Electronic Supplementary Material (ESI) for ChemComm.


# Supporting Information

## Olefin hydroboration catalyzed by an Iron-borane complex

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## Experimental Procedures

All commercially purchased starting materials were used as received unless otherwise stated. All manipulations were performed using standard Schlenk techniques or an Mbraun glovebox, under an atmosphere of dry $N_2$. Dry solvents (THF, $Et_2O$, Pentane, $C_6H_6$, $CH_3CN$, toluene and $CH_2Cl_2$) were obtained using innovative technologies anhydrous engineering solvent purification systems, subsequently degassed and left over 3 Å activated sieves before being transferred to a potassium mirror, except for $CH_2Cl_2$. All other solvents used were of HPLC grade, unless otherwise stated. Solvents removed under "reduced pressure" were by rotary evaporation and "*in vacuo*" under high vacuum via Schlenk line. THF-$d_8$, $C_6D_6$ and $CDCl_3$ were dried over activated 3 Å molecular sieves and degassed by sparging with dry $N_2$. All glassware and stirrer bars were flame dried with a blowtorch under a vacuum before use. Column chromatography: Flash column chromatography with silica gel 60. Mixtures of solvents used are noted in brackets.

$^1H$, $^{11}B$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a bruknmer advance III HD 400 spectrometer (operating frequencies: 399.78 MHz, 128.25 MHz, 100.53 MHz and 161.83 ppm, respectively). $^1H$ and $^{13}C\{^1H\}$ NMR chemical shifts were internally referenced to the residual solvent resonances ($CDCl_3$ (Chloroform-d): $^1H$ δ = 7.26 ppm, $^{13}C\{^1H\}$ δ = 77.16 ppm; $C_6D_6$ (benzene-$d_6$): $^1H$ δ = 7.16 ppm, $^{13}C\{^1H\}$ δ = 128.02 ppm), THF-$d_8$ (Tetrahydrofuran-$d_8$): $^1H$ δ = 3.58, 1.73 ppm, $^{13}C\{^1H\}$ δ = 67.57, 25.37 ppm). NMR samples were prepared under an inert atmosphere in 5 mm J. Youngs NMR tubes. Data was analysed using MestReNova V14.0.0 software. ATR-IR spectra were recorded as microcrystalline powders using a Bruker Tensor 27 spectrometer.

## Synthesis of [{($^{iPr}$DPB$^{Ph}$)Fe}$_2$(μ-1,2-$N_2$)] Pre-Catalyst Complex A

The $^{iPr}$DPB$^{Ph}$ ligand (1.33 g, 2.81 mmol) and $FeBr_2$ (0.602 g, 2.81 mmol) were stirred at rt in THF (80 mL) until all solids dissolved into a yellow solution. Volatiles were removed *in vacuo* generating yellow/orange solids, this was left under a vacuum for 30 min after all solvents were visibly removed. $Et_2O$ (100 mL) was added to the solids and stirred vigorously for 1 h to produce a bright yellow precipitate, volatiles were removed *in vacuo* and the remaining solids were subsequently dissolved in benzene (100 mL) and allowed to stir overnight before being added to a 1% Na/Hg amalgam (Na: 291 mg, 0.013 mol) and left to stir for 16 h at rt. The dark red solution was filtered through Celite® and volatiles were removed *in vacuo*. Dark brown/red solids were washed in pentane (20 mL), solids were dried *in vacuo* before being washed in cold $Et_2O$ (2 x 10 mL) (0.974 g, 1.83 mmol, 65%). **$^1$H NMR** (400 MHz, $C_6D_6$) δ 135.00, 44.52, 34.77, 28.38, 26.50, 7.46, 0.32, –1.45, –2.28, –6.25, –9.23, –76.98 ppm. Data is consistent with literature.[1]

## Synthesis of [($\eta^3$-$H_2$$^{ipr}$DPB)Fe($\eta^3$-$H_2$Bpin)] Complex B

Complex **B** was prepared by dissolving complex **A** (20 mg, 0.034 mmol) and HBpin (32 µL, 0.219 mmol) in $C_6D_6$ (0.6 mL) and heating at 50 °C for 24 h. Volatiles were removed *in vacuo* to reveal a purple oil which was then dissolved in hexane and filtered through a short pad of silica (1.0 cm in a pipette). Volatiles were removed *in vacuo* to furnish complex **B** as a dark pink amorphous solid. Slow evaporation from a concentrated solution of diethyl ether gave pink single crystals suitable for XRD (23 mg, 0.029 mmol, 85%). **$^1$H NMR** (400 MHz, $C_6D_6$) δ 8.55 (d, *J* = 7.5 Hz, 2H), 7.77 – 7.63 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 2H), 3.00 (heptet, *J* = 7.0 Hz, 4H), 1.36 (q, *J* = 7.2 Hz, 12H), 1.14 (q, *J* = 8.2 Hz, 12H), 1.10 (s, 12H), -16.71 (s, 2H), -20.69 (s, 2H). **$^{13}$C{$^1$H} NMR** (101 MHz, $C_6D_6$) δ 156.9, 147.6 – 146.8 (m), 130.3 (t, $J_{C\text{-}P}$ = 7.8 Hz), 129.6, 129.5, 126.3 (t, $J_{C\text{-}P}$ = 2.6 Hz), 81.7, 26.4 (t, $J_{C\text{-}P}$ = 9.5 Hz), 24.5, 19.9 (t, $J_{C\text{-}P}$ = 2.4 Hz), 18.8. **$^{11}$B NMR** (128 MHz, $C_6D_6$) δ 48.0, 36.1. **$^{31}$P NMR** (162 MHz, $C_6D_6$) δ 98.1 (2P, t, $^2J_{P\text{-}H}$ = 17 Hz). IR ($cm^{-1}$) 1820 (b, Fe-H). HRMS (ESI) m/z calcd for [M] 584.16, found $[M+H]^-$ 585.30, $[M+Na]^-$ 607.29. Anal,: calcd for $C_{30}H_{52}B_2FeO_2P_2$: C 61.68, H 8.97, Fe 9.56; found: C 61.69, H 9.12, Fe 9.42.

## Deuterium Labelling Experiment of Complex B using DBpin

DBpin was synthesised according to literature and used as a known concentration in a solution of $C_6D_6$.[2]

Complex **B** was prepared dissolving complex **A** (20 mg, 0.034 mmol) and DBpin solution (0.217 mmol) in $C_6D_6$ and heating to 50 °C for 24 h. Volatiles were removed *in vacuo* to reveal a purple oil which was then dissolved in hexane and filtered through a short pad of silica (1.0 cm in a pipette in a glovebox). Volatiles were removed *in vacuo* to furnish complex **B** as a dark pink amorphous solid (20 mg, 0.0253 mmol, 74%). **$^{31}$P NMR** (162 MHz, $C_6D_6$) δ 98.03. **$^2$H NMR** (61 MHz, $C_6D_6$) δ –17.01, –21.07.

## General Crystallographic Methods

The crystal data for [($\eta^3$-$H_2$$^{ipr}$DPB)Fe($\eta^3$-$H_2$Bpin)] is recorded in XRD experimental parameters. The crystals were examined using an Agilent Supernova diffractometer, equipped with an Eos CCD area detector and a microfocus source with Mo Kα radiation (λ = 0.71073 Å). Intensities were integrated from data recorded on 1° frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. A Gaussian grid face-indexed with a beam profile was applied for all structures.[3] The structures were solved in olex2.solve[4] and the data sets were refined by full-matrix least-squares on all $F^2$ values[5], with anisotropic displacement parameters for all non-hydrogen atoms, and with constrained riding hydrogen geometries; $U_{iso}$(H) was set at 1.2 (1.5 for methyl groups) times $U_{eq}$ of the parent atom. CrysAlisPro6[3] was used for control and integration, and SHELXL[5] was employed through OLEX2[6] for structure solution and refinement. ORTEP-3[7] was employed for molecular graphics. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via deposition number 2260204.

**XRD Experimental Parameters for Complex B**

| | |
|---|---|
| Empirical formula | $C_{30}H_{52}B_2FeO_2P_2$ |
| Formula weight | 584.12 |
| Temperature/K | 99.97(10) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 9.6026(3) |
| b/Å | 10.9986(3) |
| c/Å | 29.9514(8) |
| α/° | 90 |
| β/° | 94.869(3) |
| γ/° | 90 |
| Volume/Å$^3$ | 3151.93(16) |
| Z | 4 |
| $\rho_{calcd\ g/cm3}$ | 1.231 |
| μ, mm$^{-1}$ | 0.605 |
| F(000) | 1256 |
| No. of reflections collected | 26248 |
| Independent reflections $R_{int}$ | 7510, 0.0431 |
| No. of params, restraints | 7510/0/362 |
| GOF | 1.054 |
| R, $_wR^2$ ($F^2 > 2\sigma(F^2)$) | (0.0379, 0.0789) |
| R, $_wR^2$ (all data) | (0.0498, 0.0848) |
| Max., min. diff map, e Å$^{-3}$ | 0.45 -0.40 |

[a] Conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$; $S = [\Sigma w(F_o^2 - F_c^2)^2 / \text{no. data} - \text{no. params})]^{1/2}$ for all data.

## Table of Optimizations

**Table 1:** Optimized conditions

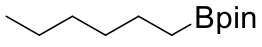
| Entry | Fe (mol%) | HBpin Equiv | Solvent | Temp (°C) | Time (h) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | 5 | 1.1 | benzene | 50 | 15 | 83 |
| 2 | 5 | 1.1 | toluene | 50 | 15 | 79 |
| 3 | 5 | 1.1 | methylcyclohexane | 50 | 15 | 81 |
| 4 | 5 | 1.1 | diethyl ether | 50 | 15 | 68 |
| 5 | 5 | 1.1 | hexane | 50 | 15 | 24 |
| 6 | 5 | 1.1 | neat | 50 | 15 | 98 |
| 7 | 4 | 1.1 | neat | 50 | 15 | 68 |
| 8 | 3 | 1.1 | neat | 50 | 15 | 47 |
| 9 | 2 | 1.1 | neat | 50 | 15 | 19 |
| 10 | 5 | 1.1 | neat | 50 | 1 | 18 |
| 11 | 5 | 1.1 | neat | 50 | 3 | 29 |
| 12 | 5 | 1.1 | neat | 50 | 6 | 45 |
| 13 | 5 | 1.1 | neat | r.t | 30 | 9 |
| 14 | 5 | 1.0 | neat | 50 | 15 | 96 |
| 15 | 5 | 1.2 | neat | 50 | 15 | 95 |
| 16 | 5 | 1.5 | neat | 50 | 15 | 95 |

## General Procedure for the Hydroboration of Olefins

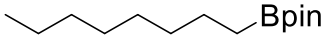
In a nitrogen filled glovebox, an oven dried J-Youngs NMR tube was charged with $[\{(^{iPr}DPB^{Ph})Fe\}_2(\mu\text{-}1,2\text{-}N_2)]$ (0.01 mmol), HBpin (0.225 mmol), substrate (0.205 mmol). The reaction mixture was added to an oil bath (50 °C) for 15 h. Crude NMR was taken in $C_6D_6$ with toluene as an internal standard, volatiles were removed under reduced pressure, mixture was suspended in $Et_2O$ and filtered through a short pad of silica (2.0 cm in a pipette), in some cases the product was purified by flash chromatography.

## Characterization data of Hydroborated Products of Olefins

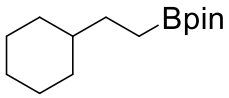
Spectroscopic data is in accordance to literature.[8]



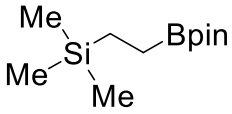

**2a**, 2-Hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared according to the general procedure using hexene (25 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h to furnish product **2a** (36 mg, 0.170 mmol, 83%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 1.45 – 1.35 (m, 2H), 1.31 – 1.25 (m, 6H), 1.24 (s, 12H), 0.90 – 0.83 (m, 3H), 0.76 (t, *J* = 7.8 Hz, 2H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 82.9, 32.2, 31.7, 24.9, 24.7, 24.1, 22.7, 14.2 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 34.1 ppm.



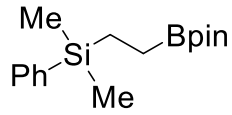

**2b**, 4,4,5,5-Tetramethyl-2-octyl-1,3,2-dioxaborolane was prepared according to the general procedure using octene (32 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h to furnish product **2b** (43 mg, 0.179 mmol, 87%). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 1.38 (q, *J* = 7.3 Hz, 2H), 1.32 – 1.24 (22H), 0.91 – 0.81 (m, 3H), 0.76 (t, *J* = 7.8 Hz, 2H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 82.9, 32.6, 32.1, 29.5, 29.4, 24.9, 24.2, 22.8, 14.3 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 34.2 ppm.



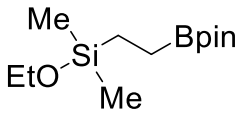

**2c**, 2-(2-Cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared according to the general procedure using vinylcyclohexane (28 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h to furnish product **2c** (47 mg, 0.197 mmol, 96%). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 1.73 – 1.65 (m, 4H), 1.65 – 1.57 (m, 1H), 1.35 – 1.27 (m, 2H), 1.24 (s, 12H), 1.20 – 1.04 (m, 4H), 0.84 (t, *J* = 11.6 Hz, 2H), 0.78 – 0.73 (m, 2H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 82.9, 40.1, 33.1, 31.5, 26.9, 26.6, 24.9. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 34.3.



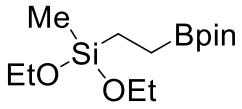

**2d**, Trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was prepared according to the general procedure using vinyltrimethylsilane (30 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h to furnish product **2d** (46 mg, 0.202 mmol, 98%). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 1.24 (s, 12H), 0.76 – 0.66 (m, 2H), 0.58 – 0.48 (m, 2H), –0.05 (s, 9H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 83.0, 24.9, 24.7, 9.4, –2.0 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 34.2 ppm. **$^{29}$Si NMR** (79 MHz, $CDCl_3$) δ 3.13 ppm.



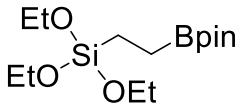

**2e**, Dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was prepared according to the general procedure using dimethylphenylvinylsilane (37 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h to furnish product **2e** (49 mg, 0.169 mmol, 82%). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.37 – 7.31 (m, 3H), 1.24 (s, 12H), 0.86 – 0.72 (m, 4H), 0.26 (s, 6H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 139.5, 133.8, 128.8, 127.7, 83.0, 24.9, 8.54, –3.4 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 34.3 ppm. **$^{29}$Si NMR** (79 MHz, $CDCl_3$) δ –1.30 ppm.



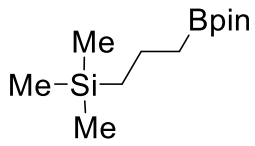

**2f**, Ethoxydimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2o-yl)ethyl)silane was prepared according to the general procedure using dimethylethoxyvinylsilane (34 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h to furnish product **2f** (48 mg, 0.186 mmol, 91%). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 3.63 (q, *J* = 7.0 Hz, 2H), 1.23 (s, 12H), 1.15 (t, *J* = 7.0 Hz, 3H), 0.79 – 0.69 (m, 2H), 0.67 – 0.59 (m, 2H), 0.06 (s, 6H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 83.1, 58.3, 24.9, 18.7, 8.9, –2.4 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 34.3 ppm. **$^{29}$Si NMR** (79 MHz, $CDCl_3$) δ 18.13 ppm. HRMS (ESI) m/z calcd for [M] 258.24, found $[M\text{-}C_2H_5]^+$ 229.14.



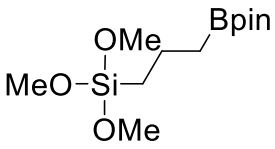

**2g**, Diethoxy(methyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was prepared according to the general procedure using diethoxymethylvinylsilane (38 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 70 °C for 3 h to furnish product **2g** (53 mg, 0.184 mmol, 90%). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 3.73 (q, *J* = 7.0 Hz, 4H), 1.22 (s, 12H), 1.18 (t, *J* = 7.0 Hz, 6H), 0.83 – 0.74 (m, 2H), 0.71 – 0.61 (m, 2H), 0.08 (s, 3H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 83.1, 58.1, 24.9, 24.7, 18.5, 6.4, –5.3 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 34.2 ppm. **$^{29}$Si NMR** (79 MHz, $CDCl_3$) δ –3.86 ppm.



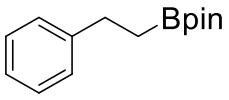

**2h**, Triethoxy(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)silane was prepared according to the general procedure using triethoxyvinlysilane (43 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 70 °C for 3 h to furnish product **2h** (51 mg, 0.160 mmol, 78%). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 3.79 (q, *J* = 7.0 Hz, 6H), 1.22 (s, 12H), 1.19 (t, *J* = 7.0 Hz, 9H), 0.87 – 0.78 (m, 2H), 0.73 – 0.61 (m, 2H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 83.0, 58.4, 24.9, 18.4, 3.1 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 34.1 ppm. **HRMS (ESI)** m/z calc for [M] 288.19, found $[M+Na]^-$ 311.18.



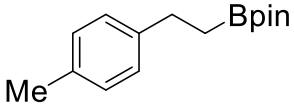

**2i**, Trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane was prepared according to the general procedure using allyltrimethylsilane (33 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 70 °C for 3 h to furnish product **2i** (41 mg, 0.169 mmol, 83%). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 1.43 (dd, *J* = 16.0, 8.2 Hz, 2H), 1.23 (s, 12H), 0.82 (t, *J* = 7.7 Hz, 2H), 0.57 – 0.46 (m, 2H), –0.04 (s, 9H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 82.9, 24.9, 24.7, 20.2, 18.7, –1.5 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 34.0 ppm. **$^{29}$Si NMR** (79 MHz, $CDCl_3$) δ 0.72 ppm.



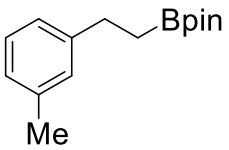

**2j**, Trimethoxy(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane was prepared according to the general procedure using allyltrimethoxysilane (35 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 70 °C for 3 h to furnish product **2j** (37 mg, 0.127 mmol, 62%). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 3.54 (s, 9H), 1.63 – 1.45 (m, 2H), 1.22 (s, 12H), 0.84 (t, *J* = 7.7 Hz, 2H), 0.73 – 0.63 (m, 2H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 83.0, 50.5, 24.9, 24.7, 17.4, 12.1 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 34.2 ppm. **$^{29}$Si NMR** (79 MHz, $CDCl_3$) δ –41.60 ppm.



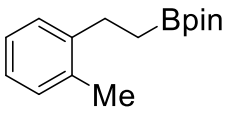

**2k**, 4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane was prepared according to the general procedure using styrene (23 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h and purified by flash chromatography ($SiO_2$, hexane/ethyl acetate 92:8) to furnish product **2k** (45 mg, 0.194 mmol, 95%). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 4H), 7.16 – 7.08 (m, 1H), 2.77 – 2.69 (m, 2H), 1.20 (s, 12H), 1.17 – 1.09 (m, 2H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 144.5, 128.3, 128.1, 125.6, 83.2, 30.1, 24.9 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 33.9 ppm.



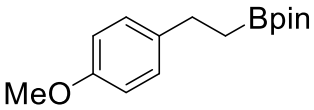

**2l**, 4,4,5,5-Tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane was prepared according to the general procedure using 4-methylstyrene (27 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h and purified by flash chromatography ($SiO_2$, hexane/ethyl acetate 92:8) to furnish product **2l** (49 mg, 0.199 mmol, 97%). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.10 (q, *J* = 8.2 Hz, 4H), 2.76 – 2.68 (m, 2H), 2.32 (s, 3H), 1.24 (s, 12H), 1.18 – 1.09 (m, 2H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 141.5, 134.9, 129.0, 127.9, 83.2, 29.6, 24.9, 21.1 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 33.9 ppm.



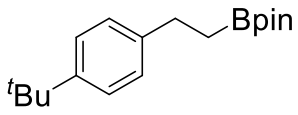

**2m,** 4,4,5,5-Tetramethyl-2-(3-methylphenethyl)-1,3,2-dioxaborolane was prepared according to the general procedure using 3-methylstyrene (27 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h and purified by flash chromatography ($SiO_2$, hexane/ethyl acetate 92:8) to furnish product **2m** (49 mg, 0.199 mmol, 97%). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.5 Hz, 1H), 7.07 – 6.94 (m, 2H), 2.76 – 2.68 (m, 2H), 2.33 (s, 3H), 1.24 (s, 7H), 1.19 – 1.09 (m, 1H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$) δ 144.5, 137.7, 128.9, 128.2, 126.3, 125.1, 83.2, 29.9, 24.9, 21.5 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 33.9 ppm.



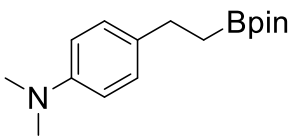

**2n,** 4,4,5,5-Tetramethyl-2-(2-methylphenethyl)-1,3,2-dioxaborolane was prepared according to the general procedure using 2-methylstyrene (27 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h and purified by flash chromatography ($SiO_2$, hexane/ethyl acetate 92:8) to furnish product **2n** (44 mg, 0.179 mmol, 87%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.2 Hz, 1H), 7.14 – 7.05 (m, 3H), 2.72 (t, *J* = 8.0 Hz, 2H), 2.33 (s, 3H), 1.25 (s, 12H), 1.11 (t, *J* = 8.3 Hz, 2H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 142.6, 135.9, 130.0, 128.2, 125.9, 125.7, 83.2, 27.3, 24.9, 19.4 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 33.9 ppm.



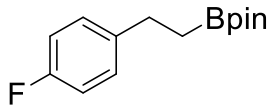

**2o**, 2-(4-Methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared according to the general procedure using 4-methoxystyrene (28 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h and purified by flash chromatography ($SiO_2$, hexane/ethyl acetate 92:8) to furnish product **2o** (50 mg, 0.191 mmol, 93%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.15 – 7.13 (m, 2H), 6.84 – 6.76 (m, 2H), 3.78 (s, 3H), 2.75 – 2.64 (m, 2H), 1.22 (s, 12H), 1.15 – 1.09 (m, 2H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 157.7, 136.7, 129.0, 113.7, 83.3, 55.4, 29.2, 24.9 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 33.9 ppm.



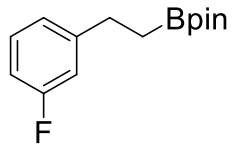

**2p**, 2-(4-(*Tert*-butyl)phenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared according to the general procedure using 4-*tert*-butylstyrene (37 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h and purified by flash chromatography ($SiO_2$, hexane/ethyl acetate 92:8) to furnish product **2p** (45 mg, 0.157 mmol, 76%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 2.77 – 2.69 (m, 2H), 1.32 (s, 9H), 1.23 (s, 12H), 1.19 – 1.11 (m, 2H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 148.4, 141.5, 127.8, 125.2, 83.2, 34.4, 31.6, 29.5, 24.9 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 33.9 ppm.



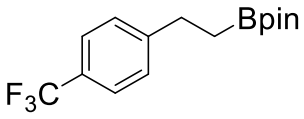

**2q**, *N,N*-Dimethyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)anilinewas prepared according to the general procedure using *N,N*-dimethyl-4-vinylaniline (30 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h and purified by flash chromatography ($SiO_2$, hexane/ethyl acetate 92:8) to furnish product **2q** (49 mg, 0.178 mmol, 85%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 2.91 (s, 6H), 2.71 – 2.63 (m, 2H), 1.24 (s, 12H), 1.16 – 1.08 (m, 2H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 149.0, 133.1, 128.6, 113.2, 83.1, 41.2, 29.0, 24.9 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 34.03 ppm.



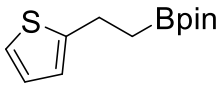

**2r**, 2-(4-Fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared according to the general procedure using 4-fluorostyrene (25 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h and purified by flash chromatography ($SiO_2$, hexane/ethyl acetate 92:8) to furnish product **2r** (44 mg, 0.176 mmol, 86%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.02 – 6.83 (m, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 1.21 (s, 12H), 1.12 (t, *J* = 8.1 Hz, 2H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 161.2 (d, *J* = 242.6 Hz), 140.1 (d, *J* = 2.9 Hz), 129.4 (d, *J* = 7.8 Hz), 114.9 (d, *J* = 21.0 Hz), 83.3, 29.3, 24.9 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 33.8 ppm.



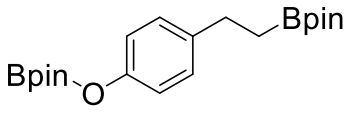

**2s**, 2-(3-Fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared according to the general procedure using 3-fluorostyrene (25 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h and purified by flash chromatography ($SiO_2$, hexane/ethyl acetate 92:8) to furnish product **2s** (43 mg, 0.172 mmol, 84%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.92 (dt, *J* = 10.3, 2.3 Hz, 1H), 6.84 (td, *J* = 8.3, 2.7 Hz, 1H), 2.74 (t, *J* = 8.1 Hz, 2H), 1.22 (s, 12H), 1.17 – 1.09 (m, 2H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 162.9 (d, *J* = 244.5 Hz), 147.0 (d, *J* = 6.8 Hz), 129.5 (d, *J* = 8.3 Hz), 123.7 (d, *J* = 2.9 Hz), 114.9 (d, *J* = 21.0 Hz), 112.3 (d, *J* = 21.0 Hz), 83.2, 29.8, 24.8 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 33.8 ppm.




**2t**, 4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenethyl)-1,3,2-dioxaborolane was prepared according to the general procedure using 4-trifluoromethylstyrene (30 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h and purified by flash chromatography ($SiO_2$, hexane/ethyl acetate 92:8) to furnish product **2t** (47 mg, 0.157 mmol, 76%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 2.80 (t, *J* = 8.2 Hz, 2H), 1.21 (s, 12H), 1.15 (t, *J* = 8.1 Hz, 2H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 148.6, 128.5, 125.2 (q, *J* = 3.9 Hz), 83.4, 30.0, 24.9 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 33.7 ppm.




**2u**, 4,4,5,5-Tetramethyl-2-(2-(thiophen-2-yl)ethyl)-1,3,2-dioxaborolane was prepared according to the general procedure using 2-vinylthiophene (20 µL, 0.205 mmol) and HBpin (32 µL, 0.225 mmol) at 50 °C for 15 h and purified by flash chromatography ($SiO_2$, hexane/ethyl acetate 92:8) to furnish product **2u** (38 mg, 0.160 mmol, 78%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 6.4 Hz, 1H), 6.93 – 6.86 (m, 1H), 6.80 (d, *J* = 4.5 Hz, 1H), 2.96 (t, *J* = 8.0 Hz, 2H), 1.23 (m, 14H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 147.9, 126.7, 123.5, 122.7, 83.4, 24.9, 24.5 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 33.7 ppm.




**2v**, 4,4,5,5-Tetramethyl-2-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenoxy)-1,3,2-dioxaborolane was prepared according to the general procedure using 4-acetoxystyrene (31 µL, 0.205 mmol) and HBpin (90 µL, 0.620 mmol) at 50 °C for 15 h. Volatiles were removed *in vacuo*, the mixture was suspended in diethyl ether and filtered through a short plug of Celite in a glove box and volatiles were removed *in vacuo* to furnish product **2v** (46 mg, 0.123 mmol, 60%). Broad **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.13 (s, 2H), 7.00 (s, 2H), 2.71 (s, 2H), 1.33 – 1.24 (m, 24H), 1.14 (s, 2H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$) δ 150.7, 138.3, 128.1, 118.5, 82.8, 82.4, 28.6, 24.3, 24.1, 12.7 ppm. **$^{11}$B NMR** (128 MHz, $CDCl_3$) δ 33.9, 21.9 ppm.

**Deuterium Labelling Hydroboration Experiment with DBpin**

In a nitrogen filled glovebox, an oven dried J-Youngs NMR tube was charged with [{($^{iPr}$DPB$^{Ph}$)Fe}$_2$(μ-1,2-$N_2$)] (0.01 mmol), DBpin solution (0.225 mmol) and vinyltrimethylsilane (30 μL, 0.205 mmol). The reaction mixture was added to an oil bath (50 °C) for 15 h. Crude NMR was taken in $C_6D_6$ with toluene as an internal standard, volatiles were removed under reduced pressure, mixture was suspended in $Et_2O$ and filtered through a short pad of silica (2.0 cm in a pipette) further purification was required by flash chromatography ($SiO_2$, hexane/ethyl acetate 92:8) to furnish product ***d*-2d** (44 mg, 0.191 mmol, 93%). **$^2$H NMR** (61 MHz, $C_6D_6$) δ 0.85 (s, 0.67D), 0.68 (s, 1D).

**Infrared Spectroscopy**

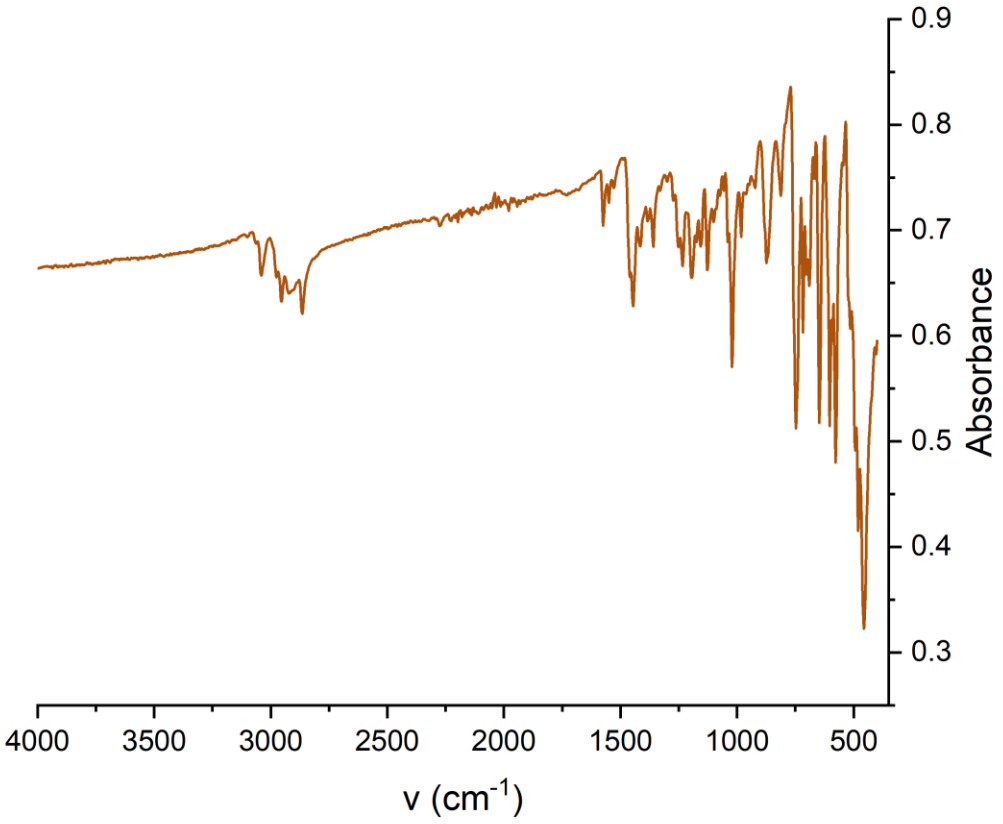



**Figure S1:** Infrared spectrum of complex **A**

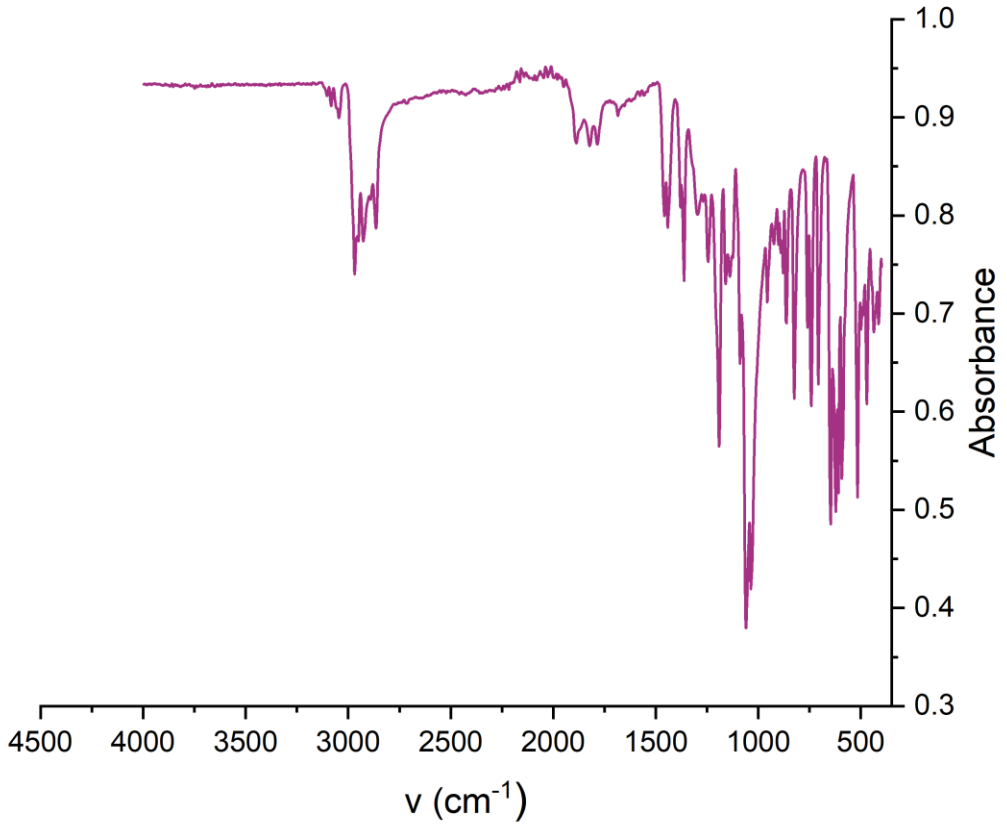



**Figure S2:** Infrared spectrum of complex **B**

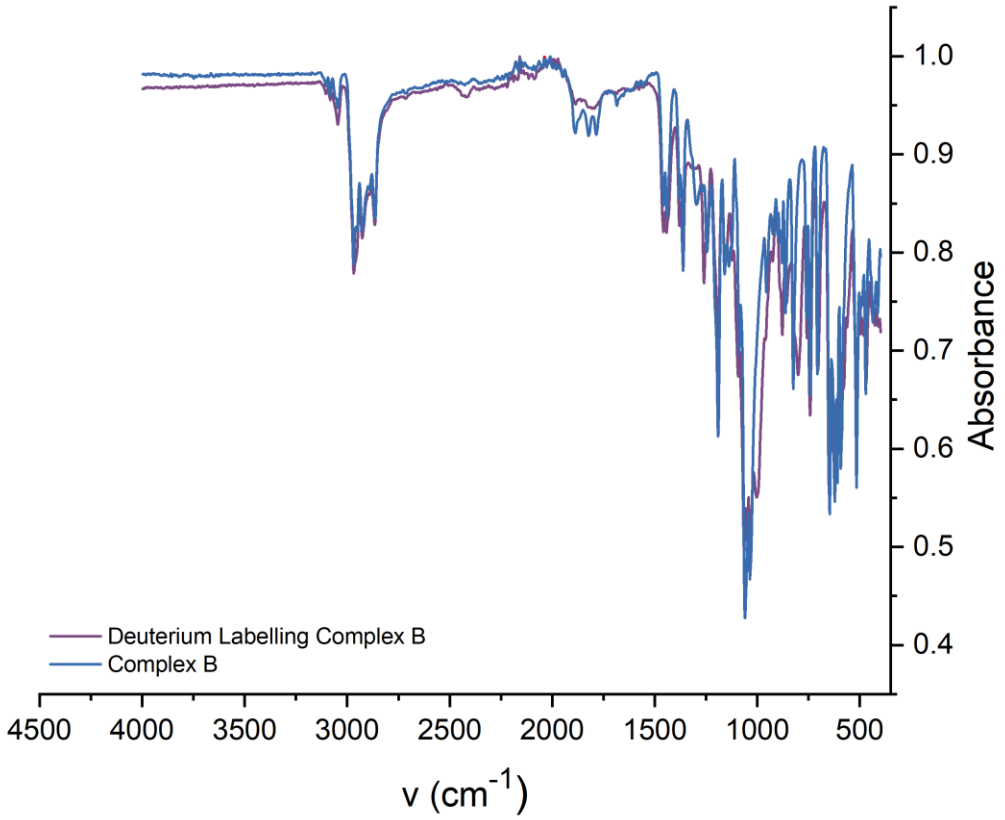



**Figure S3:** Infrared spectrum of complex **B** and deuterium labelled complex **B**

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## NMR Spectra of Compounds

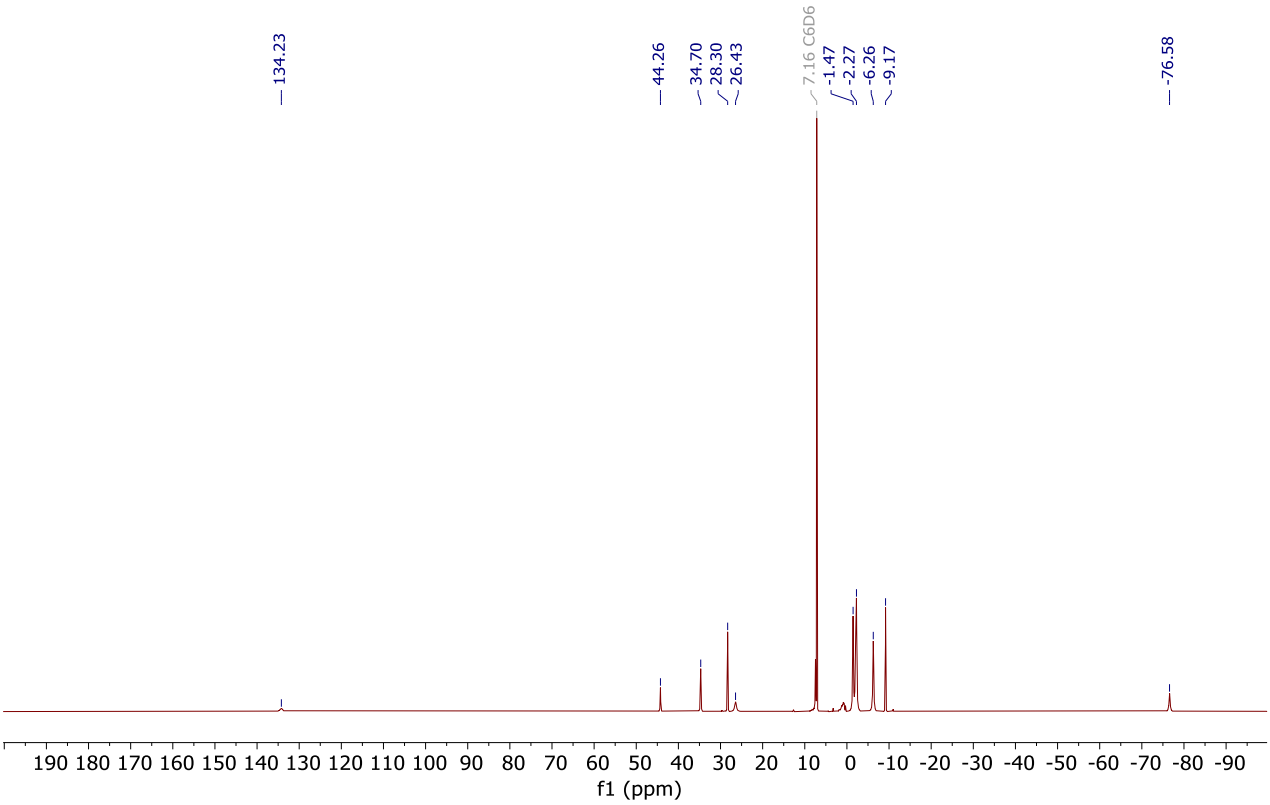


**Figure S4:** $^{1}$H NMR spectrum ($C_6D_6$) of pre-catalyst **[{(($^{iPr}$DPB$^{Ph}$)Fe}$_2$(μ-1,2-N$_2$)]** complex **A**

