Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Transition metal- and solvent-free double hydroboration of nitriles

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General considerations

All reactions were performed in oven dried apparatus under an inert, argon, atmosphere. All reagents were purchased from commercial vendors and were used as received without any purification or drying. $NaHBEt_3$ was purchased as a 1 M solution in THF from Sigma Aldrich. ^{1}H, $^{13}C\{^{1}H\}$ and ^{11}B NMR spectra were recorded on a Jeol 400 MHz spectrometer at 298K. ^{1}H NMR spectra were referenced to the solvent residual peak ($CDCl_3$, δ 7.26 ppm) and $^{13}C\{^{1}H\}$ NMR spectra were referenced to the solvent residual peak ($CDCl_3$, δ 77.16 ppm). Coupling constants *J* are reported in Hz. NMR multiplicities are as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, sept = septet. Melting points were analyzed on a Mel-Temp instrument from Barnstead International, Iowa, USA.

General procedure for hydroboration of nitriles (For NMR yields)

In an inert atmosphere glovebox, organic nitrile (1 eq, 0.25 mmol), HBpin (2.5-4.0 eq., 0.625-1 mmol, 80 mg-128 mg, 91 μL-145 μL) and $NaHBEt_3$ (0.05 eq., 0.0125 mmol, 12.5 μL) were charged to an oven dried *J*-young tube. The reaction mixture was allowed to stand at room temperature or heated in a pre-heated oil bath at 80 ^{o}C for substrates **1k**-**1m** and **1s-1v** till the solid product precipitates out or the entire reaction mixture solidifies (0.5 min-24h). Then, 20 μL of mesitylene was added as an internal standard and the reaction mixture was diluted with ~ 0.5-0.6 ml of $CDCl_3$. Subsequently, the *J*-young was shaken vigorously to dissolve all the solid formed and ^{1}H spectra was recorded to evaluate the NMR yield.

General procedure for hydroboration of nitriles (For isolated yields)

In an inert atmosphere glovebox, organic nitrile (1 eq, 0.5 mmol), HBpin (2.5-4 eq., 1.25-2 mmol, 160-256 mg, 182 μL-290 μL) and $NaHBEt_3$ (0.05 eq., 0.025mmol, 25 μL) were charged to an oven dried screw cap vial. The reaction mixture was allowed to stand at room temperature or heated in a pre-heated oil bath at 80 ^{o}C for substrates **1k**-**1m** till the solid product precipitates out or the entire reaction mixture solidifies (0.5 min-24h).

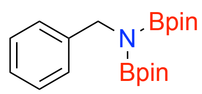
General procedure for isolation of the products (except **2k**, **2l** and **2n**)

After the solid formation was observed in the screw cap vial, 0.5 ml of dry hexanes was added, and the vial was placed inside the Glove-box freezer at -30 ^{o}C. 30 minutes later, the vial was removed from the freezer and hexanes was decanted out from the solid. The solid was then dried using external glovebox vacuum pump to remove any residual hexanes. The solid product thus obtained was weighed and melting point,^{11}B, ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded.

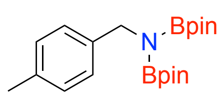
General procedure for isolation of the products **2l** and **2n**

After the solid formation was observed in the screw cap vial, 0.5 ml of dry pentane was added, and vial was placed inside the Glove-box freezer at -30 ^{o}C for crystallization. After 24 hours, the crystals were picked and dried using external glovebox vacuum pump to remove any residual pentane. The solid product thus obtained was weighed and melting point,^{11}B, ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded.

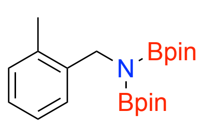
Spectral data for diborylated amine products



2a (Yield: 128 mg, 71%, white solid, m. pt: 85°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.29-7.27 (m, 2H), 7.22 (t, 2H, *J* = 7.4 Hz), 7.15-7.11 (m, 1H), 4.22 (s, 2H), 1.18 (s, 24H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 143.12, 127.87, 127.58, 126.13, 82.40, 47.32, 24.57. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 24.70. Spectral data matches the literature report.[1]

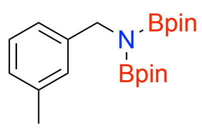


2b (Yield: 153 mg, 83%, white solid, m. pt: 111°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.18 (d, 2H, *J* = 7.96 Hz), 7.03 (d, 2H, *J* = 7.84 Hz), 4.18 (s, 2H), 2.28 (s, 3H), 1.18 (s, 24H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 140.14, 135.48, 128.55, 127.51, 82.35, 46.96, 24.59, 21.14. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 24.81. Spectral data matches the literature report.[1]

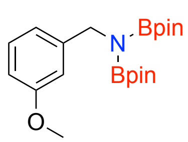


2c (Yield:159 mg, 85%, white solid, m. pt: 96°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.22 (d, 1H, *J* = 7.36 Hz), 7.11-7.03 (m, 3H), 4.21 (s, 2H), 2.28 (s, 3H), 1.16 (s, 24H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 140.72, 135.26, 129.56, 126.23,

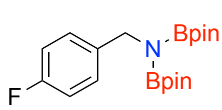
125.76, 125.45, 82.39, 44.88, 24.50, 19.23. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 24.80. Spectral data matches the literature report.[1]



2d (Yield: 156 mg, 84%, white solid, m. pt: 68°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.12-7.06 (m, 3H), 6.95 (d, 1H, *J* = 7.08 Hz), 4.19 (s, 2H), 2.28 (s, 3H), 1.18 (s, 24H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 143.02, 137.29, 128.35, 127.77, 126.81, 124.57, 82.38, 47.19, 24.57, 21.47. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 25.03. Spectral data matches the literature report.[1]

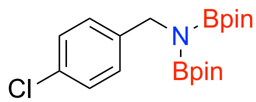


2e (Yield: 184 mg, 95%, white solid, m. pt: 89°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.13 (t, 1H, *J* = 7.76 Hz), 6.89-6.86 (m, 2H), 6.70-6.68 (m, 1H), 4.19 (s, 2H), 3.75 (s, 3H), 1.18 (s, 24H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 159.41, 144.81, 128.82, 120.05, 112.75, 112.16, 82.41, 55.17, 47.35, 24.59. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 24.74. Spectral data matches the literature report.[2]

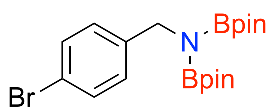


2f (Yield: 140 mg, 75%, white solid, m. pt: 96°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.26-7.23 (m, 2H), 6.92-6.87 (m, 2H), 4.15 (s, 2H), , 1.18 (s, 24H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 161.59 (d, $J_{C\text{-}F}$ = 244.42 Hz), 138.91 (d, $J_{C\text{-}F}$ = 3.03

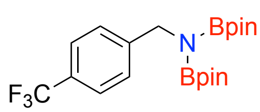
Hz), 129.24 (d, J_{C-F} = 8.08 Hz), 114.53 (d, J_{C-F} = 21.21 Hz), , 82.47, 46.64, 24.57. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 24.68. Spectral data matches the literature report.



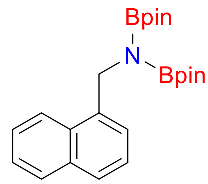
2g (Yield: 182 mg, 93%, white solid, m. pt: 125°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.20 (q, 4H, J = 6.92 Hz), 4.15 (s, 2H), 1.17 (s, 24H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 141.65, 131.79, 129.01, 127.97, 82.52, 46.72, 24.57. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 24.90. Spectral data matches the literature report.[1]



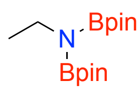
2h (Yield: 187 mg, 86%, white solid, m. pt: 147°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.23 (d, 2H, J = 8.40 Hz), 7.05 (d, 2H, J = 8.40 Hz), 4.03 (s, 2H), 1.06 (s, 24H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 142.17, 130.93, 129.40, 119.92, 82.53, 46.76, 24.58. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 24.78. Spectral data matches the literature report.[3]



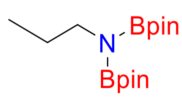
2i (Yield: 187 mg, white solid, m. pt: 135°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.48 (d, 2H, J = 8.32 Hz), 7.38 (d, 2H, J = 8.12 Hz), 4.25 (s, 2H), 1.18 (s, 24 H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 147.15, 128.44 (q, J_{C-F} = 32.32 Hz), 127.67, 124.54 (d, J_{C-F} = 272.7 Hz), 124.85 (q, J_{C-F} = 4.04 Hz), 124.83, 82.61 47.04, 24.75. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 24.96. Spectral data matches the literature report.[2]



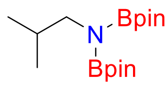
2j (Yield: 177 mg, 86% pale yellow solid, m. pt: 205°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.14 (d, 1H, *J* = 7.92 Hz), 7.83 (d, 1H, *J* = 7.04 Hz), 7.68 (d, 1H, *J* = 7.72 Hz), 7.48- 7.36 (m, 4H), 4.75 (s, 2H), 1.17 (s, 24H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 138.24, 133.56, 131.35, 128.54, 126.63, 125.44, 125.4, 125.29, 123.74, 123.54, 82.49, 44.85, 24.54. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 25.01. Spectral data matches the literature report.[3]



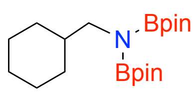
2k (74% yield, white crystal, m. pt: 91°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 3.03 (q, 2H, *J* = 7.08 Hz), 1.20 (s, 24H), 1.00 (t, 3H, *J* = 7.08 Hz). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 82.07, 38.65, 24.65, 18.72. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 24.73. Spectral data matches the literature report.[1]



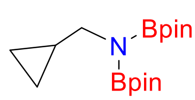
2l (Yield: 151 mg, 98% yield, white powder, m. pt: 52°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 2.96 (t, 2H, *J* = 3.72 Hz), 1.41- 1.34 (m, 2H), 1.19 (s, 24H), 0.83-0.79 (m, 3H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 82.05, 45.39, 26.06, 24.55, 11.18. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 24.81. Spectral data matches the literature report.[3]



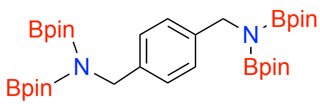
2m (Yield: 159 mg, 98%, white solid, m. pt: 42°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 2.82 (d, 2H, *J* = 7.0 Hz), 1.59 (sept, 1H, *J* = 6.64 Hz), 1.19 (s, 24H), 0.79 (d, 6H, *J* = 6.72 Hz). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 82.08, 51.08, 30.82, 24.53, 19.96. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 24.66. Spectral data matches the literature report.[1]



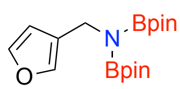
2n (Yield: 177mg, 97%, white solid, m. pt: 67°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 2.84 (d, 2H, *J* = 7.04 Hz), 1.21 (s, 24H), 1.66-1.59 (m, 5H), 1.19 (s, 24H), 0.87-0.79 (m, 2H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 82.06, 49.77, 40.57, 30.61, 26.85, 26.23, 24.53. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 25.05. Spectral data matches the literature report.[1]



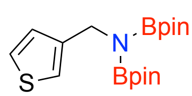
2o (Yield: 156mg, 97%, white solid, m. pt: 44°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 2.87 (d, 2H, *J* = 6.8 Hz), 1.19 (s, 24 H), 0.93-0.84 (m, 1H), 0.31 -0.27 (m, 2H), 0.18-0.16 (m, 2H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 82.15, 48.04, 24.58, 14.26, 3.23. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 24.72.



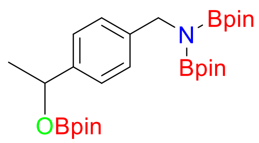
2p (NMR Yield: 90%)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.09 (s, 4H), 4.10 (s, 4 H), 1.10 (s, 48H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 140.73, 126.92, 82.21, 46.94, 24.49. ^{11}B could not be assigned since the peak due to B-N bond was obscured by the unreacted HBpin peak. Spectral data matches the literature report.[3]



2q (Yield: 164mg, 94%, white solid, m. pt: 98°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.26-7.24 (m, 2H), 6.35 (s, 1H), 4.00 (s, 2H), 1.19 (s, 24H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 142.21, 139.77, 126.82, 110.86, 82.41, 38.19, 24.62. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 24.88.

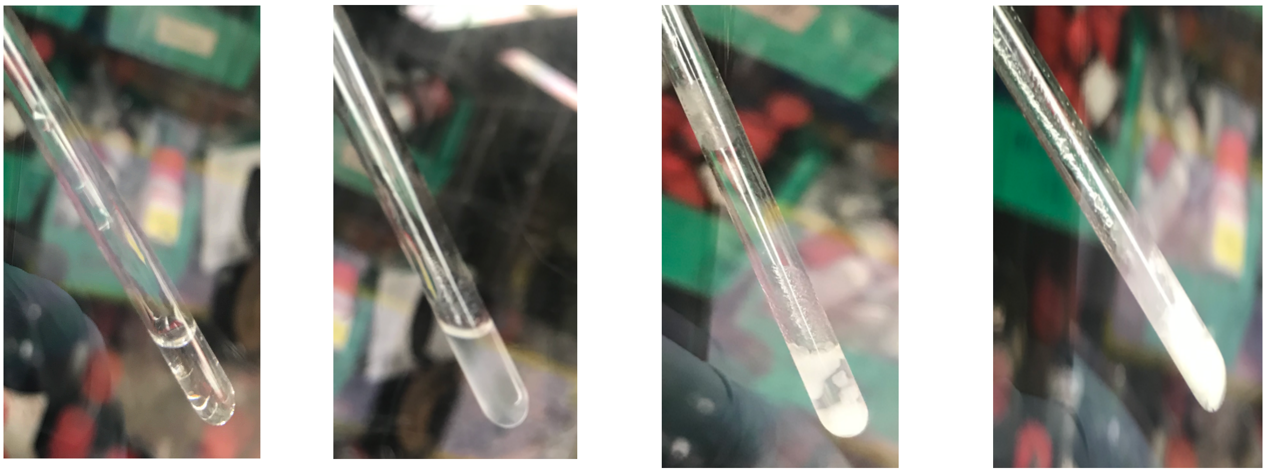


2r (Yield: 126 mg, 69%, white solid, m. pt: 115°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.04-7.01 (m, 1H), 6.94-6.90 (m, 2H), 4.06 (s, 2H), 1.08 (s, 24H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 144.24, 127.99, 124.64, 121.11, 82.42, 42.56, 24.60. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 24.89. Spectral data matches the literature report.[3]



2s (Yield: 259 mg, 98%, white solid, m. pt: 104°C)
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.24-7.19 (m, 4H), 5.18 (q, 1H, *J* = 6.44 Hz), 4.18 (s, 2H), 1.44 (d, 3H, *J* = 6.40 Hz), 1.21-1.17 (m, 36 H).^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 298 K): δ 142.39, 142.00, 127.42, 124.91, 82.73, 82.37,72.61, 47.03, 25.49, 24.65. ^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$, 298K): δ 24.92, 21.17. Spectral data matches the literature report.[3]

Depiction of formation of the product using Benzonitrile as an example

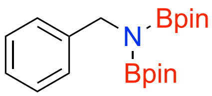


a) b) c) d)

Figure S1

a) Initial mixing of Benzonitrile, HBpin and $NaHBEt_3$ at t = 0 sec
b) Seconds after the mixing the solution starts to become turbid
c) Formation of product seen as a white solid
d) In ~2 minutes the entire reaction mixture solidified indicating the completion of the reaction

^{11}B, ^{1}H and ^{13}C spectra for diborylated amine products



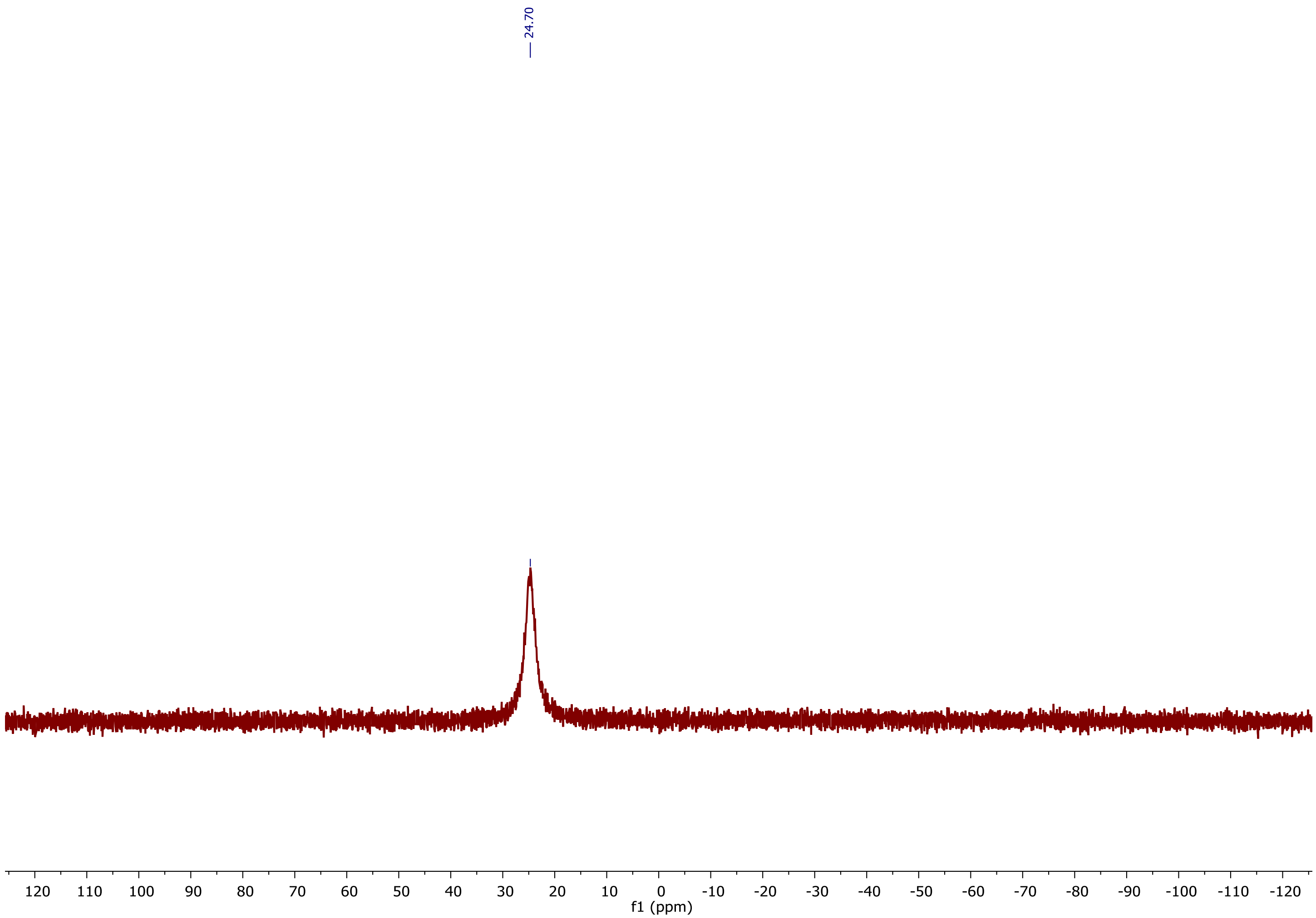
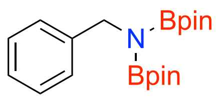


Figure S2: ^{11}B NMR spectrum of **2a**



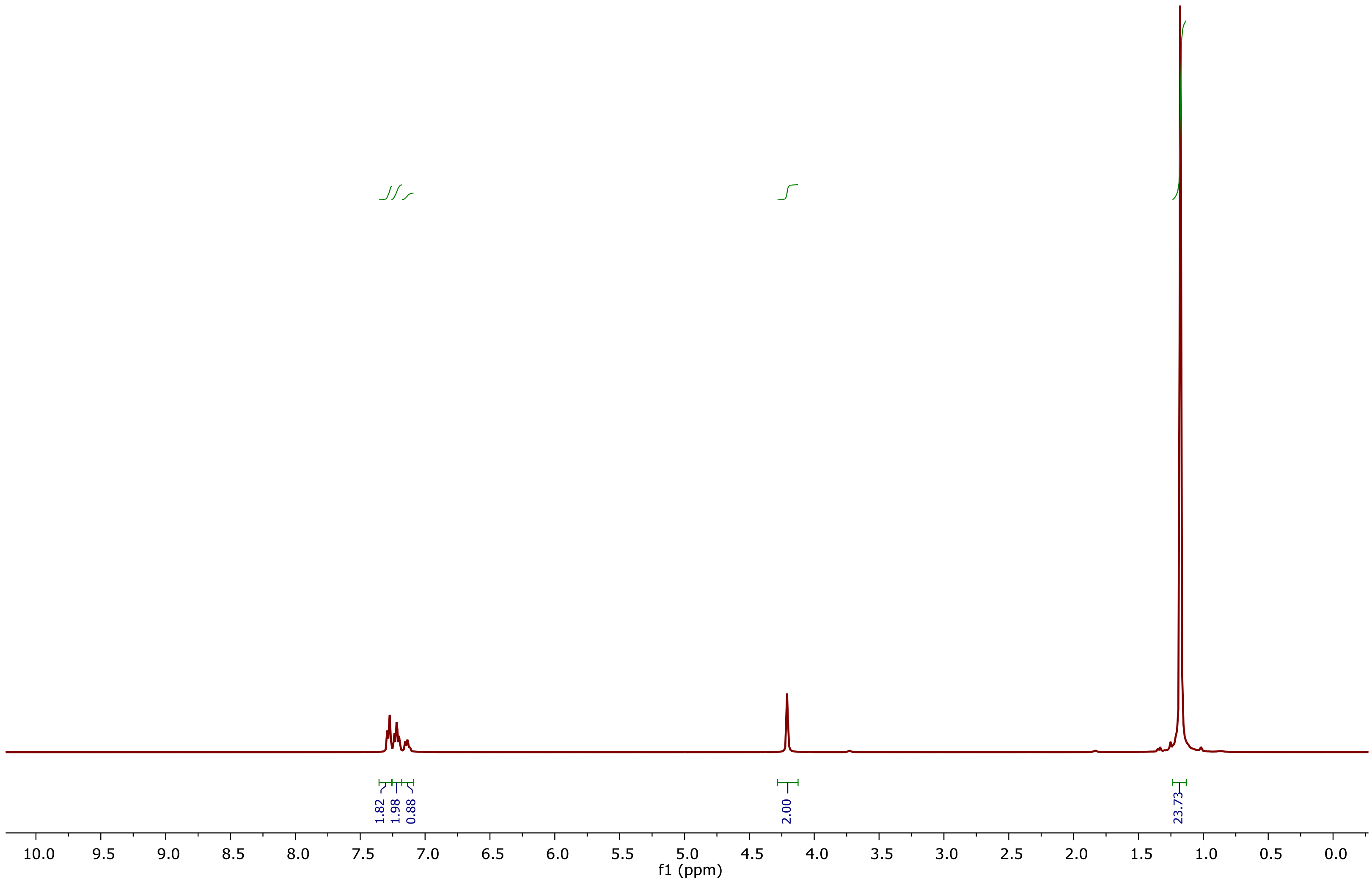


Figure S3: ^{1}H NMR spectrum of **2a**.

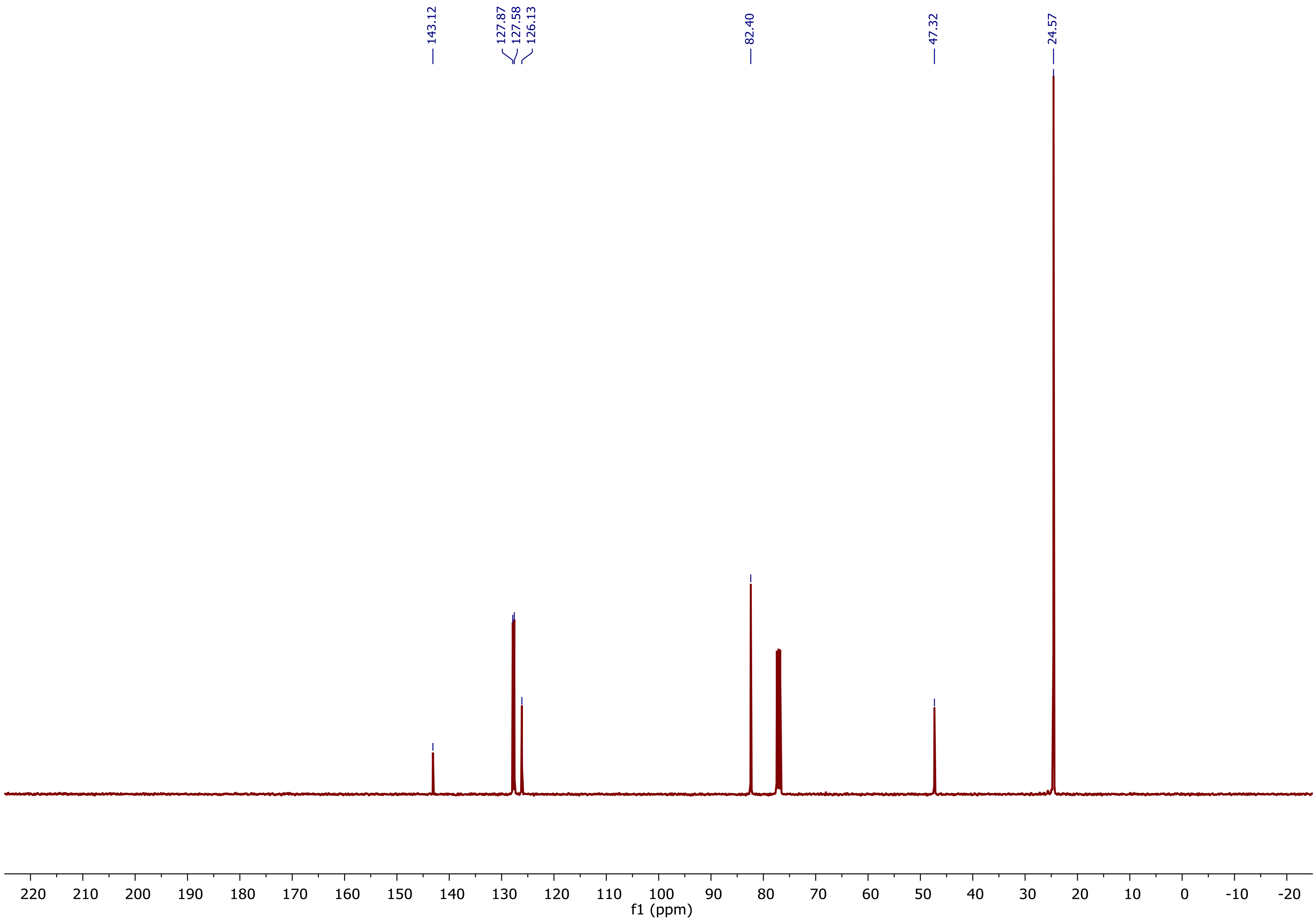
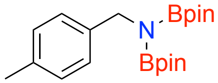


Figure S4: ^{13}C NMR spectrum of **2a**.



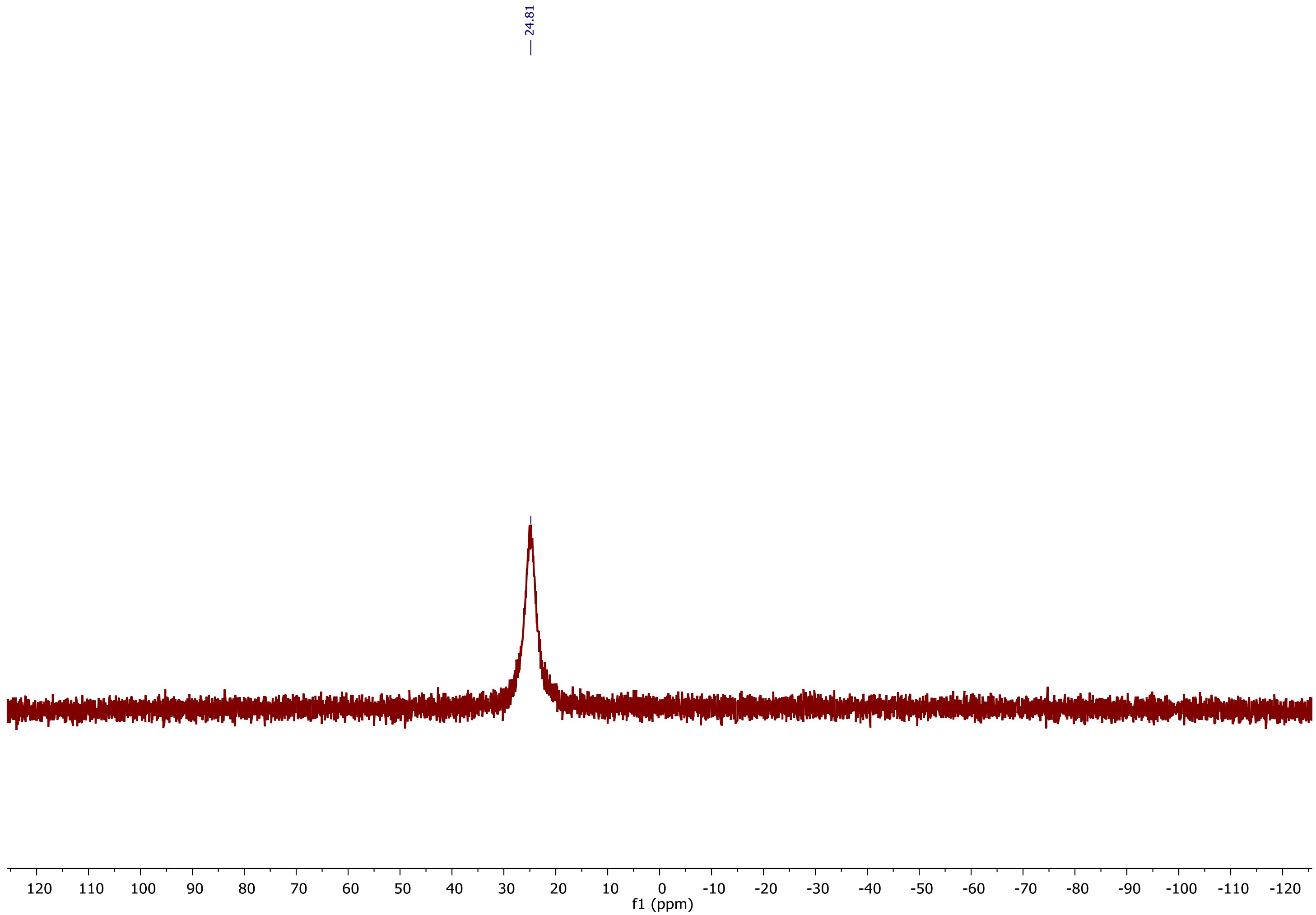


Figure S5: ^{11}B NMR spectrum of **2b**

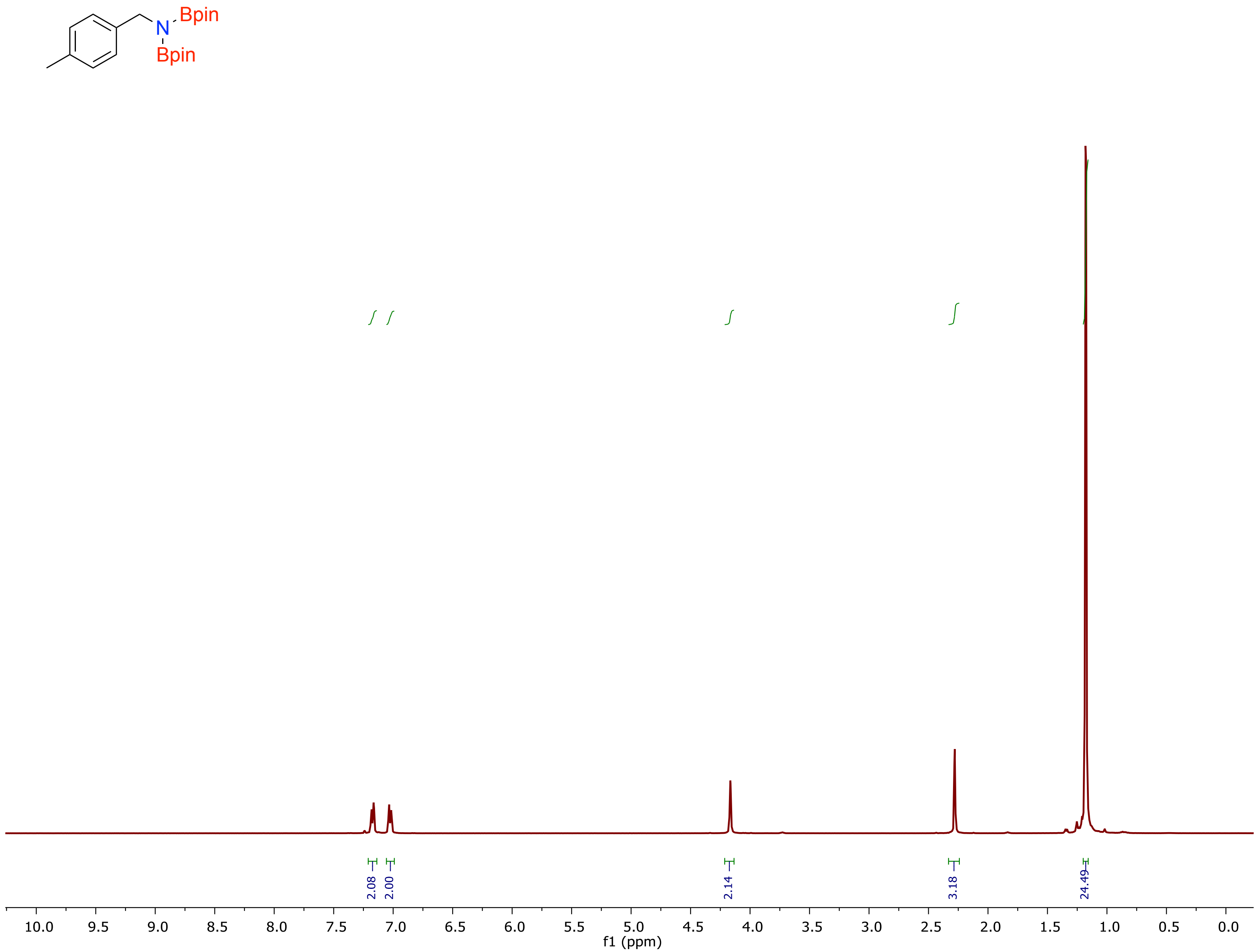


Figure S6: ^{1}H NMR spectrum of **2b**.

