Iridium-Catalyzed, Substrate-Directed C–H Borylation Reactions of Benzylic Amines

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Supporting Information

Contents:

General methods

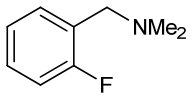
All procedures involving air- or moisture-sensitive reagents were performed in oven-dried glassware under purified nitrogen, either in an MBraun inert atmosphere glovebox or by standard Schlenk techniques. All solvents were dried and degassed by standard procedures unless employed for extraction or purification. In all procedures, unless otherwise noted, concentration was performed by rotary evaporation. TLC analysis was performed on Whatman 60 Å silica layer fluorescence UV plates or Fluka 60 Å neutral or basic aluminum oxide layer fluorescence UV plates. Flash column chromatography was carried out on hand-packed columns of aluminum oxide, basic or neutral, Brockman I, 50-200 μm, 60 Å or hand packed columns of silica gel, 40-63μm, 60 Å.

NMR spectra were collected on a ^{UNITY}Inova spectrometer at 500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR or on a Mercury spectrometer at 100 MHz for ^{13}C NMR, 128 MHz for ^{11}B NMR. The ^{11}B NMR spectra were processed by adding 15 points of backward linear prediction to remove the glass peaks from the broadband probe. ^{1}H NMR spectra are referenced to $CDCl_3$ at 7.26 ppm, or to an internal tetramethylsilane (TMS) standard at 0.00 ppm. The ^{1}H NMR spectral data are reported as follows: chemical shift ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, hex = hextet, sep = septet, oct = octet, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra are referenced to $CDCl_3$ at 77.0 ppm. ^{11}B NMR spectra were referenced to an external $BF_3{\cdot}Et_2O$ sample in $CDCl_3$ (0.0 ppm). Attenuated total reflection IR (ATR-IR) spectra were obtained with a Jasco FT-IR-480 plus and absorptions reported in cm^{-1}.

All deuterated solvents (except chloroform-*d*) were distilled from CaH_2, degassed and stored in a glovebox. Bis(pinacolato)diboron, 2-(aminomethyl)pyridine, 2-[(dimethylaminomethyl)]pyridine, $[Ir(\mu\text{-OMe})(COD)]_2$, 4,4'-di-*tert*-butylbipyridine, ethylenediamine, *o*-phenylenediamine, 2-(diphenylphosphino)ethylamine, 4-trifluoromethyl-1,2-phenylenediamine, and all required benzylbromides were purchased and employed without purification. Benzylamines **3a** and **3e** were purchased from commercial sources and liquids were distilled and degassed before being taken into the glovebox. Benzylic amines[1] **3b**,[2] **3d**,[3] **3f**,[4] **3g**,[2] **3i**,[2] **3j**,[5] **5c**[6,7] and pyridine hydrazone **S-14**[8] were synthesized by known procedures.

General Procedure A for the Synthesis of Benzylamines[1]

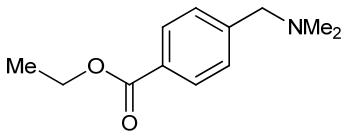
A solution of benzylbromide (5 mmol) and dimethylamine (5.4 mL, 42.7 mmol, 40% w/v in water) in ethanol was heated at reflux temperature for 4 h, cooled, and acidified to pH 1 with 12 M hydrochloric acid. The solution was concentrated *in vacuo* and then basified to pH 14 with 1 M aqueous sodium hydroxide. The aqueous layer was extracted with diethyl ether (3 × 20 mL) and the combined organic phase was washed with saturated aqueous sodium chloride (3 × 30 mL) and water (3 × 30 mL) and then dried ($MgSO_4$). The solution was filtered through Celite and rinsed with diethyl ether, and then concentrated *in vacuo*. The product was purified by silica gel chromatography (short plug) with 400 mL CH_2Cl_2 (discarded) followed by 1500 mL of a 1% solution of triethylamine in ethyl acetate to provide the benzylic amine upon concentrating *in vacuo*.



3c

2-fluoro-*N*, *N*-dimethylbenzylamine (3c)[9]

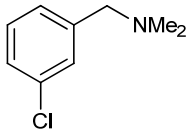
General Procedure A was followed to provide **3c** as a colorless oil (1.046 g, 33%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 1H), 7.23 (m, 1H), 7.10 (m, 1H), 7.03 (m, 1H), 3.49 (s, 2H), 2.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, J = 246.2 Hz), 133.1 (d, J = 4.4 Hz), 128.8 (d, J = 8.1 Hz), 125.4 (d, J = 13.5 Hz), 123.8 (d, J = 3.7 Hz), 115.2 (d, J = 22.1 Hz), 56.6 (d, J = 2.2 Hz), 45.2; IR (neat) 2818, 2769, 1489, 1455, 1366, 1227, 1024, 861, 754 cm^{-1}.



3h

4-(dimethylaminomethyl)ethylbenzoate (3h)

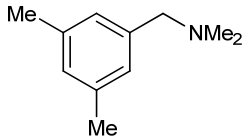
General Procedure A was followed to provide **3h** as a yellow oil (4.599 g, 51%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 4.36 (q, *J* = 7.3 Hz, 2H), 3.46 (s, 2H), 2.23 (s, 6H), 1.38 (t, *J* = 7.3 Hz, 3H); ^{13}C (125 MHz, $CDCl_3$) δ 166.6, 144.2, 129.6, 129.4, 128.9, 64.1, 60.9, 45.4, 14.4; IR (neat) 2977, 2768, 1715, 1611, 1270, 864, 755, 700, 521; HRMS (CI) calcd for $(C_{12}H_{17}NO_2 + H)^+$ 208.1338, found 208.1344.



3k

3-chloro-*N*,*N*-dimethylbenzylamine (3k)

General Procedure A was followed to provide **3k** as a yellow oil (1.398 g, 40%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.29-7.20 (m, 3H), 3.42 (s, 2H), 2.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 134.4, 129.7, 129.2, 127.4, 127.3, 64.0, 45.6; IR (neat) 2771, 1620, 1495, 1359, 1096, 1032, 877, 777, 683 cm^{-1}.



3l

3,5-dimethyl-*N*,*N*-dimethylbenzylamine (3l)

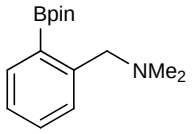
General Procedure A was followed to provide **3l** as a colorless oil (2.329 g, 66%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (s, 2H), 6.90 (s, 1H), 3.34 (s, 2H), 2.30 (s, 6H), 2.24 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 137.7, 128.6, 126.9, 64.5, 45.5, 21.2; IR (neat) 2942, 2771, 1739, 1456, 1238, 1043, 729 cm^{-1}; HRMS (CI) calcd for $(C_{11}H_{17}N + H)^+$ 164.1439, found 164.1438.

General Procedure B for Reactions Monitored by NMR Spectroscopy

To a PTFE-valved NMR tube (J. Young tube), was added B_2pin_2 (0.021 g, 0.082 mmol), [Ir(μ-OMe)(COD)]$_2$ (0.001 g, 0.002 mmol), ligand (0.004 mmol), *N*,*N*-dimethylbenzylamine (0.025 mL, 0.166 mmol), and cyclohexane-d_{12} (0.50 mL). The sealed J. Young tube was heated to 70 °C in an oil bath and periodically cooled to monitor reaction progress by ^{1}H NMR spectroscopy.

General Procedure C for the C–H Borylation of Benzylic Amines:

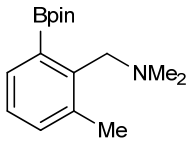
To a 50 mL PTFE-valved reaction tube, equipped with a stir bar and charged with [Ir(μ-OMe)(COD)]$_2$ (0.020 g, 0.015 mmol), was added 2-(aminomethyl)pyridine (0.0062 mL, 0.030 mmol), B_2pin_2 (0.423 g, 1.67 mmol), benzylamine (2.00 mmol), and 4.0 mL of methylcyclohexane. After 16 h at 70 °C, the volatiles were removed *in vacuo*. Purification by flash column chromatography provided the corresponding boronate ester. The carbon directly attached to the boron atom was not seen by ^{13}C NMR spectroscopy in all cases.[7]



1a

Borylation of *N*,*N*-dimethylbenzylamine (1a)

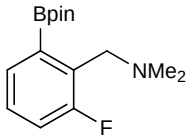
General procedure C was followed with *N*,*N*-dimethylbenzylamine (0.240 mL, 2.00 mmol). Purification by basic alumina flash column chromatography (98:1:1 CH_2Cl_2:MeOH:NEt_3) provided **1a** as a white solid (0.381 g, 73%): mp 60–63 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.1 Hz, 1H,), 7.19 (m, 2H), 7.00 (d, *J* = 7.6 Hz, 1H), 3.85 (s, 2H), 2.56 (s, 6H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 134.5, 131.5, 127.5, 127.3, 123.1, 80.5, 65.4, 45.7, 26.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 14.8; IR (ATR) 2987, 1472, 1357, 1149, 1042, 853, 752, 691 cm^{-1}; HRMS (CI) calcd for $(C_{15}H_{24}BNO_2 + H)^+$ 262.1981, found 262.1982.



1b

Borylation of *N*,*N*-dimethyl-2-methylbenzylamine (1b)

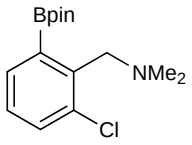
General Procedure C was followed with *N*,*N*-dimethyl-2-methylbenzylamine (0.298 g, 2.00 mmol). Purification by basic alumina flash column chromatography (98.5:0.5:1 CH_2Cl_2:MeOH:NEt_3) provided **1b** as a white solid (0.400 g, 73%): mp 106–110 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.3 Hz, 1H), 3.83 (s, 2H), 2.60 (s, 6H), 2.13 (s, 3H), 1.29 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 131.3, 128.5, 128.4, 127.3, 80.1, 64.2, 45.9, 26.8, 18.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 13.5; IR (ATR): 2977, 2928, 1460, 1242, 1085, 781, 694, 611 cm^{-1}; HRMS (CI) calcd for ($C_{16}H_{26}BNO_2$ + H)$^+$ 276.2138, found 276.2137.



1c

Borylation of 2-fluoro-*N*,*N*-dimethylbenzylamine (1c)

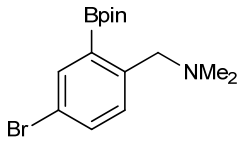
General Procedure C was followed with 2-fluoro-*N*,*N*-dimethylbenzylamine (0.306 g, 2.00 mmol). Purification by basic alumina flash column chromatography (98.5:0.5:1 CH_2Cl_2:MeOH:NEt_3) provided **1c** as a white solid (0.414 g, 74%): mp 79–81 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.3 Hz, 1H), 7.20 (m, 1H), 6.85 (t, *J* = 8.8 Hz, 1H), 3.91 (s, 2H), 2.59 (s, 6H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3 (d, *J* = 247.4 Hz), 129.2 (d, *J* = 5.9 Hz), 126.6 (d, *J* = 2.9 Hz), 125.0 (d, *J* = 12.5 Hz), 113.6 (d, *J* = 19.2 Hz), 80.4, 60.5, 45.8, 26.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 14.0; IR (ATR) 2968, 1575, 1467, 1347, 1236, 1152, 1089, 1046, 978, 907, 844, 784, 733 608 cm^{-1}; HRMS (CI) calcd for ($C_{15}H_{23}BFNO_2$ + H)$^+$ 280.1887, found 280.1887.



1d

Borylation of 2-chloro-*N*,*N*-dimethylbenzylamine (1d)

General Procedure C was followed with 2-chloro-*N*,*N*-dimethylbenzylamine (0.339 g, 2.00 mmol). Purification by basic alumina flash column chromatography (99:0.5:0.5 CH_2Cl_2:MeOH:NEt_3) provided **1d** as an off-white solid (0.449 g, 76%): mp 69–72 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (m, 1H), 7.19 (m, 2H), 3.95 (s, 2H), 2.63 (s, 6H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 129.3, 129.2, 129.1, 127.4, 80.4, 63.8, 45.9, 26.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 14.6; IR (thin film) 3055, 2991, 2934, 1561, 1461, 1440, 1341, 1266, 1239, 1058, 963, 731, 697, 605 cm^{-1}; HRMS (CI) calcd for $(C_{15}H_{23}BClNO_2 + H)^+$ 296.1591, found 296.1587.

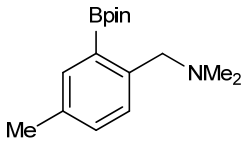


1f

Borylation of 4-bromo-*N*,*N*-dimethylbenzylamine (1f)

General Procedure C was followed with 4-bromo-*N*,*N*-dimethylbenzylamine (0.428 g, 2.00 mmol). Purification by basic alumina flash column chromatography (98.5:0.5:1 CH_2Cl_2:MeOH:NEt_3) provided **1f** as a white solid (0.252 g, 37%): mp 133–135 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.28 (dd, J = 8.0, 1.5 Hz, 1H), 6.88 (d, J = 8.0 Hz), 3.79 (s, 2H), 2.56 (s, 6H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 134.2, 130.3, 124.6, 121.9, 80.5, 64.9, 46.7, 26.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 13.8; IR (ATR) 2975, 2927, 1461,

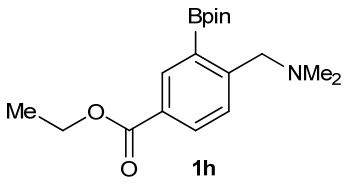
1152, 1086, 963, 694 cm^{-1}; HRMS (CI) calcd for $(C_{15}H_{23}BBrNO_2 + H)^+$ 340.1086, found 340.1084.



1g

Borylation of *N*,*N*-dimethyl-4-methylbenzylamine (1g)

General Procedure C was followed with *N*,*N*-dimethyl-4-methylbenzylamine (0.298 g, 2.00 mmol). Purification by basic alumina flash column chromatography (98.5:0.5:1.0 CH_2Cl_2:MeOH:NEt_3) provided a 74:26 mixture of **1g**:**2g** as a white solid (0.449 g, 81%): mp 89–96 °C; IR (thin film) 2971, 2928, 1580, 1459, 1359, 1247, 1149, 1042, 965, 852, 737, 683 cm^{-1}; ^{11}B NMR (128 MHz, $CDCl_3$) δ 15.4. **1g**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (s, 1H), 6.98 (dd, *J* = 7.6, 1.0 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 3.79 (s, 2H), 2.52 (s, 6H), 2.30 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 135.0, 132.1, 128.2, 122.9, 80.4, 65.1, 45.5, 26.5, 21.3; HRMS (CI) calcd for $(C_{16}H_{26}BNO_2 + H)^+$ 276.2138, found 276.2134. **2g (**characteristic spectral data): ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (s, 2H), 4.10 (s, 2H), 2.59 (s, 6H), 1.29 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 136.3, 135.2, 81.4, 66.3, 45.7, 25.8, 21.1.

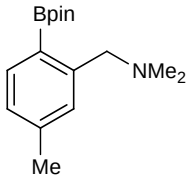


1h

Borylation of 4-(dimethylaminomethyl)ethylbenzoate (1h)

General Procedure C was followed with (4-dimethylaminomethyl)ethylbenzoate (0.474 g, 2.00 mmol). Purification by basic alumina flash column chromatography (99:0.5:0.5

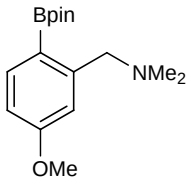
CH_2Cl_2:MeOH:NEt_3) followed by Kugelrohr distillation (0.5 mmHg , up to 90 °C to remove **2h**) provided **1h** as a pale yellow oil (0.326 g, 49%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 1.7 Hz, 1H), 7.89 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 2H), 2.57 (s, 6H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.32 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 144.7, 132.8, 129.5, 129.2, 122.8, 80.6, 65.2, 60.5, 45.7, 26.4, 14.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 14.4; IR (neat) 2965, 1712, 1605, 1365, 1239, 1210, 1099, 908, 848, 784, 761, 726, 627 cm^{-1}; HRMS (CI) calcd for $(C_{16}H_{26}BNO_2 + H)^+$ 334.2193, found 334.2193.