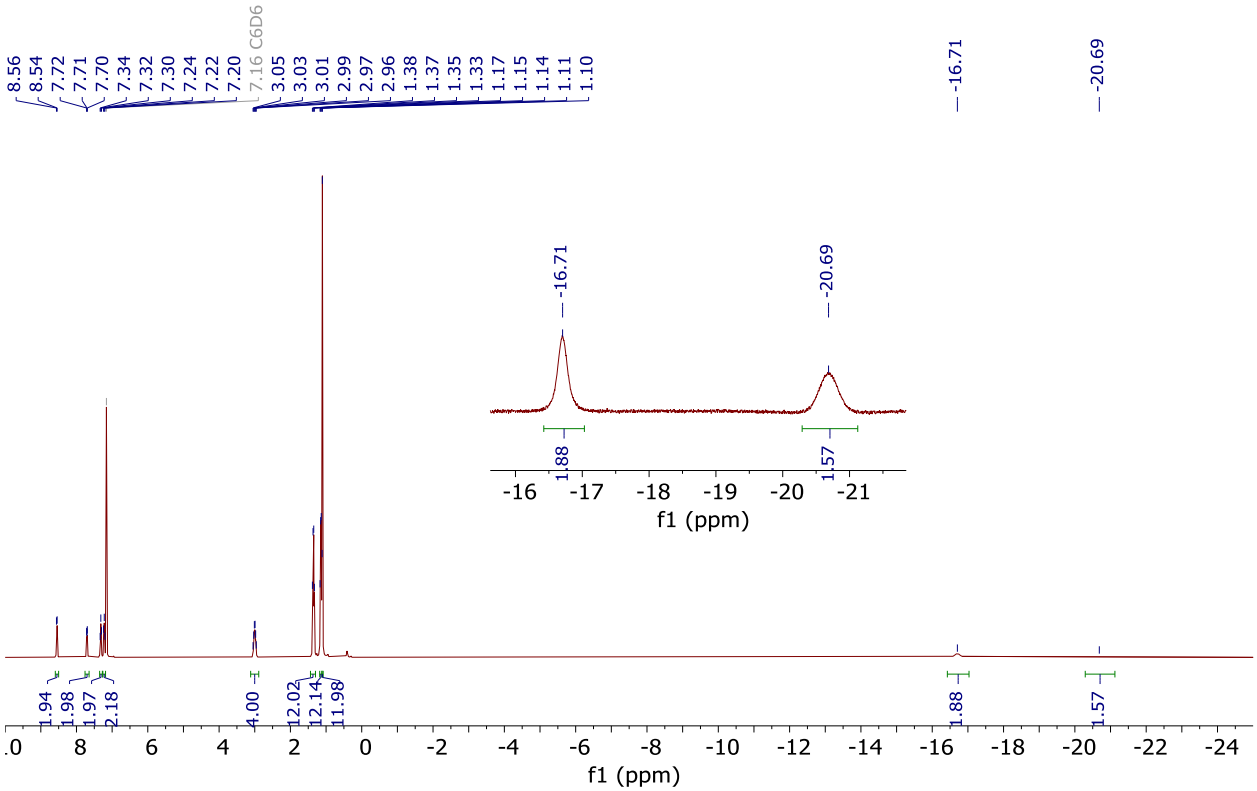


**Figure S5:** $^{1}H$ NMR spectrum ($C_6D_6$) of complex **B**

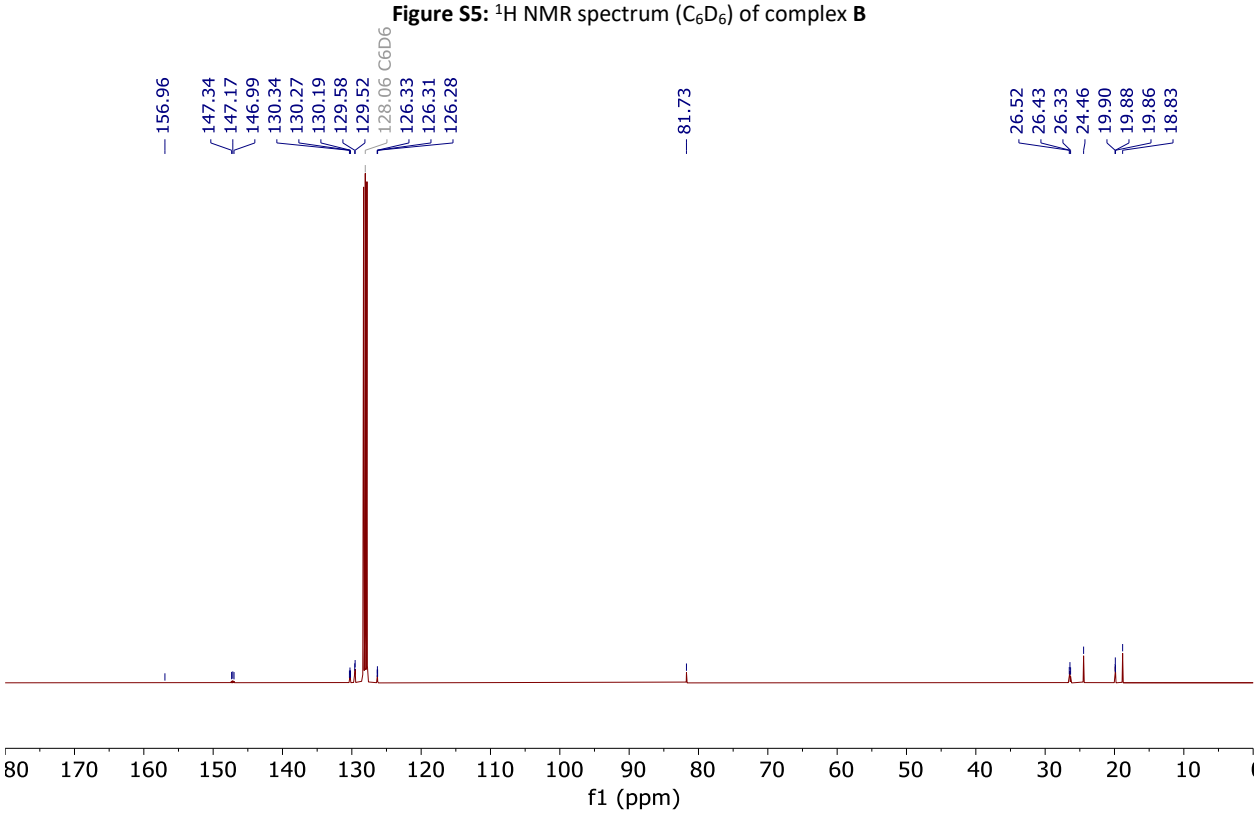


**Figure S6:** $^{13}C\{^{1}H\}$ NMR spectrum ($C_6D_6$) of complex **B**

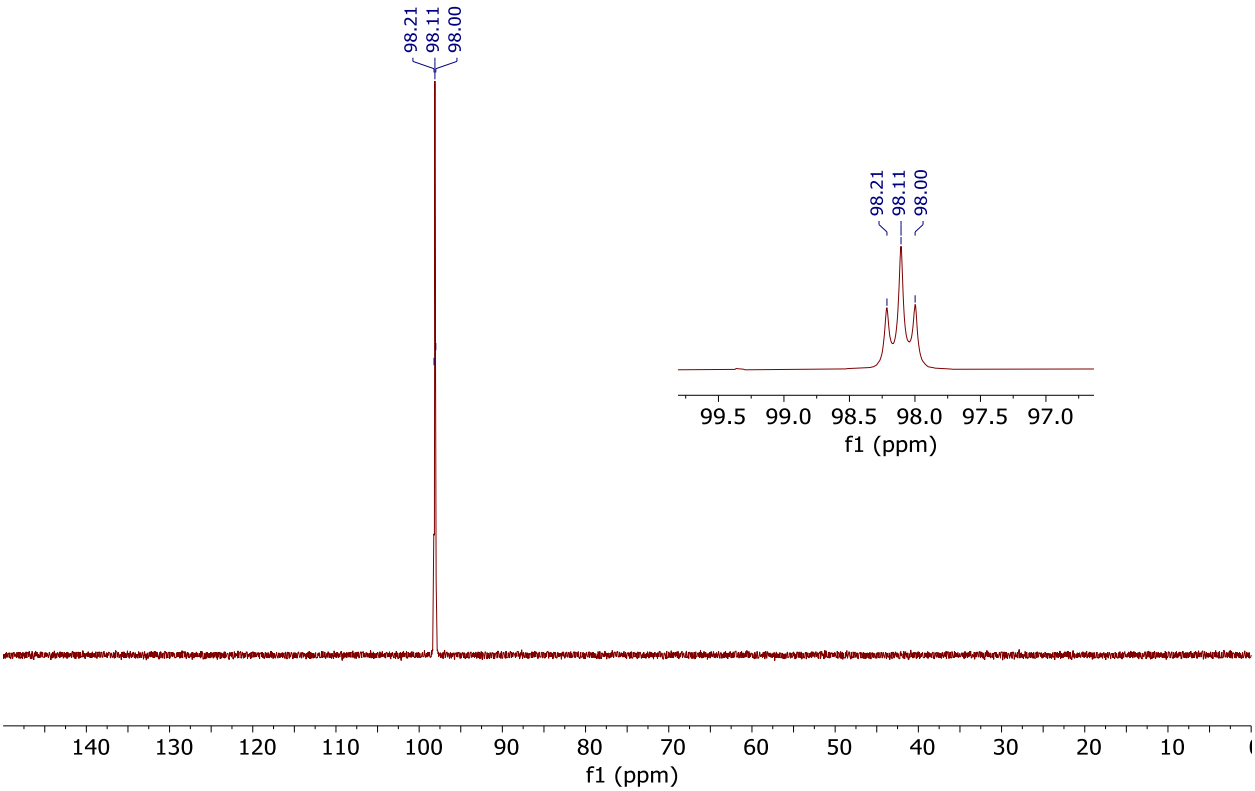


**Figure S7:** $^{31}P$ NMR spectrum ($C_6D_6$) of complex **B**

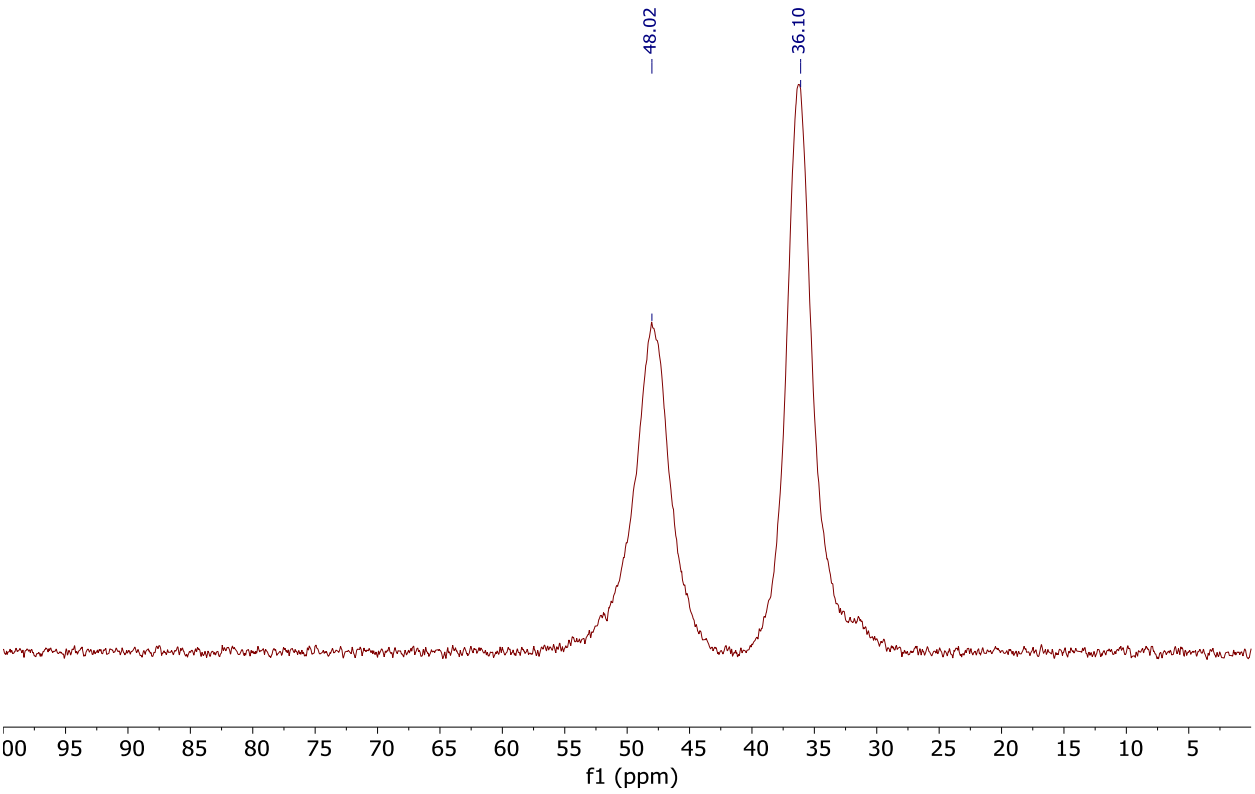


**Figure S8:** $^{11}B$ NMR ($C_6D_6$) of complex **B**

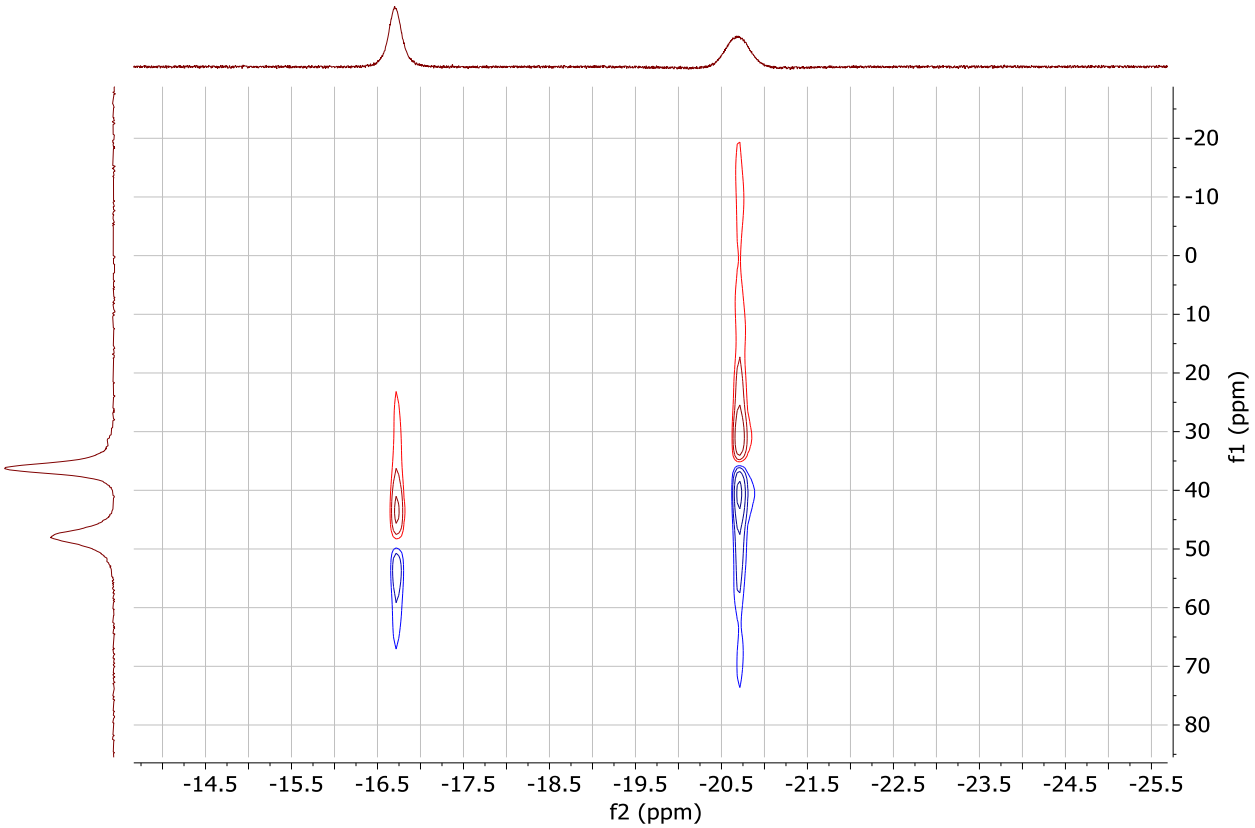


**Figure S9:** $^{1}H$ $^{11}B$ HMQC spectrum ($C_6D_6$) of complex **B**

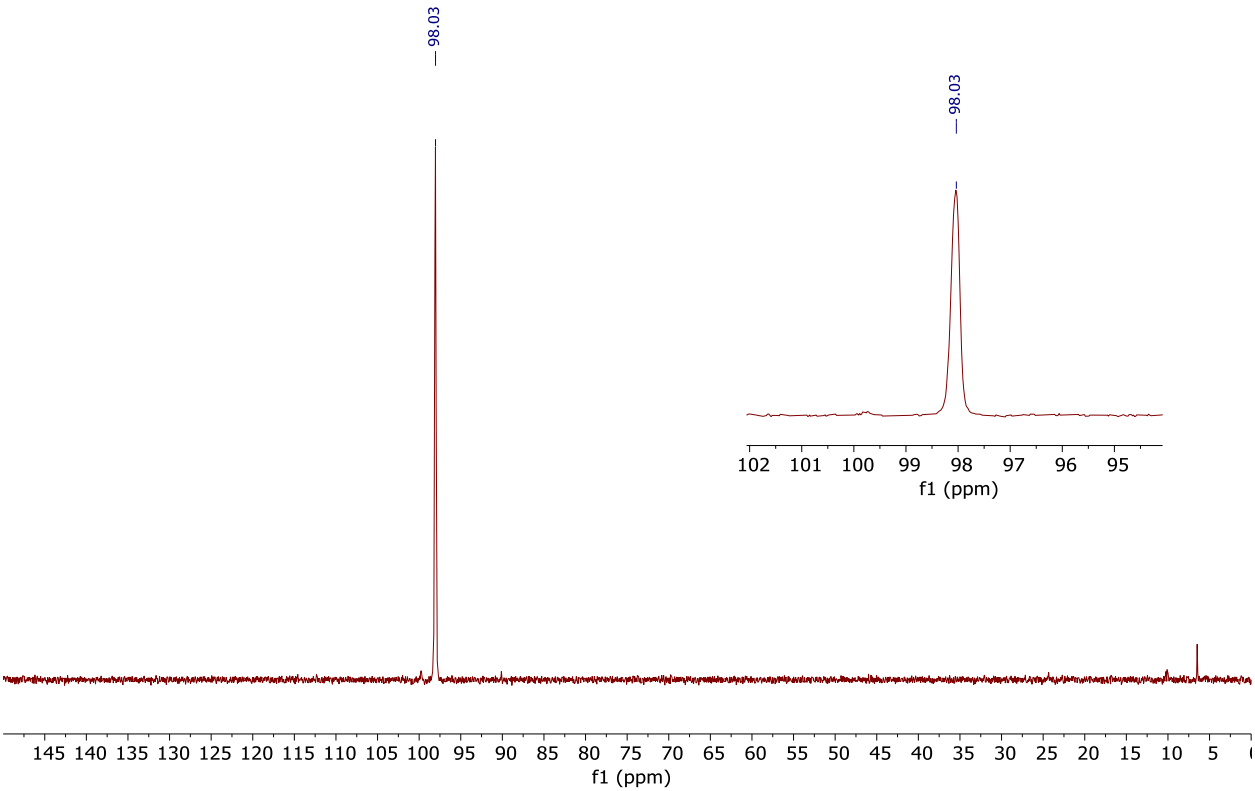


**Figure S10:** $^{31}P$ NMR spectrum ($C_6D_6$) of complex **B** made with DBpin

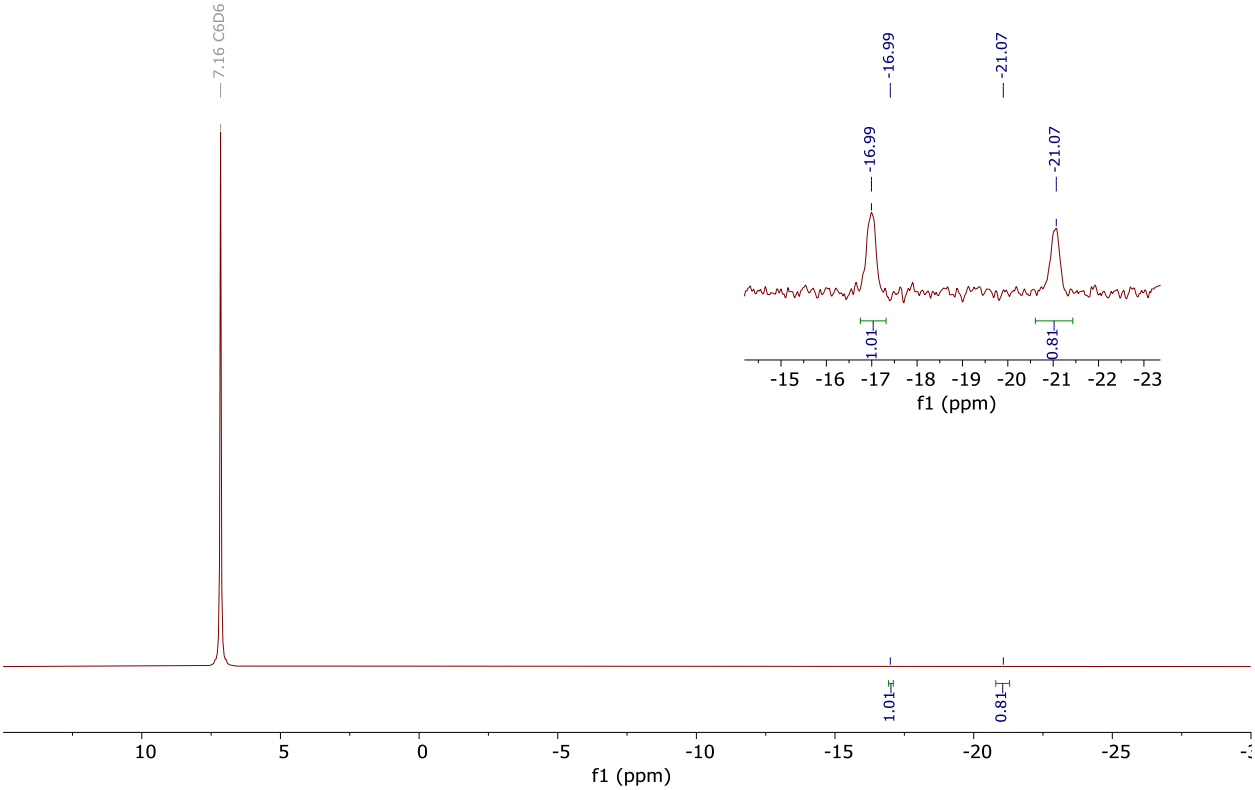


**Figure S11:** $^{2}H$ NMR spectrum of complex **B** made with DBpin

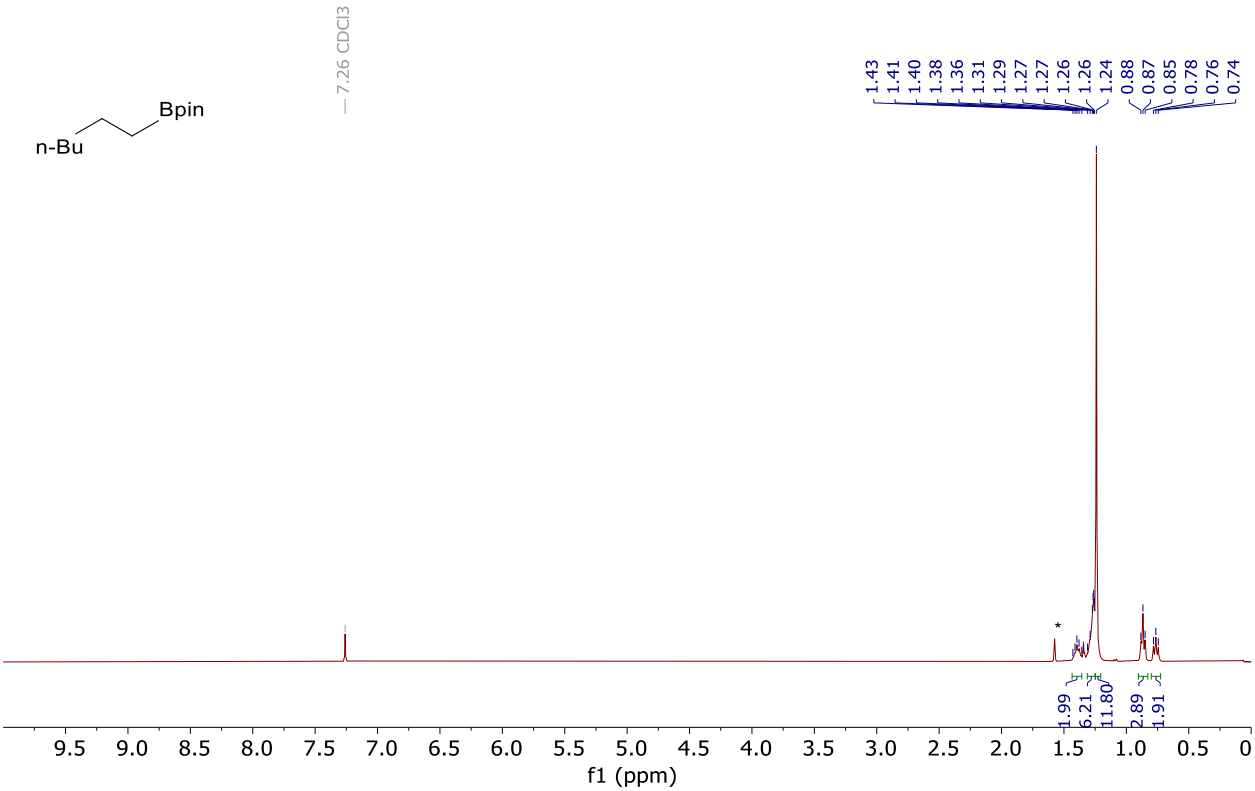


**Figure S12:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2a**

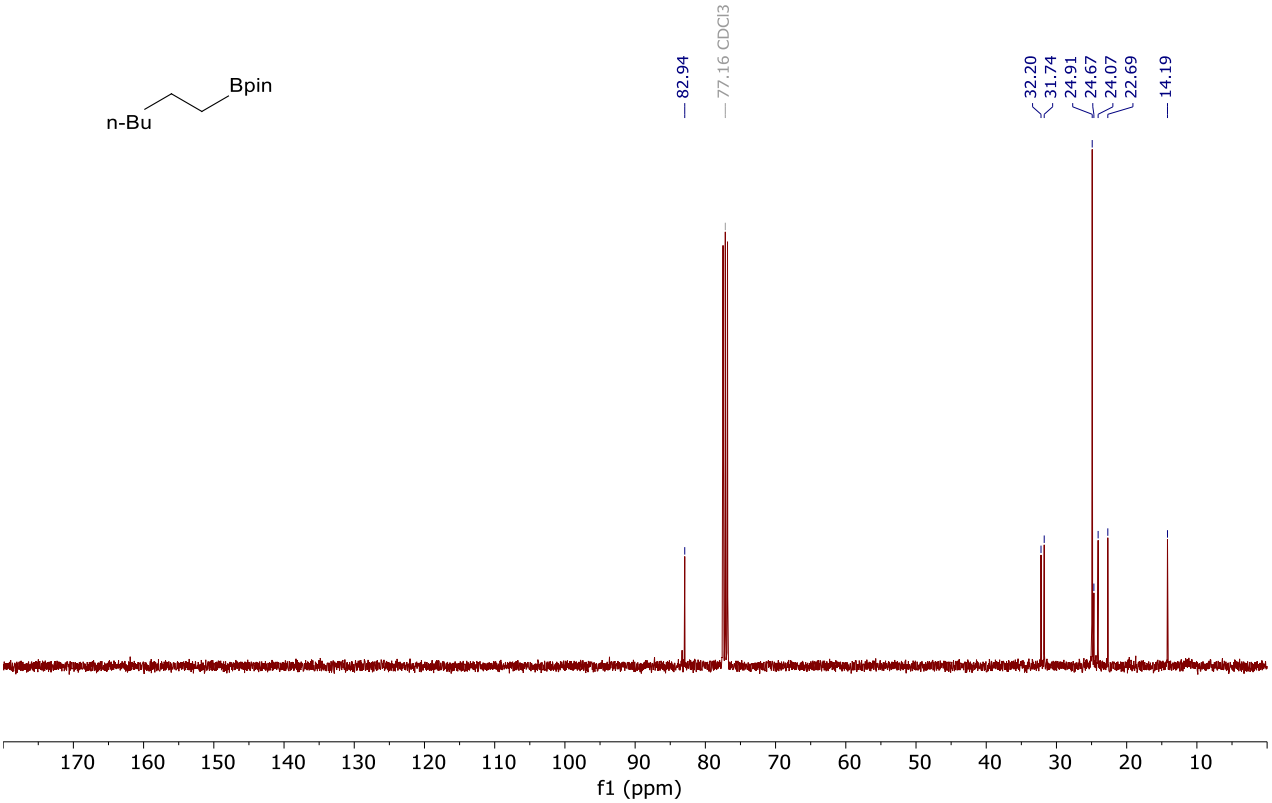


**Figure S13:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2a**

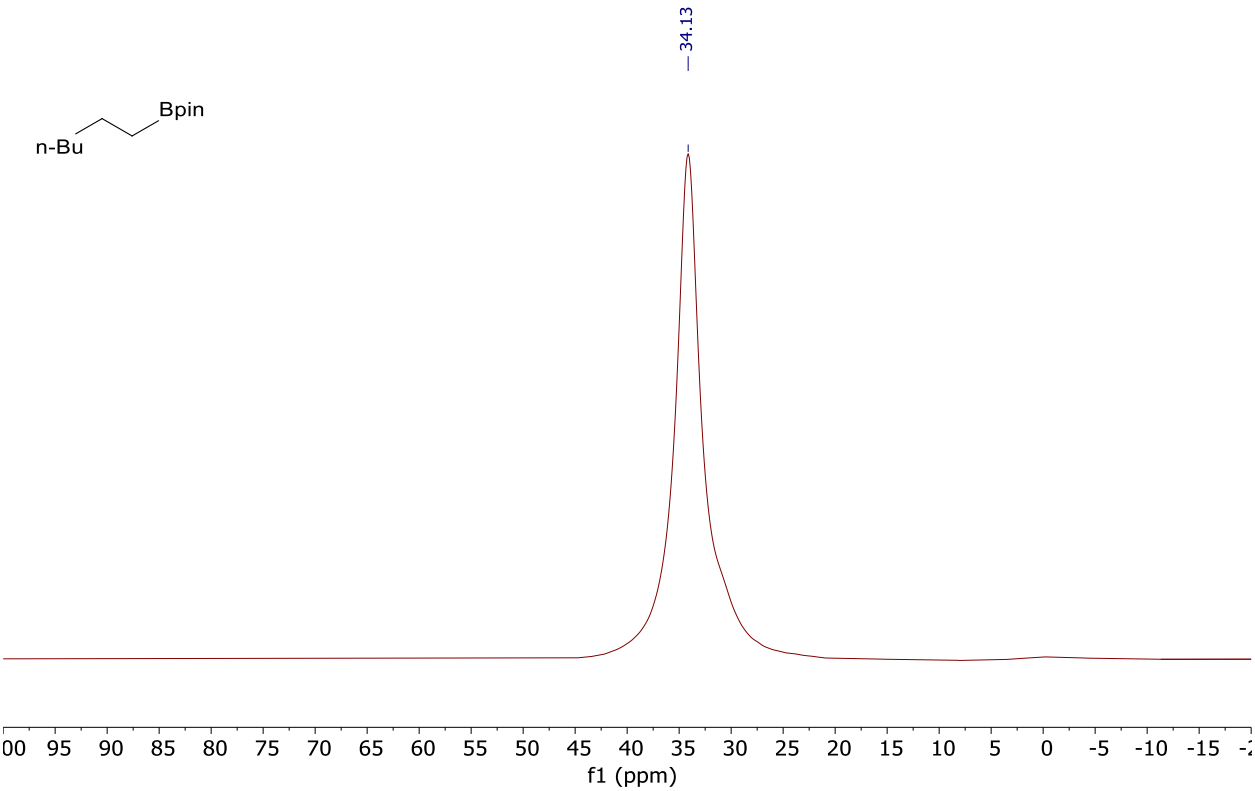


**Figure S14:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2a**

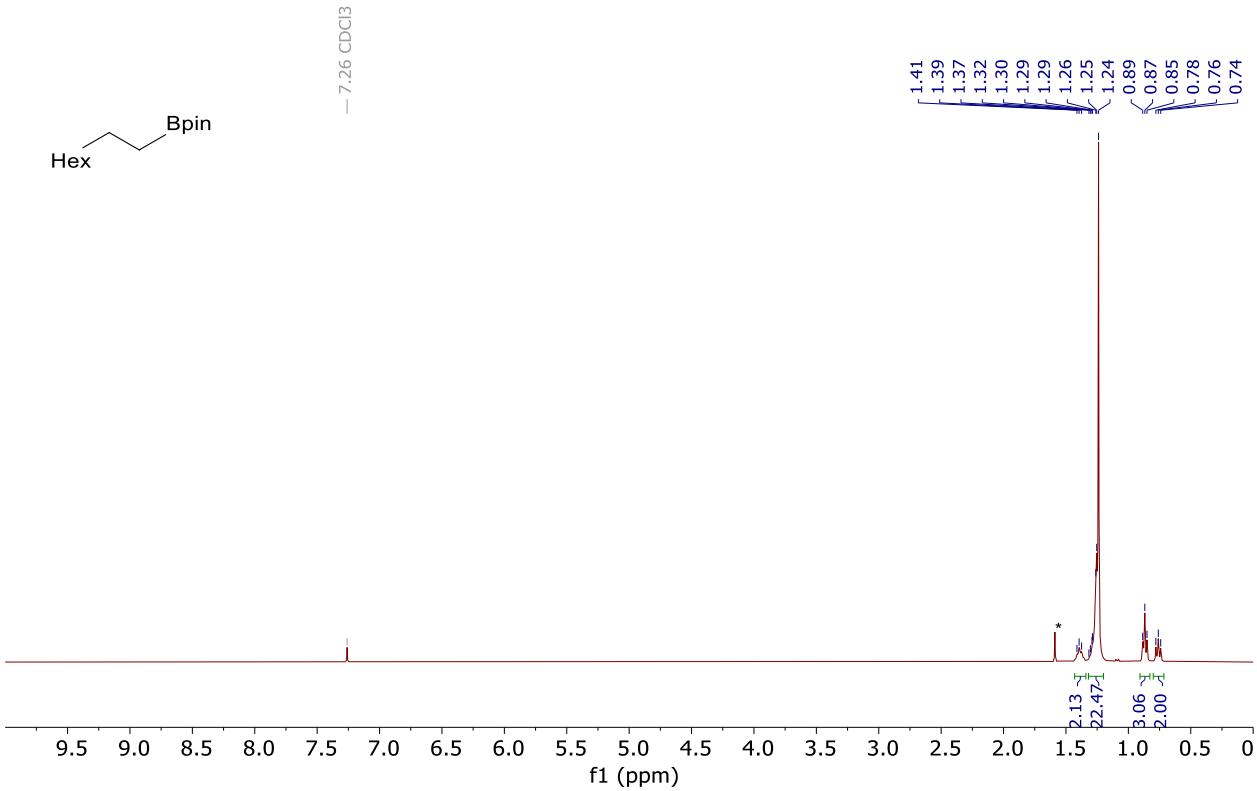


**Figure S15:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2b**

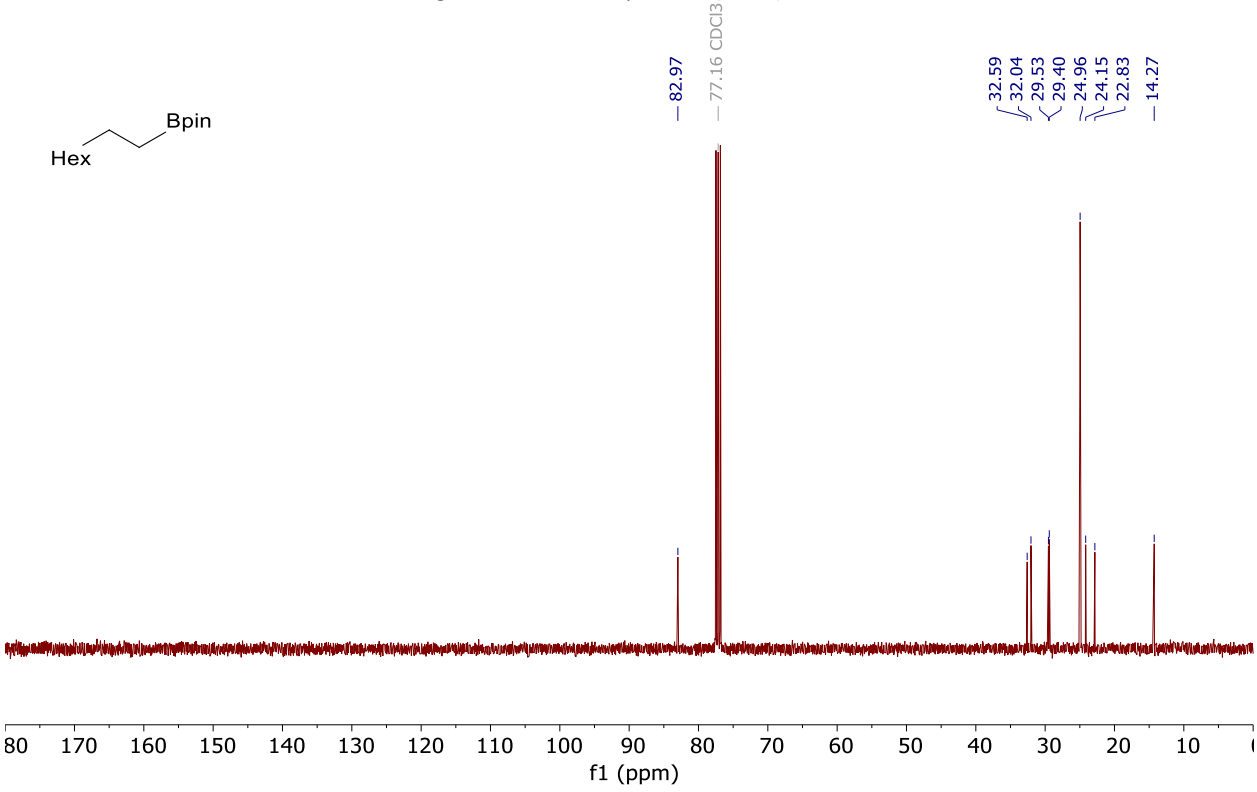


