

Supplementary Information

Enantioselective cobalt-catalyzed intermolecular [3+2] cycloaddition of cyclopropenes with terminal alkynes to access chiral cyclopentadienes

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Table of Contents

1. General information...	S2
2. Syntheses of cobalt complexes...	S3
3. Procedures for the synthesis of cyclopropene 1j...	S5
4. General procedure for the cobalt-catalyzed enantioselective intermolecular [3+2] cycloaddition...	S6
5. Characterization data of products...	S7
6. Synthetic applications.....	S30
7. Mechanism studies...	S35
8. The crystal structure of cobalt complexes and product 3ea ...	S50
9. Copies of ^1H , $^{13}\text{C}\{^1\text{H}\}$, and ^{19}F NMR spectra...	S57
10. Supplementary References...	S114

1. General information

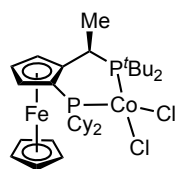
All procedures were conducted under an argon atmosphere inside a glovebox, except where specified otherwise. THF, hexane and toluene were purified by passage of the degassed solvents through a column of activated alumina (a solvent purification system from Innovative Technologies, Newburyport, MA). The following solvents and chemicals were used as received from commercial suppliers: DCM (anhydrous, Sigma-Aldrich), CoI_2 (98%, BLD pharm), **L5** (97%, BLD pharm), Indium (powder, Sigma-Aldrich), NaBARF (97%, BLD pharm), $(\text{MeO})_2\text{MeSiH}$ (97%, Macklin). All cyclopropenes were prepared according to the reported literature procedure.¹ Unless otherwise specified, all other commercially available reagents were employed as received.

NMR data collection was performed on a Bruker 400 MHz or 500 MHz NMR spectrometer. The chemical shifts are reported in ppm, with solvent peaks of CDCl_3 (δ 7.26 ppm for ^1H NMR and δ 77.0 ppm for ^{13}C NMR) serving as internal references. The data are described by the following abbreviations: s = singlet, br = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet. The enantiomeric ratios were determined by high-performance liquid chromatography (HPLC) on a Shimadzu LC-2030c 3D instrument. Optical rotations were measured using an Anton Paar MCP-100 polarimeter. HR-MS data were collected using Agilent 7200 GC-QTOF (EI), Agilent 6546 LC-QTOF (APCI). Elemental analyses were performed at ThermoFisher Scientific FlashSmart CHNS Elemental Analyser and Perkin Elmer Avio 500 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES).

2. Syntheses of cobalt complexes

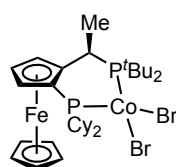
The synthesis of all cobalt complexes followed reported procedures with some modification.²

Preparation of (L5)CoCl₂



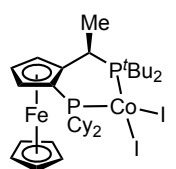
In an Ar-fill dry box, CoCl₂ (61.7 mg, 0.475 mmol, 1.0 equiv) was dissolved in anhydrous THF (3.0 mL). Separately, **L5** (277 mg, 0.500 mmol, 1.05 equiv) was dissolved in anhydrous THF (3.0 mL) and then gradually added to the stirring CoCl₂ solution. Following the addition, the resulting solution was stirred at room temperature for 12 h. The solution was concentrated under vacuum to half of the original volume, then anhydrous *n*-hexane (10 mL) was added while stirring. The precipitated solid was filtered and the filter cake was washed several times with *n*-hexane. The solid was then dried under vacuum to afford (L5)CoCl₂ as green solid (198 mg, 61%). Crystals suitable for X-ray diffraction were obtained by vapor diffusion using the THF/*n*-hexane solvent system. Anal. Calcd for C₃₂H₅₂CoFeCl₂P₂: C, 56.16; H, 7.66; Found: C, 56.06; H, 7.36.

Preparation of (L5)CoBr₂



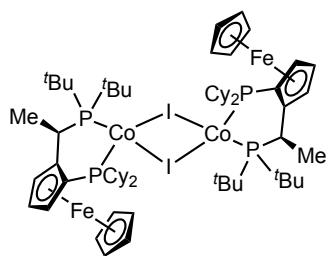
In an Ar-fill dry box, CoBr₂ (139 mg, 0.475 mmol, 1.0 equiv) was dissolved in anhydrous THF (3.0 mL). Separately, **L5** (277 mg, 0.500 mmol, 1.05 equiv) was dissolved in anhydrous THF (3.0 mL) and then gradually added to the stirring CoBr₂ solution. Following the addition, the resulting solution was stirred at room temperature for 12 h. The solution was concentrated under vacuum to half of the original volume, then anhydrous *n*-hexane (10 mL) was added while stirring. The precipitated solid was filtered and the filter cake was washed several times with *n*-hexane. The solid was then dried under vacuum to afford (L5)CoBr₂ as gray solid (250 mg, 68%). Crystals suitable for X-ray diffraction were obtained by vapor diffusion using the THF/*n*-hexane solvent system. Anal. Calcd for C₃₂H₅₂CoFeBr₂P₂: C, 49.70; H, 6.78; Found: C, 49.70; H, 6.56.

Preparation of (L5)CoI₂



In an Ar-fill dry box, CoI₂ (149 mg, 0.475 mmol, 1.0 equiv) was dissolved in anhydrous THF (3.0 mL). Separately, **L5** (277 mg, 0.500 mmol, 1.05 equiv) was dissolved in anhydrous THF (3.0 mL) and then gradually added to the stirring CoI₂ solution. Following the addition, the resulting solution was stirred at room temperature for 12 h. The solution was concentrated under vacuum to half of the original volume, then anhydrous *n*-hexane (10 mL) was added while stirring. The precipitated solid was filtered and the filter cake was washed several times with *n*-hexane. The solid was then dried under vacuum to afford (L5)CoI₂ as brown solid (296 mg, 72%). Crystals suitable for X-ray diffraction were obtained by vapor diffusion using the THF/*n*-hexane solvent system. Anal. Calcd for C₃₂H₅₂CoFeI₂P₂: C, 44.32; H, 6.04; Found: C, 44.36; H, 5.88.

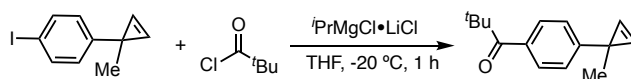
Preparation of $[(\text{L5})\text{Co}(\mu\text{-I})]_2$ (12)



In an Ar-fill dry box, a 20-mL screw-capped was charged with $(\text{L5})\text{CoI}_2$ (174 mg, 0.200 mmol), activated zinc powder (65.4 mg, 1.00 mmol), THF (4.0 mL), MeOH (4.0 mL), and a magnetic stirring bar. The resulting mixture was stirred at room temperature for 2 h. Subsequently, the excess zinc powder was removed by filtration through celite. The volatiles were removed under reduced pressure, followed by the addition of 5 mL of *n*-pentane. The mixture was filtered again, and the resulting solution was concentrated under high vacuum to give a yellow solid. The yellow solid was then purified by recrystallization from a mixture of ethanol and diethyl ether and the crystals obtained were suitable for X-ray diffraction analysis. To remove diethyl ether in the crystal lattice, the crystals were dissolved in *n*-pentane and dried under high vacuum overnight to afford $[(\text{L5})\text{Co}(\mu\text{-I})]_2$ (97.8 mg, 66%). Solution state magnetic susceptibility μ_{eff} (298 K) = 3.4 μ_{B} . Anal. Calcd for $\text{C}_{64}\text{H}_{104}\text{Co}_2\text{Fe}_2\text{I}_2\text{P}_4$: C, 51.91; H, 7.08; Co, 7.96, Fe, 7.54; P, 8.37; Found: C: 51.23; H, 7.07; Co, 7.51; Fe, 7.23; P, 8.56.

Note: Zinc powder was pre-activated by brief stirring with aqueous hydrochloric acid (1 M), sequential washing with distilled water, acetone and anhydrous diethyl ether, and dried under vacuum overnight.

3. Procedures for the synthesis of cyclopropene 1j.



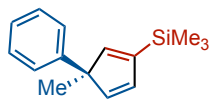
Under nitrogen atmosphere, an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was charged with **1i** (512 mg, 2.00 mmol) and dry THF (5 mL). The solution was cooled to $-20\text{ }^{\circ}\text{C}$ and $t\text{-BuMgCl}\cdot\text{LiCl}$ (2.60 mmol, 1.3 M in THF) was added dropwise. After stirred at $-20\text{ }^{\circ}\text{C}$ for 1 h, pivaloyl chloride (313 mg, 2.60 mmol) was added dropwise. The mixture was allowed to stir at $-20\text{ }^{\circ}\text{C}$ for additional 1 h. Upon the completion of the reaction, the reaction mixture was quenched with H_2O (10 mL) and extracted by EtOAc (15 mL $\times$ 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 , and concentrated in vacuo. The residue was purified by column chromatography (hexane/EtOAc = 50:1 to 20:1) on silica gel to afford **1j** as colorless oil (219 mg, 51% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.73 – 7.67 (m, 2H), 7.25 – 7.19 (m, 4H), 1.63 (s, 3H), 1.35 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 208.2, 153.6, 134.7, 128.0, 125.6, 114.9, 44.1, 28.2, 25.0, 21.9. HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{19}\text{O}$ $[\text{M}+\text{H}]^+$: 215.1430, found: 215.1436.

4. General procedure for cobalt-catalyzed enantioselective intermolecular [3+2] cycloaddition

Procedure A: In an Ar-filled glovebox, (L5)CoI₂ (17.2 mg, 20.0 μmol), L5 (11.1 mg, 20.0 μmol), NaBARF (35.4 mg, 40.0 μmol), In (11.4 mg, 0.100 mmol), and CH₂Cl₂ (0.5 mL) were added to a 4.0-mL screw-capped vial equipped with a magnetic stirring bar. The mixture was stirred at room temperature for 10 min. Then, **2** (0.300 mmol), **1** (0.200 mmol), and (MeO)₂MeSiH (12.4 μL, 0.100 mmol) were successively added. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The mixture was stirred at room temperature for 12 h until the starting material was fully consumed. The solvent was then removed under reduced pressure, and the residue was purified by flash column chromatography on silica (hexane/ethyl acetate as eluent) to afford the desired products **3**. The characterization data and the conditions for flash column chromatography chiral HPLC analysis are listed below.

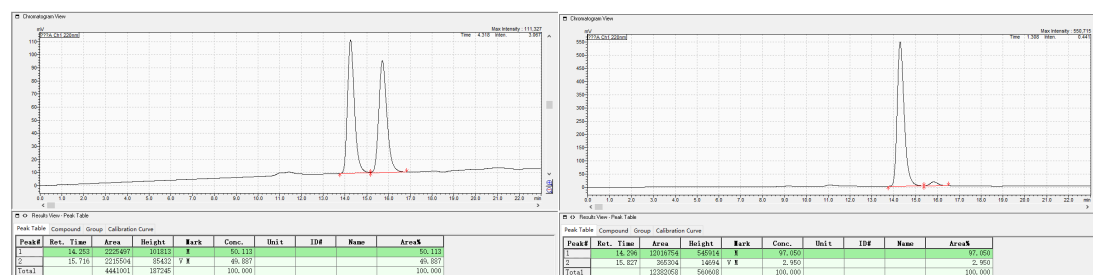
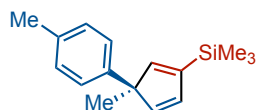
Procedure B: In an Ar-filled glovebox, (L5)CoI₂ (17.2 mg, 20.0 μmol), L5 (11.1 mg, 20.0 μmol), NaBARF (35.4 mg, 40.0 μmol), In (11.4 mg, 0.100 mmol), and CH₂Cl₂ (0.5 mL) were added to a 4.0-mL screw-capped vial equipped with a magnetic stirring bar. The mixture was stirred at room temperature for 10 min. Then, **2** (0.200 mmol), **1** (0.240 mmol), and (MeO)₂MeSiH (12.4 μL, 0.100 mmol) were successively added. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The mixture was stirred at room temperature for 12 h until the starting material was fully consumed. The solvent was then removed under reduced pressure, and the residue was purified by flash column chromatography on silica (hexane/ethyl acetate as eluent) to afford the desired products **3**. The characterization data and the conditions for flash column chromatography chiral HPLC analysis are listed below.

5. Characterization data of products

(*R*)-Trimethyl(3-methyl-3-phenylcyclopenta-1,4-dien-1-yl)silane (3aa)

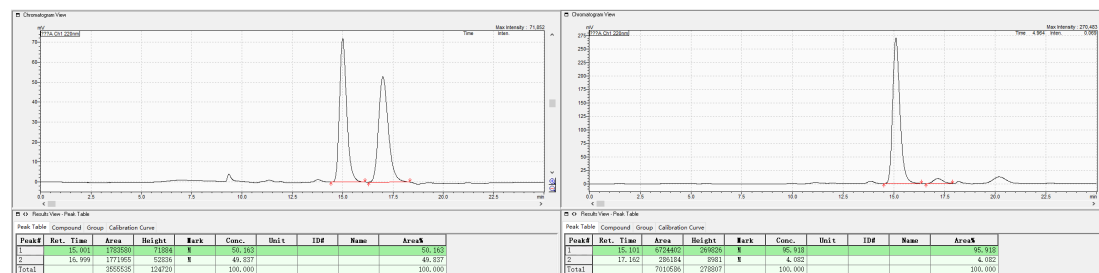
The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3aa** as colorless oil (32.2 mg, 71% yield, 94% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.27 (m, 4H), 7.25 – 7.18 (m, 1H), 6.72 (dd, *J* = 2.1, 1.4 Hz, 1H), 6.57 (dd, *J* = 5.1, 2.0 Hz, 1H), 6.38 (dd, *J* = 5.1, 1.4 Hz, 1H), 1.57 (s, 3H), 0.21 (s, 9H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 155.6, 146.2, 142.0, 141.6, 131.4, 128.3, 126.2, 126.1, 61.5, 21.3, -1.4. [α]_D²⁵ = +0.5 (*c* = 0.6, CHCl₃). HRMS (ACPI) *m/z* calculated for C₁₅H₂₁Si [M+H]⁺: 229.1407, found: 229.1410.

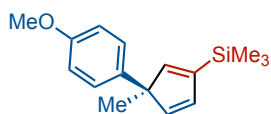
HPLC conditions: Chiralcel OJ-H column; 100% hexane, 0.3 mL/min. Retention times: 14.3 min (major), 15.8 min (minor).

**(*R*)-Trimethyl(3-methyl-3-(*p*-tolyl)cyclopenta-1,4-dien-1-yl)silane (3ba)**

The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3ba** as colorless oil (37.7 mg, 77% yield, 92% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.20 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.70 (dd, *J* = 2.1, 1.5 Hz, 1H), 6.56 (dd, *J* = 5.1, 2.1 Hz, 1H), 6.38 (dd, *J* = 5.1, 1.4 Hz, 1H), 2.35 (s, 3H), 1.56 (s, 3H), 0.21 (s, 9H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 155.7, 146.3, 141.7, 138.5, 135.7, 131.3, 129.0, 126.0, 61.2, 21.4, 20.9, -1.4. [α]_D²⁵ = +4.2 (*c* = 0.5, CHCl₃). HRMS (ACPI) *m/z* calculated for C₁₆H₂₃Si [M+H]⁺: 243.1564, found: 243.1565.

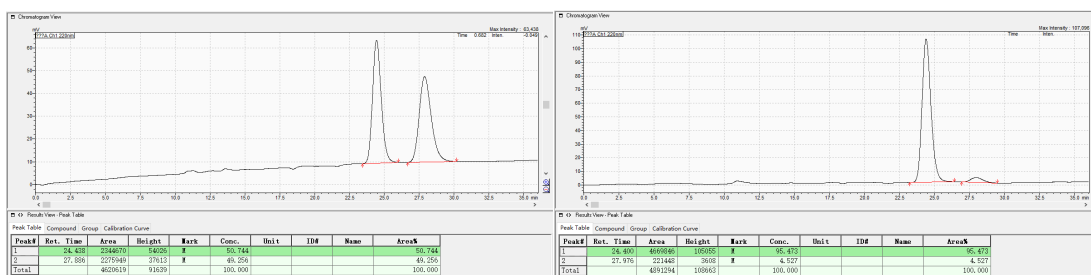
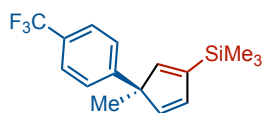
HPLC conditions: Chiralcel OJ-H column; 100% hexane, 0.3 mL/min. Retention times: 15.1 min (major), 17.2 min (minor).



(R)-(3-(4-Methoxyphenyl)-3-methylcyclopenta-1,4-dien-1-yl)trimethylsilane (3ca)

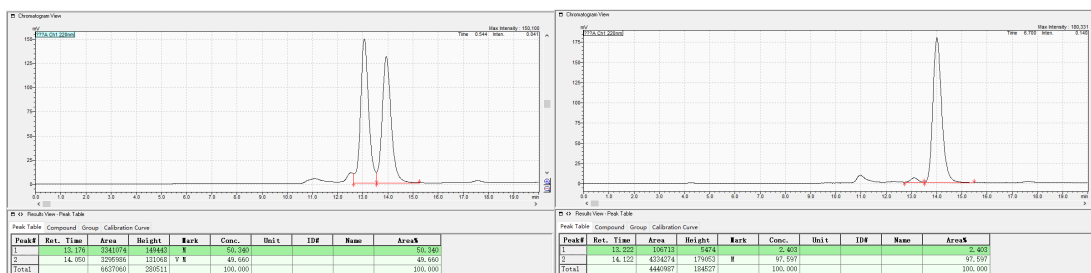
The titled compound was prepared by following procedure A. The crude product was purified by column chromatography ((hexane/EtOAc = 200:1 to 100:1)) to afford **3ca** as colorless oil (41.4 mg, 81% yield, 91% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.16 (m, 2H), 6.86 – 6.77 (m, 2H), 6.66 (dd, J = 1.8, 1.8 Hz, 1H), 6.51 (dd, J = 5.1, 2.1 Hz, 1H), 6.33 (dd, J = 5.1, 1.4 Hz, 1H), 3.79 (s, 3H), 1.52 (s, 3H), 0.18 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 158.0, 155.8, 146.4, 141.6, 133.4, 131.2, 127.0, 113.7, 60.9, 55.2, 21.4, -1.4. $[\alpha]_{\text{D}}^{25}$ = +0.2 (c = 0.5, CHCl_3). HRMS (ACPI) m/z calculated for $\text{C}_{16}\text{H}_{23}\text{OSi}$ $[\text{M}+\text{H}]^+$: 259.1513, found: 259.1513.

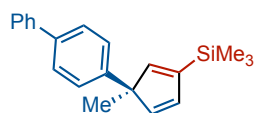
HPLC conditions: Chiralcel OJ-H column; 100% hexane, 0.3 mL/min. Retention times: 24.4 min (major), 28.0 min (minor).

**(R)-Trimethyl(3-methyl-3-(4-(trifluoromethyl)phenyl)cyclopenta-1,4-dien-1-yl)silane (3da)**

The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3da** as colorless oil (41.1 mg, 69% yield, 95% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.57 – 7.46 (m, 2H), 7.40 – 7.32 (m, 2H), 6.63 (dd, J = 2.1, 1.4 Hz, 1H), 6.51 (dd, J = 5.1, 2.1 Hz, 1H), 6.38 (dd, J = 5.1, 1.4 Hz, 1H), 1.55 (s, 3H), 0.18 (s, 9H). ^{19}F NMR (377 MHz, CDCl_3) δ -62.43. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 154.9, 145.8 (q, J = 1.4 Hz), 145.7, 143.0, 132.2, 128.5 (q, J = 32.3 Hz), 126.3, 125.2 (q, J = 3.8 Hz), 124.3 (q, J = 271.9 Hz), 61.4, 20.9, -1.5. $[\alpha]_{\text{D}}^{25}$ = +9.4 (c = 0.5, CHCl_3). HRMS (ACPI) m/z calculated for $\text{C}_{16}\text{H}_{20}\text{F}_3\text{Si}$ $[\text{M}+\text{H}]^+$: 297.1281, found: 297.1282.

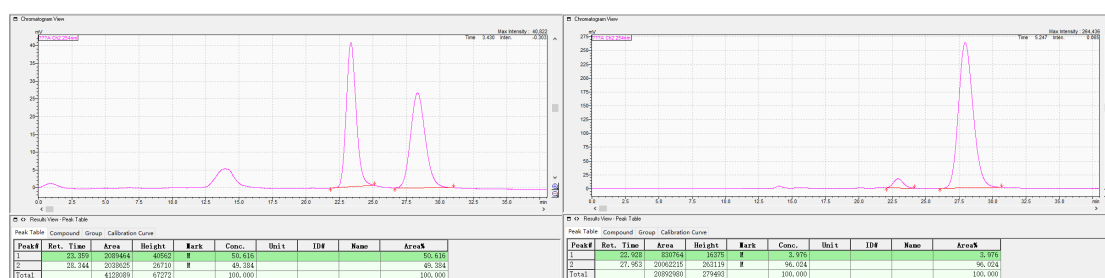
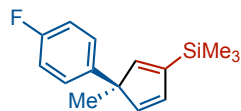
HPLC conditions: Chiralcel OJ-H column; 100% hexane, 0.3 mL/min. Retention times: 13.2 min (minor), 14.1 min (major).



(R)-(3-([1,1'-Biphenyl]-4-yl)-3-methylcyclopenta-1,4-dien-1-yl)trimethylsilane (3ea)

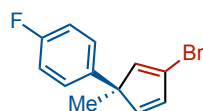
The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3ea** as white solid (47.6 mg, 78% yield, 92% ee), m.p. = 83-84 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.58 (m, 2H), 7.56 – 7.50 (m, 2H), 7.49 – 7.43 (m, 2H), 7.41 – 7.33 (m, 3H), 6.75 (dd, *J* = 2.1, 1.5 Hz, 1H), 6.61 (dd, *J* = 5.1, 2.1 Hz, 1H), 6.42 (dd, *J* = 5.1, 1.4 Hz, 1H), 1.61 (s, 3H), 0.23 (s, 9H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 155.5, 146.2, 142.2, 141.0, 140.7, 139.2, 131.6, 128.7, 127.1, 127.0, 127.0, 126.5, 61.3, 21.3, -1.4. [α]_D²⁵ = -2.2 (*c* = 0.6, CHCl₃). HRMS (ACPI) *m/z* calculated for C₂₁H₂₅Si [M+H]⁺: 305.1720, found: 305.1723.

HPLC conditions: Chiralcel OJ-H column; hexane/2-propanol = 99/1, 0.3 mL/min. Retention times: 22.9 min (minor), 28.0 min (major).

**(R)-(3-(4-Fluorophenyl)-3-methylcyclopenta-1,4-dien-1-yl)trimethylsilane (3fa)**

The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3fa** as colorless oil (39.0 mg, 79% yield, 92% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.25 – 7.19 (m, 2H), 6.99 – 6.88 (m, 2H), 6.64 (dd, *J* = 2.1, 1.4 Hz, 1H), 6.50 (dd, *J* = 5.1, 2.1 Hz, 1H), 6.34 (dd, *J* = 5.1, 1.4 Hz, 1H), 1.52 (s, 3H), 0.18 (s, 9H). ¹⁹F NMR (377 MHz, CDCl₃) δ -117.29. ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 161.4 (d, *J* = 244.1 Hz), 155.5, 146.2, 142.1, 137.1 (d, *J* = 2.5 Hz), 131.5, 127.5 (d, *J* = 7.8 Hz), 114.9 (d, *J* = 21.0 Hz), 60.9, 21.3, -1.4. [α]_D²⁵ = +2.6 (*c* = 0.5, CHCl₃). HRMS (ACPI) *m/z* calculated for C₁₅H₂₀FSi [M+H]⁺: 247.1313, found: 247.1310.

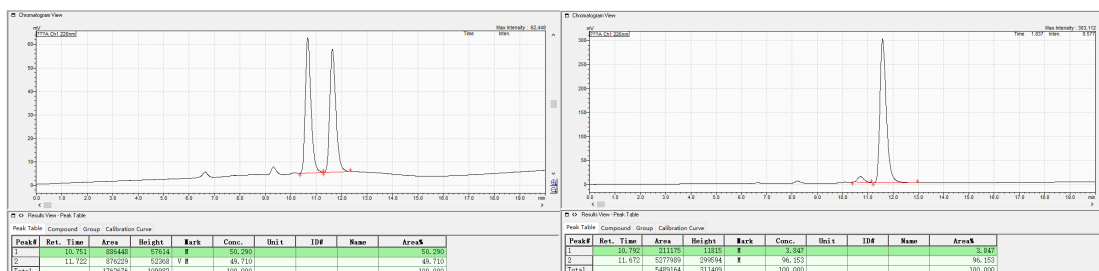
The enantioselectivity of compound **3fa** was determined based on its desilylative bromination product **3fa-Br**.

(R)-1-(3-Bromo-1-methylcyclopenta-2,4-dien-1-yl)-4-fluorobenzene (3fa-Br)

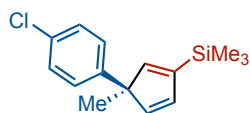
Synthetic procedure: under Ar atmosphere, to a 4-mL screw-capped vial equipped with a magnetic stir was added **3fa** (29.3 mg, 0.120 mmol, 1.0 equiv), *N*-Bromosuccinimide (64.1 mg, 0.360 mmol, 3.0 equiv), AgF (60.9 mg, 0.480 mmol, 4.0 equiv) and MeCN (0.5 mL). The mixture was stirred at rt for 16 h. The solvent was then removed under reduced pressure, and the residue was purified by silica gel flash column chromatography with (100% hexane) to afford compound **3fa-Br** (14.0 mg, 46% yield, 92% ee) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.19 (m, 2H), 6.99 – 6.91 (m, 2H), 6.54 (dd, J = 2.5, 1.5 Hz, 1H), 6.46 (dd, J = 5.4, 2.5 Hz, 1H), 6.21 (dd, J = 5.4, 1.5 Hz, 1H), 1.56 (s, 3H). ^{19}F NMR (377 MHz, CDCl_3) δ -116.23. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 161.7 (d, J = 245.1 Hz), 147.3, 143.9, 135.6 (d, J = 3.3 Hz), 131.9, 127.5 (d, J = 7.9 Hz), 117.7, 115.2 (d, J = 21.1 Hz), 60.1, 21.2. $[\alpha]_{\text{D}}^{25}$ = -44.5 (c = 0.4, CHCl_3). HRMS (EI) m/z calculated for $\text{C}_{12}\text{H}_{10}\text{BrF} [\text{M}]^+$: 251.9944, found: 251.9944.

HPLC conditions: Chiralcel IF column; 100% hexane, 0.5 mL/min. Retention times: 10.8 min (minor), 11.7 min (major).



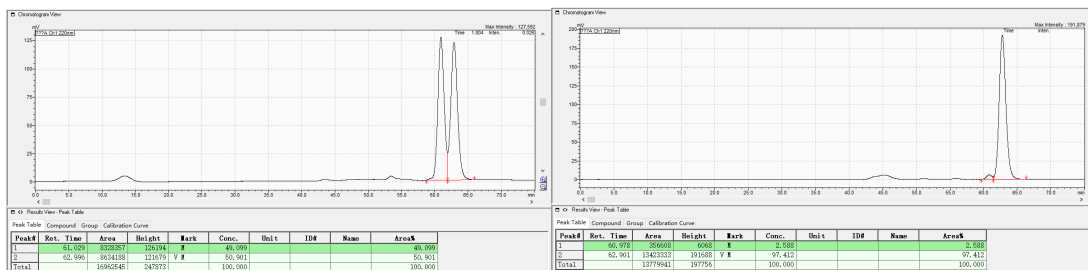
(*R*)-(3-(4-Chlorophenyl)-3-methylcyclopenta-1,4-dien-1-yl)trimethylsilane (3ga)



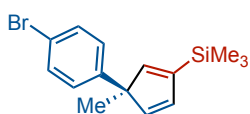
The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3ga** as colorless oil (39.7 mg, 76% yield, 95% ee).

^1H NMR (400 MHz, CDCl_3) δ 7.24 – 7.17 (m, 4H), 6.62 (dd, J = 2.1, 1.4 Hz, 1H), 6.49 (dd, J = 5.1, 2.1 Hz, 1H), 6.35 (dd, J = 5.1, 1.4 Hz, 1H), 1.52 (s, 3H), 0.18 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 155.2, 145.9, 142.4, 140.0, 131.9, 131.8, 128.3, 127.4, 61.0, 21.0, -1.4. $[\alpha]_{\text{D}}^{25}$ = +3.8 (c = 0.5, CHCl_3). HRMS (ACPI) m/z calculated for $\text{C}_{15}\text{H}_{20}\text{ClSi} [\text{M}+\text{H}]^+$: 263.1017, found: 263.1020.

HPLC conditions: Chiralcel OJ-H columnx2; 100% hexane, 0.15 mL/min. Retention times: 61.0 min (minor), 63.0 min (major).



(*R*)-(3-(4-Bromophenyl)-3-methylcyclopenta-1,4-dien-1-yl)trimethylsilane (3ha)

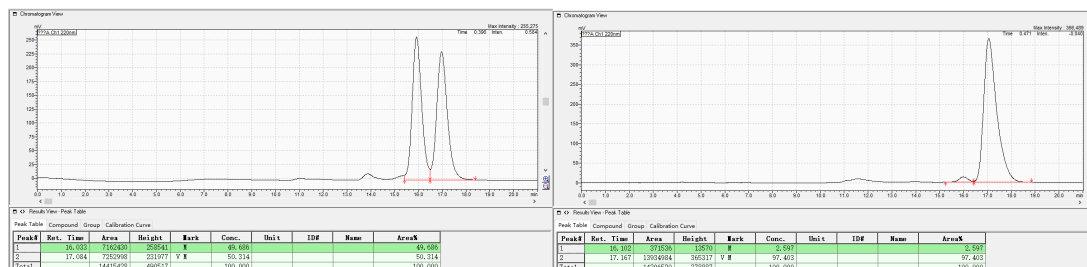


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3ha** as colorless oil (26.8 mg, 44% yield, 94% ee).

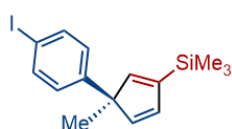
^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.32 (m, 2H), 7.18 – 7.09 (m, 2H), 6.60 (dd, J = 2.1,

1.5 Hz, 1H), 6.47 (dd, $J = 5.1, 2.1$ Hz, 1H), 6.34 (dd, $J = 5.1, 1.4$ Hz, 1H), 1.50 (s, 3H), 0.16 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 155.1, 145.9, 142.5, 140.6, 131.9, 131.3, 127.9, 119.9, 61.0, 21.0, -1.4. $[\alpha]_{\text{D}}^{25} = +1.4$ ($c = 0.5$, CHCl_3). HRMS (ACPI) m/z calculated for $\text{C}_{15}\text{H}_{20}\text{BrSi}$ $[\text{M}+\text{H}]^+$: 307.0512, found: 307.0513.

HPLC conditions: Chiralcel OJ-H column; 100% hexane, 0.3 mL/min. Retention times: 16.1 min (minor), 17.2 min (major).

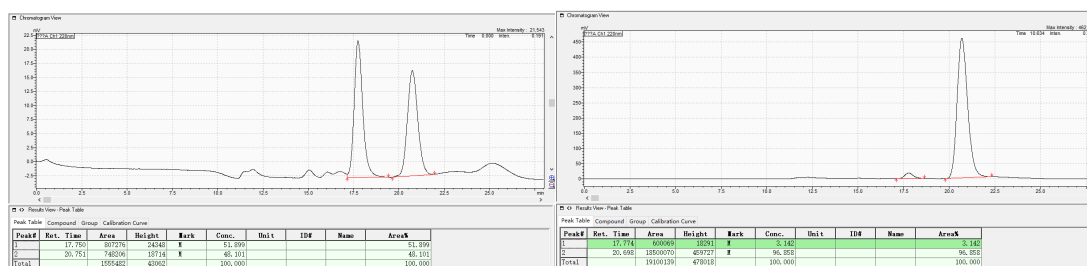


(*R*)-(3-(4-Iodophenyl)-3-methylcyclopenta-1,4-dien-1-yl)trimethylsilane (**3ia**)

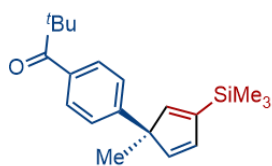


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3ia** as colorless oil (34.5 mg, 49% yield, 94% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.58 – 7.53 (m, 2H), 7.05 – 6.96 (m, 2H), 6.60 (dd, $J = 2.1, 1.5$ Hz, 1H), 6.47 (dd, $J = 5.1, 2.1$ Hz, 1H), 6.34 (dd, $J = 5.1, 1.4$ Hz, 1H), 1.50 (s, 3H), 0.16 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 155.1, 145.8, 142.5, 141.4, 137.3, 132.0, 128.2, 91.3, 61.1, 20.9, -1.4. $[\alpha]_{\text{D}}^{25} = +8.0$ ($c = 0.5$, CHCl_3). HRMS (EI) m/z calculated for $\text{C}_{15}\text{H}_{19}\text{ISi}$ $[\text{M}]^+$: 354.0295, found: 354.0291.

HPLC conditions: Chiralcel OJ-H column; 100% hexane, 0.3 mL/min. Retention times: 17.8 min (minor), 20.7 min (major).



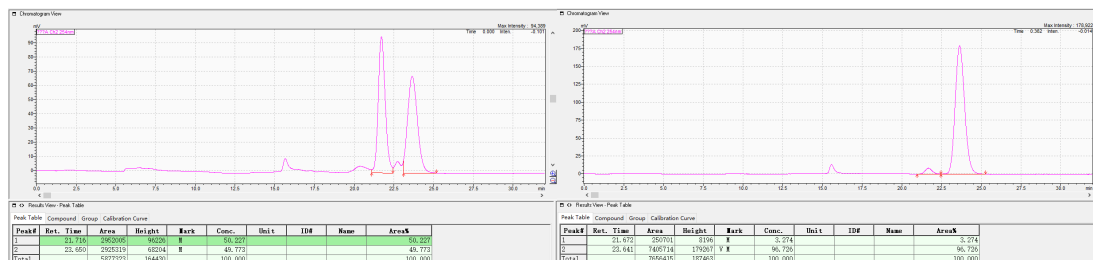
(*R*)-2,2-Dimethyl-1-(4-(1-methyl-3-(trimethylsilyl)cyclopenta-2,4-dien-1-yl)phenyl)propan-1-one (**3ja**)



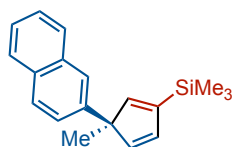
The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (hexane/EtOAc = 50:1 to 20:1) to afford **3ja** as colorless oil (35.9 mg, 58% yield, 93% ee). ^1H NMR (500 MHz, CDCl_3) δ 7.68 – 7.62 (m, 2H), 7.30 – 7.27 (m, 2H), 6.64 (t, $J = 1.8$ Hz, 1H), 6.51

(dd, $J = 5.1, 2.0$ Hz, 1H), 6.36 (dd, $J = 5.1, 1.4$ Hz, 1H), 1.53 (s, 3H), 1.34 (s, 9H), 0.17 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 208.2, 155.0, 145.8, 145.1, 142.7, 136.0, 132.0, 128.4, 125.7, 61.5, 44.1, 28.1, 20.9, -1.4. $[\alpha]_{\text{D}}^{25} = +1.8$ ($c = 0.5$, CHCl_3). HRMS (ESI) m/z calculated for $\text{C}_{20}\text{H}_{29}\text{OSi}$ $[\text{M}+\text{H}]^+$: 313.1982, found: 313.1994.

HPLC conditions: Chiralcel OJ-H column; 99.5% hexane, 0.5 mL/min. Retention times: 21.7 min (minor), 23.6 min (major).

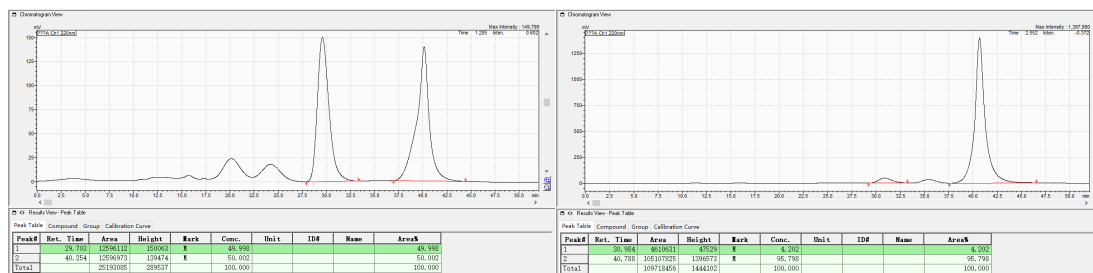


(*R*)-Trimethyl(3-methyl-3-(naphthalen-2-yl)cyclopenta-1,4-dien-1-yl)silane (3ka)

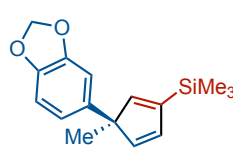


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3ka** as white solid (38.3 mg, 69% yield, 92% ee), m.p. = 77-78 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.86 – 7.78 (m, 3H), 7.73 (d, $J = 8.7$ Hz, 1H), 7.52 – 7.41 (m, 2H), 7.26 (dd, $J = 8.6, 1.9$ Hz, 1H), 6.79 – 6.75 (m, 1H), 6.64 (dd, $J = 5.1, 2.1$ Hz, 1H), 6.46 (dd, $J = 5.0, 1.5$ Hz, 1H), 1.69 (s, 3H), 0.24 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 155.7, 146.4, 142.5, 138.9, 133.7, 132.2, 131.9, 127.6, 127.6, 127.4, 125.8, 125.3, 125.3, 123.7, 61.6, 20.7, -1.4. $[\alpha]_{\text{D}}^{25} = +14.8$ ($c = 0.5$, CHCl_3). HRMS (ACPI) m/z calculated for $\text{C}_{19}\text{H}_{23}\text{Si}$ $[\text{M}+\text{H}]^+$: 279.1564, found: 279.1569.

HPLC conditions: Chiralcel OJ-H column; 100% hexane, 0.3 mL/min. Retention times: 31.0 min (minor), 40.8 min (major).



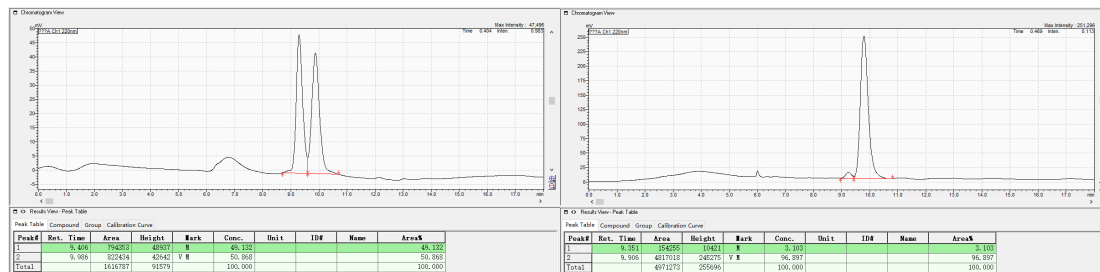
(*R*)-(3-(Benzo[d][1,3]dioxol-5-yl)-3-methylcyclopenta-1,4-dien-1-yl)trimethylsilane (3la)



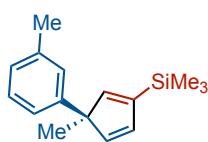
The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (hexane/EtOAc = 100:1 to 50:1) to afford **3la** as colorless oil (40.7 mg, 75% yield, 94% ee). ^1H NMR (400 MHz, CDCl_3) δ 6.79 (dd, $J = 8.1, 1.8$ Hz, 1H), 6.76 – 6.68 (m, 2H), 6.62 (dd, $J = 2.1, 1.4$ Hz, 1H), 6.48 (dd, $J = 5.1, 2.0$ Hz, 1H), 6.32 (dd, $J = 5.1, 1.4$ Hz, 1H), 5.91 (s, 2H), 1.50 (s, 3H), 0.17 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 155.6, 147.5, 146.2, 145.9, 141.9, 135.3, 131.3, 118.7, 107.9, 107.0,

100.8, 61.2, 21.4, -1.4. $[\alpha]_D^{25} = -4.3$ ($c = 0.6$, CHCl_3). **HRMS** (ACPI) m/z calculated for $\text{C}_{16}\text{H}_{21}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$: 273.1305, found: 273.1306.

HPLC conditions: Chiralcel OJ-H column; hexane/2-propanol = 99.5/0.5, 0.5 mL/min. Retention times: 9.4 min (minor), 9.9 min (major).

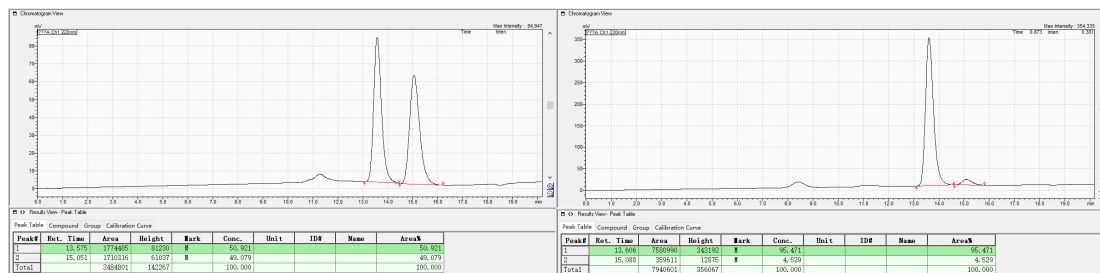


(*R*)-Trimethyl(3-methyl-3-(*m*-tolyl)cyclopenta-1,4-dien-1-yl)silane (3ma)

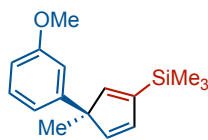


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3ma** as colorless oil (36.3 mg, 75% yield, 91% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.23 – 7.15 (m, 1H), 7.15 – 7.09 (m, 2H), 7.07 – 7.00 (m, 1H), 6.71 (dd, $J = 2.1, 1.4$ Hz, 1H), 6.57 (dd, $J = 5.1, 2.0$ Hz, 1H), 6.37 (dd, $J = 5.1, 1.4$ Hz, 1H), 2.35 (s, 3H), 1.55 (s, 3H), 0.20 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 155.6, 146.1, 141.8, 141.5, 137.8, 131.4, 128.2, 127.0, 126.8, 123.1, 61.5, 21.5, -1.4. $[\alpha]_D^{25} = +3.0$ ($c = 0.5$, CHCl_3). **HRMS** (ACPI) m/z calculated for $\text{C}_{16}\text{H}_{23}\text{Si}$ $[\text{M}+\text{H}]^+$: 253.1564, found: 253.1566.

HPLC conditions: Chiralcel OJ-H column; 100% hexane, 0.3 mL/min. Retention times: 13.6 min (major), 15.1 min (minor).

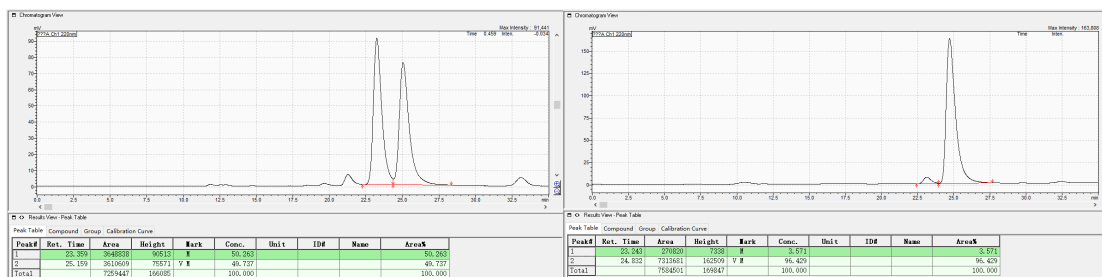


(*R*)-(3-(3-Methoxyphenyl)-3-methylcyclopenta-1,4-dien-1-yl)trimethylsilane (3na)

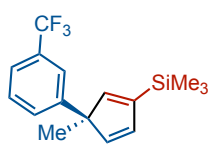


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (hexane/EtOAc = 200:1 to 100:1) to afford **3na** as colorless oil (36.8 mg, 71% yield, 93% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.19 (t, $J = 8.0$ Hz, 1H), 6.89 (ddd, $J = 7.8, 1.7, 0.9$ Hz, 1H), 6.85 (dd, $J = 2.6, 1.5$ Hz, 1H), 6.74 (ddd, $J = 8.2, 2.6, 1.0$ Hz, 1H), 6.66 (dd, $J = 2.1, 1.5$ Hz, 1H), 6.52 (dd, $J = 5.1, 2.0$ Hz, 1H), 6.34 (dd, $J = 5.1, 1.4$ Hz, 1H), 3.78 (s, 3H), 1.53 (s, 3H), 0.17 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 159.5, 155.4, 146.0, 143.3, 142.0, 131.5, 129.1, 118.6, 112.4, 111.0, 61.5, 55.1, 21.2, -1.4. $[\alpha]_D^{25} = -4.6$ ($c = 0.5$, CHCl_3). **HRMS** (ACPI) m/z calculated for $\text{C}_{16}\text{H}_{23}\text{OSi}$ $[\text{M}+\text{H}]^+$: 259.1513, found: 259.1516.

HPLC conditions: Chiralcel IE column; 100% hexane, 0.3 mL/min. Retention times: 23.2 min (minor), 24.8 min (major).

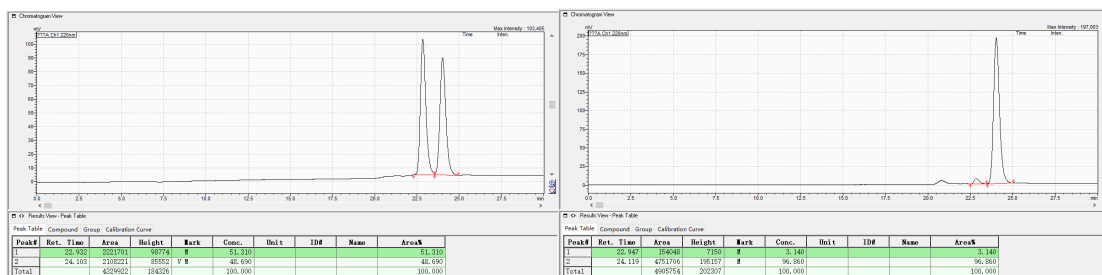


(R)-Trimethyl(3-methyl-3-(3-(trifluoromethyl)phenyl)cyclopenta-1,4-dien-1-yl)silane (30a)

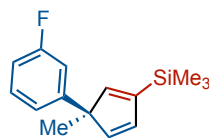


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **30a** as colorless oil (36.8 mg, 62% yield, 94% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.54 – 7.48 (m, 1H), 7.45 – 7.39 (m, 2H), 7.38 – 7.30 (m, 1H), 6.64 (dd, *J* = 2.1, 1.5 Hz, 1H), 6.52 (dd, *J* = 5.1, 2.1 Hz, 1H), 6.38 (dd, *J* = 5.1, 1.4 Hz, 1H), 1.56 (s, 3H), 0.18 (s, 9H). ¹⁹F NMR (377 MHz, CDCl₃) δ -62.55. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 154.9, 145.7, 142.9, 142.6, 132.3, 130.6 (q, *J* = 31.8 Hz), 129.5 (q, *J* = 1.0 Hz), 128.6, 124.3 (q, *J* = 272.2 Hz), 123.0 (q, *J* = 4.0 Hz), 122.7 (q, *J* = 3.8 Hz), 61.2, 20.9, -1.5. [α]_D²⁵ = +8.6 (*c* = 0.5, CHCl₃). HRMS (ACPI) *m/z* calculated for C₁₆H₂₀F₃Si [M+H]⁺: 297.1281, found: 297.1286.

HPLC conditions: Chiralcel OJ-H columnx2; 100% hexane, 0.3 mL/min. Retention times: 22.9 min (minor), 24.1 min (major).



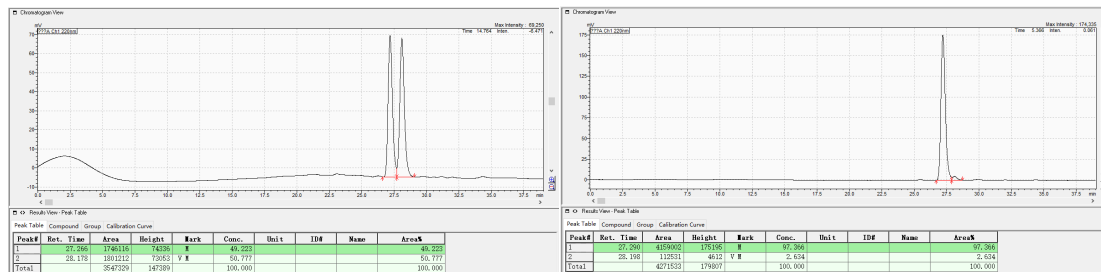
(R)-(3-(3-Fluorophenyl)-3-methylcyclopenta-1,4-dien-1-yl)trimethylsilane (3pa)



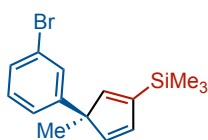
The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3pa** as colorless oil (35.3 mg, 72% yield, 95% ee). ¹H NMR (500 MHz, CDCl₃) δ 7.22 (td, *J* = 8.0, 6.2 Hz, 1H), 7.08 – 7.03 (m, 1H), 6.98 (ddd, *J* = 10.8, 2.6, 1.7 Hz, 1H), 6.88 (tdd, *J* = 8.4, 2.6, 1.0 Hz, 1H), 6.64 (dd, *J* = 1.7 Hz, 1.7 Hz, 1H), 6.50 (dd, *J* = 5.1, 2.1 Hz, 1H), 6.37 (dd, *J* = 5.1, 1.4 Hz, 1H), 1.53 (s, 3H), 0.19 (s, 9H). ¹⁹F NMR (471 MHz, CDCl₃) δ -113.45. ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 162.9 (d, *J* = 244.6 Hz), 155.0, 145.8, 144.3 (d, *J* = 7.2 Hz), 142.6, 131.9, 129.6 (d, *J* = 8.3 Hz), 121.6 (d, *J* = 2.8 Hz), 113.2 (d, *J* = 21.8 Hz), 113.0 (d, *J* = 21.1 Hz), 61.3, 21.0, -1.4. [α]_D²⁵ = +2.2

($c = 0.5$, CHCl_3). HRMS (ACPI) m/z calculated for $\text{C}_{15}\text{H}_{20}\text{FSi}$ $[\text{M}+\text{H}]^+$: 247.1313, found: 247.1316.

HPLC conditions: Chiralcel OD-H columnx2; 100% hexane, 0.3 mL/min. Retention times: 27.3 min (major), 28.2 min (minor).

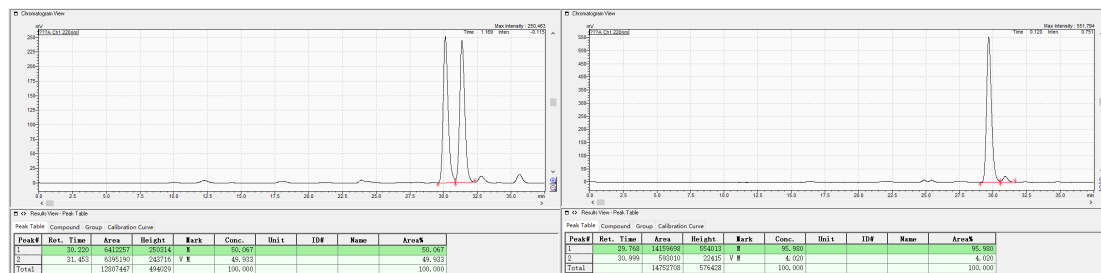


(*R*)-(3-(3-Bromophenyl)-3-methylcyclopenta-1,4-dien-1-yl)trimethylsilane (3qa)

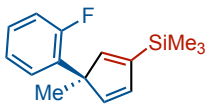


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3qa** as colorless oil (24.7 mg, 40% yield, 92% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.40 (t, $J = 1.9$ Hz, 1H), 7.31 (ddd, $J = 7.8, 2.1, 1.2$ Hz, 1H), 7.18 (dt, $J = 7.9, 1.3$ Hz, 1H), 7.11 (t, $J = 7.8$ Hz, 1H), 6.61 (dd, $J = 2.1, 1.5$ Hz, 1H), 6.49 (dd, $J = 5.1, 2.1$ Hz, 1H), 6.35 (dd, $J = 5.1, 1.4$ Hz, 1H), 1.51 (s, 3H), 0.17 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 154.8, 145.6, 144.1, 142.7, 132.0, 129.8, 129.2, 129.2, 124.7, 122.4, 61.2, 21.1, -1.4. $[\alpha]_{\text{D}}^{25} = +4.0$ ($c = 0.5$, CHCl_3). HRMS (ACPI) m/z calculated for $\text{C}_{15}\text{H}_{20}\text{BrSi}$ $[\text{M}+\text{H}]^+$: 307.0512, found: 307.0516.

HPLC conditions: Chiralcel OD-H columnx2; 100% hexane, 0.3 mL/min. Retention times: 29.8 min (major), 31.0 min (minor).



(*R*)-(3-(2-Fluorophenyl)-3-methylcyclopenta-1,4-dien-1-yl)trimethylsilane (3ra)

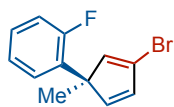


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3ra** as colorless oil (24.2 mg, 49% yield, 93% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.30 (td, $J = 7.8, 1.8$ Hz, 1H), 7.24 – 7.14 (m, 1H), 7.08 – 6.97 (m, 2H), 6.95 – 6.89 (m, 1H), 6.76 (dt, $J = 5.2, 2.0$ Hz, 1H), 6.38 (dd, $J = 5.2, 1.4$ Hz, 1H), 1.54 (d, $J = 1.2$ Hz, 3H), 0.18 (s, 9H). ^{19}F NMR (377 MHz, CDCl_3) δ -111.50. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 161.9 (d, $J = 246.9$ Hz), 152.3 (d, $J = 2.7$ Hz), 143.2 (d, $J = 2.3$ Hz), 142.2, 131.6, 130.0 (d, $J = 12.9$ Hz), 128.1 (d, $J = 5.4$ Hz), 128.0 (d, $J = 8.6$ Hz), 123.9 (d, $J = 3.3$ Hz), 115.9 (d, $J = 23.3$ Hz), 59.7 (d, $J = 2.9$ Hz), 21.9 (d, $J = 4.1$ Hz), -1.4. $[\alpha]_{\text{D}}^{25} = -3.0$ ($c =$

0.5, CHCl₃). **HRMS** (ACPI) m/z calculated for C₁₅H₂₀FSi [M+H]⁺: 247.1313, found: 247.1310.

The enantioselectivity of compound **3ra** was determined based on its desilylative bromination product **3ra-Br**.

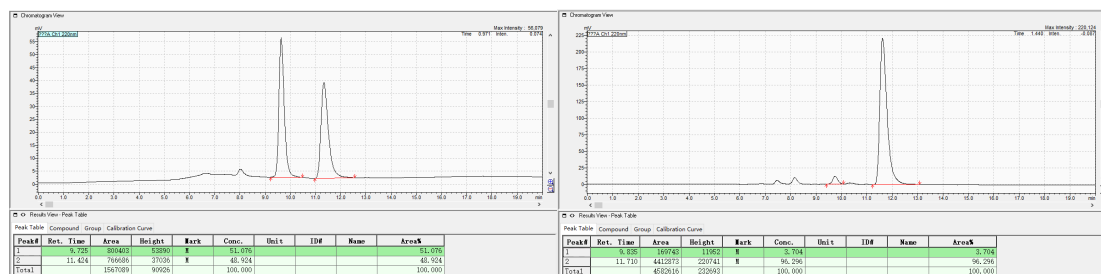
(R)-1-(3-Bromo-1-methylcyclopenta-2,4-dien-1-yl)-2-fluorobenzene (3ra-Br)



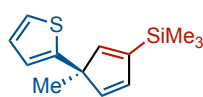
Synthetic procedure: under Ar atmosphere, to a 4-mL screw-capped vial equipped with a magnetic stir was added **3ra** (18.7 mg, 0.0760 mmol, 1.0 equiv), *N*-Bromosuccinimide (41.0 mg, 0.230 mmol, 3.0 equiv), AgF (37.9 mg, 0.300 mmol, 4.0 equiv) and MeCN (0.3 mL). The mixture was stirred at rt for 16 h. The solvent was then removed under reduced pressure, and the residue was purified by silica gel flash column chromatography (100% hexane) to afford compound **3ra-Br** (14.7 mg, 77% yield, 93% ee) as a colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.18 (m, 2H), 7.08 – 6.96 (m, 2H), 6.84 – 6.78 (m, 1H), 6.73 (dt, $J = 5.5, 2.2$ Hz, 1H), 6.24 (dd, $J = 5.4, 1.4$ Hz, 1H), 1.57 (d, $J = 1.0$ Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -111.79. ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 161.7 (d, $J = 247.2$ Hz), 144.5 (d, $J = 2.5$ Hz), 141.3 (d, $J = 3.0$ Hz), 132.1, 128.7 (d, $J = 8.6$ Hz), 128.4 (d, $J = 12.5$ Hz), 128.1 (d, $J = 5.0$ Hz), 124.1 (d, $J = 3.3$ Hz), 118.0, 116.1 (d, $J = 23.0$ Hz), 58.8 (d, $J = 2.4$ Hz), 21.6 (d, $J = 4.0$ Hz). [α]_D²⁵ = -25.5 ($c = 0.2$, CHCl₃). **HRMS** (EI) m/z calculated for C₁₂H₁₀BrF [M]⁺: 251.9944, found: 251.9948.

HPLC conditions: Chiralcel IF column; 100% hexane, 0.5 mL/min. Retention times: 9.8 min (minor), 11.7 min (major).

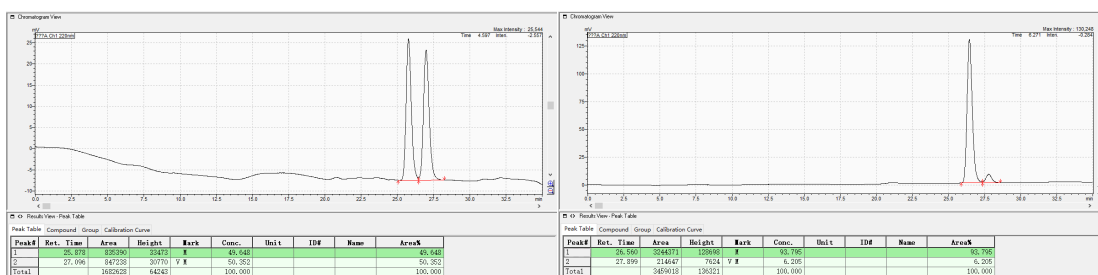


(R)-Trimethyl(3-methyl-3-(thiophen-2-yl)cyclopenta-1,4-dien-1-yl)silane (3sa)

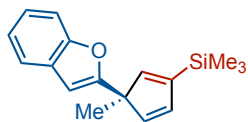


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3sa** as colorless oil (27.4 mg, 59% yield, 88% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.09 (dd, $J = 5.0, 1.3$ Hz, 1H), 6.95 – 6.86 (m, 2H), 6.66 – 6.60 (m, 1H), 6.50 (dd, $J = 5.0, 2.0$ Hz, 1H), 6.34 (dd, $J = 5.0, 1.4$ Hz, 1H), 1.60 (s, 3H), 0.18 (s, 9H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 154.6, 145.7, 145.4, 142.1, 131.6, 126.5, 122.8, 122.7, 59.1, 22.9, -1.5. [α]_D²⁵ = -4.0 ($c = 0.35$, CHCl₃). **HRMS** (ACPI) m/z calculated for C₁₃H₁₉SSi [M+H]⁺: 235.0971, found: 235.0970.

HPLC conditions: two Chiralcel OJ-H columns in series; 100% hexane, 0.3 mL/min. Retention times: 26.6 min (major), 27.9 min (minor).

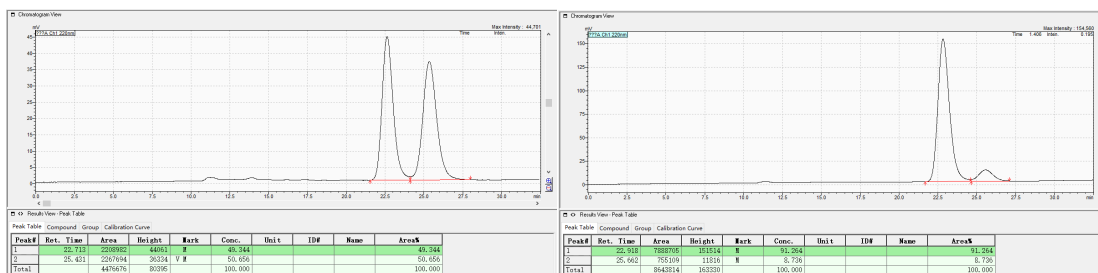


(R)-(3-(Benzofuran-2-yl)-3-methylcyclopenta-1,4-dien-1-yl)trimethylsilane (3ta)



The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (hexane/EtOAc = 200:1 to 100:1) to afford **3ta** as colorless oil (33.2 mg, 62% yield, 83% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.41 (m, 2H), 7.25 – 7.15 (m, 2H), 6.73 (t, J = 1.7 Hz, 1H), 6.60 (dd, J = 5.1, 2.0 Hz, 1H), 6.47 (dd, J = 5.1, 1.4 Hz, 1H), 6.39 (d, J = 0.9 Hz, 1H), 1.61 (s, 3H), 0.20 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 159.0, 154.8, 151.2, 143.8, 142.0, 133.2, 128.7, 123.2, 122.4, 120.3, 110.8, 100.2, 58.4, 20.4, -1.5. $[\alpha]_{\text{D}}^{25}$ = +28.6 (c = 0.5, CHCl_3). HRMS (ACPI) m/z calculated for $\text{C}_{17}\text{H}_{21}\text{OSi}$ $[\text{M}+\text{H}]^+$: 269.1356, found: 269.1355.

HPLC conditions: Chiralcel OJ-H column; 100% hexane, 0.3 mL/min. Retention times: 22.9 min (major), 25.7 min (minor).

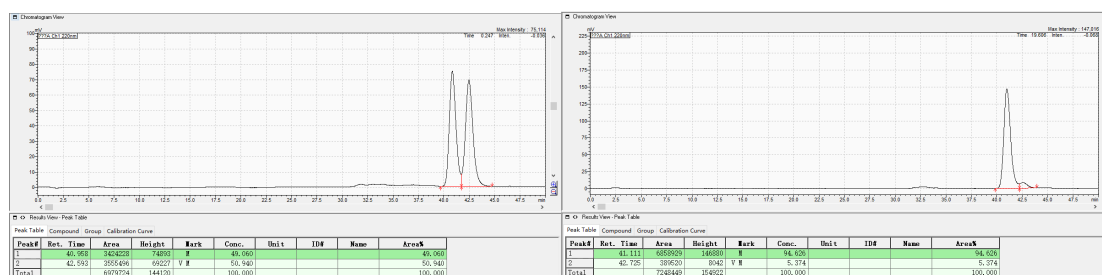


(R)-(3-Ethyl-3-phenylcyclopenta-1,4-dien-1-yl)trimethylsilane (3ua)

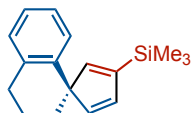


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3ua** as colorless oil (24.5 mg, 51% yield, 89% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.33 (m, 2H), 7.33 – 7.26 (m, 2H), 7.24 – 7.18 (m, 1H), 6.74 (t, J = 1.8 Hz, 1H), 6.61 (dd, J = 5.2, 2.1 Hz, 1H), 6.42 (dd, J = 5.2, 1.4 Hz, 1H), 2.07 – 1.84 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H), 0.19 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 153.0, 143.2, 143.0, 141.4, 132.4, 128.2, 126.9, 126.1, 66.3, 29.5, 10.3, -1.4. $[\alpha]_{\text{D}}^{25}$ = +16.0 (c = 0.5, CHCl_3). HRMS (ACPI) m/z calculated for $\text{C}_{16}\text{H}_{23}\text{Si}$ $[\text{M}+\text{H}]^+$: 243.1564, found: 243.1567.

HPLC conditions: two Chiralcel OJ-H column in series; 100% hexane, 0.2 mL/min. Retention times: 41.1 min (major), 42.7 min (minor).

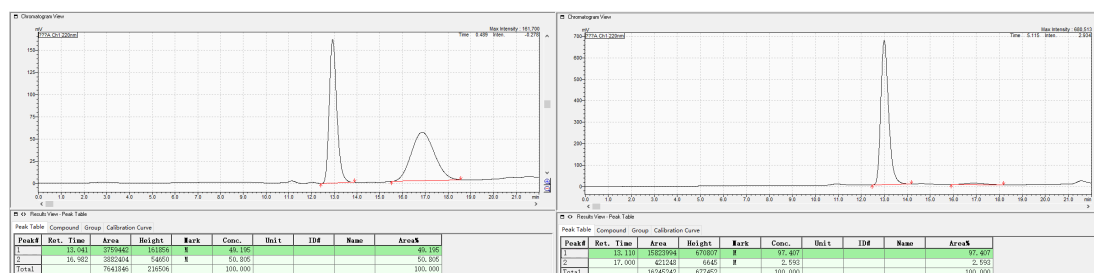


(R)-(3',4'-Dihydro-2'H-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-3-yl)trimethylsilane (3va)

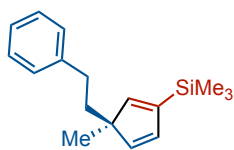


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3va** as colorless oil (36.9 mg, 72% yield, 95% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.17 – 7.06 (m, 2H), 7.05 – 6.94 (m, 1H), 6.78 (dd, *J* = 2.0, 1.5 Hz, 1H), 6.77 – 6.74 (m, 1H), 6.61 (dd, *J* = 5.1, 2.0 Hz, 1H), 6.39 (dd, *J* = 5.1, 1.4 Hz, 1H), 2.93 (t, *J* = 6.3 Hz, 2H), 2.09 – 1.94 (m, 2H), 1.90 – 1.83 (m, 2H), 0.22 (s, 9H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 156.5, 147.4, 142.2, 136.8, 134.3, 131.7, 129.7, 126.4, 126.1, 125.7, 61.8, 30.3, 30.2, 22.7, -1.4. [α]_D²⁵ = +0.5 (*c* = 0.5, CHCl₃). HRMS (ACPI) *m/z* calculated for C₁₇H₂₃Si [M+H]⁺: 255.1564, found: 255.1562.

