Supporting Information

Bench-stable frustrated Lewis pair chemistry: fluoroborate salts as precatalysts for the C-H borylation of heteroarenes

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Contents

1. Materials and Methods

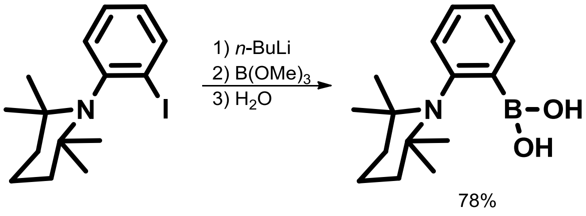
Toluene and hexanes used in the synthesis of **2** were purified by distillation over Na/benzophenone. Chloroform used in catalytic reactions was dried by distillation over P_2O_5. $CDCl_3$ used for the kinetic catalytic reactions and deprotection investigations was similarly treated. $CDCl_3$ used for product and precatalyst characterization was used as received from Sigma-Aldrich. C_6D_6 was dried over Na/K alloy and distilled.

NMR spectra were recorded on an Agilent Technologies NMR spectrometer at 500 MHz (^{1}H), 125.758 MHz (^{13}C), 160.46 MHz (^{11}B) and on a Varian Inova NMR AS400 spectrometer, at 400.0 MHz (^{1}H), 100.580 MHz (^{13}C). ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR chemical shifts are referenced to residual protons or carbons in deuterated solvent. $^{11}B\{^{1}H\}$ was calibrated using an external reference of $BF_3.Et_2O$. Multiplicities are reported as singlet (s), broad singlet (s, br) doublet (d), triplet (t), multiplet (m). Chemical shifts are reported in ppm. Coupling constants are reported in Hz. Mass Spectrometry analyses were carried out on an Agilent Technologies 6210 LC Time of Flight Mass Spectrometer. Gas chromatography was carried out on a Thermo-Fisher Trace GC Ultra with an ITQ 900 MS, using electronic impact as an ionization source (precision +/- 0.2 uma).

Al_2O_3 was purchased from Sigma-Aldrich and activated by heating in a Schlenk flask at 300 °C under vacuum (20 millitorr) for 16 hours. Heteroaromatic substrates were purchased from Sigma-Aldrich. 1-methylpyrrole was distilled from KOH and flame-dried $MgSO_4$. 2-Tertbutylfuran and 1-methylindole were used as received. 1-Benzylpyrrole and 2-(trimethylsilyloxy)furanwere passed through a short pad of alumina before use. 3,4-Ethylenedioxythiophene was distilled before use. Pinacolborane was purchased from Sigma-Aldrich and used as received. 2-TMP-iodobenzene was synthesized according to a reported procedure.[1]

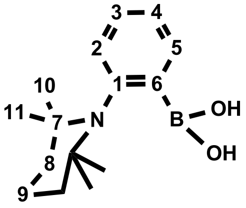
2. Synthesis of precatalysts

(2-TMP-benzene) boronic acid (**2**):



4.3 g (12.5 mmol) of 2-TMP-iodobenzene was dissolved in *ca.* 40 mL of dry hexanes and *n*-BuLi (5 mL of a 2.5 M solution in hexanes, 1 eq.) was added at -78 °C. The reaction mixture was left warming while stirring for approximately 4h until it reached room temperature and a white precipitate formed. The solvent was removed and *ca.* 40 mL of toluene was added. The reaction mixture was then cooled to -78 °C, 3 equivalents (4.3 mL) of $B(OMe)_3$ were subsequently added and the reaction was left to warm to room temperature and stirred overnight (*ca.* 16h). The next morning, water (*ca.* 40 mL) was added and the mixture was stirred for 3h. The reaction mixture was then extracted three times with $CHCl_3$ and the combined organic fractions were dried with $MgSO_4$. 3.03 g of a white powder were obtained after evaporation that was identified by ^{1}HNMR as a methanol adduct of the target compound.

Trituration of the solid in 50 mL of water and evaporation under vacuum at 50°C gave the target compound as a white powder (2.54 g, 78% yield). A suitable single crystal for XRD were obtained by slow evaporation of an acetone solution at room temperature.



^{1}H-NMR 500MHz: δ 9.05 (s, broad, 2H, OH); 7.98 (d, $^3J_{H\text{-}H}$= 7Hz, 1H, H2 or H5); 7.44-7.37 (m, 2H, H3 or H4 and H2 or H5); 7.29 (t, $^3J_{H\text{-}H}$=7Hz, 1H, H3 or H4); 2.02-1.90 (m, 1H, H9); 1.81-1.66 (m, 5H, H8 and H9); 1.43 (s, 6H, H10 or H11); 0.88 (s, 6H, H10 or H11).

^{13}C {^{1}H} (126 MHz): δ 151.5 (s, 1C, C1); 135.1, 130.3, 129.4, 126.0 (s, 4C, C2, C3, C4 and C5); 56.7 (s, 2C, C7); 41.7 (s, 2C, C8); 32.0 (s, 2C, C10 or C11); 25.0 (s, 2C, C10 or C11); 18.1 (s, 1C, C9). C6 was not observed.

^{11}B {^{1}H} (160 MHz): δ 29.8 (s, 1B).

Elemental analysis calcd. for $C_{15}H_{24}B_1N_1O_2$: C, 68.98; H, 9.26; N, 5.36%. Found: C, 68.97; H, 9.30; N, 5.36.

$[M+H]^+$ = 262.2115 (calc.: 262.19785)

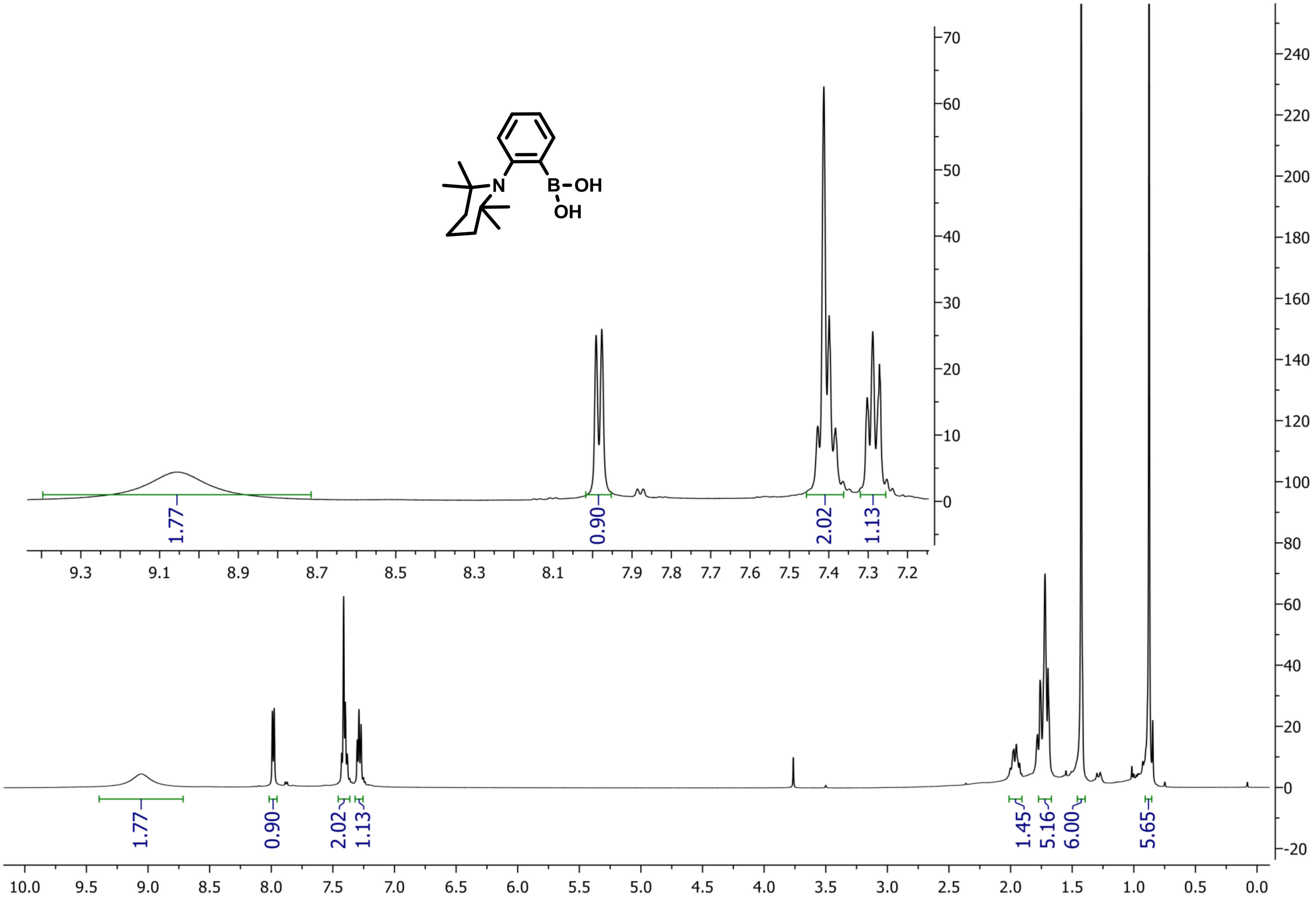


Figure S1: ^{1}H NMR (CDCl$_3$, 500 MHz) of **2**.

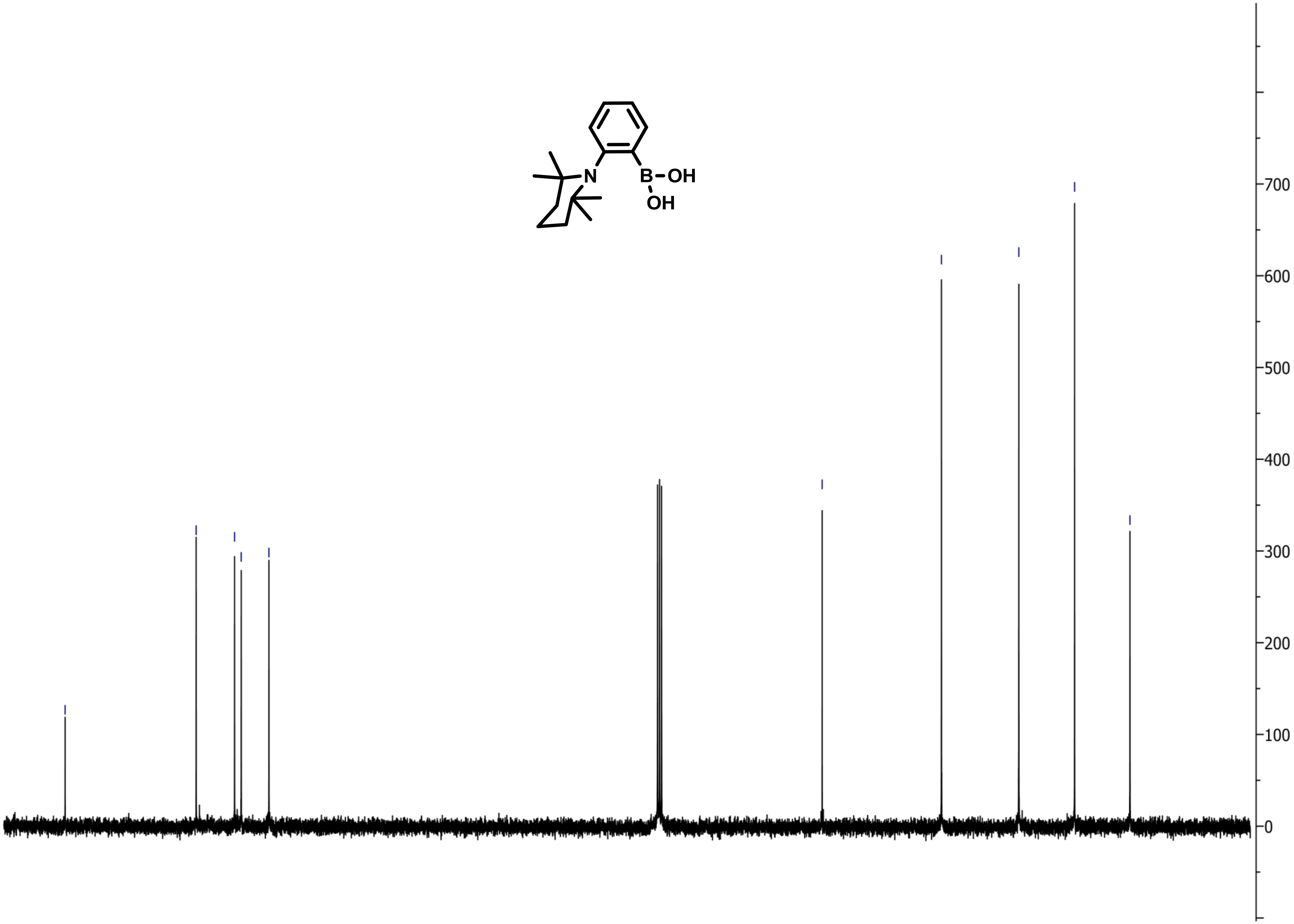


Figure S2: ^{13}C NMR ($CDCl_3$, 125.7 MHz) of **2**.

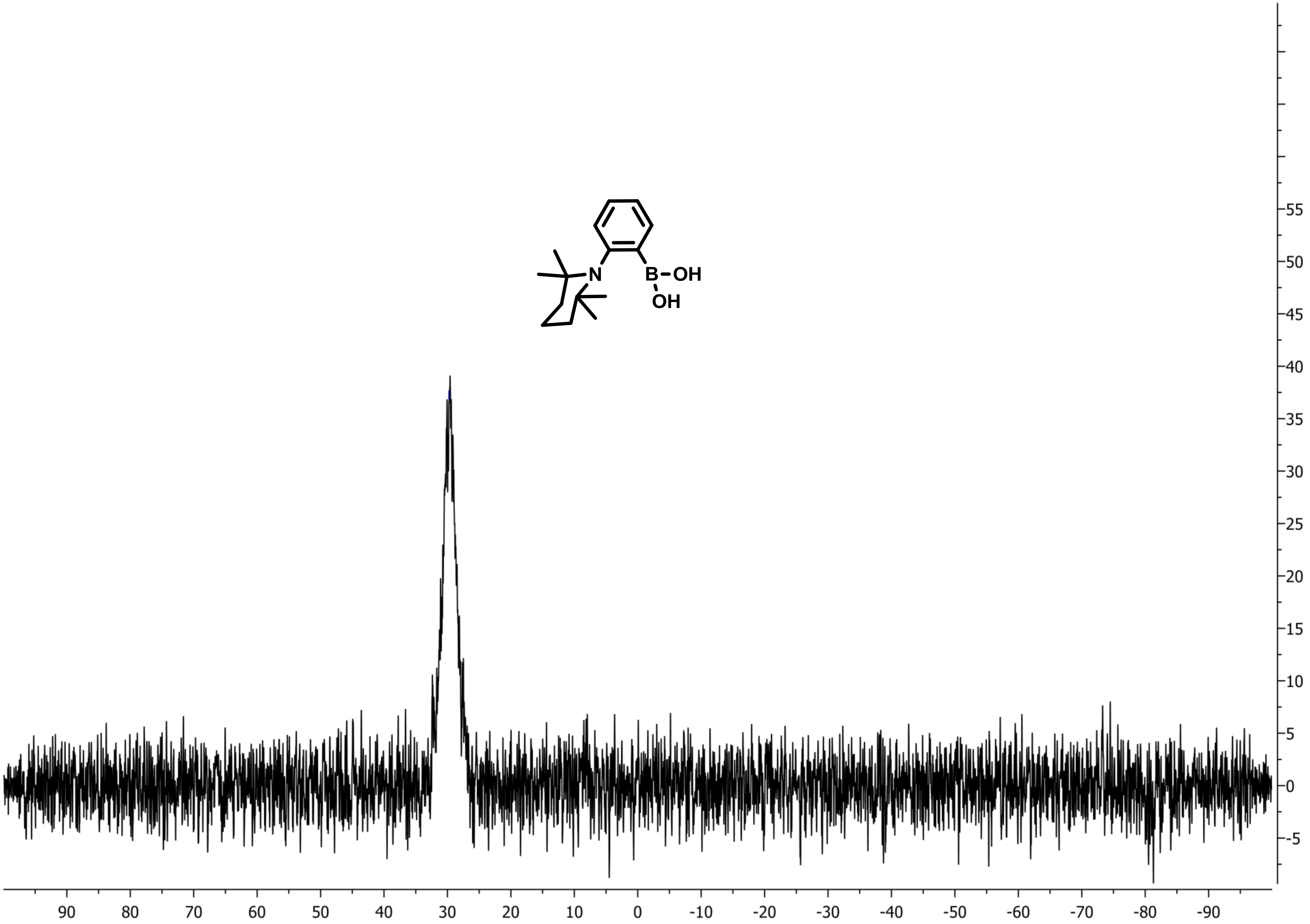
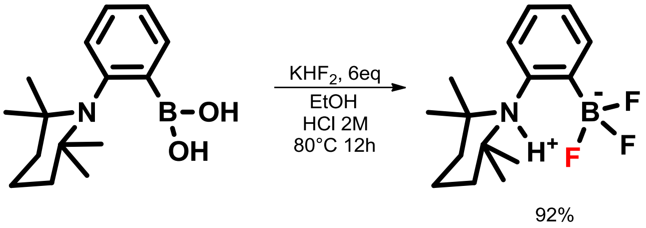


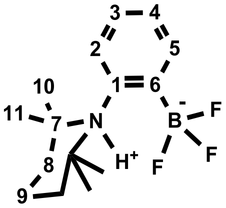
Figure S3: ^{11}B NMR (CDCl$_3$, 160.4 MHz) of **2**.

1-(trifluoroborato)-2-TMP-benzene (**3a**):



To a solution of **2** (250 mg, 0.95 mmol) in methanol (10 mL), were added KHF_2 (445 mg, 5.7 mmol) and 1 mL of a 2M HCl solution in water. The reaction mixture was sonicated for 30 min and stirred at 80°C for 12h. After evaporation of the volatiles *in vacuo*, a white solid was obtained and extracted three times with $CHCl_3$. The combined organic fractions were dried to yield 250 mg (92% yield) of the target compound.

A suitable single crystal for XRD were obtained by slow evaporation of an acetone solution at room temperature.



^{1}H-NMR 500MHz: δ 9.7 (d, broad, J=12Hz, 1H, NH); 7.81 (d, $^3J_{H-H}$=7Hz, 1H, H2 or H5); 7.41 (t, $^3J_{H-H}$=7Hz, 1H, H2 or H5); 7.32-7.22 (m, 2H, H3 or H4 and H2 or H5); 2.04-1.95 (m, 5H, H8 and H9); 1.89-1.83 (m, 1H, H9); 1.65 (s, 6H, H10 or H11); 1.22 (s, 6H, H10 or H11).

^{13}C {^{1}H} (126 MHz): δ 136.6 (s, 1C, C1); 135.5, 129.2, 127.0, 121.1 (s, 4C, C2, C3, C4 and C5); 67.8 (s, 1C, C7); 39.6 (s, 2C, C8); 30.3 (s, 2C, C10 or C11); 23.5 (s, 2C, C10 or C11); 16.5 (s, 1C, C9).

^{19}F {^{1}H} (470 MHz): δ -134.0 (m).

^{11}B {^{1}H} (160 MHz): δ 3.3 (m).

