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Supporting Information

The Intramolecular Reaction of Acetophenone *N*-Tosylhydrazone and Vinyl: Brønsted Acid-Promoted Cationic Cyclization toward Polysubstituted Indenes

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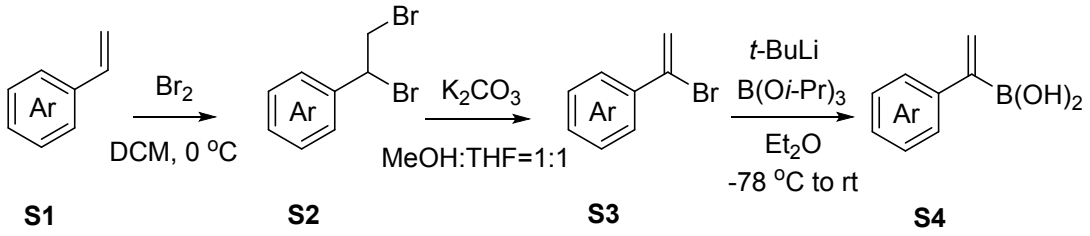
1. General considerations:

Unless otherwise noted, all the reactions were carried out using standard Schlenk technique，and all chemicals were purchased from commercial suppliers and used without further purification. The ^{1}H NMR spectra were recorded on a 300 MHz or 400 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 75 MHz or 100 MHz. NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.26 ppm) or DMSO-d_6 (2.50 or 39.52 ppm) as the internal standard. The coupling constants J are given in Hz. Gas chromatography mass spectrometry (GC-MS) were obtained by GCMS-QP2010 SE. High-resolution mass spectra (HRMS) were obtained using an agilent 6230 TOF focus spectrometer (ESI). Column chromatography was performed using EM Silica gel 60 (300-400 mesh), and the eluent was a mixture of petroleum ether (PE) and ethyl acetate (EA).

2. General Synthetic Procedures

2.1 Synthetic procedures for (1-arylvinyl)boronic acids[1]



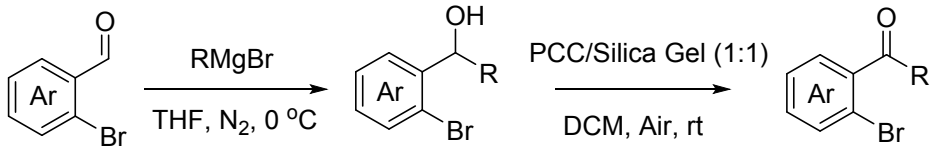
Step 1: S1 (1.0 equiv.) in DCM was cooled to 0 °C and Br_2 (1.2 equiv.) was added via syringe and the reaction was stirred at 0 °C for 1 hour. After completion of the reaction, it was quenched with saturated $Na_2S_2O_3$ solution until the solution became colorless. The resulting solutions was then filtered through a pad celite and washed with DCM. The layers were then separated and the aqueous layer was extracted with DCM. The combined organic layers were then washed with saturated brine, dried over Na_2SO_4 and concentrated to obtain a white solid.

Step 2: **S2** (1.0 equiv.) was stirred in a solution of 1:1 methanol and THF at room temperature. Potassium carbonate (2.0 equiv.) was added to the stirred solution until the reaction was complete judged by TLC. The reaction was then quenched with deionized water to remove volatiles. The resulting aqueous layer was extracted with

ether and then the combined organic layers were then washed with saturated brine, dried over Na_2SO_4 and concentrated in vacuo to obtain an oily liquid.

Step 3: S3 (1.0 equiv.) in dry diethyl ether was put under Nitrogen atmosphere in a 2-neck flask and cooled to -78 ^oC. A 1.7 M solution of *t*-BuLi in pentanes (2.1 equiv.) was added dropwise and the solution was stirred at -78 ^oC for 30 minutes. Tri-isopropylborate (1.2 equiv.) was added dropwise to the solution over 30 minutes. After the addition was complete, the solution was stirred at -78 ^oC for 2 hours after which the solution was removed from the cold bath and stirred at room temperature overnight. To the resulting yellow-orange solution was added 1.0 M HCl solution and was stirred for 2 hours. The layers were separated and the aqueous layer was extracted with ether. The combined organic layers were then washed with 1.0 M NaOH solution and the layers were separated. The aqueous layer was acidified to pH≈1.0 and extracted with ethyl acetate. The combined organic layers were then washed with brine, dried over Na_2SO_4, and concentrated. The crude product was directly carried on without purification.

2.2 Synthetic procedures for substituted 1-(2-bromophenyl)ethanones[2]



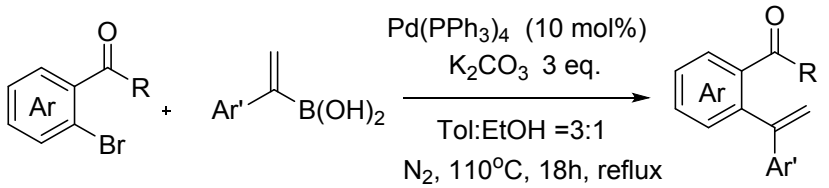
S5 **S6** **S7**

Step 1: To a solution of **S5** derivatives (20 mmol) in THF (20 mL) was added RMgBr (24.0 mmol) dropwise at 0 ^oC under N_2, and stirred at the same temperature. After the reaction was completed, the reaction was quenched with saturated NH_4Cl solution and extracted with EtOAc. The combined organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by silica gel chromatography column.

Step 2: To a solution of **S6** (15 mmol) in DCM was added a mixture of PCC (45.0 mmol) and silica gel [PCC/silica gel = 1/1 (w/w)]. The resulted reaction mixture was

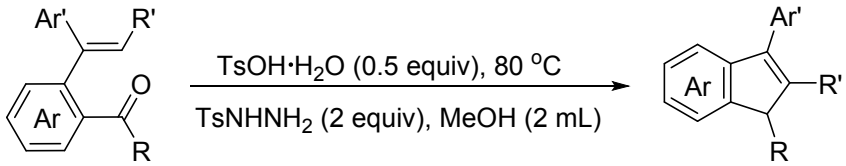
stirred at room temperature. Upon completion, the reaction mixture was then filtered through a pad of silica gel with EtOAc as eluent. The resulting solution was concentrated, and the residue was purified by silica gel chromatography column.

2.3 Synthetic procedures for 1[3]



To a stirred solution of aryl bromide (1.0 equiv.) and aryl boronic acid (1.2 equiv.) in a toluene/ethanol (3/1) mixture was added K_2CO_3 (3.0 equiv.) and $Pd(PPh_3)_4$ (0.1 equiv). The resulting suspension was heated at 110 °C under nitrogen atmosphere for 18 h. The solvent was removed under reduced pressure and the crude residue was redissolved in H_2O (100 mL) and extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with brine (100 mL) and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and purified by column chromatography.

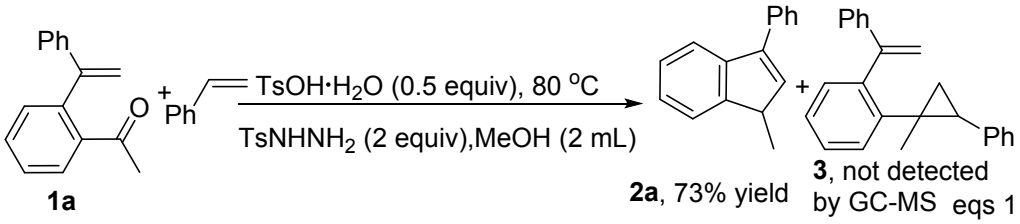
2.4 Synthetic procedure for 2



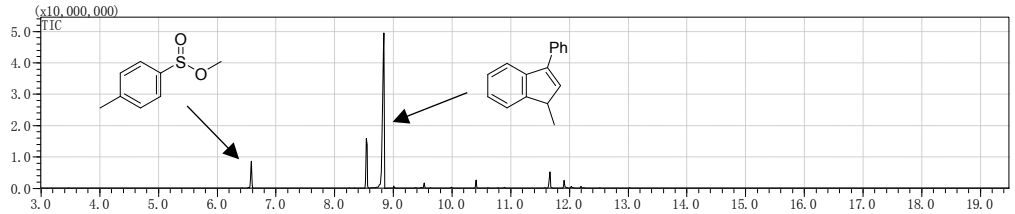
1 **2**

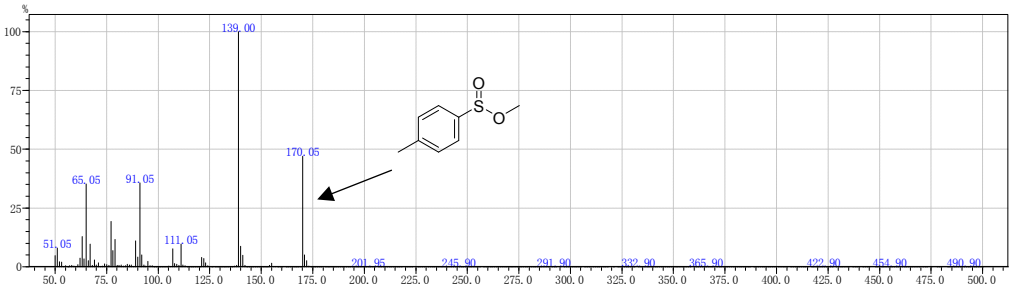
To an oven-dried Schlenk tube equipped with a magnetic stirring bar was added sequentially *o*-(1-arylvinyl) acetophenone **1** (0.1 mmol), $TsNHNH_2$ (0.2 mmol), TsOH‧H_2O (0.5 equiv), and MeOH (2.0 mL). The reaction vessel was evacuated to about -0.1 MPa (last 30 seconds per time) and backfilled with N_2 (1 atm) in three times. The reaction mixture was stirred at 80 °C in an oil bath under nitrogen for 6 hours. After the completion of the reaction, the mixture was purified by flash column chromatography on silica gel with PE as the eluent to give the desired products **2**.

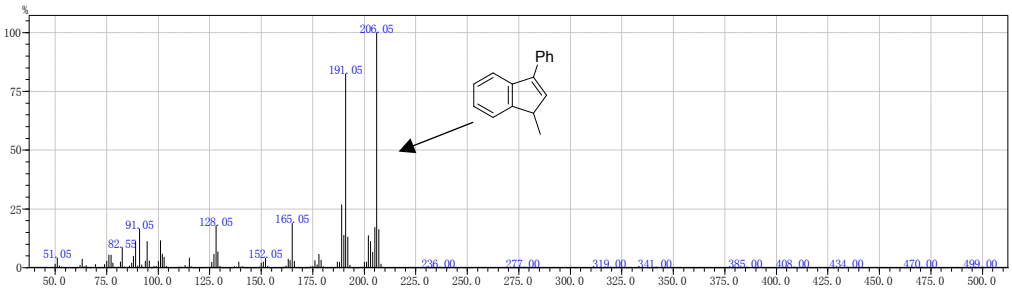
3. Mechanism study

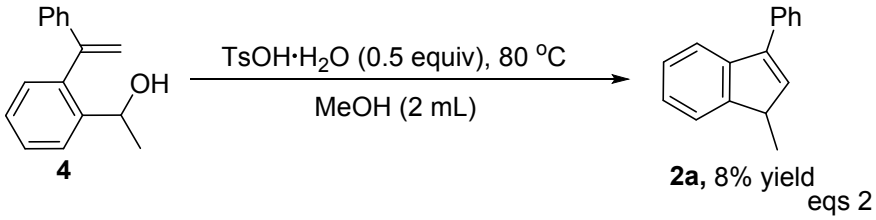


eqs 1

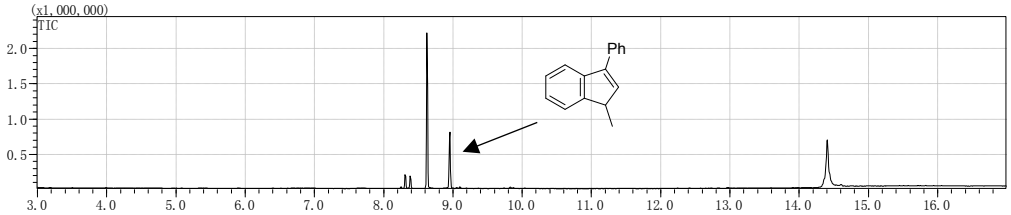


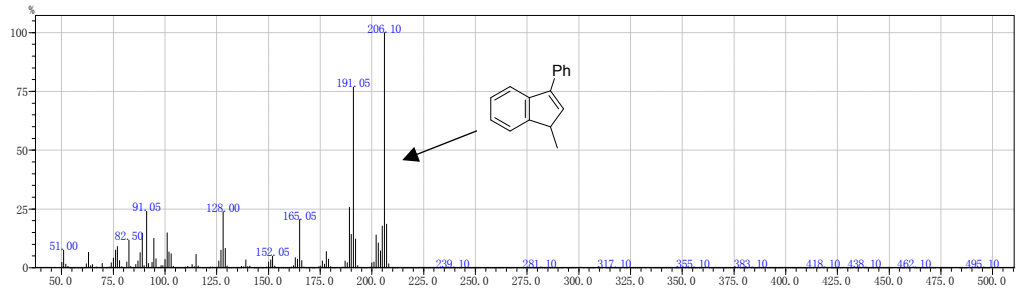


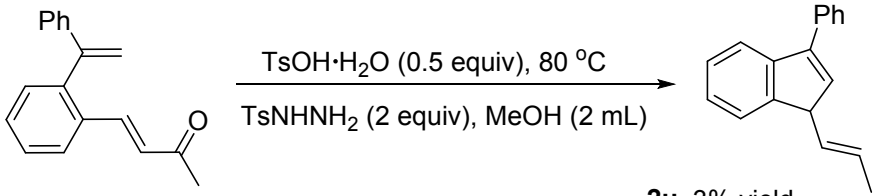




eqs 2



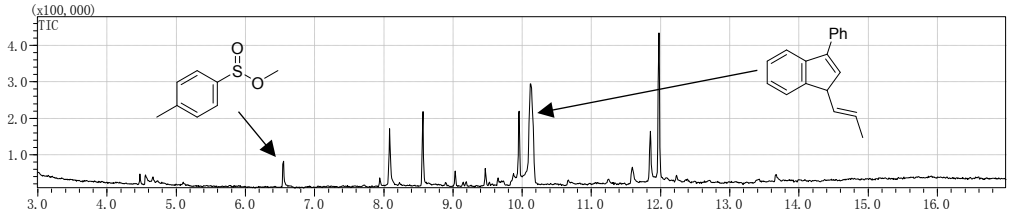


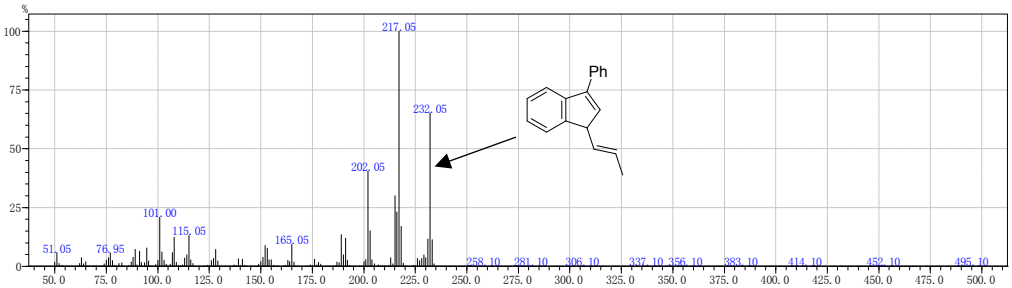


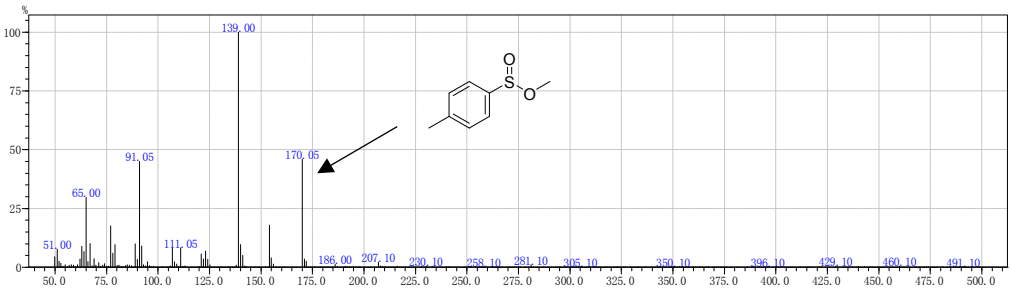
1u

2u, 3% yield

eqs 3

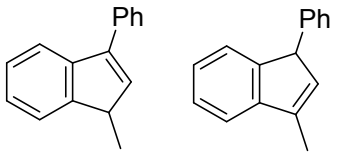






4. Characterization Data for the Products

1-methyl-3-phenyl-1*H*-indene (2a):



5.6 : 1

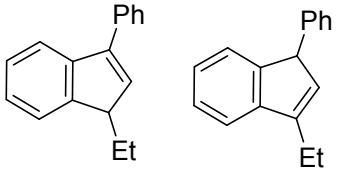
Flash column chromatography on a silica gel (petroleum ether) give **2a** (16.7 mg, 81% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67-7.59 (m, 3H), 7.55-7.47 (m, 3H), 7.44-7.28 (m, 3.9H), 7.25-7.14 (m, 0.72H), 6.56 (d, J = 2.0 Hz, 1H), 6.32-6.30 (m, 0.18H), 4.60-4.58 (m, 0.18H), 3.68-3.61 (m, 1H), 2.26 (s, 0.54H), 1.45 (d, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 145.6, 143.5, 143.2, 140.3, 139.8, 138.3, 136.2, 134.7, 128.8, 128.7, 128.0, 127.9, 127.8, 126.8, 126.5, 125.4, 125.3, 123.9, 123.2, 120.6, 119.2, 55.3, 44.2, 16.4, 13.2.

HRMS (EI) m/z calcd for $C_{16}H_{14}^+$ [M^+]: 206.1090; found: 206.1092.