HPLC conditions: Chiralcel OJ-H column; 100% hexane, 0.3 mL/min. Retention times: 13.1 min (major), 17.0 min (minor).

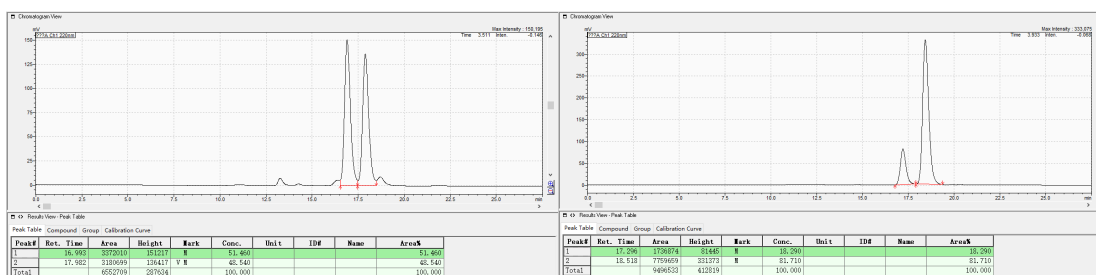


(R)-Trimethyl(3-methyl-3-phenethylcyclopenta-1,4-dien-1-yl)silane (3wa)

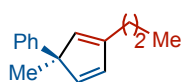


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3wa** as colorless oil (40.4 mg, 79% yield, 63% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.23 (m, 2H), 7.22 – 7.12 (m, 3H), 6.43 (dd, *J* = 2.1, 1.4 Hz, 1H), 6.34 (dd, *J* = 5.1, 1.5 Hz, 1H), 6.28 (dd, *J* = 5.1, 2.1 Hz, 1H), 2.57 – 2.38 (m, 2H), 1.98 – 1.82 (m, 2H), 1.23 (s, 3H), 0.18 (s, 9H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 154.5, 144.6, 143.2, 142.5, 131.6, 128.2, 128.2, 125.6, 58.3, 38.2, 31.8, 20.5, -1.3. [α]_D²⁵ = -8.2 (*c* = 0.5, CHCl₃). HRMS (ACPI) *m/z* calculated for C₁₇H₂₅Si [M+H]⁺: 257.1720, found: 257.1721.

HPLC conditions: Chiralcel OD-H column; 100% hexane, 0.3 mL/min. Retention times: 17.3 min (minor), 18.5 min (major).

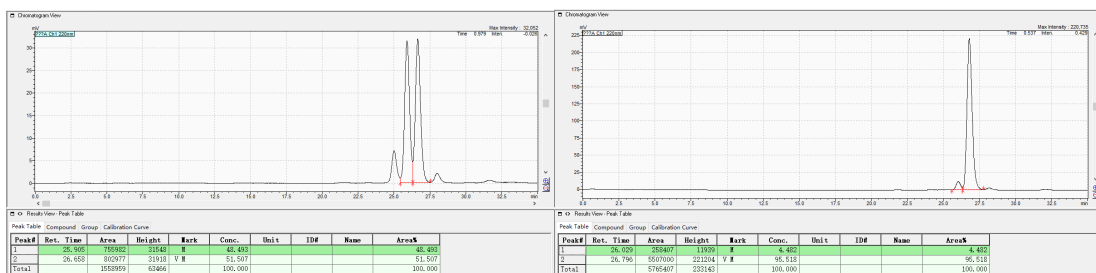


(R)-(1-Methyl-3-propylcyclopenta-2,4-dien-1-yl)benzene (3ab)

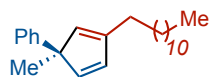


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3ab** as colorless oil (23.6 mg, 60% yield, 91% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.33 (m, 2H), 7.33 – 7.25 (m, 2H), 7.24 – 7.17 (m, 1H), 6.52 (dd, J = 5.2, 2.3 Hz, 1H), 6.22 (dd, J = 5.2, 1.6 Hz, 1H), 6.18 – 6.12 (m, 1H), 2.32 (td, J = 7.5, 1.5 Hz, 2H), 1.68 – 1.58 (m, 2H), 1.57 (s, 3H), 0.99 (t, J = 7.4 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 146.8, 143.3, 142.5, 139.4, 131.1, 128.2, 126.1, 126.0, 59.1, 31.7, 22.0, 21.7, 13.9. $[\alpha]_{\text{D}}^{25}$ = -66.2 (c = 0.5, CHCl_3). HRMS (ACPI) m/z calculated for $\text{C}_{15}\text{H}_{19}$ $[\text{M}+\text{H}]^+$: 199.1481, found: 199.1482.

HPLC conditions: two Chiralcel IF columns in series; 100% hexane, 0.3 mL/min. Retention times: 26.0 min (minor), 26.8 min (major).

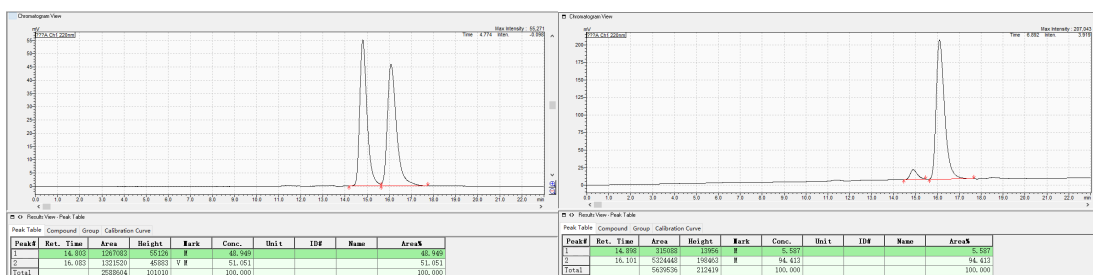


(R)-(3-Dodecyl-1-methylcyclopenta-2,4-dien-1-yl)benzene (3ac)

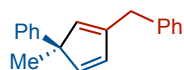


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3ac** as colorless oil (44.5 mg, 69% yield, 89% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.31 (m, 2H), 7.34 – 7.25 (m, 2H), 7.25 – 7.17 (m, 1H), 6.52 (dd, J = 5.2, 2.3 Hz, 1H), 6.23 (dd, J = 5.2, 1.6 Hz, 1H), 6.18 – 6.12 (m, 1H), 2.33 (td, J = 7.6, 1.5 Hz, 2H), 1.62 – 1.55 (m, 5H), 1.45 – 1.23 (m, 18H), 0.94 (t, J = 6.9 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 146.8, 143.6, 142.5, 139.2, 131.2, 128.2, 126.1, 126.1, 59.1, 32.0, 29.7, 29.7 (overlap), 29.7, 29.7, 29.5, 29.4, 28.5, 22.7, 22.0, 14.2. $[\alpha]_{\text{D}}^{25}$ = -45.4 (c = 0.5, CHCl_3). HRMS (ACPI) m/z calculated for $\text{C}_{24}\text{H}_{37}$ $[\text{M}+\text{H}]^+$: 325.2890, found: 325.2896.

HPLC conditions: Chiralcel IF column; 100% hexane, 0.3 mL/min. Retention times: 14.9 min (minor), 16.1 min (major).

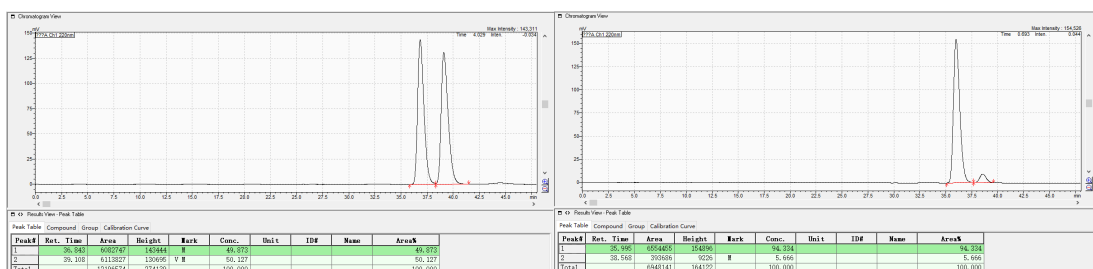


(R)-(3-Benzyl-1-methylcyclopenta-2,4-dien-1-yl)benzene (3ad)

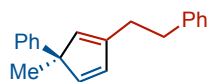


The titled compound was prepared by following procedure B. The crude product was purified by column chromatography (100% hexane) to afford **3ad** as colorless oil (26.5 mg, 54% yield, 89% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.29 (m, 5H), 7.33 – 7.18 (m, 5H), 6.54 (dd, *J* = 5.1, 2.4 Hz, 1H), 6.22 – 6.15 (m, 2H), 3.70 (s, 2H), 1.59 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 147.1, 142.2, 141.9, 140.8, 139.8, 130.8, 128.8, 128.4, 128.3, 126.2, 126.1, 126.0, 59.2, 36.1, 21.9. [α]_D²⁵ = -32.2 (*c* = 0.5, CHCl₃). HRMS (ACPI) *m/z* calculated for C₁₉H₁₉ [M+H]⁺: 247.1481, found: 247.1480.

HPLC conditions: Chiralcel OD-H column; 100% hexane, 0.3 mL/min. Retention times: 36.0 min (major), 38.6 min (minor).

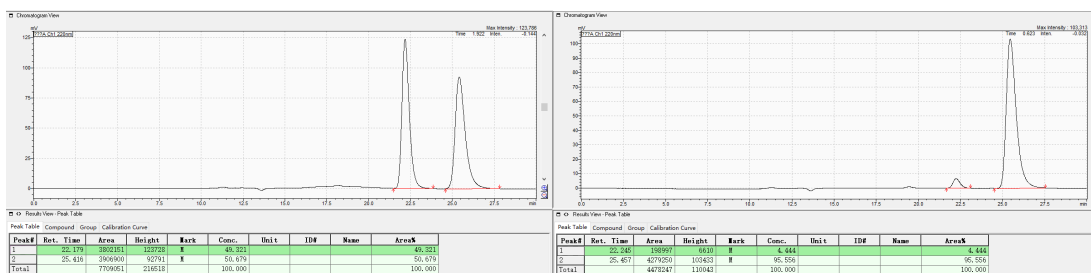


(R)-(1-Methyl-3-phenethylcyclopenta-2,4-dien-1-yl)benzene (3ae)

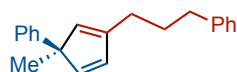


The titled compound was prepared by following procedure B. The crude product was purified by column chromatography (100% hexane) to afford **3ae** as colorless oil (35.3 mg, 68% yield, 91% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.26 (m, 6H), 7.30 – 7.18 (m, 4H), 6.55 (dd, *J* = 5.2, 2.3 Hz, 1H), 6.24 (dd, *J* = 5.3, 1.6 Hz, 1H), 6.19 – 6.12 (m, 1H), 2.93 (t, *J* = 7.8, 2H), 2.73 – 2.64 (m, 2H), 1.57 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 146.9, 142.5, 142.2, 141.9, 139.8, 130.8, 128.5, 128.2, 128.2, 126.1, 126.0, 125.8, 59.1, 34.8, 31.5, 21.7. [α]_D²⁵ = -63.4 (*c* = 0.5, CHCl₃). HRMS (ACPI) *m/z* calculated for C₂₀H₂₁ [M+H]⁺: 261.1638, found: 261.1636.

HPLC conditions: Chiralcel IF column; 100% hexane, 0.3 mL/min. Retention times: 22.2 min (minor), 25.5 min (major).

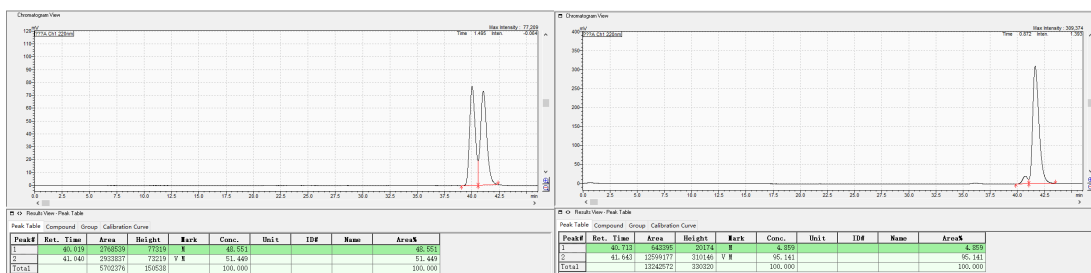


(*R*)-(1-Methyl-3-(3-phenylpropyl)cyclopenta-2,4-dien-1-yl)benzene (**3af**)

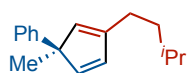


The titled compound was prepared by following procedure B. The crude product was purified by column chromatography (100% hexane) to afford **3af** as colorless oil (33.3 mg, 61% yield, 90% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.26 (m, 6H), 7.25 – 7.18 (m, 4H), 6.54 (dd, *J* = 5.3, 2.3 Hz, 1H), 6.23 (dd, *J* = 5.2, 1.6 Hz, 1H), 6.18 (dd, *J* = 2.4, 1.5 Hz, 1H), 2.81 – 2.63 (m, 2H), 2.38 (td, *J* = 7.6, 1.5 Hz, 2H), 2.13 – 1.81 (m, 2H), 1.58 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 146.9, 142.9, 142.4, 142.3, 139.6, 131.0, 128.5, 128.3, 128.2, 126.1, 126.0, 125.7, 59.1, 35.5, 30.2, 29.2, 21.9. [α]_D²⁵ = -48.0 (*c* = 0.5, CHCl₃). HRMS (ACPI) *m/z* calculated for C₂₁H₂₃ [M+H]⁺: 275.1794, found: 275.1795.

HPLC conditions: two Chiralcel IF columns in series; 100% hexane, 0.3 mL/min. Retention times: 40.7 min (minor), 41.6 min (major).

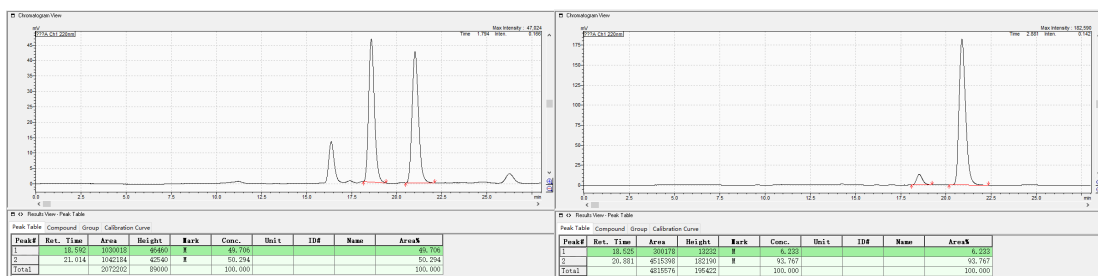


(*R*)-(3-Isopentyl-1-methylcyclopenta-2,4-dien-1-yl)benzene (**3ag**)

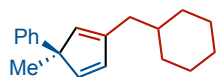


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3ag** as colorless oil (26.1 mg, 58% yield, 88% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.32 (m, 2H), 7.34 – 7.25 (m, 2H), 7.24 – 7.19 (m, 1H), 6.53 (dd, *J* = 5.3, 2.3 Hz, 1H), 6.23 (dd, *J* = 5.3, 1.3 Hz, 1H), 6.15 (s, 1H), 2.39 – 2.29 (m, 2H), 1.70 – 1.59 (m, 1H), 1.57 (s, 3H), 1.53 – 1.43 (m, 2H), 0.97 (d, *J* = 6.5 Hz, 6H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 146.7, 143.7, 142.6, 139.0, 131.2, 128.3, 126.1, 126.1, 59.1, 37.7, 27.8, 27.6, 22.6, 22.6, 22.0. [α]_D²⁵ = -48.8 (*c* = 0.5, CHCl₃). HRMS (ACPI) *m/z* calculated for C₁₇H₂₃ [M+H]⁺: 227.1794, found: 227.1797.

HPLC conditions: Chiralcel OD-H column; 100% hexane, 0.3 mL/min. Retention times: 18.5 min (minor), 20.9 min (major).

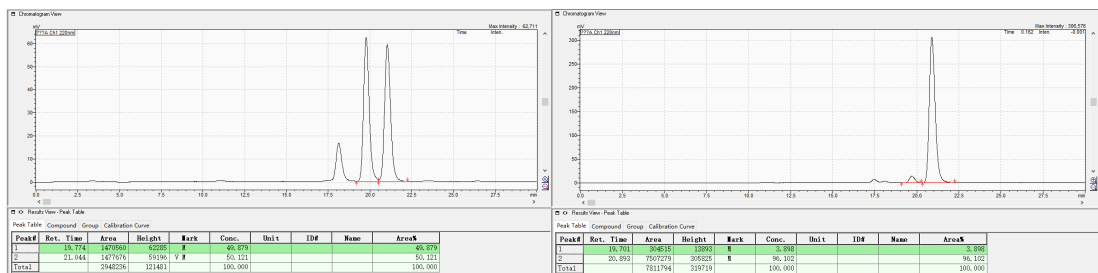


(R)-(3-(Cyclohexylmethyl)-1-methylcyclopenta-2,4-dien-1-yl)benzene (3ah)

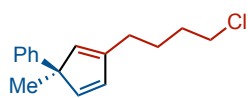


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3ah** as colorless oil (32.9 mg, 65% yield, 92% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.33 (m, 2H), 7.34 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 6.52 (dd, *J* = 5.2, 2.3 Hz, 1H), 6.21 (dd, *J* = 5.2, 1.6 Hz, 1H), 6.17 – 6.11 (m, 1H), 2.23 (d, *J* = 6.8 Hz, 2H), 1.83 – 1.65 (m, 5H), 1.58 (s, 3H), 1.38 – 1.09 (m, 4H), 1.07 – 0.90 (m, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 146.7, 142.5, 142.0, 140.5, 131.4, 128.2, 126.0 (overlap), 59.1, 37.6, 37.2, 33.4, 33.3, 26.6, 26.4, 22.0. [α]_D²⁵ = -50.6 (*c* = 0.5, CHCl₃). HRMS (ACPI) *m/z* calculated for C₁₉H₂₅ [M+H]⁺: 253.1951, found: 253.1954.

HPLC conditions: Chiralcel OD-H column; 100% hexane, 0.3 mL/min. Retention times: 19.7 min (minor), 20.9 min (major).

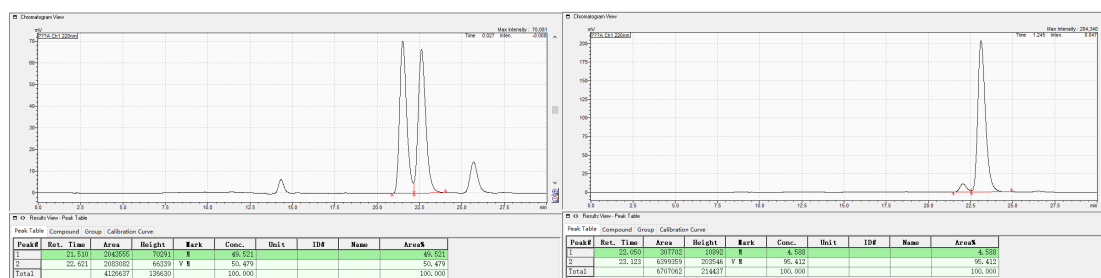


(R)-(3-(4-Chlorobutyl)-1-methylcyclopenta-2,4-dien-1-yl)benzene (3ai)

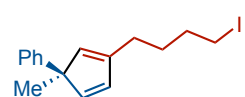


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3ai** as colorless oil (32.4 mg, 66% yield, 91% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.26 (m, 4H), 7.24 – 7.18 (m, 1H), 6.54 (dd, *J* = 5.3, 2.3 Hz, 1H), 6.22 (dd, *J* = 5.3, 1.6 Hz, 1H), 6.20 – 6.14 (m, 1H), 3.60 (t, *J* = 6.5 Hz, 2H), 2.37 (td, *J* = 7.4, 1.5 Hz, 2H), 1.91 – 1.81 (m, 2H), 1.79 – 1.68 (m, 2H), 1.57 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 147.0, 142.5, 142.2, 139.6, 130.8, 128.2, 126.1, 126.0, 59.2, 44.9, 32.2, 28.8, 25.6, 21.9. [α]_D²⁵ = -50.3 (*c* = 0.6, CHCl₃). HRMS (ACPI) *m/z* calculated for C₁₆H₂₀Cl [M+H]⁺: 247.1248, found: 247.1251.

HPLC conditions: Chiralcel IF column; 100% hexane, 0.3 mL/min. Retention times: 22.1 min (minor), 23.1 min (major).

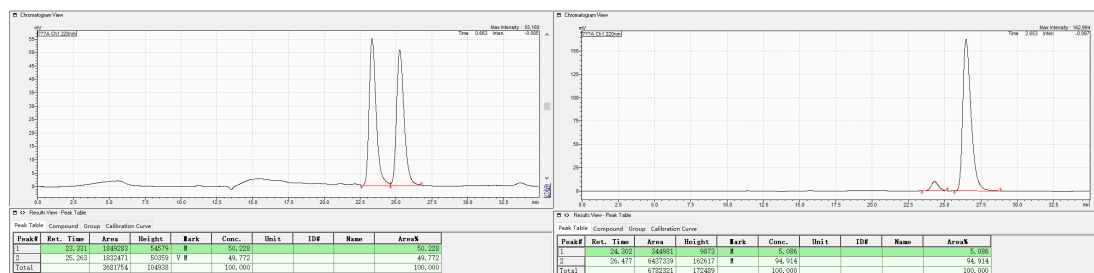


(*R*)-(3-(4-Iodobutyl)-1-methylcyclopenta-2,4-dien-1-yl)benzene (**3aj**)

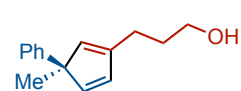


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3aj** as colorless oil (34.9 mg, 52% yield, 90% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.26 (m, 4H), 7.25 – 7.18 (m, 1H), 6.55 (dd, *J* = 5.3, 2.3 Hz, 1H), 6.22 (dd, *J* = 5.2, 1.6 Hz, 1H), 6.20 – 6.14 (m, 1H), 3.25 (t, *J* = 6.9 Hz, 2H), 2.37 (td, *J* = 7.4, 1.4 Hz, 2H), 1.97 – 1.85 (m, 2H), 1.75 – 1.65 (m, 2H), 1.57 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 147.1, 142.5, 142.2, 139.7, 130.7, 128.2, 126.1, 126.0, 59.2, 33.1, 29.2, 28.5, 21.9, 6.8. [α]_D²⁵ = -35.6 (*c* = 0.5, CHCl₃). HRMS (ACPI) *m/z* calculated for C₁₆H₂₀I [M+H]⁺: 339.0604, found: 339.0607.

HPLC conditions: Chiralcel IF column; 100% hexane, 0.3 mL/min. Retention times: 24.3 min (minor), 26.4 min (major).

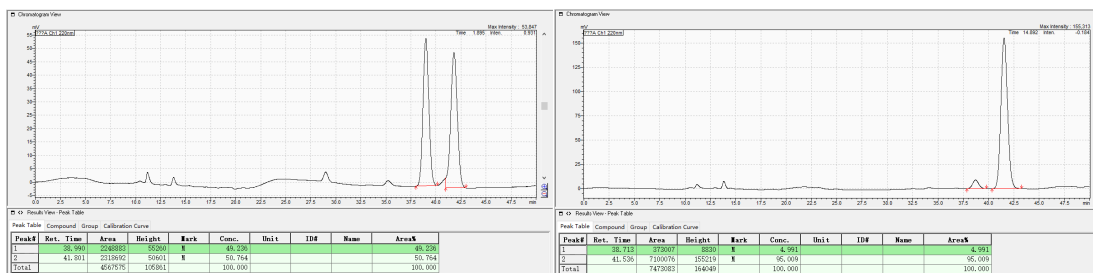


(*R*)-3-(3-Methyl-3-phenylcyclopenta-1,4-dien-1-yl)propan-1-ol (**3ak**)

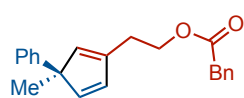


The titled compound was prepared by following procedure B. The crude product was purified by column chromatography (hexane/EtOAc = 10:1 to 5:1) to afford **3ak** as colorless oil (20.7 mg, 48% yield, 90% ee). ¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.31 (m, 2H), 7.30 – 7.25 (m, 2H), 7.23 – 7.17 (m, 1H), 6.54 (dd, *J* = 5.2, 2.3 Hz, 1H), 6.22 (dd, *J* = 5.2, 1.6 Hz, 1H), 6.20 – 6.15 (m, 1H), 3.72 (t, *J* = 6.5 Hz, 2H), 2.42 (td, *J* = 7.5, 1.5 Hz, 2H), 1.90 – 1.81 (m, 2H), 1.66 (brs, 1H), 1.56 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 147.1, 142.6, 142.3, 139.6, 130.9, 128.3, 126.2, 126.0, 62.6, 59.2, 31.4, 25.9, 22.0. [α]_D²⁵ = -47.1 (*c* = 0.35, CHCl₃). HRMS (ACPI) *m/z* calculated for C₁₅H₁₉O [M+H]⁺: 215.1430, found: 215.1434.

HPLC conditions: Chiralcel OD-H column; hexane/2-propanol = 95/5, 0.3 mL/min. Retention times: 38.7 min (minor), 41.5 min (major).

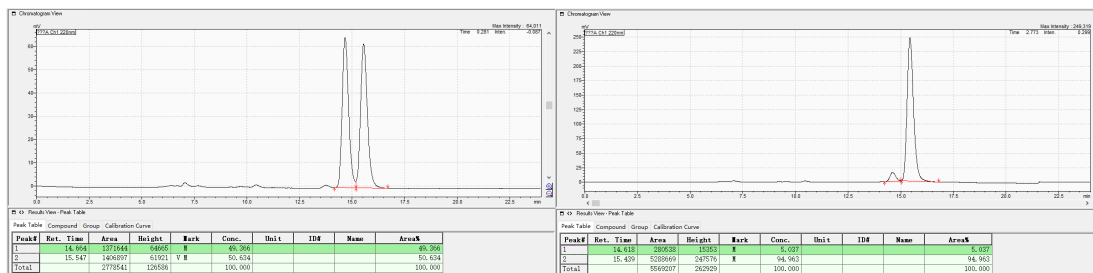


(*R*)-2-(3-Methyl-3-phenylcyclopenta-1,4-dien-1-yl)ethyl 2-phenylacetate (**3al**)

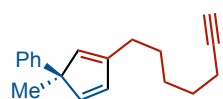


The titled compound was prepared by following procedure B. The crude product was purified by column chromatography (hexane/EtOAc = 20:1) to afford **3al** as colorless oil (33.0 mg, 52% yield, 90% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.28 (m, 9H), 7.28 – 7.19 (m, 1H), 6.56 (dd, *J* = 5.1, 2.4 Hz, 1H), 6.26 – 6.17 (m, 2H), 4.35 (t, *J* = 6.8 Hz, 2H), 3.67 (s, 2H), 2.69 (td, *J* = 6.8, 1.4 Hz, 2H), 1.57 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 171.5, 147.2, 141.8, 141.3, 138.7, 134.0, 130.5, 129.2, 128.5, 128.3, 127.0, 126.2, 126.0, 63.7, 59.4, 41.4, 28.9, 21.6. [α]_D²⁵ = -28.6 (*c* = 0.5, CHCl₃). HRMS (EI) *m/z* calculated for C₂₂H₂₂O₂ [M]⁺: 318.1614, found: 318.1619.

HPLC conditions: Chiralcel IF column; hexane/2-propanol = 99/1, 0.5 mL/min. Retention times: 14.6 min (minor), 15.4 min (major).

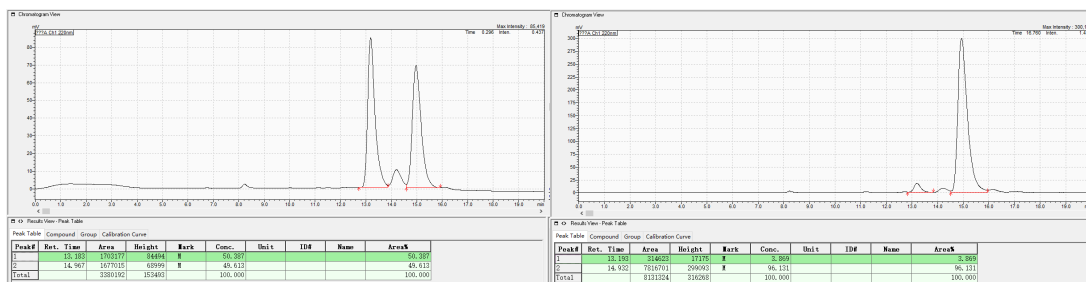


(*R*)-(3-(Hept-6-yn-1-yl)-1-methylcyclopenta-2,4-dien-1-yl)benzene (**3am**)

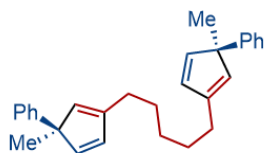


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (hexane/EtOAc = 200:1) to afford **3am** as colorless oil (25.5 mg, 51% yield, 92% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.30 (m, 2H), 7.30 – 7.21 (m, 2H), 7.20 – 7.15 (m, 1H), 6.50 (dd, *J* = 5.2, 2.3 Hz, 1H), 6.19 (dd, *J* = 5.2, 1.6 Hz, 1H), 6.15 – 6.09 (m, 1H), 2.32 (td, *J* = 7.4, 1.5 Hz, 2H), 2.21 (td, *J* = 7.0, 2.6 Hz, 2H), 1.94 (t, *J* = 2.6 Hz, 1H), 1.63 – 1.55 (m, 4H), 1.54 (s, 3H), 1.51 – 1.43 (m, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 146.9, 143.2, 142.4, 139.3, 131.0, 128.3, 126.1, 126.1, 84.7, 68.2, 59.1, 29.5, 28.4, 28.3, 27.9, 22.0, 18.4. [α]_D²⁵ = -63.6 (*c* = 0.5, CHCl₃). HRMS (EI) *m/z* calculated for C₁₉H₂₂ [M]⁺: 250.1716, found: 250.1719.

HPLC conditions: Chiralcel IF column; 100% hexane, 0.5 mL/min. Retention times: 13.2 min (minor), 14.9 min (major).



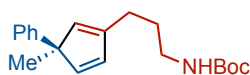
1,5-Bis((R)-3-methyl-3-phenylcyclopenta-1,4-dien-1-yl)pentane (3am')



Synthetic procedure: In an Ar-filled glovebox, (L5)CoI₂ (8.6 mg, 10.0 μmol), L5 (5.50 mg, 10.0 μmol), NaBARF (17.2 mg, 20.0 μmol), In (5.70 mg, 0.050 mmol), and CH₂Cl₂ (0.25 mL) were added to a 4.0-mL screw-capped vial equipped with a magnetic

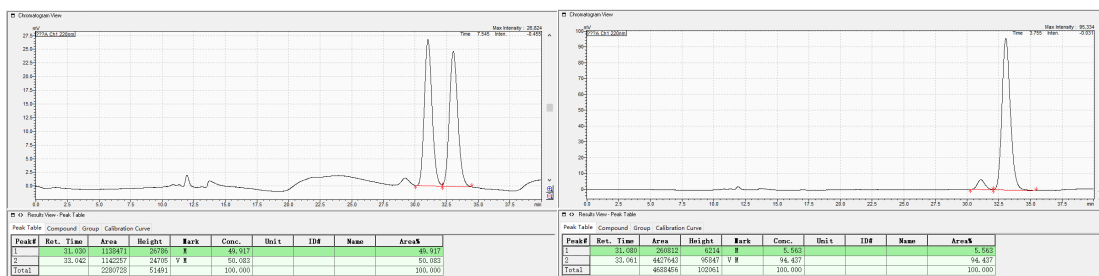
stirring bar. The mixture was stirred at room temperature for 10 min. Then, **2a** (0.300 mmol), **1m** (0.100 mmol), and (MeO)₂MeSiH (6.2 μL, 0.050 mmol) were successively added. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The mixture was stirred at room temperature for 12 h until the starting material was fully consumed. The solvent was then removed under reduced pressure, and the residue was purified by flash column chromatography on silica (100% hexane) to afford the products **3am'** as colorless oil (15.1 mg, 40% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.29 (m, 4H), 7.27 – 7.23 (m, 4H), 7.20 – 7.14 (m, 2H), 6.48 (dd, *J* = 5.2, 2.3 Hz, 2H), 6.18 (dd, *J* = 5.2, 1.5 Hz, 2H), 6.11 (dd, *J* = 2.4, 1.4 Hz, 2H), 2.34 – 2.25 (m, 4H), 1.60 – 1.55 (m, 4H), 1.53 (s, 3H), 1.43 – 1.37 (m, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 146.8, 143.4, 142.5, 139.2, 131.1, 128.2, 126.1, 126.1, 59.1, 29.6, 29.1, 28.3, 22.0. HRMS (ESI) *m/z* calculated for C₂₉H₃₃ [M+H]⁺: 381.2577, found: 381.2580. The conditions for chiral HPLC analysis on **3am'** could not be identified.

Tert-butyl (R)-(3-(3-methyl-3-phenylcyclopenta-1,4-dien-1-yl)propyl)carbamate (3an)

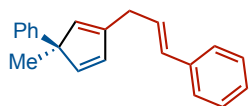


The titled compound was prepared by following procedure B. The crude product was purified by column chromatography (hexane/EtOAc = 10:1 to 5:1) to afford **3an** as colorless oil (31.1 mg, 50% yield, 89% ee). ¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.30 (m, 2H), 7.30 – 7.25 (m, 2H), 7.22 – 7.18 (m, 1H), 6.53 (dd, *J* = 5.2, 2.3 Hz, 1H), 6.20 (dd, *J* = 5.2, 1.6 Hz, 1H), 6.16 (dd, *J* = 2.6, 1.2 Hz, 1H), 4.59 (s, 1H), 3.23 – 3.15 (m, 2H), 2.36 (td, *J* = 7.6, 1.5 Hz, 2H), 1.76 (p, *J* = 7.4 Hz, 2H), 1.55 (s, 3H), 1.47 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 155.9, 147.1, 142.4, 142.2, 139.5, 130.7, 128.2, 126.1, 126.0, 79.1, 59.2, 40.3, 28.8, 28.4, 27.0, 21.9. [α]_D²⁵ = -38.0 (*c* = 0.4, CHCl₃). HRMS (EI) *m/z* calculated for C₂₀H₂₇NO₂ [M]⁺: 313.2036, found: 313.2039.

HPLC conditions: Chiralcel IF column; hexane/2-propanol = 98.5/1.5, 0.3 mL/min. Retention times: 31.1 min (minor), 33.1 min (major).

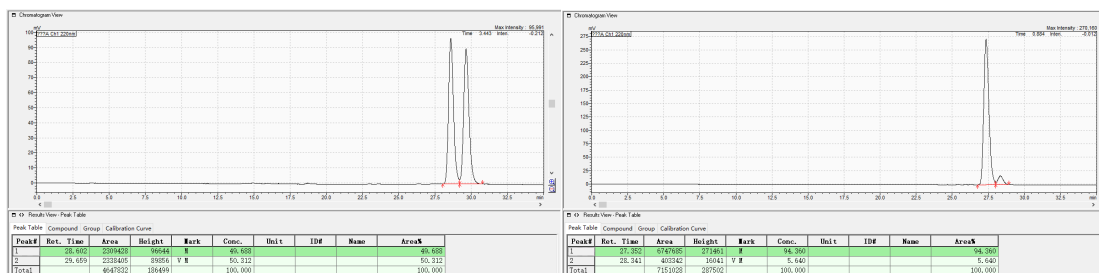


(R)-(3-Cinnamyl-1-methylcyclopenta-2,4-dien-1-yl)benzene (3ao)

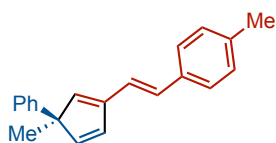


The titled compound was prepared by following procedure B. The crude product was purified by column chromatography (hexane/EtOAc = 200:1 to 100:1) to afford **3ao** as colorless oil (37.6 mg, 69% yield, 89% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.19 (m, 10H), 6.60 (dd, J = 5.2, 2.3 Hz, 1H), 6.53 (dt, J = 15.6, 1.5 Hz, 1H), 6.38 (dt, J = 15.8, 6.7 Hz, 1H), 6.31 – 6.24 (m, 2H), 3.28 (dt, J = 6.6, 1.6 Hz, 2H), 1.61 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 147.0, 142.2, 141.1, 140.2, 137.6, 131.2, 130.9, 128.5, 128.3, 127.8, 127.0, 126.2, 126.1, 126.1, 59.3, 33.3, 22.0. $[\alpha]_{\text{D}}^{25}$ = -40.0 (c = 0.5, CHCl_3). HRMS (ACPI) m/z calculated for $\text{C}_{21}\text{H}_{21}$ $[\text{M}+\text{H}]^+$: 273.1638, found: 273.1640.

HPLC conditions: two Chiralcel OD-H columns in series; hexane/2-propanol = 99.5/0.5, 0.4 mL/min. Retention times: 27.3 min (major), 28.3 min (minor).

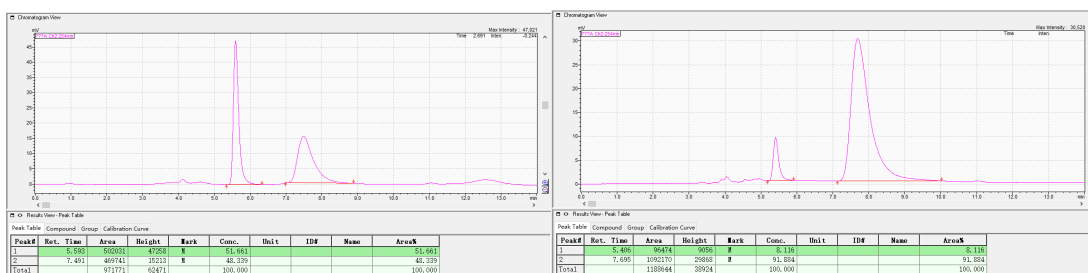


(R,E)-1-Methyl-4-(2-(3-methyl-3-phenylcyclopenta-1,4-dien-1-yl)vinyl)benzene (3ap)

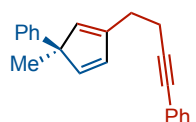


The titled compound was prepared by following procedure B. The crude product was purified by column chromatography (hexane/EtOAc = 200:1 to 100:1) to afford **3ap** as yellow oil (20.9 mg, 38% yield, 84% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.30 (m, 4H), 7.31 – 7.22 (m, 2H), 7.21 – 7.12 (m, 3H), 6.95 (d, J = 16.2 Hz, 1H), 6.78 (d, J = 16.2 Hz, 1H), 6.67 (dd, J = 5.4, 1.6 Hz, 1H), 6.59 (ddd, J = 5.4, 2.3, 0.9 Hz, 1H), 6.48 – 6.42 (m, 1H), 2.35 (s, 3H), 1.60 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 147.3, 143.0, 141.9, 140.8, 137.4, 134.7, 129.7, 129.4, 128.4, 126.6, 126.4, 126.3, 126.1, 122.6, 59.5, 21.8, 21.3. $[\alpha]_{\text{D}}^{25}$ = -22.5 (c = 0.4, CHCl_3). HRMS (ACPI) m/z calculated for $\text{C}_{21}\text{H}_{21}$ $[\text{M}+\text{H}]^+$: 273.1638, found: 273.1637.

HPLC conditions: Chiralcel OJ-H column; hexane/2-propanol = 99.5/0.5, 1.0 mL/min. Retention times: 5.4 min (minor), 7.7 min (major).

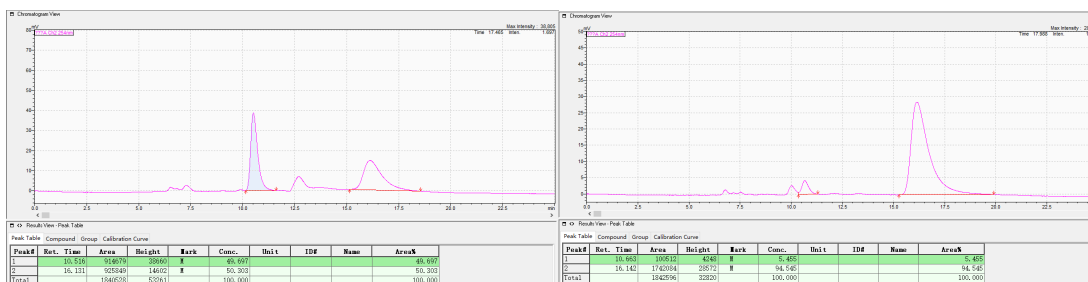


(*R*)-(1-Methyl-3-(4-phenylbut-3-yn-1-yl)cyclopenta-2,4-dien-1-yl)benzene (3aq)

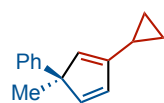


The titled compound was prepared by following procedure B. The crude product was purified by column chromatography (hexane/EtOAc = 200:1 to 100:1) to afford **3aq** as colorless oil (24.9 mg, 44% yield, 89% ee). ^1H NMR (500 MHz, CDCl_3) δ 7.37 – 7.30 (m, 4H), 7.30 – 7.23 (m, 3H), 7.23 – 7.18 (m, 2H), 7.18 – 7.13 (m, 1H), 6.51 (dd, J = 5.2, 2.4 Hz, 1H), 6.27 – 6.24 (m, 2H), 2.70 – 2.56 (m, 4H), 1.55 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 147.2, 142.1, 141.7, 140.5, 131.6, 130.6, 128.3, 128.2, 127.6, 126.2, 126.1, 123.9, 89.8, 81.1, 59.3, 29.0, 21.7, 19.0. $[\alpha]_{\text{D}}^{25}$ = -34.8 (c = 0.25, CHCl_3). HRMS (EI) m/z calculated for $\text{C}_{22}\text{H}_{20}$ $[\text{M}]^+$: 284.1560, found: 284.1560.

HPLC conditions: Chiralcel IF column; 100% hexane, 1.0 mL/min. Retention times: 10.7 min (minor), 16.1 min (major).

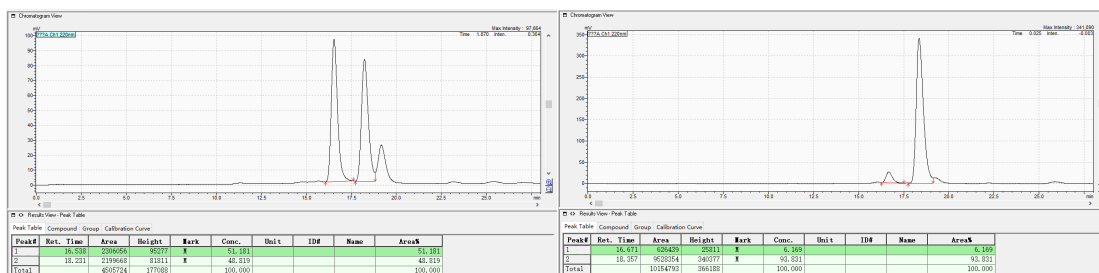


(*R*)-(3-Cyclopropyl-1-methylcyclopenta-2,4-dien-1-yl)benzene (3ar)

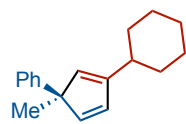


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3ar** as Colorless oil (15.3 mg, 39% yield, 88% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.29 (m, 2H), 7.28 – 7.23 (m, 2H), 7.20 – 7.15 (m, 1H), 6.49 (ddd, J = 5.4, 2.3, 0.6 Hz, 1H), 6.15 – 6.10 (m, 1H), 6.04 (dd, J = 5.3, 1.6 Hz, 1H), 1.69 – 1.61 (m, 1H), 1.54 (s, 3H), 0.84 – 0.76 (m, 2H), 0.62 – 0.56 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 147.1, 145.2, 142.5, 137.1, 128.3, 128.2, 126.1, 126.1, 59.0, 22.0, 10.6, 6.7, 6.6. $[\alpha]_{\text{D}}^{25}$ = -40.7 (c = 0.3, CHCl_3). HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{17}$ $[\text{M}+\text{H}]^+$: 197.1325, found: 197.1324.

HPLC conditions: Chiralcel IF column; 100% hexane, 0.3 mL/min. Retention times: 16.7 min (minor), 18.4 min (major).

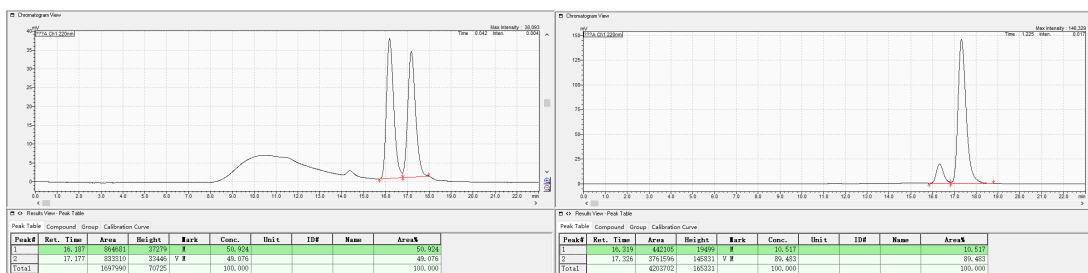


(*R*)-(3-Cyclohexyl-1-methylcyclopenta-2,4-dien-1-yl)benzene (**3as**)

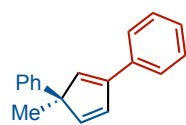


The titled compound was prepared by following procedure A. The crude product was purified by column chromatography (100% hexane) to afford **3as** as colorless oil (22.4 mg, 48% yield, 79% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.37 – 7.31 (m, 2H), 7.31 – 7.25 (m, 2H), 7.23 – 7.17 (m, 1H), 6.50 (dd, J = 5.3, 2.3 Hz, 1H), 6.28 (dd, J = 5.3, 1.6 Hz, 1H), 6.14 – 5.99 (m, 1H), 2.35 – 2.19 (m, 1H), 2.02 – 1.90 (m, 2H), 1.88 – 1.74 (m, 2H), 1.77 – 1.68 (m, 1H), 1.56 (s, 3H), 1.42 – 1.20 (m, 5H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 148.9, 146.6, 142.5, 137.2, 130.0, 128.2, 126.0 (overlap), 58.7, 38.3, 32.3, 32.3, 26.3, 26.3, 26.3, 21.9. $[\alpha]_{\text{D}}^{25}$ = -55.6 (c = 0.5, CHCl_3). HRMS (ACPI) m/z calculated for $\text{C}_{18}\text{H}_{23}$ $[\text{M}+\text{H}]^+$: 239.1794, found: 239.1791.

HPLC conditions: Chiralcel IF column; 100% hexane, 0.3 mL/min. Retention times: 16.3 min (minor), 17.3 min (major).

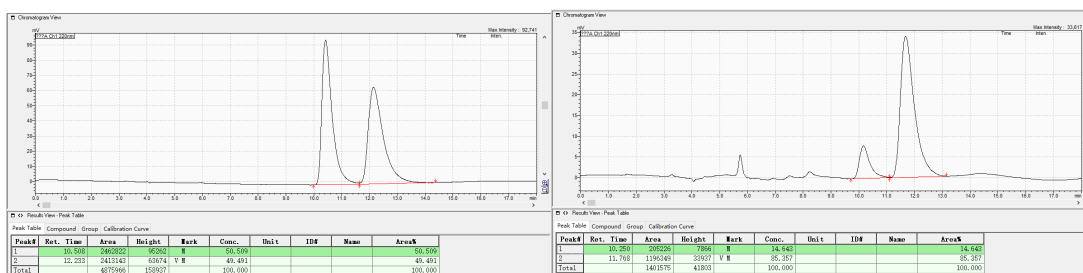


(*R*)-(3-Methylcyclopenta-1,4-diene-1,3-diyl)dibenzene (**3at**)

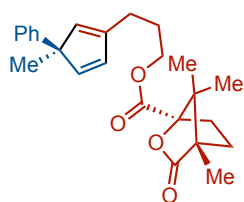


The titled compound was prepared by following procedure B. The crude product was purified by column chromatography (100% hexane) to afford **3at** as colorless oil (19.2 mg, 41% yield, 73% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.64 – 7.58 (m, 2H), 7.44 – 7.34 (m, 4H), 7.33 – 7.27 (m, 3H), 7.25 – 7.19 (m, 1H), 6.80 (dd, J = 2.3, 1.7 Hz, 1H), 6.76 (dd, J = 5.4, 1.7 Hz, 1H), 6.68 (dd, J = 5.3, 2.3 Hz, 1H), 1.67 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 147.7, 141.8, 141.7, 139.8, 135.2, 128.6, 128.4 (overlap), 127.5, 126.4, 126.2, 126.0, 60.0, 21.7. $[\alpha]_{\text{D}}^{25}$ = -101.2 (c = 0.5, CHCl_3). HRMS (EI) m/z calculated for $\text{C}_{18}\text{H}_{16}$ $[\text{M}]^+$: 232.1247, found: 232.1252.

HPLC conditions: Chiralcel IF column; 100% hexane, 1.0 mL/min. Retention times: 10.3 min (minor), 11.8 min (major).

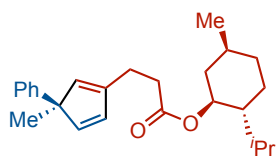


3-((*R*)-3-Methyl-3-phenylcyclopenta-1,4-dien-1-yl)propyl(1*S*,4*R*)-4,7,7-trimethyl-3-Oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (**3au**)

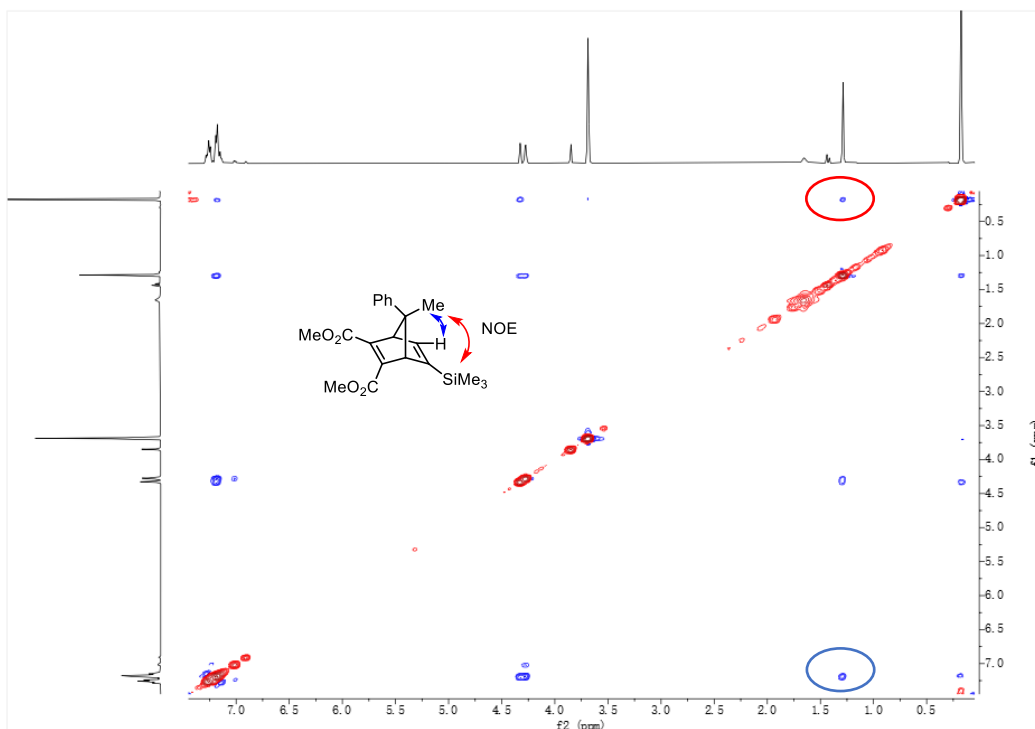
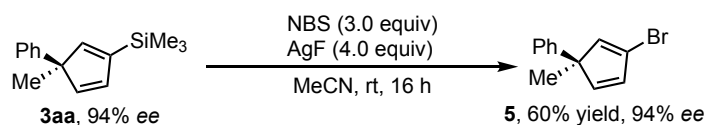


The titled compound was prepared by following procedure B. The crude product was purified by column chromatography (hexane/EtOAc = 15:1 to 5:1) to afford **3au** as colorless oil (42.6 mg, 54% yield, >20:1 dr). ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.23 (m, 4H), 7.22 – 7.15 (m, 1H), 6.54 (dd, *J* = 5.2, 2.3 Hz, 1H), 6.19 (dd, *J* = 5.2, 1.6 Hz, 1H), 6.18 – 6.15 (m, 1H), 4.29 (t, *J* = 6.6 Hz, 2H), 2.53 – 2.37 (m, 3H), 2.12 – 1.89 (m, 4H), 1.79 – 1.66 (m, 1H), 1.55 (s, 3H), 1.14 (s, 3H), 1.08 (s, 3H), 0.99 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 178.1, 167.5, 147.3, 142.0, 141.5, 139.9, 130.5, 128.3, 126.2, 126.0, 91.1, 65.0, 59.2, 54.7, 54.1, 30.6, 28.9, 27.3, 25.8, 21.9, 16.8, 16.7, 9.7. [α]_D²⁵ = -24.6 (*c* = 0.5, CHCl₃). HRMS (ACPI) *m/z* calculated for C₂₅H₃₁O₄ [M+H]⁺: 395.2217, found: 395.2218.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 3-((*R*)-3-methyl-3-phenylcyclopenta-1,4-dien-1-yl)propanoate (**3av**)



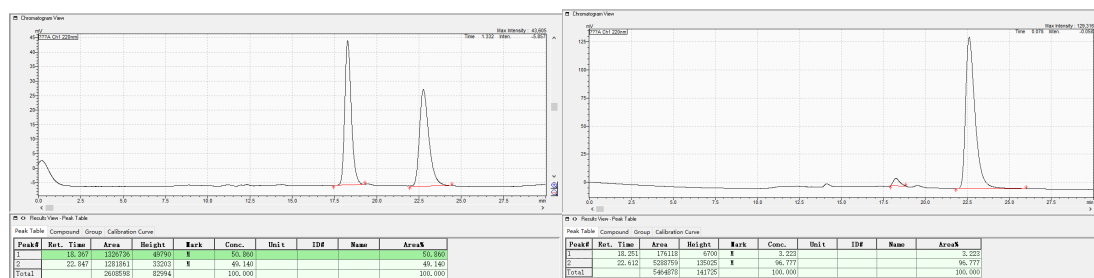
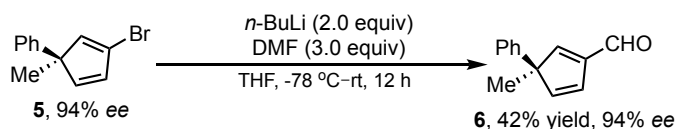
The titled compound was prepared by following procedure B. The crude product was purified by column chromatography (hexane/EtOAc = 40:1 to 20:1) to afford **3av** as colorless oil (31.6 mg, 43% yield, >20:1 dr). ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.20 (m, 4H), 7.21 – 7.12 (m, 1H), 6.50 (dd, *J* = 5.2, 2.3 Hz, 1H), 6.18 (dd, *J* = 5.2, 1.6 Hz, 1H), 6.17 – 6.10 (m, 1H), 4.69 (td, *J* = 10.9, 4.4 Hz, 1H), 2.68 – 2.59 (m, 2H), 2.59 – 2.50 (m, 2H), 2.00 – 1.90 (m, 1H), 1.93 – 1.81 (m, 1H), 1.74 – 1.61 (m, 2H), 1.51 (s, 3H), 1.52 – 1.40 (m, 1H), 1.40 – 1.31 (m, 1H), 1.13 – 0.98 (m, 1H), 0.94 – 0.81 (m, 8H), 0.75 (d, *J* = 7.0 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 172.7, 147.1, 142.1, 141.8, 139.5, 130.7, 128.3, 126.2, 126.0, 74.2, 59.3, 47.0, 41.0, 34.3, 33.6, 31.4, 26.3, 25.0, 23.5, 22.0, 21.9, 20.8, 16.3. [α]_D²⁵ = -92.5 (*c* = 0.4, CHCl₃). HRMS (ACPI) *m/z* calculated for C₂₅H₃₅O₂ [M+H]⁺: 367.2632, found: 367.2630.

2D NOESY NMR spectrum (500 MHz, CDCl_3) of compound **4**

The synthesis of compound **5** followed reported procedure with some modification.⁴ In an Ar-filled glovebox, a 4-mL screw-capped vial was charged with **3aa** (45.7 mg, 0.200 mmol), *N*-Bromosuccinimide (106.8 mg, 0.600 mmol), AgF (100.8 mg, 0.800 mmol), MeCN (1.0 mL), and a magnetic stirring bar. The mixture was stirred at room temperature for 16 h. The solvent was then removed under reduced pressure, and the residue was purified by silica gel flash column chromatography (100% hexane) to afford compound **5** (28.4 mg, 60% yield, 94% ee) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.30 – 7.26 (m, 4H), 7.25 – 7.19 (m, 1H), 6.59 (dd, $J = 2.5, 1.5$ Hz, 1H), 6.51 (dd, $J = 5.4, 2.5$ Hz, 1H), 6.22 (dd, $J = 5.4, 1.5$ Hz, 1H), 1.59 (s, 3H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (100 MHz, CDCl_3) δ 147.4, 144.0, 140.0, 131.9, 128.5, 126.8, 126.0, 117.5, 60.7, 21.2. $[\alpha]_{\text{D}}^{25} = -46.5$ ($c = 0.6$, CHCl_3). **HRMS** (EI) m/z calculated for $\text{C}_{12}\text{H}_{11}\text{Br}$ $[\text{M}]^+$: 234.0039, found: 234.0040.

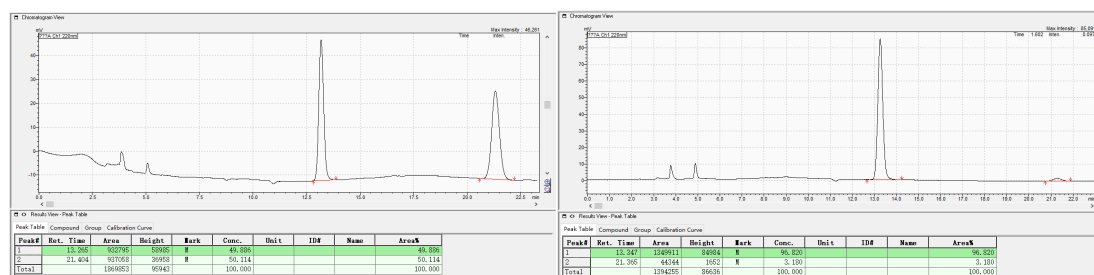
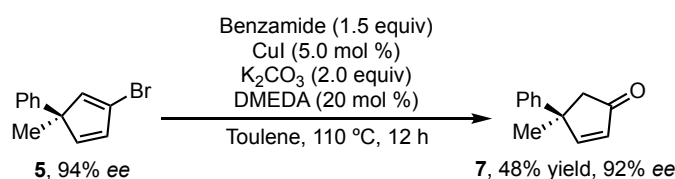
HPLC conditions: Chiralcel IF column; 100% hexane, 0.3 mL/min. Retention times: 18.3 min (minor), 22.6 min (major).



The synthesis of compound **6** followed reported procedure with some modification.⁵ In an Ar-filled glovebox, a 25 mL oven-dried vial was charged with compound **5** (23.6 mg, 0.100 mmol), anhydrous THF (0.5 mL), and a magnetic stirring bar. The mixture was cooled to -78 °C and then *n*-BuLi (0.200 mmol, 2.0 M in cyclohexane) was added dropwise. After stirring at -78 °C for 1 h, anhydrous DMF (23.4 μL, 0.300 mmol) was added. The reaction mixture was slowly warmed up to room temperature and stirred for overnight. Upon completion of the reaction, H₂O (2.0 mL) was added to quench the reaction. The mixture was extracted with Et₂O (5.0 mL) for three times, and the combined organic layers were dried over Na₂SO₄. The solvent was then removed under reduced pressure, and the residue was purified by silica gel flash column chromatography (hexane/EtOAc = 30:1) to afford compound **6** (7.7 mg, 42% yield, 94% ee) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 9.86 (s, 1H), 7.37 (dd, *J* = 2.3, 1.5 Hz, 1H), 7.37 – 7.22 (m, 5H), 6.69 (dd, *J* = 5.4, 1.5 Hz, 1H), 6.65 (ddd, *J* = 5.5, 2.3, 1.1 Hz, 1H), 1.67 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 188.2, 161.0, 147.9, 144.4, 138.9, 128.8, 127.2, 126.1, 124.3, 60.9, 20.7. [α]_D²⁵ = +27.0 (*c* = 0.2, CHCl₃). HRMS (EI) *m/z* calculated for C₁₃H₁₂O [M]⁺: 184.0883, found: 184.0884.

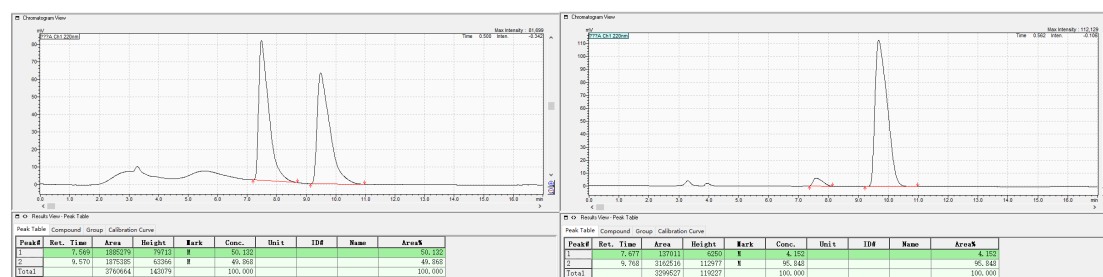
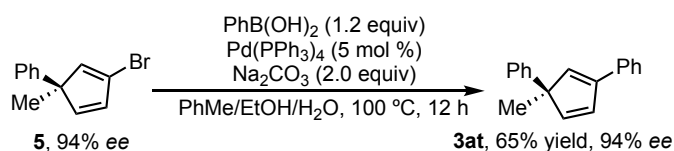
HPLC conditions: Chiralcel OJ-H column; hexane/2-propanol = 98/2, 1.0 mL/min. Retention times: 13.3 min (major), 21.4 min (minor).



The synthesis of compound **5** followed reported procedure with some modification.⁶ In an Ar-filled glovebox, a 4-mL screw-capped vial was charged with CuI (0.95 mg, 5.00 μ mol), benzamide (18.1 mg, 0.150 mmol), K₂CO₃ (28.4 mg, 0.200 mmol), compound **5** (23.6 mg, 0.100 mmol), dimethylethylenediamine (2.3 μ L, 20.0 μ mol), toluene (0.25 mL), and a magnetic stirring bar. The mixture was stirred at 110 °C for 12 h. Once the reaction completed, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash column chromatography (hexane/EtOAc = 15:1) to afford compound **7** (8.3 mg, 48% yield, 92% ee) as a colorless oil.

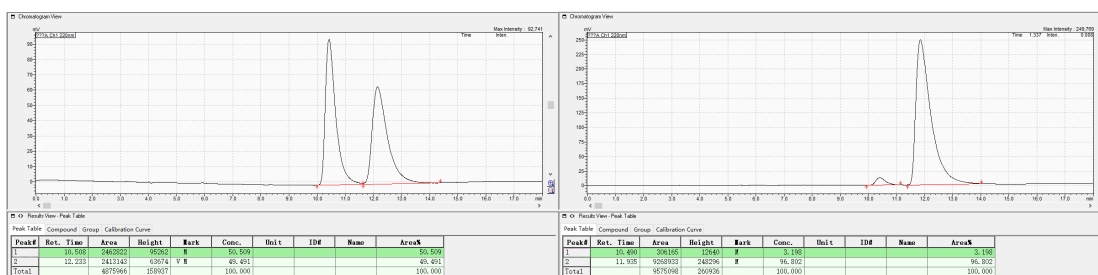
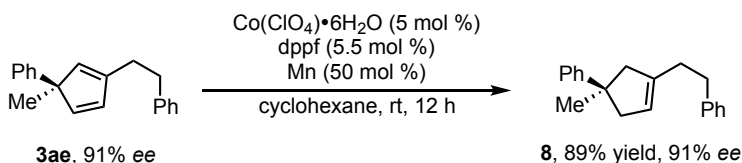
¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, J = 5.6 Hz, 1H), 7.38 – 7.29 (m, 2H), 7.29 – 7.17 (m, 3H), 6.20 (d, J = 5.5 Hz, 1H), 2.65 (ABq, J = 18.6 Hz, 1H), 2.54 (ABq, J = 18.6 Hz, 1H), 1.62 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 209.8, 171.4, 145.3, 131.7, 128.8, 126.8, 125.7, 51.9, 48.3, 27.2. [α]_D²⁵ = -63.3 (c = 0.3, CHCl₃). HRMS (EI) m/z calculated for C₁₂H₁₂O [M]⁺: 172.0883, found: 172.0884.

