

# **Enantio- and Regioselective CuH-Catalyzed Hydroamination of Alkenes**

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## Supporting Information

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**1. General Information.** Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.<sup>1</sup> All solvents were purified according to the method of Grubbs.<sup>2</sup> Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished using force-flow chromatography on Silicycle silica gel according to the method of Still.<sup>3</sup> Thin-layer chromatography (TLC) was performed on Silicycle 250  $\mu\text{m}$  silica gel plates. Compounds were visualized by irradiation with UV light,  $\text{I}_2$ , or by treatment with a solution of phosphomolybdic acid in ethanol followed by heating. Yields refer to pure compounds, unless otherwise indicated.

$^1\text{H}$  NMR spectra were recorded on a Bruker 400 and are referenced relative to residual  $\text{CDCl}_3$  proton signals at  $\delta$  7.26 ppm.  $^{19}\text{F}$  NMR spectra were recorded on a Bruker 400 and are referenced relative to  $\text{CFCl}_3$  ( $\delta$  0.0 ppm). Data for  $^1\text{H}$  and  $^{19}\text{F}$  NMR are reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, ap = apparent), integration, coupling constant (Hz) and assignment.  $^{13}\text{C}$  spectra were recorded on a Bruker 400 and are referenced relative to  $\text{CDCl}_3$  at  $\delta$  77.16 ppm. Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift and multiplicity where appropriate. IR spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer (iD5 ATR, diamond) and are reported in terms of frequency of absorption ( $\text{cm}^{-1}$ ). GC analyses were performed on an Agilent 6890 gas chromatograph with an FID detector using a J & W DB-1 column (10 m, 0.1 mm I.D.). Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. High Resolution Mass spectra were obtained from on a Bruker Daltonics APEXIV 4.7 Tesla Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS). High pressure liquid chromatography (HPLC) was performed on Hewlett-Packard 1100 Series chromatographs using a chiral column (25 cm) and guard column (5 cm) as noted for each compound. Optical rotations were measured on a Jasco P-1010 polarimeter with  $[\alpha]_D$  values reported in degrees; concentration (c) is in g/100 mL. For *N*-(1-

(1) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*. 3<sup>rd</sup> ed., Pergamon Press, Oxford, 1988.

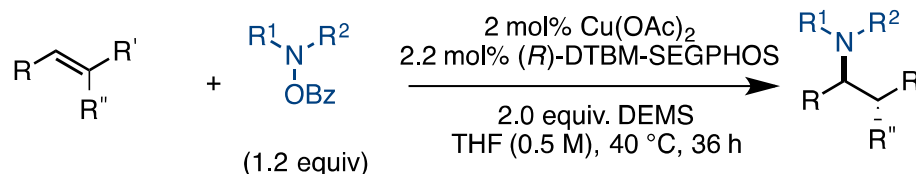
(2) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallic*. **1996**, *15*, 1518.

(3) Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

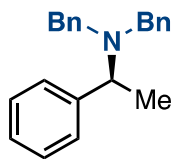
phenylethyl)amine (**3r**, **u**), the enantiomeric excesses were determined by  $^1\text{H}$  NMR analysis using our previously published procedure.<sup>4</sup>

## 2. CuH-Catalyzed Hydroamination of Alkenes

### General Procedure for CuH-Catalyzed Hydroamination of Styrenes and Alkenes.



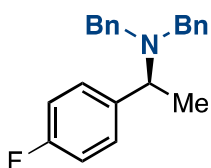
**General procedure for the enantioselective CuH catalyzed hydroamination of styrenes:** In a glove-box,  $\text{Cu}(\text{OAc})_2$  (3.6 mg, 2 mol%) and (*R*)-DTBM-SEGPHOS (25.9 mg, 2.2 mol%) were added to a screw-cap test tube. The tube was then sealed and taken out from the glove-box and THF (2.0 mL, 0.5 M) was added. The mixture was stirred for 15 min, then DEMS (diethoxymethylsilane, 270 mg, 320  $\mu\text{L}$ , 2.0 equiv.) was added dropwise and the stirring was continued for another 10 min at rt before being added by a syringe to another screw-cap test tube containing styrene (104 mg, 1.0 mmol, 1.0 equiv.) and *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv.). The reaction tube was stirred at 40°C for 36 h. The reaction mixture was diluted with EtOAc, quenched with 2 mL  $\text{Na}_2\text{CO}_3$  solution. Dodecane (100  $\mu\text{L}$ ) was added as the internal standard for GC yield determination. The product was purified by chromatography on silica gel (5-10% EtOAc/hexane).



**(*S*)-*N,N*-dibenzyl-1-phenylethan-1-amine (Table 2, entry 3a).** Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% (*R*)-DTBM-SEGPHOS, styrene (104 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol,

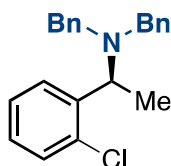
<sup>4</sup> Lee, N. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 5985–5986.

1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a liquid in 95% and 86% yield. IR (thin film) 3028, 2820, 1493, 1452, 1123, 1027, 742, 695  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.46 – 7.18 (m, 15H), 3.94 (q,  $J = 6.9$  Hz, 1H), 3.63 (d,  $J = 14.0$  Hz, 2H), 3.48 (d,  $J = 13.6$  Hz, 2H), 1.46 (d,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.86, 140.56, 128.77, 128.31, 128.15, 128.08, 126.85, 126.83, 56.30, 53.71, 13.91. HRMS (DART-TOF) calculated for  $\text{C}_{22}\text{H}_{23}\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  302.1903, found 302.1901. Anal. Calcd. for  $\text{C}_{22}\text{H}_{23}\text{N}$ : C, 87.66; H, 7.69. Found: C, 87.64; H, 7.79.  $[\alpha]_{\text{D}}^{25} = -97.1$  ( $c = 1.29$ ,  $\text{CHCl}_3$ ); HPLC analysis (OD-H, 3% IPA/hexane, 0.8 mL/min, 220 nm) indicated 97% ee:  $t_{\text{R}}$  (major) = 4.8 minutes,  $t_{\text{R}}$  (minor) = 5.4 minutes.

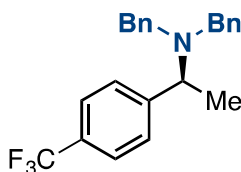


**(R)-N,N-dibenzyl-1-(4-fluorophenyl)ethan-1-amine (Table 2, entry 3b).** Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% (*R*)-DTBM-SEGPHOS, 4-fluorostyrene (122.1 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a liquid in 86% and 85% yield. IR (thin film) 1602, 1506, 1453, 1221, 807, 740, 697  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.44 – 7.37 (m, 6H), 7.36 – 7.30 (m, 4H), 7.28 – 7.21 (m, 2H), 7.05 (t,  $J = 8.7$  Hz, 2H), 3.93 (q,  $J = 6.9$  Hz, 1H), 3.60 (d,  $J = 13.8$  Hz, 2H), 3.49 (d,  $J = 13.8$  Hz, 2H), 1.45 (d,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 161.84 (d,  $J = 244.6$  Hz), 140.37, 138.72 (d,  $J = 3.0$  Hz), 129.54 (d,  $J = 7.8$  Hz), 128.75, 128.36, 126.95, 114.80 (d,  $J = 20.9$  Hz), 55.53, 53.60, 13.49;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -116.43; HRMS (ESI-TOF) calculated for  $\text{C}_{22}\text{H}_{22}\text{FN}$   $[\text{M}+\text{H}]^+$   $m/z$  320.1809, found 320.1807. Anal. Calcd. for  $\text{C}_{26}\text{H}_{25}\text{N}$ : C, 82.72; H, 6.94. Found: C, 82.54; H, 6.82.  $[\alpha]_{\text{D}}^{25} = -79.6$  ( $c = 1.10$ ,  $\text{CHCl}_3$ );

HPLC analysis (OD-H, 5% IPA/hexane, 0.8 mL/min, 220 nm) indicated 97% ee:  $t_R$  (major) = 4.8 minutes,  $t_R$  (minor) = 5.5 minutes.

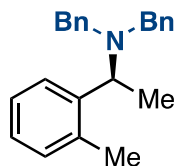


**(R)-N,N-dibenzyl-1-(2-chlorophenyl)ethan-1-amine (Table 2, entry 3c).** Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% (*R*)-DTBM-SEGPPOS, 2-chlorostyrene (138.6 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a white solid in 79 % and 92% yield. m.p. 67-68°C. IR (thin film,  $\text{CHCl}_3$ ) 3025, 2802, 1493, 1453, 1367, 1035, 746, 696  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.78 (dd,  $J = 7.8, 1.7$  Hz, 1H), 7.48 – 7.41 (m, 5H), 7.41 – 7.33 (m, 5H), 7.33 – 7.27 (m, 2H), 7.27 – 7.21 (m, 1H), 4.51 (q,  $J = 6.8$  Hz, 1H), 3.84 (d,  $J = 14.1$  Hz, 2H), 3.69 (d,  $J = 14.2$  Hz, 2H), 1.45 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.12, 140.30, 134.17, 129.84, 128.85, 128.14, 127.95, 126.77, 126.76, 56.79, 54.96, 18.15; HRMS (DART-TOF) calculated for  $\text{C}_{22}\text{H}_{22}\text{ClN}$   $[\text{M}+\text{H}]^+$   $m/z$  336.1514, found 336.1513. Anal. Calcd. for  $\text{C}_{22}\text{H}_{22}\text{ClN}$ : C, 78.67; H, 6.60. Found: C, 78.64; H, 6.71.  $[\alpha]_D^{25} = +53.0$  ( $c = 1.13$ ,  $\text{CHCl}_3$ ); HPLC analysis (OD-H, 3% IPA/hexane, 0.8 mL/min, 220 nm) indicated 92% ee:  $t_R$  (major) = 5.2 minutes,  $t_R$  (minor) = 5.8 minutes.



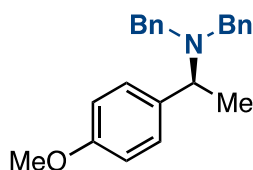
**(R)-N,N-dibenzyl-1-(4-(trifluoromethyl)phenyl)ethan-1-amine (Table 2, entry 3d).** Prepared following the general procedure using 4 mol%  $\text{Cu}(\text{OAc})_2$ , 4.4% (*R*)-DTBM-

SEGPLHOS, 4-(trifluoromethyl)styrene (172.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a liquid in 92% and 84% yield. IR (thin film) 3028, 2973, 2804, 1323, 1162, 1120, 1069, 1016, 737, 696 1453, 1367, 1035, 843, 746, 696  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.72 – 7.64 (m, 2H), 7.64 – 7.58 (m, 2H), 7.50 – 7.43 (m, 4H), 7.42 – 7.35 (m, 4H), 7.35 – 7.29 (m, 2H), 4.05 (q,  $J$  = 6.8 Hz, 1H), 3.68 (d,  $J$  = 13.8 Hz, 2H), 3.58 (d,  $J$  = 13.8 Hz, 2H), 1.53 (d,  $J$  = 6.9 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 147.45 (q,  $J$  = 1.3 Hz), 140.08, 129.07 (q,  $J$  = 32.2 Hz), 128.76, 128.45, 128.33, 127.09, 125.05 (q,  $J$  = 3.8 Hz), 124.52 (q,  $J$  = 272.7 Hz), 56.02, 53.76, 13.16;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$ : -62.11; HRMS (ESI-TOF) calculated for  $\text{C}_{23}\text{H}_{22}\text{F}_3\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  370.1777, found 370.1775. Anal. Calcd. for  $\text{C}_{23}\text{H}_{22}\text{F}_3\text{N}$ : C, 74.78; H, 6.00. Found: C, 74.81; H, 6.14.  $[\alpha]_{\text{D}}^{25} = -93.8$  ( $c$  = 1.12,  $\text{CHCl}_3$ ); HPLC analysis (OD-H, 3% IPA/hexane, 0.8 mL/min, 220 nm) indicated 95% ee:  $t_{\text{R}}$  (major) = 4.8 minutes,  $t_{\text{R}}$  (minor) = 6.5 minutes.

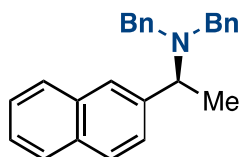


**(*S*)-*N,N*-dibenzyl-1-(*o*-tolyl)ethan-1-amine (Table 2, entry 3e).** Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% (*R*)-DTBM-SEGPLHOS, 2-methylstyrene (118.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a white solid in 85% and 74% yield. m.p.: 83.5-84.0 °C. IR (thin film,  $\text{CHCl}_3$ ) 3026, 2970, 2801, 1739, 1494, 1453, 1377, 741, 677  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.54 (d,  $J$  = 7.5 Hz, 1H), 7.33 – 7.29 (m, 8H), 7.28 – 7.18 (m, 3H), 7.18 – 7.15 (m, 2H), 4.14 (q,  $J$  = 6.8 Hz, 1H), 3.68 (d,  $J$  = 13.6 Hz, 2H), 3.63 (d,  $J$  = 13.7 Hz,

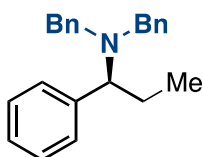
2H), 2.19 (s, 3H), 1.44 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.22, 140.38, 137.27, 130.69, 129.15, 128.11, 127.19, 126.79, 126.68, 125.60, 54.95, 54.50, 19.55, 14.44; HRMS (ESI-TOF) calculated for  $\text{C}_{23}\text{H}_{25}\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  316.2060, found 316.2057. Anal. Calcd. for  $\text{C}_{23}\text{H}_{25}\text{N}$ : C, 87.57; H, 7.99. Found: C, 87.68; H, 7.96.  $[\alpha]_{\text{D}}^{25} = +34.8$  ( $c = 0.92$ ,  $\text{CHCl}_3$ ); HPLC analysis (OJ, 3% IPA/hexane, 0.8 mL/min, 220 nm) indicated 92% ee:  $t_{\text{R}}$  (major) = 6.2 minutes,  $t_{\text{R}}$  (minor) = 8.7 minutes.



**(S)-N,N-dibenzyl-1-(4-methoxyphenyl)ethan-1-amine (Table 2, entry 3f).** Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% (*R*)-DTBM-SEGPPOS, 4-vinylanisole (134.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 5-10% EtOAc in hexane to provide the title compound as a liquid in 89% and 88% yield. IR (thin film) 3025, 2960, 2833, 1510, 1244, 1176, 1028, 832, 739, 697  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.47 – 7.39 (m, 4H), 7.39 – 7.30 (m, 6H), 7.28 – 7.20 (m, 2H), 6.93 (d,  $J = 8.7$  Hz, 2H), 3.92 (q,  $J = 6.9$  Hz, 1H), 3.85 (s, 3H), 3.63 (d,  $J = 13.8$  Hz, 2H), 3.49 (d,  $J = 13.9$  Hz, 2H), 1.45 (d,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 158.46, 140.64, 134.84, 129.14, 128.74, 128.28, 126.81, 113.39, 55.55, 55.28, 53.58, 13.96; HRMS (DART-TOF) calculated for  $\text{C}_{23}\text{H}_{25}\text{NO}$   $[\text{M}+\text{H}]^+$   $m/z$  332.2009, found 332.2006. Anal. Calcd. for  $\text{C}_{23}\text{H}_{25}\text{NO}$ : C, 83.34; H, 7.60. Found: C, 83.28; H, 7.60.  $[\alpha]_{\text{D}}^{25} = -117.3$  ( $c = 0.93$ ,  $\text{CHCl}_3$ ); HPLC analysis (OJ, 10% IPA/hexane, 0.8 mL/min, 220 nm) indicated 99% ee:  $t_{\text{R}}$  (major) = 9.0 minutes,  $t_{\text{R}}$  (minor) = 17.9 minutes.



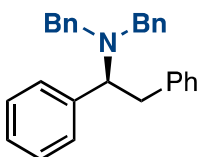
**(S)-N,N-dibenzyl-1-(naphthalen-2-yl)ethanamine (Table 3, entry 3g).** Prepared following the general procedure using 2 mol% Cu(OAc)<sub>2</sub>, 2.2% (*R*)-DTBM-SEGPHOS, 2-vinylnaphthalene (154 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a colorless crystal in 83% and 89% yield. m. p. 123~124 °C. IR (thin film) 3057, 3024, 2968, 1500, 1453, 1379, 1124, 857, 819, 582, 579, 560, 557 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.90 (dd, *J* = 7.6, 3.3 Hz, 3H), 7.85 – 7.80 (m, 1H), 7.72 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.48 (m, 4H), 7.38 (m, 4H), 7.32 – 7.26 (m, 2H), 4.16 (q, *J* = 6.8 Hz, 1H), 3.70 (d, *J* = 13.6 Hz, 2H), 3.63 (d, *J* = 13.6 Hz, 2H), 1.61 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 140.83, 140.52, 133.28, 132.71, 128.86, 128.34, 128.02, 127.67, 127.31, 126.91, 126.10, 125.94, 125.64, 56.35, 53.76, 13.24. HRMS (DART-TOF) calculated for C<sub>26</sub>H<sub>25</sub>N [M+H]<sup>+</sup> m/z 352.2060, found 352.2059. Anal. Calcd. for C<sub>26</sub>H<sub>25</sub>N: C, 87.57; H, 7.99. Found: C, 87.45; H, 8.16. [α]<sub>D</sub><sup>25</sup> = -149.63 (c = 1.00, CHCl<sub>3</sub>); HPLC analysis (OJ, 10% IPA/hexane, 0.8 mL/min, 220 nm) indicated 97% ee: t<sub>R</sub> (major) = 10.9 minutes, t<sub>R</sub> (minor) = 36.2 minutes.



**(S)-N,N-dibenzyl-1-phenylpropan-1-amine (Table 2, 3h & 3l).** Prepared following the general procedure using 2 mol% Cu(OAc)<sub>2</sub>, 2.2% (*R*)-DTBM-SEGPHOS, *trans*-β-methylstyrene or *cis*-β-methylstyrene (118.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a liquid. 97% and 98% yields from *trans*-β-methylstyrene; 89% and 87% from *cis*-β-methylstyrene. IR (thin film) 3025, 2960, 2930, 2800, 1493, 1452, 1027, 739, 695 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.47

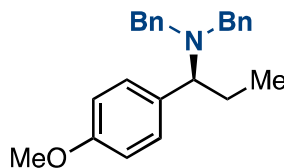


– 7.39 (m, 6H), 7.35 (t,  $J = 7.5$  Hz, 5H), 7.30 – 7.23 (m, 4H), 3.87 (d,  $J = 13.8$  Hz, 2H), 3.64 (t,  $J = 7.5$  Hz, 1H), 3.20 (d,  $J = 13.9$  Hz, 2H), 2.12 (dt,  $J = 13.7, 7.3$  Hz, 1H), 1.96 – 1.75 (m, 1H), 0.97 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.56, 139.08, 129.07, 128.80, 128.25, 127.95, 126.98, 126.75, 63.83, 53.74, 24.31, 11.81; HRMS (DART-TOF) calculated for  $\text{C}_{23}\text{H}_{25}\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  316.2060, found 316.2053. Anal. Calcd. for  $\text{C}_{23}\text{H}_{25}\text{N}$ : C, 87.57; H, 7.99. Found: C, 87.45; H, 8.16.  $[\alpha]_{\text{D}}^{25} = -112.9$  ( $c = 1.19$ ,  $\text{CHCl}_3$ ); HPLC analysis (OD-H, 5% IPA/hexane, 0.8 mL/min, 220 nm) indicated >99% ee (from *trans*-), 96% ee (from *cis*-):  $t_{\text{R}}$  (major) = 4.8 minutes,  $t_{\text{R}}$  (minor) = 5.6 minutes.

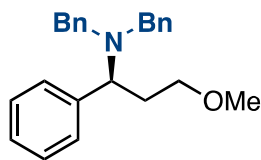


**(S)-N,N-dibenzyl-1,2-diphenylethan-1-amine (Table 2, 3i & 3m).** Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% (*R*)-DTBM-SEGPHOS, *trans*-stilbene or *cis*-stilbene (180.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a white solid. 95% and 94% yields from *trans*-stilbene; 93% and 93% from *cis*-stilbene. m. p. 73.5-74.0 °C. IR (thin film,  $\text{CHCl}_3$ ) 3025, 1493, 1452, 1028, 740, 695  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.43 (t,  $J = 7.7$  Hz, 2H), 7.38 – 7.21 (m, 16H), 7.14 (d,  $J = 7.7$  Hz, 2H), 4.11 (t,  $J = 7.7$  Hz, 1H), 3.94 (d,  $J = 13.9$  Hz, 2H), 3.44 (dd,  $J = 14.0, 8.4$  Hz, 1H), 3.25 (d,  $J = 14.0$  Hz, 2H), 3.13 (dd,  $J = 14.0, 6.9$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.10, 139.96, 138.57, 129.69, 129.17, 128.76, 128.28, 128.13, 128.07, 127.26, 126.83, 126.04, 63.32, 53.69, 37.75; HRMS (DART-TOF) calculated for  $\text{C}_{28}\text{H}_{27}\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  378.2216, found 378.2203. Anal. Calcd. for  $\text{C}_{28}\text{H}_{27}\text{N}$ : C, 89.08; H, 7.21. Found: C, 89.13; H, 7.29.  $[\alpha]_{\text{D}}^{25} = -55.7$  ( $c = 0.97$ ,  $\text{CHCl}_3$ ); HPLC analysis (OD-H, 5% IPA/hexane, 0.8 mL/min, 220 nm) indicated >99% ee (from *trans*-), 89% ee (from *cis*):  $t_{\text{R}}$  (major) = 5.2 minutes,  $t_{\text{R}}$  (minor)

= 6.5 minutes.

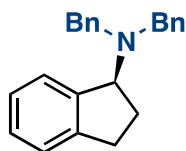


**(S)-N,N-dibenzyl-1-(4-methoxyphenyl)propan-1-amine (Table 2, 3j).** Prepared following the general procedure using 2 mol% Cu(OAc)<sub>2</sub>, 2.2% (*R*)-DTBM-SEGPHOS, trans-anethole (148.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a colorless liquid in 91% and 92% yield. IR (thin film) 2932, 2832, 1510, 1453, 1247, 1178, 1037, 826, 741, 697 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.56 – 7.46 (m, 4H), 7.45 – 7.35 (m, 4H), 7.35 – 7.27 (m, 2H), 7.27 – 7.20 (m, 2H), 7.04 – 6.95 (m, 2H), 3.91 (d, *J* = 13.9 Hz, 2H), 3.91 (s, 3H), 3.66 (t, *J* = 7.5 Hz, 1H), 3.25 (d, *J* = 13.9 Hz, 2H), 2.16 (dt, *J* = 13.7, 7.3 Hz, 1H), 1.95 – 1.78 (m, 1H), 1.02 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 158.60, 140.70, 131.22, 130.09, 128.84, 128.29, 126.78, 113.34, 63.17, 55.29, 53.75, 24.55, 11.91; HRMS (DART-TOF) calculated for C<sub>24</sub>H<sub>27</sub>NO [M+H]<sup>+</sup> *m/z* 346.2165, found 346.2171. Anal. Calcd. for C<sub>24</sub>H<sub>27</sub>NO: C, 83.44; H, 7.88. Found: C, 83.58; H, 7.82. [α]<sub>D</sub><sup>25</sup> = -137.0 (c = 1.95, CHCl<sub>3</sub>); HPLC analysis (OJ, 10% EtOH/hexane, 0.8 mL/min, 220 nm) indicated >99% ee: t<sub>R</sub> (major) = 8.3 minutes, t<sub>R</sub> (minor) = 23.6 minutes.



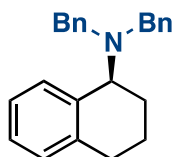
**(S)-N,N-dibenzyl-3-methoxy-1-phenylpropan-1-amine (Table 3, entry 3k).** Prepared following the general procedure using 2 mol% Cu(OAc)<sub>2</sub>, 2.2% (*R*)-DTBM-SEGPHOS, (*E*)-(3-methoxyprop-1-en-1-yl)benzene (148.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40

°C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a colorless liquid in 94% and 95% yield. IR (thin film) 2932, 2832, 1493, 1452, 1113, 739, 696  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.50 – 7.42 (m, 6H), 7.42 – 7.35 (m, 5H), 7.34 – 7.26 (m, 4H), 4.00 – 3.85 (m, 3H), 3.56 – 3.47 (m, 2H), 3.33 (d,  $J = 0.9$  Hz, 3H), 3.23 (d,  $J = 13.8$  Hz, 2H), 2.45 (ddd,  $J = 13.9, 7.6, 6.4$  Hz, 1H), 2.21 – 1.96 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.32, 138.49, 129.05, 128.85, 128.33, 128.10, 127.26, 126.90, 70.58, 58.94, 58.59, 53.82, 31.61; HRMS (DART-TOF) calculated for  $\text{C}_{24}\text{H}_{27}\text{NO}$   $[\text{M}+\text{H}]^+$   $m/z$  346.2165, found 346.2162. Anal. Calcd. for  $\text{C}_{24}\text{H}_{27}\text{NO}$ : C, 83.44; H, 7.88. Found: C, 83.17; H, 8.02.  $[\alpha]_{\text{D}}^{25} = -89.9$  ( $c = 0.91$ ,  $\text{CHCl}_3$ ); HPLC analysis (OD-H, 3% IPA/hexane, 0.8 mL/min, 220 nm) indicated >99% ee:  $t_{\text{R}}$  (major) = 6.0 minutes,  $t_{\text{R}}$  (minor) = 6.7 minutes.



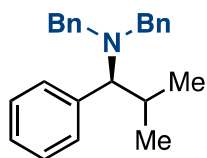
**(S)-N,N-dibenzyl-2,3-dihydro-1H-inden-1-amine (Table 3, entry 3n).** Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% (*R*)-DTBM-SEGPHOS, s indene (116.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF 2 mL for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a white solid in 95% and 73% yield. m. p. 89-90 °C. IR (thin film) 3024, 2934, 2798, 1493, 1452, 1372, 1117, 1027, 742, 696  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.71 – 7.59 (m, 1H), 7.56 (m, 4H), 7.40 (m, 4H), 7.33 – 7.19 (m, 5H), 4.57 (t,  $J = 7.8$  Hz, 1H), 3.67 (d,  $J = 13.6$  Hz, 2H), 3.50 (d,  $J = 13.6$  Hz, 2H), 3.03 (dt,  $J = 16.1, 6.4$  Hz, 1H), 2.86 (dt,  $J = 16.3, 8.5$  Hz, 1H), 2.21 (tdd,  $J = 8.3, 6.4, 1.7$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 144.51, 143.69, 140.47, 128.66, 128.33, 127.39, 126.88, 126.48, 124.72, 124.62, 64.65, 54.31, 30.61, 23.46; HRMS (DART-TOF) calculated for  $\text{C}_{23}\text{H}_{23}\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  314.1903, found 314.1902. Anal. Calcd. for  $\text{C}_{23}\text{H}_{23}\text{N}$ : C, 88.13; H, 7.40. Found: C, 87.84; H, 7.31.  $[\alpha]_{\text{D}}^{25} = -99.4$  ( $c = 1.35$ ,  $\text{CHCl}_3$ ); HPLC analysis (OJ, 5%

IPA/hexane, 0.8 mL/min, 220 nm) indicated 97% ee:  $t_R$  (major) = 5.9 minutes,  $t_R$  (minor) = 7.6 minutes.