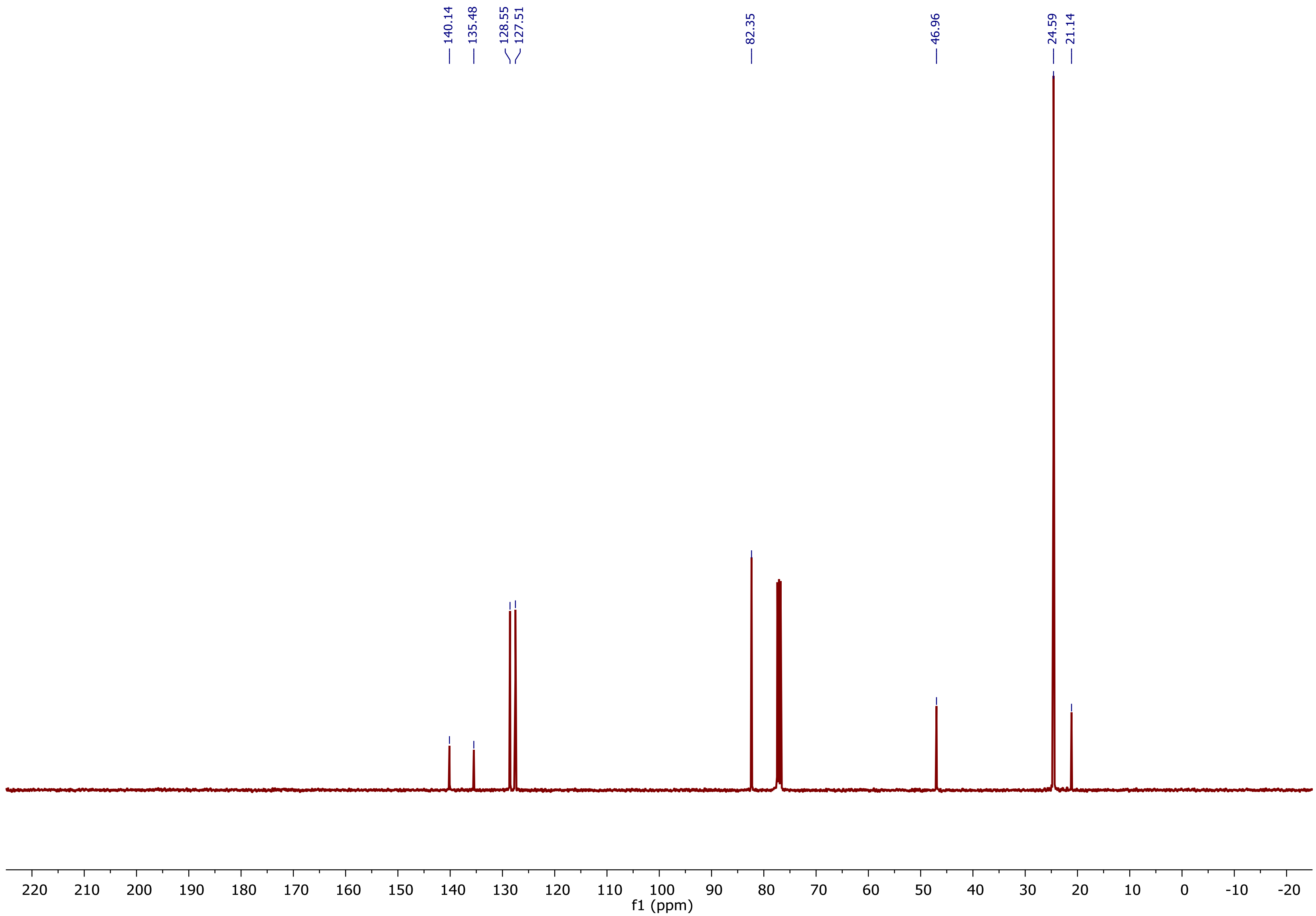
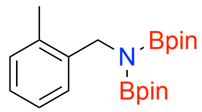


Figure S7: ^{13}C NMR spectrum of **2b.**



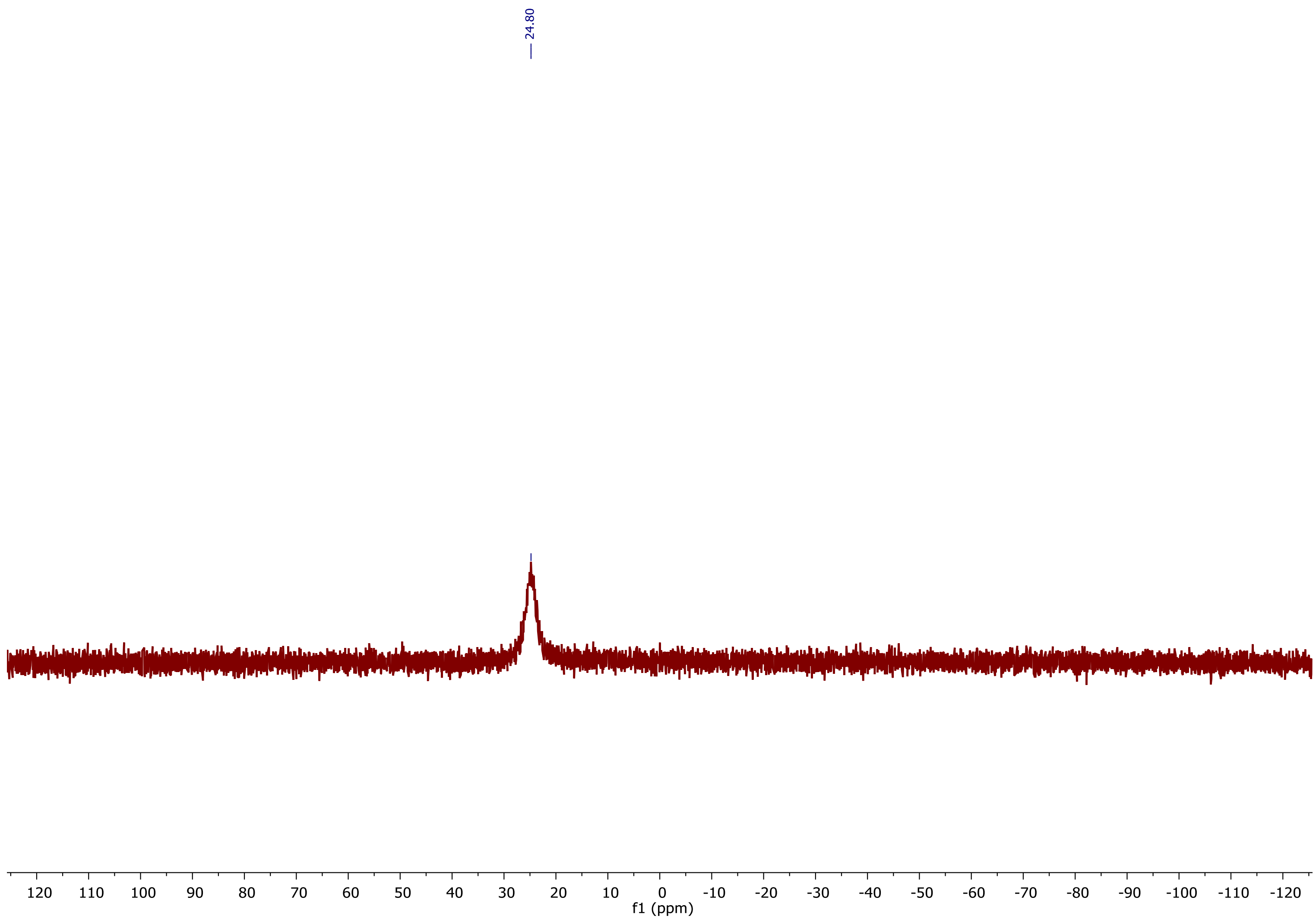


Figure S8: ^{11}B NMR spectrum of **2c**

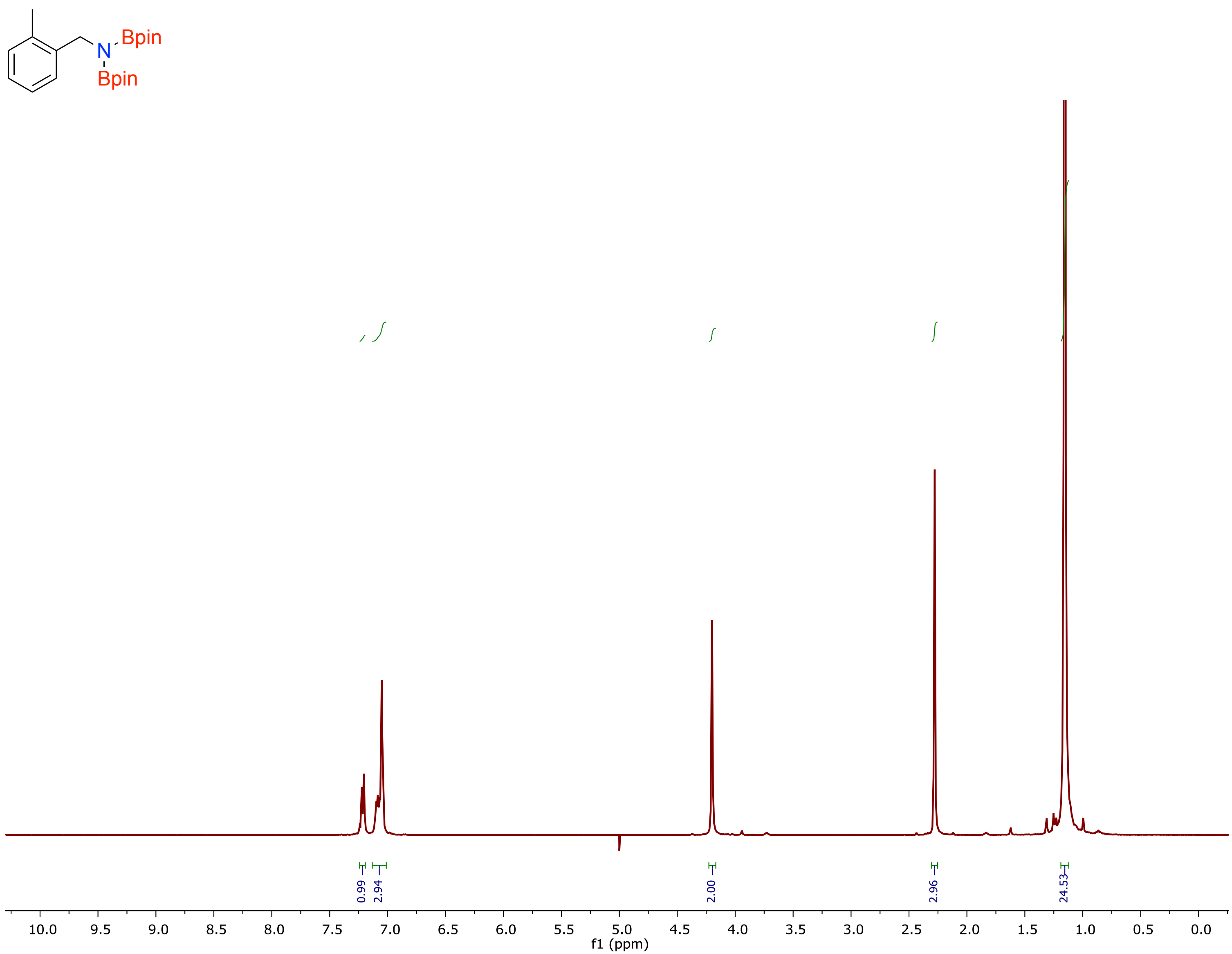


Figure S9: ^{1}H NMR spectrum of **2c**.

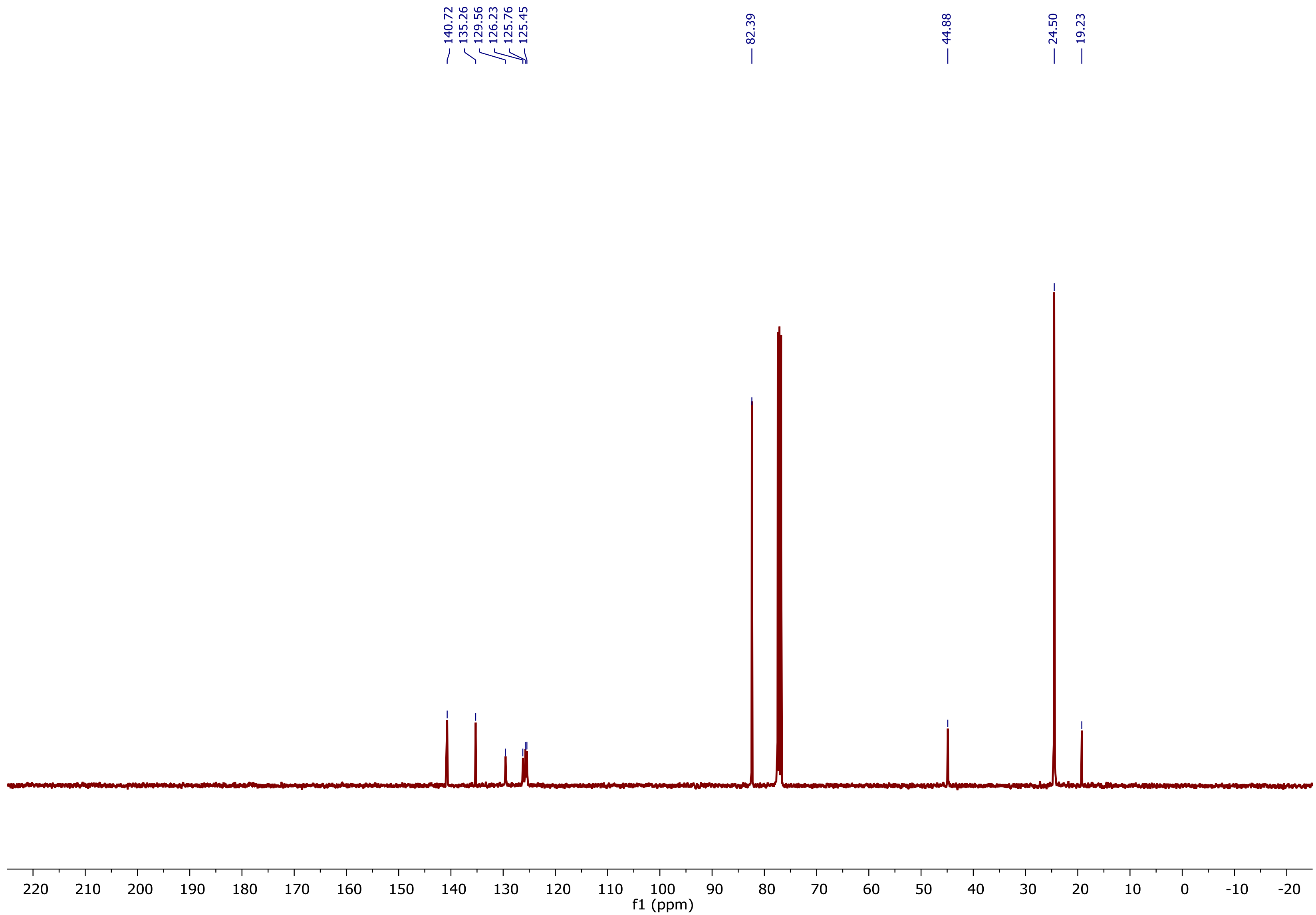


Figure S10: ^{13}C NMR spectrum of **2c**.

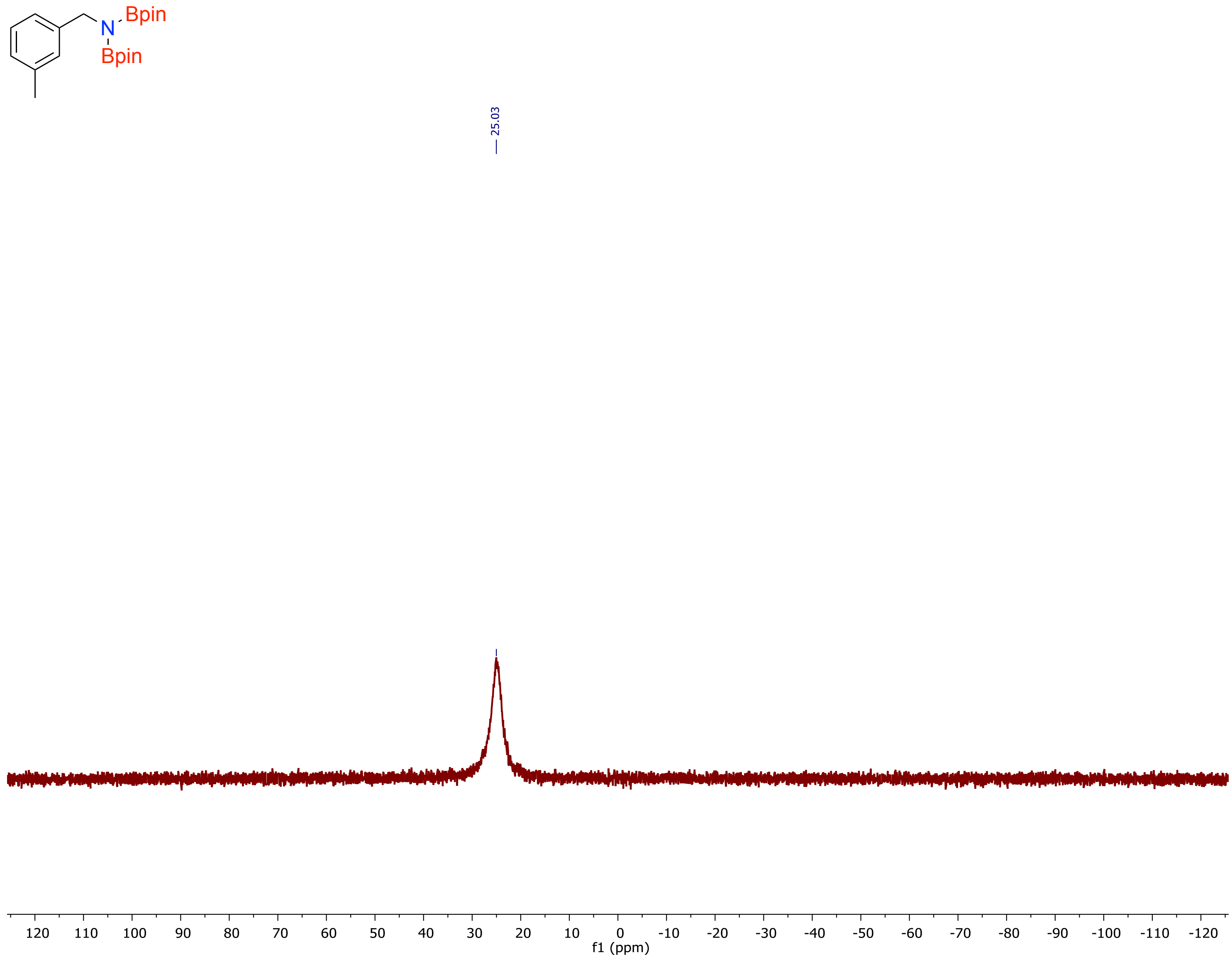


Figure S11: ^{11}B NMR spectrum of **2d**

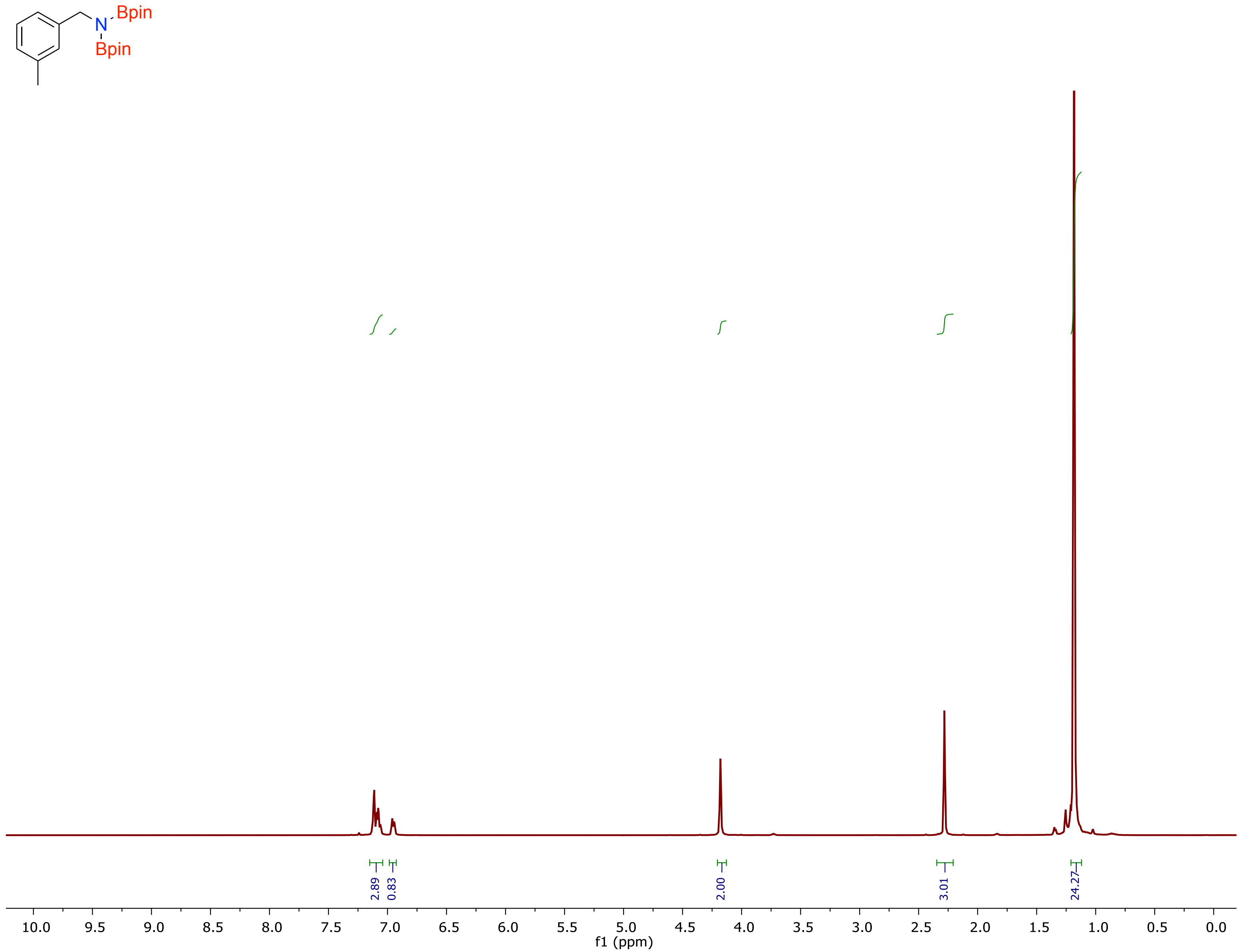


Figure S12: ^{1}H NMR spectrum of **2d**.

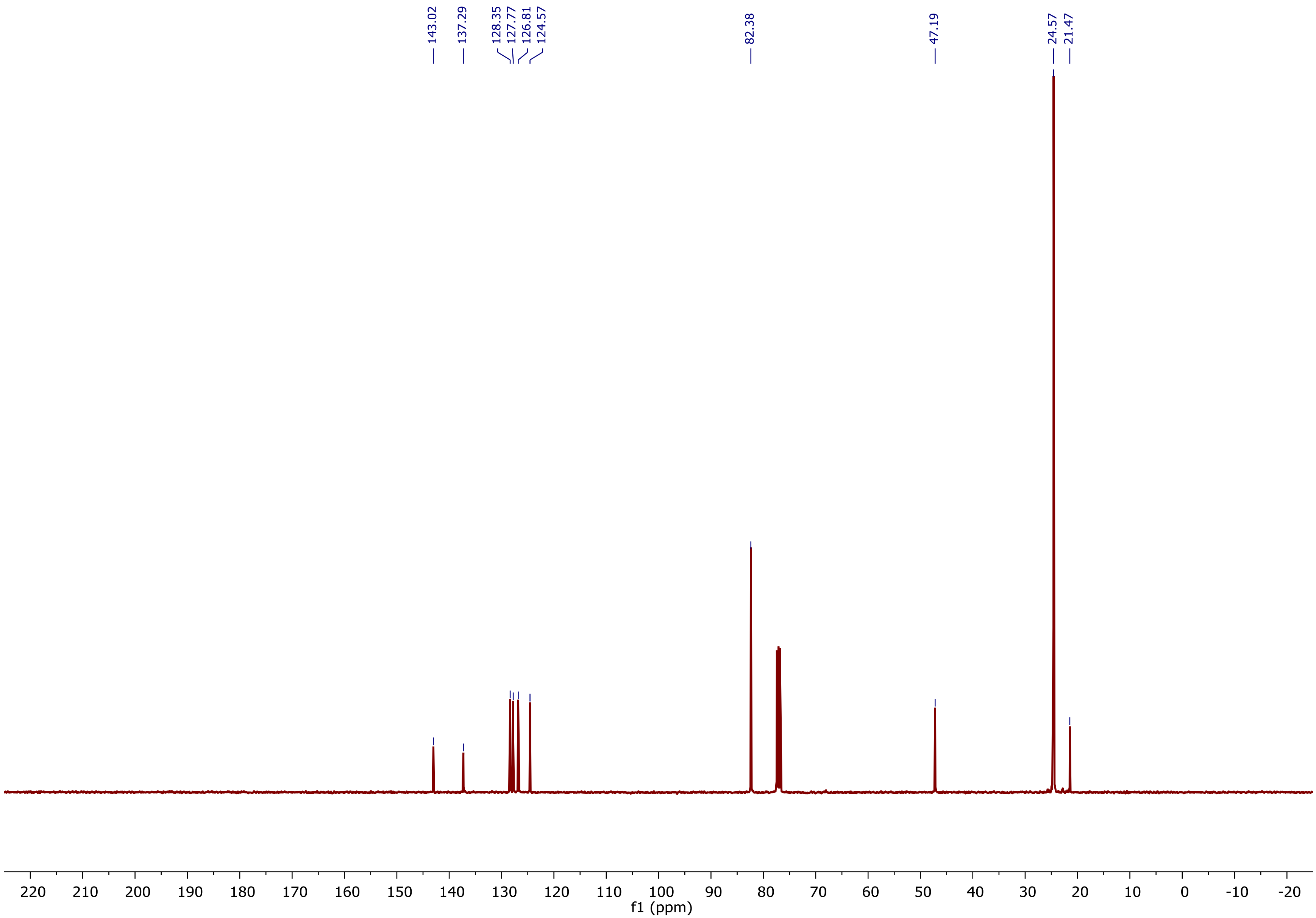
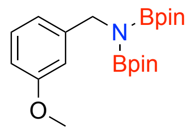


Figure S13: ^{13}C NMR spectrum of **2d**.



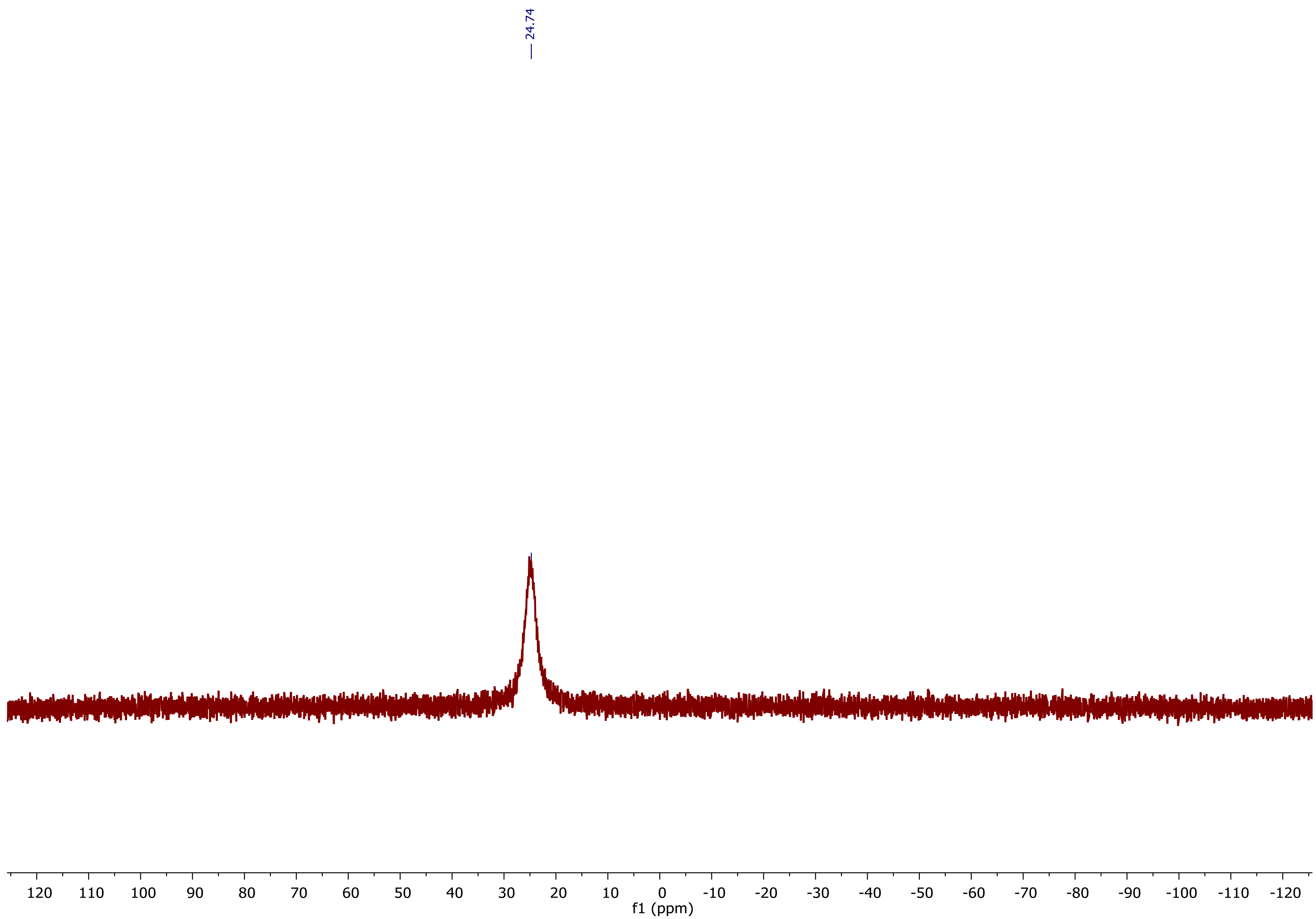
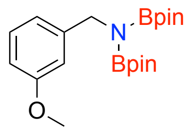


Figure S14: ^{11}B NMR spectrum of **2e**



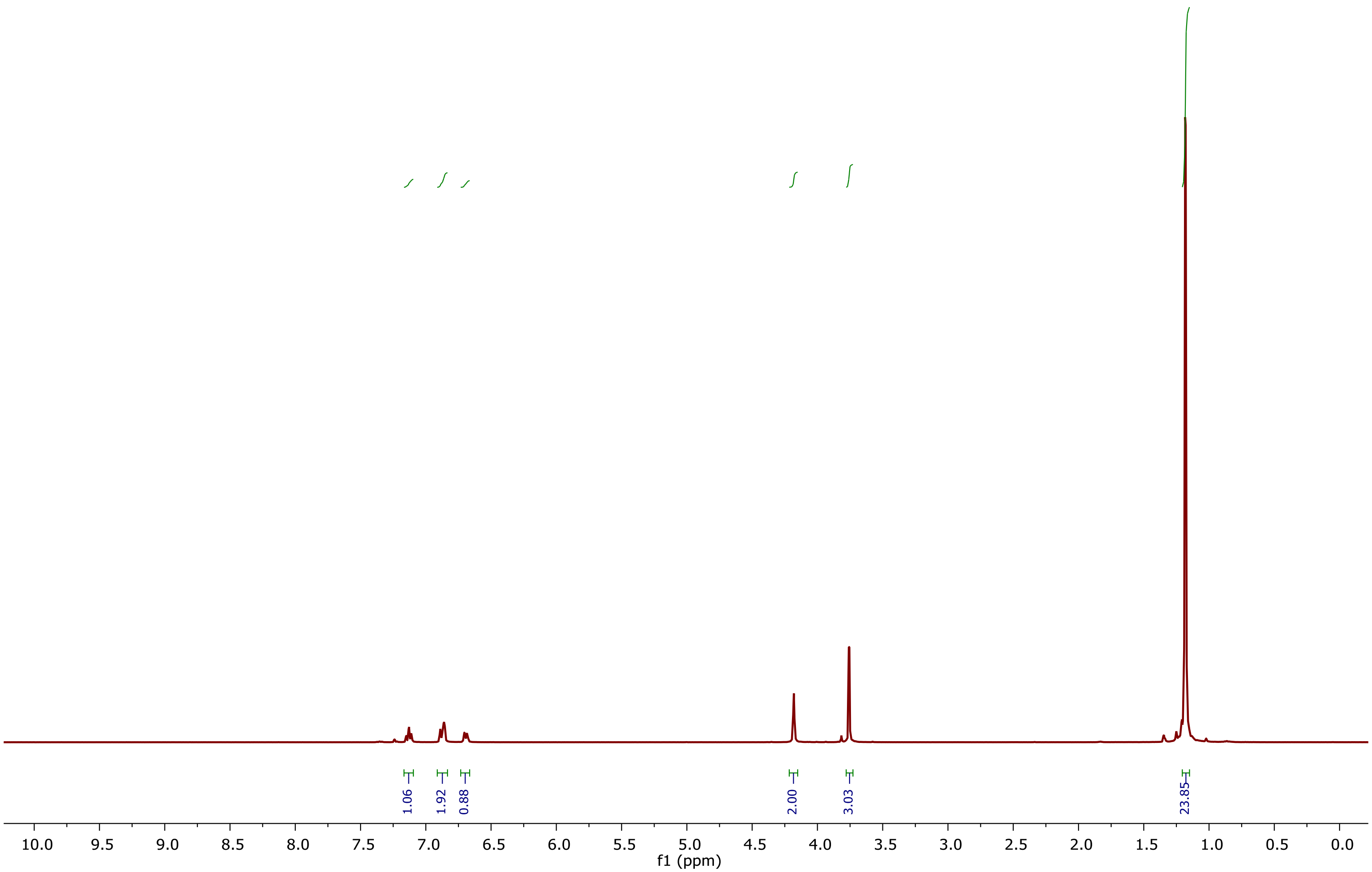


Figure S15: ^{1}H NMR spectrum of **2e**.

