Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Iron/Zinc-Catalyzed Benzannulation Reaction of 2-(2-Oxo-alkyl)benzketones Leading to Naphthalene and Isoquinoline Derivatives

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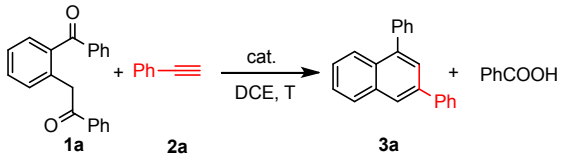
Contents

1. Condition optimization.

Table S1. Optimization of reaction conditions.[a]



entry	Cat.	**1a**:**2a**	Solvent	T/°C	Yield[b]
1	$FeCl_3$(5%)	1:1.1	DCE	r.t.	trace
2	$FeCl_3$(5%)	1:1.1	DCE	60	53%
3	$FeCl_3$(5%)	1:1.1	DCE	80	56%
4	$FeCl_3$(10%)	1:1.1	DCE	80-100	80%[c]
5	**$FeCl_3$(10%)**	**1:2.0**	**DCE**	**80**	**88%[c]**
6	**$ZnCl_2$(10%)**	**1:2.0**	**DCE**	**80**	**87%[c]**
7	$CuCl_2$(10%)	1:2.0	DCE	80	trace
8	$FeCl_3$(10%)	1:2.0	DCM	80	65%
9	$FeCl_3$(10%)	1:2.0	THF	80	trace
10	None	1:2.0	DCE	80	NR
11	TfOH(20%)	1:2.0	DCE	80-100	trace
12	TFA(20%)	1:2.0	DCE	80-100	trace

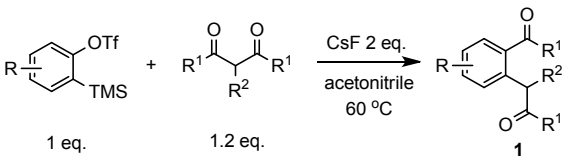
[a] [**1a**] = 0.25 M.;
[b] The yields were determined by ^{1}H NMR;
[c] Isolated yield;

2. General information.

All reactions were carried out under an inert atmosphere of dry N_2 in Schlenk tube. ^1H, ^{13}C, ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ^1H; 100 MHz for ^{13}C; 376 MHz for ^{19}F), ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Infrared (IR) spectra were recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra were obtained using ESI mass spectrometer. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. Aryne precursors[1] and 2-(alkanoyl phenyl) ethyl ketones (**1a**, **1n**)[2a] were prepared according to the method of reference.

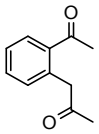
3. Experimental details

3.1 General Procedure for the Preparation of 1



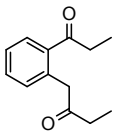
To the solution of β-diketone (0.3 mmol) and CsF (0.5 mmol) in anhydrous acetonitrile (2 mL), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.25 mmol) was added at room temperature under N_2. The reaction mixture was stirred at 60 °C for 2 h and then quenched with saturated NH_4Cl aqueous solution. The mixture was extracted with ethyl acetate. Combined organic layers were dried over anhydrous sodium sulfate, and evaporated. Crude products were purified by column chromatography (ethyl acetate/petroleum ether = 1:10) to afford the 2-(alkanoyl phenyl) ethyl ketones **1**.

2-(Acetylmethyl) acetophenone (1l).[2a]



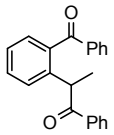
Yellow oil (22 mg, 50%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.7 Hz, 1H), 7.47 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 7.4 Hz, 1H), 4.03 (s, 2H), 2.58 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7, 201.0, 136.6, 135.1, 133.0, 132.2, 130.2, 127.3, 49.5, 30.0, 28.6.

2-(Acetylethyl) propiophenone (1m).



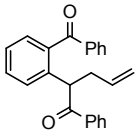
Yellow oil (31 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.7 Hz, 1H), 7.44 (t, J = 7.3 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.5 Hz, 1H), 4.00 (s, 2H), 2.96 (q, J = 7.2 Hz, 2H), 2.59 (q, J = 7.3 Hz, 2H), 1.15 (t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 204.3, 137.3, 134.8, 134.5, 132.8, 131.6, 129.0, 127.0, 48.1, 35.8, 33.8, 8.3, 7.72; IR (KBr) ν_{max} 2927, 1800, 1735, 1705, 1682, 1465, 1376, 845, 771, 750, 732; HRMS (ESI) calcd. for $C_{13}H_{17}O_2$ $[M+H]^+$: 205.1223, found 205.1227.

2-(Benzoylphenyl)-1-phenylpropan-1-one (1o).[2b]



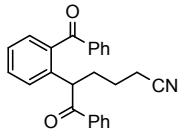
To the solution of 2-methyl-1,3-diphenylpropane-1,3-dione (0.25 mmol) and CsF (0.63 mmol) in anhydrous acetonitrile (2 mL), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.31 mmol) was added at room temperature under N_2. The reaction mixture was stirred at 80 ^{o}C for 4 h and then quenched with saturated NH_4Cl aqueous solution. The mixture was extracted with ethyl acetate. Combined organic layers were dried over anhydrous sodium sulfate, and evaporated. Crude products were purified by column chromatography (ethyl acetate/petroleum ether = 1:30) to afford **1o**. Yellow oil (49 mg, 63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.8 Hz, 2H), 7.83 (d, J = 7.8 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.46-7.36 (m, 2H), 7.32-7.28 (m, 5H), 5.15 (q, J = 6.7 Hz, 1H), 1.50 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 198.3, 140.8, 137.7, 137.4, 136.3, 133.5, 132.7, 131.0, 130.5, 129.5, 129.4, 128.8, 128.5, 128.4, 128.3, 128.2, 125.9, 43.5, 19.5.

2-(Benzoylphenyl) phenylpent-4-en-1-one (1r)



To the solution of 2-allyl-1,3-diphenylpropane-1,3-dione[3] (0.25 mmol) and CsF (0.63 mmol) in anhydrous acetonitrile (2 mL), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (0.31 mmol) was added at room temperature under N_2. The reaction mixture was stirred at 80 ^{o}C for 4 h and then quenched with saturated NH_4Cl aqueous solution. The mixture was extracted with ethyl acetate. Combined organic layers were dried over anhydrous sodium sulfate, and evaporated. Crude products were purified by column chromatography (ethyl acetate/petroleum ether = 1:30) to afford **1r**. Yellow oil (42.2 mg, 64%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.9 Hz, 2H), 7.79 (d, J = 7.8 Hz, 2H), 7.73 (d, J = 7.9 Hz, 1H), 7.60 (t, J = 7.3 Hz, 1H), 7.50-7.22 (m, 8H), 5.69 (td, J = 17.0, 6.9 Hz, 1H), 5.23 (t, J = 7.1 Hz, 1H), 4.96-4.78 (m, 2H), 2.71 (ddt, J = 163.0, 13.9, 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 198.3, 138.6, 137.8, 137.6, 136.5, 135.7, 133.3, 132.8, 131.1, 130.6, 129.8, 128.9, 128.6, 128.4, 128.3, 126.0, 117.0, 48.4, 38.4; IR (KBr) ν_{max} 3063, 2925, 1736, 1683, 1590, 1579, 1447, 1316, 1267, 1211, 1180, 999, 845, 705; HRMS (ESI) calcd. for $C_{24}H_{21}O_2$ $[M+H]^+$: 341.1536, found 341.1541.

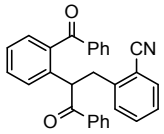
5-(2-Benzoylphenyl)-6-oxo-6-phenylhexanenitrile 1s



Thick oil (57 mg, 52%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.8 Hz, 2H), 7.81 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.4 Hz,

1H), 7.51 (d, J = 7.7 Hz, 2H), 7.40 (dd, J = 15.9, 7.2 Hz, 4H), 7.28 (dd, J = 11.7, 7.6 Hz, 3H), 5.14 (dd, J = 7.7, 6.2 Hz, 1H), 2.40 – 2.28 (m, 3H), 2.05 – 1.94 (m, 1H), 1.83 – 1.71 (m, 1H), 1.65 – 1.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 198.2, 138.5, 137.6, 137.5, 136.3, 133.6, 133.0, 131.4, 130.5, 130.1, 128.7, 128.6, 128.5, 128.4, 126.3, 119.4, 47.7, 33.1, 23.6, 17.1; IR (KBr) ν_{max} 3063, 2937, 1677, 1587, 1446, 1277, 761, 700; HRMS (ESI) calcd. for $C_{25}H_{21}NNaO_2$ $[M+Na]^+$: 390.1465, found 390.1466.

2-(2-(2-Benzoylphenyl)-3-oxo-3-phenylpropyl)benzonitrile 1t

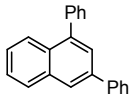


Yellow solid (62.2 mg, 50%, m.p. = 119-120 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.3 Hz, 2H), 7.55 (dd, J = 7.9, 6.6 Hz, 4H), 7.47 – 7.36 (m, 5H), 7.27 (dd, J = 14.3, 7.0 Hz, 4H), 7.22 – 7.14 (m, 2H), 7.01 (td, J = 7.6, 1.2 Hz, 1H), 5.80 (t, J = 7.4 Hz, 1H), 3.73 (dd, J = 14.2, 7.1 Hz, 1H), 3.35 (dd, J = 14.2, 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 197.5, 143.0, 137.8, 137.4, 136.9, 136.1, 133.1, 133.0, 132.6, 132.3, 131.6, 130.4, 129.9, 129.2, 129.0, 128.4, 128.2, 126.7, 126.3, 117.8, 113.2, 48.9, 38.4; IR (KBr) ν_{max} 3064, 1667, 1589, 1446, 1256, 931, 762, 700; HRMS (ESI) calcd. for $C_{29}H_{21}NNaO_2$ $[M+Na]^+$: 438.1465, found 438.1471.

3.2 General Procedure for the Preparation of Product 3a-p

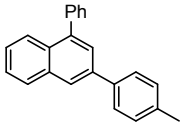
To a DCE (1 mL) solution of **1** (0.25 mmol) in Schlenk tube with a magnetic bar was added $FeCl_3$ (10 mol%) and arylethynylene (2 eq.) under N_2. The reaction mixture was stirred at 80-100 °C, followed by TLC. After the substrates were completely consumed, then the solvent was evaporated under vacuum, and the mixture was purified by chromatography (SiO_2) with eluent of petroleum ether, the products were obtained.

1,3-Diphenylnaphthalene (3a).[4a]



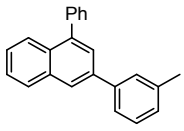
Yellow solid (61.6 mg, 88%): ^{1}H NMR δ 8.10 (s, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 7.1 Hz, 2H), 7.76 (d, J = 1.8 Hz, 1H), 7.62-7.44 (m, 9H), 7.41 (t, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 140.8, 140.7, 138.0, 134.2, 130.9, 130.1, 128.8, 128.6, 128.3, 127.4, 127.3, 126.7, 126.2, 126.1, 125.9, 125.4.

1-Phenyl-3-(p-tolyl) naphthalene (3b).



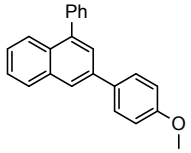
Thick oil (53.7 mg, 73%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.75 (s, 1H), 7.69 (d, J = 7.9 Hz, 2H), 7.60-7.52 (m, 5H), 7.49 (d, J = 7.1 Hz, 1H), 7.46 (d, J = 7.3 Hz, 1H), 7.32 (d, J = 7.9 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 138.0, 137.9, 137.2, 134.2, 130.8, 130.1, 129.6, 128.5, 128.3, 127.3, 127.2, 126.6, 126.1, 125.9, 125.8, 125.0; IR (KBr) ν_{max} 3054, 3028, 2922, 2856, 1598, 1492, 1446, 1395, 1186, 1113, 1027, 968, 889, 785, 752, 702; HRMS (ESI) calcd. for $C_{23}H_{19}$ $[M+H]^+$: 295.1481, found 295.1482.

1-Phenyl-3-(m-tolyl) naphthalene (3c).



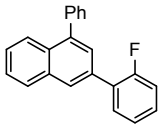
Thick oil (63.2 mg, 86%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.99 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.75 (s, 1H), 7.60 (d, J = 9.6 Hz, 4H), 7.55 (t, J = 7.4 Hz, 3H), 7.51-7.37 (m, 3H), 7.23 (d, J = 7.5 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 140.8, 138.4, 138.1, 134.2, 130.8, 130.1, 128.8, 128.6, 128.3, 128.2, 127.3, 126.7, 126.2, 126.0, 125.9, 125.3, 124.5, 21.5; IR (KBr) ν_{max} 3053, 2922, 1700, 1599, 1491, 1400, 1264, 1094, 1028, 972, 882, 785, 766, 751; HRMS (ESI) calcd. for $C_{23}H_{19}$ $[M+H]^+$: 295.1481, found 295.1480.

3-(4-Methoxyphenyl)-1-phenylnaphthalene (3d).[4a]



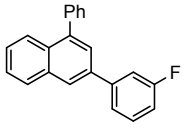
To a DCE (1 mL) solution of **1a** (0.25 mmol) in Schlenk tube with a magnetic bar was added $ZnCl_2$ (10 mol%) and ethynyl-4-methoxybenzene (2eq.) under N_2. The reaction mixture was stirred at 100 ^{o}C, followed by TLC. After the substrates were completely consumed, then the solvent was evaporated under vacuum, and the mixture was purified by chromatography (SiO_2) with eluent of petroleum ether, the product was obtained. Thick oil (64.3 mg, 83%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 7.2 Hz, 3H), 7.59-7.47 (m, 6H), 7.45-7.40 (m, 1H), 7.04 (d, J = 7.9 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 140.8, 137.6, 134.2, 133.4, 130.6, 130.4, 130.1, 128.4, 128.3, 127.3, 126.5, 126.1, 125.9, 125.8, 124.6, 114.3, 55.4.

3-(2-Fluorophenyl)-1-phenylnaphthalene (3e).



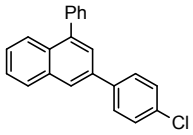
Thick oil (57.4 mg, 77%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.99 (t, J = 7.9 Hz, 2H), 7.70 (s, 1H), 7.66-7.46 (m, 8H), 7.43-7.34 (m, 1H), 7.30-7.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0 (d, J_{C-F} = 248.0 Hz), 140.5 (d, J_{C-F} = 10.1 Hz), 133.9, 132.8, 131.1 (d, J_{C-F} = 3.4 Hz), 131.0, 130.1, 129.1 (d, J_{C-F} = 8.3 Hz), 129.0, 128.8, 128.6, 128.3, 128.0 (d, J_{C-F} = 2.7 Hz), 127.7 (d, J_{C-F} = 3.1 Hz), 127.4, 126.4, 126.2, 125.9, 124.4 (d, J_{C-F} = 3.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.5; IR (KBr) ν_{max} 3056, 2961, 2924, 2853, 1701, 1579, 1455, 1389, 1237, 1153, 969, 857, 757; HRMS (ESI) calcd. for $C_{22}H_{15}FNa$ $[M+Na]^+$: 321.1050, found 321.1048.

3-(3-Fluorophenyl)-1-phenylnaphthalene (3f).



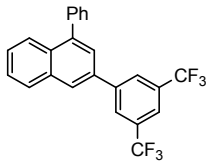
Yellow solid (61.6 mg, 88%, m.p. 73-74 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.98 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H), 7.70 (s, 1H), 7.58-7.52 (m, 6H), 7.49-7.42 (m, 4H), 7.09 (td, J = 8.4, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (d, $J_{C\text{-}F}$ = 245.7 Hz), 143.2 (d, $J_{C\text{-}F}$ = 7.6 Hz), 141.1, 140.5, 136.7, 134.1, 131.1, 130.3 (d, $J_{C\text{-}F}$ = 8.4 Hz), 130.0, 128.6, 128.3, 127.5, 126.3 (d, $J_{C\text{-}F}$ = 9.5 Hz), 125.9, 125.5, 123.0 (d, $J_{C\text{-}F}$ = 2.7 Hz), 114.3 (d, $J_{C\text{-}F}$ = 6.5 Hz), 114.1 (d, $J_{C\text{-}F}$ = 5.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.9; IR (KBr) ν_{max} 3054, 2920, 1700, 1630, 1544, 1400, 1372, 1180, 1136, 1026, 899, 786, 755, 702; HRMS (ESI) calcd. for $C_{22}H_{15}FNa$ $[M+Na]^+$: 321.1050, found 321.1051.

3-(4-Chlorophenyl)-1-phenylnaphthalene (3g).[4b]



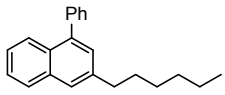
Thick oil (70.8 mg, 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.97 (d, J = 8.1 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.70 (s, 1H), 7.68 (d, J = 2.6 Hz, 2H), 7.58-7.51 (m, 5H), 7.49-7.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 140.5, 139.3, 136.7, 134.1, 133.6, 131.0, 130.0, 129.0, 128.6, 128.5, 128.3, 127.5, 126.4, 126.3, 126.2, 125.9, 125.3.

3-(3,5-Bis(trifluoromethyl) phenyl)-1-phenylnaphthalene (3h).



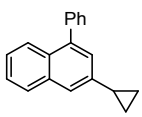
Yellow solid (31.2 mg, 30%, m.p. 128-129 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 2H), 8.10 (s, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.90 (s, 1H), 7.67 (s, 1H), 7.61-7.47 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 141.8, 140.1, 134.9, 134.0, 132.2 (q, $J_{C\text{-}F}$ = 33.2 Hz), 131.5, 130.0, 128.8, 128.5, 127.7, 127.4 (d, $J_{C\text{-}F}$ = 3.6 Hz), 127.1, 126.8, 126.1 (d, $J_{C\text{-}F}$ = 2.9 Hz), 125.7, 124.2 (q, $J_{C\text{-}F}$ = 268.1 Hz) 121.0 (m); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8; IR (KBr) ν_{max} 3054, 3028, 2925, 1702, 1543, 1400, 1371, 1337, 1179, 1026, 900, 845, 754; HRMS (ESI) calcd. for $C_{24}H_{14}F_6$ $[M+H]^+$: 417.1072, found 417.1070.

3-Hexyl-1-phenylnaphthalene (3i).



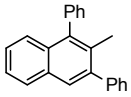
Thick oil (61.2 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (t, J = 9.1 Hz, 2H), 7.66 (s, 1H), 7.56-7.43 (m, 6H), 7.39 (t, J = 7.1 Hz, 1H), 7.33 (d, J = 1.4 Hz, 1H), 2.83 (t, J=8 Hz, 2H), 1.85-1.69 (m, 2H), 1.50-1.31 (m,6H), 0.93 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 140.1, 140.0, 134.1, 130.2, 130.1, 128.6, 128.2, 127.8, 127.1, 126.0, 125.8, 125.7, 125.1, 36.1, 31.8, 31.3, 29.1, 22.6, 14.1; IR (KBr) ν_{max} 3056, 2955, 2927, 2855, 1701, 1625, 1574, 1493, 1393, 1073, 1030, 878, 784, 749; HRMS (ESI) calcd. for $C_{22}H_{25}$ $[M+H]^+$: 289.1951, found 289.1951.

3-Cyclopropyl-1-phenylnaphthalene (3j).



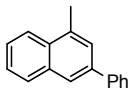
Thick oil (34.2 mg, 56%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.82 (m, 2H), 7.58 (s, 1H), 7.53-7.44 (m, 6H), 7.37 (t, J = 7.6 Hz, 1H), 7.18 (s, 1H), 2.19-2.05 (m, 1H), 1.07 (q, J = 5.4 Hz, 2H), 0.88 (q, J = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 140.9, 140.2, 134.0, 130.1, 130.0, 128.2, 127.6, 127.2, 125.9, 125.8, 125.7, 125.0, 123.4, 15.6, 9.2; IR (KBr) ν_{max} 3056, 2923, 2852, 1701, 1650, 1558, 1541, 1508, 1492, 1459, 1398, 1213, 869, 750; HRMS (ESI) calcd. for $C_{19}H_{17}$ $[M+H]^+$: 245.1325, found 244.1230.

2-Methyl-1,3-diphenylnaphthalene (3k).



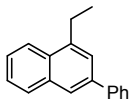
Thick oil (52.9 mg, 72%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.1 Hz, 1H), 7.76 (s, 1H), 7.52 (t, J = 7.3 Hz, 2H), 7.48-7.31 (m, 11H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 141.1, 140.4, 139.1, 132.3, 131.6, 130.2, 129.5, 128.5, 128.1, 127.7, 127.0, 126.9, 126.3, 125.7, 125.2, 19.2; IR (KBr) ν_{max} 3056, 2957, 2921, 2852, 1737, 1599, 1490, 1376, 1186, 1075, 967, 854, 788; HRMS (ESI) calcd. for $C_{23}H_{19}$ $[M+H]^+$: 295.1481, found 295.1481.

1-Methyl-3-phenylnaphthalene (3l).[4c]



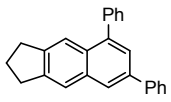
Yellow solid (28,9 mg, 53%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.03 (m, 1H), 7.96-7.91 (m, 2H), 7.76 (d, J = 7.3 Hz, 2H), 7.64 (s, 1H), 7.57-7.49 (m, 4H), 7.41 (t, J = 7.4 Hz, 1H), 2.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 138.2, 134.8, 133.9, 131.8, 128.8, 128.7, 127.4, 127.2, 126.3, 126.0, 125.8, 124.2, 124.0, 19.5.

1-Ethyl-3-phenylnaphthalene (3m).[4d]



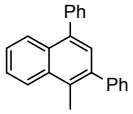
Thick oil (23.2 mg, 40%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.13 (m, 1H), 8.01-7.93 (m, 2H), 7.84-7.78 (m, 2H), 7.71 (s, 1H), 7.63-7.53 (m, 4H), 7.45 (t, J = 7.4 Hz, 1H), 3.26 (q, J = 7.5 Hz, 2H), 1.52 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 140.8, 138.3, 134.2, 131.0, 129.1, 128.8, 127.4, 127.2, 125.8, 125.7, 124.7, 124.3, 123.6, 26.1, 15.1.

5,7-Diphenyl-2,3-dihydro-1H-cyclopenta[b]naphthalene (3n).



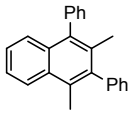
Thick oil (59.2 mg, 74%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.82- 7.74 (m, 3H), 7.72 (s, 1H), 7.64 (s, 1H), 7.61-7.44 (m, 7H), 7.38 (t, J = 7.4 Hz, 1H), 3.05 (dt, J = 36.3, 7.2 Hz, 4H), 2.15 (p, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 143.7, 141.3, 141.2, 140.3, 136.9, 133.7, 130.3, 130.1, 128.8, 128.2, 127.3, 127.2, 125.8, 125.1, 122.8, 120.1, 32.9, 32.6, 26.1; IR (KBr) ν_{max} 3055, 3030, 2953, 2841, 1747, 1599, 1480, 1389, 1265, 1075, 888, 762; HRMS (ESI) calcd. for $C_{25}H_{21}$ $[M+H]^+$: 321.1638, found 321.1640.

1-Methyl-2,4-diphenylnaphthalene (3o).[4e]



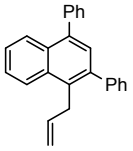
White solid (45.6 mg, 62%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.56-7.29 (m, 12H), 2.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 140.7, 138.6, 138.1, 133.3, 130.9, 130.3, 130.2, 129.8, 129.3, 128.2, 128.1, 127.1, 126.8, 126.6, 126.1, 125.5, 124.8, 16.4.

1,3-Dimethyl-2,4-diphenylnaphthalene (3p).[4f]



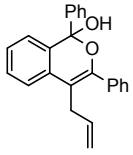
Yellowish crystal (53.9 mg, 70%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.4 Hz, 1H), 7.54-7.35 (m, 10H), 7.32 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 6.7 Hz, 1H), 2.44 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 140.6, 140.3, 136.8, 132.3, 132.2, 132.1, 131.0, 130.9, 130.4, 129.4, 128.4, 126.9, 126.8, 126.7, 125.3, 125.1, 124.3, 19.9, 16.8.

1-Allyl-2,4-diphenylnaphthalene (3r).



Thick oil (48 mg, 60%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.61-7.52 (m, 3H), 7.51-7.39 (m, 10H), 6.26-6.05 (m, 1H), 5.13 (d, J = 10.2 Hz, 1H), 4.95 (d, J = 17.2 Hz, 1H), 3.84 (d, J = 3.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 140.7, 138.6, 138.1, 133.3, 130.9, 130.3, 130.2, 129.8, 129.3, 128.2, 128.1, 127.1, 126.8, 126.6, 126.1, 125.5, 124.8, 16.4; IR (KBr) ν_{max} 3058, 2922, 1774, 1718, 1686, 1637, 1559, 1510, 1263, 1032, 912, 760, 701; HRMS (ESI) calcd. for $C_{25}H_{21}$ $[M+H]^+$: 321.1638, found 321.1634.

4-Allyl-1,3-diphenyl-1H-isochromen-1-ol (1r').



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.2 Hz, 2H), 7.62 (d, J = 6.9 Hz, 1H), 7.49-7.33 (m, 8H), 7.16 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 7.7 Hz, 1H), 6.17-6.04 (m, 1H), 5.19 (d, J = 12.3 Hz, 2H), 3.46 (s, 1H), 3.39 (d, J = 3.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 141.8, 137.1, 135.3, 132.8, 130.9, 128.9, 128.8, 128.7, 128.6, 128.0, 127.2, 126.6, 125.8, 122.9, 116.4, 108.7, 99.3, 31.7; IR (KBr) ν_{max} 3449, 3059, 2923, 1754, 1718, 1680, 1633, 1550, 1521, 1260, 1037, 910, 758, 698; HRMS (ESI) calcd. for $C_{24}H_{21}O_2$ $[M+H]^+$: 341.1536, found 341.1532.

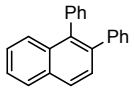
3.3 General Procedure for the Preparation of Product 3s-v

To a DCE (1 mL) solution of **1** (0.25 mmol) in Schlenk tube with a magnetic bar was added $FeCl_3$ (10 mol%), TFA (20%) and aldehyde/ketone (2 eq.) under N_2. The reaction mixture was stirred at 100 °C, followed by TLC. After the substrates were completely consumed, then the solvent was evaporated under vacuum, and the mixture was purified by chromatography (SiO_2) with eluent of petroleum ether, the products were obtained.

1-Phenylnaphthalene (3s).[4g]

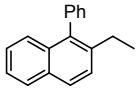
White solid (33.7 mg, 66%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.57-7.50 (m, 6H), 7.47-7.45 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 140.2, 133.8, 131.6, 130.1, 128.2, 127.6, 127.2, 126.9, 126.0, 125.7, 125.4.

1,2-Diphenylnaphthalene (3t).[4h]



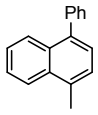
White solid (57.4 mg, 82%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.94 (m, 2H), 7.75 (d, J = 8.5 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H), 7.55 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.38-7.33 (m, 3H), 7.30-7.20 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 139.0, 138.3, 137.6, 132.8, 132.7, 131.4, 130.1, 128.3, 127.9, 127.8, 127.7, 126.8, 126.7, 126.2, 126.1, 125.7.

2-Ethyl-1-phenylnaphthalene (3u).[4i]



Thick oil (38.3 mg, 66%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J= 4 Hz, 1H), 7.86 (d, J = 3.2 Hz, 1H), 7.57-7.31 (m, 9H), 2.59 (q, J = 7.5 Hz, 2H), 1.17 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 139.3, 137.5, 133.1, 131.9, 130.3, 128.2, 127.7, 127.6, 127.1, 127.0, 126.4, 125.7, 124.8, 27.0, 16.0.

1-Methyl-4-phenylnaphthalene (3v).[4j]

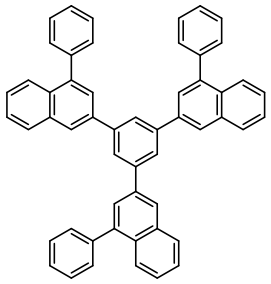


Thick oil (30 mg, 55%):^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.59-7.46 (m, 6H), 7.45-7.31 (m, 3H), 2.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 138.7, 133.8, 132.8, 131.7, 130.2, 128.2, 127.1, 126.7, 126.6, 126.2, 125.6, 124.4, 19.6.

3.4 General Procedure for the Preparation of Product 3q

To a DCE (5 mL) solution of **1** (4.5 eq.) in Schlenk tube with a magnetic bar was added $FeCl_3$ (20 mol%) and 1,3,5-triethynylbenzene (0.27 mmol) under N_2. The reaction mixture was stirred at 100 °C, followed by TLC. After the substrates were completely consumed, and was then quenched with distilled water. The mixture was extracted with dichloromethane. Combined organic layers were dried over anhydrous sodium sulfate, and evaporated. Crude products were purified by column chromatography (dichloromethane /petroleum ether = 1:4), the product was obtained.

1,3,5-Tris(4-phenylnaphthalen-2-yl)benzene (3q).

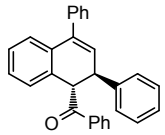


White solid (135 mg, 73%, m.p. >350 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 3H), 8.13 (s, 3H), 8.03 (d, J = 8.1 Hz, 3H), 7.94 (d, J = 8.4 Hz, 3H), 7.87 (d, J = 1.4 Hz, 3H), 7.64-7.41 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 141.2, 140.6, 137.9, 134.2, 131.1, 130.2, 128.7, 128.4, 127.4, 126.7, 126.3, 126.2, 126.0, 125.9, 125.8; IR (KBr) ν_{max} 3030, 2954, 2921, 2850, 1796, 1718, 1651, 1522, 1438, 1219, 964, 842, 700; HRMS (ESI) calcd. for $C_{54}H_{37}$ $[M+H]^+$: 685.2890, found 685.2887.

3.5 General Procedure for the Preparation of Product 4a-h

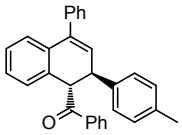
To a DCE (1 mL) solution of **1** (0.25 mmol) in Schlenk tube with a magnetic bar was added $ZnCl_2$ (10 mol%) and styrene derivatives (2 eq.) under N_2. The reaction mixture was stirred at 100 °C, followed by TLC. After the substrates were completely consumed, the solvent was evaporated under vacuum, and the mixture was purified by chromatography (SiO_2) with eluent of ethyl acetate/petroleum ether = 1:30, the products were obtained.

(*Trans*-)(2,4-diphenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4a).[5]



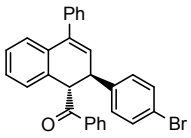
Thick oil (89 mg, *dr* = 76:24, 92%). The relative chemistry of product **4a** was determined by comparing the NMR data with those in the literature (*Org. Lett.* **2017**, *19*, 2470−2473), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.3 Hz, 2H), 7.45 – 7.39 (m, 1H), 7.29 (7.35 – 7.24, 7H), 7.19 – 6.97 (m, 8H), 6.82 (d, J = 7.3 Hz, 1H), 5.93 (d, J = 4.1 Hz, 1H), 5.02 (d, J = 9.2 Hz, 1H), 4.23 (dd, J = 9.2, 4.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 142.6, 139.9, 139.7, 137.5, 134.8, 133.6, 133.0, 129.6, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.8, 127.4, 127.3, 126.9, 126.0, 53.8, 44.2.

(*Trans*-)phenyl (4-phenyl-2-(p-tolyl)-1,2-dihydronaphthalen-1-yl) methanone (4b)..



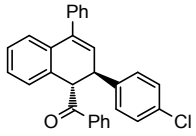
Thick oil (76 mg, *dr* = 74:26, 76%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.4 Hz, 2H), 7.59-7.55 (m, 1H), 7.53-7.35 (m, 7H), 7.24-7.11 (m,4H), 7.05 (d, J = 7.7 Hz,2H), 6.95 (d, J = 7.4 Hz, 2H), 6.04 (d, J = 4.2 Hz, 1H), 5.12 (d, J = 8.8 Hz, 1H), 4.32 (dd, J = 8.8, 4.1 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 140.0, 139.6, 139.5, 137.4, 136.5, 134.9, 133.6, 133.0, 129.8, 129.3, 128.8, 128.7, 128.5, 128.3, 128.0, 127.9, 127.8, 127.4, 127.3, 125.9, 53.9, 43.8, 21.0; IR (KBr) ν_{max} 3057, 3026, 2922, 1681, 1513, 1487, 1342, 1270, 1110, 1025, 998, 941, 910, 816, 768; HRMS (ESI) calcd. for $C_{30}H_{24}ONa$ $[M+Na]^+$: 423.1719, found 423.1727.

