Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Rhodium-Catalyzed Formal [2+2+1] Annulation of Arylboronic Acids with Alkynes

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1. General information

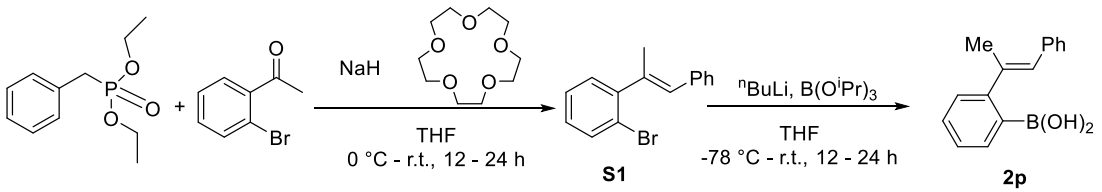
All air-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or argon. Oil bath is used as the heat source for all the reactions that requiring heating. NMR spectra were recorded on Bruker AVANCE AV-400 spectrometer (400 MHz for ^{1}H, 101 MHz for ^{13}C) or Bruker AVANCE AV-300 spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C). Chemical shifts were reported in δ (ppm) referenced to the residual solvent peak of $CDCl_3$ (δ 7.26) for ^{1}H NMR and $CDCl_3$ (δ 77.0) for ^{13}C NMR, the residual solvent peak of DMSO-d6 (δ 2.50) for ^{1}H NMR and DMSO-d6 (δ 40.0) for ^{13}C NMR. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Coupling constants were reported in Hertz (Hz). High resolution mass spectra (HRMS) were obtained on Waters XEVO G2-S TOF or Agilent 6520B Q-FOF (ESI). For thin layer chromatography (TLC), Yantai pre-coated TLC plates (HSGF 254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with $KMnO_4$ followed by heating. Column chromatography separations were performed on silica gel (300–400 mesh). Unless otherwise noted, all commercialized reagents were used as received without further purification.

2. Materials

All solvents were purchased from commercial suppliers and degassed with N_2 before use. Rhodium complex $[Rh(OH)(cod)]_2$ was prepared according to the reported procedure.[1] Alkynes were purchased from commercial suppliers or prepared according to literature methods.[2-8] Most organoboronic acids were purchased from commercial suppliers and used as received.

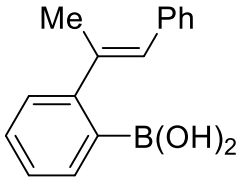
Arylboronic acids **2p** and **2q** were prepared according to the following procedures:

2.1 Synthesis of (*E*)-(2-(1-phenylprop-1-en-2-yl)phenyl)boronic acid (2p)



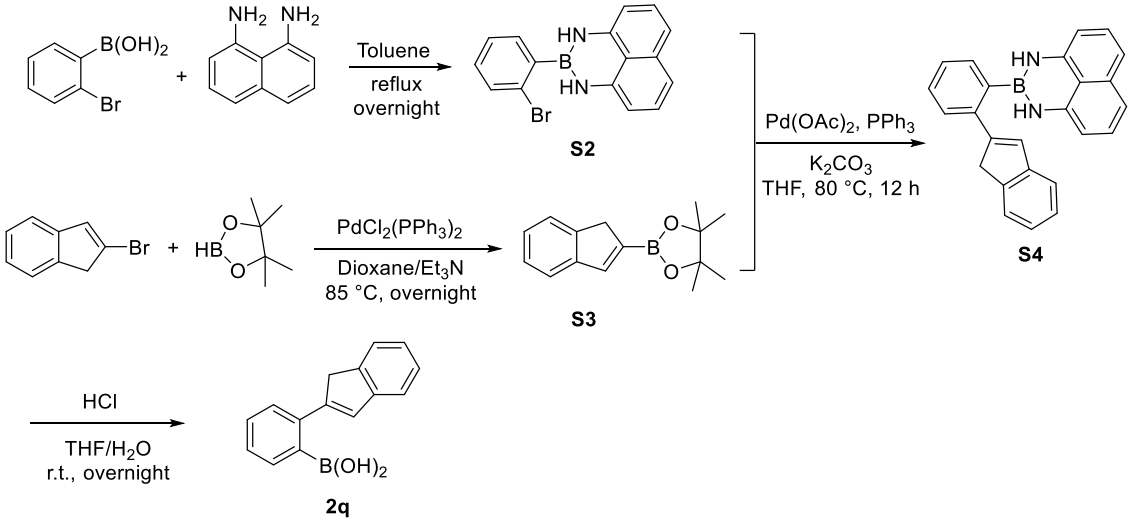
A solution of NaH (6.0 mmol) and 1,4,7,10,13-pentaoxacyclopentadecane (6.0 mmol, 1.2 equiv) in anhydrous THF (20 mL) was added diethyl benzylphosphonate (5.5 mmol, 1.1 equiv) at 0 ℃ under argon. After stirring for 30 min at 0 ℃, 1-(2-bromophenyl)ethan-1-one (5.0 mmol, 1.0 equiv) was added slowly. The reaction mixture was allowed to warm to room temperature and stirred until judged complete by TLC analysis (12-24 h). The reaction mixture was then cooled to 0 ℃ and quenched with aqueous ammonium chloride (20 mL). The biphasic solution was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with brine (20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via flash column chromatography eluting with petroleum ether to afford colorless oil **S1** in 55% yield. The NMR data was consistent with the reported literature.[9] To a solution of **S1** (754 mg, 2.8 mmol, 1.0 equiv) in THF (10 mL) was added ^{n}BuLi (3.1 mmol, 1.1 equiv) at -78 ℃ under argon. After stirring for 30 min at the same temperature, the triisopropyl borate (4.2 mmol, 1.5 equiv) was added dropwise to the reaction mixture. The reaction mixture was allowed to warm to room temperature and stirred until judged complete by TLC analysis (12-24 h). The reaction mixture was then cooled to 0 ℃ and quenched with saturated aqueous solution of ammonium chloride (15 mL). The biphasic solution was extracted with ethyl acetate (3 × 15 mL). The combined organic phases were washed with brine (15 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via flash column chromatography eluting with a mixture of petroleum ether and ethyl acetate to give (*E*)-(2-(1-phenylprop-1-en-2-yl)phenyl)boronic acid (**2p**) in 79% yield.

(*E*)-(2-(1-phenylprop-1-en-2-yl)phenyl)boronic acid (2p)



Colorless oil; 526.6 mg, 79% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.27 (td, *J* = 7.4, 1.3 Hz, 1H), 7.17 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.14 – 7.05 (m, 4H), 6.92 – 6.87 (m, 2H), 6.54 (d, *J* = 1.6 Hz, 1H), 2.21 (d, *J* = 1.5 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 138.1, 137.1, 133.1, 129.9, 128.6, 128.3, 128.2, 128.12, 128.08, 126.6, 122.6, 26.4. HRMS (ESI) calcd for $C_{15}H_{15}BO_2Na^+$ $(M+Na)^+$: 261.1057, found: 261.1064.

2.2 Synthesis of (2-(1*H*-inden-2-yl)phenyl)boronic acid (2q)



In a 100 mL round-bottom flask equipped with a Dean-Stark apparatus, a solution of (2-bromophenyl)boronic acid (10.0 mmol, 1.0 equiv) in toluene (30 mL) was treated with 1,8-diaminonaphthalene (11.0 mmol, 1.1 equiv), which was added in one portion. The reaction mixture was stirred overnight under reflux condition. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The residue was extracted with H_2O and ethyl acetate. The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via flash column chromatography eluting with a mixture of petroleum ether and ethyl acetate to give white solid **S2** in 85% yield. The NMR data was consistent with the reported literature.[10]

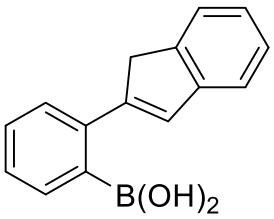
To a solution of $PdCl_2(PPh_3)_2$ (0.2 mmol, 0.03 equiv) in dioxane (25 mL) was added 2-bromo-1*H*-indene (6.3 mmol, 1.0 equiv), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9.4

mmol, 1.5 equiv) and triethylamine (2.6 mL) at room temperature under argon. The reaction mixture was warmed to 85 ℃. After stirring overnight, the mixture was quenched with saturated sodium chloride solution and extracted with ethyl acetate. The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via flash column chromatography eluting with a mixture of petroleum ether and ethyl acetate to give product **S3** in 60% yield. The NMR data was consistent with the reported literature.[11]

In a 50 mL Schlenk tube, a solution of $Pd(OAc)_2$ (0.13 mmol, 0.05 equiv), PPh_3 (0.25 mmol, 0.1 equiv) and K_3PO_4 (7.5 mmol, 3.0 equiv) in THF (20 mL) was added **S2** (2.5 mmol, 1.0 equiv) and **S3** (3.7 mmol, 1.5 equiv) under nitrogen. The mixture was allowed to warm to 80 ℃. After stirring for 12 h, the mixture was quenched with water and extracted with ethyl acetate. The combined organic phases were washed with bine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via flash column chromatography eluting with a mixture of petroleum ether and ethyl acetate to give product **S4** in 68% yield.

To a solution of **S4** (1.7 mmol) in THF was added HCl (5 M), then the reaction was stirred overnight at room temperature. The resulting reaction was extracted with HCl (2 M) and ethyl acetate. The combined organic phases were washed with bine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified via flash column chromatography eluting with a mixture of petroleum ether and ethyl acetate to give (2-(1*H*-inden-2-yl)phenyl)boronic acid (**2q**) in 51% yield.

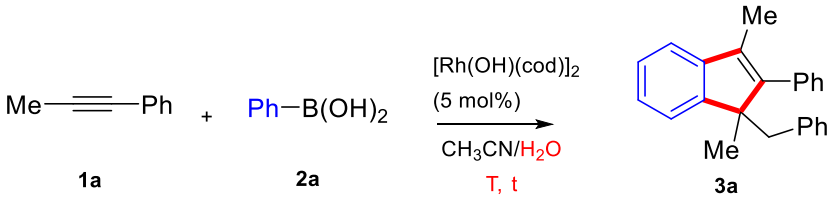
(2-(1*H*-inden-2-yl)phenyl)boronic acid (2q)



White solid, mp: 160 – 161 ℃; 205 mg, 51% yield. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.16 (s, 2H), 7.53 – 7.43 (m, 2H), 7.39 – 7.30 (m, 3H), 7.26 – 7.19 (m, 2H), 7.14 (td, J = 7.4, 1.3 Hz, 1H), 7.03 (s, 1H), 3.81 (s, 2H).^{13}C NMR (75 MHz, DMSO-d_6) δ 149.31, 145.09, 143.28, 138.54, 131.98, 128.12, 127.65, 126.94, 126.44, 124.45, 123.60, 120.73, 40.25. HRMS (ESI) calcd for $C_{15}H_{14}BO_2^+$ $(M+H)^+$: 237.1081, found: 237.1093.

3. Evaluation of reaction conditions for the synthesis of indene 3a

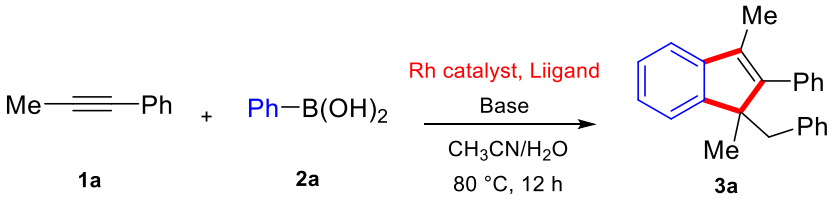
Table S1. Evaluation of temperature, amount of water, and reaction time[a]



Entry	Temp. (°C)	H_2O (mL)	Time (h)	Yield (%) (3a)[b]
1	40	0.1	12	15
2	60	0.1	12	65
3	80	0.1	12	97
4	80	0.5	12	43
5	80	0.05	12	95
6	80	0	12	8
7	80	0.1	8	93
8	80	0.1	4	89

[a]Reaction conditions: **1a** (0.60 mmol), **2a** (0.20 mmol) and Rh catalyst (5 mol%) in CH_3CN (1.0 mL)/H_2O (as indicated). [b]Isolated yield.

Table S2. Evaluation of catalysts and ligand[a]

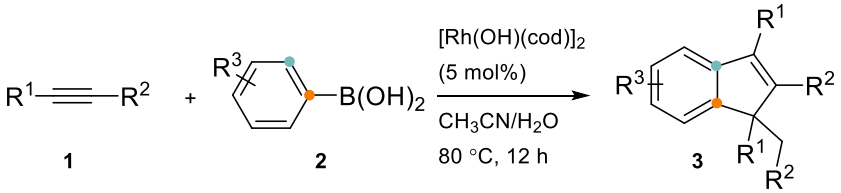


Entry	Rh catalyst	Ligand	Base	Yield (%) (3a)[c]
1	$[Rh(OH)(cod)]_2$	——	——	97
2[b]	$[Rh(OH)(cod)]_2$	——	——	53

3	$[RhCl(cod)]_2$	——	——	n.d.
4	$[RhCl(cod)]_2$	——	KOH (20 mmol%)	85
5	$[Rh(OH)(cod)]_2$	binap (12 mmol%)	——	n.d.
6	$[Rh(OH)(cod)]_2$	dppf (12 mmol%)	——	n.d.
7	$[Rh(OH)(cod)]_2$	segphos (12 mmol%)	——	n.d

[a]Reaction conditions: **1a** (0.60 mmol), **2a** (0.20 mmol) and Rh catalyst (5 mol%) in CH_3CN/H_2O (1.0 mL/0.1mL) at 80 ℃ for 12 h. The catalyst was generated in situ by mixing $[Rh(OH)(cod)]_2$ with bisphosphine ligand in THF at 30 for 30 min, then THF was removed. [b]2.5 mmol% catalyst was added. [c]Isolated yield.

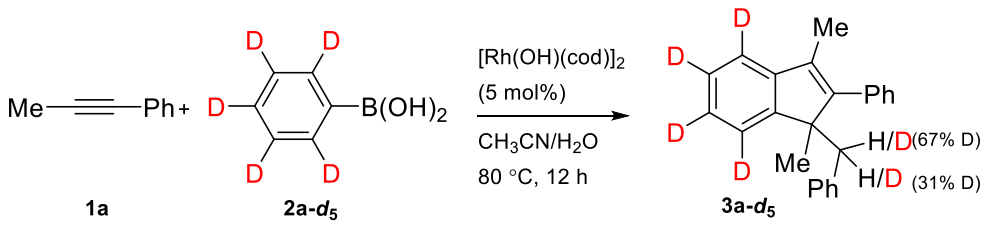
4. Procedures for Scheme 2



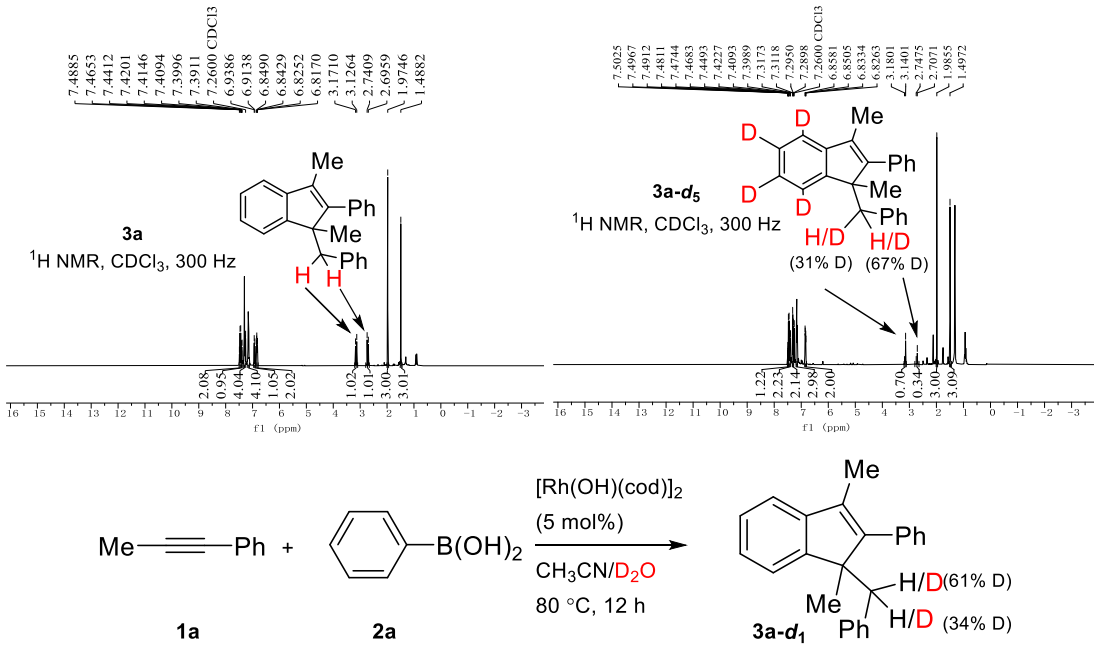
$[Rh(OH)(cod)]_2$ (4.6 mg, 0.01 mmol, 5 mol%), **1** (0.6 mmol), and **2** (0.20 mmol) were placed in an oven-dried Schlenk tube under nitrogen. CH_3CN/H_2O (1.0 mL/0.1 mL) was added and the reaction mixture was stirred at 80 ℃ for 12 h. Upon completion, the reaction mixture was diluted with ethyl acetate (5 mL) and water (5 mL). The layers were separated and the aqueous layer was extracted again with ethyl acetate for two more times (5 mL × 2). The combined organic phases were concentrated in vacuo, and the residue was purified by silica gel chromatography eluting with petroleum ether to give **3**.

5. Procedures for Scheme 3

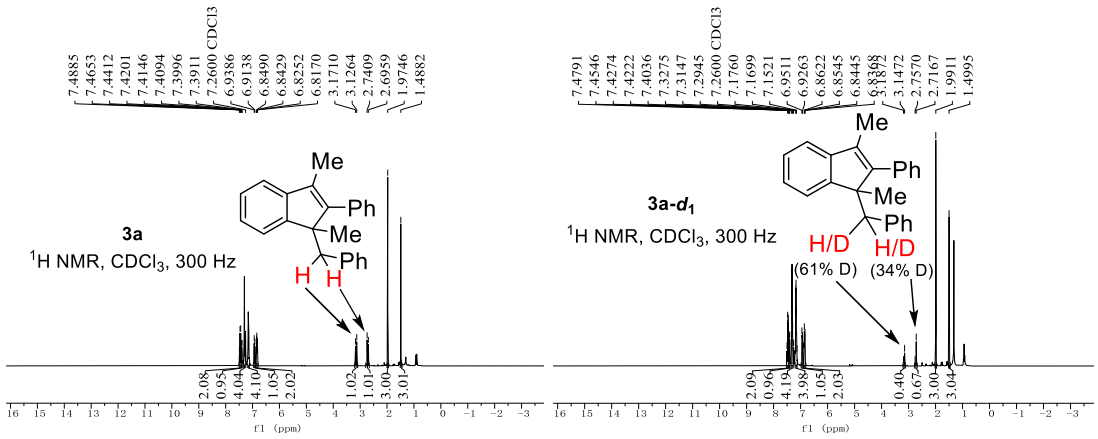
5.1 Deuterium-labelling experiment



[Rh(OH)(cod)]$_2$ (4.6 mg, 0.01 mmol, 5 mol%), **1a** (0.6 mmol), and **2a-*d*$_5$** (0.20 mmol) were placed in an oven-dried Schlenk tube under nitrogen. CH_3CN/H_2O (1.0 mL/0.1 mL) was added and the reaction mixture was stirred at 80 ℃ for 12 h. Upon completion, the reaction mixture was diluted with ethyl acetate (5 mL) and water (5 mL). The layers were separated and the aqueous layer was extracted again with ethyl acetate for two more times (5 mL × 2). The combined organic phases were concentrated in vacuo, and the residue was purified by silica gel chromatography eluting with petroleum ether to give **3a-*d*$_5$**. The deuterium incorporation of **3a-*d*$_5$** was determined by ^{1}H NMR analysis.

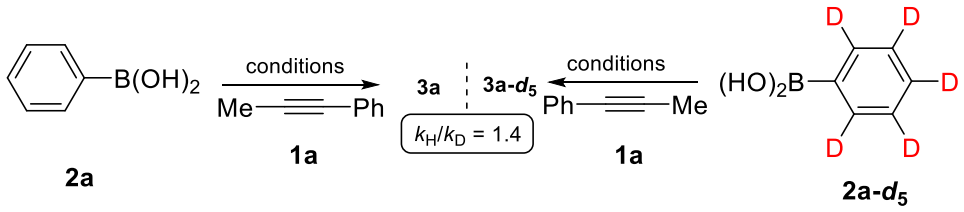


[Rh(OH)(cod)]$_2$ (4.6 mg, 0.01 mmol, 5 mol%), **1a** (0.6 mmol), and **2a** (0.20 mmol) were placed in an oven-dried Schlenk tube under nitrogen. CH_3CN/D_2O (1.0 mL/0.1 mL) was added and the reaction mixture was stirred at 80 ℃ for 12 h. Upon completion, the reaction mixture was diluted with ethyl acetate (5 mL) and water (5 mL). The layers were separated and the aqueous layer was extracted again with ethyl acetate for two more times (5 mL × 2). The combined organic phases were concentrated in vacuo, and the residue was purified by silica gel chromatography eluting with petroleum ether to give **3a-*d*$_1$**. The deuterium incorporation of **3a-*d*$_1$** was determined by ^{1}H NMR analysis.