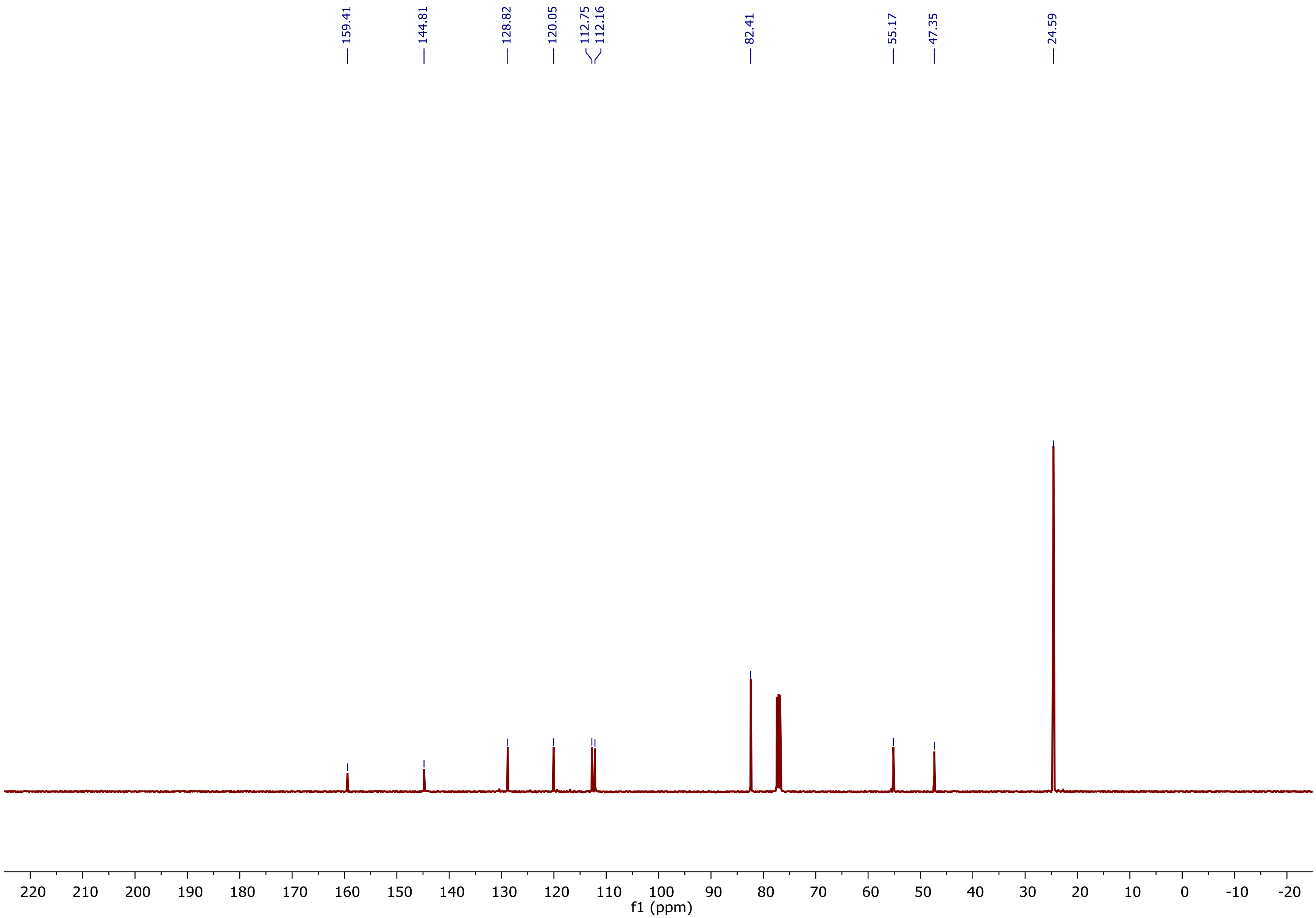
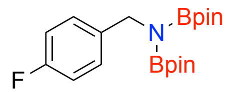


Figure S16: ^{13}C NMR spectrum of **2e**.



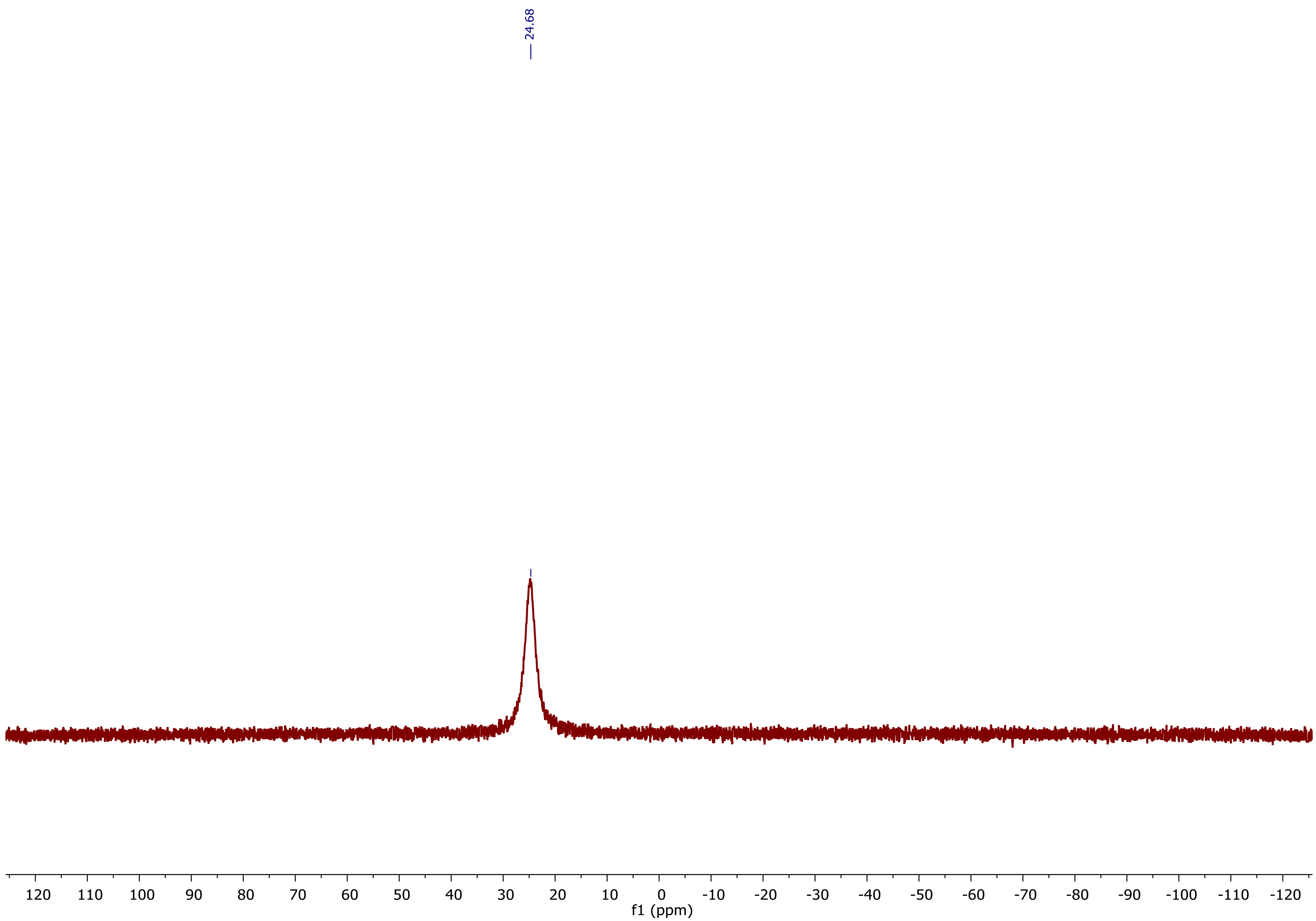
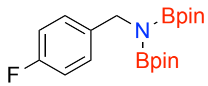


Figure S17: ^{11}B NMR spectrum of **2f**



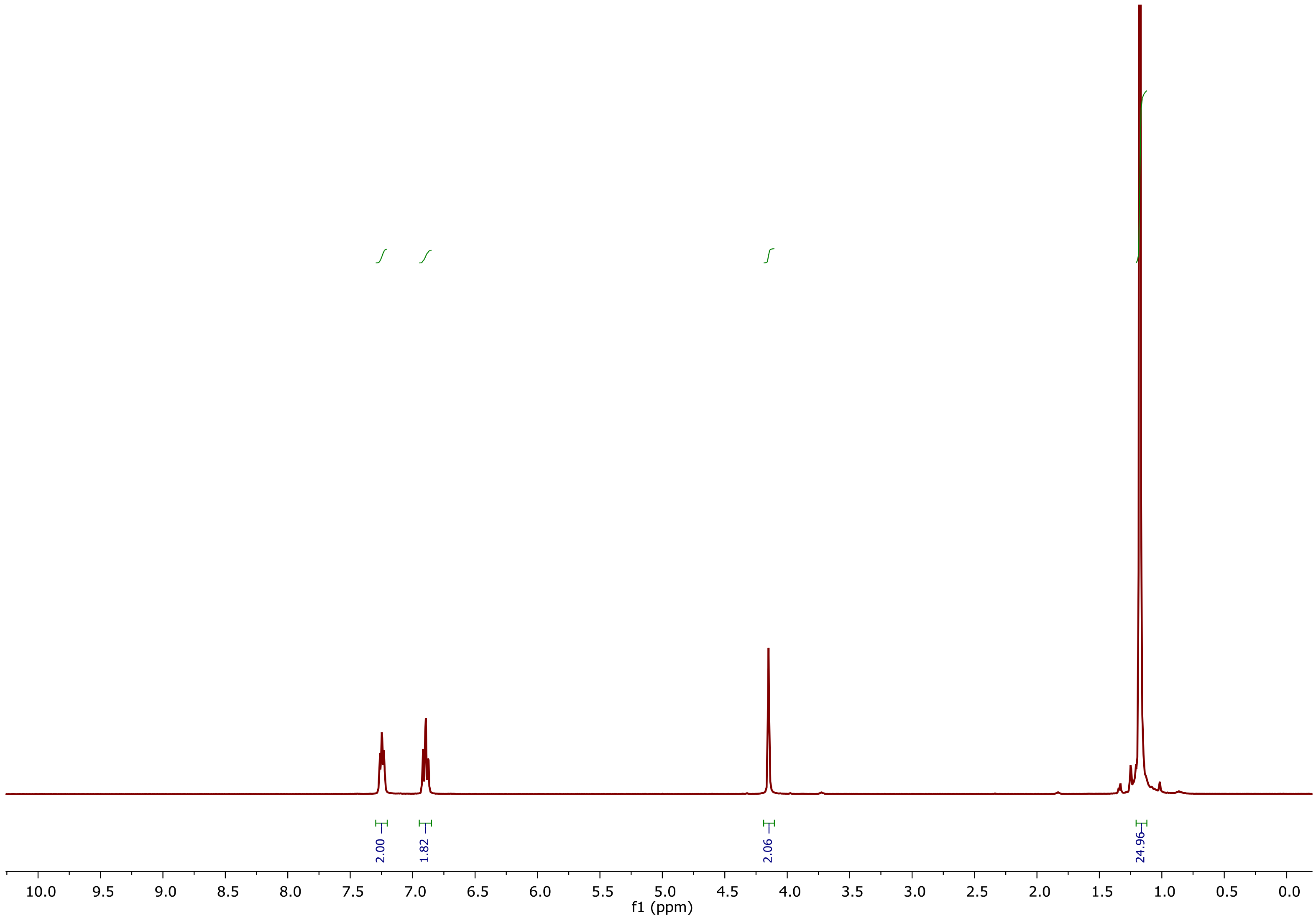


Figure S18: ^{1}H NMR spectrum of **2f.**

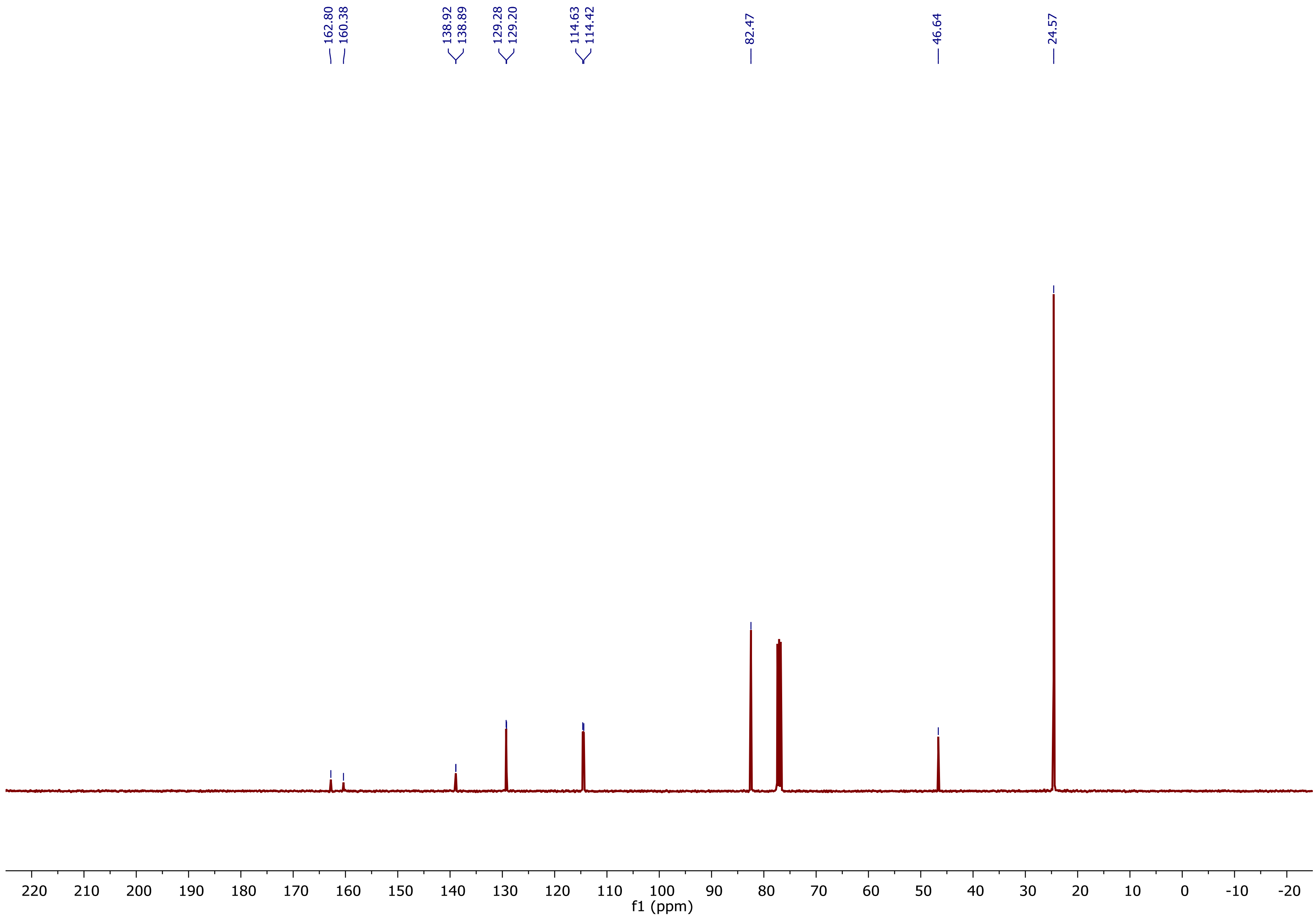


Figure S19: ^{1}H NMR spectrum of **2f.**

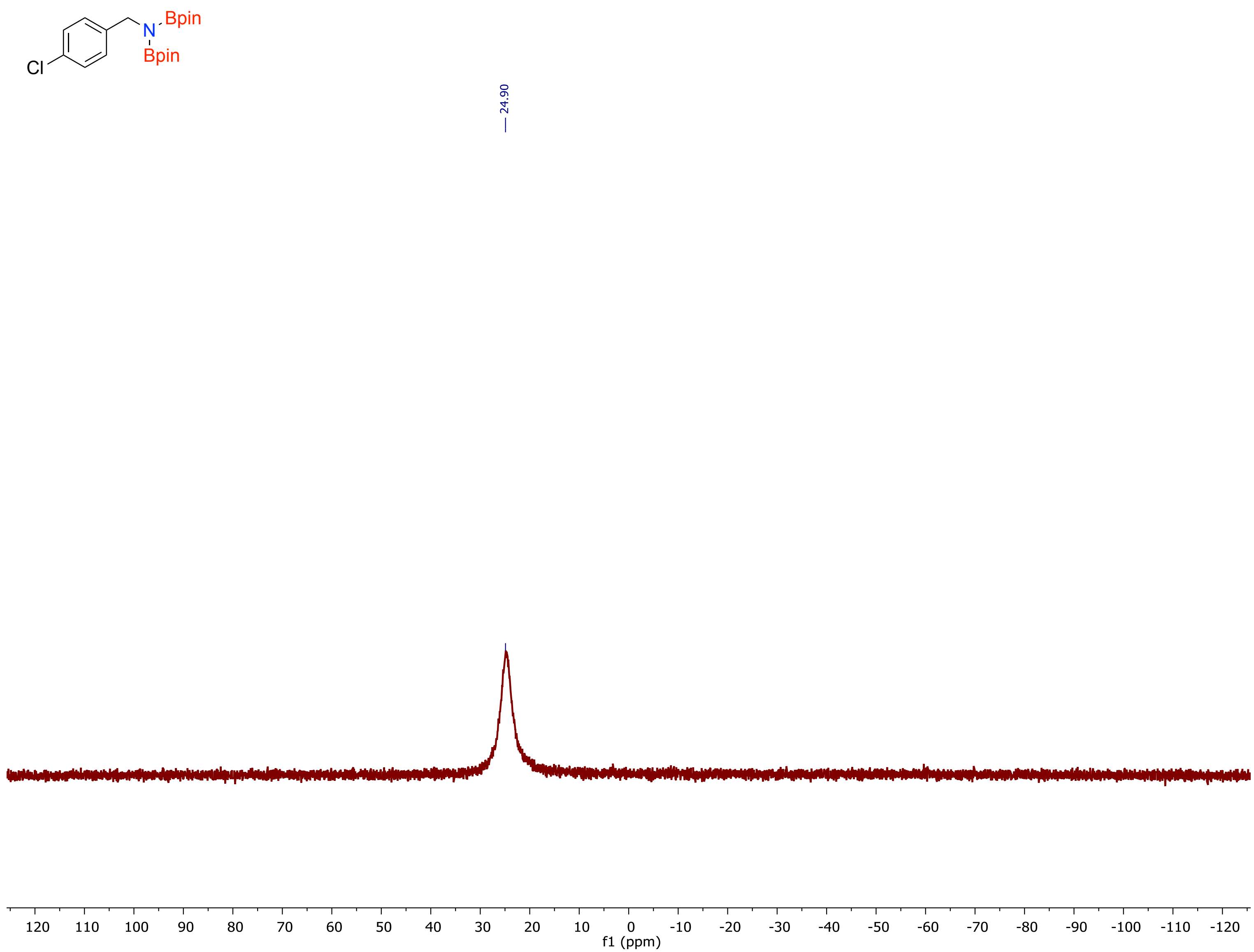
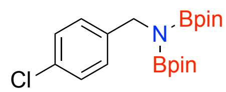


Figure S20: ^{11}B NMR spectrum of **2g**



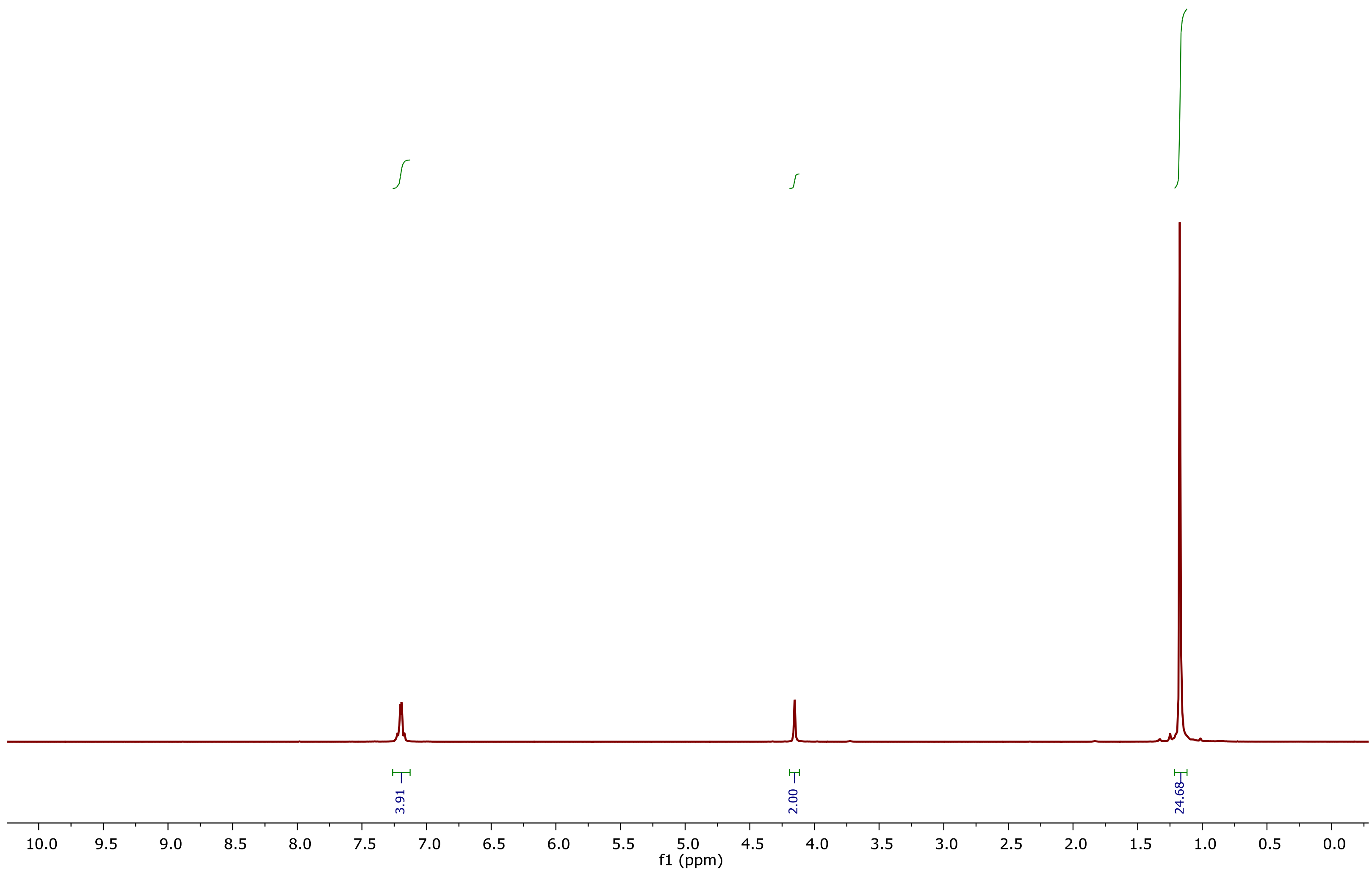


Figure S21: ^{1}H NMR spectrum of **2g.**

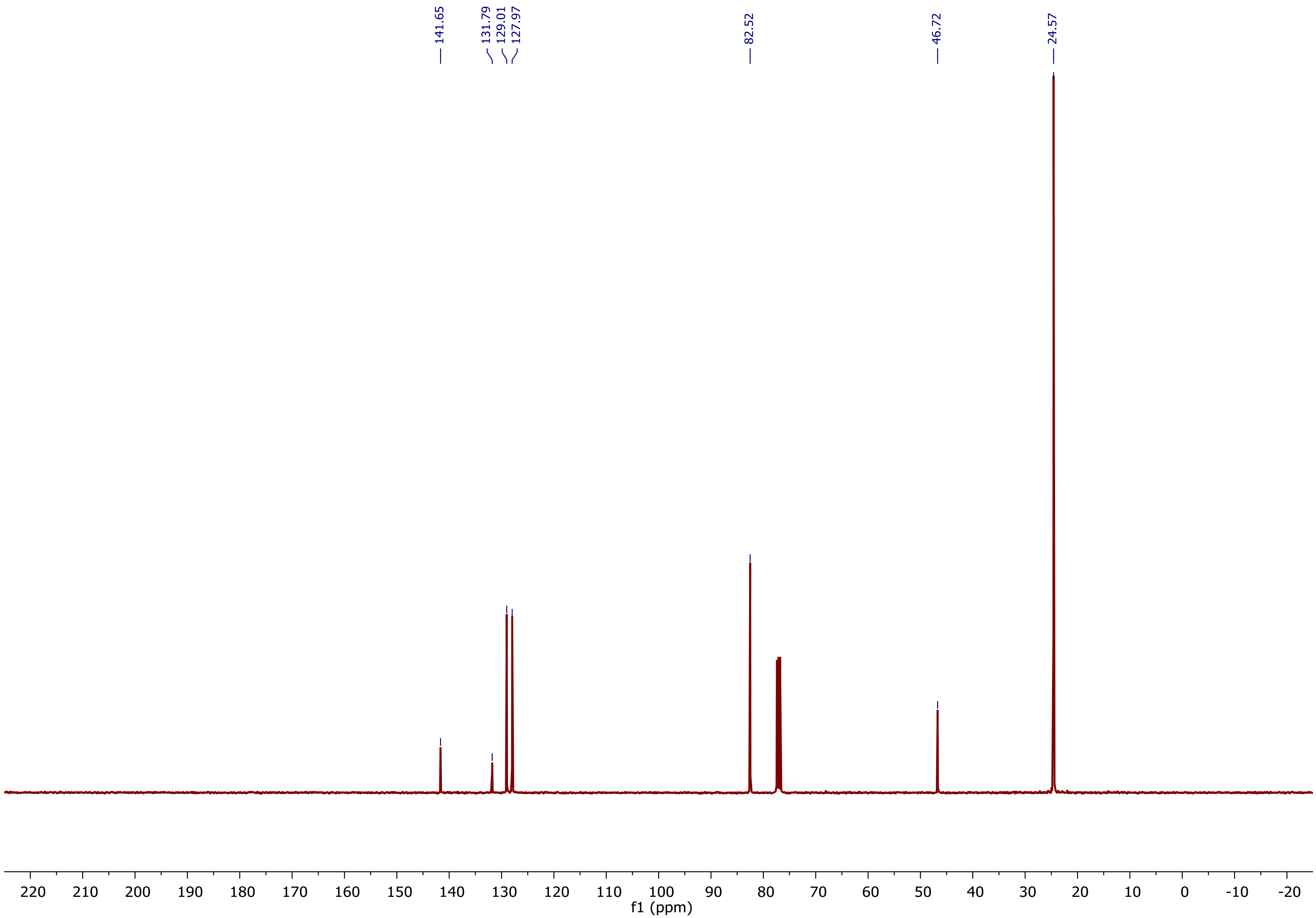
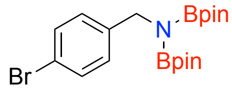


Figure S22: ^{13}C NMR spectrum of **2g**.