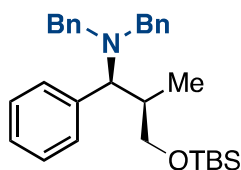
**(S)-N,N-dibenzyl-1,2,3,4-tetrahydronaphthalen-1-amine (Table 3, entry 3o).**

Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% (*R*)-DTBM-SEGPHOS, 1,2-dihydronaphthalene (130.2 mg, 1.0 mmol, 1.0 equiv), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a colorless liquid in 92% and 82% yield. IR (thin film) 2928, 1493, 1452, 1366, 1121, 1027, 973, 740, 696 $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.07 (dt,  $J = 7.8, 1.2$  Hz, 1H), 7.53 (d,  $J = 7.3$  Hz, 4H), 7.38 (dd,  $J = 8.2, 6.9$  Hz, 4H), 7.32 – 7.22 (m, 3H), 7.17 (tt,  $J = 7.3, 1.1$  Hz, 1H), 7.09 (d,  $J = 7.9$  Hz, 1H), 4.00 (dd,  $J = 10.2, 5.7$  Hz, 1H), 3.87 (d,  $J = 13.6$  Hz, 2H), 3.54 (d,  $J = 13.6$  Hz, 2H), 2.91 – 2.66 (m, 2H), 2.32 – 2.14 (m, 1H), 2.06 (dtt,  $J = 13.7, 5.6, 3.1$  Hz, 1H), 1.85 (tdd,  $J = 12.5, 10.1, 2.8$  Hz, 1H), 1.76 – 1.58 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.51, 139.20, 138.84, 128.76, 128.69, 128.34, 128.10, 126.88, 126.22, 126.02, 56.45, 53.77, 30.27, 22.37, 20.67; HRMS (DART-TOF) calculated for  $\text{C}_{24}\text{H}_{25}\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  328.2060, found 328.2068. Anal. Calcd. for  $\text{C}_{24}\text{H}_{25}\text{N}$ : C, 88.03; H, 7.70. Found: C, 87.77; H, 7.74.  $[\alpha]_D^{25} = -77.0$  ( $c = 1.09$ ,  $\text{CHCl}_3$ ); HPLC analysis (OJ, 3% IPA/hexane, 0.8 mL/min, 220 nm) indicated 86% ee:  $t_R$  (major) = 5.8 minutes,  $t_R$  (minor) = 7.7 minutes.



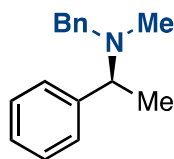
**(S)-N,N-dibenzyl-2-methyl-1-phenylpropan-1-amine (Table 2, 3p).** Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% (*R*)-DTBM-SEGPHOS,

2-methyl-1-phenylpropene (132.2 mg, 1.0 mmol, 1.0 equiv., *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a colorless liquid in 77% and 76% yield. IR (thin film) 3025, 2955, 1493, 1452, 1092, 1069, 1121, 1028, 761, 696 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.47 (d, *J* = 7.6 Hz, 4H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 5H), 7.29 – 7.22 (m, 2H), 7.15 (d, *J* = 6.9 Hz, 2H), 3.93 (d, *J* = 13.8 Hz, 2H), 3.22 (d, *J* = 10.9 Hz, 1H), 3.00 (d, *J* = 13.9 Hz, 2H), 2.54 – 2.35 (m, 1H), 1.31 (d, *J* = 6.5 Hz, 3H), 0.63 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 140.45, 137.03, 129.68, 128.89, 128.37, 127.91, 126.97, 126.82, 69.37, 53.68, 28.68, 21.29, 20.92; HRMS (DART-TOF) calculated for C<sub>24</sub>H<sub>27</sub>N [M+H]<sup>+</sup> *m/z* 330.2216, found 330.2216. Anal. Calcd. for C<sub>24</sub>H<sub>25</sub>N: C, 87.49; H, 8.26. Found: C, 87.29; H, 8.43. [α]<sub>D</sub><sup>25</sup> = -114.5 (c = 1.14, CHCl<sub>3</sub>); HPLC analysis (OD-H, 5% IPA/hexane, 0.8 mL/min, 220 nm) indicated >99% ee, single isomer: *t*<sub>R</sub> (major) = 4.7 minutes, *t*<sub>R</sub> (minor) = 6.1 minutes.

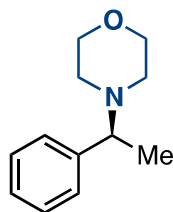


**(1*S*,2*R*)-*N,N*-dibenzyl-3-((*tert*-butyldimethylsilyl)oxy)-2-methyl-1-phenylpropan-1-amine (Table 2, 3q).** Prepared following the general procedure using 2 mol% Cu(OAc)<sub>2</sub>, 2.2% (*R*)-DTBM-SEGPHOS, (*E*)-*tert*-butyldimethyl((2-methyl-3-phenylallyl)oxy)silane (262.5 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a colorless solid in 84% and 82% yield. m. p. 93~94 °C. IR (thin film) 2955, 2927, 2855, 1494, 1453, 1257, 1084, 834, 763, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.45 – 7.37 (m, 6H), 7.37 – 7.30 (m, 5H), 7.29 – 7.21 (m, 2H), 7.20 – 7.13 (m, 2H), 4.49 (dd, *J* = 9.8, 3.9 Hz, 1H), 3.93 (d, *J* = 13.9 Hz, 2H), 3.54 – 3.33 (m, 2H), 3.01

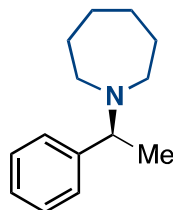
(d,  $J = 13.9$  Hz, 2H), 2.60 – 2.44 (m, 1H), 0.97 (s, 9H), 0.66 (d,  $J = 6.5$  Hz, 3H), 0.12 (d,  $J = 5.2$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.05, 135.91, 129.73, 128.72, 128.29, 127.87, 127.04, 126.80, 66.74, 65.63, 53.70, 36.07, 26.14, 18.55, 15.68, -5.13, -5.17. HRMS (DART-TOF) calculated for  $\text{C}_{30}\text{H}_{41}\text{NOSi}$   $[\text{M}+\text{H}]^+$   $m/z$  460.3030, found 460.3026. Anal. Calcd. for  $\text{C}_{30}\text{H}_{41}\text{NOSi}$ : C, 78.38; H, 8.99. Found: C, 78.54; H, 9.01.  $[\alpha]_{\text{D}}^{25} = -73.5$  ( $c = 0.86$ ,  $\text{CHCl}_3$ ); HPLC analysis (OD-H, 3% IPA/hexane, 0.8 mL/min, 220 nm) indicated >99% ee, single isomer:  $t_{\text{R}}$  (major) = 4.3 minutes,  $t_{\text{R}}$  (minor) = 4.9 minutes.



**(S)-N-benzyl-N-methyl-1-phenylethanamine (Table 3, entry 3r).** Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% (R)-DTBM-SEGPHOS, styrene (104 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N*-benzyl-*N*-methylhydroxylamine (290 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a colorless liquid crystal in 90% and 84% yield. IR (thin film) 2971, 2784, 1494, 1451, 1074, 1028, 761, 735, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.44 (m, 2H) 7.42 – 7.22 (m, 8H), 3.69 – 3.64 (q,  $J = 6.7$  Hz, 1H), 3.63 – 3.59 (d,  $J = 13.3$  Hz, 1H), 3.35 – 3.32 (d,  $J = 13.3$  Hz, 1H), 2.16 (s, 3H), 1.46 – 1.44 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 128.89, 128.31, 128.3, 127.8, 126.9, 126.9, 63.4, 59.0, 38.5, 18.5; HRMS (DART-TOF) calculated for  $\text{C}_{16}\text{H}_{19}\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  226.1590, found 226.1582. Anal. Calcd. for  $\text{C}_{16}\text{H}_{19}\text{N}$ : C, 82.70; H, 11.28. Found: C, 82.64; H, 11.28.  $[\alpha]_{\text{D}}^{25} = -15.3$  ( $c = 1.02$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR analysis of the amine and (R) and (S)-*O*-acetylmandelic acid indicated 94% ee.



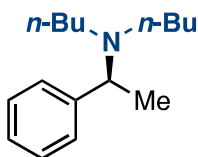
**(S)-4-(1-phenylethyl)morpholine (Table 3, entry 3s).** Prepared following the general procedure using 2 mol% Cu(OAc)<sub>2</sub>, 2.2% (R)-DTBM-SEGPBOS, styrene (104 mg, 1.0 mmol, 1.0 equiv.), morpholino benzoate (207.23 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a liquid in 88% and 85% yield. IR (thin film) 2957, 2851, 2803, 1450, 1116, 946, 865, 759, 700 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.39 – 7.31 (m, 4H), 7.29 – 7.23 (m, 1H), 3.72 (dd, *J* = 5.3, 4.1 Hz, 4H), 3.33 (q, *J* = 6.7 Hz, 1H), 2.62 – 2.45 (m, 2H), 2.45 – 2.30 (m, 2H), 1.38 (d, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 144.05, 128.33, 127.61, 127.00, 67.22, 65.40, 51.37, 19.96; HRMS (DART-TOF) calculated for C<sub>12</sub>H<sub>17</sub>NO [M+H]<sup>+</sup> *m/z* 192.1383, found 192.1381. Anal. Calcd. for C<sub>12</sub>H<sub>17</sub>NO: C, 75.35; H, 8.96. Found: C, 75.09; H, 8.81. [α]<sub>D</sub><sup>24</sup> = –36.5 (c = 0.98, CHCl<sub>3</sub>); [α]<sub>D</sub><sup>25</sup> = –41.0 (c = 1.10, EtOH); Literature [α]<sub>D</sub><sup>25</sup> = –41.6 (c = 1.10, EtOH)<sup>5</sup>. ee: 98%. GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm, chiralsil-DEX CB), H2 2.7 mL/min, programmed from 100 ° to 125 ° at 0.5 °/min; t<sub>R</sub> (minor) = 28.41 min, and t<sub>R</sub> (major) = 29.24 min.



**(S)-1-(1-phenylethyl)azepane (Table 3, entry 3t).** Prepared following the general

<sup>5</sup> Kawaguchi, M.; Ohashi, J.; Kawakami, Y.; Yamamoto, Y.; Oda, J. *Synthesis*, 1985, 701.

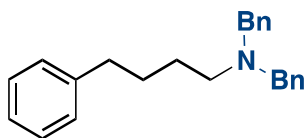
procedure using 2 mol% Cu(OAc)<sub>2</sub>, 2.2% (*R*)-DTBM-SEGPHOS, styrene (104 mg, 1.0 mmol, 1.0 equiv), azepan-1-yl benzoate (219 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 20-50% EtOAc in hexane to provide the title compound as a liquid in 86% yield for both runs. IR (thin film) 2922, 1492, 1451, 1128, 909, 762, 697 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.43 – 7.37 (m, 2H), 7.37 – 7.30 (m, 2H), 7.28 – 7.21 (m, 1H), 3.80 (q, *J* = 6.7 Hz, 1H), 2.66 (s, 4H), 1.62 (s, 8H), 1.39 (d, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ: 144.94, 127.95, 127.60, 126.46, 63.21, 52.06, 28.96, 27.07, 18.26; HRMS (DART-TOF) calculated for C<sub>14</sub>H<sub>21</sub>N [M+H]<sup>+</sup> *m/z* 204.1747, found 204.1745. Anal. Calcd. for C<sub>14</sub>H<sub>21</sub>N: C, 82.70; H, 10.41. Found: C, 82.58; H, 10.47. [α]<sub>D</sub><sup>25</sup> = +6.5 (c = 1.10, CHCl<sub>3</sub>); ee~99%. GC condition: Varian CP7502 column (25 m×0.25 mm×0.25 μm, chiralsil-DEX CB), H<sub>2</sub> 2.7 mL/min, programmed from 100 ° to 125 ° at 0.5 °/min; *t*R = 35.2 min (minor) and *t*R = 35.8 min (major).



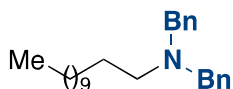
**(*S*)-*N*-butyl-*N*-(1-phenylethyl)butan-1-amine (Table 3, entry 3u).** Prepared following the general procedure using 2 mol% Cu(OAc)<sub>2</sub>, 2.2% (*R*)-DTBM-SEGPHOS, styrene (104 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibutylhydroxylamine (249 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was quenched with Na<sub>2</sub>CO<sub>3</sub> solution, and the crude product extracted with ethyl acetate (x3) (NB: This step is necessary to remove N-OBz compounds). The reaction was then purified by an acid-base treatment, where the amine was first protonated with dilute HCl solution and the aqueous layer washed with ethyl acetate (x1), then treated with 1 M NaOH to deprotonate the amine. The aqueous layer was then extracted with EtOAc (x3), and the organic combined and concentrated to give the pure product as a yellow liquid in 90% yields (for both runs). IR (thin film) 2955, 2929, 2871, 1452, 1367, 1081, 776, 759, 697,



553  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.42 (m, 2H), 7.39 – 7.31 (m, 2H), 7.30 – 7.22 (m, 1H), 3.90 (q,  $J = 6.8$  Hz, 1H), 2.58 – 2.47 (m, 2H), 2.42 (m, 2H), 1.54 – 1.41 (m, 4H), 1.38 (m, 3H), 1.36 – 1.18 (m, 4H), 0.92 (t,  $J = 7.3$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 145.00, 127.89, 127.76, 126.39, 58.96, 49.65, 30.0, 20.62, 16.49, 14.14; HRMS (DART-TOF) calculated for  $\text{C}_{24}\text{H}_{27}\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  234.2216, found 234.2209. Anal. Calcd. for  $\text{C}_{16}\text{H}_{27}\text{N}$ : C, 83.76; H, 11.10. Found: C, 83.63; H, 11.28.  $[\alpha]_{\text{D}}^{25} = +2.9$  ( $c = 0.57$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR analysis of the amine and (*R*) and (*S*)-*O*-acetylmandelic acid indicated 90% ee.

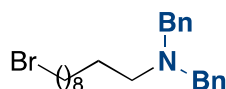


***N,N*-dibenzyl-4-phenylbutan-1-amine (Table 4, entry 5a).** Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% ( $\pm$ )-DTBM-SEGPHOS, but-3-en-1-ylbenzene (132.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40  $^\circ\text{C}$ . The reaction mixture was purified by flash chromatography on silica gel using 0-5% Ether in hexane to provide the title compound as a colorless liquid in 90% and 87% yield. IR (thin film) 2933, 2792, 1494, 1451, 1125, 1027, 732  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.51 – 7.09 (m, 15H), 3.61 (s, 4H), 2.58 (t,  $J = 7.4$  Hz, 2H), 2.51 (t,  $J = 6.8$  Hz, 2H), 1.74 – 1.58 (m, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.74, 140.10, 128.91, 128.52, 128.34, 128.27, 126.87, 125.71, 58.47, 53.20, 35.73, 29.00, 26.65; HRMS (DART-TOF) calculated for  $\text{C}_{24}\text{H}_{27}\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  330.2216, found 330.2215. Anal. Calcd. for  $\text{C}_{24}\text{H}_{27}\text{N}$ : C, 87.49; H, 8.26. Found: C, 87.48; H, 8.27.

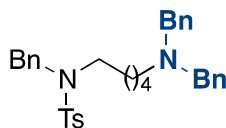


***N,N*-dibenzyl-dodecan-1-amine (Table 4, entry 5b).** Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% ( $\pm$ )-DTBM-SEGPHOS, dodec-1-ene (168.3

mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound as a colorless liquid in 94% and 95% yield. IR (thin film) 2922, 2852, 1494, 1452, 1028, 734, 696  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.60 – 7.09 (m, 10H), 3.58 (s, 4H), 2.43 (t,  $J = 7.2$  Hz, 2H), 1.67 – 1.42 (m, 2H), 1.41 – 1.09 (m, 18H), 0.92 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.11, 128.79, 128.13, 126.71, 58.29, 53.43, 31.97, 29.71, 29.68(3C), 29.54, 29.40, 27.29, 27.00, 22.74, 14.17; HRMS (Dart-TOF) calculated for  $\text{C}_{26}\text{H}_{39}\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  366.3155, found 366.3147. Anal. Calcd. for  $\text{C}_{26}\text{H}_{39}\text{N}$ : C, 85.42; H, 10.75. Found: C, 85.40; H, 10.78.

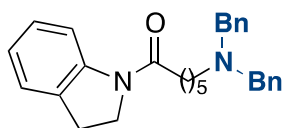


***N,N*-dibenzyl-10-bromodecan-1-amine (Table 4, entry 5c).** Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% ( $\pm$ )-DTBM-SEGPHOS, 10-bromo-1-decene (219.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 5-10% Ethyl acetate in hexane to provide the title compound as a colorless liquid in 89% and 90% yield. IR (thin film) 2925, 2853, 1494, 1452, 742, 696  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.44 – 7.38 (m, 4H), 7.34 (t,  $J = 7.4$  Hz, 4H), 7.28 (s, 2H), 3.58 (s, 4H), 3.44 (t,  $J = 6.8$  Hz, 2H), 2.43 (t,  $J = 7.2$  Hz, 2H), 1.84 – 1.90 (m, 2H), 1.59 – 1.48 (m, 2H), 1.48 – 1.37 (m, 2H), 1.37 – 1.17 (m, 10H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.10, 128.81, 128.18, 126.76, 58.38, 53.42, 34.06, 32.91, 29.58, 29.50, 29.48, 28.83, 28.25, 27.28, 27.06; HRMS (DART-TOF) calculated for  $\text{C}_{24}\text{H}_{34}\text{NBr}$   $[\text{M}+\text{H}]^+$   $m/z$  416.1947, found 416.1943. Anal. Calcd. for  $\text{C}_{24}\text{H}_{34}\text{NBr}$ : C, 69.22; H, 8.23. Found: C, 69.51; H, 8.13.



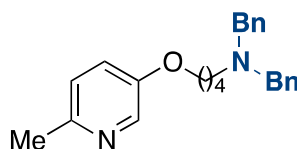
***N*-benzyl-*N*-(5-(dibenzylamino)pentyl)-4-methylbenzenesulfonamide (Table 4, 5d).**

Prepared following the general procedure using 2 mol% Cu(OAc)<sub>2</sub>, 2.2% (±)-DTBM-SEGPHOS, *N*-benzyl-4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide (329.5 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 10-15% EtOAc in hexane (contain 0.5% TEA) to provide the title compound as a colorless liquid in 95% and 95% yield. IR (thin film) 2932, 1494, 1338, 1155, 1090, 734 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.73 (m, 2H), 7.46 – 7.14 (m, 17H), 4.29 (s, 2H), 3.50 (s, 4H), 3.16 – 2.95 (t, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 2.29 (t, *J* = 7.2 Hz, 2H), 1.42 – 1.19 (m, 4H), 1.17 – 0.96 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 143.13, 139.93, 137.17, 136.66, 129.69, 128.74, 128.52, 128.25, 128.17, 127.70, 127.19, 126.78, 58.27, 53.18, 51.92, 48.11, 27.87, 26.53, 24.31, 21.55; HRMS (DART-TOF) calculated for C<sub>33</sub>H<sub>38</sub>N<sub>2</sub>O<sub>2</sub>S [M+H]<sup>+</sup> *m/z* 527.2727, found 527.2738.



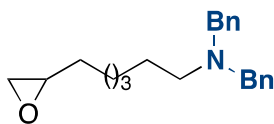
**6-(dibenzylamino)-1-(indolin-1-yl)hexan-1-one (Table 4, 5e).** Prepared following the general procedure using 2 mol% Cu(OAc)<sub>2</sub>, 2.2% (±)-DTBM-SEGPHOS, 1-(indolin-1-yl)hex-5-en-1-one (215.3 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 15-20% EtOAc in hexane (contain 0.5% TEA) to provide the title compound as a colorless liquid in 85% and 91% yield. IR (thin film) 2932, 1658, 1598, 1481, 1404, 1262, 747, 697 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.29 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 4H), 7.34 (t, *J* = 7.5 Hz, 4H), 7.30 – 7.17 (m, 4H), 7.09 – 6.99 (m, 1H), 4.01 (t, *J* = 8.5 Hz, 1.78 H) &

4.17 (m, 0.22 H) due to rotamer, 3.61 (s, 4H), 3.20 (t,  $J = 8.5$  Hz, 1.78 H) & 3.07 (m, 0.22H) due to rotamer, 2.49 (t,  $J = 7.2$  Hz, 2H), 2.38 (t,  $J = 7.5$  Hz, 1.78H) & 2.65 (m, 0.22H) due to rotamer, 1.79 – 1.66 (m, 2H), 1.66 – 1.53 (m, 2H), 1.47 – 1.35 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 171.40, 143.20, 140.02, 131.09, 128.87, 128.23, 127.60, 126.84, 124.55, 123.51, 117.06, 58.44, 53.43, 48.03, 35.97, 28.10, 27.12, 27.04, 24.55; HRMS (DART-TOF) calculated for  $\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$   $m/z$  413.2587, found 413.2595. Anal. Calcd. for  $\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}$ : C, 81.28; H, 7.83. Found: C, 81.28; H, 7.83.

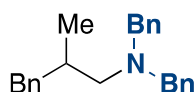


***N,N*-dibenzyl-4-((6-methylpyridin-3-yl)oxy)butan-1-amine (Table 4, entry 5f).**

Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% ( $\pm$ )-DTBM-SEGPHOS, 5-(but-3-en-1-yloxy)-2-methylpyridine (163.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 20-50% EtOAc in hexane (contain 0.5% TEA) to provide the title compound as a colorless liquid in 92% yield for both runs. IR (thin film) 2942, 2793, 1494, 1262, 825  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.15 (dd,  $J = 2.6, 1.0$  Hz, 1H), 7.42 – 7.35 (m, 4H), 7.35 – 7.29 (m, 4H), 7.28 – 7.22 (m, 2H), 7.08 – 6.99 (m, 2H), 3.85 (t,  $J = 6.3$  Hz, 2H), 3.59 (s, 4H), 2.51 (s, 3H), 2.50 (t,  $J = 6.9$  Hz, 2H), 1.86 – 1.76 (m, 2H), 1.73 – 1.66 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 153.20, 150.10, 139.85, 136.79, 128.86, 128.45, 128.22, 126.88, 123.24, 121.96, 67.99, 58.43, 52.56, 26.73, 23.42, 23.36; HRMS (DART-TOF) calculated for  $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$   $m/z$  361.2274, found 361.2270. Anal. Calcd. for  $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}$ : C, 79.96; H, 7.83. Found: C, 79.83; H, 7.75.

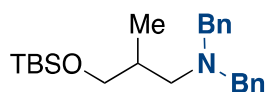


***N,N*-dibenzyl-6-(oxiran-2-yl)hexan-1-amine (Table 4, 5g).** Prepared following the general procedure using 2 mol% Cu(OAc)<sub>2</sub>, 2.2% (±)-DTBM-SEGPHOS, 1,2-epoxy-7-octene (126.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 5-10% EtOAc in hexane (contain 0.5% TEA) to provide the title compound as a colorless liquid in 90% and 91% yield. IR (thin film) 2928, 2855, 2790, 1494, 1128, 1028, 743, 697 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.40 (d, *J* = 6.7 Hz, 4H), 7.34 (t, *J* = 7.4 Hz, 4H), 7.26 (t, *J* = 7.2 Hz, 2H), 3.58 (s, 4H), 2.96 – 2.87 (m, 1H), 2.77 (dd, *J* = 5.0, 4.0 Hz, 1H), 2.48 (dd, *J* = 5.0, 2.7 Hz, 1H), 2.44 (t, *J* = 7.2 Hz, 2H), 1.62 – 1.37 (m, 6H), 1.37 – 1.22 (m, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 140.03, 128.77, 128.14, 126.74, 58.36, 53.25, 52.31, 47.07, 32.47, 29.24, 27.12, 26.91, 25.96; HRMS (DART-TOF) calculated for C<sub>22</sub>H<sub>29</sub>NO [M+H]<sup>+</sup> *m/z* 324.2322, found 324.2314.



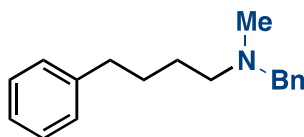
***N,N*-dibenzyl-2-methyl-3-phenylpropan-1-amine (Table 4, 5h).** Prepared following the general procedure using 2 mol% Cu(OAc)<sub>2</sub>, 2.2% (±)-DTBM-SEGPHOS, (2-methylallyl)benzene (132.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (1 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 5-10% EtOAc in hexane to provide the title compound as a colorless liquid in 87% and 90% yields. IR (thin film) 3025, 2795, 1494, 1452, 1066, 1028, 735, 697 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.46 – 7.40 (m, 4H), 7.36 (t, *J* = 7.4 Hz, 4H), 7.28 (s, 4H), 7.22 (d, *J* = 7.3 Hz, 1H), 7.15 – 7.08 (m, 2H), 3.62 (d, *J* = 13.6 Hz, 2H), 3.58 (d, *J* = 13.6 Hz, 2H), 2.97 (dd, *J* = 13.1, 4.6 Hz, 1H), 2.38 (dd, *J* = 12.5, 7.3 Hz, 1H), 2.29 (dd, *J* = 12.4, 6.9

Hz, 1H), 2.15 (dd,  $J = 13.1, 9.1$  Hz, 1H), 2.11 – 1.99 (m, 1H), 0.86 (d,  $J = 6.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 141.64, 139.96, 129.26, 129.04, 128.28, 128.22, 126.91, 125.70, 60.72, 59.08, 41.50, 33.68, 18.09; HRMS (DART-TOF) calculated for  $\text{C}_{24}\text{H}_{27}\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  330.2216, found 330.2203. Anal. Calcd. for  $\text{C}_{24}\text{H}_{27}\text{N}$ : C, 87.49; H, 8.26 Found: C, 87.59; H, 8.24.



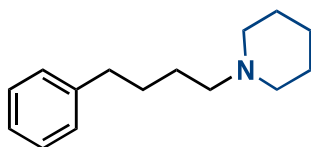
***N,N*-dibenzyl-3-((*tert*-butyldimethylsilyloxy)-2-methylpropan-1-amine (Table 4, 5i).**

Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% ( $\pm$ )-DTBM-SEGPHOS, *tert*-butyldimethyl((2-methylallyl)oxy)silane (132.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-dibenzylhydroxylamine (381 mg, 1.2 mmol, 1.2 equiv), THF (1 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 5-10% EtOAc in hexane to provide the title compound as a colorless liquid in 88% an 87% yield. IR (thin film) 2927, 1452, 1250, 1086, 834, 773, 743, 696  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.39 – 7.27 (m, 8H), 7.25 – 7.19 (m, 2H), 3.63 – 3.54 (m, 3H), 3.47 (d,  $J = 13.6$  Hz, 2H), 3.28 (dd,  $J = 9.8, 6.7$  Hz, 1H), 2.37 (dd,  $J = 12.6, 6.7$  Hz, 1H), 2.18 (dd,  $J = 12.5, 7.6$  Hz, 1H), 1.99 – 1.85 (m, 1H), 0.87 (m, 3H), 0.87 (s, 9H), 0.01 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 140.01, 128.99, 128.23, 126.86, 67.12, 58.99, 57.51, 34.43, 26.12, 18.49, 15.80, -5.19; HRMS (DART-TOF) calculated for  $\text{C}_{24}\text{H}_{37}\text{NOSi}$   $[\text{M}+\text{H}]^+$   $m/z$  384.2717, found 384.2718.

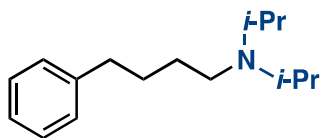


***N*-benzyl-*N*-methyl-4-phenylbutan-1-amine (Table 5, 5j).** Prepared following the general procedure using 2 mol%  $\text{Cu}(\text{OAc})_2$ , 2.2% ( $\pm$ )-DTBM-SEGPHOS, *but-3-en-1-ylbenzene* (132.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N*-benzyl-*N*-methylhydroxylamine (290 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C.

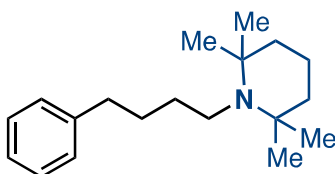
The reaction mixture was purified by flash chromatography on silica gel using 20-50% EtOAc in hexane (contain 0.5% TEA) to provide the title compound as a colorless liquid in 91% and 92% yield. IR (thin film) 2937, 2785, 1495, 1452, 1027, 736, 697  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.37 – 7.25 (m, 7H), 7.24 – 7.17 (m, 3H), 3.51 (s, 2H), 2.64 (t,  $J = 7.6$  Hz, 2H), 2.42 (t,  $J = 7.6$  Hz, 2H), 2.21 (s, 3H), 1.74 – 1.64 (m, 2H), 1.64 – 1.54 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.67, 139.32, 129.14, 128.50, 128.34, 128.27, 126.97, 125.73, 62.50, 57.35, 42.34, 35.90, 29.30, 27.10; HRMS (DART-TOF) calculated for  $\text{C}_{18}\text{H}_{23}\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  254.1903, found 254.1897. Anal. Calcd. for  $\text{C}_{18}\text{H}_{23}\text{N}$ : C, 85.32; H, 9.15 Found: C, 85.06; H, 9.14.