Elemental analysis calcd. for $C_{15}H_{23}B_1N_1F_3$: C, 63.18; H, 8.13; N, 4.91%. Found: C, 63.02; H, 8.67; N, 4.98.

$[M-H]^-$ = 284.1810 (calc.: 284.1797)

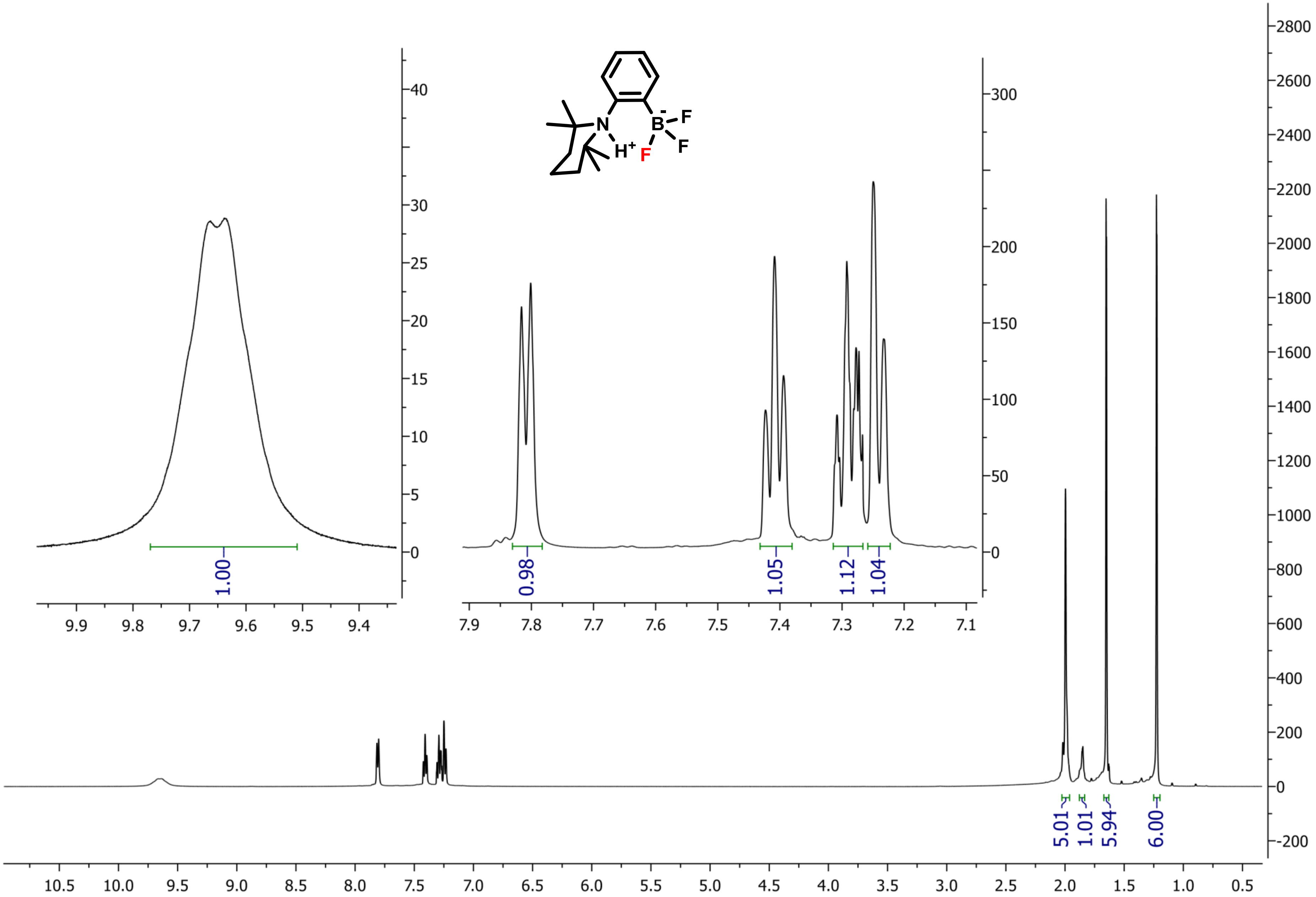


Figure S4: ^{1}H NMR (CDCl$_3$, 500 MHz) of **3a**.

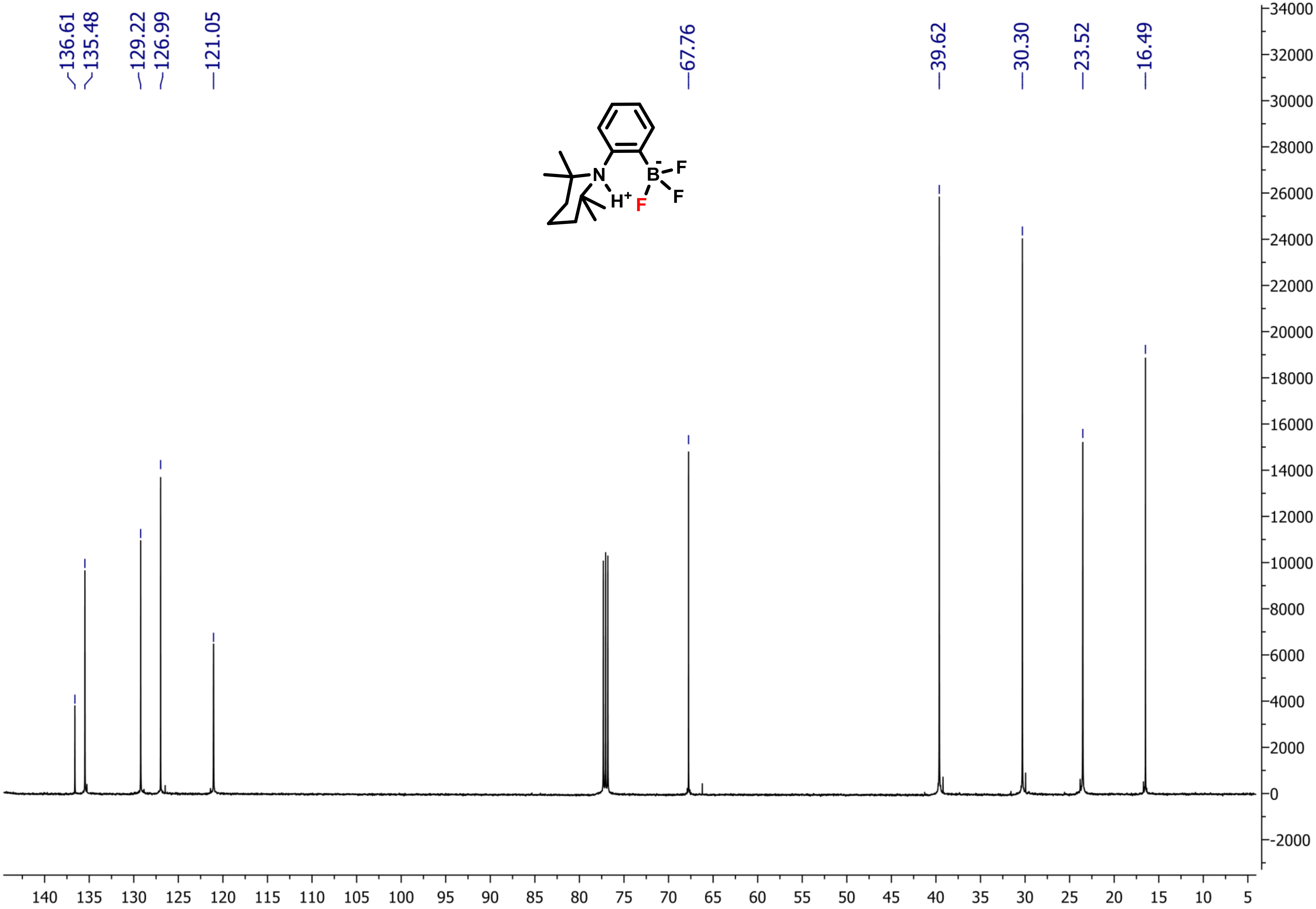


Figure S5: ^{13}C NMR (CDCl$_3$, 125.7 MHz) of **3a**.

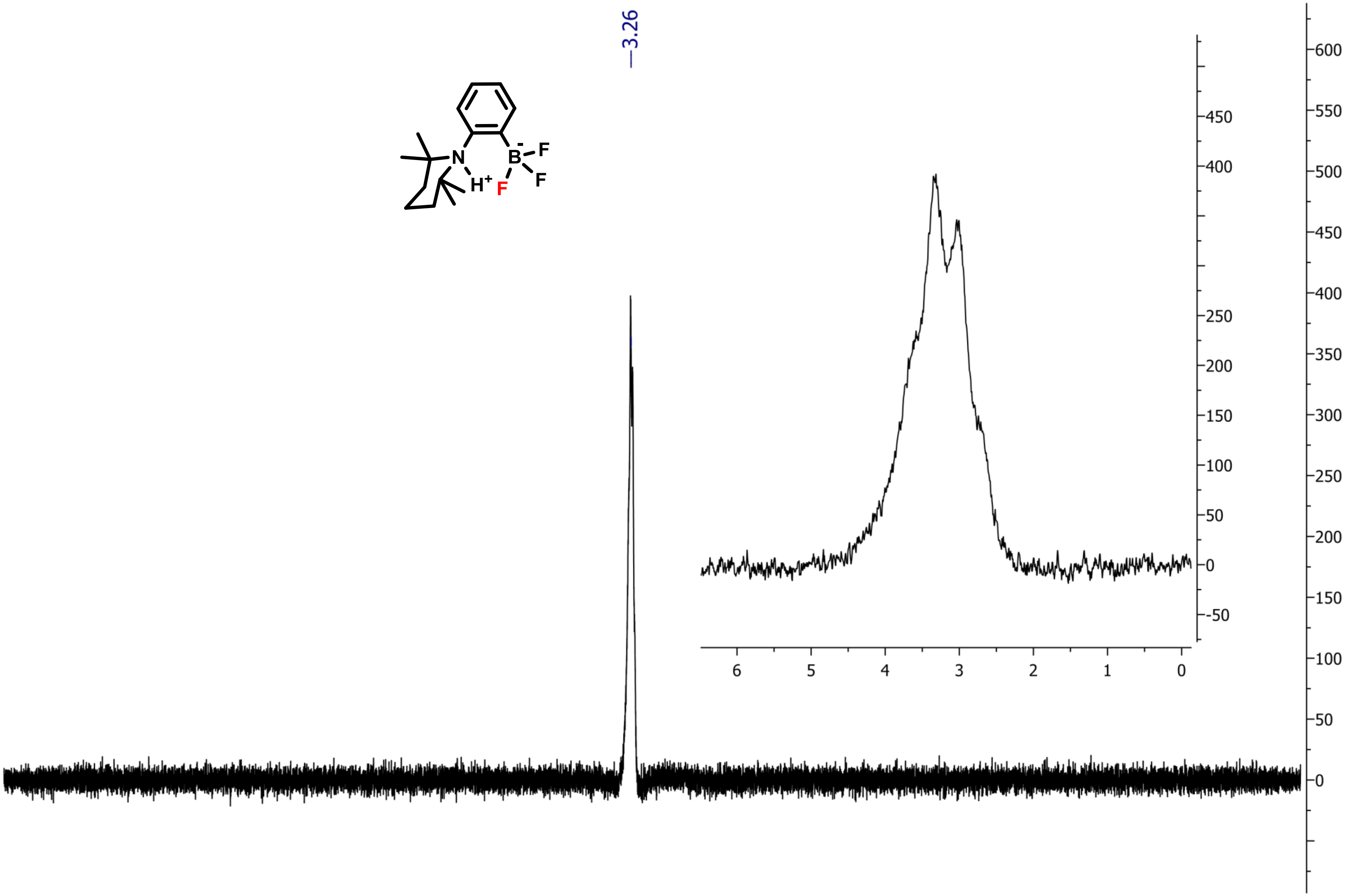


Figure S6: ^{11}B NMR (CDCl$_3$, 160.4 MHz) of **3a**.

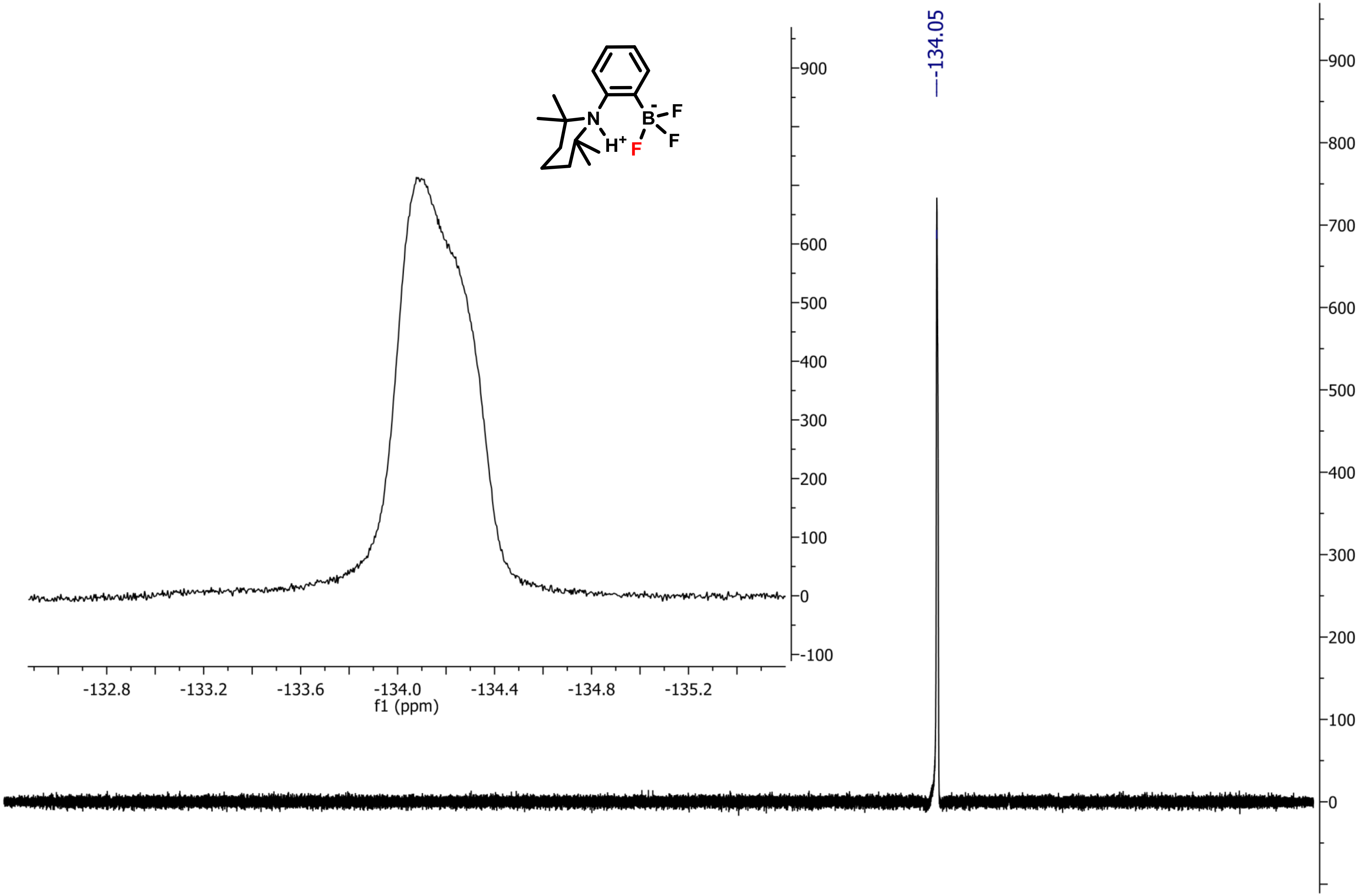
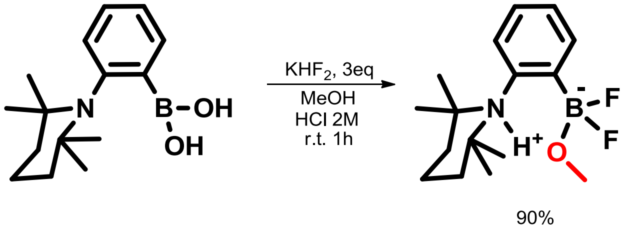


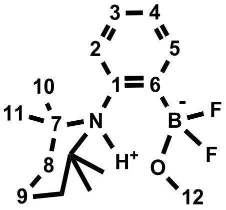
Figure S7: ^{19}F NMR (CDCl$_3$, 470.4 MHz) of **3a**.

1-(difluoromethoxyborato)-2-TMP-benzene (**3b**):



To solution of **2** (500 mg, 1.91 mmol) in methanol (10 mL), were added KHF_2 (445 mg, 5.7 mmol) and 1 mL of a 2M HCl solution in water. The reaction mixture was sonicated for 5 min and stirred at room temperature for one hour. After evaporation of the volatiles *in vacuo*, a white solid was obtained and extracted three times with $CHCl_3$. The organic fractions were combined and evaporated to give 514 mg (90% yield) of the target compound.

A suitable single crystal for XRD were obtained from a saturated toluene solution at -35°C.



^{1}H-NMR 500MHz: δ 13.0 (s, broad, 1H, NH); 7.83 (d, $^3J_{H\text{-}H}$=7Hz, 1H, H2 or H5); 7.37 (t, $^3J_{H\text{-}H}$=7Hz, 1H, H2 or H5); 7.24-7.16 (m, 2H, H3 or H4 and H2 or H5); 3.58 (s, 3H, H12); 2.03-1.87 (m, 6H, H8 and H9); 1.60 (s, 6H, H10 or H11); 1.17 (s, 6H, H10 or H11).

^{13}C {^{1}H} (126 MHz): δ 137.7 (t, $^3J_{C\text{-}F}$ =4Hz, 1C, C1); 137.7, 135.2, 128.8, 121.4 (s, 4C, C2, C3, C4 and C5); 65.5 (s, 1C, C7); 47.1 (t, $^3J_{C\text{-}F}$=5Hz, 2C, C12); 39.5 (s, 2C, C8); 29.8 (s, 2C, C10 or C11); 23.8 (s, 2C, C10 or C11); 16.8 (s, 1C, C9).

^{19}F {^{1}H} (470 MHz): δ -147.8 (q, $^1J_{F\text{-}B}$=58Hz).

^{11}B {^{1}H} (160 MHz): δ 3.4 (t, $^1J_{B\text{-}F}$ =59Hz).

Elemental analysis calcd. for $C_{16}H_{26}B_1N_1F_2O_1$: C, 64.66; H, 8.82; N, 4.71%. Found: C, 64.31; H, 9.21; N, 4.79.

