

Iron-Catalyzed Benzannulation Reactions of 2-Alkylbenzaldehydes and Alkynes Leading to Naphthalene Derivatives

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Table of Contents

INDEX

1. General Remarks.....	S1
2. Typical Procedure for Substrates Preparation	S1
3. General Procedure for the FeCl ₃ -Catalyzed Benzannulation of 2-Alkylbenzaldehydes with Alkynes.....	S2
4. NMR Spectra of Compounds.....	S9
5. References.....	S41

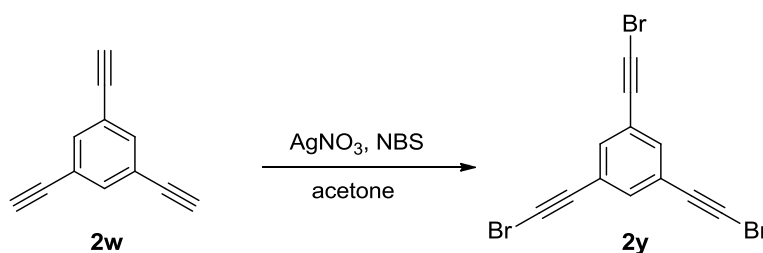
1. General Remarks.

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ^1H NMR, ^{13}C NMR and ^{19}F NMR (400 and 100 MHz, 376 MHz respectively) spectra were recorded in CDCl_3 . ^1H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl_3 at 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (CDCl_3 at 77.20 ppm). ^{19}F NMR chemical shifts were determined relative to CFCl_3 as external standard. Melting points were recorded on a Buchi Melting Point B-545. IR spectra were recorded on a Perkin Elmer BX FT-IR spectrophotometer.

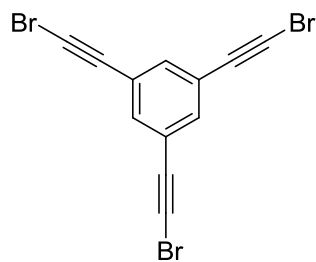
2. Typical Procedure for Substrates Preparation.

The syntheses of compounds 2-Alkylbenzaldehydes (**1a-e**)¹, bromoalkynes (**2p-s**)² and Alkynes (**2w**³, **2x**⁴, **2z**³) have been reported and will not be discussed here.

The synthesis of 1,3,5-tris(bromoethynyl)benzene (**2y**)



To the mixture of 1,3,5-triethynylbenzene (1 eq.), NBS (3.3 eq.) and 5 mL acetone, AgNO_3 (5 mol%) was added and the mixture was stirred at room temperature for three hours. After completion the reaction, the solvent was evaporated and extracted with 10 mL petroleum ether (60-90 °C), then evaporated the solvent and the residue was the title product (silvery white solid, 81%).

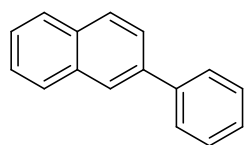


1,3,5-Tris(bromoethynyl)benzene(2y)

Silvery white solid, M.p. 115-120 °C, yield 76%. ¹H NMR (400 MHz, CDCl₃) δ 7.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 135.2, 123.5, 78.1, 52.1; IR (KBr) ν_{max} 2925, 2853, 2201, 1637, 1580, 1457, 1413, 1131, 876, 675, 617 cm⁻¹; MS (EI) 384 ([M]⁺); HRMS (EI) calcd. for C₁₂H₃Br₃ ([M]⁺): 383.7785; Found: 383.7789.

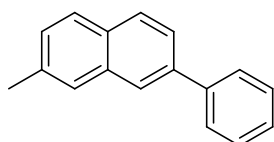
3. General Procedure for the FeCl₃-Catalyzed [4+2] Benzannulation of 2-(2-Oxoethyl)benzaldehydes with Alkynes.

To a Schlenk tube were added 2-Alkylbenzaldehydes **1** (0.2 mmol), alkyne **2** (1.1 equiv), FeCl₃ (5 mol%), and ClCH₂CH₂Cl (3 mL). Then the tube was charged with argon, and was stirred at Optimal temperature until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted in diethyl ether, and washed with brine. The aqueous phase was reextracted with EtOAc. The combined organic extracts were dried over Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10 : 1) to afford the desired product.



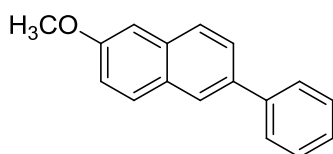
2-Phenylnaphthalene(3a)⁵

Yield 98%. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (s, 1H), 7.92-7.81 (m, 3H), 7.72 (t, *J* = 8.4 Hz, 3H), 7.51-7.42 (m, 4H), 7.36 (t, *J* = 7.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 141.2, 138.6, 133.8, 132.7, 128.9, 128.5, 128.3, 127.7, 127.5, 127.4, 126.4, 126.0, 125.9, 125.7.



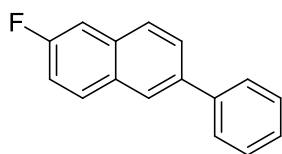
2-Methyl-6-phenylnaphthalene(3b)⁶

Yield 77%. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.78-7.63 (m, 5H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 2.52 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 141.3, 138.6, 135.95, 133.9, 130.9, 128.8, 128.2, 128.1, 127.4, 127.4, 127.2, 127.1, 125.2, 124.7, 21.7.



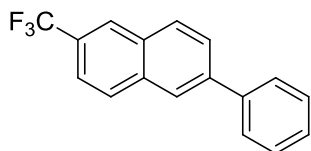
2-Methoxy-6-phenylnaphthalene(3c)⁷

Yield 60%. ¹H NMR (400 MHz, CDCl₃) δ 7.97 (s, 1H), 7.79 (t, *J* = 7.0 Hz, 2H), 7.70 (dd, *J* = 7.7, 4.5 Hz, 3H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 10.1 Hz, 2H), 3.93 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 157.7, 141.2, 136.4, 133.8, 129.7, 129.2, 128.8, 127.2, 127.2, 127.0, 126.0, 125.6, 119.1, 105.6, 55.3.



2-Fluoro-6-phenylnaphthalene(3d)⁸

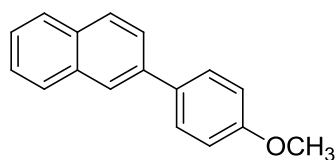
Yield 80%. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 1H), 7.96-7.87 (m, 2H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.54 (dd, *J* = 12.7, 4.9 Hz, 3H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.35 (dd, *J* = 12.1, 5.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 162.0, 159.5, 140.8, 138.0, 138.0, 133.3, 133.2, 130.7, 130.6, 130.5, 128.9, 127.8, 127.8, 127.4, 127.3, 126.6, 125.7, 116.8, 116.6, 110.8, 110.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -114.4.



2-Phenyl-6-(trifluoromethyl)naphthalene(3e)

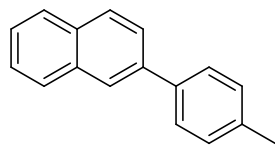
Yellow solid, M.p. 127-128 °C, yield 99%. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (s, 1H), 7.98 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.1 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 140.8, 140.4, 134.9, 131.3, 129.3, 129.2, 129.0, 127.9, 127.5, 126.9, 125.6, 125.5, 125.4,

125.4, 125.4, 121.9, 121.9, 121.8, 121.8; ^{19}F NMR (376 MHz, CDCl_3) δ -62.20. IR (KBr) ν_{max} 2924, 2853, 2361, 1632, 1475, 1448, 1373, 1326, 1189, 1157, 1122, 1066, 892, 825, 756, 688, 473 cm^{-1} ; MS (EI) 272 ($[\text{M}]^+$); HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{11}\text{F}_3$ ($[\text{M}]^+$): 272.0813; Found: 272.0817.



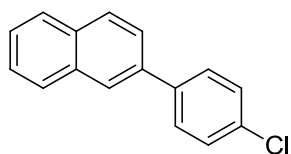
2-(P-methoxyphenyl)naphthalene(3f)⁹

Yield 73%. ^1H NMR (400 MHz, CDCl_3) δ 7.98 (s, 1H), 7.86 (dd, J = 15.6, 8.8 Hz, 3H), 7.71 (d, J = 8.5 Hz, 1H), 7.66 (d, J = 8.6 Hz, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.02 (d, J = 8.6 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 138.1, 133.7, 133.6, 132.3, 128.4, 128.3, 128.0, 127.6, 126.2, 125.6, 125.4, 125.0, 114.3, 55.4.



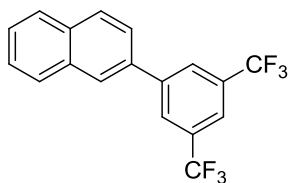
2-(P-tolyl)naphthalene(3g)⁹

Yield 84%. ^1H NMR (400 MHz, CDCl_3) δ 8.01 (s, 1H), 7.91-7.81 (m, 3H), 7.73 (d, J = 8.5 Hz, 1H), 7.61 (d, J = 7.9 Hz, 2H), 7.47 (t, J = 6.6 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.5, 138.3, 137.1, 133.7, 132.5, 129.6, 128.3, 128.1, 127.6, 127.2, 126.2, 125.8, 125.6, 125.4, 21.1.



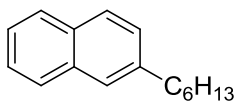
2-(4-Chlorophenyl)naphthalene(3h)¹⁰

Yield 89%. ^1H NMR (400 MHz, CDCl_3) δ 7.99 (s, 1H), 7.88 (dd, J = 17.6, 8.4 Hz, 3H), 7.68 (d, J = 8.5 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.54-7.46 (m, 2H), 7.44 (d, J = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.5, 137.3, 133.6, 133.5, 132.7, 129.0, 128.6, 128.6, 128.2, 127.6, 126.4, 126.1, 125.7, 125.2.



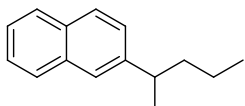
2-(3,5-Bis(trifluoromethyl)phenyl)naphthalene(3i)

Colorless solid, M.p. 92-93 °C, yield 99%. ¹H NMR (400 MHz, CDCl₃) δ 8.17 (s, 2H), 8.10 (s, 1H), 8.03-7.90 (m, 4H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.63-7.55 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 143.2, 135.4, 133.5, 133.2, 132.3, 132.0, 129.2, 128.3, 127.7, 127.4, 127.4, 126.9, 126.9, 126.5, 124.7, 120.9, 120.9, 120.9; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.7; IR (KBr) ν_{\max} 3060, 2924, 1631, 1378, 1272, 1127, 896, 824, 747, 476 cm⁻¹; MS (EI) 340 ([M]⁺); HRMS (EI) calcd. for C₁₈H₁₀F₆ ([M]⁺): 340.0687; Found: 340.0686.



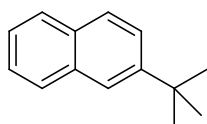
2-Hexylnaphthalene(3j)⁵

Yield 92%. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (dd, *J* = 15.1, 8.4 Hz, 3H), 7.60 (s, 1H), 7.46-7.36 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 1H), 2.76 (t, *J* = 7.7 Hz, 2H), 1.74-1.63 (m, 2H), 1.41-1.28 (m, 6H), 0.89 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 140.5, 133.6, 131.9, 127.7, 127.6, 127.5, 127.4, 126.3, 125.8, 125.0, 36.1, 31.8, 31.4, 29.0, 22.6, 14.1.



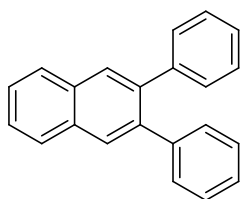
2-(Pentan-2-yl)naphthalene(3k)

Yield 63%. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (t, *J* = 7.8 Hz, 3H), 7.60 (s, 1H), 7.48-7.37 (m, 2H), 7.35 (d, *J* = 8.5 Hz, 1H), 2.95-2.79 (m, 1H), 1.63 (ddd, *J* = 13.0, 11.8, 7.3 Hz, 2H), 1.31 (d, *J* = 6.9 Hz, 3H), 1.26-1.19 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.3, 133.6, 132.1, 127.8, 127.5, 127.5, 125.8, 125.7, 125.1, 125.0, 40.5, 39.8, 22.3, 20.8, 14.1.



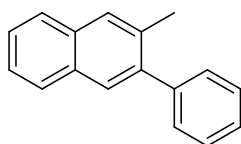
2-tert-Butyl-naphthalene(3l)⁵

Yield 92%. ¹H NMR (400 MHz, CDCl₃) δ 7.77-7.81 (m, 4H), 7.55-7.59 (m, 1H), 7.40-7.45 (m, 2H), 1.53 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 148.5, 133.4, 131.7, 127.9, 127.5, 127.3, 125.8, 125.2, 124.8, 122.8, 34.8, 31.2.



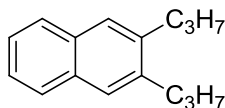
2,3-Diphenyl-naphthalene(3m)⁵

Yield 74%. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (m, 4H), 7.52-7.44 (m, 2H), 7.22 (m, 10H); ¹³C NMR (100 MHz, CDCl₃) δ 141.5, 139.2, 132.8, 130.0, 129.5, 127.9, 127.8, 126.6, 126.3.



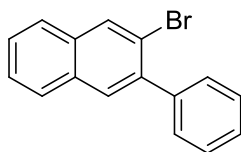
2-Methyl-3-phenyl-naphthalene(3n)¹¹

Yield 90%. ¹H NMR (400 MHz, CDCl₃) δ 7.78-7.80 (m, 2H), 7.69-7.71 (m, 2H), 7.38-7.45 (m, 7H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 141.9, 141.0, 134.0, 133.0, 132.1, 129.4, 128.5, 128.3, 128.2, 127.7, 127.0, 126.0, 125.5, 21.2.



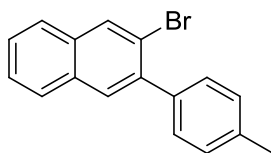
2,3-Dipropyl-naphthalene(3o)⁵

Yield 83%. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (dd, *J* = 5.6, 2.8 Hz, 2H), 7.59 (s, 2H), 7.36 (dd, *J* = 5.8, 2.7 Hz, 2H), 2.74 (t, *J* = 7.7 Hz, 4H), 1.71 (dd, *J* = 15.0, 7.5 Hz, 4H), 1.03 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 139.4, 132.2, 127.0, 125.0, 35.0, 24.2, 14.3.



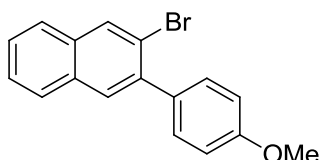
2-Bromo-3-phenyl-naphthalene(3p)¹¹

Yield 80%. ¹H NMR (400 MHz, CDCl₃) δ 8.19 (s, 1H), 7.83-7.75 (m, 3H), 7.53-7.41 (m, 7H); ¹³C NMR (100MHz, CDCl₃) δ 141.1, 140.1, 133.6, 132.3, 131.6, 123.0, 129.7, 128.0, 127.9, 127.7, 126.9, 126.7, 126.7, 120.8.



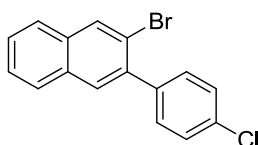
2-Bromo-3-(p-tolyl)naphthalene(3q)

Yellow oil, yield 74%. ^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 1H), 7.78-7.70 (m, 3H), 7.46 (dd, $J = 6.2, 3.2$ Hz, 2H), 7.37 (d, $J = 7.9$ Hz, 2H), 7.24 (d, $J = 7.8$ Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.1, 138.2, 137.4, 133.5, 132.3, 131.6, 129.9, 129.6, 128.7, 127.8, 126.8, 126.7, 126.6, 121.1, 21.3; IR (KBr) ν_{max} 3045, 2925, 2863, 2355, 1908, 1588, 1501, 1440, 1223, 1124, 1050, 953, 885, 817, 745, 572, 477 cm^{-1} ; MS (EI) 296 ($[\text{M}]^+$); HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{13}\text{Br}$ ($[\text{M}]^+$): 296.0201; Found: 296.0196.



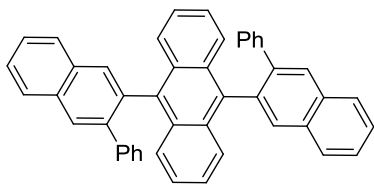
2-Bromo-3-(4-methoxyphenyl)naphthalene(3r)

Yellow solid, M.p. 93-94 $^{\circ}\text{C}$, yield 60%. ^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 1H), 7.78-7.70 (m, 3H), 7.46 (dd, $J = 6.2, 3.2$ Hz, 2H), 7.37 (d, $J = 7.9$ Hz, 2H), 7.24 (d, $J = 7.8$ Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.1, 138.2, 137.4, 133.5, 132.3, 131.6, 129.9, 129.6, 128.7, 127.8, 126.8, 126.7, 126.6, 121.1; IR (KBr) ν_{max} 2926, 2354, 1613, 1509, 1450, 1249, 1180, 1031, 952, 884, 826, 747, 575, 478 cm^{-1} ; MS (EI) 312 ($[\text{M}]^+$); HRMS (EI) calcd. for $\text{C}_{17}\text{H}_{13}\text{OBr}$ ($[\text{M}]^+$): 312.0150; Found: 312.0146.



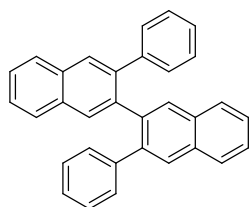
2-Bromo-3-(4-chlorophenyl)naphthalene(3s)

Yellow solid, M.p. 92-95 $^{\circ}\text{C}$, yield 79%. ^1H NMR (400 MHz, CDCl_3) δ 8.16 (s, 1H), 7.81-7.72 (m, 3H), 7.49 (dd, $J = 6.1, 3.2$ Hz, 2H), 7.44-7.36 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.4, 138.8, 133.8, 133.6, 132.2, 131.7, 131.1, 129.9, 128.2, 127.8, 127.1, 126.8, 126.7, 120.4; IR (KBr) ν_{max} 2922, 2355, 1639, 1489, 1093, 950, 880, 822, 740, 548, 474 cm^{-1} ; MS (EI) 316 ($[\text{M}]^+$); HRMS (EI) calcd. for $\text{C}_{16}\text{H}_{10}\text{ClBr}$ ($[\text{M}]^+$): 315.9654; Found: 315.9649.



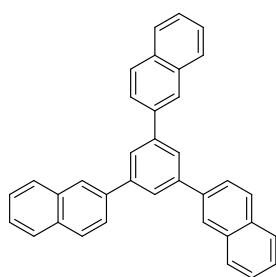
9,10-Bis(3-phenylnaphthalen-2-yl)anthracene(3u)

Yellow solid, M.p. 310-315 °C, yield 51%. ¹H NMR (400 MHz, CDCl₃) δ 8.07 (s, 2H), 8.03 (d, *J* = 7.9 Hz, 2H), 7.87 (dd, *J* = 13.6, 5.5 Hz, 4H), 7.66-7.53 (m, 8H), 7.23-7.14 (m, 4H), 7.09-6.88 (m, 7H), 6.83 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100MHz, CDCl₃) δ 141.6, 140.9, 136.2, 135.9, 133.2, 132.5, 131.6, 130.2, 129.0, 128.7, 128.5, 127.9, 127.7, 127.6, 127.3, 127.1, 126.5, 126.3, 126.3, 124.9, 124.8; IR (KBr) ν_{\max} 3056, 2957, 2921, 2852, 1735, 1651, 1459, 1378, 1261, 1095, 1022, 802, 754, 698, 577, 477 cm⁻¹; MS (EI) 582 ([M]⁺); HRMS (EI) calcd. for C₄₆H₃₀ ([M]⁺): 582.2348; Found: 582.2342.



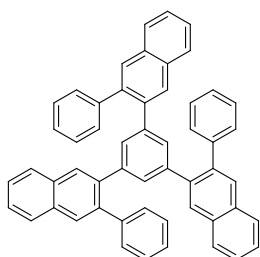
3,3'-Diphenyl-2,2'-binaphthalene(3v)⁹

Yield 75%. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 2H), 7.92 (d, *J* = 7.5 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.60 (s, 2H), 7.54-7.46 (m, 4H), 7.05 (dd, *J* = 10.6, 4.1 Hz, 2H), 6.92 (dd, *J* = 11.0, 4.2 Hz, 4H), 6.63-6.56 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 140.7, 139.7, 139.1, 133.0, 132.7, 130.8, 129.3, 128.8, 127.8, 127.6, 127.5, 126.1, 126.1, 126.0.



1,3,5-Tri(naphthalen-2-yl)benzene(3w)

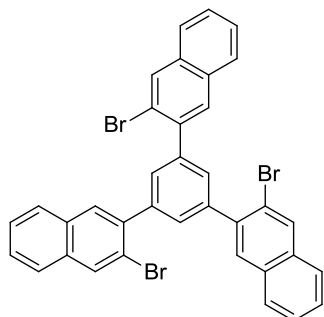
Yield 73%. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (s, 3H), 8.07 (s, 3H), 8.01-7.89 (m, 12H), 7.57-7.49 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 142.5, 138.4, 133.7, 132.8, 128.6, 128.2, 127.7, 126.4, 126.1, 126.1, 125.7, 125.7.



1,3,5-Tris(3-phenylnaphthalen-2-yl)benzene(3x)⁹

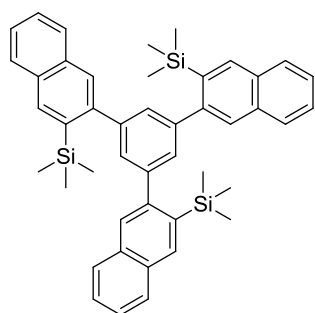
Yield 85%. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 6.6 Hz, 6H), 7.78-7.73 (m, 3H), 7.51-7.47 (m, 6H), 7.42-7.38 (m, 9H), 7.25 (s, 3H), 7.19 (dd, *J* = 6.4, 2.7 Hz, 6H), 6.94 (s, 3H); ¹³C

NMR (100 MHz, CDCl₃) δ 141.7, 140.4, 139.0, 138.7, 132.7, 132.6, 130.4, 130.1, 129.3, 129.1, 128.0, 127.7, 127.6, 126.6, 126.2, 126.2.



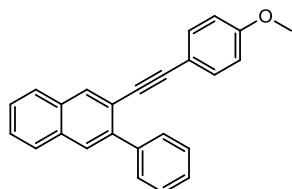
1,3,5-Tris(3-bromonaphthalen-2-yl)benzene(3y)

Yellow solid, M.p. 234-235 °C, yield 56%. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (s, 3H), 7.98 (s, 3H), 7.82 (ddd, *J* = 20.6, 5.8, 3.2 Hz, 6H), 7.70 (s, 3H), 7.51 (dd, *J* = 6.2, 3.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 140.3, 139.5, 133.6, 132.3, 131.7, 130.3, 127.9, 126.9, 126.7, 126.6, 120.8; IR (KBr) ν_{\max} 2924, 2352, 1638, 1103, 468 cm⁻¹; MS (EI) 690 ([M]⁺); HRMS (EI) calcd. for C₃₆H₂₁Br₃ ([M]⁺): 689.9193; Found: 689.9194.



((5-(1-(Trimethylsilyl)naphthalen-2-yl)-1,3-phenylene)bis(naphthalene-3,2-diyl))bis(trimethylsilane)(3z)

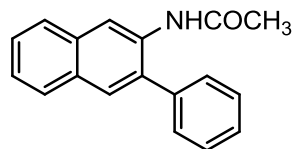
Yellow solid, M.p. 214-216 °C, yield 87%. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (s, 3H), 7.90 (dd, *J* = 12.4, 7.8 Hz, 6H), 7.85 (s, 3H), 7.58-7.50 (m, 9H), 0.24 (s, 27H); ¹³C NMR (100 MHz, CDCl₃) δ 144.0, 142.1, 135.6, 134.6, 131.9, 130.5, 128.3, 126.9, 126.6, 126.2, 125.5, 124.6, 0.0; IR (KBr) ν_{\max} 3051, 2956, 2902, 1739, 1715, 1576, 1485, 1410, 1247, 1015, 881, 837, 759, 644, 475 cm⁻¹; MS(ESI-TOF) 672([M]⁺); HRMS (ESI-TOF) calcd. for C₄₅H₄₈Si₃ ([M]⁺): 672.3064; Found: 672.3061.



