Supporting Information

Spontaneous ^{15}N Nuclear Spin Hyperpolarization in Metal-Free Activation of Parahydrogen by Molecular Tweezers

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1 Materials and Experimental Methods

1.1 General information

NMR experiments were performed on a 300 MHz Bruker AV 300 NMR spectrometer equipped with a broad-band 10 mm RF probe. **1**-**3** *ansa*-aminoboranes were synthesized using procedures described below. The standard temperature control unit of the NMR spectrometer was used for cooling and heating the samples.

High-purity commercially available H_2 gas was used for producing parahydrogen-enriched H_2 referred to in the main text as "para-H_2". The enrichment was performed with a Bruker parahydrogen generator, which produced H_2 gas with 91 % of para-H_2.

1.2 NMR experiments

In a typical workflow, parahydrogen, obtained as described in the previous section, was bubbled trough 0.05 M solution of *ansa*-aminoborane compound (**1**-**3**) in degassed methylene chloride-d_2 in a 5 mm sample tube with a screw cap (Wilmad) inside the NMR magnet for ca. 5 s, and then the para-H_2 flow was abruptly switched off and an NMR experiment was started. The bubbling procedure was performed under elevated pressure (3.2 bar) in the same manner as explained in details in Ref.[S1] Parahydrogen was supplied to the bottom of the sample tube through a 1/32" PTFE tubing. The sample temperature was varied in the experiments when it was required.

1.2.1 ^{1}H NMR spectra acquired at 20 ºC after para-H_2 bubbling

^{1}H NMR spectra acquired after para-H_2 bubbling for **1**, **2** and **3** are shown in Figure S1. The corresponding ^{15}N spectra are presented in Figure 2 of the main text. In all cases, the antiphase doublet shape signal with J^{H1N} splitting for N-H proton reveals the presence of the longitudinal two spin order ($I_z^{H1}.I_z^N$) formed after para-H_2 bubbling. J^{H1N} spin-spin constants for **1**-H_2, **2**-H_2 and **3**-H_2 were 69.5, 70.4 and 71.3 Hz, respectively.

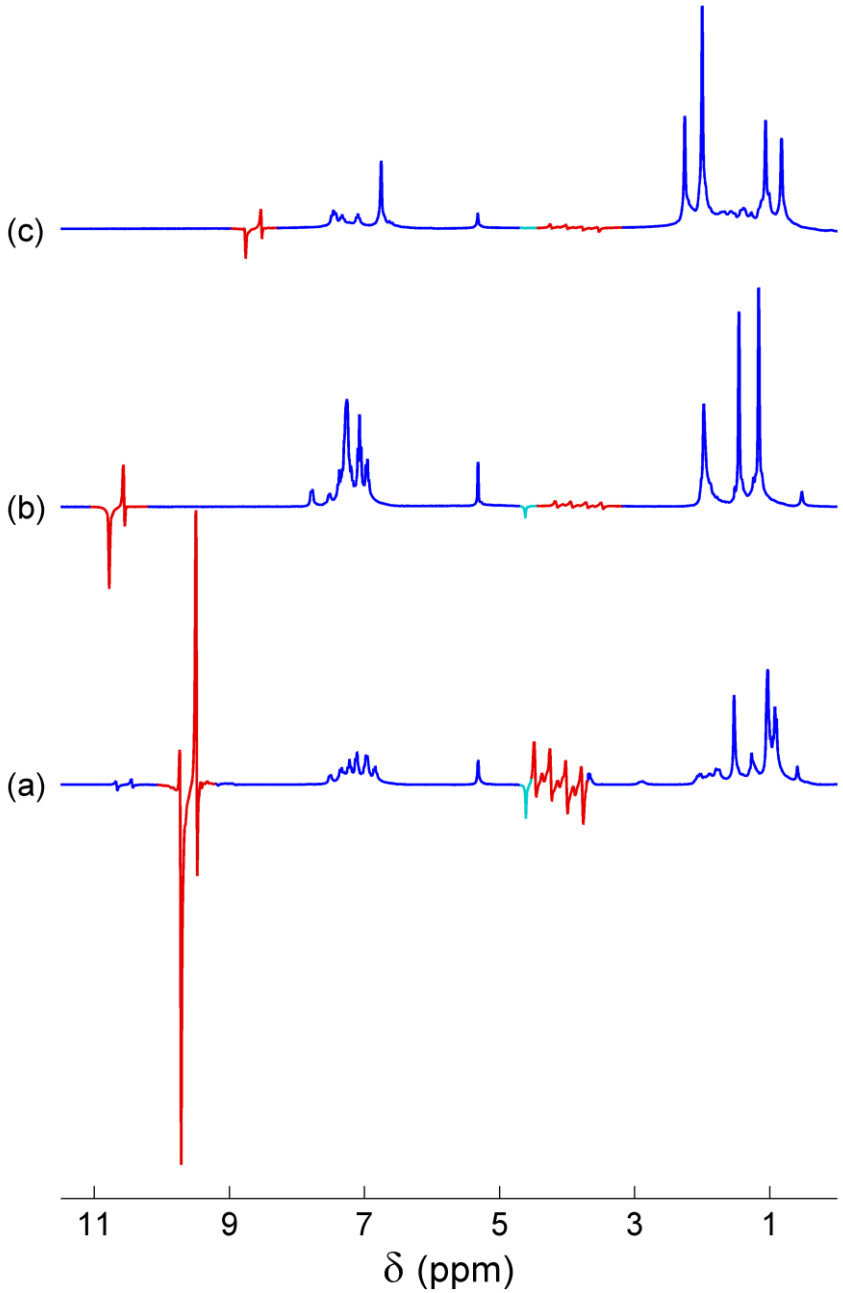


Figure S1. ^{1}H NMR spectra obtained after para-H_2 bubbling through 0.05 M solution of **2** (a), **1** (b) and **3** (c) in methylene chloride-d_2. The spectra were acquired right after the bubbling using the $\pi/4$-pulse. The red color highlights the polarized ^{1}H signals of -N-H..H-B- of AABs. The cyan colored signal corresponds to ortho-H_2.

1.2.2 ^{11}B NMR spontaneous hyperpolarization

A weaker effect of spontaneous hyperpolarization of ^{11}B nuclei was also observed under the same conditions as were utilized in ^{15}N experiments. Figure S2 shows NMR spectra corresponding to thermally polarized (a) and hyperpolarized H_2 adduct with **2**. The signal enhancements detected in ^{11}B spectra were on the order of 10-fold for the AABs under study. This effect was relatively weak compared to ^{15}N hyperpolarization.

