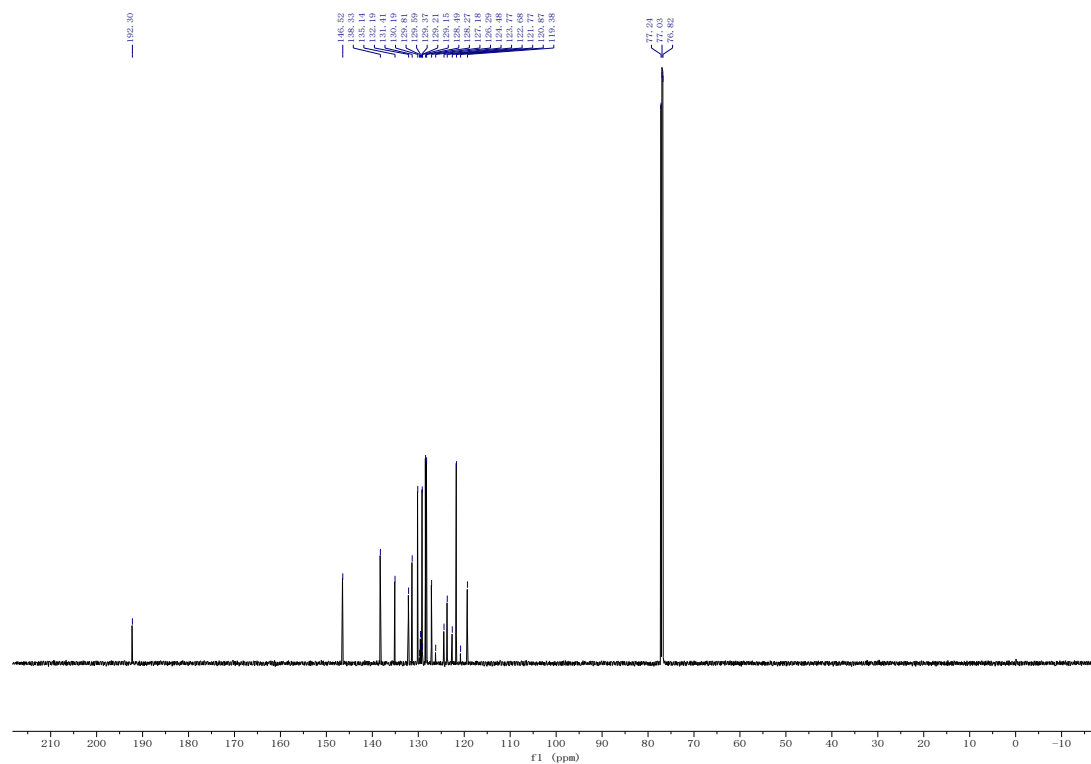
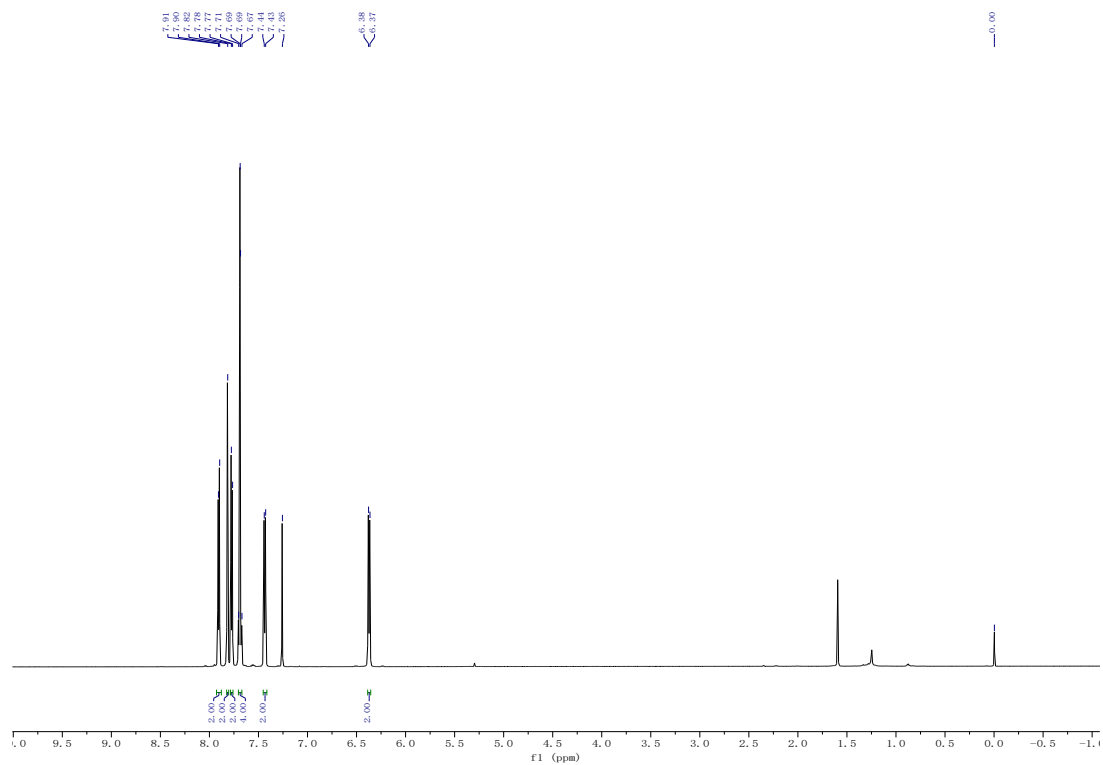
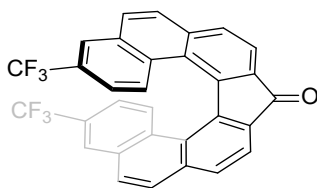


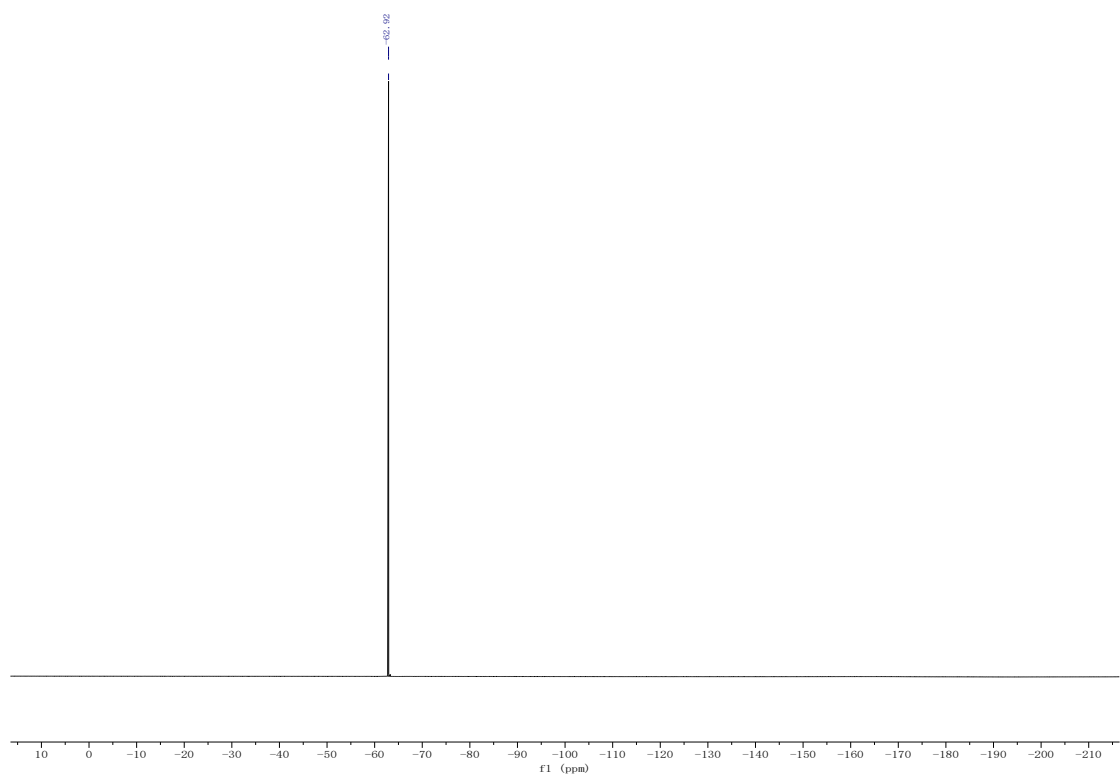


(*M*)-3,15-dimethoxy-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A10)

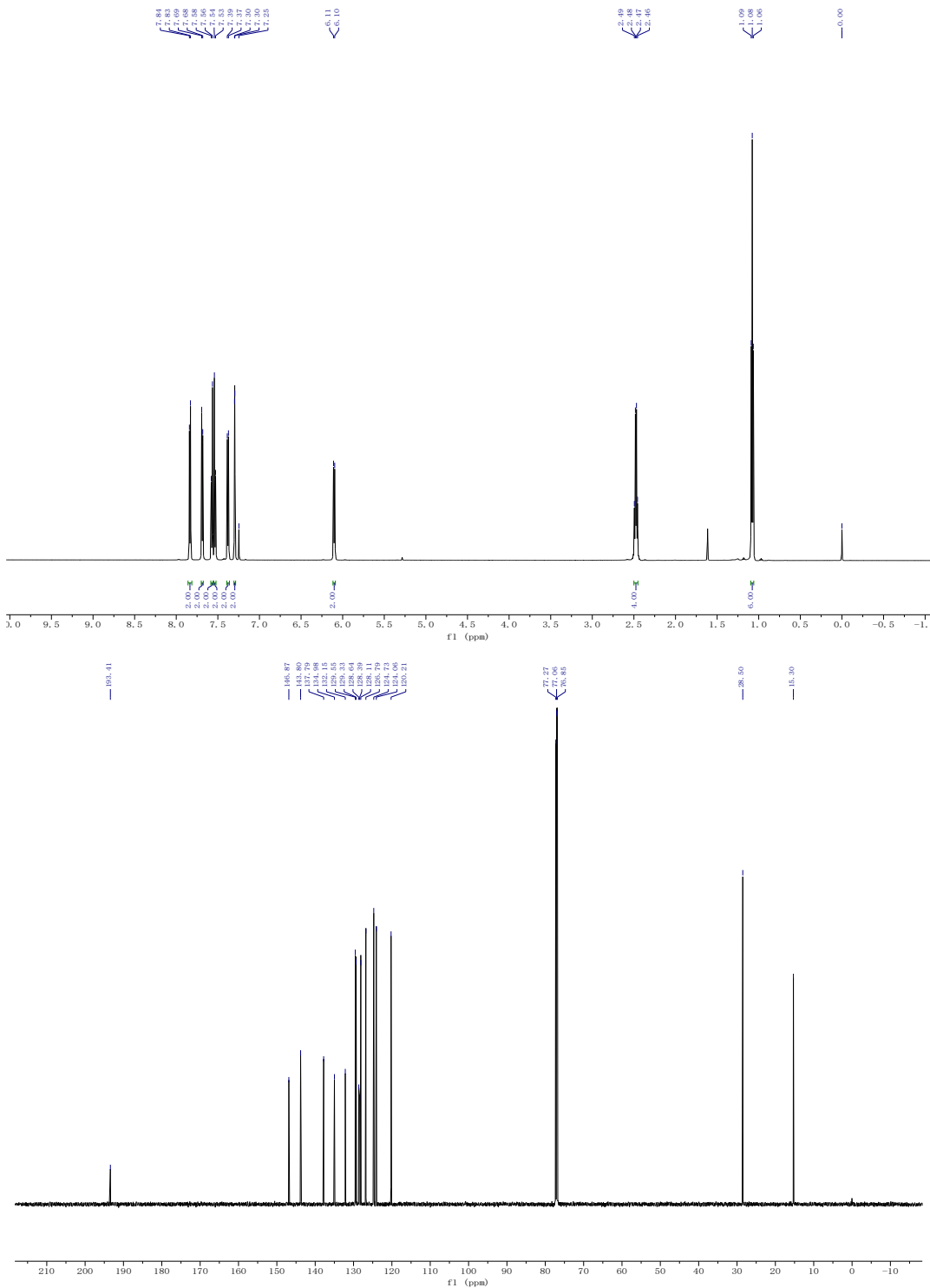
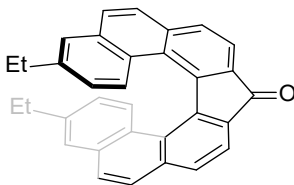


(*M*)-3,15-bis(trifluoromethyl)-9H-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A11)

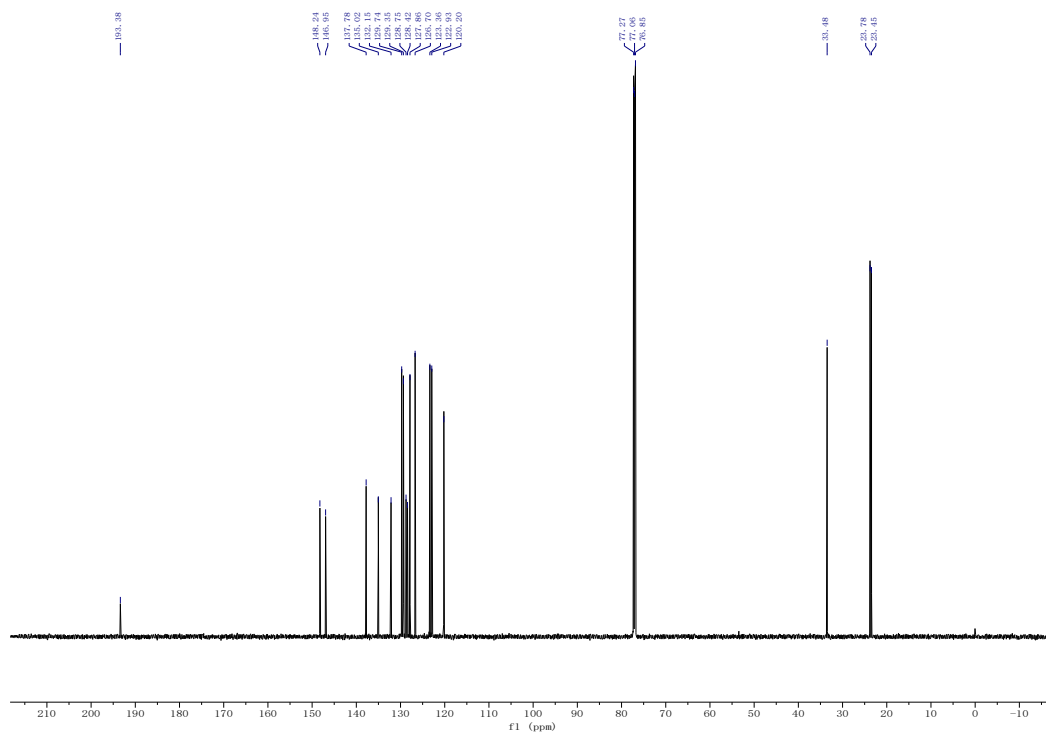
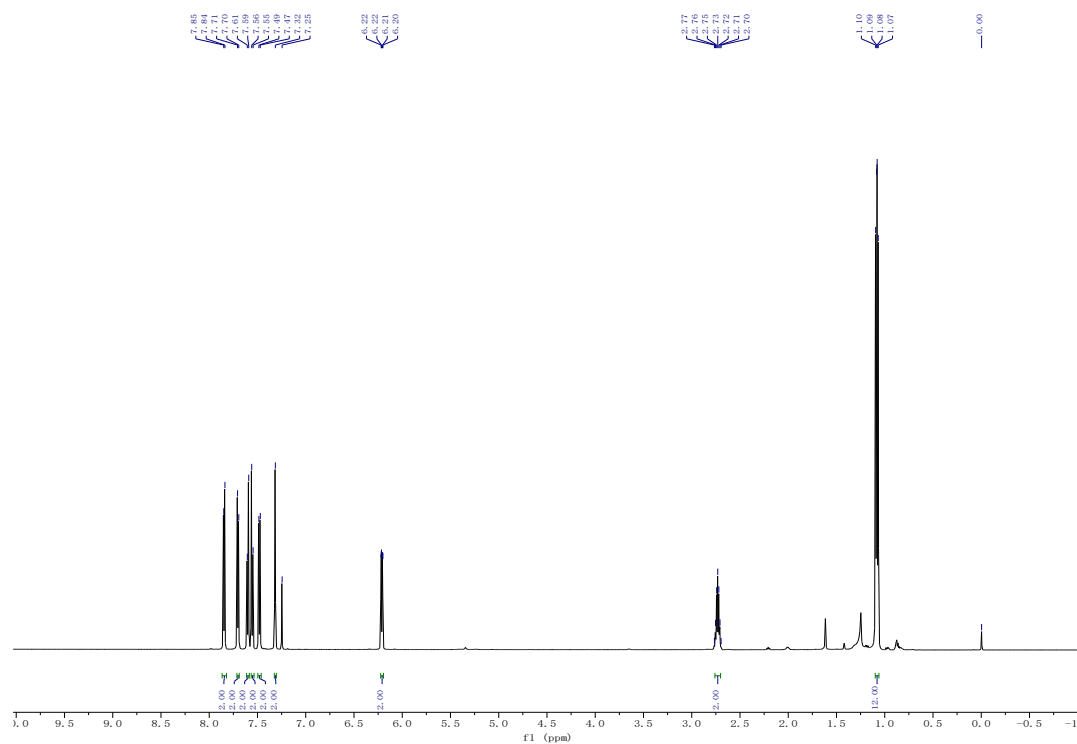
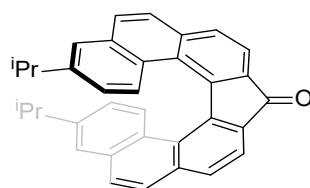




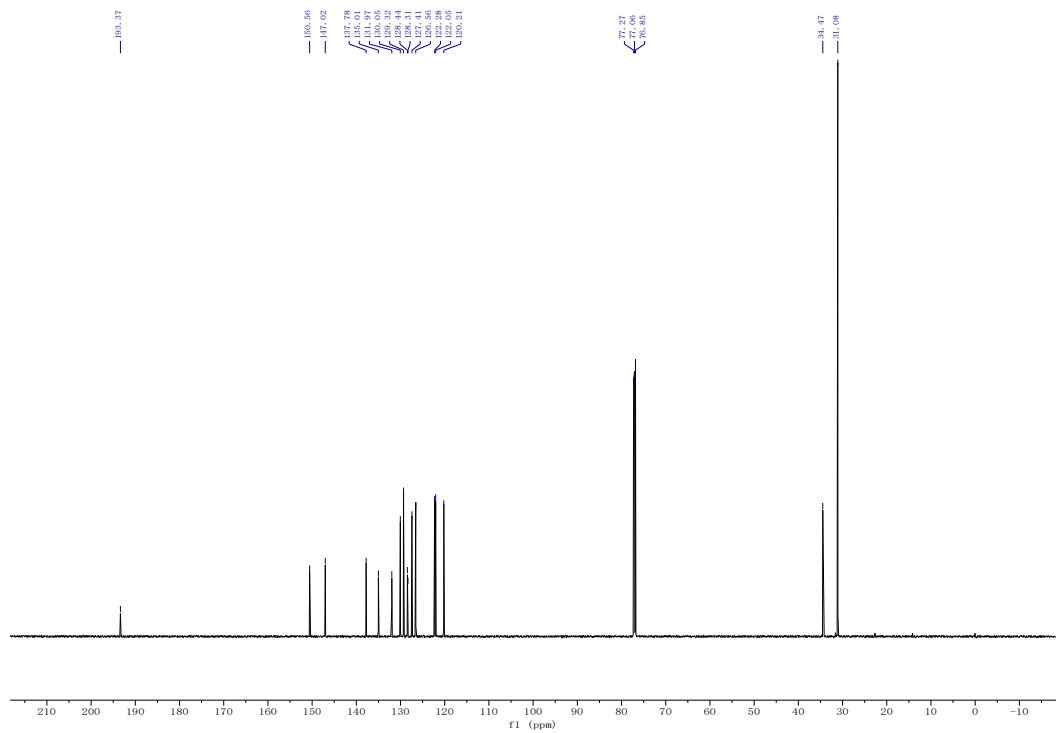
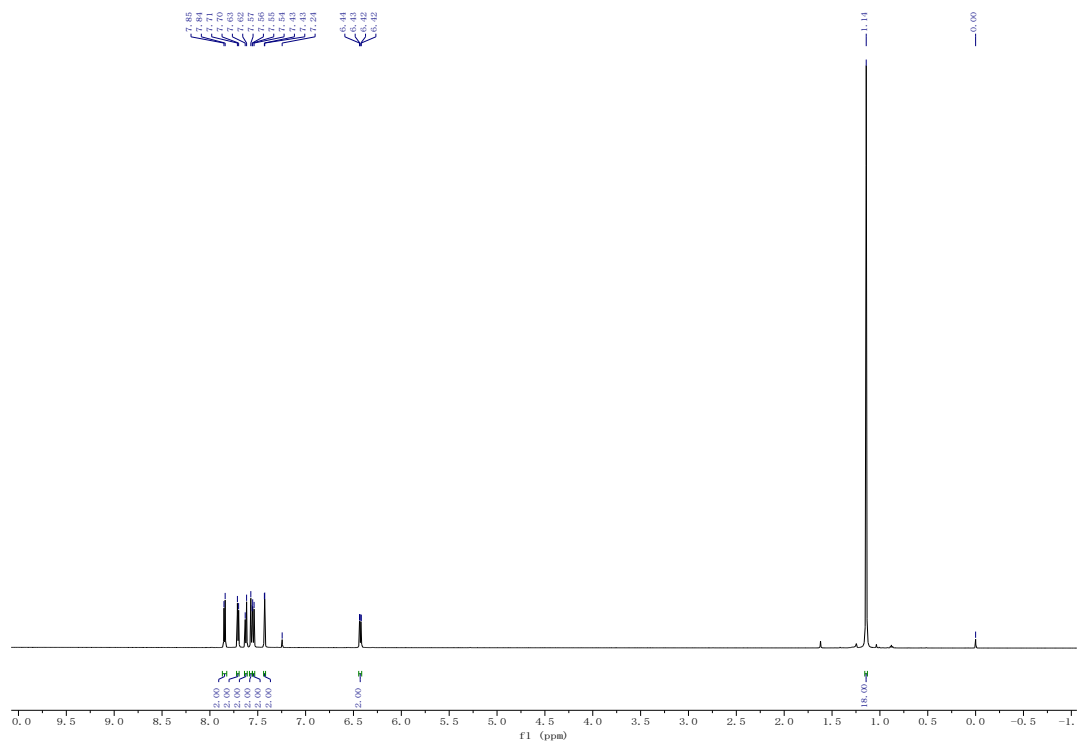
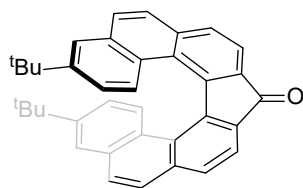
(M)-3,15-diethyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A12)



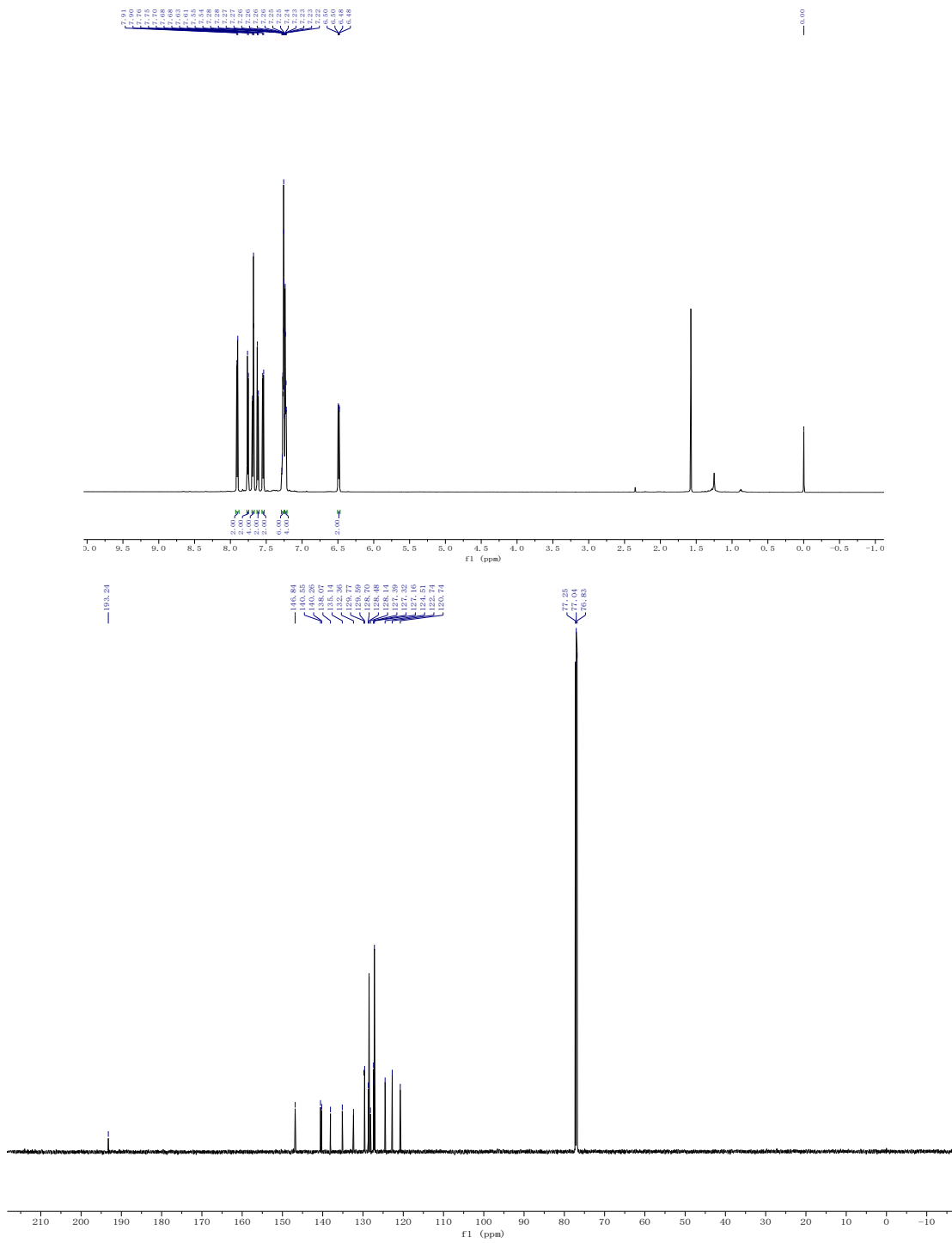
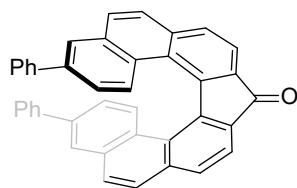
(*M*)-3,15-diisopropyl-9H-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A13)



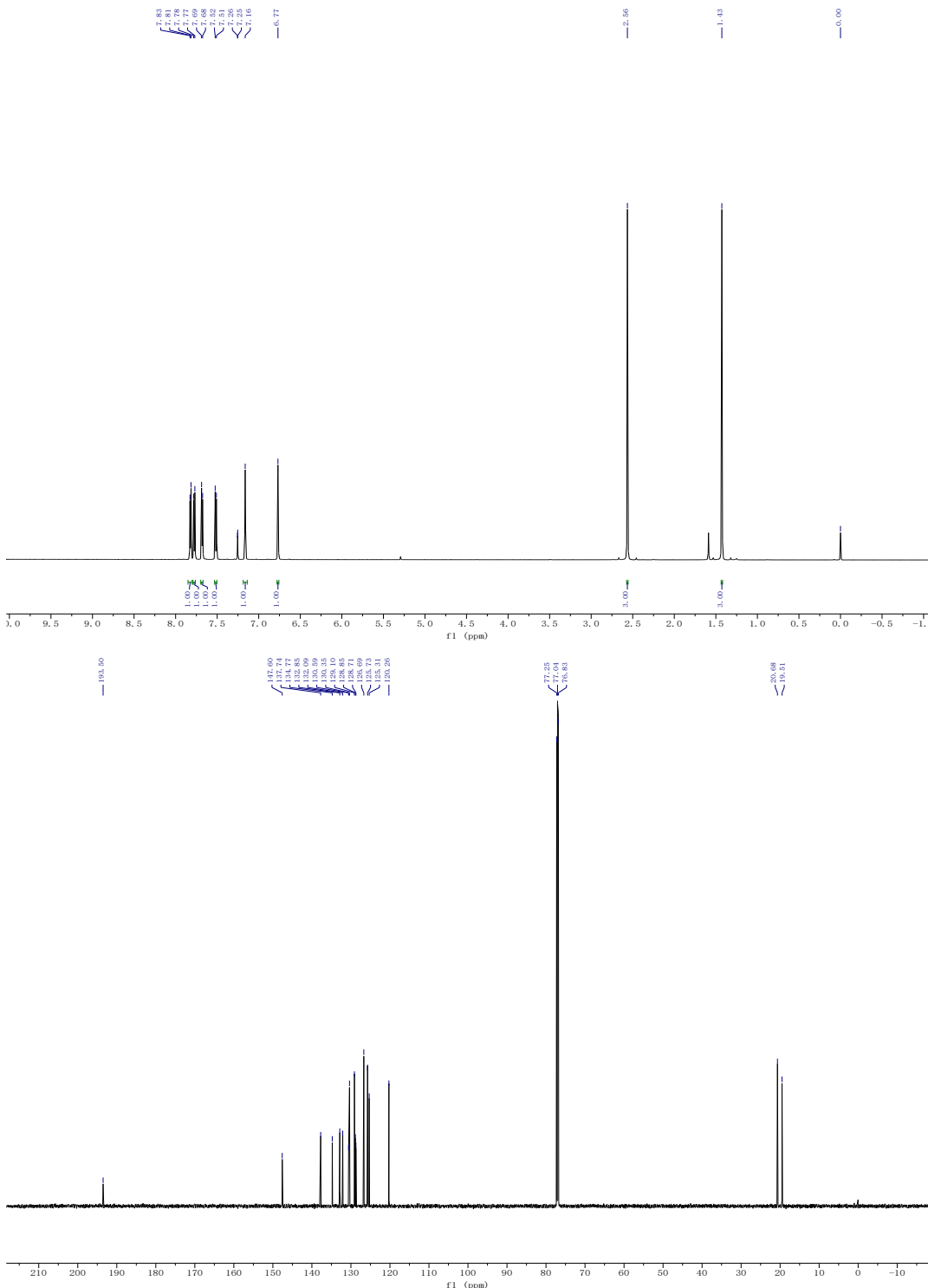
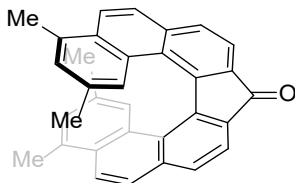
(M)-3,15-di-*tert*-butyl-9H-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-one (A14)



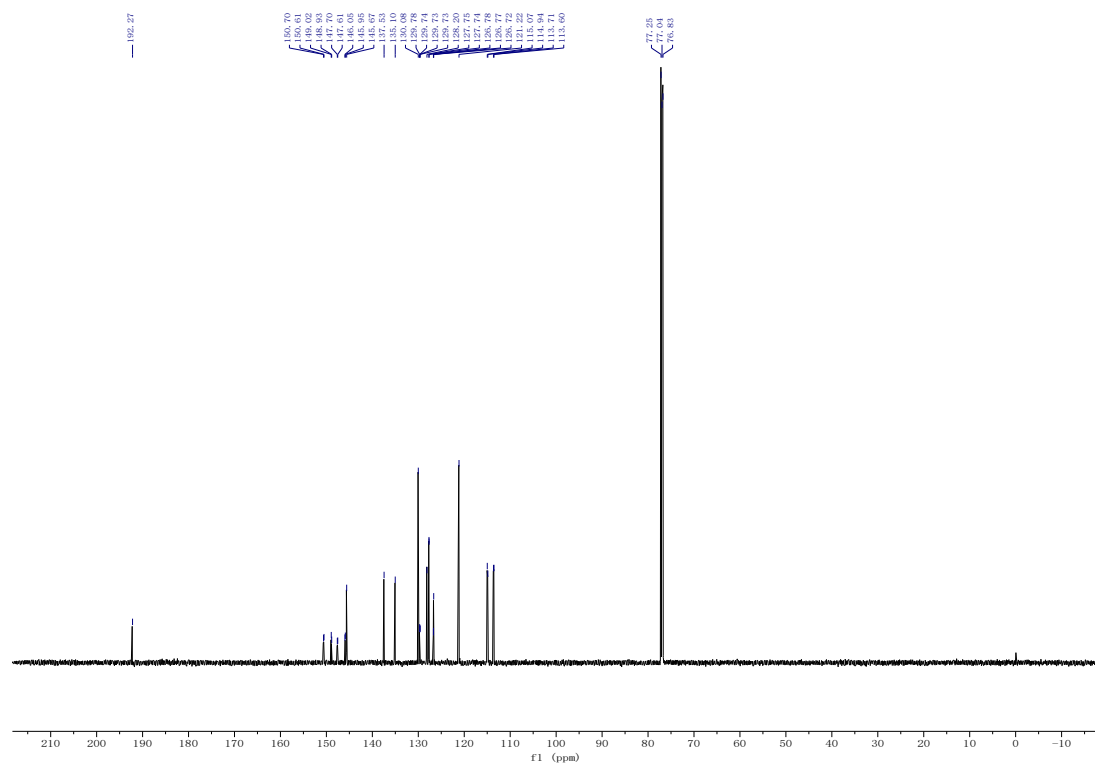
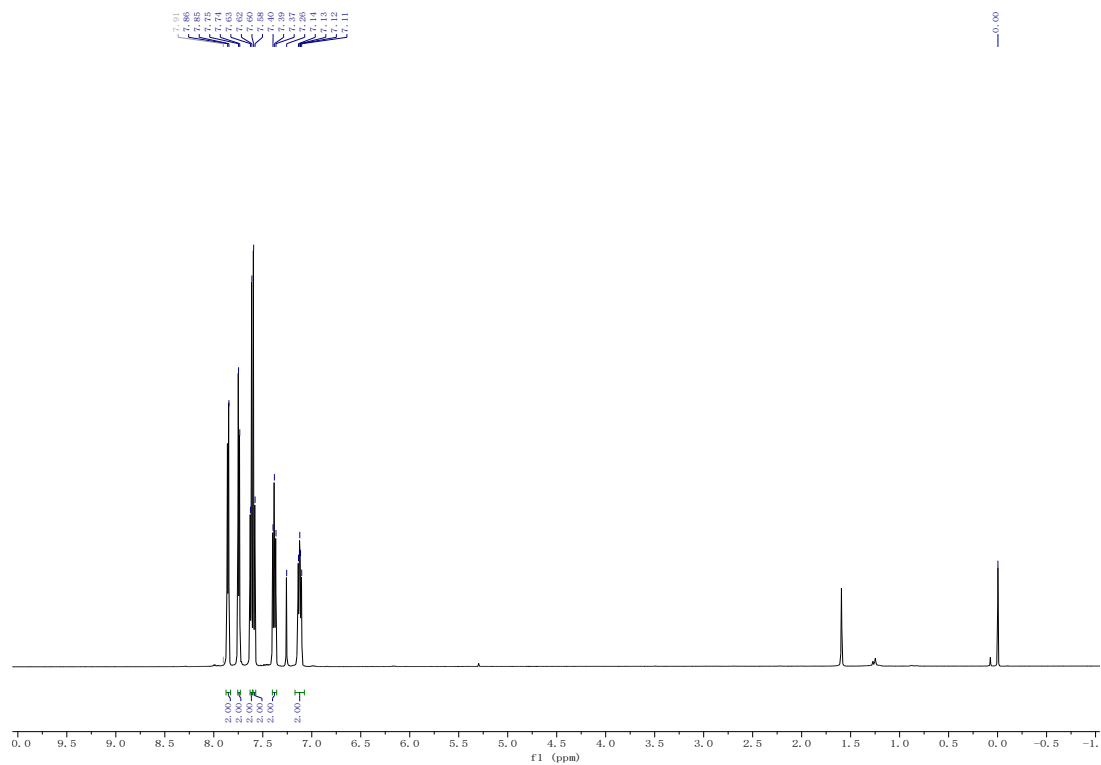
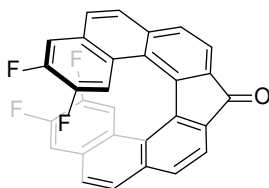
(M)-3,15-diphenyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A15)

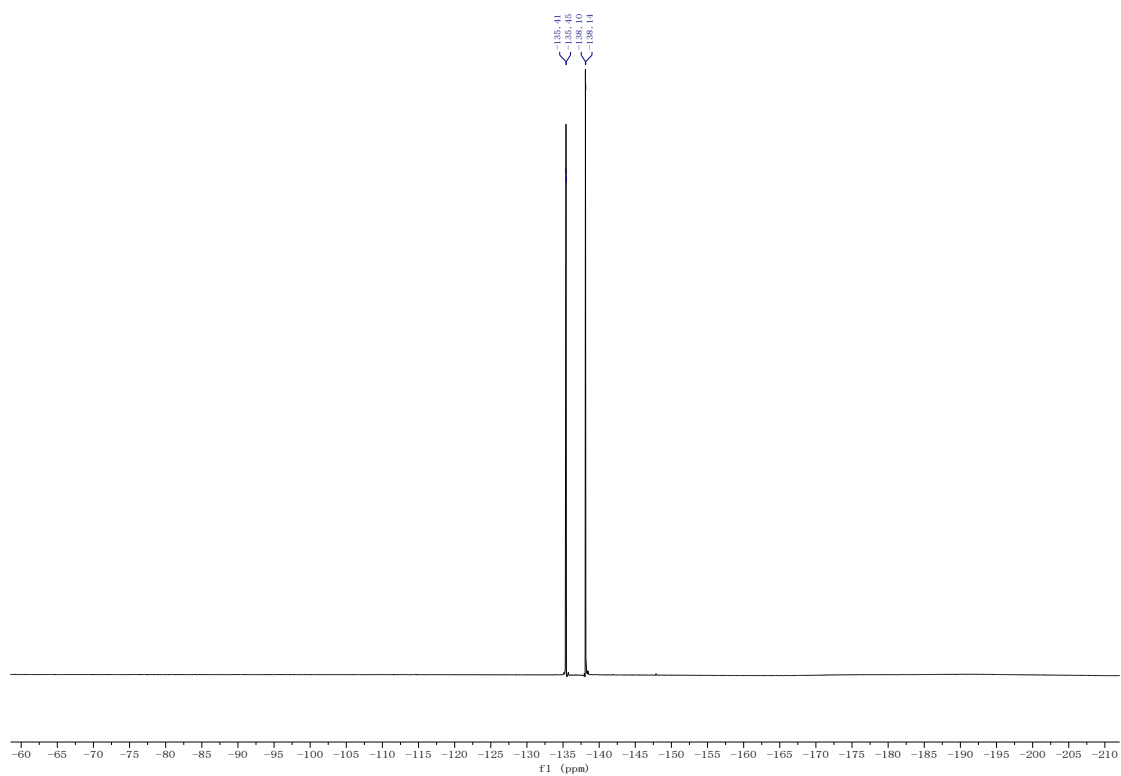


(M)-2,4,14,16-tetramethyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A16)

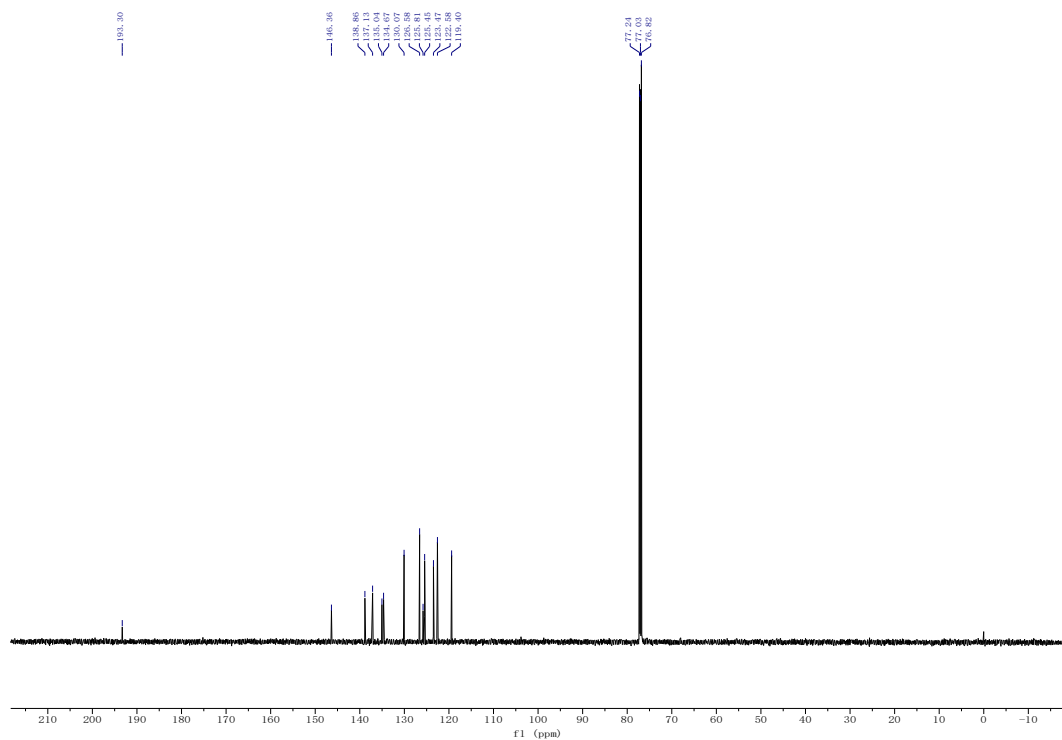
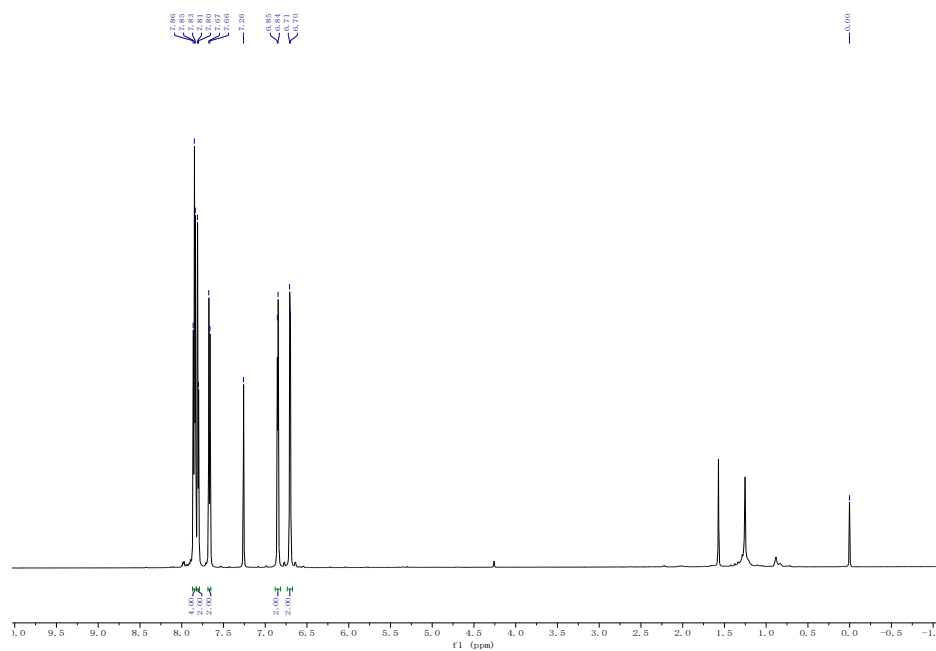
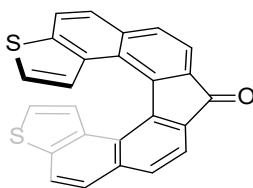


(M)-2,3,15,16-tetrafluoro-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one (A17)

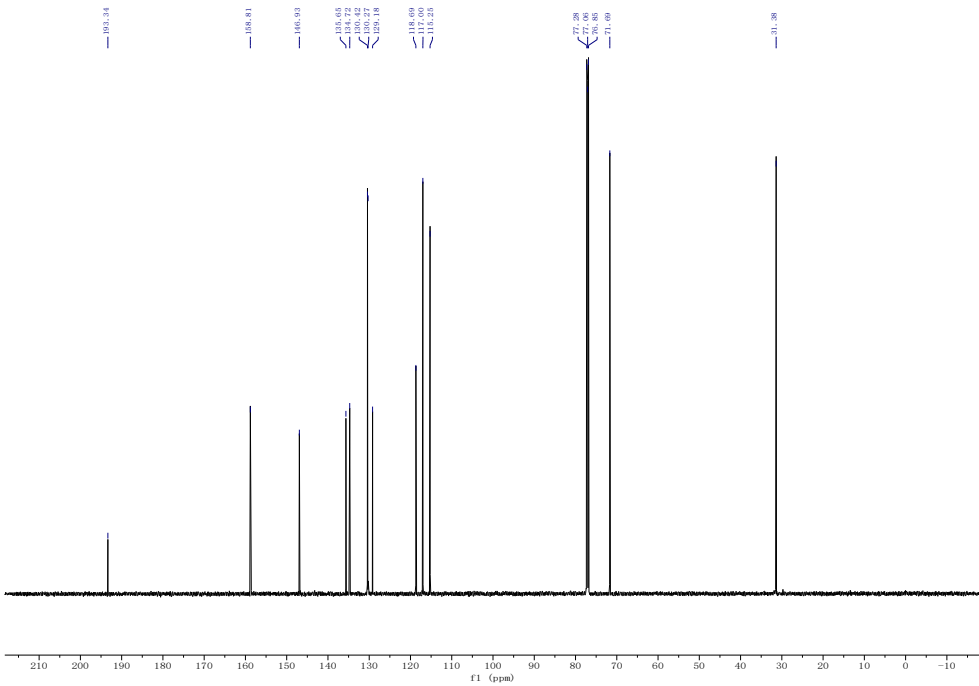
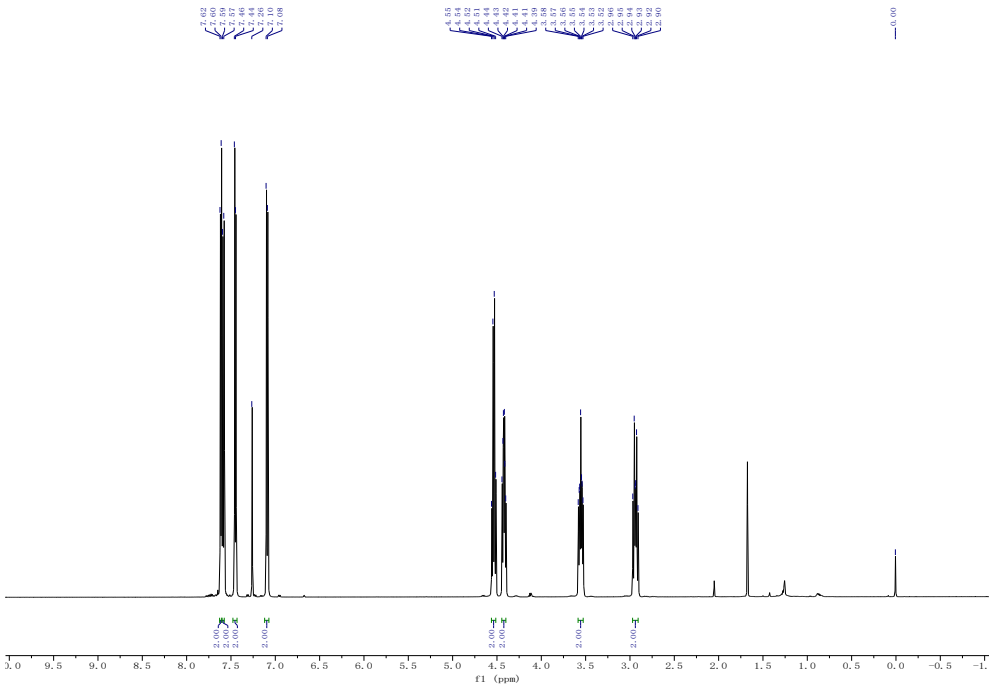
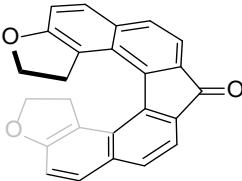