**1-(4-phenylbutyl)piperidine (Table 5, 5k).** Prepared following the general procedure using 4 mol%  $\text{Cu}(\text{OAc})_2$ , 4.4% ( $\pm$ )-DTBM-SEGPHOS, but-3-en-1-ylbenzene (132.2 mg, 1.0 mmol, 1.0 equiv.), piperidin-1-yl benzoate (246.3 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40  $^\circ\text{C}$ . The reaction mixture was purified by flash chromatography on silica gel using 10-20% EtOAc in hexane (contain 1% TEA) to provide the title compound as a colorless liquid in 99% yield for both runs. IR (thin film) 2931, 1738, 1453, 1350, 1122, 1039, 745  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.35 – 7.25 (m, 2H), 7.25 – 7.15 (m, 3H), 2.65 (t,  $J = 7.5$  Hz, 2H), 2.40 – 2.33 (m, 4H), 2.33 (t,  $J = 7.5$  Hz, 2H), 1.73 – 1.51 (m, 8H), 1.51 – 1.39 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 142.52, 128.39, 128.23, 125.63, 59.44, 54.68, 35.91, 29.63, 26.67, 26.02, 24.53; HRMS (DART-TOF) calculated for  $\text{C}_{15}\text{H}_{23}\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  218.1903, found 218.1895. Anal. Calcd. for  $\text{C}_{15}\text{H}_{23}\text{N}$ : C, 82.89; H, 10.67 Found: C, 82.76; H, 10.69.



***N,N*-diisopropyl-4-phenylbutan-1-amine (Table 5, 5l).** Prepared following the general procedure using 4 mol% Cu(OAc)<sub>2</sub>, 4.4% (±)-DTBM-SEGPHOS, *but-3-en-1-yl*benzene (132.2 mg, 1.0 mmol, 1.0 equiv.), *O*-benzoyl-*N,N*-diisopropylhydroxylamine (246.3 mg, 1.2 mmol, 1.2 equiv), THF (1 mL) for 36 h at 40 °C. The reaction mixture was purified by flash chromatography on silica gel using 20-50% EtOAc in hexane (contain 1% TEA) to provide the title compound as a colorless liquid in 97% yield for both runs. IR (thin film) 2961, 2933, 1453, 1384, 1360, 1206, 1158, 742, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.33 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 3.13 – 2.89 (m, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.43 (t, *J* = 7.6 Hz, 2H), 1.69 – 1.57 (m, 2H), 1.55 – 1.40 (m, 2H), 1.02 (d, *J* = 6.6 Hz, 12H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 142.91, 128.40, 128.23, 125.57, 48.40, 45.10, 35.99, 31.13, 29.33, 20.71; HRMS (DART-TOF) calculated for C<sub>16</sub>H<sub>27</sub>N [M+H]<sup>+</sup> *m/z* 234.2216, found 234.2213. Anal. Calcd. for C<sub>16</sub>H<sub>27</sub>N: C, 82.34; H, 11.66 Found: C, 82.086; H, 11.66.



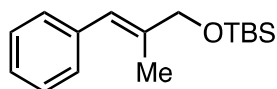
**2,2,6,6-Tetramethyl-1-(4-phenylbutyl)piperidine (Table 5, 5m).** Prepared following the general procedure using 4 mol% Cu(OAc)<sub>2</sub>, 4.4% (±)-DTBM-SEGPHOS, *but-3-en-1-yl*benzene (132.2 mg, 1.0 mmol, 1.0 equiv.), 2,2,6,6-tetramethylpiperidin-1-yl benzoate (314 mg, 1.2 mmol, 1.2 equiv), THF (2 mL) for 36 h at 40 °C. The reaction mixture was quenched with Na<sub>2</sub>CO<sub>3</sub> solution, and the crude product extracted with EtOAc (x3) (NB: This step is necessary to remove N-OBz compounds). The reaction was then purified by an acid-base treatment, where the amine was first protonated with dilute HCl solution and the aqueous layer washed with EtOAc (x1), then treated with 1 M NaOH to deprotonate



the amine. The aqueous layer was then extracted with EtOAc (x3), and the organic combined and concentrated to give the pure product as a yellow liquid in 83% and 76% yields. IR (thin film) 2963, 2925, 2868, 1453, 1377, 1359, 1350, 1261, 1175, 1129, 1108, 1025, 746, 697  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.38 – 7.26 (m, 2H), 7.24 – 7.18 (m, 3H), 2.65 (t,  $J = 7.5$  Hz, 2H), 2.47 – 2.35 (m, 2H), 1.60 – 1.50 (m, 6H), 1.47 – 1.39 (m, 4H), 1.05 (s, 12H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 143.05, 128.44, 128.33, 125.67, 54.58, 45.12, 41.28, 36.12, 35.87, 29.55, 27.63, 17.92; HRMS (DART-TOF) calculated for  $\text{C}_{19}\text{H}_{31}\text{N}$   $[\text{M}+\text{H}]^+$   $m/z$  274.2529, found 274.2519.

### 3. Substrate Preparation

Synthesis of substrates **1q**:



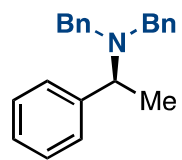
**(E)-tert-butyldimethyl((2-methyl-3-phenylallyl)oxy)silane (Table 2, 1q)** To a 50 mL round-bottom flask containing trans-2-Methyl-3-phenyl-2-propen-1-ol (2.964 g, 20 mmol, 1.00 equiv), imidazole (26 mmol, 1.3 equiv.) was added DMF (20 mL). Then TBSCl (3.62 g, 24 mmol, 1.2 equiv.) was added in one portion. The mixture was allowed to stir overnight. It was then diluted with ethyl acetate and washed with water, extracted 2 times with ethyl acetate and the combined organic layers were washed with brine and dried over  $\text{NaSO}_4$ . The mixture was purified by flash chromatography on silica gel using 0-5% EtOAc in hexane to provide the title compound in 90% yield as a colorless oil. IR (thin film) 2957, 2928, 2855, 1257, 1110, 1076, 835, 776  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.40 – 7.29 (m, 4H), 7.23 (t,  $J = 7.1$  Hz, 1H), 6.56 (s, 1H), 4.26 – 4.14 (m, 2H), 1.86 (d,  $J = 1.3$  Hz, 3H), 0.98 (s, 9H), 0.15 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$ : 138.17, 137.62, 129.03, 128.19, 126.25, 123.83, 68.64, 26.12, 18.61, 15.15, -5.09; HRMS (DART-TOF) calculated for  $\text{C}_{16}\text{H}_{26}\text{OSi}$   $[\text{M}+\text{H}]^+$   $m/z$  263.1826, found 263.1889.

**4. Spectroscopic Data.**

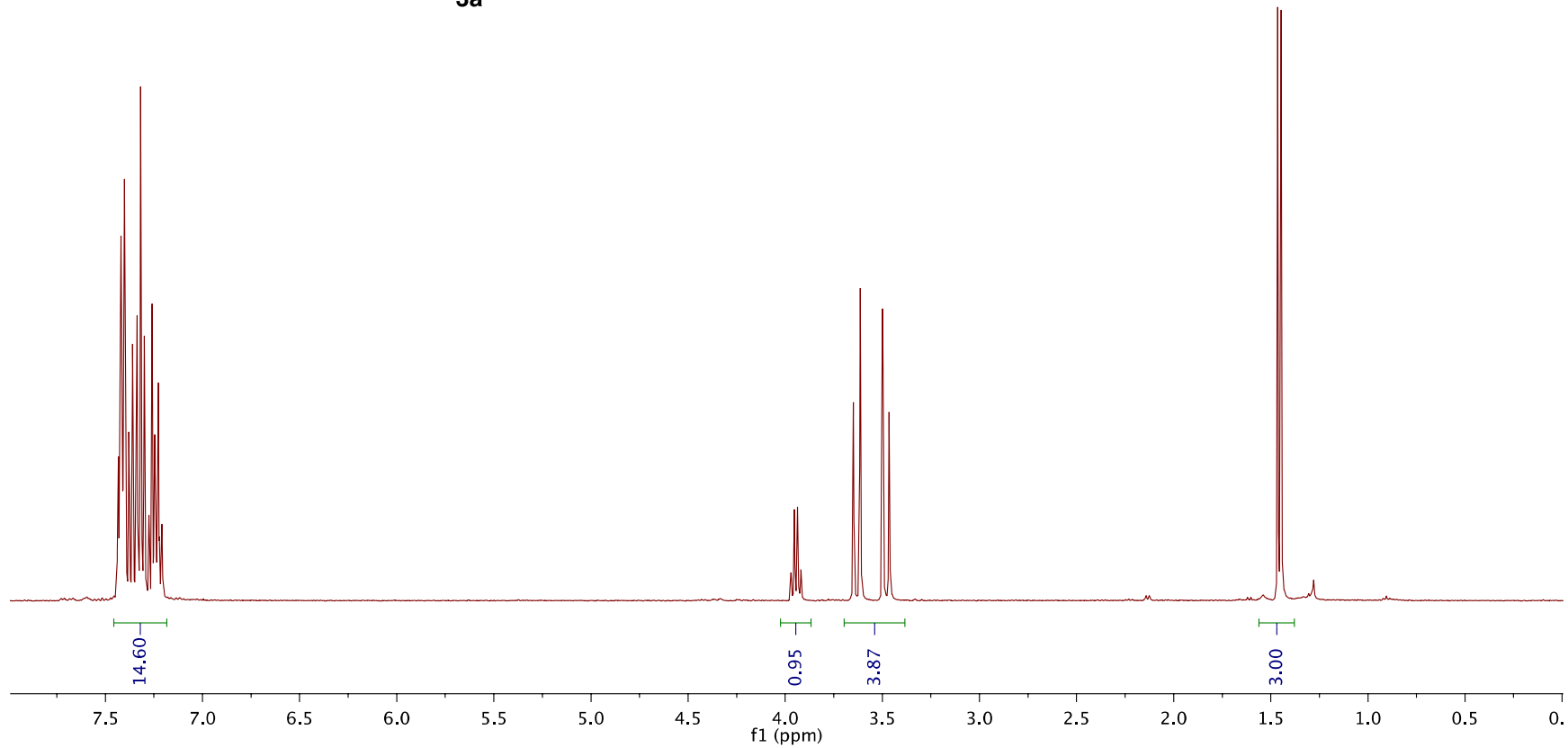
$^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  NMR and HPLC spectra are included below.

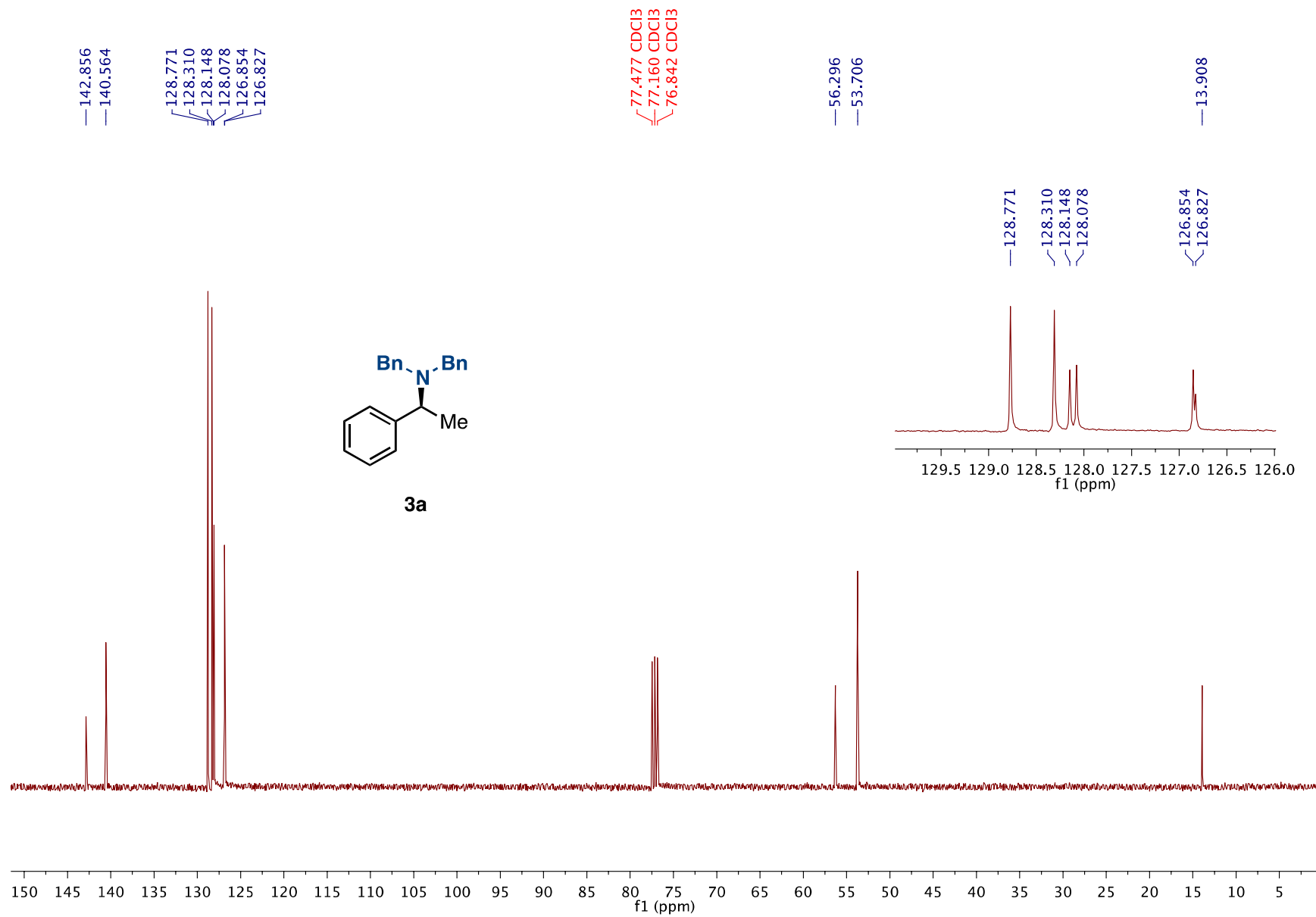
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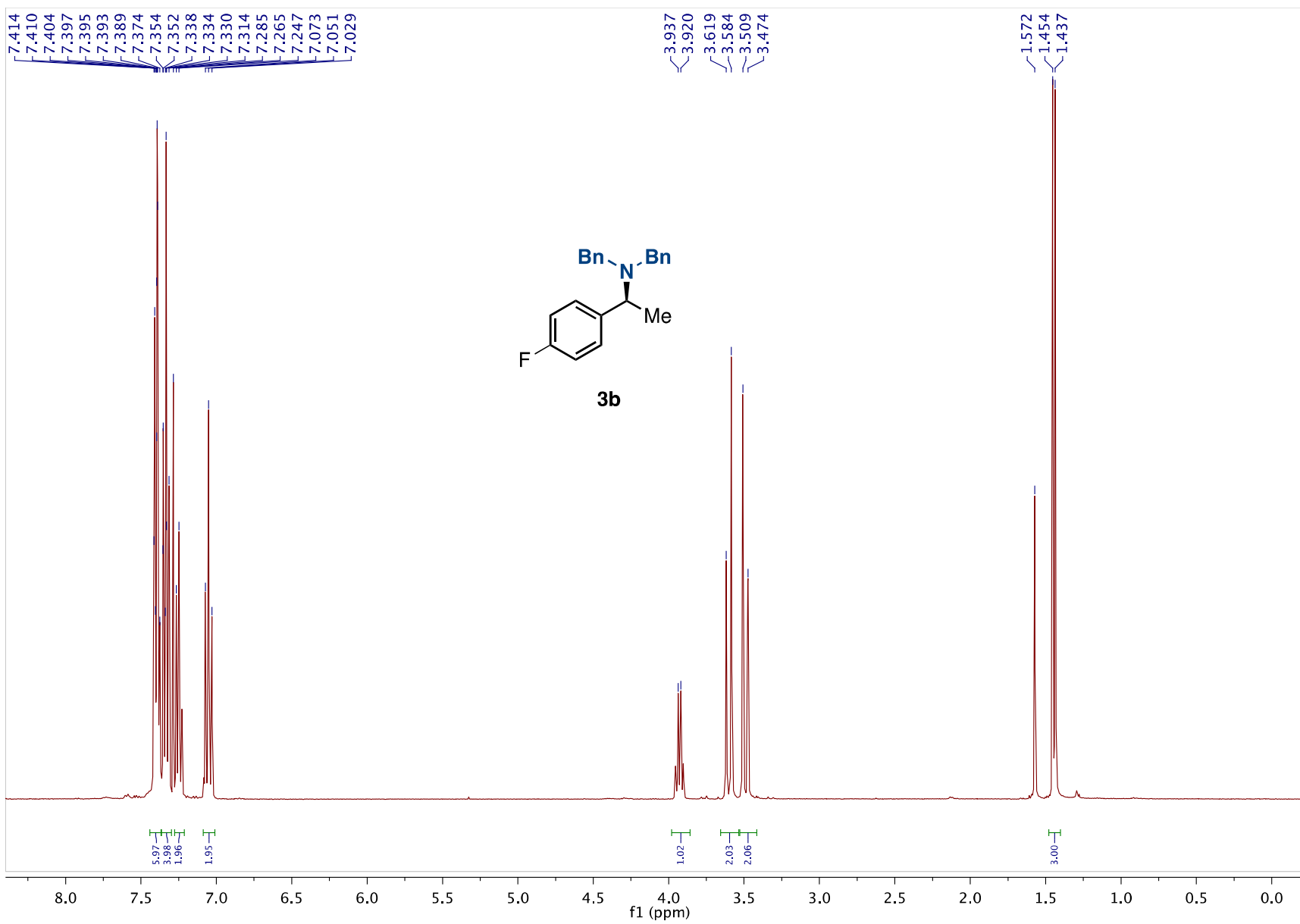
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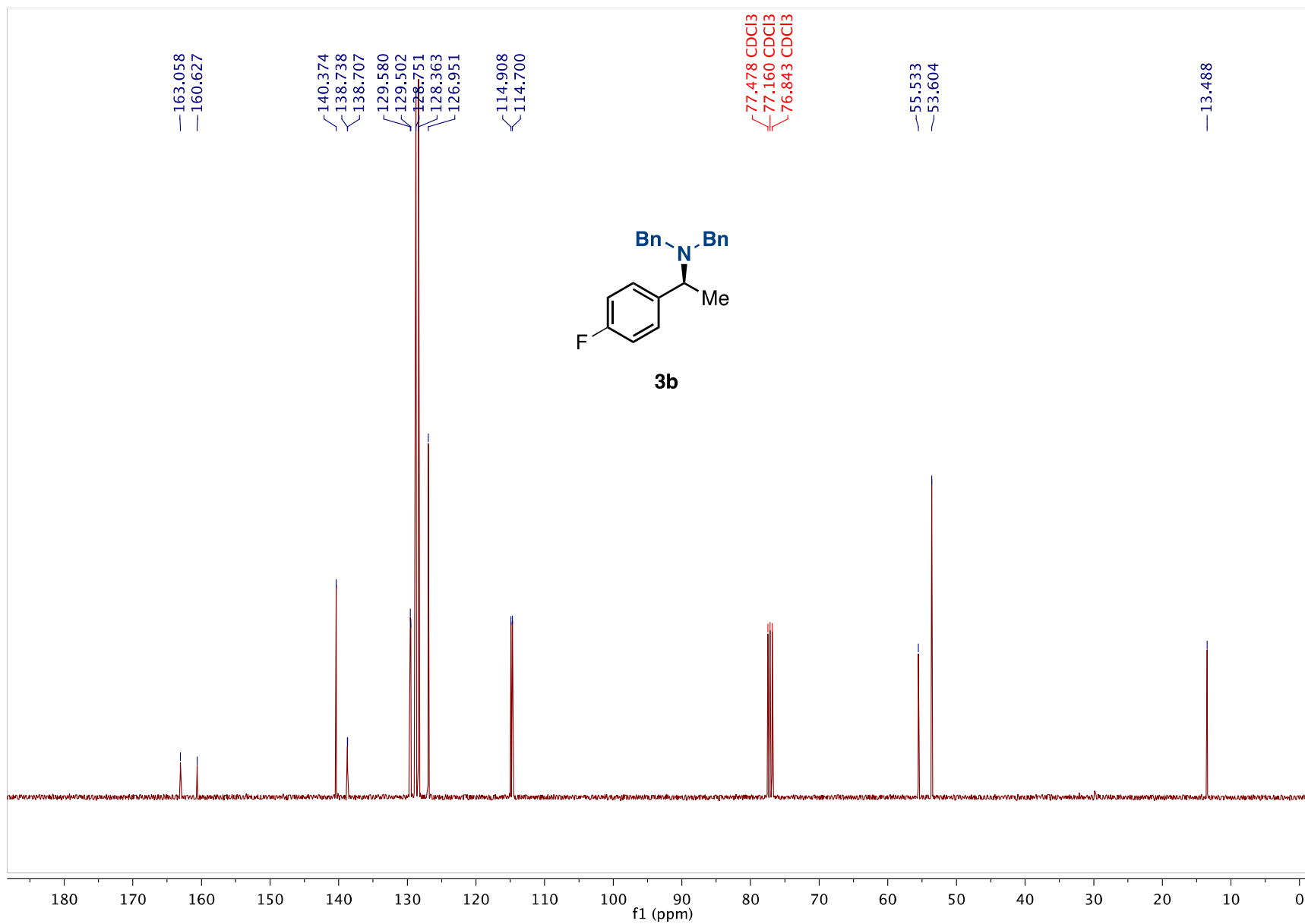