$[M\text{-}H]^-$ = 296.2018 (calc.: 296.1997)

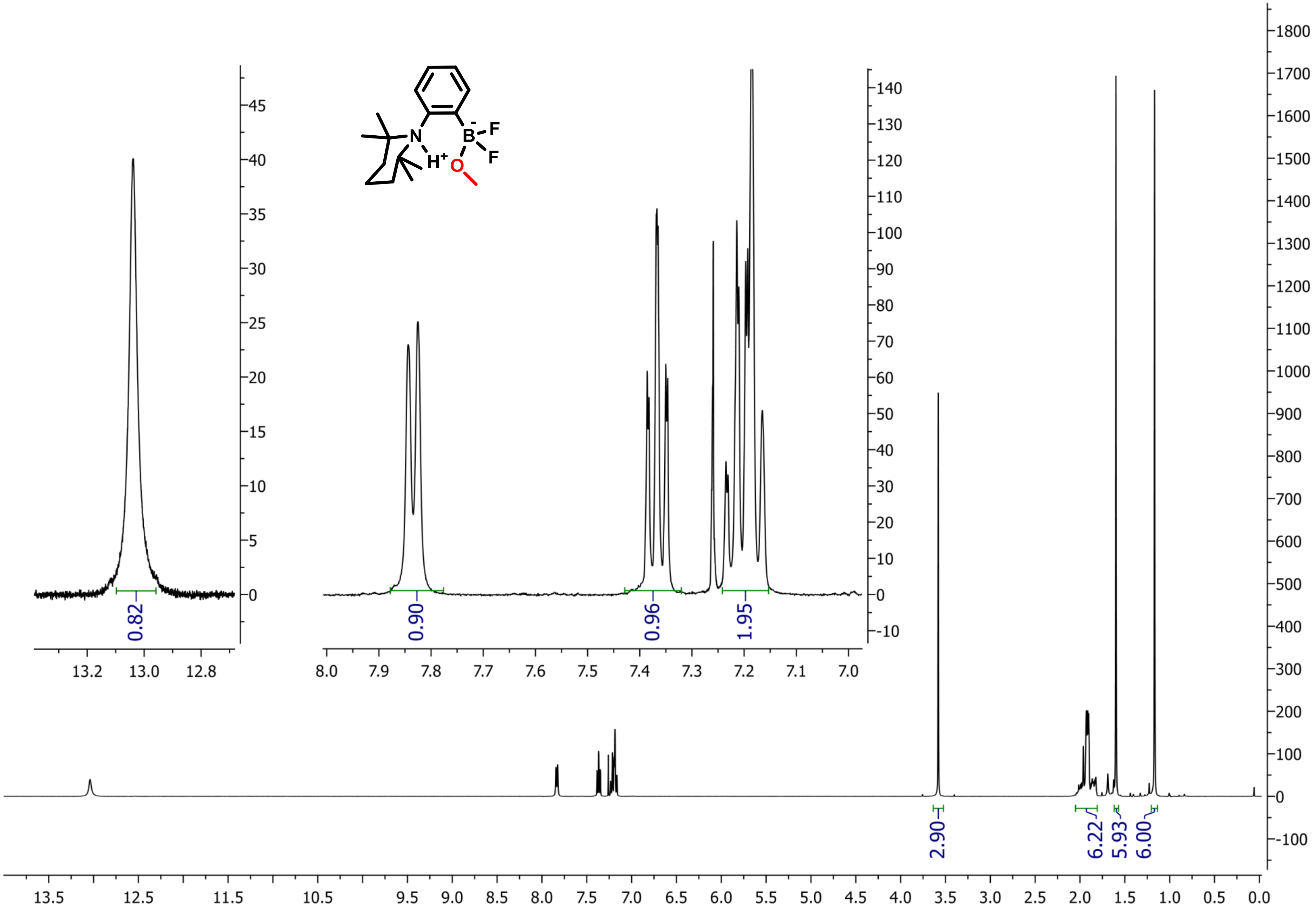


Figure S8: ^{1}H NMR (CDCl$_3$, 500 MHz) of **3b**.

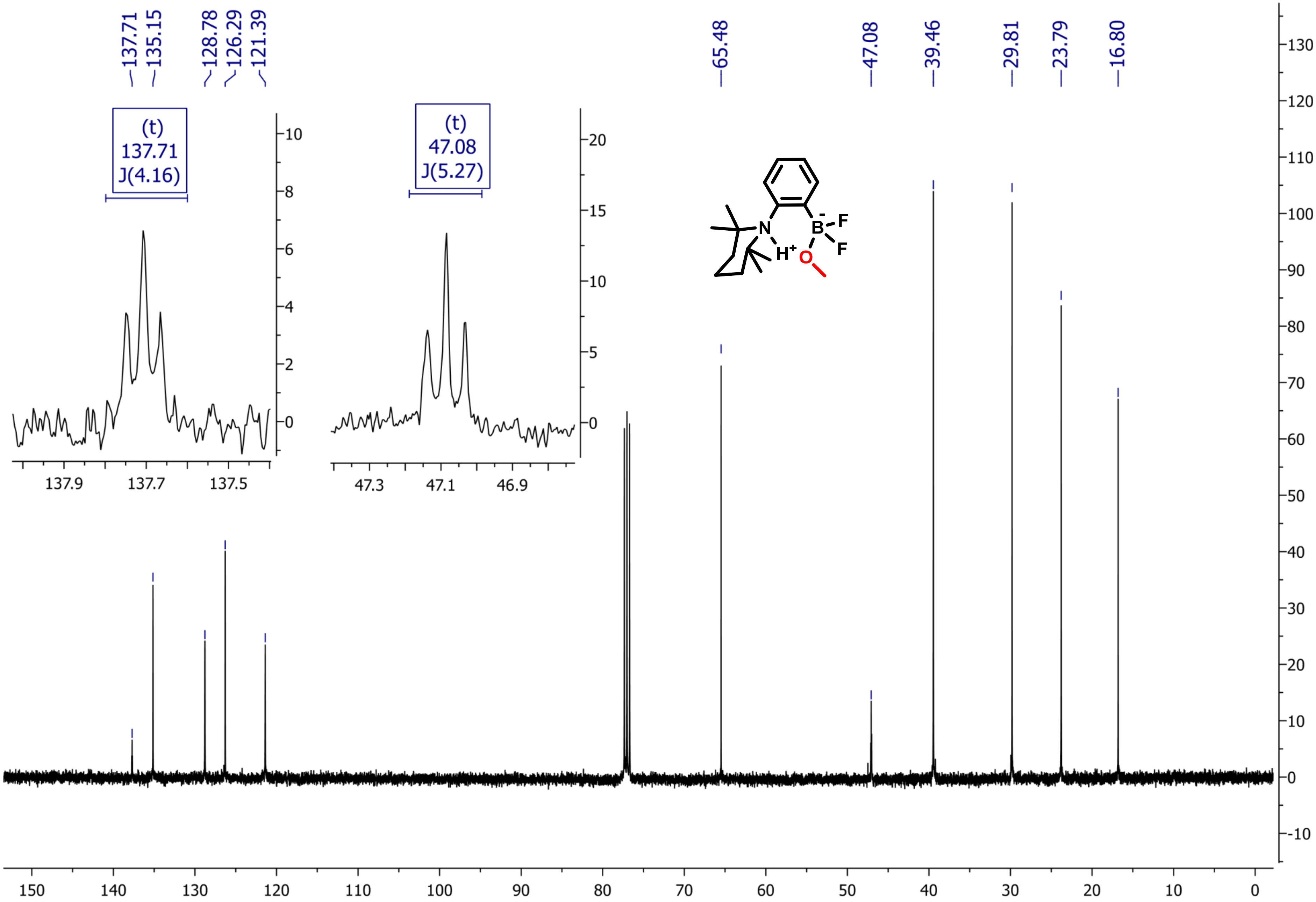


Figure S9: ^{13}C NMR (CDCl$_3$, 125.7 MHz) of **3b**.

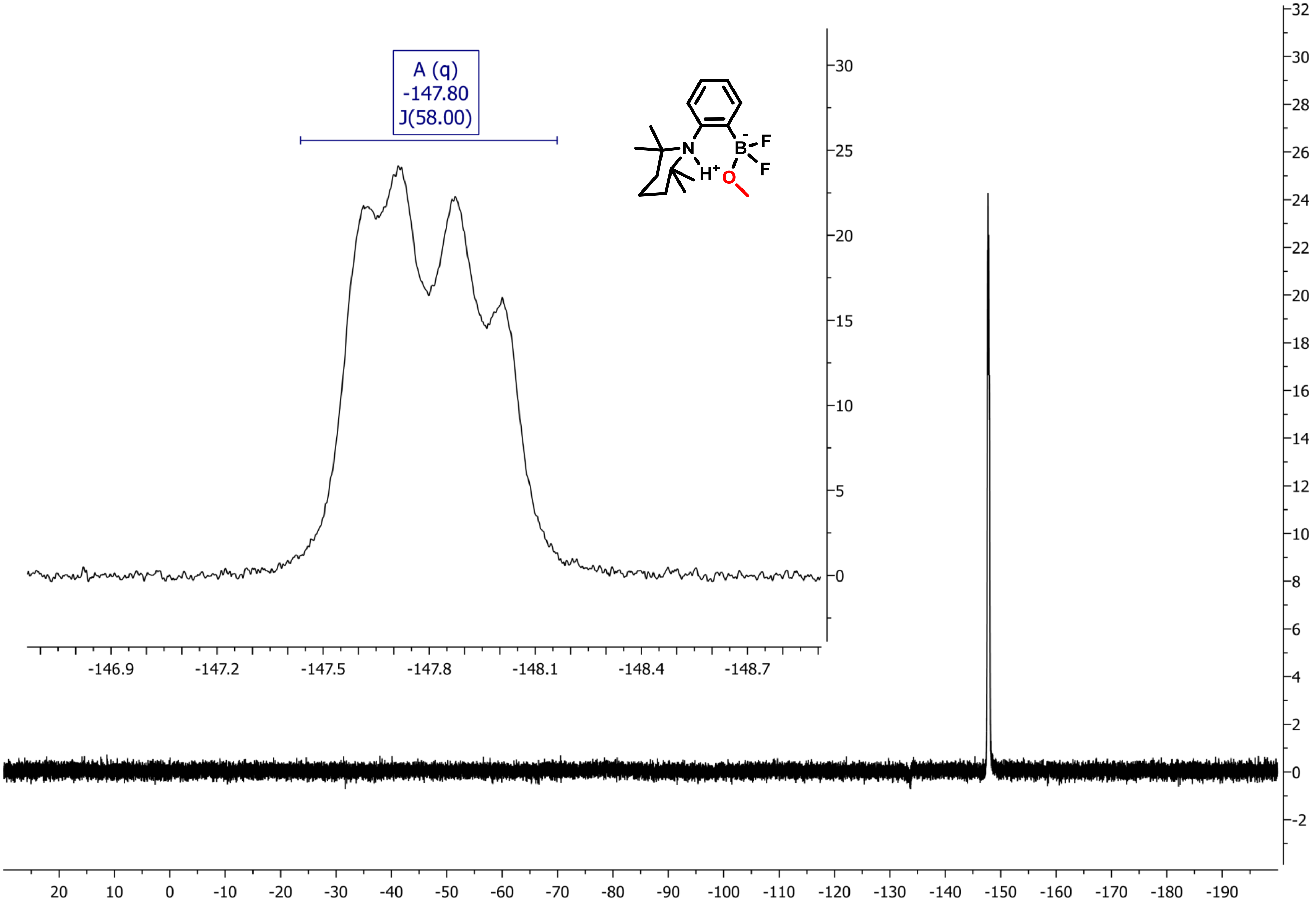


Figure S10: ^{19}F NMR (CDCl$_3$, 470.4 MHz) of **3b**.

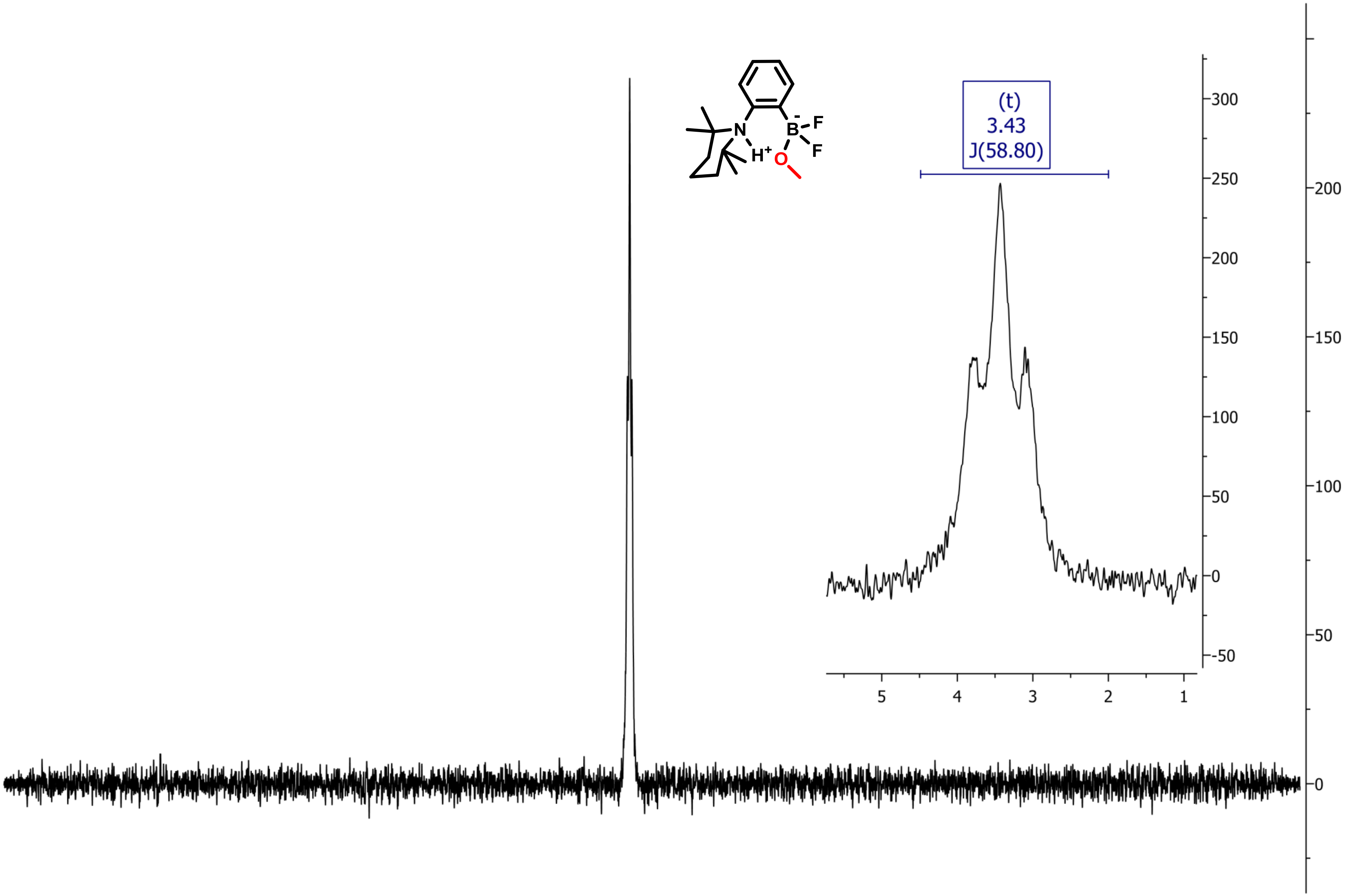
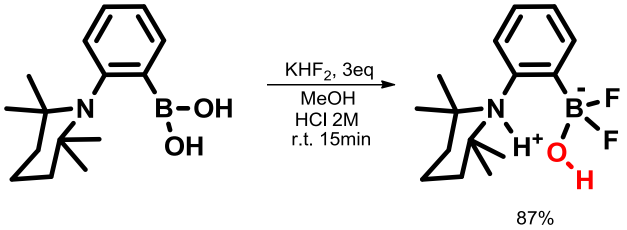
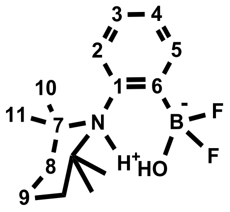


Figure S11: ^{11}B NMR (CDCl$_3$, 160.4 MHz) of **3b**.

1-(difluorohydroxyborato)-2-TMP-benzene (**3c**):



To solution of **2** (500 mg, 1.91 mmol) in THF:H_2O (20 mL of a 5:1 mixture), was added KHF_2 (445 mg, 5.7 mmol). The reaction mixture was stirred at room temperature for 15 minutes, then with $CHCl_3$ (3 x 15 mL). After evaporation of the volatiles *in vacuo*, 470 mg (87 %) of a white solid was obtained, which was identified as the target compound.



^{1}H-NMR 500MHz: δ 12.6 (s, broad, 1H, NH); 7.89 (d, $^3J_{H\text{-}H}$=7Hz, 1H, H2 or H5); 7.41 (t, $^3J_{H\text{-}H}$=7Hz, 1H, H2 or H5); 7.26-7.21 (m, 2H, H3 or H4 and H2 or H5); 2.39 (s, broad, 1H, OH); 2.11-1.81 (m, 6H, H8 and H9); 1.65 (s, 6H, H10 or H11); 1.26 (s, 6H, H10 or H11).

^{13}C {^{1}H} (126 MHz): δ 137.6 (t, J=4Hz, 1C, C1); 135.4, 129.0, 126.4, 121.3 (s, 4C, C2, C3, C4 and C5); 66.2 (s, 1C, C7); 39.2 (s, 2C, C8); 30.0 (s, 2C, C10 or C11); 23.8 (s, 2C, C10 or C11); 16.8 (s, 1C, C9).

^{19}F {^{1}H} (470 MHz): δ -133.9 (q, $^1J_{F\text{-}B}$=53 Hz).

^{11}B {^{1}H} (160 MHz): δ 3.5 (t, $^1J_{B\text{-}F}$ =61 Hz).

Elemental analysis calcd. for $C_{15}H_{24}B_1N_1F_2O_1$: C, 63.62; H, 8.54; N, 4.95%. Found: C, 63.60; H, 8.84; N, 4.89.

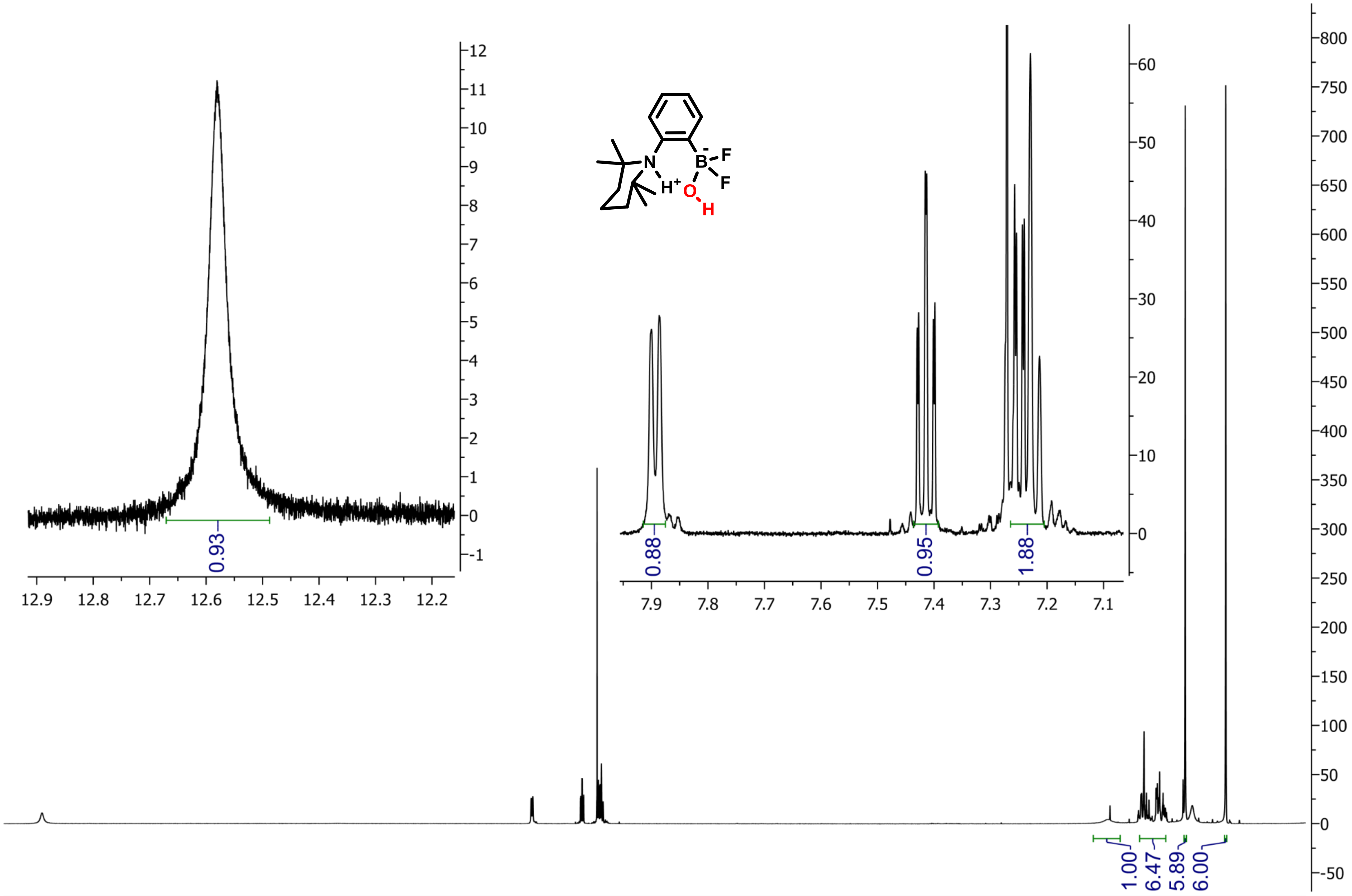


Figure S12: ^{1}H NMR ($CDCl_3$, 500 MHz) of **3c**.

