Electronic Supporting Information

Copper-catalyzed borylative aminomethylation of C–C double and triple bonds with *N,O*-acetal

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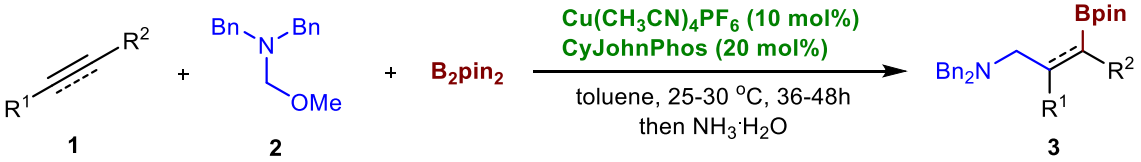
Contents

1. General considerations

Unless otherwise noted, all reactions were performed under an argon atmosphere (purity ≥ 99.999%) using standard Schlenk-type tubes on a dual-manifold Schlenk line. All the solvents were refluxed with CaH_2 for 12 h, then distilled, further degassed by bubbling with argon for 20 minutes at room temperature, and stored with activated 4 Å molecular sieves. Isolated yields were determined after purification of the crude product by column chromatography with 10 ~ 40 μm silica gel. Various reagents were purchased from commercial sources and used without further purification. *N*,*N*-dibenzyl-1-methoxymethanamine was synthesized according to reported method.[1]

^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{11}B NMR spectra were recorded on Bruker Avance III HD 400 and Bruker Avance III HD 500 spectrometer with complete proton decoupling. All NMR data were obtained in $CDCl_3$ at ambient temperature. High-resolution mass spectrum (HRMS) were recorded on a solariX-70FT-MS and TSQ Fortis MS. X-ray crystallographic analysis was carried out by Bruker APEII CCD. Infrared spectra were obtained on a Thermo Scientific Nicolet iS10 FT-IR spectrometer.

2. General procedure for copper-catalyzed borylative aminomethylation of alkenes, alkynes and allenes

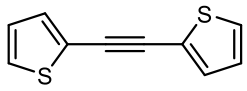


To an oven-dried Schlenk tube equipped with a magnetic stir bar, $Cu(CH_3CN)_4PF_6$ (0.02 mmol, 7.5 mg), Cy-JohnPhos (0.04 mmol, 14.0 mg), B_2pin_2(0.3 mmol, 76.5 mg) and unsaturated hydrocarbon **1** (0.2 mmol, if solid) were added. The tube was evacuated and backfilled with argon (this process was repeated three times). Then toluene (1.0 mL) was added into the tube. The resulting mixture was stirred at room temperature for 20 minutes, then unsaturated hydrocarbon **1** (0.2 mmol, if liquid) and *N*,*N*-dibenzyl-1-methoxymethanamine **2** (0.3 mmol, 73.0 mg) were added under a flow of argon. After stirring at 25–30 °C for 36 hours (if alkynes, stirring for 48 hours), ammonium hydroxide (0.1 mL, 25% $NH_3·H_2O$) was introduced to quench the reaction. Further stirring for 30 minutes, the mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were concentrated in vacuo and the residue was purified with column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to give the designed products **3**. If products **3** were from alkenes, the silica gel powder was soaked overnight in petroleum ether solution containing Et_3N (0.25 vol%).

3. Characterization data of compounds

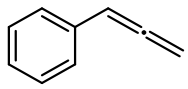
3.1 Characterization of substrates

1,2-di(thiophen-2-yl)ethyne[2]**:**



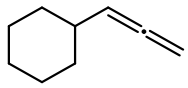
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.30 (dd, *J* = 5.2, 1.0 Hz, 2H), 7.28 (dd, *J* = 3.6, 0.9 Hz, 2H), 7.01 (dd, *J* = 5.1, 3.7 Hz, 2H).

Propa-1,2-dien-1-ylbenzene[3]**:**



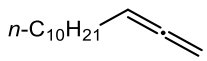
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.29 – 7.28 (m, 4H), 7.21 – 7.16 (m, 1H), 6.15 (t, *J* = 6.8 Hz, 1H), 5.13 (d, *J* = 6.8 Hz, 2H).

Propa-1,2-dien-1-ylcyclohexane[3]**:**



^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.08 (q, *J* = 6.5 Hz, 1H), 4.68 (dd, *J* = 6.7, 3.2 Hz, 2H), 2.02 – 1.94 (m, 1H), 1.77 – 1.69 (m, 4H), 1.65 – 1.61 (m, 1H), 1.31 – 1.23 (m, 2H), 1.21 – 1.13 (m, 1H), 1.11 – 1.06 (m, 2H).

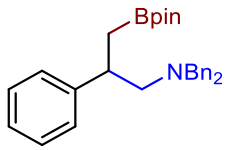
Trideca-1,2-diene [4]



^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.12 – 5.06 (m, 1H), 4.65 – 4.63 (m, 2H), 2.02 – 1.96 (m, 2H), 1.43 – 1.37 (m, 2H), 1.33 – 1.26 (m, 14H), 0.88 (t, *J* = 7.0 Hz, 3H).

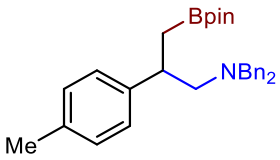
3.2 Characterization of γ-amino boronates 3 from borylaminomethylation.

***N*,*N*-dibenzyl-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (3a):**



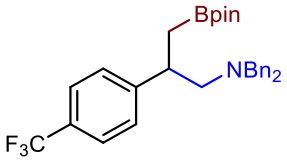
Purification by column chromatograph on silica gel (petroleum ether (0.25 vol% Et_3N)/ethyl acetate = 120/1) gave **3a** as a colorless oil (66.2 mg 75%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.23 – 7.20 (m, 7H), 7.18-7.16 (m, 6H), 7.08 (d, *J* = 7.1 Hz, 2H), 3.59 (d, *J* = 13.8 Hz, 2H), 3.47 (d, *J* = 13.8 Hz, 2H), 3.20 – 3.15 (m, 1H), 2.57 (dd, *J* = 12.6, 8.2 Hz, 1H), 2.49 (dd, *J* = 12.6, 7.0 Hz, 1H), 1.31 (dd, *J* = 15.6, 6.4 Hz, 1H), 1.05 (s, 6H), 1.04 (s, 6H), 0.96 (dd, *J* = 15.7, 9.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 145.87, 139.74, 128.83, 128.06, 128.00, 127.92, 126.63, 125.92, 82.94, 62.09, 58.44, 39.72, 24.72, 24.65, 17.05. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 33.49. **HRMS** (ESI) m/z: calculated for $[C_{29}H_{36}BNO_2 + H]^+$ 442.2917, found 442.2916. **IR** (film): *v* (cm^{-1}) = 3025, 2983, 2935, 2794, 1601, 1493, 1452, 1370, 1315, 1214, 1144, 1030, 965, 844, 738, 699.

***N*,*N*-dibenzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(*p*-tolyl)propan-1-amine (3b):**



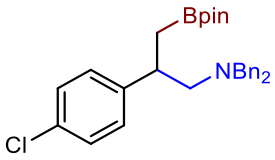
Purification by column chromatograph on silica gel (petroleum ether (0.25 vol% Et_3N)/ethyl acetate = 120/1) afforded **3b** as a colorless oil (44.6 mg, 49%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = δ 7.22 – 7.16 (m, 10H), 7.02 (d, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 3.57 (d, *J* = 13.9 Hz, 2H), 3.50 (d, *J* = 13.8 Hz, 2H), 3.18 – 3.12 (m, 1H), 2.54 (dd, *J* = 12.6, 7.9 Hz, 1H), 2.47 (dd, *J* = 12.5, 7.2 Hz, 1H), 2.32 (s, 3H), 1.31 (dd, *J* = 15.8, 6.6 Hz, 1H), 1.07 (s, 6H), 1.06 (s, 6H), 0.94 (dd, *J* = 15.4, 9.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 142.82, 139.75, 135.15, 128.83, 128.55, 128.00, 127.75, 126.57, 82.89, 62.14, 58.40, 39.22, 24.71, 24.65, 21.08, 17.04. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 32.62. **HRMS** (ESI) m/z: calculated for $[C_{30}H_{38}BNO_2 + H]^+$ 456.3068, found 456.3050. **IR** (film): *v* (cm^{-1}) = 3025, 2977, 2928, 2791, 1514, 1494, 1452, 1370, 1322, 1145, 1028, 967, 846, 812 745, 698.

***N*,*N*-dibenzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-(trifluoromethyl)phenyl)propan-1-amine (3c):**



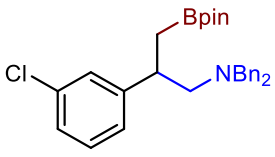
Purification by column chromatograph on silica gel (petroleum ether (0.25 vol% Et_3N)/ethyl acetate = 120/1) afforded **3c** as a colorless oil (75.1 mg, 74%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.17 (m, 6H), 7.14 – 7.09 (m, 6H), 3.69 (d, *J* = 13.7 Hz, 2H), 3.35 (d, *J* = 13.7 Hz, 2H), 3.23 – 3.19 (m, 1H), 2.60 (dd, *J* = 12.6, 9.4 Hz, 1H), 2.49 (dd, *J* = 12.7, 5.8 Hz, 1H), 1.24 – 1.20 (m, 1H), 1.07 (s, 6H), 1.06 (s, 6H), 0.95 (dd, *J* = 15.6, 9.2 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.30, 139.43, 128.75, 128.29, 128.13 (q, *J* = 31.9 Hz), 128.08, 126.75, 124.56 (q, *J* = 271.6 Hz), 124.73 (q, *J* = 3.7 Hz), 83.13, 61.75, 58.57, 39.72, 24.66, 24.64, 16.97. **^{19}F NMR** (471 MHz, CDCl3) δ = -62.13. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 32.94. **HRMS** (ESI) m/z: calculated for $[C_{30}H_{35}BF_3NO_2 + H]^+$ 510.2791, found 510.2795. **IR** (film): *v* (cm^{-1}) = 3027, 2978, 2931, 2795, 1618, 1494, 1451, 1371, 1325, 1144, 1122, 1068, 966, 836, 743. 698.

***N*,*N*-dibenzyl-2-(4-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (3d):**



Purification by column chromatograph on silica gel (petroleum ether (0.25 vol% Et_3N)/ethyl acetate = 120/1) afforded **3d** as a colorless oil (66.5 mg, 70%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.22– 7.12 (m, 12H), 6.96 (d, *J* = 8.4 Hz, 2H), 3.64 (d, *J* = 13.7 Hz, 2H), 3.37 (d, *J* = 13.7 Hz, 2H), 3.21 – 3.07 (m, 1H), 2.55 (dd, *J* = 12.6, 9.0 Hz, 1H), 2.45 (dd, *J* = 12.7, 6.2 Hz, 1H), 1.25 – 1.18 (m, 1H), 1.07 (s, 6H), 1.05 (s, 6H), 0.91 (dd, *J* = 15.6, 9.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 144.56, 139.58, 131.41, 129.38, 128.82, 128.12, 127.95, 126.76, 83.08, 61.94, 58.57, 39.23, 24.78, 24.72, 17.14. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 32.07. **HRMS** (ESI) m/z: calculated for $[C_{29}H_{35}BClNO_2 + H]^+$ 476.2522, found 476.2508. **IR** (film): *v* (cm^{-1}) = 3026, 2977, 2931, 2792, 1492, 1451, 1370, 1321, 1212, 1144, 1091, 1014, 967, 846, 745, 698.

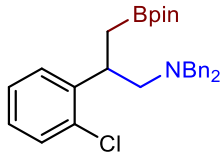
***N*,*N*-dibenzyl-2-(3-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (3e):**



Purification by column chromatograph on silica gel (petroleum ether (0.25 vol% Et_3N)/ethyl acetate = 120/1) afforded **3e** as a colorless oil (54.2 mg, 57%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.24 – 7.12 (m, 12H), 7.04

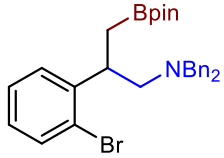
(s, 1H), 6.93 (d, *J* = 6.7 Hz, 1H), 3.66 (d, *J* = 13.7 Hz, 2H), 3.38 (d, *J* = 13.7 Hz, 2H), 3.29 – 3.13 (m, 1H), 2.58 (dd, *J* = 12.5, 9.1 Hz, 1H), 2.47 (dd, *J* = 12.7, 6.2 Hz, 1H), 1.25 – 1.20 (m, 1H), 1.08 (s, 6H), 1.07 (s, 6H), 0.92 (dd, *J* = 15.6, 9.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 148.05, 139.50, 133.60, 129.09, 128.75, 128.23, 128.09, 126.72, 126.20, 125.98, 83.06, 61.56, 58.49, 39.53, 24.71, 24.64, 17.10. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 32.92. **HRMS** (ESI) m/z: calculated for $[C_{29}H_{35}BClNO_2 + H]^+$ 476.2522, found 476.2507. **IR** (film): *v* (cm^{-1}) = 3027, 2977, 2931, 2793, 1596, 1494, 1453, 1371, 1321, 1212, 1144, 1028, 967, 845, 745, 697.

***N*,*N*-dibenzyl-2-(2-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (3f):**



Purification by column chromatograph on silica gel (petroleum ether (0.25 vol% Et_3N)/ethyl acetate = 120/1) afforded **3f** as a colorless oil (54.4 mg, 57%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.32 – 7.31 (m, 1H), 7.25 – 7.15 (m, 10H), 7.10 – 7.04 (m, 2H), 6.96 – 6.90 (m, 1H), 3.91 – 3.77 (m, 1H), 3.59 (d, *J* = 13.7 Hz, 2H), 3.51 (d, *J* = 13.7 Hz, 2H), 2.61 (dd, *J* = 12.4, 7.9 Hz, 1H), 2.45 (dd, *J* = 12.6, 7.2 Hz, 1H), 1.36 (dd, *J* = 15.5, 6.0 Hz, 1H), 1.06 (s, 6H), 1.02 (s, 6H), 0.96 (dd, *J* = 15.4, 10.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 143.13, 139.69, 134.20, 129.05, 128.92, 128.52, 128.01, 126.84, 126.62, 82.97, 61.18, 58.50, 35.07, 24.65, 24.52, 16.31. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 33.52. **HRMS** (ESI) m/z: calculated for $[C_{29}H_{35}BClNO_2 + H]^+$ 476.2522, found 476.2506. **IR** (film): *v* (cm^{-1}) = 3026, 2977, 2928, 2794, 1494, 1451, 1370, 1323, 1211, 1144, 1035, 967, 846, 748, 698.

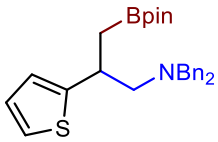
***N*,*N*-dibenzyl-2-(2-bromophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (3g):**



Purification by column chromatograph on silica gel (petroleum ether (0.25 vol% Et_3N)/ethyl acetate = 120/1) afforded **3g** as a colorless oil (61.5 mg, 59%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.51 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.25 – 7.21 (m, 8H), 7.21 – 7.16 (m, 2H), 7.13 – 7.10 (m, 1H), 7.02 – 6.99 (m, 1H), 6.91 (dd, *J* = 7.7, 1.5 Hz, 1H), 3.84 – 3.78 (m, 1H), 3.57 (s, 4H), 2.61 (dd, *J* = 12.6, 7.6 Hz, 1H), 2.44 (dd, *J* = 12.7, 7.5 Hz,

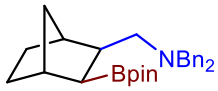
1H), 1.38 (dd, *J* = 15.5, 6.1 Hz, 1H), 1.06 (s, 6H), 1.02 (s, 6H), 0.96 (dd, *J* = 15.5, 10.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 144.73, 139.71, 132.39, 128.95, 128.61, 128.03, 127.29, 127.25, 126.64, 125.24, 82.98, 61.23, 58.53, 37.89, 24.66, 24.52, 16.48. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 33.95. **HRMS** (ESI) m/z: calculated for $[C_{29}H_{35}BBrNO_2 + H]^+$ 520.2017, found 520.1993. **IR** (film): *v* (cm^{-1}) = 3026, 2977, 2928, 2793, 1494, 1470, 1370, 1322, 1211, 1144, 1021, 967, 846, 747, 698.

***N*,*N*-dibenzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-2-yl)propan-1-amine (3i):**



Purification by column chromatograph on silica gel (petroleum ether (0.25 vol% Et_3N)/ethyl acetate = 120/1) afforded **3i** as a colorless oil (24.3 mg, 27%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.25 (d, *J* = 3.8 Hz, 8H), 7.22 – 7.17 (m, 2H), 7.08 (d, *J* = 5.1 Hz, 1H), 6.87 (dd, *J* = 4.9, 3.6 Hz, 1H), 6.75 (d, *J* = 3.4 Hz, 1H), 3.59 (d, *J* = 13.8 Hz, 2H), 3.54 (d, *J* = 13.8 Hz, 2H), 3.49 – 3.42 (m, 1H), 2.62 (dd, *J* = 12.6, 7.6 Hz, 1H), 2.53 (dd, *J* = 12.6, 7.2 Hz, 1H), 1.43 – 1.36 (m, 1H), 1.12 (s, 6H), 1.10 (s, 6H), 1.03 (dd, *J* = 15.7, 9.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 149.91, 139.45, 128.90, 128.06, 126.67, 126.08, 123.36, 122.40, 83.05, 62.94, 58.37, 35.20, 24.70, 24.67, 18.13. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 30.01. **HRMS** (ESI) m/z: calculated for $[C_{27}H_{34}BNO_2S + H]^+$ 448.2476, found 448.2459. **IR** (film): *v* (cm^{-1}) = 3026, 2977, 2929, 2795, 1494, 1453, 1371, 1322, 1263, 1144, 1028, 967, 846, 746, 698.

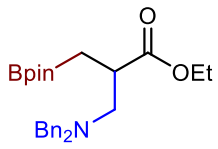
***N*,*N*-dibenzyl-1-((1S,4R)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[2.2.1]heptan-2-yl)methanamine (3k):**



Purification by column chromatograph on silica gel (petroleum ether/ethyl acetate = 40/1) afforded **3k** as a colorless oil (25.1 mg, 29%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 7.3 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 4H), 7.21 (t, *J* = 7.2 Hz, 2H), 3.81 (d, *J* = 13.7 Hz, 2H), 3.21 (d, *J* = 13.7 Hz, 2H), 2.41 (d, *J* = 3.5 Hz, 1H), 2.35 – 2.30 (m, 1H), 2.16 (dd, *J* = 12.2, 5.2 Hz, 1H), 2.11 (d, *J* = 2.4 Hz, 1H), 1.99 – 1.94 (m, 1H), 1.54 – 1.44 (m, 2H), 1.23 – 1.22 (m, 1H), 1.17 (s, 6H), 1.13 (s, 6H), 1.11 – 1.07 (m, 2H), 1.01 (d, *J* = 8.6 Hz, 1H), 0.94 (d, *J* = 9.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 139.83, 129.01, 128.03, 126.67, 82.70, 58.15,

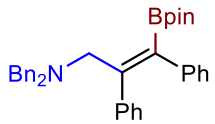
57.39, 43.28, 38.96, 38.57, 34.80, 31.73, 29.93, 25.05, 24.80. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 34.29. **HRMS** (ESI) m/z: calculated for $[C_{28}H_{38}BNO_2 + H]^+$ 432.3068, found 432.3052. **IR** (film): *ν* (cm^{-1}) = 3026, 2942, 2866, 2791, 1601, 1494, 1452, 1368, 1318, 1143, 1028, 973, 858, 745, 698.

Ethyl 3-(dibenzylamino)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)propanoate (3l):



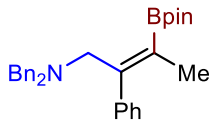
Purification by column chromatograph on silica gel (petroleum ether/ethyl acetate = 20/1) afforded **3l** as a colorless oil (56.9 mg, 65%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.32 – 7.26 (m, 8H), 7.23 – 7.18 (m, 2H), 4.15 – 4.03 (m, 2H), 3.65 (d, *J* = 13.7 Hz, 2H), 3.45 (d, *J* = 13.7 Hz, 2H), 2.94 – 2.88 (m, 1H), 2.78 (dd, *J* = 12.5, 8.7 Hz, 1H), 2.48 – 2.40 (m, 1H), 1.24 – 1.21 (m, 3H), 1.20 (s, 6H), 1.19 (s, 6H), 1.04 –0.94 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 175.88, 139.29, 128.96, 128.08, 126.81, 83.20, 60.17, 58.16, 57.80, 40.10, 24.80, 24.77, 14.23. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 33.63. **HRMS** (ESI) m/z: calculated for $[C_{26}H_{36}BNO_4 + H]^+$ 438.2810, found 438.2789. **IR** (film): *ν* (cm^{-1}) = 3027, 2977, 2926, 2798, 1731, 1494, 1452, 1370, 1320, 1143, 967, 846, 745, 698.

(*E*)-*N*,*N*-dibenzyl-2,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-2-en-1-amine (3m):



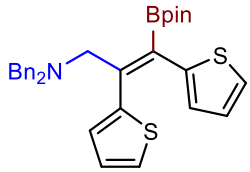
Purification by column chromatograph on silica gel (petroleum ether/ethyl acetate = 30/1 to 15/1) afforded **3m** as a colorless oil (62.7 mg, 61%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.21 – 7.18 (m, 6H), 7.12 – 7.11 (m, 4H), 7.09 – 7.03 (m, 5H), 7.01 – 6.96 (m, 3H), 6.72 – 6.71 (m, 2H), 3.71 (s, 4H), 3.61 (s, 2H), 1.28 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 146.34, 141.06, 139.82, 138.23, 129.80, 129.35, 129.24, 127.96, 127.48, 127.22, 127.02, 126.19, 125.38, 82.97, 59.88, 58.02, 25.46. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 27.69. **HRMS** (ESI) m/z: calculated for $[C_{35}H_{38}BNO_2 + H]^+$ 516.3068, found 516.3055. **IR** (film): *ν* (cm^{-1}) = 3024, 2976, 2925, 2791, 1597, 1492, 1443, 1344, 1303, 1141, 970, 845, 740, 698.

(*E*)-*N*,*N*-dibenzyl-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-amine (3n):



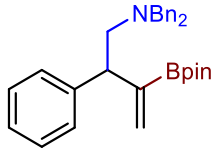
Purification by column chromatograph on silica gel (petroleum ether/ethyl acetate = 35/1 to 15/1) afforded **3n** as a colorless oil (57.1 mg, 63%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.32 – 7.26 (m, 3H), 7.18 – 7.13 (m, 6H), 7.04 – 7.02 (m, 4H), 6.97 – 6.96 (m, 2H), 3.52 (s, 4H), 3.50 (s, 2H), 1.63 (s, 3H), 1.33 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 150.69, 141.80, 139.78, 128.78, 128.58, 127.89, 127.57, 126.49, 126.27, 83.27, 59.30, 57.64, 25.01, 18.21. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 31.08. **HRMS** (ESI) m/z: calculated for $[C_{30}H_{36}BNO_2 + H]^+$ 454.2912, found 454.2893. **IR** (film): *ν* (cm^{-1}) = 3025, 2977, 2922, 2789, 1597, 1493, 1452, 1348, 1302, 1273, 1127, 968, 863, 742, 698.

(*Z*)-*N*,*N*-dibenzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-di(thiophen-2-yl)prop-2-en-1-amine (3p):



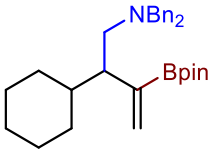
Purification by column chromatograph on silica gel (petroleum ether/ethyl acetate = 20/1) afforded **3p** as a colorless oil (42.2 mg, 40%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.31 – 7.29 (m, 4H), 7.25 – 7.22 (m, 6H), 7.15 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.10 (dd, *J* = 5.0, 1.0 Hz, 1H), 6.89 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.80 – 7.78 (m, 2H), 6.54 – 6.53 (m, 1H), 3.95 (s, 4H), 3.60 (s, 2H), 1.26 (s, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 142.39, 140.19, 136.39, 136.06, 130.80, 128.14, 127.63, 126.31, 126.08, 125.93, 125.52, 125.05, 82.25, 59.90, 58.40, 26.22. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 22.41. **HRMS** (ESI) m/z: calculated for $[C_{31}H_{34}BNO_2S_2 + H]^+$ 528.2197, found 528.2191. **IR** (film): *ν* (cm^{-1}) = 3026, 2976, 2925, 2795, 1588, 1454, 1371, 1331, 1271, 1144, 1075, 967, 851, 744, 697.

***N*,*N*-dibenzyl-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-amine (3q):**



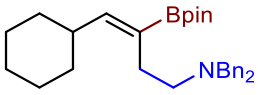
Purification by column chromatograph on silica gel (petroleum ether/ethyl acetate = 50/1 to 30/1) afforded **3q** as a colorless oil (65.3 mg, 72%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.24 – 7.14 (m, 13H), 7.10 – 7.06 (m, 2H), 5.81 (d, *J* = 2.5 Hz, 1H), 5.48 (d, *J* = 1.6 Hz, 1H), 3.87 (t, *J* = 7.7 Hz, 1H), 3.70 (d, *J* = 13.8 Hz, 2H), 3.40 (d, *J* = 13.8 Hz, 2H), 2.93 – 2.85 (m, 2H), 1.17 (s, 6H), 1.13 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 143.11, 139.55, 129.07, 128.93, 128.78, 127.96, 127.78, 126.61, 125.80, 83.34, 58.07, 57.54, 48.53, 24.72, 24.63. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 30.63. **HRMS** (ESI) m/z: calculated for $[C_{30}H_{36}BNO_2 + H]^+$ 454.2912, found 454.2901. **IR** (film): *ν* (cm^{-1}) = 3026, 2977, 2929, 2792, 1601, 1494, 1453, 1371, 1330, 1144, 1028, 966, 863, 746, 698.

***N*,*N*- dibenzyl-2-cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-amine (3r):**



Purification by column chromatograph on silica gel (petroleum ether/ethyl acetate = 50/1 to 25/1) afforded **3r** as a colorless oil (37.5 mg, 41%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.32 – 7.31 (m, 4H), 7.29 – 7.26 (m, 4H), 7.21 – 7.18 (m, 2H), 5.86 (d, *J* = 3.5 Hz, 1H), 5.43 (d, *J* = 3.5 Hz, 1H), 3.57 (d, *J* = 13.7 Hz, 2H), 3.41 (d, *J* = 13.7 Hz, 2H), 2.62 – 2.59 (m, 2H), 2.32 – 2.28 (m, 1H), 1.74 – 1.57 (m, 4H), 1.49 – 1.37 (m, 3H), 1.18 (s, 6H), 1.17 (s, 6H), 1.08 – 1.02 (m, 2H), 0.90 – 0.82 (m, 1H), 0.75 – 0.67 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 139.78, 130.11, 129.19, 127.92, 126.55, 82.93, 57.86, 55.75, 49.62, 39.82, 31.98, 30.73, 26.73, 26.56, 24.86, 24.55. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 30.23 **HRMS** (ESI) m/z: calculated for $[C_{30}H_{42}BNO_2 + H]^+$ 460.3381, found 460.3371. **IR** (film): *ν* (cm^{-1}) = 2975, 2923, 2849, 2793, 1603, 1494, 1449, 1370, 1304, 1143, 1028, 967, 856, 746, 698.

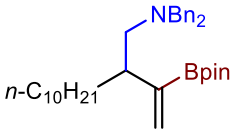
***N*,*N*- dibenzyl-4-cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-amine (3s):**



Purification by column chromatograph on silica gel (petroleum ether/ethyl acetate = 50/1 to 25/1) gave the mixture (**3s** and **3r**) as a colorless oil (HNMR, **3s** : **3r** = 1 : 1.8, 58.6 mg, 64%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.40 (d, *J* = 7.4 Hz, 4H), 7.32 – 7.26 (m, 4H), 7.22 – 7.18 (m, 2H), 6.05 (d, *J* = 9.4 Hz, 1H), 3.65 (s, 4H), 2.38 (s, 4H), 2.20 – 2.13 (m, 4H), 1.28 – 1.21 (m, 2H), 1.17 (s, 6H), 1.16 (s, 6H), 1.13 – 0.98 (m, 5H). **^{13}C**

NMR (126 MHz, $CDCl_3$) δ = 152.42, 140.00, 128.84, 128.09, 126.67, 82.95, 58.02, 53.38, 37.53, 32.77, 26.03, 25.86, 25.70, 24.71.

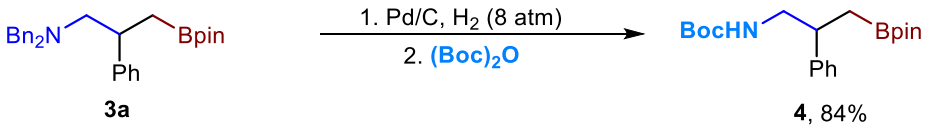
***N*,*N*-dibenzyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)dodecan-1-amine (3t):**



Purification by column chromatograph on silica gel (petroleum ether/ethyl acetate = 60:1 to 25:1) afforded **3t** as a colorless oil (44.5 mg, 43%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.34 – 7.33 (m, 4H), 7.29 – 7.25 (m, 4H), 7.21 – 7.18 (m, 2H), 5.81 (d, *J* = 3.4 Hz, 1H), 5.50 (d, *J* = 3.3 Hz, 1H), 3.57 (d, *J* = 13.7 Hz, 2H), 3.47 (d, *J* = 13.7 Hz, 2H), 2.47 – 2.46 (m, 2H), 1.57 – 1.51 (m, 1H), 1.33 – 1.21 (m, 18H), 1.18 (s, 6H), 1.15 (s, 6H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 139.86, 129.42, 129.08, 127.97, 126.57, 82.96, 58.74, 58.20, 44.06, 32.20, 31.96, 29.81, 29.72, 29.70, 29.64, 29.38, 27.38, 24.79, 24.63, 22.72, 14.15. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 31.58. **HRMS** (ESI) m/z: calculated for $[C_{34}H_{52}BNO_2 + H]^+$ 518.4164, found 518.4157. **IR** (film): *ν* (cm^{-1}) = 3027, 2925, 2853, 2793, 1609, 1494, 1453, 1370, 1306, 1143, 1028, 967, 855, 803, 745, 698.

4. Further functionalization reactions

***Tert*-butyl (2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate (4):**



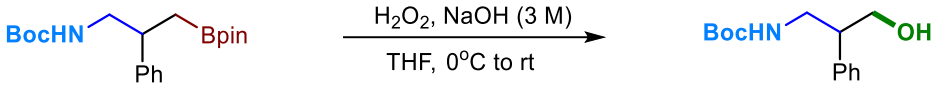
3a **4**, 84%

The following procedure was adapted from a previously-published method.[5] To a high pressure reactor equipped with a magnetic stirring bar, was added **3a** (0.5 mmol, 221 mg), wet 10% Pd/C (20 wt%, 45 mg) and MeOH (2.0 mL). The reactor was filled with H_2 to reach a pressure of 8.0 atm and stirred for 24 h at room temperature. Then the reaction mixture was diluted with 2.0 mL of CH_2Cl_2. *N*,*N*-diisopropylethylamine (DIPEA, 0.75 mmol, 131 uL,) and di-*tert*-butyl dicarbonate (Boc_2O, 0.6 mmol, 131 mg,) were added in sequence at room temperature. The mixture was stirred 12 h at room temperature and then filtered through a pad of Celite to remove Pd/C, and the solid was washed with MeOH. The filtrate was concentrated under

vacuum, and the residue was purified with column chromatography on silica gel using petroleum ether/ethyl acetate (PE/EA= 8:1) as the eluent to give the designed product **4** (151.5mg, 84% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ = δ 7.29 – 7.26 (m, 2H), 7.22 – 7.17 (m, 3H), 4.55 (s, 1H), 3.40 – 3.35 (m, 1H), 3.36 – 3.21 (m, 1H), 3.05 – 2.99 (m, 1H), 1.39 (s, 9H), 1.23 – 1.13 (m, 2H), 1.12 (s, 6H), 1.10 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 155.79, 144.33, 128.38, 127.58, 126.44, 83.18, 78.93, 48.12, 41.50, 28.39, 24.73, 24.62, 16.48. **^{11}B NMR** (128 MHz, $CDCl_3$) δ = 33.16. **HRMS** (ESI) m/z: calculated for $[C_{20}H_{32}BNO_4 + Na]^+$ 384.2316, found 384.2298. **IR** (film): *v* (cm^{-1}) = 2977, 2929, 1716, 1508, 1453, 1366, 1312, 1248, 1168, 1144, 968, 846,700.

***Tert*-butyl (3-hydroxy-2-phenylpropyl)carbamate (5):**

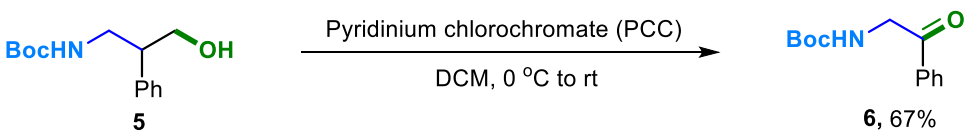


4 **5**, 89%

The following procedure was adapted from a previously-published method.[6] A 25 mL Schlenk tube was charged with compound **4** (0.2 mmol, 72.5 mg) and tetrahydrofuran (THF, 1.5 mL). While stirring at 0 °C, NaOH (3 M, 0.8 mL) was added dropwise followed by H_2O_2 solution (30% in water, 0.4 mL). After stirring at ambient temperature for 30 minutes, the mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were concentrated in vacuo and the residue was purified with column chromatography on silica gel using petroleum ether/ethyl acetate (PE/EA= 3:1) as the eluent to give the designed product **5** (44.7 mg, 89%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.34 – 7.31 (m, 2H), 7.27 – 7.22 (m, 3H), 4.76 (s, 1H), 3.80 (d, *J* = 5.5 Hz, 2H), 3.50 – 3.44 (m, 2H), 3.19 (s, 1H), 2.94 – 2.89 (m, 1H), 1.44 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 157.11, 140.61, 128.74, 128.03, 127.05, 79.90, 63.46, 48.36, 42.23, 28.36. **HRMS** (ESI) m/z: calculated for $[C_{14}H_{21}NO_3 + Na]^+$ 274.1413, found 274.1402. **IR** (film): *v* (cm^{-1}) =3367, 2977, 2931, 1692, 1513, 1453, 1366, 1251, 1169, 1037, 937, 861, 758, 700.

***Tert*-butyl (2-oxo-2-phenylethyl)carbamate (6):**

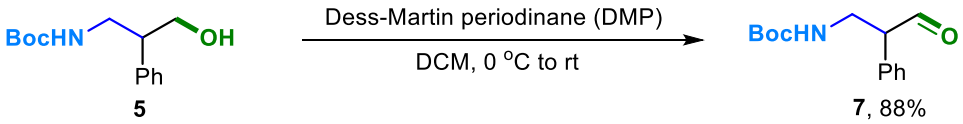


5 **6**, 67%

The following procedure was adapted from a previously-published method.[7] Pyridinium chlorochromate (PCC, 0.6 mmol, 130 mg) was added portionwisely over 5 minutes to a solution of **5** (0.2 mmol, 51 mg) in dry CH_2Cl_2 (1.2 mL) at 0 °C. After stirring at ambient temperature for 24 h, $NaHCO_3$ (0.5 mL, saturated solution) and $Na_2S_2O_3$ (0.5 mL, saturated solution) were introduced to the reaction mixture. Further stirring for 10 minutes, the mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were concentrated in vacuo and the residue was purified with column chromatography on silica gel using petroleum ether/ethyl acetate (PE/EA= 6:1 to 2:1) as the eluent to give the designed product **6** (31.4 mg, 67%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 7.6 Hz, 2H), 7.63 – 7.60 (m, 1H), 7.51 – 7.48 (m, 2H), 5.55 (s, 1H), 4.67 (d, *J* = 4.3 Hz, 2H), 1.48 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 194.46, 155.77, 134.54, 133.96, 128.89, 127.84, 79.86, 47.53, 28.38. **HRMS** (ESI) m/z: calculated for $[C_{13}H_{17}NO_3 + Na]^+$ 258.1101, found 258.1093. **IR** (film): *ν* (cm^{-1}) = 2977, 2918, 1689, 1503, 1449, 1365, 1223, 1170, 1056, 868, 756, 689.

***Tert*-butyl (3-oxo-2-phenylpropyl)carbamate (7):**

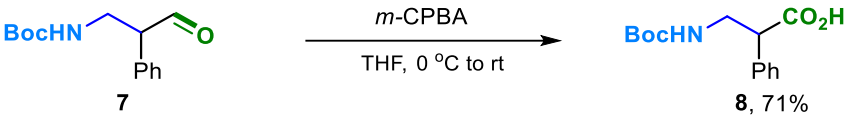


5 **7**, 88%

The following procedure was adapted from a previously-published method.[8] Dess-Martin periodinane (DMP, 0.3 mmol, 128 mg) was added portionwisely over 5 minutes to a solution of **5** (0.2 mmol, 51 mg) in dry CH_2Cl_2 (1.2 mL) at 0 °C. After stirring at ambient temperature for 3 hours, $NaHCO_3$ (0.5 mL, saturated solution) and $Na_2S_2O_3$ (0.5 mL, saturated solution) were introduced to the reaction mixture. Further stirring for 10 minutes, the mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were concentrated in vacuo and the residue was purified with column chromatography on silica gel using petroleum ether/ethyl acetate (PE/EA= 6:1) as the eluent to give the designed product **7** (43.7 mg, 88%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.73 (s, 1H), 7.40 – 7.32 (m, 3H), 7.18 (d, *J* = 7.3 Hz, 2H), 4.92 (s, 1H), 3.92 – 3.89 (m, 1H), 3.69 – 3.64 (m, 1H), 3.51 – 3.46 (m, 1H), 1.41 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 200.15, 155.78, 133.63, 129.31, 129.06, 128.13, 79.52, 59.14, 40.93, 28.36. **HRMS** (ESI) m/z: calculated for $[C_{14}H_{19}NO_3 + Na]^+$ 272.1257, found 272.1250. **IR** (film): *ν* (cm^{-1}) = 2976, 2931, 1715, 1505, 1454, 1366, 1252, 1169, 855, 756, 700.

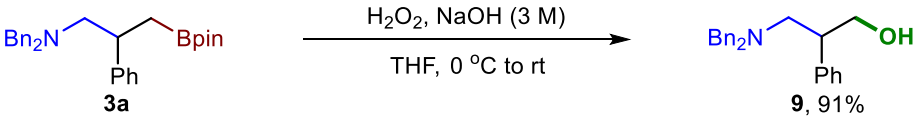
3-((Tert-butoxycarbonyl)amino)-2-phenylpropanoic acid (8):



The following procedure was adapted from a previously-published method.[9] 3-Chloroperbenzoic acid (*m*-CPBA) (1.0 mmol, 85%, 203 mg) was added portionwisely over 5 minutes to a solution of **7** (0.2 mmol, 50 mg) in dry THF (0.5 ml) at 0 °C. After stirring at ambient temperature for 24 h, $Na_2S_2O_3$ (0.5 mL, saturated solution) was introduced to the reaction mixture. Further stirring for 10 minutes, the mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were concentrated in vacuo and the residue was purified with column chromatography on silica gel using petroleum ether/ethyl acetate (PE/EA= 6:1 to 2:1) as the eluent to give the designed product **8** (37.5 mg, 71%) as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 10.69 (s, 1H), 7.33 – 7.26 (m, 5H), 6.90 (s, 0.5H), 4.99 (s, 0.5H), 3.90 – 3.91 (m, 1H), 3.58 – 3.51 (m, 2H), 1.46 – 1.42 (m, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 177.79, 176.42, 158.01, 155.84, 135.91, 128.95, 128.10, 127.86, 81.44, 79.82, 52.45, 51.61, 44.64, 43.15, 28.36. **HRMS** (ESI) m/z: calculated for $[C_{14}H_{19}NO_4 + Na]^+$ 288.1206, found 288.1196. **IR** (film): *v* (cm^{-1}) = 2977, 2924, 1712, 1515, 1455, 1395, 1367, 1253, 1167, 1063, 699.

3-(dibenzylamino)-2-phenylpropan-1-ol (9):

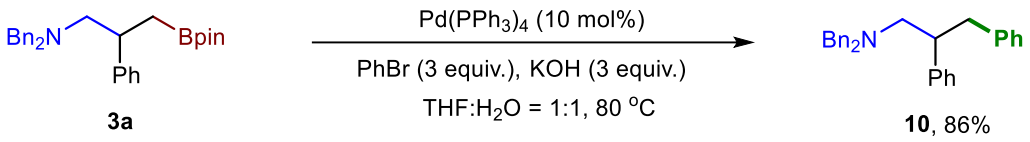


The following procedure was adapted from a previously-published method.[6] A 25 mL Schlenk tube charged with **3a** (0.2 mmol, 88.5 mg) was dissolved in THF (1.5 mL). While stirring at 0 °C, NaOH (3 M, 0.8 mL) was added dropwise followed by H_2O_2 solution (30% in water, 0.4 mL). After stirring at ambient temperature for 30 min, the mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were concentrated in vacuo and the residue was purified with column chromatography on silica gel using petroleum ether/ethyl acetate (PE/EA= 8:1) as the eluent to give the designed product **9** (60.4 mg, 91%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.37 – 7.24 (m, 12H), 7.21 – 7.18 (m, 1H), 7.04 (d, *J* = 7.3 Hz, 2H), 5.36 (s, 1H), 4.04 (d, *J* = 13.1 Hz, 2H), 3.76 – 3.73 (m, 1H), 3.71 – 3.67 (m, 1H), 3.33 – 3.28 (m, 1H), 3.25

(d, *J* = 13.1 Hz, 2H), 3.05 (t, *J* = 12.1 Hz, 1H), 2.66 – 2.62 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 140.59, 137.88, 129.34, 128.60, 128.58, 127.62, 127.49, 126.91, 69.25, 59.91, 59.11, 43.87. **IR** (film): *v* (cm^{-1}) =3027, 2925, 2827, 1601, 1494, 1452, 1372, 1129, 1028, 968, 748, 698.

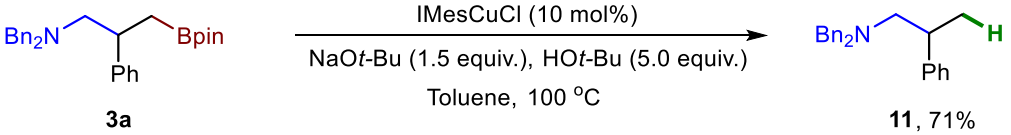
***N*,*N*-Dibenzyl-2,3-diphenylpropan-1-amine (10):**



The following procedure was adapted from a previously-published method.[10] An oven-dried 25 mL Schlenk tube were charged with **3a** (0.1 mmol, 44.5 mg), KOH (0.3 mmol, 17.0 mg) and $Pd(PPh_3)_4$ (0.01 mmol, 12.0 mg). The tube was evacuated and backfilled with argon (this process was repeated three times). THF (1.0 mL, degassed), bromobenzene (0.3mmol, 32 μL) and H_2O (1.0 mL, degassed) were added under an argon atmosphere. The reaction tube was sealed and stirred at 80 °C for 24 h. After cooling to room temperature, 1 mL H_2O was added and the reaction mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were concentrated in vacuo, and the residue was purified by chromatography on silica gel (petroleum ether / ethyl acetate = 25/1 to 15/1) to give the desired product **10** (33.6 mg, 86%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.27 – 7.07 (m, 16H), 6.95 – 6.90 (m, 4H), 3.55 (d, *J* = 13.6 Hz, 2H), 3.50 (d, *J* = 13.6 Hz, 2H), 3.13 – 3.06 (m, 2H), 2.70 – 2.60 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 143.73, 140.77, 139.63, 129.06, 128.94, 128.19, 128.14, 128.04, 128.02, 126.80, 126.13, 125.67, 59.46, 58.84, 46.40, 40.92. **HRMS** (ESI) m/z: calculated for $[C_{29}H_{29}N + H]^+$ 392.2372, found 392.2354. **IR** (film): *v* (cm^{-1}) =3026, 2928, 2795, 1601, 1494, 1452, 1373, 1257, 1125, 1072, 1028, 971, 840, 740, 696.