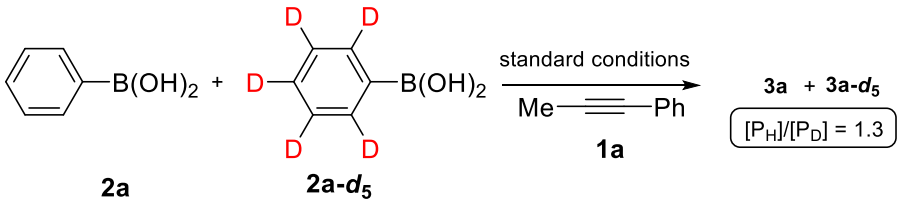
5.2 Kinetic isotope effect study

Parallel reaction:



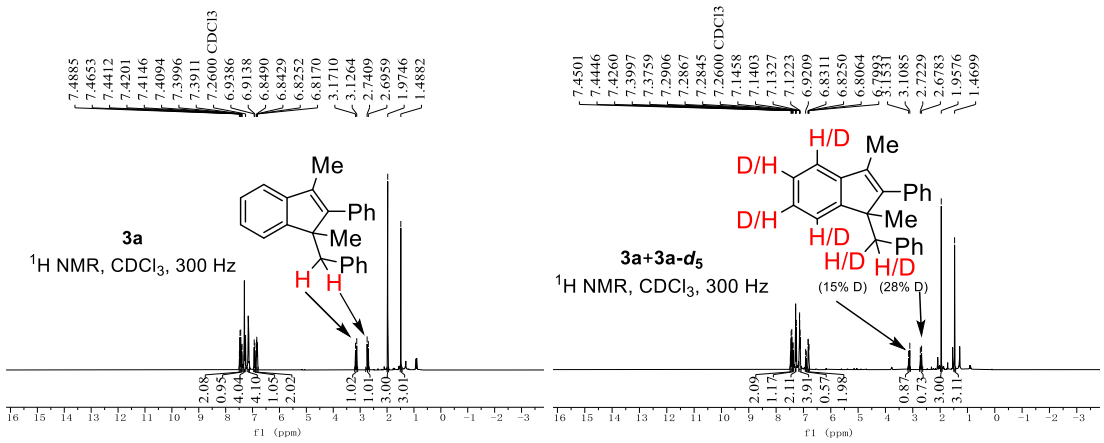
[Rh(OH)(cod)]$_2$ (4.6 mg, 0.01 mmol, 5 mol%), **1a** (0.6 mmol), and **2a**/**2a-*d*$_5$** (0.20 mmol) were placed in an oven-dried Schlenk tube under nitrogen. CH_3CN/H_2O (1.0 mL/0.1 mL) was added and the reaction mixture was stirred at 80 °C for 2 h. The reaction mixture was diluted with ethyl acetate (5 mL) and water (5 mL). The layers were separated and the aqueous layer was extracted again with ethyl acetate for two more times (5 mL × 2). The combined organic phases were concentrated in vacuo, and the residue was purified by silica gel chromatography eluting with petroleum ether to give **3a** in 33% yield/**3a-*d*$_5$** in 23% yield.

Intermolecular competition reaction:

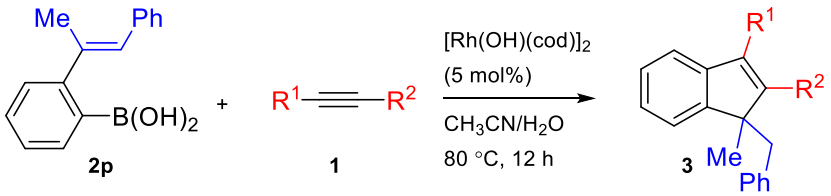


[Rh(OH)(cod)]$_2$ (4.6 mg, 0.01 mmol, 5 mol%), **1a** (0.2 mmol), **2a** (0.2 mmol), and **2a-*d*$_5$** (0.2 mmol) were placed in an oven-dried Schlenk tube under nitrogen. CH_3CN/H_2O (1.0 mL/0.1 mL) was added and the reaction mixture was stirred at 80 °C for 12 h. The

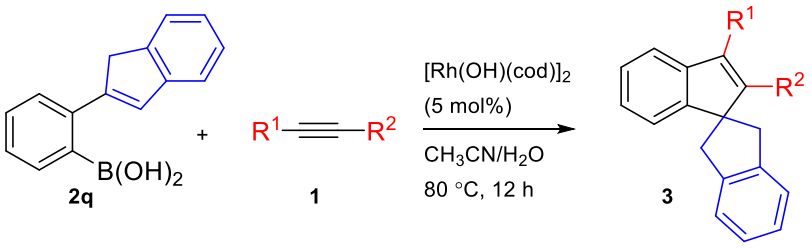
reaction mixture was diluted with ethyl acetate (5 mL) and water (5 mL). The layers were separated and the aqueous layer was extracted again with ethyl acetate for two more times (5 mL × 2). The combined organic phases were concentrated in vacuo, and the residue was purified by silica gel chromatography eluting with petroleum ether to give **3a**+**3a-*d*$_5$**. The deuterium incorporation of **3a**+**3a-*d*$_5$** was determined by ^{1}H NMR analysis.



6. Procedures for Scheme 5



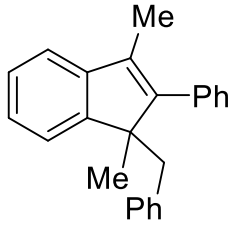
$[Rh(OH)(cod)]_2$ (4.6 mg, 0.01 mmol, 5 mol%) and **1** (0.30 mmol) were placed in an oven-dried Schlenk tube under nitrogen. A solution of **2p** (47.6 mg, 0.20 mmol) in CH_3CN (1.0 mL) and H_2O (0.1 mL) was added and the reaction mixture was stirred at 80 ℃ for 12 h. Upon completion, the reaction mixture was diluted with ethyl acetate (5 mL) and water (5 mL). The layers were separated and the aqueous layer was extracted again with ethyl acetate for two more times (5 mL × 2). The combined organic phases were concentrated in vacuo, and the residue was purified by silica gel chromatography eluting with petroleum ether to give **3**.



[Rh(OH)(cod)]$_2$ (4.6 mg, 0.01 mmol, 5 mol%), **2q** (47.2 mg, 0.20 mmol) and **1** (0.30 mmol) were placed in an oven-dried Schlenk tube under nitrogen. CH_3CN /H_2O (1.0 mL/0.1 mL) was added and the reaction mixture was stirred at 80 ℃ for 12 h. Upon completion, the reaction mixture was diluted with ethyl acetate (5 mL) and water (5 mL). The layers were separated and the aqueous layer was extracted again with ethyl acetate for two more times (5 mL × 2). The combined organic phases were concentrated in vacuo, and the residue was purified by silica gel chromatography eluting with petroleum ether to give **3**.

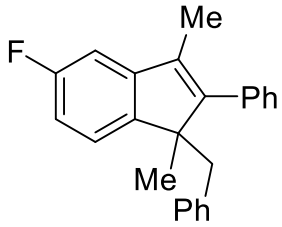
7. Characterization of the products

1-benzyl-1,3-dimethyl-2-phenyl-1*H*-indene (3a)



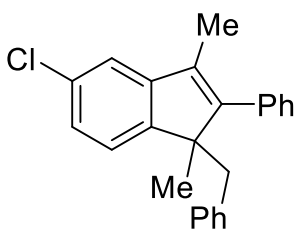
Colorless oil; 60.2 mg, 97% yield; 294.7 mg, 95% yield at 1.0 mmol scale. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.43 – 7.38 (m, 1H), 7.34 – 7.29 (m, 3H), 7.29 – 7.27 (m, 1H), 7.19 (d, *J* = 3.0 Hz, 1H), 7.16 – 7.11 (m, 3H), 6.93 (d, *J* = 7.4 Hz, 1H), 6.85 – 6.81 (m, 2H), 3.15 (d, *J* = 13.4 Hz, 1H), 2.72 (d, *J* = 13.5 Hz, 1H), 1.97 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.4, 150.2, 144.8, 138.4, 137.1, 134.1, 130.5, 129.9, 128.3, 127.4, 127.1, 126.7, 126.1, 124.7, 123.2, 119.2, 55.0, 43.7, 23.2, 11.3. HRMS (ESI) calcd for $C_{24}H_{23}^{+}$ $(M+H)^{+}$: 311.1794, found: 311.1797.

1-benzyl-5-fluoro-1,3-dimethyl-2-phenyl-1*H*-indene (3b)



Colorless oil; 54.5 mg, 82% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 2H), 7.43 – 7.38 (m, 1H), 7.29 (d, *J* = 1.7 Hz, 2H), 7.19 – 7.12 (m, 3H), 6.96 (dd, *J* = 9.0, 2.2 Hz, 1H), 6.86 – 6.74 (m, 4H), 3.10 (d, *J* = 13.4 Hz, 1H), 2.67 (d, *J* = 13.4 Hz, 1H), 1.93 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.7 (d, $^{1}J_{C\text{-}F}$ = 240.8 Hz), 152.5, 146.8 (d, $^{3}J_{C\text{-}F}$ = 8.2 Hz), 145.4 (d, $^{4}J_{C\text{-}F}$ = 2.2 Hz), 138.2, 136.7, 133.5 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 130.5, 129.8, 128.4, 127.5, 127.4, 126.3, 123.9 (d, $^{3}J_{C\text{-}F}$ = 8.2 Hz), 110.9 (d, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 106.4 (d, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 54.6, 43.7, 23.0, 11.3. HRMS (ESI) calcd for $C_{24}H_{22}F^{+}$ $(M+H)^{+}$: 329.1700, found: 329.1692.

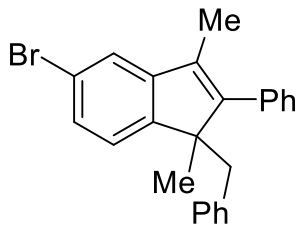
1-benzyl-5-chloro-1,3-dimethyl-2-phenyl-1*H*-indene (3c)



Colorless oil; 40.6 mg, 59% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.42 – 7.36 (m, 1H), 7.27 (d, *J* = 1.7 Hz, 1H), 7.25 (d, *J* = 1.7 Hz, 2H), 7.19 – 7.12 (m, 3H), 7.10 (dd, *J* = 7.9, 2.0 Hz, 1H), 6.86 – 6.79 (m, 2H), 6.76 (d, *J*

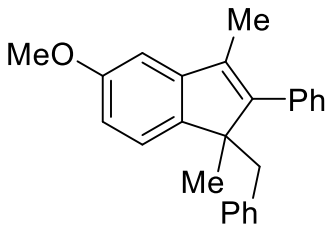
= 8.0 Hz, 1H), 3.09 (d, *J* = 13.5 Hz, 1H), 2.66 (d, *J* = 13.5 Hz, 1H), 1.93 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2, 148.4, 146.6, 138.0, 136.5, 133.3, 132.6, 130.5, 129.8, 128.4, 127.6, 127.4, 126.3, 124.4, 124.2, 119.5, 54.8, 43.6, 22.9, 11.2. HRMS (ESI) calcd for $C_{24}H_{22}Cl^+$ $(M+H)^+$: 345.1405, found: 345.1404.

1-benzyl-5-bromo-1,3-dimethyl-2-phenyl-1*H*-indene (3d)



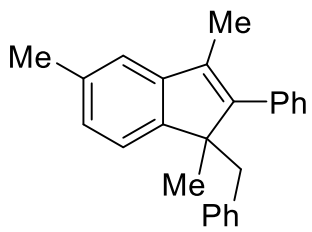
Colorless oil; 34.9 mg, 45% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.41 – 7.36 (m, 2H), 7.26 – 7.22 (m, 3H), 7.17 – 7.12 (m, 3H), 6.86 – 6.77 (m, 2H), 6.70 (d, *J* = 7.9 Hz, 1H), 3.08 (d, *J* = 13.4 Hz, 1H), 2.65 (d, *J* = 13.5 Hz, 1H), 1.91 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2, 148.9, 146.9, 138.0, 136.5, 133.3, 130.5, 129.8, 128.4, 127.6, 127.4, 127.2, 126.3, 124.7, 122.5, 120.7, 54.9, 43.5, 22.8, 11.3. HRMS (ESI) calcd for $C_{24}H_{22}Br^+$ $(M+H)^+$: 389.0899, 391.0879, found: 389.0896, 391.0883.

1-benzyl-5-methoxy-1,3-dimethyl-2-phenyl-1*H*-indene (3e)



Colorless oil; 57.8 mg, 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.41 – 7.38 (m, 1H), 7.28 (d, *J* = 1.7 Hz, 2H), 7.17 – 7.14 (m, 3H), 6.88 – 6.82 (m, 3H), 6.77 (d, *J* = 8.1 Hz, 1H), 6.70 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.87 (s, 3H), 3.10 (d, *J* = 13.4 Hz, 1H), 2.66 (d, *J* = 13.4 Hz, 1H), 1.95 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 151.8, 146.2, 142.4, 138.5, 137.1, 133.8, 130.5, 129.9, 128.3, 127.4, 127.2, 126.1, 123.7, 109.9, 105.1, 55.6, 54.4, 43.9, 23.2, 11.3. HRMS (ESI) calcd for $C_{25}H_{25}O^+$ $(M+H)^+$: 341.1900, found: 341.1906.

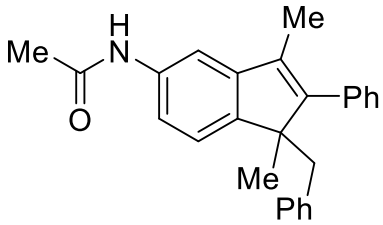
1-benzyl-1,3,5-trimethyl-2-phenyl-1*H*-indene (3f)



Colorless oil; 49.3 mg, 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.41 – 7.37 (m, 1H), 7.28 (d, *J* = 1.7 Hz, 2H), 7.17 – 7.12 (m, 4H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.89 – 6.82 (m, 2H), 6.77 (d, *J* = 7.6 Hz, 1H), 3.11 (d, *J* = 13.4 Hz, 1H), 2.67 (d, *J* = 13.4 Hz, 1H), 2.44 (s, 3H),

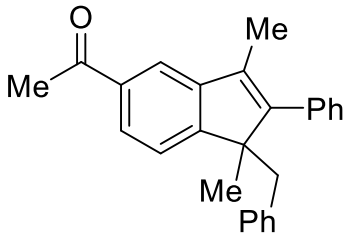
1.95 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.8, 147.4, 144.9, 138.5, 137.2, 136.3, 134.0, 130.6, 129.9, 128.2, 127.4, 127.1, 126.1, 125.4, 123.0, 120.0, 54.6, 43.8, 23.3, 21.7, 11.3. HRMS (ESI) calcd for $C_{25}H_{25}^+$ $(M+H)^+$: 325.1951, found: 325.1950.

_N_-(1-benzyl-1,3-dimethyl-2-phenyl-1_H_-inden-5-yl)acetamide (3g)



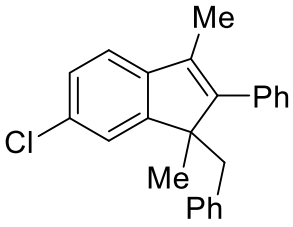
White solid, mp: 182 – 183 ℃; 58.0 mg, 79% yield. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.90 (s, 1H), 7.52 – 7.43 (m, 3H), 7.40 – 7.36 (m, 1H), 7.30 – 7.26 (m, 3H), 7.06 – 7.03 (m, 3H), 6.97 (d, J = 8.1 Hz, 1H), 6.72 – 6.69 (m, 2H), 3.10 (d, J = 13.6 Hz, 1H), 2.74 (d, J = 13.7 Hz, 1H), 2.03 (s, 3H), 1.84 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.0, 149.9, 144.6, 144.4, 138.1, 137.8, 136.3, 133.5, 129.6, 129.3, 128.3, 127.2, 127.1, 126.0, 122.3, 115.6, 110.2, 54.3, 42.9, 24.1, 24.0, 11.2. HRMS (ESI) calcd for $C_{26}H_{26}NO^+$ $(M+H)^+$: 368.2009, found: 368.2015.

1-(1-benzyl-1,3-dimethyl-2-phenyl-1_H_-inden-5-yl)ethan-1-one (3h)



Colorless oil; 62.0 mg, 88% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (dd, J = 7.9, 1.6 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.42 – 7.36 (m, 2H), 7.31 (d, J = 7.9 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.19 – 7.08 (m, 3H), 6.81 – 6.77 (m, 2H), 3.14 (d, J = 13.4 Hz, 1H), 2.67 (d, J = 13.4 Hz, 1H), 2.50 (s, 3H), 1.96 (s, 3H), 1.48 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.4, 154.8, 150.1, 149.8, 138.0, 136.4, 133.9, 133.6, 130.5, 129.6, 128.4, 128.0, 127.6, 126.5, 123.2, 119.1, 55.3, 43.6, 26.8, 22.7, 11.3. HRMS (ESI) calcd for $C_{26}H_{25}O^+$ $(M+H)^+$: 353.1900, found: 353.1909.

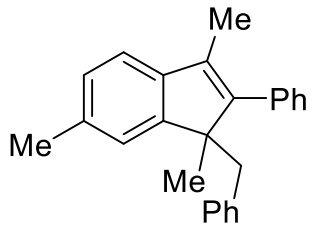
1-benzyl-6-chloro-1,3-dimethyl-2-phenyl-1_H_-indene (3i)



Colorless oil; 50.2 mg, 73% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.41 – 7.37 (m, 1H), 7.28 – 7.24 (m, 3H), 7.19 – 7.13 (m, 4H), 6.85 (d, J = 1.9 Hz, 1H), 6.83 – 6.79 (m, 2H), 3.10 (d, J = 13.5 Hz, 1H), 2.70 (d, J =

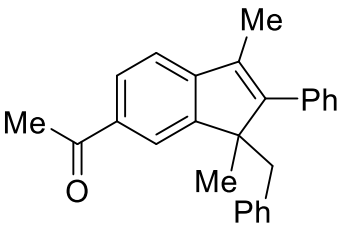
13.5 Hz, 1H), 1.93 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.0, 150.8, 143.3, 137.8, 136.6, 133.5, 130.6, 130.4, 129.8, 128.3, 127.6, 127.3, 126.8, 126.4, 123.7, 120.1, 55.2, 43.6, 23.0, 11.3. HRMS (ESI) calcd for $C_{24}H_{22}Cl^+$ $(M+H)^+$: 345.1405, found: 345.1405.

1-benzyl-1,3,6-trimethyl-2-phenyl-1*H*-indene (3j)



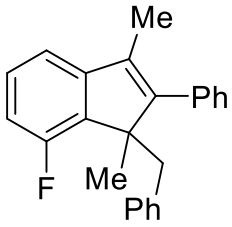
Colorless oil; 60.3 mg, 93% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.40 – 7.35 (m, 1H), 7.27 (d, *J* = 1.7 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.20 – 7.14 (m, 3H), 7.11 (d, *J* = 9.1 Hz, 2H), 6.83 – 6.79 (m, 2H), 6.72 (s, 1H), 3.13 (d, *J* = 13.5 Hz, 1H), 2.70 (d, *J* = 13.5 Hz, 1H), 2.36 (s, 3H), 1.94 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.5, 149.3, 142.2, 138.5, 137.2, 134.3, 134.0, 130.5, 130.0, 128.2, 127.3, 127.3, 127.0, 126.1, 124.1, 118.9, 54.8, 43.8, 23.4, 21.7, 11.4. HRMS (ESI) calcd for $C_{25}H_{25}^+$ $(M+H)^+$: 325.1951, found: 325.1959.

1-(1-benzyl-1,3-dimethyl-2-phenyl-1*H*-inden-6-yl)ethan-1-one (3k)



White solid, mp: 172 – 173 ℃; 58.5 mg, 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.42 – 7.36 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.20 – 7.08 (m, 3H), 6.81 – 6.77 (m, 2H), 3.14 (d, *J* = 13.4 Hz, 1H), 2.68 (d, *J* = 13.4 Hz, 1H), 2.50 (s, 3H), 1.97 (s, 3H), 1.48 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.4, 154.8, 150.1, 149.8, 138.0, 136.4, 133.9, 133.6, 130.5, 129.6, 128.4, 128.0, 127.6, 126.5, 123.2, 119.1, 55.3, 43.6, 26.8, 22.7, 11.3. HRMS (ESI) calcd for $C_{26}H_{25}O^+$ $(M+H)^+$: 353.1900, found: 353.1906.

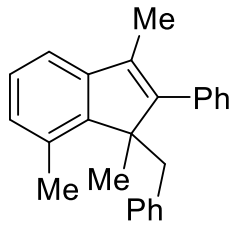
1-benzyl-7-fluoro-1,3-dimethyl-2-phenyl-1*H*-indene (3l)



Colorless oil; 26.9 mg, 41% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.39 (d, *J* = 5.1 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.23 – 7.18 (m, 1H), 7.03 – 6.98 (m, 3H), 6.95 (d, *J* = 7.4 Hz, 1H), 6.92 – 6.83 (m, 1H), 6.80 (d, *J* = 7.7 Hz, 2H), 3.42 (d,

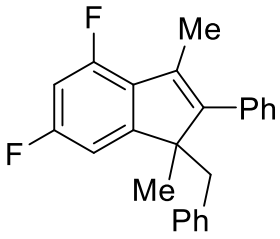
J = 13.9 Hz, 1H), 3.05 (d, *J* = 13.9 Hz, 1H), 1.90 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6 (d, $^{1}J_{C\text{-}F}$ = 244.5 Hz), 149.6, 147.8 (d, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 138.0, 136.3, 135.0, 134.83, 134.80, 129.9, 129.5, 129.1, 128.6 (d, $^{3}J_{C\text{-}F}$ = 8.2 Hz), 128.2, 128.0 (d, $^{2}J_{C\text{-}F}$ = 19.5 Hz), 127.3, 125.9, 115.0 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 112.6 (d, $^{2}J_{C\text{-}F}$ = 21.7 Hz), 56.3 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 41.8, 23.1, 11.6. HRMS (ESI) calcd for $C_{24}H_{22}F^+$ $(M+H)^+$: 329.1700, found: 329.1681.

1-benzyl-1,3,7-trimethyl-2-phenyl-1*H*-indene (3m)



Colorless oil; 22.7 mg, 35% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 2H), 7.38 – 7.33 (m, 1H), 7.25 – 7.18 (m, 3H), 7.07 (d, *J* = 6.9 Hz, 1H), 7.04 – 6.94 (m, 4H), 6.74 – 6.70 (m, 2H), 3.49 (d, *J* = 14.9 Hz, 1H), 3.06 (d, *J* = 14.9 Hz, 1H), 2.51 (s, 3H), 1.87 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3, 147.3, 145.6, 138.8, 137.0, 134.8, 132.6, 130.2, 128.8, 128.2, 128.1, 127.5, 127.1, 126.8, 125.9, 117.0, 56.5, 40.7, 22.7, 19.3, 11.5. HRMS (ESI) calcd for $C_{25}H_{25}^+$ $(M+H)^+$: 325.1951, found: 325.1953.