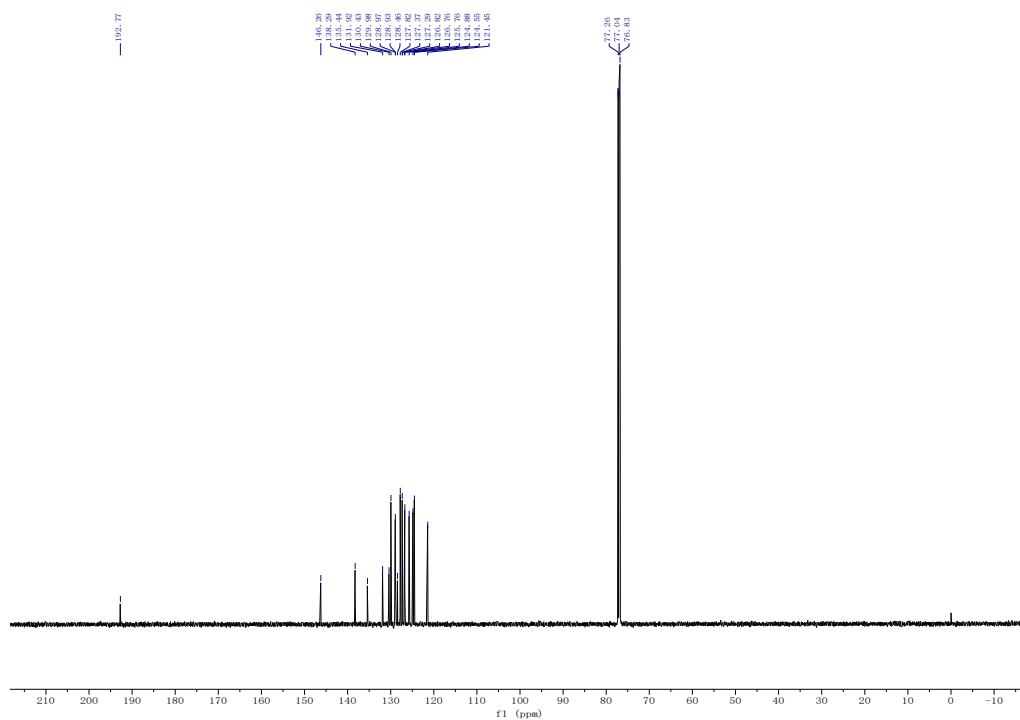
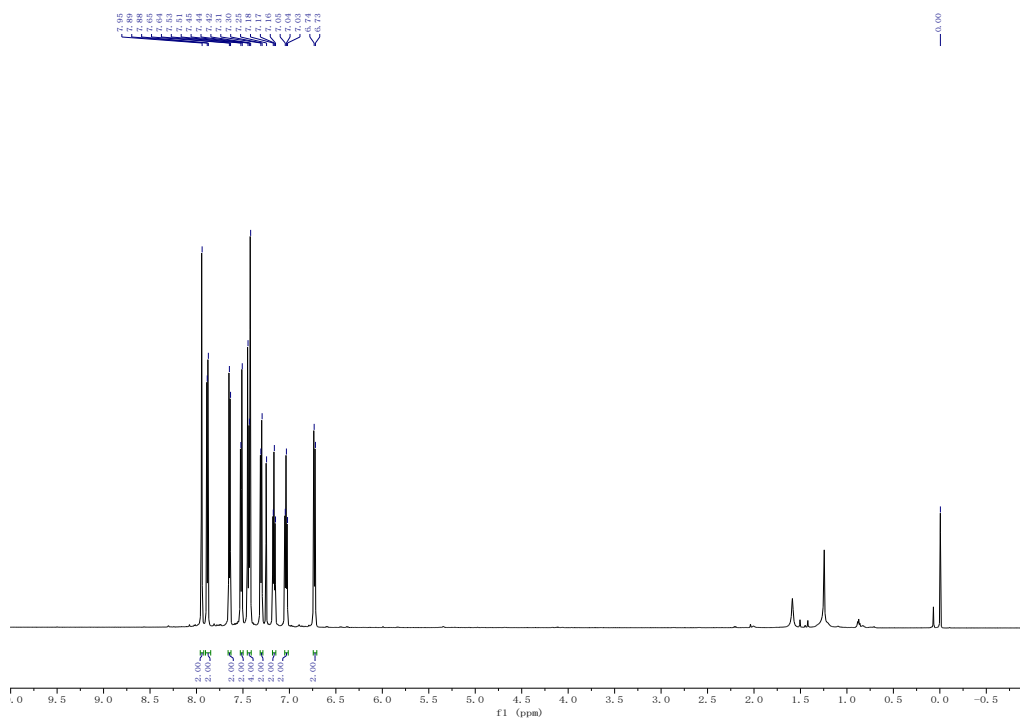
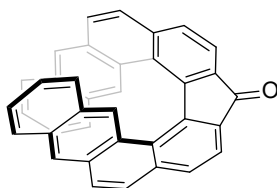
(M)-8H-dibenzo[b]thieno[5,4-c:4',5'-g]fluoren-8-one (A18)



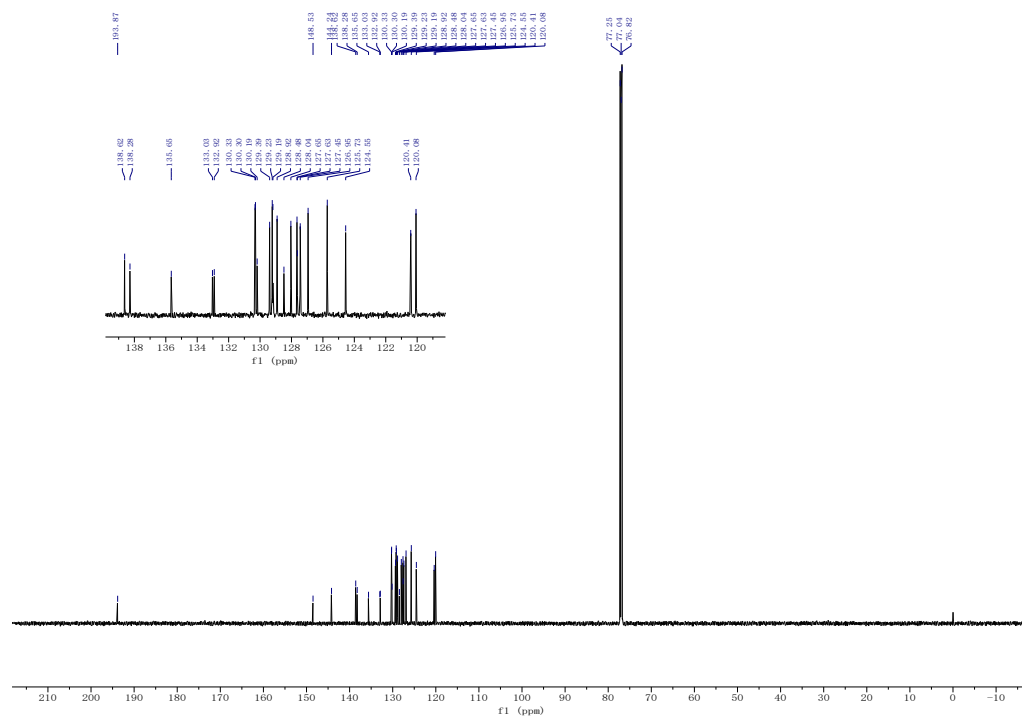
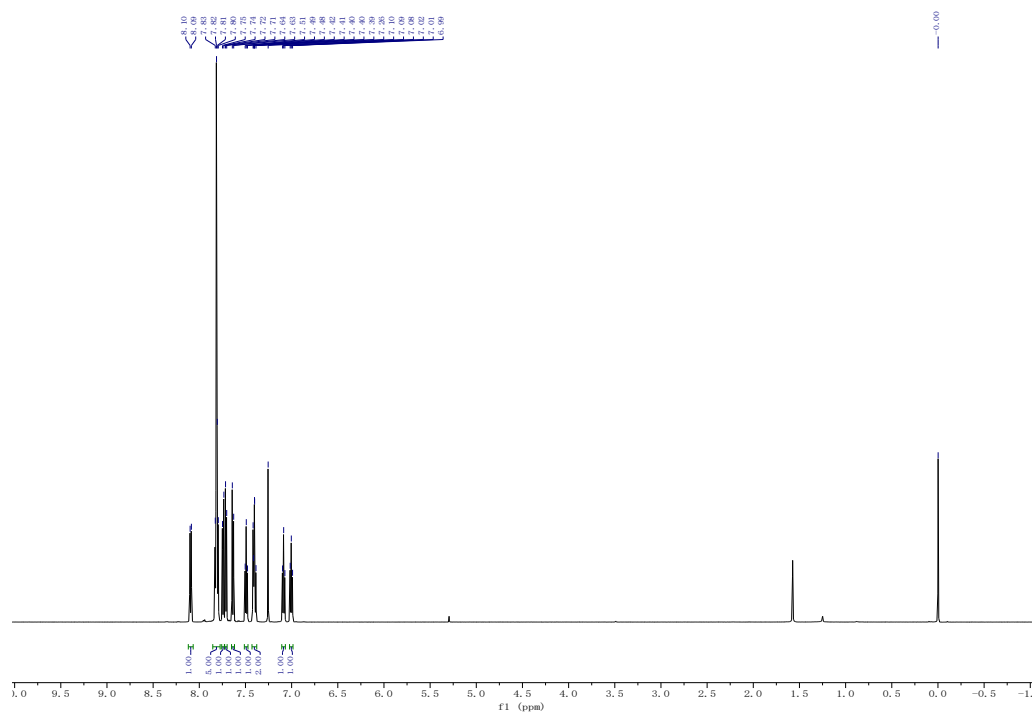
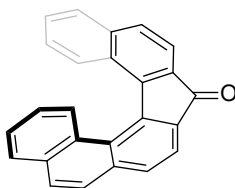
(M)-1,2,14,15-tetrahydro-8H-dibenzo[b]furan[5,4-c:4',5'-g]fluoren-8-one (A19)



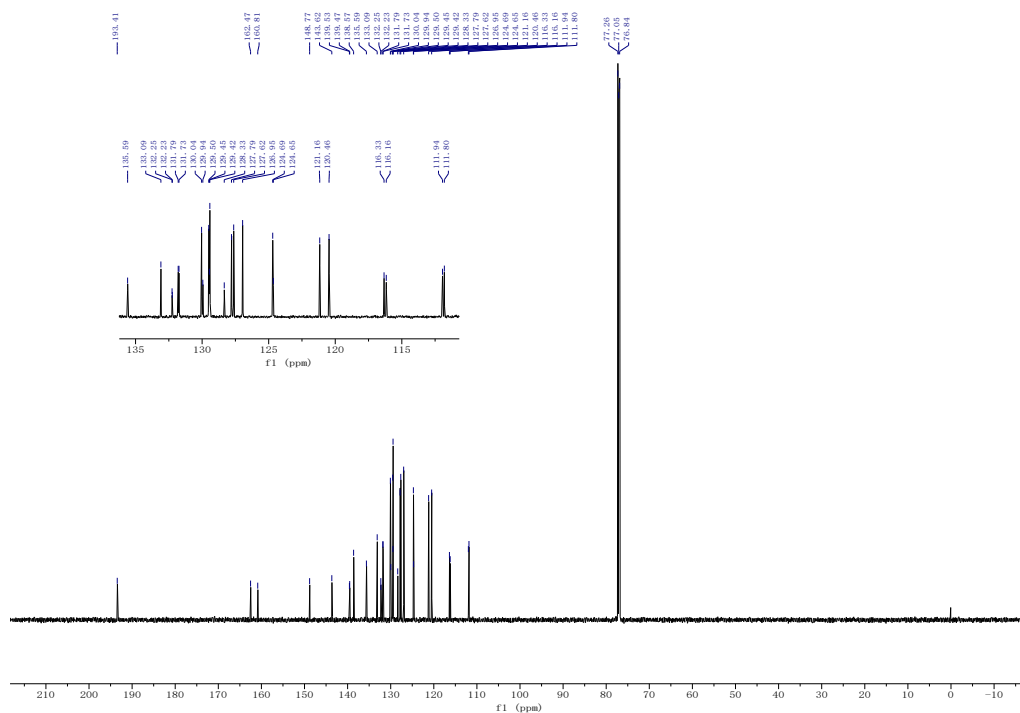
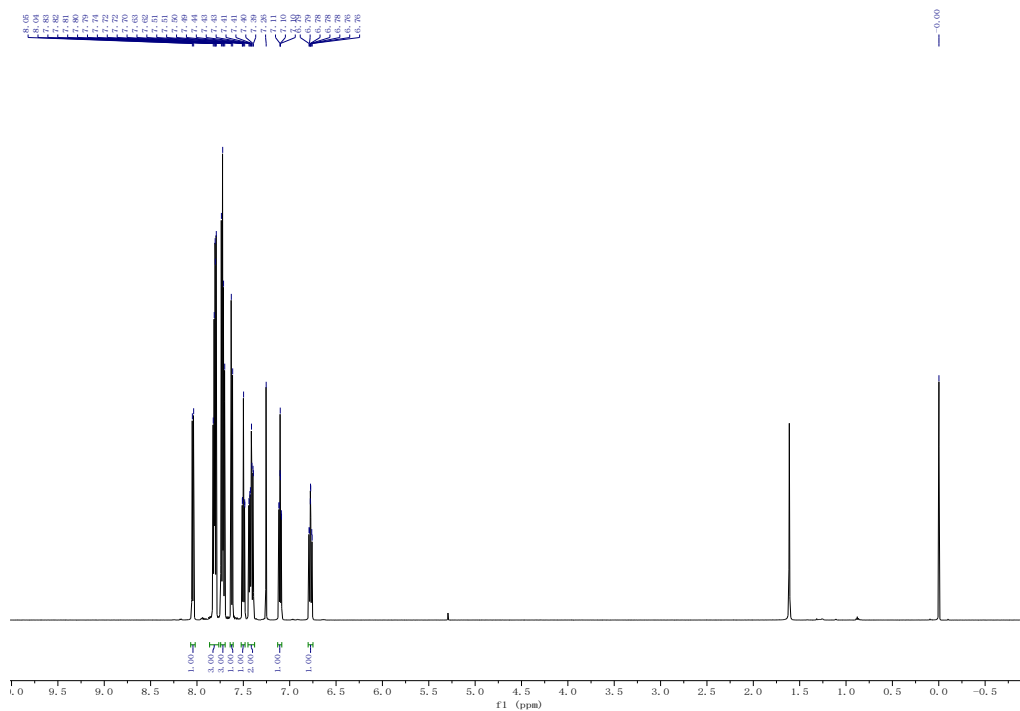
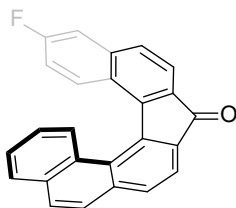
(M)-3H-cyclopenta[2,1-a:3,4-a']ditetraphen-3-one (A20)

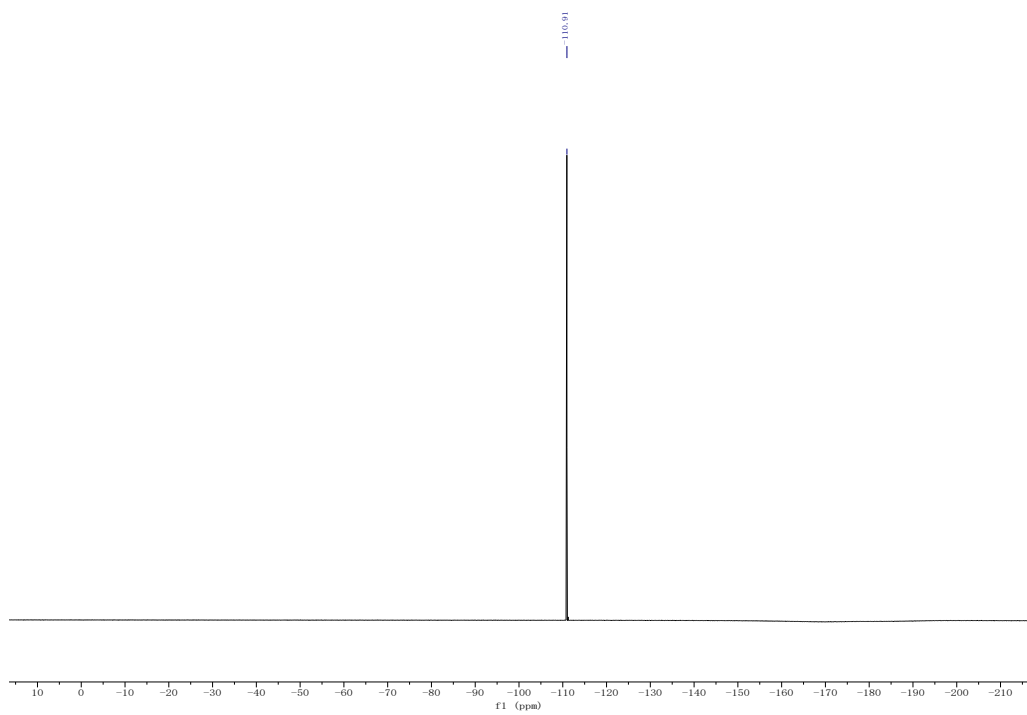


(M)-9H-benzo[6,7]indeno[2,1-c]phenanthren-9-one (A21)

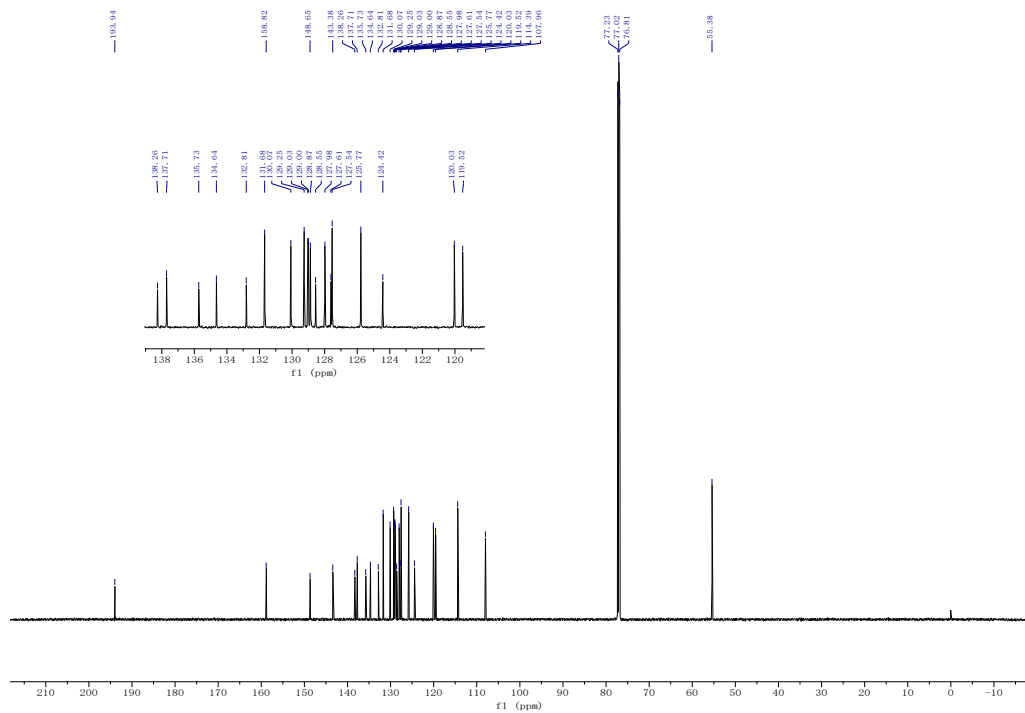
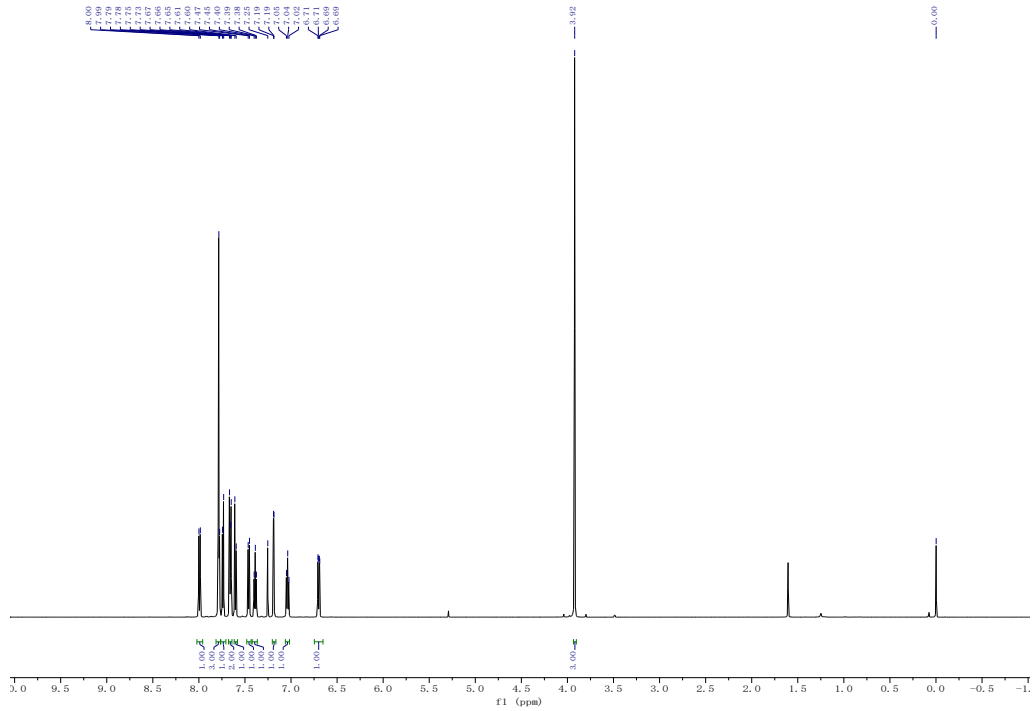
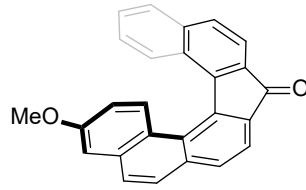


(M)-13-fluoro-9H-benzo[6,7]indeno[2,1-c]phenanthren-9-one (A22)

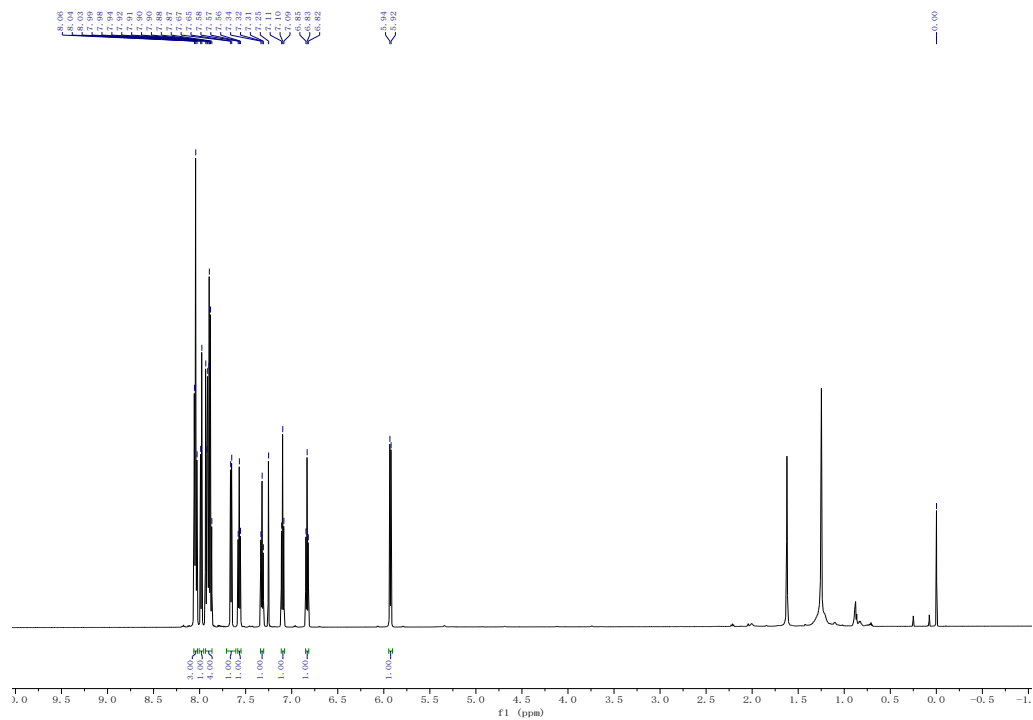
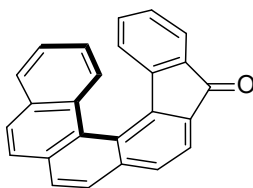




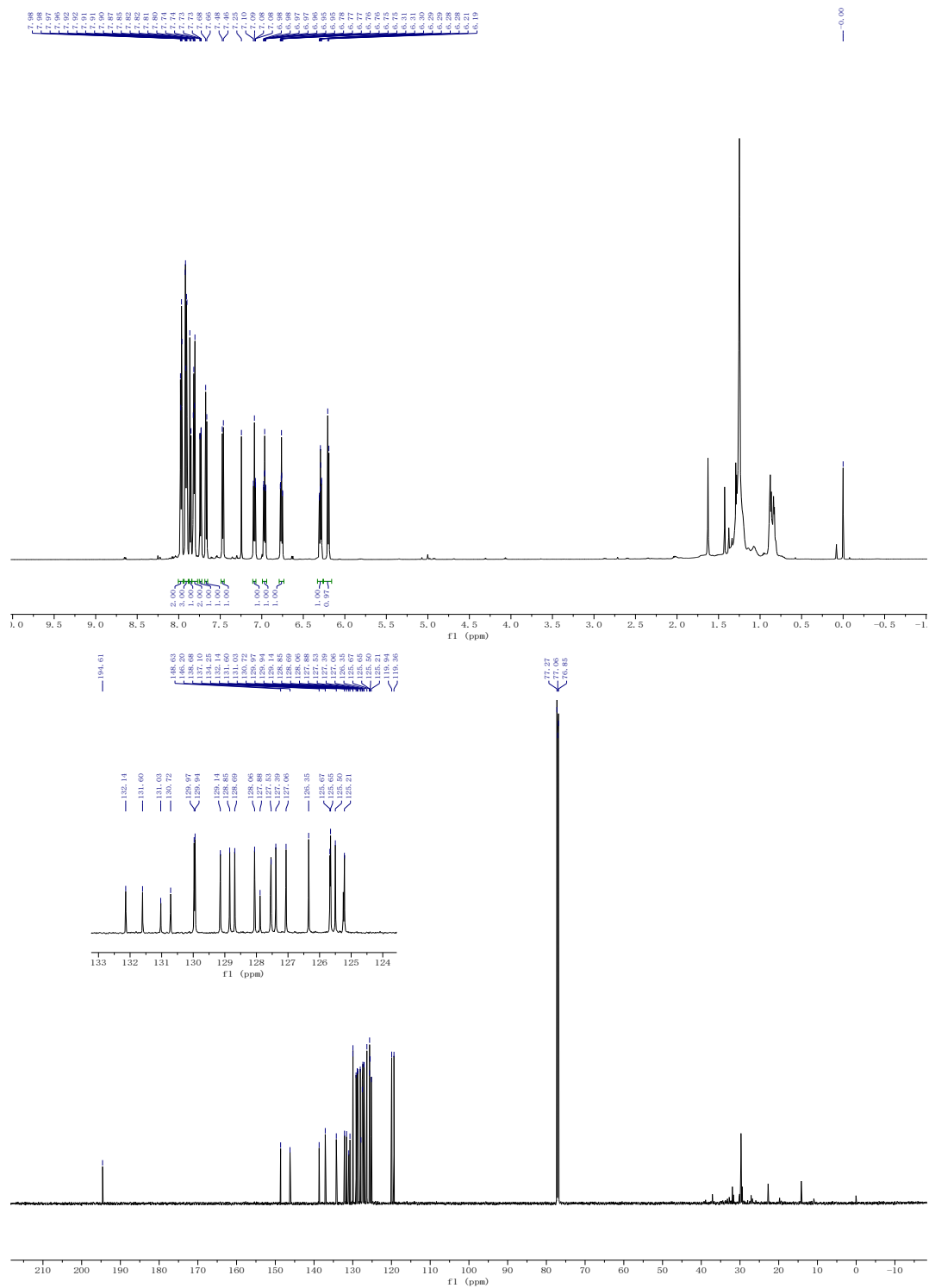
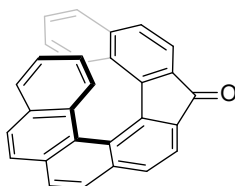
(*M*)-13-methoxy-9H-benzo[6,7]indeno[2,1-c]phenanthren-9-one (A23)



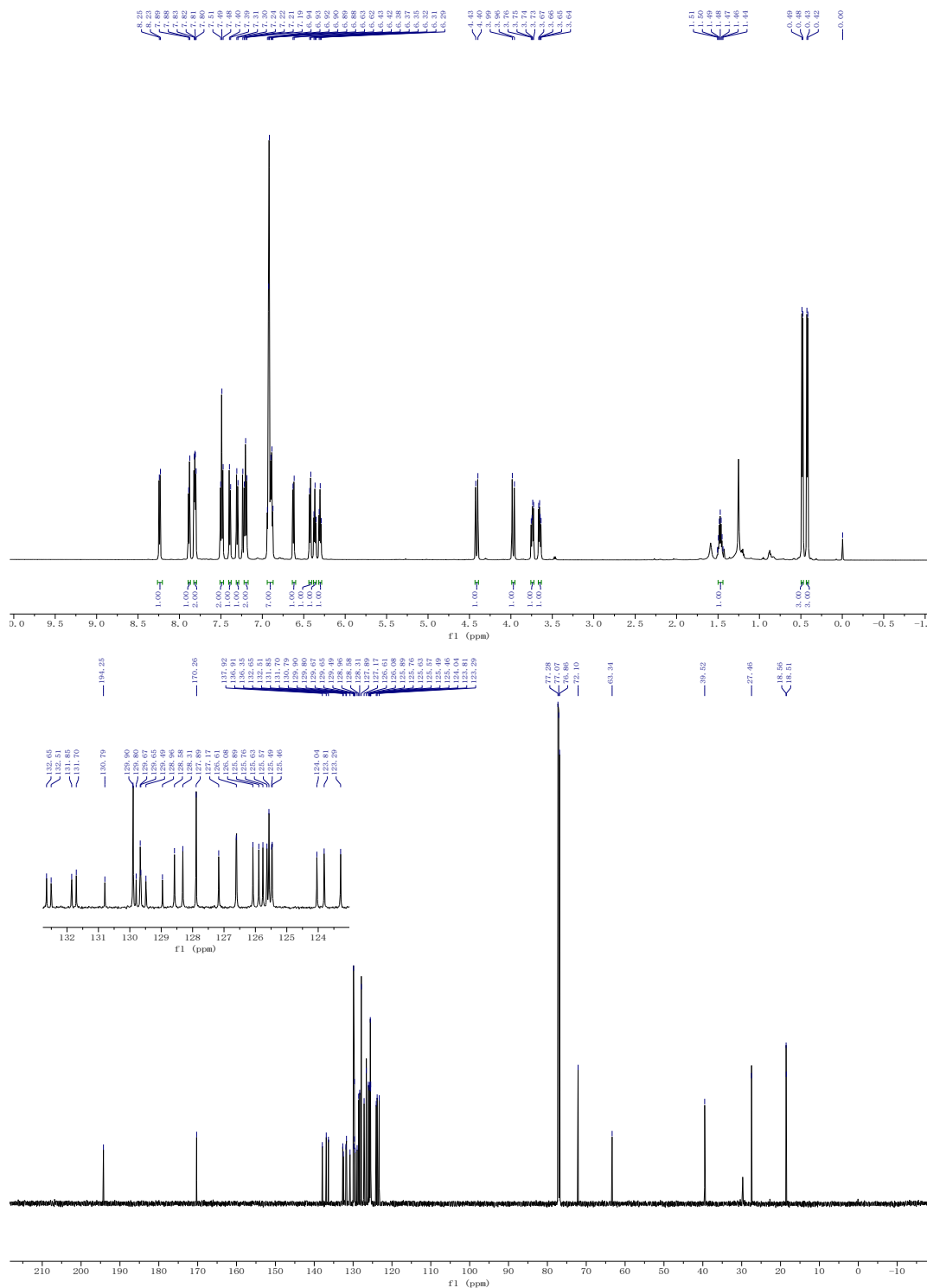
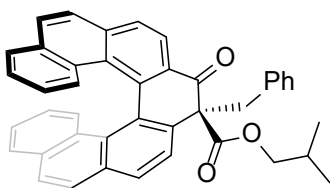
(*M*)-7H-benzo[*c*]indeno[1,2-*g*]phenanthren-7-one (*M*-A24)



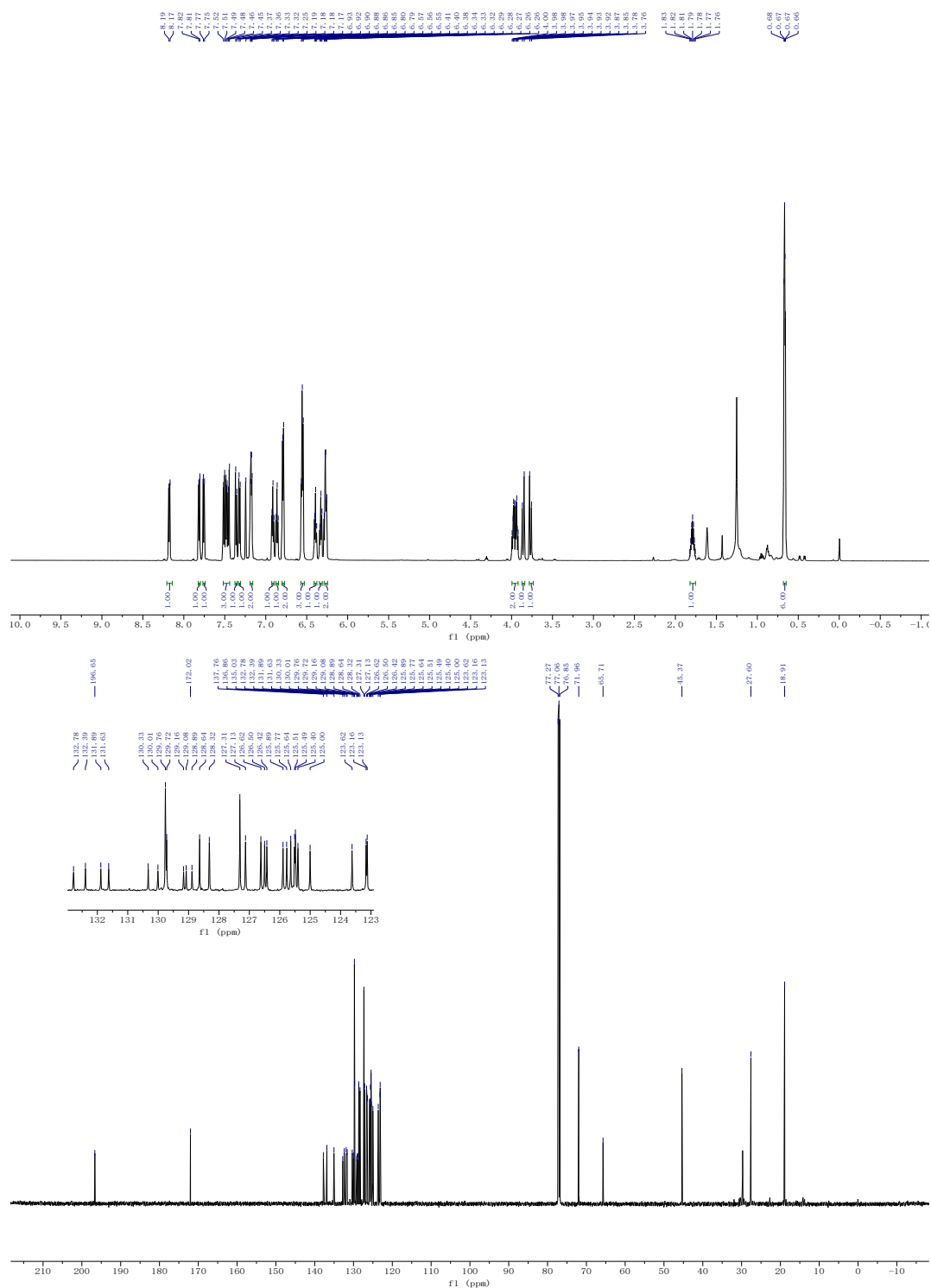
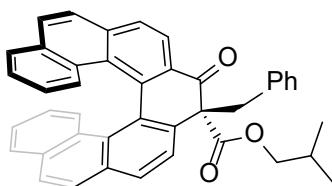
(M)-7H-benzo[c]benzo[6,7]indeno[1,2-g]phenanthren-7-one (M-A25)



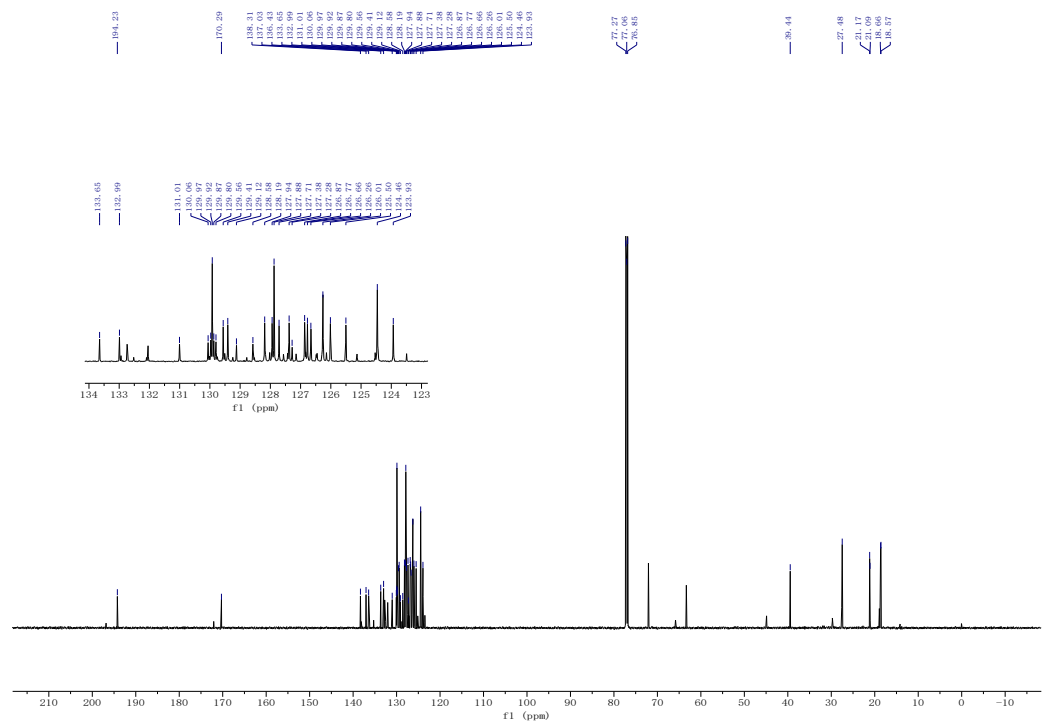
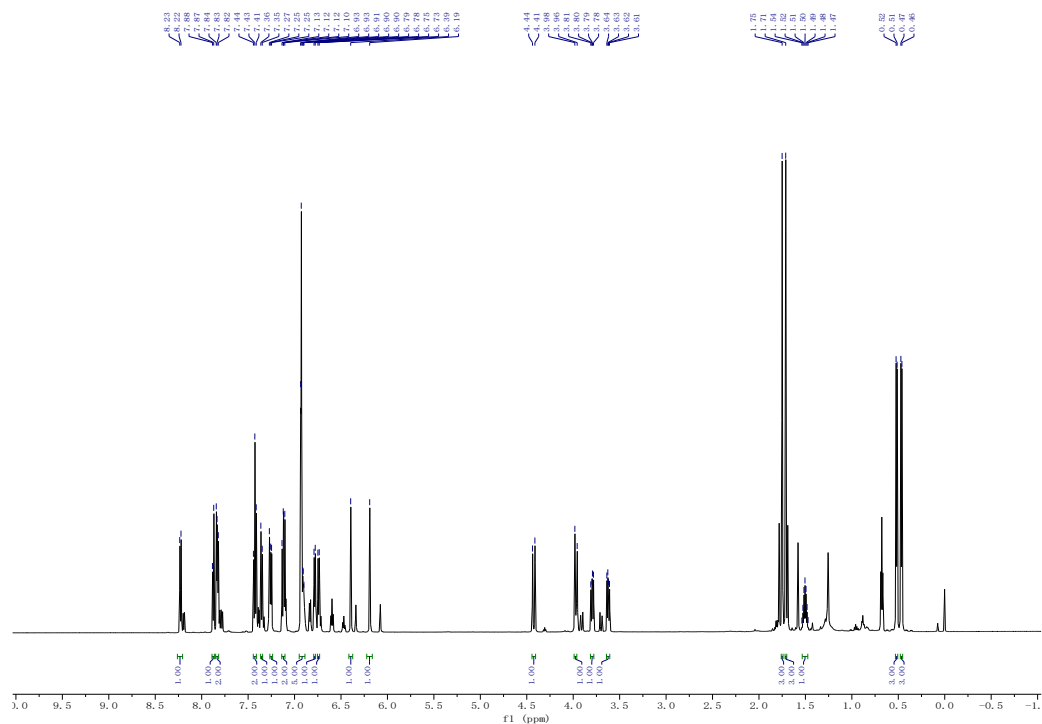
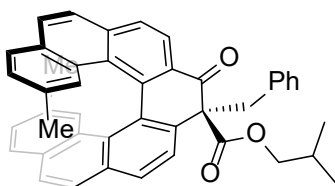
isobutyl (*P, S*)-9-benzyl-2,17-dimethyl-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (C1)



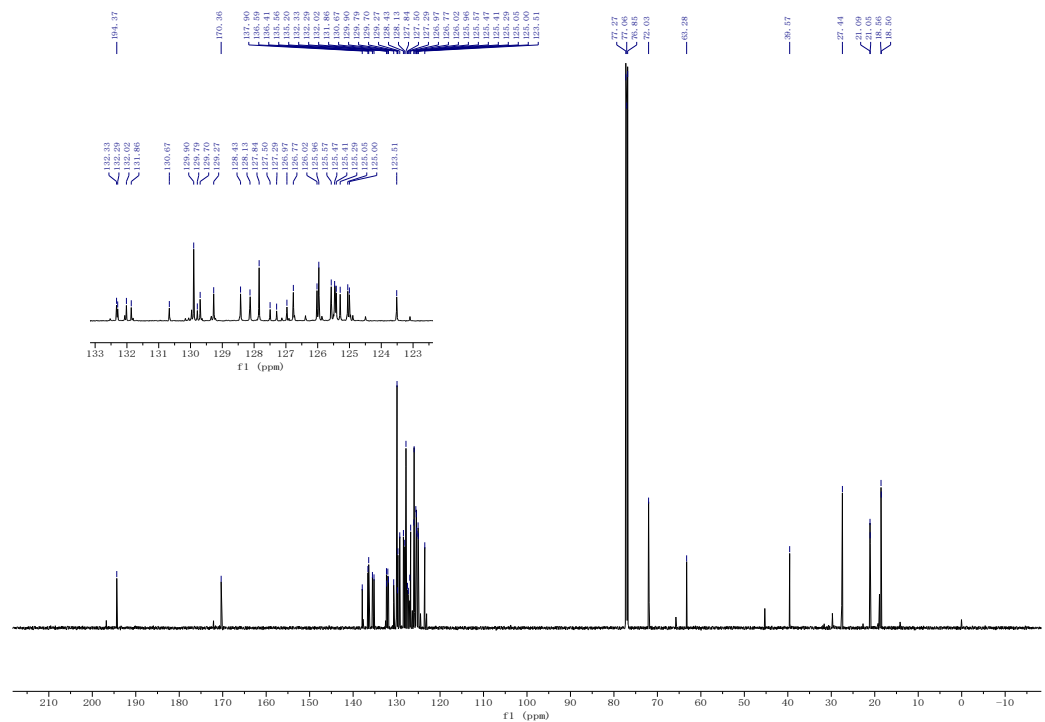
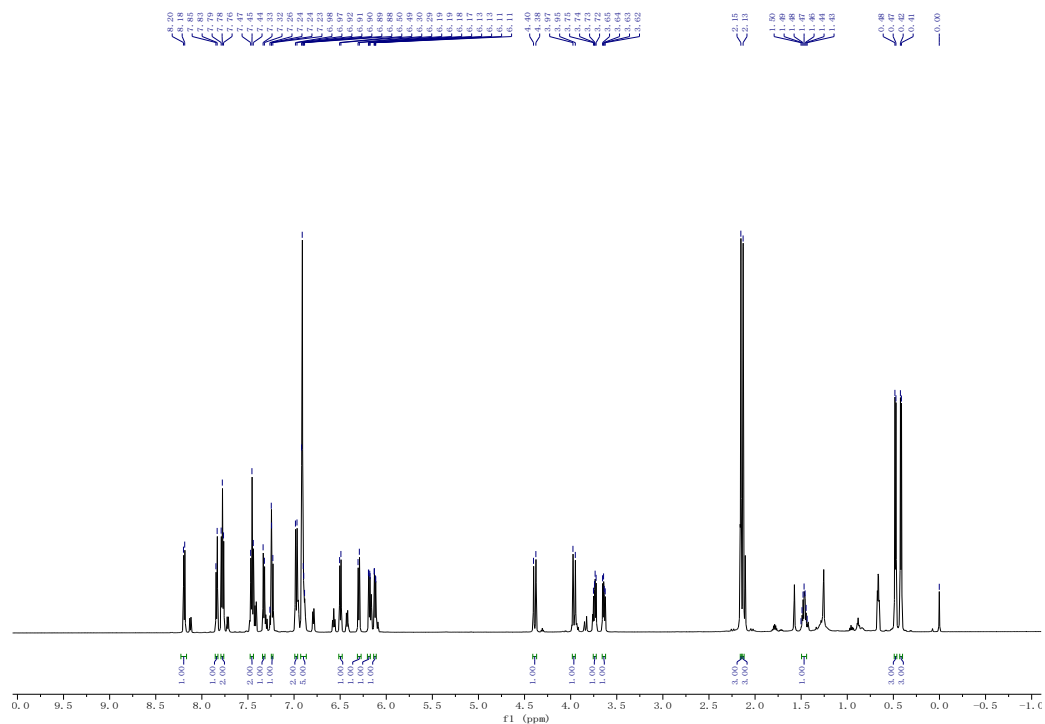
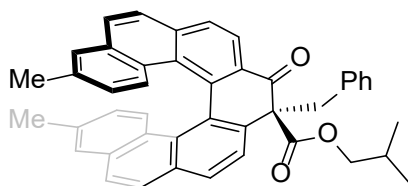
isobutyl (*P, R*)-9-benzyl-2,17-dimethyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C1)



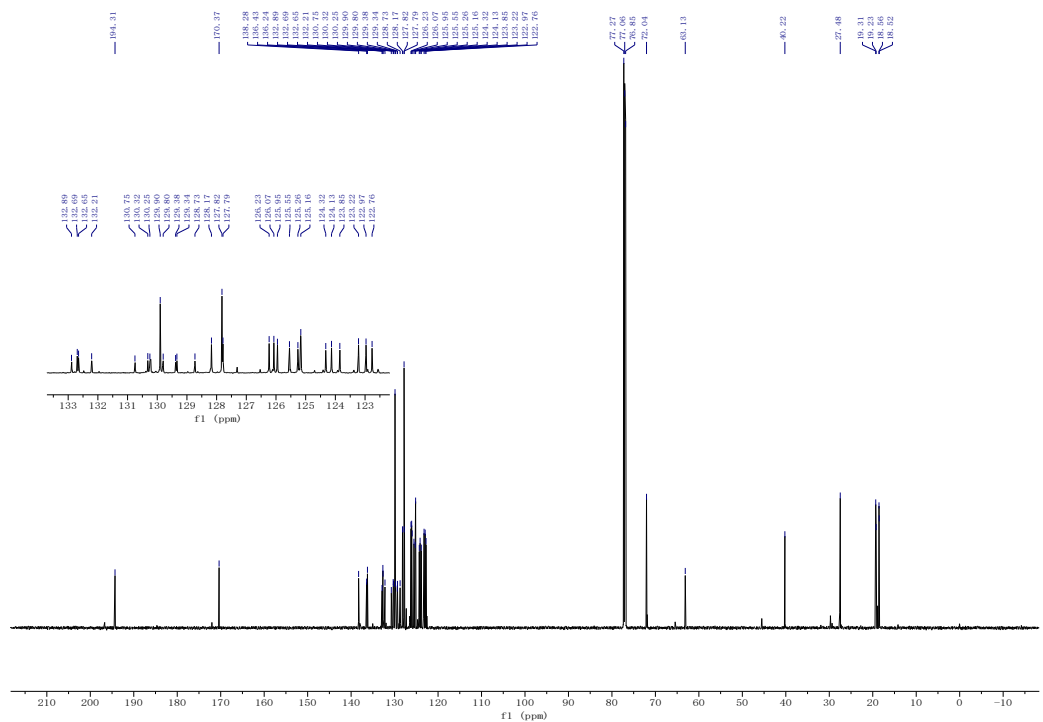
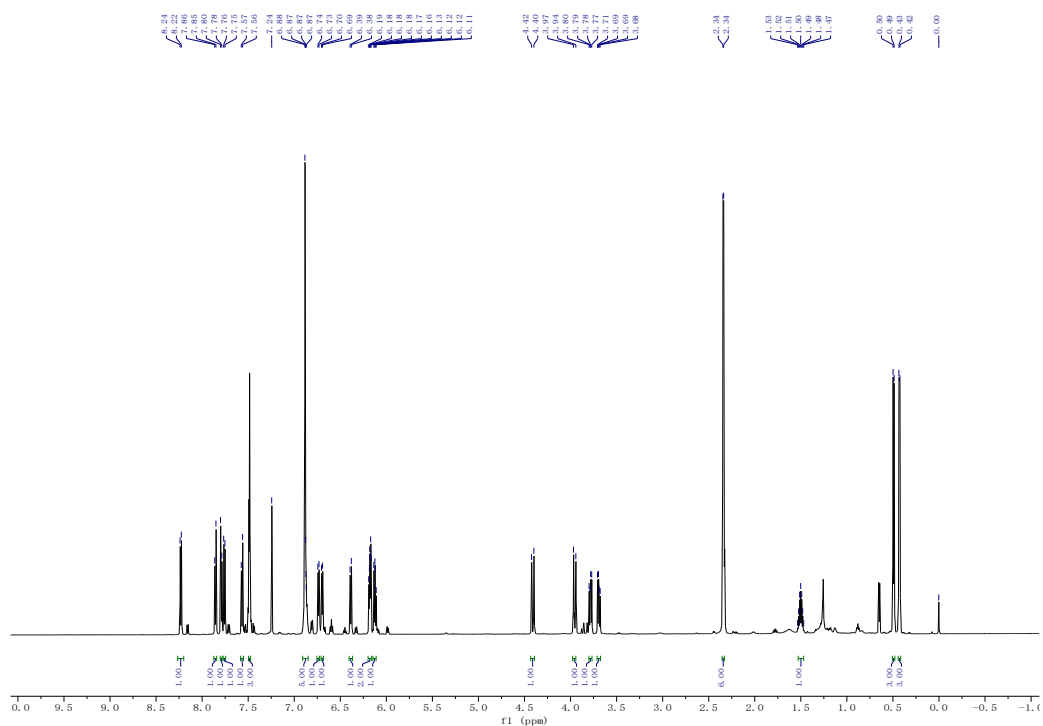
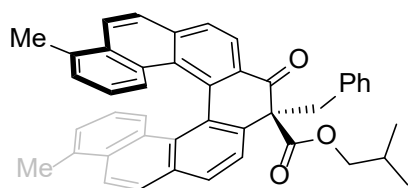
isobutyl (*P*, *S*)-9-benzyl-2,17-dimethyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C2)