1i

Borylation of *N*,*N*-dimethyl-3-methylbenzylamine (1i)

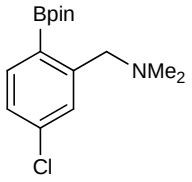
General Procedure C was followed with *N*,*N*-dimethyl-3-methylbenzylamine (0.298 g, 2.00 mmol). Purification by basic alumina flash column chromatography (98.5:0.5:0.5 CH_2Cl_2:MeOH:NEt_3) provided **1i** as a white solid (0.302 g, 55%): mp 89–96 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.83 (s, 1H), 3.78 (s, 2H), 2.51 (s, 6H), 2.29 (s, 3H), 1.30 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 137.1, 131.5, 128.0, 124.0, 80.4, 65.1, 45.6, 26.4, 21.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 16.0; IR (thin film) 2967, 2890, 1613, 1458, 1381, 1145, 1118, 988, 849, 815, 775 cm^{-1}; HRMS (CI) calcd for $(C_{16}H_{26}BNO_2 + H)^+$ 276.2138, found 276.2130.



1j

Borylation of 3-methoxy-*N*,*N*-dimethylbenzylamine (1j)

General Procedure C was followed with 3-methoxy-*N*,*N*-dimethylbenzylamine (0.331 g, 2.00 mmol). Purification by basic alumina flash column chromatography (98.5:0.5:1.0 CH_2Cl_2:MeOH:NEt_3) followed by Kugelrohr distillation (0.5 mmHg, up to 90 °C to remove **2j**) provided a 89:11 mixture of **1j:4j** as a pale yellow oil (0.476 g, 82%): IR (neat) 2973, 2833, 1604, 1463, 1347, 1300, 1242, 1150, 1118, 1025, 860, 733, 695, 635 cm^{-1}. **1j:** ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 (d *J* = 7.8 Hz, 1H), 6.78 (dd, *J* = 7.1, 1.6 Hz, 1H), 6.60 (s, 1H), 3.77 (s, 2H), 2.50 (s, 6H), 1.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 144.7, 132.8, 129.6, 129.2, 122.9, 80.7, 65.2, 60.3, 45.7, 26.6, 14.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 17.4; HRMS (CI) calcd for $(C_{16}H_{26}BNO_3 + H)^+$ 292.2087, found 292.2085. **4j (**characteristic spectral data**):** ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 9.1 Hz, 1H), 7.13 (t, *J* = 9.8 Hz, 1H), 6.64 (d, *J* = 8.8 Hz, 1H), 3.78 (s, 2H), 2.54 (s, 6H), 1.34 (s, 12H).

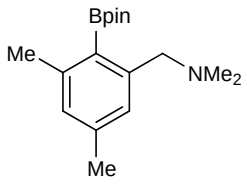


1k

Borylation of 3-chloro-*N*,*N*-dimethylbenzylamine (1k)

General Procedure C was followed with 3-chloro-*N*,*N*-dimethylbenzylamine (0.340 g, 2.00 mmol). Purification by basic alumina flash column chromatography (98.5:0.5:1

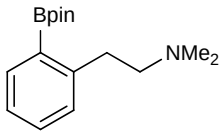
CH_2Cl_2:MeOH:NEt_3) provided a 85:15 of **1k**:**4k** as a white solid (0.320 g, 54%)**:** mp 69–72 °C; ^{11}B NMR (128 MHz, $CDCl_3$) δ 14.6; IR (ATR) 2920, 1360, 1151, 1040, 781, 689 cm^{-1}. **1k:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 9.5 Hz, 1H), 7.17 (dd, *J* = 9.5, 1.6 Hz, 1H), 6.99 (s, 1H), 3.80 (s, 2H), 2.54 (s, 6H), 1.27 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 133.2 132.7, 127.5, 123.1, 80.5, 64.7, 45.7, 26.5; HRMS (CI) calcd for $(C_{15}H_{23}BClNO_2 + H)^+$ 296.1591, found 196.1587. **4k** (characteristic spectral data)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 9.1 Hz, 1H), 7.09 (t, *J* = 9.7 Hz, 1H), 6.87 (d, *J* = 8.9 Hz, 1H), 3.74 (s, 2H), 2.53 (s, 6H), 1.38 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 133.2, 129.0, 128.7, 121.5, 80.1, 64.0, 45.2, 27.5.



1l

Borylation of *N*,*N*-dimethyl-3,5-dimethylbenzylamine (1l)

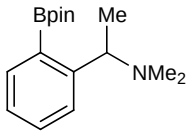
General Procedure C was followed with *N*,*N*-dimethyl-3,5-dimethylbenzylamine (0.298 g, 2.00 mmol). Purification by basic alumina flash column chromatography (99.0:0.5:0.5 CH_2Cl_2:MeOH:NEt_3) provided **1l** as a yellow oil (0.424 g, 73%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80 (s, 1H), 6.63 (s, 1H), 3.63 (s, 2H), 2.46 (s, 3H), 2.45 (s, 6H), 2.23 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 141.1, 137.0, 130.0, 121.9, 80.9, 64.1, 45.2, 27.9, 21.1, 20.5; ^{11}B NMR (128 MHz, $CDCl_3$) δ 17.9; IR (thin film) 2970, 1613, 1456, 1143, 1039, 857, 633 cm^{-1}; HRMS (CI) calcd for $(C_{17}H_{28}BNO_2 + H)^+$ 290.2295, found 290.2293.



6a

Borylation of *N,N*-dimethylphenethylamine (6a)

General Procedure C was followed with *N,N*-dimethylphenethylamine (0.298 g, 2.00 mmol). Purification by basic alumina flash column chromatography (97.5:1.5:1.0 CH_2Cl_2:MeOH:NEt_3) followed by Kugelrohr distillation (0.5 mmHg, 45 °C to remove **5a**) provided **6a** as a yellow oil (0.253g, 51%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 6.2 Hz, 1H), 7.29 (t, *J* = 1.5 Hz, 1H), 7.15 (m, 2H), 3.07 (m, 2H), 2.66 (m, 2H), 2.38 (s, 6H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 135.6, 130.0, 129.0, 125.7, 82.8, 61.3, 45.2, 32.4, 25.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 25.2; IR (neat) 2976, 1599, 1441, 1346, 1142, 860, 660 cm^{-1}; HRMS (CI) calcd for $(C_{16}H_{26}BNO_2 + H)^+$ 276.2138, found 276.2137.

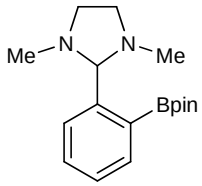


6b

Borylation of *N,N*-dimethyl-1-phenylethylamine (6b)

General Procedure C was followed with *N,N*-dimethyl-1-phenylethylamine (0.298 g, 2.00 mmol). Purification by basic alumina flash column chromatography (98.5:0.5:1.0 CH_2Cl_2:MeOH:NEt_3) provided **6b** as a light yellow oil (0.475 g, 86%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.1 Hz, 1H), 7.20 (m, 2H), 6.99 (d, *J* = 7.3 Hz, 1H), 4.12 (q, *J* = 7.3 Hz, 1H), 2.42 (s, 6H), 1.43 (d, *J* = 7.1 Hz, 3H), 1.31 (s, 6H), 1.29 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 130.5, 127.3, 121.5, 79.9, 65.9, 40.9, 27.2, 26.4, 12.0; ^{11}B NMR (128 MHz,

$CDCl_3$) δ 13.3; IR (neat) 2970, 1444, 1381, 1148, 1040, 730, 616 cm^{-1}; HRMS (CI) calcd for $(C_{16}H_{26}BNO_2 + H)^+$ 276.2138, found 276.2132.



6c

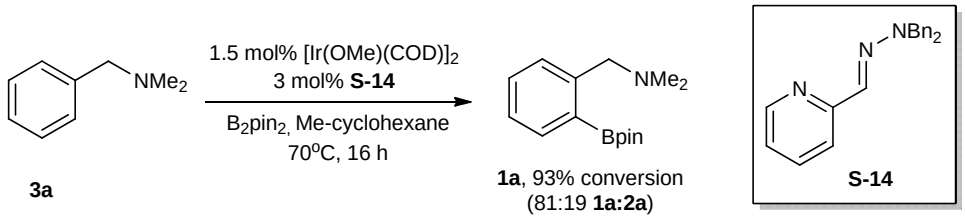
Borylation of *N*,*N*-dimethyl-2-(1,4-dimethylimidizole)benzylamine (6c)

General Procedure C was followed with *N*,*N*-dimethyl-2-(1,4-dimethylimidizole)benzylamine (0.350 g, 2.00 mmol). Purification by basic alumina flash column chromatography (98.5:0.5:1.0 CH_2Cl_2:MeOH:NEt_3) provided a 88:12 mixture of **6c**:**7c** as a pale yellow solid (0.429g, 71%): mp 94–98 °C; IR (ATR) 2974, 1461, 1241, 1085, 962, 692 cm^{-1}. **6c:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 7.15 Hz, 1H), 3.86 (s, 1H), 3.75 (m, 2H), 2.71 (m, 2H), 2.45 (s, 6H), 1.29 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 131.7, 128.7, 126.9, 123.9, 99.1, 80.2, 53.4, 41.6, 25.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ 14.7; HRMS (CI) calcd for $(C_{17}H_{27}BN_2O_2 + H)^+$ 303.2247, found 303.2250. **7c** (characteristic spectral data): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.3 Hz, 2H), 7.30 (m, 1H), 3.86 (s, 1H), 3.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 134.6, 127.9, 93.9, 81.6, 53.7, 42.0, 25.5; ^{11}B NMR (128 MHz, $CDCl_3$) δ 22.6.

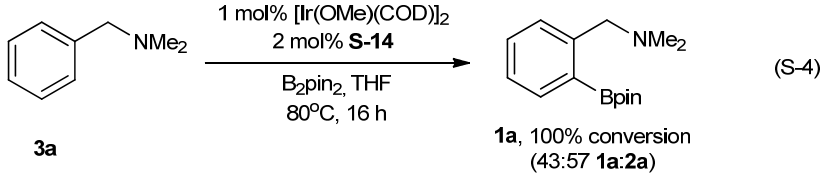
Comparison Reactions with Ligand S-14

Pyridine hydrazone ligand **S-14** (Scheme S-3) was used by Fernandez and Lassaletta in the directed C–H borylation of aryl hydrazones.[8] For comparison, this ligand was used with benzylamine **3a** under Lassaleatta's conditions (eq S-4) and under the reaction conditions reported in this manuscript (Scheme S-3). In both cases significant quantities of bis borylation product **2a** was observed.

Scheme S-3. Borylation of *N*,*N*-dimethylbenzylamine with Lassaletta's pyridine hydrazone ligand **S-14**.

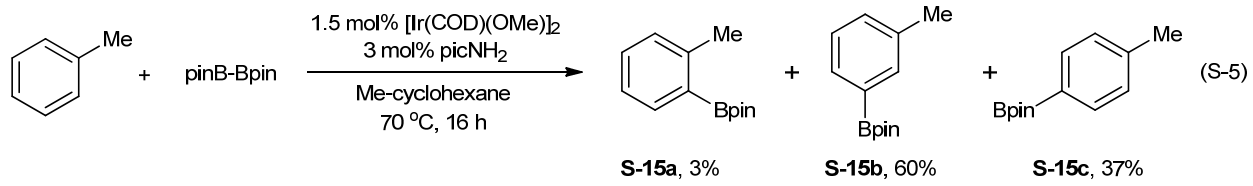


General procedure C was followed using pyridine hydrazone ligand **S-14** (0.019 g, 0.064 mmol), [Ir(μ-OMe)(COD)]$_2$ (0.020 g, 0.030 mmol), B_2pin_2 (0.424 g, 1.67 mmol) and *N*,*N*-dimethylbenzylamine (0.271 g, 2.00 mmol). The crude reaction mixture was examined by ^{1}H NMR spectroscopy showing 93% conversion and an 81:19 mixture of **1a**:**2a**.



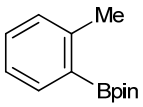
To a 25 mL PTFE-valved reaction tube, equipped with a stir bar and charged with [Ir(μ-OMe)(COD)]$_2$ (0.007 g, 0.011 mmol), B_2pin_2 (0.508 g, 2.00 mmol), **S-14** (0.006 g, 0.020 mmol), and *N*,*N*-dimethylbenzylamine (0.271 g, 2.00 mmol). After 16 h at 80 °C the crude reaction

mixture was examined by ^{1}H NMR spectroscopy showing 100% conversion and a 43:57 mixture of **1a:2a**.



Non-Selective C–H Borylation of Toluene.

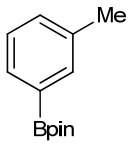
In an inert atmosphere glovebox, a 25 mL PTFE-valved reaction tube, equipped with a stir bar, was charged with [Ir(μ-OMe)(COD)]$_2$ (0.008 g, 0.012 mmol), B_2pin_2 (0.0635 g, 0.250 mmol), 2-(aminomethyl)pyridine (0.25 M, 0.100 mL, 0.025 mmol) solution in methylcyclohexane), and toluene (0.053 mL, 0.50 mmol). The sealed flask was heated to 115 °C for 23 h. The reaction mixture was transferred to a round bottom flask and the solvent was removed *in vacuo* to provide a mixture of **S-15a–c**. Purification by silica gel flash column chromatography (50:50 CH_2Cl_2:hexanes) provided a 3:60:37 mixture of **S-15a**:**S-15b**:**S-15c** as a colorless liquid (0.037 g, 67%):



S-15a

4,4,5,5-tetramethyl-2-*o*-tolyl-1,3,2-dioxaborolane (S-15a)[10]

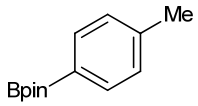
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 1H), 7.25–7.23 (m, 1H), 7.16 (m, 2H), 2.52 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.9, 130.8, 129.8, 124.7, 83.4, 24.9, 22.2 (carbon directly attached to boron was not observed)[7]; ^{11}B NMR (160 MHz, $CDCl_3$) δ 31.0.



S-15b

4,4,5,5-tetramethyl-2-*m*-tolyl-1,3,2-dioxaborolane (S-15b)[10]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63–7.60 (m, 2H), 7.26 (m, 2H), 2.30 (s, 3H), 1.33 (s, 12 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.1, 135.3, 132.0, 131.8, 127.7, 83.7, 24.7, 21.3 (carbon directly attached to boron was not observed)[7]; ^{11}B NMR (160 MHz, $CDCl_3$) δ 31.0.



S-15c

4,4,5,5-tetramethyl-2-*p*-tolyl-1,3,2-dioxaborolane (S-15c)[10]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0, 2H), 7.18 (d, J = 8.0, 2H), 2.34 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 134.8, 128.5, 83.6, 24.7, 21.7 (carbon directly attached to boron was not observed)[7]; ^{11}B NMR (160 MHz, $CDCl_3$) δ 31.0.