1-ethyl-3-phenyl-1*H*-indene (2b):



5.6 : 1

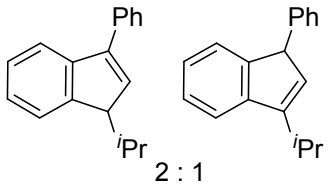
Flash column chromatography on a silica gel (petroleum ether) give **2b** (19.1 mg, 87% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68-7.59 (m, 3H), 7.54-7.47 (m, 3H), 7.44-7.27 (m, 3.9H), 7.25-7.14 (m, 0.72H), 6.64 (d, J = 2.2 Hz, 1H), 6.32-6.30 (m, 0.18H), 4.60-4.58 (m, 0.18H), 3.58-3.53 (m, 1H), 2.68-2.64 (m, 0.36H), 2.14-2.04 (m, 1H), 1.74-1.64 (m, 1H), 1.39-1.34 (m, 0.54H), 1.10-1.04 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 145.9, 145.0, 144.1, 143.5, 140.3, 136.1, 136.0, 132.6, 129.1, 128.6, 128.6, 127.8, 127.7, 127.6, 126.7, 126.6, 126.4, 125.2, 125.0, 123.9, 123.3, 120.3, 119.1, 55.1, 50.8, 24.8, 20.7, 12.4, 11.9.

HRMS (EI) m/z calcd for $C_{17}H_{16}^+$ [M^+]: 220.1247; found: 220.1248

1-isopropyl-3-phenyl-1*H*-indene (2c):



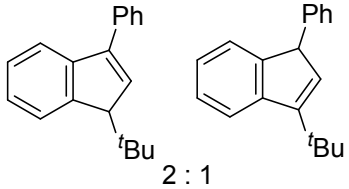
Flash column chromatography on a silica gel (petroleum ether) give **2c** (13.3 mg, 57% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63-7.53 (m, 3H), 7.50-7.44 (m, 3H), 7.42-7.36 (m, 1.5H), 7.32-7.28 (m, 2H), 7.25-7.19 (m, 2.5H), 7.18-7.15 (m, 0.5H), 7.13-7.09 (m, 1H), 6.56 (d, J = 2.0 Hz, 1H), 6.26-6.25 (m, 0.5H), 4.53 (s, 0.5H), 3.54-3.52 (m, 1H), 3.03-2.95 (m, 0.5H), 2.48-2.39 (m, 1H), 1.34 (d, J = 7.0 Hz, 1.5H), 1.32 (d, J = 6.4 Hz, 1.5H), 1.20 (d, J = 6.8 Hz, 3H), 0.69 (d, J = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.8, 149.3, 148.0, 144.9, 144.4, 144.0, 140.3, 136.2, 133.9, 131.2, 128.6, 128.5, 127.8, 127.7, 127.6, 126.6, 126.5, 126.3, 125.1, 124.9, 124.0, 123.4, 120.2, 119.6, 55.8, 54.9, 30.5, 26.9, 21.8, 17.8.

HRMS (EI) m/z calcd for $C_{18}H_{18}^+$ [M^+]: 234.1403; found: 234.1405.

1-(tert-butyl)-3-phenyl-1*H*-indene (2d):



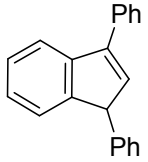
Flash column chromatography on a silica gel (petroleum ether) give **2d** (12.9 mg, 52% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66-7.59 (m, 3.5H), 7.55-7.35 (m, 4.5H), 7.34-7.28 (m, 2H), 7.25-7.08 (m, 3.5H), 6.61 (d, J = 1.9 Hz, 1H), 6.26 (d, J = 1.9 Hz, 0.5H), 4.50 (d, J = 2.1 Hz, 0.5H), 3.39 (d, J = 2.0 Hz, 1H), 1.43 (s, 4.5H), 1.10 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 150.2, 146.8, 144.5, 144.4, 143.4, 140.3, 136.2, 135.3, 131.9, 128.6, 128.5, 128.5, 127.8, 127.8, 127.6, 126.7, 126.3, 126.1, 125.2, 124.7, 124.5, 124.2, 122.3, 120.2, 60.2, 54.4, 34.7, 33.2, 29.5, 28.7.

HRMS (ESI) m/z calcd for $C_{19}H_{21}^+$ [M+H^+] : 249.1638; found: 249.1638.

1,3-diphenyl-1*H*-indene (2e):



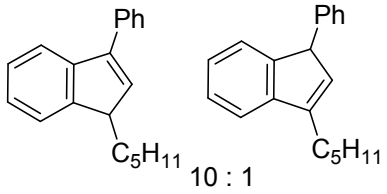
Flash column chromatography on a silica gel (petroleum ether) give **2e** (12.9 mg, 48% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70-7.67 (m, 3H), 7.50-7.39 (m, 3H), 7.36-7.26 (m, 5H), 7.25-7.18 (m, 3H), 6.66 (d, J = 2.2 Hz, 1H), 4.73 (d, J = 2.2 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3, 144.6, 143.2, 139.5, 136.3, 135.6, 128.7, 128.6, 128.0, 127.8, 127.8, 126.9, 126.7, 125.6, 124.3, 120.6, 55.4.

HRMS (EI) m/z calcd for $C_{21}H_{16}^+$ [M^+]: 268.1247; found: 268.1248.

1-pentyl-3-phenyl-1*H*-indene (2f):



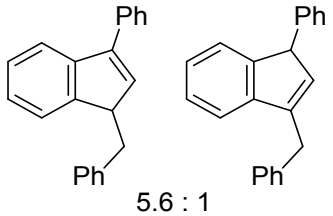
Flash column chromatography on a silica gel (petroleum ether) give **2f** (19.4 mg, 74% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68-7.60 (m, 3H), 7.56-7.48 (m, 3H), 7.44-7.29 (m, 3.5H), 7.23-7.15 (m, 0.4H), 6.66 (s, 1H), 6.31 (s, 0.1H), 4.60 (s, 0.1H), 3.63-3.59 (m, 1H), 2.67-2.62 (m, 0.2H), 1.67-1.47 (m, 3.4H), 1.42-1.36 (m, 4H), 0.98-0.94 (m, 3.3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 145.2, 144.6, 144.1, 143.5, 140.4, 136.6, 136.3, 133.6, 128.8, 128.7, 128.0, 127.9, 127.7, 126.8, 126.7, 126.5, 125.4, 125.2, 124.1, 123.4, 120.5, 119.4, 55.3, 49.6, 32.4, 32.1, 32.0, 27.8, 27.7, 22.8, 14.3.

HRMS (EI) m/z calcd for $C_{20}H_{22}^+$ [M^+]: 262.1716; found: 262.1715.

1-benzyl-3-phenyl-1*H*-indene (2g):



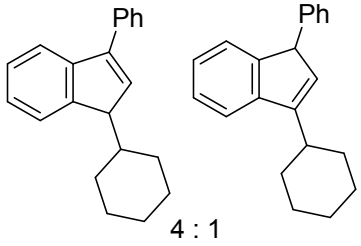
Flash column chromatography on a silica gel (petroleum ether) give **2g** (18.3 mg, 65% yield) as as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60-7.56 (m, 3H), 7.48-7.43 (m, 2H), 7.40-7.27 (m, 9.26H), 7.25-7.20 (m, 1.54H), 7.19-7.11 (m, 0.72H), 6.49 (d, J = 1.9 Hz, 1H), 6.23 (s, 0.18H), 4.60 (s, 0.18H), 3.97 (s, 0.36H), 3.86-3.81 (m, 1H), 3.27-3.21 (m, 1H), 2.82-2.75 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 144.2, 143.6, 141.6, 140.5, 136.0, 135.8, 129.3, 129.1, 128.8, 128.7, 128.6, 128.5, 128.0, 127.9, 127.8, 126.9, 126.8, 126.5, 126.4, 125.5, 125.2, 124.1, 123.7, 120.7, 119.8, 55.3, 51.0, 38.4, 34.5.

HRMS (EI) m/z calcd for $C_{22}H_{18}^+$ [M^+]: 282.1043; found: 282.1042.

1-cyclohexyl-3-phenyl-1*H*-indene (2h):



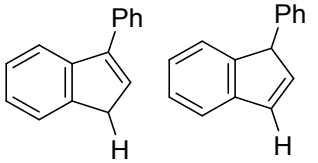
Flash column chromatography on a silica gel (petroleum ether) give **2h** (9.3 mg, 34% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65-7.54 (m, 3H), 7.53-7.44 (m, 3H), 7.41-7.28 (m, 3.5H), 7.25-7.10 (m, 1.75H), 6.59 (d, J = 2.8 Hz, 1H), 6.25 (s, 0.25H), 4.54 (s, 0.25H), 3.52 (d, J = 3.9 Hz, 1H), 2.68-2.62 (m, 0.25H), 2.16-1.98 (m, 2.5H), 1.90-1.66 (m, 3H), 1.51-1.28 (m, 5H), 1.21-0.95 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 148.0, 144.6, 144.1, 140.4, 136.3, 134.8, 131.6, 128.7, 128.7, 128.0, 127.9, 127.7, 126.8, 126.6, 126.4, 125.2, 125.0, 124.1, 123.6, 120.3, 119.6, 55.6, 55.1, 41.0, 37.1, 32.6, 28.5, 27.1, 26.9, 26.7.

HRMS (EI) m/z calcd for $C_{21}H_{22}^+$ [M^+]: 274.1716; found: 274.1716.

3-phenyl-1*H*-indene (2i):



3.4 : 1

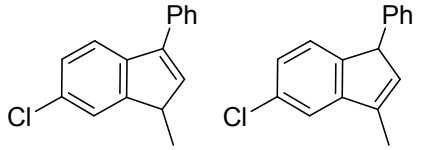
Flash column chromatography on a silica gel (petroleum ether) give **2i** (7.3 mg, 38% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.65-7.60 (m, 3H), 7.58-7.44 (m, 3H), 7.43-7.27 (m, 4.5H), 7.21-7.11 (m, 1.2H), 6.94-6.91 (m, 0.3H), 6.63-6.62 (m, 0.3H), 6.61-6.59 (m, 1H), 4.63-4.61 (m, 0.3H), 3.53 (d, J = 2.2 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 144.8, 143.9, 139.8, 139.3, 136.2, 131.5, 131.0, 128.7, 128.6, 128.1, 127.8, 127.7, 127.6, 126.8, 126.8, 126.2, 125.3, 124.9, 124.1, 123.9, 121.2, 120.3, 56.5, 38.2.

HRMS (EI) m/z calcd for $C_{15}H_{12}^+$ [M^+]: 192.0934; found: 192.0930.

6-chloro-1-methyl-3-phenyl-1*H*-indene (2j):



3.4 : 1

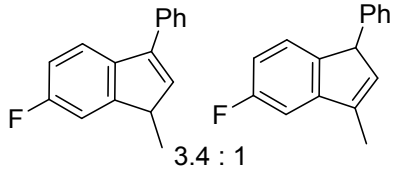
Flash column chromatography on a silica gel (petroleum ether) give **2j** (17.3 mg, 72% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59-7.56 (m, 2H), 7.49-7.44 (m, 4H), 7.41-7.36 (m, 1H), 7.31-7.22 (m, 2.2H), 7.14-7.07 (m, 1.2H), 6.52 (d, J = 2.2 Hz, 1H), 6.33-6.31 (m, 0.3H), 4.53-4.51 (m, 0.3H), 3.63-3.56 (m, 1H), 2.19 (s, 0.9H), 1.40 (d, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 142.8, 141.6, 138.4, 136.4, 135.6, 131.4, 131.2, 128.84, 128.8, 128.0, 127.8, 127.7, 127.0, 126.6, 125.2, 124.8, 123.7, 121.4, 119.6, 54.9, 44.1, 16.2, 13.0.

HRMS (EI) m/z calcd for $C_{16}H_{13}Cl^+$ [M^+]: 240.0700; found: 240.0701.

6-fluoro-1-methyl-3-phenyl-1*H*-indene (2k):



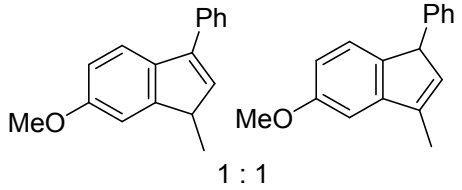
Flash column chromatography on a silica gel (petroleum ether) give **2j** (16.8 mg, 75% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61-7.58 (m, 2H), 7.49-7.44 (m, 3H), 7.41-7.36 (m, 1H), 7.31-7.27 (m, 0.6H), 7.25-7.09 (m, 2.3H), 7.04-6.98 (m, 1.2H), 6.88-6.82 (m, 0.3H), 6.49 (d, J = 2.0 Hz, 1H), 6.36-6.34 (m, 0.3H), 4.52 (s, 0.3H), 3.62-3.55 (m, 1H), 2.19 (s, 0.9H), 1.40 (d, J = 7.6Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8 (d, $J_{C\text{-}F}$ = 242.0 Hz), 152.6, 152.5, 142.8, 139.8, 139.0, 138.9, 137.7, 137.6, 136.8, 135.9, 128.8, 128.7, 127.9, 127.8, 127.7, 126.9, 124.7 (d, $J_{C\text{-}F}$ = 8.9 Hz), 121.2 (d, $J_{C\text{-}F}$ = 8.7 Hz), 113.2 (d, $J_{C\text{-}F}$ = 22.5 Hz), 111.8 (d, $J_{C\text{-}F}$ = 22.7 Hz), 110.9 (d, $J_{C\text{-}F}$ = 22.9 Hz), 106.5 (d, $J_{C\text{-}F}$ = 23.2 Hz), 54.7, 44.1, 16.4, 13.0.

HRMS (EI) m/z calcd for $C_{16}H_{13}F^+$ [M^+]: 224.0996; found: 224.0997.

6-methoxy-1-methyl-3-phenyl-1*H*-indene (2l):



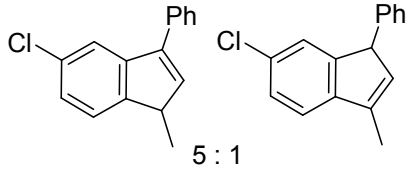
Flash column chromatography on a silica gel (petroleum ether) give **2l** (8.5 mg, 36% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66-7.62 (m, 2H), 7.50-7.37 (m, 4H), 7.32-7.27 (m, 2H), 7.25-7.21 (m, 1H), 7.17-7.10 (m, 4H), 6.94-6.88 (m, 2H), 6.77-6.73 (m, 1H), 6.44 (d, J = 1.8 Hz, 1H), 6.33-6.31 (m, 1H), 4.55-4.52 (m, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.63-3.56 (m, 1H), 2.23 (s, 3H), 1.42 (d, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 158.4, 152.4, 147.2, 143.0, 141.1, 140.6, 139.5, 136.3, 136.2, 136.1, 128.7, 128.7, 127.9, 127.7, 127.7, 126.7, 124.4, 121.0, 111.7, 110.7, 109.9, 105.3, 55.8, 55.7, 54.6, 44.1, 16.7, 13.2.

HRMS (EI) m/z calcd for $C_{17}H_{16}O^+$ [M^+]: 236.1196; found: 236.1202.

5-chloro-1-methyl-3-phenyl-1*H*-indene (2m):



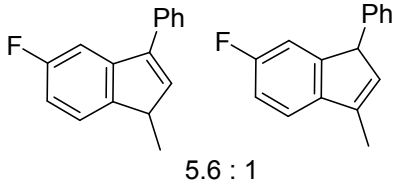
Flash column chromatography on a silica gel (petroleum ether) give **2l** (14.9 mg, 62% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58-7.55 (m, 2H), 7.51-7.44 (m, 3H), 7.41-7.36 (m, 2H), 7.30-7.27 (m, 0.6H), 7.25-7.18 (m, 1.6H), 7.11-7.08 (m, 0.4H), 6.56 (d, J = 2.1 Hz, 1H), 6.27-6.25 (m, 0.2H), 4.53-4.51 (m, 0.2H), 3.62-3.54 (m, 1H), 2.19 (s, 0.6H), 1.38 (d, J = 7.6Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.4, 148.4, 144.8, 142.7, 139.6, 139.1, 135.3, 134.9, 132.4, 131.3, 128.7, 128.7, 127.9, 127.7, 127.6, 126.9, 126.8, 125.0, 124.2, 123.9, 120.7, 119.9, 55.0, 43.8, 16.1, 13.0.

HRMS (EI) m/z calcd for $C_{16}H_{13}Cl^+$ [M^+]: 240.0700; found: 240.0699.

5-fluoro-1-methyl-3-phenyl-1*H*-indene (2n):



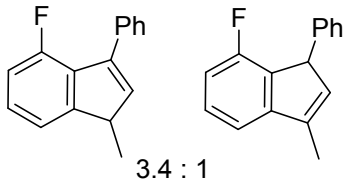
Flash column chromatography on a silica gel (petroleum ether) give **2m** (15.5 mg, 69% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59-7.56 (m, 2H), 7.49-7.44 (m, 2H), 7.42-7.37 (m, 2H), 7.31-7.27 (m, 0.36H), 7.25-7.22 (m, 1.36H), 7.12-7.09 (m, 0.36H), 7.03-6.92 (m, 1.36H), 6.60 (d, J = 2.0 Hz, 1H), 6.25-6.23 (m, 0.18H), 4.53-4.51 (m, 0.18H), 3.62-3.54 (m, 1H), 2.20 (s, 0.54H), 1.39 (d, J = 7.6Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, $J_{C\text{-}F}$ = 240.0 Hz), 151.0, 150.9, 145.7, 145.1, 145.0, 143.0, 142.9, 140.1, 139.6, 139.1, 135.6, 134.3, 128.8, 128.0, 127.9, 127.7, 127.0, 123.8 (d, $J_{C\text{-}F}$ = 9.2 Hz), 119.8 (d, $J_{C\text{-}F}$ = 8.7 Hz), 113.5 (d, $J_{C\text{-}F}$ = 22.5 Hz), 111.8 (d, $J_{C\text{-}F}$ = 22.8 Hz), 111.7 (d, $J_{C\text{-}F}$ = 23.3 Hz), 107.8 (d, $J_{C\text{-}F}$ = 23.8 Hz), 55.2, 43.7, 16.4, 13.2.

HRMS (EI) m/z calcd for $C_{16}H_{13}F^+$ [M^+]: 224.0996; found: 224.0994.