***(Trans-)*(2-(4-bromophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4c)**.



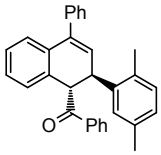
Thick oil (101 mg, *dr* = 64:36, 87%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.4 Hz, 2H), 7.74 (d, J = 7.5 Hz, 1H), 7.50-7.41 (m, 6H), 7.41-7.38 (m, 1H), 7.36-7.34 (m, 2H), 7.21-7.15 (m, 3H), 7.04 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 7.4 Hz, 1H), 5.99 (d, J = 4.0 Hz, 1H), 5.09 (d, J = 9.6 Hz, 1H), 4.34 (dd, J = 9.8, 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 141.8, 140.2, 139.7, 137.5, 134.7, 133.3, 131.7, 131.4, 130.6, 130.0, 129.1, 128.9, 128.8, 128.5, 128.4, 128.3, 128.0, 127.8, 127.7, 127.5, 126.2, 120.8, 53.7, 43.7; IR (KBr) ν_{max} 3060, 2922, 1770, 1740, 1646, 1549, 1516, 1449, 1342, 1215, 1072, 940, 821, 770, 741, 698; HRMS (ESI) calcd. for $C_{29}H_{21}BrONa$ $[M+Na]^+$: 487.0668, found 487.0671.

***(Trans-)*(2-(4-chlorophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4d).**.



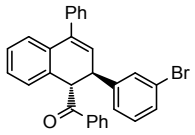
Thick oil (95 mg, *dr* = 66:34, 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 7.6 Hz, 1H), 7.58 (t, J = 7.3 Hz, 1H), 7.52-7.39 (m, 7H), 7.40-7.33 (m, 1H), 7.29-7.09 (m, 5H), 6.95 (d, J = 7.4 Hz, 1H), 6.01 (d, J = 3.9 Hz, 1H), 5.10 (d, J = 9.6 Hz, 1H), 4.36 (dd, J = 9.3, 4.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 141.2, 140.1, 139.7, 137.4, 134.7, 133.5, 133.2, 132.7, 132.6, 130.2, 129.5, 129.1, 128.8, 128.7, 128.4, 128.3, 128.2, 127.9, 127.7, 127.6, 127.4, 126.1, 53.7, 43.6; IR (KBr) ν_{max} 3059, 3028, 2925, 1682, 1595, 1488, 1446, 1344, 1213, 1094, 1012, 769, 698; HRMS (ESI) calcd. for $C_{29}H_{22}ClO$ $[M+H]^+$: 421.1354, found 421.1354.

***(Trans-)*(2-(2,5-dimethylphenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4e)**.



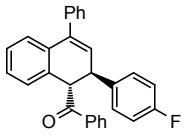
Yellow solid (65 mg, *dr* = 79:21, 63%, m.p. 160-161 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.4 Hz, 2H), 7.60-7.50 (m, 2H), 7.50-7.37 (m, 6H), 7.23-7.09 (m, 4H), 7.01-6.96 (m, 2H), 6.87 (d, J = 8.0 Hz, 1H), 6.00 (d, J = 3.5 Hz, 1H), 5.32 (d, J = 10.9 Hz, 1H), 4.63 (dd, J = 11.1, 3.4 Hz, 1H), 2.35 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 140.5, 139.9, 139.0, 138.0, 135.4, 134.6, 134.5, 133.0, 132.7, 131.2, 130.6, 128.8, 128.6, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.4, 127.3, 127.1, 126.0, 52.5, 40.1, 21.0, 19.4; IR (KBr) ν_{max} 3057, 3026, 2923, 2865, 1682, 1959, 1682, 1598, 1496, 1343, 1218, 1106, 997, 810, 770, 737; HRMS (ESI) calcd. for $C_{31}H_{27}O$ $[M+H]^+$: 415.2056, found 415.2056.

***(Trans-)*(2-(3-bromophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4f)**.



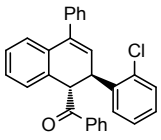
Thick oil (108 mg, *dr* = 67:33, 93%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.4 Hz, 2H), 7.72 (d, J = 7.4 Hz, 1H), 7.58 (t, J = 7.4 Hz, 1H), 7.51-7.41 (m, 7H), 7.30 (d, J = 8.4 Hz, 1H), 7.23-7.15 (m, 4H), 7.08 (t, J = 7.8 Hz, 1H), 6.96 (d, J = 6.9 Hz, 1H), 6.01 (d, J = 3.9 Hz, 1H), 5.13 (d, J = 9.9 Hz, 1H), 4.35 (dd, J = 9.9, 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 145.0, 140.2, 139.6, 137.5, 134.6, 133.4, 133.2, 131.2, 130.1, 130.0, 128.8, 128.4, 128.3, 128.2, 128.1, 128.0, 127.6, 127.5, 127.4, 126.9, 126.1, 122.5, 53.6, 44.0; IR (KBr) ν_{max} 3059, 3028, 2924, 1681, 1592, 1479, 1423, 1267, 1073, 997, 836, 771, 740, 696; HRMS (ESI) calcd. for $C_{29}H_{21}BrONa$ $[M+Na]^+$: 487.0668, found 487.0672.

***(Trans-)*(2-(4-fluorophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4g)**.



Thick oil (88 mg, *dr* = 74:26, 87%):^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.4 Hz, 2H), 7.71 (t, J = 12.4 Hz, 1H), 7.48-7.40 (m, 7H), 7.28-7.24 (m, 2H), 7.20-7.13 (m, 4H), 6.96-6.90 (m, 2H), 6.02 (d, J = 3.9 Hz, 1H), 5.11 (d, J = 9.7 Hz, 1H), 4.37 (dd, J = 9.8, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 161.7 (d, J_{C-F} = 245.3 Hz), 139.8 (d, J_{C-F} = 17.0 Hz), 138.4, 137.5, 134.7, 133.6, 133.2, 129.7 (d, J_{C-F} = 7.9 Hz), 129.6, 128.8, 128.7 (d, J_{C-F} = 3.7 Hz), 128.3 (d, J_{C-F} = 3.2 Hz), 128.2, 127.9, 127.7, 127.5, 127.4, 126.0, 115.4 (d, J_{C-F} = 21.3 Hz), 54.0, 43.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.7; IR (KBr) ν_{max} 2060, 3030, 2924, 1680, 1600, 1508, 1418, 1270, 1161, 1073, 998, 909, 835, 737, 697; HRMS (ESI) calcd. for $C_{29}H_{22}FO$ $[M+H]^+$: 405.1649, found 405.1648.

***(Trans-)*(2-(2-chlorophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4h)**.



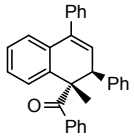
Thick oil (99 mg, *dr* = 72:28, 94%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 2H), 7.53-7.47 (m, 2H), 7.43-7.32 (m, 7H), 7.24-7.18 (m, 2H), 7.13-7.02 (m, 4H), 6.93 (d, J = 7.3 Hz, 1H), 5.96 (d, J = 4.8 Hz, 1H), 5.15 (d, J = 6.6 Hz, 1H), 4.79 (t, J = 5.2 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 200.3, 140.1, 139.8, 139.1, 137.3, 134.8, 133.4, 133.0, 132.7, 130.0, 129.6, 128.8, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 127.4, 127.0, 126.2, 51.6, 39.8; IR (KBr) ν_{max} 3060, 3027, 2924,

1682, 1596, 1477, 1444, 1395, 1269, 1209, 1041, 996, 910, 762, 698; HRMS (ESI) calcd. for $C_{29}H_{22}ClO$ $[M+H]^+$: 421.1354, found 421.1354.

3.6 General Procedure for the Preparation of Product 4i-j

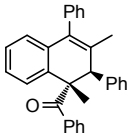
To a DCE (1 mL) solution of **1** (0.25 mmol) in Schlenk tube with a magnetic bar was added $ZnCl_2$ (10 mol%) and styrene derivatives (2 eq.) under N_2. The reaction mixture was stirred at 120 °C, followed by TLC. After the substrates were completely consumed, then the solvent was evaporated under vacuum, and the mixture was purified by chromatography (SiO_2) with eluent of ethyl acetate/petroleum ether = 1:30, the products were obtained.

***(Trans-)*1-methyl-2,4-diphenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4i).**



Thick oil (78 mg, *dr* = 94:6, 78%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.9 Hz, 2H), 7.53-7.42 (m, 4H), 7.38-7.33 (m, 5H), 7.28-7.17 (m, 6H), 6.98 (d, J = 7.0 Hz, 2H), 6.24 (d, J = 4.0 Hz, 1H), 4.87 (d, J = 4.0 Hz, 1H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.6, 140.0, 139.8, 138.9, 138.6, 137.6, 133.6, 131.2, 130.6, 129.7, 129.5, 128.7, 128.3, 128.1, 128.0, 127.8, 127.5, 127.4, 127.2, 127.1, 126.2, 56.6, 48.5, 21.2; IR (KBr) ν_{max} 3061, 3026, 2927, 1677, 1593, 1488, 1448, 1228, 1079, 1036, 768, 702; HRMS (ESI) calcd. for $C_{30}H_{25}O$ $[M+H]^+$: 401.1900, found 401.1899.

***(Trans-)*1,3-dimethyl-2,4-diphenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4j).**

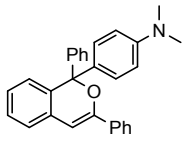


Thick oil (42.4 mg, *dr* = 90:10, 41%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.26 (m, 6H), 7.17-7.09(m, 10H), 7.00 (dd, J = 7.8, 1.6 Hz, 1H), 6.62-6.57 (m, 1H), 4.17 (s, 1H), 1.66 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 139.7, 139.1, 139.0, 138.5, 137.2, 135.1, 134.5, 130.3, 129.8, 128.3, 128.0, 127.8, 127.5, 127.4, 127.3, 127.1, 126.8, 126.7, 125.4, 55.8, 54.9, 21.5, 20.3; IR (KBr) ν_{max} 3062, 3027, 2975, 2925, 2857, 1674, 1592, 1487, 1448, 1230, 1074, 962, 763, 704; HRMS (ESI) calcd. for $C_{31}H_{27}O$ $[M+H]^+$: 415.2056, found 415.2057.

3.7 General Procedure for the Preparation of Product 6

To a DCE (1 mL) solution of **1** (0.25 mmol) in Schlenk tube with a magnetic bar was added $FeCl_3$ (10 mol%) and N,N-dimethylaniline (2eq.) under N_2. The reaction mixture was stirred at 100 °C, followed by TLC. After the substrates were completely consumed, then the solvent was evaporated under vacuum, and the mixture was purified by chromatography (SiO_2) with eluent of petroleum ether, the product was obtained.

4-(1,3-Diphenyl-1H-isochromen-1-yl)-N,N-dimethylaniline (6).

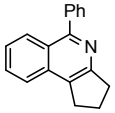


Yellow solid (63.5mg, 63%, m.p. 145-146 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.4 Hz, 2H), 7.43-7.22 (m, 10H), 7.18 (d, J = 7.6 Hz, 1H), 7.10 (d, J = 7.8 Hz, 2H), 6.70 (d, J = 7.6 Hz, 1H), 6.64 (d, J = 8.0 Hz, 2H), 6.50 (s, 1H), 2.94 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 149.8, 144.4, 134.6, 133.9, 131.9, 131.4, 129.4, 128.6, 128.2, 128.0, 127.5, 127.3, 125.9, 125.0, 123.9, 111.2, 101.4, 87.3, 40.4; IR (KBr) ν_{max} 3085, 3027, 2923, 1681, 1592, 1486, 1446, 1343, 1213, 1104, 1008, 940, 822, 770, 739, 698; HRMS (ESI) calcd. for $C_{29}H_{25}NONa$ $[M+Na]^+$: 426.1828, found 426.1836.

3.8 General Procedure for the Preparation of Product 7a-b

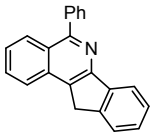
To a DCE (1 mL) solution of **1** (0.25 mmol) in Schlenk tube with a magnetic bar was added $FeCl_3$ (10 mol%) under N_2. The reaction mixture was stirred at 100 °C, followed by TLC. After the substrates were completely consumed, saturated potassium carbonate was added. The mixture was extracted with dichloromethane, combined organic layers were dried over anhydrous sodium sulfate, and evaporated., and the mixture was purified by chromatography (SiO_2) with eluent of ethyl acetate/petroleum ether = 1:30, the products were obtained.

5-phenyl-2,3-dihydro-1H-cyclopenta[c]isoquinoline 7a



Yellow solid (53.9 mg, 88%, m.p. = 80-81 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.3 Hz, 1H), 7.67 (dd, J = 9.9, 8.3 Hz, 3H), 7.47 (ddd, J = 17.4, 14.9, 7.1 Hz, 4H), 3.29 (t, J = 7.3 Hz, 4H), 2.37 – 2.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 156.9, 140.0, 134.3, 130.0, 129.9, 129.4, 128.4, 128.2, 128.2, 125.6, 125.2, 123.6, 34.9, 29.1, 22.5; IR (KBr) ν_{max} 3051, 2920, 1616, 1555, 1367, 1274, 1021, 756, 695; HRMS (ESI) calcd. for $C_{18}H_{16}N$ $[M+H]^+$: 246.1277, found 246.1278.

5-phenyl-11H-indeno[1,2-c]isoquinoline 7b



Yellow solid (70.3 mg, 96%, m.p. = 160-161 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.5 Hz, 1H), 8.12 (d, J = 8.6 Hz, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.74 – 7.68 (m, 1H), 7.64 (d, J = 7.3 Hz, 1H), 7.59 – 7.50 (m, 3H), 7.50 – 7.43 (m, 2H), 7.39 (td, J = 7.4, 1.2 Hz, 1H), 4.17 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 153.3, 143.0, 142.3, 140.0, 134.4, 130.3, 129.0, 128.5, 128.3, 127.5, 127.1, 126.0, 125.6, 124.9, 123.5, 120.7, 33.3; IR (KBr) ν_{max} 3058, 2924, 1710, 1615, 1560, 1381, 1343, 761, 698; HRMS (ESI) calcd. for $C_{22}H_{16}N$ $[M+H]^+$: 294.1277, found 246.1283.

4. References

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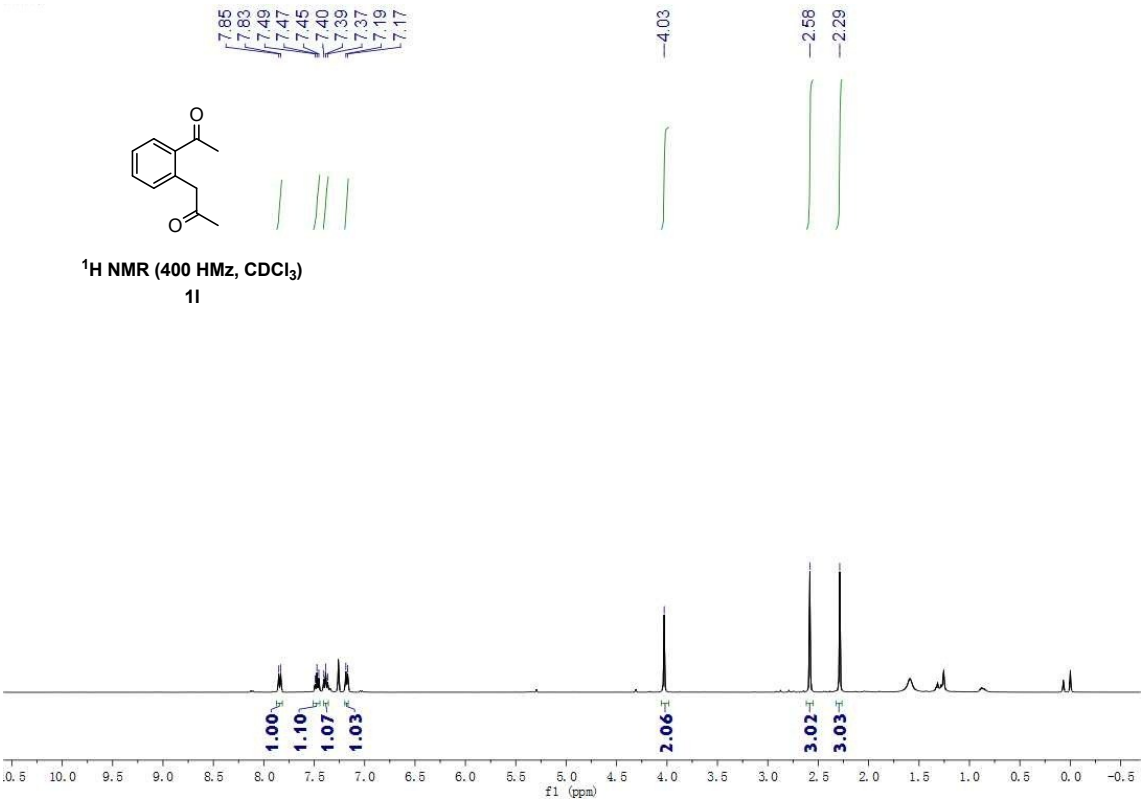
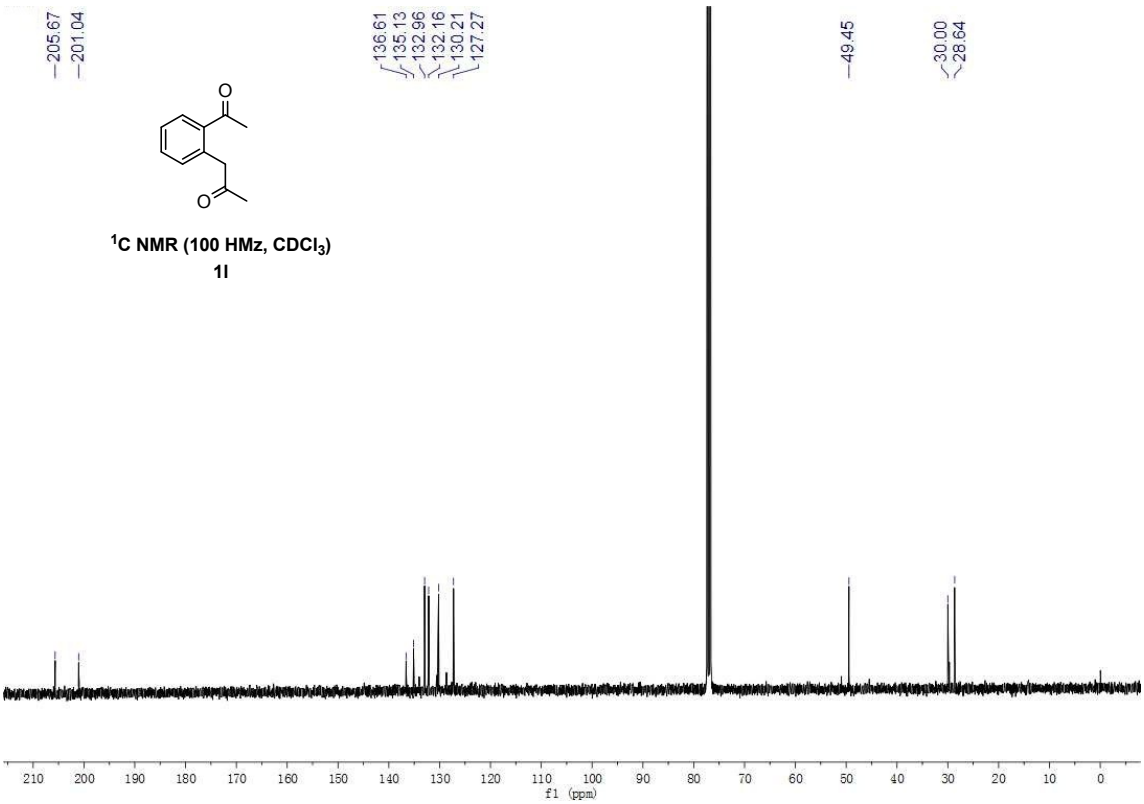
[5] a) S. Perveen, Z. Zhao, G. Zhang, J. Liu, M. Anwar, and X. Fang, *Org. Lett*. 2017, **19**, 2470−2473; b) N. Asao, T. Kasahara, Y. Yamamoto, *Angew. Chem. Int. Ed*. 2003, **42**, 3504-3506; c) S. Zhu, R. Liang, H. Jiang, W. Wu, *Angew. Chem. Int. Ed.* 2012, **51**, 10861-10865.

5. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra

2-(Acetylmethyl) acetophenone (1l).

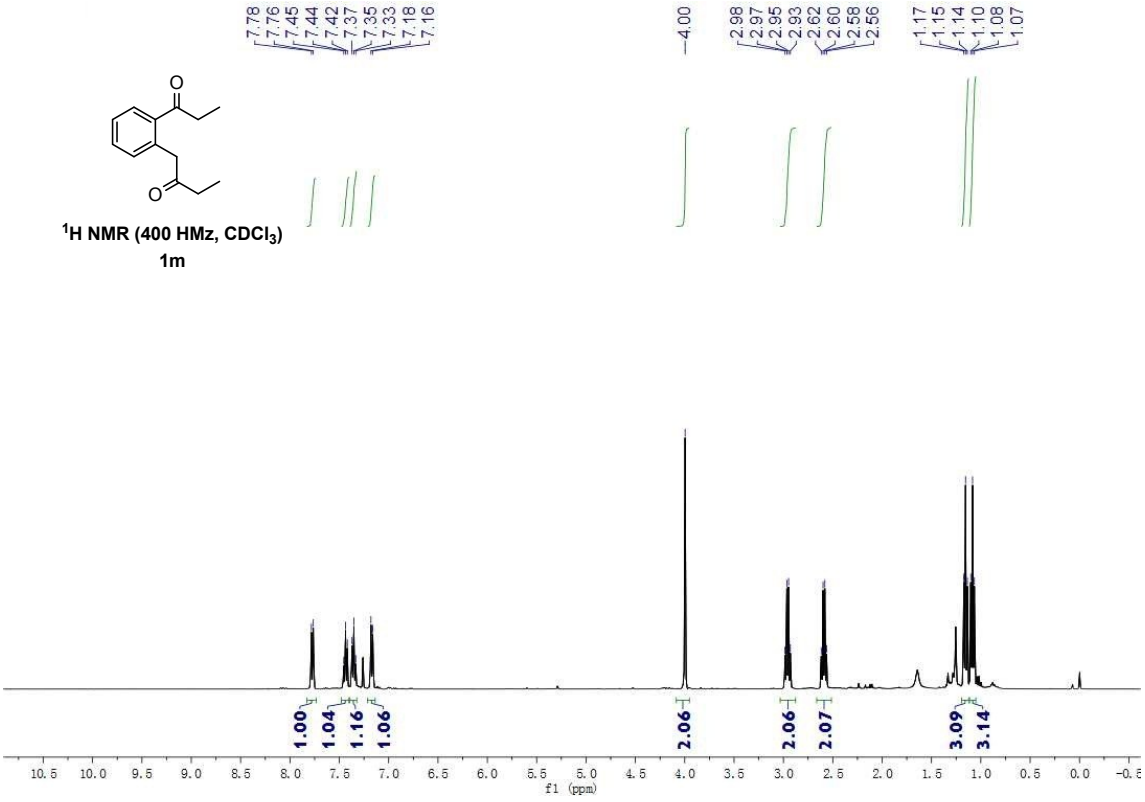


^{1}H NMR (400 HMz, $CDCl_3$)
1l

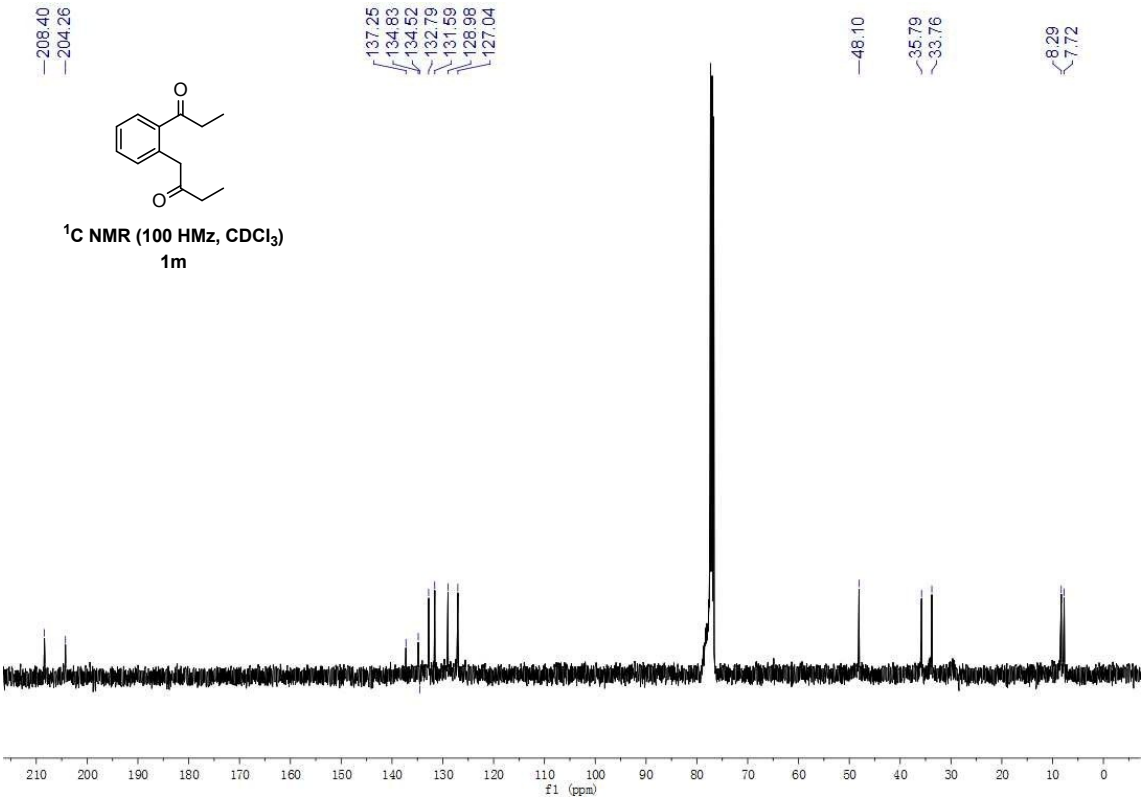


^{1}C NMR (100 HMz, $CDCl_3$)
1l

2-(Acetylethyl) propiophenone (1m).

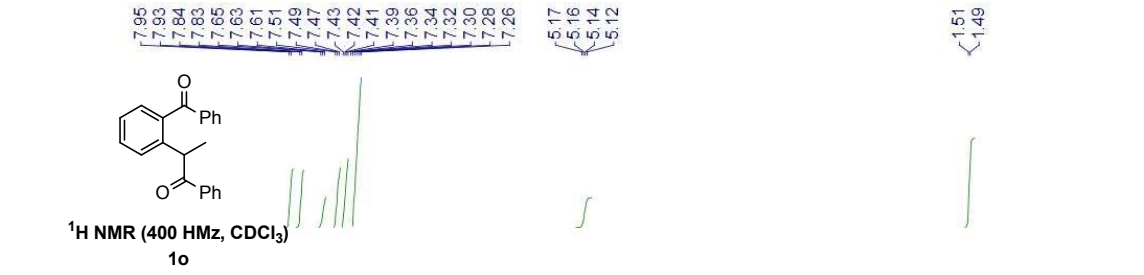


^{1}H NMR (400 HMz, $CDCl_3$)
1m



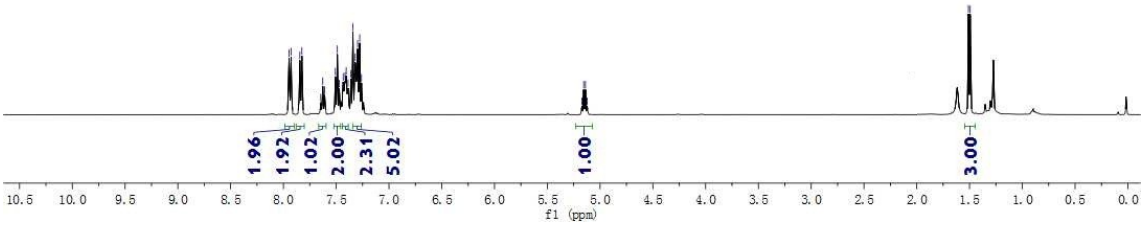
^{1}C NMR (100 HMz, $CDCl_3$)
1m

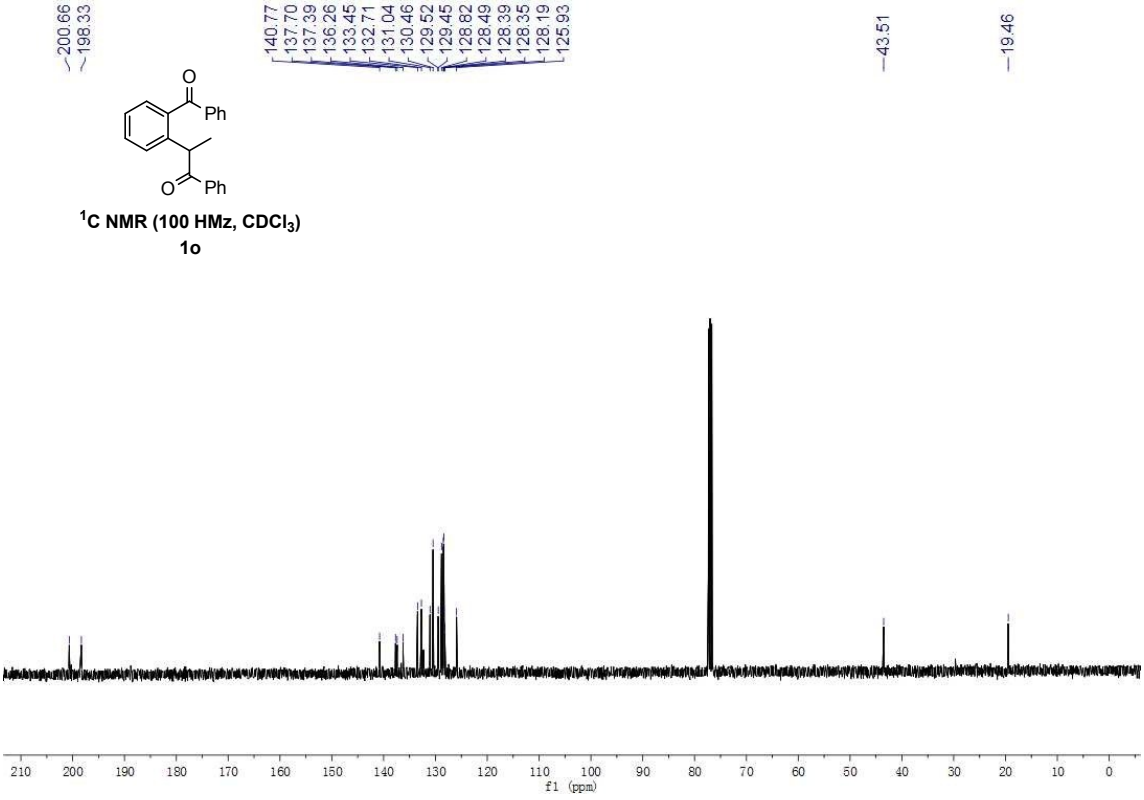
2-(Benzoylphenyl)-1-phenylpropan-1-one (1o).



