

Supporting Information

Synthesis of 2-phenylnaphthalenes from styrene oxides using recyclable bronsted acidic [HNMP]⁺HSO₄⁻ ionic liquid

Kishor V. Wagh and Bhalchandra M. Bhanage*

Department of Chemistry, Institute of Chemical Technology, N.
Parekh Marg, Matunga, Mumbai 400019, India.

Tel.: +91-22-3361 2601; fax: +91-22-3361 1020; E-mail: bhalchandra_bhanage@yahoo.com,
bm.bhanage@gmail.com.

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I. General information:

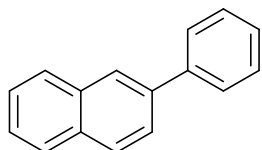
All reagents were purchased from Sigma-Aldrich and Alfa Aesar. Solvents purchased from commercial suppliers and used without further purification. GC equipped flame ionization detector with a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 μm) was carried out for gas chromatography analysis. GC-MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness 0.25 μm df) (column flow 2 mLmin⁻¹, 80 °C to 240 °C at 10°/min rise). Products were purified by flash chromatography on 60-120 mesh silica gels, SiO₂. ¹H and ¹³C NMR spectra were recorded at 400 and 500 MHz (¹H NMR), 100 MHz (¹³C NMR) frequency in CDCl₃. All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All reagents were weighed and handled in air.

II. Typical procedure for the synthesis of 2-phenylnaphthalenes from styrene oxides:

A mixture of 1a (1 mmol), and [HNMP]⁺HSO₄⁻ (4 mmol) was stirred at 100 °C in a sealed 10 mL tube for 8 h. The progress of the reaction was monitored by gas chromatography. After the completion of reaction, it was cooled to room temperature. The reaction mixture was extracted with diethyl ether (3 × 8 mL) and the combined organic layers was washed with water (10 mL). The organic layer was dried over anhydrous Na₂SO₄ and evaporated under the reduced pressure to furnish the crude product. It was purified by column chromatography (silica gel, 60–120 mesh; petroleum ether) to give the corresponding product 2a in 80% yield. The structure of the product was confirmed by GC-MS, ¹H NMR, ¹³C NMR spectroscopic techniques. The purity of the compound was determined by GC-MS analysis.

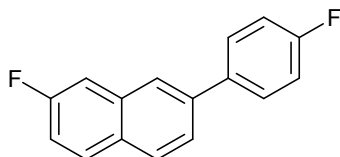
III.Characterization data of compounds:

2-phenylnaphthalene (2a)



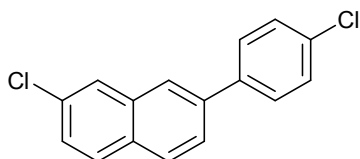
^1H NMR (CDCl_3 , 500 MHz) δ 8.06(s, 1H), 7.94-7.87(m, 3H), 7.77-7.73(m, 3H), 7.53-7.48(m, 4H), 7.41-7.38(t, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 141.13, 138.56, 133.67, 132.61, 128.84, 128.39, 128.18, 127.62, 127.41, 127.33, 126.26, 125.91, 125.79, 125.58. GC-MS (EI) m/z (%) = 204 (100.0) $[\text{M}]^+$, 205 (M+1, 16.4), 202 (35.4), 102 (10.3), 89 (8.1).

2-fluoro-7-(4-fluorophenyl)naphthalene (2b)



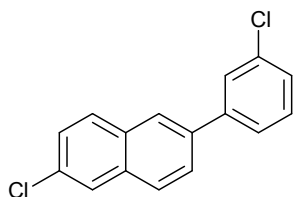
^1H NMR (CDCl_3 , 500 MHz) δ 7.92-7.90(m, 2H), 7.87-7.84(dd, 1H), 7.69-7.64(m, 3H), 7.51-7.49(d, 1H), 7.29-7.25(m, 1H), 7.19-7.17(t, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) 163.63, (d, $^1J_{\text{CF}} = 206$ Hz), 161.67, 138.64, 136.89, 136.86, 134.45, 134.48, 130.07, 130.00, 129.50, 129.02, 128.95, 128.47, 124.97, 124.93, 124.72, 116.35 (d, $^2J_{\text{CF}} = 25$ Hz), 115.77 (d, $^2J_{\text{CF}} = 21$ Hz), 111.07 (d, $^2J_{\text{CF}} = 20$ Hz). GC-MS (EI) m/z (%) = 240 (100.0) $[\text{M}]^+$, 241 (M+1, 17.3), 238 (30.5), 220 (6.2), 207 (1.7), 120 (10.5), 110 (6.7), 57 (3.0).

2-chloro-7-(4-chlorophenyl)naphthalene (2c)



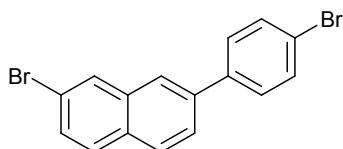
^1H NMR (CDCl_3 , 400 MHz) δ 7.89-7.86(m, 3H), 7.79-7.77(d, 1H), 7.68-7.66(d, 1H), 7.62-7.60(d, 2H), 7.43-7.40(m, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) 139.04, 138.39, 134.20, 133.78, 132.18, 130.82, 129.23, 129.06, 128.61, 128.48, 127.01, 126.79, 125.51, 124.79. GC-MS (EI) m/z (%) = 272 (100.0) $[\text{M}]^+$, 273 (M+1, 17.4), 274 (M+2, 66.5), 236 (10.8), 202 (51.1), 136 (10.7), 118 (11.0), 100 (26.5), 88 (6.5).

2-chloro-6-(3-chlorophenyl)naphthalene (2d)



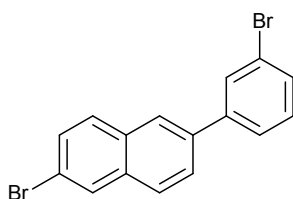
^1H NMR (CDCl_3 , 400 MHz) δ 8.00(s, 1H), 7.86-7.83(m, 3H), 7.74-7.69(m, 2H), 7.59-7.57(d, 1H), 7.43-7.37(m, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) 142.51, 137.44, 134.82, 133.36, 131.97, 131.79, 130.12, 129.78, 129.02, 127.78, 127.54, 127.46, 127.42, 126.40, 126.30, 125.85, 125.47. GC-MS (EI) m/z (%) = 272 (100.0) $[\text{M}]^+$, 273 (M+1, 17.0), 274 (M+2, 65.7), 236 (9.6), 202 (50.9), 136 (9.0), 118 (9.6), 100 (23.7), 87 (6.8), 75 (6.5).

2-bromo-7-(4-bromophenyl)naphthalene (2e)



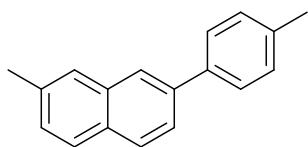
^1H NMR (CDCl_3 , 400 MHz) δ 8.04 (s, 1H), 7.83-7.81(d, 2H), 7.73-7.67(m, 2H), 7.61-7.59(d, 2H), 7.56-7.53(m, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) 139.48, 138.37, 134.66, 132.02, 131.82, 130.11, 129.50, 129.31, 128.95, 128.57, 127.97, 125.59, 124.69, 121.98, 120.46. GC-MS (EI) m/z (%) = 360 (9.3) $[\text{M}]^+$, 361 (M+1, 100.0), 362 (M+2, 16.4), 359 (51.4), 202 (62.5), 180 (9.7), 150 (3.5), 101 (45.9), 88 (15.7).

2-bromo-6-(3-bromophenyl)naphthalene (2f)



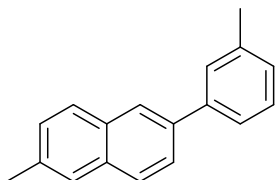
^1H NMR (CDCl_3 , 400 MHz) δ 8.04 (s, 1H), 7.97(s, 1H), 7.83-7.79(m, 2H), 7.75-7.73(d, 1H), 7.70-7.68(dd, 1H), 7.61-7.55(m, 2H), 7.51-7.49(d, 1H), 7.38-7.31(dd, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) 142.74, 137.43, 133.77, 131.93, 130.47, 130.40, 130.34, 129.87, 129.85, 129.70, 127.70, 126.25, 125.93, 125.90, 123.03, 120.19. GC-MS (EI) m/z (%) = 360 (51.9) $[\text{M}]^+$, 361 (M+1, 9.6), 362 (M+2, 100.0), 202 (67.3), 181 (9.7), 150 (4.8), 101 (51.9), 88 (16.7).

