Suplementary materials for

Hydrogen activation by 2-boryl-*N*,*N*-dialkylanilines: a revision of Piers' *ansa*-aminoborane

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Crystal structure determinations

Crystal structure studies of 2, $2H_2$ and 3: The single-crystal X-ray diffraction studies of **2 and $2H_2$** were carried out on a Bruker-Nonius Kappa-CCD diffractometer and **3** on a Bruker-Nonius APEXIIat 123(2) K using MoK_α radiation (λ = 0.71073 Å). Direct Methods (SHELXS-97) were used for structure solution, and full-matrix least-squares refinement on F^2 (SHELXL-97). [G. M. Sheldrick, Acta Crystallogr. **2008**, **A64**, 112-122] H atoms were localized by difference Fourier synthesis and refined using a riding model (H(N) and H(B) free).

2: colorless crystals, $C_{27}H_{22}BF_{10}N$, M = 561.27, crystal size 0.32 x 0.16 x 0.08 mm, monoclinic, space group $P2_1/c$ (No.14): a = 7.8910(5) Å, b = 17.3435(15) Å, c = 17.8672(15) Å, β = 101.330(7)°, V = 2397.6(3) Å^3, Z = 4, ρ (calc) = 1.555 Mg m^{-3}, F(000) = 1144, μ = 0.144 mm^{-1}, 25679 reflections ($2\theta_{max}$ = 55°), 5411 unique [R_{int} = 0.062], 352 parameters, R1 ($I > 2\sigma(I)$) = 0.058, wR2 (*all data*) = 0.121, GooF = 1.03, largest diff. peak and hole 0.292 and –0.271e Å^{-3}.

$2H_2$: colorless crystals, $C_{27}H_{24}BF_{10}N$ – 0.5 C_6D_6, M = 605.35, crystal size 0.30 x 0.15 x 0.10 mm, triclinic, space group P-1 (No.2): a = 10.944(1) Å, b = 11.974(1) Å, c = 12.513(1) Å, α = 117.39(1)°, β = 98.29(1)°, γ = 106.57(1)°, V = 1320.4(2) Å^3, Z = 2, ρ (calc) = 1.523 Mg m^{-3}, F(000) = 618, μ = 0.137 mm^{-1}, 20736 reflections ($2\theta_{max}$ = 55°), 6029 unique [R_{int} = 0.032], 385 parameters, R1 ($I > 2\sigma(I)$) = 0.044, wR2 (*all data*) = 0.112, GooF = 1.03, largest diff. peak and hole 0.320 and –0.230 e Å^{-3}.

3: colorless crystals, $C_{20}H_{10}BF_{10}N$, M = 465.10, crystal size 0.32 x 0.16 x 0.08 mm, monoclinic, space group $P2_1/c$ (No.14): a = 9.8216(4) Å, b = 35.0210(15) Å, c = 11.1291(4) Å, β = 107.047(2)°V = 3659.8(3) Å^3, Z = 8, ρ (calc) = 1.688 Mg m^{-3}, F(000) = 1856, μ = 0.170 mm^{-1}, 18746 reflections ($2\theta_{max}$ = 55°), 8151 unique [R_{int} = 0.031], 581 parameters, R1 ($I > 2\sigma(I)$) = 0.051, wR2 (*all data*) = 0.111, GooF = 1.11, largest diff. peak and hole 0.300 and –0.319 e Å^{-3}.

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 875800 (**2**), CCDC 875801 (**$2H_2$**) and CCDC 975802 (**3**), respectively. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

Experimental details

All the solvents were dried by conventional methods and stored over molecular sieves. Deutereited solvent were dried by standing over molecular sieves (3 Å) and used without additional purification. All operations were performed under argon atmosphere by conventional Schlenk technique or in a glove box (Mbraun Unilab). Reagents were purchased from Sigma-Aldrich, Acros Organics (*n*-butyllithium, boron trichloride solution), Strem (dimethyltin dichloride) and dried by conventional methods if needed.

NMR spectra were recorded at Varian Mercury 300 MHz NMR (^{1}H, ^{13}C, ^{19}F) or Varian Inova 500 MHz (^{1}H, ^{13}C, ^{10}B) spectrometers and were referenced to solvent (^{1}H, ^{13}C) or external standard (^{10}B, ^{19}F). ^{13}C spectra were ^{1}H decoupled and ^{10}B spectra were not ^{1}H decoupled, if not otherwise stated.

Hydrogen (5.0) was purchased from AGA and dried additionally by passing through the cylinder with molecular sieves. Hydrogenations (at 2 bar) were performed in thick-wall 25 ml Schlenk vessels or in J. Young valve NMR tubes purchased from Wilmad. Schlenk vessels were equiped with gas-tight teflon valves and Glindemann PTFE sealing rings.

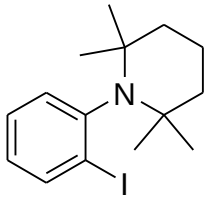
Chloro[bis(pentafluorophenyl)]borane was prepared as described.[1]

Starting imines and enamines have been prepared by conventional methods: **12**, **13**, **16**, **17** by the TsOH-catalyzed condensation of the respective amines and the carbonyl compounds with removal of water by either azeotropic distillation or molecular sieves or sodium sulfate. **15** by a condensation of *N*-vinylpyrrolidin-2-one with ethyl benzoate.[2] **14** by a decarboxylation of 2-phenyl-4-quinolinecarboxylic acid.

1-(2-iodophenyl)-2,2,6,6-tetramethylpiperidine (7)

[1] D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492.

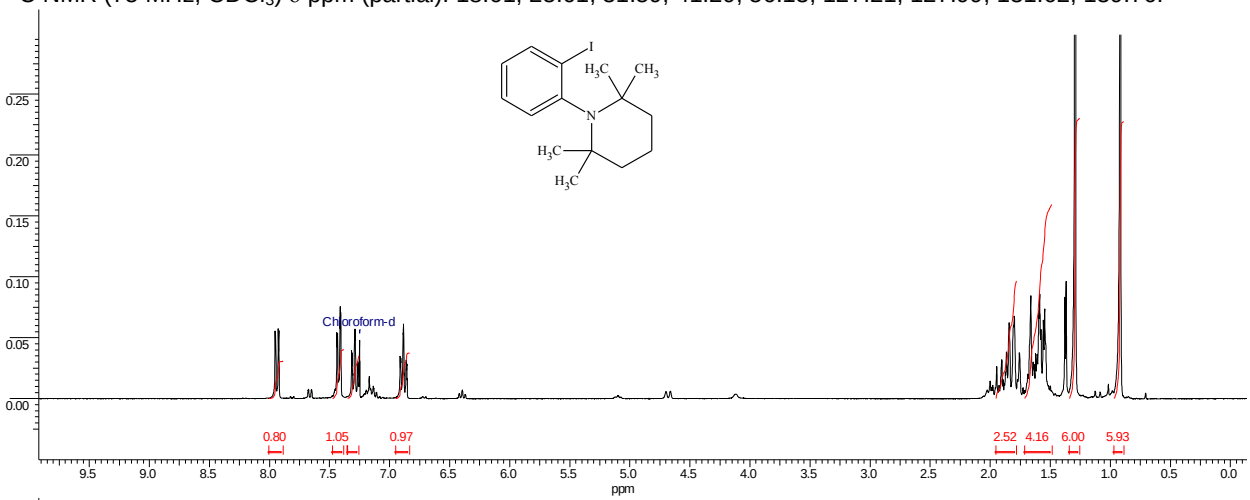
[2] Kirk L. Sorgi, Cynthia A. Maryanoff, David F. McComsey, and Bruce E. Maryanoff, *Org. Synth.* 1998, **75**, 215