^{1}H NMR (400 HMz, $CDCl_3$)

1o

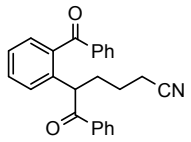




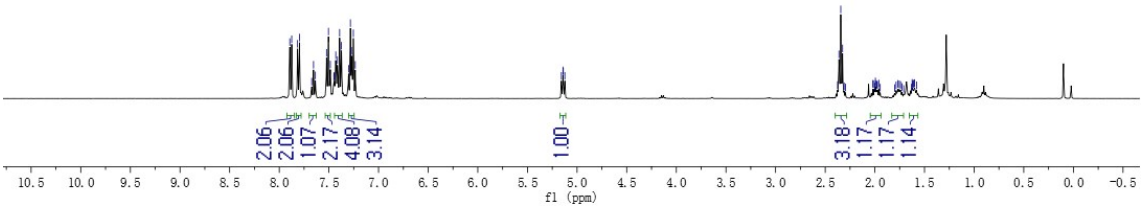
^{1}C NMR (100 HMz, $CDCl_3$)

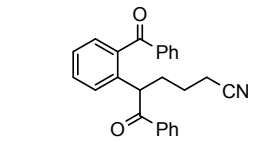
1o

5-(2-Benzoylphenyl)-6-oxo-6-phenylhexanenitrile 1s

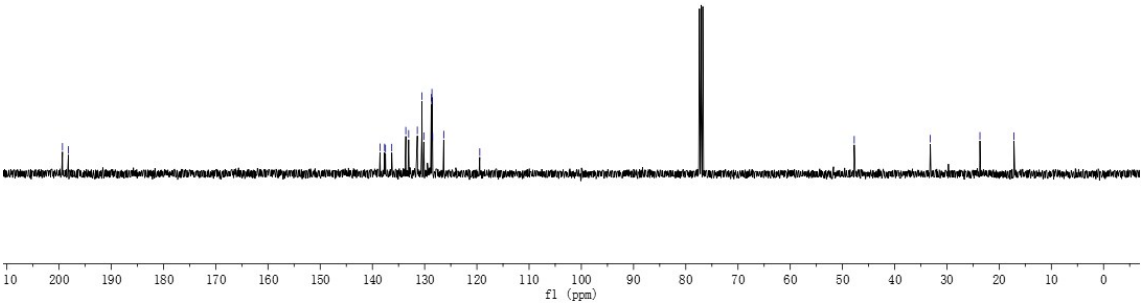


^{1}H NMR (400 MHz, $CDCl_3$)
1s

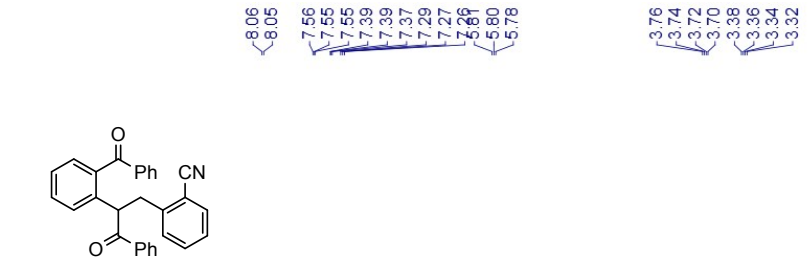




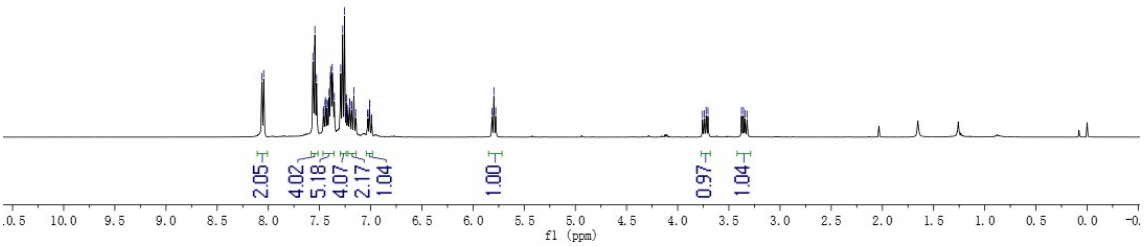
^{13}C NMR (100 MHz, $CDCl_3$)
1s

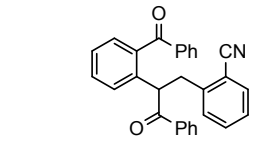


2-(2-(2-benzoylphenyl)-3-oxo-3-phenylpropyl)benzonitrile 1t

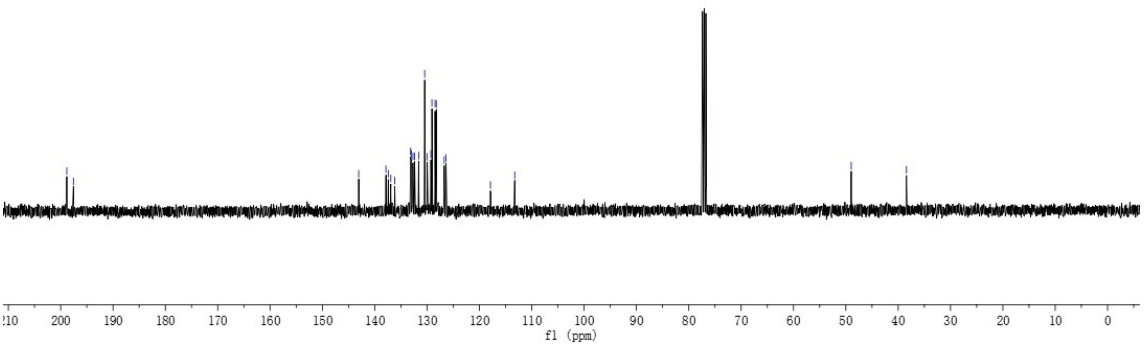


^{1}H NMR (400 MHz, $CDCl_3$)
1t

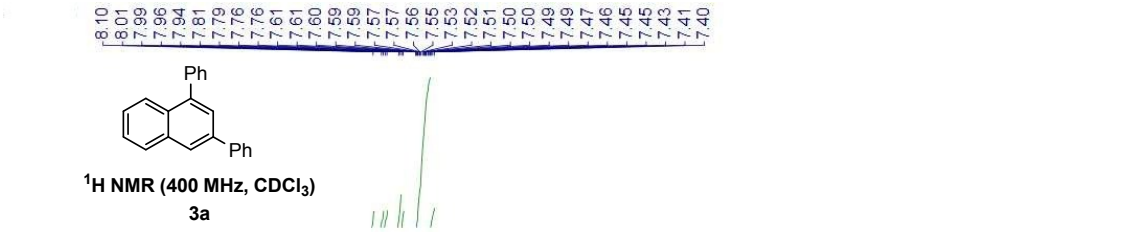




^{13}C NMR (100 MHz, $CDCl_3$)
1t

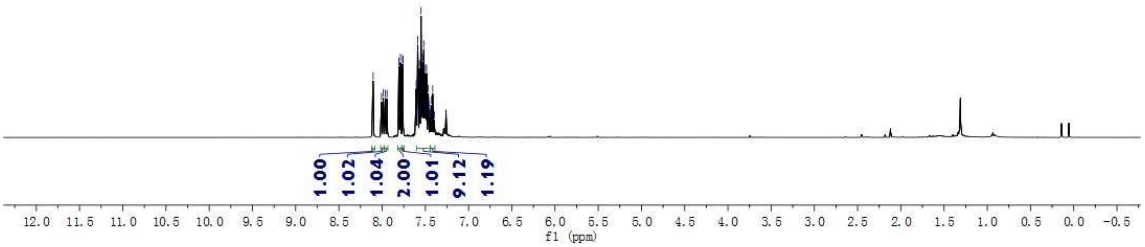


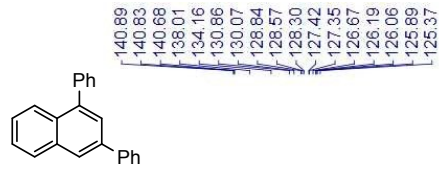
1,3-Diphenylnaphthalene (3a)



^{1}H NMR (400 MHz, $CDCl_3$)

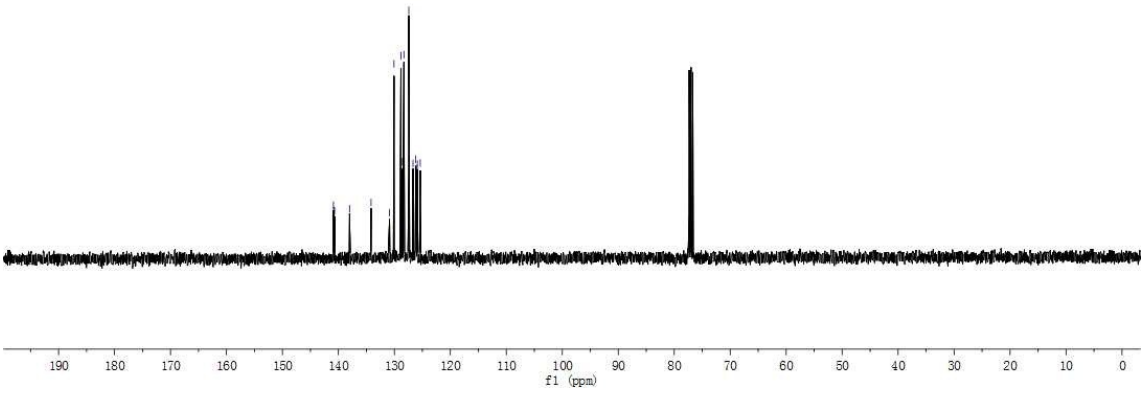
3a



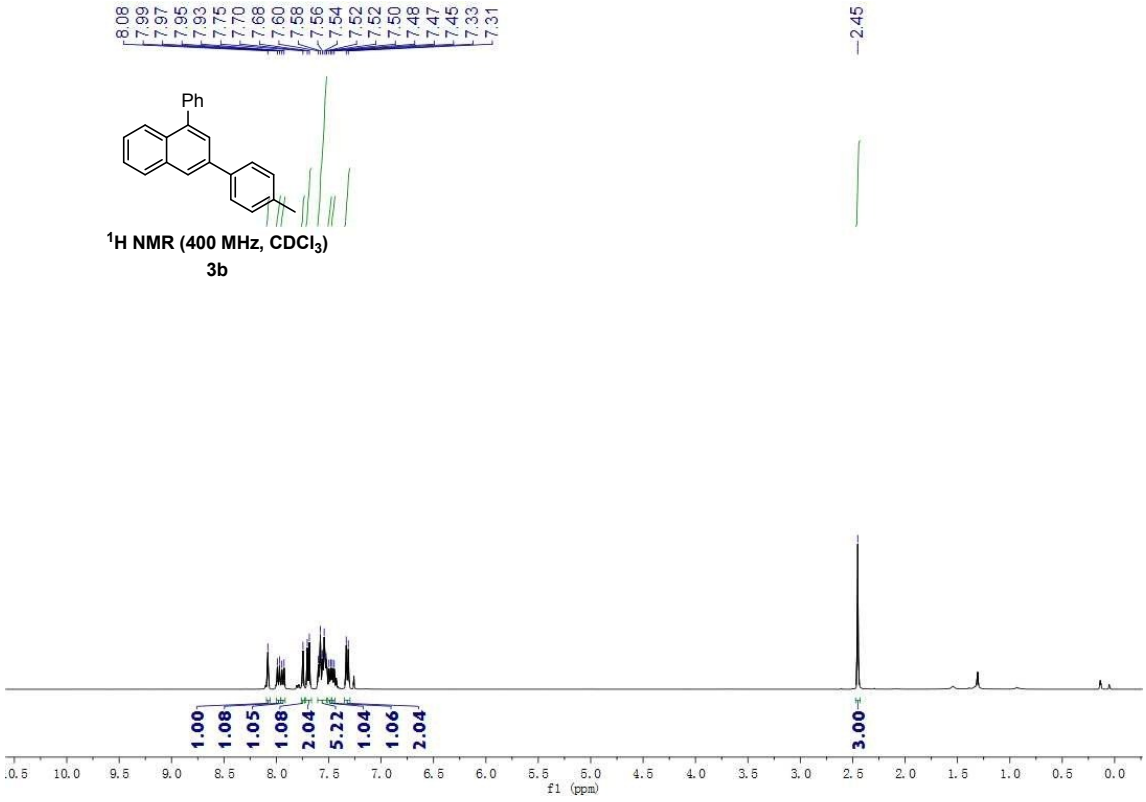


^{13}C NMR (100 MHz, $CDCl_3$)

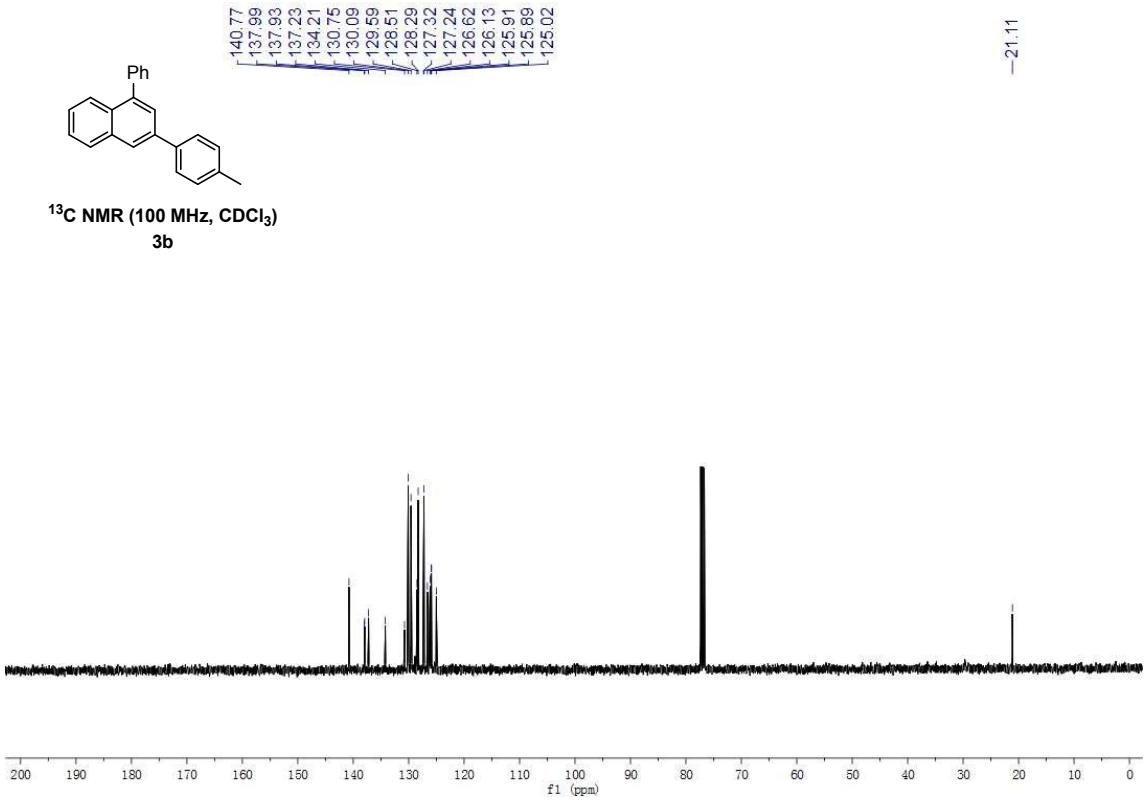
3a



1-Phenyl-3-(p-tolyl) naphthalene (3b).

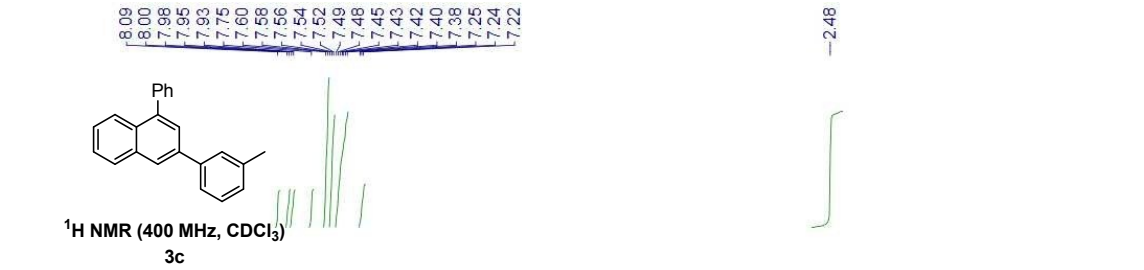


^{1}H NMR (400 MHz, $CDCl_3$)
3b

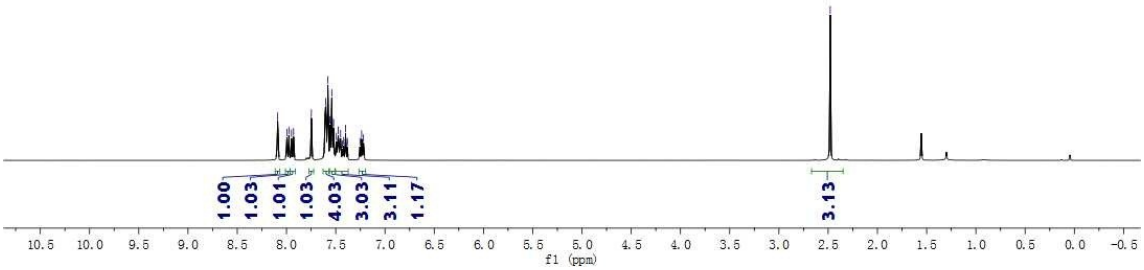


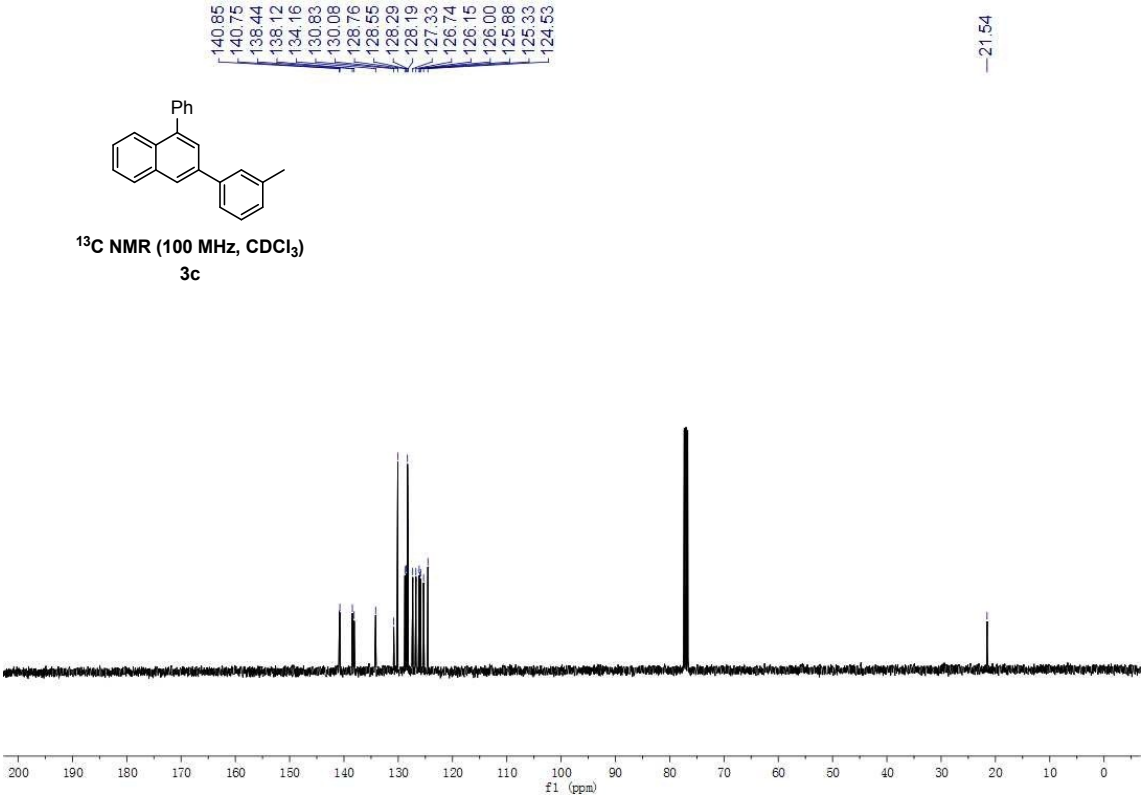
^{13}C NMR (100 MHz, $CDCl_3$)
3b

1-Phenyl-3-(m-tolyl) naphthalene (3c).



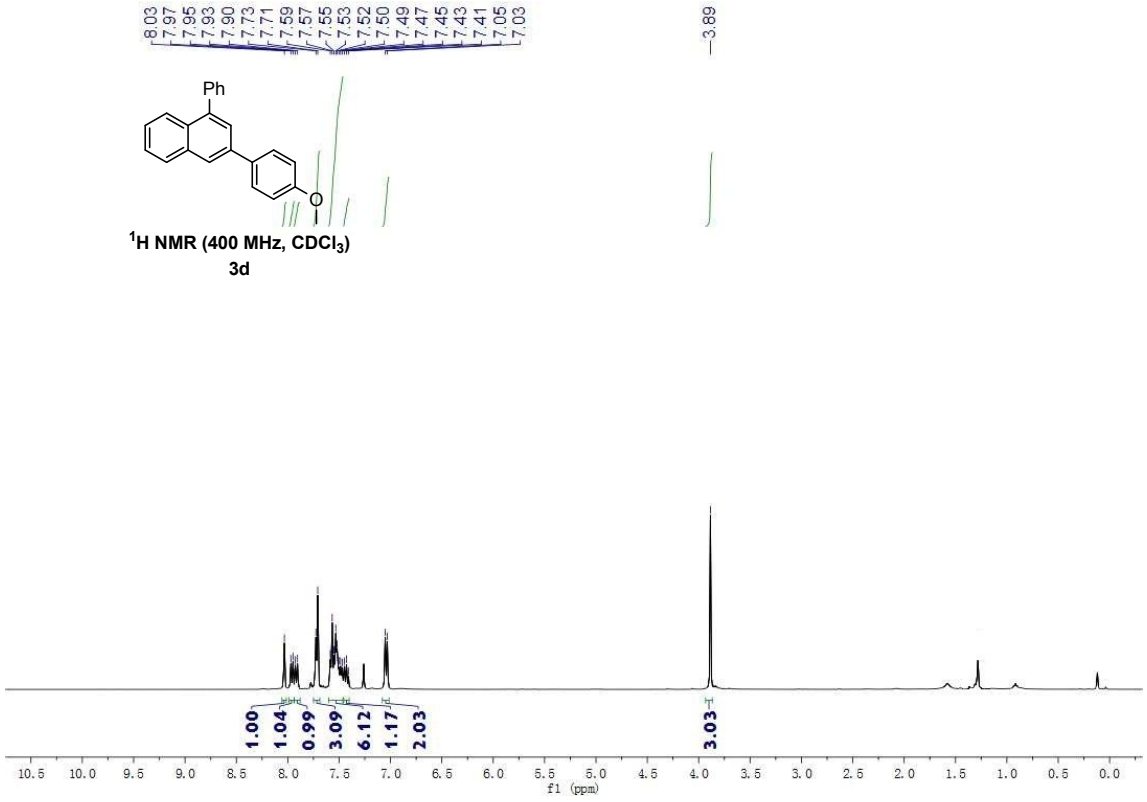
^{1}H NMR (400 MHz, $CDCl_3$)
3c



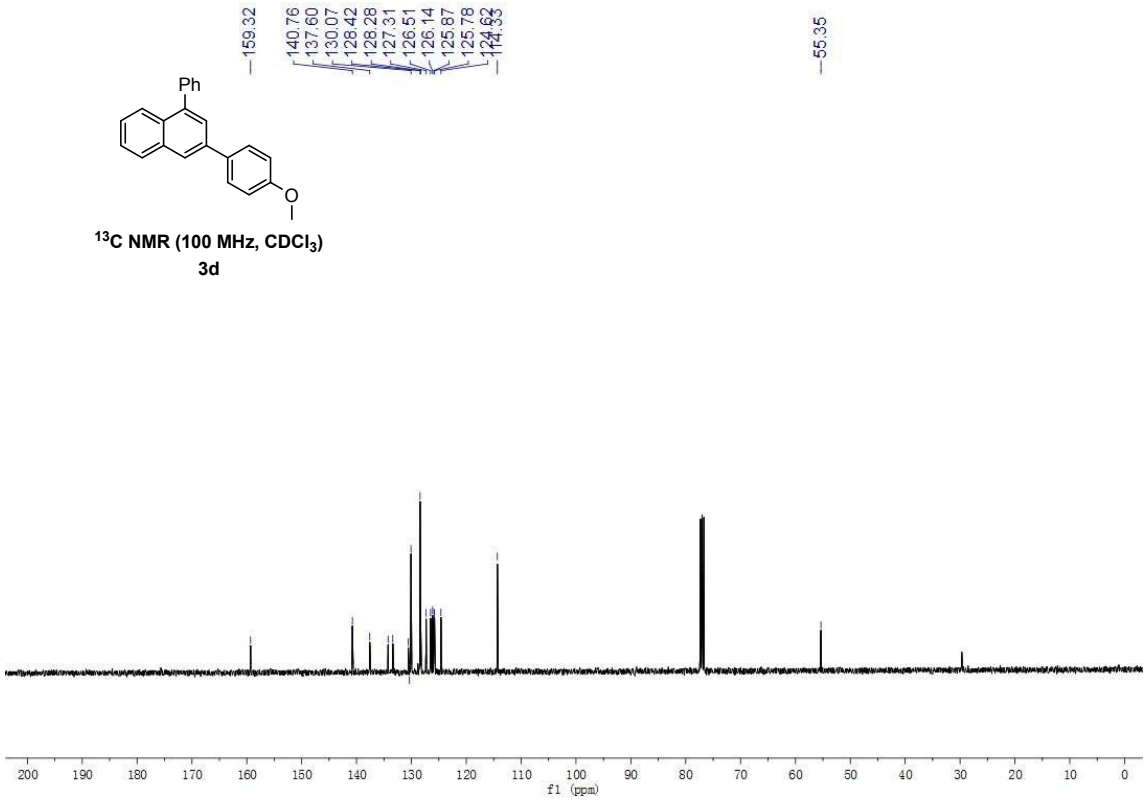


^{13}C NMR (100 MHz, $CDCl_3$)
3c

3-(4-Methoxyphenyl)-1-phenylnaphthalene (3d).

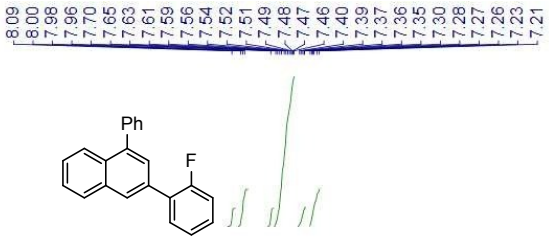


^{1}H NMR (400 MHz, $CDCl_3$)
3d

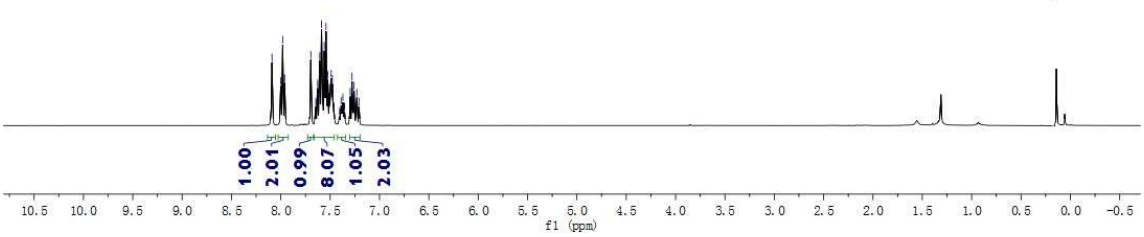


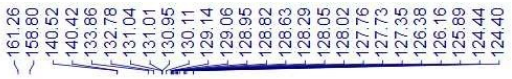
^{13}C NMR (100 MHz, $CDCl_3$)
3d

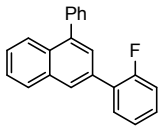
3-(2-Fluorophenyl)-1-phenylnaphthalene (3e).



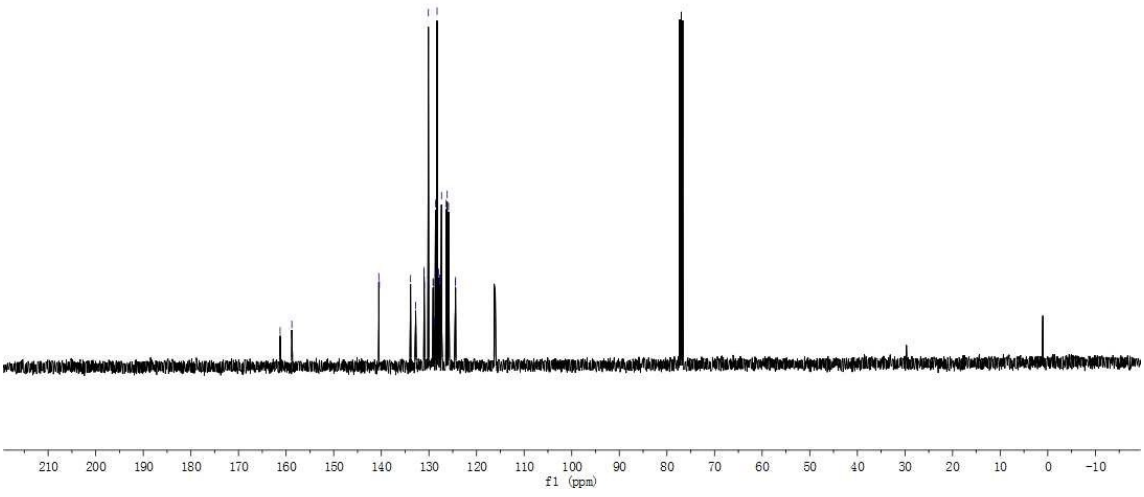
^{1}H NMR (400 MHz, $CDCl_3$)
3e

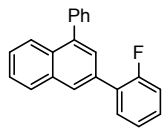






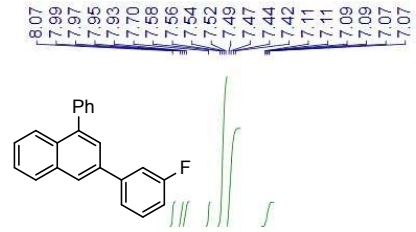
^{13}C NMR (100 MHz, $CDCl_3$)
3e



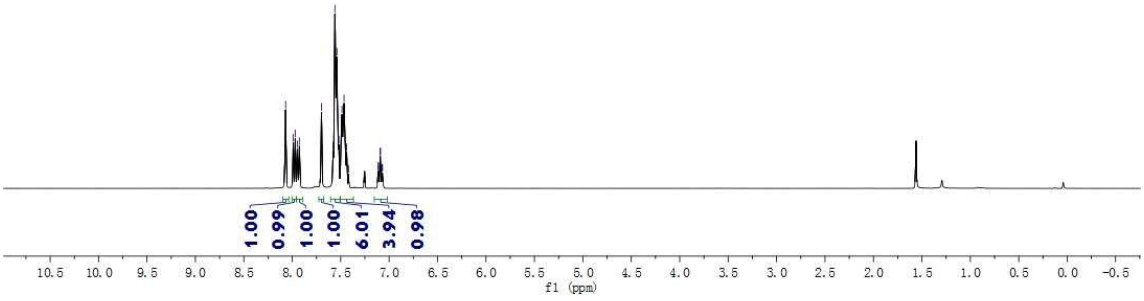


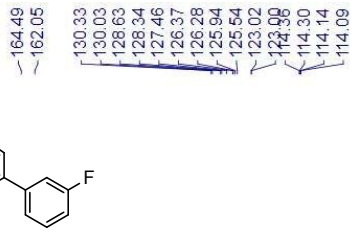
^{19}F NMR (376 MHz, CDCl3)
3e

3-(3-Fluorophenyl)-1-phenylnaphthalene (3f).