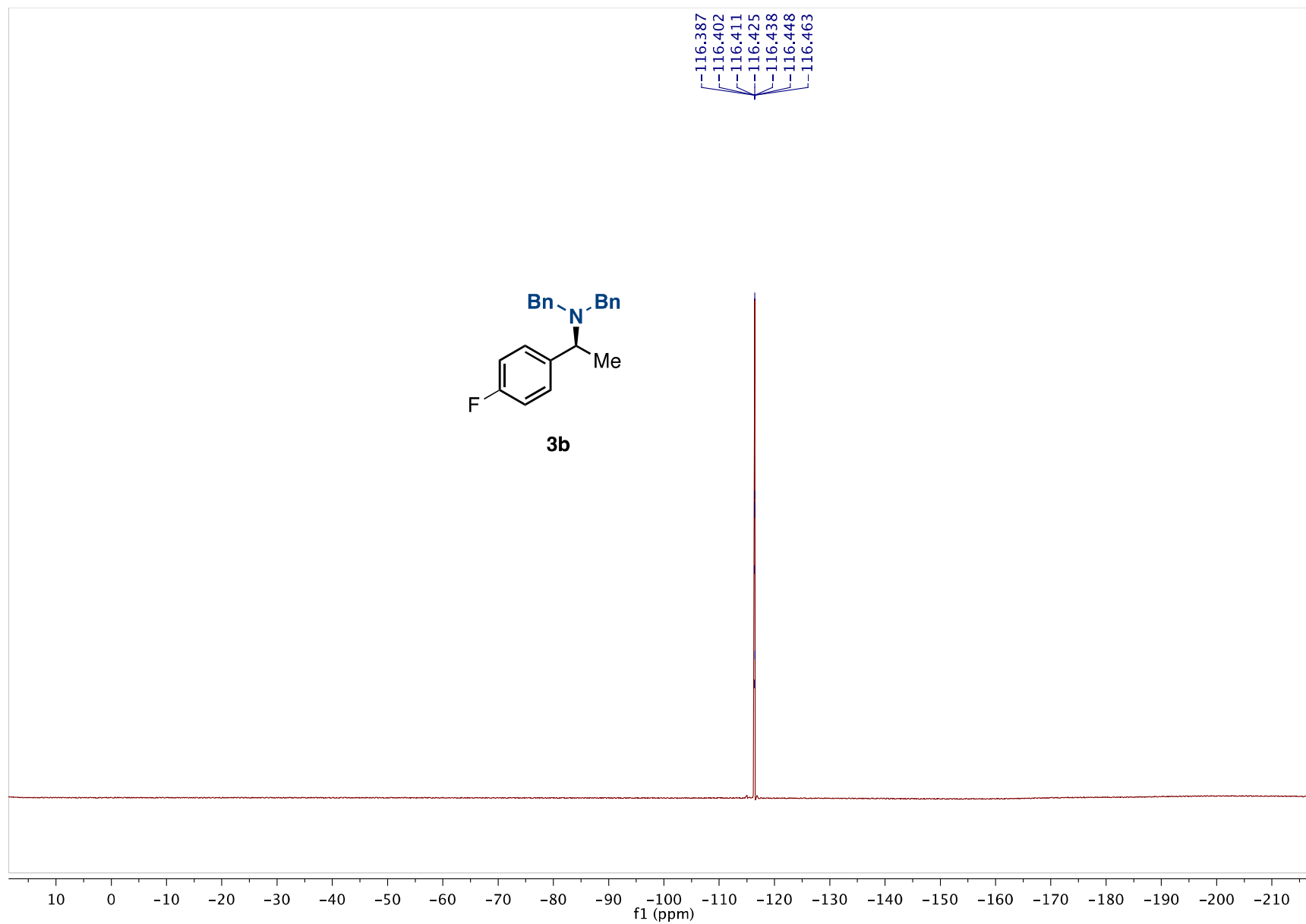
**3a**

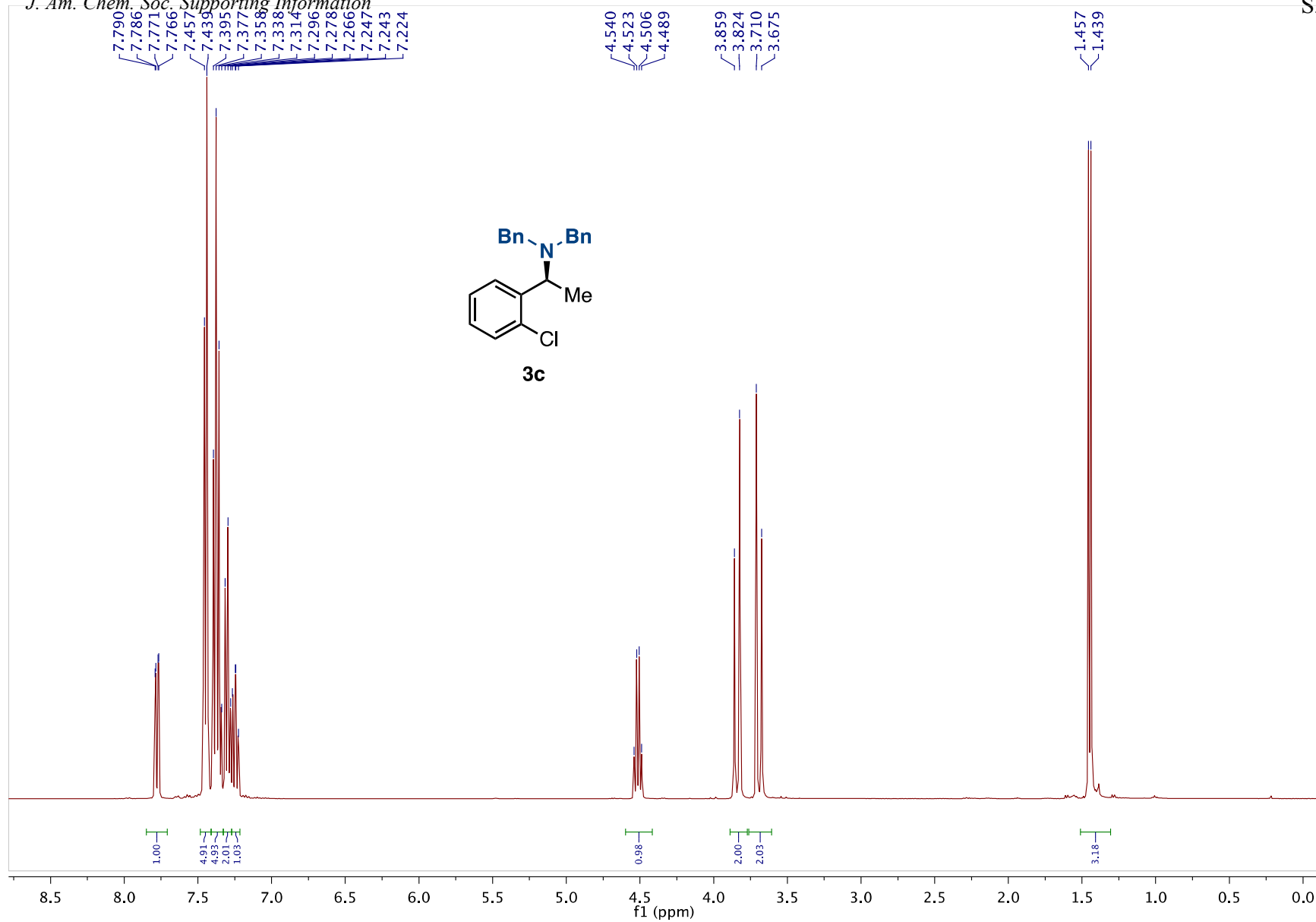




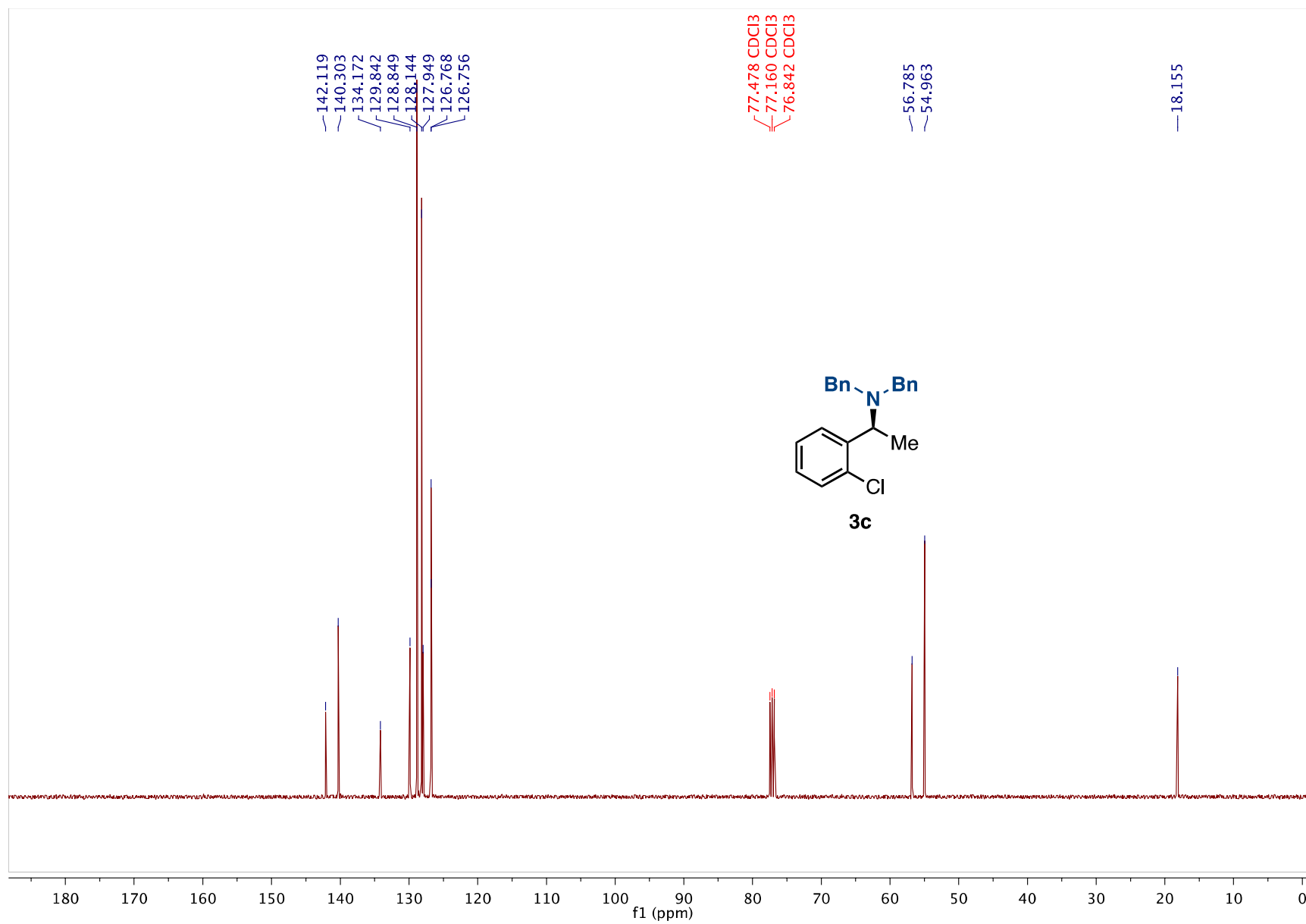


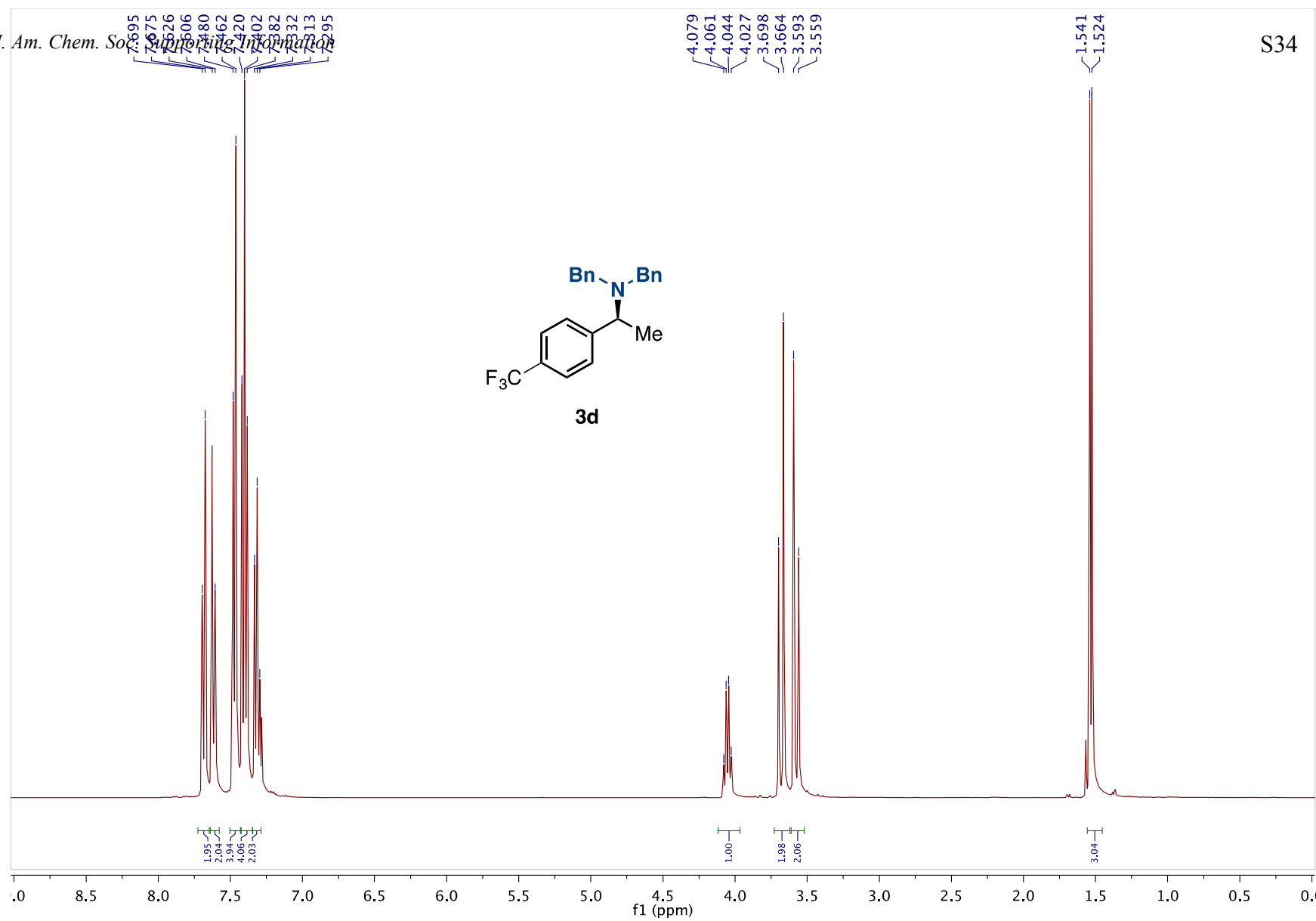


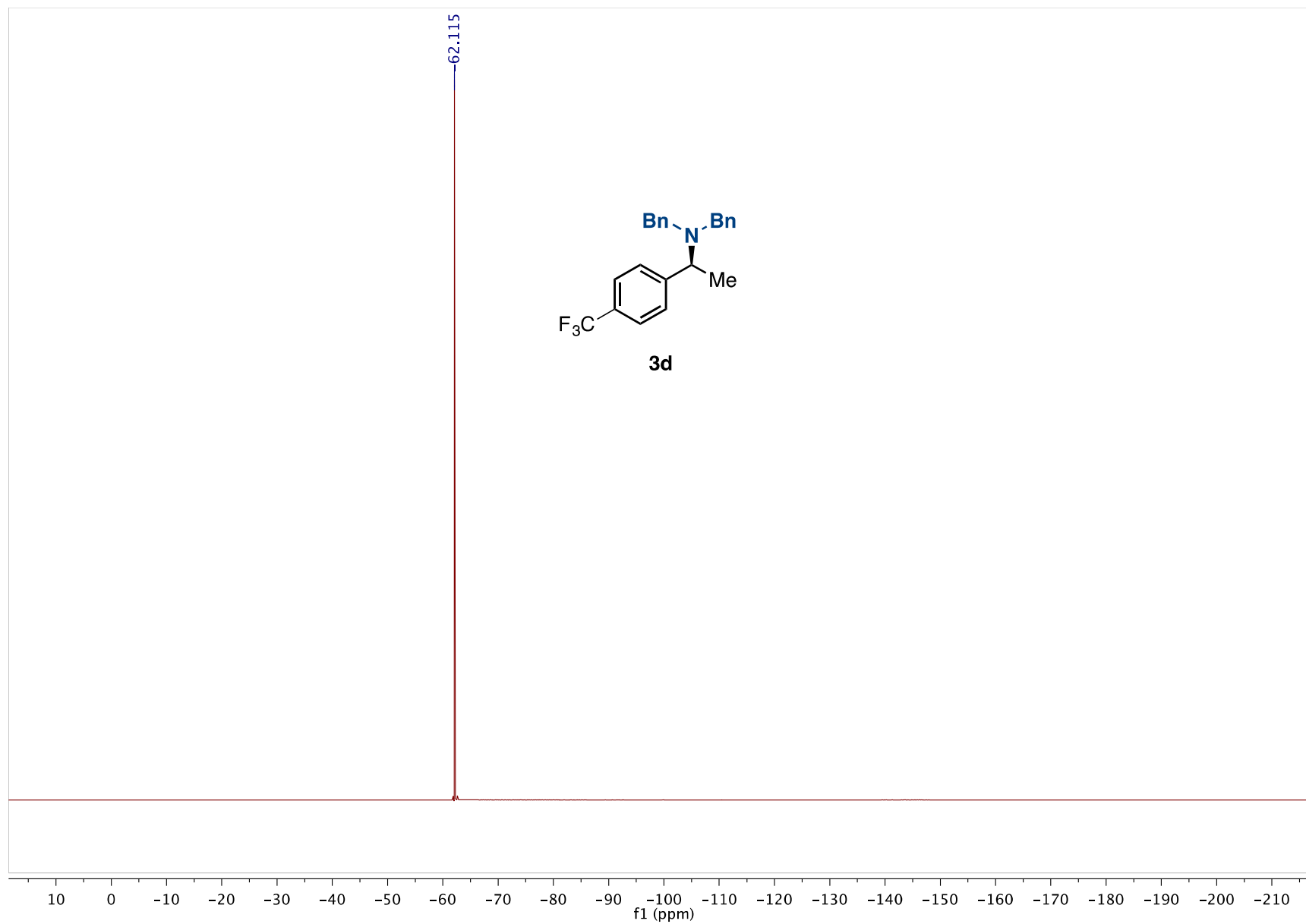


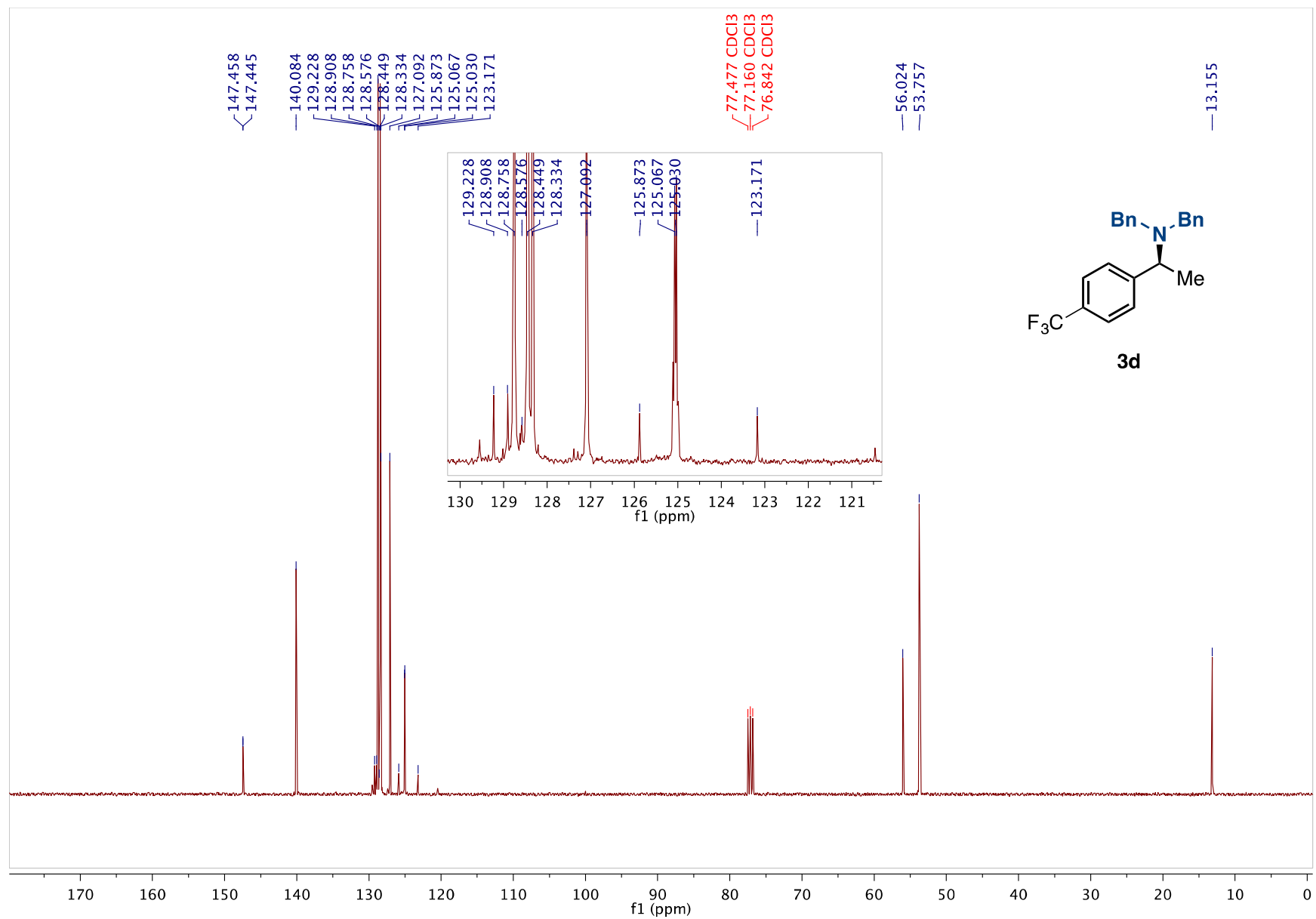


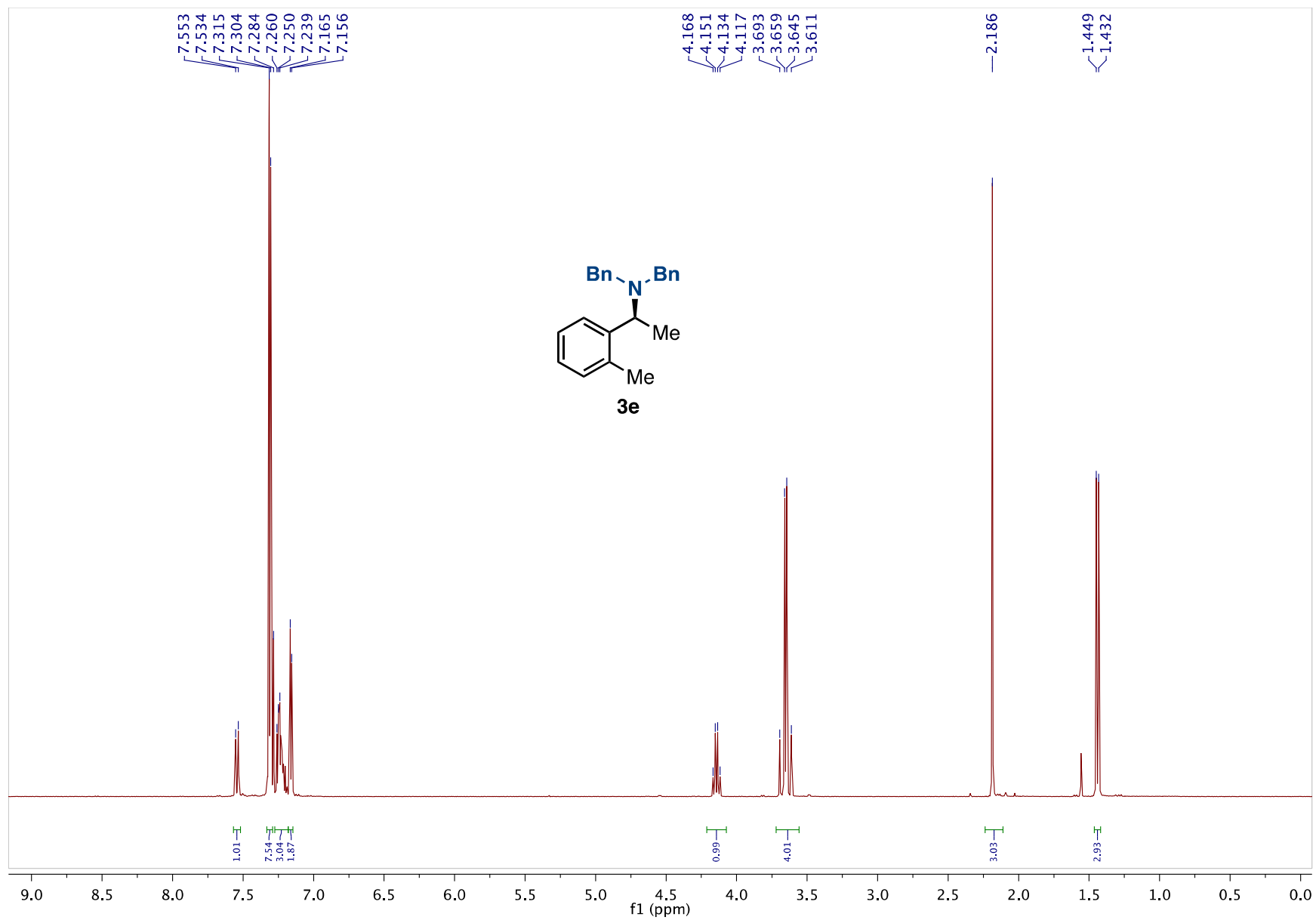


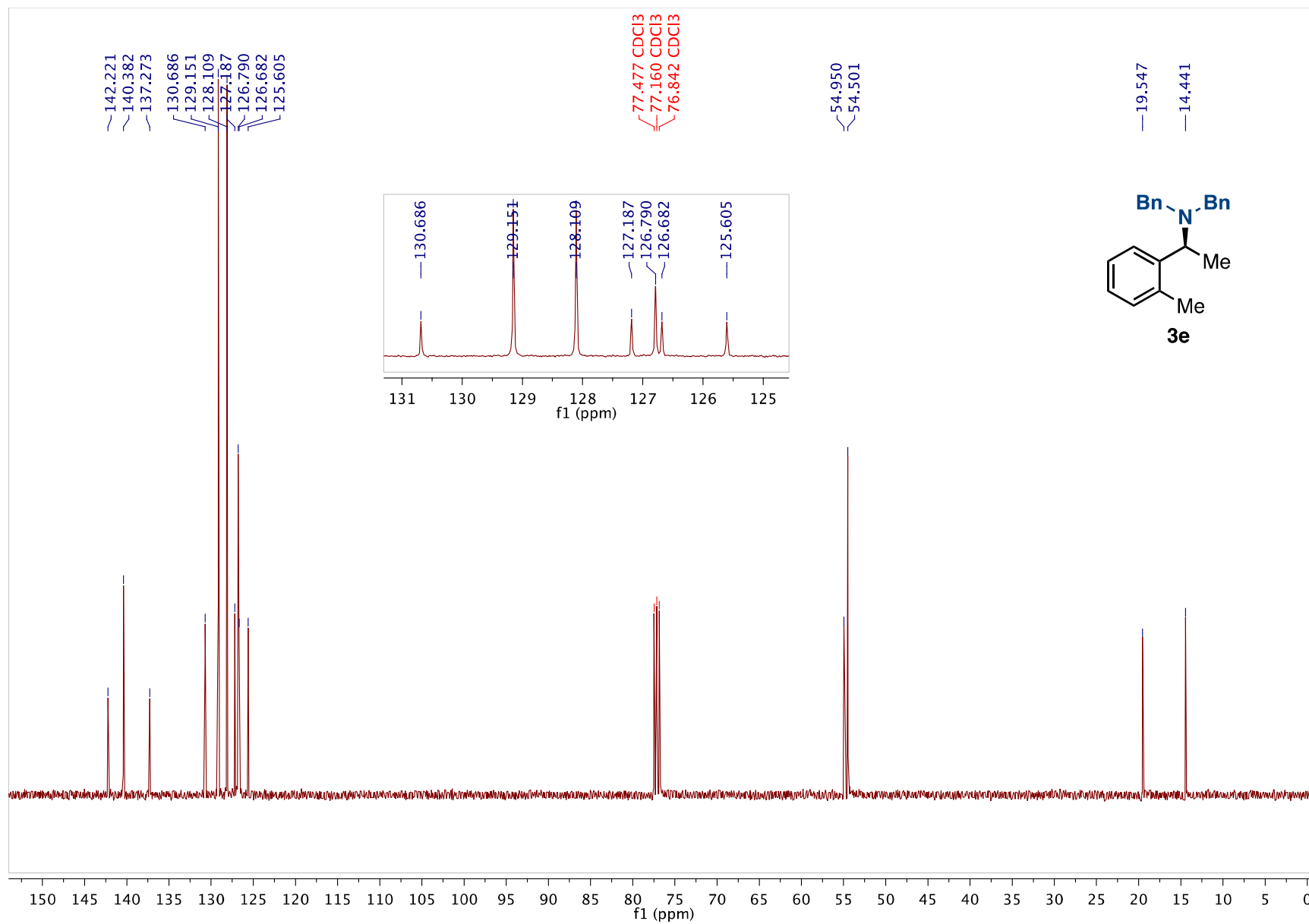


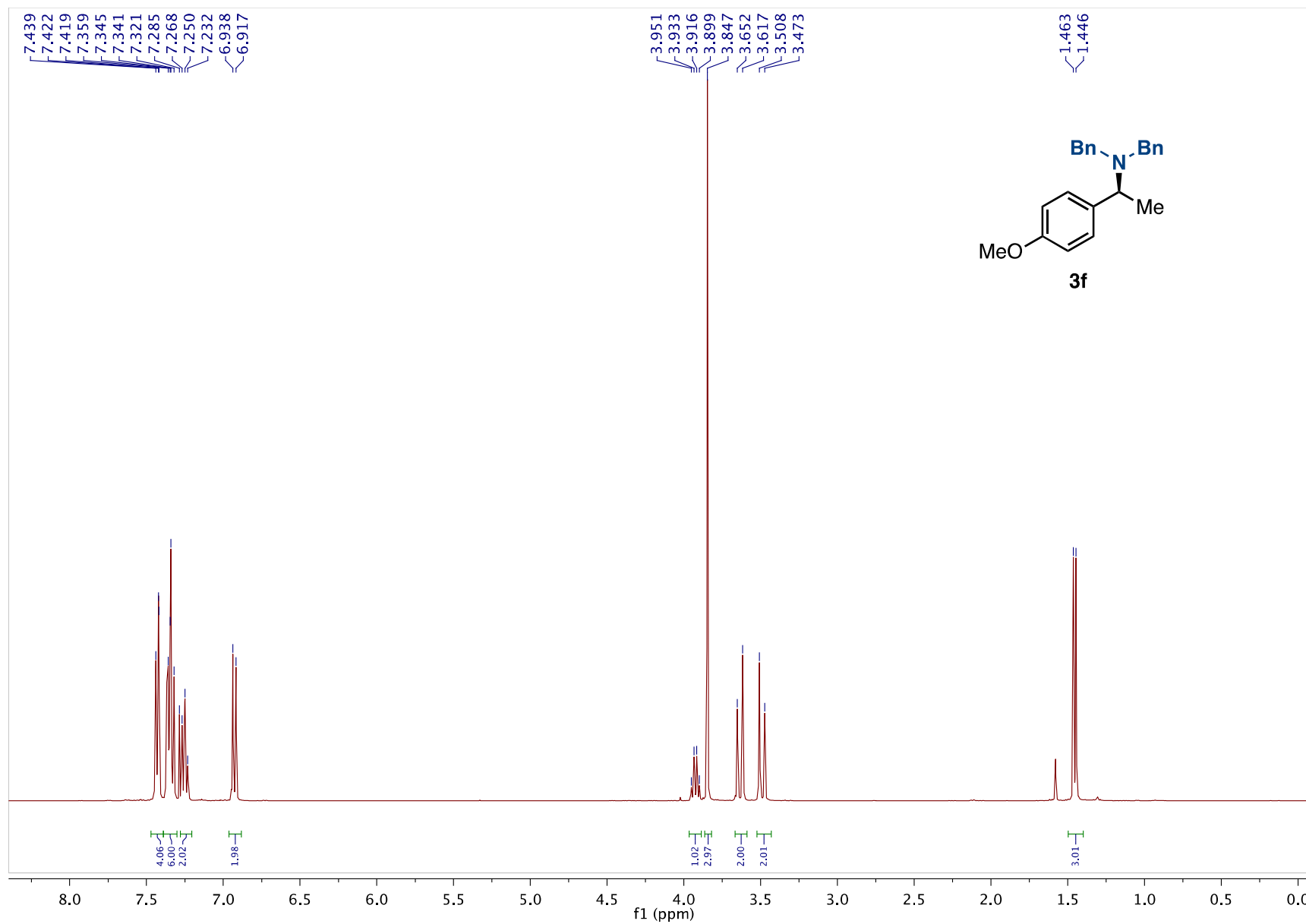


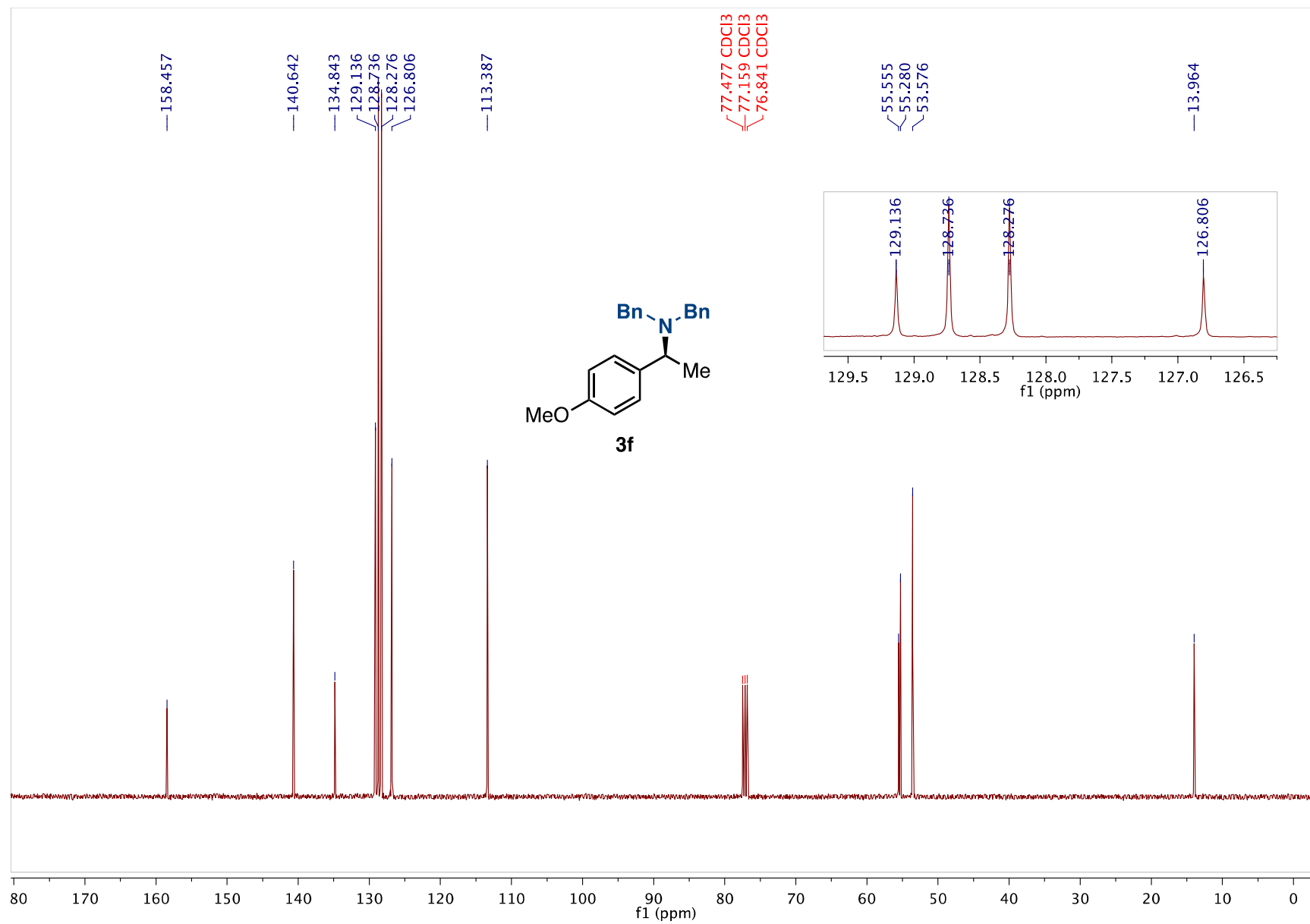




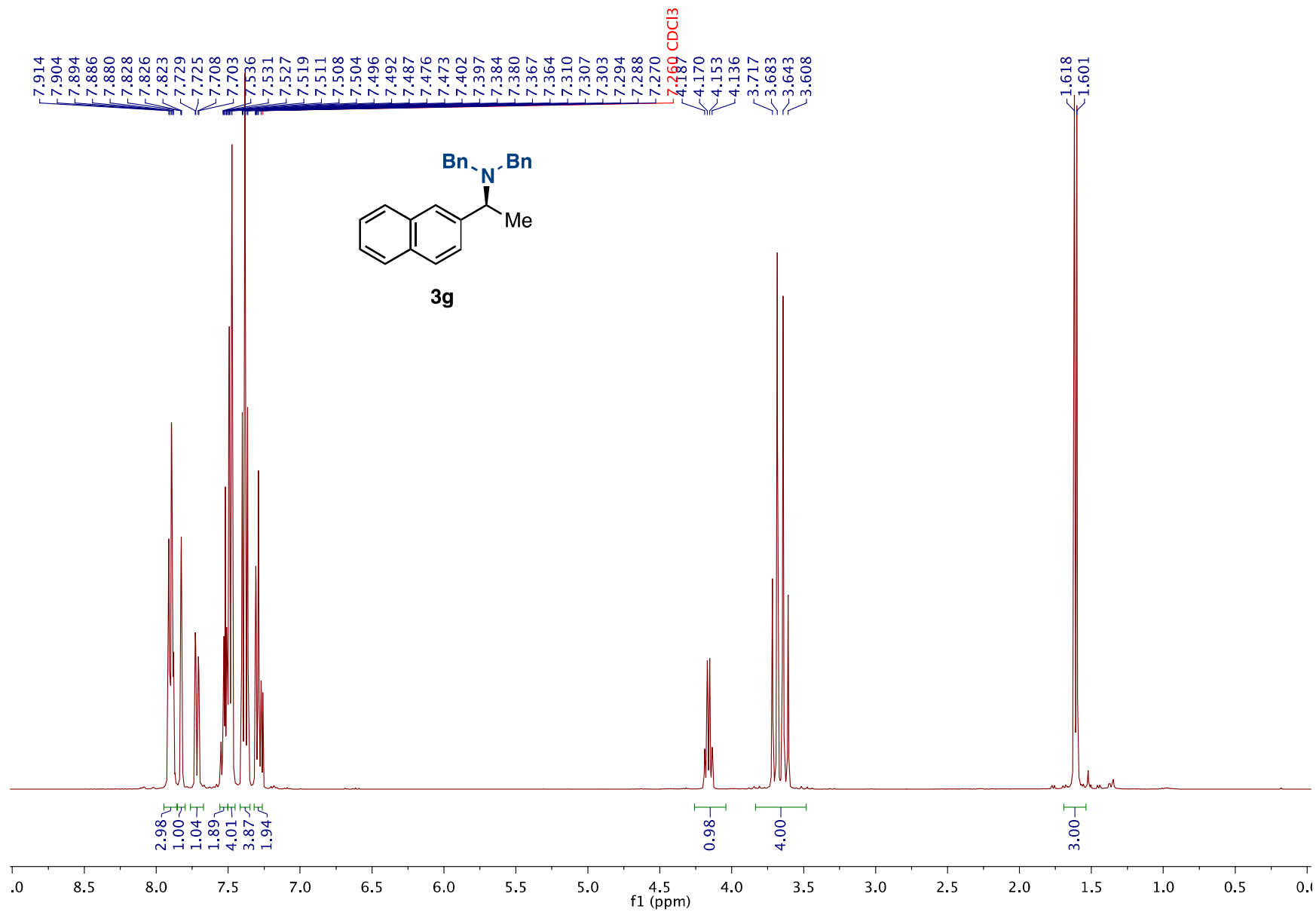