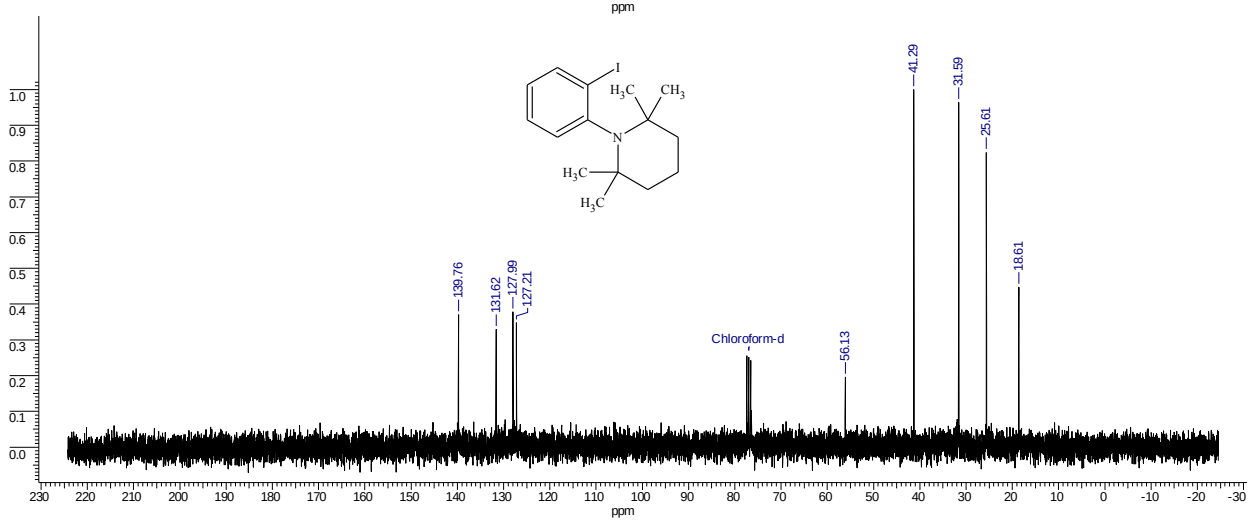


was prepared by a modified procedure.[3] 14.1 g of 2,2,6,6-tetramethylpiperidine (0.1 mol), followed by 150 ml of THF, were placed into a three-neck flask equipped with an internal thermometer. The reaction mixture was cooled to -40 °C with stirring and 40 ml of 2.5M buthyllithium solution in hexane were added via syringe. Temperature grew up to -20 °C and the reaction mixture was stirred at this temperature for additional 20 min. The reaction was cooled to -50 °C and 40.8 g of iodobenzene (0.2 mol) in 50 ml of THF were added via syringe, maintaining temperature below -40 °C. The reaction mixture was then stirred at -40 °C for 1 h and left stirred immersed in a thermally isolated cooling bath over night. 10 ml of aq. NH_4Cl followed by 100 ml of hexane were added and, after several minutes of stirring, the organic layer was separated in a separatory funnel. The aqueous layer was additionally washed with 50 ml of hexane; the organic extracts were combined, dried over Na_2SO_4 and rotavapored. A remaining oil was vacuum-distilled (1 torr) to give some recovered iodobenzene (40 °C), then *N*-phenyl-2,2,6,6-tetramethylpiperidine together with biphenyl (70-100 °C) and the title compound (120 °C) of 95% purity as a yellowish oil (32%).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 0.92 (s, 6 H), 1.30 (s, 6 H), 1.50-1.70 (m, 4H), 1.80-1.95 (m, 2H), 6.89 (tm, *J*=7.5 Hz, 1 H), 7.30 (tm, *J*=7.5 Hz, 1 H), 7.42 (dm, *J*=7.8 Hz, 1 H) 7.94 (dm, *J*=7.8 Hz, 1 H).

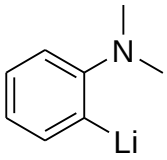
^{13}C NMR (75 MHz, $CDCl_3$) δ ppm (partial): 18.61, 25.61, 31.59, 41.29, 56.13, 127.21, 127.99, 131.62, 139.76.





[3] S. Tripathy, R. LeBlanc, and T. Durst, *Org. Lett.*, 1999, **1**, 1973–1975.

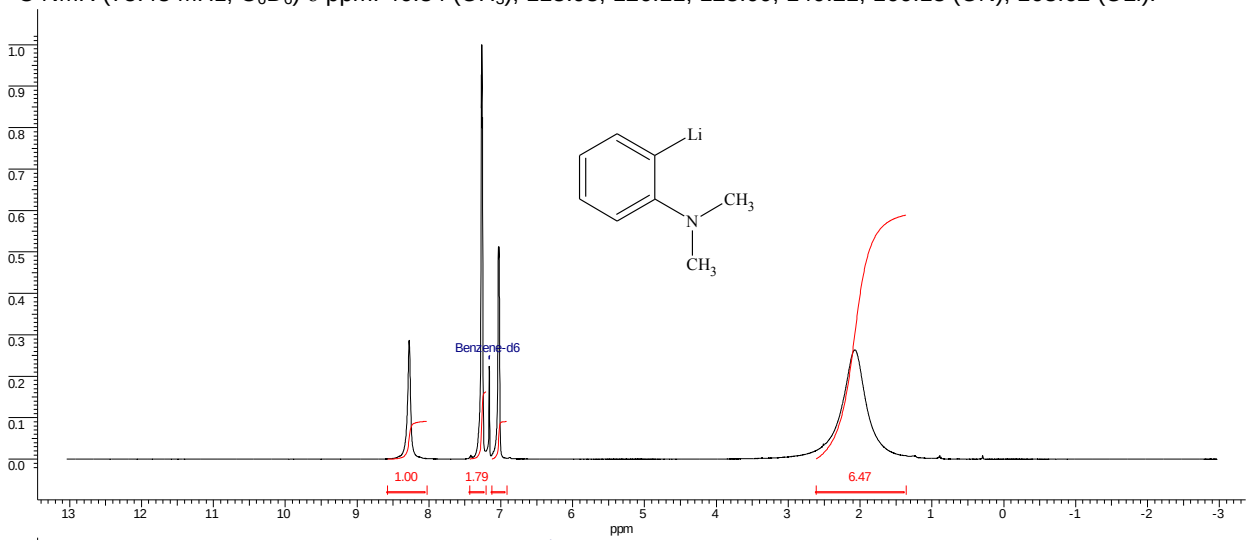
[2-(dimethylamino)phenyl]lithium (10)

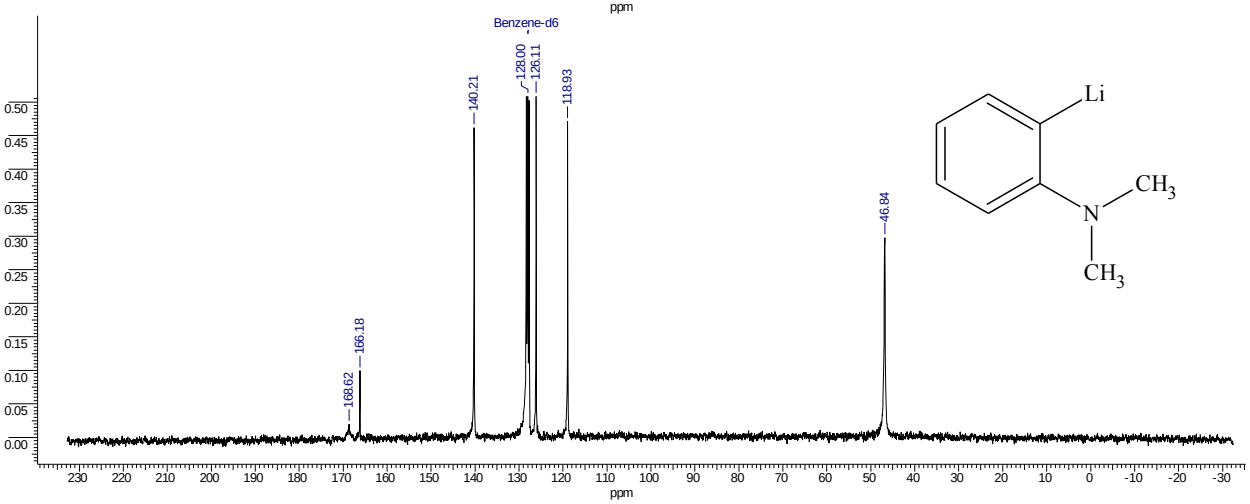


Into a 100 ml Schlenk flask 7.23 g of 2-bromo-*N*,*N*-dimethylaniline (36.1 mmol) and 30 ml of hexane were placed. It was cooled in a ice bath and 22.6 ml of 1.6M buthyllithium (36.1 mmol) solution were added in small portions using syringe during 15 min and stirred with ice bath cooling for another 3 h. Hexane was evaporated in vacuo almost to dryness leaving a white slurry which was transferred to a glass filter and thoroughly washed with 4-6 ml portions of hexane (totally around 30 ml). The white solid was dried in vacuo, 4.13 g (90%).

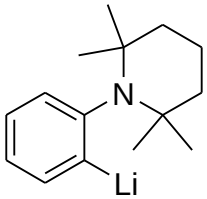
^{1}H NMR (500 MHz, C_6D_6) δ ppm: 2.02 (br. s., 6 H), 7.02 (m, 1 H), 7.34 (m, 2 H), 8.27 (s, 1 H).

^{13}C NMR (75.43 MHz, C_6D_6) δ ppm: 46.84 (*C*H$_3$), 118.93, 126.11, 128.00, 140.21, 166.18 (*C*N), 168.62 (*C*Li).