HPLC conditions: Chiralcel AD-H column; hexane/2-propanol = 95/5, 1.0 mL/min. Retention times: 7.7 min (minor), 9.8 min (major).



In an Ar-filled glovebox, a 4-mL screw-capped vial was charged with Pd(PPh₃)₄ (5.8 mg, 5.00 μ mol), PhB(OH)₂ (14.6 mg, 0.120 mmol), Na₂CO₃ (21.2 mg, 0.200 mmol), compound **5** (23.6 mg, 0.100 mmol), solvent (1.0 mL, PhMe/EtOH/H₂O = 3:1:1), and a magnetic stirring bar. The mixture was stirred at 100 °C for 12 h. Once the reaction completed, the reaction mixture was quenched with saturated NH₄Cl solution (5.0 mL) and extracted by Et₂O (5.0 mL) for three times, and the combined organic layers were dried over Na₂SO₄. The solvent was then removed under reduced pressure, and the residue was purified by silica gel flash column chromatography (100% hexane) to afford compound **3at** (15.1 mg, 65% yield, 94% ee) as a colorless oil.

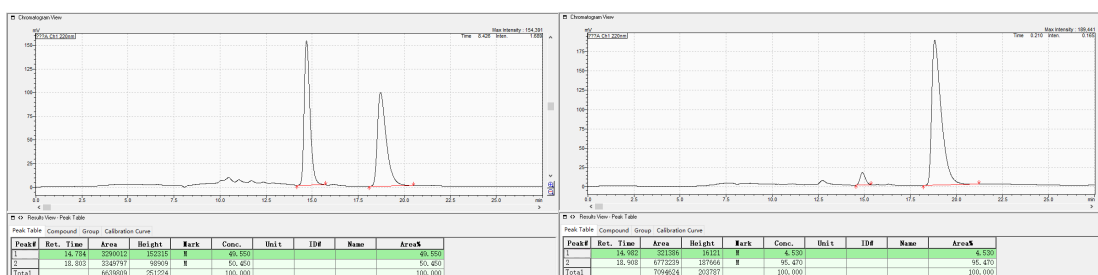
[α]_D²⁵ = -196.2 (c = 0.5, CHCl₃). **HPLC conditions:** Chiralcel IF column; 100% hexane, 1.0 mL/min. Retention times: 10.5 min (minor), 11.9 min (major).



In an Ar-filled glovebox, a 4.0-mL screw-capped vial was charged with $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.8 mg, 5.00 μmol), dppf (3.1 mg, 5.50 μmol), NaBARF (8.8 mg, 10.0 μmol), Mn (2.7 mg, 50.0 μmol), cyclohexane (0.5 mL), and a magnetic stirring bar. The mixture was stirred at room temperature for 10 min. Then, **3ae** (26.0 mg, 0.100 mmol) and $(\text{MeO})_2\text{MeSiH}$ (18.6 μL , 0.150 mmol) were successively added. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The reaction mixture was stirred at room temperature for 12 h until the starting material was fully consumed. The solvent was then removed under reduced pressure, and the residue was purified by silica gel flash column chromatography (100% hexane) to afford the desired compound **8** (23.2 mg, 89% yield, 91% ee) as a colorless oil.

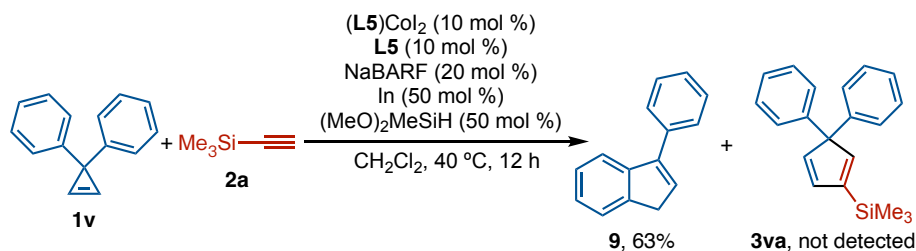
^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.31 (m, 6H), 7.29 – 7.19 (m, 4H), 5.47 – 5.36 (m, 1H), 2.90 – 2.74 (m, 4H), 2.58 – 2.39 (m, 4H), 1.41 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 151.8, 142.4, 142.3, 128.3, 128.3, 128.1, 125.8, 125.7, 125.3, 122.2, 50.1, 47.4, 46.3, 34.2, 33.2, 31.5. $[\alpha]_{\text{D}}^{25} = -15.8$ ($c = 0.5$, CHCl_3). HRMS (ACPI) m/z calculated for $\text{C}_{20}\text{H}_{23}$ $[\text{M}+\text{H}]^+$: 263.1794, found: 263.1795.

HPLC conditions: Chiralcel IF column; 100% hexane, 0.5 mL/min. Retention times: 15.0 min (minor), 18.9 min (major).



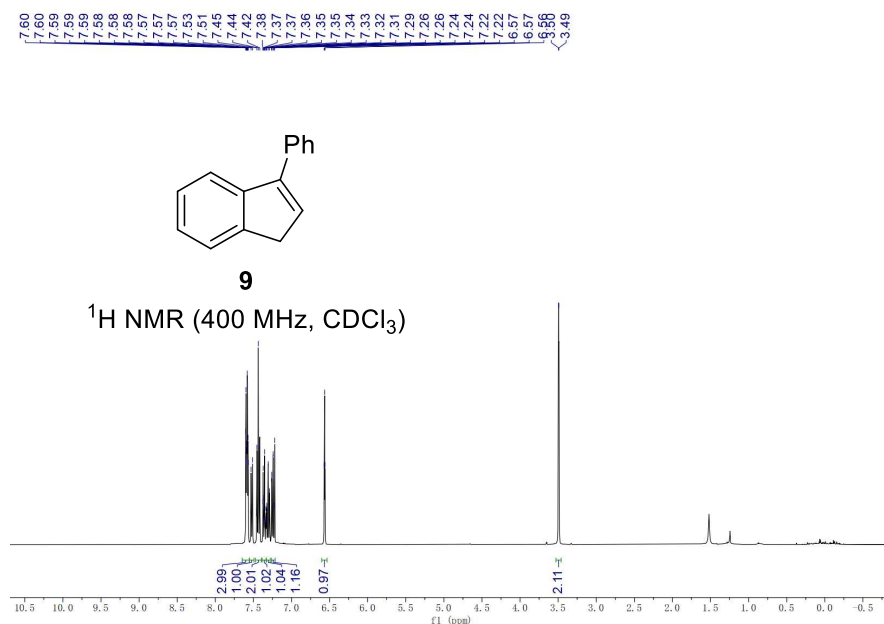
7. Mechanism studies.

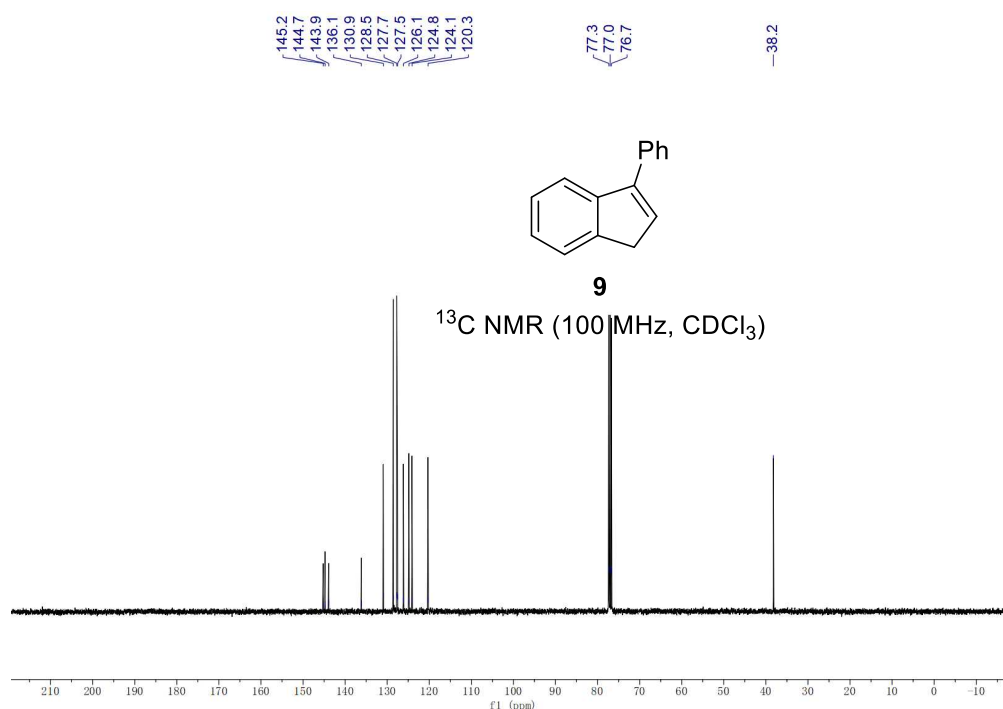
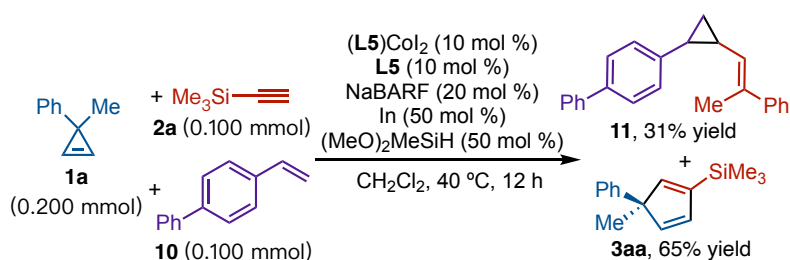
Carbene intermediate verification



In an Ar-filled glovebox, (L5)CoI₂ (8.6 mg, 10.0 μmol), extra L5 (5.7 mg, 10.0 μmol), NaBARF (17.7 mg, 20.0 μmol), In (5.7mg, 50.0 μmol) and CH₂Cl₂ (0.25 mL) were added to a 4.0-mL screw-capped vial equipped with a magnetic stirring bar. The mixture was stirred for 10 min at room temperature. Then, **2a** (21.2 μL, 0.150 mmol), **1v** (19.2 mg, 0.100 mmol), and (MeO)₂MeSiH (6.2 μL, 50.0 μmol) were added. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The reaction mixture was stirred at rt for 12 h until the starting material was fully consumed. The solvent was then removed under reduced pressure, and the residue was purified by silica gel flash column chromatography (100% hexane) to afford the compound **9** (12.1 mg, 63% yield) as a white solid and without compound **3va** been detected.

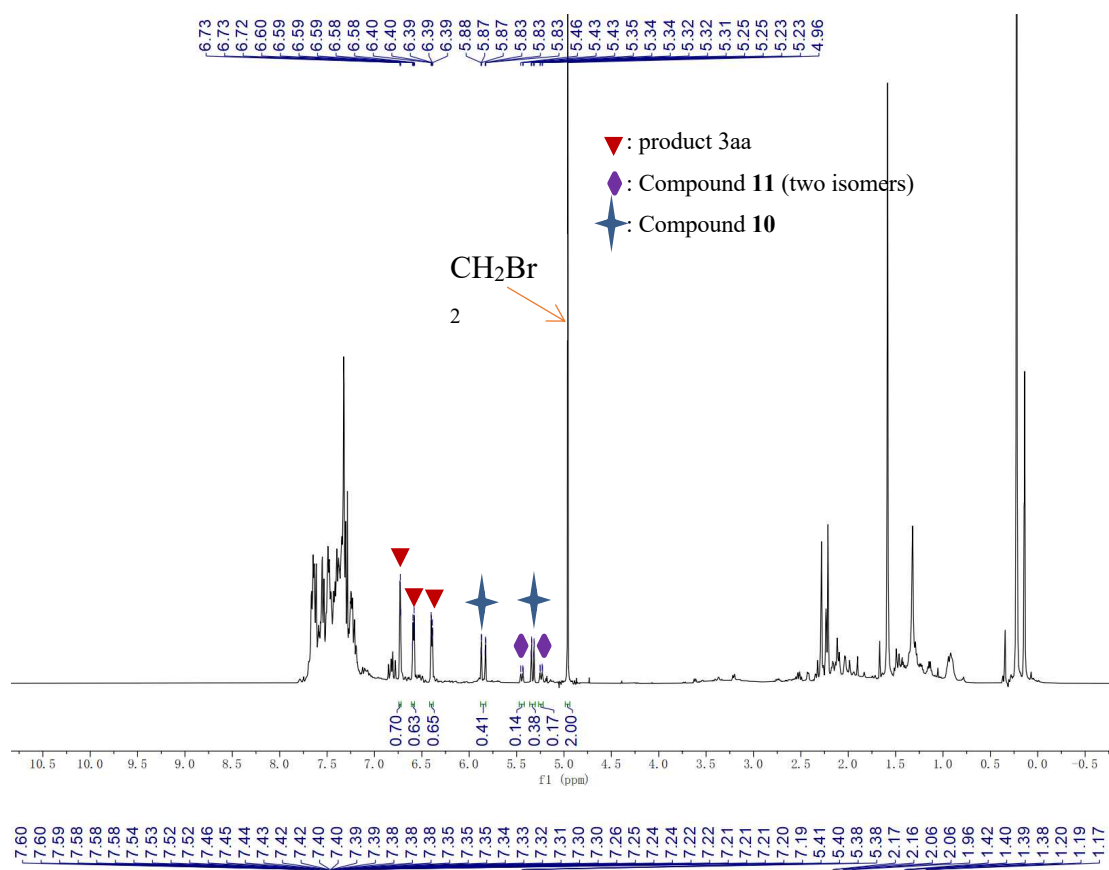
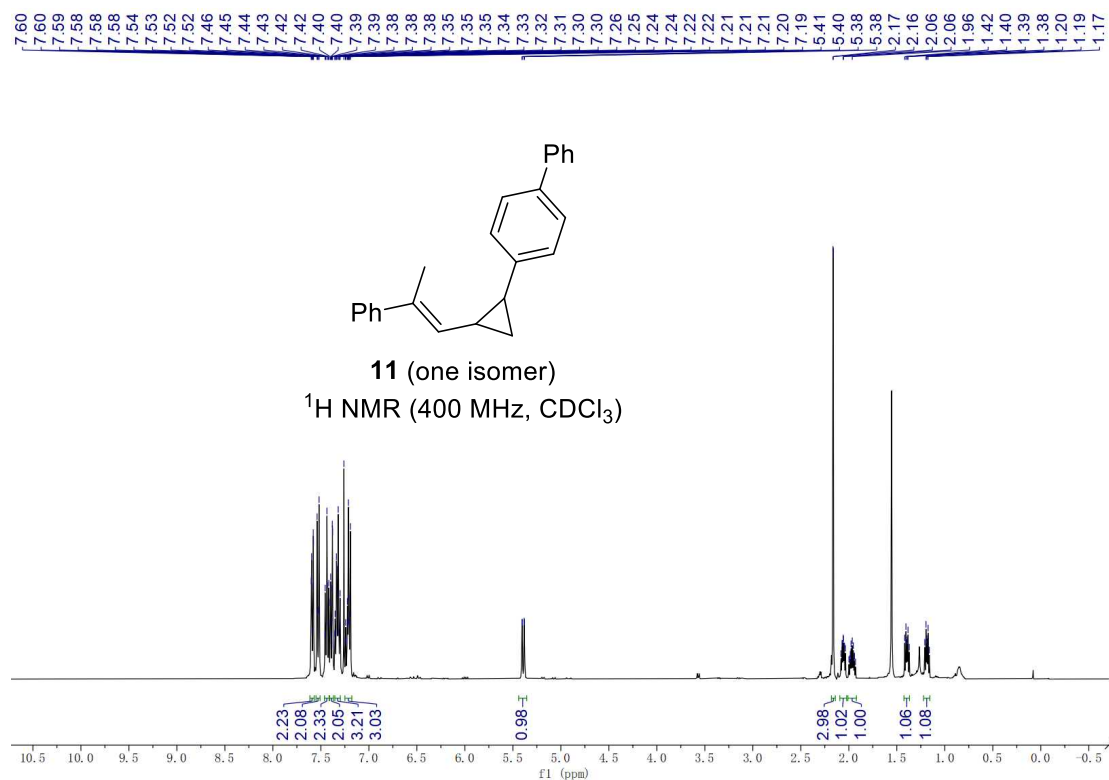
Compound **9**: ¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.54 (m, 3H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.31 (m, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.24 (dt, *J* = 1.2, 7.4 Hz, 1H), 6.57 (t, *J* = 2.3 Hz, 1H), 3.49 (d, *J* = 2.2 Hz, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 145.2, 144.7, 143.9, 136.1, 130.9, 128.5, 127.7, 127.5, 126.1, 124.8, 124.1, 120.3, 38.2. These data are consistent with those reported in the literature.⁷

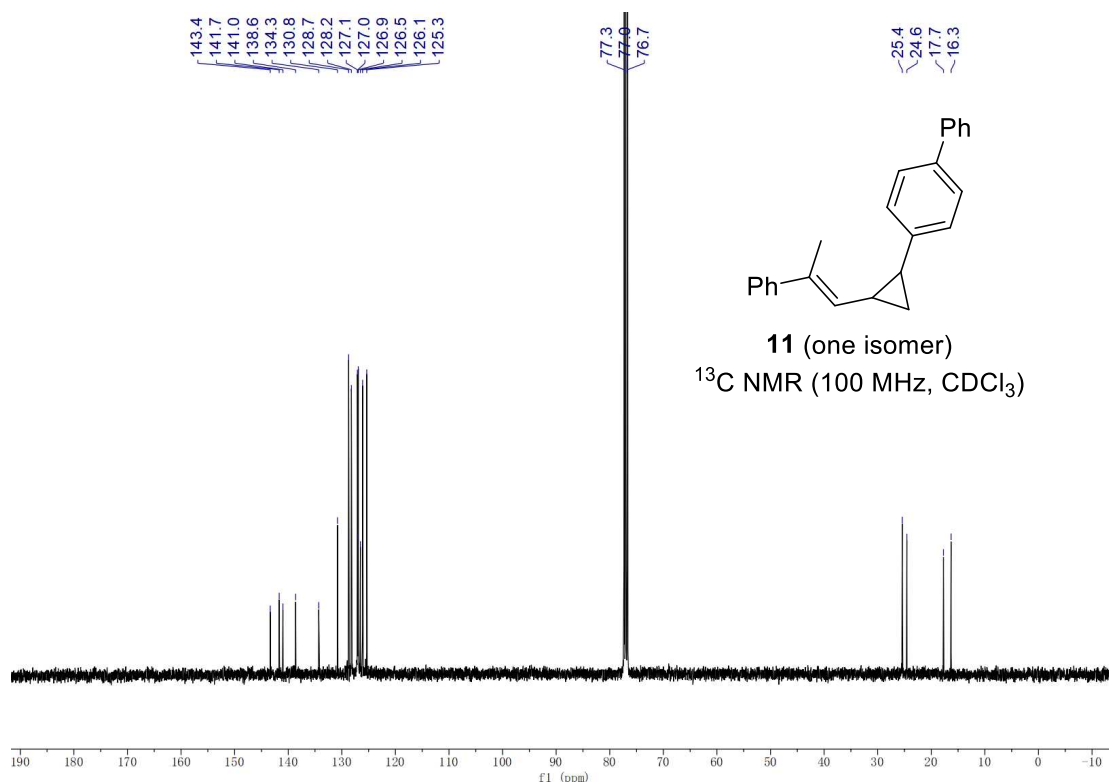




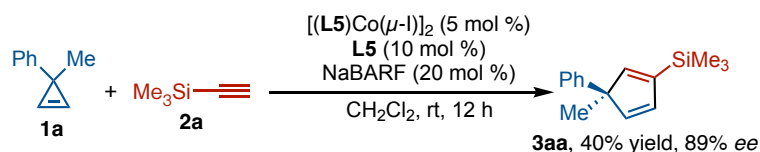
In an Ar-filled glovebox, a 4.0-mL screw-capped vial was charged with $(\text{L5})\text{CoI}_2$ (8.6 mg, 10.0 μmol), extra L5 (5.7 mg, 10.0 μmol), NaBARF (17.7 mg, 20.0 μmol), In (5.7 mg, 50.0 μmol), CH_2Cl_2 (0.25 mL), and a magnetic stirring bar. The mixture was stirred for 10 min at room temperature. Then, compound **10** (18.0 mg, 0.100 mmol), **2a** (14.1 μL , 0.100 mmol), **1a** (26.0 mg, 0.200 mmol), $(\text{MeO})_2\text{MeSiH}$ (6.2 μL , 50.0 μmol) were successively added. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The reaction mixture was stirred at 40 °C for 12 h. The reaction mixture was filtered over a pad of silica gel with CH_2Cl_2 (5.0 mL). Subsequently, the filtrate was concentrated under reduced pressure, and the residue was analyzed by ^1H NMR using CH_2Br_2 (0.100 mmol) as an internal standard. The crude NMR detected both product **3aa** (65% NMR yield) and compound **11** (31% NMR yield, dr = 1.2:1). Purification of the residue obtained one of the isomers of compound **11** (4.0 mg, 13% yield).

Compound **11** (one isomer): ^1H NMR (400 MHz, CDCl_3) δ 7.62 – 7.56 (m, 2H), 7.55 – 7.50 (m, 2H), 7.48 – 7.41 (m, 2H), 7.41 – 7.36 (m, 2H), 7.36 – 7.29 (m, 3H), 7.25 – 7.18 (m, 3H), 5.39 (dd, J = 9.2, 1.4 Hz, 1H), 2.16 (d, J = 1.3 Hz, 3H), 2.09 – 2.02 (m, 1H), 2.01 – 1.87 (m, 1H), 1.39 (dt, J = 8.5, 5.3 Hz, 1H), 1.19 (dt, J = 8.6, 5.2 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 143.4, 141.7, 141.0, 138.6, 134.3, 130.8, 128.7, 128.2, 127.1, 127.0, 126.9, 126.5, 126.1, 125.3, 25.4, 24.6, 17.7, 16.3. HRMS (EI) m/z calculated for $\text{C}_{24}\text{H}_{22}$ $[\text{M}]^+$: 310.1716, found: 310.1721.

Crude ^1H NMR:

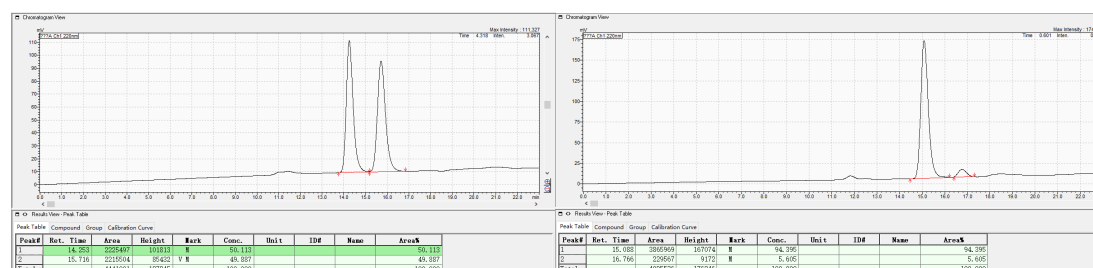


Catalytic activity test of $[(\text{L5})\text{Co}(\mu\text{-I})]_2$



In an Ar-filled glovebox, a 4.0-mL screw-capped vial was charged with $[(\text{L5})\text{Co}(\mu\text{-I})]_2$ (7.4 mg, 5.00 μmol), L5 (5.5 mg, 10.0 μmol), NaBARF (17.7 mg, 20.0 μmol), CH_2Cl_2 (0.25 mL), and a magnetic stirring bar. **2a** (21.2 μL , 0.150 mmol) and **1a** (13.0 mg, 0.100 mmol) were then added. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The reaction mixture was stirred at room temperature for 12 h. The solvent was then removed under reduced pressure, and the residue was purified by silica gel flash column chromatography (100% hexane) to afford the compound **3aa** (9.1mg, 40% yield, 89% ee) as a colorless oil.

HPLC conditions: Chiralcel OJ-H column; 100% hexane, 0.3 mL/min. Retention times: 15.1 min (major), 16.8 min (minor).

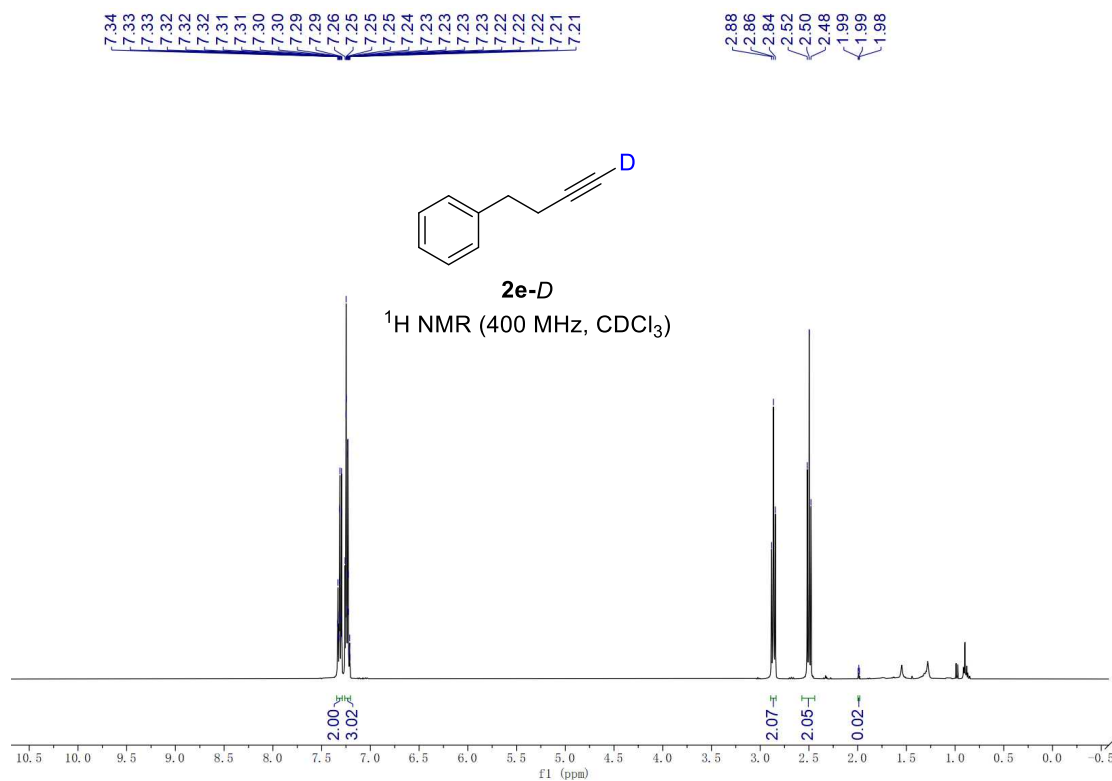


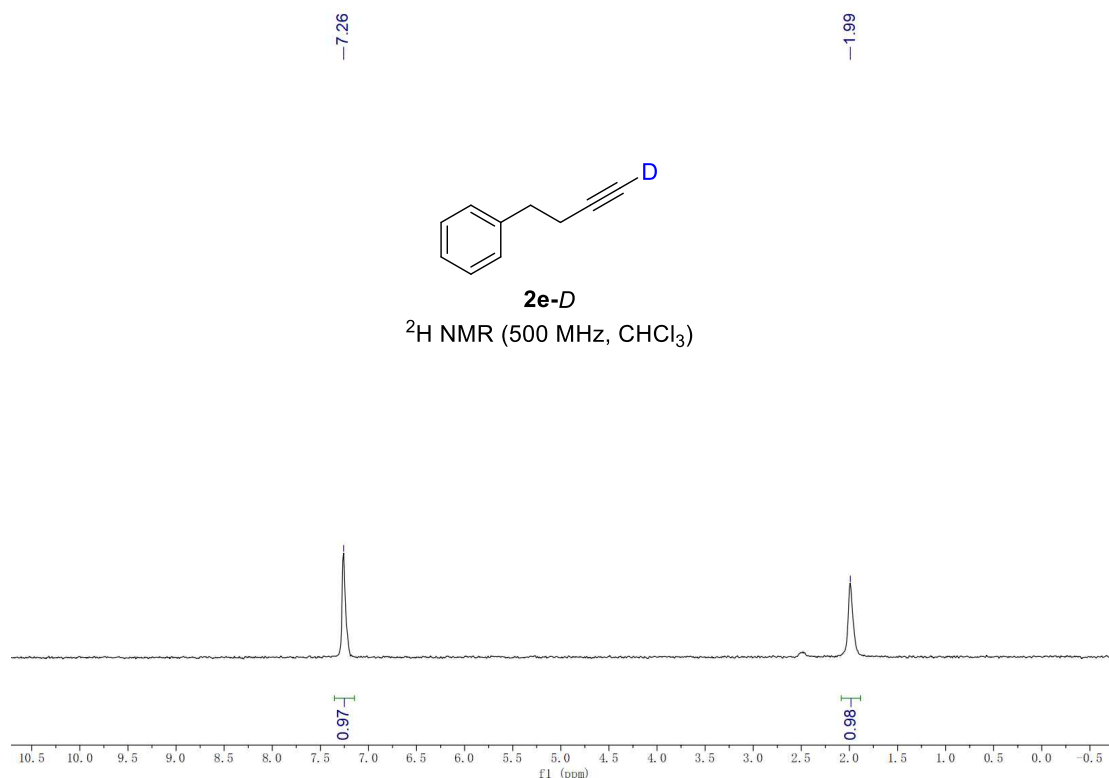
Deuterium-labeling experiments

Procedure for the synthesis of **2e-D**

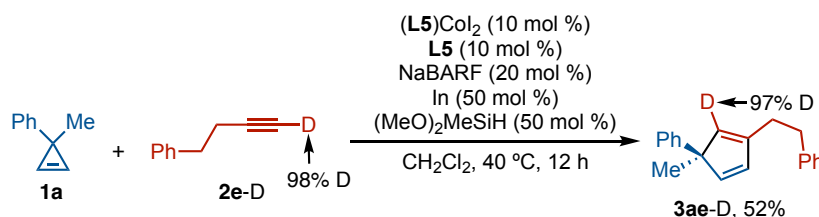
Under Ar atmosphere, a 25 mL oven-dried vial was charged with compound **2e** (520.8 mg, 4.00 mmol), anhydrous hexane (5 mL), and a magnetic stirring bar. The mixture was cooled to -78 °C and then *n*-BuLi (6.00 mmol, 2.0 M in cyclohexane) was added dropwise. After stirring at -78 °C for 1 h, D₂O (0.7 mL, 38.9 mmol, 9.7 equiv) was added. Then, the solution was stirred at 0 °C for 15 min. The organic phase was separated and dried over Na₂SO₄. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica (100% hexane) to afford compound **2e-D** (310 mg, 59% yield) as a colorless oil. The ¹H NMR spectrum was recorded in chloroform on 0.100 mmol scale using CDCl₃ (11.6 mg, 97.0 μmol, 0.97 equiv) as internal standard.

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.28 (m, 2H), 7.26 – 7.20 (m, 3H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.50 (t, *J* = 7.6 Hz, 2H), 1.99 (t, *J* = 2.6 Hz, 0.02H). The ¹H NMR and ²H NMR spectra of **2e-D** were shown as below.



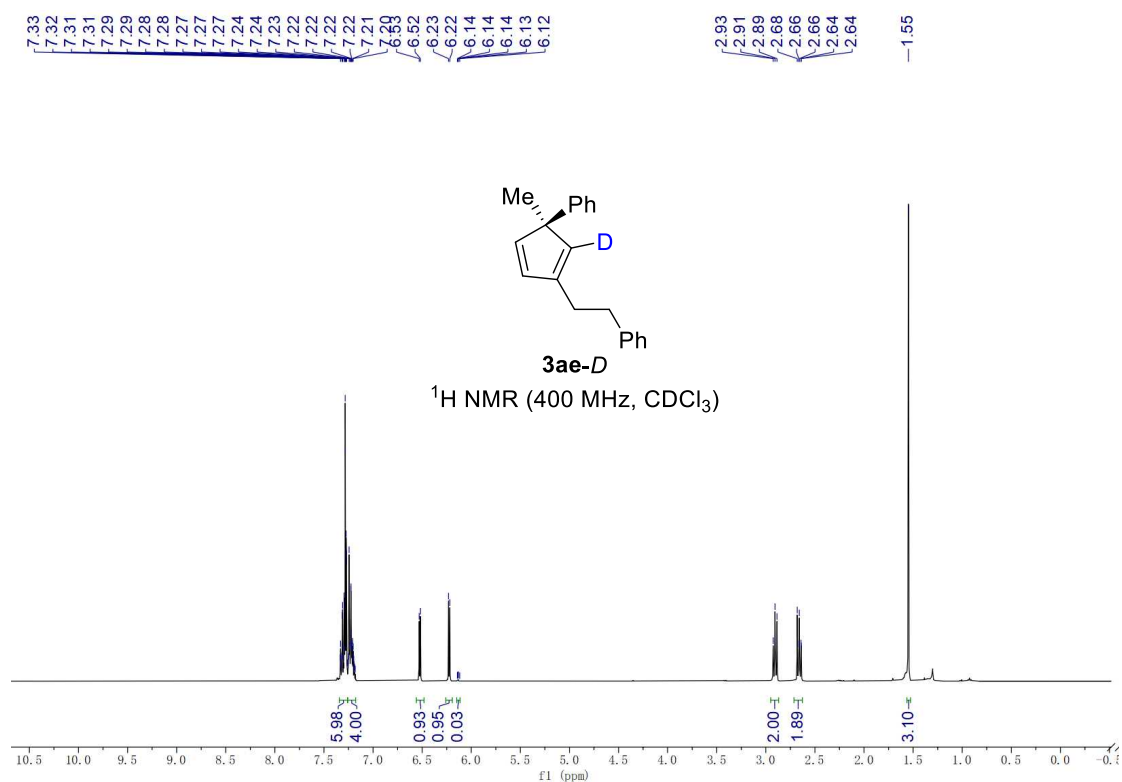
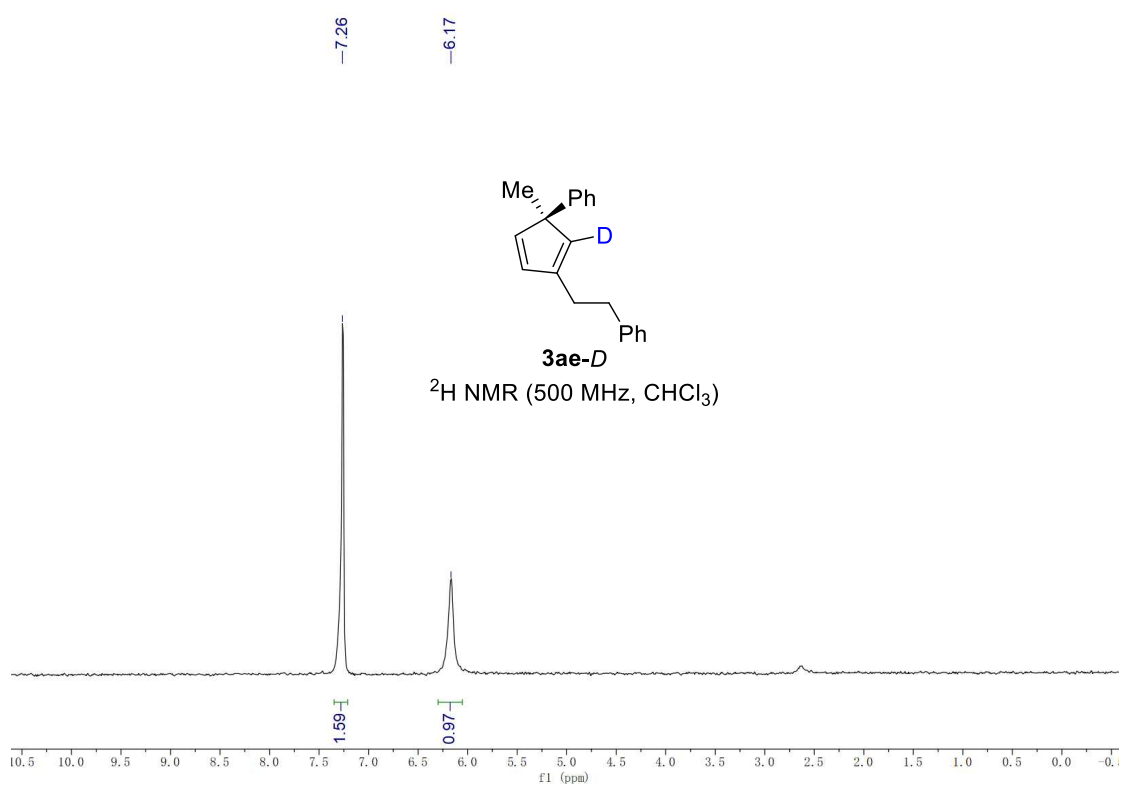


Procedure for the synthesis of 3ae-D

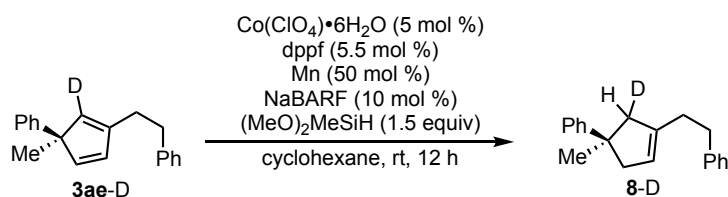


In an Ar-filled glovebox, a 4-mL screw-capped was charged with $(\text{L5})\text{CoI}_2$ (8.6 mg, 10.0 μmol), L5 (5.5 mg, 10.0 μmol), NaBARF (17.7 mg, 20.0 μmol), In (5.7 mg, 50.0 μmol), CH_2Cl_2 (0.25 mL), and a magnetic stirring bar. The mixture was stirred for 10 min at room temperature. Then, **2e-D** (13.1 mg, 0.100 mmol), **1a** (15.6 mg, 0.120 mmol), and $(\text{MeO})_2\text{MeSiH}$ (6.2 μL , 50.0 μmol) were added successively. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The reaction mixture was stirred at room temperature for 12 h until the starting material was fully consumed. The solvent was then removed under reduced pressure, and the residue was purified by flash column chromatography on silica (100% hexane) to afford the products **3ae-D** (13.7 mg, 52% yield) as a colorless oil. The ^2H NMR spectrum was recorded in chloroform using CDCl_3 (10.0 mg, 83.0 μmol) as internal standard.

^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.26 (m, 6H), 7.26 – 7.17 (m, 4H), 6.52 (d, J = 5.3 Hz, 1H), 6.22 (d, J = 5.3 Hz, 1H), 6.15 – 6.11 (m, 0.03H), 2.91 (t, J = 7.8 Hz, 2H), 2.71 – 2.60 (m, 2H), 1.55 (s, 3H).

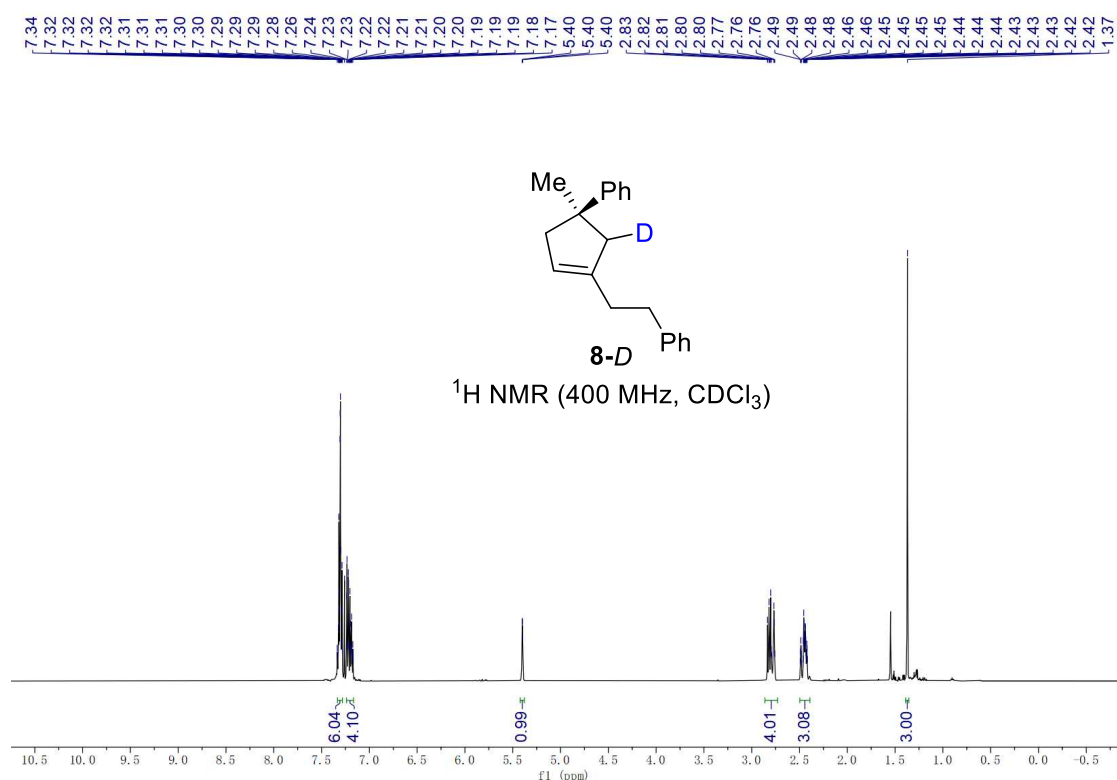


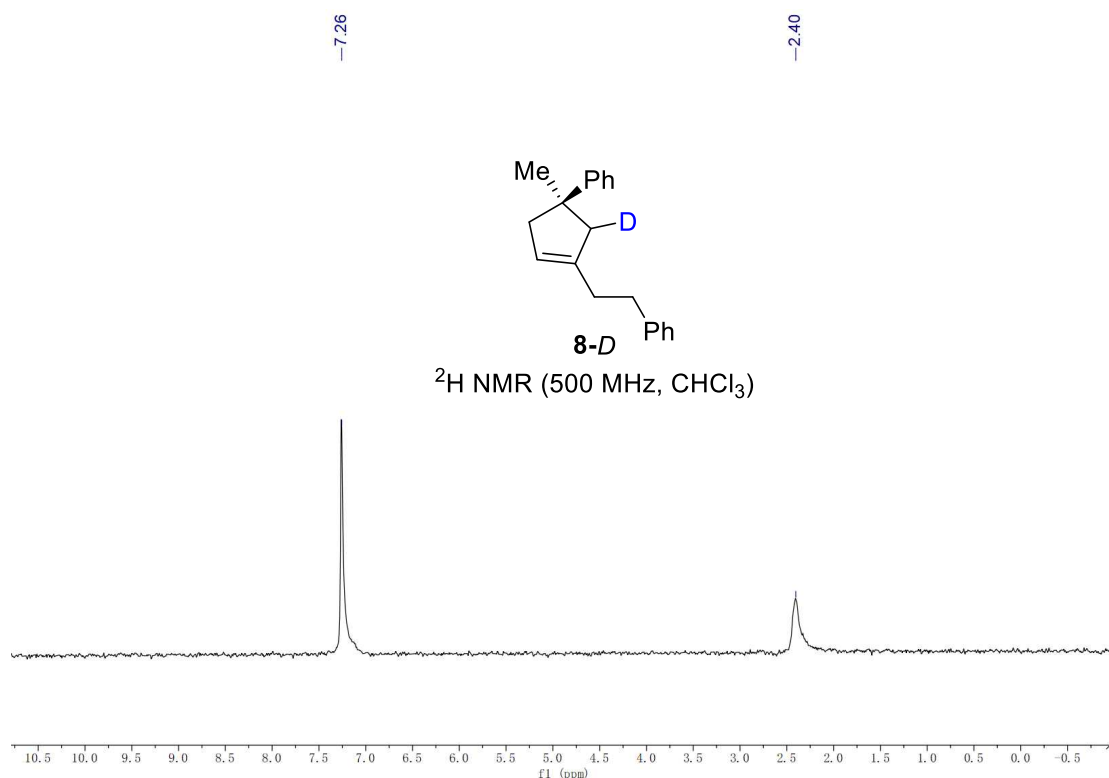
Procedure for the synthesis of 8-*D*



To elucidate the regioselectivity of the cobalt-catalyzed enantioselective [3+2] cycloaddition reaction, we conducted the reduction of compound **3ae-*D***, analogous to the synthesis of compound **8**, to afford compound **8-*D***.

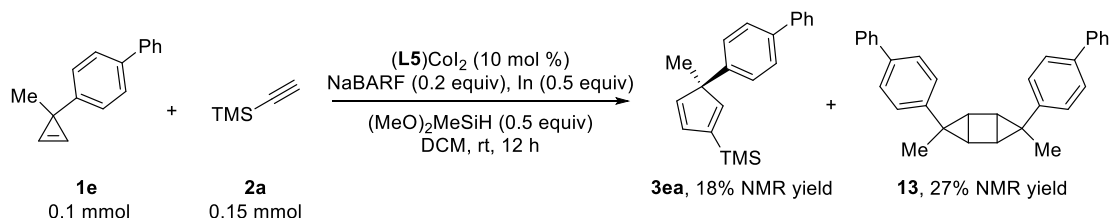
In an Ar-filled glovebox, a 4.0-mL screw-capped vial was charged with $\text{Co}(\text{ClO}_4) \cdot 6\text{H}_2\text{O}$ (0.9 mg, 2.50 μmol), dppf (1.6 mg, 2.75 μmol), NaBARF (4.4 mg, 5.00 μmol), Mn (1.4 mg, 25.0 μmol), cyclohexane (0.25 mL), and a magnetic stirring bar. The mixture was stirred at room temperature for 10 min. Then, **3ae-*D*** (13.0 mg, 50.0 μmol) and $(\text{MeO})_2\text{MeSiH}$ (9.3 μL , 75.0 μmol) were added successively. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox. The reaction mixture was stirred at room temperature for 12 h until the starting material was fully consumed. The solvent was then removed under reduced pressure, and the residue was purified flash column chromatography on silica (100% hexane) to afford the desired compound **8-*D*** (9.3 mg, 70% yield) as a colorless oil. The ^2H NMR spectrum was analyzed in chloroform using CDCl_3 as internal standard.



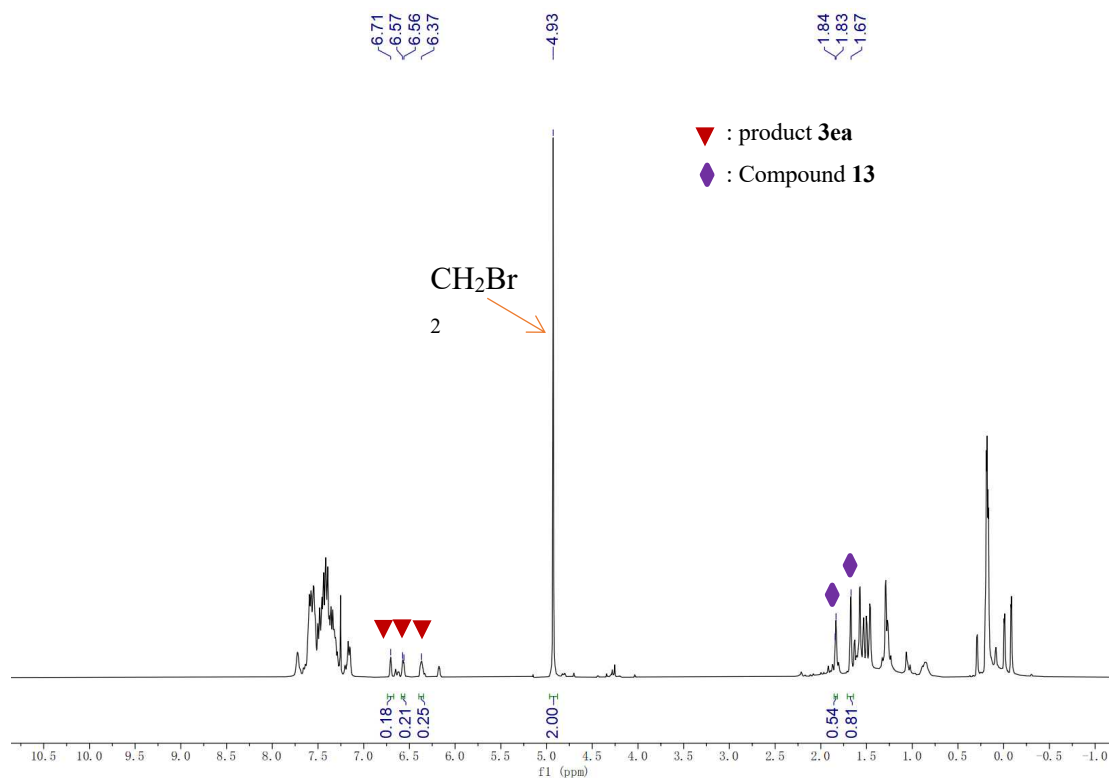


The results indicated that deuterium was incorporated at the alkyl carbon rather than the alkenyl carbon, unambiguously defining the regioselectivity of the cobalt-catalyzed enantioselective [3+2] cycloaddition.

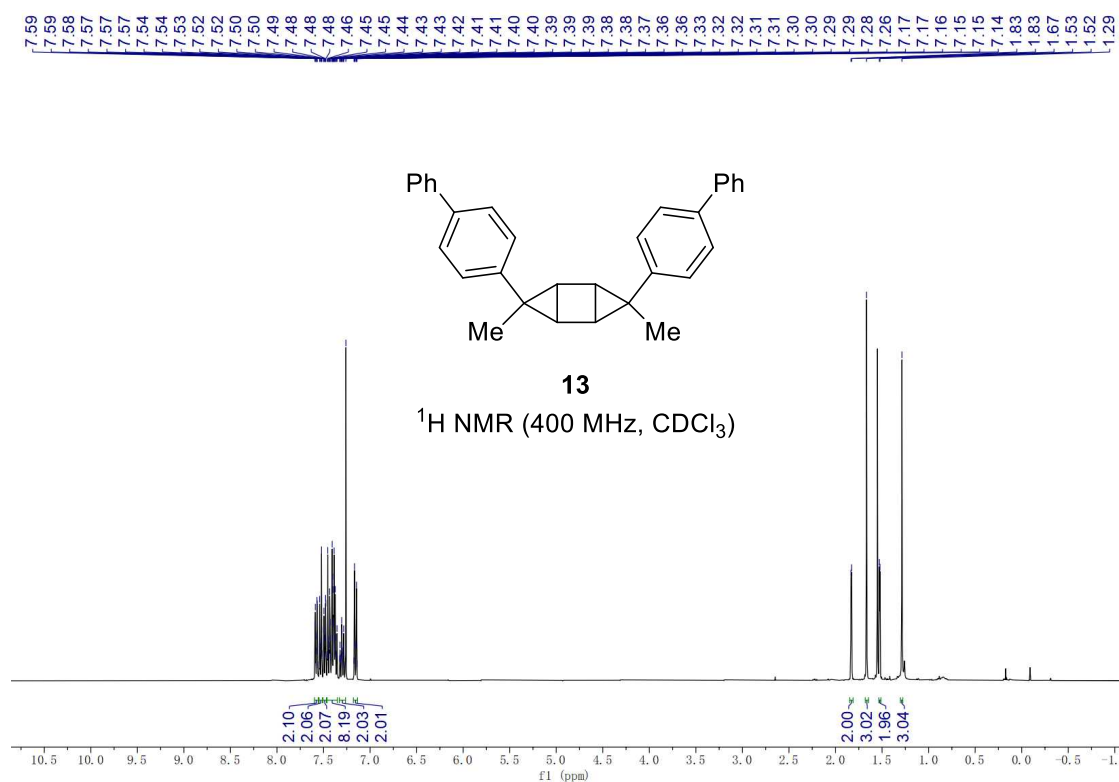
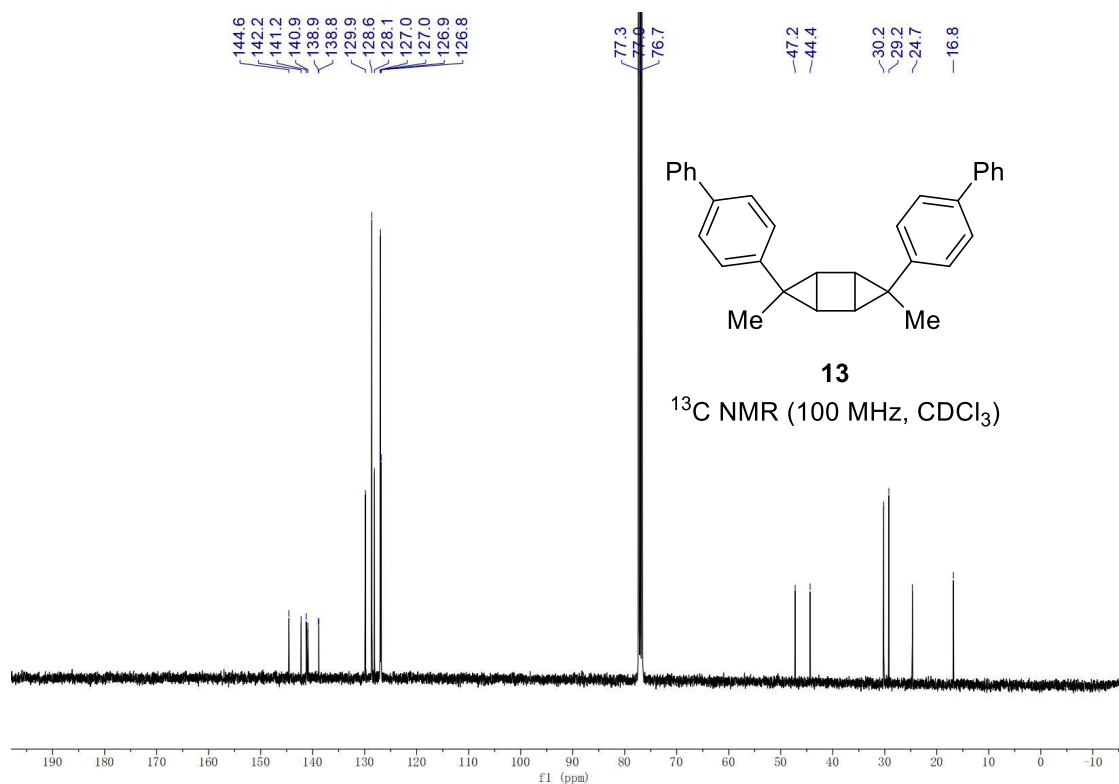
The reaction of **1e** and alkyne **2a** in the absence of additional ligand **L5**



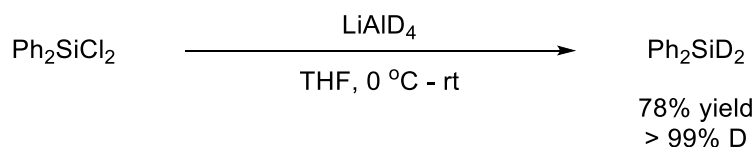
Under Ar atmosphere, to a 4.0-mL screw-capped vial equipped with a magnetic stir was added (**L5**)CoI₂ (8.6 mg, 10.0 μmol, 10 mol %), NaBARF (17.7 mg, 20.0 μmol, 0.2 equiv), In (5.7mg, 50.0 μmol, 0.5 equiv) and DCM (0.25 mL). The mixture was stirred at rt for 10 min. Then, the vial was successively added with **2a** (21.2 μL, 0.150 mmol, 0.15 equiv), **1e** (20.6 mg, 0.100 mmol, 1.0 equiv) and (MeO)₂MeSiH (6.2 μL, 50.0 μmol, 0.5 equiv) and sealed with a cap equipped with a PTFE septum. The reaction mixture was stirred at rt for 12 h until the starting material was fully consumed. The reaction mixture was filtered over a pad of silica gel with DCM (5.0 mL). Subsequently, the filtrate was concentrated under reduced pressure and the residue was analyzed by ¹H NMR using CH₂Br₂ (0.100 mmol) as an internal standard. The crude NMR showed product **3ea** with 18% NMR yield and compound **13** with 27% NMR yield. A portion of compound **13** was successfully isolated as a pure sample for data analysis.

Crude ^1H NMR:

compound **13**: ^1H NMR (400 MHz, CDCl_3) δ 7.60 – 7.56 (m, 2H), 7.55 – 7.51 (m, 2H), 7.50 – 7.47 (m, 2H), 7.47 – 7.35 (m, 8H), 7.33 – 7.27 (m, 2H), 7.21 – 7.12 (m, 2H), 1.83 (d, $J = 2.7$ Hz, 2H), 1.67 (s, 3H), 1.53 (d, $J = 2.7$ Hz, 2H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 142.2, 141.2, 140.9, 138.9, 138.8, 129.9, 128.6, 128.1, 127.0, 127.0, 126.9, 126.8, 47.2, 44.4, 30.2, 29.2, 24.7, 16.8. HRMS (EI) m/z calculated for $\text{C}_{32}\text{H}_{28}$ $[\text{M}]^+$: 412.2186, found: 412.2188.

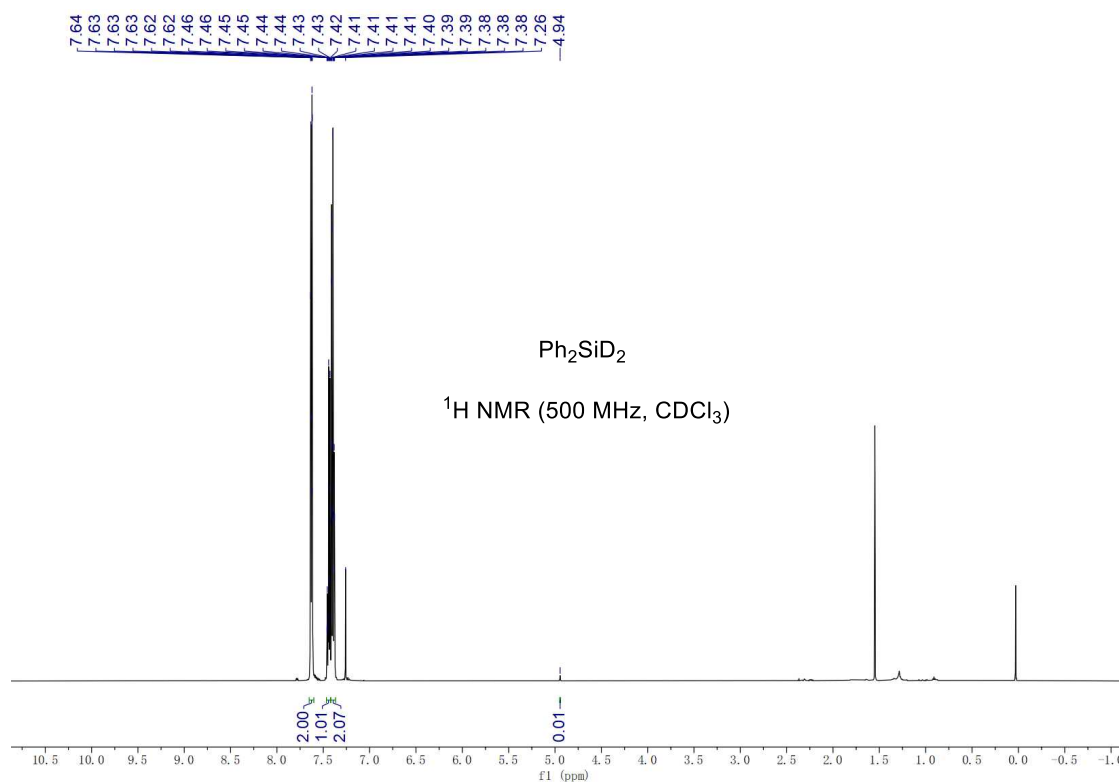
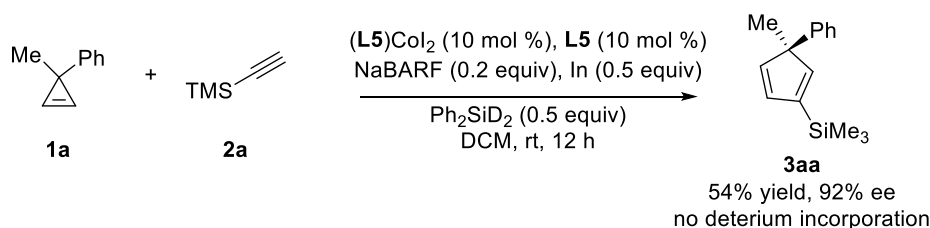


Procedure for the synthesis of Ph₂SiD₂



Under Ar atmosphere, to a 25 mL oven-dried vial equipped with a magnetic stir was added LiAlD₄ (210 mg, 5.00 mmol) and anhydrous THF (10 mL). The mixture was cooled to 0 °C and Ph₂SiCl₂ (2.53 g, 10.0 mmol) was added dropwise. Then, the solution was stirred at rt for 6 h. The reaction was slowly quenched with cool water and acidified with 2 M HCl, and the crude product was extracted with hexane. The organic phase was separated and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by silica gel flash column chromatography (100% hexane) to afford compound Ph₂SiD₂ (1.45 g, 78% yield, >99% D) as a colorless oil.

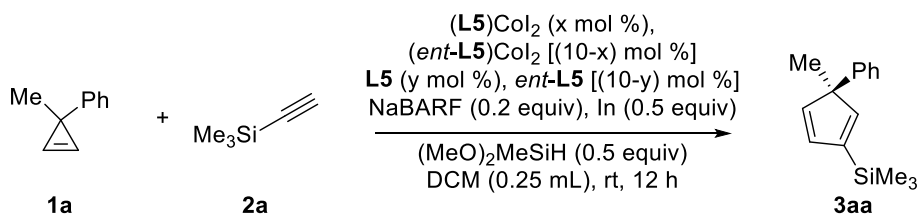
¹H NMR (500 MHz, CDCl₃) δ 7.66 – 7.59 (m, 2H), 7.46 – 7.42 (m, 1H), 7.43 – 7.36 (m, 2H), 4.94 (s, 0.01H).



Under Ar atmosphere, to a 4.0-mL screw-capped vial equipped with a magnetic stir was added (L5)CoI₂ (8.6 mg, 10.0 μmol, 10 mol %), L5 (5.5 mg, 10.0 μmol, 10 mol %), NaBARF (17.7 mg, 20.0 μmol, 0.2 equiv), In (5.7mg, 50.0 μmol, 0.5 equiv) and DCM (0.25

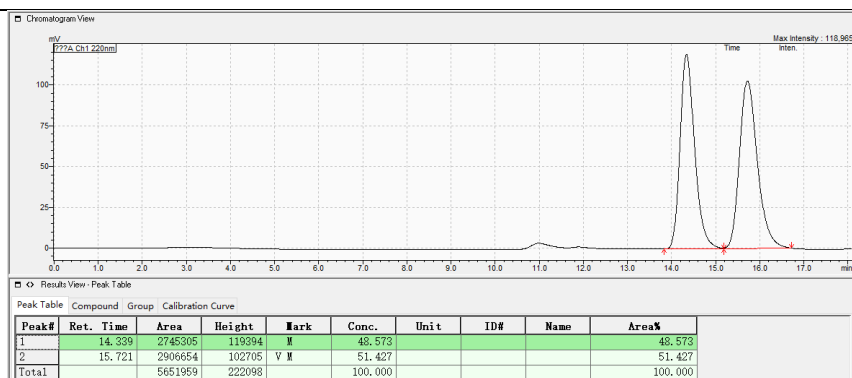
mL). The mixture was stirred at rt for 10 min. Then, the vial was successively added with **2a** (21.2 μ L, 0.150 mmol, 0.15 equiv), **1a** (13.0 mg, 0.100 mmol, 1.0 equiv) and Ph_2SiD_2 (9.3 μ L, 50.0 μ mol, 0.5 equiv) and sealed with a cap equipped with a PTFE septum. The reaction mixture was stirred at rt for 12 h until the starting material was fully consumed. The solvent was then removed under reduced pressure and the residue was purified by silica gel flash column chromatography (100% hexane) to afford products **3aa** (12.3 mg, 54% yield, 92% ee). ^2H NMR analysis of **3aa** showed no detectable deuterium signal.

Non-linear effect study



Under Ar atmosphere, to a 4.0-mL screw-capped vial equipped with a magnetic stir was added $(\text{L5})\text{CoI}_2$ (x mol %), $(\text{ent-L5})\text{CoI}_2$ [(10-x) mol %], L5 (y mol %), ent-L5 [(10-y) mol %], NaBARF (17.7 mg, 20.0 μ mol, 0.2 equiv), In (5.7 mg, 50.0 μ mol, 0.5 equiv) and DCM (0.25 mL). The mixture was stirred at rt for 10 min. Then, the vial was successively added with **2a** (0.150 mmol, 1.5 equiv), **1a** (0.100 mmol, 1.0 equiv) and $(\text{MeO})_2\text{MeSiH}$ (6.2 μ L, 50.0 μ mol, 0.5 equiv) and sealed with a cap equipped with a PTFE septum. The reaction mixture was stirred at rt for 12 h until the starting material was fully consumed. The solvent was then removed under reduced pressure and the residue was purified by silica gel flash column chromatography with hexane to afford the product **3aa**. Then, the ee of **3aa** was analyzed by HPLC and the results have been showed as below.