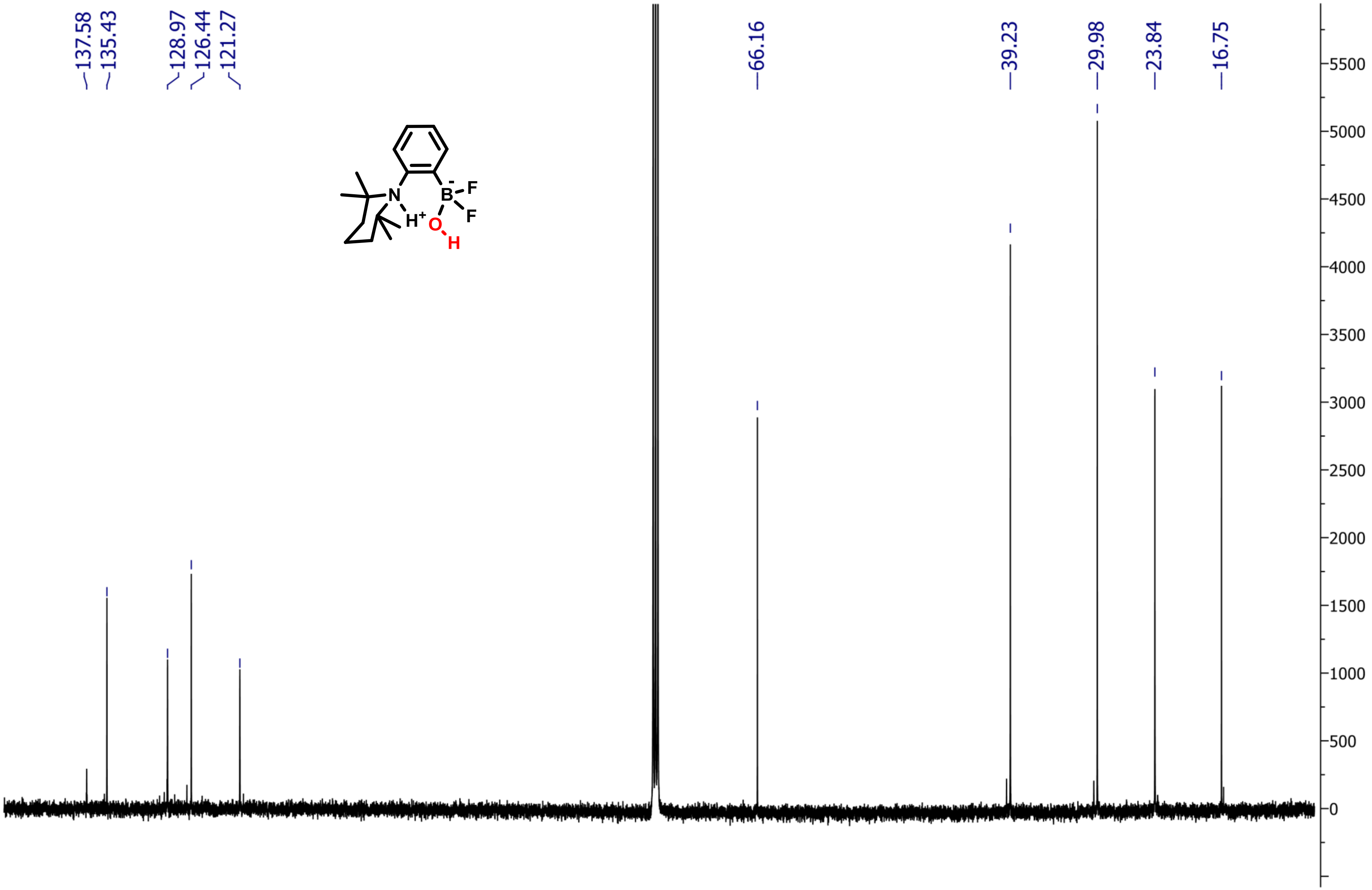


Figure S13: ^{13}C NMR (CDCl$_3$, 125.7 MHz) of **3c**.

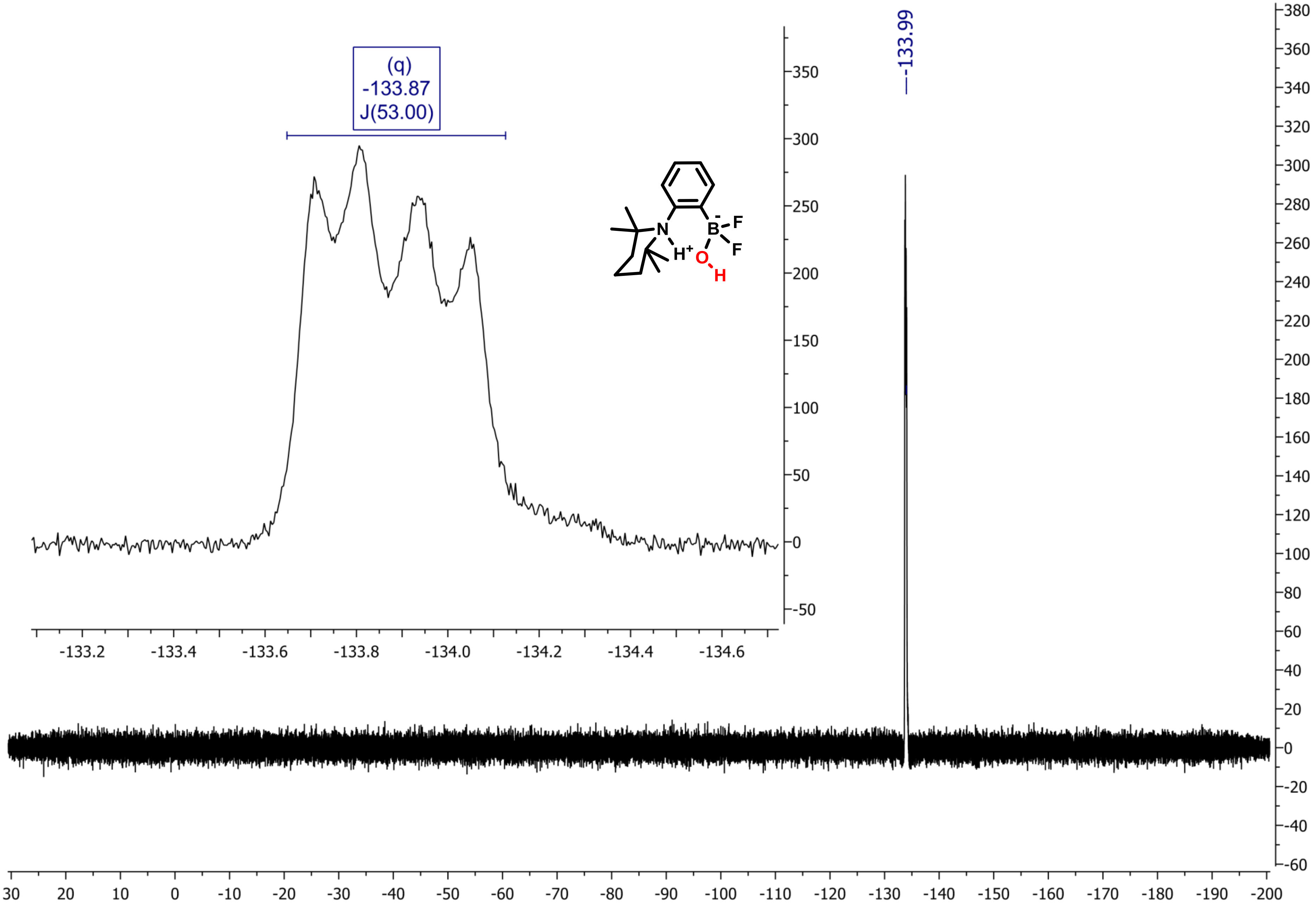


Figure S14: ^{19}F NMR ($CDCl_3$, 470.4 MHz) of **3c**.

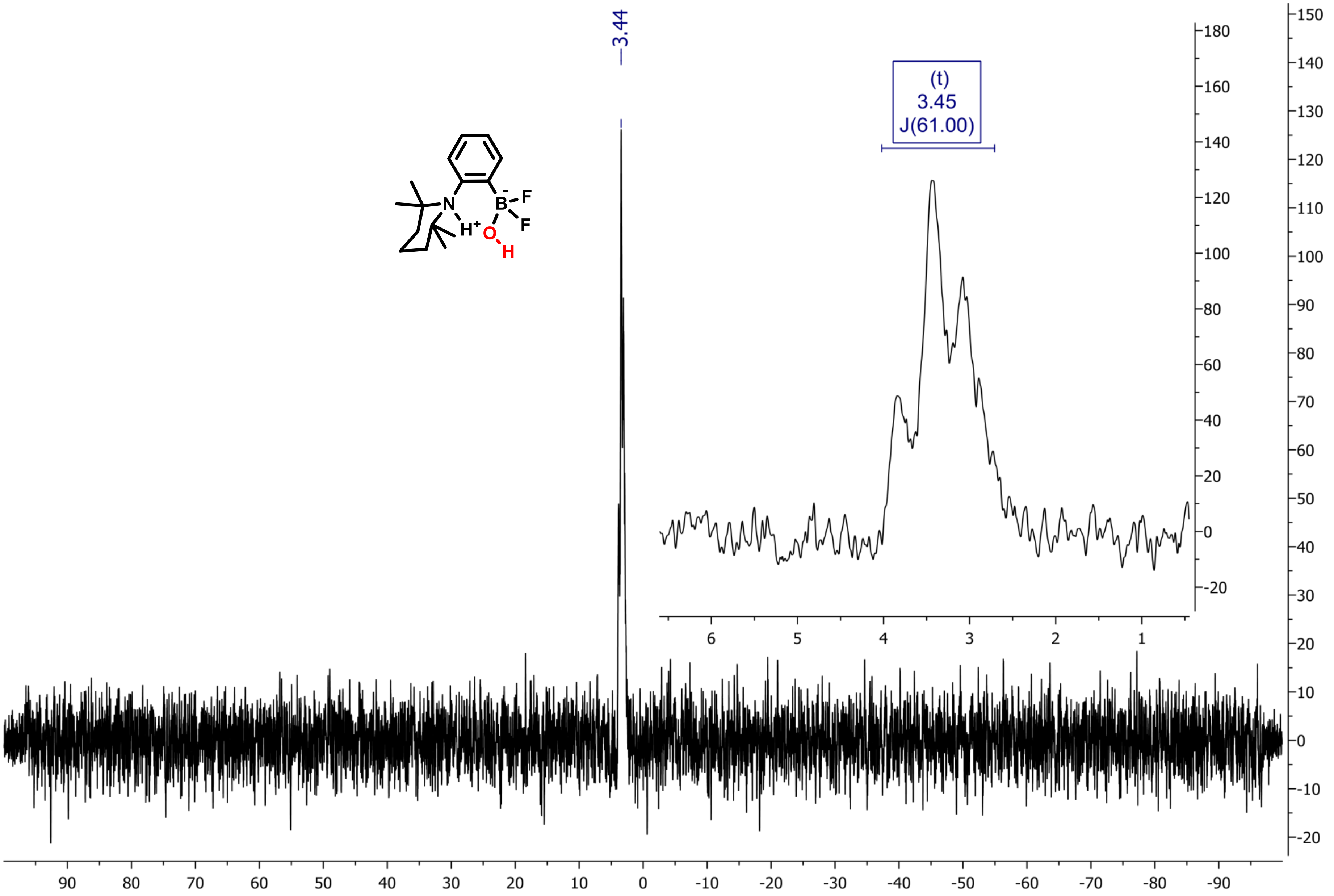


Figure S15: ^{11}B NMR (CDCl$_3$, 160.4 MHz) of **3c.**

3. Validation of the catalytic method

General method for the ^{1}H NMR monitoring of the borylation reactions

In the glovebox, a solution of hexamethylbenzene (internal standard) and of catalyst or precatalyst (**1**, **3a-c**) (0.01 mmol) in 0.4 mL $CDCl_3$ was prepared and introduced to a J-Young NMR tube. To this tube were added HBpin (28.3 µL, 14.9 mg, 0.195 mmol) and 1-methylpyrrole (18.3 µL, 15.8 mg, 0.195 mmol) by automatic syringe.

The J-Young was inserted in NMR spectrometer at 80°C and ^{1}H NMR spectra were acquired at intervals for 12 hours, along with ^{19}F NMR spectra. The yields were calculated according to the conversion of HBpin as measured against the internal standard.

Evidence for the deprotection of fluoroborate salts using HBpin.

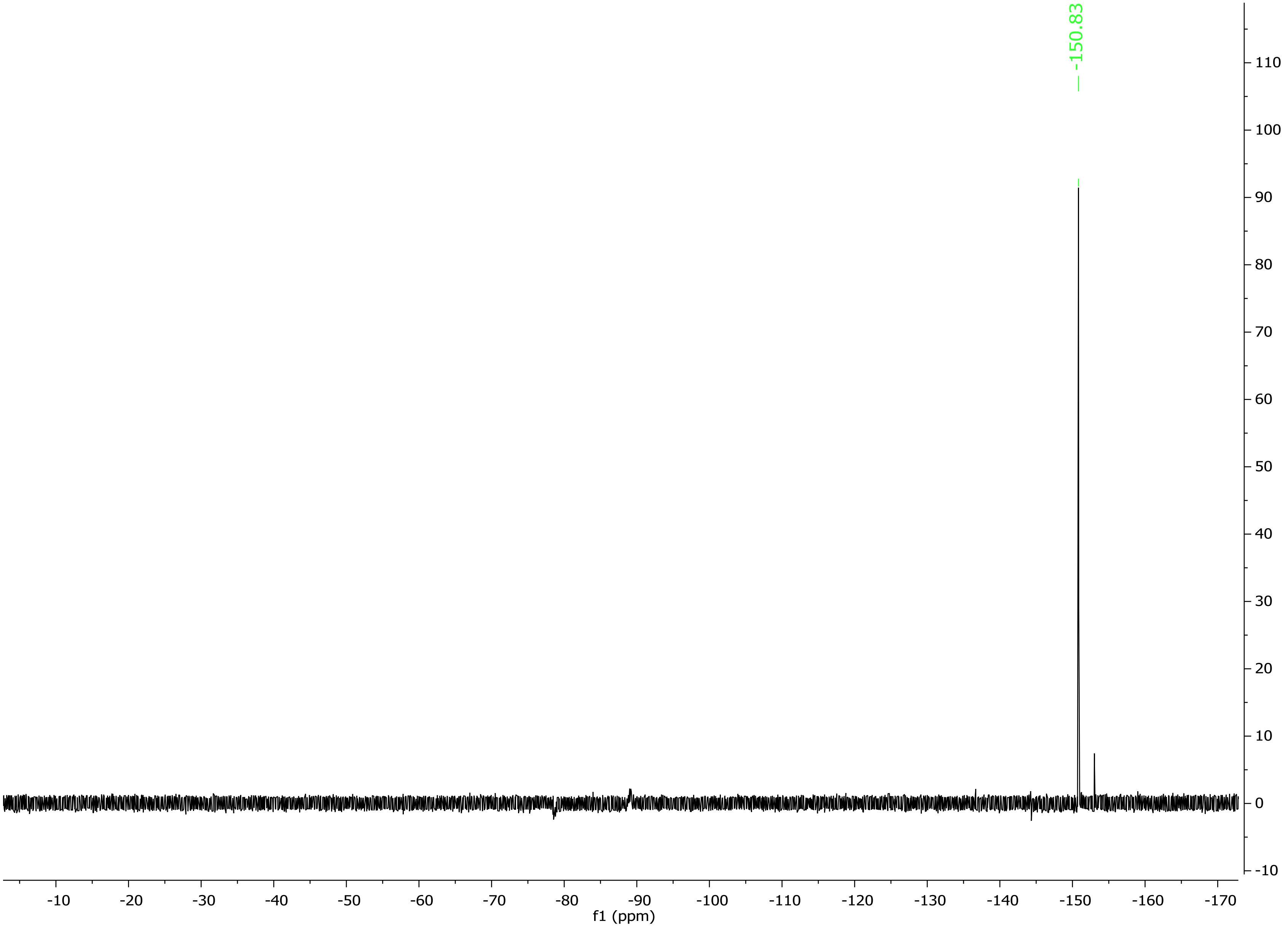


Figure S16: ^{19}F NMR ($CDCl_3$, 470.6 MHz) spectrum of the reaction mixture of **3b** with 20 equivalents of HBpin after one hour. The signal at 150.8 ppm is assigned to FBpin.