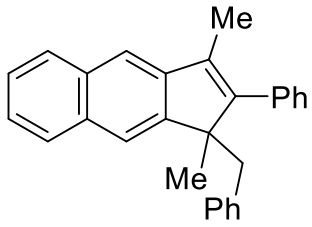
1-benzyl-4,6-difluoro-1,3-dimethyl-2-phenyl-1*H*-indene (3n)



Colorless oil; 23.5 mg, 34% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 2H), 7.42 – 7.38 (m, 1H), 7.27 – 7.22 (m, 2H), 7.20 – 7.15 (m, 3H), 6.88 – 6.81 (m, 2H), 6.74 – 6.66 (m, 1H), 6.42 (dd, *J* = 8.3, 2.2 Hz, 1H), 3.07 (d, *J* = 13.6 Hz, 1H), 2.71 (d, *J* = 13.6 Hz, 1H), 2.08 (s, 3H), 1.43 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9 (dd, $J_{C\text{-}F}$ = 244.5 Hz, 10.5 Hz), 156.6 (dd, $J_{C\text{-}F}$ = 249.0 Hz, 11.2 Hz, 1C), 154.8 (dd, $J_{C\text{-}F}$ = 6.0 Hz, 8.2 Hz, 1C), 150.2 (dd, $J_{C\text{-}F}$ = 3.7 Hz, 3.7 Hz, 1C) 137.5, 136.1, 131.6 (dd, $J_{C\text{-}F}$ = 4.5 Hz, 1.5 Hz, 1C) 130.4, 130.0, 128.7, 128.4, 128.2, 127.7, 127.5, 126.9 (dd, $J_{C\text{-}F}$ = 12.7 Hz, 3.0 Hz, 1C), 126.5, 107.3 (dd, $J_{C\text{-}F}$ =

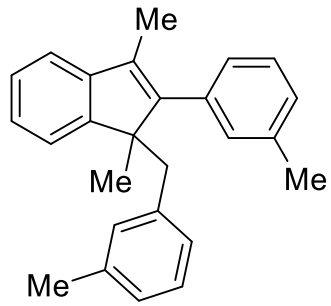
23.2 Hz, 3.7 Hz, 1C), 102.3 (t, J_{C-F} = 25.5 Hz, 1C), 56.0, 43.6, 23.3, 13.5 (d, J_{C-F} = 3.7 Hz, 1C). HRMS (ESI) calcd for $C_{24}H_{21}F_2^+$ $(M+H)^+$: 347.1606, found: 347.1606.

1-benzyl-1,3-dimethyl-2-phenyl-1*H*-cyclopenta[*b*]naphthalene (3o)



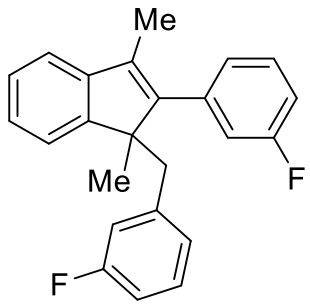
Colorless oil; 66.3 mg, 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 1H), 7.78 – 7.72 (m, 1H), 7.67 (s, 1H), 7.52 – 7.45 (m, 3H), 7.44 – 7.38 (m, 2H), 7.34 – 7.29 (m, 2H), 7.24 (s, 1H), 7.18 – 7.09 (m, 3H), 6.88 – 6.80 (m, 2H), 3.22 (d, *J* = 13.5 Hz, 1H), 2.74 (d, *J* = 13.5 Hz, 1H), 2.06 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 148.4, 144.1, 138.3, 137.0, 134.2, 133.5, 132.0, 130.7, 129.9, 128.3, 128.2, 128.0, 127.5, 127.3, 126.2, 125.3, 124.9, 121.8, 116.9, 54.4, 44.3, 24.1, 11.4. HRMS (ESI) calcd for $C_{28}H_{25}^+$ $(M+H)^+$: 361.1951, found: 361.1949.

1,3-dimethyl-1-(3-methylbenzyl)-2-(m-tolyl)-1*H*-indene (3p)



Yellow oil; 61.5 mg, 91% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 3H), 7.22 – 7.14 (m, 2H), 7.09 (d, *J* = 7.0 Hz, 2H), 7.05 – 6.97 (m, 2H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.69 – 6.60 (m, 2H), 3.11 (d, *J* = 13.4 Hz, 1H), 2.65 (d, *J* = 13.3 Hz, 1H), 2.45 (s, 3H), 2.25 (s, 3H), 1.97 (s, 3H), 1.48 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 150.7, 150.3, 144.8, 138.3, 137.6, 137.1, 136.7, 133.8, 131.6, 130.6, 128.1, 127.8, 127.5, 127.2, 127.0, 126.8, 126.7, 124.5, 123.2, 119.1, 55.0, 43.7, 23.1, 21.7, 21.5, 11.4. HRMS (ESI) calcd for $C_{26}H_{27}^+$ $(M+H)^+$: 339.2107, found: 339.2116.

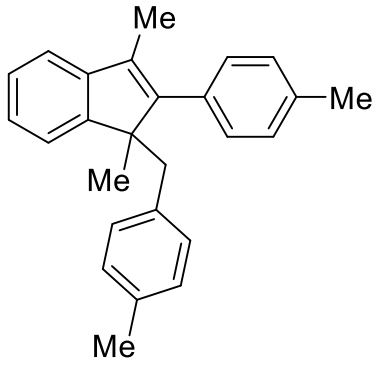
1-(3-fluorobenzyl)-2-(3-fluorophenyl)-1,3-dimethyl-1*H*-indene (3q)



Yellow oil; 68.5 mg, 99% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 1H), 7.33– 7.28 (m, 2H), 7.24 – 7.17 (m, 1H), 7.13 – 7.00 (m, 4H), 7.00 – 6.94 (m, 1H), 6.88 – 6.79 (m, 1H), 6.55 (d, *J* = 7.7 Hz, 1H), 6.44 (d, *J* = 10.4 Hz, 1H), 3.14 (d, *J* = 13.6 Hz, 1H), 2.73 (d, *J* = 13.6 Hz, 1H), 1.97 (s, 3H), 1.50 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8 (d,

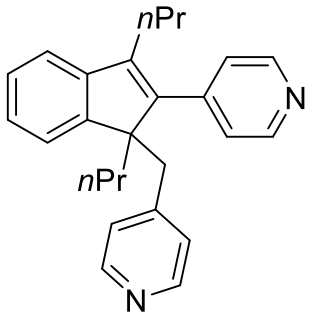
$^{1}J_{C\text{-}F}$ = 244.5 Hz), 162.2 (d, $^{1}J_{C\text{-}F}$ = 243.0 Hz), 161.1, 160.6, 149.9, 148.2 (d, $^{4}J_{C\text{-}F}$ = 2.2 Hz), 144.4, 140.6 (d, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 139.1 (d, $^{3}J_{C\text{-}F}$ = 8.2 Hz), 135.3, 129.8 (d, $^{3}J_{C\text{-}F}$ = 8.2 Hz), 128.7 (d, $^{3}J_{C\text{-}F}$ = 8.2 Hz), 127.0, 126.0 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 125.7 (d, $^{4}J_{C\text{-}F}$ = 2.2 Hz), 125.2, 122.8, 119.6, 116.9 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 116.7 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 114.1 (d, $^{2}J_{C\text{-}F}$ = 20.2 Hz), 113.1 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 55.0, 43.5 (d, $^{4}J_{C\text{-}F}$ = 1.5 Hz), 23.6, 11.4. HRMS (ESI) calcd for $C_{24}H_{21}F_2^+$ $(M+H)^+$: 347.1606, found: 347.1607.

1,3-dimethyl-1-(4-methylbenzyl)-2-(p-tolyl)-1*H*-indene (3r)



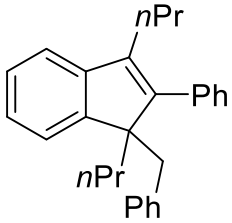
Yellow oil; 39.2 mg, 58% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 4H), 7.20 – 7.17 (m, 2H), 7.16 – 7.11 (m, 1H), 6.97 – 6.89 (m, 3H), 6.73 (d, *J* = 8.0 Hz, 2H), 3.09 (d, *J* = 13.5 Hz, 1H), 2.65 (d, *J* = 13.5 Hz, 1H), 2.45 (s, 3H), 2.30 (s, 3H), 1.96 (s, 3H), 1.45 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 150.6, 150.3, 144.9, 136.7, 135.5, 135.3, 134.1, 133.7, 130.4, 129.8, 129.0, 128.1, 126.6, 124.5, 123.2, 119.1, 55.0, 43.3, 23.0, 21.4, 21.2, 11.4. HRMS (ESI) calcd for $C_{26}H_{27}^+$ $(M+H)^+$: 339.2107, found: 339.2116.

4-(1,3-dimethyl-1-(pyridin-4-ylmethyl)-1*H*-inden-2-yl)pyridine (3s)



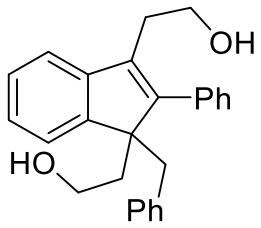
Yellow oil; 53.0 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 6.1 Hz, 2H), 8.21 (d, *J* = 6.2 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.26 – 7.23 (m, 1H), 7.20 (dt, *J* = 7.1, 1.1 Hz, 1H), 7.08 – 6.99 (m, 2H), 6.49 – 6.38 (m, 2H), 3.19 (d, *J* = 13.8 Hz, 1H), 2.78 (d, *J* = 13.8 Hz, 1H), 2.40 – 2.30 (m, 2H), 2.05 – 1.97 (m, 2H), 1.48 – 1.30 (m, 2H), 1.09 – 0.96 (m, 1H), 0.78 (t, *J* = 7.3 Hz, 6H), 0.70 – 0.62 (m, 1H).^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 148.7, 148.7, 146.5, 145.0, 144.5, 143.7, 142.7, 127.2, 125.9, 125.0, 124.3, 122.2, 120.4, 59.3, 43.2, 39.6, 28.1, 22.4, 16.8, 14.31, 14.27. HRMS (ESI) calcd for $C_{26}H_{29}N_2^+$ $(M+H)^+$: 369.2325, found: 369.2329.

1-benzyl-2-phenyl-1,3-dipropyl-1*H*-indene (3t)



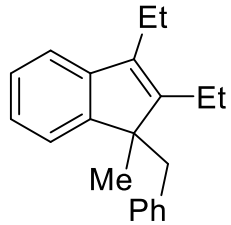
Yellow oil; 54.2 mg, 74% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.40 – 7.34 (m, 1H), 7.30 – 7.27 (m, 2H), 7.21 – 7.14 (m, 3H), 7.13 – 7.05 (m, 3H), 6.96 (d, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 5.7 Hz, 2H), 3.15 (d, *J* = 13.6 Hz, 1H), 2.71 (d, *J* = 13.6 Hz, 1H), 2.43 – 2.29 (m, 2H), 2.02 – 1.88 (m, 2H), 1.54 – 1.39 (m, 2H), 1.16 – 1.01 (m, 1H), 0.85 – 0.76 (m, 6H), 0.71 – 0.57 (m, 1H).^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 147.7, 145.2, 140.4, 138.1, 137.2, 130.5, 129.7, 128.2, 127.3, 127.0, 126.4, 126.0, 124.5, 123.1, 119.5, 59.4, 43.9, 38.3, 28.1, 22.4, 17.0, 14.5, 14.4. HRMS (ESI) calcd for $C_{28}H_{31}^{+}$ $(M+H)^{+}$: 367.2420, found: 367.2419.

2,2'-(1-benzyl-2-phenyl-1*H*-indene-1,3-diyl)bis(ethan-1-ol) (3u)



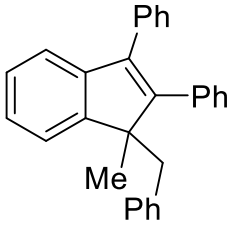
Yellow oil; 68.1 mg, 92% yield. ^{1}H NMR (300 MHz, DMSO-d_6) δ7.50 – 7.41 (m, 3H), 7.32 – 7.25 (m, 4H), 7.17 – 7.14 (m, 2H), 7.06 – 6.99 (m, 3H), 6.63 (d, *J* = 6.1 Hz, 2H), 4.61 (t, *J* = 5.4 Hz, 1H), 4.30 (t, *J* = 5.1 Hz, 1H), 3.35 – 3.26 (m, 2H), 3.16 (d, *J* = 13.7 Hz, 1H), 3.10 – 3.05 (m, 1H), 2.78 (d, *J* = 13.7 Hz, 1H), 2.67 – 2.60 (m, 3H), 2.24 – 2.13 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 148.2, 147.7, 144.1, 137.1, 136.5, 136.0, 129.7, 129.2, 128.4, 127.3, 127.1, 126.6, 126.0, 124.7, 122.5, 119.4, 59.8, 57.2, 56.6, 43.0, 38.8, 29.8. HRMS (ESI) calcd for $C_{26}H_{27}O_2^{+}$ $(M+H)^{+}$: 371.2006, found: 371.2011.

1-benzyl-2,3-diethyl-1-methyl-1*H*-indene (3v)



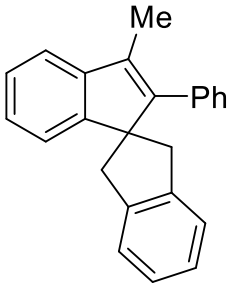
Colorless oil; 51.4 mg, 93% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.07 (m, 4H), 7.07 – 6.97 (m, 3H), 6.73 – 6.66 (m, 2H), 3.15 (d, *J* = 13.1 Hz, 1H), 2.87 (d, *J* = 13.1 Hz, 1H), 2.57 – 2.39 (m, 2H), 2.39 – 2.29 (m, 2H), 1.41 (s, 3H), 1.18 (t, *J* = 7.6 Hz, 3H), 0.90 (t, *J* = 7.6 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 150.4, 149.6, 144.7, 138.1, 138.0, 129.6, 127.1, 126.4, 125.8, 123.7, 122.2, 118.3, 54.9, 44.4, 22.8, 19.0, 18.4, 15.1, 13.2. HRMS (ESI) calcd for $C_{21}H_{25}^{+}$ $(M+H)^{+}$: 277.1951, found: 277.1953.

1-benzyl-1-methyl-2,3-diphenyl-1*H*-indene (3w)



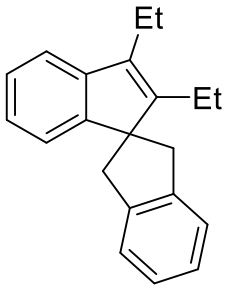
White solid, mp: 134 – 135 ℃; 47.4 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 1H), 7.26 – 7.23 (m, 5H), 7.23 – 7.18 (m, 4H), 7.17 – 7.07 (m, 6H), 6.84 – 6.77 (m, 2H), 3.23 (d, *J* = 13.5 Hz, 1H), 2.95 (d, *J* = 13.5 Hz, 1H), 1.60 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 150.7, 143.8, 139.9, 137.9, 136.7, 135.4, 130.3, 130.2, 129.6, 128.2, 128.0, 127.4, 127.03, 127.01, 126.8, 126.2, 125.1, 123.2, 120.7, 55.6, 44.2, 23.5. HRMS (ESI) calcd for $C_{29}H_{25}^{+}$ $(M+H)^{+}$: 373.1951, found: 373.1955.

3-methyl-2-phenyl-1',3'-dihydro-1,2'-spirobi[indene] (3x)



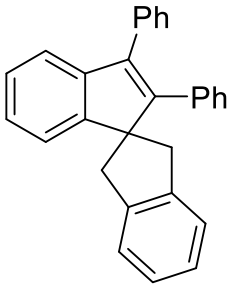
White solid, mp: 139 – 140 ℃; 39.0 mg, 64% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.33 – 7.26 (m, 3H), 7.24 – 7.14 (m, 6H), 7.05 (td, *J* = 7.2, 1.7 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 3.52 (d, *J* = 15.6 Hz, 2H), 2.97 (d, *J* = 15.6 Hz, 2H), 2.02 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8, 148.1, 143.8, 143.3, 136.8, 134.7, 130.1, 128.4, 127.1, 126.9, 126.5, 125.5, 124.7, 120.4, 119.1, 61.9, 40.6, 11.5. HRMS (ESI) calcd for $C_{24}H_{21}^{+}$ $(M+H)^{+}$: 309.1638, found: 309.1638.

2,3-diethyl-1',3'-dihydro-1,2'-spirobi[indene] (3y)



Colorless oil; 42.6 mg, 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 4H), 7.26 – 7.21 (m, 2H), 7.06 – 6.93 (m, 2H), 3.33 (d, *J* = 15.9 Hz, 2H), 3.08 (d, *J* = 15.9 Hz, 2H), 2.57 (q, *J* = 7.6 Hz, 2H), 2.31 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H), 1.10 (t, *J* = 7.6 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 149.5, 143.8, 143.5, 137.6, 126.62, 126.60, 124.7, 124.5, 120.5, 118.4, 60.8, 41.3, 18.8, 18.7, 15.0, 14.1, 13.9. HRMS (ESI) calcd for $C_{21}H_{23}^{+}$ $(M+H)^{+}$: 275.1794, found: 275.1811.

2,3-diphenyl-1',3'-dihydro-1,2'-spirobi[indene] (3z)



White solid, mp: 193 – 194 ℃; 58.1 mg, 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 3H), 7.36 – 7.28 (m, 5H), 7.26 – 7.15 (m, 8H), 7.12 (td, *J* = 7.4, 1.2 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 3.68 (d, *J* = 15.8 Hz, 2H), 3.15 (d, *J* = 15.8 Hz, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3, 149.3, 143.1, 142.7, 139.7, 136.3, 135.2, 130.4, 129.6, 128.3, 128.1, 127.2, 127.0, 126.9, 126.6, 125.9, 124.8, 120.7, 120.6, 62.1, 41.1. HRMS (ESI) calcd for $C_{29}H_{23}^{+}$ $(M+H)^{+}$: 371.1794, found: 371.1808.

8. References

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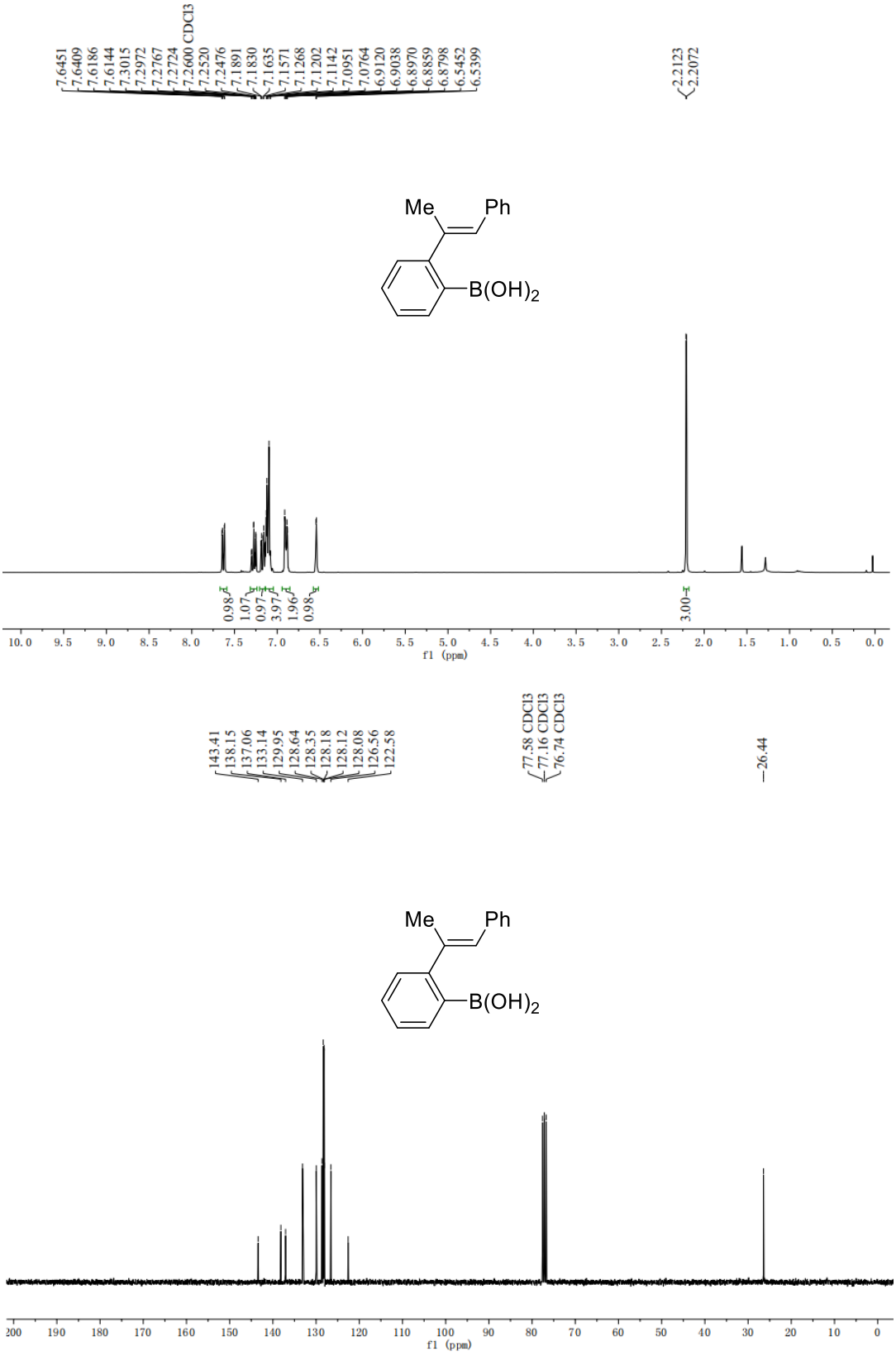
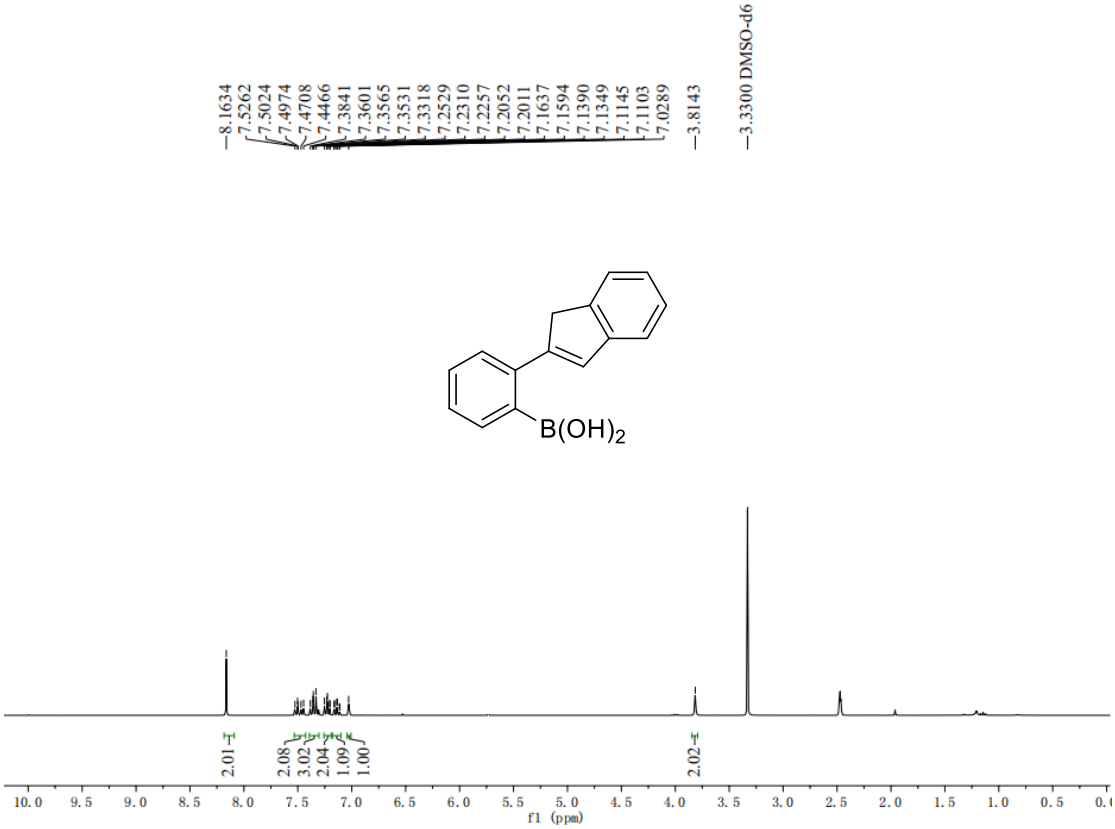
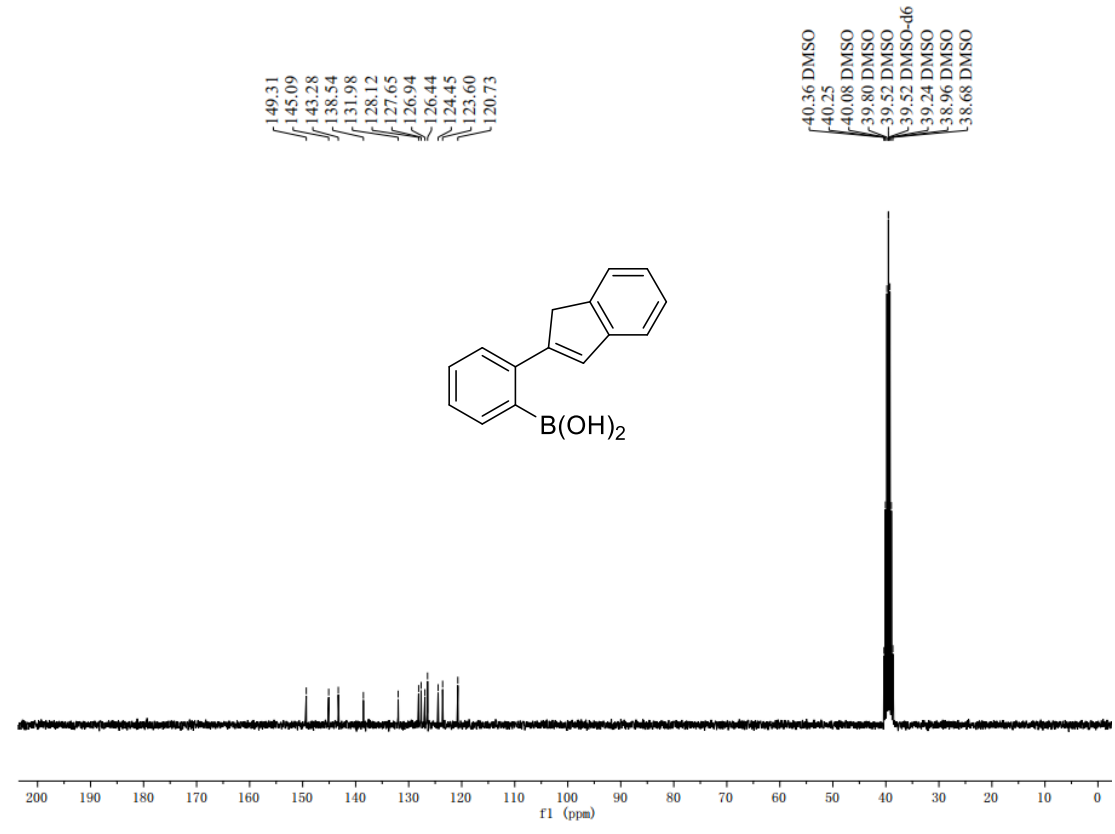
9. NMR spectra