***N*,*N*-Dibenzyl-2-phenylpropan-1-amine (11):**

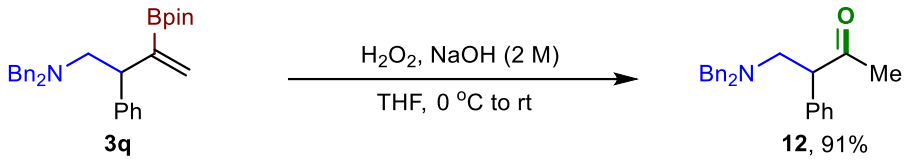


The following procedure was adapted from a previously-published method.[11] To an oven-dried 25 mL Schlenk tube were charged with **3a** (0.1 mmol, 45 mg), IMesCuCl (0.01 mmol, 5.0 mg) and $NaOBu^t$ (0.15 mmol, 15.0 mg). The tube was evacuated and backfilled with argon (this process was repeated three times).

Toluene (1.0 mL, degassed) and HOBu^t (0.5 mmol, 48 uL) were added under an argon atmosphere. The reaction tube was sealed and stirred at 100 °C for 48 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo, and the residue was purified by chromatography on silica gel (petroleum ether / ethyl acetate == 50:1) to give the desired product **11** (22.4 mg, 71%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.29 – 7.17 (m, 13H), 7.08 – 7.04 (m, 2H), 3.56 (d, *J* = 13.7 Hz, 2H), 3.52 (d, *J* = 13.7 Hz, 2H), 3.04 – 2.96 (m, 1H), 2.57 (dd, *J* = 12.6, 7.3 Hz, 1H), 2.49 (dd, *J* = 12.7, 7.8 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 146.02, 139.76, 128.83, 128.15, 128.08, 127.45, 126.72, 126.00, 61.52, 58.71, 38.09, 19.89. **HRMS** (ESI) m/z: calculated for $[C_{23}H_{25}N + H]^+$ 316.2060, found 316.2052. **IR** (film): *v* (cm^{-1}) = 3026, 2959, 2926, 2793, 1602, 1494, 1452, 1371, 1126, 1027, 974, 743, 697.

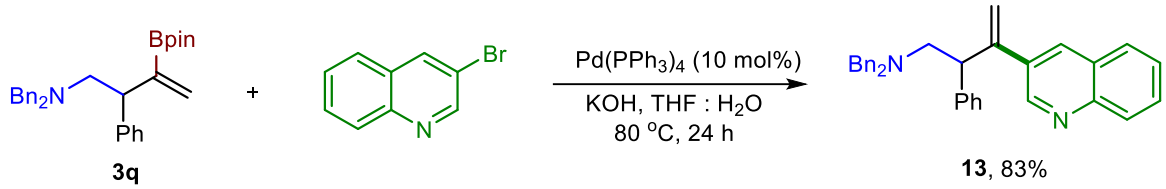
4-(Dibenzylamino)-3-phenylbutan-2-one (12):



The following procedure was adapted from a previously-published method.[12] To a solution of **3q** (0.2 mmol, 91 mg) in THF (1.0 mL) at 0 °C, were added H_2O_2 (30% in water, 0.2 mL) and NaOH (0.5 mL of a 2 M aqueous solution). The reaction mixture was stirred at ambient temperature for 30 minutes and then extracted with Et_2O (3 x 5 mL). The organic layers were combined, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 25 / 1) to afford the desired product **12** (62.8 mg, 91%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.29 – 7.18 (m, 13H), 7.07 – 7.05 (m, 2H), 3.85 (t, *J* = 7.5 Hz, 1H), 3.59 (d, *J* = 13.5 Hz, 2H), 3.52 (d, *J* = 13.5 Hz, 2H), 3.22 (dd, *J* = 13.1, 8.2 Hz, 1H), 2.79 (dd, *J* = 13.1, 6.9 Hz, 1H), 1.90 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 207.89, 139.32, 137.38, 128.99, 128.73, 128.41, 128.18, 127.30, 126.96, 59.04, 58.24, 56.13, 28.88. **HRMS** (ESI) m/z: calculated for $[C_{24}H_{25}NO + H]^+$ 344.2009, found 344.1996. **IR** (film): *v* (cm^{-1}) =3027, 2924, 2799, 1710, 1600, 1494, 1452, 1353, 1354, 1127, 1072, 1028, 971, 746, 698.

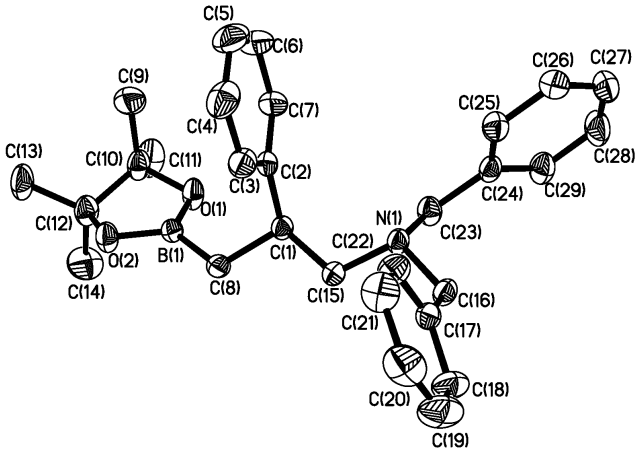
***N*,*N*-dibenzyl-2-phenyl-3-(quinolin-3-yl)but-3-en-1-amine (13):**



The following procedure was adapted from a previously-published method.[10] An oven-dried 25 mL Schlenk tube were charged with **3q** (0.2 mmol, 91 mg), KOH (0.6 mmol, 35.0 mg) and $Pd(PPh_3)_4$ (0.02 mmol, 24.0 mg). The tube was evacuated and backfilled with argon (this process was repeated three times). THF (2.0 mL, degassed), 3-bromoquinoline (0.6mmol, 82 μL) and H_2O (2.0 mL, degassed) were added under an argon atmosphere. The reaction tube was sealed and stirred at 80 °C for 24 h. After cooling to room temperature, 2 mL H_2O was added and the reaction mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were concentrated in vacuo, and the residue was purified by chromatography on silica gel (petroleum ether / ethyl acetate = 8 / 1) to give the desired product **13** (75.2mg, 83%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.80 (d, *J* = 2.2 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 1.7 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.49 – 7.46 (m, 1H), 7.27 – 7.11 (m, 15H), 5.53 (s, 1H), 5.20 (s, 1H), 4.13 (t, *J* = 7.4 Hz, 1H), 3.64 (d, *J* = 13.6 Hz, 2H), 3.55 (d, *J* = 13.6 Hz, 2H), 3.02 (dd, *J* = 12.9, 7.0 Hz, 1H), 2.92 (dd, *J* = 12.9, 8.1 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 149.87, 147.22, 146.82, 141.49, 139.40, 135.06, 132.57, 129.10, 129.04, 128.91, 128.53, 128.38, 128.16, 127.98, 127.56, 126.88, 126.64, 126.62, 116.06, 59.34, 59.04, 48.61. **HRMS** (ESI) m/z: calculated for $[C_{33}H_{30}N_2+H]^+$ 455.2481, found 455.2460. **IR** (film): *v* (cm^{-1}) =3026, 2925, 2797, 1622, 1492, 1452, 1372, 1242, 1126, 1075, 1028, 972, 907, 787, 748, 698.

5. X-Ray data of 3a



CCDC 2047479 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

6. References

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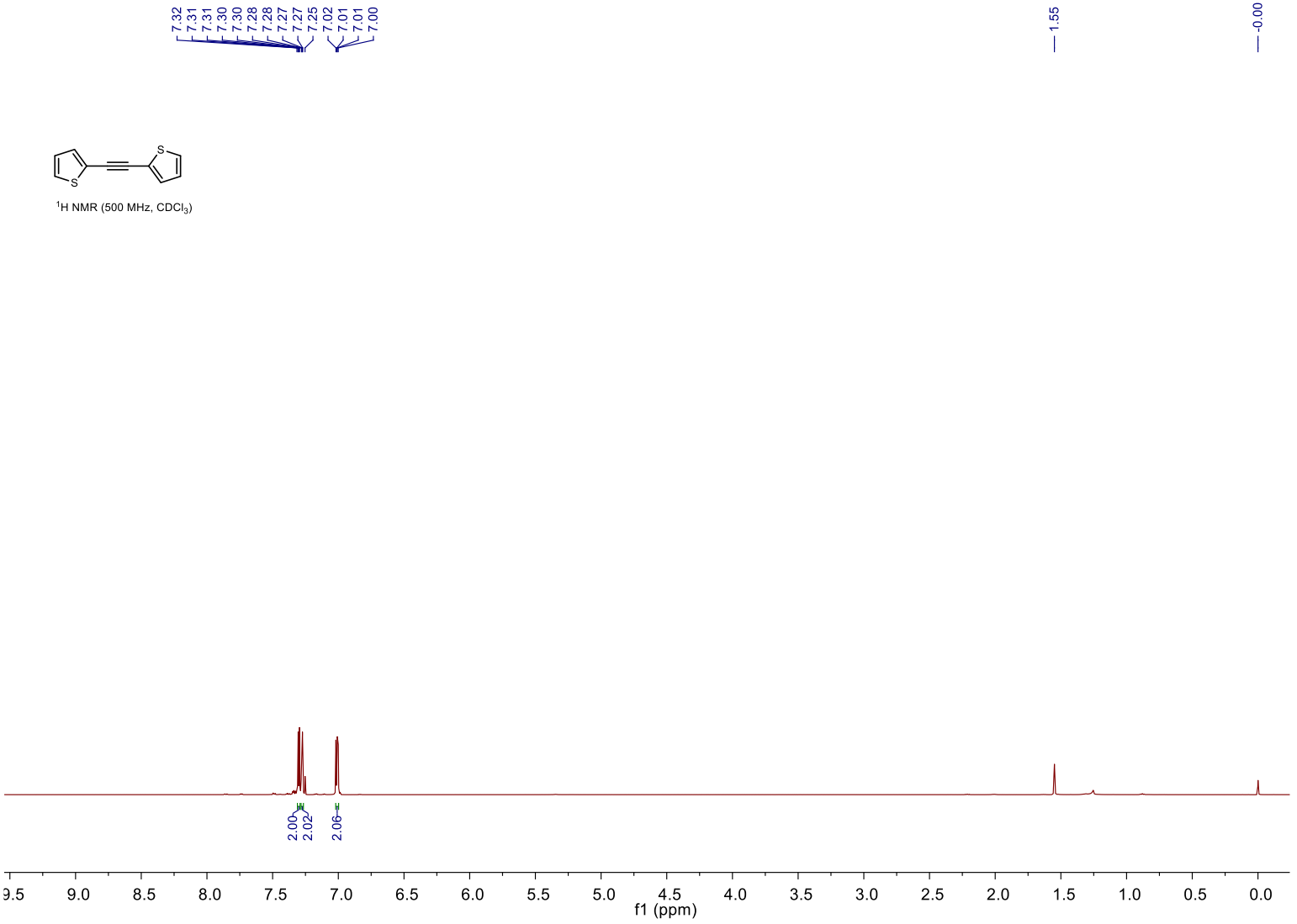
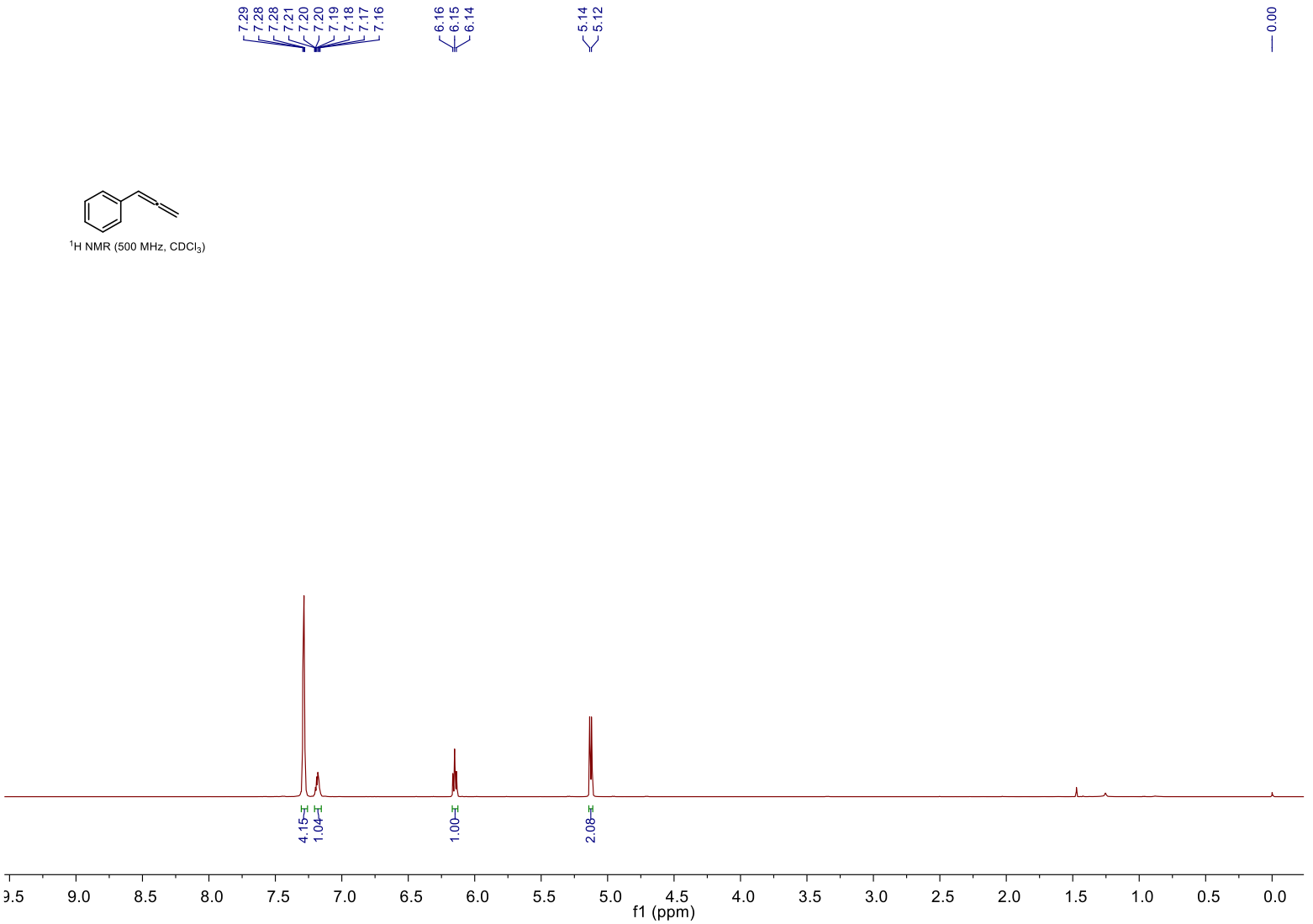
7. Spectroscopic data (NMR spectra)

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6.14
5.14
5.12
0.00
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1.00
2.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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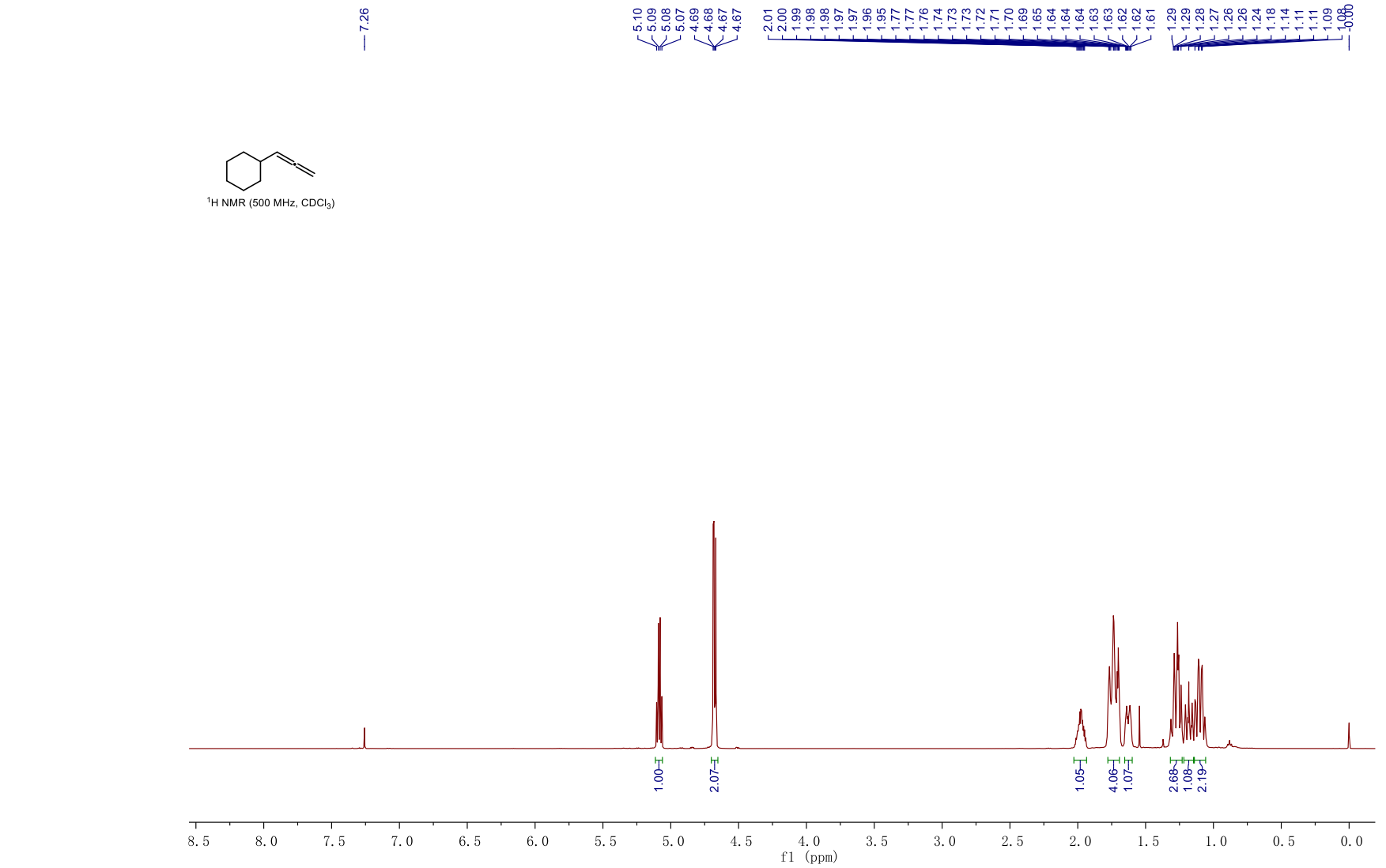
f1 (ppm)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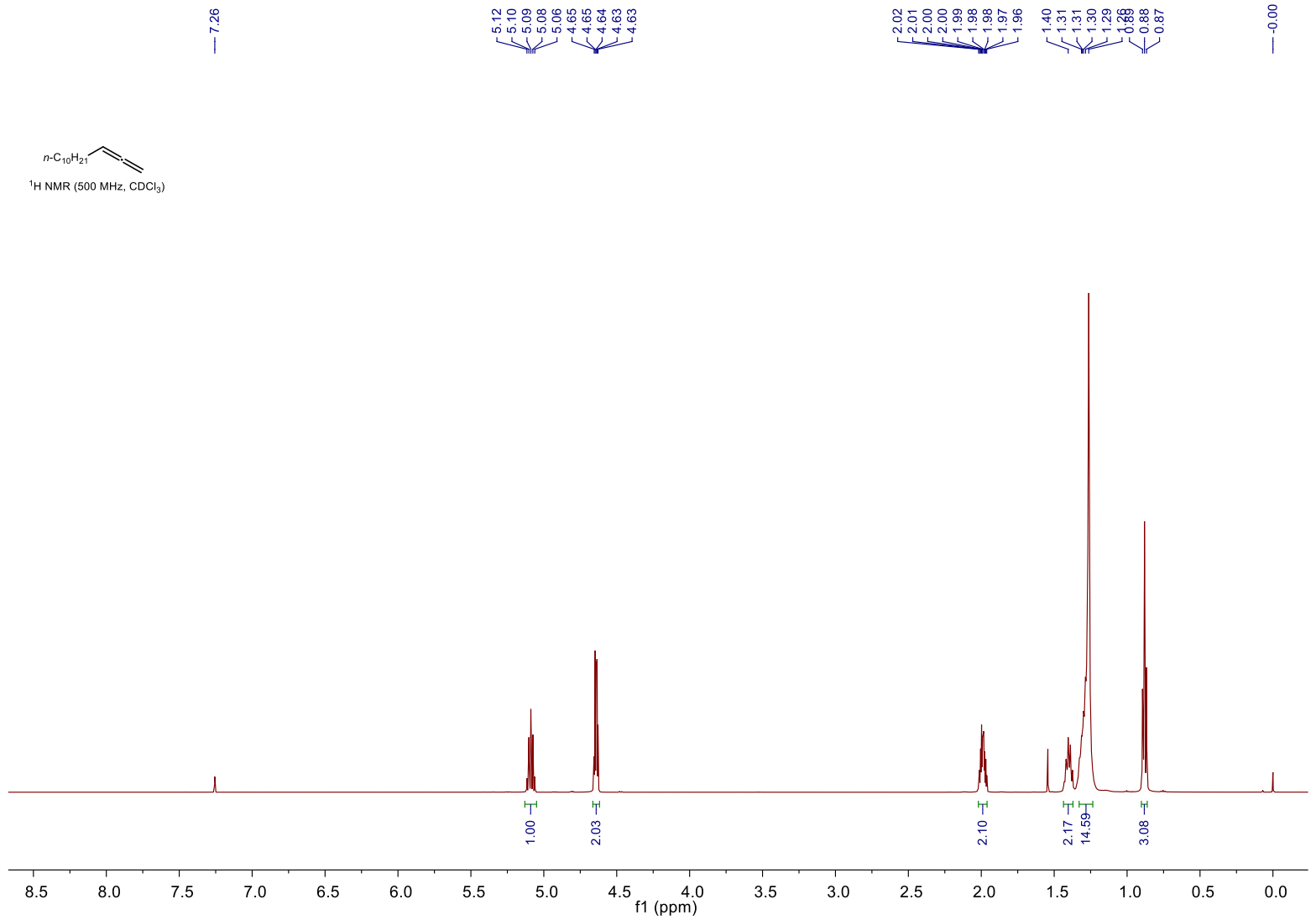
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1.98
1.97
1.96
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1.30
1.29
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0.88
0.87
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n-C10H21
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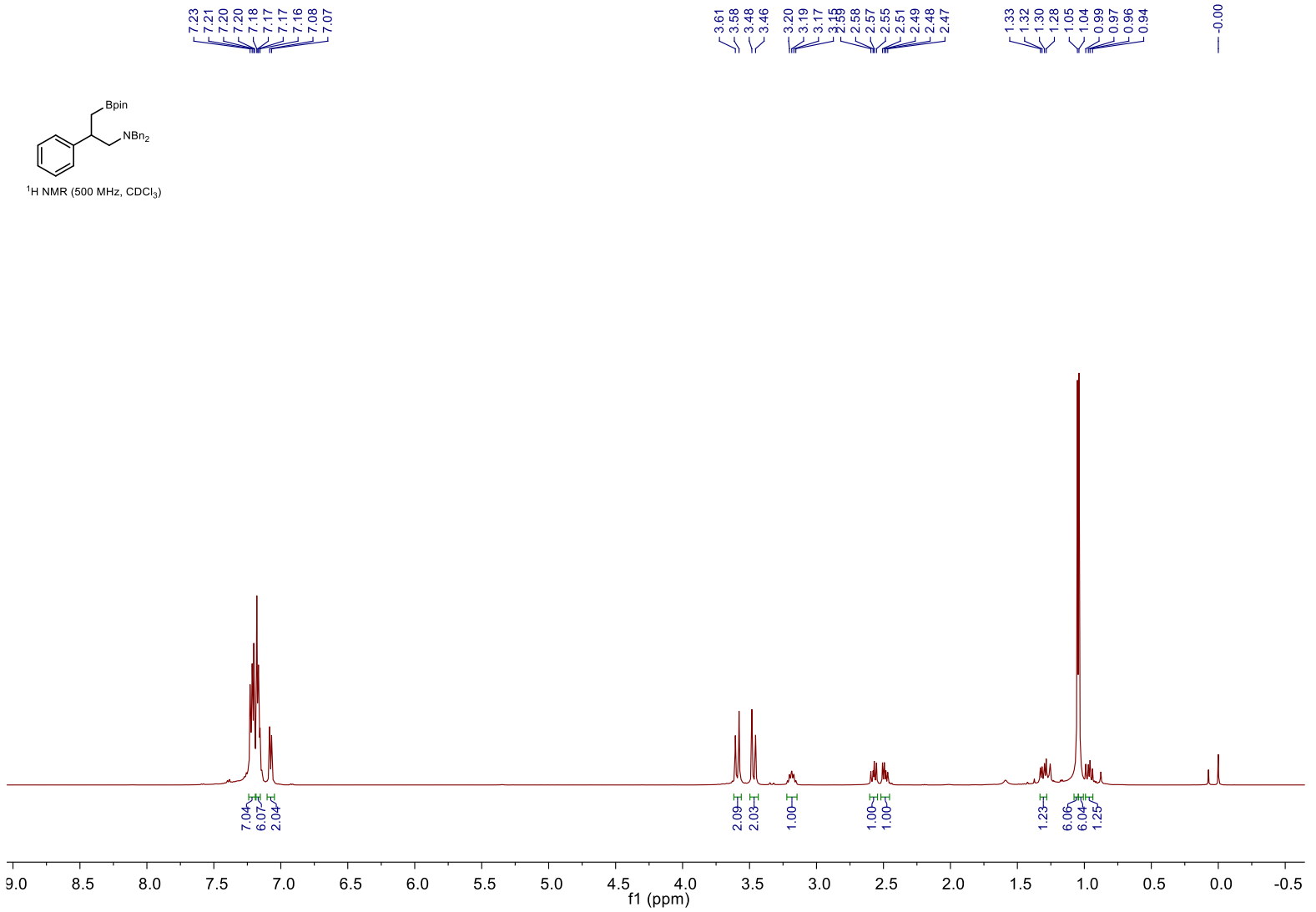
f1 (ppm)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2.03
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6.06
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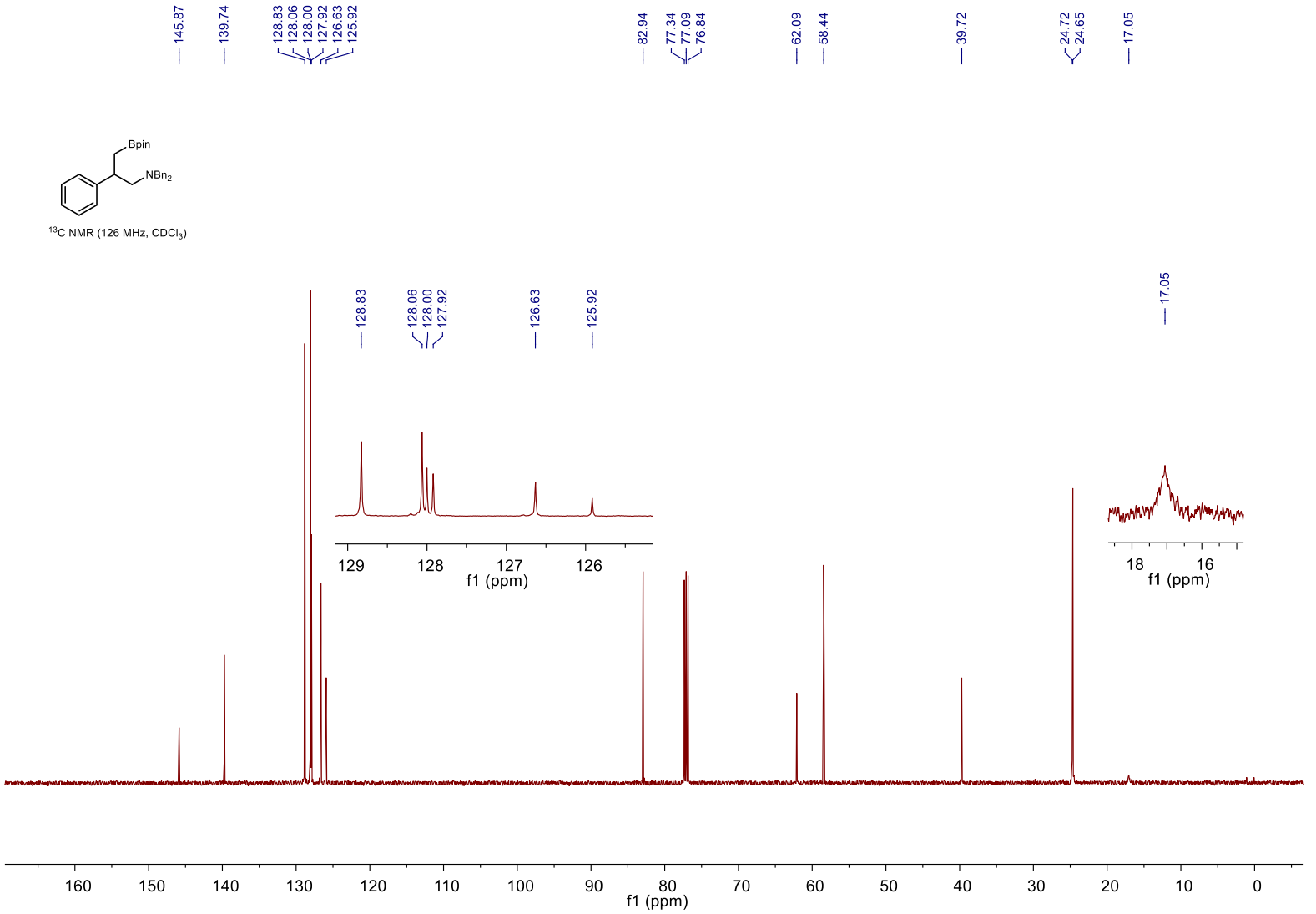
f1 (ppm)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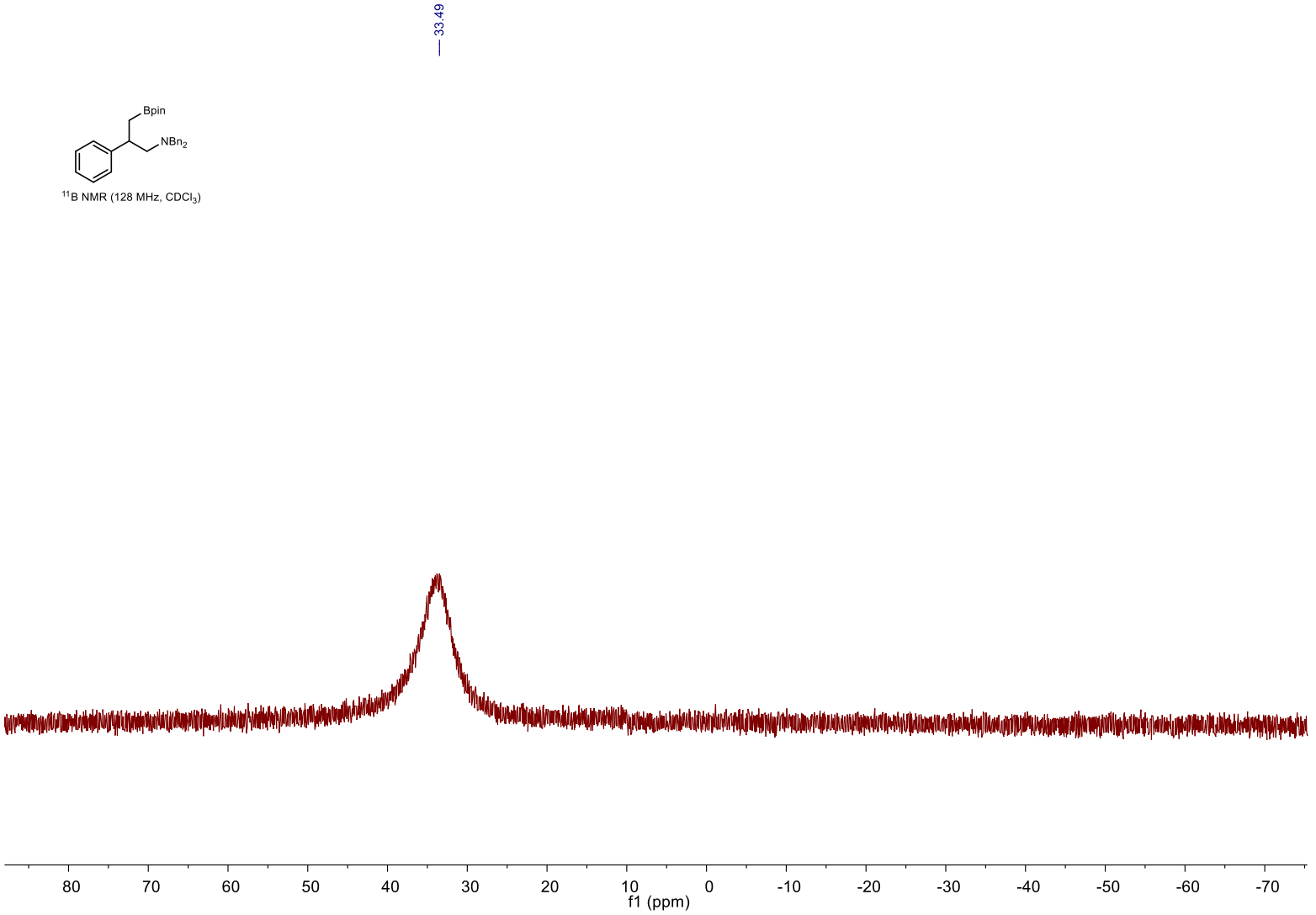
13C NMR (126 MHz, CDCl3)
f1 (ppm)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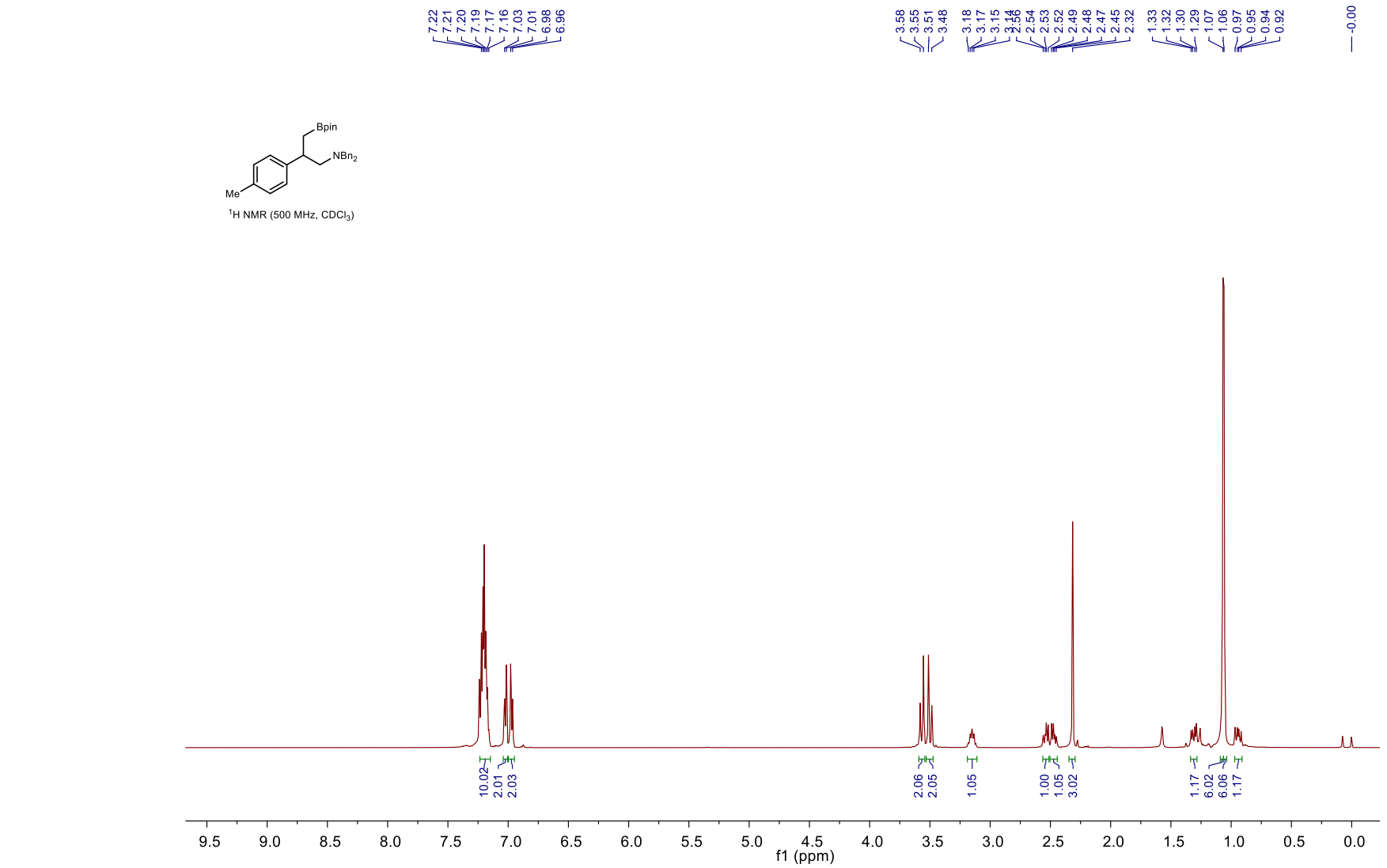
f1 (ppm)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2.49
2.48
2.47
2.45
2.32
1.33
1.32
1.30
1.29
1.07
1.06
0.97
0.95
0.94
0.92
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Bpin
NBn2
Me
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2.03
2.06
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1.05
1.00
1.05
3.02
1.17
6.02
6.06
1.17
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9.0
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8.0
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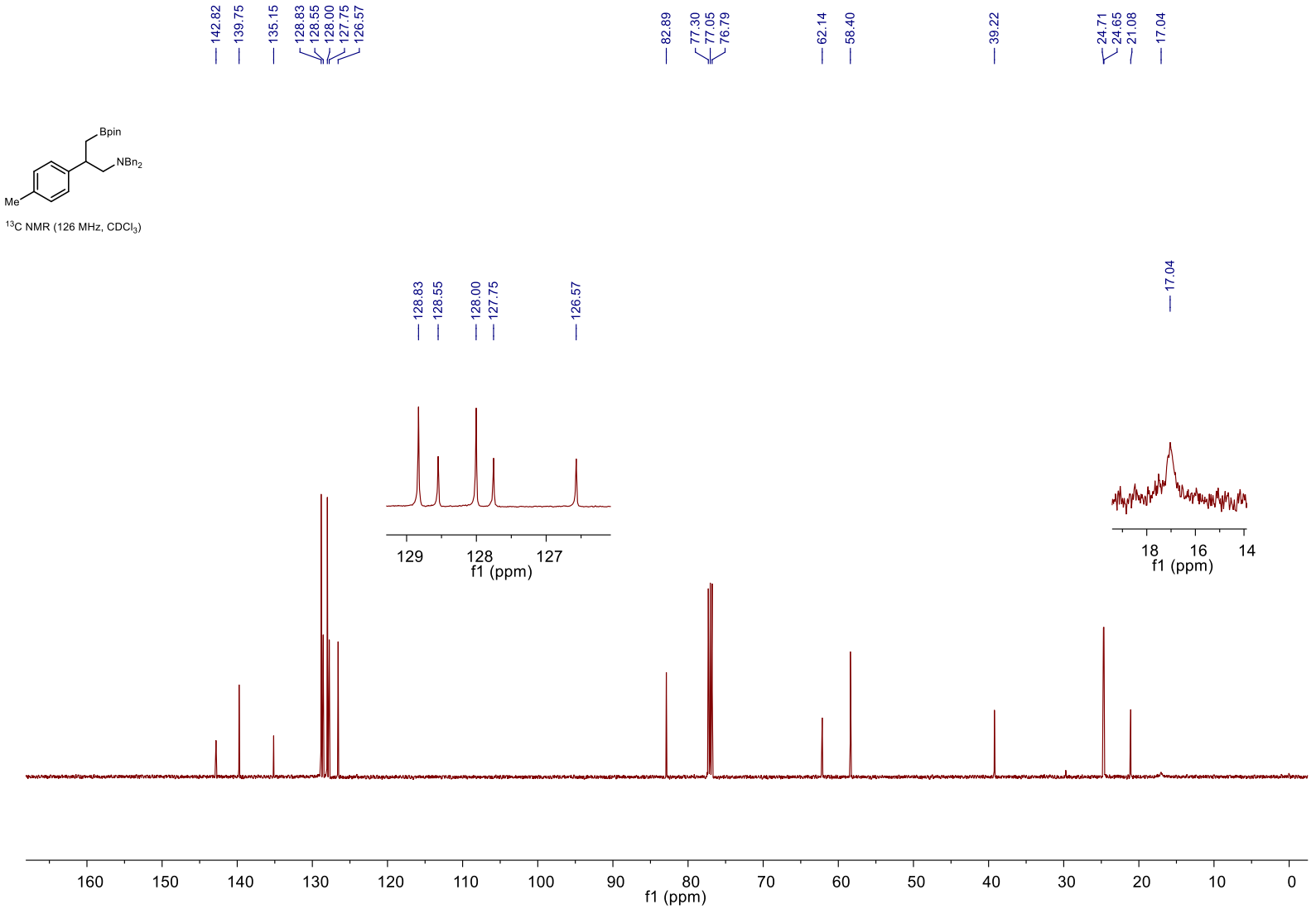
f1 (ppm)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21.08
17.04
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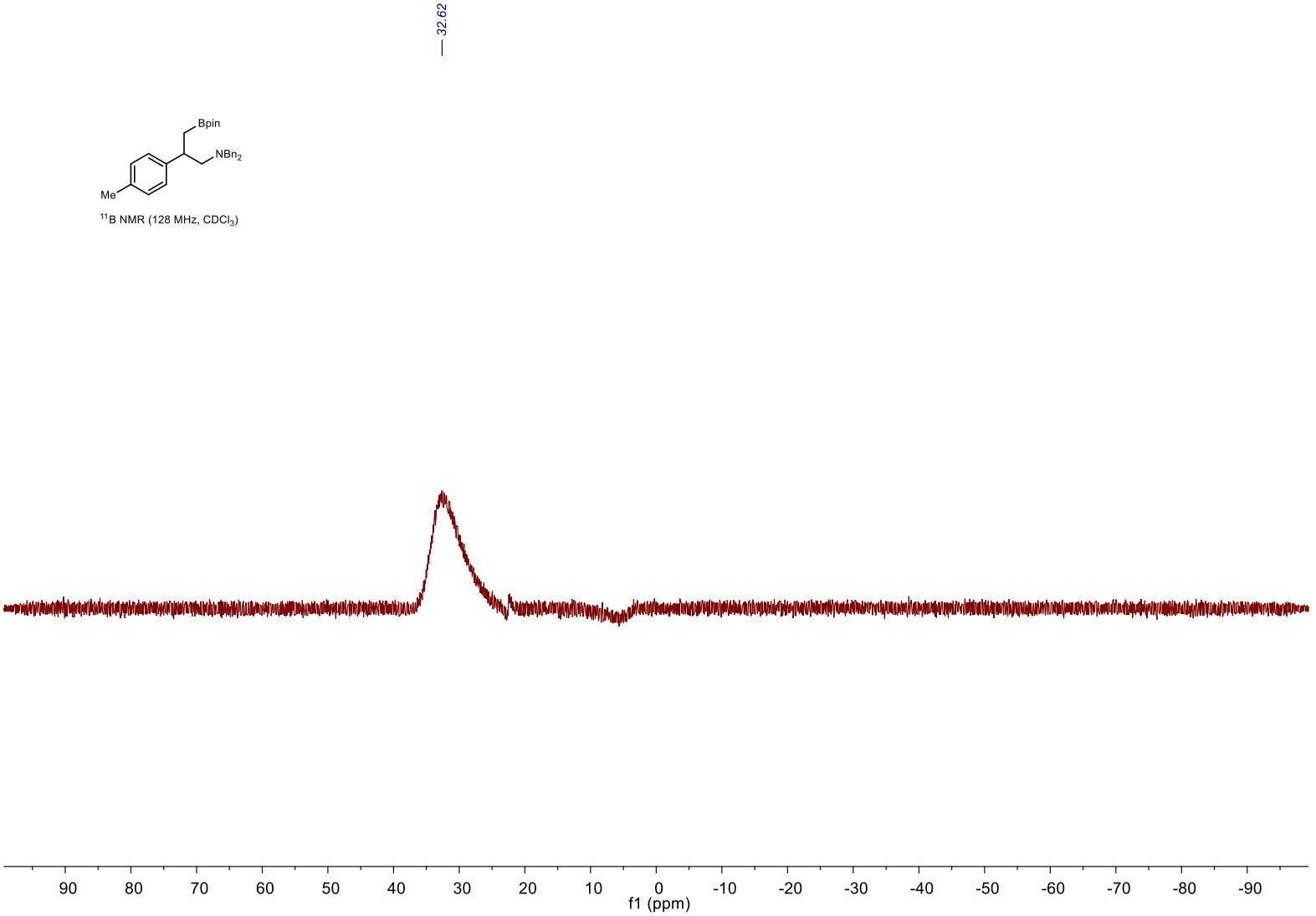
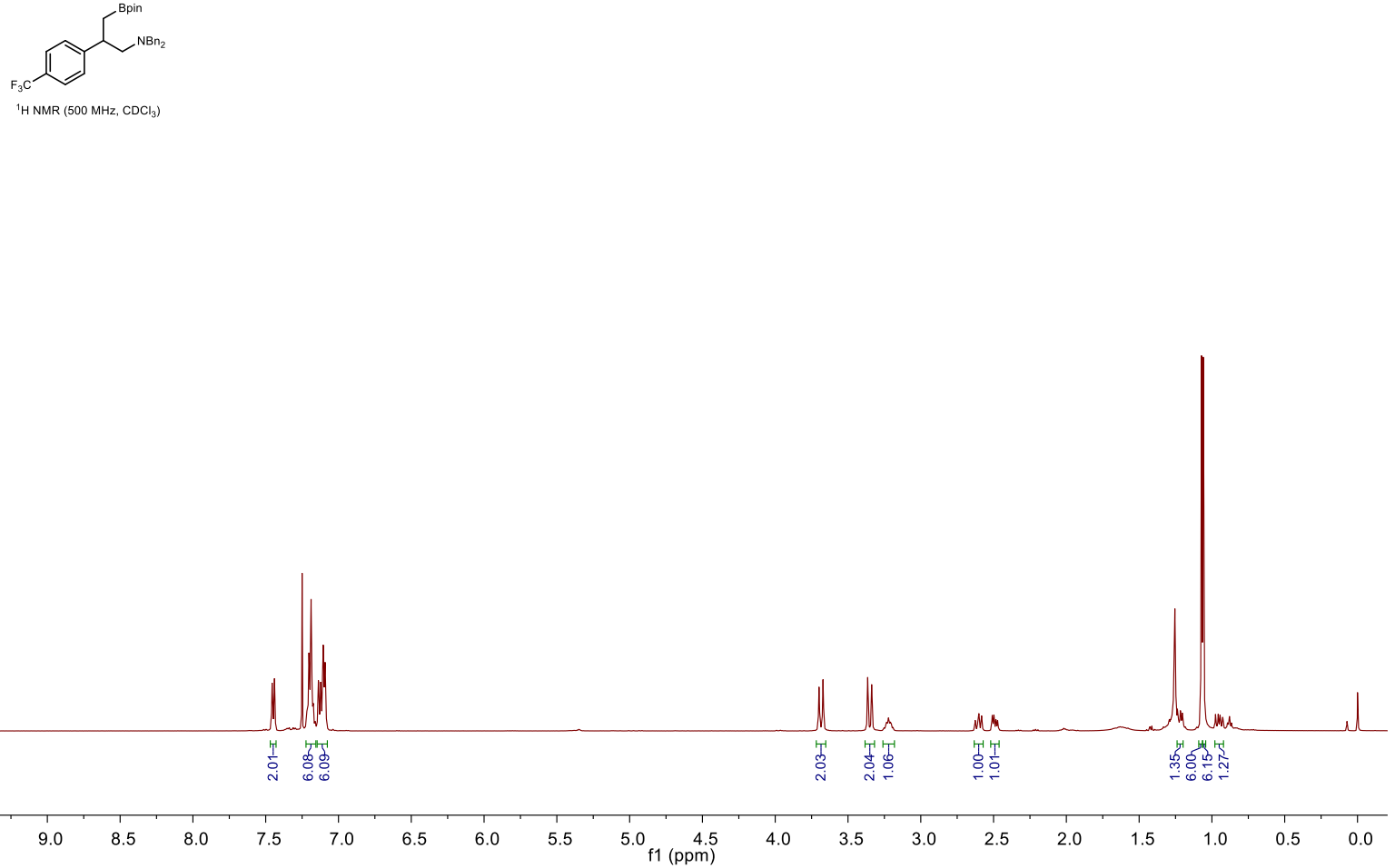
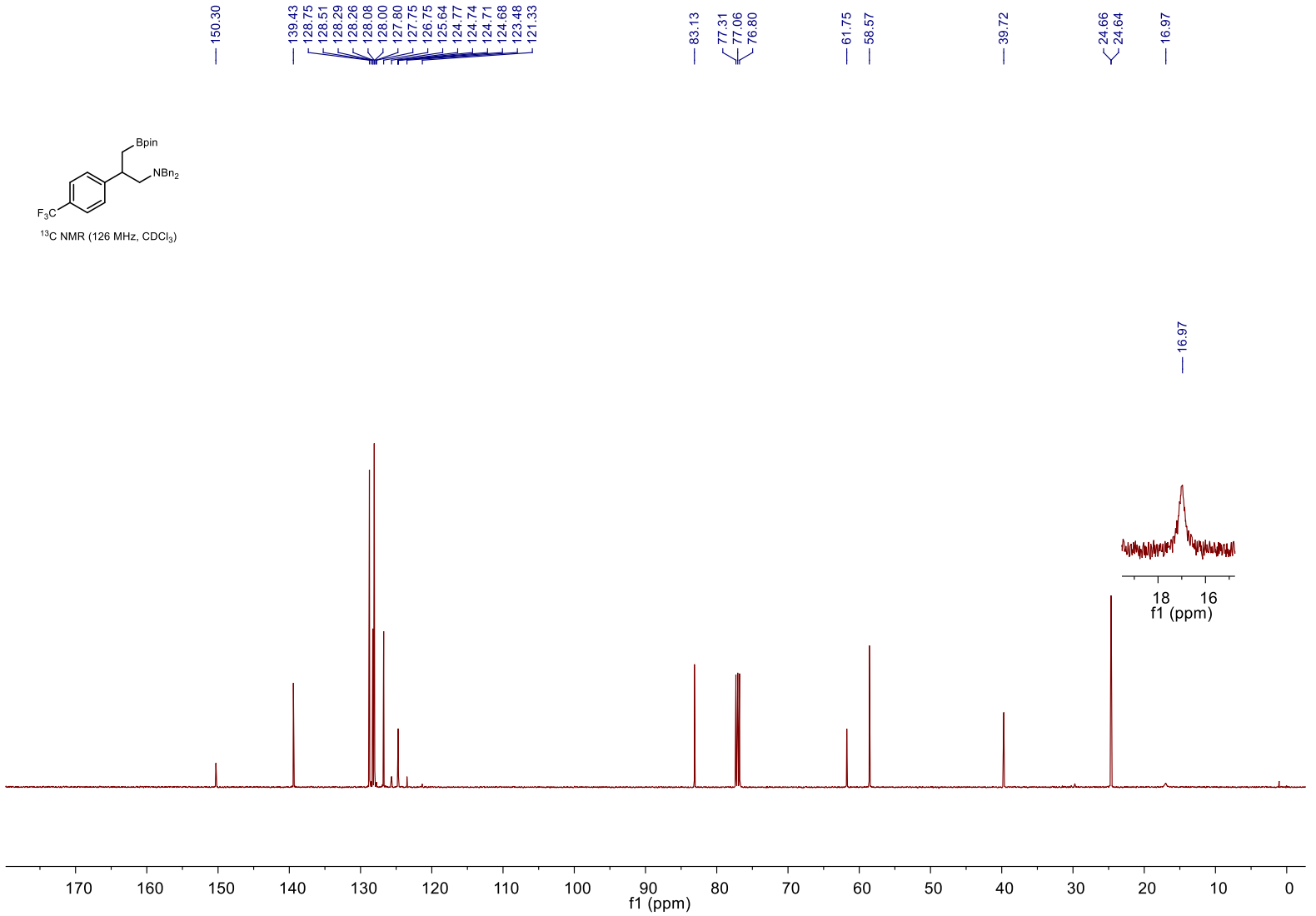
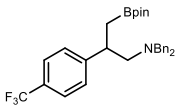
Me
13C NMR (126 MHz, CDCl3)
f1 (ppm)