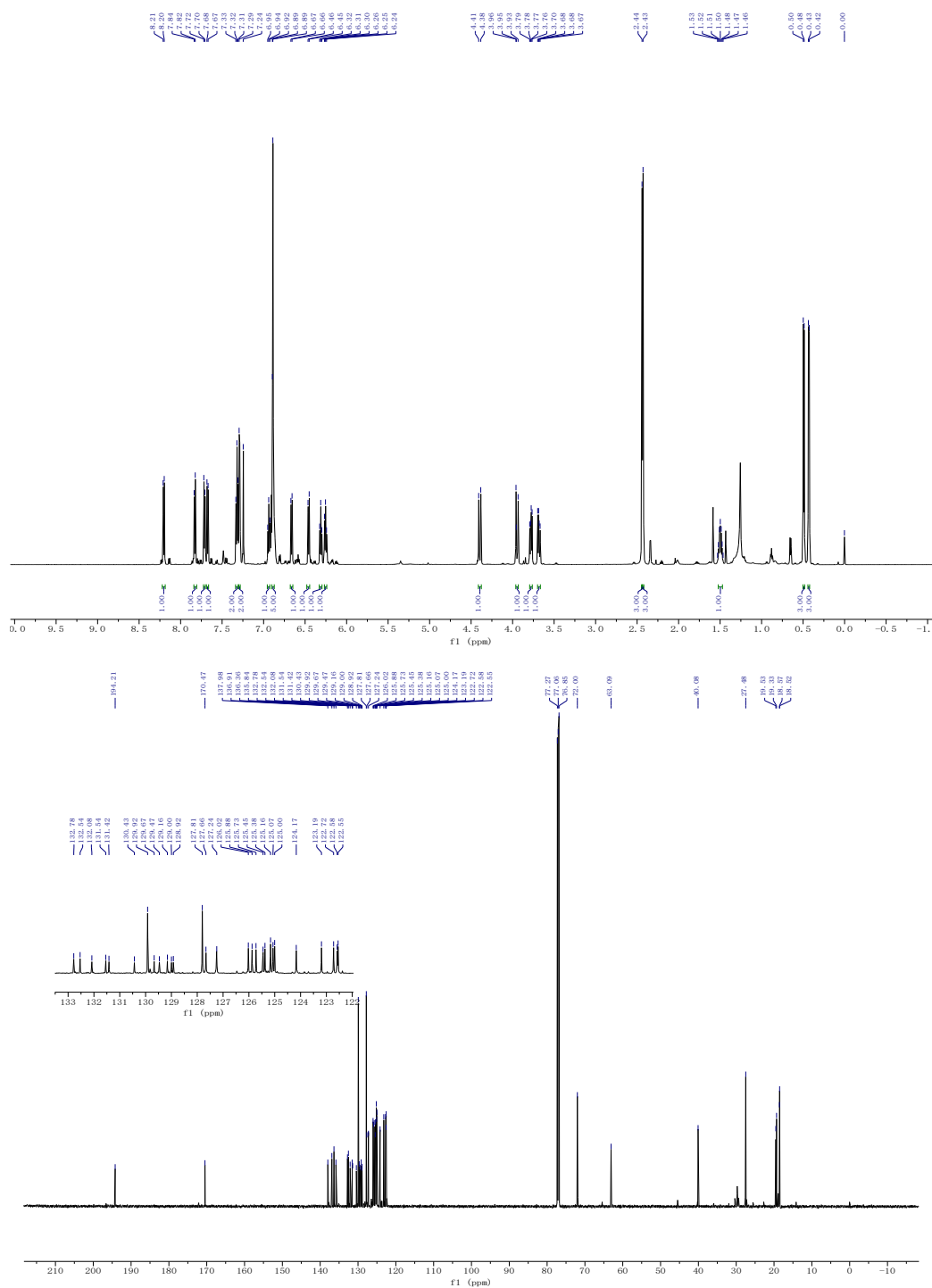
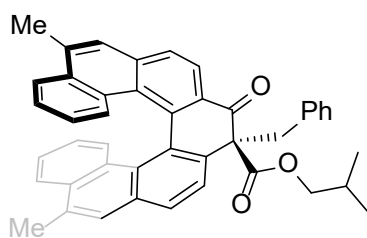
isobutyl (*P, S*)-9-benzyl-3,16-dimethyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C3)



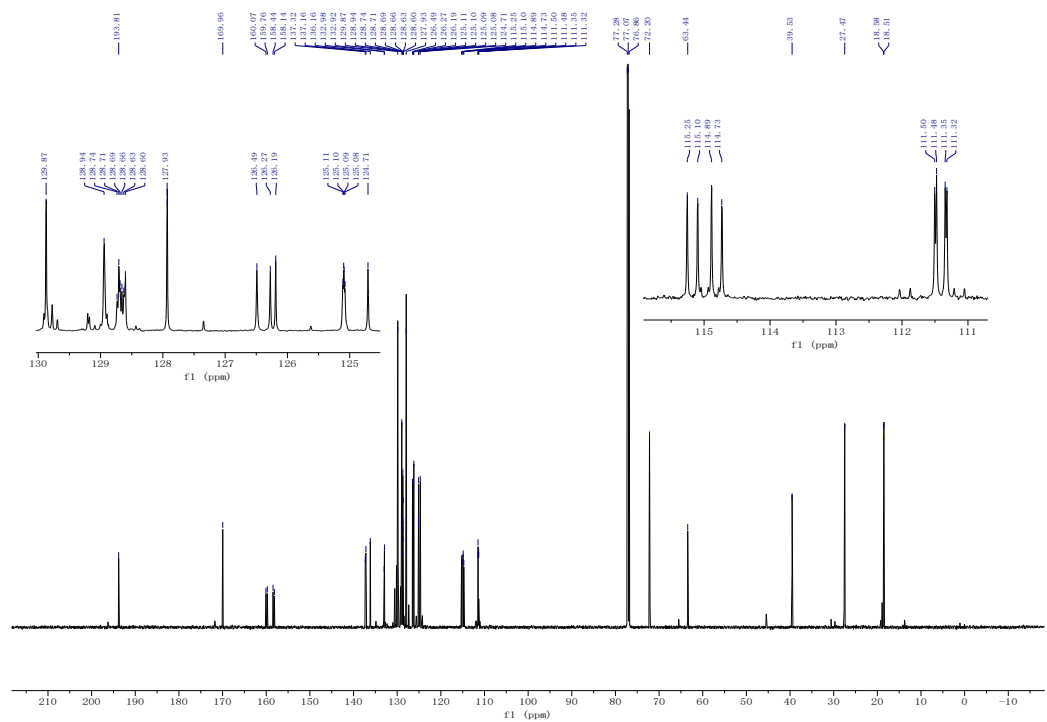
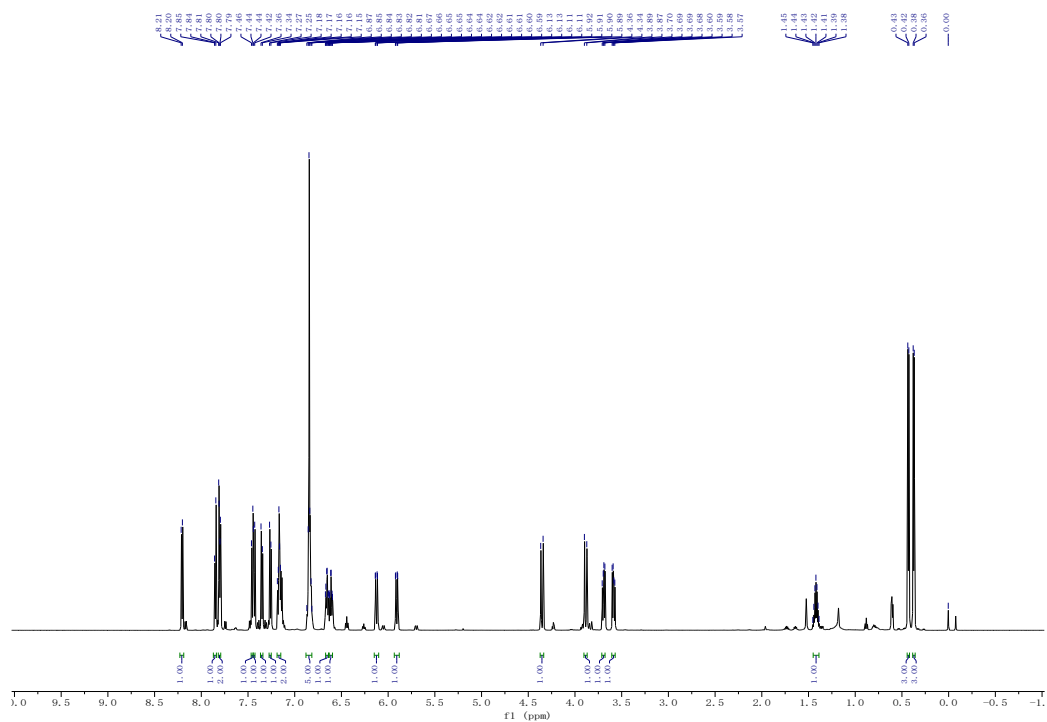
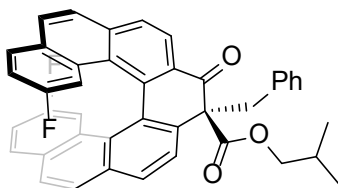
isobutyl (*P, S*)-9-benzyl-4,15-dimethyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C4)



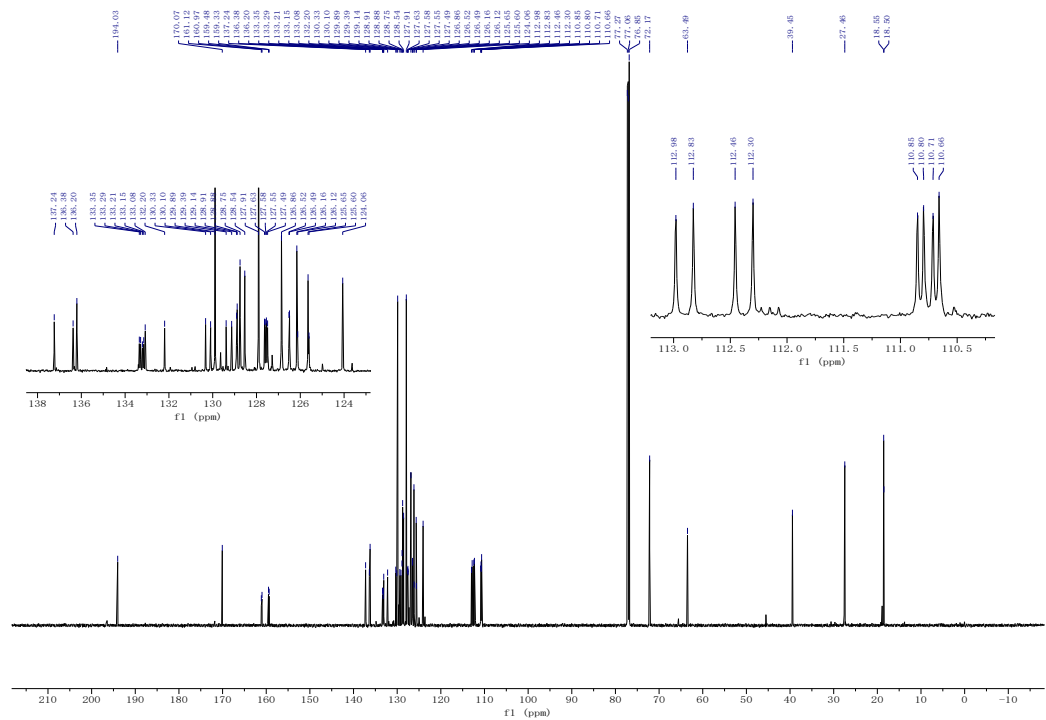
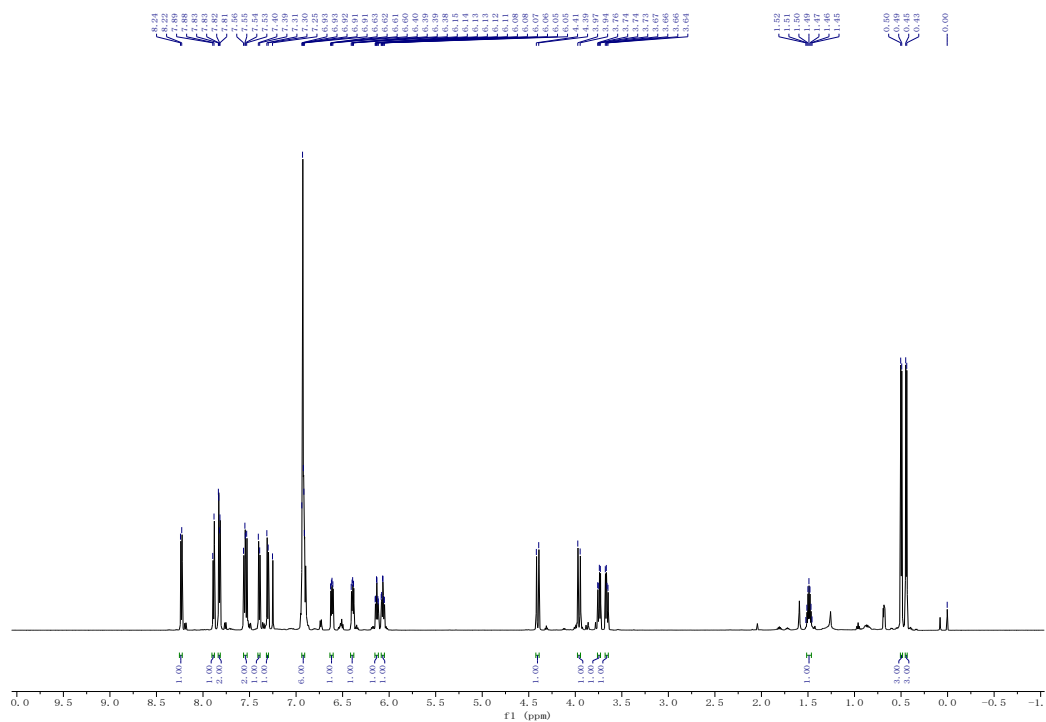
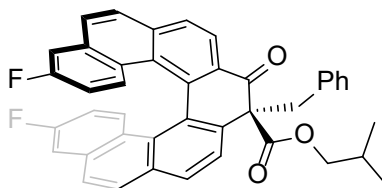
isobutyl (*P*, *S*)-9-benzyl-5,14-dimethyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C5)



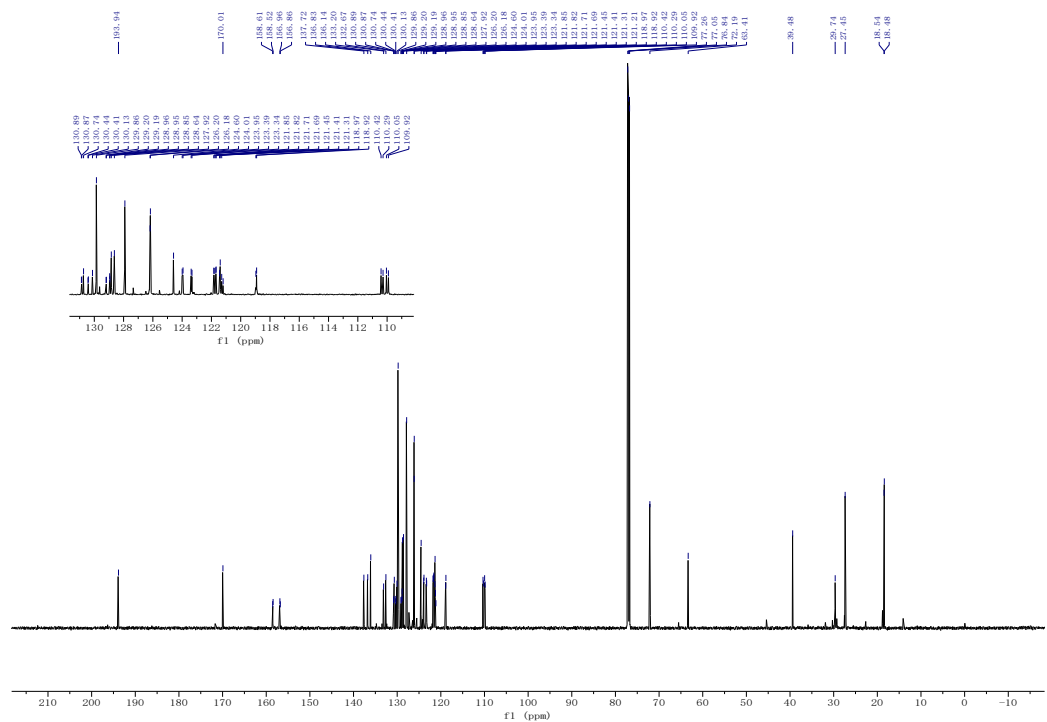
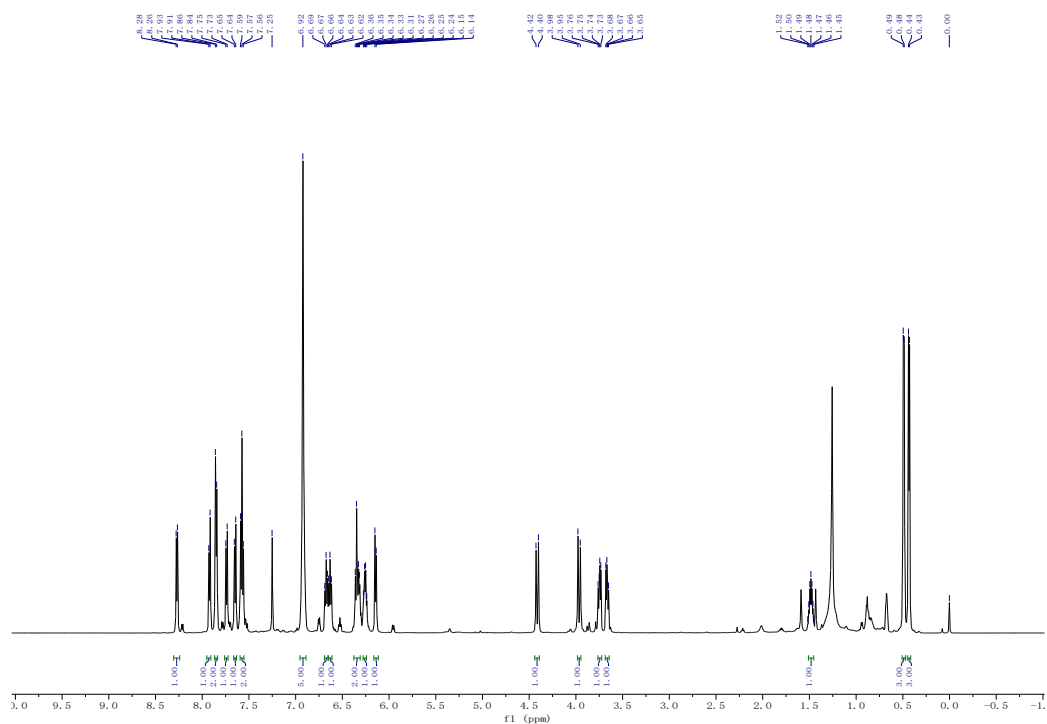
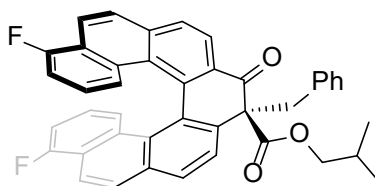
isobutyl (*P*, *S*)-9-benzyl-2,17-difluoro-10-oxo-9,10-dihydrobenzo [1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C7)

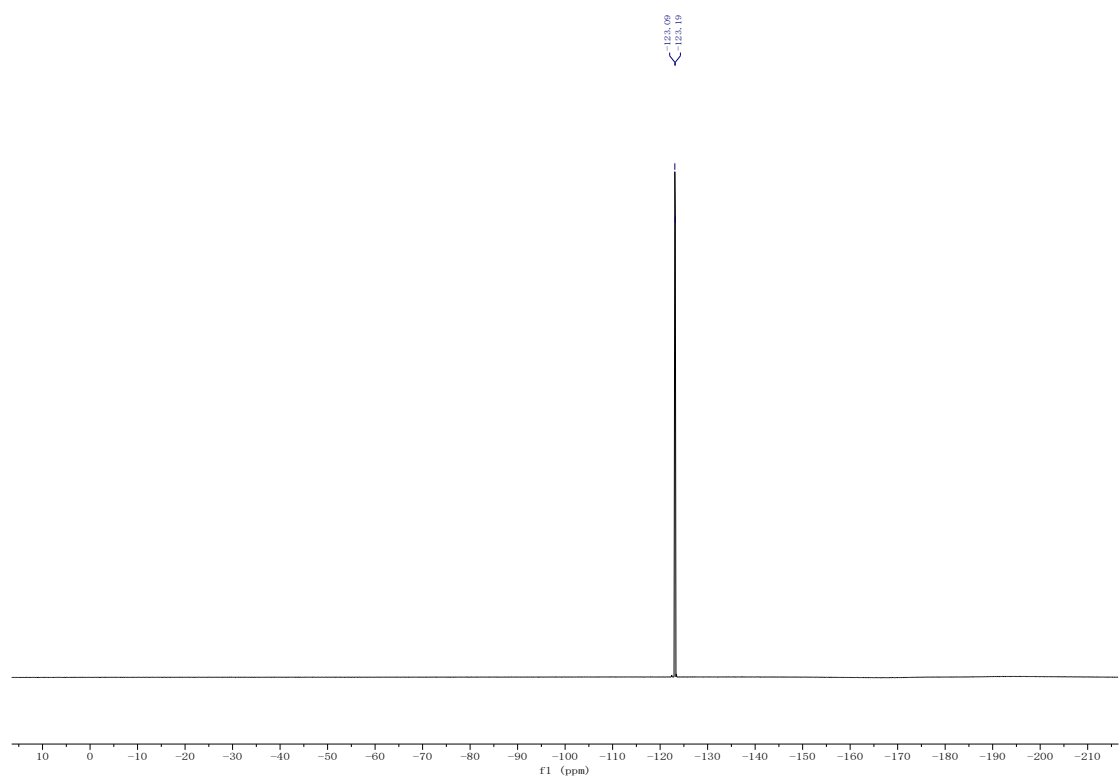


isobutyl (*P, S*)-9-benzyl-3,16-difluoro-10-oxo-9,10-dihydrobenzo [1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C8)

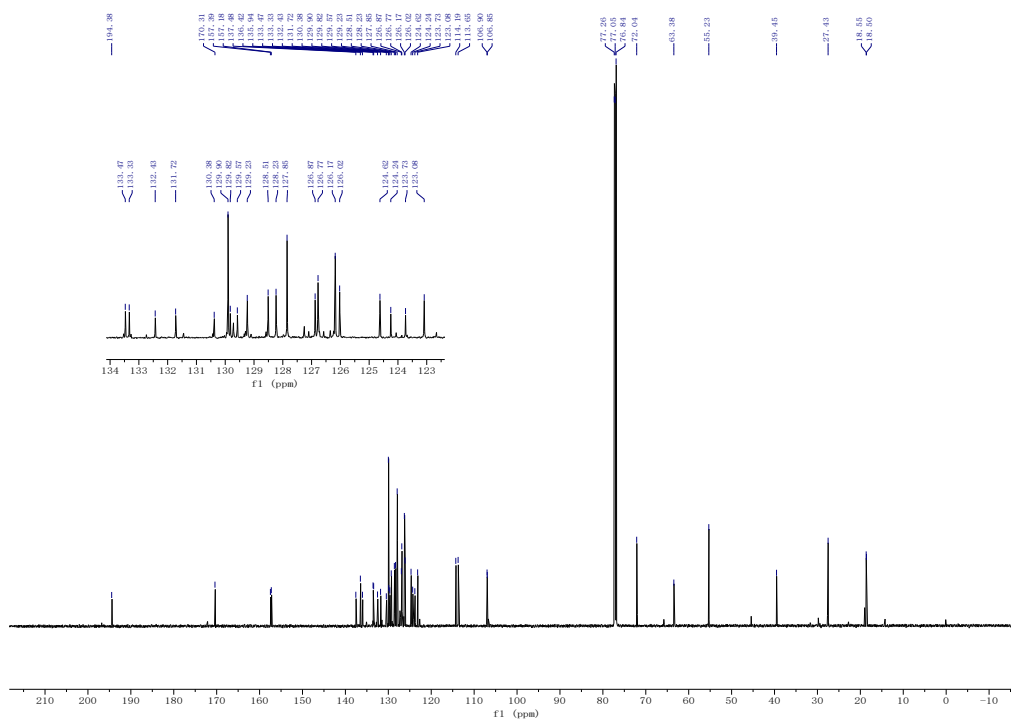
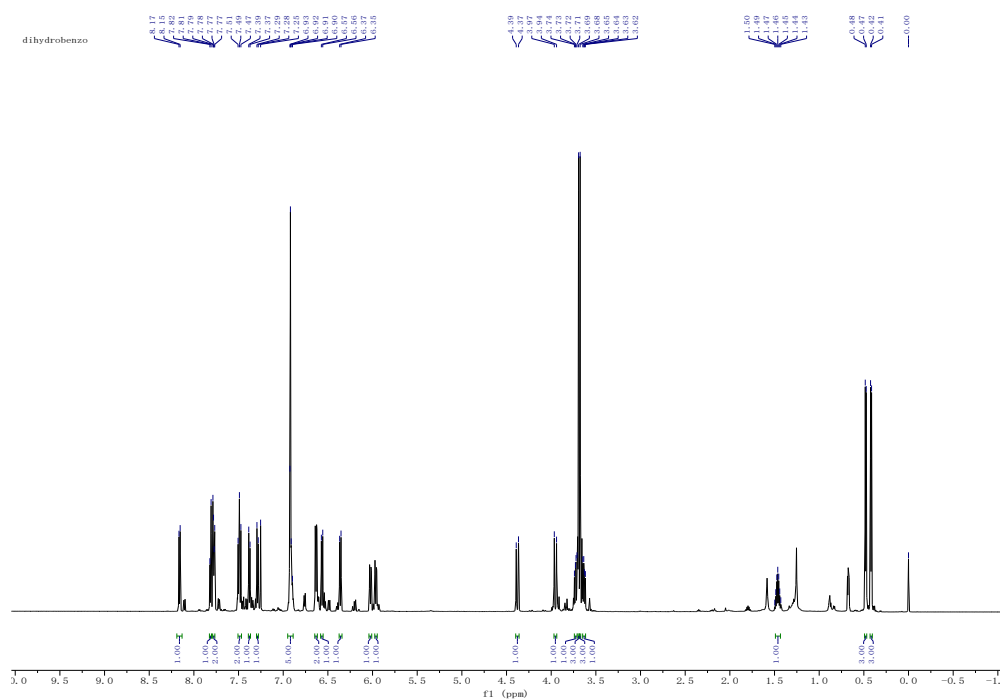
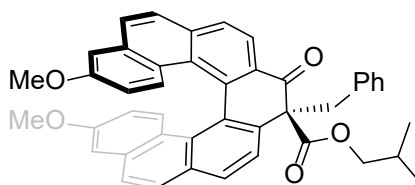


isobutyl (*P*, *S*)-9-benzyl-4,15-difluoro-10-oxo-9,10-dihydrobenzo [1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C9)

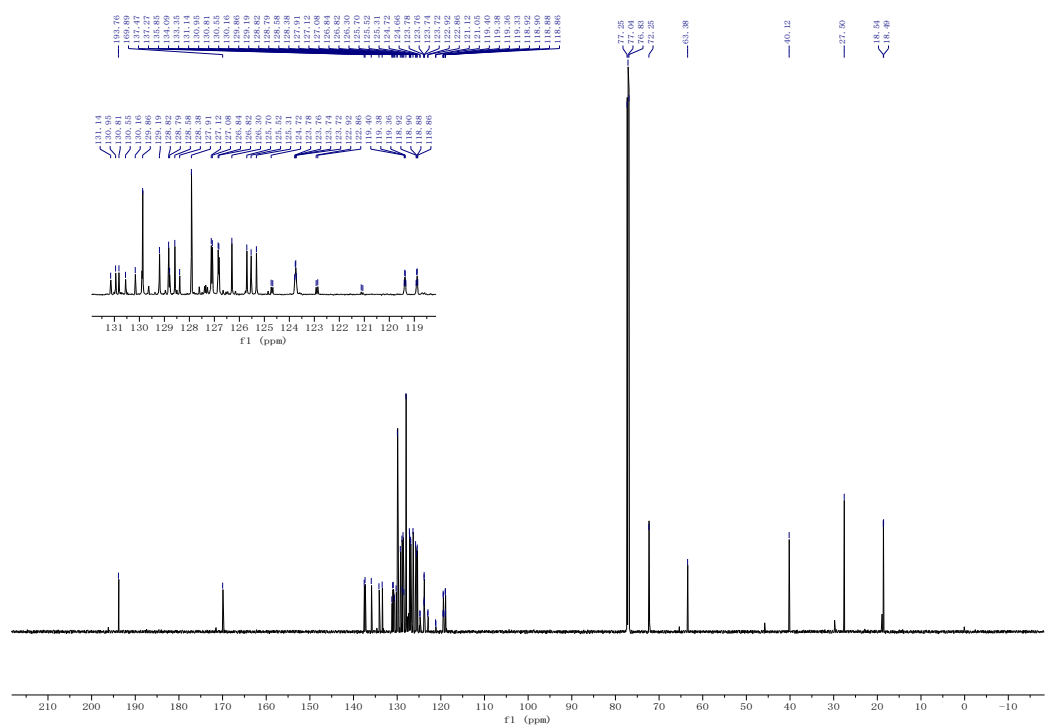


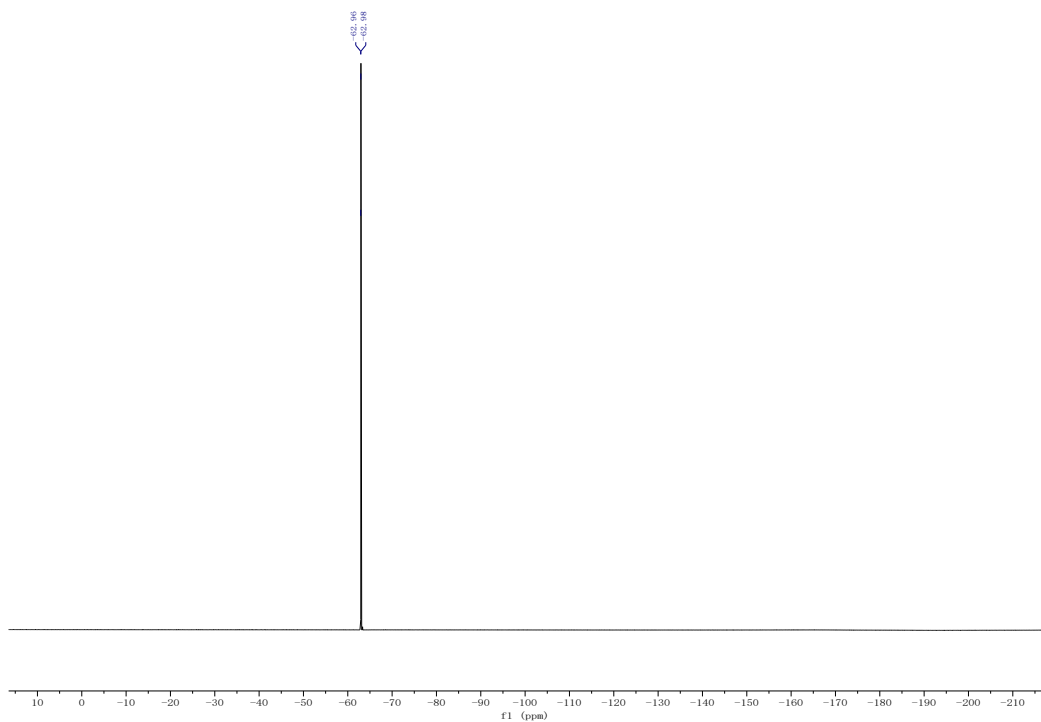


(C10)

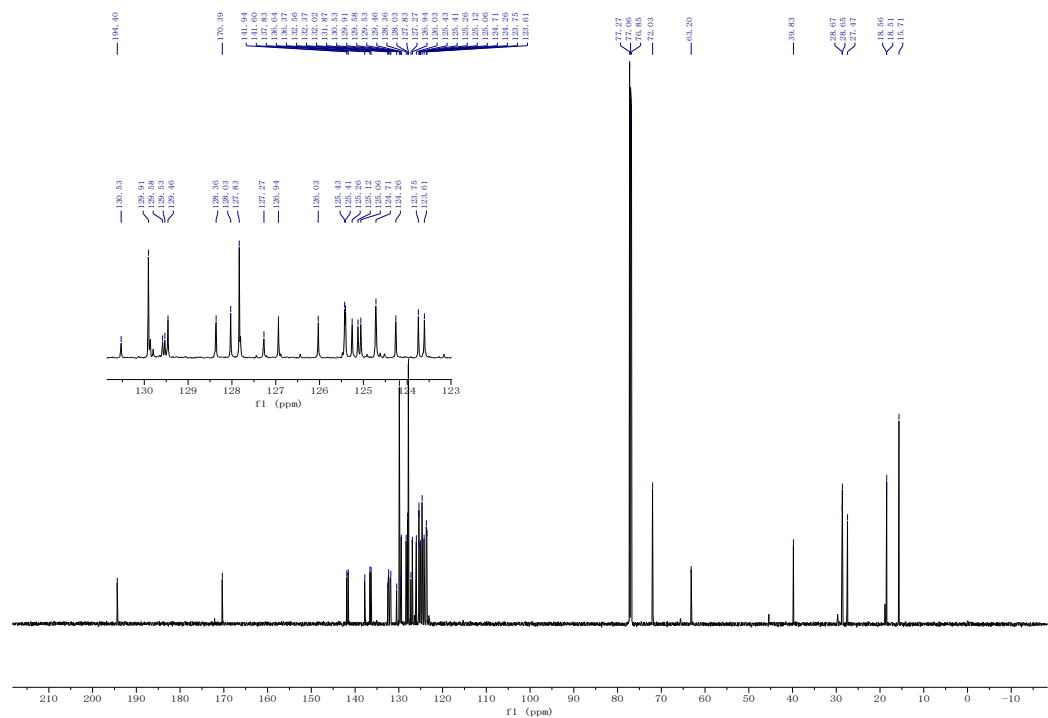
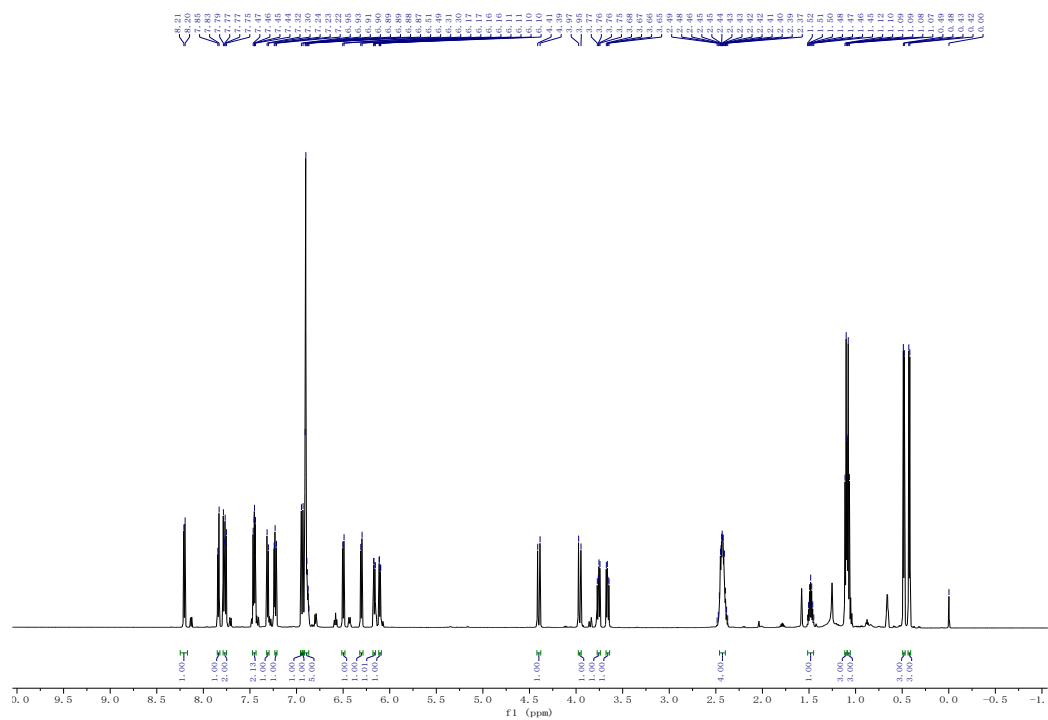
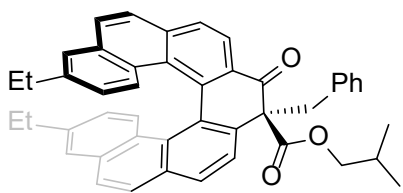


The chemical structure shows a macrocyclic compound with two CF_3 groups. The macrocycle is formed by a series of fused rings, including a central benzene ring. The structure is shown with a chiral auxiliary, a phenyl group (Ph), and an isopropoxy group (OCH(CH₃)₂) attached to the macrocycle. The auxiliary is shown with a dashed bond to the macrocycle and a solid bond to the isopropoxy group, indicating its stereochemistry.

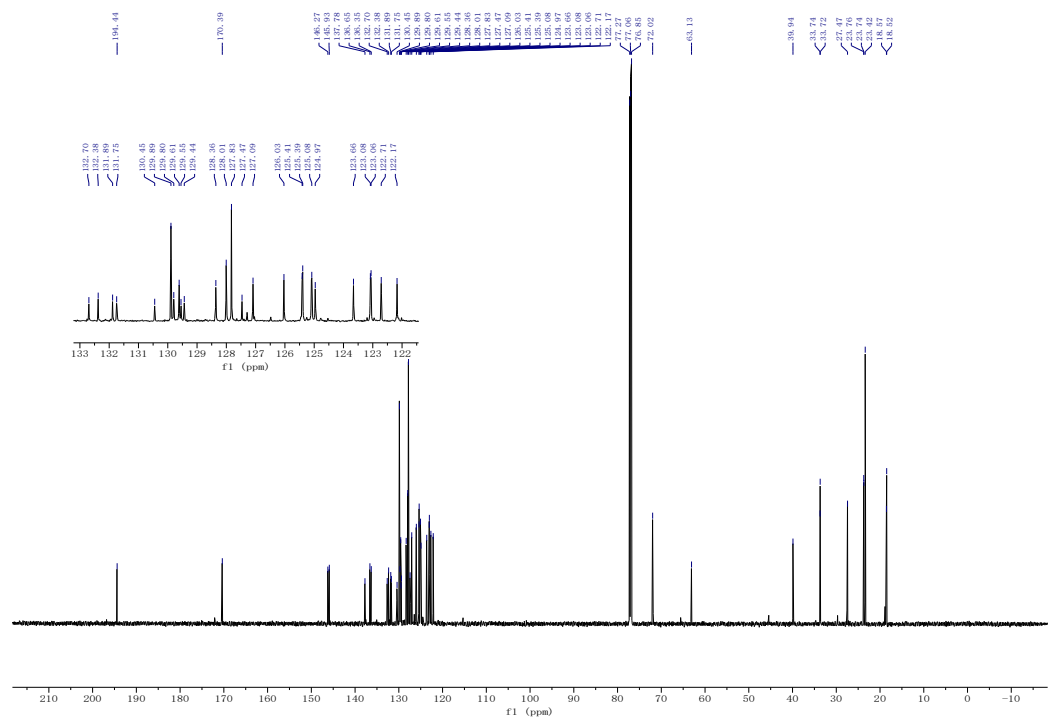
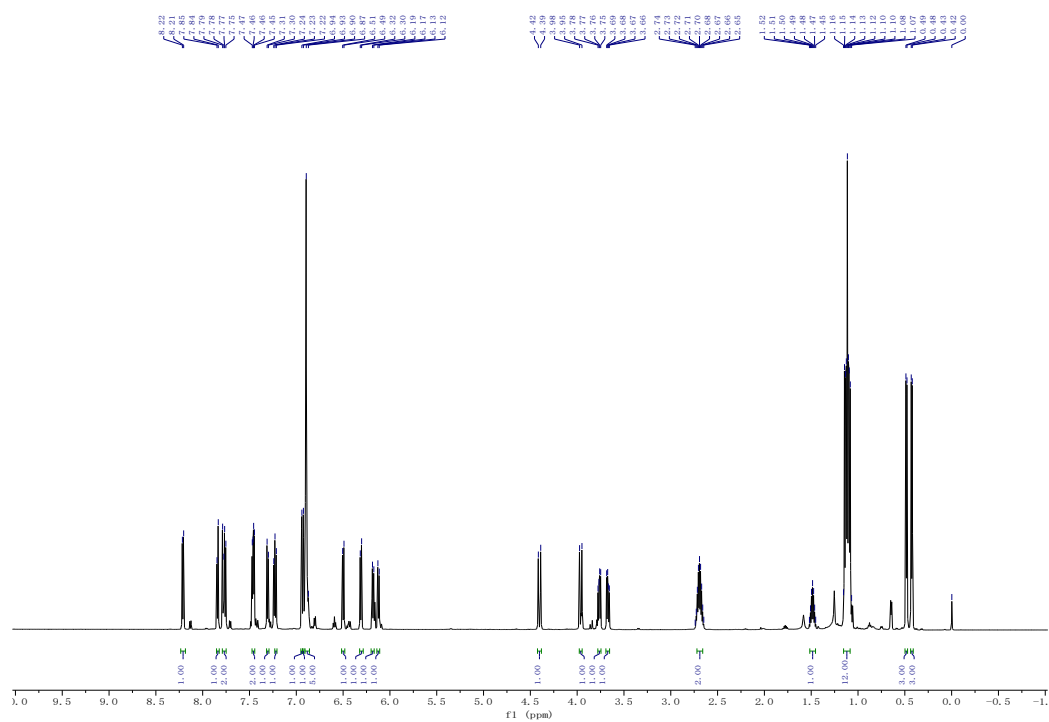
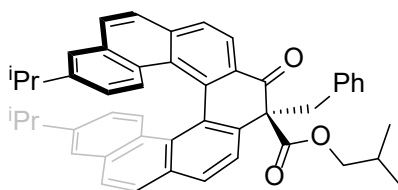




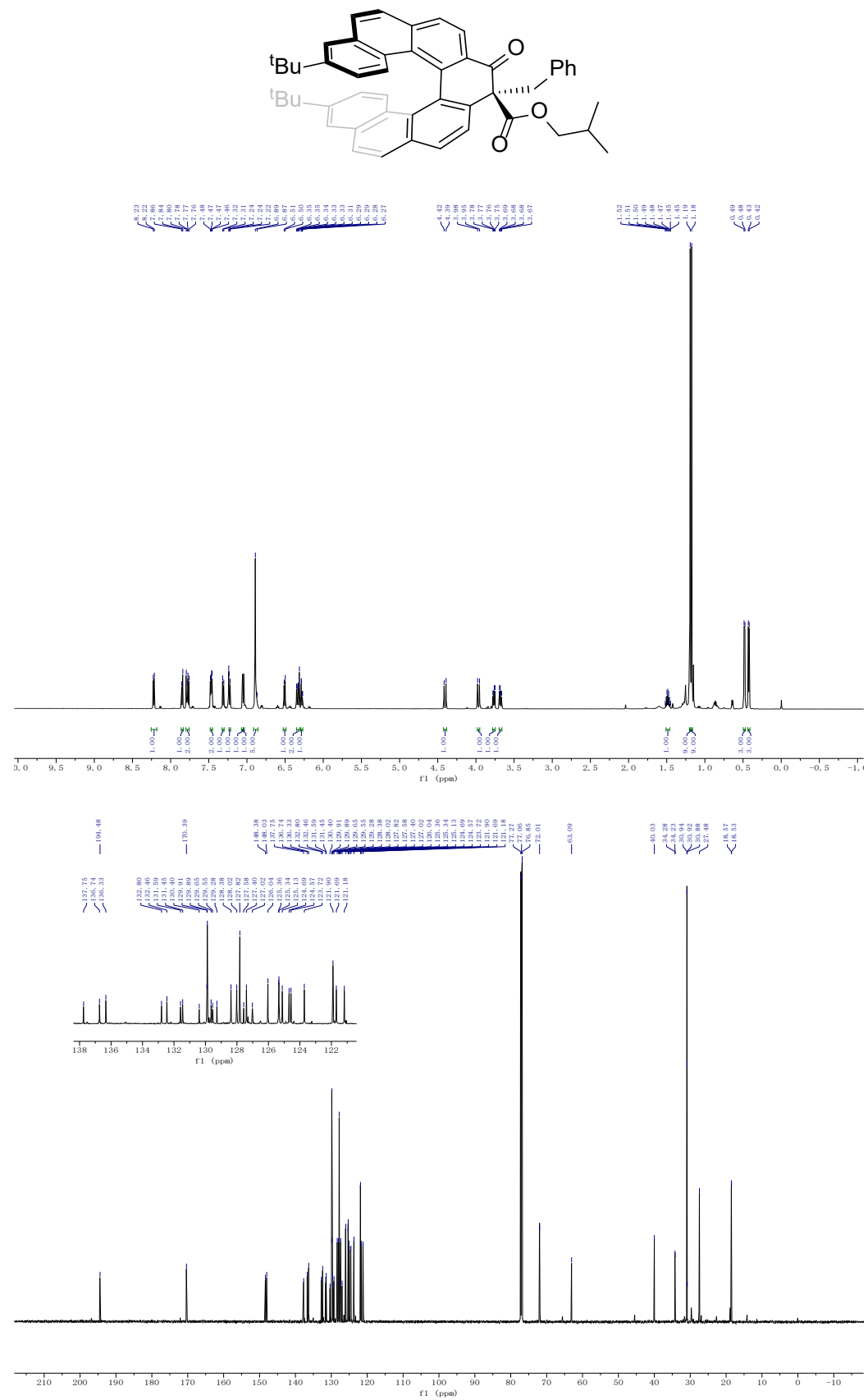
isobutyl (*P*, *S*)-9-benzyl-3,16-diethyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C12)