2p ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)

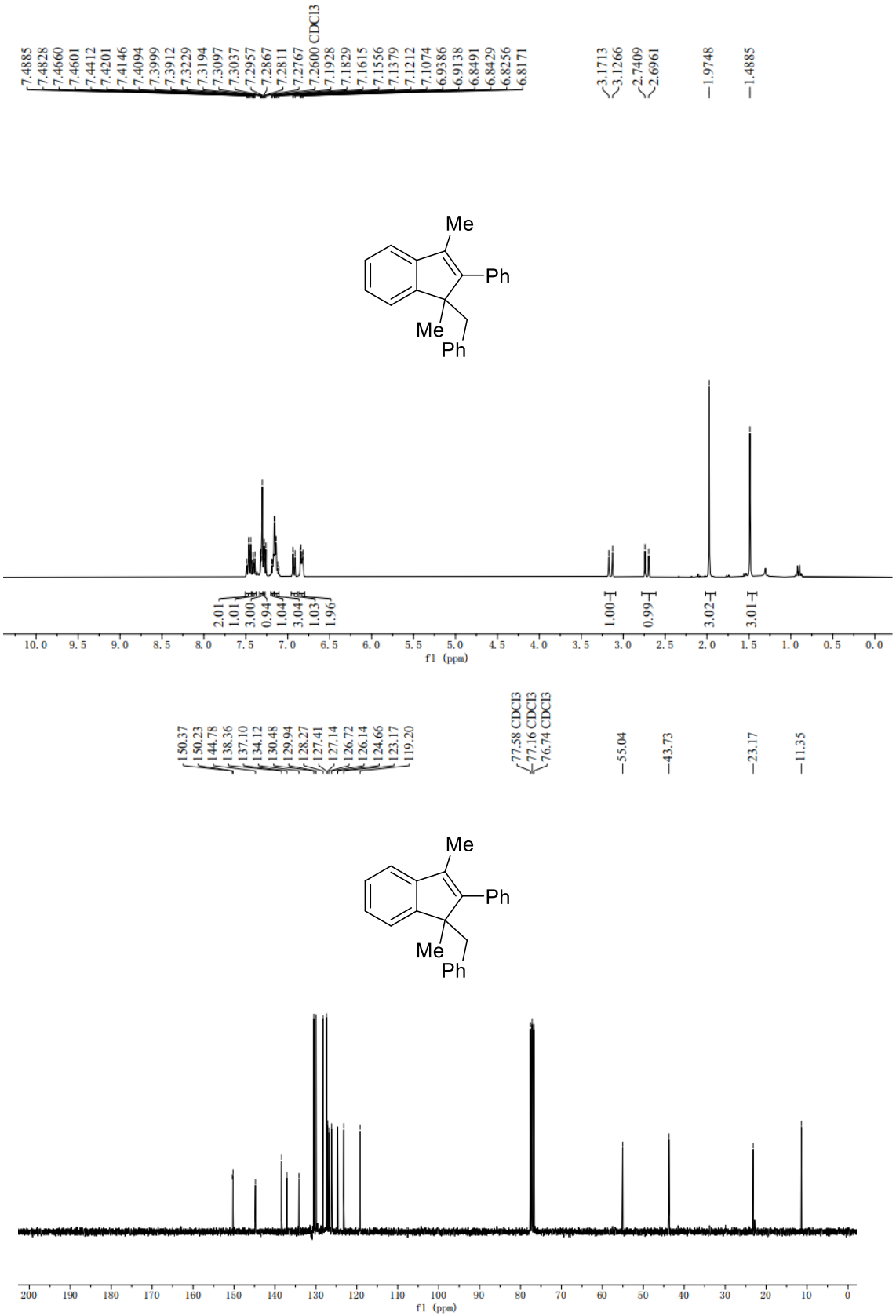


2q ^{1}H NMR (300 MHz, DMSO-d_6)/ ^{13}C NMR (75 MHz, DMSO-d_6)

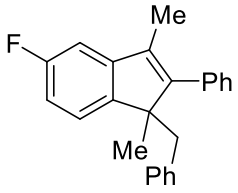


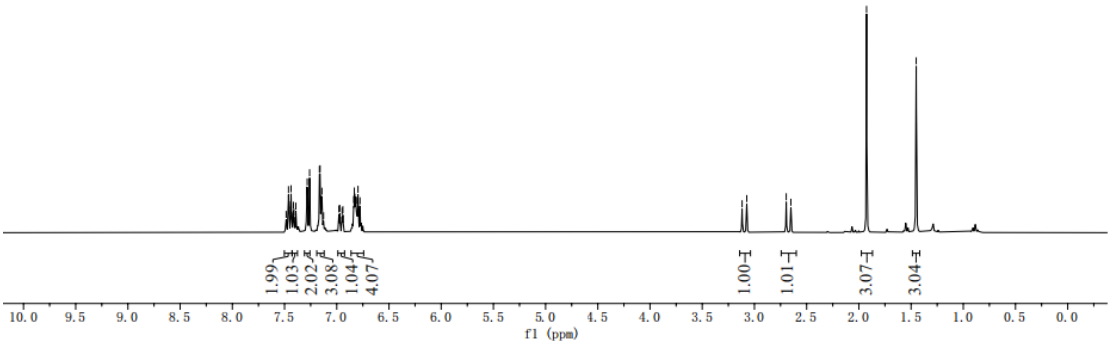


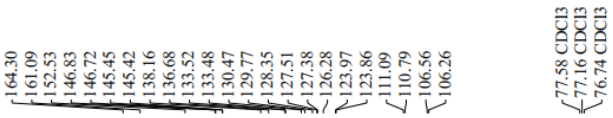
3a ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)

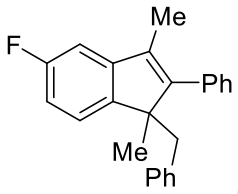


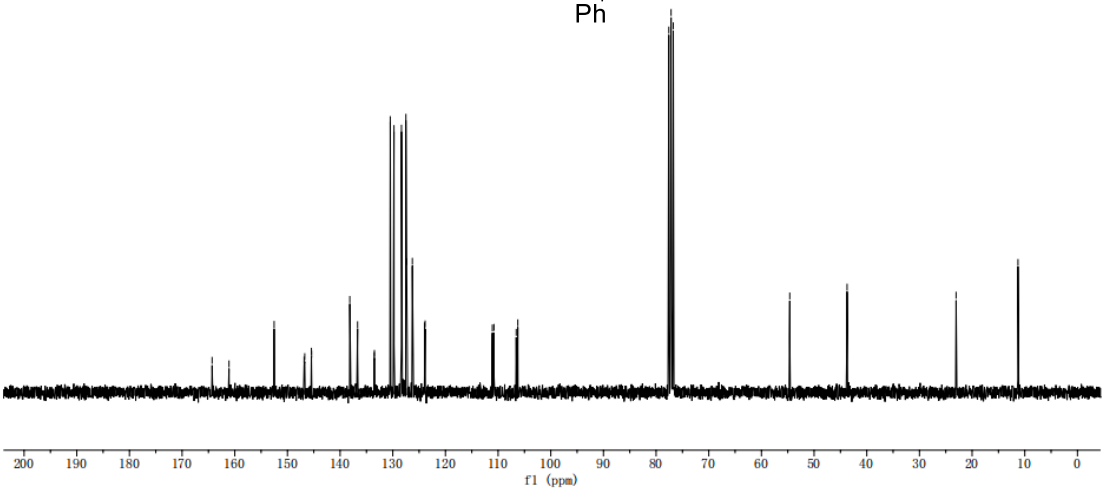
3b ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)



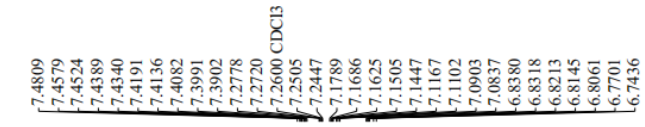


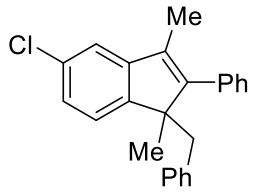


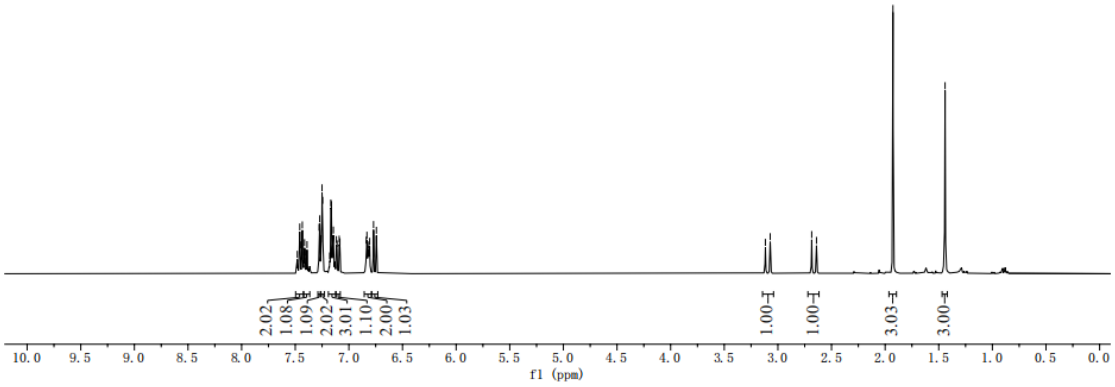


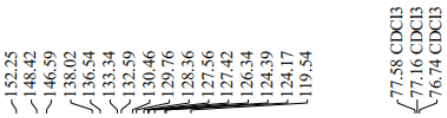


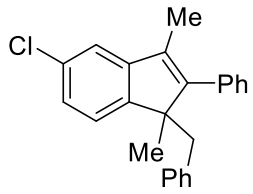
3c ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)

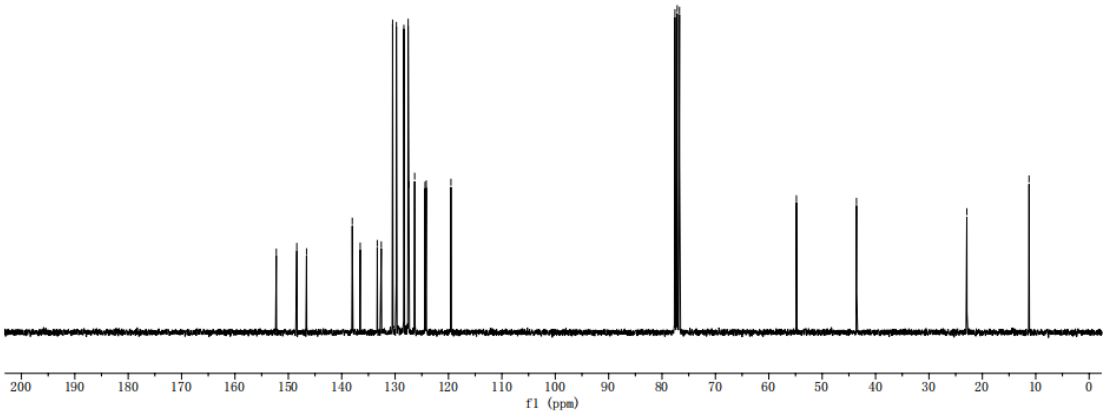




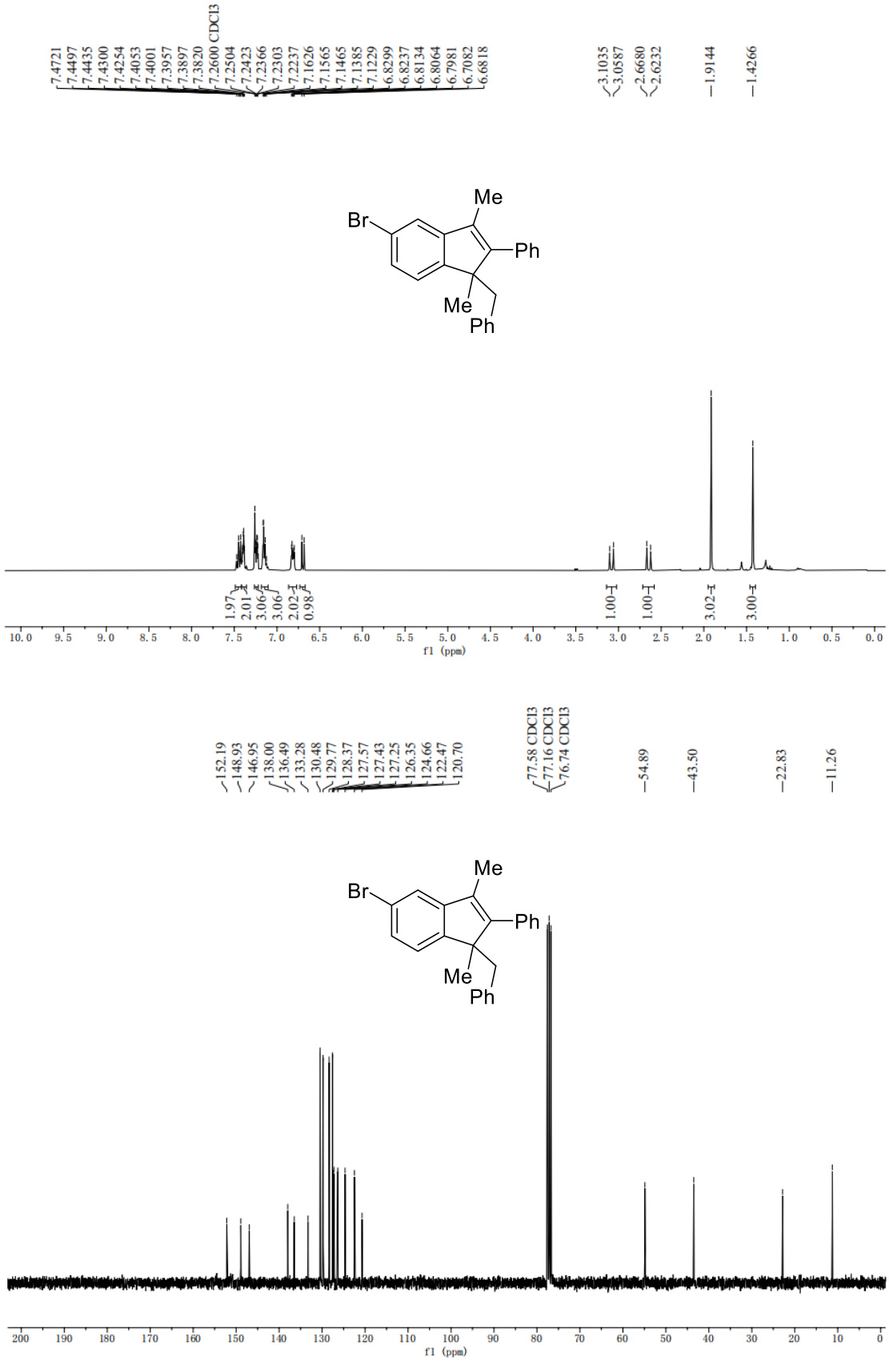




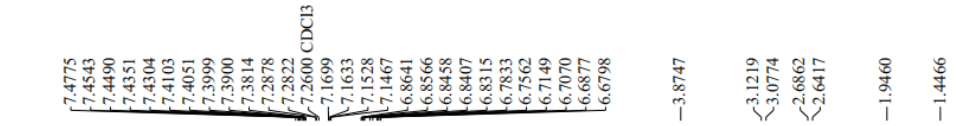


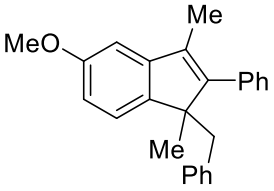


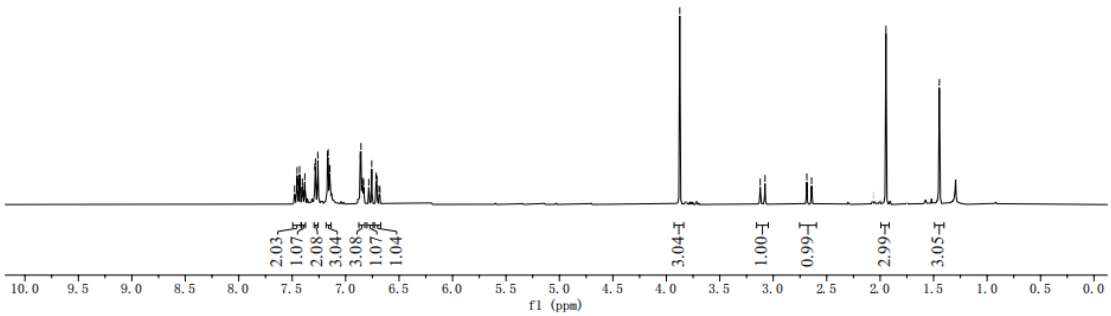
3d ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)

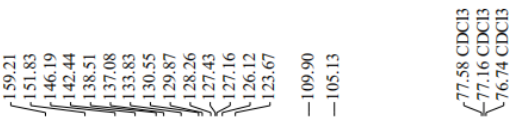


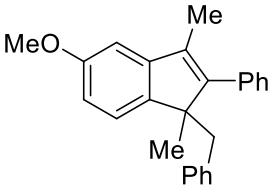
3e ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)