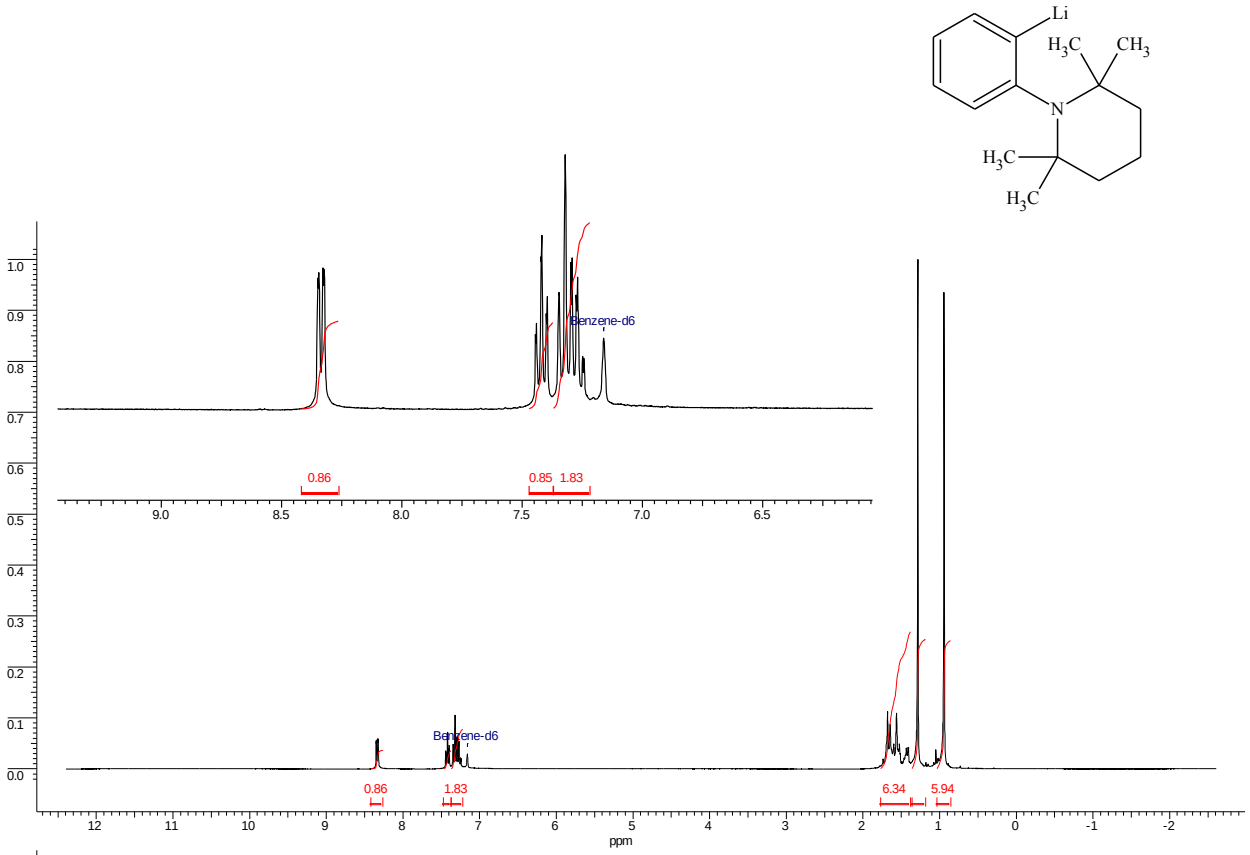
[2-(2,2,6,6-tetramethylpiperidin-1-yl)phenyl]lithium (9)

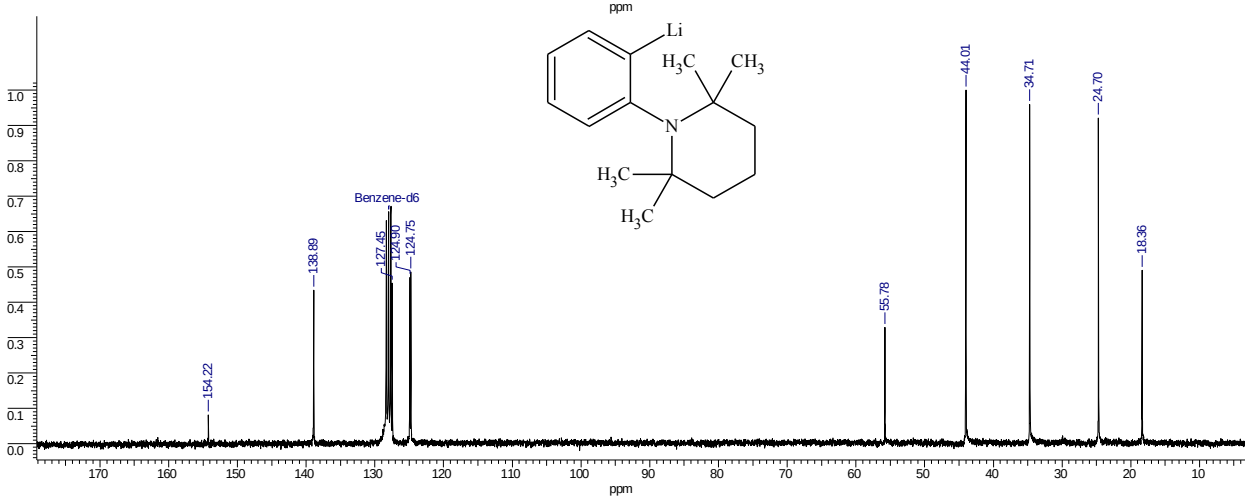


Was prepared similar to [2-(dimethylamino)phenyl]lithium. 8.3 g of 1-(2-iodophenyl)-2,2,6,6-tetramethylpiperidine (24.2

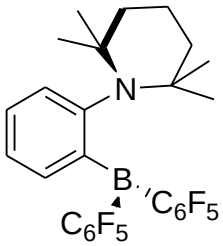
mmol) in 75 ml of hexane were treated with 15.1 ml of 1.6M buthyllithium solution in hexane with ice bath cooling. The mixture was stirred at +5 °C for additional 4 h, then cooled to -30 °C and filtered. The white precipitate was washed with 4x10 ml of cold (-30 °C) hexane and dried in vacuum to give 5.22 g (97%) of a white powder.

^{1}H NMR (300 MHz, C_6D_6) δ ppm: 0.93 (s, 6 H), 1.28 (s, 6 H), 1.40-1.75 (m, 6 H), 7.20-7.37 (m, 2 H), 7.42 (tm, *J*=6.6 Hz, 1 H), 8.32 (dm, *J*=6.6 Hz, 1 H).
^{13}C NMR (75.43 MHz, C_6D_6) δ ppm (partial): 18.36, 24.70, 34.71, 44.01, 55.78, 124.75, 124.90, 127.45, 138.89, 154.22.



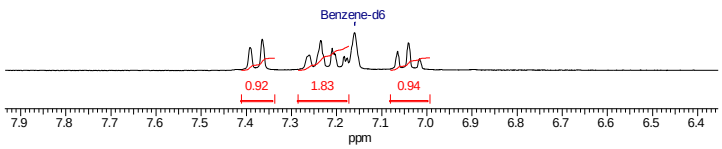


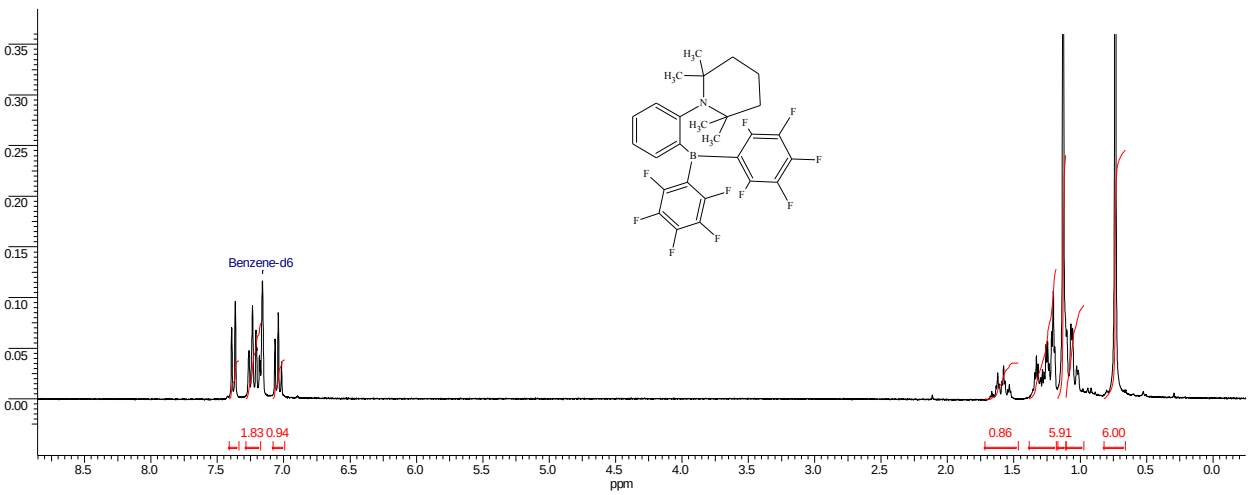
1-{2-[bis(pentafluorophenyl)boryl]phenyl}-2,2,6,6-tetramethylpiperidine (2)