2-((4-methoxyphenyl)ethynyl)-3-phenylnaphthalene(4)

Yellow oil, yield 82%. ¹H NMR (400 MHz, CDCl₃) δ 8.15 (s, 1H), 7.83 (dd, *J* = 7.0, 3.9 Hz, 3H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.53-7.45 (m, 4H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.5, 140.6, 140.61, 132.8, 132.8, 132.3, 132.2, 129.7, 128.2, 127.8, 127.8, 127.4, 127.3,

126.8, 126.4, 120.4, 115.6, 113.9, 92.8, 88.4, 55.3; IR(KBr) ν_{\max} 3053, 2929, 2850, 2209, 1601, 1507, 1453, 1251, 1175, 1030, 893, 830, 756, 700, 536, 480 cm^{-1} ; MS(EI) 334 ($[\text{M}]^+$); HRMS(EI) calcd. for $\text{C}_{25}\text{H}_{18}\text{O}$ ($[\text{M}]^+$): 334.1358; found: 334.1360.

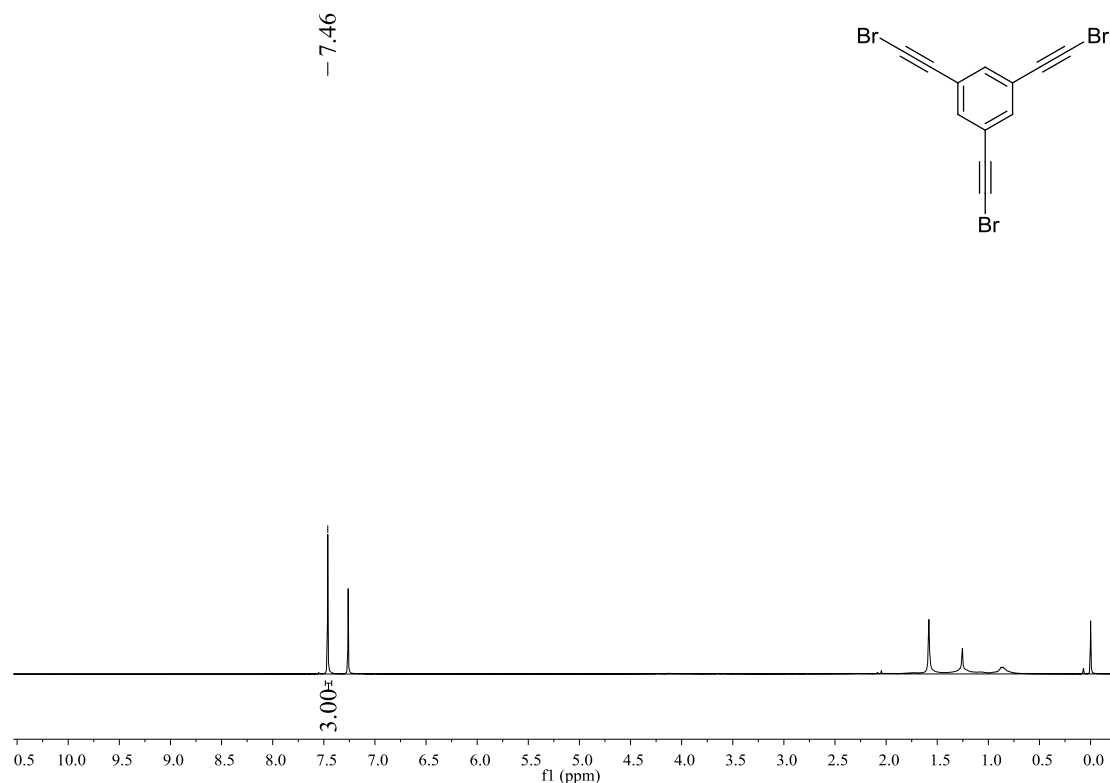


N-(3-phenylnaphthalen-2-yl)acetamide(5)

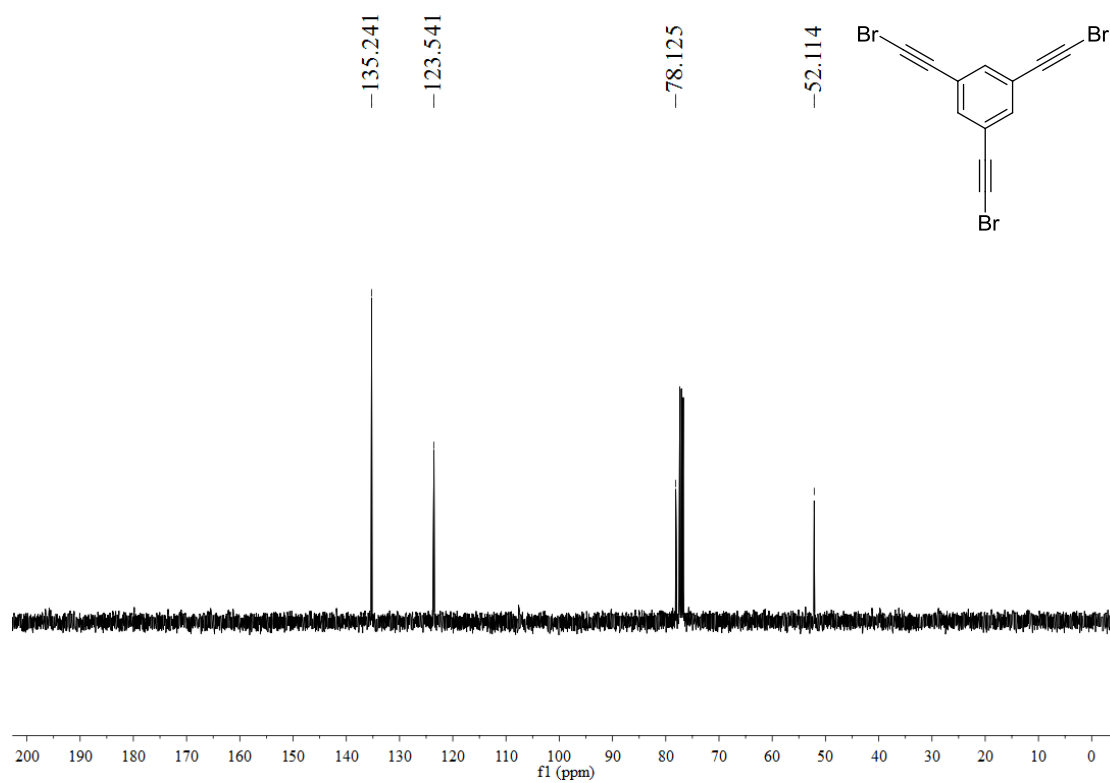
Yellow solid, M.p. 137-139 °C, yield 80%. ^1H NMR (400 MHz, CDCl_3) δ 8.72 (s, 1H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.67 (d, $J = 7.9$ Hz, 1H), 7.61 (s, 1H), 7.46-7.29 (m, 8H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.34, 137.97, 133.43, 132.61, 132.19, 130.30, 129.48, 129.18, 128.23, 127.79, 127.48, 126.54, 125.45, 118.26, 118.21, 24.77; IR(KBr) ν_{\max} 3418, 3235, 3046, 2926, 2350, 1663, 1531, 1372, 1276, 1017, 891, 755, 697, 610, 485 cm^{-1} ; MS(EI) 261 ($[\text{M}]^+$); HRMS(EI) calcd. for $\text{C}_{18}\text{H}_{15}\text{NO}$ ($[\text{M}]^+$): 261.1154; found: 261.1157.

4. ^1H NMR and ^{13}C NMR Spectra of Compounds.

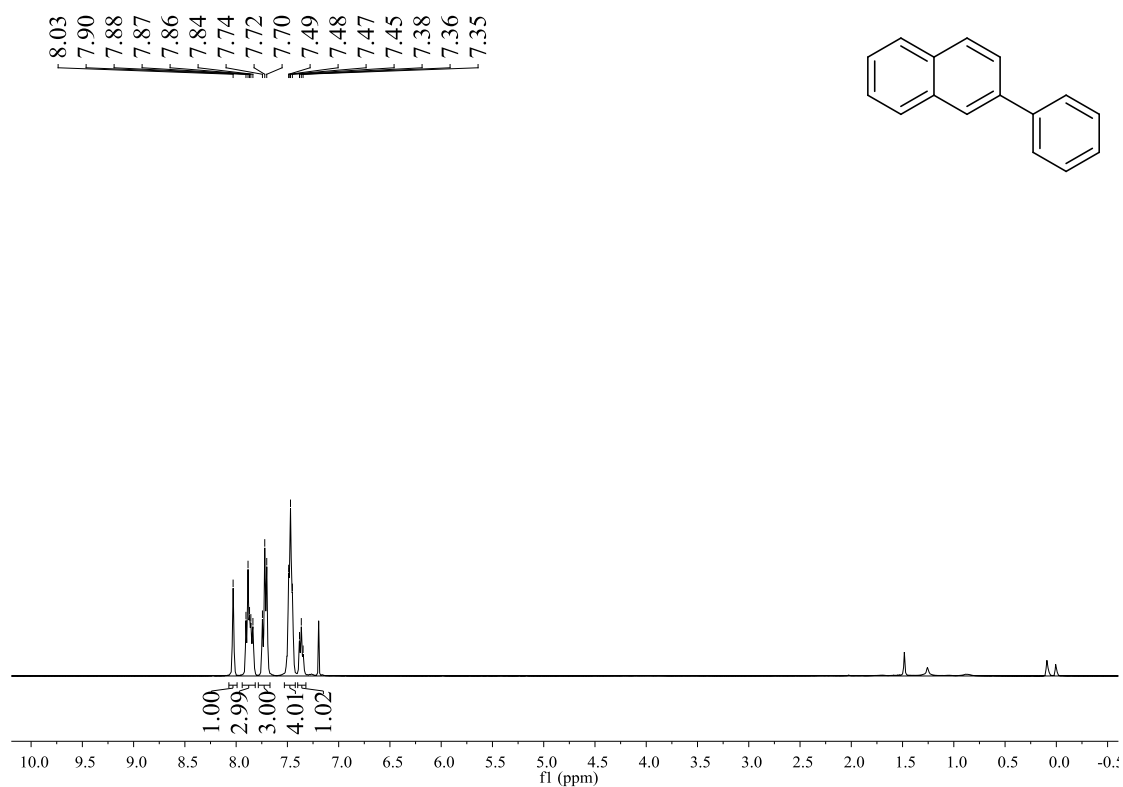
1,3,5-Tris(bromoethynyl)benzene(2y) ^1H NMR (400 MHz, CDCl_3)



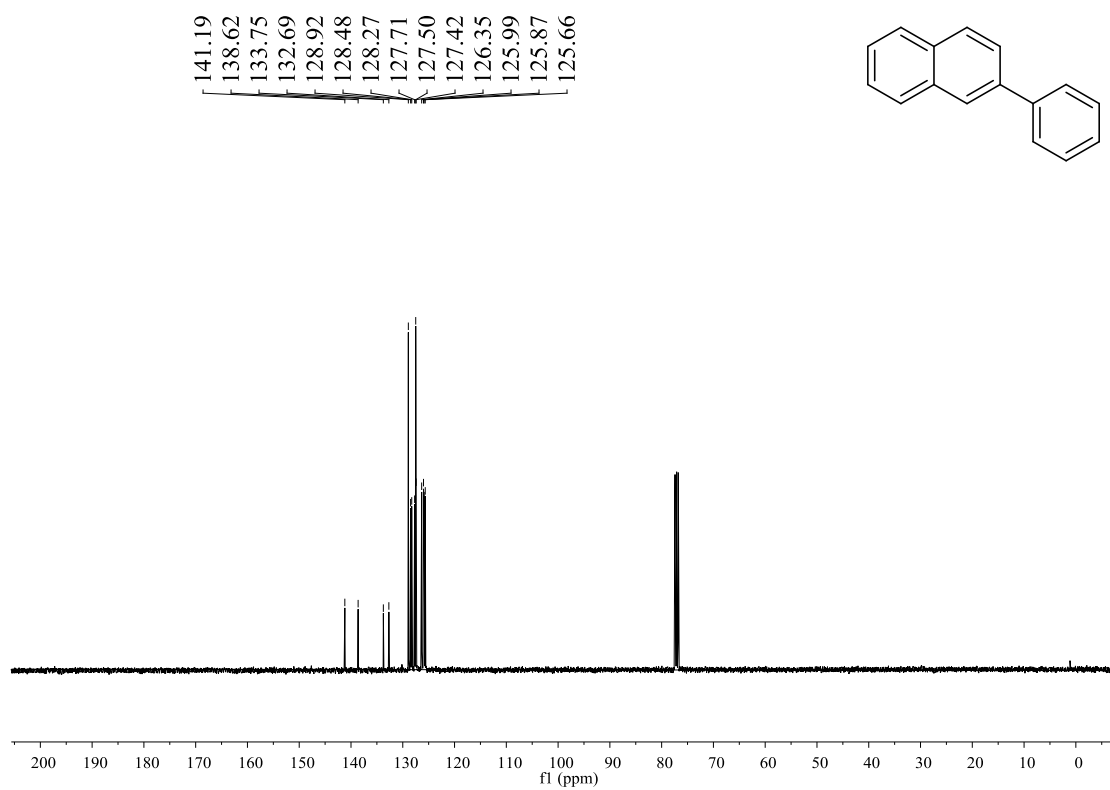
1,3,5-Tris(bromoethynyl)benzene(2y) ^{13}C NMR (100 MHz, CDCl_3)



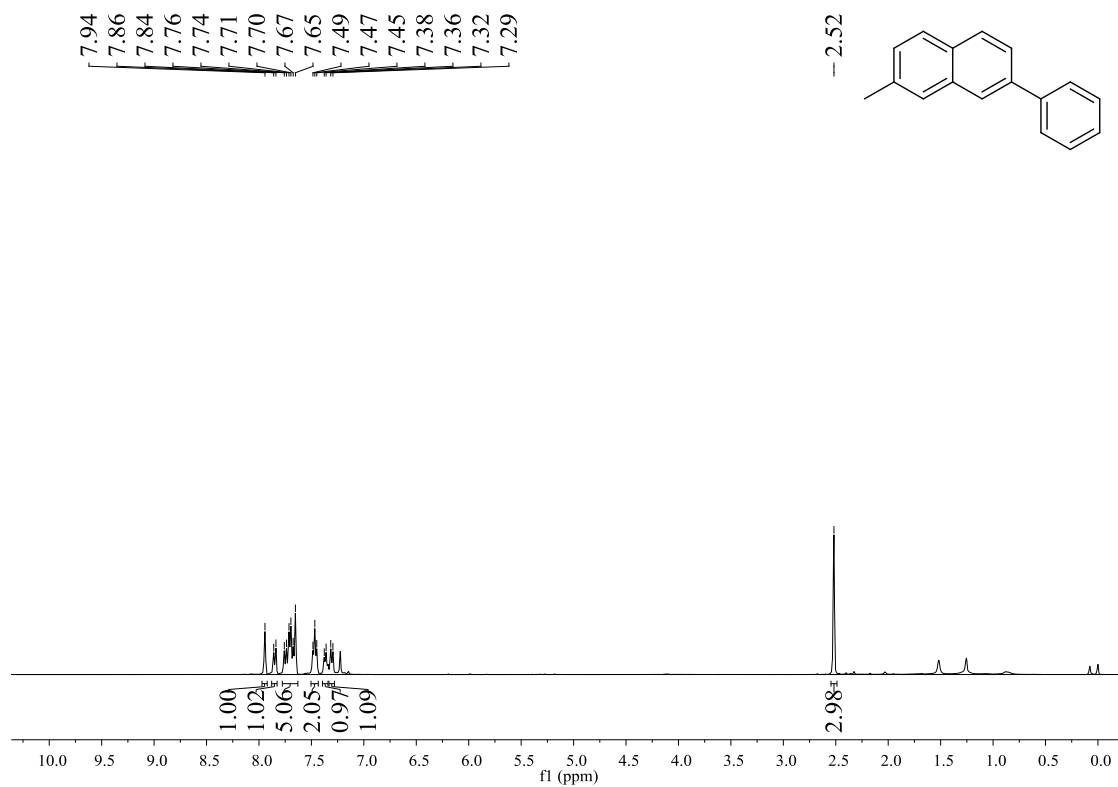
2-Phenylnaphthalene(3a) ¹H NMR (400 MHz, CDCl₃)



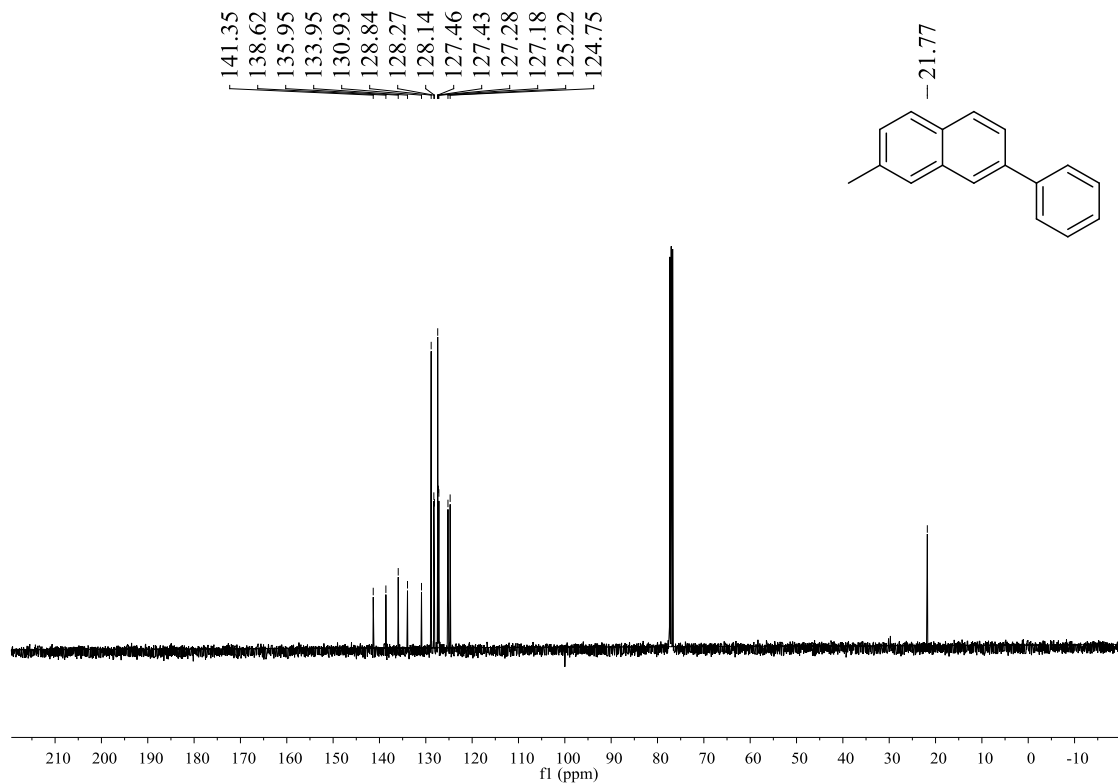
2-Phenylnaphthalene(3a) ¹³C NMR (100 MHz, CDCl₃)



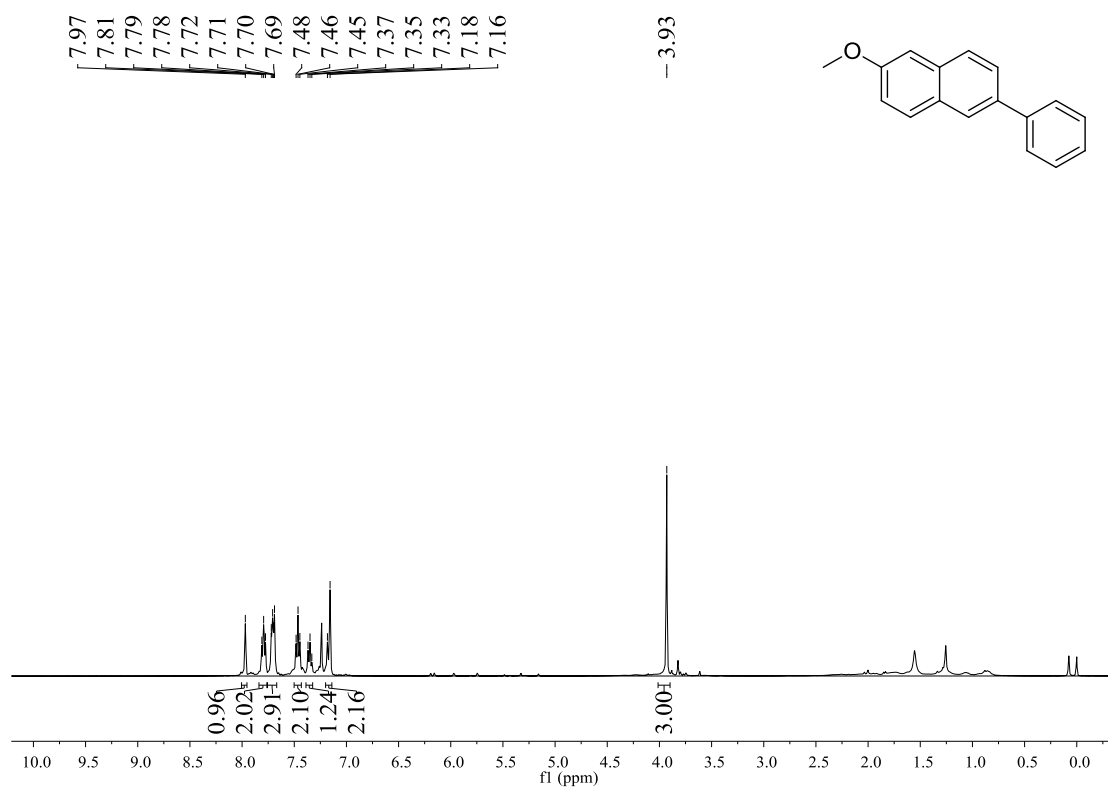
2-Methyl-6-phenylnaphthalene(3b) ^1H NMR (400 MHz, CDCl_3)



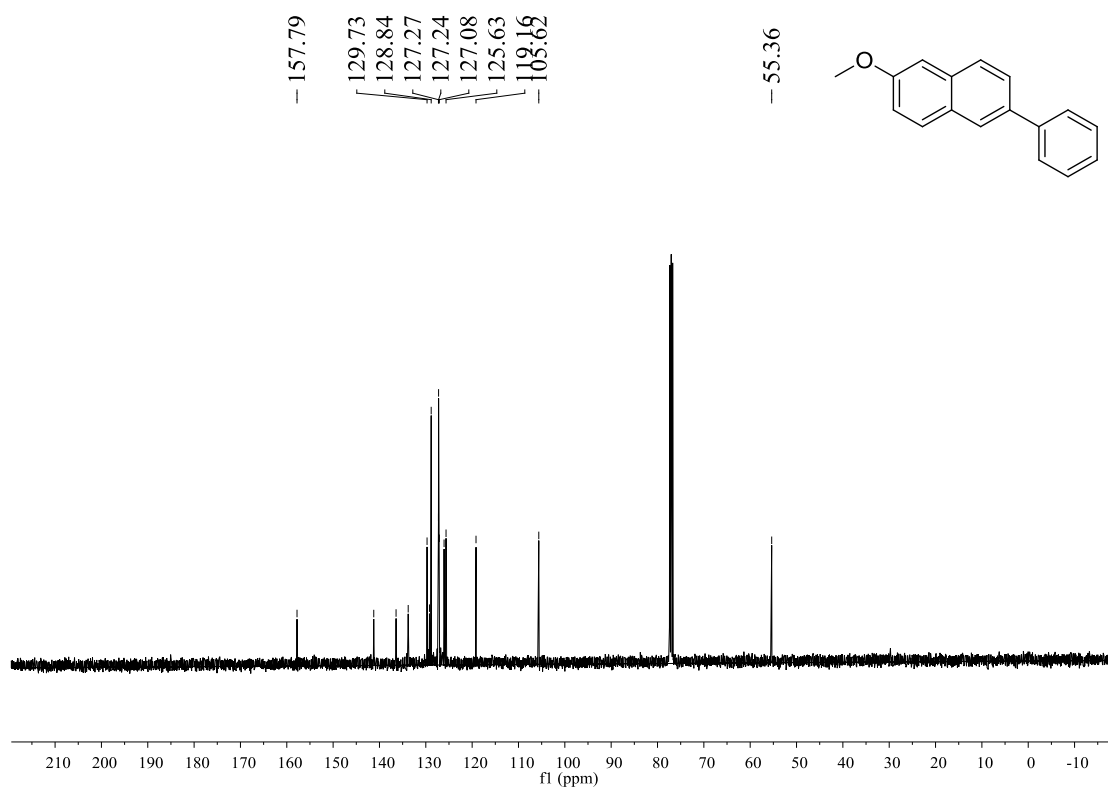
2-Methyl-6-phenylnaphthalene(3b) ^{13}C NMR (100 MHz, CDCl_3)