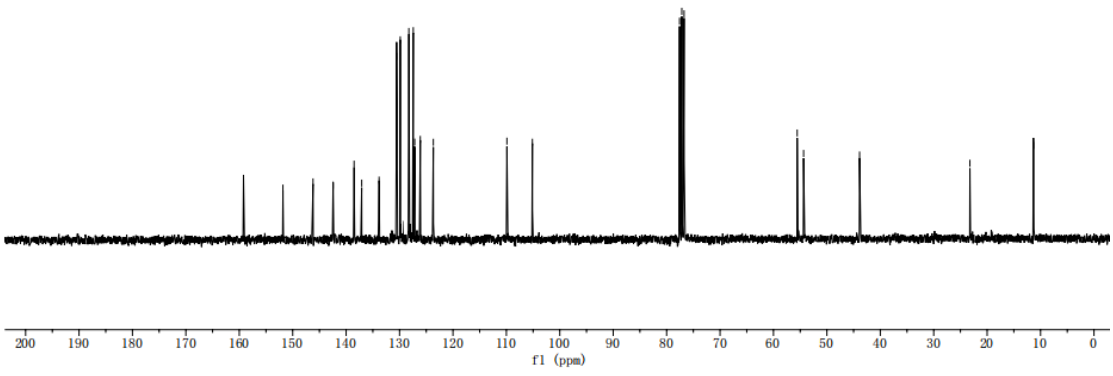




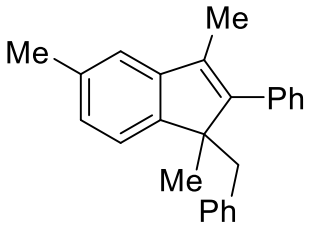


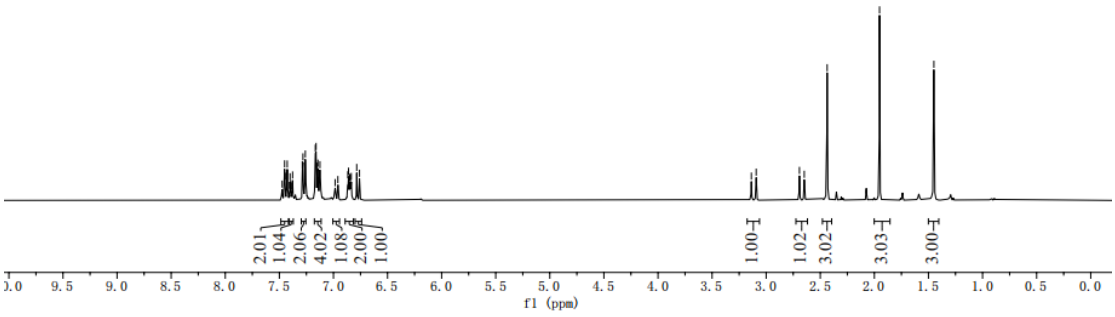


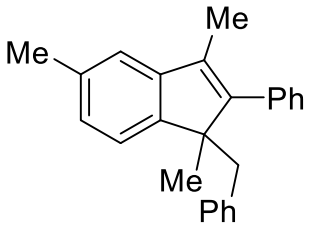


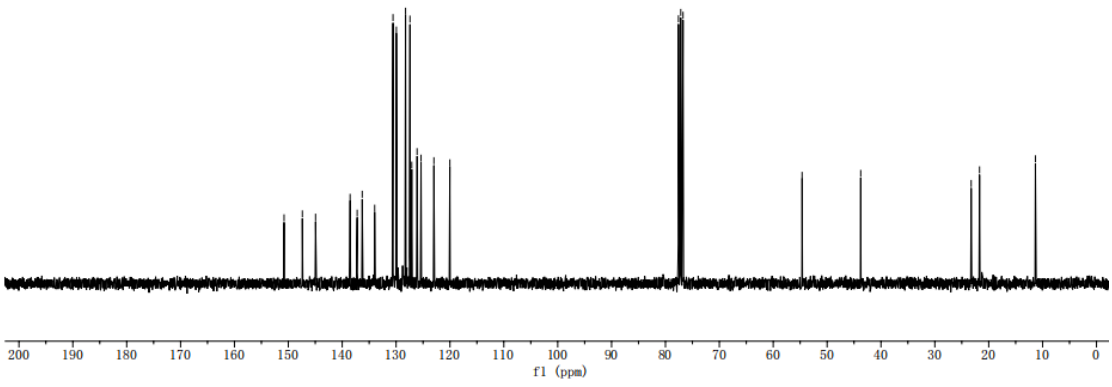


3f ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)

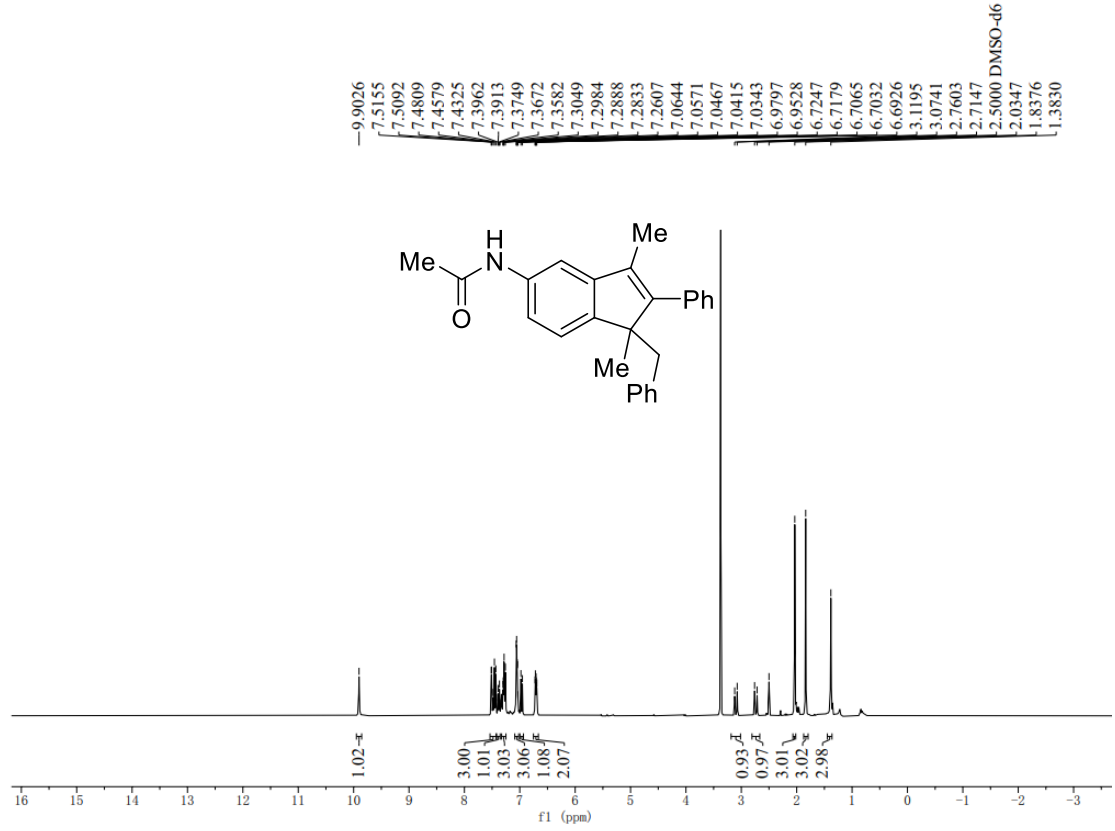


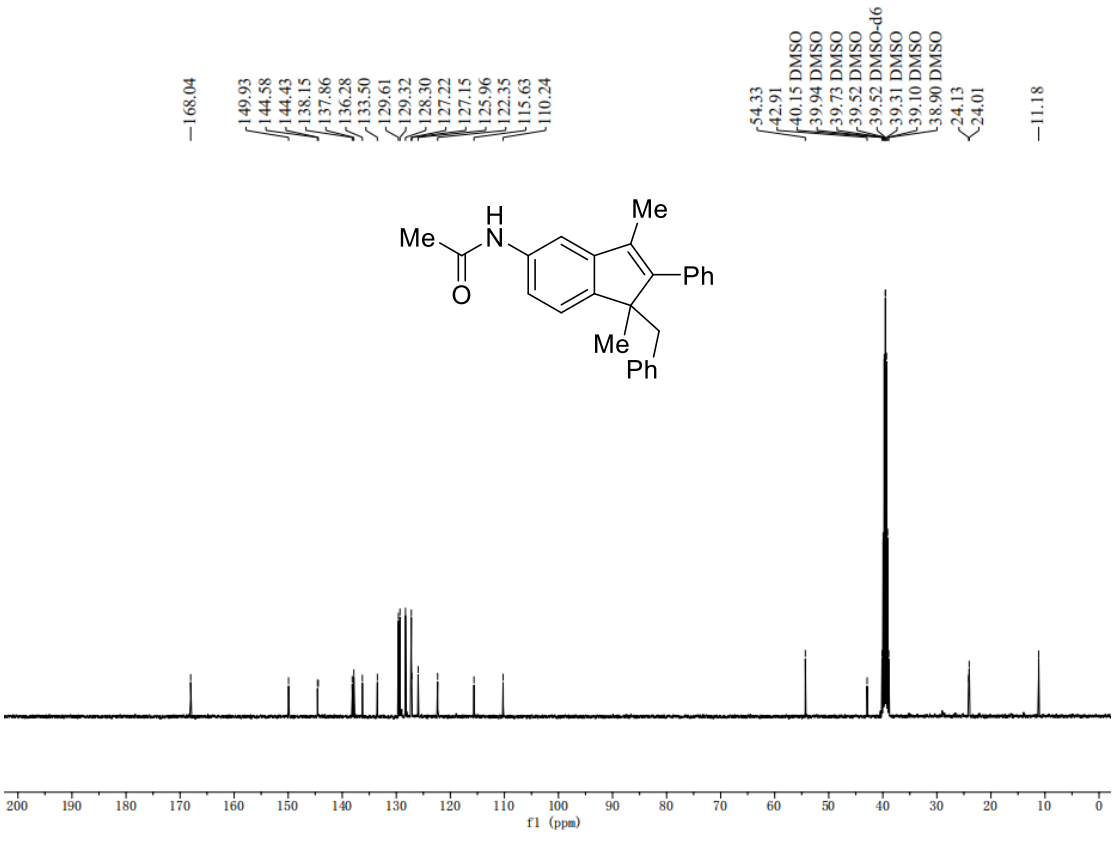




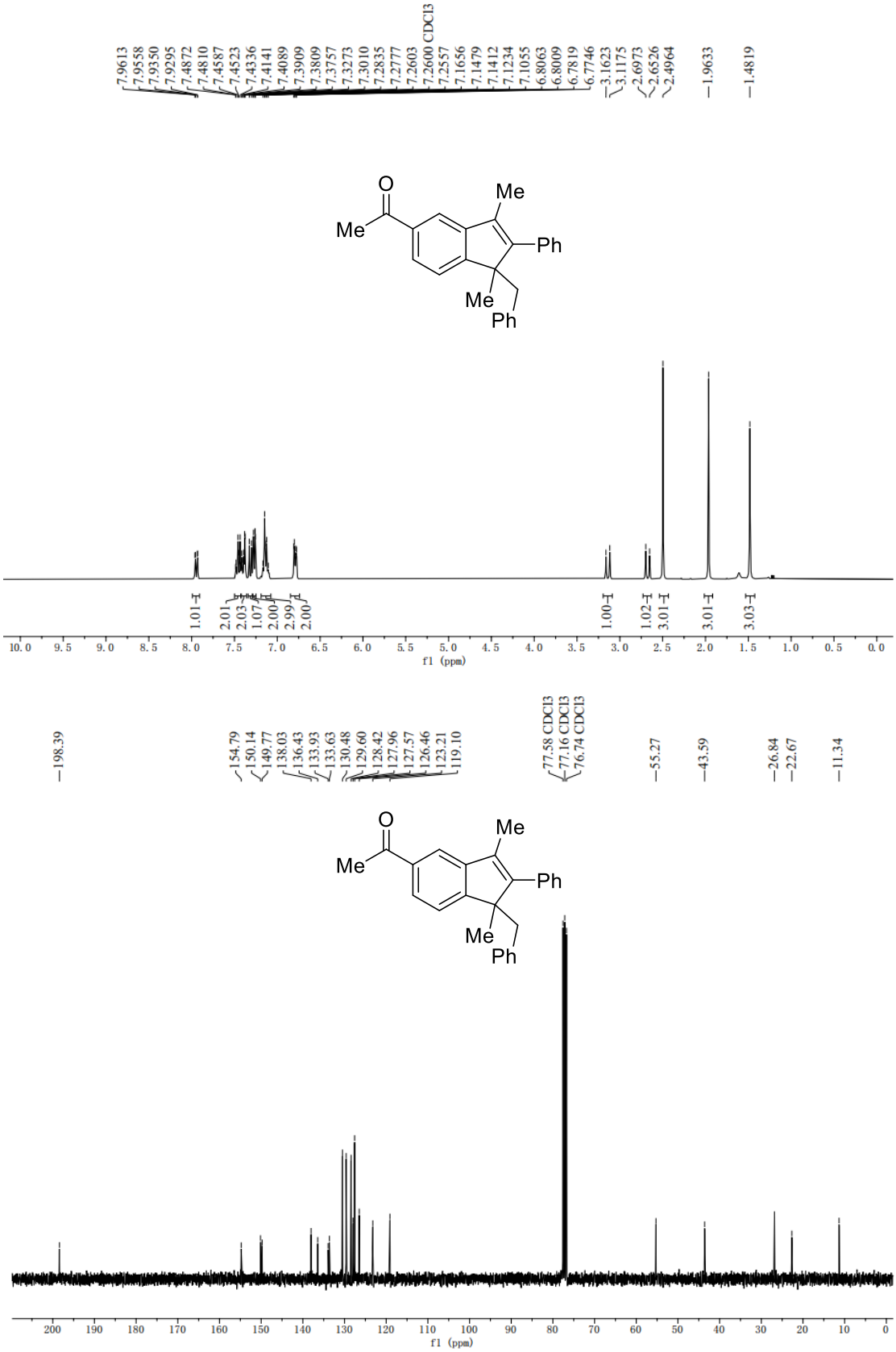


3g ^{1}H NMR (300 MHz, DMSO-d_6)/ ^{13}C NMR (101 MHz, DMSO-d_6)

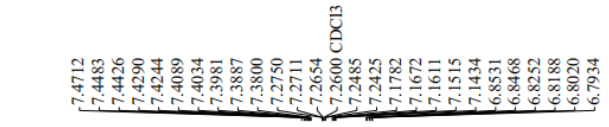


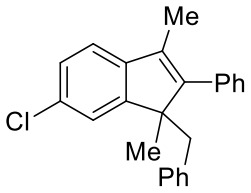


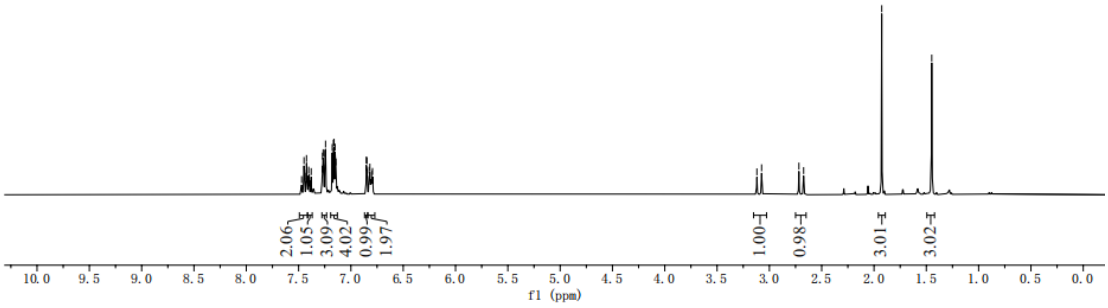
3h ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)

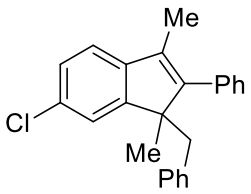


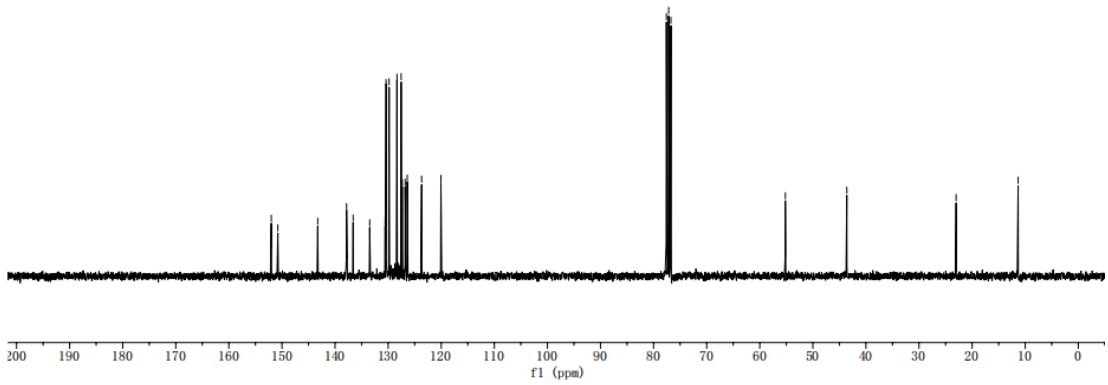
3i ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)



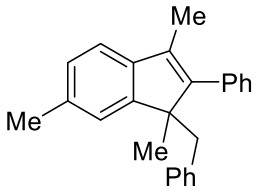


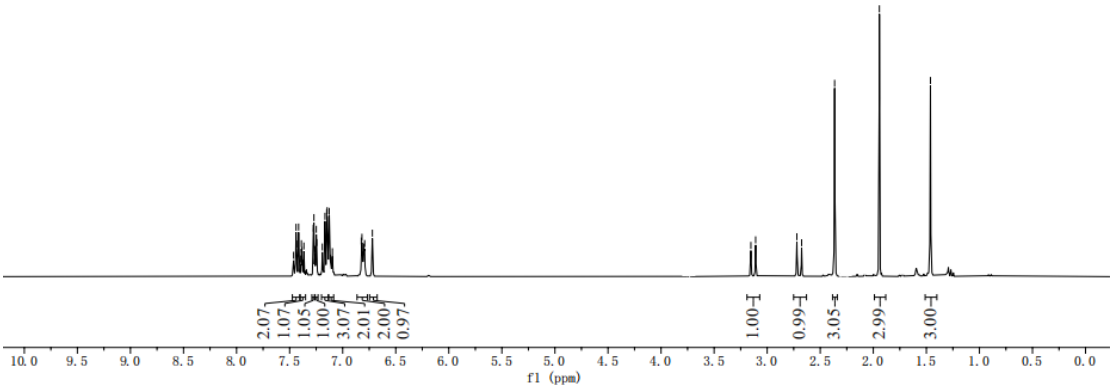


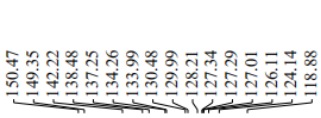


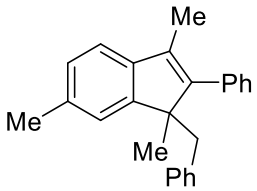


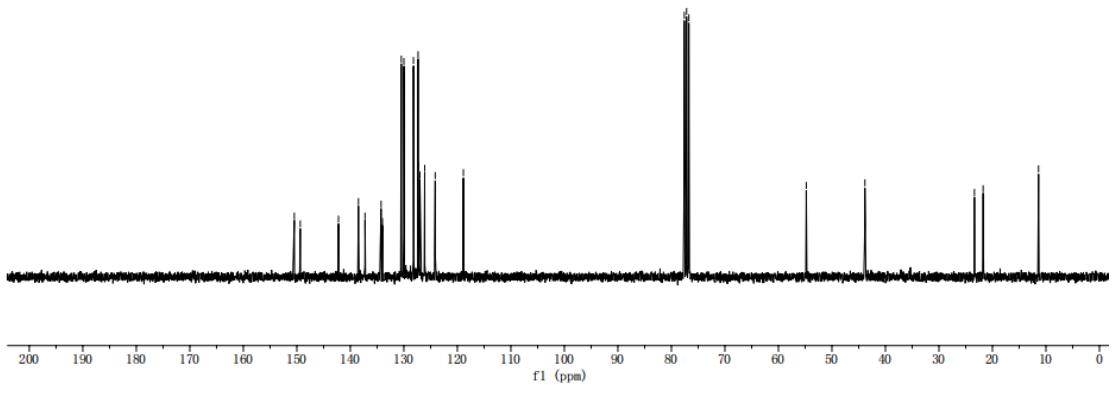
3j ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)