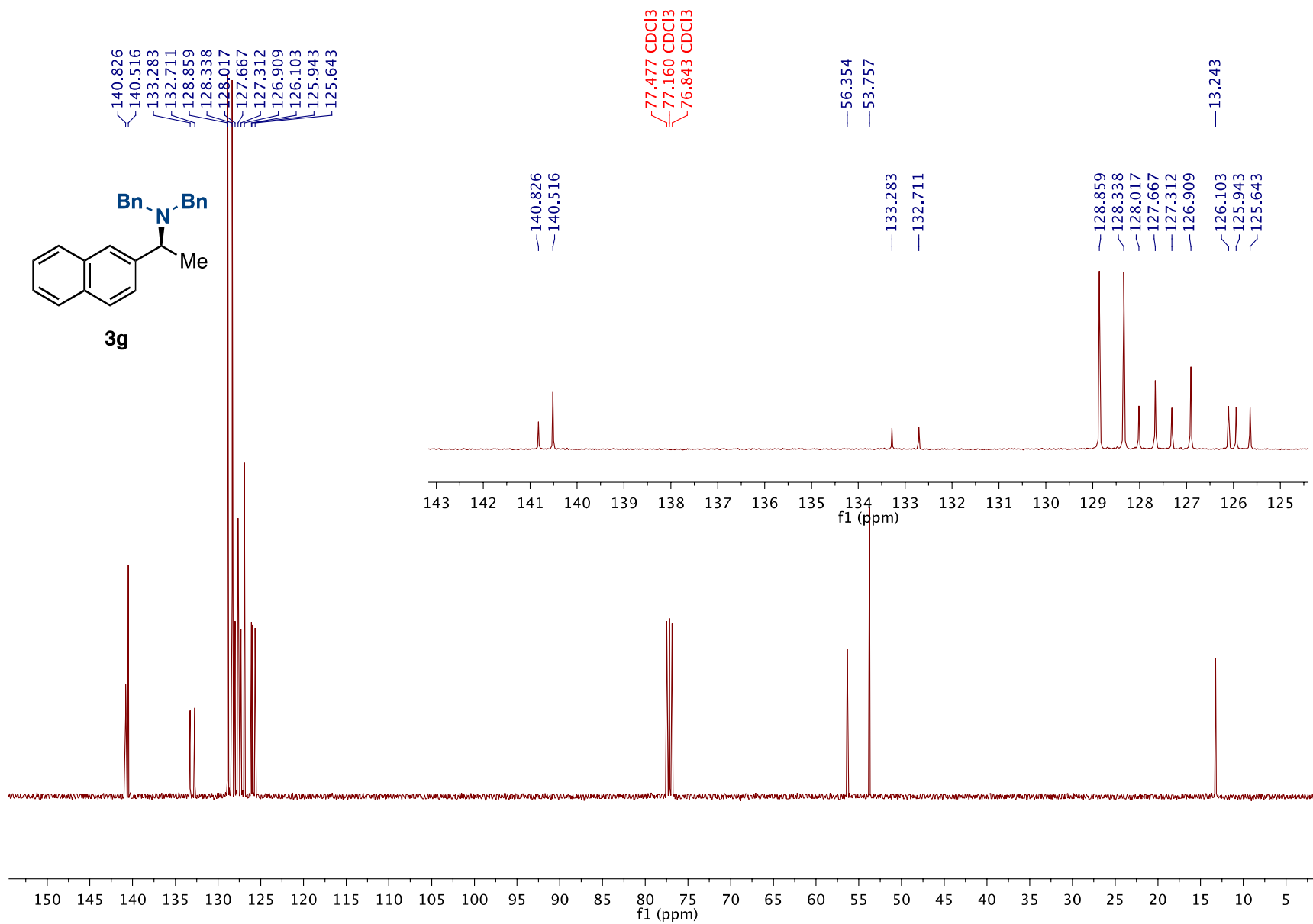


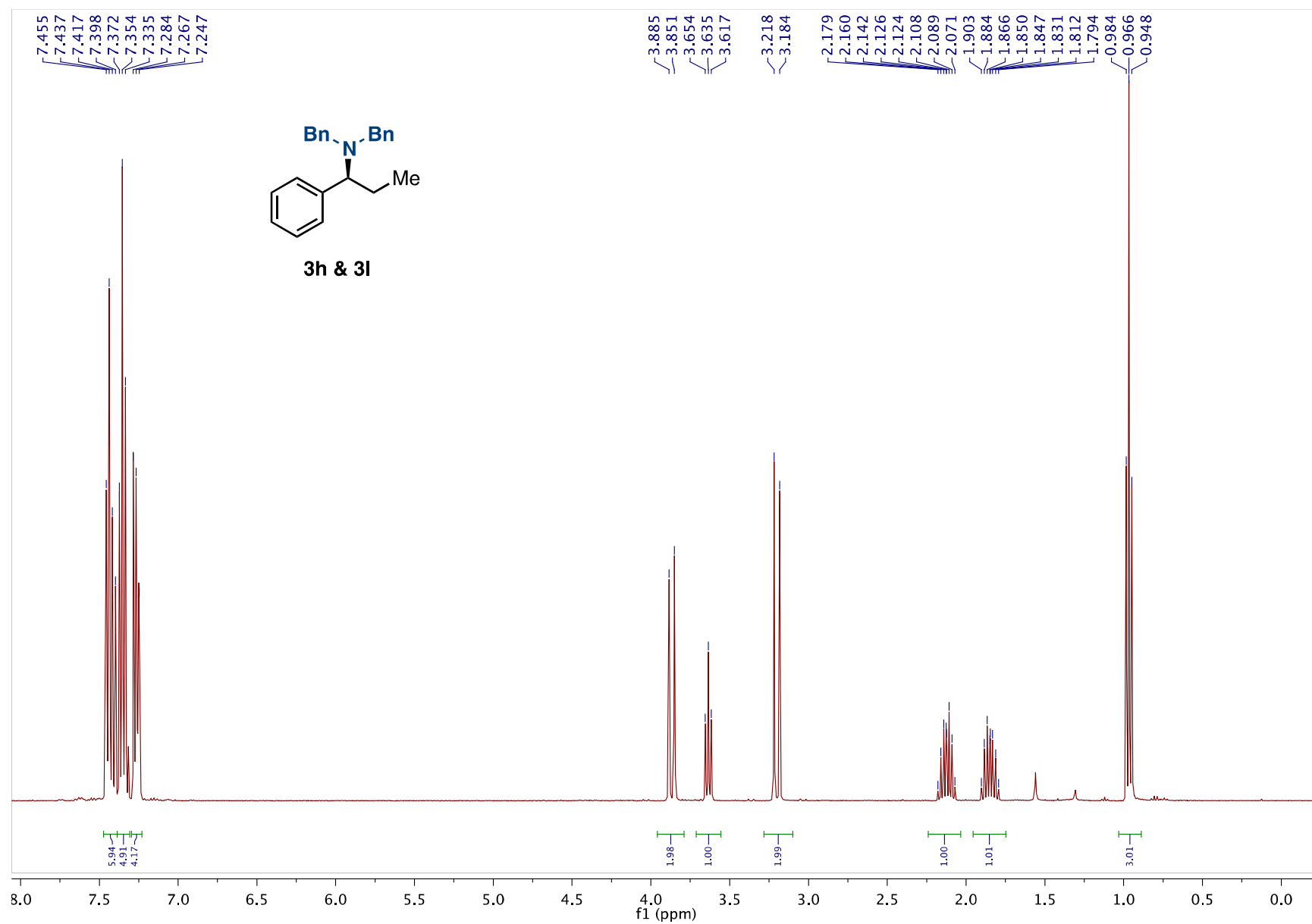


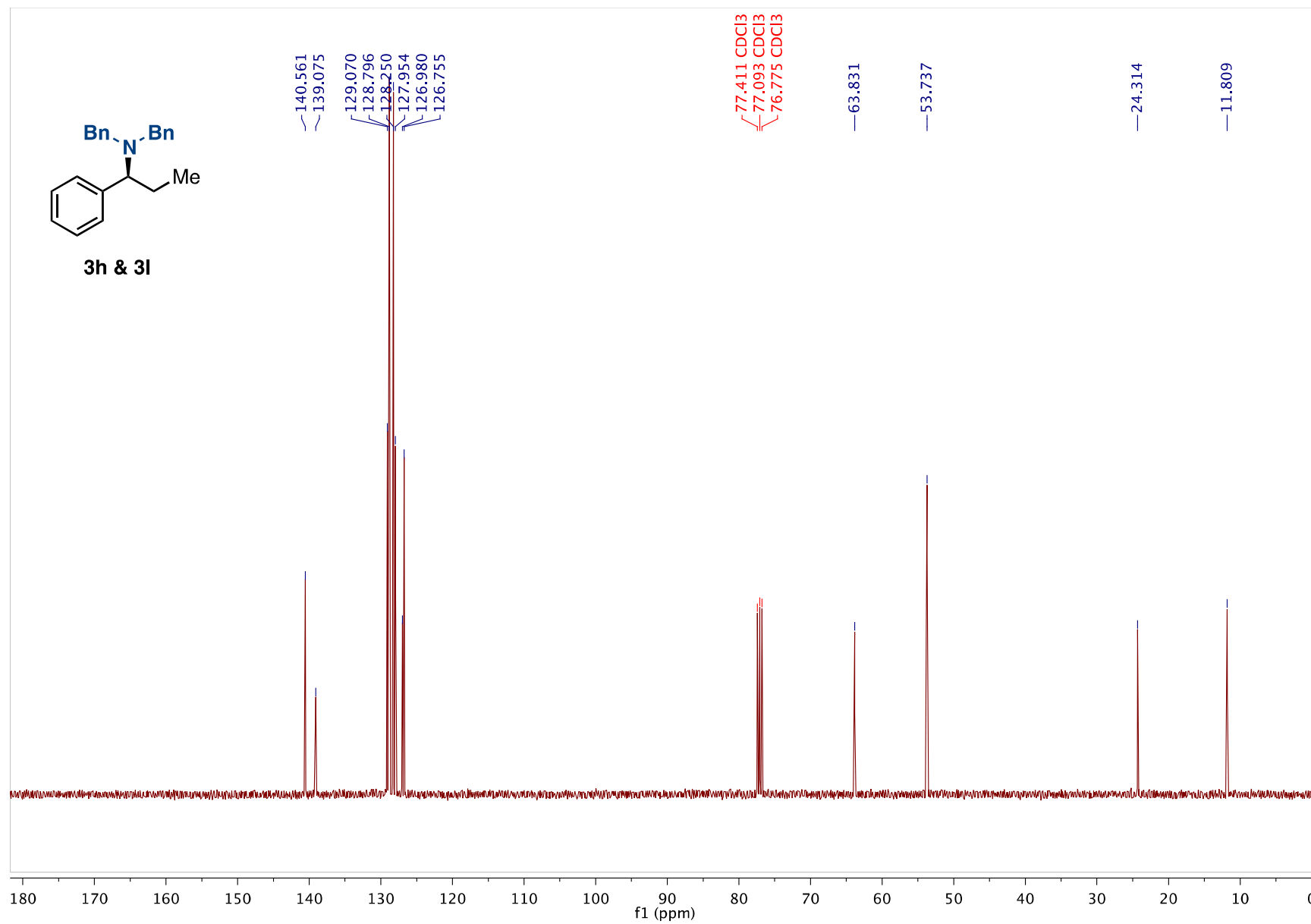


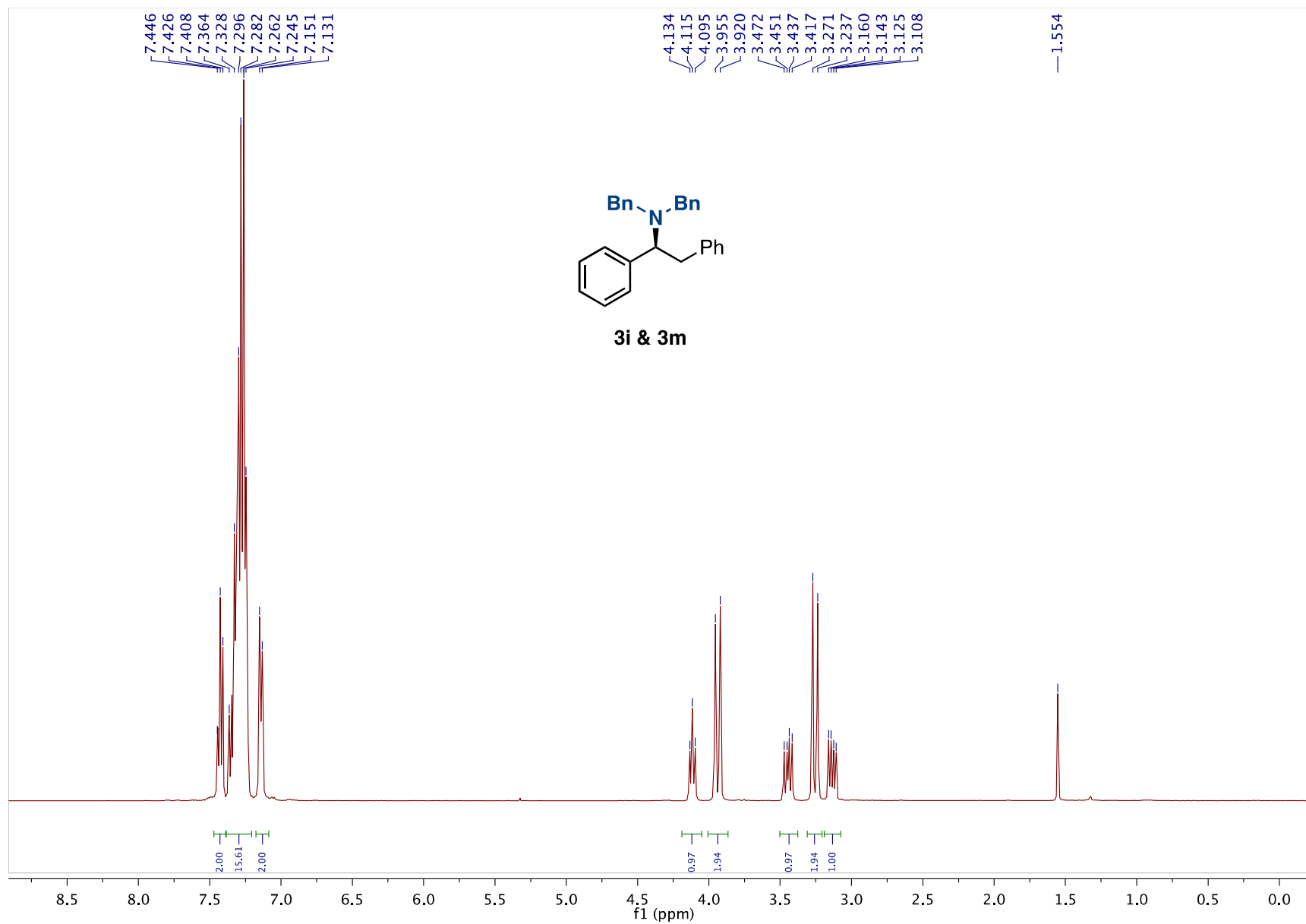


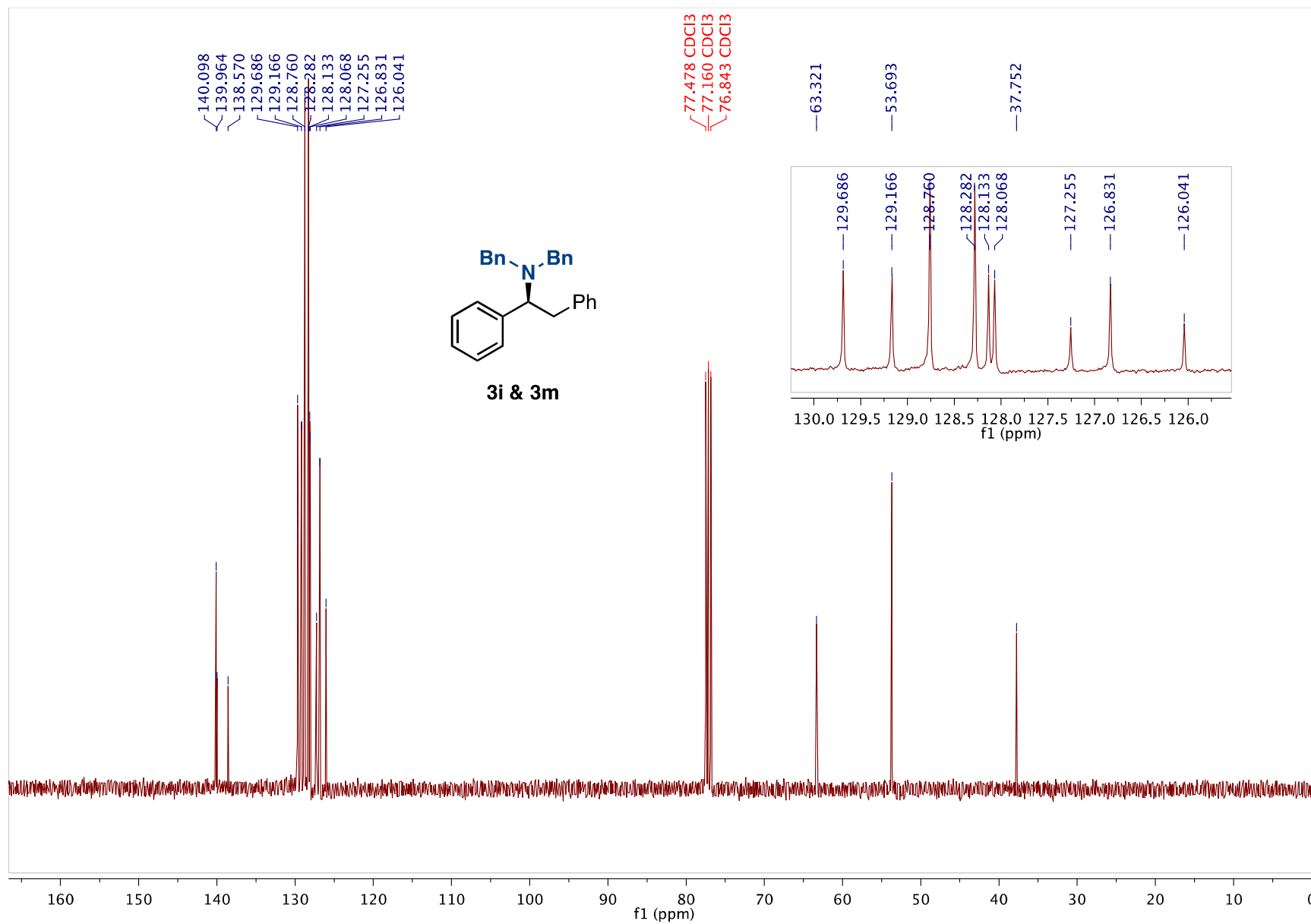


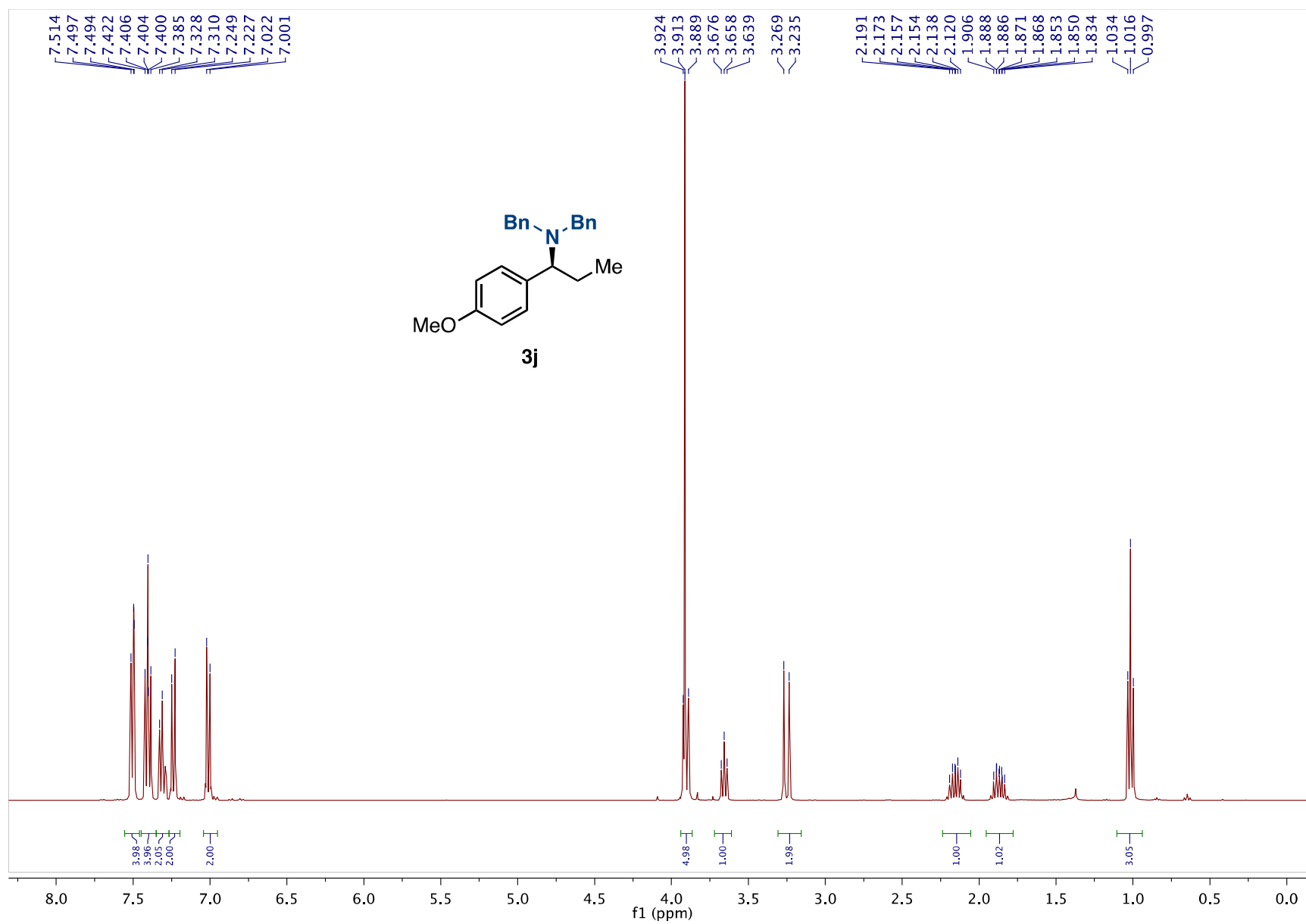


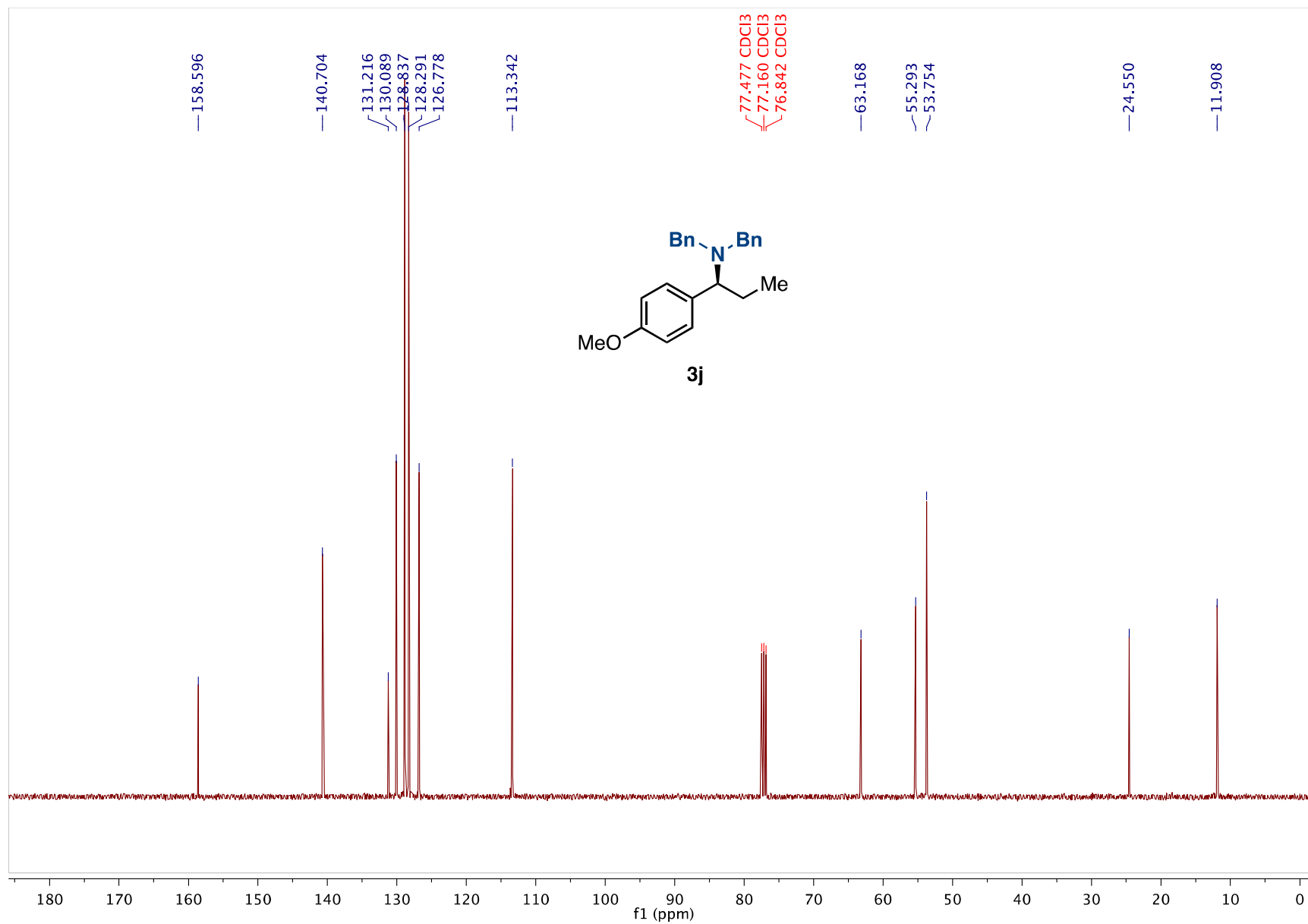




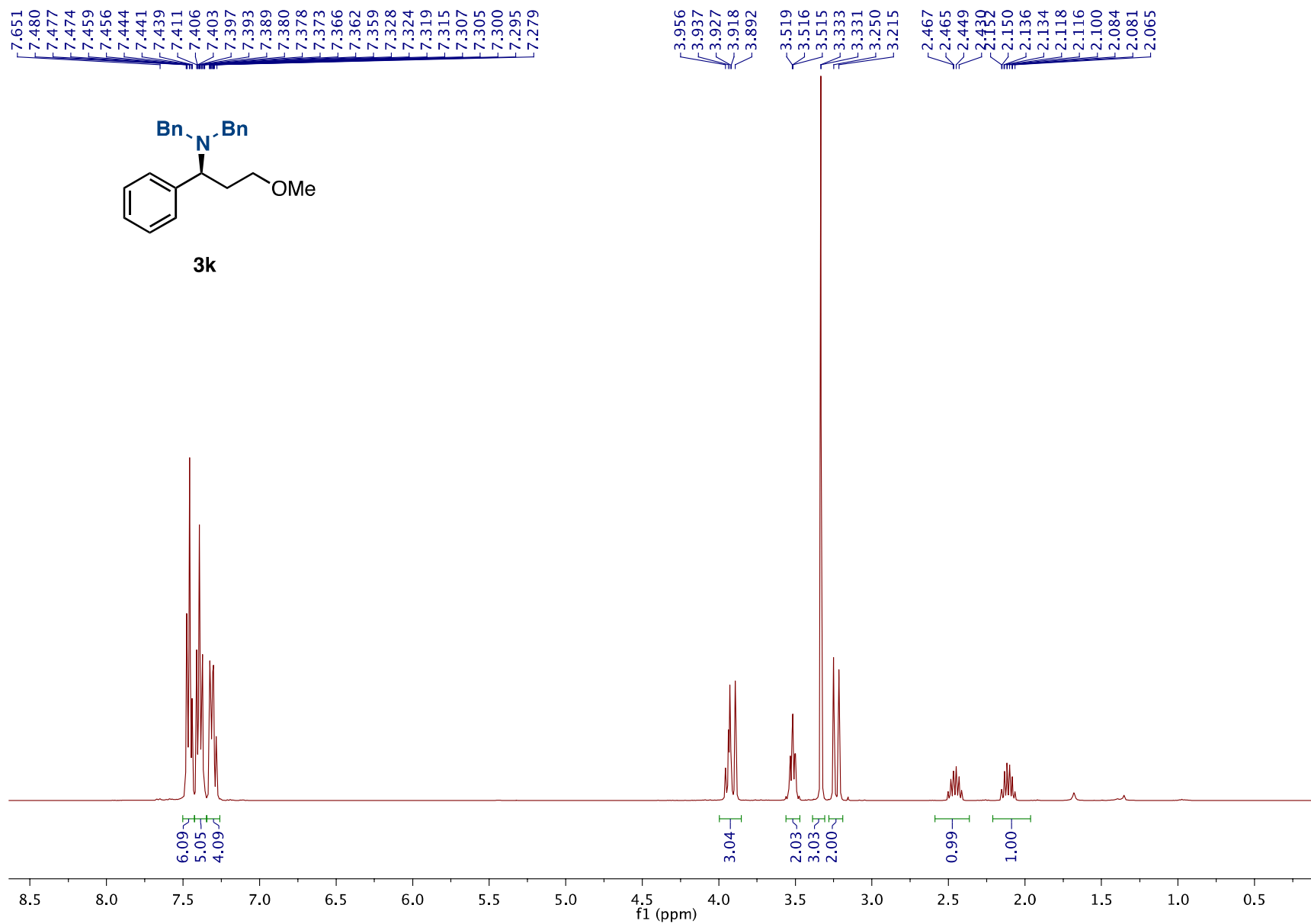


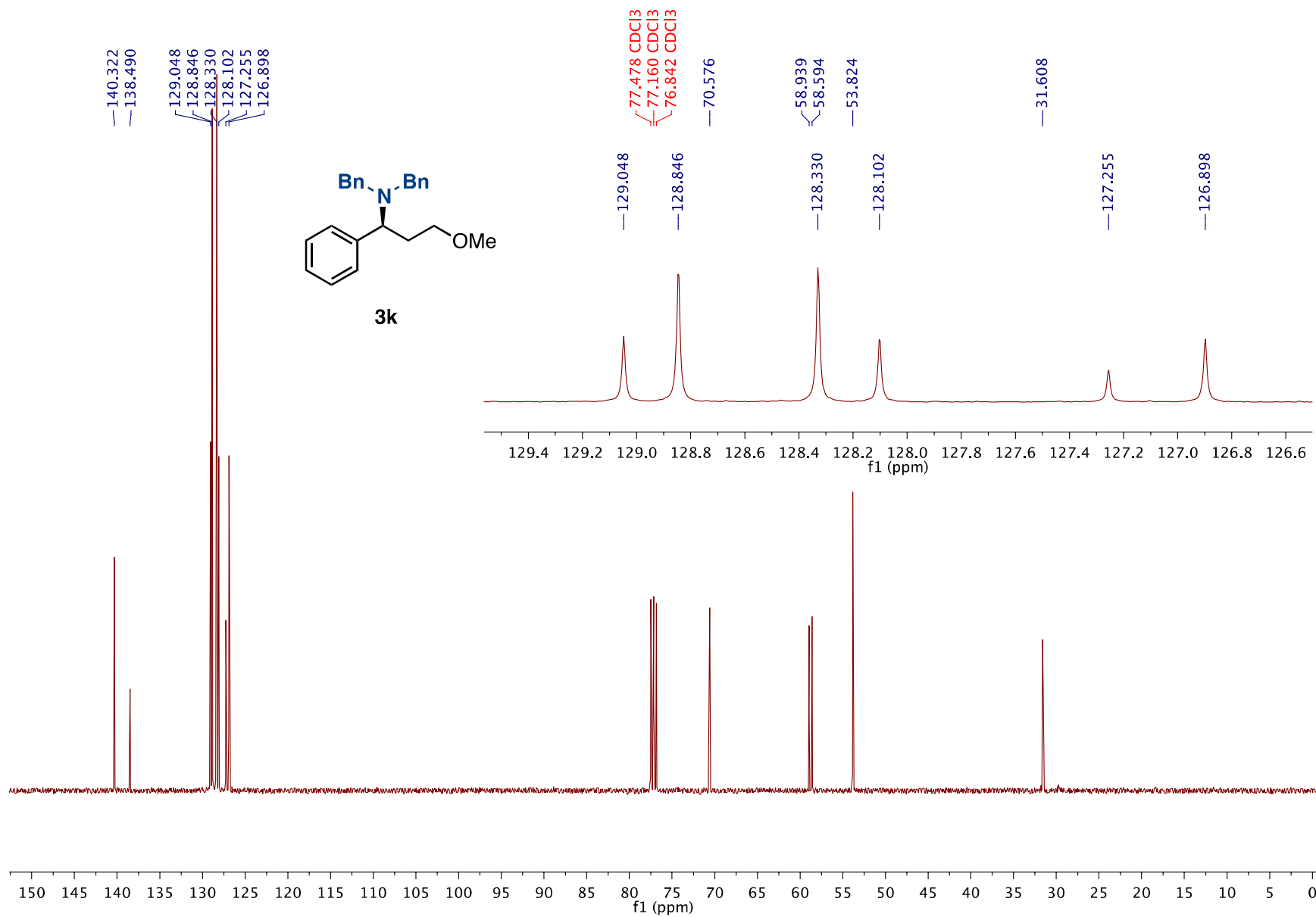










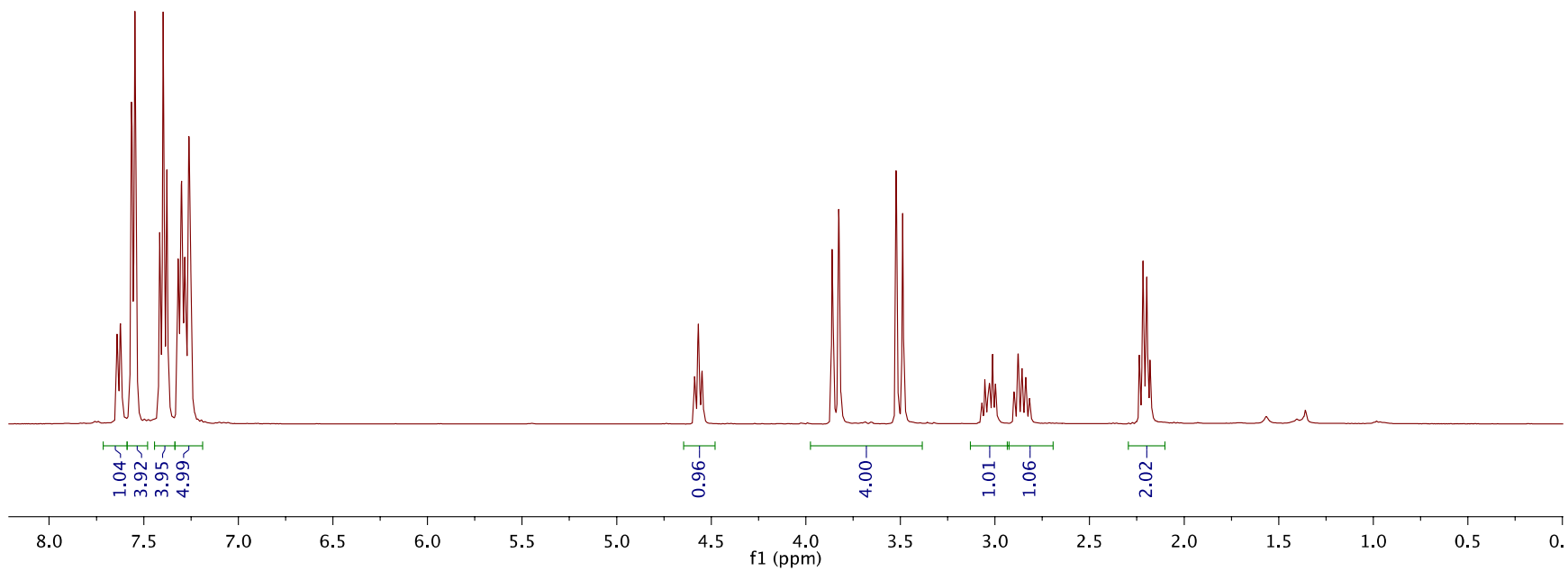
