Electronic Supplementary Information

Synthesis of Tetrasubstituted Benzenes via Rhodium(I)-Catalysed Ring-Opening Benzannulation of Cyclobutenols with Alkynes

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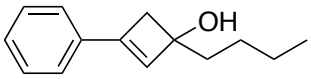
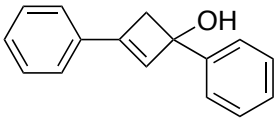
General. All reactions were carried out with standard Schlenk techniques under an argon or nitrogen atmosphere. Column chromatography was carried out on Wakogel® C-200 (75–150 μm). Preparative thin-layer chromatography was performed on Wakogel® B-5F. Proton chemical shifts were referenced to residual $CHCl_3$ signal at 7.26 ppm. Carbon chemical shifts were referenced to $CDCl_3$ at 77.0 ppm or internal $SiMe_4$ at 0.0 ppm.

Materials. Cyclobutenols **1** were prepared by the literature method[1] via nucleophilic addition of organolithium reagents to the corresponding cyclobutenones.[2] Diarylacetylenes were prepared by the literature method.[3] All other reagents and solvents were obtained from commercial sources and used without further purification.

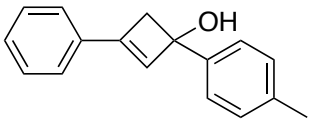
1 M. Murakami, Y. Miyamoto and Y. Ito, *J. Am. Chem. Soc.*, 2001, **123**, 6441.
2 R. L. Danheiser, S. Savariar and D. D. Cha, *Org. Synth.*, 1990, **68**, 32.
3 M. J. Mio, L. C. Kopel, J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth and P. A. Grieco, *Org. Lett.*, 2002, **4**, 3199.



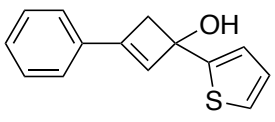
1-Butyl-3-phenylcyclobut-2-enol[1] (1a): Mp 73–75 °C; IR (KBr, ν/cm^{-1}): 3278, 2931, 1157, 752, 690.



1,3-Diphenylcyclobut-2-enol (1b): Mp 103–106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.26 (s, 1H), 3.14 (d, J = 12.0 Hz, 1H), 3.23 (d, J = 12.5 Hz, 1H), 6.65 (s, 1H), 7.24–7.42 (m, 6H), 7.43–7.48 (m, 2H), 7.55–7.60 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 47.1, 76.3, 125.3, 125.5, 127.3, 128.3, 128.4, 128.8, 130.5, 133.5, 143.8, 147.8; IR (KBr, ν/cm^{-1}): 3255, 1115, 883, 752, 694; HRMS (MALDI) calcd for $C_{16}H_{14}NaO$ $[M + Na]^+$ 245.0937, found 245.0929.

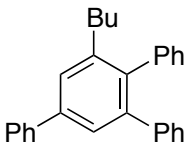


3-Phenyl-1-(*p*-tolyl)cyclobut-2-enol (1c): Mp 112–116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.25 (s, 1H), 2.35 (s, 3H), 3.13 (d, J = 12.6 Hz, 1H), 3.21 (d, J = 12.6 Hz, 1H), 6.64 (s, 1H), 7.18 (d, J = 7.8 Hz, 2H), 7.31–7.50 (m, 7H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.1, 47.0, 76.2, 125.3, 125.5, 128.4, 128.8, 129.0, 130.6, 133.6, 136.9, 140.9, 147.7; IR (KBr, ν/cm^{-1}): 3255, 1111, 887, 818, 756, 694; HRMS (MALDI) calcd for $C_{17}H_{16}ONa$ $[M + Na]^+$ 259.1093, found 259.1083.



3-Phenyl-1-(thiophen-2-yl)cyclobut-2-enol (1d): Mp 71–72 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.47 (s, 1H), 3.20 (dd, *J* = 12.6, 0.6 Hz, 1H), 3.32 (d, *J* = 12.6 Hz, 1H), 6.59 (s, 1H), 6.97 (dd, *J* = 5.0, 3.4 Hz, 1H), 7.07 (dd, *J* = 3.6, 1.2 Hz), 7.24 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.33–7.47 (m, 5H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 48.4, 74.4, 123.1, 124.5, 125.9, 126.8, 128.6, 128.9, 131.7, 133.9, 147.7, 149.8; IR (KBr, ν/cm^{-1}): 3240, 1103, 949, 841, 756, 694; HRMS (MALDI) calcd for $C_{14}H_{12}ONaS$ $[M + Na]^+$ 251.0501, found 251.0502.

General Procedure for the Rhodium(I)-Catalysed [4+2] Annulation of Cyclobutenols 1 with Alkynes 2. A Schlenk tube was charged with cyclobutenol **1** (0.100 mmol), $[Rh(OH)(cod)]_2$ (2.5 µmol, 5 mol% Rh), *rac*-BINAP (method A, none; method B, 6.0 µmol), and alkyne (0.120 mmol) (liquid substrates were added via syringe after toluene). The tube was evacuated and backfilled with nitrogen. Toluene (0.50 mL) was added via syringe through the septum. The mixture was stirred at rt for 10–15 min, and then heated at 110 °C. For the reaction using method A, silica gel (100–150 mg) was added, and the mixture was further heated at 110 °C for 1–3 h. The reaction mixture was filtered through a plug of Florisil® washing with AcOEt, and the filtrate was concentrated in vacuo. Purification by preparative TLC on silica gel afforded tetrasubstituted benzene **2**.

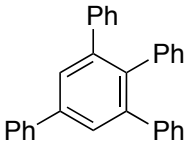


1-Butyl-2,3,5-triphenylbenzene (3a). The general procedure (method A; method B) was followed using **1a** (20.2 mg, 0.100 mmol; 20.2 mg, 0.100 mmol), **2a** (20.8 mg, 0.117 mmol; 22.1 mg, 0.124 mmol), $[Rh(OH)(cod)]_2$ (1.3 mg, 2.8 µmol, 5.7 mol% Rh; 1.2 mg, 2.6

μmol, 5.3 mol% Rh), *rac*-BINAP (–; 3.6 mg, 5.8 μmol) and toluene (0.50 mL; 0.50 mL) for 2 h; 4 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 40:1) yielded **3a** (31.4 mg, 0.087 mmol, 87%; 33.3 mg, 0.092 mmol, 92%) as a pale yellow oil.

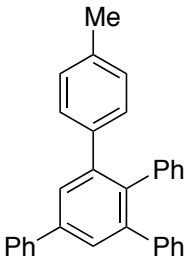
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.79 (t, J = 7.2 Hz, 3H), 1.24 (sext, J = 7.3 Hz, 2H), 1.44–1.56 (m, 2H), 2.52–2.61 (m, 2H), 7.06–7.28 (m, 10H), 7.32–7.41 (m, 1H), 7.42–7.58 (m, 4H), 7.69 (d, J = 7.2 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.8, 22.6, 33.5, 33.6, 126.1, 126.3, 126.4, 126.9, 127.2, 127.3, 127.4, 127.5, 128.7, 129.8, 130.6, 139.3, 139.7, 140.0, 140.9, 141.8, 142.1, 142.2; HRMS (EI) calcd for $C_{28}H_{26}$ $[M]^+$ 362.2029, found 362.2034.

The reaction of **1a** (19.8 mg, 0.098 mmol) and **2a** (22.1 mg, 0.118 mmol) performed in 1,4-dioxane (0.5 mL) at 100 °C for 5.5 h in the presence of $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh) and *rac*-BINAP (3.5 mg, 5.6 μmol) afforded **3a** (8.5 mg, 0.023 mmol, 24%) and (*E*)-2-phenyloct-2-en-4-one (**4a**, 12.7 mg, 0.063 mmol, 64%).

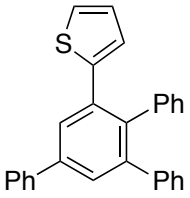


1,2,3,5-Tetraphenylbenzene[4] (3b). The general procedure (method A) was followed using **1b** (22.2 mg, 0.100 mmol), **2a** (21.1 mg, 0.118 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh) and toluene (0.50 mL) for 2.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 40:1) yielded **3b** (35.4 mg, 0.093 mmol, 93%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84–6.91 (m, 2H), 6.97–7.03 (m, 3H), 7.15–7.23 (m, 10H), 7.34–7.41 (m, 1H), 7.43–7.50 (m, 2H), 7.68–7.74 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 125.9, 126.3, 127.17, 127.21, 127.5, 127.6, 128.3, 128.8, 129.9, 131.6, 138.1, 139.2, 140.1, 140.4, 141.9, 142.4.

4 (*a*) T. Zimmermann and G. W. Fischer, *J. Prakt. Chem.*, 1987, **329**, 975; (*b*) C. P. G. Rühle, J. Niere, P. D. Morrison, R. C. Jones, T. Caradoc-Davies, A. J. Canty, M. G. Gardiner, V.-A. Tolhurst and P. J. Marriott, *Anal. Chem.*, 2010, **82**, 4501.

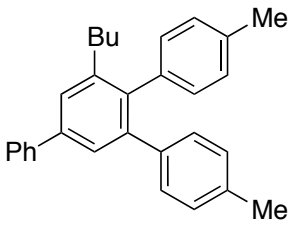


1-(4-Methylphenyl)-2,3,5-triphenylbenzene (3c). The general procedure (method A) was followed using **1c** (23.2 mg, 0.098 mmol), **2a** (21.2 mg, 0.119 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh) and toluene (0.50 mL) for 2 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 20:1) yielded **3c** (31.0 mg, 0.078 mmol, 80%) as a white solid. Mp 144–146 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3H), 6.88–6.95 (m, 2H), 6.98–7.09 (m, 7H), 7.12–7.24 (m, 5H), 7.35–7.43 (m, 1H), 7.44–7.52 (m, 2H), 7.68–7.76 (m, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.1, 125.8, 126.2, 127.15, 127.22, 127.5, 127.6, 128.1, 128.3, 128.4, 128.8, 129.8, 129.9, 131.6, 135.9, 138.1, 138.9, 139.3, 140.0, 140.5, 142.0, 142.3, 142.4; HRMS (MALDI) calcd for $C_{31}H_{24}Na$ $[M + Na]^+$ 419.1770, found 419.1774.

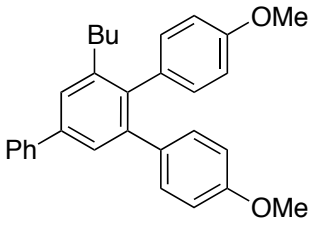


1,2,5-Triphenyl-3-(thiophen-2-yl)benzene (3d). The general procedure (method A) was followed using **1d** (21.6 mg, 0.095 mmol), **2a** (21.4 mg, 0.120 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh) and toluene (0.50 mL) for 1 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 20:1) yielded **3d** (25.0 mg, 0.064 mmol, 68%) as a white solid. Mp 168–171 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.66–6.72 (m, 1H), 6.82–6.90 (m, 1H), 6.96–7.05 (m, 2H), 7.07–7.24 (m, 9H), 7.35–7.53 (m, 3H), 7.63–7.75 (m, 3H), 7.80–7.86 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 125.7, 126.4, 126.5, 126.6, 127.18, 127.20, 127.5,

127.55, 127.61, 128.4, 128.6, 128.9, 129.8, 131.3, 134.9, 138.3, 139.2, 140.2, 140.3, 141.6, 142.8, 143.4; HRMS (MALDI) calcd for $C_{28}H_{20}NaS$ $[M + Na]^+$ 411.1178, found 411.1171.

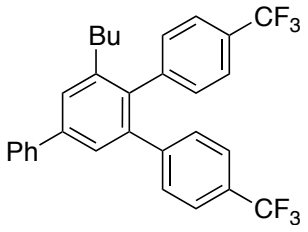


1-Butyl-2,3-bis(4-methylphenyl)-5-phenylbenzene (3f). The general procedure (method B) was followed using **1a** (20.1 mg, 0.099 mmol), **2b** (24.8 mg, 0.120 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh), *rac*-BINAP (3.8 mg, 6.1 μmol) and toluene (0.50 mL) for 4 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 40:1) yielded **3f** (29.1 mg, 0.075 mmol, 75%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83 (t, J = 7.2 Hz, 3H), 1.27 (sext, J = 7.4 Hz, 2H), 1.46–1.58 (m, 2H), 2.29 (s, 3H), 2.34 (s, 3H), 2.53–2.61 (m, 2H), 6.95–7.08 (m, 8H), 7.34–7.41 (m, 1H), 7.44–7.51 (m, 3H), 7.55 (d, J = 2.1 Hz, 1H), 7.67–7.73 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.9, 21.1, 21.2, 22.6, 33.6, 33.7, 126.5, 126.7, 127.1, 127.2, 128.2, 128.3, 128.7, 129.7, 130.4, 135.5, 135.6, 136.7, 139.27, 139.28, 139.7, 141.0, 142.0, 142.2; HRMS (EI) calcd for $C_{30}H_{30}$ $[M]^+$ 390.2342, found 390.2352.