**Figure S16:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2b**

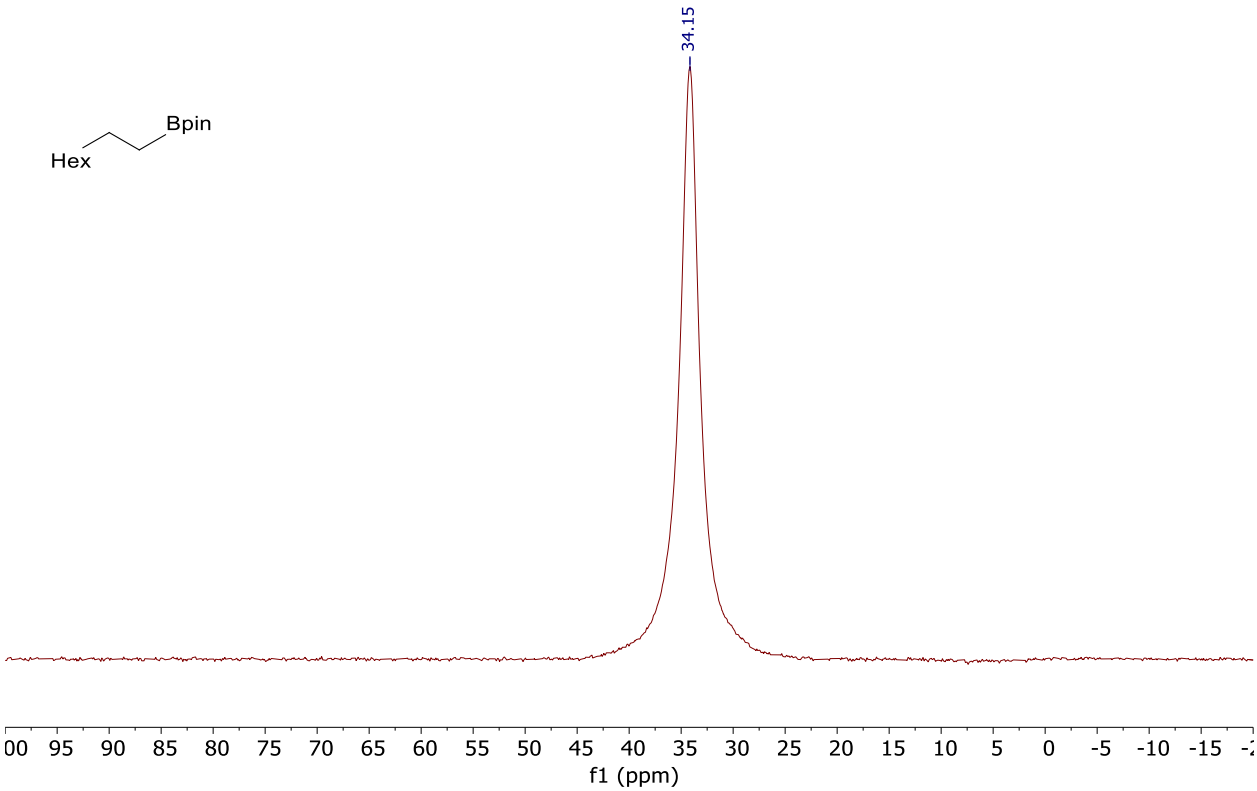


**Figure S17:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2b**

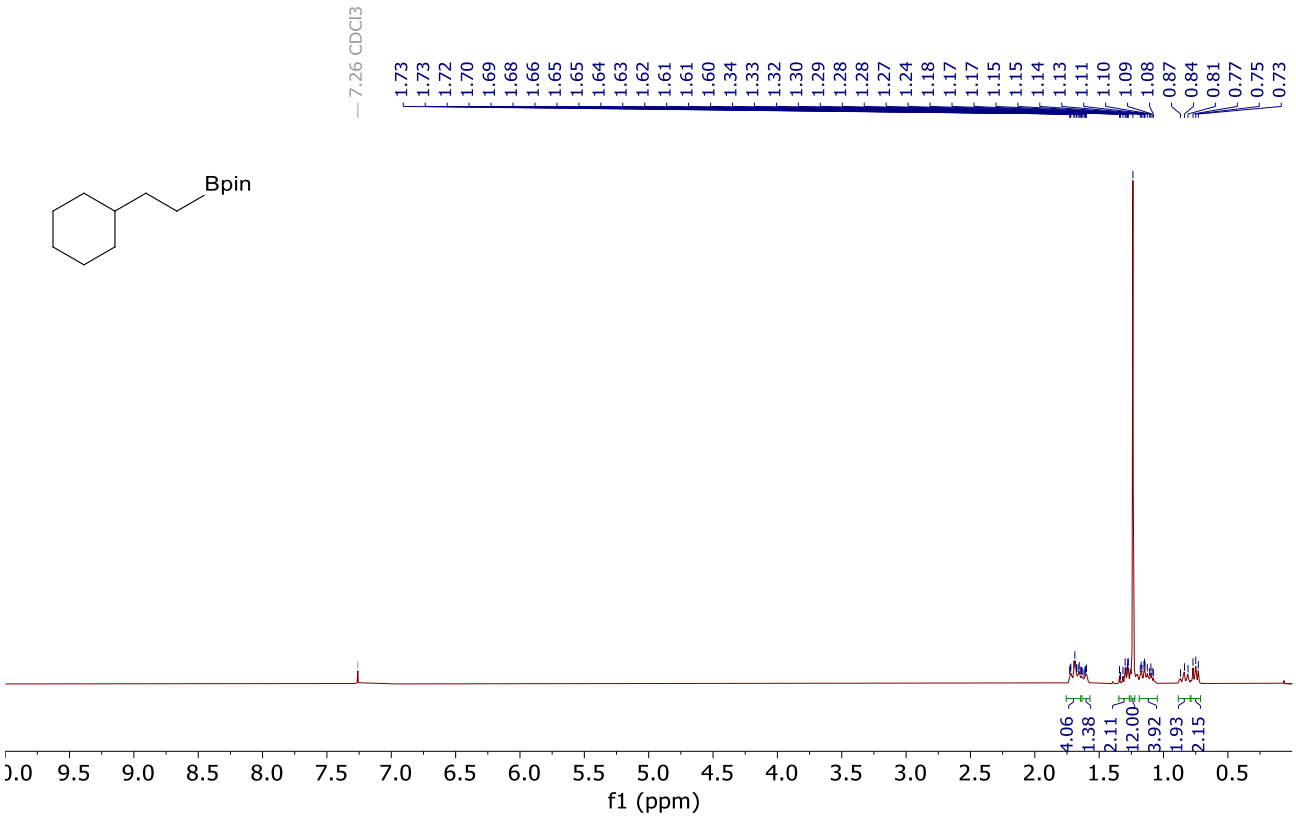


**Figure S18:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2c**

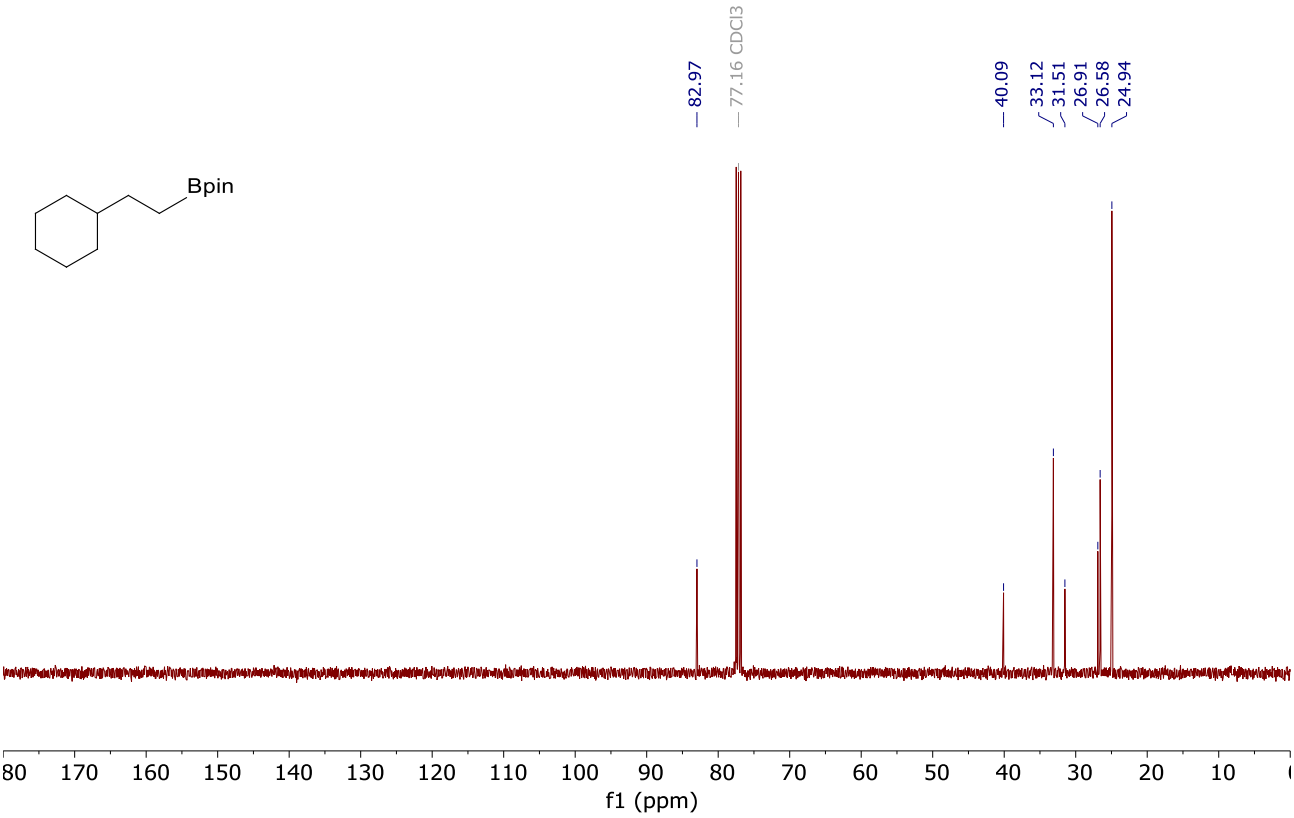


**Figure S19:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2c**

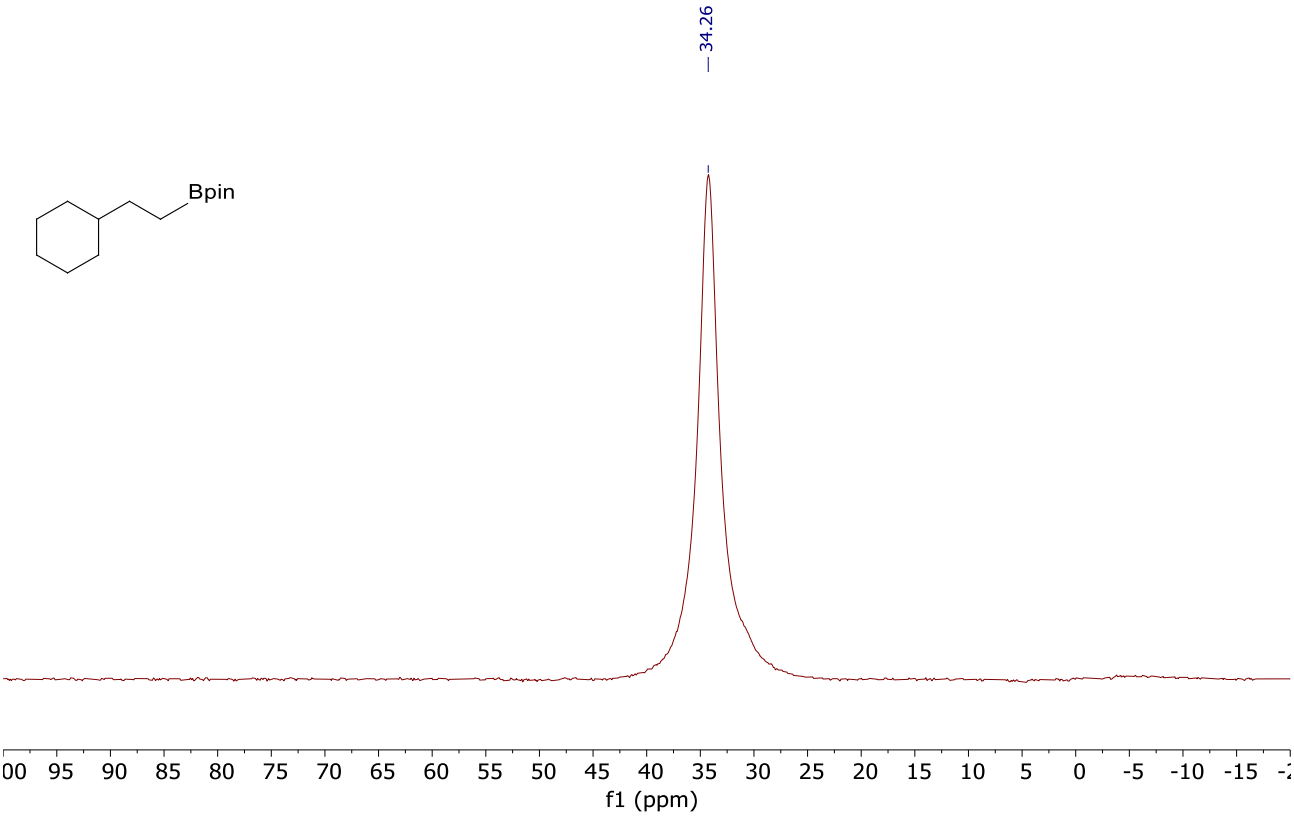


**Figure S20:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2c**

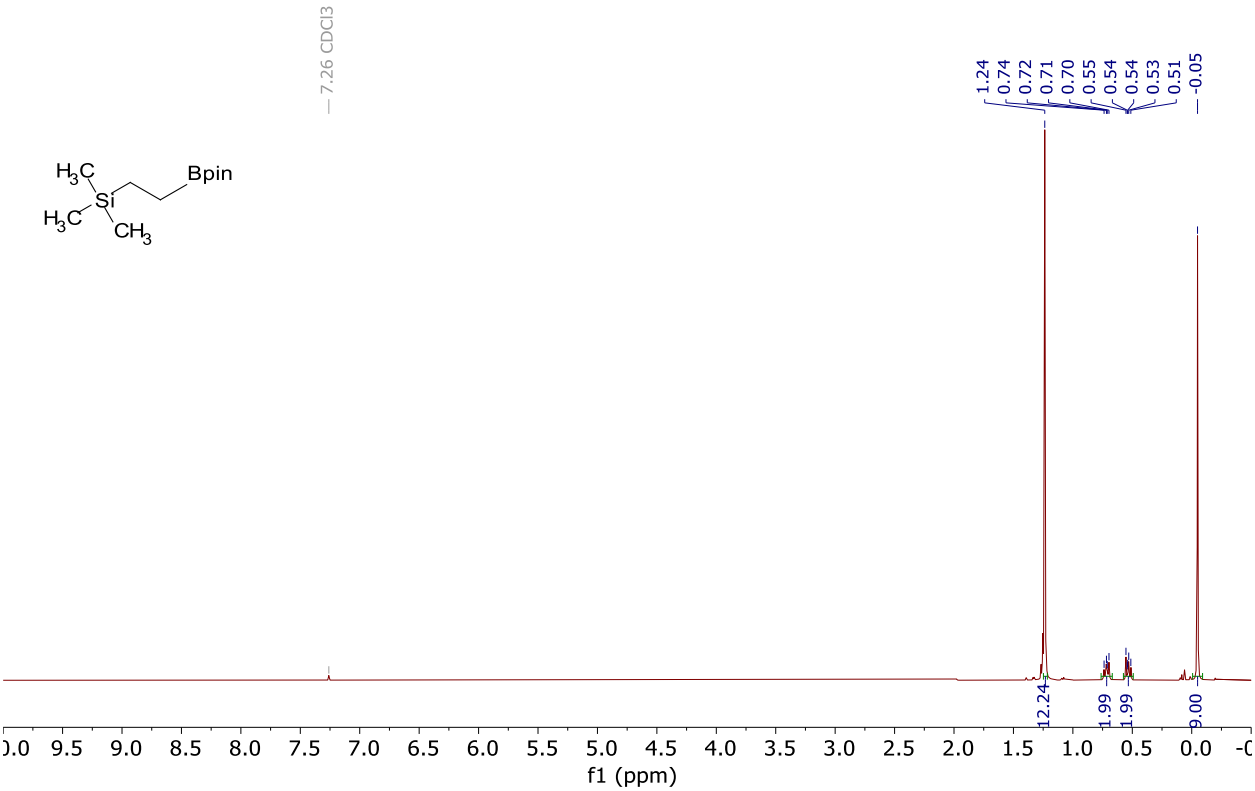


**Figure S21**: $^{1}H$ NMR spectrum ($CDCl_3$) of **2d**

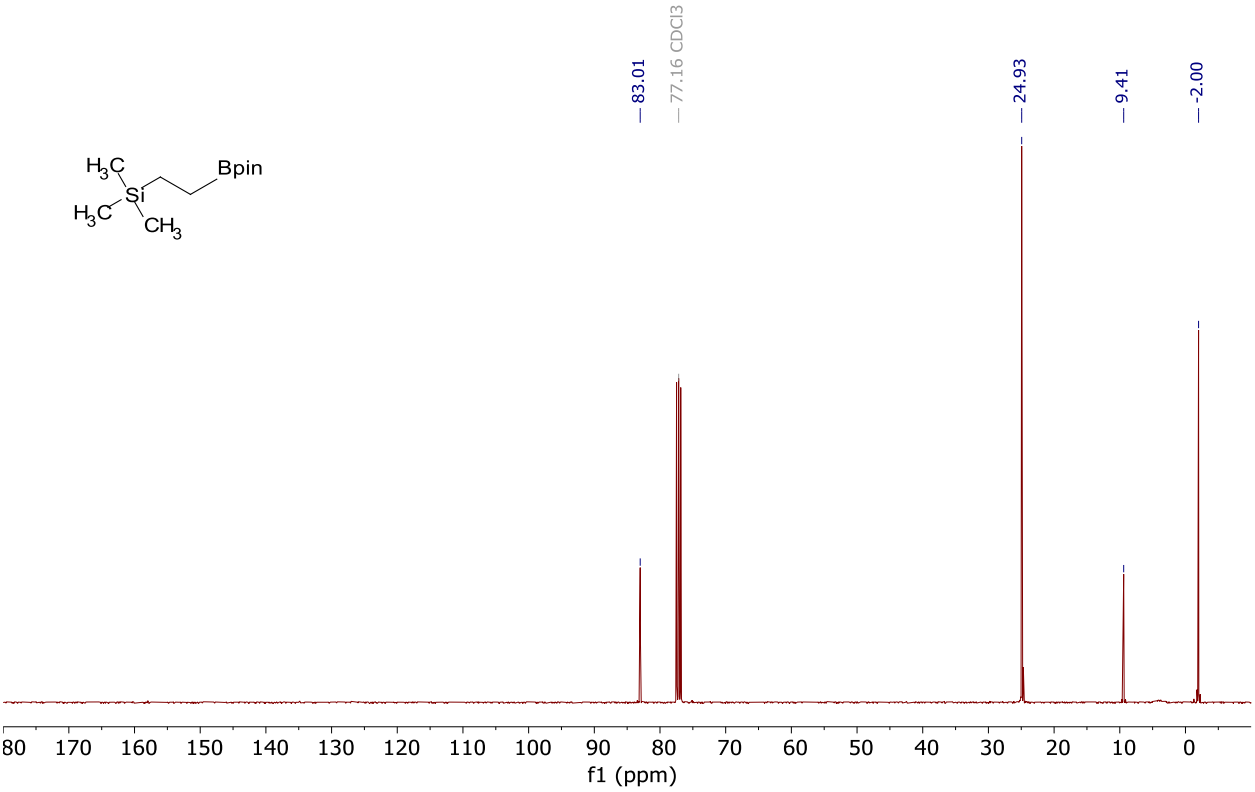


**Figure S22:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2d**

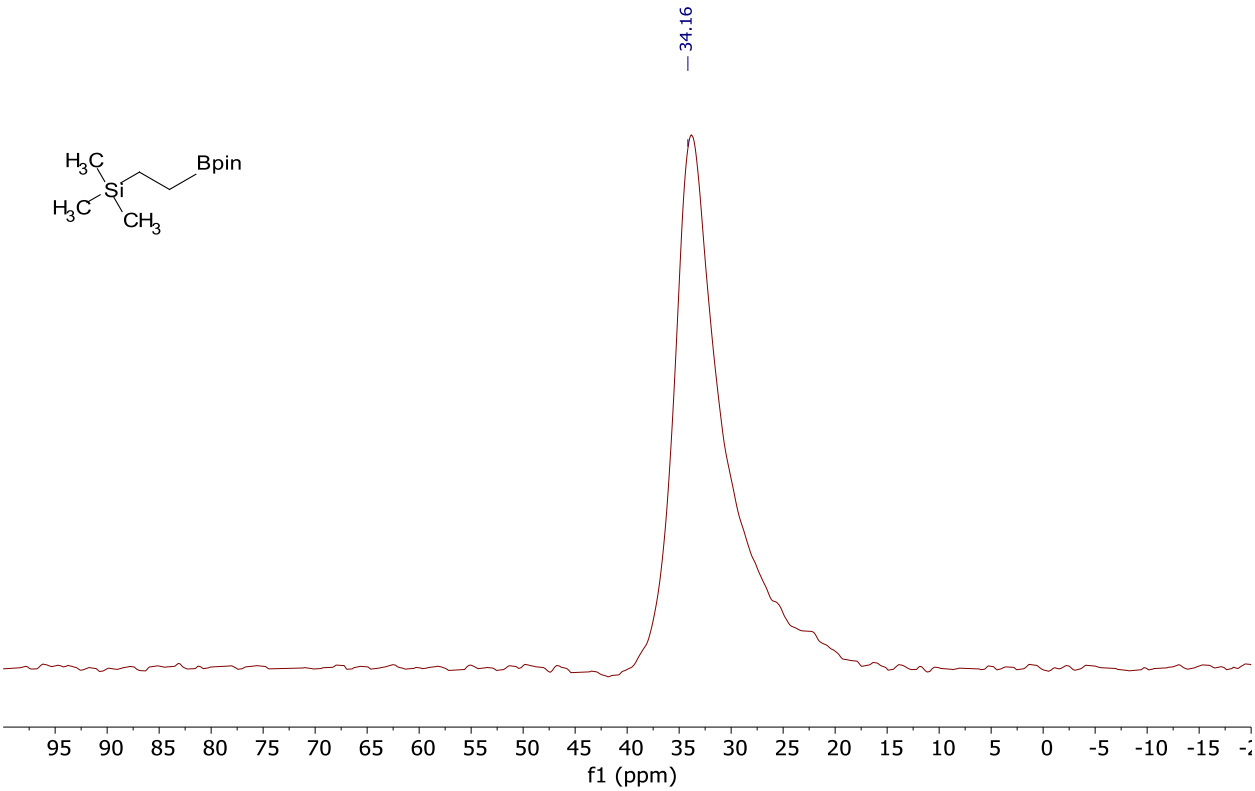


**Figure S23**: $^{11}B$ NMR spectrum ($CDCl_3$) of **2d**

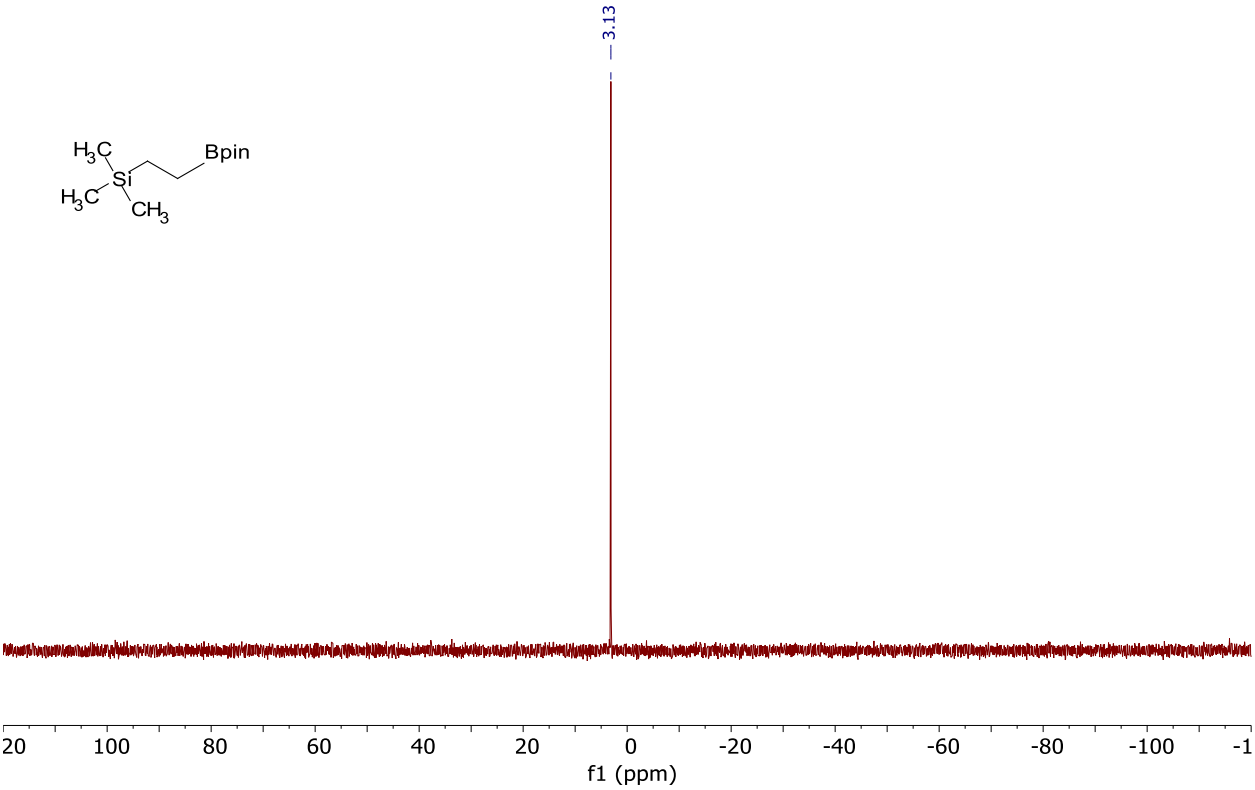


**Figure S24:** $^{29}Si$ NMR spectrum ($CDCl_3$) of **2d**

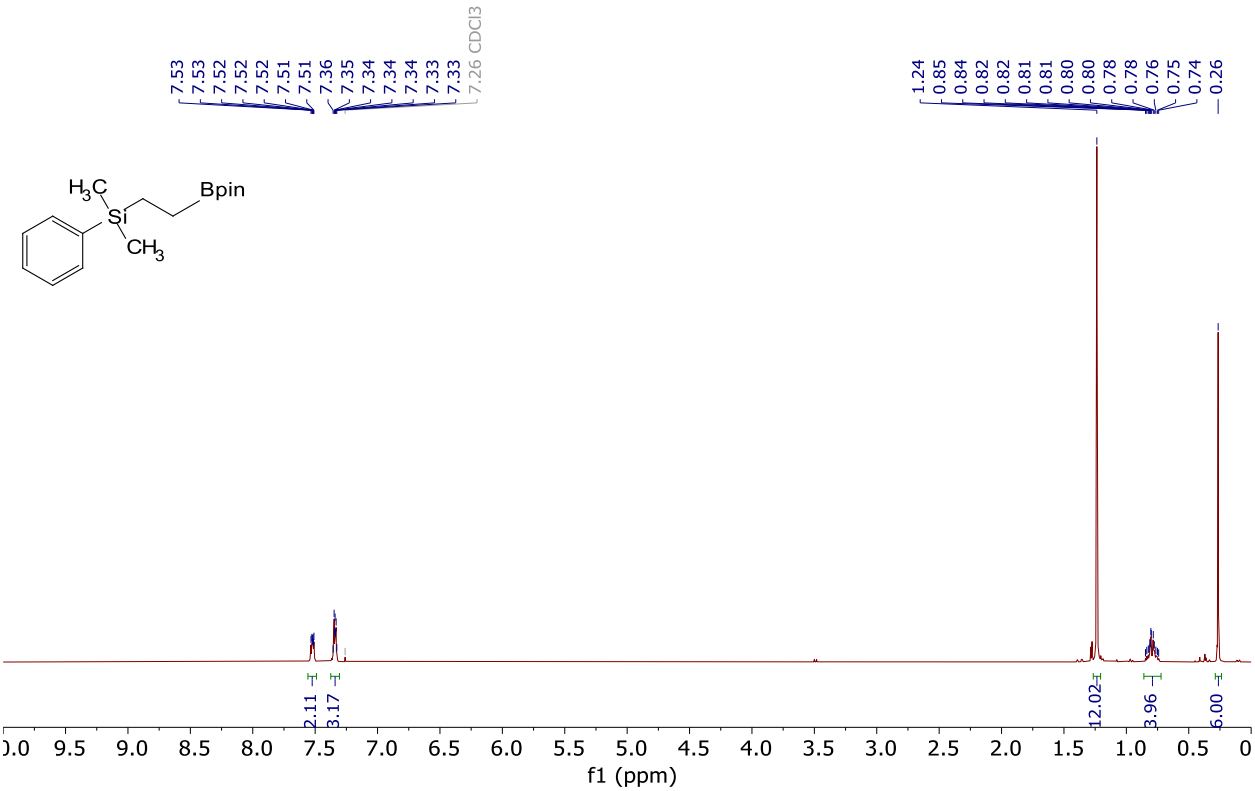


**Figure S25:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2e**

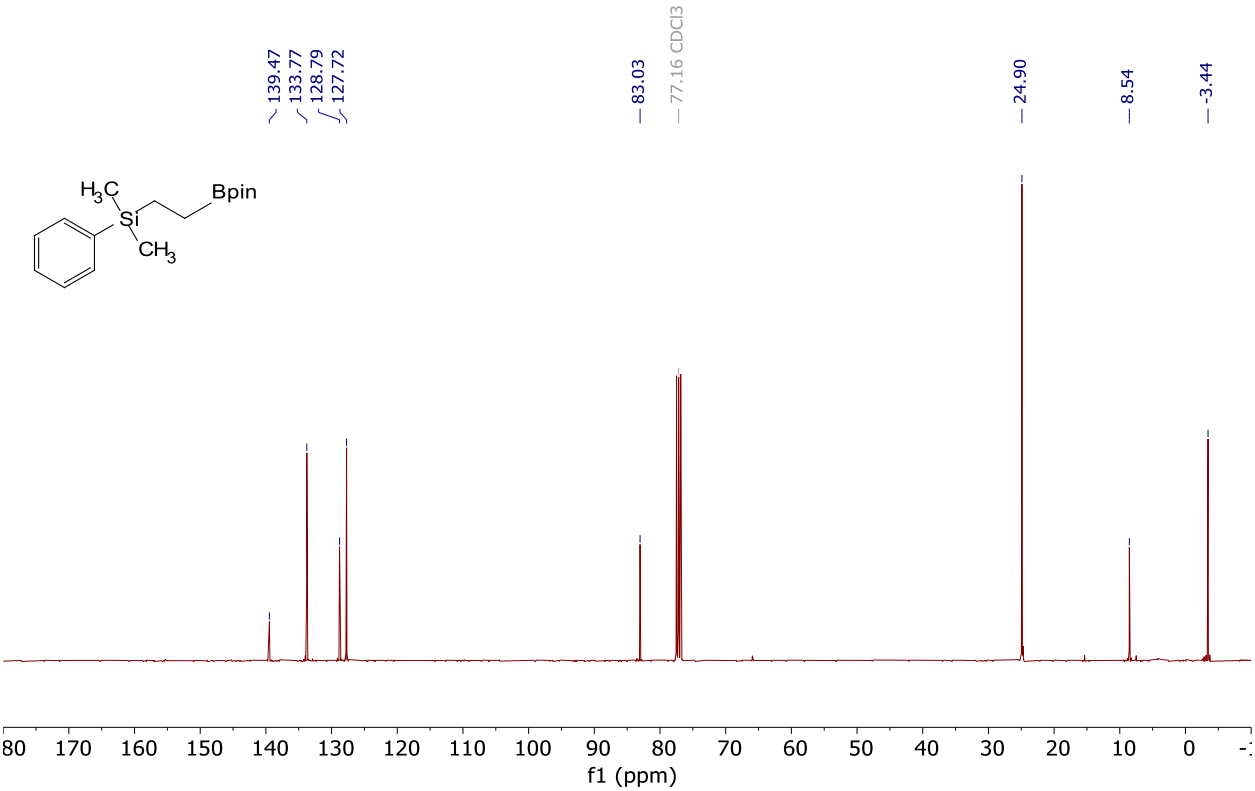


**Figure S26:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2e**

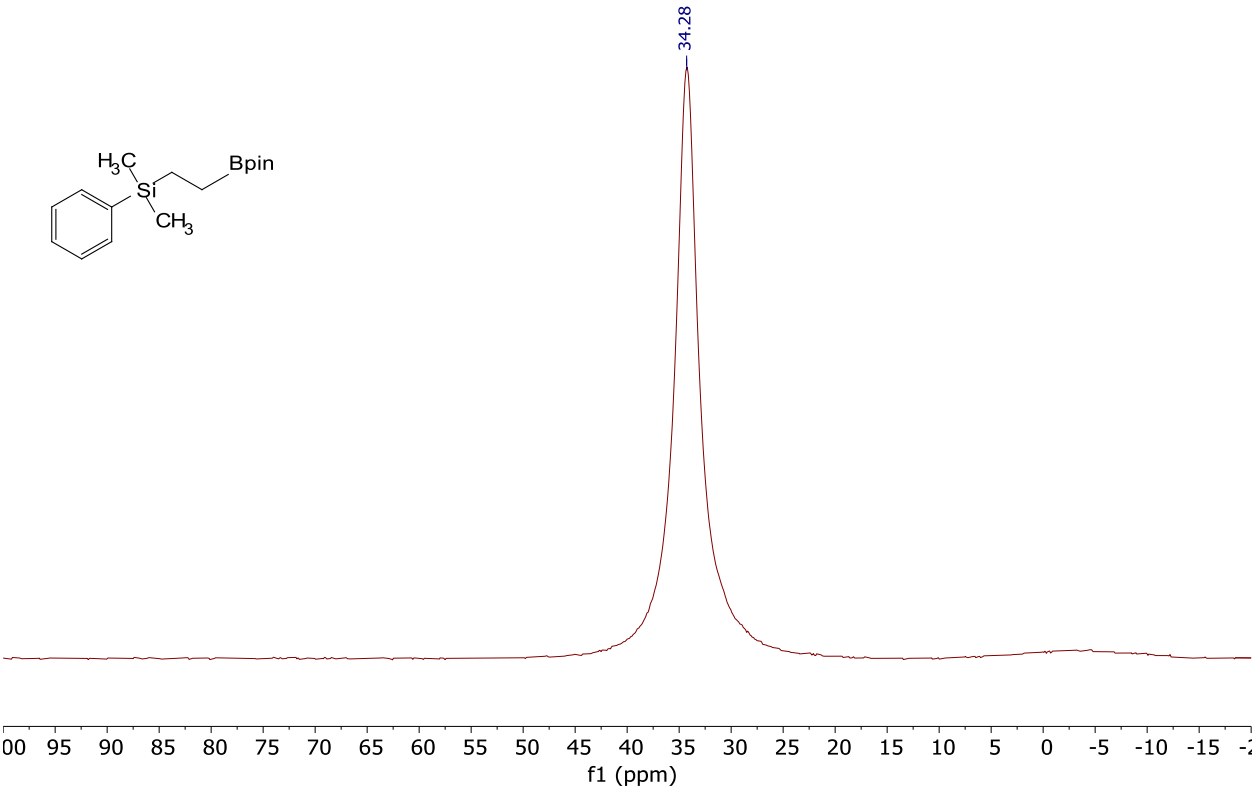


**Figure S27:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2e**

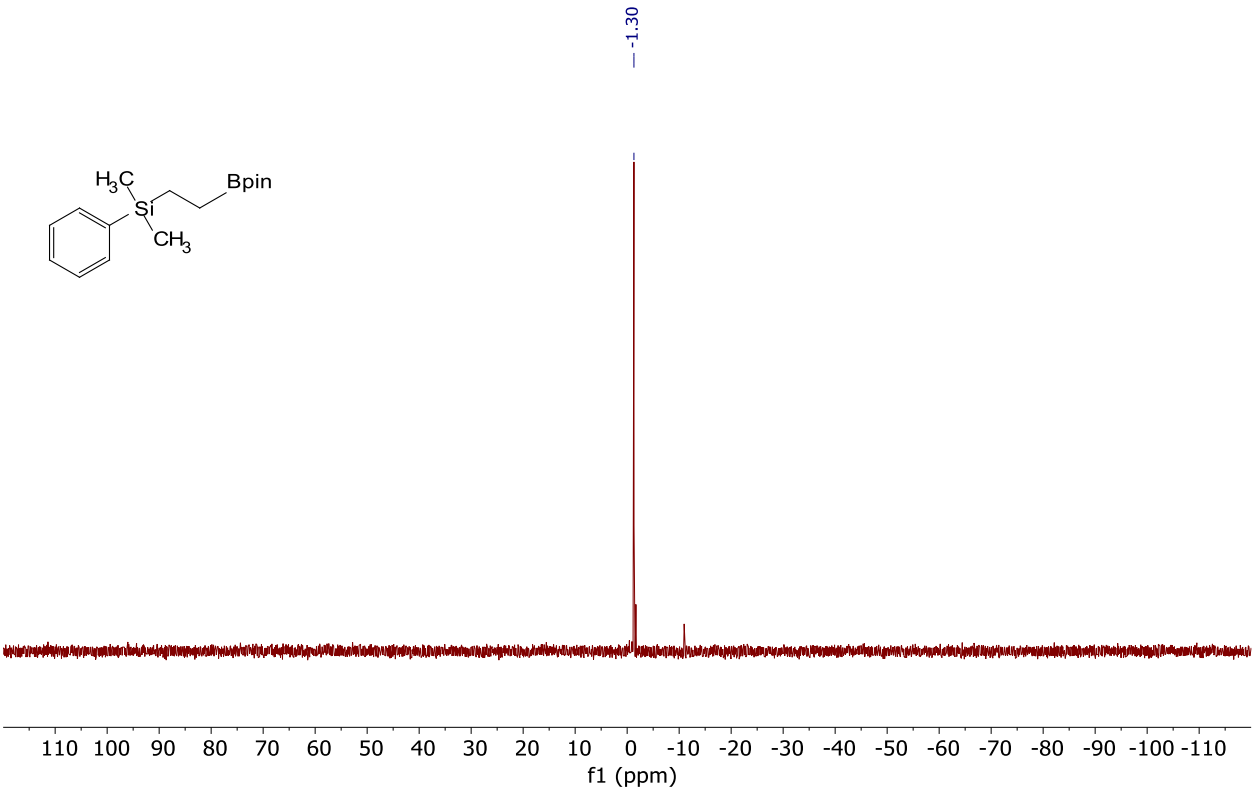