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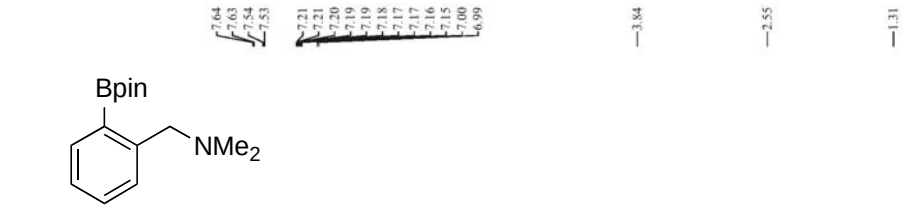
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Bpin
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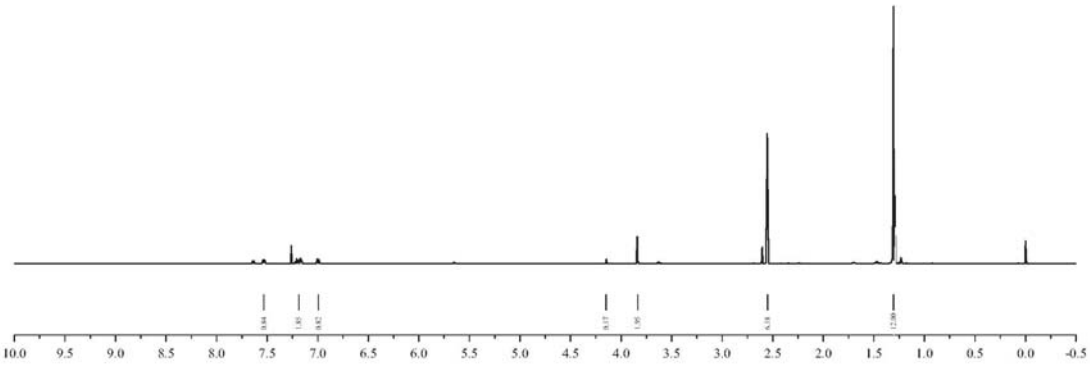
1a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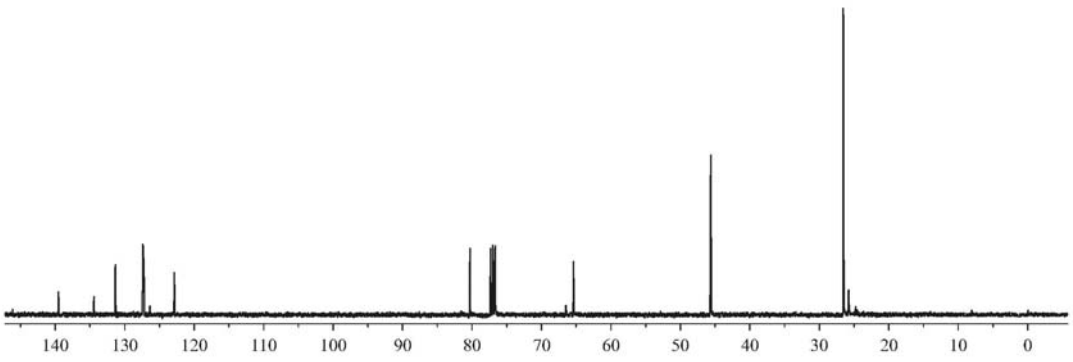
26.55
Bpin
NMe2

1a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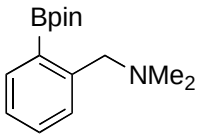
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NMe2

1a

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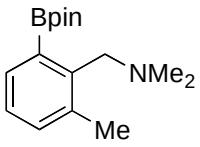
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Me

1b

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0.91
1.80
2.03
6.09
12.00
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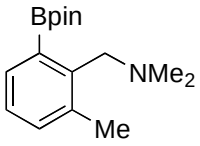
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Me

1b

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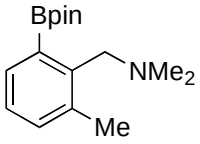
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1b

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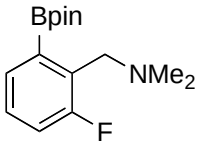
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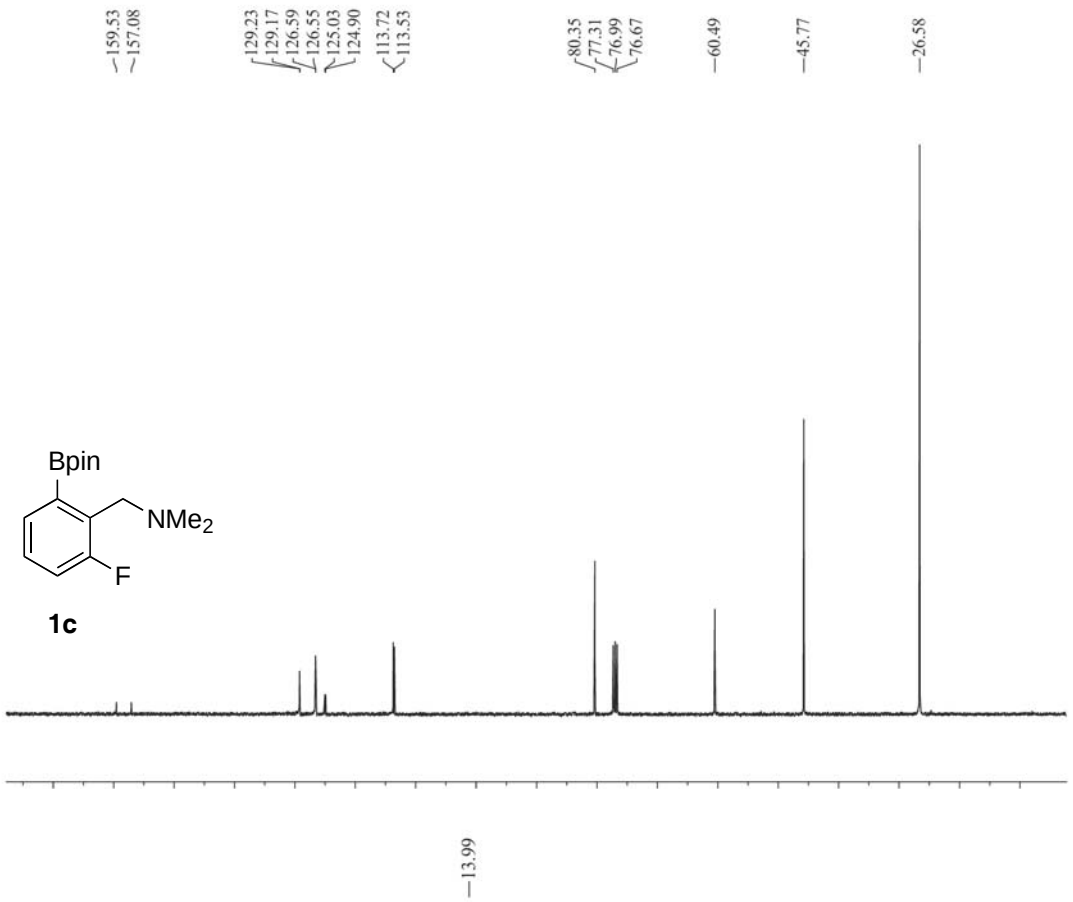
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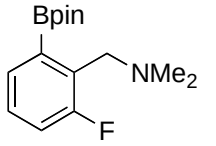
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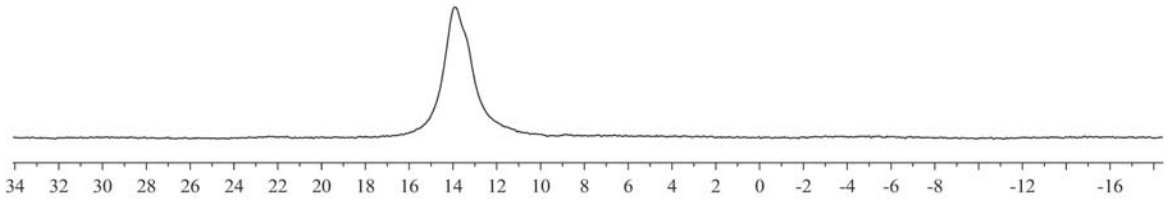
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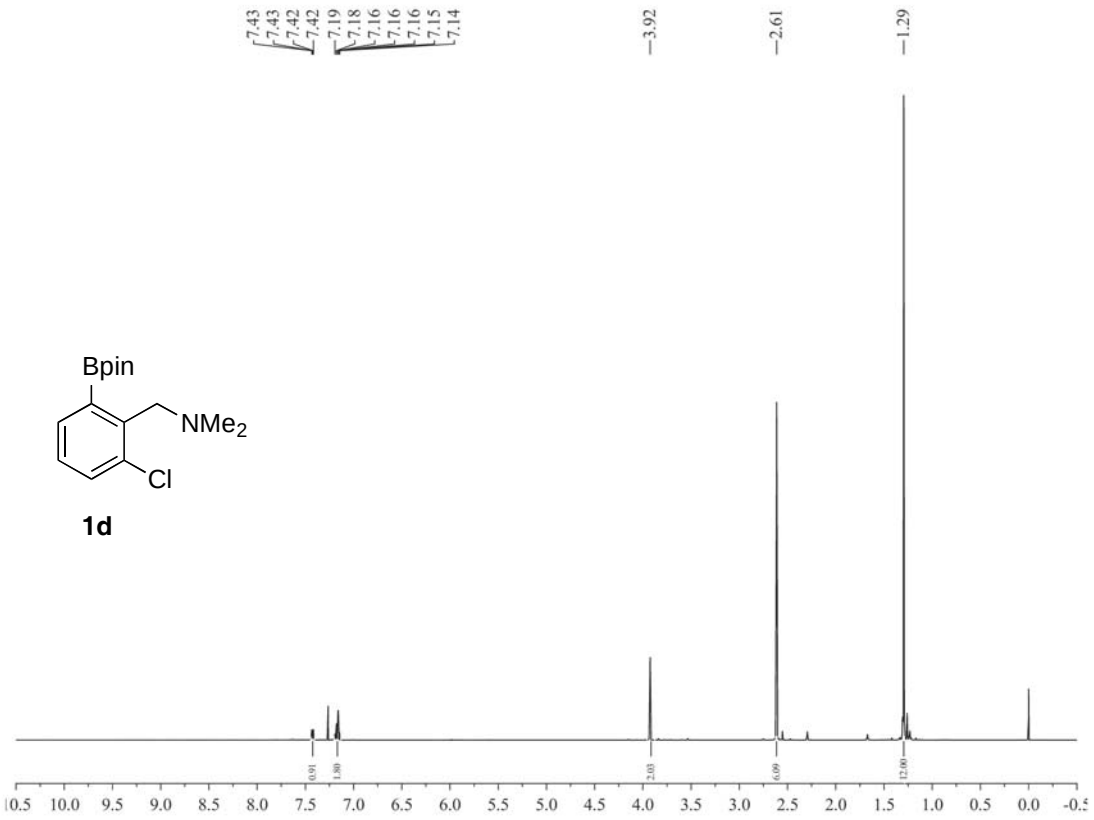
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Cl
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2.03
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12.00
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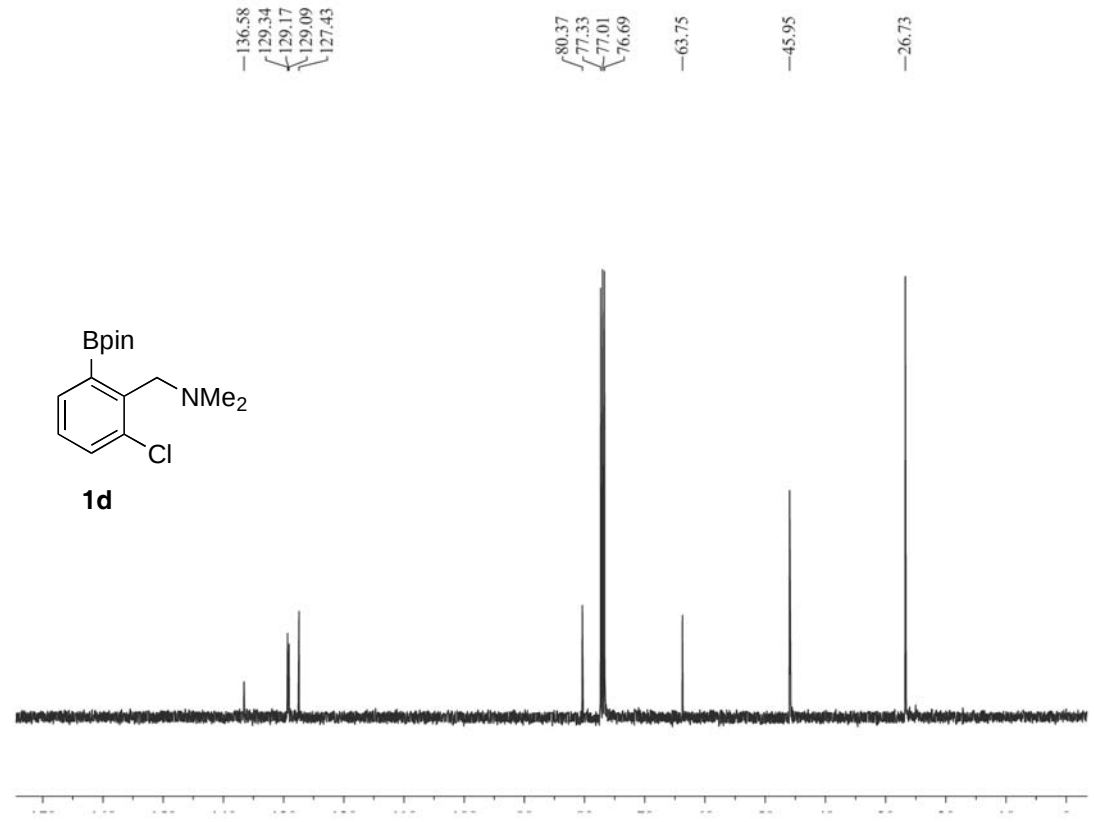
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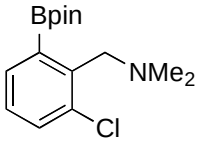
NMe2
Cl
1d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Cl

1d

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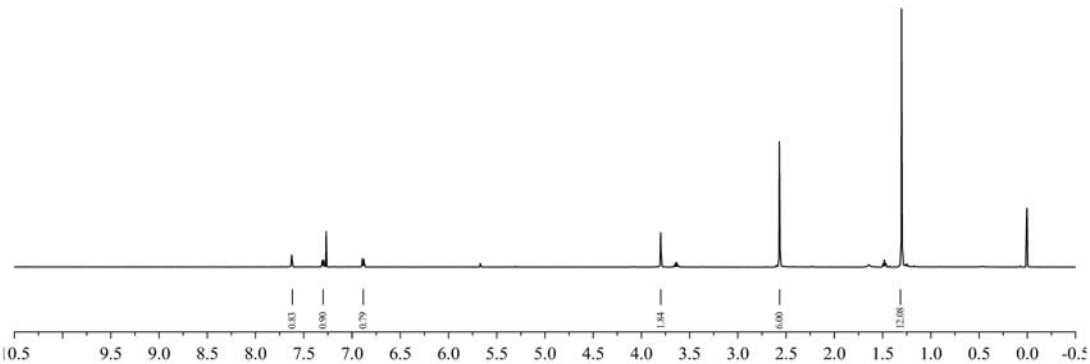
Br