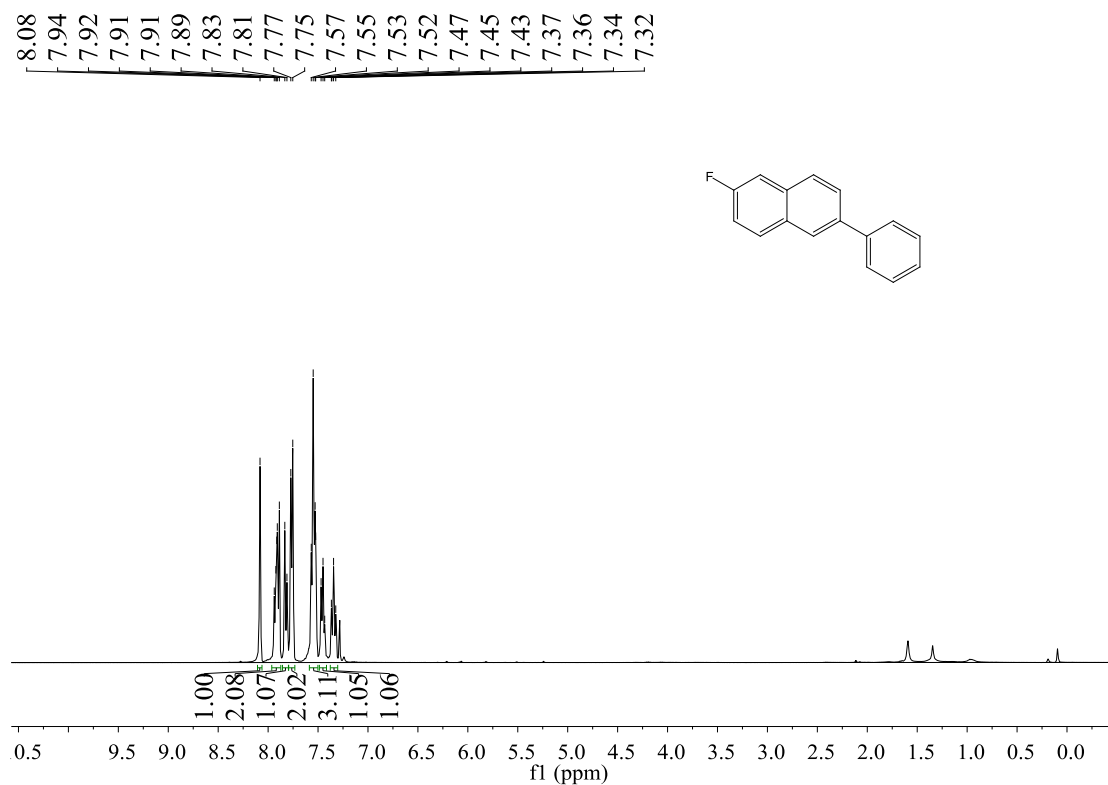
2-Methoxy-6-phenylnaphthalene(3c) ^1H NMR (400 MHz, CDCl_3)



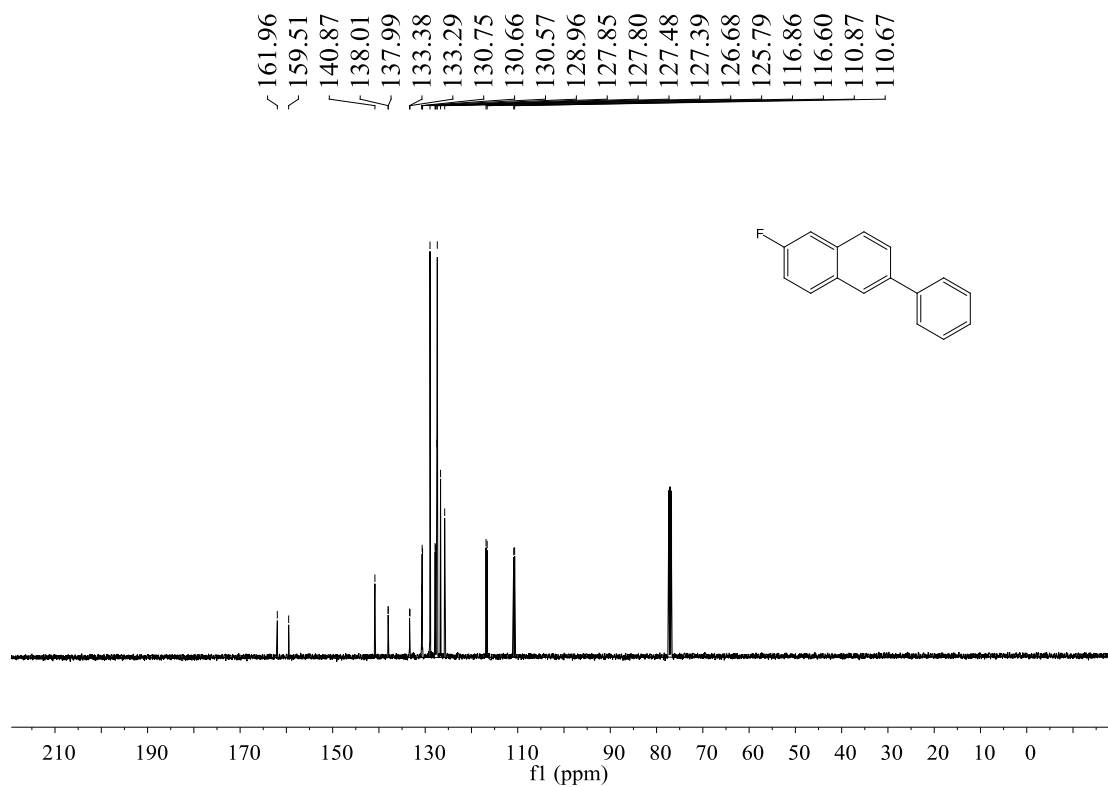
2-Methoxy-6-phenylnaphthalene(3c) ^{13}C NMR (100 MHz, CDCl_3)



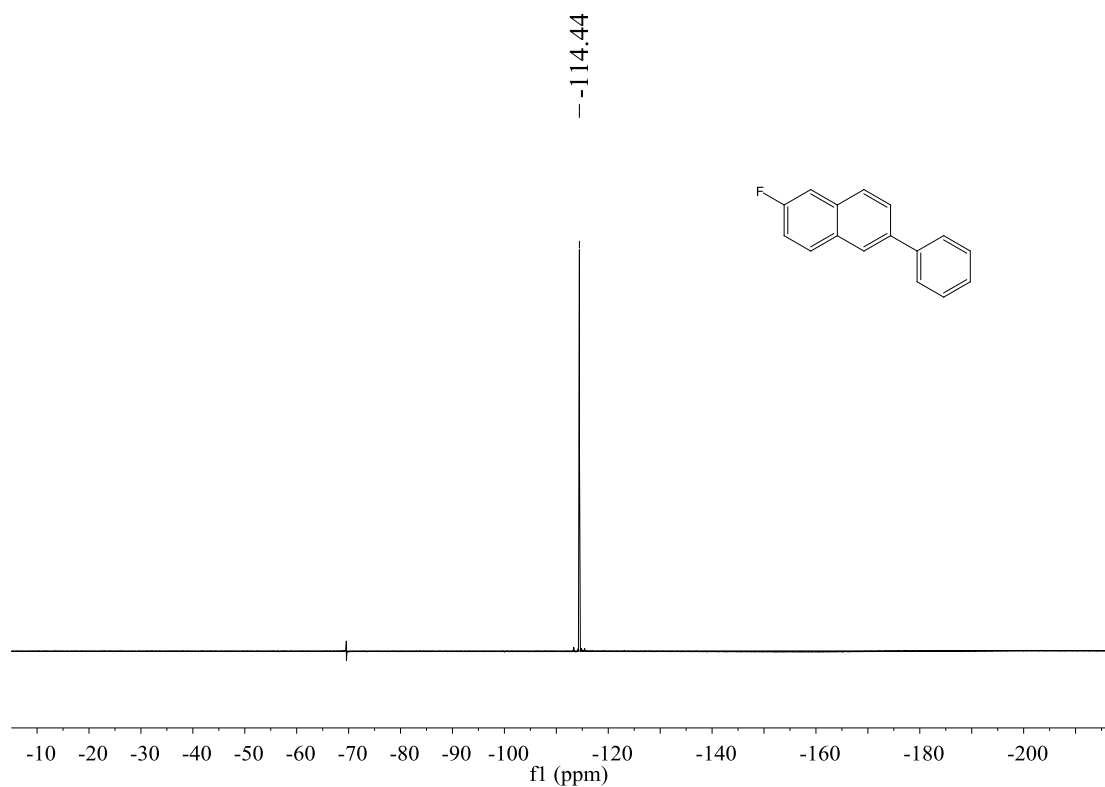
2-Fluoro-6-phenylnaphthalene(3d) ¹H NMR (400 MHz, CDCl₃)



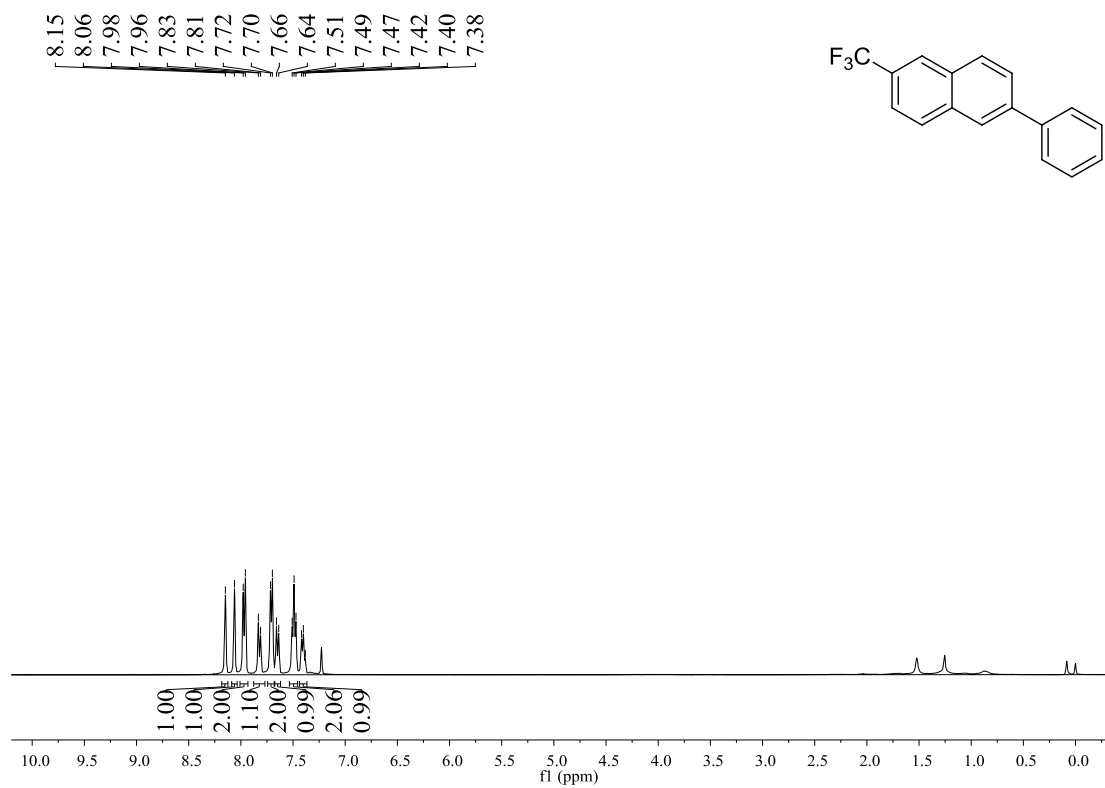
2-Fluoro-6-phenylnaphthalene(3d) ¹³C NMR (100 MHz, CDCl₃)



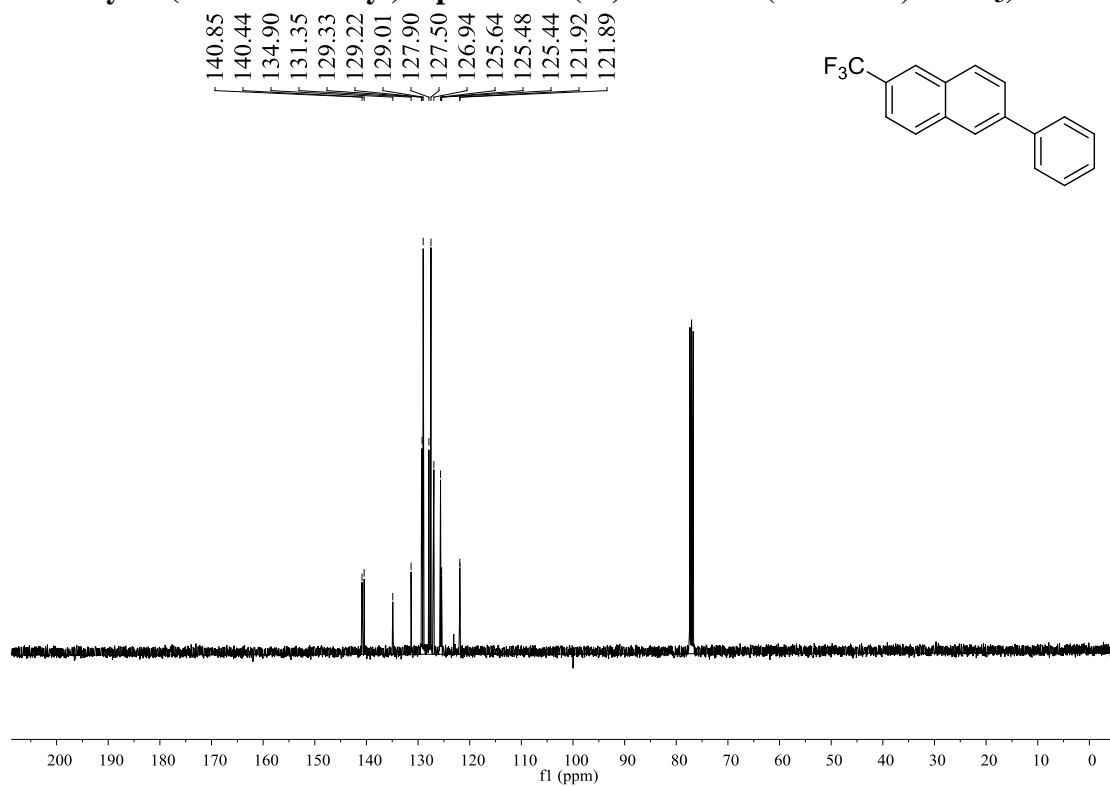
2-Fluoro-6-phenylnaphthalene(3d) ^{19}F NMR(376 MHz, CDCl_3)



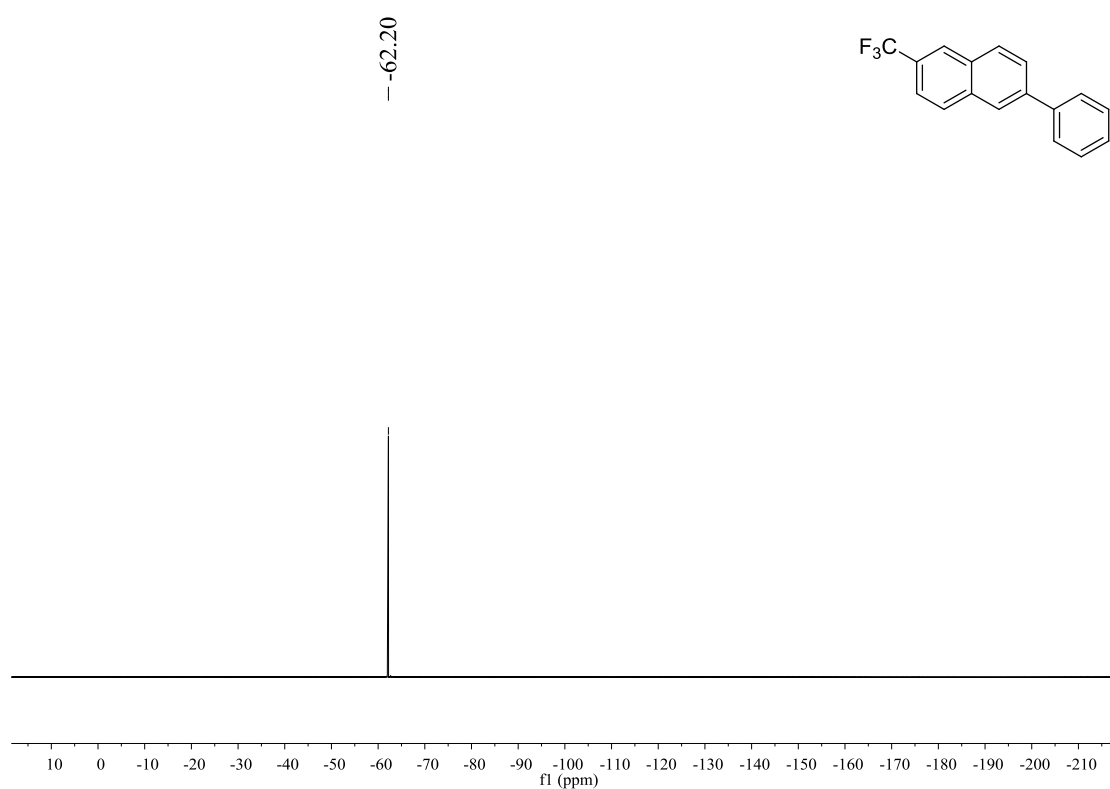
2-Phenyl-6-(trifluoromethyl)naphthalene(3e) ^1H NMR (400 MHz, CDCl_3)



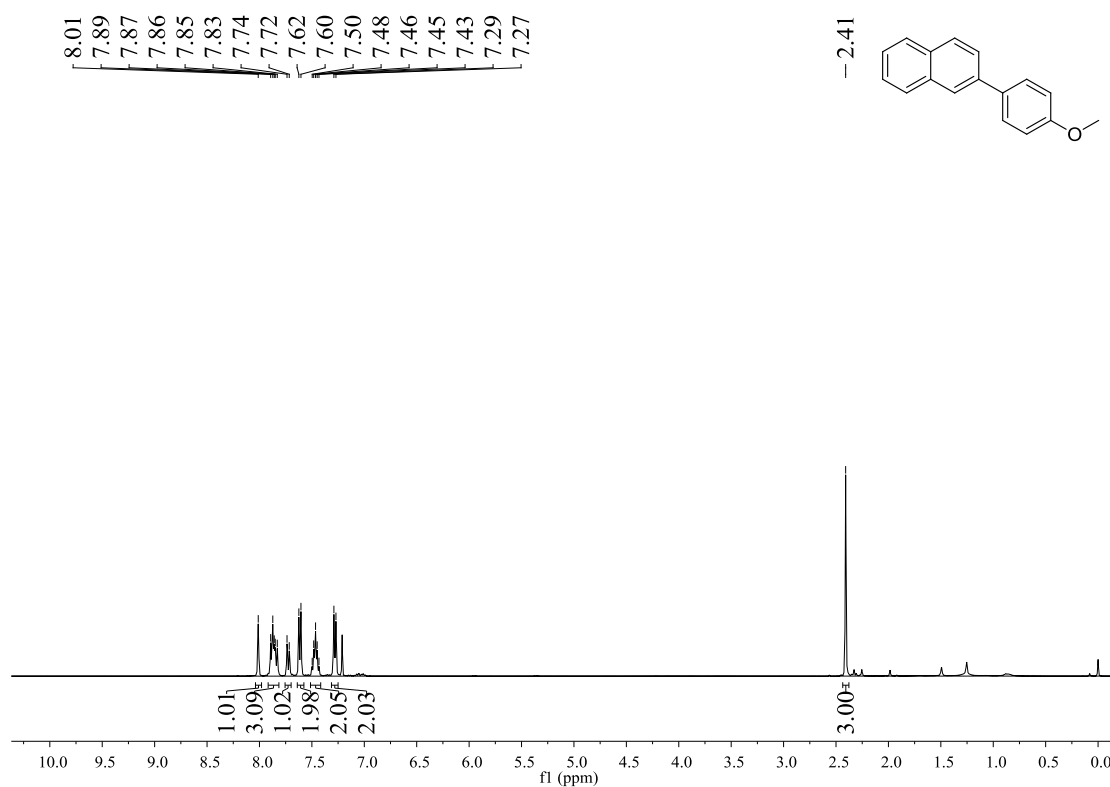
2-Phenyl-6-(trifluoromethyl)naphthalene(3e) ^{13}C NMR (100 MHz, CDCl_3)



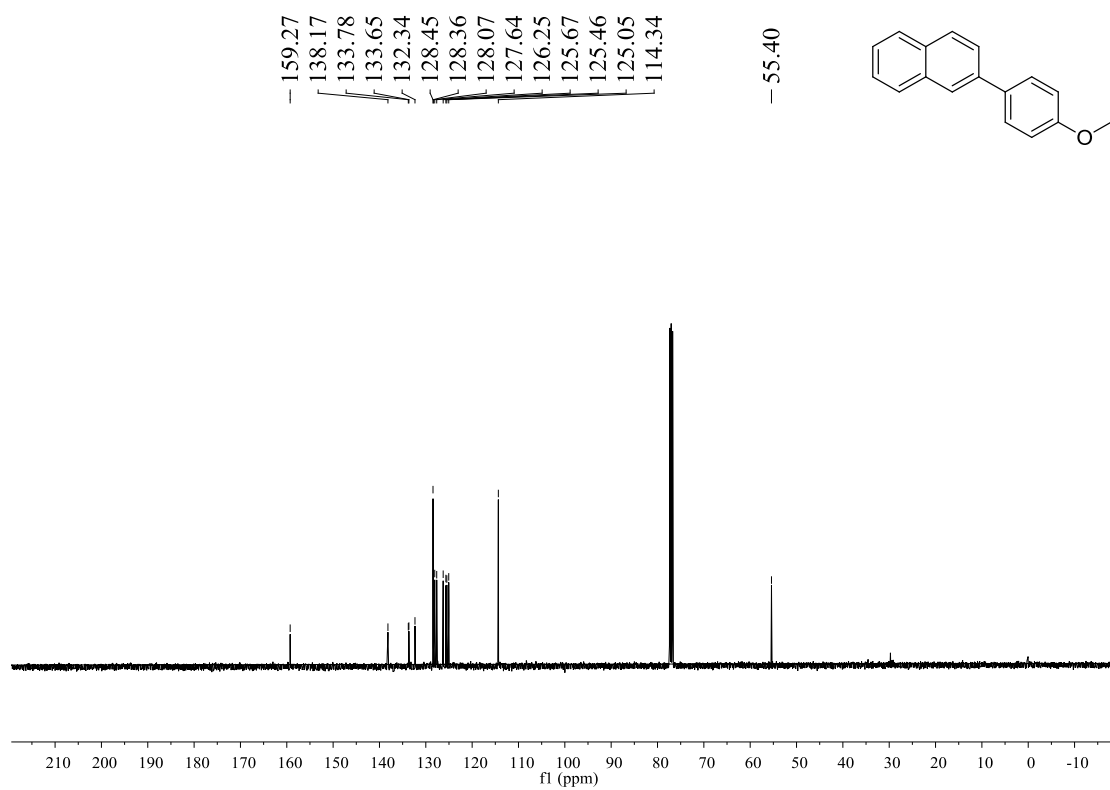
2-Phenyl-6-(trifluoromethyl)naphthalene(3e) ^{19}F NMR(376 MHz, CDCl_3)