**Figure S28:** $^{29}Si$ NMR spectrum ($CDCl_3$) of **2e**

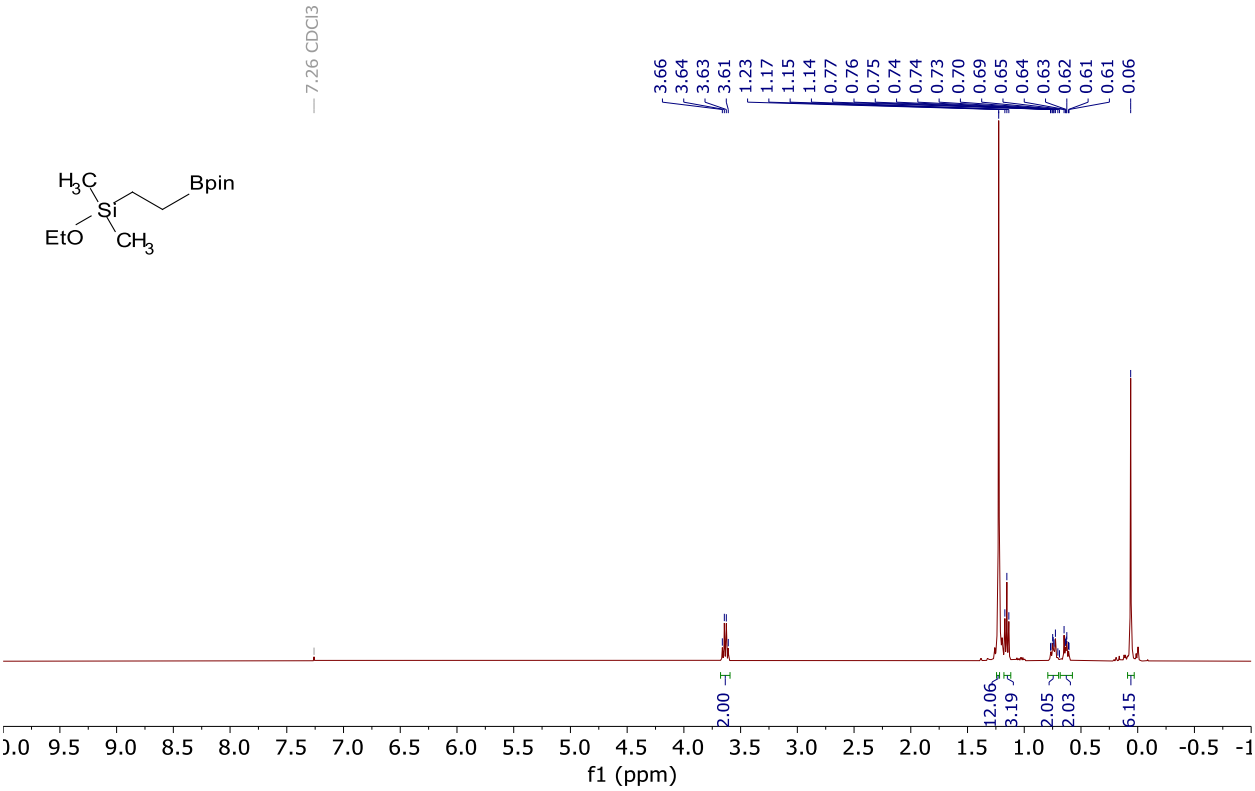


**Figure S29:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2f**

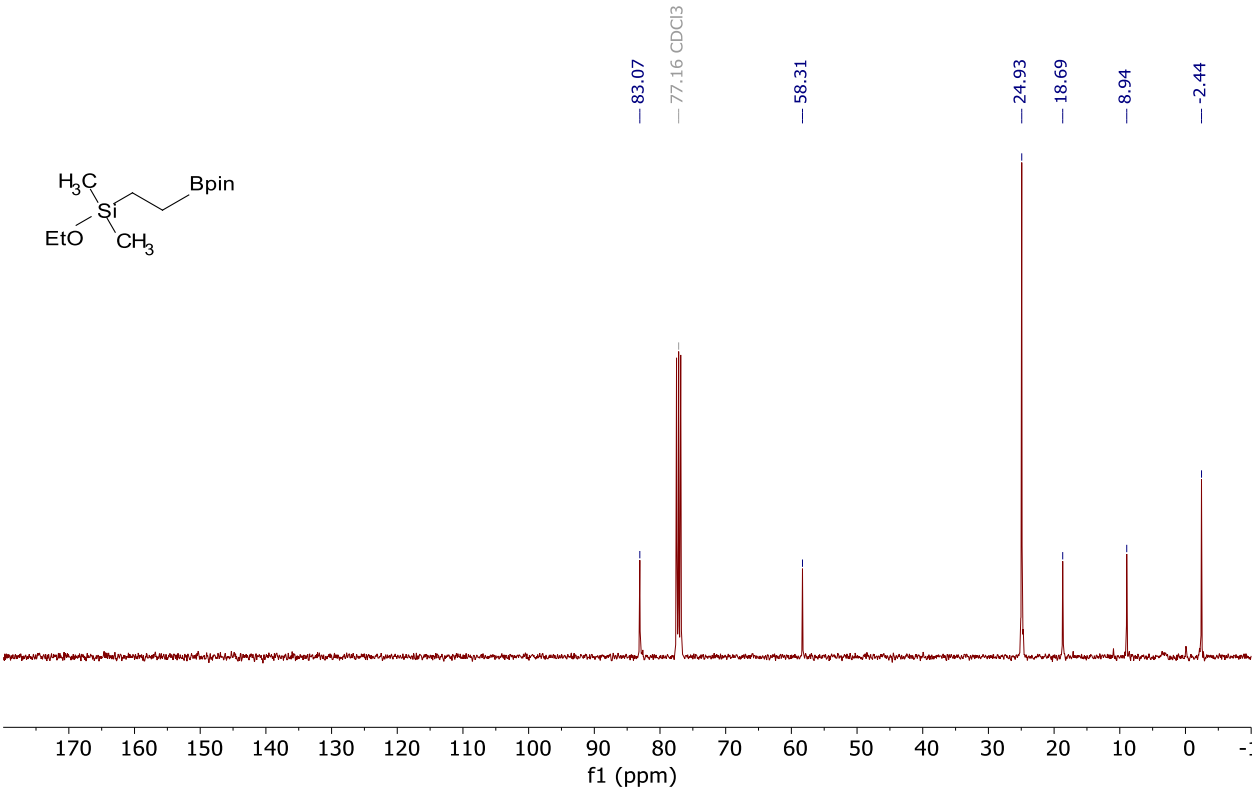


**Figure S30:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2f**

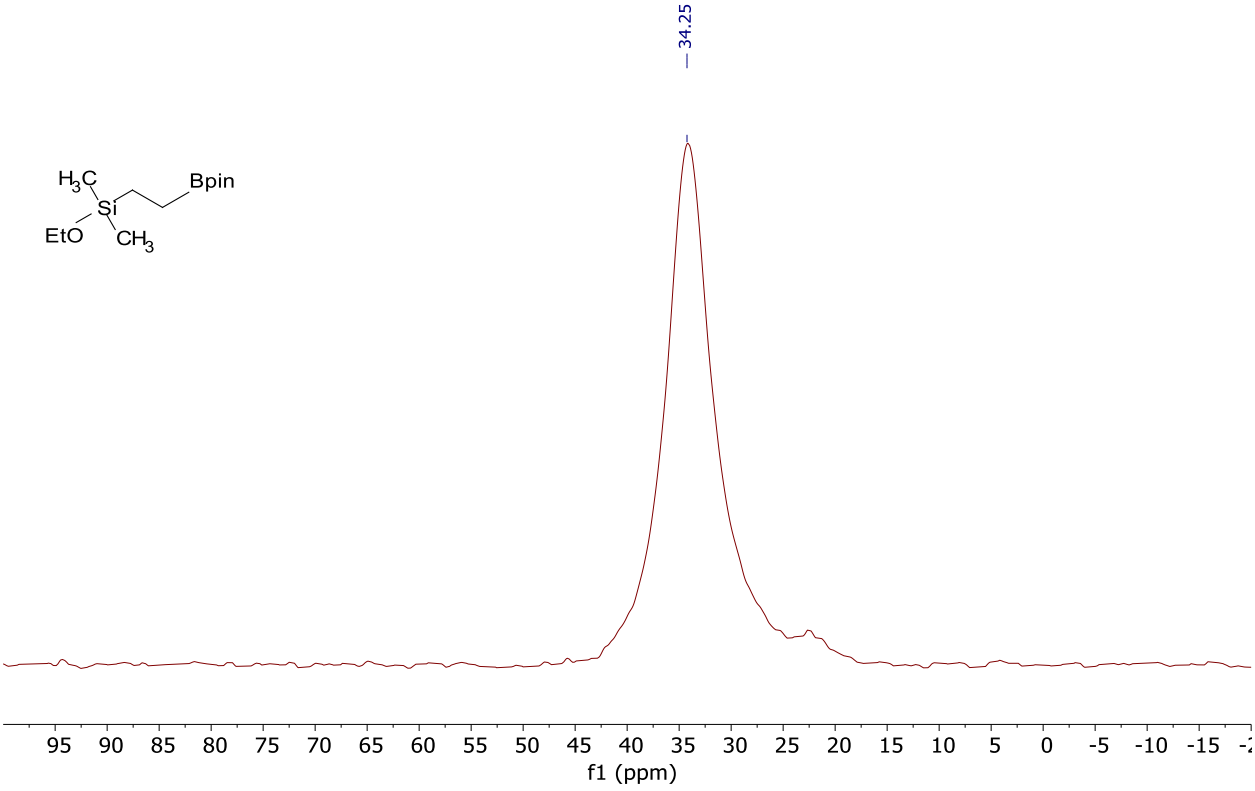


**Figure S31:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2f**

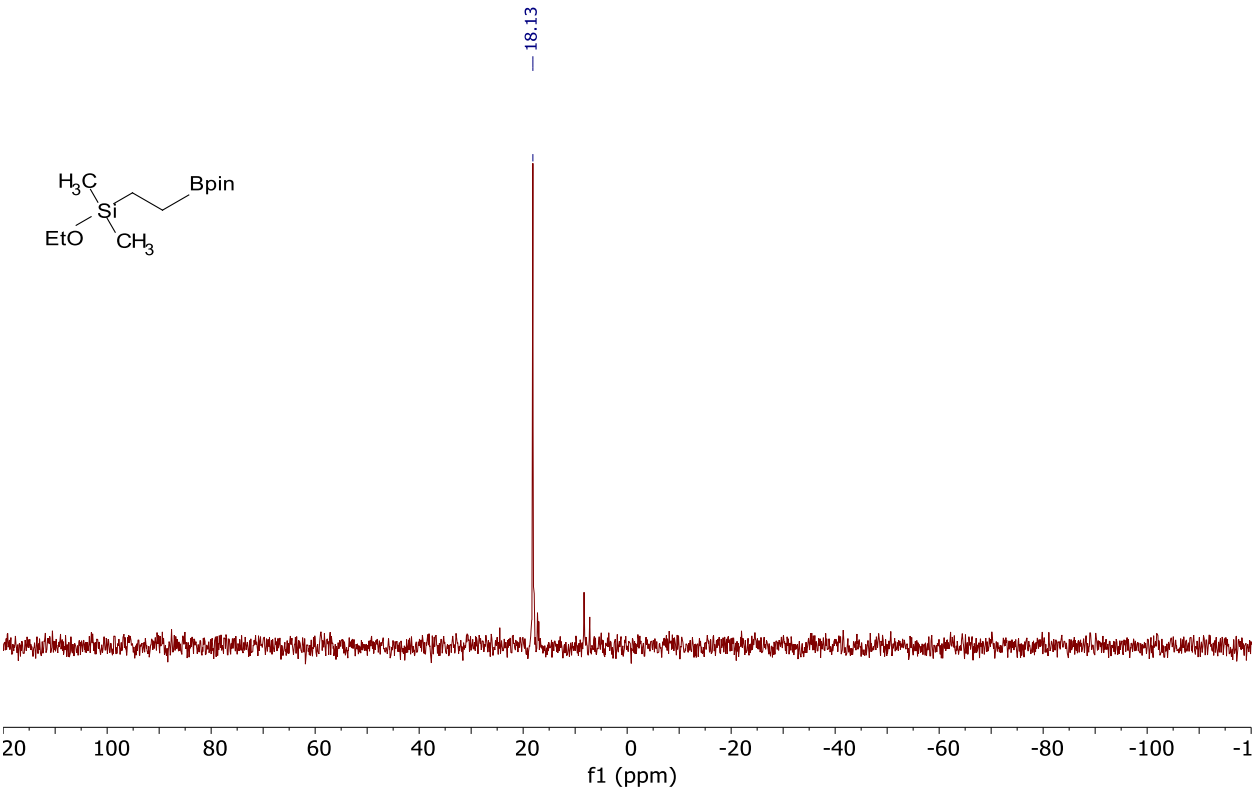


**Figure S32:** $^{29}Si$ NMR spectrum ($CDCl_3$) of **2f**

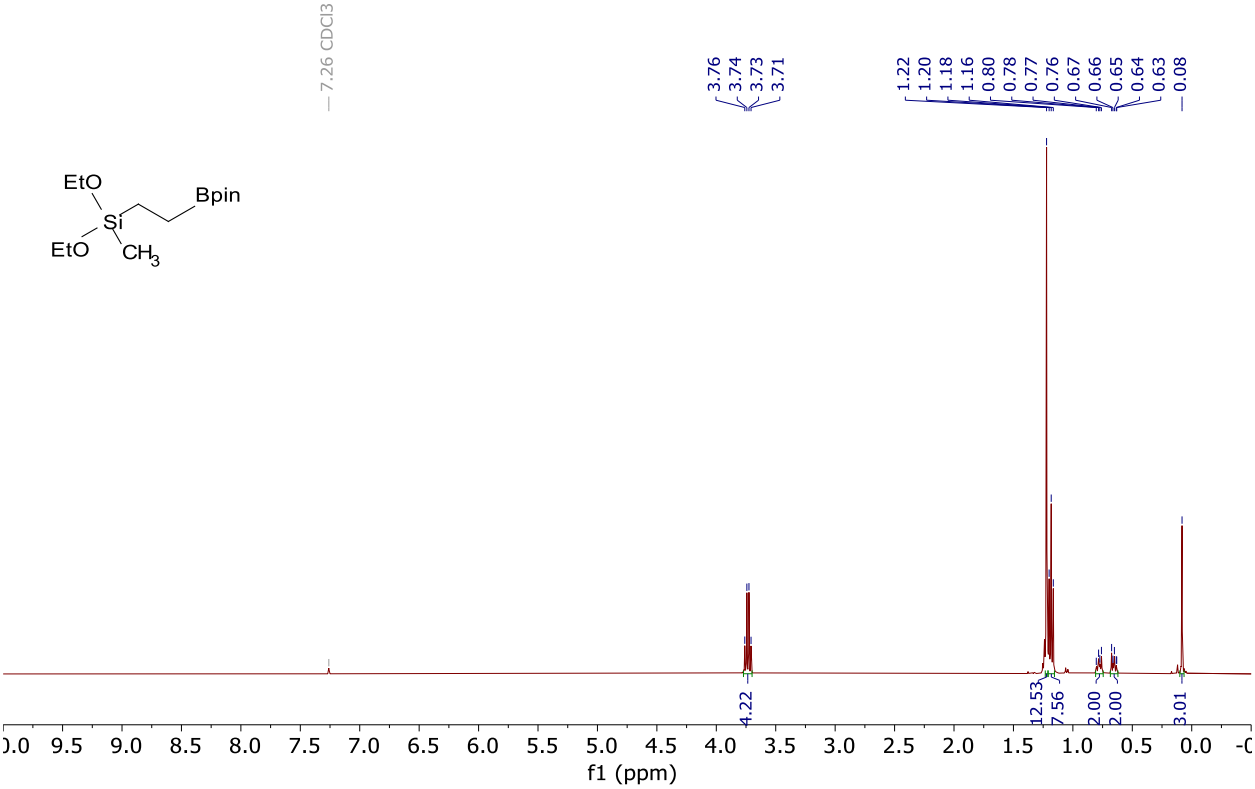


**Figure S33:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2g**

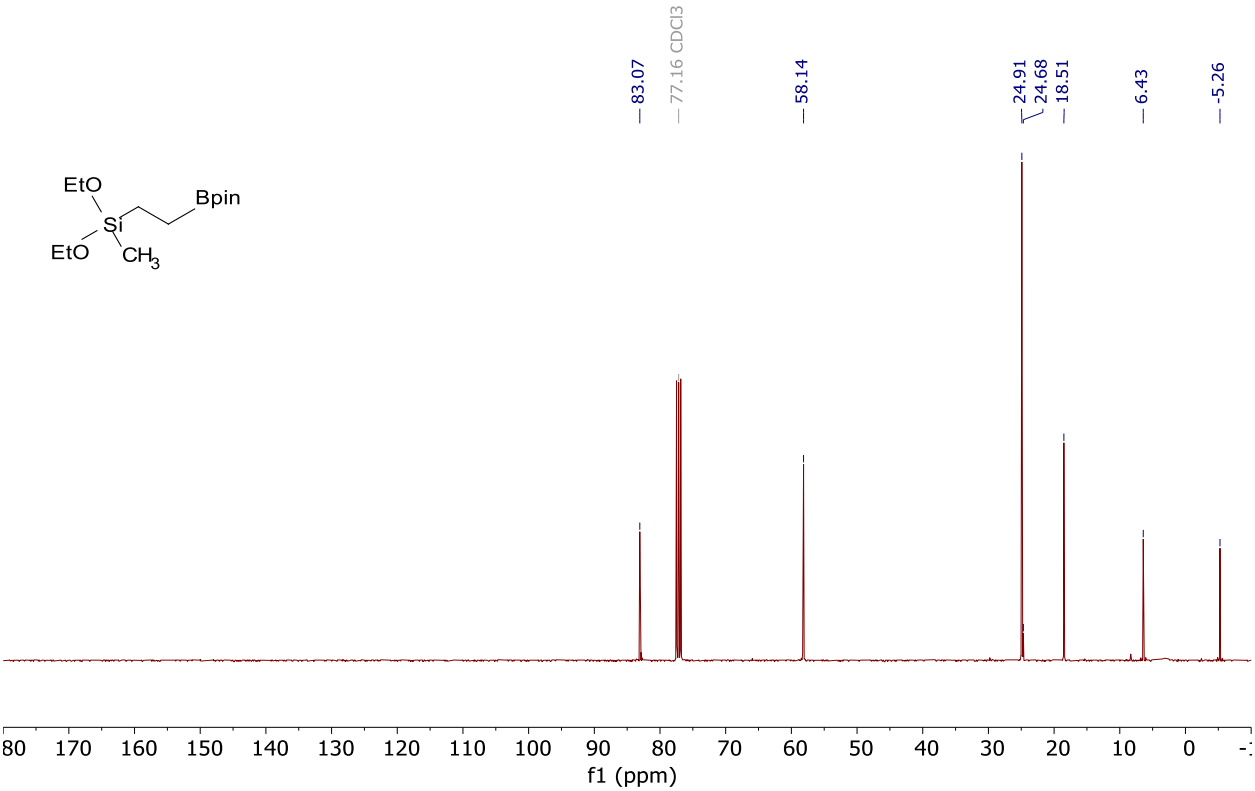


**Figure S34:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2g**

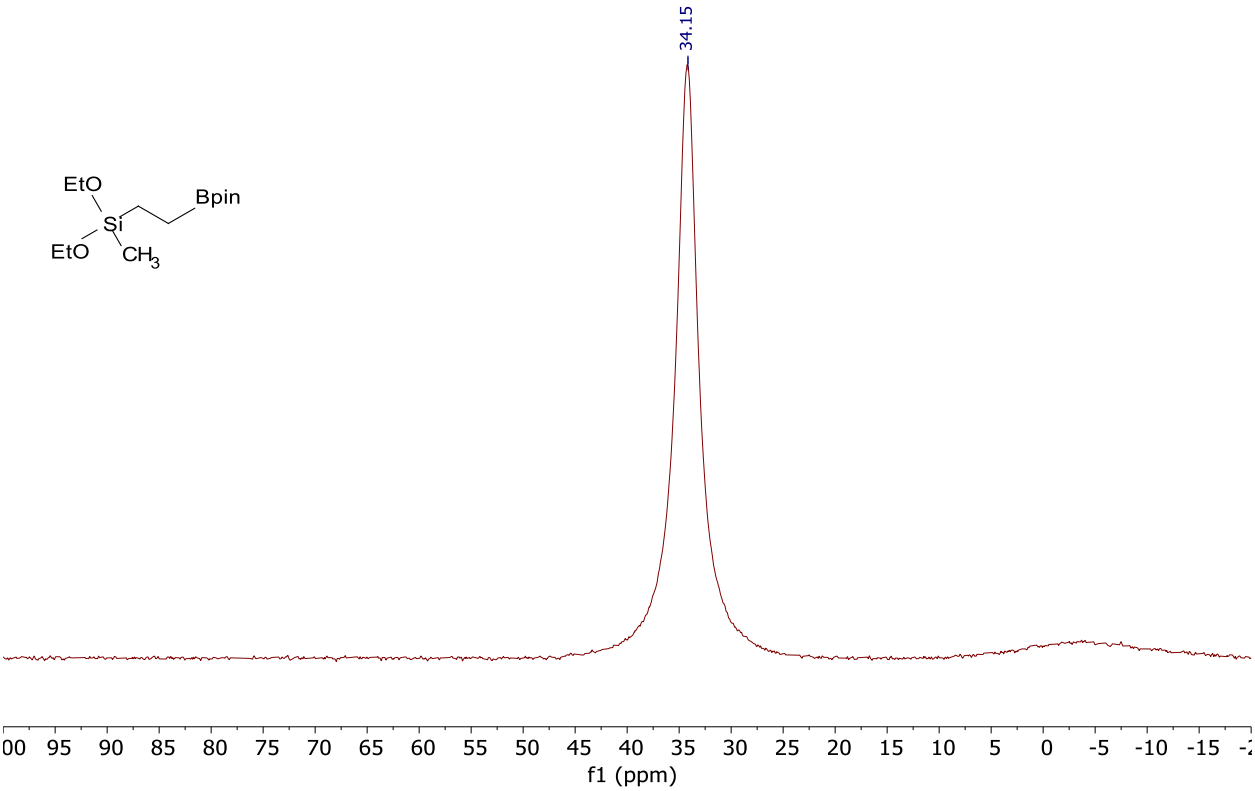


**Figure S35:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2g**

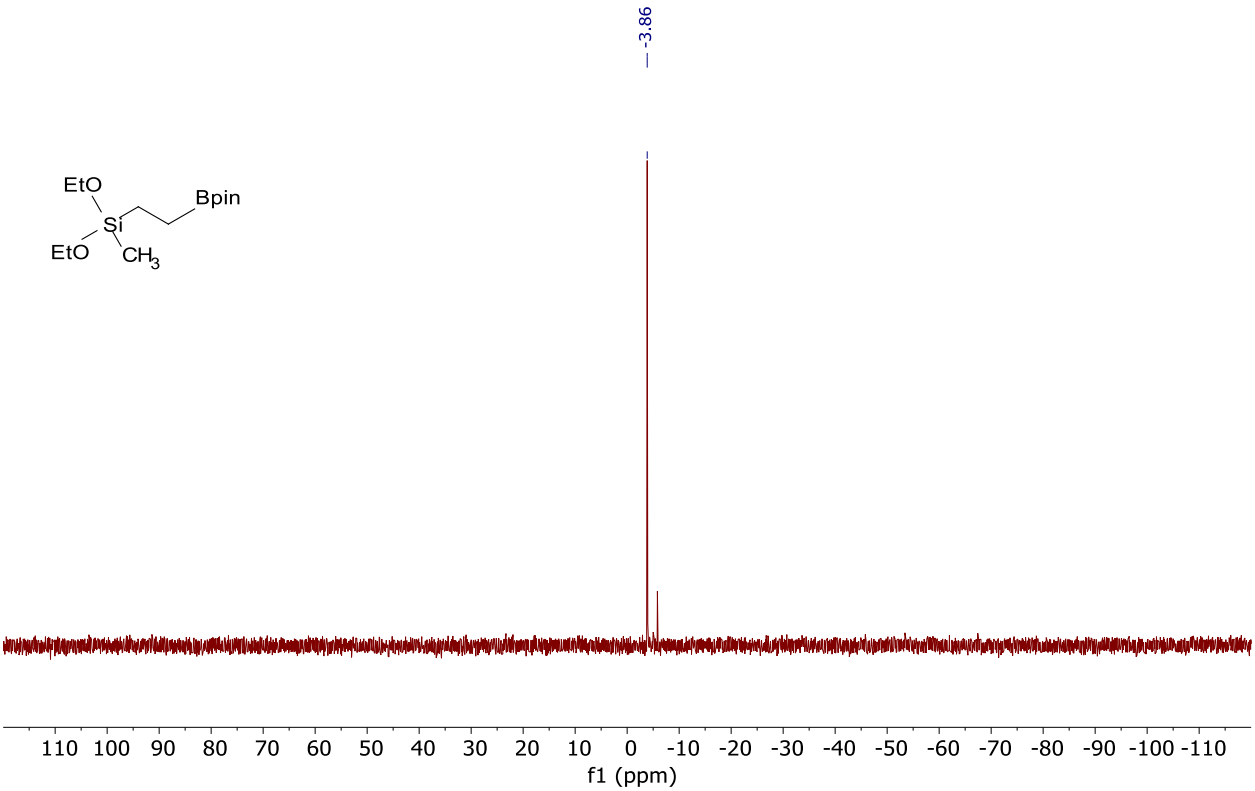


**Figure S36:** $^{29}Si$ NMR spectrum ($CDCl_3$) of **2g**

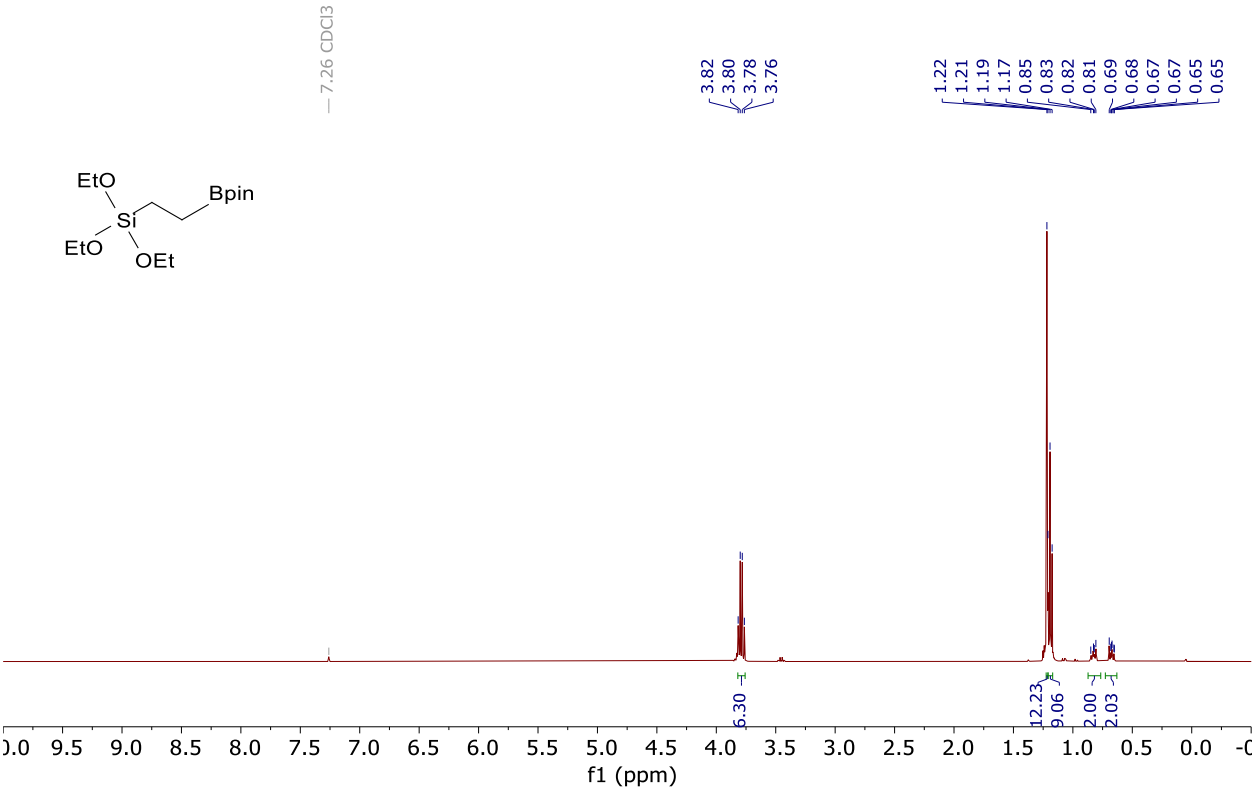


**Figure S37:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2h**

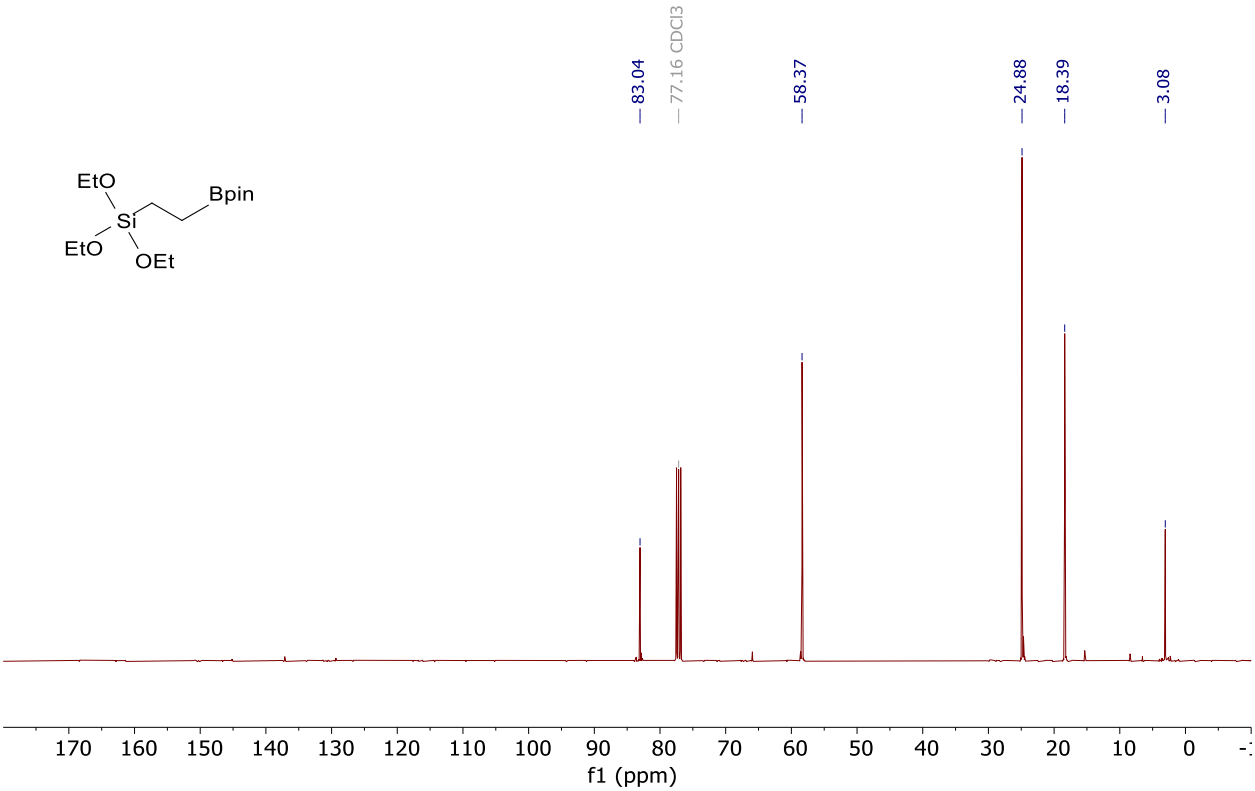


**Figure S38:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2h**

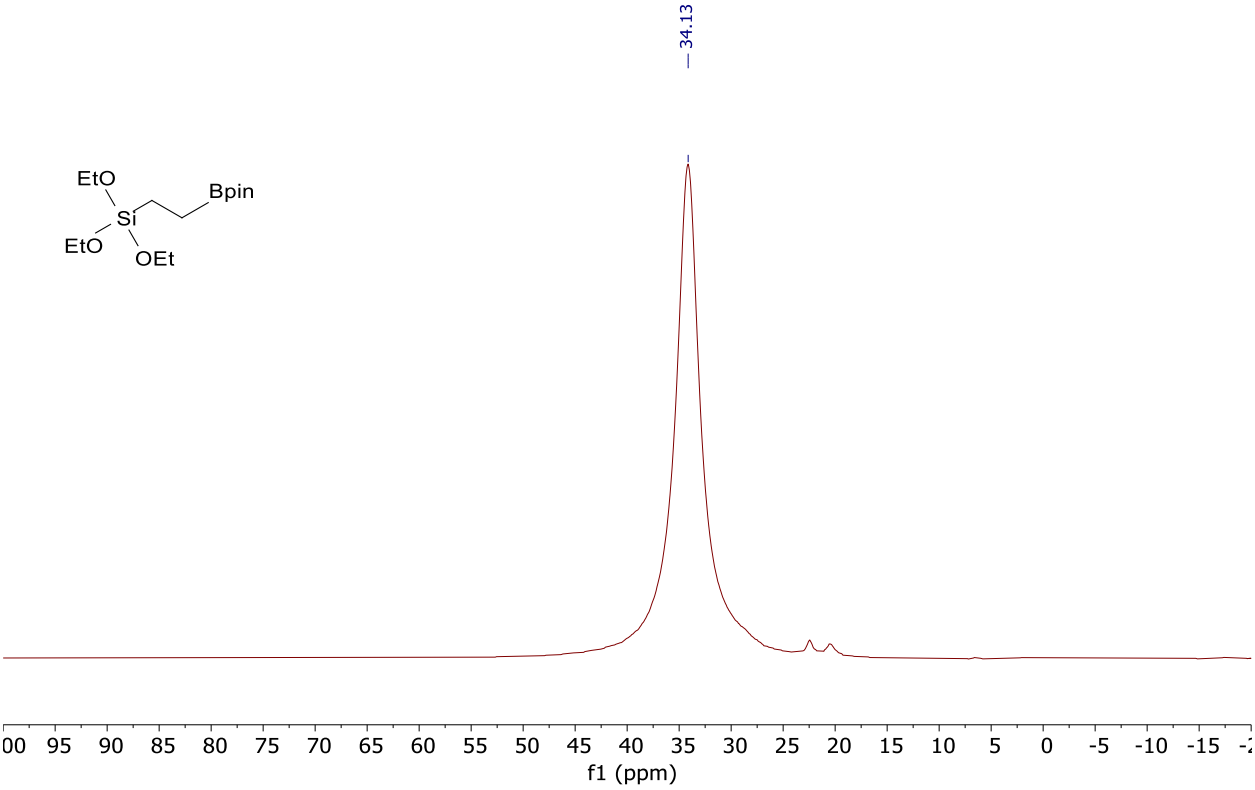