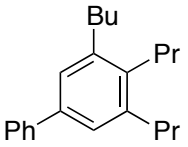


1-Butyl-2,3-bis(4-methoxyphenyl)-5-phenylbenzene (3g). The general procedure (method B) was followed using **1a** (20.4 mg, 0.101 mmol), **2c** (29.0 mg, 0.122 mmol), $[Rh(OH)(cod)]_2$ (1.2 mg, 2.6 μmol, 5.3 mol% Rh), *rac*-BINAP (3.7 mg, 5.9 μmol) and

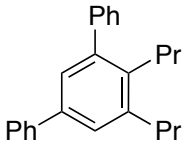
toluene (0.50 mL) for 2.5 h. Purification by preparative TLC on silica gel (hexane:$CHCl_3$ = 1:3) yielded **3g** (40.4 mg, 0.096 mmol, 95%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (t, J = 7.2 Hz, 3H), 1.26 (sext, J = 7.5 Hz, 2H), 1.44–1.57 (m, 2H), 2.52–2.61 (m, 2H), 3.76 (s, 3H), 3.80 (s, 3H), 6.68–6.75 (m, 2H), 6.77–6.83 (m, 2H), 6.97–7.08 (m, 4H), 7.33–7.40 (m, 1H), 7.43–7.54 (m, 4H), 7.66–7.72 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.9, 22.6, 33.6, 33.7, 55.1 [overlapping], 112.9, 113.0, 126.4, 126.6, 127.1, 127.2, 128.7, 130.9, 131.6, 132.1, 134.7, 138.9, 139.8, 141.0, 142.0, 142.2, 157.8, 157.9; HRMS (MALDI) calcd for $C_{30}H_{30}O_2Na$ $[M + Na]^+$ 445.2138, found 445.2137.



1-Butyl-2,3-bis(4-methoxyphenyl)-5-phenylbenzene (3h). The general procedure (method A) was followed using **1a** (10.0 mg, 0.049 mmol), **2d** (18.4 mg, 0.059 mmol), $[Rh(OH)(cod)]_2$ (0.5 mg, 1.1 μmol, 4.4 mol% Rh) and toluene (0.50 mL) for 2 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 80:1) yielded **3h** (23.0 mg, 0.046 mmol, 93%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.79 (t, J = 7.4 Hz, 3H), 1.23 (sext, J = 7.3 Hz, 2H), 1.41–1.53 (m, 2H), 2.47–2.57 (m, 2H), 7.16–7.24 (m, 4H), 7.36–7.59 (m, 8H), 7.59 (d, J = 1.8 Hz, 1H), 7.64–7.69 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.8, 22.5, 33.4, 33.6, 124.1 (q, $^1J_{C–F}$ = 271.8 Hz) [overlapping], 124.6 (q, $^3J_{C–F}$ = 3.7 Hz), 124.8 (q, $^3J_{C–F}$ = 3.7 Hz), 126.4, 127.2, 127.7, 127.8, 128.6 (q, $^2J_{C–F}$ = 32.4 Hz), 128.88, 128.94 (q, $^2J_{C–F}$ = 32.4 Hz), 130.0, 130.9, 137.6, 140.4, 140.7, 140.9, 141.9, 143.2 (q), 145.2 (q); HRMS (MALDI) calcd for $C_{30}H_{24}F_6Na$ $[M + Na]^+$ 521.1674, found 521.1702.

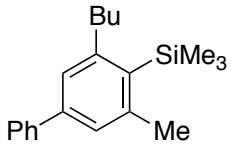


1-Butyl-5-phenyl-2,3-dipropylbenzene (3i). The general procedure (method A; method B) was followed using **1a** (20.4 mg, 0.101 mmol; 19.8 mg, 0.098 mmol), **2e** (13.8 mg, 0.125 mmol; 13.8 mg, 0.125 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh; 1.2 mg, 2.6 μmol, 5.3 mol% Rh), *rac*-BINAP (–; 3.9 mg, 6.3 μmol) and toluene (0.50 mL; 0.5 mL) for 2 h; 4 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 40:1) yielded **3i** (26.8 mg, 0.091 mmol, 90%; 16.4 mg, 0.056 mmol, 57%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.3 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H), 1.40–1.76 (m, 8H), 2.60–2.72 (m, 6H), 7.26 (s, 1H+1H), 7.28–7.35 (m, 1H), 7.39–7.47 (m, 2H), 7.57–7.64 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.0, 14.5, 14.9, 23.0, 24.5, 24.8, 30.8, 33.0, 34.0, 35.5, 125.7, 125.8, 126.7, 127.0, 128.6, 137.7, 138.2, 141.2, 141.4, 141.5; HRMS (EI) calcd for $C_{22}H_{30}$ $[M]^+$ 294.2342, found 294.2347.



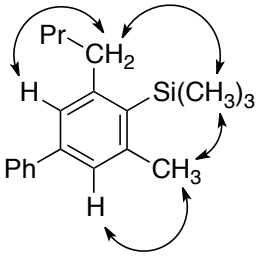
1,5-Diphenyl-2,3-dipropylbenzene (3j). The general procedure (method B) was followed using **1b** (22.2 mg, 0.100 mmol), **2e** (15.0 mg, 0.136 mmol), $[Rh(OH)(cod)]_2$ (1.2 mg, 2.6 μmol, 5.3 mol% Rh), *rac*-BINAP (3.6 mg, 5.8 μmol) and toluene (0.50 mL) for 1 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 15:1) yielded **3j** (11.4 mg, 0.036 mmol, 36%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.3 Hz, 3H), 1.38–1.49 (m, 2H), 1.75 (sext, *J* = 7.5 Hz, 2H), 2.52–2.62 (m, 2H), 2.68–2.78 (m, 2H), 7.24–7.46 (m, 10H), 7.58–7.65 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 14.5, 14.6, 24.5, 24.9, 31.5, 35.4, 126.59, 126.62, 126.95, 126.98, 127.1, 127.9,

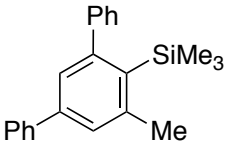
128.6, 129.3, 137.5, 137.9, 141.0, 141.5, 142.9, 143.1; HRMS (MALDI) calcd for $C_{24}H_{26}Na$ $[M + Na]^+$ 337.1927, found 337.1936.



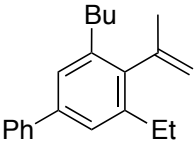
1-Butyl-3-methyl-5-phenyl-2-(trimethylsilyl)benzene (3k). The general procedure (method A; method B) was followed using **1a** (20.0 mg, 0.099 mmol; 20.2 mg, 0.100 mmol), **2f** (14.2 mg, 0.127 mmol; 13.0 mg, 0.116 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.9 mol% Rh; 1.1 mg, 2.4 μmol, 4.8 mol% Rh), *rac*-BINAP (–; 3.6 mg, 5.8 μmol) and toluene (0.5 mL; 0.50 mL) for 1 h; 1 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 12:1) yielded **3k** (27.2 mg, 0.092 mmol, 93%; 14.7 mg, 0.050 mmol, 50%) as a pale yellow oil. Regioisomeric ratio of **3k** was determined to be 90:10; >99:1 by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.44 (s, 9H), 0.96 (t, J = 7.3 Hz, 3H), 1.44 (sext, J = 7.7 Hz, 2H), 1.56–1.64 (m, 2H), 2.54 (s, 3H), 2.76–2.82 (m, 2H), 7.22 (s, 1H), 7.25 (s, 1H), 7.34 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.2 Hz, 2H), 7.60 (d, J = 7.5 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 3.7, 14.1, 22.9, 25.0, 35.9, 36.8, 125.89, 125.90, 127.1, 127.2, 128.6, 135.0, 140.9, 141.3, 144.7, 150.2; HRMS (MALDI) calcd for $C_{20}H_{28}NaSi$ $[M + Na]^+$ 319.1852, found 319.1864.

The regiochemistry of **3k** was determined by NOESY experiments.



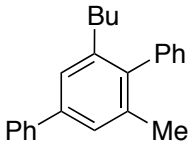


1-Methyl-3,5-diphenyl-2-(trimethylsilyl)benzene (3l). The general procedure (method A; method B) was followed using **1b** (21.9 mg, 0.099 mmol; 22.3 mg, 0.100 mmol), **2f** (13.4 mg, 0.119 mmol; 15.9 mg, 0.142 mmol), $[Rh(OH)(cod)]_2$ (1.0 mg, 2.2 μmol, 4.4 mol% Rh; 1.1 mg, 2.4 μmol, 4.8 mol% Rh), *rac*-BINAP (–; 3.8 mg, 6.1 μmol) and toluene (0.50 mL; 0.50 mL) for 2.5 h; 3.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 50:1) yielded **3l** (27.0 mg, 0.085 mmol, 87%; 20.3 mg, 0.064 mmol, 64%) as a pale yellow oil. Regioisomeric ratio of **3l** was determined to be 92:8; 93:7 by ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 9H), 2.64 (s, 3H), 7.29–7.47 (m, 10H), 7.60–7.66 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 2.3, 24.6, 126.4, 127.0, 127.1, 127.4, 127.6, 127.8, 128.7, 129.5, 135.7, 140.5, 140.6, 145.2, 145.6, 150.6; HRMS (MALDI) calcd for $C_{22}H_{24}NaSi$ $[M + Na]^+$ 339.1539, found 339.1531.



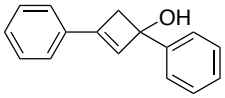
1-Butyl-3-ethyl-5-phenyl-2-(prop-1-en-2-yl)benzene (3m). The general procedure (method A) was followed using **1a** (20.3 mg, 0.100 mmol), **2g** (12.0 mg, 0.127 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh) and toluene (0.50 mL) for 1 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 40:1) yielded **3m** (21.7 mg, 0.078 mmol, 78%) as a pale yellow oil. Regioisomeric ratio of **3m** was determined to be 93:7 by ^{1}H NMR analysis. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, J = 7.4 Hz, 3H), 1.27 (t, J = 7.5 Hz, 3H), 1.43 (sext, J = 7.4 Hz, 2H), 1.55–1.71 (m, 2H), 2.05 (s, 3H), 2.58–2.75 (m, 4H), 4.86 (s, 1H), 5.34 (s, 1H), 7.27–7.40 (m, 3H), 7.40–7.50 (m, 2H), 7.57–7.68 (m, 2H); ^{13}C NMR (75.5 MHz,

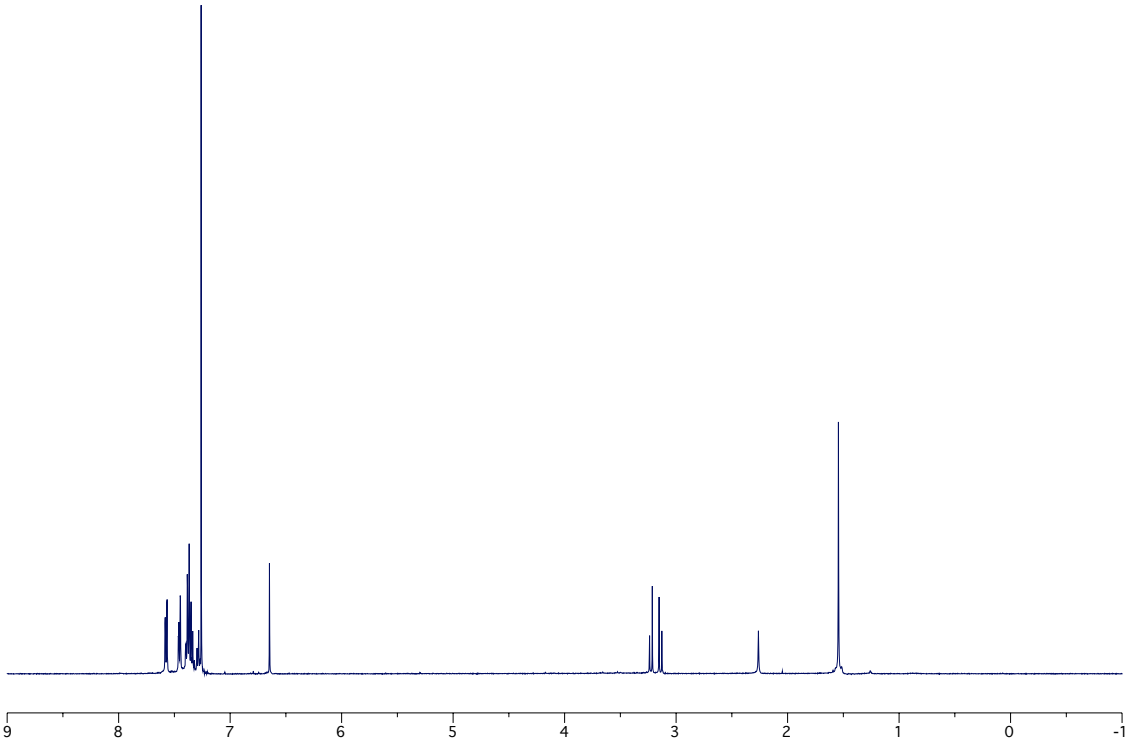
$CDCl_3$) δ 14.0, 16.4, 23.0, 25.3, 26.2, 33.0, 34.5, 115.6, 124.5, 125.1, 126.9, 127.1, 128.6, 139.5, 140.1, 141.3, 141.4, 141.5, 143.8; HRMS (MALDI) calcd for $C_{21}H_{26}Na$ $[M + Na]^+$ 301.1927, found 301.1940.