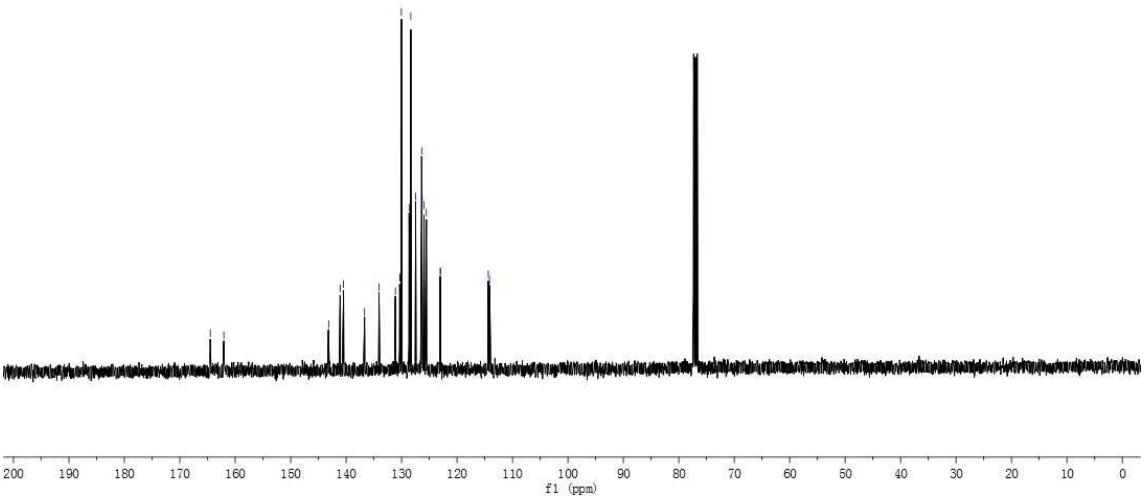


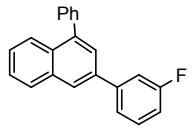
^{1}H NMR (400 MHz, $CDCl_3$)
3f





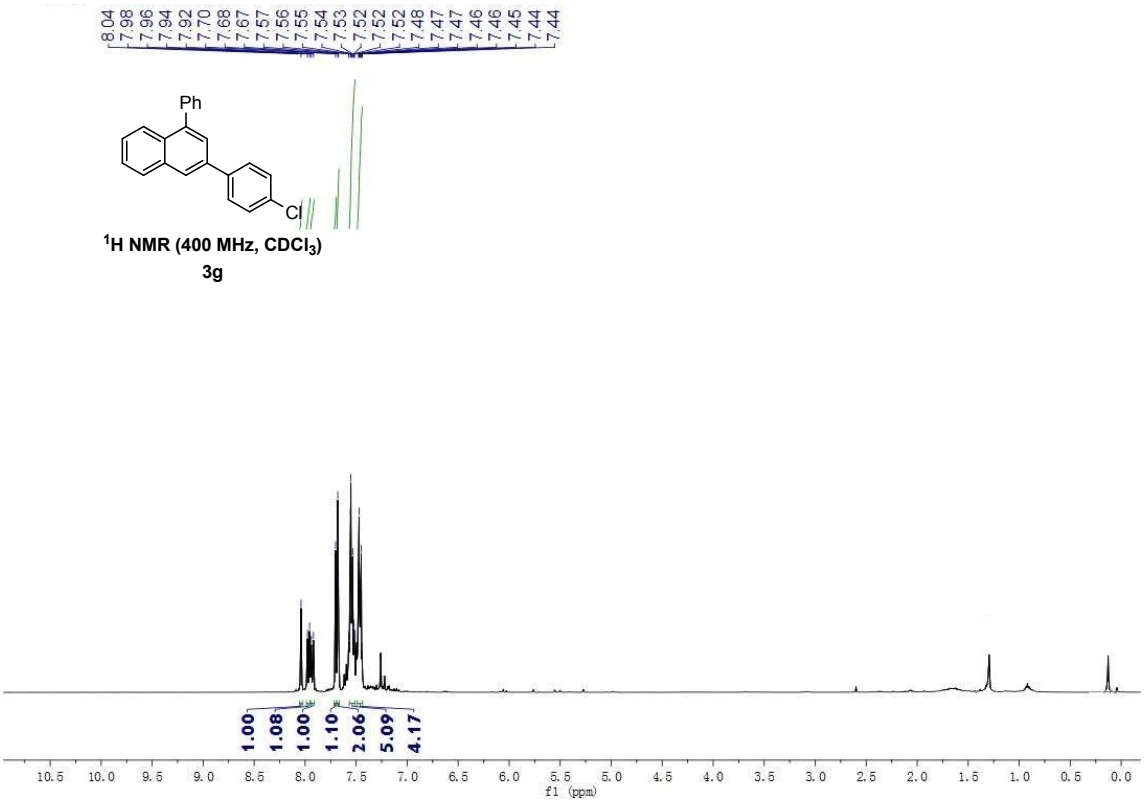
^{13}C NMR (100 MHz, $CDCl_3$)
3f



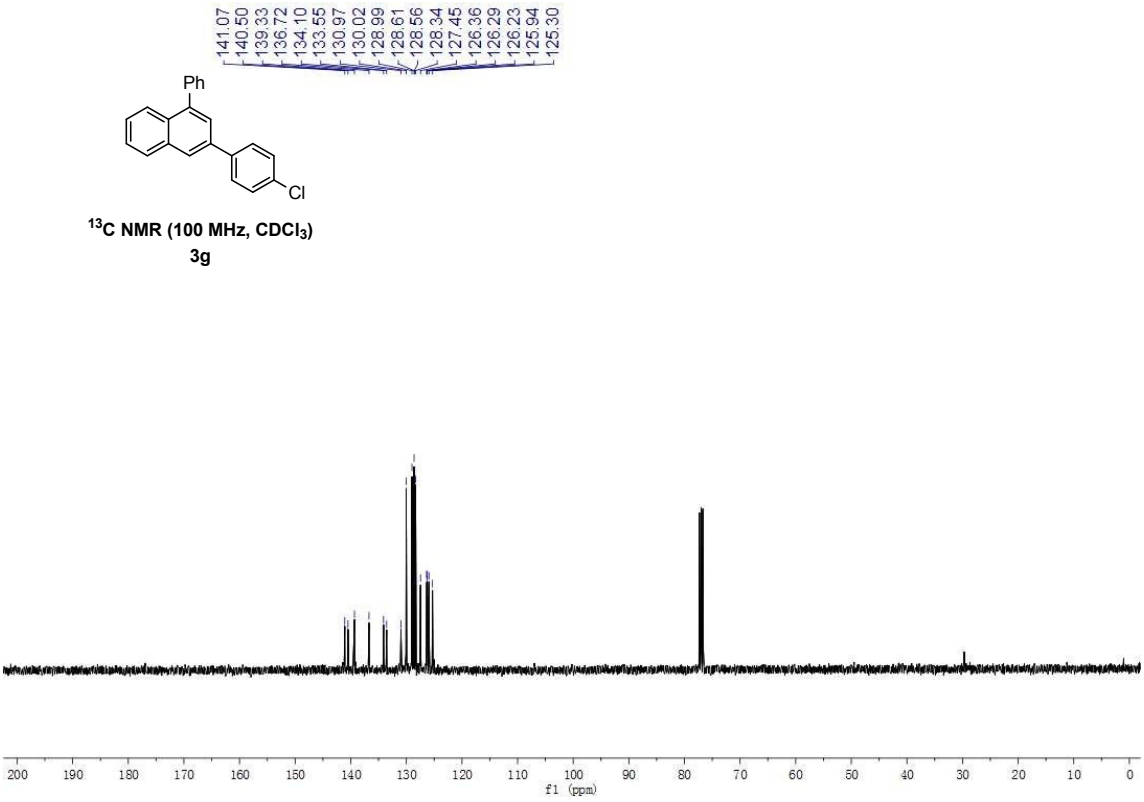


^{19}F NMR (376 MHz, CDCl3)
3f

3-(4-Chlorophenyl)-1-phenylnaphthalene (3g).

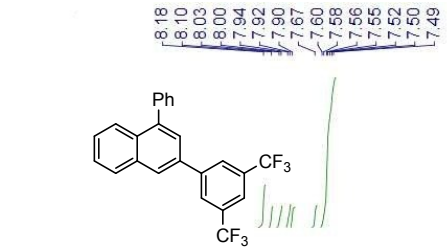


^{1}H NMR (400 MHz, $CDCl_3$)
3g

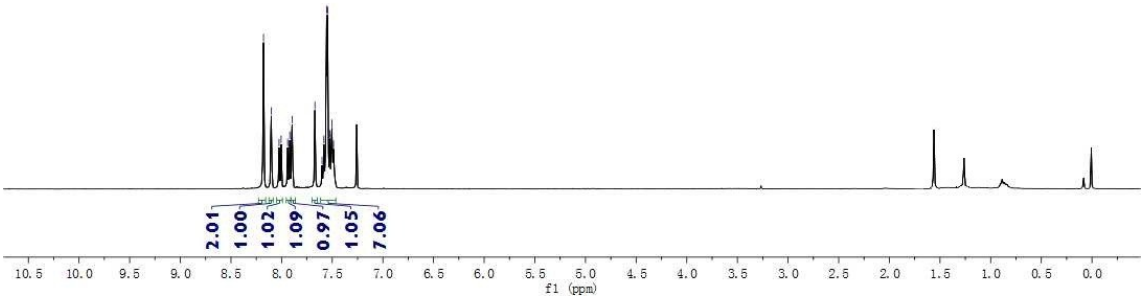


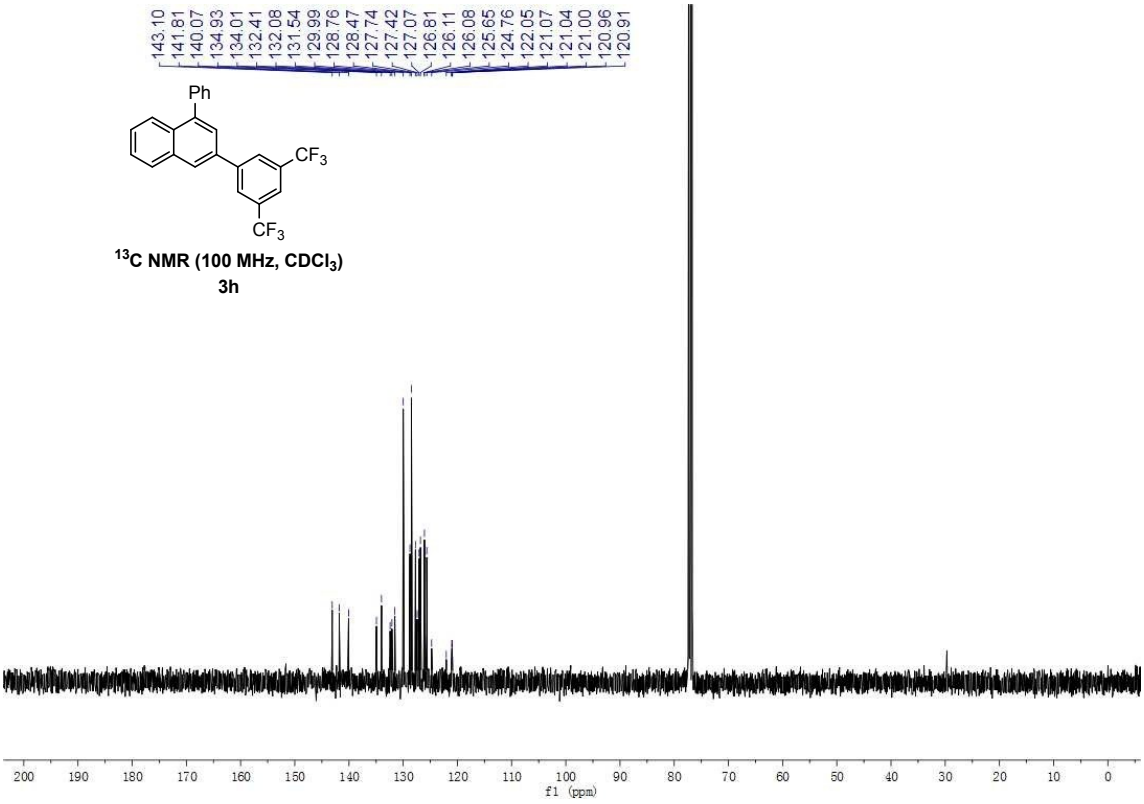
^{13}C NMR (100 MHz, $CDCl_3$)
3g

3-(3,5-Bis(trifluoromethyl)phenyl)-1-phenylnaphthalene (3h)

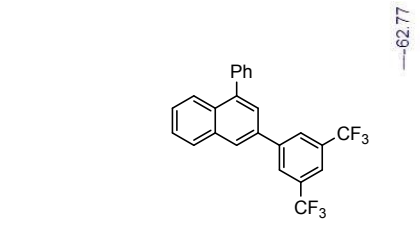


^{1}H NMR (400 MHz, $CDCl_3$)
3h





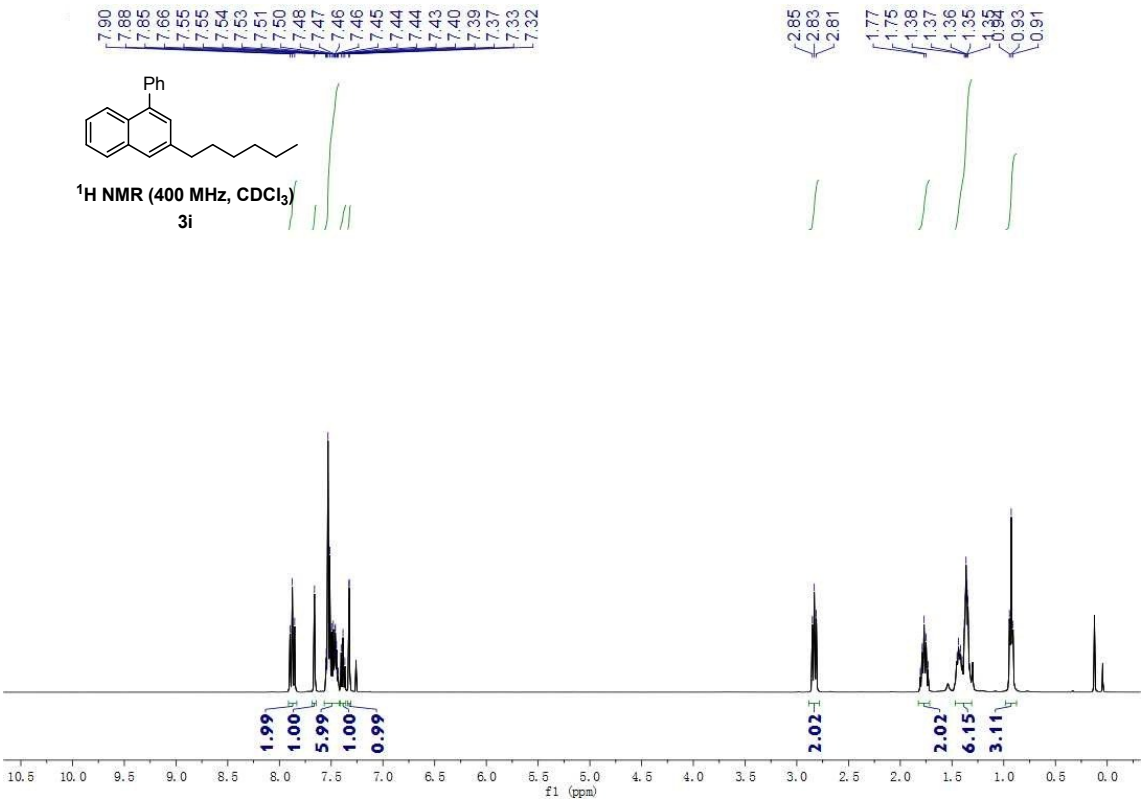
^{13}C NMR (100 MHz, $CDCl_3$)
3h



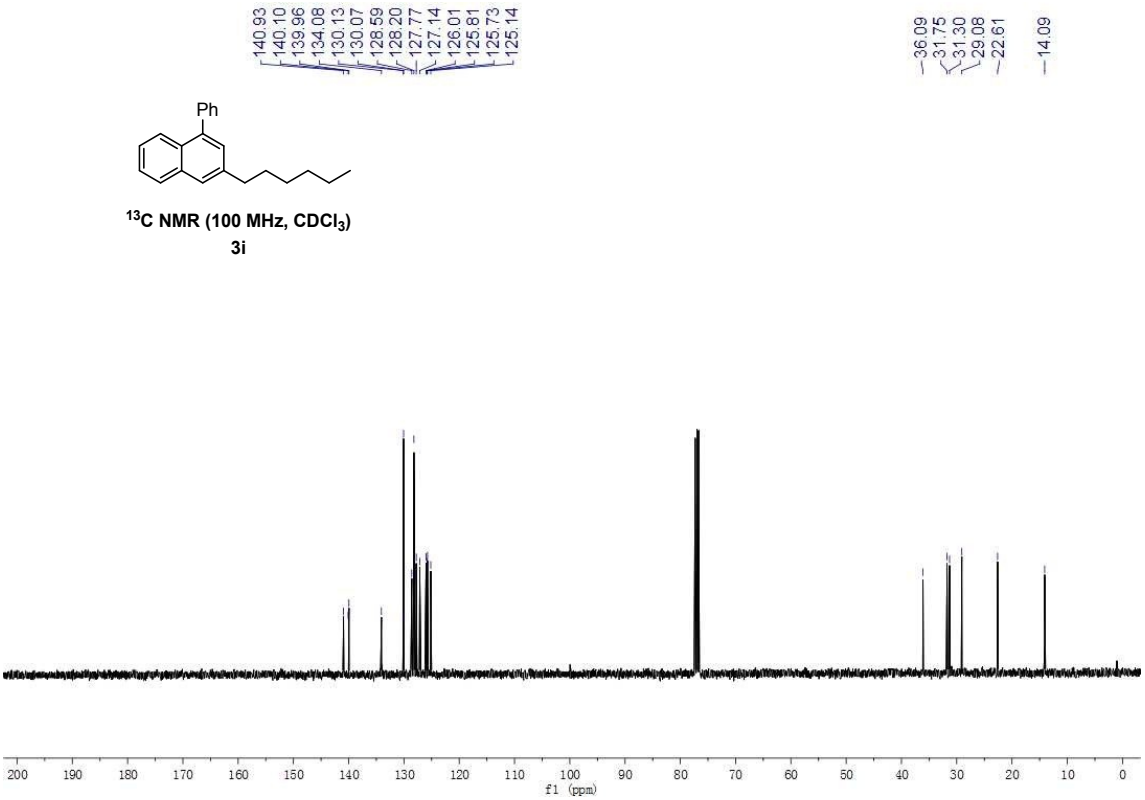
^{19}F NMR (376 MHz, CDCl3)

3h

3-Hexyl-1-phenylnaphthalene (3i).

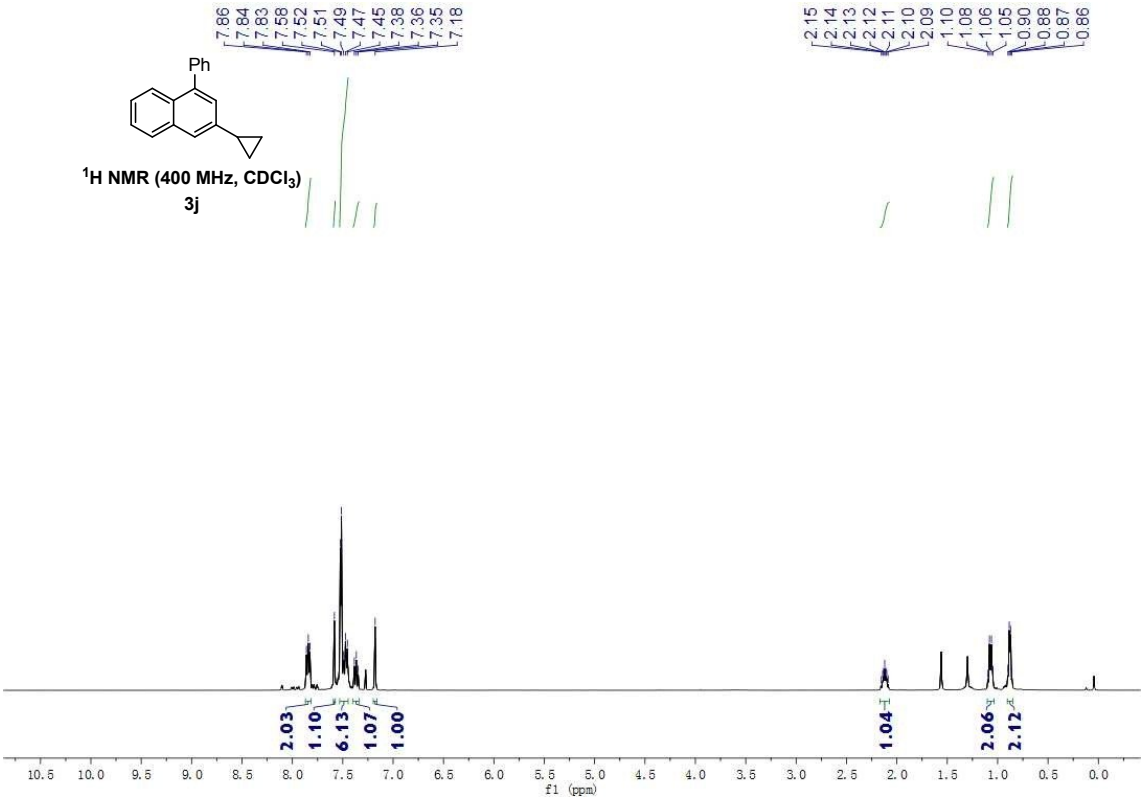


^{1}H NMR (400 MHz, $CDCl_3$)
3i

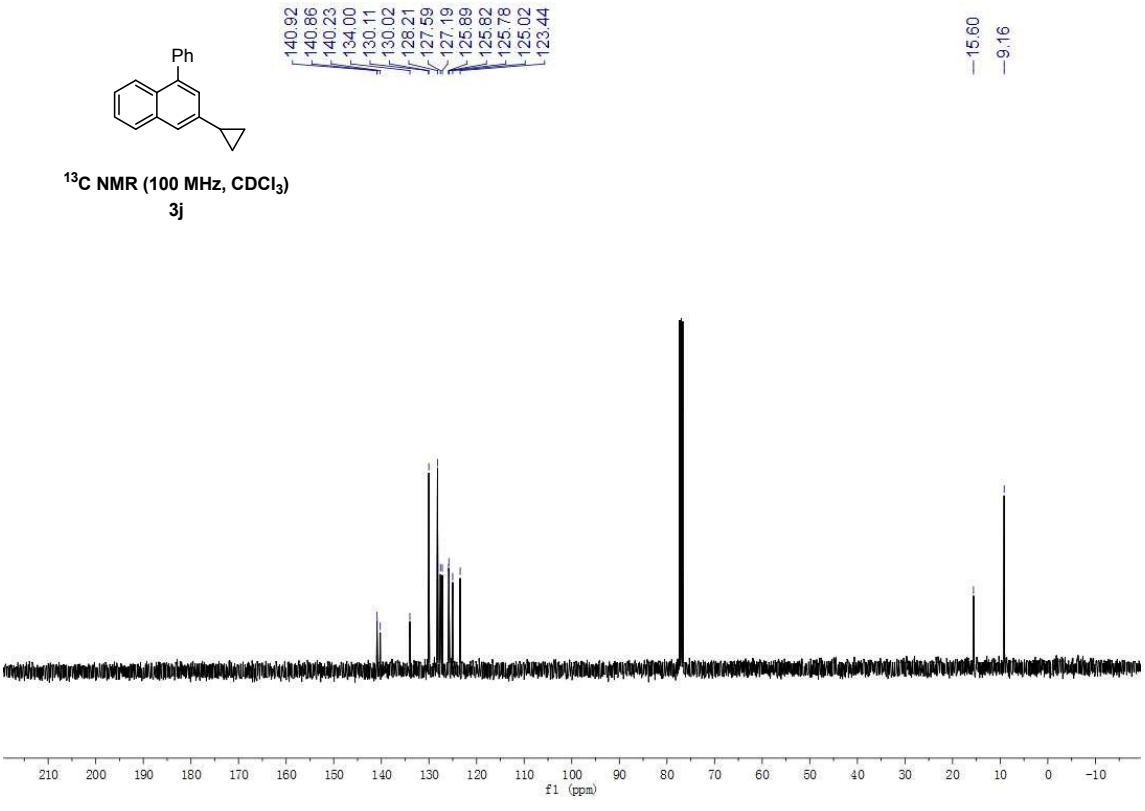


^{13}C NMR (100 MHz, $CDCl_3$)
3i

2-Cyclopropyl-1-phenylnaphthalene (3j).

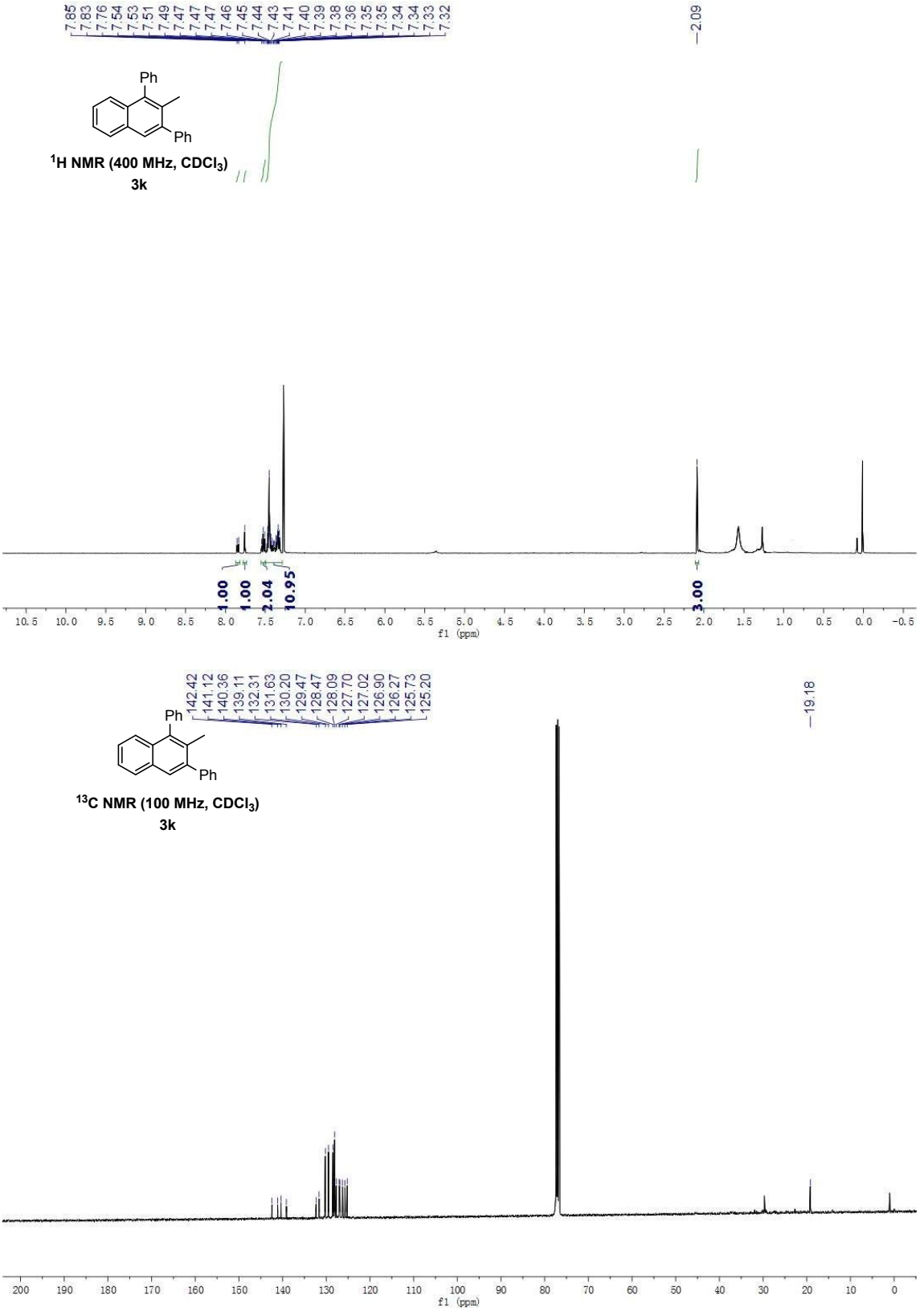


^{1}H NMR (400 MHz, $CDCl_3$)
3j



^{13}C NMR (100 MHz, $CDCl_3$)
3j

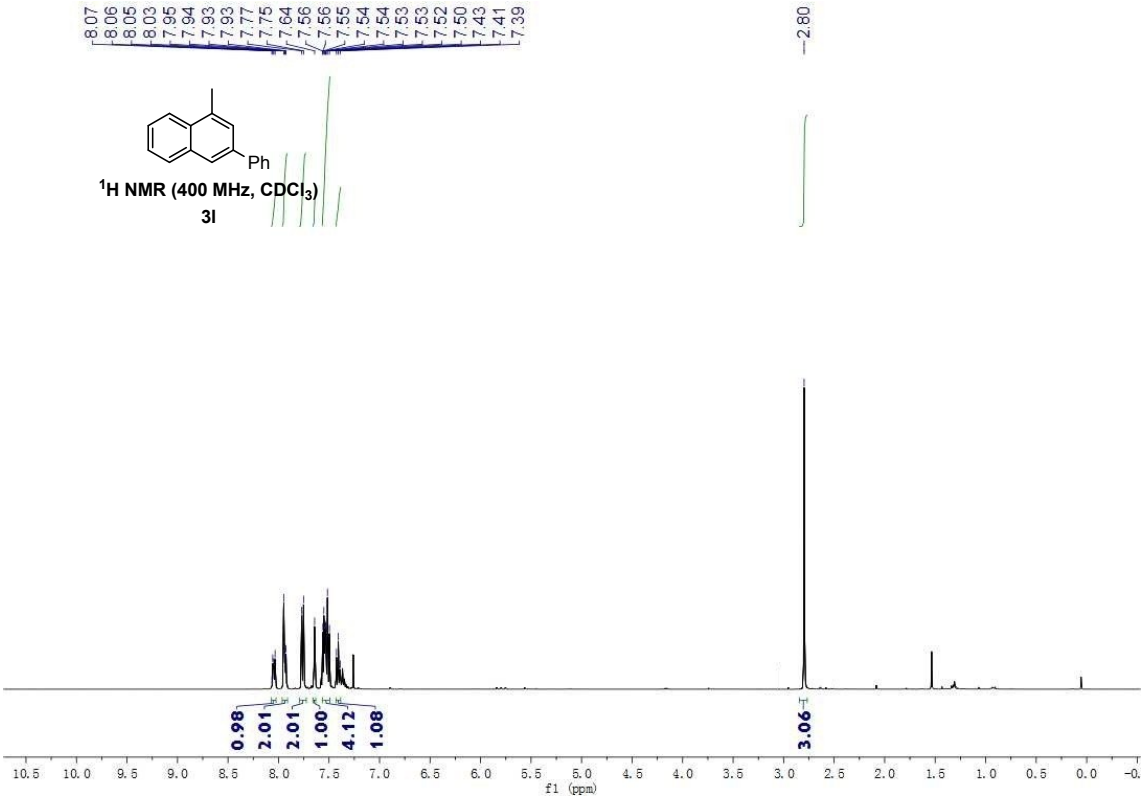
2-Methyl-1,3-diphenylnaphthalene (3k).



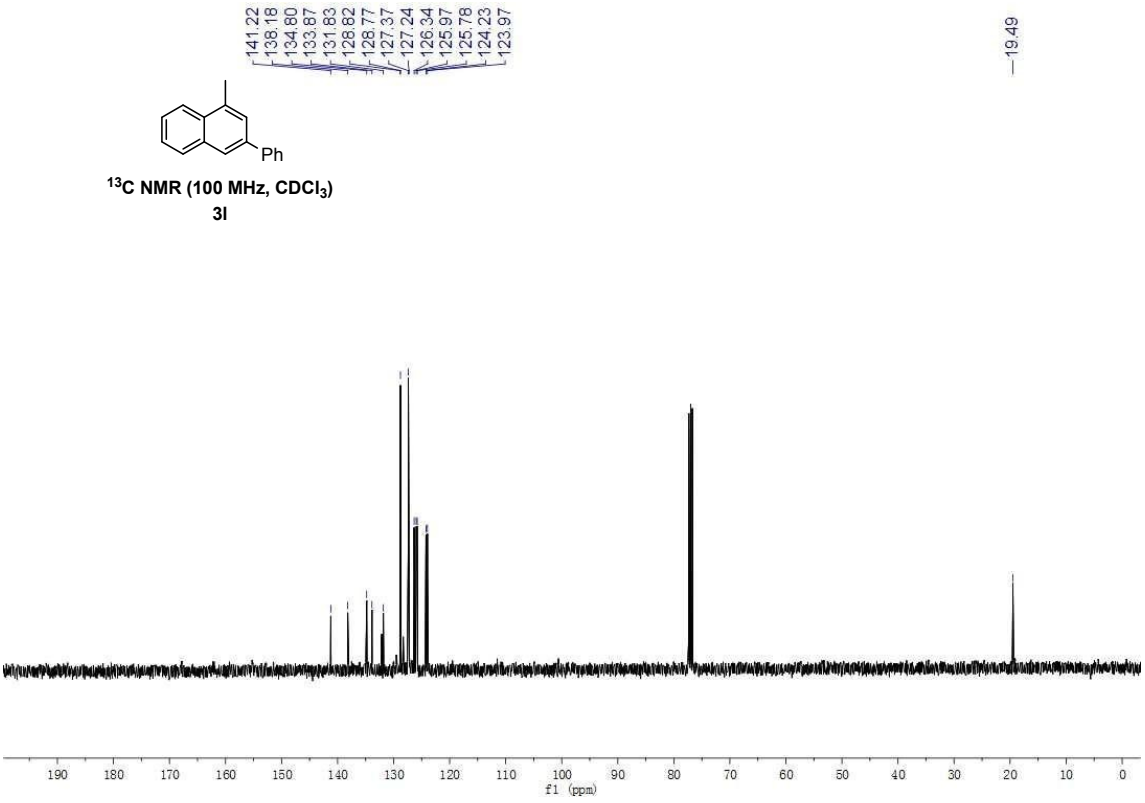
^{1}H NMR (400 MHz, $CDCl_3$)
3k

^{13}C NMR (100 MHz, $CDCl_3$)
3k

1-Methyl-3-phenylnaphthalene (3l).

