# Supporting Information

## Weakly Stabilized Primary Borenium Cations and their Dicationic Dimers

Aleksandrs Prokofjevs, Jeff W. Kampf, Andrey Solovyev, Dennis P. Curran,* and Edwin Vedejs*

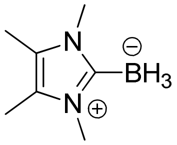
# Table of Contents

# General Remarks

All reactions were performed at room temperature (unless otherwise stated), under an atmosphere of dry nitrogen, either in a glovebox, or using standard Schlenk techniques. Nuclear magnetic resonance experiments were performed at the following frequencies: $^{1}H$ 700 MHz or 400 MHz; $^{11}B$ and $^{11}B\{^{1}H\}$ 225 MHz, 128 MHz or 96 MHz; $^{13}C\{^{1}H\}$ 176 MHz or 101 MHz; $^{19}F$ 471 MHz or 376 MHz. All spectra were recorded in $CDCl_3$, $d_5$-PhBr, $CD_2Cl_2$ or $CH_2Cl_2$ and referenced to the $^{1}H$ signal of internal $Me_4Si$ according to IUPAC recommendations,[22] using a $\Xi$ (referencing parameter) of 32.083974 for $BF_3$–$OEt_2$ ($^{11}B$), a $\Xi$ of 25.145020 for $Me_4Si$ ($^{13}C$), and a $\Xi$ of 94.094011 for $CCl_3F$ ($^{19}F$). When the internal $Me_4Si$ reference could not be used, residual solvent peaks in $^{1}H$ NMR spectra were referenced instead. Hexanes, $CH_2Cl_2$, and THF were dried by passing through a column of activated alumina. Hexanes and $CH_2Cl_2$ were further dried by storing over activated 3Å molecular sieves in the glovebox. Commercially available NMR grade deuterated solvents (Cambridge Isotope Laboratories), as well as benzene and fluorobenzene were not distilled; instead they were simply dried over a large amount of activated 3Å molecular sieves in the glovebox. All other reagents were used as received from commercial suppliers, or prepared according to published procedures.[23]

# NHC Boranes

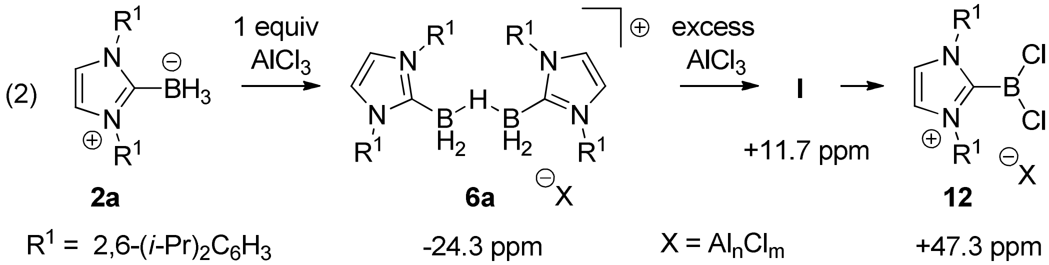
## *Preparation of 2e*



A solution of $LiN(SiMe_3)_2$ (7.06 g, 42.2 mmol) in 20 mL of dry THF was cannulated into a slurry of thoroughly dried 1,3,4,5-tetramethylimidazolium iodide (9.68g, 38.4 mmol) in 20 mL of dry THF at −78 °C. After stirring at −78 °C for 1 h, neat $Me_2S–BH_3$ (4.3 mL, 42.2 mmol) was added dropwise, and the resulting mixture was allowed to warm up to rt. The resulting clear yellowish solution was stirred at rt for 1 h, during which time it developed a white precipitate. Following careful quenching with 100 mL of brine (frothing!) the reaction mixture was extracted with $CH_2Cl_2$ (1x70 mL, then 2x40 mL). The combined organic extracts were dried with $MgSO_4$, then filtered and concentrated. Crystallization of the resulting solid from hexanes/$CHCl_3$ mixture provided 4.94g (93%) of **2e** as an off-white crystalline solid in two crops. The product was additionally recrystallized from hexanes/$CHCl_3$ before use in sensitive electrophilic activations. The compound was identical to that reported previously according to NMR data.[24]

$^1$H NMR (700 MHz, $CDCl_3$): δ 3.62 (s, 6H), 2.12 (s, 6H), 1.3-0.8 ppm (m, 3H). $^{11}$B NMR (225 MHz, $CDCl_3$): δ −36.9 ppm (q, J = 86 Hz). $^{13}$C NMR (176 MHz, $CDCl_3$): δ 169.7-168.6 (m), 123.0, 32.4, 8.7 ppm. HRMS (EI+): m/z calculated for $C_9H_{22}BNNa$ $[M-H]^+$ 137.1250, found 137.1257 (+5 ppm).

## NHC Borane activations with $TiCl_4$ and $AlCl_3$



*Generation of* ***6a*** *with $TiCl_4$:* A solution of $TiCl_4$ (1 M in $CH_2Cl_2$, 0.1 mL, 0.1 mmol) was added to a solution of NHC–$BH_3$ **2a** (40.5 mg, 0.10 mmol) in $CH_2Cl_2$ (1 mL) at 0 °C. The vigorous evolution of $H_2$ gas was immediately observed. After 5 min, $^{11}B$ NMR analysis of the yellow crude mixture showed the complete conversion of **2a** to **6a**. The structure of the counterion was not established. No further reaction was observed with excess $TiCl_4$ (up to 5 equiv).

$^{11}B$ NMR (128 MHz, $CH_2Cl_2$): δ −24.6 ppm (br s). $^{13}C$ NMR (101 MHz, $CH_2Cl_2$): δ 144.6, 132.0, 130.8, 124.2, 124.1, 28.4, 25.1, 21.9 ppm.

*Generation of* ***6a*** *with $AlCl_3$:* $CD_2Cl_2$ (0.5 mL) was added to a mixture of solid NHC–$BH_3$ **2a** (30 mg, 0.075 mmol) and $AlCl_3$ (10 mg, 0.075 mmol). Intense gas bubbling was observed. The $^{13}C$ and $^{11}B$ NMR spectra of the light yellow reaction mixture were identical to those of **6a** obtained in the reaction with $TiCl_4$.

$^{1}H$ NMR (400 MHz, $CD_2Cl_2$): δ 7.47 (br t, $J$ = 7.2 Hz, 4H), 7.18 (br d, $J$ = 6.0 Hz, 8H), 7.12 (s, 4H), 2.12 (br s, 8H), 1.02 (d, $J$ = 4.4 Hz, 24H), 0.96 ppm (d, $J$ = 4.4 Hz, 24H). $^{11}B$ NMR (128 MHz, $CD_2Cl_2$): δ −24.3 ppm (br s). $^{13}C$ NMR (100 MHz, $CD_2Cl_2$): δ 144.8, 132.3, 131.0, 124.5, 124.3, 28.7, 25.3, 22.1 ppm.

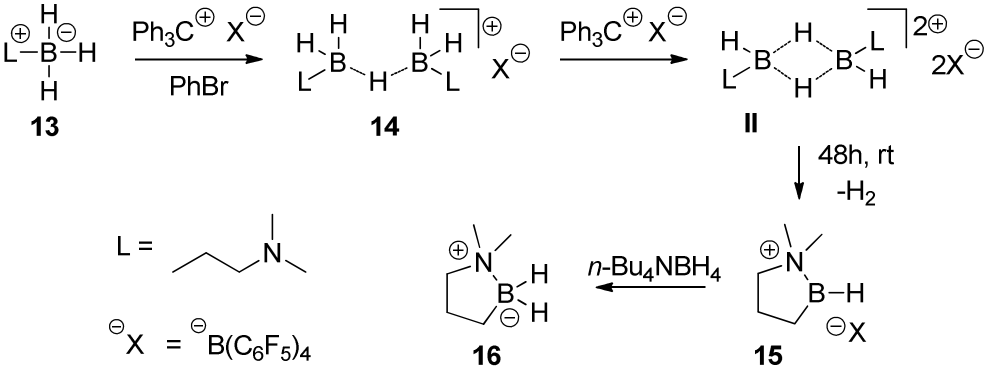
*Generation of* ***I*** *with $AlCl_3$:* $CH_2Cl_2$ (0.5 mL) was added to a mixture of solid **2a** (30 mg, 0.075 mmol) and $AlCl_3$ (50 mg, 0.37 mmol). Intense gas bubbling was observed. $^{11}B$ NMR analysis of the light yellow reaction mixture showed a major signal at +11.7 ppm, tentatively assigned as dication **I**, but the identity of the anion was not established.

$^{11}B$ NMR (128 MHz, $CH_2Cl_2$): δ +11.7 ppm (br s). $^{13}C$ NMR (101 MHz, $CH_2Cl_2$): δ 143.8, 133.6, 129.7, 129.3, 125.7, 29.1, 24.5, 23.1 ppm.

*Generation of **12**:* A solution of **I** in $CH_2Cl_2$ was prepared from **2a** as described above. This solution was kept at rt overnight. The transformation was monitored by the $^{11}B$ NMR spectroscopy. The starting signal at +11 ppm slowly disappeared. After 24 h, the only signal in $^{11}B$ NMR (96 MHz, $CH_2Cl_2$) was a singlet at +47.3 ppm. The tentative structure of $[NHC–BCl_2]^+ X^-$ **12** was assigned. An attempt to grow crystals of **12** for the X-ray crystallographic analysis outside the glovebox resulted in the complete conversion of **12** to an imidazolium salt $[NHC–H]^+X^-$ after 12 days in solution at rt.

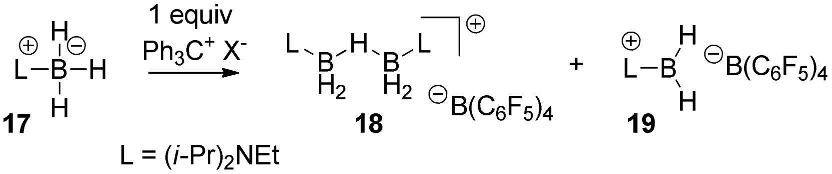
# Amine Borane Activation with $Ph_3C^+ [B(C_6F_5)_4]^-$

### *Activation of 13. Generation of 14, II, 15 and 16*



Every possible effort was made to protect the reaction mixture from exposure to air and moisture. The reaction was set up in a dry J. Young NMR tube under $N_2$ atmosphere in a glovebox. The NMR tube was dried in a heating oven at ca. 200 °C overnight, and the fitted Teflon valve was dried in a dessicator over Drierite. Commercial grade $d_5$-PhBr (Cambridge Isotope Laboratories) was not distilled, but rather simply dried with freshly activated molecular sieves in the glovebox. The reaction tube was charged with a solution of $Ph_3C^+ [B(C_6F_5)_4]^-$ (56.0 mg, 60.7 µmol) in 0.6 mL $d_5$-PhBr. To this solution neat *n*-$PrNMe_2$–$BH_3$ (**13**) (5.5 mg, 54.5 µmol) was added in one portion. No substantial exotherm was observed, potentially due to the small scale of the reaction. The tube was immediately sealed with the fitted Teflon valve, and then shaken vigorously for ca. 1 min. Formation of **II** (δ +13.2 ppm) as a transient intermediate in addition to the expected **14** (δ −0.9 ppm) was evident from the $^{11}B$ NMR spectra taken after ca. 30 min following mixing of the reagents. After 48 h at rt the signals corresponding to **14** and **II** were almost entirely replaced by a peak at +67.4 ppm assigned as **15**. Formation of the known **16**[25] was established by NMR spectroscopy upon quenching the reaction mixture with excess *n*-$Bu_4NBH_4$.