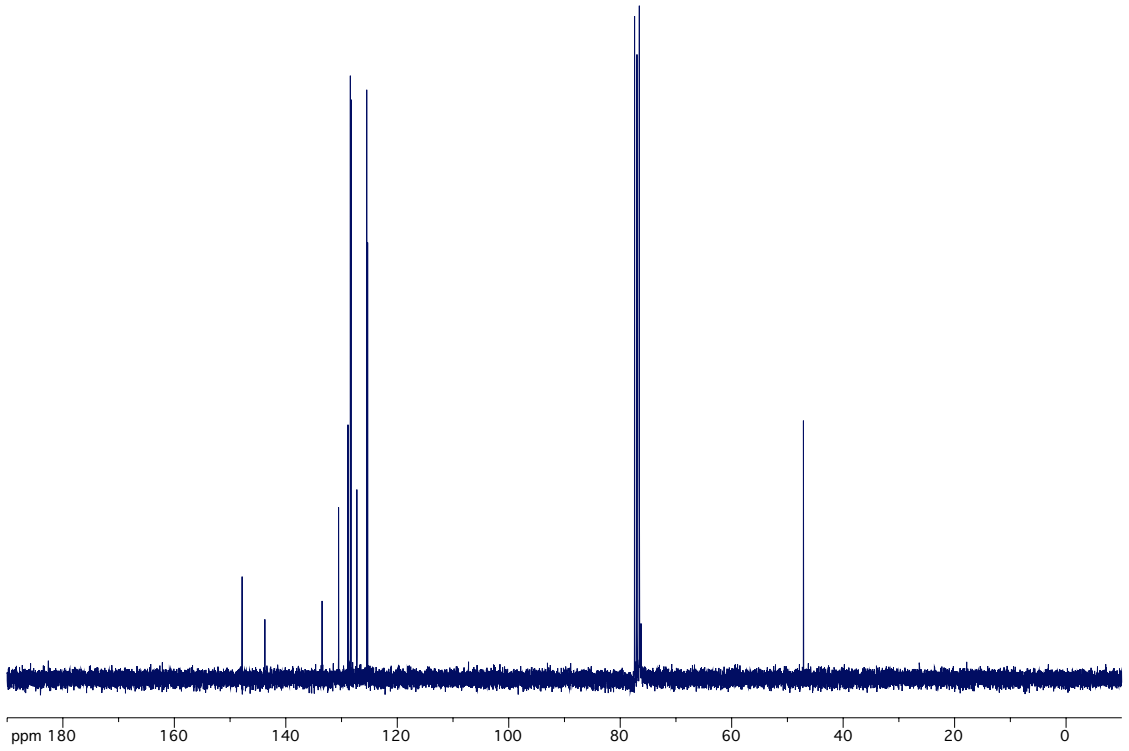


1-Butyl-3-methyl-2,5-diphenylbenzene (3n). The general procedure (method A) was followed using **1a** (20.2 mg, 0.100 mmol), **2h** (13.1 mg, 0.113 mmol), $[Rh(OH)(cod)]_2$ (1.1 mg, 2.4 μmol, 4.8 mol% Rh) and toluene (0.50 mL) for 2.5 h. Purification by preparative TLC on silica gel (hexane:AcOEt = 20:1) yielded **3n** (11.6 mg, 0.039 mmol, 39%) as a pale yellow oil and **4a** (8.9 mg, 0.044 mmol, 44%) as a pale yellow oil. Regioisomeric ratio of **3n** was determined to be 87:13 by ^1H NMR analysis. ^1H NMR (300 MHz, $CDCl_3$) δ 0.78 (t, J = 7.2 Hz, 3H), 1.21 (sext, J = 7.3 Hz, 2H), 1.45 (quint, J = 7.6 Hz, 2H), 2.91 (s, 3H), 2.34–2.48 (m, 2H), 7.17–7.24 (m, 2H), 7.32–7.52 (m, 8H), 7.62–7.69 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.8, 21.2, 22.5, 33.4, 33.6, 125.3, 126.0, 126.6, 127.06, 127.1, 128.2, 128.7, 129.4, 136.7, 139.9, 140.5, 140.6, 141.3, 141.4; HRMS (MALDI) calcd for $C_{23}H_{24}Na$ $[M + Na]^+$ 323.1770, found 323.1782.

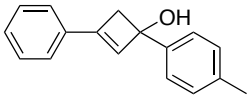
1b

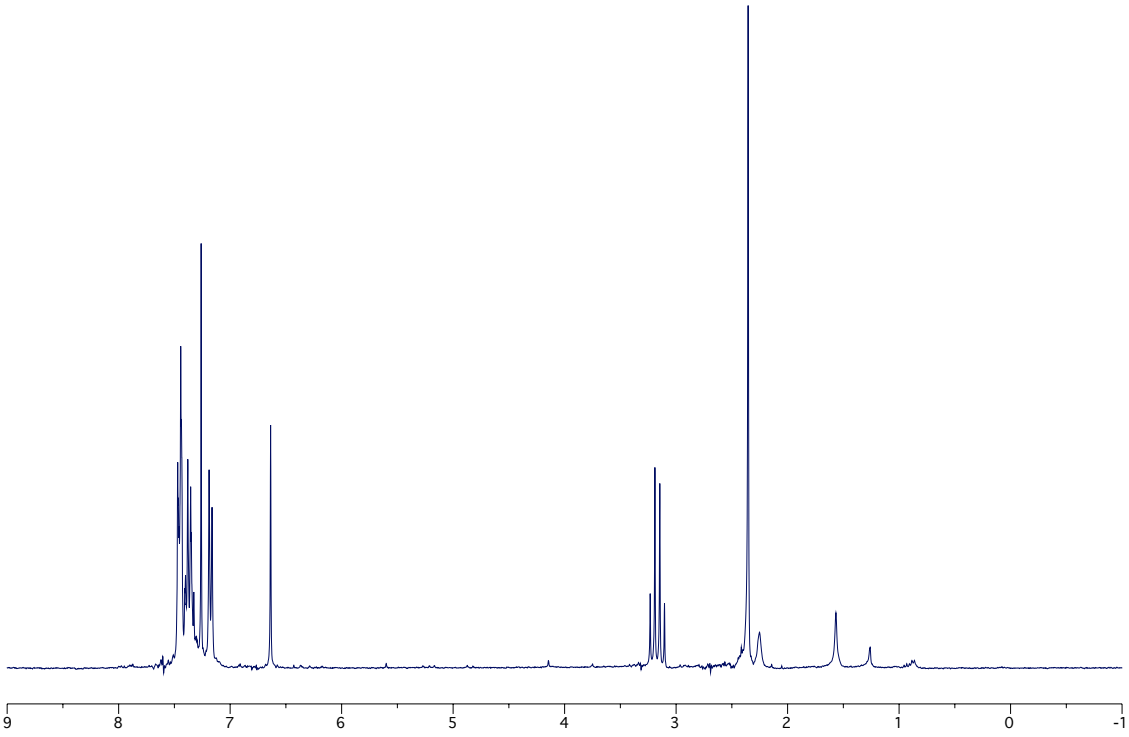


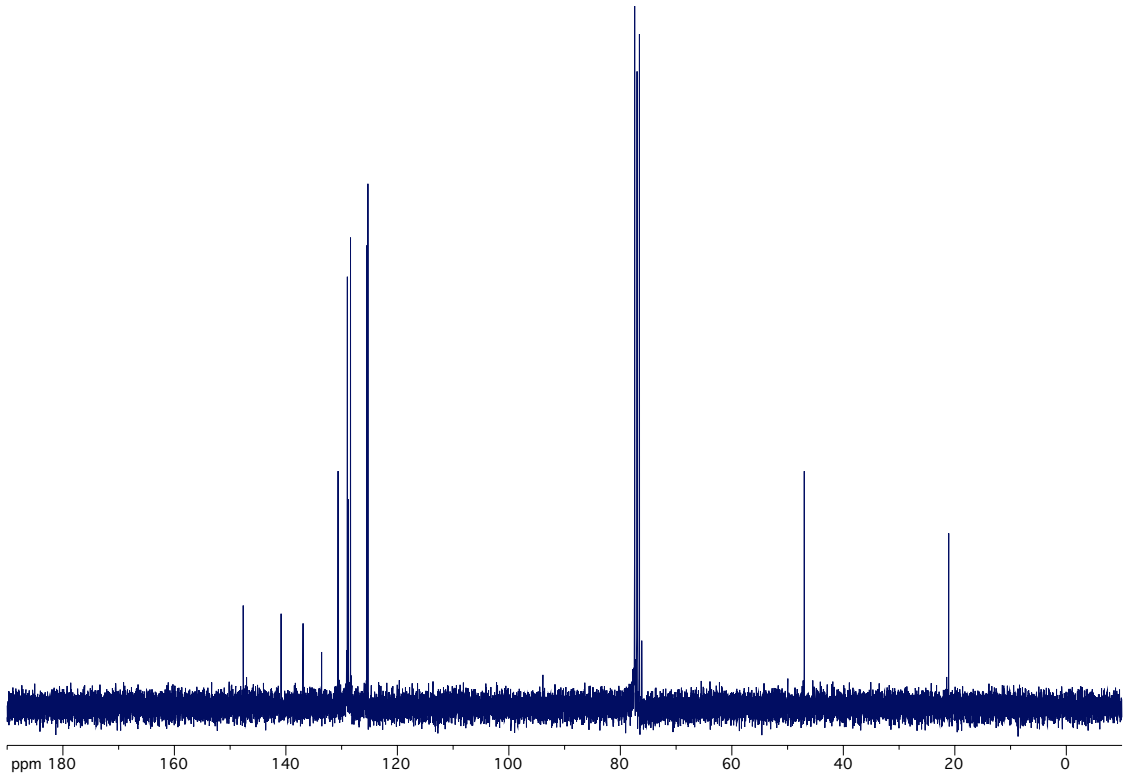




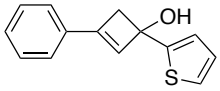
1c

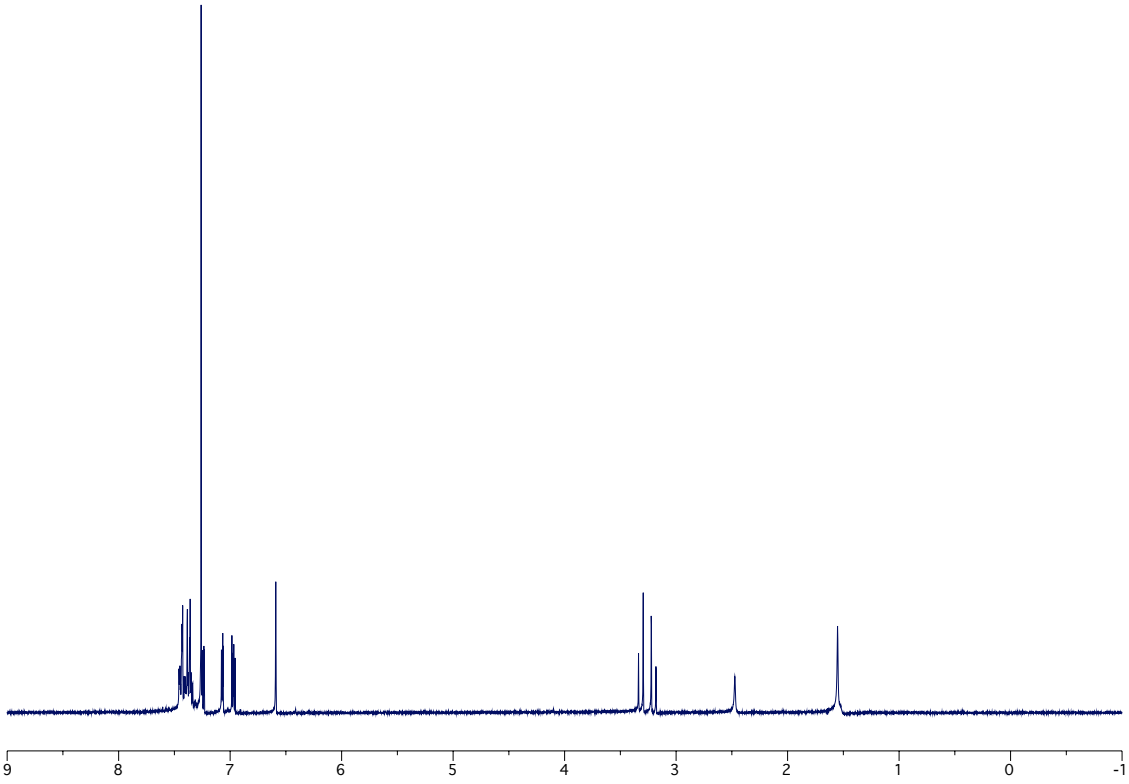


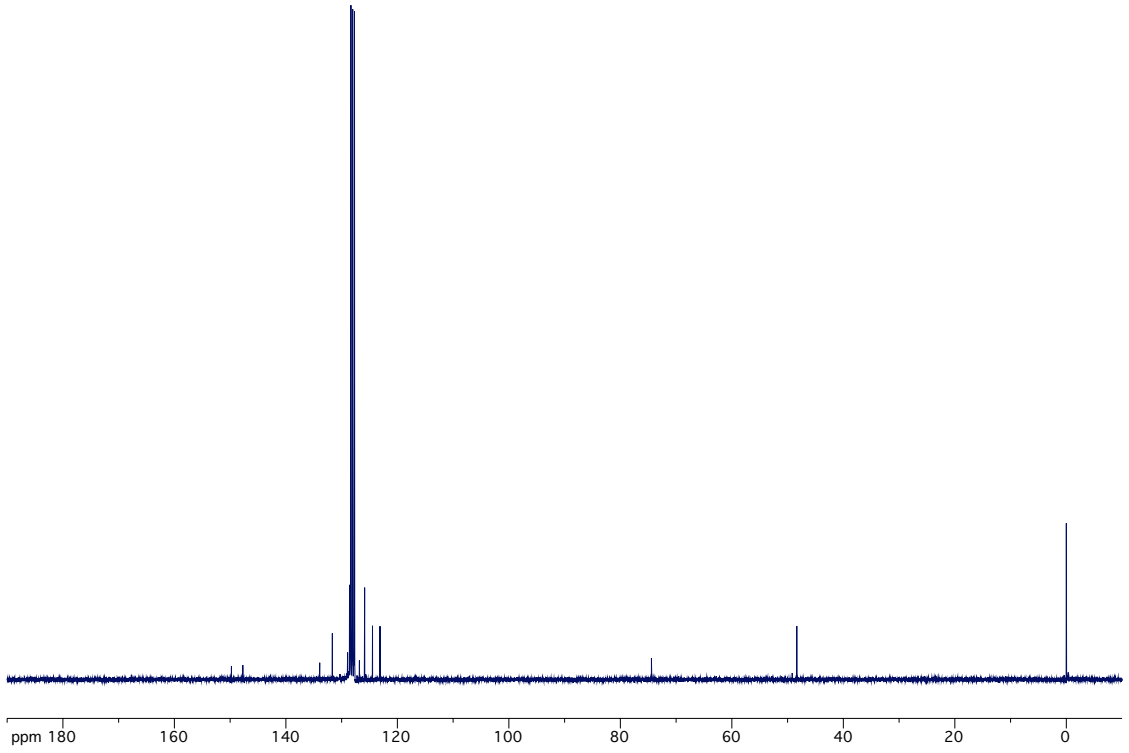




1d







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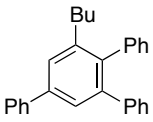