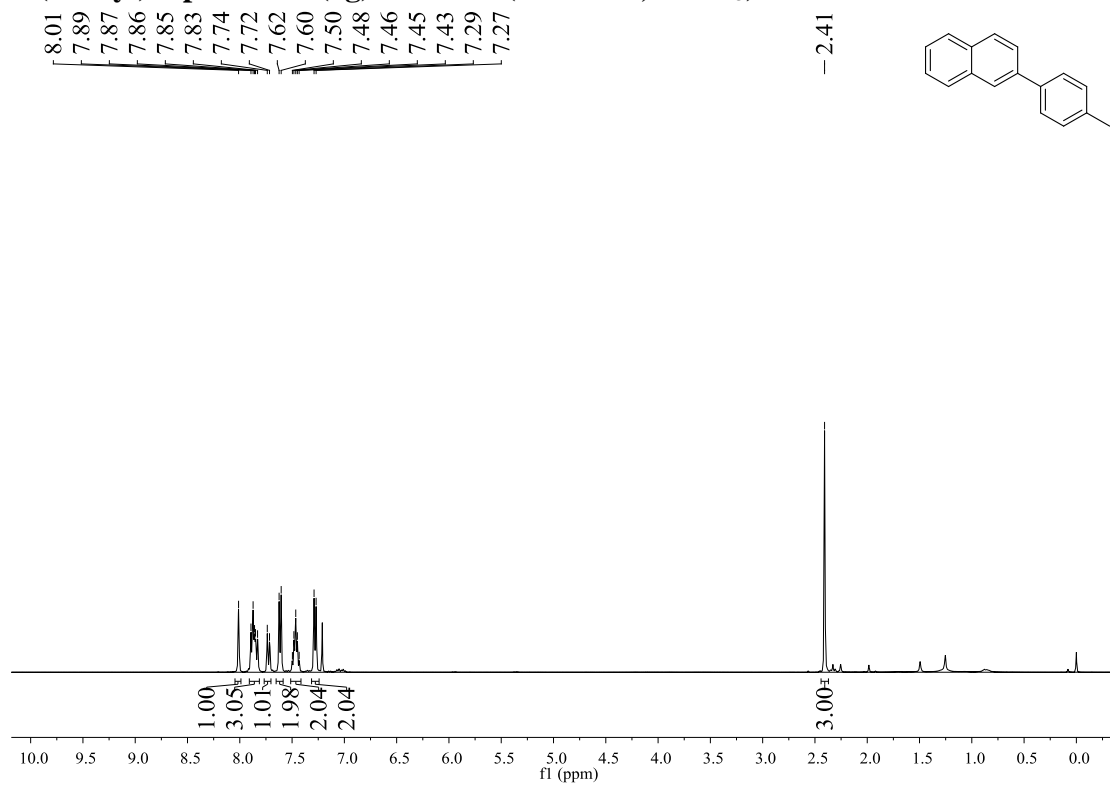
2-P-methoxyphenylnaphthalene(3f) ^1H NMR (400 MHz, CDCl_3)



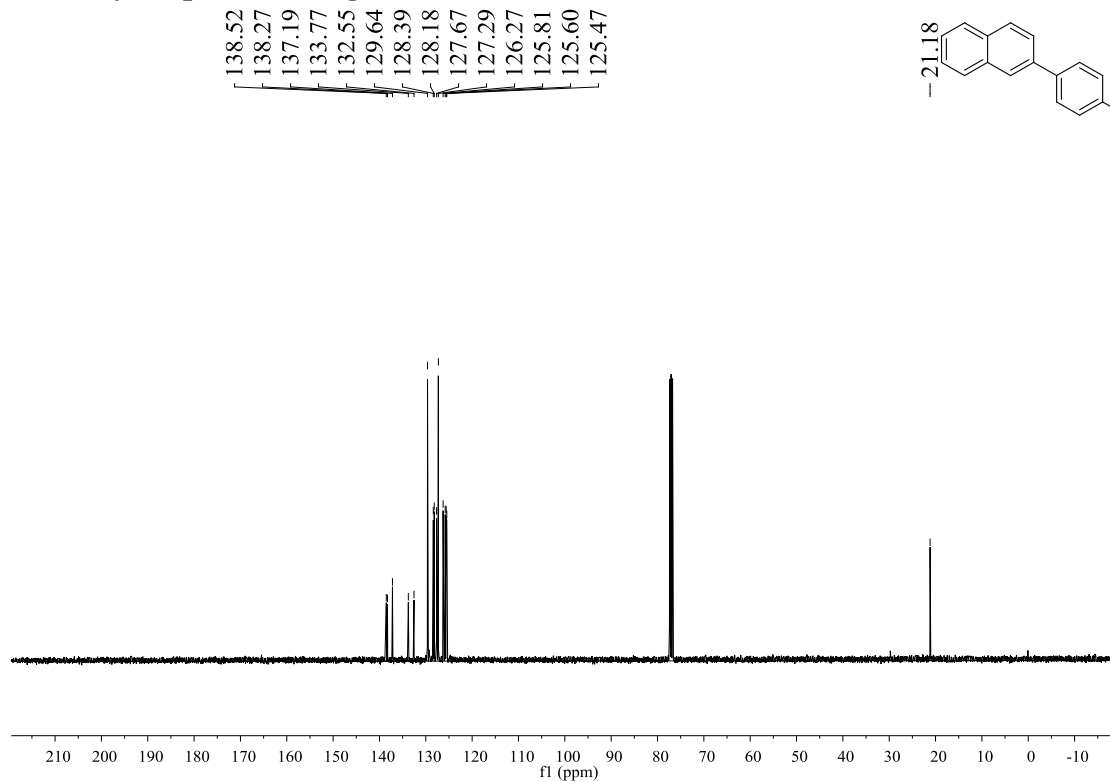
2-P-methoxyphenylnaphthalene(3f) ^{13}C NMR (100 MHz, CDCl_3)



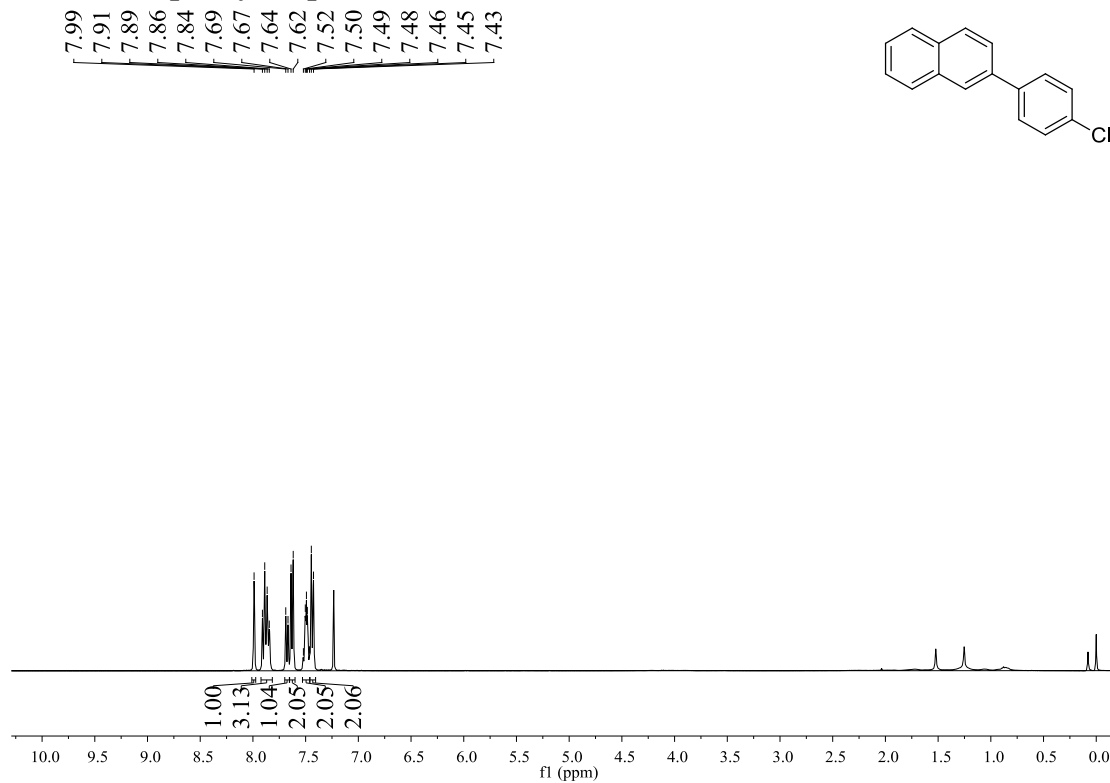
2-(P-tolyl)naphthalene(3g) ^1H NMR (400 MHz, CDCl_3)



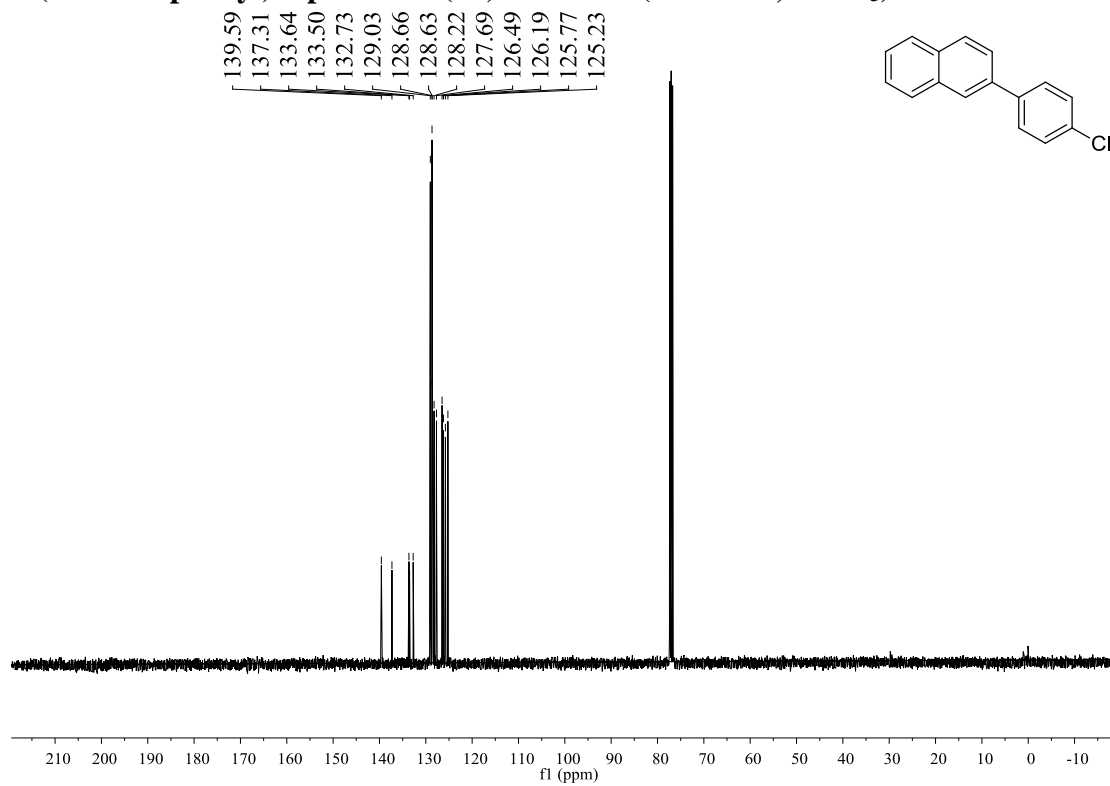
2-(P-tolyl)naphthalene(3g) ^{13}C NMR (100 MHz, CDCl_3)



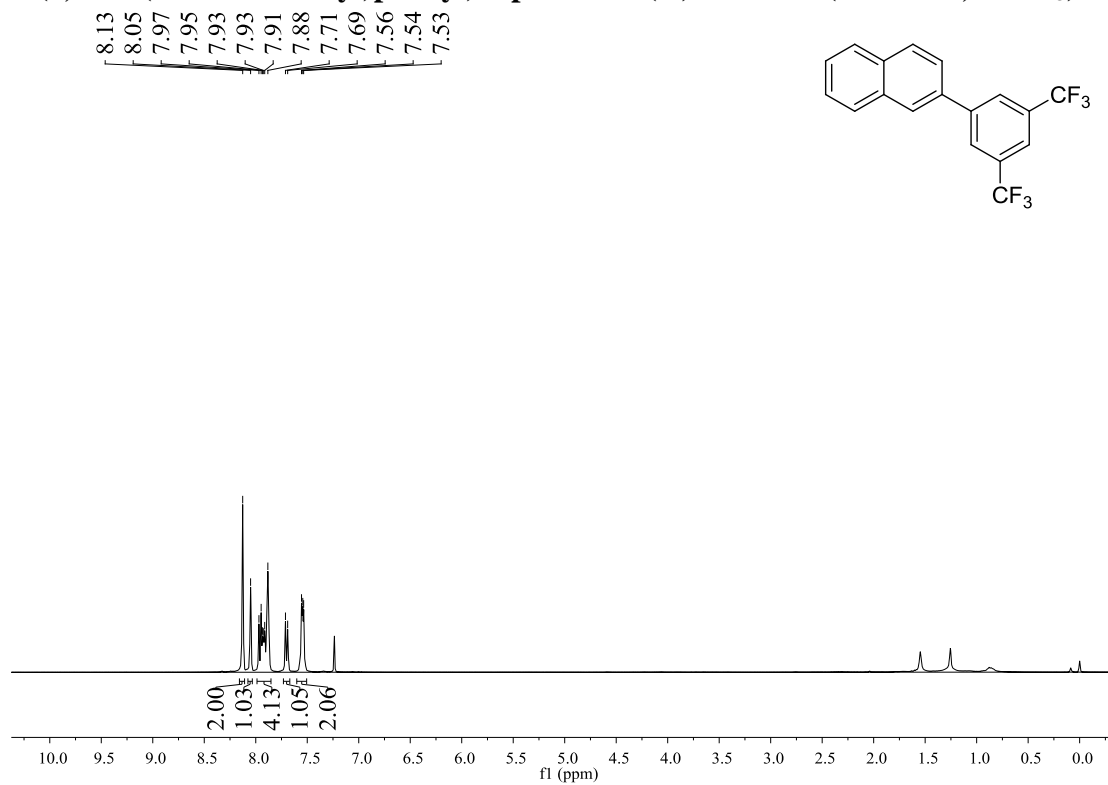
2-(4-Chlorophenyl)naphthalene(3h) ¹H NMR (400 MHz, CDCl₃)



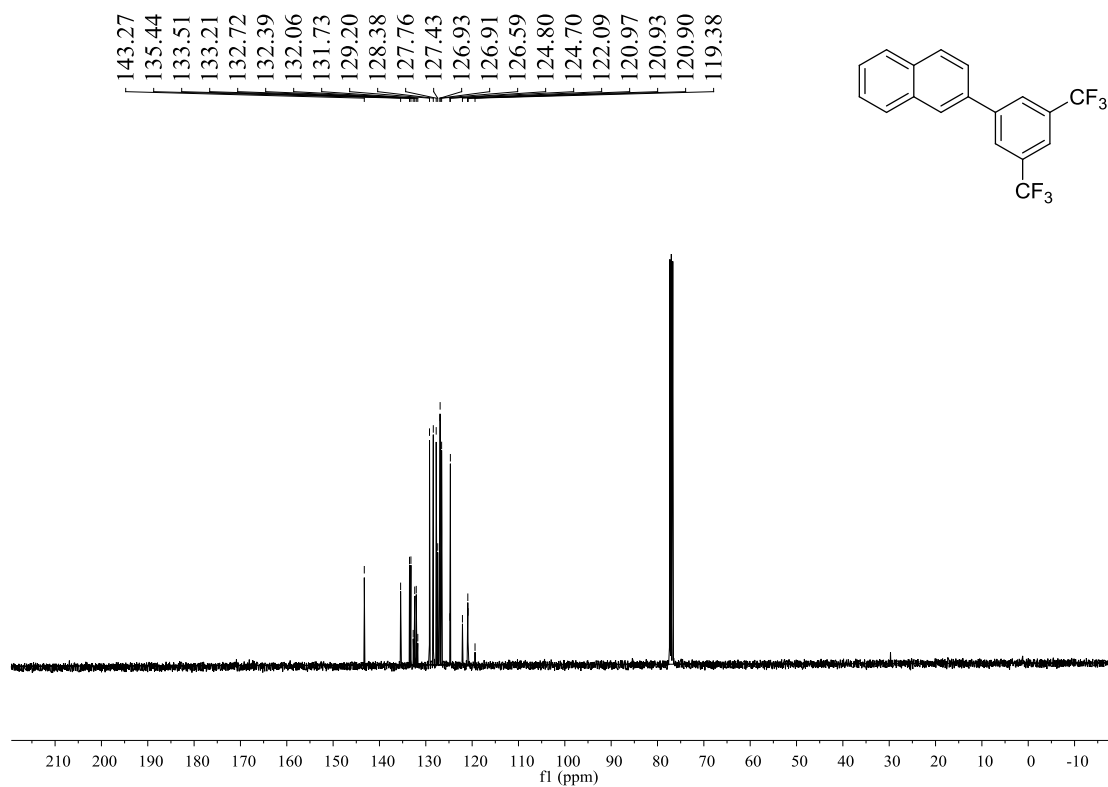
2-(4-Chlorophenyl)naphthalene(3h) ¹³C NMR (100 MHz, CDCl₃)



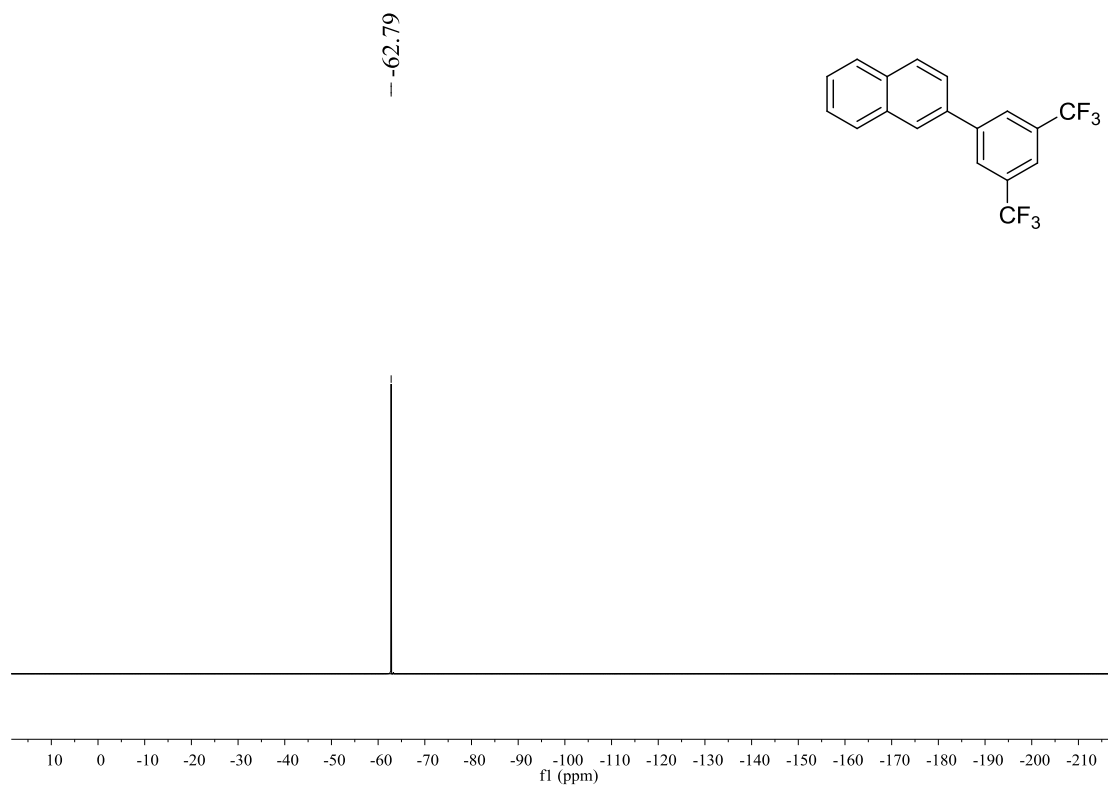
2-(3,5-Bis(trifluoromethyl)phenyl)naphthalene(3i) ^1H NMR (400 MHz, CDCl_3)



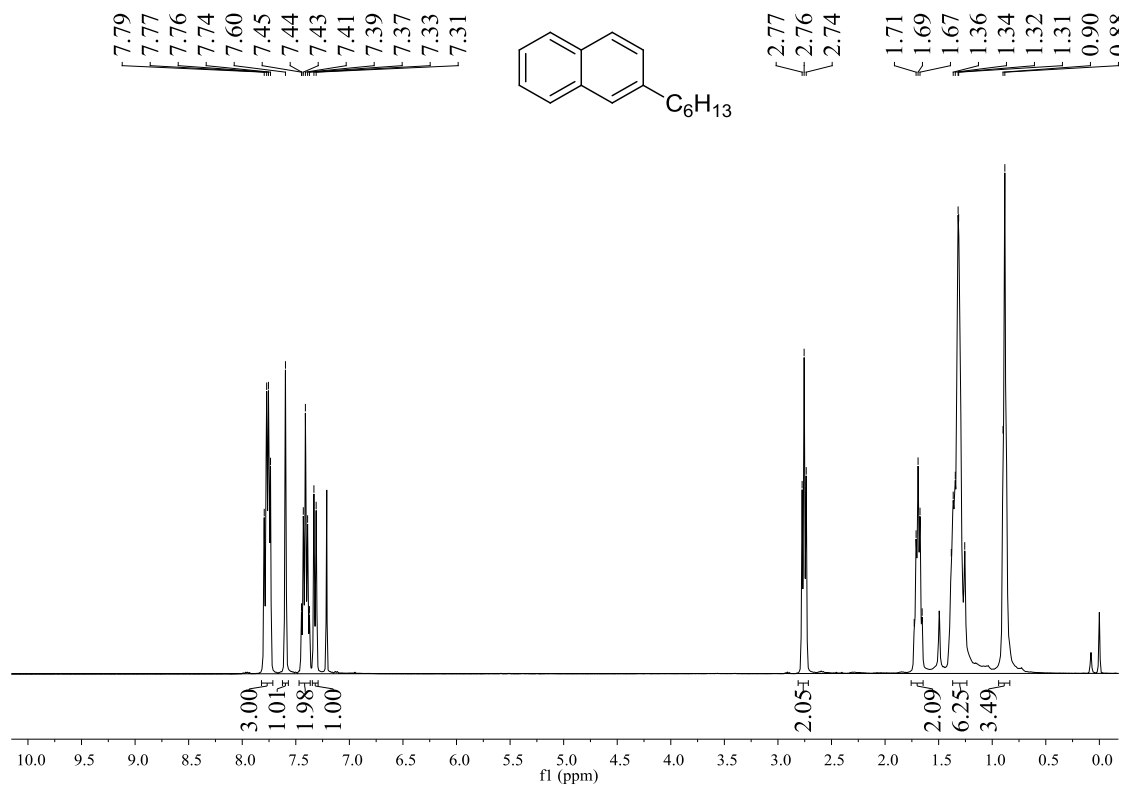
2-(3,5-Bis(trifluoromethyl)phenyl)naphthalene(3i) ^{13}C NMR (100 MHz, CDCl_3)



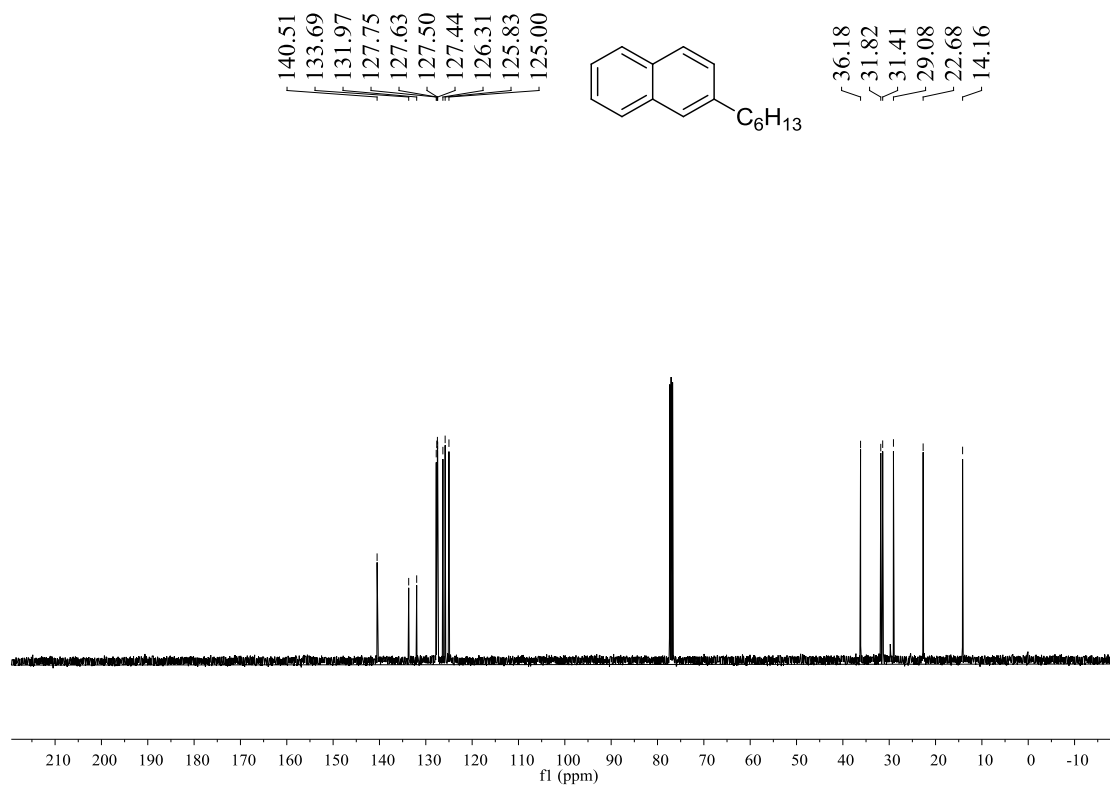
2-(3,5-Bis(trifluoromethyl)phenyl)naphthalene(3i) ^{19}F NMR (376 MHz, CDCl_3)