### *Activation of 17. Generation of 18 and 19*

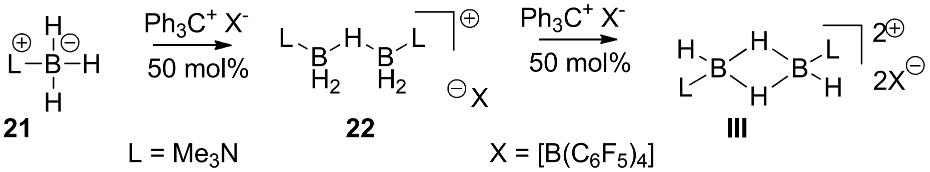


Every possible effort was made to protect the reaction mixture from exposure to air and moisture. The reaction was set up in a dry J. Young NMR tube under $N_2$ atmosphere in a glovebox. The NMR tube was dried in a heating oven at ca. 200 °C overnight, and the fitted Teflon valve was dried in a dessicator over Drierite. Commercial grade ($i$Pr)$_2$EtN–BH$_3$ (**17**) was used without further purification. Commercial grade $d_5$-PhBr (Cambridge Isotope Laboratories) was not distilled, but rather simply dried with freshly activated molecular sieves in the glovebox. The reaction tube was charged with a solution of Ph$_3$C$^+$ [B(C$_6$F$_5$)$_4$]$^-$ (48.0 mg, 52.0 μmol) in 0.6 mL $d_5$-PhBr. To this solution neat ($i$Pr)$_2$EtN–BH$_3$ (**17**) (9.1 μL, 52.0 μmol) was added via a microsyringe in one portion. No substantial exotherm was observed, potentially due to the small scale of the reaction. The tube was immediately sealed with the fitted Teflon valve, and then shaken vigorously for ca. 1 min. Since primary borenium **19** is very unstable under the reaction conditions, all NMR spectra had to be acquired within the first 10 minutes following mixing the reagents to obtain reasonable quality data. The following NMR spectra were acquired: (1) $^1$H NMR (ca. 3 sec total acquisition time) at 3 min counting from the moment of addition of **17** to the solution of the trityl reagent; (2) $^{11}$B NMR (ca. 7 min total acquisition time) at 3–10 min counting from the moment addition of **17** to the solution of the trityl reagent.

While overlaps in the $^1$H spectrum did not allow to fully assign the peaks of the ($i$Pr)$_2$EtN fragment, observation of a broad signal at δ 5.2–4.3 ppm serves as a clear indication for the formation of a tricoordinate B–H species in the course of the reaction. To illustrate the reasoning behind this assignment, the $^1$H NMR B–H signal of tricoordinate borenium **11** also appears as a broad peak around δ 5.2–4.3 ppm (in $d_5$-PhBr), while the B–H signals of other plausible species with larger coordination numbers at B appear noticeably upfield from that (cf. δ $^1$H 3.5–2.7 ppm for dication **III** in $d_5$-PhBr). Integration of the peaks at δ 5.2–4.3 ppm (BH$_2$ of **19**) and −2.8 (bridging H of **18**) in the $^1$H spectrum suggests a ca. 3.9:1 molar ratio of **18** and **19**. The molar ratio of **18** to **19** determined by the integration of peaks at δ −0.5 and +53.9 ppm, respectively, in the $^{11}$B NMR is comparable (4.3:1), supporting the assignment of the peak at δ $^{11}$B +53.9 ppm as the primary borenium species. The $^{11}$B NMR spectrum at that time also showed two minor peaks at δ +19.1 and +15.0 ppm whose intensity gradually increased along with the disappearance of **19**. Monitoring the progress of the reaction over time suggests that these two peaks apparently correspond to some unidentified decomposition products. Aside from the integration, the gradual disappearance of the peak at δ $^{11}$B +53.9 ppm due to decomposition appears to parallel the disappearance of the broad peak at δ $^1$H 5.2–4.3 ppm, suggesting that the two peaks likely arise from the same compound. The spectral data summarized below lists only those peaks that can be reasonably assigned as arising from the cation of **19**. The signals corresponding to Ph$_3$CH, Ph$_3$C$^+$, **18** and [B(C$_6$F$_5$)$_4$]$^-$ counterion are omitted.

$^{1}$H NMR (700 MHz, $d_5$-PhBr): δ 5.2-4.3 ppm (br m, 2H). $^{11}$B NMR (225 MHz, $d_5$-PhBr): δ +53.9 ppm.

### *Activation of 21. Generation of 22 and III. Quenching of III*



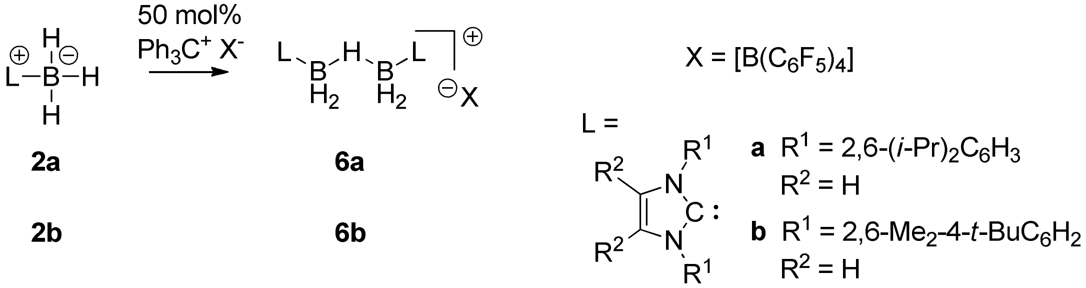
Every possible effort was made to protect the reaction mixture from exposure to air and moisture. The reaction was set up in a dry J. Young NMR tube under $N_2$ atmosphere in a glovebox. The NMR tube was dried in a heating oven at ca. 200 °C overnight, and the fitted Teflon valve was dried in a dessicator over Drierite. Commercial grade $Me_3N–BH_3$ (**21**) (Aldrich) was used without further purification. Commercial grade $d_5$-PhBr (Cambridge Isotope Laboratories) was not distilled, but rather simply dried with freshly activated molecular sieves in the glovebox. The reaction tube was charged with a mixture of solid **21** (3.4 mg, 48.0 μmol) and $Ph_3C^+$ $[B(C_6F_5)_4]^-$ (44.3 mg, 48.0 μmol). The solid mixture was then dissolved by adding 0.6 mL of anhydrous $d_5$-PhBr to the tube in one portion at rt. No substantial exotherm was observed, potentially due to the small scale of the reaction. The tube was immediately sealed with the fitted Teflon valve, and then shaken vigorously for ca. 1 min. After 2.5–3 h at rt a ca. 3:1 ratio of **22**:**III** was reached as evidenced by $^{11}$B NMR (peaks at δ −0.4 and +12.9 ppm, respectively). At this point only $Ph_3CH$, unreacted $Ph_3C^+$, **22** and **III** were present in the reaction mixture according to $^{1}$H NMR data. After 24h following mixing the reagents the molar ratio of 1:2.4 (**22**:**III**) was reached. At this point a minor peak (<5% of the combined intensity of the peaks assigned as **III** and **22**) of an unidentified product at δ +4.8 ppm was also apparent in $^{11}$B NMR. The spectral data summarized below are for the dication of **III** only. The signals corresponding to $Ph_3CH$, $Ph_3C^+$, **22** and $[B(C_6F_5)_4]^-$ counterion are omitted.

$^{1}$H NMR (700 MHz, $d_5$-PhBr): δ 3.6-2.7 (br m, 2H), 2.08 ppm (s, 9H). $^{11}$B NMR (225 MHz, $d_5$-PhBr): δ 12.9 ppm (unres m). $^{13}$C NMR (176 MHz, $d_5$-PhBr): δ 50.3 ppm.

The following quenching experiment (reaction of **III** with **21** to generate **22**) was performed as an additional consistency check confirming the stoichiometry of **III**. The reaction tube was charged with a mixture of solid **21** (7.4 mg, 0.102 mmol) and $Ph_3C^+$ $[B(C_6F_5)_4]^-$ (93.9 mg, 0.102 mmol). The solid mixture was then dissolved by adding 0.6 mL of anhydrous $d_5$-PhBr to the tube in one portion at rt. No substantial exotherm was observed, potentially due to the small scale of the reaction. The tube was immediately sealed with the fitted Teflon valve, and then shaken vigorously for ca. 1 min. After 2 h at rt ca. 3:1 ratio of **22**:**III** was reached as evidenced by $^{11}$B NMR (peaks at $\delta$ −0.4 and +12.9 ppm, respectively). At this point only $Ph_3CH$, unreacted $Ph_3C^+$, **22** and **III** were present in the reaction mixture according to $^1$H NMR data. The reaction tube was opened in the glovebox, and solid **21** (12.5 mg, 0.171 mmol) was added in one portion. The reaction tube was immediately sealed, and then shaken vigorously for ca. 1 min. According to the high quality $^1$H and $^{11}$B NMR spectra acquired shortly after the addition of **21**, the only species present in the reaction mixture at that time were $Ph_3CH$, excess **21** and **22** in a ca. 1:1.5 molar ratio, as well as $[B(C_6F_5)_4]^-$ counterion. No other signals were detected.

# NHC Borane Activation with $Ph_3C^+ [B(C_6F_5)_4]^-$

## *Activation of 2a and 2b. Generation of 6a and 6b*



Every possible effort was made to protect the reaction mixtures from exposure to air and moisture. The reactions were set up in dry J. Young NMR tubes under $N_2$ atmosphere in a glovebox. The NMR tubes were dried in a heating oven at ca. 200 °C overnight, and the fitted Teflon valves were dried in a dessicator over Drierite. $Ph_3C^+ [B(C_6F_5)_4]^-$ (Strem) was used without further purification. Commercial grade $d_5$-PhBr and $CD_2Cl_2$ (Cambridge Isotope Laboratories) were not distilled, but rather simply dried with freshly activated molecular sieves in the glovebox.

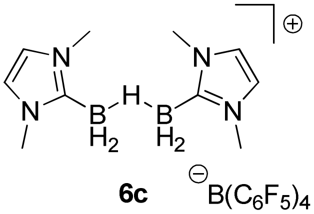
*General Procedure.* The reaction tube was charged with a mixture of solid NHC borane and $Ph_3C^+ [B(C_6F_5)_4]^-$. The solid mixture was then dissolved by adding 0.6 mL of solvent to the tube in one portion at rt. No substantial exotherm was observed, potentially due to the small scale of the reaction. The tube was immediately sealed with the fitted Teflon valve, and then shaken vigorously for ca. 1 min.