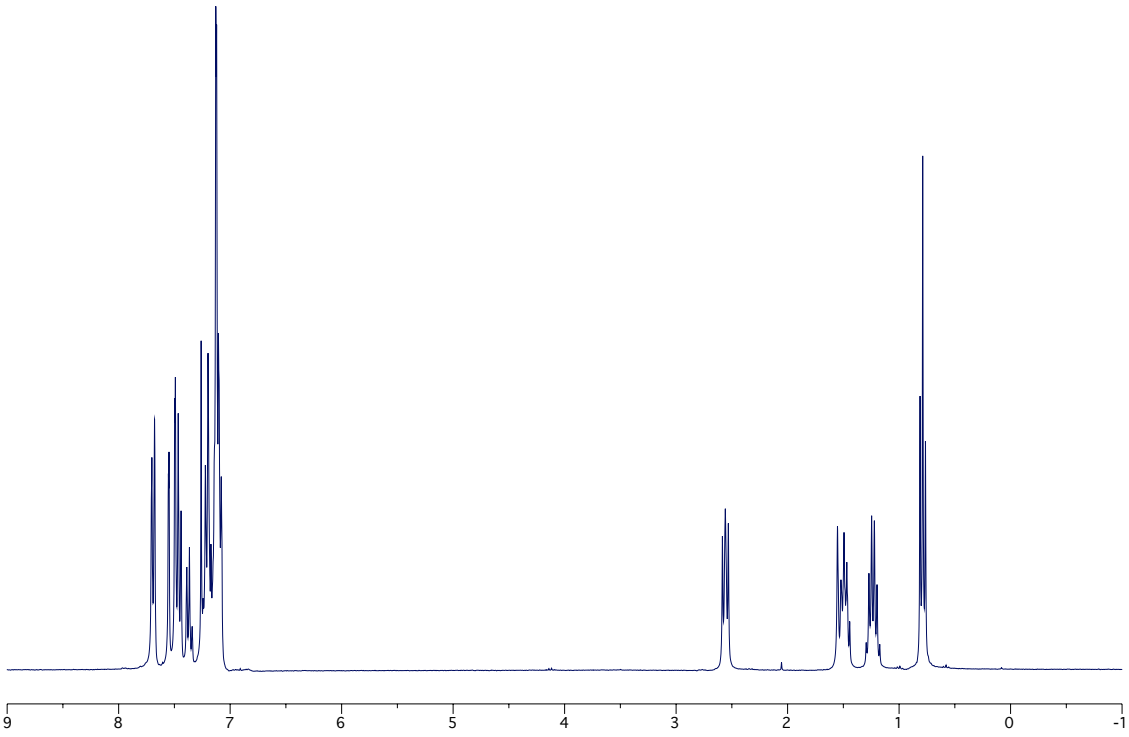

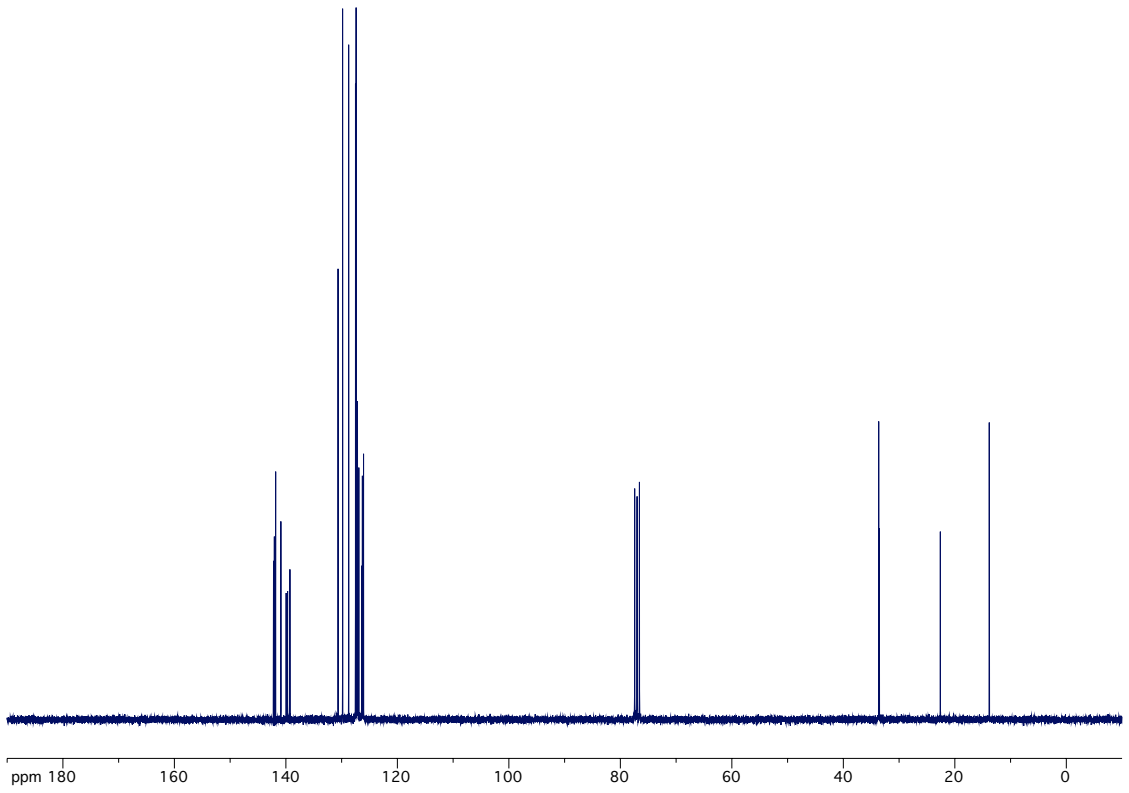

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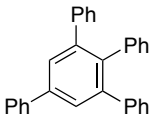

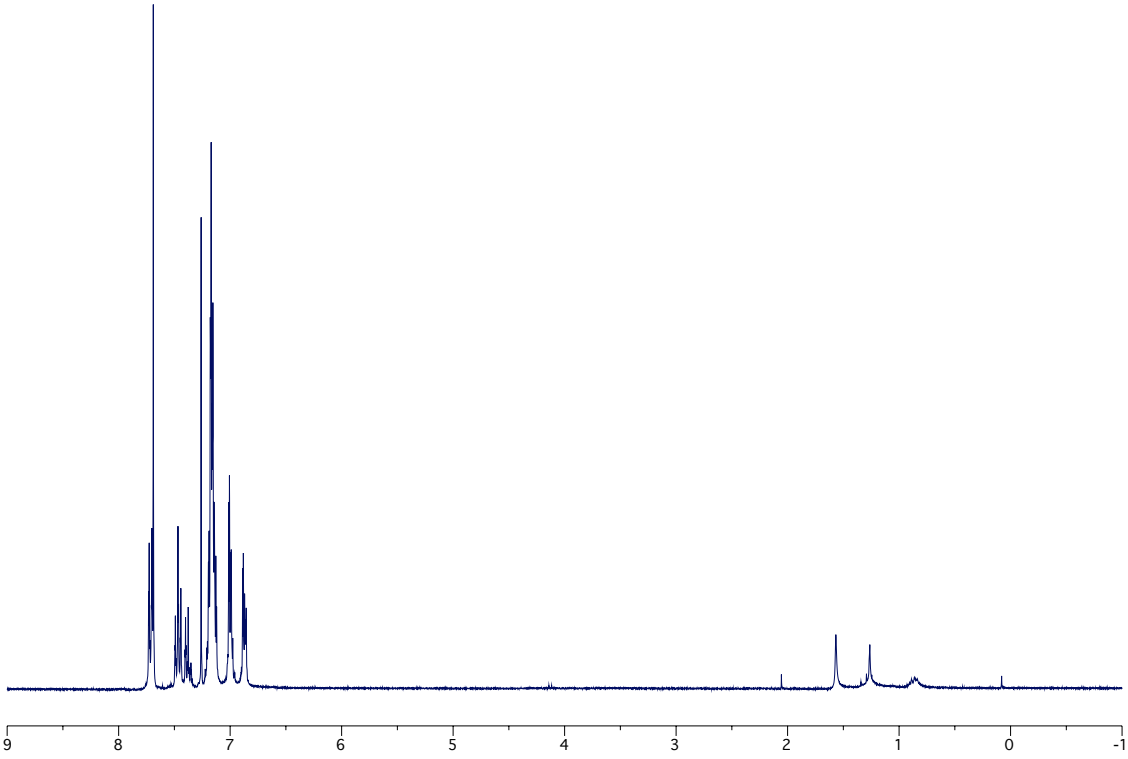

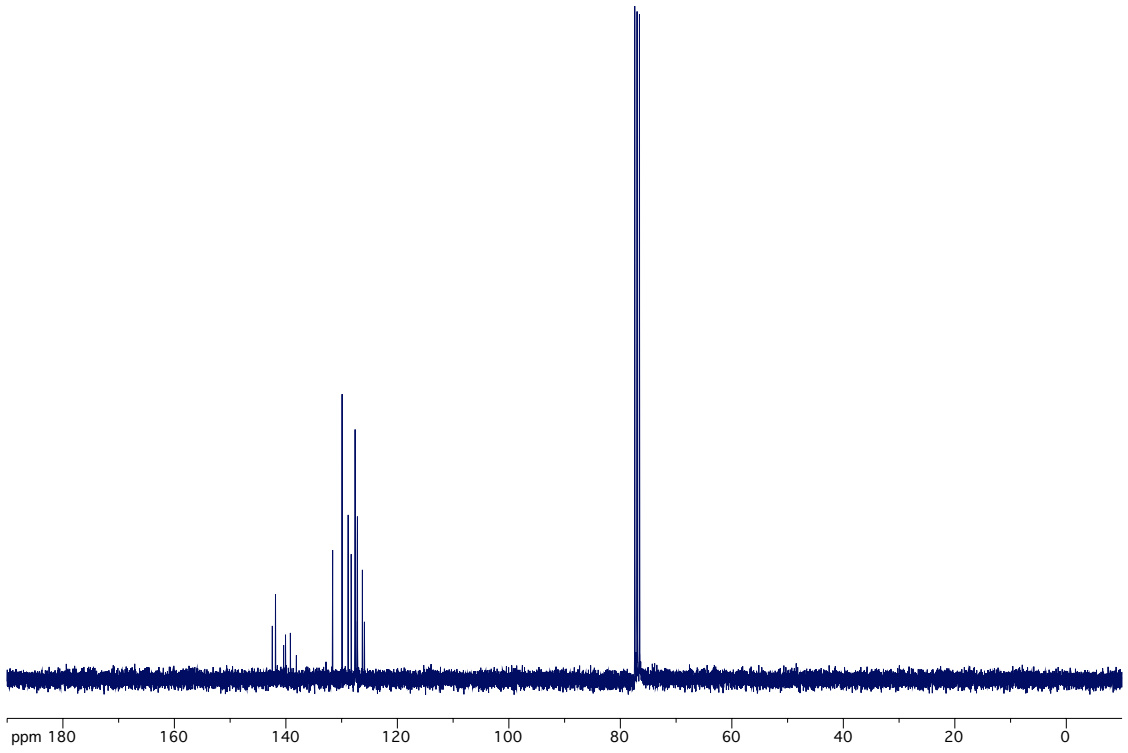

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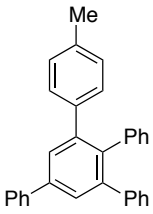