4-fluoro-1-methyl-3-phenyl-1*H*-indene (2o):



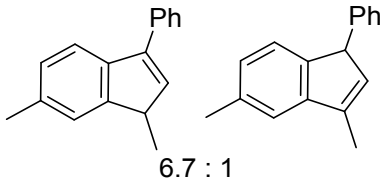
Flash column chromatography on a silica gel (petroleum ether) give **3n** (9.4 mg, 42% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60-7.55 (m, 2H), 7.44-7.35 (m, 3H), 7.33-7.26 (m, 0.9H), 7.25-7.18 (m, 2.3H), 7.15-7.11 (m, 1H), 7.01-6.94 (m, 0.9H), 6.88-6.82 (m, 0.3H), 6.41 (d, J = 2.1 Hz, 1H), 6.26-6.24 (m, 0.3H), 4.74-4.72 (m, 0.3H), 3.68-3.59 (m, 1H), 2.20 (s, 0.9H), 1.39 (d, J = 7.6Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.8 (d, $J_{C\text{-}F}$ = 248.5 Hz), 153.7, 153.6, 141.9, 141.8, 139.5, 139.4, 138.1, 136.3, 135.6, 129.1 (d, $J_{C\text{-}F}$ = 7.1 Hz), 128.5, 128.2 (d, $J_{C\text{-}F}$ = 3.6 Hz), 127.9, 127.6, 127.5, 126.8, 126.7, 118.9 (d, $J_{C\text{-}F}$ = 3.2 Hz), 115.2 (d, $J_{C\text{-}F}$ = 2.9 Hz), 114.1 (d, $J_{C\text{-}F}$ = 21.7 Hz), 112.7 (d, $J_{C\text{-}F}$ = 20.7 Hz), 52.8, 44.6, 16.3, 13.0.

HRMS (EI) m/z calcd for $C_{16}H_{13}F^+$ [M^+]: 224.0996; found: 224.0997.

1,6-dimethyl-3-phenyl-1*H*-indene (2p):



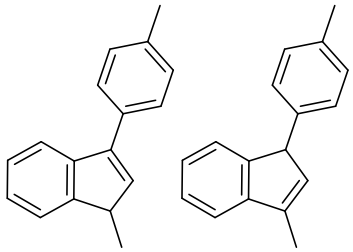
Flash column chromatography on a silica gel (petroleum ether) give **3qa** (17.2 mg, 78% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69-7.64 (m, 2H), 7.54-7.48 (m, 2H), 7.46-7.40 (m, 3H), 7.35-7.26 (m, 0.6H), 6.57-6.54 (m, 1H), 6.26-6.23 (m, 0.15H), 4.57-4.55 (m, 0.15H), 3.66-3.59 (m, 1H), 2.48-2.45 (m, 3H), 2.39-2.37 (m, 0.45H), 2.27-2.24 (m, 0.45H), 1.46-1.41 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 143.4, 138.6, 136.3, 136.2, 135.1, 133.7, 128.7, 128.1, 127.9, 127.7, 127.5, 126.8, 126.0, 124.8, 122.9, 121.3, 118.9, 55.1, 43.9, 21.8, 16.6, 13.2.

HRMS (EI) m/z calcd for $C_{17}H_{16}^+$ [M^+]: 220.1247; found: 220.1247.

1-methyl-3-(p-tolyl)-1*H*-indene (2q):



3.4 : 1

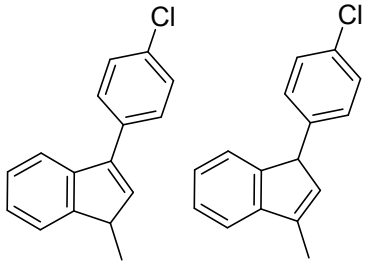
Flash column chromatography on a silica gel (petroleum ether) give **2p** (16.0 mg,73% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60-7.49 (m, 4H), 7.35-7.27 (m, 4.6H), 7.25-7.15 (m, 0.6H), 7.11-7.01 (m, 1.2H), 6.51 (d, J = 1.8 Hz, 1H), 6.28-6.26 (m, 0.3H), 4.54 (d, J = 3.1 Hz, 0.3H), 3.64-3.57 (m, 1H), 2.44 (s, 3H), 2.33 (s, 0.9H), 2.23 (s, 0.9H), 1.42 (d, J =7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 149.0, 145.6, 143.3, 139.6, 137.7, 137.5, 136.3, 134.9, 133.2, 129.4, 129.4, 127.8, 127.7, 126.7, 126.5, 125.3, 125.1, 123.8, 123.1, 120.6, 119.2, 54.9, 44.1, 21.5, 21.2, 16.4,13.1.

HRMS (EI) m/z calcd for $C_{17}H_{16}^+$ [M^+]: 220.1247; found: 220.1247.

3-(4-chlorophenyl)-1-methyl-1*H*-indene (2r):



5.6 : 1

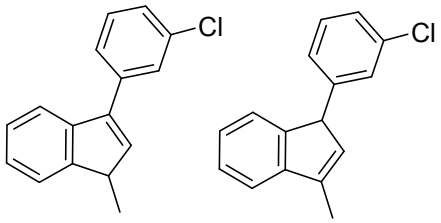
Flash column chromatography on a silica gel (petroleum ether) give **2r** (18.9 mg, 79% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.58-7.50 (m, 4H), 7.46-7.43 (m, 2H), 7.37-7.28 (m, 2.36H), 7.26-7.19 (m, 0.72H), 7.07-7.04 (m, 0.36H), 6.54 (d, J = 2.2 Hz, 1H), 6.25-6.23 (m, 0.18H), 4.53-4.51 (m, 0.18H), 3.66-3.58 (m, 1H), 2.24 (s, 0.54H), 1.42 (d, J =7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 142.8, 142.4, 138.7, 134.6, 134.2, 133.5, 129.3, 129.2, 128.9, 128.9, 127.0, 126.6, 125.5, 125.5, 123.8, 123.3, 120.3, 119.3, 54.5, 44.3, 16.3, 13.2.

HRMS (EI) m/z calcd for $C_{16}H_{13}Cl^+$ [M^+]: 240.0700; found: 240.0707.

3-(3-chlorophenyl)-1-methyl-1*H*-indene (2s):



5.6 : 1

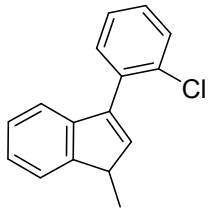
Flash column chromatography on a silica gel (petroleum ether) give **2s** (13.4 mg, 56% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.63-7.49 (m, 4H), 7.42-7.28 (m, 4.36H), 7.26-7.19 (m, 0.72H), 7.10-7.03 (m, 0.36H), 6.56 (d, J = 2.2 Hz, 1H), 6.25-6.23 (m, 0.18H), 4.53-4.51 (m, 0.18H), 3.66-3.59 (m, 1H), 2.24 (s, 0.54H), 1.42 (d, J =7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 137.8, 137.5, 134.4, 133.2, 129.9, 129.1, 125.2, 123.2, 123.1, 123.0, 122.3, 122.3, 121.9, 121.5, 121.2, 120.8, 120.7, 119.1, 118.5, 115.6, 114.6, 45.0, 39.5, 11.5, 8.4.

HRMS (EI) m/z calcd for $C_{16}H_{13}Cl^+$ [M^+]: 240.0700; found: 240.0700.

3-(2-chlorophenyl)-1-methyl-1*H*-indene (2t):



Flash column chromatography on a silica gel (petroleum ether) give **2t** (8.9 mg, 37% yield) as a colorless oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53-7.47 (m, 2H), 7.43-7.39 (m, 1H), 7.35-7.30 (m, 2H), 7.28-7.25 (m, 2H), 7.20-7.15 (m, 1H), 6.53 (d, J = 2.0 Hz, 1H), 3.72-3.63 (m, 1H), 1.43 (d, J =7.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.2, 143.5, 140.9, 140.4, 135.0, 133.3, 131.0, 129.9, 128.8, 126.6, 126.2, 125.1, 122.8, 120.8, 44.5, 16.1.

HRMS (EI) m/z calcd for $C_{16}H_{13}Cl^+$ [M^+]: 240.0700; found: 240.0702.

References:

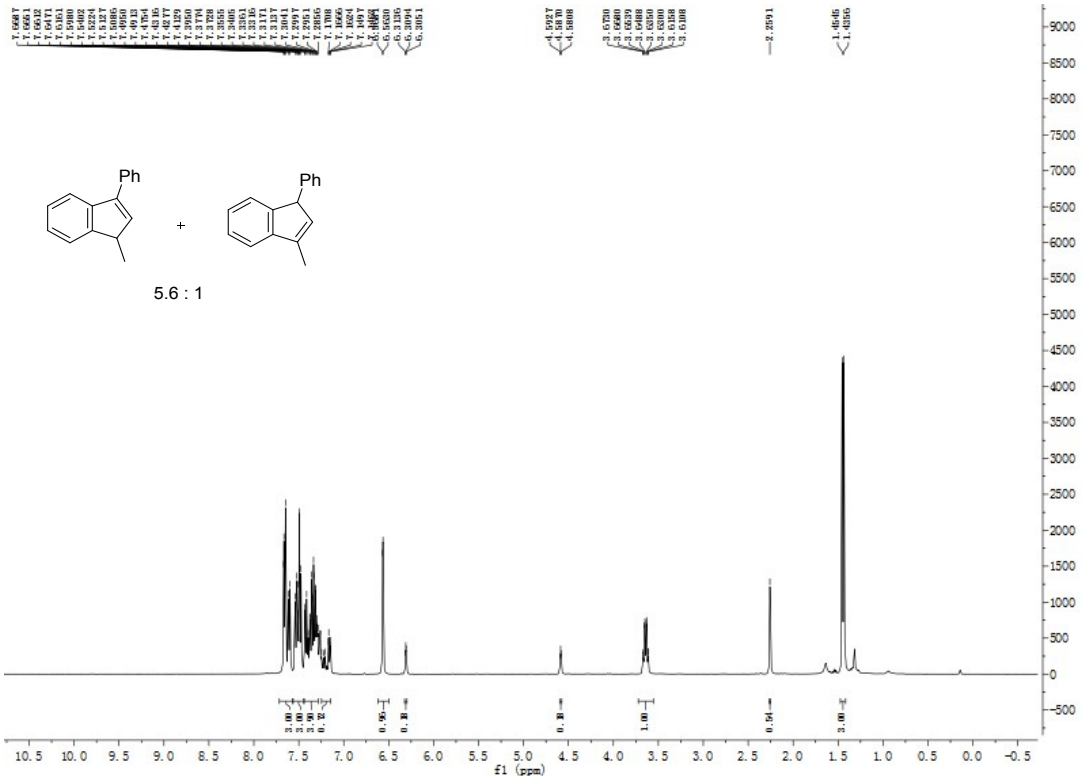
(1) E. J. T. Phipps and T. Rovis, *J. Am. Chem. Soc.,* 2019, **141**, 6807–6811.

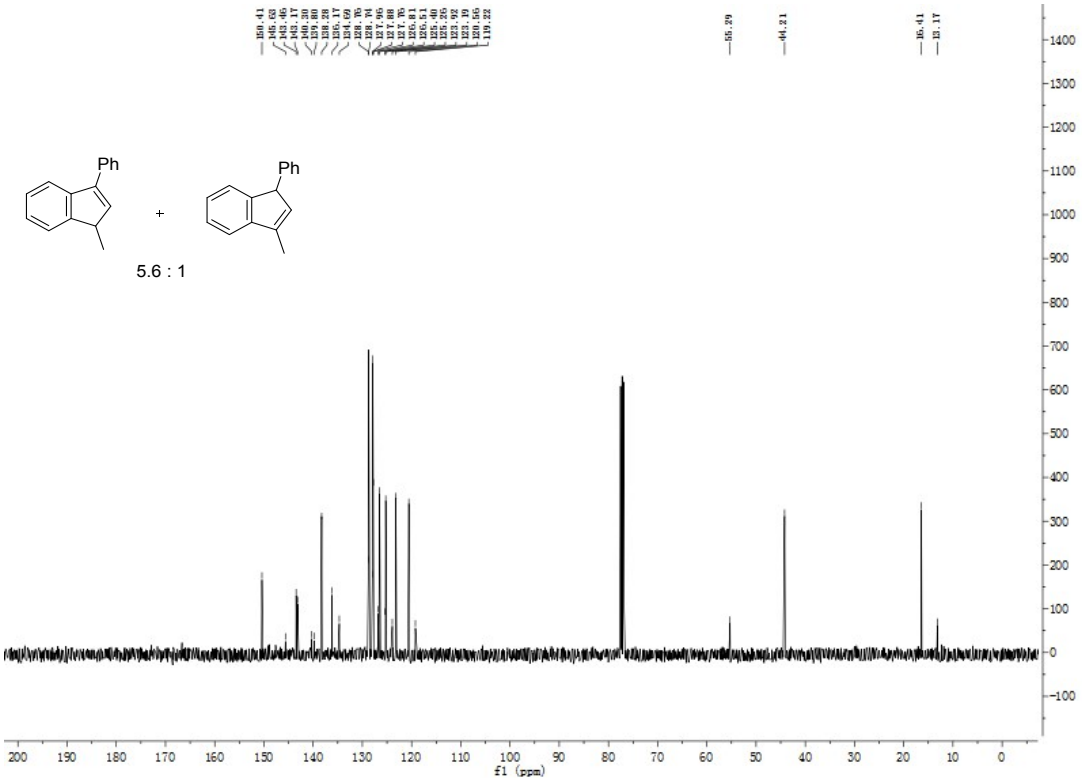
(2) X. Chang, P.-L. Ma, H.-C. Chen, C.-Y. Li and P. Wang, *Angew. Chem. Int. Ed.,* 2020, **59**, 8937–8940.

(3) Y.-T. Jiang, Z.-Z. Yu, Y.-K. Zhang, and B. Wang, *Org. Lett.,* 2018, **20**, 3728−3731.

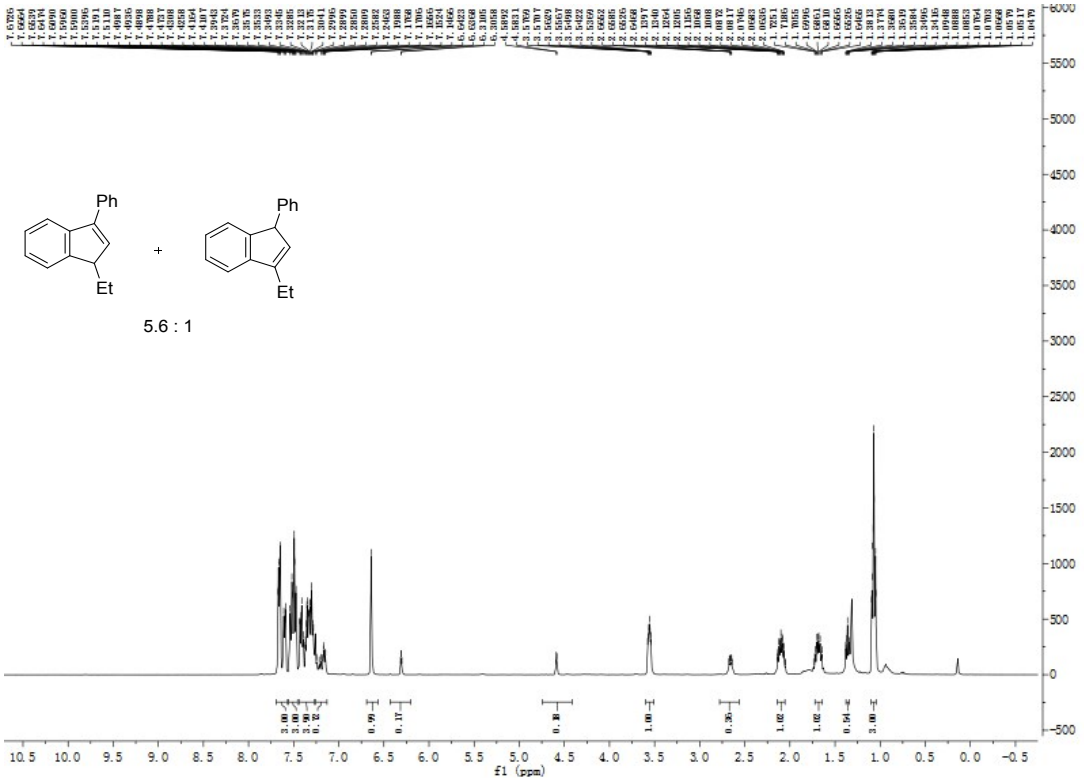
5. ^{1}H NMR, ^{13}C NMR Spectra

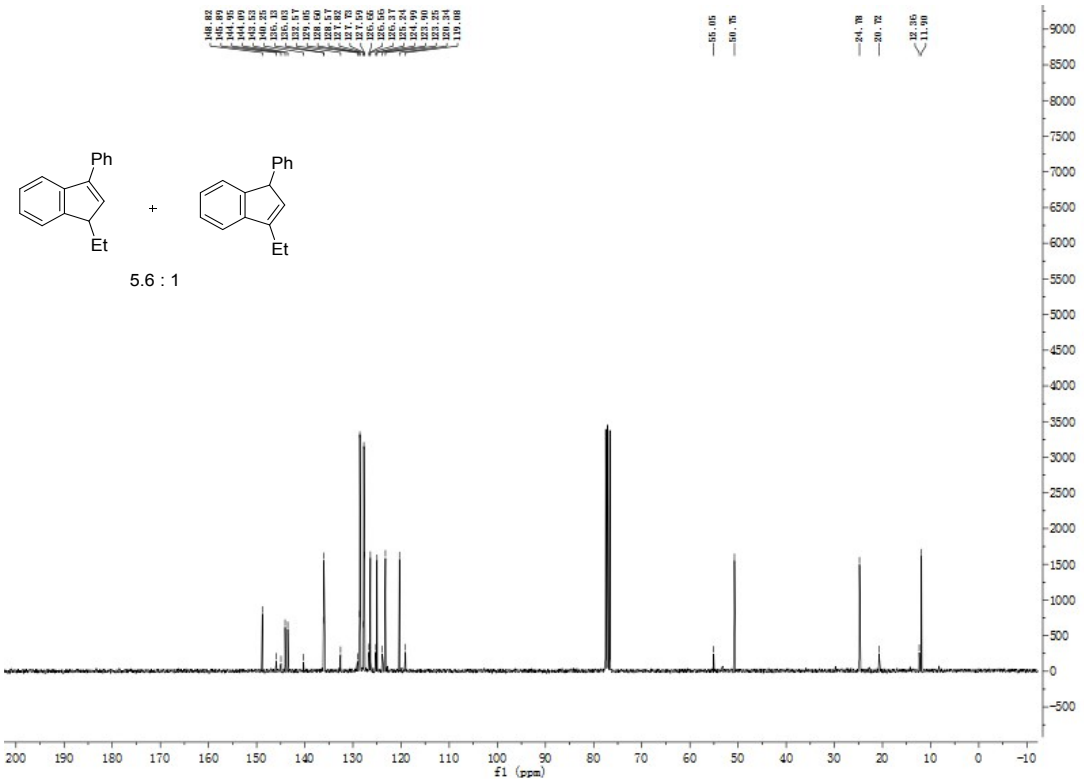
1-methyl-3-phenyl-1*H*-indene (2a):