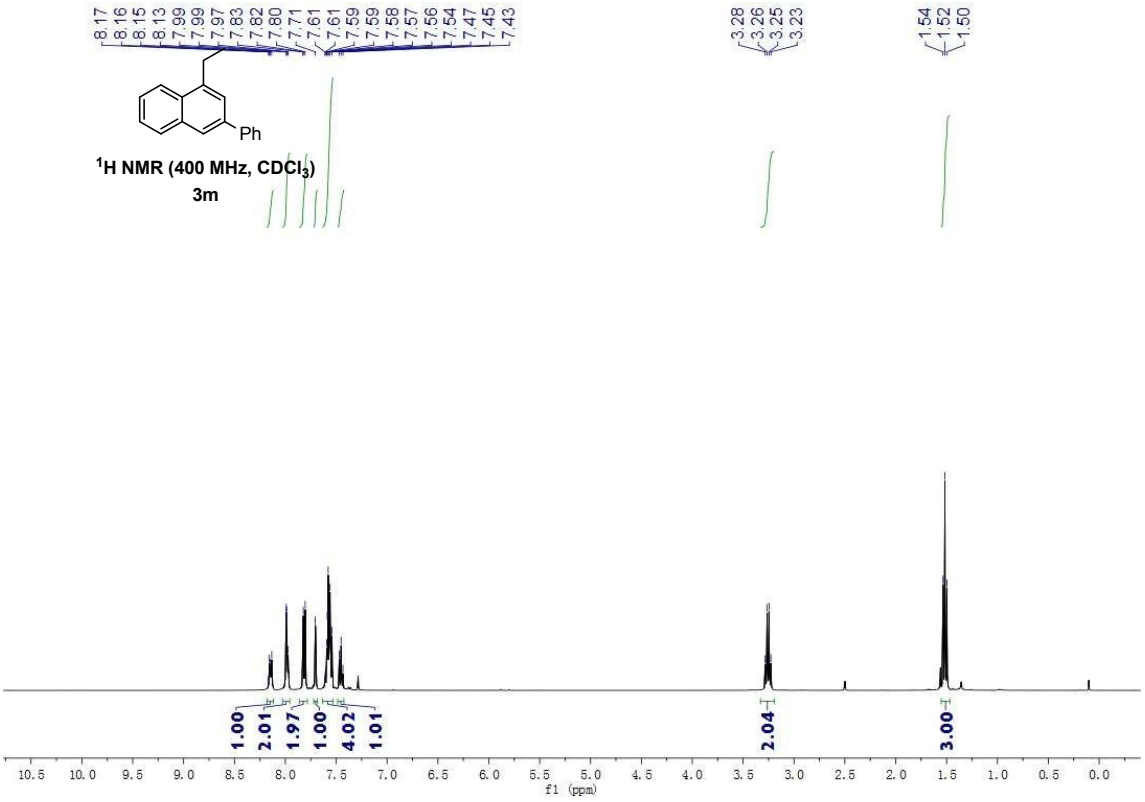


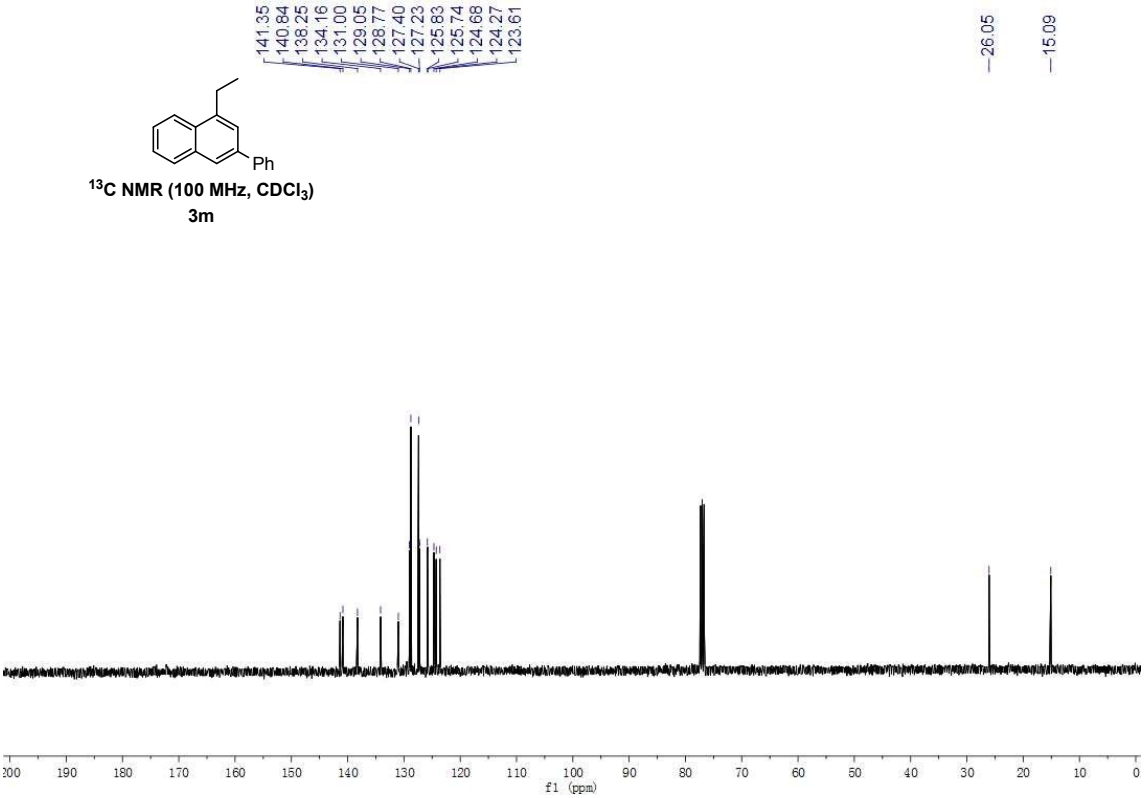
^{1}H NMR (400 MHz, $CDCl_3$)
3l



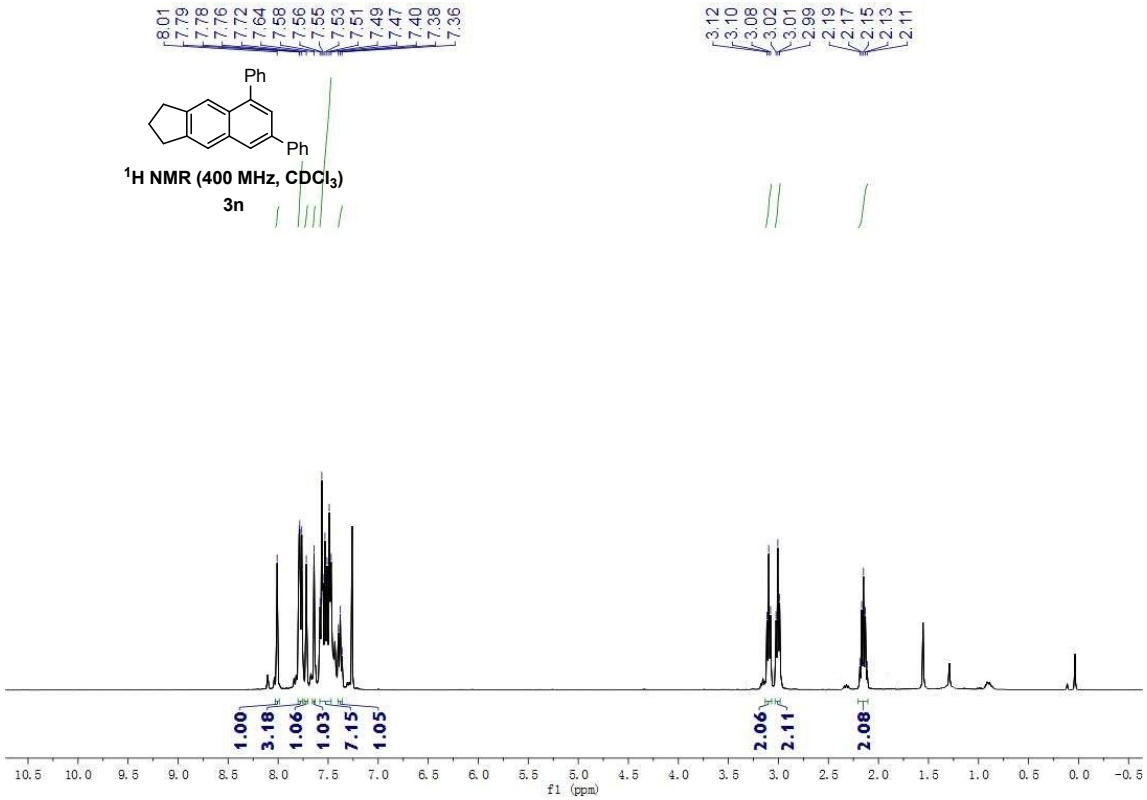
^{13}C NMR (100 MHz, $CDCl_3$)
3l

1-Ethyl-3-phenylnaphthalene (3m).



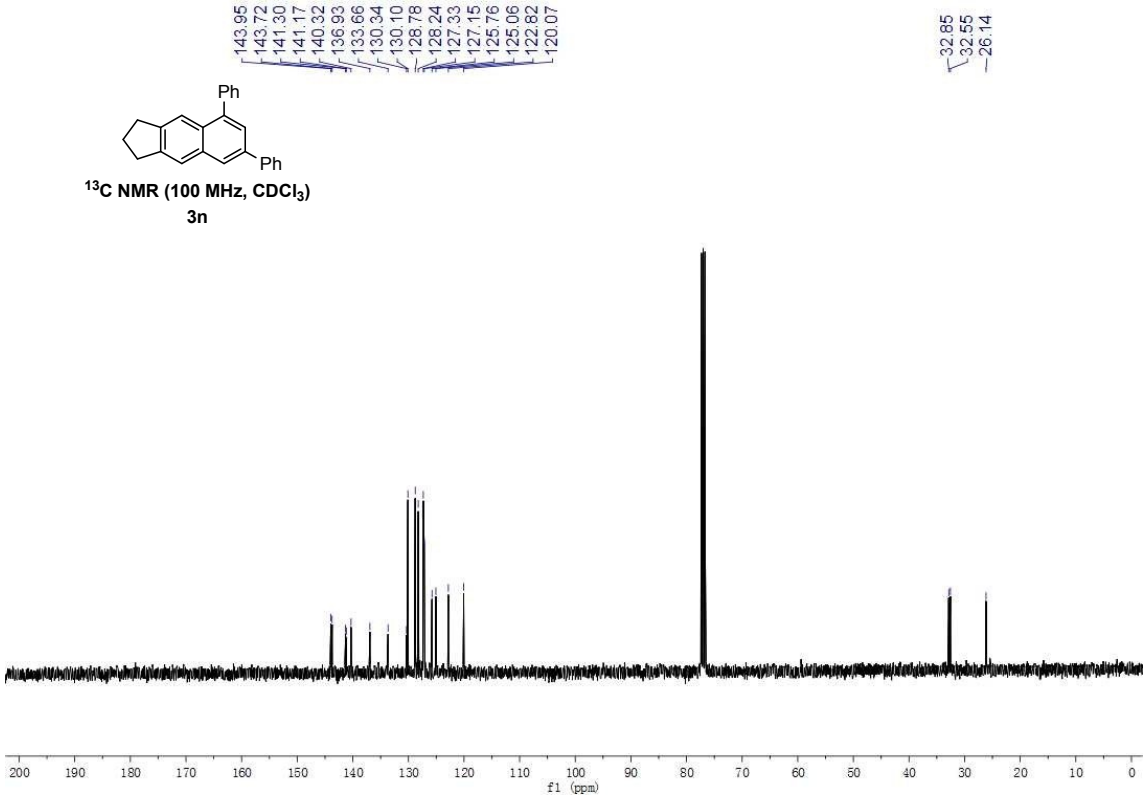


5,7-Diphenyl-2,3-dihydro-1H-cyclopenta[b]naphthalene (3n).



^{1}H NMR (400 MHz, $CDCl_3$)

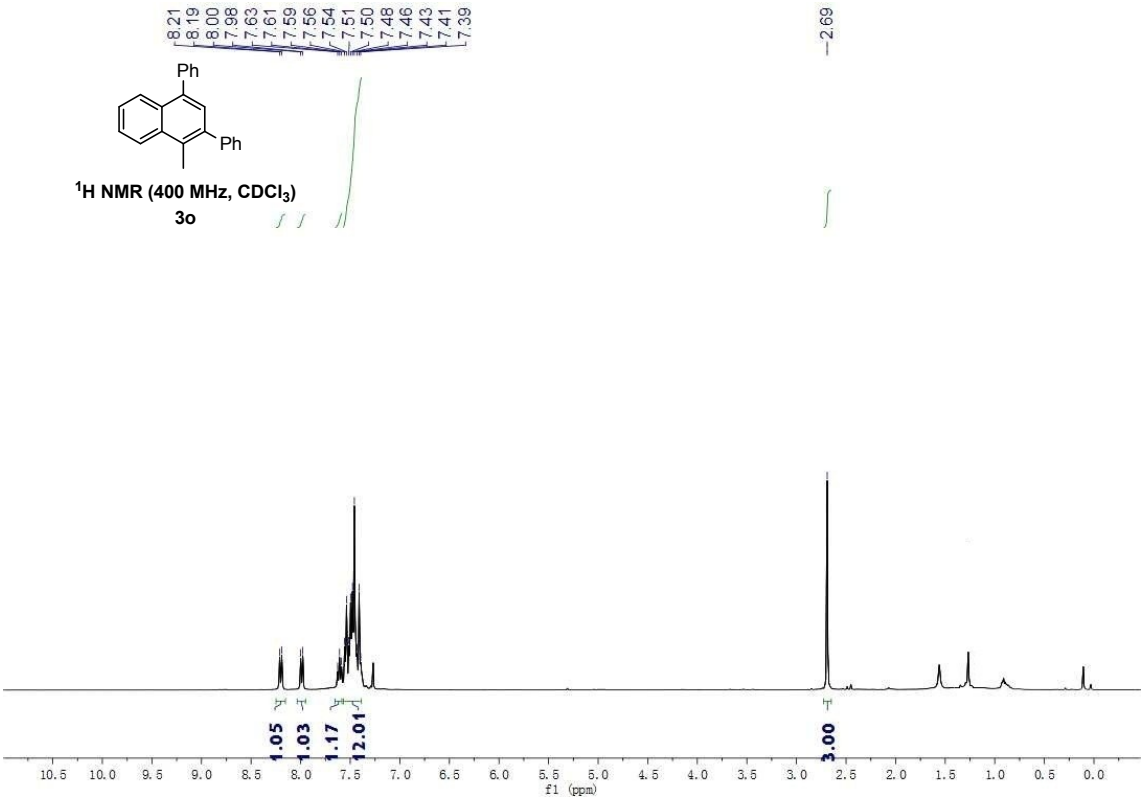
3n



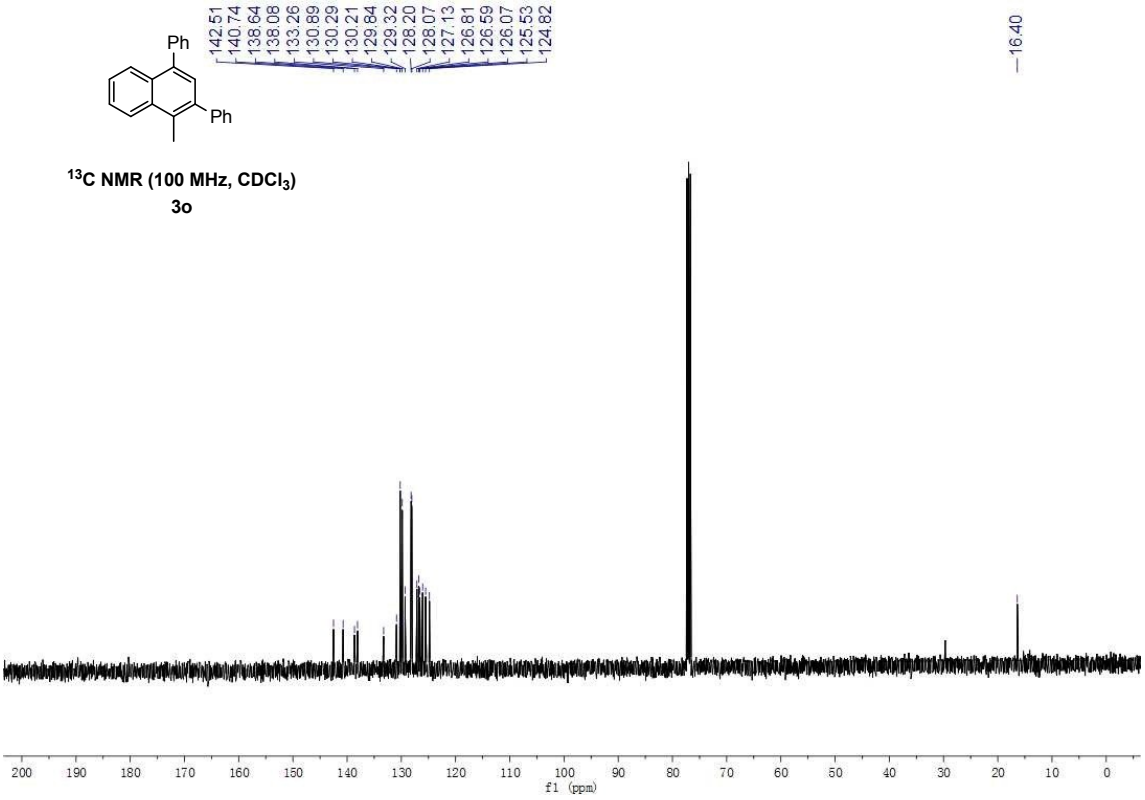
^{13}C NMR (100 MHz, $CDCl_3$)

3n

1-Methyl-2,4-diphenylnaphthalene (3o).

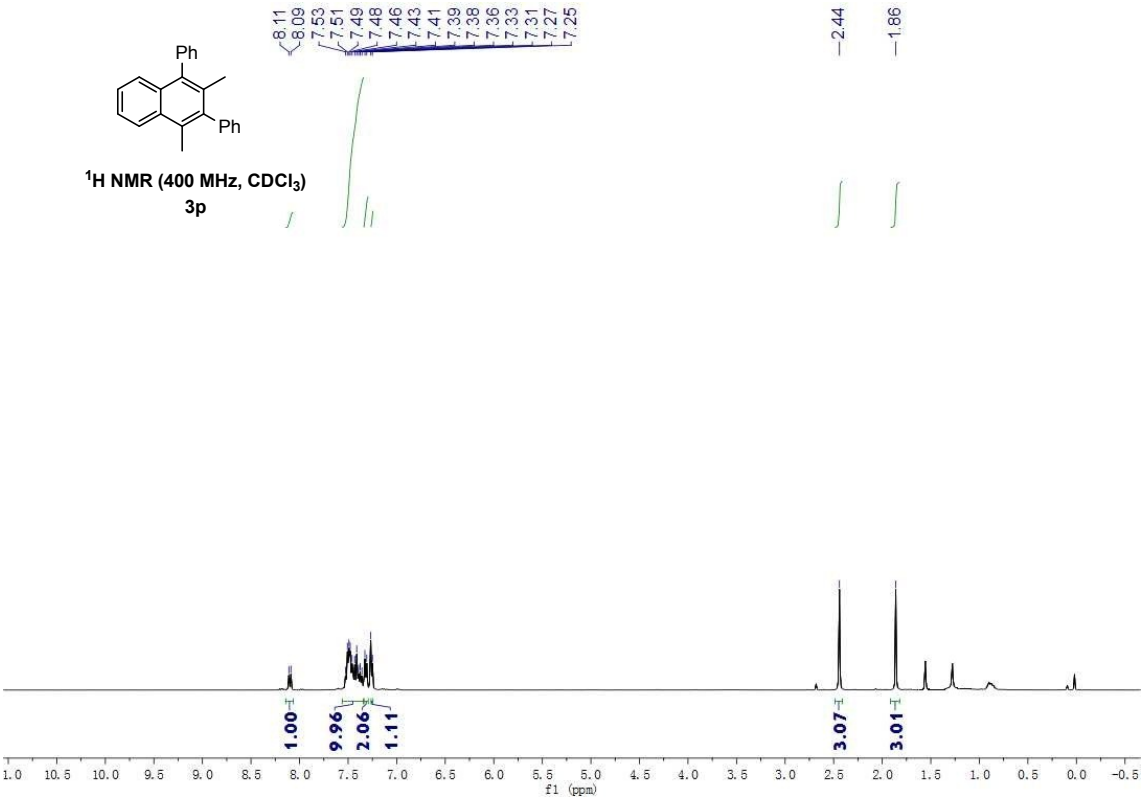


^{1}H NMR (400 MHz, $CDCl_3$)
3o

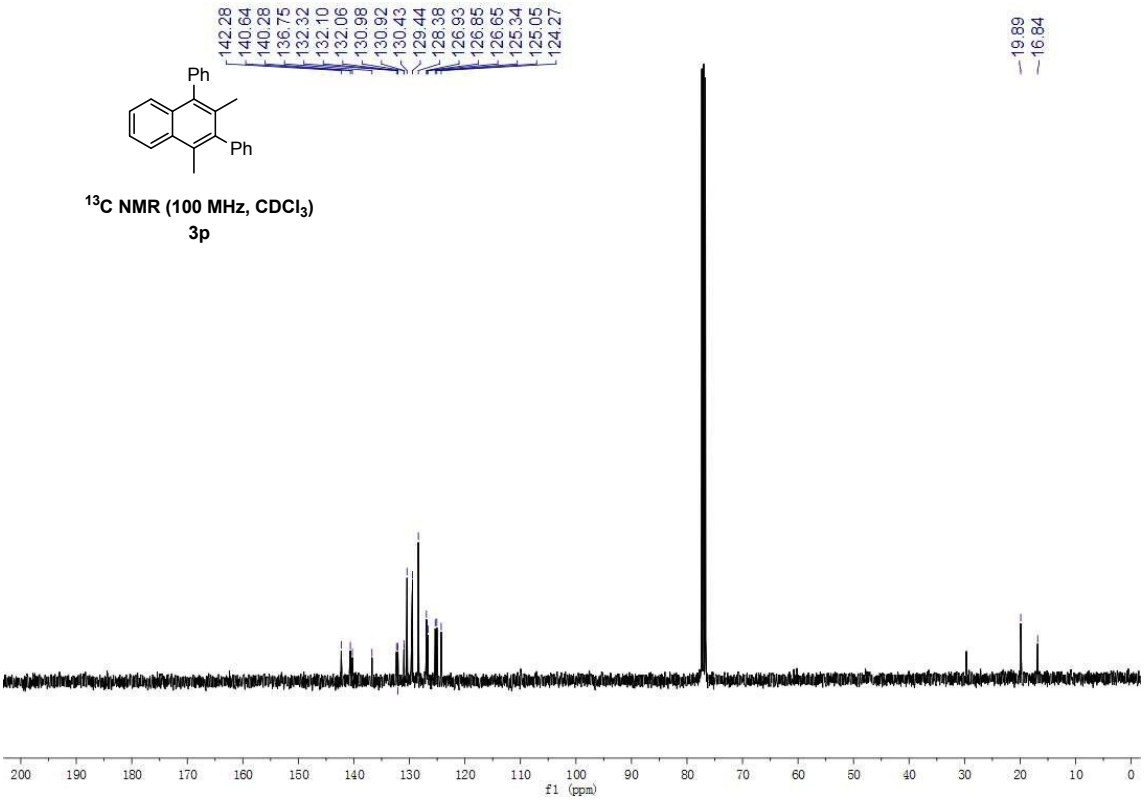


^{13}C NMR (100 MHz, $CDCl_3$)
3o

1,3-Dimethyl-2,4-diphenylnaphthalene (3p).

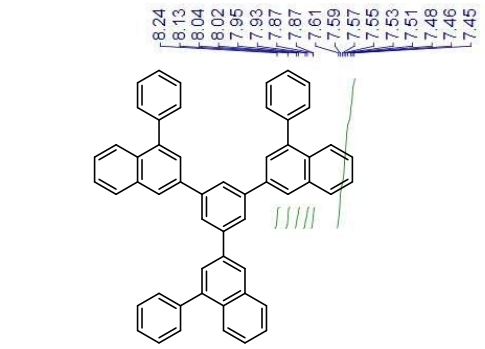


^{1}H NMR (400 MHz, $CDCl_3$)
3p

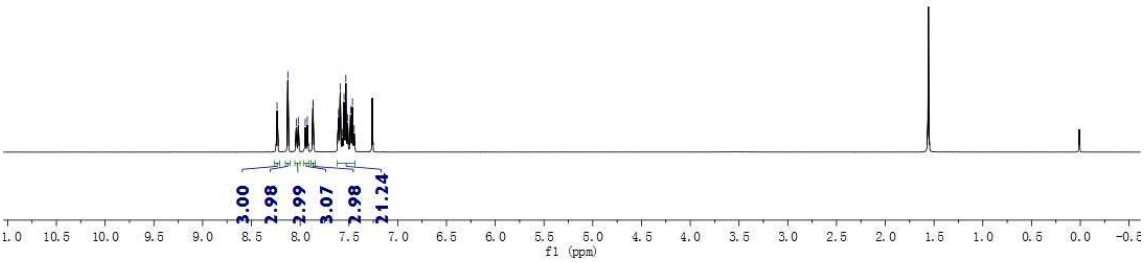


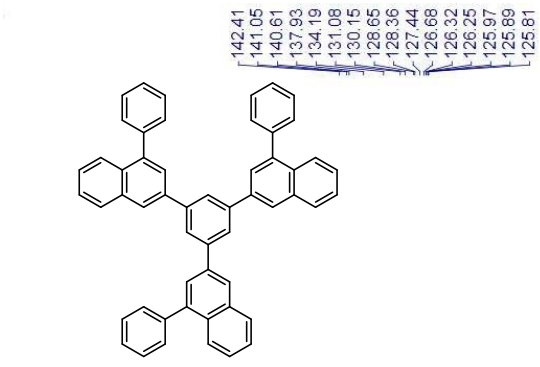
^{13}C NMR (100 MHz, $CDCl_3$)
3p

1,3,5-Tris(4-phenylnaphthalen-2-yl)benzene (3q).



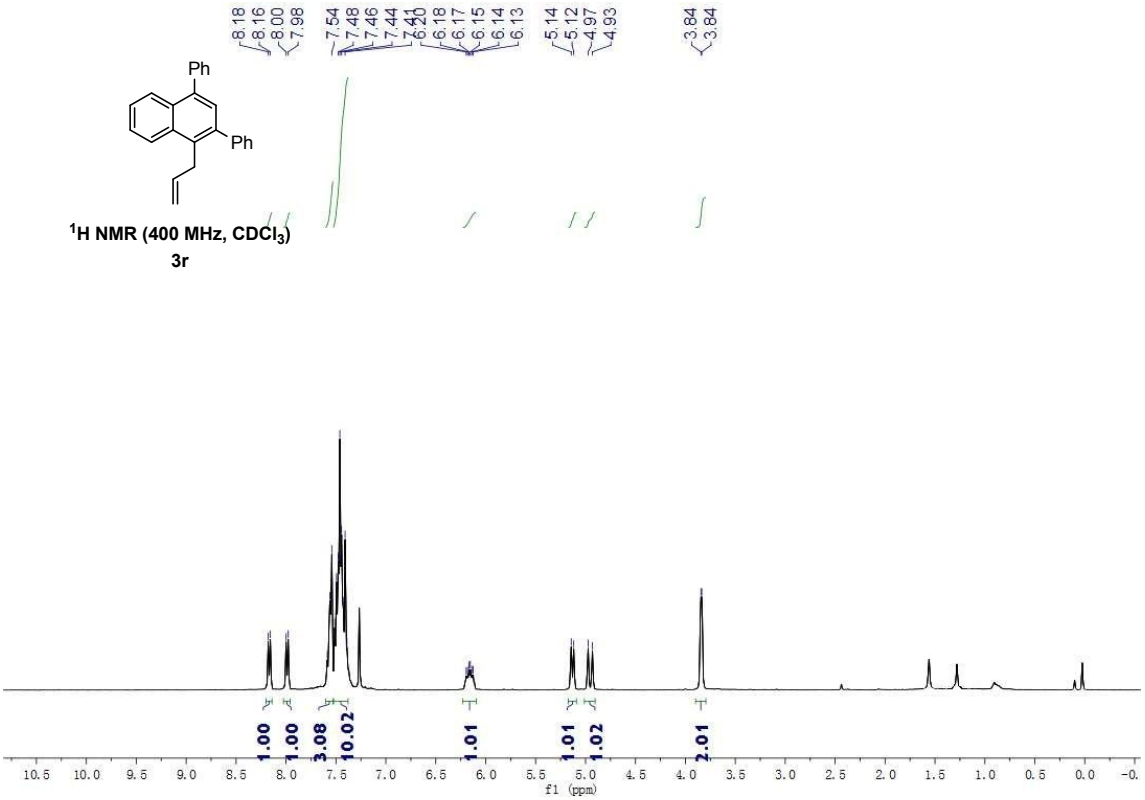
^{1}H NMR (400 MHz, $CDCl_3$)
3q



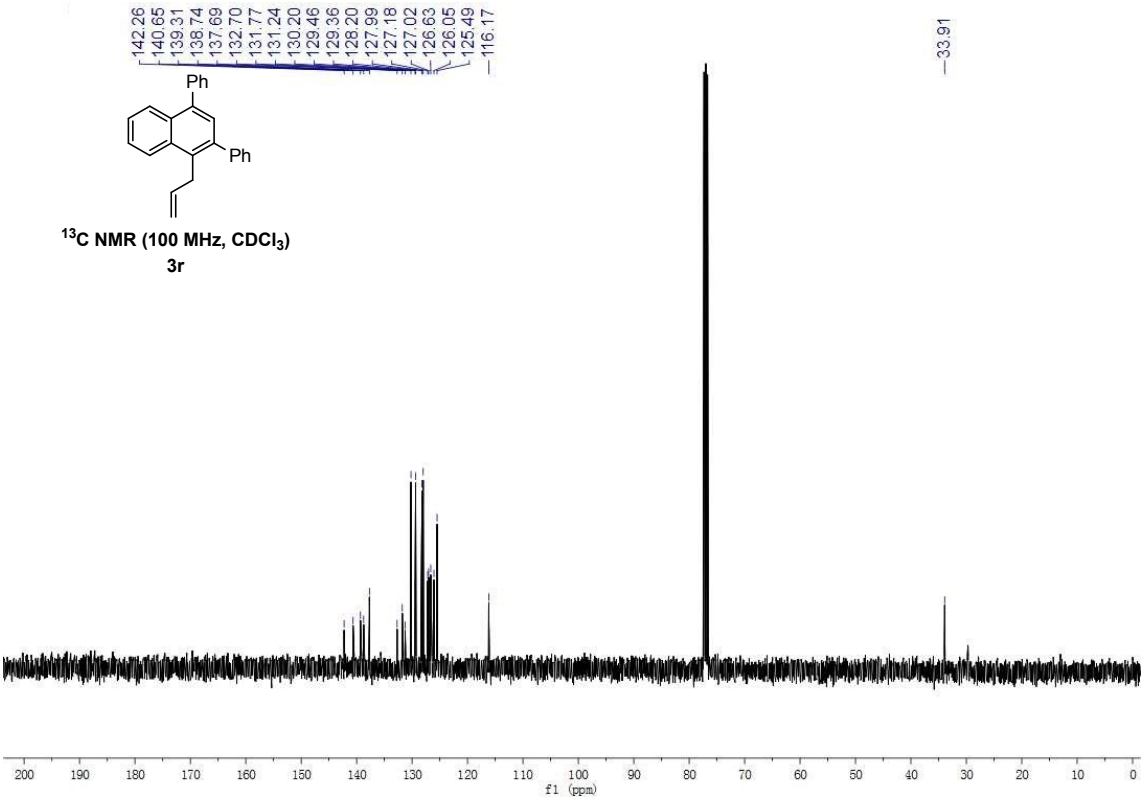


^{13}C NMR (100 MHz, $CDCl_3$)
3q

1-Allyl-2,4-diphenylnaphthalene (3r).