**6a** (in $d_5$-PhBr): The reaction was performed in $d_5$-PhBr solvent (0.6 mL). The following reagents were used: **2a** (27.4 mg, 68.1 μmol), $Ph_3C^+ [B(C_6F_5)_4]^-$ (31.4 mg, 34.0 μmol). NMR assay shortly following the mixing of reagents indicated clean formation of H-bridged cation **6a** ($[B(C_6F_5)_4]^-$ salt) along with $Ph_3CH$ byproduct. $^{11}B$ NMR (225 MHz, $d_5$-PhBr): δ −16.1 (s), −24.6 ppm (br s).

**6a** (in $CD_2Cl_2$): The reaction was performed in $CD_2Cl_2$ solvent (0.6 mL). The following reagents were used: **2a** (24.9 mg, 61.9 μmol), $Ph_3C^+ [B(C_6F_5)_4]^-$ (28.6 mg, 31.0 μmol). NMR assay shortly following the mixing of reagents indicated clean formation of H-bridged cation **6a** ($[B(C_6F_5)_4]^-$ salt) along with $Ph_3CH$ byproduct. $^{11}B$ NMR (128 MHz, $CD_2Cl_2$): δ −16.7 (s), −24.6 ppm (br s).

**6b**: The reaction was performed in $d_5$-PhBr solvent (0.6 mL). The following reagents were used: **2b** (25.0 mg, 62.1 μmol), $Ph_3C^+ [B(C_6F_5)_4]^-$ (28.7 mg, 31.1 μmol). NMR assay shortly following the mixing of reagents indicated clean formation of H-bridged cation **6b** ($[B(C_6F_5)_4]^-$ salt) along with $Ph_3CH$ byproduct. $^{11}B$ NMR (225 MHz, *d5*-PhBr): δ −16.1 (s), −24.6 ppm (br s).

## *Activation of 2c. Isolation of 6c*

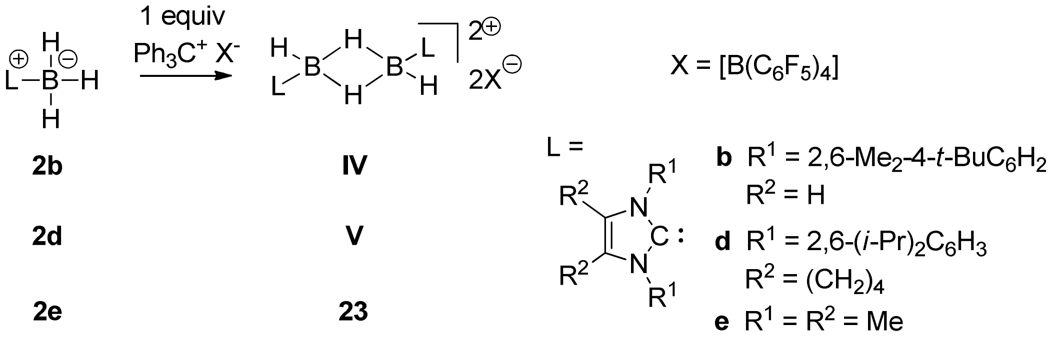


**6c**

Every possible effort was made to protect the reaction mixture from exposure to air and moisture. The reaction was performed under $N_2$ atmosphere in a glovebox. Disposable glassware flame-dried at the glass softening temperature was used. Commercial grade $Ph_3C^+$ $[B(C_6F_5)_4]^-$ (Strem) was used without further purification. Commercial grade anhydrous benzene (Aldrich) was additionally dried with freshly activated molecular sieves in the glovebox. To a mixture of solid $Ph_3C^+$ $[B(C_6F_5)_4]^-$ (0.461 g, 0.500 mmol) and **2c** (0.115 g, 1.05 mmol) 2 mL of dry PhH was added at rt, which resulted in formation of a two-layer liquid. No substantial exotherm was observed, potentially due to the small scale of the reaction. After stirring for ca. 10 min at room temperature, the two-layer mixture was diluted with 2 mL of dry hexanes. The clear top layer contained triphenylmethane and was discarded, and the bottom layer of the crude product was washed with 4x2 mL of dry hexanes. The crude product crystallized on trituration with hexanes. Drying in the glovebox produced 0.437 g (97%) of **6c** as a highly sensitive white solid. Layering a $CH_2Cl_2$ solution of the product with hexanes at room temperature produced single crystals suitable for X-ray crystallographic analysis. X-ray crystallography confirmed the proposed connectivity in the cation, although severe disorder did not allow to solve the structure fully.

$^1H$ NMR (700 MHz, *d5*-PhBr): δ 6.29 (s, 4H), 3.26 (s, 12H), 2.7-1.6 (br m, 4H), −2.2-−3.8 ppm (br s, 1H). $^{11}B$ NMR (225 MHz, *d5*-PhBr): δ −16.2 (s), −22.1 ppm (br m). $^{13}C$ NMR (176 MHz, *d5*-PhBr): δ 158.1-156.1 (br m), 149.7-147.5 (m), 139.4-137.5 (m), 137.5-135.5 (m), 125.2-123.7 (m), 121.7, 35.4 ppm. $^{19}F$ NMR (471 MHz, *d5*-PhBr): δ −131.8 (m), −162.0 (t, J = 20.9 Hz), −166.0 ppm (m).

## *Activation of 2b, 2d and 2e. Generation of IV, V, and 23*



Every possible effort was made to protect the reaction mixtures from exposure to air and moisture. The reactions were set up in dry J. Young NMR tubes under $N_2$ atmosphere in a glovebox. The NMR tubes were dried in a heating oven at ca. 200 °C overnight, and the fitted Teflon valves were dried in a dessicator over Drierite. $Ph_3C^+$ $[B(C_6F_5)_4]^-$ (Strem) was used without further purification. Commercial grade $d_5$-PhBr and $CD_2Cl_2$ (Cambridge Isotope Laboratories) were not distilled, but rather simply dried with freshly activated molecular sieves in the glovebox.

*General Procedure.* The reaction tube was charged with a mixture of solid NHC borane and $Ph_3C^+$ $[B(C_6F_5)_4]^-$. The solid mixture was then dissolved by adding 0.6 mL of solvent to the tube in one portion at rt. No substantial exotherm was observed, potentially due to the small scale of the reaction. The tube was immediately sealed with the fitted Teflon valve, and then shaken vigorously for ca. 1 min.

**IV** (in $d_5$-PhBr): The reaction was performed in $d_5$-PhBr solvent (1.0 mL). The following reagents were used: **2b** (25.0 mg, 62.1 μmol), $Ph_3C^+$ $[B(C_6F_5)_4]^-$ (57.3 mg, 62.1 μmol). Formation of dication **IV** was found to be somewhat slow. Thus, after ca. 1.5 h at rt following the mixing of reagents the reaction mixture was found to contain **6b** and **IV** ($[B(C_6F_5)_4]^-$ salts) in a ca. 1:1.4 ratio, along with $Ph_3CH$ byproduct and unreacted $Ph_3C^+$. After 17 h at rt $^{11}B$ NMR assay indicated clean formation of **IV**. $^{11}B$ NMR (128 MHz, $d_5$-PhBr): δ 11.9 (br s), −16.2 ppm (s).

**IV** (in $CD_2Cl_2$): The reaction was performed in $CD_2Cl_2$ solvent (0.6 mL). The following reagents were used: **2b** (30.8 mg, 76.5 μmol), $Ph_3C^+$ $[B(C_6F_5)_4]^-$ (66.8 mg, 72.4 μmol). Formation of dication **IV** was found to be somewhat slow. Thus, after 15 min at rt following the mixing of reagents the reaction mixture was found to contain **6b** and **IV** ($[B(C_6F_5)_4]^-$ salts) in a ca. 1.5:1 ratio, along with $Ph_3CH$

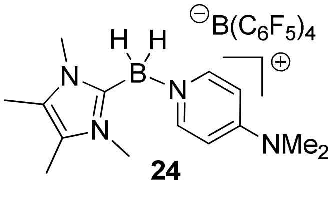
byproduct and unreacted $Ph_3C^+$. After 26 h at rt $^{11}B$ NMR assay indicated clean formation of **IV**. $^{11}B$ NMR (225 MHz, $CD_2Cl_2$): δ 12.4 (br s), −16.7 ppm (s).

**V** (in $d_5$-PhBr): The reaction was performed in $d_5$-PhBr solvent (0.6 mL). The following reagents were used: **2d** (20.6 mg, 45.1 μmol), $Ph_3C^+$ $[B(C_6F_5)_4]^-$ (41.6 mg, 45.1 μmol). NMR assay shortly following the mixing of reagents indicated clean formation of dication **V** ($[B(C_6F_5)_4]^-$ salt) along with $Ph_3CH$ byproduct. $^{11}B$ NMR (225 MHz, $d_5$-PhBr): δ 8.0 (br s), −16.1 ppm (s).

**V** (in $CD_2Cl_2$): The reaction was performed in $CD_2Cl_2$ solvent (0.6 mL). The following reagents were used: **2d** (20.6 mg, 45.1 μmol), $Ph_3C^+$ $[B(C_6F_5)_4]^-$ (46.8 mg, 50.7 μmol). NMR assay shortly following the mixing of reagents indicated clean formation of dication **V** ($[B(C_6F_5)_4]^-$ salt) along with $Ph_3CH$ byproduct. Some unreacted $Ph_3C^+$ was also observed. $^{11}B$ NMR (225 MHz, $CD_2Cl_2$): δ 9.9 (br s), −16.7 ppm (s).

**23**: The reaction was performed in $CD_2Cl_2$ solvent (0.6 mL). The following reagents were used: **2e** (9.9 mg, 71.7 μmol), $Ph_3C^+$ $[B(C_6F_5)_4]^-$ (66.1 mg, 71.7 μmol). Addition of the solvent to the solid mixture produced a clear solution, which turned into a slush of fine crystals within ca. 1 min at rt. NMR assay shortly following the mixing of reagents indicated clean formation of dication **23** ($[B(C_6F_5)_4]^-$ salt) along with $Ph_3CH$ byproduct, although $^{13}C$ NMR data could not be acquired due to very low solubility of the product, as well as its gradual conversion to $[NHC–BCl_2]^+$ over time. $^1H$ NMR (700 MHz, $CD_2Cl_2$): δ 3.82 (s, 6H), 2.37 ppm (s, 6H). $^{11}B$ NMR (225 MHz, $CD_2Cl_2$): δ 10.6 (br s), −16.7 ppm (s).

## *Quenching Studies with 23. Preparation of 24*



**24**

*Quenching of **23** with 4-dimethylaminopyridine.* Every possible effort was made to protect the reaction mixture from exposure to air and moisture. The reaction was set up in dry J. Young NMR tubes under $N_2$ atmosphere in a glovebox. The NMR tube was dried in a heating oven at ca. 200 °C overnight, and the fitted Teflon valve was dried in a dessicator over Drierite. $Ph_3C^+$ $[B(C_6F_5)_4]^-$ (Strem) was used without further purification. Commercial grade $d_5$-PhBr (Cambridge Isotope Laboratories) was not distilled, but rather simply dried with freshly activated molecular sieves in the glovebox. The reaction tube was charged with a mixture of solid **2e** (8.3 mg, 60.1 μmol) and $Ph_3C^+$ $[B(C_6F_5)_4]^-$ (55.4 mg, 60.1 μmol). The solid mixture was then dissolved by adding anhydrous *d*$_5$-PhBr (1.0 mL) to the tube in one portion at rt. No substantial exotherm was observed, potentially due to the small scale of the reaction. The tube was immediately sealed with the fitted Teflon valve, and then shaken vigorously for ca. 1 min. Formation of dication **23** $[B(C_6F_5)_4]^-$ salt was evident from the formation of a fine crystalline precipitate in the reaction tube. Addition of excess DMAP (ca. 1.5 equiv) along with ca. 1 mL *d*$_5$-PhBr resulted in dissolution of the crystalline solid. $^{11}$B NMR assay indicated clean formation of boronium salt **24** (δ −14.7 ppm, compared to an independently prepared sample).