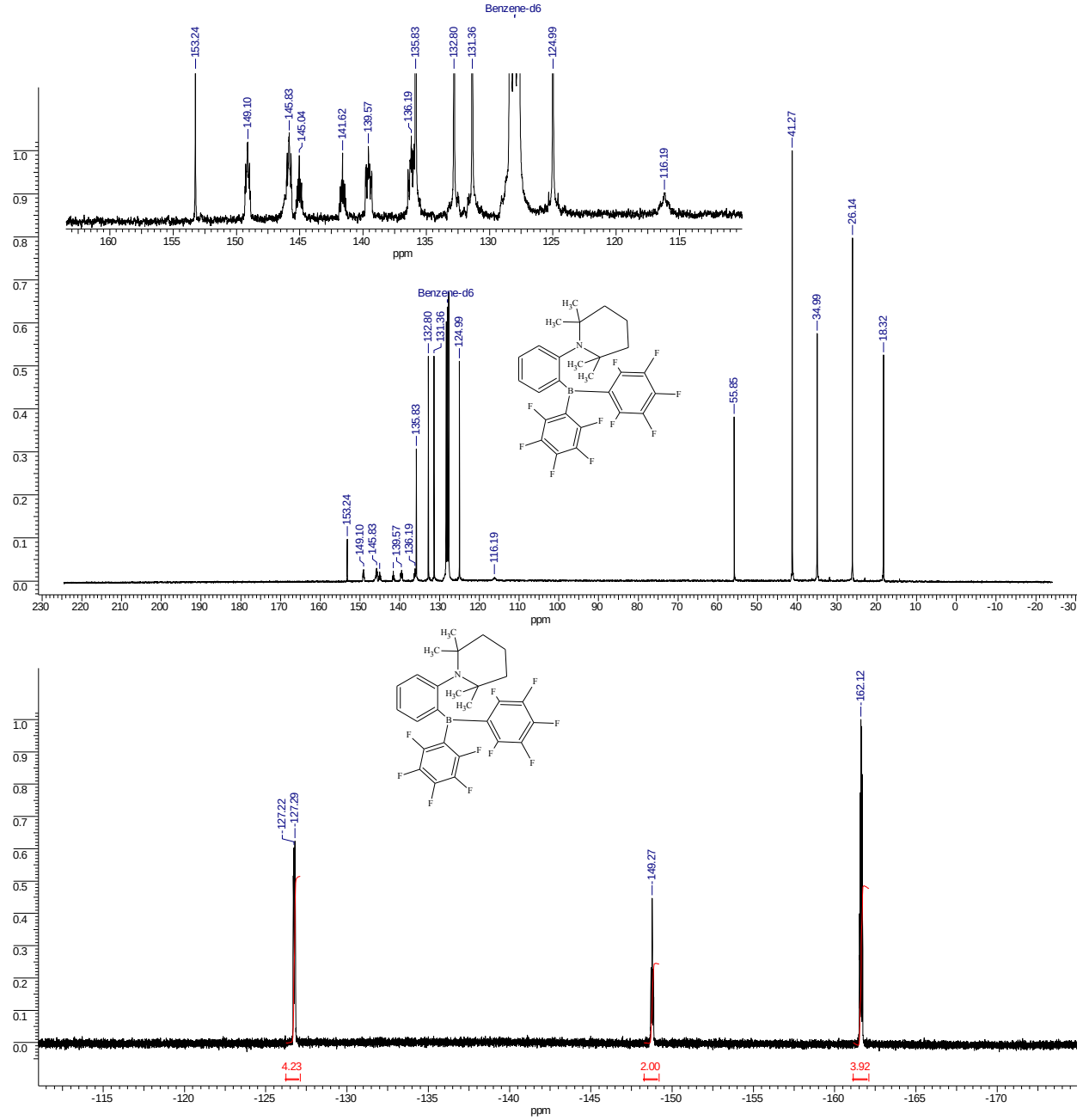


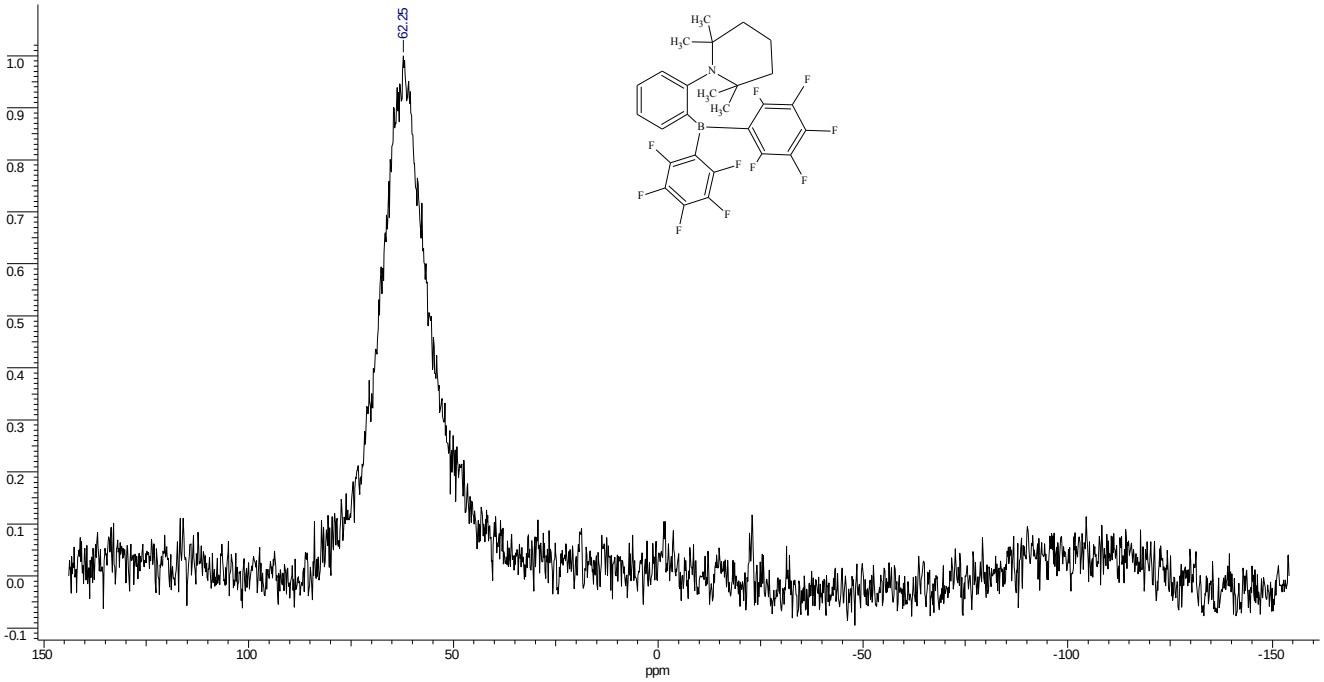
In two separate Schlenk tubes 1.17 g of [2-(2,2,6,6-tetramethylpiperidin-1-yl)phenyl]lithium (5.26 mmol) was suspended in 15 ml of toluene, and 2 g of chloro[bis(pentafluorophenyl)]borane dissolved in 25 ml of toluene. Both tubes were cooled to -80 °C and the suspension of the lithium compound was added to the chloroborane via cannula in one portion. The resultant reaction mixture was allowed to warm to room temperature naturally and stirred over night, then evaporated to a half of the volume and 20 ml of hexane were aded. Lithium chloride was filtered off and the residue evaporated to give the title compound as spectroscopically pure orange crystalls (2.95 g, 100%). The solid may contain some residual toluene and minor amounts of a polymeric tar, in this case additional purification can be performed; the crude material was redissolved in hot hexane and filtered hot, then evaporated and dried in vacuum at 50 °C. An analytical sample was prepared by recrystallization from 5 ml of hexane (1.53 g, 52%). The recrystallizing material should be free of toluene as it is occluded into the crystals. The crystals suitable for X-ray diffraction analysis were collected from the recrystallization crop.

^{1}H NMR (300 MHz, C_6D_6), δ ppm: 0.73 (s, 6 H), 1.0-1.35 (m, 5H), 1.14 (s, 6 H), 1.50-1.70 (m, 1 H), 7.04 (t, *J*=7.14 Hz, 1 H), 7.23 (m, 2 H), 7.38 (d, *J*=8.24 Hz, 1 H)
^{13}C NMR (75 MHz, C_6D_6), δ ppm: 18.32 (s), 26.14 (s), 34.99 (s), 41.27 (s), 55.85 (s), 116.19 (pseudo-t), 124.99 (s), 131.36 (s), 132.80 (s), 135.83 (s), 137.88 (dm, J=255 Hz), 143.33 (dm, J=257 Hz), 147.47 (dm, J=247 Hz), 153.24 (s).
^{19}F NMR (282 MHz, C_6D_6), δ ppm: -127.2 (dm, J=23 Hz, 4F), -149.3 (d, J=20.5 Hz, 2F), -162.1 (m, 4F).
^{10}B NMR (282 MHz, C_6D_6), δ ppm: 62.3 (br. s. $\nu_{1/2}$~630 Hz).
HRMS-ESI^{+}: found 562.1781, calc. 562.1758 for $[C_{27}H_{23}BF_{10}N]^{+}$, $[M+H]^{+}$.