2-methyl-7-(p-tolyl)naphthalene (2g)



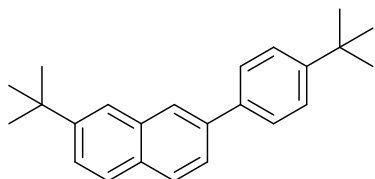
^1H NMR (CDCl_3 , 400 MHz) δ 7.94 (s, 1H), 7.86-7.85(d, 1H), 7.77-7.75(d, 1H), 7.68-7.66(m, 2H), 7.63-7.62(d, 2H), 7.32-7.29(m, 3H), 2.54(s, 3H), 2.43(s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) 138.48, 138.38, 137.03, 135.83, 133.93, 130.74, 129.52, 128.05, 128.02, 127.39, 127.20, 127.06, 124.80, 124.65, 21.74, 21.11. GC-MS (EI) m/z (%) = 232 (100.0) $[\text{M}]^+$, 233 (M+1, 19.6) , 215 (23.4), 202 (10.7), 189 (3.7), 115 (12.2), 101 (7.5), 89(3.5).

2-methyl-6-(m-tolyl)naphthalene (2h)



^1H NMR (CDCl_3 , 500 MHz) δ 7.99 (s, 1H), 7.83-7.79(t, 2H), 7.72-7.70(d, 1H), 7.64(s, 1H), 7.54-7.52(d, 2H), 7.39-7.33(m, 2H), 7.20-7.19(d, 1H), 2.54(s, 1H), 2.46(s, 1H). ^{13}C NMR (CDCl_3 , 100 MHz) 141.22, 138.37, 137.77, 135.52, 132.80, 131.90, 128.70, 128.50, 128.11, 127.97, 127.92, 127.64, 126.57, 125.65, 125.48, 124.43, 21.73, 21.57. GC-MS (EI) m/z (%) = 232 (100.0) $[\text{M}]^+$, 233 (M+1, 19.7) , 215 (23.7), 202 (11.1), 189 (4.2), 141 (4.1), 115 (13.6), 101 (7.0).

2-(tert-butyl)-7-(4-(tert-butyl)phenyl)naphthalene (2i)



^1H NMR (CDCl_3 , 500 MHz) δ 8.02 (s, 1H), 7.86-7.80(m, 3H), 7.71-7.67(m, 3H), 7.58-7.56(d, 1H), 7.52-7.51(d, 2H), 7.44(s, 9H), 1.39(s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) 150.23, 148.90, 138.36, 138.28, 133.64, 130.72, 127.73, 127.25, 126.97, 125.75, 125.55, 124.94, 124.74, 123.10, 34.87, 34.55, 31.38, 31.24. GC-MS (EI) m/z (%) = 316 (40.4) $[\text{M}]^+$, 317 (M+1, 16.8) , 302 (26.2), 301 (100.0), 281 (12.2), 207 (25.3), 143 (22.0), 229 (15.2), 115 (37.3), 91 (10.9), 77 (14.8).

***N*-methyl-2-pyrrolidone hydrogen sulfate [HNMP]⁺[HSO₄]⁻ ionic liquid (fresh)**

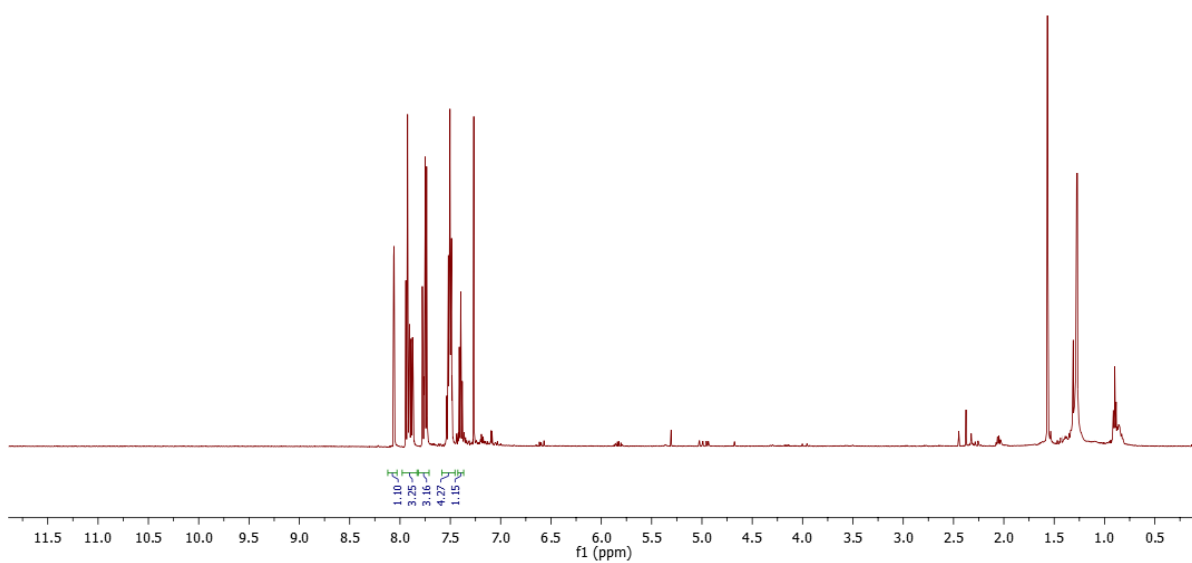
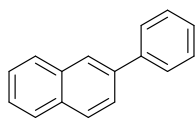
¹H NMR (D₂O, 400 MHz) δ 4.67 (bs, 1H), 3.24-3.20(t, 2H), 2.54(s, 3H), 2.17-2.13(d, 1H), 1.77-1.73(m, 2H).

***N*-methyl-2-pyrrolidone hydrogen sulfate [HNMP]⁺[HSO₄]⁻ ionic liquid (5th cycle)**

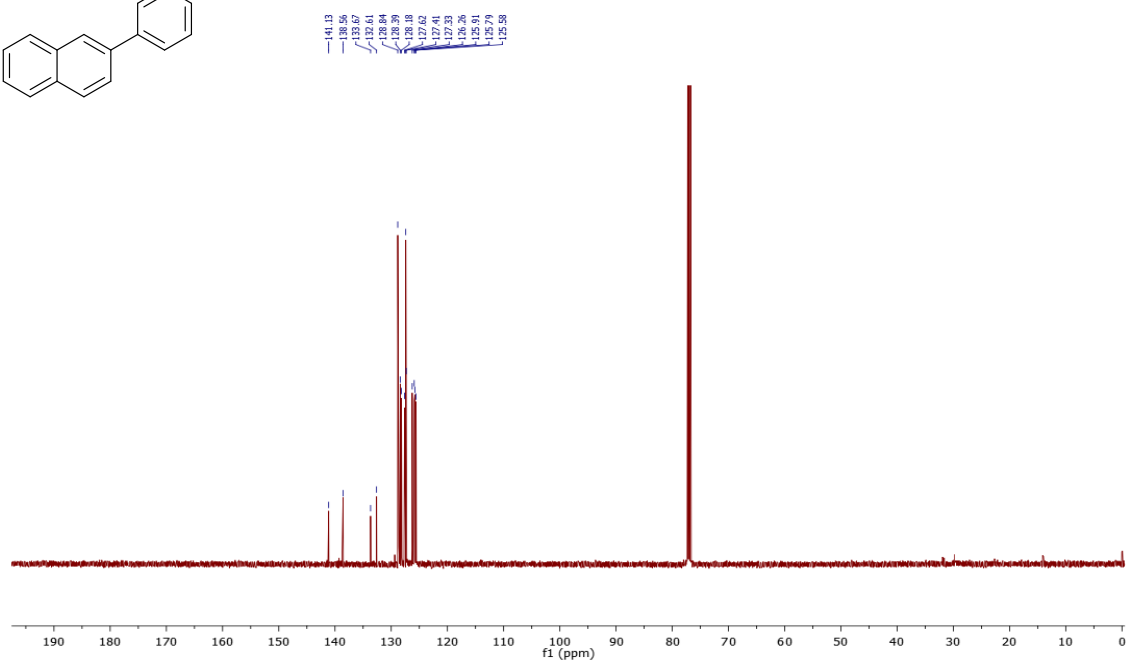
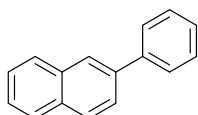
¹H NMR (D₂O, 400 MHz) δ 4.66 (bs, 1H), 3.24-3.21(t, 2H), 2.54(s, 3H), 2.18-2.14(d, 1H), 1.80-1.72(m, 2H).