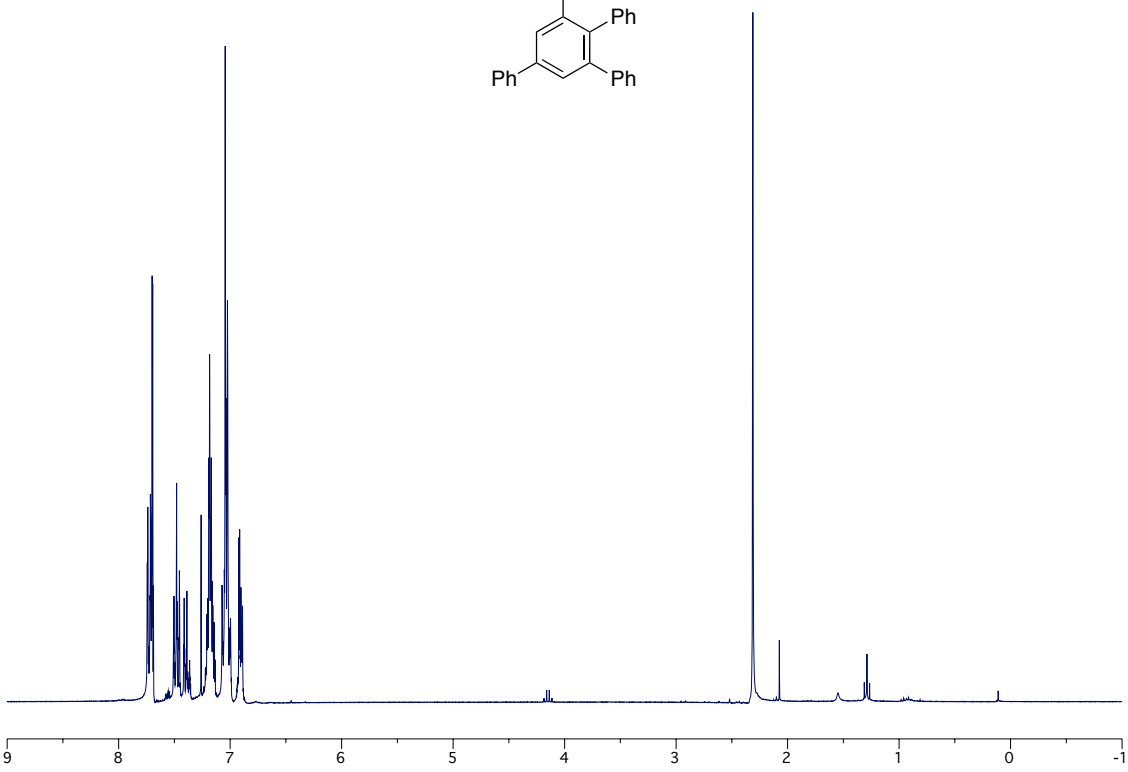

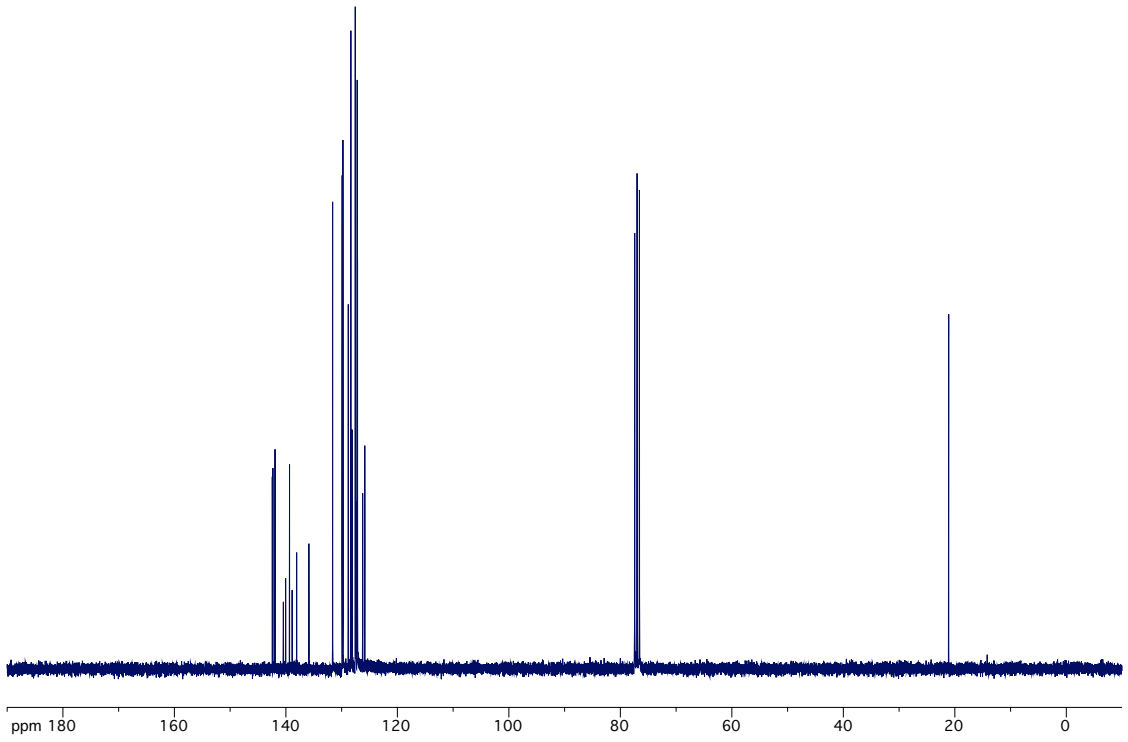

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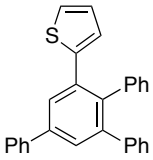

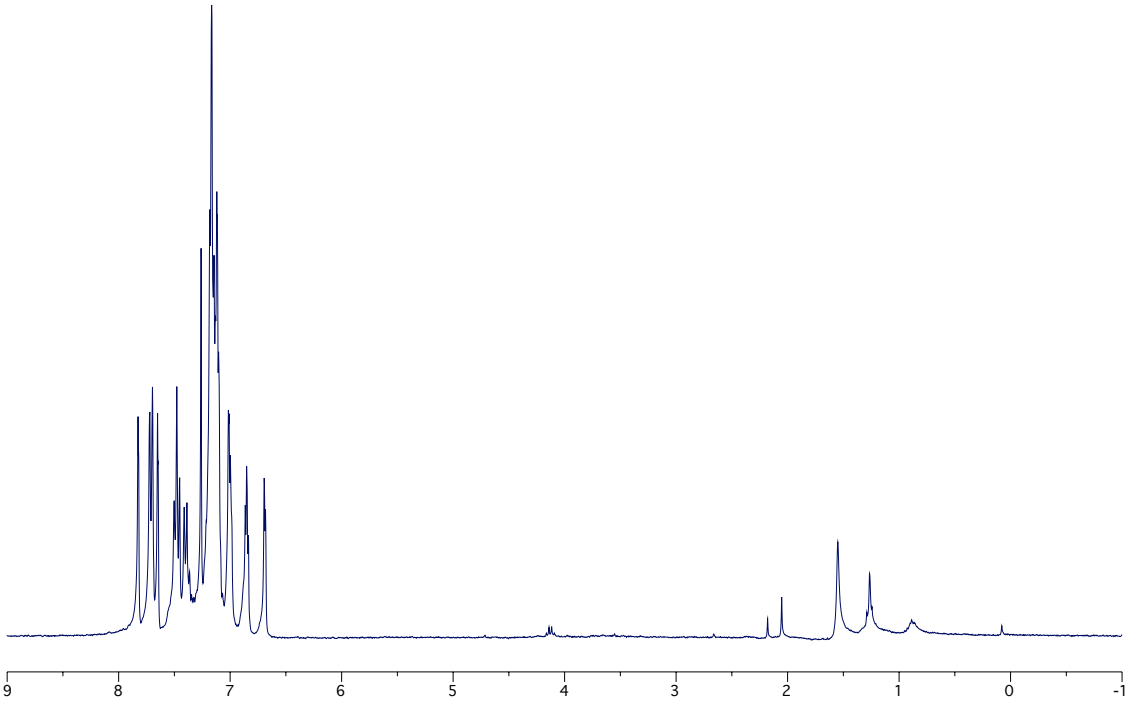

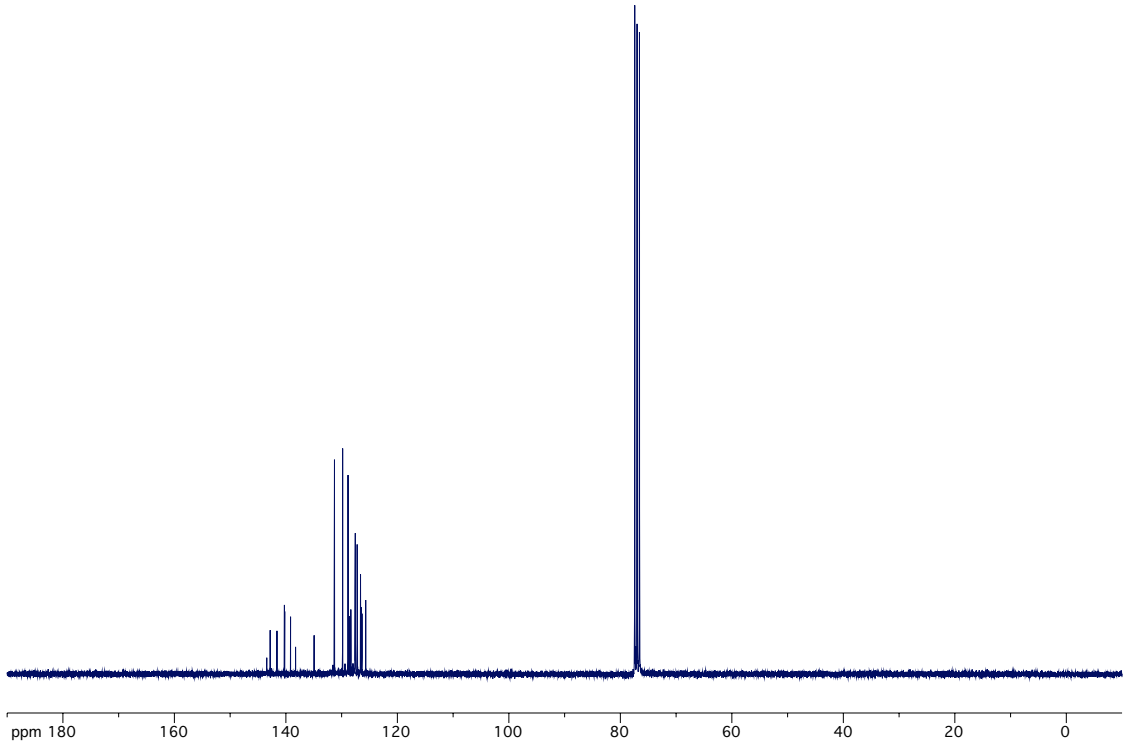

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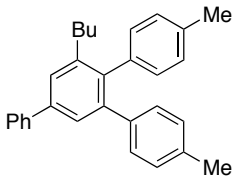

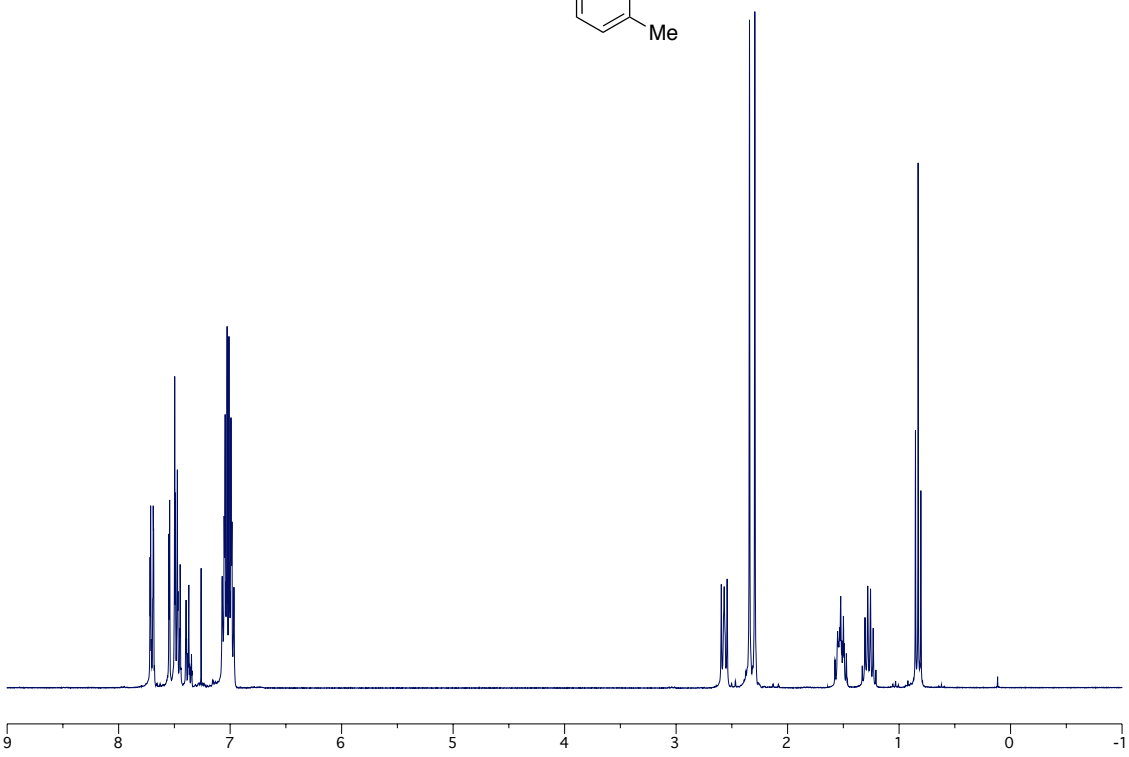

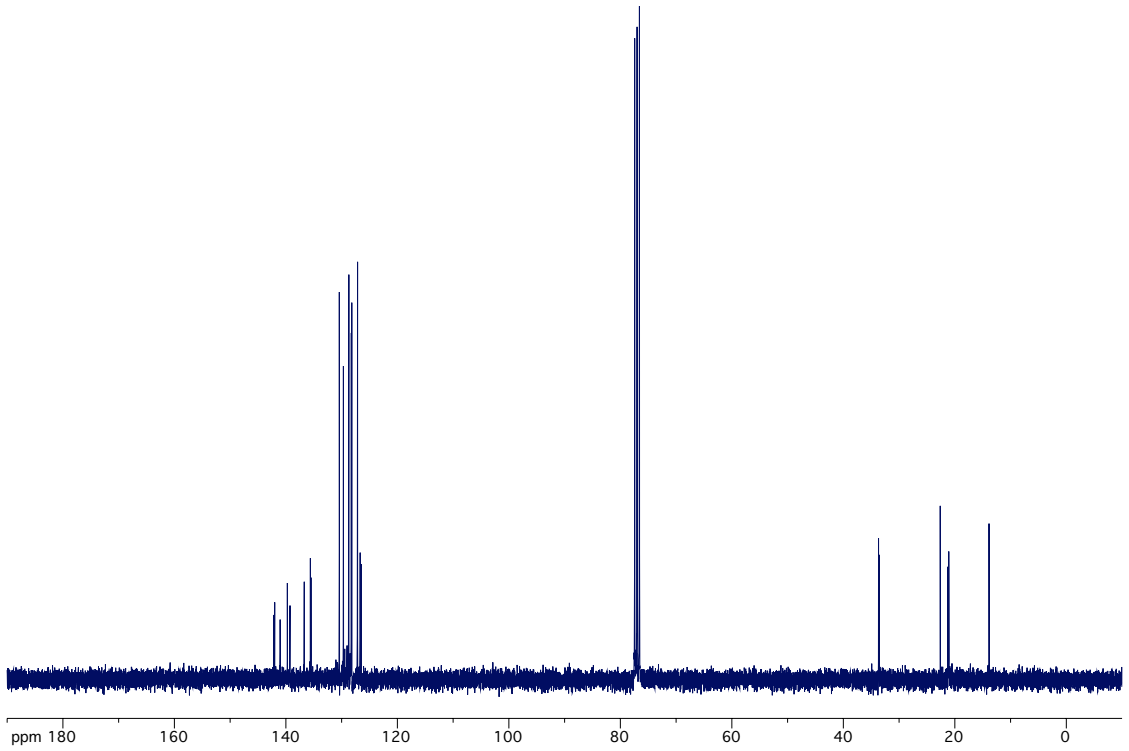

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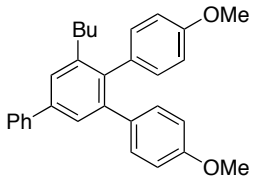