**Figure S39:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2h**

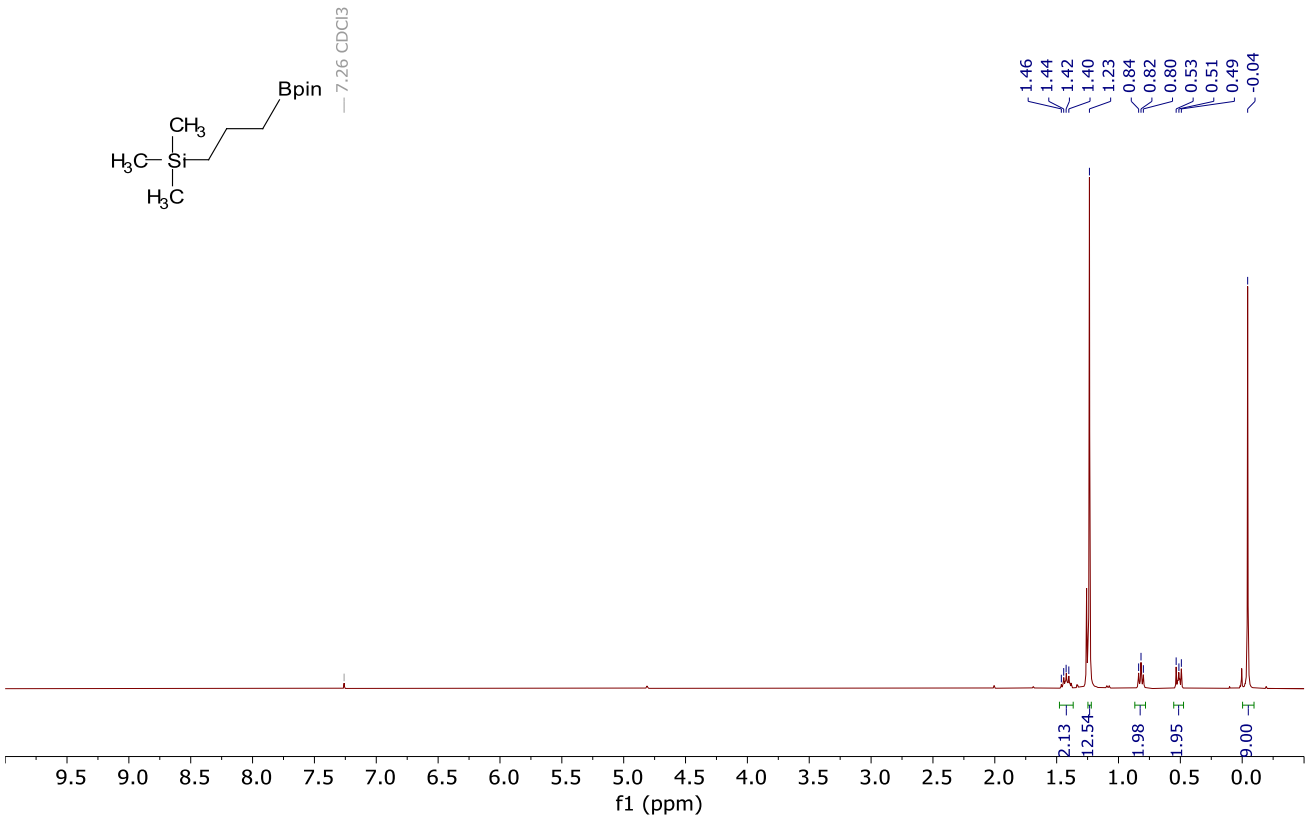


**Figure S40:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2i**

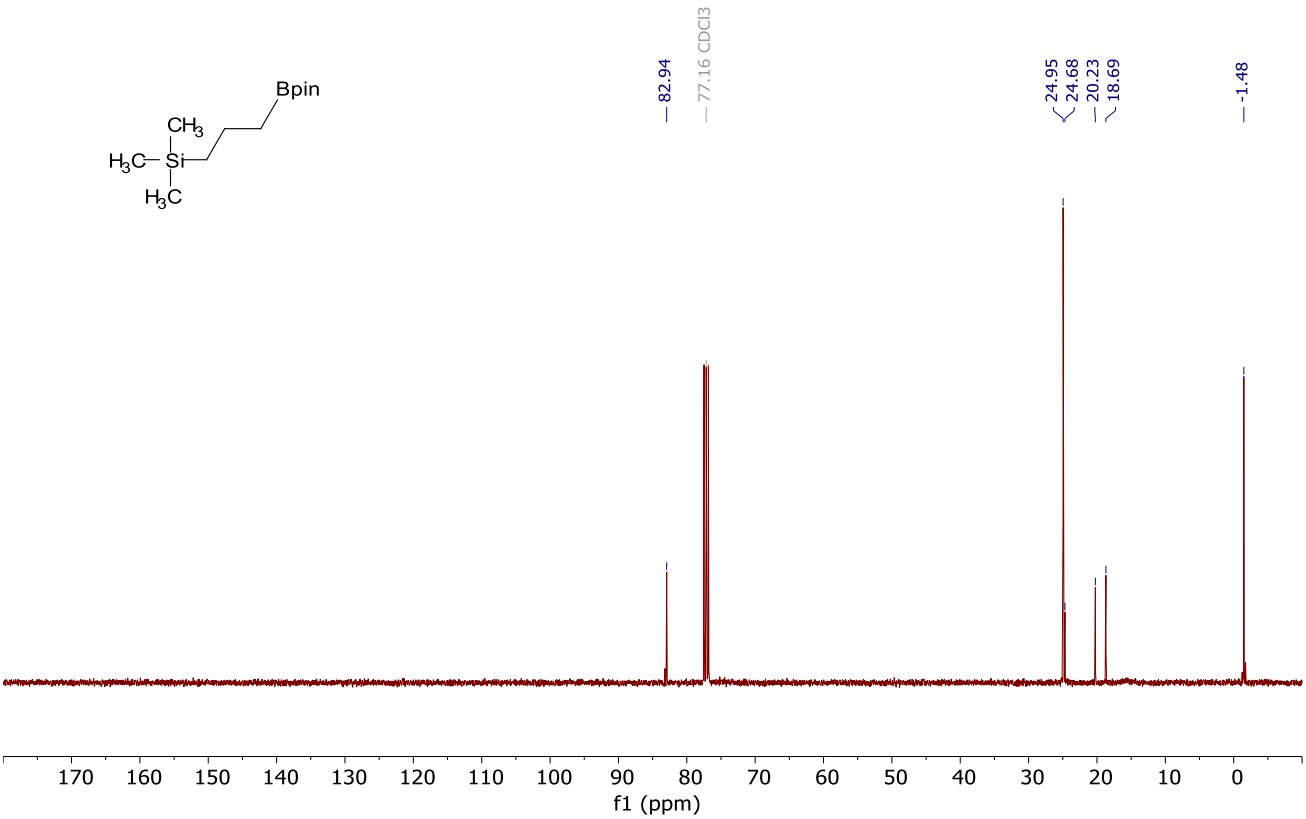


**Figure S41:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2i**

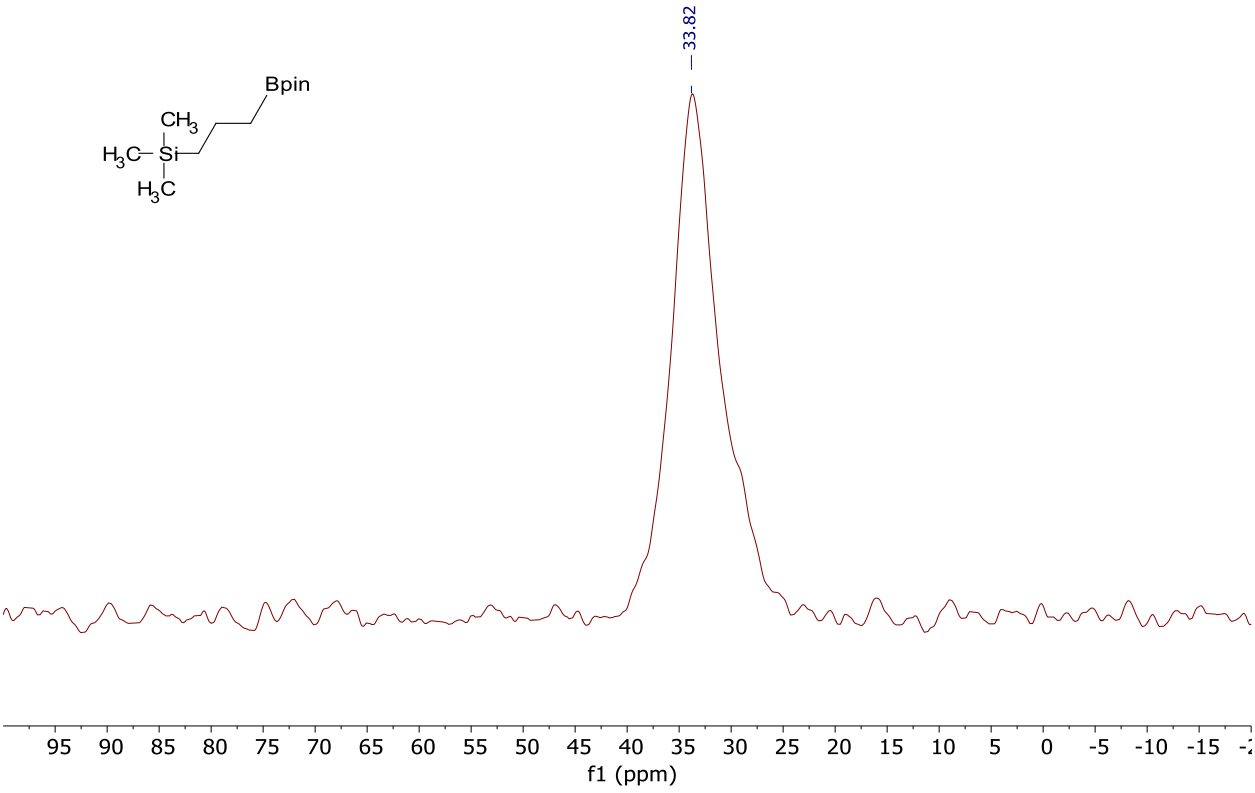


**Figure S42:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2i**

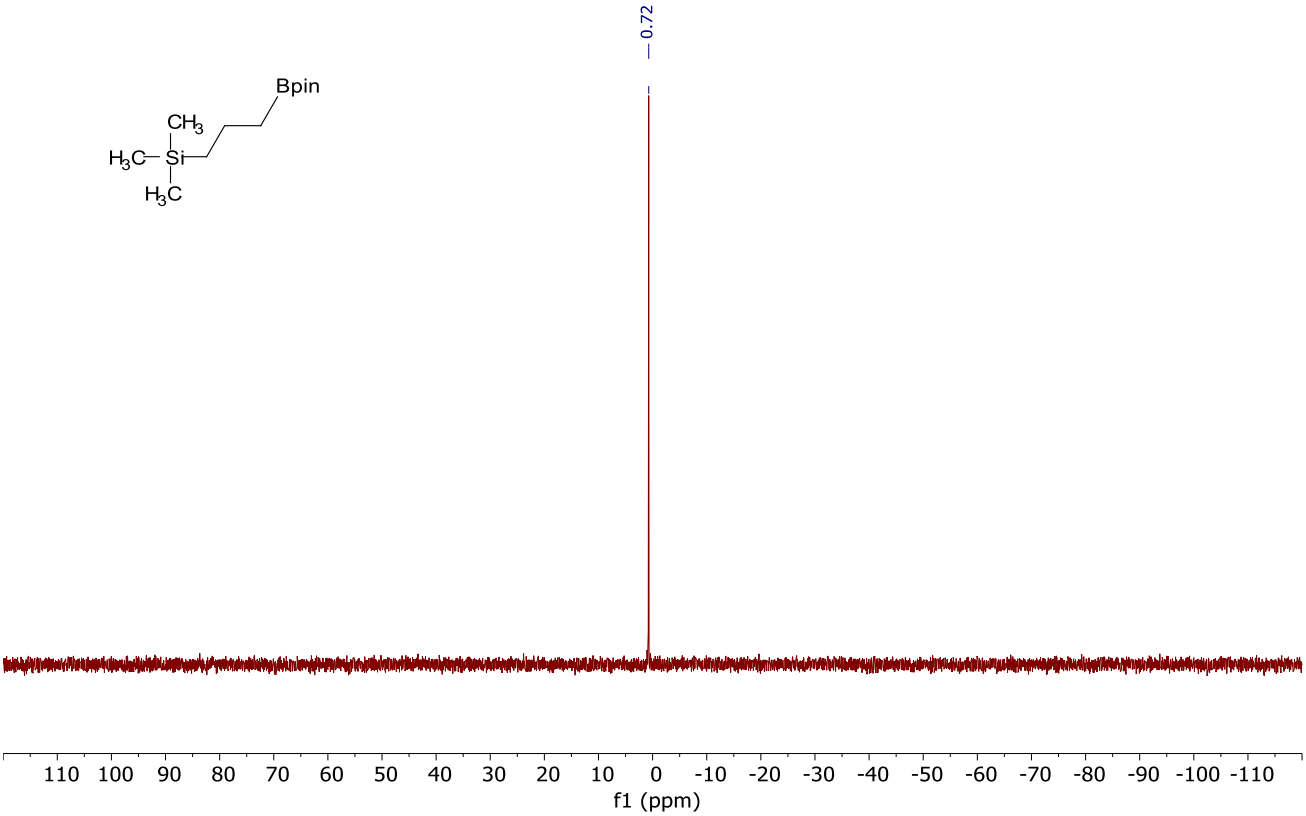


**Figure S43:** $^{29}Si$ NMR spectrum ($CDCl_3$) of **2i**

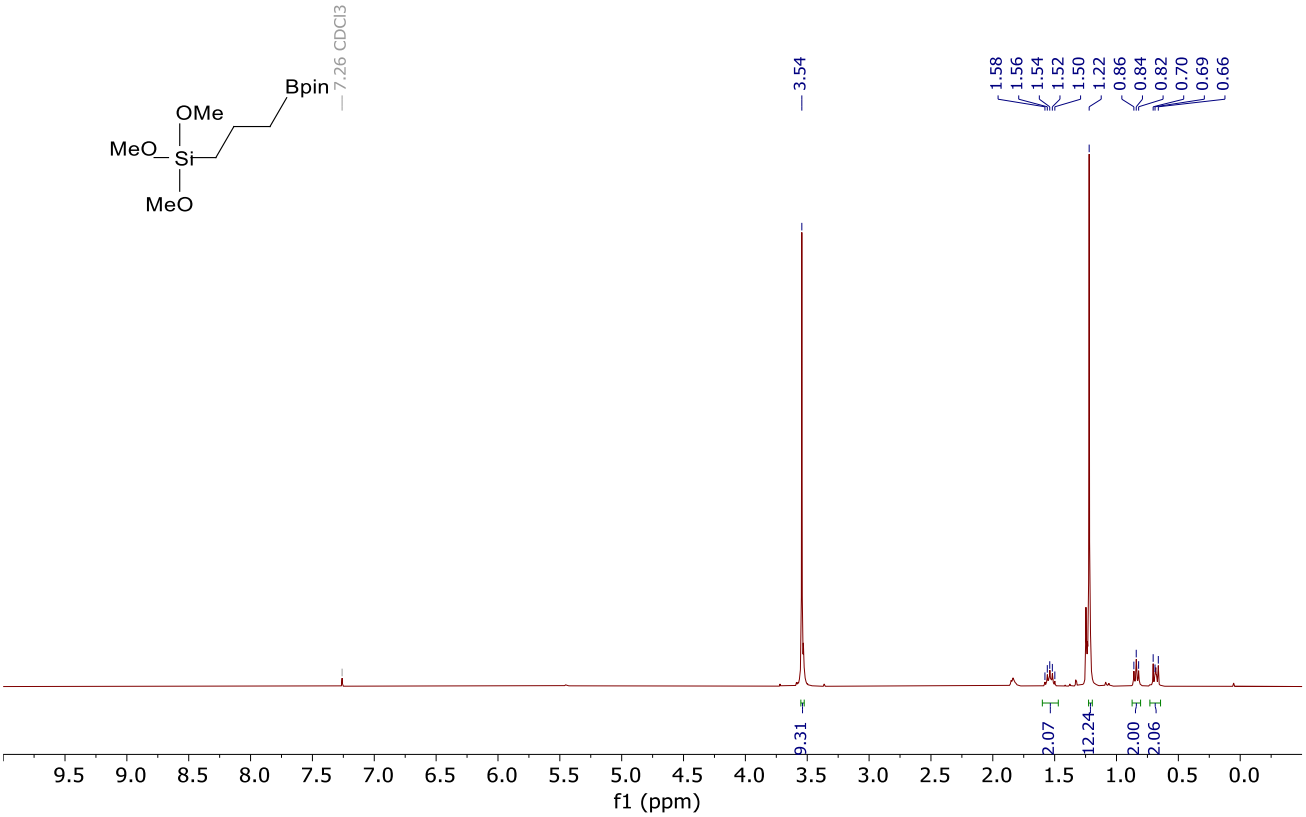


**Figure S44:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2j**

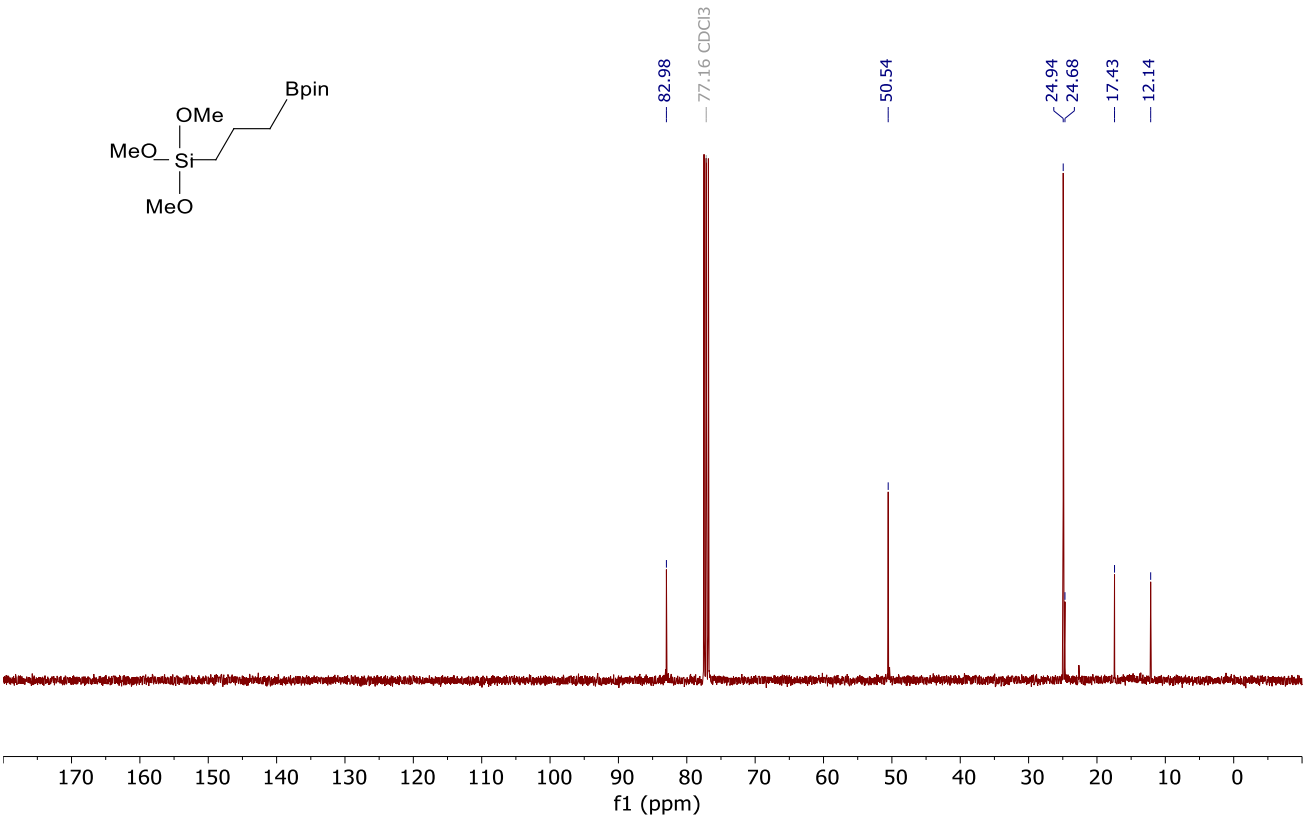


**Figure S45:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2j**

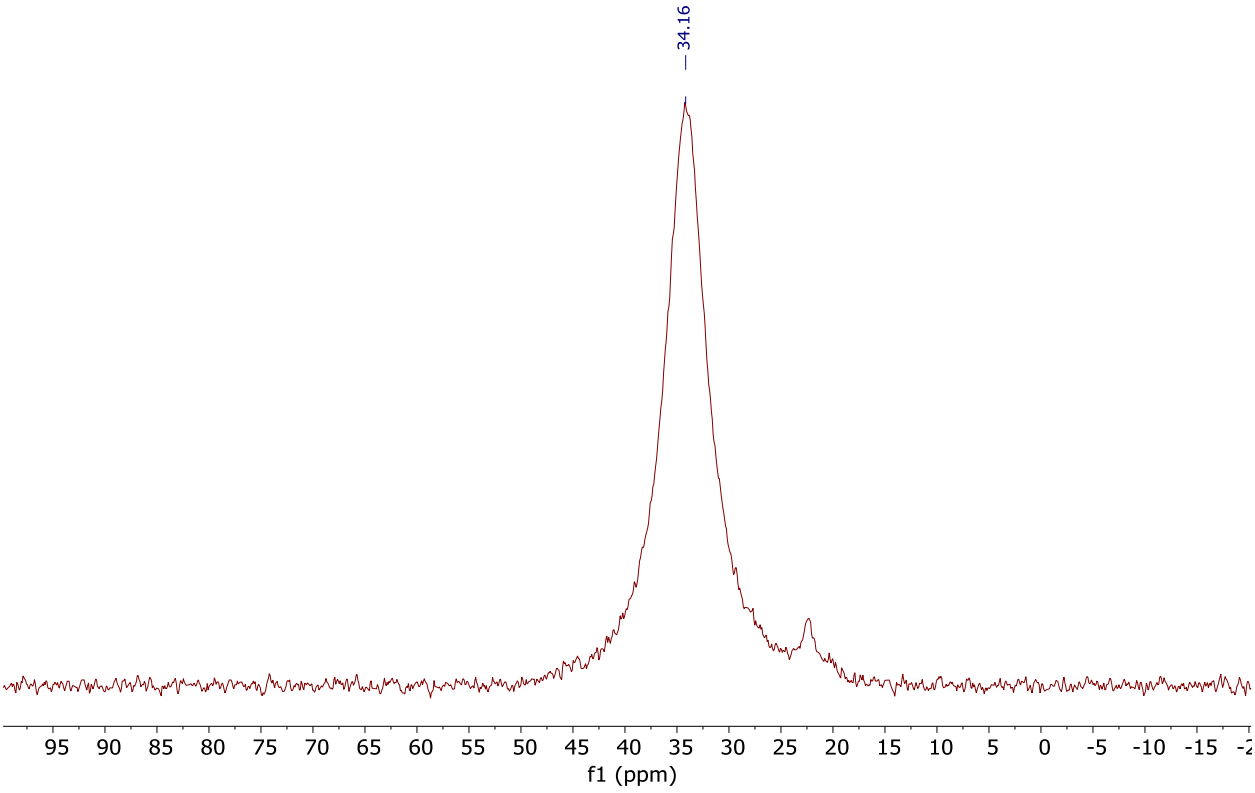


**Figure S46:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2j**

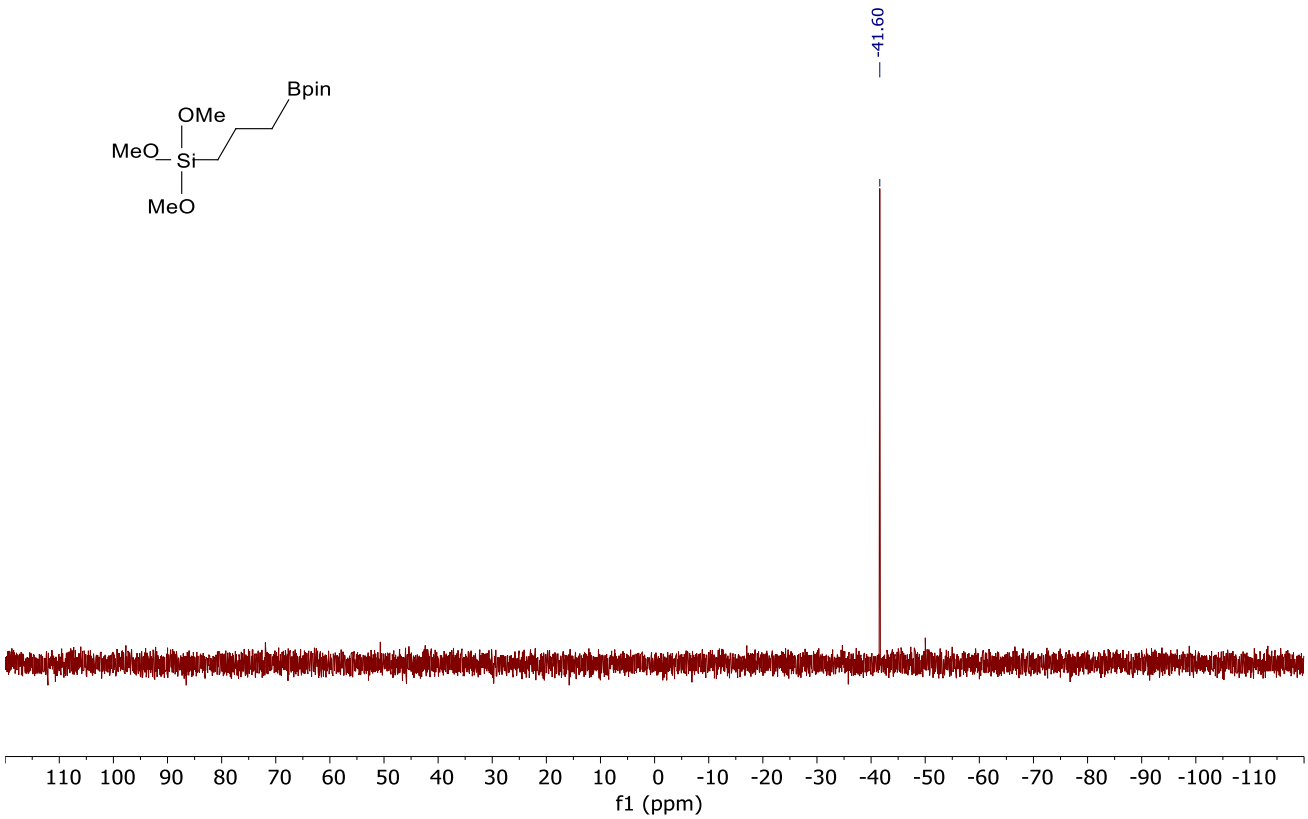


**Figure S47:** $^{29}Si$ NMR spectrum ($CDCl_3$) of **2j**

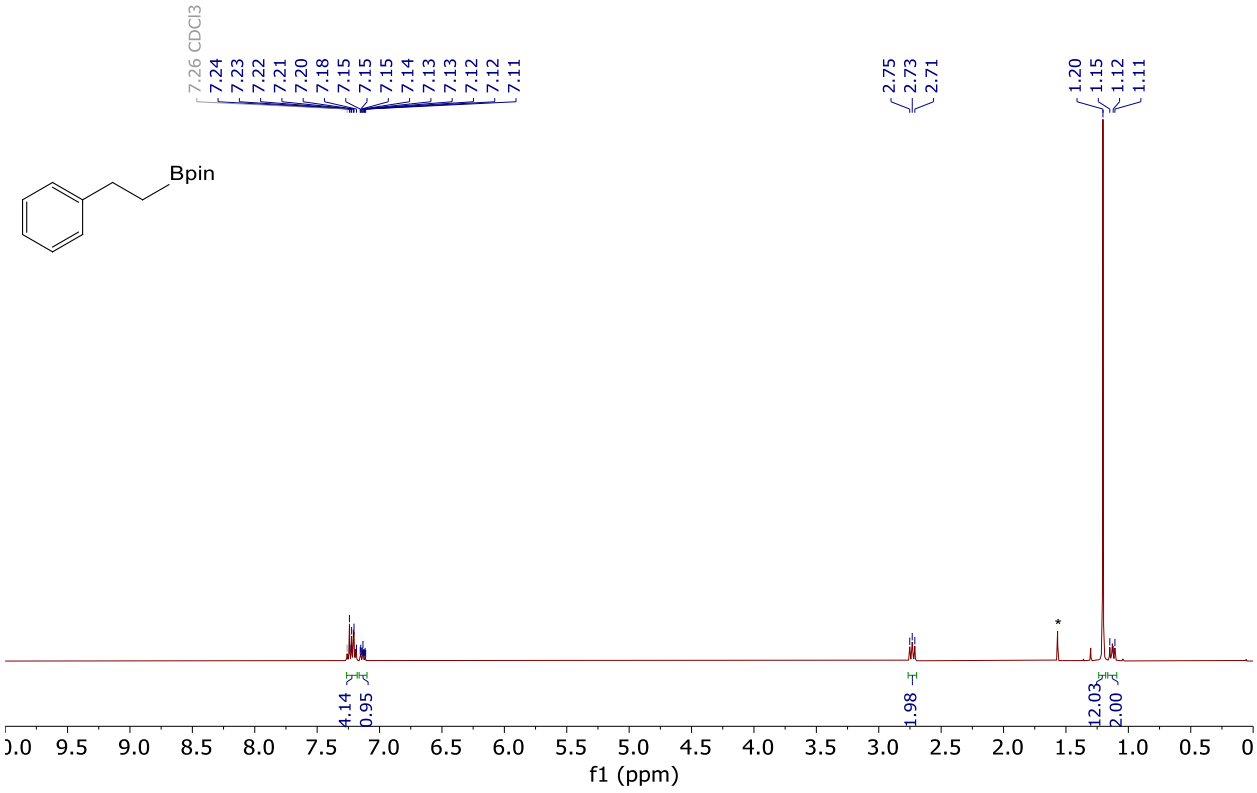


**Figure S48:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2k**

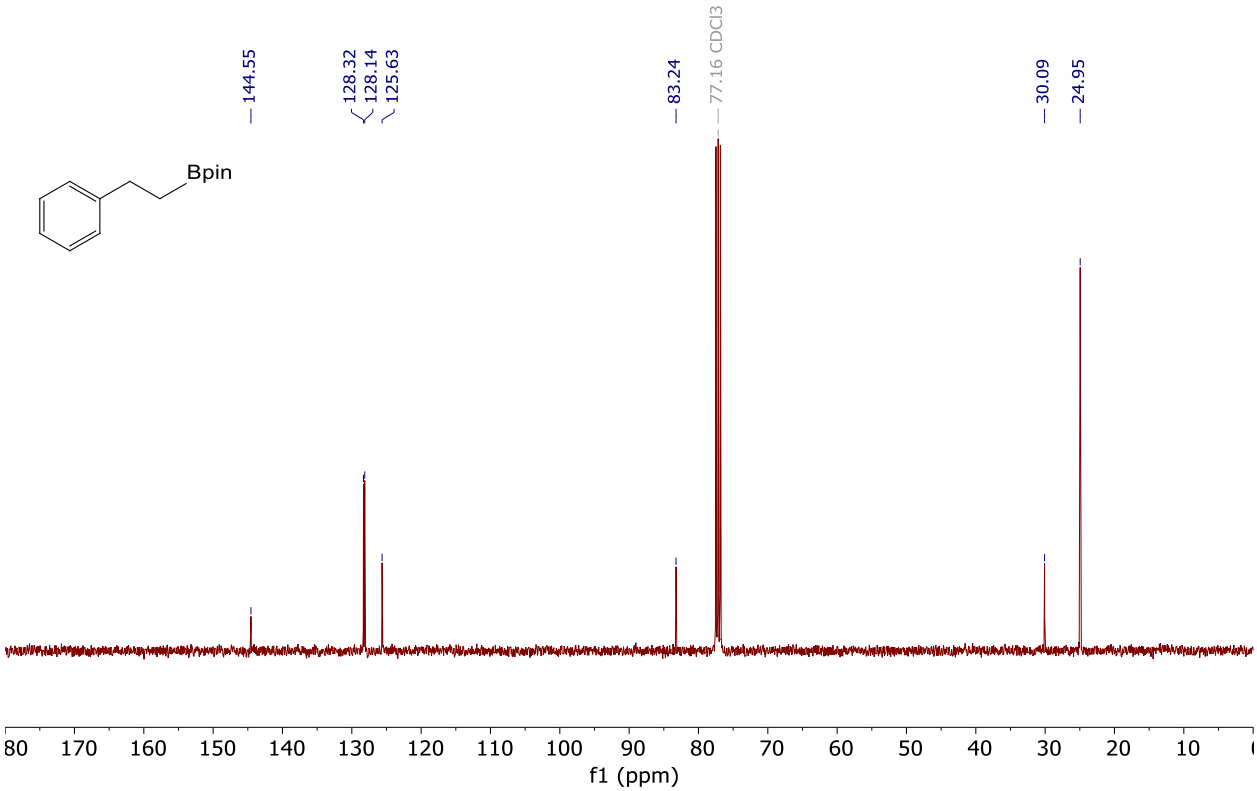


**Figure S49:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2k**

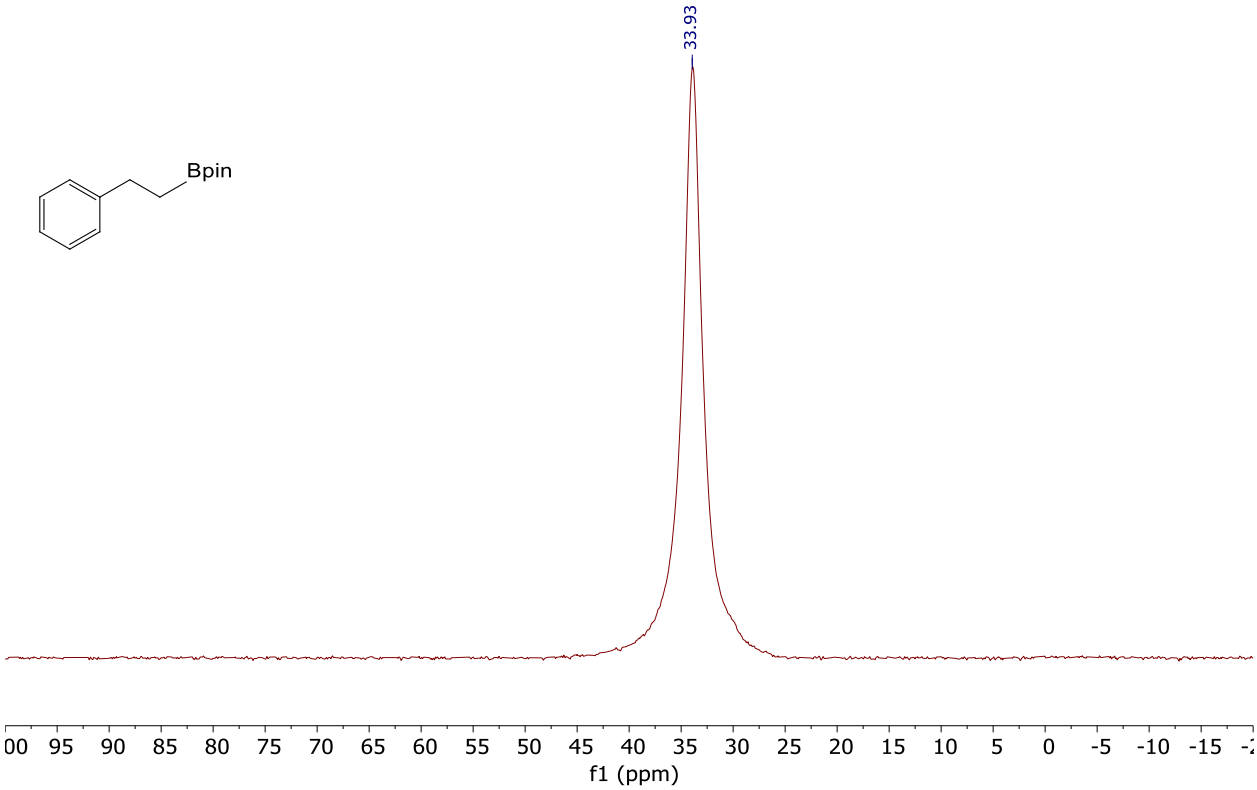


**Figure S50:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2k**

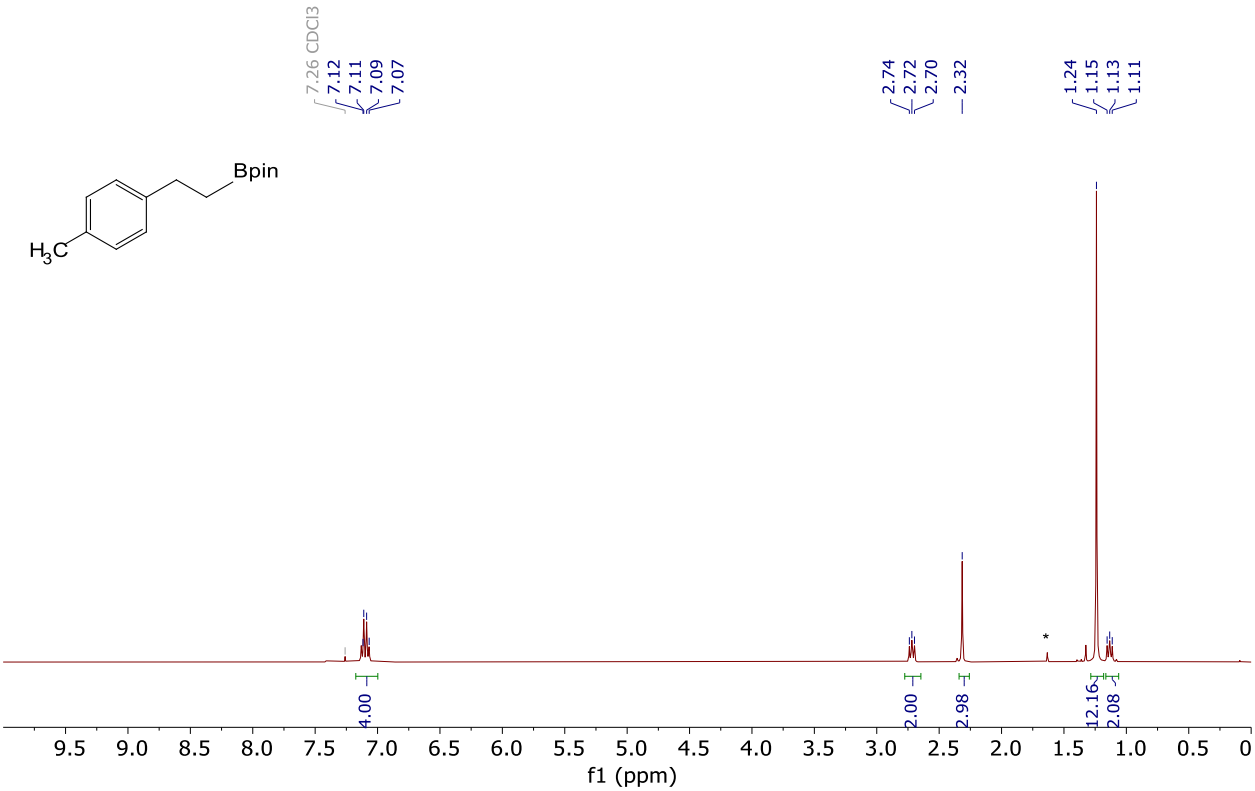