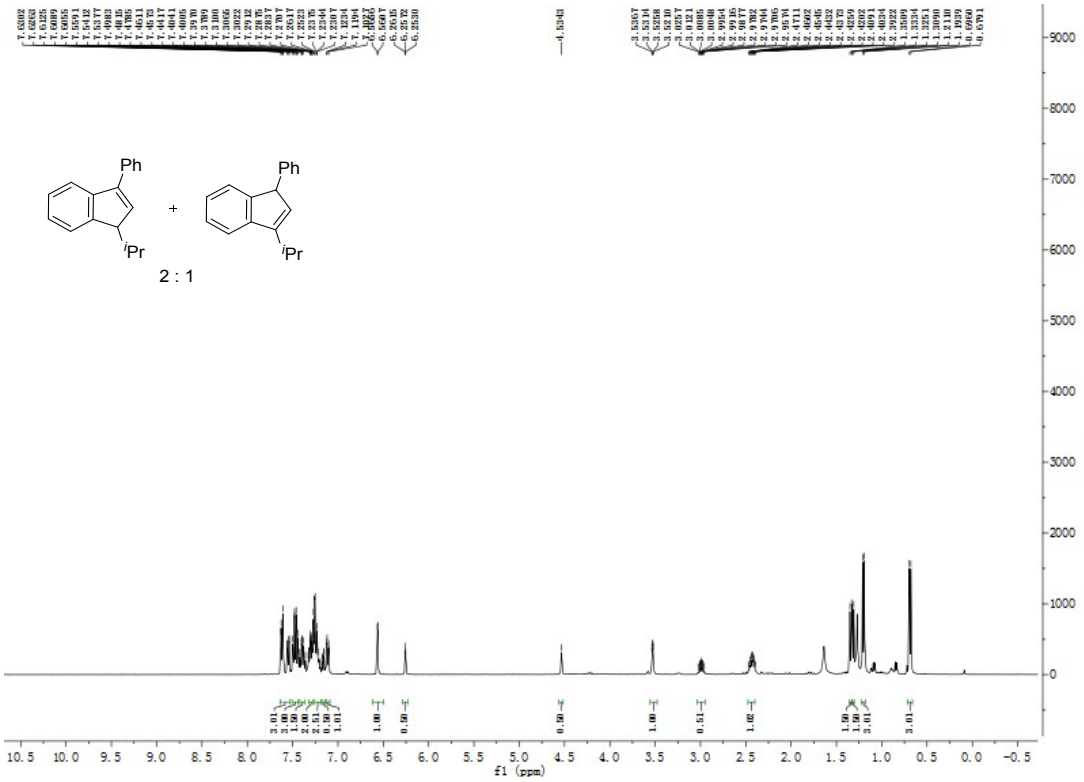


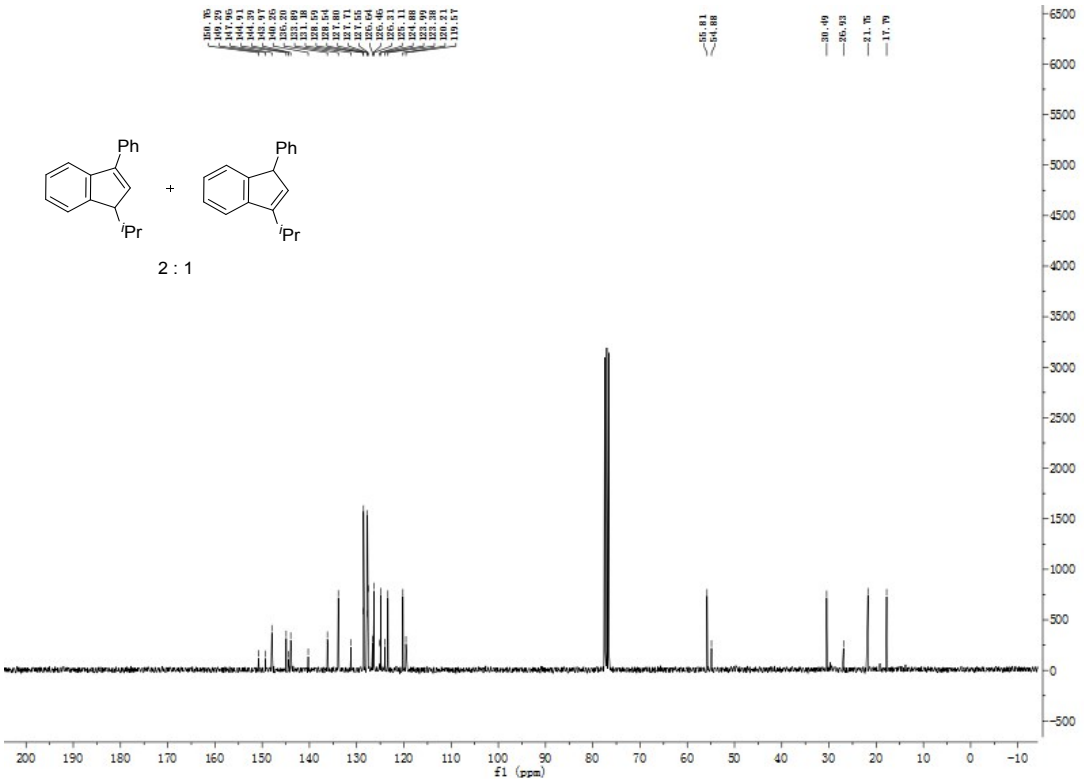
1-ethyl-3-phenyl-1*H*-indene (2b):



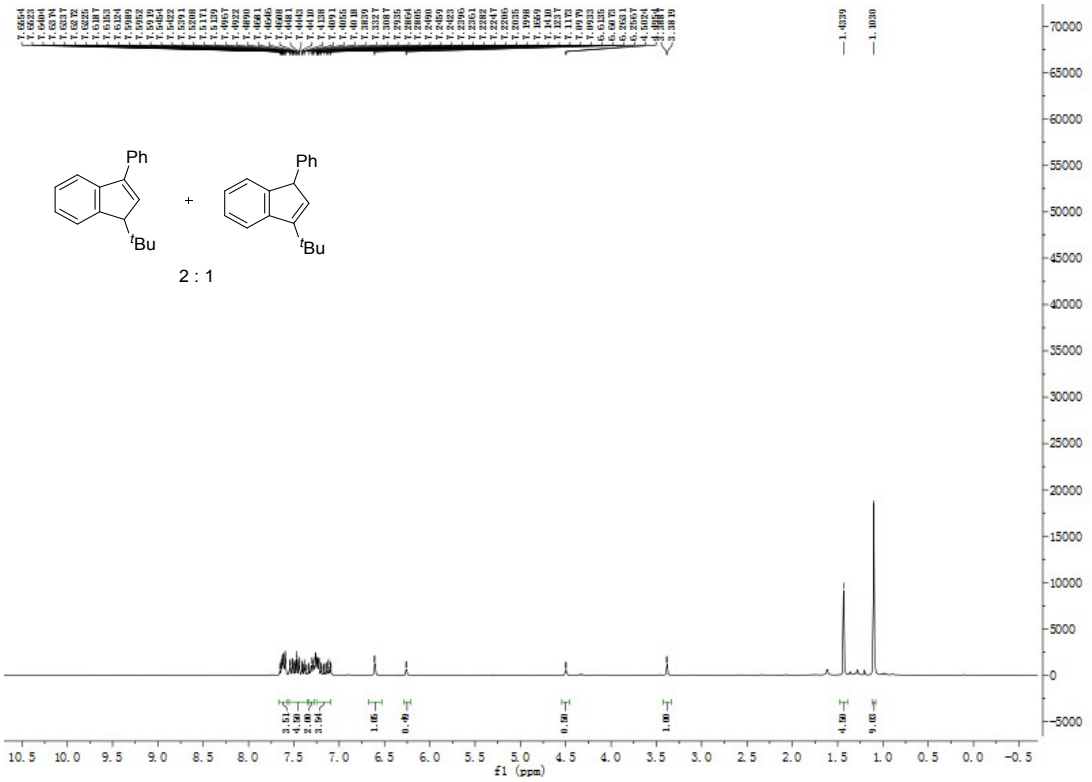


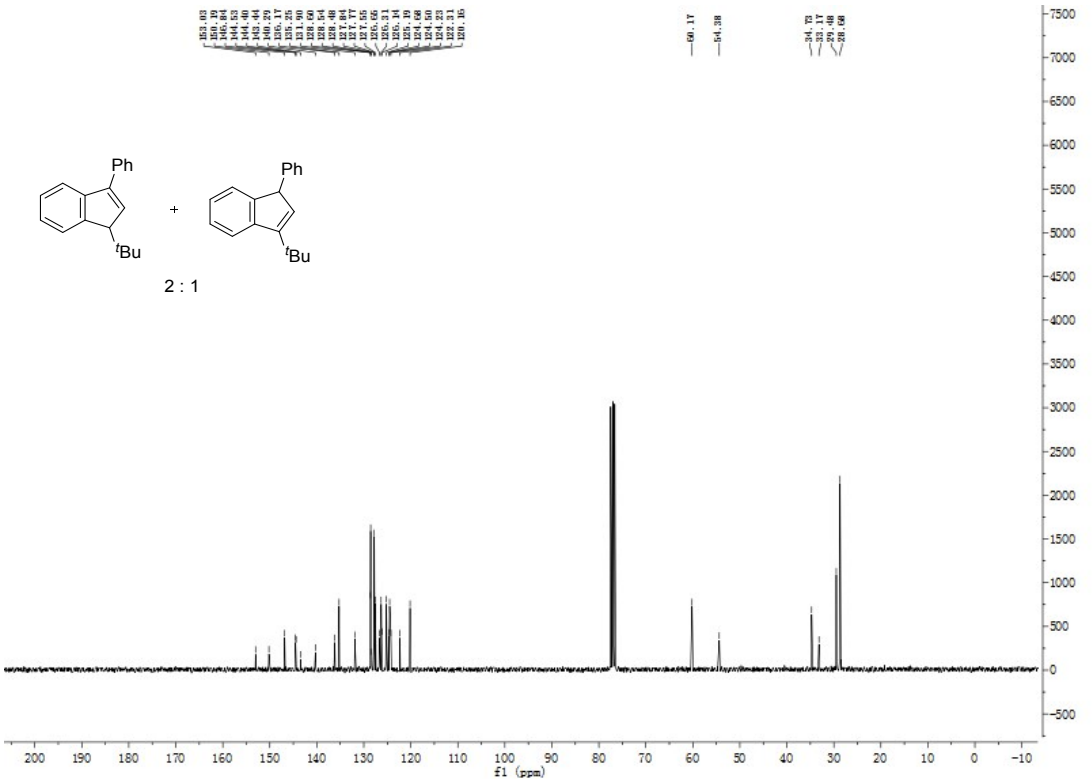
1-isopropyl-3-phenyl-1*H*-indene (2c):



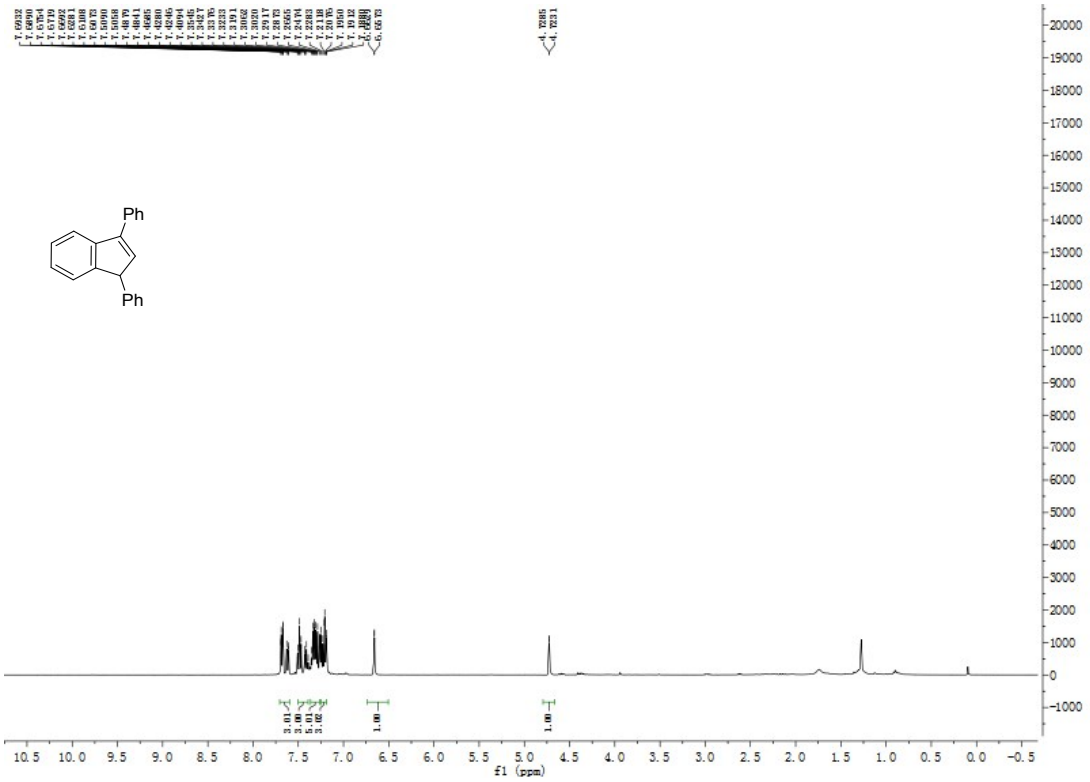


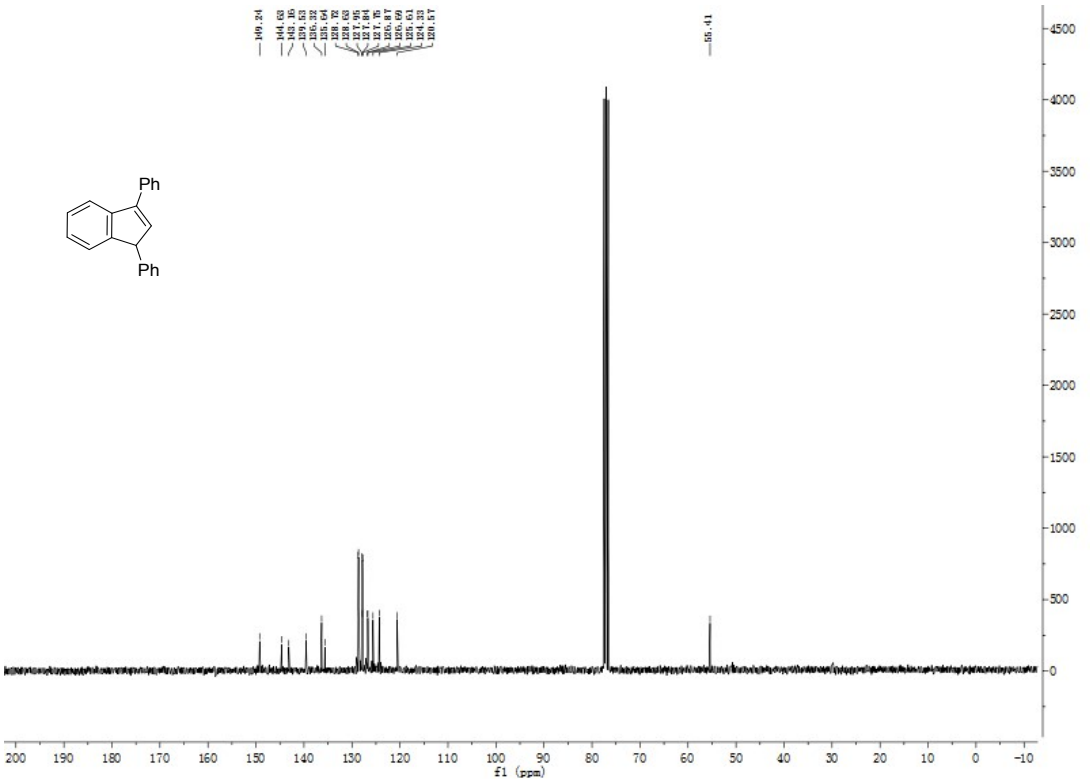
1-(tert-butyl)-3-phenyl-1*H*-indene (2d):