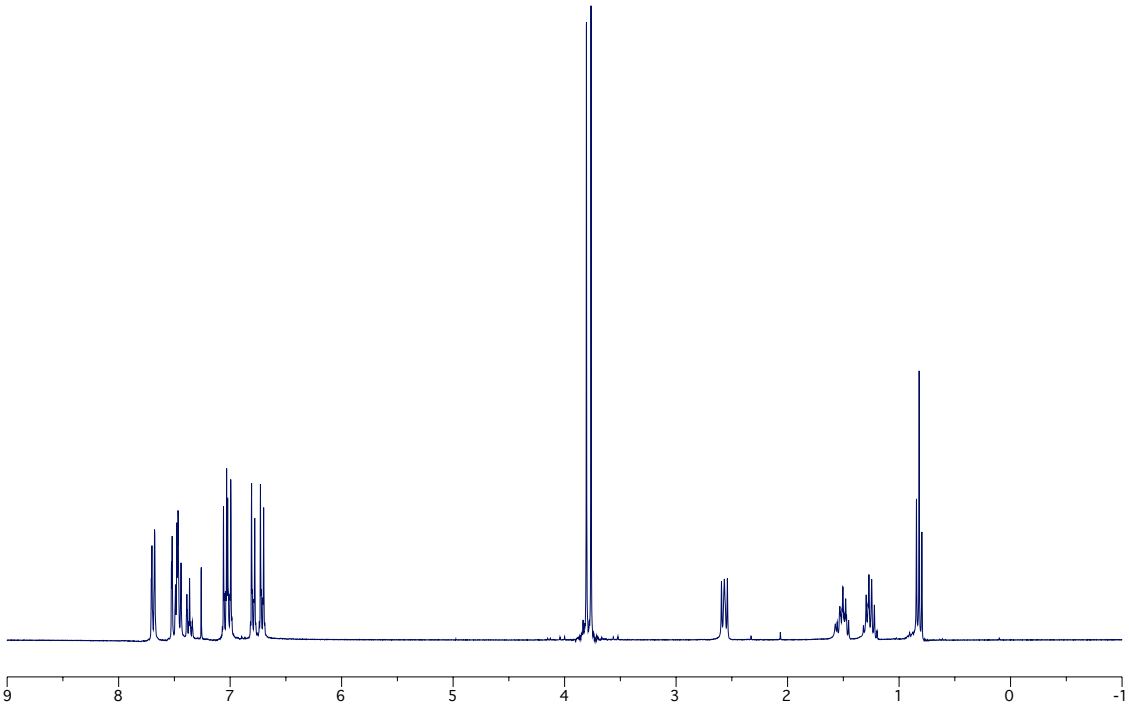

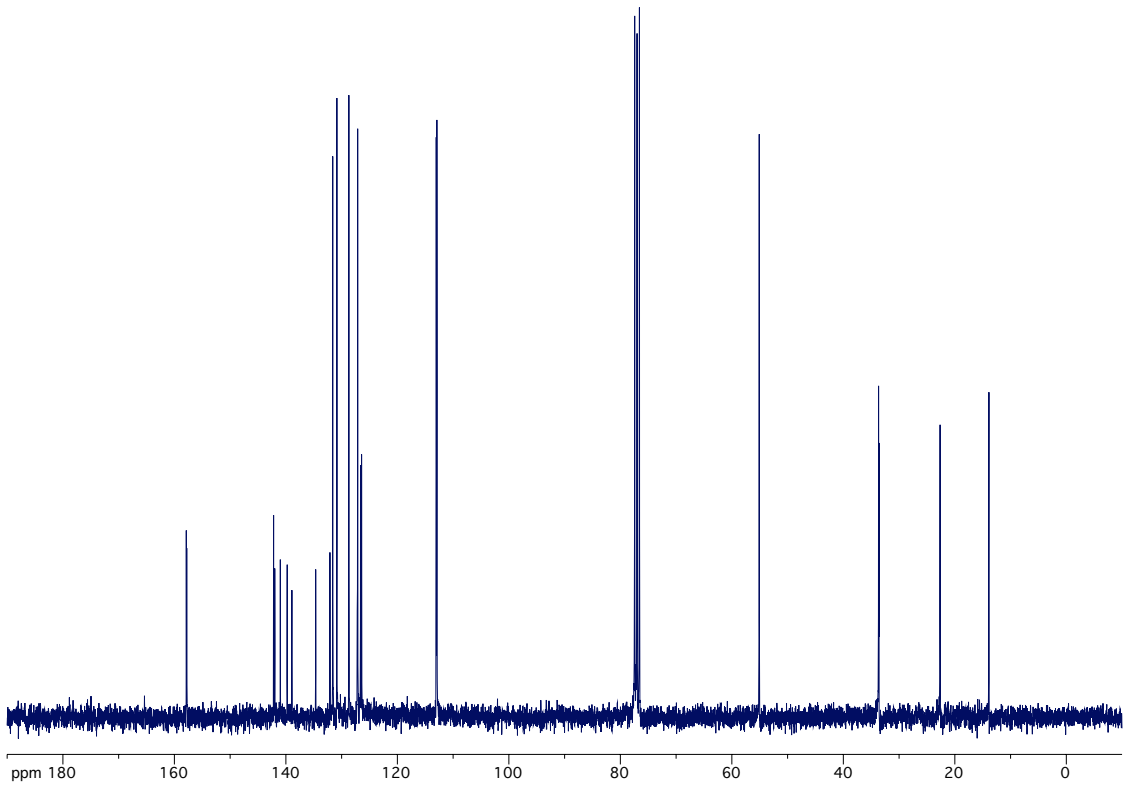

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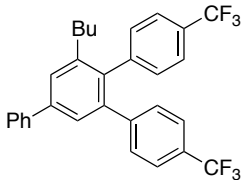

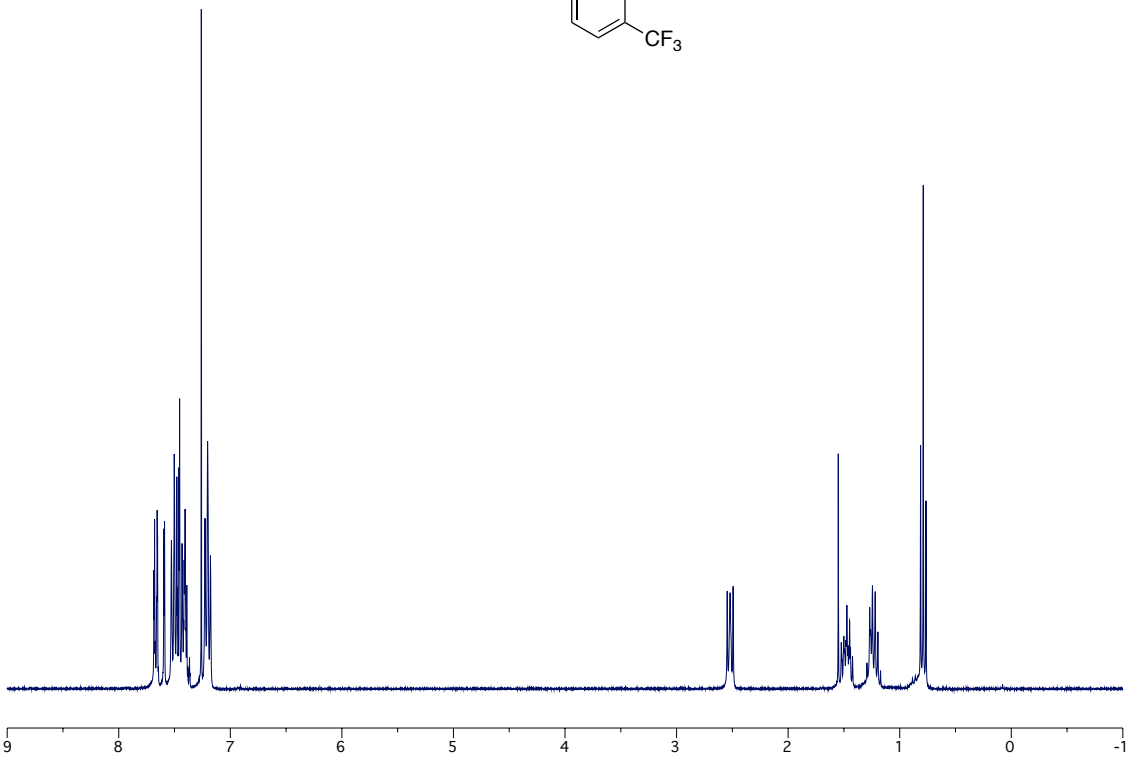

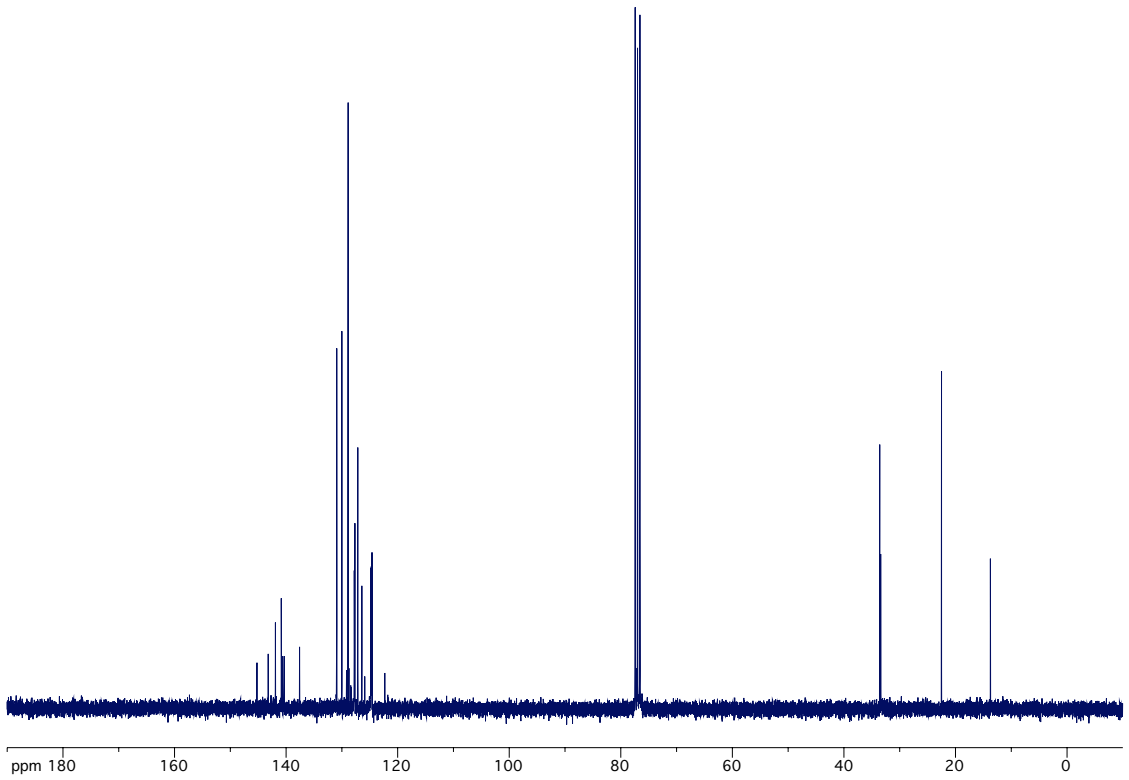

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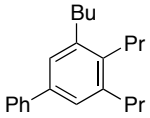