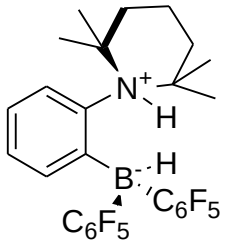








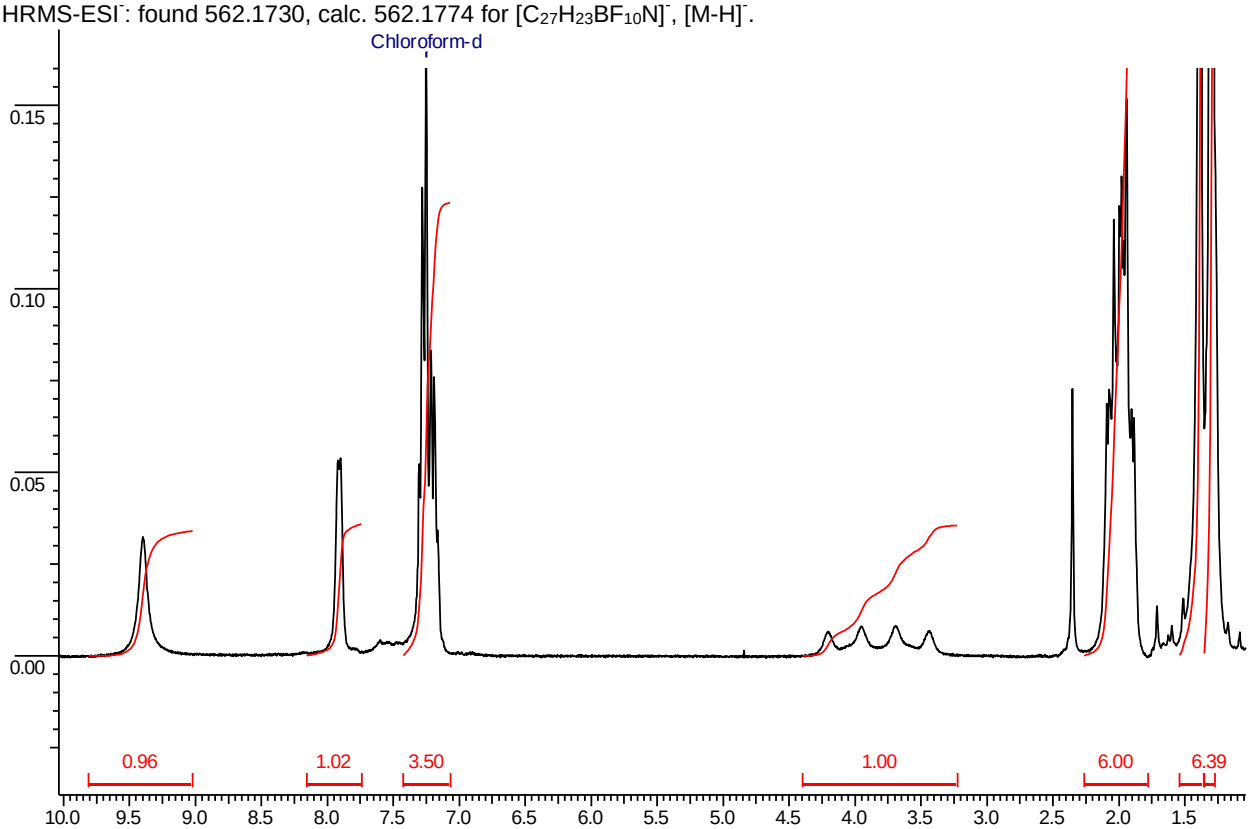
Hydrido[bis(pentafluorophenyl)][2-(2,2,6,6-tetramethylpiperidinium-1-yl)phenyl]borate(1-) ($2H_2$)

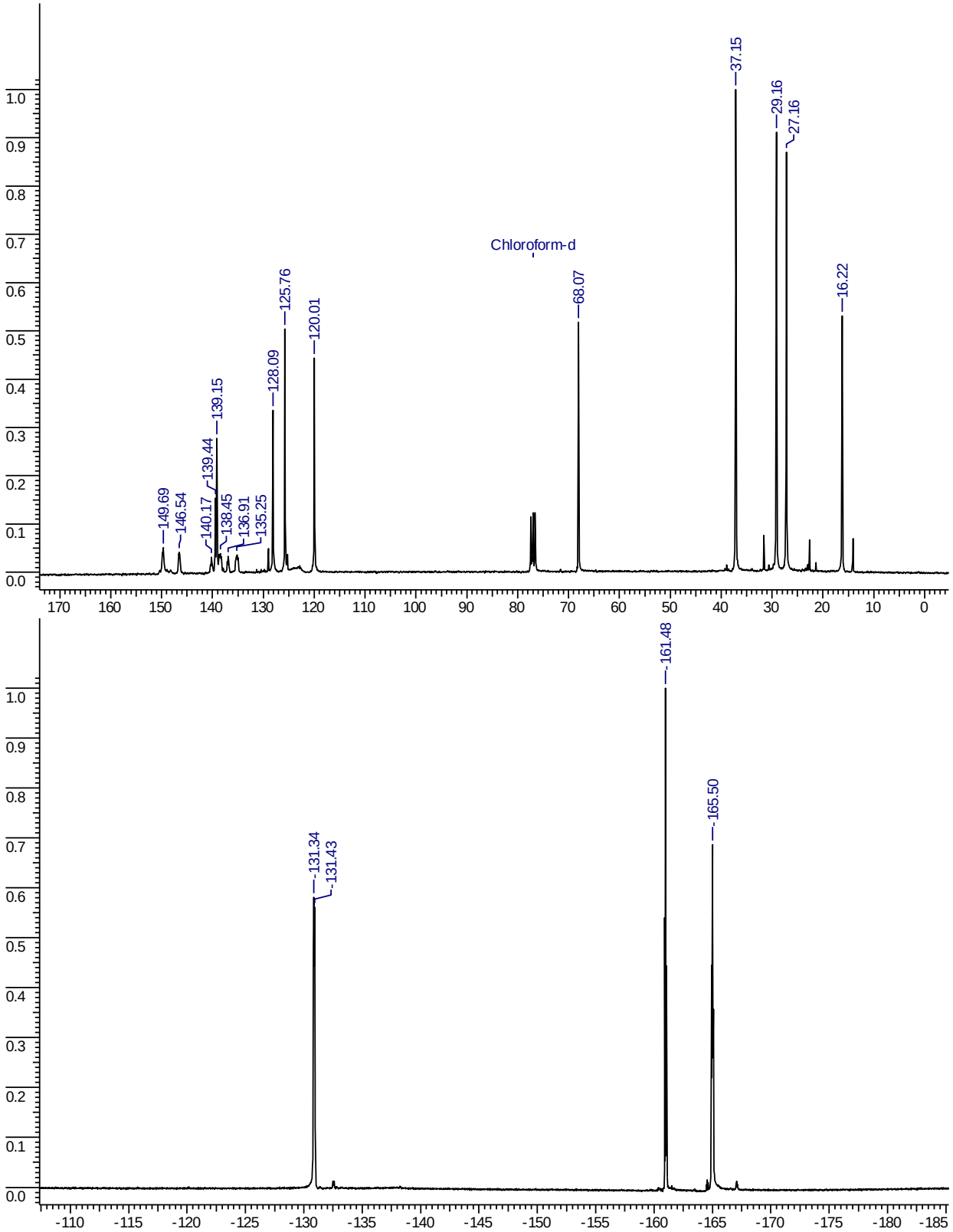


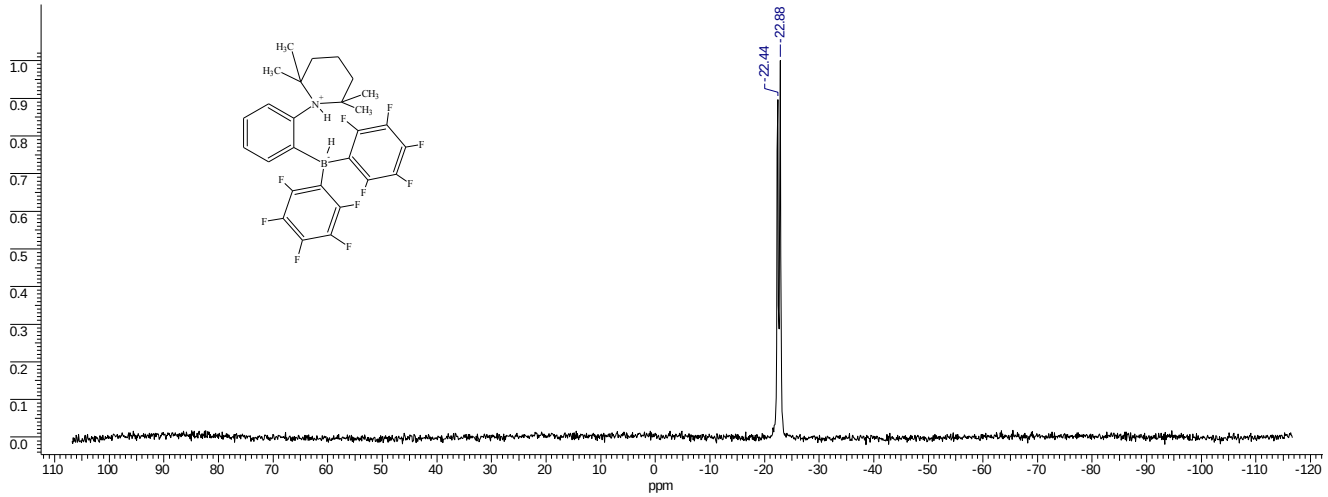
500 mg of 1-{2-[bis(pentafluorophenyl)boryl]phenyl}-2,2,6,6-tetramethylpiperidine and 5 ml of toluene were placed into a 50 ml Schlenk tube, the tube was filled with 2 bar of hydrogen by two freeze-pump-thaw cycles and stirred at room temperature for 30 min. Disappearance of the color occurred at room temperature almost instantly. The solvent was evaporated in vacuum to give the product quantatively.

Atlernatively 50 mg of pure 1-{2-[bis(pentafluorophenyl)boryl]phenyl}-2,2,6,6-tetramethylpiperidine were dissolved in 0.5 ml of C_6D_6 and placed into a J. Young valve NMR tube, filled with 2 bar of hydrogen and monitored by NMR at 70 °C. Upon cooling white crystals precipitated, which were collected and analyzed by X-ray diffraction method.