IV. Copies of ^1H NMR and ^{13}C NMR Spectra:

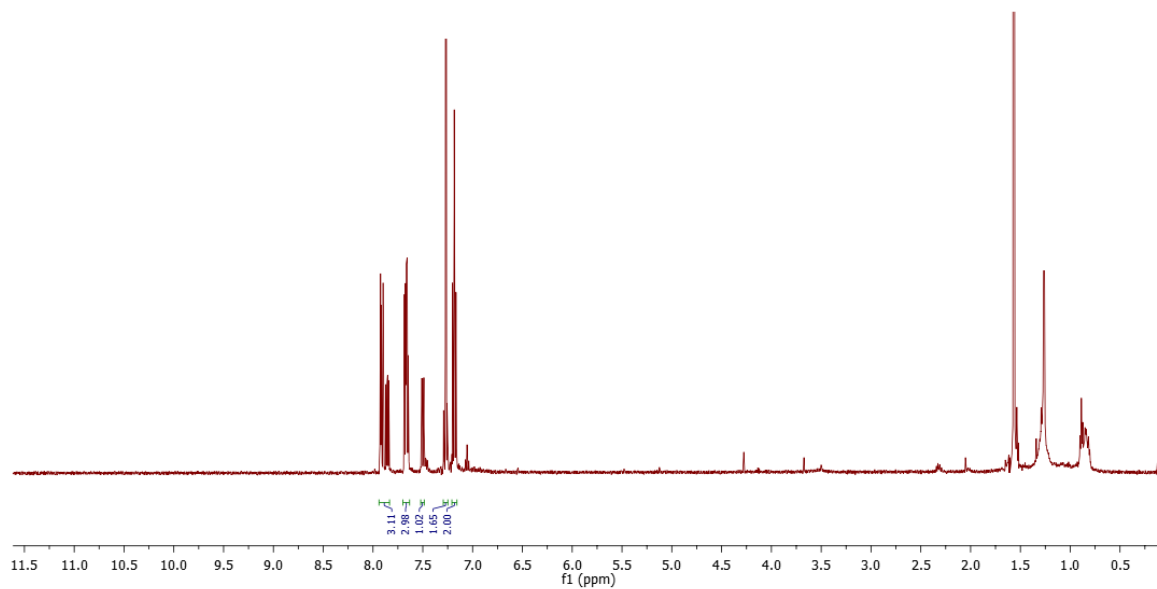
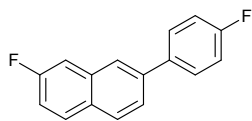
2-phenylnaphthalene (2a) ^1H



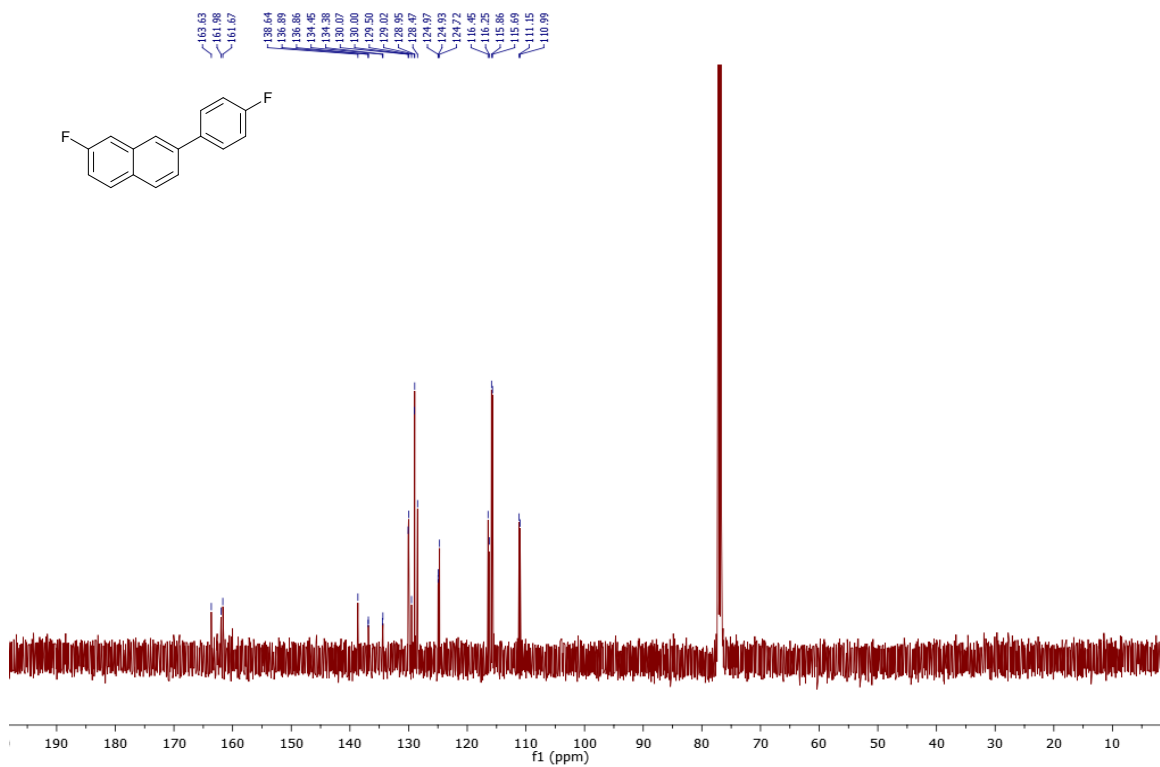
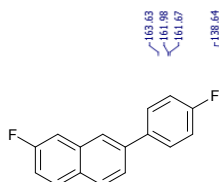
2-phenylnaphthalene (2a) ^{13}C



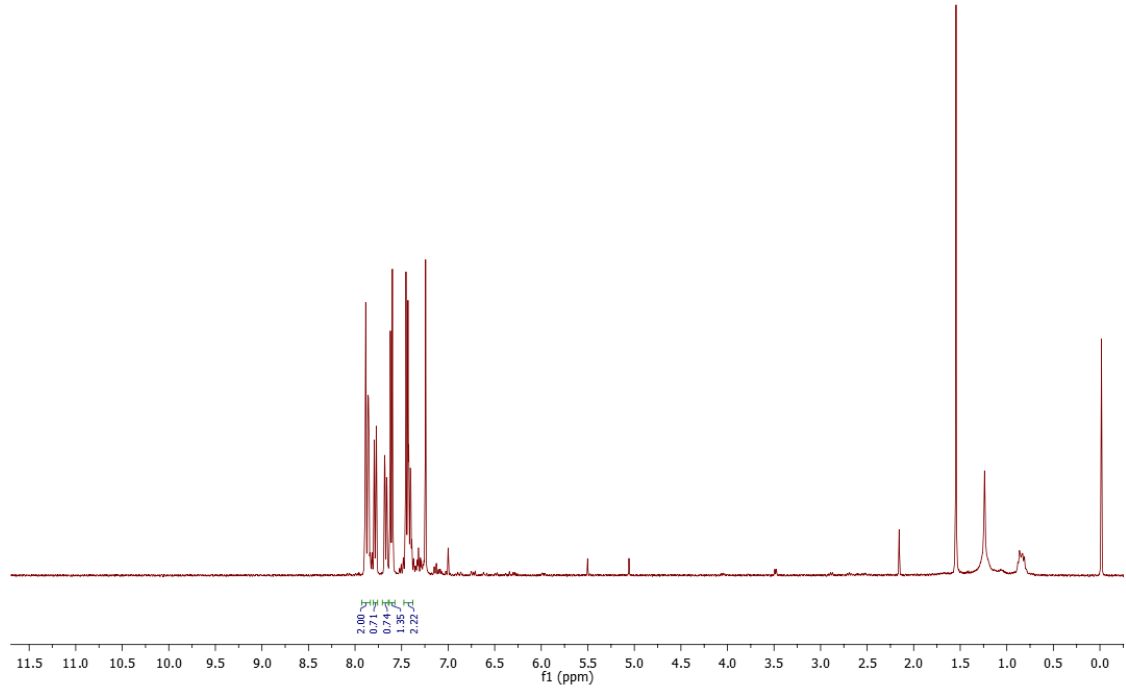
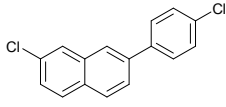
2-fluoro-7-(4-fluorophenyl)naphthalene (2b) ¹H



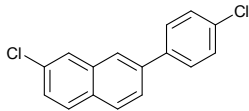
2-fluoro-7-(4-fluorophenyl)naphthalene (2b) ¹³C