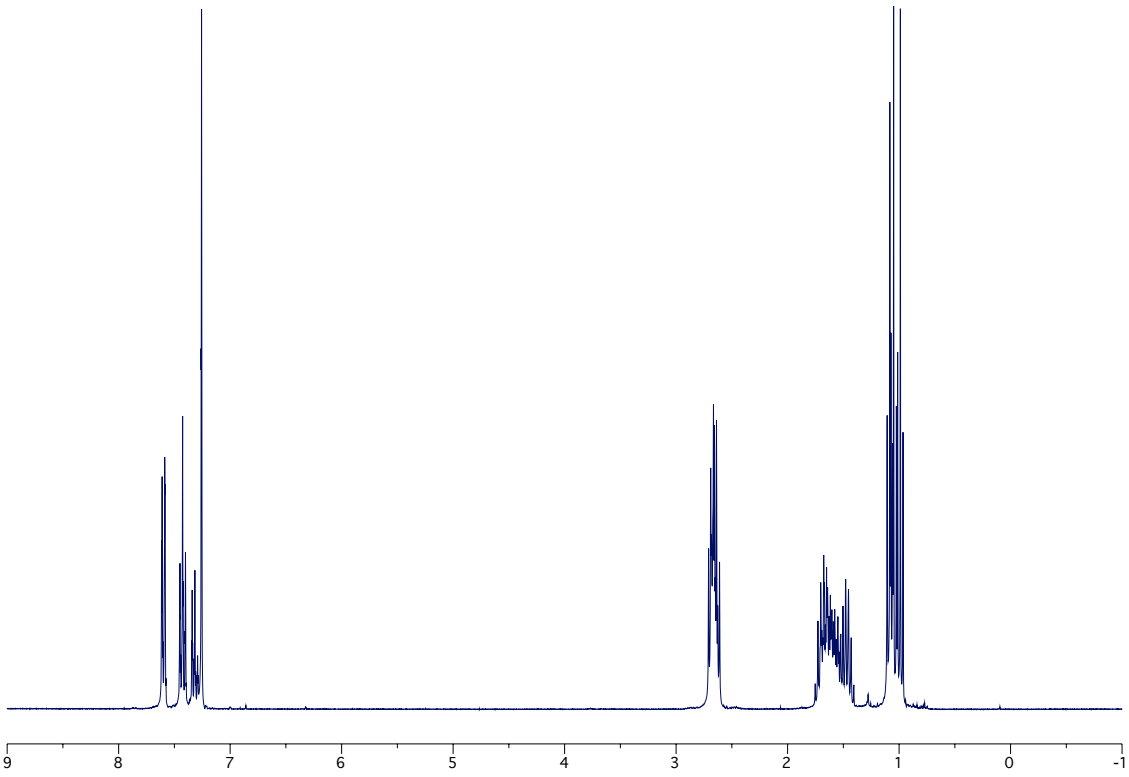

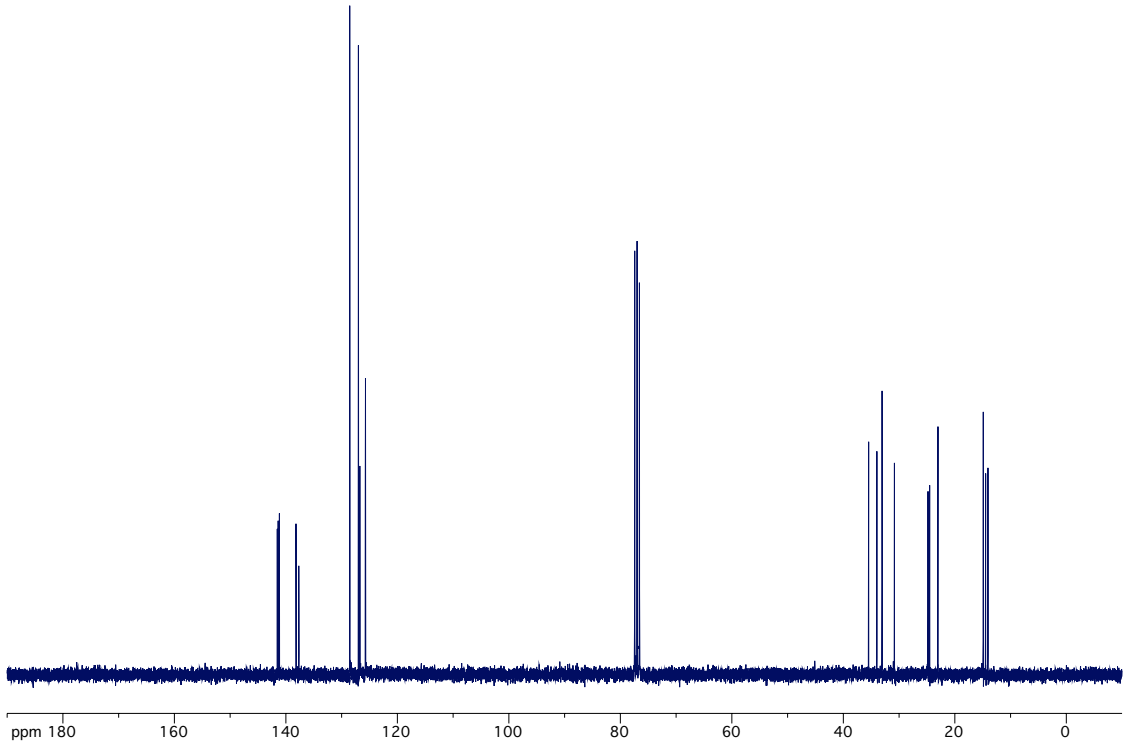

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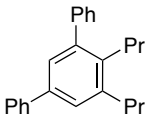