The following protocol was used to prepare the analytical sample of **24** from **6e**. A 4 mL scintillation vial was charged with a mixture of solid **2e** (34.0 mg, 0.246 mmol) and $Ph_3C^+$ $[B(C_6F_5)_4]^-$ (0.113 g, 0.123 mmol). The solid mixture was then dissolved by adding anhydrous PhF (1.0 mL) to the vial in one portion at rt. The vial was capped, and then shaken vigorously for ca. 1 min. Complete consumption of the starting $Ph_3C^+$ $[B(C_6F_5)_4]^-$ was evident from the rapid disappearance of the characteristic yellow color. To the resulting solution of **6e** solid DMAP (15.7 mg, 0.129 mmol) was added, and the mixture was shaken to accomplish full dissolution of the reagent. Addition of hexanes (2 mL) to the resulting solution precipitated a colorless oil, which was separated. The oil was dissolved in $CH_2Cl_2$ (1 mL), and the solid product was precipitated by adding 3 mL of hexanes. Separation of the solid by centrifugation, followed by two additional dissolution/precipitation cycles (1 mL $CH_2Cl_2$ + 3 mL hexanes in each precipitation) afforded 32.0 mg (28%) of the pure boronium salt. Alternatively, the boronium salt can be isolated in a nearly quantitative yield by concentrating the PhF solution after addition of DMAP, followed by repeated washing of the crude mixture with hexanes, although **2e** byproduct resulting from the cleavage of **6e** by DMAP could not be fully separated.

**24**: $^1$H NMR (700 MHz, $CHCl_3$): δ 7.67-7.64 (m, 2H), 6.50-6.46 (m, 2H), 3.60 (s, 6H), 3.2-2.7 (br m, 2H), 3.06 (s, 6H), 2.14 ppm (s, 6H). $^{11}$B NMR (225 MHz, $CHCl_3$): δ −14.7 ppm (br m), −16.7 ppm (s). $^{13}$C NMR (176 MHz, $CHCl_3$): δ 158.7-157.4 (br m), 155.3, 149.1-147.0 (m), 145.2, 139.1-137.1 (m), 137.1-135.0 (m), 126.0, 124.7-123.1 (m), 107.3, 39.3, 32.5, 8.4 ppm. $^{19}$F NMR (471 MHz, $CHCl_3$): δ −132.7 (m), −163.1 (t, J = 20.4 Hz), −167.0 ppm (m). HRMS (ES+): m/z calculated for $C_{14}H_{24}BN_4^+$ $[M]^+$ 259.2094, found 259.2094 (0 ppm).

*Quenching of* ***23*** *with n-Bu$_4$NBH$_4$.* A suspension of the finely divided crystalline dication **23** was generated as described above for the DMAP quenching experiment from **2e** (8.3 mg, 60.1 μmol) and $Ph_3C^+$ $[B(C_6F_5)_4]^-$ (55.4 mg, 60.1 μmol) and anhydrous *d*$_5$-PhBr (0.6 mL) in an NMR tube. Addition of excess n-$Bu_4NBH_4$ (23.2 mg, 90.2 μmol) along with ca. 0.4 mL $d_5$-PhBr resulted in dissolution of the crystalline solid. $^1$H and $^{11}$B NMR assay indicated clean formation of **2e** as the only product containing the NHC fragment.

*Quenching of **23** with **2e**.* A suspension of the finely divided crystalline dication **23** was generated as described above for the DMAP quenching experiment from **2e** (8.3 mg, 60.1 μmol) and $Ph_3C^+$ $[B(C_6F_5)_4]^-$ (55.4 mg, 60.1 μmol) and anhydrous $d_5$-PhBr (0.6 mL) in an NMR tube. Addition of an additional portion of solid **2e** (8.3 mg, 60.1 μmol) along with ca. 0.2 mL $d_5$-PhBr resulted in dissolution of the crystalline solids **2e** and **23**. $^1$H and $^{11}$B NMR assay indicated clean formation of **6e** as the only product containing the NHC fragment.

## Preparation and X-Ray Crystallography Details of 23 ($[Al_2Br_7]^-$ Salt)

This procedure describes preparation of crystalline $[Al_2Br_7]^-$ salt of the dication for the X-ray crystallographic study. For other applications such as the quenching experiments, $[B(C_6F_5)_4]^-$ salts of **23** were generated *in situ* as described above. Every possible effort was made to protect the reaction mixture from exposure to air and moisture. The reaction was performed under $N_2$ atmosphere in a glovebox. Disposable glassware flame-dried at the glass softening temperature was used. Commercial grade $Al_2Br_6$ (Aldrich) and $Ph_3CBr$ were used without further purification. Commercial grade fluorobenzene (Acros) was not distilled, but rather simply dried with freshly activated molecular sieves in the glovebox. The starting NHC borane **2e** was prepared as described above, crystallized from hexanes/$CHCl_3$, and dried in high vacuum before transferring into the glovebox. In a dry 4 mL scintillation vial a mixture of solid $Al_2Br_6$ (96.0 mg, 0.180 mmol) and $Ph_3CBr$ (58.2 mg, 0.180 mmol) was dissolved in 1 mL of dry PhF at rt. No substantial exotherm was observed, potentially due to the small scale of the reaction. The resulting intensively colored red-orange solution was allowed to stand at rt for 20 min, and then it was carefully layered with a solution of **2e** (24.8 mg, 0.180 mmol) in 0.5 mL of dry PhF. On standing overnight at rt in the sealed vial the reaction mixture developed a substantial amount of X-ray quality crystalline material. The quality of the crystals was found to deteriorate quickly with time, prompting immediate crystallographic analysis as soon as the sufficient crystal size is reached. X-ray crystallographic study confirmed the proposed dicationic structure of **23**.

A crystal of dimensions 0.14x0.10x0.10 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ($\lambda = 1.54187$ Å) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 3750 images were collected with an oscillation width of 1.0° in $\omega$. The exposure time was 2 sec. for the low angle images, 6 sec. for high angle. The integration of the data yielded a total of 26707 reflections to a maximum $2\theta$ value of 136.46° of which 3680 were independent and 3490 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 17391 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group $P\bar{1}$ with Z = 2 for the formula $C_{14}H_{28}B_2N_4Al_4Br_{14}$. Full matrix least-squares refinement based on $F^2$ converged at R1 =

0.0371 and wR2 = 0.0909 [based on I > 2σ(I)], R1 = 0.0394 and wR2 = 0.0926 for all data. Additional details are presented in Tables 1-5 and CIF file.

Sheldrick, G.M. SHELXTL, v. 2008/4; Bruker Analytical X-ray, Madison, WI, 2008. CrystalClear Expert 2.0 r12, Rigaku Americas and Rigaku Corporation (2011), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

Table 1. Crystal data and structure refinement for **23**.

| | |
|---|---|
| Empirical formula | $C_{14}H_{28}Al_4B_2Br_{14}N_4$ |
| Formula weight | 1500.68 |
| Temperature | 85(2) K |
| Wavelength | 1.54178 Å |
| Crystal system, space group | Triclinic, P-1 |
| Unit cell dimensions | a = 9.4348(2) Å, α = 98.386(7)°.<br>b = 9.4885(2) Å, β = 92.646(7)°.<br>c = 11.5808(8) Å, γ = 93.785(7)°. |
| Volume | 1021.78(8) Å$^3$ |
| Z, Calculated density | 1, 2.439 Mg/m$^3$ |
| Absorption coefficient | 17.238 mm$^{-1}$ |
| F(000) | 692 |
| Crystal size | 0.14 x 0.10 x 0.10 mm |
| Theta range for data collection | 4.70 to 68.23°. |
| Limiting indices | -11<=h<=11, -11<=k<=11, -13<=l<=13 |
| Reflections collected / unique | 26707 / 3680 [R(int) = 0.0745] |
| Completeness to theta = 68.23 | 98.2% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.2775 and 0.1964 |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 3680 / 0 / 184 |
| Goodness-of-fit on F$^2$ | 1.085 |
| Final R indices [I>2σ(I)] | R1 = 0.0371, wR2 = 0.0909 |
| R indices (all data) | R1 = 0.0394, wR2 = 0.0927 |
| Largest diff. peak and hole | 1.132 and -0.818 e·Å$^{-3}$ |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$ x $10^3$) for **23.**
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Br(1) | 697(1) | 6078(1) | 2111(1) | 23(1) |
| Br(2) | 2526(1) | 3062(1) | 493(1) | 30(1) |
| Br(3) | 3305(1) | 4037(1) | 3761(1) | 21(1) |
| Br(4) | 4648(1) | 6274(1) | 1535(1) | 17(1) |
| Br(5) | 4736(1) | 10223(1) | 1873(1) | 27(1) |
| Br(6) | 7610(1) | 8378(1) | 3280(1) | 23(1) |
| Br(7) | 3862(1) | 8258(1) | 4448(1) | 23(1) |
| Al(1) | 2656(1) | 4816(2) | 2071(1) | 14(1) |
| Al(2) | 5237(1) | 8457(2) | 2928(1) | 14(1) |
| N(1) | 1533(4) | -2114(5) | -1629(4) | 22(1) |
| N(2) | 22(4) | -1339(5) | -2789(4) | 21(1) |
| C(1) | 523(5) | -1161(6) | -1681(5) | 26(1) |
| C(2) | 1650(5) | -2883(5) | -2722(4) | 17(1) |
| C(3) | 690(5) | -2386(6) | -3448(4) | 17(1) |
| C(4) | 2367(7) | -2307(9) | -583(5) | 42(2) |
| C(6) | 365(6) | -2853(7) | -4731(5) | 26(1) |
| C(7) | -1095(6) | -534(6) | -3295(6) | 29(1) |
| C(11) | 2662(6) | -3988(7) | -2960(6) | 31(1) |
| B(1) | -9(7) | 57(8) | -760(6) | 31(2) |