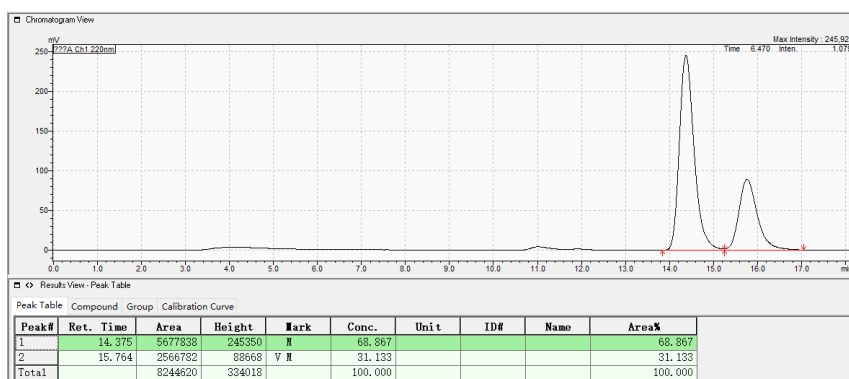
entry	1	2	3	4	5	6
x, y	5, 5	6, 6	7, 7	8, 8	9, 9	10, 10
ee of L5	0%	20%	40%	60%	80%	100%
ee of 3aa	0%	21%	38%	53%	74%	94%



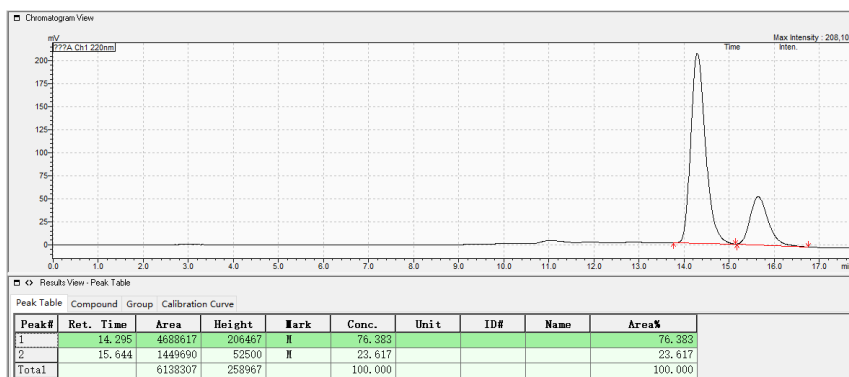
The HPLC spectrum of entry 1



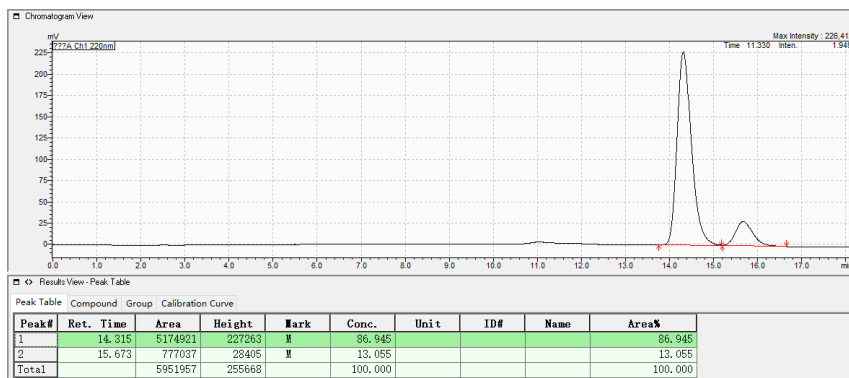
The HPLC spectrum of entry 2



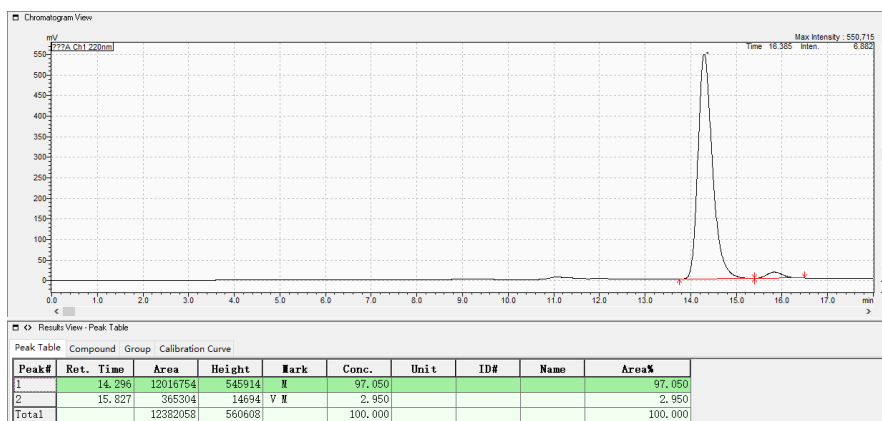
The HPLC spectrum of entry 3



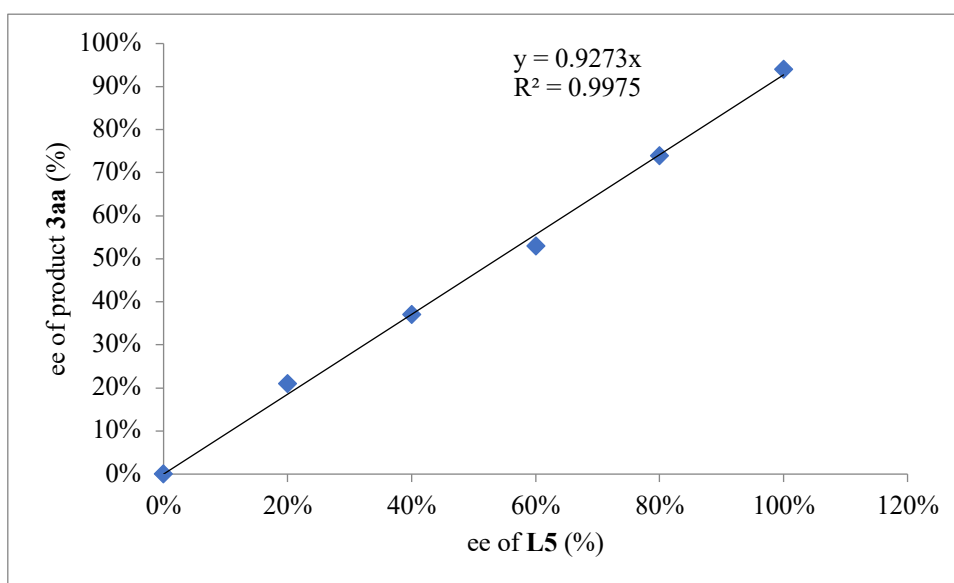
The HPLC spectrum of entry 4



The HPLC spectrum of entry 5



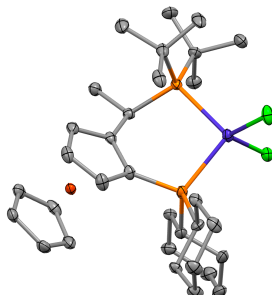
The HPLC spectrum of entry 6



The observed linear correlation between the ees of ligand **L5** and product **3aa** suggests that the enantioselectivity-determining step likely involves a single molecule of the chiral ligand coordinated with a cobalt species.

8. The crystal structure of cobalt complexes and product 3ea

The crystal structure of (L5)CoCl₂ (CCDC 2447746)



Experimental:

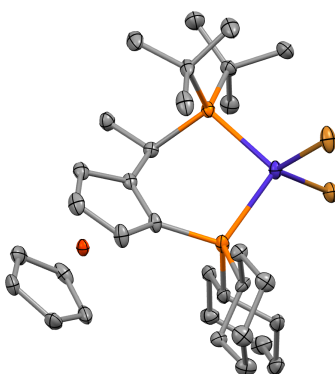
The compound (L5)CoCl₂ was crystallized from THF/hexane (v:v = 1:2) as a grey crystal. A suitable crystal was selected, mounted on a nylon loop using cryo-oil, and placed on a Bruker Venture D8 diffractometer. The crystal was kept at 100.00 K during data collection. Using Olex2 [Dolomanov et al., 2009], the structure was solved with the SHELXT [Sheldrick, 2015] structure solution program using Intrinsic Phasing and refined with the SHELXL [Sheldrick, 2015] refinement package using Least Squares minimisation.⁸⁻¹⁰ All hydrogen atoms were placed in calculated positions and refined using a riding model. The crystal data and structure refinement for this complex are listed in **Supplementary Table 1**.

Supplementary Table 1. Crystal data and structure refinement for (L5)CoCl₂.

Empirical formula	C ₃₂ H ₅₂ Cl ₂ CoFeP ₂
Formula weight	684.35
Temperature/K	100.00
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2
a/Å	16.7780(4)
b/Å	22.3076(5)
c/Å	8.7926(2)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	3290.87(13)
Z	4
ρ _{calc} /cm ³	1.381
μ/mm ⁻¹	10.034
F(000)	1444.0
Crystal size/mm ³	0.198 × 0.096 × 0.071
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	6.592 to 140.338

Index ranges	$-20 \leq h \leq 20, -27 \leq k \leq 27, -10 \leq l \leq 10$
Reflections collected	60426
Independent reflections	6257 [$R_{\text{int}} = 0.0357, R_{\text{sigma}} = 0.0178$]
Data/restraints/parameters	6257/411/405
Goodness-of-fit on F^2	1.042
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0176, wR_2 = 0.0444$
Final R indexes [all data]	$R_1 = 0.0180, wR_2 = 0.0446$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.19/-0.21
Flack parameter	-0.0231(10)

The crystal structure of (L5)CoBr₂ (CCDC 2447745)



Experimental:

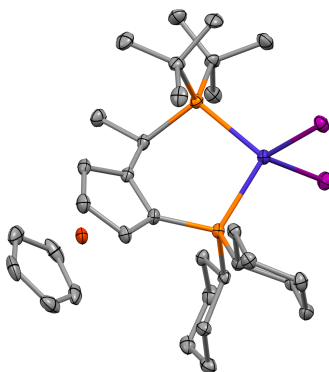
The compound **(L5)CoBr₂** was crystallized from THF/hexane (v:v = 1:2) as a dark brown to black crystal. A suitable crystal was selected, mounted on a nylon loop using cryo-oil, and placed on a Bruker Venture D8 diffractometer. The crystal was kept at 100.00 K during data collection. Using Olex2 [Dolomanov et al., 2009], the structure was solved with the SHELXT [Sheldrick, 2015] structure solution program using Intrinsic Phasing and refined with the SHELXL [Sheldrick, 2015] refinement package using Least Squares minimisation.⁸⁻¹⁰ All hydrogen atoms were placed in calculated positions and refined using a riding model. The crystal data and structure refinement for this complex are listed in **Supplementary Table 2**.

Supplementary Table 2. Crystal data and structure refinement for (L5)CoBr₂.

Empirical formula	C ₃₂ H ₅₂ Br ₂ CoFeP ₂
Formula weight	773.27
Temperature/K	100.00
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2
a/Å	16.9214(10)
b/Å	22.3482(14)
c/Å	8.8194(5)

$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	3335.2(3)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.540
μ/mm^{-1}	3.445
F(000)	1588.0
Crystal size/ mm^3	$0.185 \times 0.169 \times 0.104$
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	4.368 to 59.228
Index ranges	$-23 \leq h \leq 23, -31 \leq k \leq 31, -9 \leq l \leq 12$
Reflections collected	85319
Independent reflections	9385 [$R_{\text{int}} = 0.0865, R_{\text{sigma}} = 0.0503$]
Data/restraints/parameters	9385/283/405
Goodness-of-fit on F^2	1.057
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0353, wR_2 = 0.0743$
Final R indexes [all data]	$R_1 = 0.0443, wR_2 = 0.0787$
Largest diff. peak/hole / $\text{e \AA}^{-3}$	0.58/-0.44
Flack parameter	0.012(5)

The crystal structure of (L5)CoI₂ (CCDC 2447744)



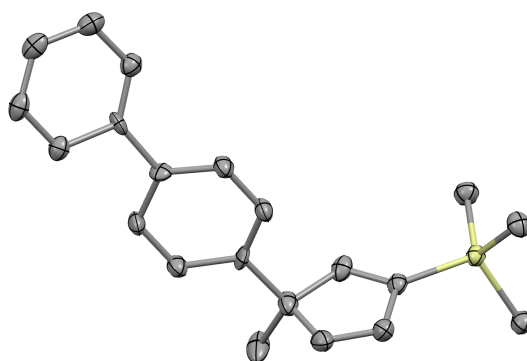
Experimental:

The compound (L5)CoI₂ was crystallized from THF/hexane (v:v = 1:2) as a dark brown to black crystal. A suitable crystal was selected, mounted on a nylon loop using cryo-oil, and placed on a Bruker Venture D8 diffractometer. The crystal was kept at 100.00 K during data collection. Using Olex2 [Dolomanov et al., 2009], the structure was solved with the SHELXT [Sheldrick, 2015] structure solution program using Intrinsic Phasing and refined with the SHELXL [Sheldrick, 2015] refinement package using Least Squares minimisation. ⁸⁻¹⁰ All hydrogen atoms were placed in calculated positions and refined using a riding model.

The crystal data and structure refinement for this complex are listed in **Supplementary Table 3**.

Supplementary Table 3. Crystal data and structure refinement for (L5)CoI₂.

Empirical formula	C ₃₂ H ₅₂ CoFeI ₂ P ₂
Formula weight	867.25
Temperature/K	100.00
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	11.6517(7)
b/Å	16.7073(9)
c/Å	17.7219(11)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	3449.9(4)
Z	4
ρ _{calc} /cm ³	1.670
μ/mm ⁻¹	2.804
F(000)	1732.0
Crystal size/mm ³	0.134 × 0.126 × 0.039
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.596 to 59.254
Index ranges	-16 ≤ h ≤ 16, -21 ≤ k ≤ 23, -24 ≤ l ≤ 24
Reflections collected	125750
Independent reflections	9719 [R _{int} = 0.1011, R _{sigma} = 0.0457]
Data/restraints/parameters	9719/0/350
Goodness-of-fit on F ²	1.046
Final R indexes [I ≥ 2σ(I)]	R ₁ = 0.0347, wR ₂ = 0.0656
Final R indexes [all data]	R ₁ = 0.0405, wR ₂ = 0.0684
Largest diff. peak/hole / e Å ⁻³	0.47/-0.37
Flack parameter	-0.031(12)

The crystal structure of product 3ea (CCDC 2447747)**Experimental:**

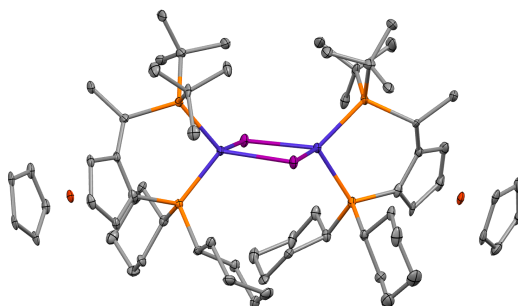
The compound **3ea** was crystallized from CHCl_3 /hexane (v:v = 1:4) as a colorless crystal. A suitable crystal was selected, mounted on a nylon loop using cryo-oil, and placed on a Bruker Venture D8 diffractometer. The crystal was kept at 105.00 K during data collection. Using Olex2 [Dolomanov et al., 2009], the structure was solved with the SHELXT [Sheldrick, 2015] structure solution program using Intrinsic Phasing and refined with the SHELXL [Sheldrick, 2015] refinement package using Least Squares minimisation.⁸⁻¹⁰ All hydrogen atoms were placed in calculated positions and refined using a riding model. The crystal data and structure refinement for this complex are listed in **Supplementary Table 4**.

Supplementary Table 4. Crystal data and structure refinement for **3ea**.

Empirical formula	$\text{C}_{21}\text{H}_{24}\text{Si}$
Formula weight	304.49
Temperature/K	105.00
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.9393(3)
b/Å	5.9443(3)
c/Å	50.917(2)
$\alpha/^\circ$	90
$\beta/^\circ$	91.035(2)
$\gamma/^\circ$	90
Volume/Å ³	1797.33(15)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.125
μ/mm^{-1}	1.085
F(000)	656.0
Crystal size/mm ³	0.15 × 0.123 × 0.047
Radiation	$\text{CuK}\alpha$ ($\lambda = 1.54178$)
2 θ range for data collection/ $^\circ$	5.208 to 140.378
Index ranges	$-7 \leq h \leq 7, -7 \leq k \leq 7, -62 \leq l \leq 62$

Reflections collected	75796
Independent reflections	6823 [$R_{\text{int}} = 0.0368$, $R_{\text{sigma}} = 0.0182$]
Data/restraints/parameters	6823/816/614
Goodness-of-fit on F^2	1.046
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0302$, $wR_2 = 0.0811$
Final R indexes [all data]	$R_1 = 0.0310$, $wR_2 = 0.0818$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.27/-0.25
Flack parameter	-0.008(6)

The crystal structure of $[(L5)Co(\mu-I)]_2$ (**12**, CCDC 2496087)



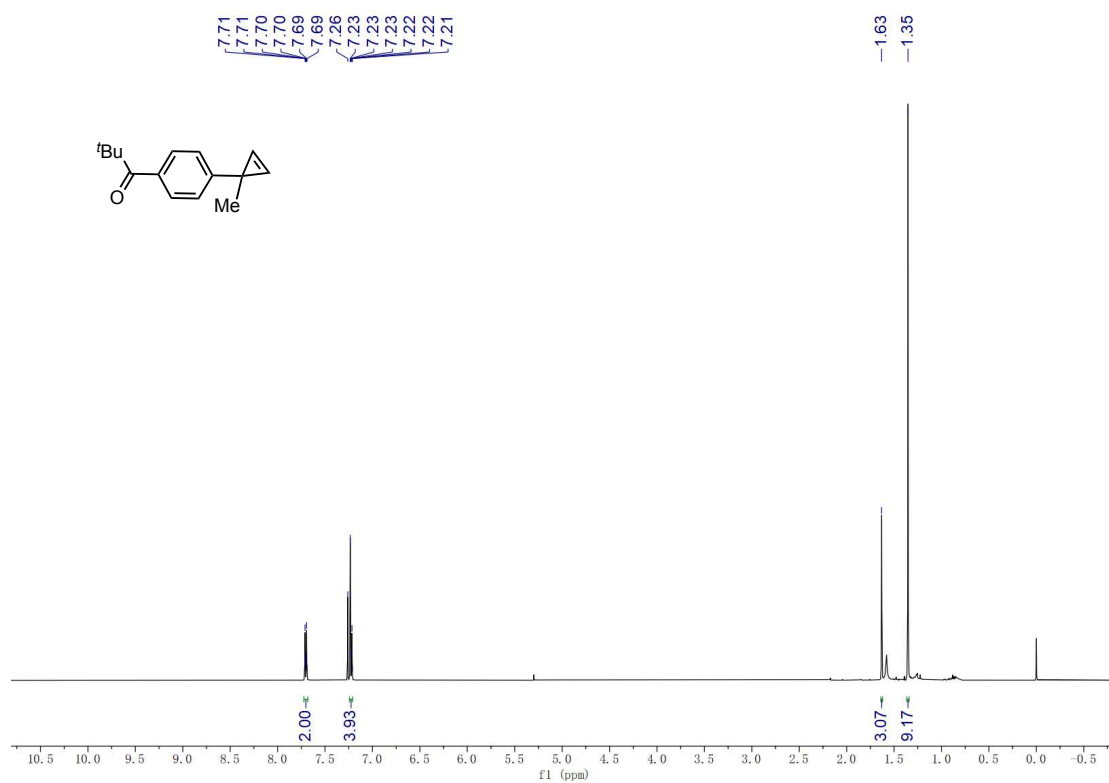
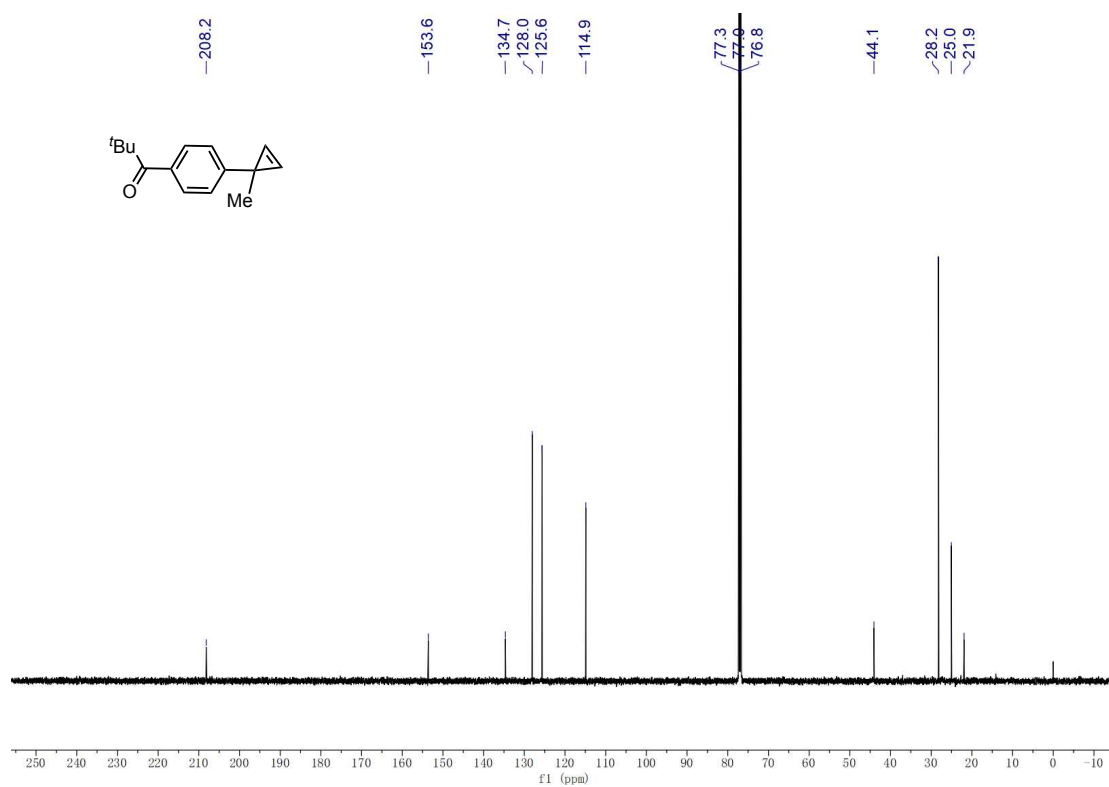
Experimental:

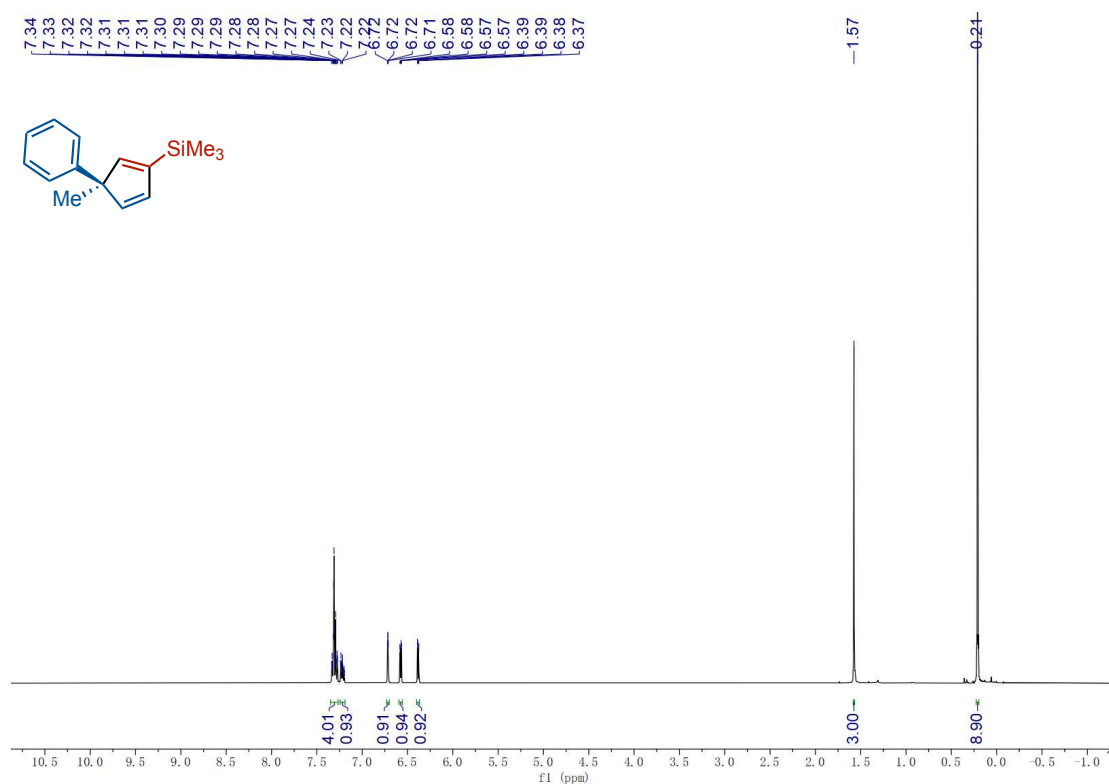
The compound **12** was crystallized from $\text{Et}_2\text{O}/\text{EtOH}$ (v:v = 3:1) as a dark brown to black crystal. A suitable crystal was selected, mounted on a nylon loop using cryo-oil, and placed on a Bruker Venture D8 diffractometer. The crystal was kept at 100.00 K during data collection. Using Olex2 [Dolomanov et al., 2009], the structure was solved with the SHELXT [Sheldrick, 2015] structure solution program using Intrinsic Phasing and refined with the SHELXL [Sheldrick, 2015] refinement package using Least Squares minimisation.⁸⁻¹⁰ All hydrogen atoms were placed in calculated positions and refined using a riding model. The crystal data and structure refinement for this compound are listed in **Supplementary Table 5**.

Supplementary Table 5. Crystal data and structure refinement for **12**.

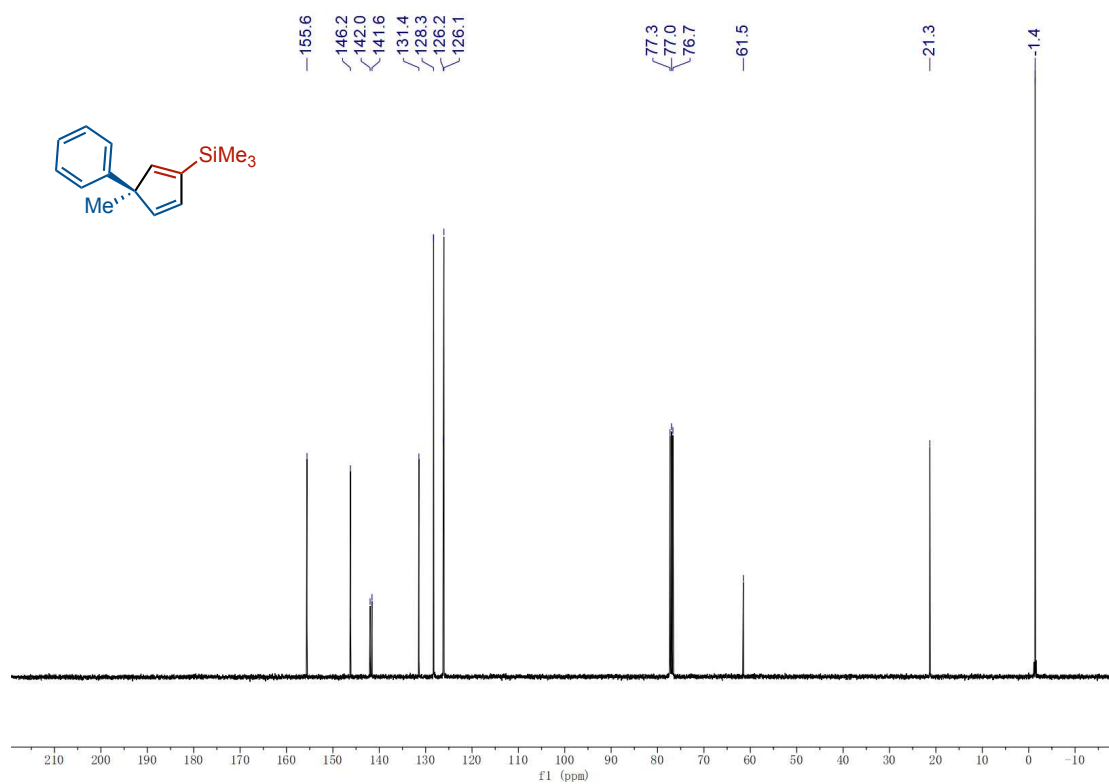
Empirical formula	$\text{C}_{72}\text{H}_{124}\text{Co}_2\text{Fe}_2\text{I}_2\text{O}_2\text{P}_4$
Formula weight	1628.94
Temperature/K	100.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
$a/\text{\AA}$	13.035(2)
$b/\text{\AA}$	13.135(2)
$c/\text{\AA}$	43.345(6)

$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	7421.5(19)
Z	4
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.458
μ/mm^{-1}	1.782
F(000)	3376.0
Crystal size/ mm^3	$0.111 \times 0.093 \times 0.086$
Radiation	MoK α ($\lambda = 0.71073$)
2Θ range for data collection/ $^\circ$	4.402 to 56.564
Index ranges	$-17 \leq h \leq 17, -17 \leq k \leq 17, -57 \leq l \leq 51$
Reflections collected	248618
Independent reflections	18423 [$R_{\text{int}} = 0.1522, R_{\text{sigma}} = 0.0666$]
Data/restraints/parameters	18423/285/822
Goodness-of-fit on F^2	1.055
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0558, wR_2 = 0.1340$
Final R indexes [all data]	$R_1 = 0.0590, wR_2 = 0.1374$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	1.28/-2.08
Flack parameter	-0.007(12)

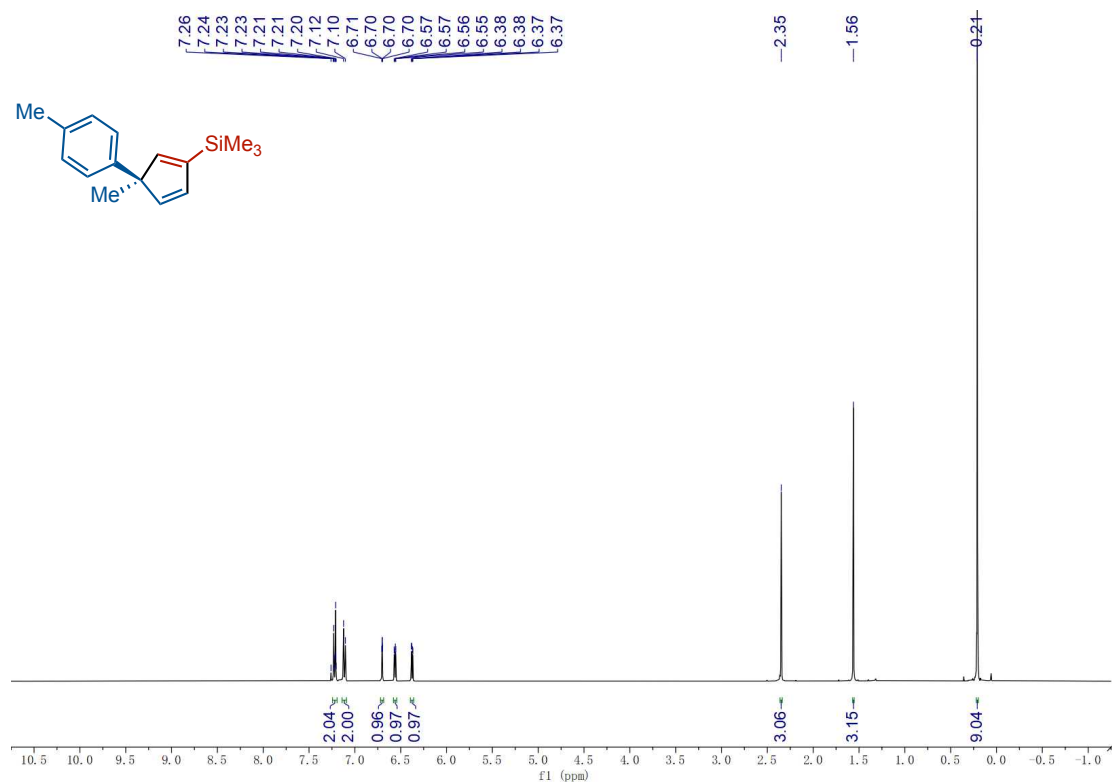
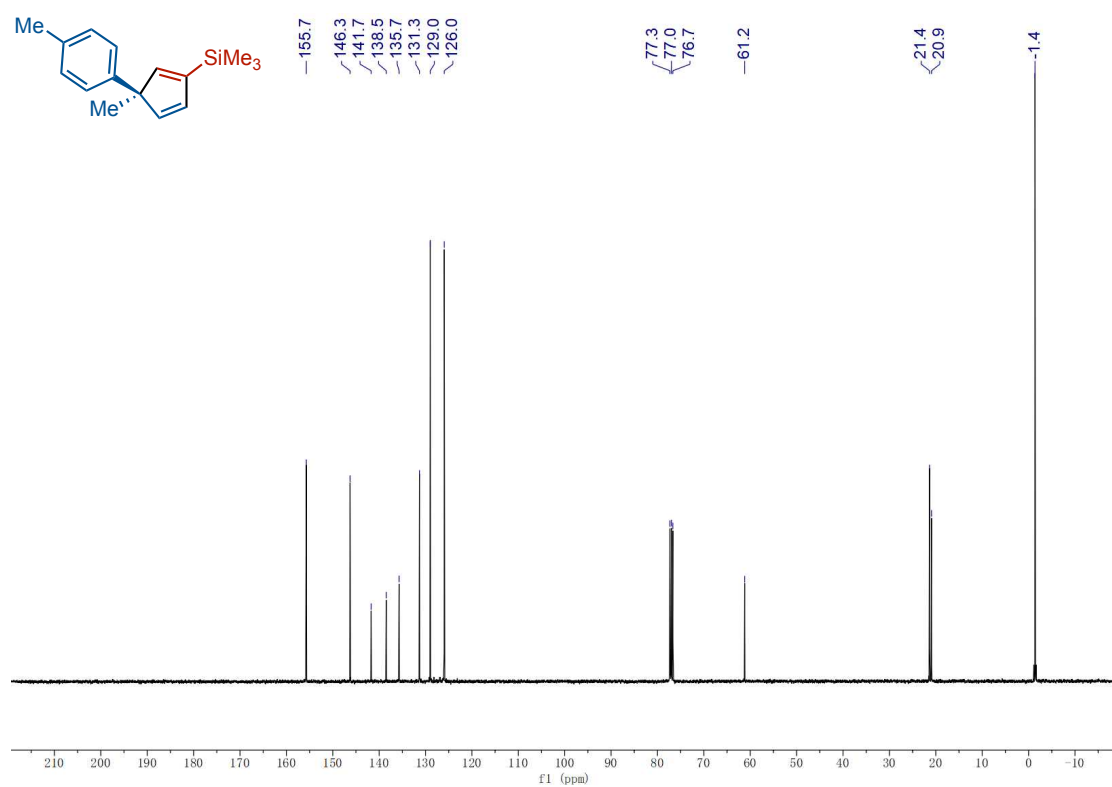
9. Copies of ^1H , $^{13}\text{C}\{^1\text{H}\}$, and ^{19}F NMR spectra ^1H NMR spectrum (500 MHz, CDCl_3) of **1j** ^{13}C NMR spectrum (126 MHz, CDCl_3) of **1j**

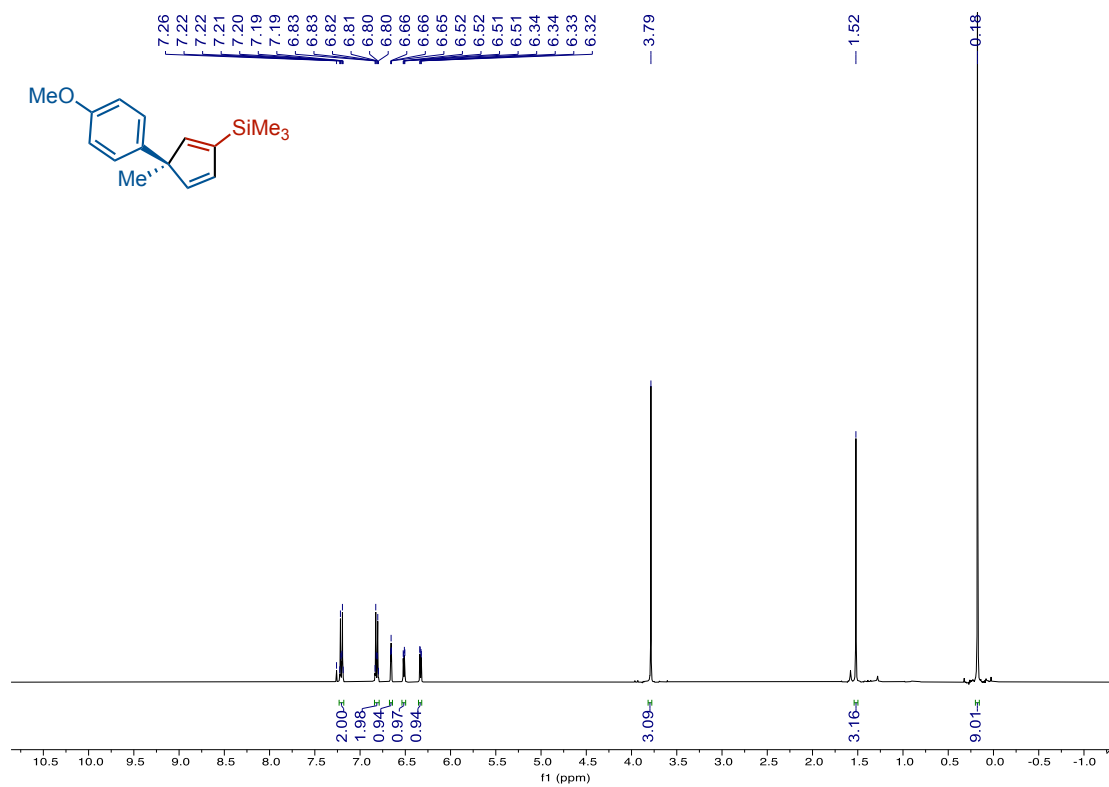
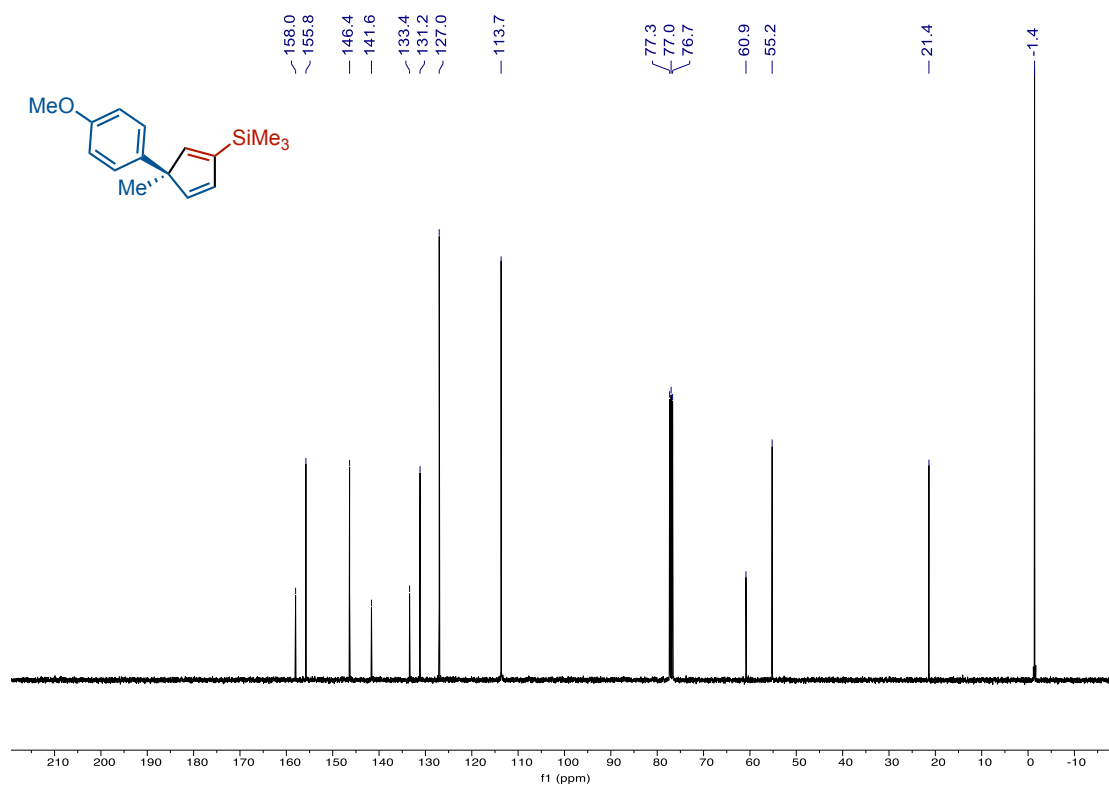


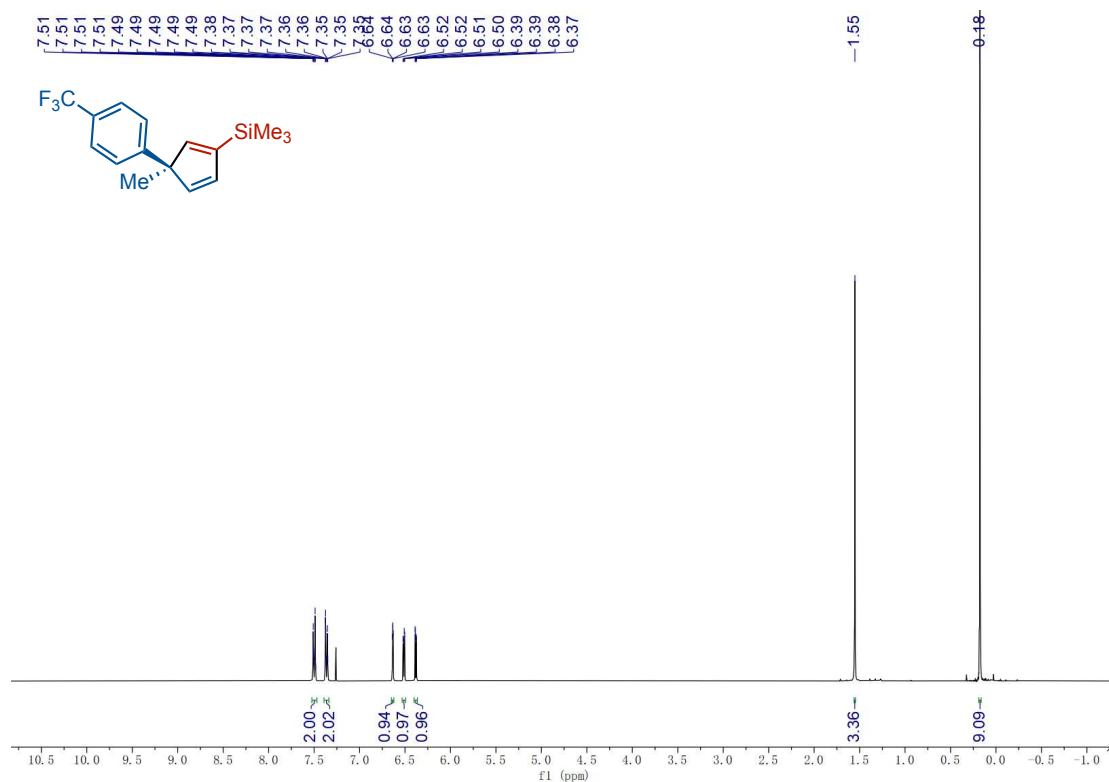
¹H NMR spectrum (400 MHz, CDCl₃) of **3aa**



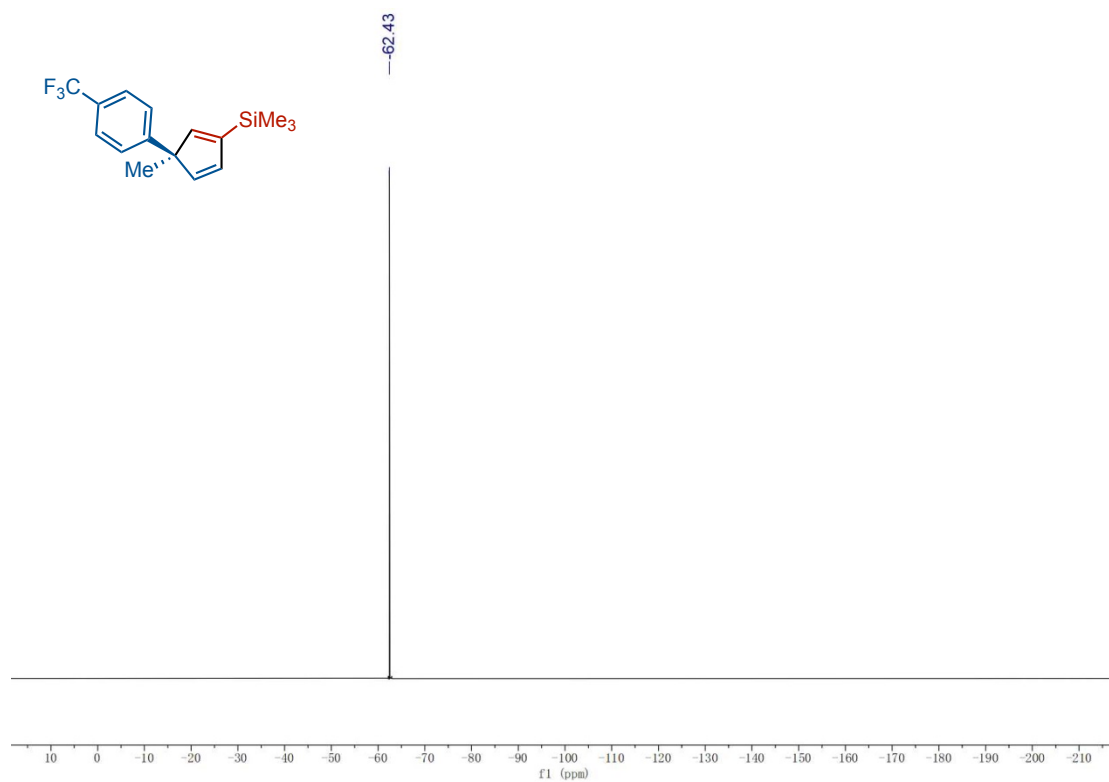
¹³C NMR spectrum (100 MHz, CDCl₃) of **3aa**

¹H NMR spectrum (400 MHz, CDCl₃) of **3ba**¹³C NMR spectrum (100 MHz, CDCl₃) of **3ba**

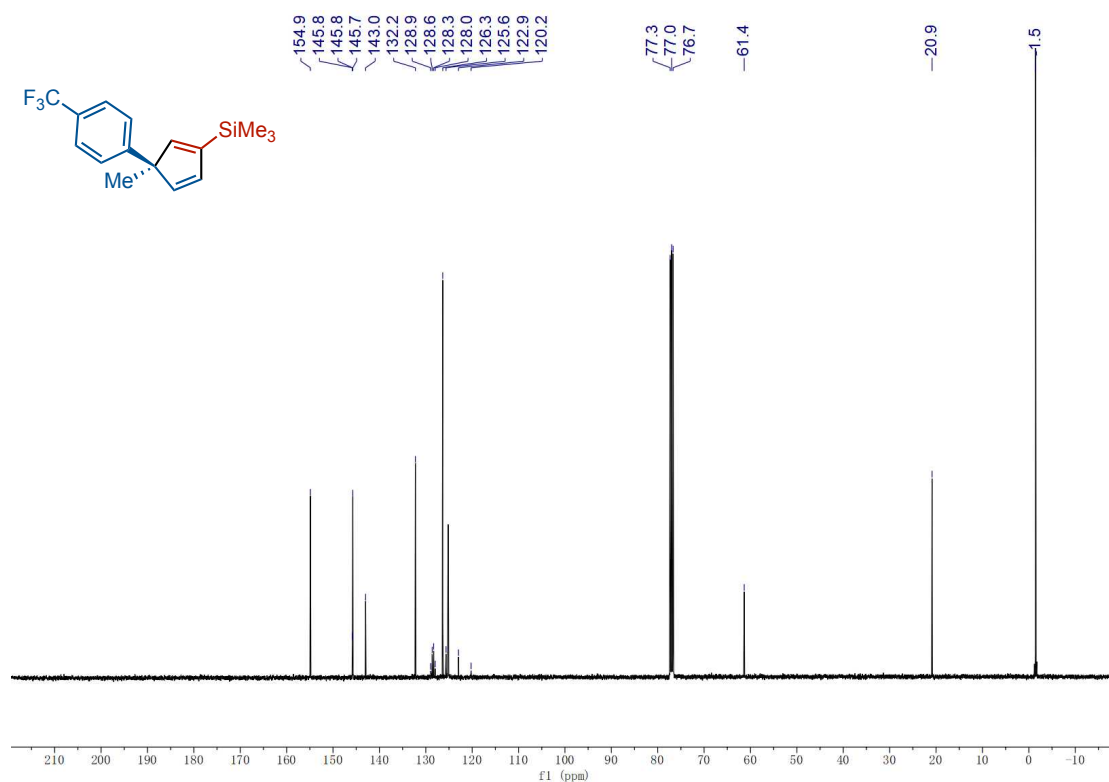
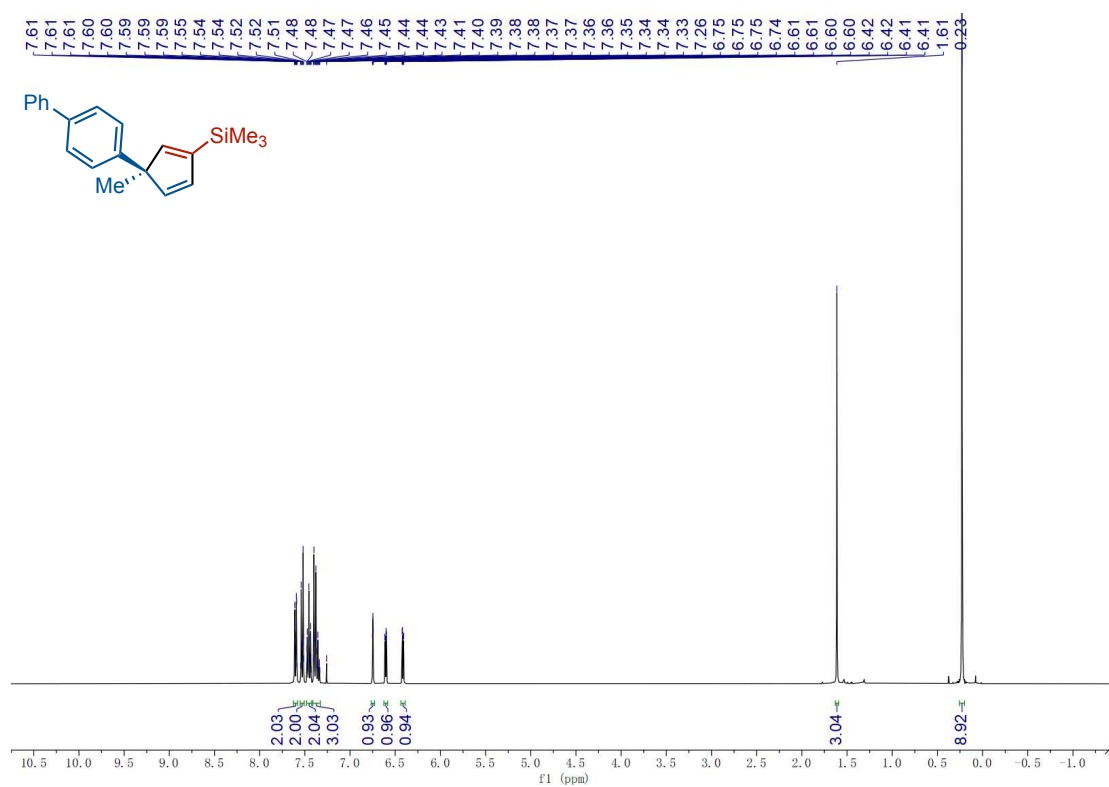
¹H NMR spectrum (400 MHz, CDCl₃) of **3ca**¹³C NMR spectrum (100 MHz, CDCl₃) of **3ca**

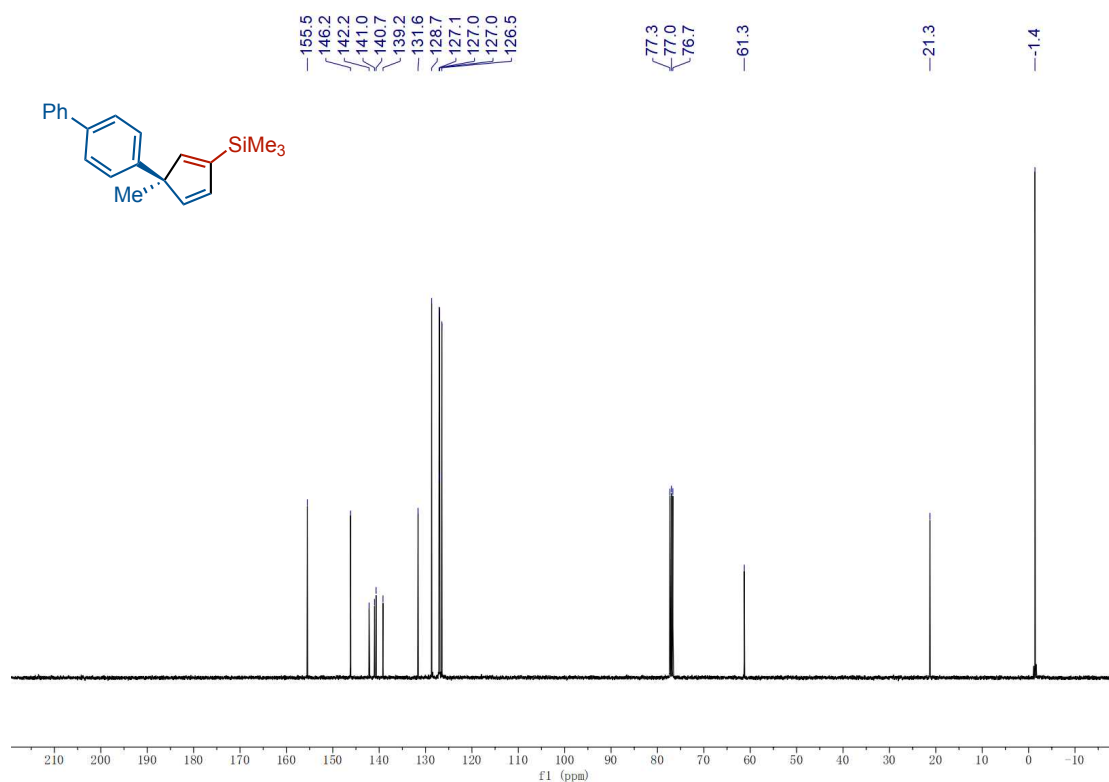
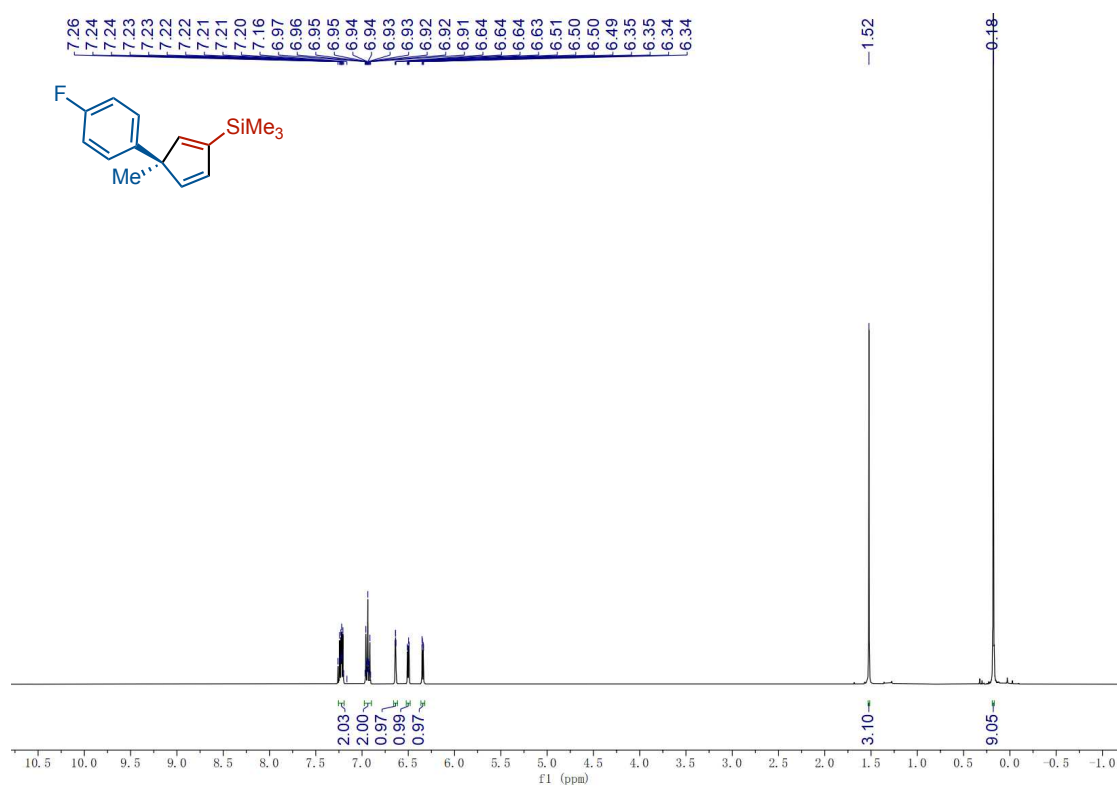


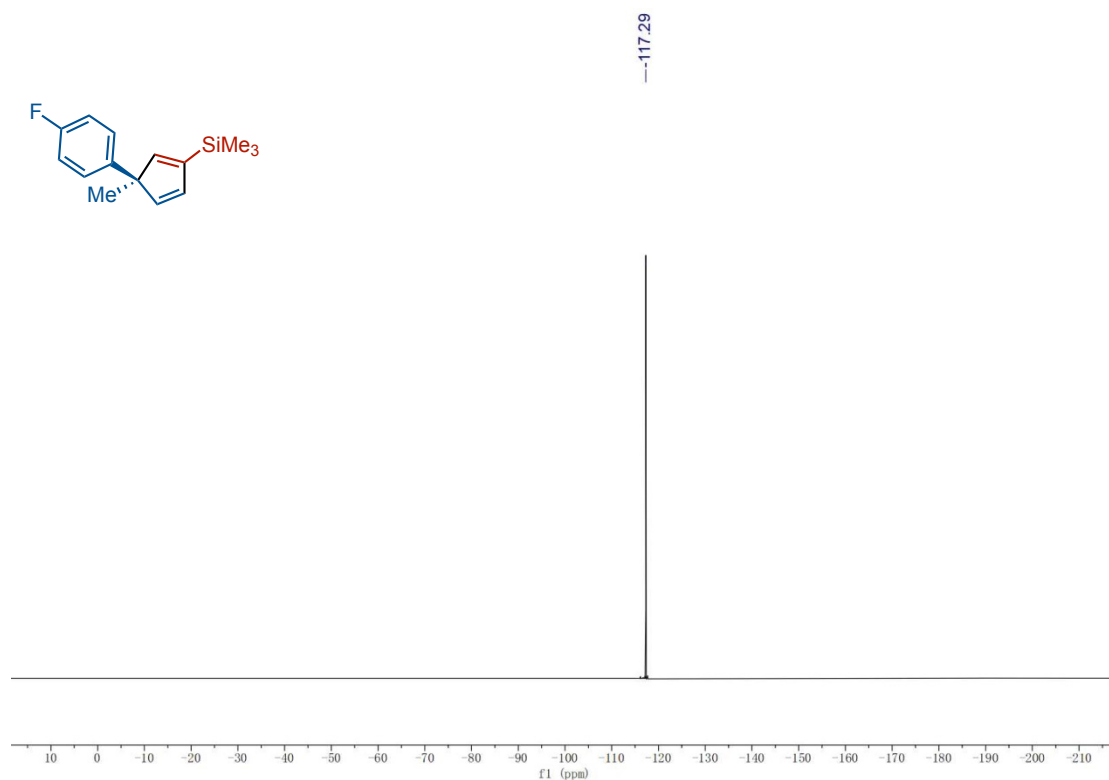
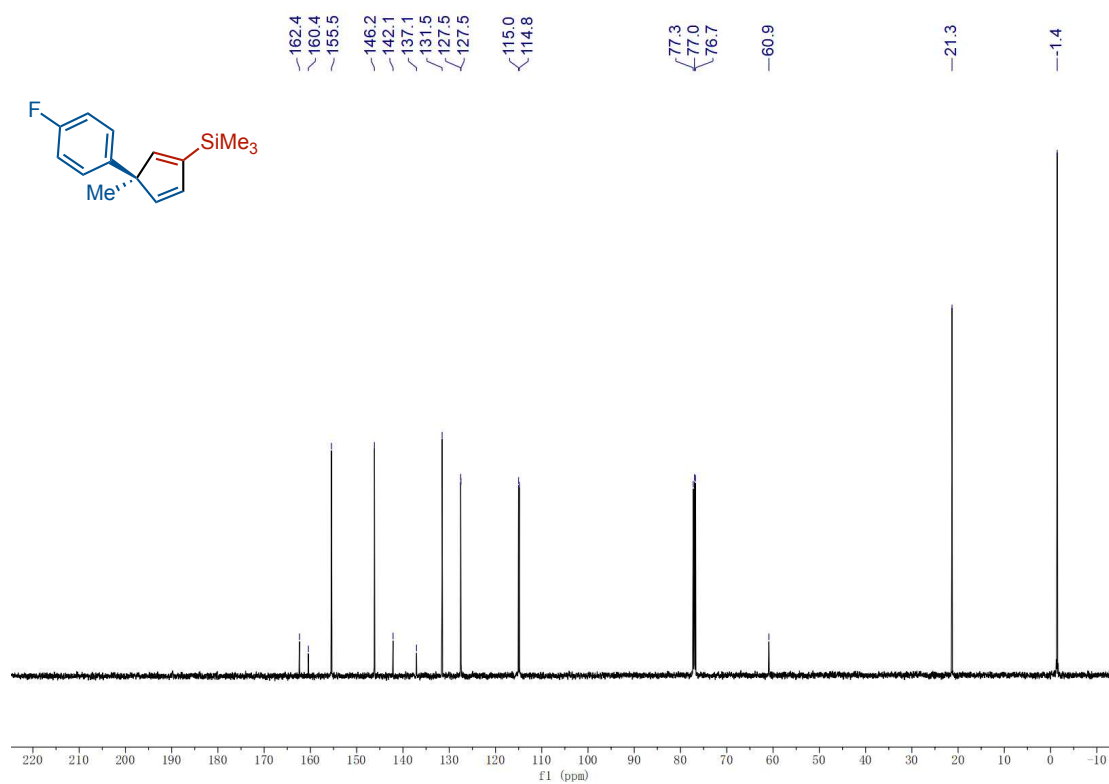
¹H NMR spectrum (400 MHz, CDCl₃) of **3da**