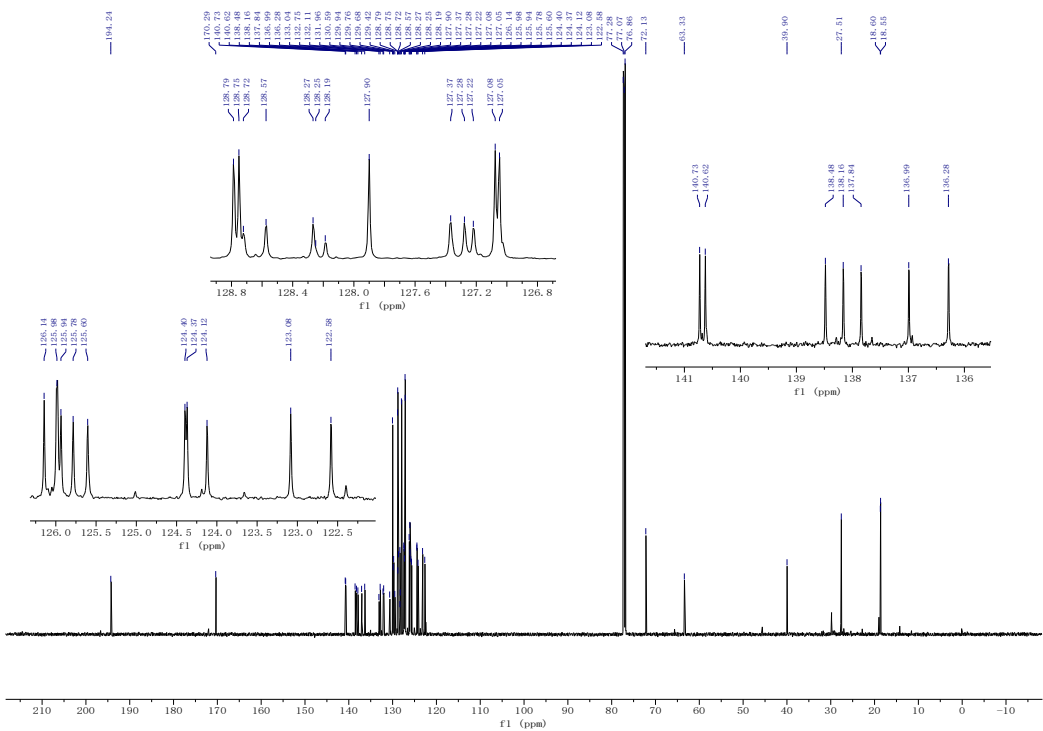
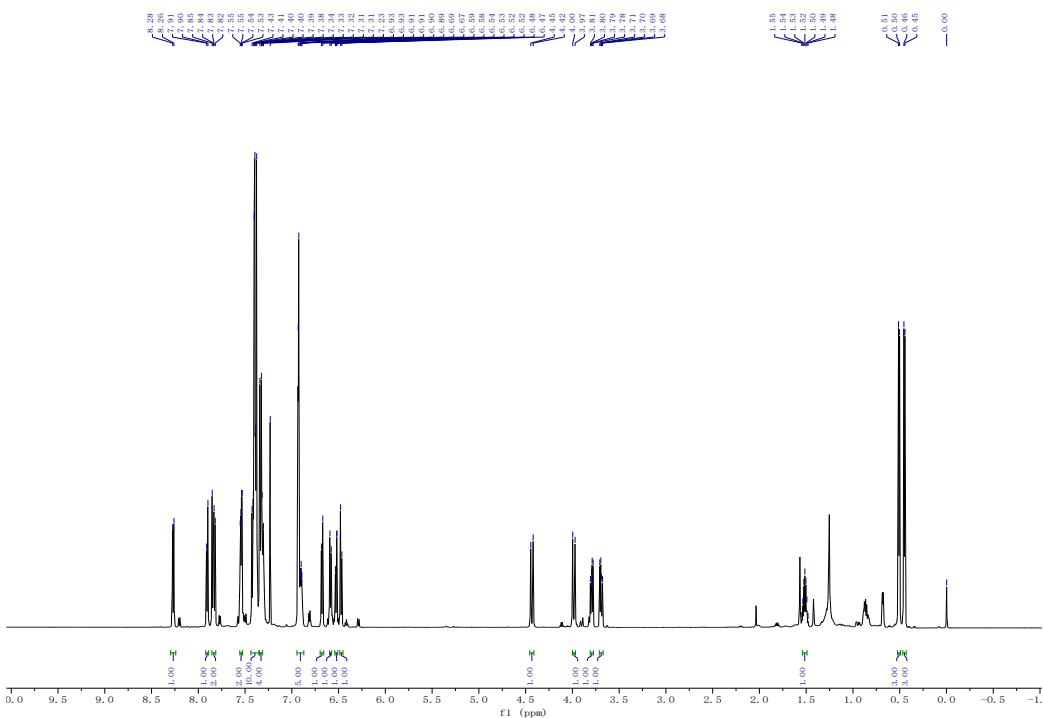


isobutyl (*P*, *S*)-9-benzyl-3,16-diisopropyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C13)

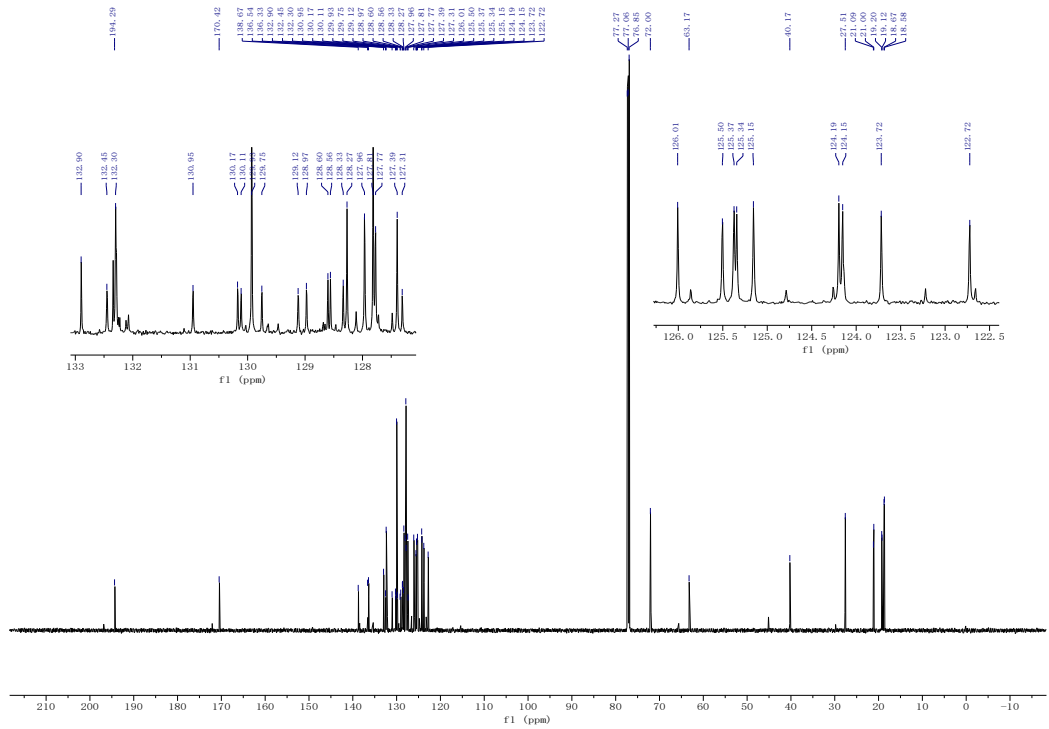
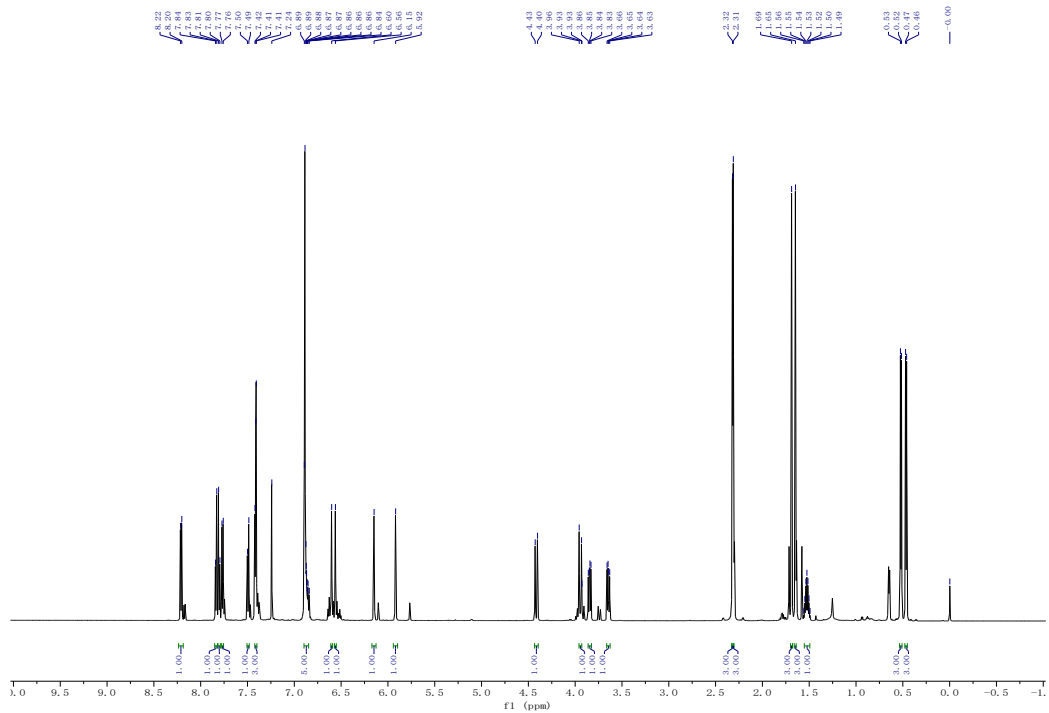
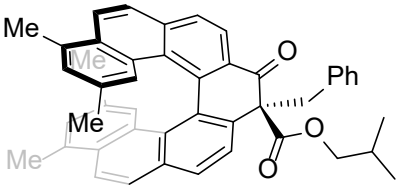


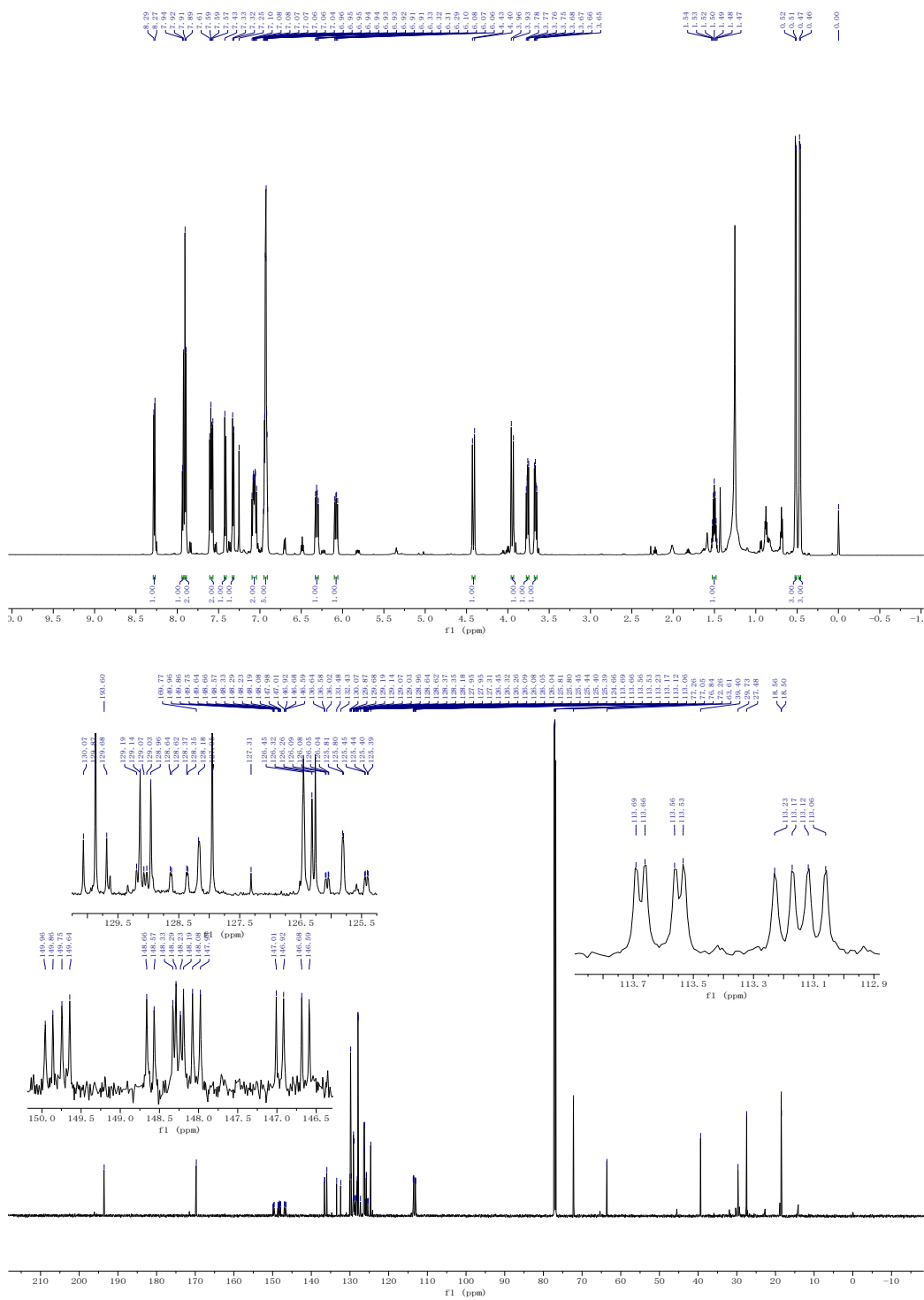
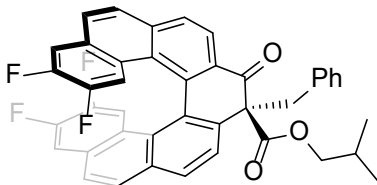
isobutyl (*P, S*)-9-benzyl-3,16-di-*tert*-butyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C14)

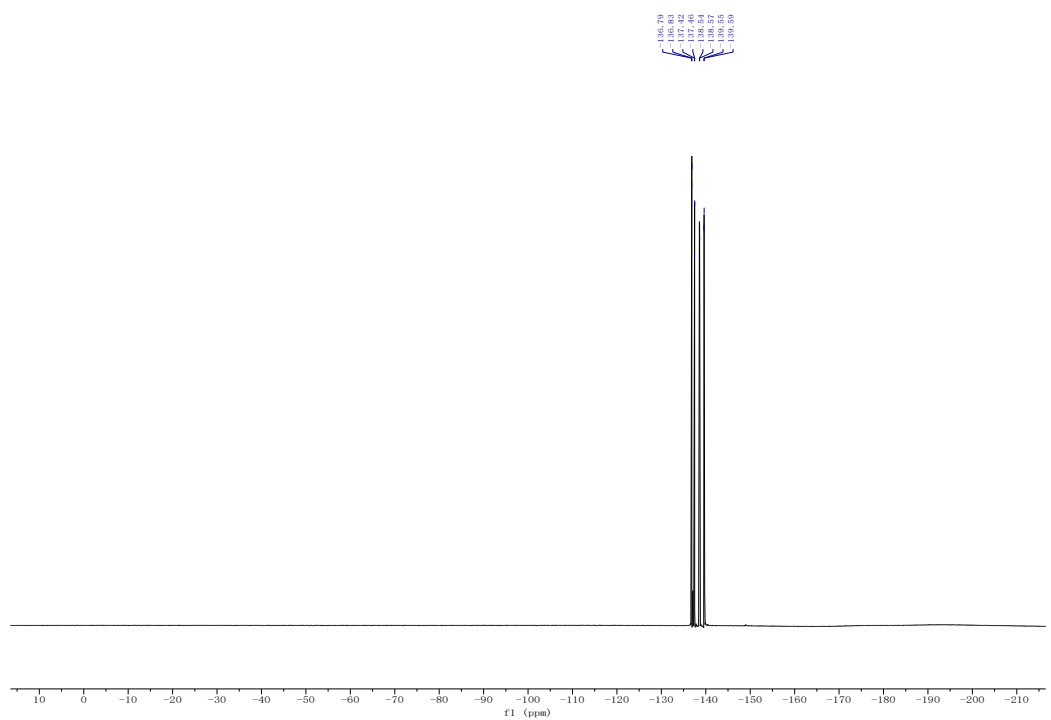


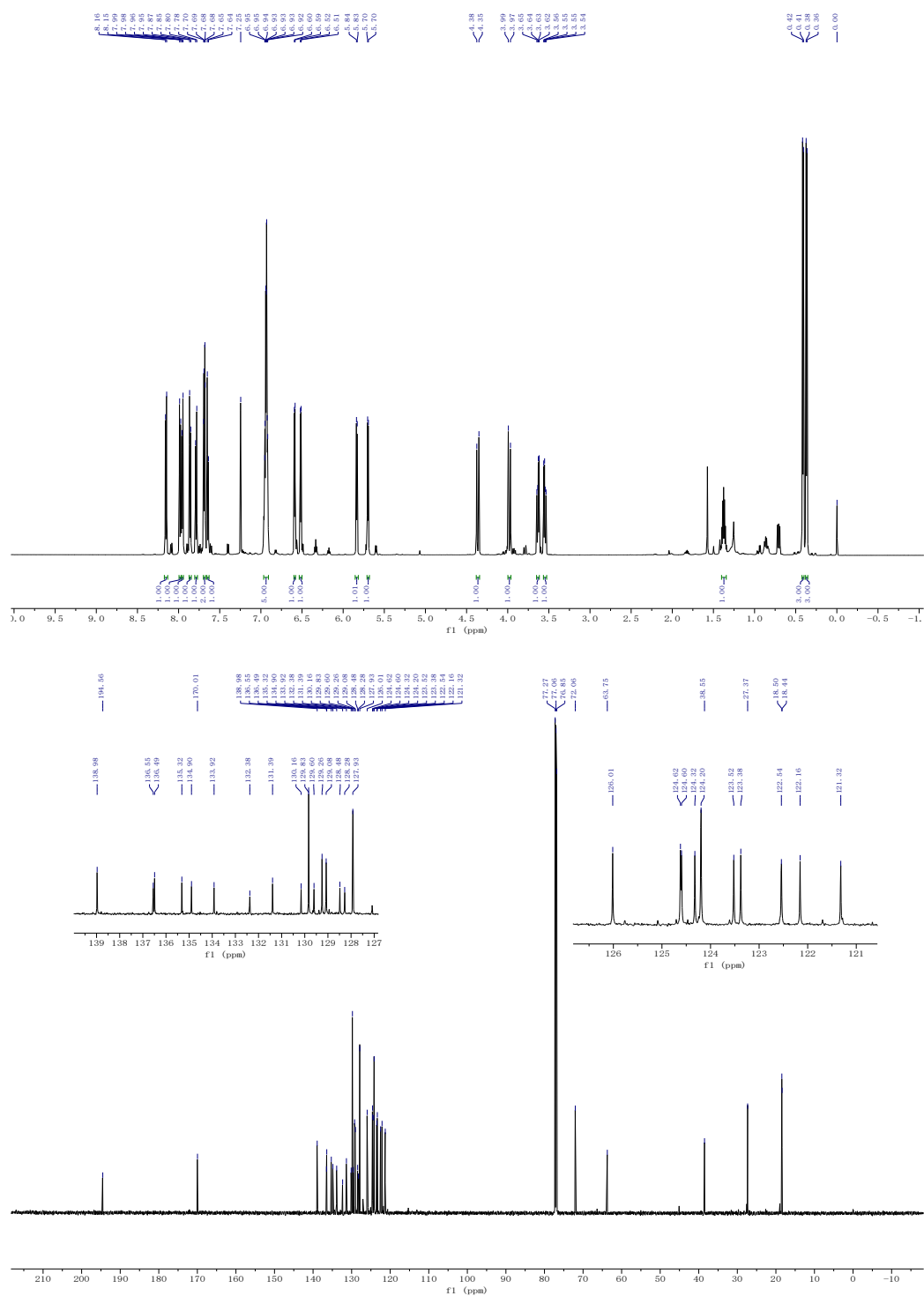
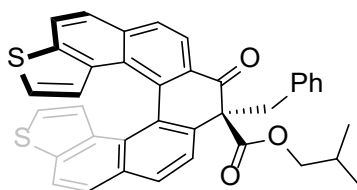


isobutyl (*P*, *S*)-9-benzyl-2,4,15,17-tetramethyl-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C16)

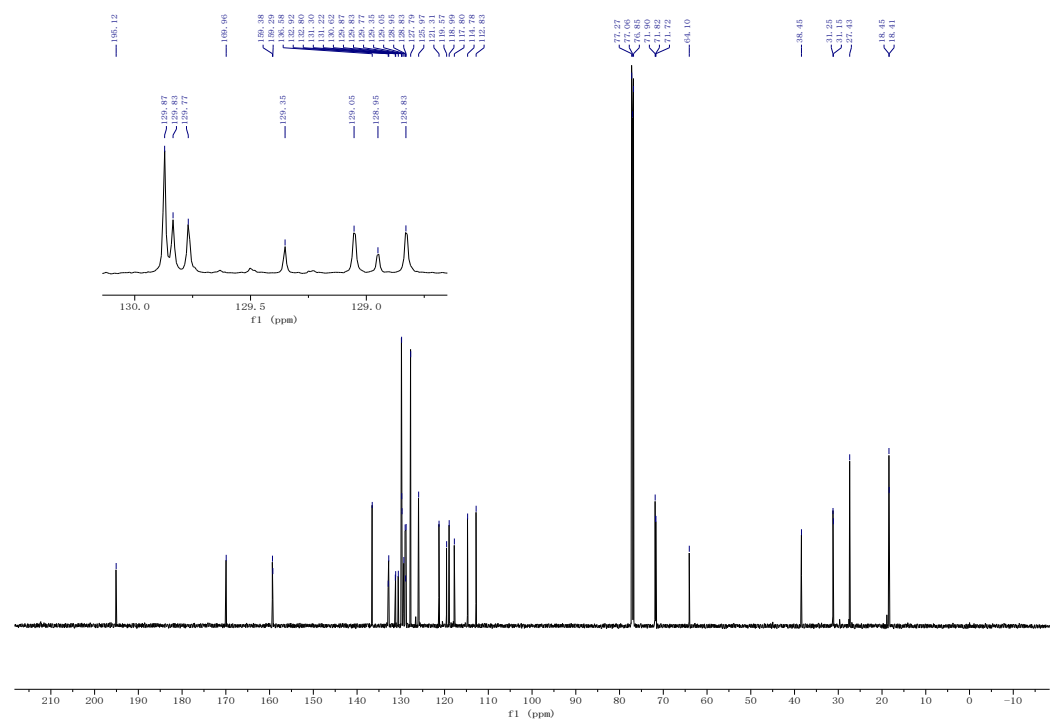
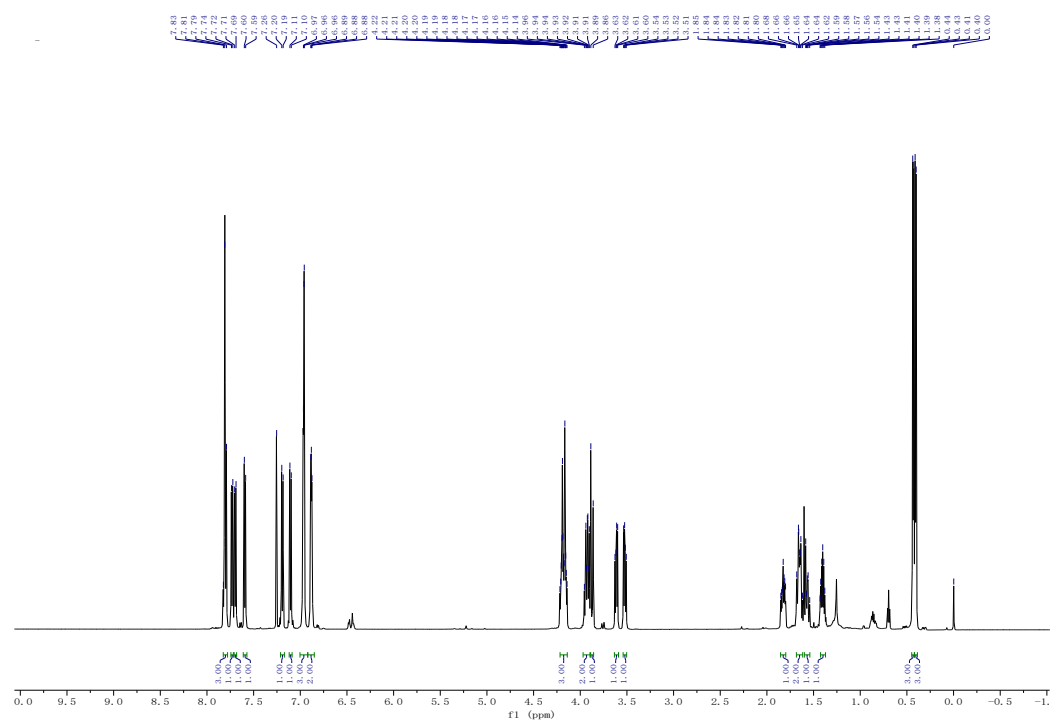
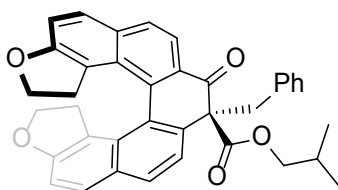


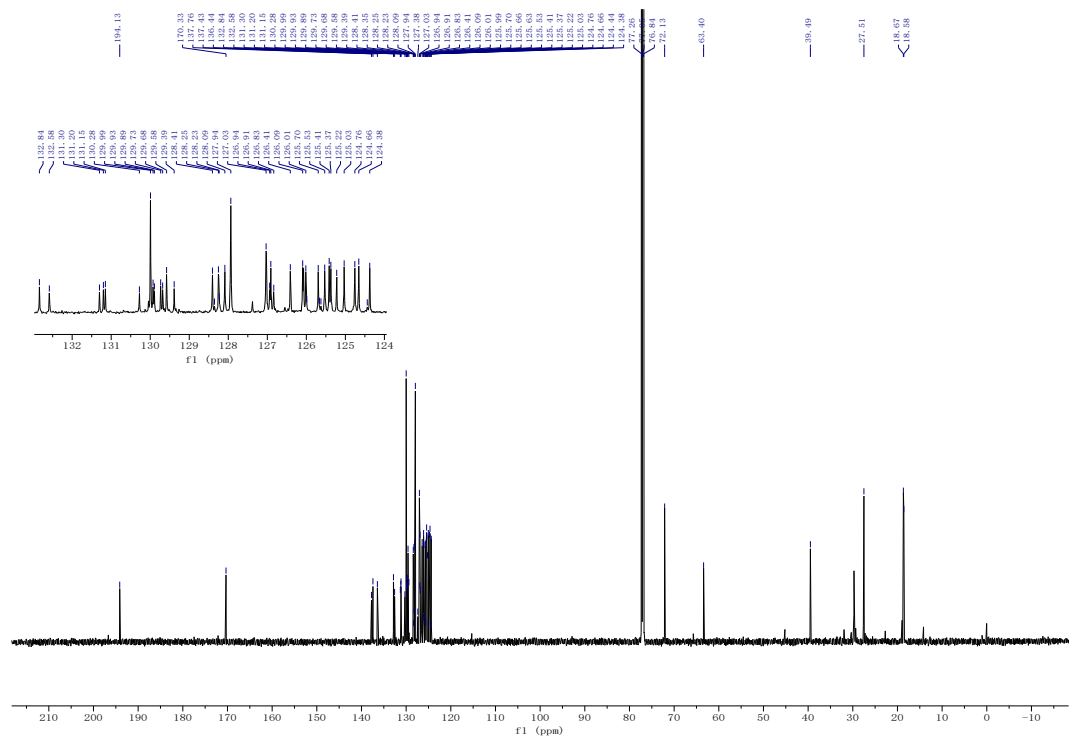
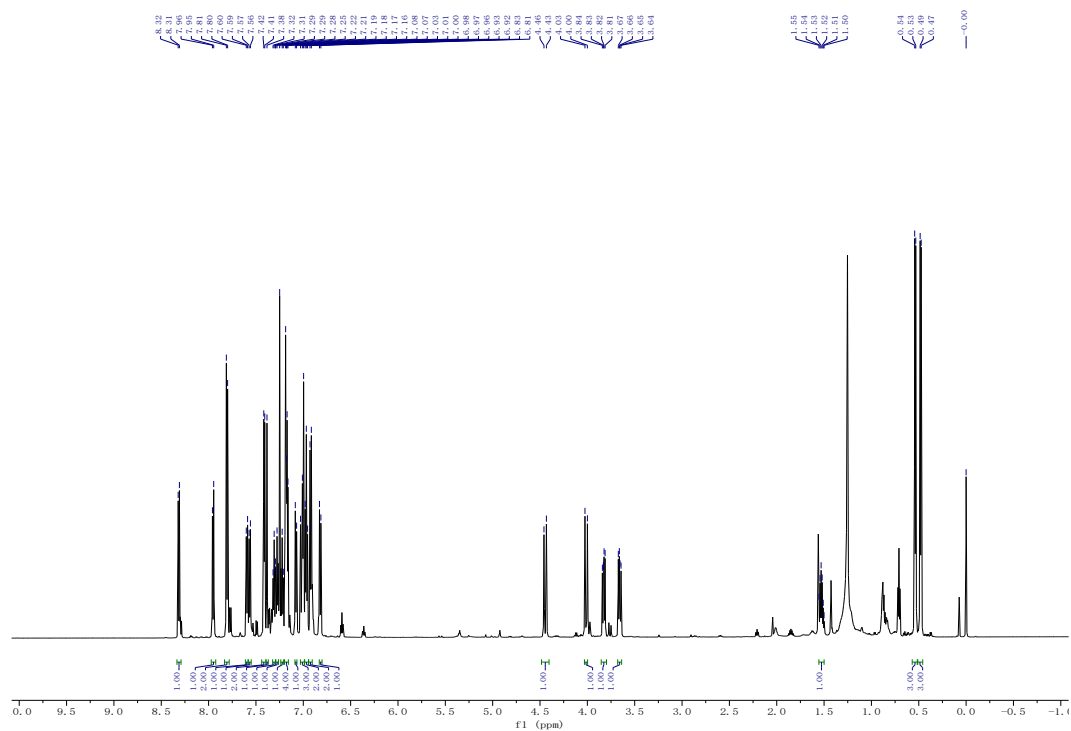
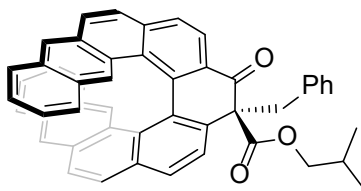
isobutyl (*P, S*)-9-benzyl-2,3,16,17-tetrafluoro-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (C17)

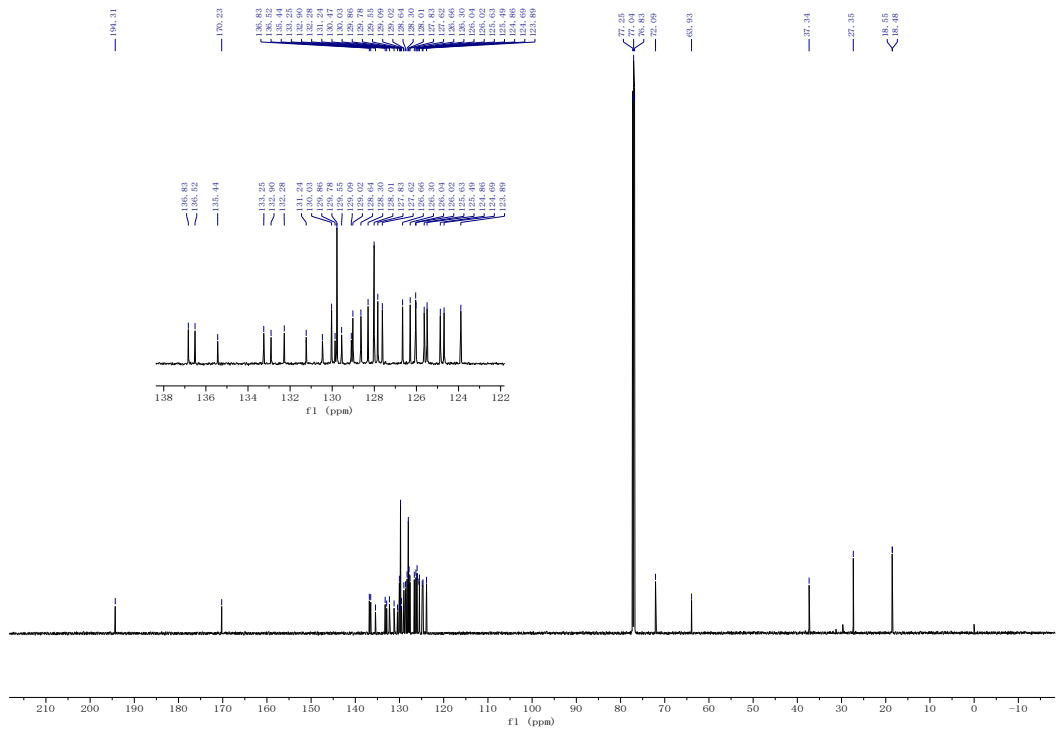
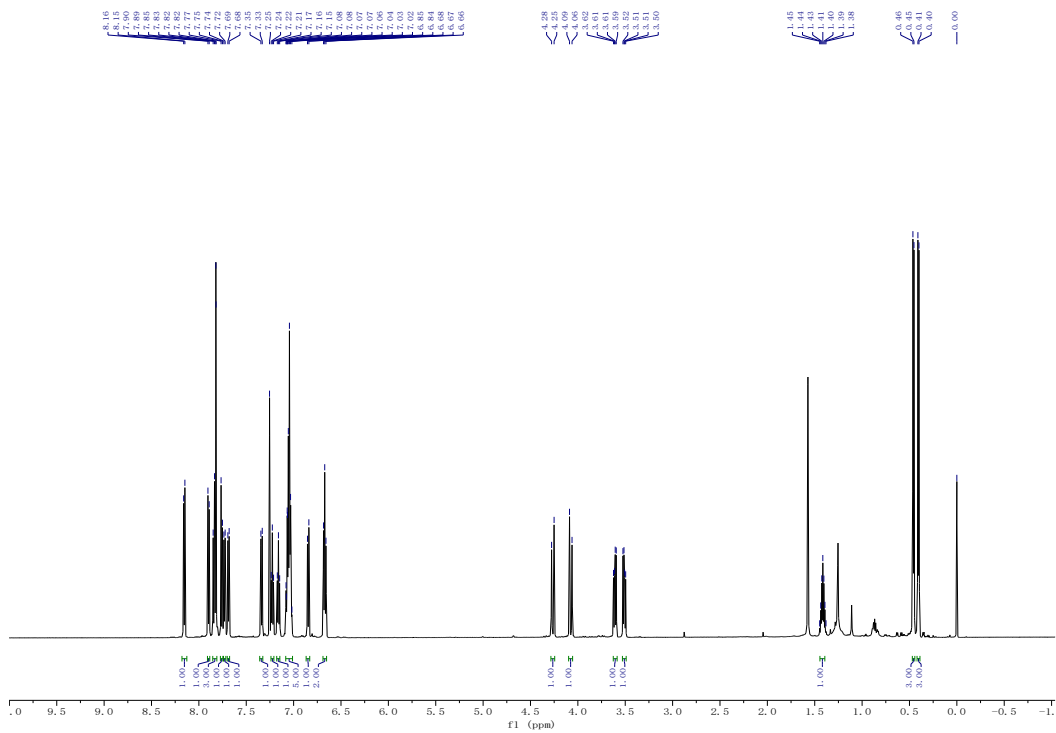
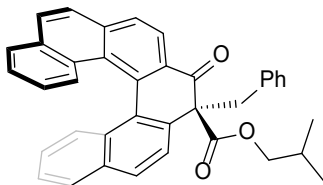


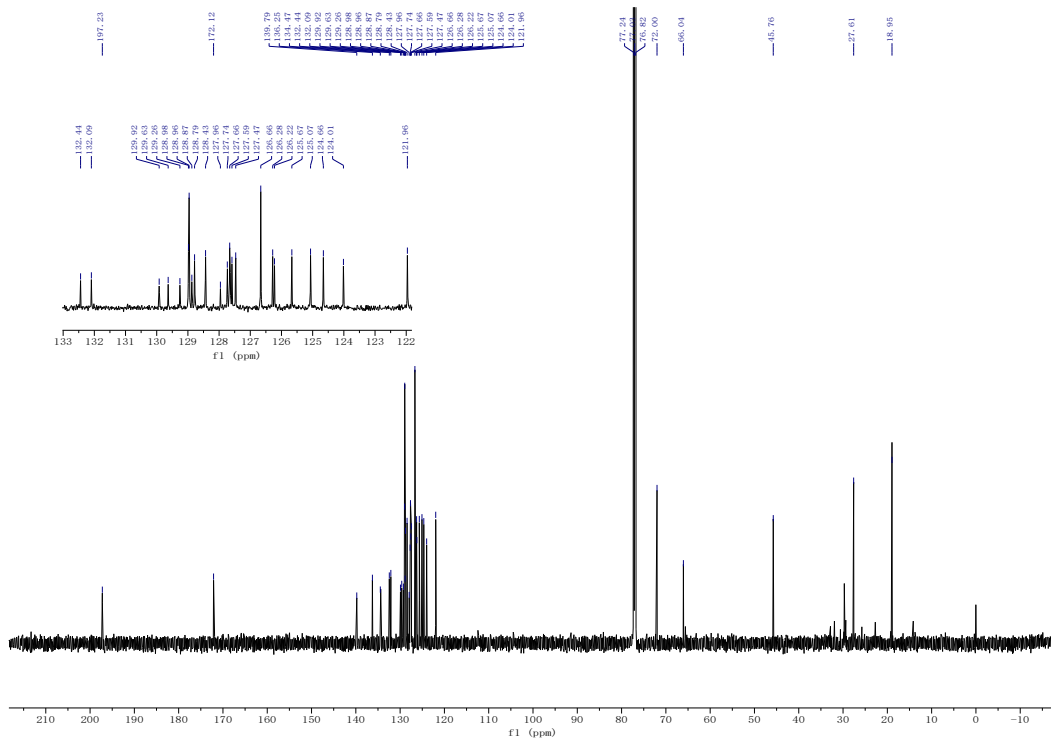
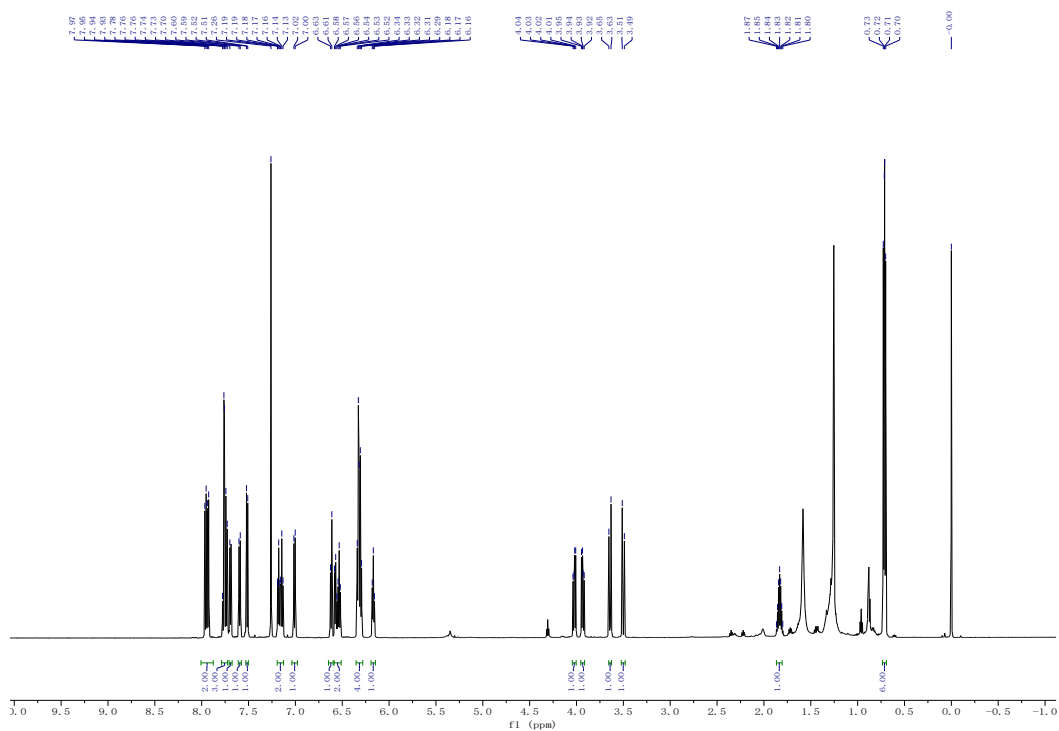
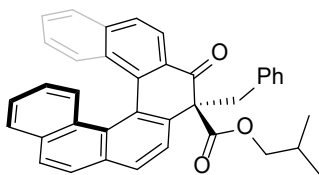
isobutyl (*P, S*)-8-benzyl-9-oxo-8,9-dihydrobenzo[*b*]thieno[5,4-*c*:4,5-*c'*]phenanthrene-8-carboxylate (C18)

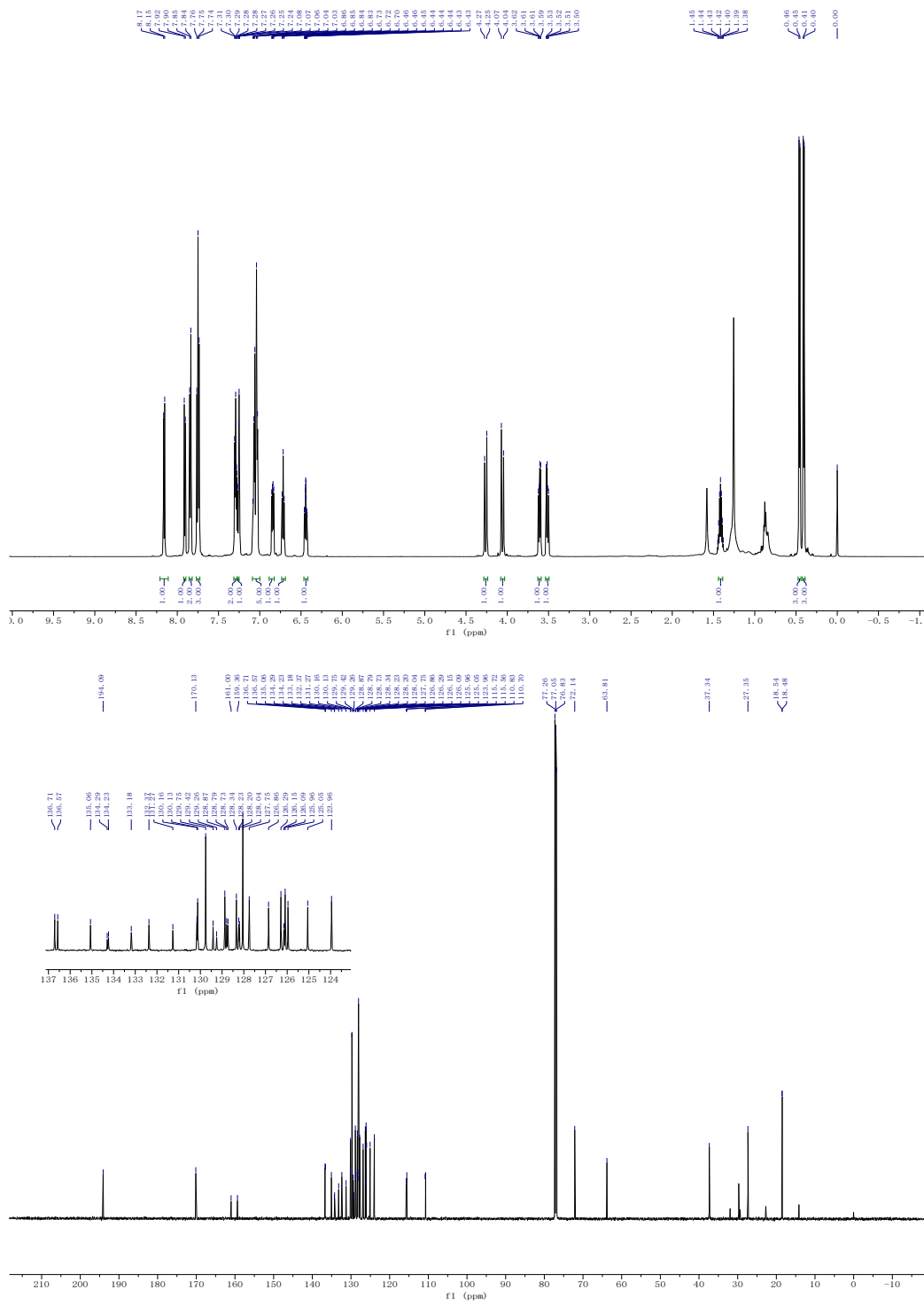
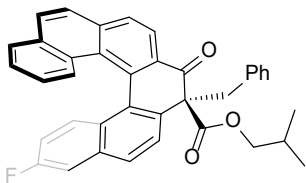
isobutyl (*P, S*)-8-benzyl-9-oxo-1,2,8,9,15,16-hexahydrobenzo[*b*]furo[5,4-*c*:4,5-*c'*]phenanthrene-8-carboxylate (C19)

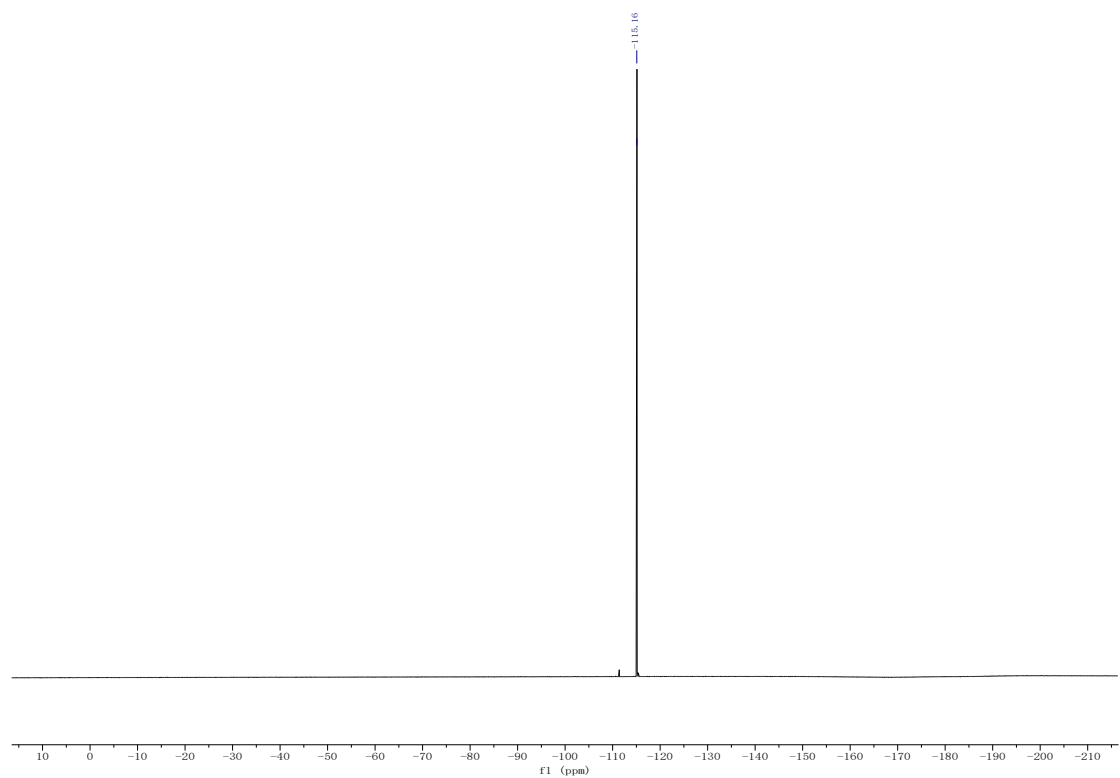


isobutyl (*P, S*)-1-benzyl-2-oxo-1,2-dihydrobenzo[2,1-a:3,4-a']ditetraphene-1-carboxylate (C20)