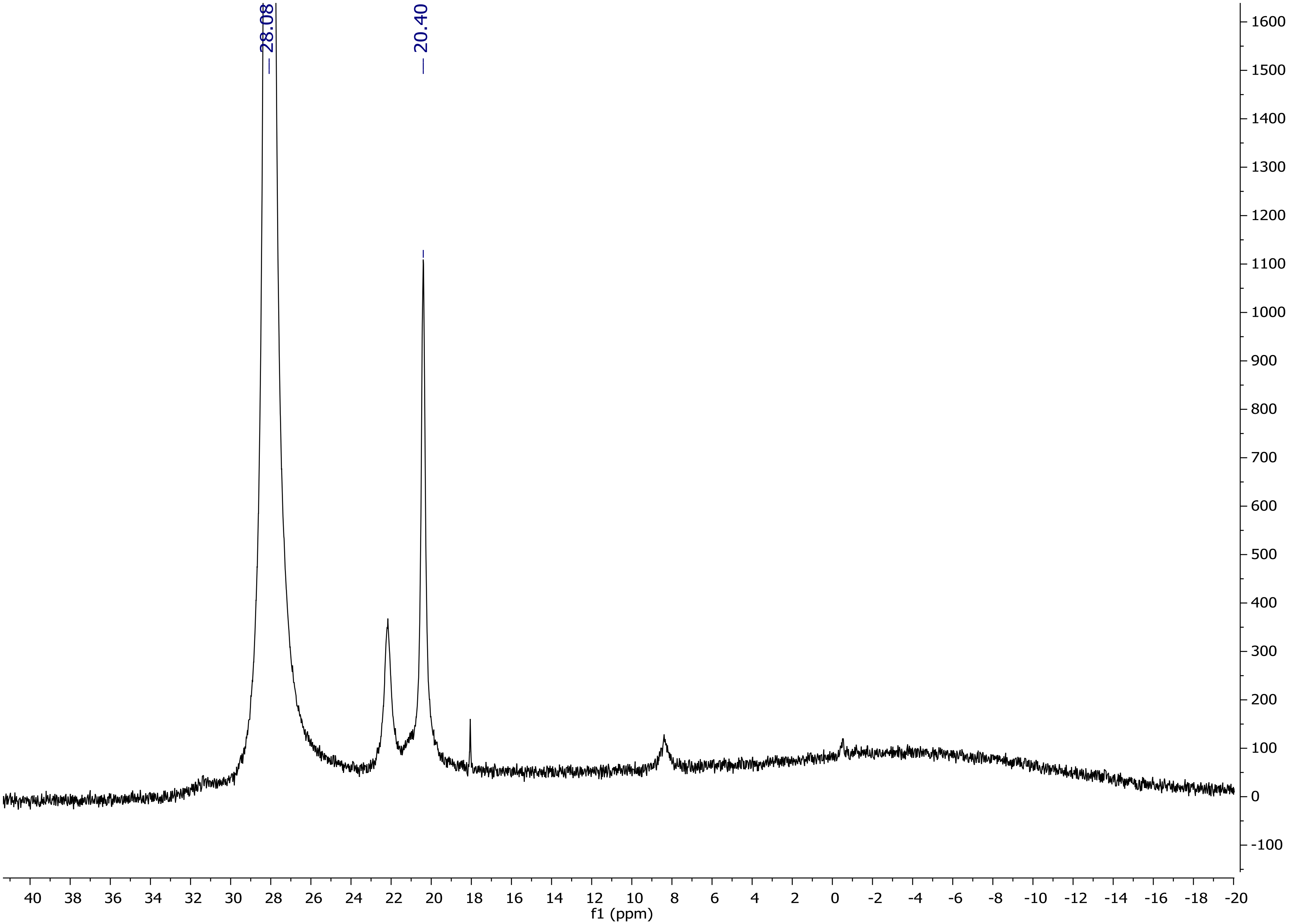


Figure S17: $^{11}B\{^1H\}$ NMR ($CDCl_3$, 160.5 MHz) spectrum of the reaction mixture of **3b** with 20 equivalents of HBpin after one hour. The resonance at 20.4 ppm is assigned to **1** and FBpin. The small resonance at -0.5 ppm is always present when **1** is present.[3]

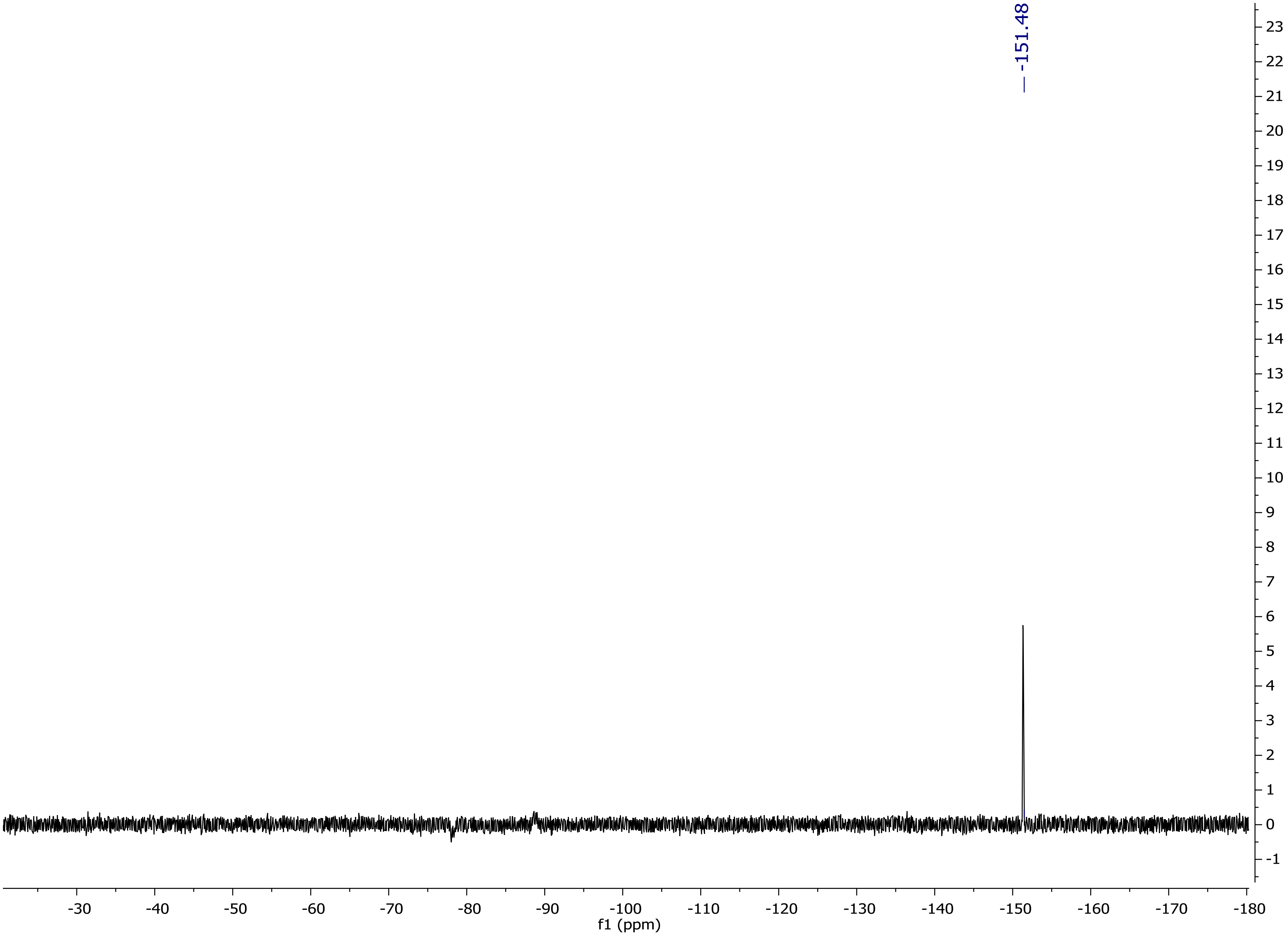
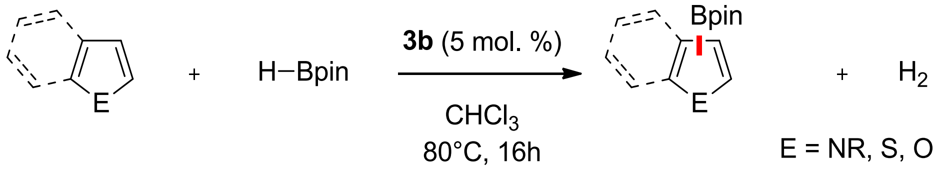


Figure S18: ^{19}F NMR ($CDCl_3$, 376.5 MHz) spectrum of an aliquot of the reaction mixture of the borylation of 1-methylpyrrole in NMR conditions after 3 hours at 80°C. The signal at 151.5 ppm is assigned to FBpin.[2]

4. Catalytic borylation reactions

General procedure for the catalytic borylation of heteroaromatic substrates

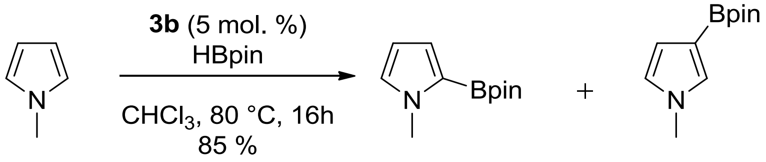


The various precatalysts **3a-c** were stored on the bench under normal atmosphere for several weeks prior to catalysis. Precatalyst **3b** (10 mg, 0.034 mmol) was introduced to an oven-dried 5 mL microwave vial containing a magnetic stirring bar, along with the heteroaromatic substrate. The vial was capped then purged with N_2 (through a needle) for at least 10 minutes before the addition of 1.6 mL of $CHCl_3$ by syringe and of pinacolborane (23 eq., 99.0 mg, 112 µL) by microsyringe. At this point, the N_2 inlet was removed. The reaction mixture was then stirred for 16 hours in a 80°C oil bath.

The resulting mixture was filtered through a short pad of silica, which was rinsed with dichloromethane. The resulting filtrate was evaporated to complete dryness *in vacuo* to afford the desired product.

The obtained products were analytically similar to the ones we previously reported.[3]

Borylation of 1-methylpyrrole



Quantity of 1-methylpyrrole: 60 µL (55 mg, 0.67mmol, 1 eq.)

Yield: 119 mg (85 %) of a 89:11 mixture of 1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole and 1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole.

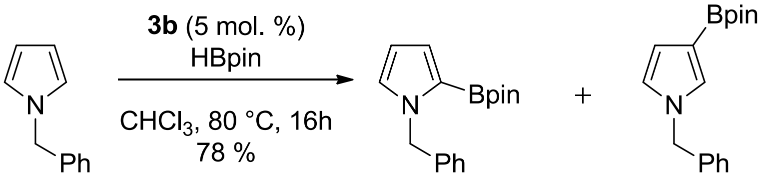
1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (m, 2H), 6.15 (m, 1H), 3.84 (s, 3H), 1.31 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 128.3, 122.0, 108.6, 83.2, 36.7, 25.0; ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) : δ 28.1.

1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (m, 1H), 6.64 (m, 1H), 6.47 (m, 1H), 3.66 (s, 3H), 1.29 (s, 12H).

Note: with longer reaction times than previously reported, a trace of 2,5-diborylation product was observed.

1-methyl-2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 2H), 3.81 (s, 3H), 1.27 (s, 12H).

Borylation of 1-benzylpyrrole



Quantity of 1-benzylpyrrole: 207 µL (211mg, 1.35mmol, 2 eq.)

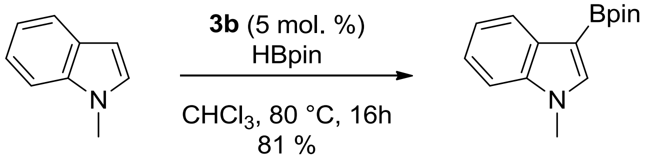
Yield: 148 mg (78 %) of a 3:2 mixture of 1-benzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole and 1-benzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole.

1-benzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.17 (m, 3H), 7.12 – 7.06 (m, 2H), 6.89 (dd, *J* = 2.4, 1.6 Hz, 1H), 6.86 (dt, *J* = 3.6, 1.9 Hz, 1H), 6.23 – 6.19 (m, 1H), 5.39 (s, 2H), 1.24 – 1.21 (m, 13H)

1-benzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 3H), 7.17 – 7.12 (m, 3H), 6.73 – 6.68 (m, 1H), 6.51 (dd, *J* = 2.6, 1.7 Hz, 1H), 5.06 (s, 2H), 1.31 (s, 12H);

Mixture: ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 139.8, 137.7, 130.4, 128.9, 128.5, 127.9, 127.7, 127.5, 127.2, 127.0, 122.4, 122.3, 114.6, 109.1, 83.3, 82.9, 53.5, 52.9, 25.0, 24.8; ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): δ 27.8.

Borylation of 1-methylindole

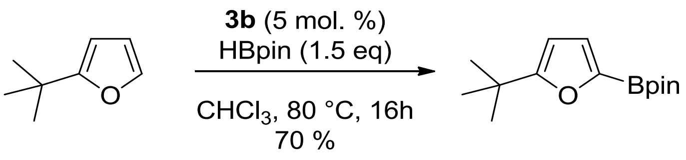


Quantity of 1-methylindole: 176 µL (185 mg, 1.35 mmol, 2 eq.)

Yield: 142 (81 %)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (ddd, *J* = 7.7, 1.4, 0.8 Hz, 1H), 7.52 (s, 1H), 7.35 – 7.31 (m, 1H), 7.25 – 7.15 (m, 2H), 3.80 (s, 3H), 1.37 (s, 12H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 138.6, 138.0, 132.6, 122.8, 121.9, 120.3, 109.3, 82.9, 33.1, 25.0; ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): δ 29.7.

Borylation of 2-tertbutylfuran



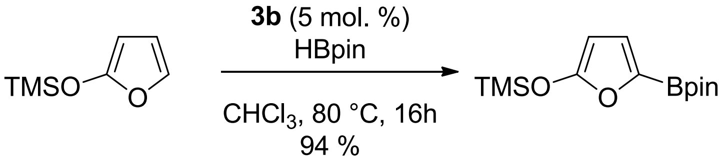
Quantity of 2-tertbutylfuran: 96 µL (83 mg, 0.67 mmol, limiting reagent)

Quantity of HBpin: 161 µL (142 mg, 1.11 mmol, (1.5 eq + 15 mol. % for deprotection))

Yield: 112 mg (70 %)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (d, *J* = 3.3 Hz, 1H), 6.02 (d, *J* = 3.3 Hz, 1H), 1.33 (s, 12H), 1.31 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.9, 124.8, 103.3, 84.0, 77.2, 33.1, 29.3, 24.9; ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): δ 27.4.

Borylation of 2-OTMS-furan



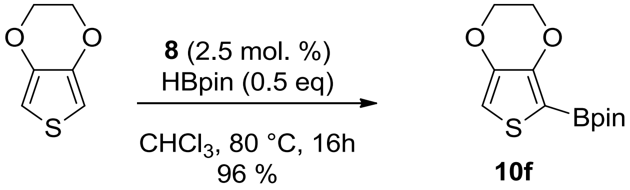
Quantity of 2-OTMS-furan: 229 µL (213 mg, 1.35 mmol, 2 eq.)

Yield: 179 mg (94 %)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 3.3, 1H), 5.18 (d, *J* = 3.3, 1H), 1.31 (s, 12H), 0.30 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 126.4, 110.2, 85.5, 83.9, 24.9, -0.1; ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): δ 26.7.

Although the product could be isolated, it tended to decompose in ambient conditions to the starting material.

Borylation of 3,4-ethylenedioxythiophene



Quantity of 3,4-ethylenedioxythiophene: 144 µL (191 mg, 1.35 mmol, 2 eq.)

Yield: 174 mg (96 %)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.63 (s, 1H), 4.31 – 4.28 (m, 2H), 4.19 – 4.17 (m, 2H), 1.34 (s, 12H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.2, 142.5, 107.6, 84.0, 65.2, 64.4, 24.9; ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$): δ 28.2.

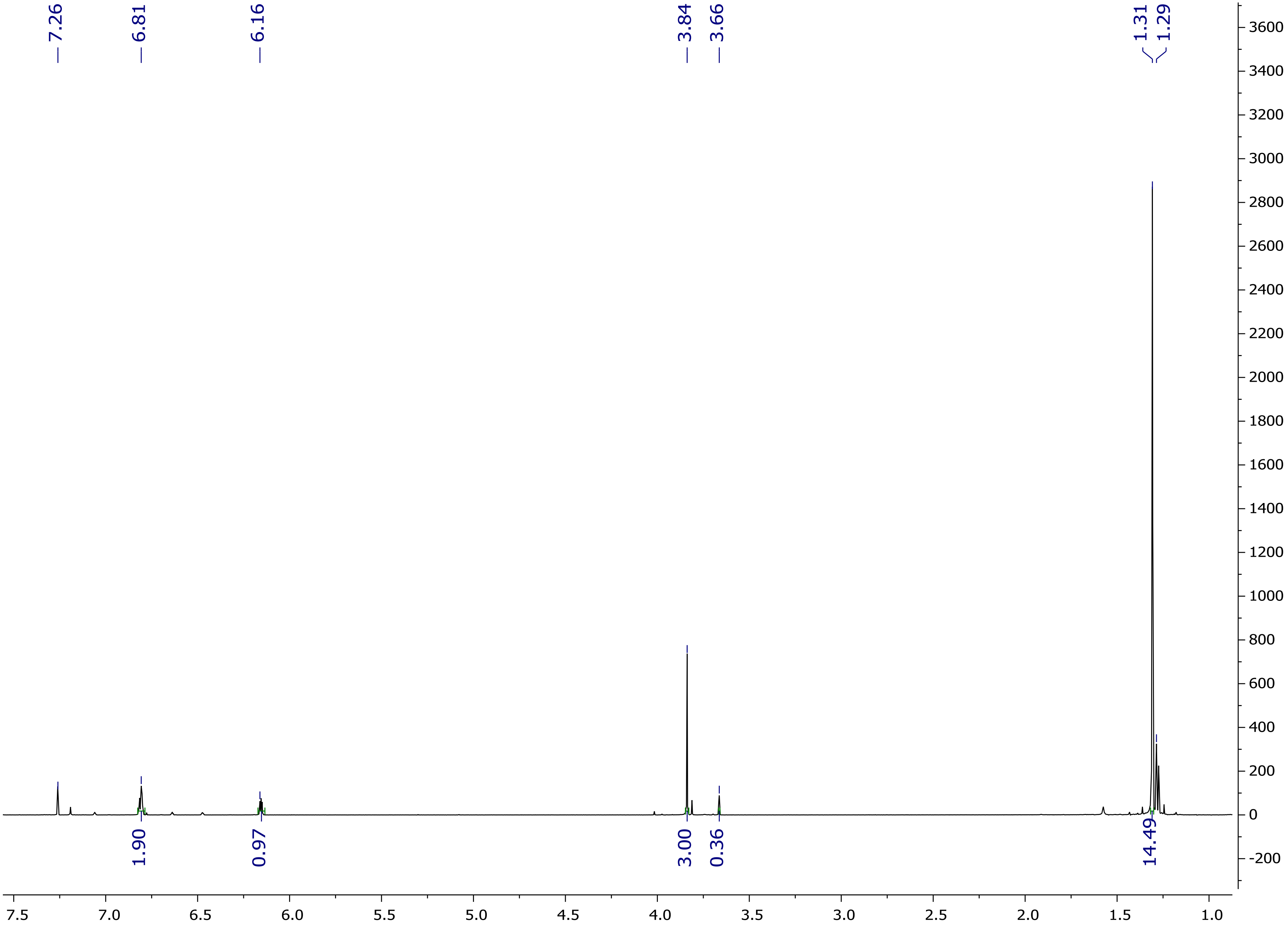


Figure S19: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of the borylation products of 1-methylpyrrole.