1f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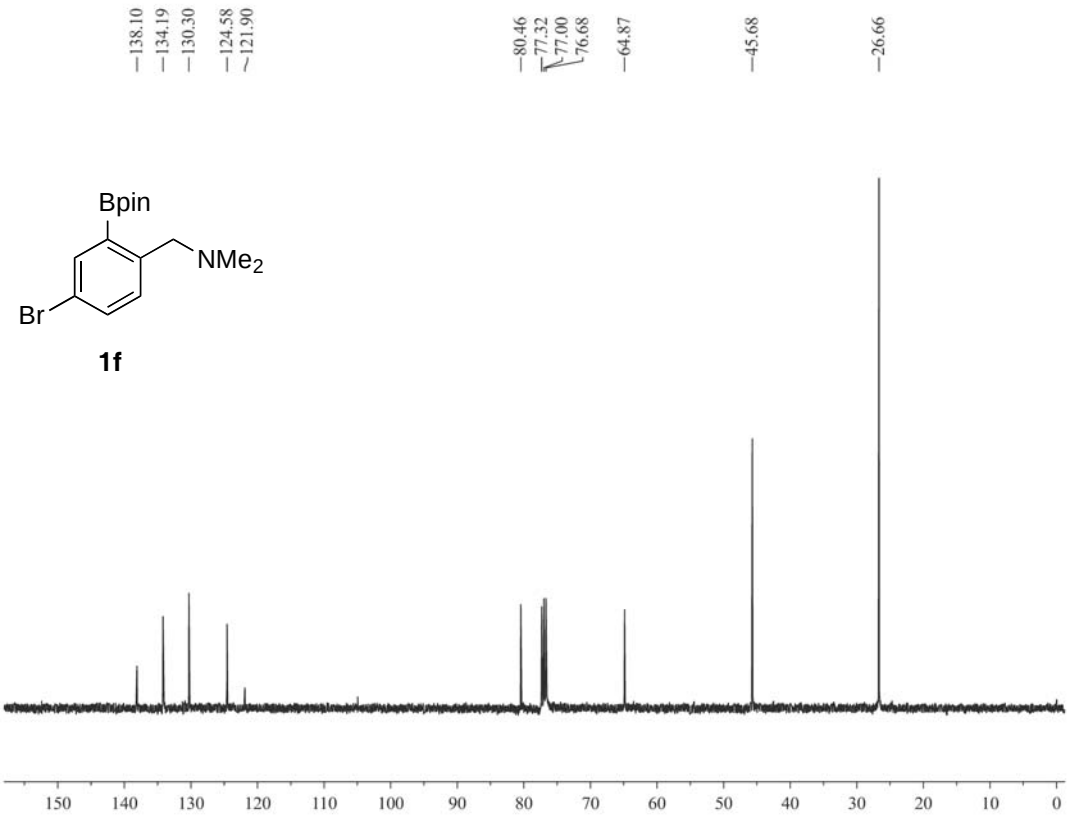
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26.66
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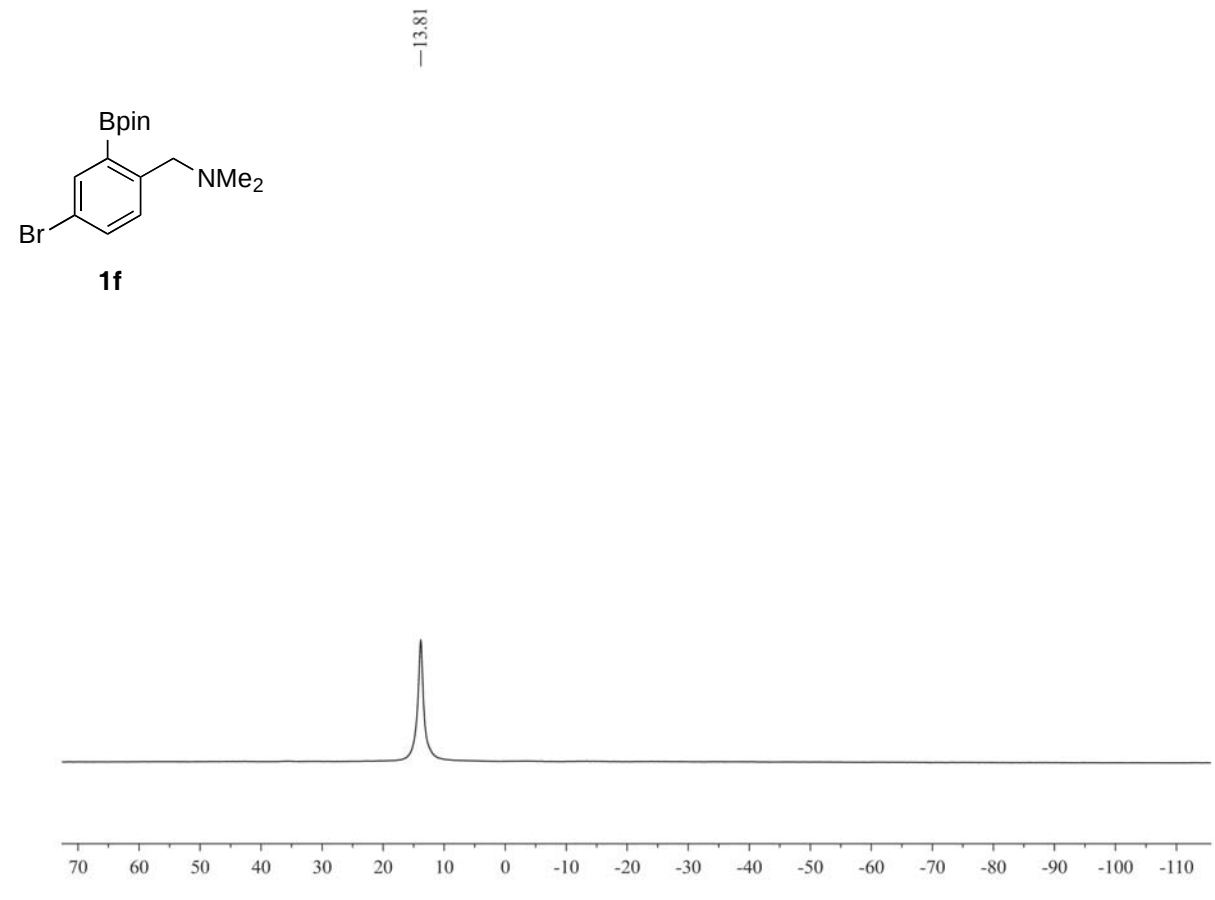
20
10
0

1f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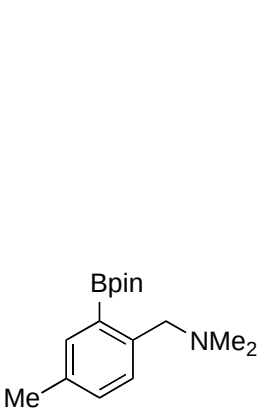
1f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1g

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4.10
3.79
2.59
2.53
2.31
1.31
1.29
0.57
0.87
0.86
0.84
0.58
2.10
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10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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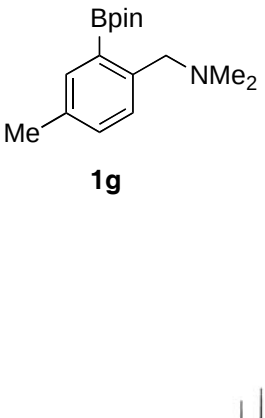
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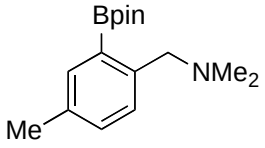
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1g

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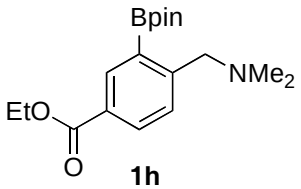
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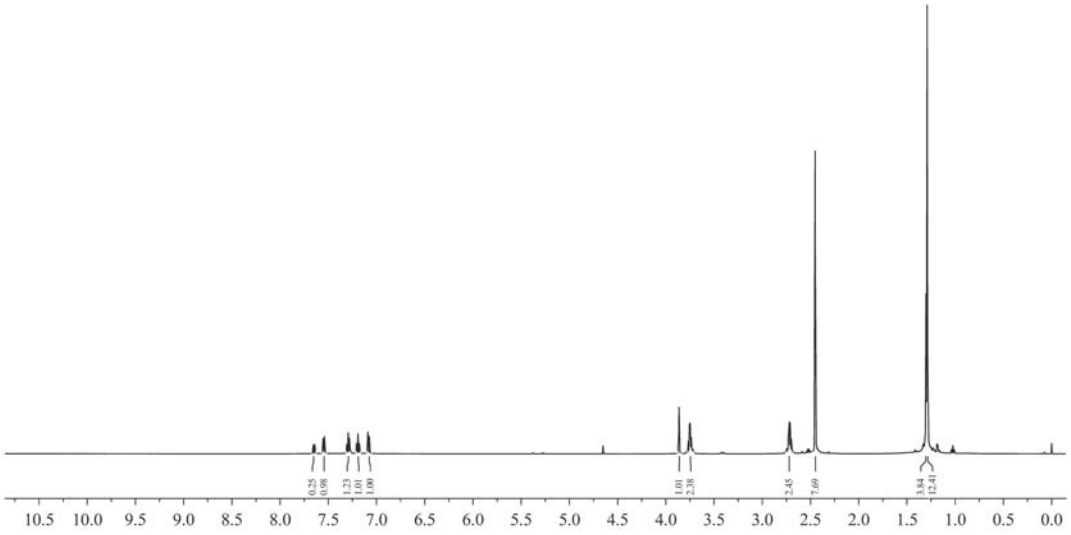
1h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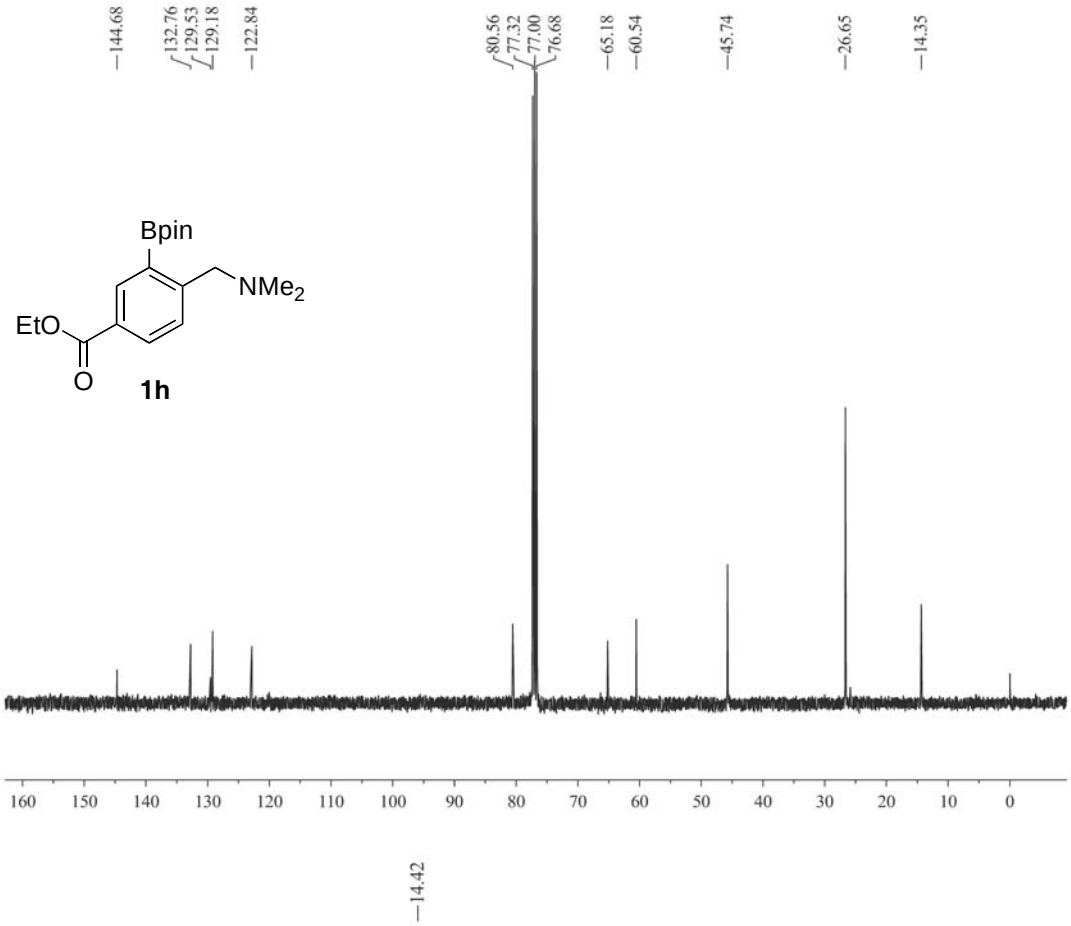
1.00
1.01
2.38
2.45
7.69
3.84
12.41
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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129.18
122.84
80.56
77.32
77.00
76.68
65.18
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26.65
14.35
Bpin
NMe2
EtO
O
1h
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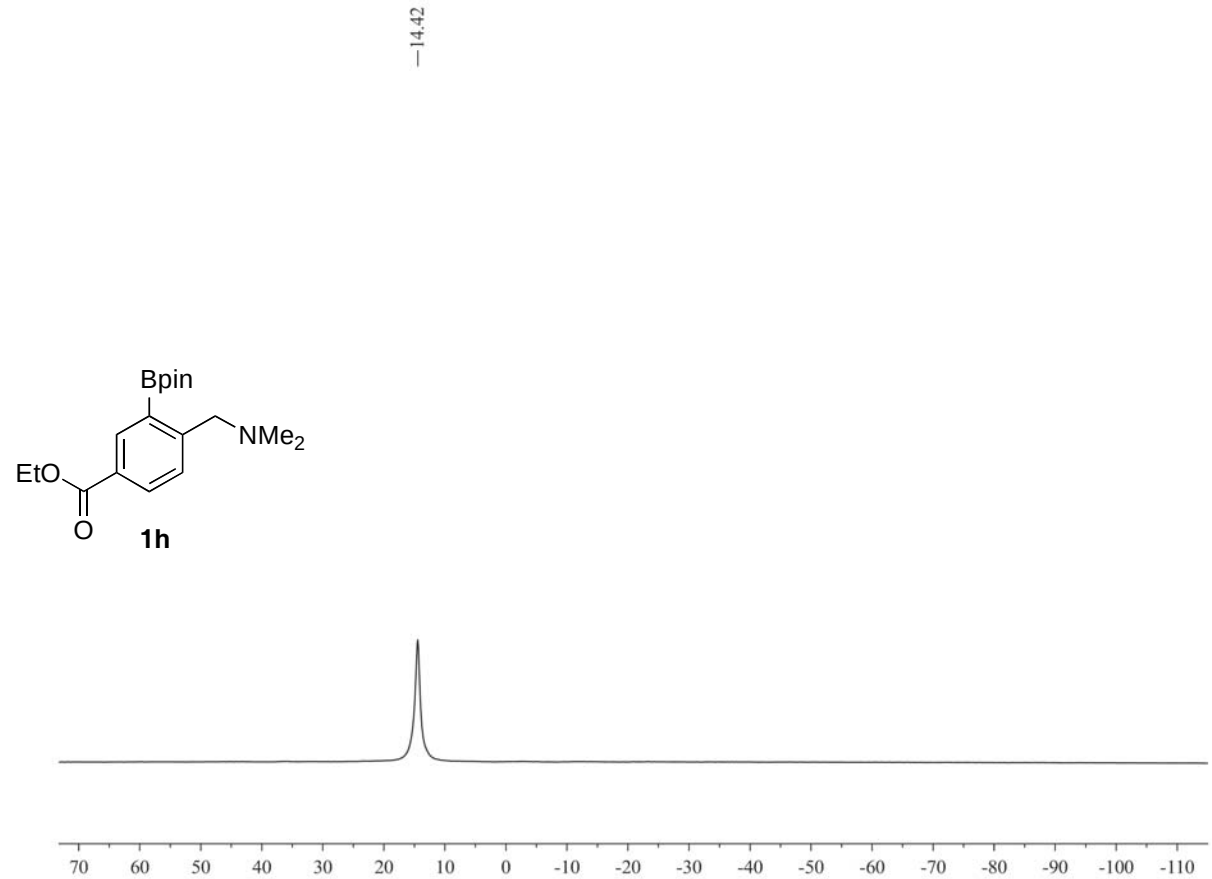
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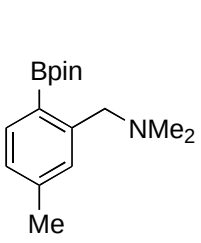
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NMe2
Me