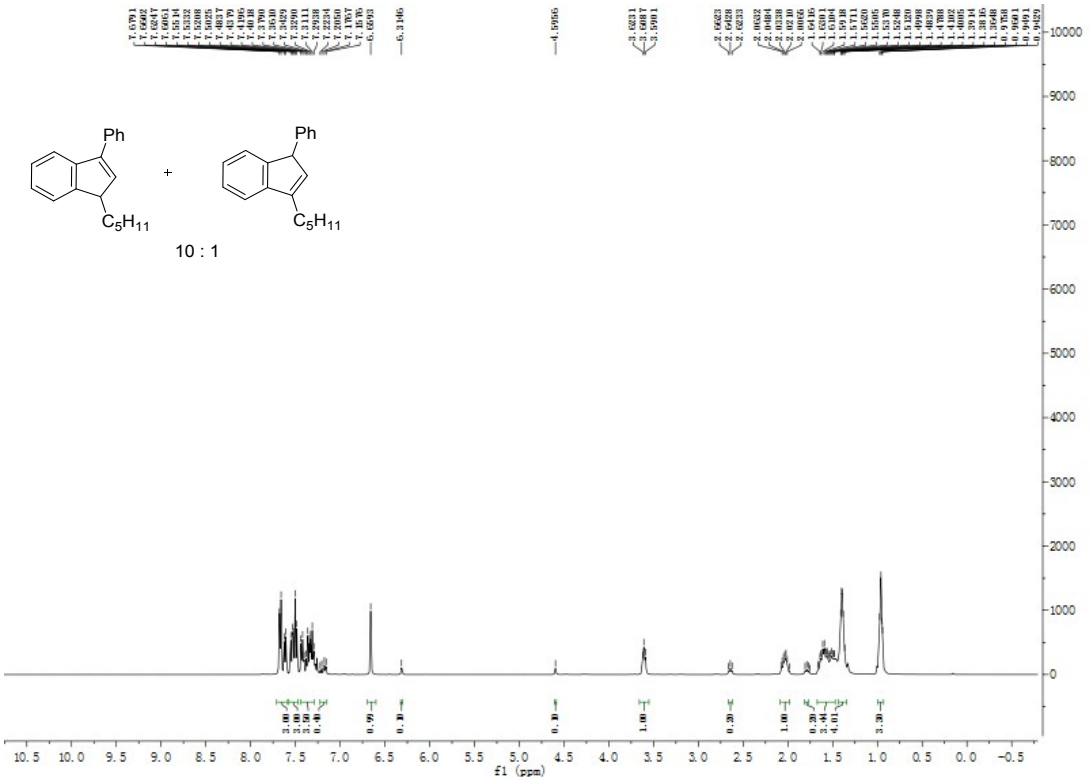


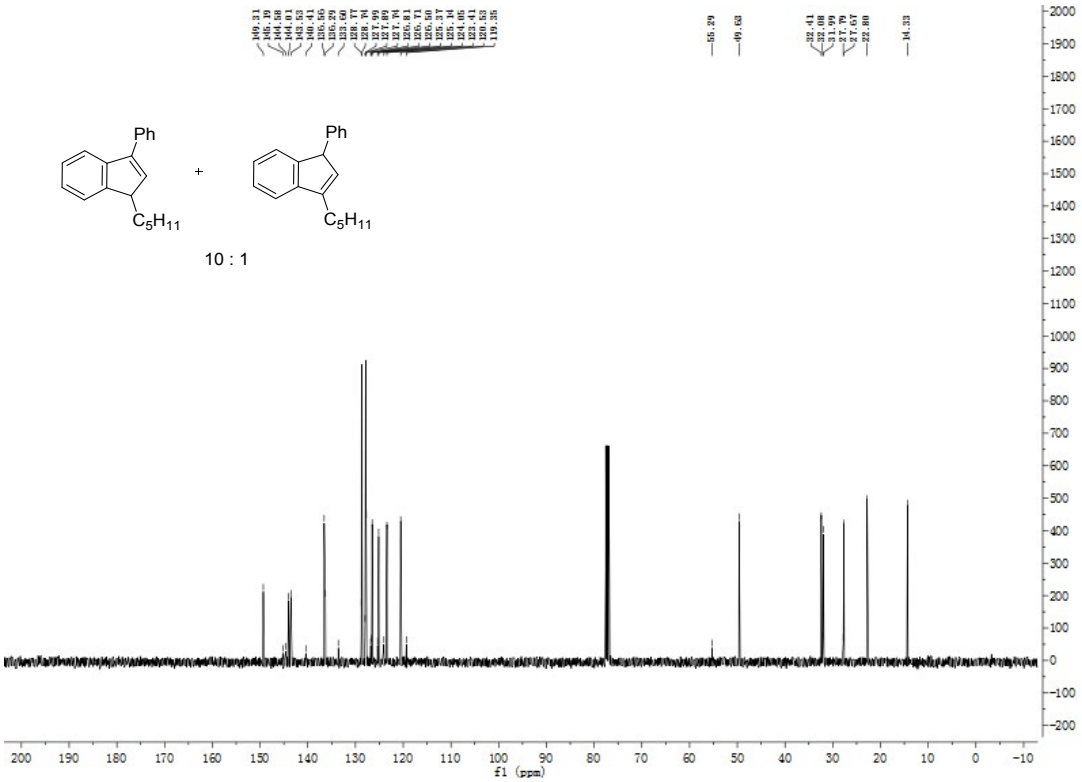
1,3-diphenyl-1*H*-indene (2e):



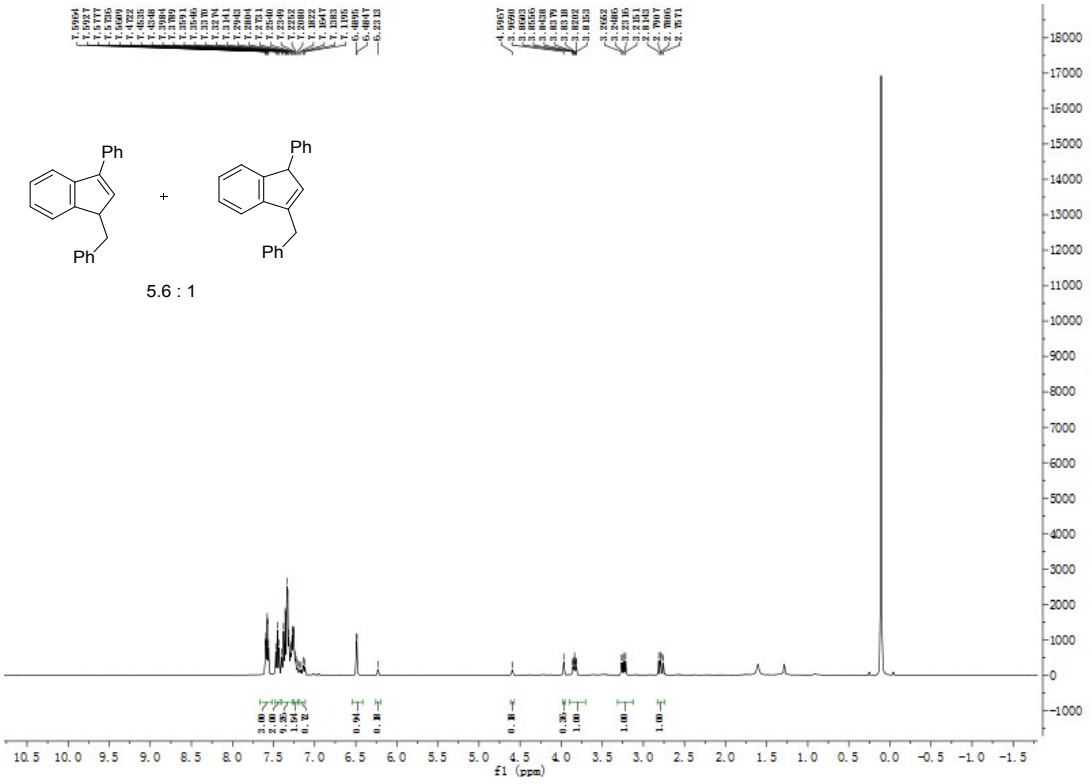


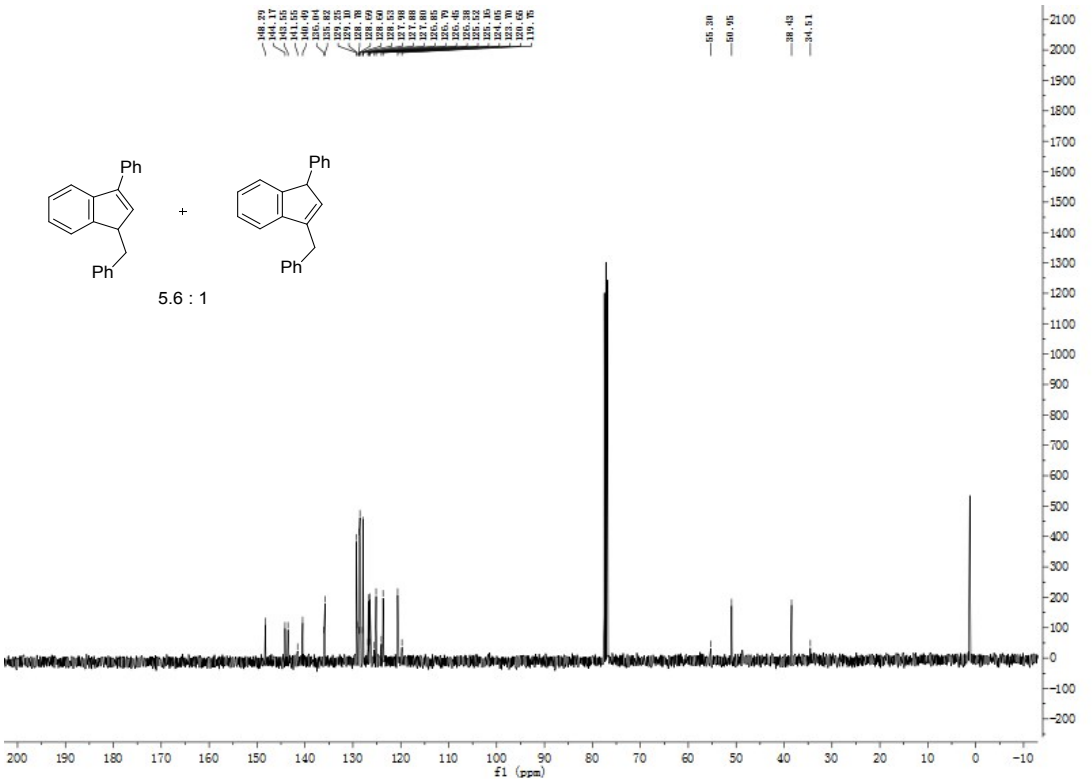
1- pentyl-3-phenyl-1*H*-indene (2f):



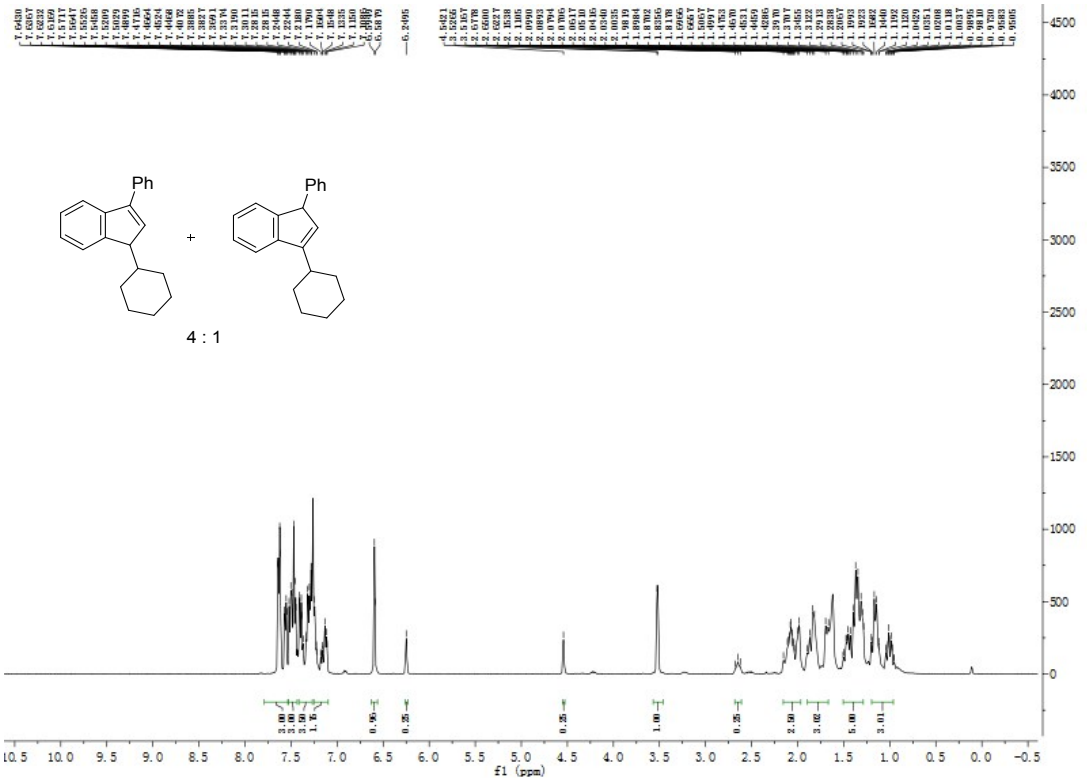


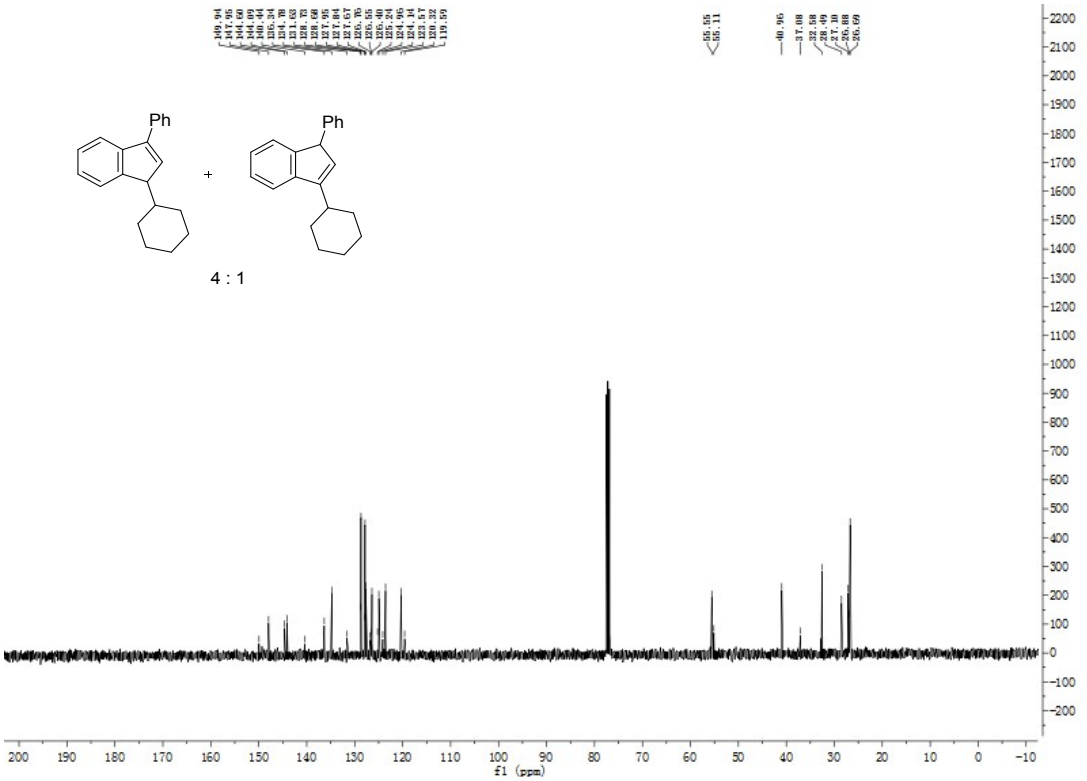
1-benzyl-3-phenyl-1*H*-indene (2g):



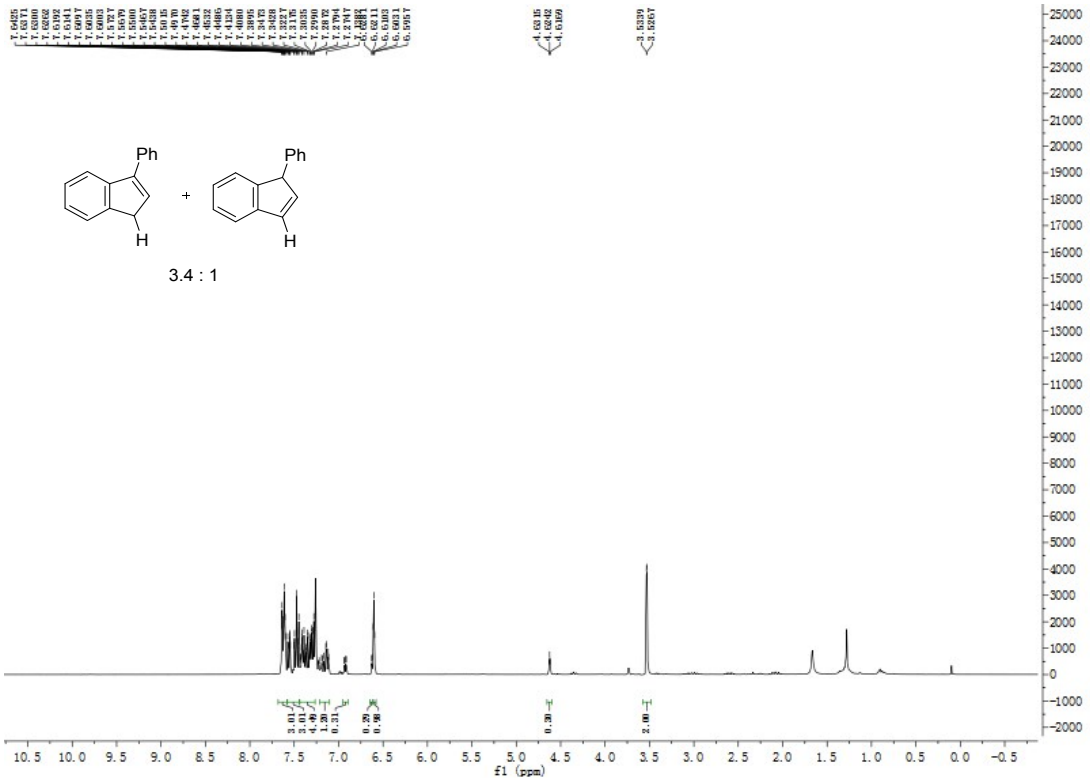


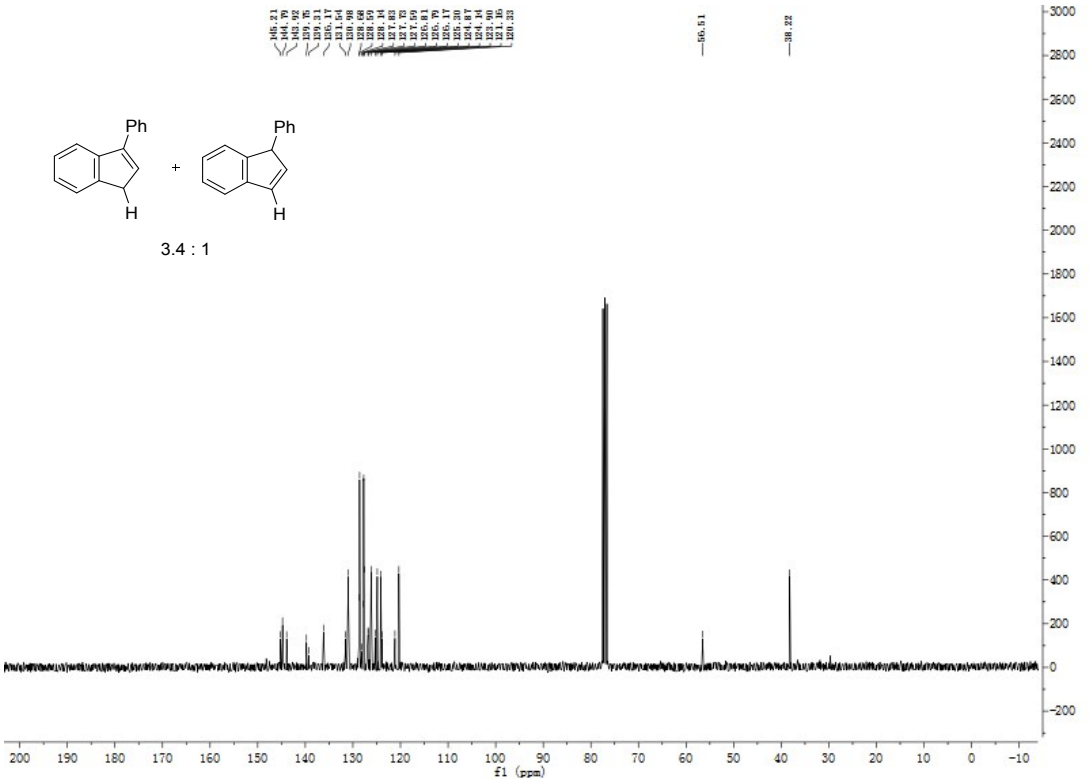
1-cyclohexyl-3-phenyl-1*H*-indene (2h):