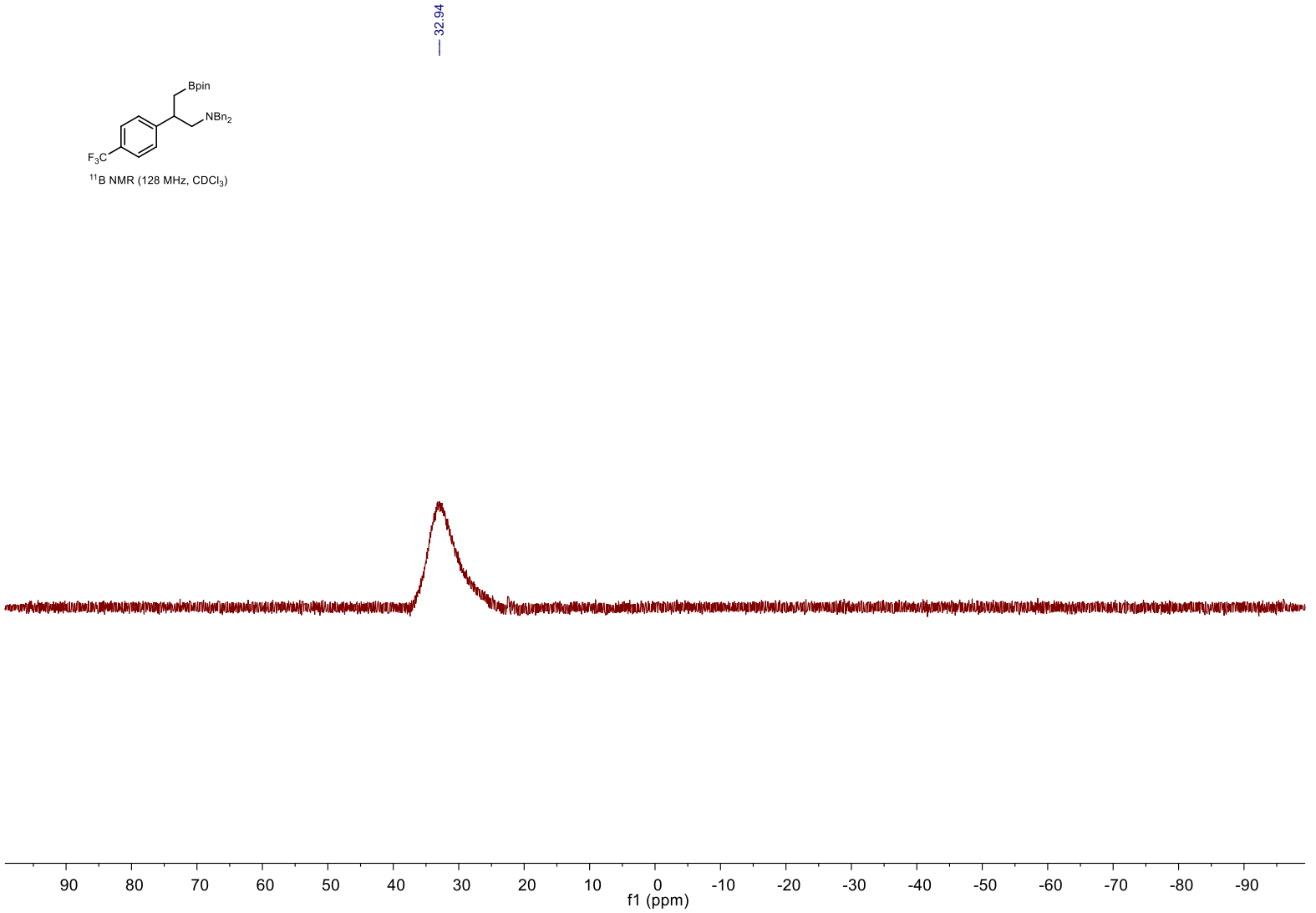

32.62
Bpin
NBn2
Me
11B NMR (128 MHz, CDCl3)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

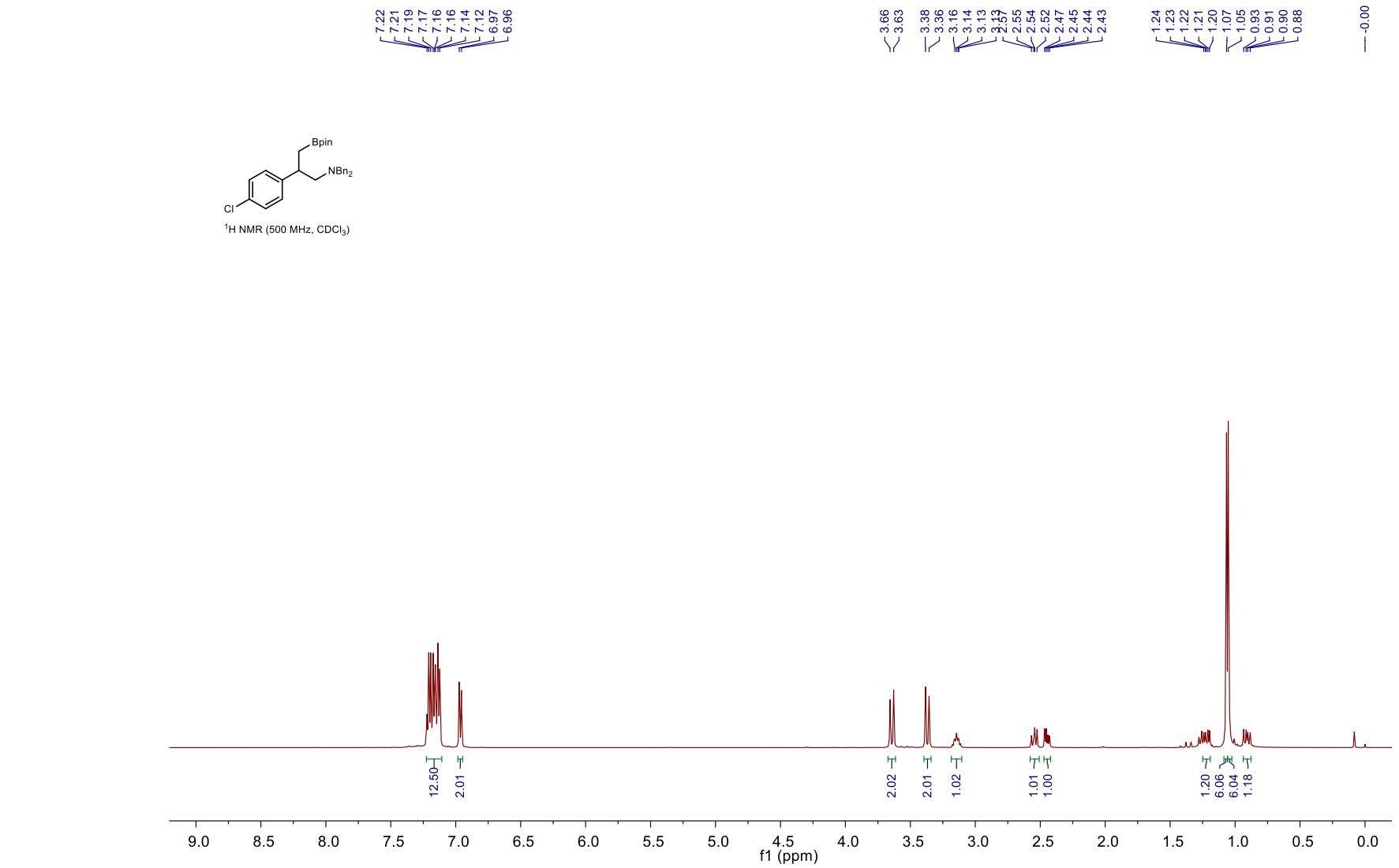

7.46
7.44
7.25
7.22
7.20
7.19
7.17
7.14
7.12
7.10
7.09
3.70
3.67
3.36
3.34
3.23
3.22
2.63
2.61
2.60
2.58
2.51
2.50
2.48
2.47
1.24
1.24
1.22
1.20
1.07
1.06
0.98
0.96
0.94
0.93
-0.00
Bpin
NBn2
F3C
1H NMR (500 MHz, CDCl3)
2.01
6.08
6.09
2.03
2.04
1.06
1.00
1.01
1.35
6.00
6.15
1.27
f1 (ppm)

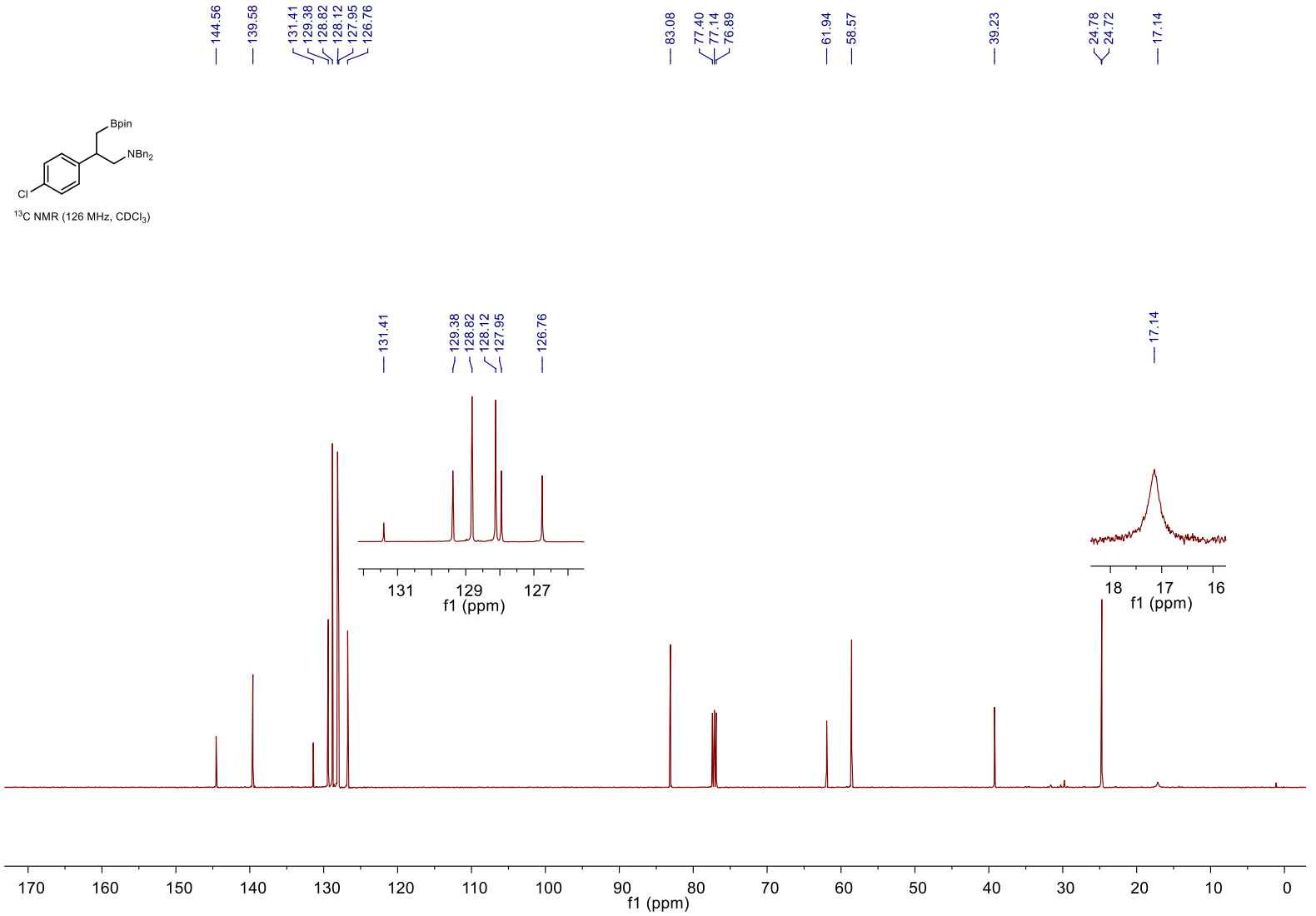

150.30
139.43
128.75
128.51
128.29
128.26
128.08
128.00
127.80
127.75
126.75
125.64
124.77
124.74
124.71
124.68
123.48
121.33
83.13
77.31
77.06
76.80
61.75
58.57
39.72
24.66
24.64
16.97
Bpin
NBn2
F3C
13C NMR (126 MHz, CDCl3)
16.97
18
16
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

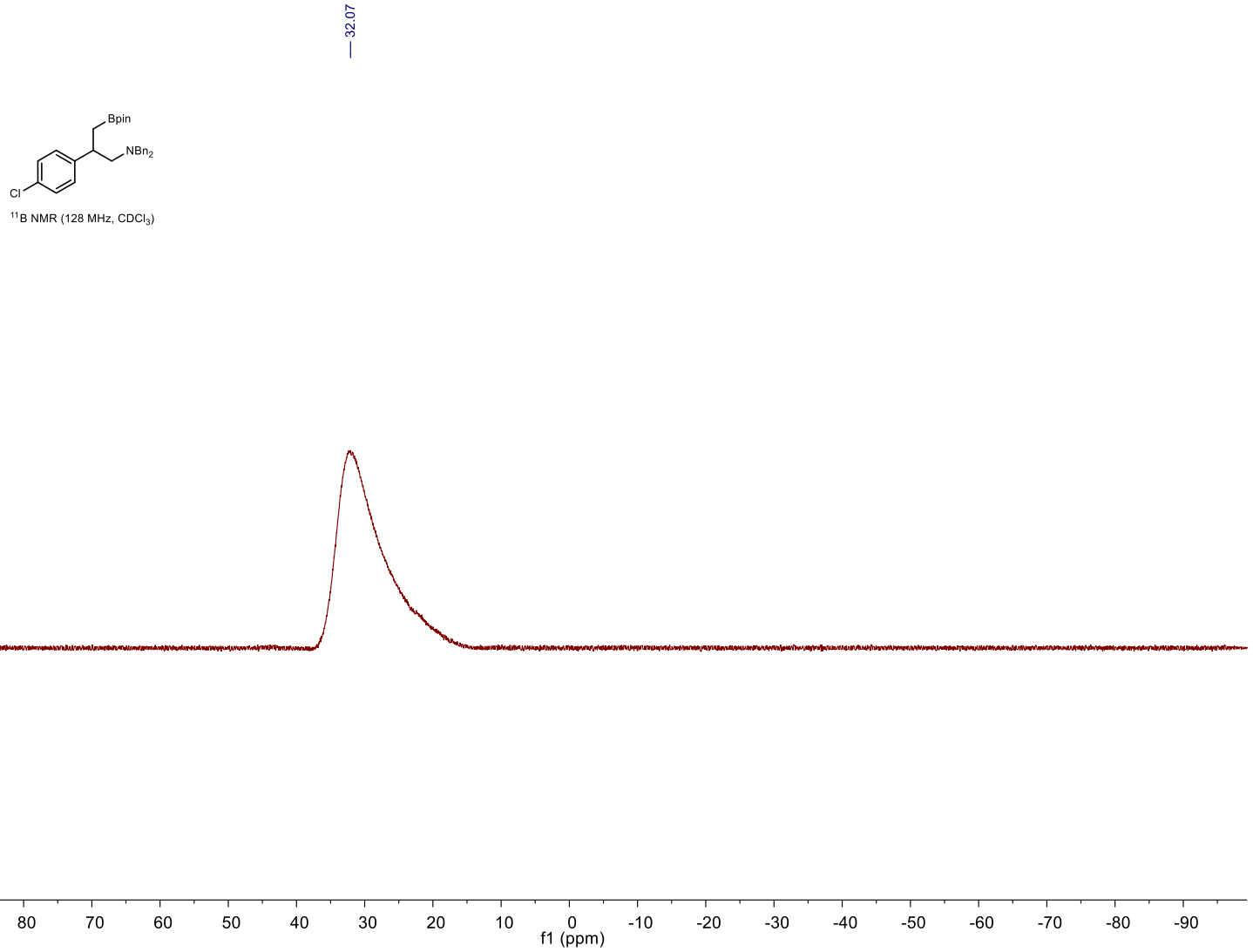


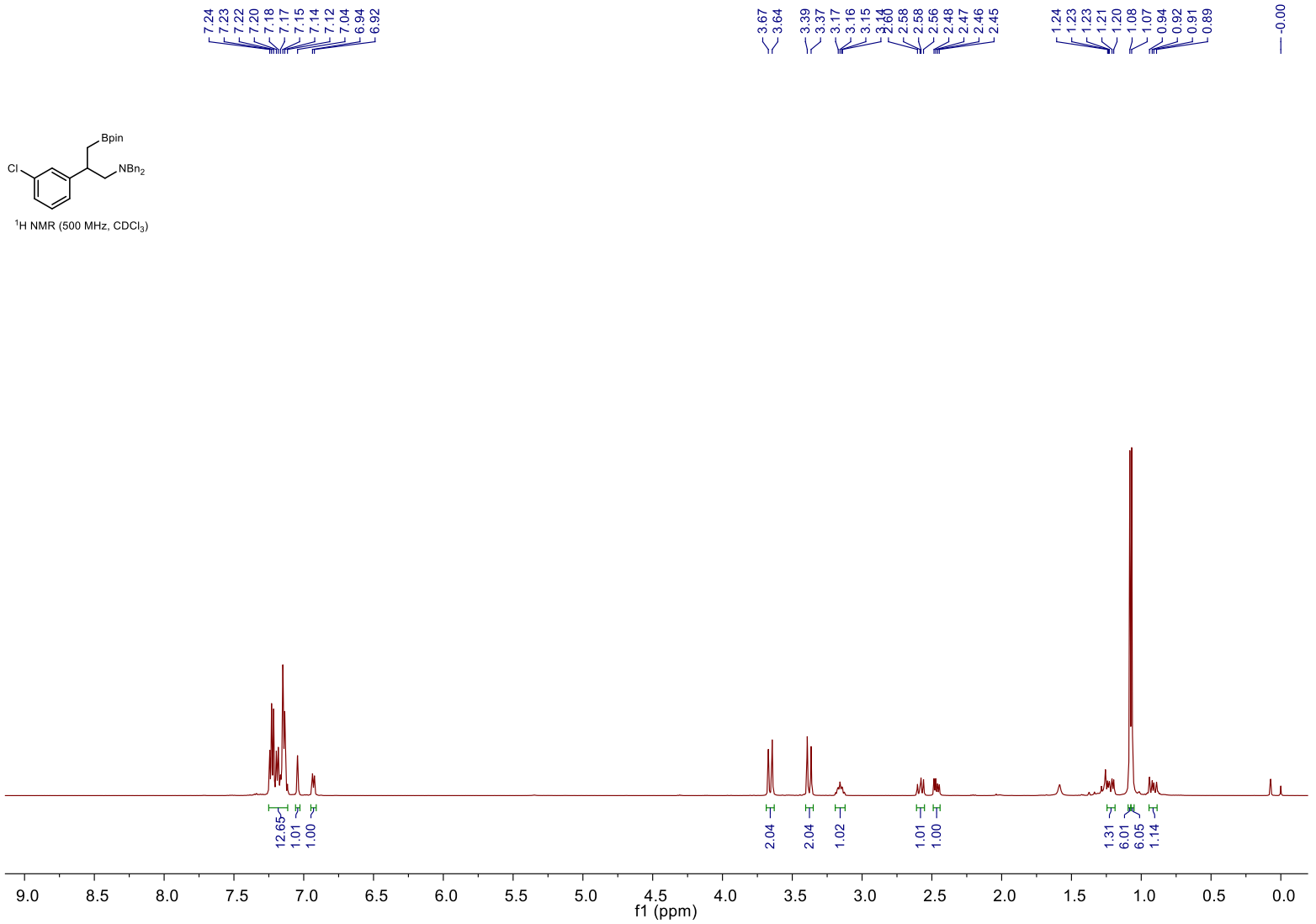
^{19}F NMR (471 MHz, $CDCl_3$)

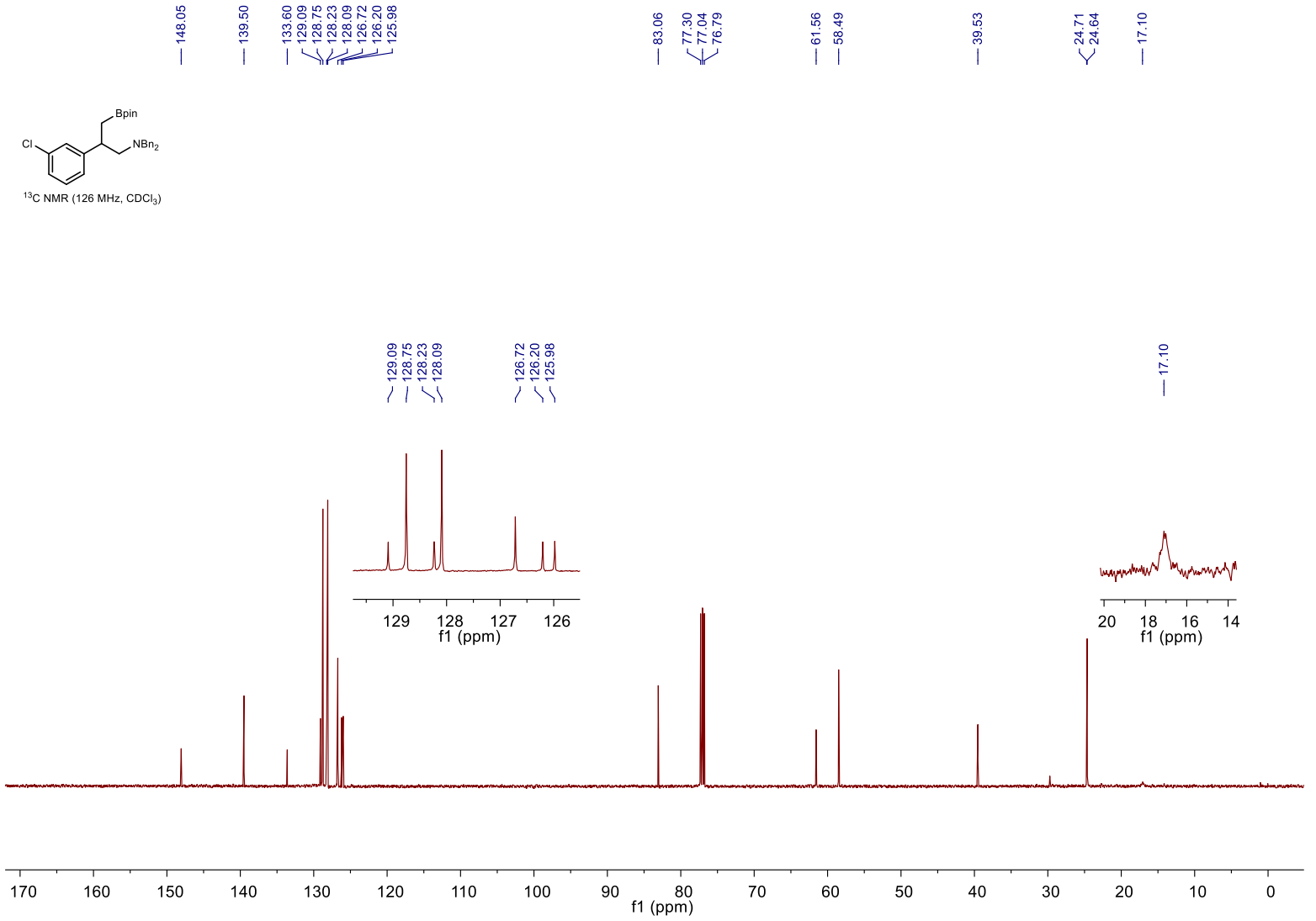

32.94
Bpin
NBn2
F3C
11B NMR (128 MHz, CDCl3)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

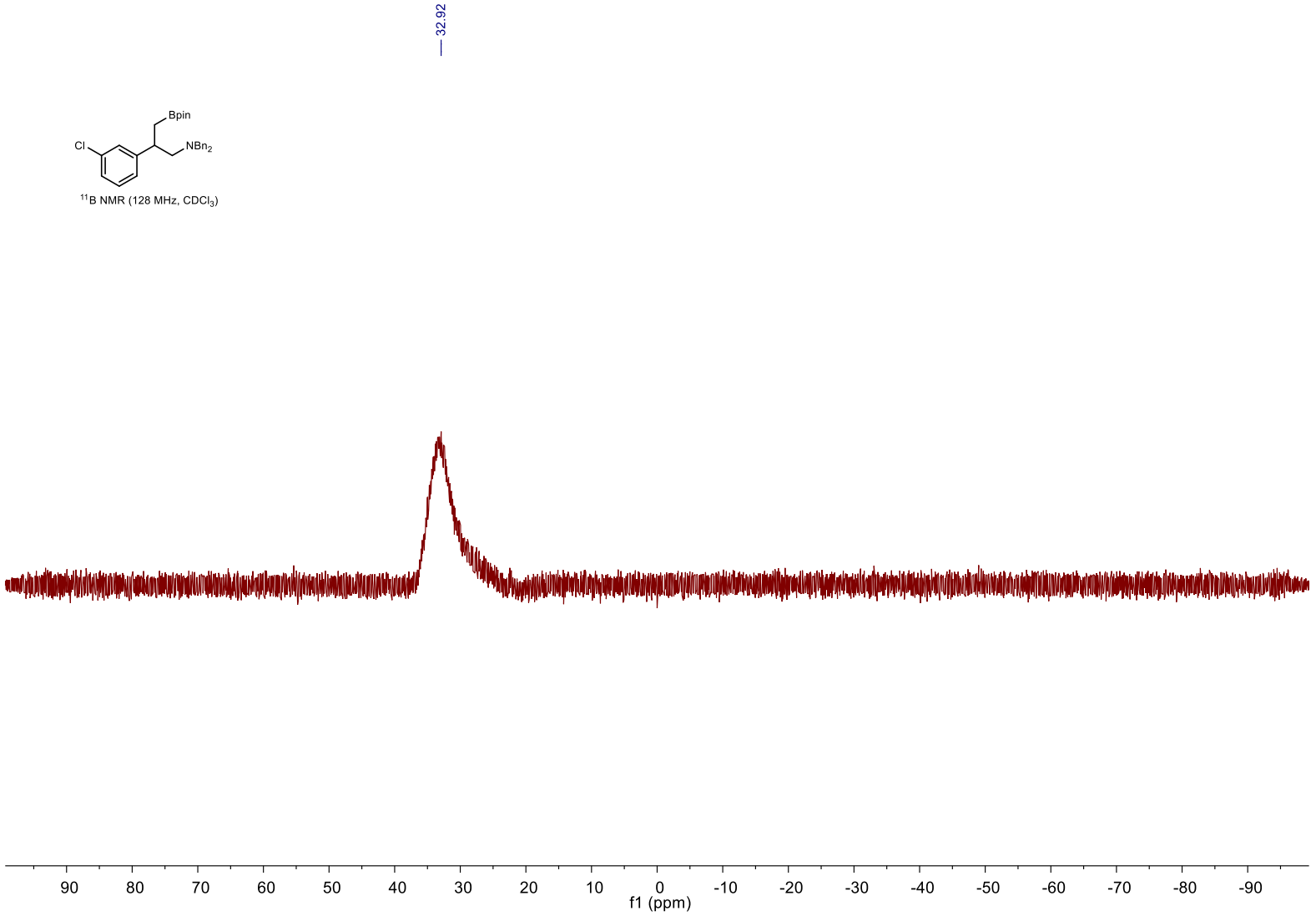

7.22
7.21
7.19
7.17
7.16
7.16
7.14
7.12
6.97
6.96
3.66
3.63
3.38
3.36
3.16
3.14
3.13
3.13
2.57
2.55
2.54
2.52
2.47
2.45
2.44
2.43
1.24
1.23
1.22
1.21
1.20
1.07
1.05
0.93
0.91
0.90
0.88
-0.00
Bpin
NBn2
Cl
1H NMR (500 MHz, CDCl3)
12.50
2.01
2.02
2.01
1.02
1.01
1.00
1.20
6.06
6.04
1.18
9.0
8.5
8.0
7.5
7.0
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
f1 (ppm)

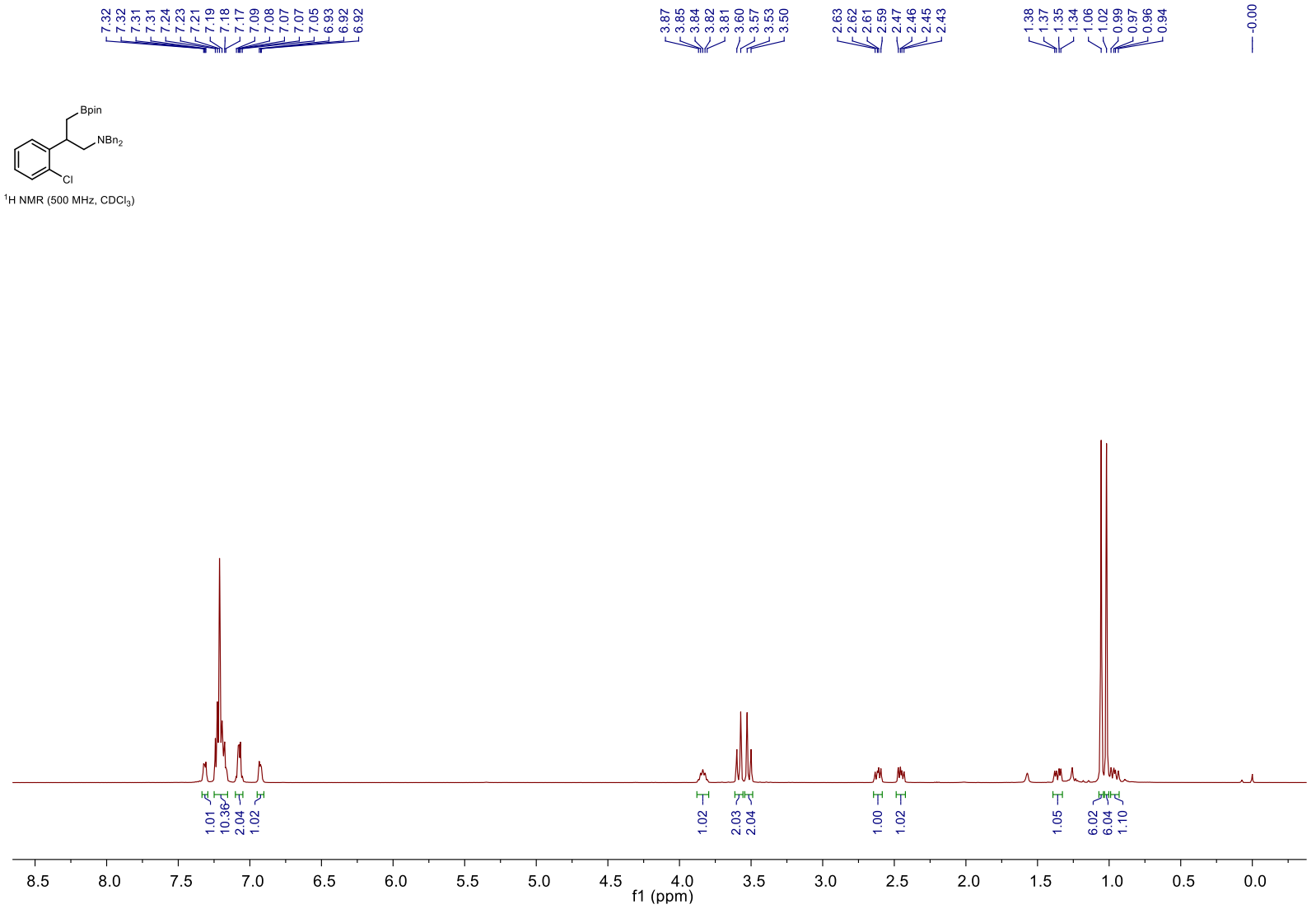

144.56
139.58
131.41
129.38
128.82
128.12
127.95
126.76
83.08
77.40
77.14
76.89
61.94
58.57
39.23
24.78
24.72
17.14
Bpin
NBn2
Cl
13C NMR (126 MHz, CDCl3)
f1 (ppm)