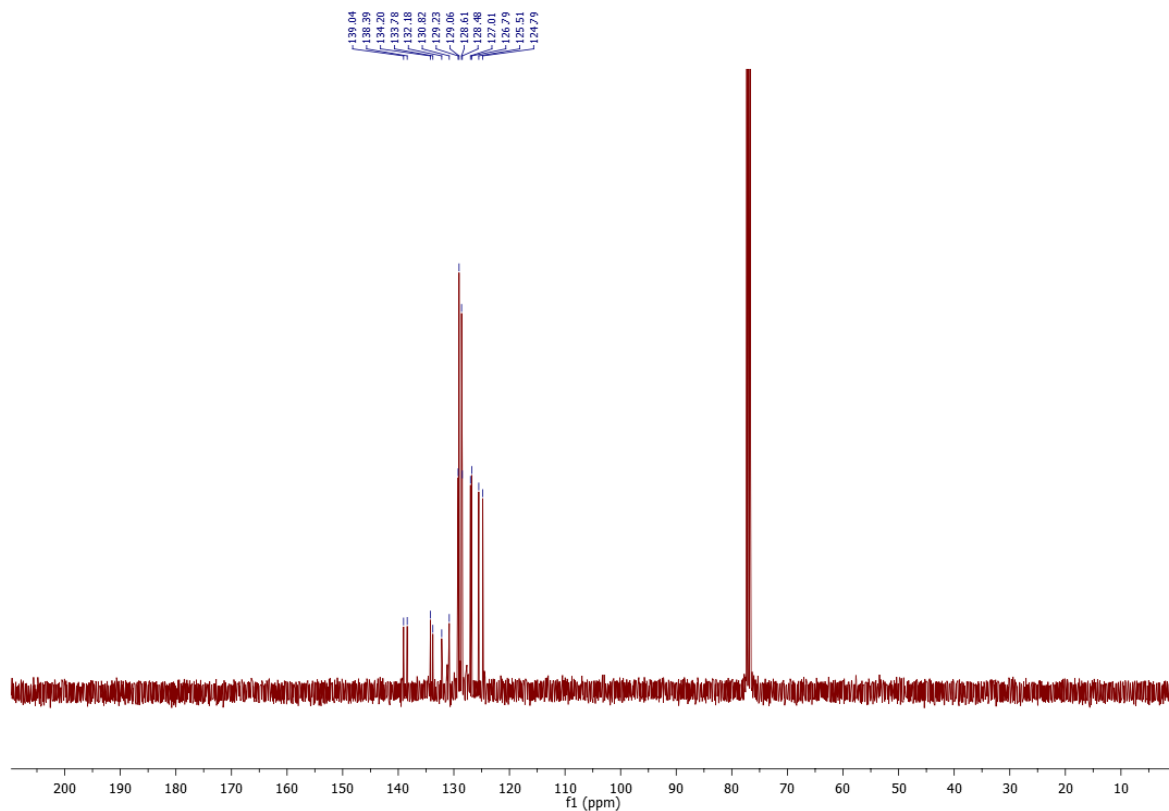


2-chloro-7-(4-chlorophenyl)naphthalene (2c) ¹H

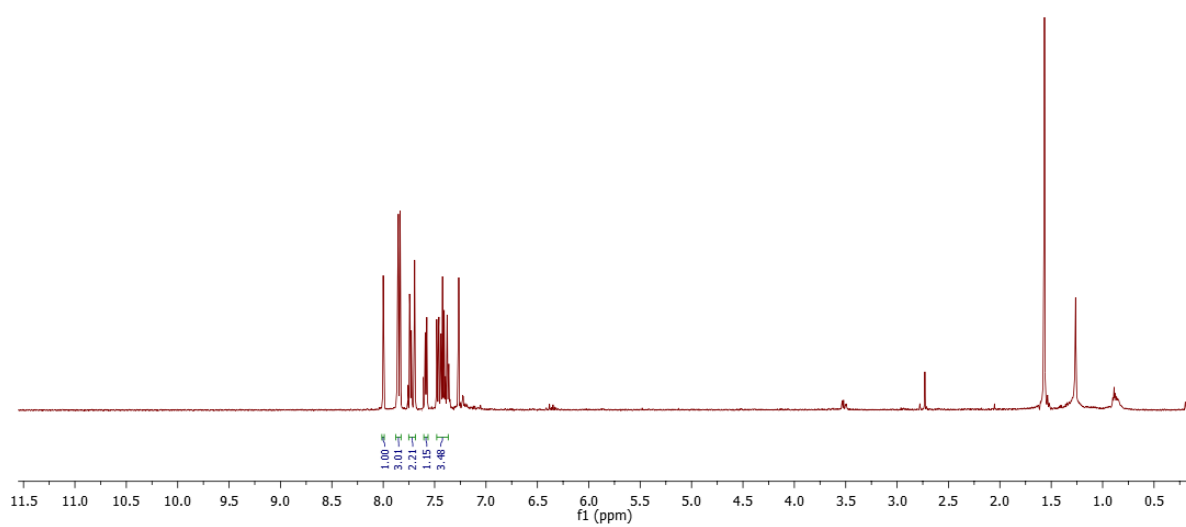
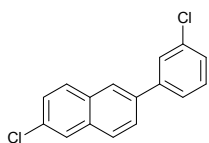


2-chloro-7-(4-chlorophenyl)naphthalene (2c) ¹³C

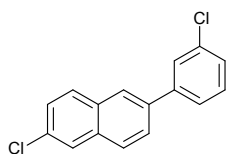


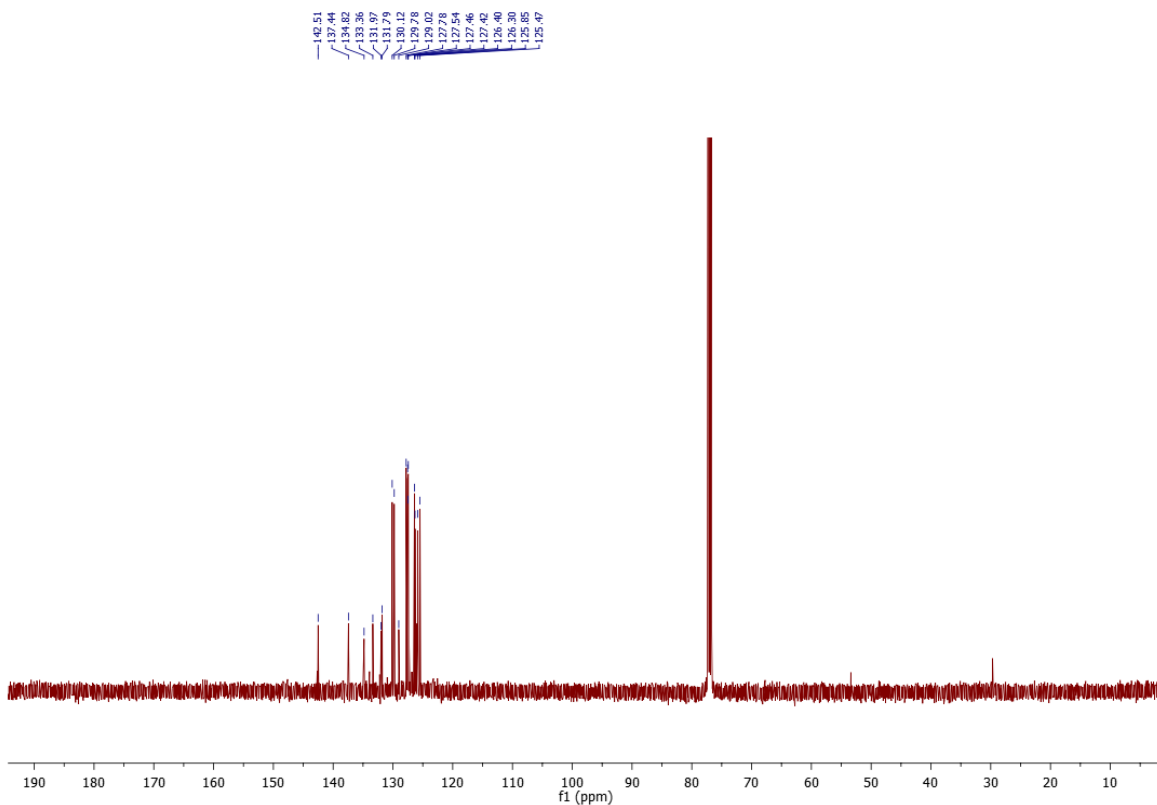


2-chloro-6-(3-chlorophenyl)naphthalene (2d) ¹H

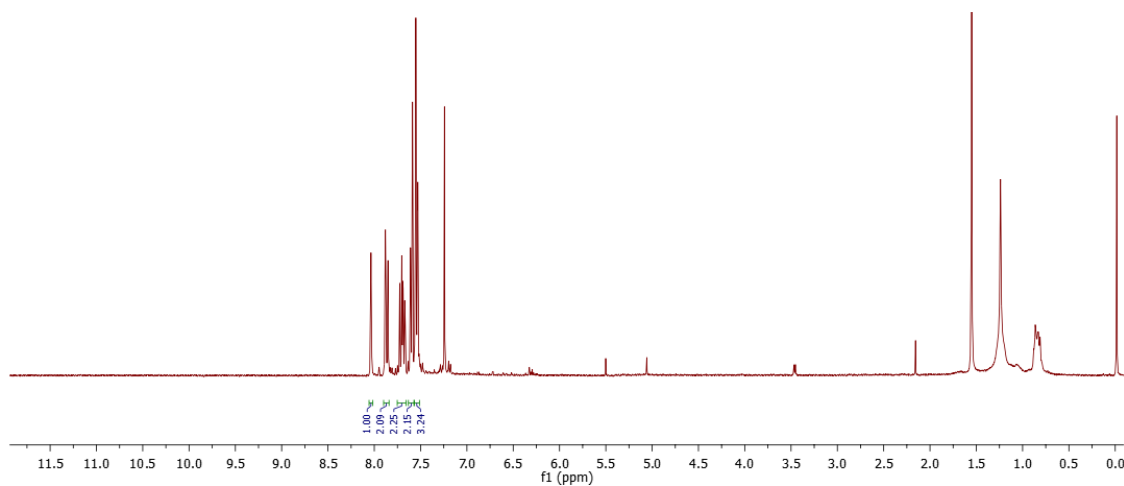
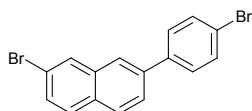