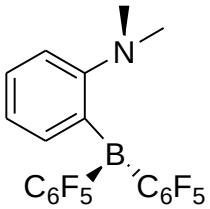
^{1}H NMR ($CDCl_3$, 300 MHz): δ ppm 1.30 (s, 6H), 1.39 (s, 6H), 1.8-2.15 (m, 6H), 3.81 (br. q. J=76 Hz, 1H, B*H*), 7.10-7.35 (m, 3H), 7.91 (d, J=6.8 Hz, 1H), 9.40 (br. s, 1H, N*H*).
^{13}C NMR ($CDCl_3$, 75 MHz): δ ppm (ppm) 16.22 (s), 27.16 (CH_3), 29.16 (s), 37.15 (s), 68.07 (s), 120.01 (s), 125.76 (s), 128.09 (s), 136.84 (d, J=248.5 Hz), 138.5 (d, J=246.8 Hz), 139.15 (m), 139.43 (s), 148.1 (d, J=237.6 Hz), 149.2 (q, J=55 Hz).
^{19}F NMR ($CDCl_3$, 282 MHz): δ ppm -131.35 (d, J=24.4 Hz, 4F, *o*-F), -161.48 (tr, J=24.4 Hz, 2F, *p*-F), -165.50 (tr. d. J=24 Hz, J,=21 Hz, 4F, *m*-F).
^{10}B NMR (C_6D_6, 53.7 MHz): δ ppm -22.7 (d, J_{BH}=23.5 Hz).
HRMS-ESI$^-$: found 562.1730, calc. 562.1774 for $[C_{27}H_{23}BF_{10}N]^-$, $[M\text{-}H]^-$.





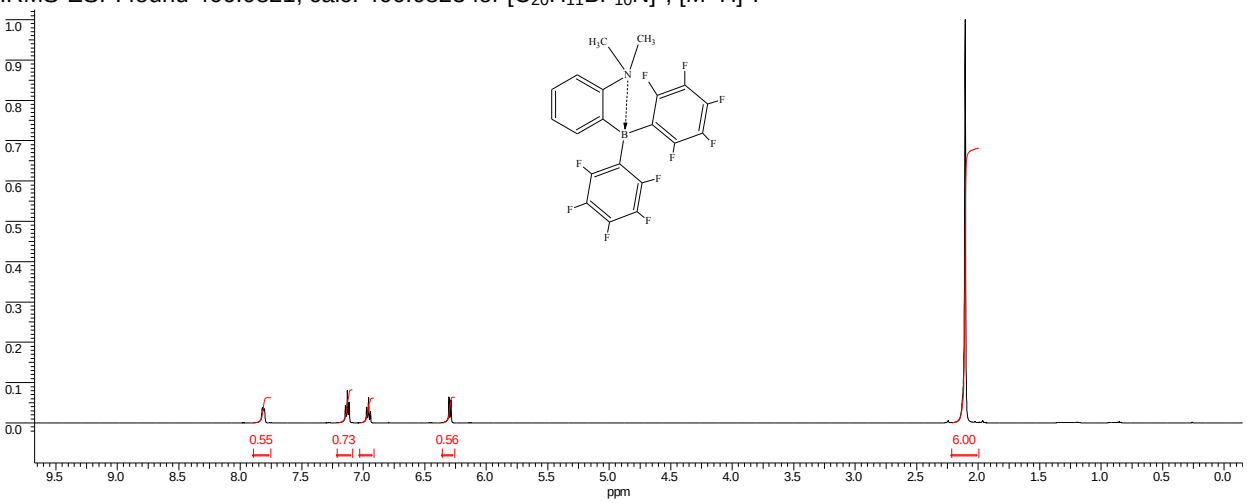


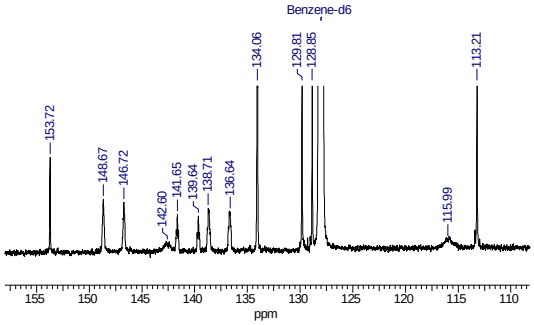
2-[bis(pentafluorophenyl)boryl]-*N*,*N*-dimethylaniline (3)

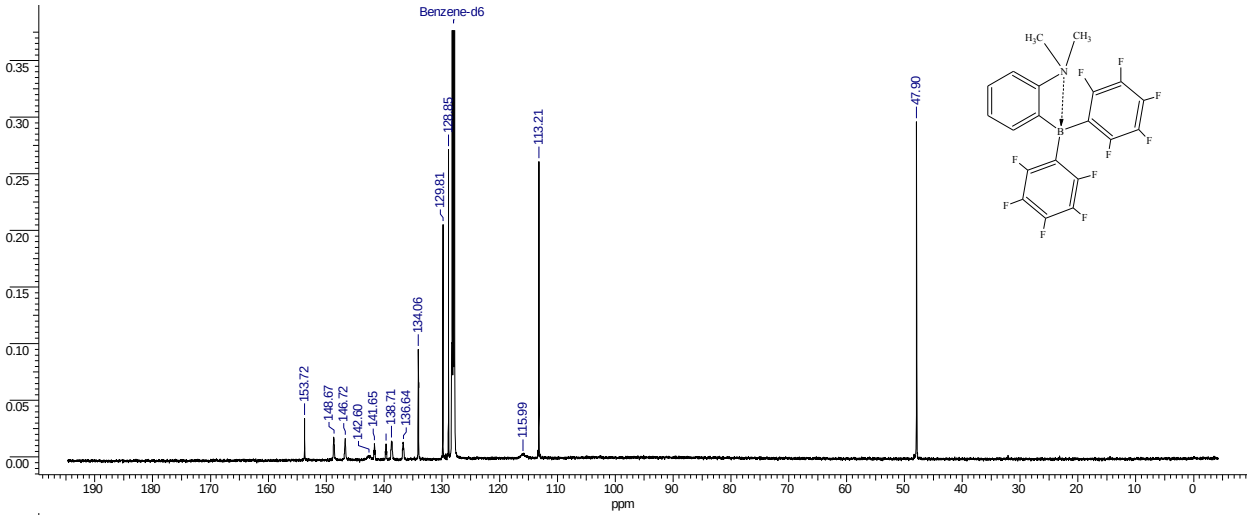


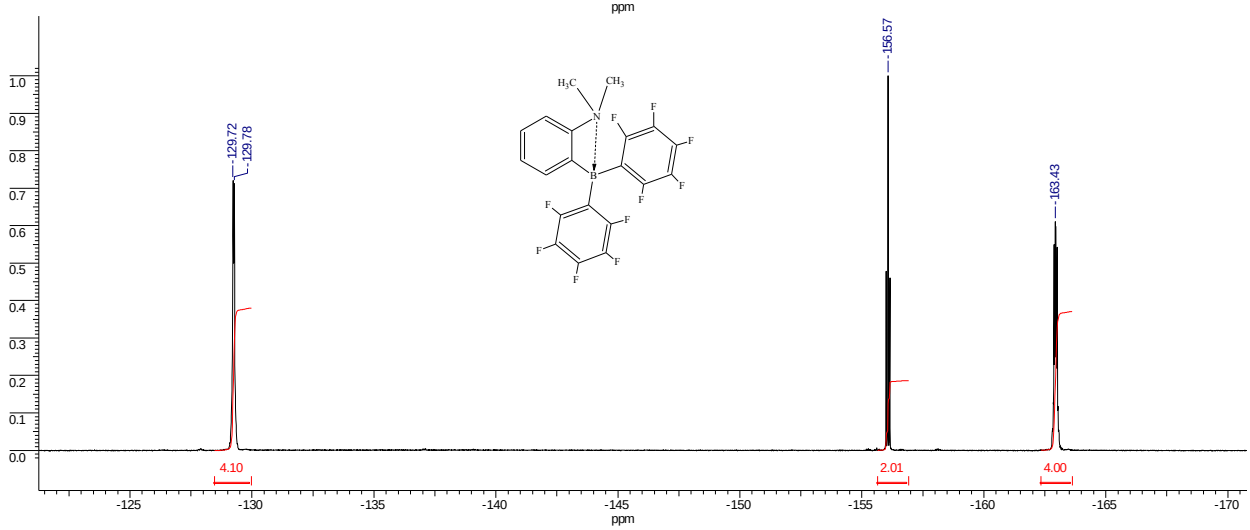
To a solution of 1520 mg of chloro[bis(pentafluorophenyl)]borane (4 mmol) in 10 ml of toluene at -90 °C a precooled to -90 °C suspension of 508 mg [2-(dimethylamino)phenyl]lithium (4 mmol) in 5 ml of toluene was added in one portion via canula. Organolithium was additionally rinsed with 5 ml of toluene and transferred to reaction Schlenk tube. Reaction was allowed to warm to room temperature naturally and stirred over night, then evaporated to a half of the volume and 5 ml of hexane were added. A precipitate was filtered off and the solvent was evaporated in vacuum to give 1820 mg of a crude compound. It was recrystalized from 5 ml of hexane and filtered. Grey crystals were redissolved in a hot 4:1 hexane-toluene mixture (10 + 5 ml) and filtered hot. A filtrate was evaporated to give 1280 mg (69 %) of white crystals.