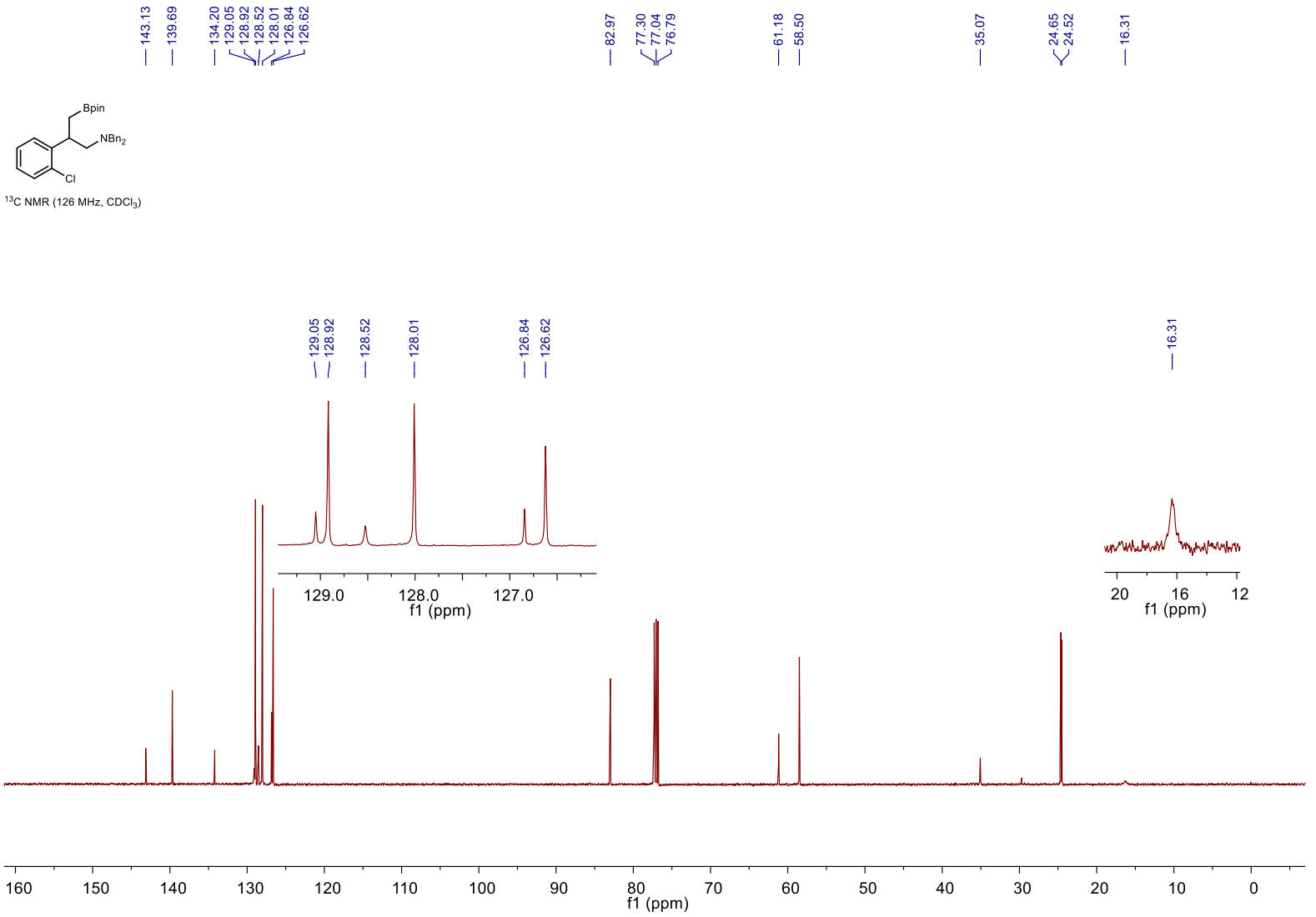

32.07
Bpin
NBn2
Cl
11B NMR (128 MHz, CDCl3)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

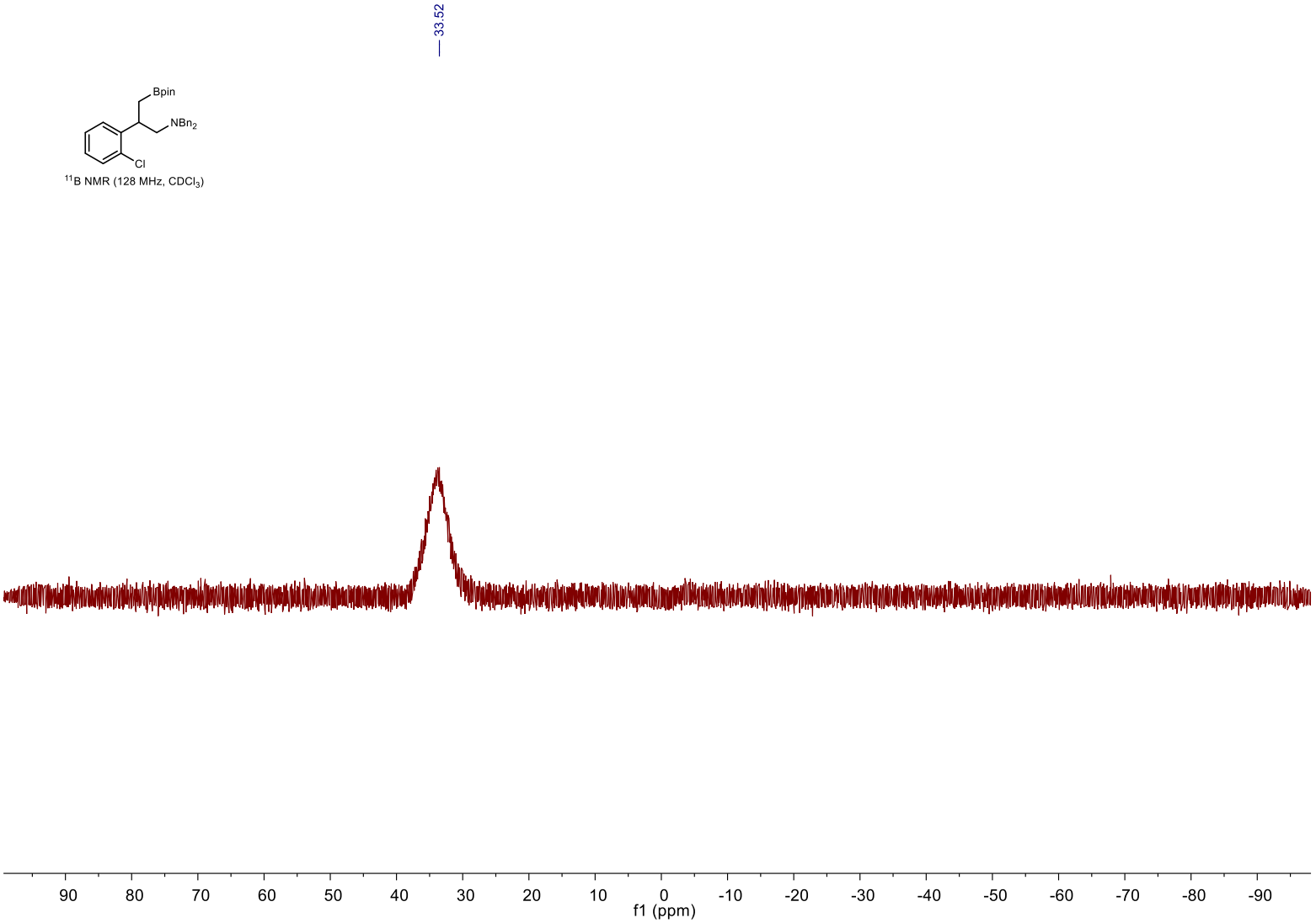

7.24
7.23
7.22
7.20
7.18
7.17
7.15
7.14
7.12
7.04
6.94
6.92
3.67
3.64
3.39
3.37
3.17
3.16
3.15
2.60
2.58
2.58
2.56
2.48
2.47
2.46
2.45
1.24
1.23
1.23
1.21
1.20
1.08
1.07
0.94
0.92
0.91
0.89
-0.00
Bpin
Cl
NBn2
1H NMR (500 MHz, CDCl3)
12.65
1.01
1.00
2.04
2.04
1.02
1.01
1.00
1.31
6.01
6.05
1.14
9.0
8.5
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
f1 (ppm)

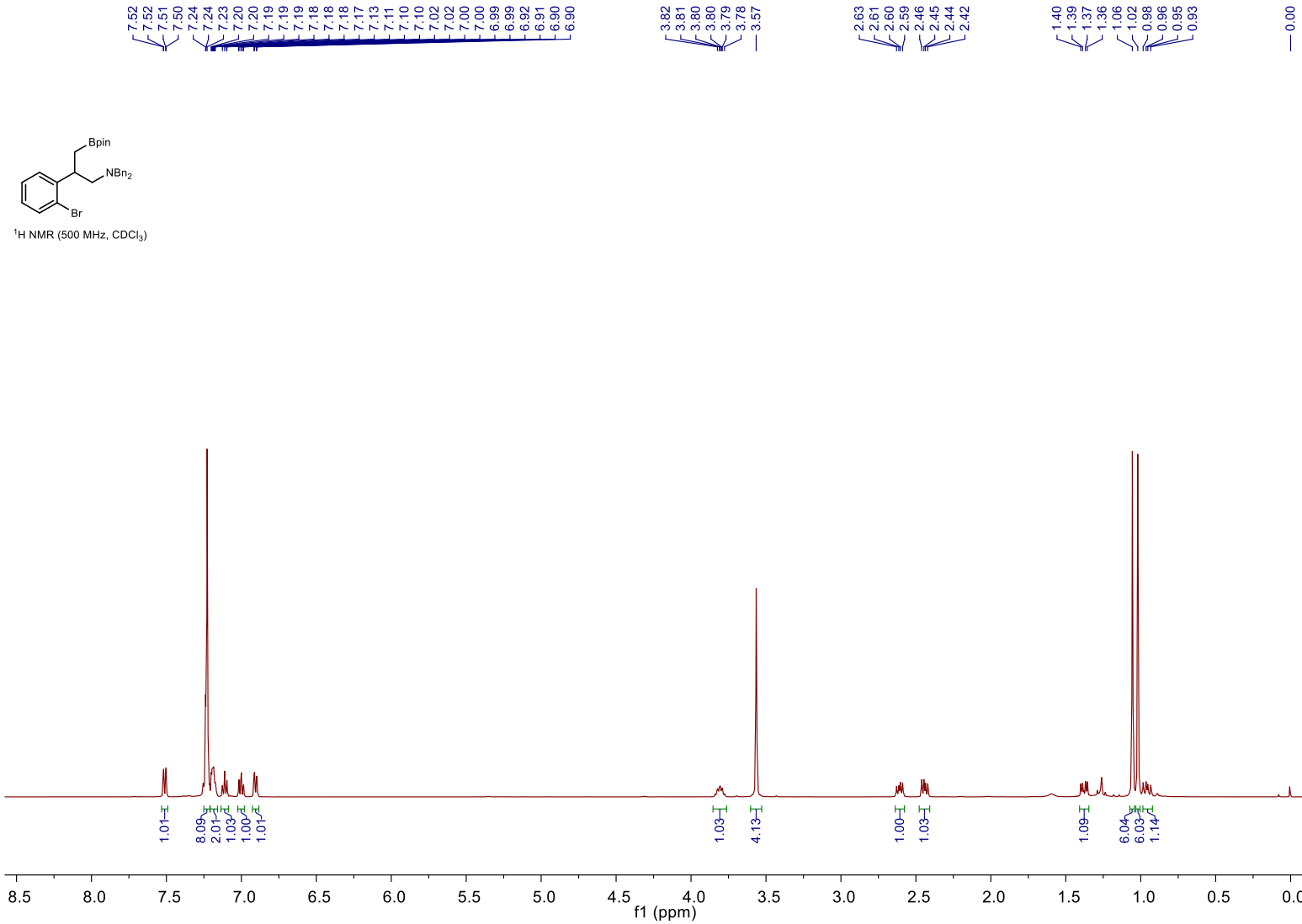

148.05
139.50
133.60
129.09
128.75
128.23
128.09
126.72
126.20
125.98
83.06
77.30
77.04
76.79
61.56
58.49
39.53
24.71
24.64
17.10
Bpin
Cl
NBn2
13C NMR (126 MHz, CDCl3)
f1 (ppm)

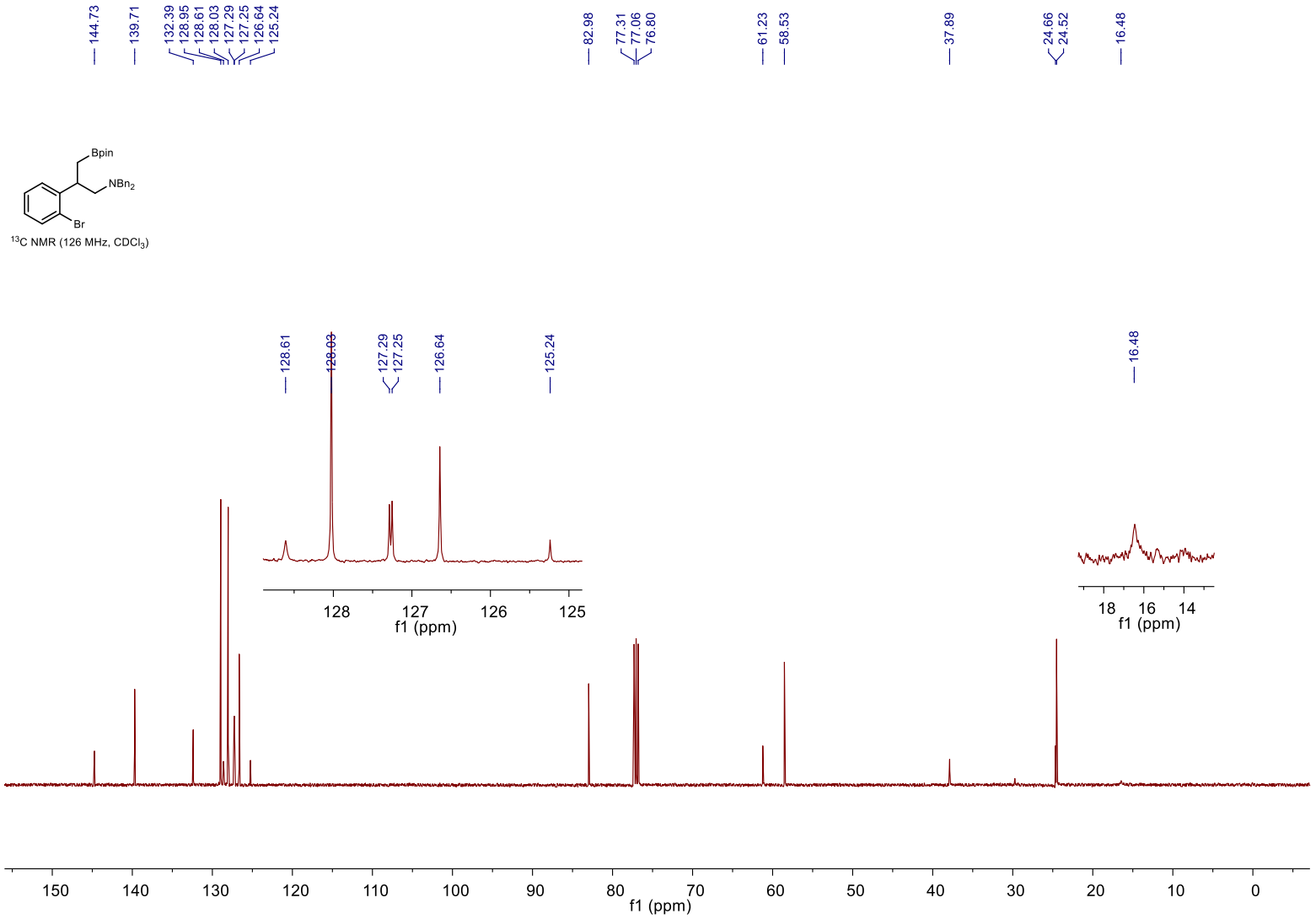

32.92
Bpin
Cl
NBn2
11B NMR (128 MHz, CDCl3)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

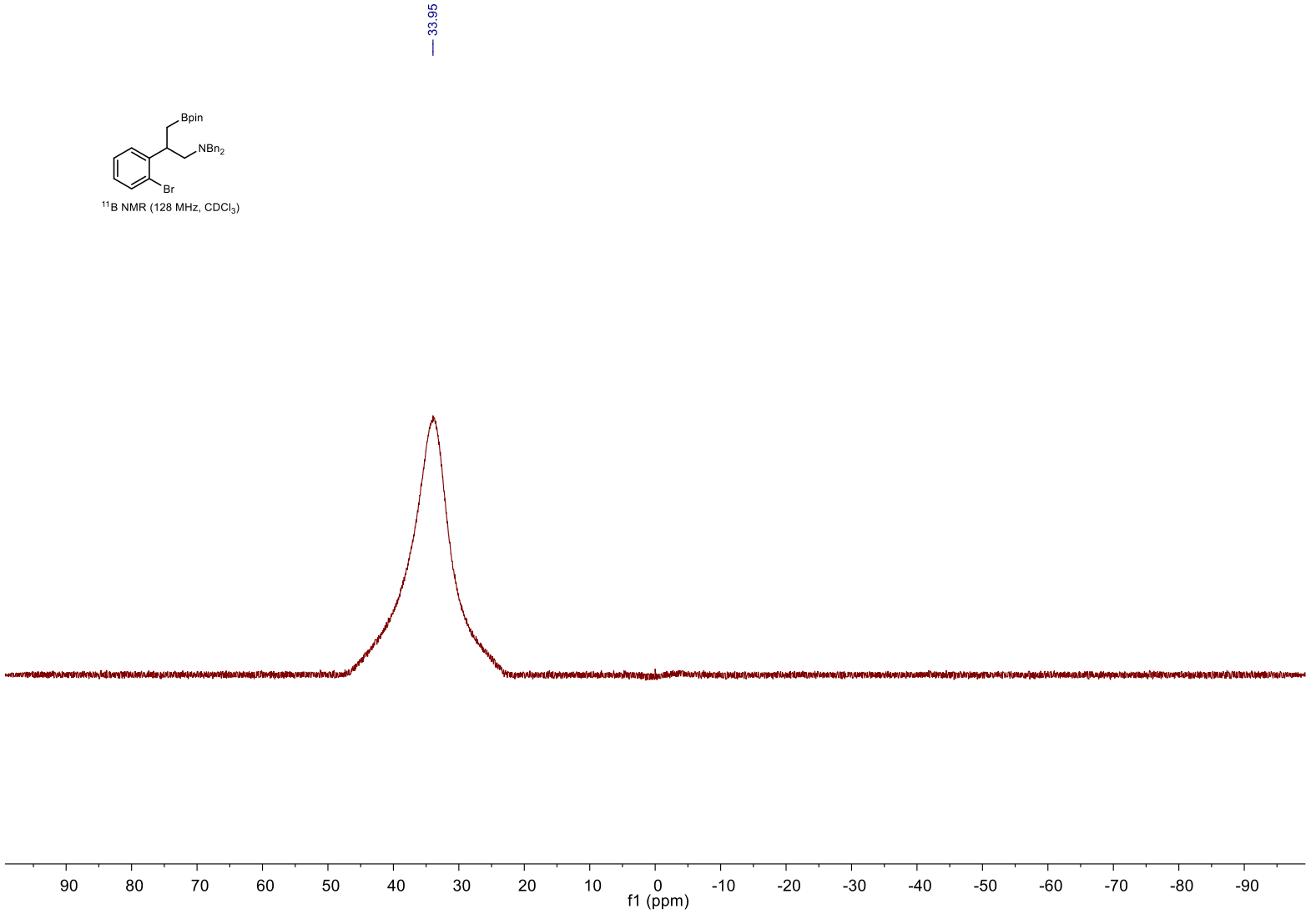

7.32
7.32
7.31
7.31
7.24
7.23
7.21
7.19
7.18
7.17
7.09
7.08
7.07
7.07
7.05
6.93
6.92
6.92
3.87
3.85
3.84
3.82
3.81
3.60
3.57
3.53
3.50
2.63
2.62
2.61
2.59
2.47
2.46
2.45
2.43
1.38
1.37
1.35
1.34
1.06
1.02
0.99
0.97
0.96
0.94
-0.00
Bpin
NBn2
Cl
1H NMR (500 MHz, CDCl3)
1.01
10.38
2.04
1.02
1.02
2.03
2.04
1.00
1.02
1.05
6.02
6.04
1.10
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
f1 (ppm)

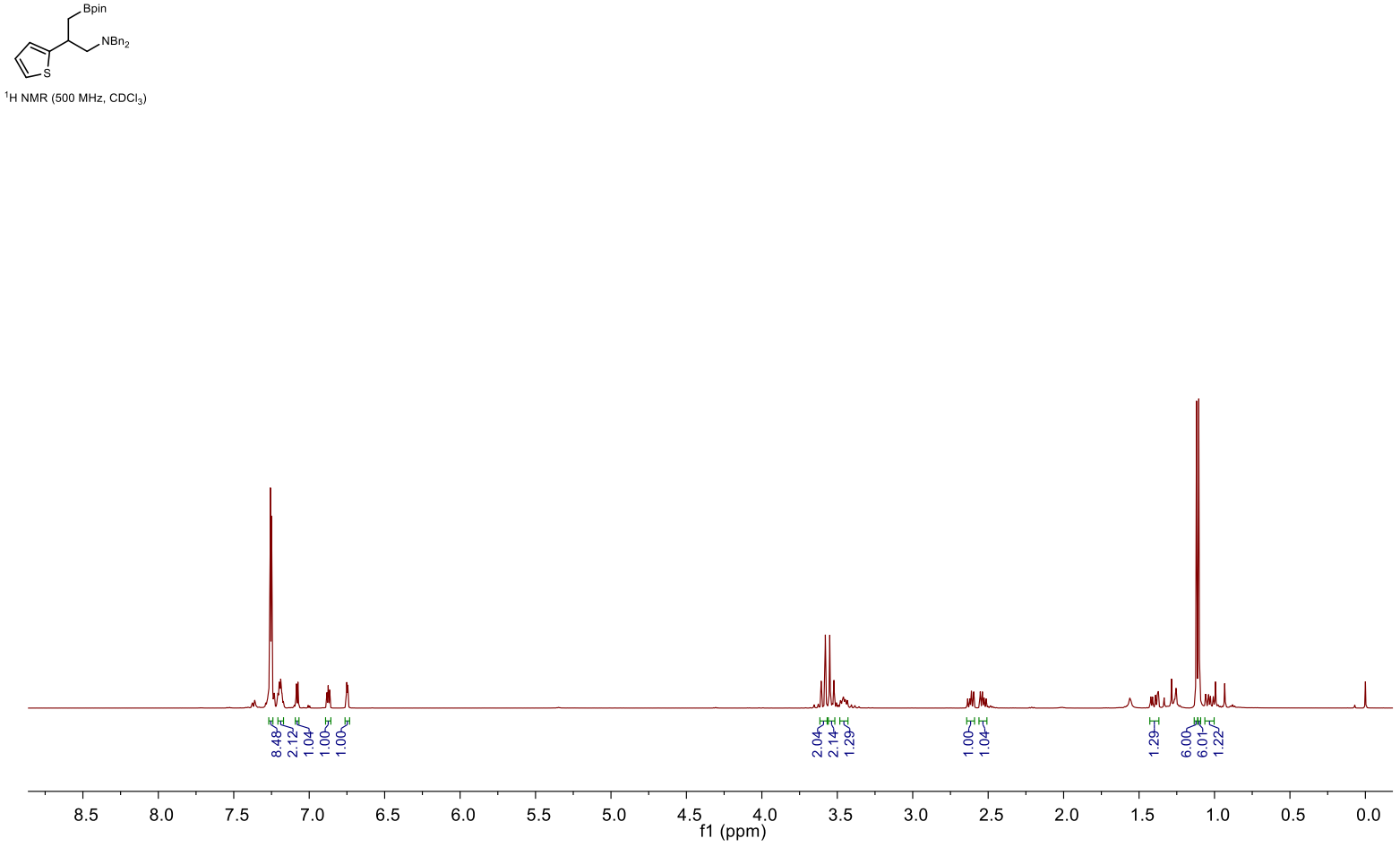

143.13
139.69
134.20
129.05
128.92
128.52
128.01
126.84
126.62
82.97
77.30
77.04
76.79
61.18
58.50
35.07
24.65
24.52
16.31
Bpin
NBn2
Cl
13C NMR (126 MHz, CDCl3)
129.0
128.0
127.0
f1 (ppm)
20
16
12
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

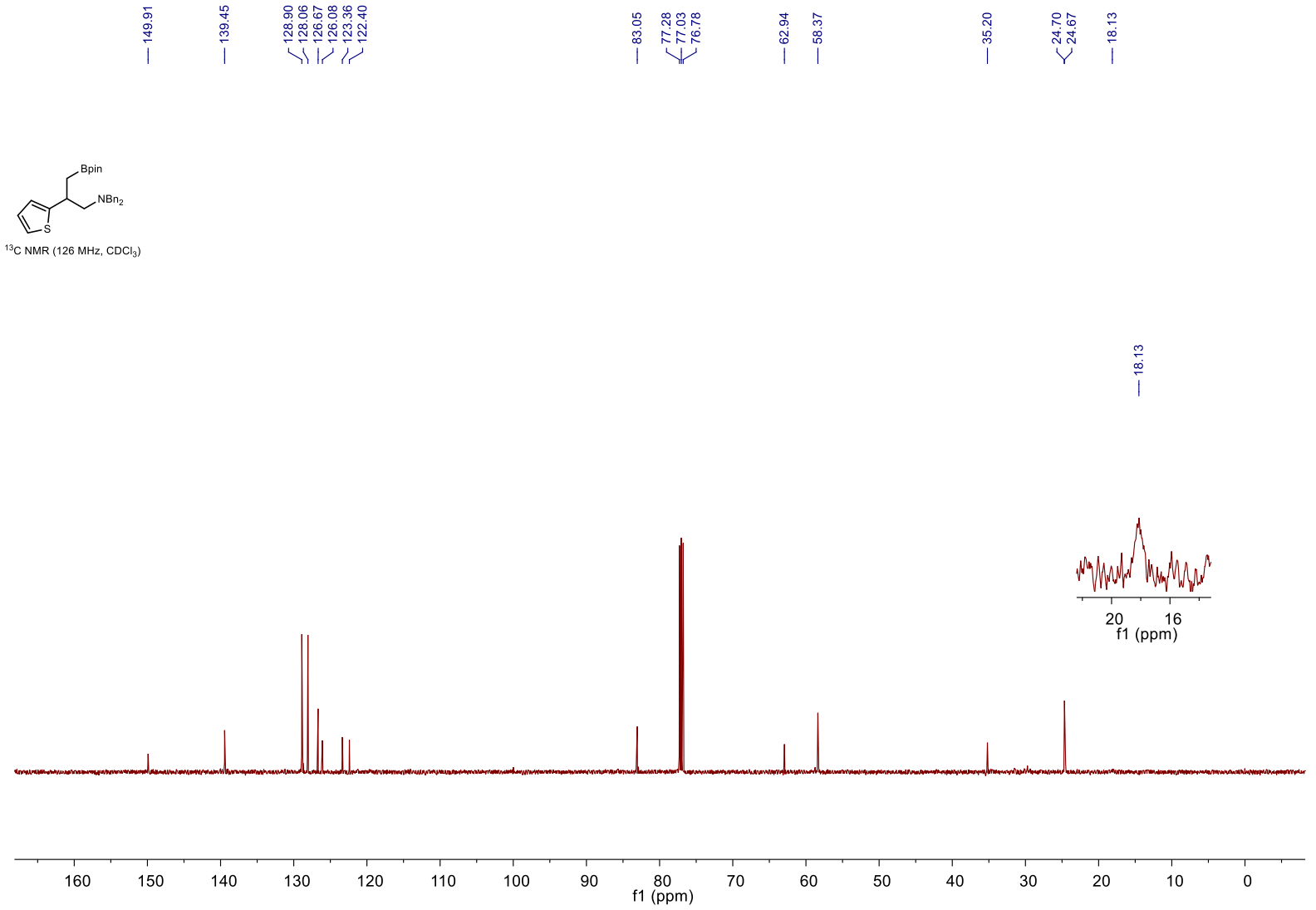

33.52
Bpin
NBn2
Cl
11B NMR (128 MHz, CDCl3)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

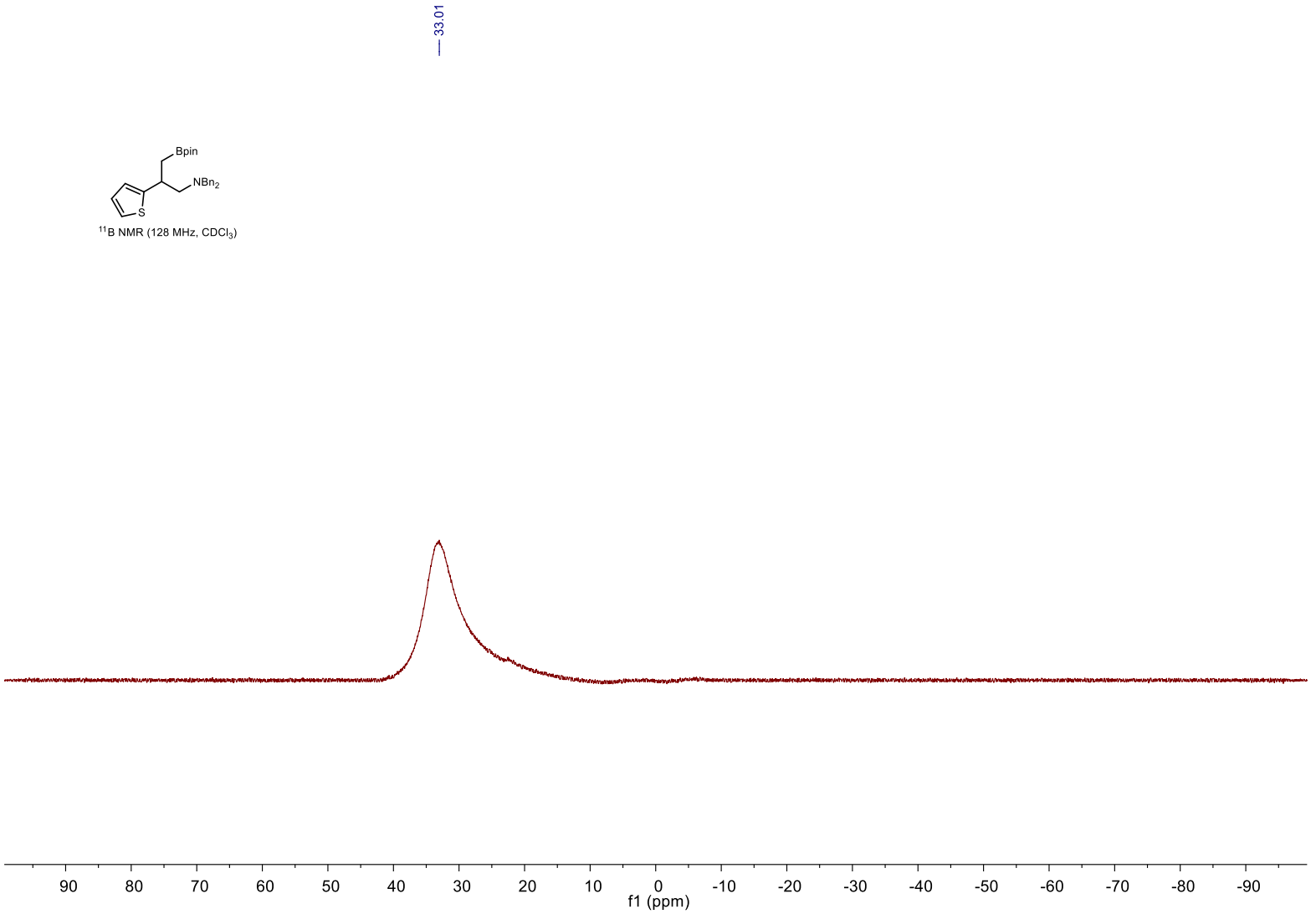

7.52
7.52
7.51
7.50
7.24
7.24
7.23
7.20
7.20
7.19
7.19
7.19
7.18
7.18
7.18
7.17
7.13
7.11
7.10
7.10
7.02
7.02
7.00
7.00
6.99
6.99
6.92
6.91
6.90
6.90
3.82
3.81
3.80
3.80
3.79
3.78
3.57
2.63
2.61
2.60
2.59
2.46
2.45
2.44
2.42
1.40
1.39
1.37
1.36
1.06
1.02
0.98
0.96
0.95
0.93
0.00
Bpin
NBn2
Br
1H NMR (500 MHz, CDCl3)
1.01
8.09
2.01
1.03
1.00
1.01
1.03
4.13
1.00
1.03
1.09
6.04
6.03
1.14
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
f1 (ppm)

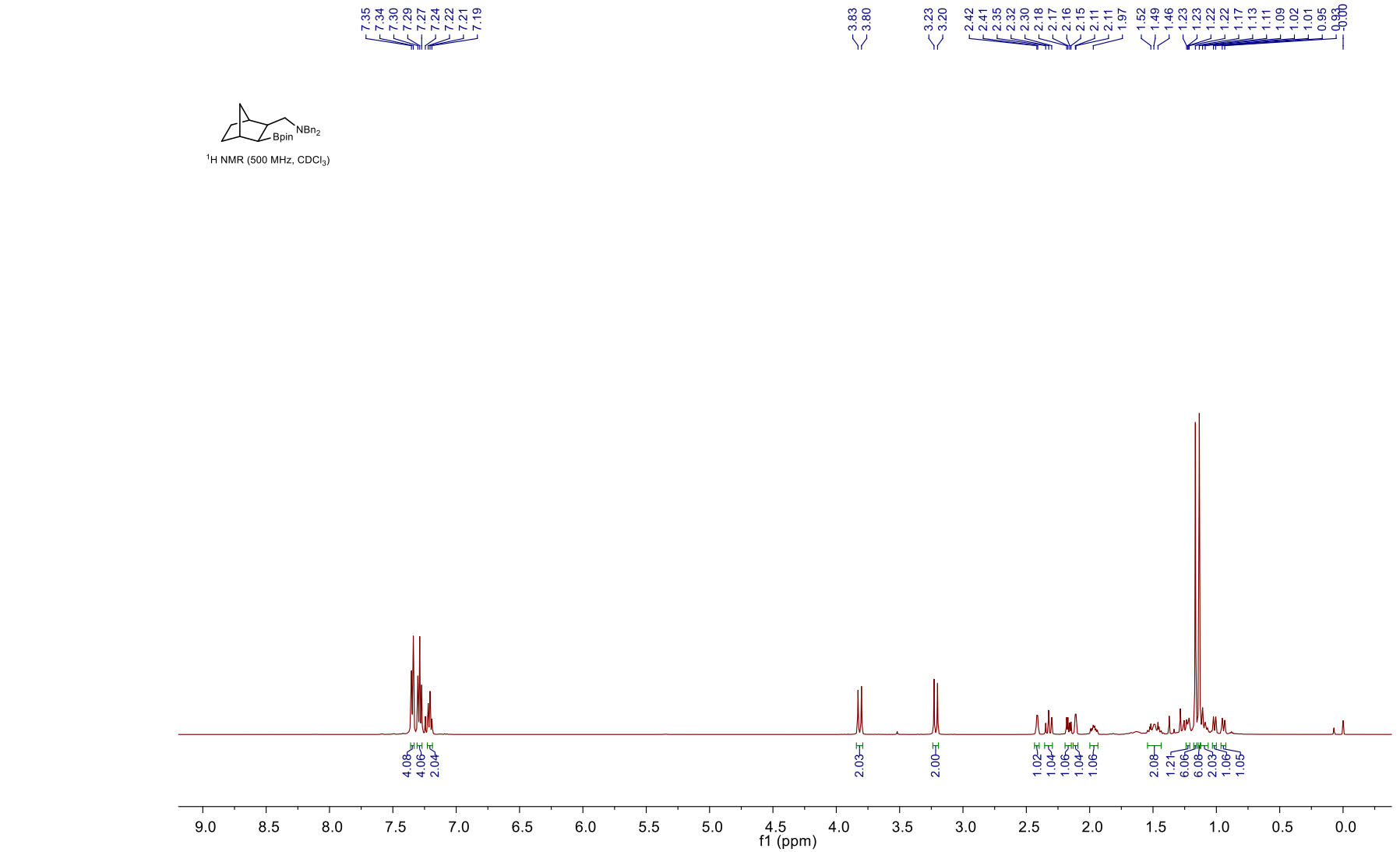

144.73
139.71
132.39
128.95
128.61
128.03
127.29
127.25
126.64
125.24
82.98
77.31
77.06
76.80
61.23
58.53
37.89
24.66
24.52
16.48
Bpin
NBn2
Br
13C NMR (126 MHz, CDCl3)
128.61
128.03
127.29
127.25
126.64
125.24
16.48
f1 (ppm)
f1 (ppm)

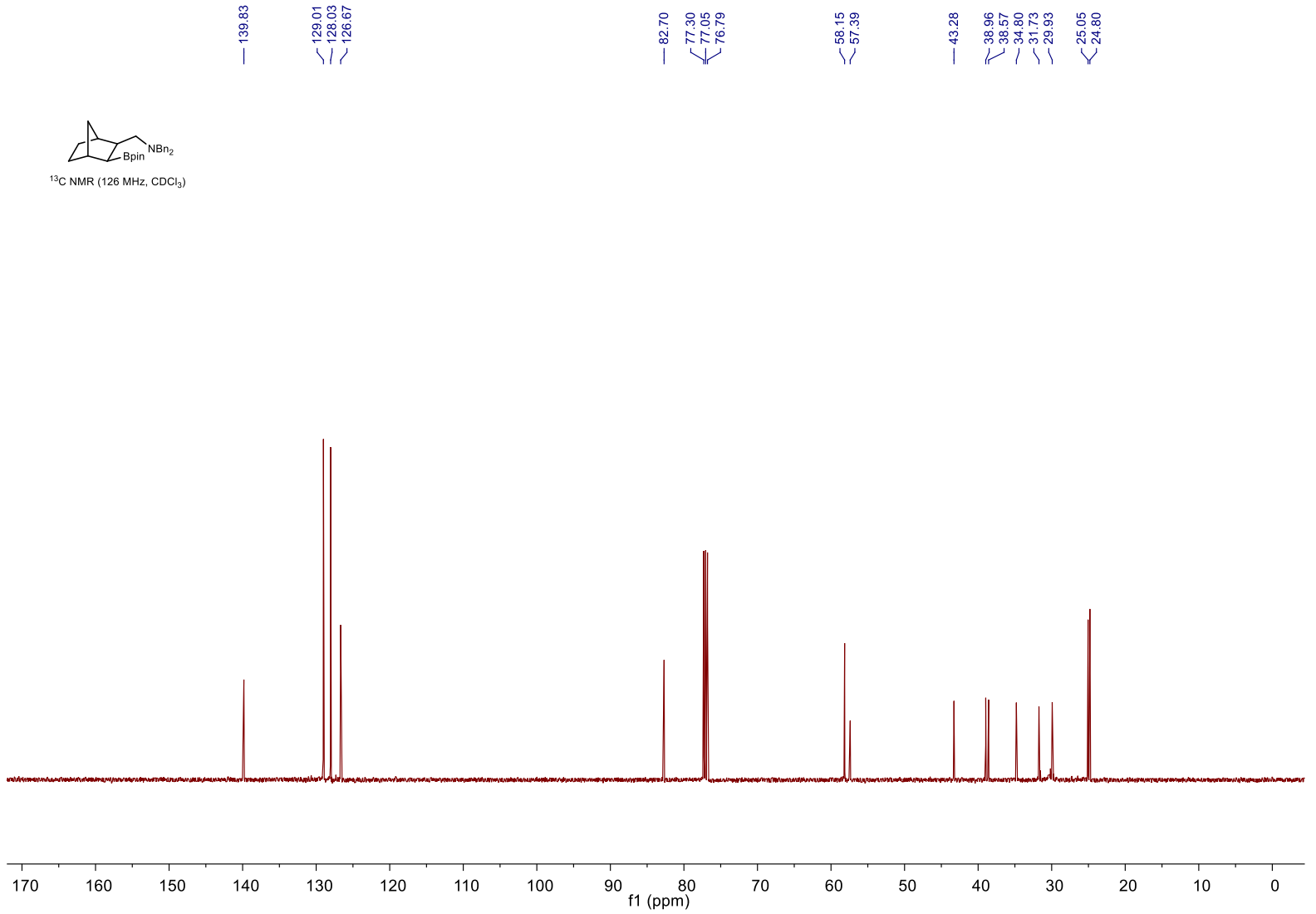

33.95
Bpin
NBn2
Br
11B NMR (128 MHz, CDCl3)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

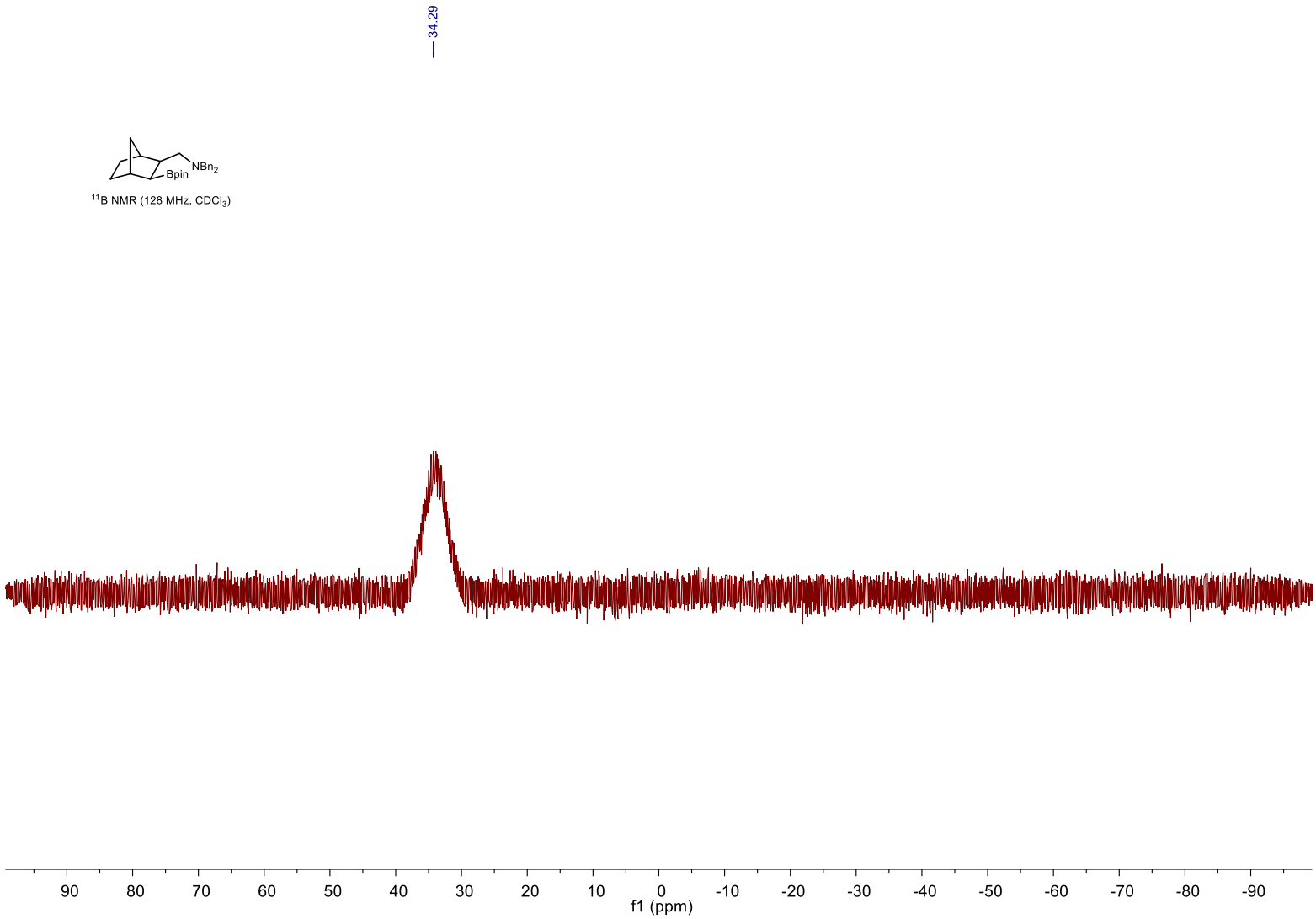

7.26
7.25
7.21
7.21
7.20
7.19
7.18
7.18
7.17
7.08
7.07
6.88
6.87
6.87
6.86
6.75
6.74
3.61
3.58
3.55
3.52
3.48
3.47
3.46
3.45
3.43
2.64
2.62
2.61
2.60
2.55
2.54
2.53
2.51
1.42
1.41
1.39
1.38
1.37
1.12
1.10
1.06
1.04
1.03
1.01
-0.00
Bpin
NBn2
S
1H NMR (500 MHz, CDCl3)
8.48
2.12
1.04
1.00
1.00
2.04
2.14
1.29
1.00
1.04
1.29
6.00
6.01
1.22
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
f1 (ppm)

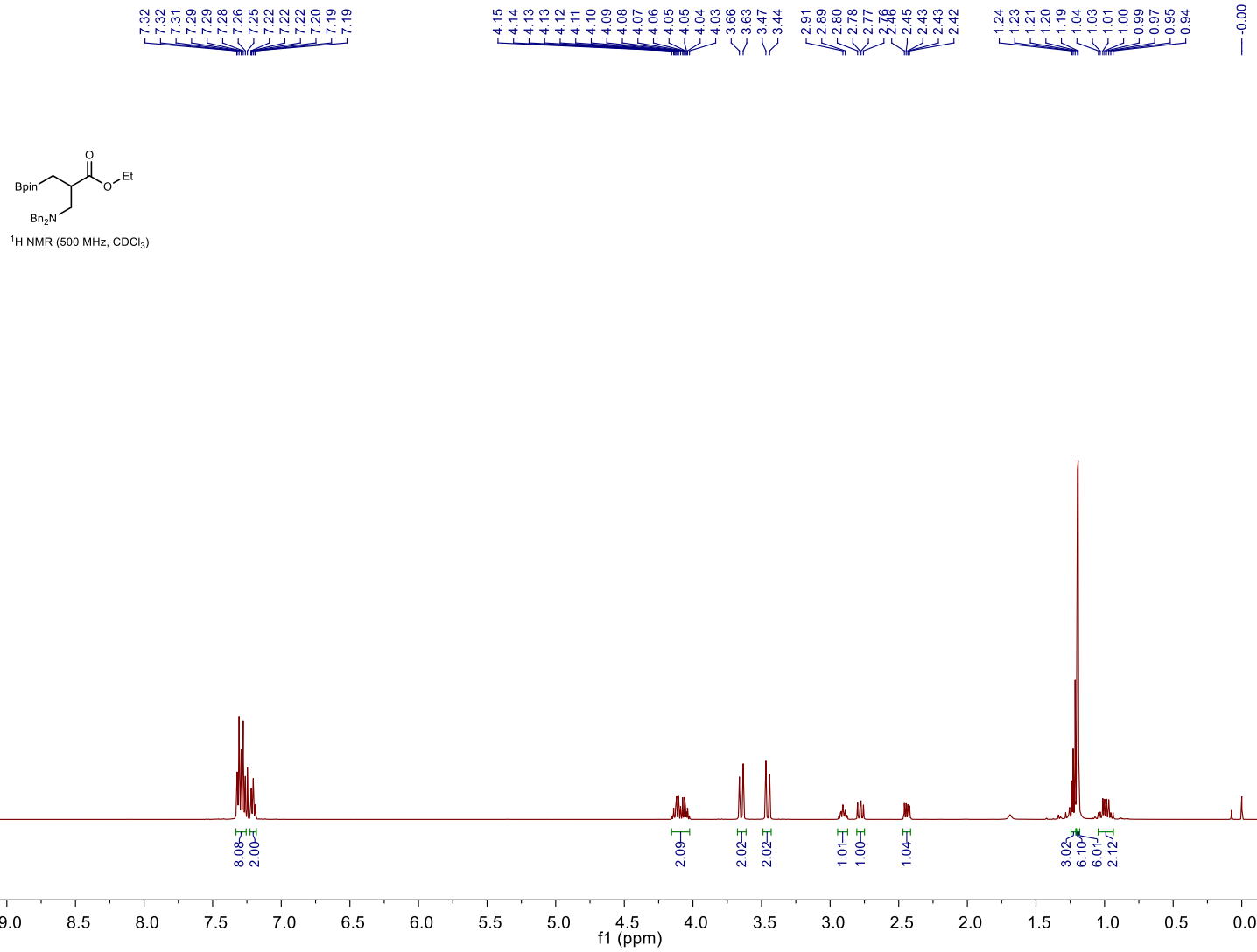

149.91
139.45
128.90
128.06
126.67
126.08
123.36
122.40
83.05
77.28
77.03
76.78
62.94
58.37
35.20
24.70
24.67
18.13
Bpin
NBn2
S
13C NMR (126 MHz, CDCl3)
18.13
20
16
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