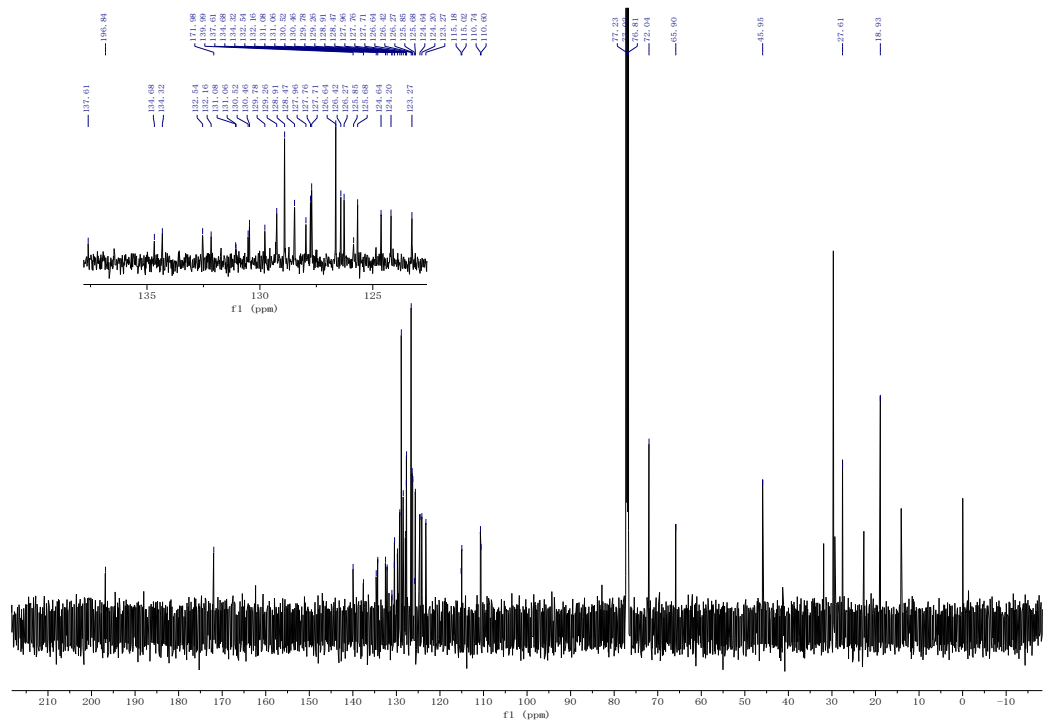
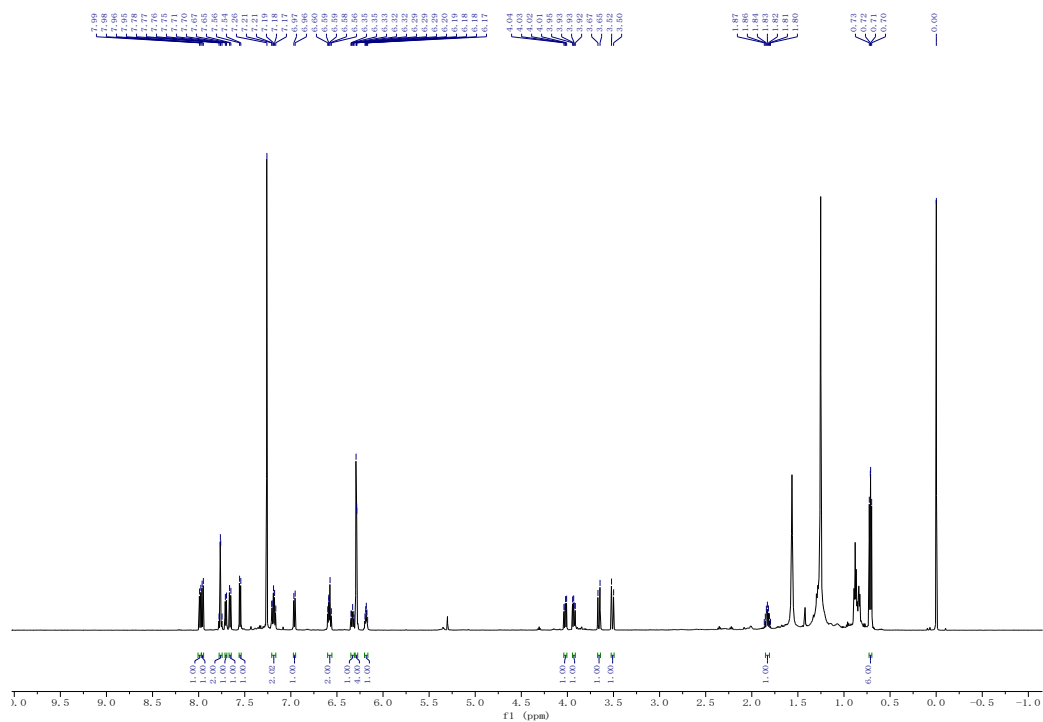
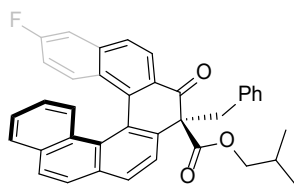
isobutyl (*P, S*)-3-benzyl-4-oxo-3,4-dihydrohexahelicene-3-carboxylate (C21)

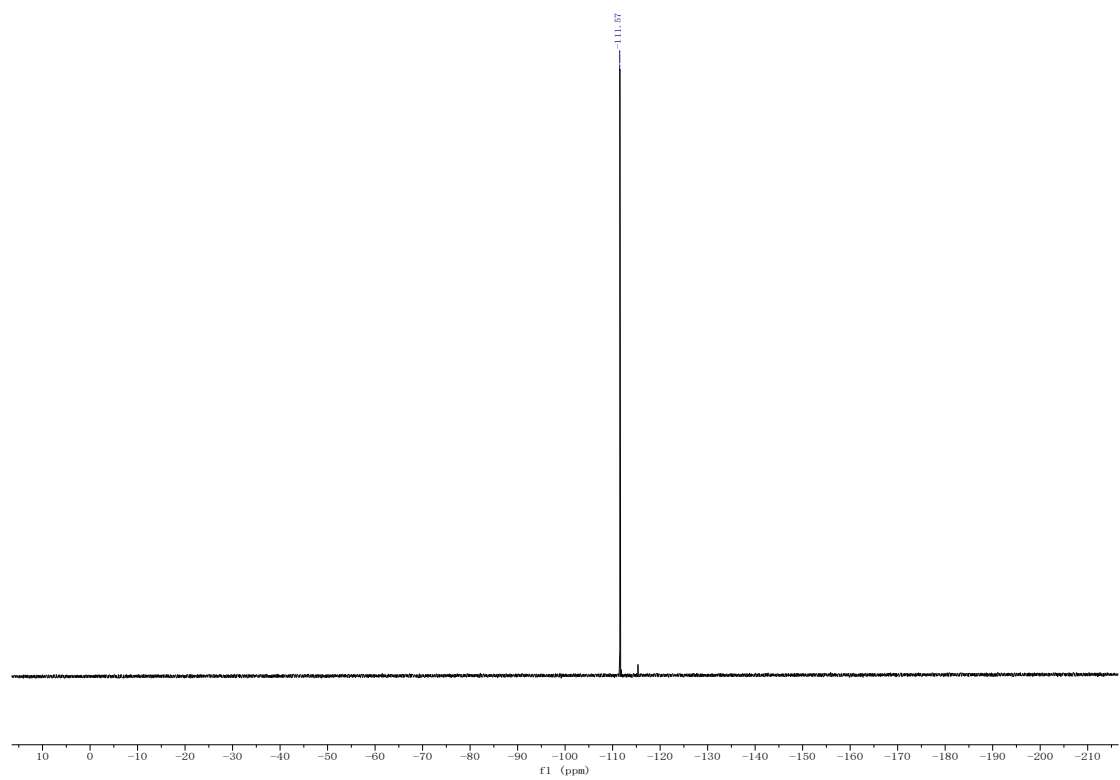
isobutyl (*M, S*)-4-benzyl-3-oxo-3,4-dihydrohexahelicene-4-carboxylate (C21')

isobutyl (*P, S*)-3-benzyl-15-fluoro-4-oxo-3,4-dihydrohexahelicene-3-carboxylate (C22)

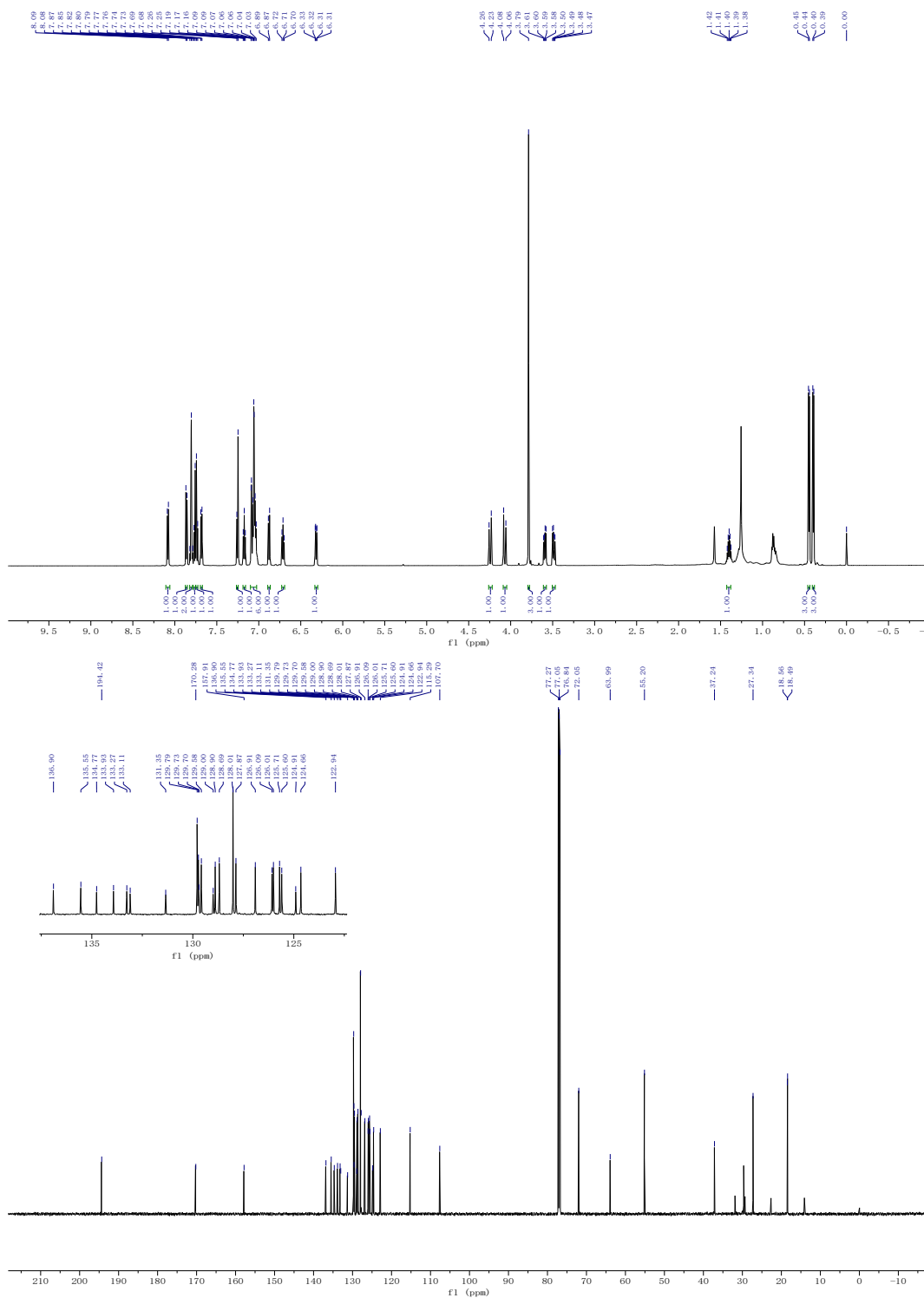
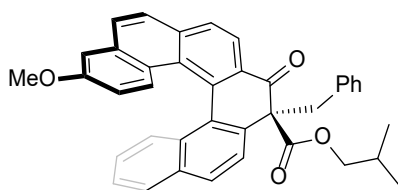


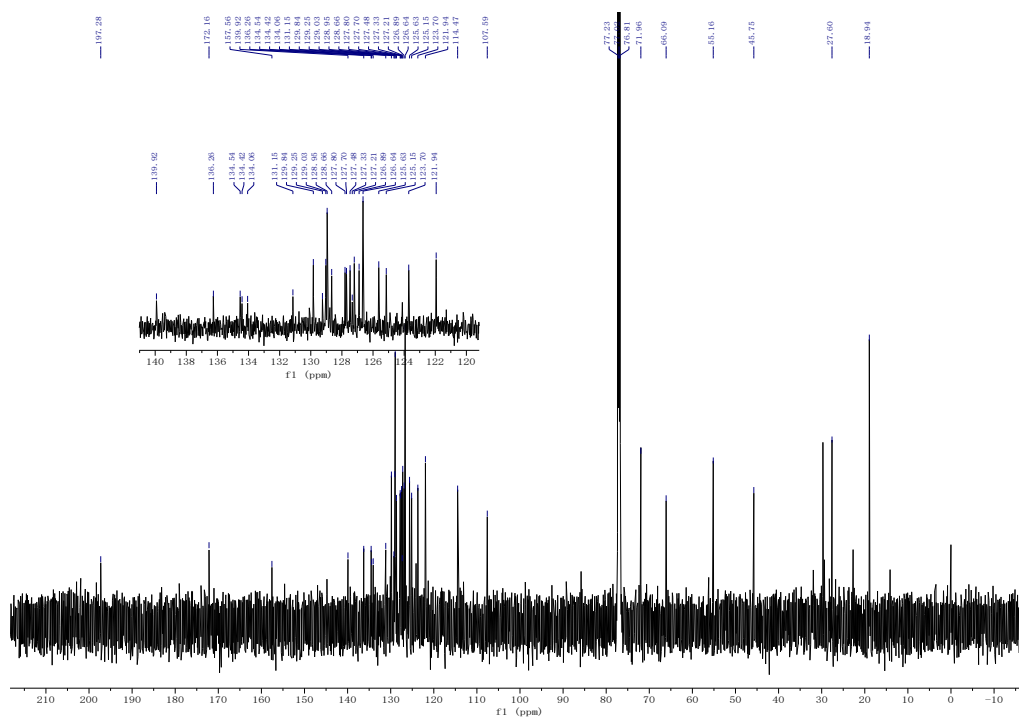
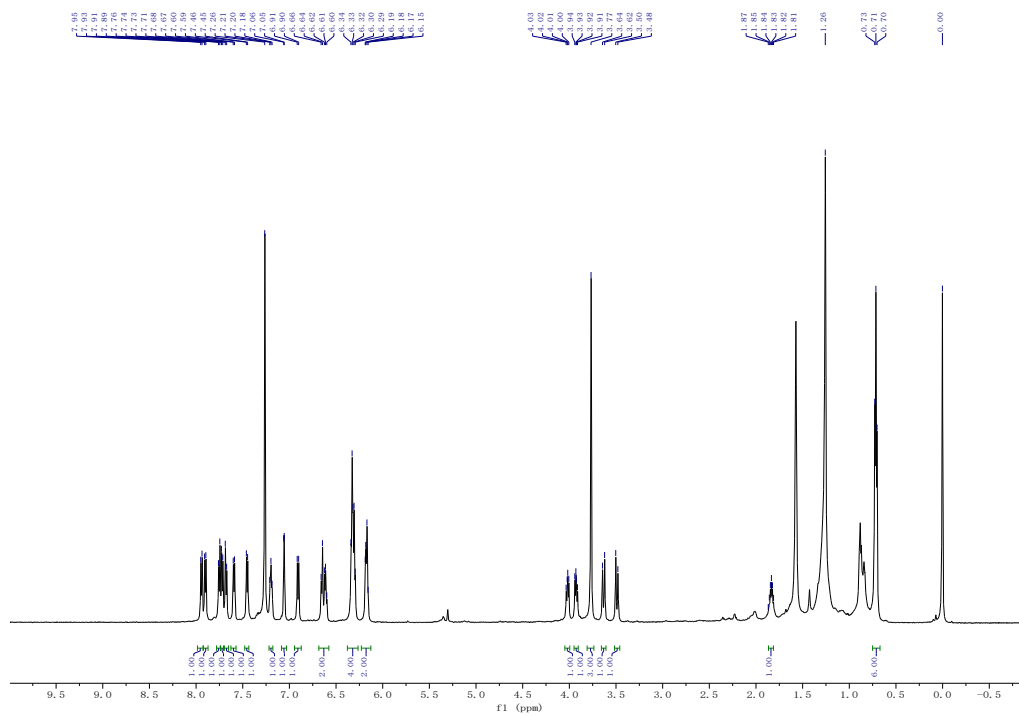
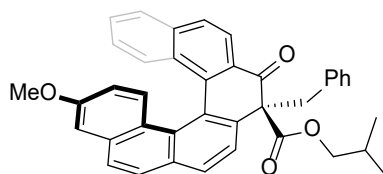
isobutyl (*M*, *S*)-4-benzyl-15-fluoro-3-oxo-3,4-dihydrohexahelicene-4-carboxylate (C22')

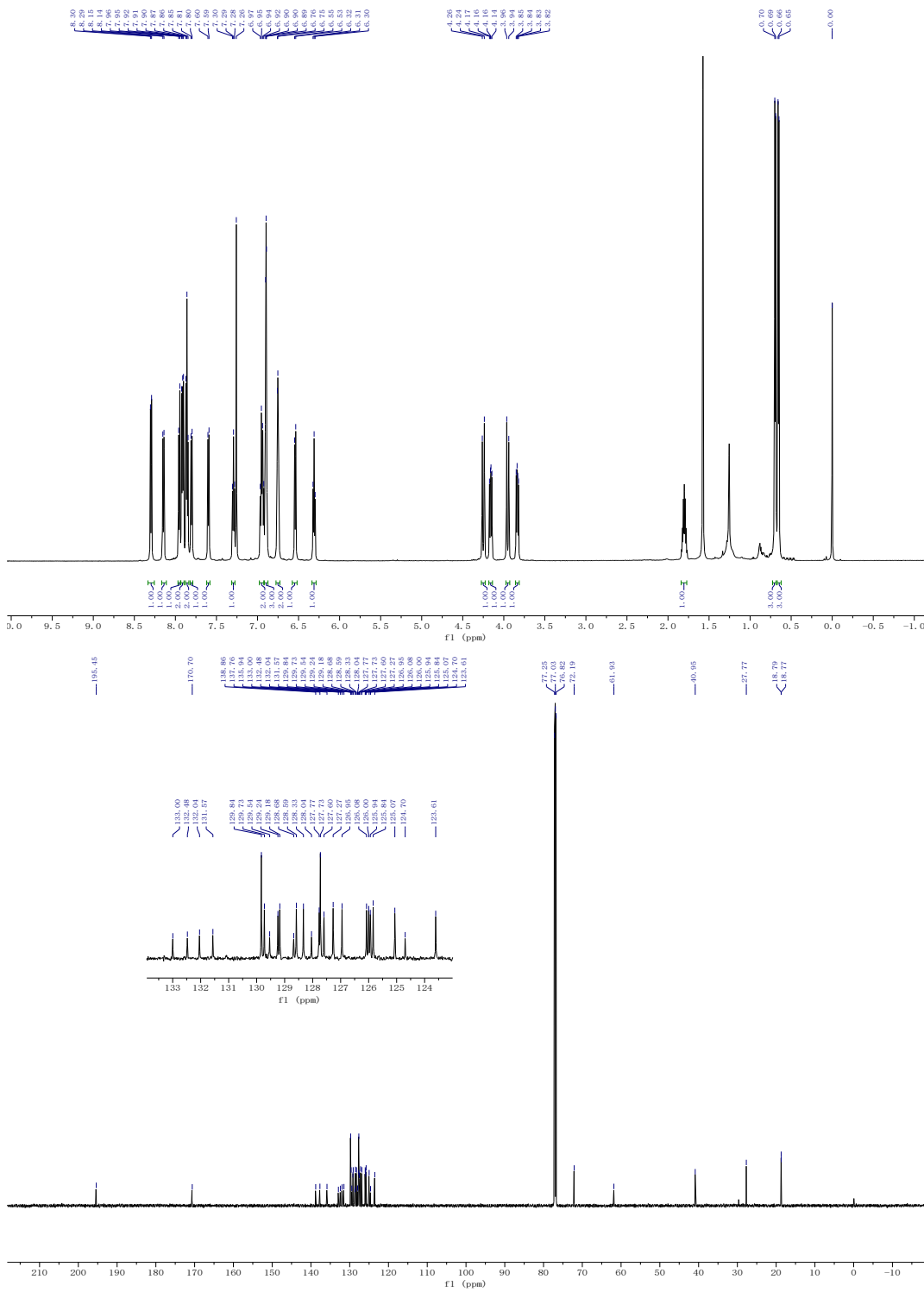
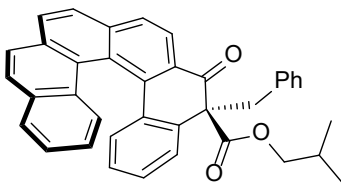




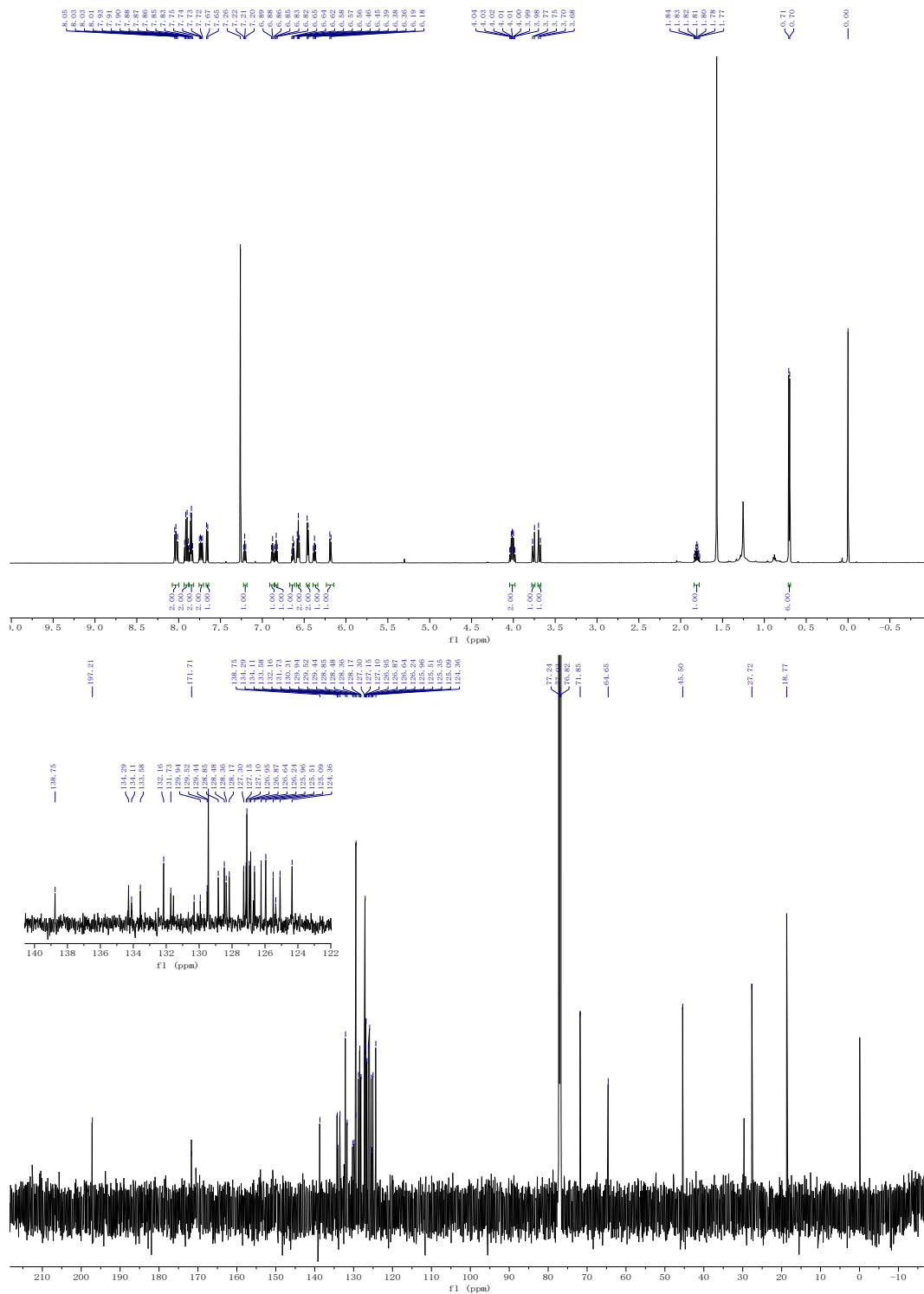
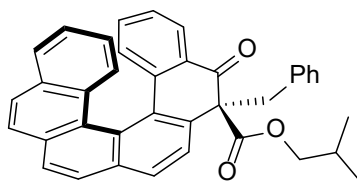
isobutyl (*P, S*)-3-benzyl-10-methoxy-4-oxo-3,4-dihydrohexahelicene-3-carboxylate (C23)



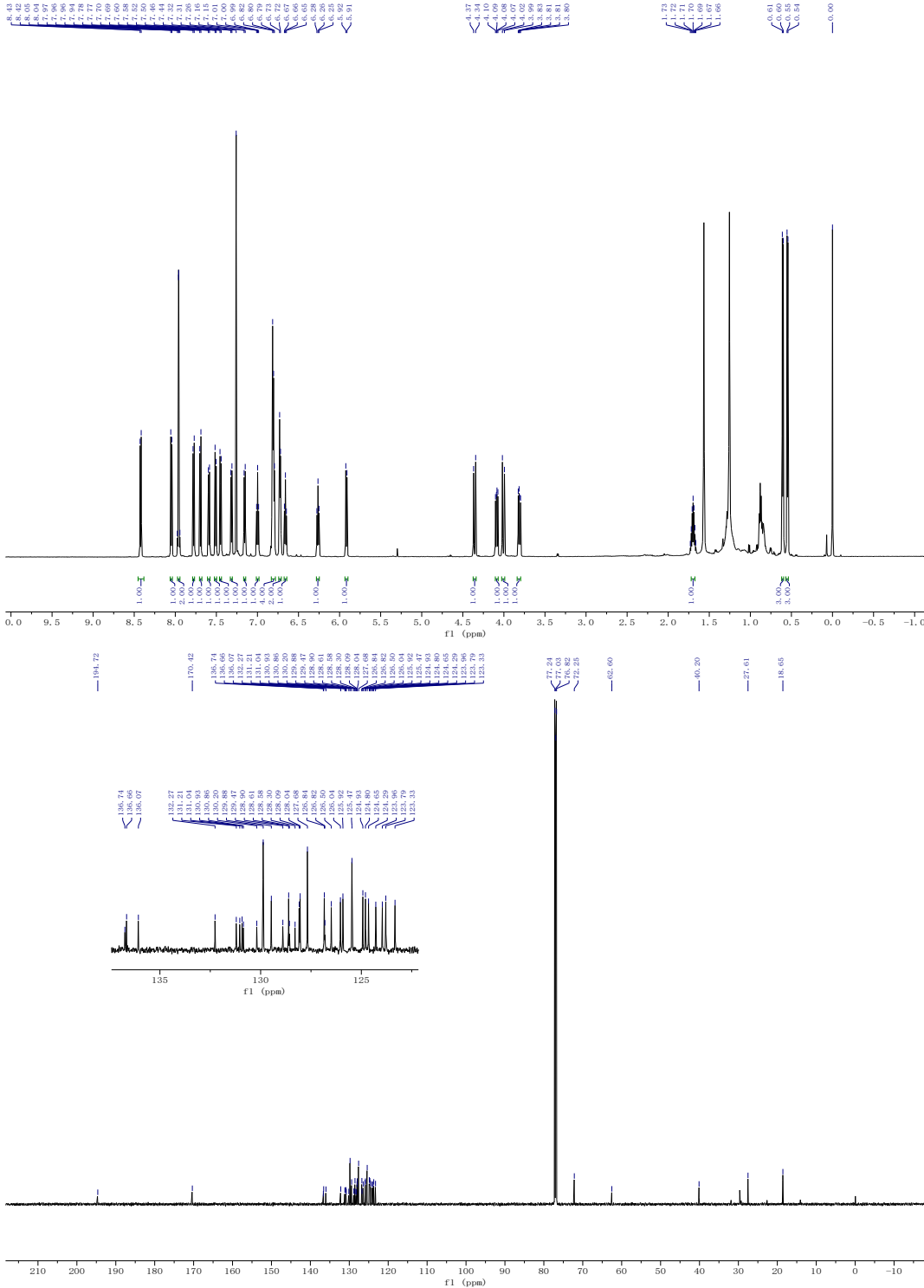
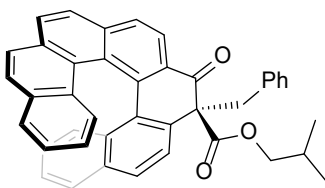
isobutyl (*M, S*)-4-benzyl-10-methoxy-3-oxo-3,4-dihydrohexahelicene-4-carboxylate (C23')

isobutyl (*P, S*)-1-benzyl-2-oxo-1,2-dihydrohexahelicene-1-carboxylate (C24)

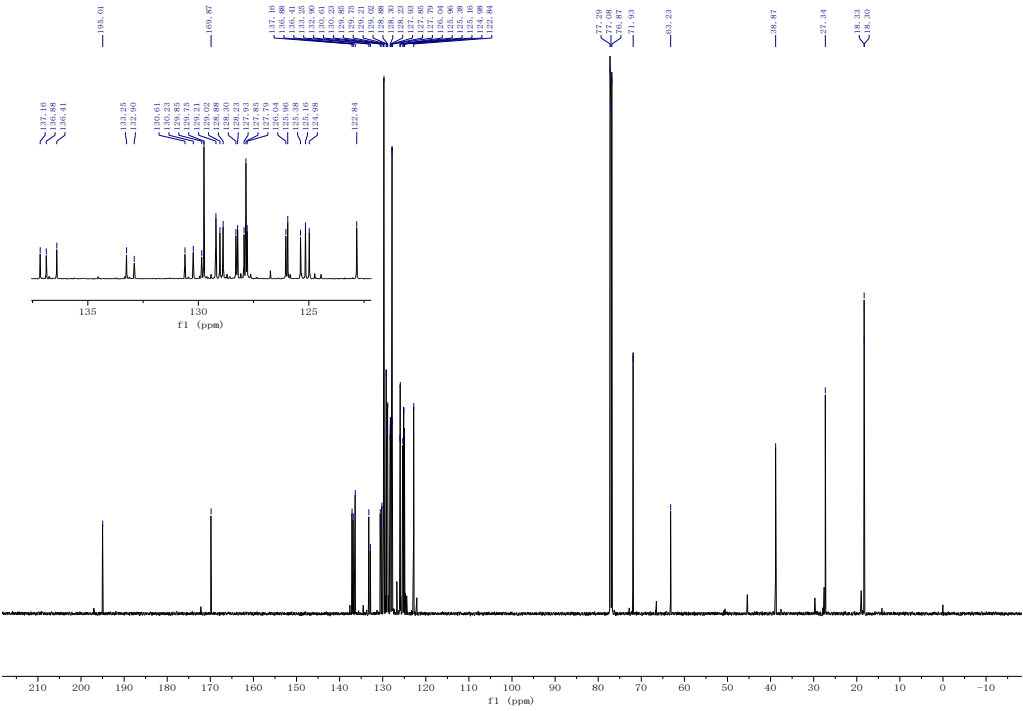
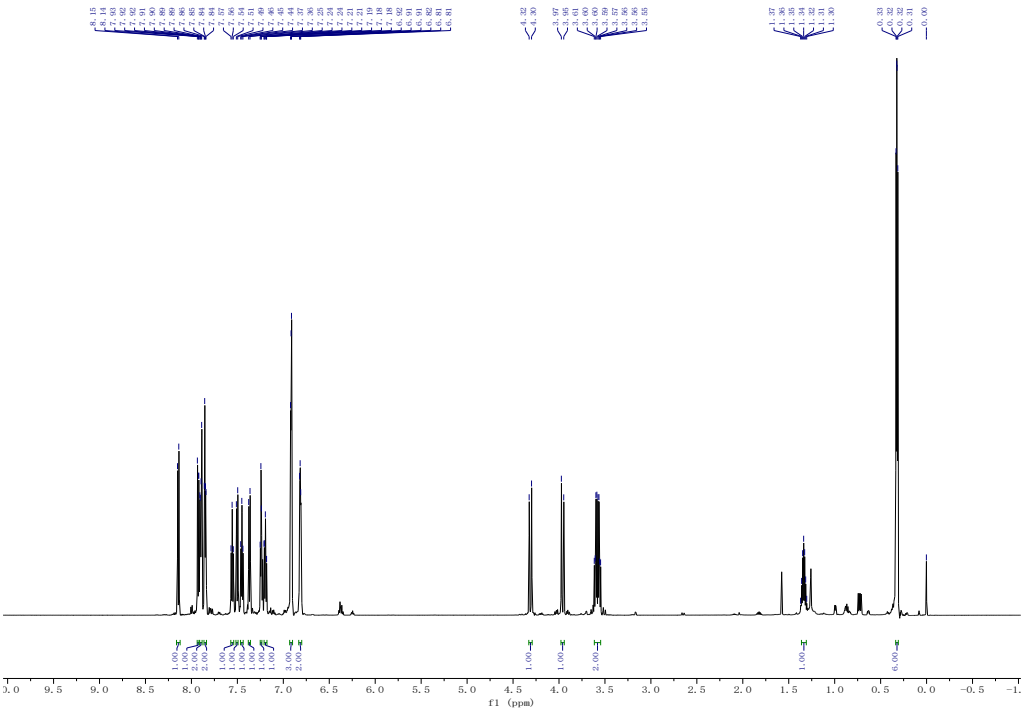
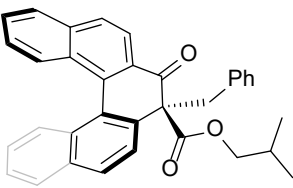
isobutyl (*M,S*)-2-benzyl-1-oxo-1,2-dihydrohexahelicene-2-carboxylate (C24')



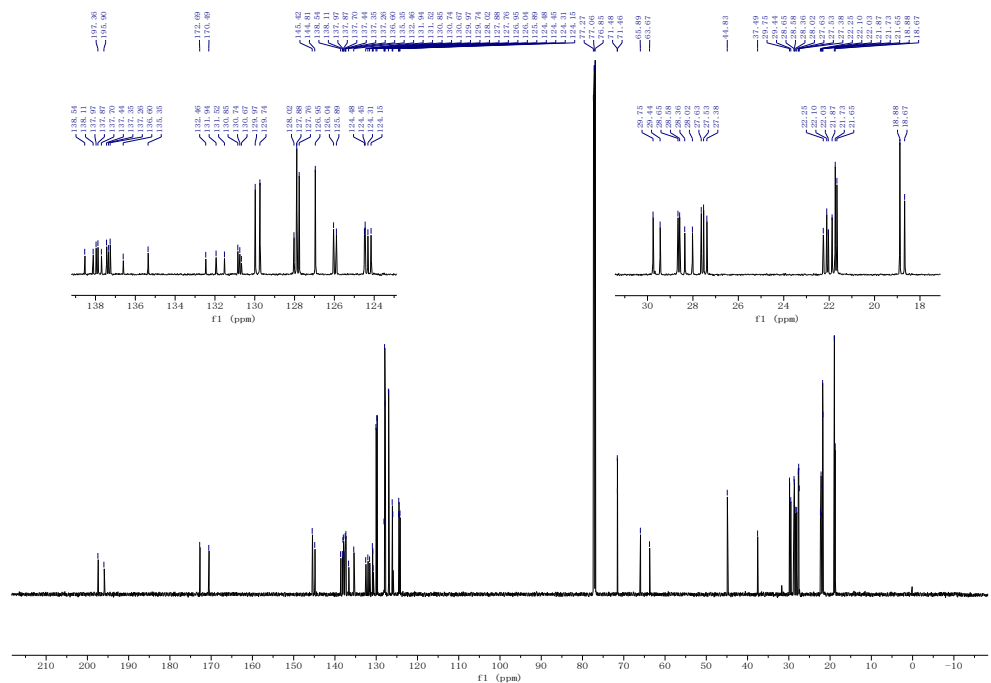
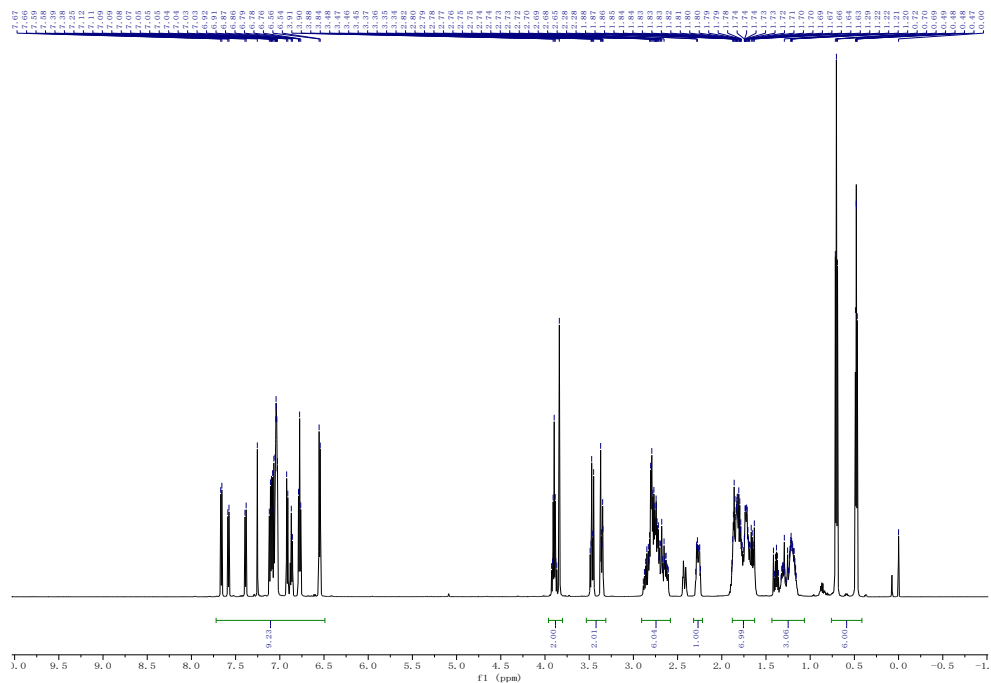
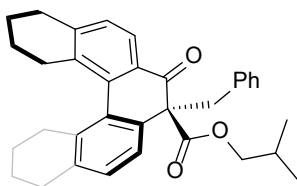
isobutyl (*P*, *S*)-7-benzyl-8-oxo-7,8-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-7-carboxylate (C25)



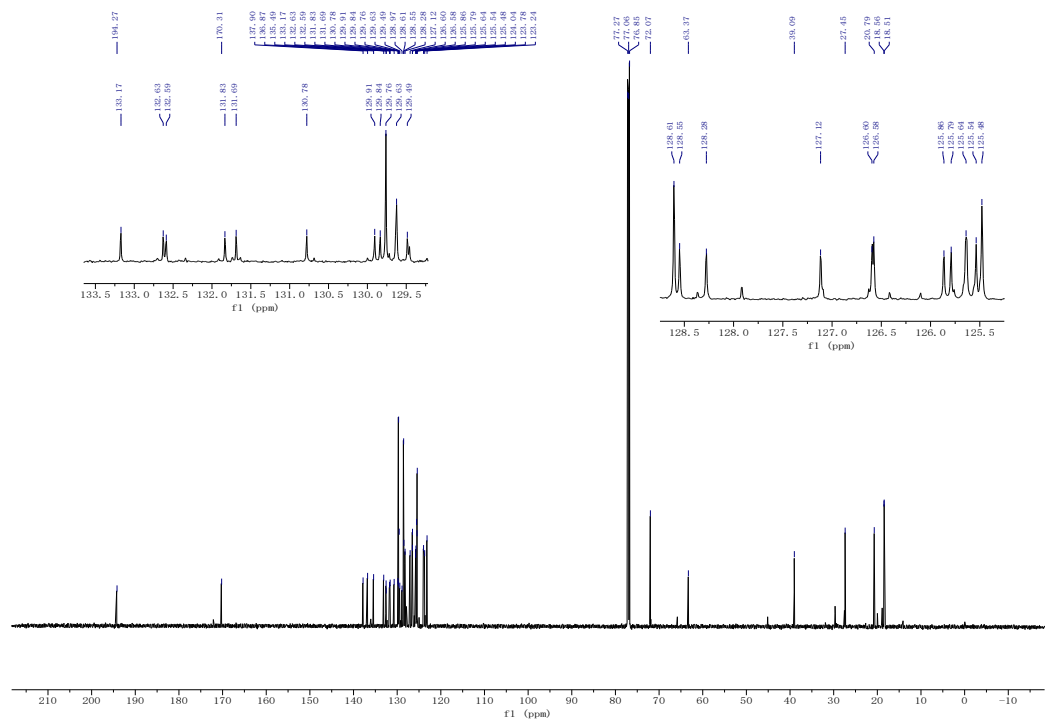
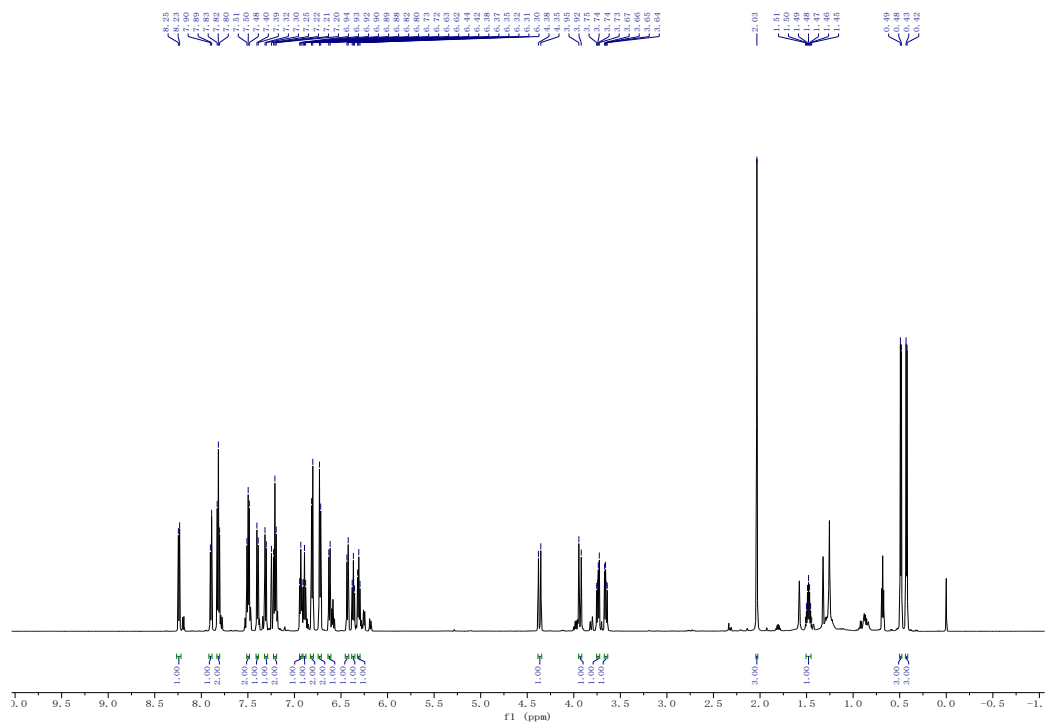
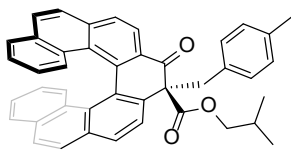
isobutyl (*P,S*)-3-benzyl-4-oxo-3,4-dihydrodibenzo[*c,g*]phenanthrene-3-carboxylate (C26)



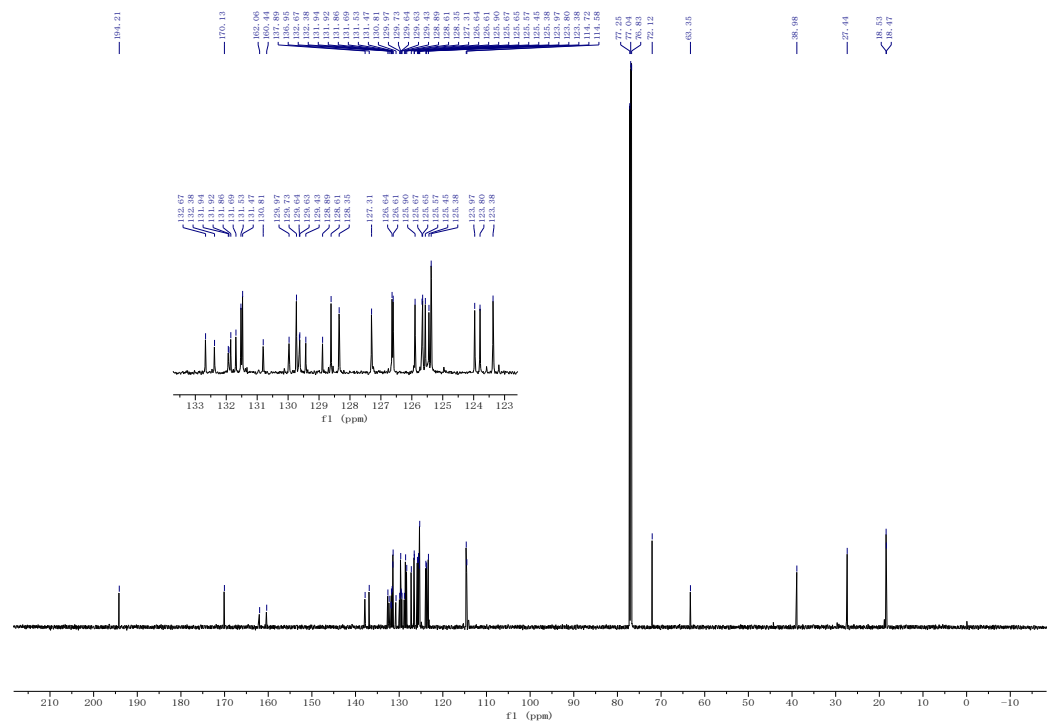
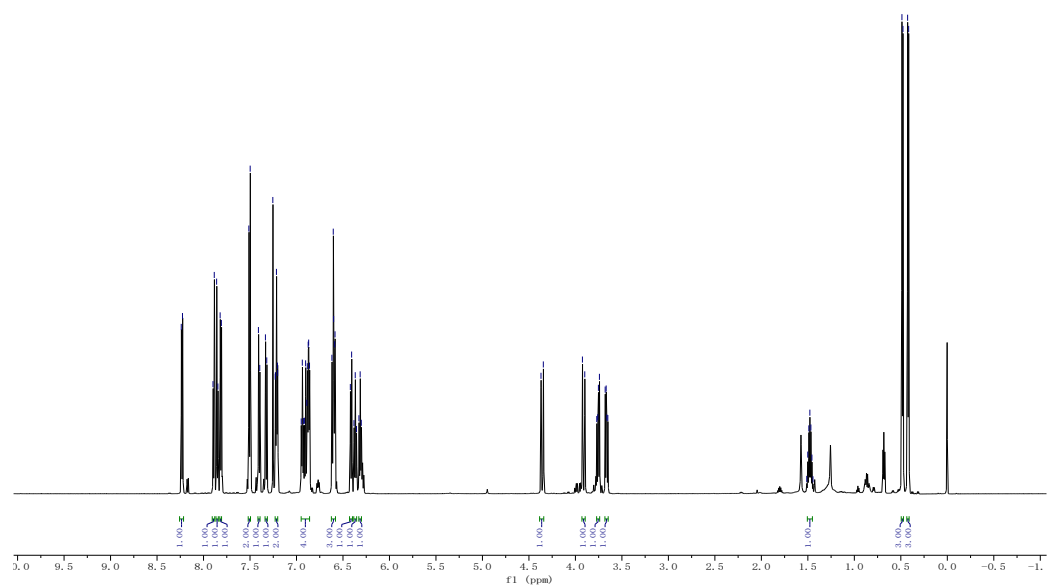
isobutyl (*P, S*)-3-benzyl-4-oxo-3,4,7,8,9,10,11,12,13,14-decahydrodibenzo[*c,g*]phenanthrene-3-carboxylate (C27)

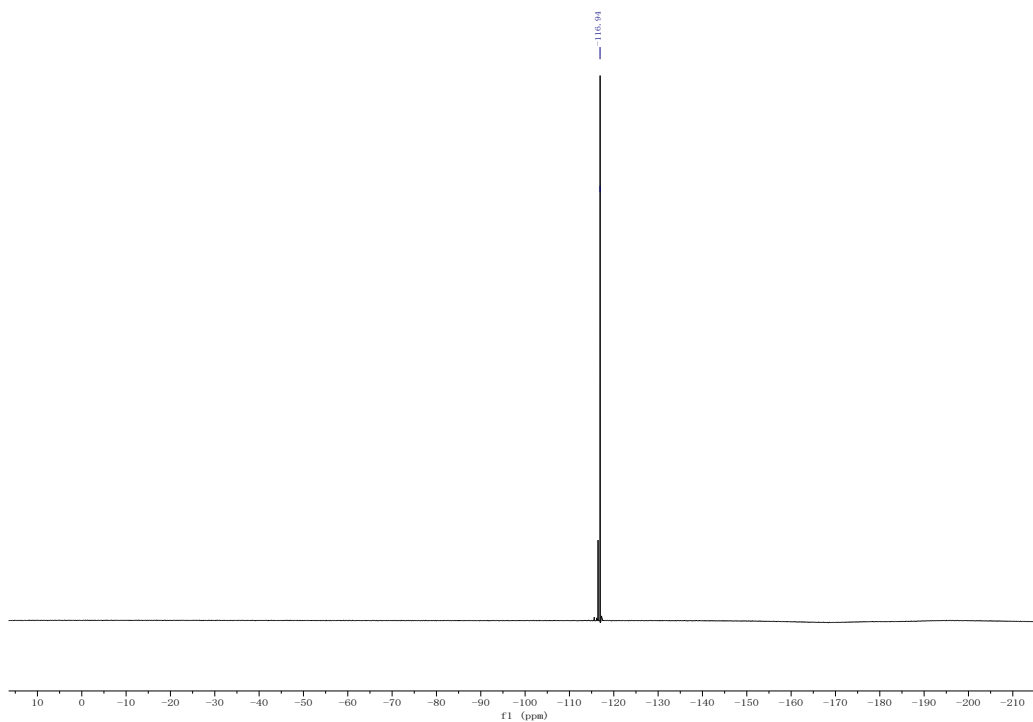


isobutyl (*P,S*)-9-(4-methylbenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D2)

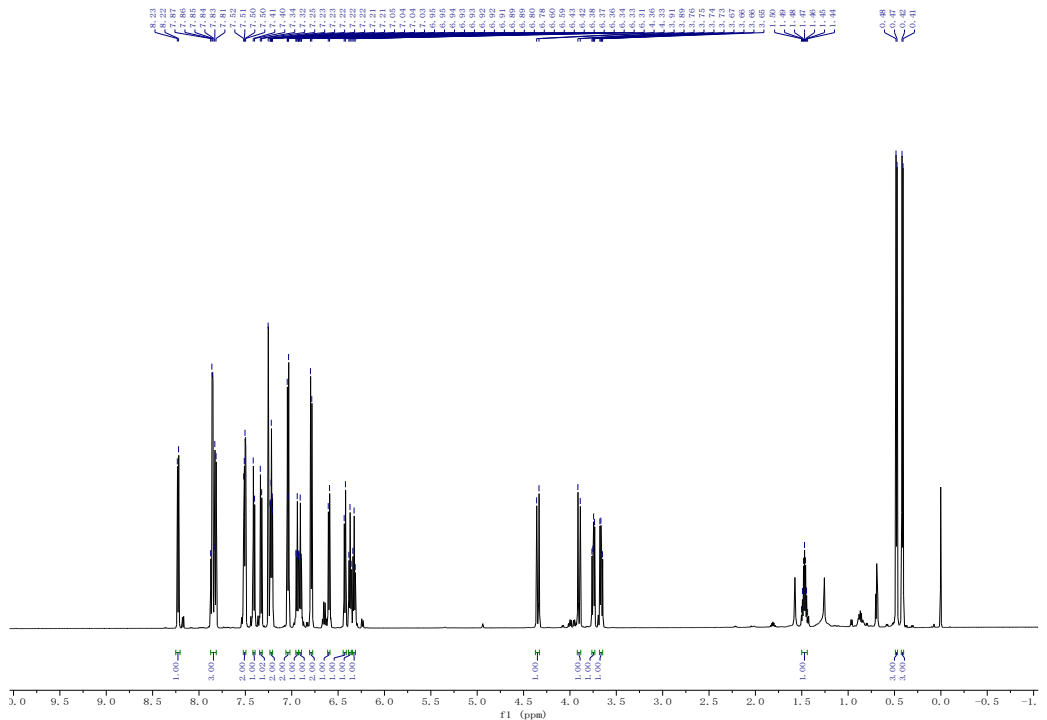
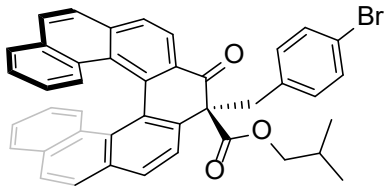


Chemical structure of compound 10 and its ^1H NMR spectrum (CDCl₃). The structure is a complex polycyclic molecule with a central five-membered ring containing a carbonyl group and a chiral center. It features a 4-fluorophenyl group and an isobutoxy group. The ^1H NMR spectrum (CDCl₃) shows peaks from 0.9 to 8.2 ppm. The spectrum includes a large multiplet between 7.2 and 7.8 ppm, a multiplet at 6.8-7.0 ppm, a multiplet at 5.5-5.8 ppm, a multiplet at 4.5-4.8 ppm, a multiplet at 3.5-3.8 ppm, a multiplet at 2.5-2.8 ppm, a multiplet at 1.8-2.1 ppm, a multiplet at 1.4-1.7 ppm, and a multiplet at 0.9-1.2 ppm.