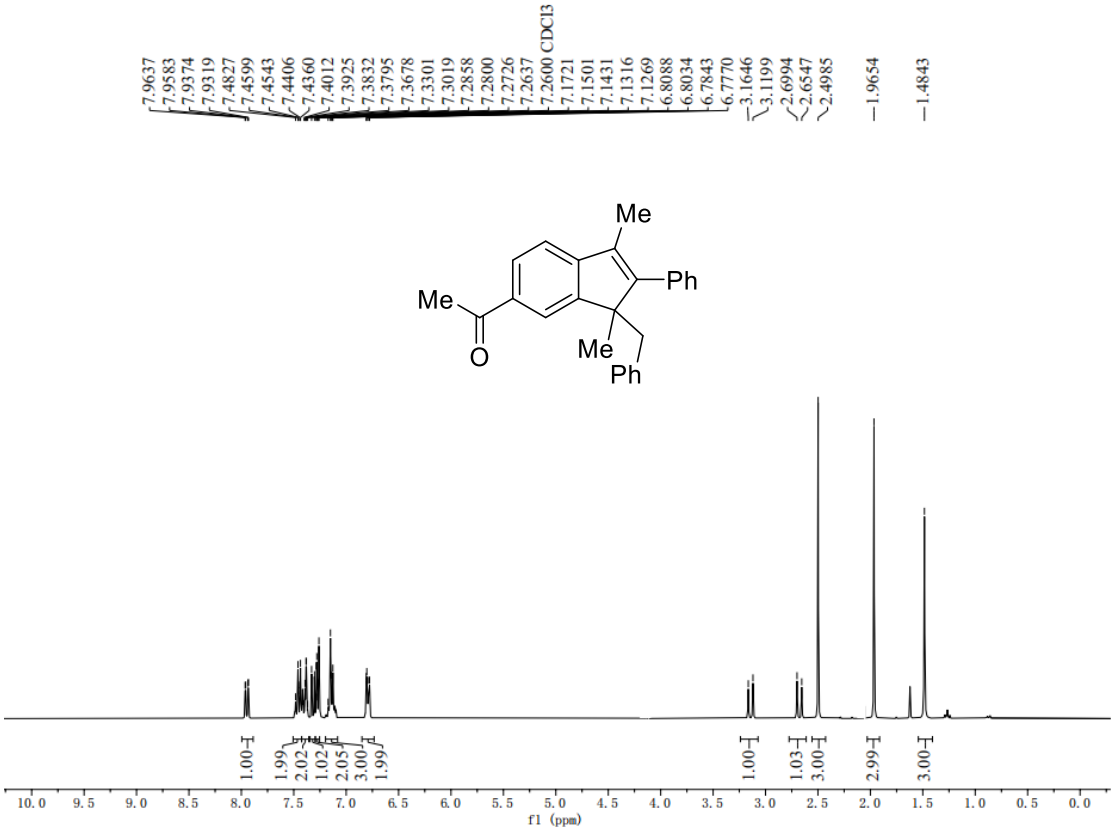


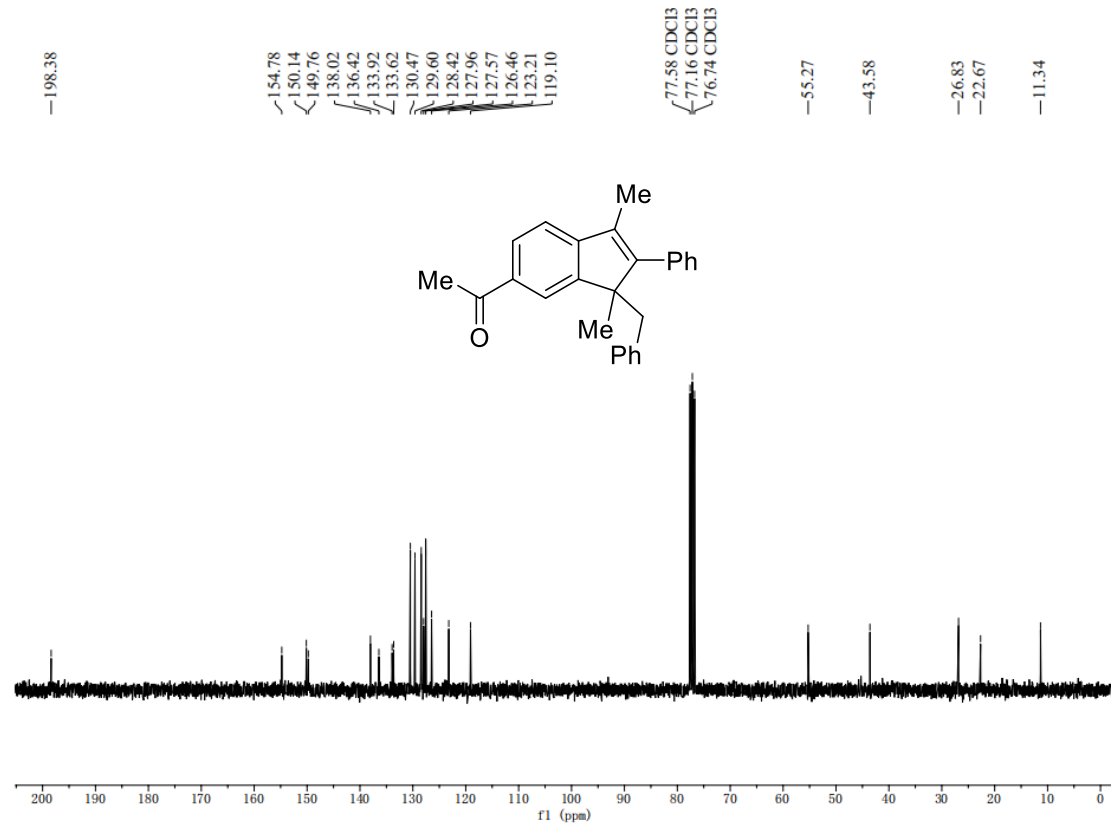




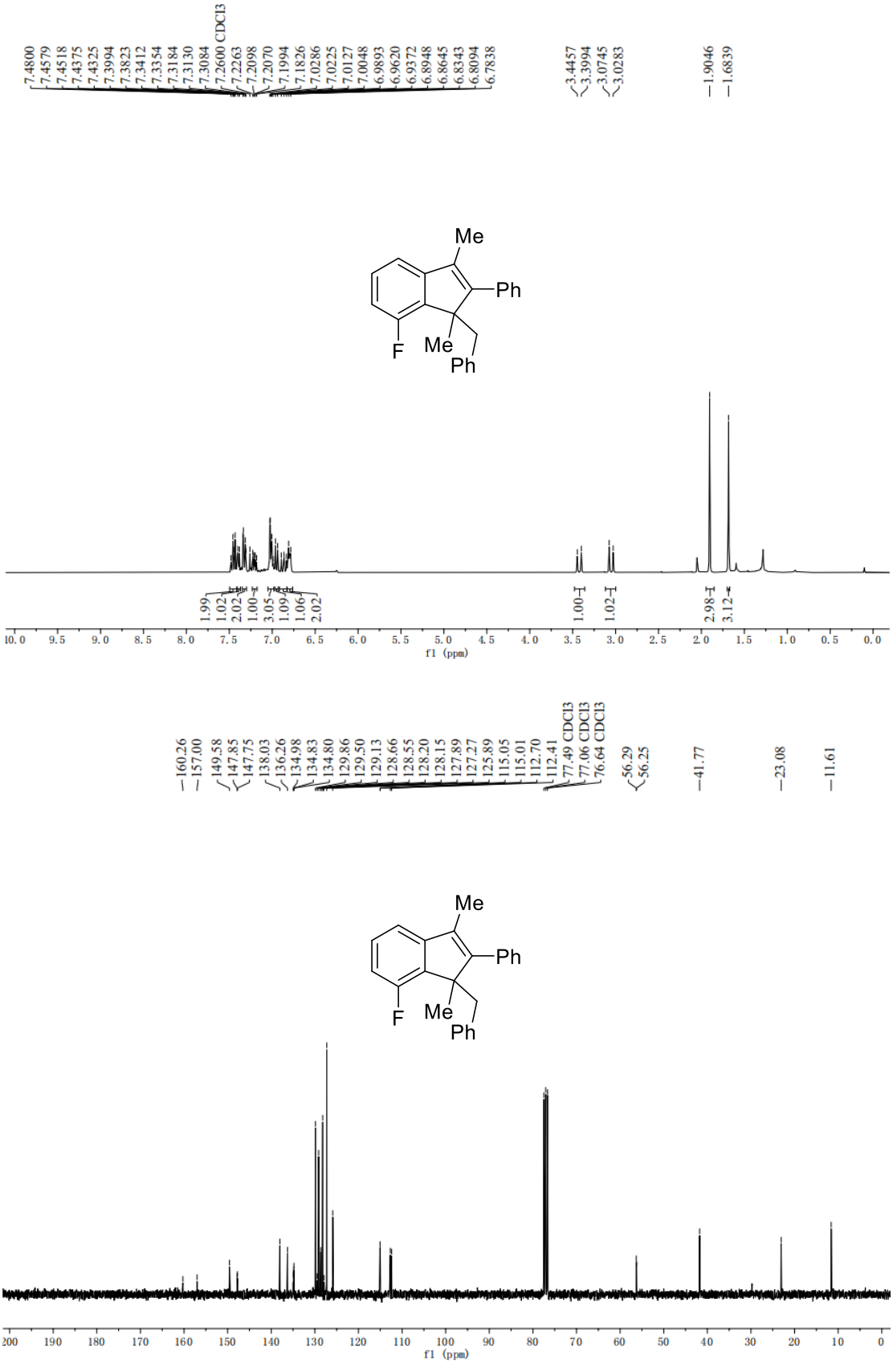


3k ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)

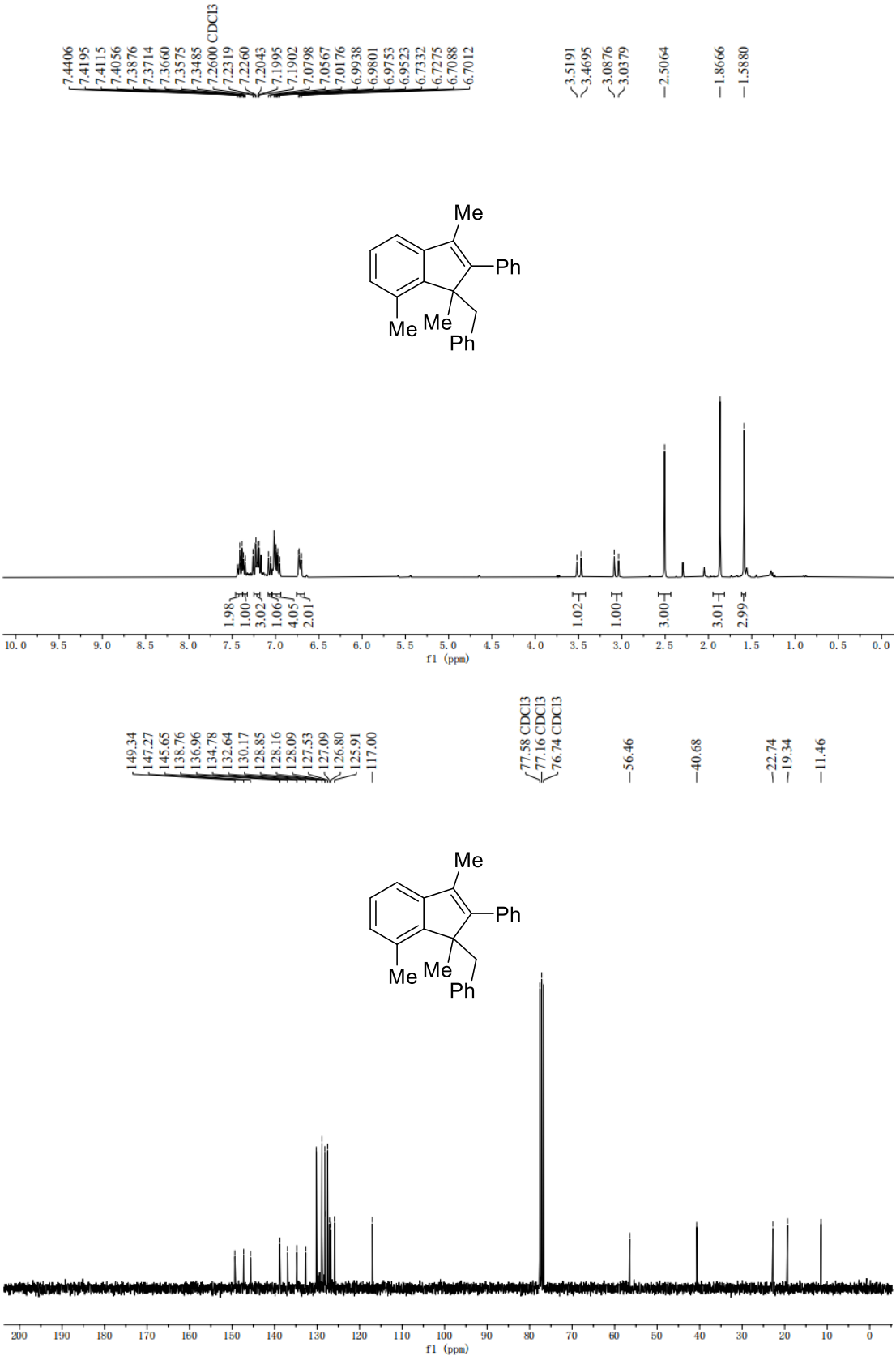




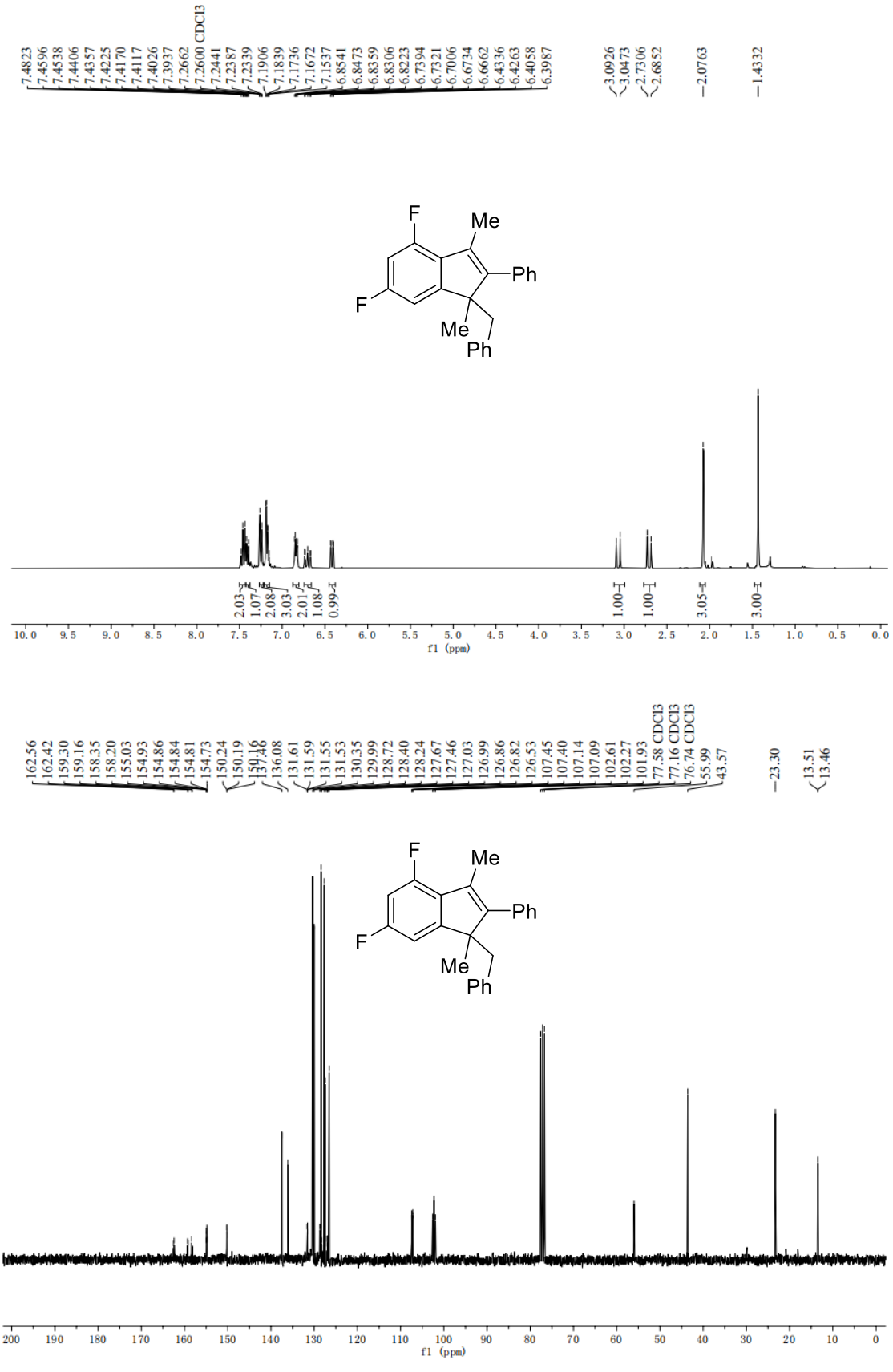
3l ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)



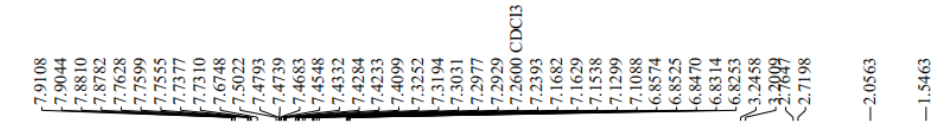
3m ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)

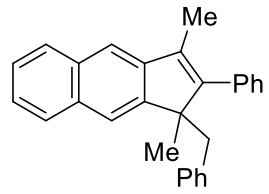


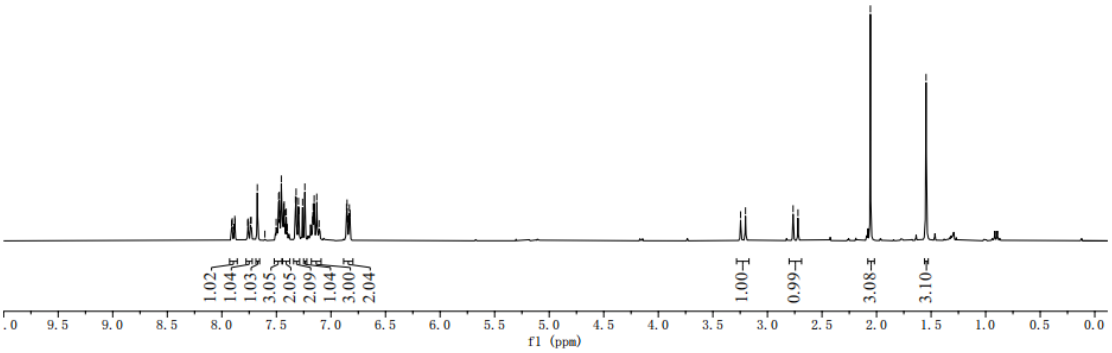
3n ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)

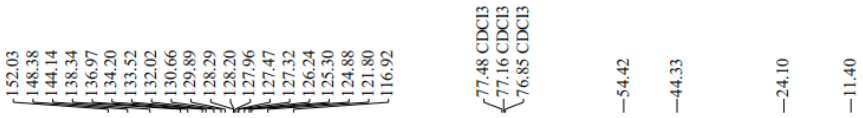


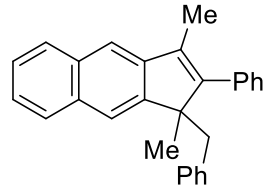
3o ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (101 MHz, Chloroform-*d*)