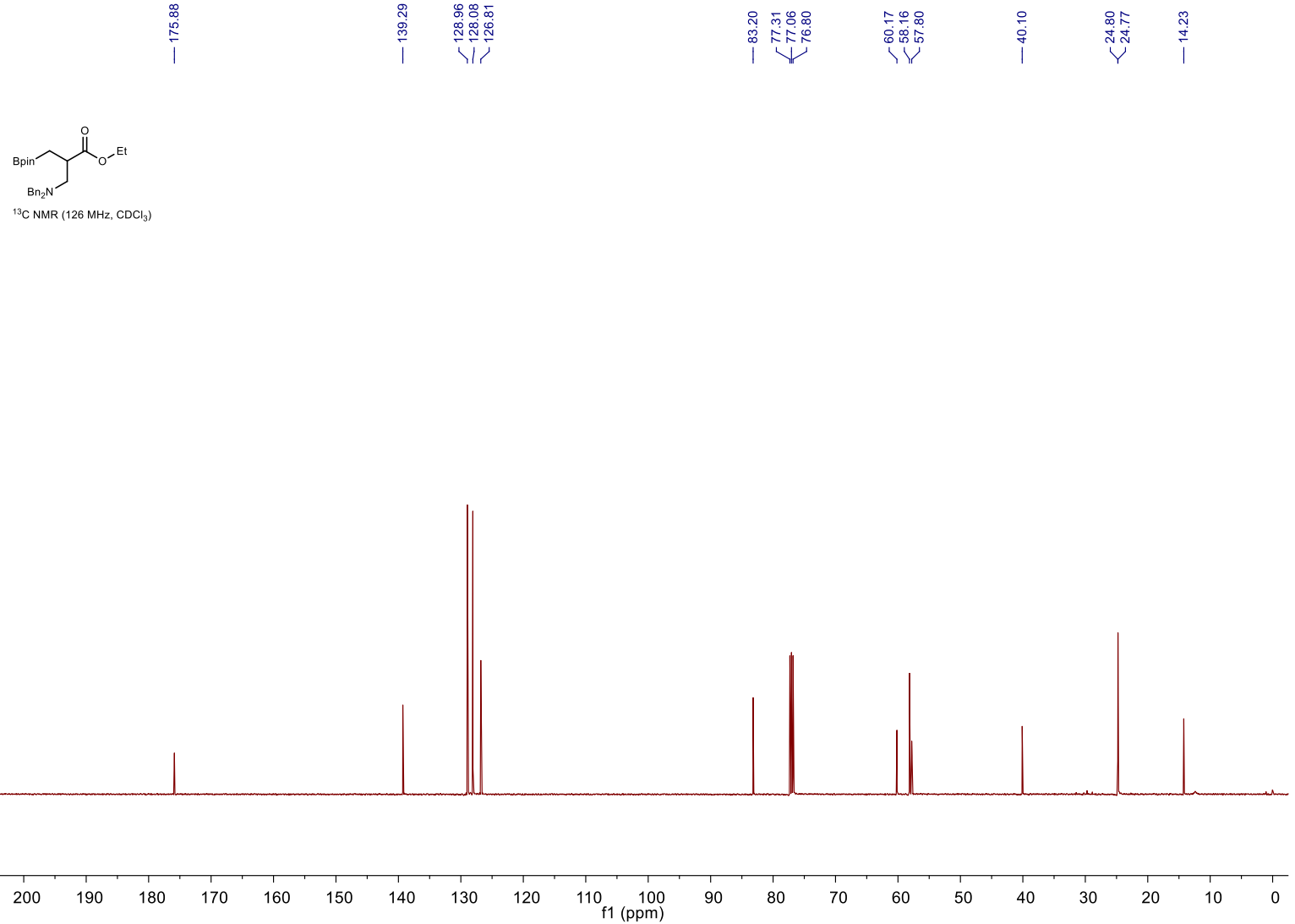

33.01
Bpin
NBn2
S
11B NMR (128 MHz, CDCl3)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

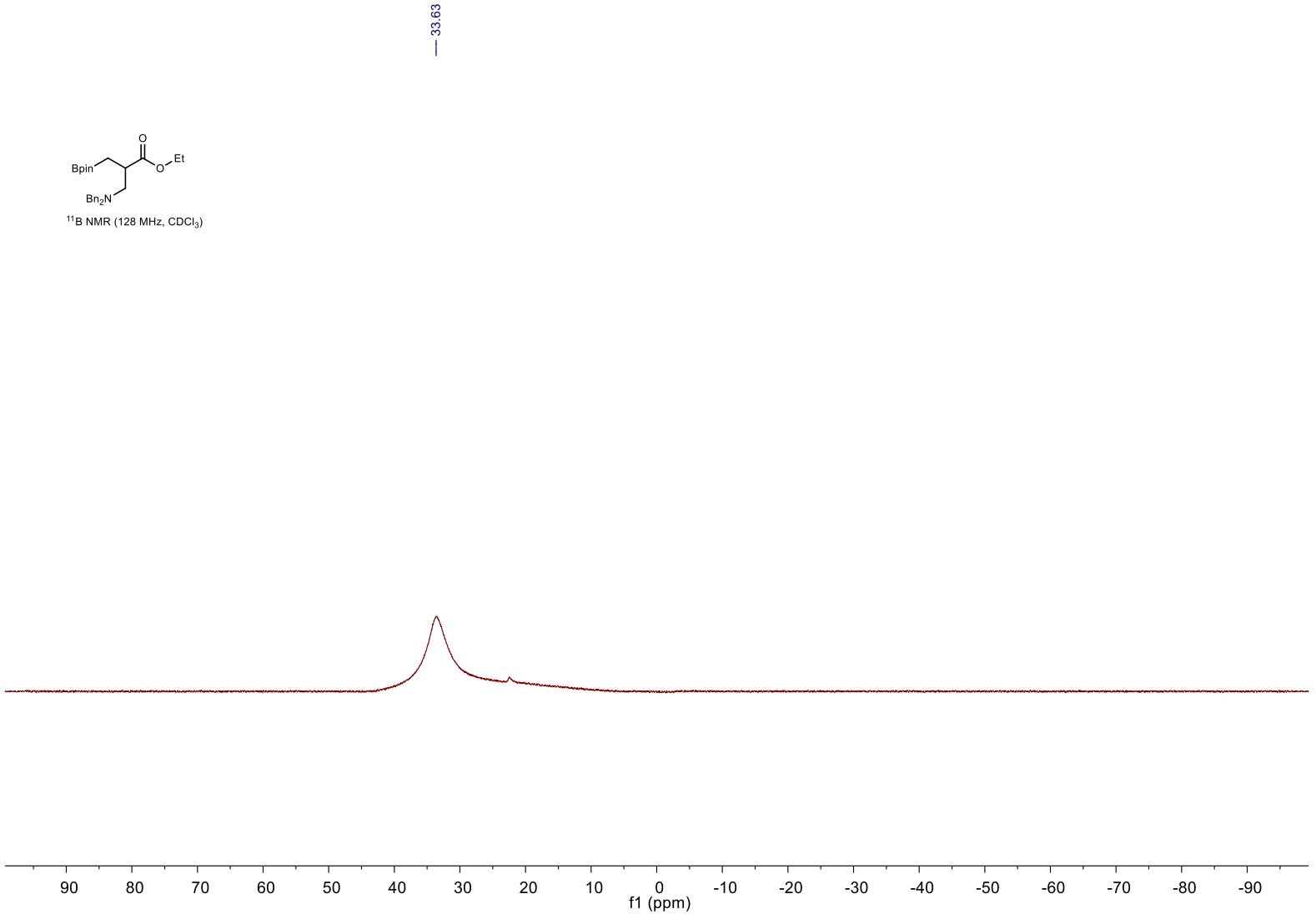

7.35
7.34
7.30
7.29
7.27
7.24
7.22
7.21
7.19
3.83
3.80
3.23
3.20
2.42
2.41
2.35
2.32
2.30
2.18
2.17
2.16
2.15
2.11
2.11
1.97
1.52
1.49
1.46
1.23
1.23
1.22
1.22
1.17
1.13
1.11
1.09
1.02
1.01
0.95
0.93
0.00
NBn2
Bpin
1H NMR (500 MHz, CDCl3)
4.08
4.06
2.04
2.03
2.00
1.02
1.04
1.06
1.04
1.06
2.08
1.21
6.06
6.08
2.03
1.06
1.05
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
f1 (ppm)

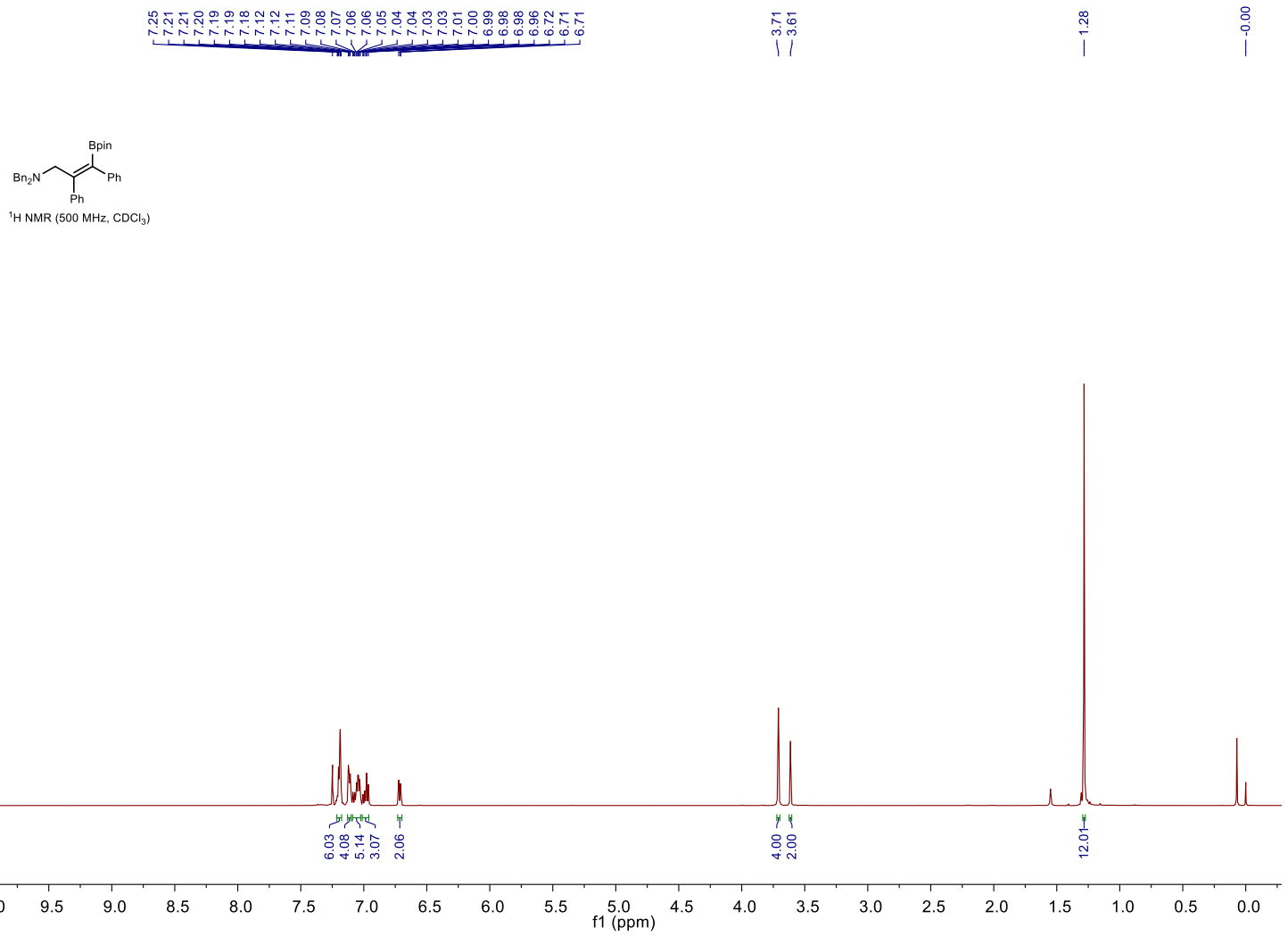

139.83
129.01
128.03
126.67
82.70
77.30
77.05
76.79
58.15
57.39
43.28
38.96
38.57
34.80
31.73
29.93
25.05
24.80
NBn2
Bpin
13C NMR (126 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

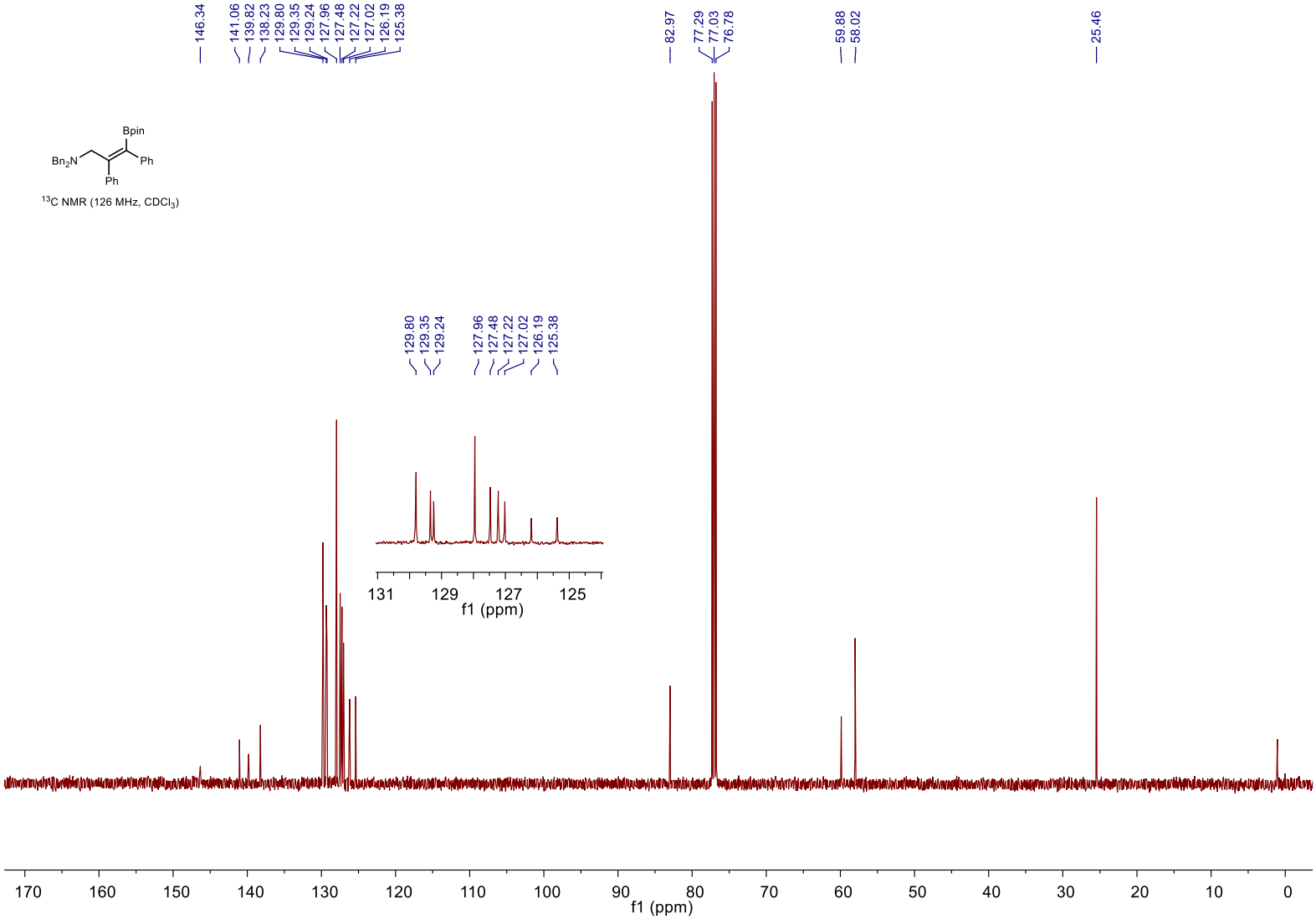

34.29
NBn2
Bpin
11B NMR (128 MHz, CDCl3)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

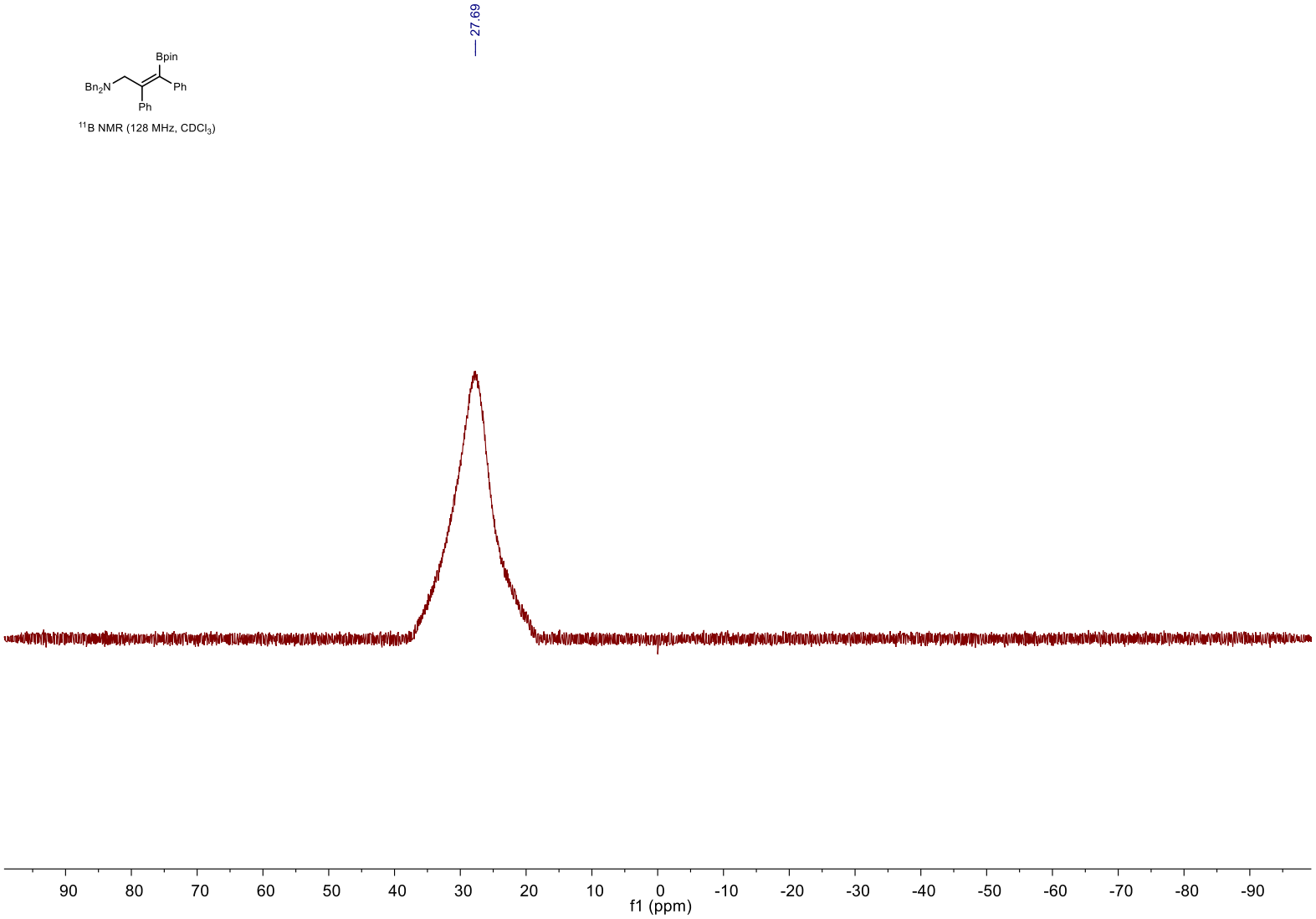

7.32
7.32
7.31
7.29
7.29
7.28
7.26
7.25
7.22
7.22
7.22
7.20
7.19
7.19
4.15
4.14
4.13
4.13
4.12
4.11
4.10
4.09
4.08
4.07
4.06
4.05
4.05
4.04
4.03
3.66
3.63
3.47
3.44
2.91
2.89
2.80
2.78
2.77
2.45
2.43
2.43
2.42
1.24
1.23
1.21
1.20
1.19
1.04
1.03
1.01
1.00
0.99
0.97
0.95
0.94
-0.00
O
Et
O
Bpin
Bn2N
1H NMR (500 MHz, CDCl3)
8.08
2.00
2.09
2.02
2.02
1.01
1.00
1.04
3.02
6.10
6.01
2.12
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
f1 (ppm)

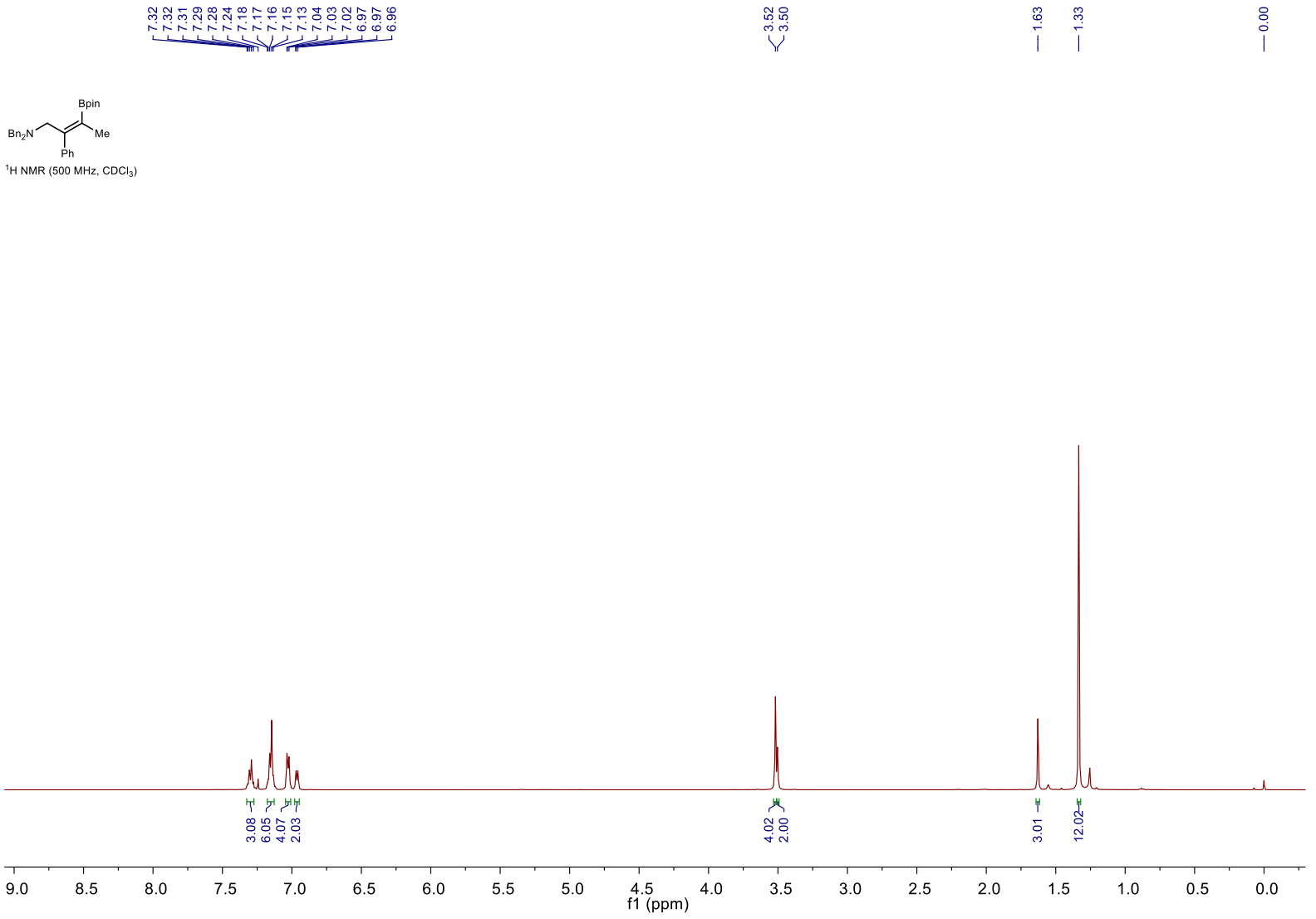

175.88
139.29
128.96
128.08
126.81
83.20
77.31
77.06
76.80
60.17
58.16
57.80
40.10
24.80
24.77
14.23
O
O
Et
Bpin
Bn2N
13C NMR (126 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

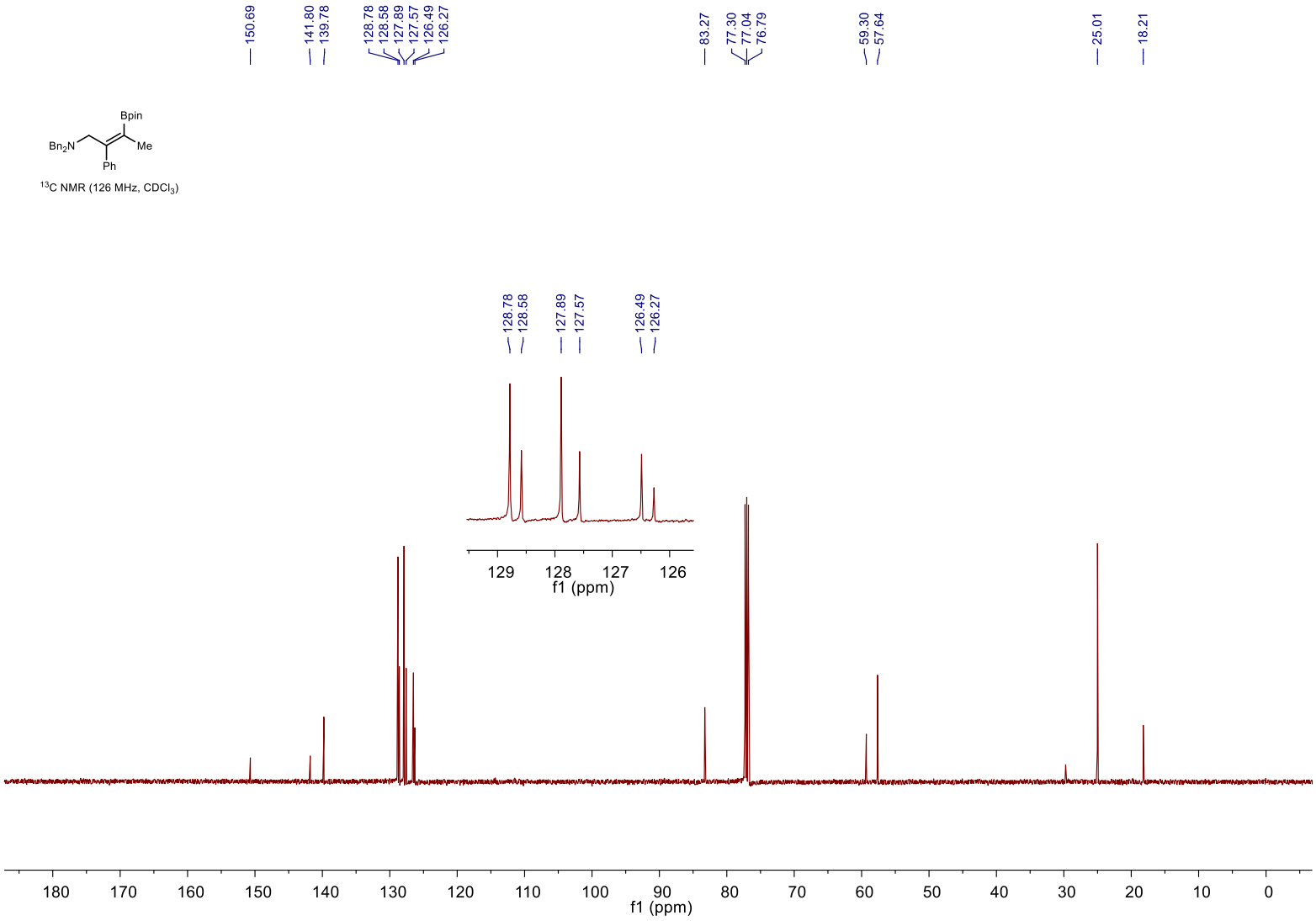

33.63
Bpin
O
O
Et
Bn2N
11B NMR (128 MHz, CDCl3)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

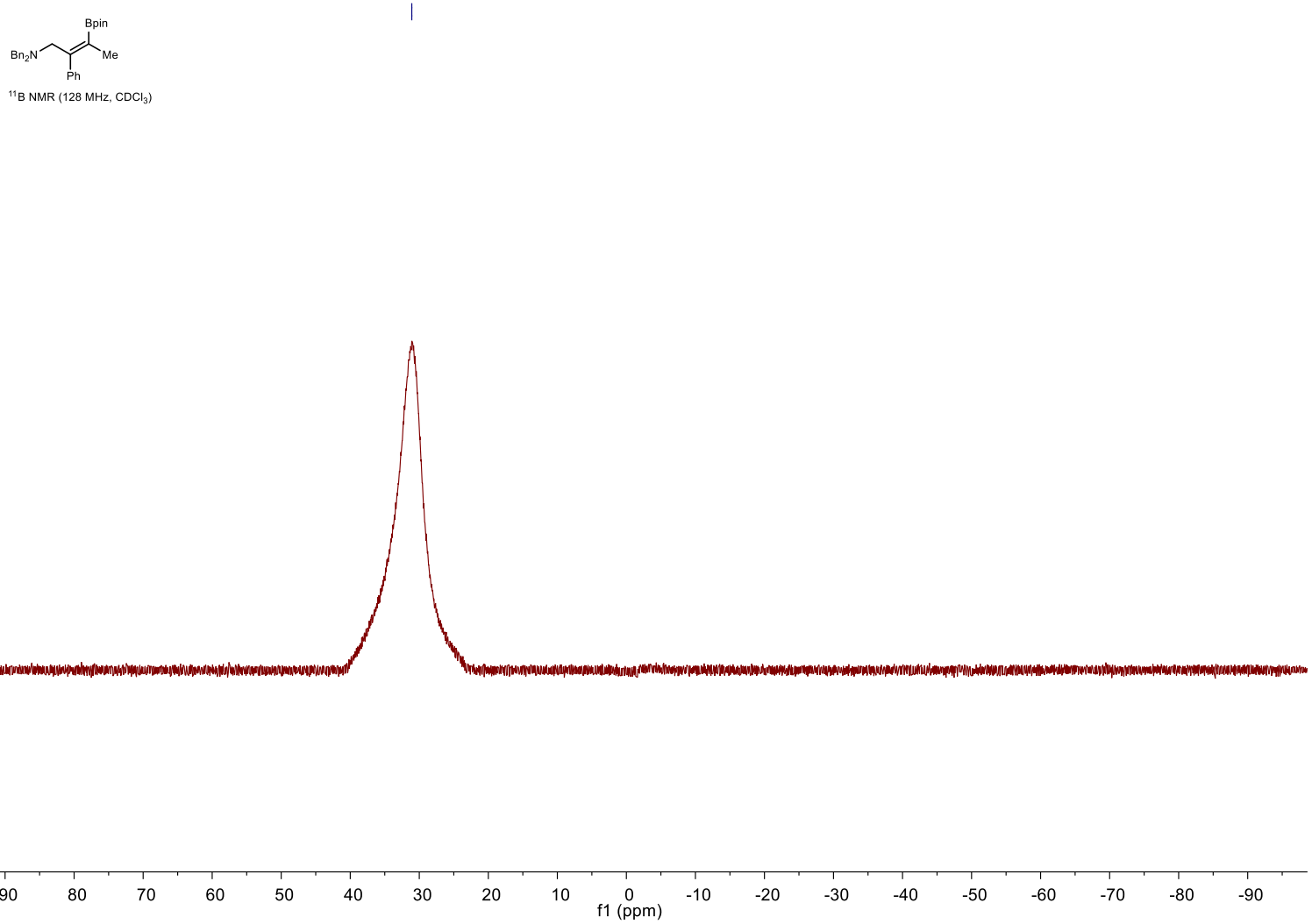

7.25
7.21
7.21
7.20
7.19
7.19
7.18
7.12
7.12
7.11
7.09
7.08
7.07
7.06
7.06
7.05
7.04
7.04
7.03
7.03
7.01
7.00
6.99
6.98
6.98
6.96
6.72
6.71
6.71
3.71
3.61
1.28
-0.00
Bpin
Bn2N
Ph
Ph
1H NMR (500 MHz, CDCl3)
6.03
4.08
5.14
3.07
2.06
4.00
2.00
12.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

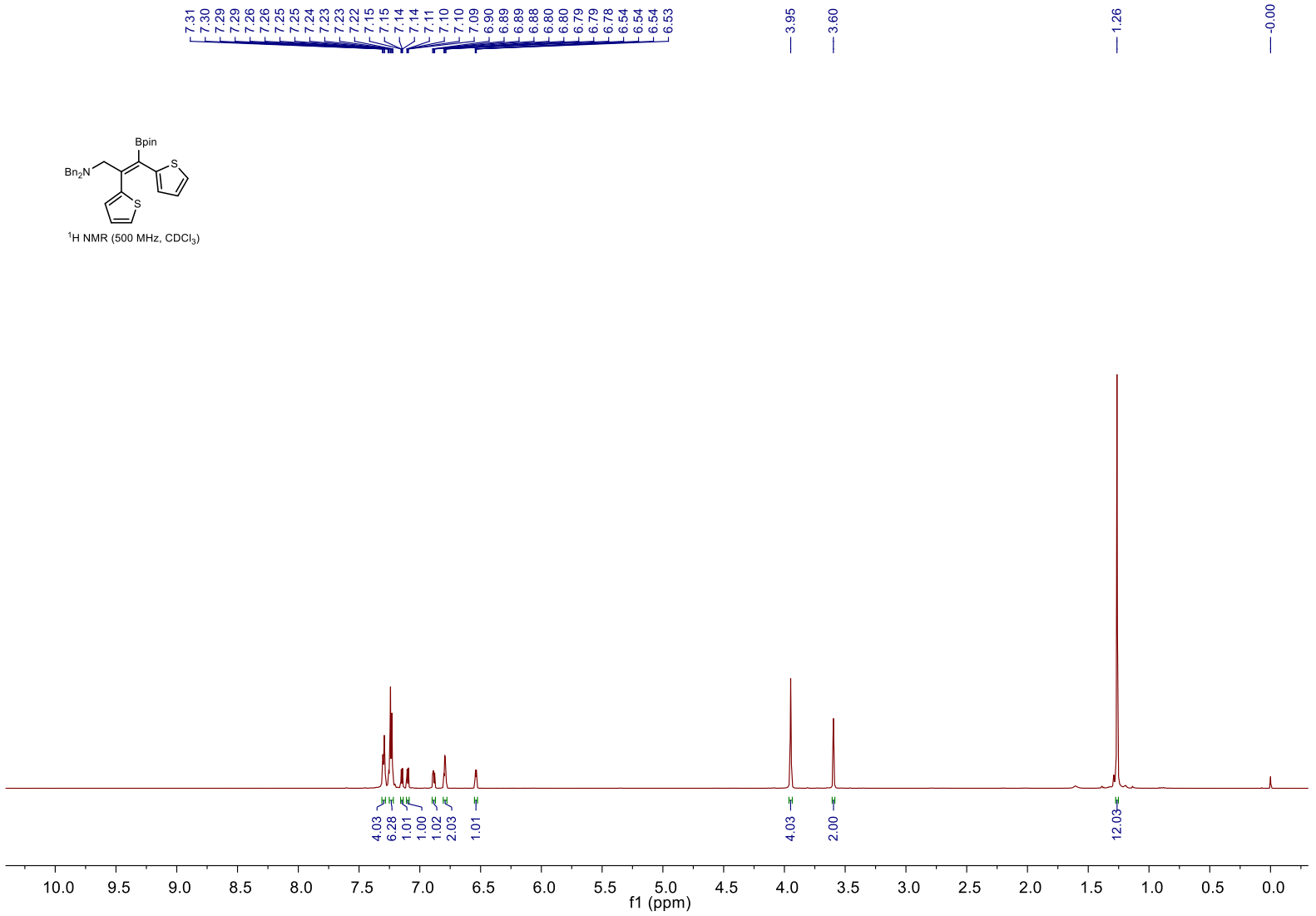

146.34
141.06
139.82
138.23
129.80
129.35
129.24
127.96
127.48
127.22
127.02
126.19
125.38
82.97
77.29
77.03
76.78
59.88
58.02
25.46
Bpin
Bn2N
Ph
Ph
13C NMR (126 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

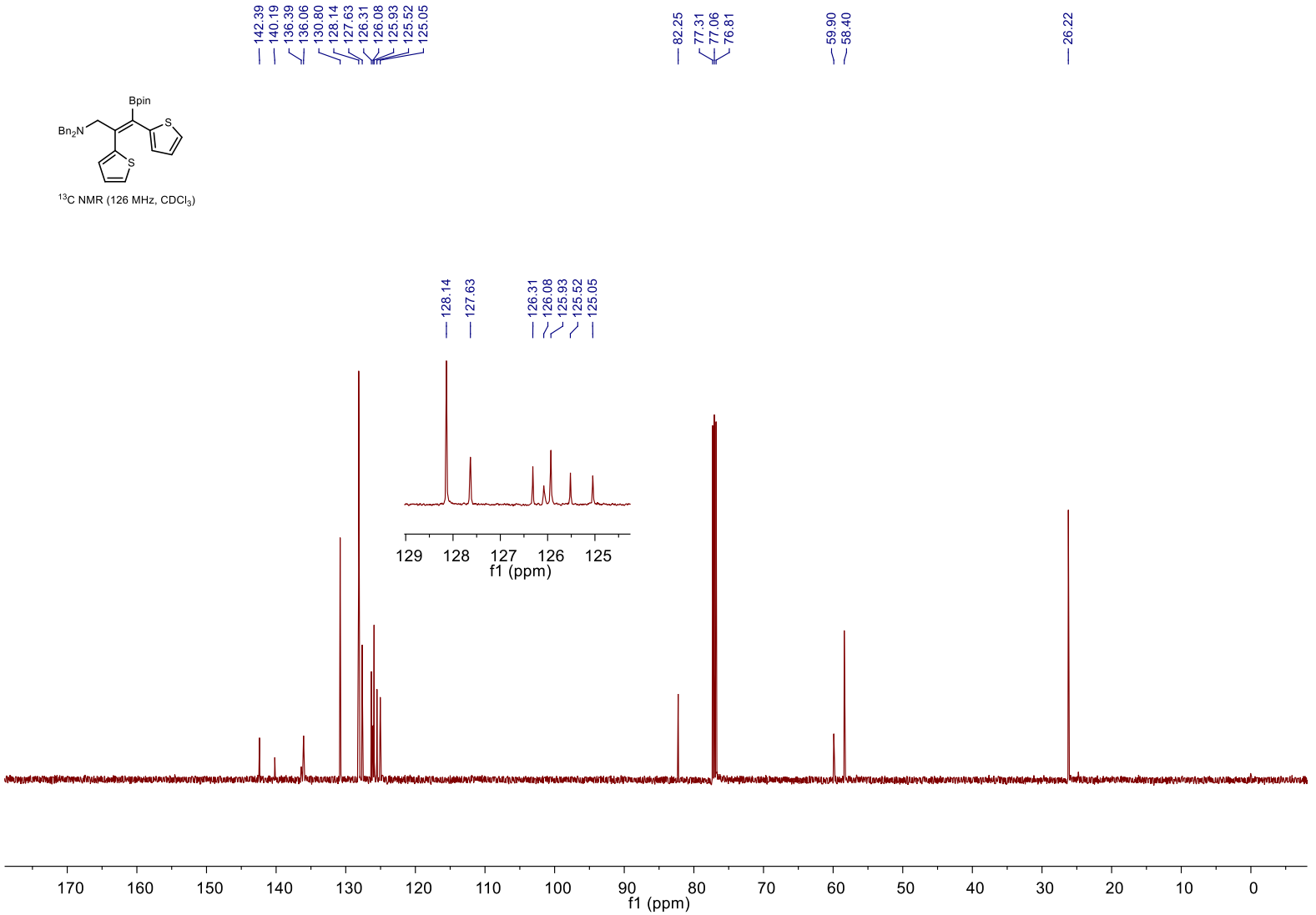

Bpin
Bn2N
Ph
Ph
11B NMR (128 MHz, CDCl3)
27.69
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

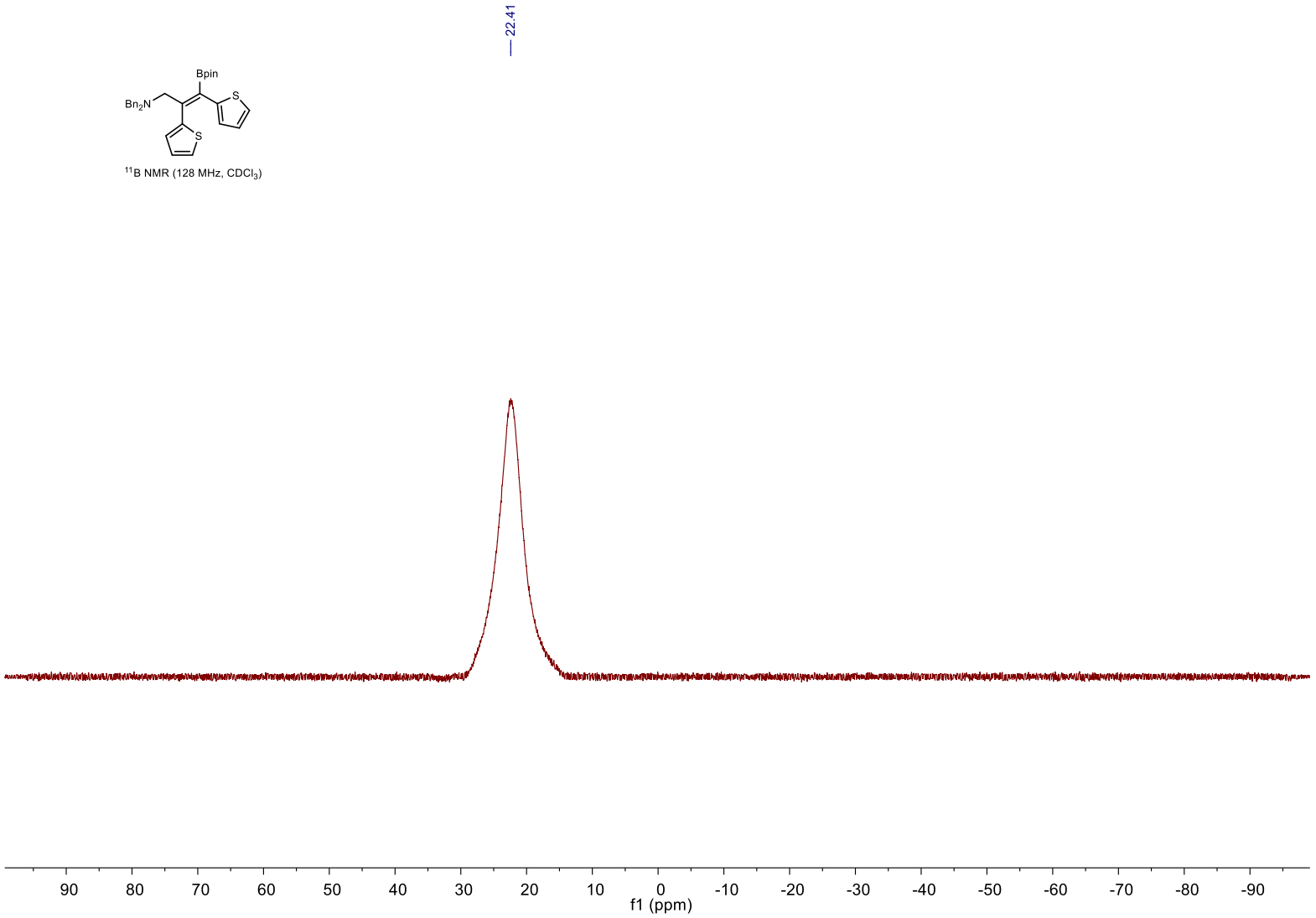

7.32
7.32
7.31
7.29
7.28
7.24
7.18
7.17
7.16
7.15
7.13
7.04
7.03
7.02
6.97
6.97
6.96
3.52
3.50
1.63
1.33
0.00
Bpin
Bn2N
Me
Ph
1H NMR (500 MHz, CDCl3)
3.08
6.05
4.07
2.03
4.02
2.00
3.01
12.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