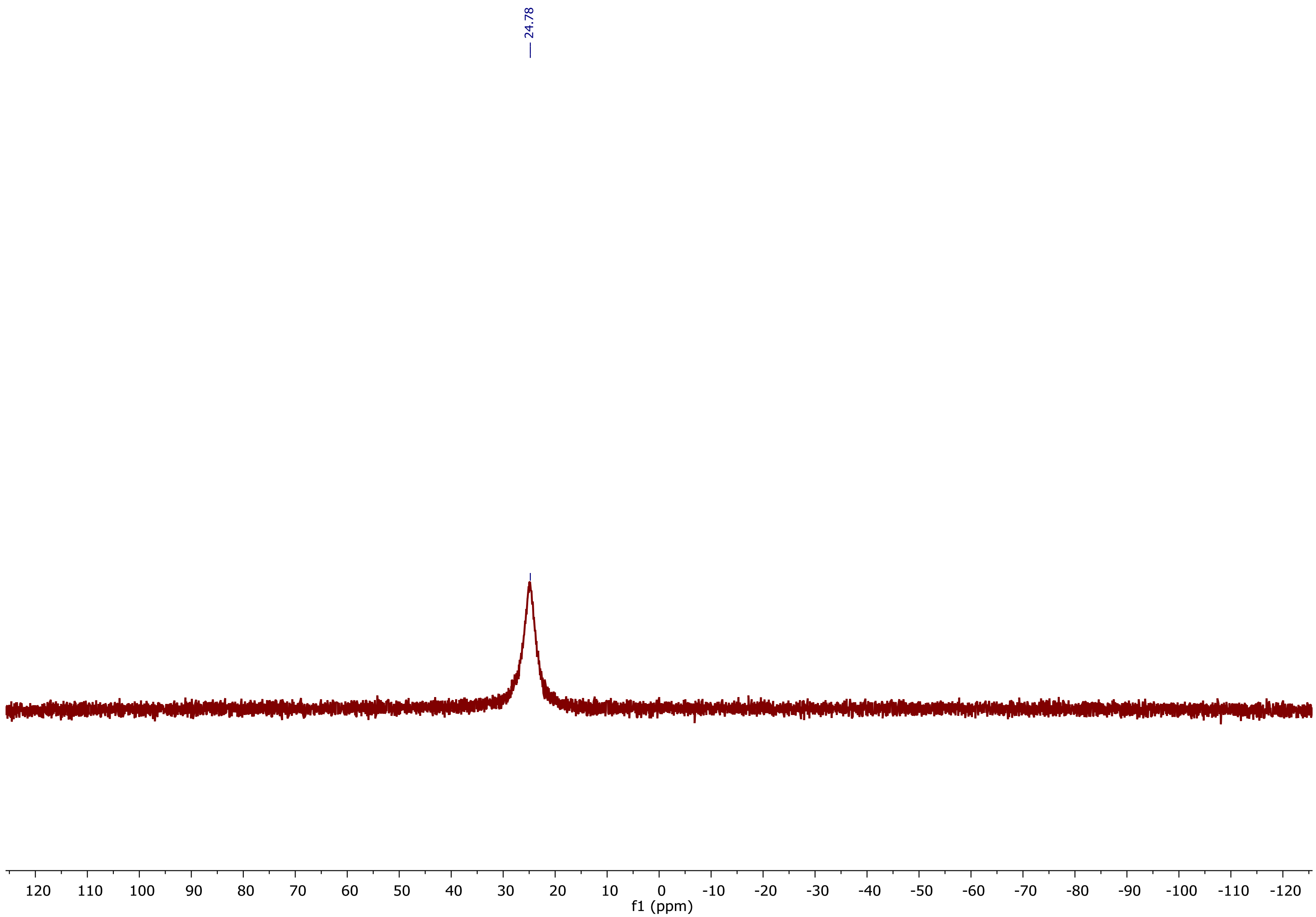
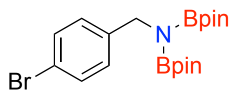


Figure S23: ^{11}B NMR spectrum of **2h.**



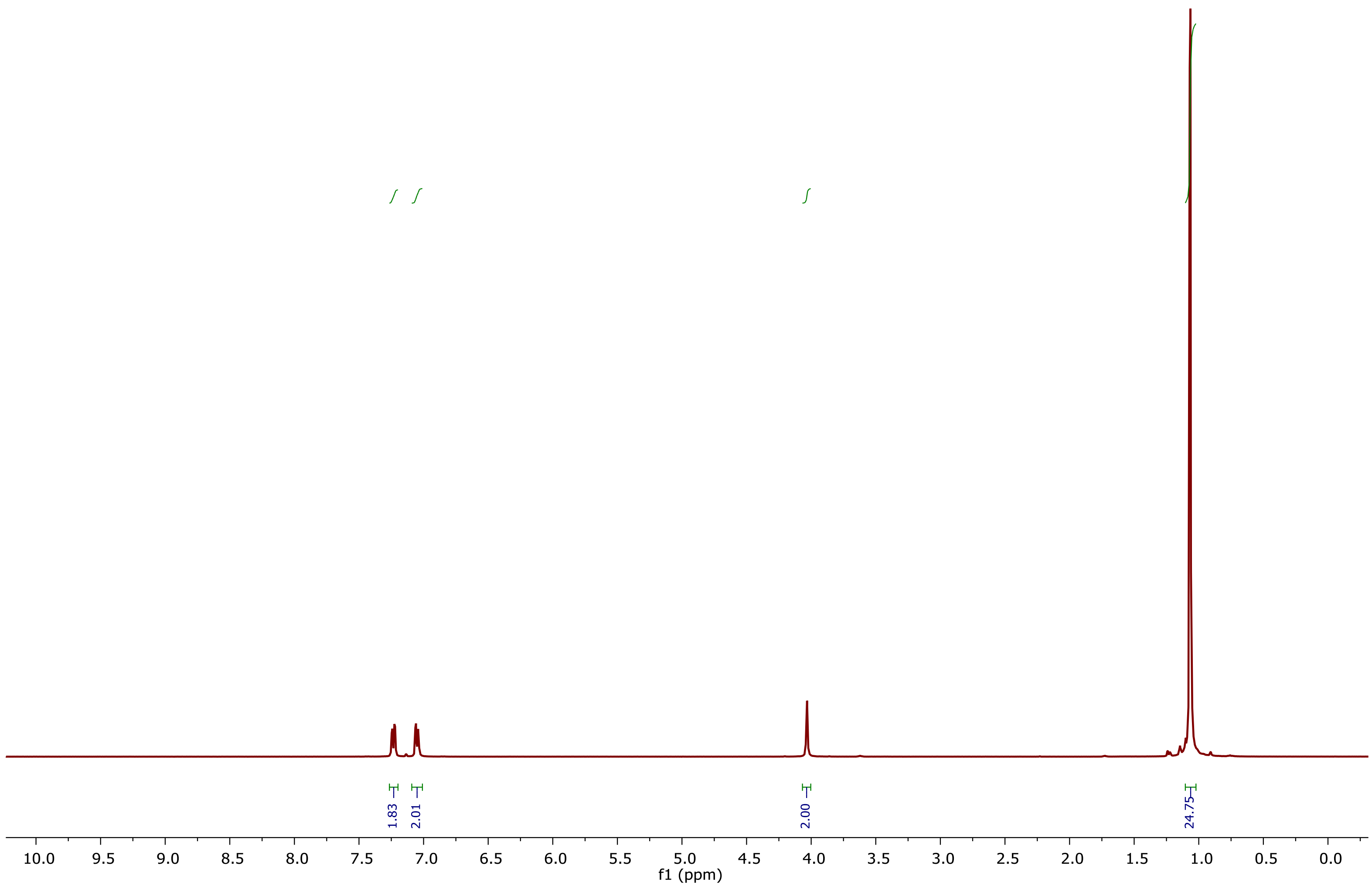


Figure S24: ^{1}H NMR spectrum of **2h.**

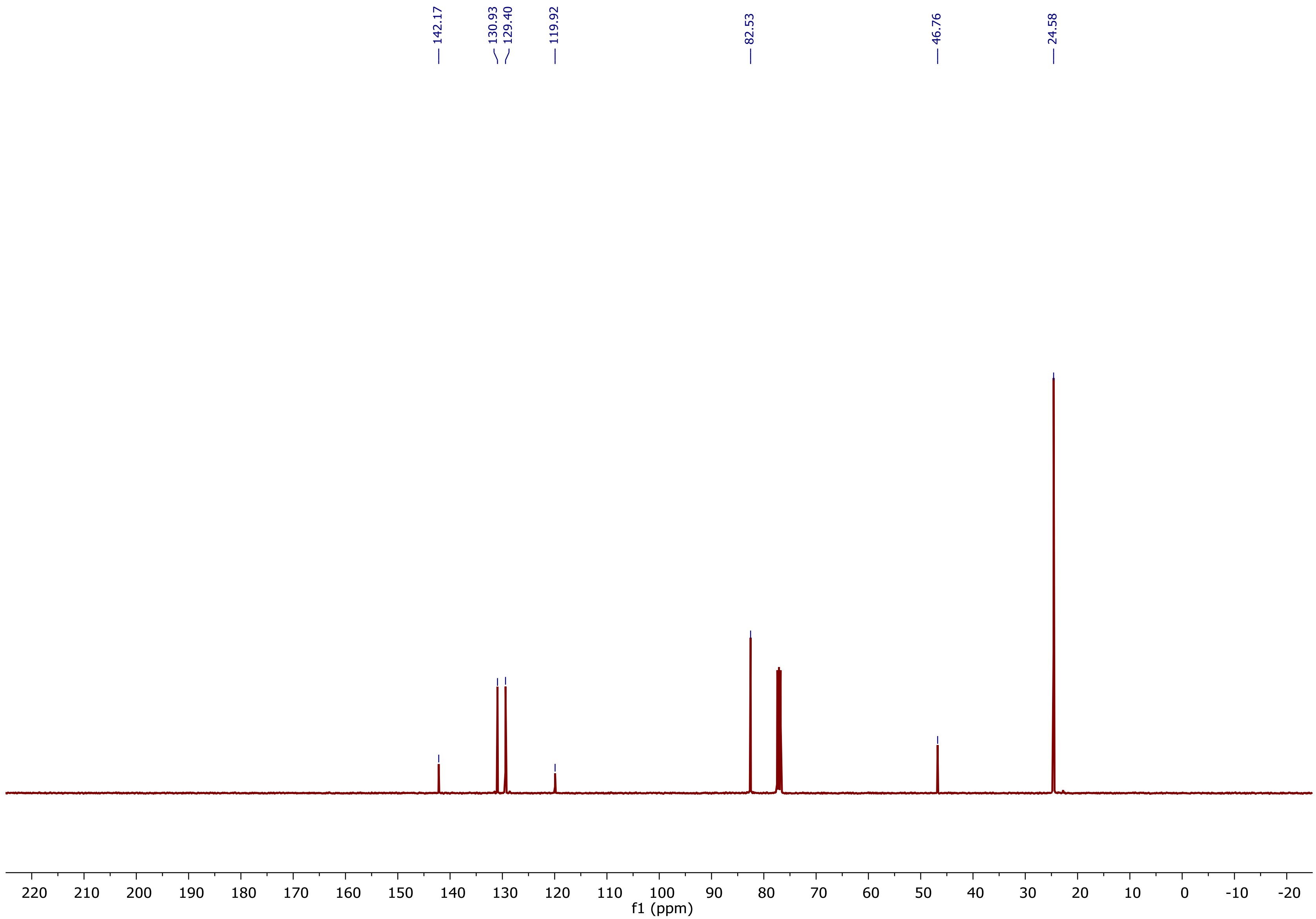


Figure S25: ^{13}C NMR spectrum of **2h.**

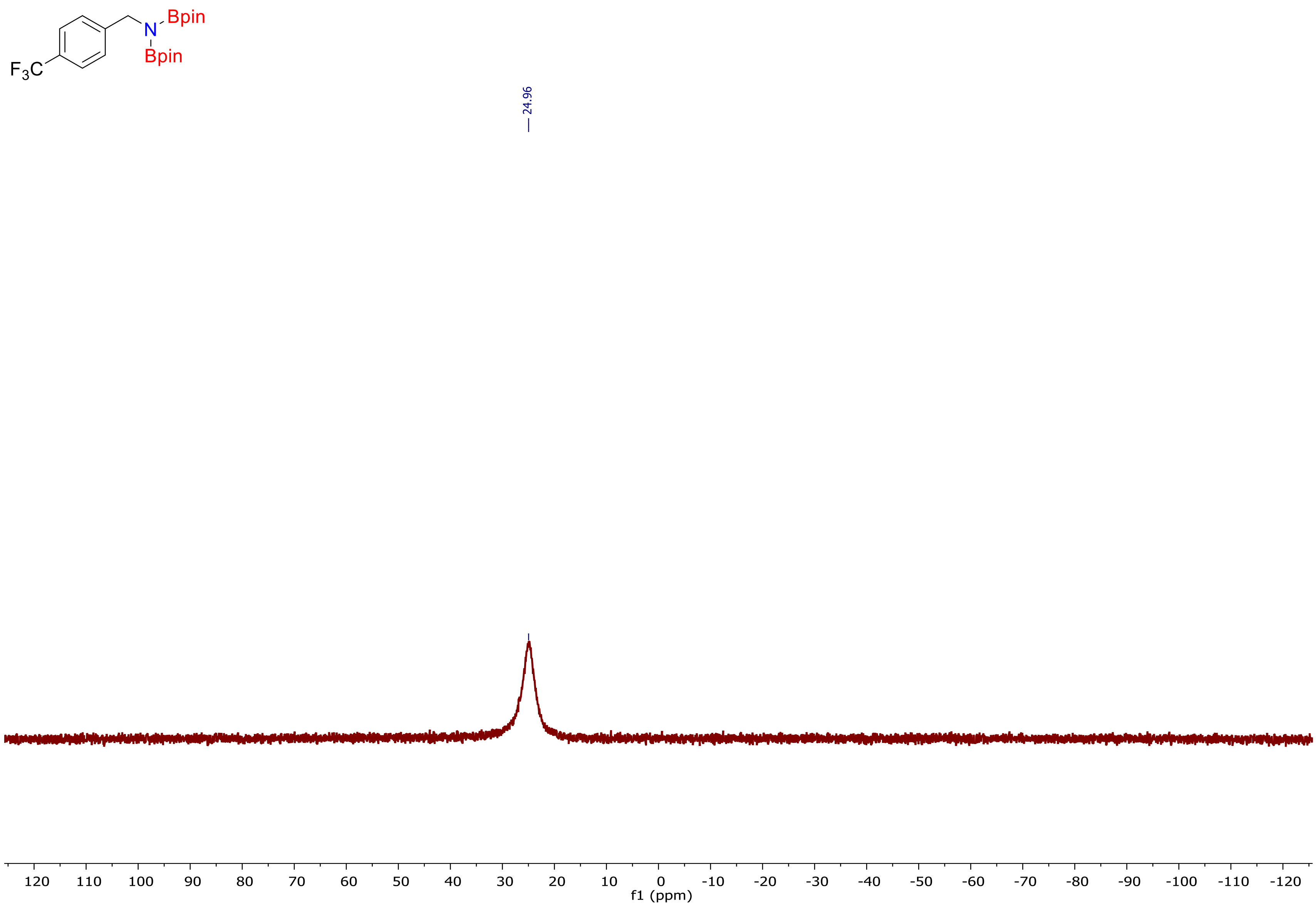
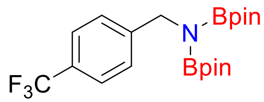


Figure S26: ^{11}B NMR spectrum of **2i**



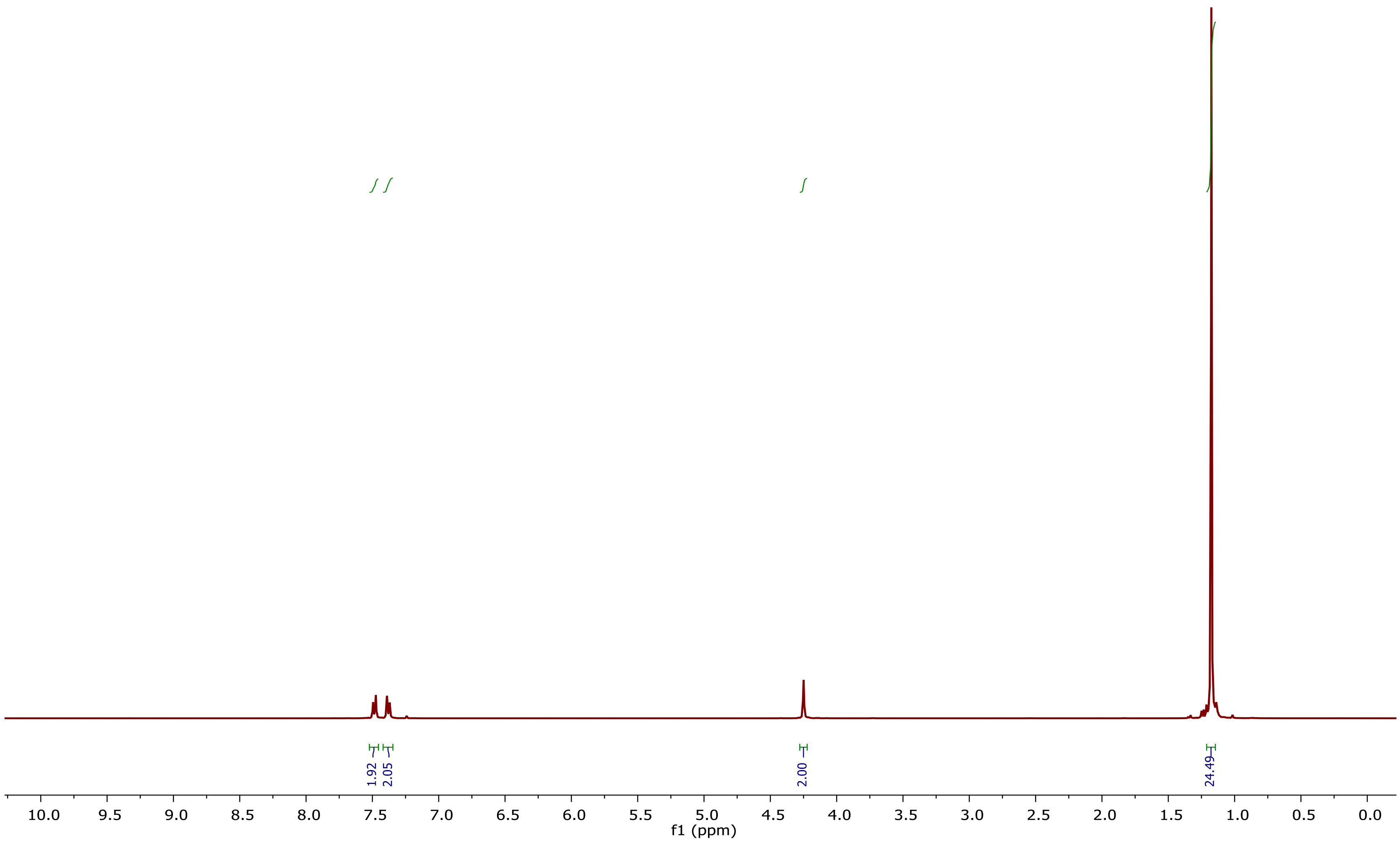


Figure S27: ^{1}H NMR spectrum of **2i**

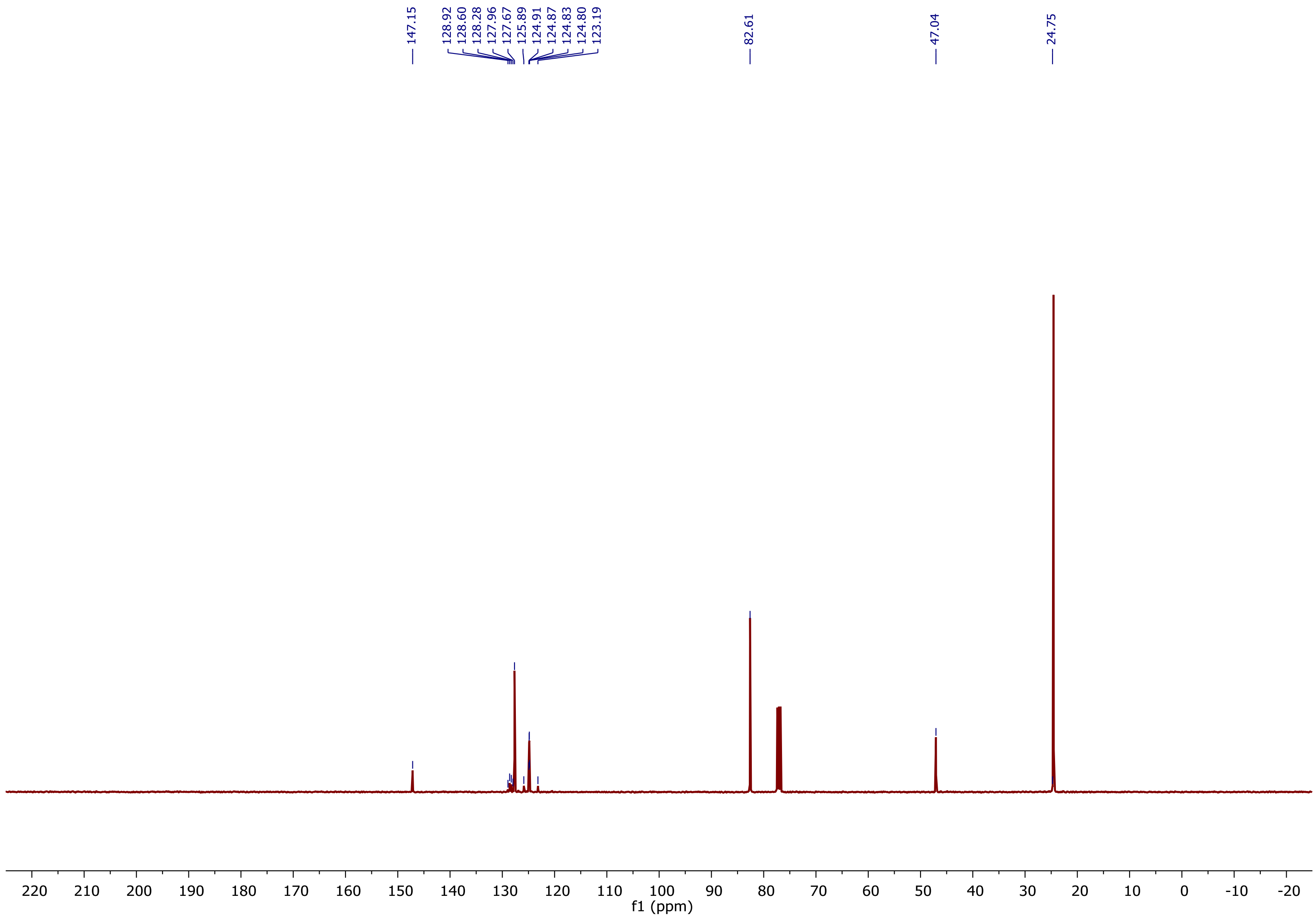
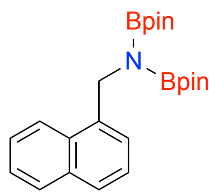


Figure S28: ^{13}C NMR spectrum of **2i**



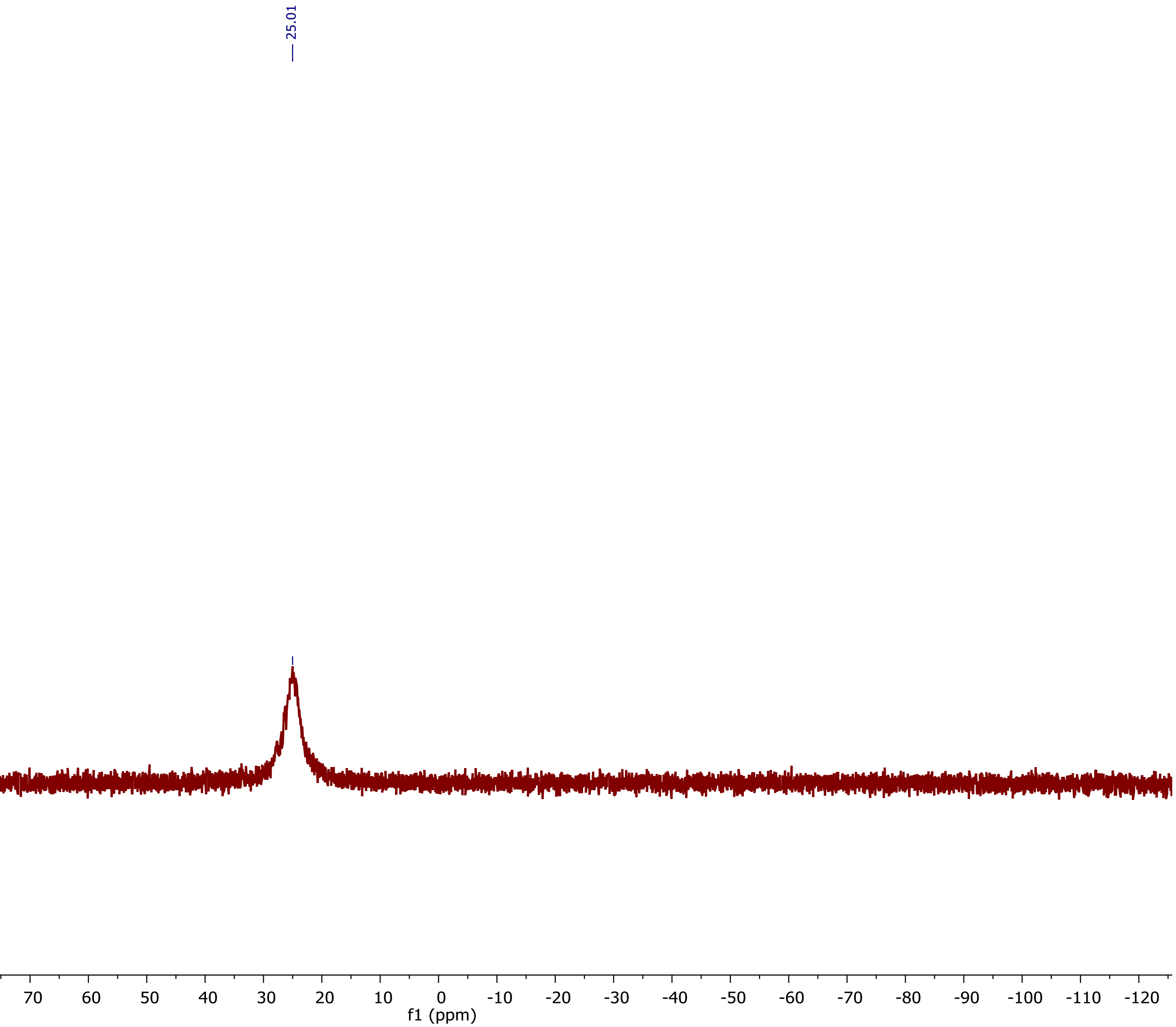
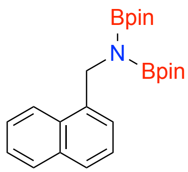


Figure S29: ^{11}B NMR spectrum of **2j**



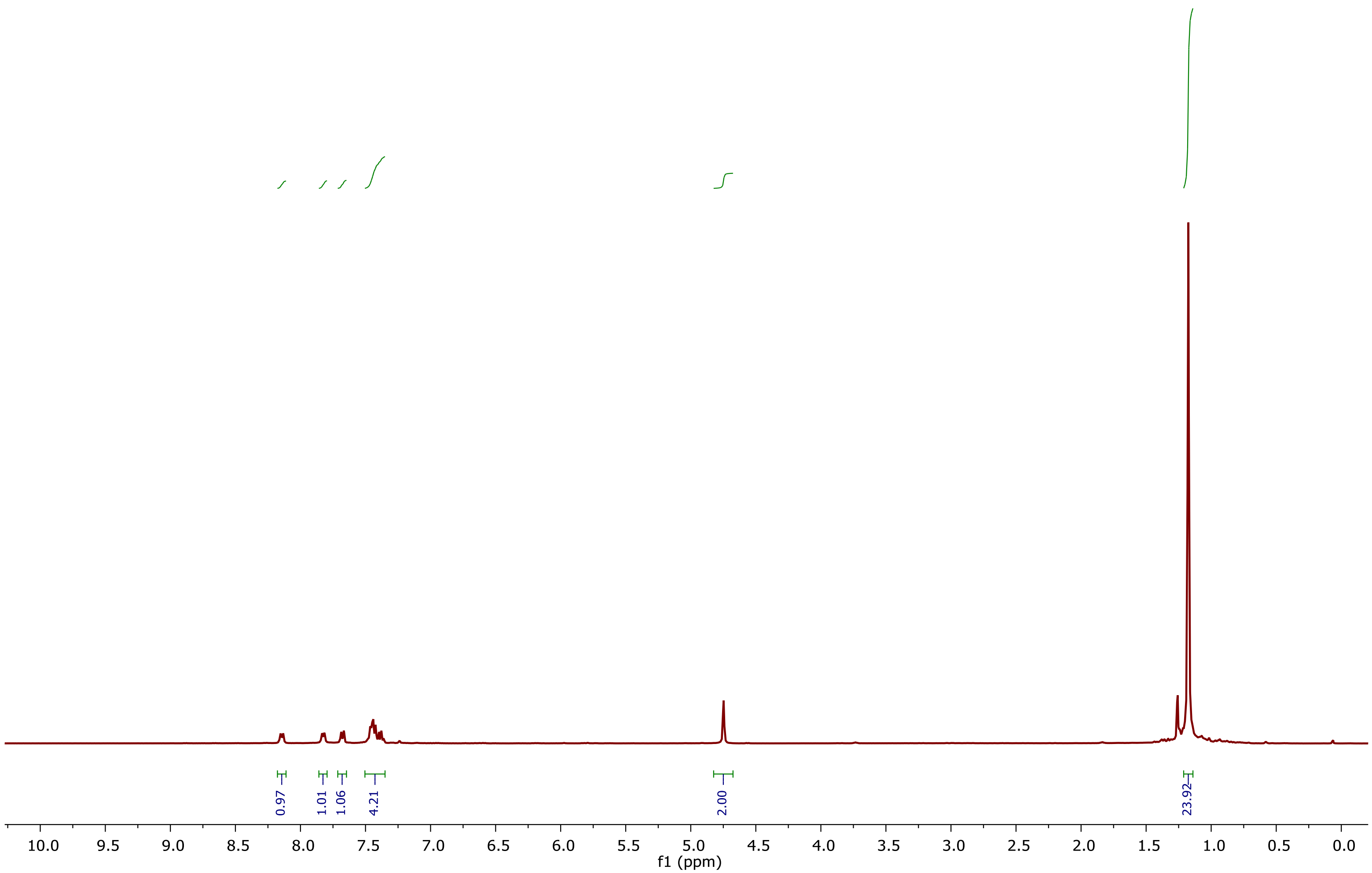


Figure S30: ^{1}H NMR spectrum of **2j.**

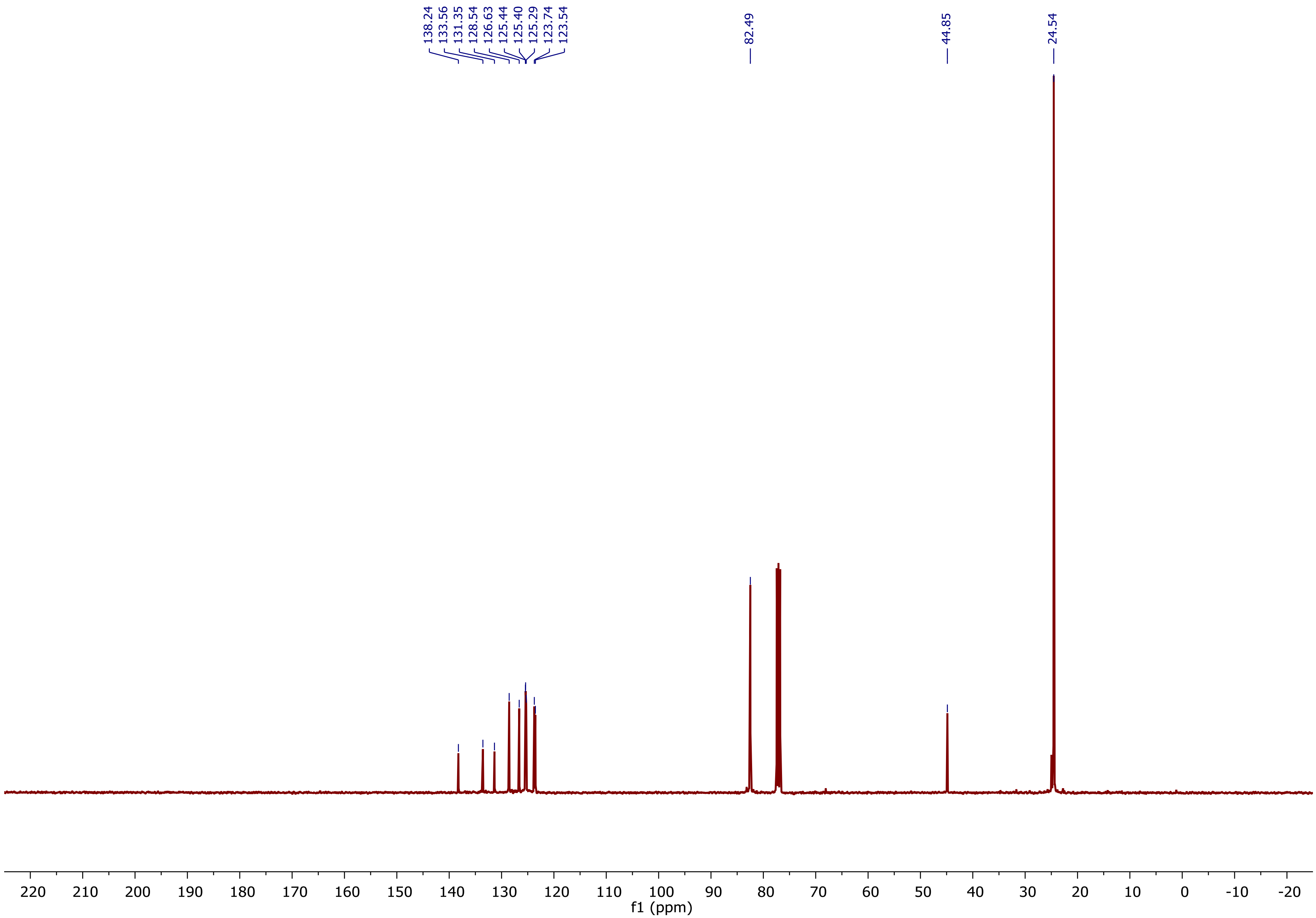


Figure S31: ^{13}C NMR spectrum of **2j.**

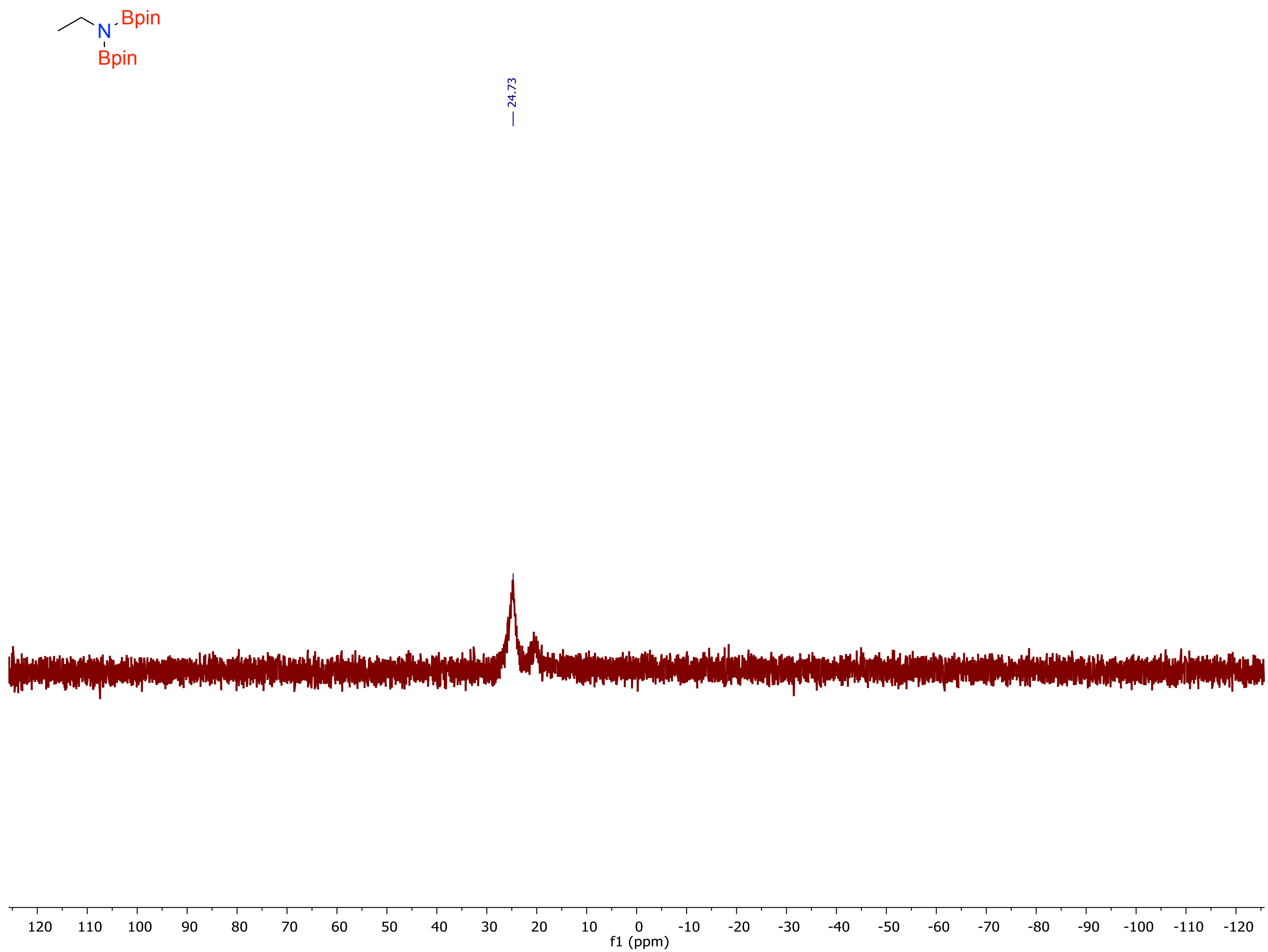
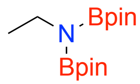