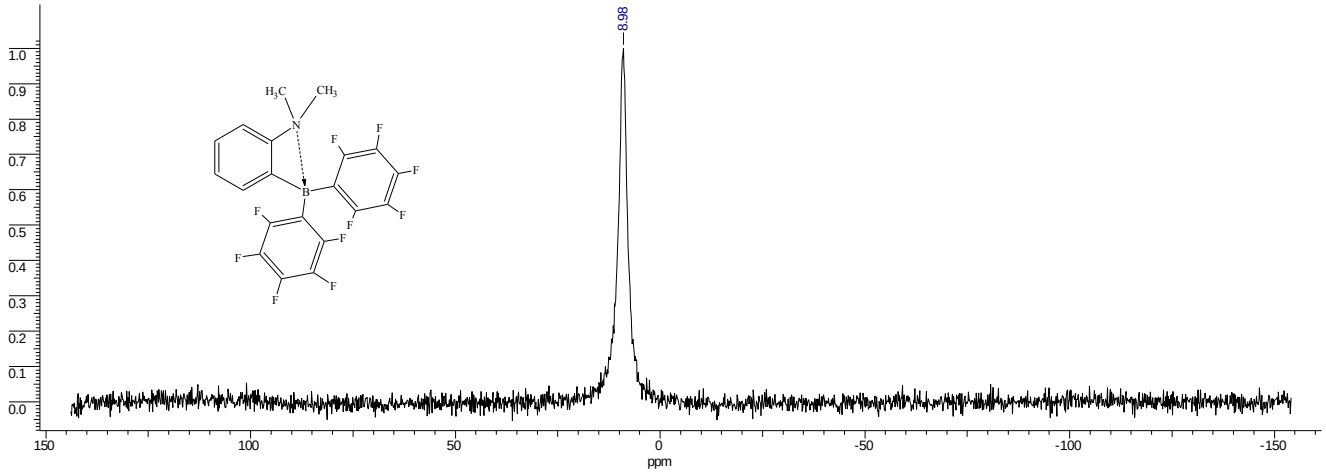
^{1}H NMR (500 MHz, C_6D_6): δ ppm 2.10 (s, 6 H), 6.30 (d, *J*=7.8 Hz, 1 H), 6.96 (t, *J*=7.8 Hz, 1 H), 7.13 (t, *J*=7.3 Hz, 1 H), 7.81 (d, *J*=6.8 Hz, 1 H).
^{13}C NMR (125.7 MHz, C_6D_6): δ ppm 47.90 (s),113.21 (s),115.99 (br. m),128.85 (s),129.81 (s),134.06 (t, J=3.8 Hz),137.68 (dm, J=250 Hz), 140.64 (dm, J=250 Hz),142.60 (br. m),147.70 (dm, J=245 Hz),153.72 (s).
^{19}F NMR (282 MHz, C_6D_6): δ ppm -129.7 (d, J=15.2 Hz, 4F, *o*-F), -156.57 (t, J=21.3 Hz, 2F, *p*-F), -163.43 (m, 4F, *m*-F).
^{10}B NMR (53.7 MHz, C_6D_6): δ ppm 9.0 (s)
HRMS-ESI^{+}: found 466.0821, calc. 466.0823 for $[C_{20}H_{11}BF_{10}N]^{+}$, $[M+H]^{+}$.



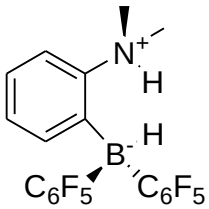








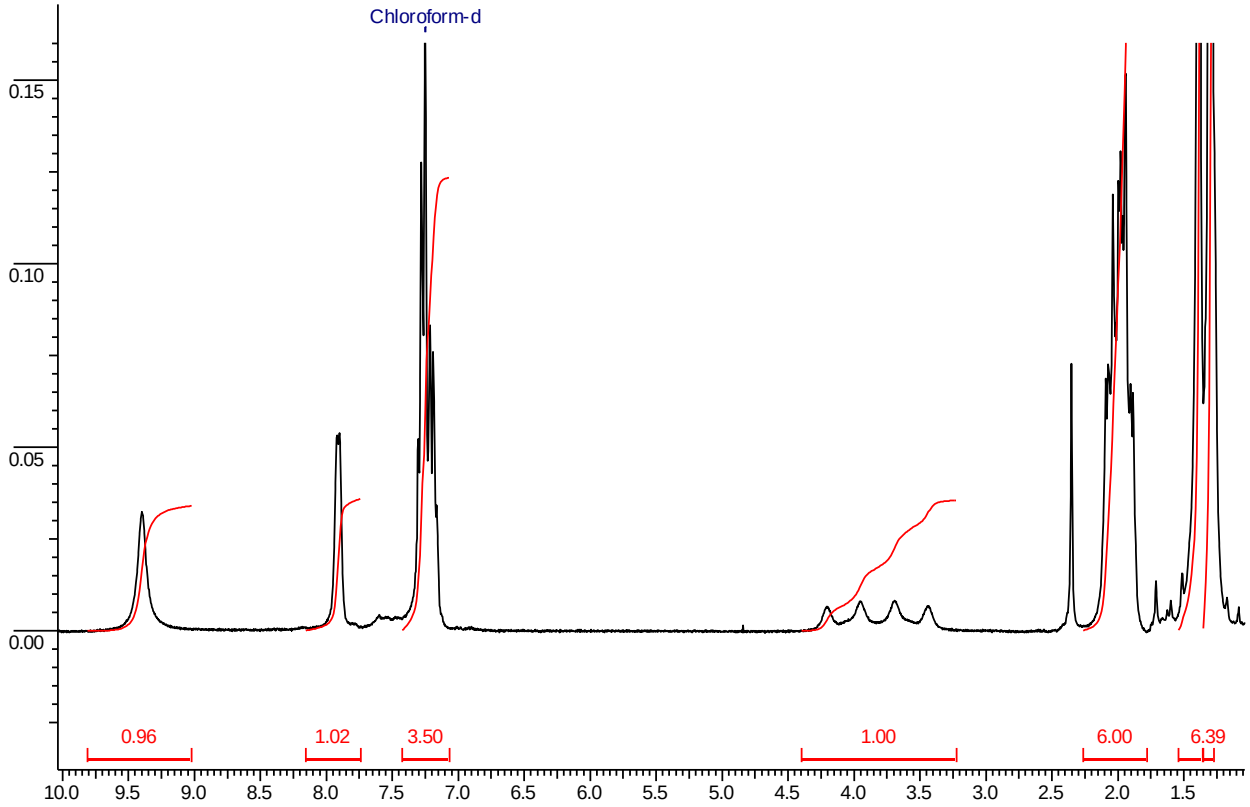
[2-(dimethylammonio)phenyl](hydrido)bis(pentafluorophenyl)borate(1-) ($3H_2$)