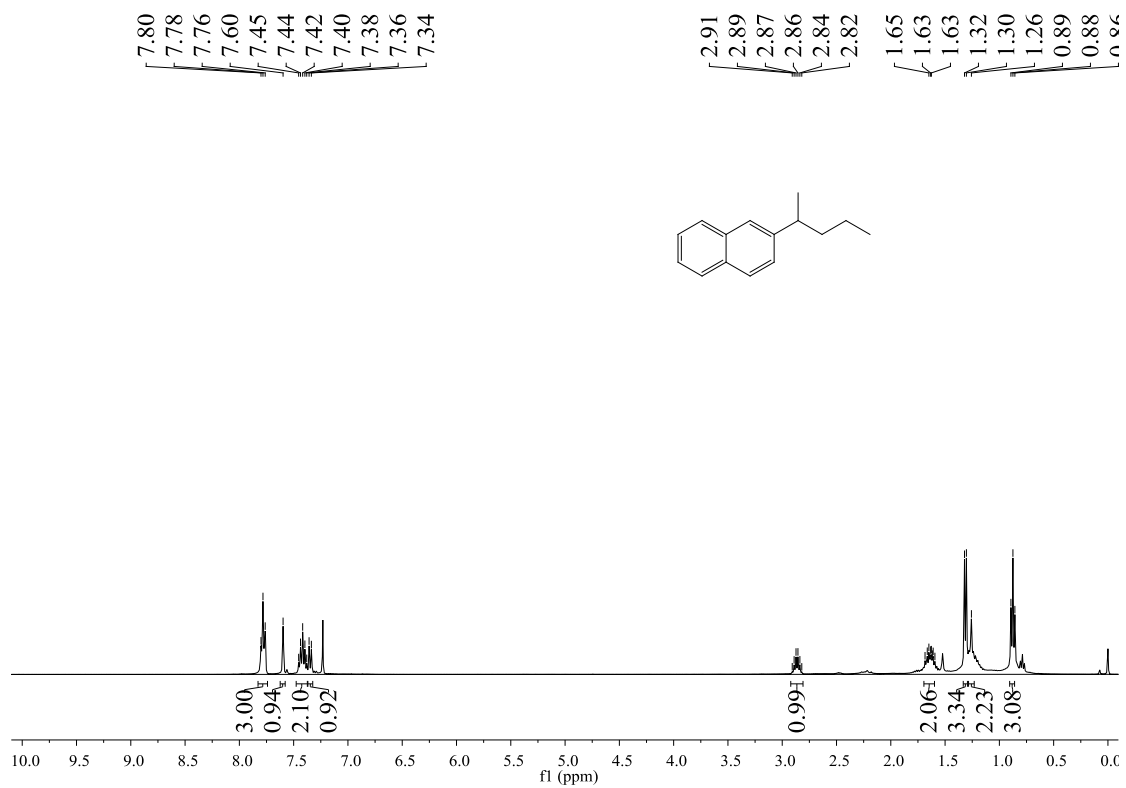
2-Hexylnaphthalene(3j) ^1H NMR (400 MHz, CDCl_3)



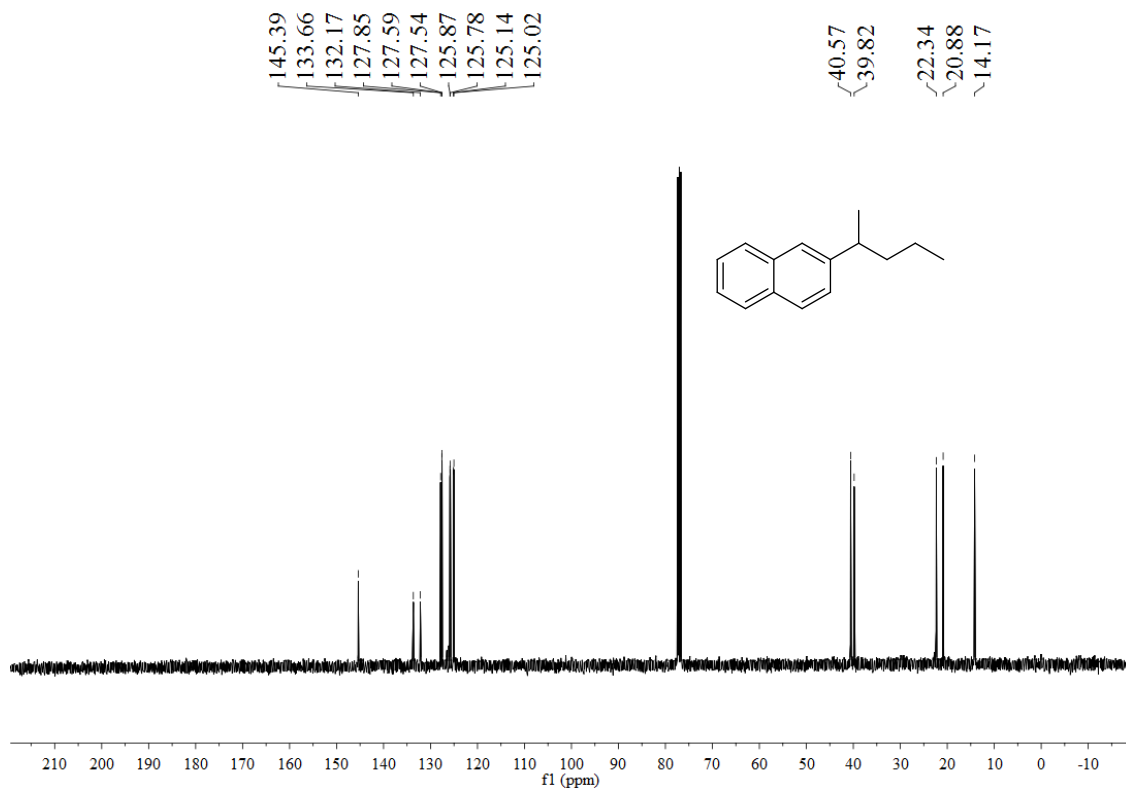
2-Hexylnaphthalene(3j) ^{13}C NMR (100 MHz, CDCl_3)



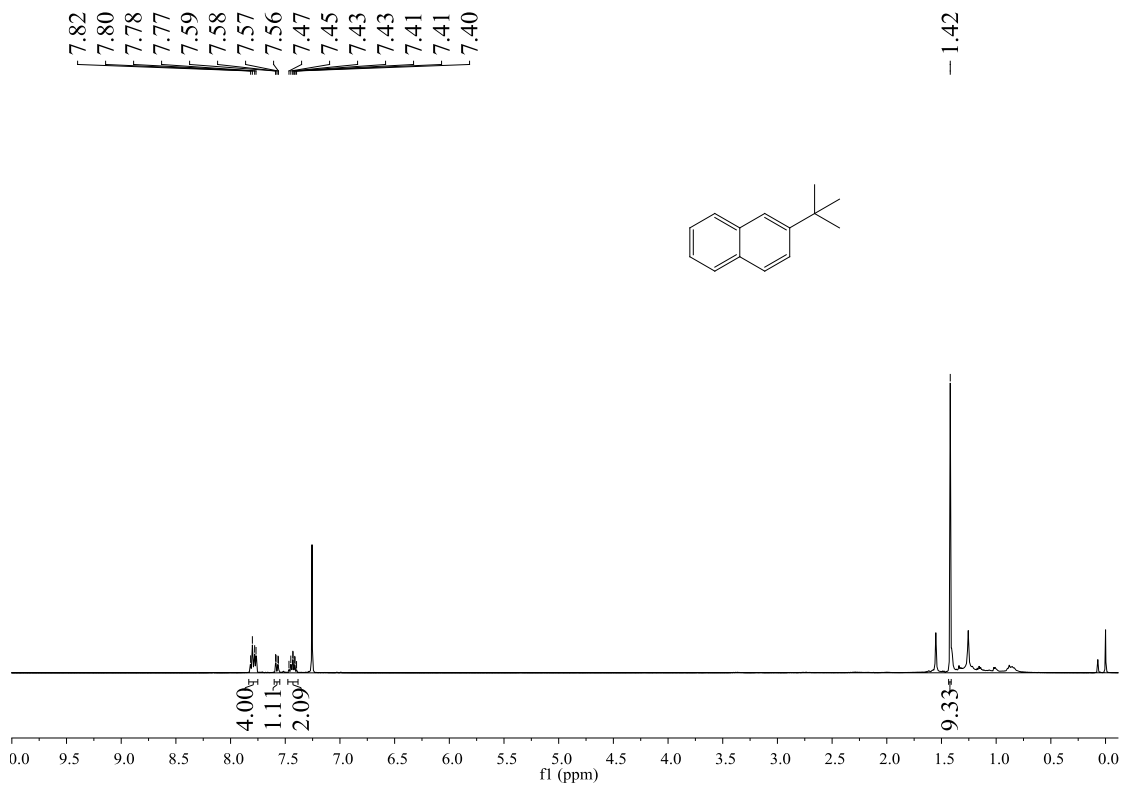
2-(Pentan-2-yl)naphthalene(3k) ^1H NMR (400 MHz, CDCl_3)



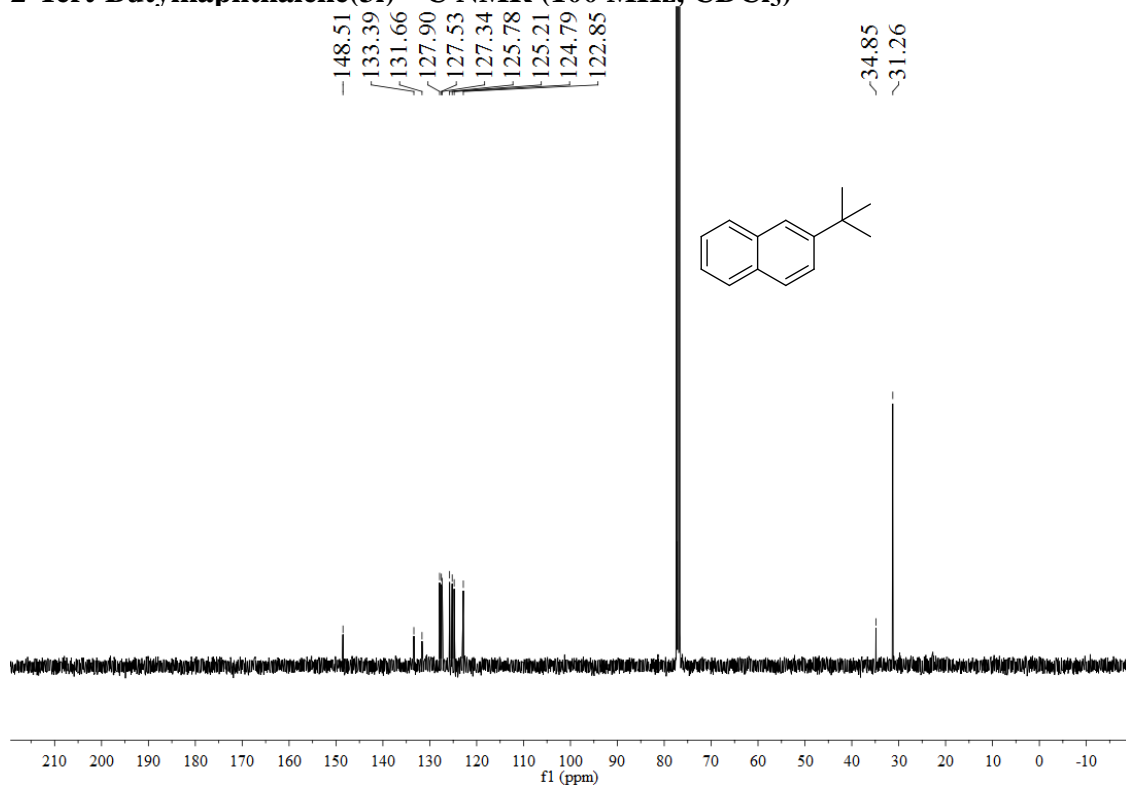
2-(Pentan-2-yl)naphthalene(3k) ^{13}C NMR (100 MHz, CDCl_3)



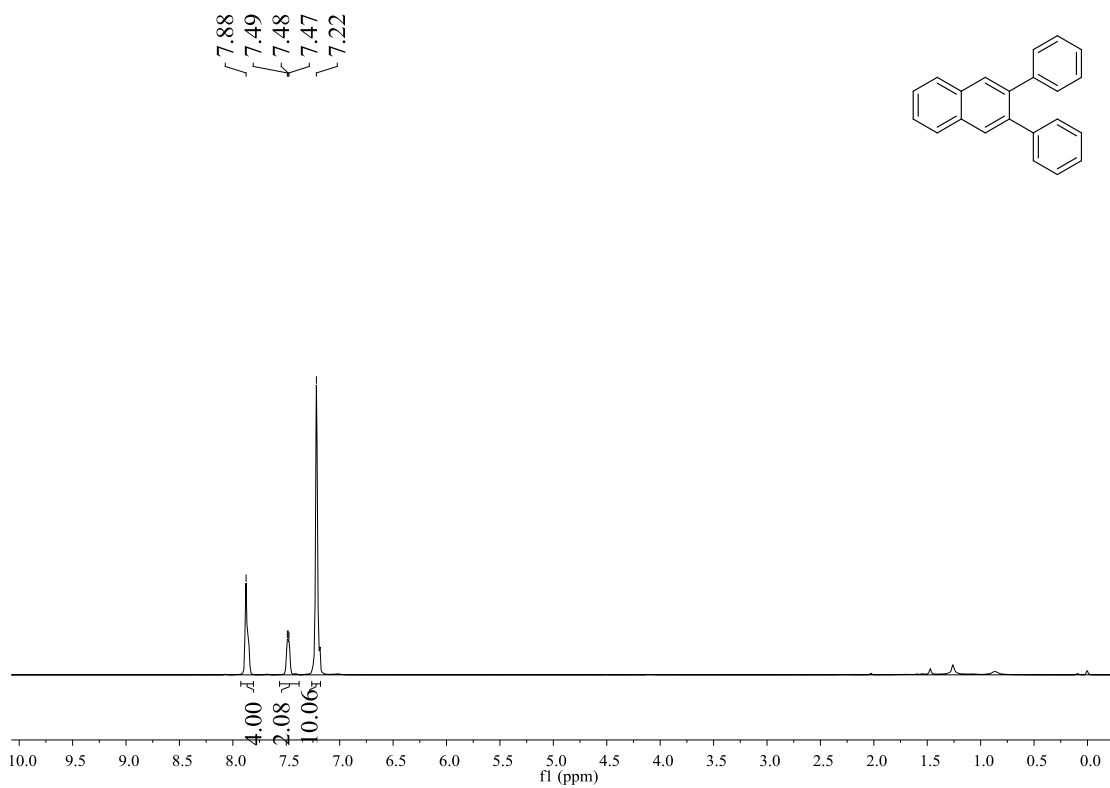
2-Tert-Butylnaphthalene(3l) ¹H NMR(400 MHz, CDCl₃)



2-Tert-Butylnaphthalene(3l) ^{13}C NMR (100 MHz, CDCl_3)

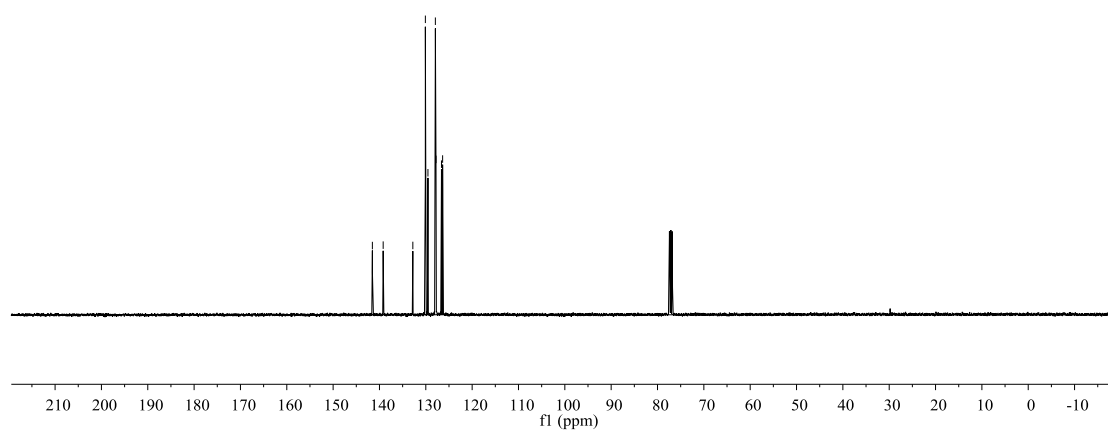
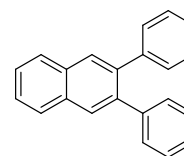


2,3-Diphenylnaphthalene(3m) ^1H NMR (400 MHz, CDCl_3)



2,3-Diphenylnaphthalene(3m) ^{13}C NMR (100 MHz, CDCl_3)

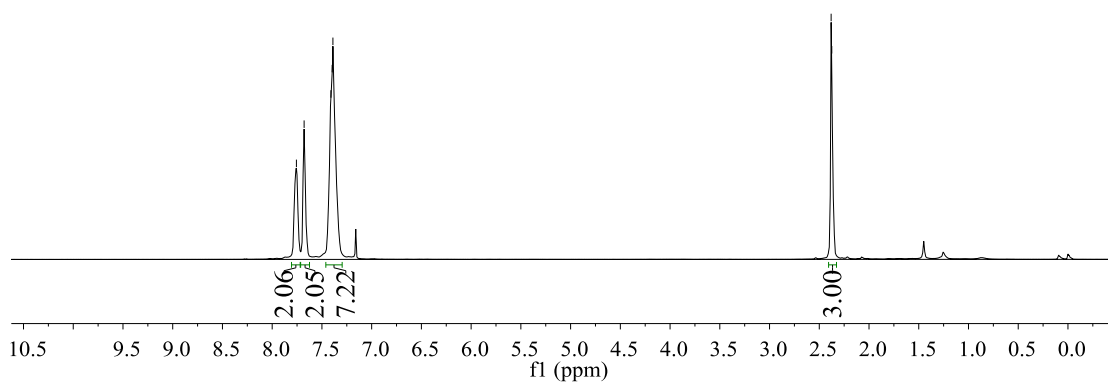
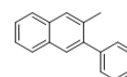
141.53
139.20
132.80
130.09
129.54
127.94
127.80
126.62
126.37



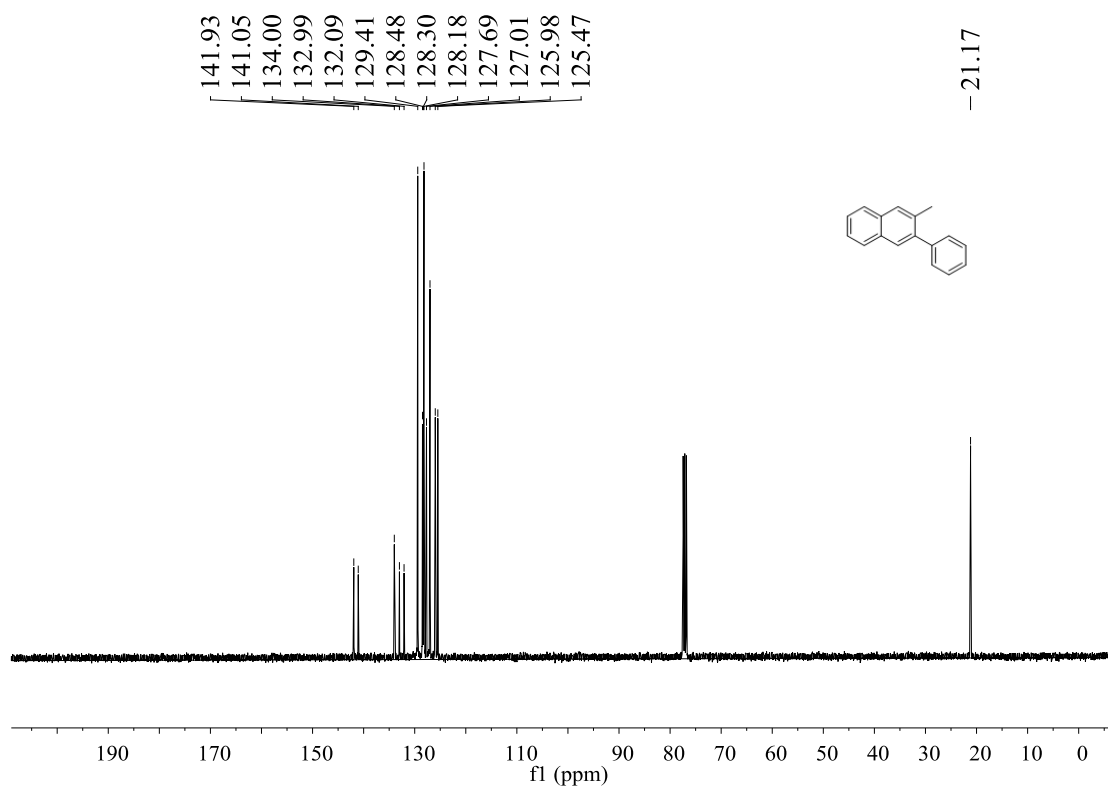
2-Methyl-3-phenylnaphthalene(3n) ^1H NMR (400 MHz, CDCl_3)