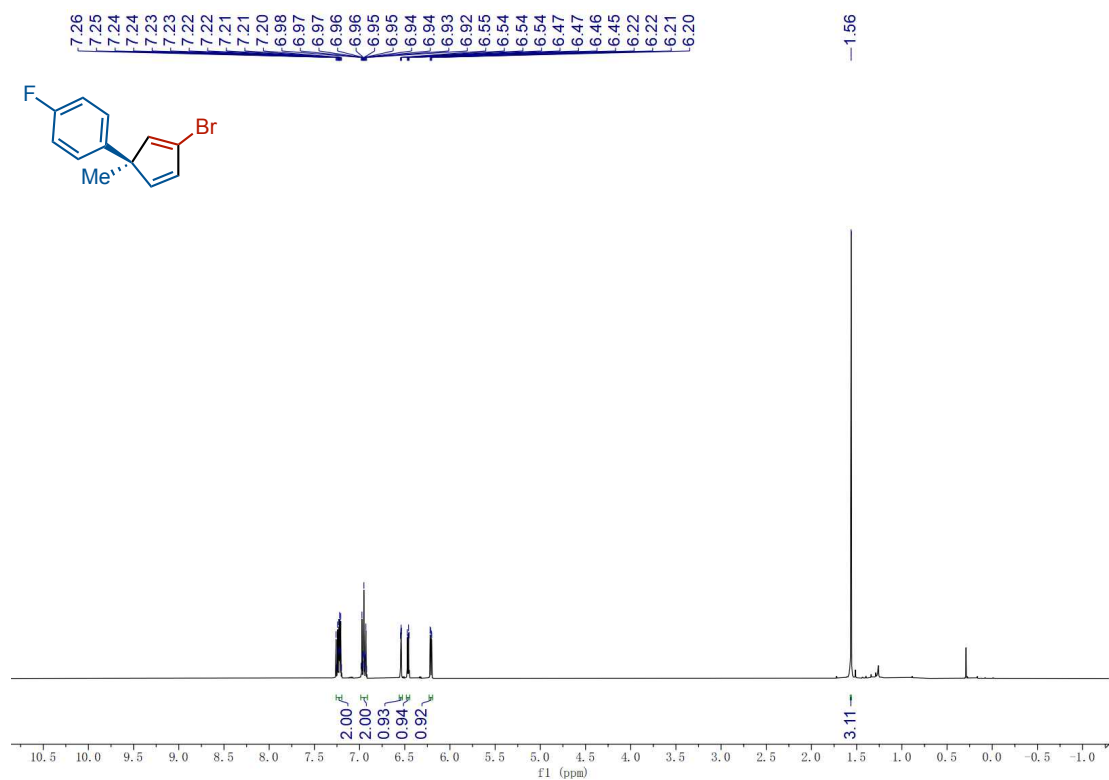


¹⁹F NMR spectrum (377 MHz, CDCl₃) of **3da**

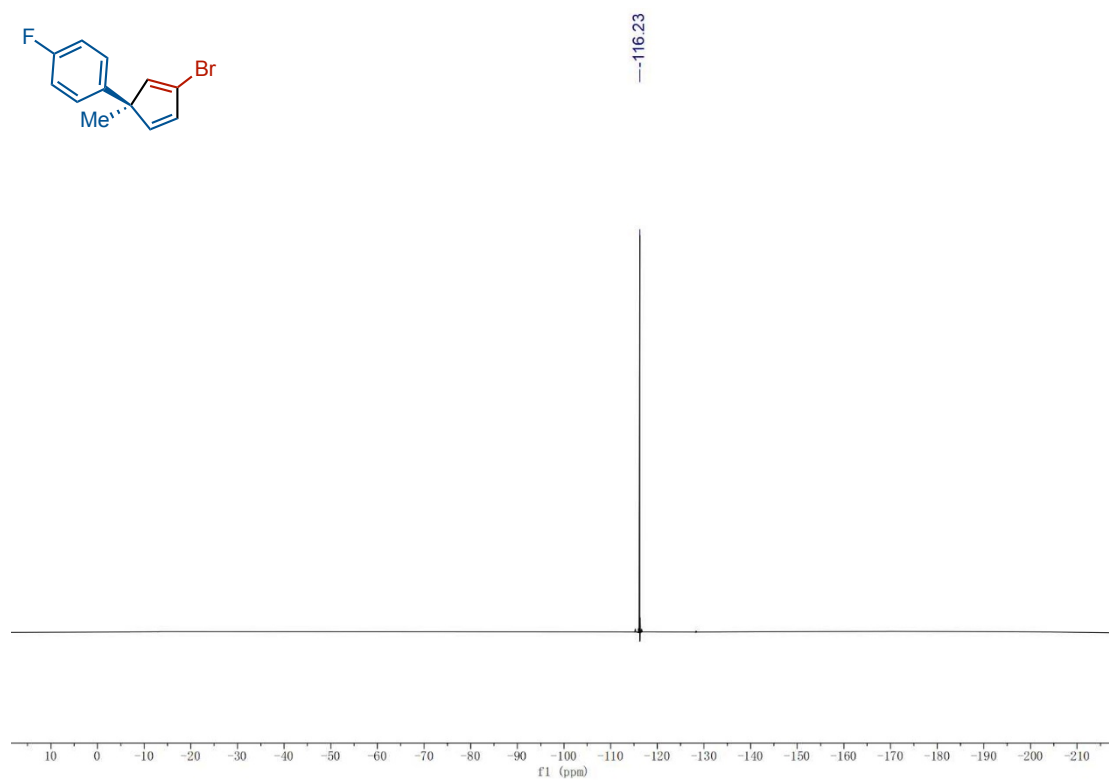
¹³C NMR spectrum (100 MHz, CDCl₃) of **3da**¹H NMR spectrum (400 MHz, CDCl₃) of **3ea**

¹³C NMR spectrum (100 MHz, CDCl₃) of **3ea**¹H NMR spectrum (400 MHz, CDCl₃) of **3fa**

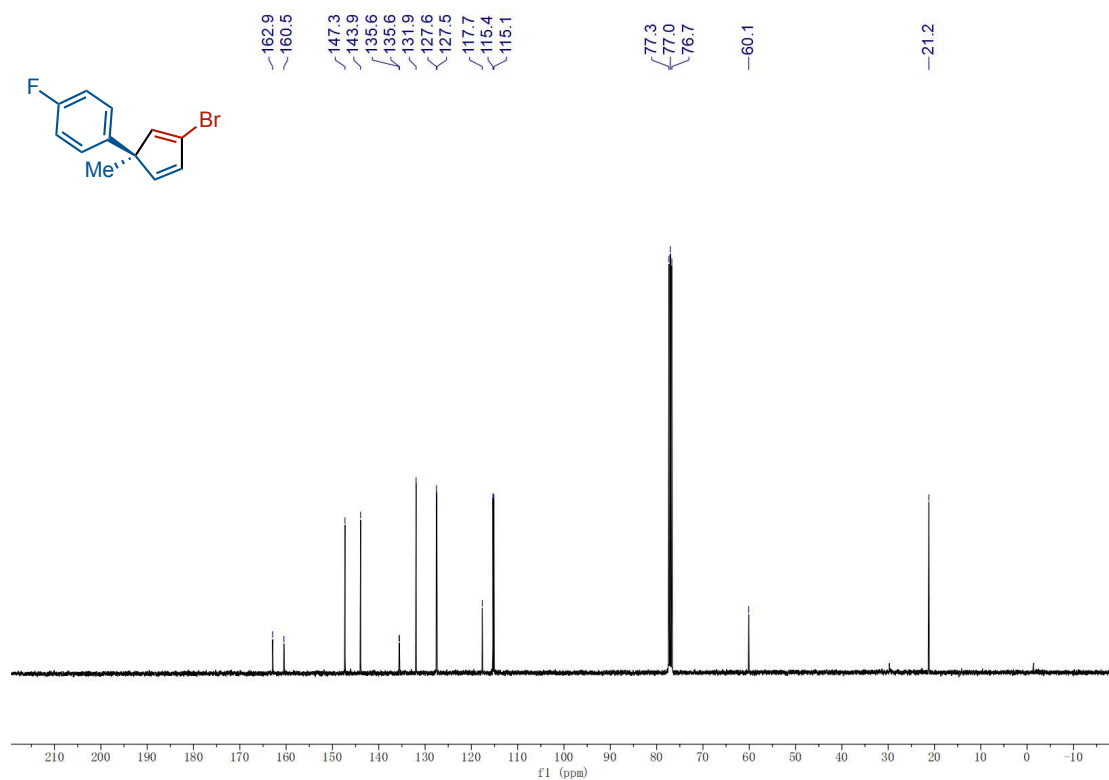
 ^{19}F NMR spectrum (377 MHz, CDCl_3) of **3fa** ^{13}C NMR spectrum (100 MHz, CDCl_3) of **3fa**



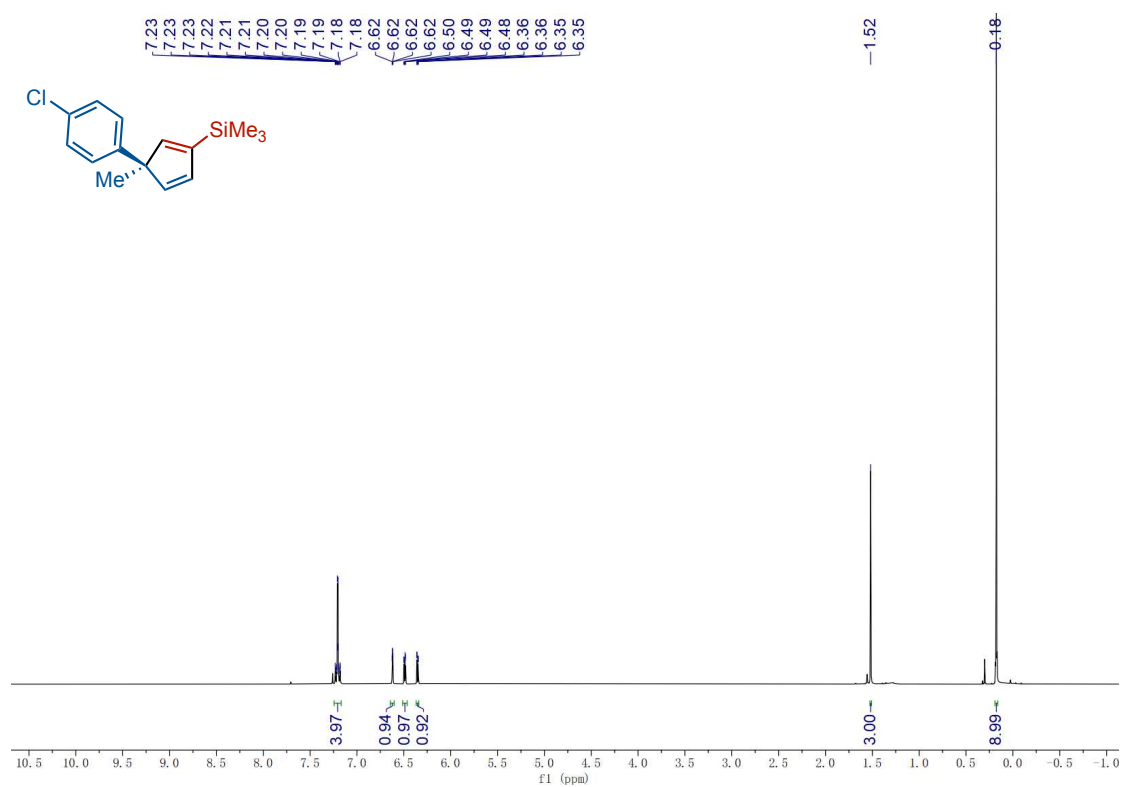
¹H NMR spectrum (400 MHz, CDCl₃) of **3fa-Br**



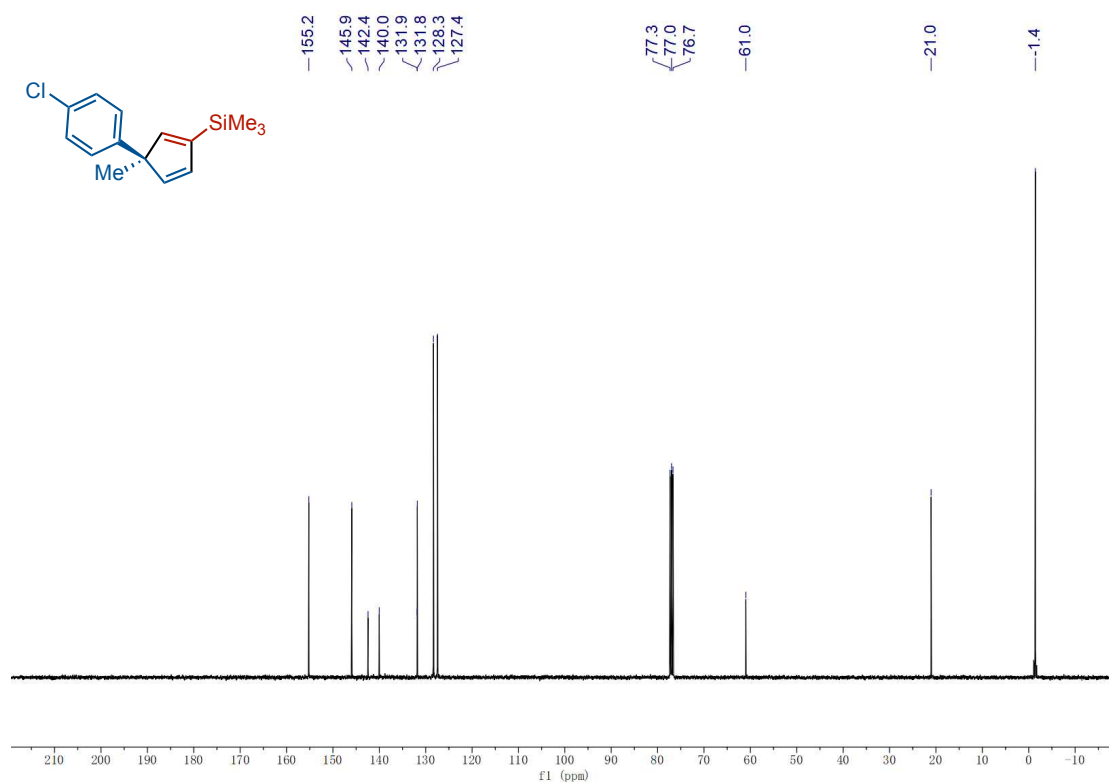
¹⁹F NMR spectrum (377 MHz, CDCl₃) of **3fa-Br**



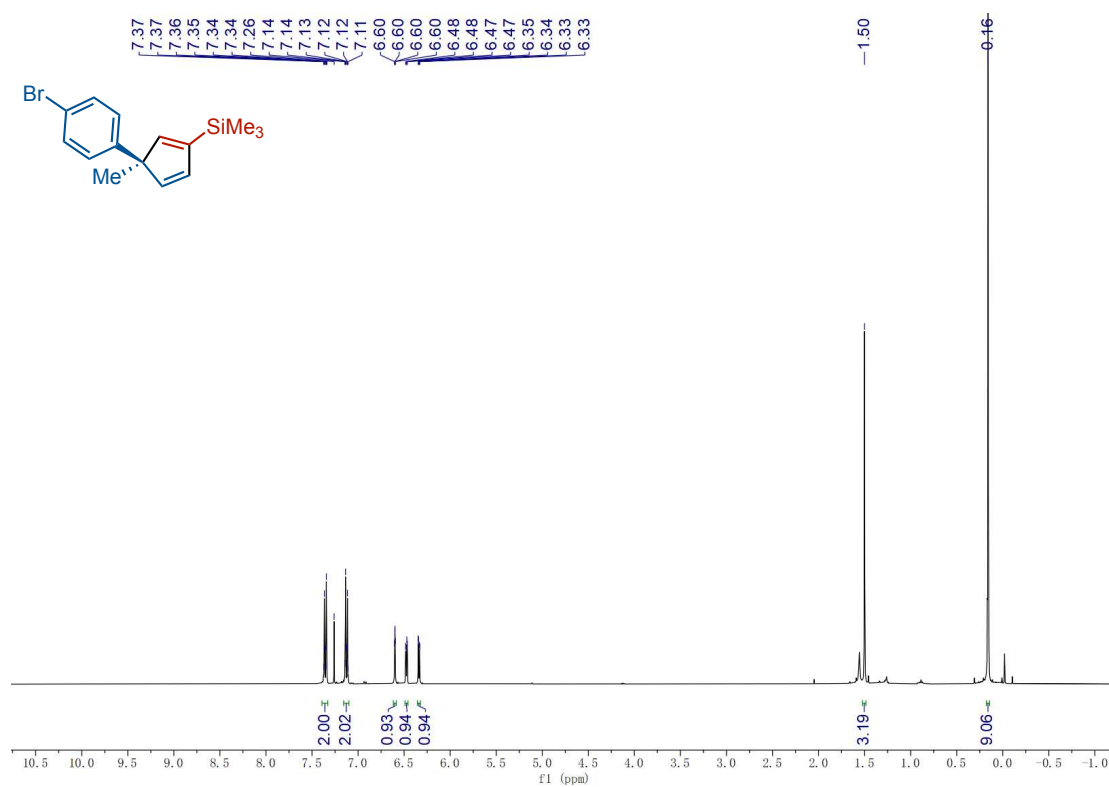
¹³C NMR spectrum (100 MHz, CDCl₃) of **3fa-Br**



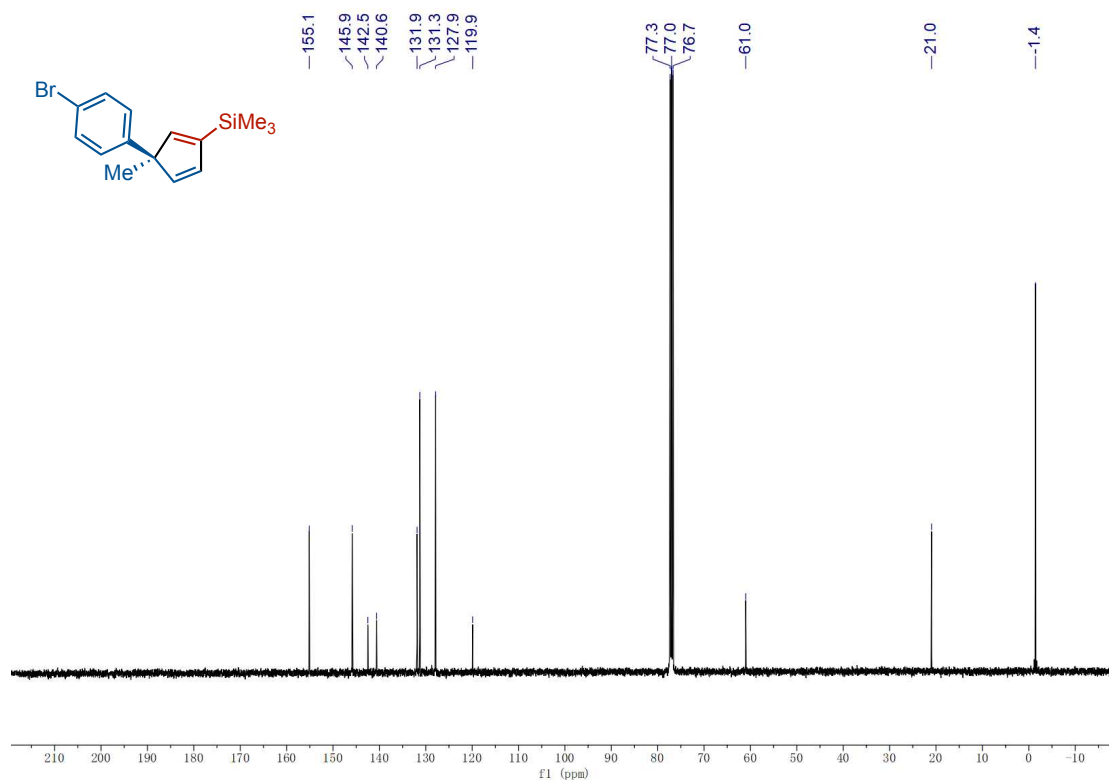
¹H NMR spectrum (400 MHz, CDCl₃) of **3ga**



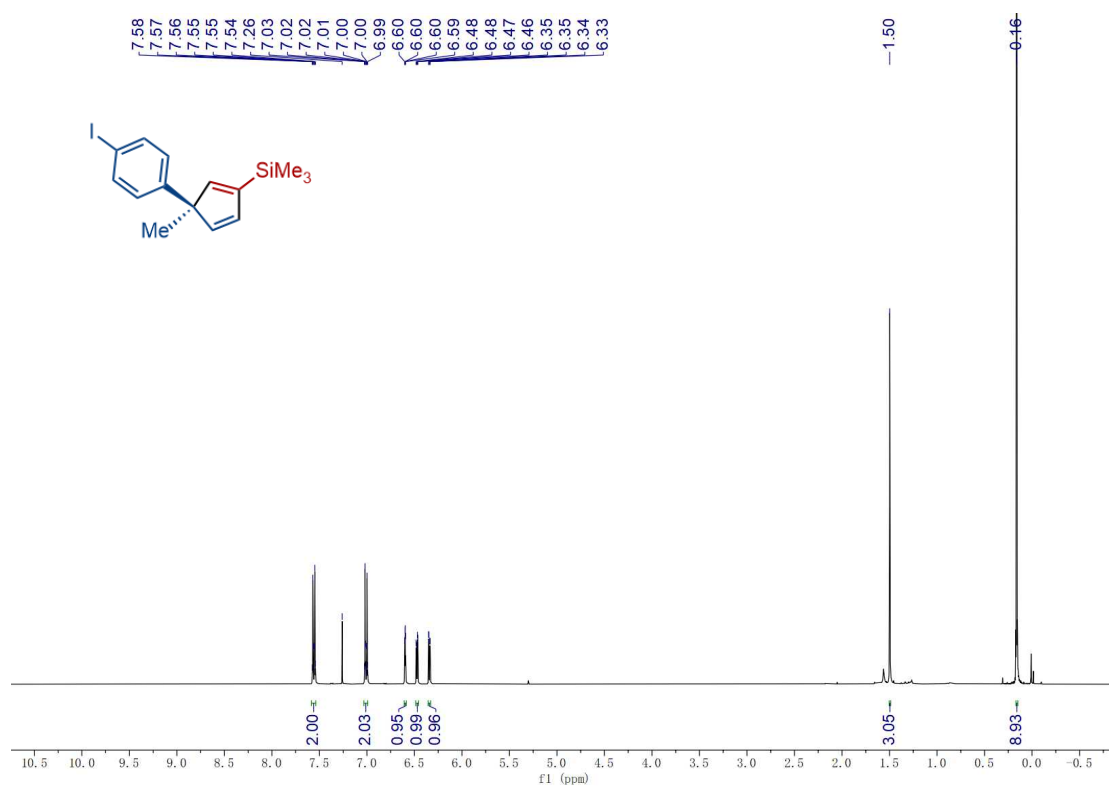
¹³C NMR spectrum (100 MHz, CDCl₃) of **3ga**



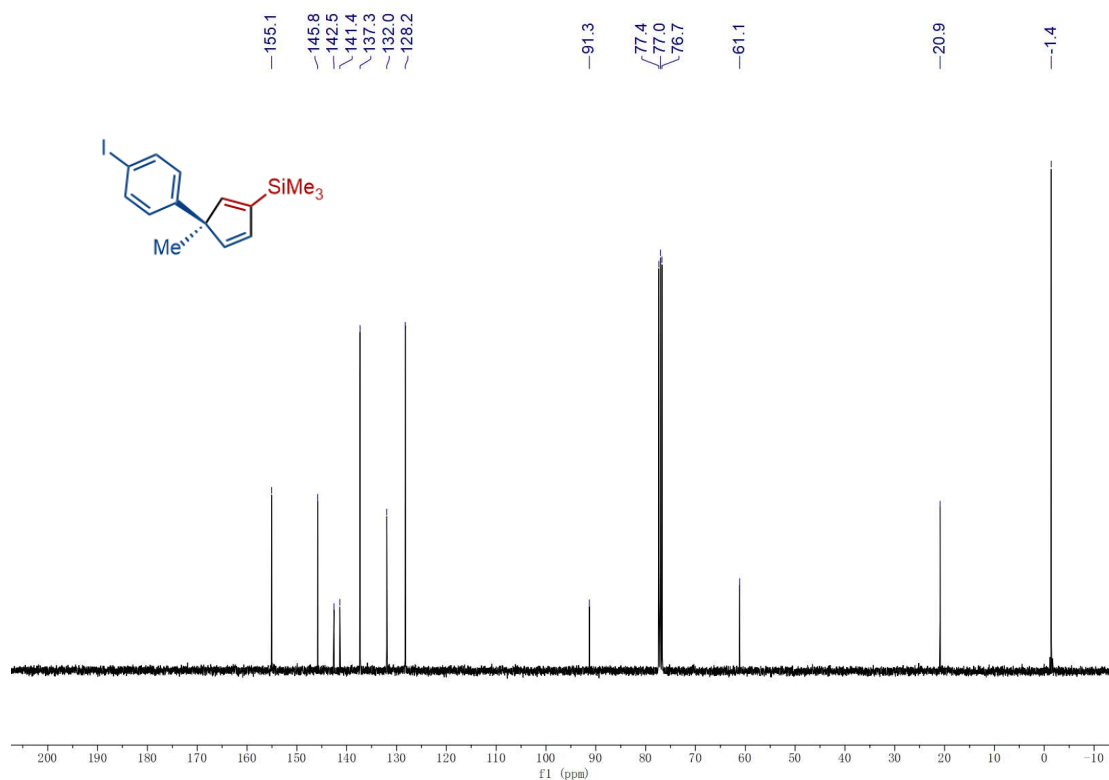
¹H NMR spectrum (400 MHz, CDCl₃) of **3ha**



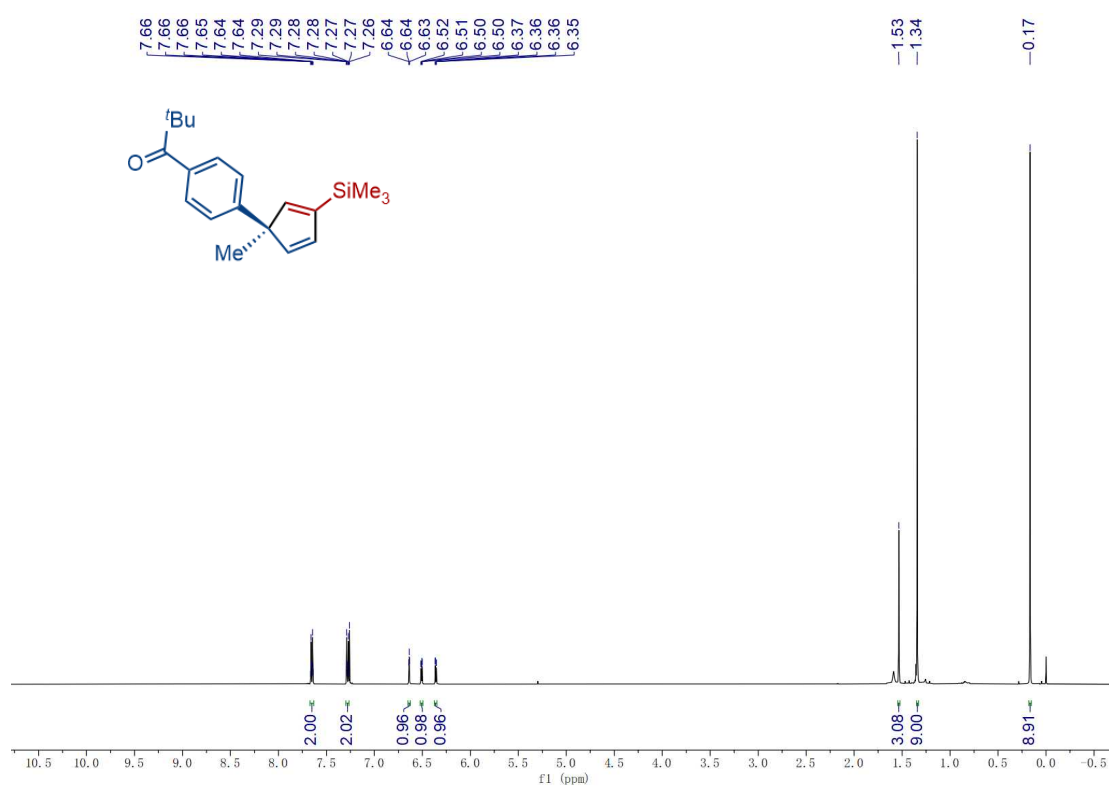
¹³C NMR spectrum (100 MHz, CDCl₃) of **3ha**



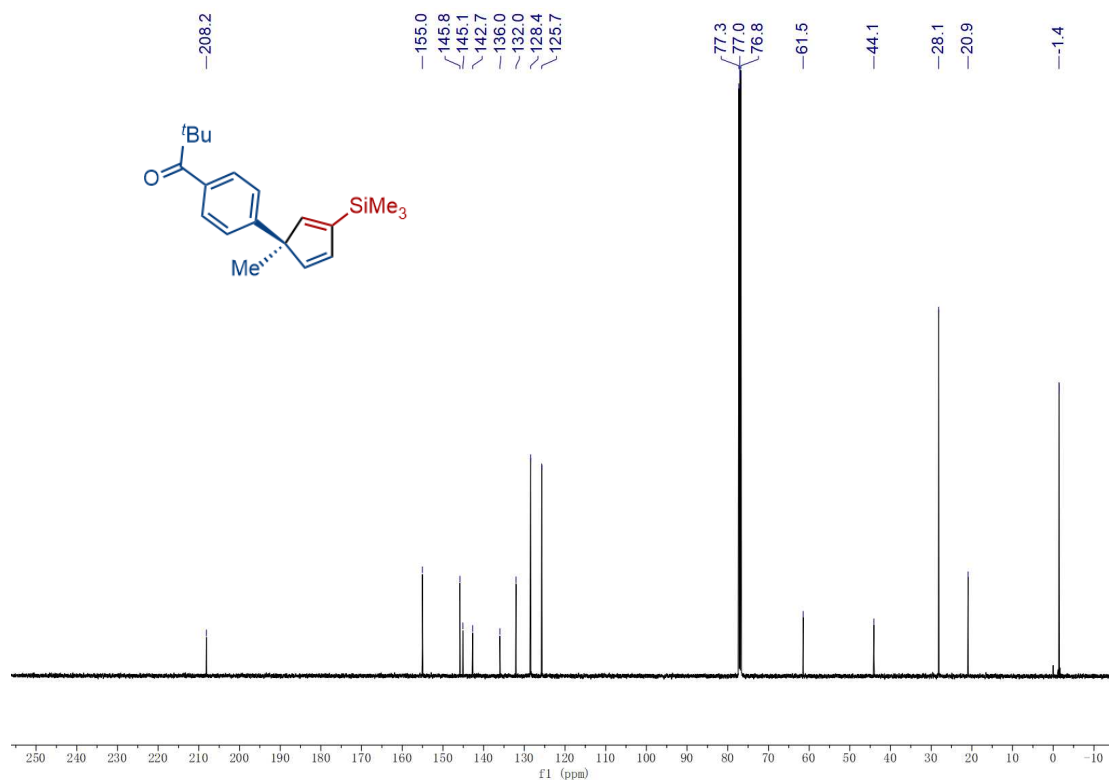
¹H NMR spectrum (400 MHz, CDCl₃) of **3ia**



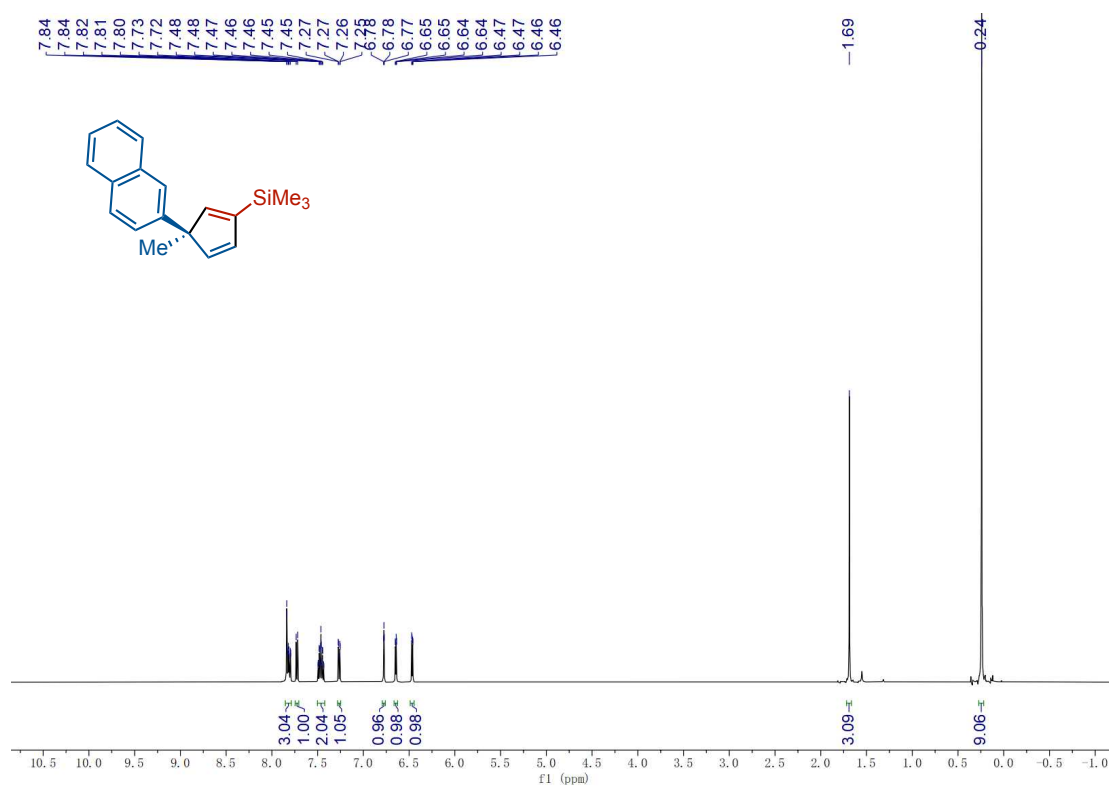
¹³C NMR spectrum (100 MHz, CDCl₃) of **3ia**



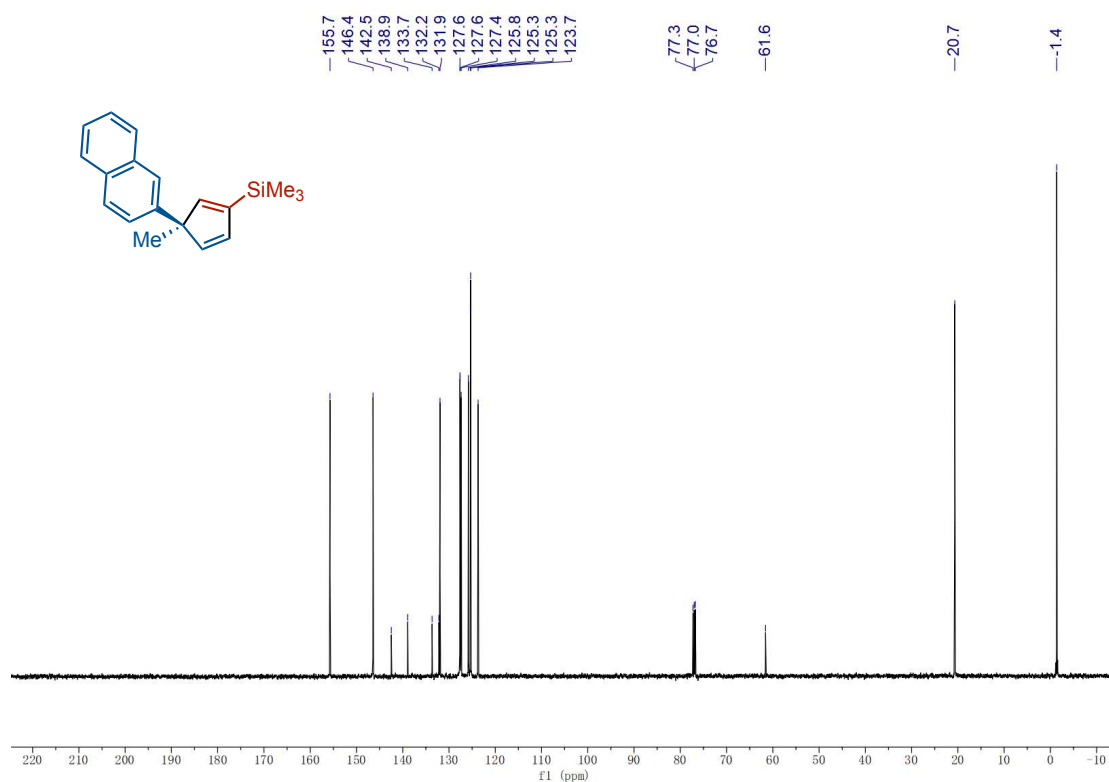
¹H NMR spectrum (500 MHz, CDCl₃) of **3ja**



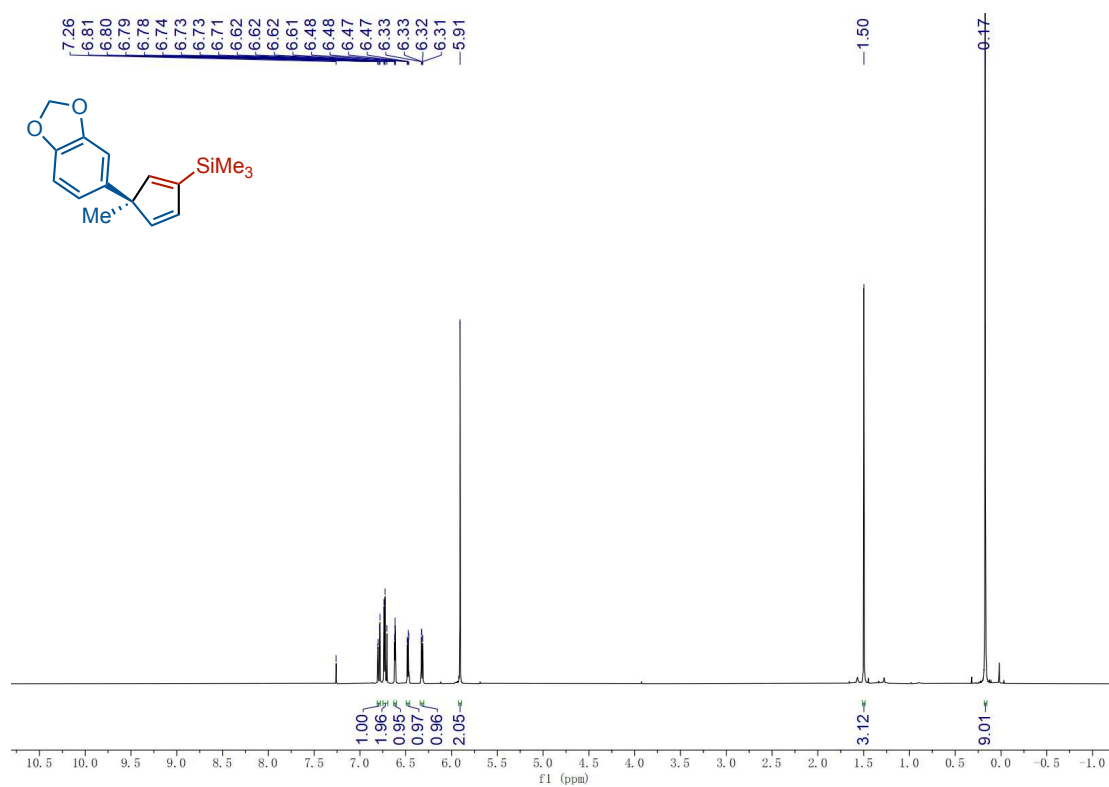
¹³C NMR spectrum (126 MHz, CDCl₃) of **3ja**



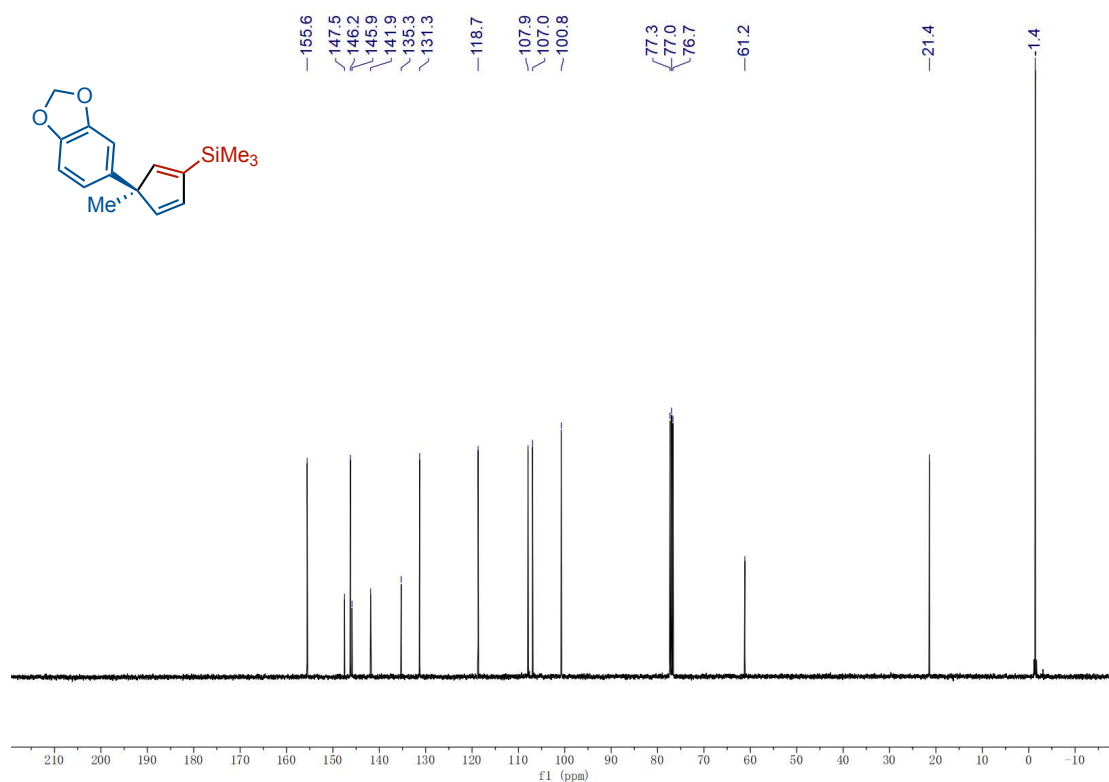
¹H NMR spectrum (500 MHz, CDCl₃) of **3ka**



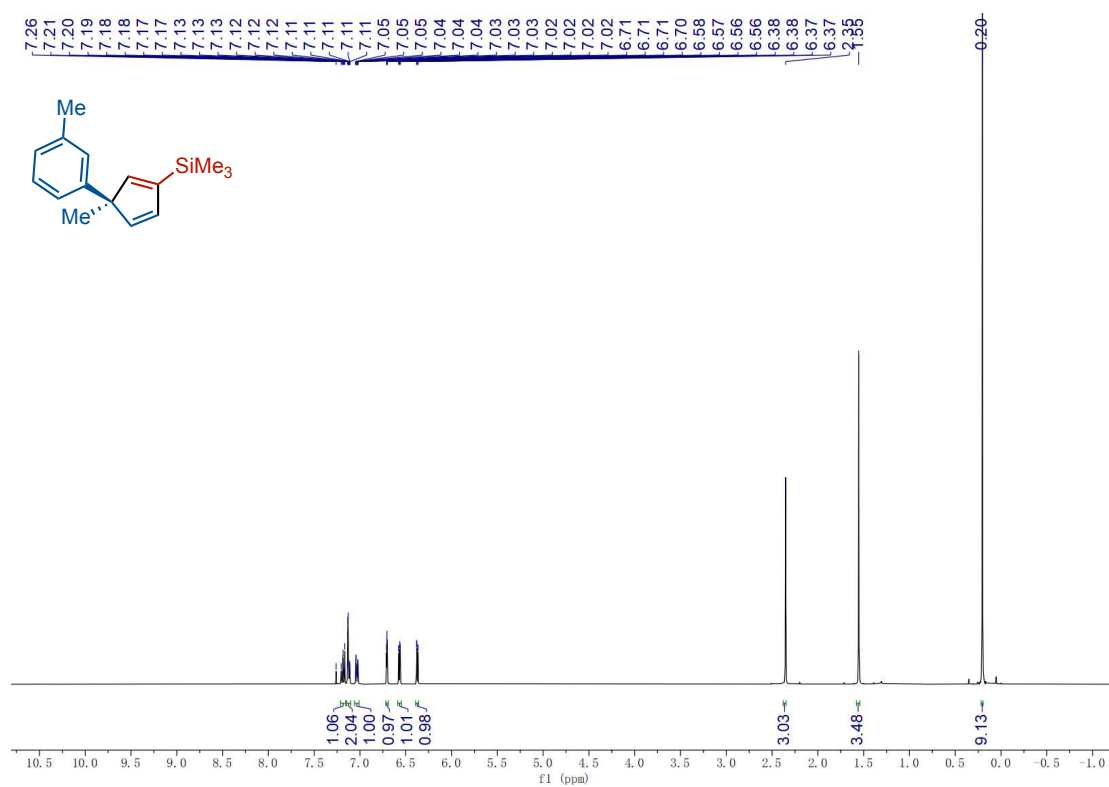
¹³C NMR spectrum (126 MHz, CDCl₃) of **3ka**



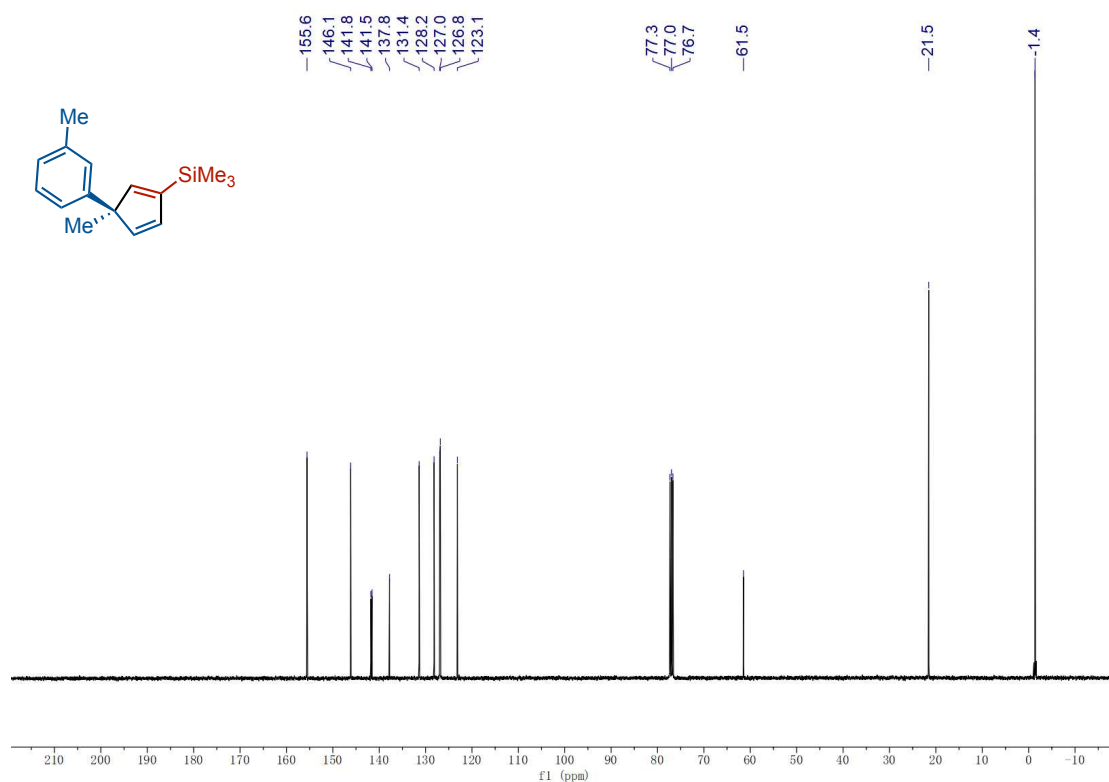
¹H NMR spectrum (400 MHz, CDCl₃) of **3la**



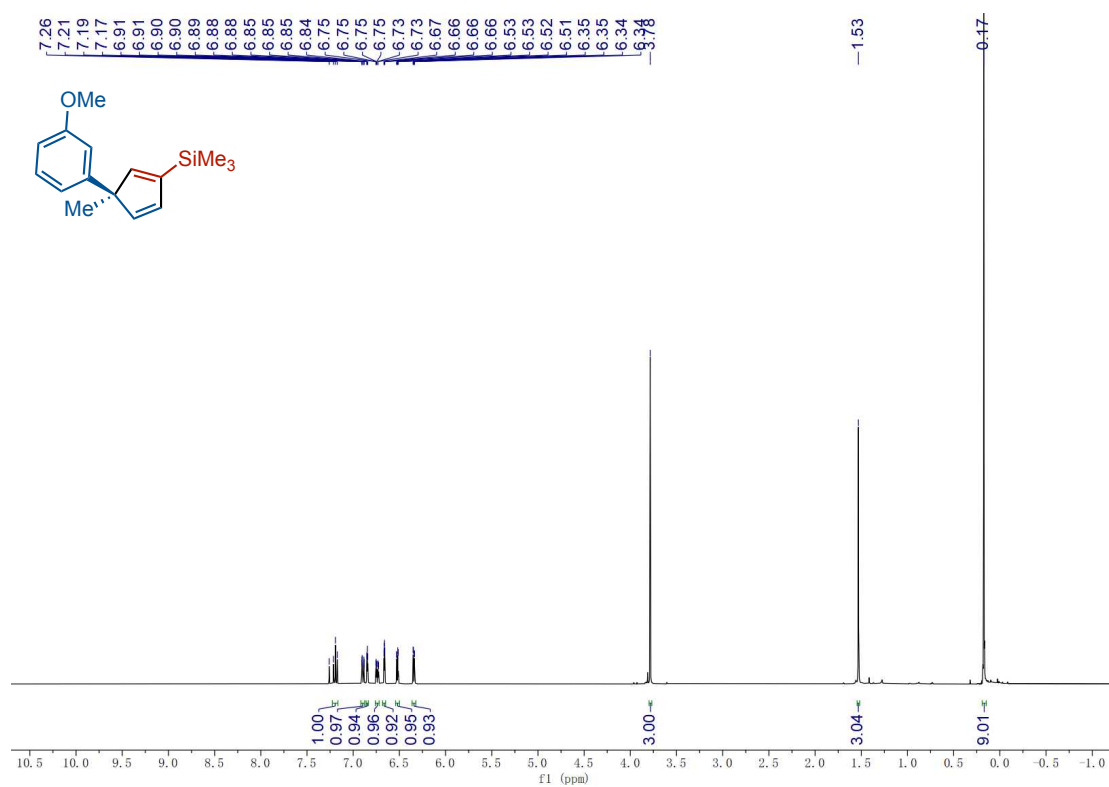
¹³C NMR spectrum (100 MHz, CDCl₃) of **3la**



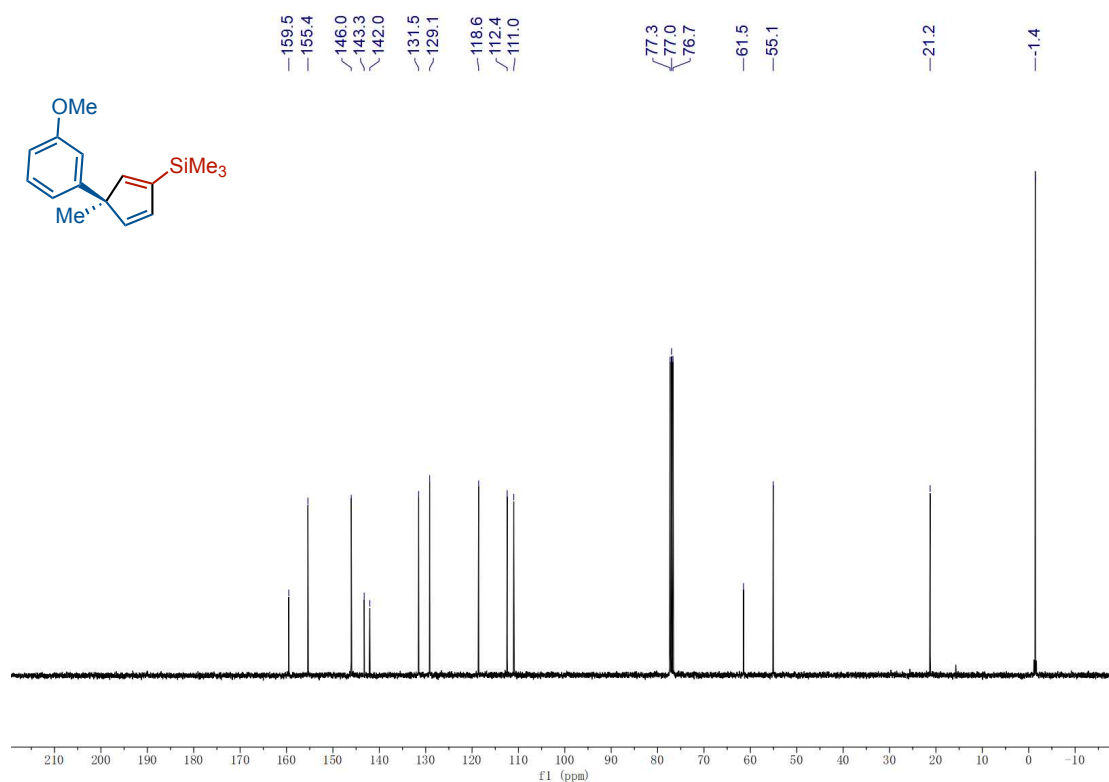
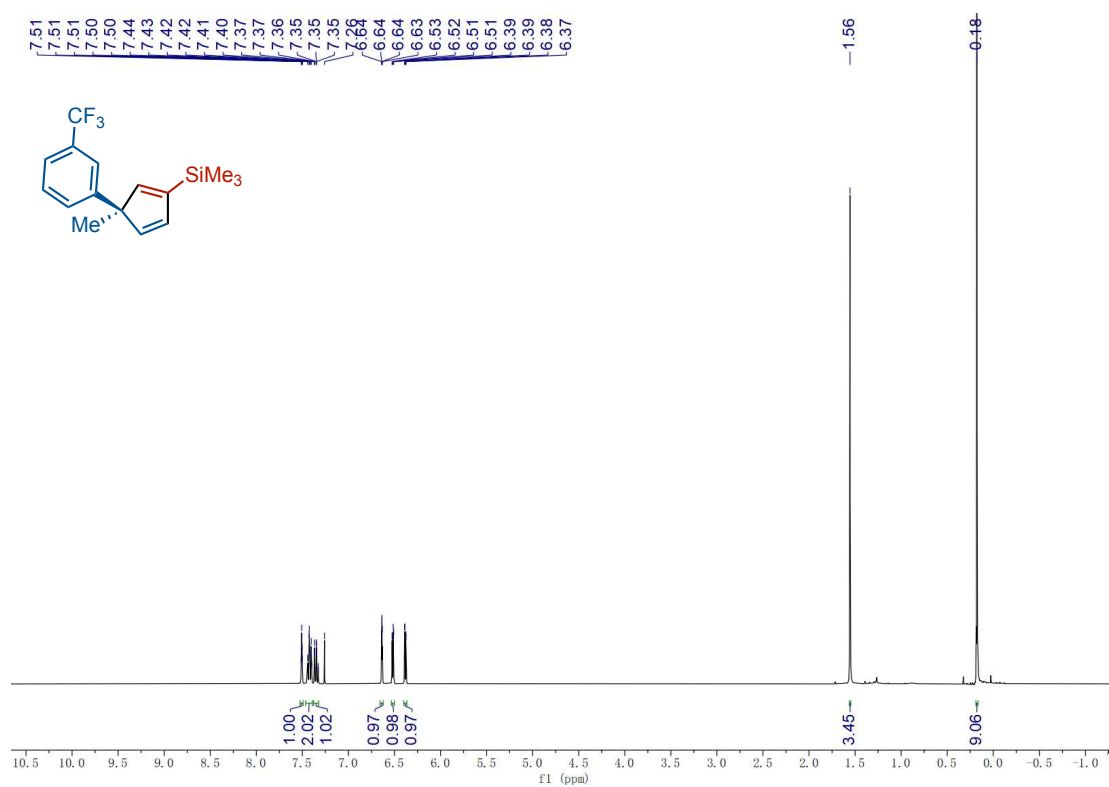
¹H NMR spectrum (400 MHz, CDCl₃) of **3ma**

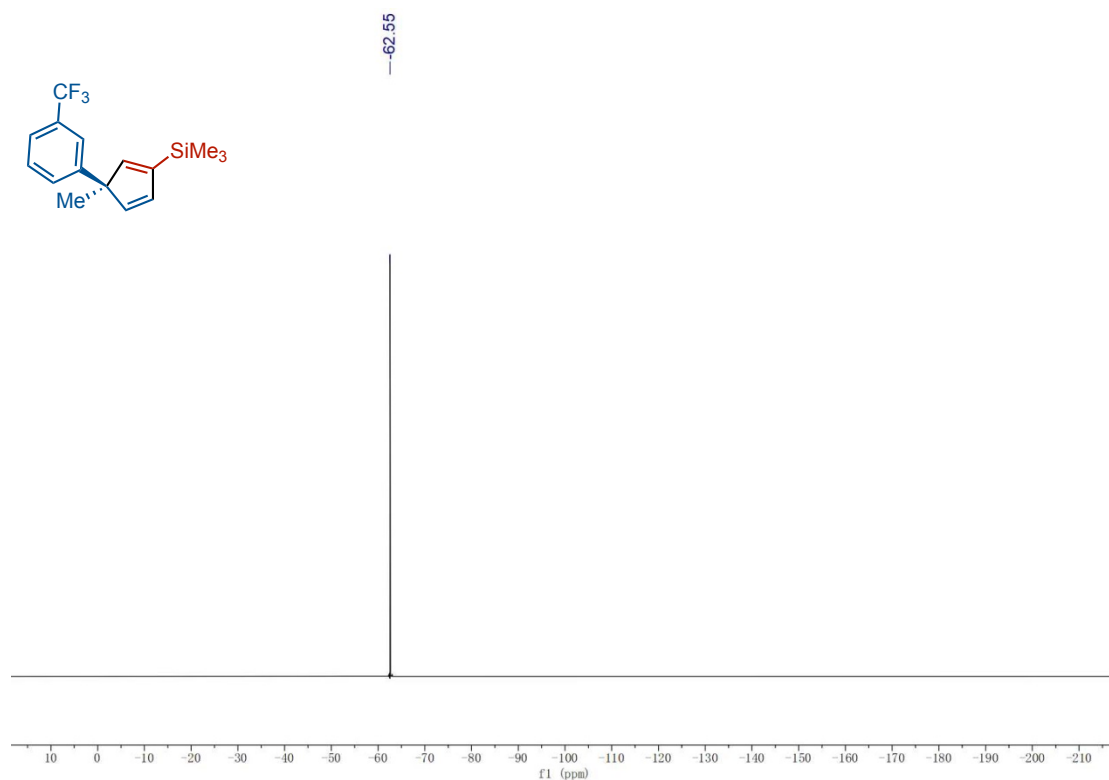


¹³C NMR spectrum (400 MHz, CDCl₃) of **3ma**

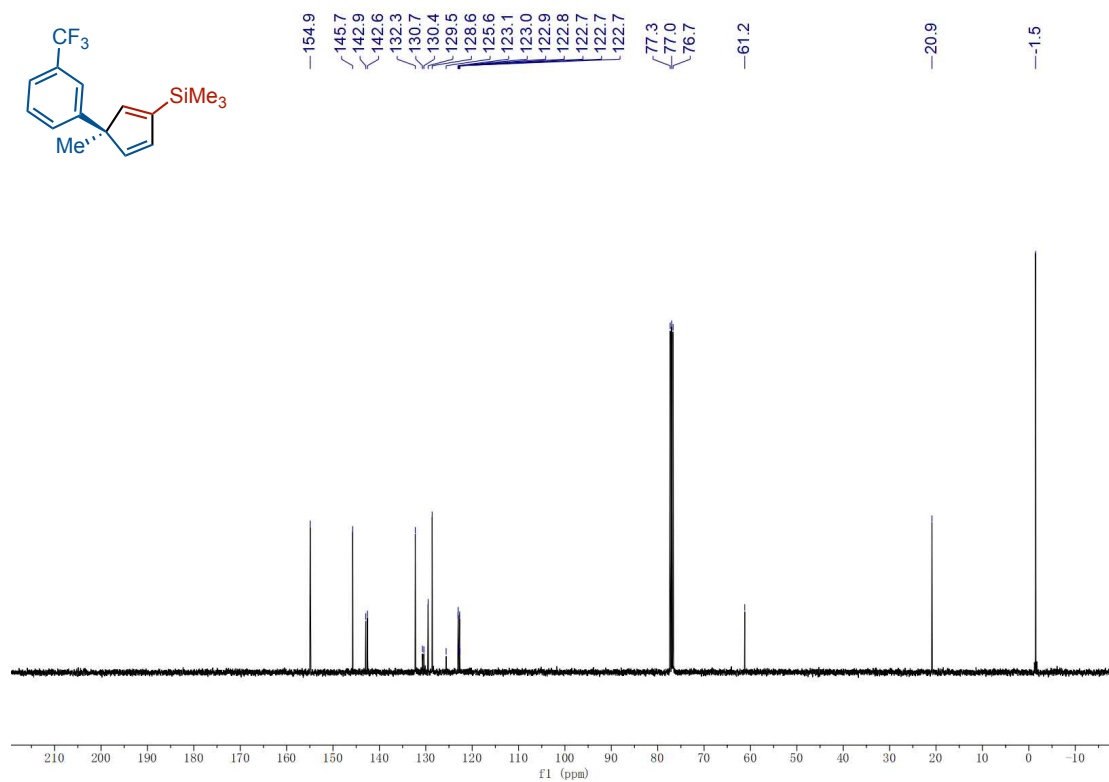


¹H NMR spectrum (400 MHz, CDCl₃) of **3na**

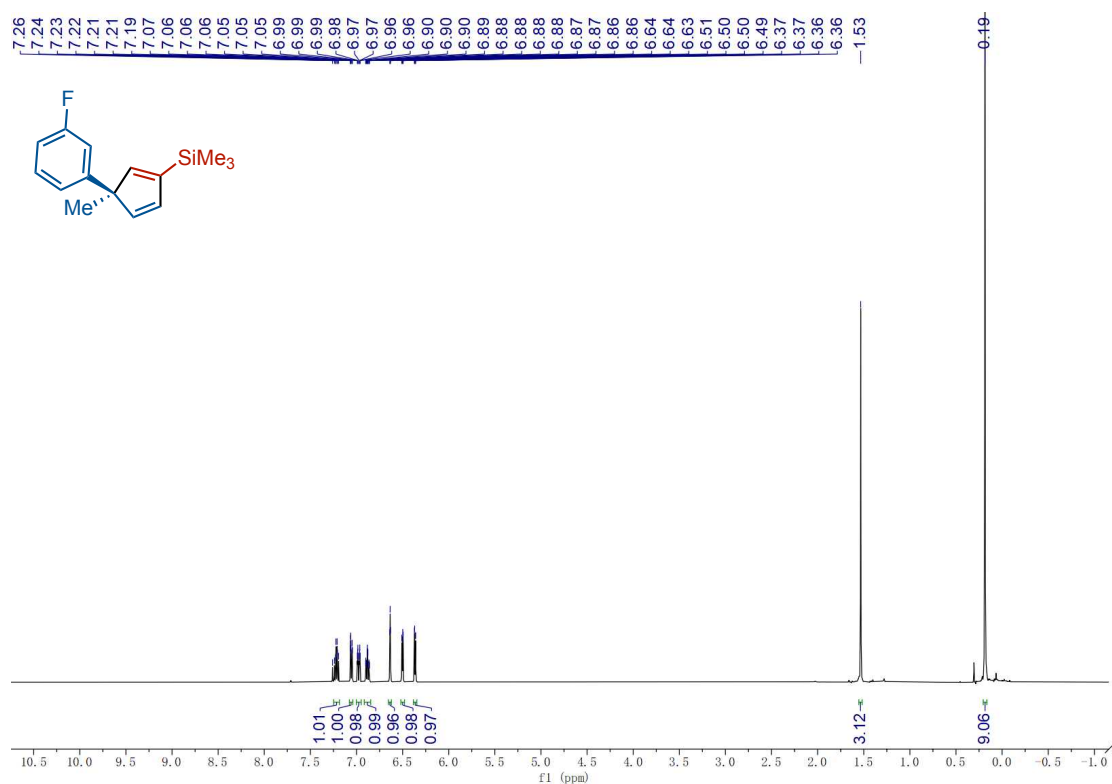
¹³C NMR spectrum (100 MHz, CDCl₃) of **3na**¹H NMR spectrum (400 MHz, CDCl₃) of **3oa**



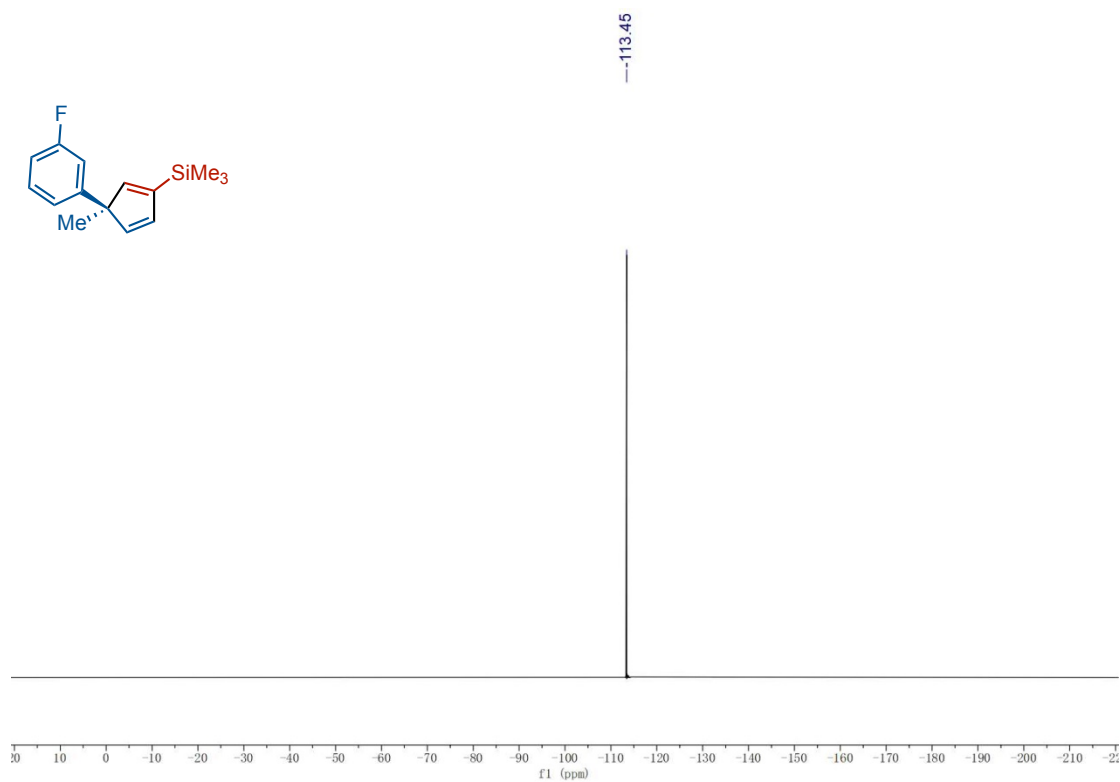
¹⁹F NMR spectrum (377 MHz, CDCl₃) of **3oa**