2-chloro-6-(3-chlorophenyl)naphthalene (2d) ¹³C

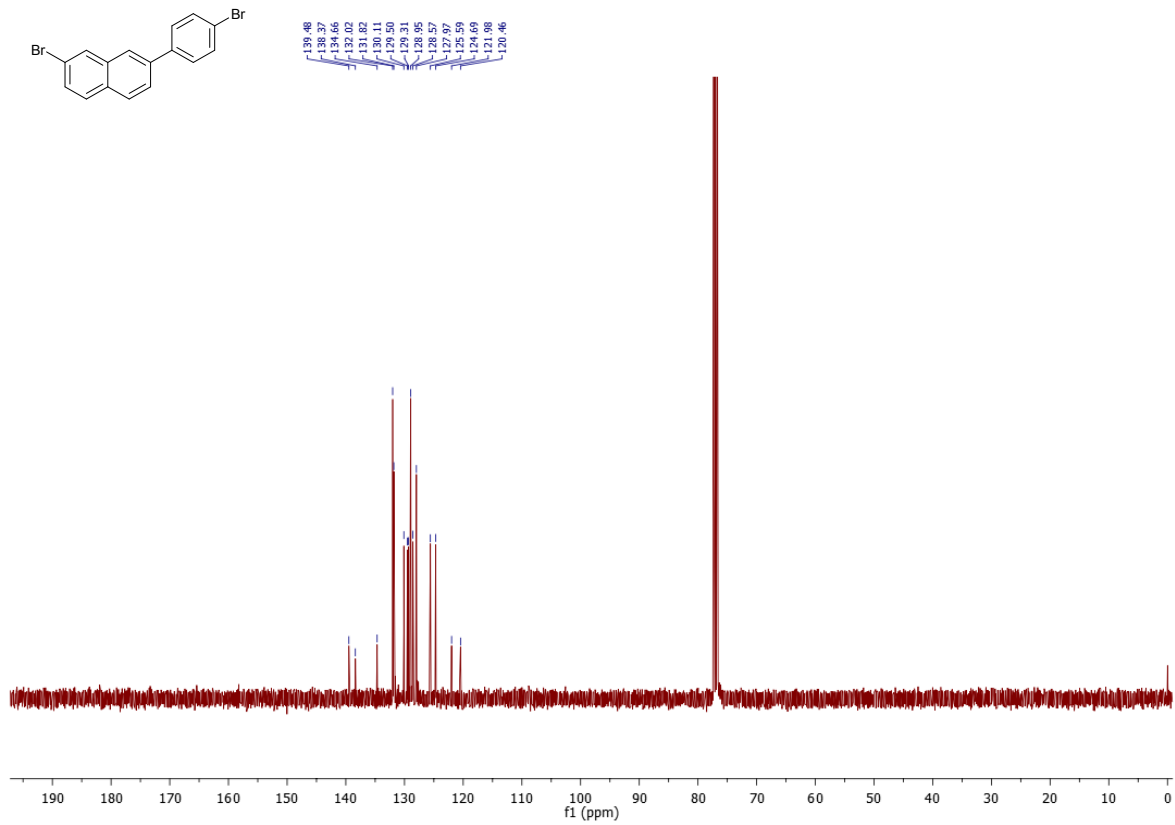




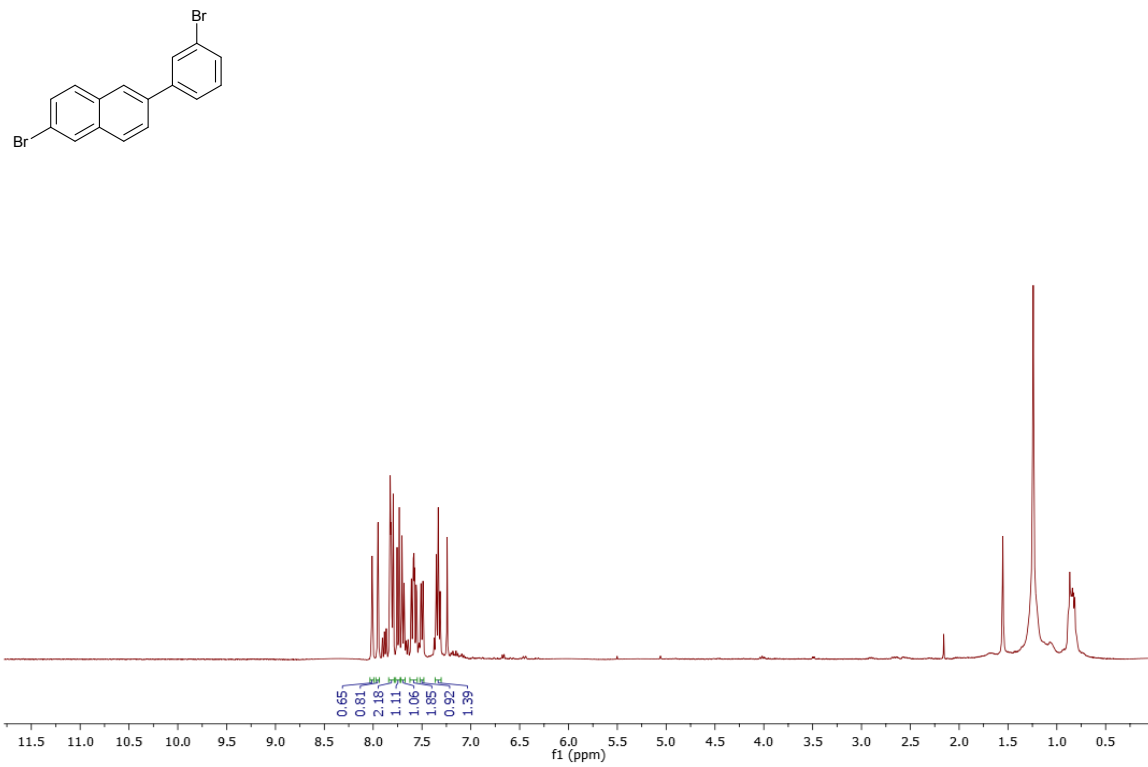
2-bromo-7-(4-bromophenyl)naphthalene (2e) ¹H