7.76
7.68
7.41
7.40
7.39

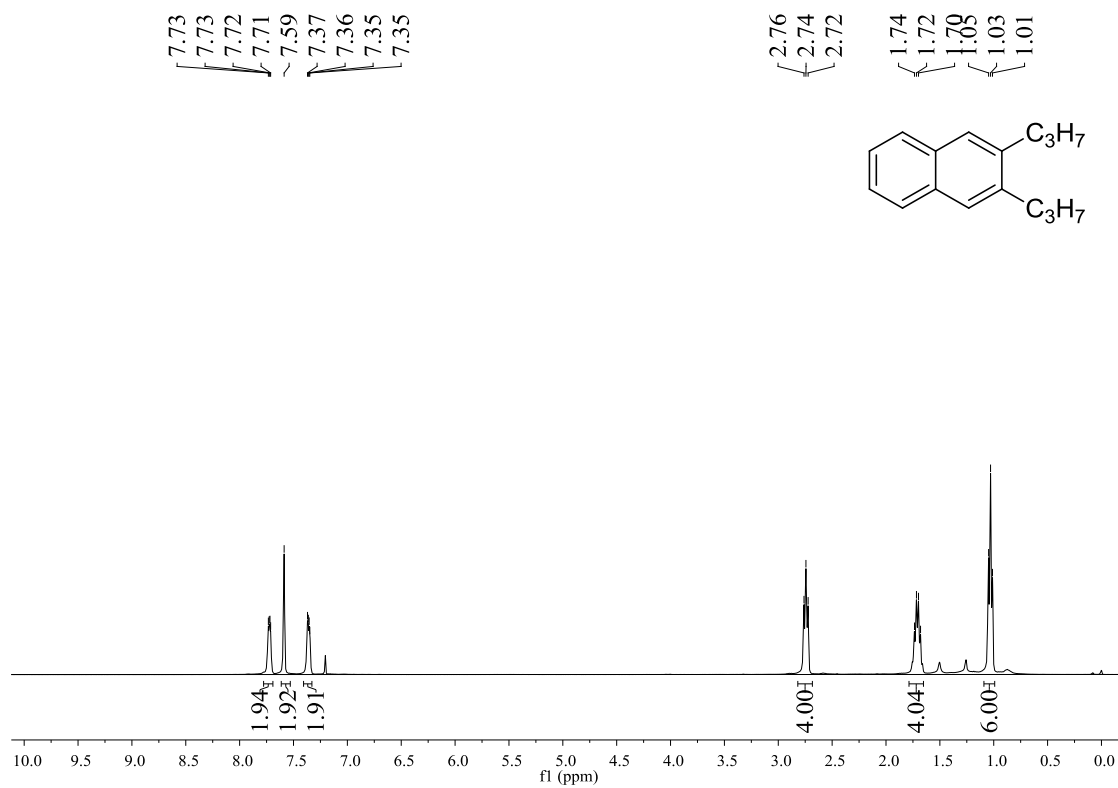
2.38
2.37



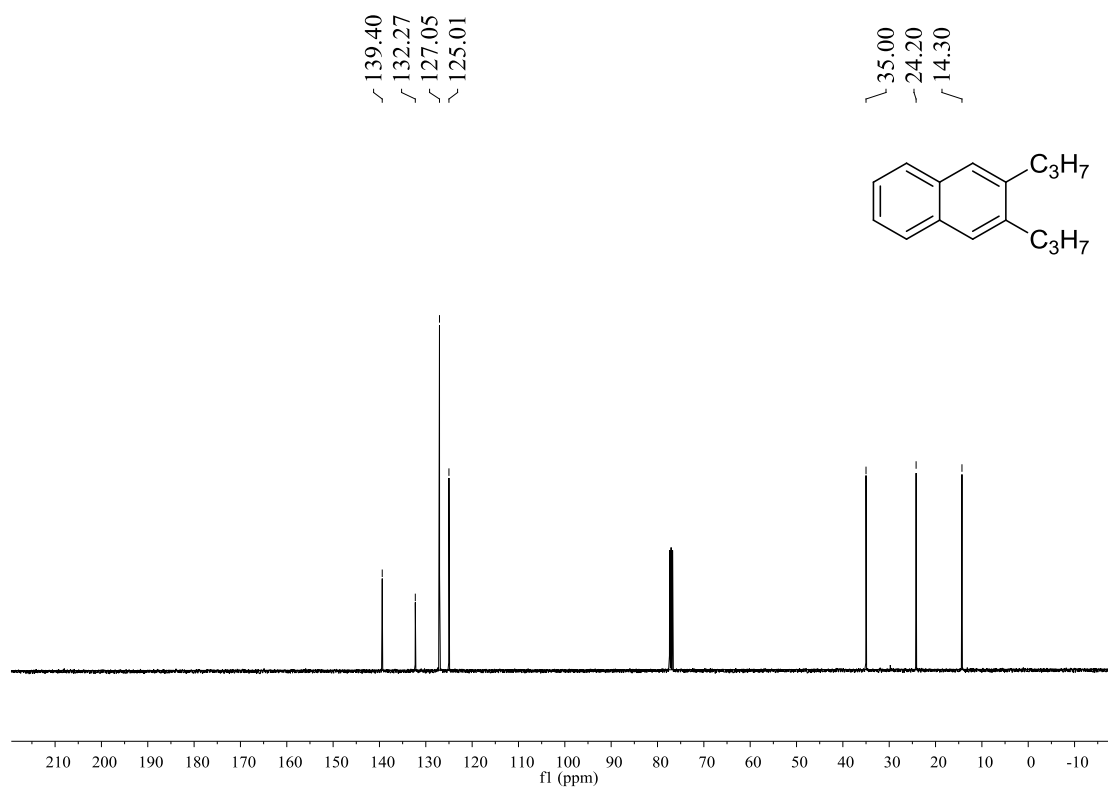
2-Methyl-3-phenylnaphthalene(3n) ^{13}C NMR (100 MHz, CDCl_3)



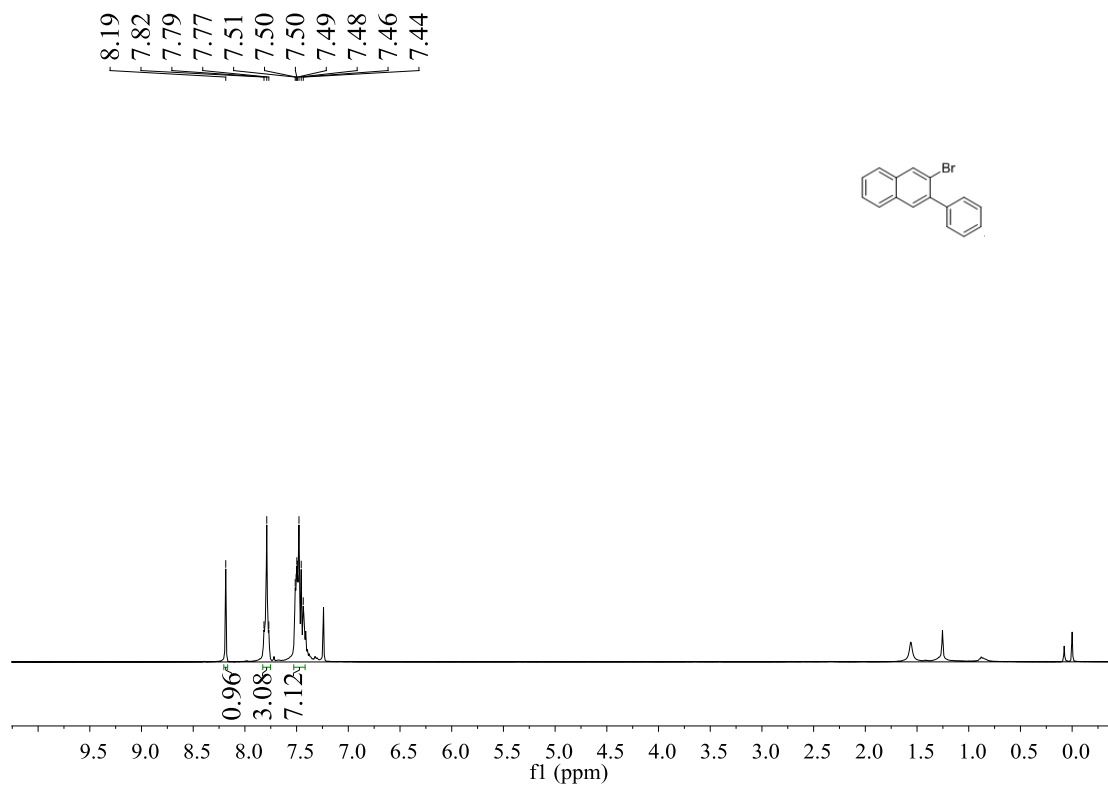
2,3-Dipropylnaphthalene(3o) ^1H NMR (400 MHz, CDCl_3)



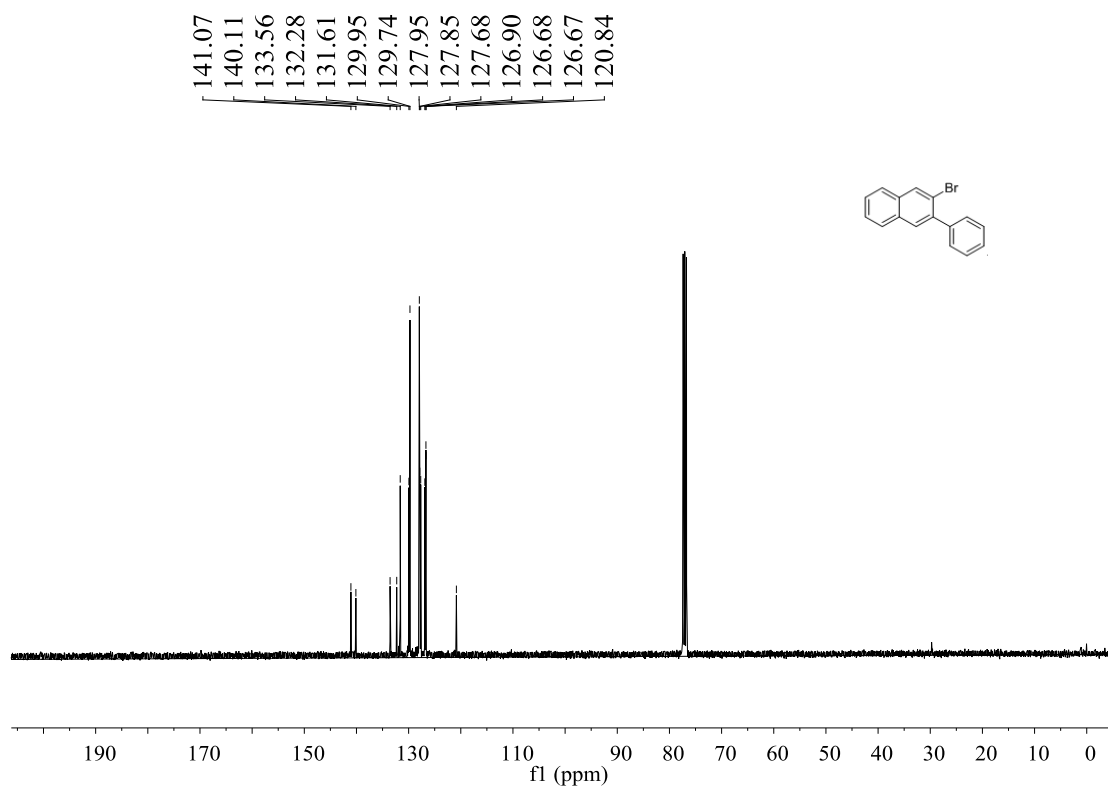
2,3-Dipropylnaphthalene(3o) ^{13}C NMR (100 MHz, CDCl_3)



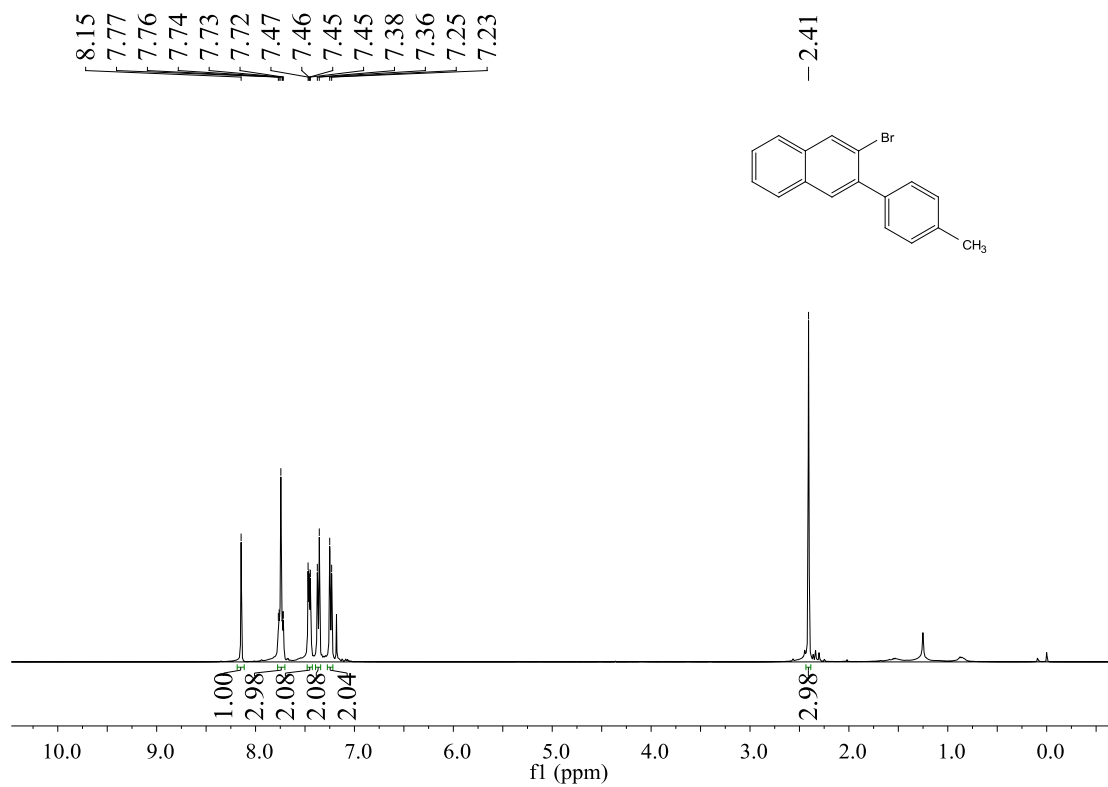
2-Bromo-3-phenylnaphthalene(3p) ^1H NMR (400 MHz, CDCl_3)



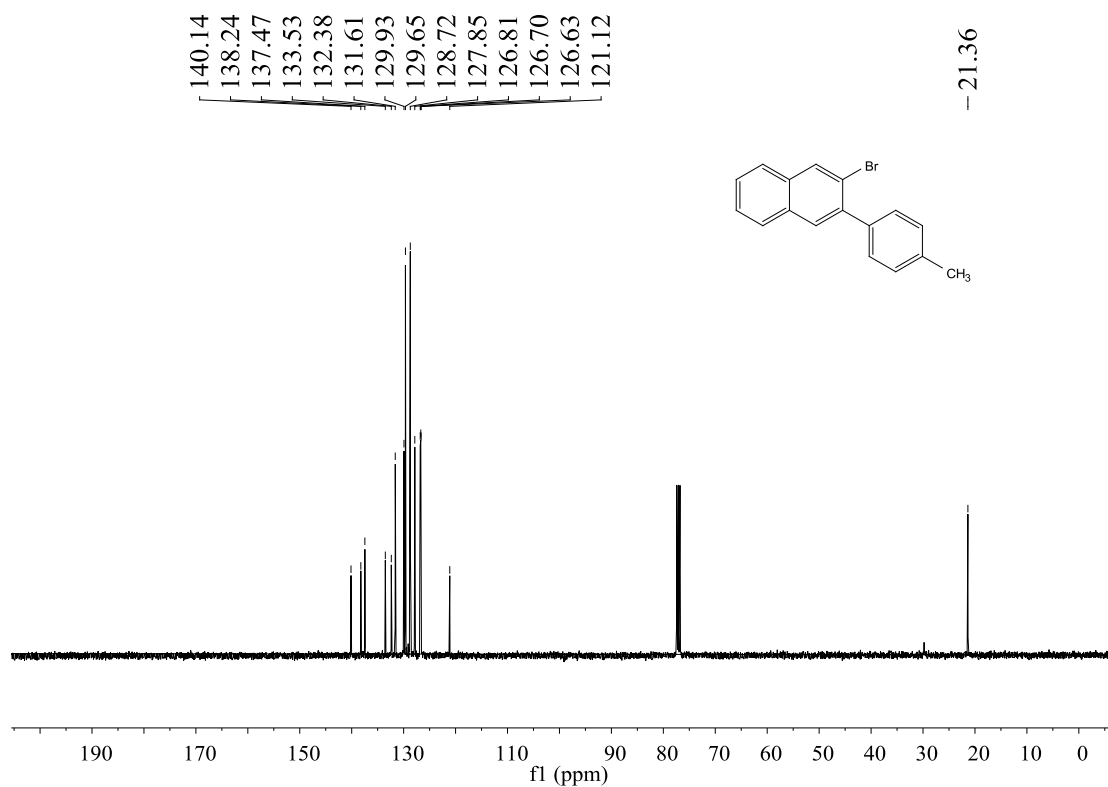
2-Bromo-3-phenylnaphthalene(3p) ^{13}C NMR (100 MHz, CDCl_3)



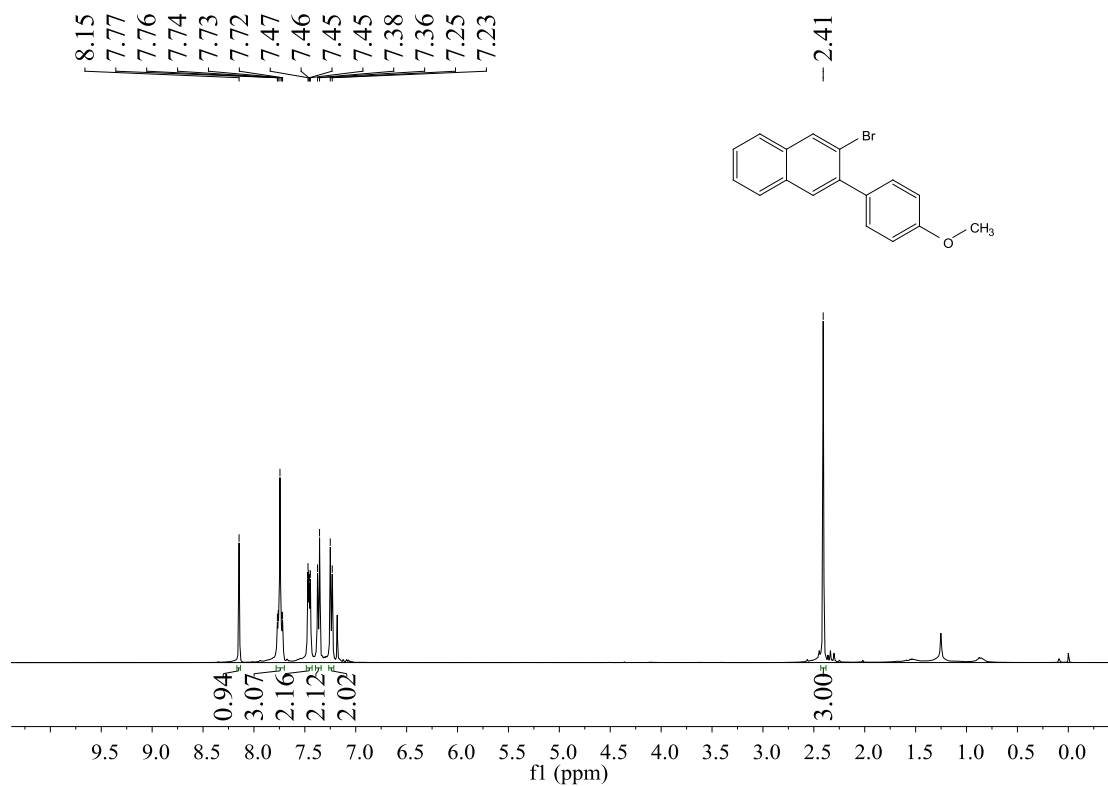
2-Bromo-3-(p-tolyl)naphthalene(3q) ^1H NMR (400 MHz, CDCl_3)



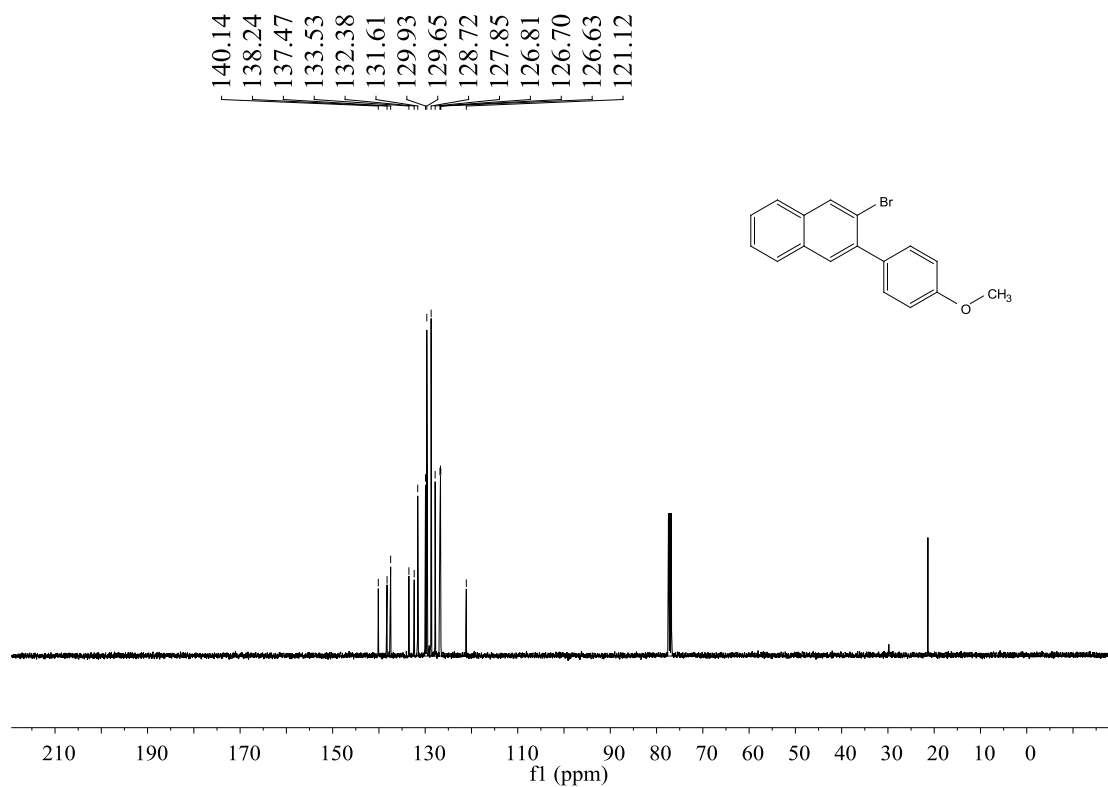
2-Bromo-3-(p-tolyl)naphthalene(3q) ^{13}C NMR (100 MHz, CDCl_3)



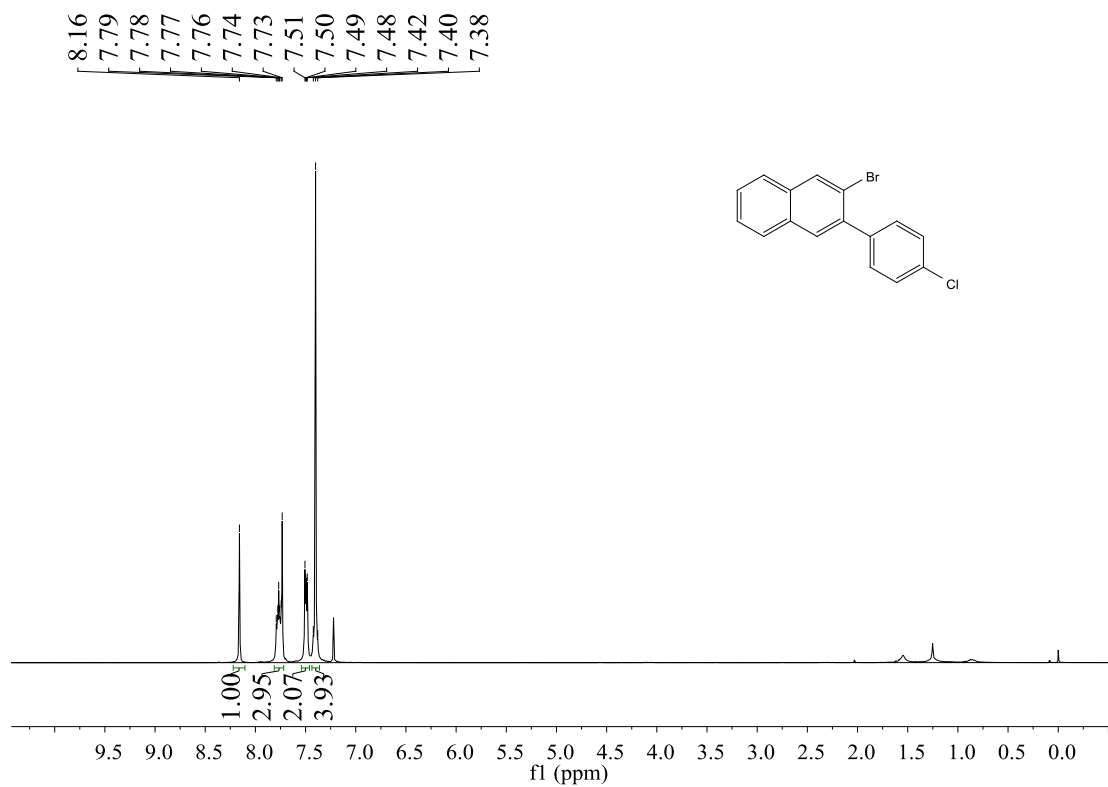
2-Bromo-3-(4-methoxyphenyl)naphthalene(3r) ^1H NMR (400 MHz, CDCl_3)



2-Bromo-3-(4-methoxyphenyl)naphthalene(3r) ^{13}C NMR (100 MHz, CDCl_3)