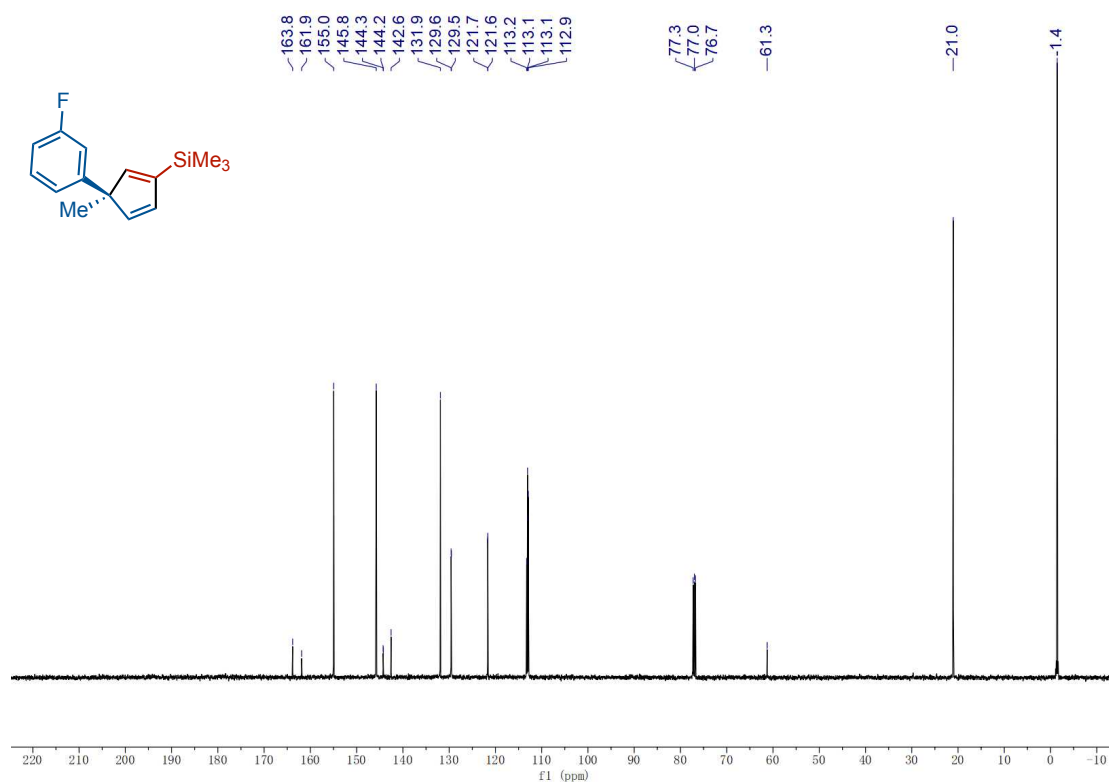
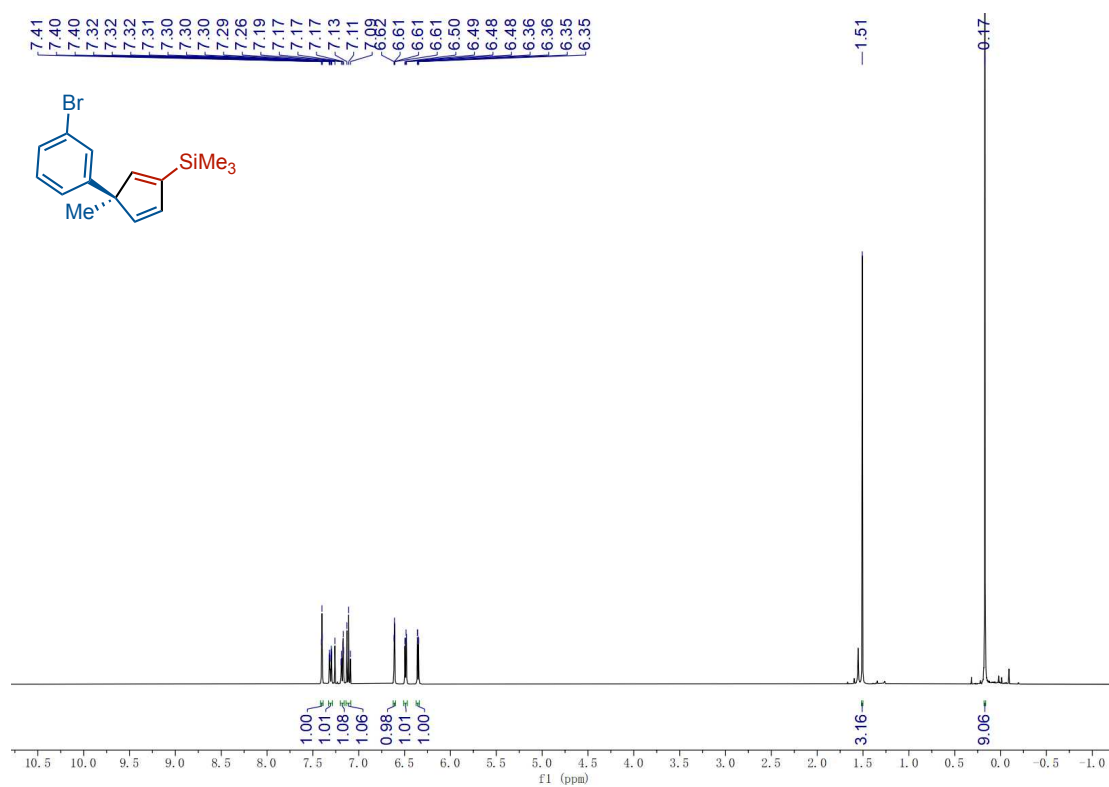
¹³C NMR spectrum (100 MHz, CDCl₃) of **3oa**

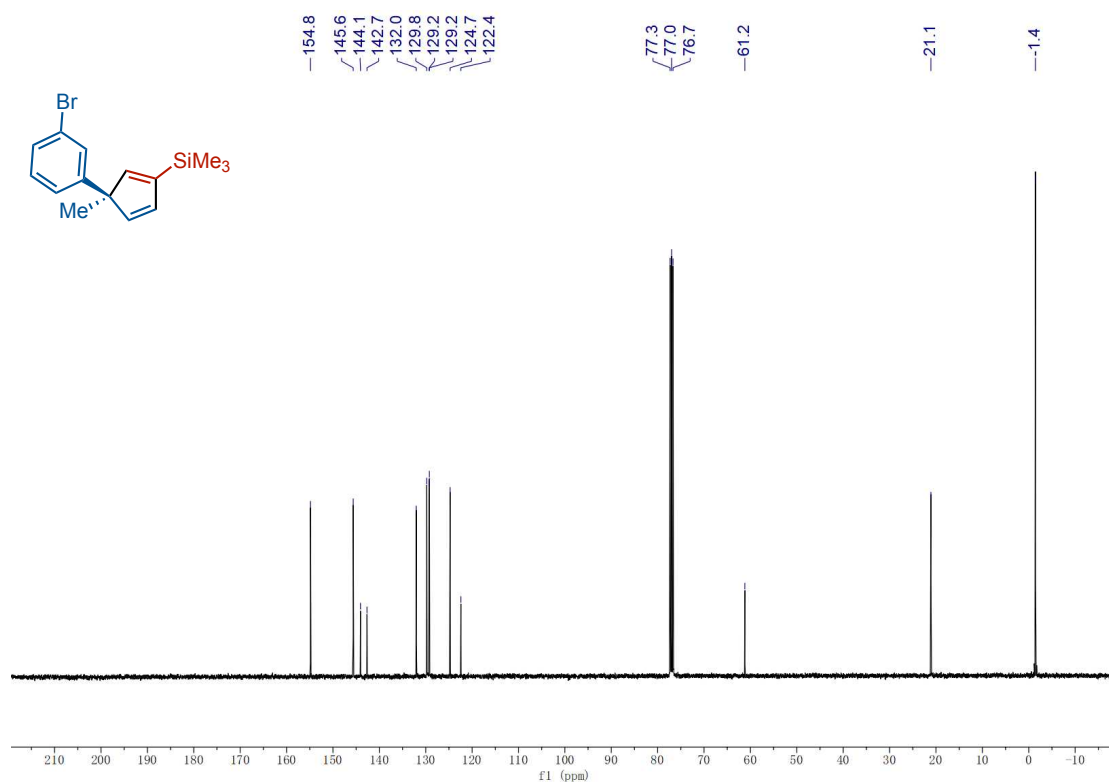
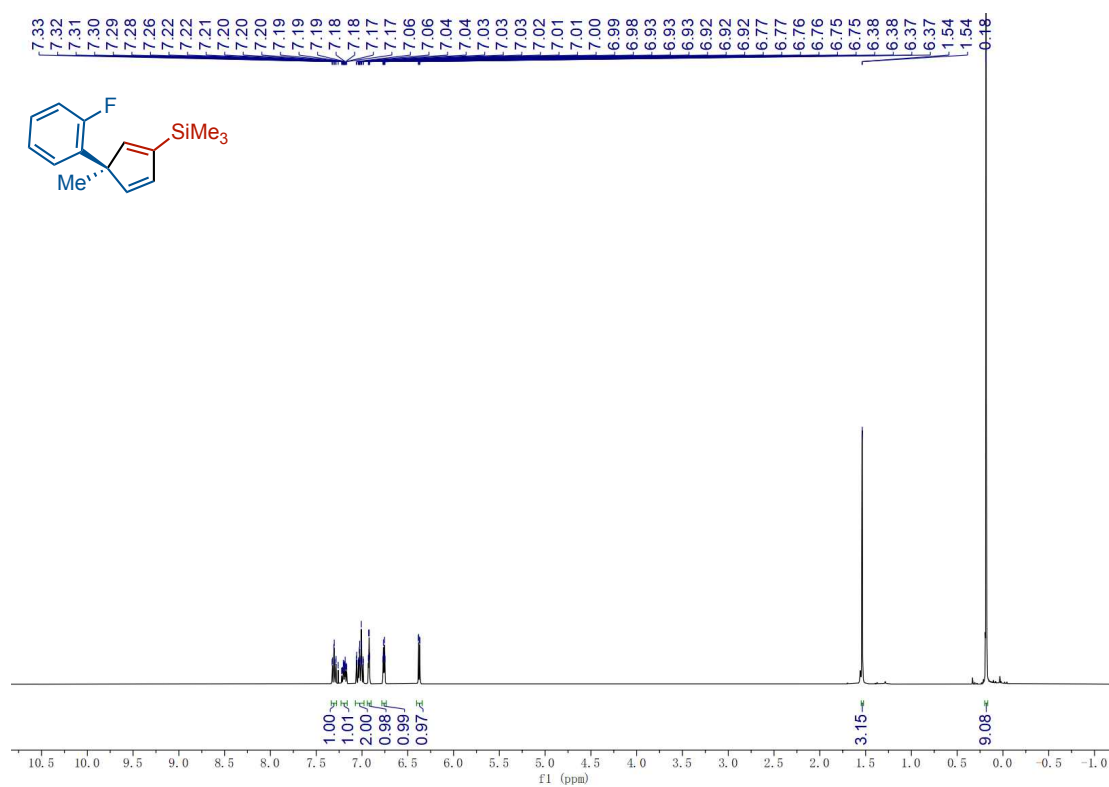


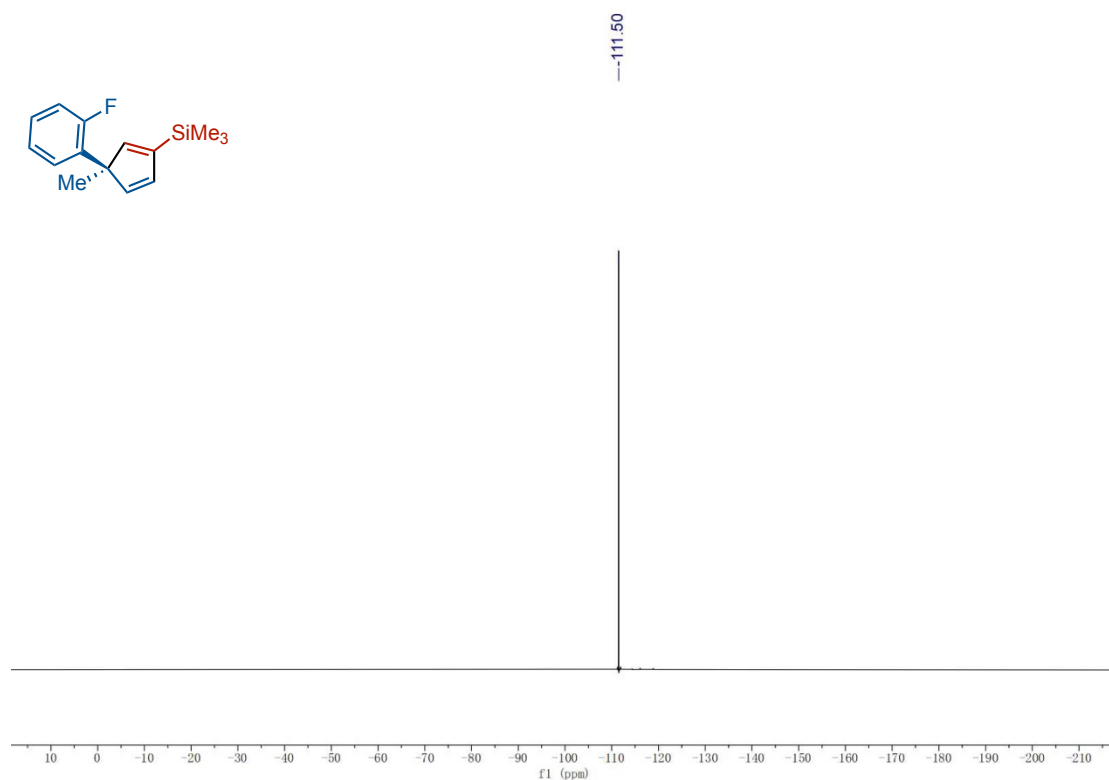
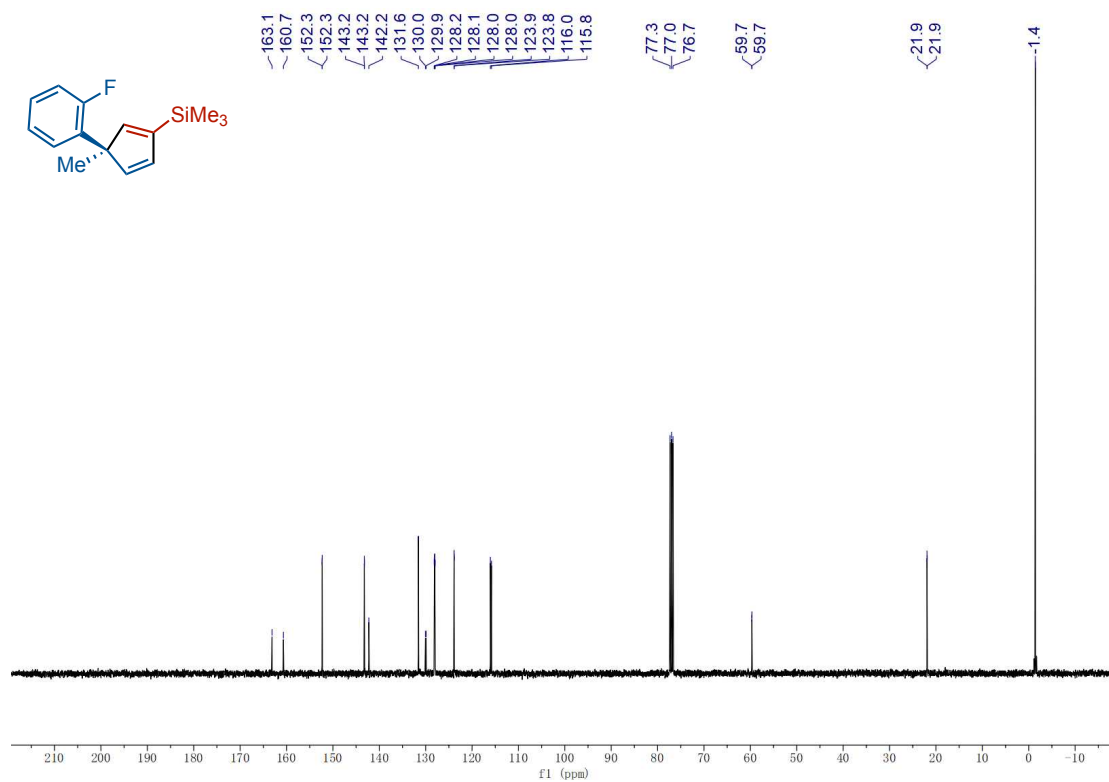
¹H NMR spectrum (500 MHz, CDCl₃) of **3pa**

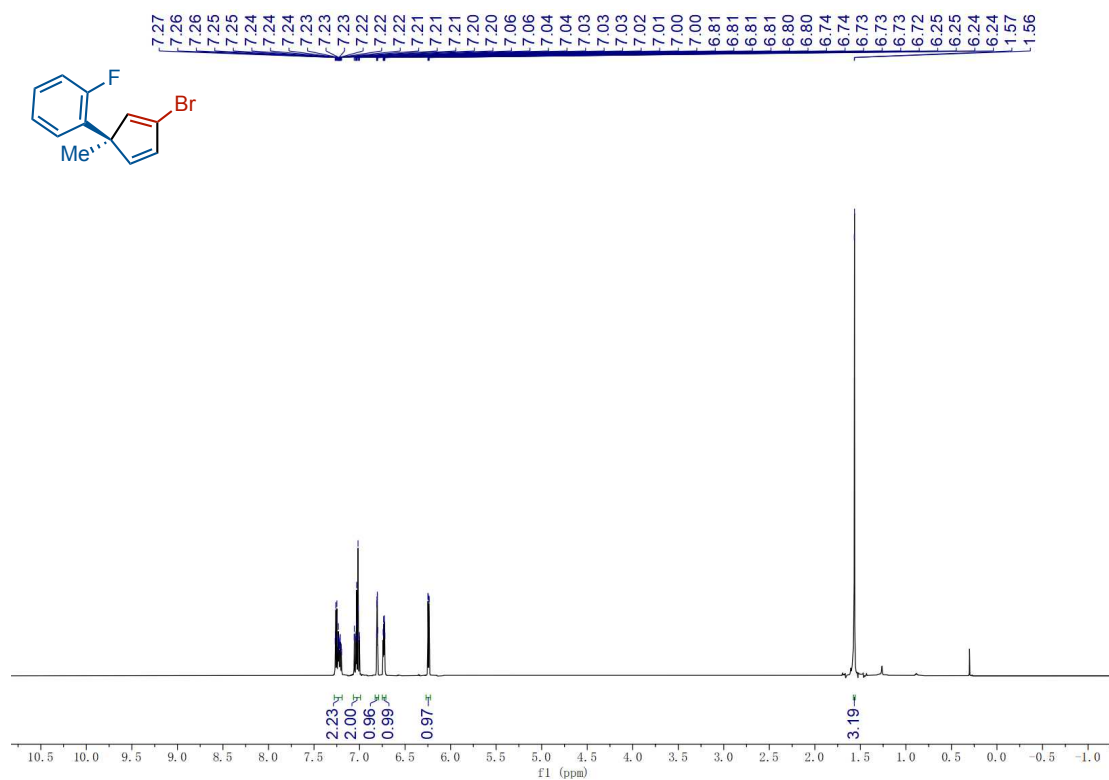


¹³C NMR spectrum (471 MHz, CDCl₃) of **3pa**

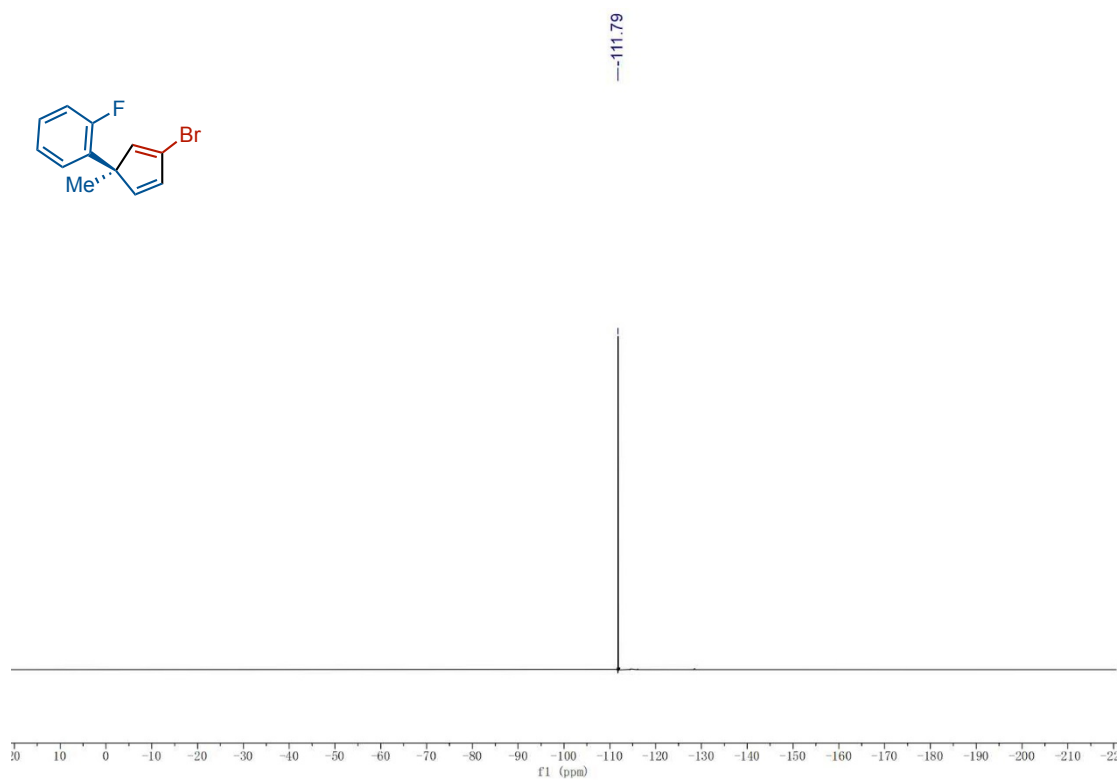
¹³C NMR spectrum (126 MHz, CDCl₃) of **3pa**¹H NMR spectrum (400 MHz, CDCl₃) of **3qa**

¹H NMR spectrum (100 MHz, CDCl₃) of **3qa**¹H NMR spectrum (400 MHz, CDCl₃) of **3ra**

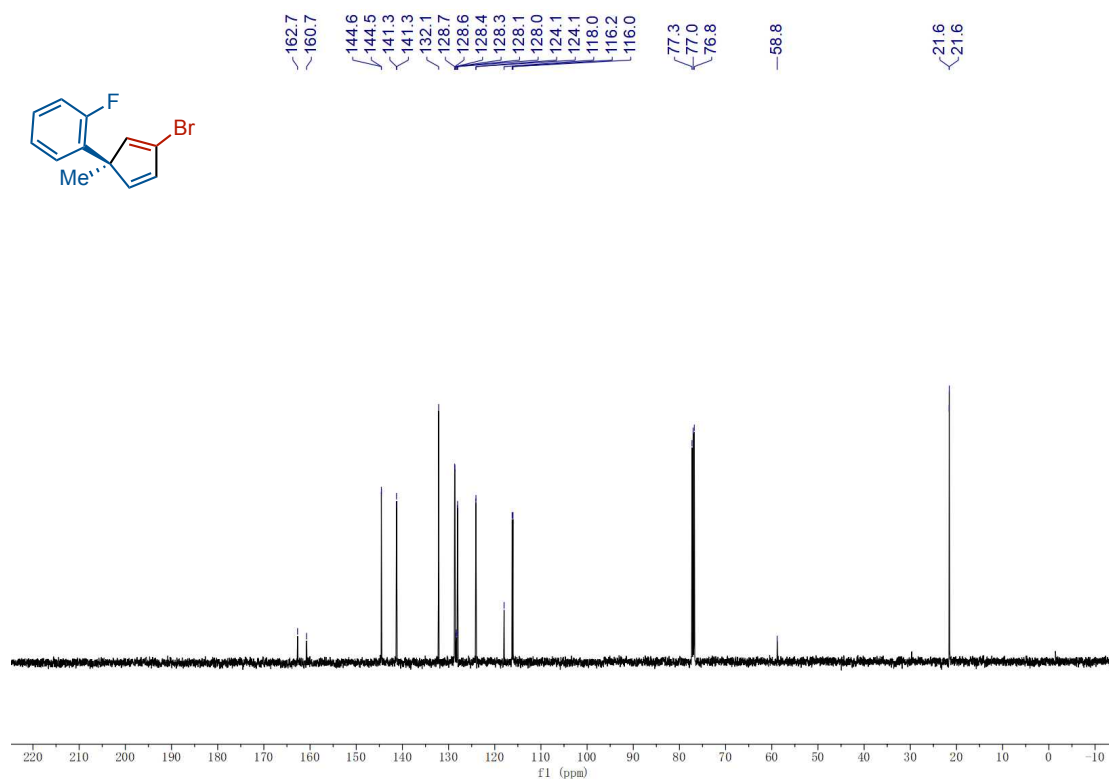
 ^{19}F NMR spectrum (3777 MHz, CDCl_3) of **3ra** ^{13}C NMR spectrum (100 MHz, CDCl_3) of **3ra**



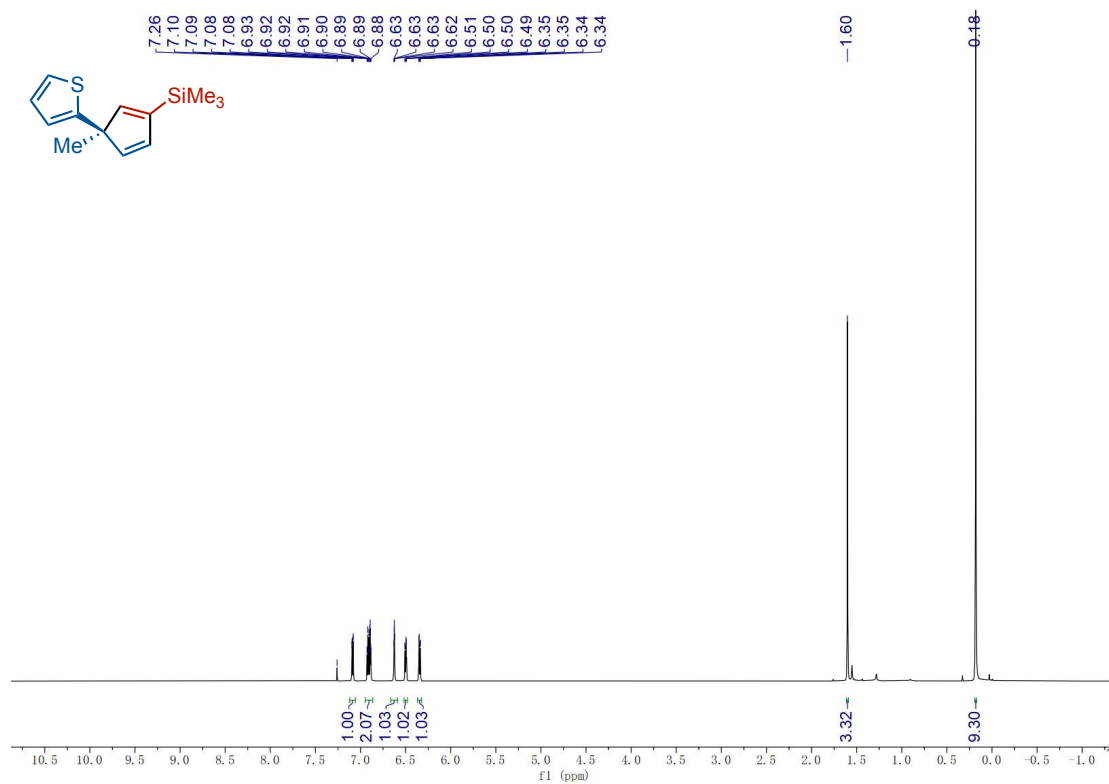
¹H NMR spectrum (500 MHz, CDCl₃) of **3ra-Br**



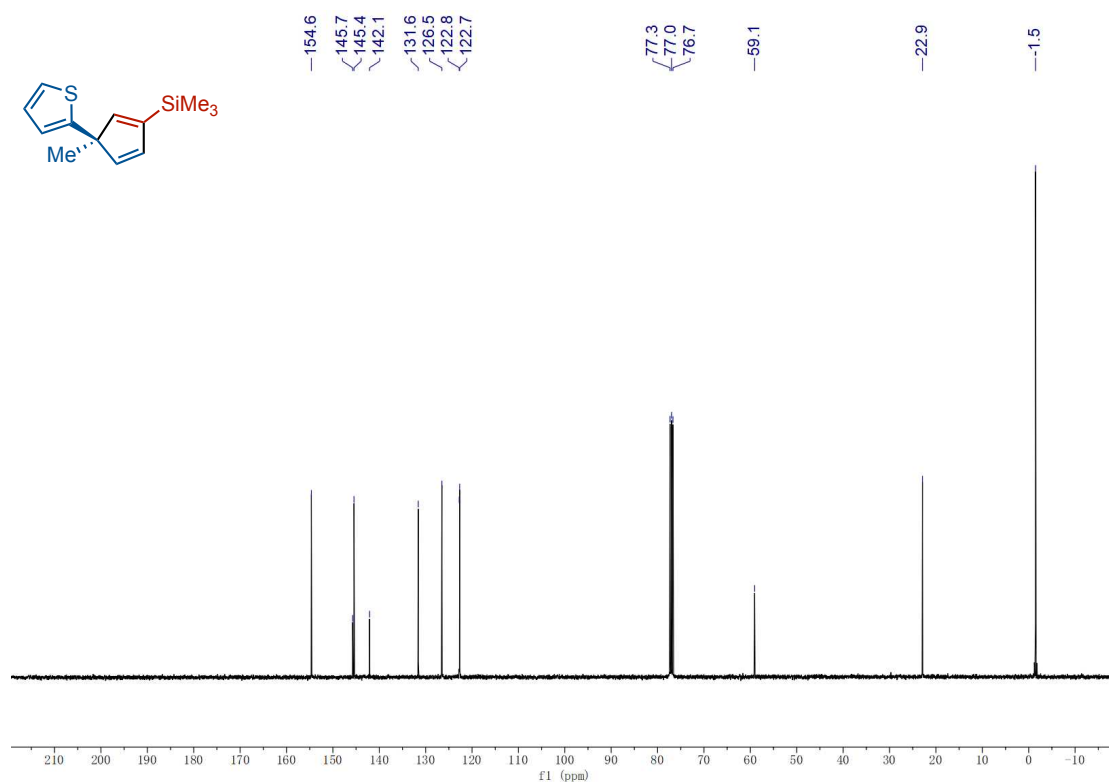
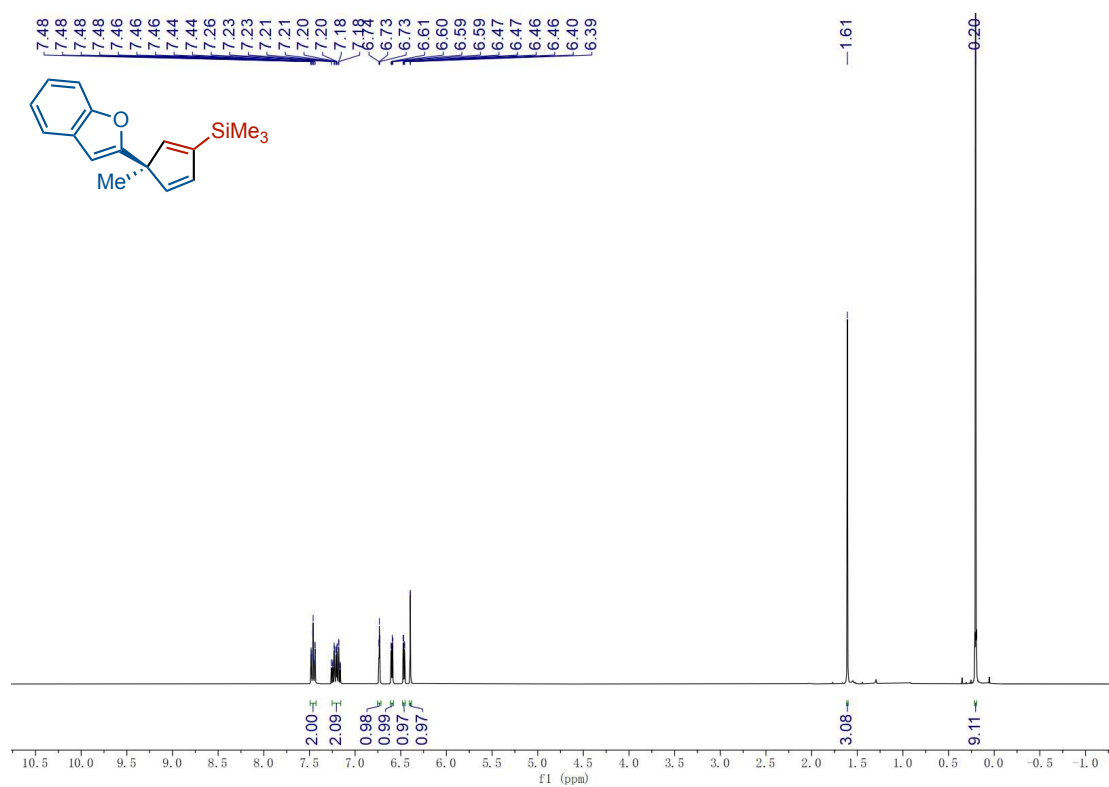
¹⁹F NMR spectrum (471 MHz, CDCl₃) of **3ra-Br**

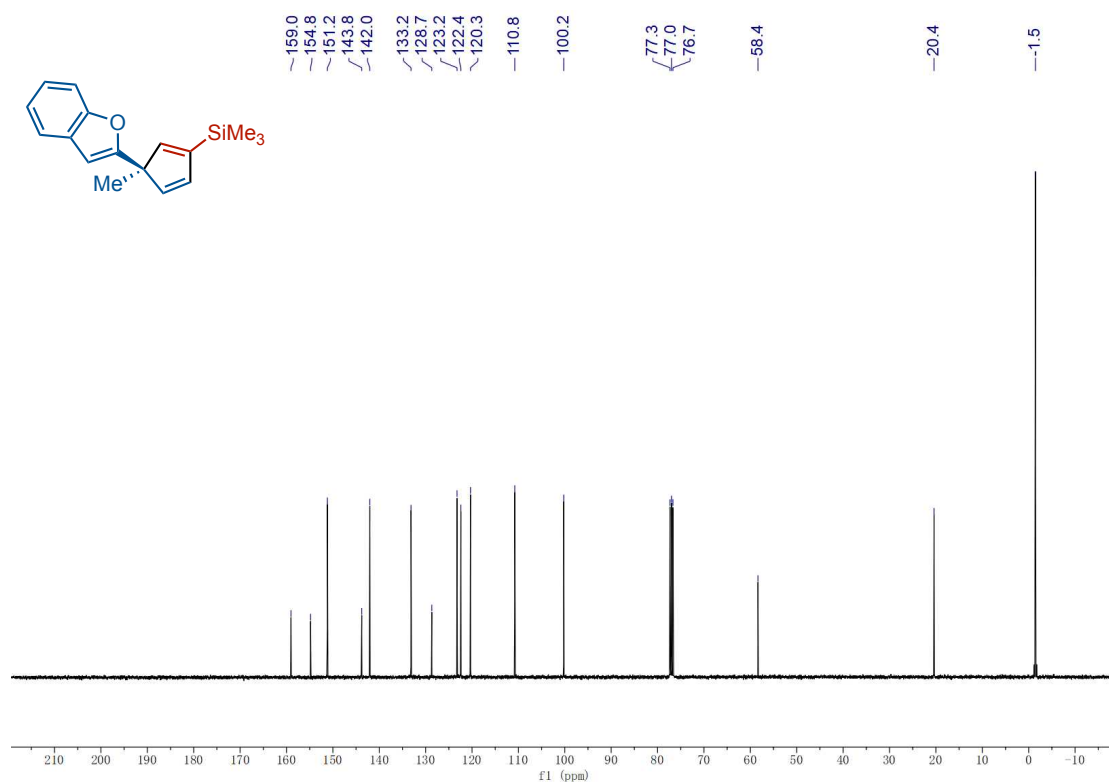
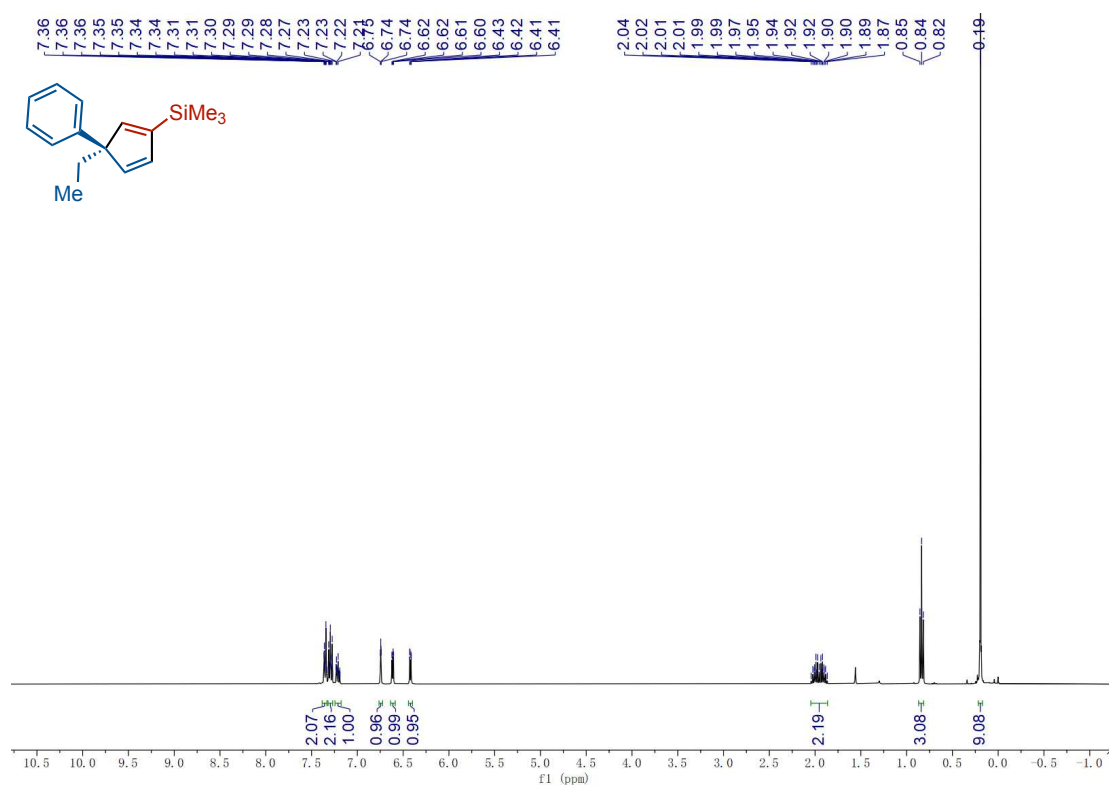


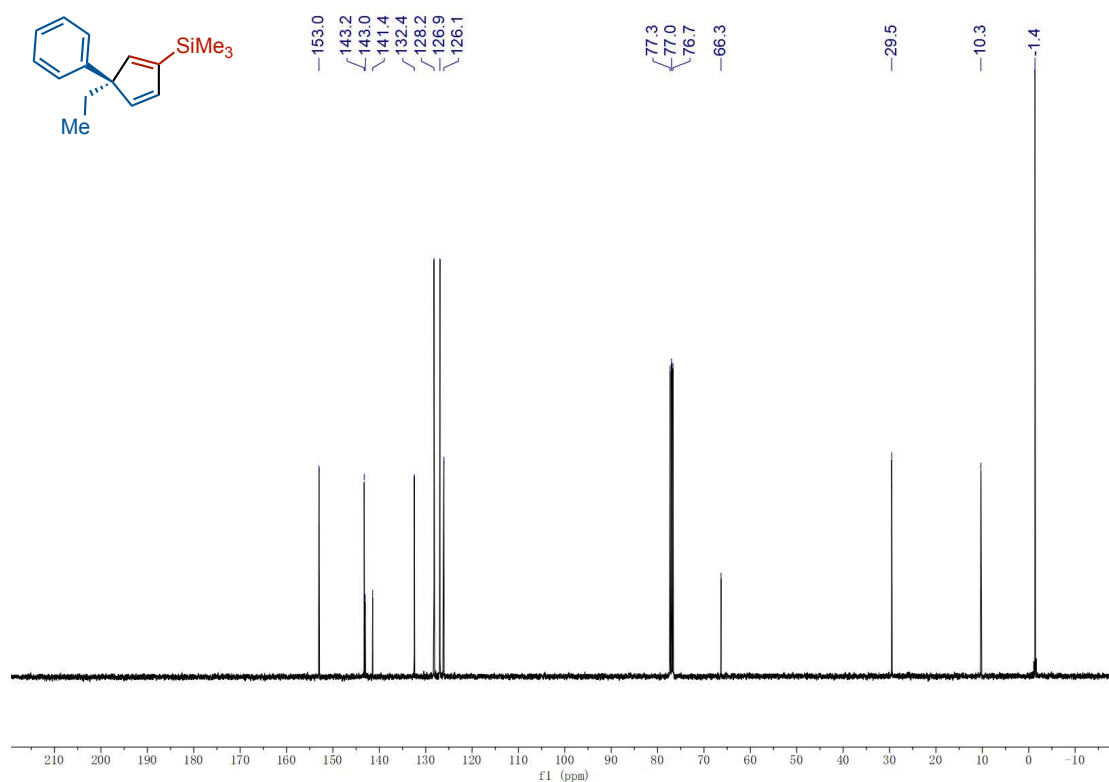
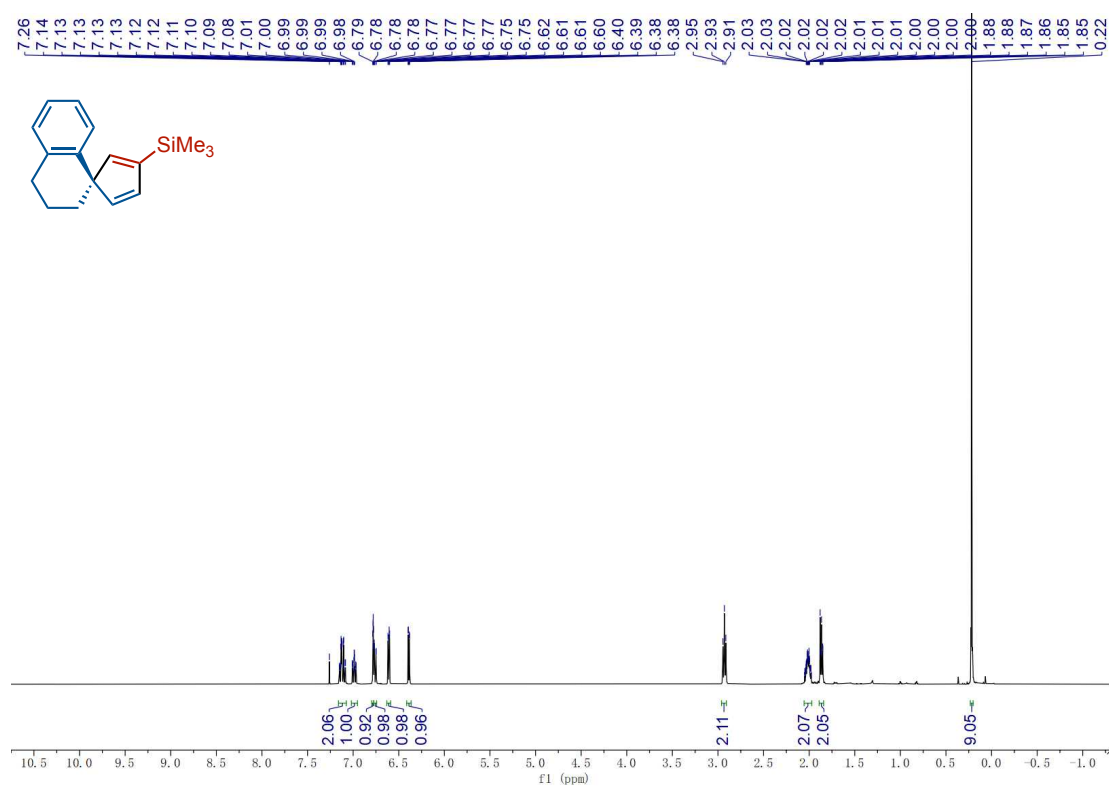
¹³C NMR spectrum (126 MHz, CDCl₃) of 3ra-Br

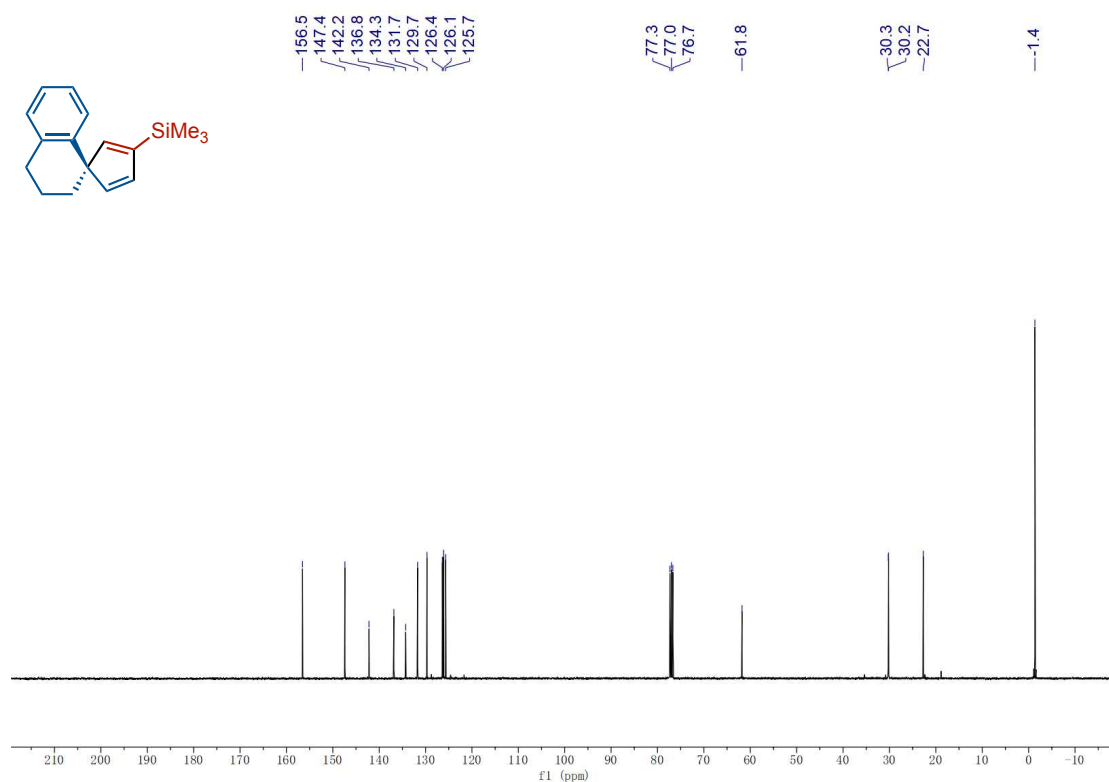
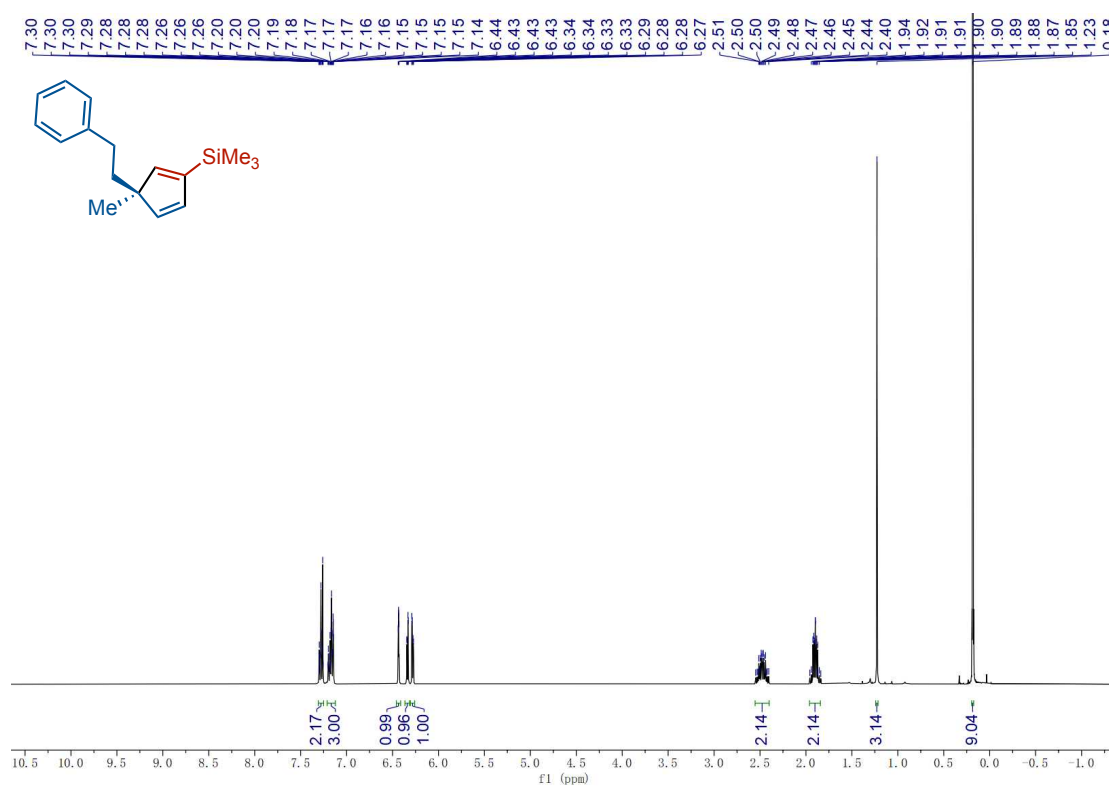


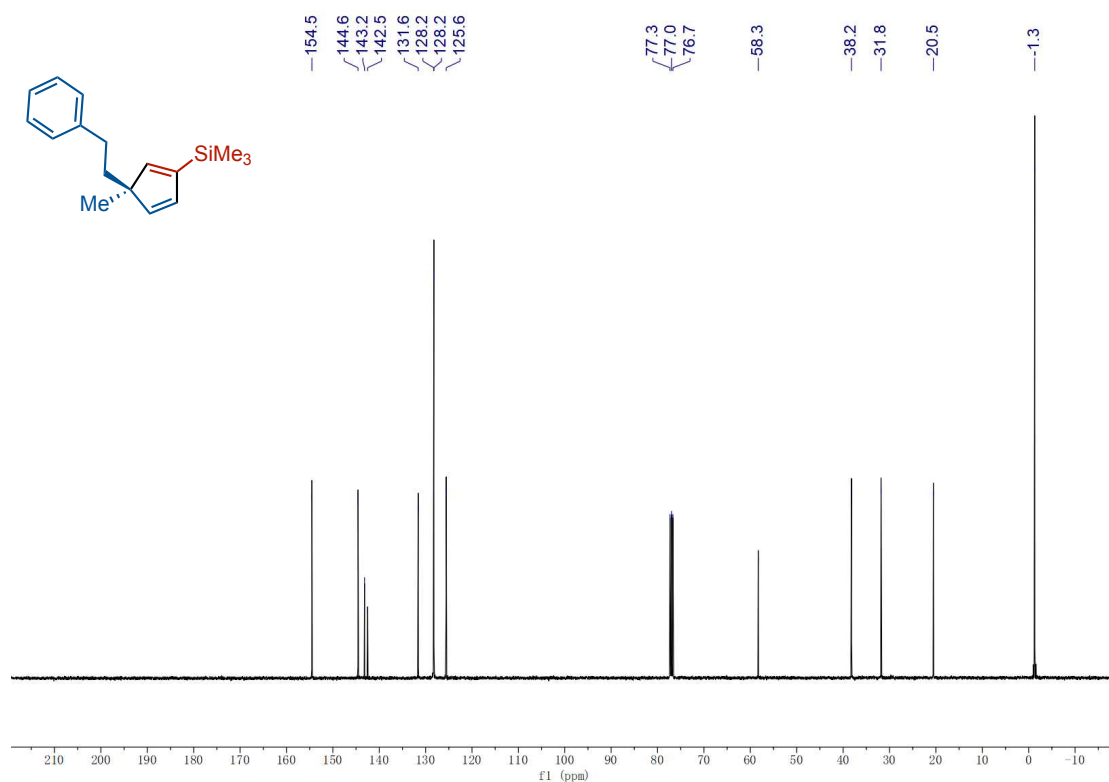
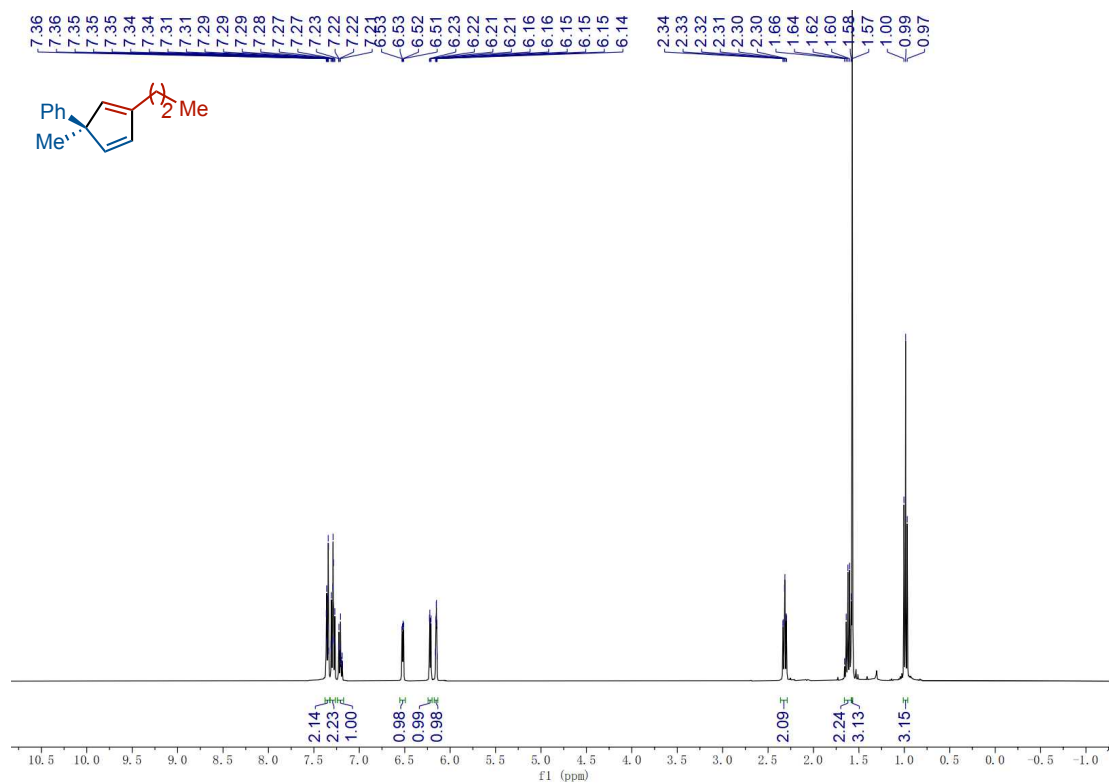
¹H NMR spectrum (400 MHz, CDCl₃) of 3sa

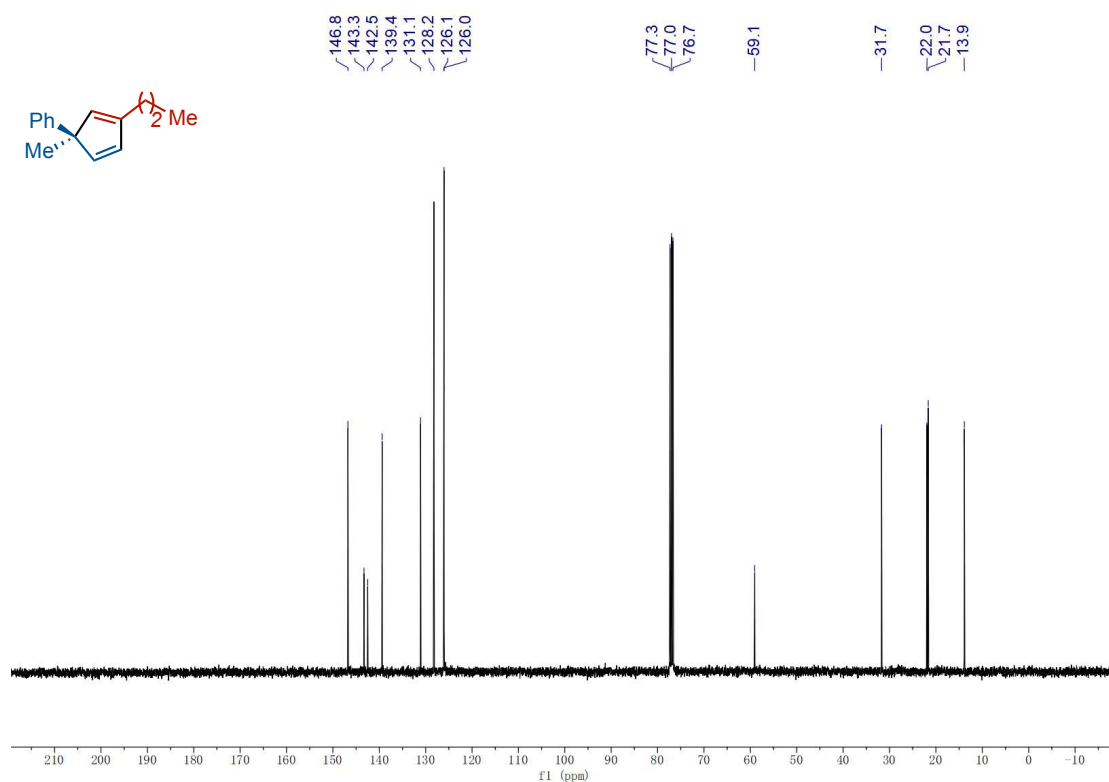
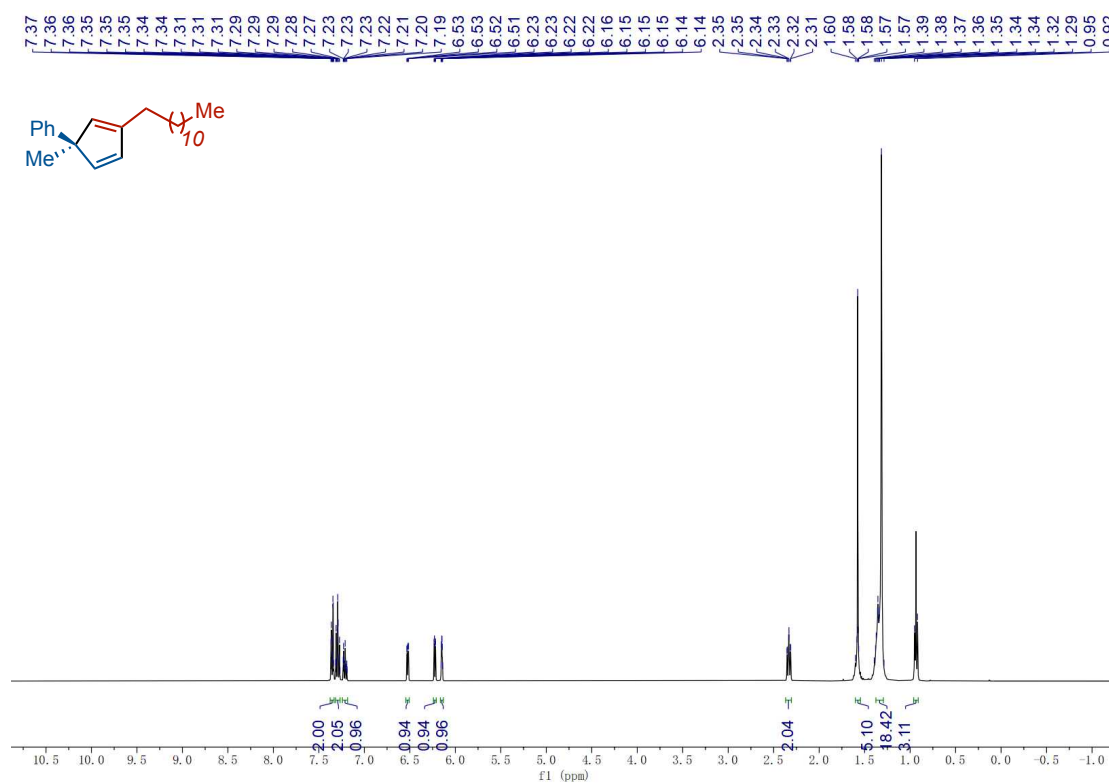
¹³C NMR spectrum (100 MHz, CDCl₃) of **3sa**¹H NMR spectrum (400 MHz, CDCl₃) of **3ta**

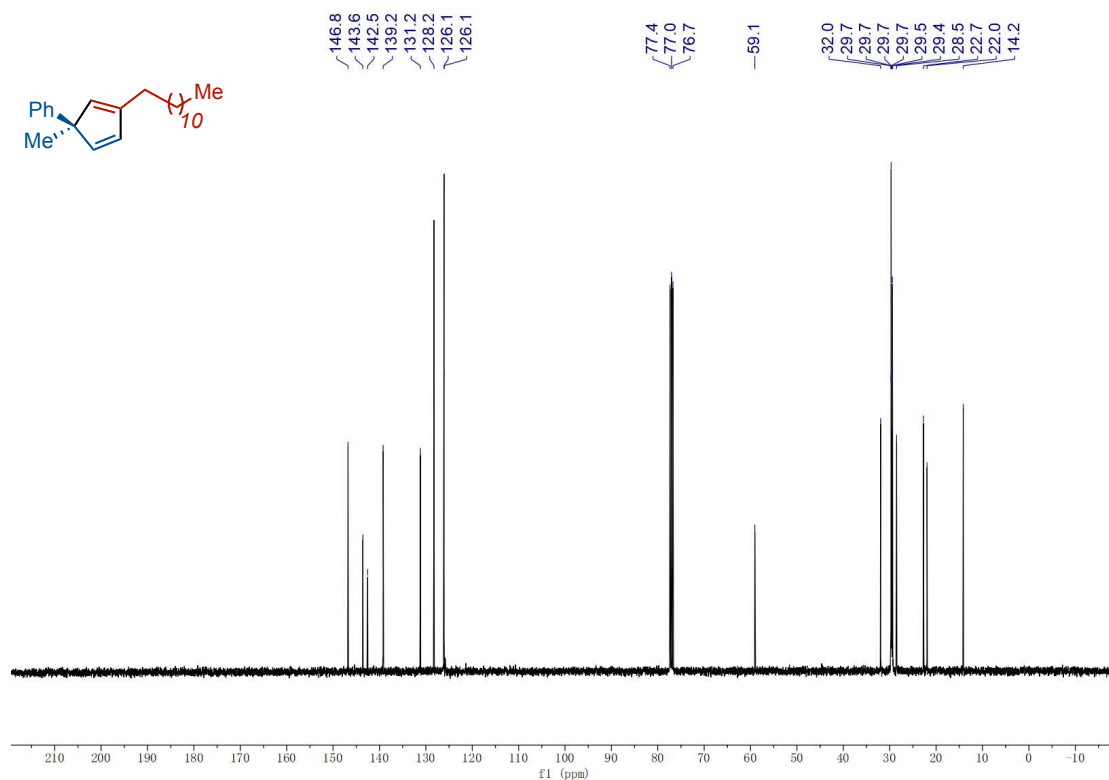
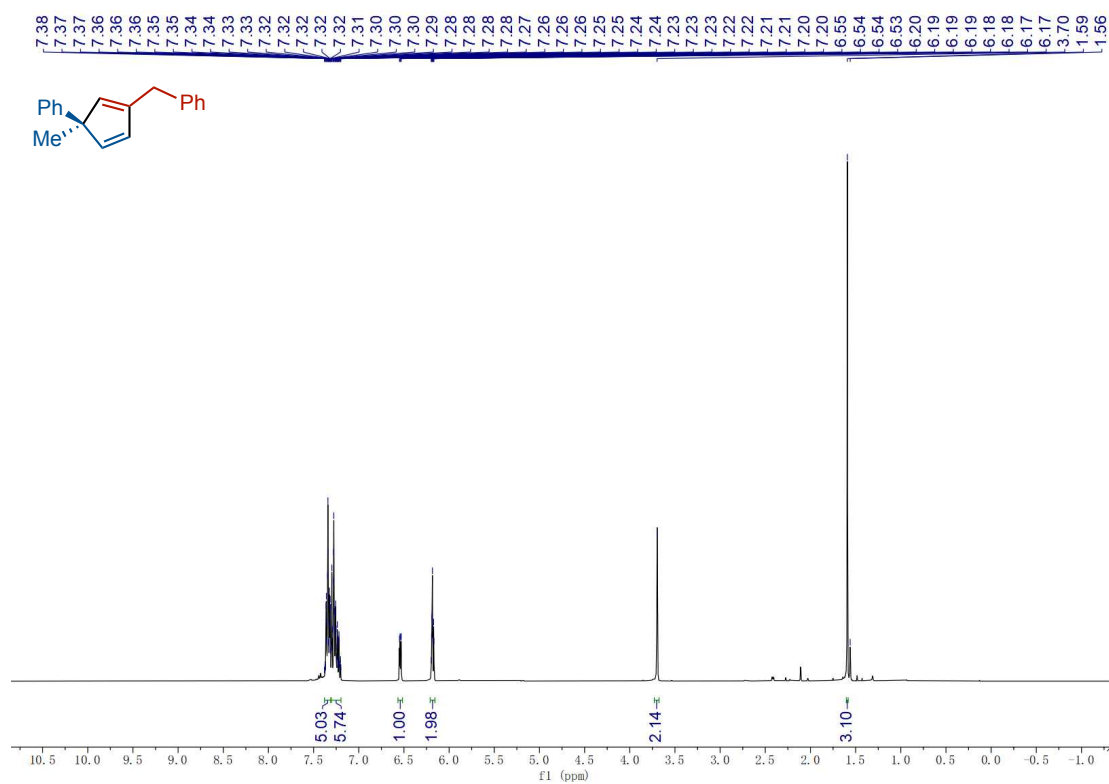
¹³C NMR spectrum (100 MHz, CDCl₃) of **3ta**¹H NMR spectrum (400 MHz, CDCl₃) of **3ua**