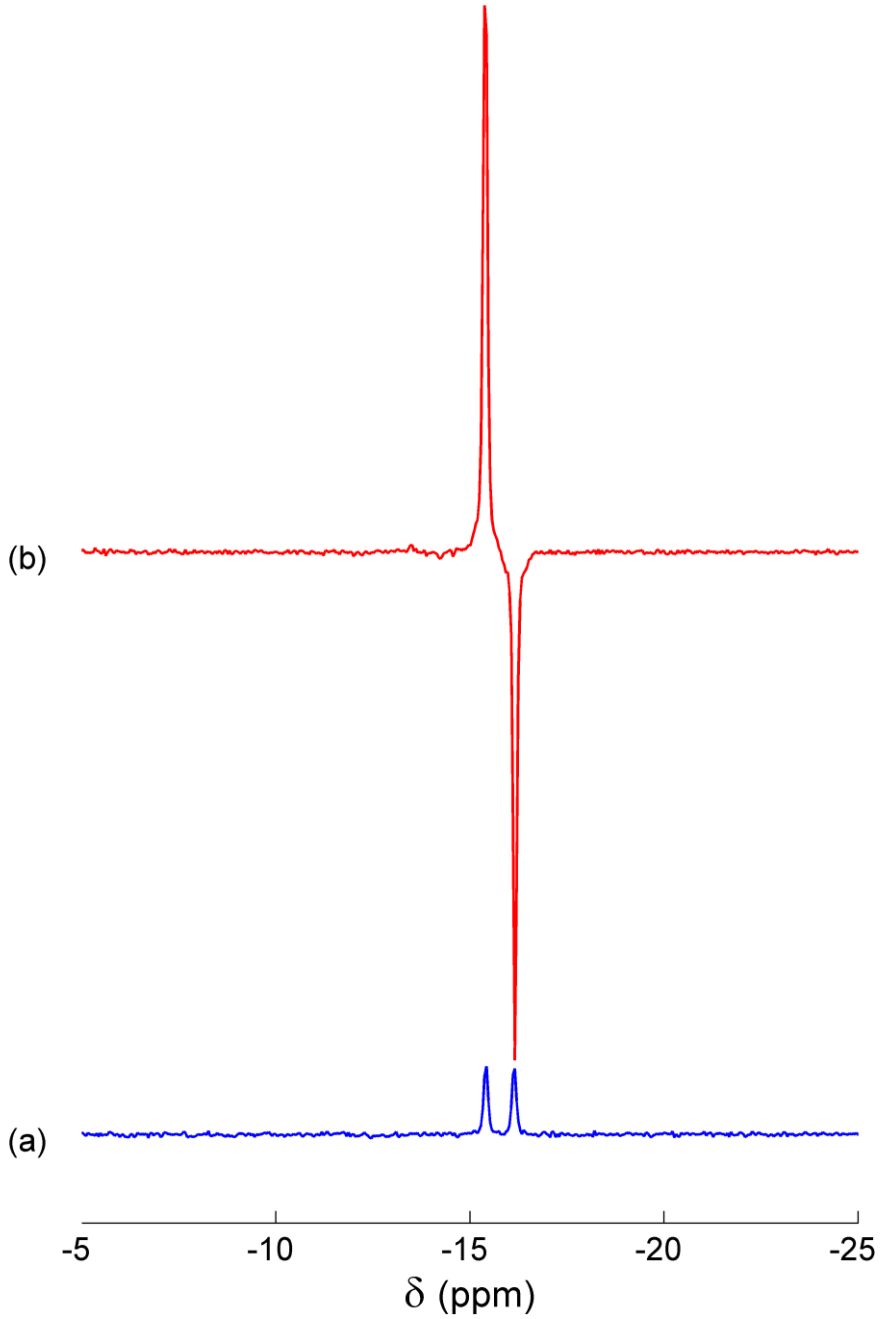


Figure S2. ^{11}B NMR spectra obtained after parahydrogen bubbling through 0.05 M solution of **2** (b) and after the relaxation to thermal equilibrium (a) at 20 ºC. The spectra were acquired right after the bubbling using the π/2-pulse. Signal enhancement was ca. 10-fold.

1.2.3 Signal enhancements

^{15}N signal enhancements were impossible to determine without extensive signal accumulation of the weak thermally polarized signals. Actually, SNR for thermal spectra was so low that no signal was evident after 8 scans for any case and only 64 and 512 scan accumulations provided a ^{15}N signal good enough for a reliable comparison with the corresponding hyperpolarized one for **1**-H_2 and **2**-H_2, respectively. For **3**-H_2 it was impossible to see any good signal after 4k scan accumulations,

because the H_2 adduct concentration was very low for this AAB at 20 ºC. However, using INEPT pulse sequence the accumulation of the spectrum took much shorter providing ca. 10-fold signal enhancement. Thus, the comparison of INEPT and PHIP provided more rapid and reliable signal enhancement determination. This latter procedure provided the following signal enhancements for the reaction performed at 20 ºC: 150 for **1**-H_2, 350 for **2**-H_2, and 300 for **3**-H_2.

1.3 Synthesis

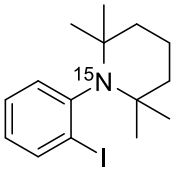
15.1 g of 2,2,6,6-tetramethylpiperidin-4-one-1-^{15}N was obtained from 10 g of ^{15}N-ammonium chloride, yield 52%. ^{1}H (300 MHz, $CDCl_3$, δ, ppm): 2.16 (s, 4H), 1.12 (s, 12H). ^{13}C (75 MHz, $CDCl_3$, δ, ppm): 210.84, 55.51 (d, J = 3.5 Hz), 54.19, 32.10 (d, J = 2.7 Hz).

9.1g of 2,2,6,6-Tetramethylpiperidine-1-^{15}N (**4**) were prepared starting from 15.0 g of 2,2,6,6-tetramethylpiperidin-4-one-1-^{15}N according to the literature procedure.[S2] Yield 66%. ^{1}H (500 MHz, $CDCl_3$, δ, ppm): 1.59 (m, 2H), 1.26 (m, 4H), 1.06 (d, J = 2.6 Hz, 12H).

Compounds **1-3** were synthesized according to the literature procedure.[S1] Synthetic operations were performed under argon atmosphere by a conventional Schlenk technique or in a glove box (Mbraun Unilab). The solvents were dried by conventional methods and stored over molecular sieves. Deuterated solvents were dried by standing over molecular sieves (3 Å) and used without additional purification. Reagents were purchased from Sigma-Aldrich.

NMR spectra were recorded using Varian Mercury 300 (^{1}H, ^{13}C) or Varian Inova 500 (^{1}H, ^{13}C, ^{11}B) spectrometers at 27 °C. ^{1}H and ^{13}C spectra were referenced to residual solvent signal and reported as parts per million relative to tetramethylsilane. ^{11}B spectra were referenced to external standard, a $BF_3{\cdot}Et_2O$ solution.