**Figure S51:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2l**

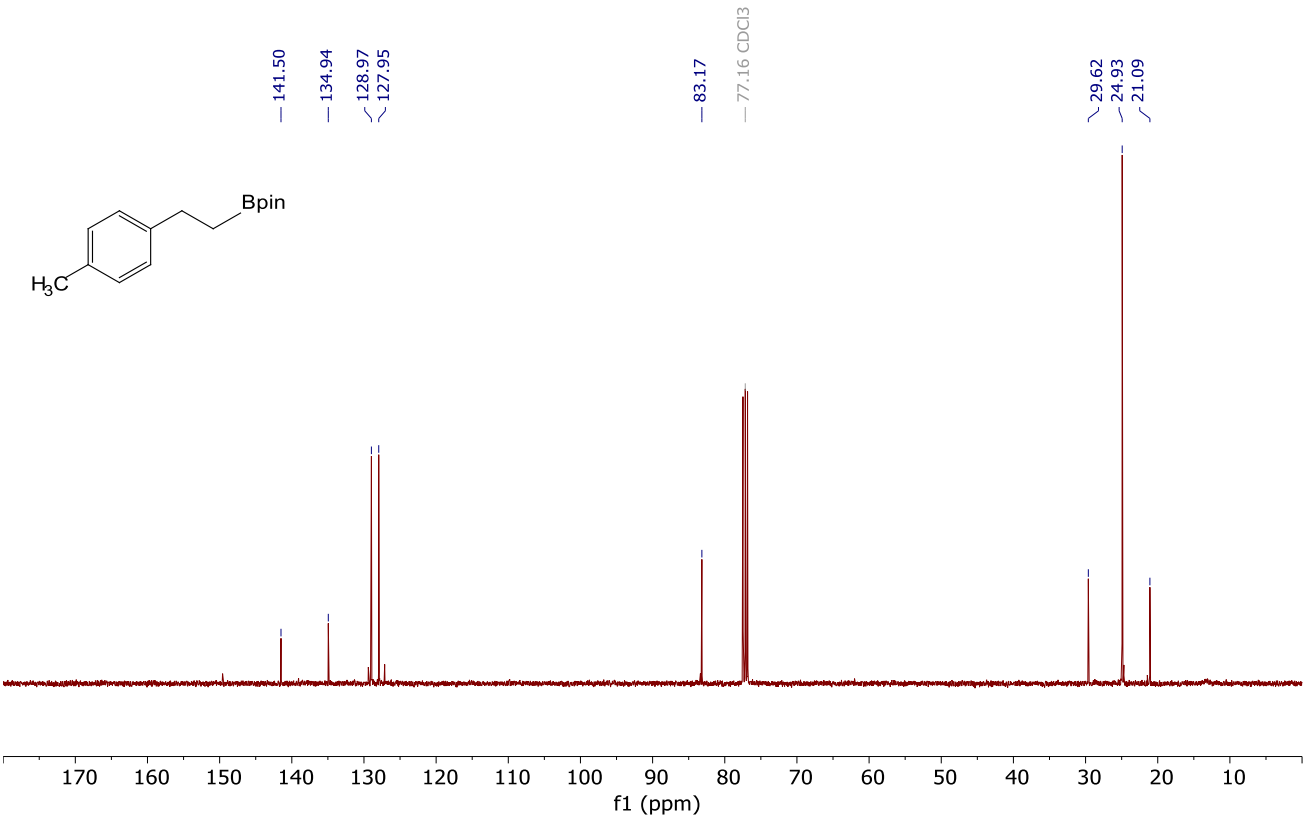


**Figure S52:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2l**

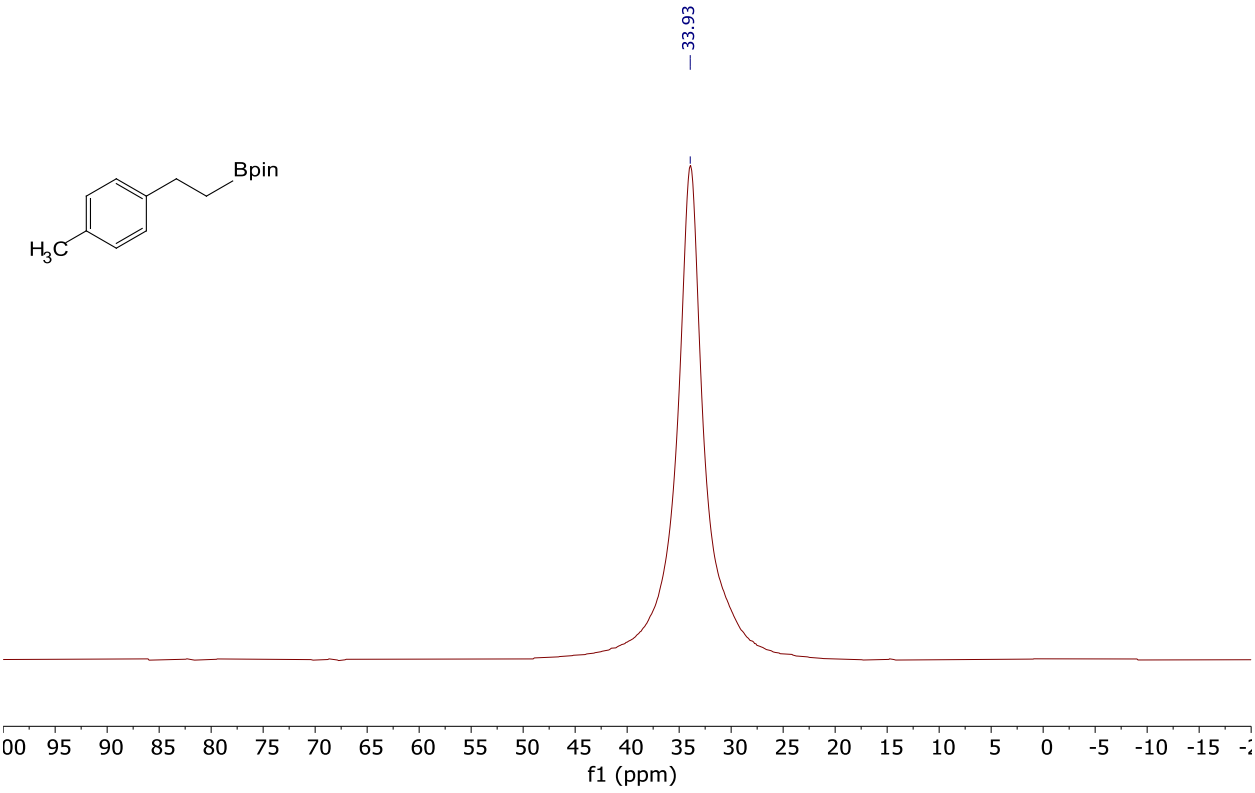


**Figure S53:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2l**

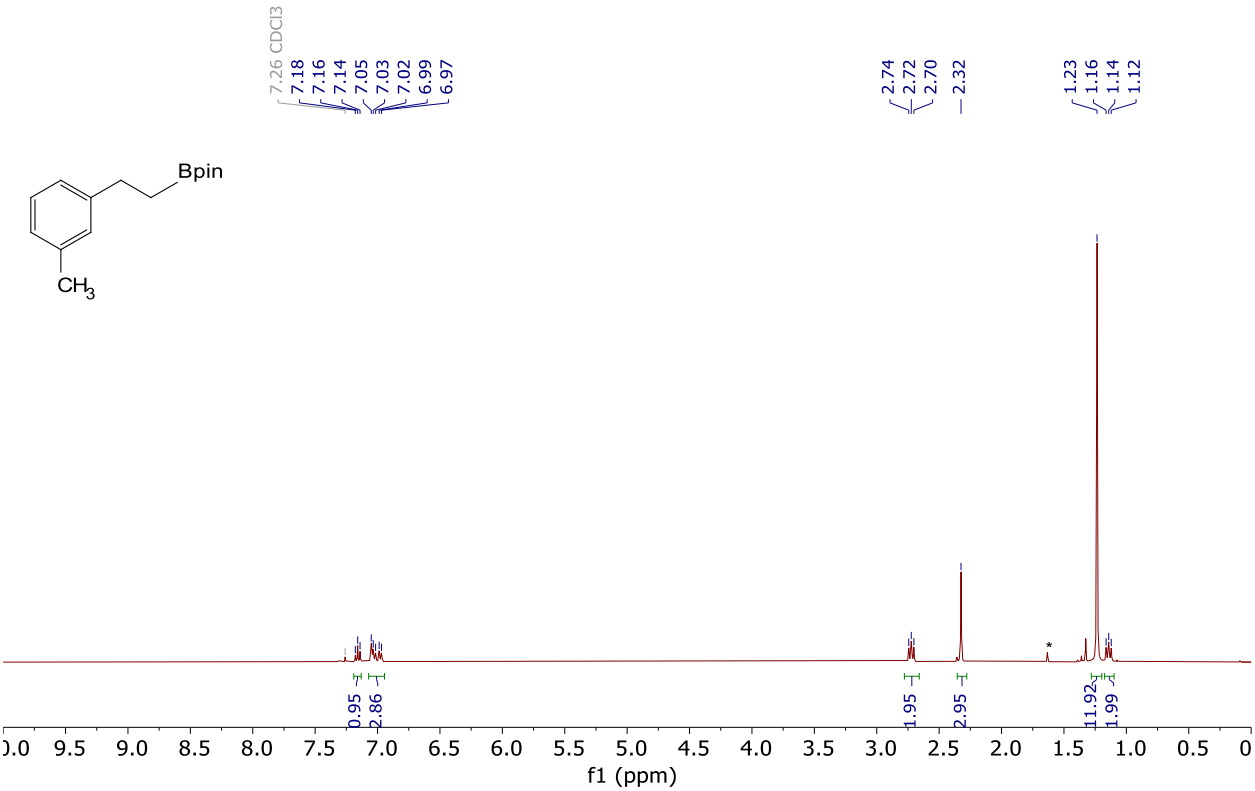


**Figure S54:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2l**

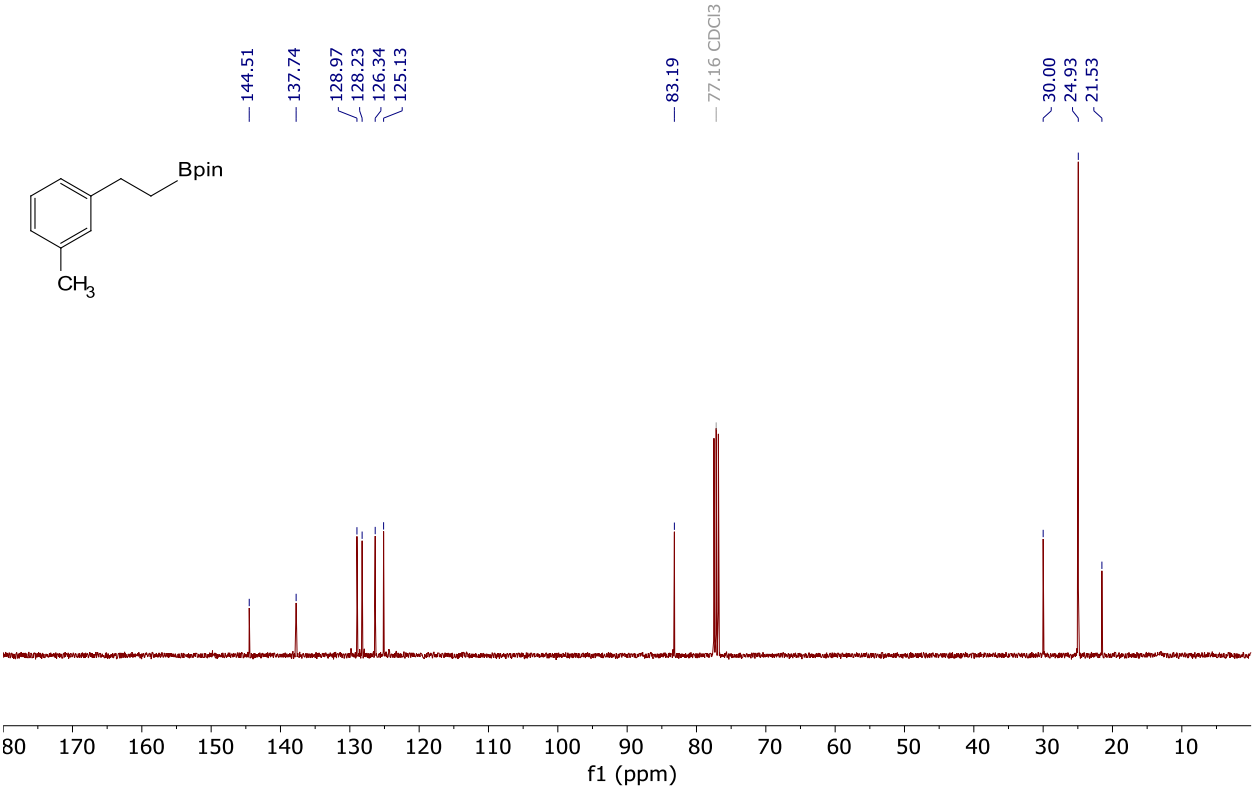


**Figure S55:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2m**

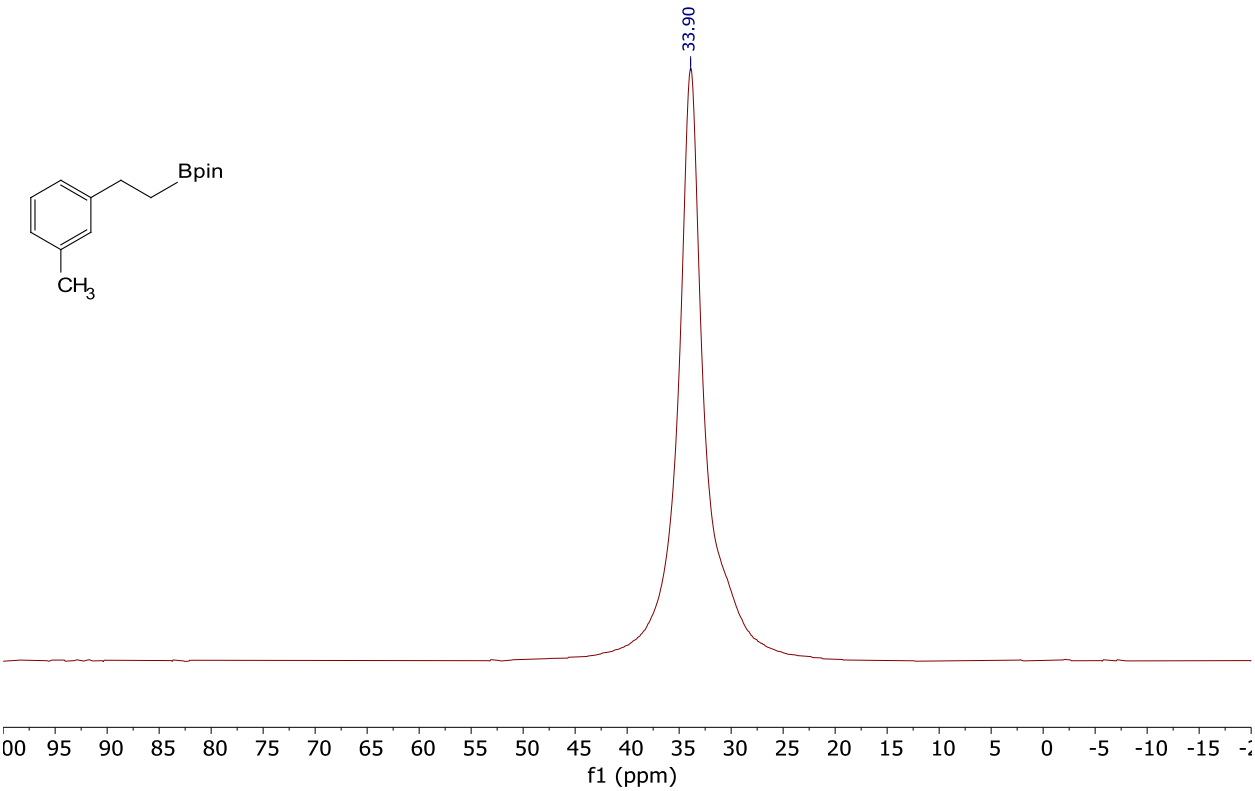


**Figure S56:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2m**

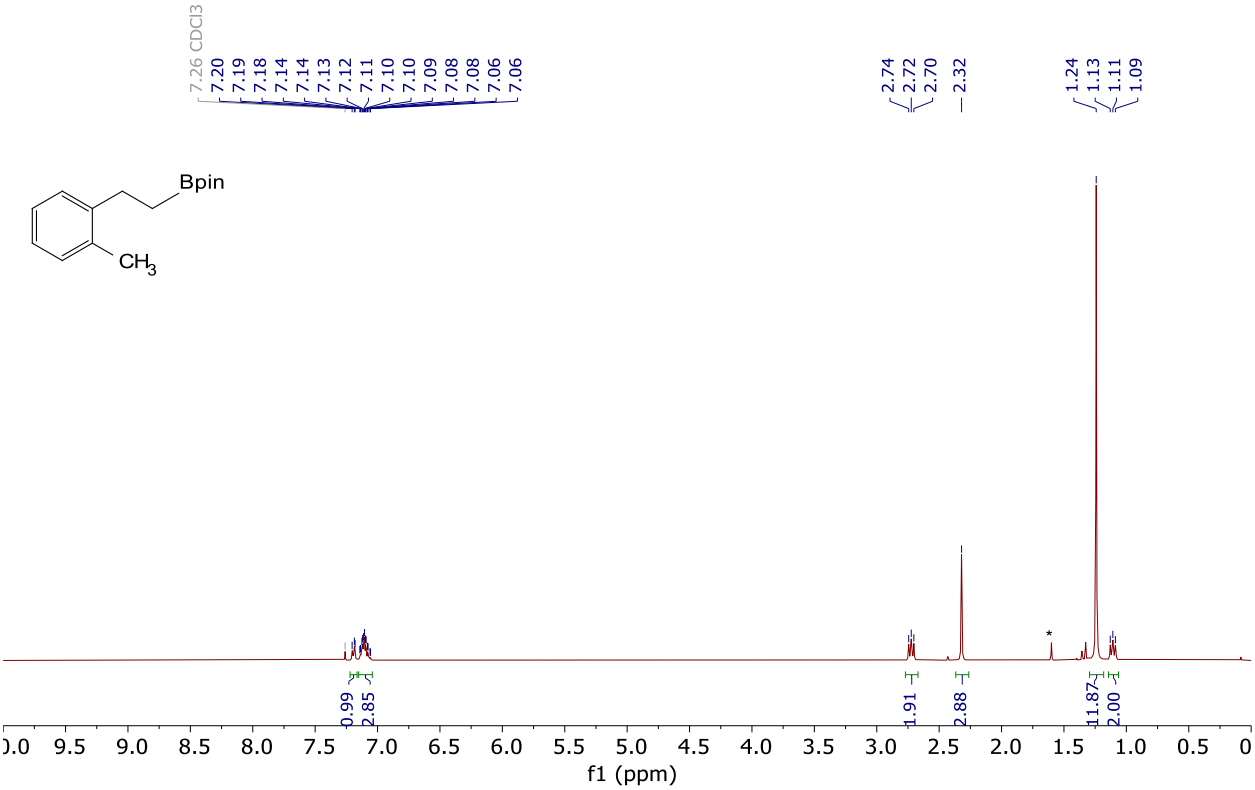


**Figure S57:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2n**

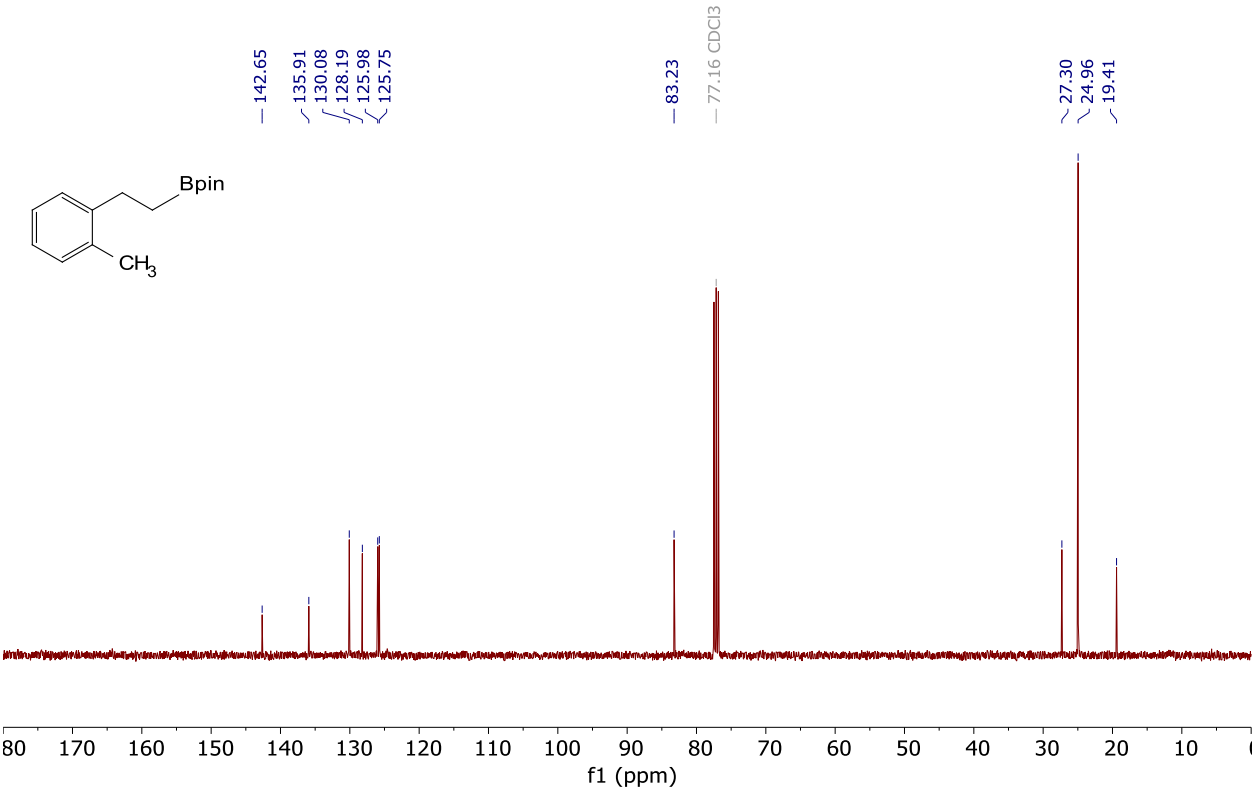


**Figure S58:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2n**

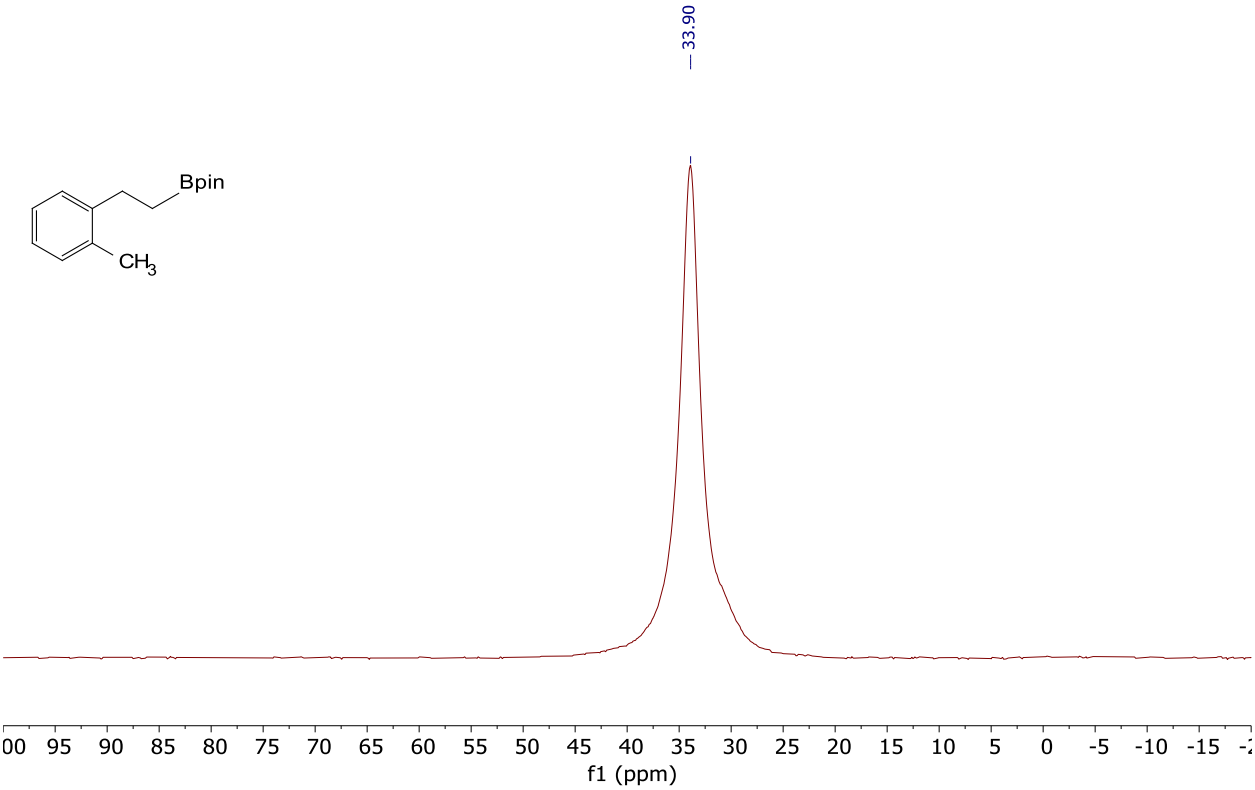


**Figure S59:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2n**

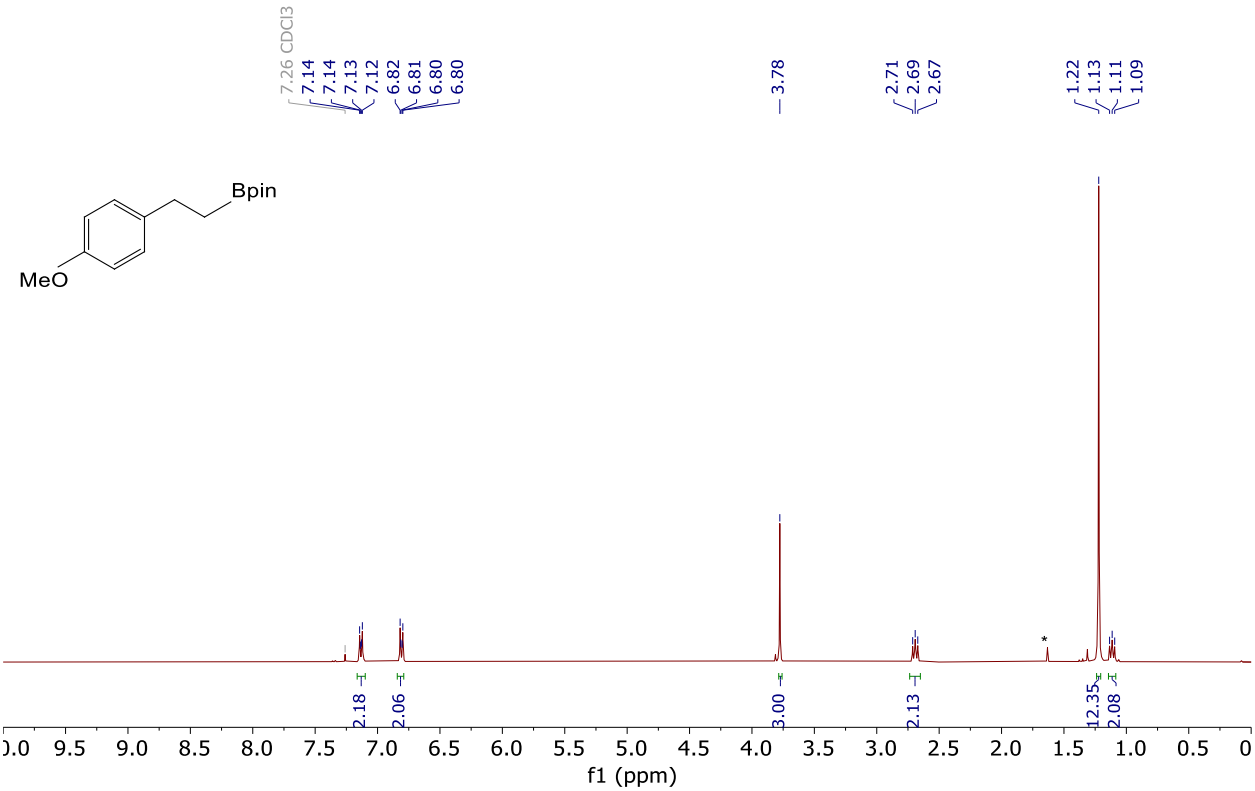


**Figure S60:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2o**

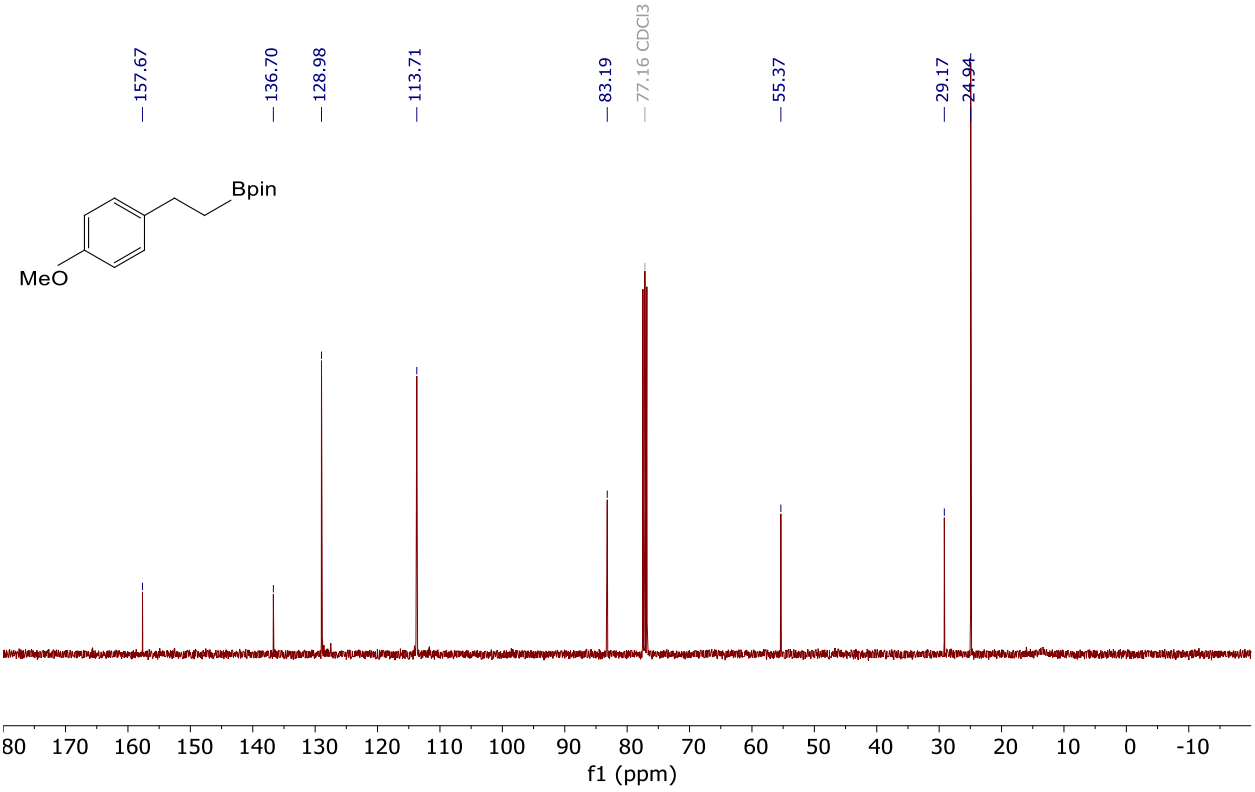


**Figure S61:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2o**

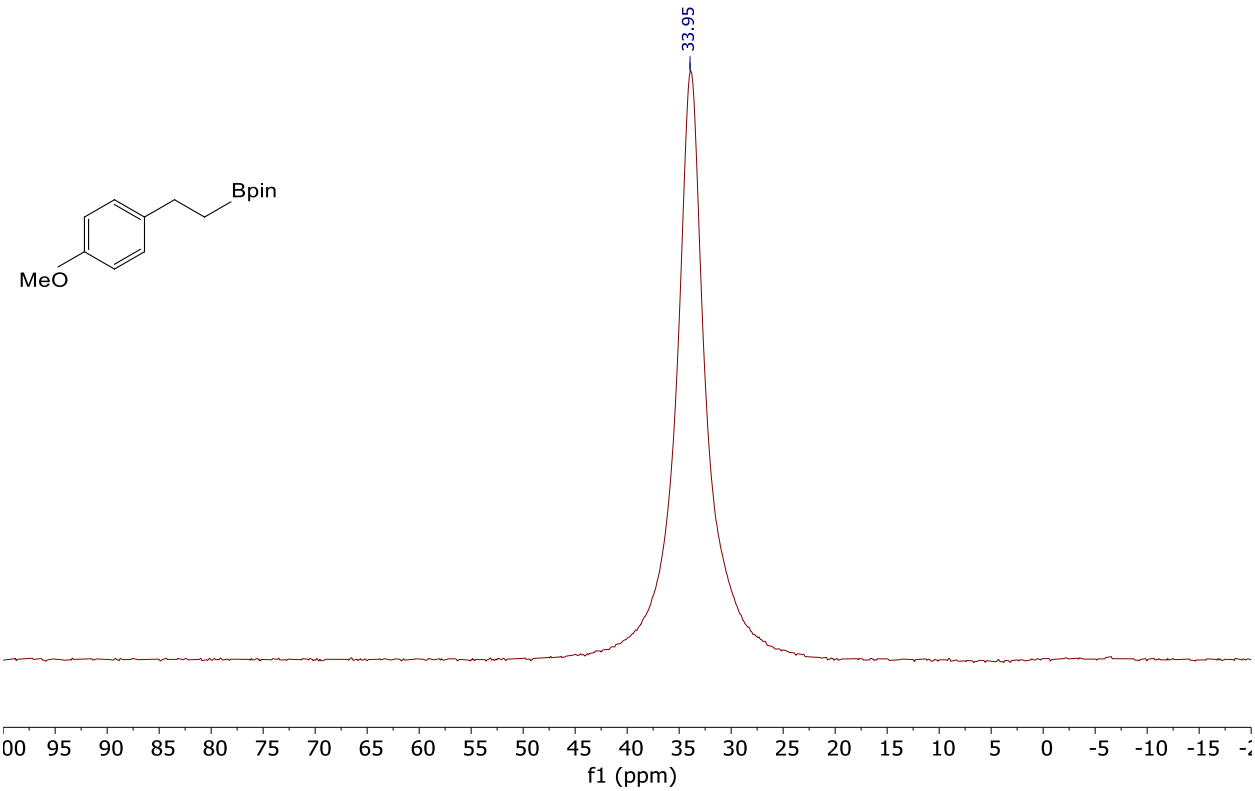