Figure S32: ^{11}B NMR spectrum of **2k**



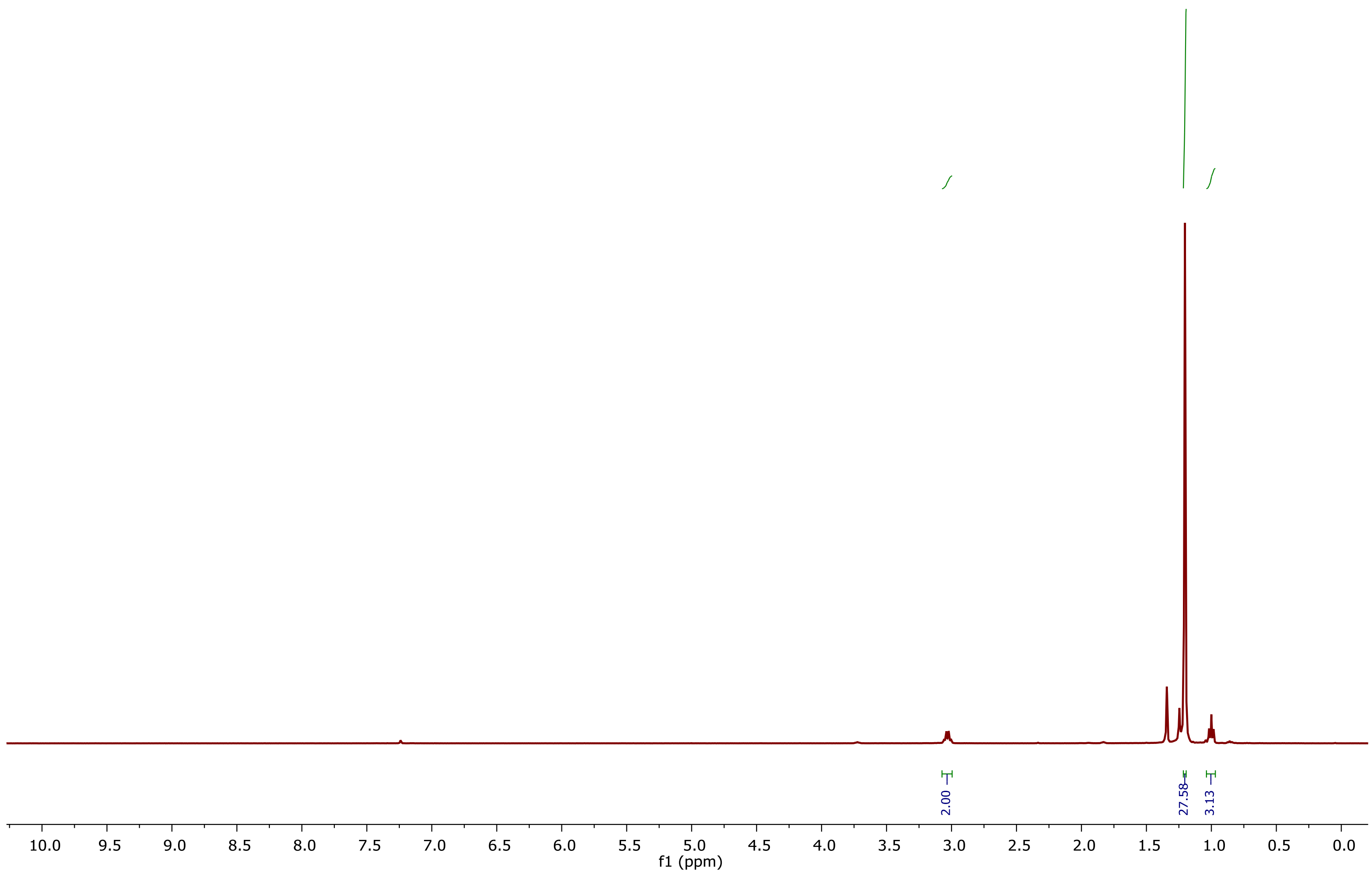


Figure S33: ^{1}H NMR spectrum of **2k**

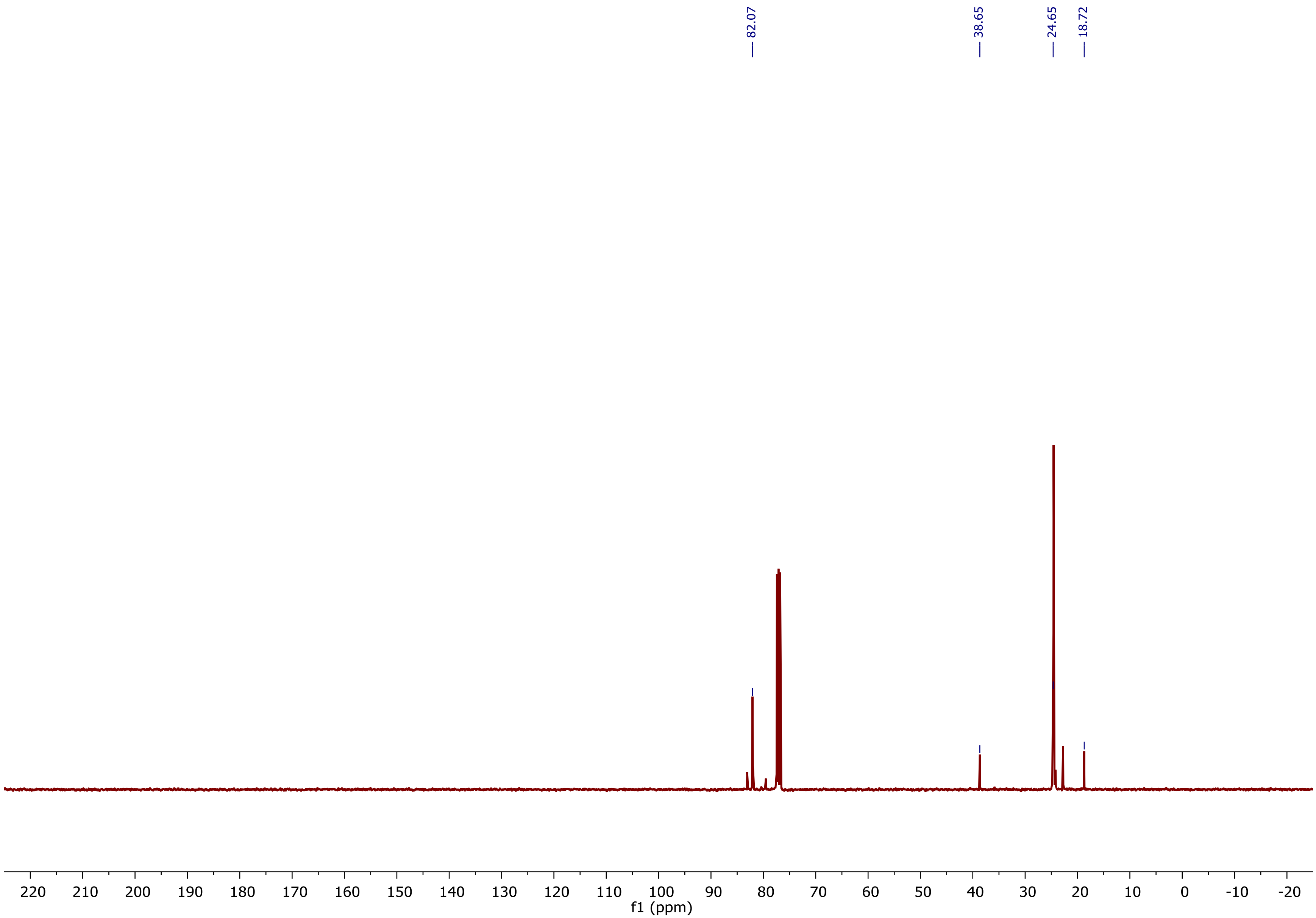


Figure S34: ^{13}C NMR spectrum of **2k**.

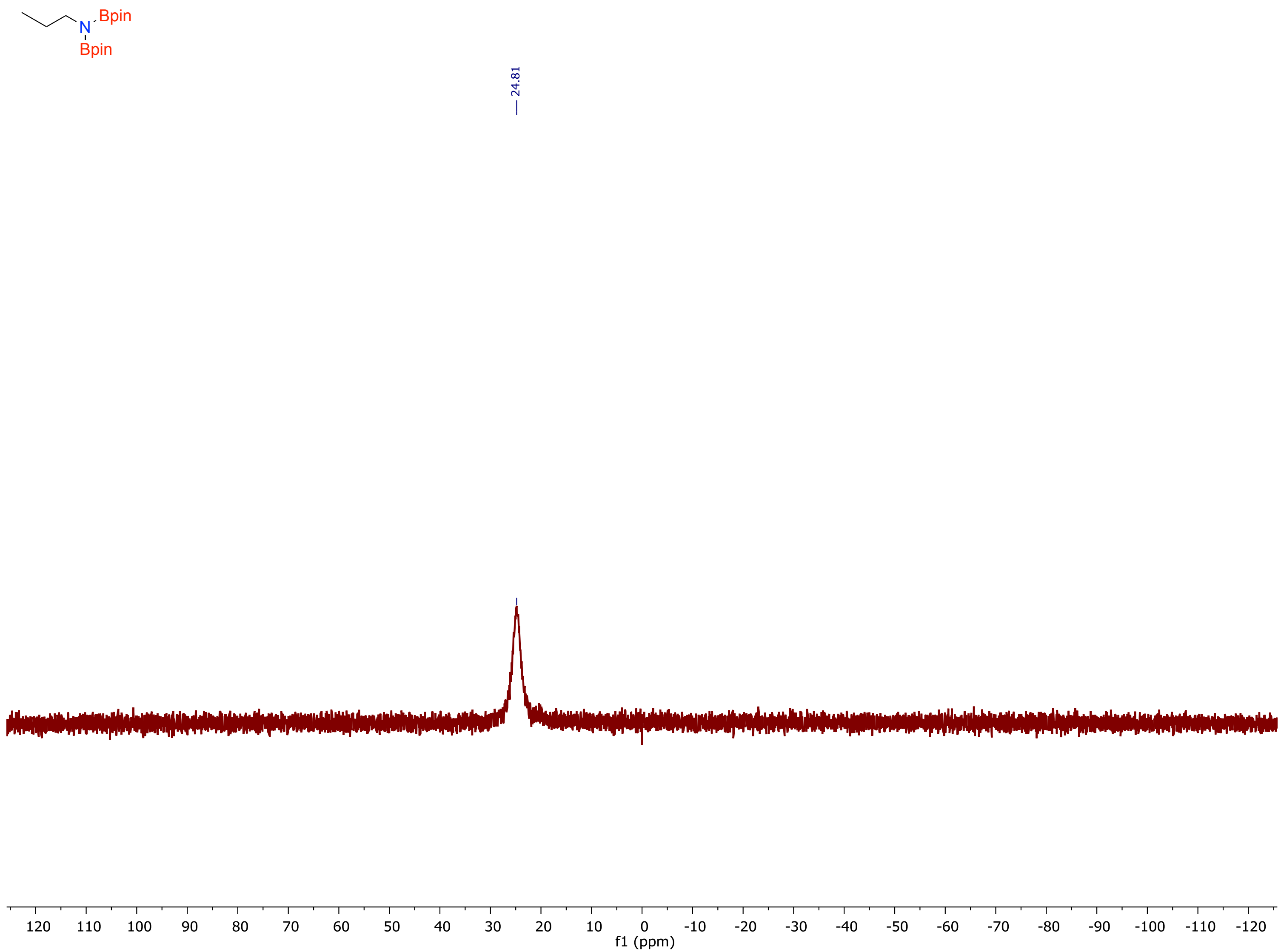
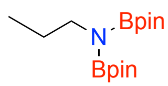


Figure S35: ^{11}B NMR spectrum of **2l**



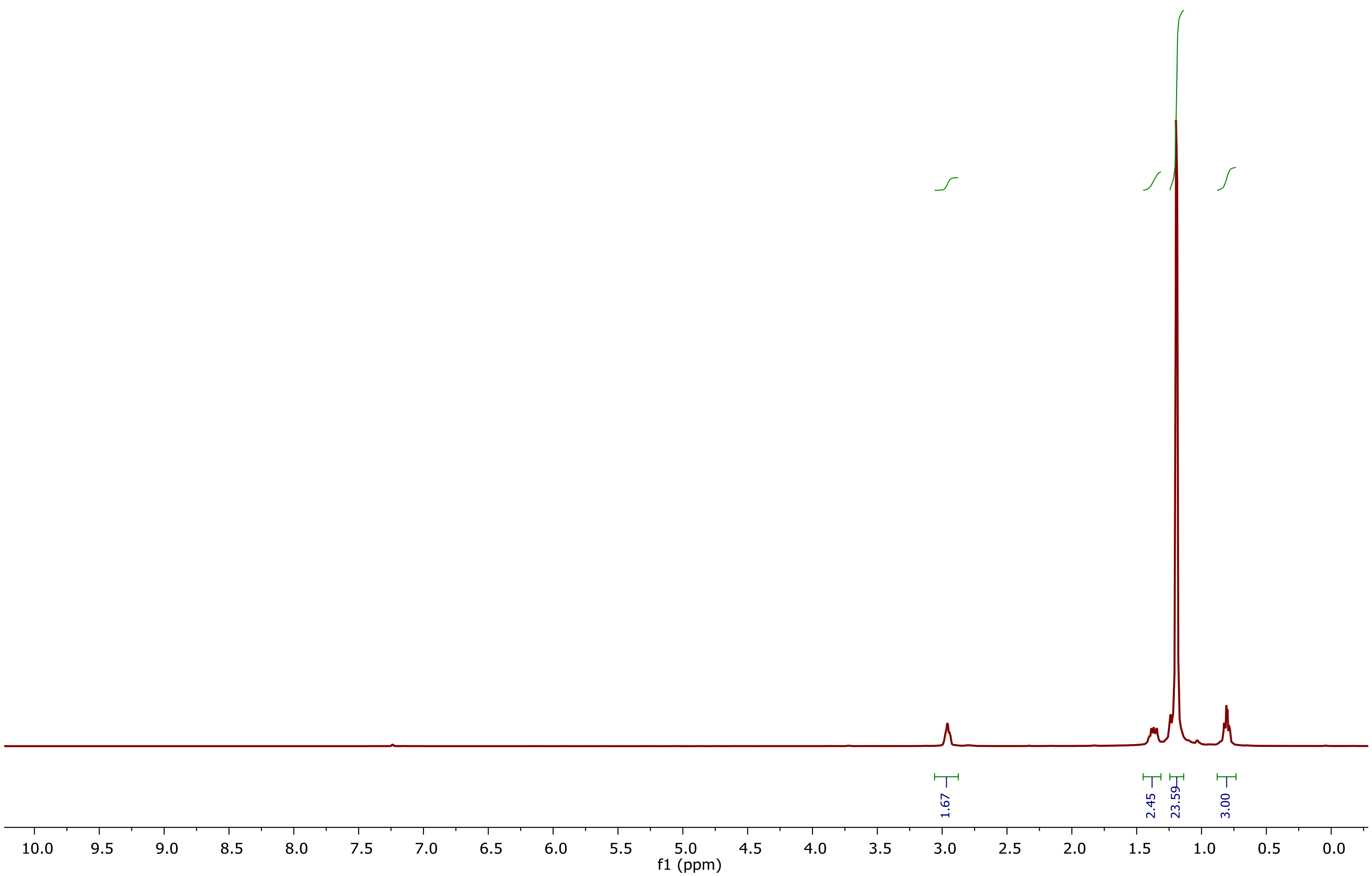


Figure S36: ^{1}H NMR spectrum of **2l.**

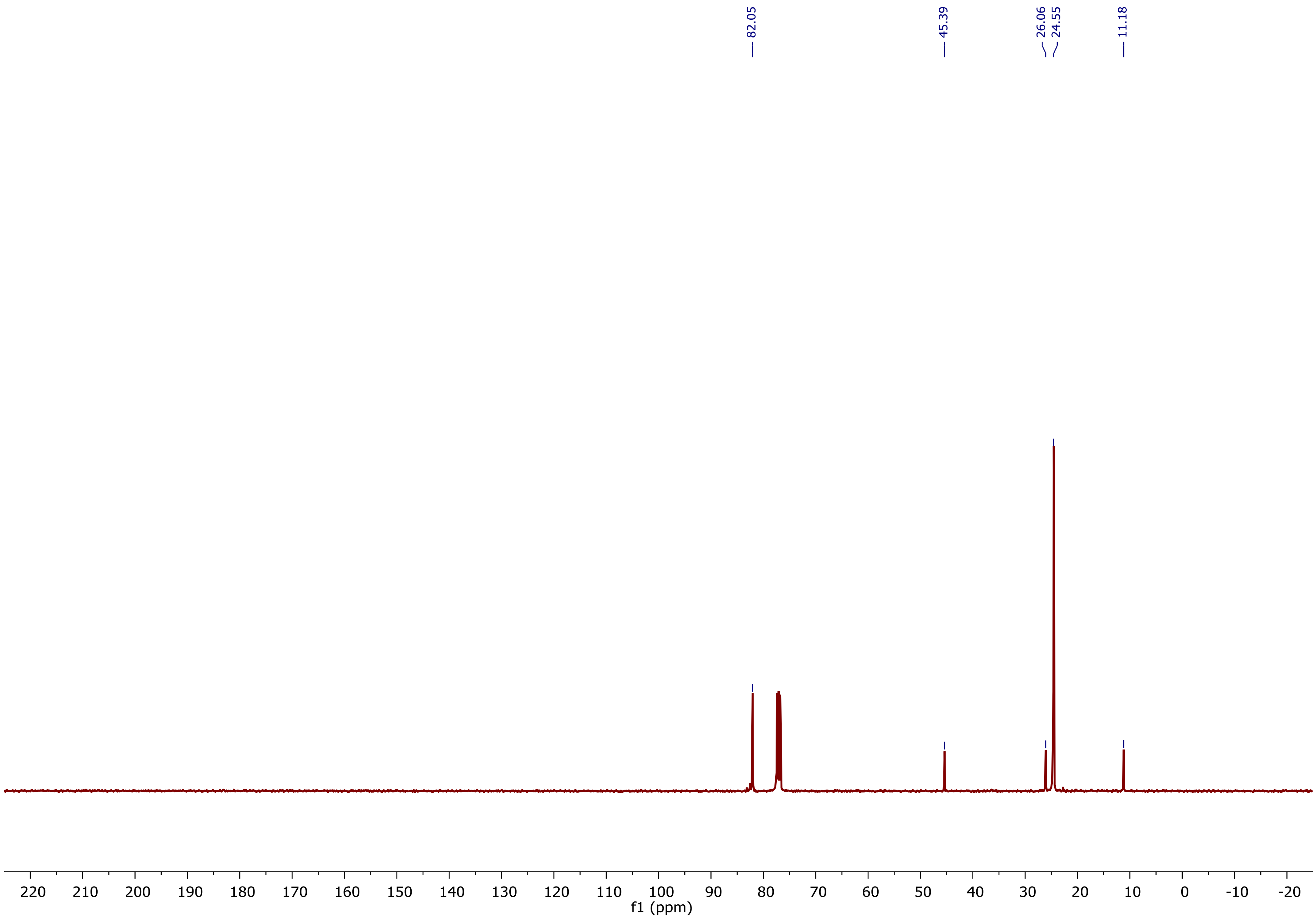
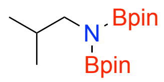


Figure S37: ^{13}C NMR spectrum of **2l**.



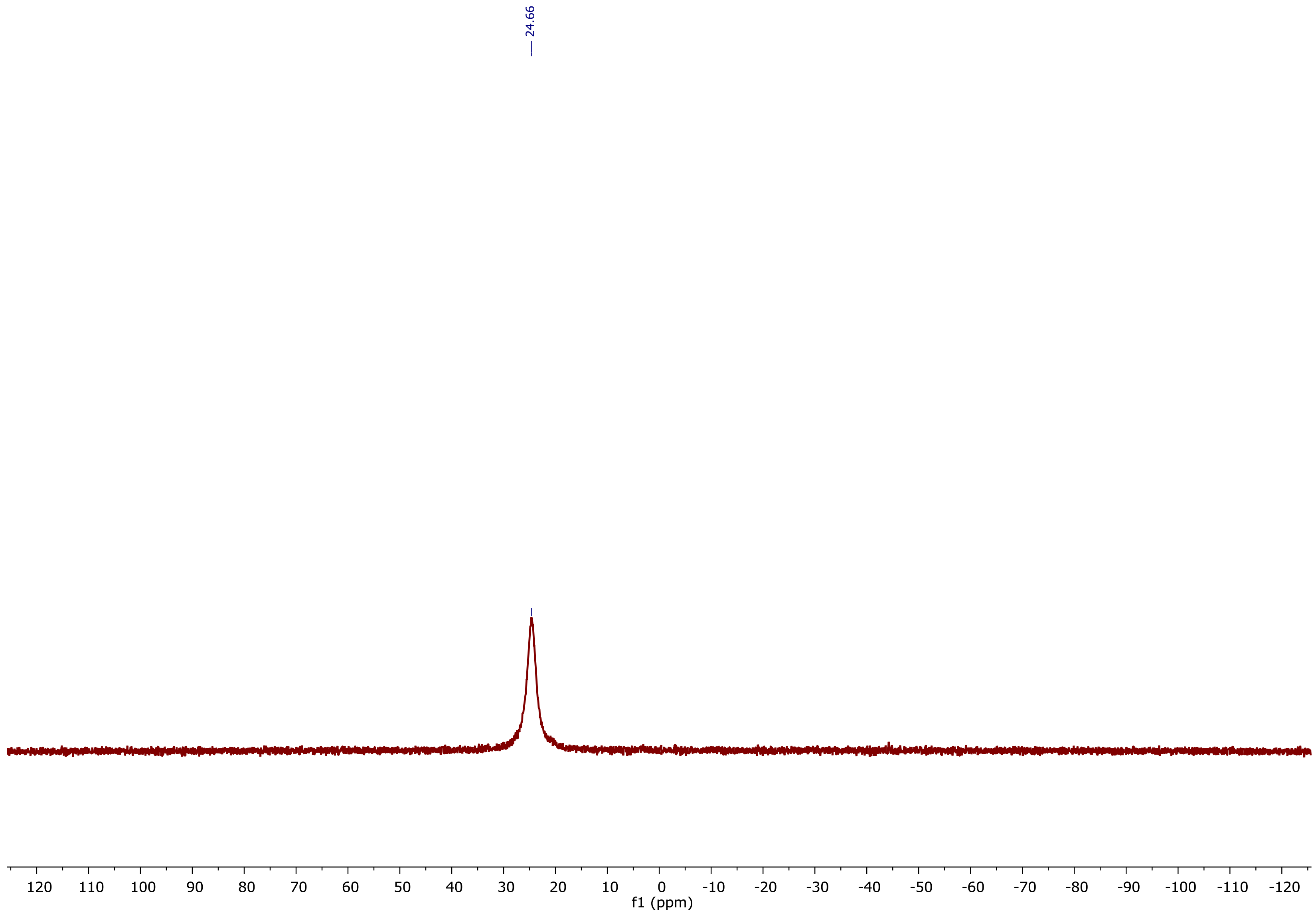
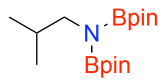


Figure S38: ^{11}B NMR spectrum of **2m**



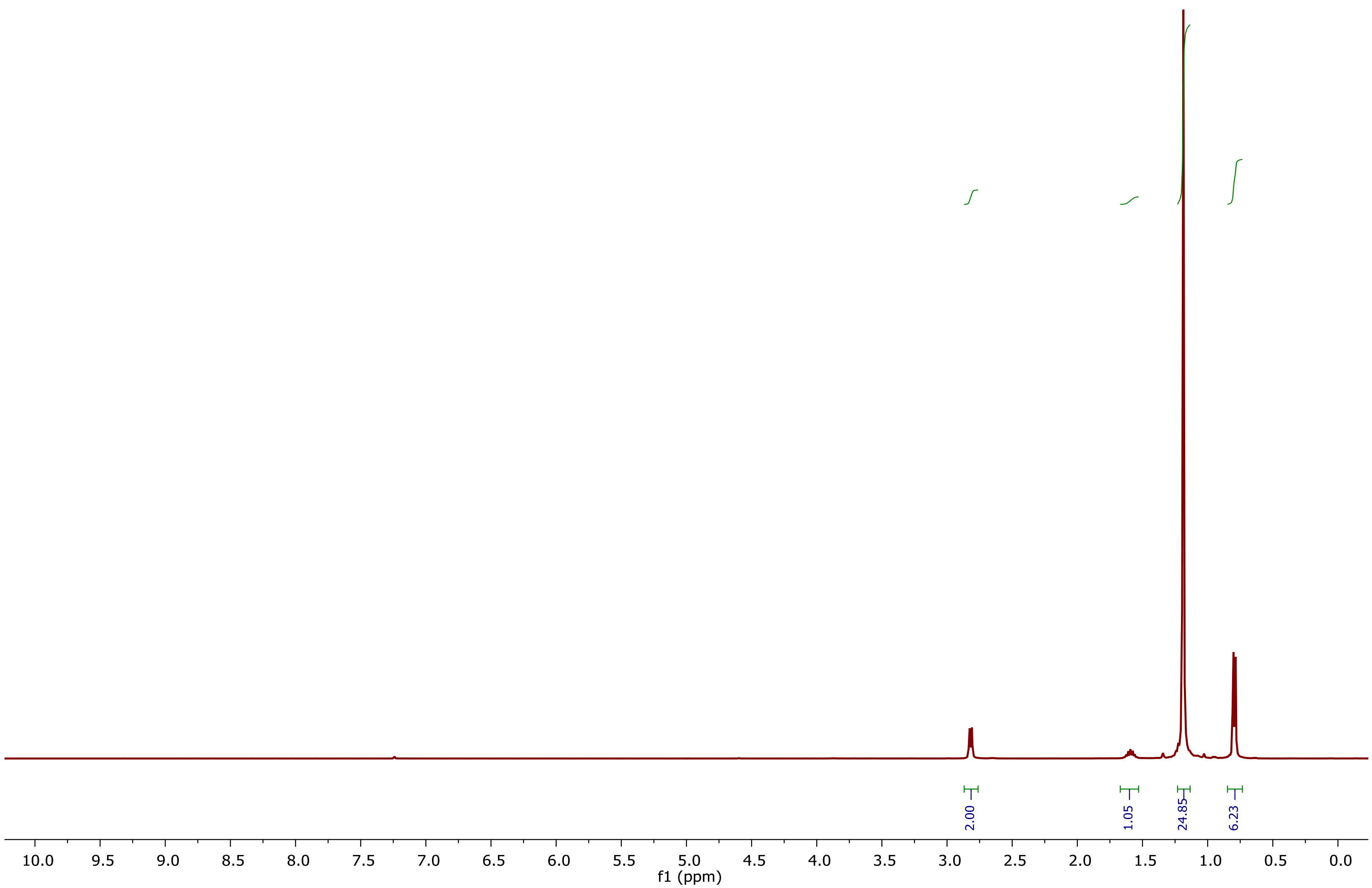


Figure S39: ^{1}H NMR spectrum of **2m.**

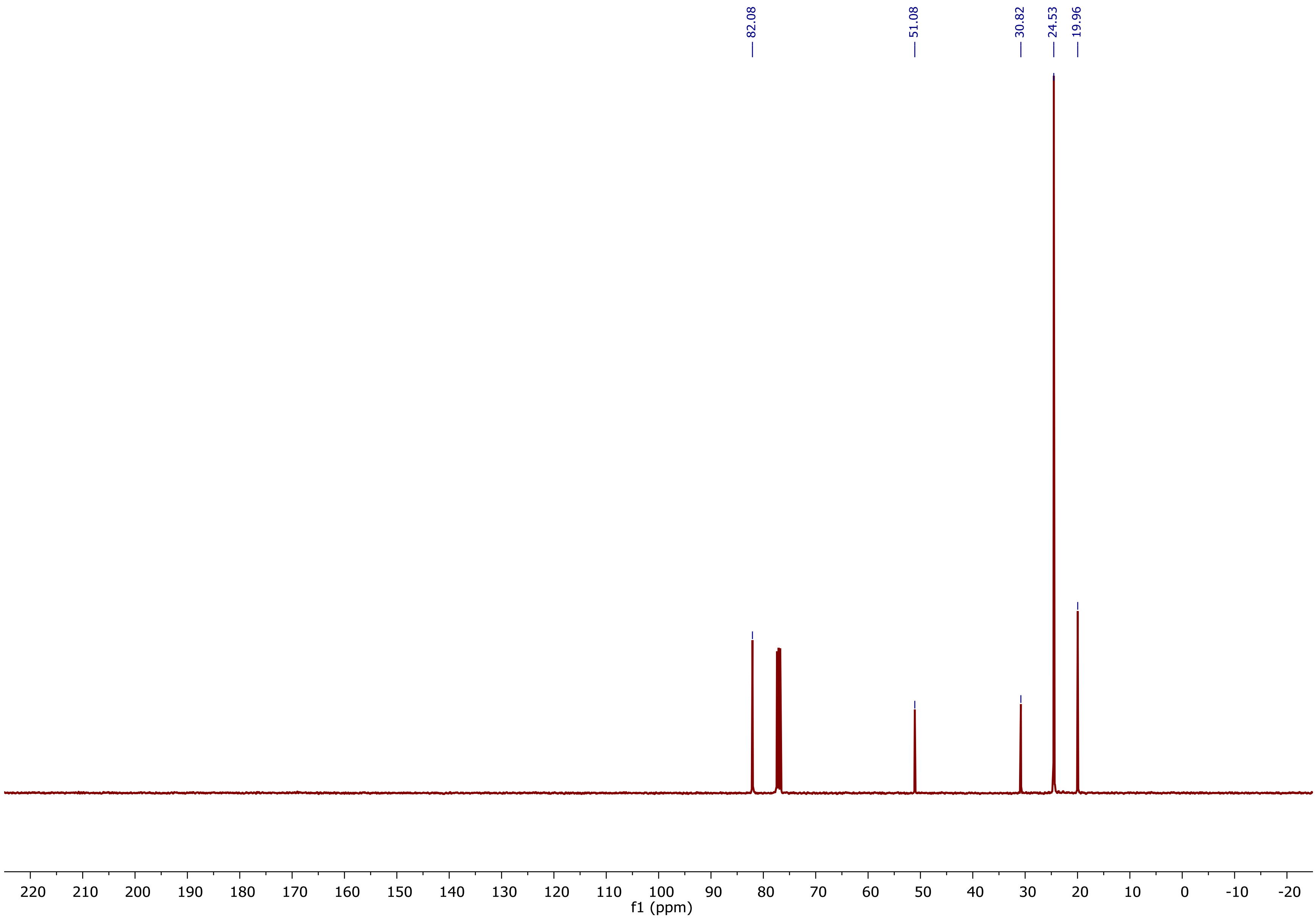
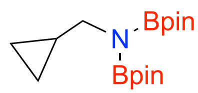


Figure S40: ^{13}C NMR spectrum of **2m**.