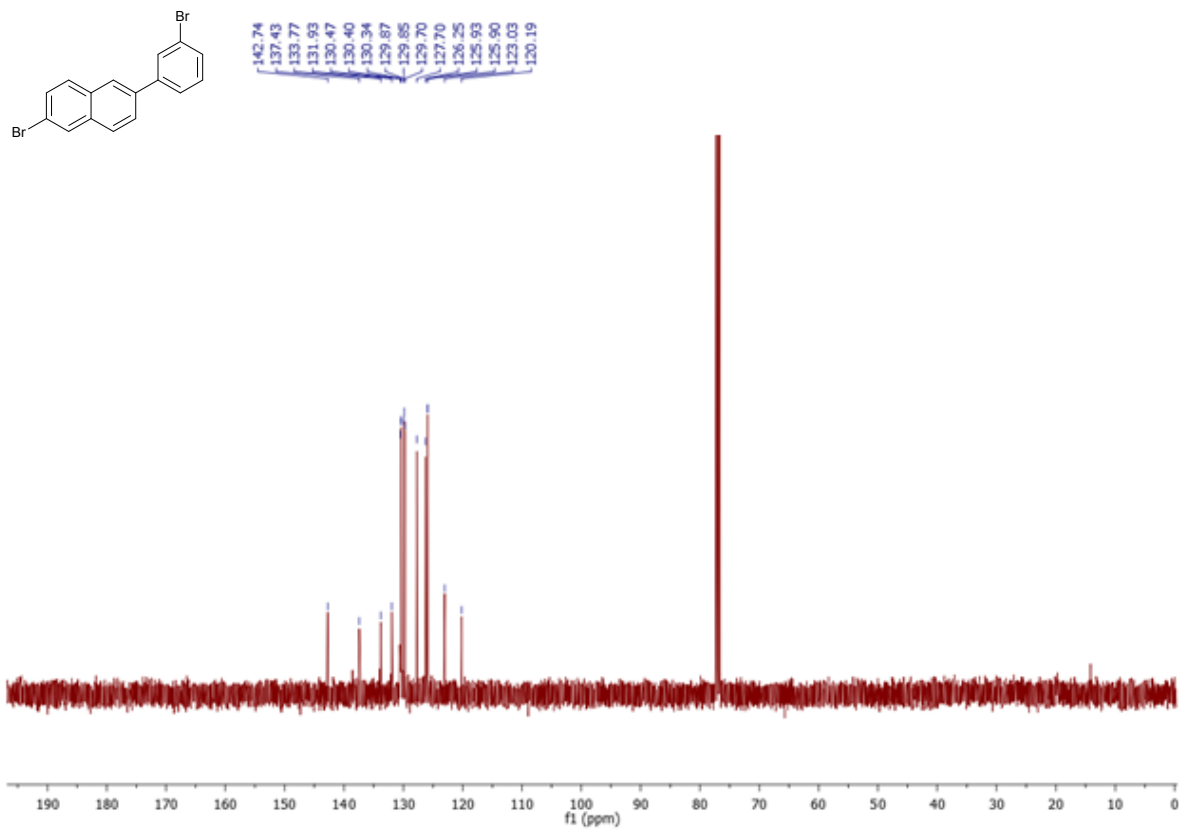
2-bromo-7-(4-bromophenyl)naphthalene (2e) ¹³C



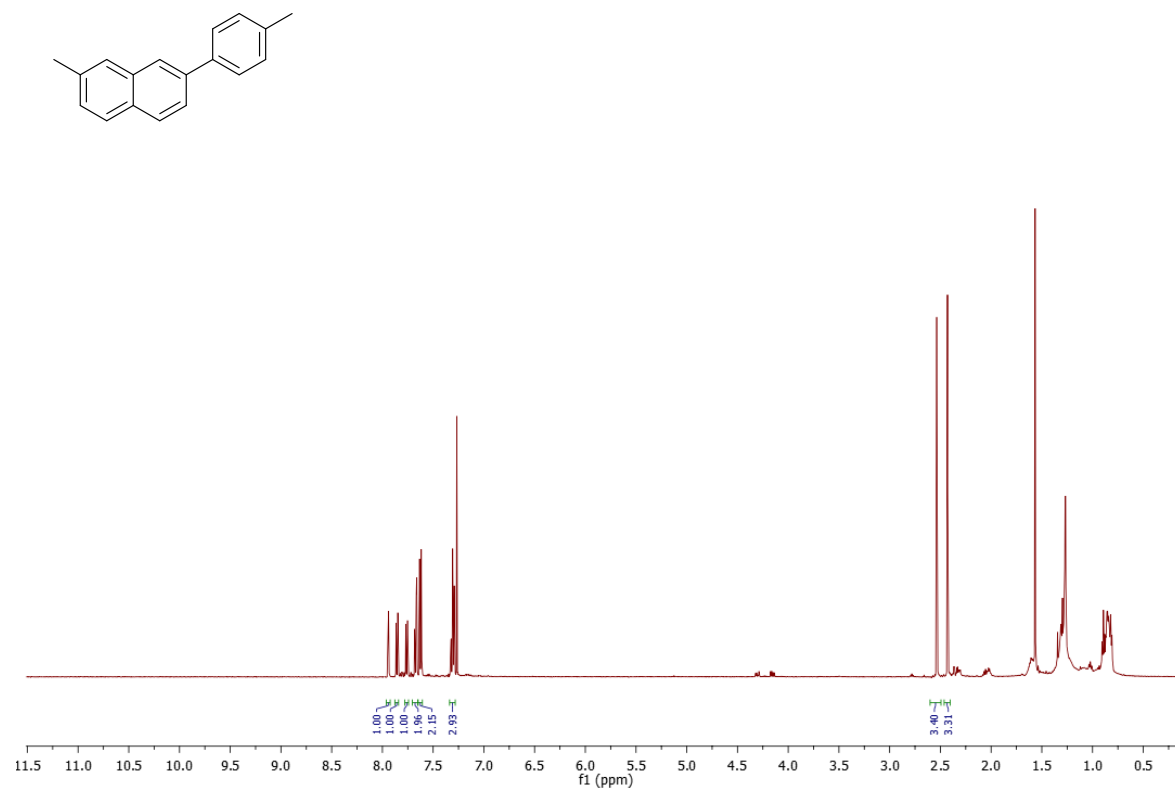
2-bromo-6-(3-bromophenyl)naphthalene (2f) ^1H



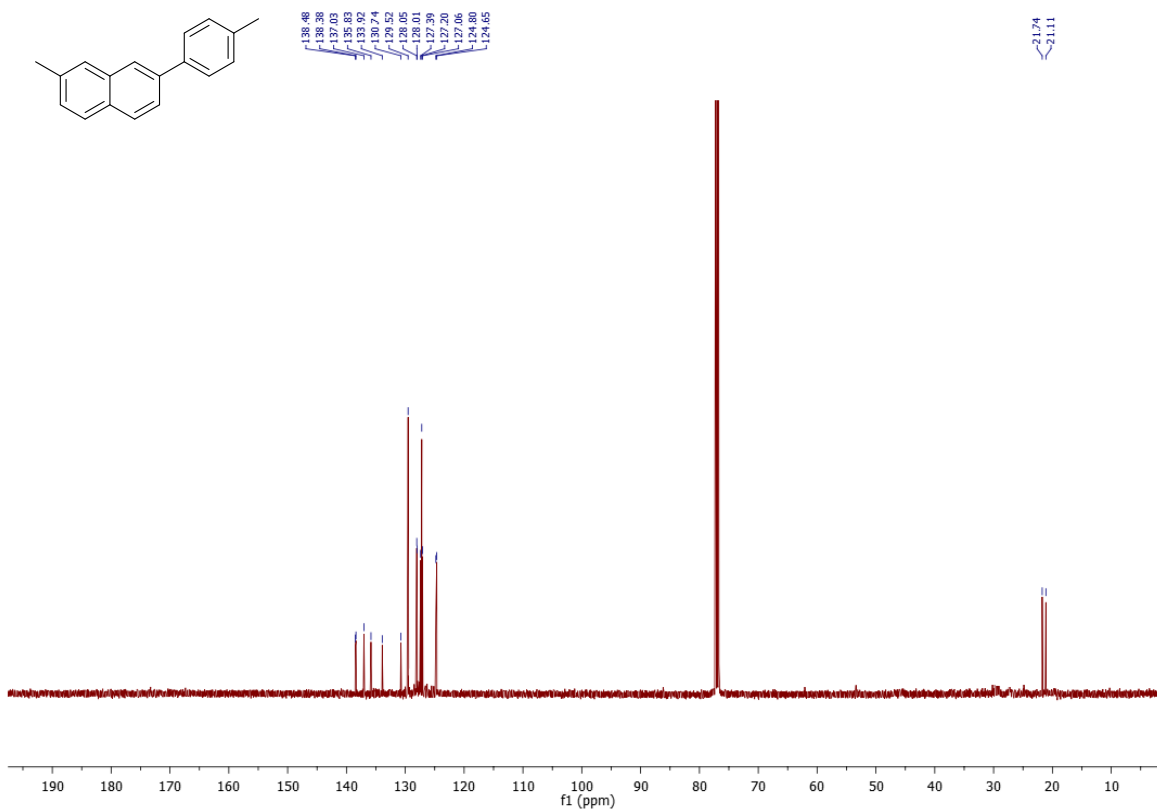
2-bromo-6-(3-bromophenyl)naphthalene (2f) ^{13}C