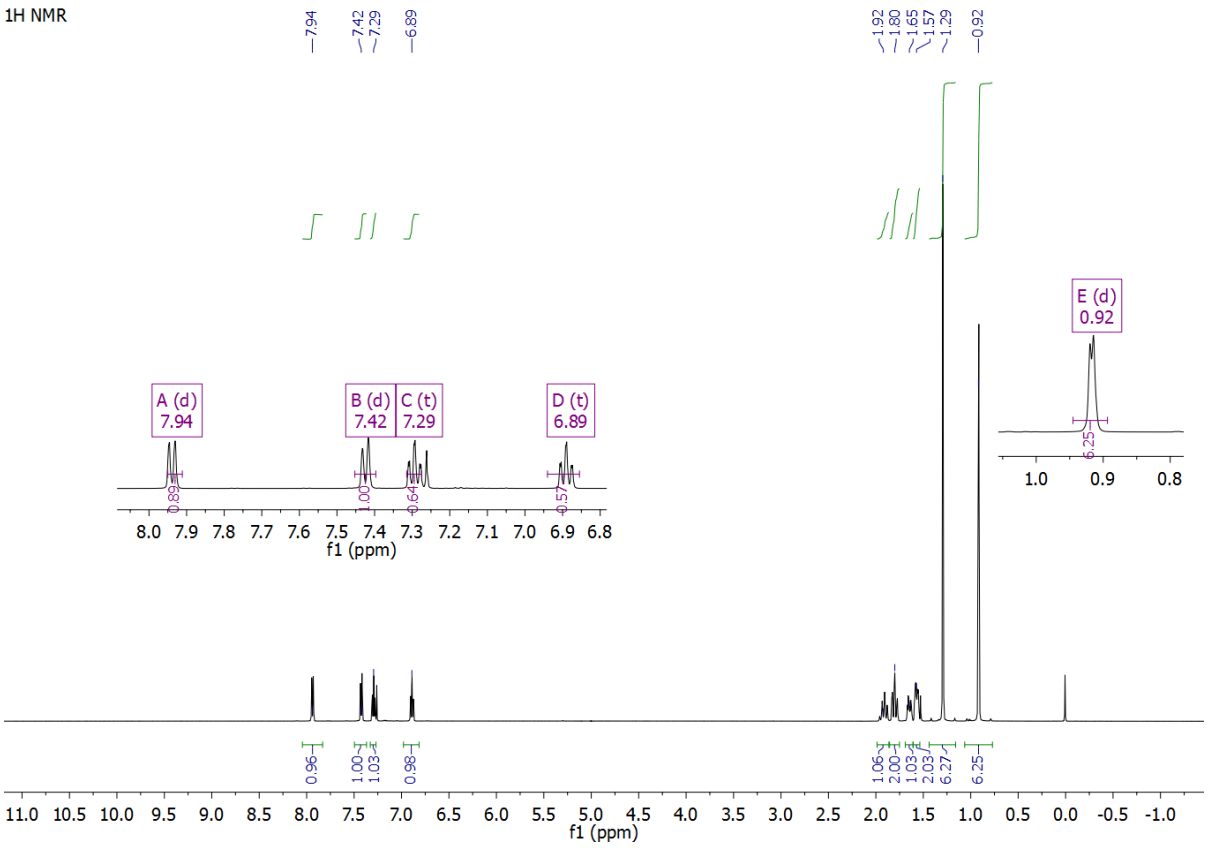
1.3.1 1-(2-iodophenyl)-2,2,6,6-tetramethylpiperidine-1-^{15}N (5)

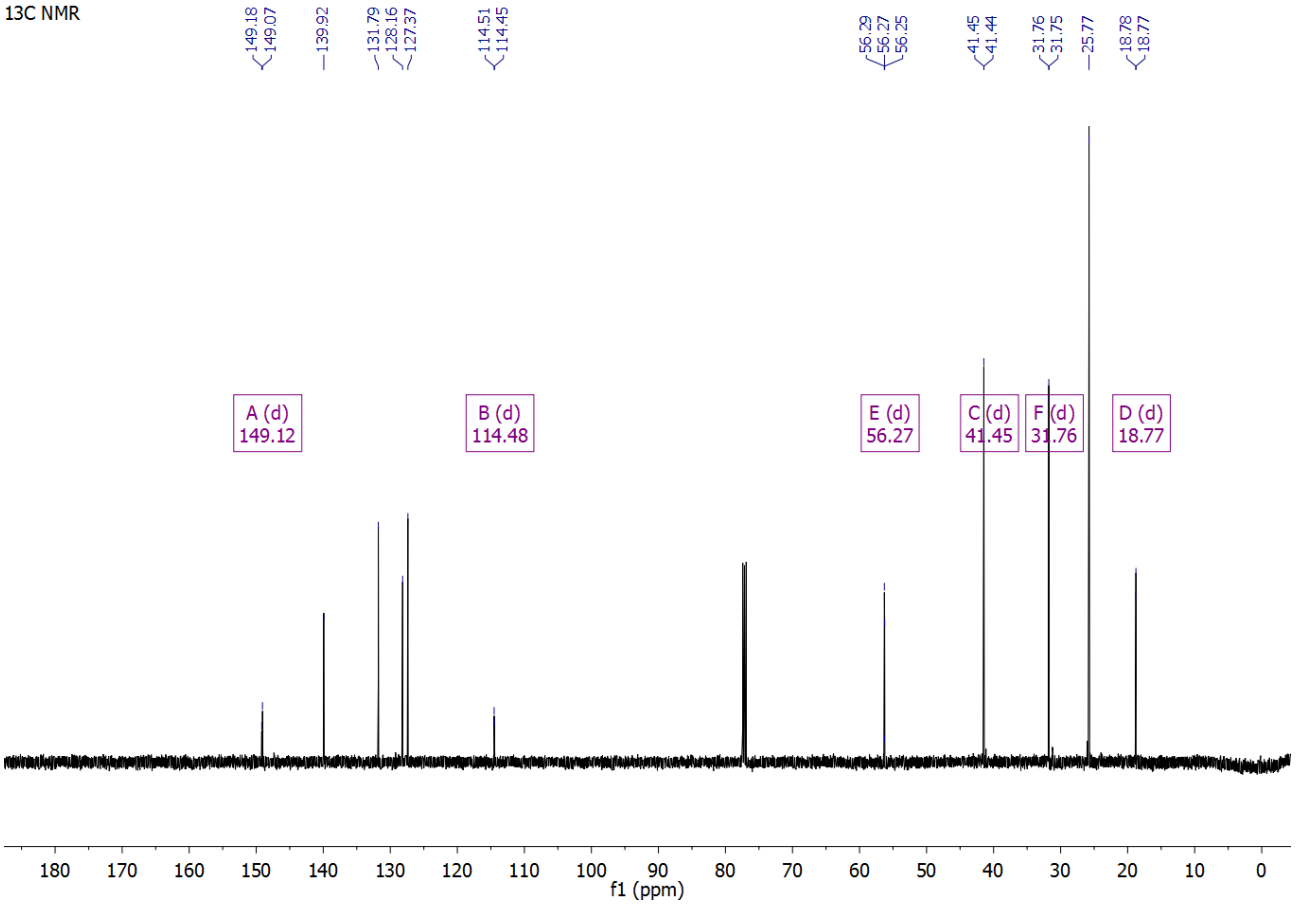


5 was prepared according to the protocol previously described for a non-labeled compound.[S3]

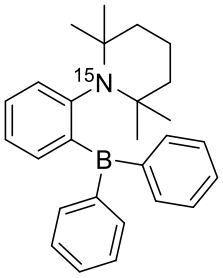
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 7.94 (dm, J = 7.9 Hz, 1H), 7.42 (dm, J = 7.9 Hz, 1H), 7.29 (tm, J = 7.6 Hz, 1H), 6.89 (tm, J = 7.6 Hz, 1H), 1.92 (m, 1H), 1.80 (m, 2H), 1.65 (m, 1H), 1.57 (m, 2H), 1.29 (s, 6H), 0.92 (d, J = 2.7 Hz, 6H)

^{13}C NMR (75 MHz, C_6D_6) δ ppm: (C-B not observed), 149.12 (d, *J* = 13.7 Hz), 139.92, 131.79, 128.16, 127.37, 114.48 (d, *J* = 6.9 Hz), 56.27 (d, *J* = 5.3 Hz), 41.45 (d, *J* = 1.9 Hz), 31.76 (d, *J* = 1.9 Hz), 25.77, 18.77 (d, *J* = 1.4 Hz)





1.3.2 1-(2-(diphenylboranyl)phenyl)-2,2,6,6-tetramethylpiperidine-1-^{15}N (1)