**Figure S62:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2o**

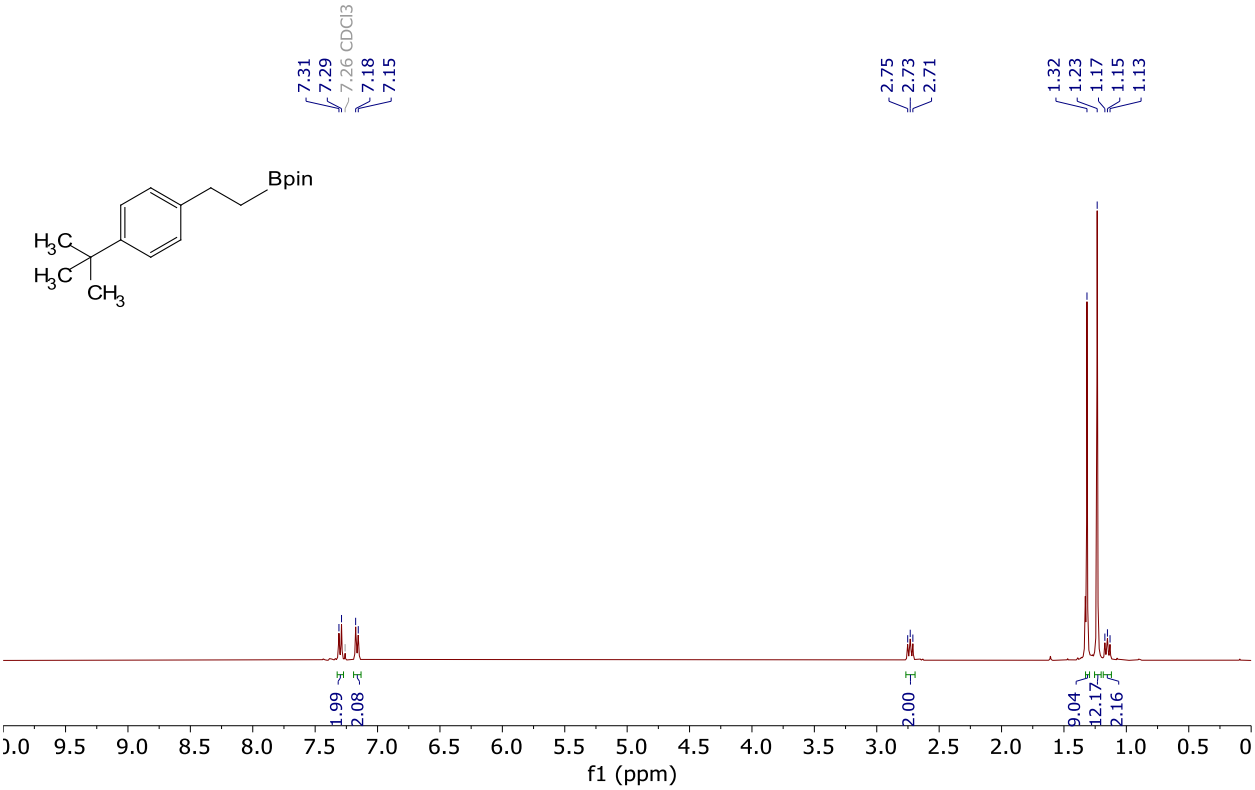


**Figure S63:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2p**

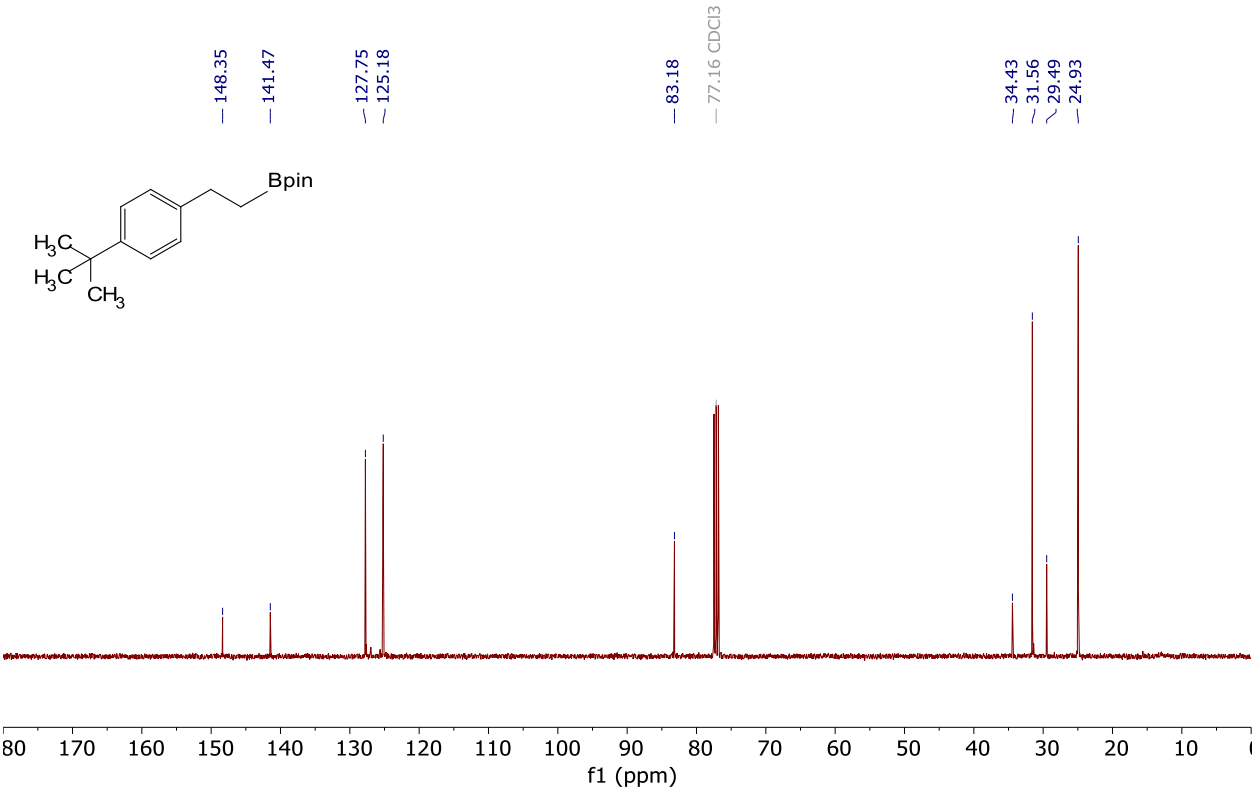


**Figure S64:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2p**

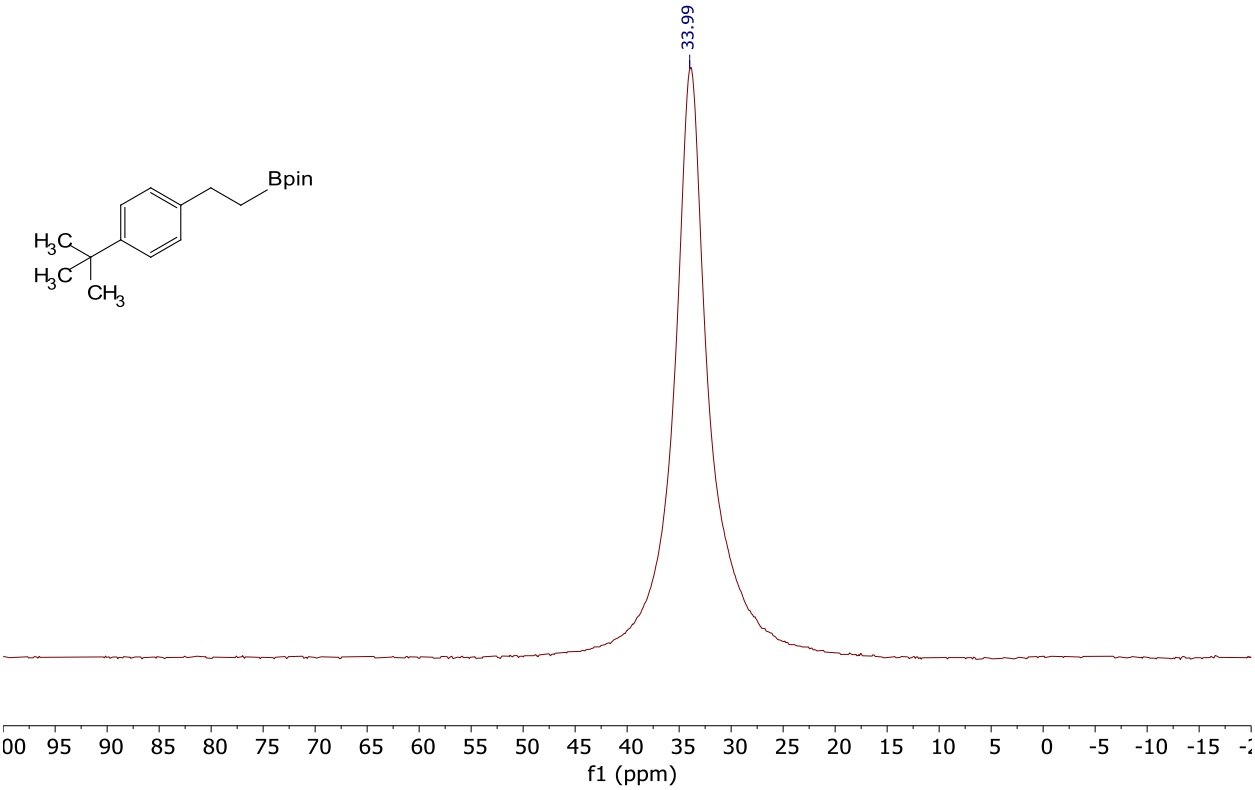


**Figure S65:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2p**

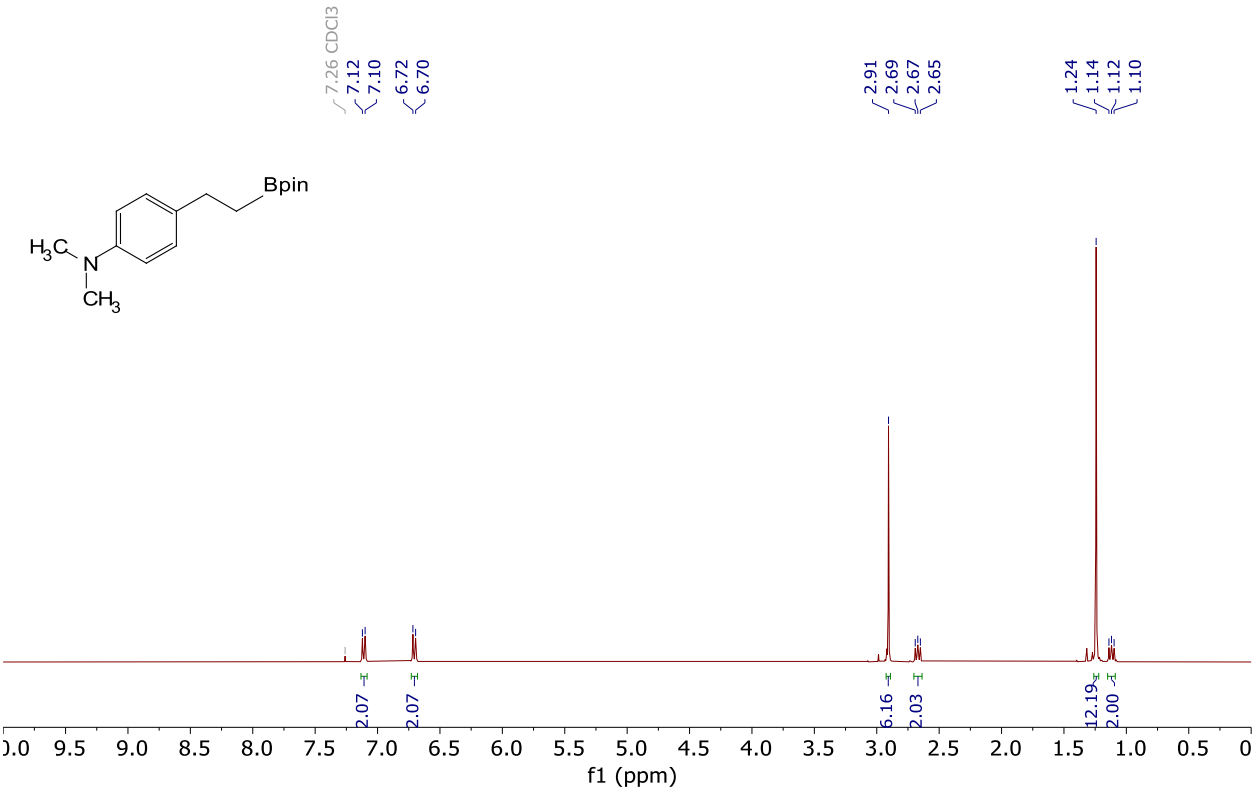


**Figure S66:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2q**

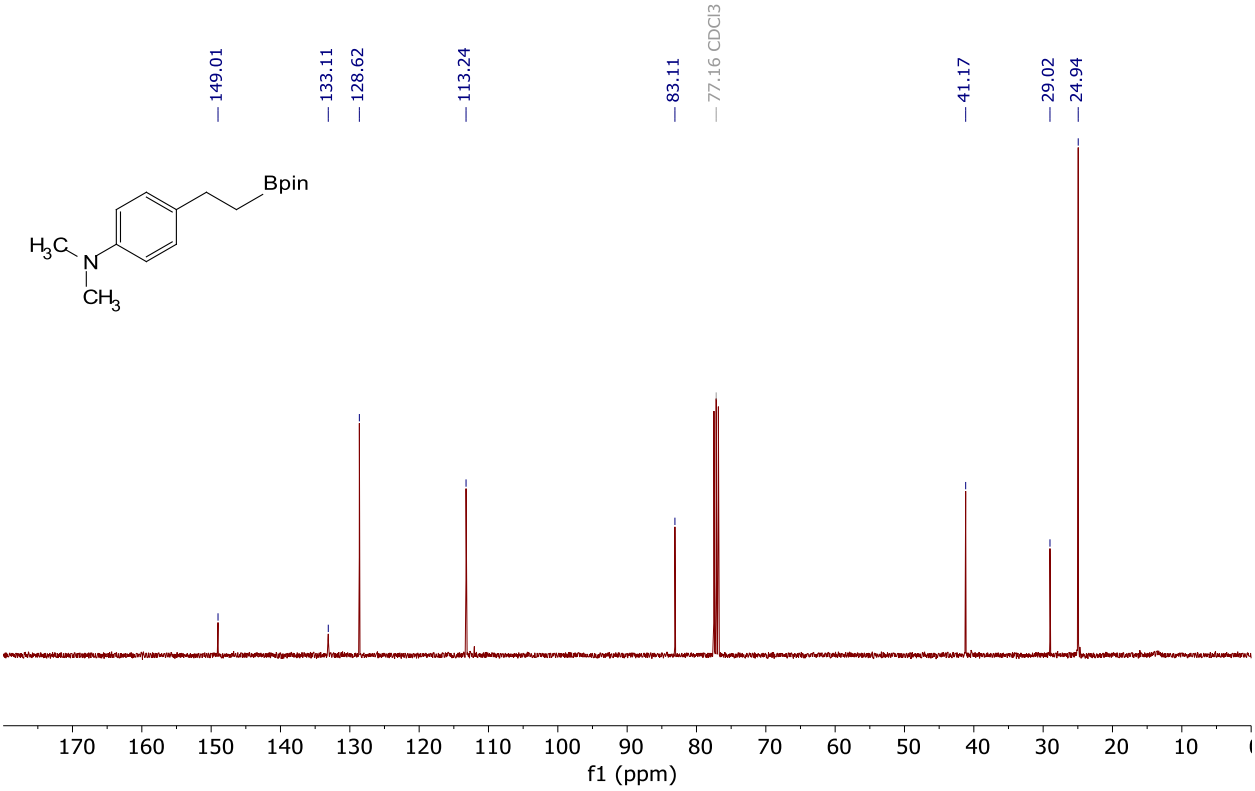


**Figure S67:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2q**

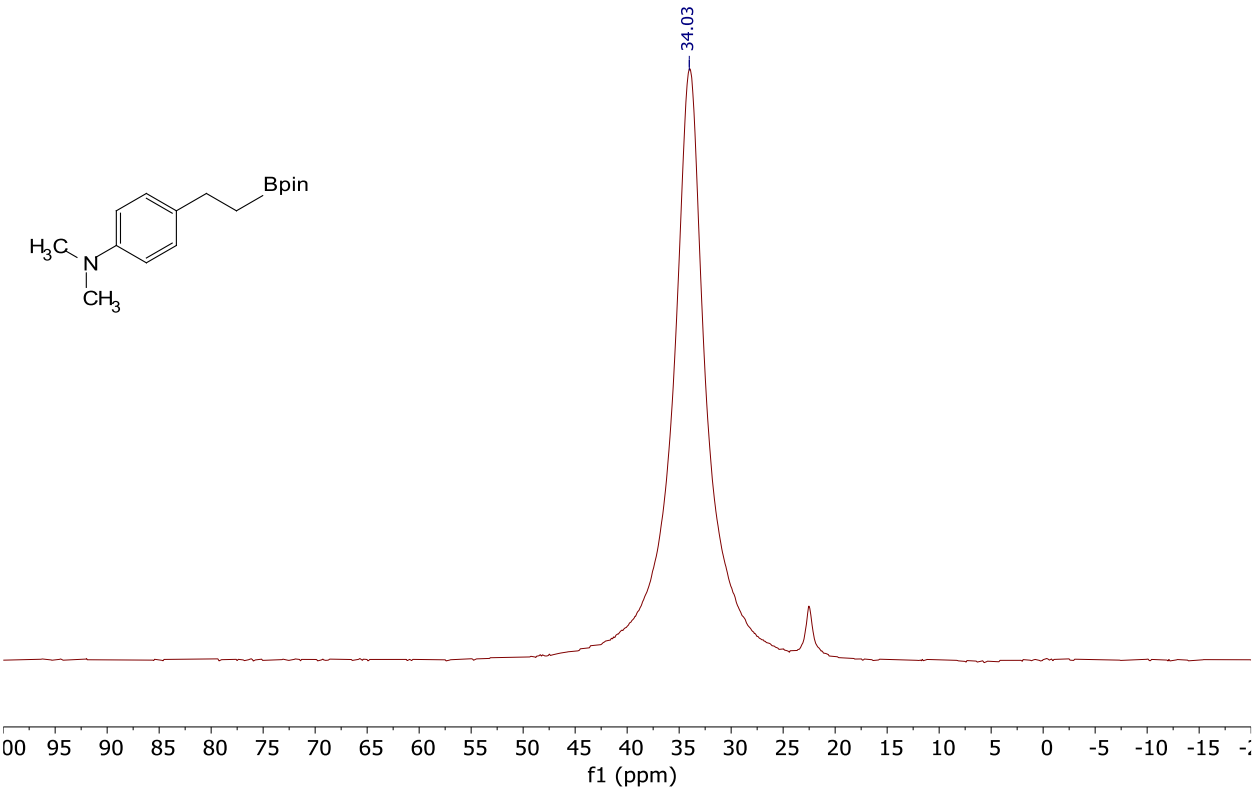


**Figure S68:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2q**

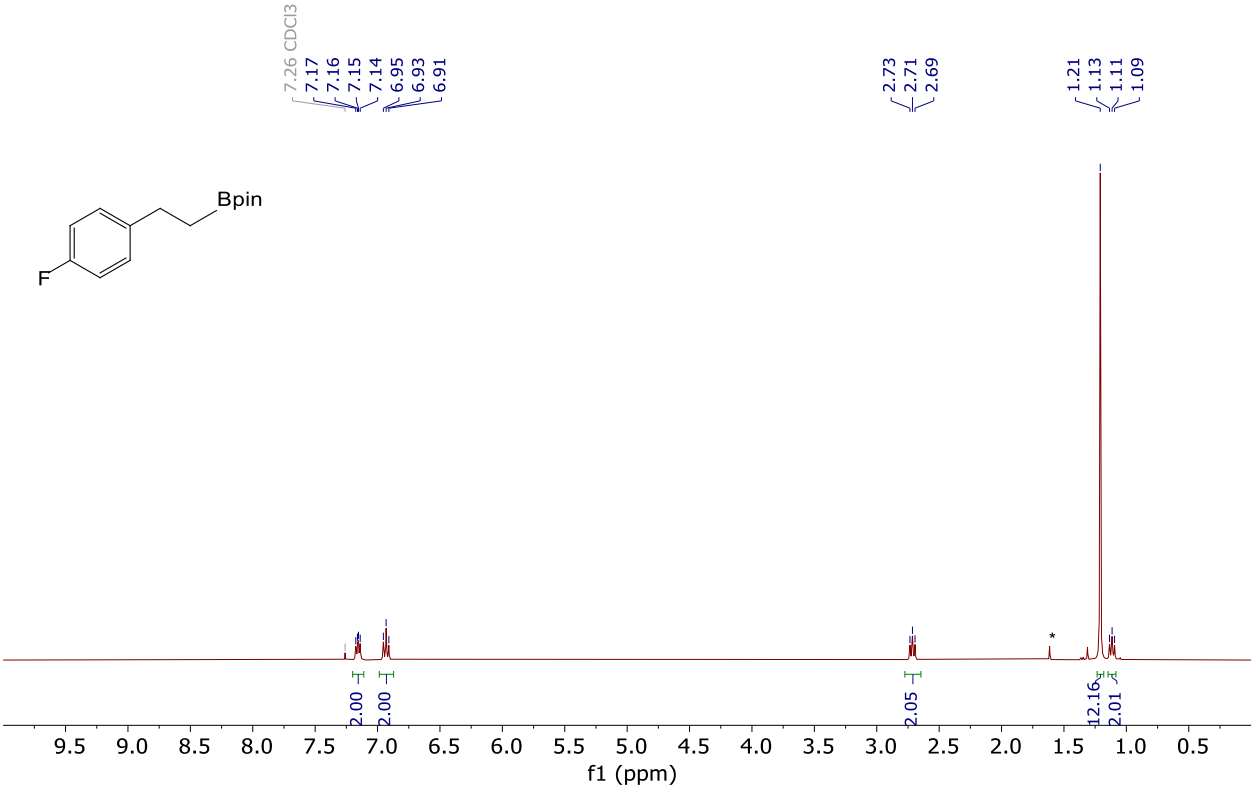


**Figure S69:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2r**

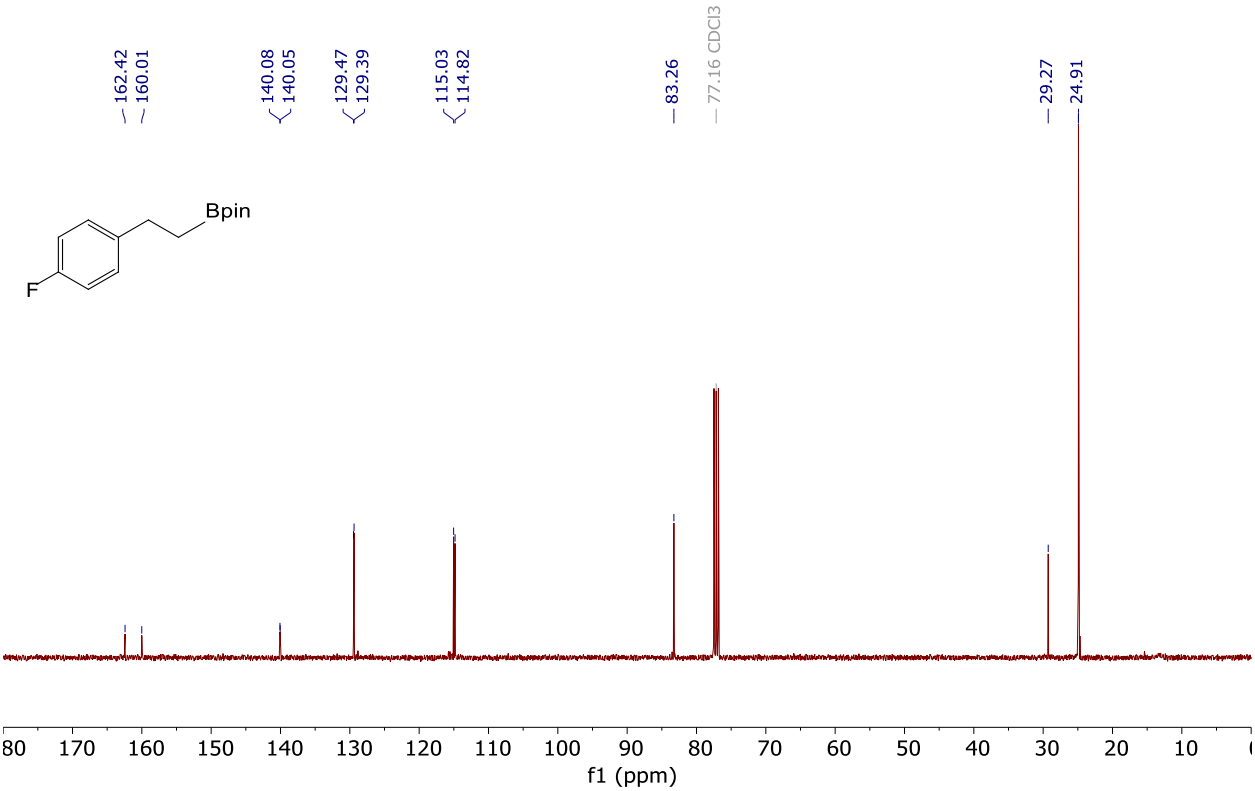


**Figure S70:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2r**

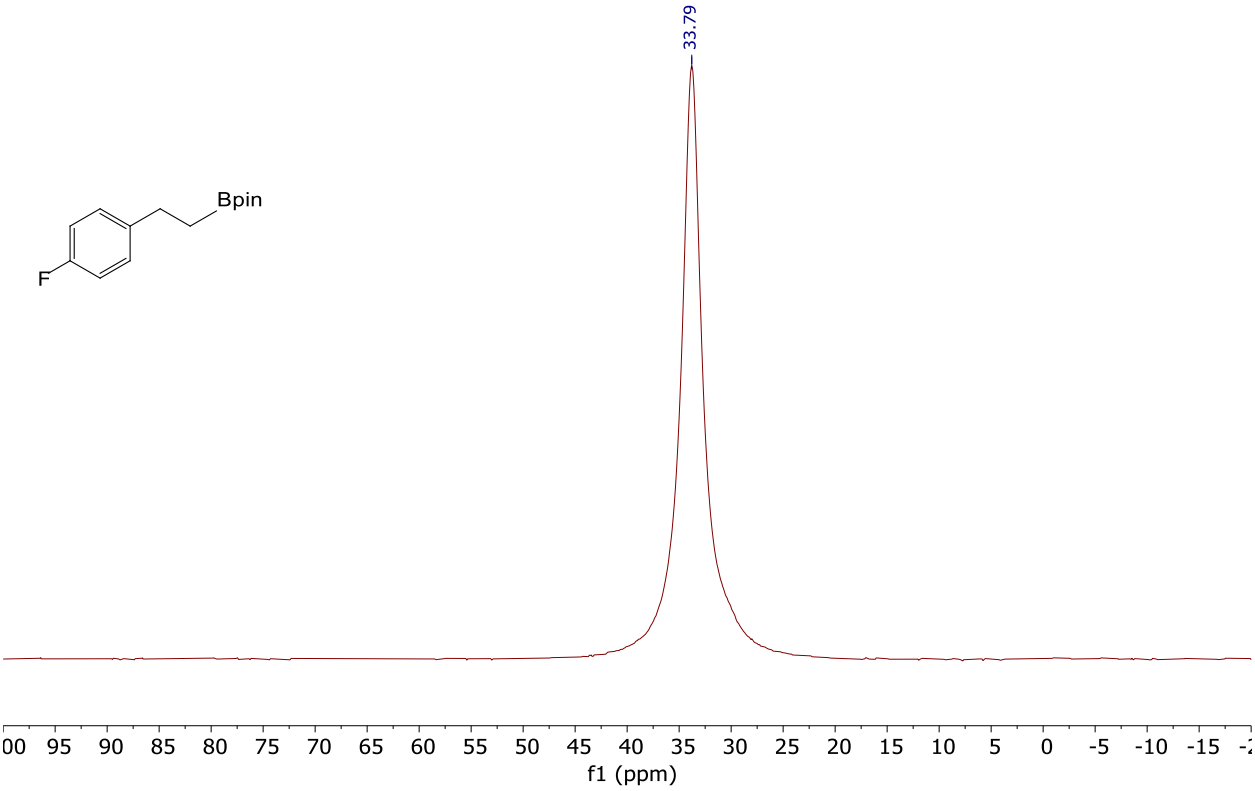


**Figure S71:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2r**

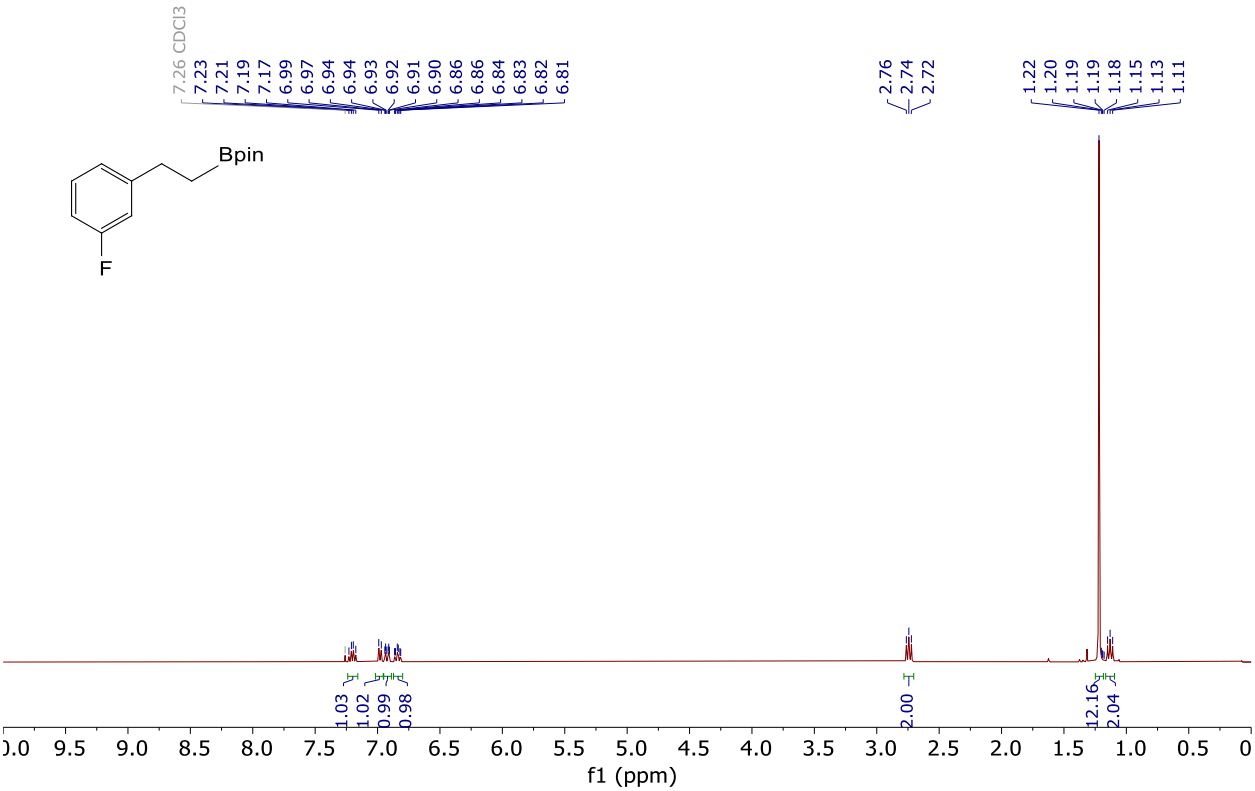


**Figure S72:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2s**

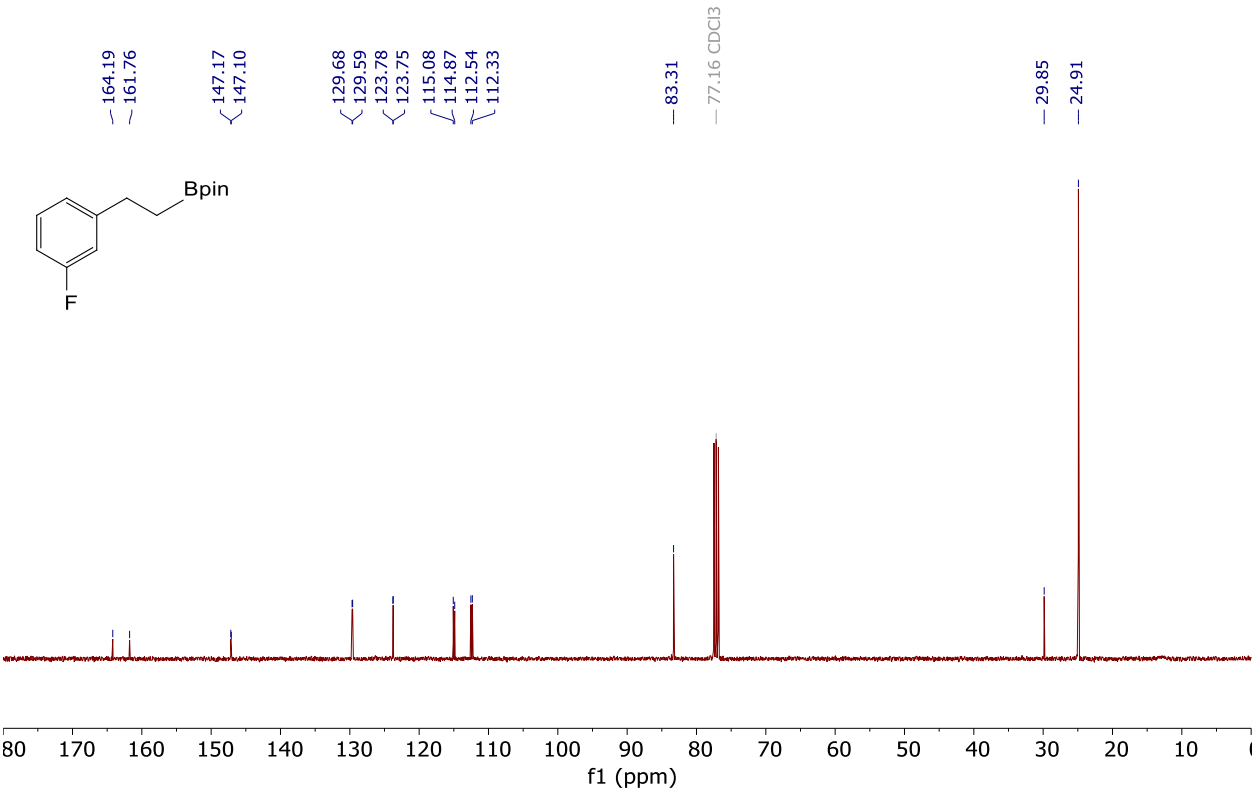