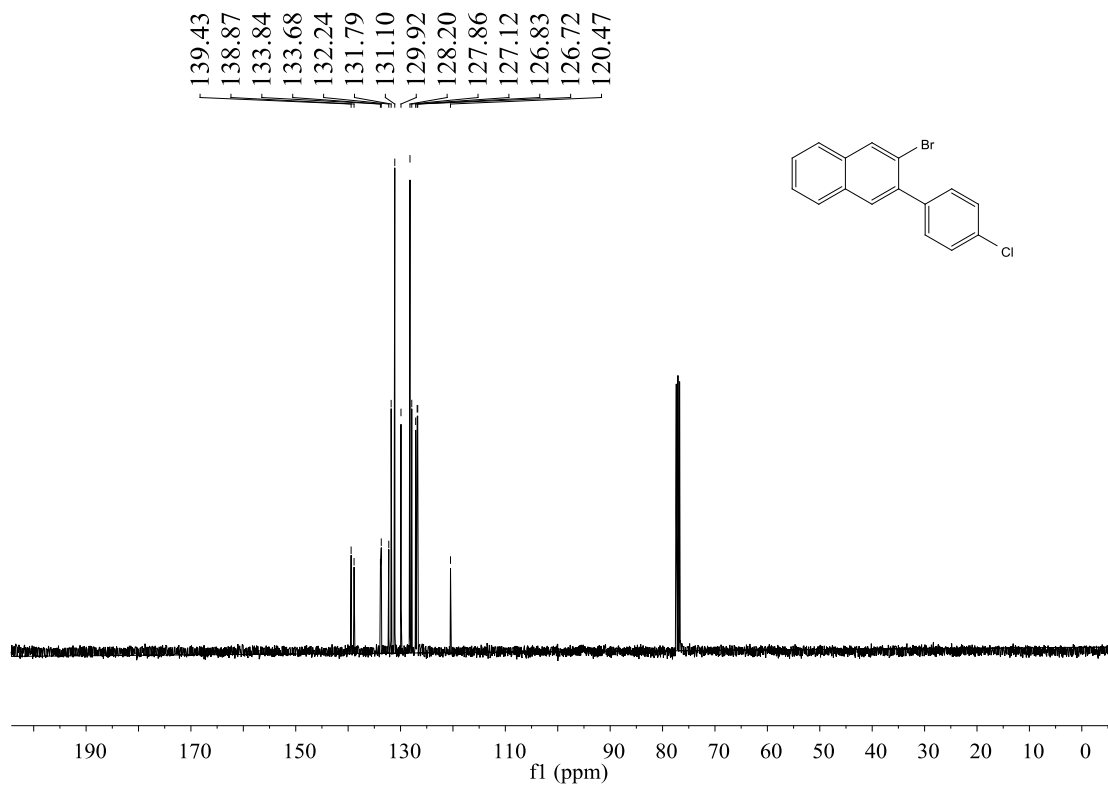


2-Bromo-3-(4-chlorophenyl)naphthalene(3s) ¹H NMR (400 MHz, CDCl₃)

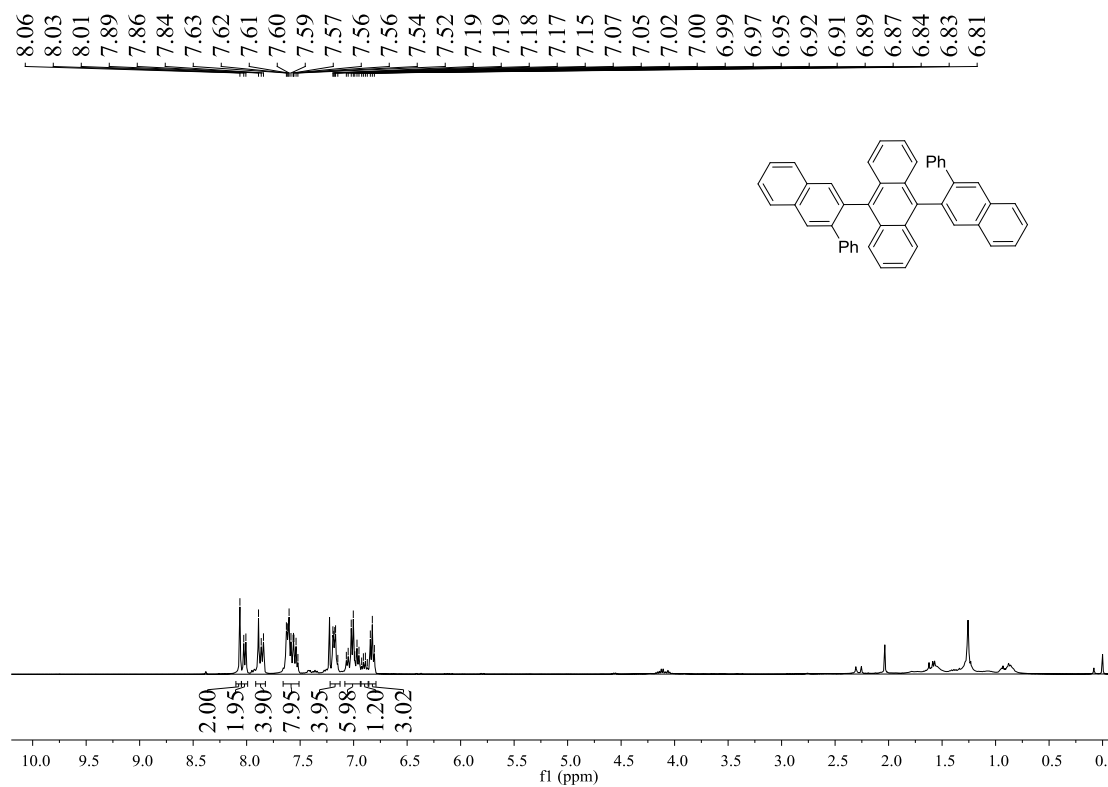


2-Bromo-3-(4-chlorophenyl)naphthalene(3s) ¹³C NMR (100 MHz, CDCl₃)

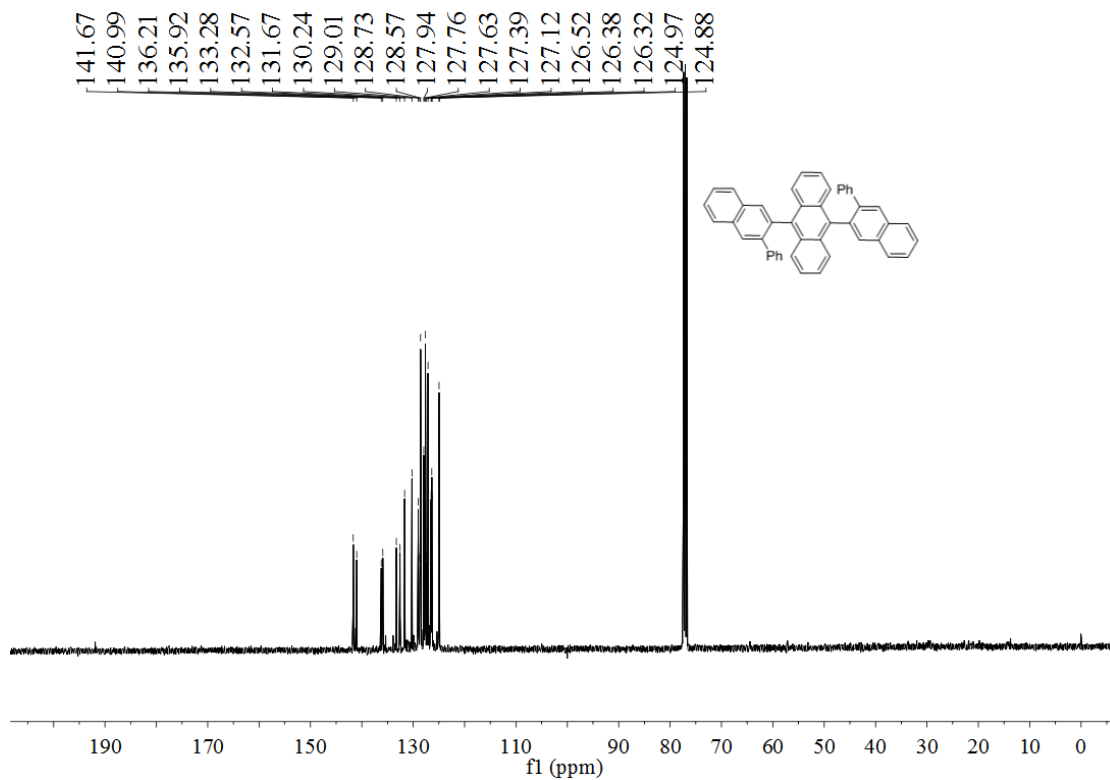
S31



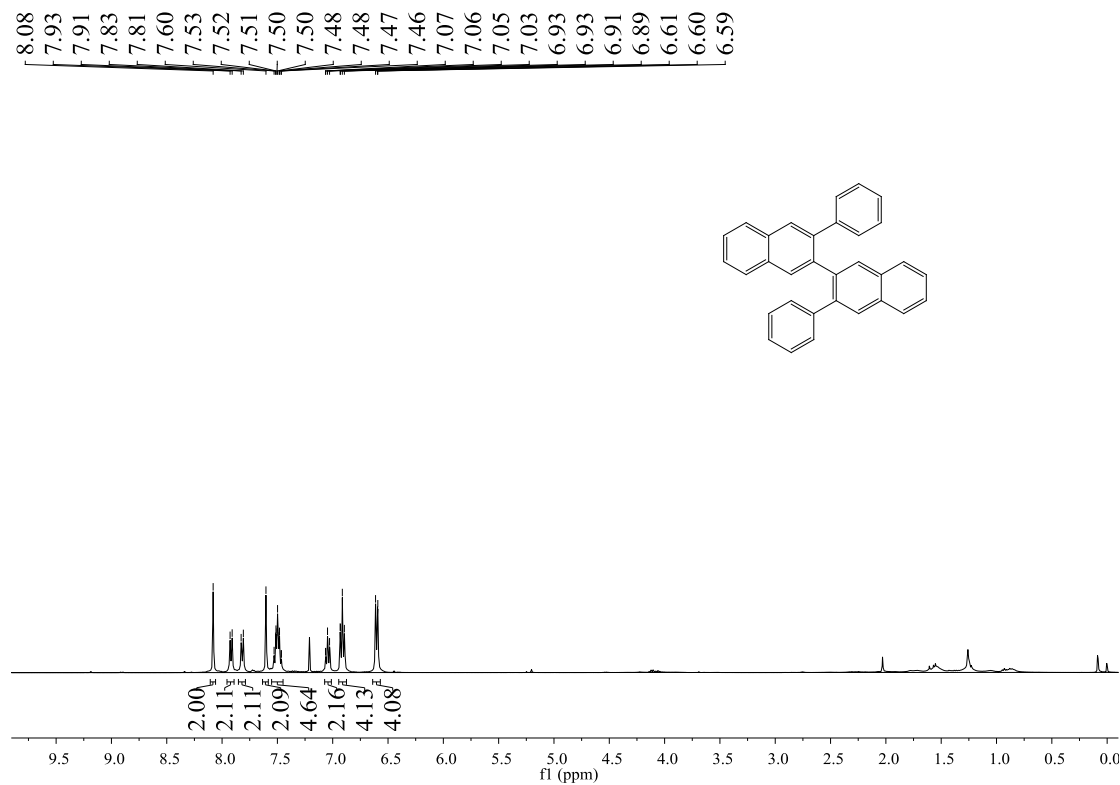
9,10-Bis(3-phenylnaphthalen-2-yl)anthracene(3u) ¹H NMR (400 MHz, CDCl₃)



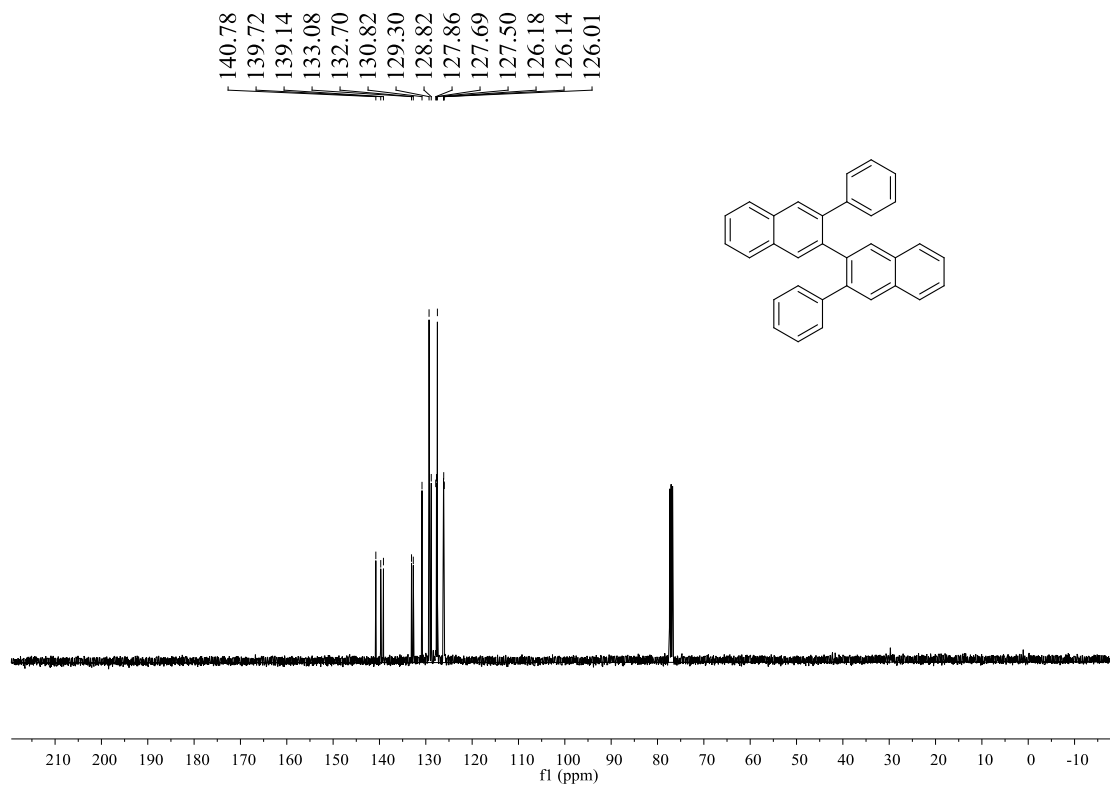
9,10-Bis(3-phenylnaphthalen-2-yl)anthracene(3u) ¹³C NMR (100 MHz, CDCl₃)



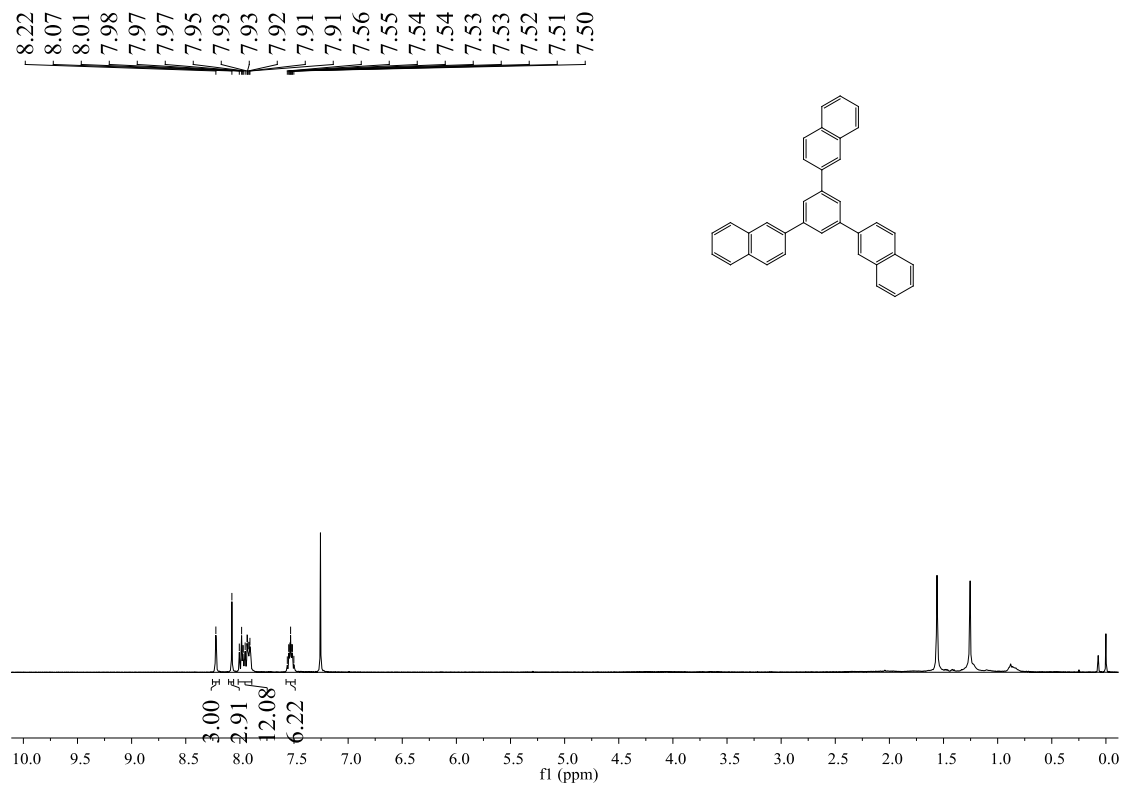
3,3'-Diphenyl-2,2'-binaphthalene(3v) ¹H NMR (400 MHz, CDCl₃)



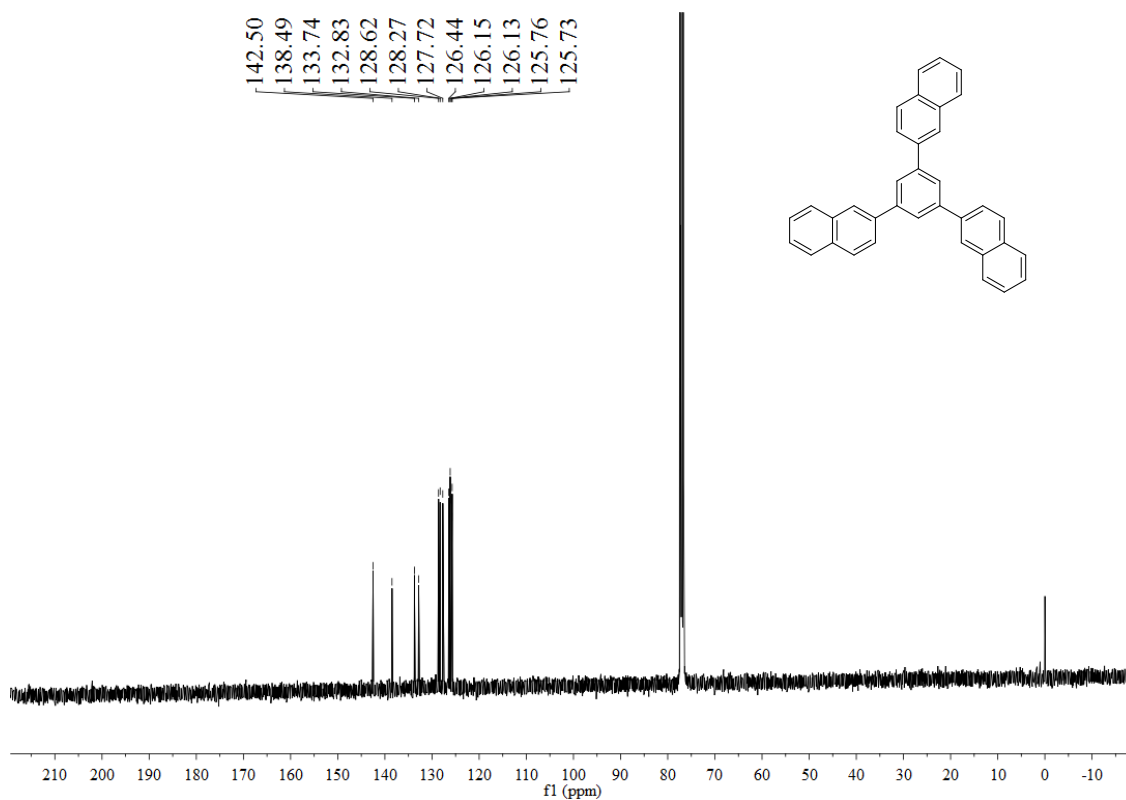
3,3'-Diphenyl-2,2'-binaphthalene(3v) ¹³C NMR (100 MHz, CDCl₃)



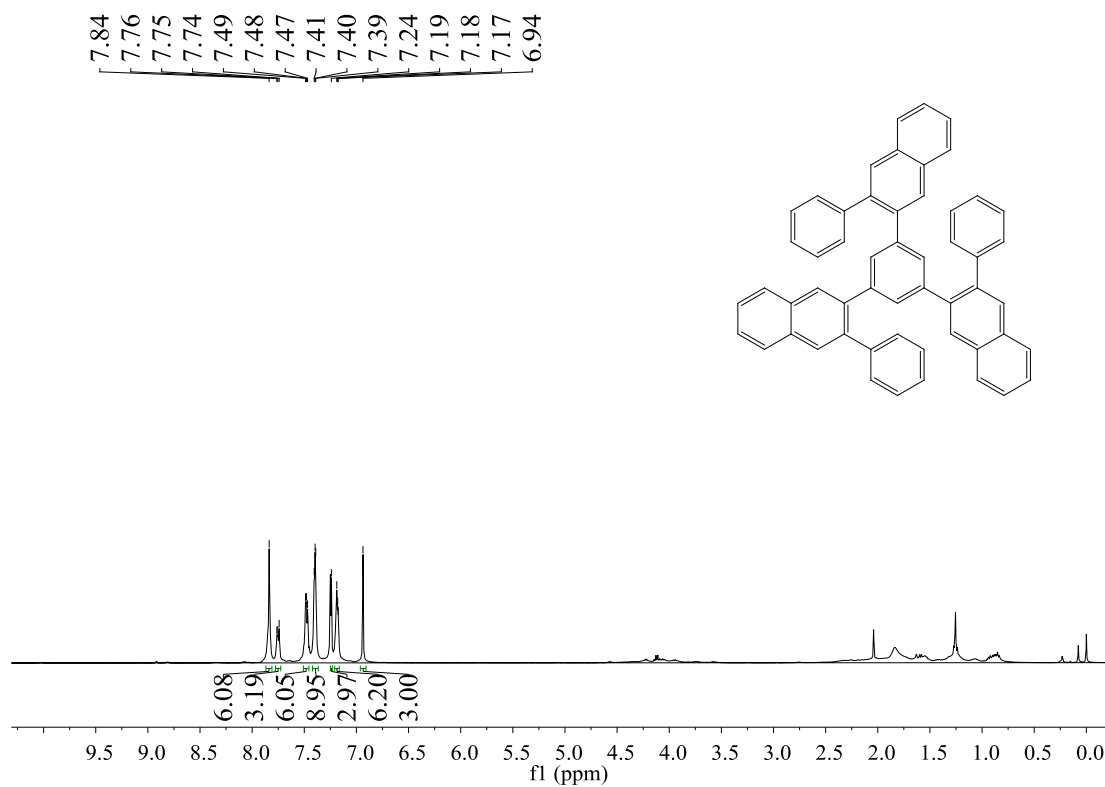
1,3,5-Tri(naphthalen-2-yl)benzene(3w) ^1H NMR (400 MHz, CDCl_3)