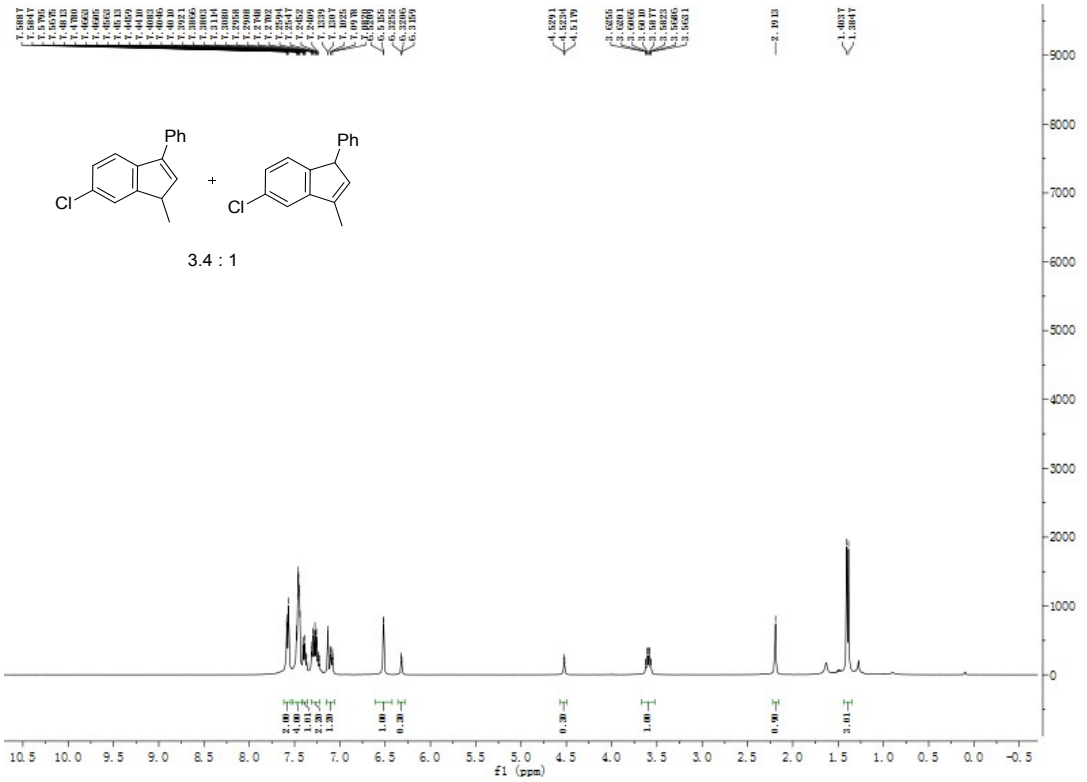


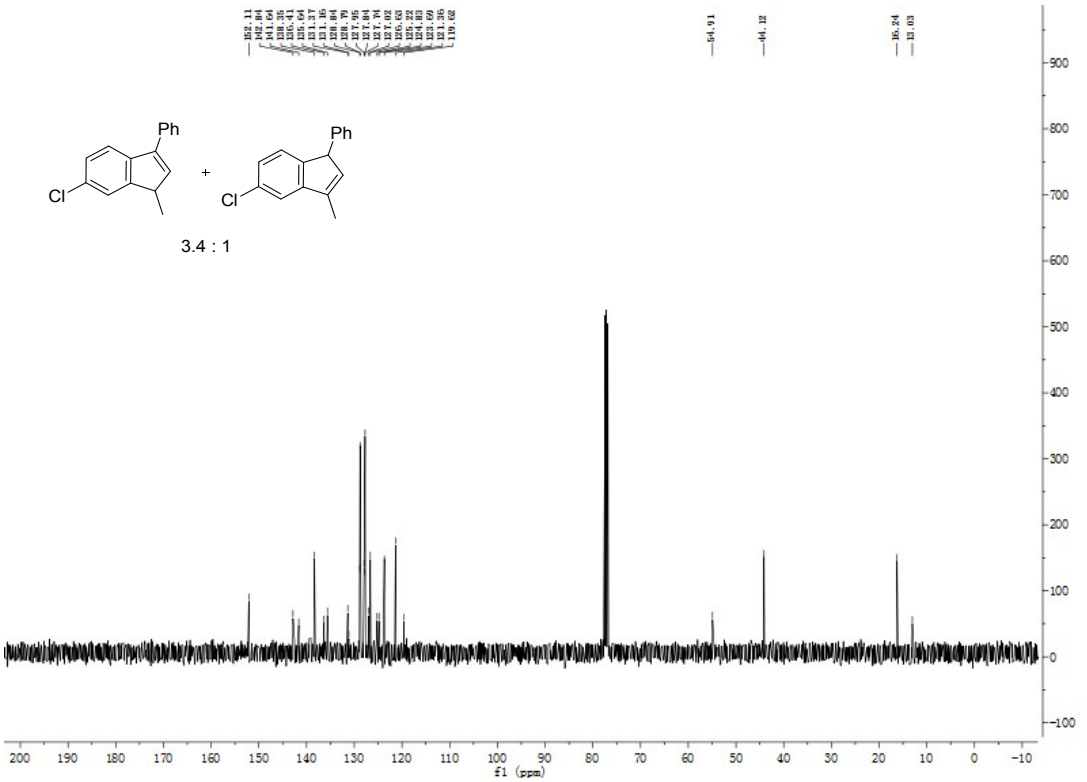
3-phenyl-1*H*-indene (2i):



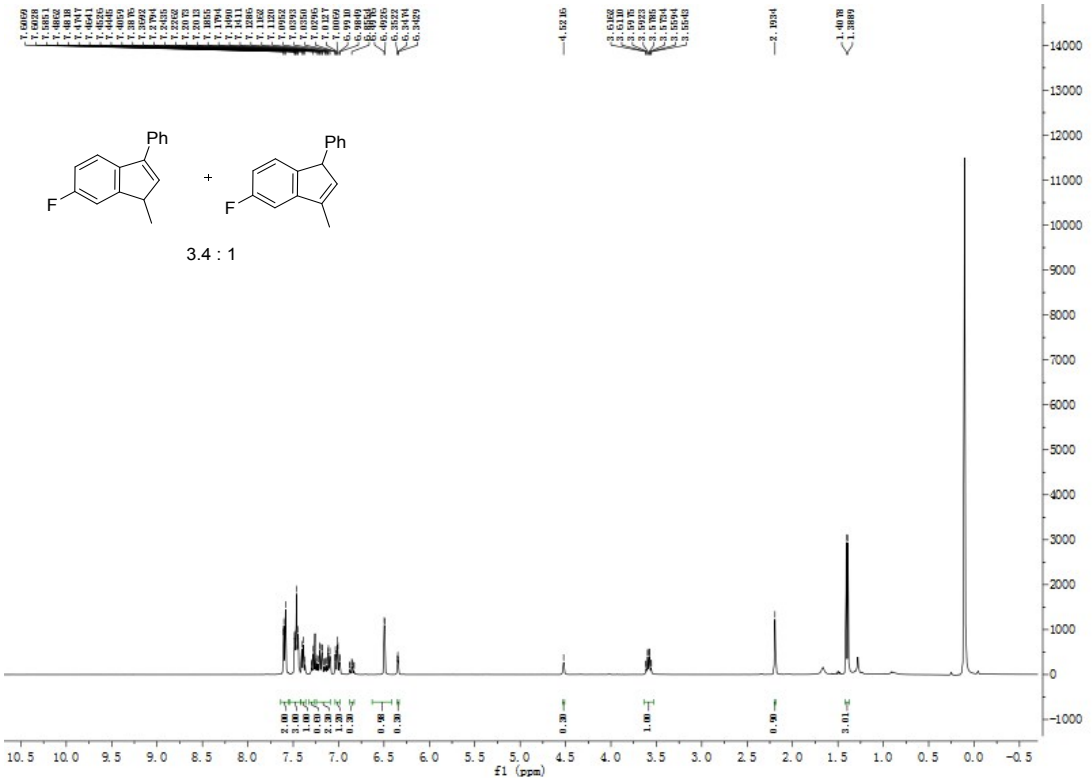


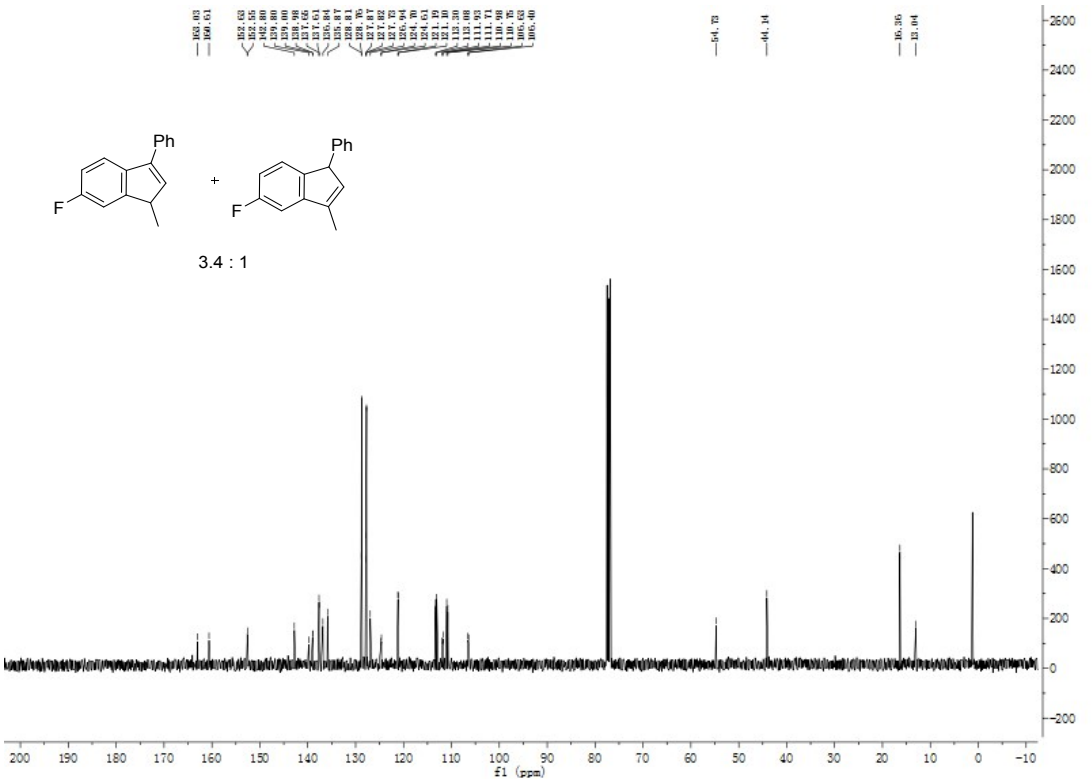
6-chloro-1-methyl-3-phenyl-1*H*-indene (2j):



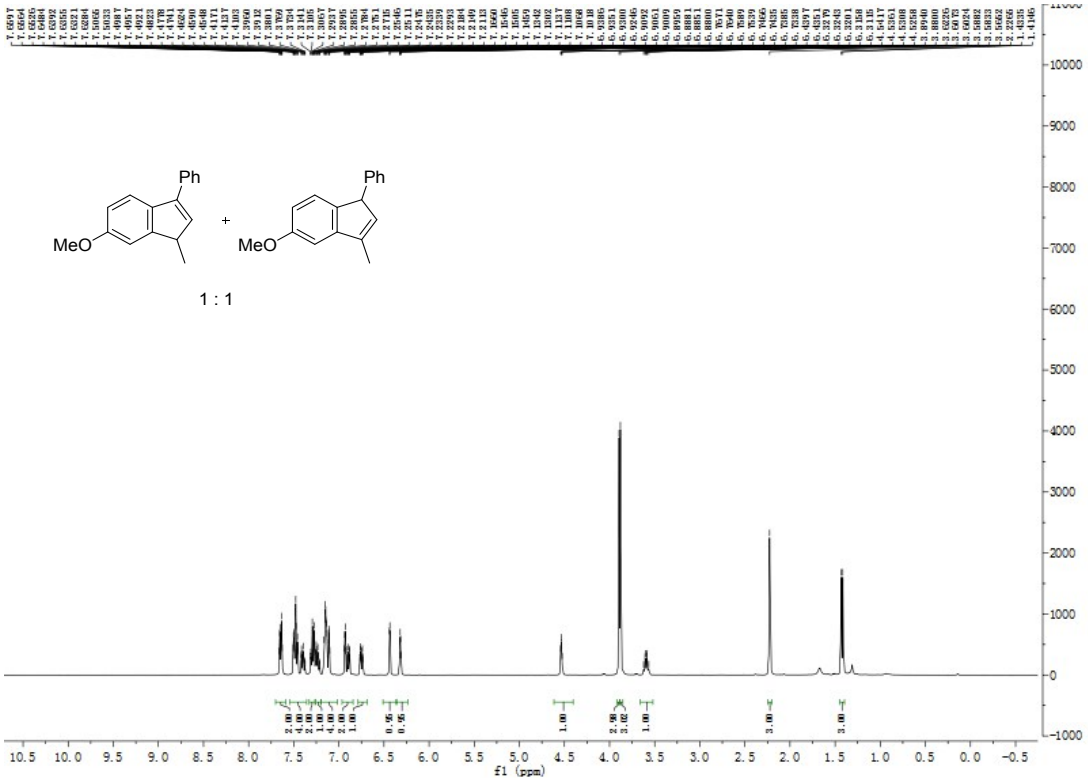


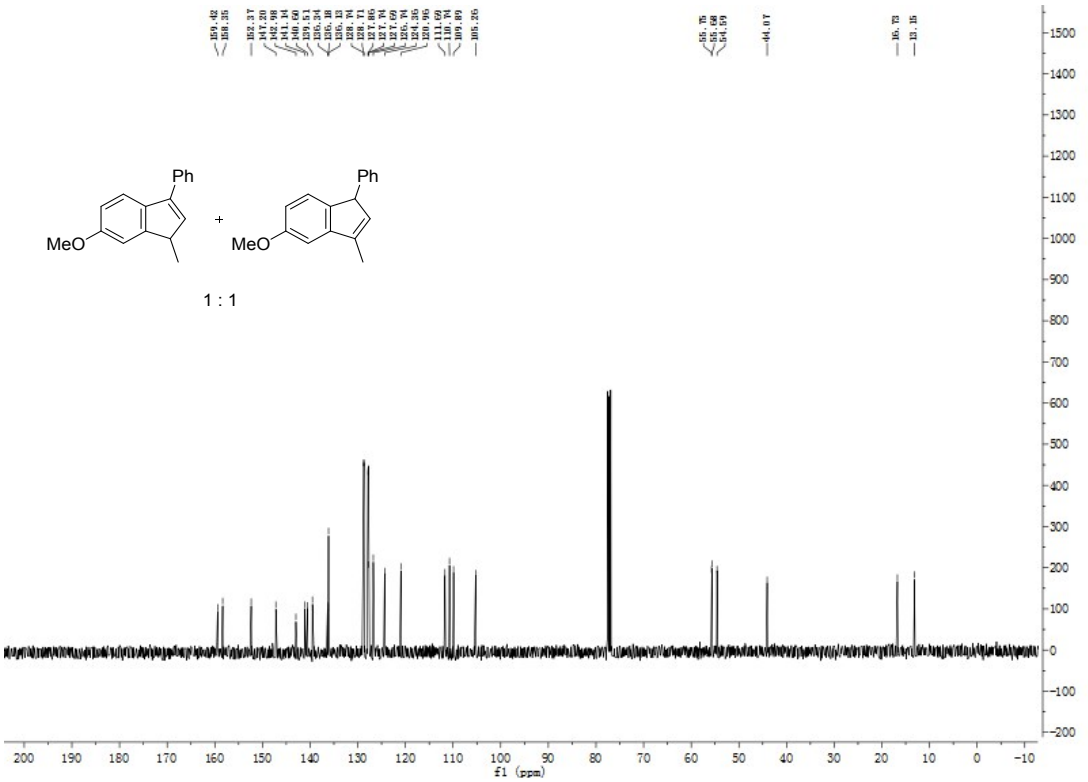
6-fluoro-1-methyl-3-phenyl-1*H*-indene (2k):