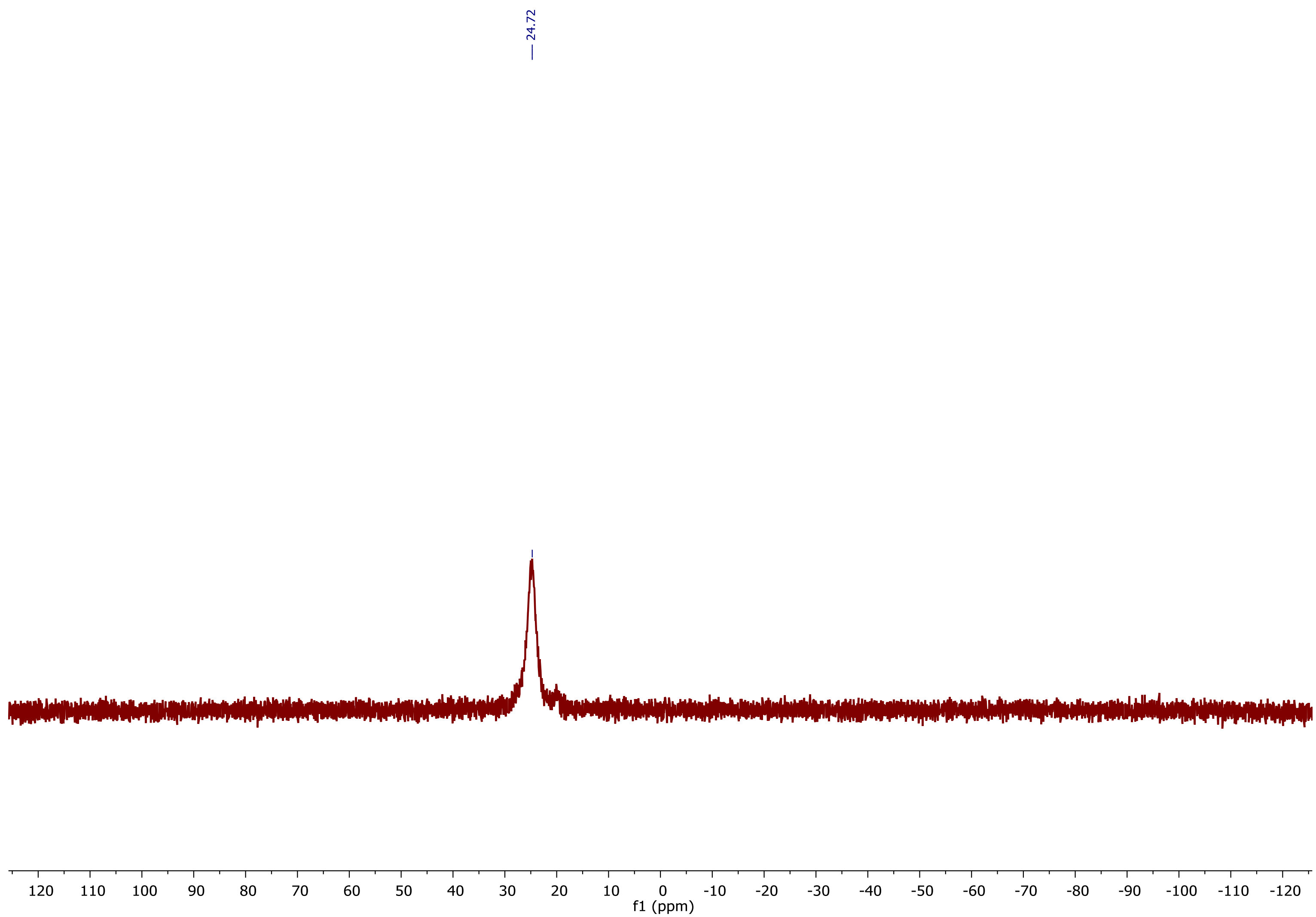
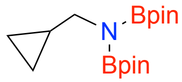


Figure S41: ^{11}B NMR spectrum of **2n.**



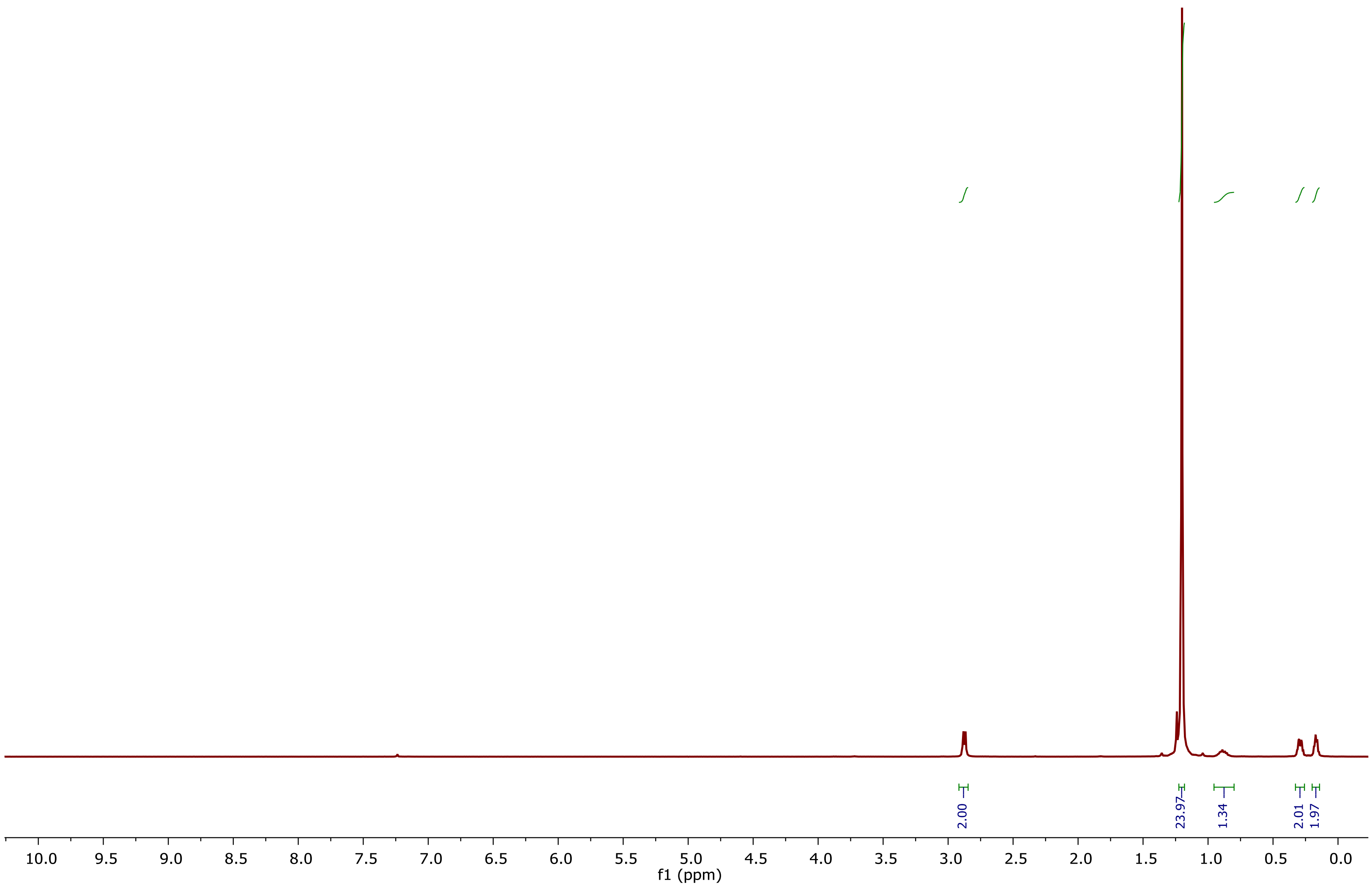


Figure S42: ^{1}H NMR spectrum of **2n.**

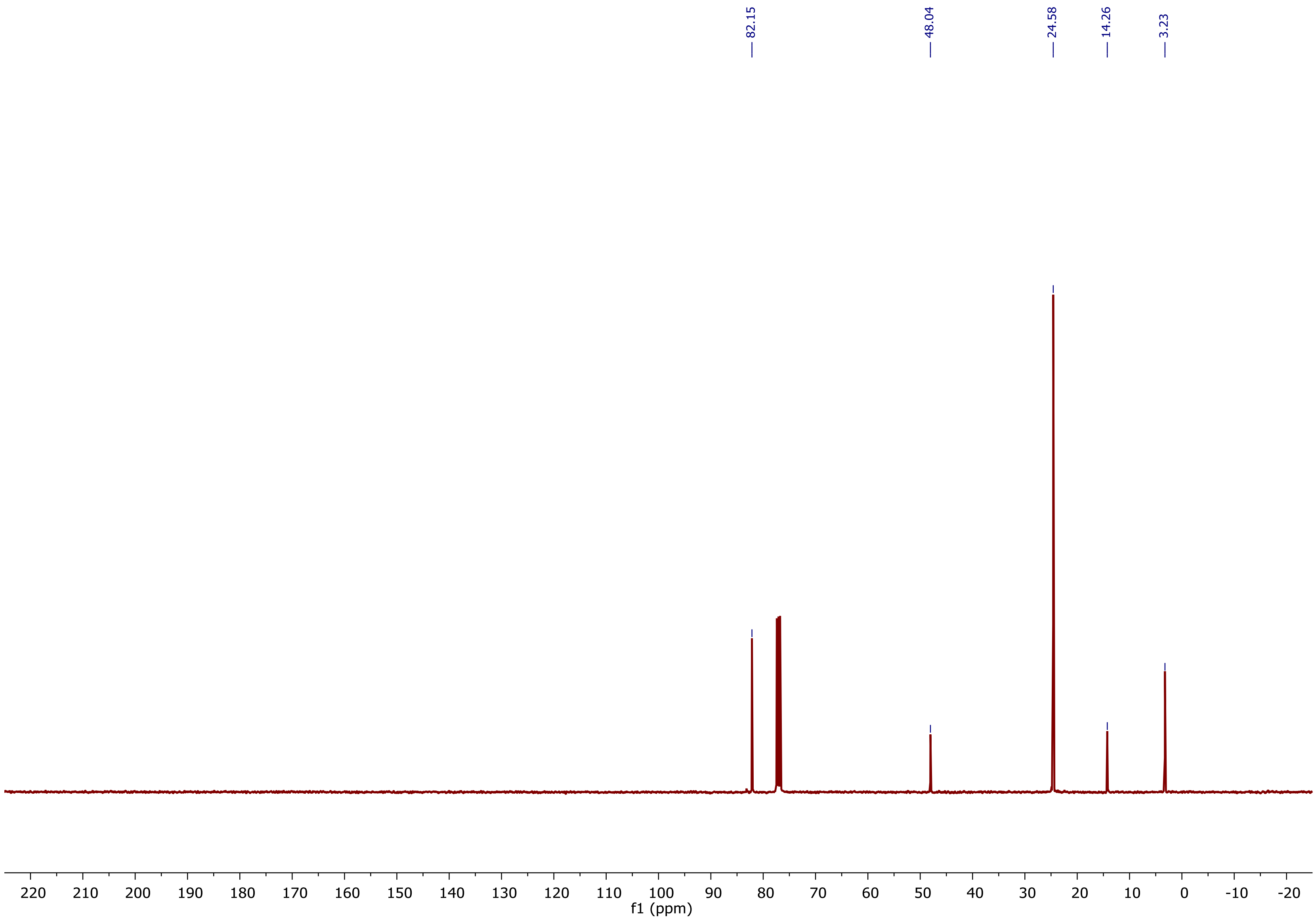


Figure S43: ^{13}C NMR spectrum of **2n**.

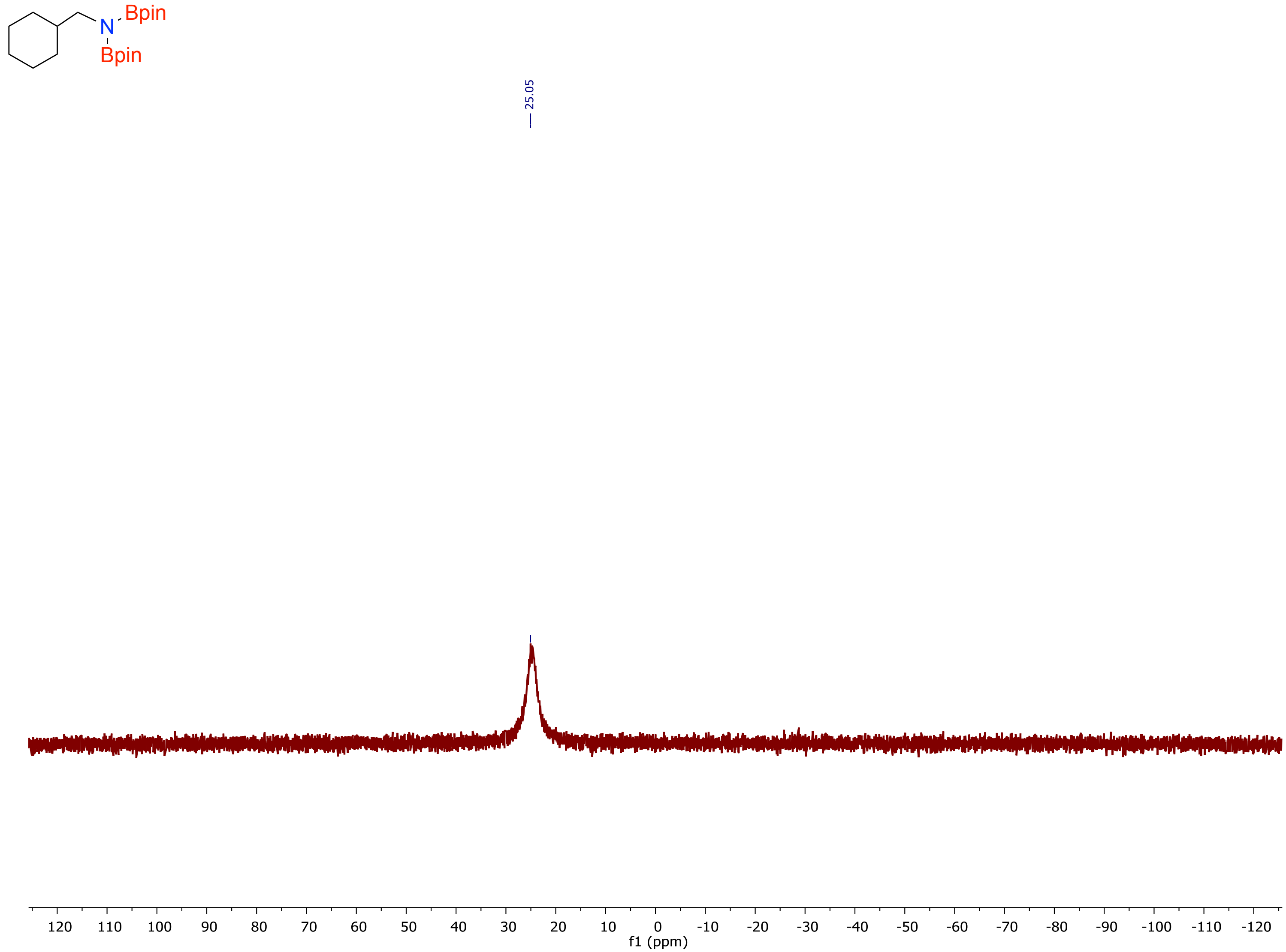
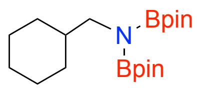


Figure S44: ^{11}B NMR spectrum of **2o.**



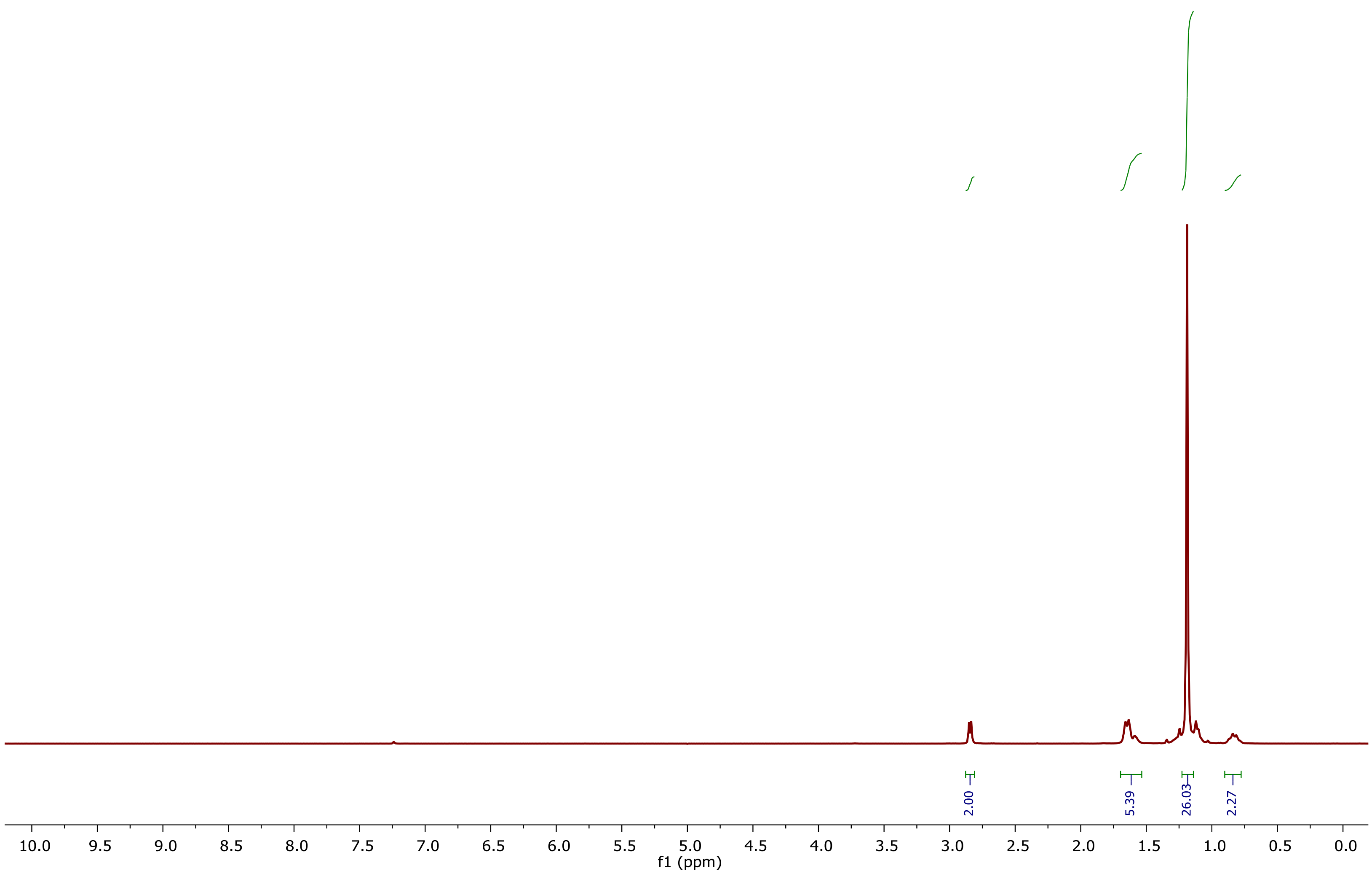


Figure S45: ^{1}H NMR spectrum of **2o.**

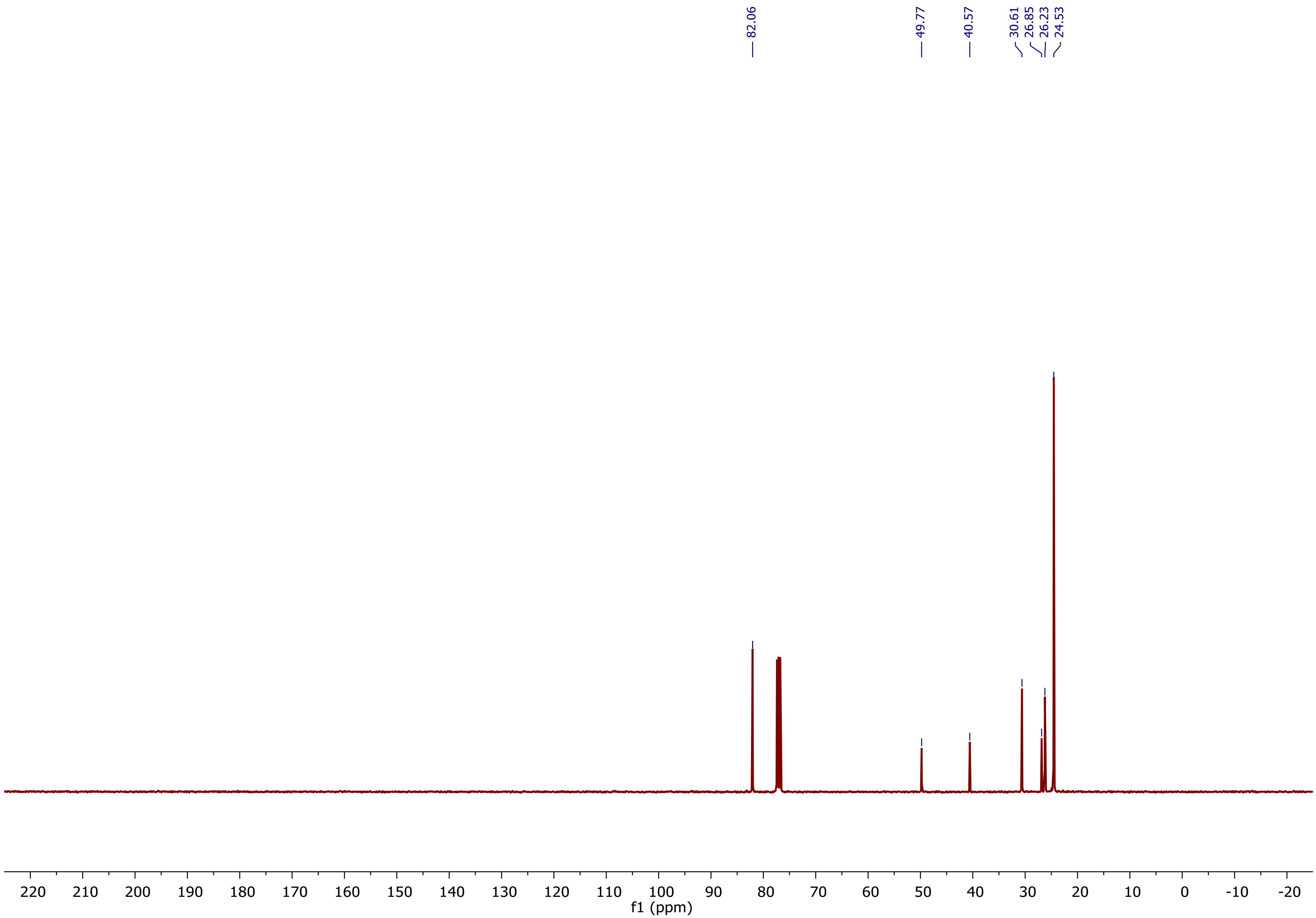
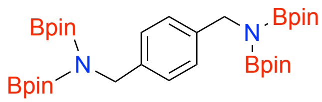


Figure S46: ^{13}C NMR spectrum of **2o**.



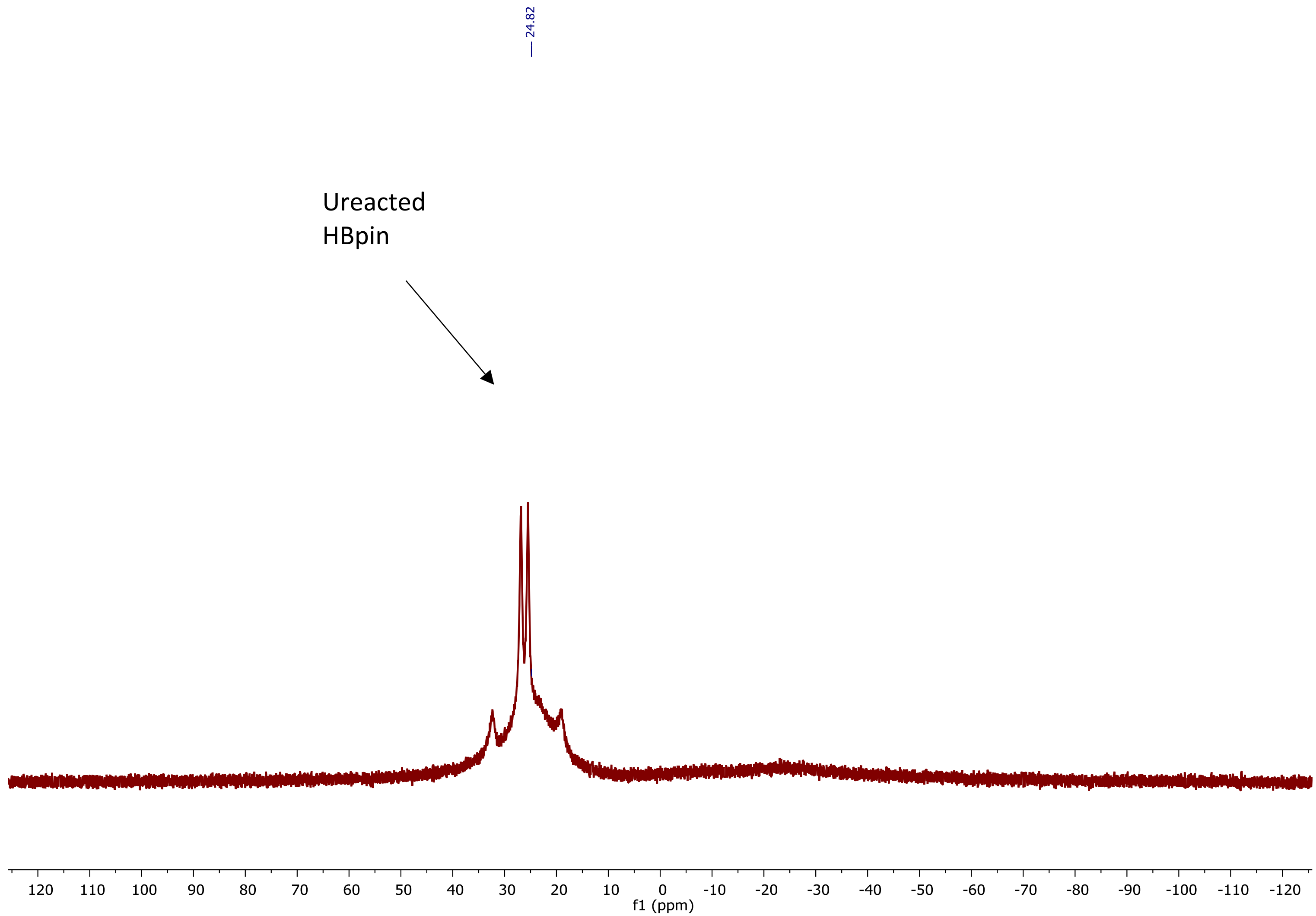


Figure S47: ^{11}B NMR spectrum of **2p.**

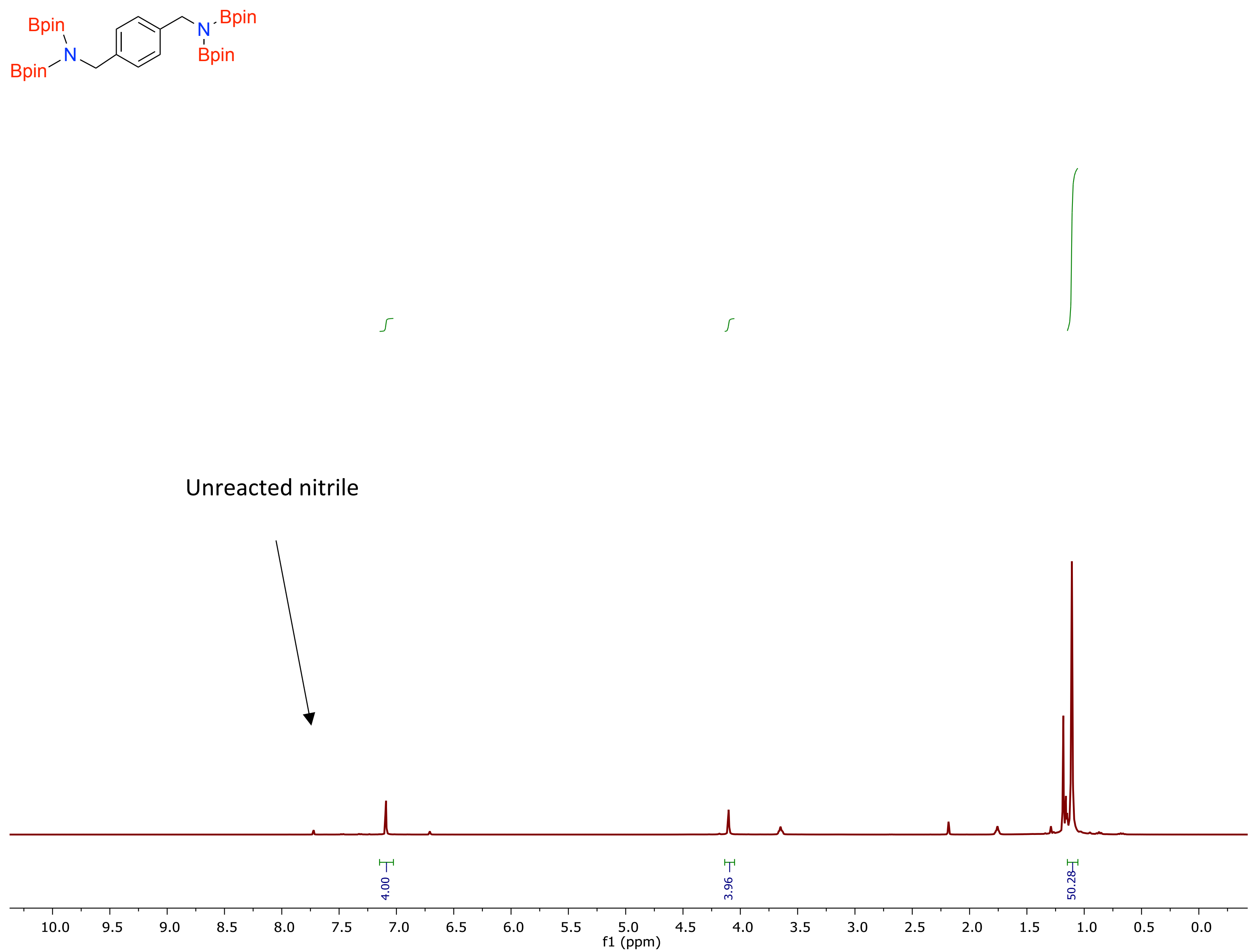


Figure S48: ^{1}H NMR spectrum of **2p.**

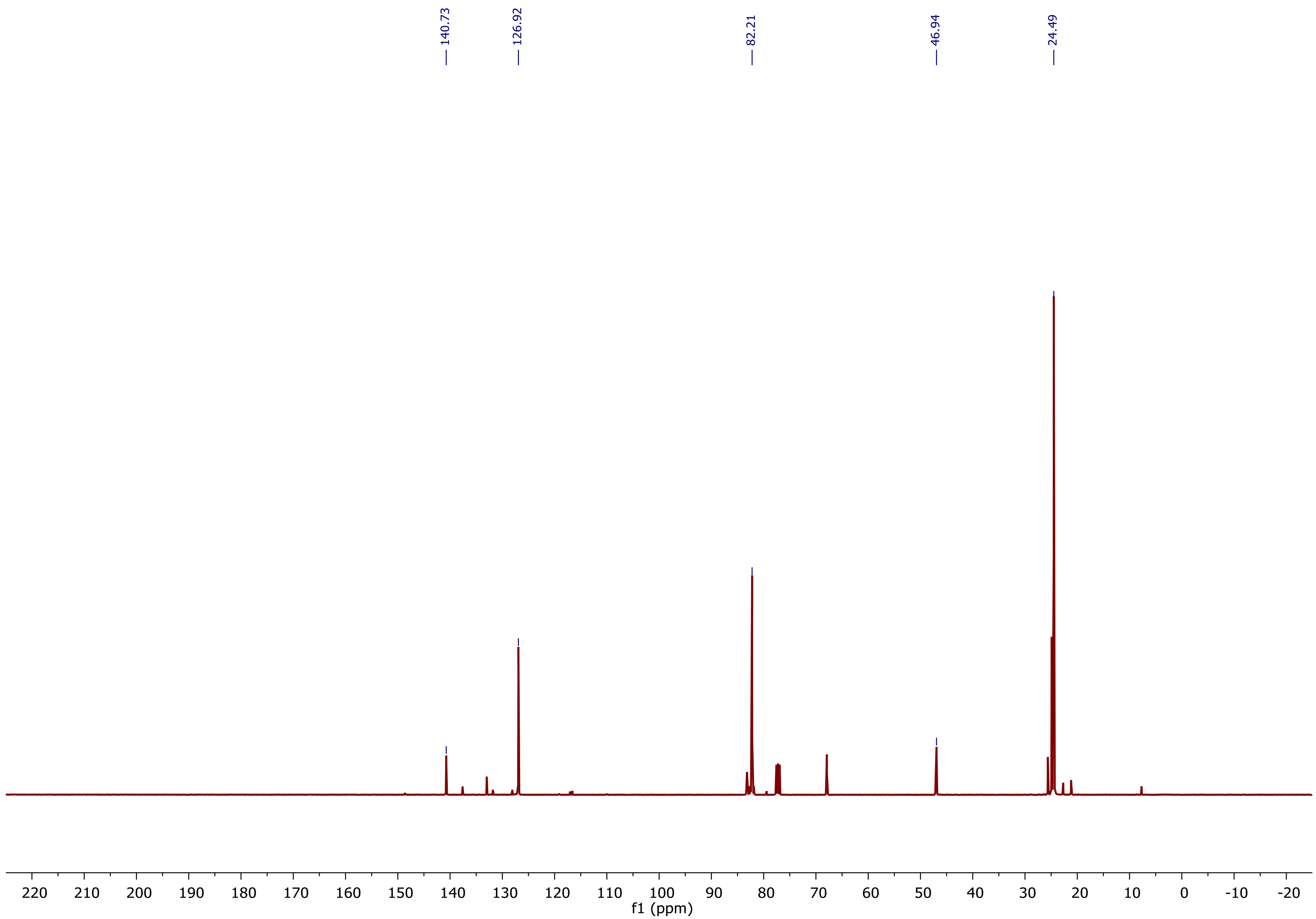
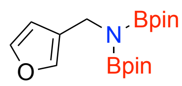