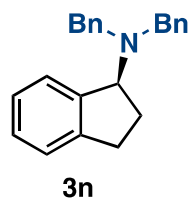


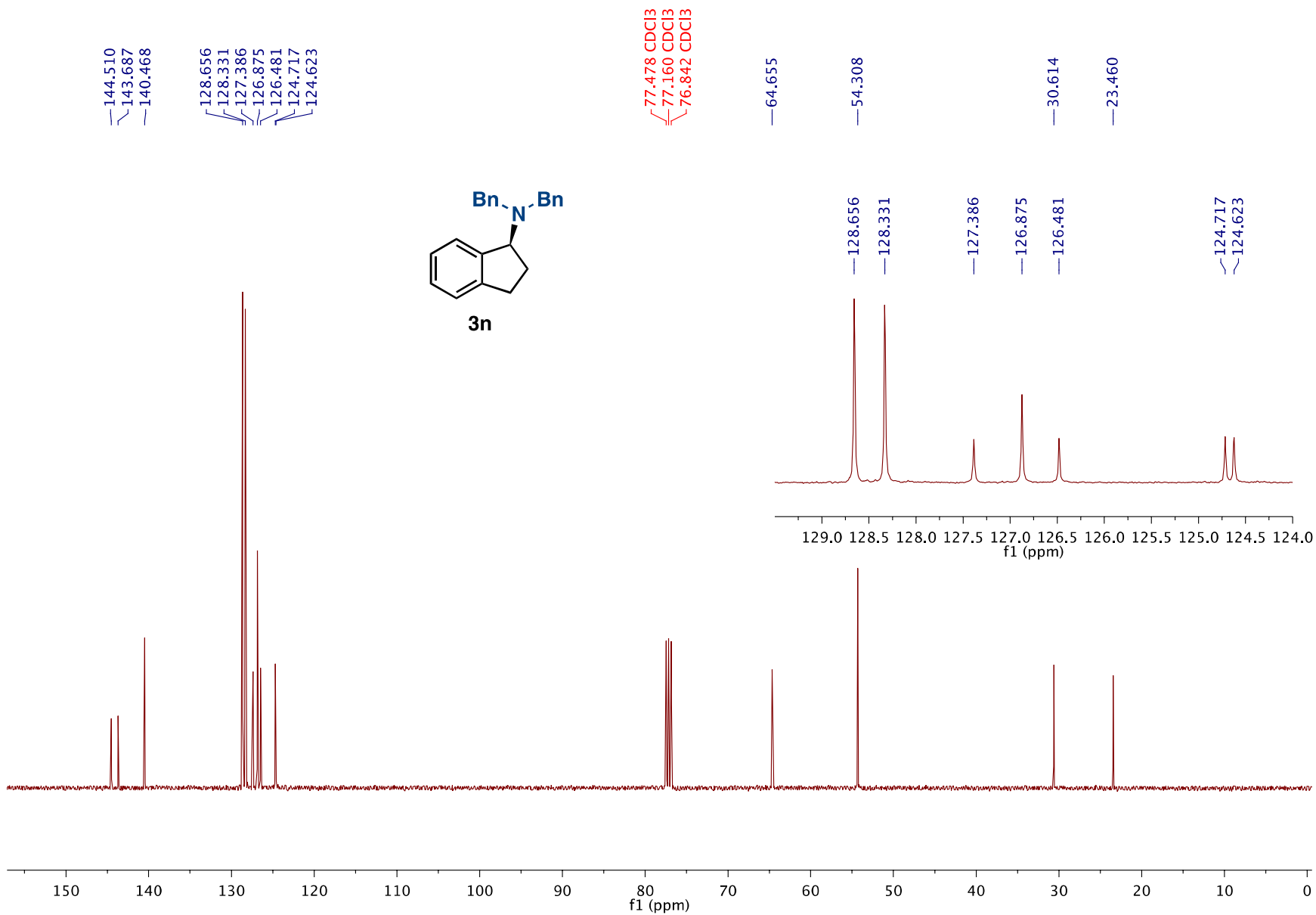
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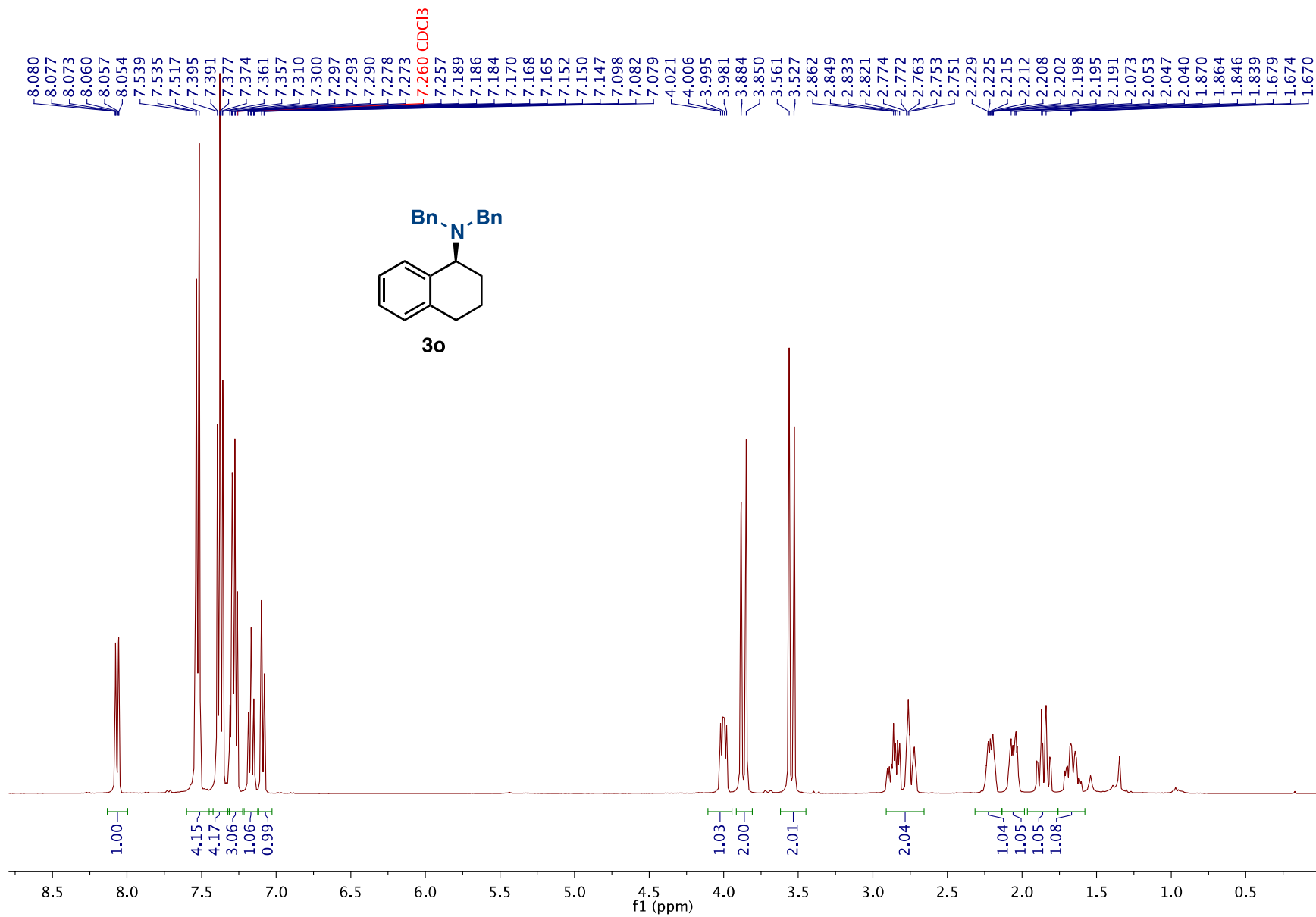
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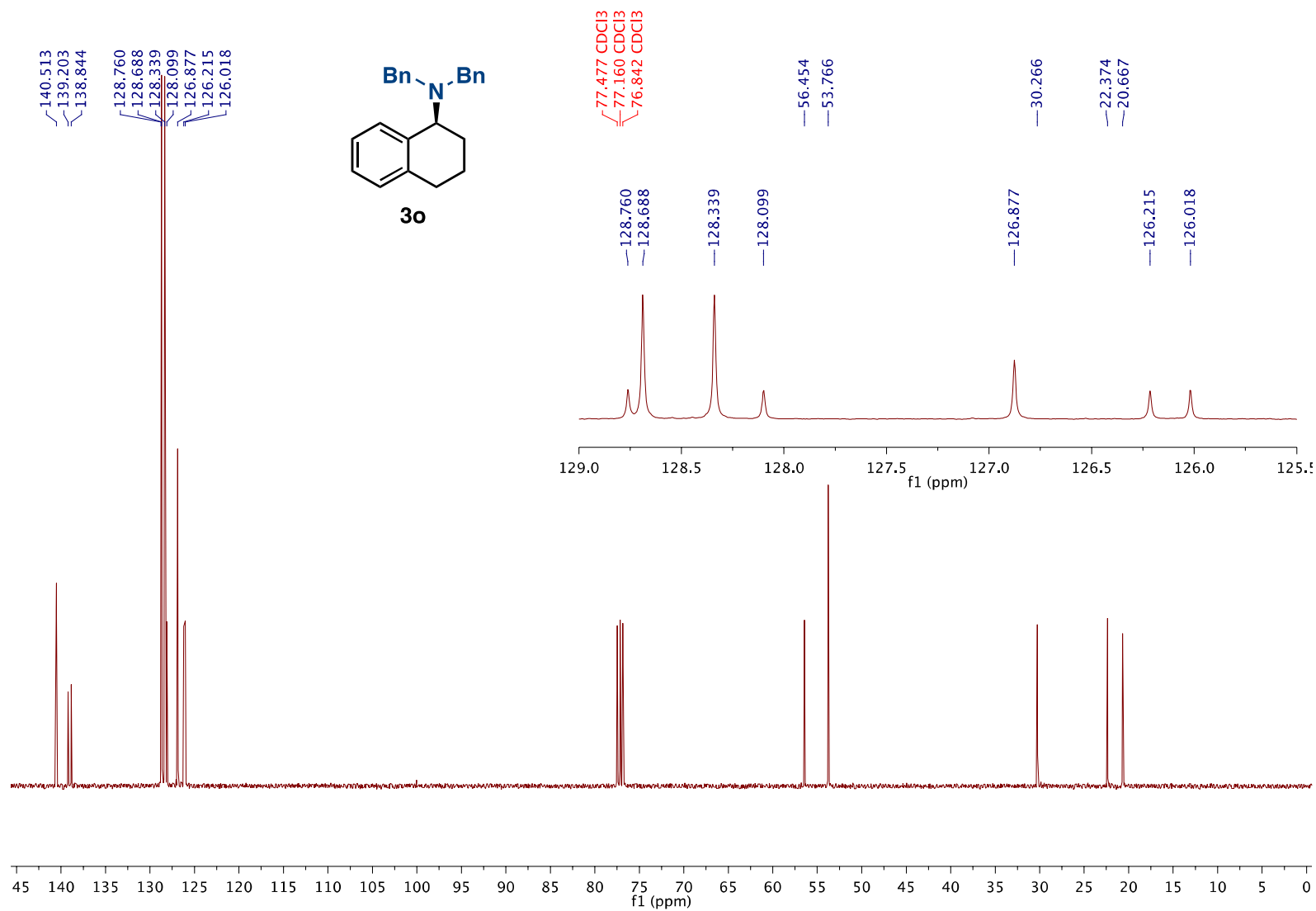
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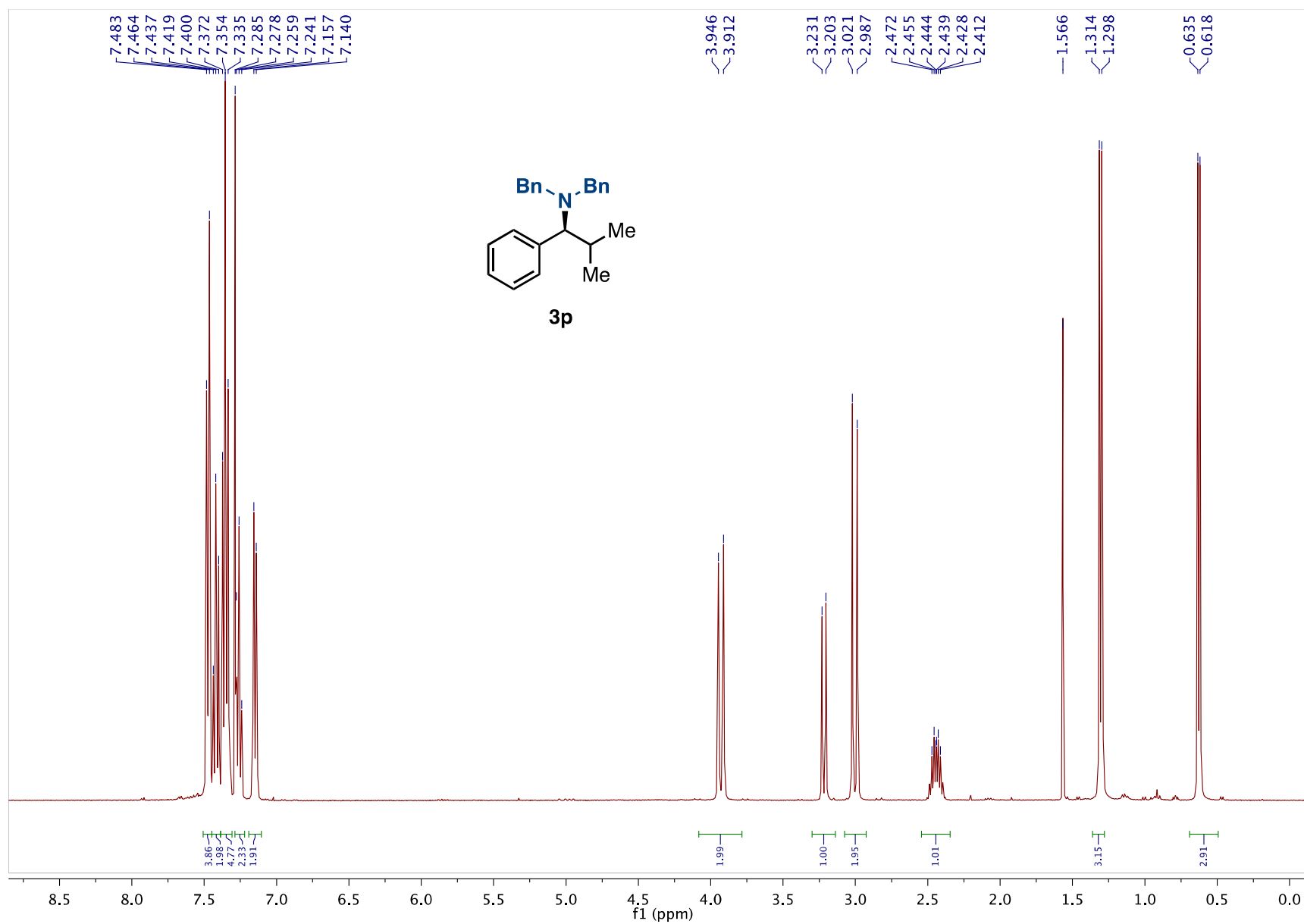
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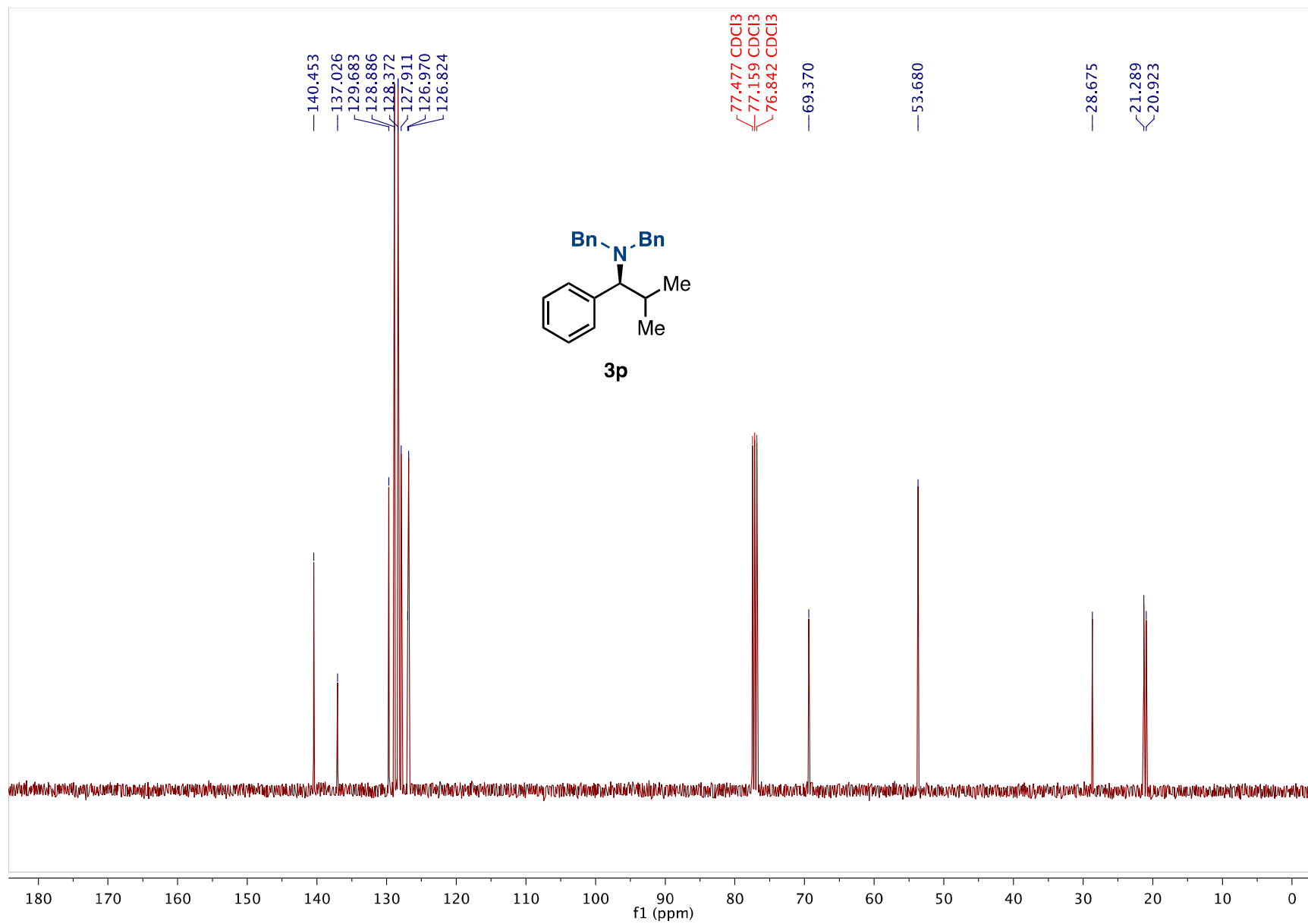