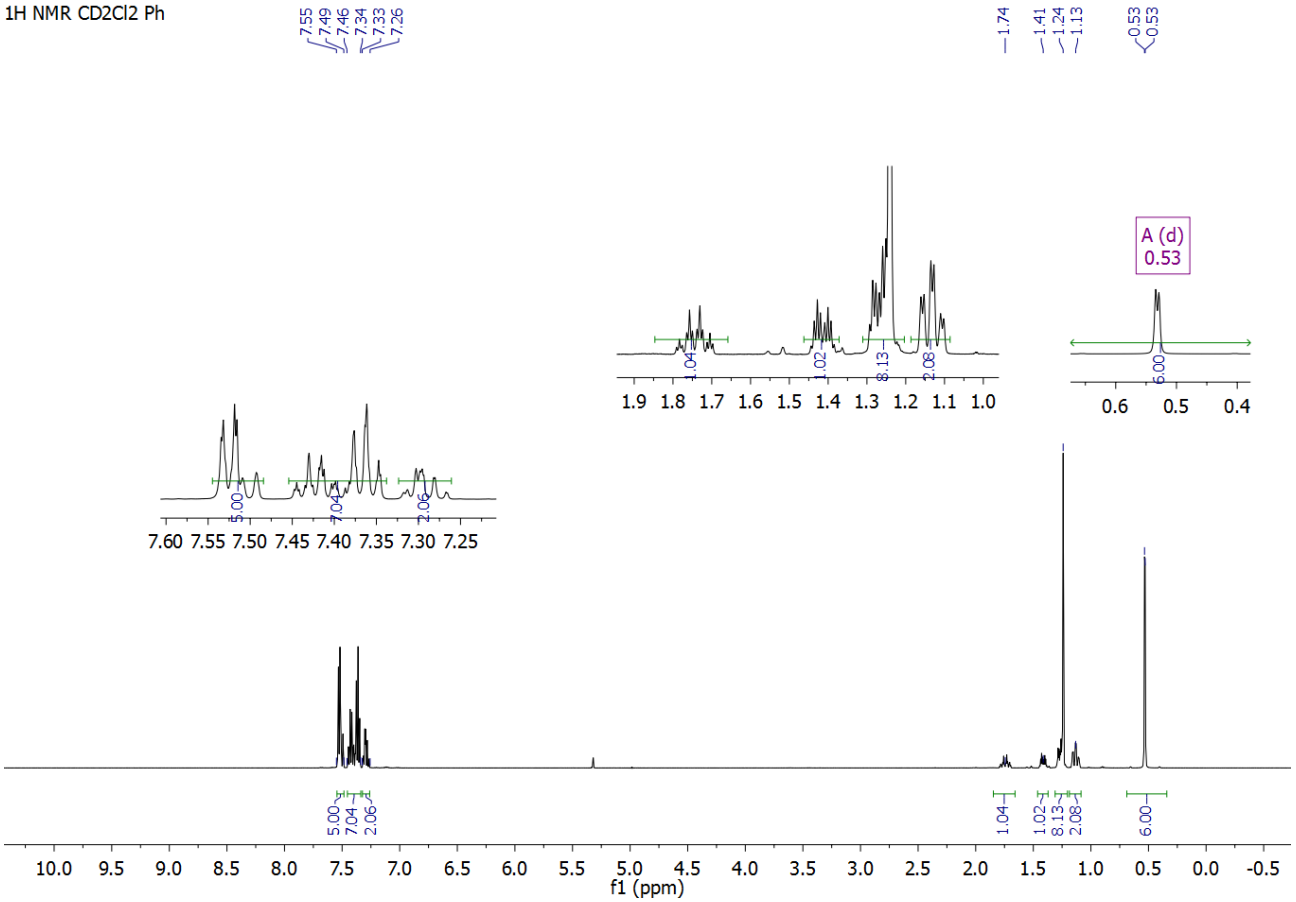
^{1}H NMR (500 MHz, CD_2Cl_2) δ ppm:7.55-7.98 (m, 5H), 7.46-7.34 (m, 7H), 7.33-7.26 (m, 2H),1.74 (m, 1H), 1.41 (m,1H), 1.30-1.23 (m, 2H), 1.24(s, 6H), 1.13, 0.53 (d, *J* = 2.7 Hz, 1H),

^{13}C NMR (75 MHz, C_6D_6) δ ppm: (C-B not observed), 151.87 (d, *J* = 9.9 Hz), 137.00, 135.01 (d, *J* = 3.3 Hz), 132.18, 130.69, 129.00, 127.62, 124.19, 56.14 (d, *J* = 4.9 Hz), 41.48 (d, *J* = 2.1 Hz), 35.45 (d, *J* = 2.4 Hz), 26.78, 18.95

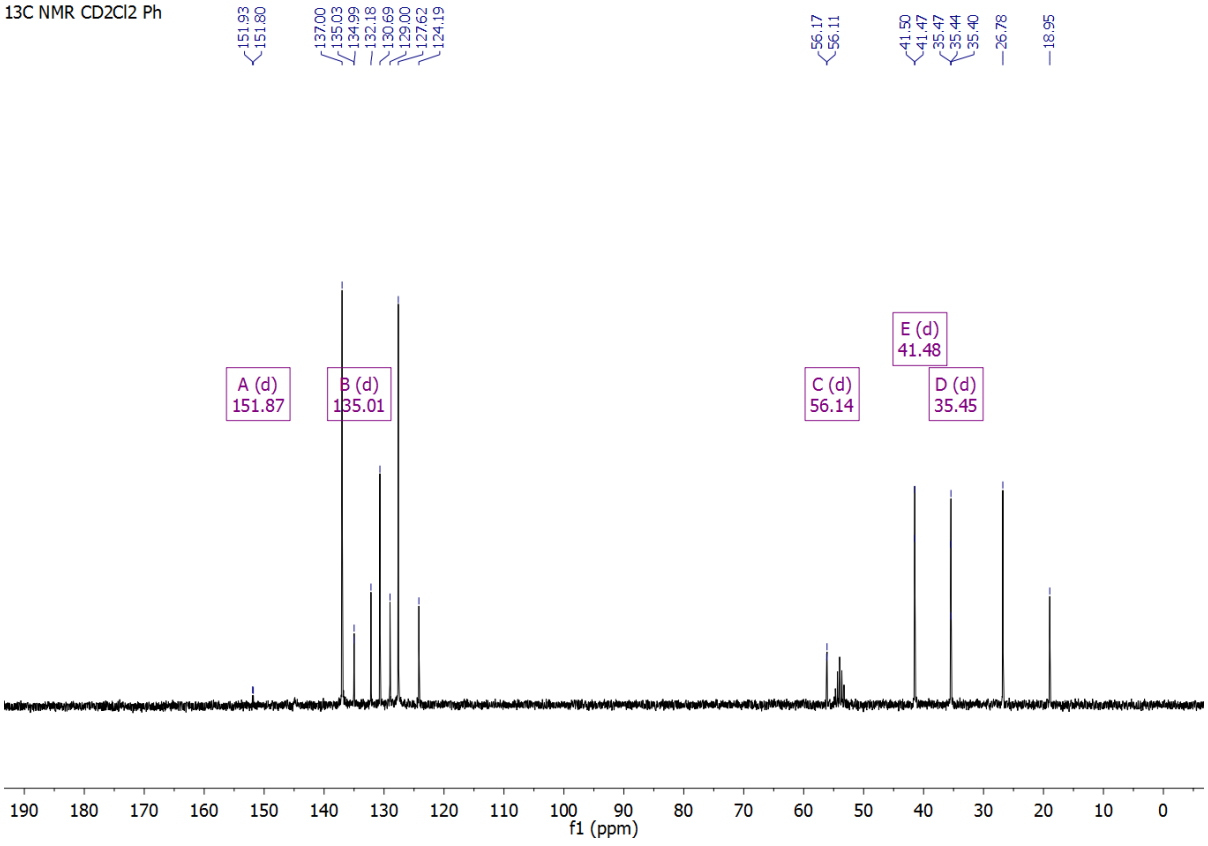
^{15}N NMR (30 MHz, CD_2Cl_2, δ, ppm): 76.45 (s)