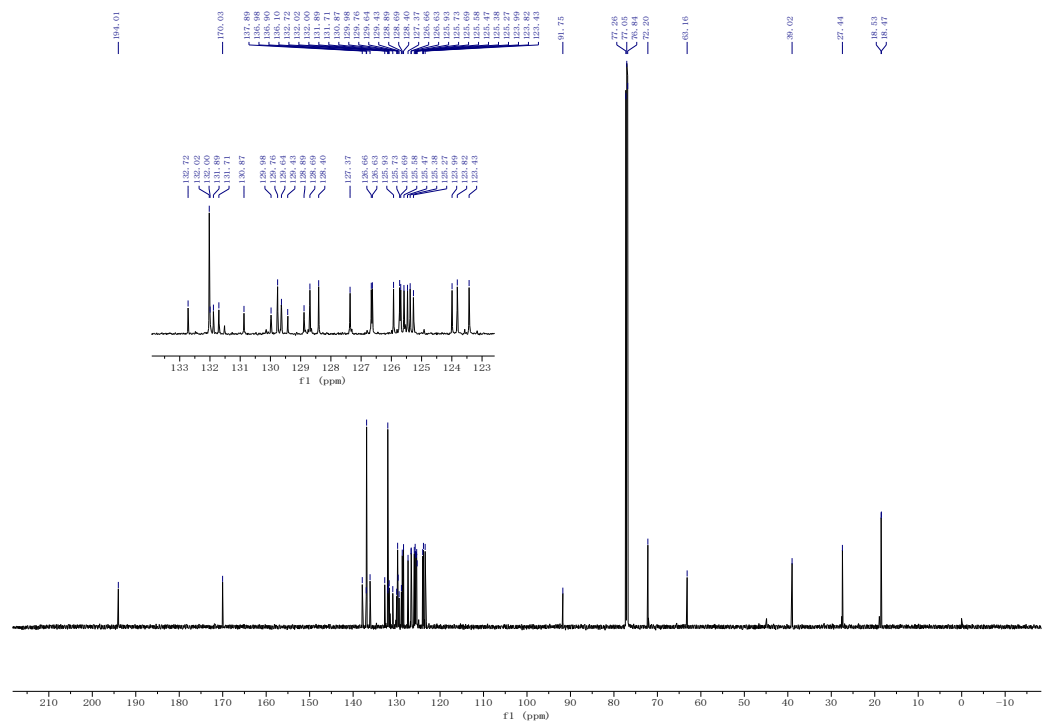
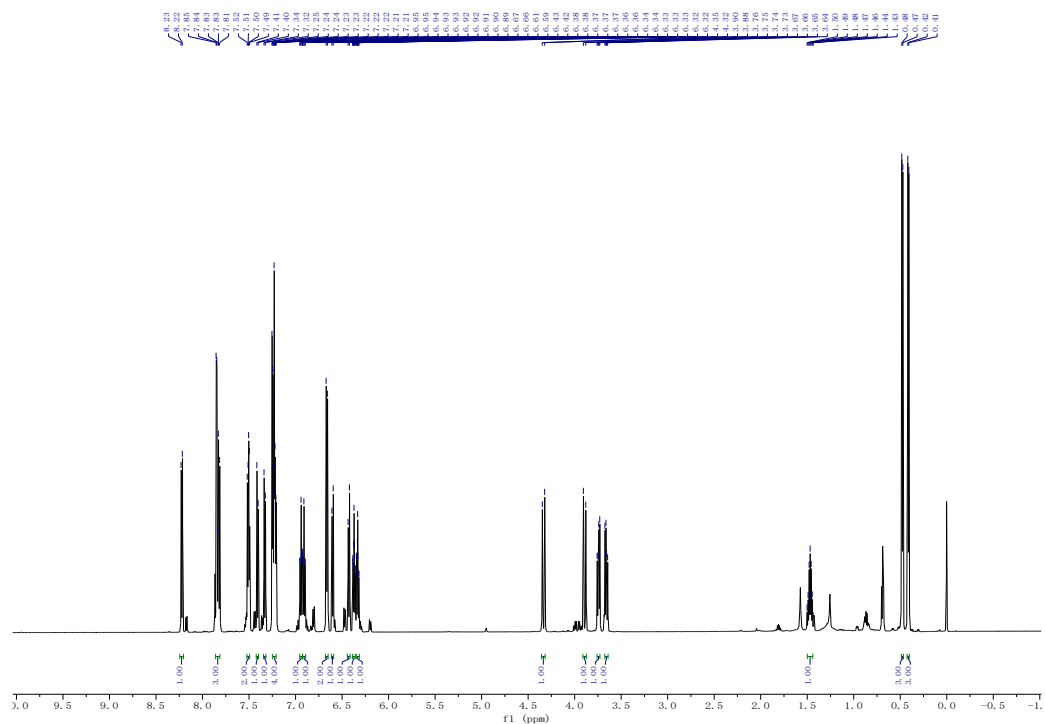
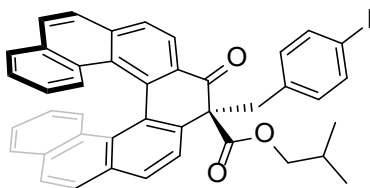




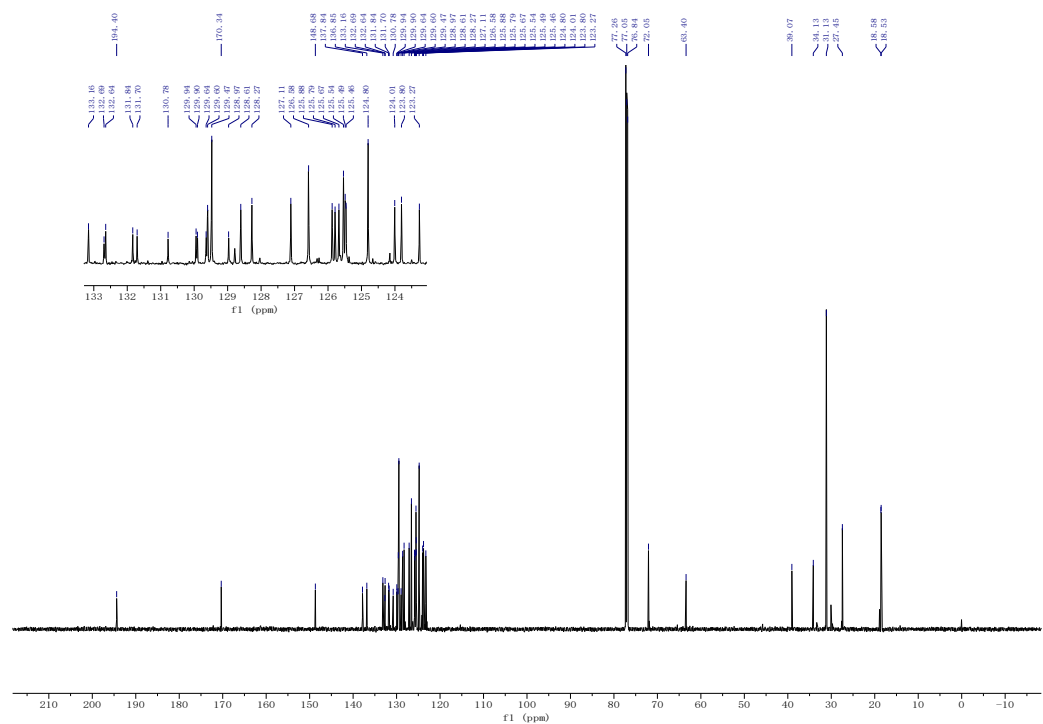
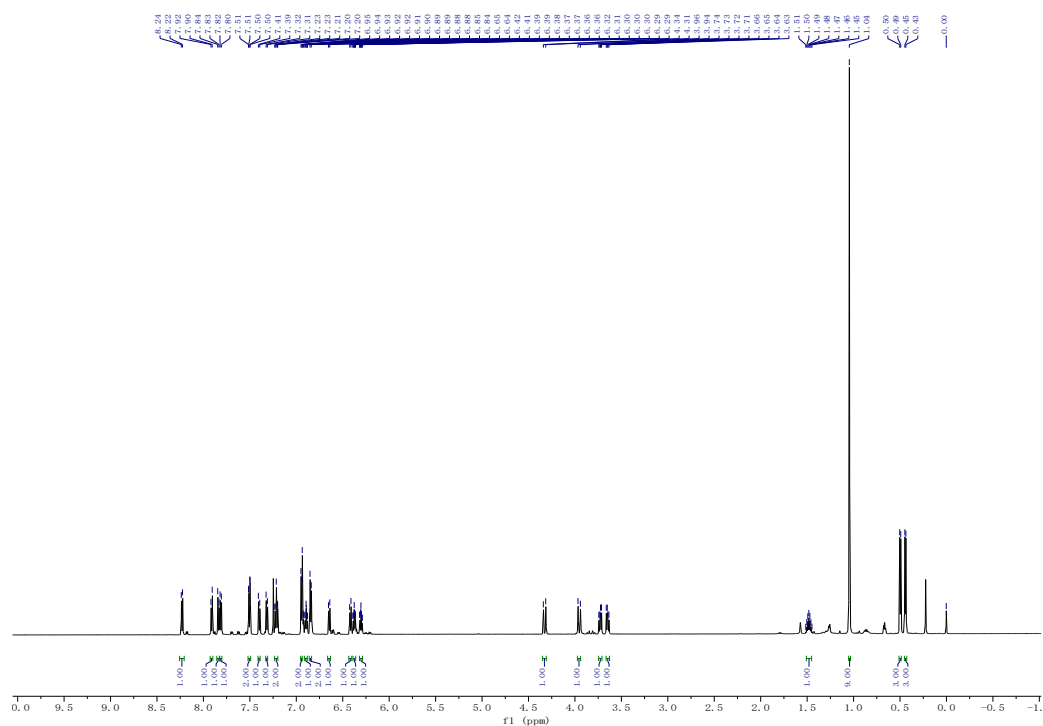
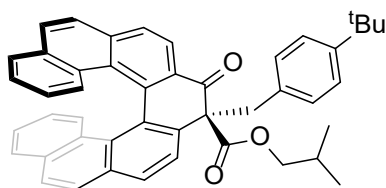
isobutyl (P, S)-9-(4-bromobenzyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D5)



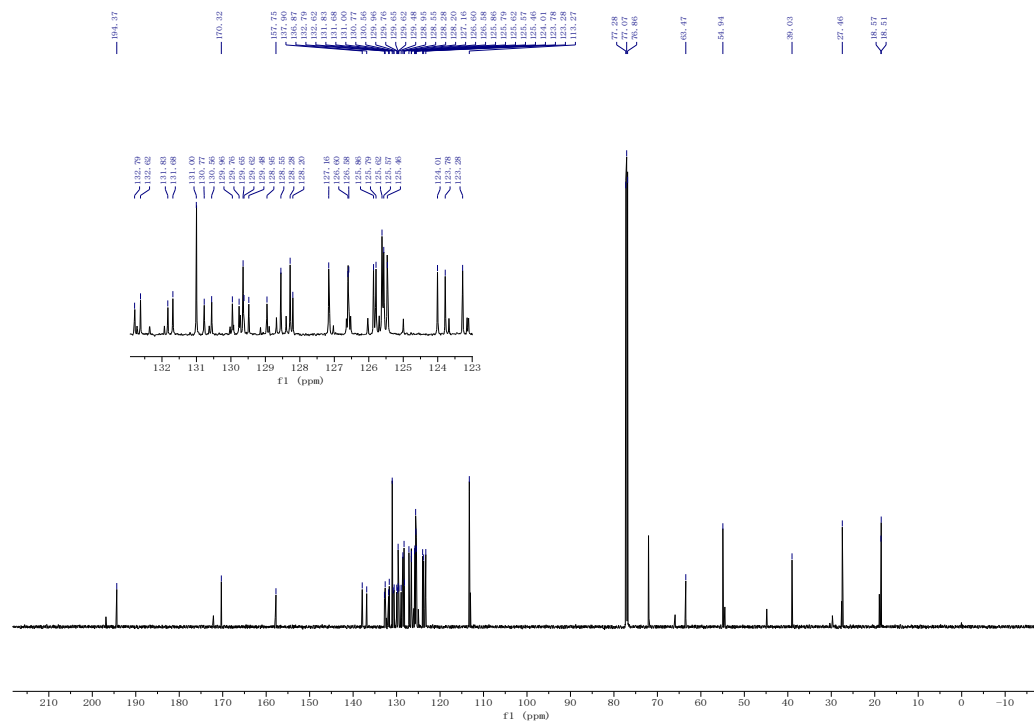
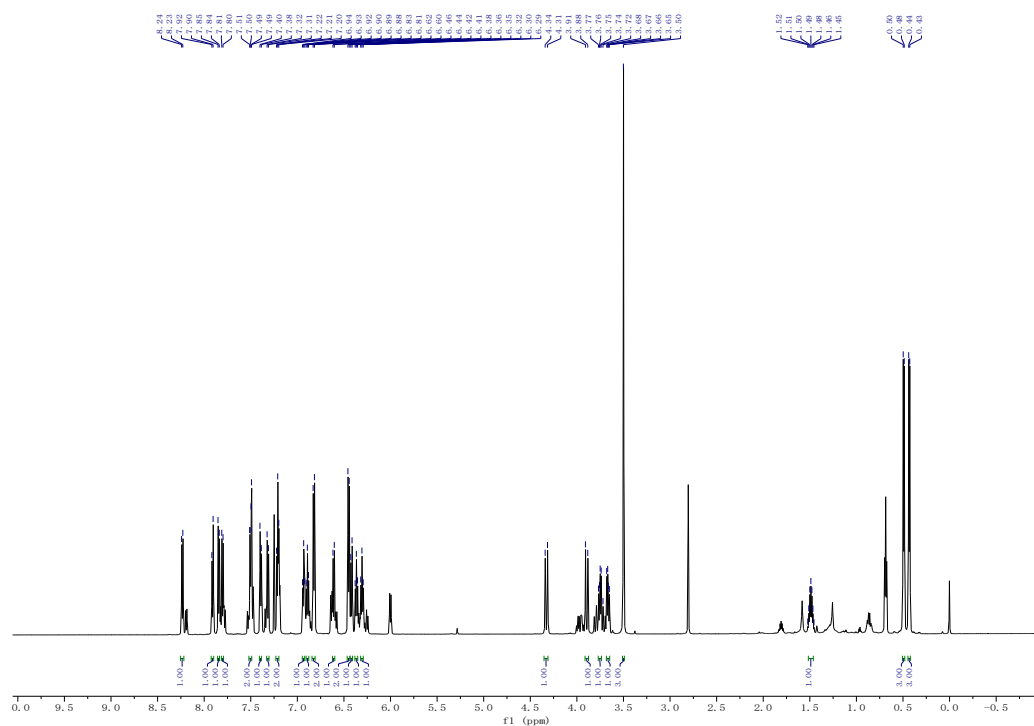
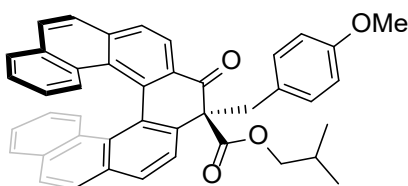
isobutyl (*P, S*)-9-(4-iodobenzyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D6)



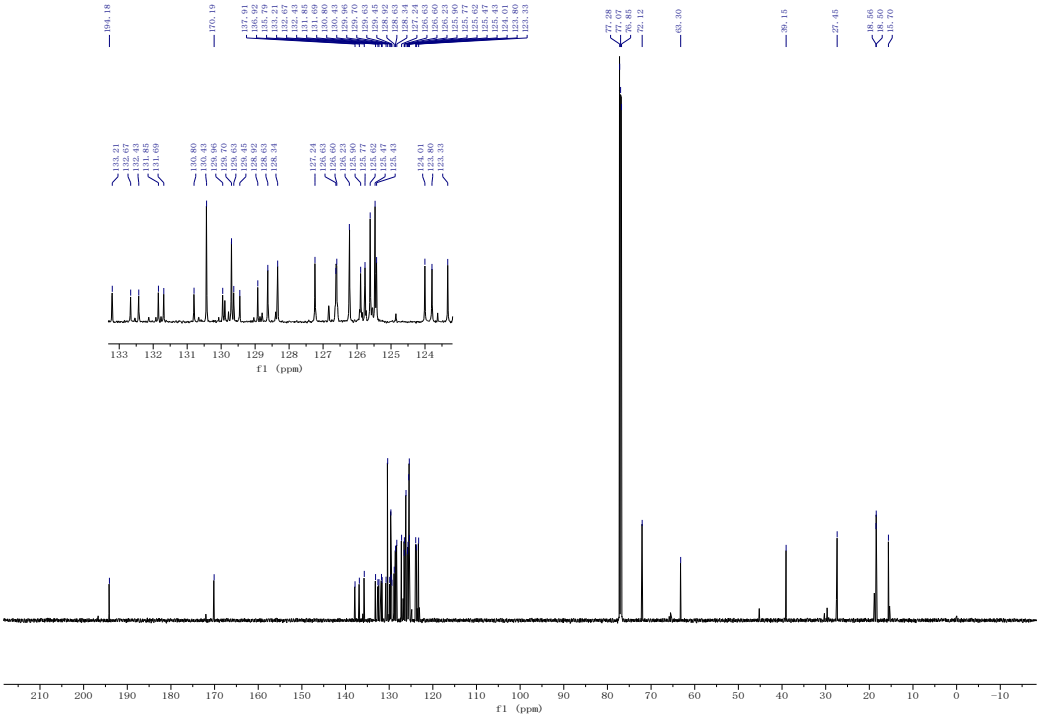
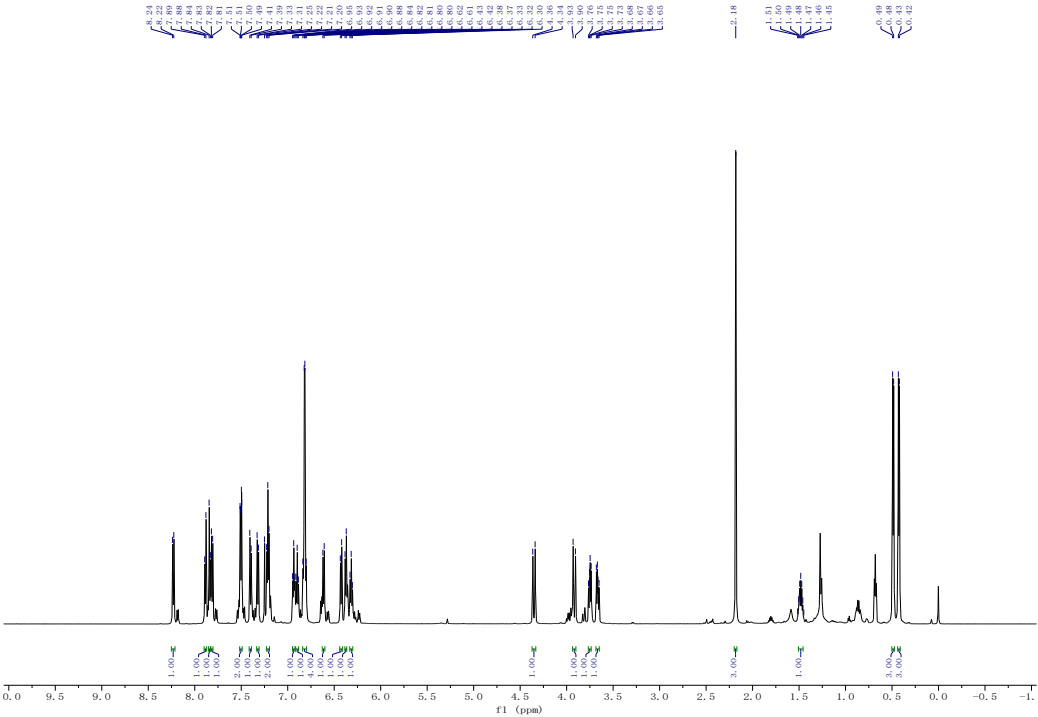
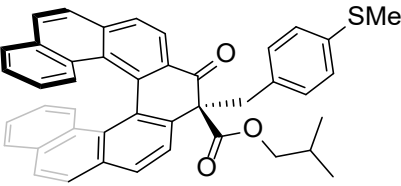
isobutyl (*P*, *S*)-9-(4-(*tert*-butyl)benzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D7)



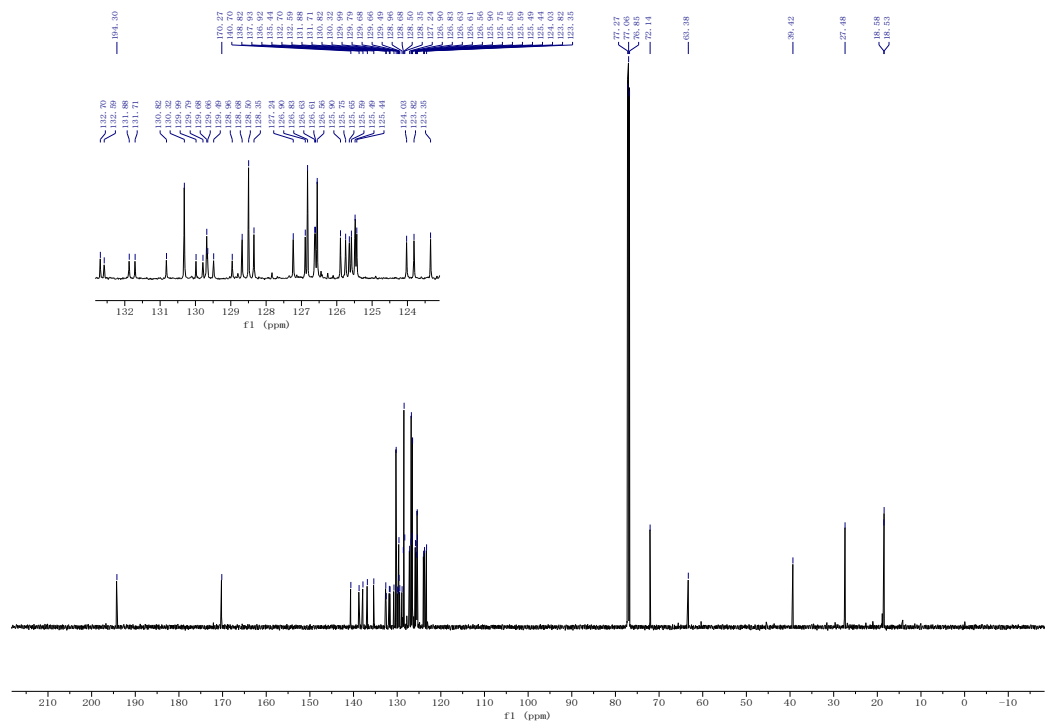
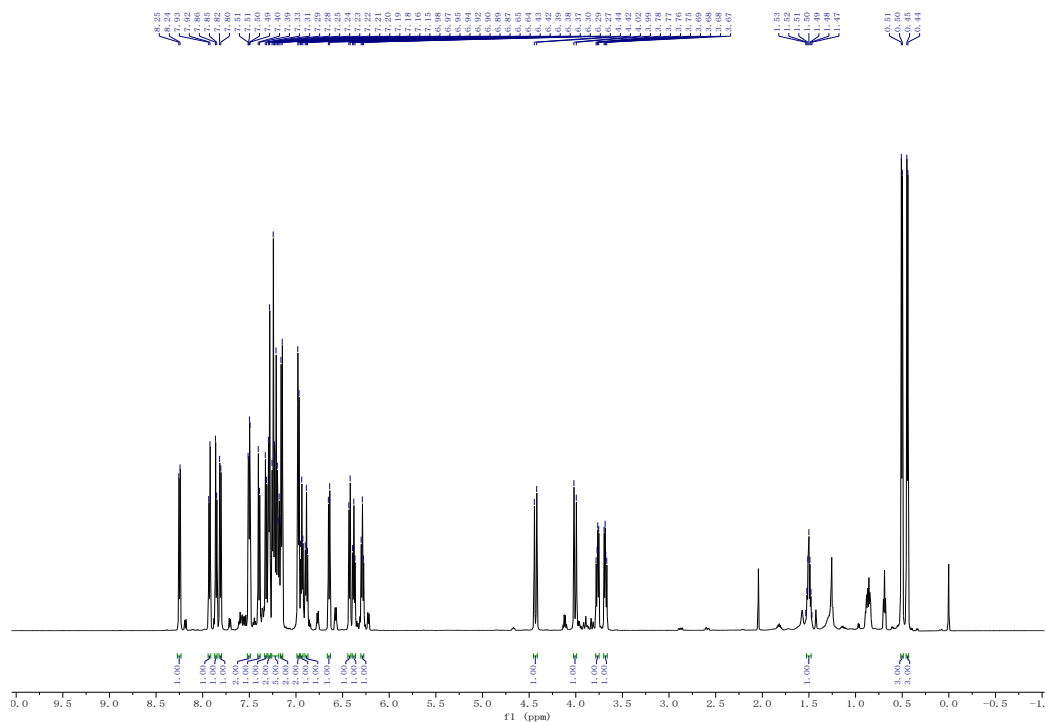
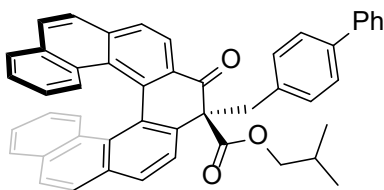
isobutyl (*P*, *S*)-9-(4-methoxybenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D8)



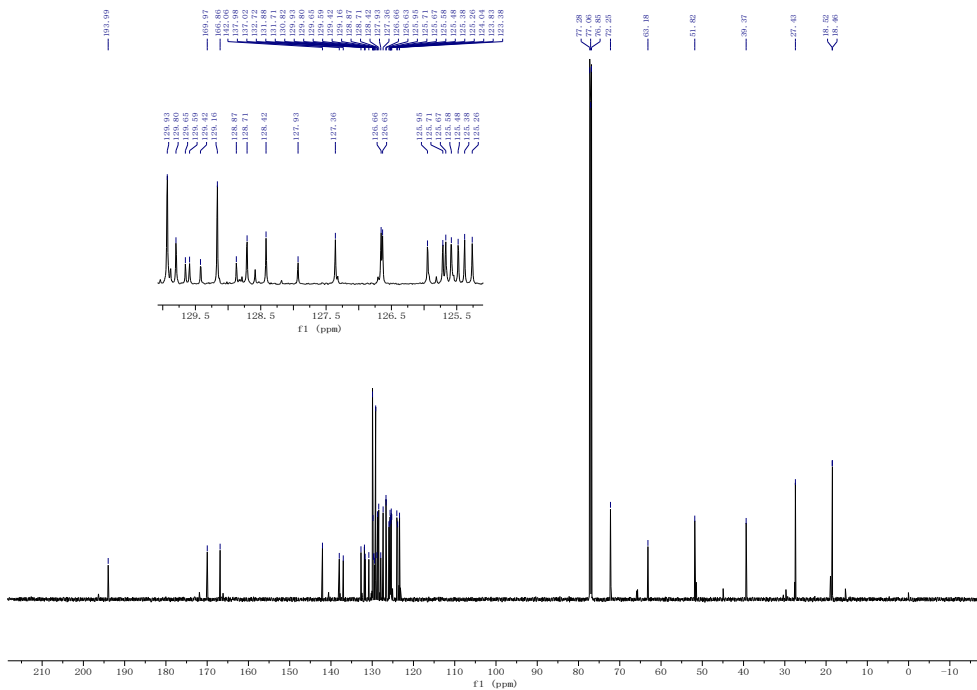
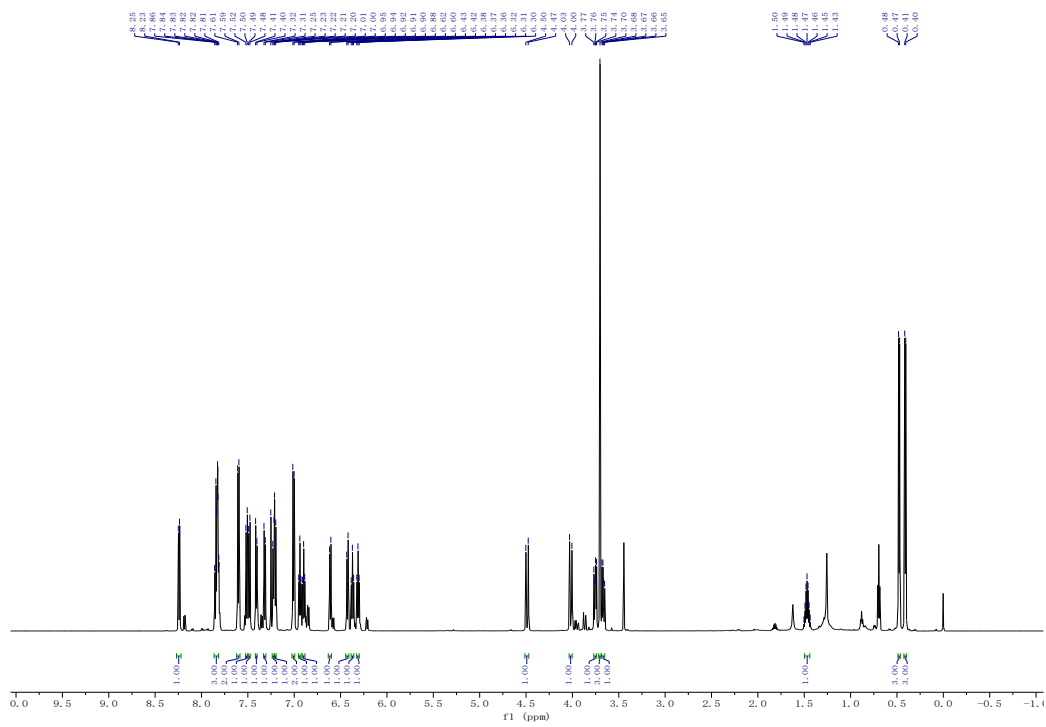
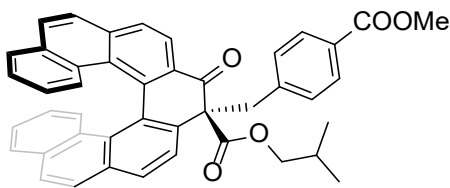
isobutyl (*P,S*)-9-(4-(methylthio)benzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D9)



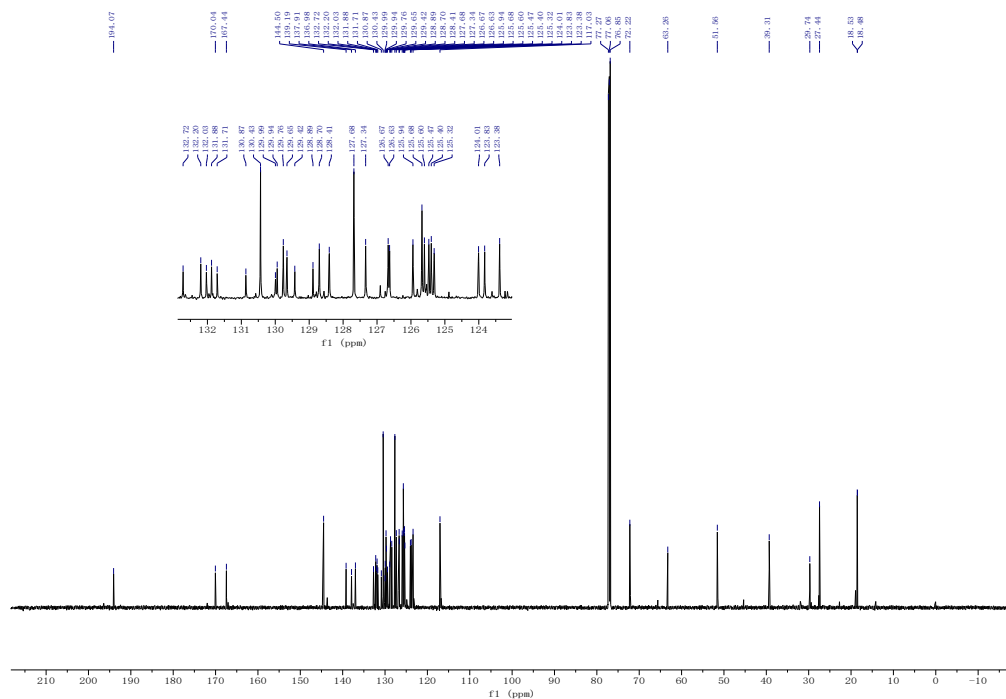
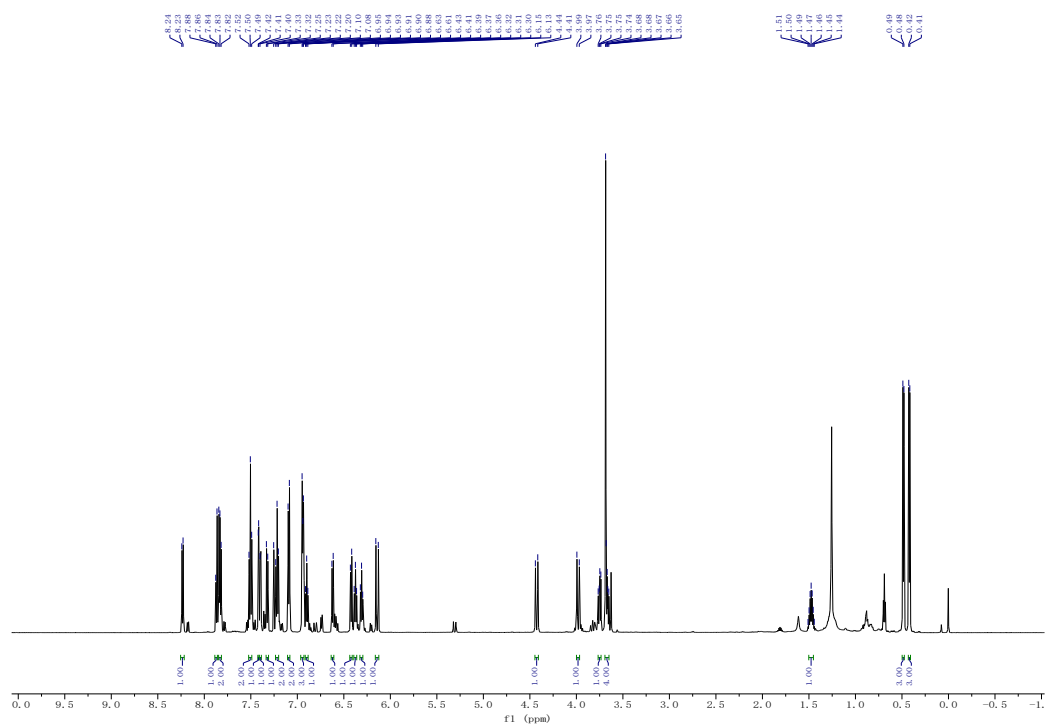
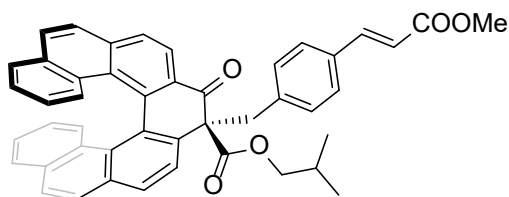
isobutyl (*P,S*)-9-(4-phenylbenzyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D10)



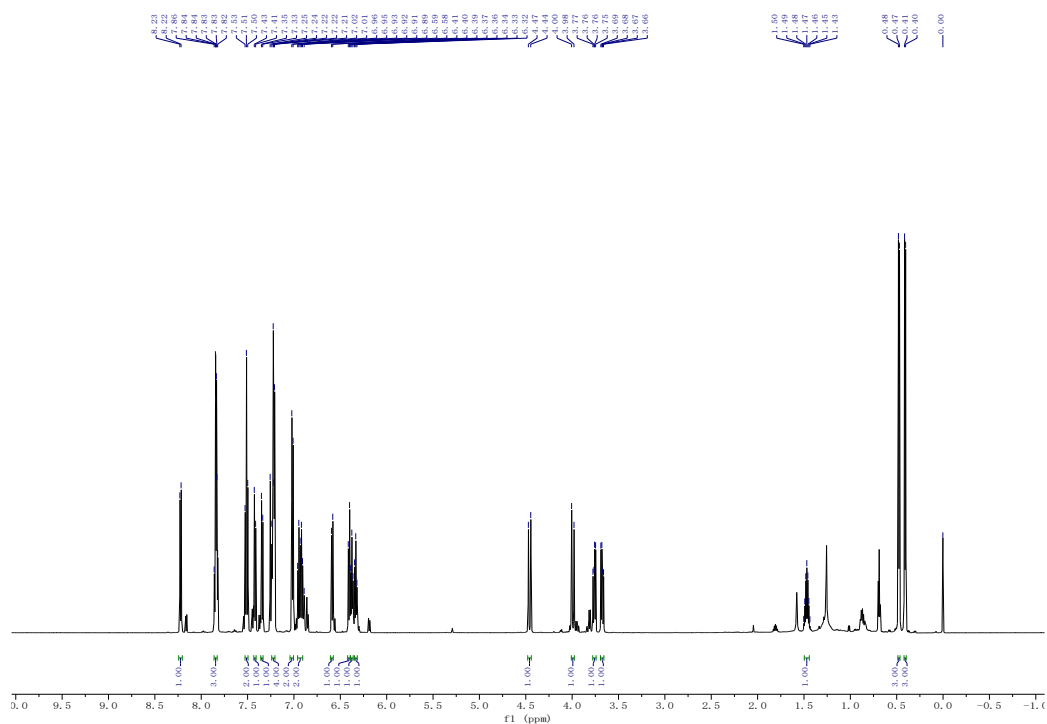
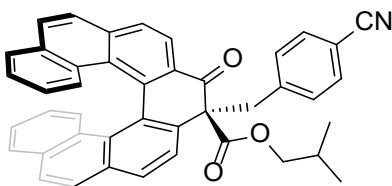
isobutyl (*P,S*)-9-(4-methoxycarbonylbenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D11)



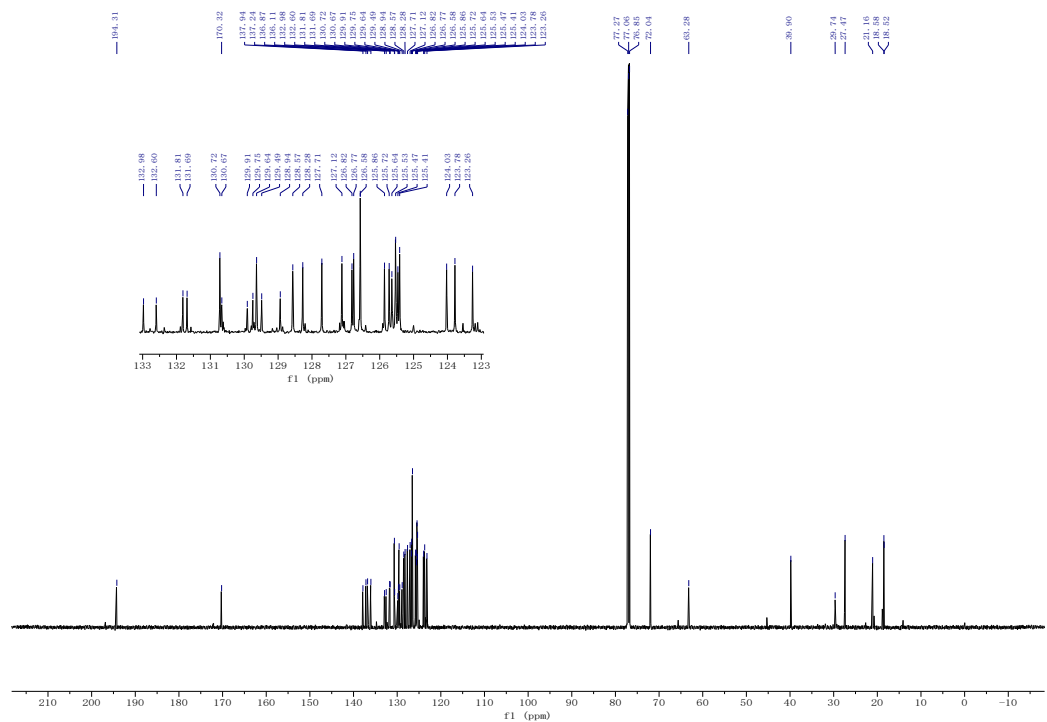
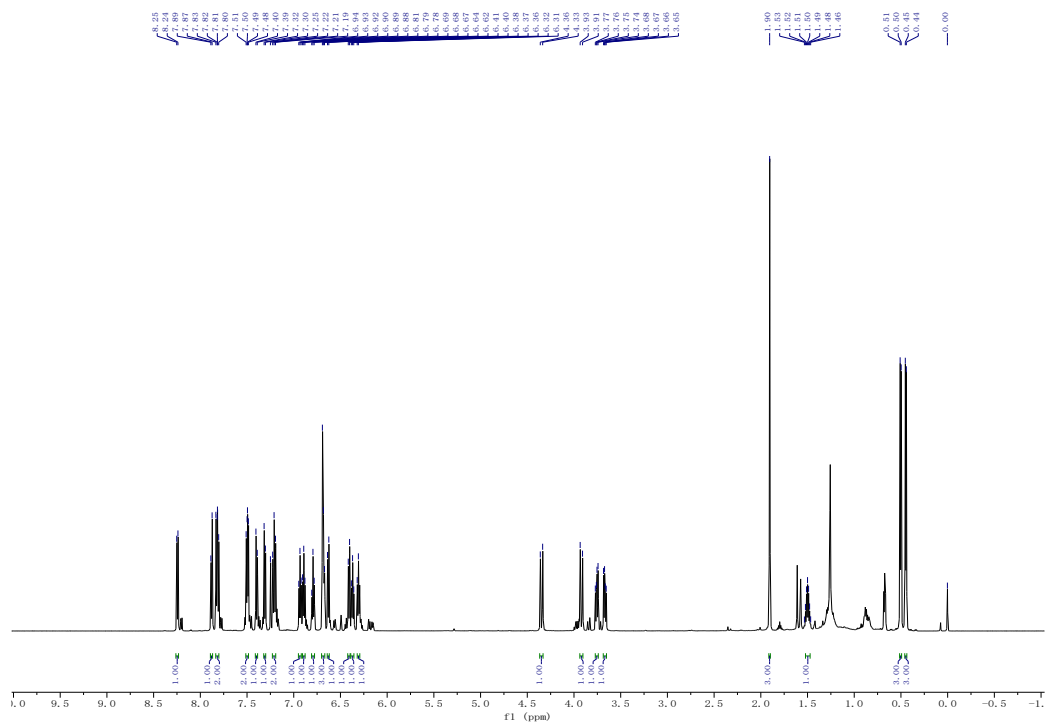
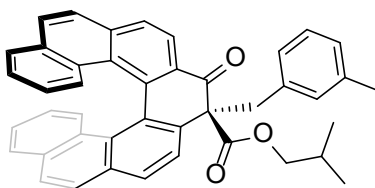
isobutyl (*P, S, E*)-9-(4- (3-methoxy-3-oxoprop-1-en-1-yl)benzyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D12)



isobutyl (*P,S*)-9-(4-cyanobenzyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D13)



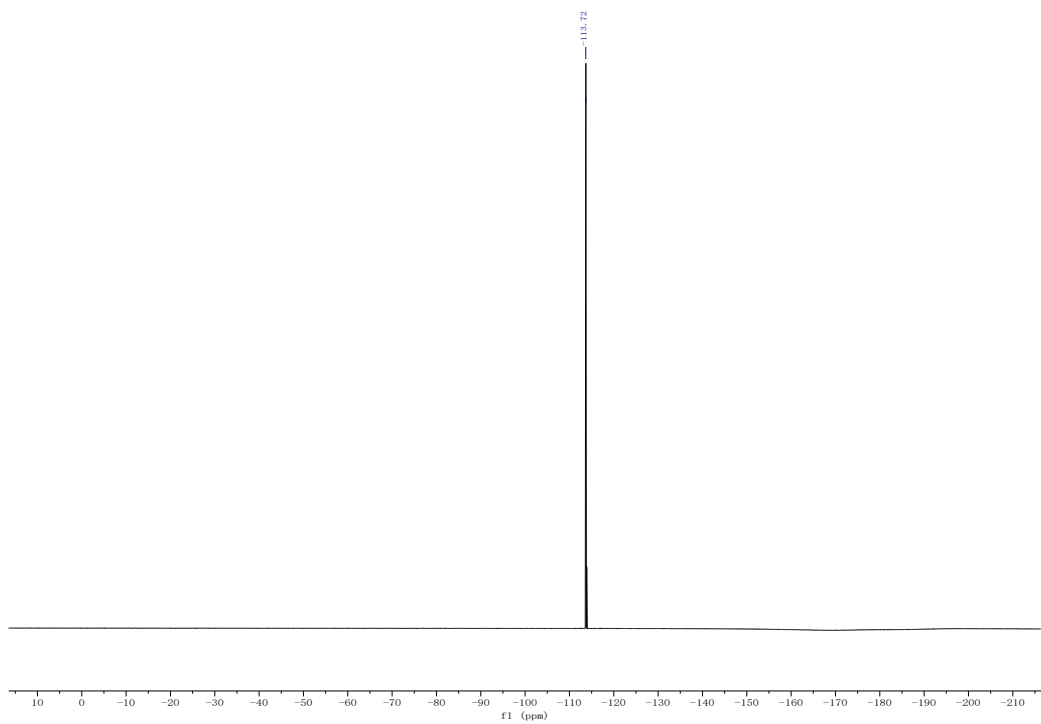
isobutyl (*P,S*)-9-(3-methylbenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D14)



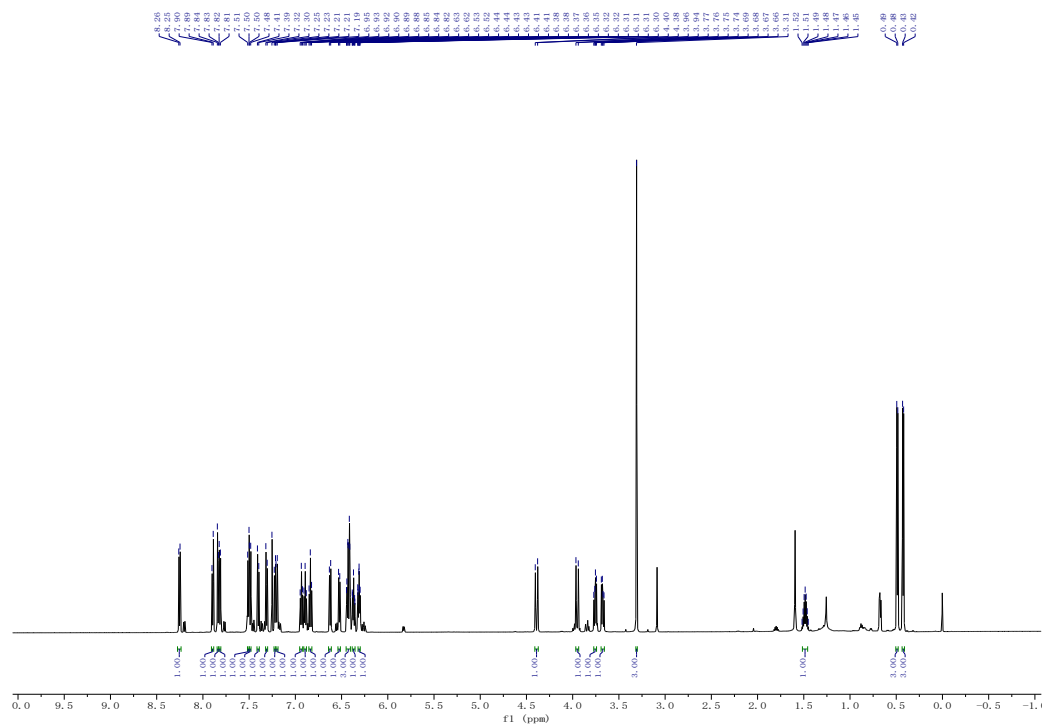
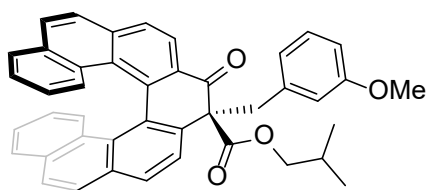
The chemical structure of compound 10 is shown at the top. It is a complex polycyclic molecule featuring a central fluorene-like core. The core is substituted with a 4-fluorophenyl group and an isopropoxy group. The structure is drawn with stereochemistry indicating a specific enantiomer.