Figure S49: ^{13}C NMR spectrum of **2p.**



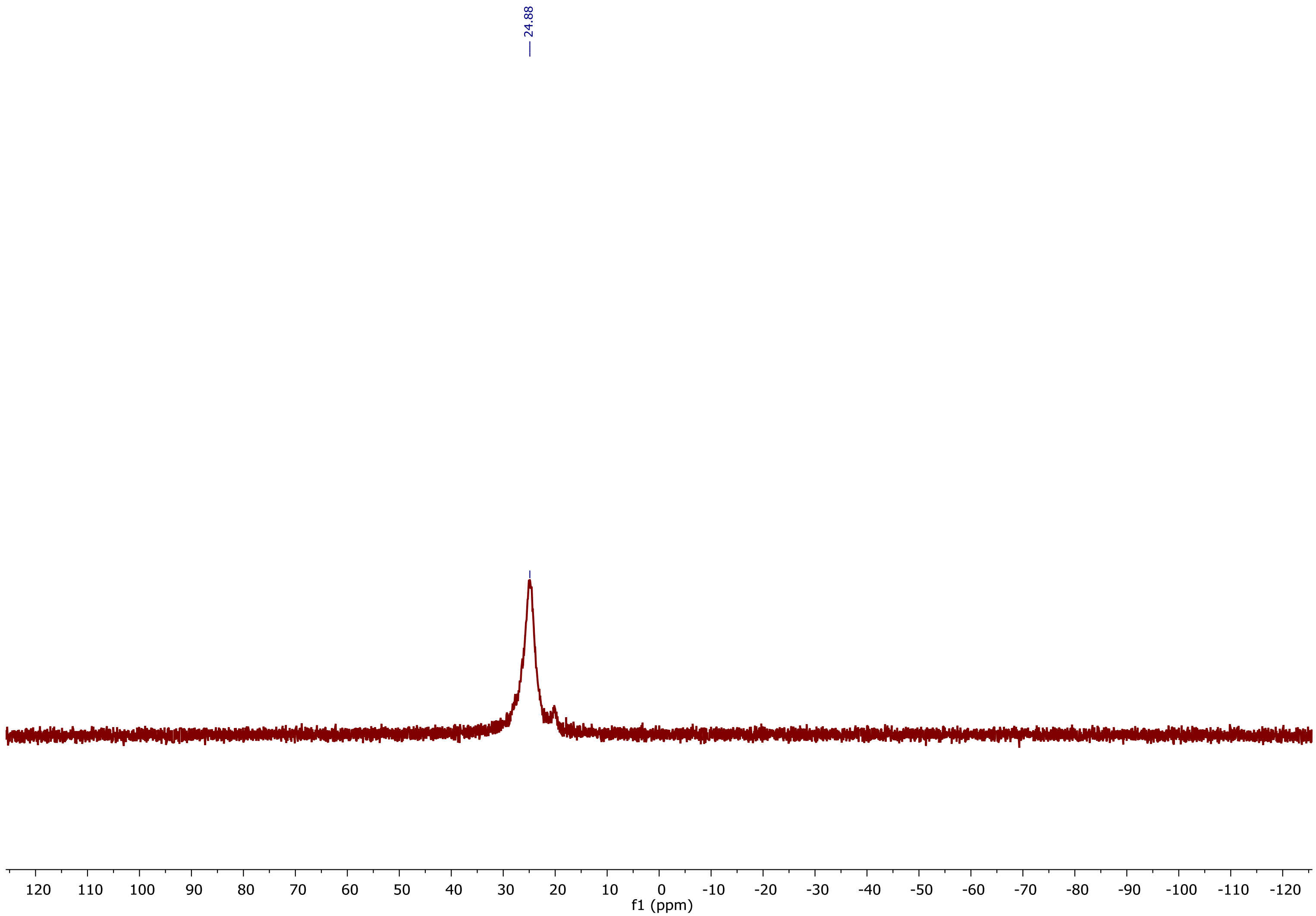
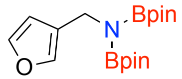


Figure S50: ^{11}B NMR spectrum of **2q.**



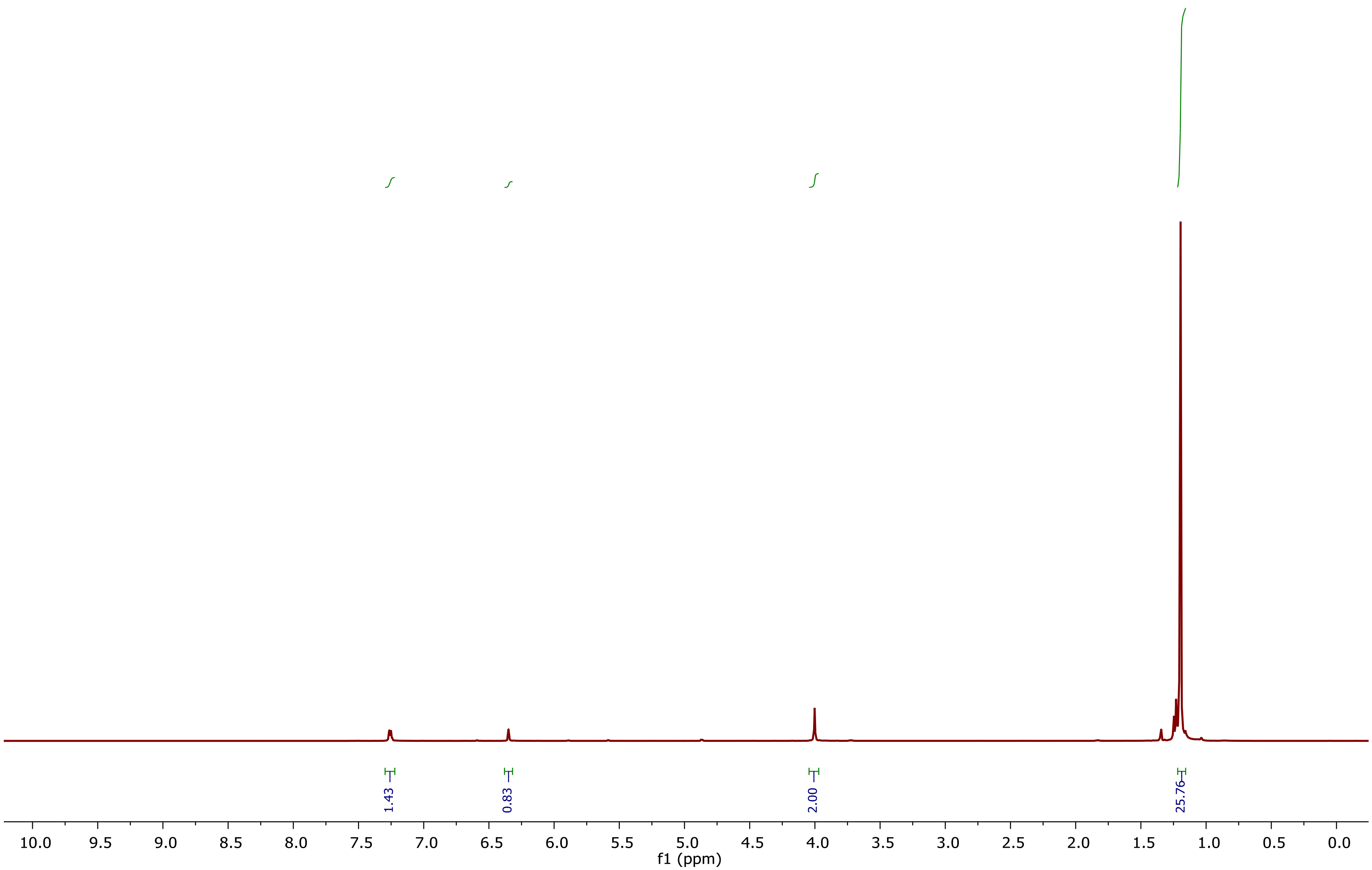


Figure S51: ^{1}H NMR spectrum of **2q.**

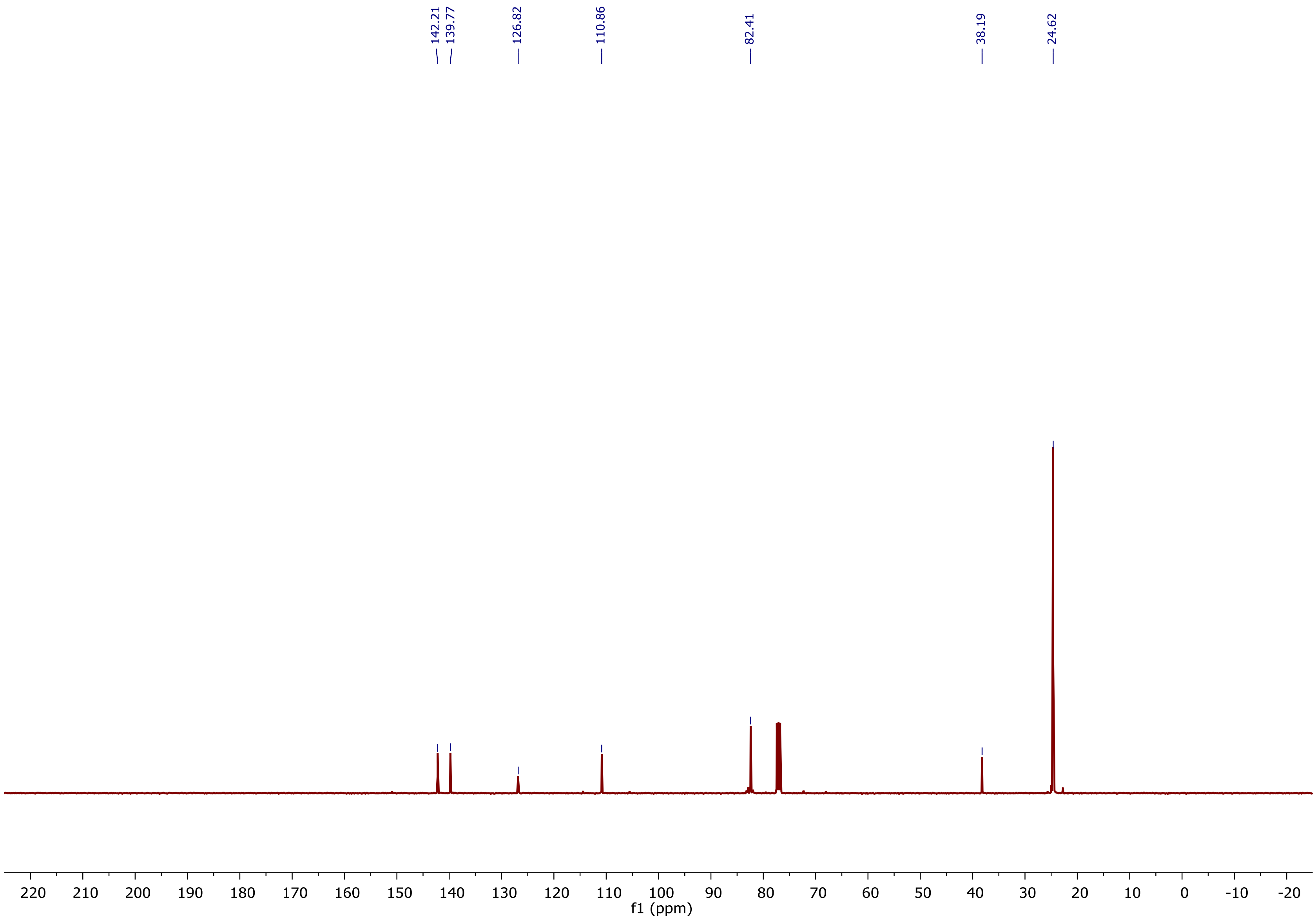


Figure S52: ^{13}C NMR spectrum of **2q.**

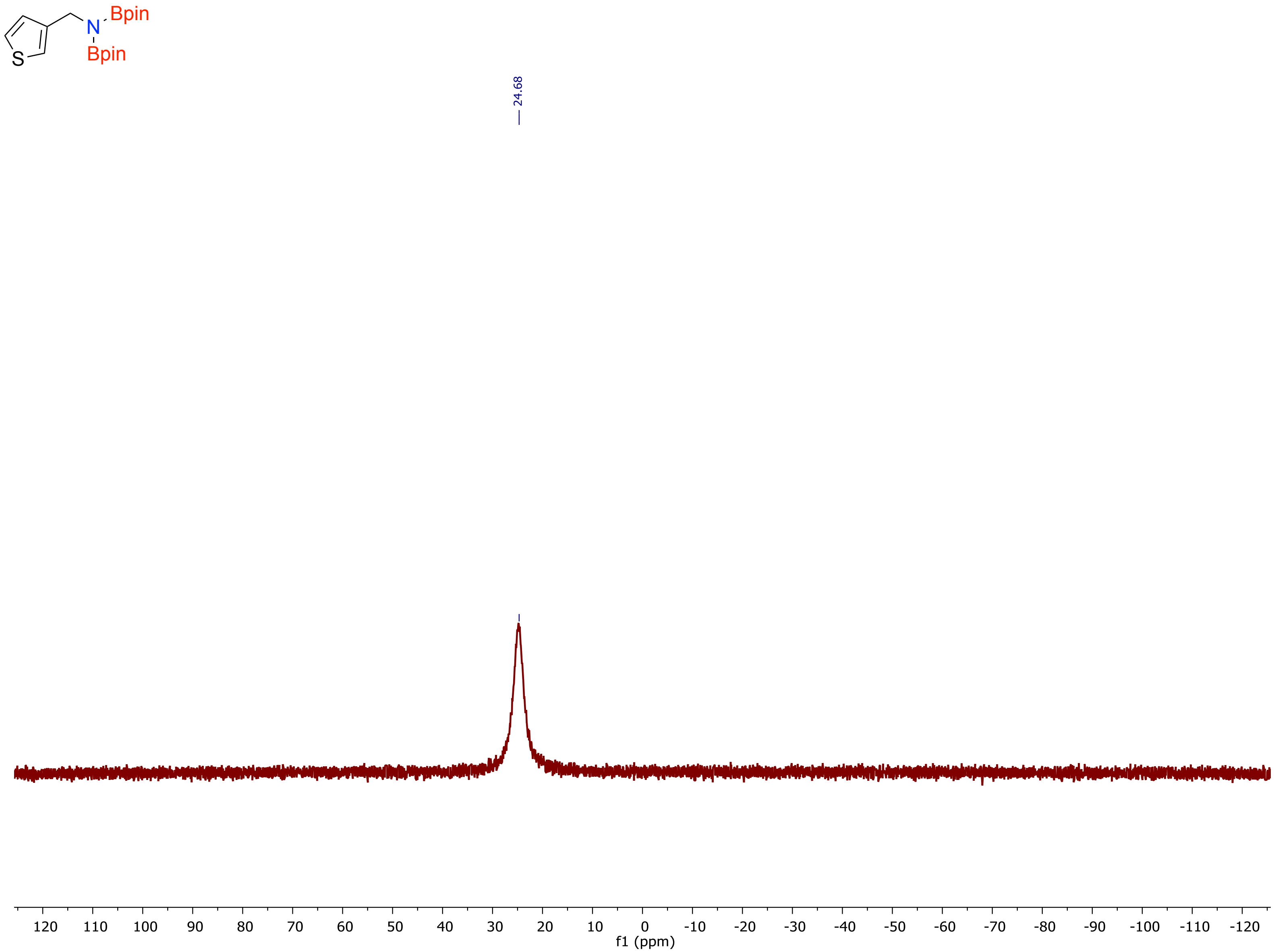
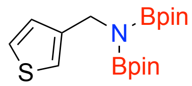


Figure S53: ^{11}B NMR spectrum of **2r.**



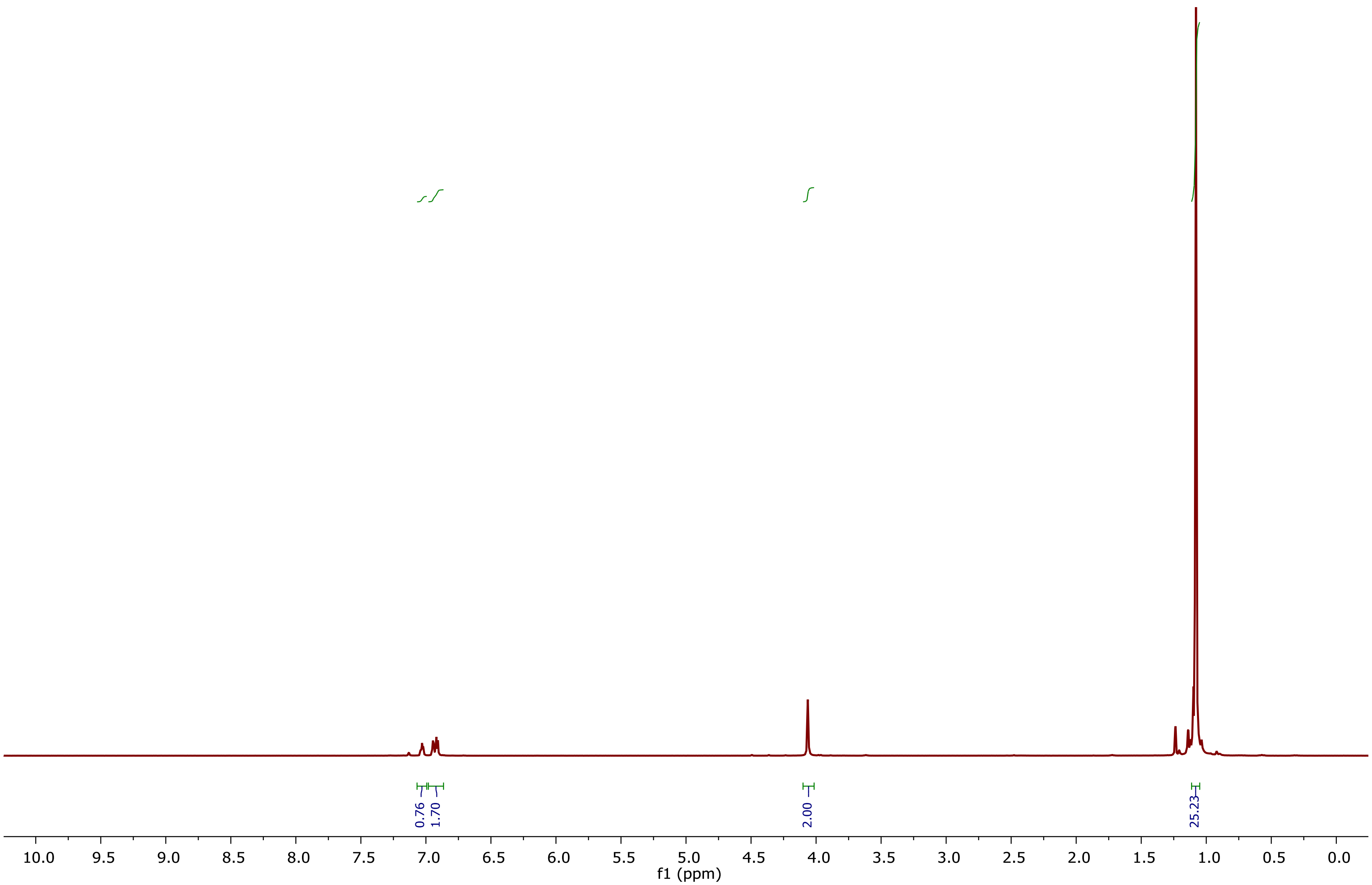


Figure S54: ^{1}H NMR spectrum of **2r.**

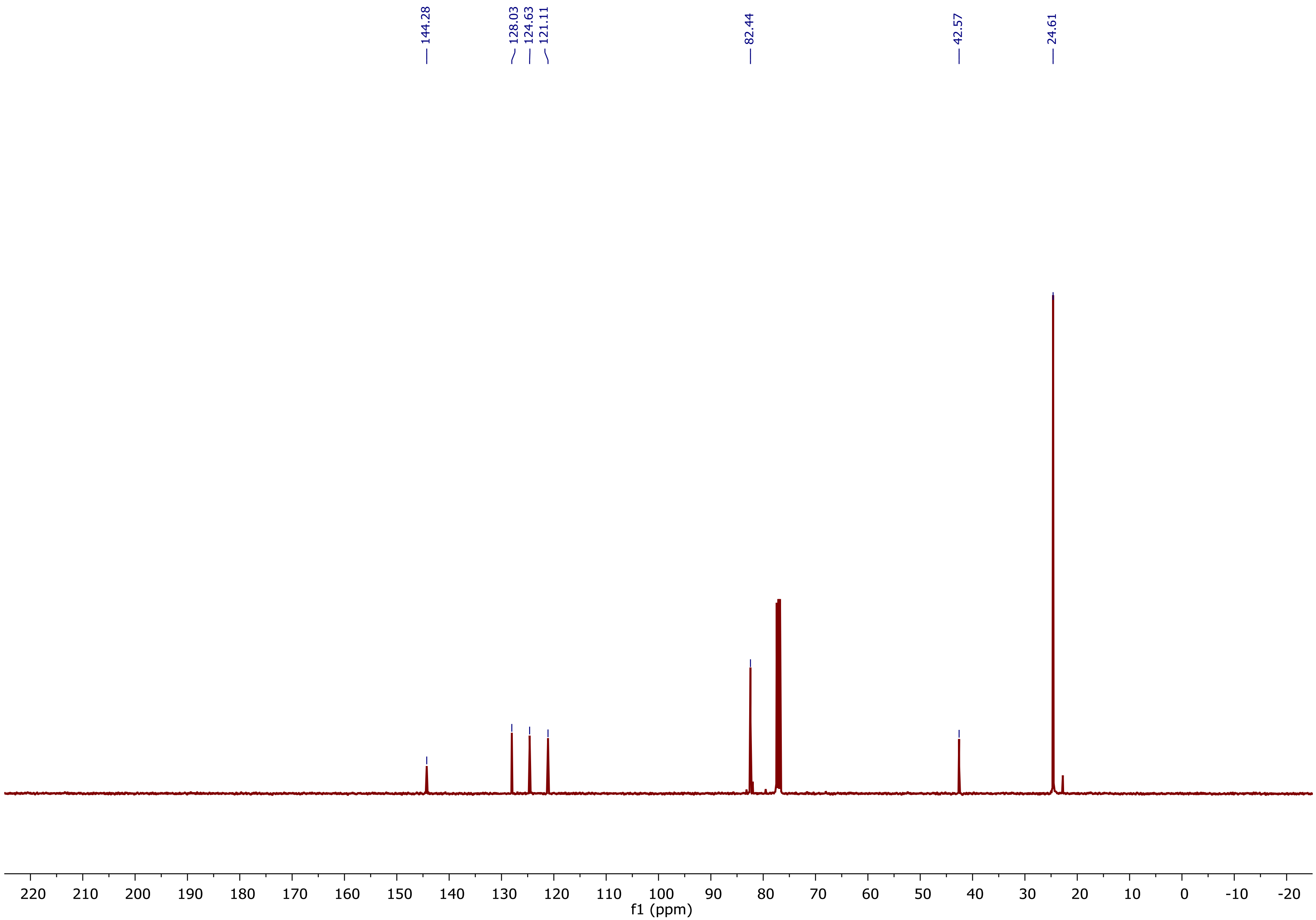
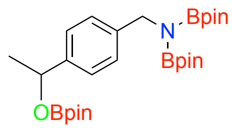


Figure S55: ^{13}C NMR spectrum of **2r.**



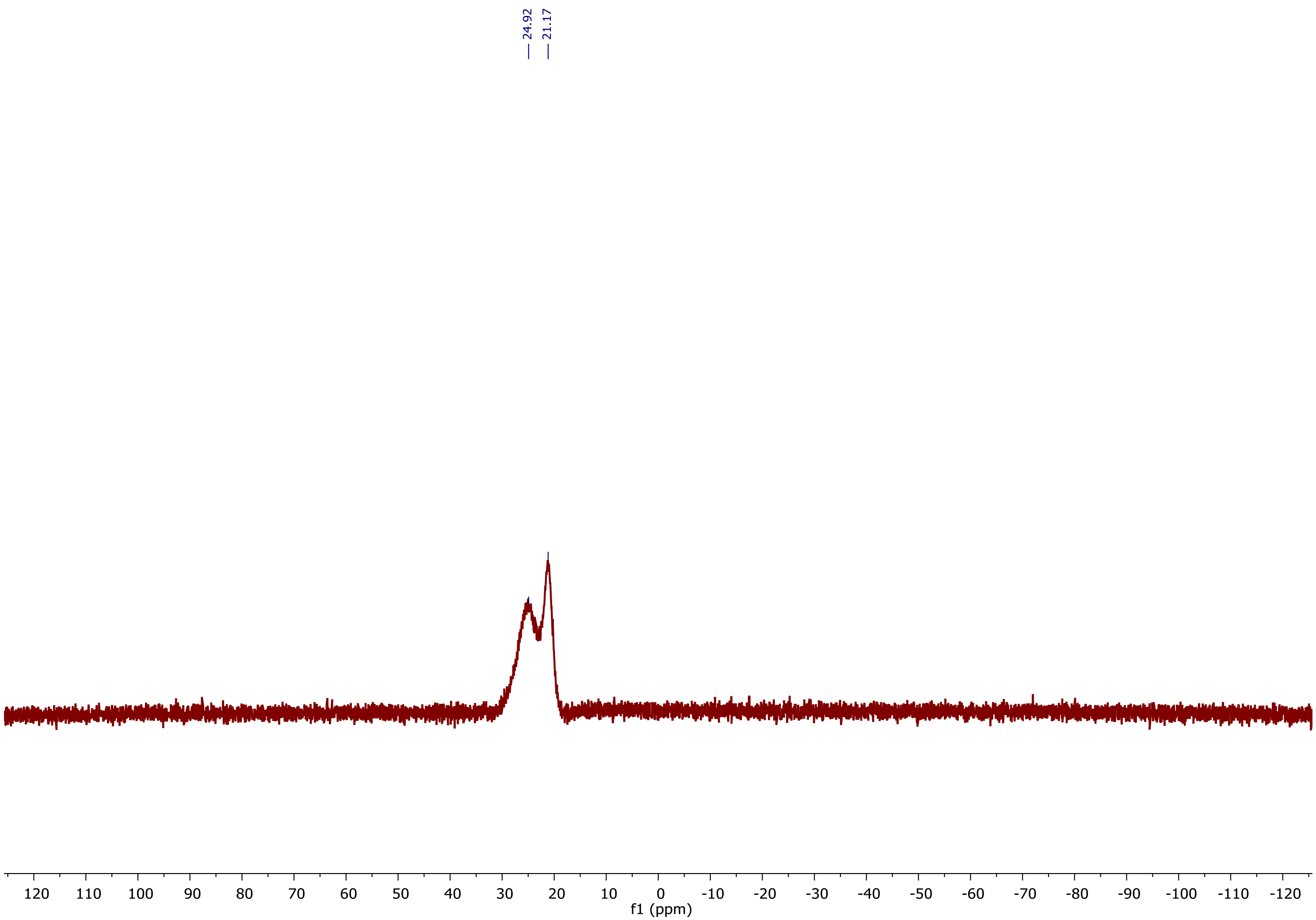
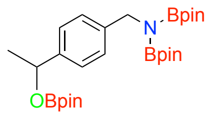


Figure S56: ^{11}B NMR spectrum of **2s.**



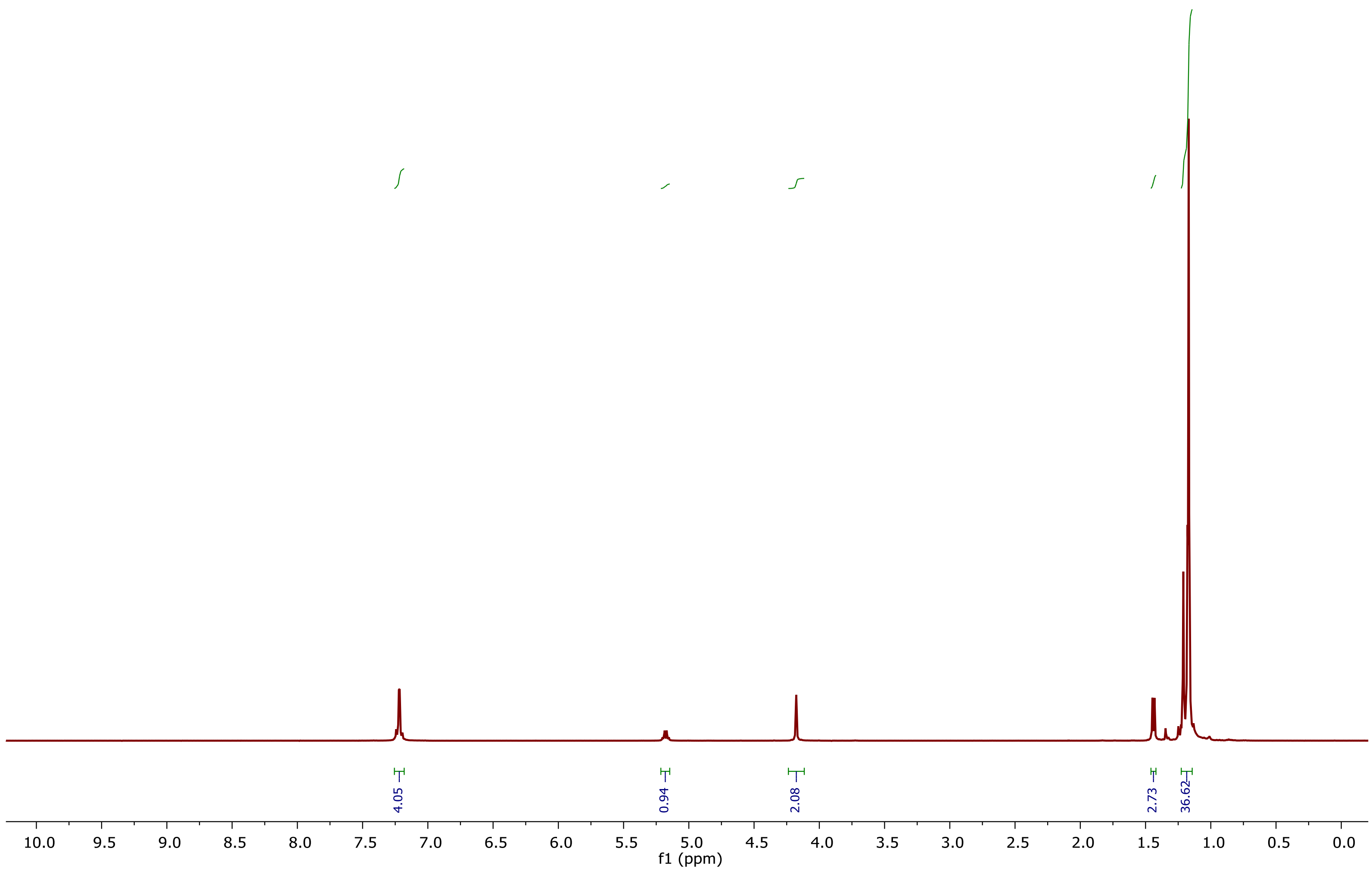


Figure S57: ^{1}H NMR spectrum of **2s.**

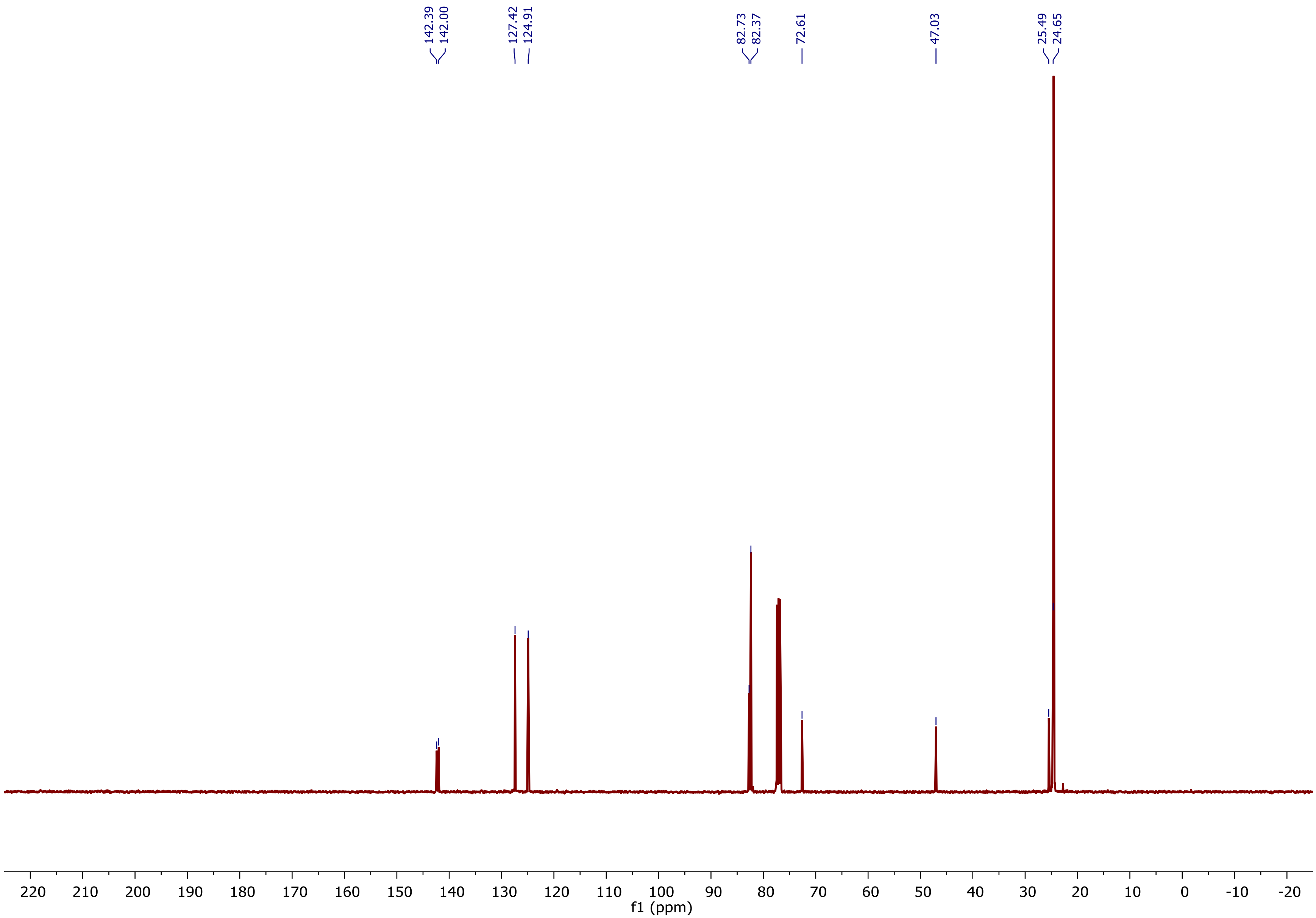
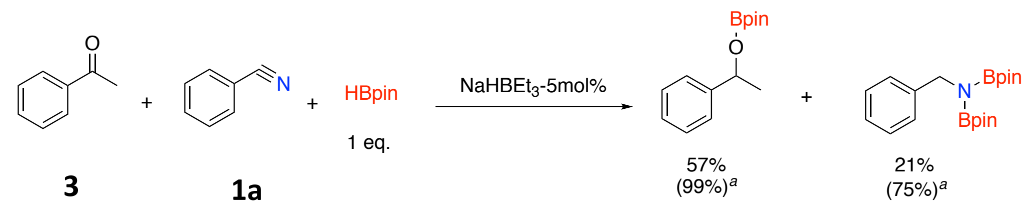