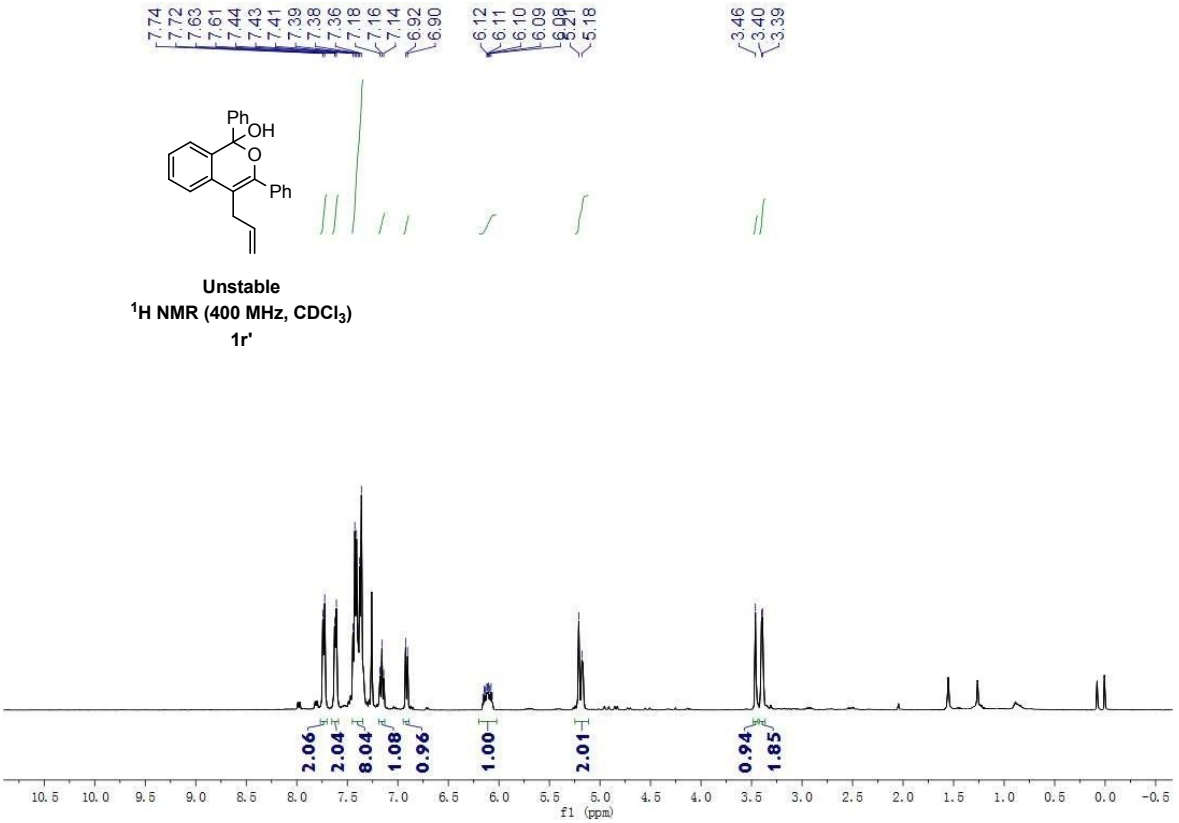


^{1}H NMR (400 MHz, $CDCl_3$)
3r

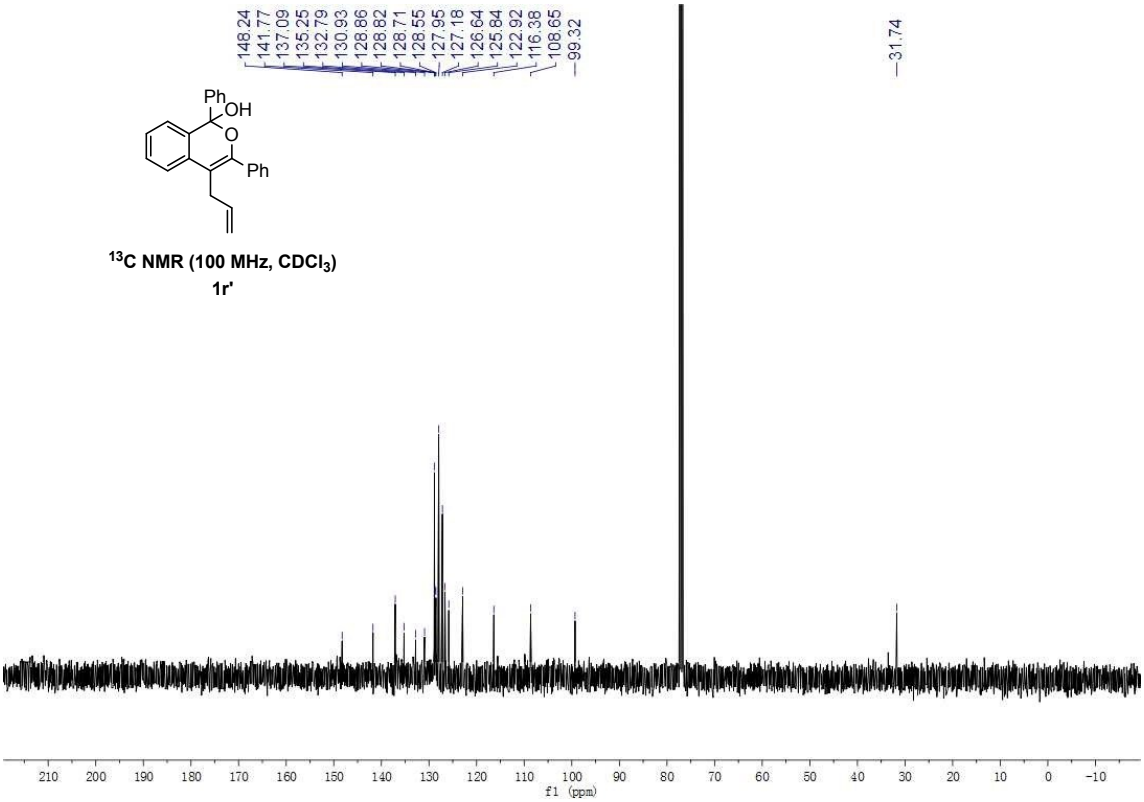


^{13}C NMR (100 MHz, $CDCl_3$)
3r

4-Allyl-1,3-diphenyl-1H-isochromen-1-ol (1r').

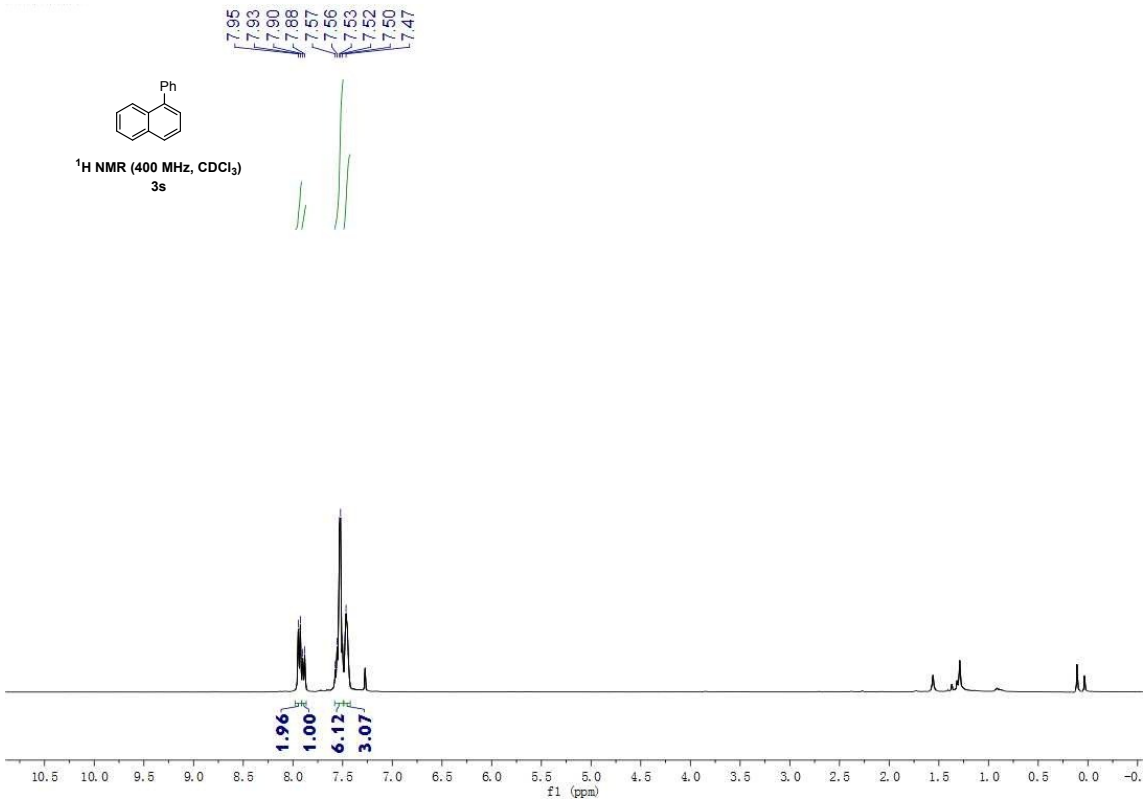


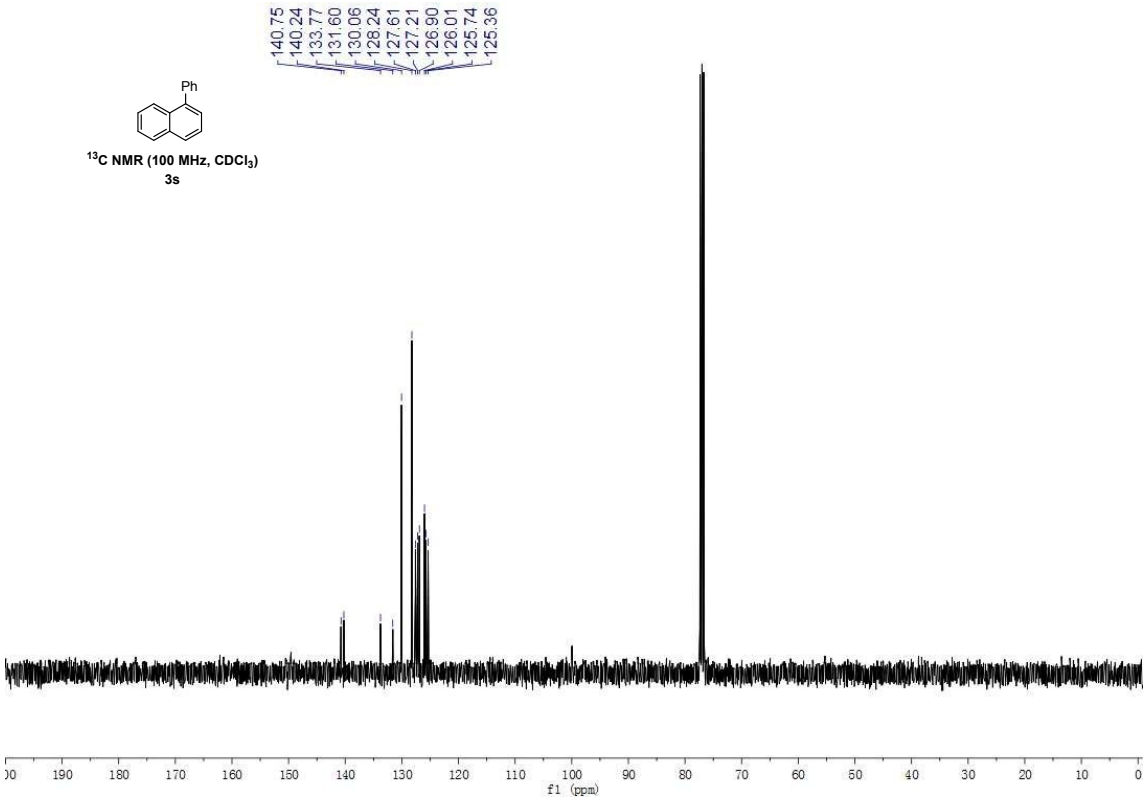
Unstable
^{1}H NMR (400 MHz, $CDCl_3$)
1r'



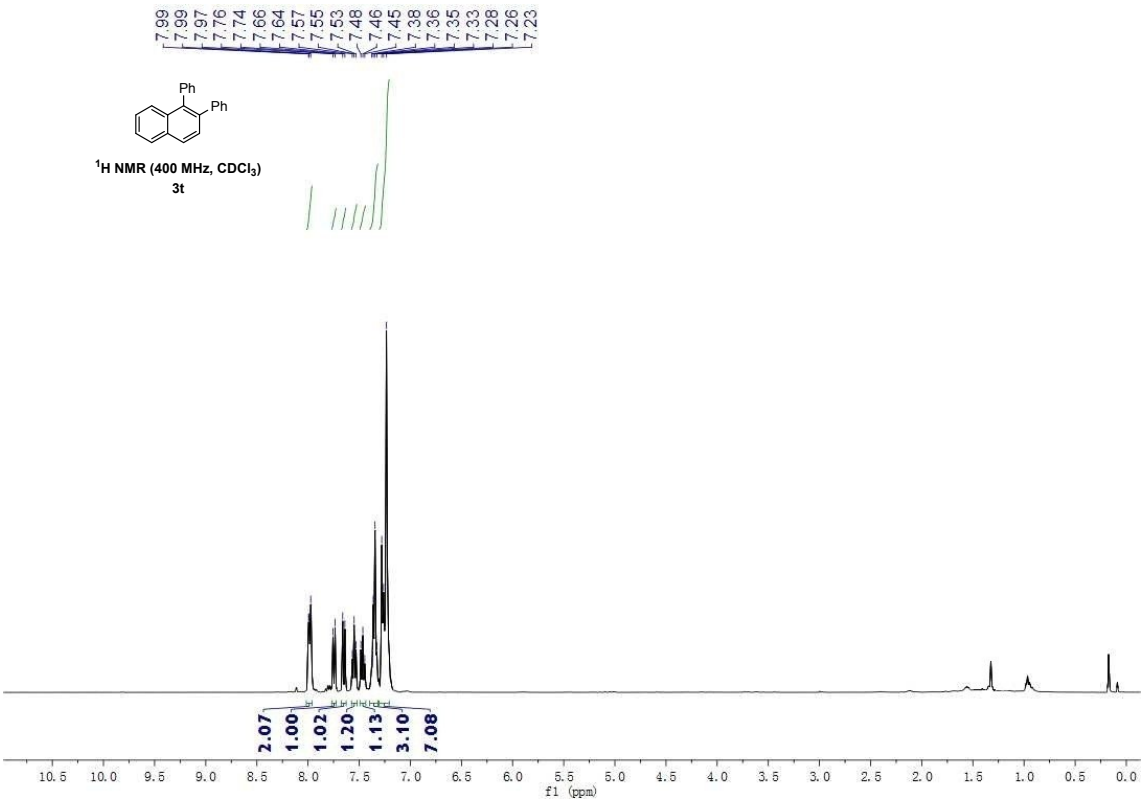
^{13}C NMR (100 MHz, $CDCl_3$)
1r'

1-Phenylnaphthalene (3s).

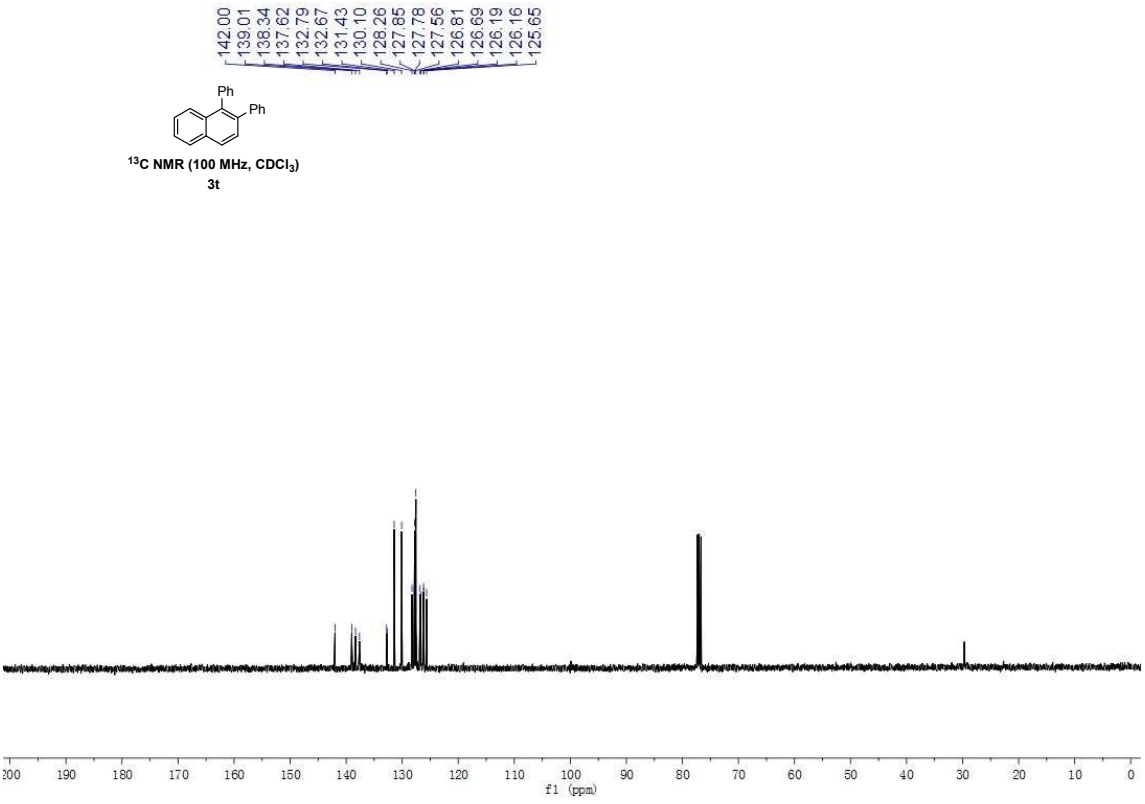




1,2-Diphenylnaphthalene (3t).

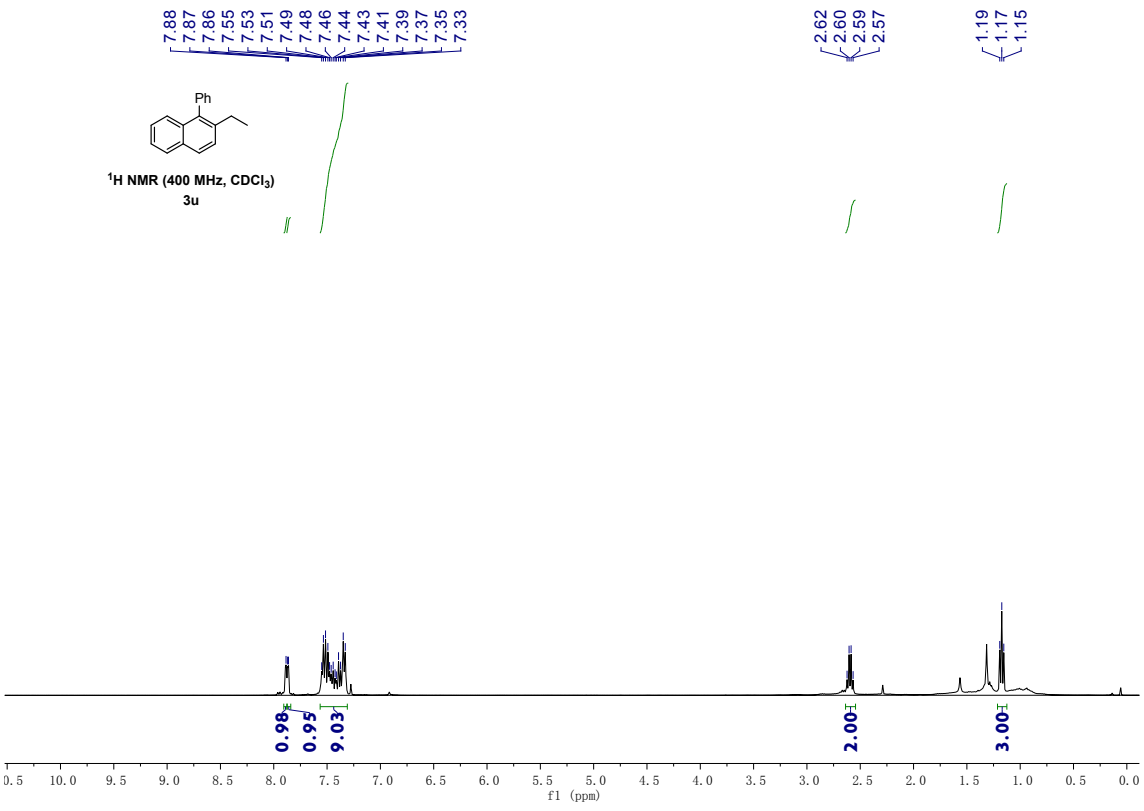


^{1}H NMR (400 MHz, $CDCl_3$)
3t

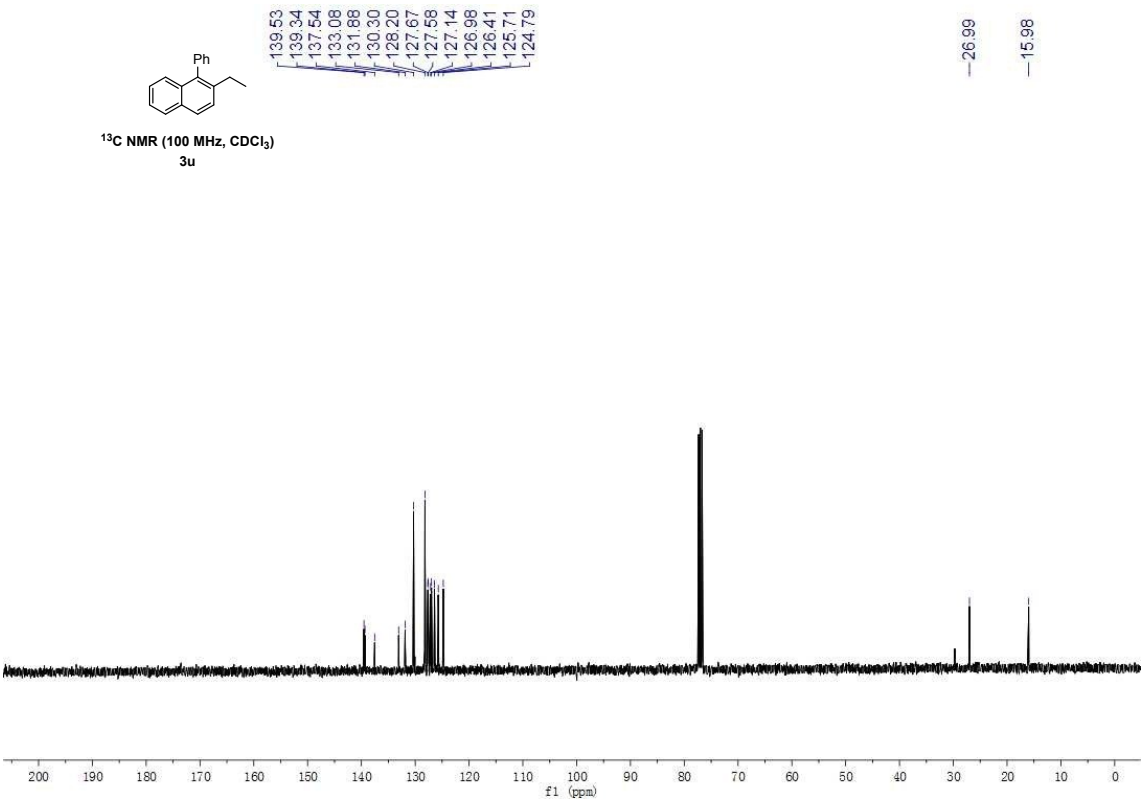


^{13}C NMR (100 MHz, $CDCl_3$)
3t

2-Ethyl-1-phenylnaphthalene (3u).

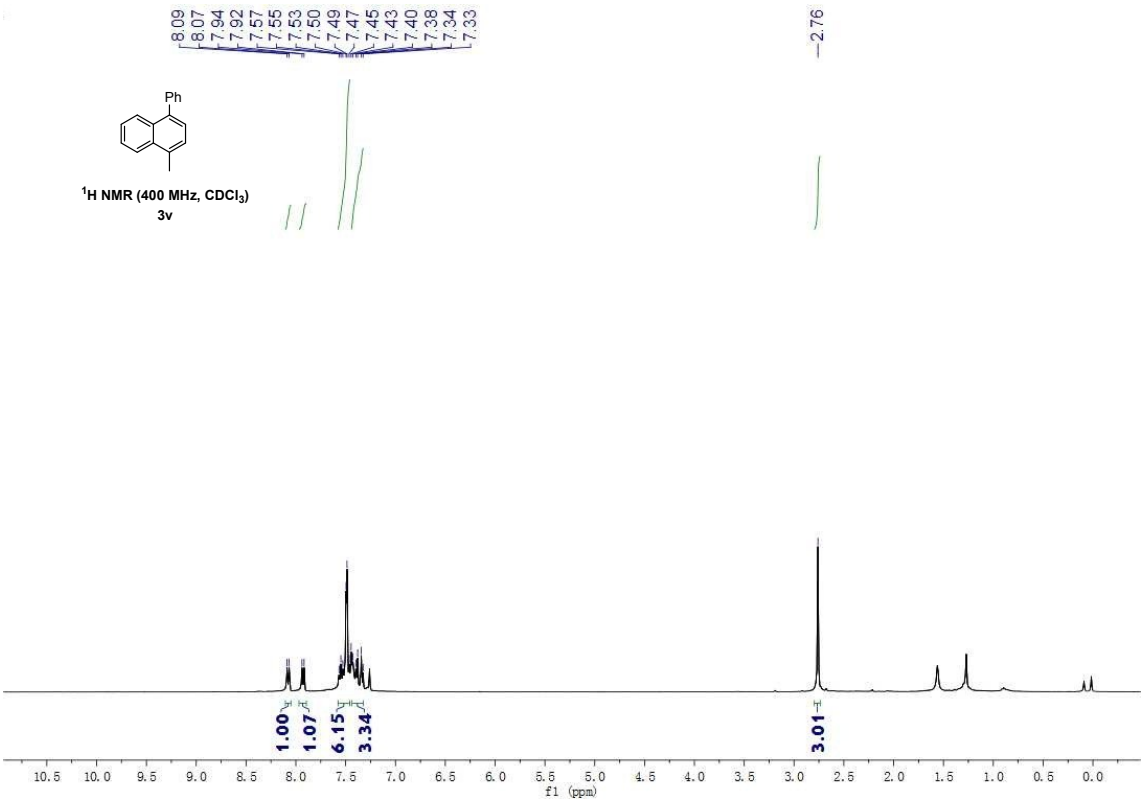


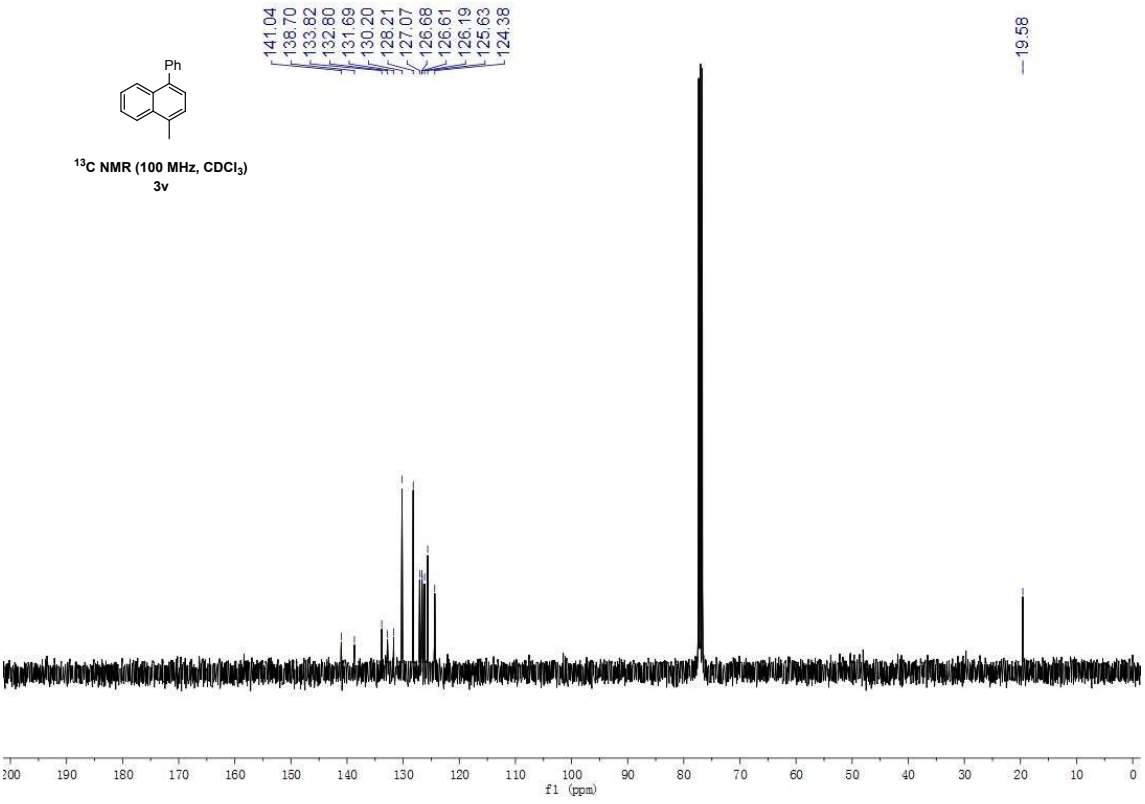
^{1}H NMR (400 MHz, $CDCl_3$)
3u



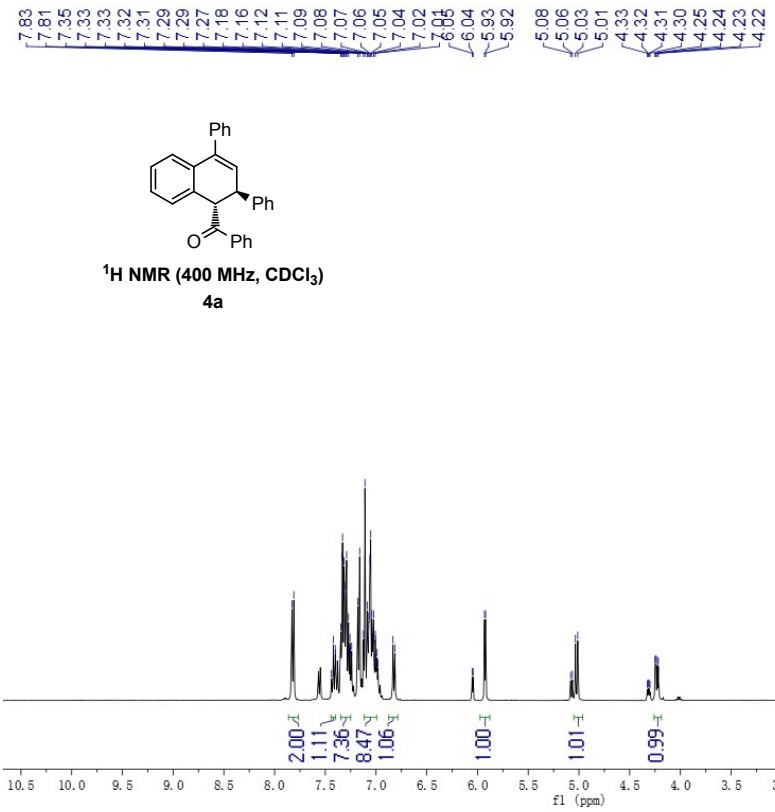
^{13}C NMR (100 MHz, $CDCl_3$)
3u

1-Methyl-4-phenylnaphthalene (3v).