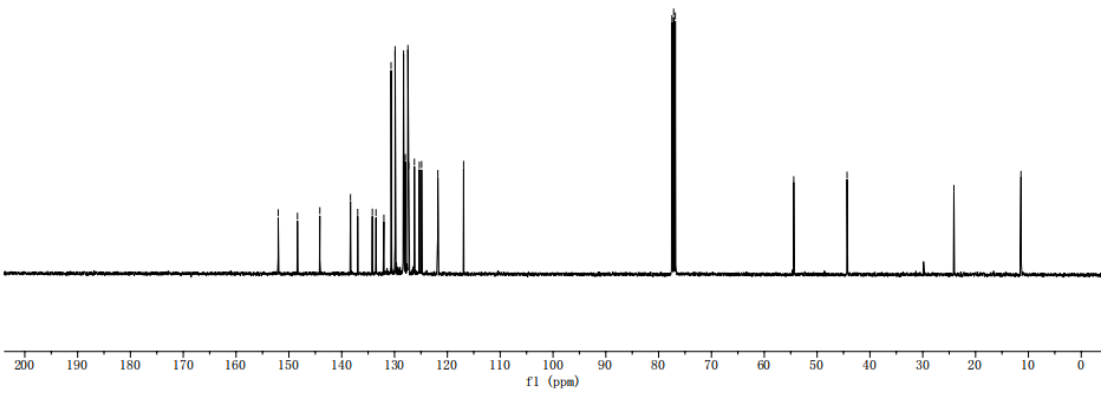




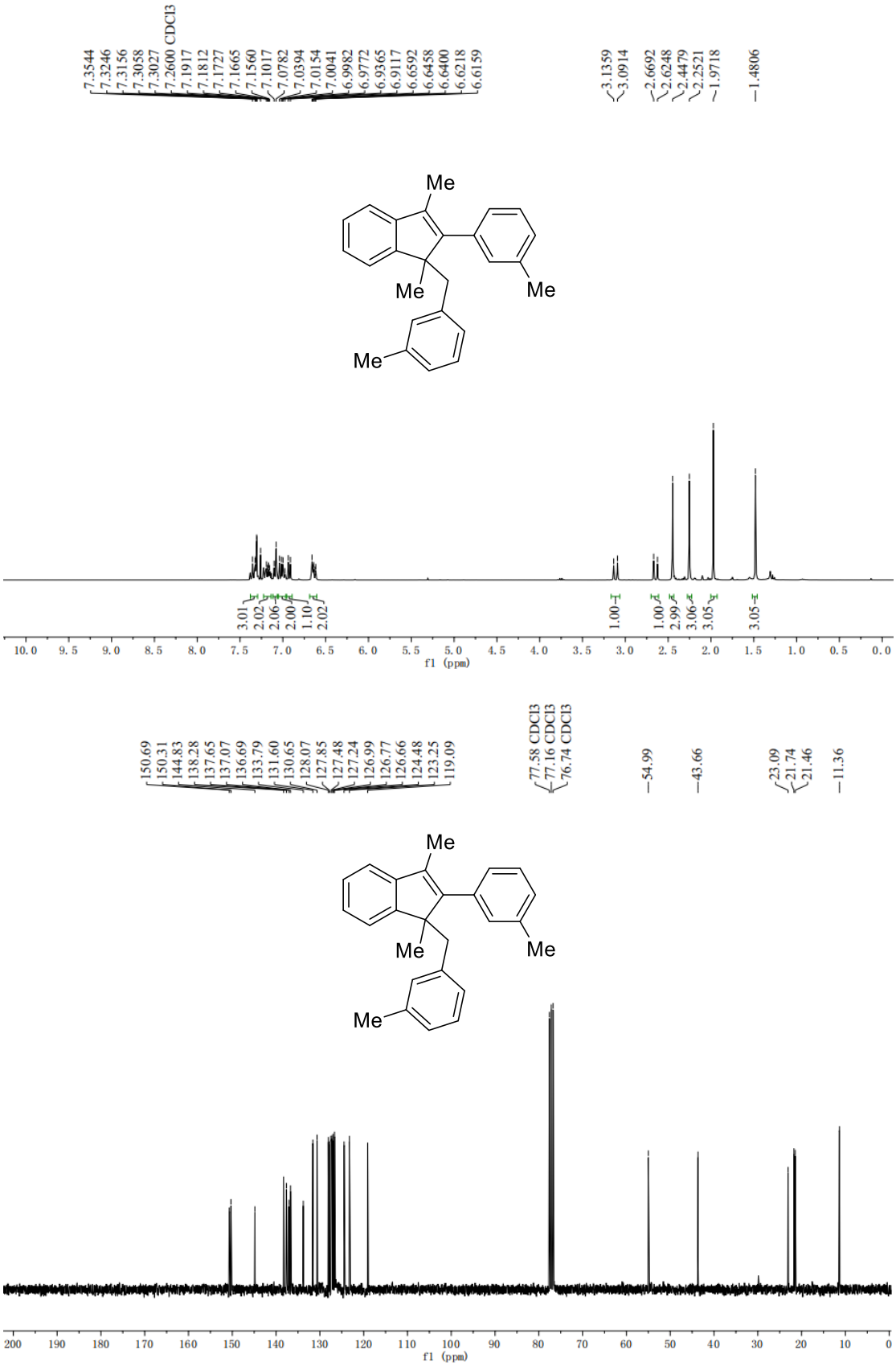




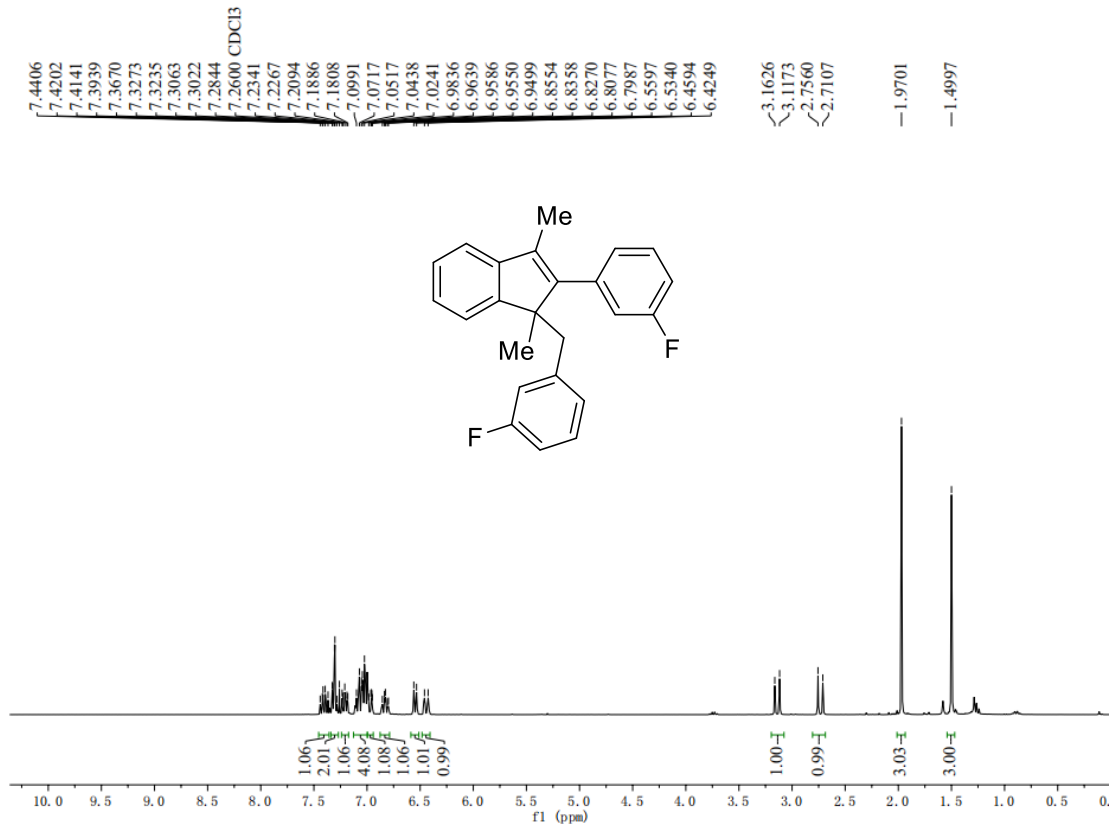


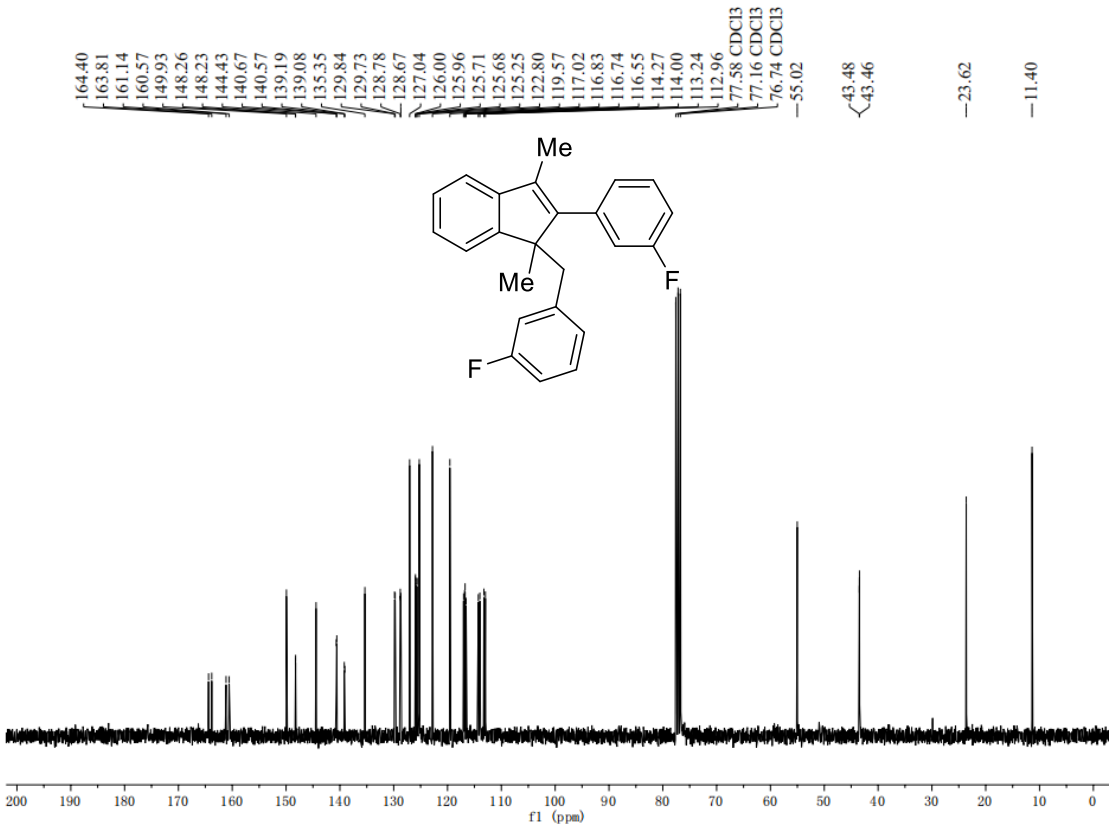


3p ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)

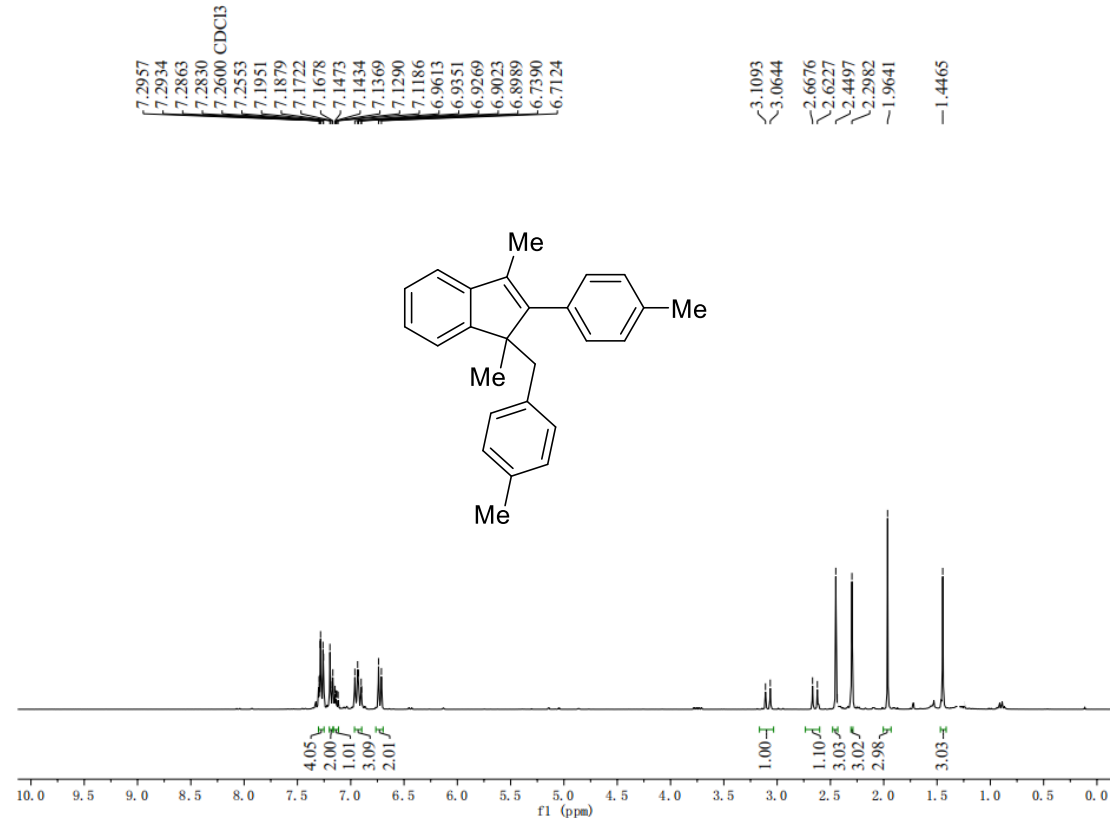


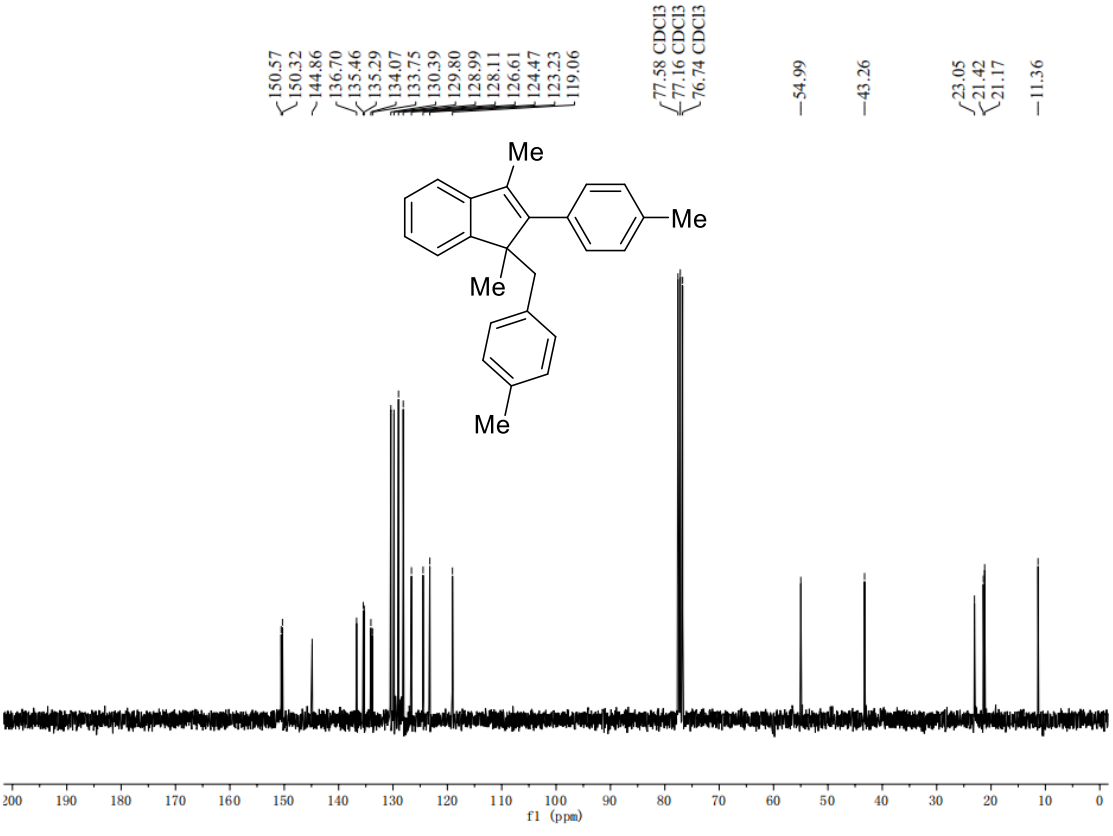
3q ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)



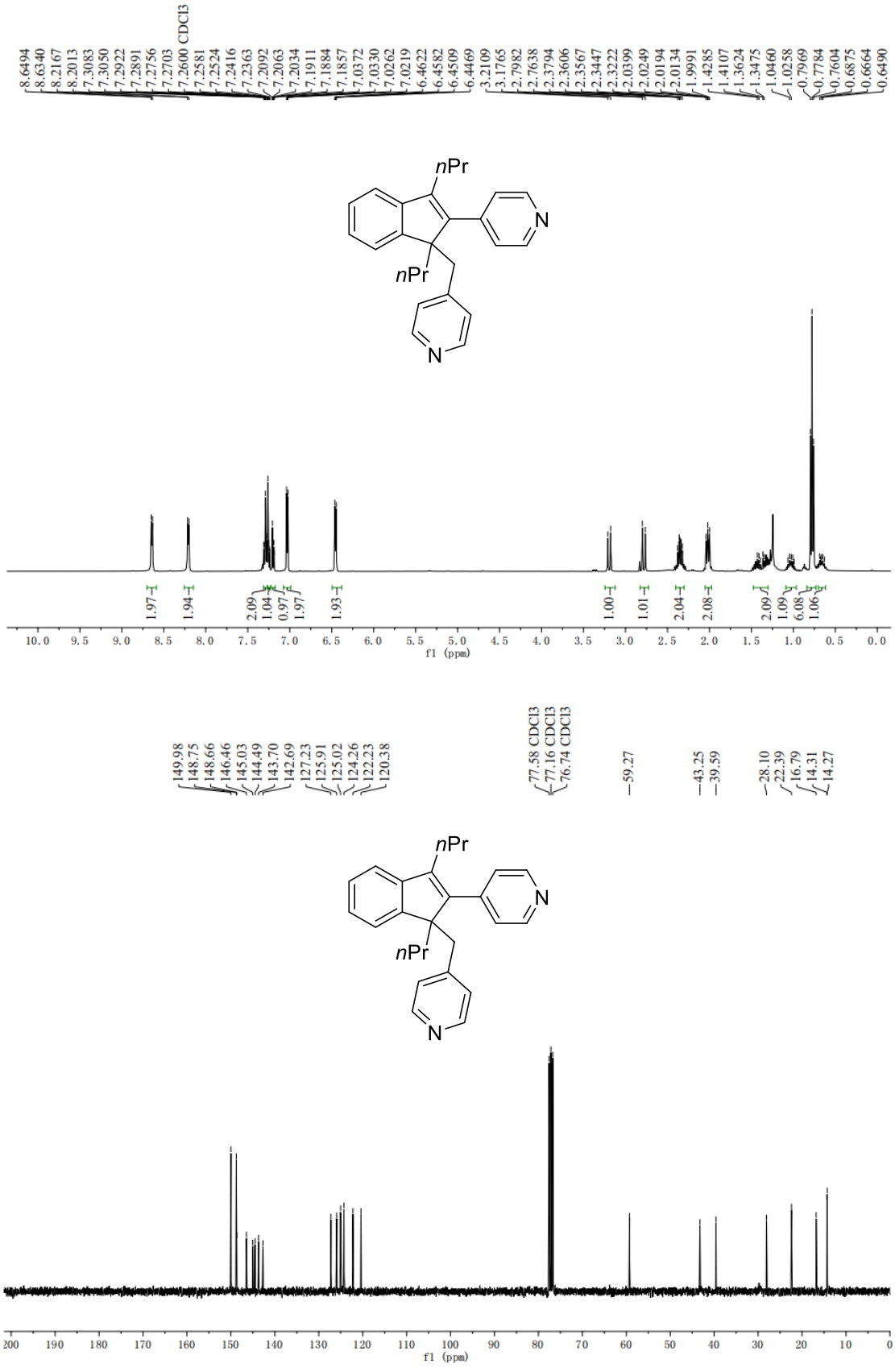


3r ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)

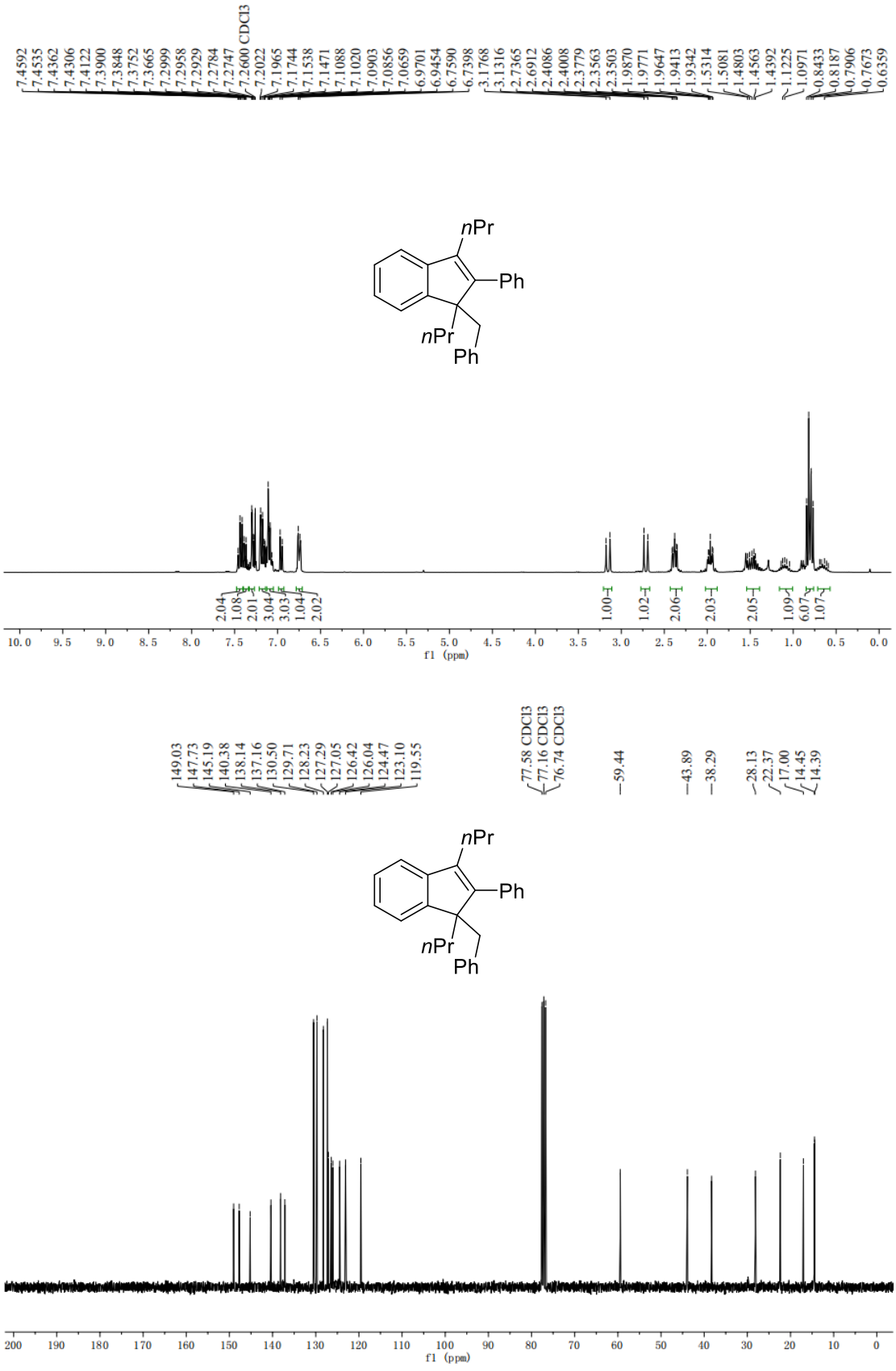




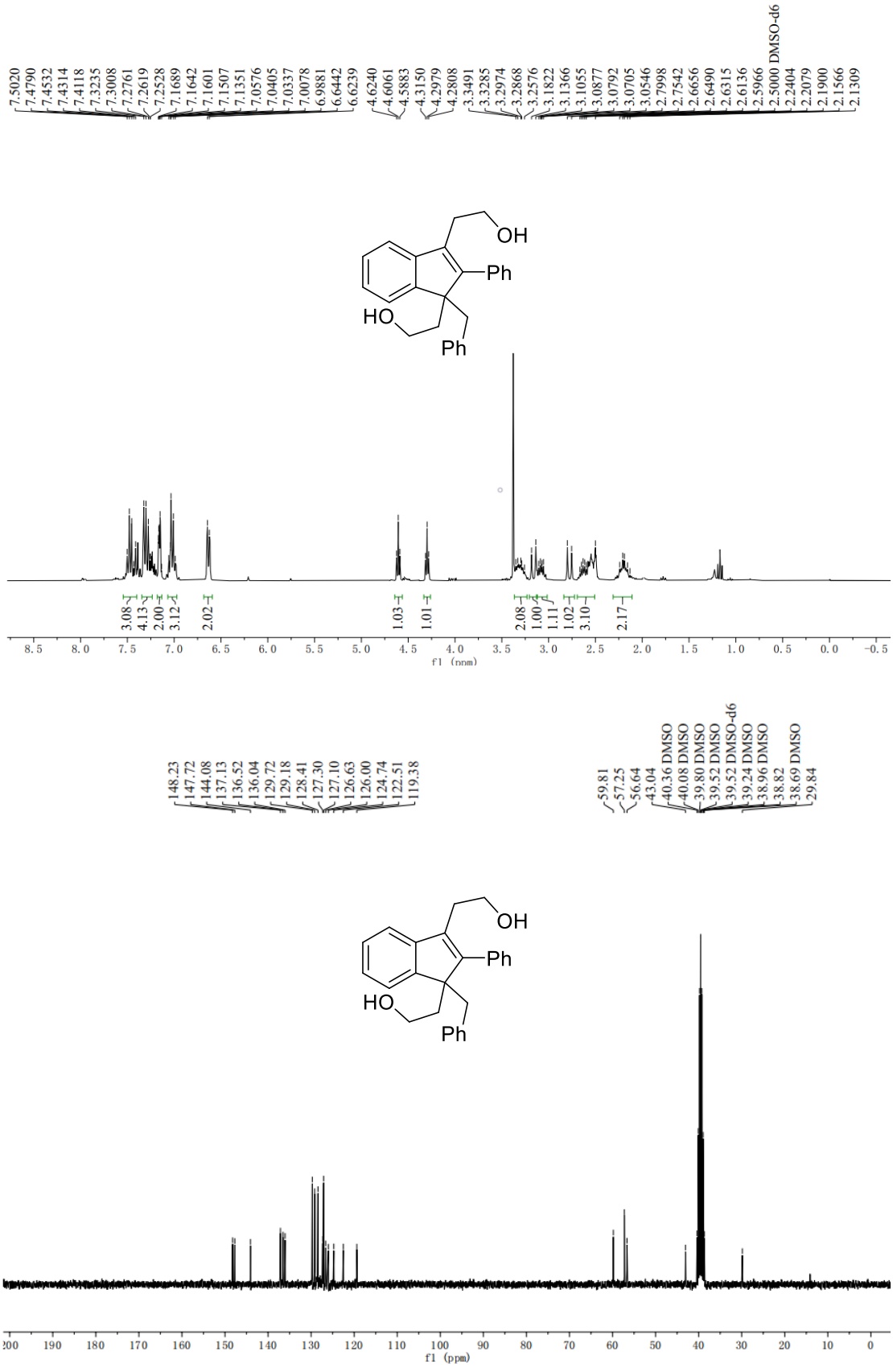
3s ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)