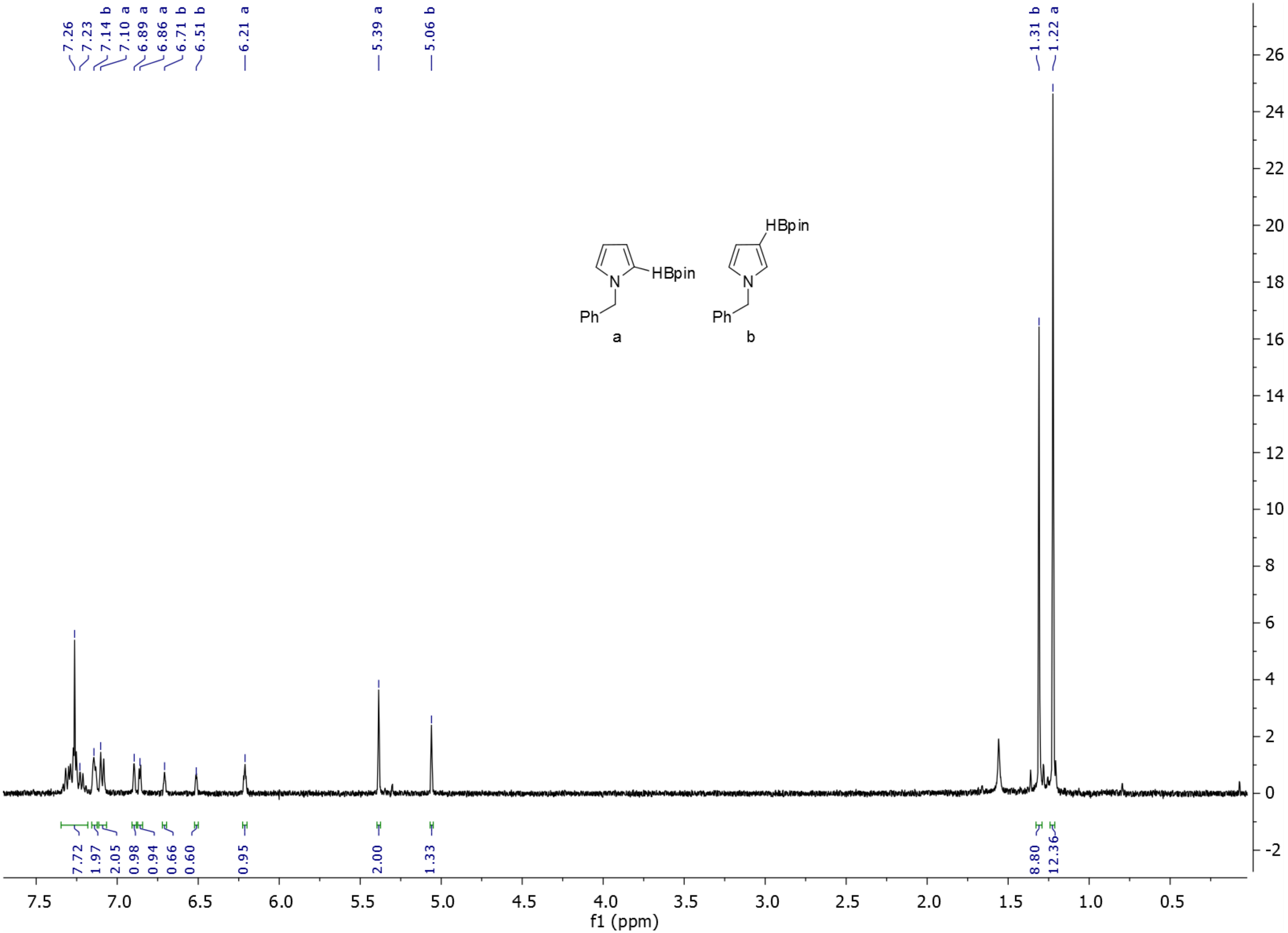


Figure S20: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of the borylation products of 1-benzylpyrrole.

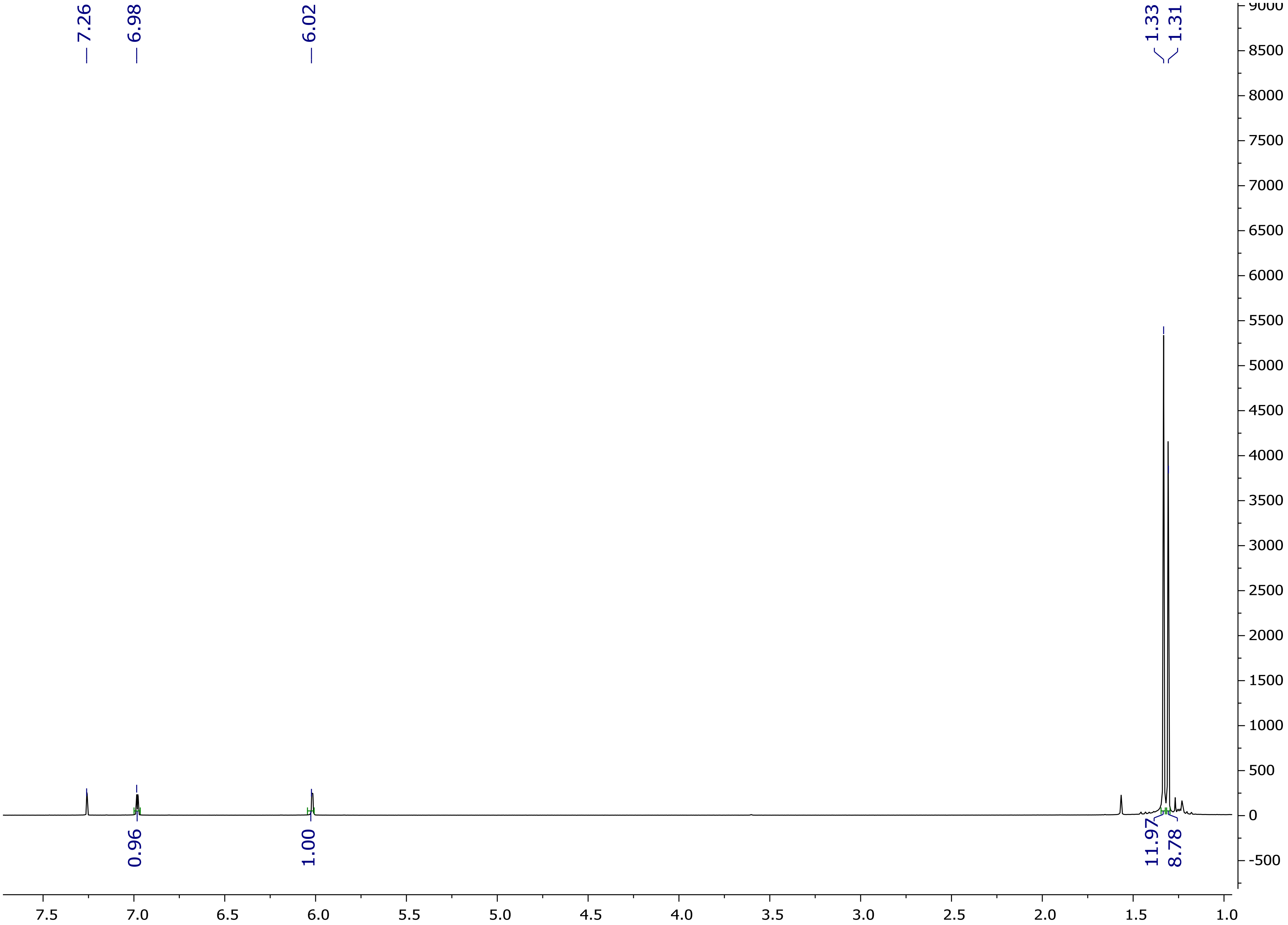


Figure S21: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of the borylation products of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(tertbutyl)furan.

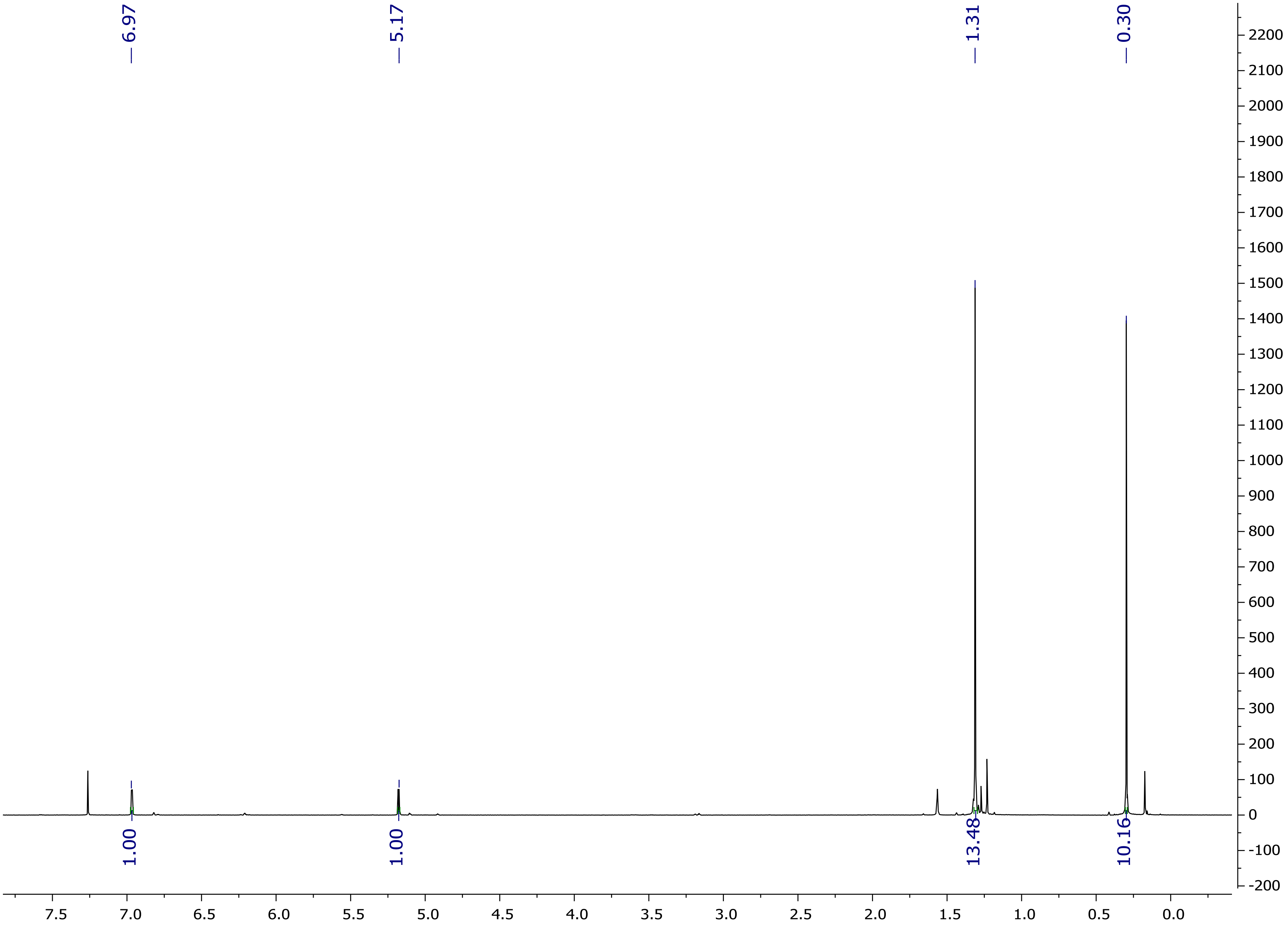


Figure S22: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of the borylation products of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trimethylsilyloxy)furan.

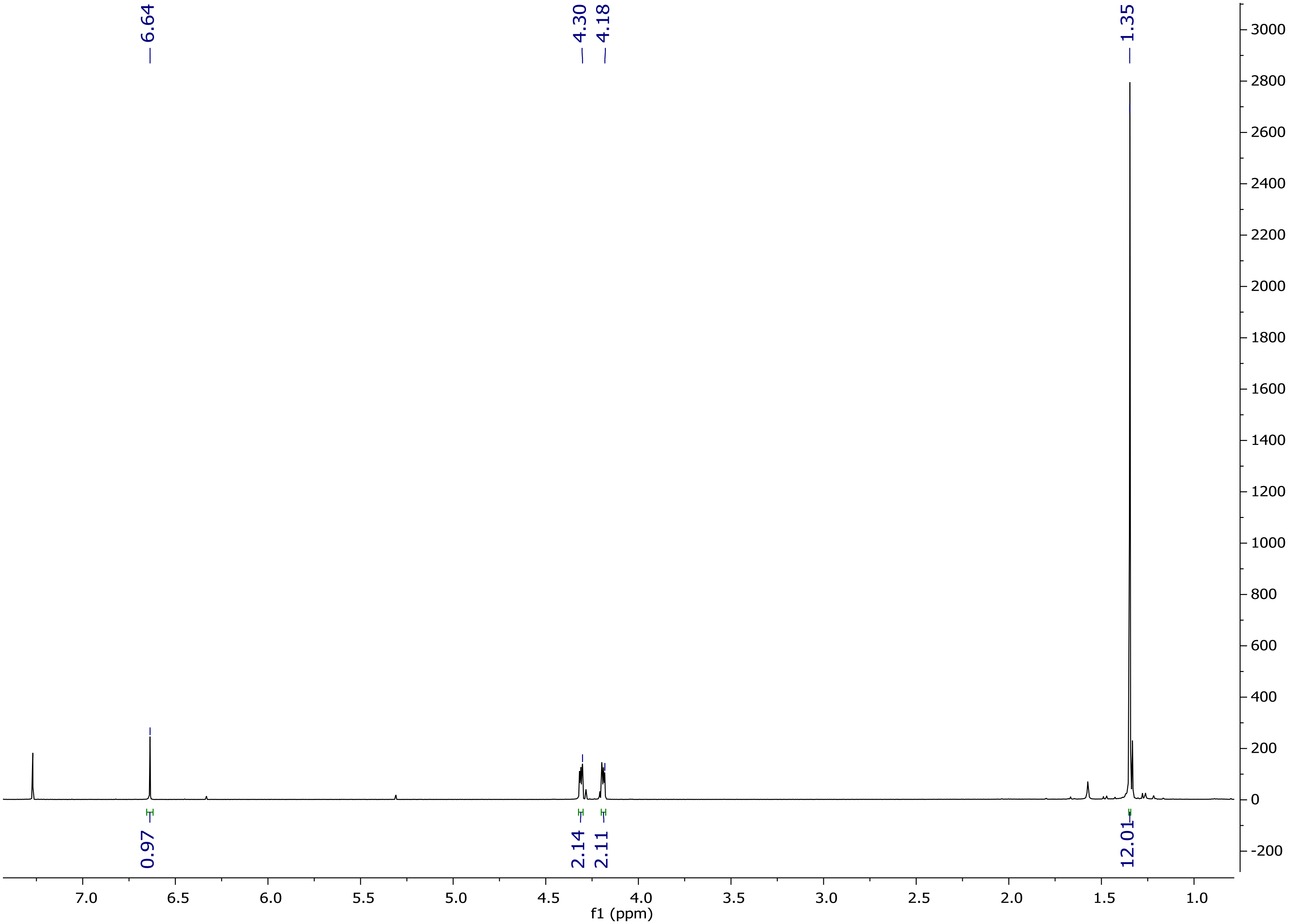


Figure S23: ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of the borylation products of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-ethylenedioxythiophene.

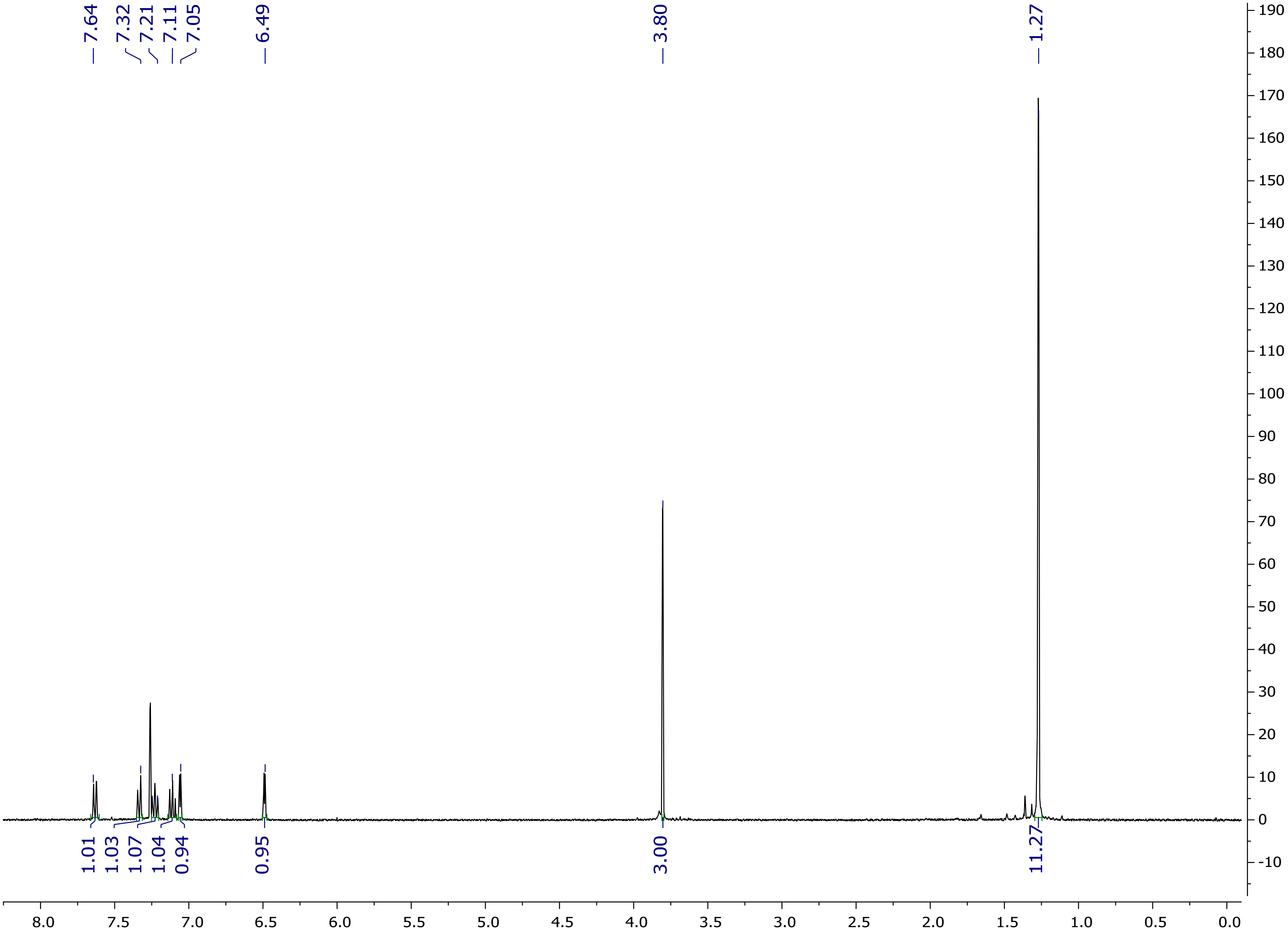


Figure S24: ^{1}H NMR (CDCl$_3$, 500 MHz) spectrum of the borylation products of 1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)indole

Crystallographic details

Crystals were mounted on CryoLoops with Paratone-N and optically aligned on a Bruker SMART APEX-II X-ray diffractometer with 1K CCD detector using a digital camera. Initial intensity measurements were performed using a fine-focused sealed tube, graphite-monochromated, X-ray source (Mo $K\alpha$, λ = 0.71073 Å) at 50 kV and 30 mA. Standard APEX-II software package was used for determining the unit cells, generating the data collection strategy, and controlling data collection. SAINT[10] was used for data integration including Lorentz and polarization corrections. Semi-empirical absorption corrections were applied using SCALE (SADABS[11]). The structures of all compounds were solved by direct methods and refined by full-matrix least-squares methods with SHELX-97[12] in the SHELXTL6.14 package. All of the H atoms on C atoms were generated geometrically and refined in riding mode. Crystallographic information for all obtained phases is summarized in Table S1. Atomic coordinates and additional structural information are provided in the .cif files of the Supporting Information. Crystallographic data have been deposited with CCDC (CCDC No. 1440668 (**2**), 1440670 (**3a**), 1440669 (**3b**)). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk, or via the Internet at www.ccdc.cam.ac.uk.