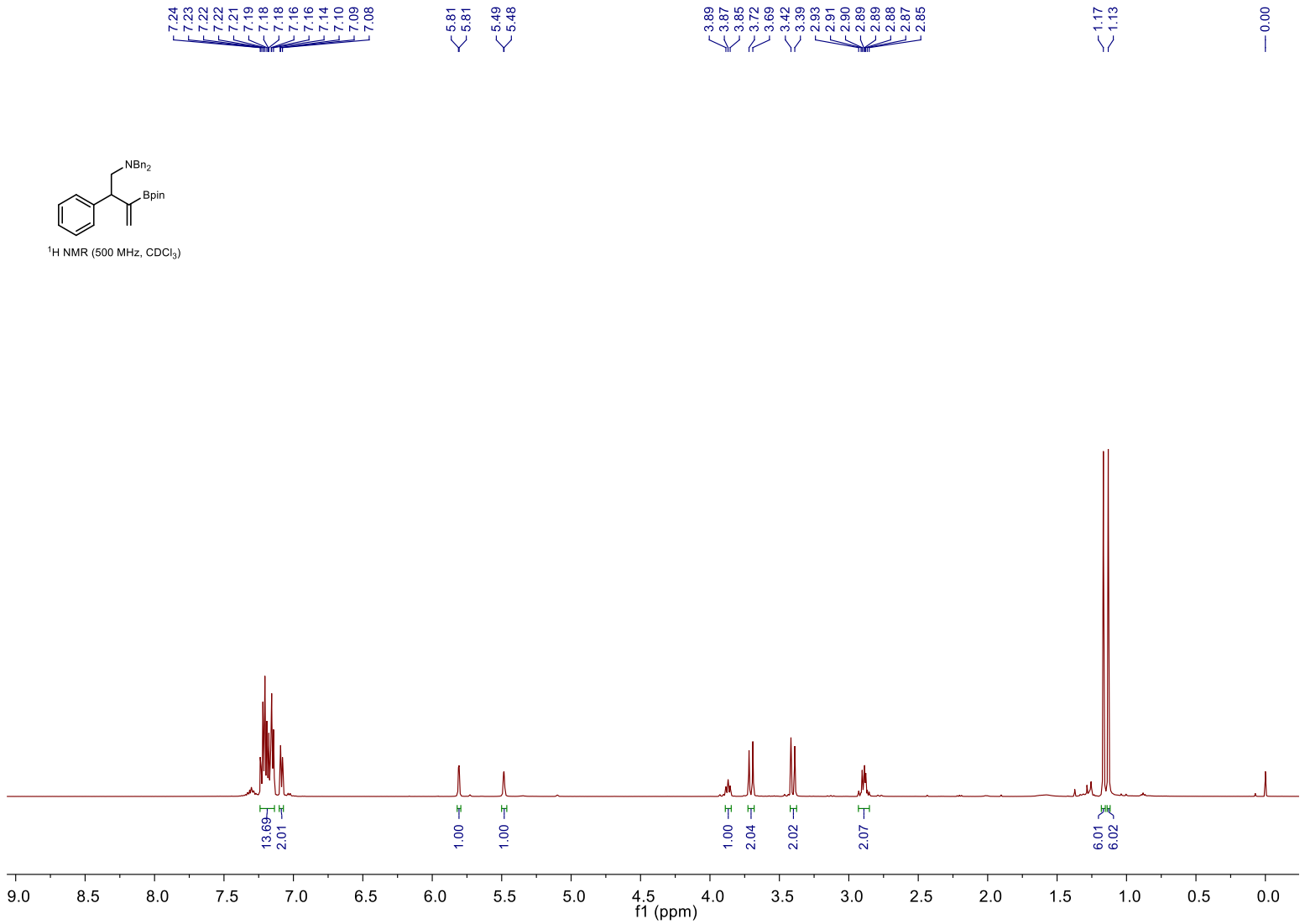

150.69
141.80
139.78
128.78
128.58
127.89
127.57
126.49
126.27
83.27
77.30
77.04
76.79
59.30
57.64
25.01
18.21
Bpin
Bn2N
Me
Ph
13C NMR (126 MHz, CDCl3)
f1 (ppm)

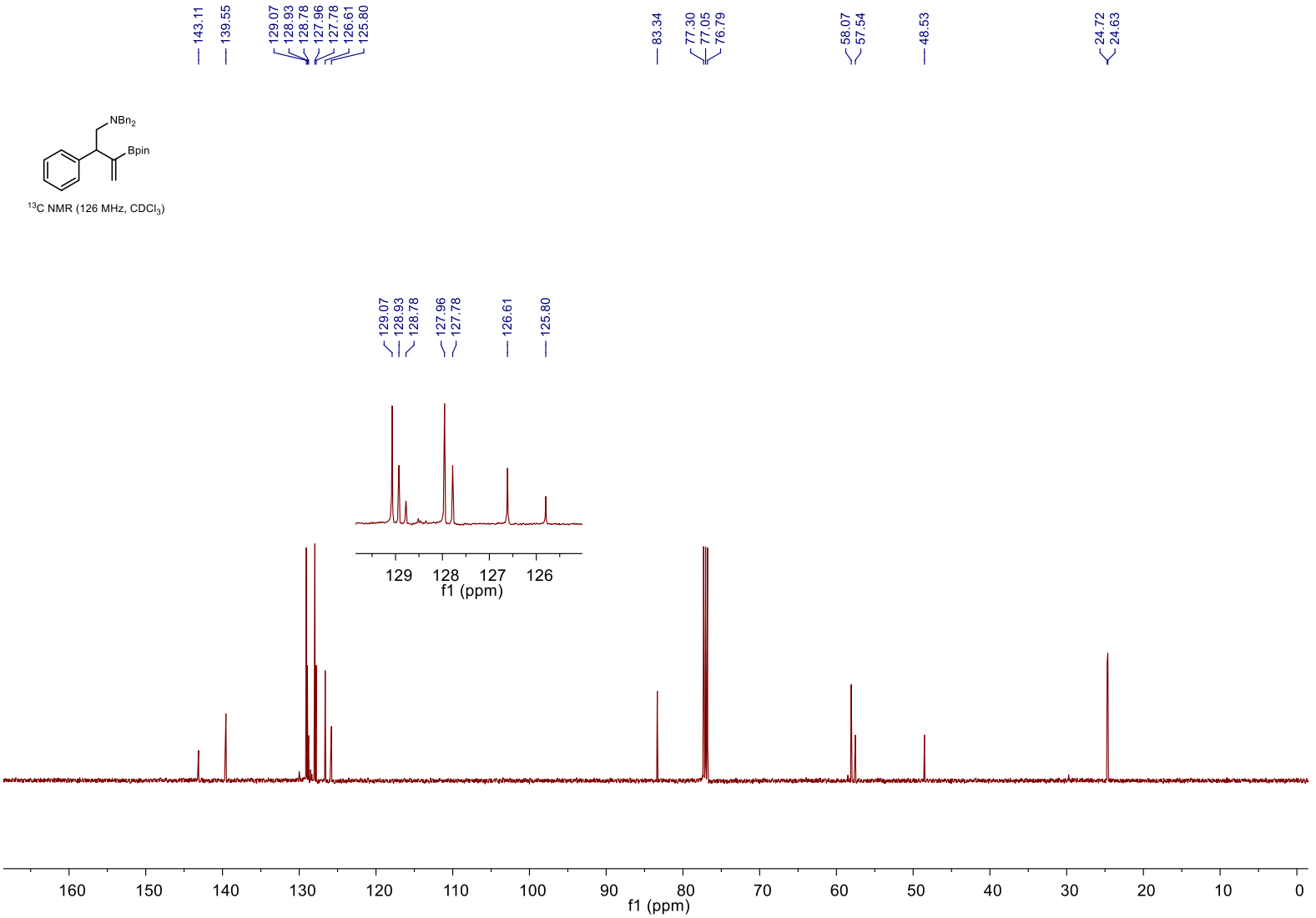

Bpin
Bn2N
Me
Ph
11B NMR (128 MHz, CDCl3)
31.08
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

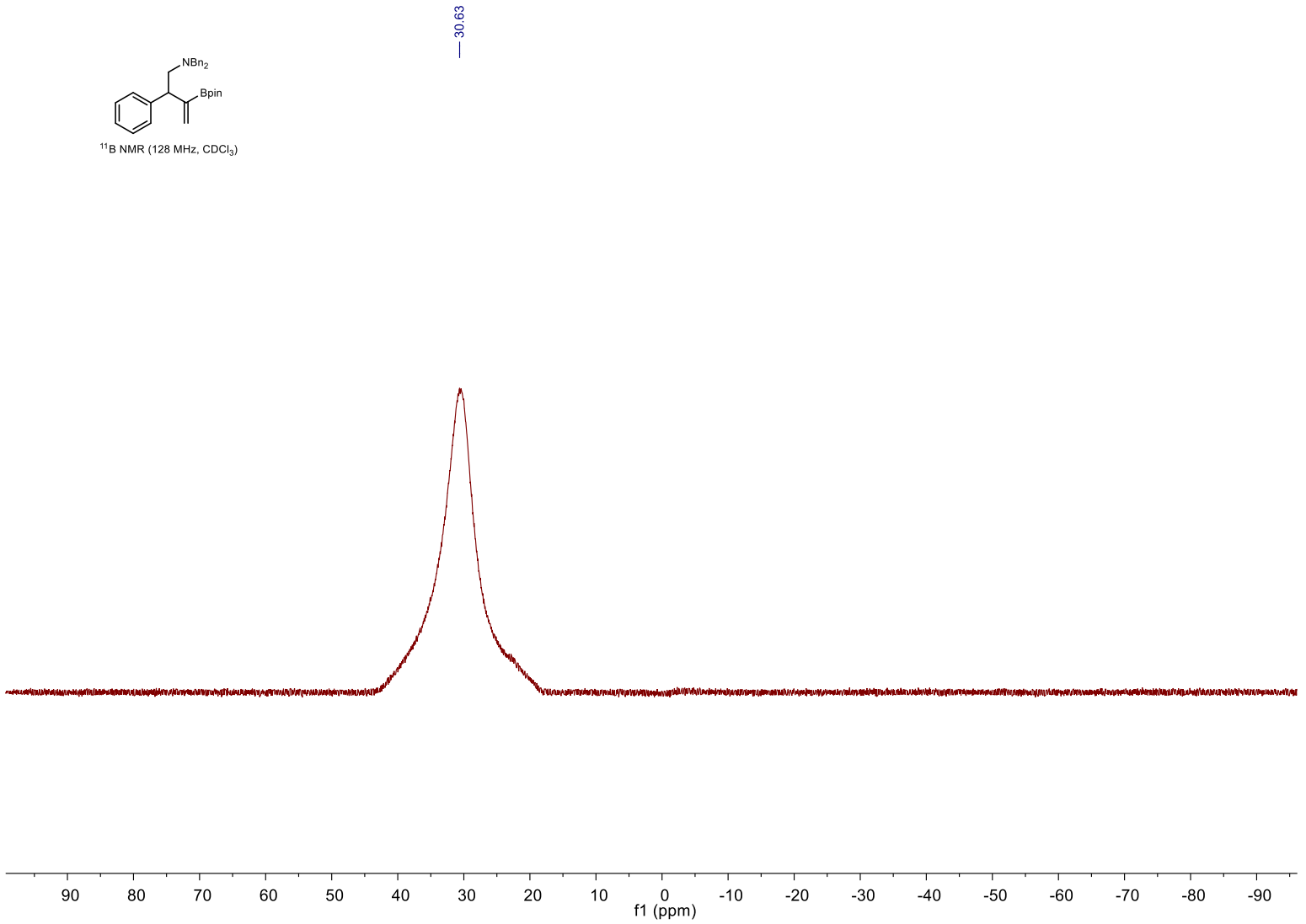

7.31
7.30
7.29
7.29
7.26
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.15
7.15
7.14
7.14
7.11
7.10
7.10
7.09
6.90
6.89
6.89
6.88
6.80
6.80
6.79
6.79
6.78
6.54
6.54
6.54
6.53
3.95
3.60
1.26
-0.00
Bpin
Bn2N
S
S
1H NMR (500 MHz, CDCl3)
4.03
6.28
1.01
1.00
1.02
2.03
1.01
4.03
2.00
12.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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
f1 (ppm)

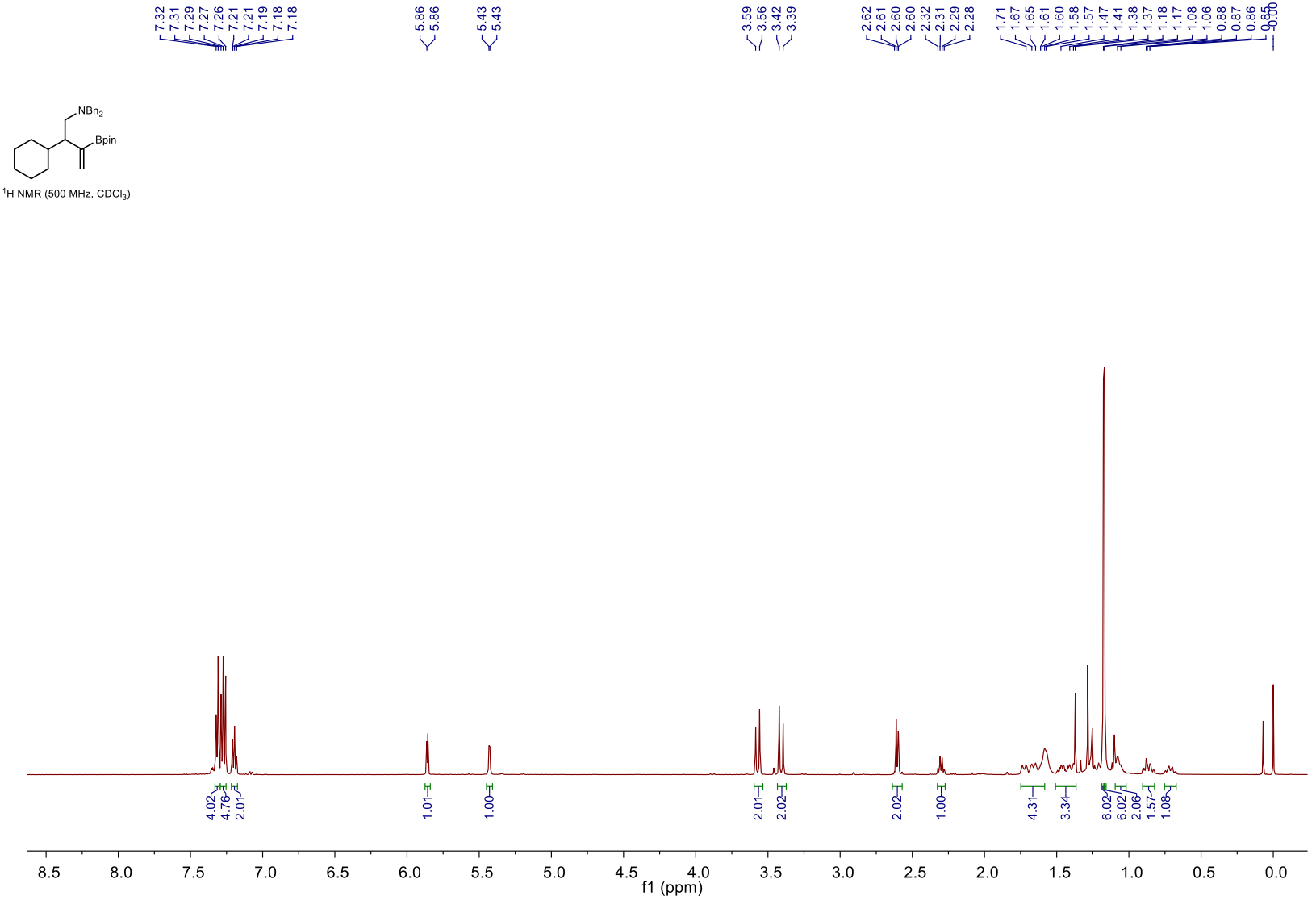

142.39
140.19
136.39
136.06
130.80
128.14
127.63
126.31
126.08
125.93
125.52
125.05
82.25
77.31
77.06
76.81
59.90
58.40
26.22
Bpin
Bn2N
S
S
13C NMR (126 MHz, CDCl3)
128.14
127.63
126.31
126.08
125.93
125.52
125.05
129 128 127 126 125
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

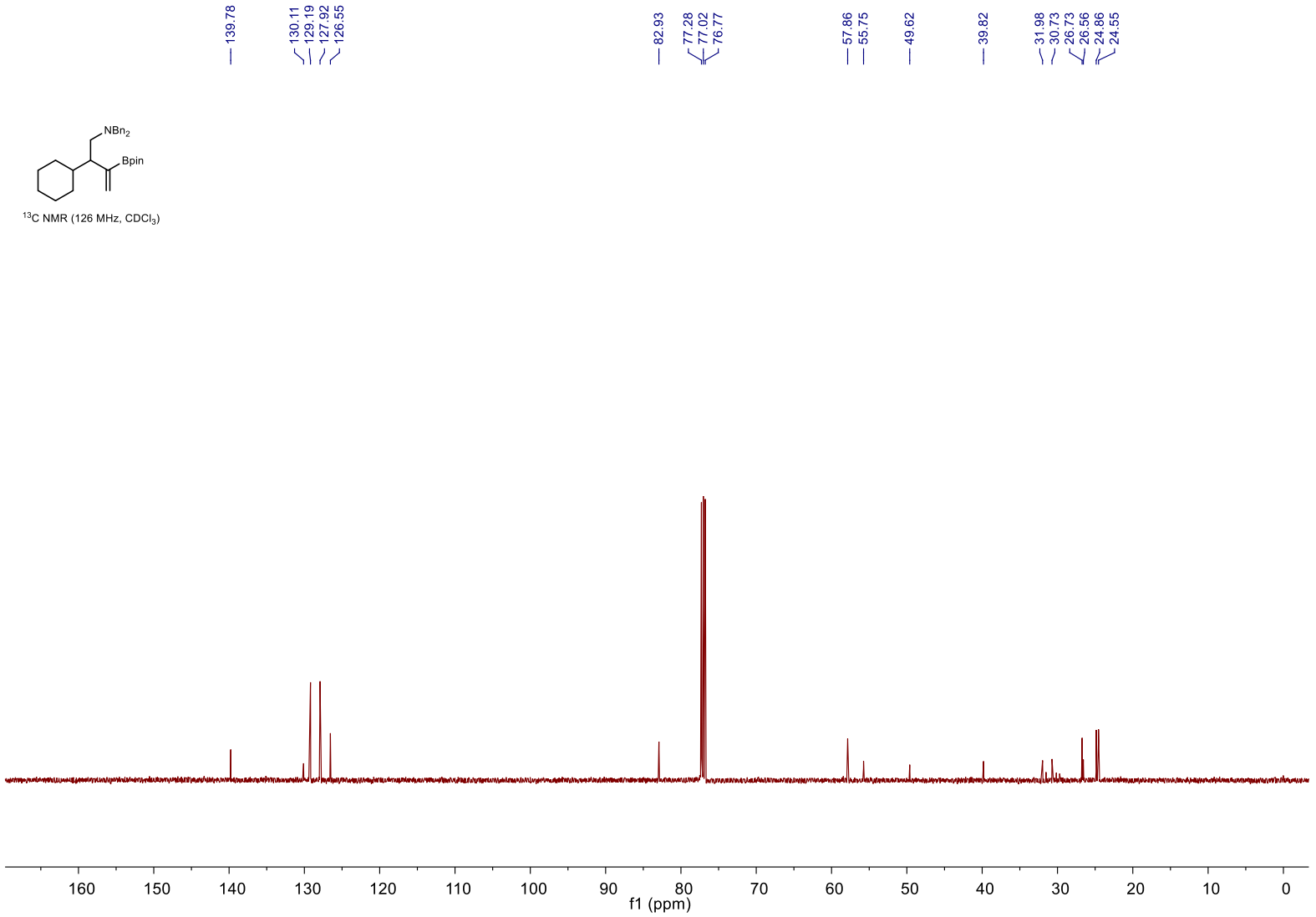

22.41
Bpin
Bn2N
S
S
11B NMR (128 MHz, CDCl3)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

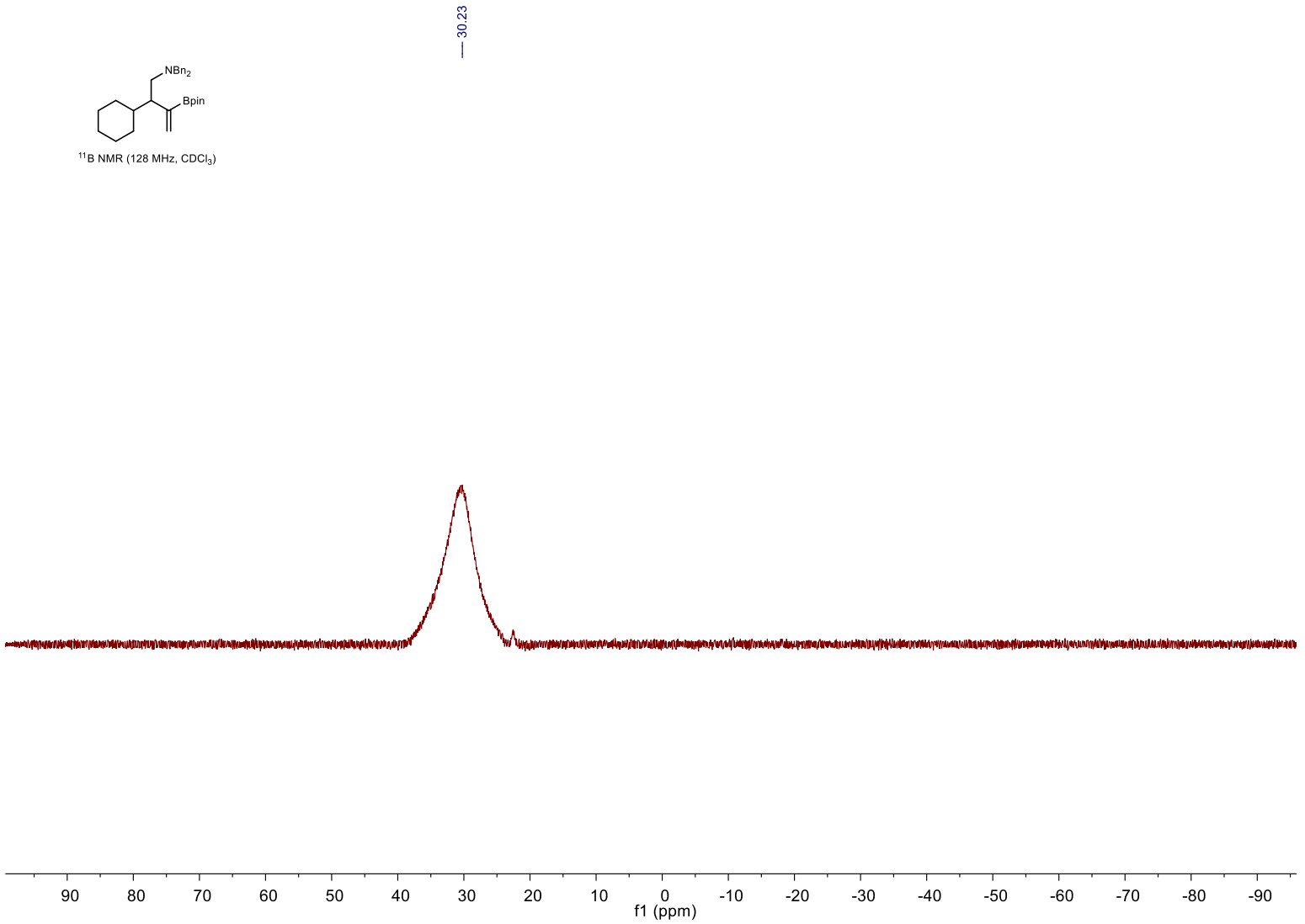

7.24
7.23
7.22
7.22
7.21
7.19
7.18
7.18
7.16
7.16
7.14
7.10
7.09
7.08
5.81
5.81
5.49
5.48
3.89
3.87
3.85
3.72
3.69
3.42
3.39
2.93
2.91
2.90
2.89
2.89
2.88
2.87
2.85
1.17
1.13
0.00
NBn2
Bpin
1H NMR (500 MHz, CDCl3)
13.69
2.01
1.00
1.00
1.00
2.04
2.02
2.07
6.01
6.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

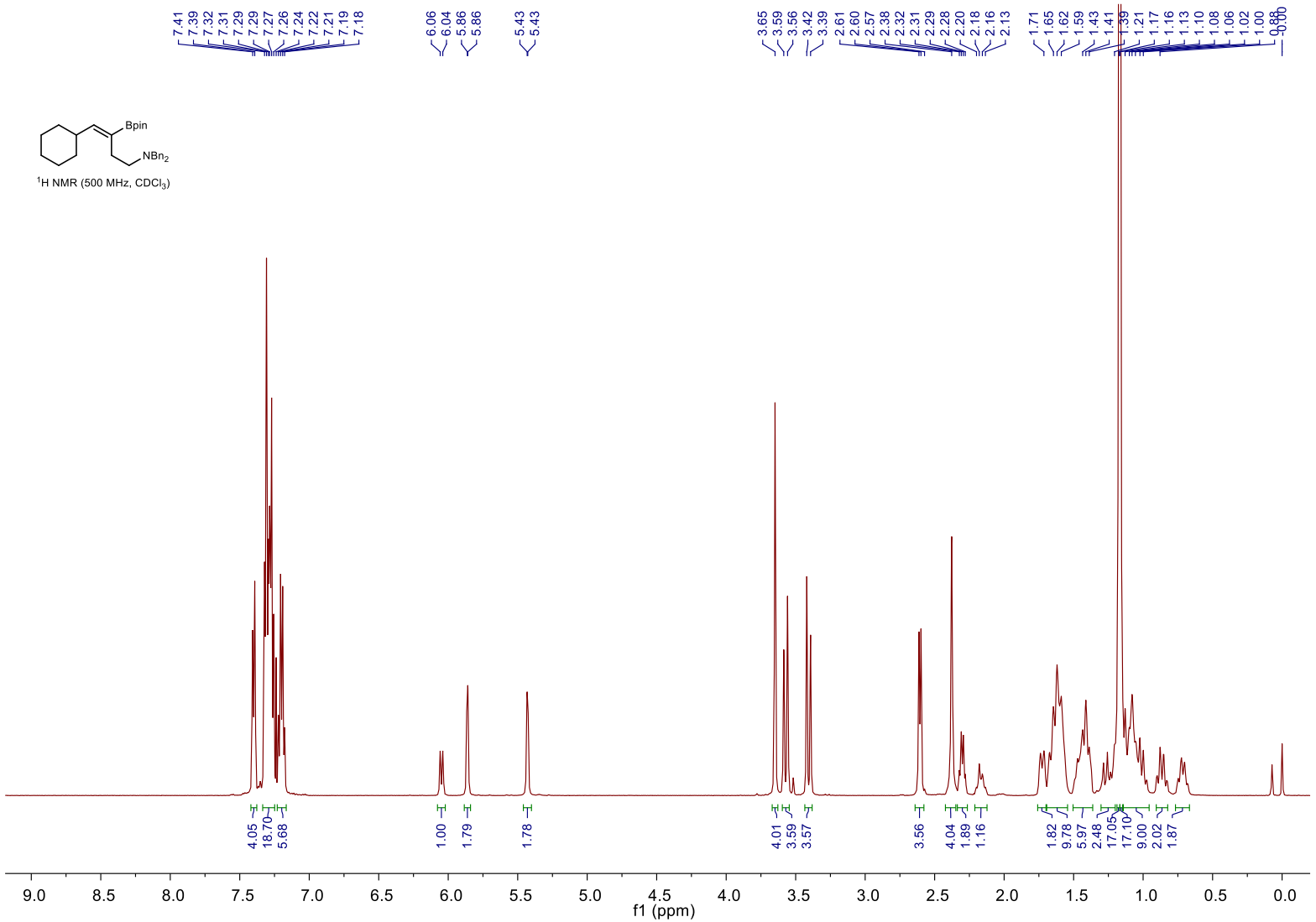

143.11
139.55
129.07
128.93
128.78
127.96
127.78
126.61
125.80
83.34
77.30
77.05
76.79
58.07
57.54
48.53
24.72
24.63
NBn2
Bpin
13C NMR (126 MHz, CDCl3)
129
128
127
126
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

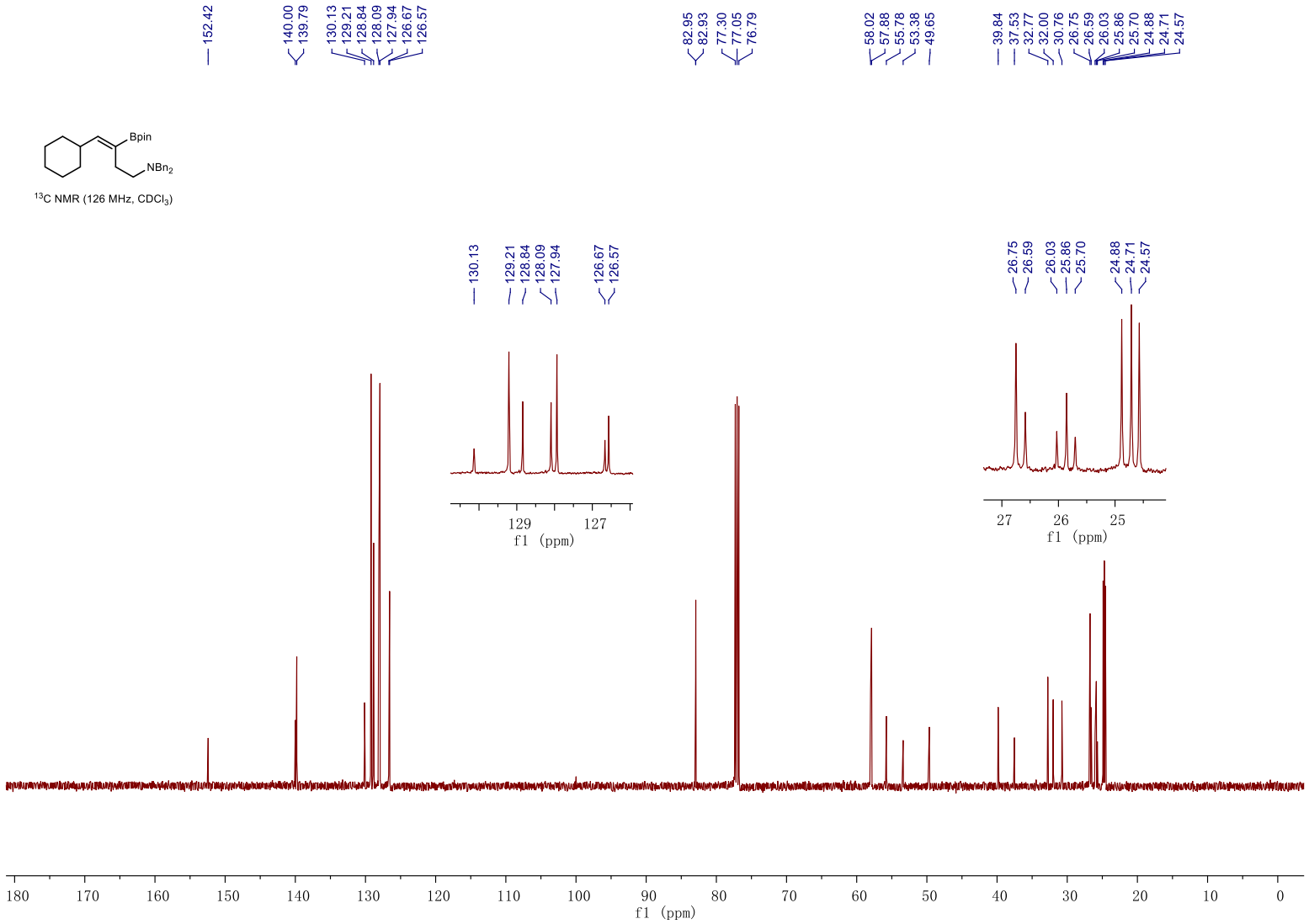

30.63
NBn2
Bpin
11B NMR (128 MHz, CDCl3)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

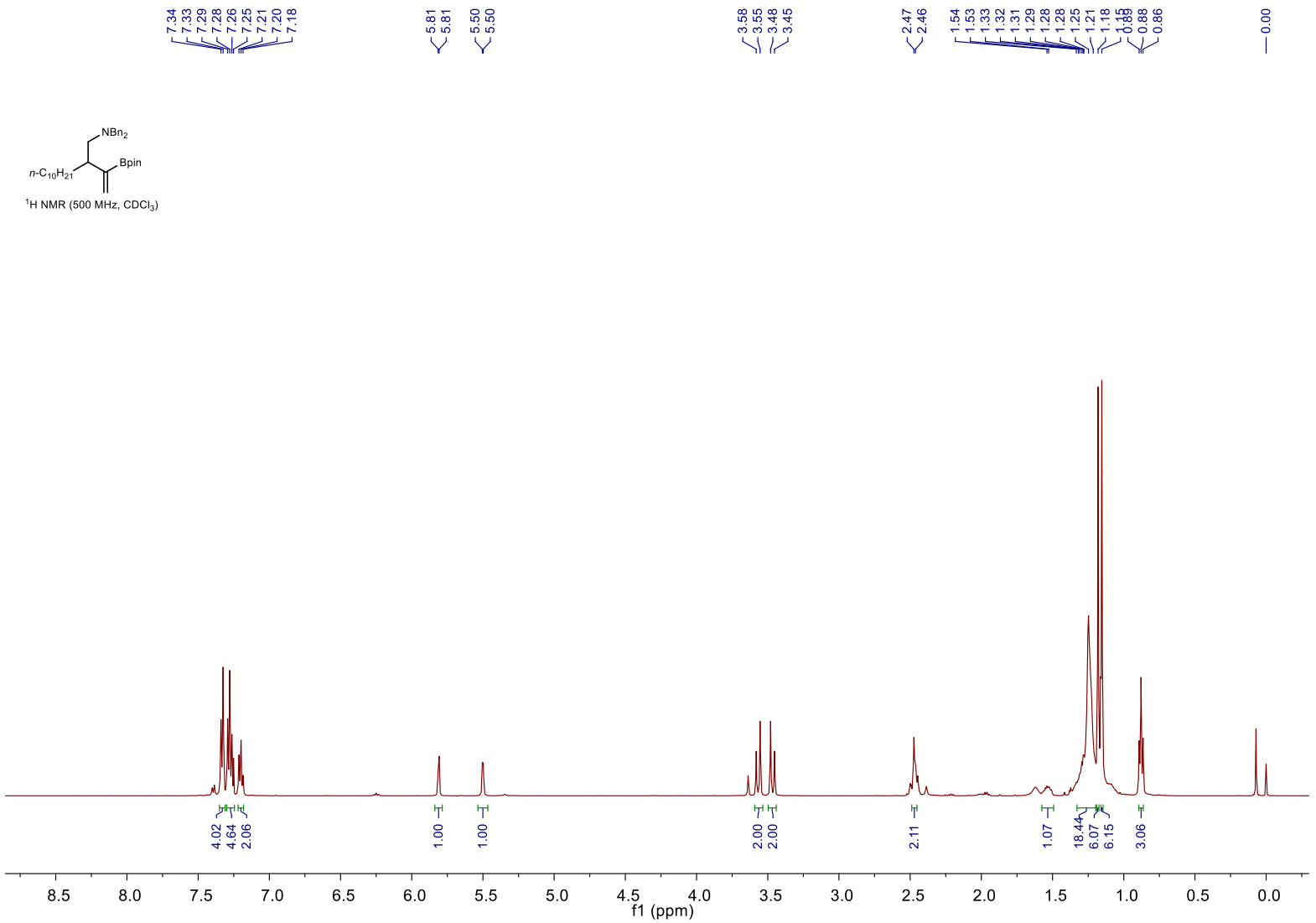

7.32
7.31
7.29
7.27
7.26
7.21
7.21
7.19
7.18
7.18
5.86
5.86
5.43
5.43
3.59
3.56
3.42
3.39
2.62
2.61
2.60
2.60
2.32
2.31
2.29
2.28
1.71
1.67
1.65
1.61
1.60
1.58
1.57
1.47
1.41
1.38
1.37
1.18
1.17
1.08
1.06
0.88
0.87
0.86
0.00
NBn2
Bpin
1H NMR (500 MHz, CDCl3)
4.02
4.76
2.01
1.01
1.00
2.01
2.02
2.02
1.00
4.31
3.34
6.02
6.02
2.06
1.57
1.08
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
f1 (ppm)

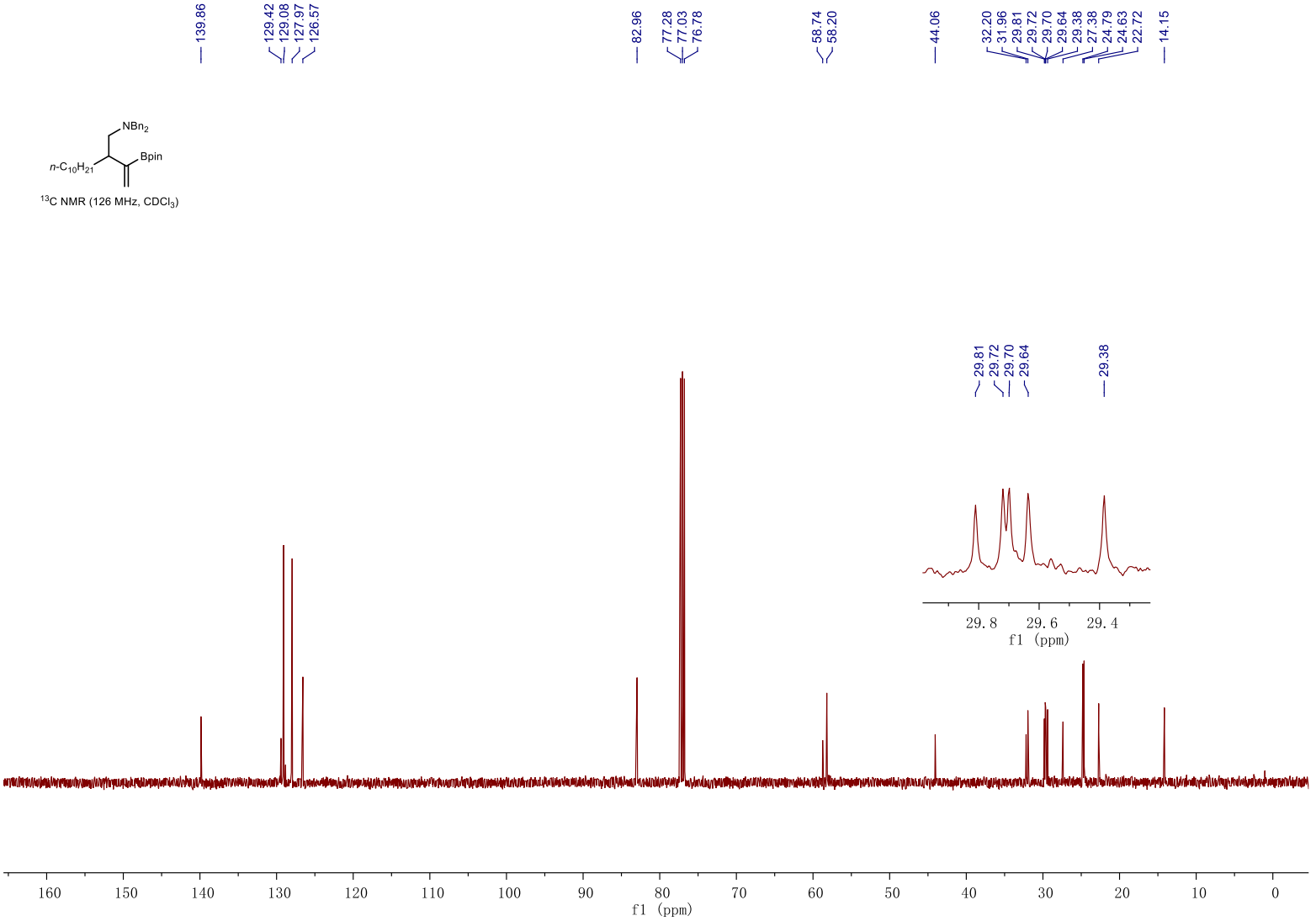

139.78
130.11
129.19
127.92
126.55
82.93
77.28
77.02
76.77
57.86
55.75
49.62
39.82
31.98
30.73
26.73
26.56
24.86
24.55
NBn2
Bpin
13C NMR (126 MHz, CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