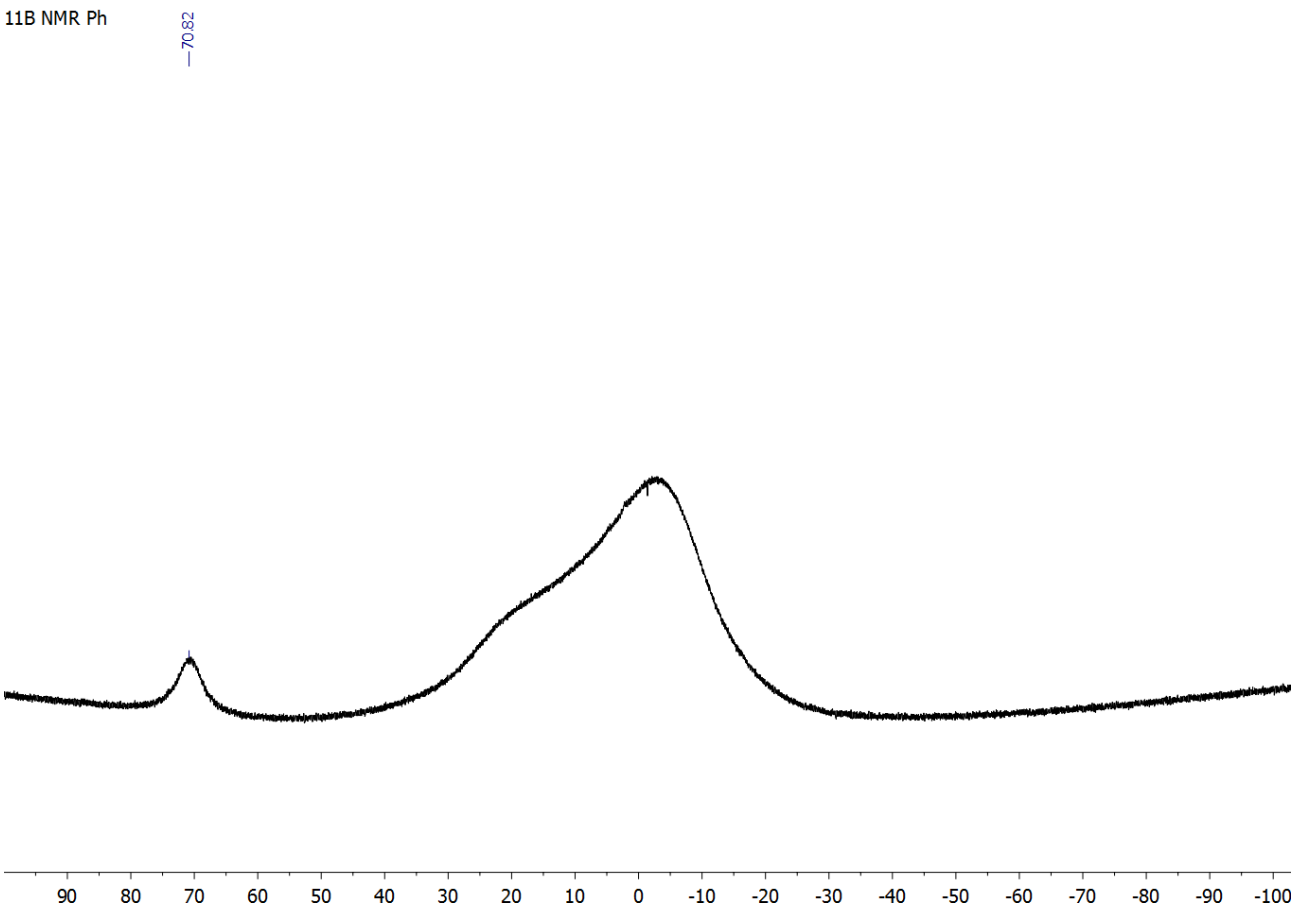
^{11}B NMR (160 MHz, CD_2Cl_2, δ, ppm): 70.82 (brs)

1H NMR CD2Cl2 Ph

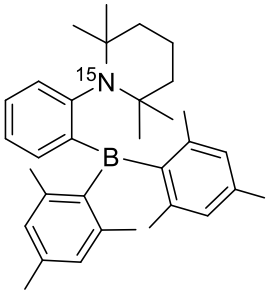


13C NMR CD2Cl2 Ph





1.3.3 1-(2-(dimesitylboranyl)phenyl)-2,2,6,6-tetramethylpiperidine-1-^{15}N (3)