Table S1. Crystal data and structure refinement for compounds **2**, **3a** and **3b**.

	2	**3a**	**3b**
Empirical formula	C15 H24 B N O2	C15 H23 B F3 N	C16 H26 B F2 N O
Formula weight	261.16	285.15	297.19
Temperature	150(2) K	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 21/n	P 2_1/c	P 21/n
Unit cell dimensions	a = 13.8539(9) Å b = 7.8160(5) Å c = 15.2430(10) Å α= γ = 90°. β= 115.8630(10)°	a = 14.8666(9) Å b = 7.6330(5) Å c = 14.4543(9) Å α= γ = 90°. β= 115.5310(10)°.	a = 7.6884(7) Å b = 13.7157(12) Å c = 15.1094(13)Å α= γ = 90°. β= 98.4350(10)°.
Volume	1485.22(17) Å^3	1480.06(16) Å^3	1576.1(2) Å^3
Z	4	4	4
Density (calculated)	1.168 Mg/m^3	1.271 Mg/m^3	1.252 Mg/m^3
Absorption coefficient	0.075 mm^{-1}	0.094 mm^{-1}	0.092 mm^{-1}
F(000)	568	608	640
Crystal size	0.65 x 0.40 x 0.08 mm^3	0.52 x 0.29 x 0.25 mm^3	0.40 x 0.40 x 0.50 mm^3
Θ range data collect.	1.660 to 33.197°	1.518 to 33.283°.	2.015 to 33.173°.
Reflections collected	20605	20569	22164
Ind. reflections	4414 [R(int) = 0.0241]	5400 [R(int) = 0.0337]	5750 [R(int) = 0.0284]
Comp. Θ = 25.242°	100.0 %	100.0 %	100.0%
Max. and min. trans.	0.7466 and 0.7043	0.6940 and 0.7466	0.6913 and 0.7466
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / rest. / para.	5426 / 0 / 178	5400/0/189	5750 / 0 / 199
Goodness-of-fit on F^2	1.015	1.003	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0427 , wR2 = 0.1166	R1 = 0.0442, wR2 = 0.1359	R1 = 0.0447, wR2 = 0.1170
R indices (all data)	R1 = 0.0537, wR2 = 0.1263	R1 = 0.0659, wR2 = 0.1535	R1 = 0.0595, wR2 = 0.1280
Largest diff. peak and hole	0.408 and -0.170 e.Å^{-3}	0.422 and -0.211 e.Å^{-3}	0.309, and -0.308 e.Å^{-3}

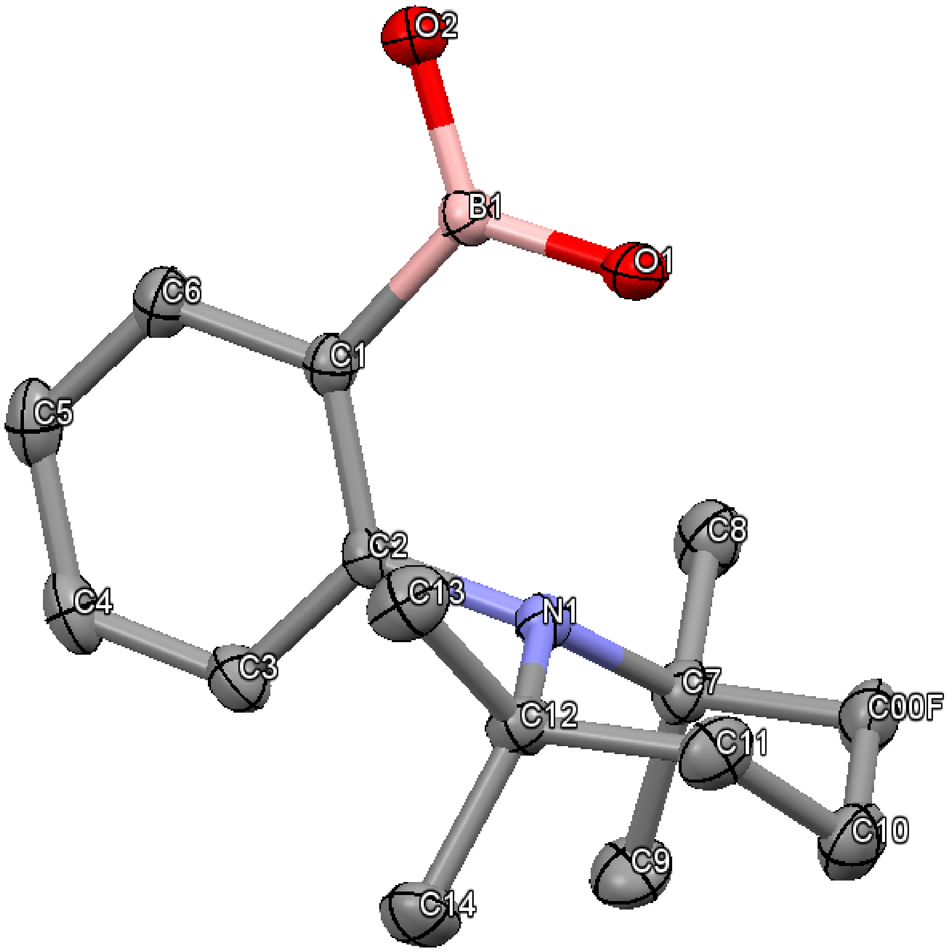


Figure S25. ORTEP structure of **2** with anisotropic atomic displacement ellipsoids at 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: O1-B1 = 1.3682(10); O2-B1 = 1.3535(10); C1-B1 = 1.5794(11); N1-C2 = 1.4595(10); O2-B1-O1 = 121.55(7); O2-B1-C1 = 118.24(7); O1-B1-C1 = 120.21(7); C2-C1-B1 = 123.41(7); C6-C1-B1 = 118.22(7); C3-C2-N1 = 122.17(7); C1-C2-N1 = 118.36(6).

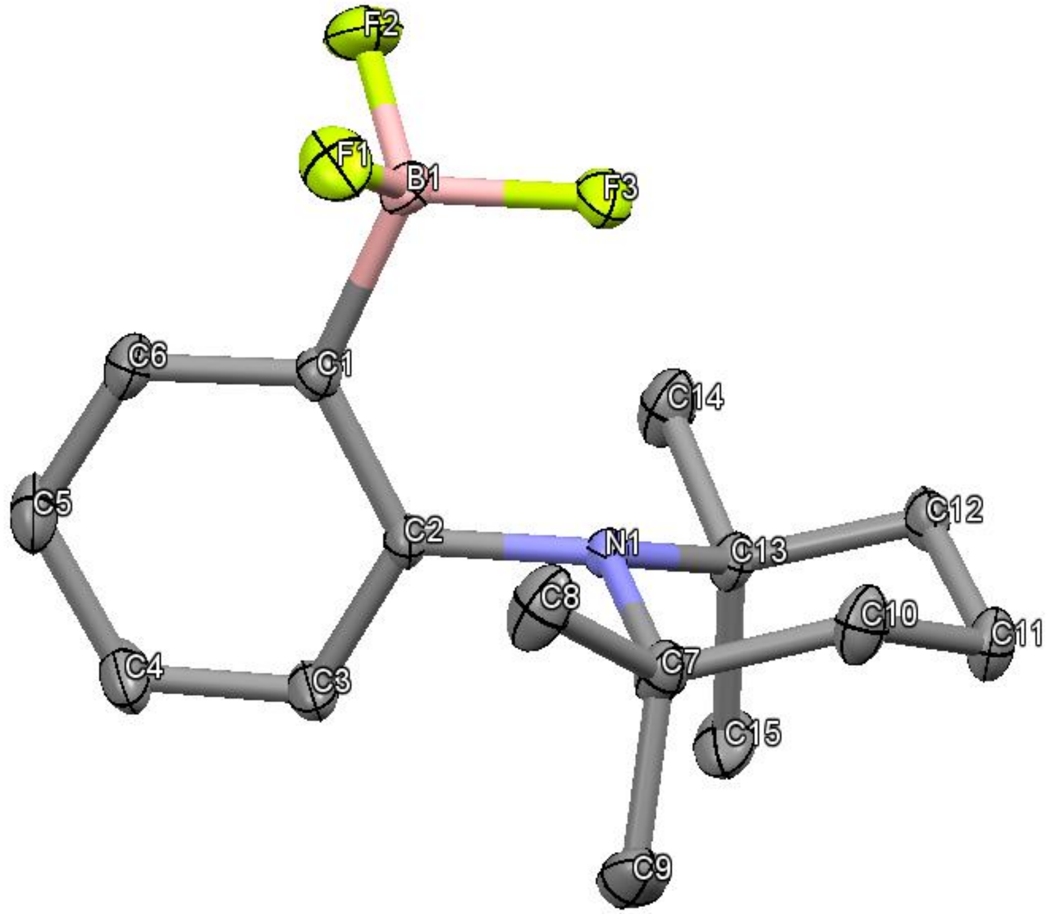


Figure S26. ORTEP structure of **3b** with anisotropic atomic displacement ellipsoids at 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]:F3-B1 = 1.4383(12); F1-B1 = 1.4066(13); F2-B1 = 1.3949(13); N1-C2 = 1.4883(11); C1-B1 = 1.6298(15); F2-B1-F1 = 108.74(8); F2-B1-F3 = 107.65(8); F1-B1-F3 = 107.46(9); F2-B1-C1 = 110.70(9); F1-B1-C1 = 109.79(8); F3-B1-C1 = 112.37(8); C2-C1-B1 = 128.39(8); C6-C1-B1 = 115.91(8); C3-C2-N1 = 120.03(8); C1-C2-N1 = 117.30(8).

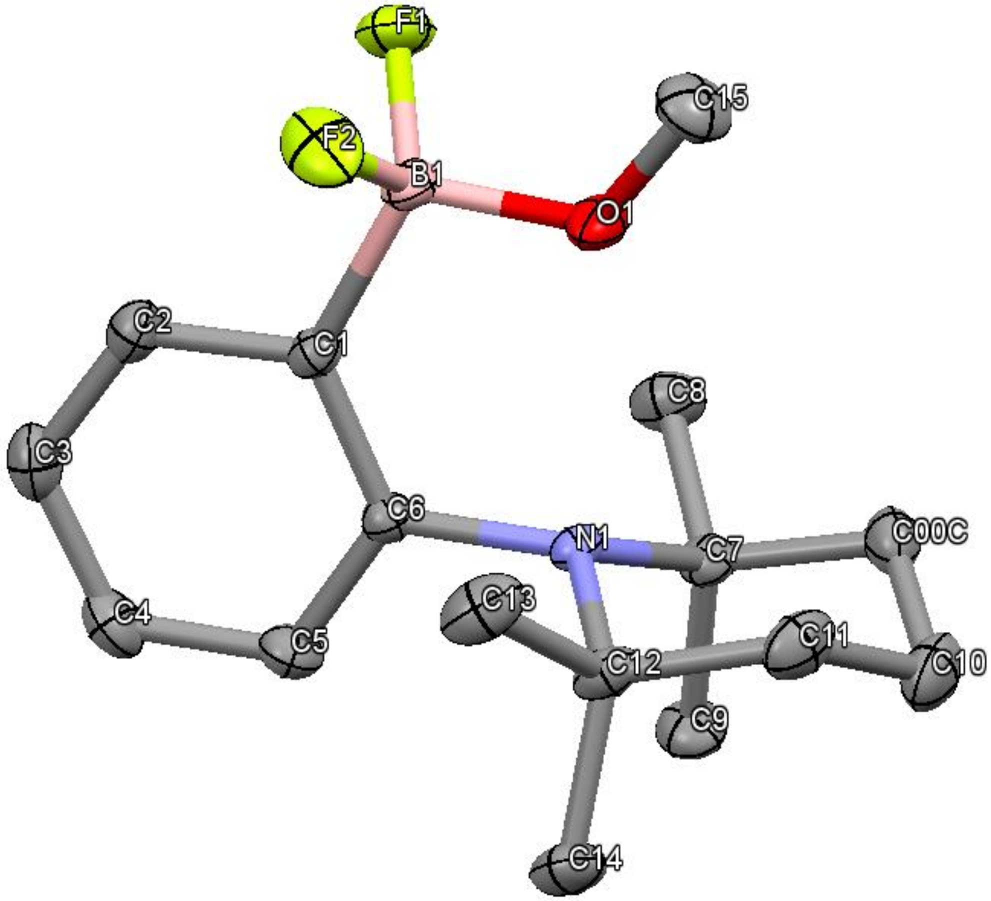


Figure S27. ORTEP structure of **3b** with anisotropic atomic displacement ellipsoids at 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: F1-B1 = 1.4164(12); F2-B1 = 1.4076(12); O1-C15 = 1.4122(12); O1-B1 = 1.4624(13); N1-C6 = 1.4864(11); C15-O1-B1 = 118.62(8); F2-B1-F1 = 107.04(8); F2-B1-O1 = 110.69(8); F1-B1-O1 = 109.12(8); F2-B1-C1 = 109.67(8); F1-B1-C1 = 109.85(8); O1-B1-C1 = 110.40(7); C6-C1-B1 = 128.32(8); C2-C1-B1 = 115.97(7); C5-C6-N1 = 120.33(8); C1-C6-N1 = 117.12(7).

Computational details

All the calculations were performed on the full structures of the reported compounds. Calculations were performed with the GAUSSIAN 09 suite of programs.[4] The ωB97XD functional[4] was used in combination with the 6-31G** basis set for all atoms.[5,6] The transition states were located and confirmed by frequency calculations (single imaginary frequency). The stationary points were characterized as minima by full vibration frequencies calculations (no imaginary frequency). All geometry optimizations were carried out without any symmetry constraints. The energies were then refined by single point calculations to include solvent effects using the SMD solvation model[7] with the experimental solvent, chloroform, at the ωB97XD /6-31+G** level of theory.[8]

Thermodynamics of the formation of 3a-c

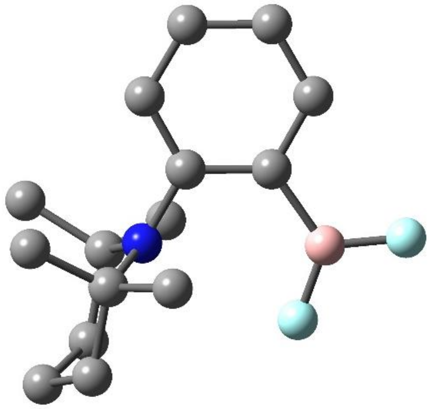
Molecular modeling was used to rationalize the observations made while making precatalysts **3a-c**. Indeed, as mentioned, the formation of trifluoroborate **3a** is majorly obtained in the case of long reaction times and/or high temperatures. By contrast, **3b** and **3c** are kinetic products that are initially formed in the mixture.

Calculations show that, after the hypothetic formation of a phenylene-bridged TMP-BF_2 FLP, the binding of HF by the latter is much more exergonic thant that of H_2O and MeOH (Table S1). This supports the observation that **3a** is thermodynamically downhill with regards to **3b-c**.

Table S2. Computed binding energies of small molecules by a TMP-BF_2 FLP.

Species	ΔH (kcal/mol)	ΔG (kcal/mol)
TMPBF2	0	0
TMPBF2 + MeOH (**3b**)	-31.42	-18.35
TMPBF2 + H_2O (**3c**)	-27.96	-17.36
TMPBF2 + HF (**3a**)	-36.13	-26.48

TMPBF2



Sum of electronic and thermal Enthalpies= -864.161431
Sum of electronic and thermal Free Energies= -864.222655

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N	3.23384600	1.91528500	0.50707200	C	3.59872000	2.32945800	2.89817500

C	3.45336200	3.82316500	2.64278800
C	2.47573800	4.03031900	1.49443300
C	3.22823300	1.00485000	-0.59150400
C	2.13284100	0.13092900	-0.77138300
C	2.14355400	-0.75799300	-1.85676900
C	3.20151200	-0.79887200	-2.75545500
C	4.27662200	0.06270600	-2.57420500
C	4.28701100	0.95247000	-1.50426000
B	0.88883800	0.07925100	0.16357000
C	5.59942500	1.78595500	1.45708600
C	3.90207000	0.05360500	1.97384700
C	4.05401800	4.12447700	-0.47439500
C	1.70940900	3.37171500	-0.76502500
H	1.30173500	-1.42920700	-1.99424600
H	3.18761400	-1.49479700	-3.58776200
H	5.11323700	0.04550000	-3.26624300
H	5.13043800	1.61962700	-1.37297800
H	2.61929000	1.92890000	3.18532300
H	4.28751300	2.13794200	3.72857600
H	3.08474300	4.32373900	3.54418700
H	4.42570900	4.27615400	2.41386100
H	2.33401400	5.09676000	1.28641900
H	1.50197400	3.62132700	1.78880800
H	4.35349500	3.66170800	-1.41807100
H	4.93730700	4.20916400	0.16042300
H	3.71440400	5.14010100	-0.70300100
H	1.95036500	2.95247000	-1.74543400
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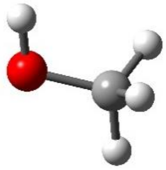
H	0.86317300	2.82242500	-0.34662100
H	5.84356400	2.83720700	1.29698200
H	5.97275900	1.21377100	0.60409500
H	6.15167000	1.45079700	2.34127600
H	4.28692000	-0.58351400	1.17323700
H	2.84658500	-0.17924500	2.13113700
H	4.44581600	-0.19437700	2.89031500
F	0.68200900	0.83332400	1.23504400
F	-0.08333300	-0.79360000	-0.10657800

MeOH



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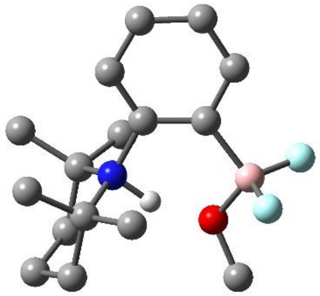
TMPBF2_MeOH



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C	3.38431600	2.46283500	2.85748900
C	3.33813300	3.95392900	2.53901500
C	2.47939100	4.19788300	1.30223300
C	3.17516500	1.00549000	-0.66426000
C	2.05158200	0.20181100	-0.88300800
C	2.12251000	-0.66162400	-1.98412400
C	3.24290500	-0.73749300	-2.80136900
C	4.34908800	0.06494000	-2.53677300
C	4.31610600	0.94675800	-1.46430400
B	0.71481400	0.10052000	0.07275300
C	5.43385400	1.78353400	1.53432700
C	3.65840200	0.12143100	2.01911600
C	4.24588800	4.06907300	-0.50699500
C	1.87987300	3.52968000	-1.03172300
H	1.25904400	-1.28454800	-2.19544300
H	3.25820900	-1.42121200	-3.64461600
H	5.23359500	0.01307300	-3.16329100
H	5.17440900	1.57596200	-1.26715300
H	2.37224200	2.11622300	3.10217100
H	4.00420900	2.27121400	3.73892000
H	2.91664400	4.49700800	3.39009600