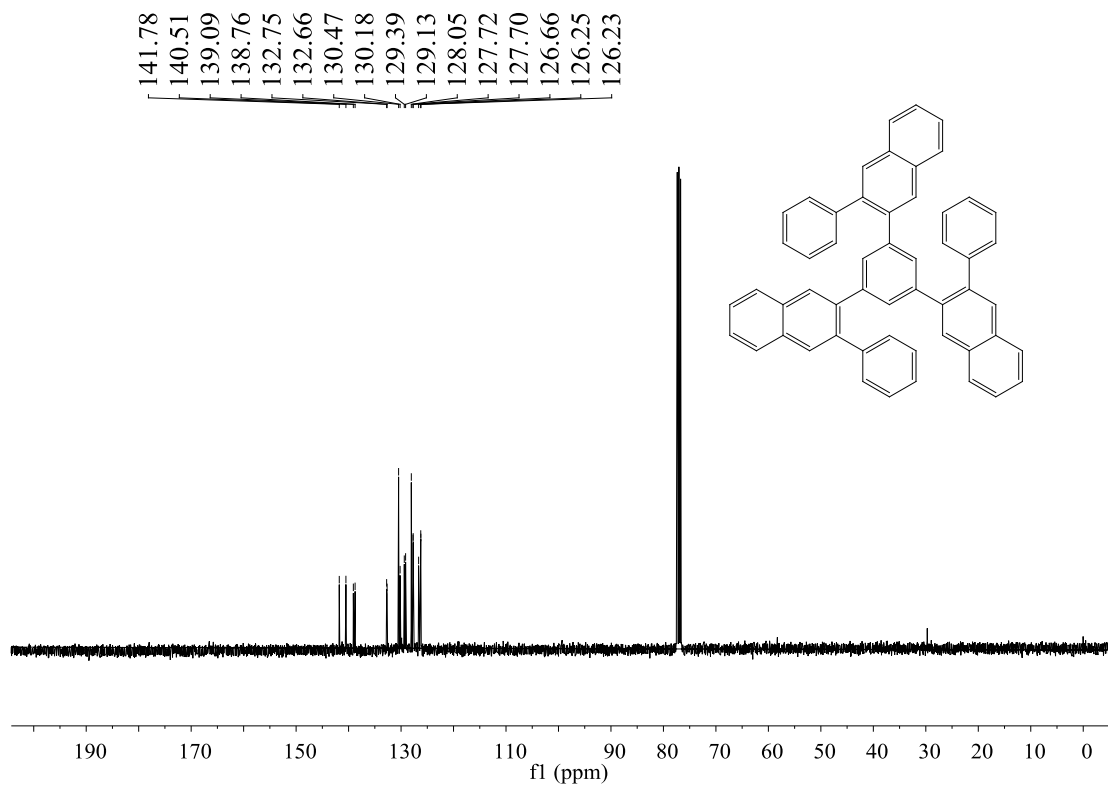
1,3,5-Tri(naphthalen-2-yl)benzene(3w) ¹³C NMR (100 MHz, CDCl₃)



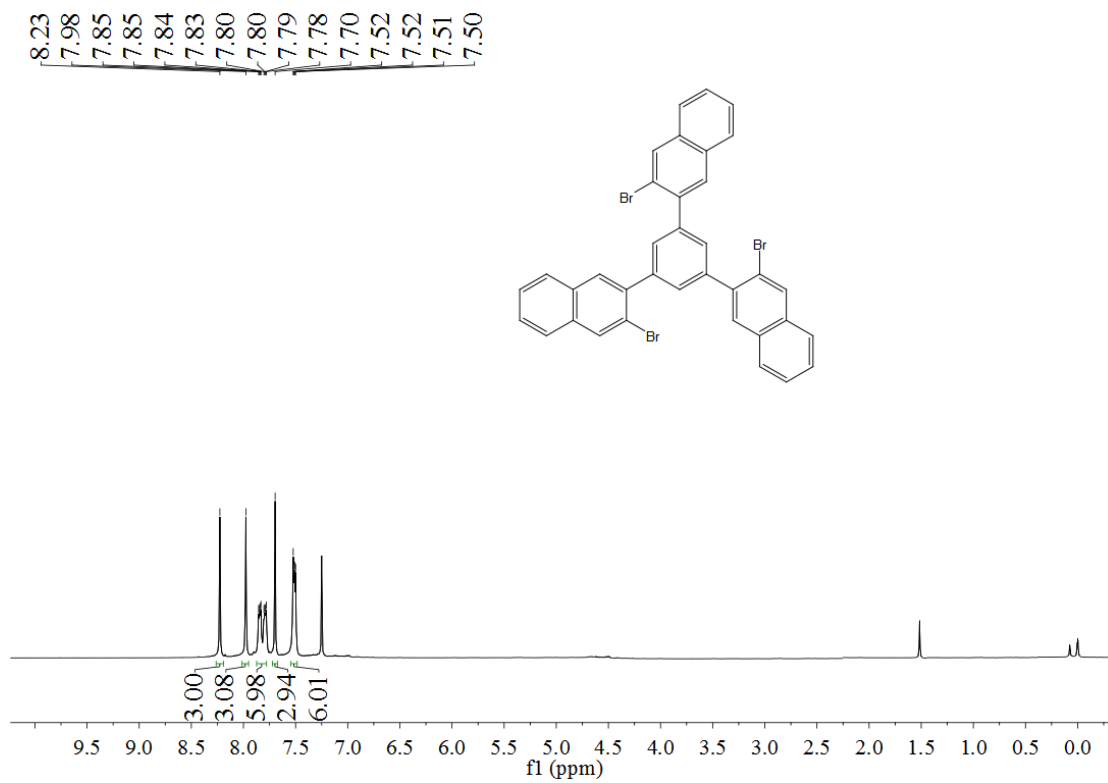
1,3,5-Tri(naphthalen-2-yl)benzene(3x) ¹H NMR (400 MHz, CDCl₃)



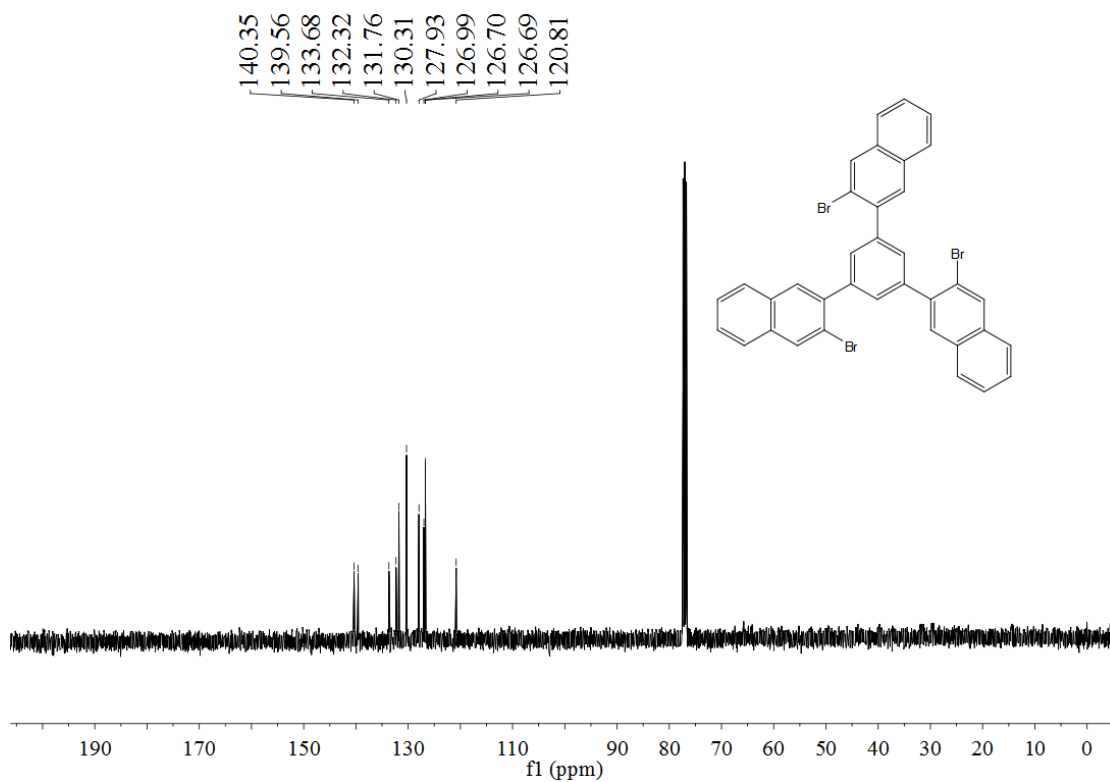
1,3,5-Tri(naphthalen-2-yl)benzene(3x) ^{13}C NMR (100 MHz, CDCl_3)



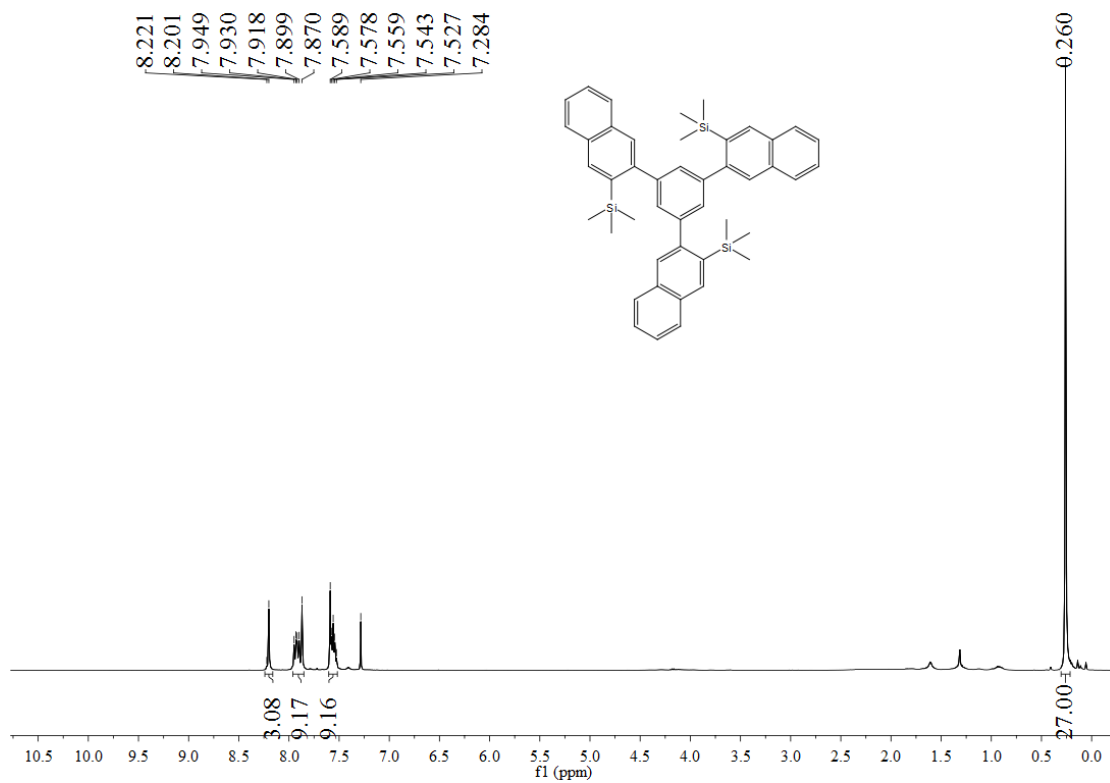
1,3,5-Tris(3-bromonaphthalen-2-yl)benzene(3y) ^1H NMR (400 MHz, CDCl_3)



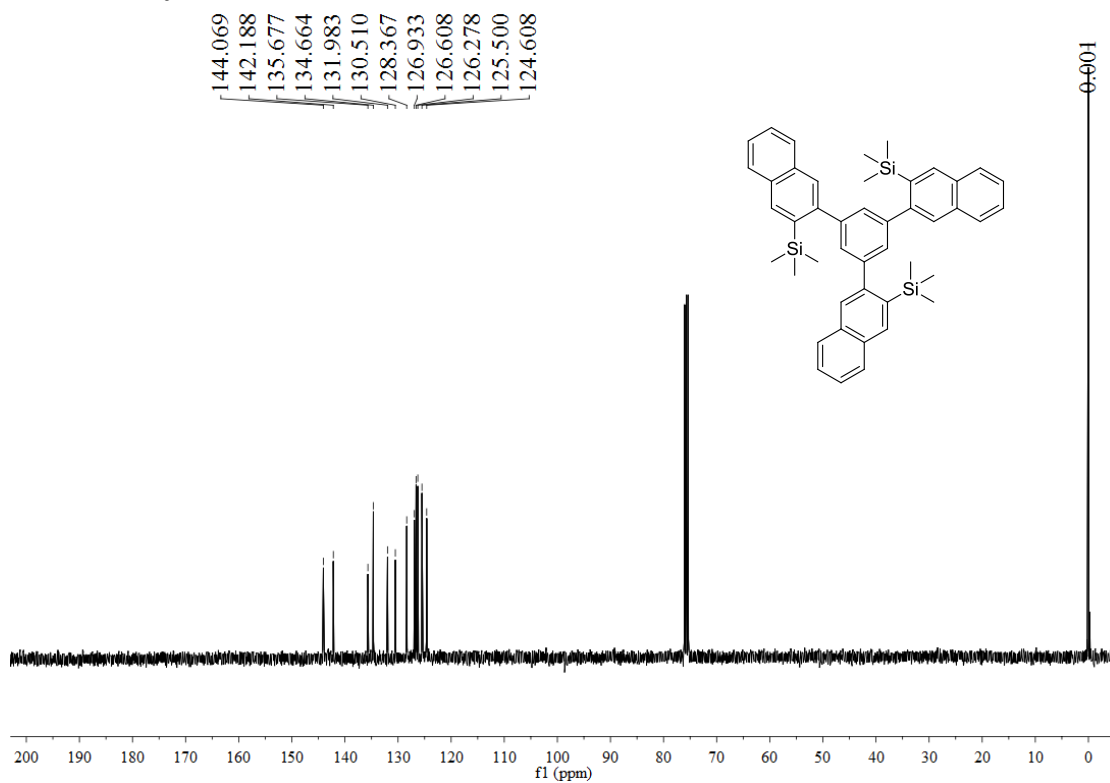
1,3,5-Tris(3-bromonaphthalen-2-yl)benzene(3y) ^{13}C NMR (100 MHz, CDCl_3)



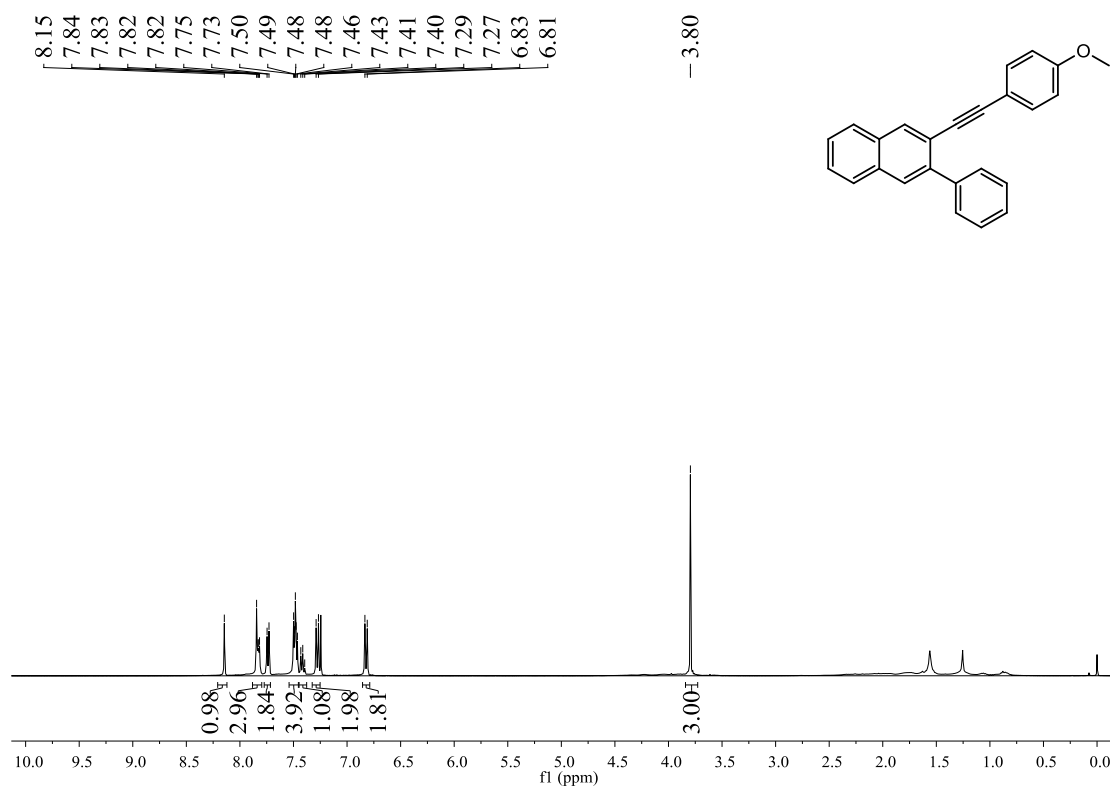
((5-(1-(Trimethylsilyl)naphthalen-2-yl)-1,3-phenylene)bis(naphthalene-3,2-diyl))bis(trimethylsilane)(3z) ^1H NMR (400 MHz, CDCl_3)



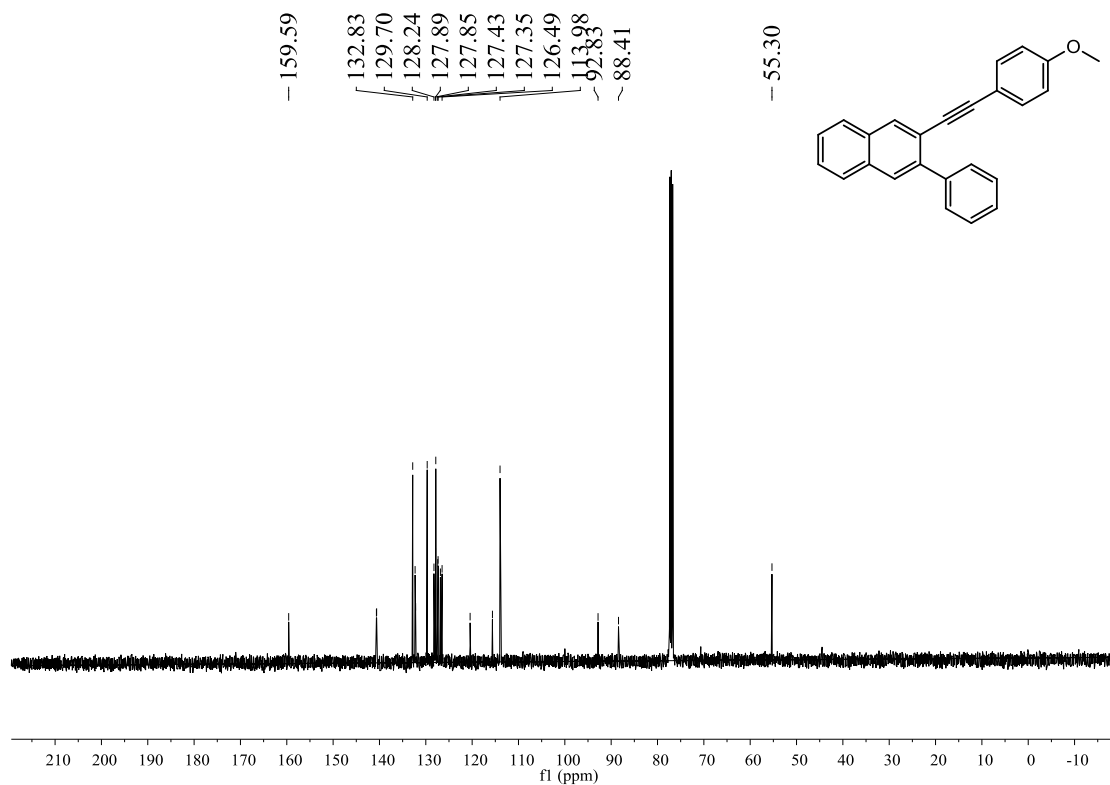
**((5-(1-(Trimethylsilyl)naphthalen-2-yl)-1,3-phenylene)bis(naphthalene-3,2-diyl))
bis(trimethylsilane)(3z) ¹³C NMR (100 MHz, CDCl₃)**



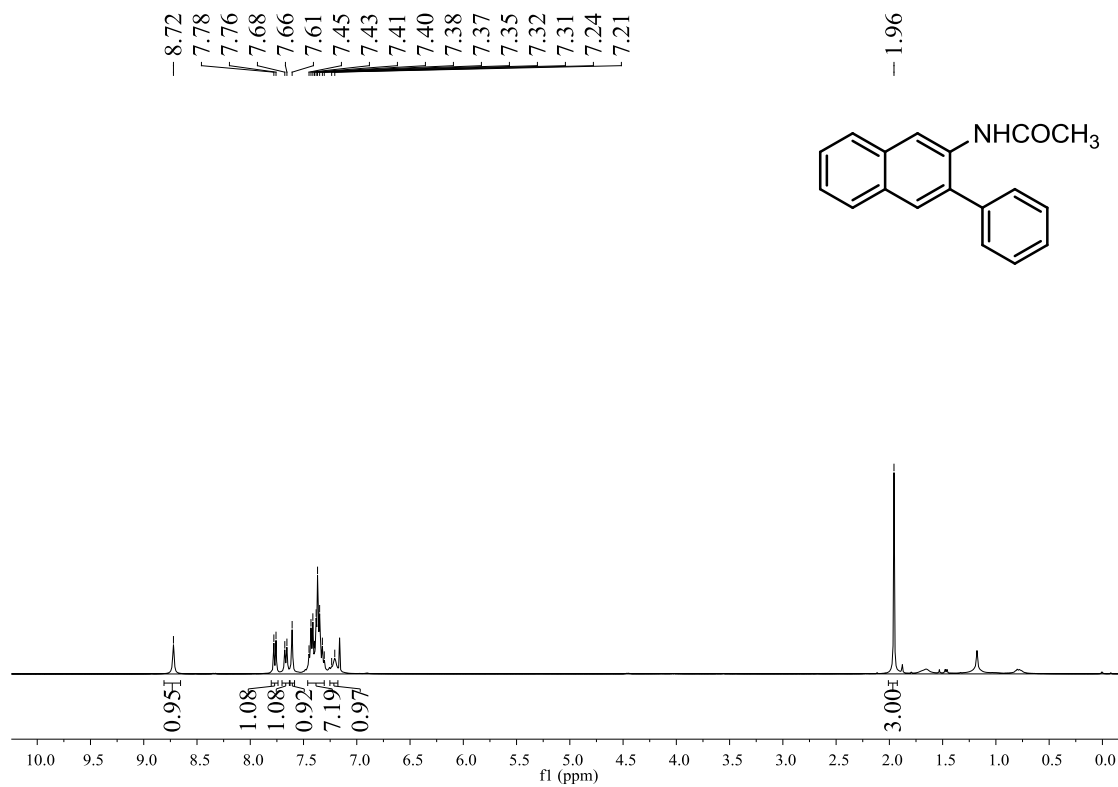
2-((4-methoxyphenyl)ethynyl)-3-phenylnaphthalene(4) ¹H NMR (400 MHz, CDCl₃)



2-((4-methoxyphenyl)ethynyl)-3-phenylnaphthalene(4) ^{13}C NMR (100 MHz, CDCl_3)



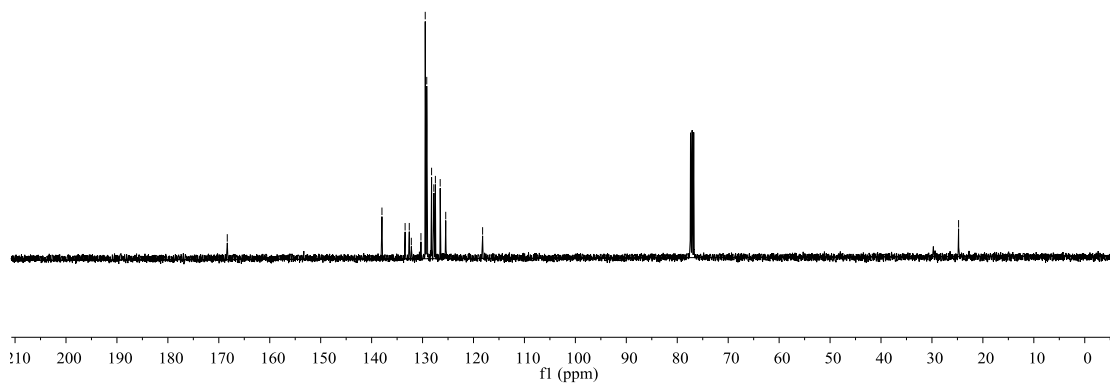
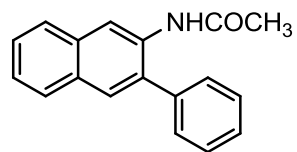
N-(3-phenylnaphthalen-2-yl)acetamide(5) ^1H NMR (400 MHz, CDCl_3)



N-(3-phenylnaphthalen-2-yl)acetamide(5) ^{13}C NMR (100 MHz, CDCl_3)

168.34
137.97
133.43
132.61
132.21
130.32
129.48
129.18
128.23
127.79
127.48
126.54
125.45
118.21

24.77



5. References.

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