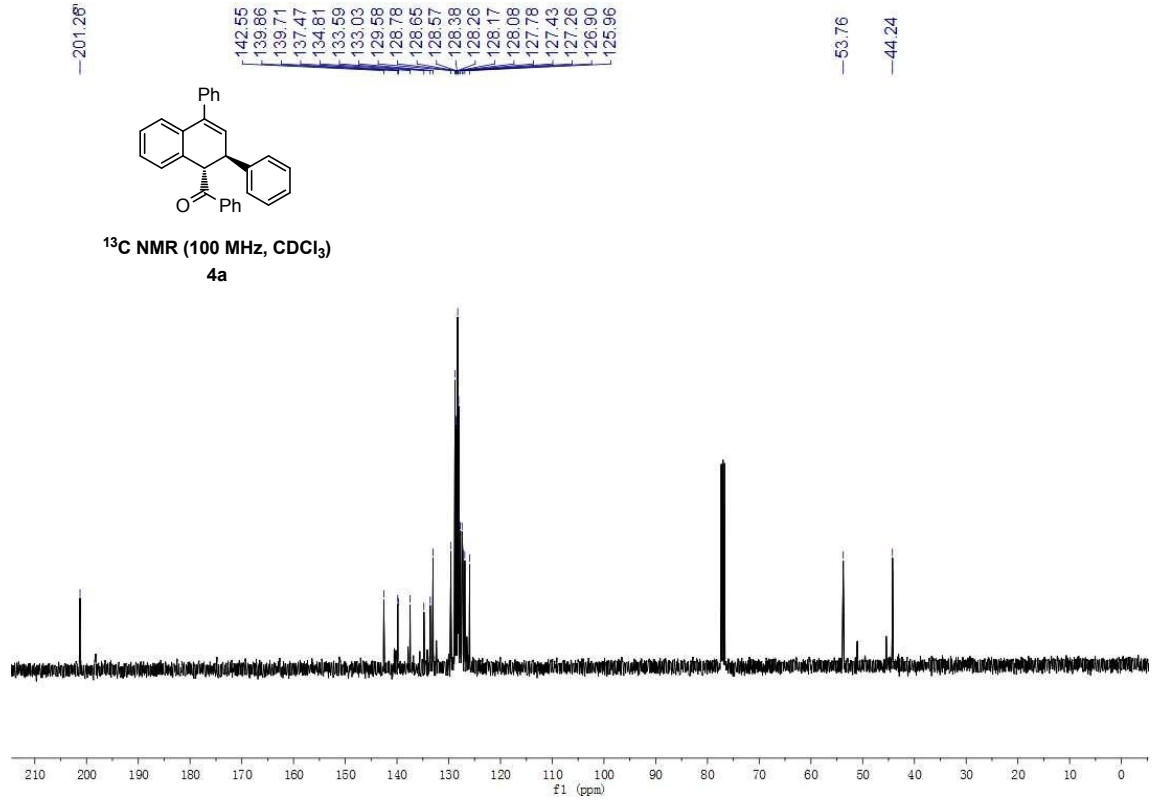




(2,4-Diphenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4a).

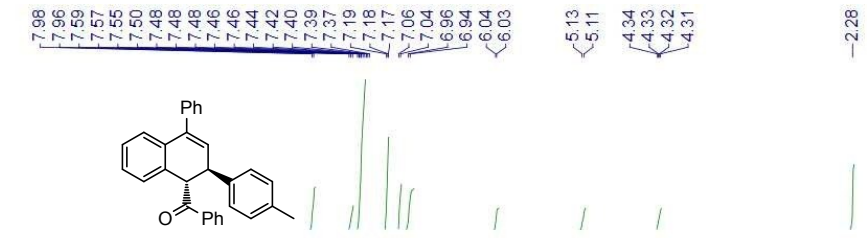


^{1}H NMR (400 MHz, $CDCl_3$)
4a

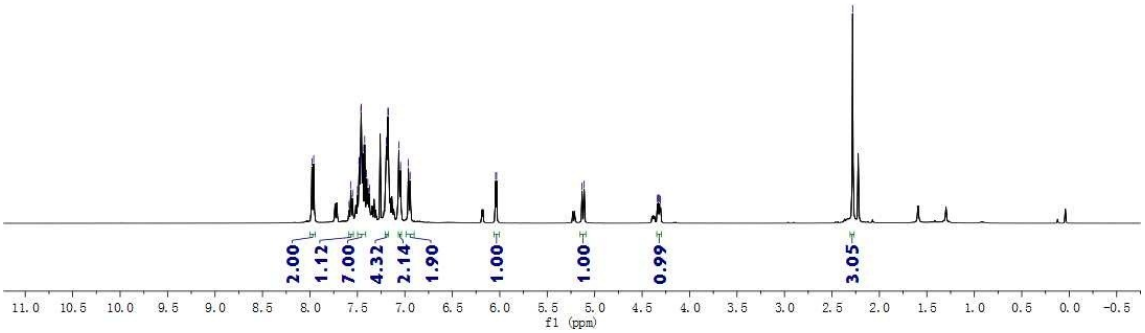


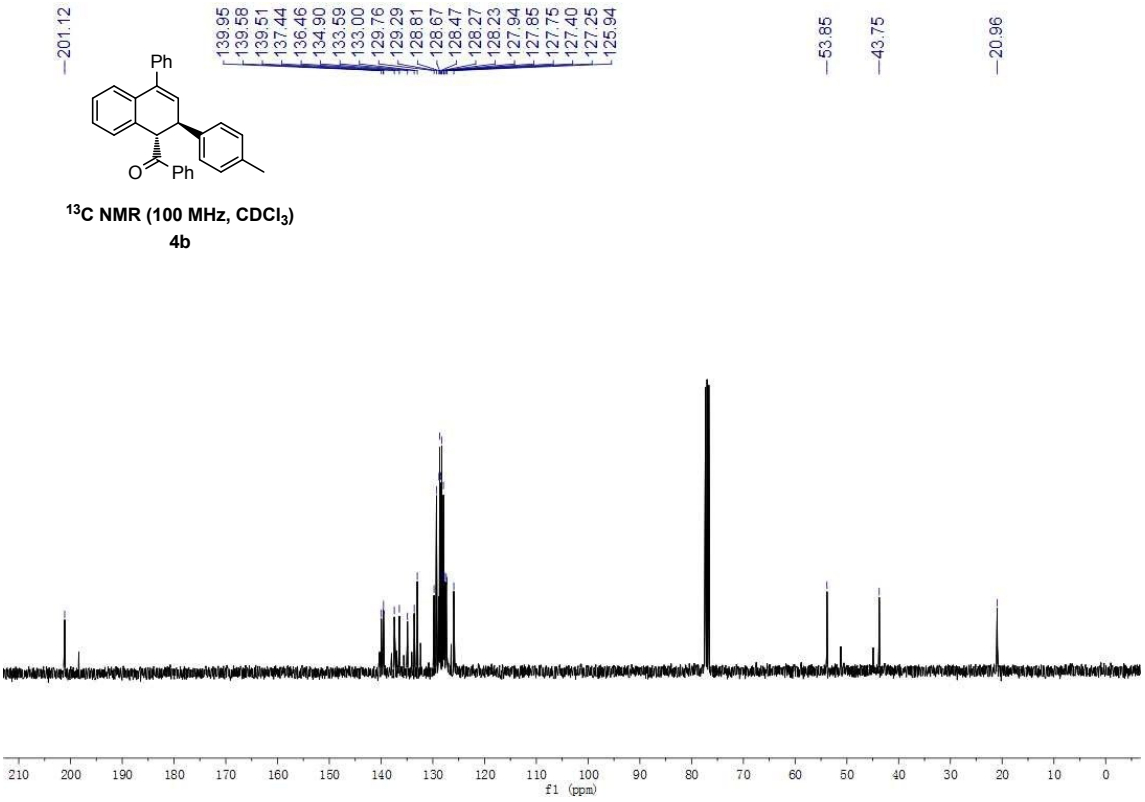
^{13}C NMR (100 MHz, $CDCl_3$)
4a

Phenyl(4-phenyl-2-(p-tolyl)-1,2-dihydronaphthalen-1-yl) methanone (4b).



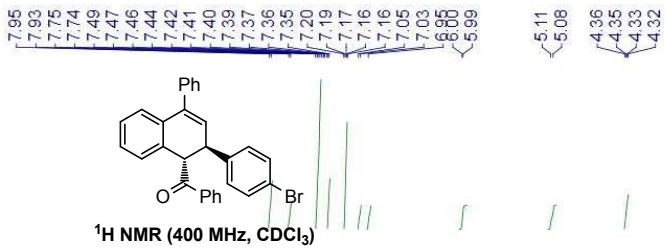
^{1}H NMR (400 MHz, $CDCl_3$)
4b





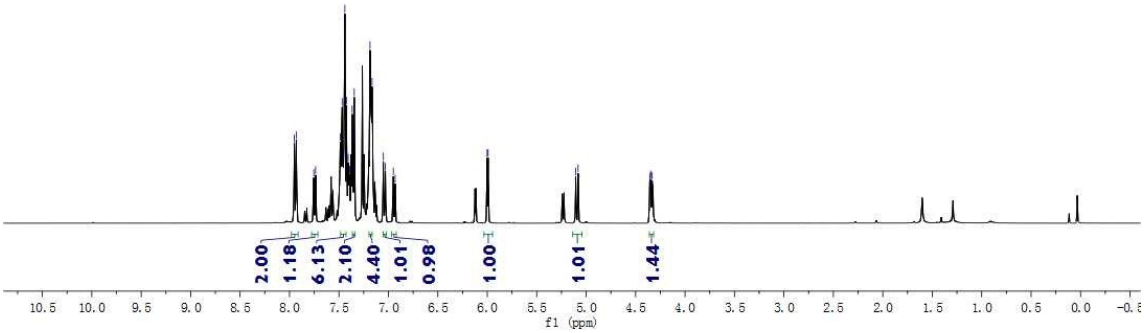
^{13}C NMR (100 MHz, $CDCl_3$)
4b

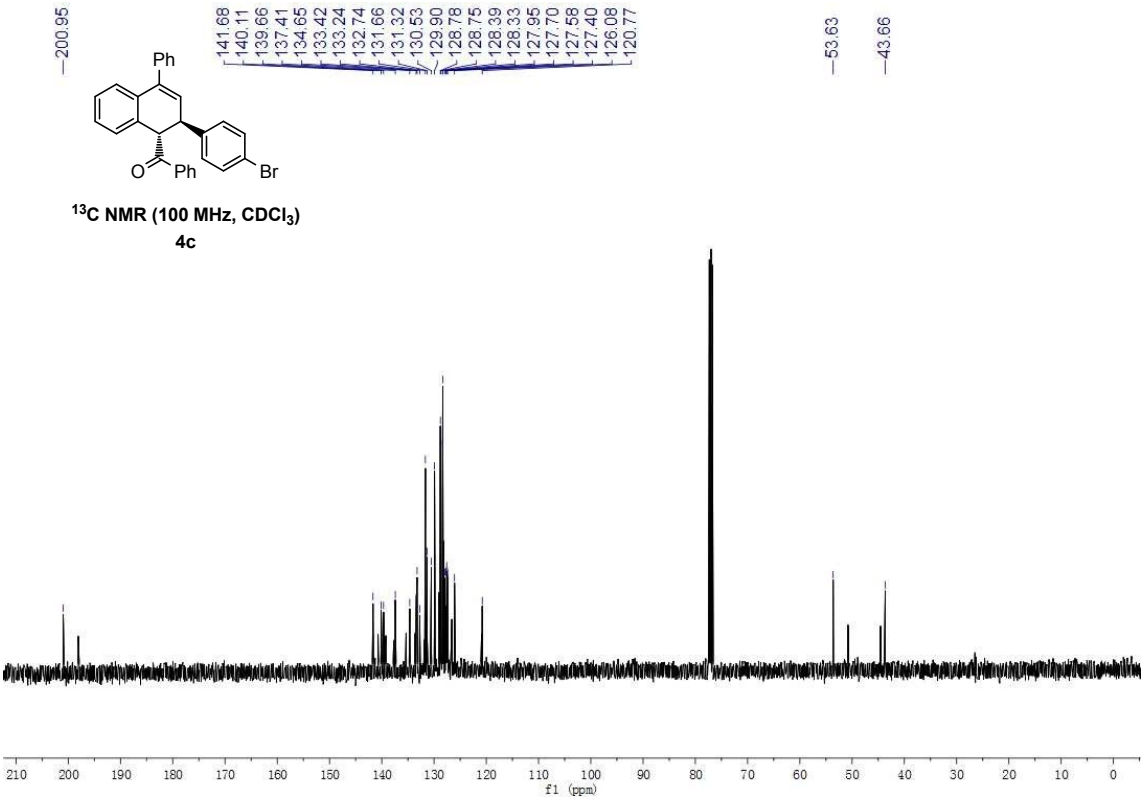
(2-(4-Bromophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4c).



^{1}H NMR (400 MHz, $CDCl_3$)

4c

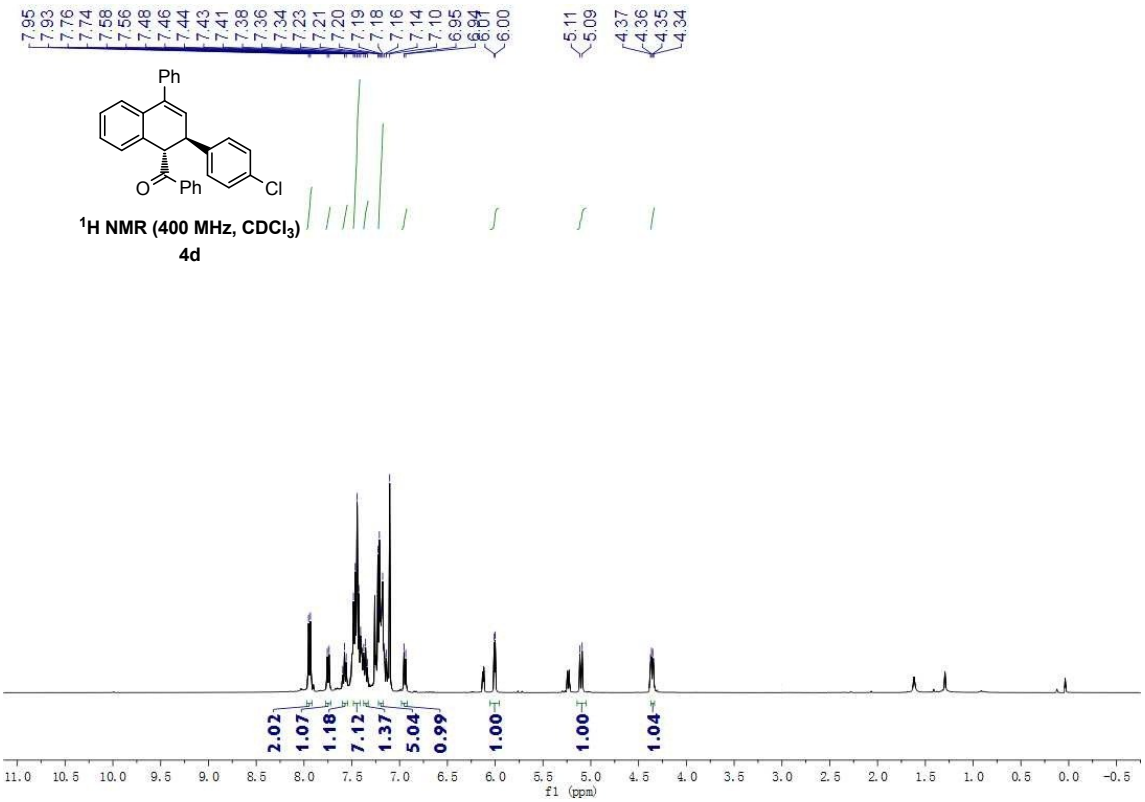




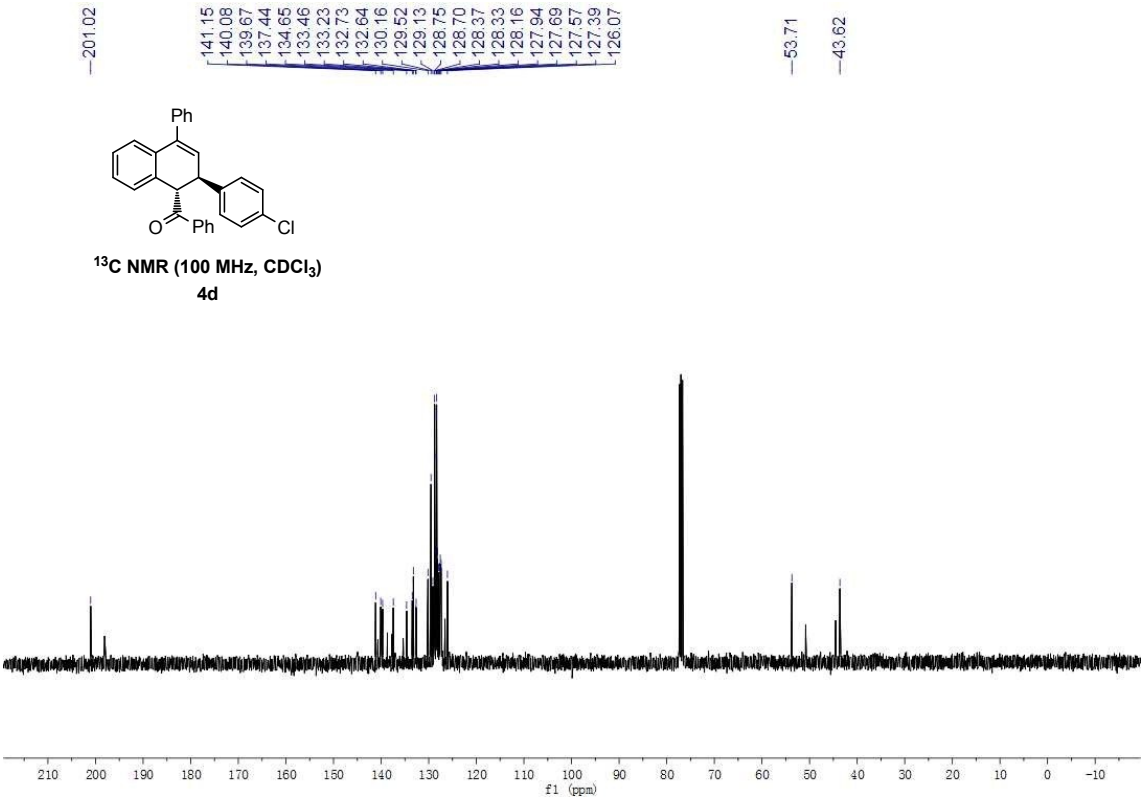
^{13}C NMR (100 MHz, $CDCl_3$)

4c

(2-(4-Chlorophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4d).

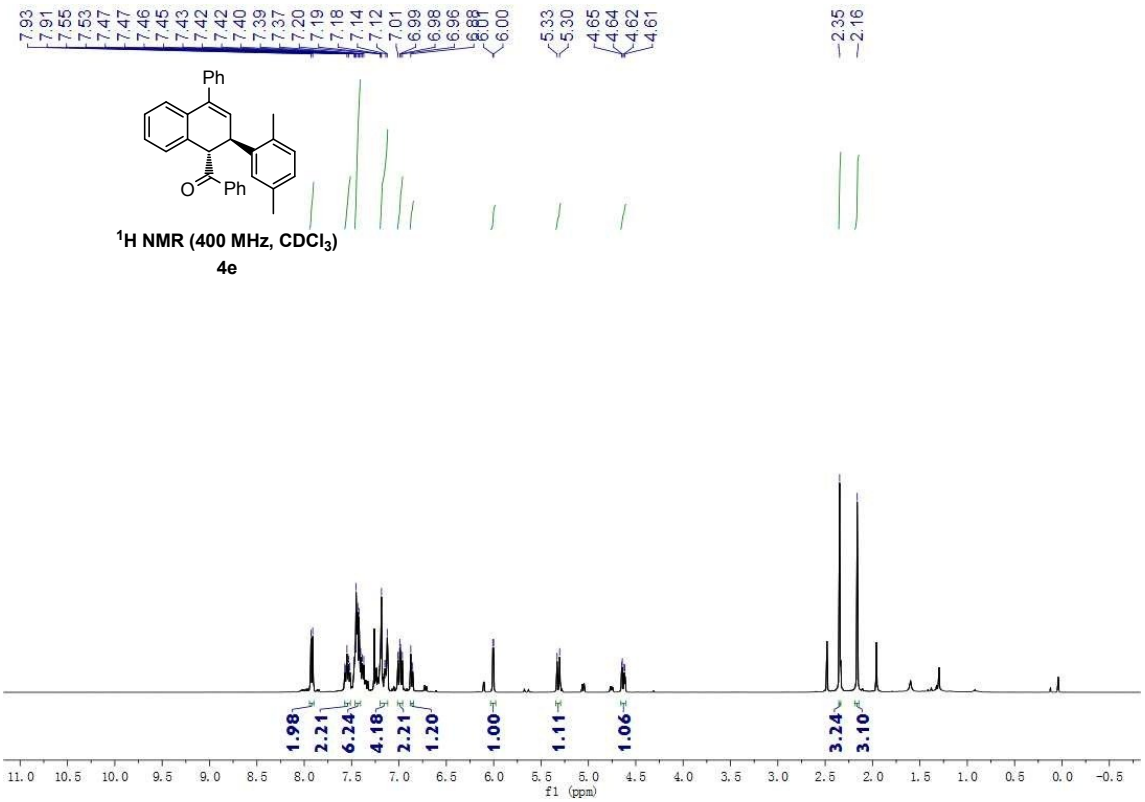


^{1}H NMR (400 MHz, $CDCl_3$)
4d



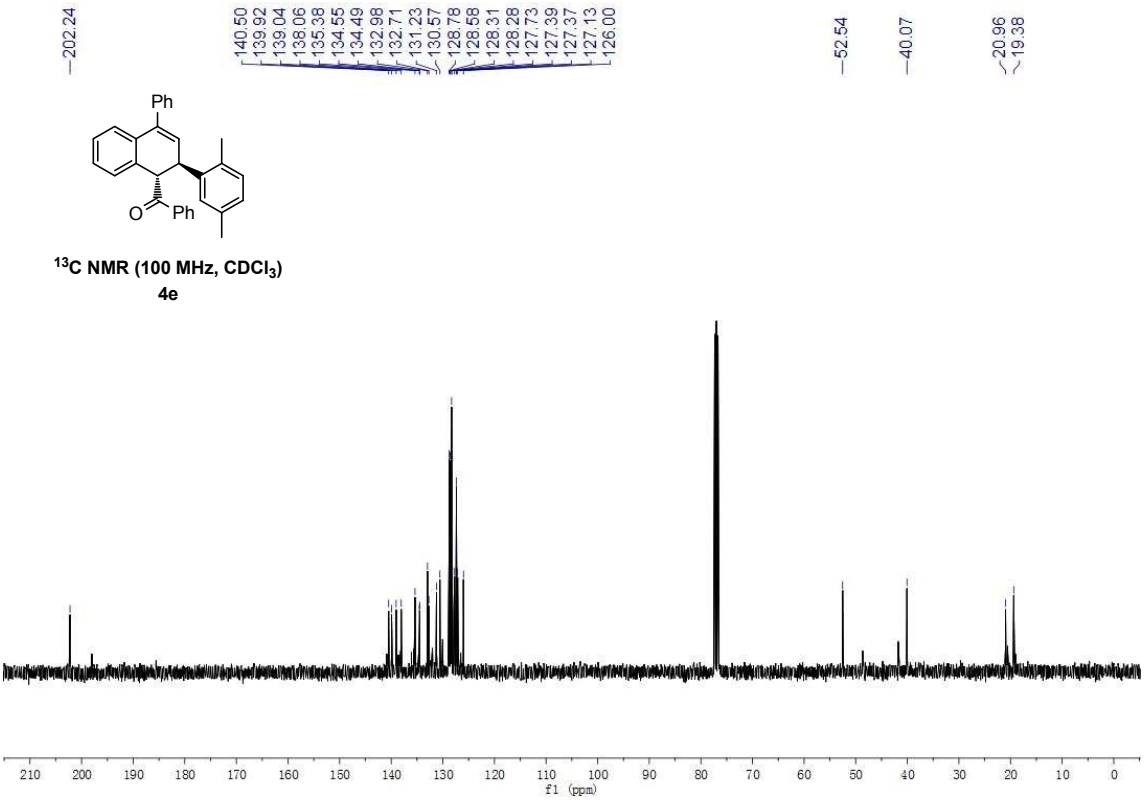
^{13}C NMR (100 MHz, $CDCl_3$)
4d

(2-(2,5-Dimethylphenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4e).



^{1}H NMR (400 MHz, $CDCl_3$)

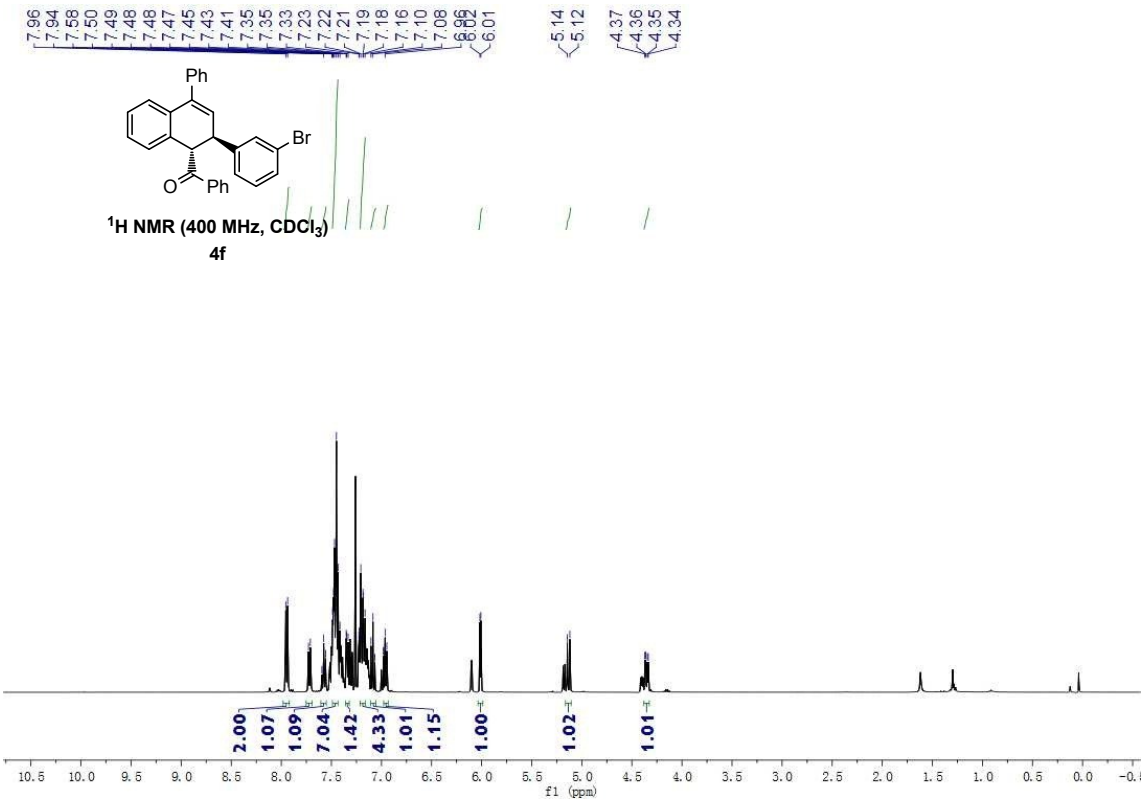
4e



^{13}C NMR (100 MHz, $CDCl_3$)

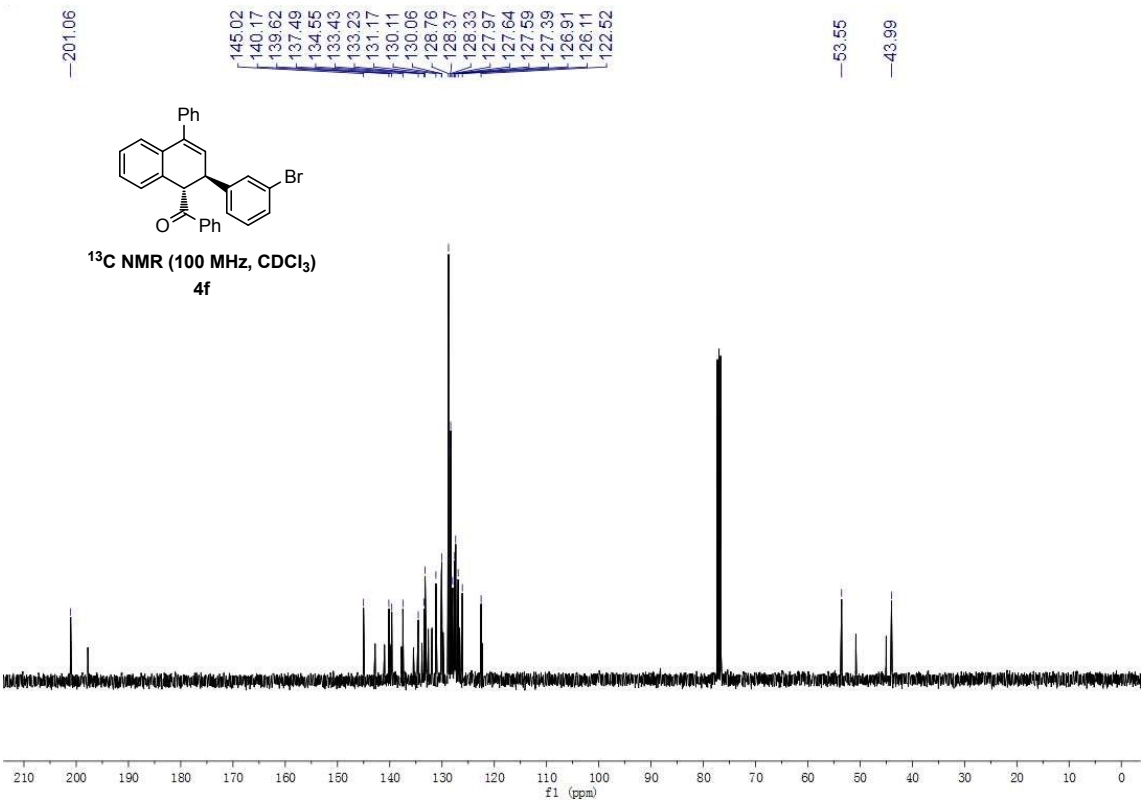
4e

(2-(3-Bromophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4f).



^{1}H NMR (400 MHz, $CDCl_3$)

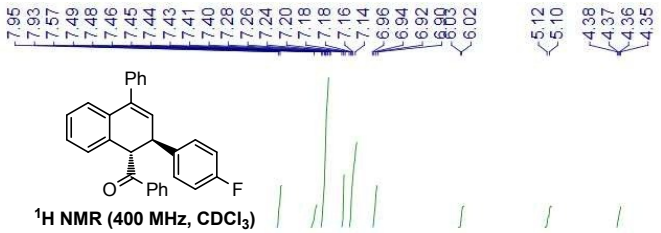
4f



^{13}C NMR (100 MHz, $CDCl_3$)

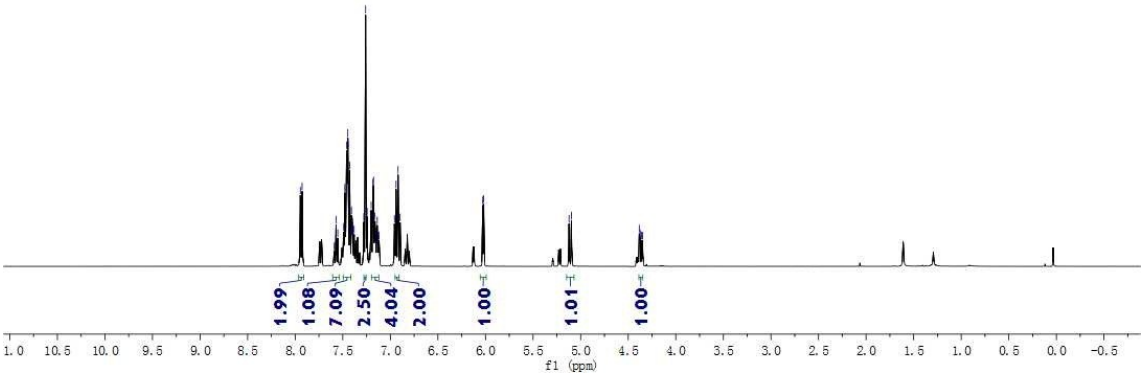
4f

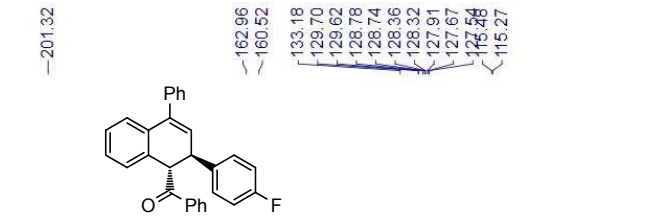
(2-(4-Fluorophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4g).