H	4.34943700	4.35045900	2.39306000
H	2.44068100	5.26413500	1.05849100
H	1.44987300	3.88248500	1.51108800
H	4.59236000	3.54808800	-1.39963400
H	5.06261700	4.12646500	0.21046400
H	4.00434000	5.09268000	-0.80672200
H	2.21695400	3.08977200	-1.97236900
H	1.65585300	4.58569500	-1.20758800
H	0.96675100	3.02236800	-0.71482500
H	5.74619600	2.82178400	1.43334700
H	5.81553900	1.21217000	0.68763000
H	5.91463100	1.38642700	2.43262200
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H	4.08409900	-0.09875200	3.00226800
H	2.09162500	1.77694200	0.80970000
F	0.86364200	-0.97850700	0.97441800
F	-0.42990400	-0.08617800	-0.69974800
O	0.61402800	1.36196700	0.86530900
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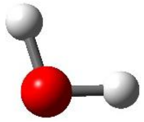
H	-0.29731800	2.35730400	2.40036600
H	-1.30475400	1.13523700	1.58785500
H	-0.01854600	0.61758400	2.69884200

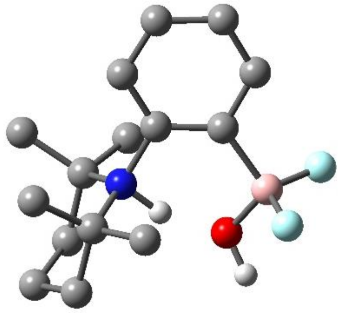
H2O



Sum of electronic and thermal Enthalpies= -76.391776
Sum of electronic and thermal Free Energies= -76.413849

O	1.69129100	-0.38241200	0.00000000
H	2.65004500	-0.33932300	0.00000000
H	1.41184600	0.53576200	0.00000000

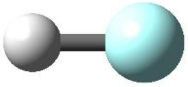
TMPBF2_H2O



Sum of electronic and thermal Enthalpies= -940.159197
Sum of electronic and thermal Free Energies= -940.226291

C	2.96379900	3.45420400	0.04144600
N	3.07772300	1.96875200	0.45738700
C	3.90902900	1.60121700	1.70383000
C	3.36707600	2.47023300	2.85103000
C	3.33271100	3.96139500	2.53080500
C	2.47894500	4.20920100	1.29116800
C	3.16952600	1.01050700	-0.67008500
C	2.04271000	0.21515600	-0.89885000
C	2.11956700	-0.65143700	-1.99717800
C	3.24838500	-0.73757900	-2.80157600
C	4.35664900	0.05914600	-2.52803900
C	4.31816600	0.94427200	-1.45856200
B	0.69271500	0.13470500	0.04080700
C	5.41937500	1.77997900	1.53948700
C	3.63566100	0.12532800	2.01546300
C	4.25153400	4.06615800	-0.51274100
C	1.88403000	3.54364600	-1.04489700
H	1.25283200	-1.26684000	-2.21641500
H	3.26827600	-1.42375300	-3.64273400
H	5.24701900	0.00054200	-3.14561200
H	5.17776300	1.56965500	-1.25535600
H	2.35062000	2.13067600	3.08636700
H	3.97877900	2.27434000	3.73717900
H	2.91233100	4.50832700	3.37998700
H	4.34740200	4.35034700	2.38810600
H	2.44710200	5.27539600	1.04627000
H	1.44784800	3.89729100	1.49576100
H	4.59486900	3.54375600	-1.40578100
H	5.06768800	4.11609400	0.20582800
H	4.01876900	5.09212400	-0.81116200
H	2.21780800	3.09115700	-1.98073200
H	1.67822800	4.60175700	-1.23031500
H	0.96018900	3.05616400	-0.72818900
H	5.73722700	2.81636200	1.43758200
H	5.80397400	1.20411000	0.69731800
H	5.89242500	1.38343200	2.44212800
H	4.11667800	-0.53061700	1.28684900
H	2.57116000	-0.11596100	2.02266600
H	4.05351700	-0.09555100	3.00185400
H	2.08239100	1.78750300	0.79682700
F	0.82172200	-0.92514000	0.97281500
F	-0.43057900	-0.07472600	-0.75458600
O	0.56798200	1.40046900	0.82703800
H	0.02897500	1.21490500	1.59991100

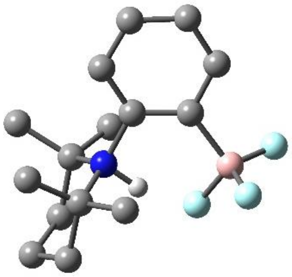
HF



Sum of electronic and thermal Enthalpies= -100.418424
Sum of electronic and thermal Free Energies= -100.438129

F	-2.50972400	0.59435500	-0.00778100
H	-3.42855100	0.59435500	-0.00778100

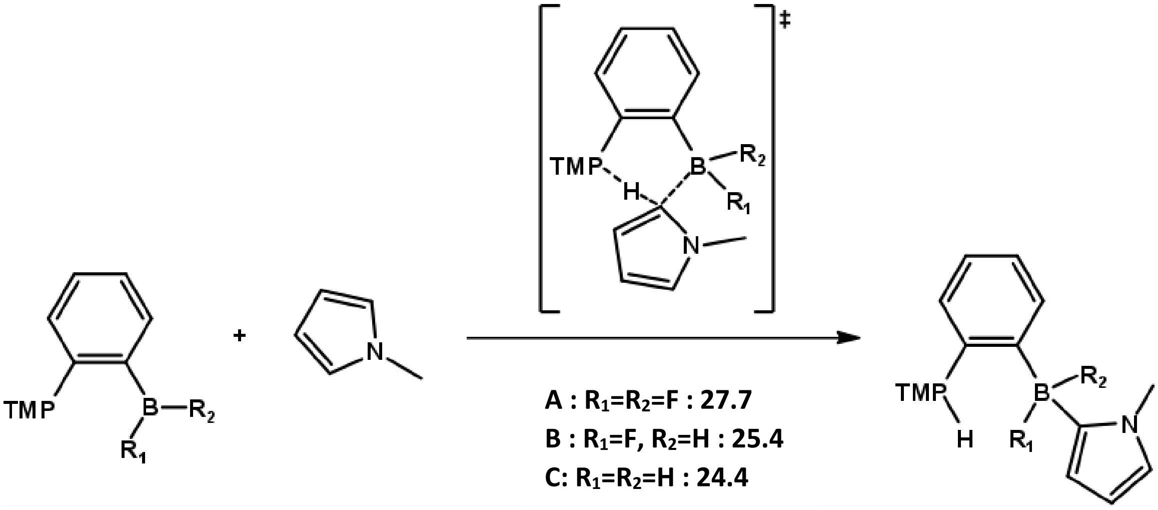
TMPBF2_HF



Sum of electronic and thermal Enthalpies= -964.198858
Sum of electronic and thermal Free Energies= -964.265107

C	2.95828700	3.44735000	0.05104800
N	3.09500600	1.95891300	0.46110700
C	3.93209600	1.59287900	1.70902100
C	3.38336400	2.45498900	2.85748100
C	3.33942800	3.94657700	2.54116500
C	2.47497800	4.19021000	1.30841900
C	3.18629500	1.00234100	-0.66898500
C	2.06027600	0.20351000	-0.88511800
C	2.13190100	-0.66624600	-1.98121900
C	3.25477900	-0.74776900	-2.79467600
C	4.36138800	0.05538200	-2.53322800
C	4.32883100	0.94285800	-1.46538400
B	0.71078200	0.12669400	0.05971500
C	5.43817600	1.78485600	1.53258400
C	3.66567700	0.11546500	2.01613200
C	4.23404100	4.07033200	-0.51419400
C	1.86380000	3.51963400	-1.02082600
H	1.26824800	-1.28836600	-2.19387700
H	3.27119000	-1.43591200	-3.63415900
H	5.24614800	-0.00054800	-3.15883400
H	5.18673700	1.57301100	-1.26964500
H	2.36929400	2.10744700	3.09169900
H	3.99724400	2.26041500	3.74227100
H	2.91909800	4.48812800	3.39347400
H	4.35024800	4.34357400	2.39313200
H	2.42848500	5.25664500	1.06731300
H	1.44891100	3.86680500	1.52179500
H	4.57607900	3.54926400	-1.40859800
H	5.05409100	4.12993000	0.19925800
H	3.98829300	5.09307500	-0.81294100
H	2.19146600	3.07547600	-1.96266800
H	1.63276900	4.57336500	-1.19939400
H	0.95478500	3.01350200	-0.69237800
H	5.74479600	2.82371100	1.42168500
H	5.82282000	1.20668000	0.69189100
H	5.92073100	1.39912400	2.43468800
H	4.13920500	-0.53749400	1.27999100
H	2.60103900	-0.12555300	2.03993900
H	4.09538400	-0.10729400	2.99678200
H	2.12057500	1.77317600	0.79289900
F	0.83678700	-0.90964500	0.98647500
F	-0.41740400	-0.00987100	-0.72144800
F	0.59317200	1.37194400	0.84255200

Transition state free energy for the C-H bond activation of N-methylpyrolle for different intermediates expected for the deprotection reaction. Computed at the ωB97Xd/6-31+G**, SMD solvent=chloroform, level of theory (energy reported in kcal/mol).

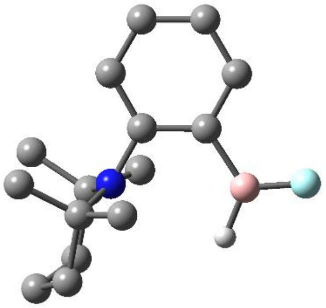


*****The most energetically favorable conformation of **A** and **B** was computed to be monomeric, but in the case of **C** the known dimeric form with bridging hydride is the most energetically favorable conformation.

Considering the energy difference between the C-H bond activation transition state of the different species, the reaction should be about 110 times slower in the case of **A** and 4 times slower in the case of **B**, compared to **C**. Since such difference in speed were not observed experimentaly, species **C** is ought to be responsible for the observed catalytic activity. However, those transition states should be accessible in the reaction condition and might have a role to play in the deprotection mechanism which remain elusive.

The structure, the sum of electronic and thermal enthalpies and the sum of electronic and thermal free energies for **1** (**C**) and N-Methylpyrolle were taken from: M.-A. Légaré, M.-A. Courtemanche, E. Rochette and F.-G. Fontaine, *Science*, 2015, **349**, 513–516.

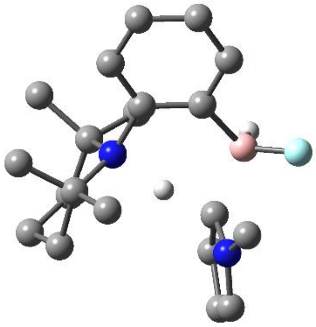
TMPBF1H1



Sum of electronic and thermal Enthalpies= -764.422438
Sum of electronic and thermal Free Energies= -764.482788

C	2.89989200	3.32391200	0.19519200
N	3.22117500	1.90868800	0.50920400
C	4.07720500	1.54235700	1.66567800
C	3.59943200	2.33057700	2.89879400
C	3.45895500	3.82389000	2.63939400
C	2.47624700	4.03096700	1.49558700
C	3.23280200	1.00304900	-0.59711200
C	2.14033600	0.12686000	-0.78267300
C	2.15735300	-0.75986500	-1.86991000
C	3.21911100	-0.79545000	-2.76381600
C	4.29131100	0.07006100	-2.57500000
C	4.29740400	0.95874100	-1.50370700
B	0.91638500	0.10903600	0.17513000
C	5.59065200	1.77160800	1.45354800
C	3.88372900	0.05032700	1.97841000
C	4.04096500	4.11583700	-0.48221900
C	1.69360200	3.36361500	-0.75599500
H	1.31553400	-1.43190600	-2.00903300
H	3.21339900	-1.48863300	-3.59873000
H	5.13052500	0.05618600	-3.26413700
H	5.13983300	1.62685600	-1.37002700
H	2.62019700	1.93568500	3.19725500
H	4.29194100	2.13854200	3.72586400
H	3.09848800	4.32989200	3.54103500
H	4.43197600	4.27093000	2.40229900
H	2.33764900	5.09708200	1.28425300
H	1.50053500	3.63082600	1.79855300
H	4.32993700	3.65363300	-1.42920400
H	4.93034700	4.19596100	0.14481200
H	3.70282000	5.13304100	-0.70600400
H	1.92907100	2.94375000	-1.73734000
H	1.38090500	4.40224500	-0.89995000
H	0.85025000	2.80893400	-0.33533400
H	5.83937900	2.82054000	1.28477800
H	5.95942900	1.19104600	0.60449800
H	6.14267500	1.44046100	2.33940200
H	4.26474900	-0.59076000	1.17928500
H	2.82560400	-0.17937500	2.13180300
H	4.42333800	-0.19920900	2.89698300
F	-0.06929400	-0.75801200	-0.08324800
H	0.77164800	0.80726500	1.13361900

TMPBF1H1_pyrolTS

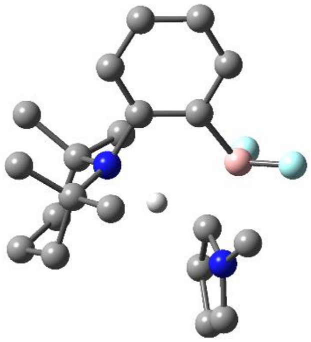


Sum of electronic and thermal Enthalpies= -1013.711481

Sum of electronic and thermal Free Energies= -1013.783945

C	-1.31904700	-2.04609900	0.54589800
C	-0.02950300	-1.65494700	0.94991800
C	1.01460300	-2.55126500	0.67817300
C	0.80784900	-3.78214600	0.07056100
C	-0.48256100	-4.16237000	-0.28265500
C	-1.54100900	-3.29496100	-0.04535200
H	2.01913200	-2.25244900	0.96198700
H	1.64519500	-4.44710200	-0.11977100
H	-0.67077400	-5.12774100	-0.74207000
C	-4.04792400	0.53357500	-0.12528800
C	-4.04842200	-1.75723900	-1.18568100
C	-2.18354300	-0.21724700	-1.57902100
H	-4.88526600	-0.46282600	3.05916300
H	-3.62636400	0.66059700	2.56568300
C	-5.01817400	0.22771400	1.00547600
H	-1.70297000	-2.38752300	3.13407300
H	-1.73440500	-0.64365200	3.35870400
H	-2.98967700	-1.64362900	4.09761400
H	-3.47922700	-3.53953400	1.61511600
H	-4.46246100	-2.90728700	2.92804200
H	-4.96810500	-2.63196400	1.27476000
H	-4.57873800	0.86793200	-1.02289700
H	-3.39069000	1.35748300	0.18135100
H	-4.70006600	-1.25575400	-1.90790100
H	-3.43502800	-2.46256300	-1.74800900
H	-4.68605700	-2.32030700	-0.51053000
H	-1.70639300	0.71827100	-1.29847400
H	-2.53958500	-3.60335500	-0.32303800
H	-1.59423600	0.06884300	1.05945200
B	0.35518000	-0.29957000	1.76612200
N	-2.42185600	-1.09508900	0.75135300
C	-3.27510100	-1.38686400	1.98818500
C	-3.17708100	-0.67687800	-0.50719400
C	-4.22025200	-0.19552100	2.23095900
C	-2.36153700	-1.51995300	3.21088200
C	-4.09341900	-2.69175100	1.92139700
H	-1.42142800	-0.97424400	-1.77636500
H	-2.73314200	-0.04246300	-2.50823800
H	-5.61595200	1.11380800	1.24094400
H	-5.72669100	-0.55347200	0.70526900
C	-0.67935800	0.98260300	1.32634200
C	-1.29682500	1.92172600	2.18416600
C	-1.32013700	3.17771900	1.58322700
H	-1.71145800	1.66901200	3.15095600
H	-1.74399600	4.09311500	1.96894600
H	0.20237900	-0.45259700	2.96289700
C	-0.66340000	3.03085200	0.36502800
H	-0.42157200	3.77386600	-0.38361100
N	-0.29336700	1.75087900	0.20654500
C	0.64482900	1.30819100	-0.81430500
H	0.46062400	1.86101300	-1.73818500
H	1.66526800	1.46299000	-0.46361200
H	0.51252900	0.24266100	-0.99308600
F	1.69063100	0.08525900	1.47476400

TMPBF2_pyrolTS



Sum of electronic and thermal Enthalpies= -1113.008931
Sum of electronic and thermal Free Energies= -1113.082247

C	-1.31193500	-2.06014300	0.55602600	H	-3.55226300	-3.52728600	1.57315300
C	-0.01888400	-1.67747500	0.95601000	H	-4.49207600	-2.88454400	2.91035200
C	1.01352600	-2.59756000	0.72614000	H	-5.01924100	-2.57073900	1.27111900
C	0.79470000	-3.84397500	0.15553700	H	-4.54685500	0.86186800	-1.05193800
C	-0.49652700	-4.20931800	-0.20809000	H	-3.34855800	1.35457900	0.14034300
C	-1.54390600	-3.31932200	-0.00900000	H	-4.67517700	-1.26985600	-1.92787500
H	2.02091600	-2.30784200	1.00925700	H	-3.42622200	-2.48917300	-1.74065000
H	1.62252200	-4.52886400	-0.00183700	H	-4.68669800	-2.31597700	-0.51666300
H	-0.69466900	-5.18248200	-0.64648800	H	-1.68441300	0.68979100	-1.32648200
H	-2.54275600	-3.61891100	-0.29439900	H	-1.39181300	-1.00958000	-1.77284600
H	-1.58873200	0.07183500	1.04243200	H	-2.69880800	-0.09224200	-2.53086400
B	0.40073200	-0.28957000	1.70846600	H	-5.56404300	1.15833200	1.21556100
N	-2.41210900	-1.10296500	0.74347400	H	-5.71132800	-0.51112300	0.69694200
C	-3.27751500	-1.38533100	1.97633000	C	-0.67125400	0.98065100	1.30582900
C	-3.15811600	-0.69082200	-0.52140100	C	-1.26909800	1.87225000	2.22587500
C	-4.19375000	-0.17168000	2.21567900	C	-1.33748700	3.14941800	1.67678900
C	-2.37234000	-1.55889500	3.19916700	H	-1.63466600	1.57184800	3.19796900
C	-4.13487500	-2.66533900	1.90028300	H	-1.76155300	4.04088900	2.11460800
C	-4.01593000	0.53358500	-0.15206600	C	-0.72561600	3.06290900	0.42940100
C	-4.03649200	-1.76949600	-1.19294600	H	-0.52869500	3.83942700	-0.29831400
C	-2.15703500	-0.25094800	-1.59430400	N	-0.33422200	1.79975800	0.20638500
H	-4.86435500	-0.42012700	3.04517100	C	0.58328300	1.42611400	-0.86090200
H	-3.58177400	0.67310200	2.54550600	H	0.31925500	1.96910700	-1.77136500
C	-4.98544500	0.25771900	0.98736400	H	1.60697000	1.65209100	-0.56201700
H	-1.78355000	-2.47664200	3.13562700	H	0.51672000	0.35533000	-1.04187400
H	-1.67194800	-0.74034800	3.33974800	F	1.69136800	0.09833600	1.31177200
H	-3.00860100	-1.62570900	4.08650300	F	0.35494600	-0.41794200	3.10621

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