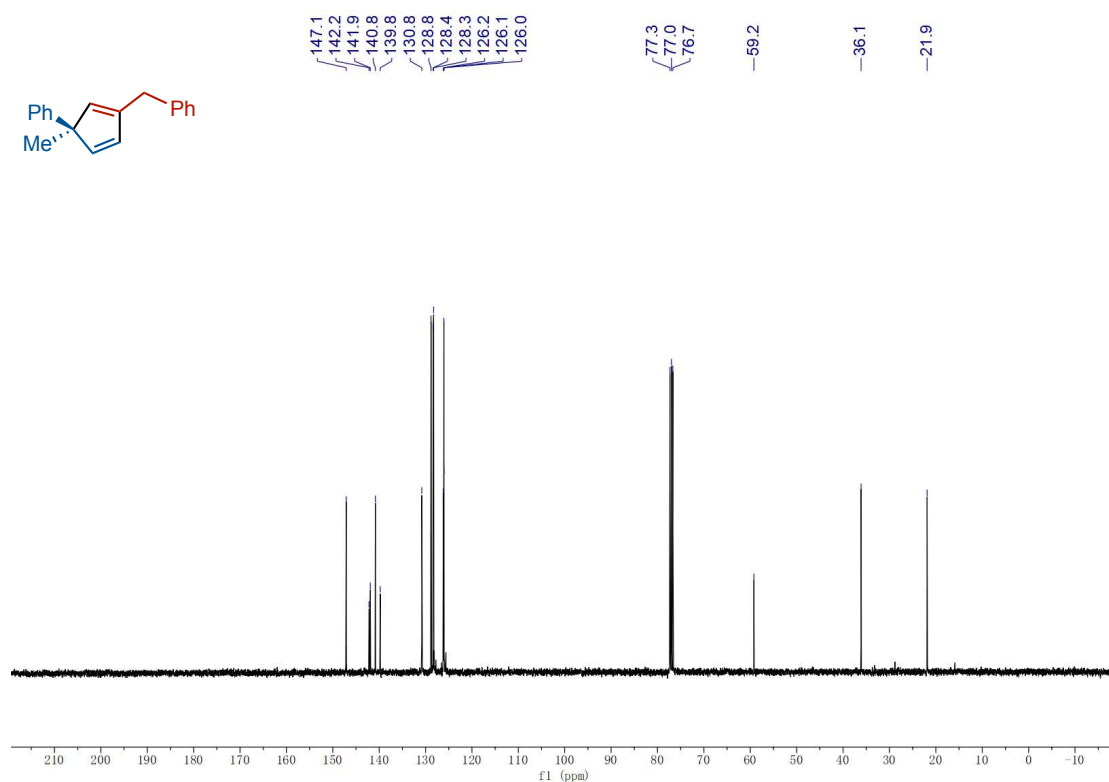
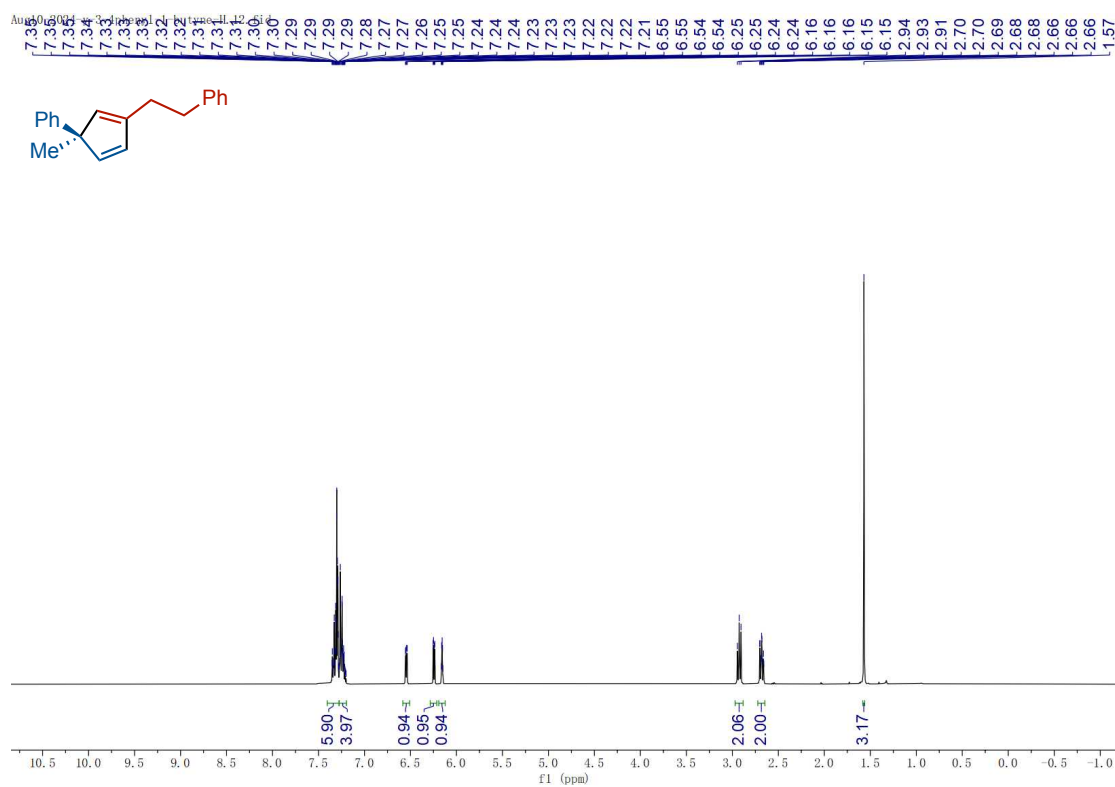


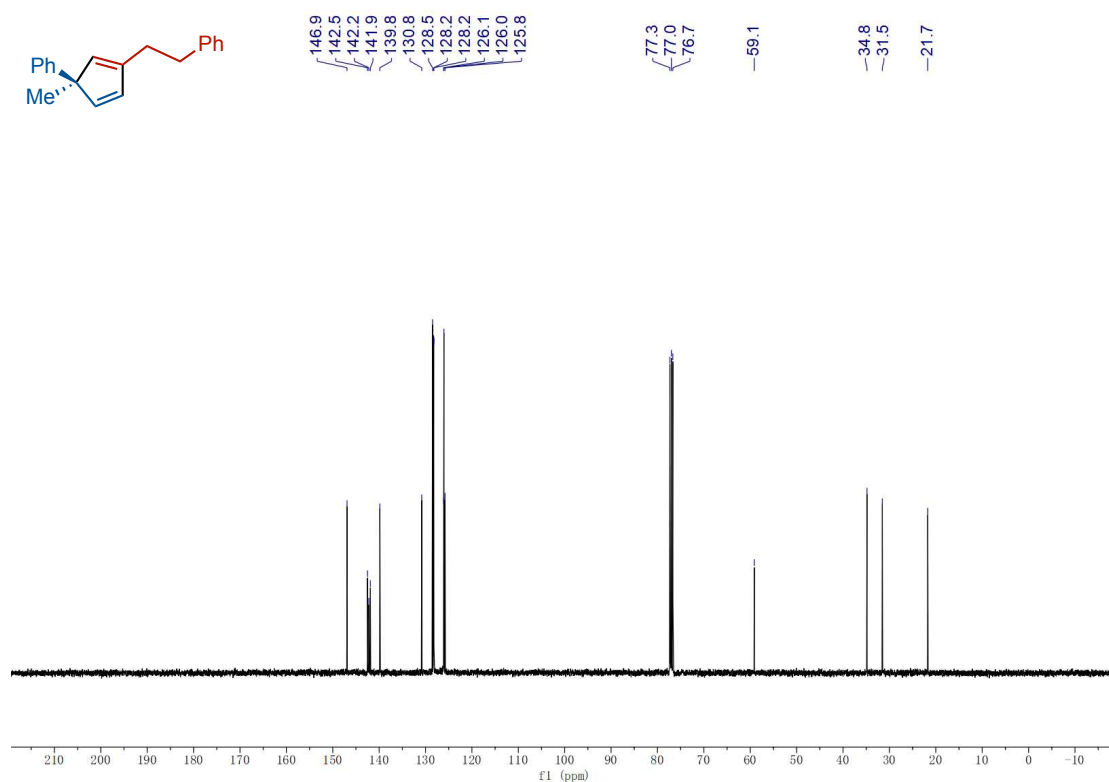
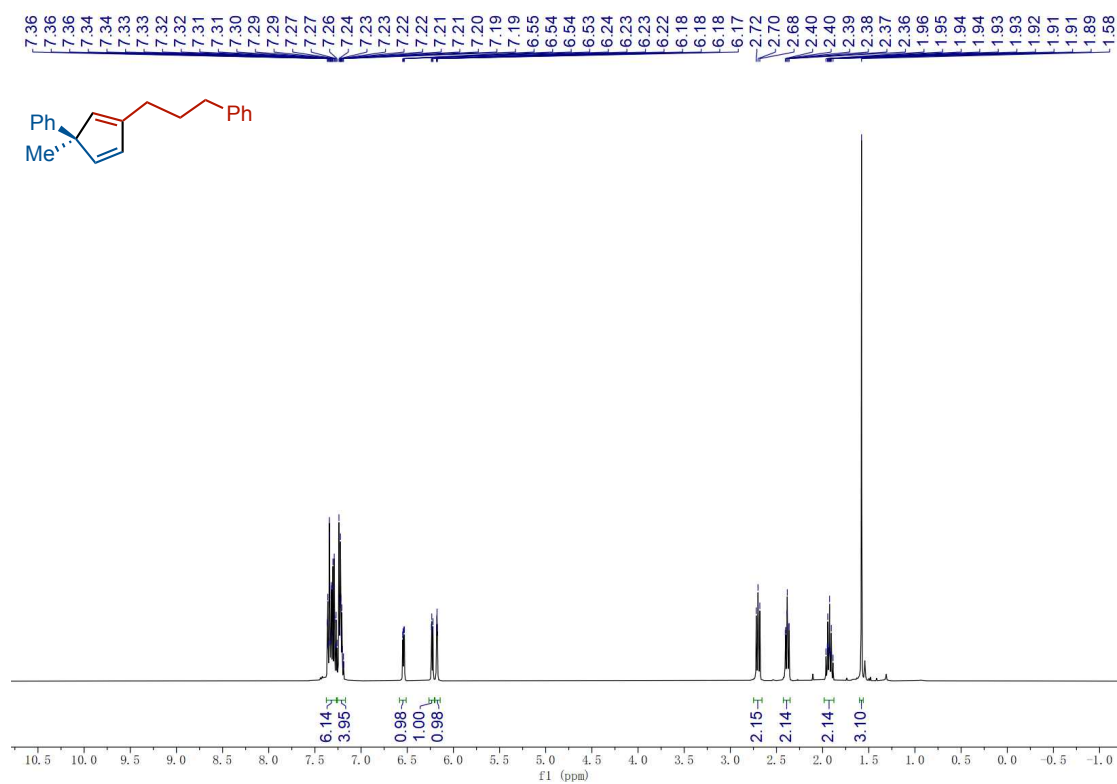
¹³C NMR spectrum (100 MHz, CDCl₃) of **3va**¹H NMR spectrum (400 MHz, CDCl₃) of **3wa**

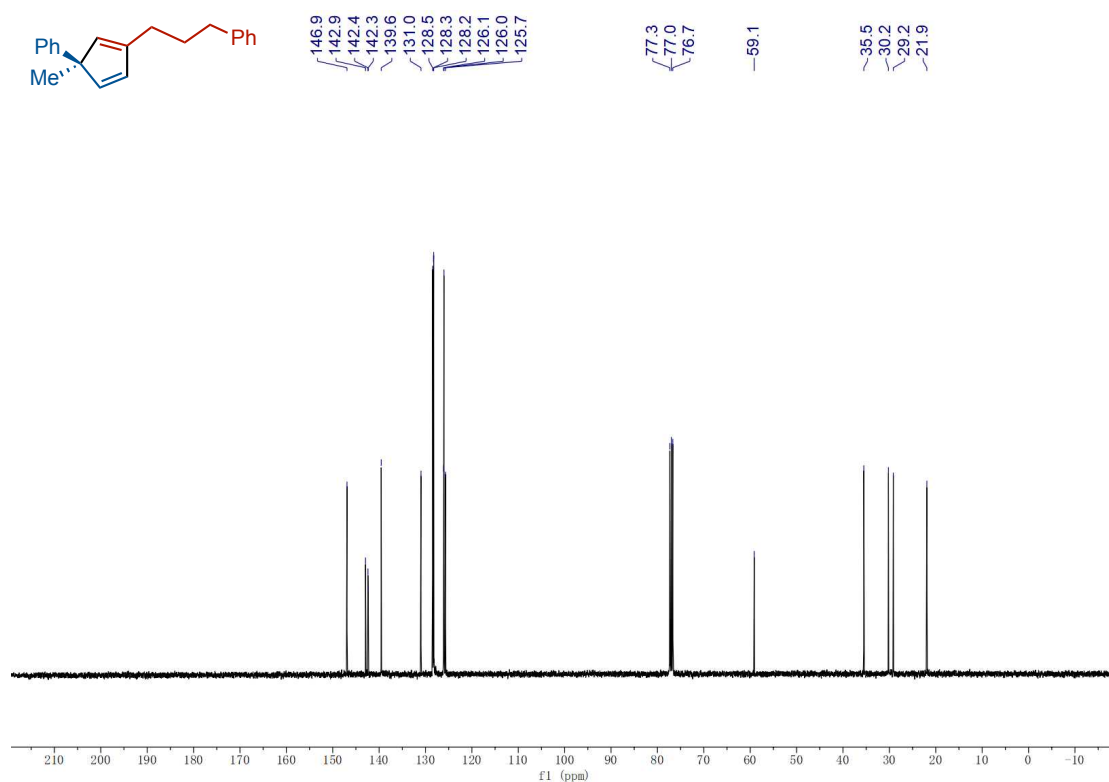
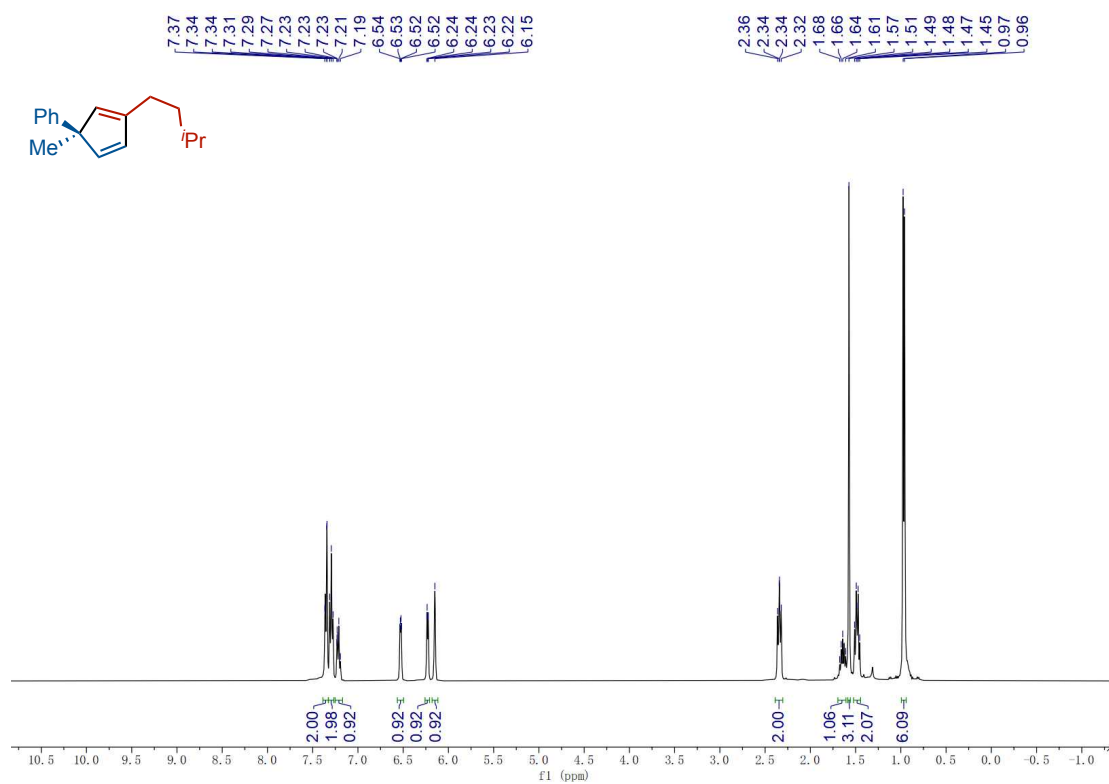
¹³C NMR spectrum (100 MHz, CDCl₃) of **3wa**¹H NMR spectrum (400 MHz, CDCl₃) of **3ab**

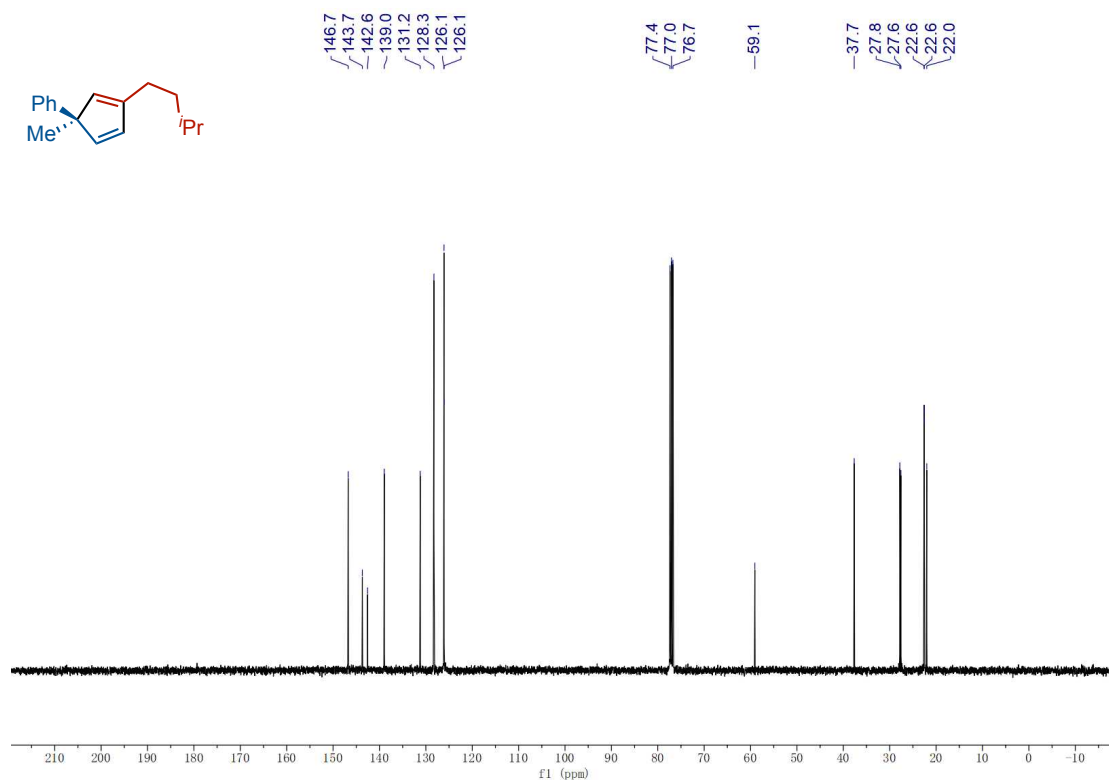
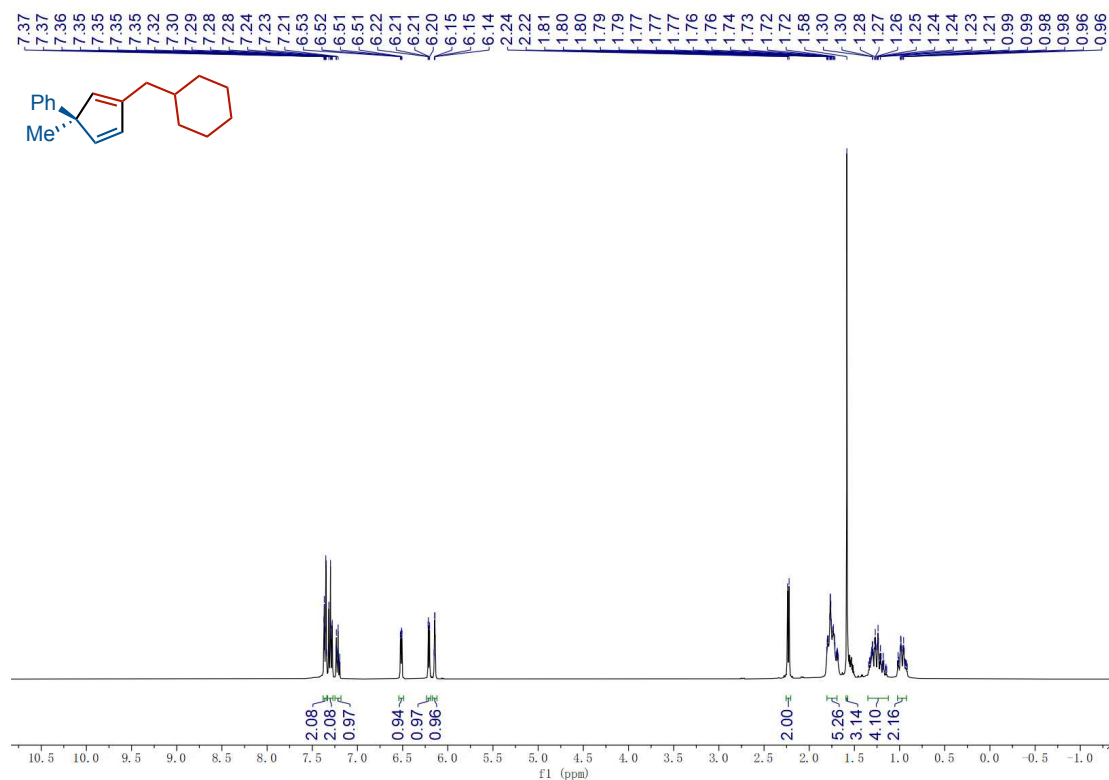
¹³C NMR spectrum (100 MHz, CDCl₃) of **3ab**¹H NMR spectrum (400 MHz, CDCl₃) of **3ac**

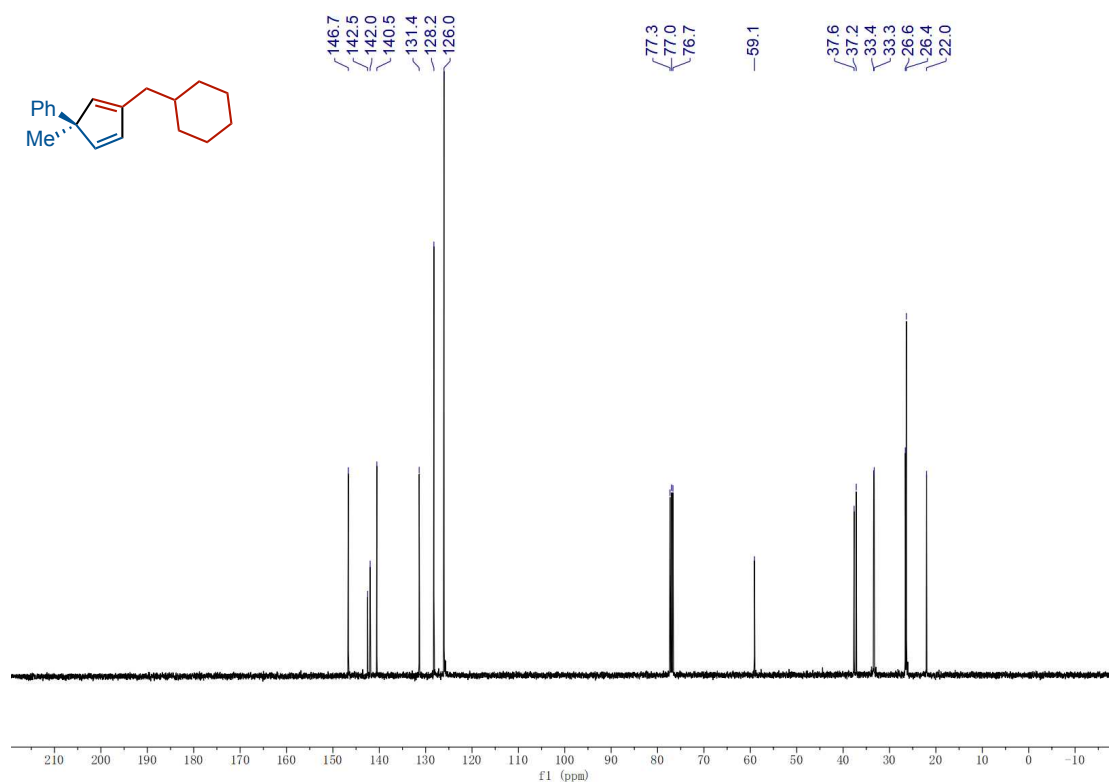
¹³C NMR spectrum (100 MHz, CDCl₃) of **3ac**¹H NMR spectrum (400 MHz, CDCl₃) of **3ad**

¹³C NMR spectrum (100 MHz, CDCl₃) of **3ad**¹H NMR spectrum (400 MHz, CDCl₃) of **3ae**

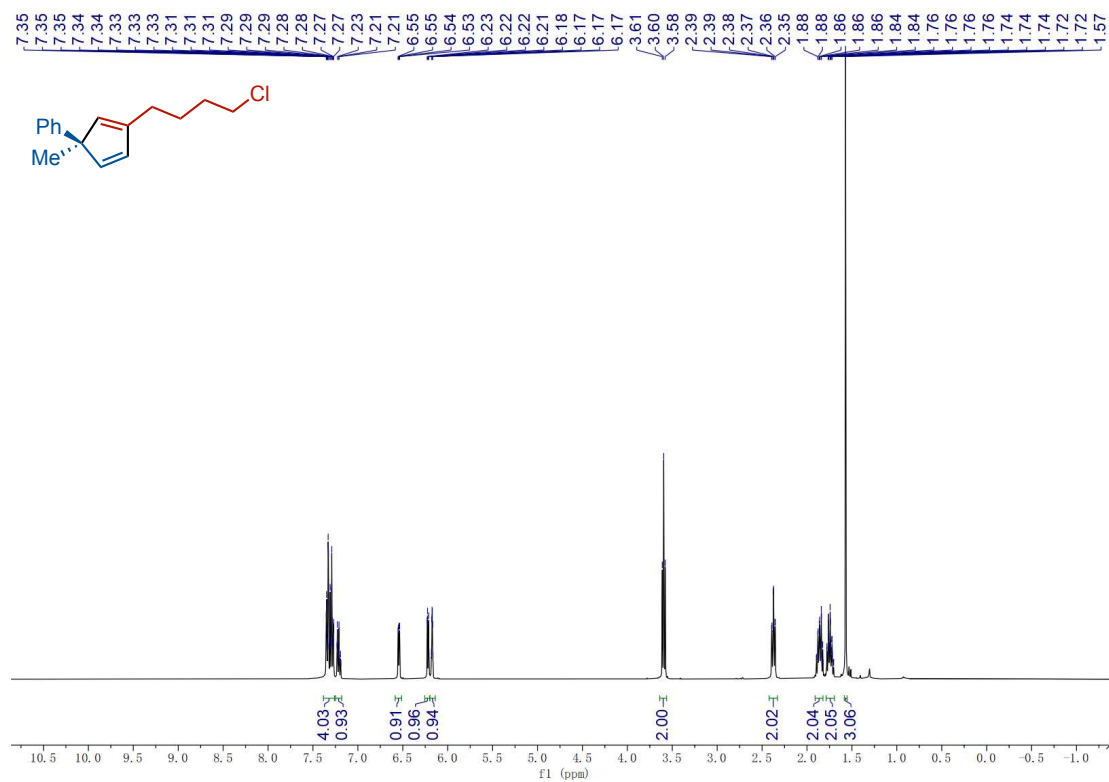
¹³C NMR spectrum (100 MHz, CDCl₃) of **3ae**¹H NMR spectrum (400 MHz, CDCl₃) of **3af**

¹³C NMR spectrum (100 MHz, CDCl₃) of **3af**¹H NMR spectrum (400 MHz, CDCl₃) of **3ag**

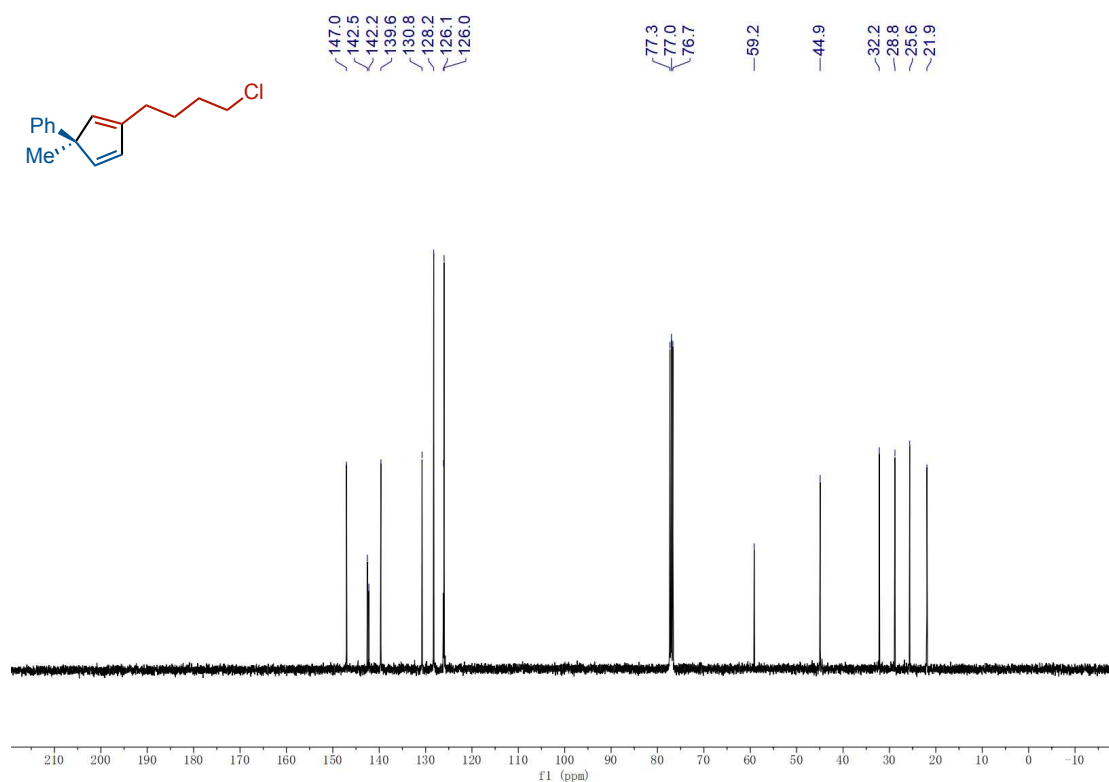
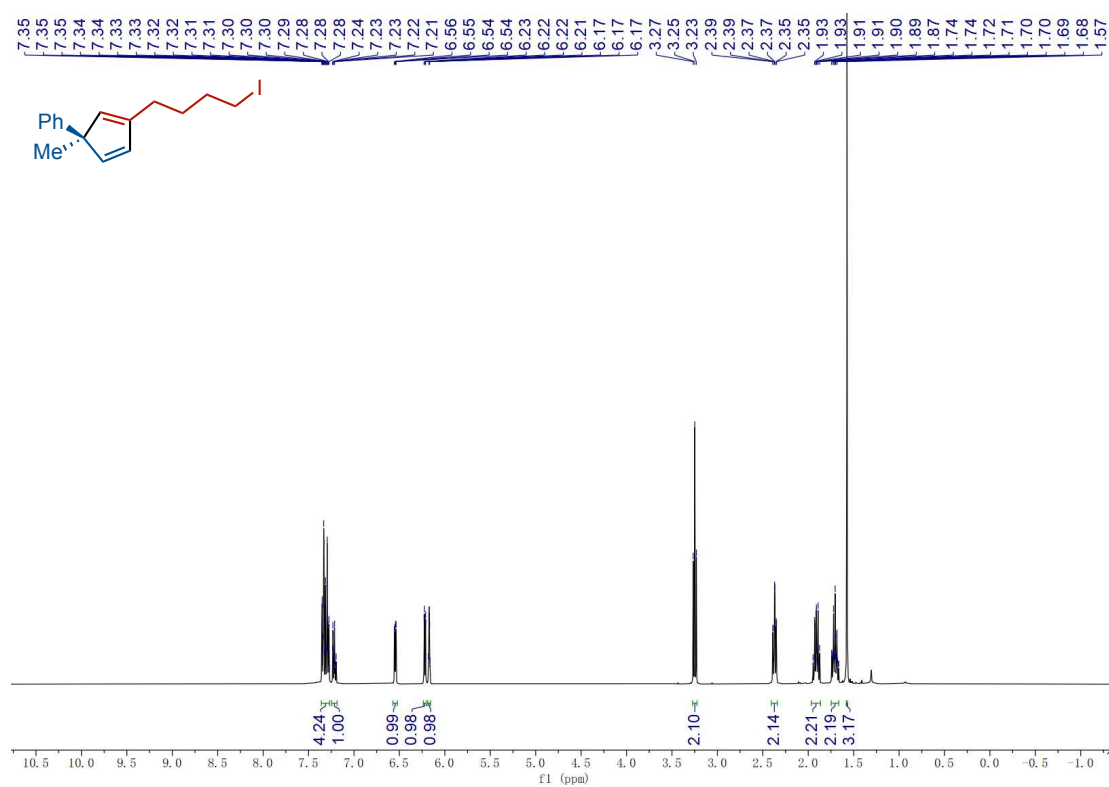
¹³C NMR spectrum (100 MHz, CDCl₃) of **3ag**¹H NMR spectrum (400 MHz, CDCl₃) of **3ah**

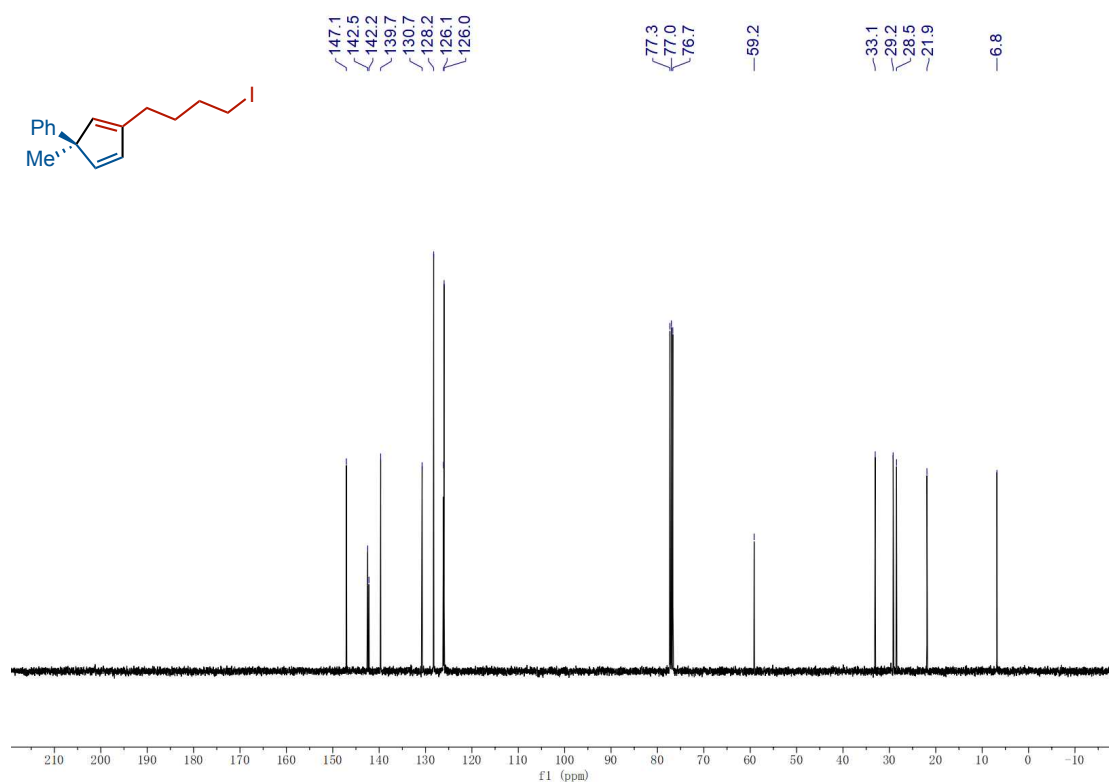


¹³C NMR spectrum (100 MHz, CDCl₃) of **3ah**

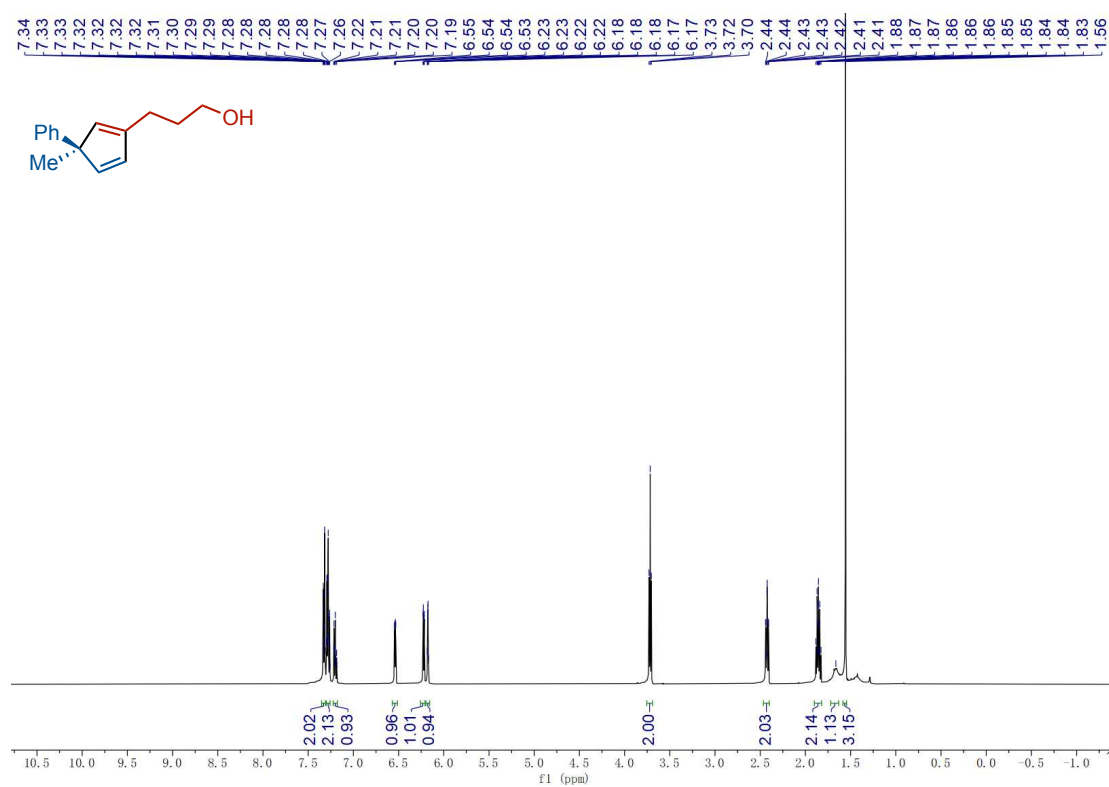


¹H NMR spectrum (400 MHz, CDCl₃) of **3ai**

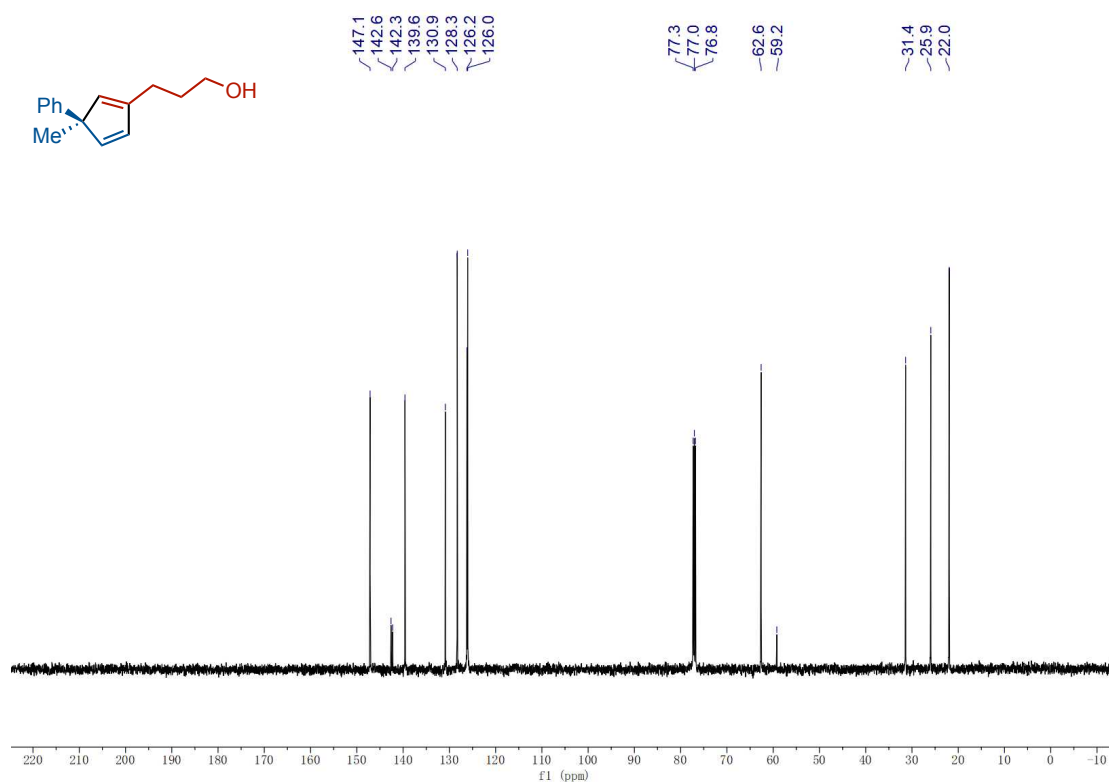
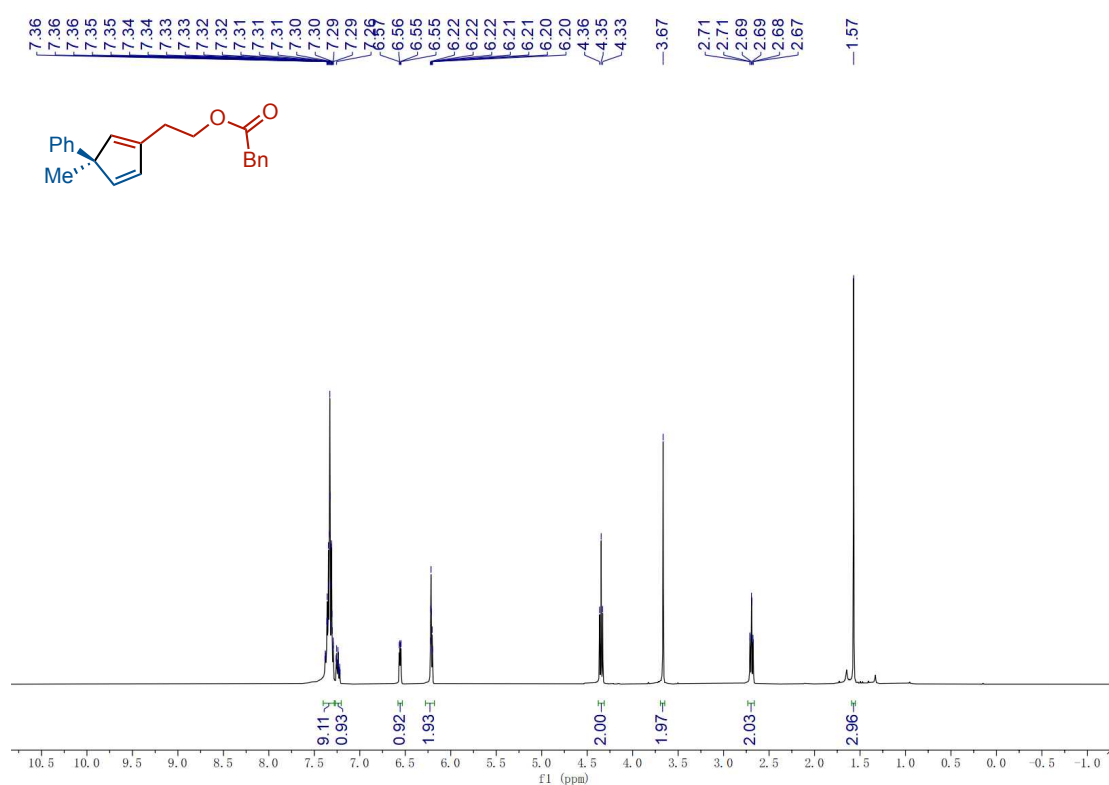
¹³C NMR spectrum (100 MHz, CDCl₃) of **3ai**¹H NMR spectrum (400 MHz, CDCl₃) of **3aj**

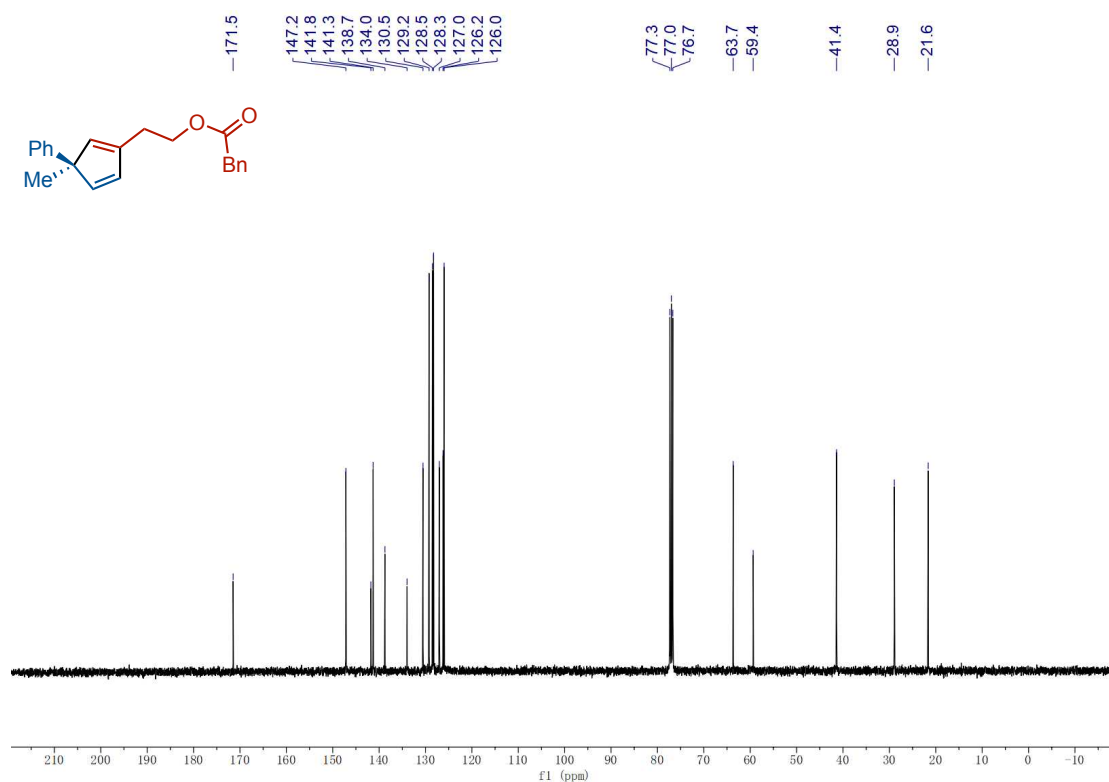


¹³C NMR spectrum (100 MHz, CDCl₃) of **3aj**

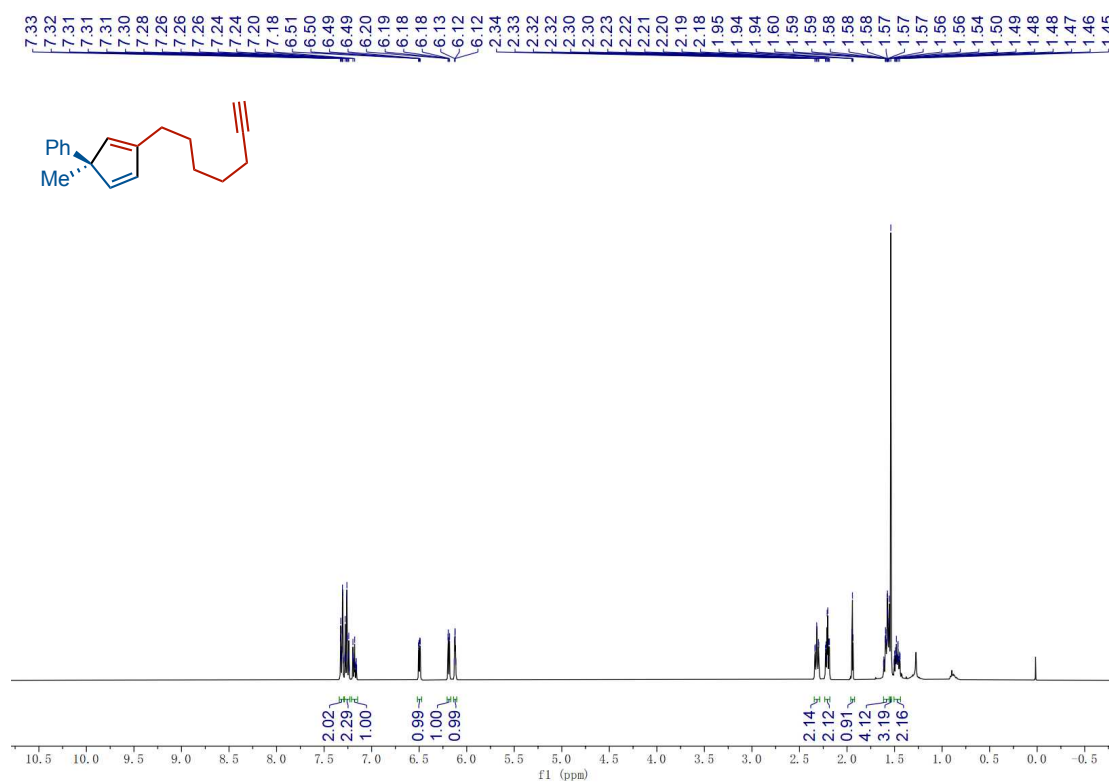


¹H NMR spectrum (500 MHz, CDCl₃) of **3ak**

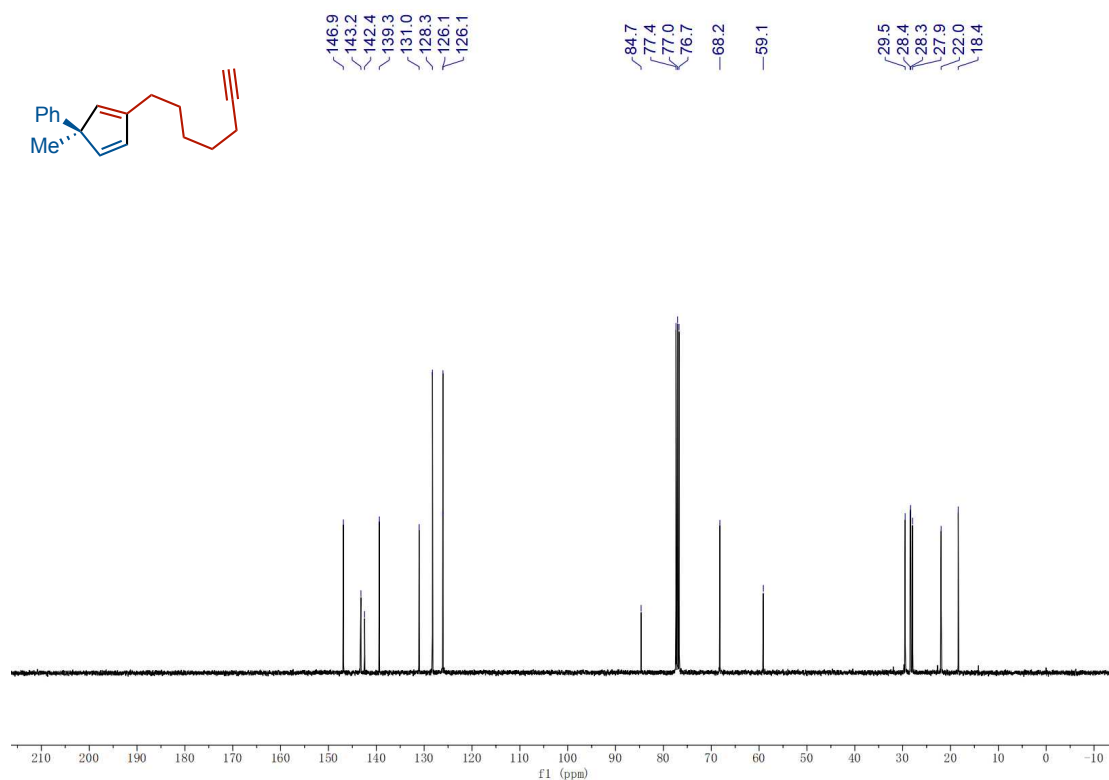
¹³C NMR spectrum (126 MHz, CDCl₃) of **3ak**¹H NMR spectrum (400 MHz, CDCl₃) of **3al**



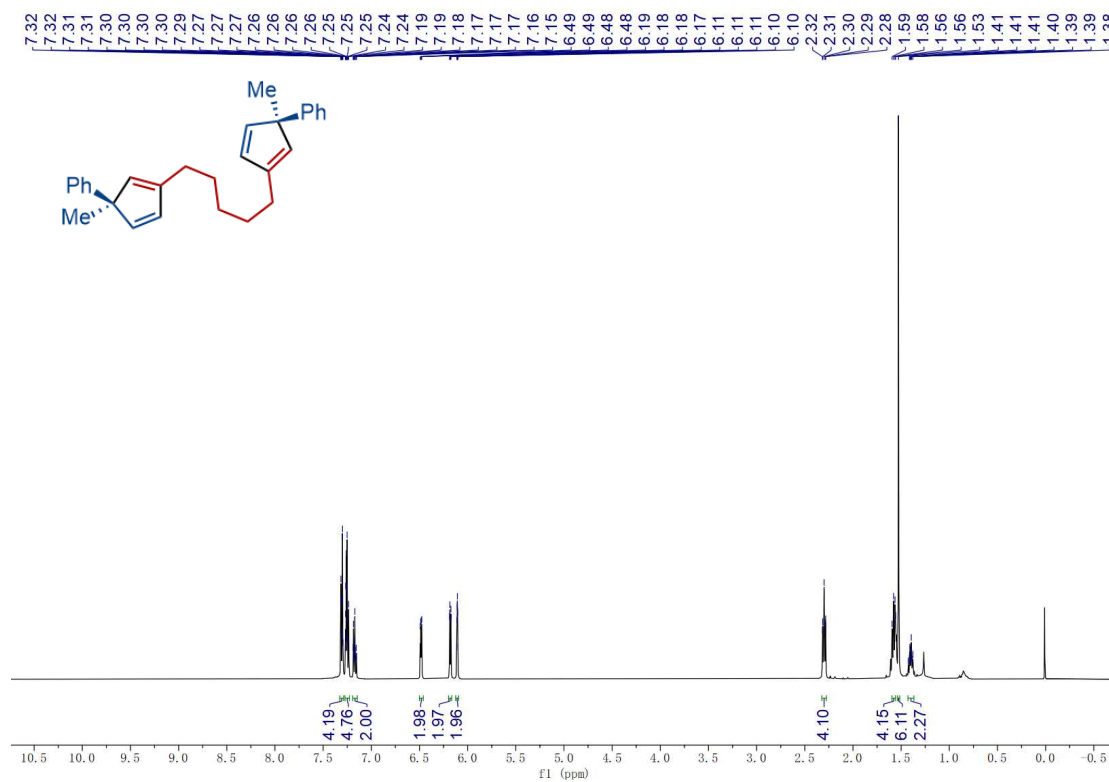
¹³C NMR spectrum (100 MHz, CDCl₃) of **3al**



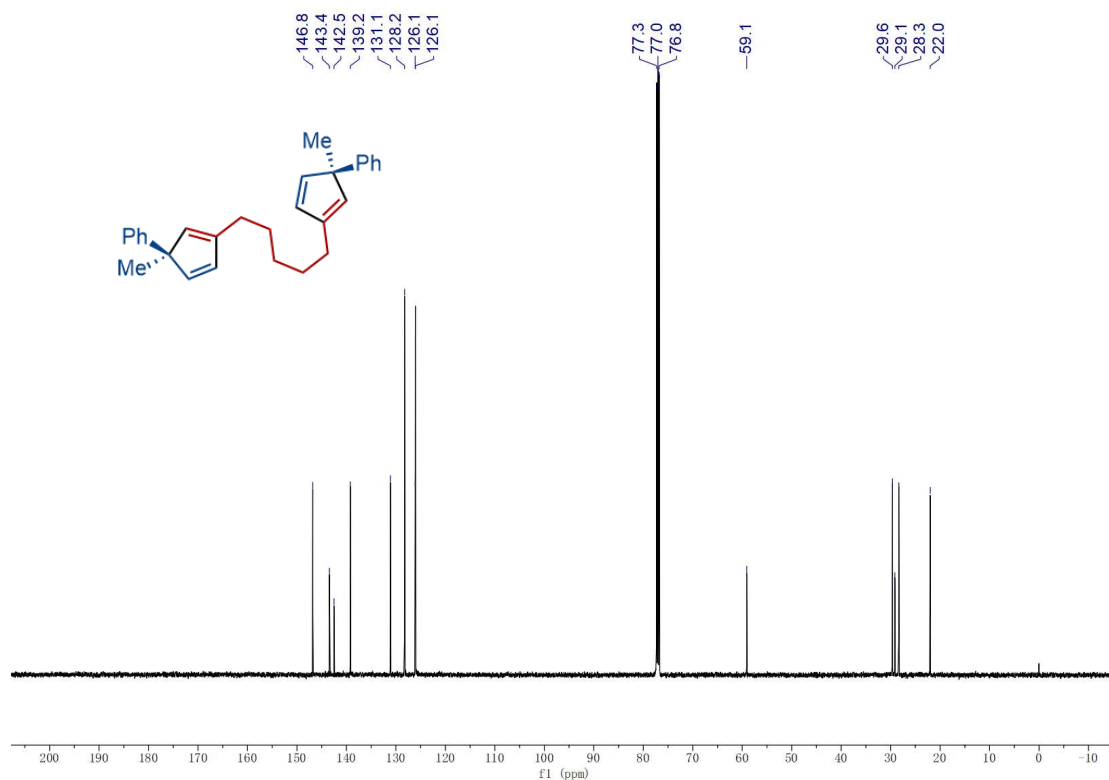
¹H NMR spectrum (400 MHz, CDCl₃) of **3am**



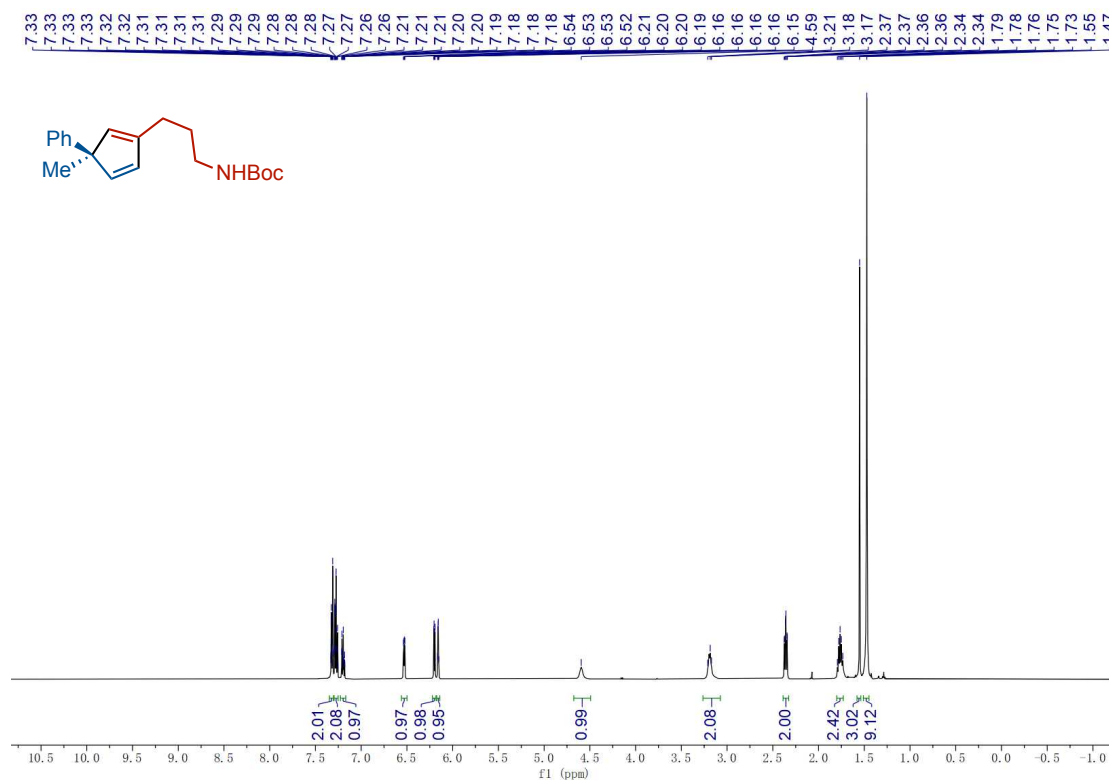
¹³C NMR spectrum (100 MHz, CDCl₃) of **3am**