The ¹H NMR spectrum (top) is recorded in CDCl₃. The x-axis represents the chemical shift in ppm, ranging from -1 to 10.0. The spectrum shows several multiplets in the aromatic region (6.5-8.5 ppm) and a cluster of peaks in the aliphatic region (3.5-4.5 ppm). Integration values are provided below the peaks.

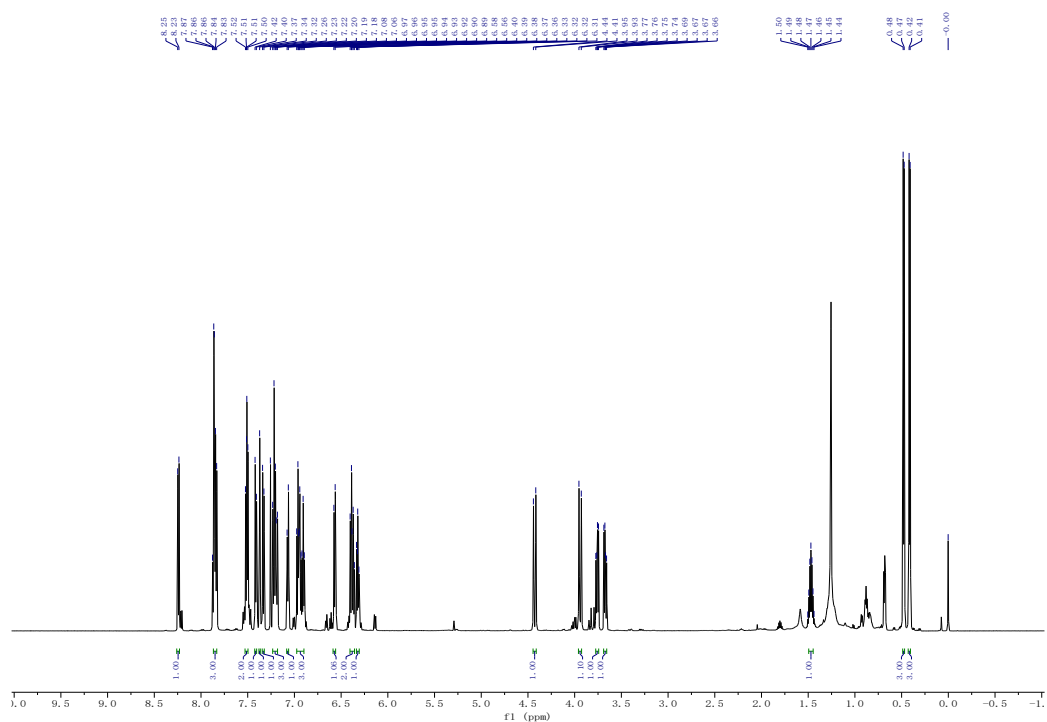
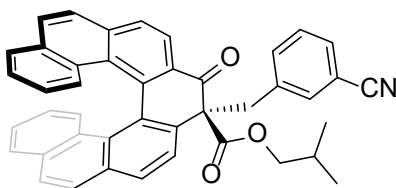
The ¹³C NMR spectrum (bottom) is recorded in CDCl₃. The x-axis represents the chemical shift in ppm, ranging from -10 to 210. The spectrum shows a large number of peaks in the aromatic region (120-140 ppm) and a few peaks in the aliphatic region (30-40 ppm). A solvent triplet for CDCl₃ is visible at 77.0 ppm.



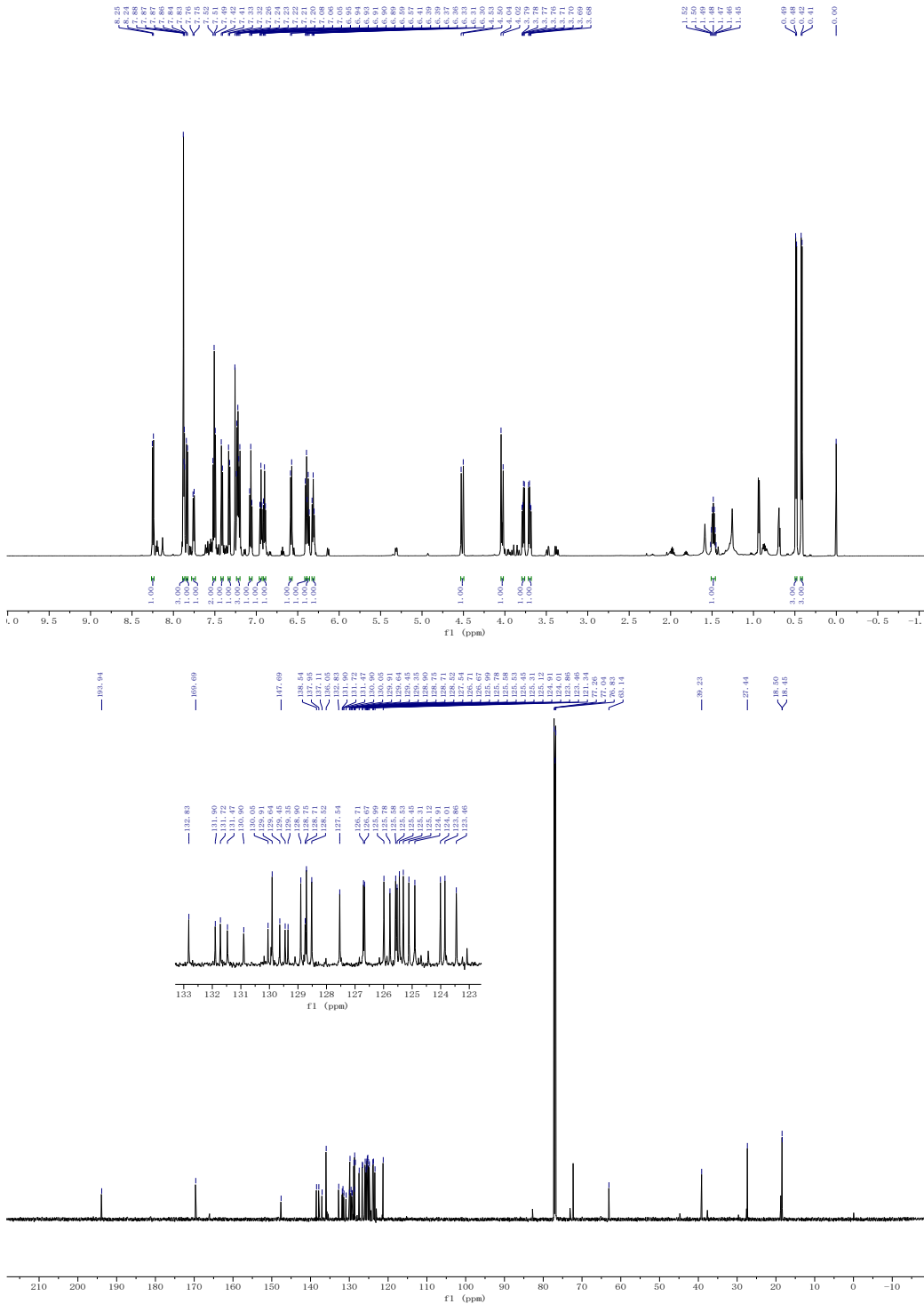
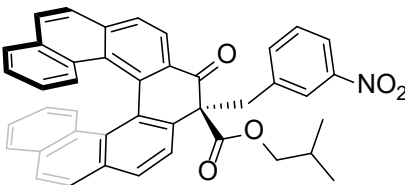
isobutyl (*P, S*)-9-(3-methoxybenzyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D16)



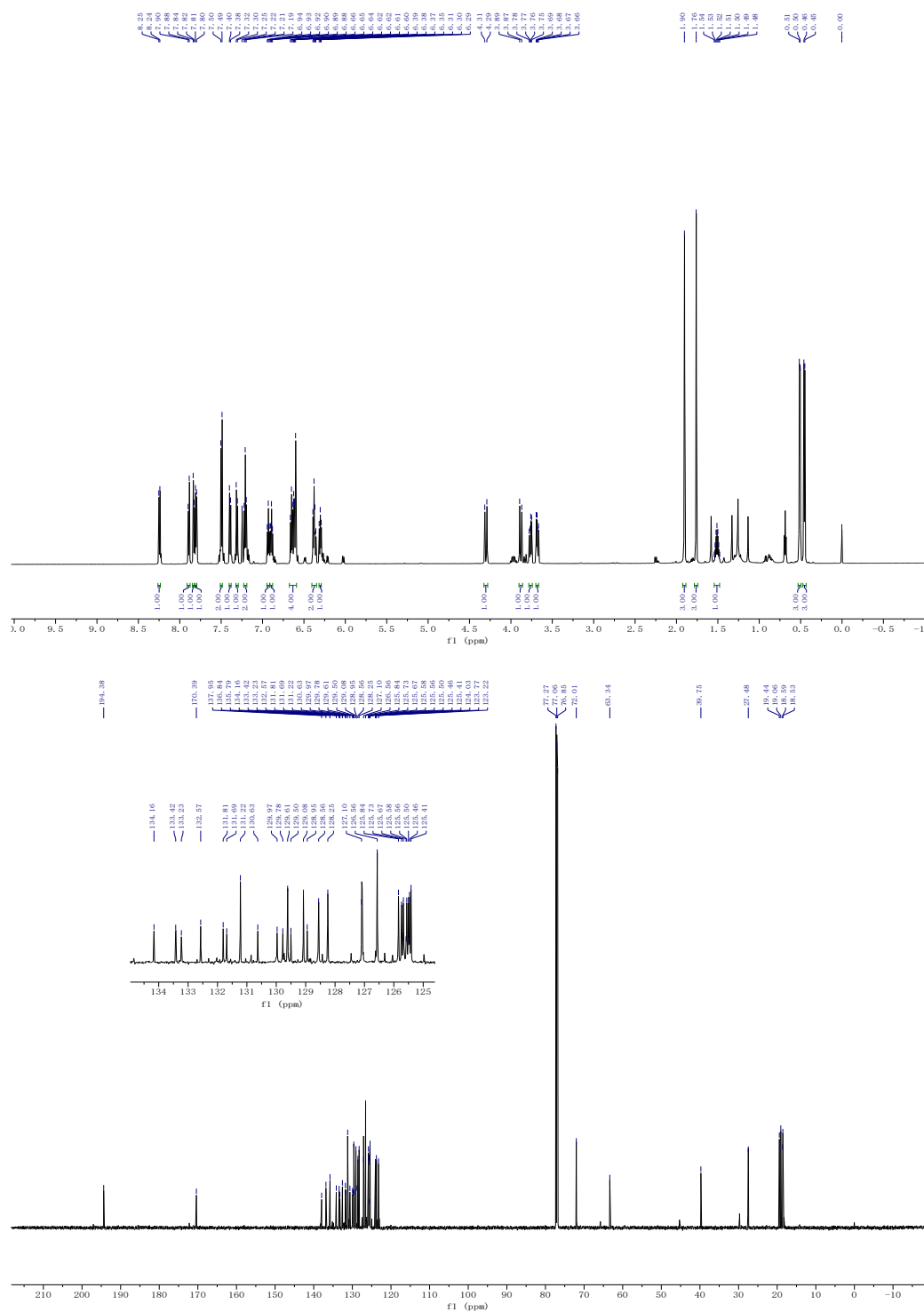
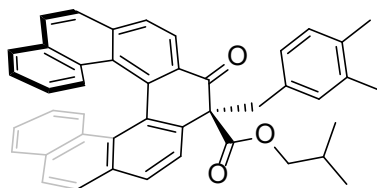
isobutyl (*P*, *S*)-9-(3-cyanobenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D17)



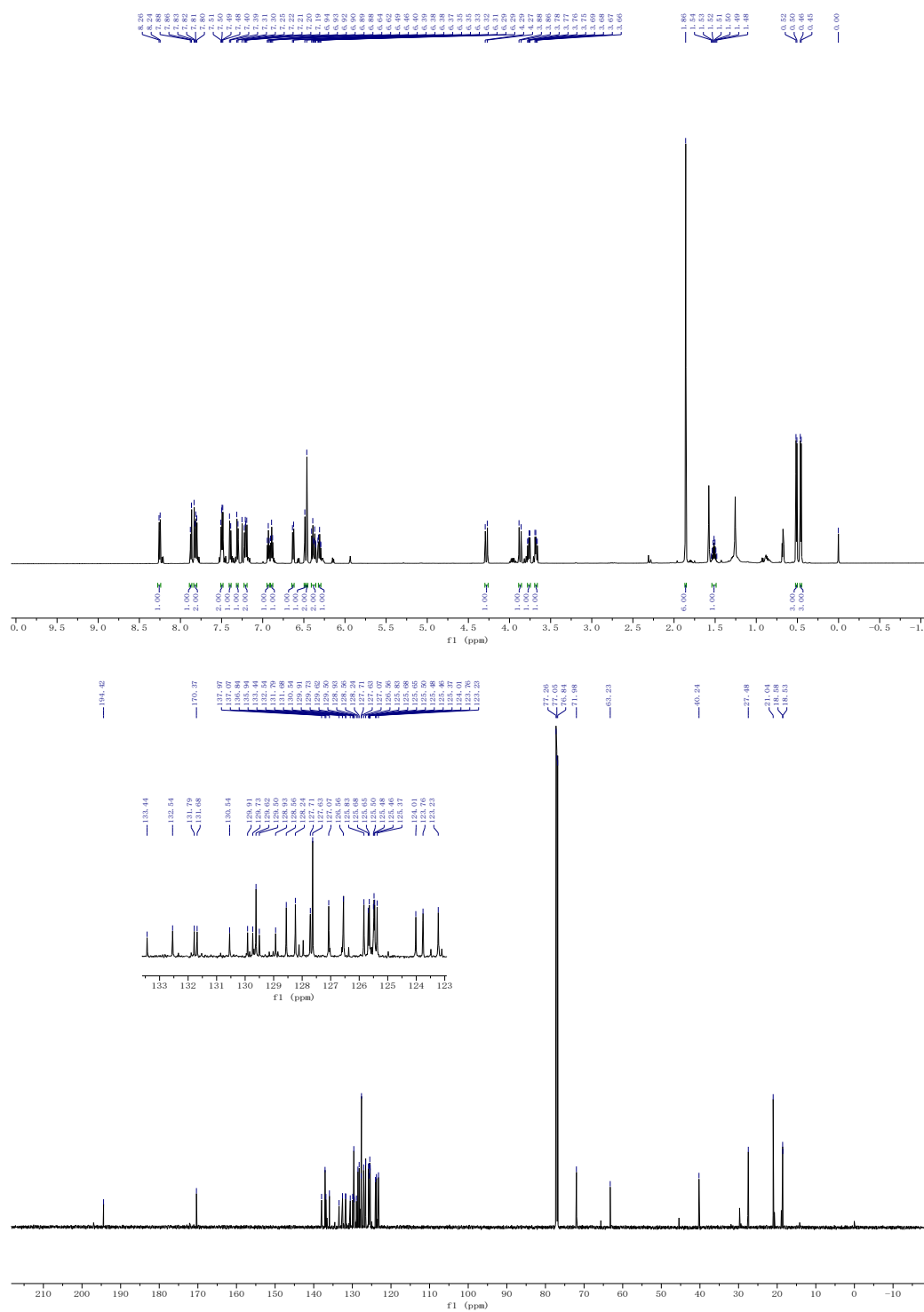
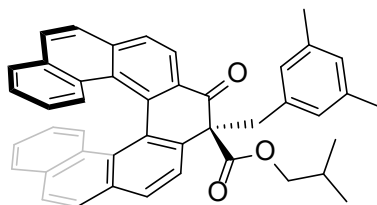
isobutyl (*P,S*)-9-(3-nitrobenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D18)



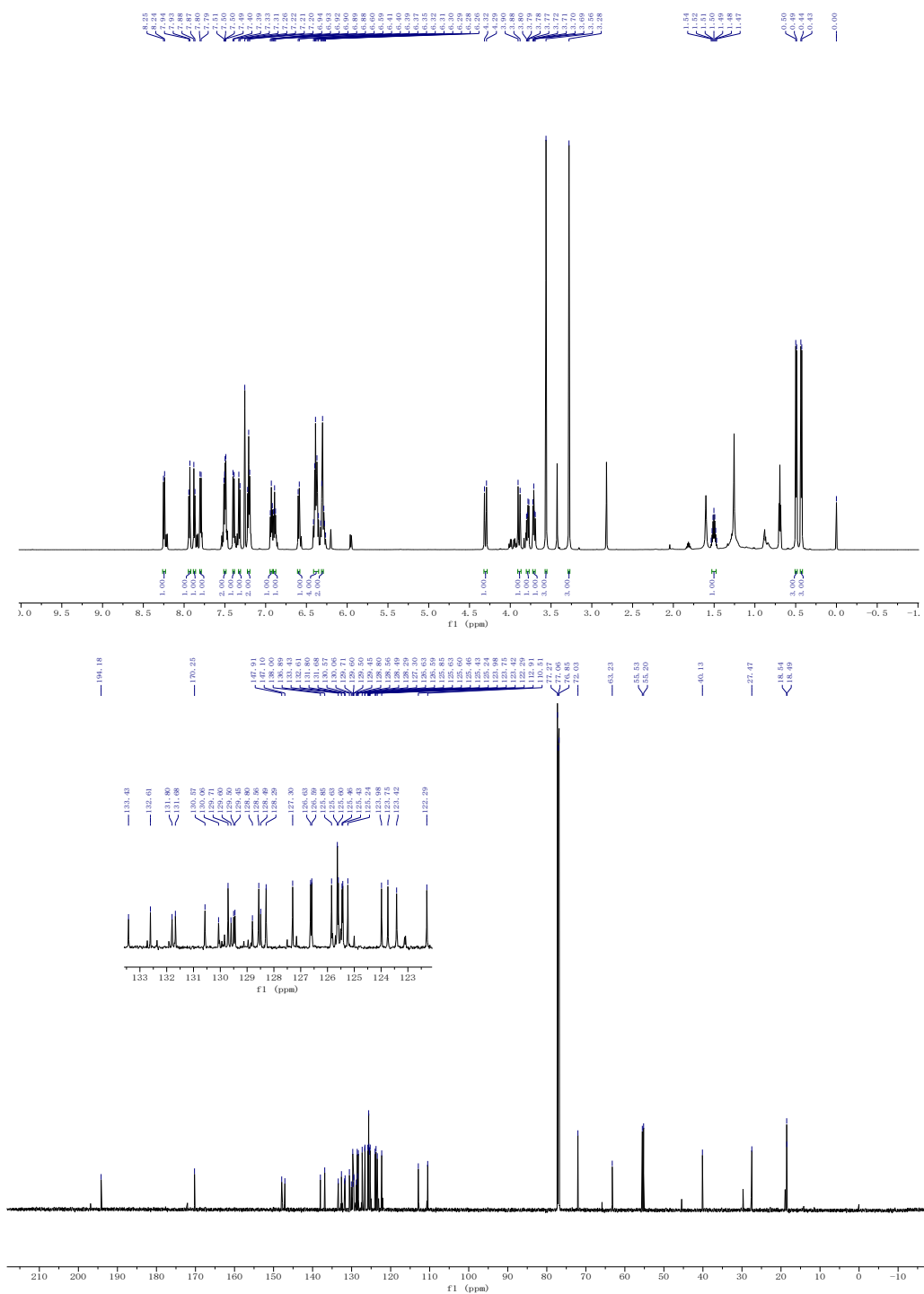
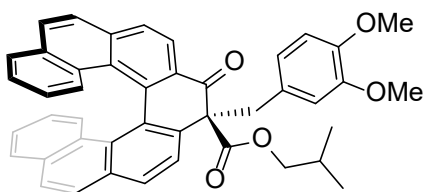
isobutyl (*P*, *S*)-9-(3,4-dimethylbenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D19)



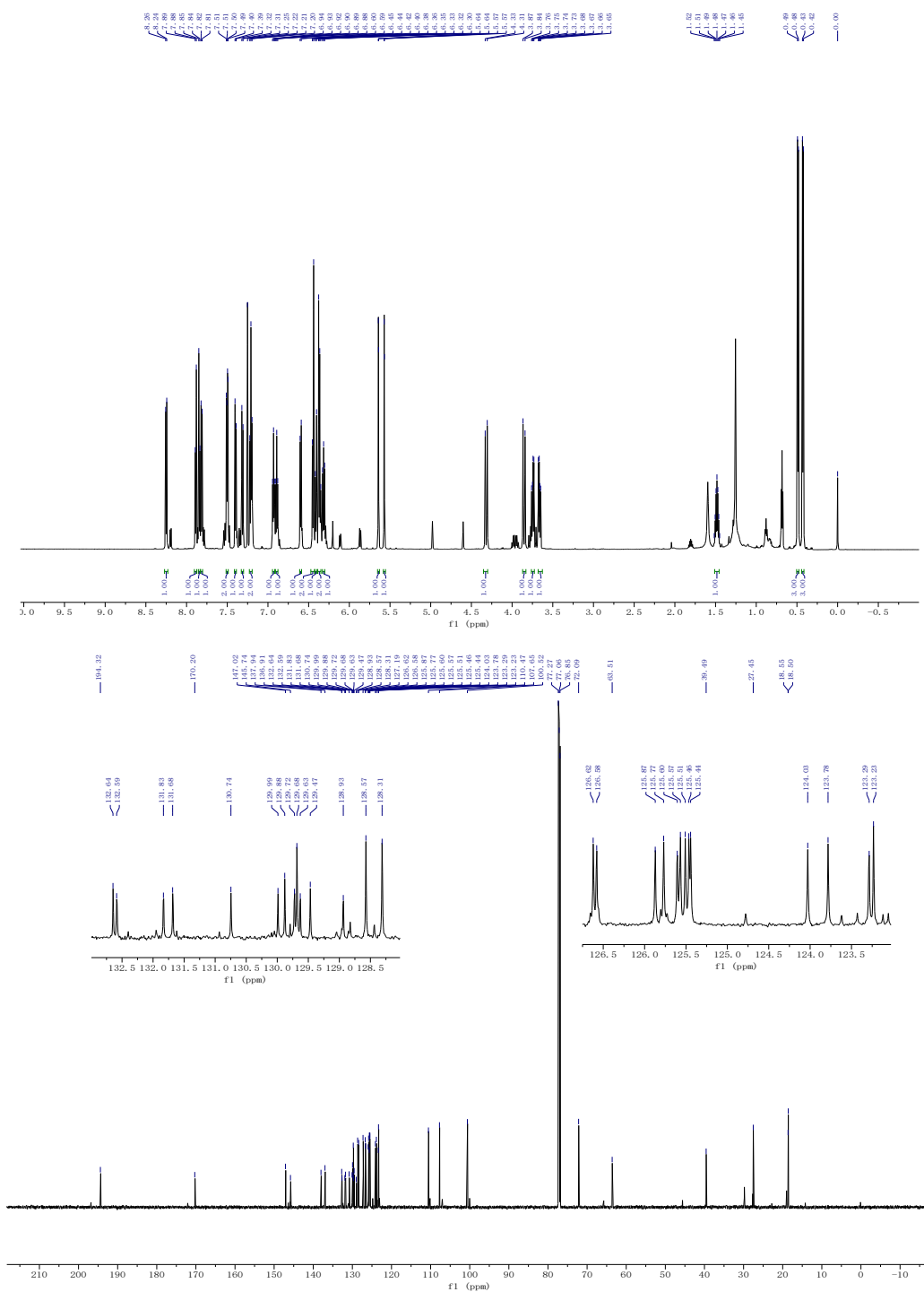
isobutyl (*P*, *S*)-9-(3,5-dimethylbenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D20)

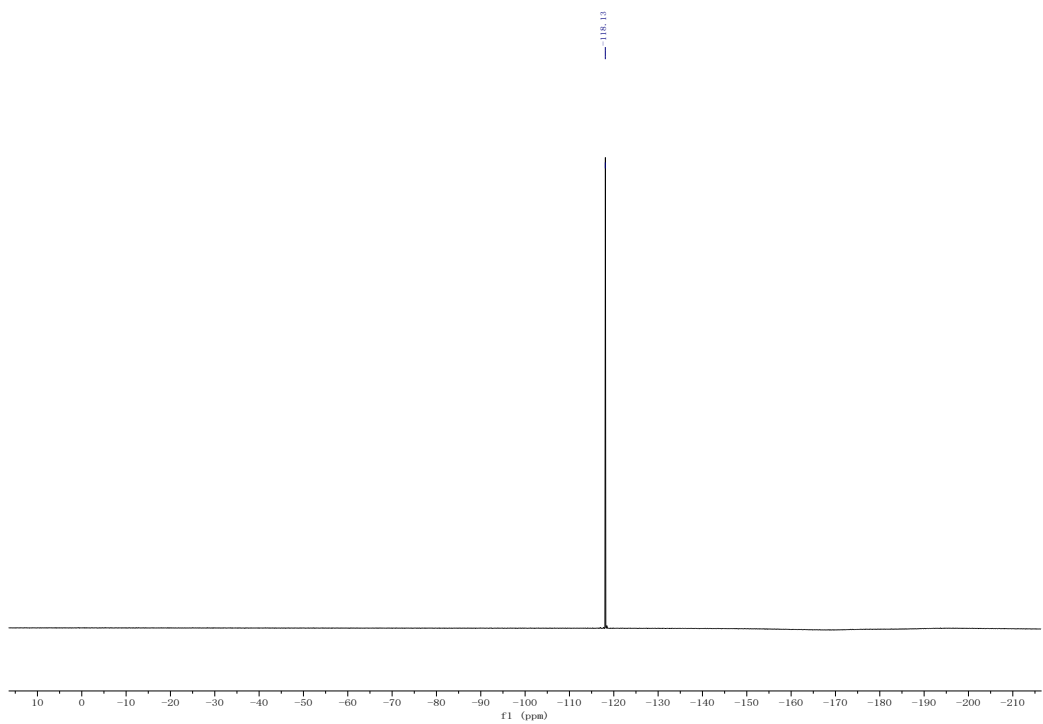


isobutyl (*P*, *S*)-9-(3,4-dimethoxybenzyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D21)

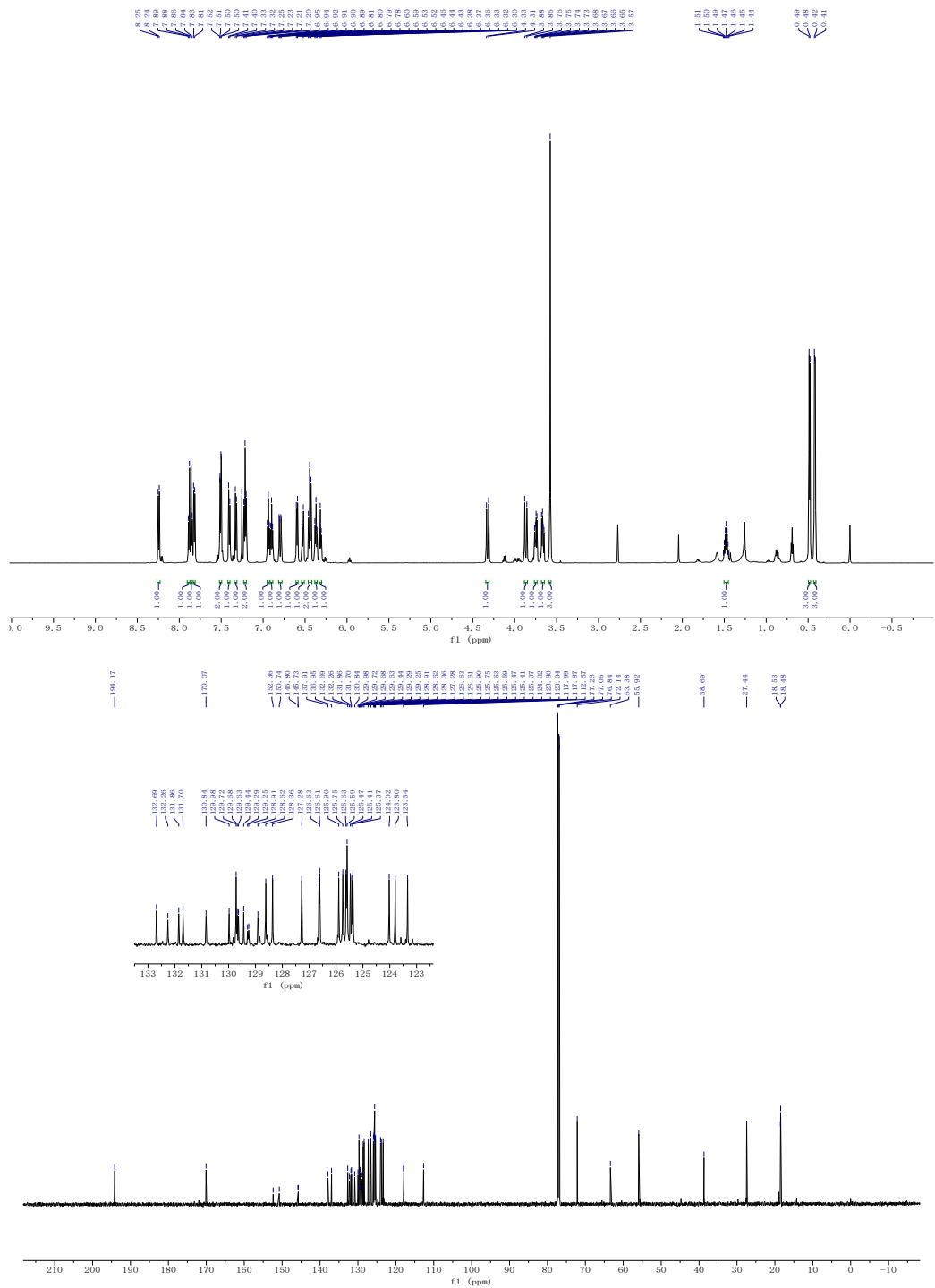
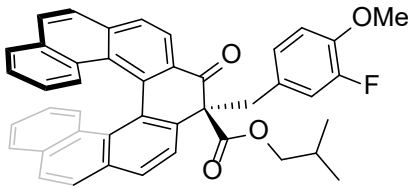


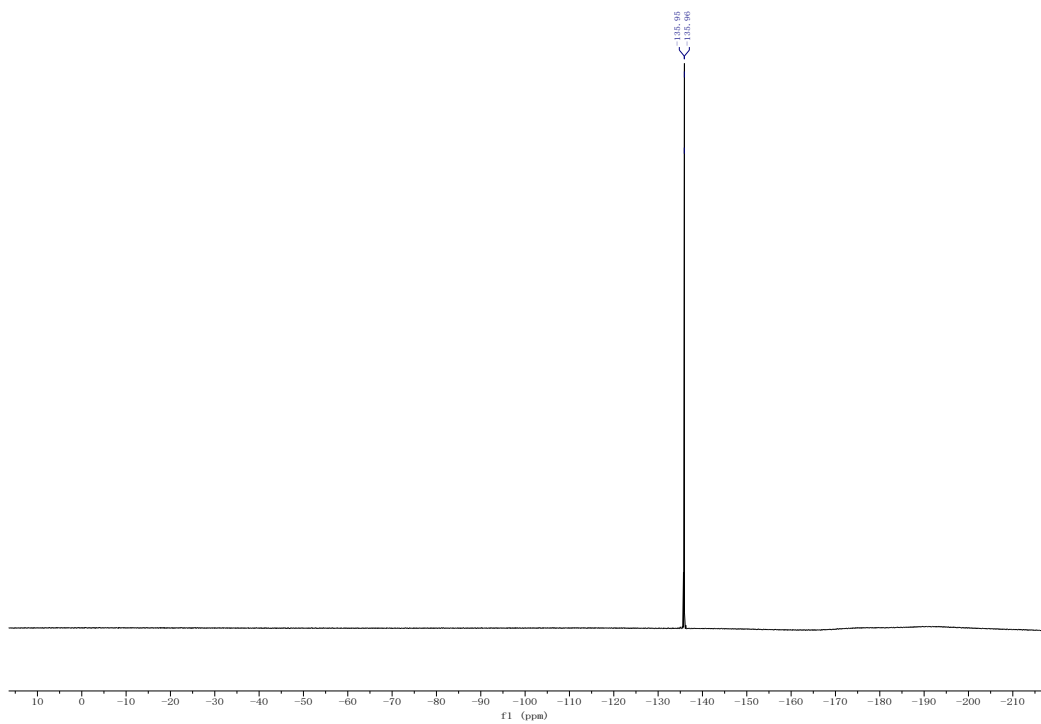
The chemical structure shows a phthalocyanine-like macrocycle with a central nitrogen atom. The macrocycle is substituted with a side chain that includes a benzodioxole ring system and an isopropoxy group. The structure is drawn in a perspective view, with the macrocycle in the foreground and the side chain extending to the right.



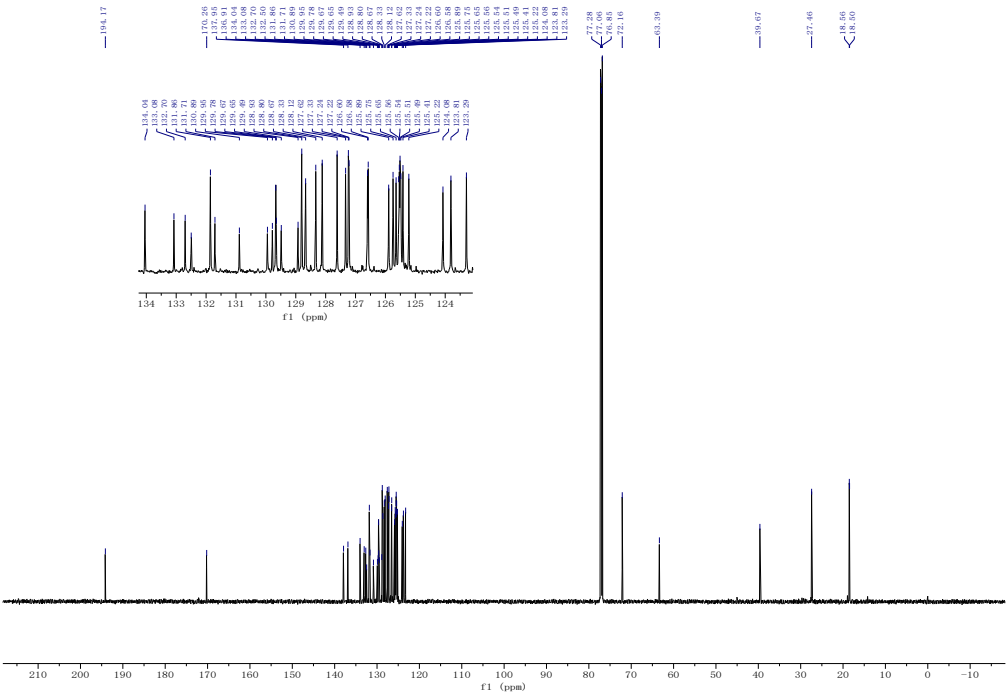
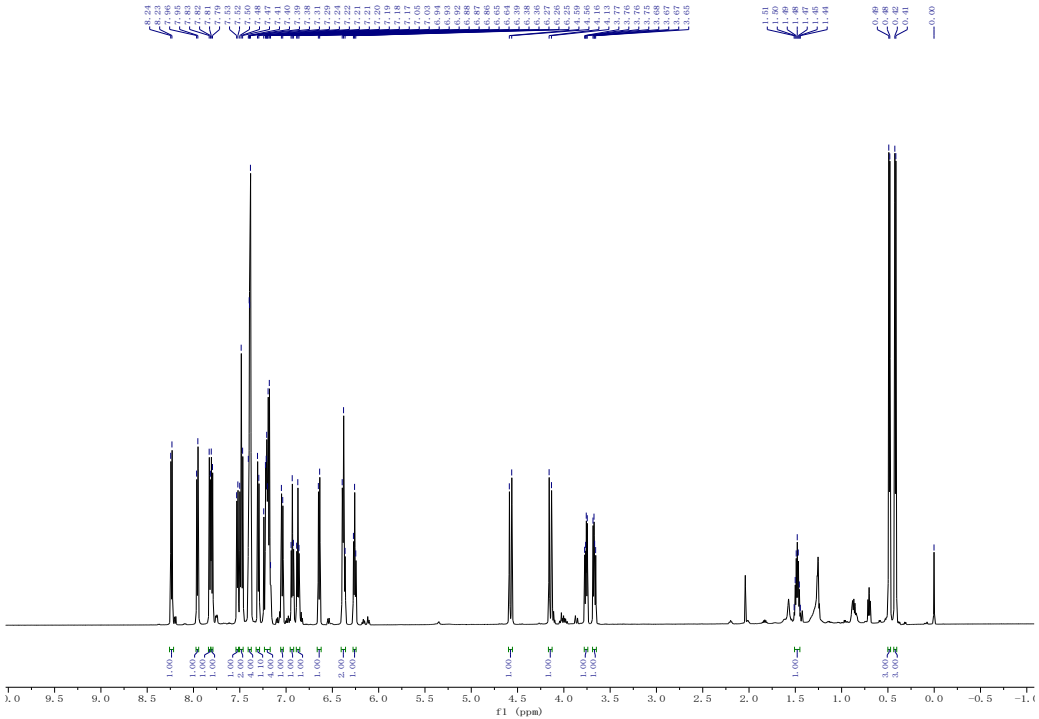
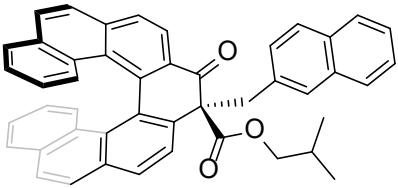


isobutyl (*P,S*)-9-(3-fluoro-4-methoxybenzyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D24)

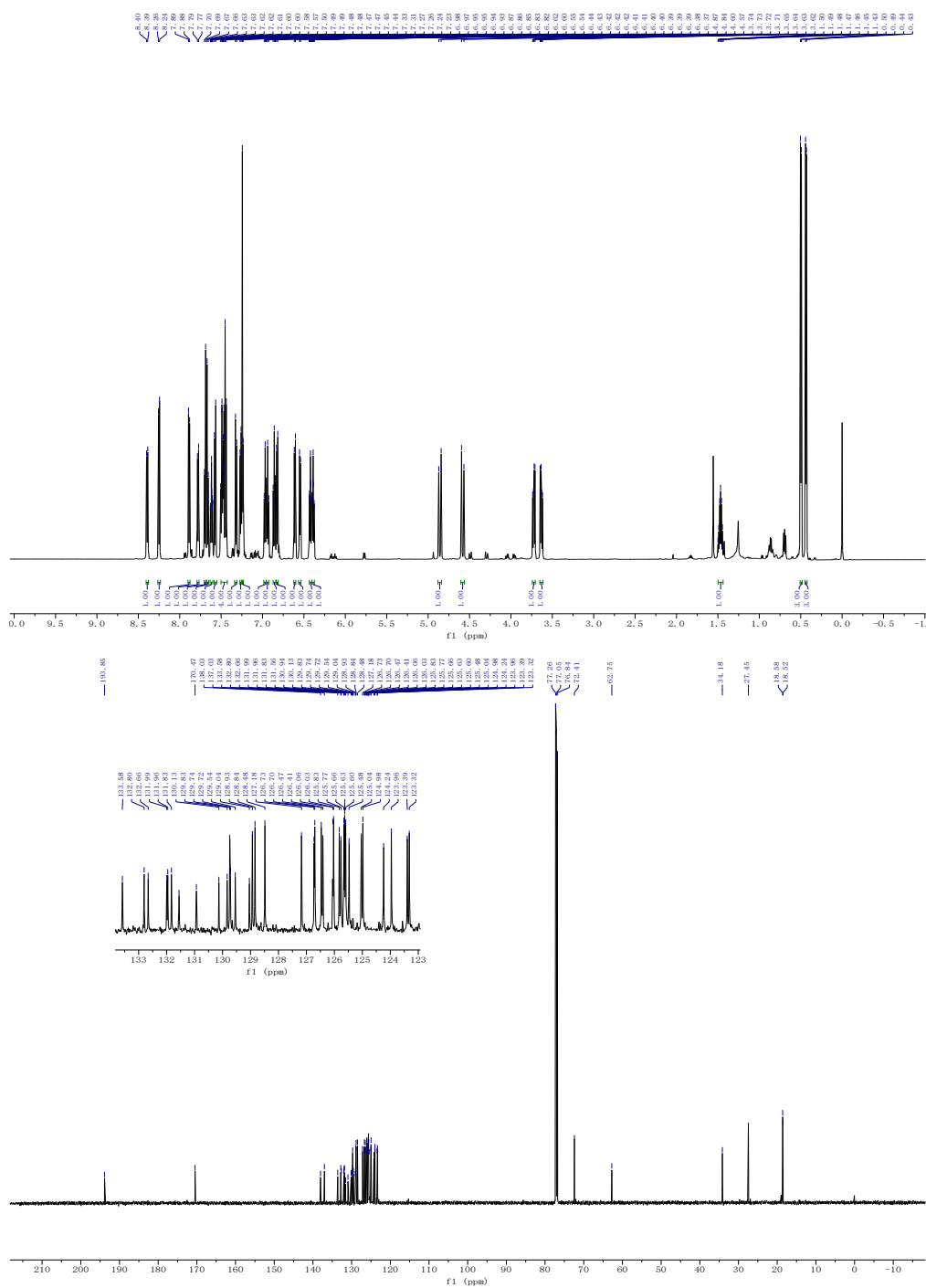
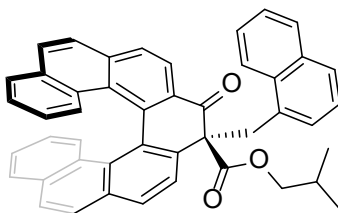




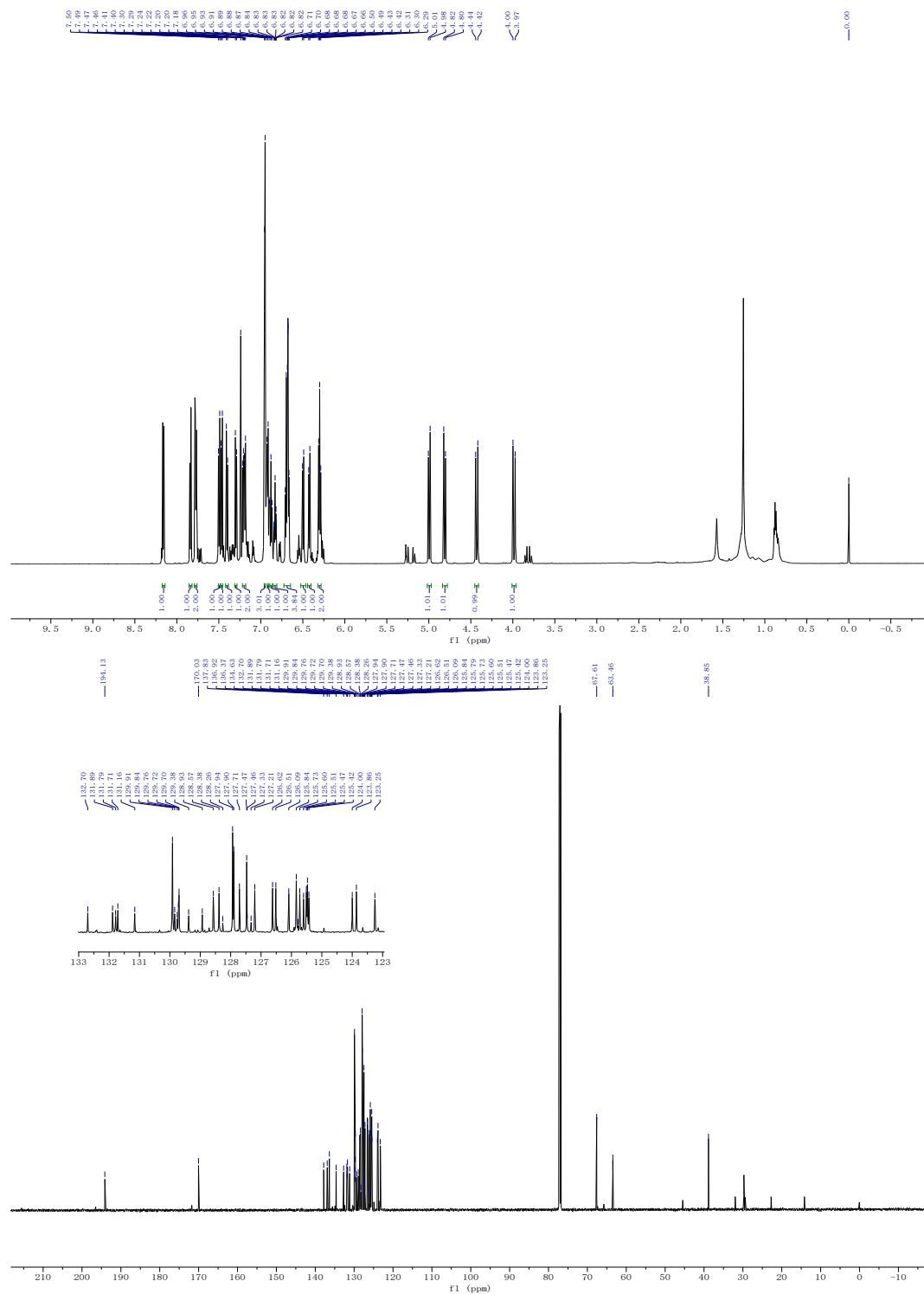
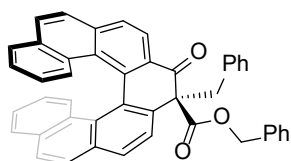
isobutyl (*P,S*)-9-(naphthalen-2-ylmethyl)-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D26)



isobutyl (*P,S*)-9-(naphthalen-1-ylmethyl)-10-oxo-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D27)