**Figure S73:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2s**

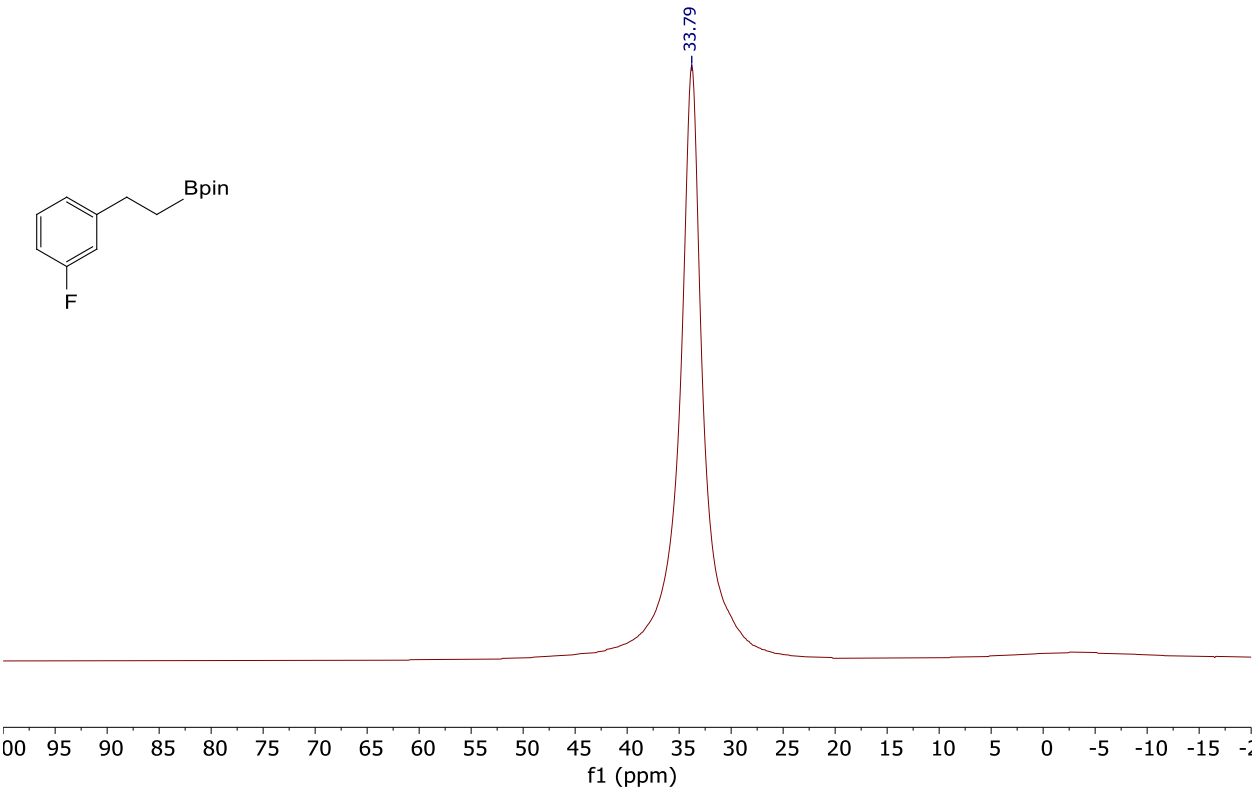


**Figure S74:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2s**

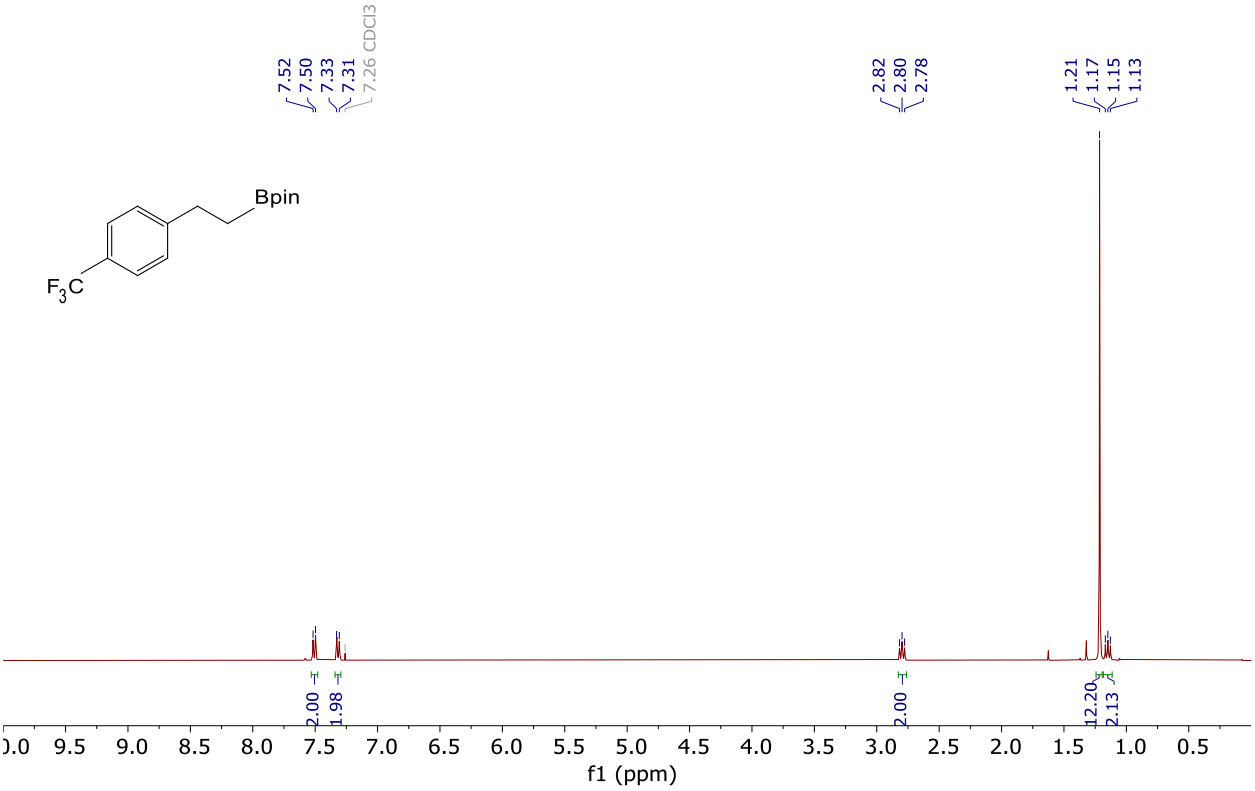


**Figure S75:** $^{1}H$ NMR spectrum ($CDCl_3$) of **2t**

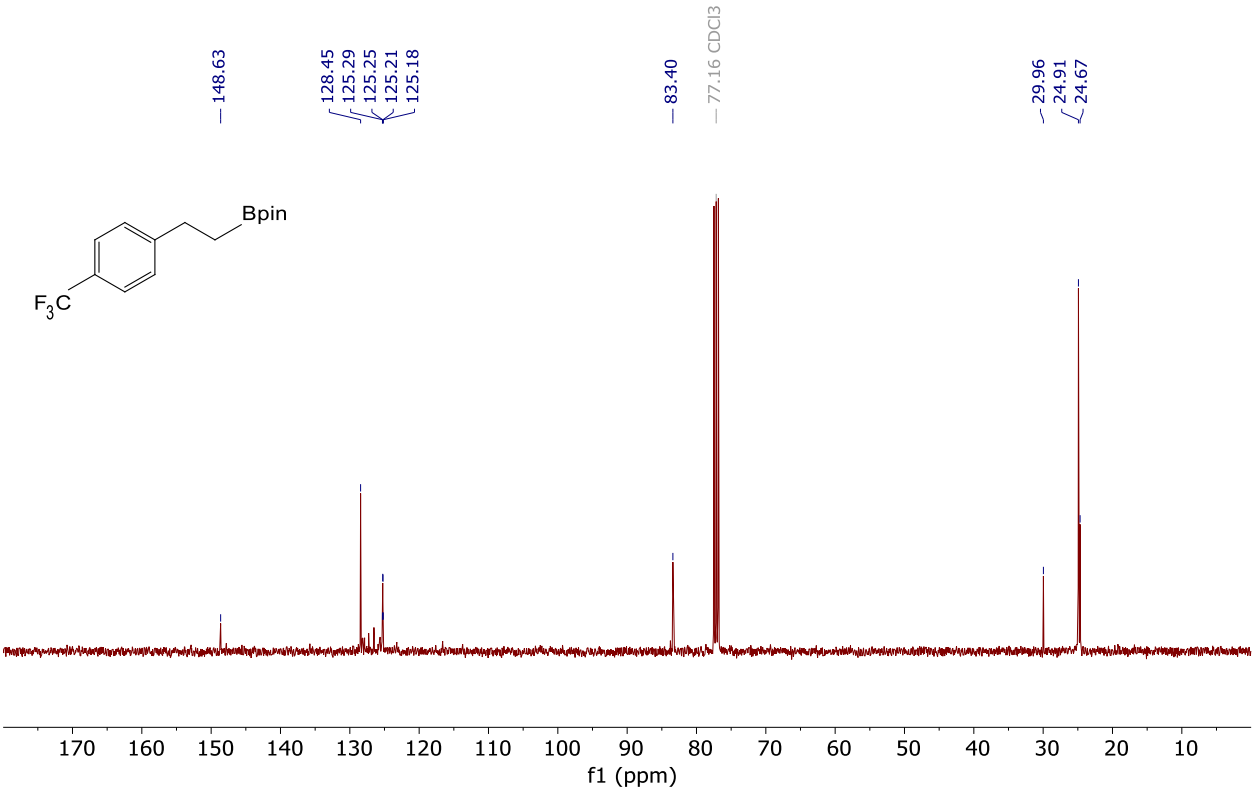


**Figure S76:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2t**

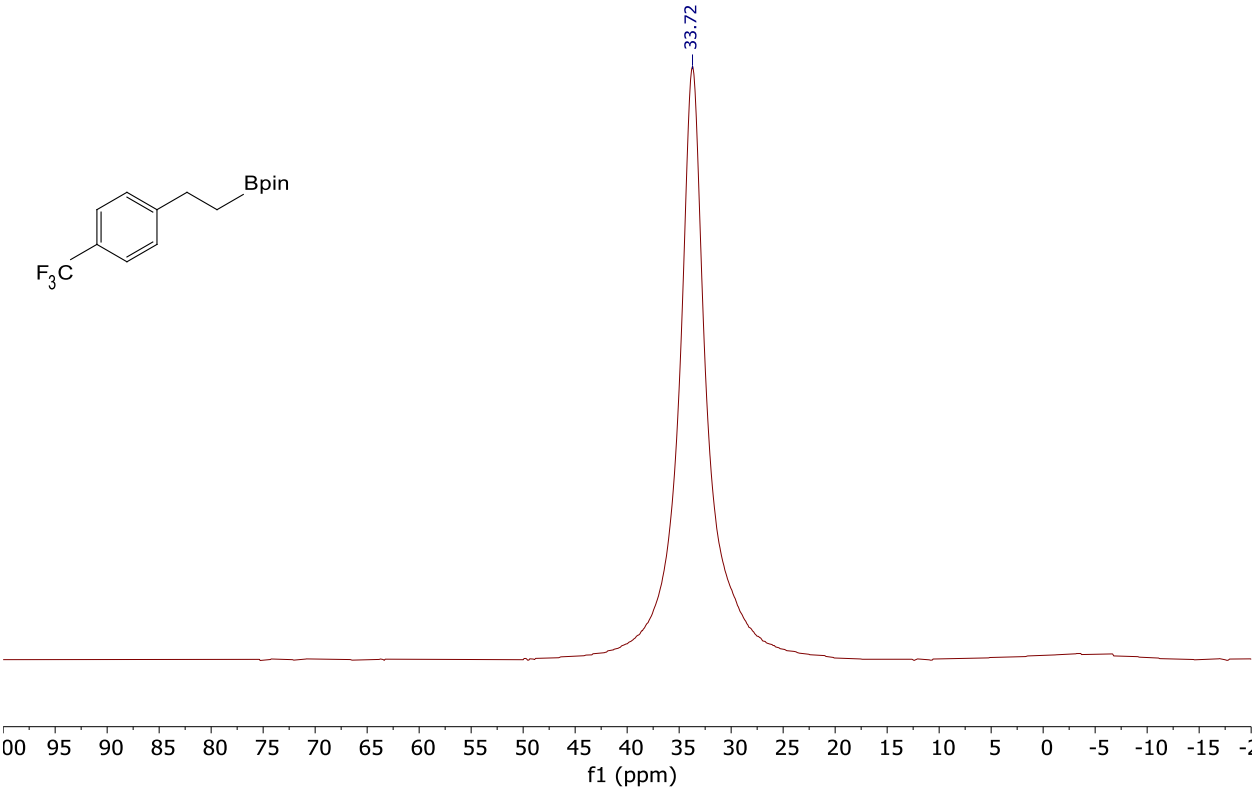


**Figure S77:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2t**

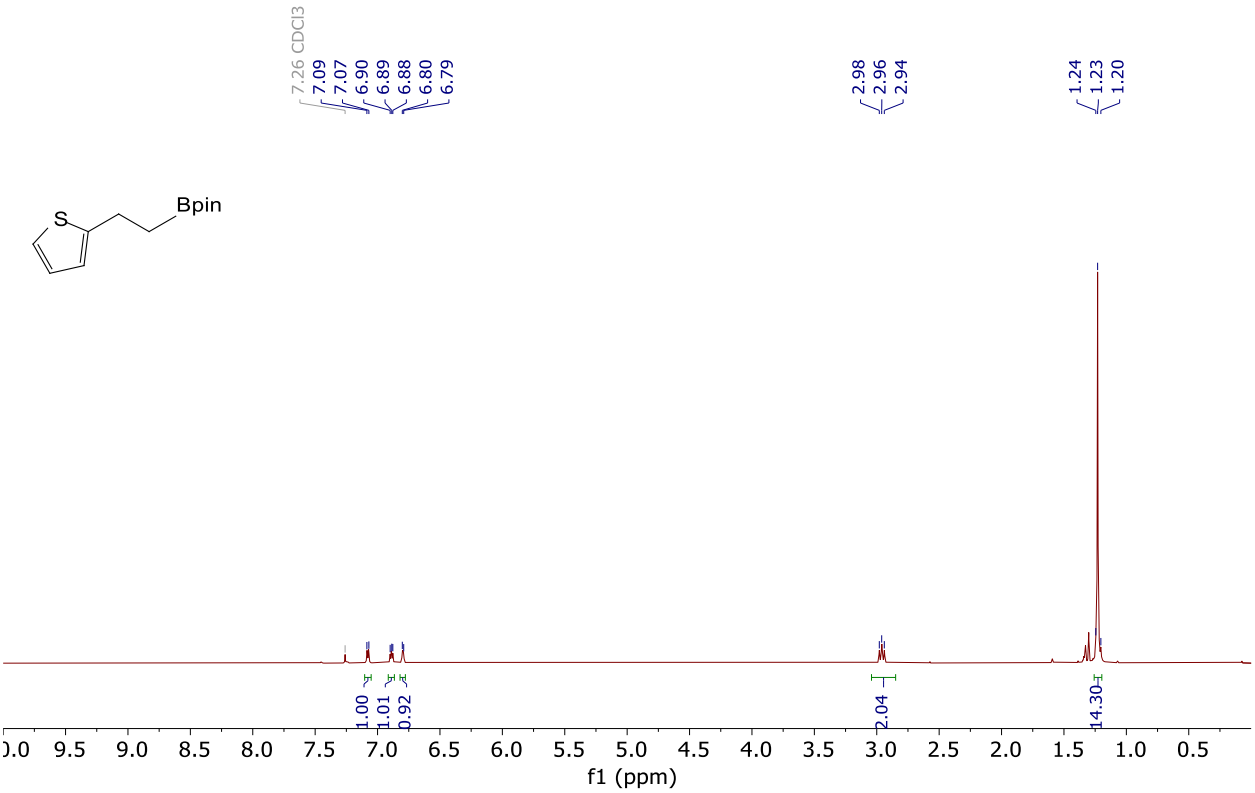


**Figure S78:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2u**

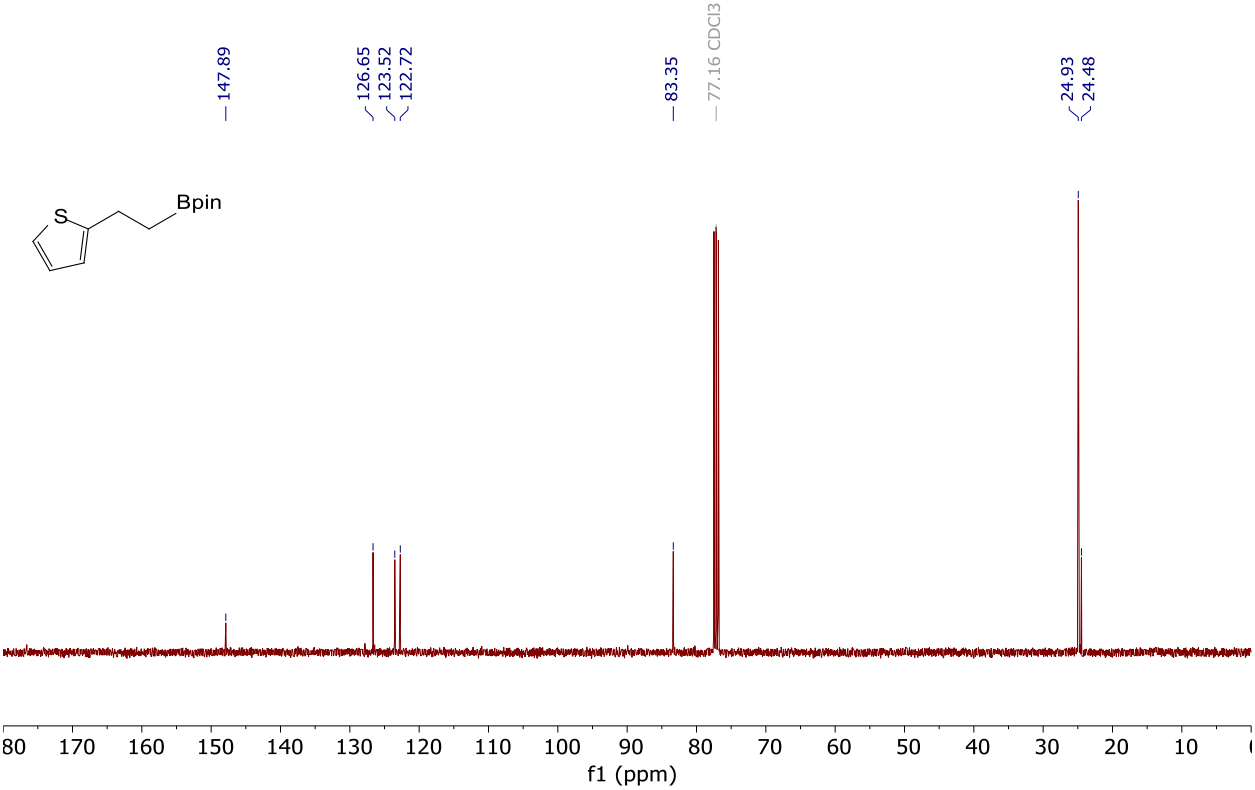


**Figure S79:** $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of **2u**

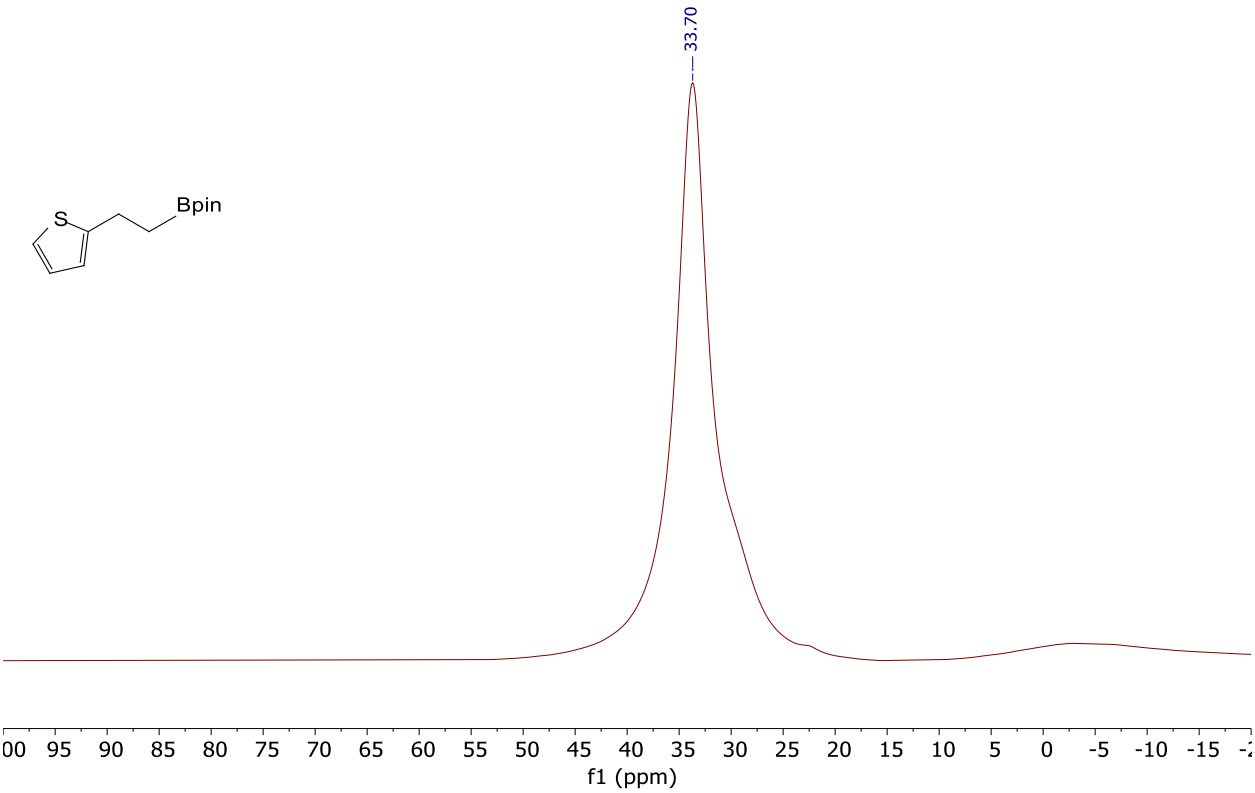


**Figure S80:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2u**

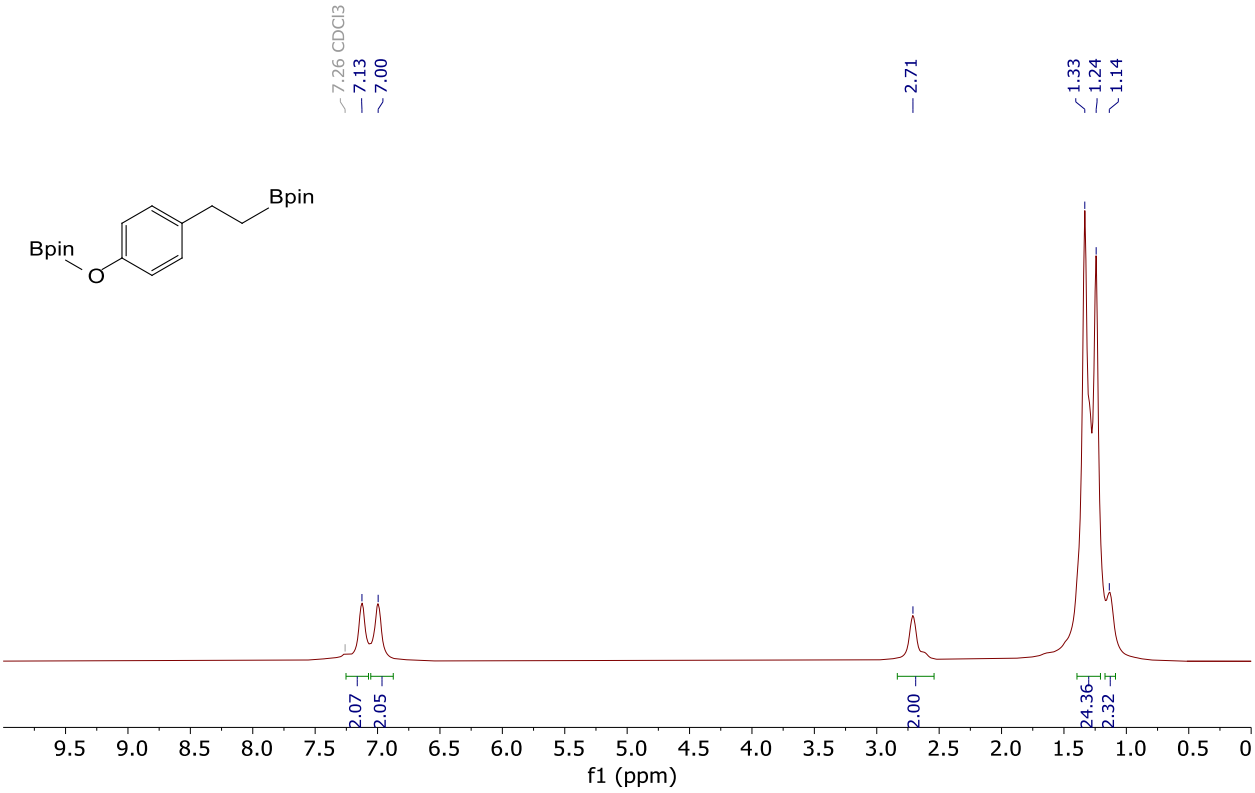


**Figure S81:** $^{1}H$ NMR Spectrum ($CDCl_3$) of **2u**

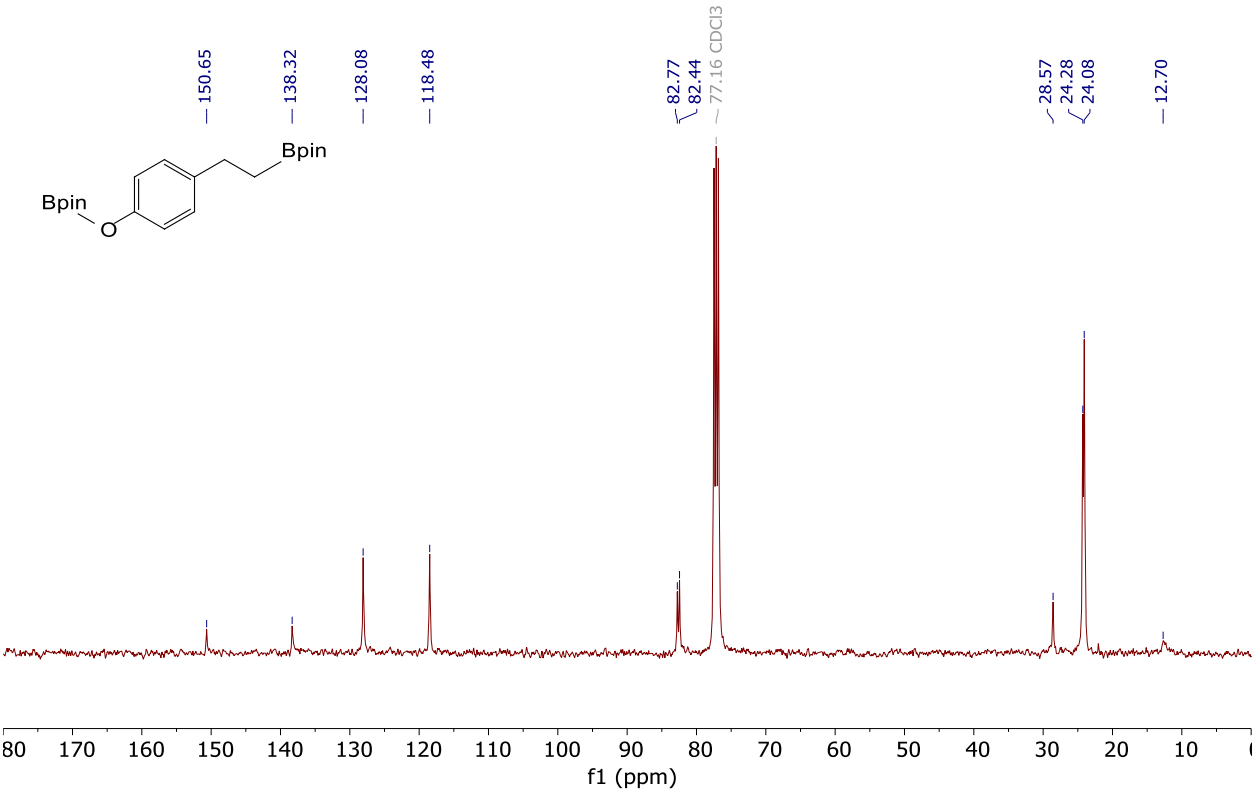


**Figure S82:** $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2v**

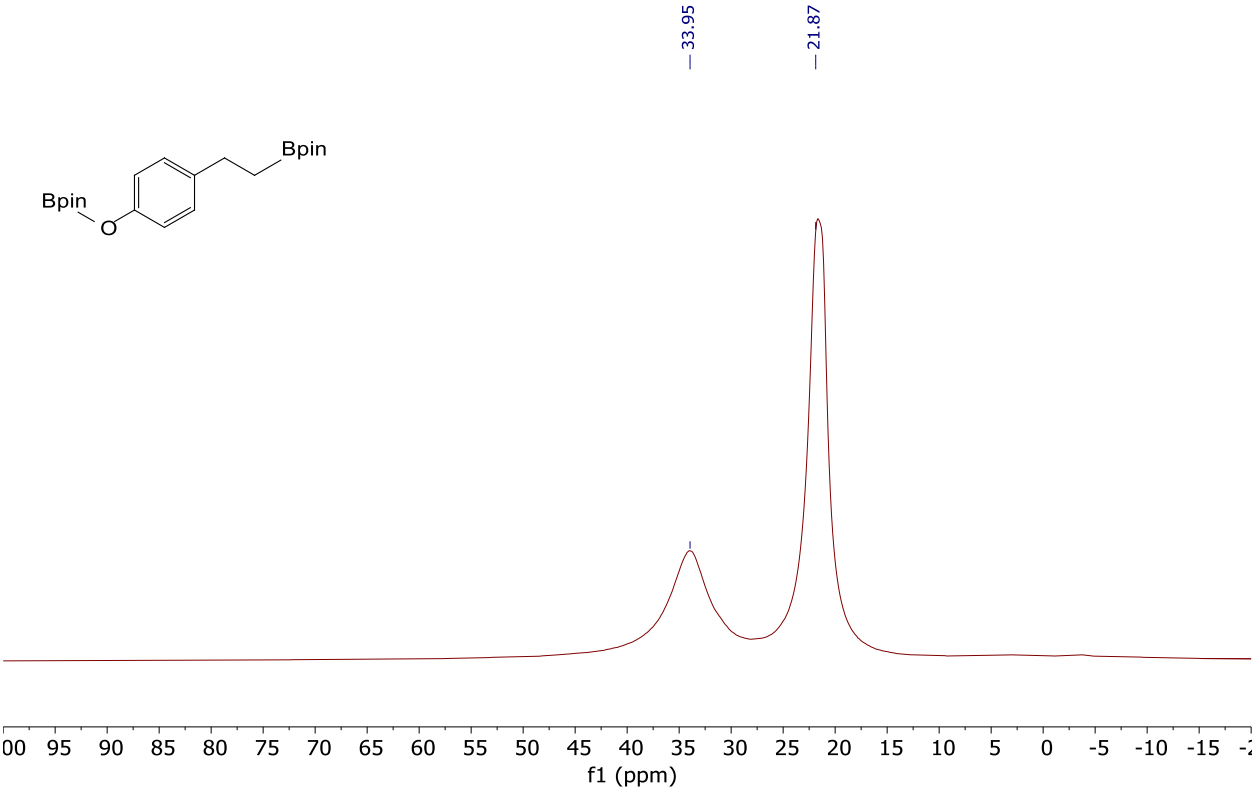


**Figure S83:** $^{11}B$ NMR spectrum ($CDCl_3$) of **2v**

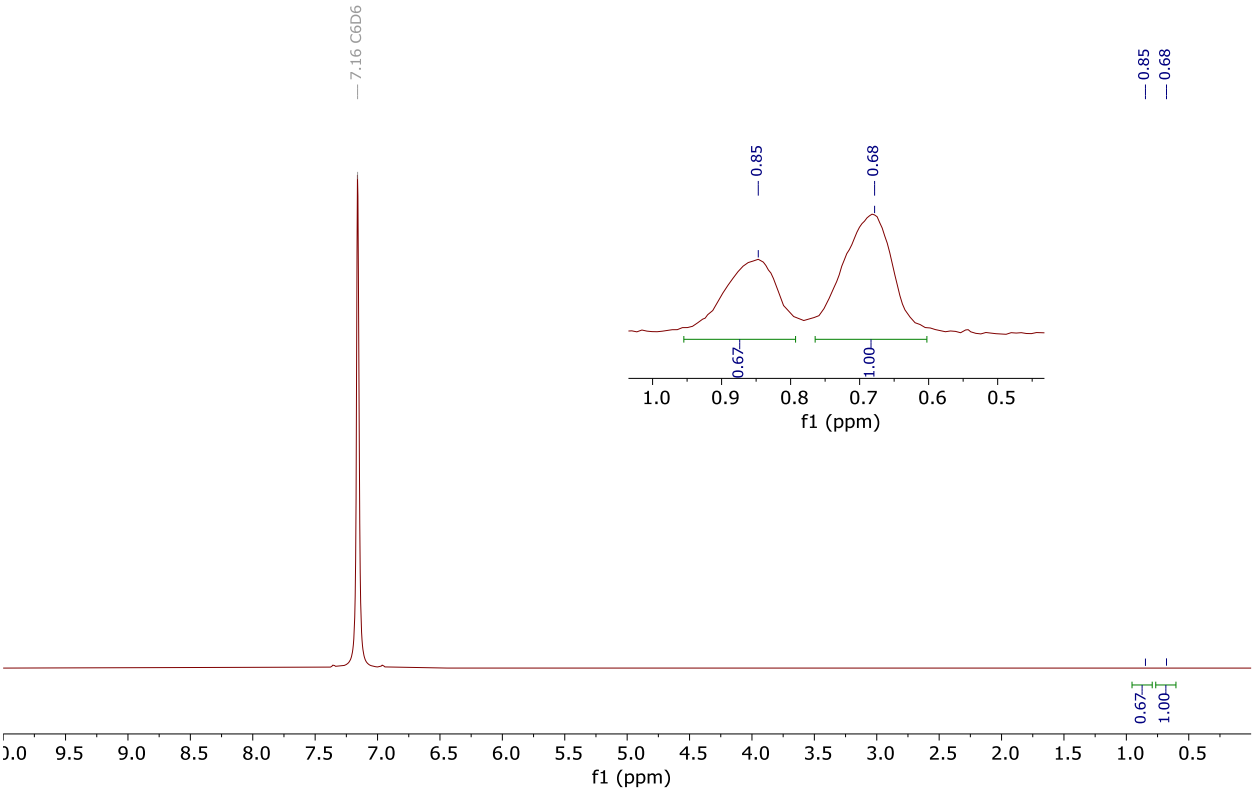


**Figure S84:** $^{2}H$ NMR spectrum ($C_6D_6$) of ***d*-2d**