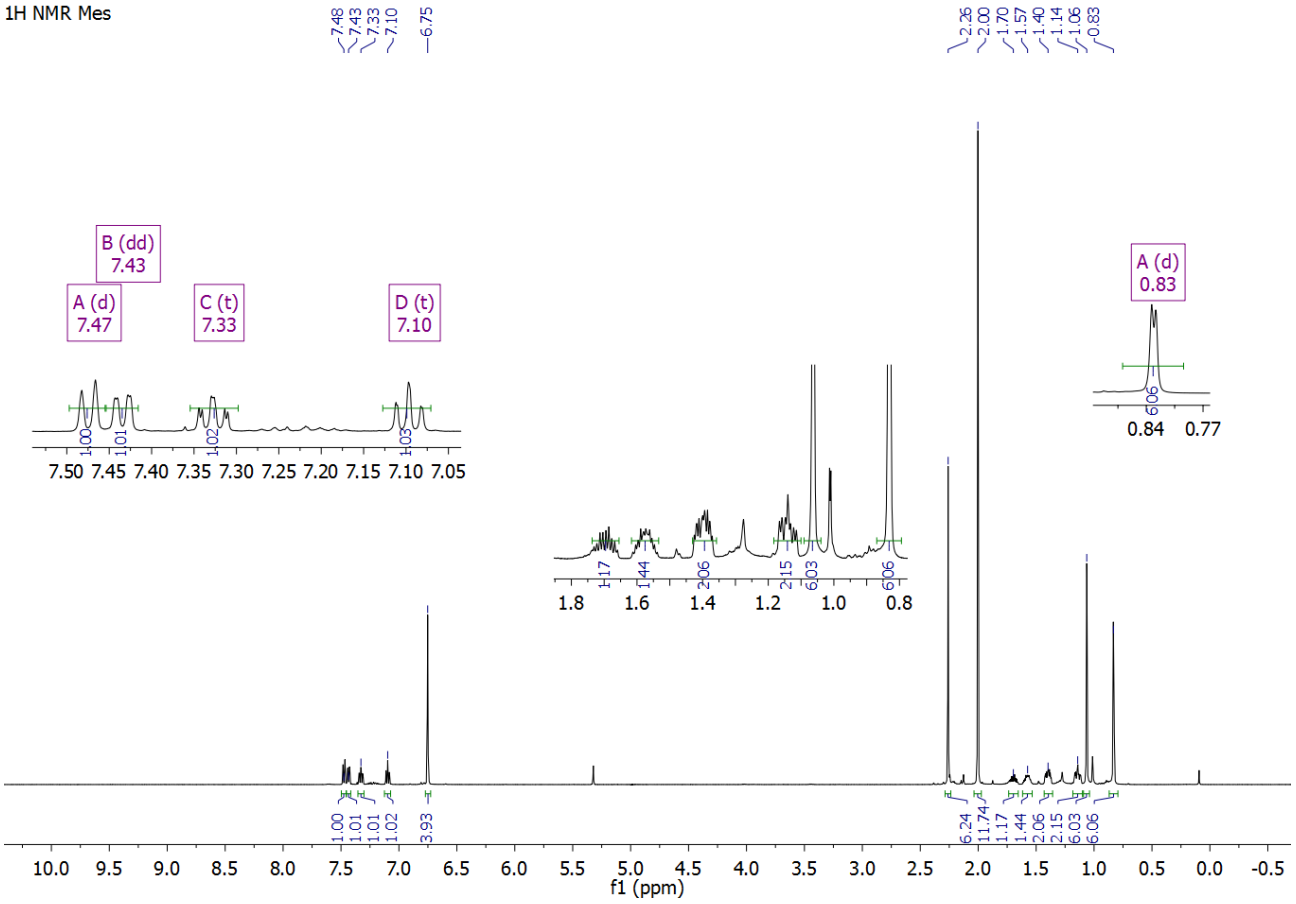


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 7.47 (d, *J* = 8.1 Hz, 1H), 7.43 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.33 (tm, *J* = 8.1, 1H), 7.10 (tm, *J* = 7.4, 1H), 6.75 (s, 4H), 2.26 (s, 6H), 2.00 (s, 12H), 1.70 (m, 1H), 1.57(m, 1H), 1.40 (m, 2H), 1.17 (m, 2H), 1.06 (s, 6H), 0.83 (d, *J* = 2.6 Hz, 6H).

^{13}C NMR (75.43 MHz, C_6D_6) δ ppm: (C-B not observed), 155.43 (d, *J* = 9.3 Hz), 142.06, 139.19, 138.04 (d, *J* = 3.0 Hz), 133.62, 130.11, 129.34,124.91, 56.19 (d, *J* = 4.7 Hz), 40.15, 34.02 (d, *J* = 3.4 Hz), 30.44, 24.95, 21.35, 18.93

^{15}N NMR (30 MHz, CD_2Cl_2, δ, ppm): 73.71 (s)

^{11}B NMR (160 MHz, CD_2Cl_2, δ, ppm): 74.88 (brs)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7.43
7.33
7.10
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2.00
1.70
1.57
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1.14
1.06
0.83
B (dd)
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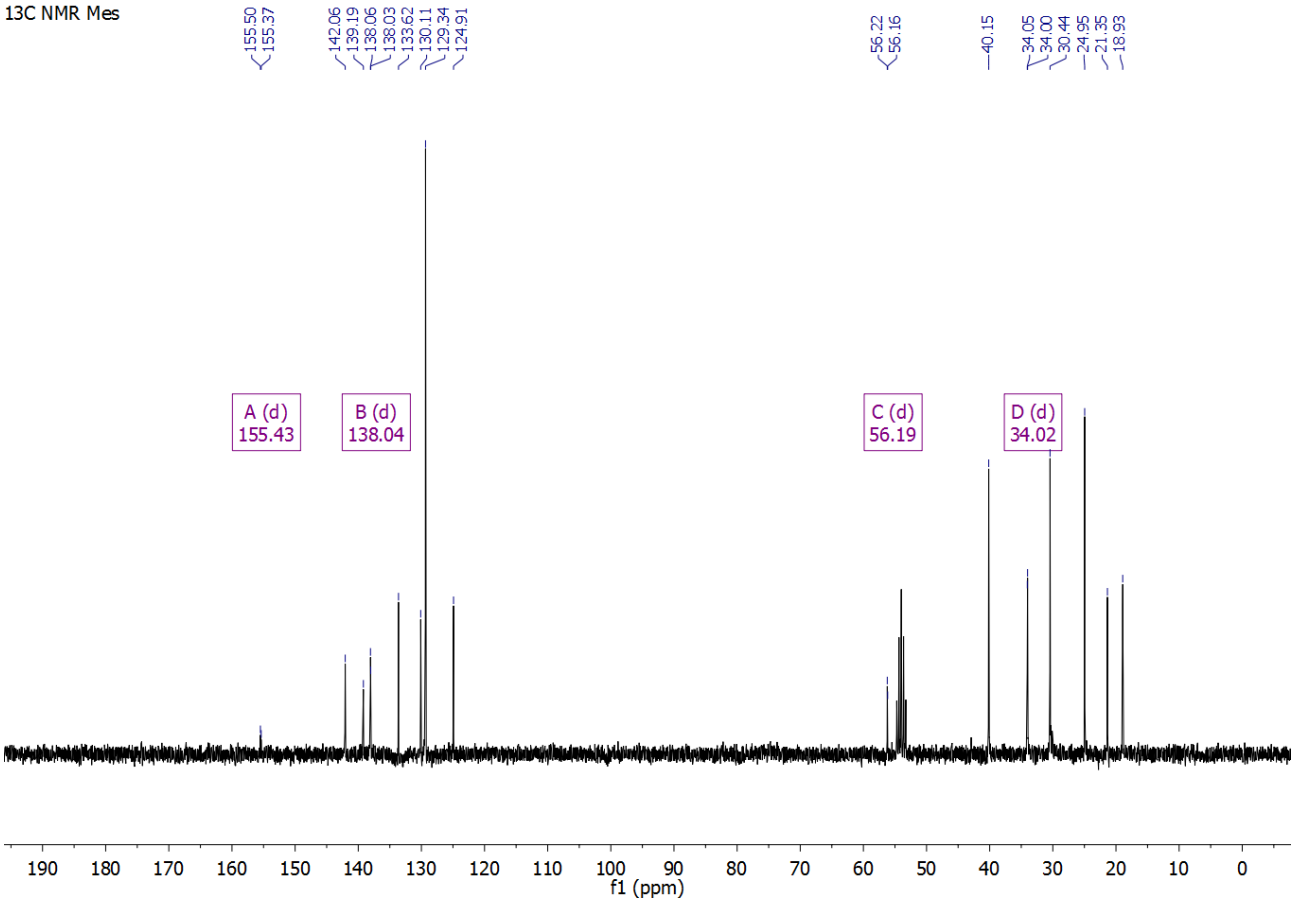
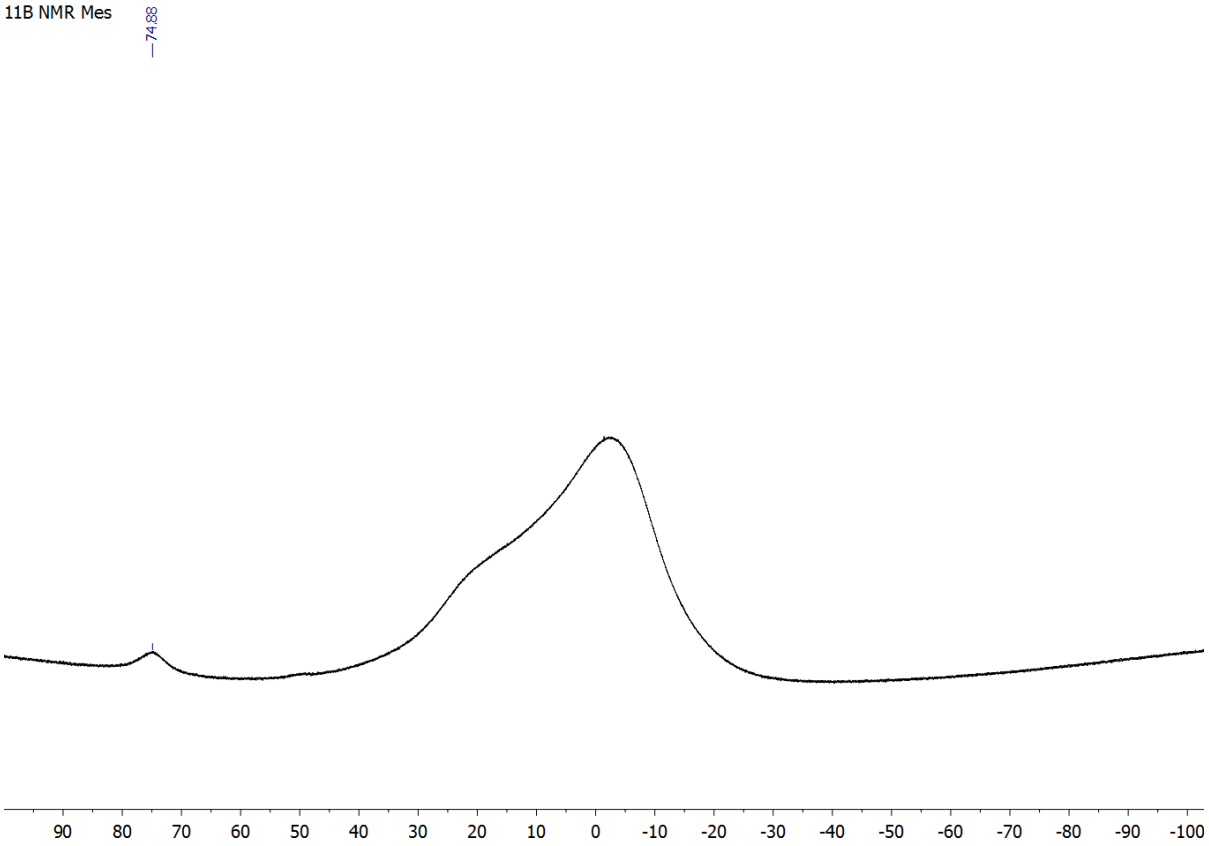
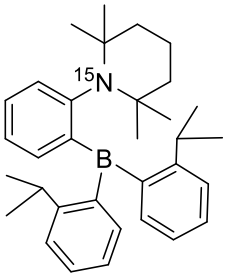
13C NMR Mes