^{1}H NMR (400 MHz, $CDCl_3$)

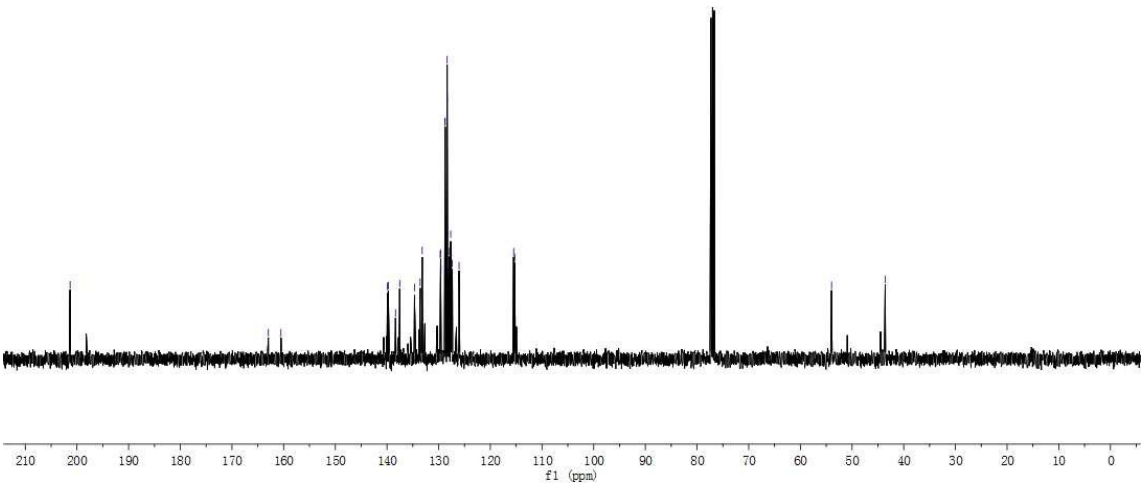
4g

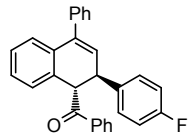




^{13}C NMR (100 MHz, $CDCl_3$)

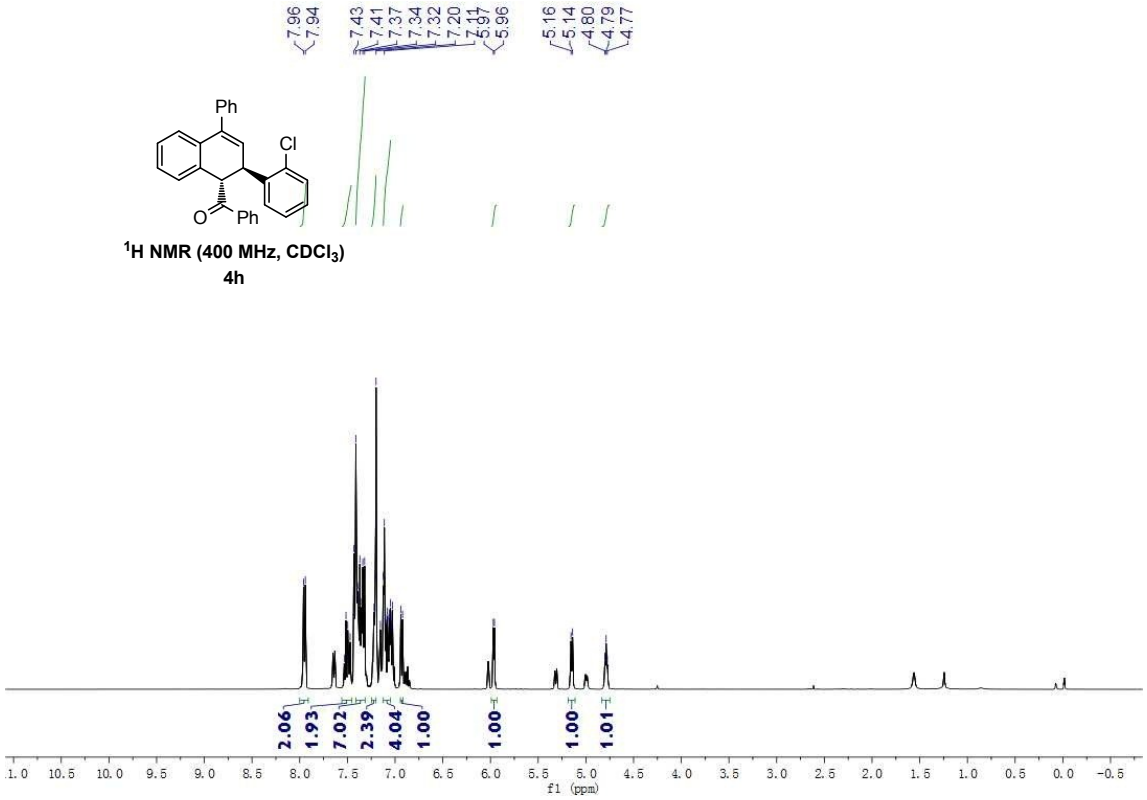
4g



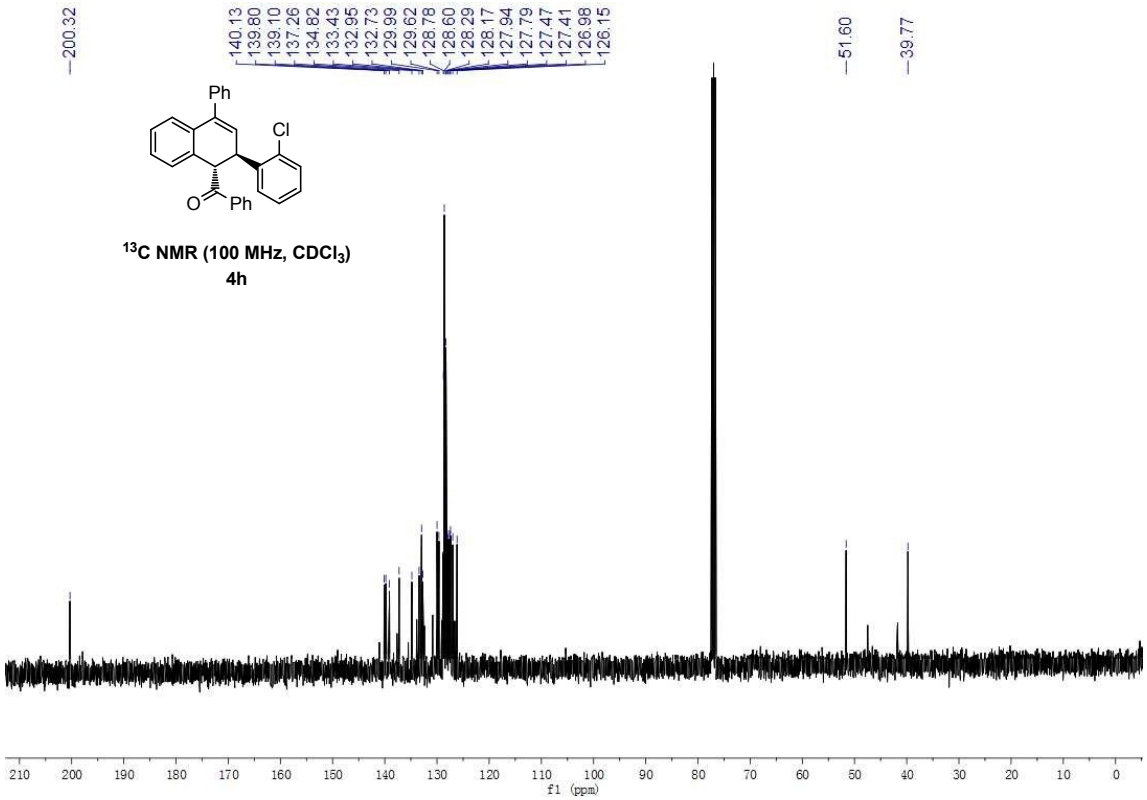


^{19}F NMR (376MHz, $CDCl_3$)
4g

(2-(2-Chlorophenyl)-4-phenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4h).

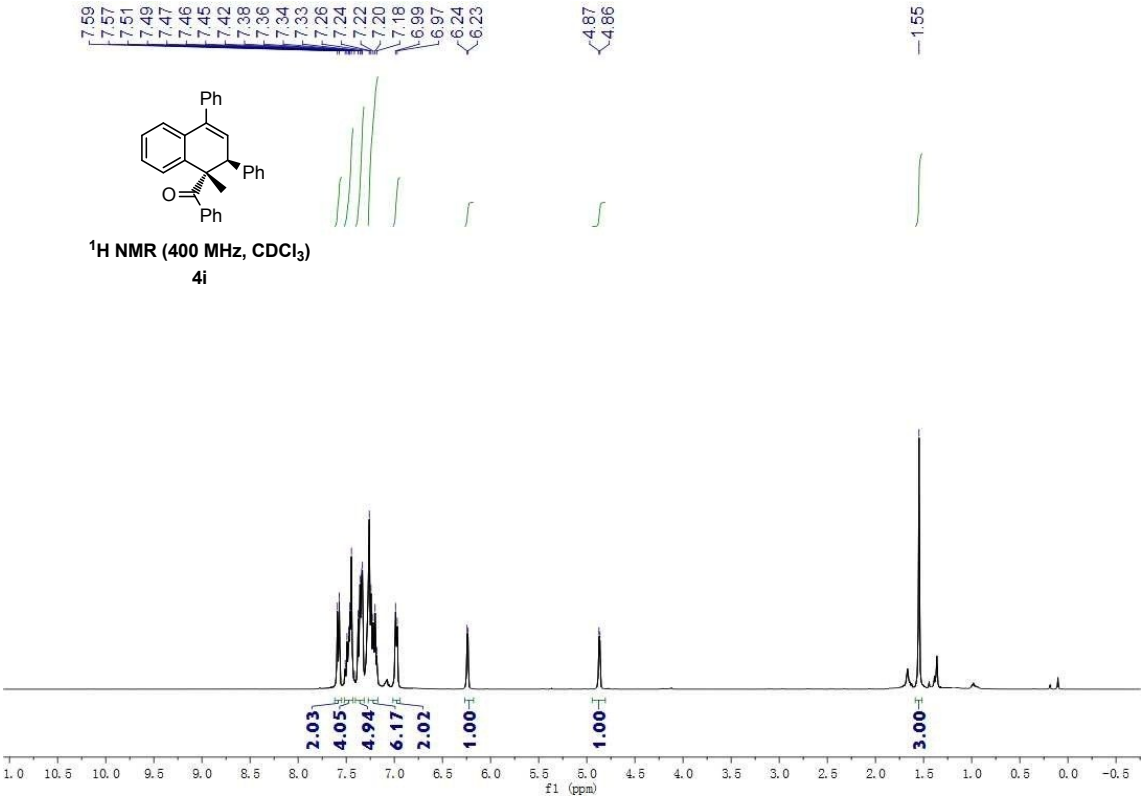


^{1}H NMR (400 MHz, $CDCl_3$)
4h

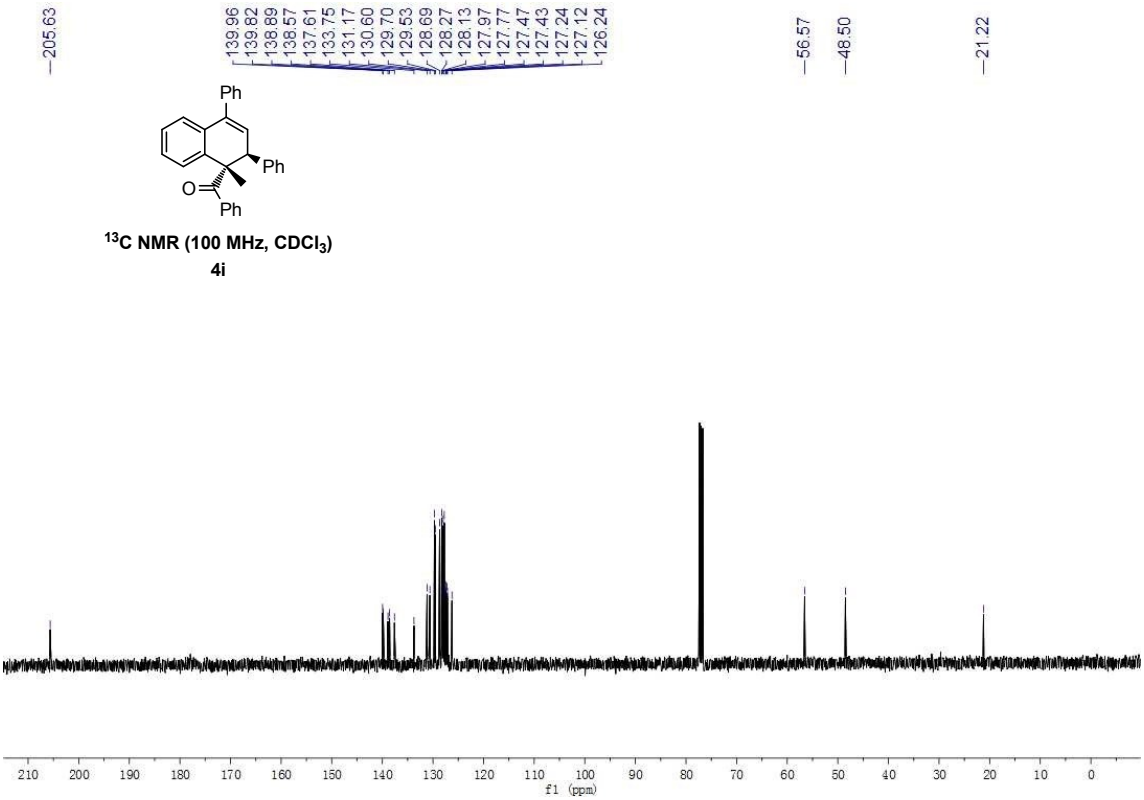


^{13}C NMR (100 MHz, $CDCl_3$)
4h

((1S,2S)-1-Methyl-2,4-diphenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4i).

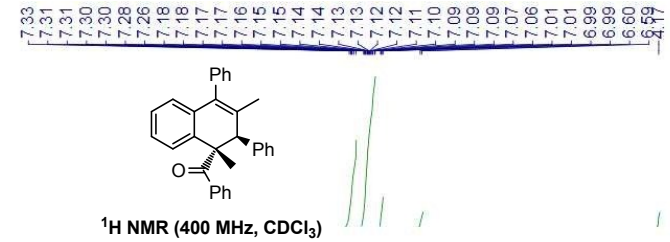


^{1}H NMR (400 MHz, $CDCl_3$)
4i

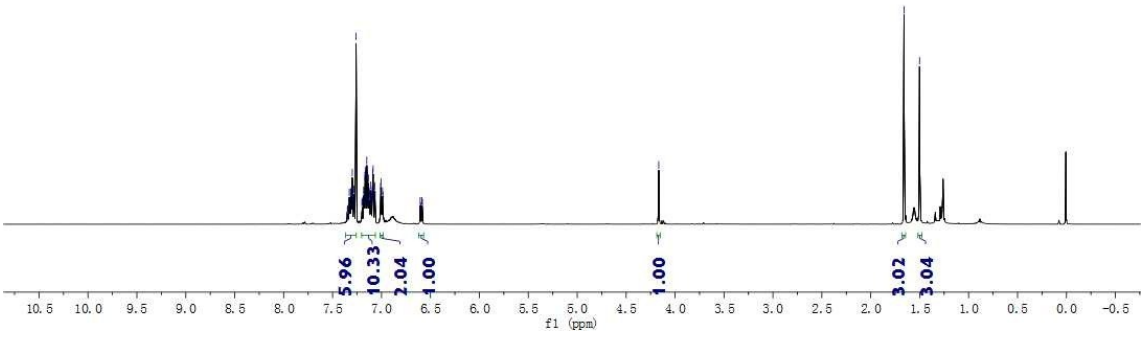


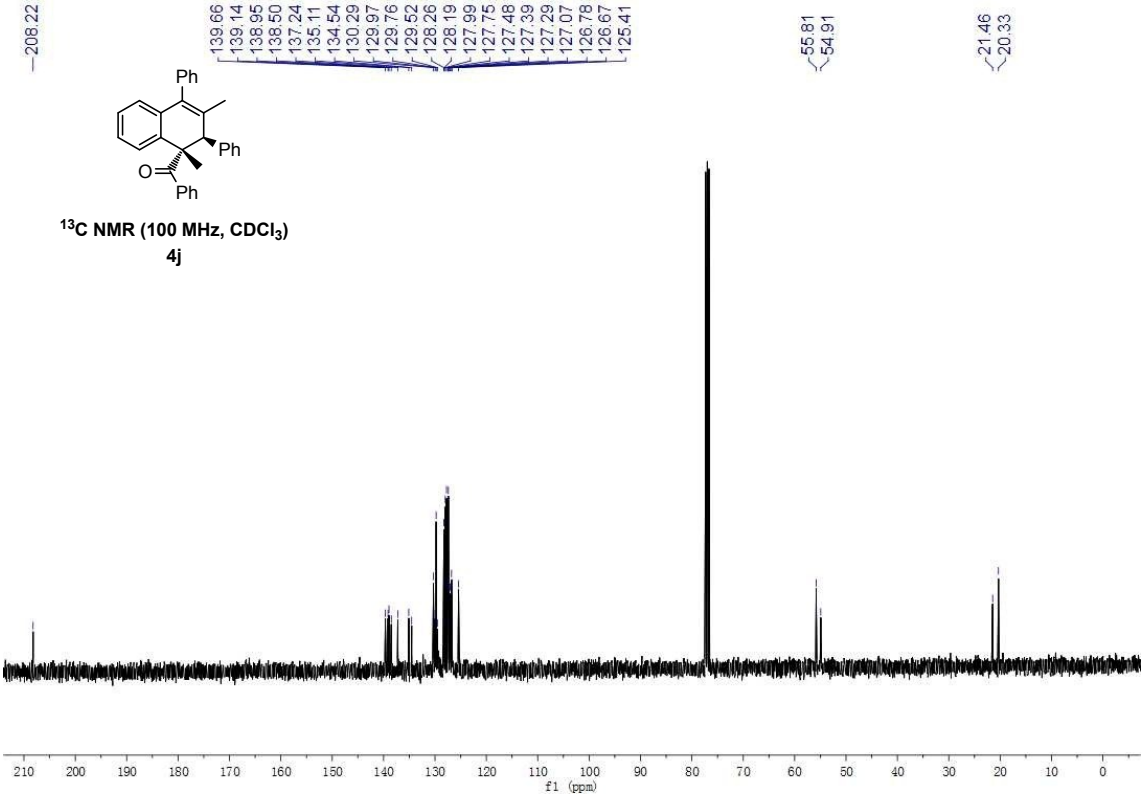
^{13}C NMR (100 MHz, $CDCl_3$)
4i

((1S,2R)-1,3-Dimethyl-2,4-diphenyl-1,2-dihydronaphthalen-1-yl) (phenyl) methanone (4j).



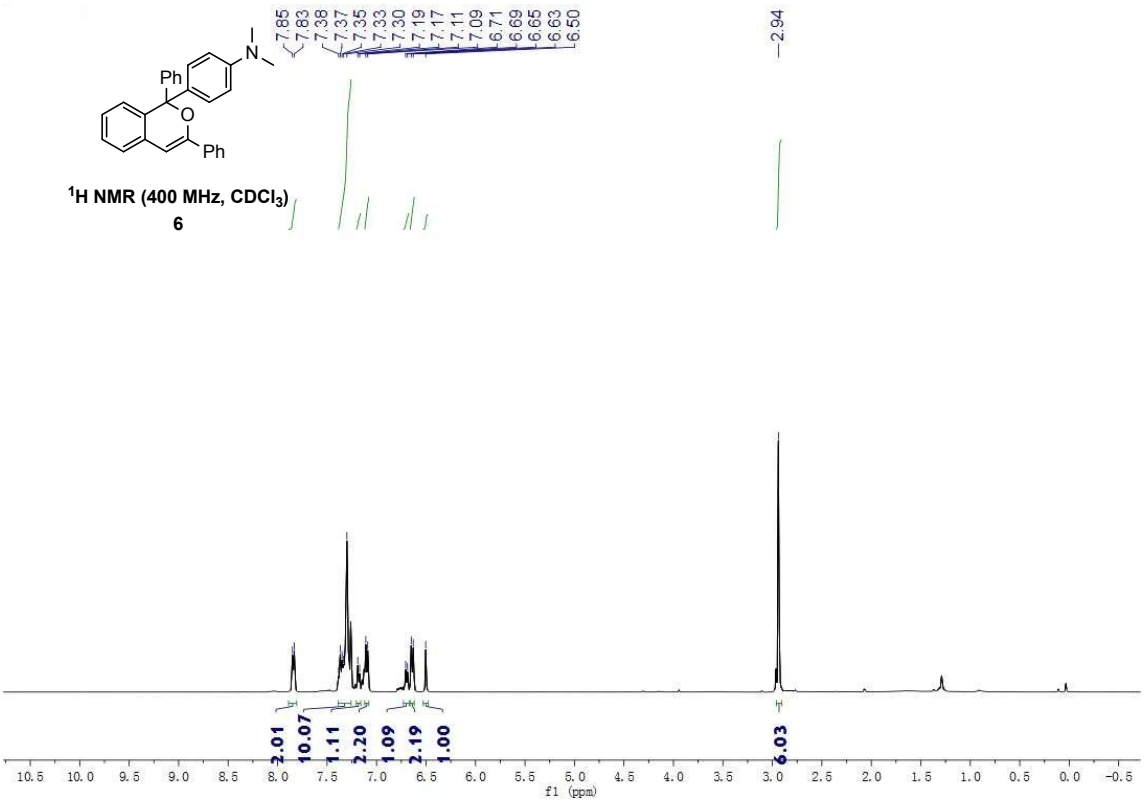
^{1}H NMR (400 MHz, $CDCl_3$)
4j



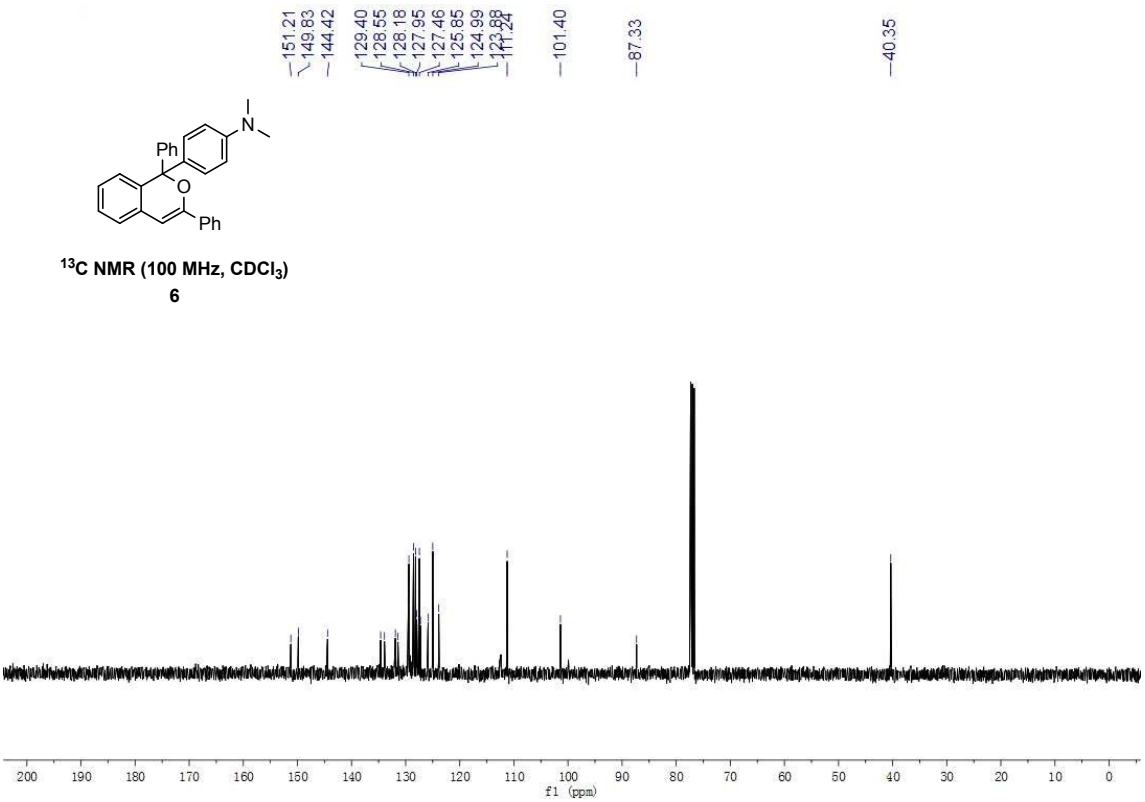


^{13}C NMR (100 MHz, $CDCl_3$)
4j

4-(1,3-Diphenyl-1H-isochromen-1-yl)-N,N-dimethylaniline (6).

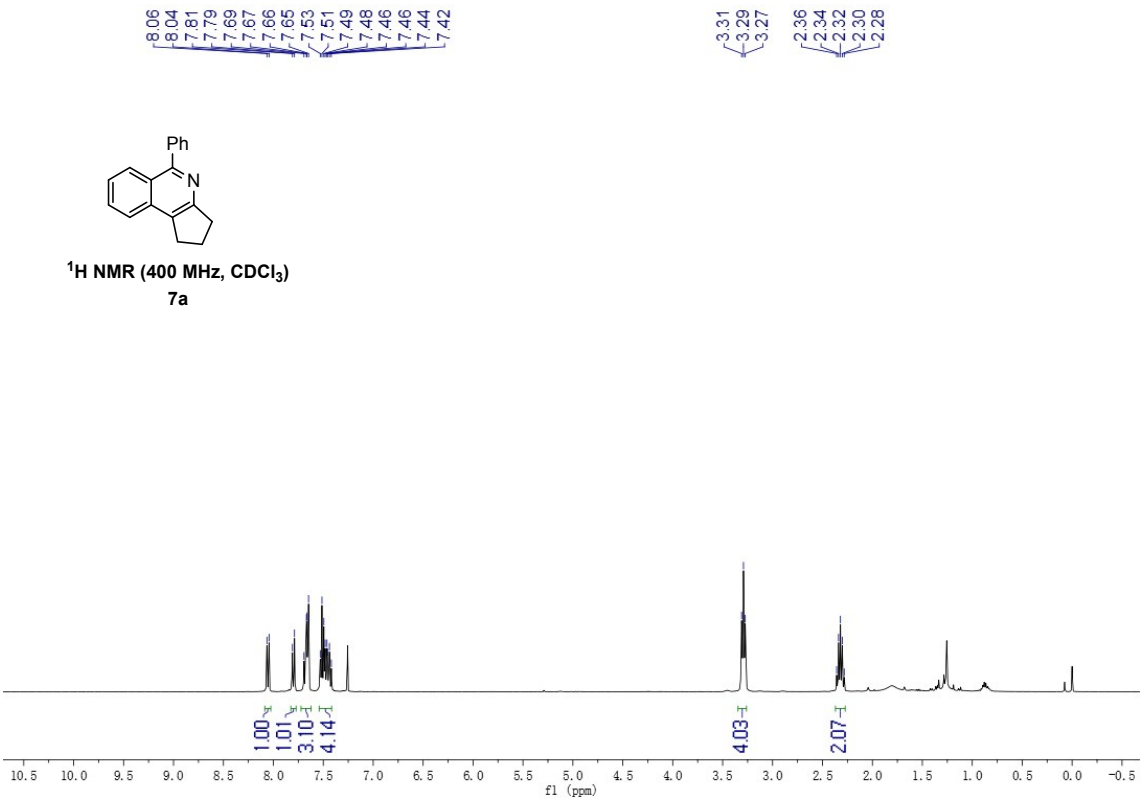


^{1}H NMR (400 MHz, $CDCl_3$)
6

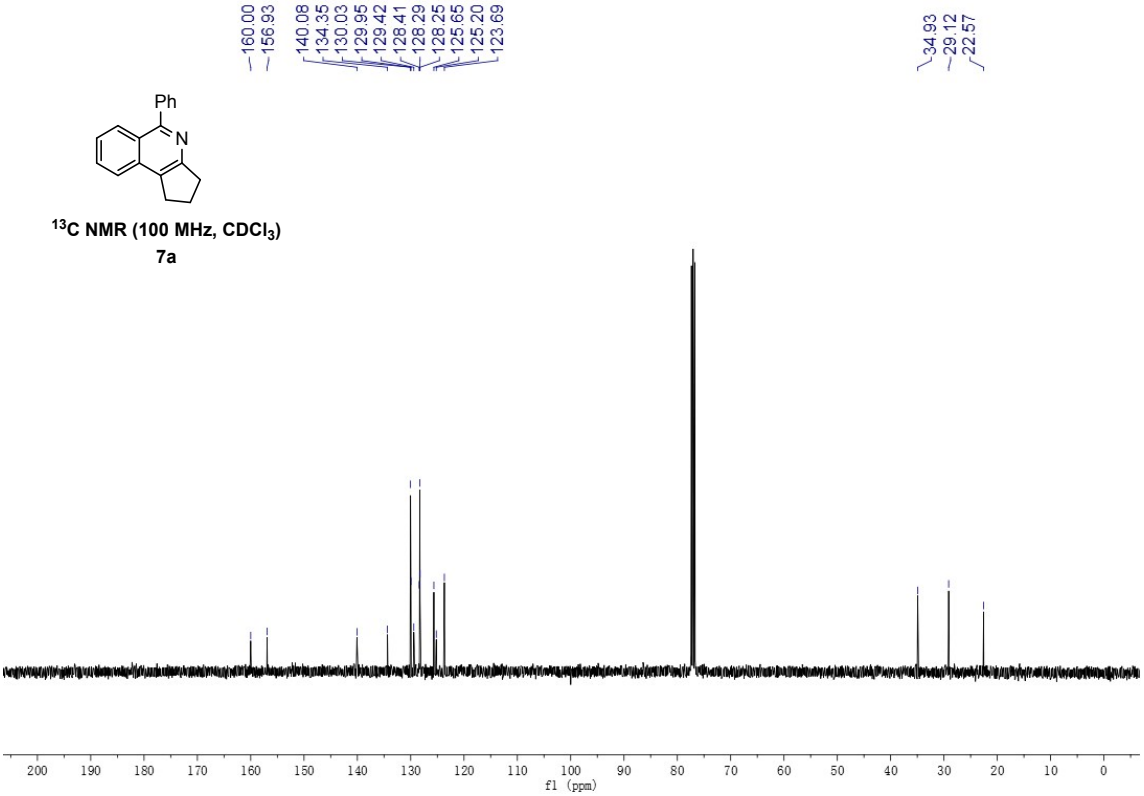


^{13}C NMR (100 MHz, $CDCl_3$)
6

5-phenyl-2,3-dihydro-1H-cyclopenta[c]isoquinoline 7a

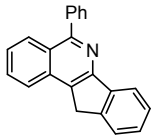


^{1}H NMR (400 MHz, $CDCl_3$)
7a

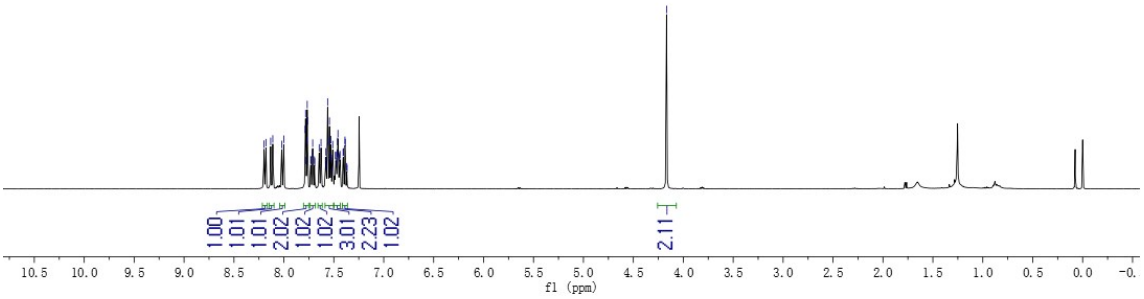


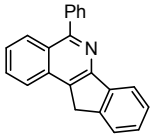
^{13}C NMR (100 MHz, $CDCl_3$)
7a

5-phenyl-11H-indeno[1,2-c]isoquinoline 7b



^{1}H NMR (400 MHz, $CDCl_3$)
7b





^{13}C NMR (100 MHz, $CDCl_3$)
7b