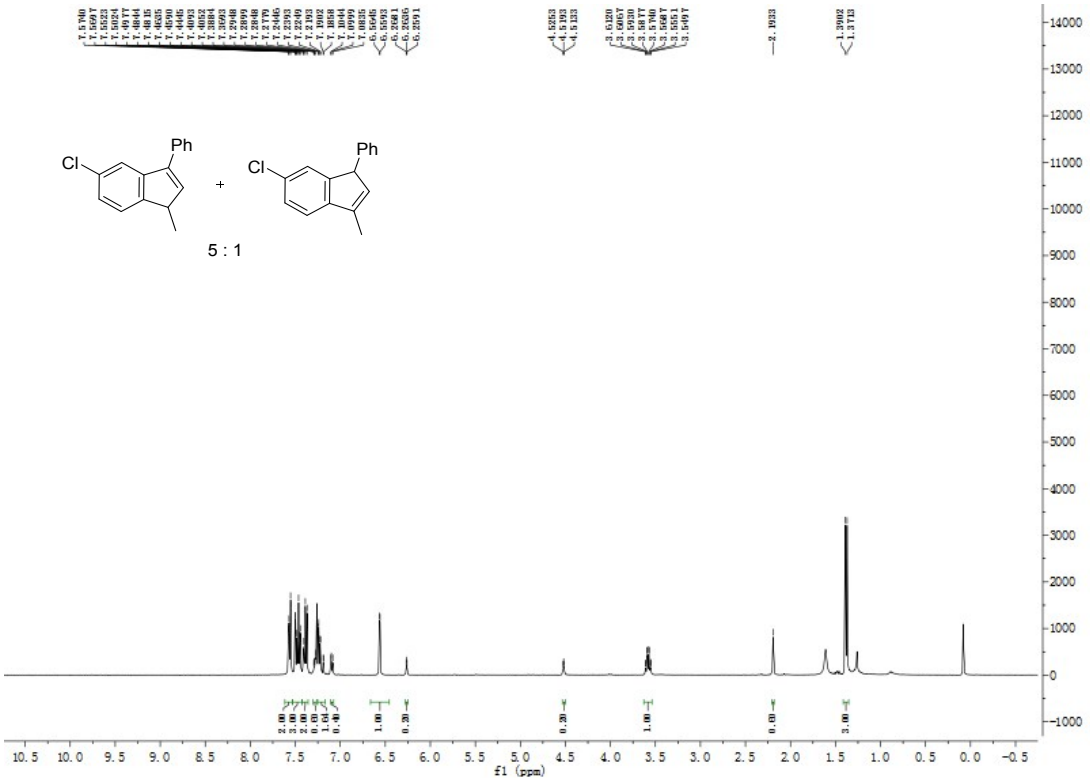


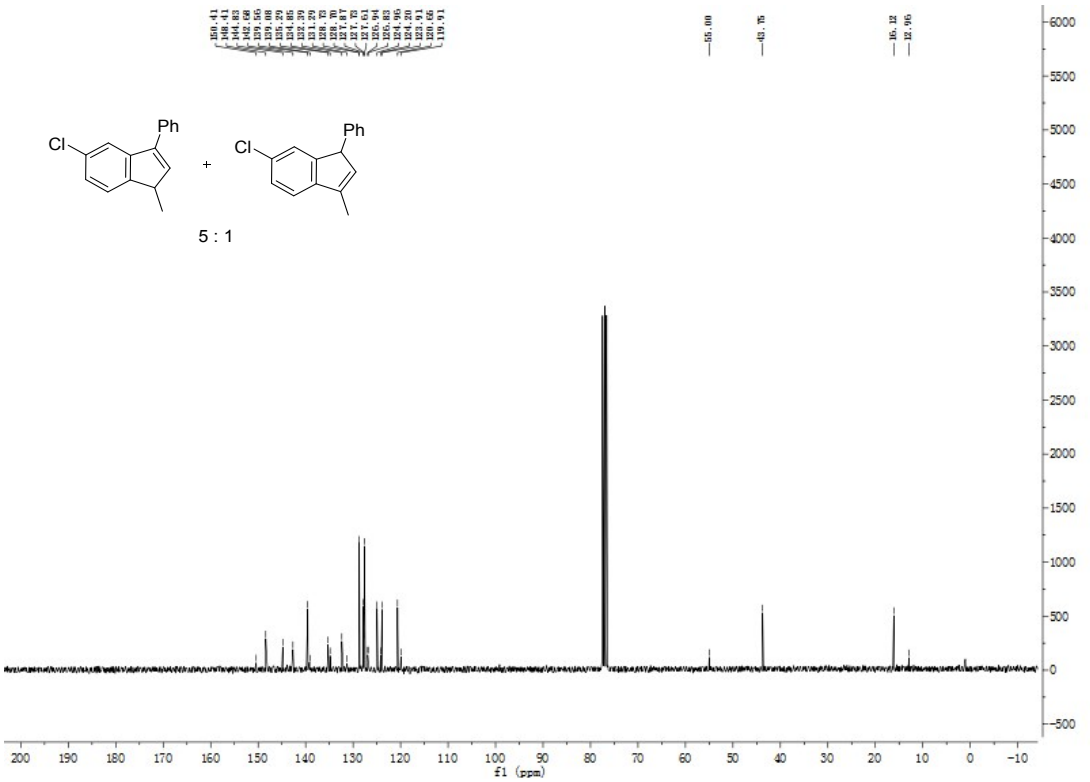
6-methoxy-1-methyl-3-phenyl-1*H*-indene (2l):



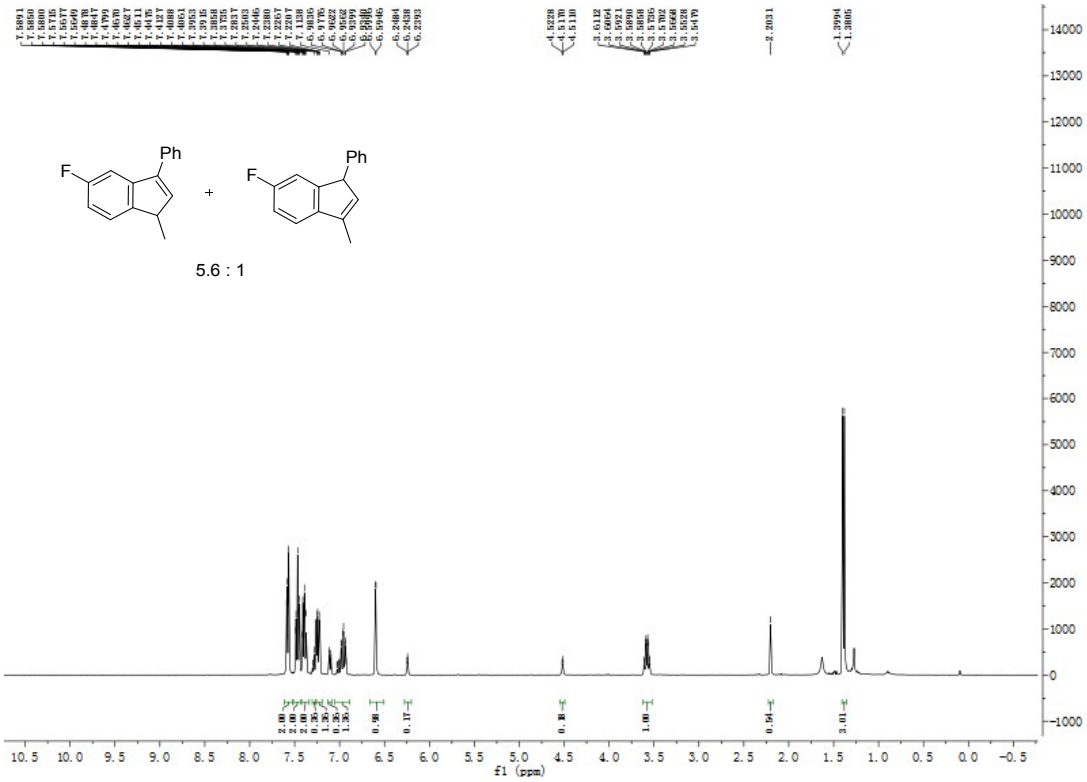


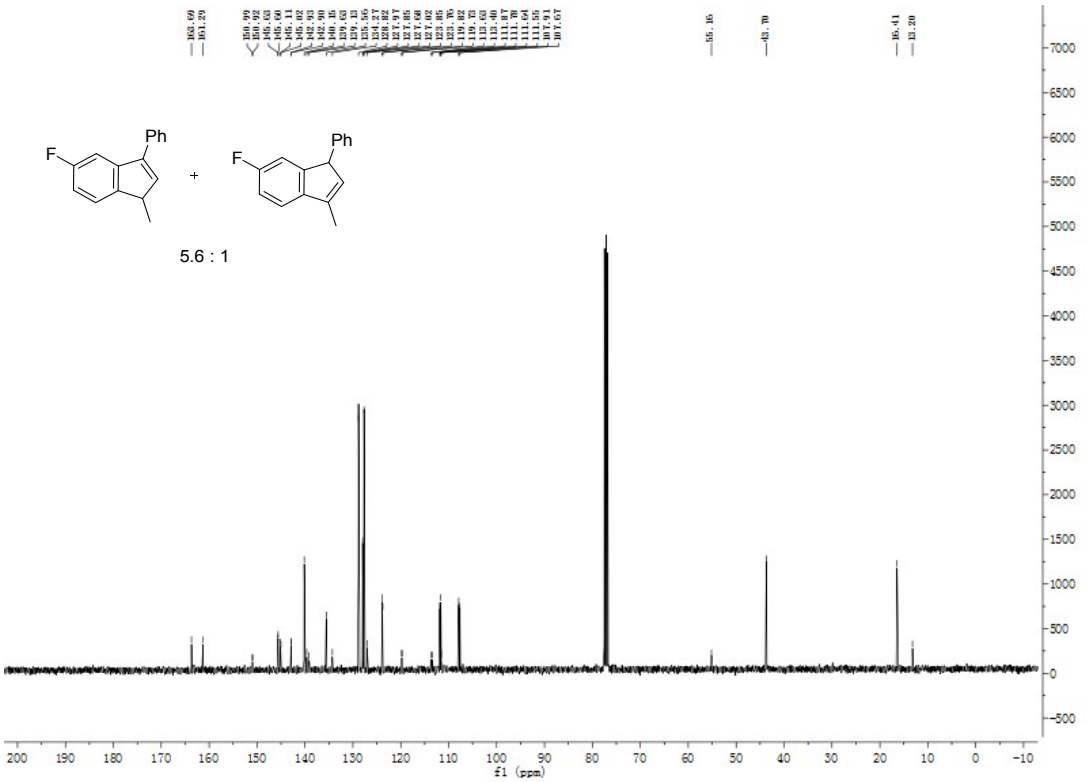
5-chloro-1-methyl-3-phenyl-1*H*-indene (2m):



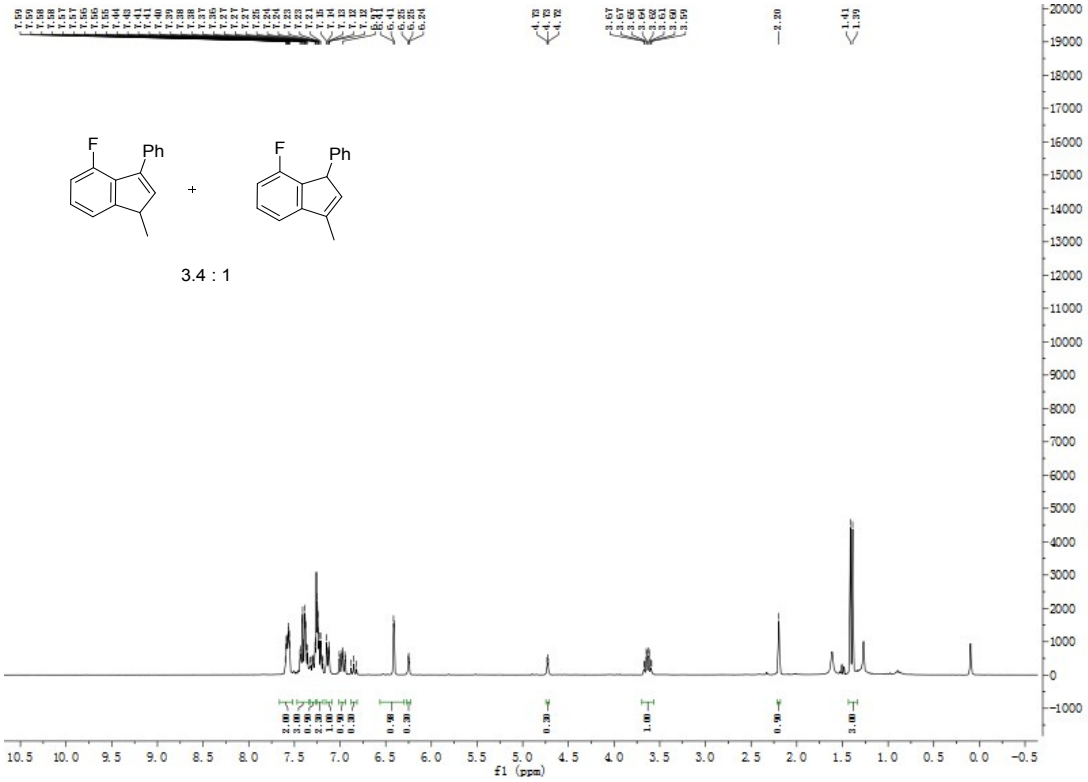


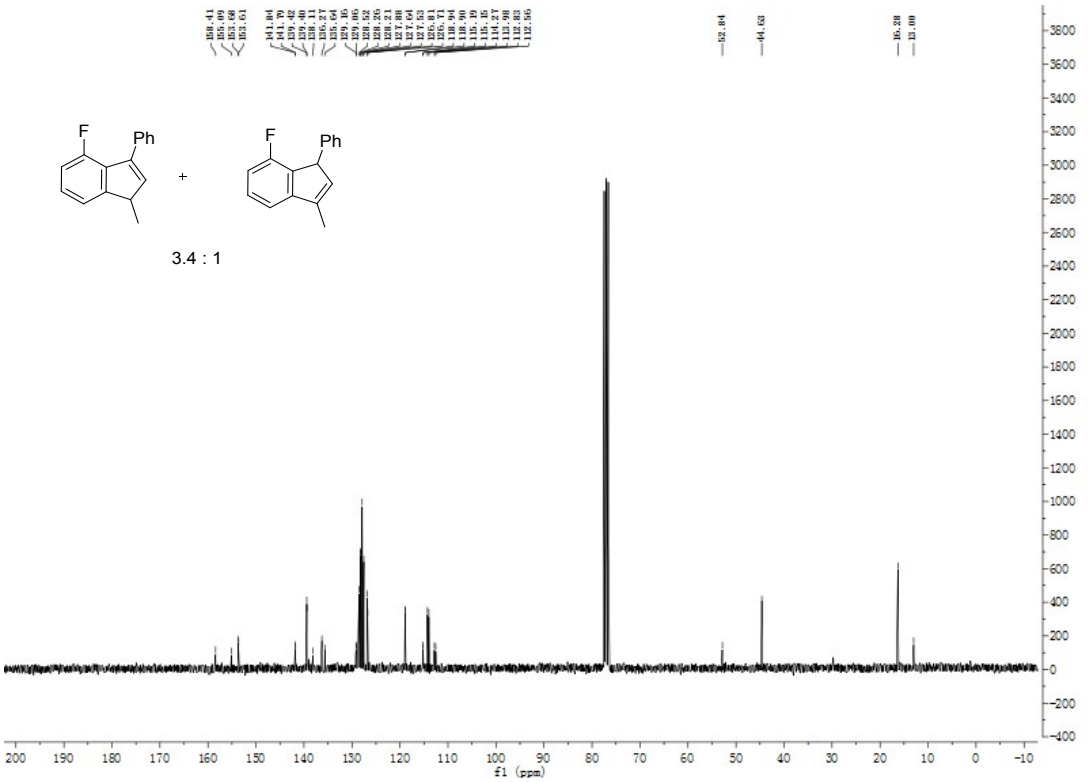
5-fluoro-1-methyl-3-phenyl-1*H*-indene (2n):



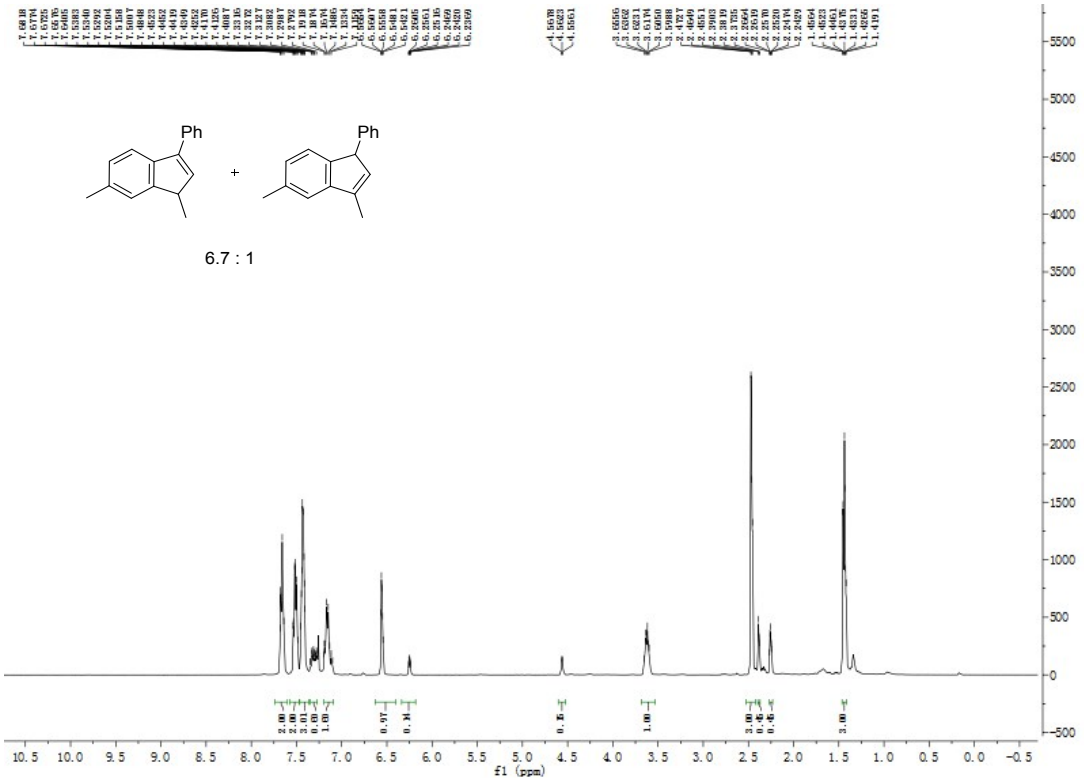


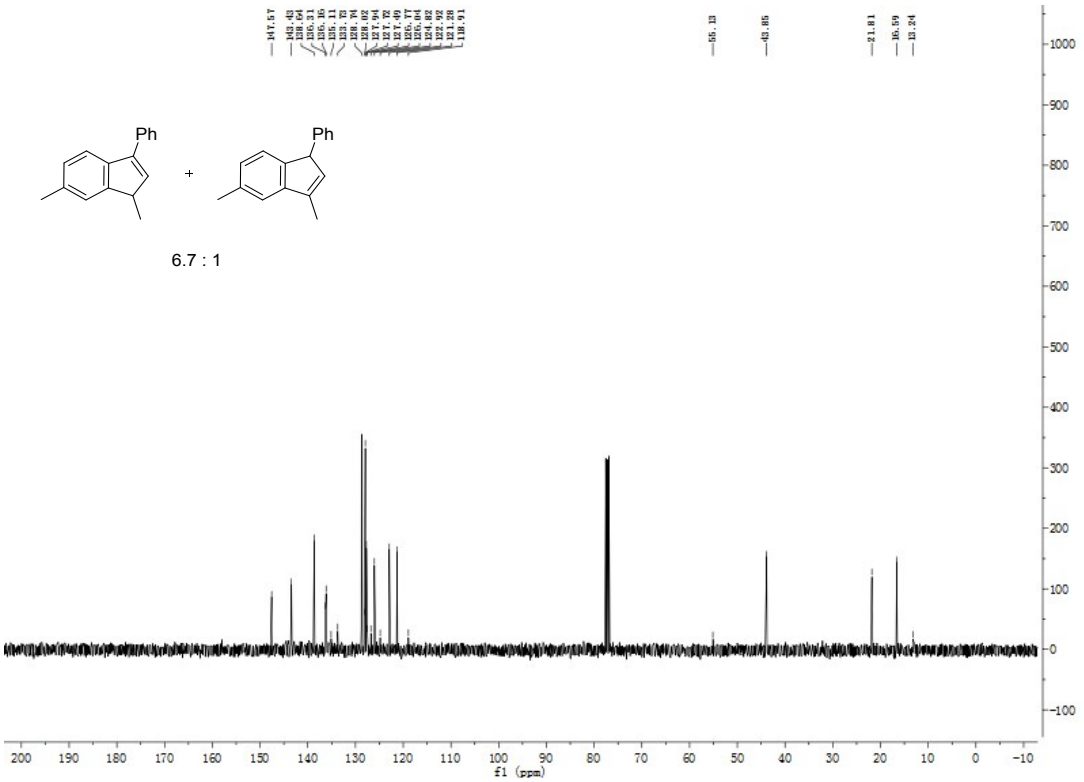
4-fluoro-1-methyl-3-phenyl-1*H*-indene (2o):