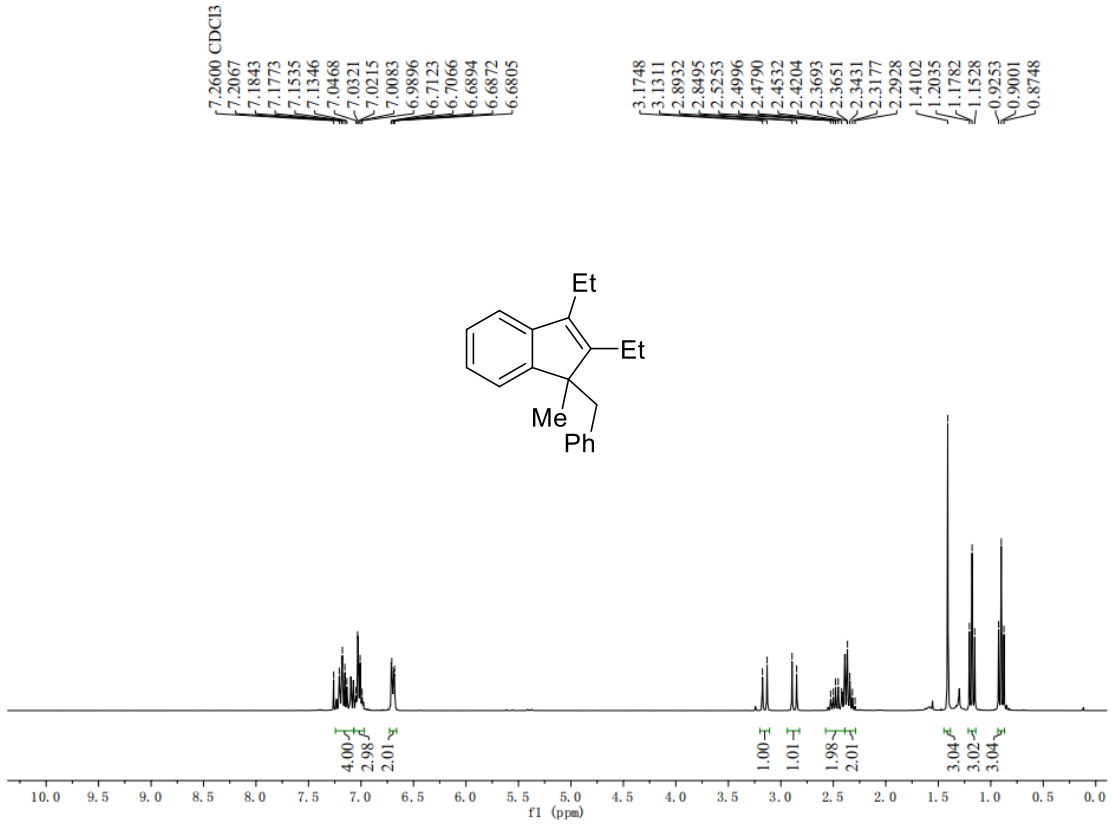
3t ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)

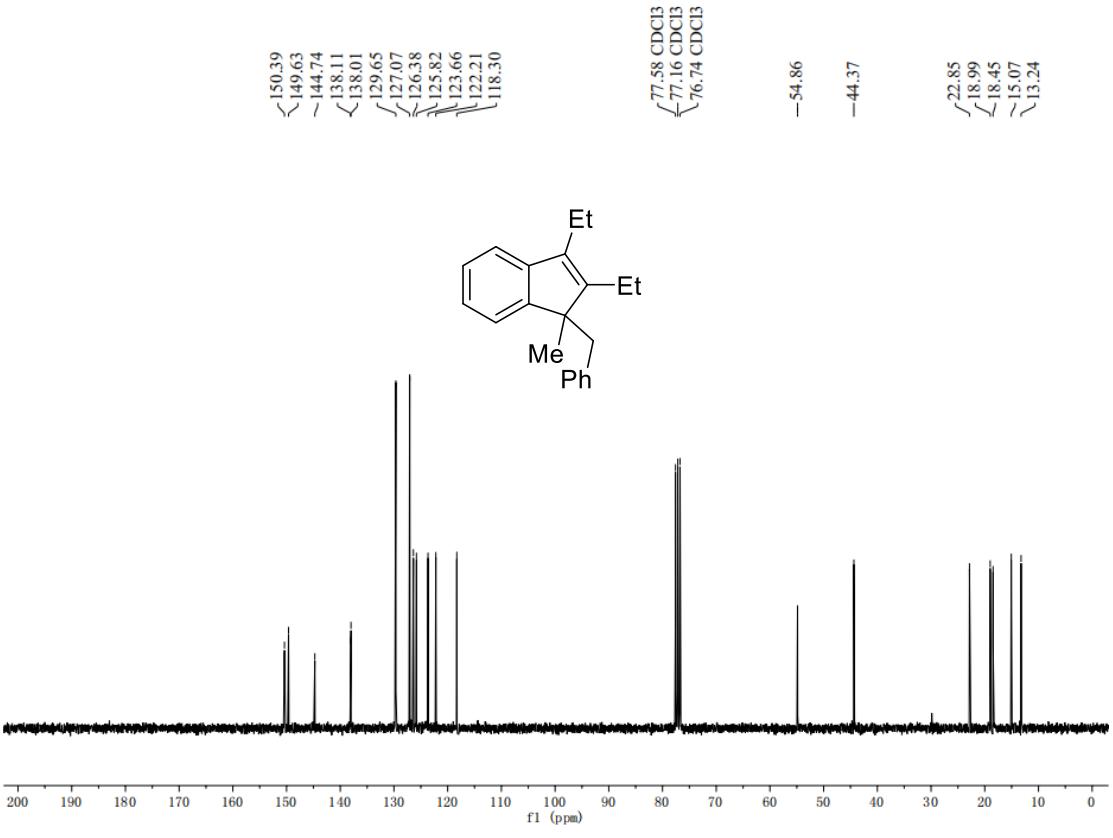


3u ^{1}H NMR (300 MHz, DMSO-d_6)/ ^{13}C NMR (75 MHz, DMSO-d_6)

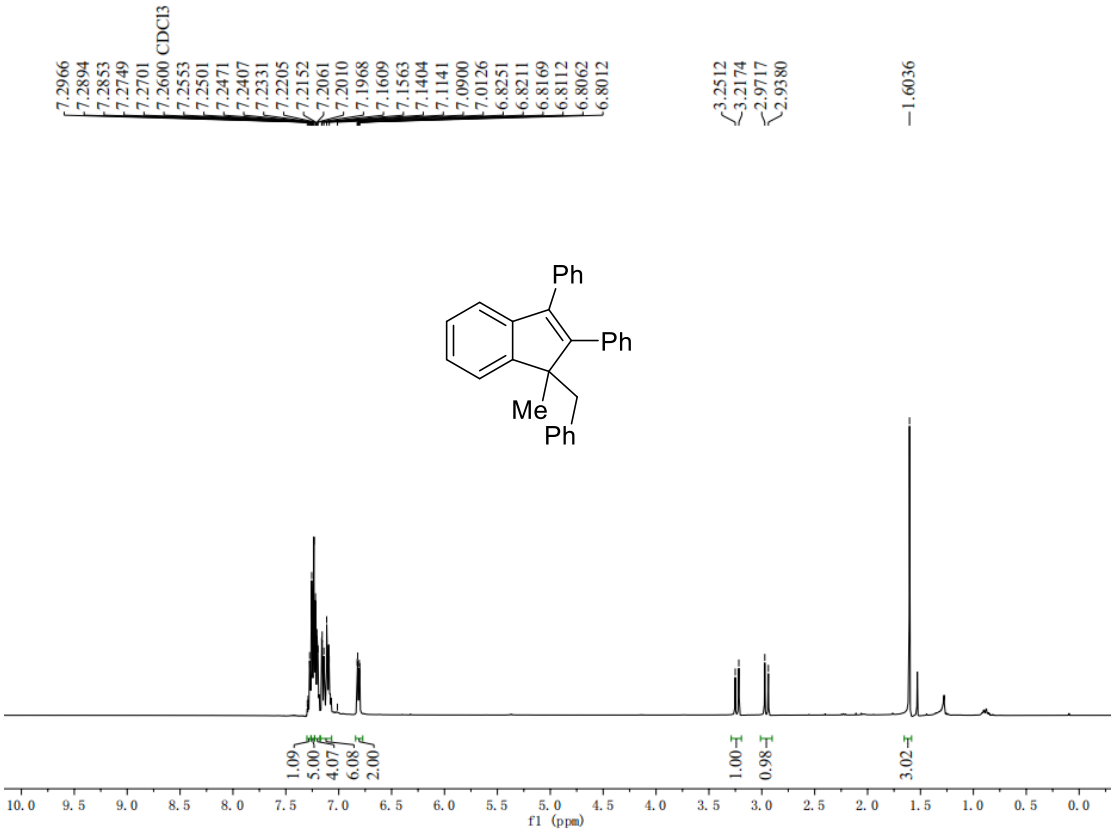


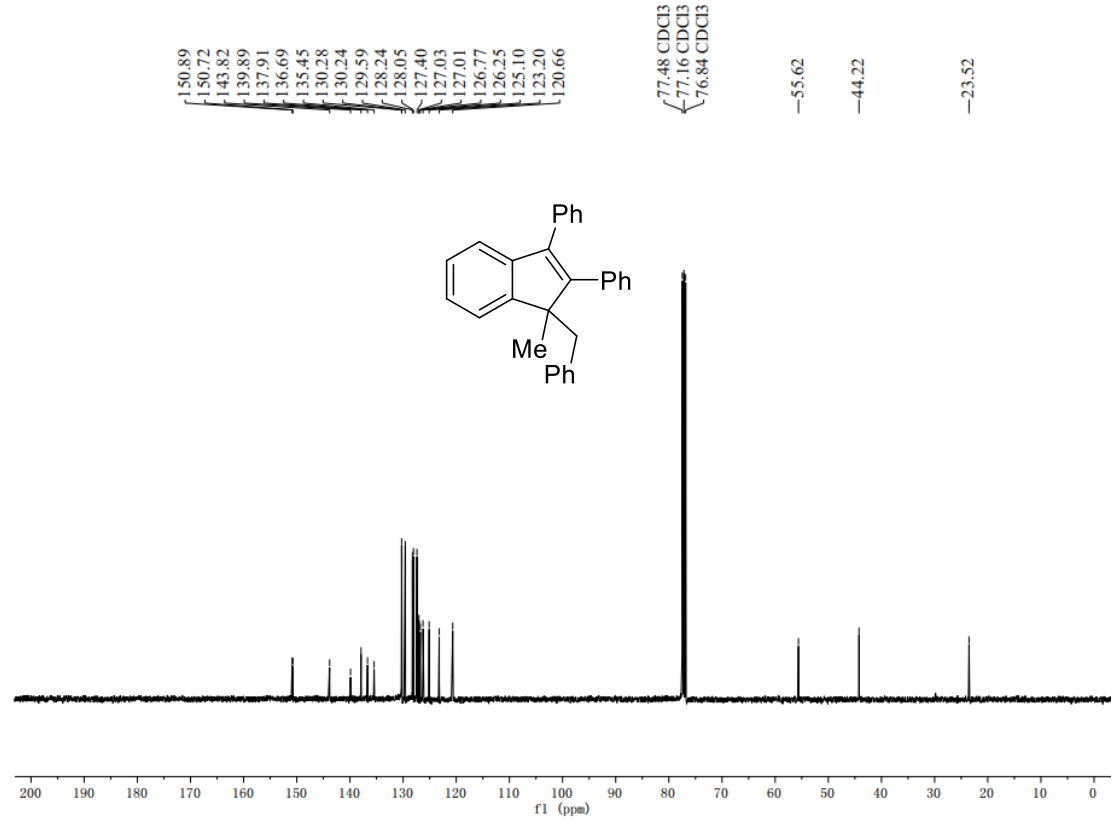
3v ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)



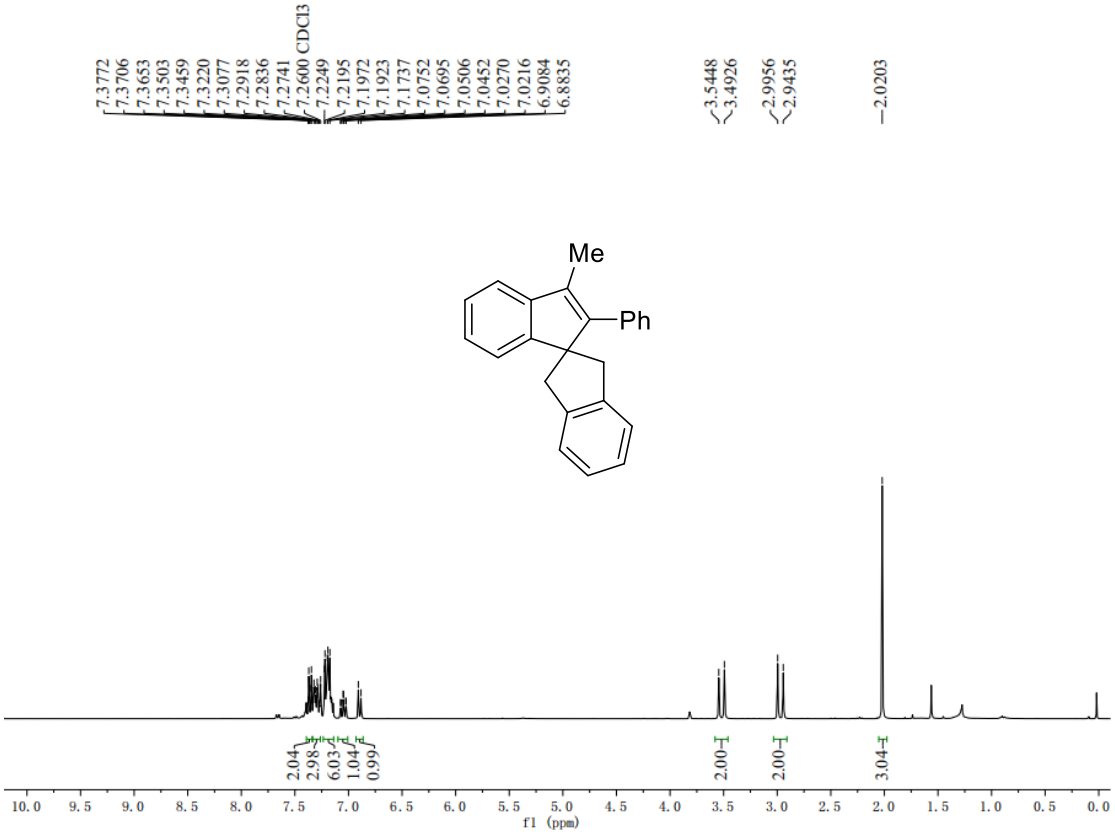


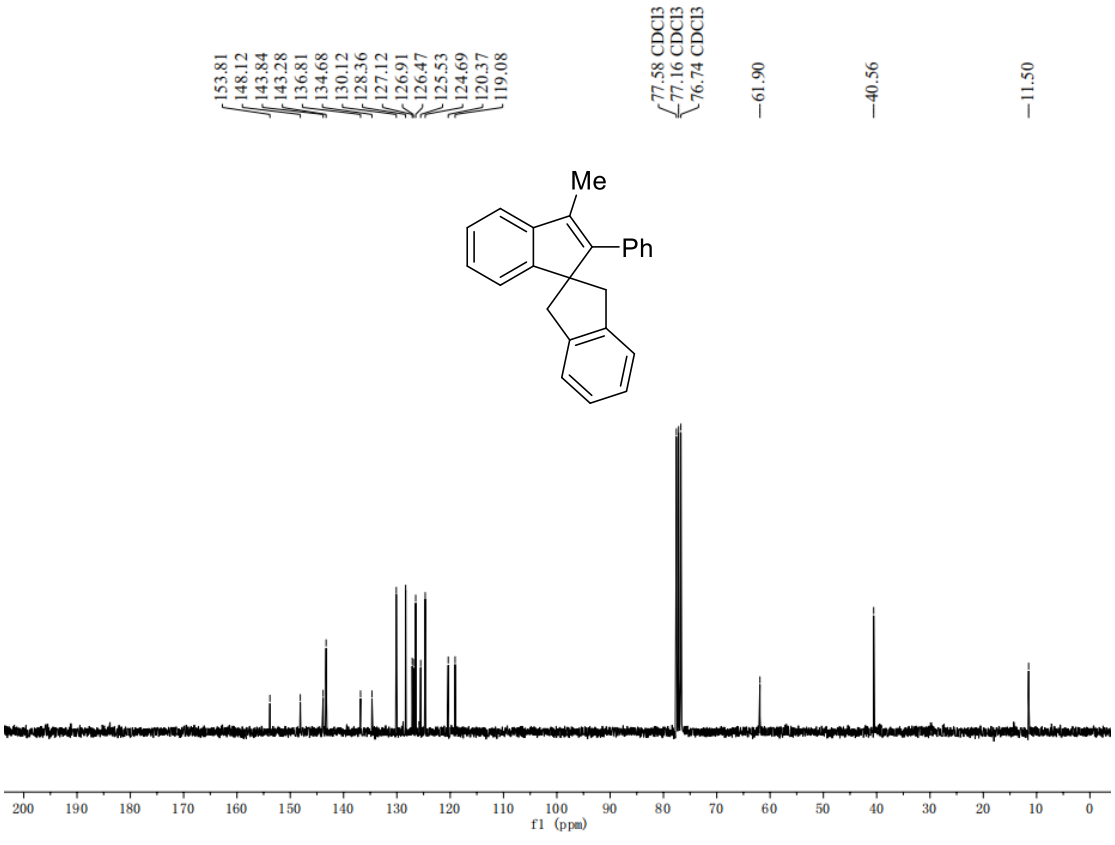
3w ^{1}H NMR (400 MHz, Chloroform-*d*)/ ^{13}C NMR (101 MHz, Chloroform-*d*)



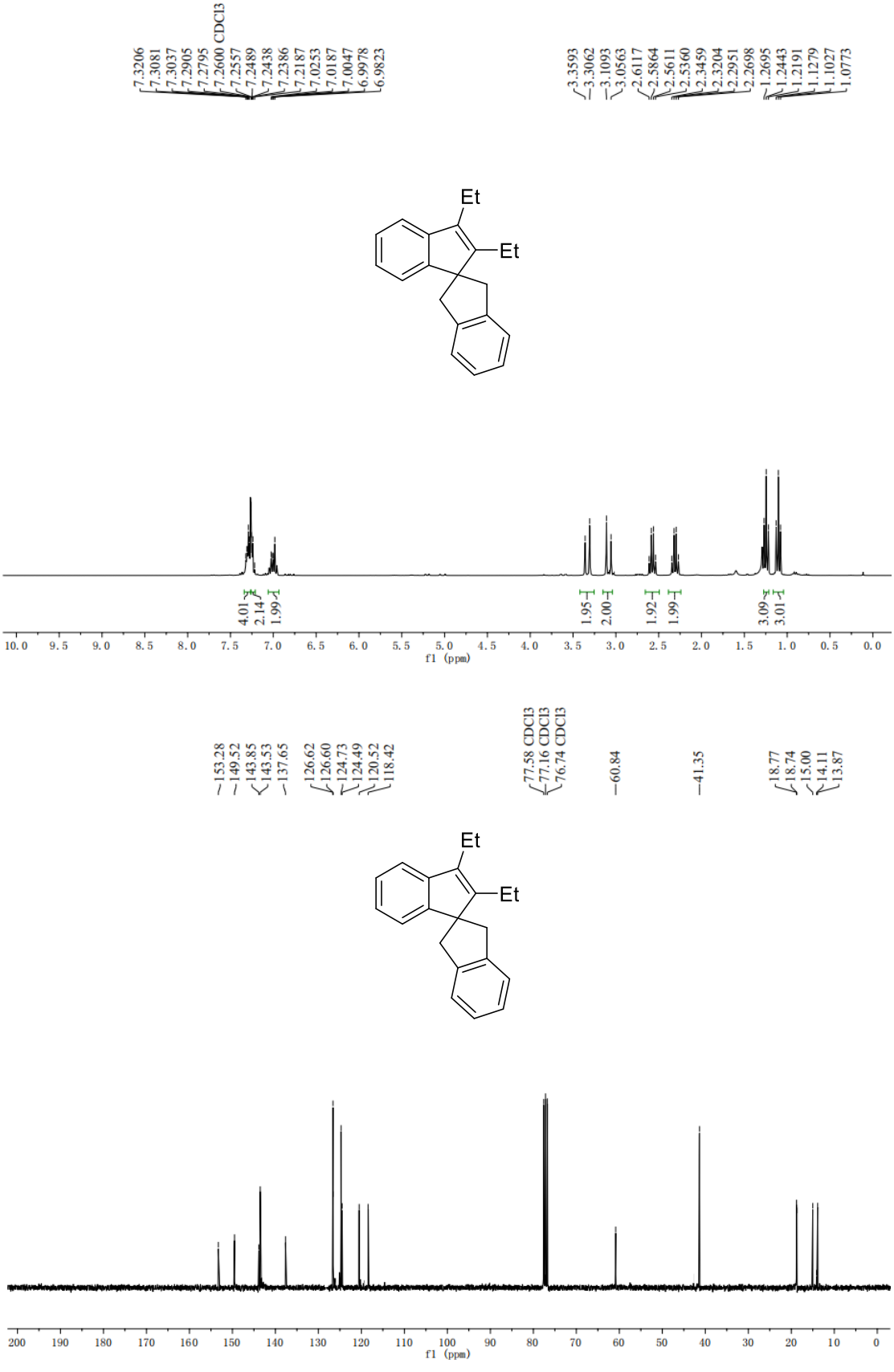


3x ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)





3y ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)



3z ^{1}H NMR (300 MHz, Chloroform-*d*)/ ^{13}C NMR (75 MHz, Chloroform-*d*)