11B NMR Mes



1.3.4 1-(2-(bis(2-isopropylphenyl)boranyl)phenyl)-2,2,6,6-tetramethylpiperidine-1-^{15}N (2)

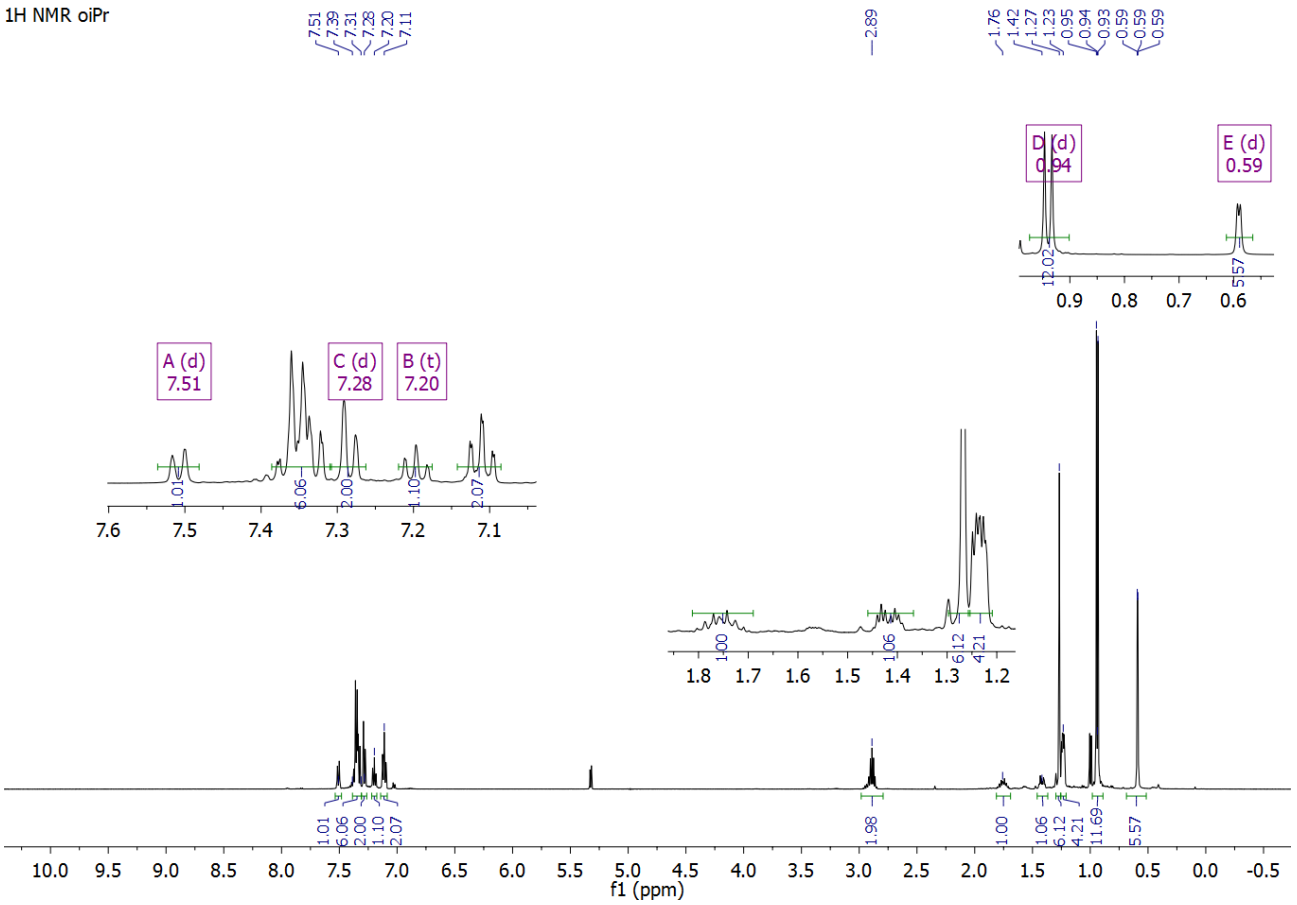


^{1}H NMR (500 MHz, CD_2Cl_2) δ ppm: 7.51 (dm, *J* = 8.2 Hz, 1H), 7.39-7.31 (m, 5H), 7.28 (d, *J* = 7.6 Hz, 4H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.11 (m, 2H), 2.89 (m, 2H), 1.76 (m, 1H), 1.42 (m, 1H), 1.27 (s, 6H), 1.23 (m, 4H), 0.94 (d, *J* = 6.8 Hz, 12H), 0.59 (d, *J* = 2.5 Hz, 11H)