Figure S58: ^{13}C NMR spectrum of **2s.**

Chemoselective experiments



[a]Yield in parenthesis are after subsequent addition of 1.5 equivalent of HBpin

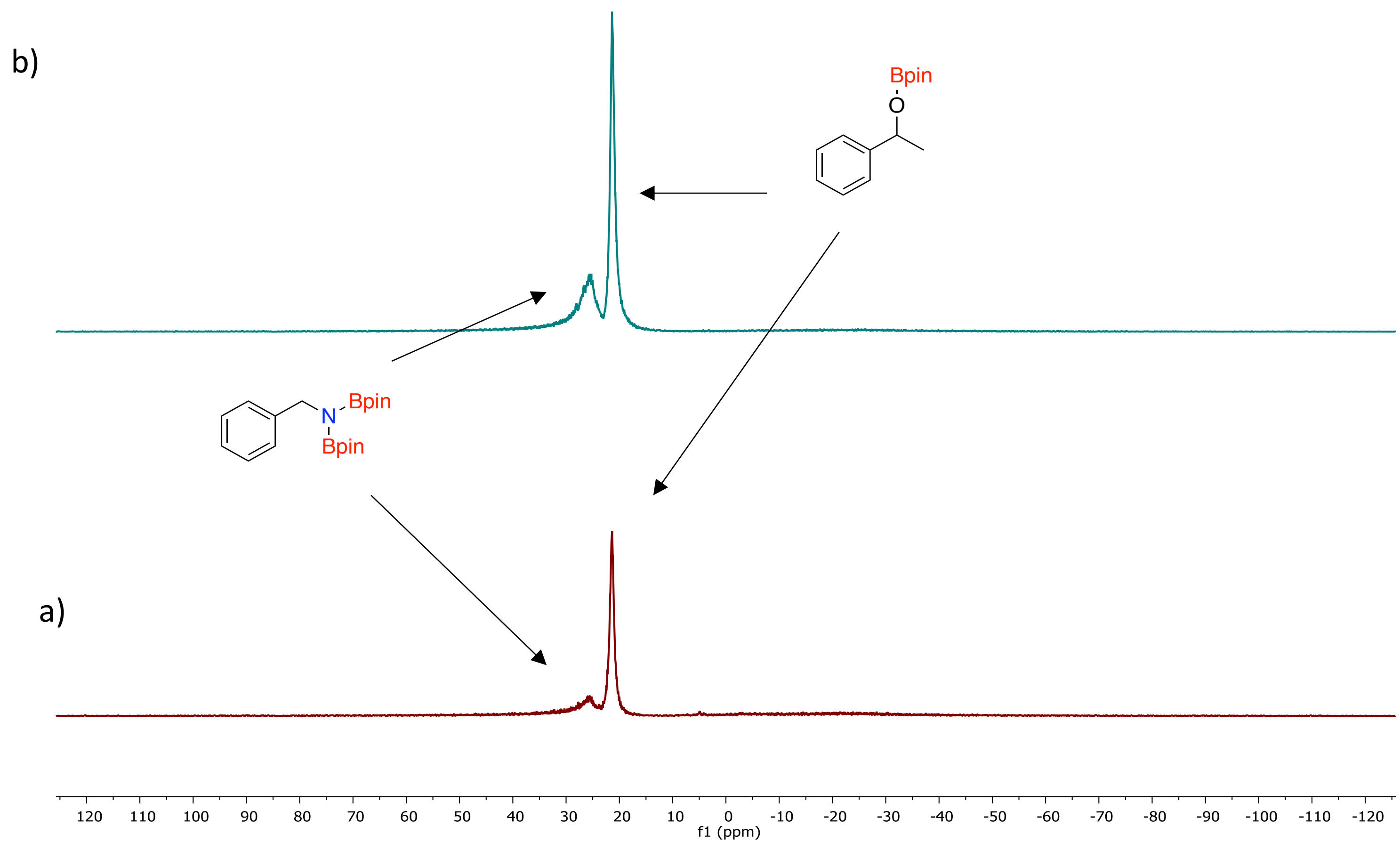


Figure S59: ^{11}B NMR spectrum of chemoselective experiment a) after addition of 1 eq. HBpin b) after subsequent addition of 1.5 eq.

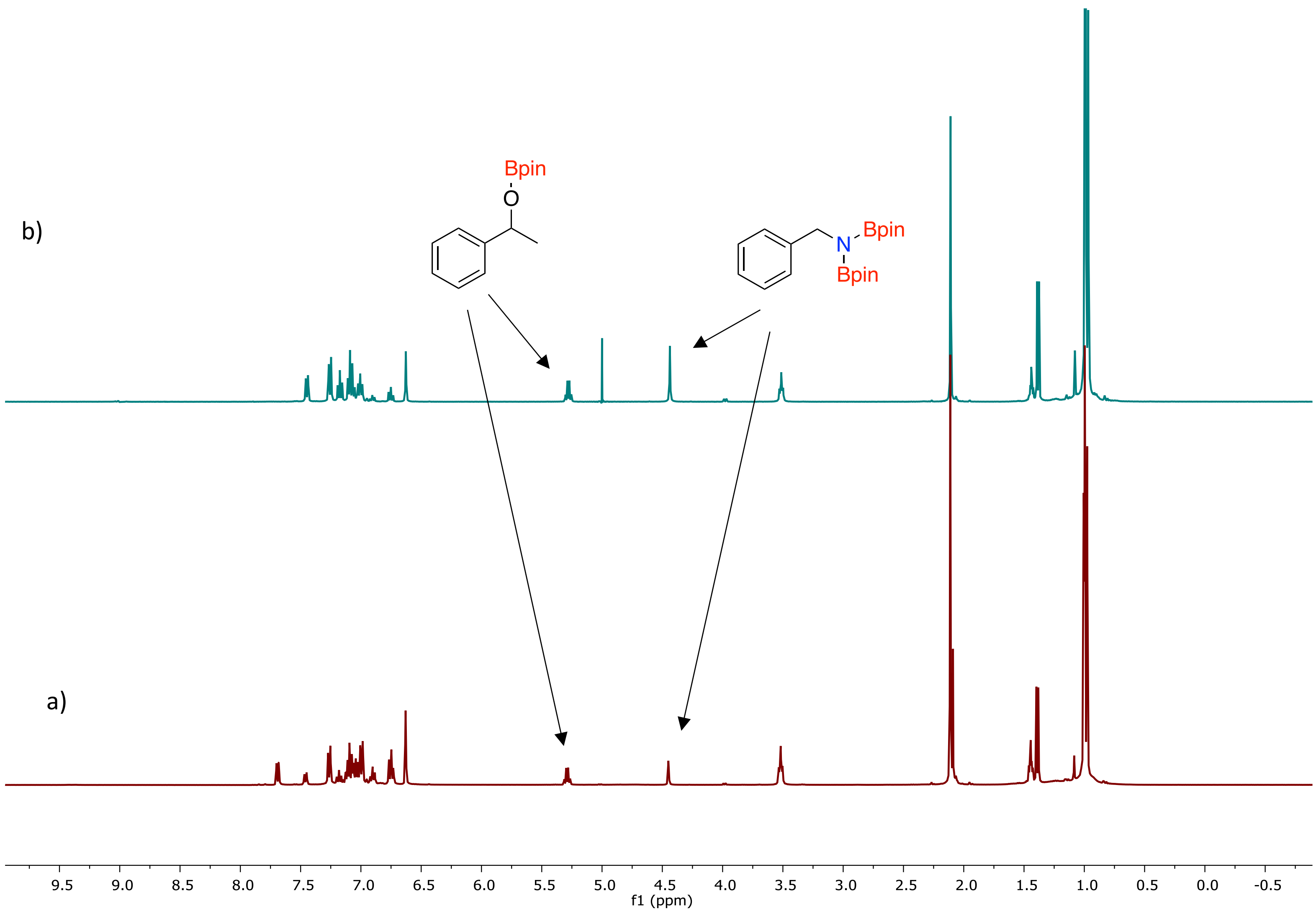


Figure S60: ^{1}H NMR spectrum of chemoselective experiment a) after addition of 1 eq. HBpin b) after subsequent addition of 1.5 eq. HBpin

Mechanistic study experiments

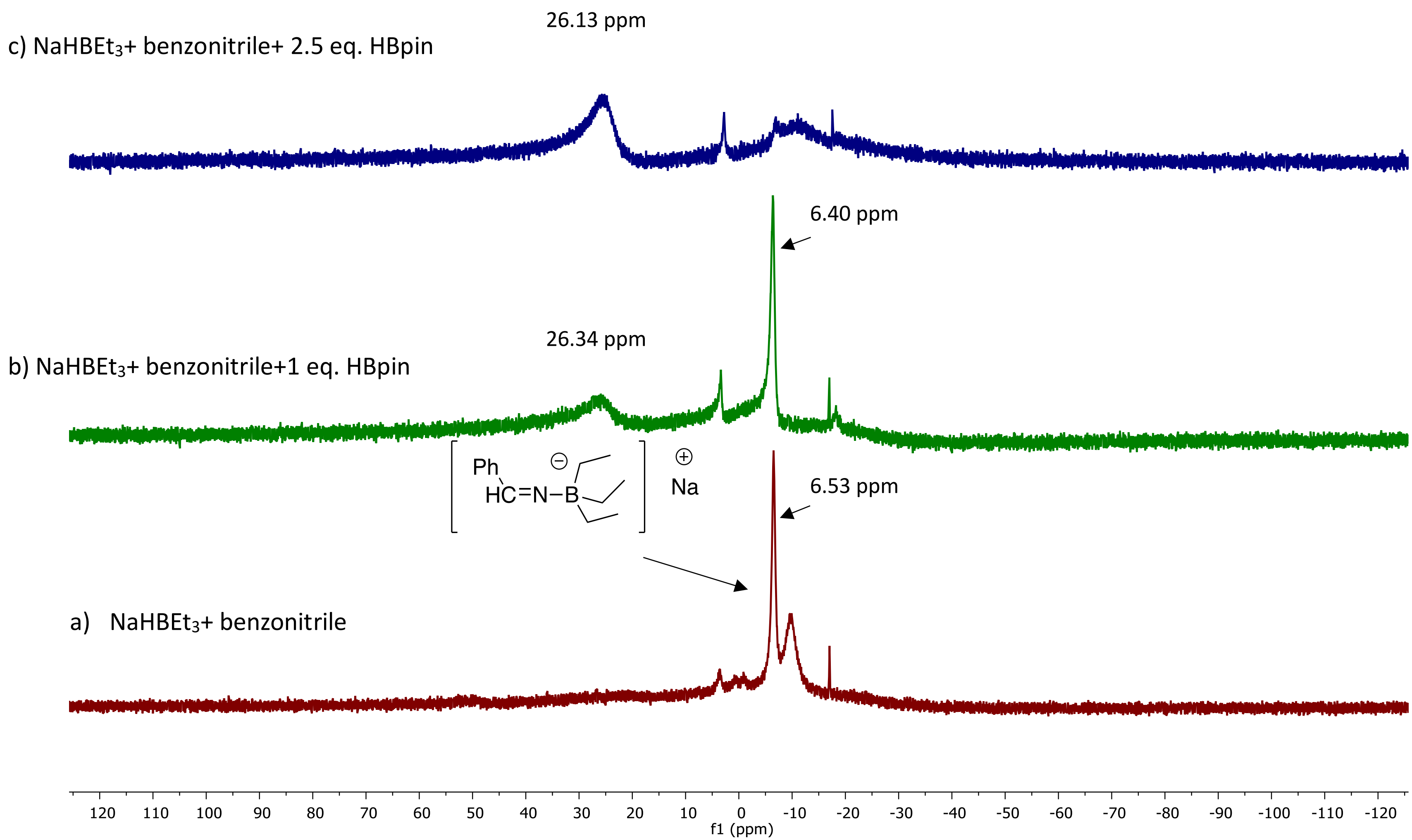


Figure S61: ^{11}B NMR spectrum of a) equimolar amount of benzonitrile and $NaHBEt_3$, b) after addition of 1 eq. of HBpin and c) after additional 1.5 eq. of HBpin.

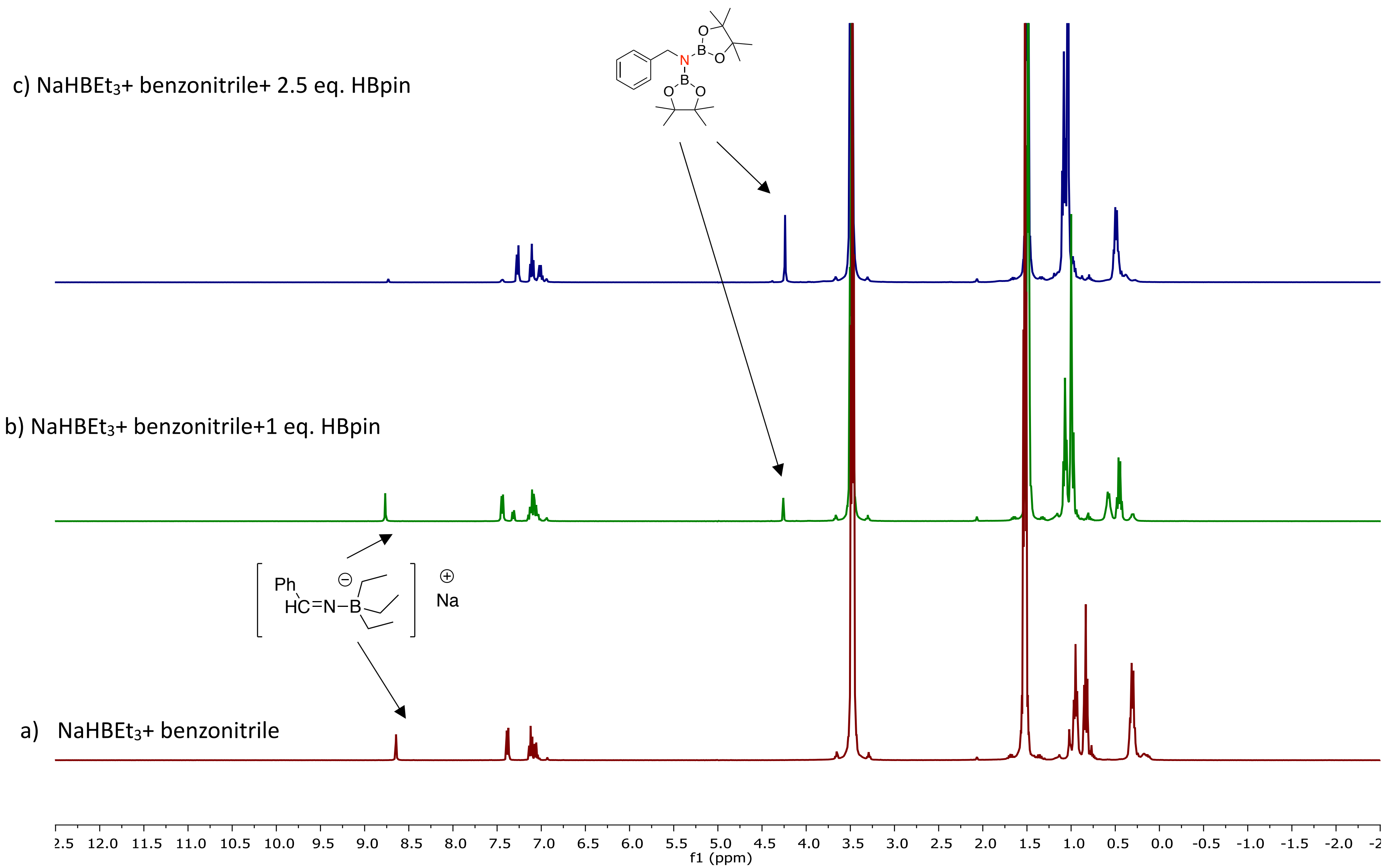
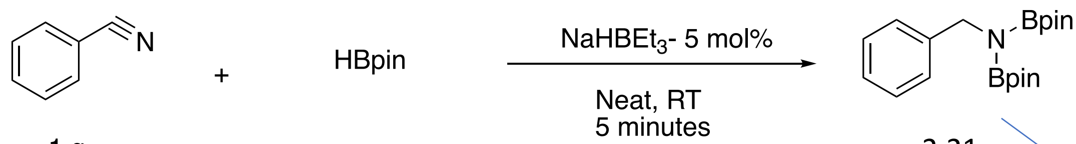


Figure S62: ^{1}H NMR spectrum of equimolar amount of a) benzonitrile and $NaHBEt_3$. b) after addition of 1 eq. of HBpin and c) after additional 1.5 eq. of HBpin.

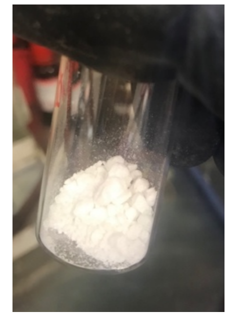
Procedure for gram scale reaction:



1 g

2.21g

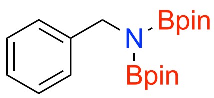
2a



In an inert atmosphere glovebox, benzonitrile (1 eq, 9.7 mmol, 103 mg), HBpin (2.5 eq., 24.25 mmol, 3.1 g, 3.52 mL) and $NaHBEt_3$ (0.05 eq., 0.485 mmol, 485 μL) were charged to an oven dried 20 ml scintillation vial. The reaction mixture was allowed to stand at room temperature for 5 minutes and the entire reaction mixture solidified. After the solid formation was observed in the vial, 0.5 ml of dry hexanes was added and the vial was placed inside Glove-box freezer at -30 ^{o}C and 30 minutes later, the vial was removed from the freezer and hexanes was decanted out from the solid and the procedure was repeated twice to remove all the $(pinB)_2O$. The solid was then dried using external glovebox vacuum pump to remove any residual hexanes. The solid product thus obtained was weighed and ^{11}B, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded.

Obtained weight: 2.21g, 63% (white solid)

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.31 (d, 2H, *J* = 8.36 Hz), 7.24-7.19 (m, 2H), 7.16-7.12 (m, 1H), 4.21 (s, 2H), 1.18 (s, 24H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ 142.13, 127.87, 127.58, 126.13, 82.40, 47.32, 24.57. $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$, 298K): δ 24.79. Spectral data matches the literature report.[1]



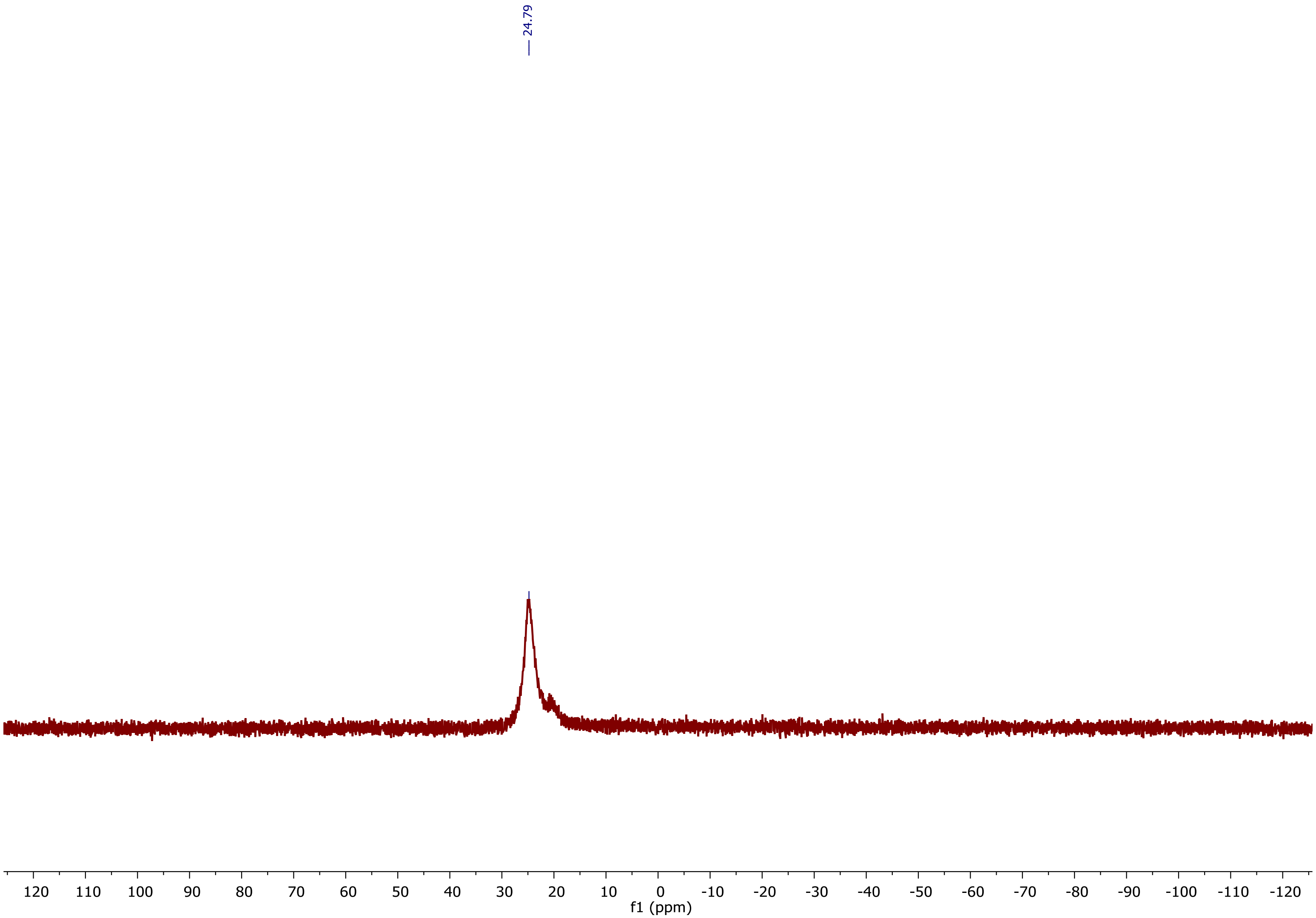
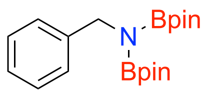


Figure S63: ^{11}B NMR spectrum of *N*-benzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine



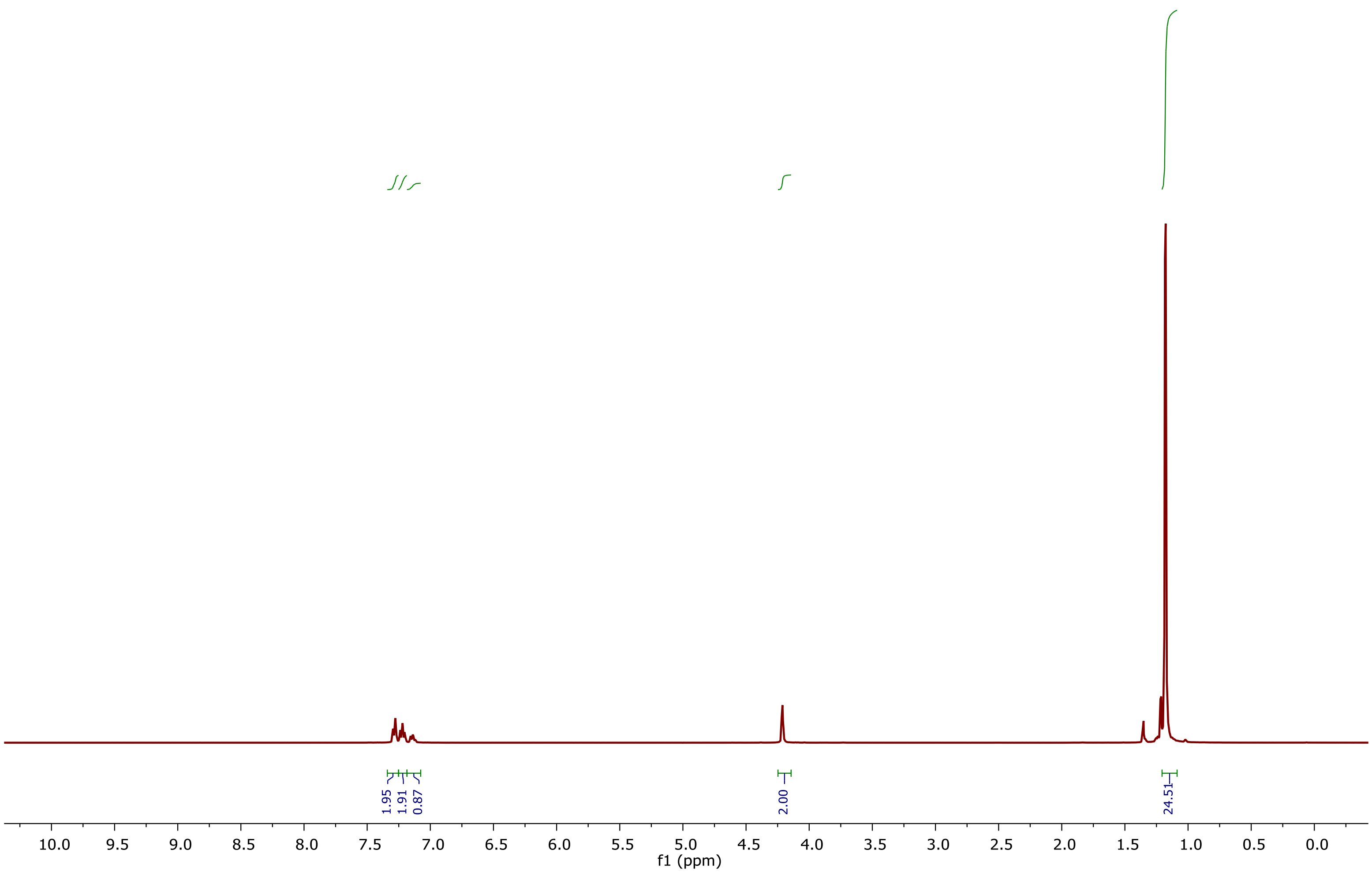


Figure S64: ^{1}H NMR spectrum of *N*-benzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine

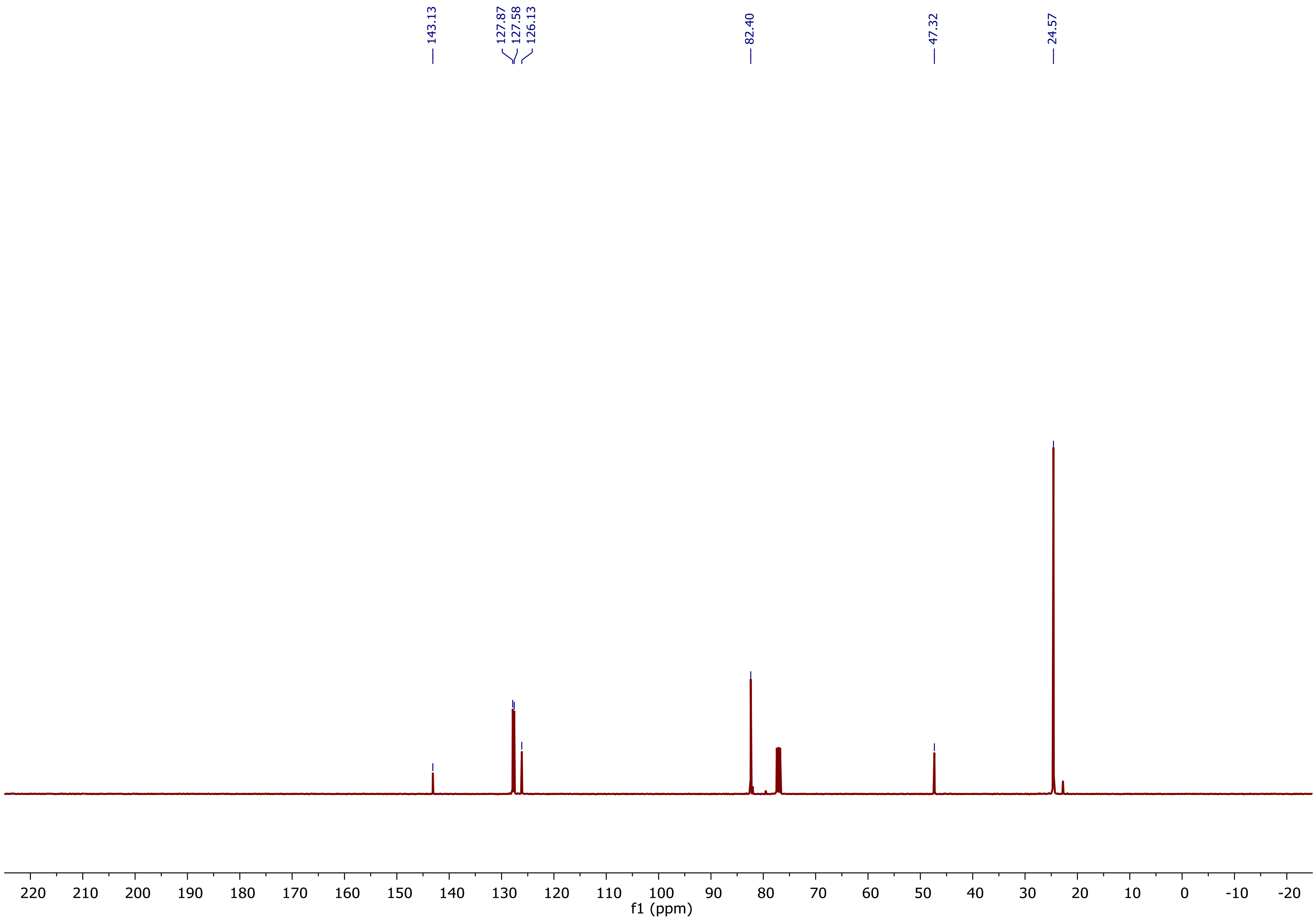


Figure S65: ^{13}C NMR spectrum of *N*-benzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine

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2. Huang Z., Wang S., Zhu X., Yuan Q., Wei Y., Zhou S., Mu X. Inorg. Chem. 2018, 57, 15069-15078
3. Saha S., Eisen M. S. ACS Catal. 2019, 9, 5947-5956