1i

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0.79
1.84
6.00
12.08
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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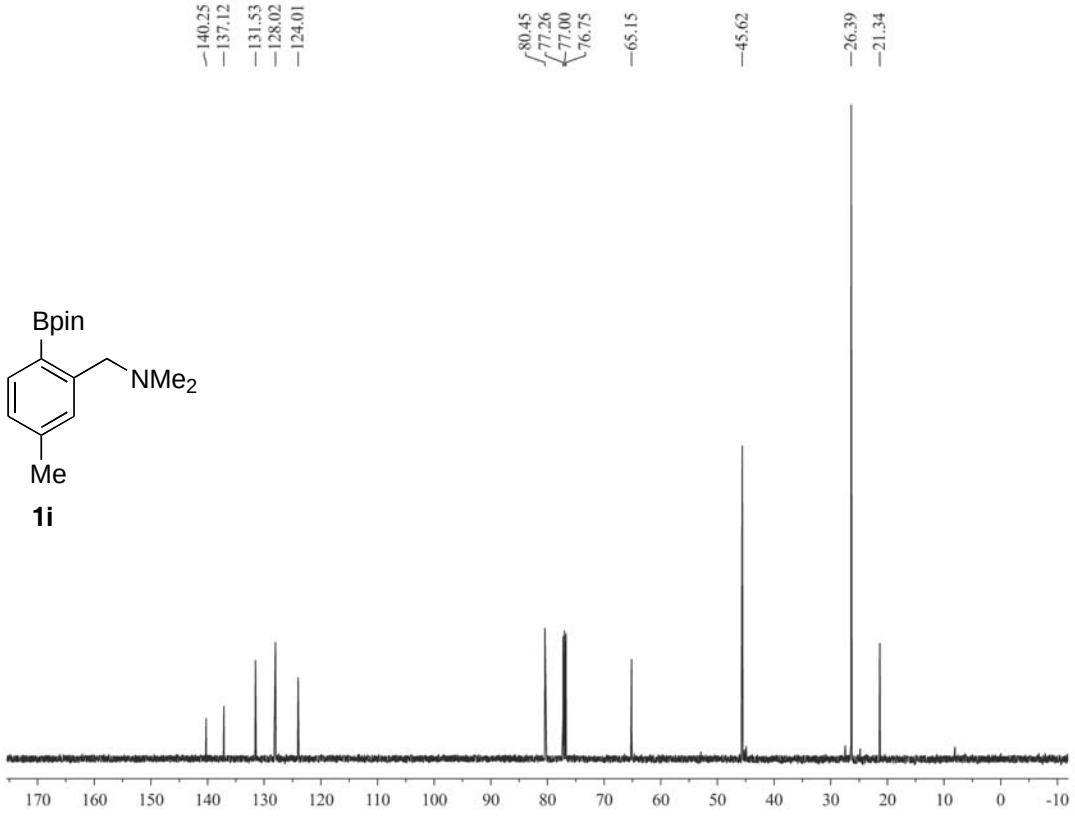
0.0
-0.5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77.26
77.00
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26.39
21.34
Bpin
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Me
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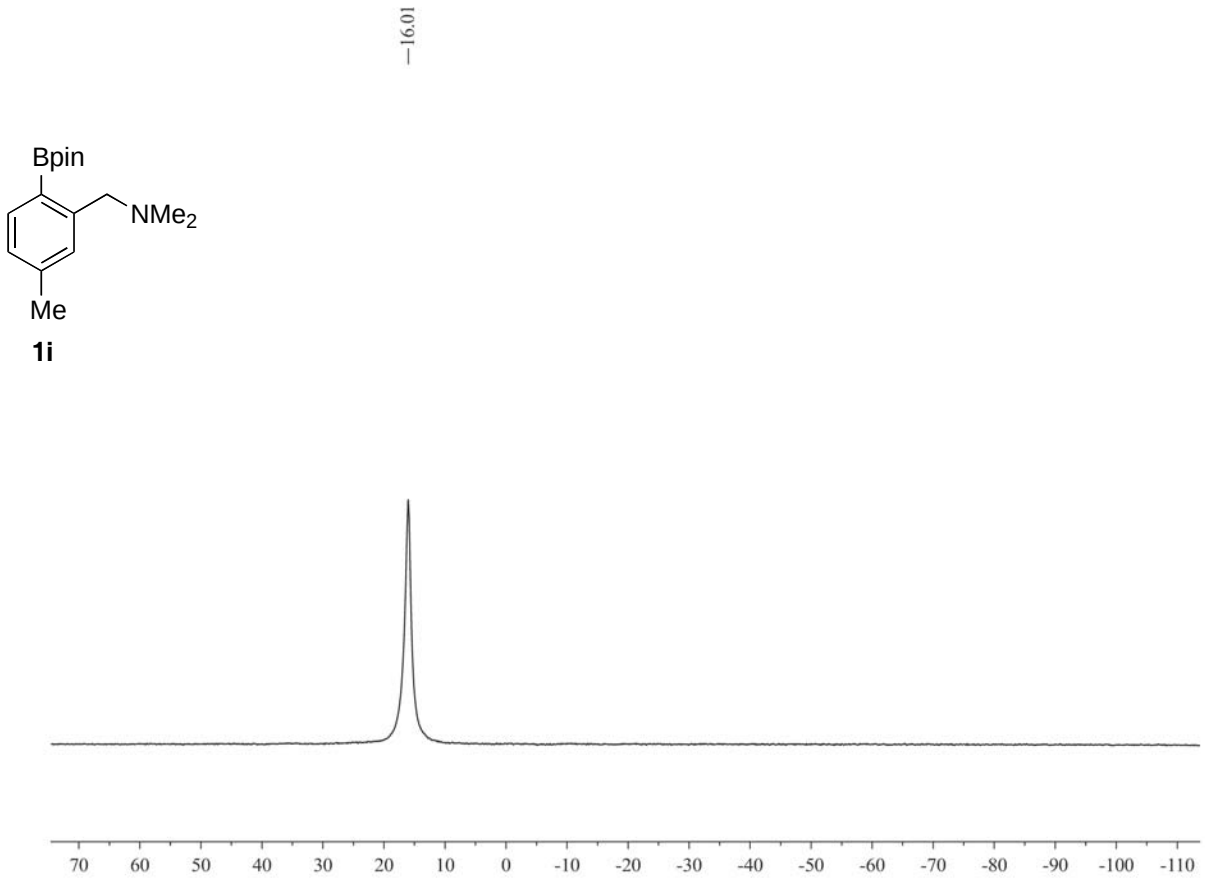
1i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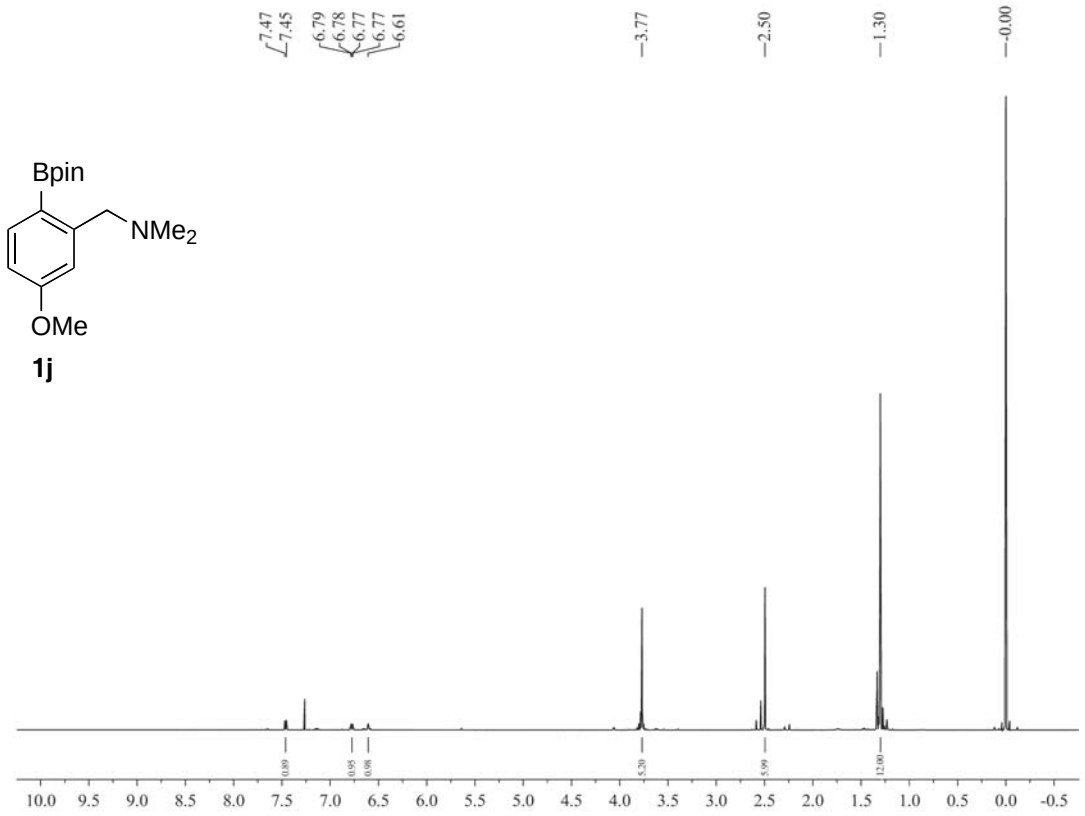
1i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6.61
3.77
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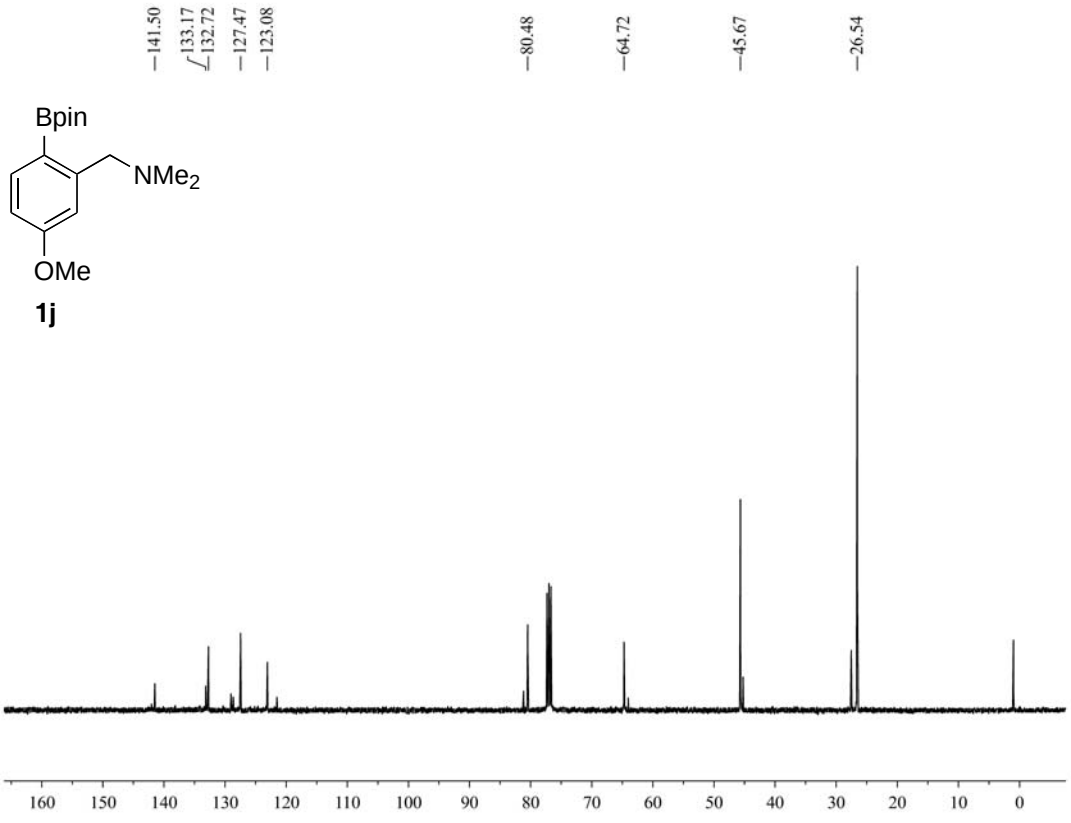
1.30
0.00
Bpin
NMe2
OMe
1j
0.89
0.95
0.98
5.20
5.99
12.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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Bpin
NMe2
OMe
1j
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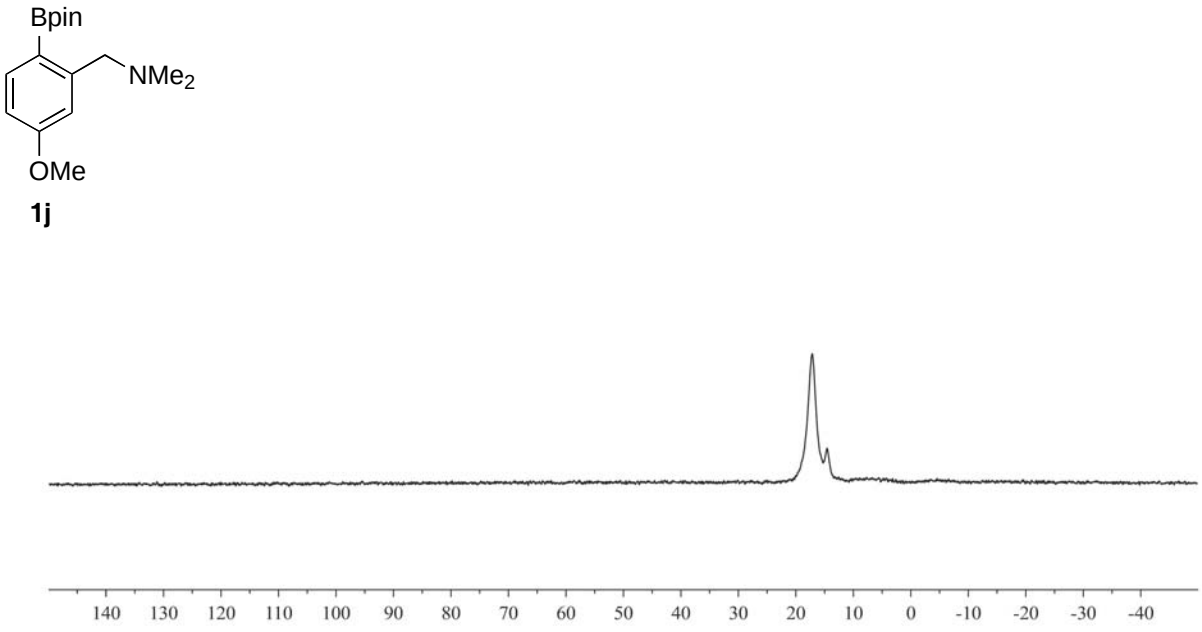
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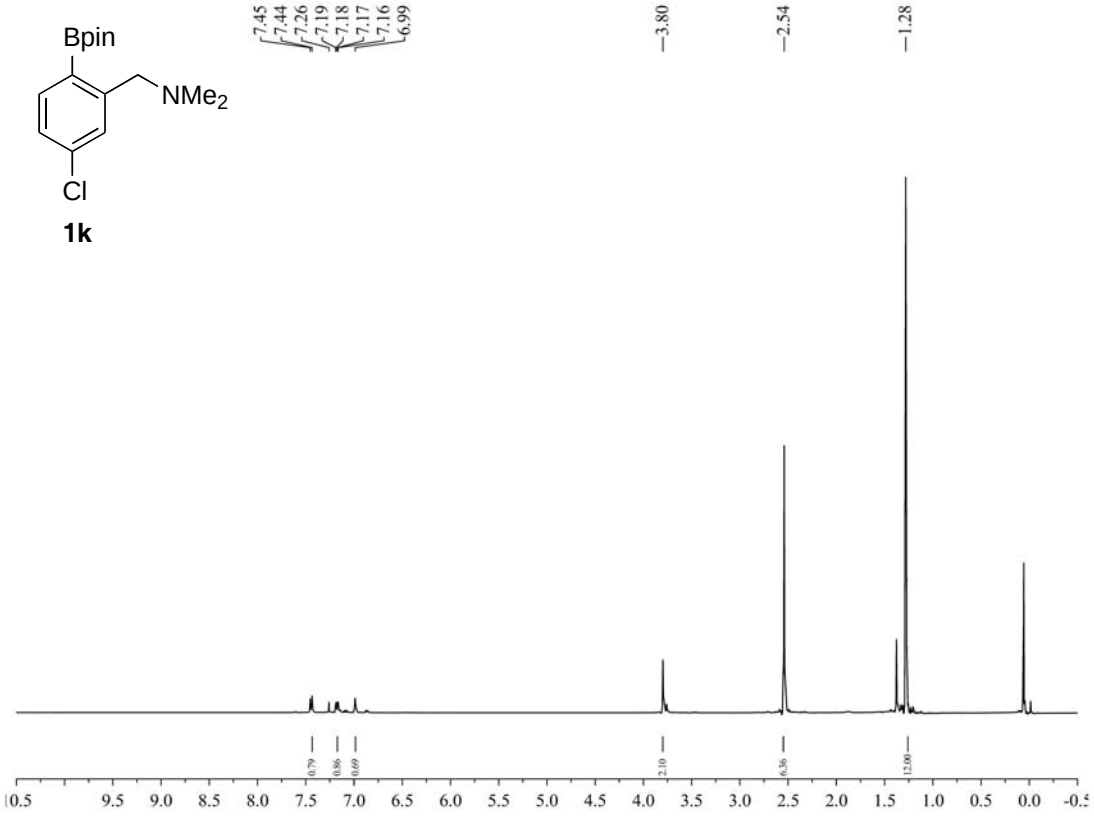
1j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NMe2
Cl
1k
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2.54
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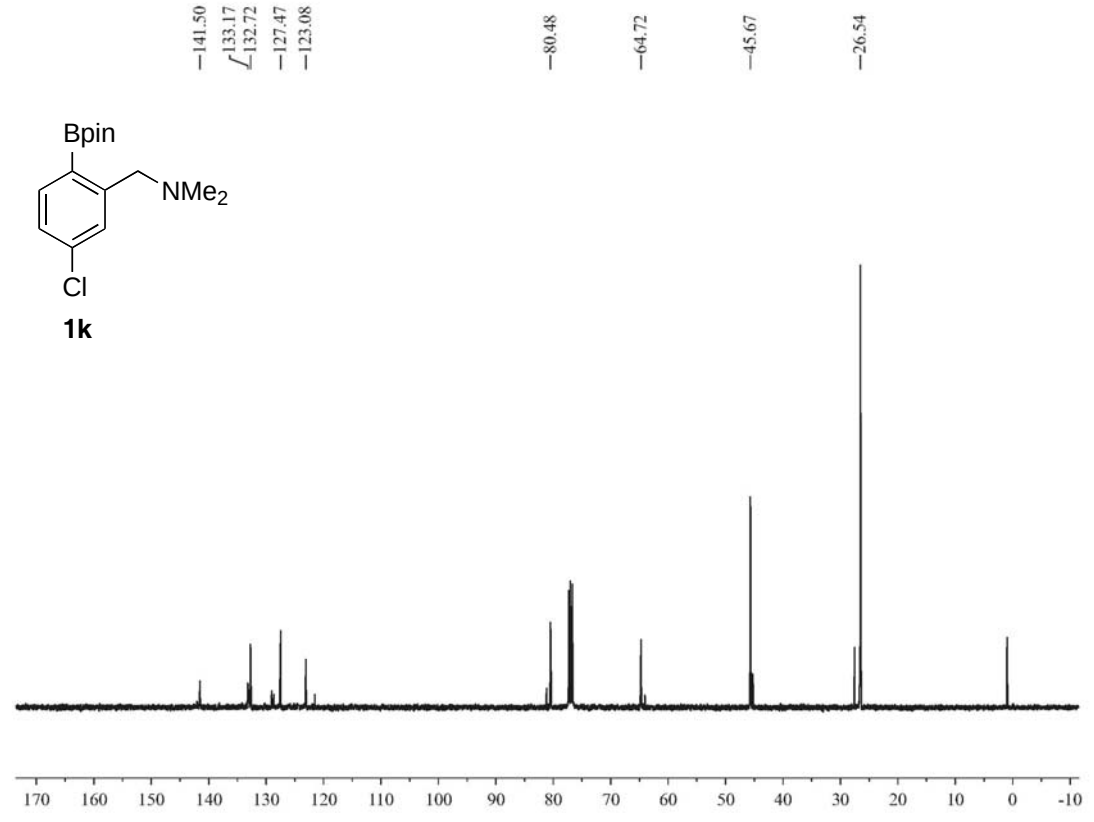
0.86
0.69
2.10
6.36
12.00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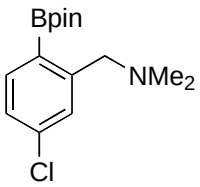
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Cl