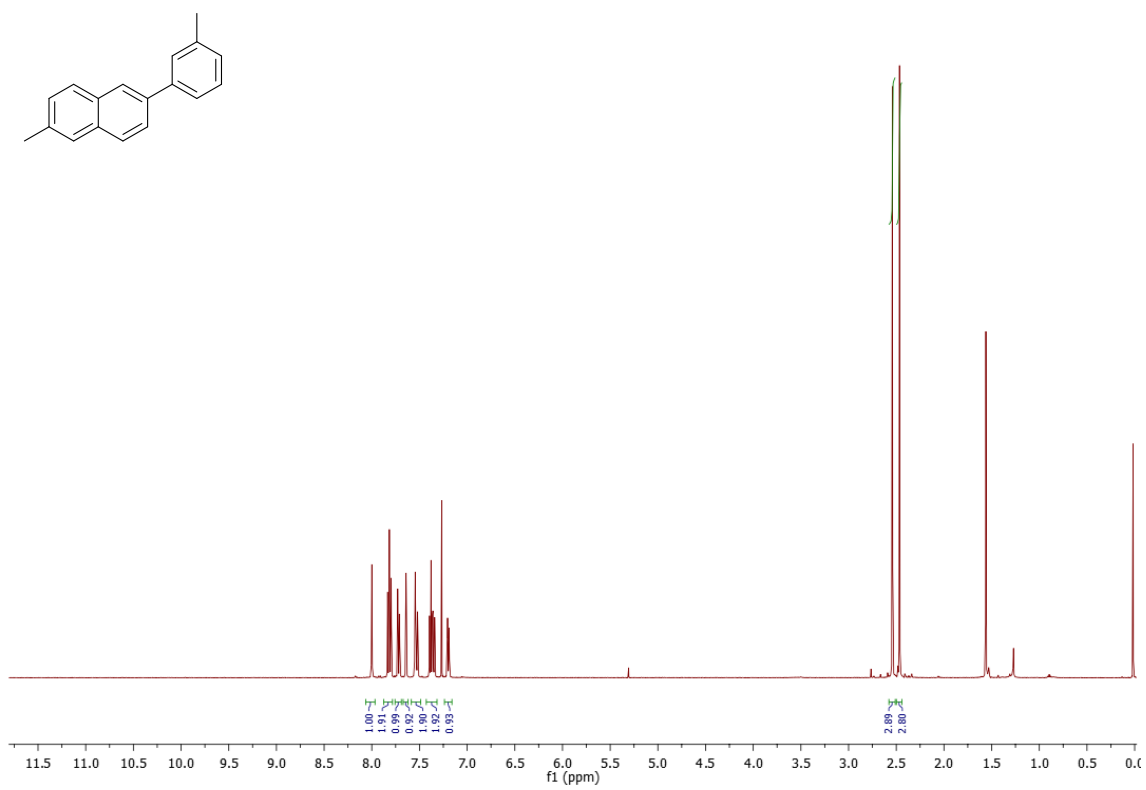
2-methyl-7-(p-tolyl)naphthalene (2g) ^1H



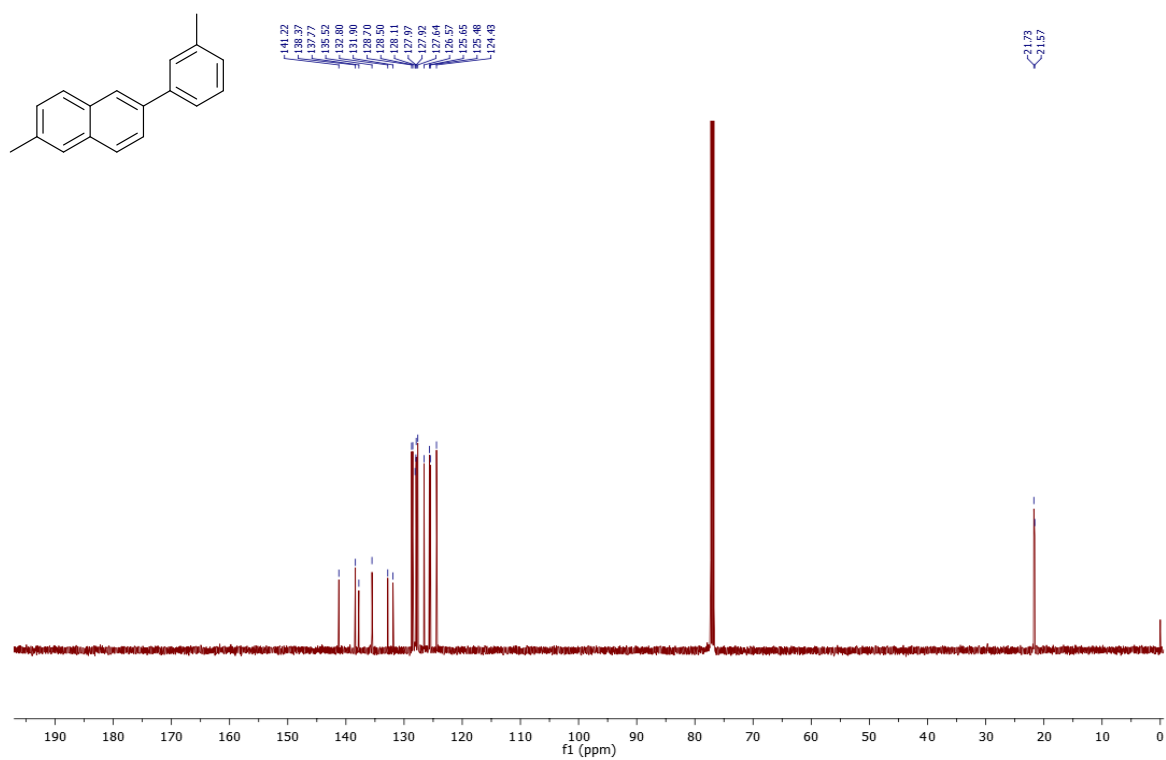
2-methyl-7-(p-tolyl)naphthalene (2g) ^{13}C