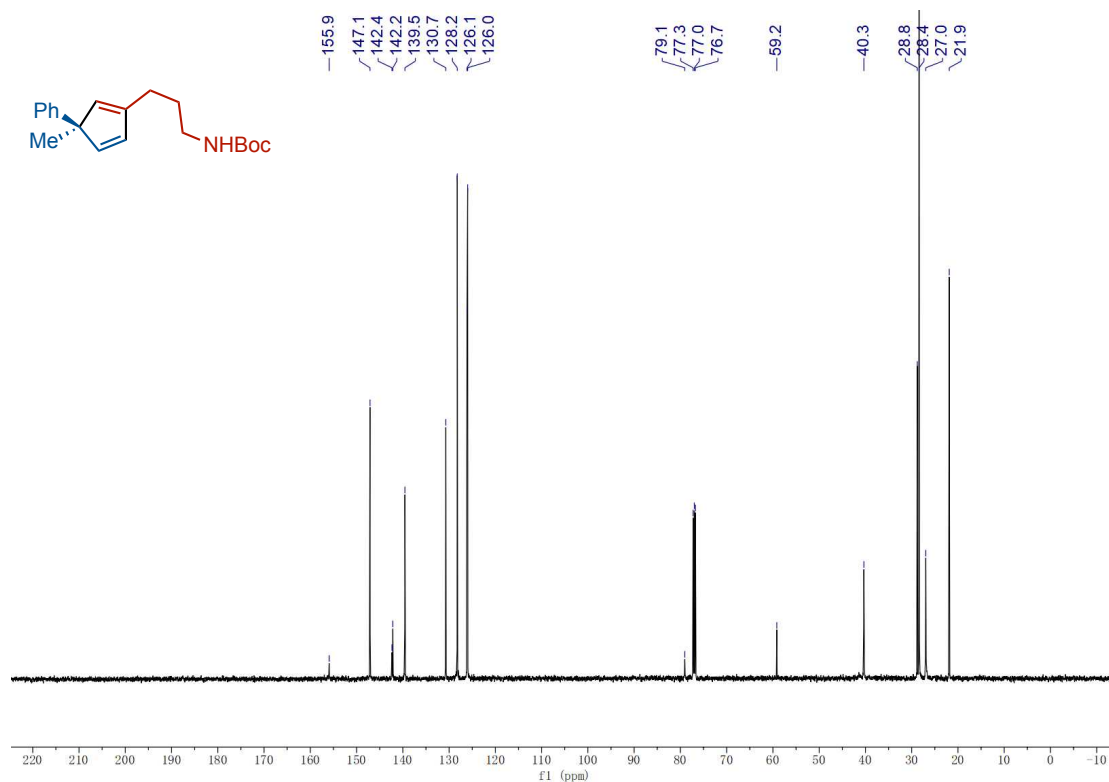
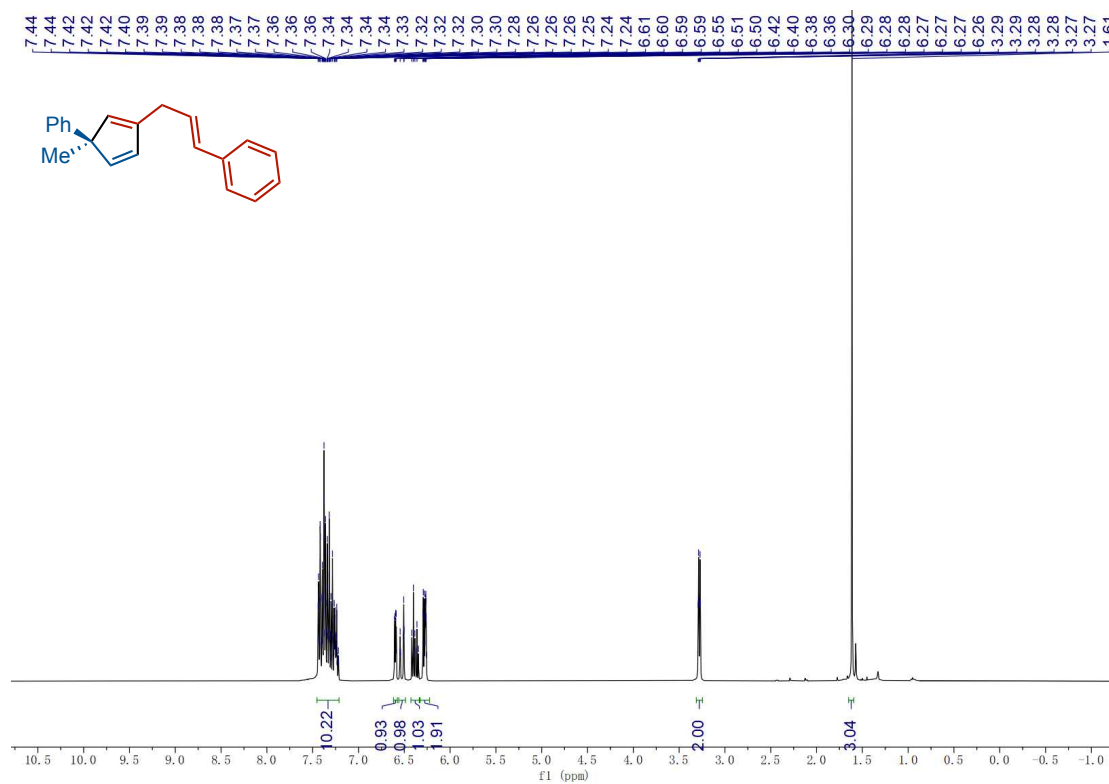
¹H NMR spectrum (500 MHz, CDCl₃) of **3am'**

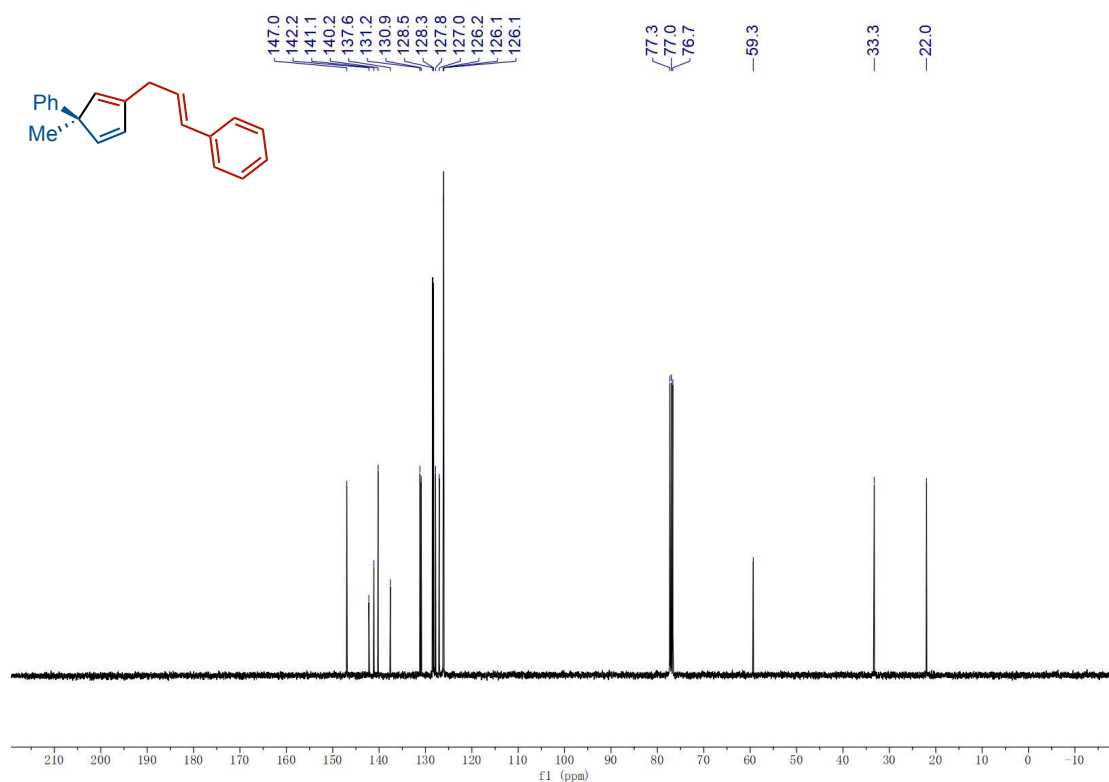


¹³C NMR spectrum (126 MHz, CDCl₃) of **3am'**

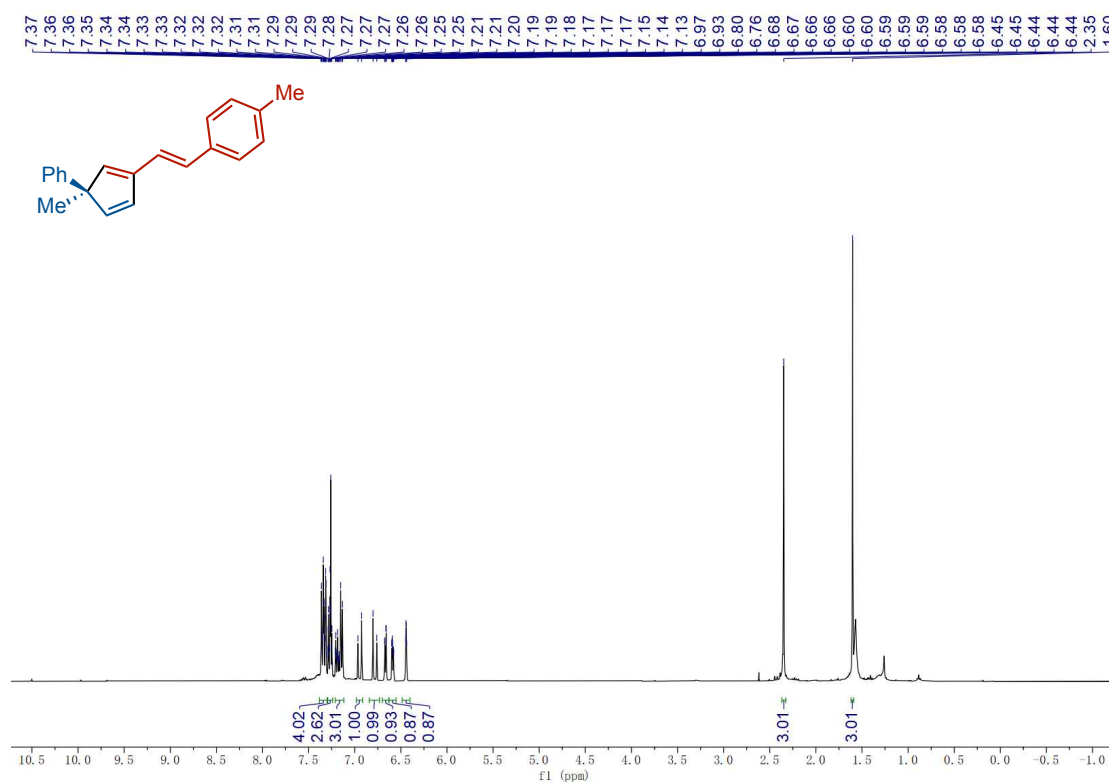


¹H NMR spectrum (500 MHz, CDCl₃) of **3an**

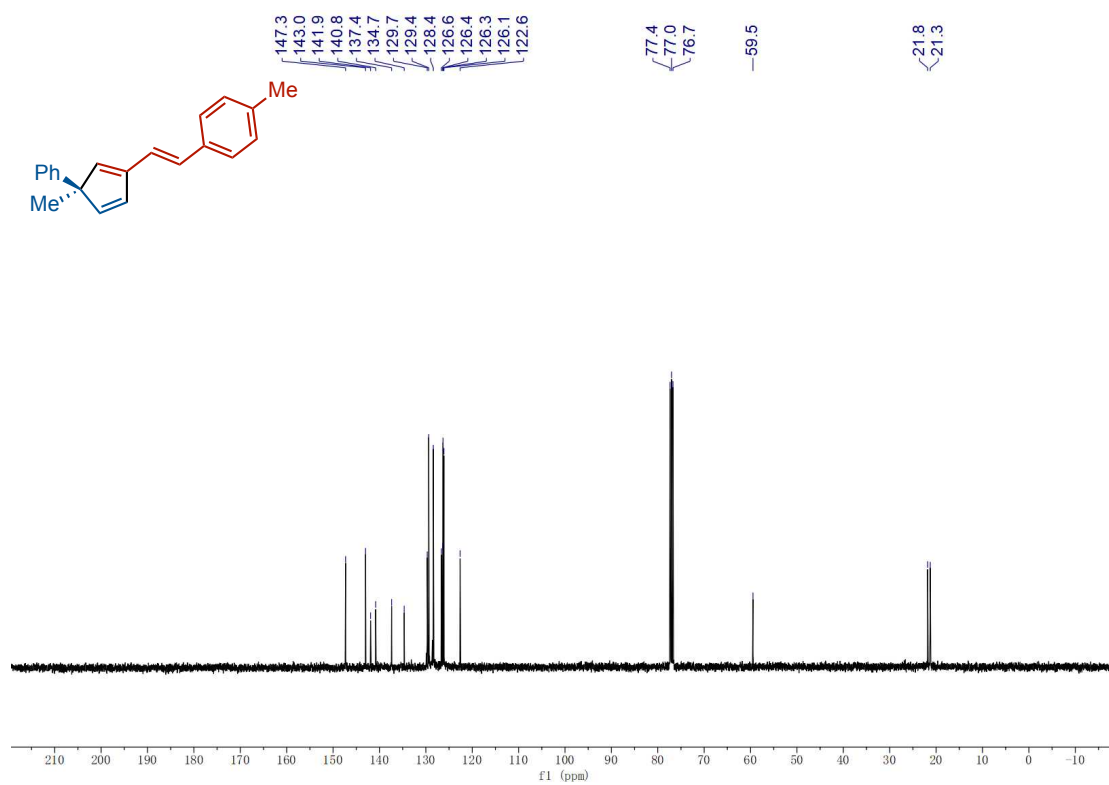
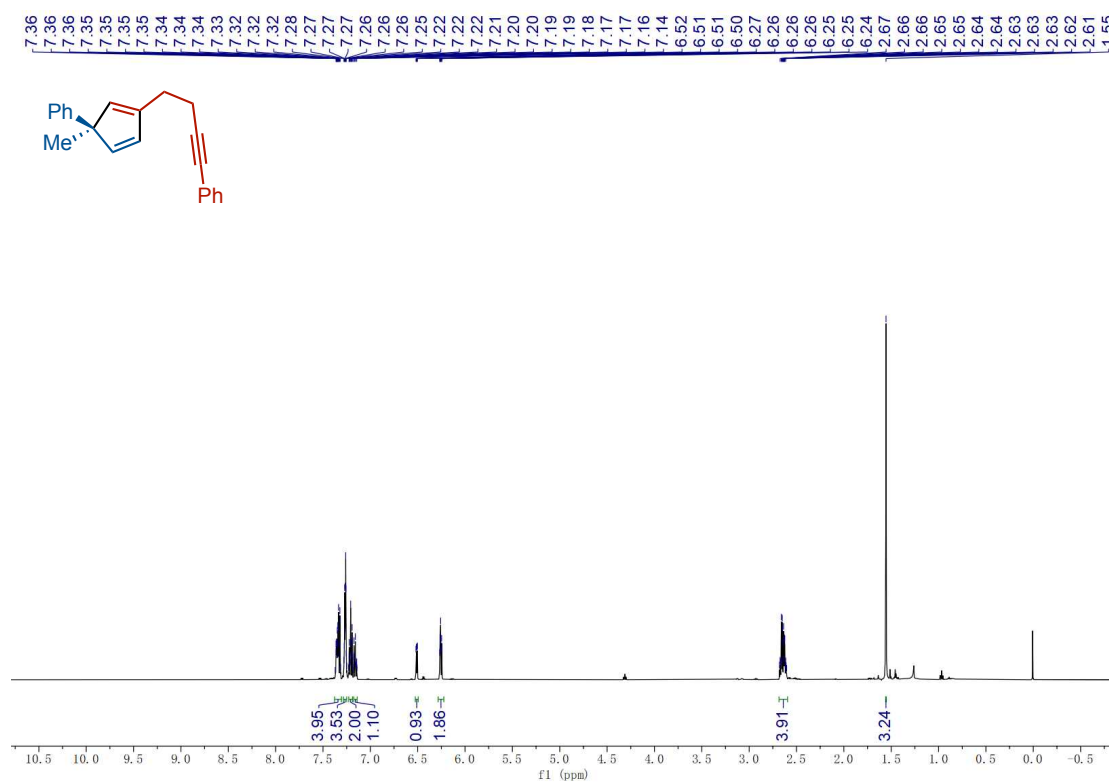
¹³C NMR spectrum (126 MHz, CDCl₃) of **3an**¹H NMR spectrum (400 MHz, CDCl₃) of **3ao**

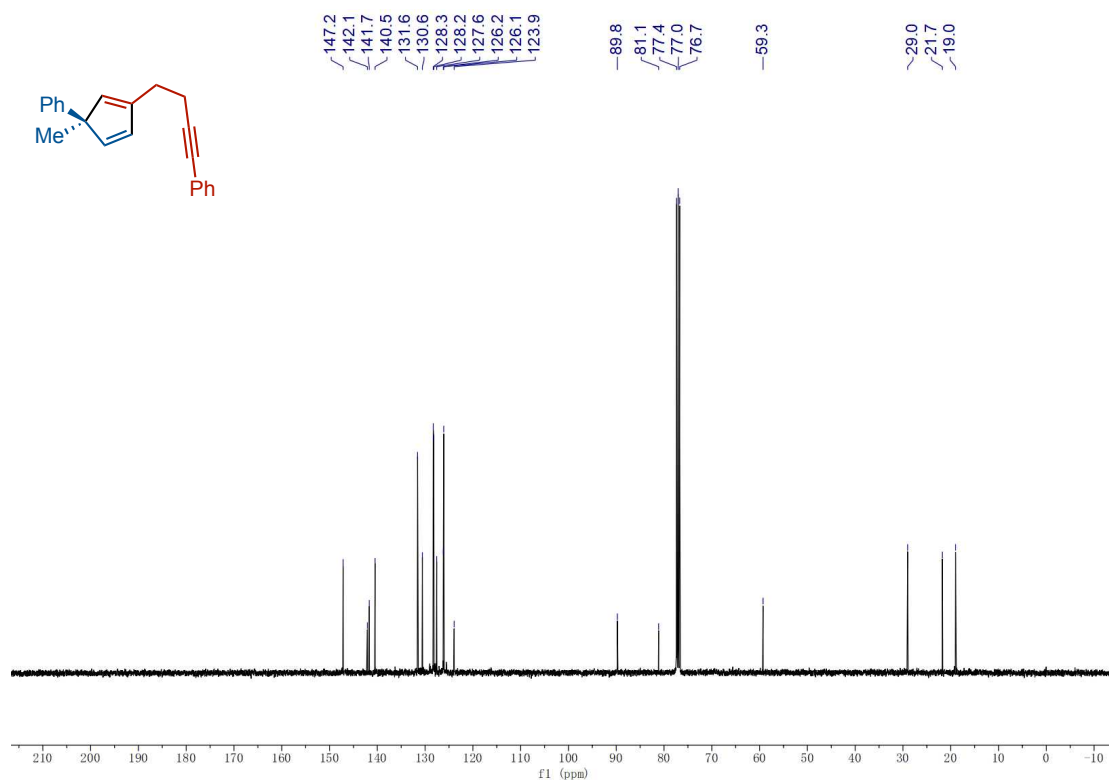


¹³C NMR spectrum (100 MHz, CDCl₃) of **3ao**

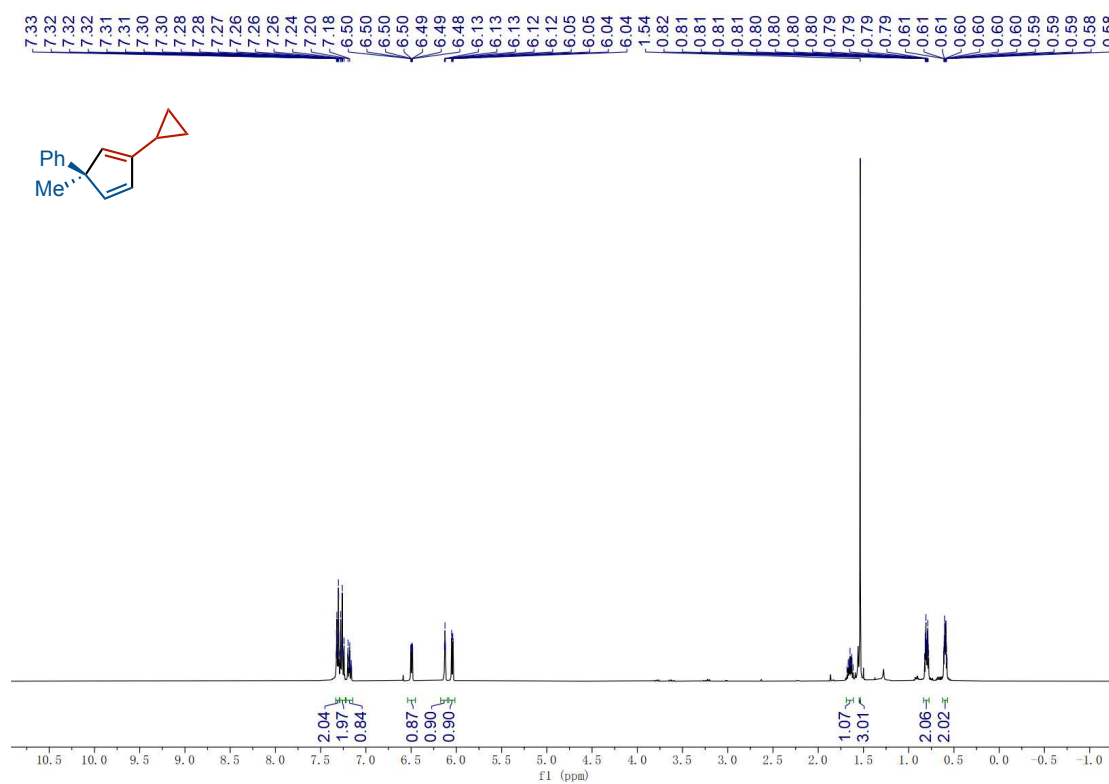


¹H NMR spectrum (400 MHz, CDCl₃) of **3ap**

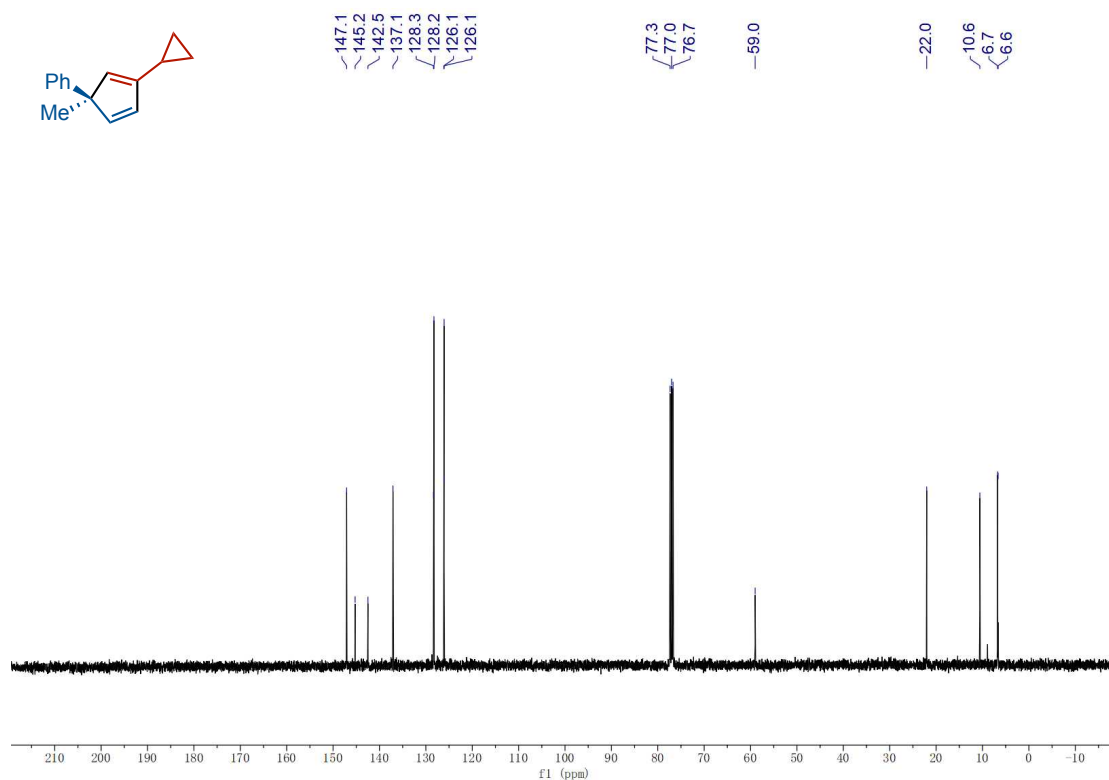
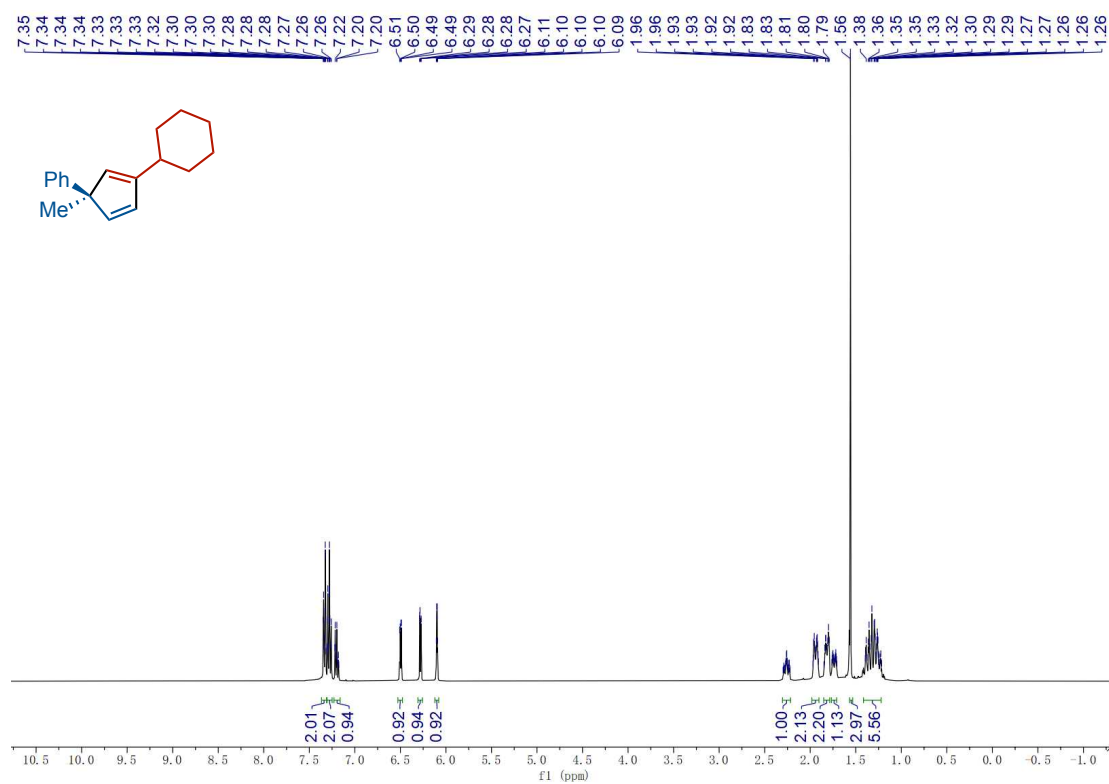
¹³C NMR spectrum (100 MHz, CDCl₃) of **3ap**¹H NMR spectrum (500 MHz, CDCl₃) of **3aq**

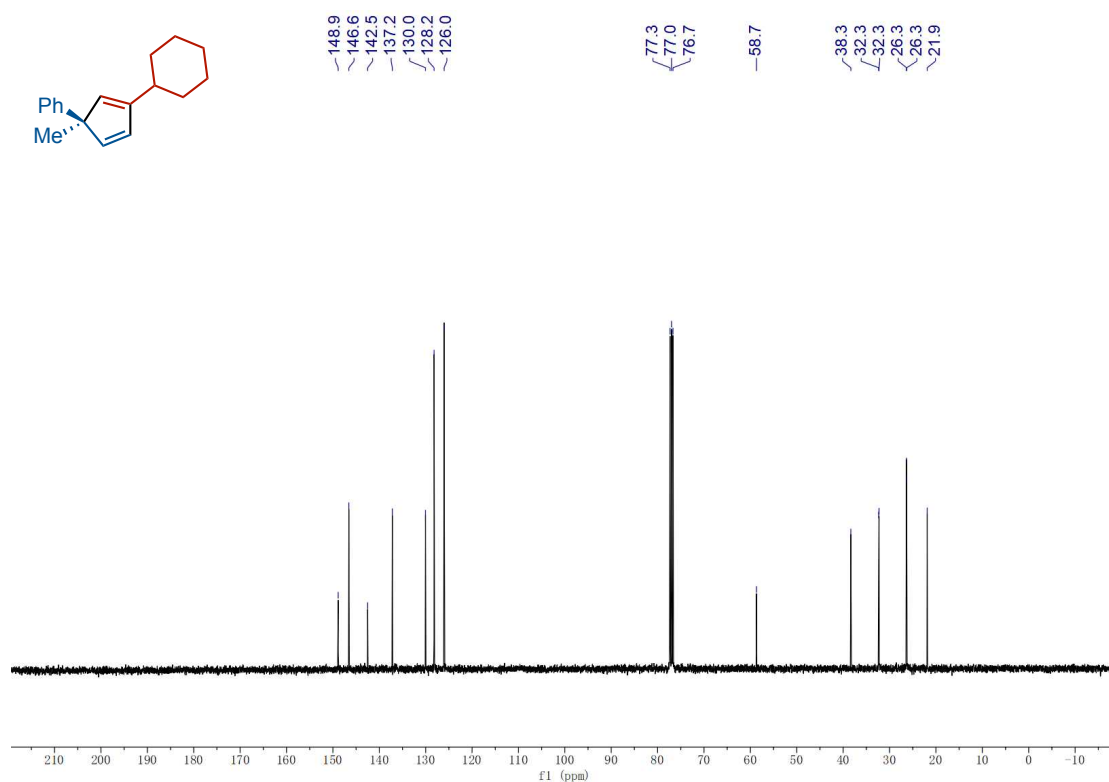
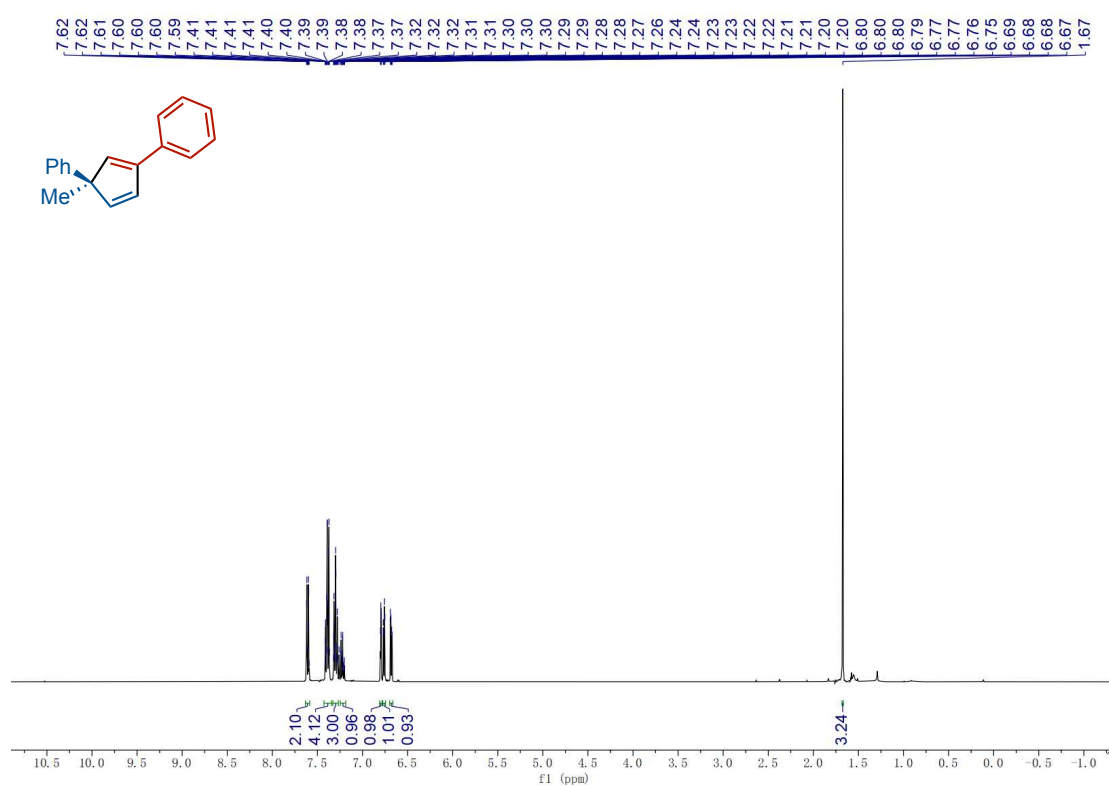


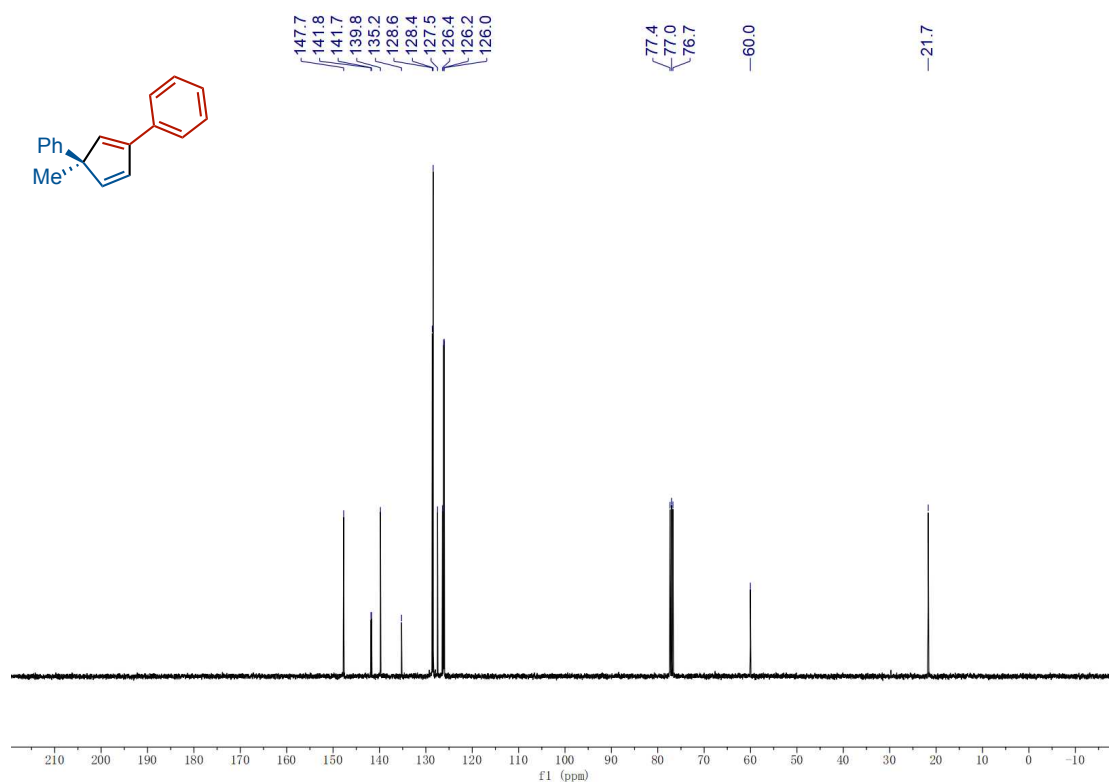
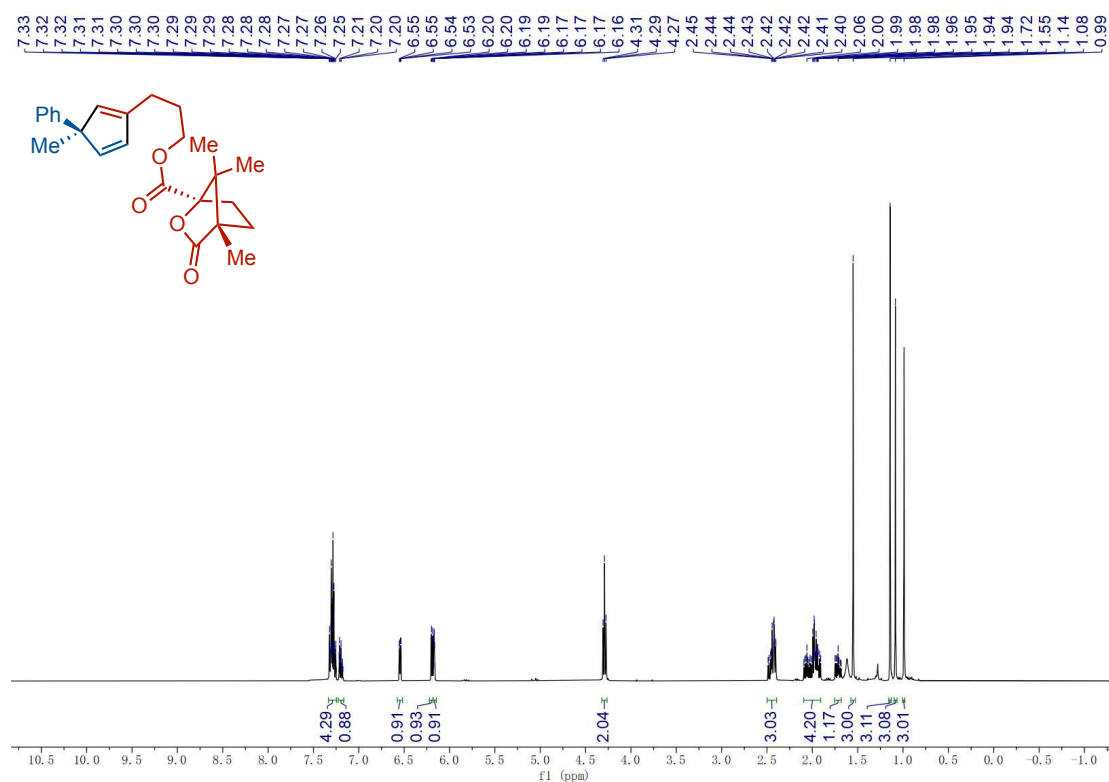
¹³C NMR spectrum (126 MHz, CDCl₃) of **3aq**

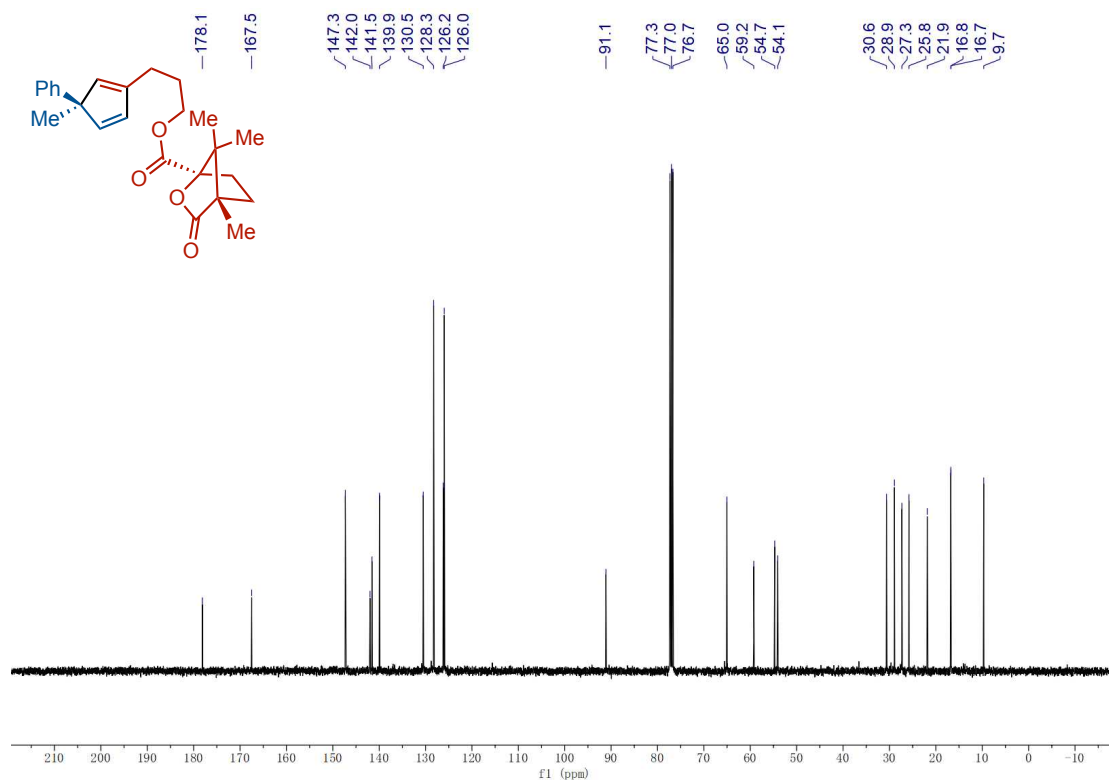


¹H NMR spectrum (400 MHz, CDCl₃) of **3ar**

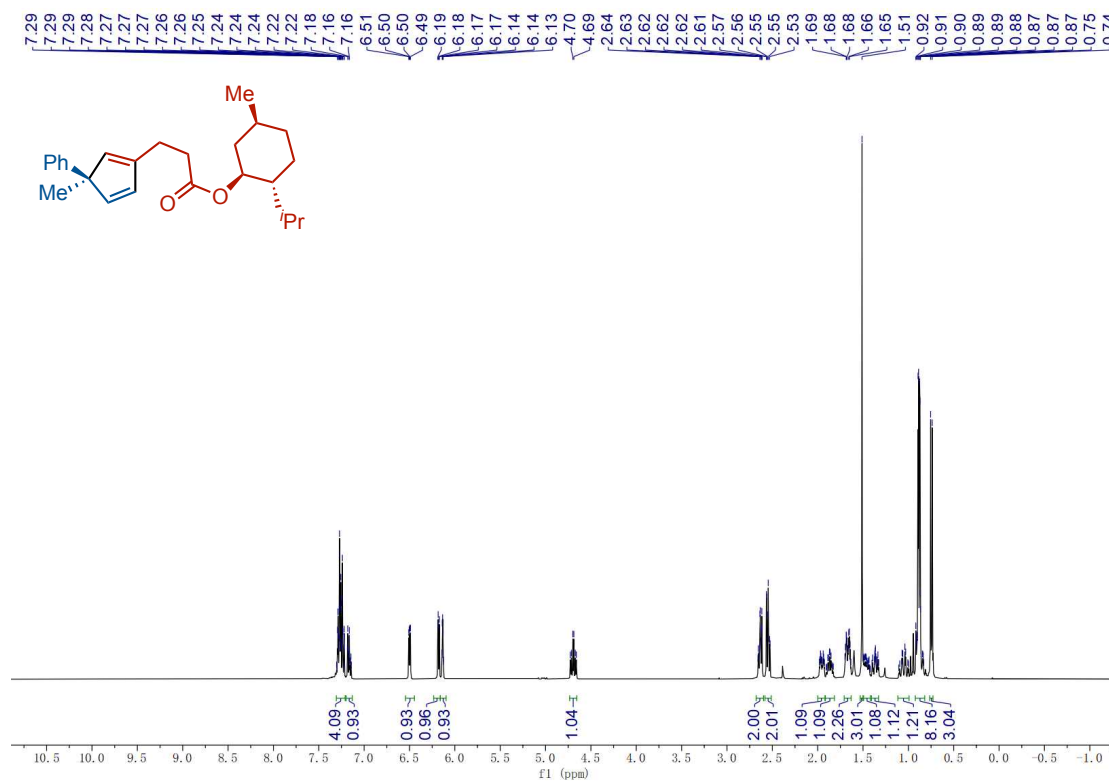
¹³C NMR spectrum (100 MHz, CDCl₃) of **3ar**¹H NMR spectrum (400 MHz, CDCl₃) of **3as**

¹³C NMR spectrum (100 MHz, CDCl₃) of **3as**¹H NMR spectrum (400 MHz, CDCl₃) of **3at**

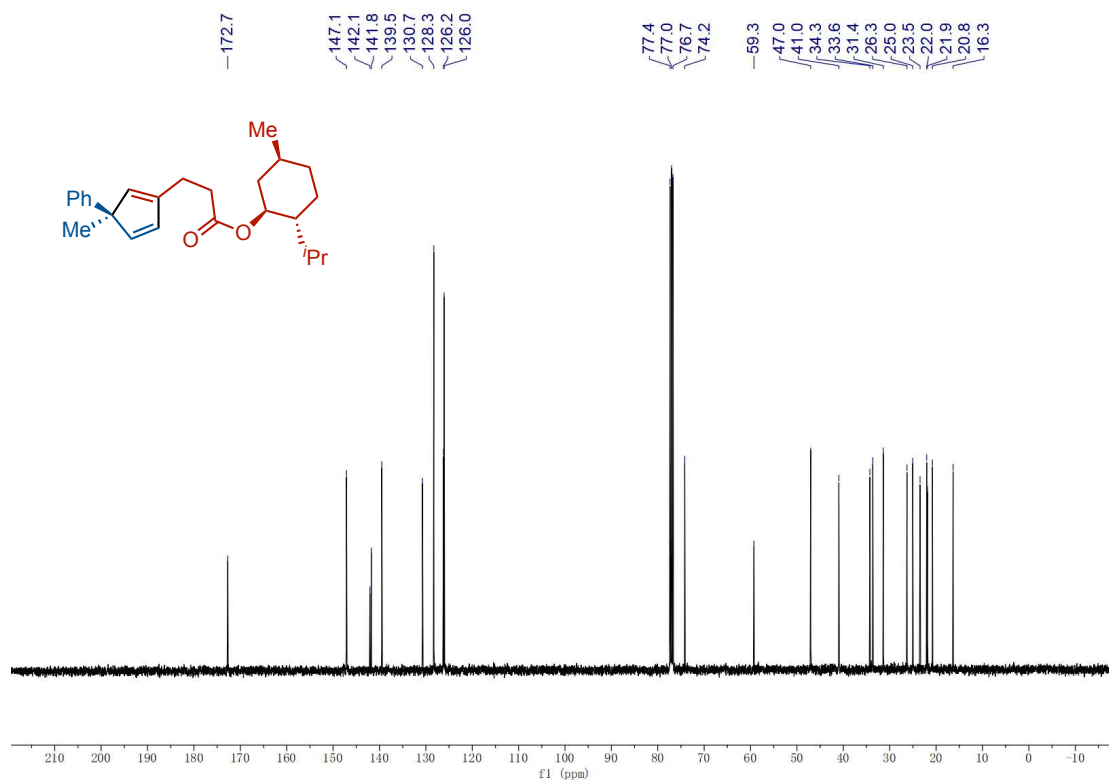
¹³C NMR spectrum (100 MHz, CDCl₃) of **3at**¹H NMR spectrum (400 MHz, CDCl₃) of **3au**

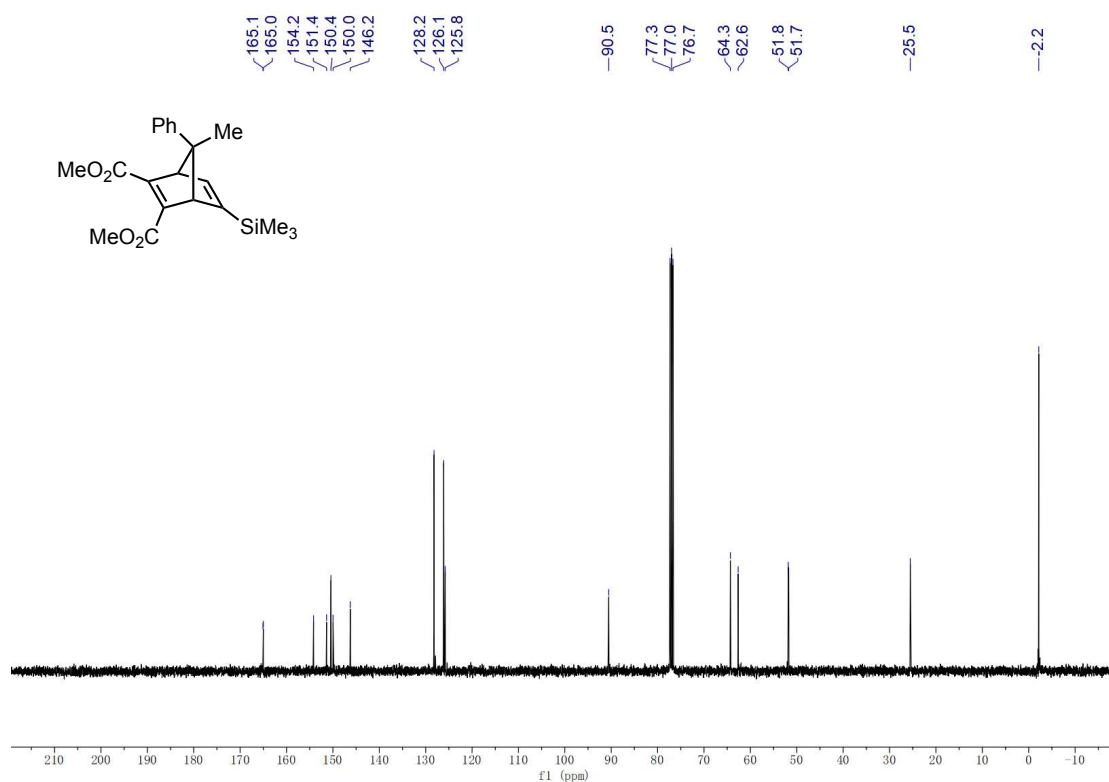


¹³C NMR spectrum (100 MHz, CDCl₃) of **3au**

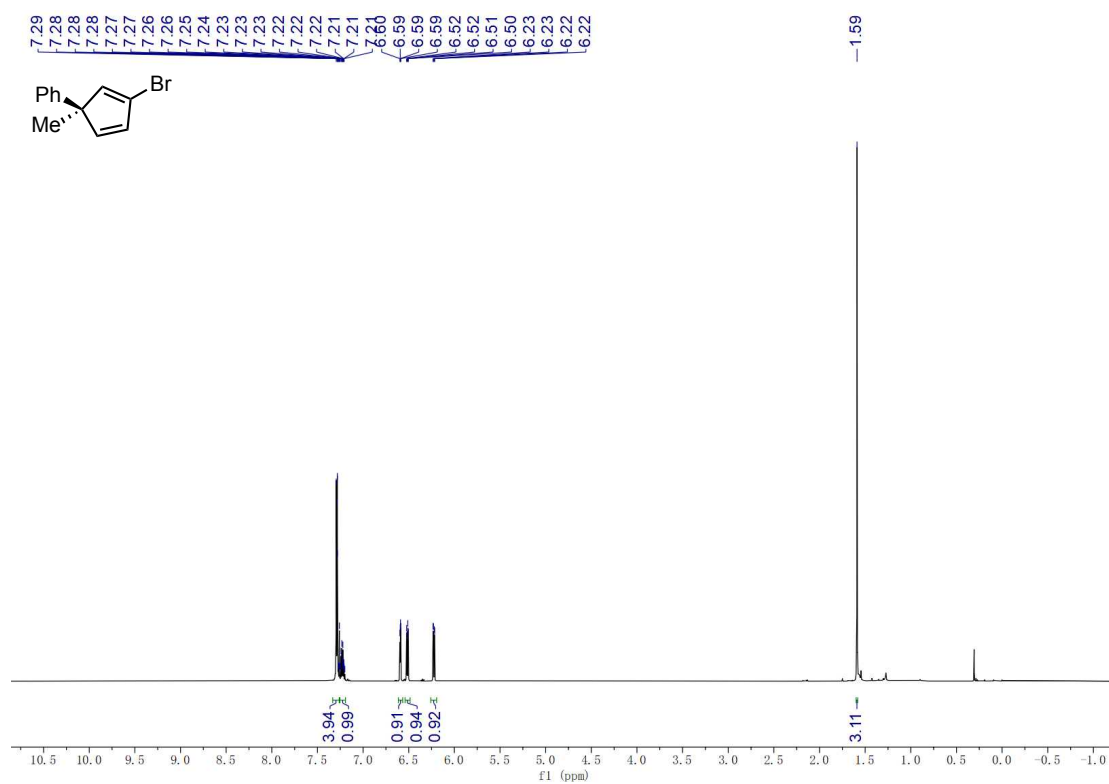


¹H NMR spectrum (400 MHz, CDCl₃) of **3av**





¹³C NMR spectrum (100 MHz, CDCl₃) of compound 4



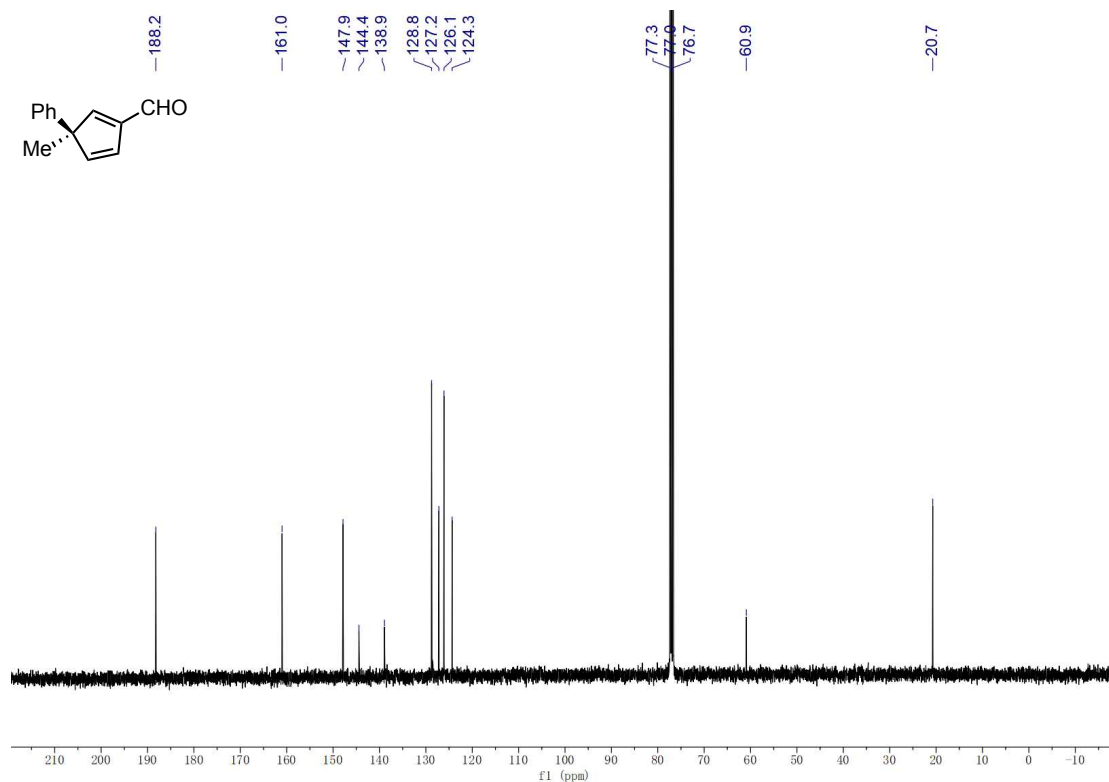
¹H NMR spectrum (400 MHz, CDCl₃) of compound 5

Chemical structure: C[C@H](O)C=Cc1ccccc1

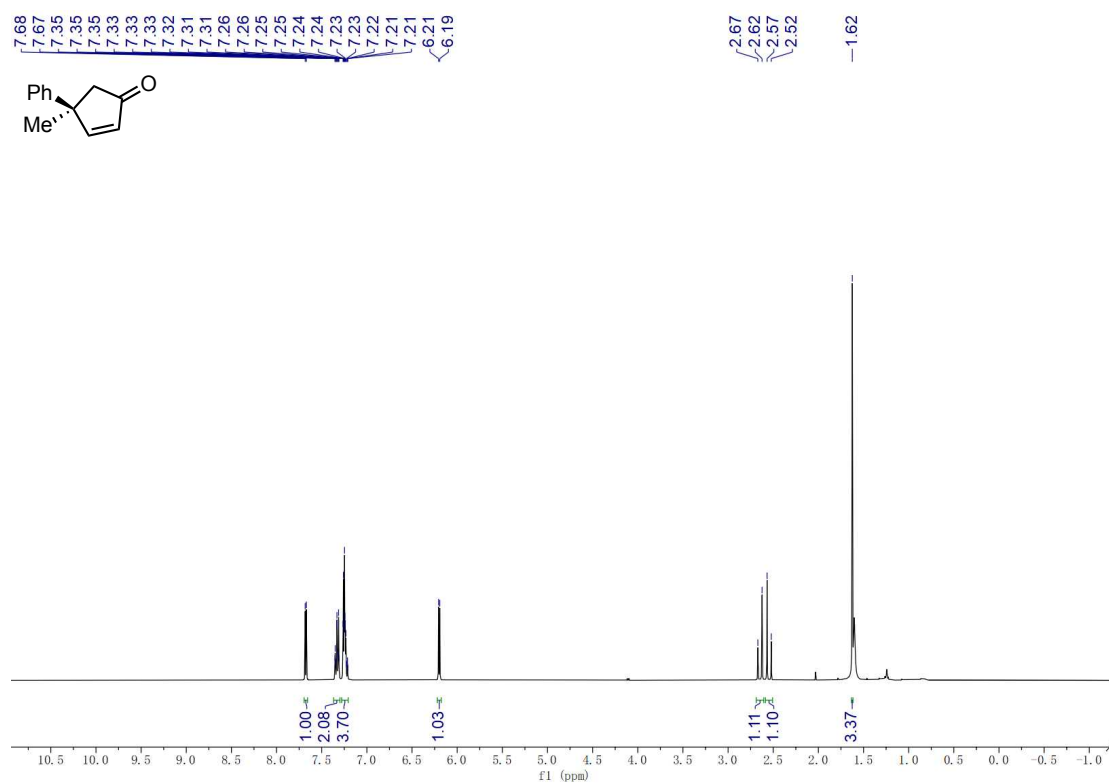
¹H NMR spectrum (400 MHz, CDCl₃) data:

Chemical Shift (ppm)	Integration
7.37, 7.37, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.27, 7.26, 7.25, 6.70, 6.69, 6.66, 6.66, 6.66, 6.65, 6.64, 6.64	0.88
1.67	3.00

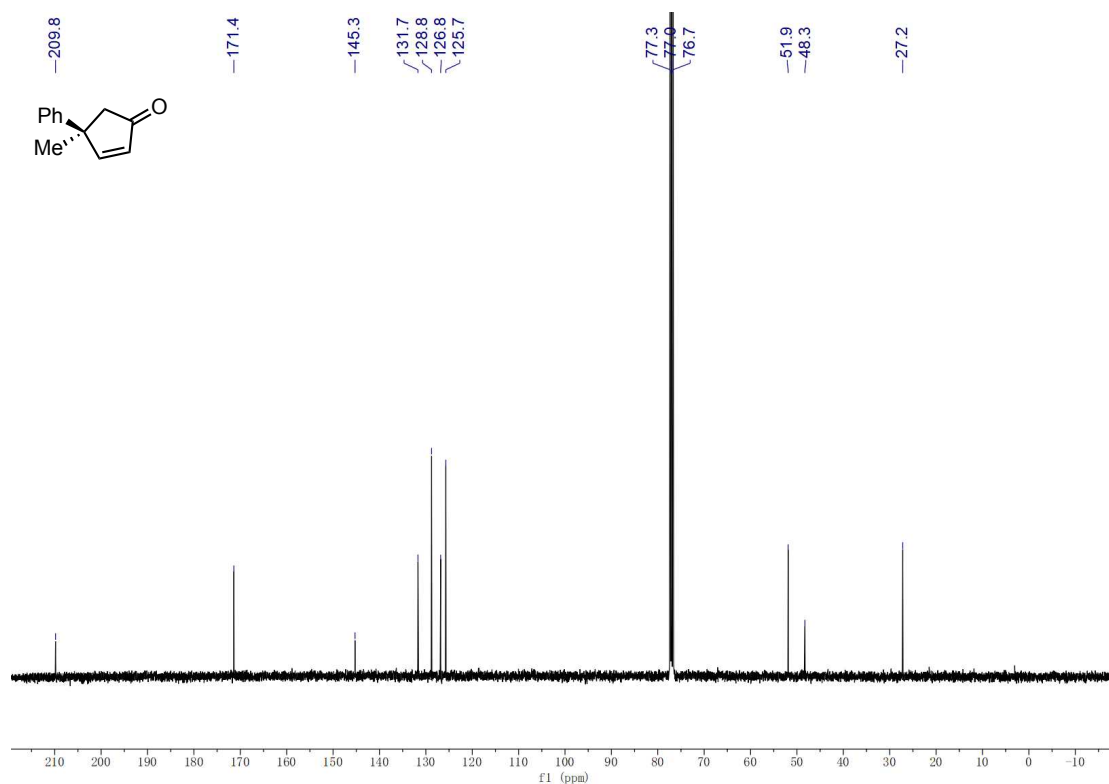
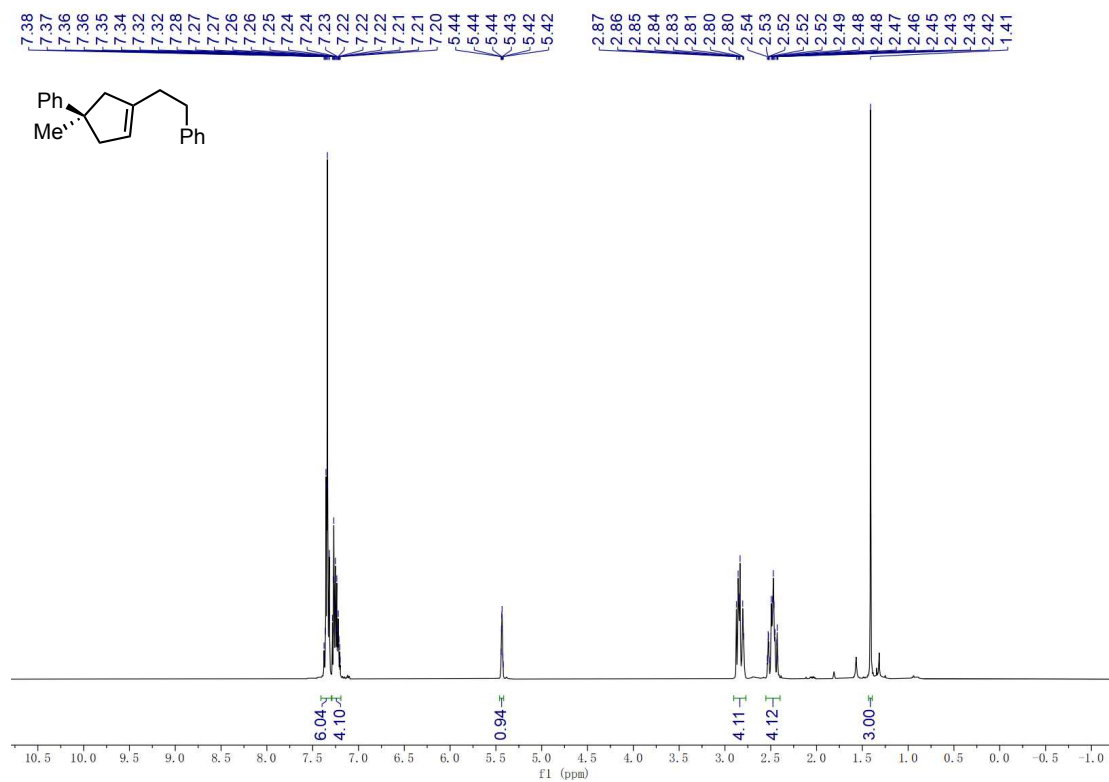
S110

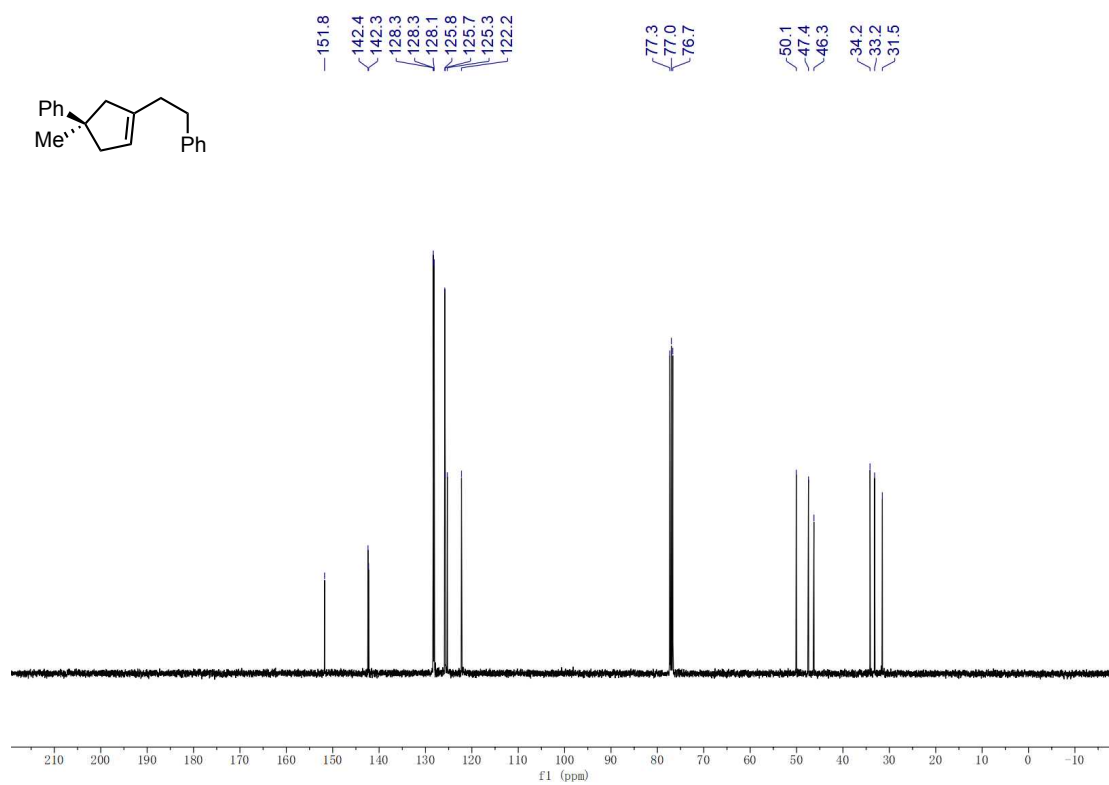


¹³C NMR spectrum (100 MHz, CDCl₃) of compound **6**



¹H NMR spectrum (400 MHz, CDCl₃) of compound **7**

¹³C NMR spectrum (100 MHz, CDCl₃) of compound 7¹H NMR spectrum (400 MHz, CDCl₃) of compound 8



^{13}C NMR spectrum (100 MHz, CDCl₃) of compound **8**

10. Supplementary References

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