1k

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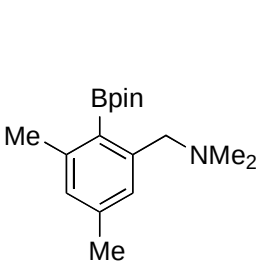
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Me
NMe2
Me

1l

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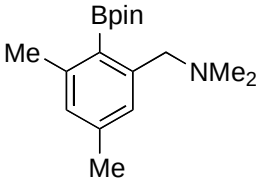
7.16
7.15
7.14
3.92
2.61
1.29
0.91
1.80
2.03
6.09
12.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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1l

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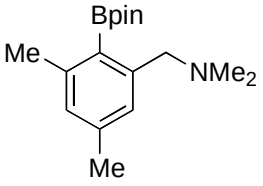
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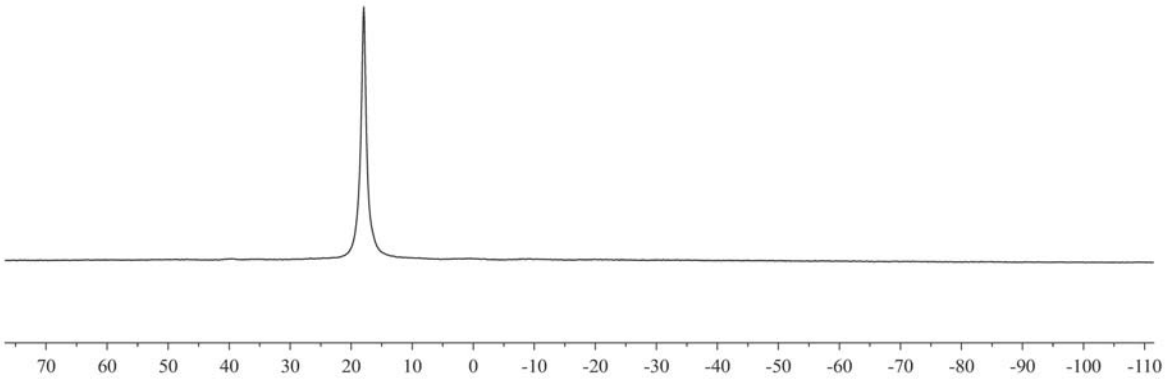
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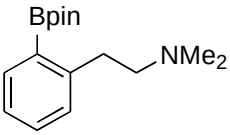
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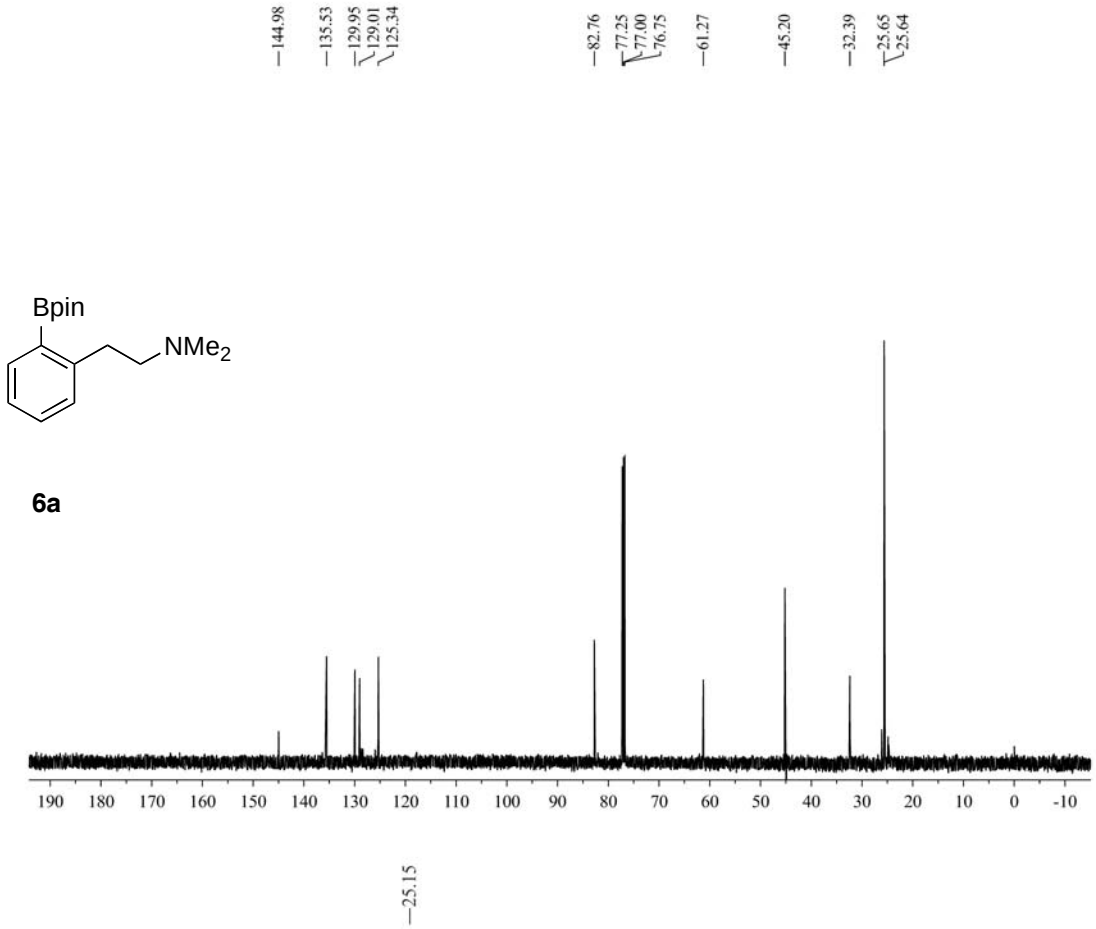
5.94
12.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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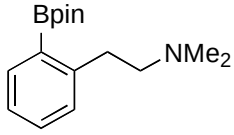
25.15

6a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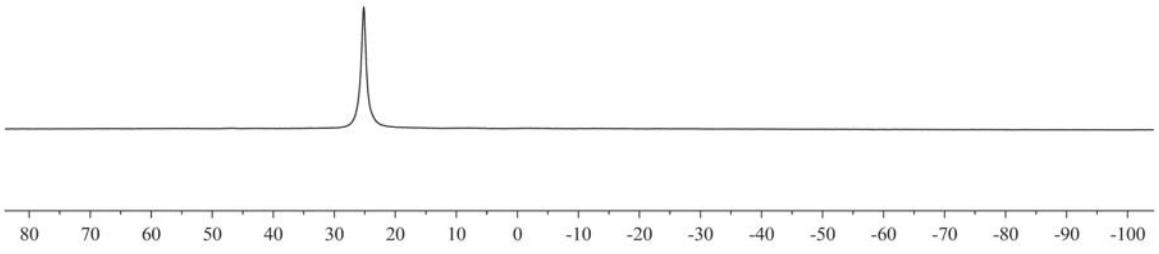
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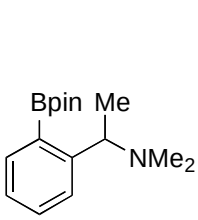
Bpin
Me
NMe2

6b

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7.15
7.14
3.92
2.61
1.29
0.91
1.80
2.03
6.09
12.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
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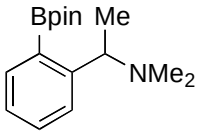
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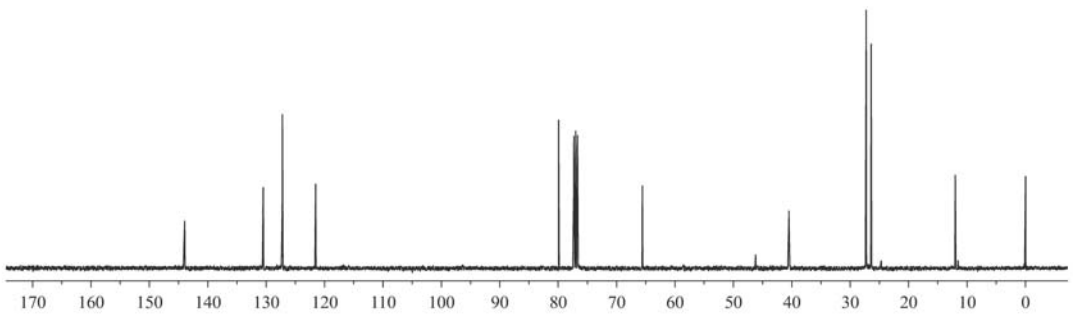
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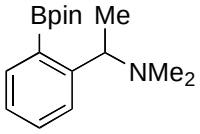
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Me
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6b

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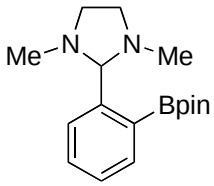
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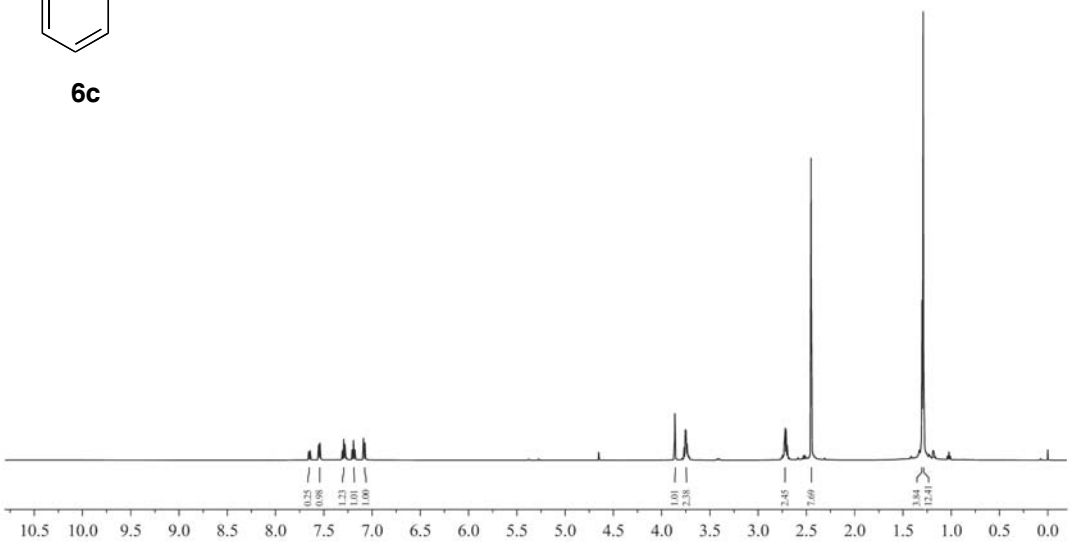
N
N
Me
Bpin