Table 3. Bond lengths [Å] and angles [°] for **23.**

| | |
|---|---|
| Br(1)-Al(1) | 2.2662(16) |
| Br(2)-Al(1) | 2.2778(14) |
| Br(3)-Al(1) | 2.2635(16) |
| Br(4)-Al(1) | 2.4178(14) |
| Br(4)-Al(2) | 2.4479(14) |
| Br(5)-Al(2) | 2.2742(17) |
| Br(6)-Al(2) | 2.2656(14) |
| Br(7)-Al(2) | 2.2564(14) |
| N(1)-C(1) | 1.361(8) |
| N(1)-C(2) | 1.379(6) |
| N(1)-C(4) | 1.455(8) |
| N(2)-C(1) | 1.330(8) |
| N(2)-C(3) | 1.368(6) |
| N(2)-C(7) | 1.489(8) |
| C(1)-B(1) | 1.579(8) |
| C(2)-C(3) | 1.360(8) |
| C(2)-C(11) | 1.470(8) |
| C(3)-C(6) | 1.499(7) |
| C(4)-H(4A) | 0.9800 |
| C(4)-H(4B) | 0.9800 |
| C(4)-H(4C) | 0.9800 |
| C(6)-H(6A) | 0.9800 |
| C(6)-H(6B) | 0.9800 |
| C(6)-H(6C) | 0.9800 |
| C(7)-H(7A) | 0.9800 |
| C(7)-H(7B) | 0.9800 |
| C(7)-H(7C) | 0.9800 |
| C(11)-H(11A) | 0.9800 |
| C(11)-H(11B) | 0.9800 |
| C(11)-H(11C) | 0.9800 |
| B(1)-B(1)#1 | 1.778(14) |
| B(1)-H(1A) | 1.25(6) |
| B(1)-H(1B) | 1.20(7) |
| | |
| Al(1)-Br(4)-Al(2) | 113.27(5) |
| Br(3)-Al(1)-Br(1) | 115.82(6) |
| Br(3)-Al(1)-Br(2) | 113.04(7) |
| Br(1)-Al(1)-Br(2) | 111.26(6) |

| | |
|---|---|
| Br(3)-Al(1)-Br(4) | 107.72(6) |
| Br(1)-Al(1)-Br(4) | 108.99(6) |
| Br(2)-Al(1)-Br(4) | 98.44(5) |
| Br(7)-Al(2)-Br(6) | 116.47(7) |
| Br(7)-Al(2)-Br(5) | 115.56(6) |
| Br(6)-Al(2)-Br(5) | 111.75(6) |
| Br(7)-Al(2)-Br(4) | 105.52(5) |
| Br(6)-Al(2)-Br(4) | 102.09(6) |
| Br(5)-Al(2)-Br(4) | 103.30(6) |
| C(1)-N(1)-C(2) | 109.8(4) |
| C(1)-N(1)-C(4) | 125.6(5) |
| C(2)-N(1)-C(4) | 124.6(5) |
| C(1)-N(2)-C(3) | 110.6(5) |
| C(1)-N(2)-C(7) | 126.8(5) |
| C(3)-N(2)-C(7) | 122.6(5) |
| N(2)-C(1)-N(1) | 106.1(4) |
| N(2)-C(1)-B(1) | 120.3(6) |
| N(1)-C(1)-B(1) | 133.4(5) |
| C(3)-C(2)-N(1) | 106.2(4) |
| C(3)-C(2)-C(11) | 130.7(5) |
| N(1)-C(2)-C(11) | 123.1(5) |
| C(2)-C(3)-N(2) | 107.3(4) |
| C(2)-C(3)-C(6) | 128.7(5) |
| N(2)-C(3)-C(6) | 124.0(5) |
| N(1)-C(4)-H(4A) | 109.5 |
| N(1)-C(4)-H(4B) | 109.5 |
| H(4A)-C(4)-H(4B) | 109.5 |
| N(1)-C(4)-H(4C) | 109.5 |
| H(4A)-C(4)-H(4C) | 109.5 |
| H(4B)-C(4)-H(4C) | 109.5 |
| C(3)-C(6)-H(6A) | 109.5 |
| C(3)-C(6)-H(6B) | 109.5 |
| H(6A)-C(6)-H(6B) | 109.5 |
| C(3)-C(6)-H(6C) | 109.5 |
| H(6A)-C(6)-H(6C) | 109.5 |
| H(6B)-C(6)-H(6C) | 109.5 |
| N(2)-C(7)-H(7A) | 109.5 |
| N(2)-C(7)-H(7B) | 109.5 |
| H(7A)-C(7)-H(7B) | 109.5 |
| N(2)-C(7)-H(7C) | 109.5 |
| H(7A)-C(7)-H(7C) | 109.5 |
| H(7B)-C(7)-H(7C) | 109.5 |
| C(2)-C(11)-H(11A) | 109.5 |
| C(2)-C(11)-H(11B) | 109.5 |
| H(11A)-C(11)-H(11B) | 109.5 |
| C(2)-C(11)-H(11C) | 109.5 |
| H(11A)-C(11)-H(11C) | 109.5 |
| H(11B)-C(11)-H(11C) | 109.5 |
| C(1)-B(1)-B(1)#1 | 122.3(8) |
| C(1)-B(1)-H(1A) | 108(3) |
| B(1)#1-B(1)-H(1A) | 44(3) |
| C(1)-B(1)-H(1B) | 121(3) |
| B(1)#1-B(1)-H(1B) | 116(3) |
| H(1A)-B(1)-H(1B) | 110(4) |

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **23**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

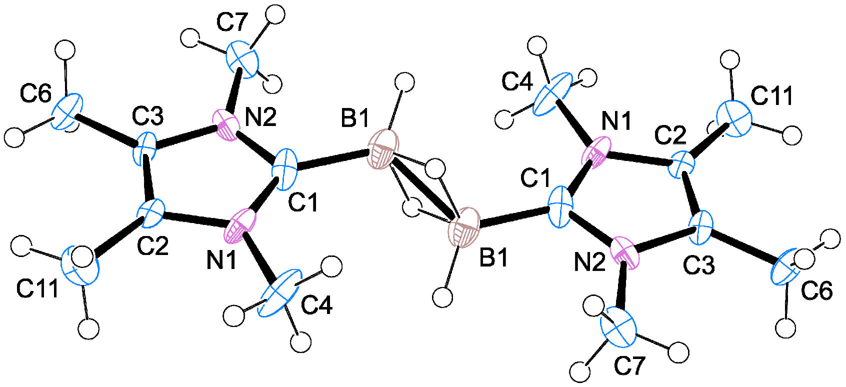
| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Br(1) | 11(1) | 35(1) | 24(1) | 7(1) | 6(1) | 3(1) |
| Br(2) | 35(1) | 27(1) | 23(1) | -11(1) | 12(1) | -17(1) |
| Br(3) | 19(1) | 27(1) | 19(1) | 7(1) | 5(1) | 0(1) |
| Br(4) | 12(1) | 22(1) | 14(1) | -2(1) | 5(1) | -7(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Br(5) | 26(1) | 24(1) | 31(1) | 9(1) | 0(1) | -1(1) |
| Br(6) | 8(1) | 32(1) | 27(1) | -4(1) | -2(1) | -3(1) |
| Br(7) | 20(1) | 26(1) | 20(1) | -5(1) | 9(1) | -8(1) |
| Al(1) | 10(1) | 18(1) | 14(1) | -1(1) | 4(1) | -4(1) |
| Al(2) | 8(1) | 18(1) | 16(1) | 2(1) | 1(1) | -2(1) |
| N(1) | 15(2) | 38(3) | 13(2) | 4(2) | 2(2) | -10(2) |
| N(2) | 14(2) | 15(2) | 32(3) | -1(2) | 9(2) | -2(2) |
| C(1) | 17(2) | 31(3) | 24(3) | -9(2) | 8(2) | -12(2) |
| C(2) | 11(2) | 21(3) | 17(2) | 3(2) | 5(2) | -8(2) |
| C(3) | 8(2) | 26(3) | 17(2) | -2(2) | 7(2) | -6(2) |
| C(4) | 28(3) | 82(5) | 15(3) | 13(3) | -2(2) | -4(3) |
| C(6) | 17(2) | 46(4) | 16(3) | 6(2) | 2(2) | 1(2) |
| C(7) | 18(3) | 27(3) | 41(3) | -1(3) | 4(2) | 1(2) |
| C(11) | 19(3) | 34(3) | 39(3) | 3(3) | -1(2) | 7(2) |
| B(1) | 24(3) | 42(4) | 26(3) | 1(3) | 8(3) | -2(3) |

Table 5. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($Å^2$ x $10^3$) for **23**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(4A) | 2689 | -1371 | -141 | 63 |
| H(4B) | 3195 | -2835 | -807 | 63 |
| H(4C) | 1780 | -2845 | -96 | 63 |
| H(6A) | 986 | -3600 | -5017 | 40 |
| H(6B) | 527 | -2035 | -5149 | 40 |
| H(6C) | -631 | -3229 | -4866 | 40 |
| H(7A) | -1989 | -694 | -2918 | 44 |
| H(7B) | -1237 | -867 | -4137 | 44 |
| H(7C) | -795 | 487 | -3163 | 44 |
| H(11A) | 2553 | -4408 | -3787 | 46 |
| H(11B) | 2473 | -4735 | -2473 | 46 |
| H(11C) | 3635 | -3559 | -2779 | 46 |
| H(1A) | -810(60) | -520(60) | -100(50) | 26(16) |
| H(1B) | -540(80) | 1070(80) | -1060(60) | 40(20) |

**Figure 1.** ORTEP plot of **23** ($Al_2Br_7^-$ salt, the counterions have been omitted for clarity)



# Computational Studies

The consistency of the observed $^{11}$B NMR chemical shifts to the proposed structures was verified by performing GIAO (Gauge-Independent Atomic Orbital) calculations. All calculations were performed using Gaussian 09, Revision A.02 suite of computational programs.[26] Ultrafine integration grids (**int=ultrafine**) and tight optimization criteria (**opt=tight**) were used. No exhaustive conformational search was performed, and the optimized structures were confirmed to be the local minima by performing frequency calculations. All calculations were performed at the M06-2X/6-311++G(3df,2p)//M06-2X/6-31+G(d,p) level of theory[27] using SMD solvation model.[28] The following reference compounds were used to estimate $^{11}$B NMR chemical shifts: **11** (δ +69.5 ppm in $d_5$-PhBr, δ +71.1 ppm in $CD_2Cl_2$) for **19** and the hypothetical primary borenium **4e**, and $B_2H_6$ (δ +17.4 ppm in $CH_2Cl_2$) for **23**.