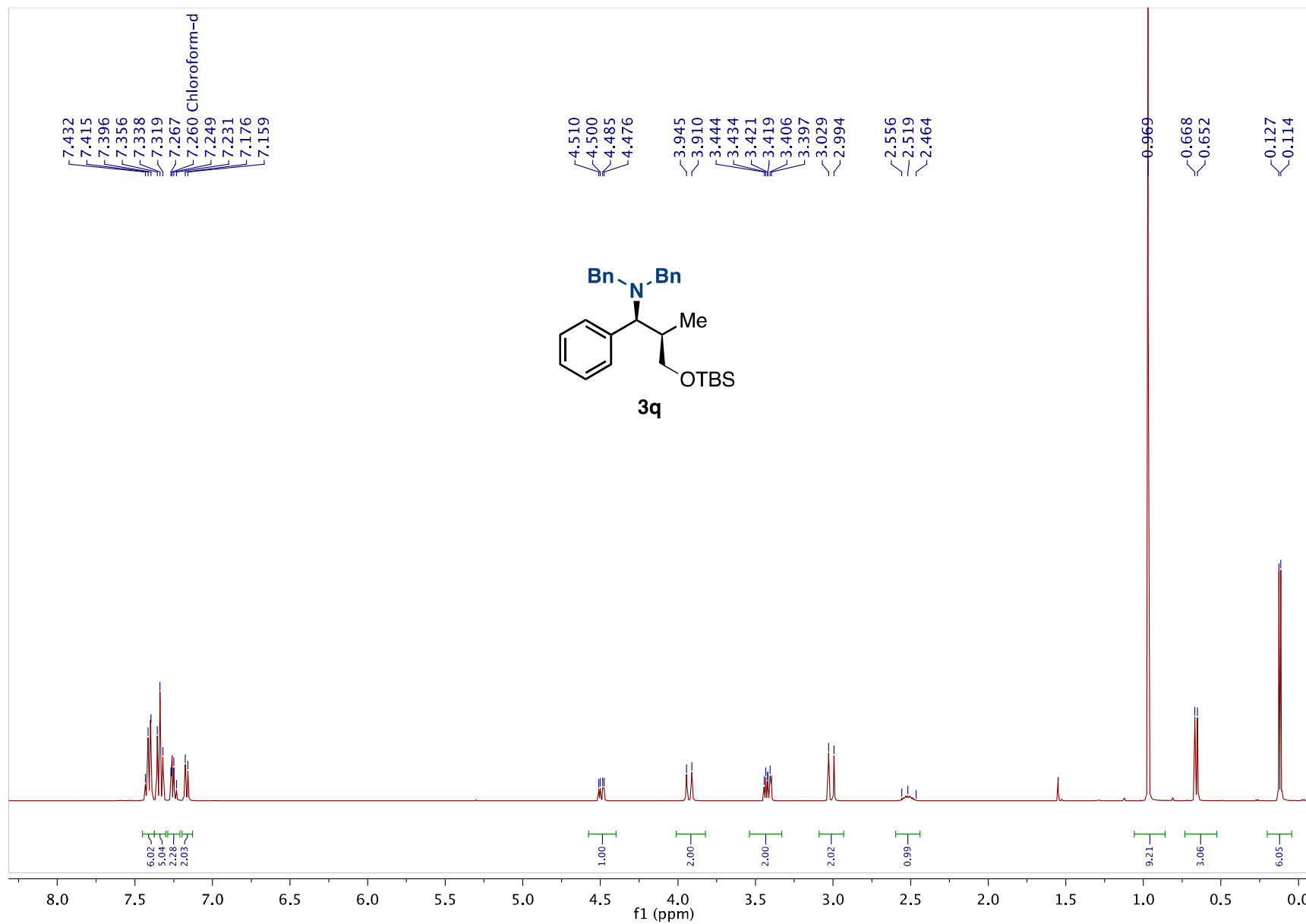


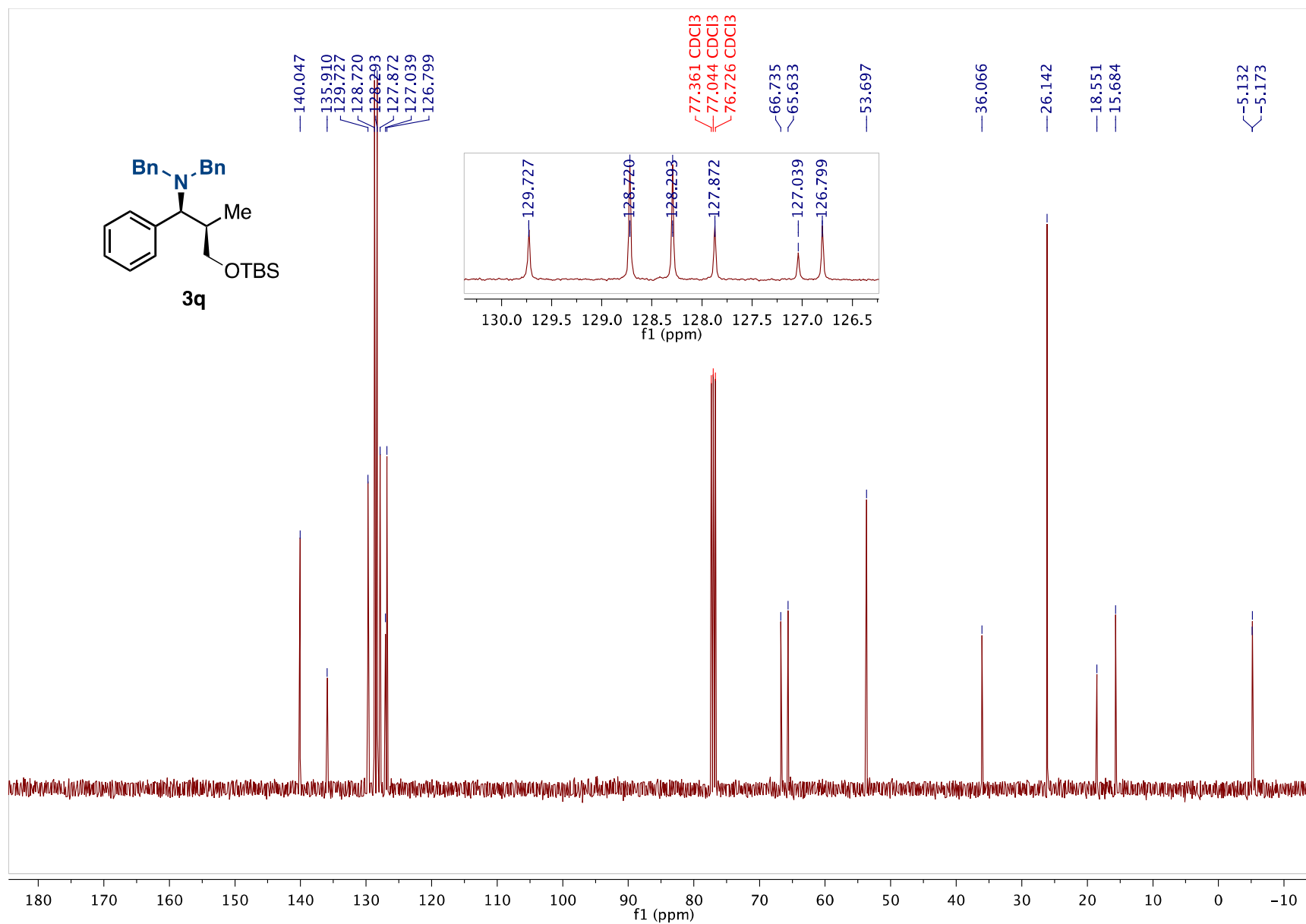


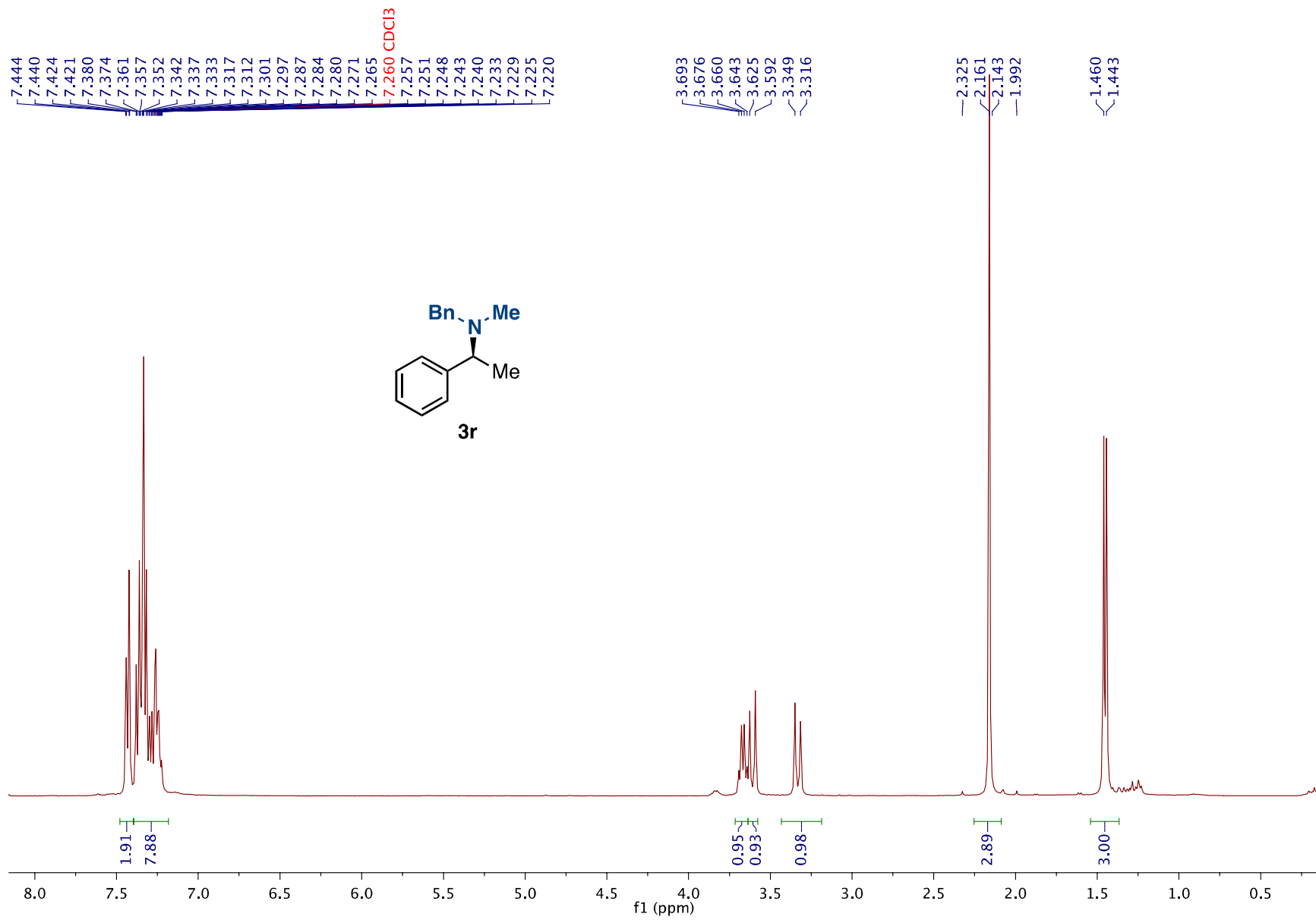


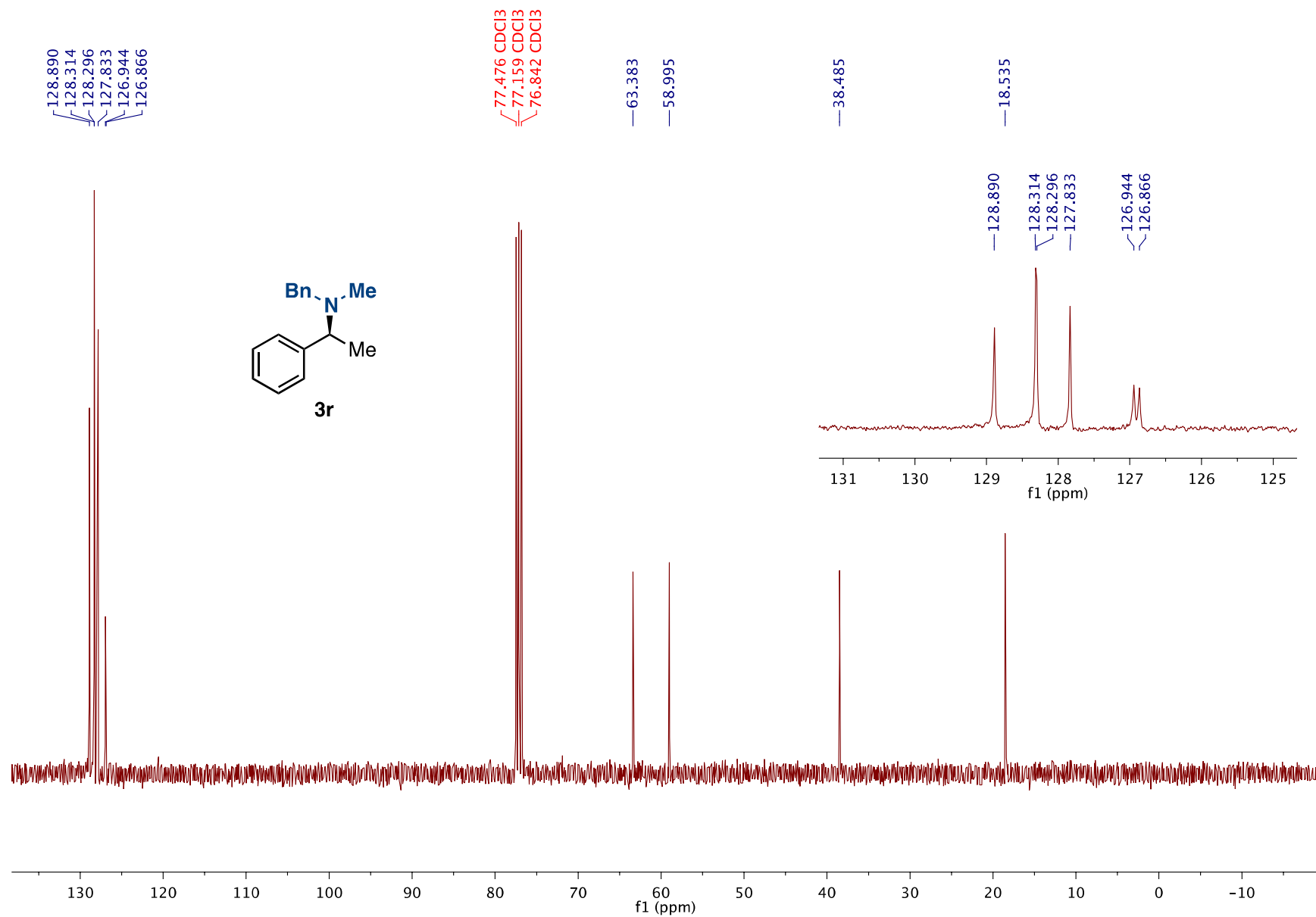




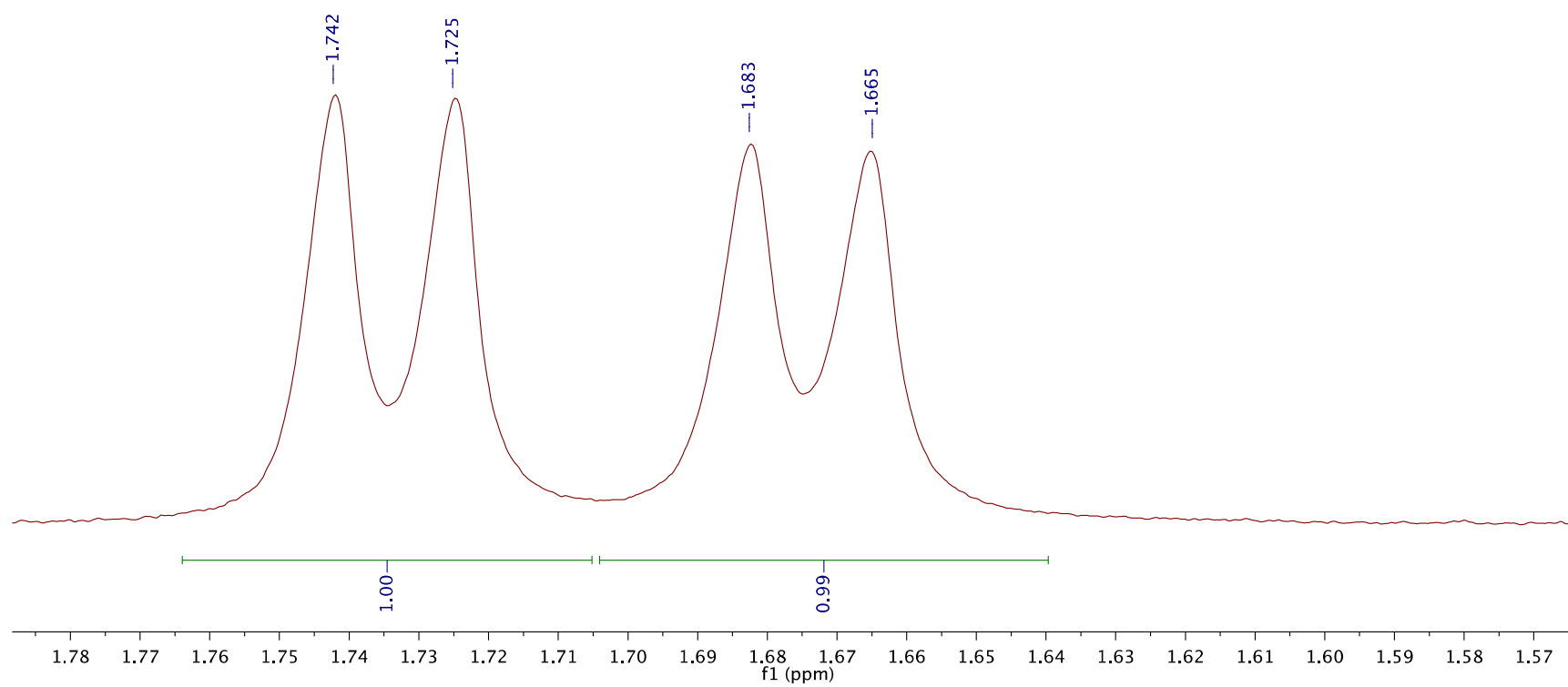




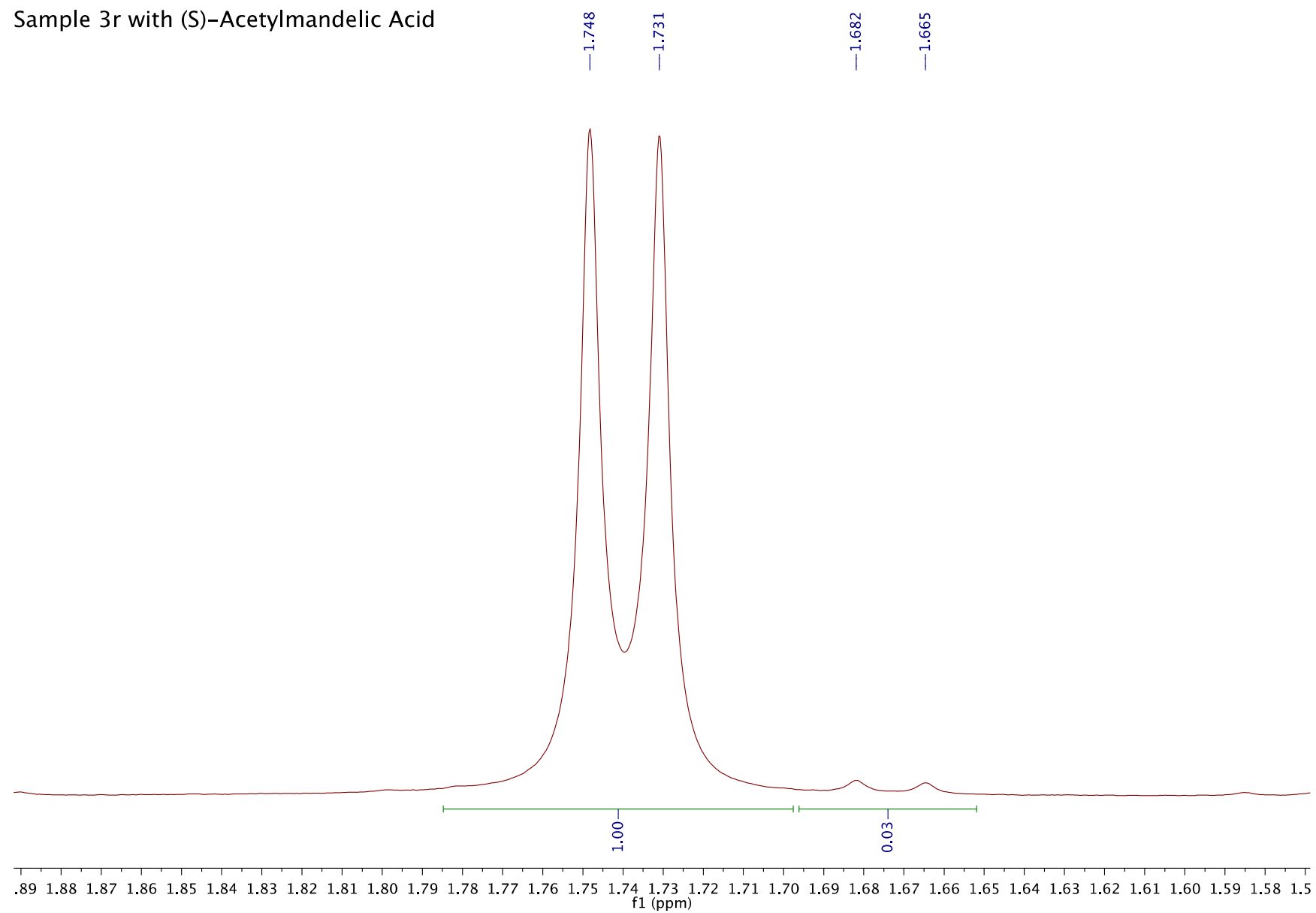


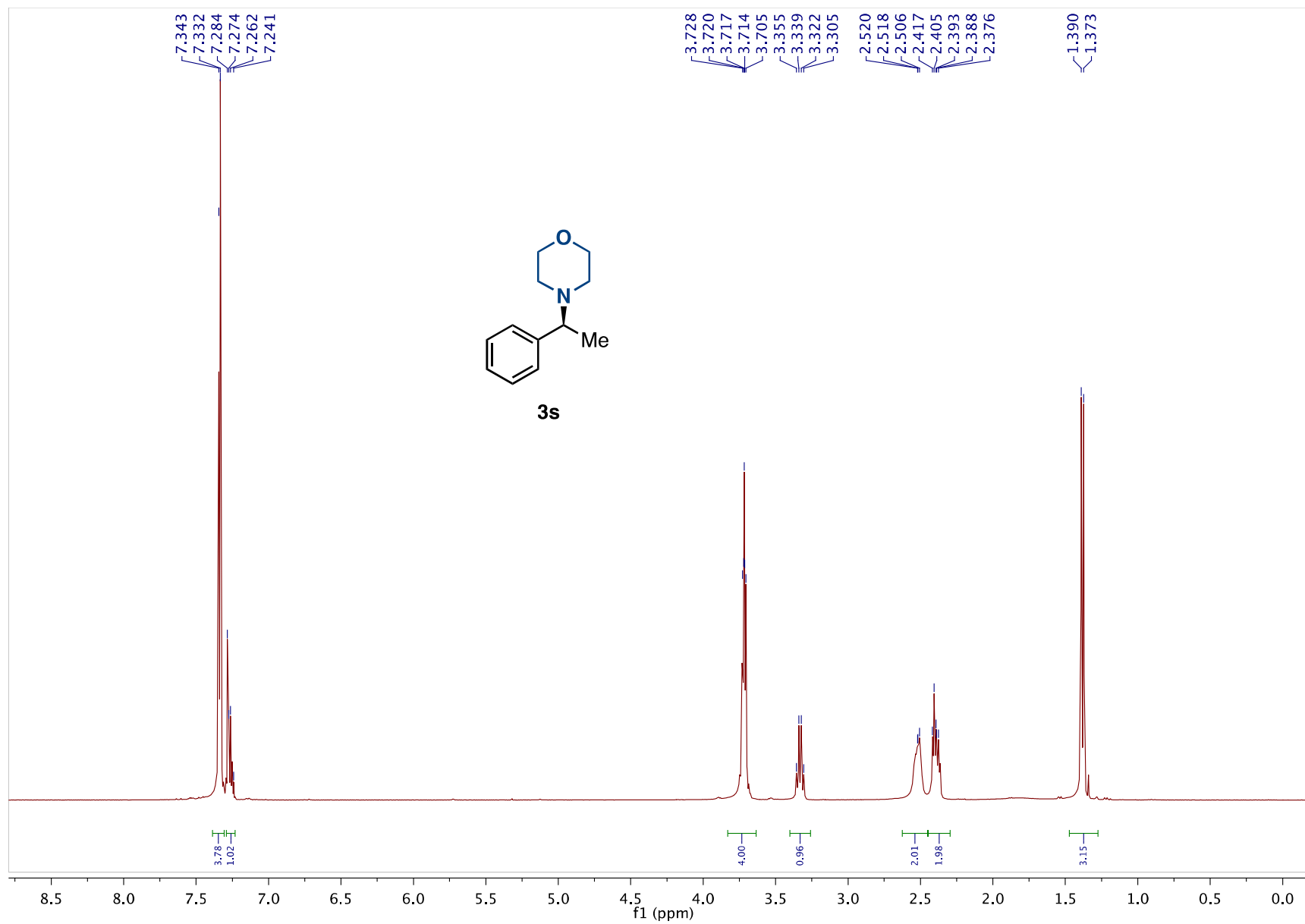


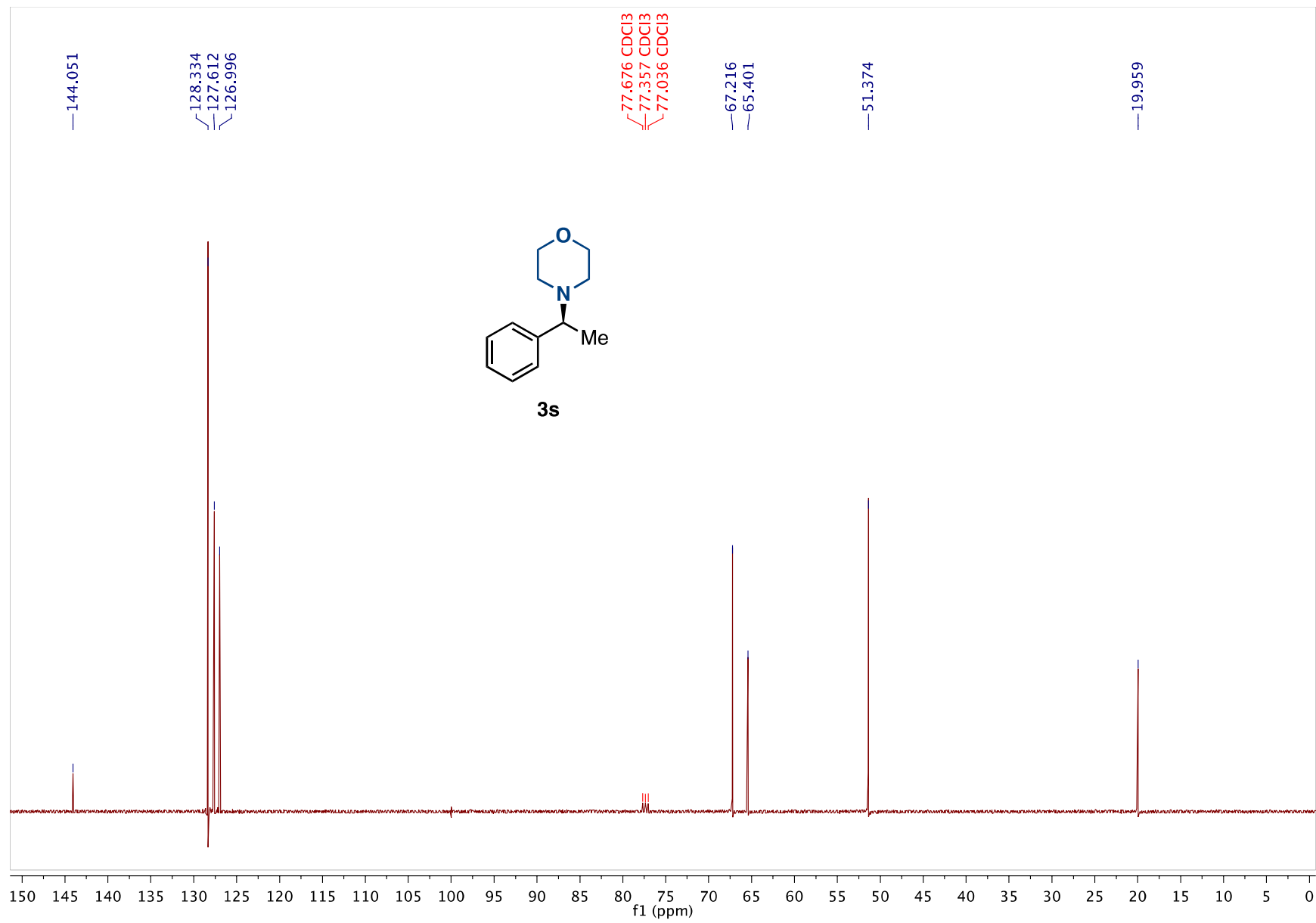
Racemic 3r with (R)-Acetylmandelic Acid