6c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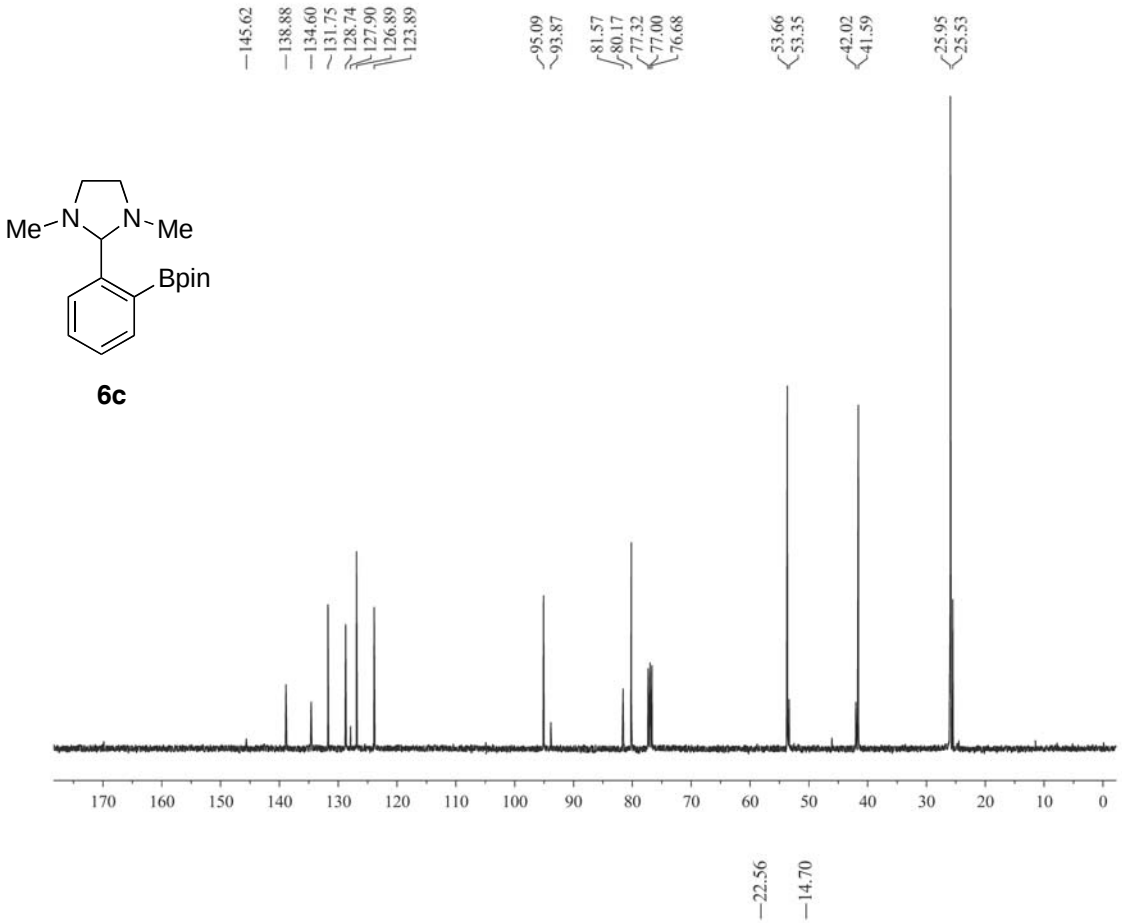
3.84
12.41
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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53.66
53.35
42.02
41.59
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N
N
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Bpin
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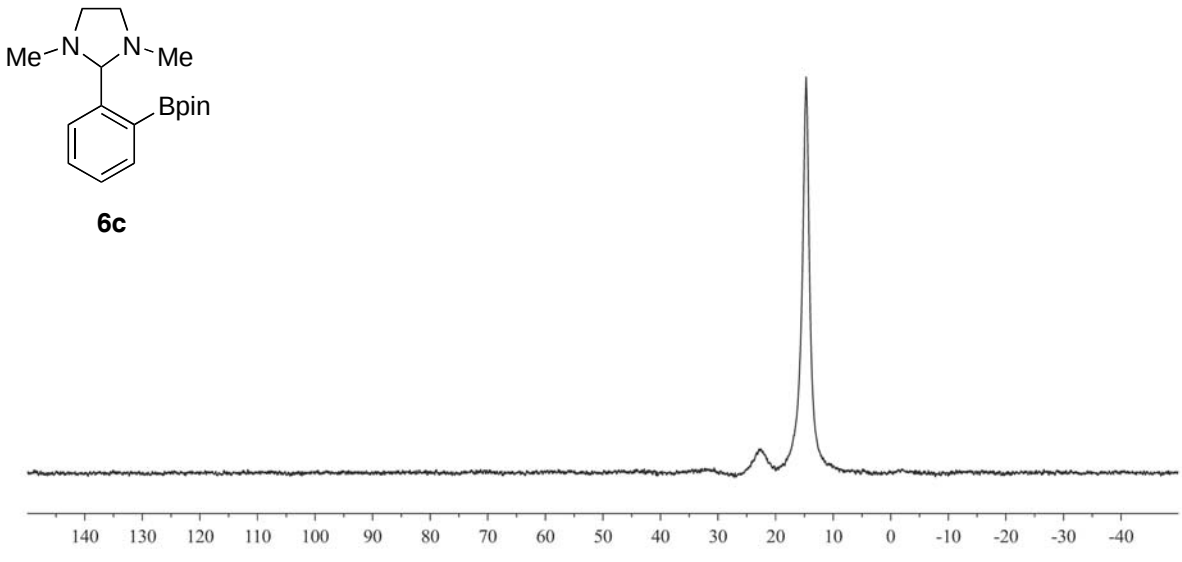
22.56
14.70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N
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Bpin
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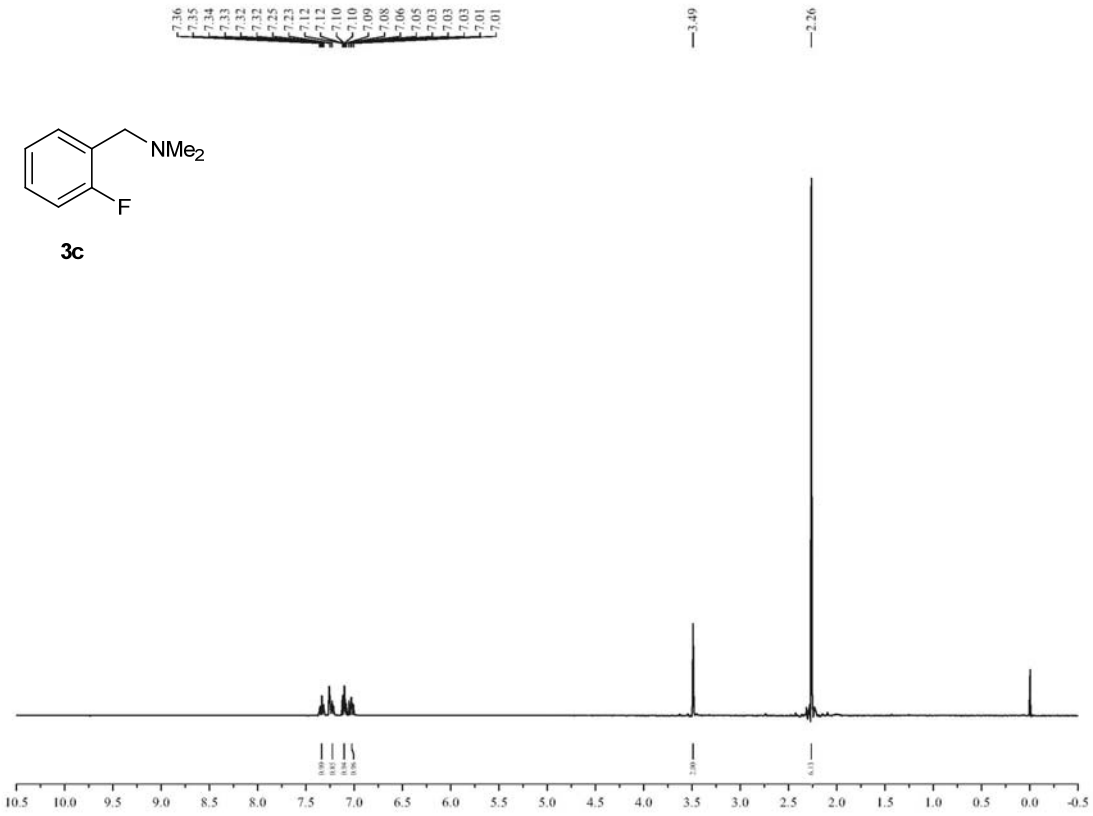
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7.35
7.34
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7.25
7.23
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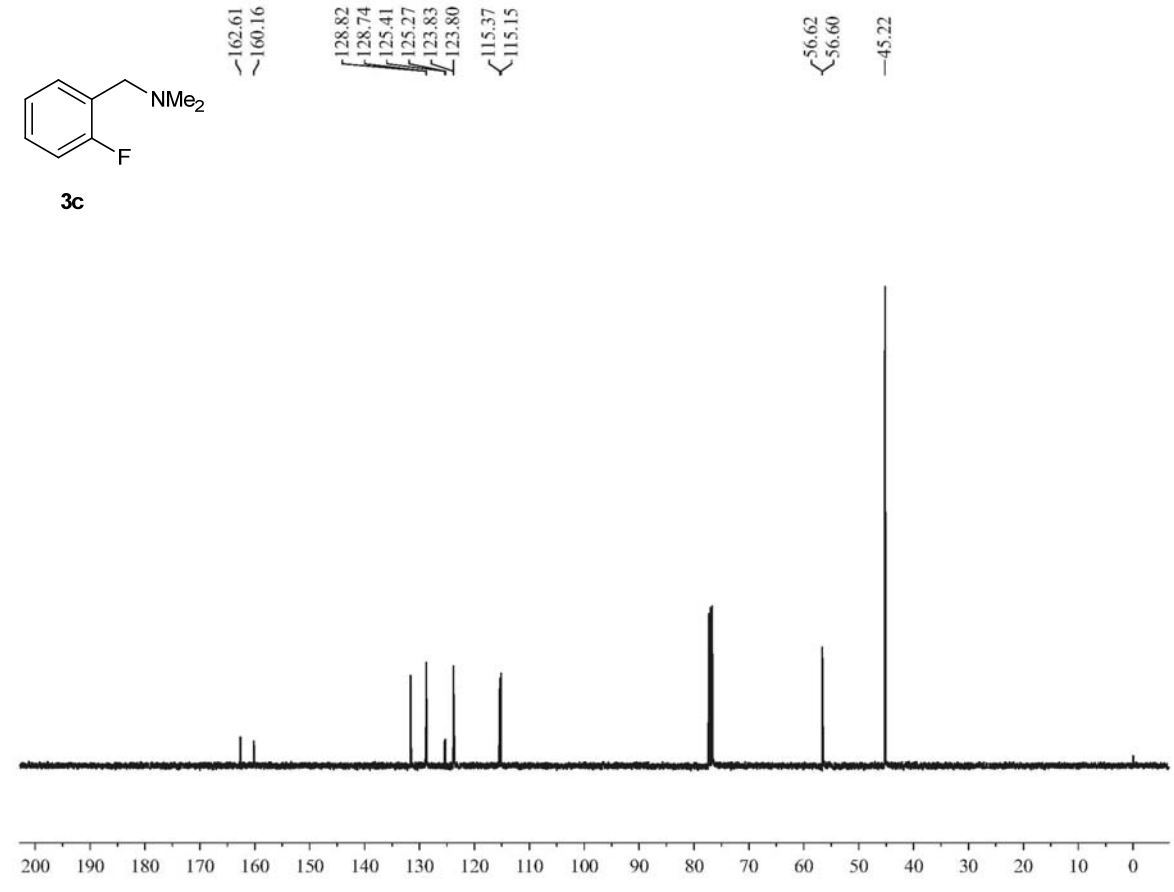
7.12
7.10
7.10
7.09
7.08
7.06
7.05
7.03
7.03
7.03
7.01
7.01
3.49
2.26
NMe2
F
3c
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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123.80
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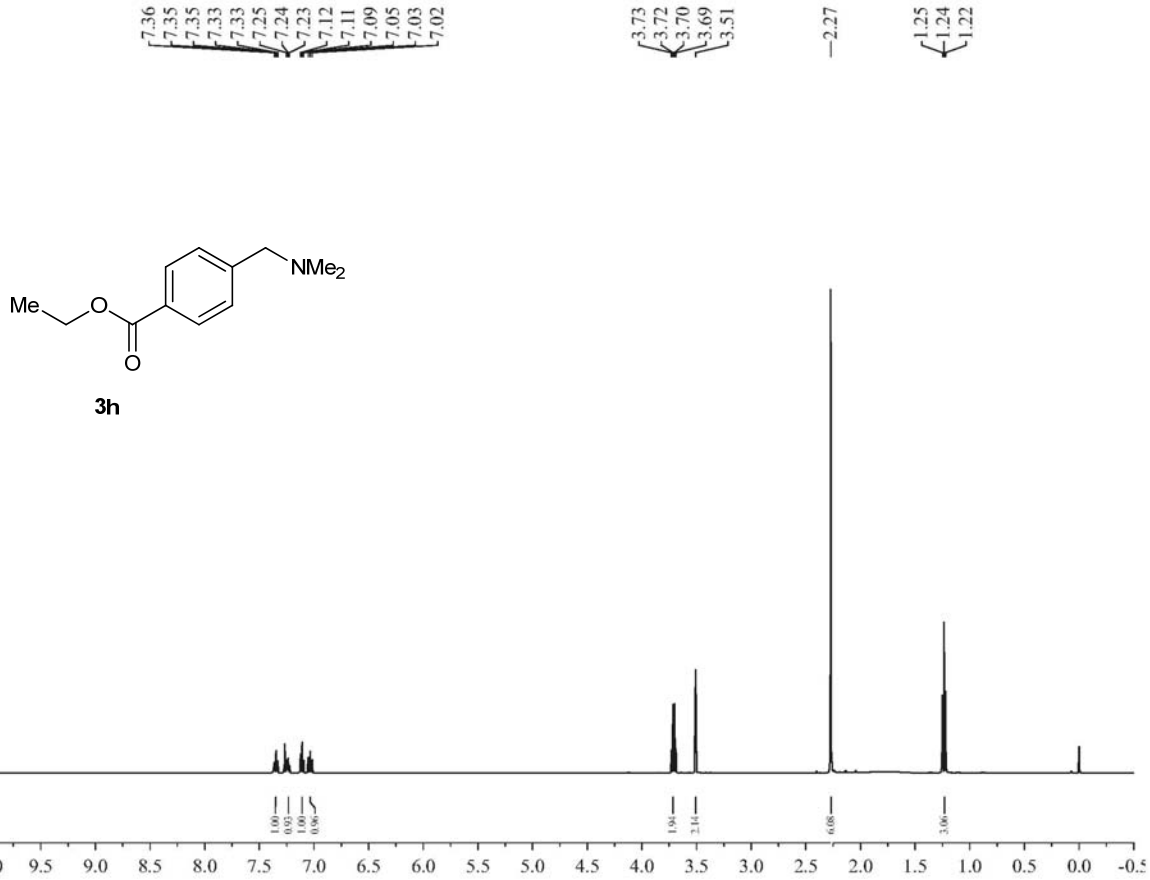
F
3c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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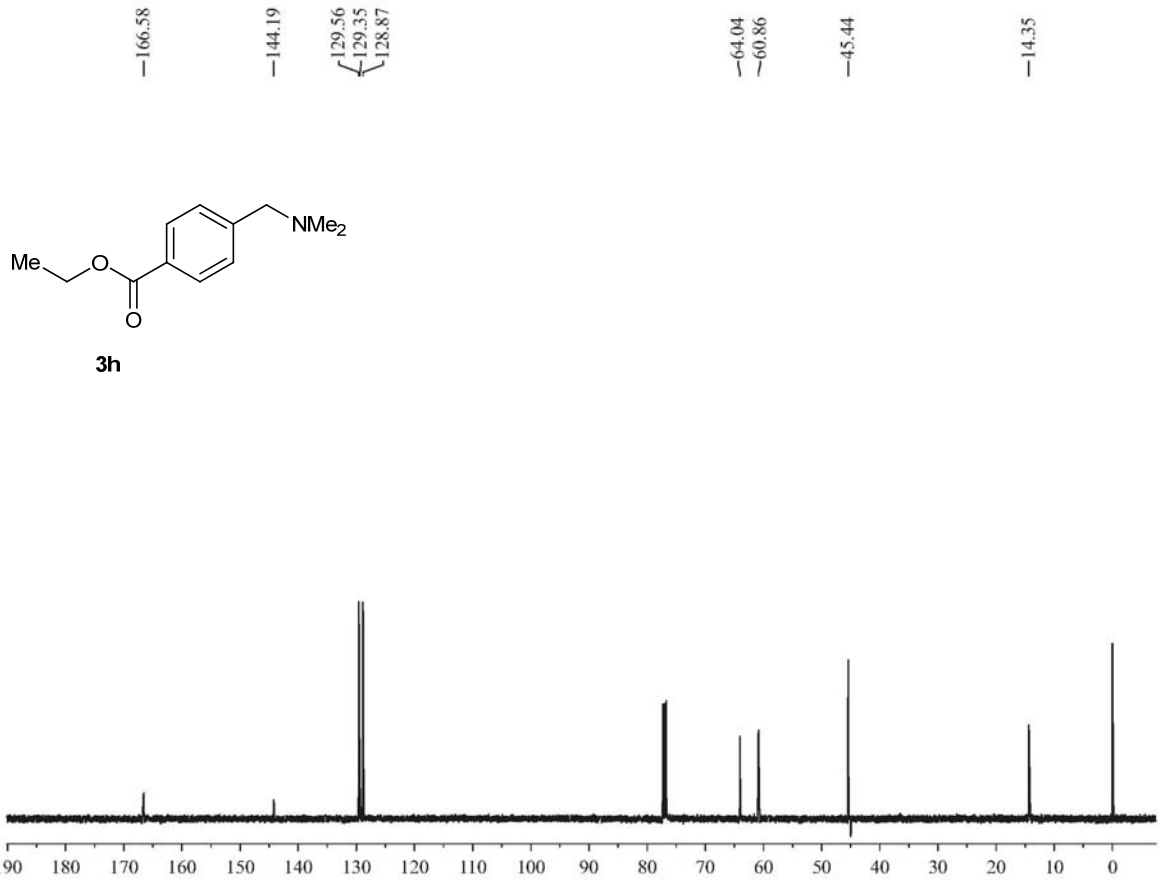
7.11
7.09
7.05
7.03
7.02
3.73
3.72
3.70
3.69
3.51
2.27
1.25
1.24
1.22
NMe2
Me
O
O
3h
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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O
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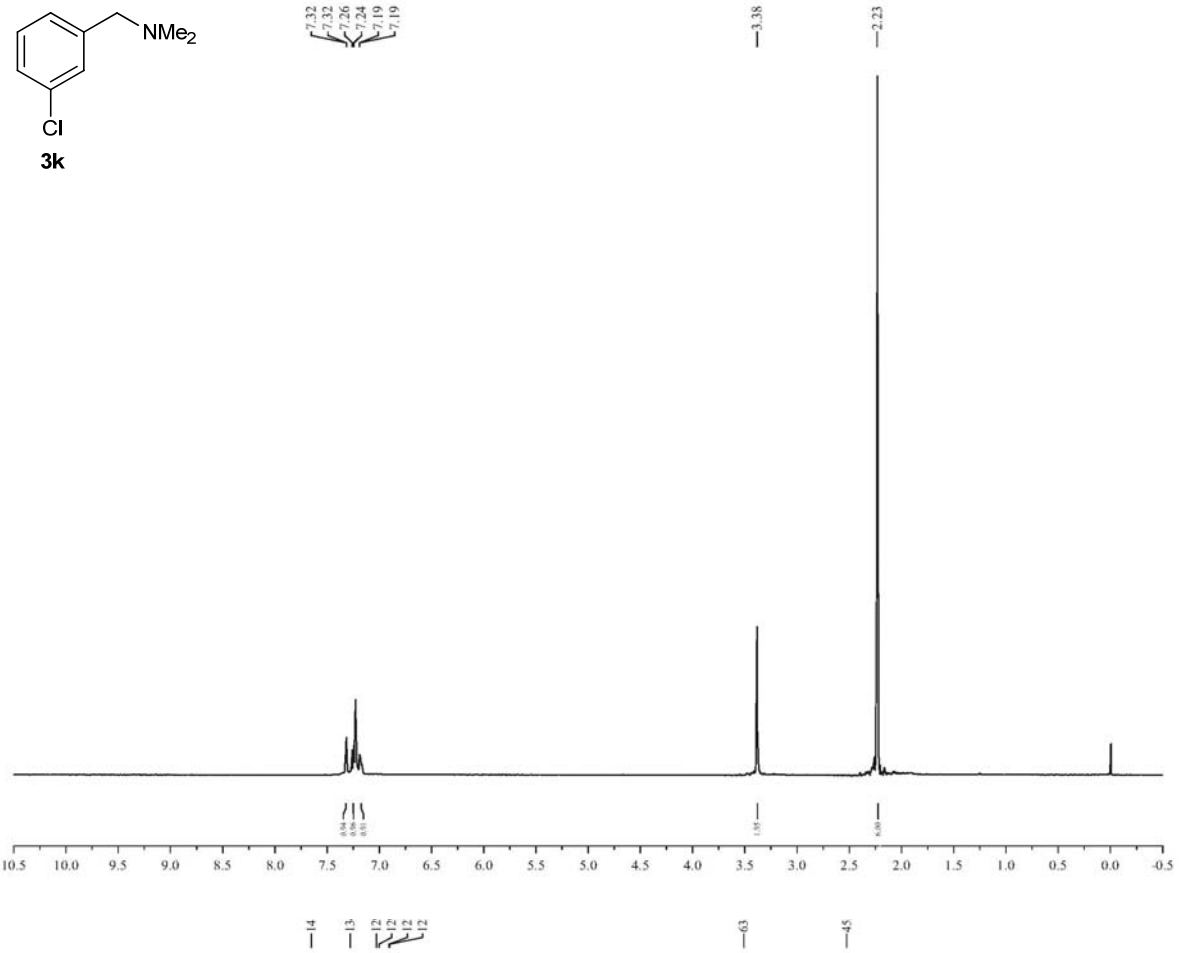
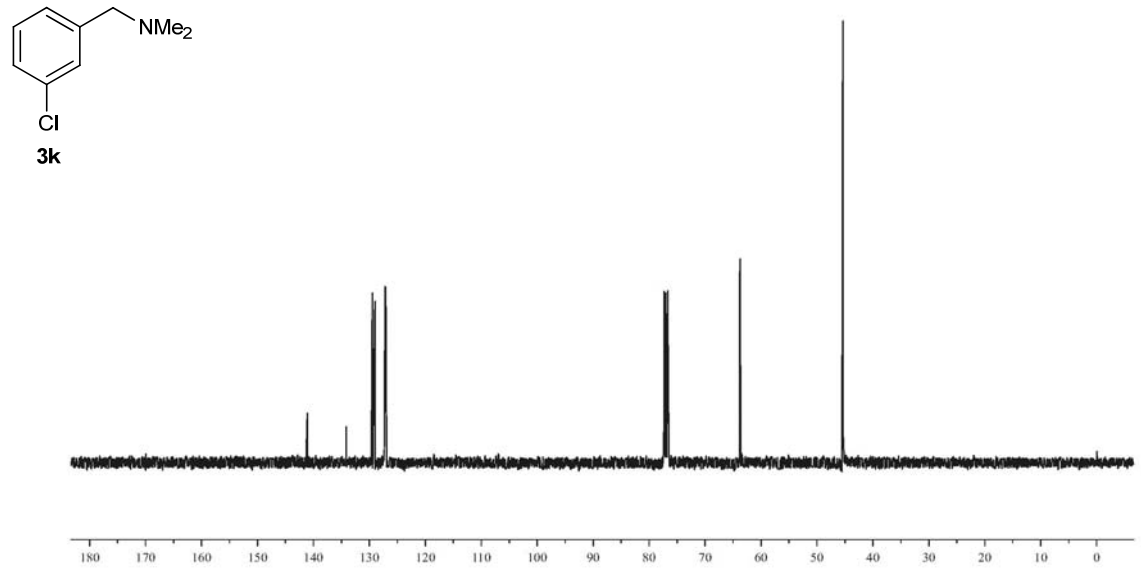
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