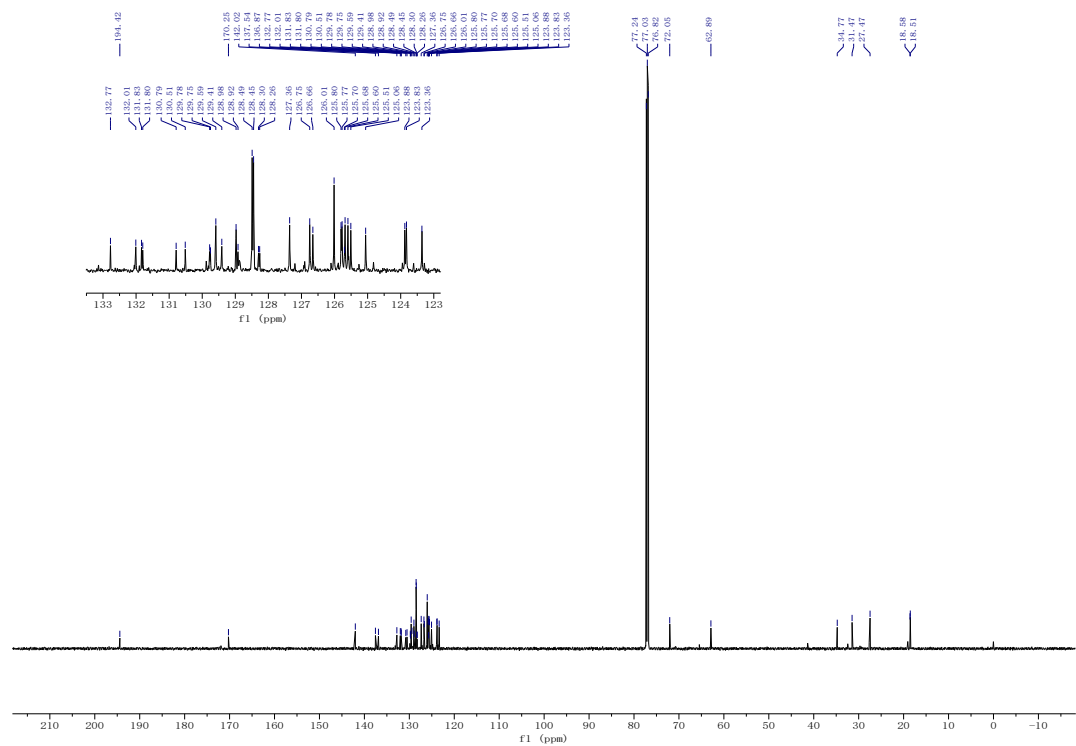
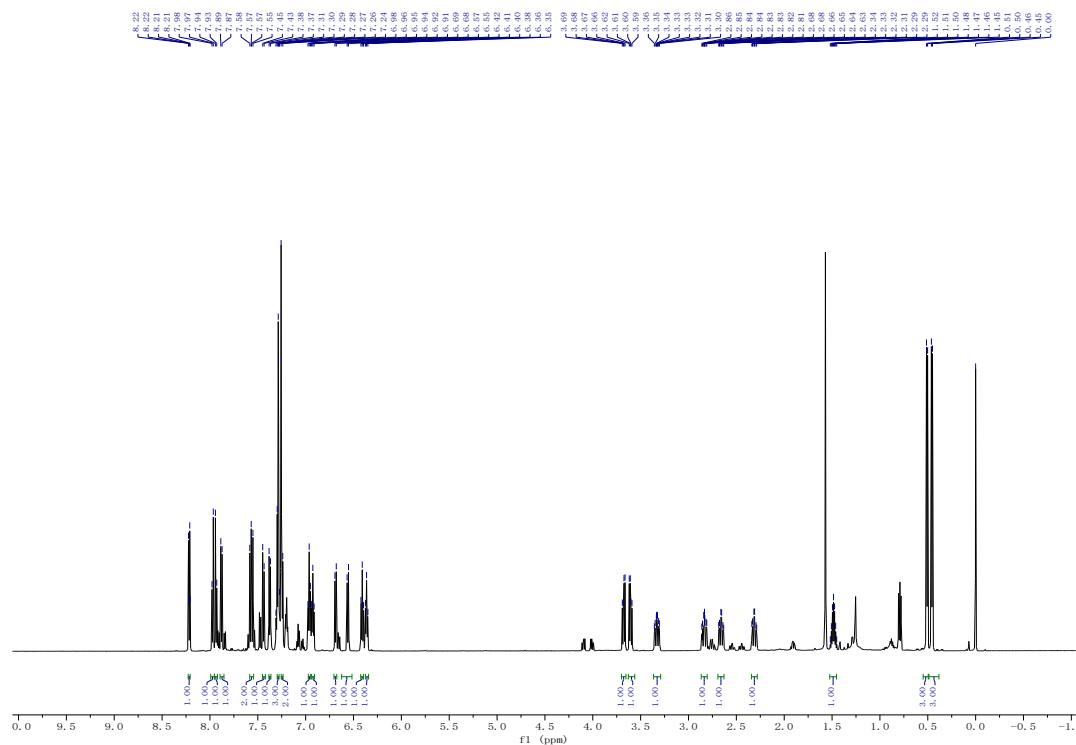
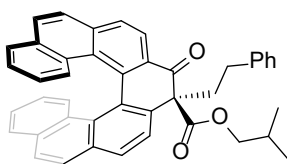


benzyl (*P,S*)-9-benzyl-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate (D29)

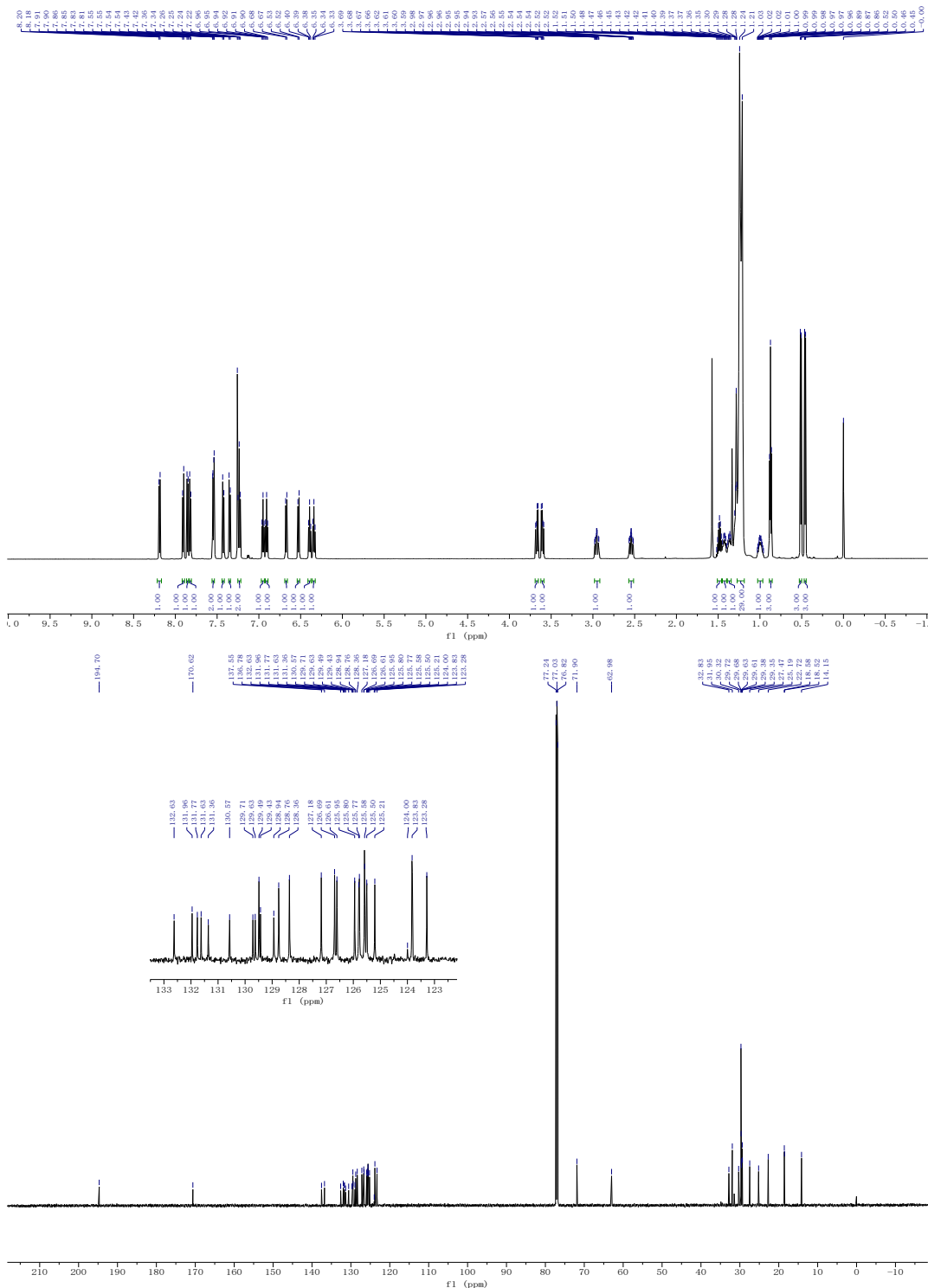
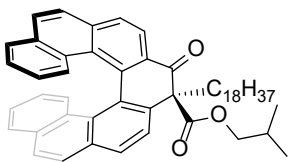


[illegible]

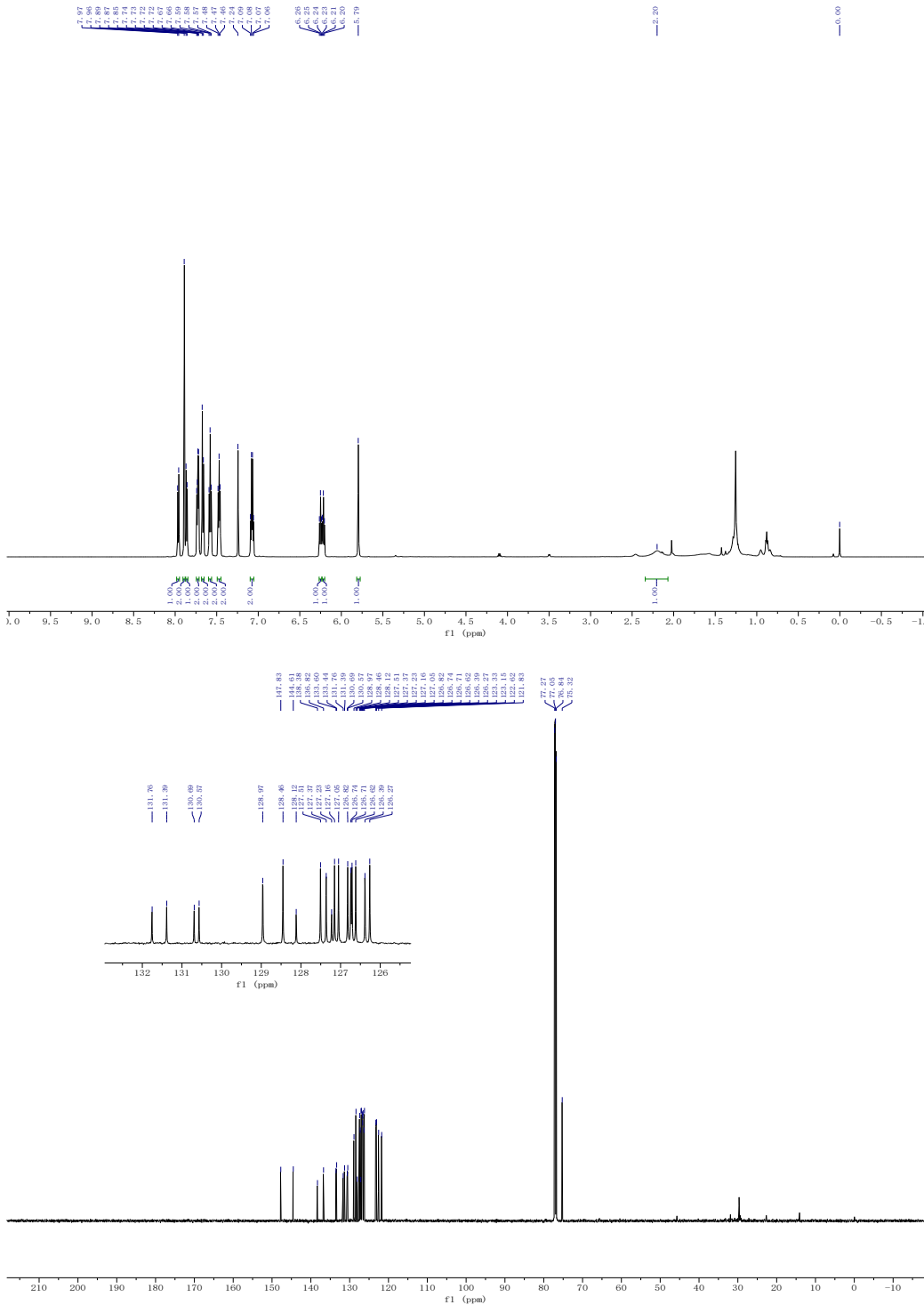
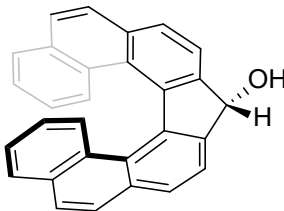
isobutyl (*P*, *S*)-10-oxo-9-phenethyl-9,10-dihydrobenzo[1,2-*c*:4,3-*c'*]diphenanthrene-9-carboxylate (D31)



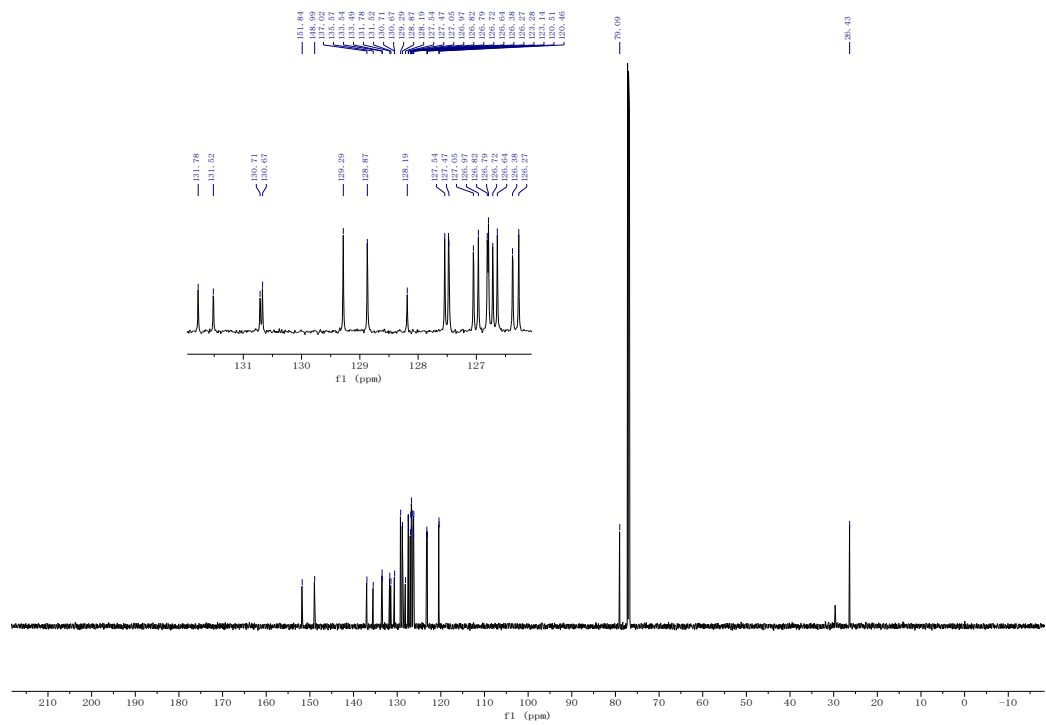
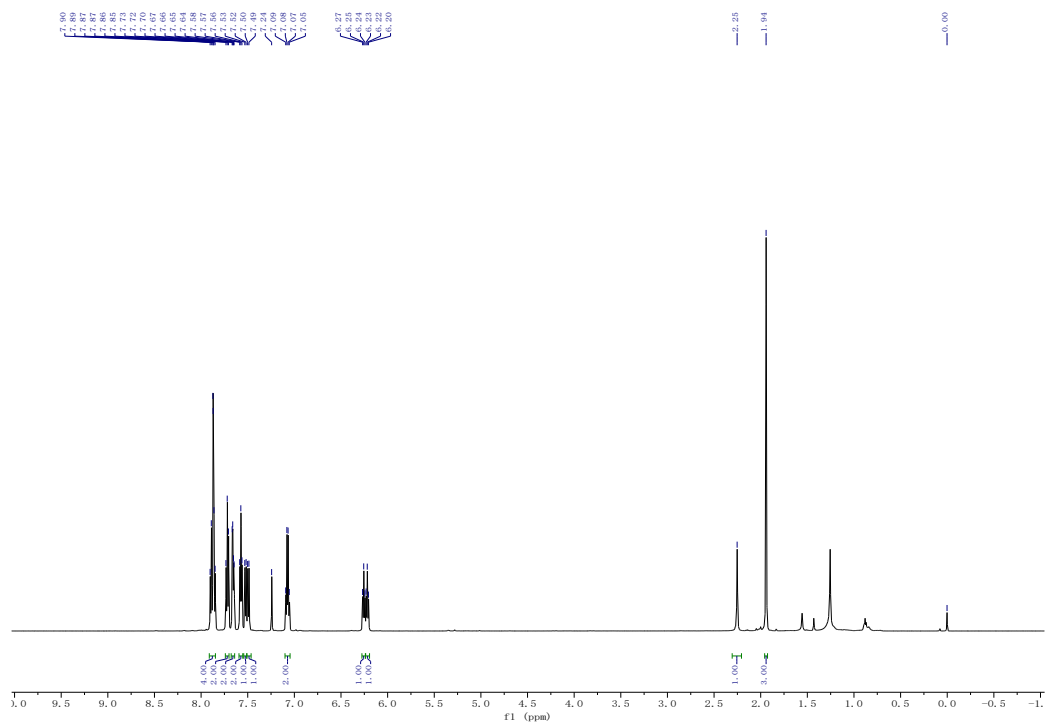
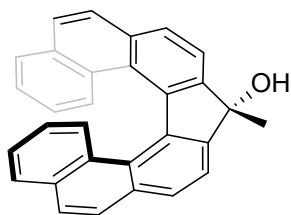
isobutyl (S)-9-octadecyl-10-oxo-9,10-dihydrobenzo[1,2-c:4,3-c']diphenanthrene-9-carboxylate(D32)



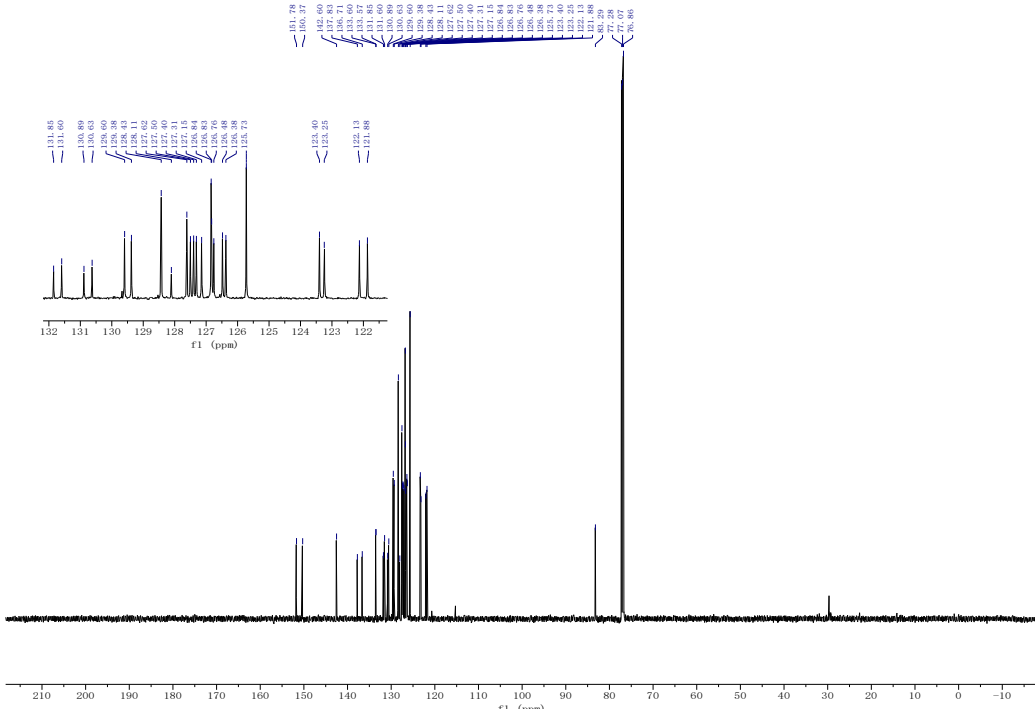
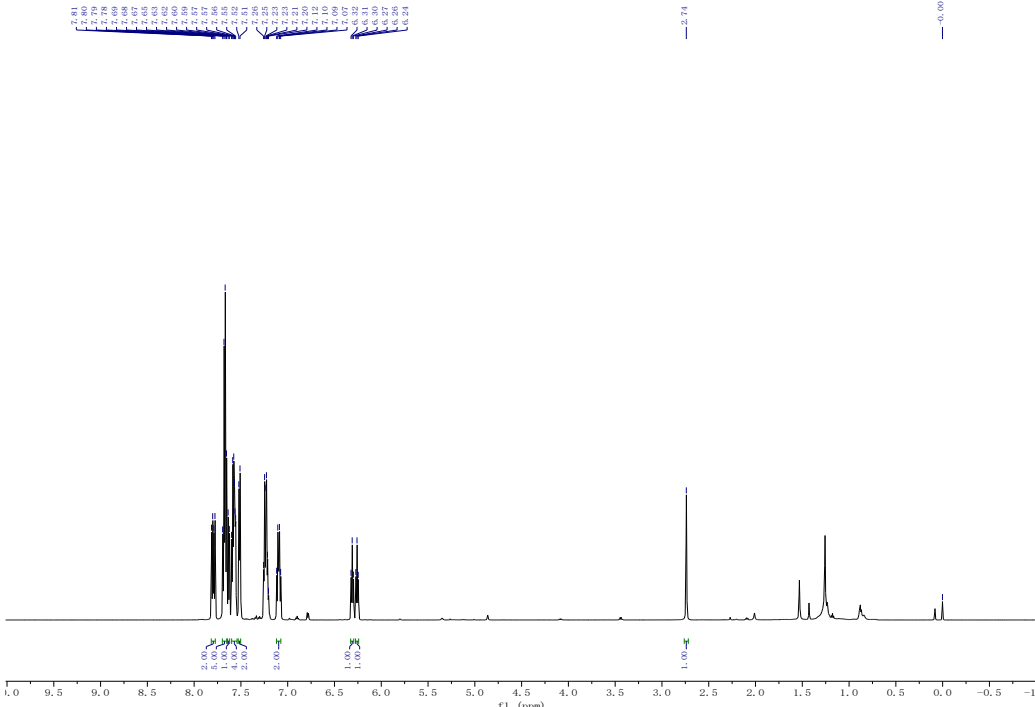
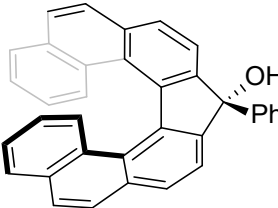
(M)-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-ol (E1)



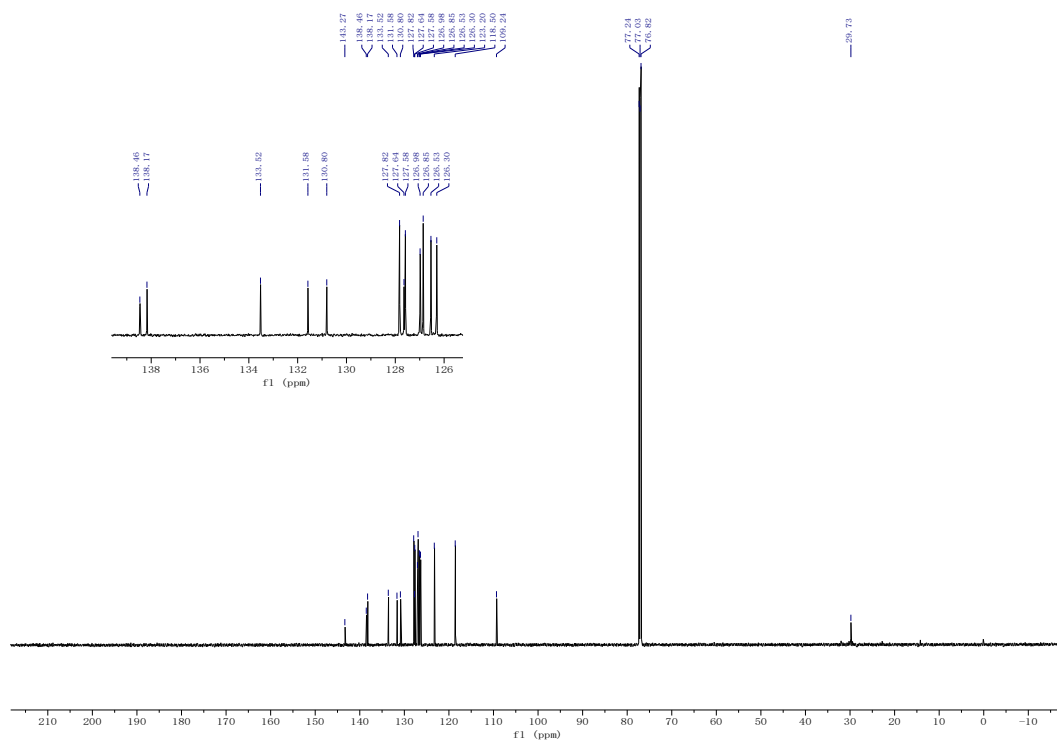
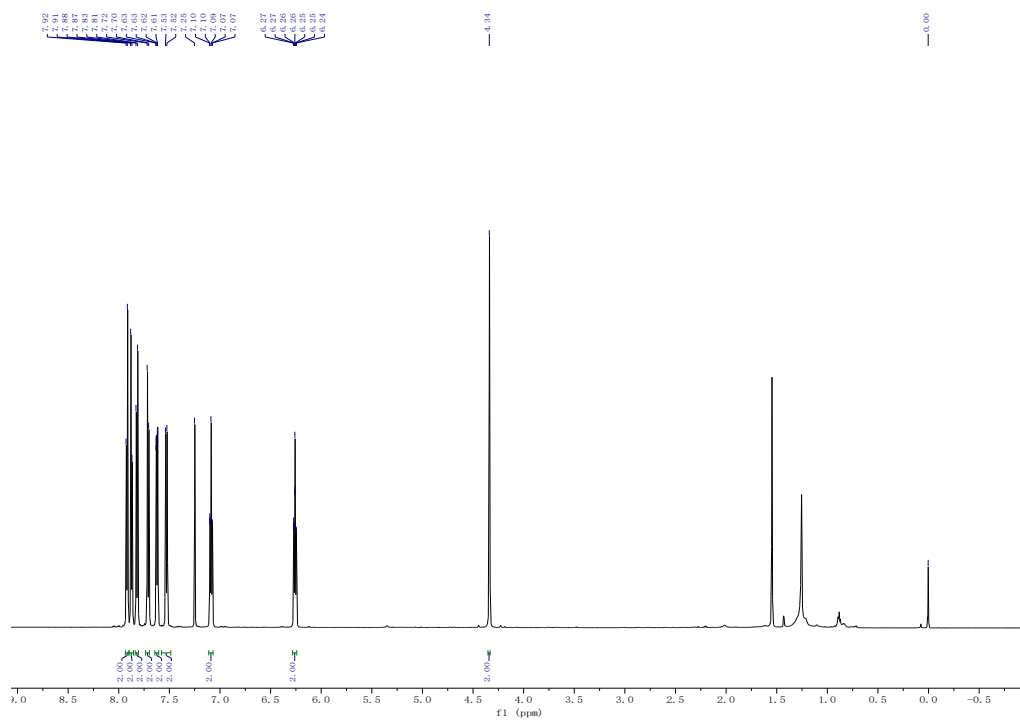
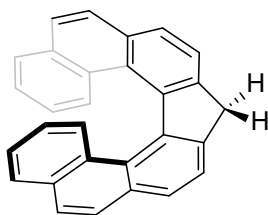
(*M*)-9-methyl-9H-cyclopenta[1,2-*c*:4,3-*c'*]diphenanthren-9-ol (E2)



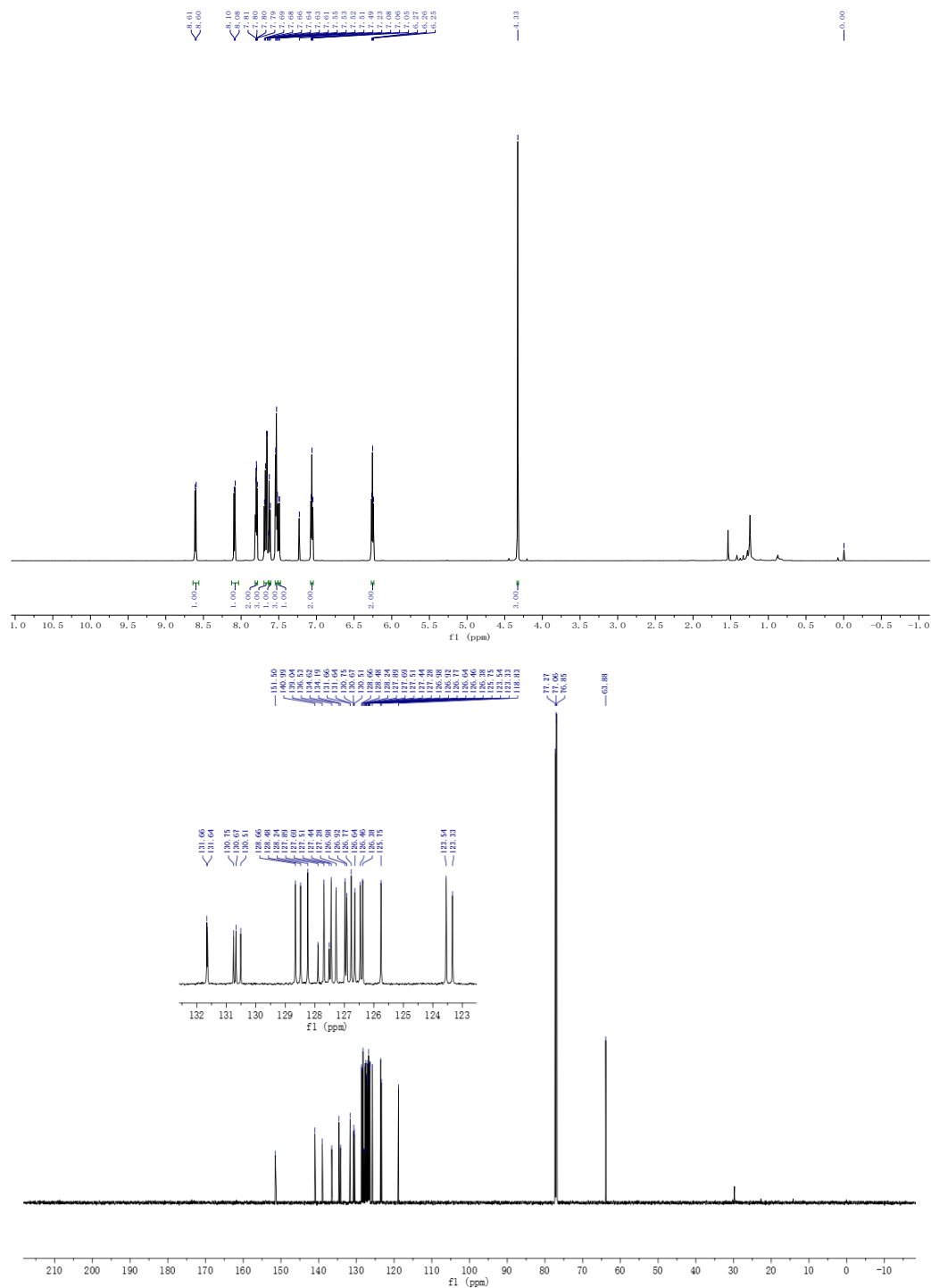
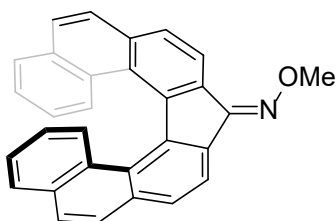
(M)-9-phenyl-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-ol (E3)



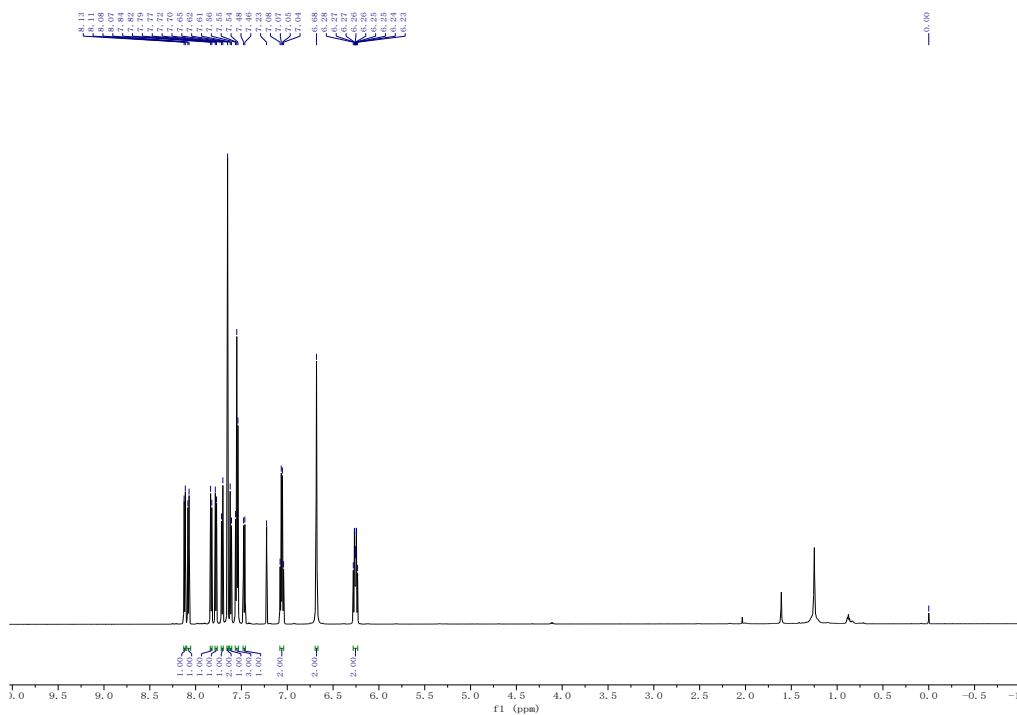
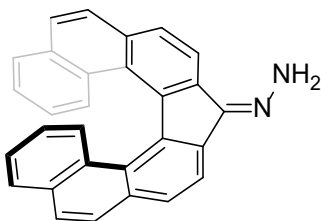
(M)-9H-cyclopenta[1,2-c:4,3-c']diphenanthrene (E4)



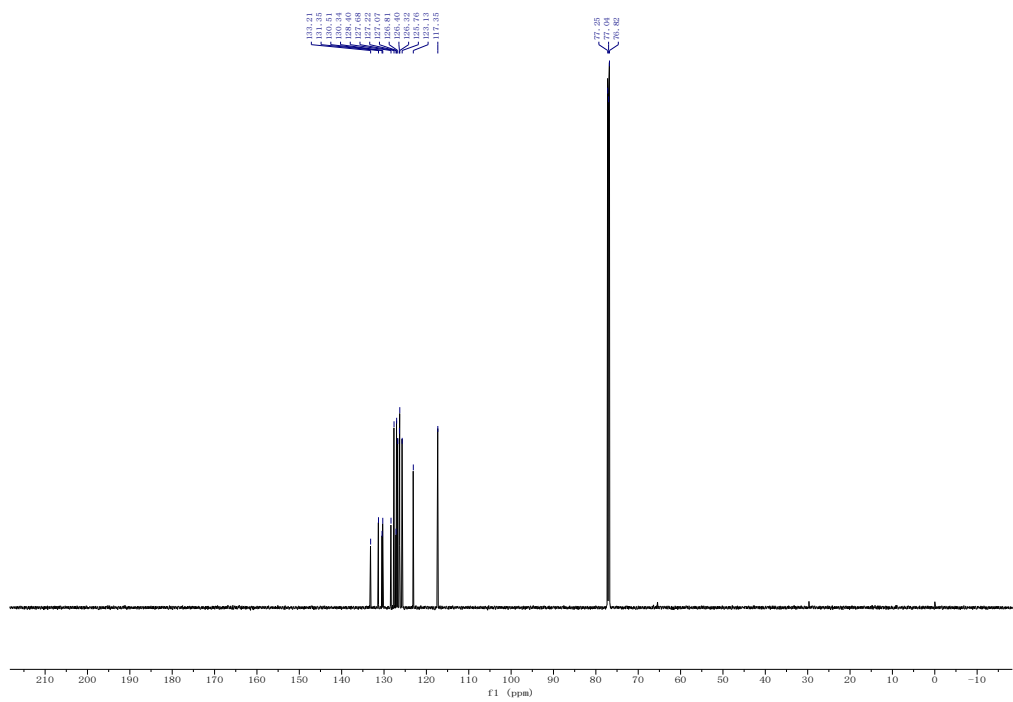
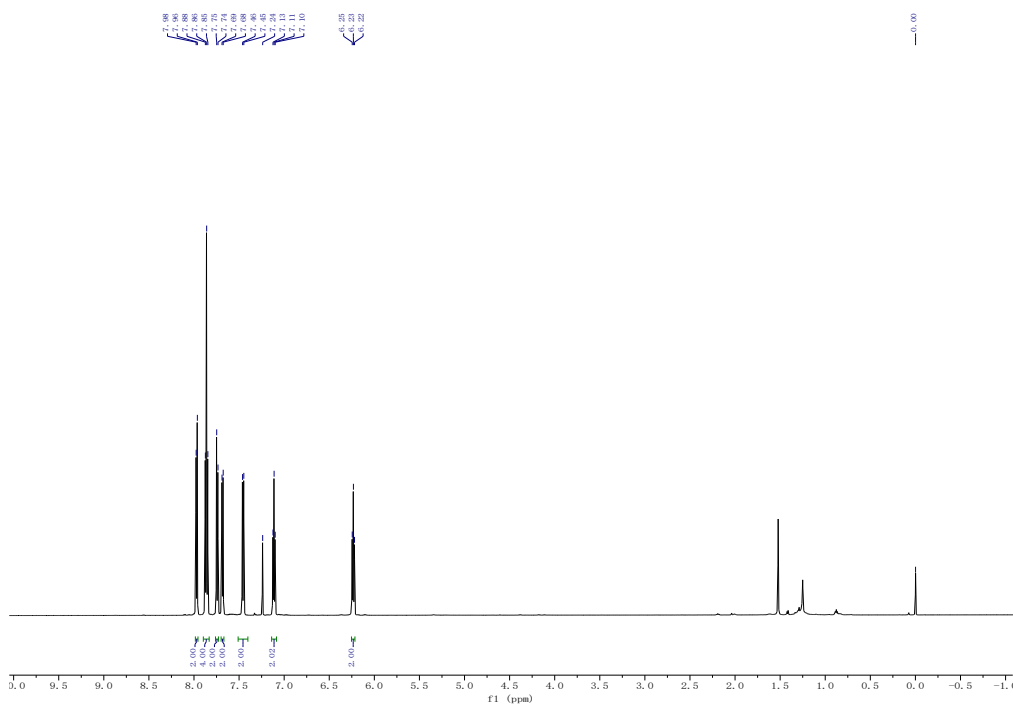
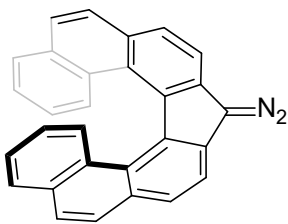
(M)-9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-one-O-methyl oxime (E5)



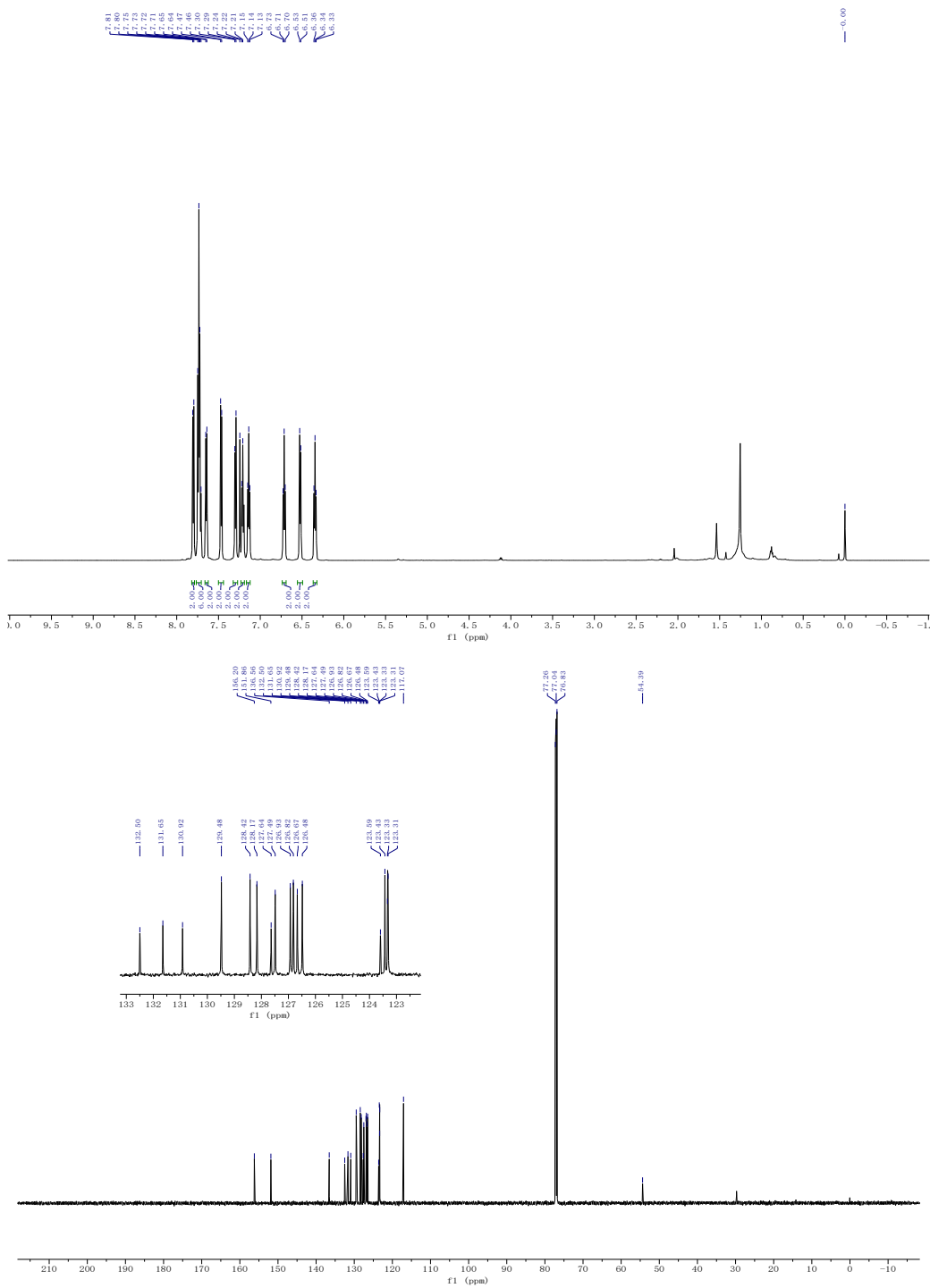
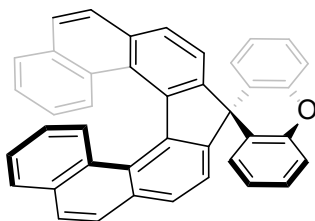
(M)-(9H-cyclopenta[1,2-c:4,3-c']diphenanthren-9-ylidene)hydrazine (E6)



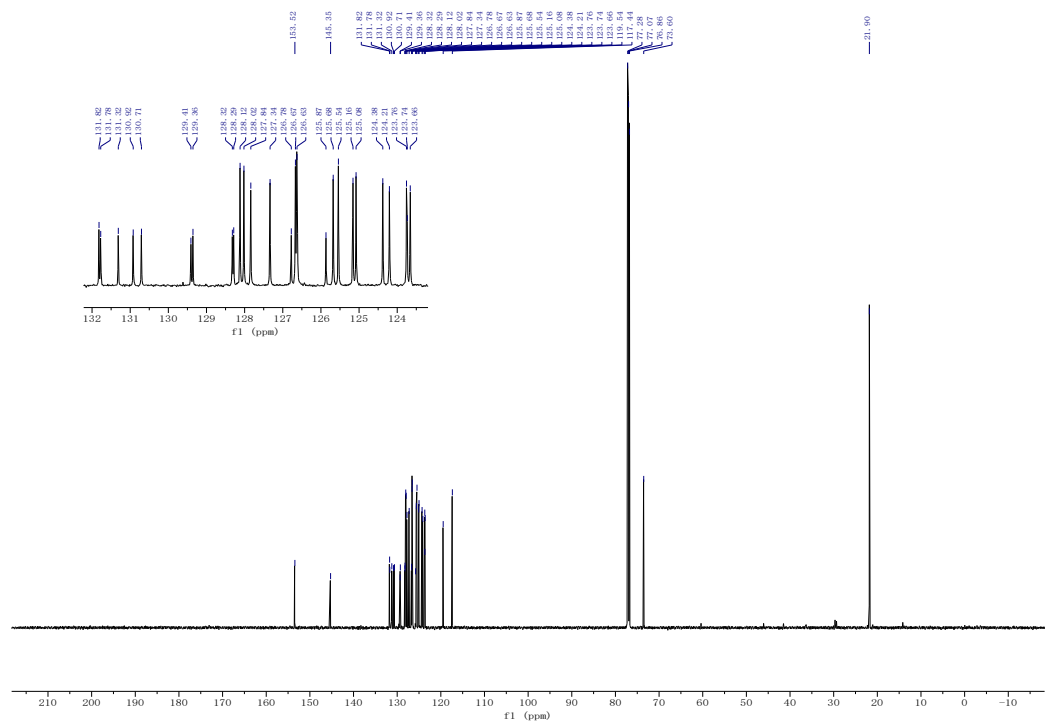
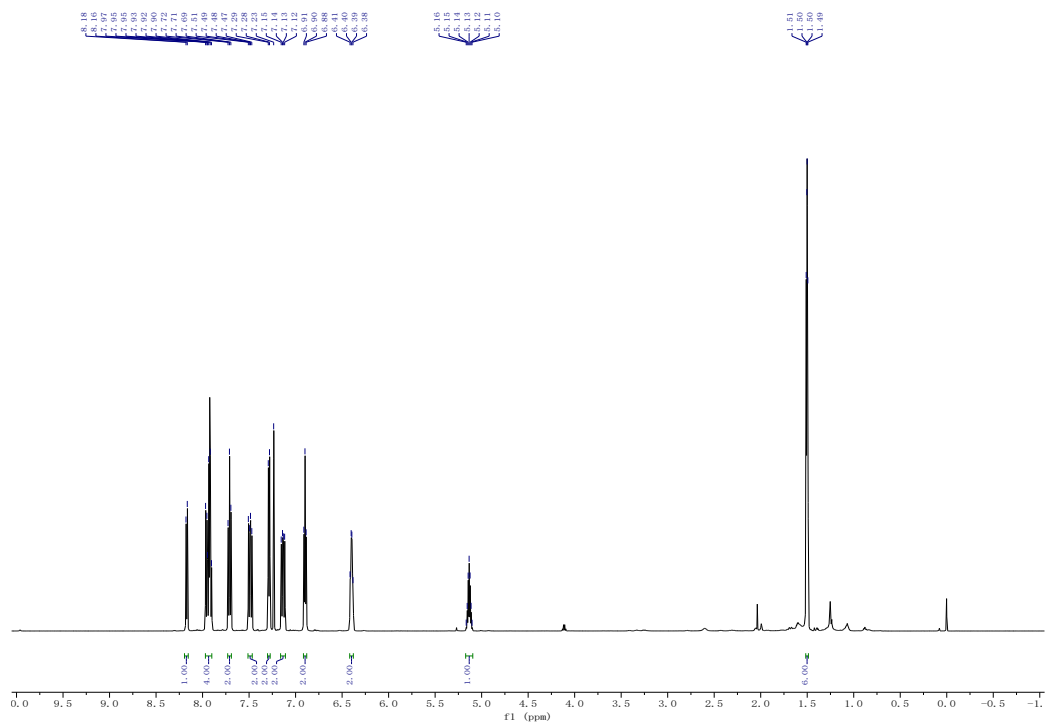
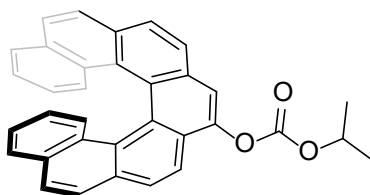
(M)-9-diazo-9H-cyclopenta[1,2-c:4,3-c']diphenanthrene (E7)



(M)-9H-cyclopenta[1,2-c:4,3-c']diphenanthrene-9-thione (E8)



(*M*)-benzo[1,2-c:4,3-c']diphenanthren-9-yl isopropyl carbonate (E9)



(P)-10-benzylbenzo[1,2-c:4,3-c']diphenanthren-9-yl trifluoromethanesulfonate (E10)