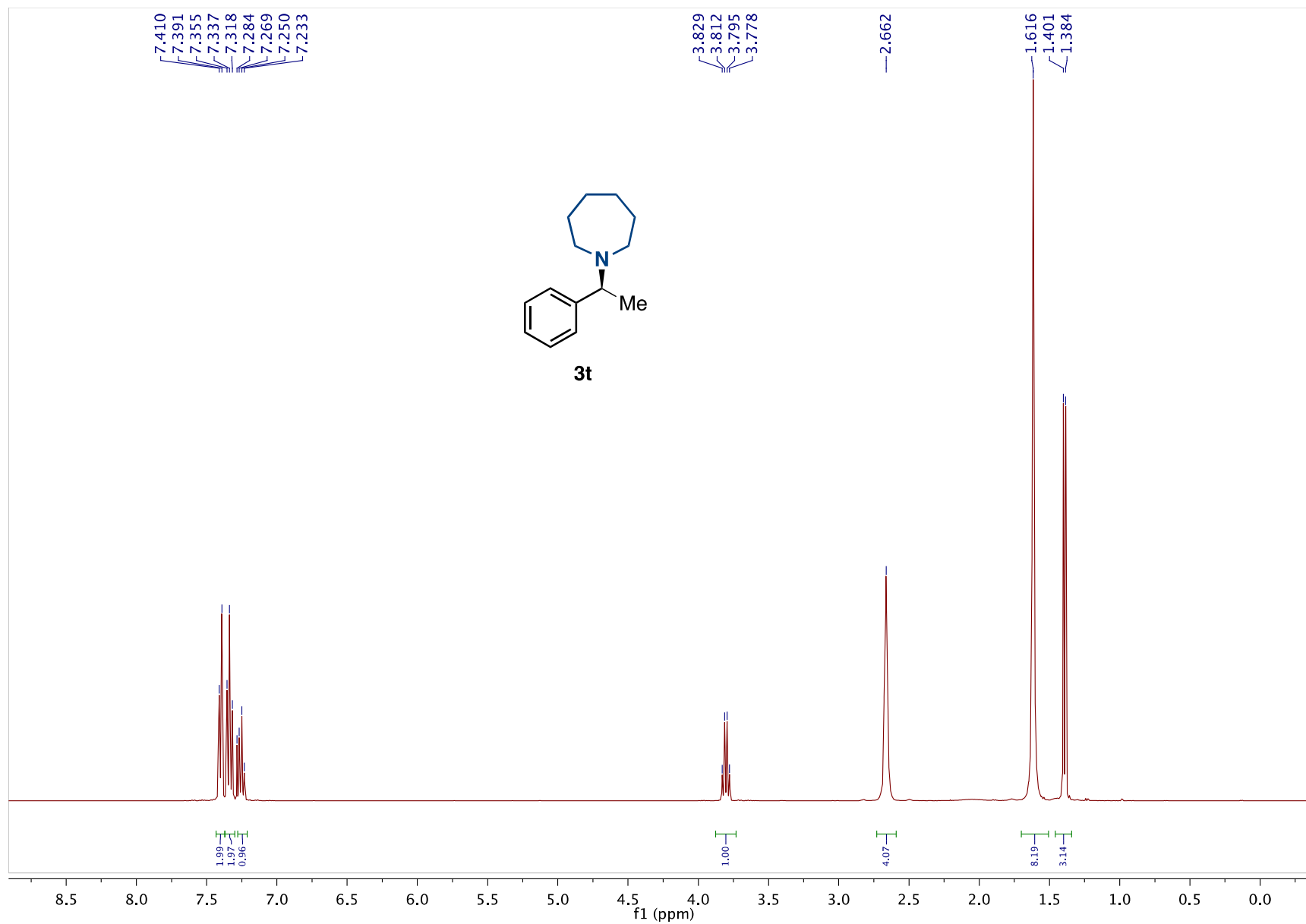
Sample 3r with (S)-Acetylmandelic Acid

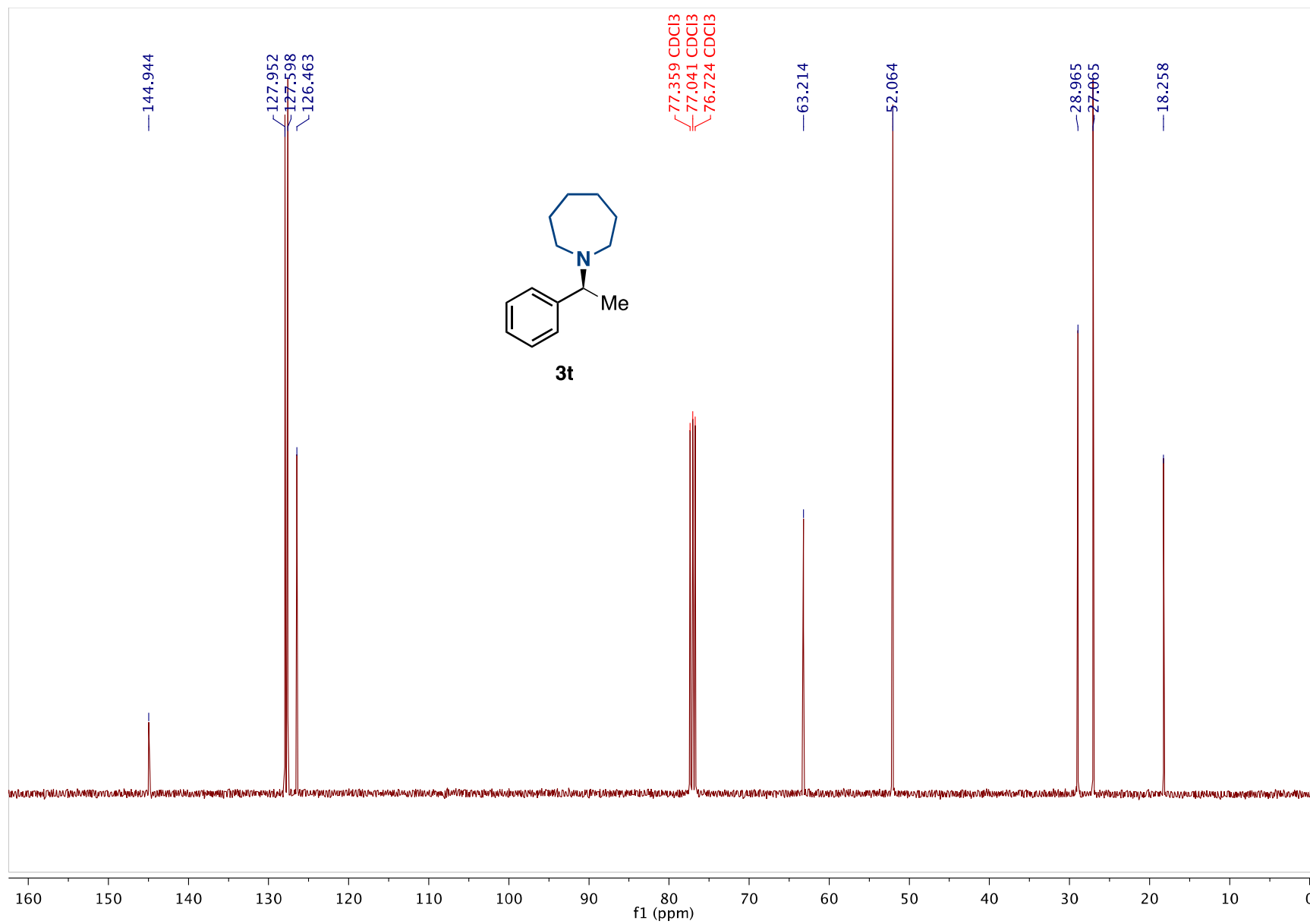


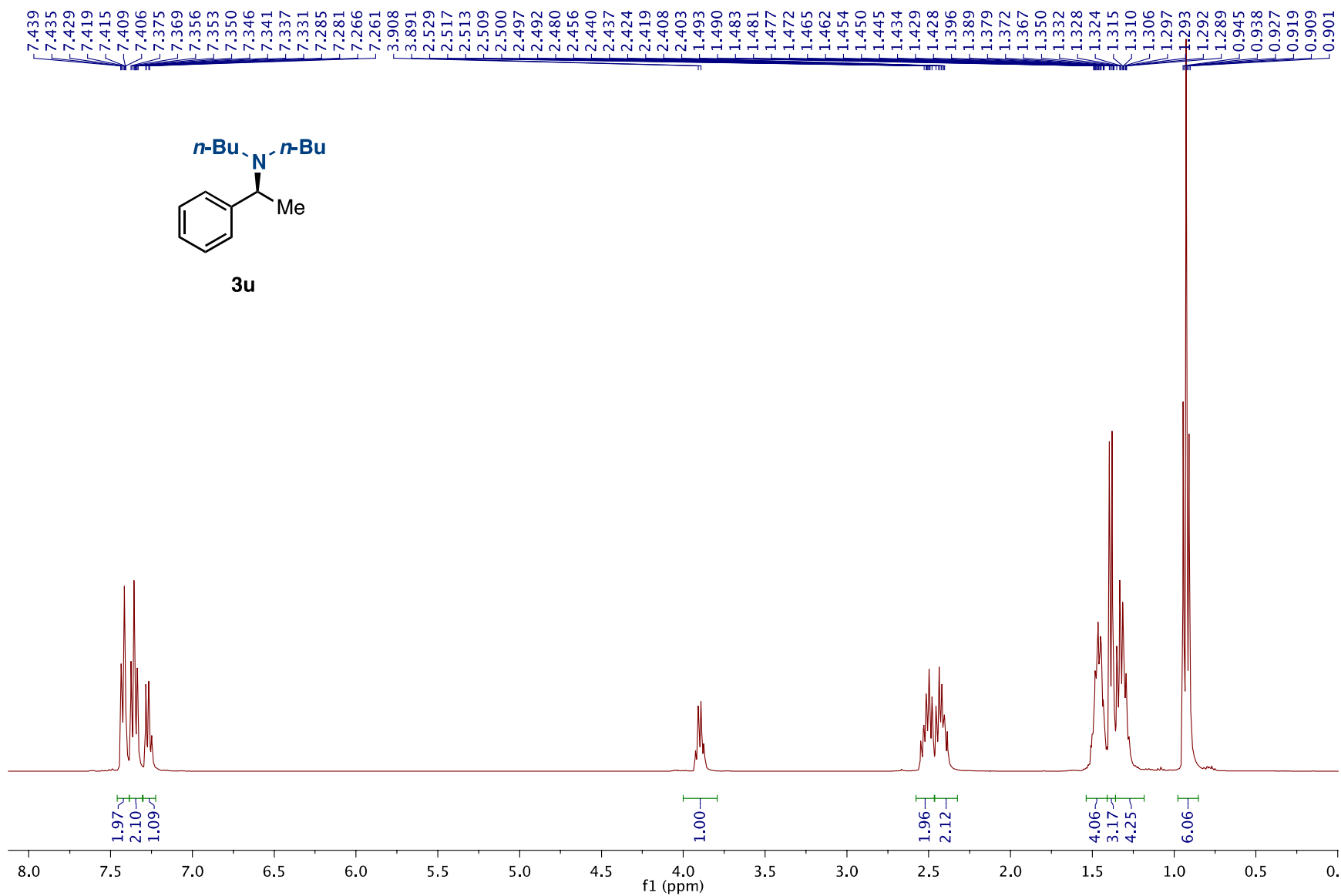


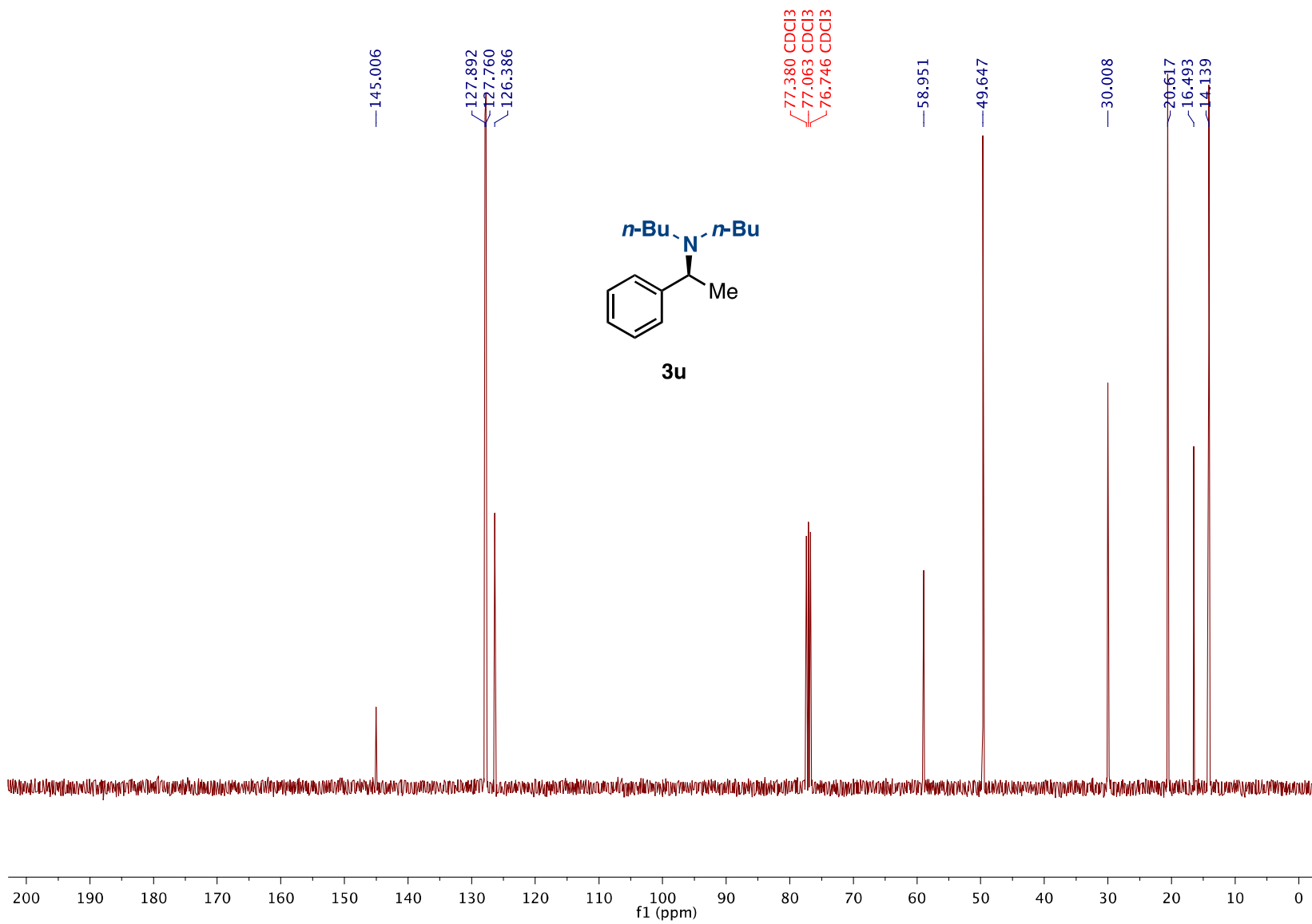




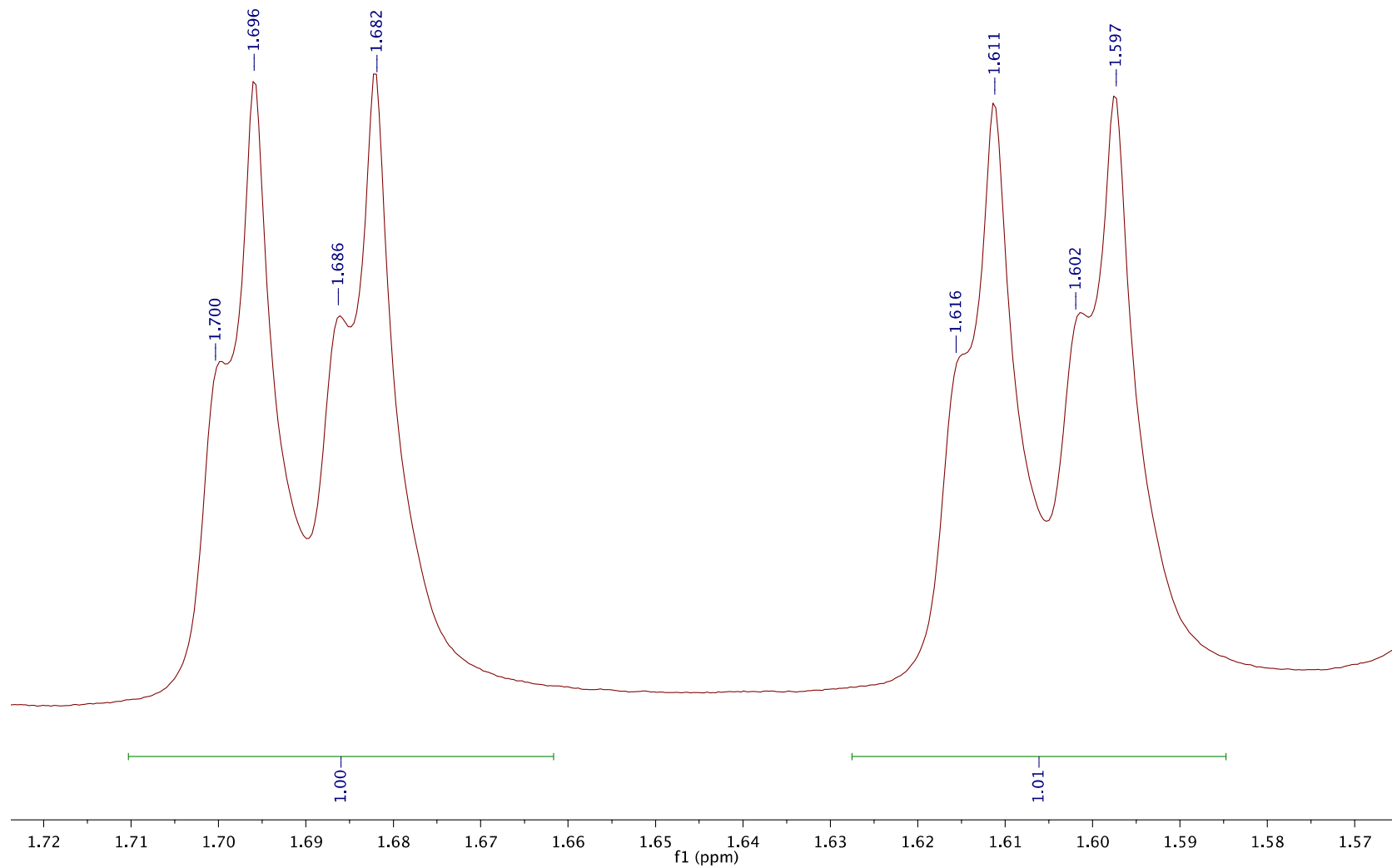








Racemic 3u with (R)-Acetylmandelic Acid



Sample of 3u with (R)-Acetylmandelic Acid