$B_2H_6$ (M06-2X/6-311++G(3df,2p)//M06-2X/6-31+G(d,p), SMD solvation ($CH_2Cl_2$)):

```
E = -53.258787
B isotropic shielding 84.9

B       -0.864999000      0.507638000      0.163691000
H        0.344376000      0.425846000     -0.338609000
H       -1.353537000      1.537414000     -0.173933000
H       -1.420687000     -0.530558000      0.001499000
B        0.710010000      0.520315000      0.917930000
H        1.265733000      1.558490000      1.080137000
H       -0.499368000      0.602107000      1.420229000
H        1.198528000     -0.509471000      1.255555000
```

**11** (M06-2X/6-311++G(3df,2p)//M06-2X/6-31+G(d,p), SMD solvation ($CH_2Cl_2$)):

```
E = -433.807690
B isotropic shielding 15.1

C        1.687883000     -1.104964000     -0.764647000
C        1.749451000      0.119444000      0.176936000
C        0.329175000      0.175215000      0.772629000
H        2.490892000     -1.141745000     -1.505647000
H        1.756127000     -2.040749000     -0.176792000
H        0.245964000     -0.516945000      1.614809000
H        0.029853000      1.174156000      1.099444000
C       -1.430061000      0.799551000     -0.933632000
C       -1.724728000     -1.195410000      0.264544000
C       -2.568793000      1.071962000      0.064076000
H       -1.807773000      0.416190000     -1.884283000
H       -0.778433000      1.652473000     -1.117937000
C       -2.660375000     -0.196556000      0.940899000
H       -1.287291000     -1.946058000      0.924195000
H       -2.205822000     -1.684717000     -0.586427000
H       -2.350185000      1.952971000      0.670574000
H       -3.493425000      1.262548000     -0.483081000
H       -2.318595000      0.008509000      1.958542000
H       -3.671642000     -0.601531000      0.998881000
N       -0.626484000     -0.319118000     -0.300052000
C        2.774800000     -0.033376000      1.299469000
H        3.783313000     -0.112423000      0.881338000
H        2.755014000      0.832116000      1.971426000
H        2.578026000     -0.933206000      1.891709000
C        2.062740000      1.374409000     -0.646643000
H        1.975017000      2.278346000     -0.034766000
H        3.085401000      1.319208000     -1.033467000
H        1.395954000      1.476778000     -1.510806000
B        0.240329000     -1.099608000     -1.297509000
H       -0.302411000     -1.585482000     -2.230006000
```

**23** (M06-2X/6-311++G(3df,2p)//M06-2X/6-31+G(d,p), SMD solvation ($CH_2Cl_2$)):

E = -818.712504
B isotropic shielding 91.5

| | | | |
|---|---|---|---|
| C | -4.343101000 | 0.685543000 | 0.071752000 |
| C | -4.193218000 | -0.676879000 | 0.107315000 |
| C | -2.156080000 | 0.240158000 | 0.256312000 |
| N | -3.077931000 | 1.220341000 | 0.172974000 |
| N | -2.839743000 | -0.922587000 | 0.221859000 |
| C | -2.282337000 | -2.274968000 | 0.282799000 |
| C | -2.827869000 | 2.659638000 | 0.135215000 |
| B | -0.606057000 | 0.516974000 | 0.360107000 |
| C | 4.343101000 | -0.685543000 | -0.071753000 |
| C | 4.193218000 | 0.676879000 | -0.107314000 |
| C | 2.156080000 | -0.240158000 | -0.256312000 |
| N | 3.077931000 | -1.220341000 | -0.172976000 |
| N | 2.839743000 | 0.922587000 | -0.221857000 |
| C | 2.282337000 | 2.274968000 | -0.282795000 |
| C | 2.827869000 | -2.659638000 | -0.135218000 |
| B | 0.606057000 | -0.516974000 | -0.360107000 |
| C | 5.559327000 | -1.536172000 | 0.042968000 |
| C | 5.210249000 | 1.762492000 | -0.047348000 |
| C | -5.210249000 | -1.762492000 | 0.047350000 |
| C | -5.559326000 | 1.536172000 | -0.042971000 |
| H | 3.102357000 | -3.046681000 | 0.847829000 |
| H | 1.775407000 | -2.852977000 | -0.323170000 |
| H | 3.430345000 | -3.144817000 | -0.904049000 |
| H | 5.732890000 | -2.104435000 | -0.876143000 |
| H | 6.433047000 | -0.910869000 | 0.229385000 |
| H | 5.463280000 | -2.247228000 | 0.868877000 |
| H | 6.196677000 | 1.328145000 | 0.119609000 |
| H | 5.242297000 | 2.328914000 | -0.983397000 |
| H | 4.996740000 | 2.458009000 | 0.769449000 |
| H | 1.388742000 | 2.280842000 | -0.903855000 |
| H | 2.048238000 | 2.625674000 | 0.723957000 |
| H | 3.022620000 | 2.931306000 | -0.737021000 |
| H | -1.775405000 | 2.852977000 | 0.323165000 |
| H | -3.102357000 | 3.046679000 | -0.847833000 |
| H | -3.430343000 | 3.144818000 | 0.904045000 |
| H | -6.433047000 | 0.910869000 | -0.229386000 |
| H | -5.732889000 | 2.104437000 | 0.876139000 |
| H | -5.463279000 | 2.247227000 | -0.868881000 |
| H | -5.242298000 | -2.328912000 | 0.983400000 |
| H | -6.196677000 | -1.328144000 | -0.119607000 |
| H | -4.996740000 | -2.458010000 | -0.769445000 |
| H | -2.048241000 | -2.625677000 | -0.723953000 |
| H | -1.388741000 | -2.280841000 | 0.903858000 |
| H | -3.022620000 | -2.931305000 | 0.737028000 |
| H | 0.061003000 | -0.483190000 | 0.858420000 |
| H | 0.242839000 | -1.508042000 | -0.894259000 |
| H | -0.242839000 | 1.508041000 | 0.894259000 |
| H | -0.061003000 | 0.483190000 | -0.858420000 |

# References:

(22) Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Goodfellow, R.; Granger, P. *Pure Appl. Chem.* **2001**, *73*, 1795.

(23) Makhlouf Brahmi, M.; Monot, J.; Desage-El Murr, M.; Curran, D. P.; Fensterbank, L.; Lacôte, E.; Malacria, M. *J. Org. Chem.* **2010**, *75*, 6983.

(24) Kuhn, N.; Henkel, G.; Kratz, T.; Kreutzberg, J.; Boese, R.; Maulitz, A. H. *Chem. Ber.* **1993**, *126*, 2041.

(25) Le Toumelin, J.-B.; Baboulène, M. *New J. Chem.* **1999**, 111.

(26) Gaussian 09, Revision A.02. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

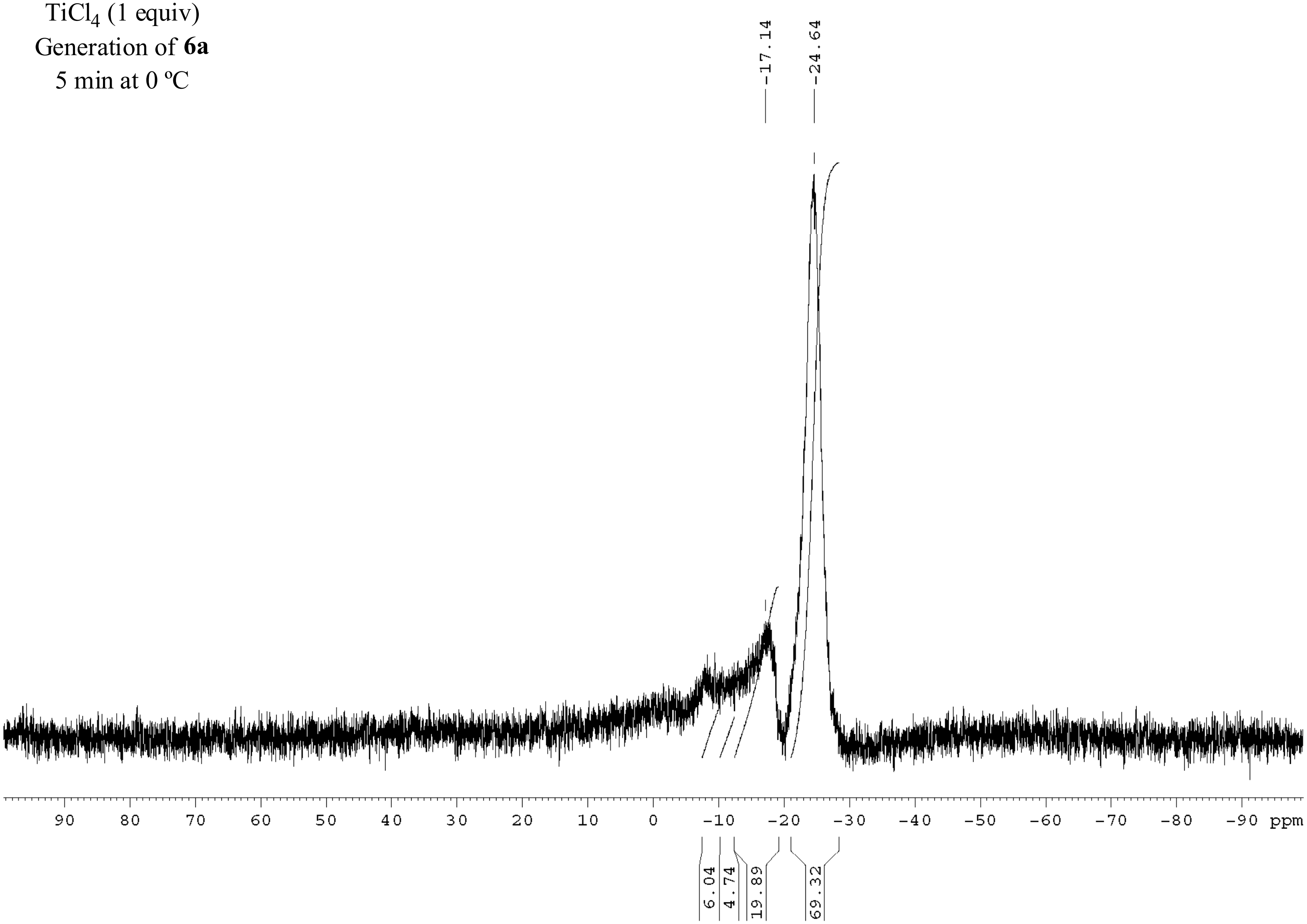
(27) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

(28) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378.