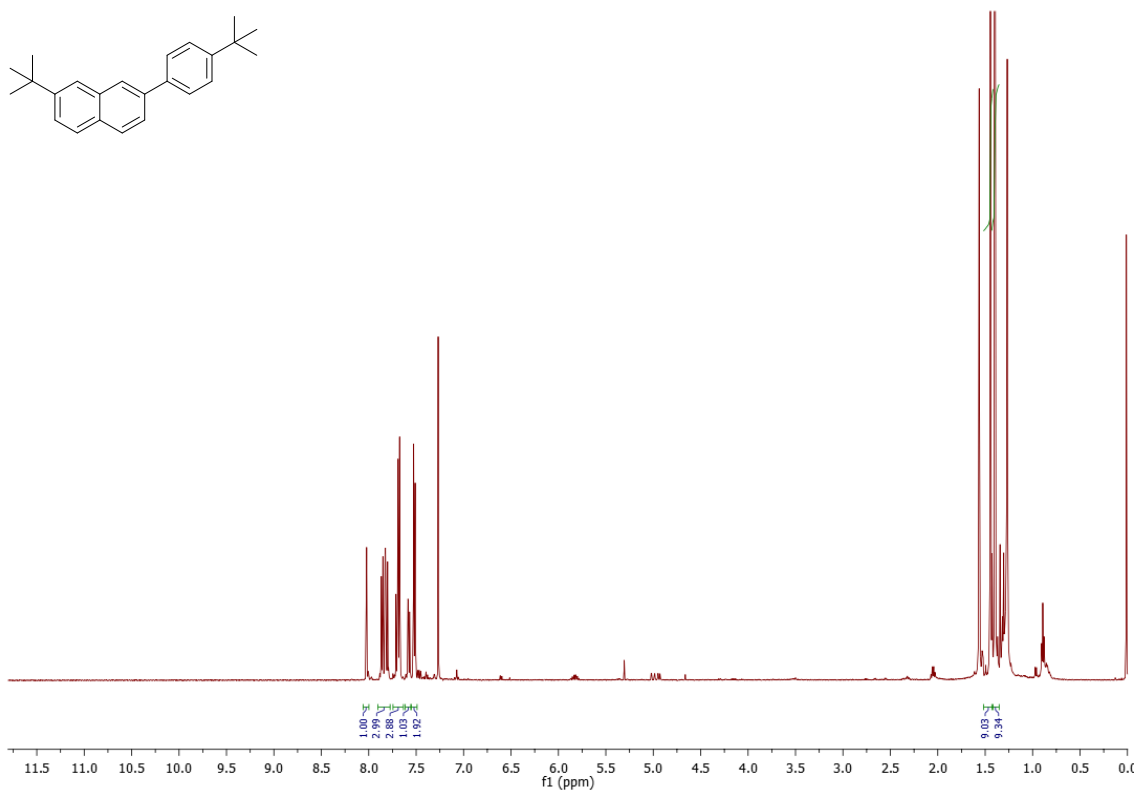
2-methyl-6-(m-tolyl)naphthalene (2h) ¹H



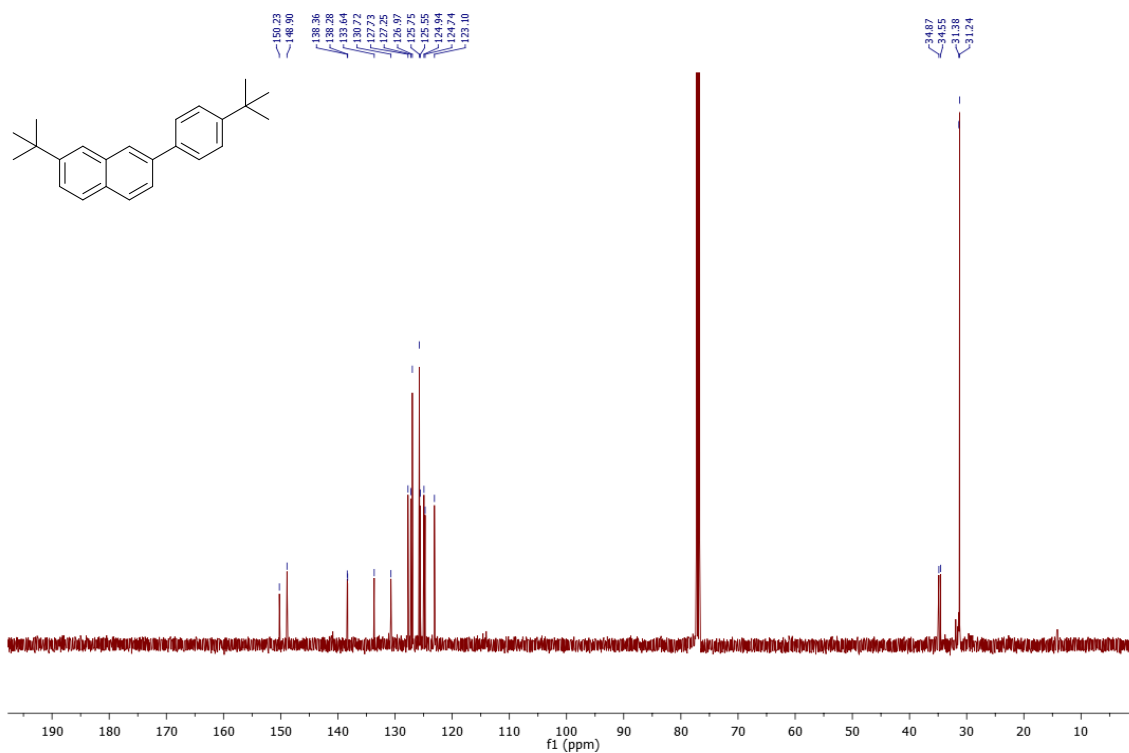
2-methyl-6-(m-tolyl)naphthalene (2h) ¹³C



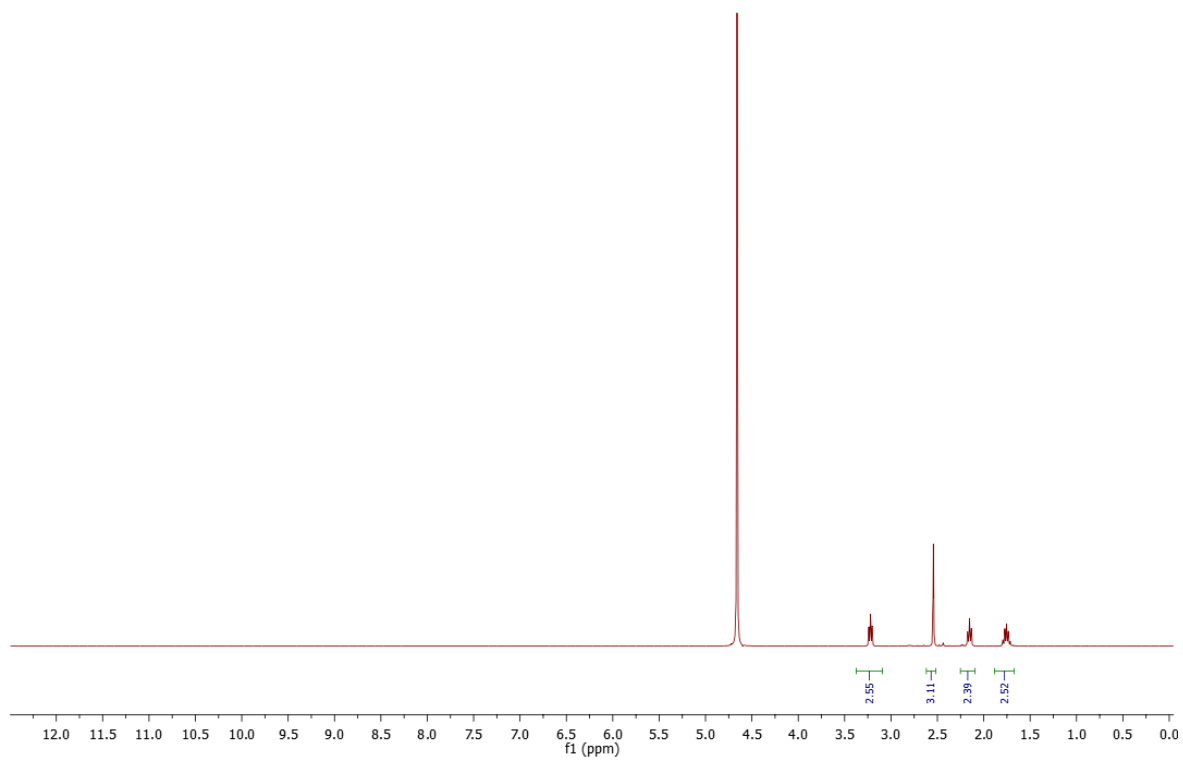
2-(tert-butyl)-7-(4-(tert-butyl)phenyl)naphthalene (2i) ¹H



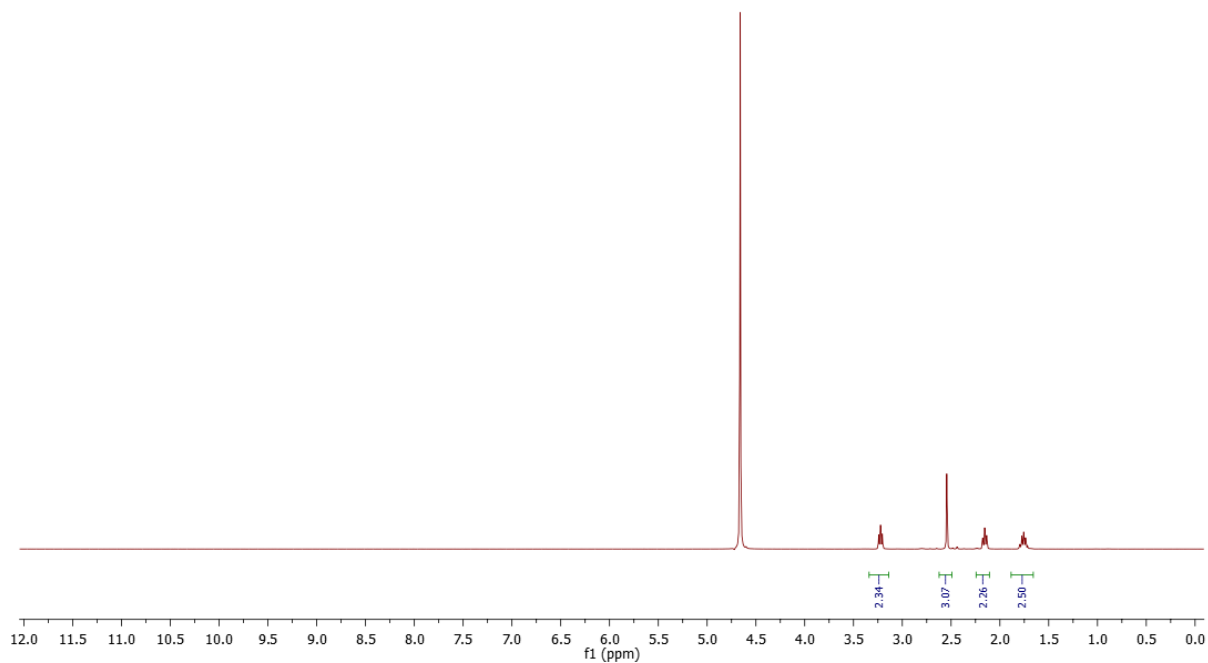
2-(tert-butyl)-7-(4-(tert-butyl)phenyl)naphthalene (2i) ¹³C



***N*-methyl-2-pyrrolidone hydrogen sulfate [HNMP]⁺[HSO₄]⁻ ionic liquid (fresh) ¹H**



N-methyl-2-pyrrolidone hydrogen sulfate [HNMP]+[HSO4]- ionic liquid (after 5th cycle) ^1H



V. GC-MS chromatogram of crude reaction mixture of model reaction