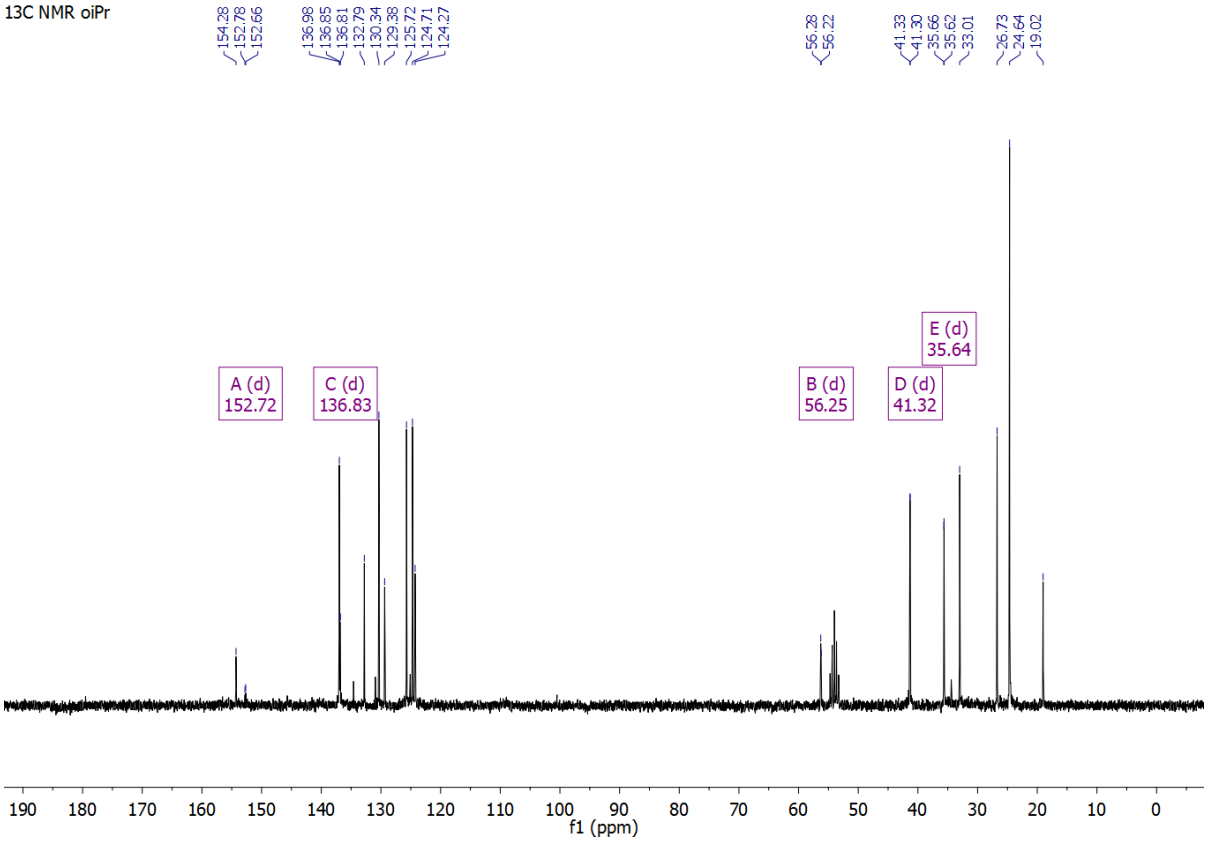
^{13}C NMR (75.43 MHz, C_6D_6) δ ppm: (C-B not observed), 154.28, 155.43 (d, *J* = 9.3 Hz), 136.98, 136.83 (d, *J* = 3.1 Hz), 132.79, 130.34, 129.38, 125.72, 124.71, 124.27, 56.25 (d, *J* = 4.9 Hz), 41.32 (d, *J* = 1.9 Hz), 35.64 (d, *J* = 2.4 Hz), 33.01, 26.73, 24.64, 19.02

^{15}N NMR (30 MHz, CD_2Cl_2, δ, ppm): 74.91 (s)

^{11}B NMR (160 MHz, CD_2Cl_2, δ, ppm): 73.40 (brs)



13C NMR oiPr



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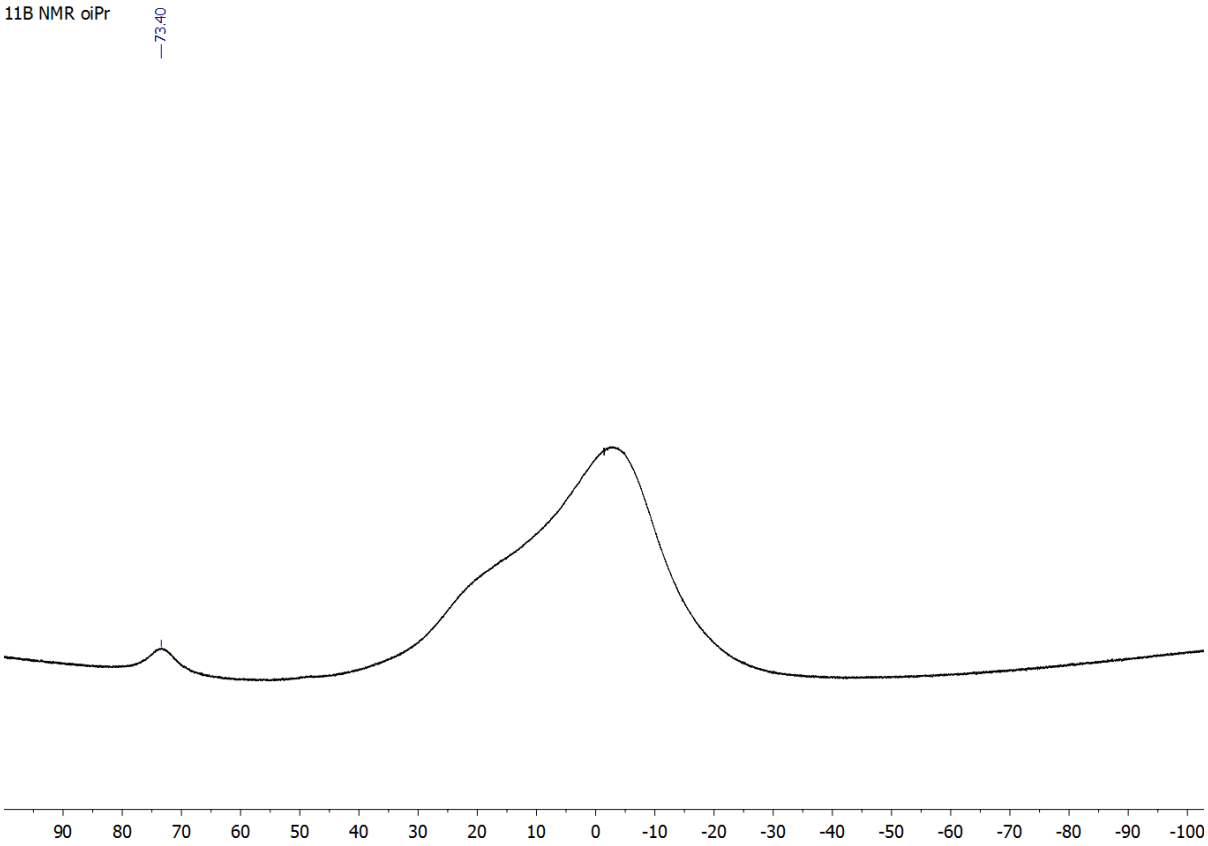

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(S2) Hall, P. L.; Gilchrist, J. H.; Harrison, A. T.; Fuller, D. J.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 9575.

(S3) Chernichenko, K.; Nieger, M.; Leskela, M.; Repo, T. *Dalton Trans.* **2012**, *41*, 9029.