# NMR Spectra

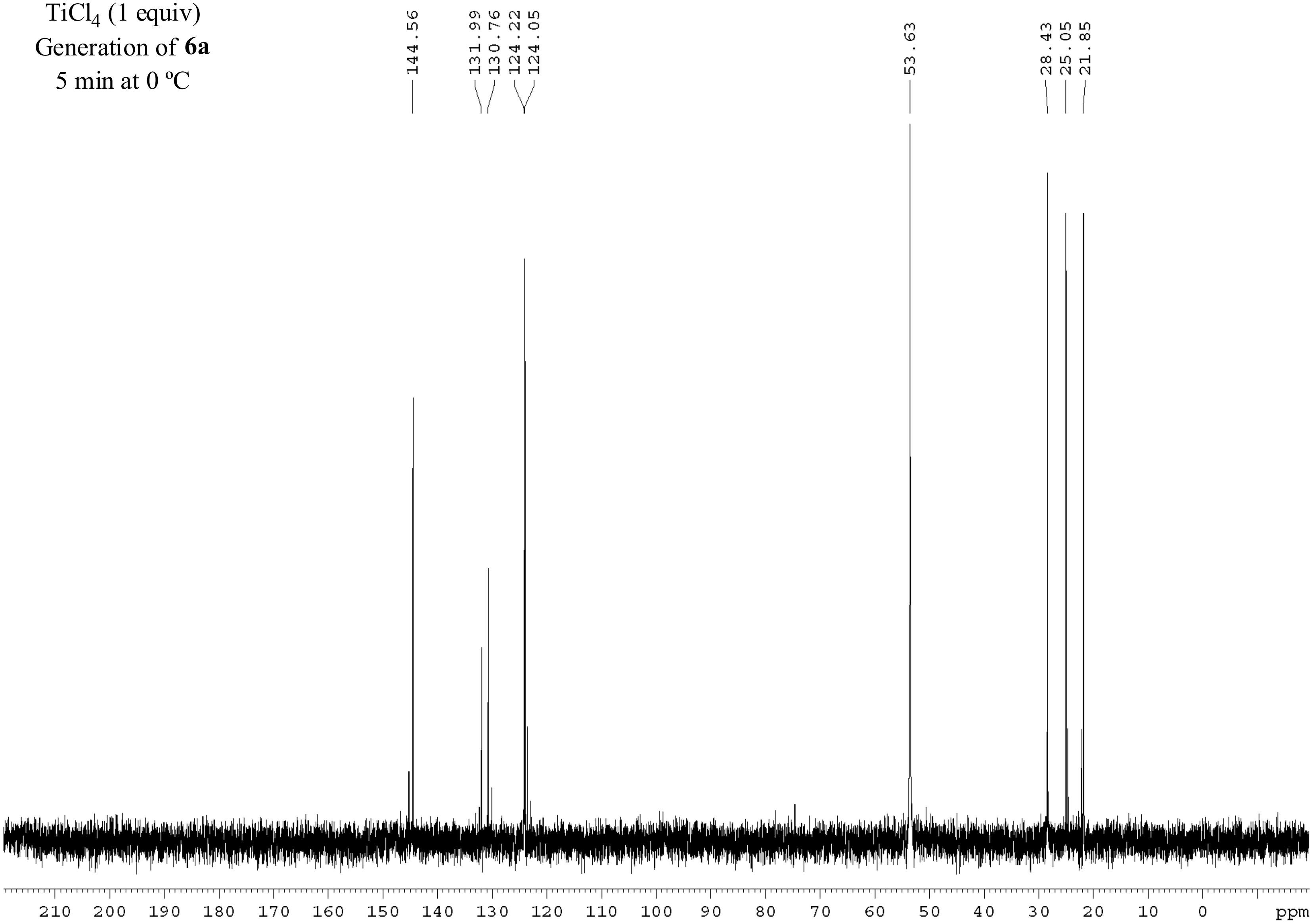
$^{11}$B NMR (128 MHz), $CH_2Cl_2$

Activation of **2a** with $TiCl_4$ (1 equiv)
Generation of **6a**
5 min at 0 ºC



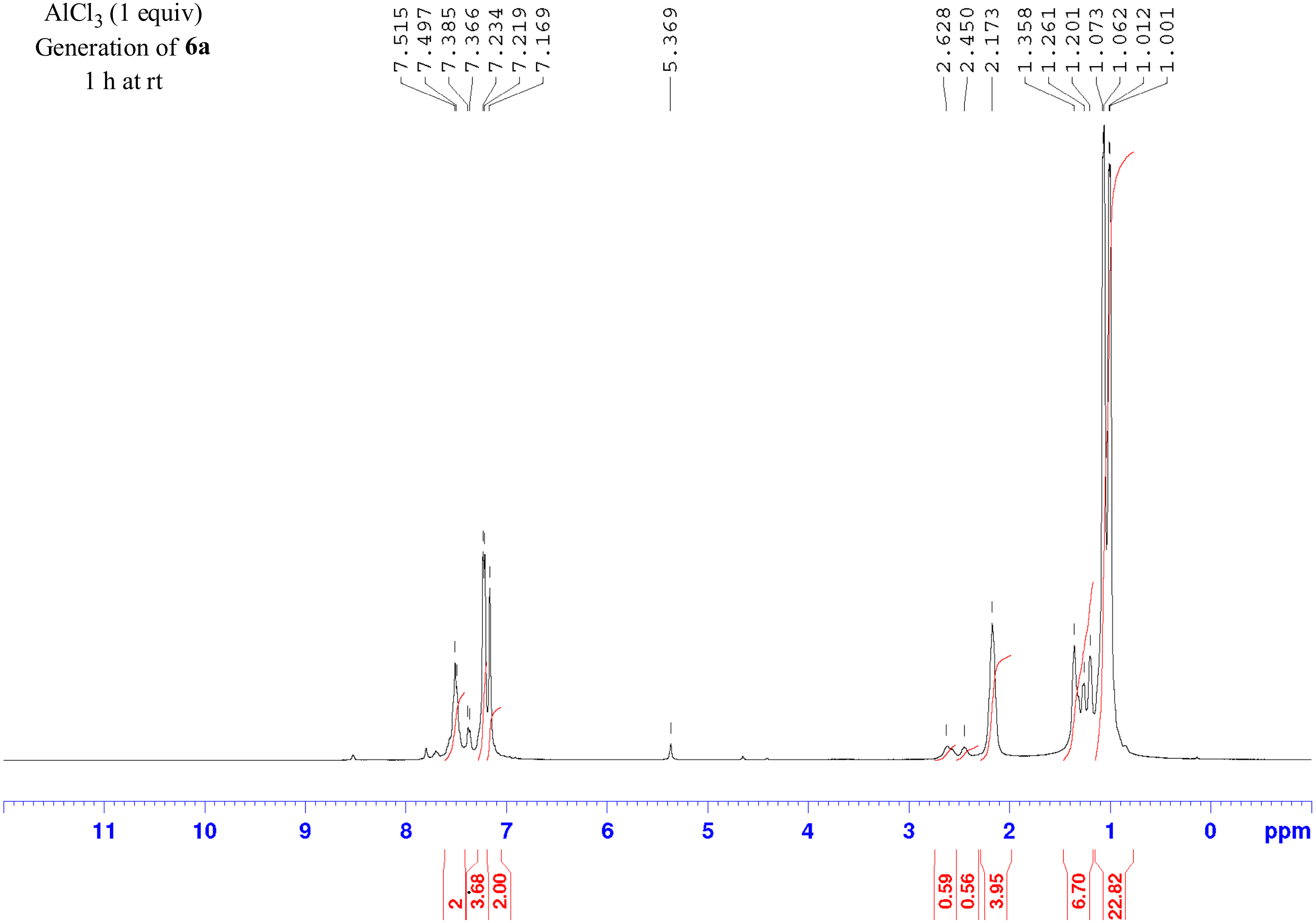
$^{13}C\{^1H\}$ NMR (101 MHz), $CH_2Cl_2$