NMe2
Cl
3k
7.32
7.32
7.26
7.24
7.19
7.19
3.38
2.23
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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Cl
3k
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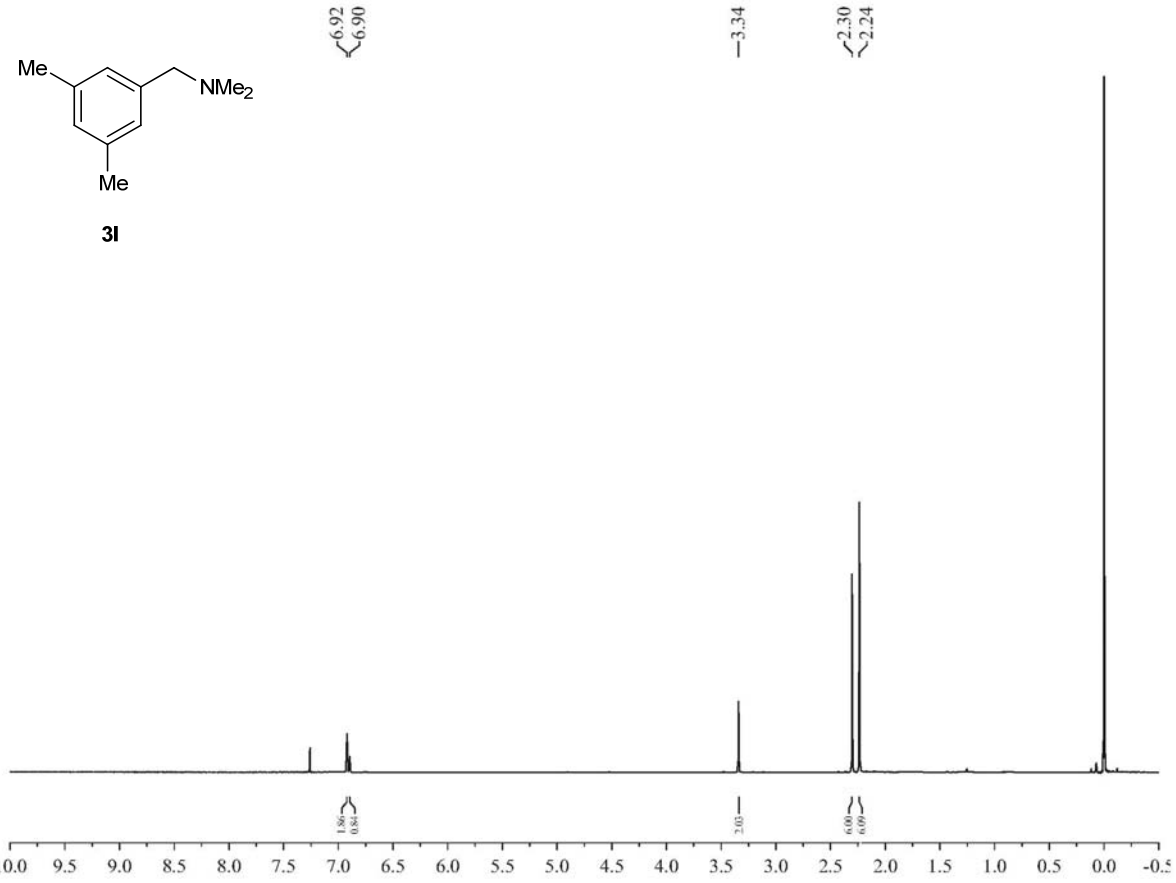
Me
NMe2
Me
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6.90
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2.30
2.24
1.86
0.84
3.03
6.00
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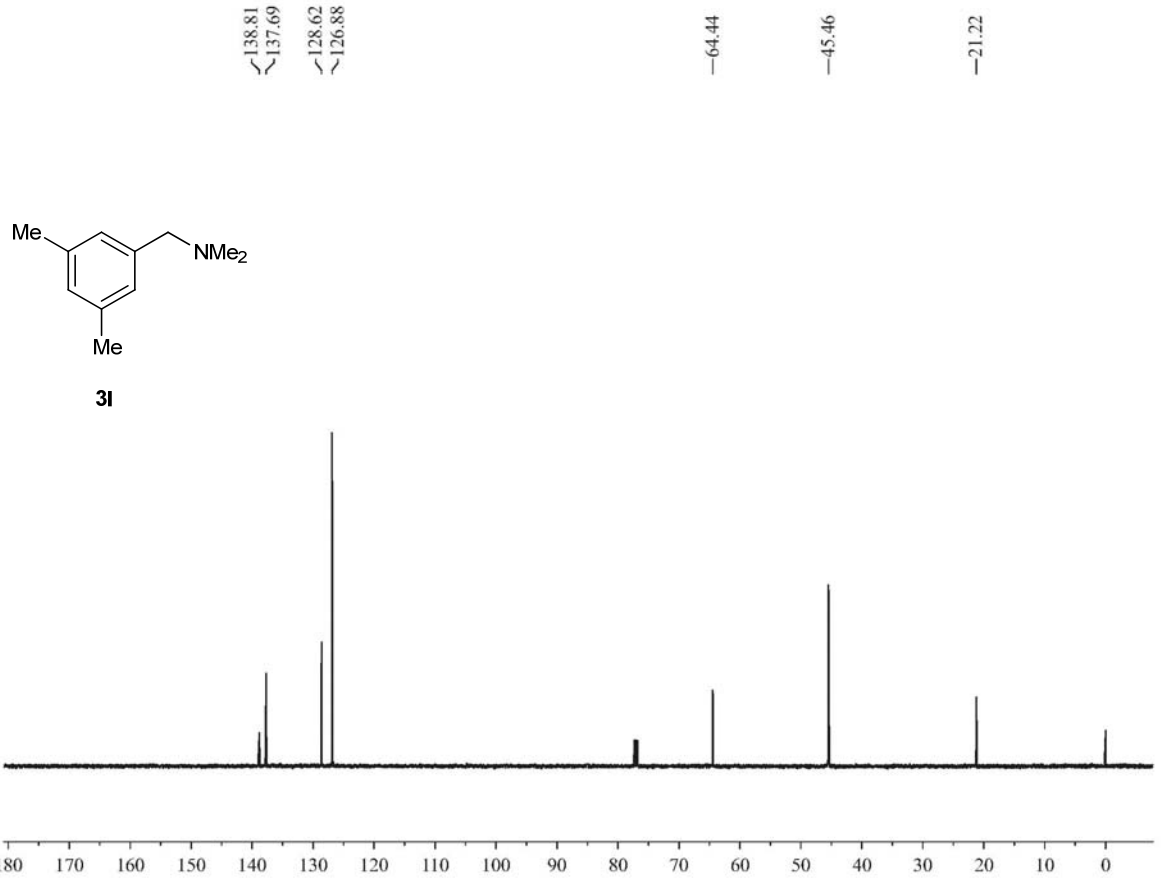
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

3l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128.62
126.88
64.44
45.46
21.22
Me
NMe2
Me
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

3l