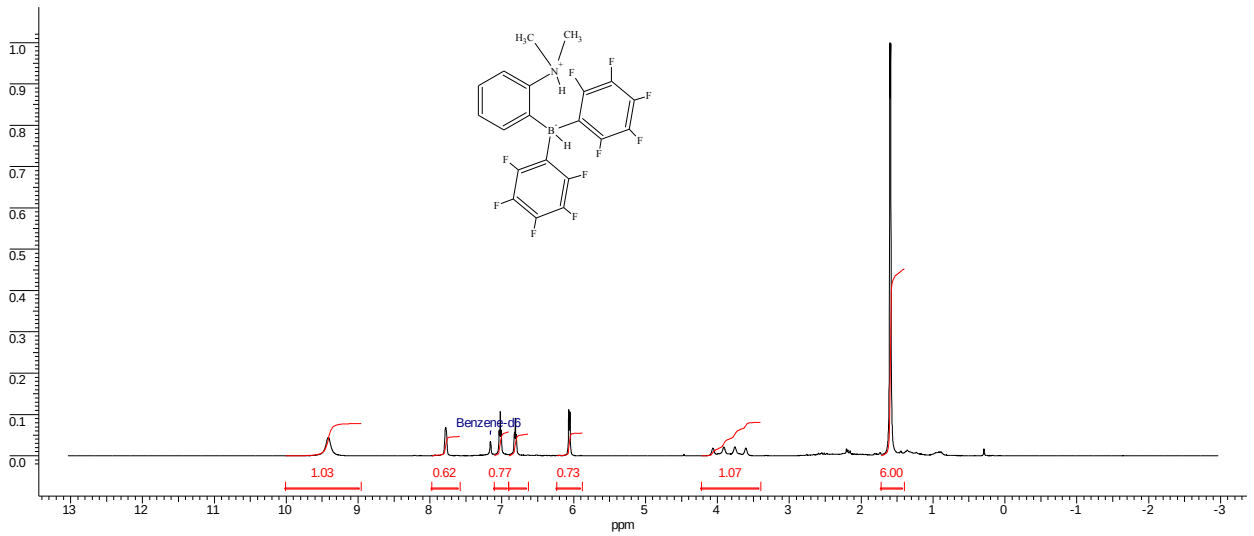


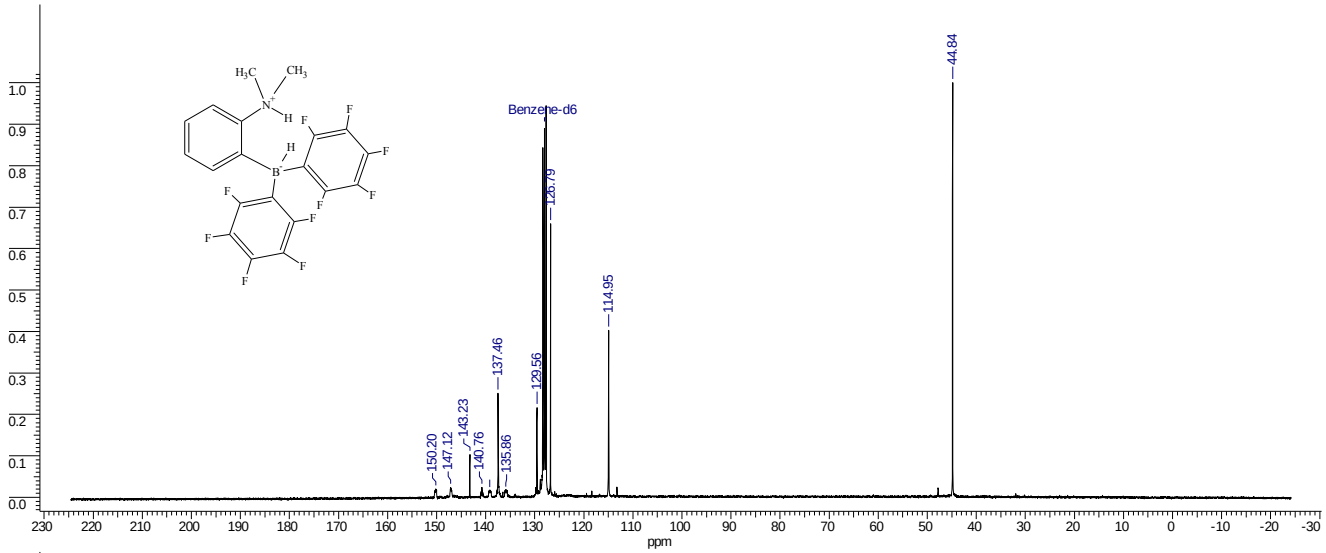
20 mg of 2-[bis(pentafluorophenyl)boryl]-*N*,*N*-dimethylaniline were dissolved in 0.5 ml of C_6D_6 and placed into a J. Young valve NMR tube. The tube was filled with 2 bar of hydrogen by three frease-pump-thaw cycles. The conversion to the title compound was monitored by NMR.

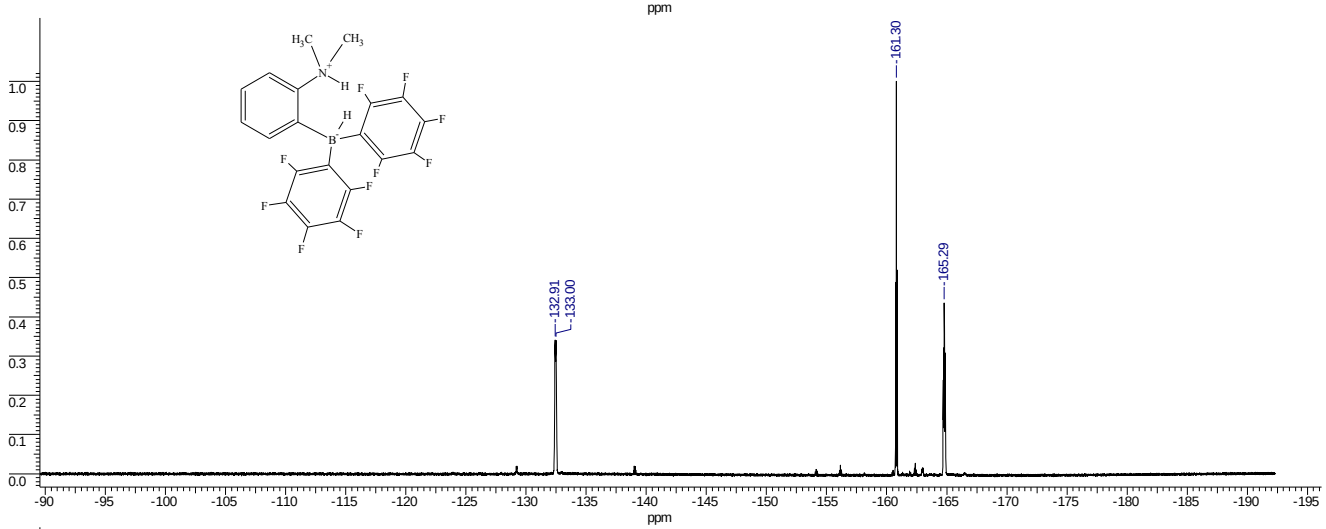
Alternatively 300 mg of 2-[bis(pentafluorophenyl)boryl]-*N*,*N*-dimethylaniline were placed into a 25 ml Schlenk tube followed by 5 ml of toluene and filled with 2 bar of hydrogen by two frease-pump-thaw cycles and stirred at room temperature for 12-24 h. The solvent was removed in vacuo to give quantatively a white solid or a colorless sticky oil crystallizing on standing.

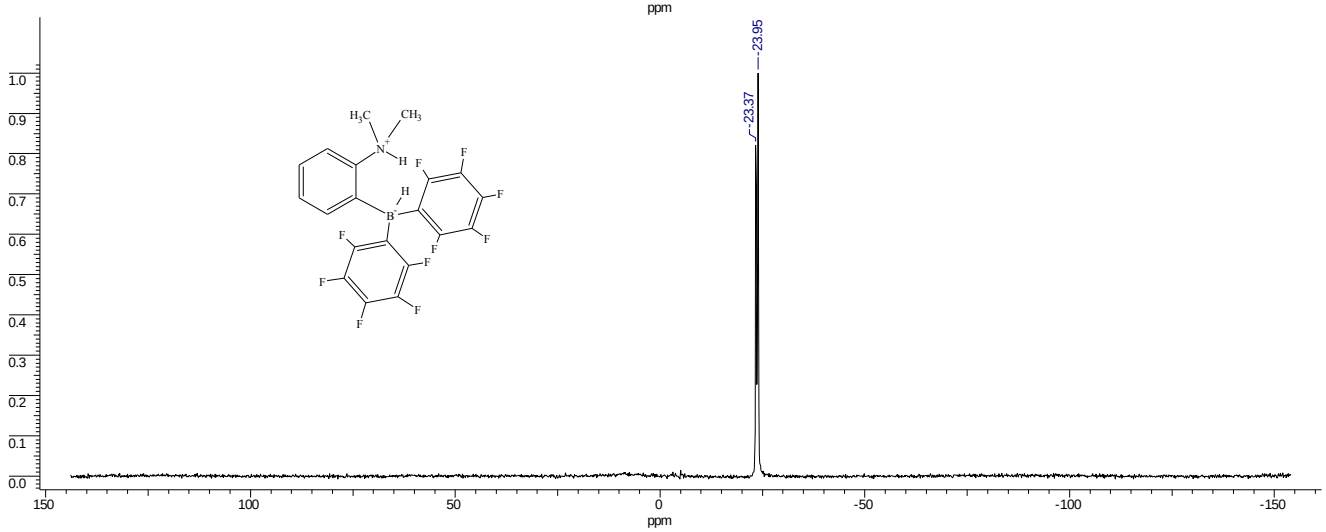
^{1}H NMR (300 MHz, C_6D_6): δ ppm 1.64 (d, J=5.2 Hz, 6H), 3.84 (q, J=76.6 Hz, 1H), 6.10 (d, J=8.2 Hz, 1H), 6.83 (t, J=7.7 Hz, 1H), 7.03 (t, J=7.4 Hz, 1H), 7.78 (br. s., 1H), 9.42 (br. s., 1H)
^{13}C NMR (75 MHz, C_6D_6): δ ppm 44.84 (s), 114.95 (s), 126.79 (s), 129.56 (s), 137.51 (d, J=247 Hz), 137.46 (s), 139.12 (d, J=247 Hz), 143.23 (s), 148.66 (d, J=232 Hz).
^{19}F NMR (282 MHz, C_6D_6): δ ppm -132.5 (d, J=23 Hz, 4F, *o*-F), -161.3 (t, J=20.6 Hz, 2F, *p*-F), -165.3 (m, 4F, *m*-F).
^{10}B NMR (53.7 MHz, C_6D_6): δ ppm -23.7 (d, J=33,3 Hz).
HRMS-ESI$^-$: found 466.0850, calc. 466.0834 for $[C_{20}H_{11}BF_{10}N]^-$, $[M\text{-}H]^-$.











Catalytic hydrogenation of imines and enamines

Into a 25-ml Schlenk tube was placed an imine or enamine (0.25 mmol), catalytic amount of the catalyst (the aminoboranes **2** or **3**, or the ammonium borohydrides **$2H_2$** or **$3H_2$**) and 1 ml of solvent (benzene-d_6 or toluene). The vessel was charged with 2 bar of hydrogen by two freeze-pump-thaw cycles and stirred at respective conditions (time and temperature). The content was then analyzed by NMR to define conversions. In case of toluene as a solvent, it was stripped off in vacuo and the sample redissolved in a deuterated solvent.