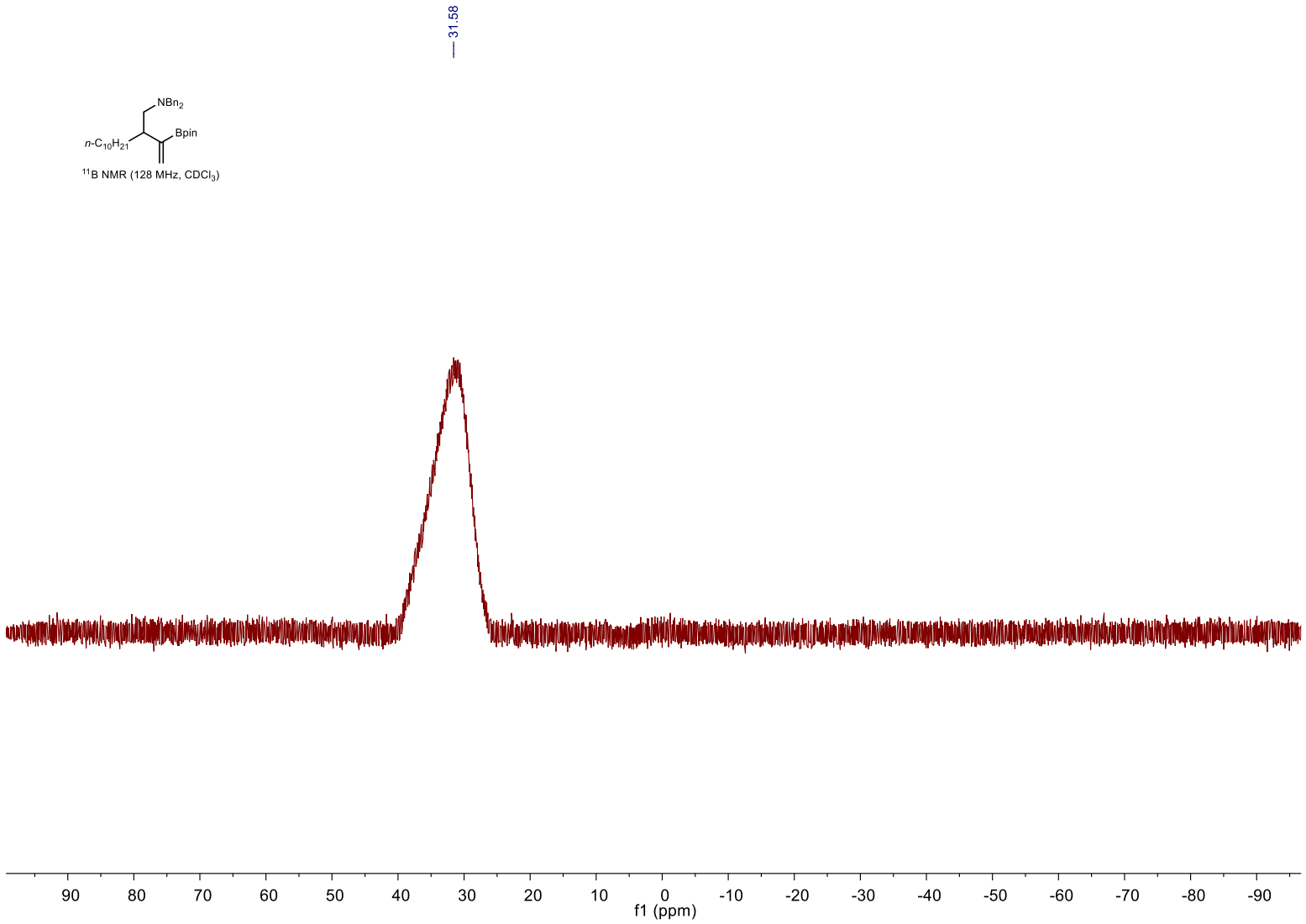

30.23
NBn2
Bpin
11B NMR (128 MHz, CDCl3)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

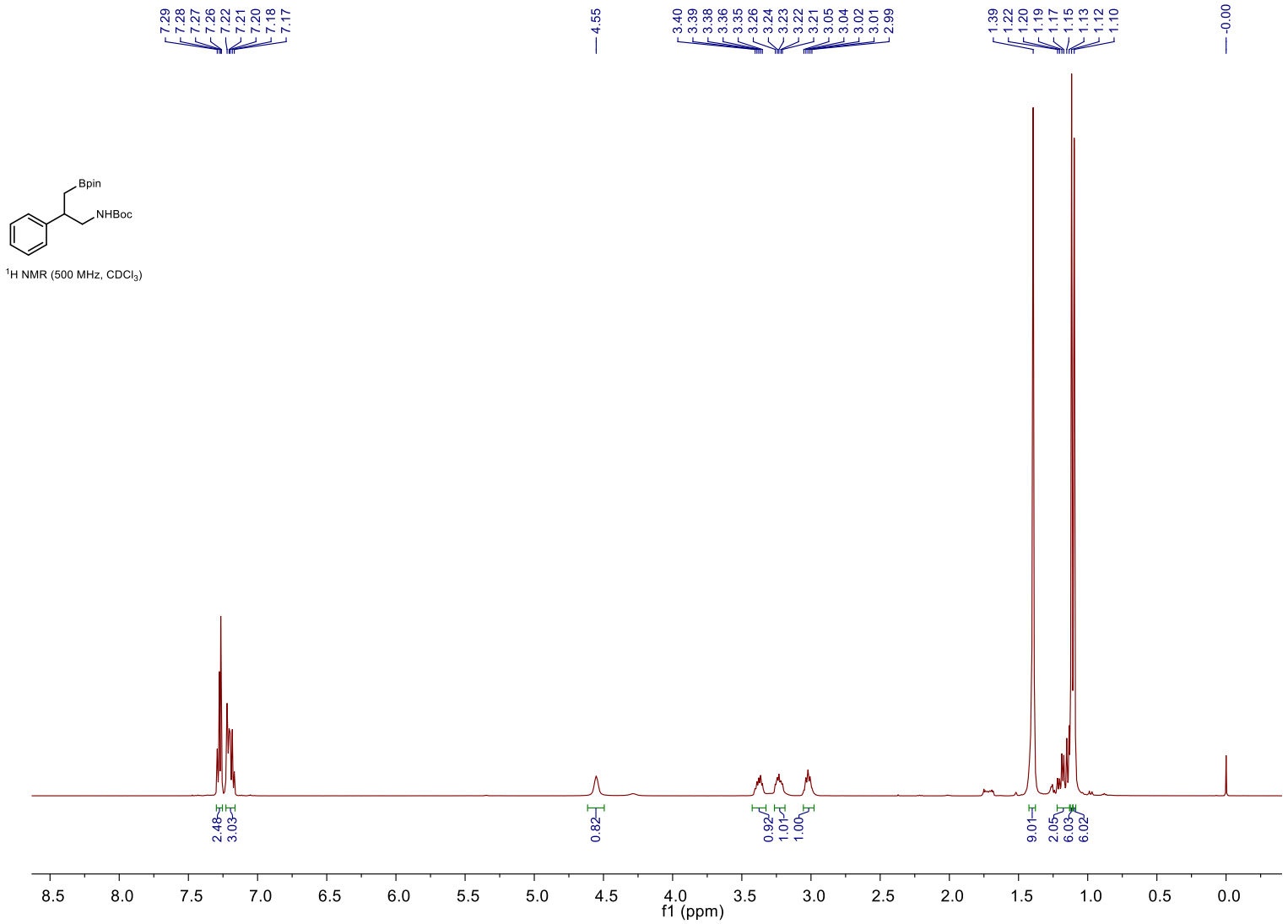

Bpin
NBn2
1H NMR (500 MHz, CDCl3)
f1 (ppm)

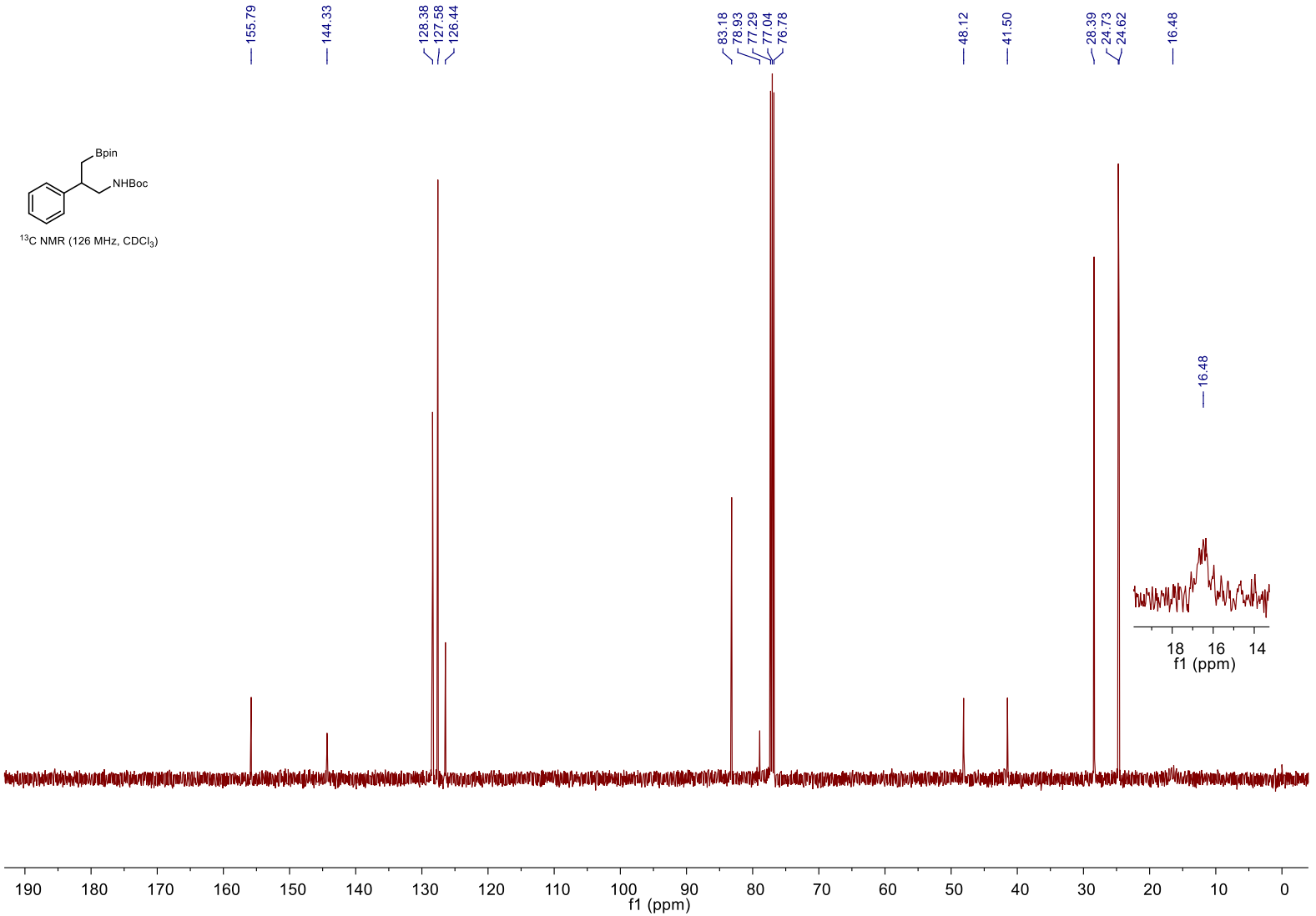

152.42
140.00
139.79
130.13
129.21
128.84
128.09
127.94
126.67
126.57
82.95
82.93
77.30
77.05
76.79
58.02
57.88
55.78
53.38
49.65
39.84
37.53
32.77
32.00
30.76
26.75
26.59
26.03
25.86
25.70
24.88
24.71
24.57
Bpin
NBn2
13C NMR (126 MHz, CDCl3)
f1 (ppm)
f1 (ppm)
f1 (ppm)

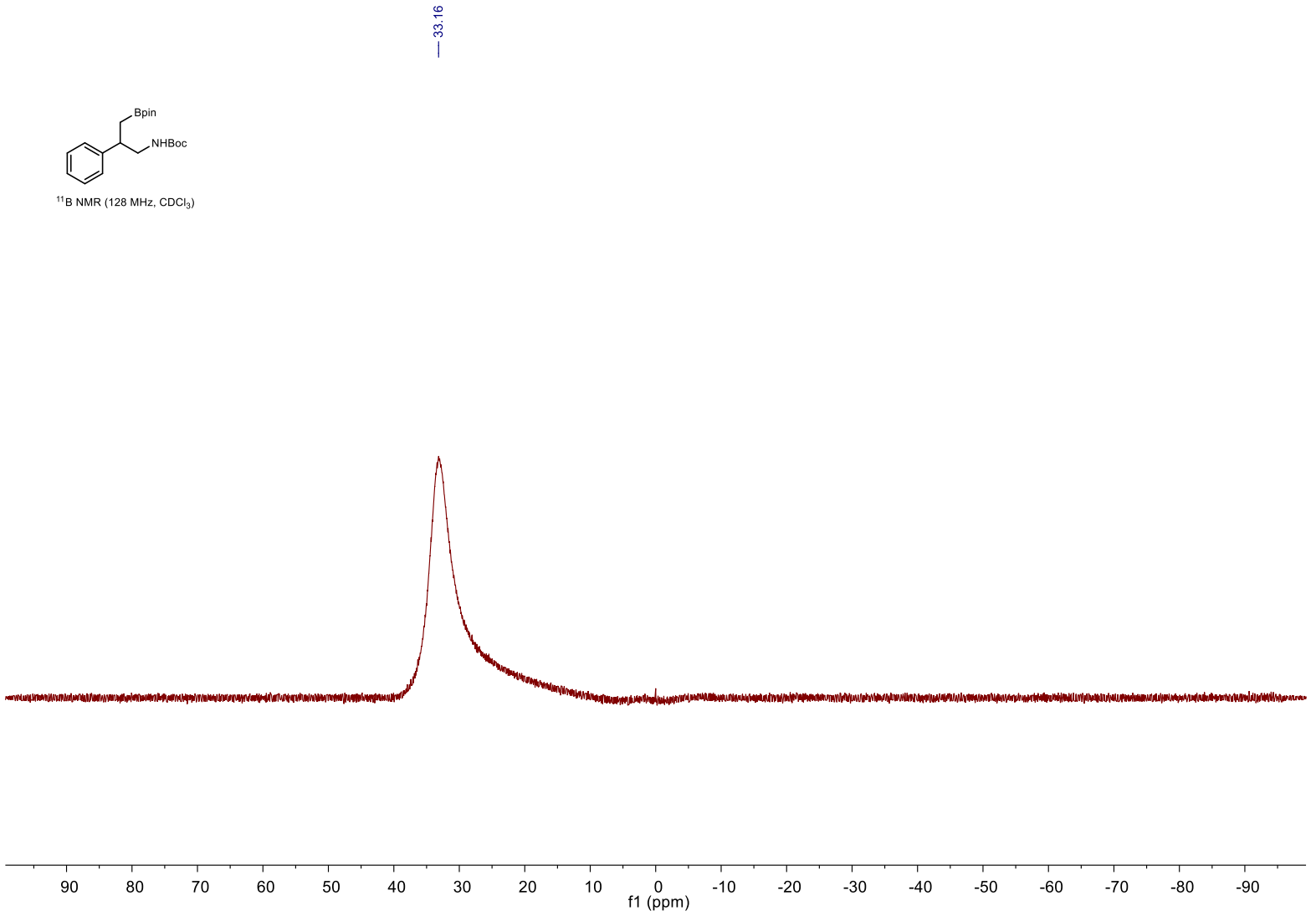

7.34
7.33
7.29
7.28
7.26
7.25
7.21
7.20
7.18
5.81
5.81
5.50
5.50
3.58
3.55
3.48
3.45
2.47
2.46
1.54
1.53
1.33
1.32
1.31
1.29
1.28
1.28
1.25
1.21
1.18
1.15
0.89
0.88
0.86
0.00
NBn2
Bpin
n-C10H21
1H NMR (500 MHz, CDCl3)
4.02
4.64
2.06
1.00
1.00
2.00
2.00
2.11
1.07
18.44
6.07
6.15
3.06
8.5
8.0
7.5
7.0
6.5
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
f1 (ppm)

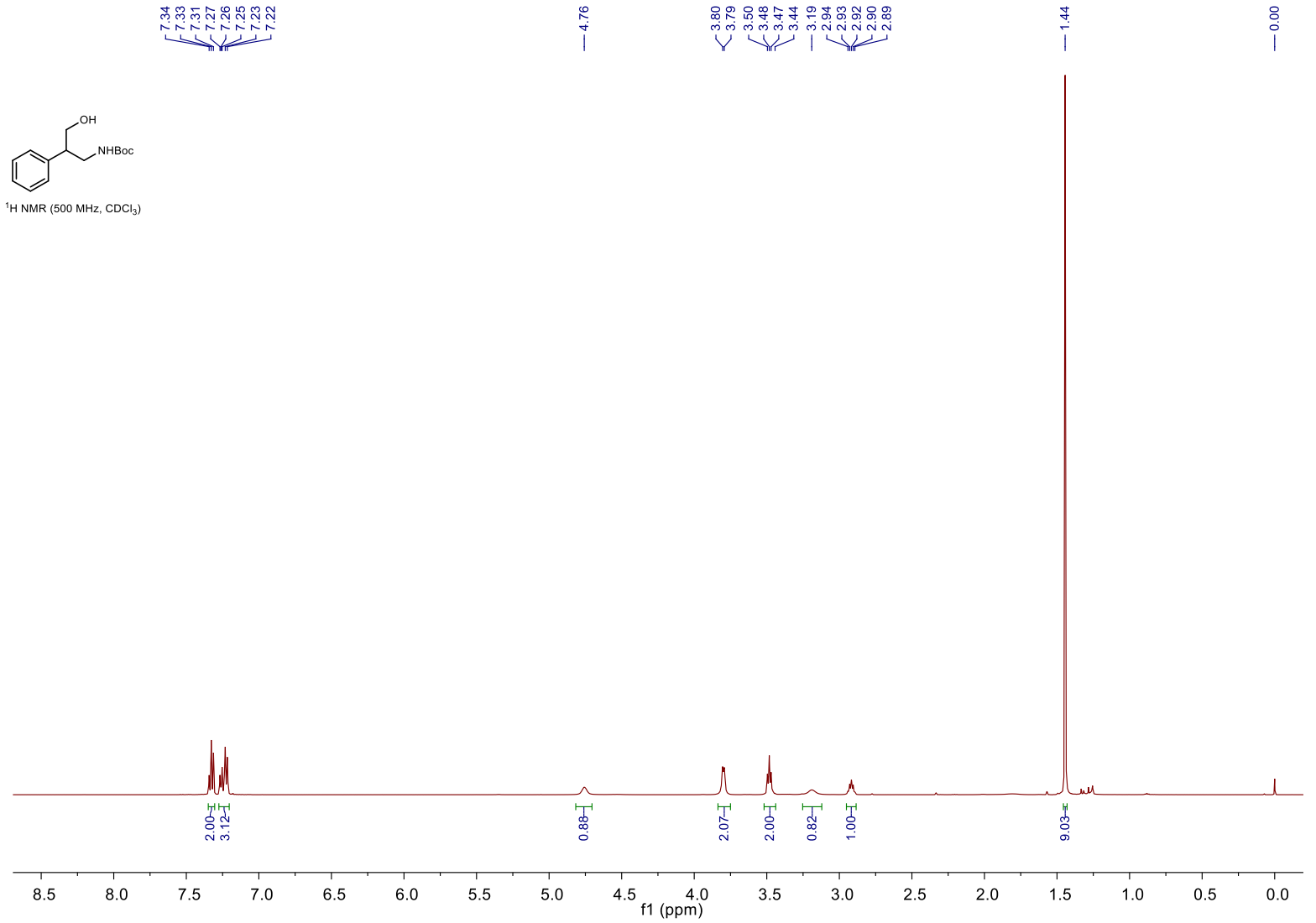

139.86
129.42
129.08
127.97
126.57
82.96
77.28
77.03
76.78
58.74
58.20
44.06
32.20
31.96
29.81
29.72
29.70
29.64
29.38
27.38
24.79
24.63
22.72
14.15
NBn2
Bpin
n-C10H21
13C NMR (126 MHz, CDCl3)
29.81
29.72
29.70
29.64
29.38
29.8
29.6
29.4
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

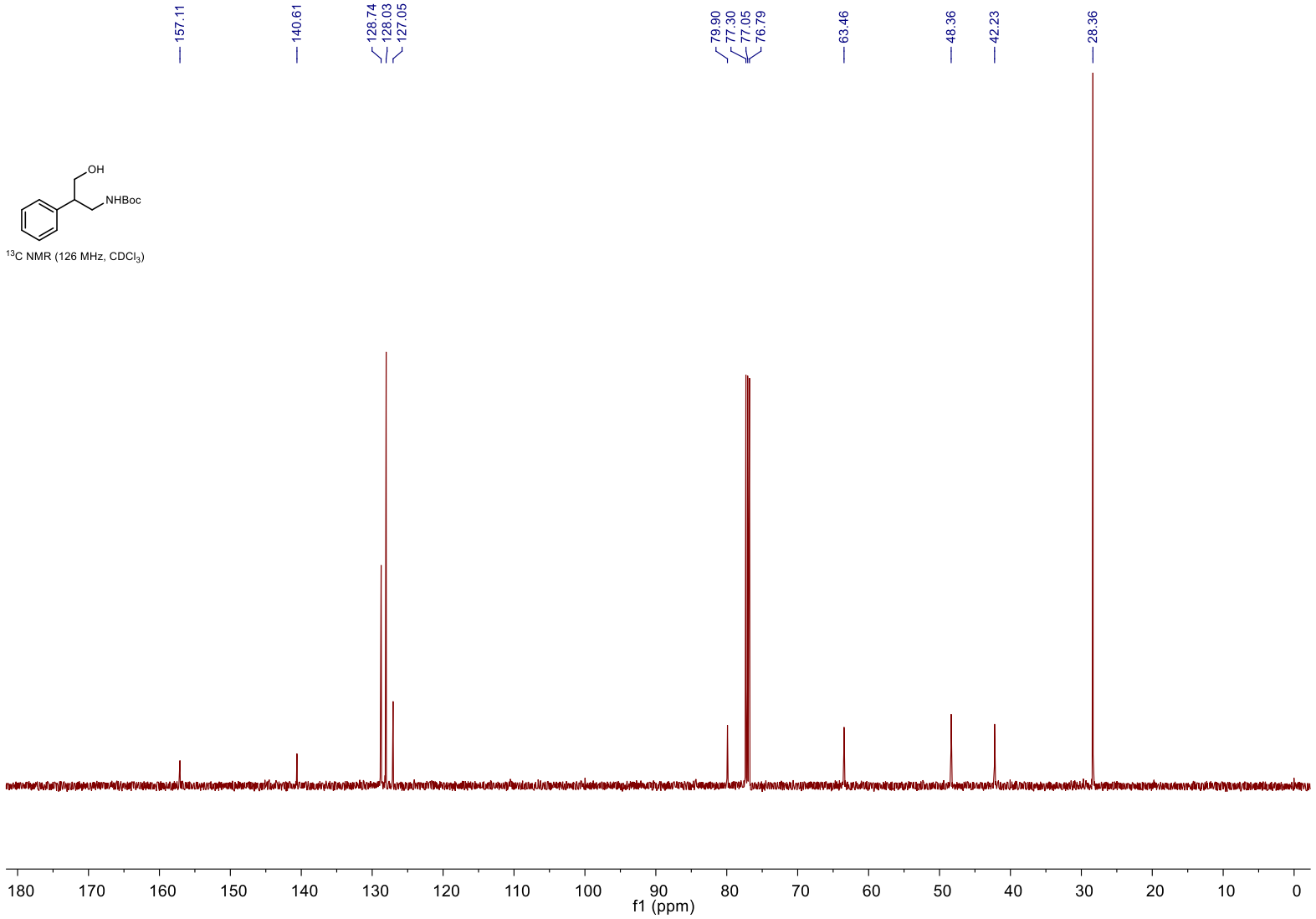

31.58
NBn2
n-C10H21
Bpin
11B NMR (128 MHz, CDCl3)
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

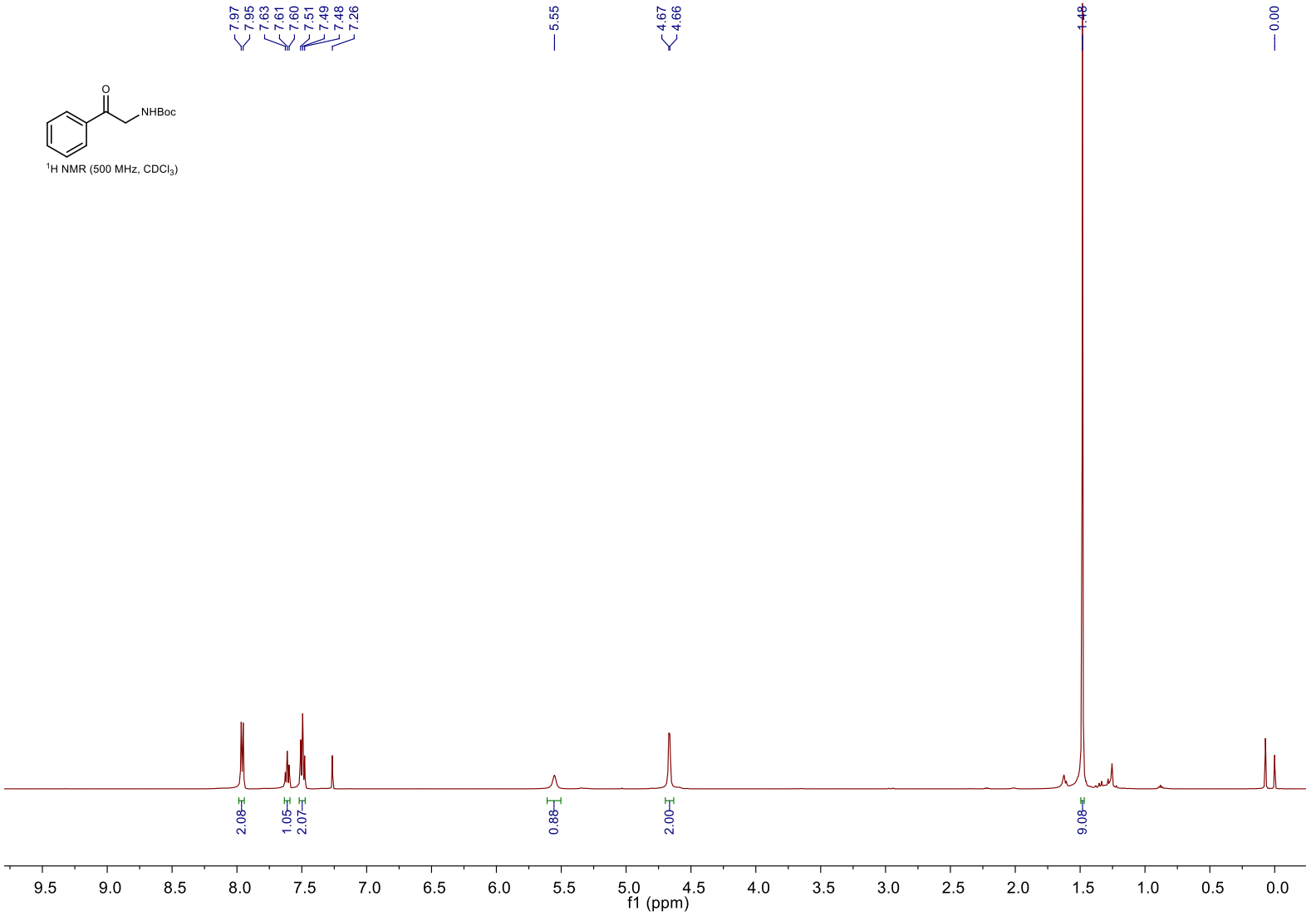

7.29
7.28
7.27
7.26
7.22
7.21
7.20
7.18
7.17
4.55
3.40
3.39
3.38
3.36
3.35
3.26
3.24
3.23
3.22
3.21
3.05
3.04
3.02
3.01
2.99
1.39
1.22
1.20
1.19
1.17
1.15
1.13
1.12
1.10
-0.00
Bpin
NHBoc
1H NMR (500 MHz, CDCl3)
2.48
3.03
0.82
0.92
1.01
1.00
9.01
2.05
6.03
6.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

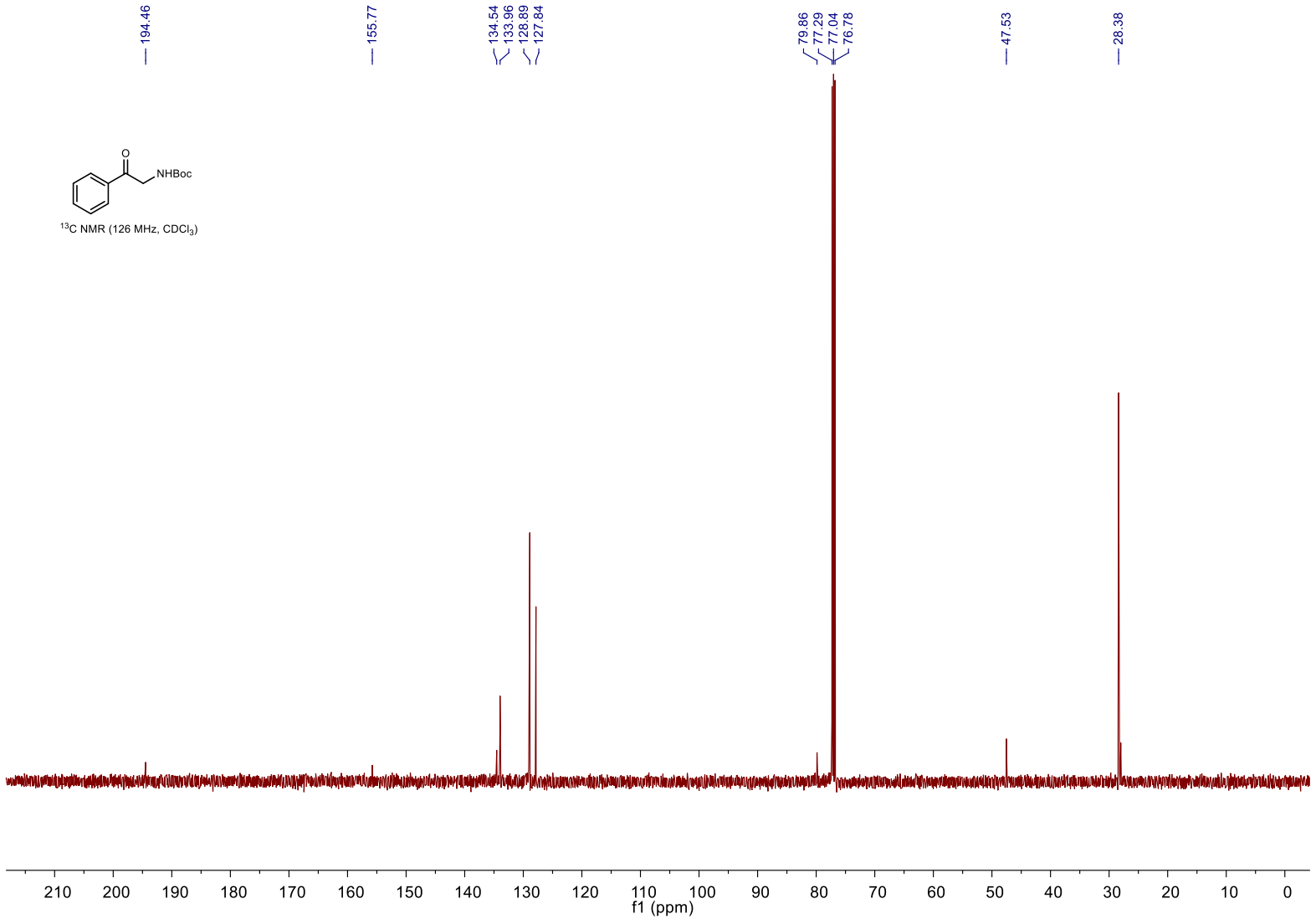

155.79
144.33
128.38
127.58
126.44
83.18
78.93
77.29
77.04
76.78
48.12
41.50
28.39
24.73
24.62
16.48
Bpin
NHBoc
^{13}C NMR (126 MHz, CDCl$_3$)
16.48
18 16 14
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

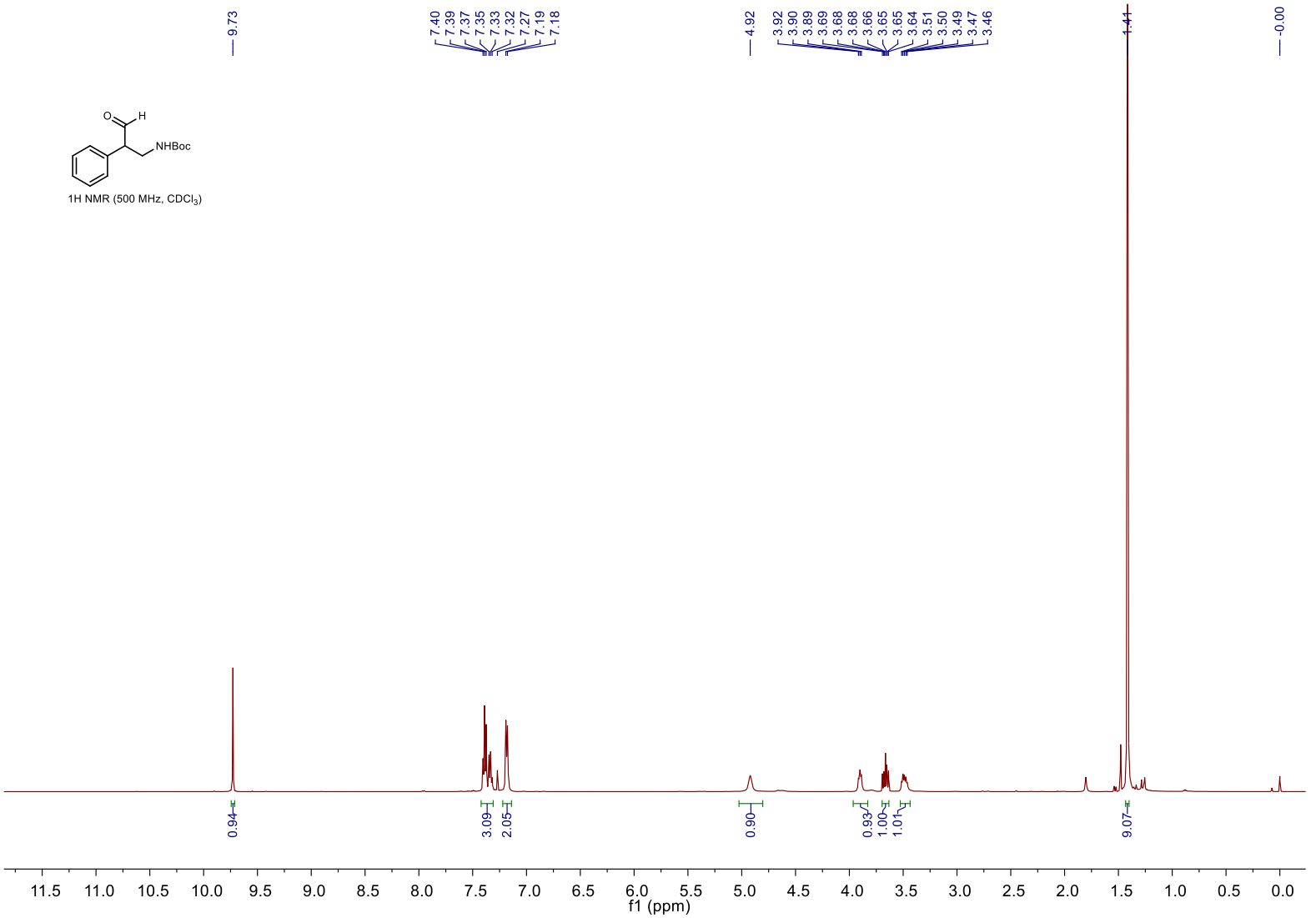

33.16
Bpin
NHBoc
^{11}B NMR (128 MHz, $CDCl_3$)
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

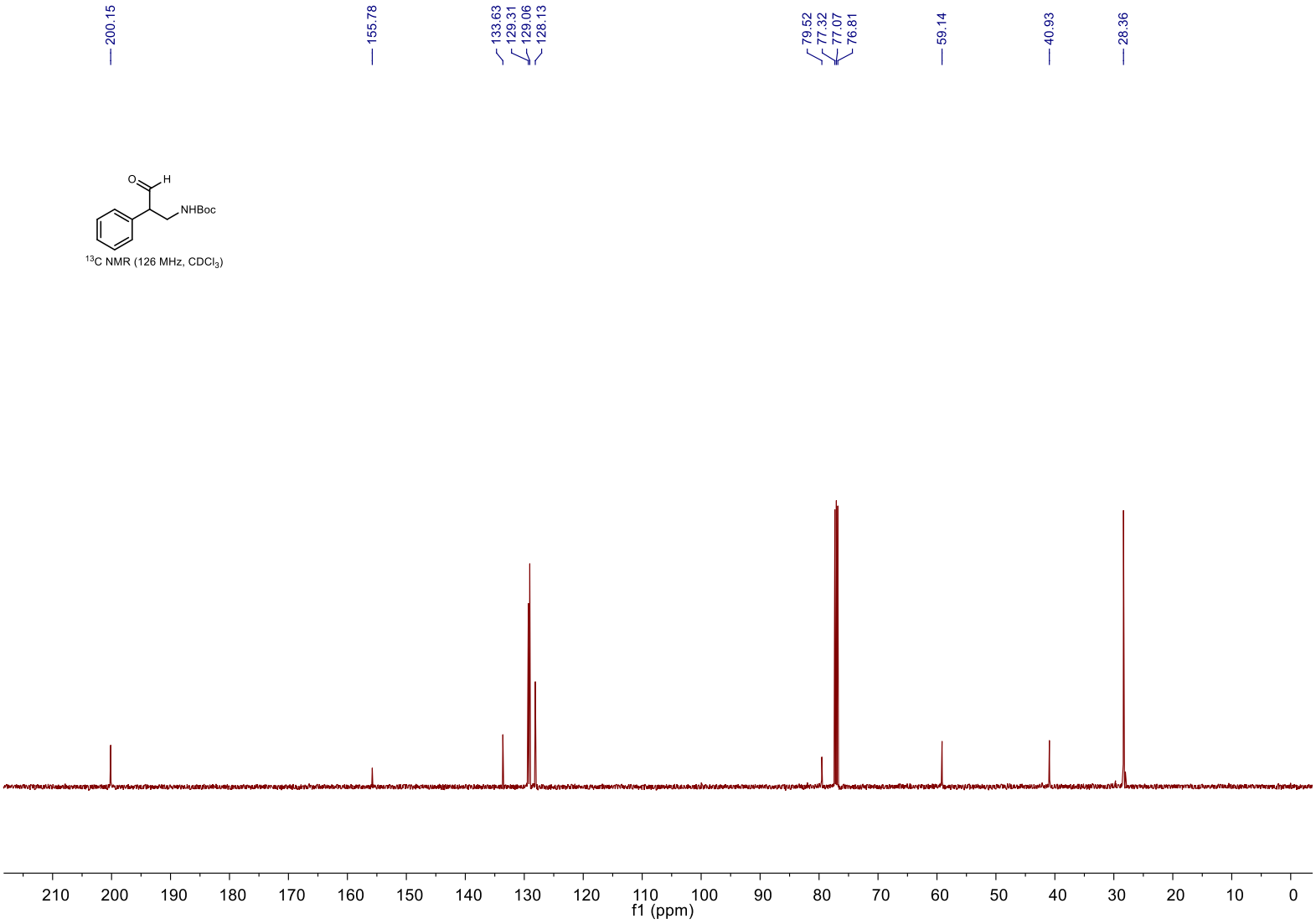

7.34
7.33
7.31
7.27
7.26
7.25
7.23
7.22
4.76
3.80
3.79
3.50
3.48
3.47
3.44
3.19
2.94
2.93
2.92
2.90
2.89
1.44
0.00
OH
NHBoc
1H NMR (500 MHz, CDCl3)
2.00
3.12
0.88
2.07
2.00
0.82
1.00
9.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

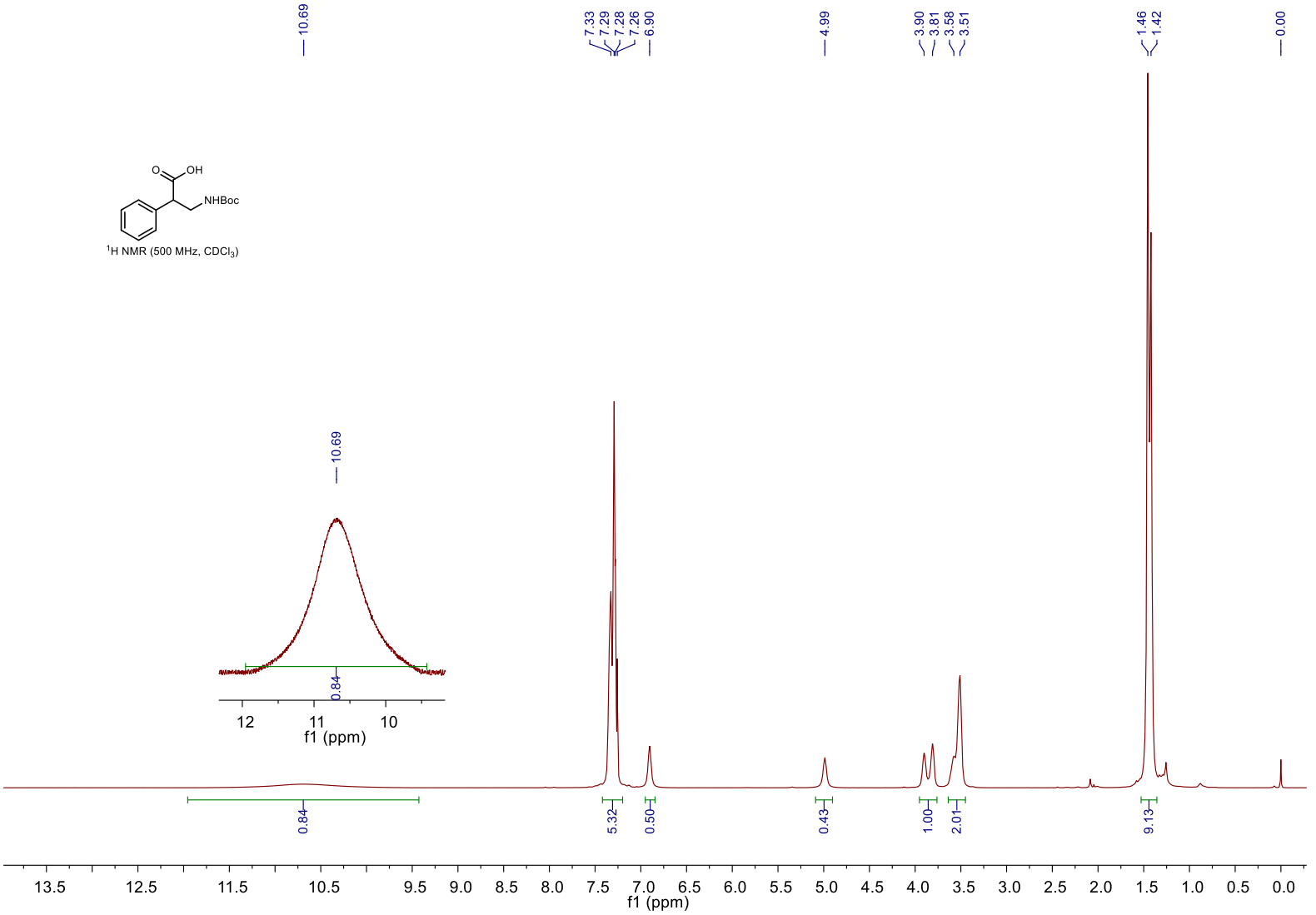

157.11
140.61
128.74
128.03
127.05
79.90
77.30
77.05
76.79
63.46
48.36
42.23
28.36
OH
NHBoc
^{13}C NMR (126 MHz, $CDCl_3$)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

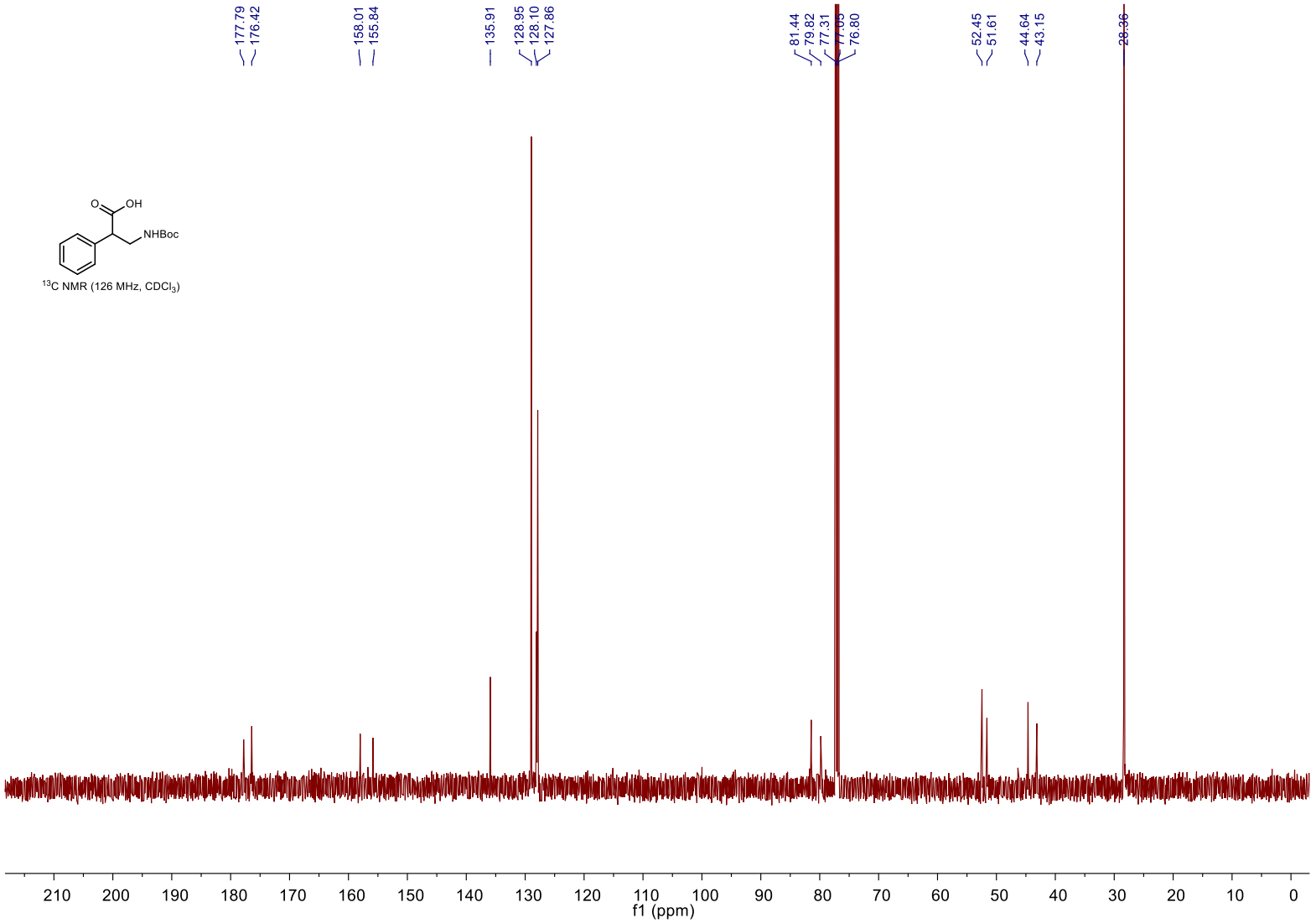

7.97
7.95
7.63
7.61
7.60
7.51
7.49
7.48
7.26
5.55
4.67
4.66
1.48
0.00
O
NHBoc
^{1}H NMR (500 MHz, CDCl$_3$)
2.08
1.05
2.07
0.88
2.00
9.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