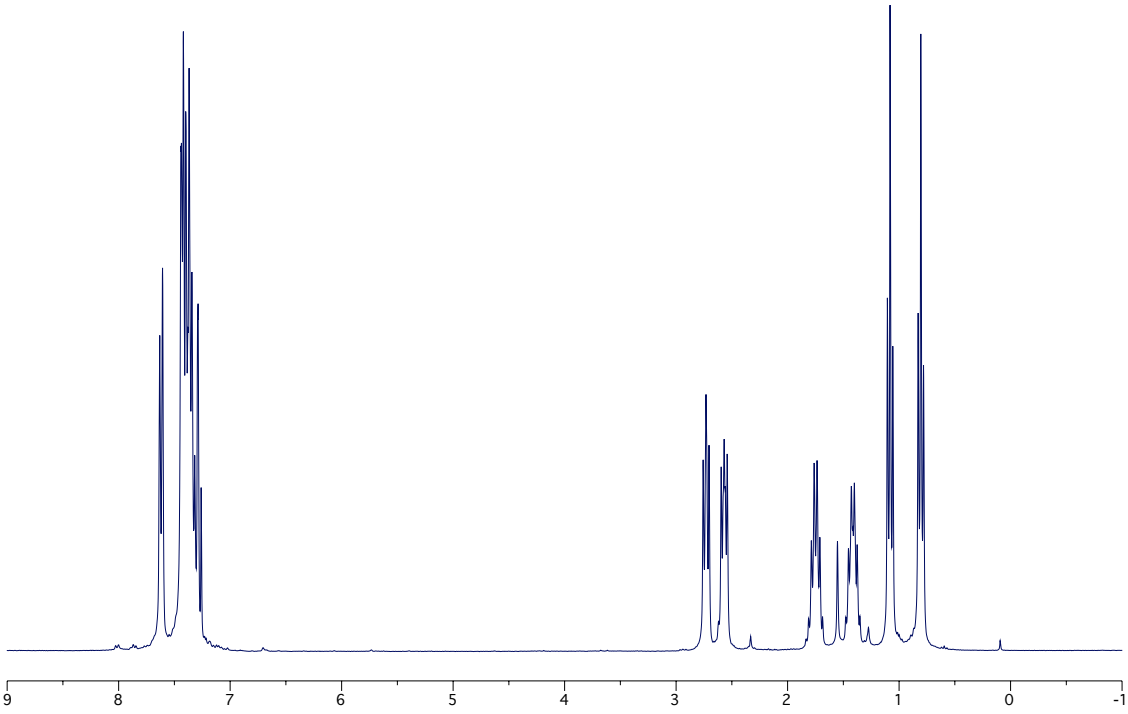

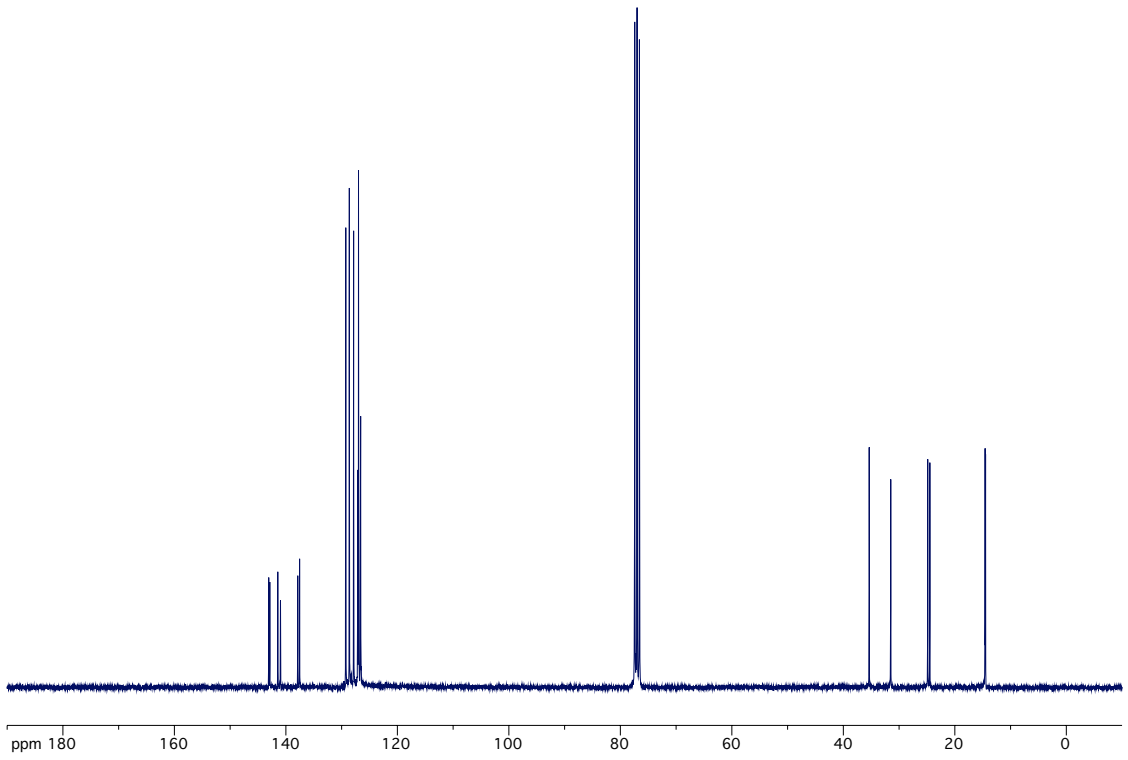

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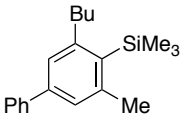
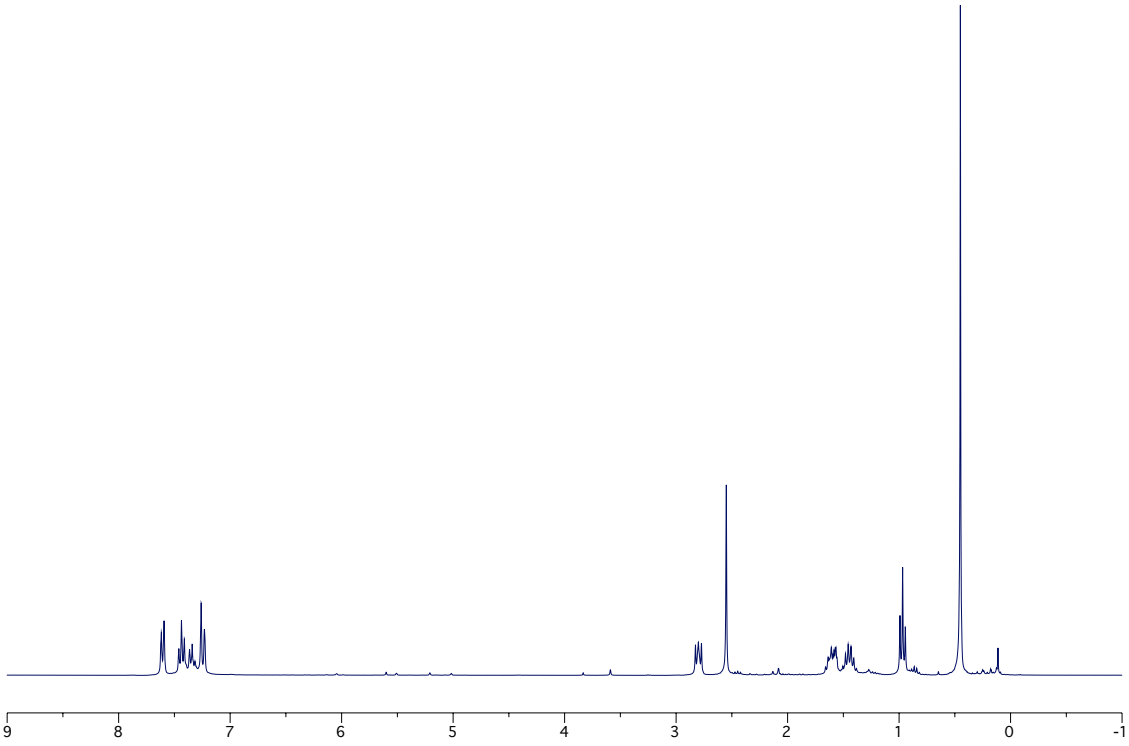
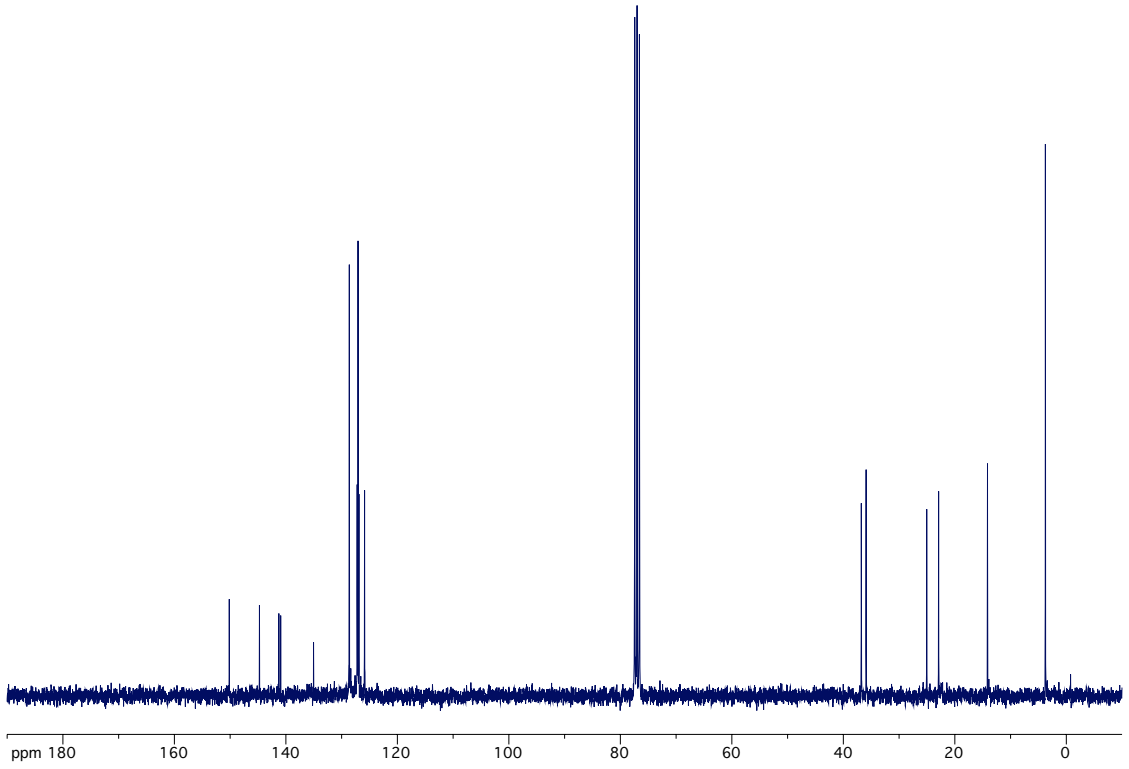
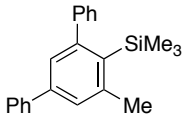
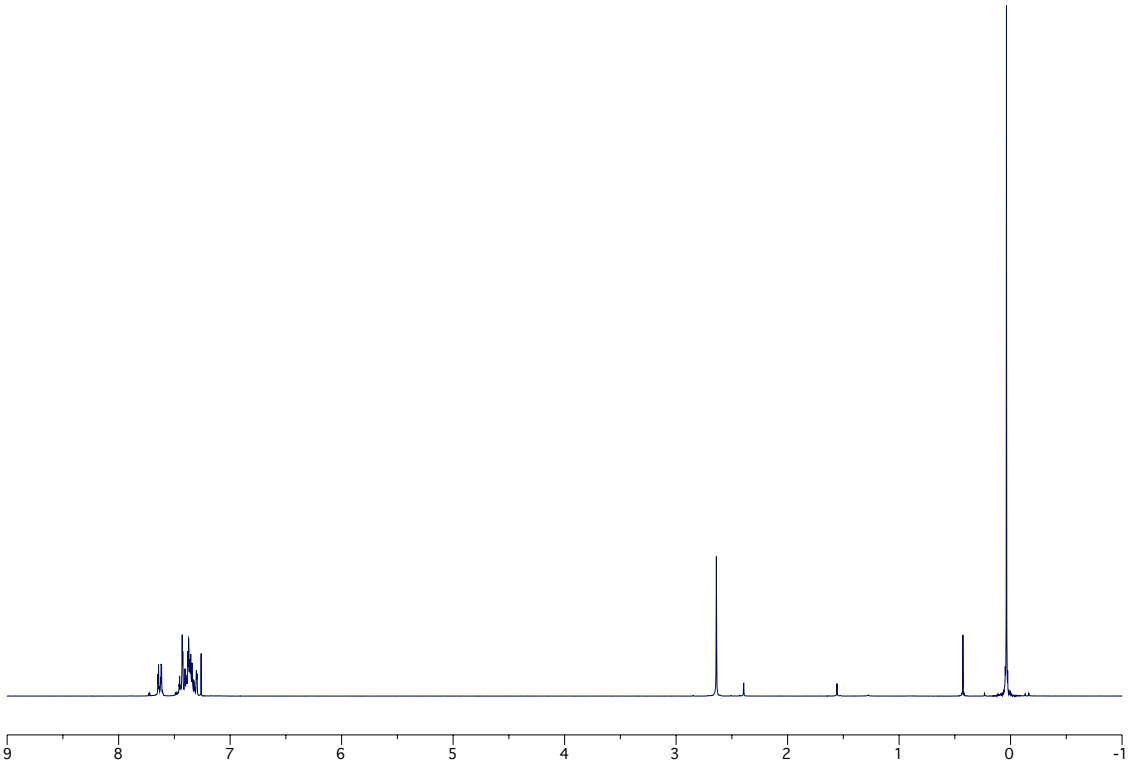


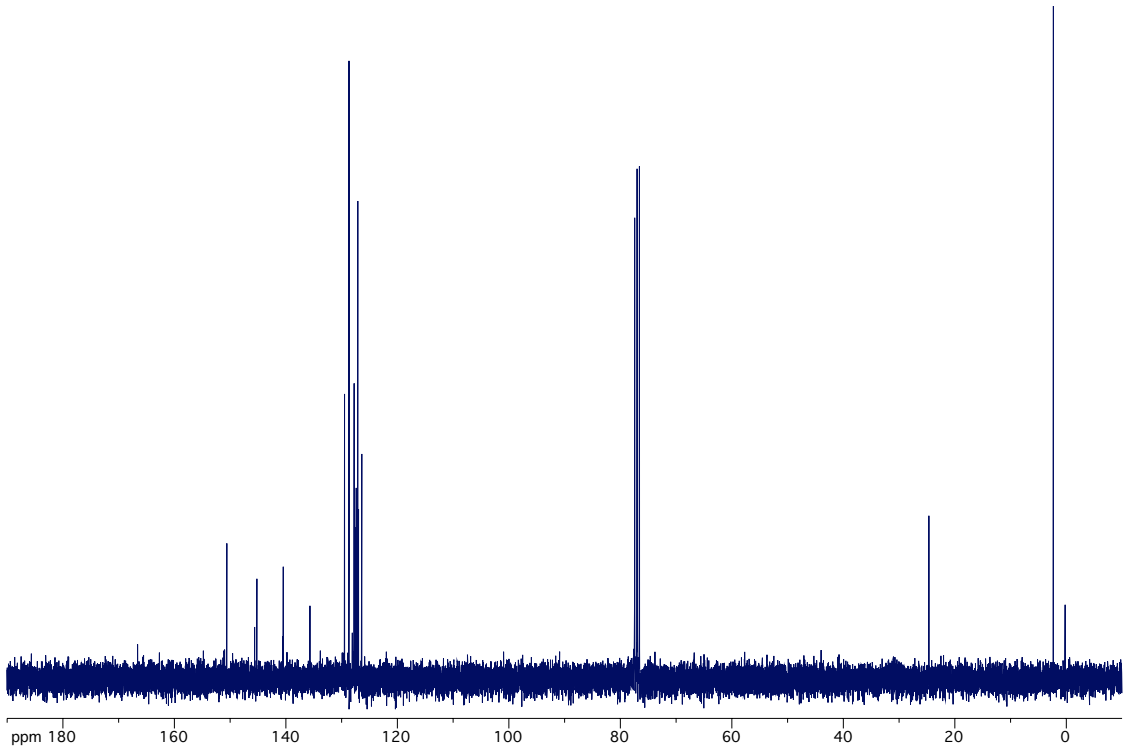




3l







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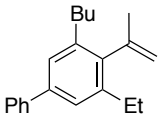

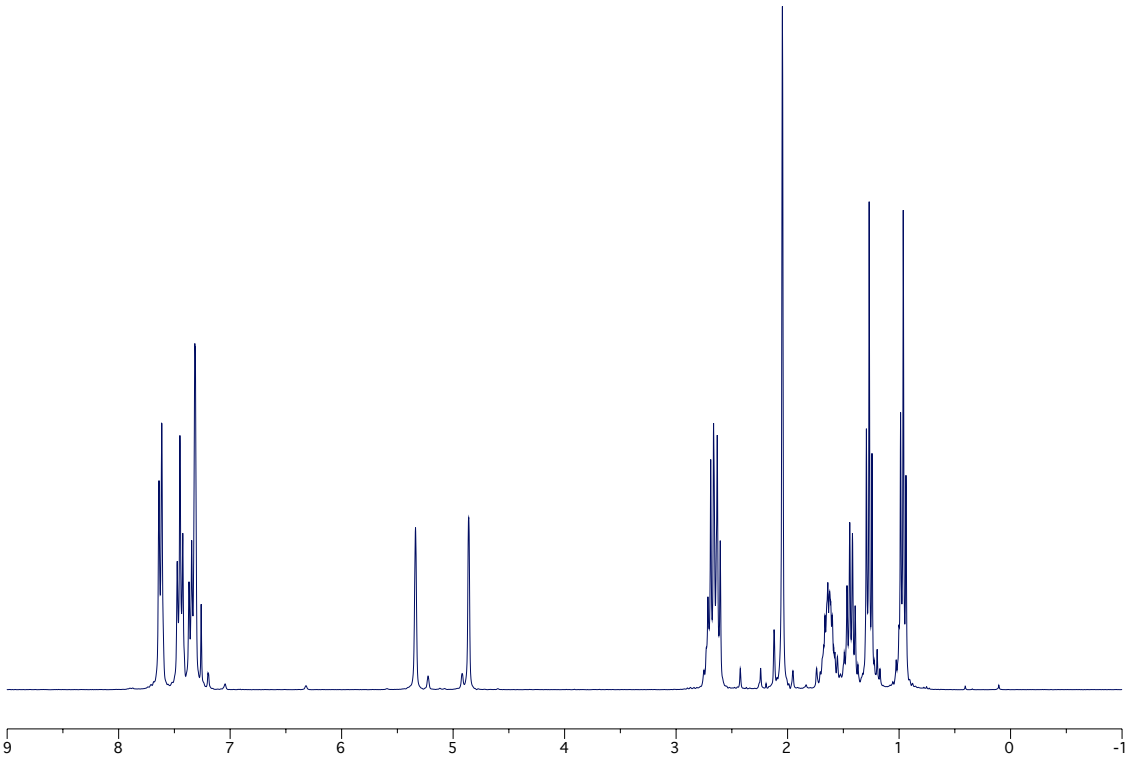

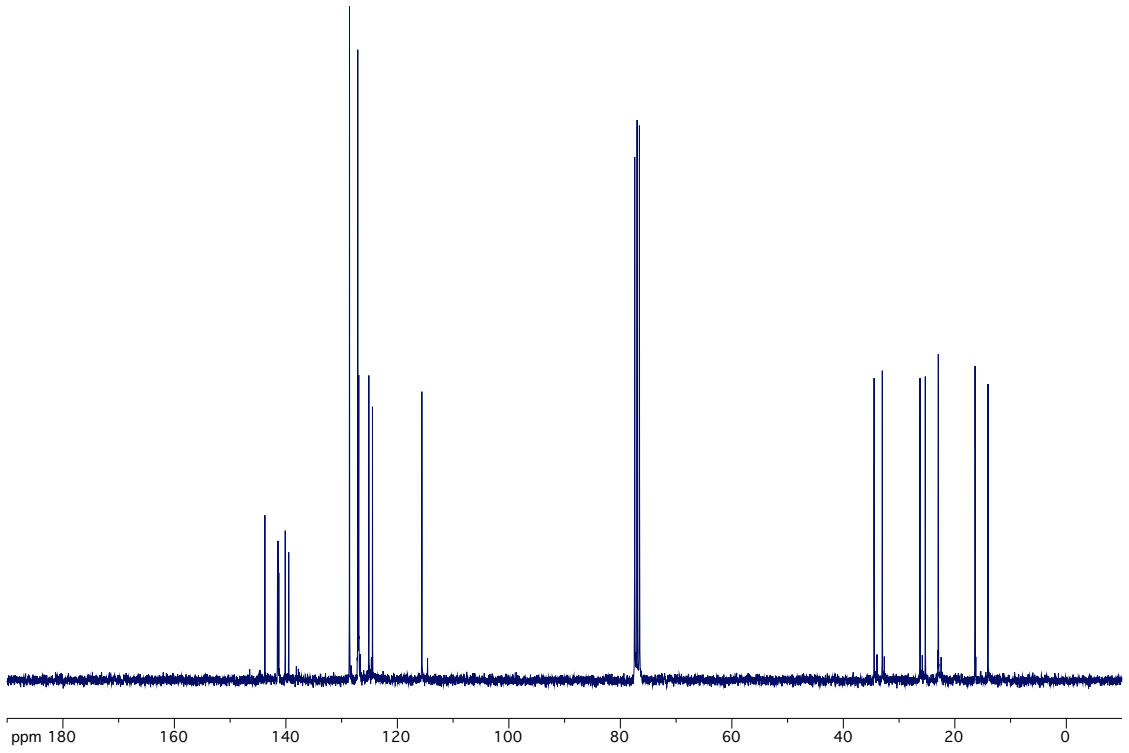

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