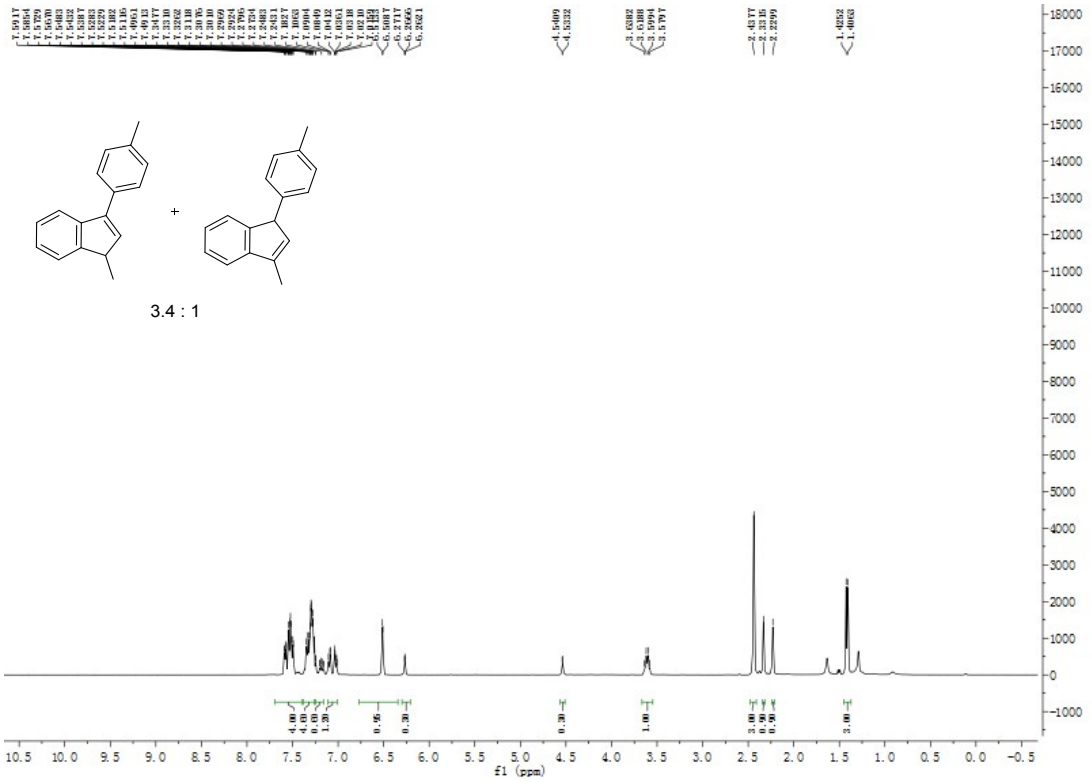


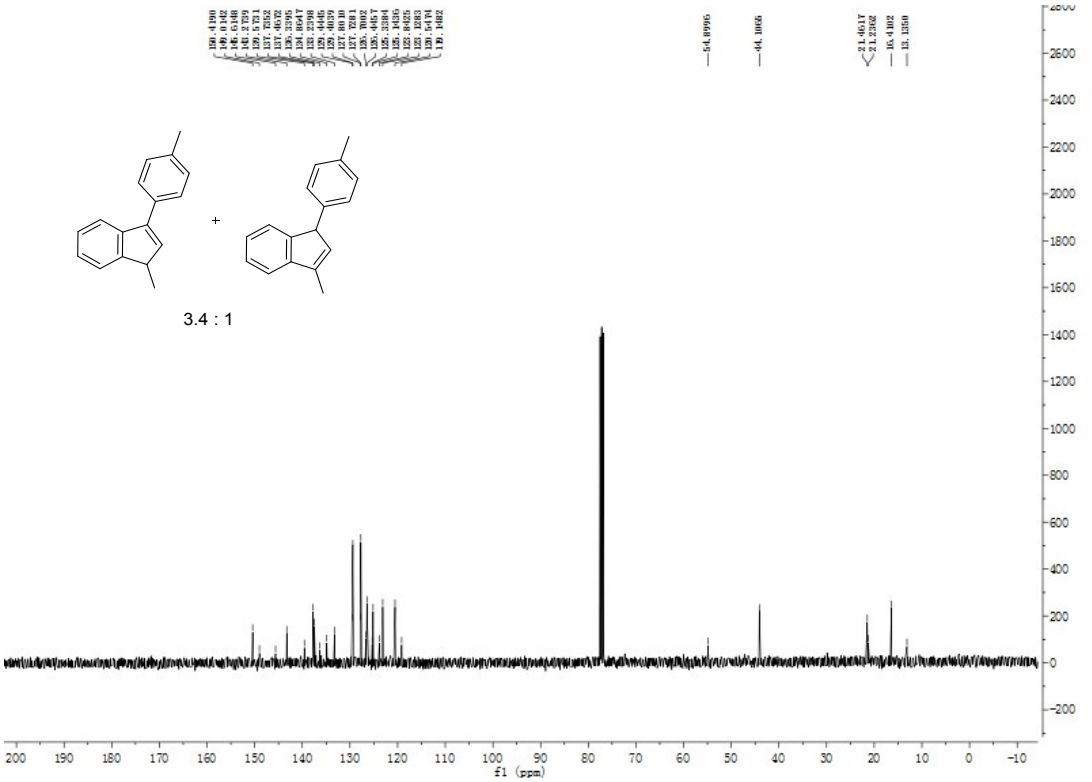
1,6-dimethyl-3-phenyl-1*H*-indene (2p):



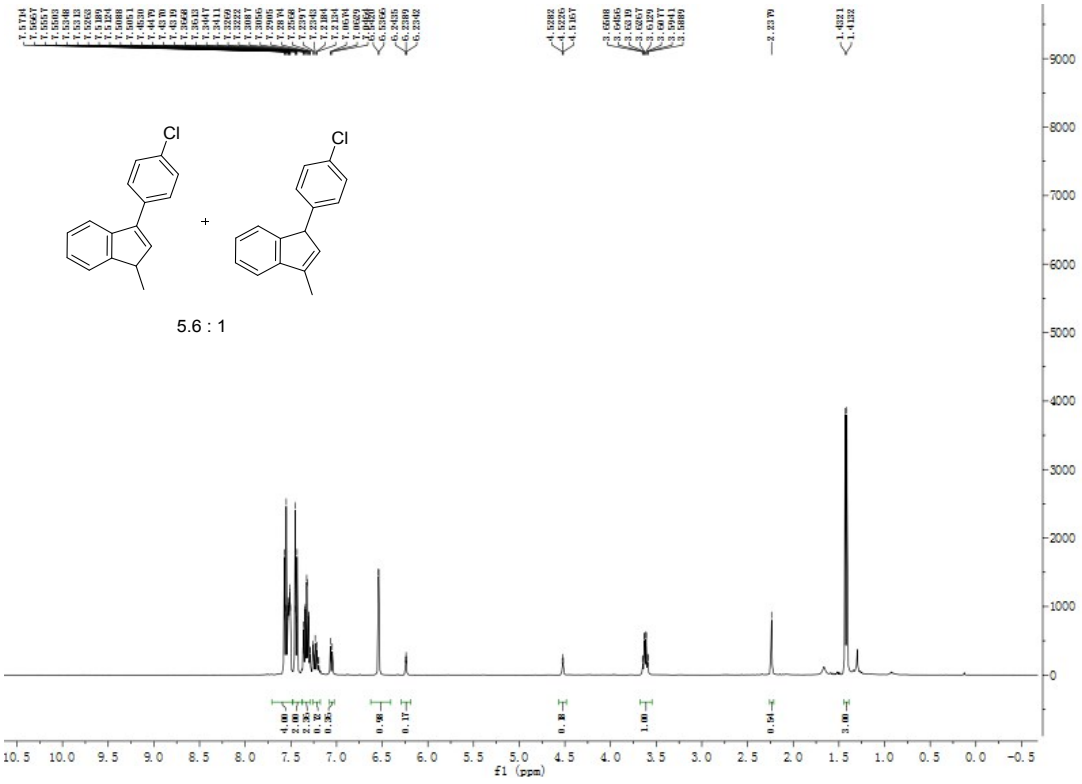


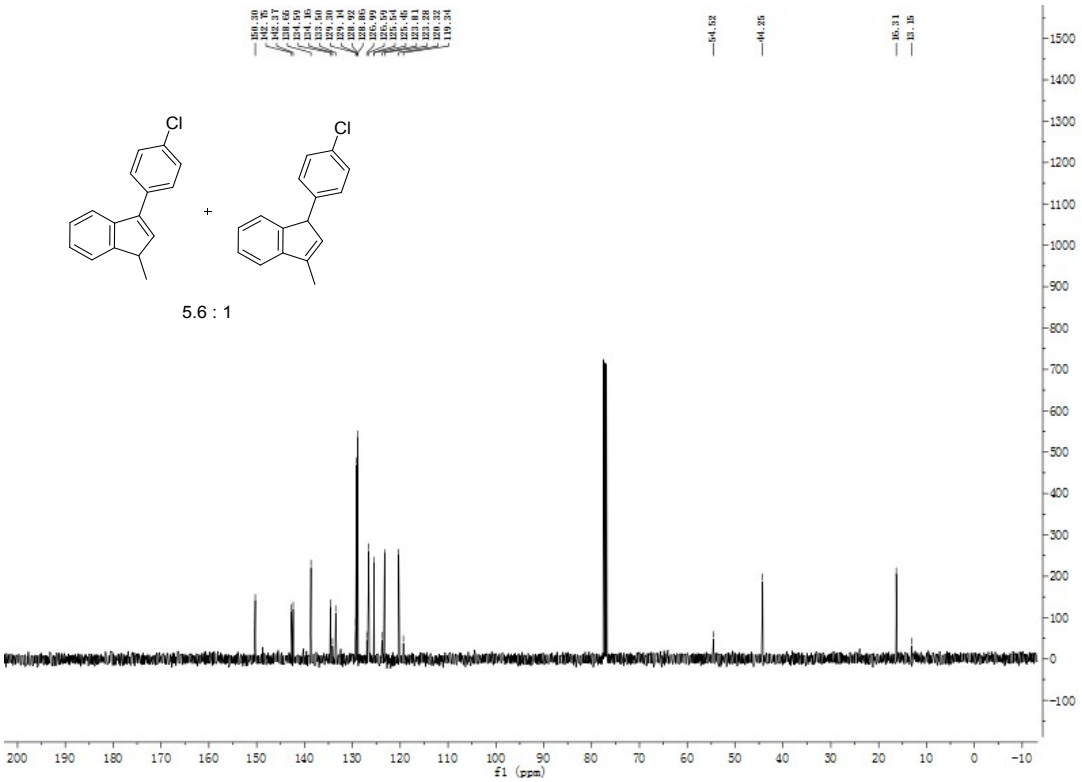
1-methyl-3-(*p*-tolyl)-1*H*-indene (2q):



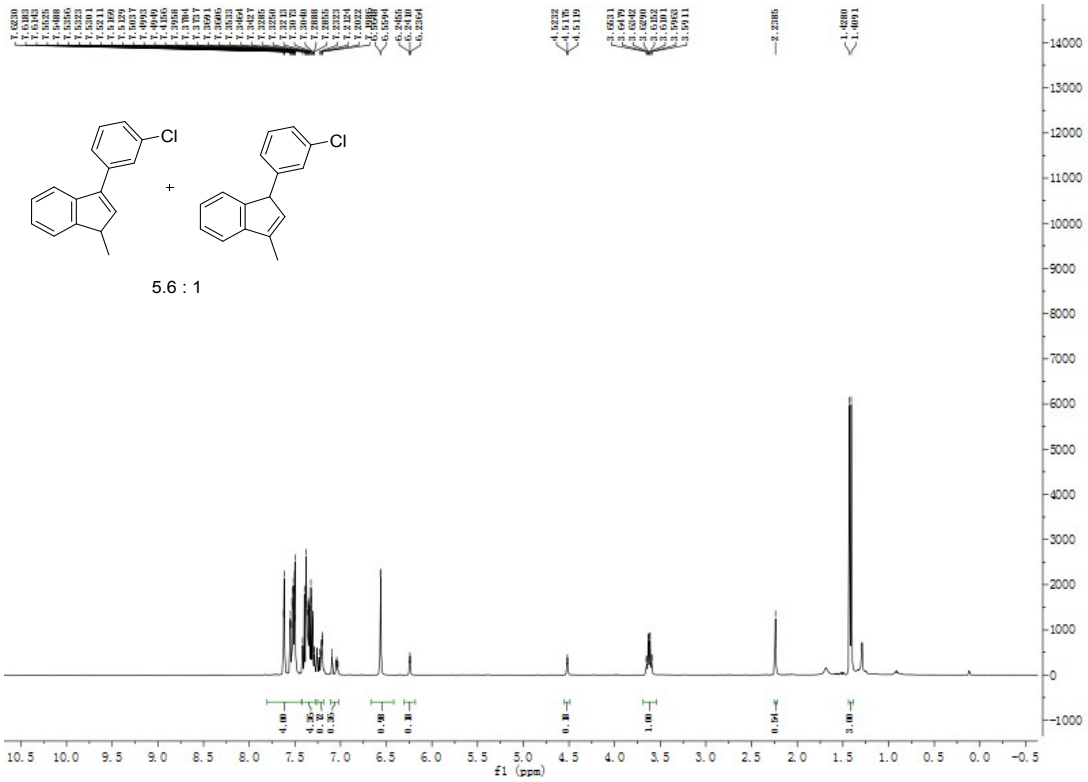


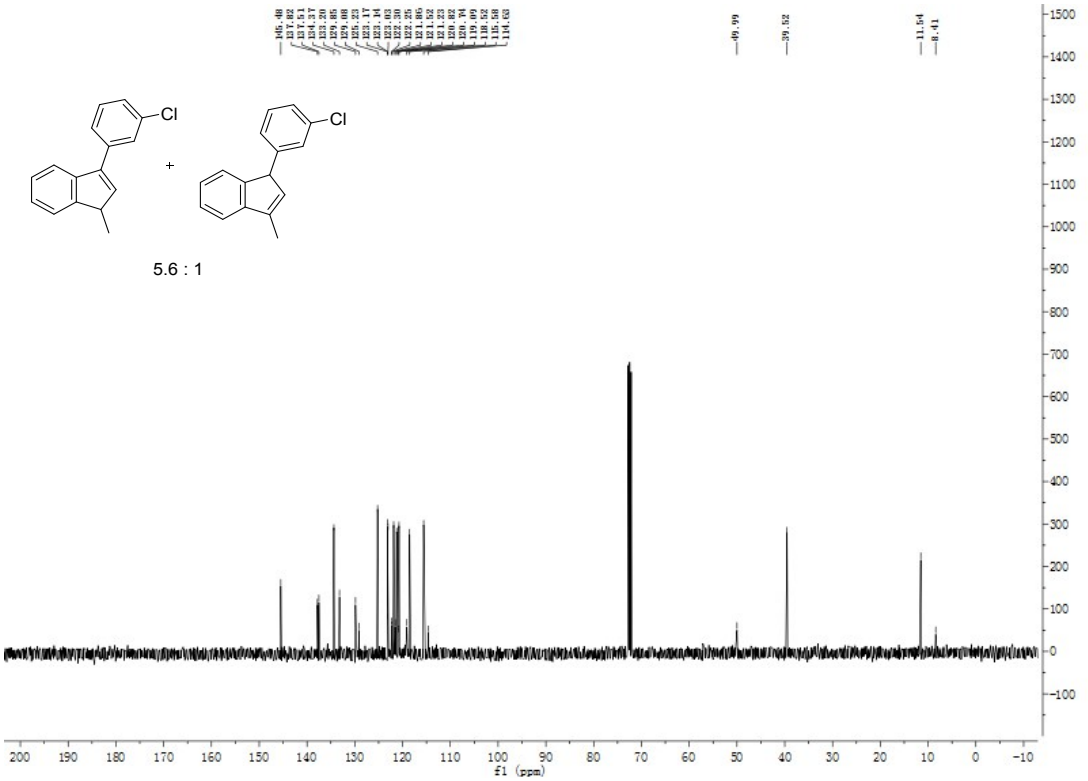
3-(4-chlorophenyl)-1-methyl-1*H*-indene (2r):





3-(3-chlorophenyl)-1-methyl-1*H*-indene (2s):





3-(2-chlorophenyl)-1-methyl-1*H*-indene (2t):