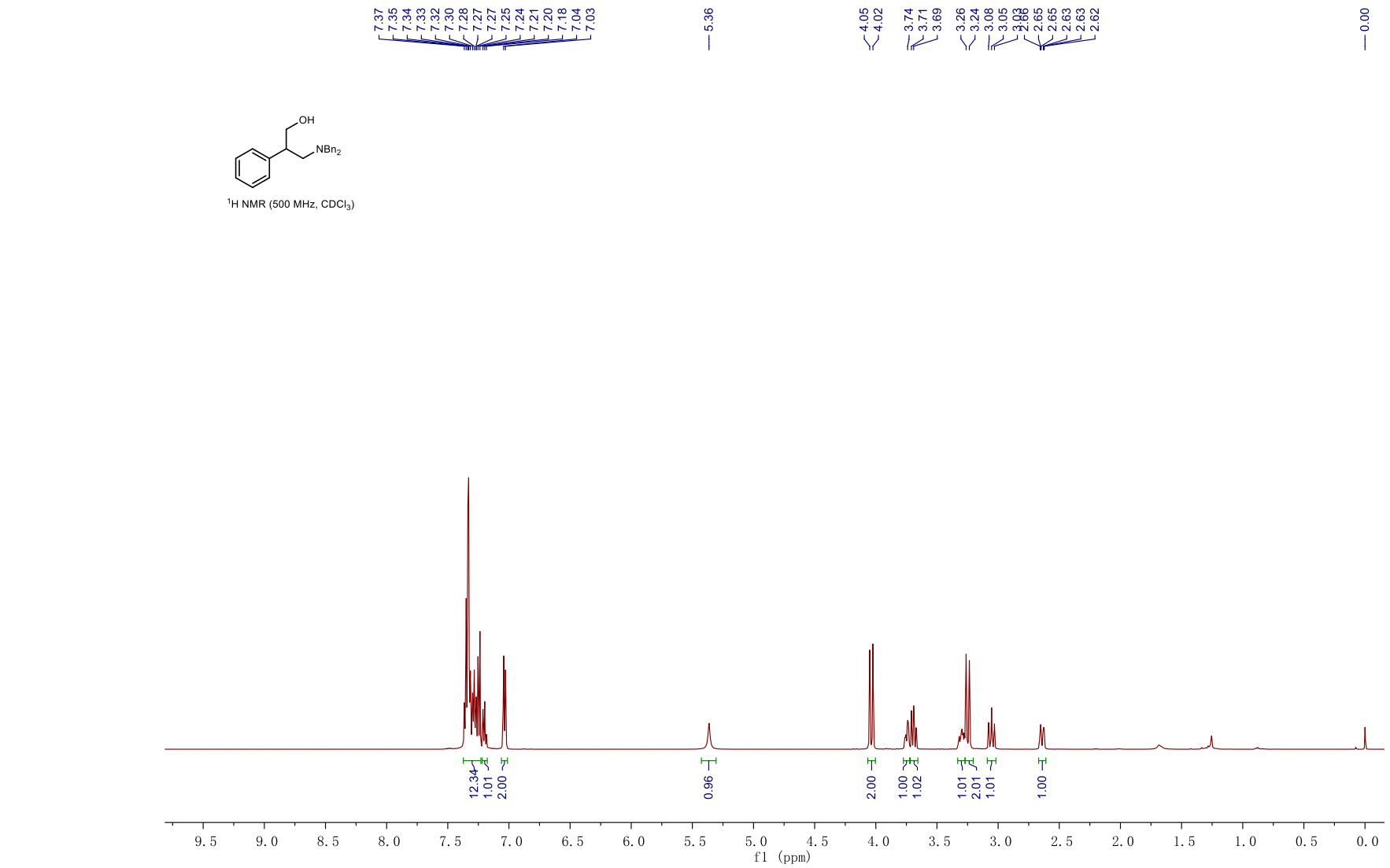

194.46
155.77
134.54
133.96
128.89
127.84
79.86
77.29
77.04
76.78
47.53
28.38
O
NHBoc
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

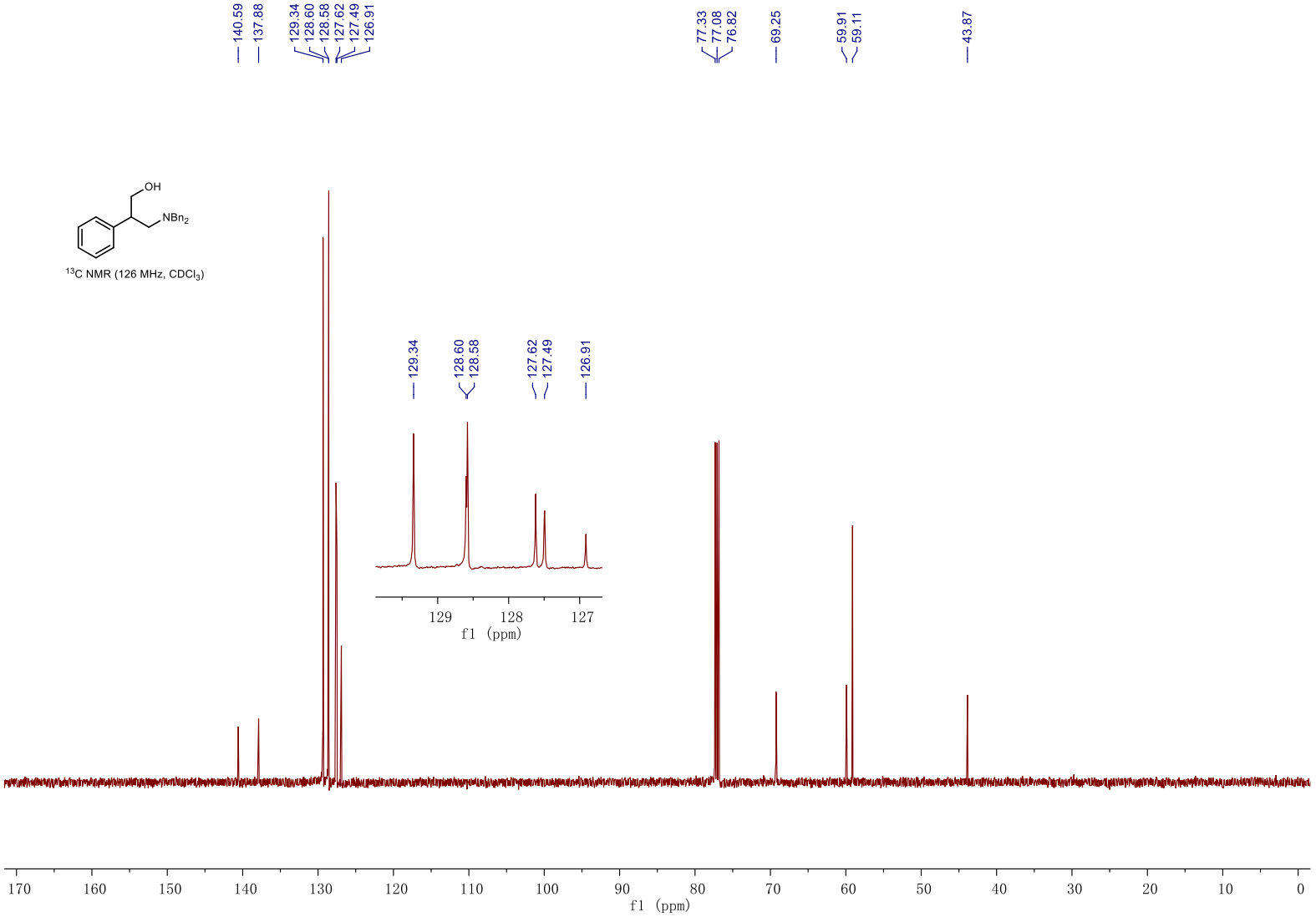

9.73
7.40
7.39
7.37
7.35
7.33
7.32
7.27
7.19
7.18
4.92
3.92
3.90
3.89
3.69
3.68
3.68
3.66
3.65
3.65
3.64
3.51
3.50
3.49
3.47
3.46
1.41
-0.00
O
H
NHBoc
1H NMR (500 MHz, CDCl3)
0.94
3.09
2.05
0.90
0.93
1.00
1.01
9.07
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

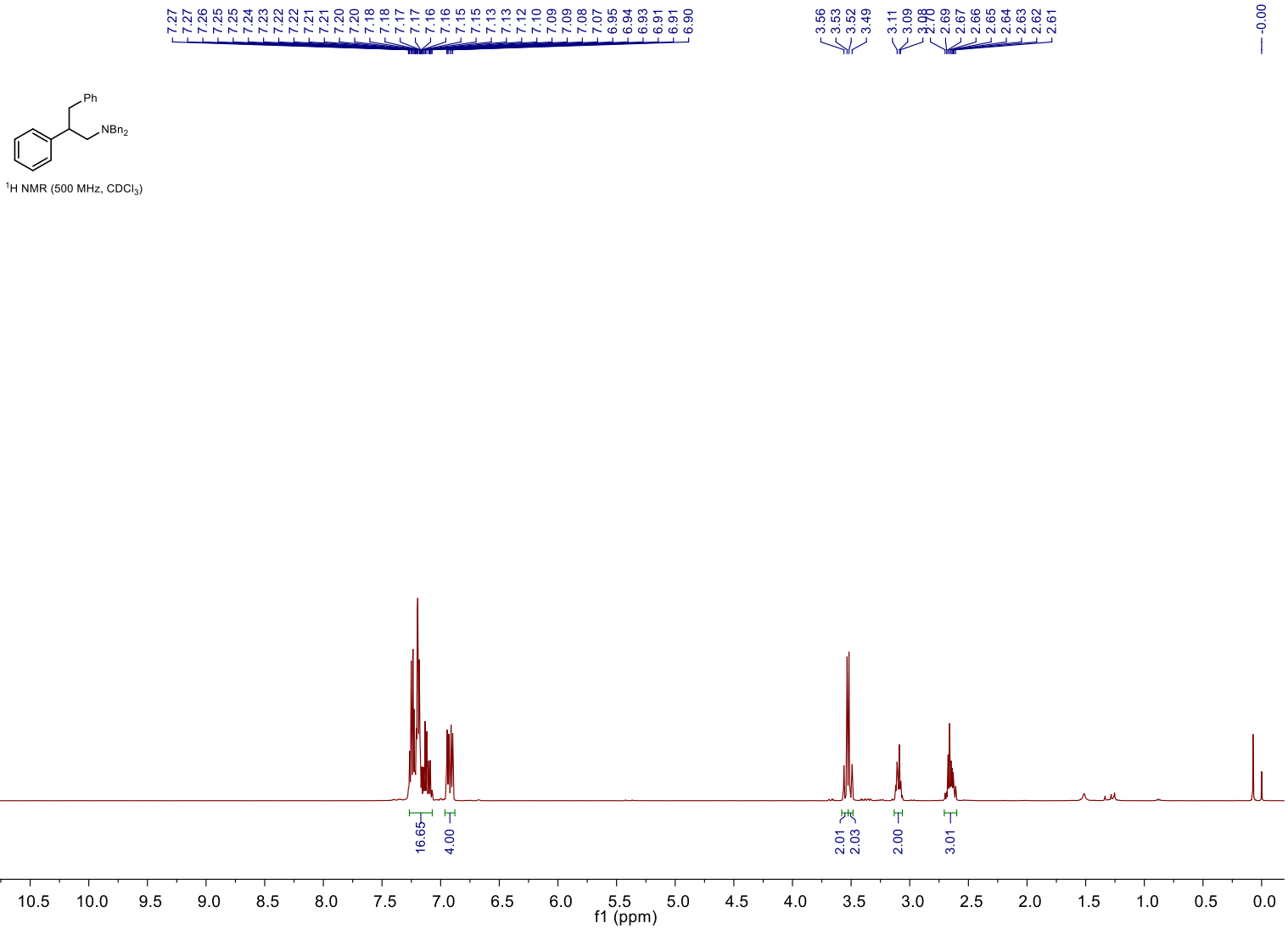

200.15
155.78
133.63
129.31
129.06
128.13
79.52
77.32
77.07
76.81
59.14
40.93
28.36
O
H
NHBoc
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

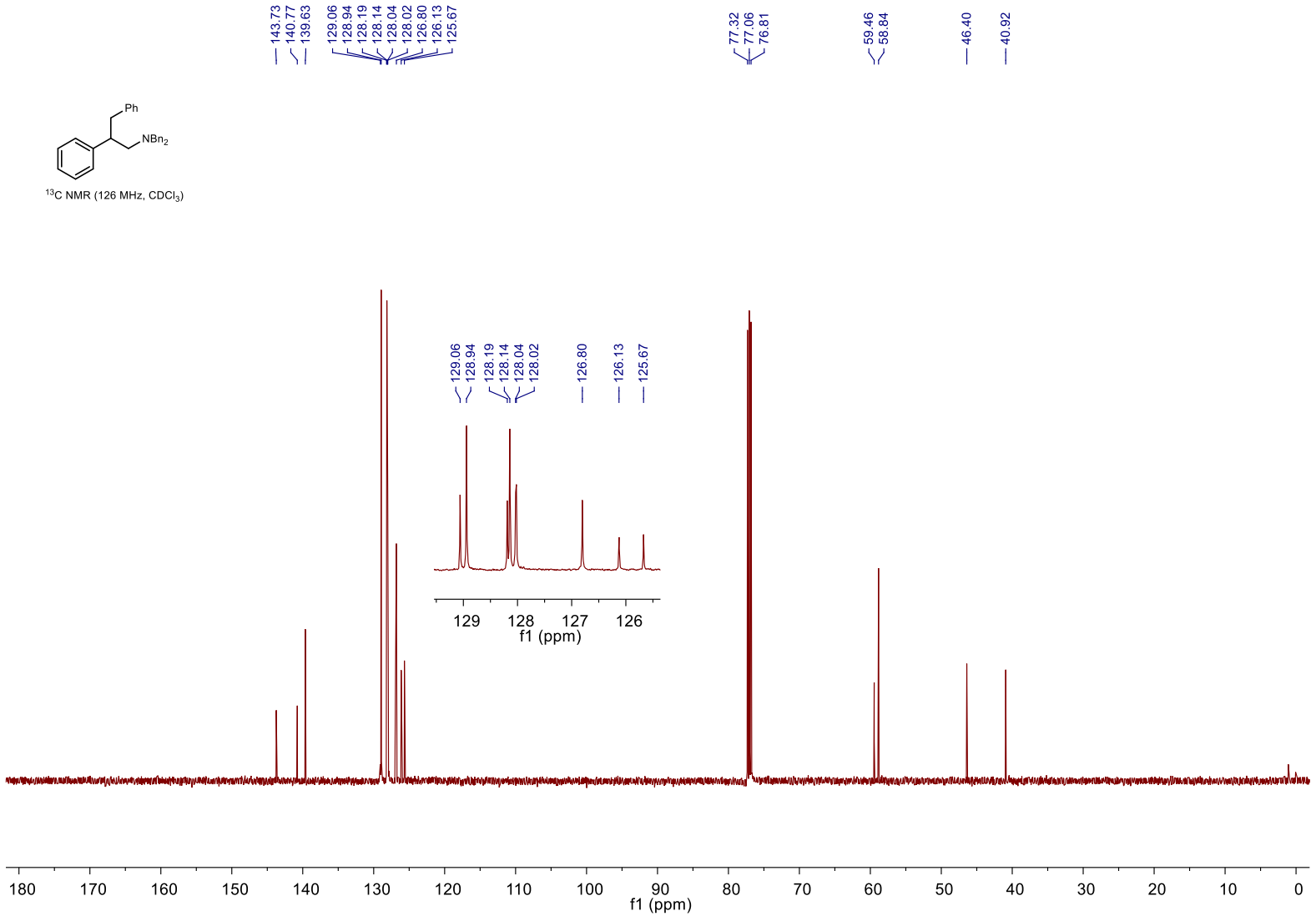

10.69
7.33
7.29
7.28
7.26
6.90
4.99
3.90
3.81
3.58
3.51
1.46
1.42
0.00
O
OH
NHBoc
1H NMR (500 MHz, CDCl3)
10.69
0.84
12
11
10
f1 (ppm)
0.84
5.32
0.50
0.43
1.00
2.01
9.13
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

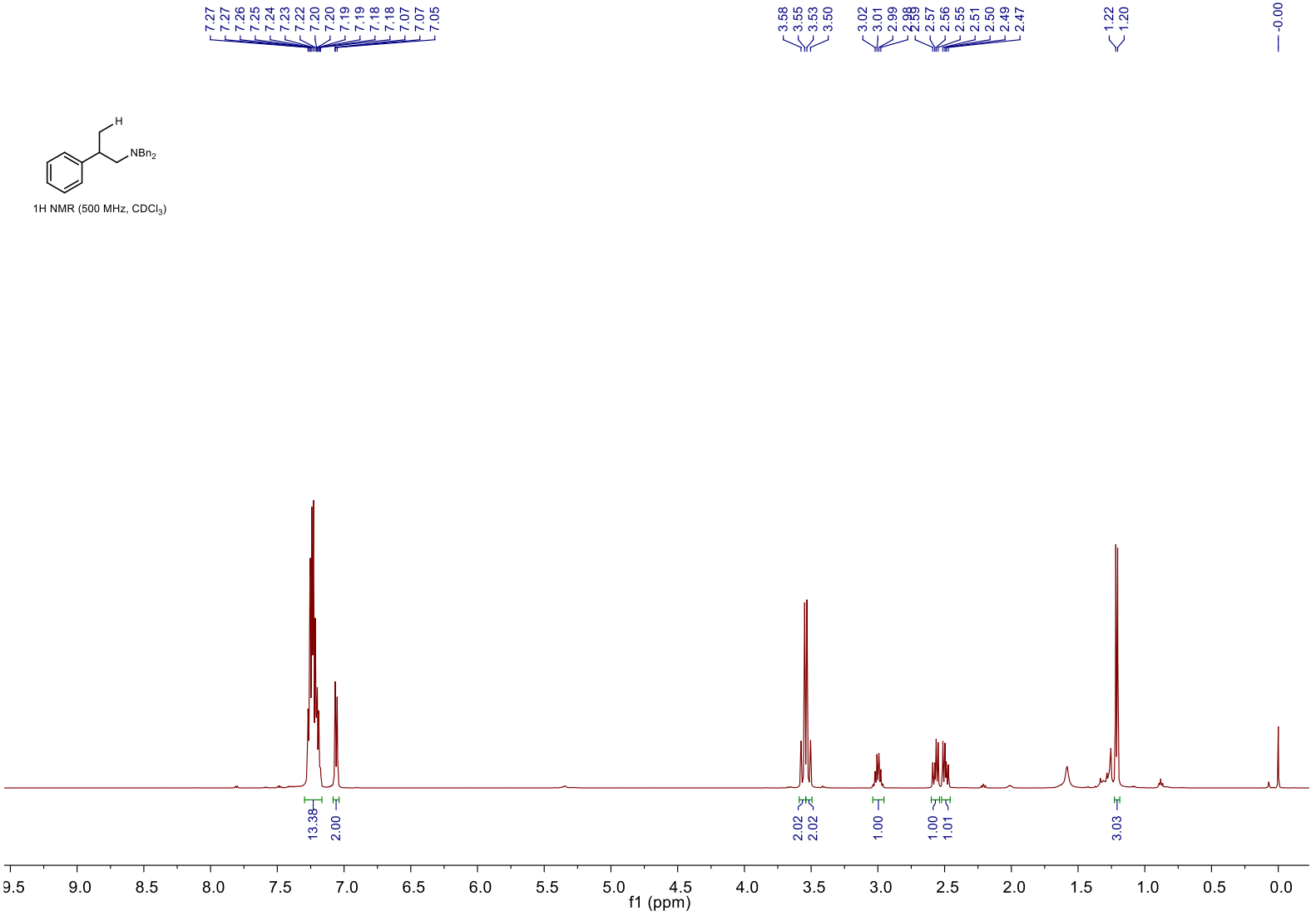

177.79
176.42
158.01
155.84
135.91
128.95
128.10
127.86
81.44
79.82
77.31
76.80
52.45
51.61
44.64
43.15
28.36
O
OH
NHBoc
13C NMR (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

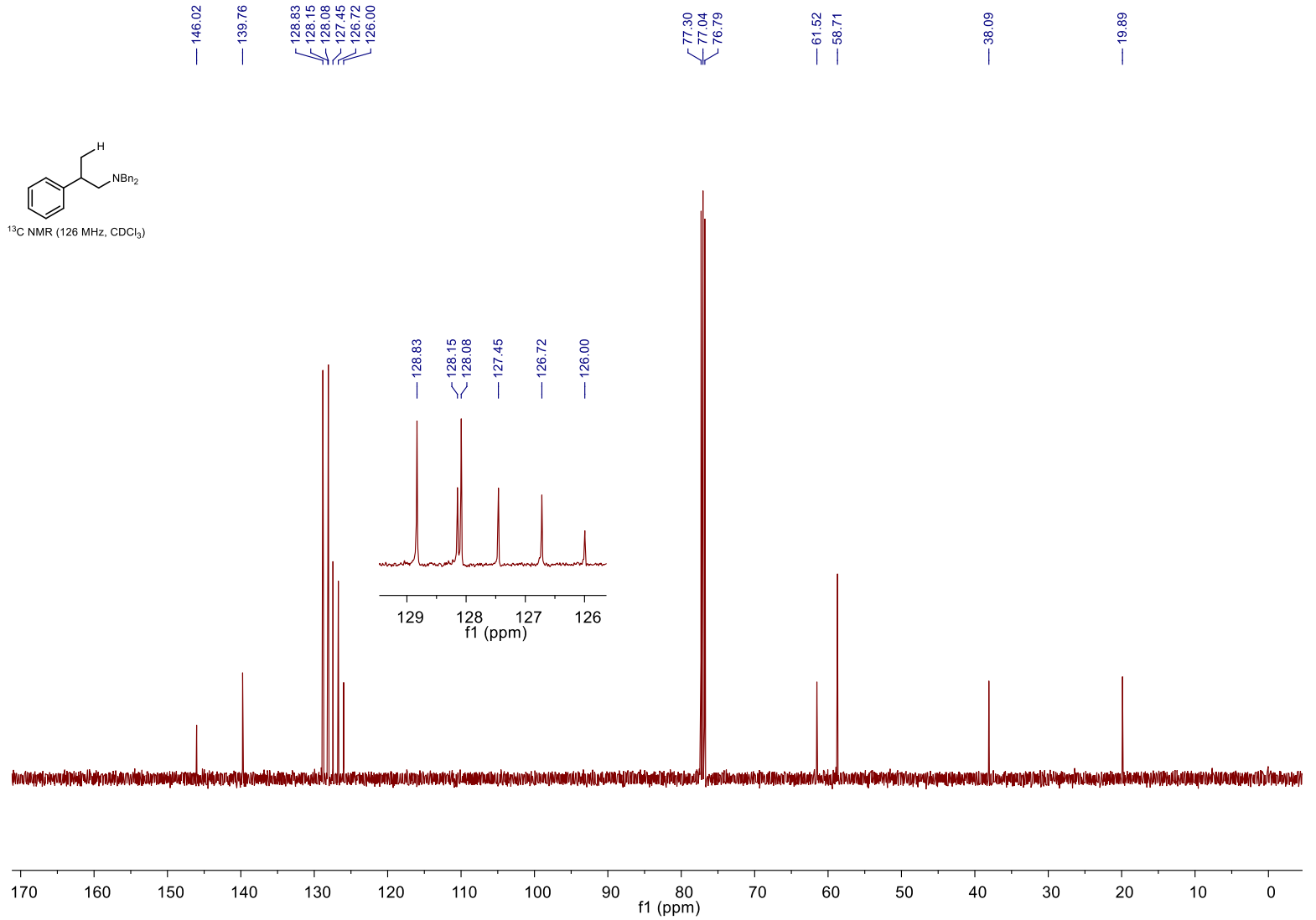

7.37
7.35
7.34
7.33
7.32
7.30
7.28
7.27
7.27
7.25
7.24
7.21
7.20
7.18
7.04
7.03
5.36
4.05
4.02
3.74
3.71
3.69
3.26
3.24
3.08
3.05
2.66
2.65
2.65
2.63
2.63
2.62
0.00
OH
NBn2
1H NMR (500 MHz, CDCl3)
12.34
1.01
2.00
0.96
2.00
1.00
1.02
1.01
2.01
1.01
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

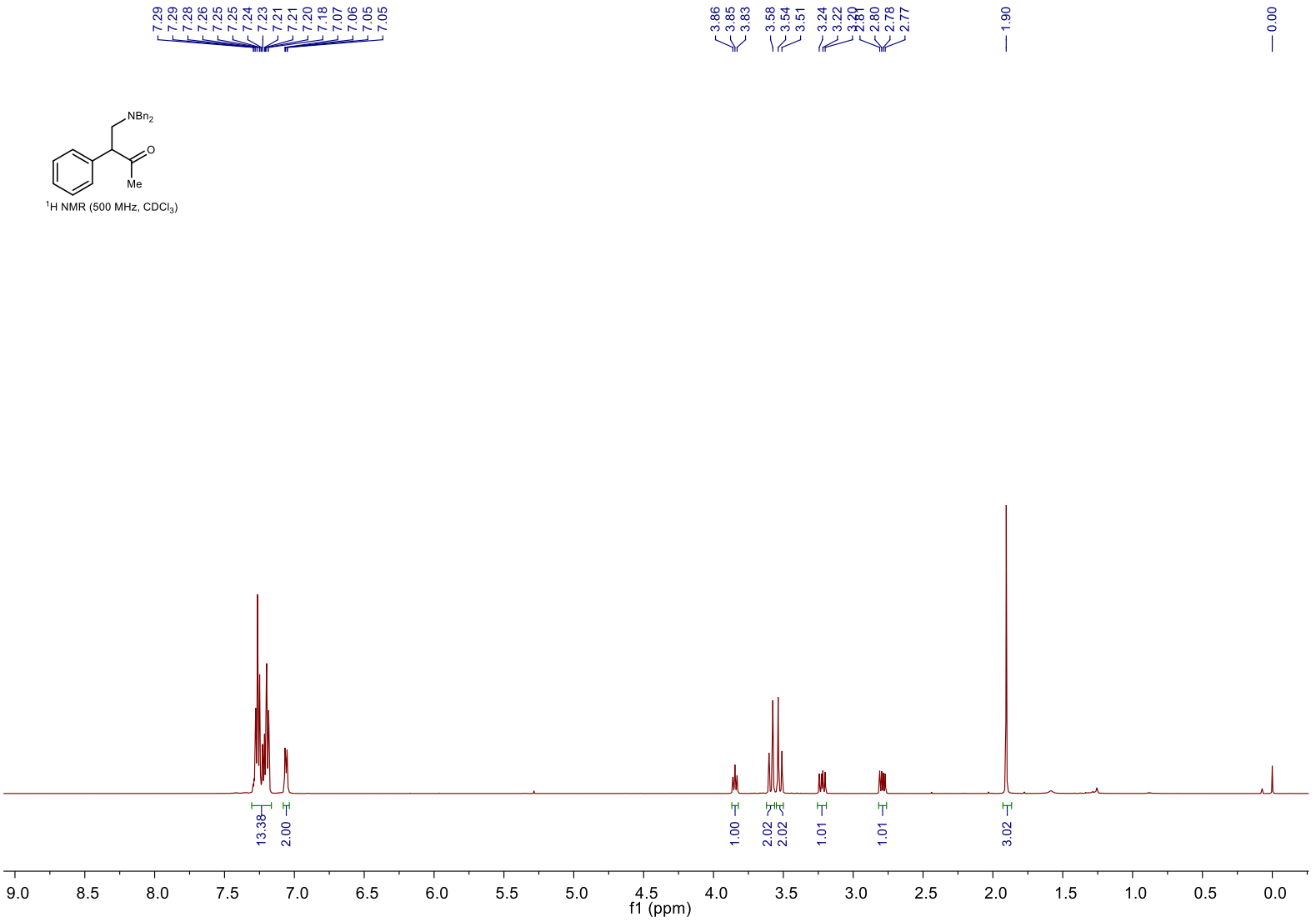

140.59
137.88
129.34
128.60
128.58
127.62
127.49
126.91
77.33
77.08
76.82
69.25
59.91
59.11
43.87
OH
NBn2
13C NMR (126 MHz, CDCl3)
129.34
128.60
128.58
127.62
127.49
126.91
129
128
127
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

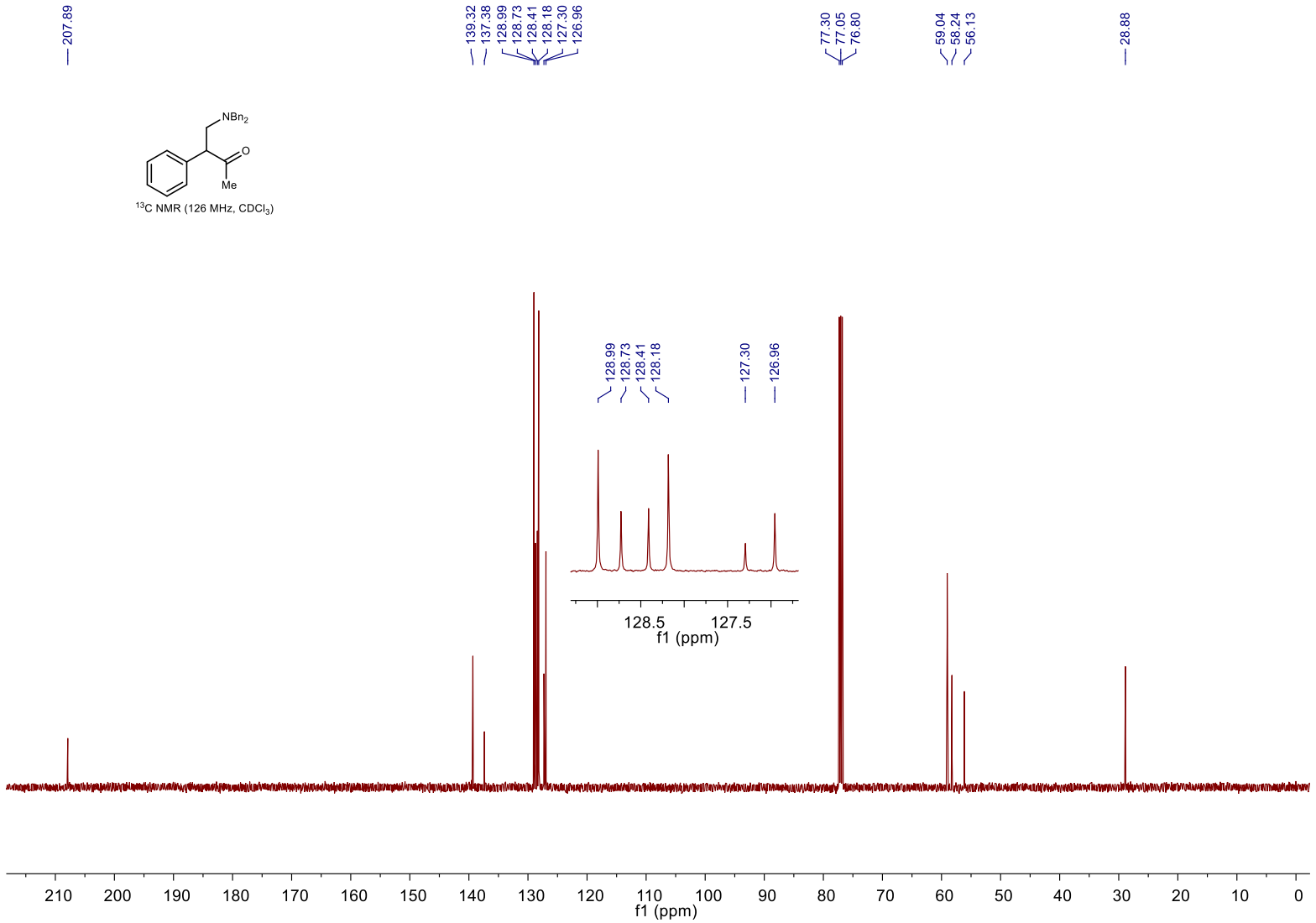

7.27
7.27
7.26
7.25
7.25
7.24
7.23
7.22
7.22
7.21
7.21
7.20
7.20
7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.13
7.13
7.12
7.10
7.09
7.09
7.08
7.07
6.95
6.94
6.93
6.91
6.91
6.90
3.56
3.53
3.52
3.49
3.11
3.09
2.69
2.67
2.66
2.65
2.64
2.63
2.62
2.61
-0.00
Ph
NBn2
1H NMR (500 MHz, CDCl3)
16.65
4.00
2.01
2.03
2.00
3.01
11.0
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
f1 (ppm)

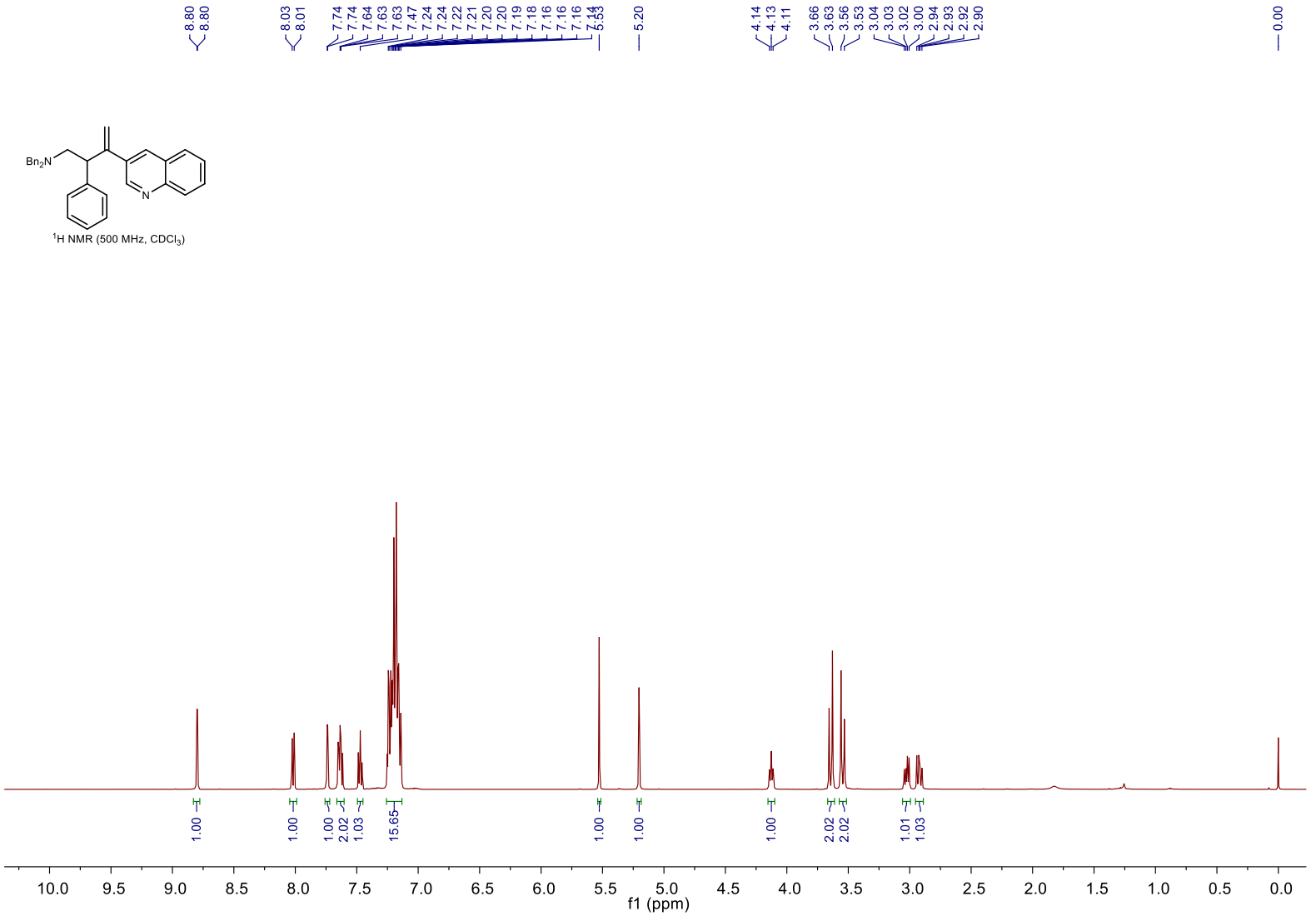

143.73
140.77
139.63
129.06
128.94
128.19
128.14
128.04
128.02
126.80
126.13
125.67
77.32
77.06
76.81
59.46
58.84
46.40
40.92
Ph
NBn2
13C NMR (126 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

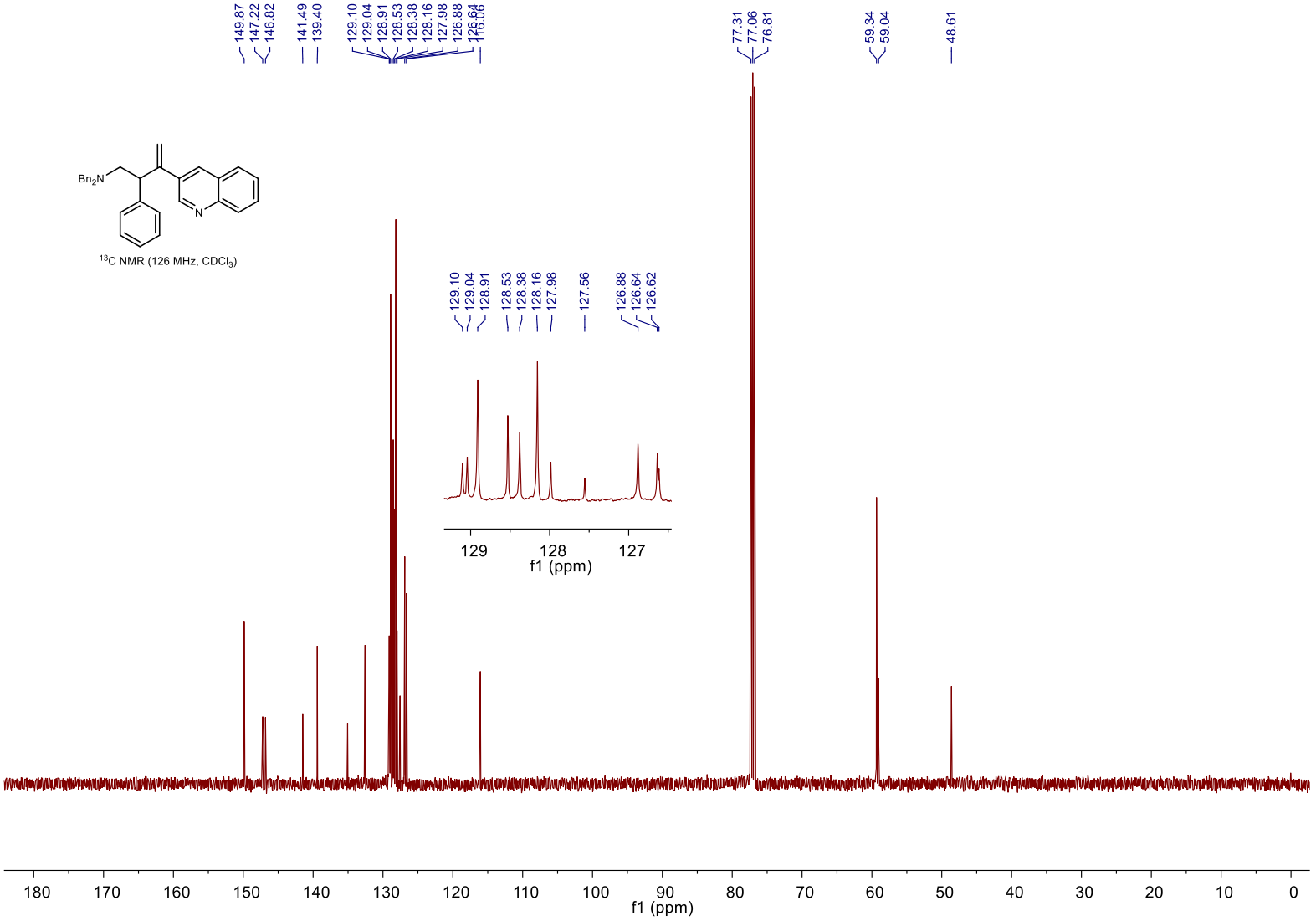

7.27
7.27
7.26
7.25
7.24
7.23
7.22
7.20
7.20
7.19
7.19
7.18
7.18
7.07
7.07
7.05
3.58
3.55
3.53
3.50
3.02
3.01
2.99
2.98
2.57
2.56
2.55
2.51
2.50
2.49
2.47
1.22
1.20
-0.00
H
NBn2
1H NMR (500 MHz, CDCl3)
13.38
2.00
2.02
2.02
1.00
1.00
1.01
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


146.02
139.76
128.83
128.15
128.08
127.45
126.72
126.00
77.30
77.04
76.79
61.52
58.71
38.09
19.89
H
NBn2
13C NMR (126 MHz, CDCl3)
129
128
127
126
f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.29
7.29
7.28
7.26
7.25
7.25
7.24
7.23
7.21
7.21
7.20
7.18
7.07
7.06
7.05
7.05
3.86
3.85
3.83
3.58
3.54
3.51
3.24
3.22
3.20
2.81
2.80
2.78
2.77
1.90
0.00
NBn2
O
Me
1H NMR (500 MHz, CDCl3)
13.38
2.00
1.00
2.02
2.02
1.01
1.01
3.02
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
f1 (ppm)


207.89
139.32
137.38
128.99
128.73
128.41
128.18
127.30
126.96
77.30
77.05
76.80
59.04
58.24
56.13
28.88
NBn2
O
Me
13C NMR (126 MHz, CDCl3)
128.5
127.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.80
8.80
8.03
8.01
7.74
7.74
7.64
7.63
7.63
7.47
7.24
7.24
7.22
7.21
7.20
7.20
7.19
7.18
7.16
7.16
7.16
7.14
5.53
5.20
4.14
4.13
4.11
3.66
3.63
3.56
3.53
3.04
3.03
3.02
3.00
2.94
2.93
2.92
2.90
0.00
Bn2N
N
1H NMR (500 MHz, CDCl3)
1.00
1.00
1.00
2.02
1.03
15.65
1.00
1.00
1.00
2.02
2.02
1.01
1.03
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
f1 (ppm)


149.87
147.22
146.82
141.49
139.40
129.10
129.04
128.91
128.53
128.38
128.16
127.98
126.88
126.64
126.06
77.31
77.06
76.81
59.34
59.04
48.61
Bn2N
N
13C NMR (126 MHz, CDCl3)
129.10
129.04
128.91
128.53
128.38
128.16
127.98
127.56
126.88
126.64
126.62
129
128
127
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)