Activation of **2a** with $TiCl_4$ (1 equiv) Generation of **6a** 5 min at 0 ºC



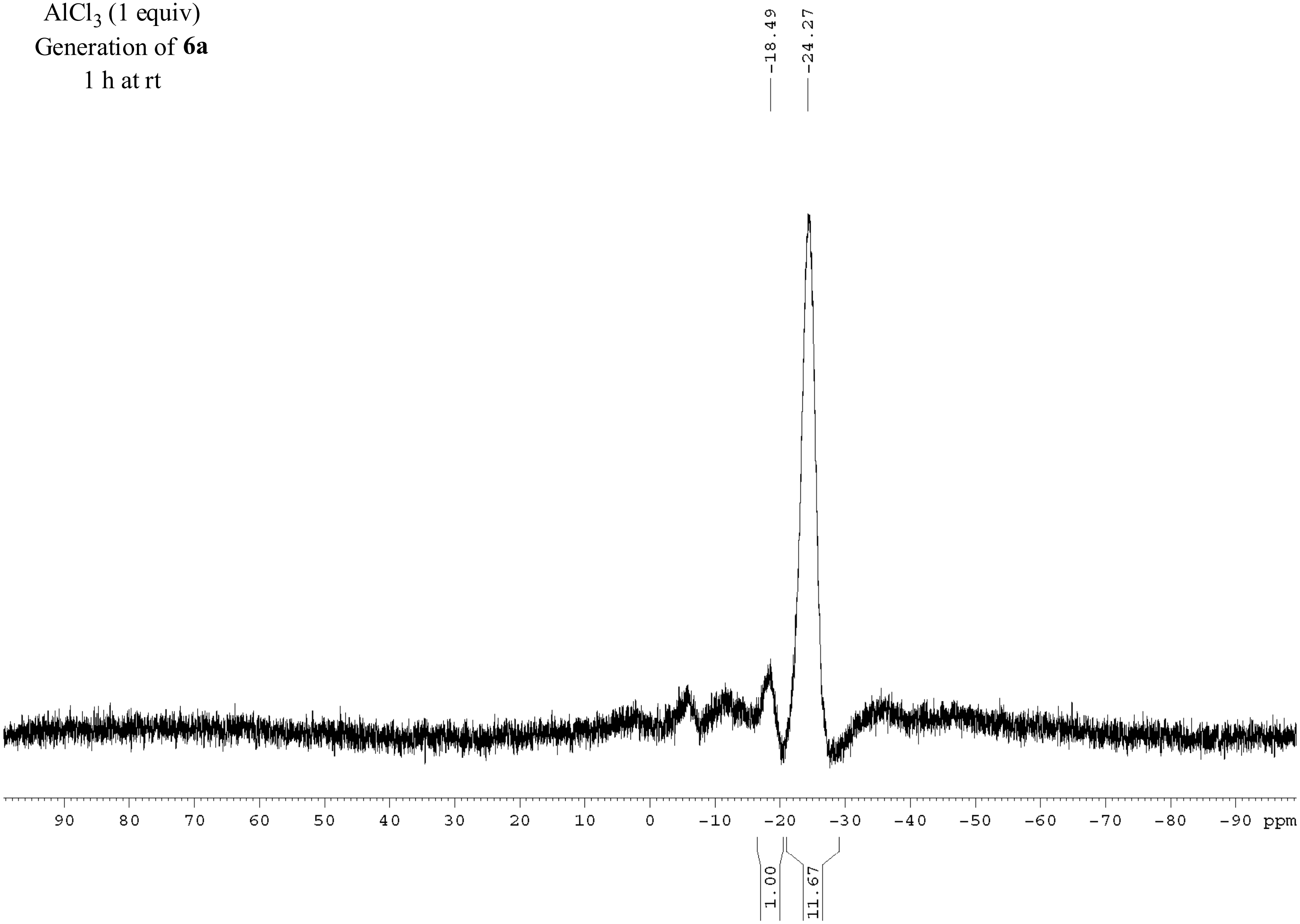
$^1$H NMR (400 MHz),
$CD_2Cl_2$

Activation of **2a** with
$AlCl_3$ (1 equiv)
Generation of **6a**
1 h at rt



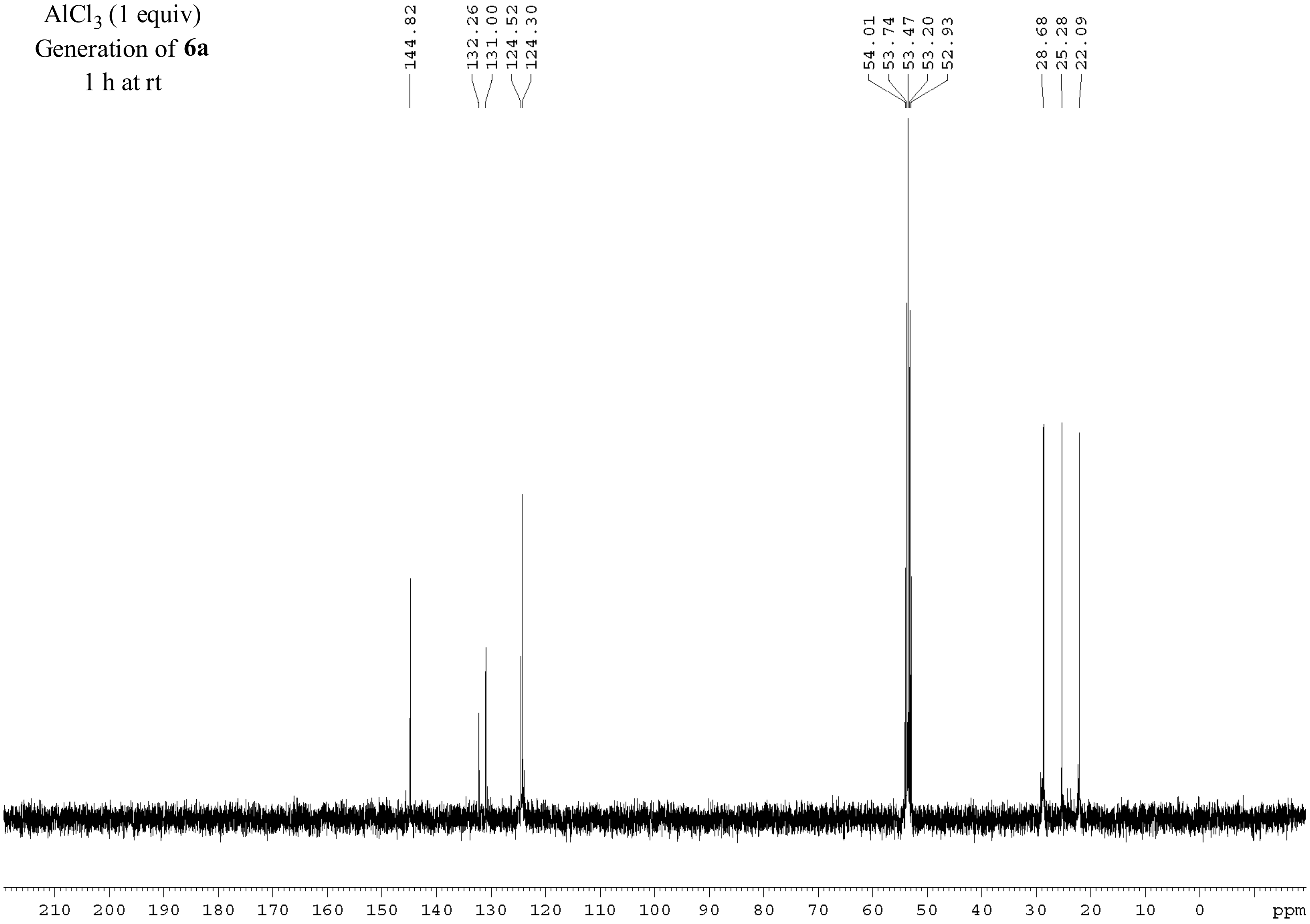
$^{11}$B NMR (128 MHz),
$CD_2Cl_2$

Activation of **2a** with
$AlCl_3$ (1 equiv)
Generation of **6a**
1 h at rt



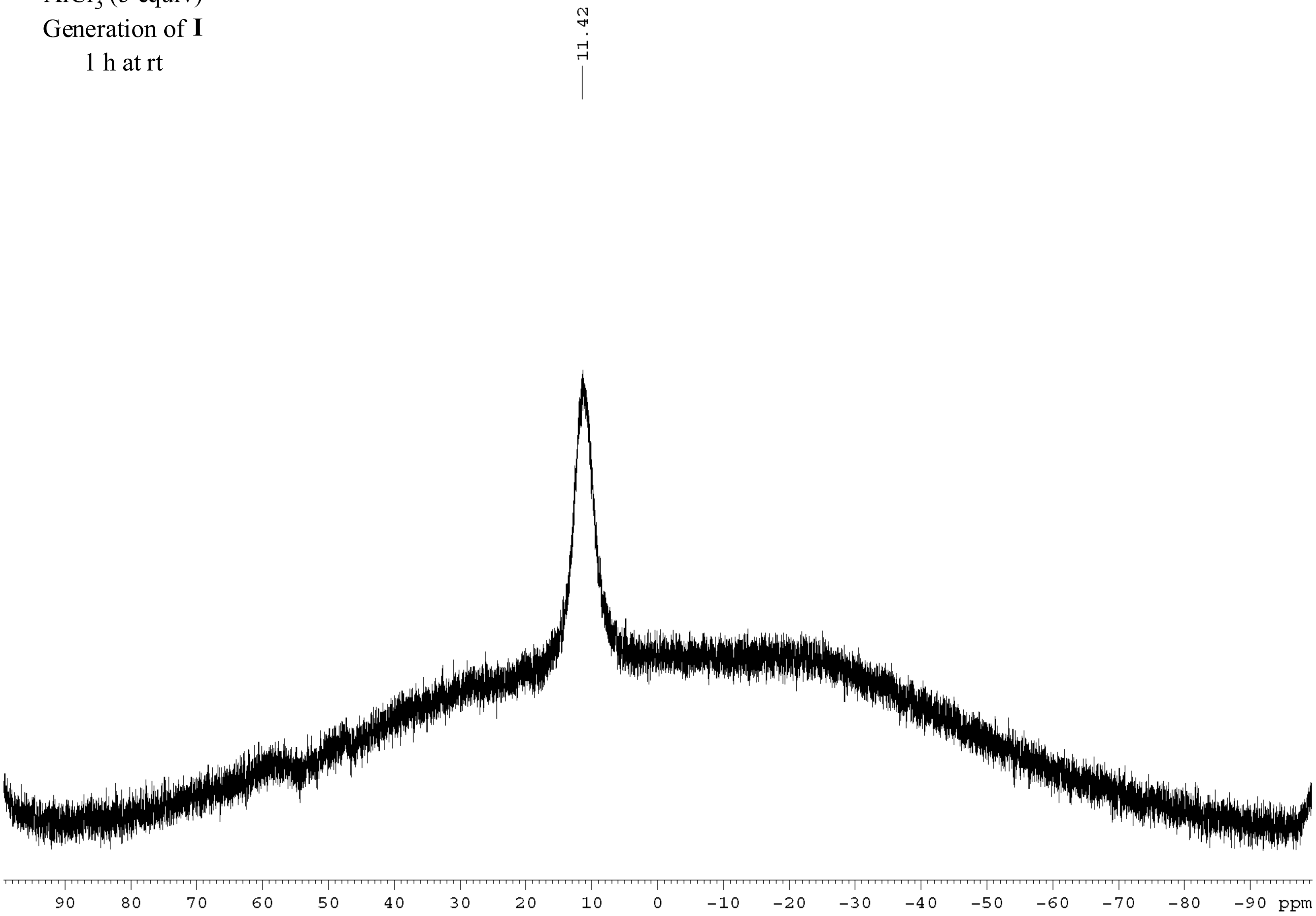
$^{13}C\{^{1}H\}$ NMR (101 MHz), $CD_2Cl_2$

Activation of **2a** with $AlCl_3$ (1 equiv)
Generation of **6a**
1 h at rt



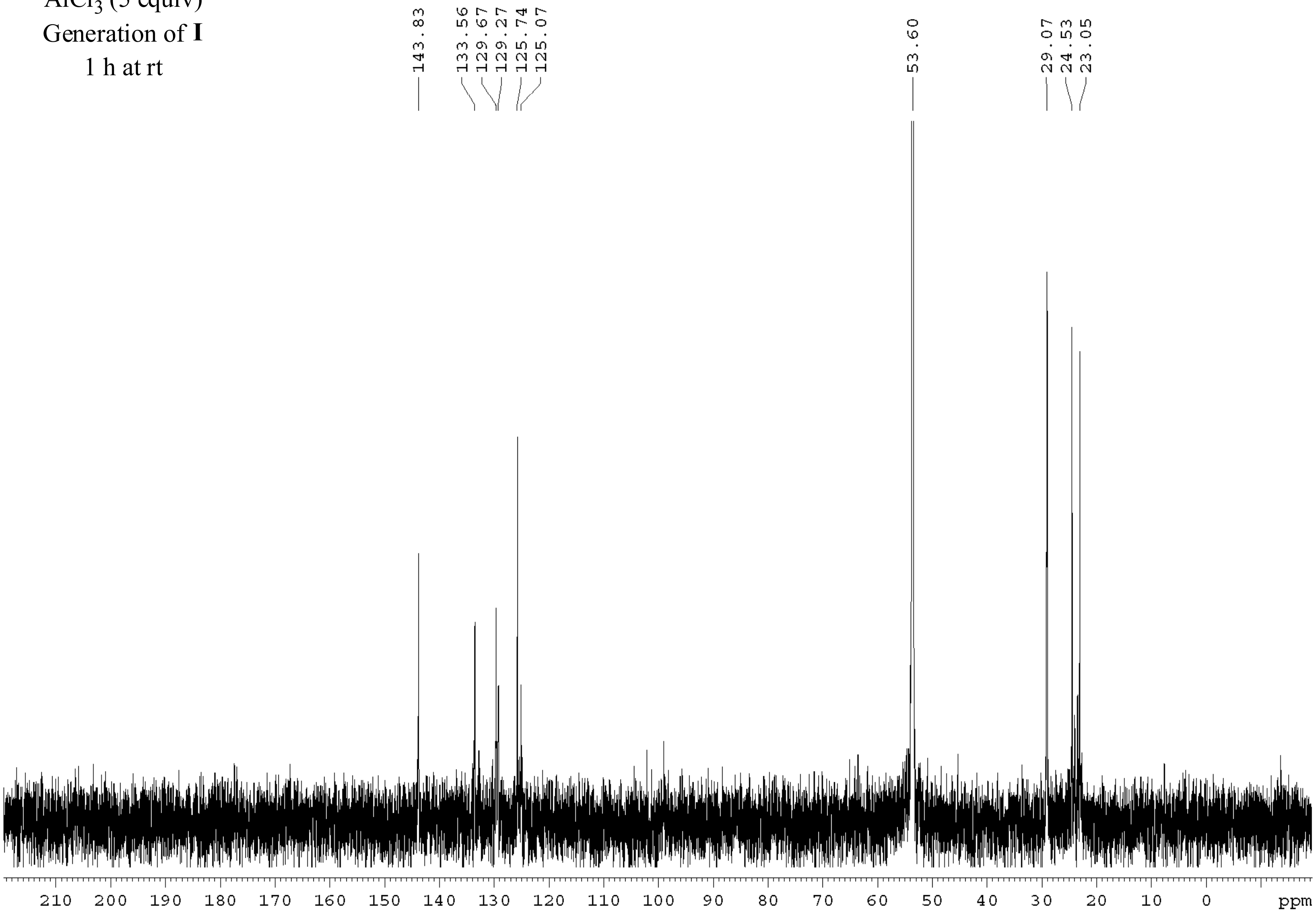
$^{11}$B NMR (128 MHz),
$CH_2Cl_2$

Activation of **2a** with
$AlCl_3$ (5 equiv)
Generation of **I**
1 h at rt



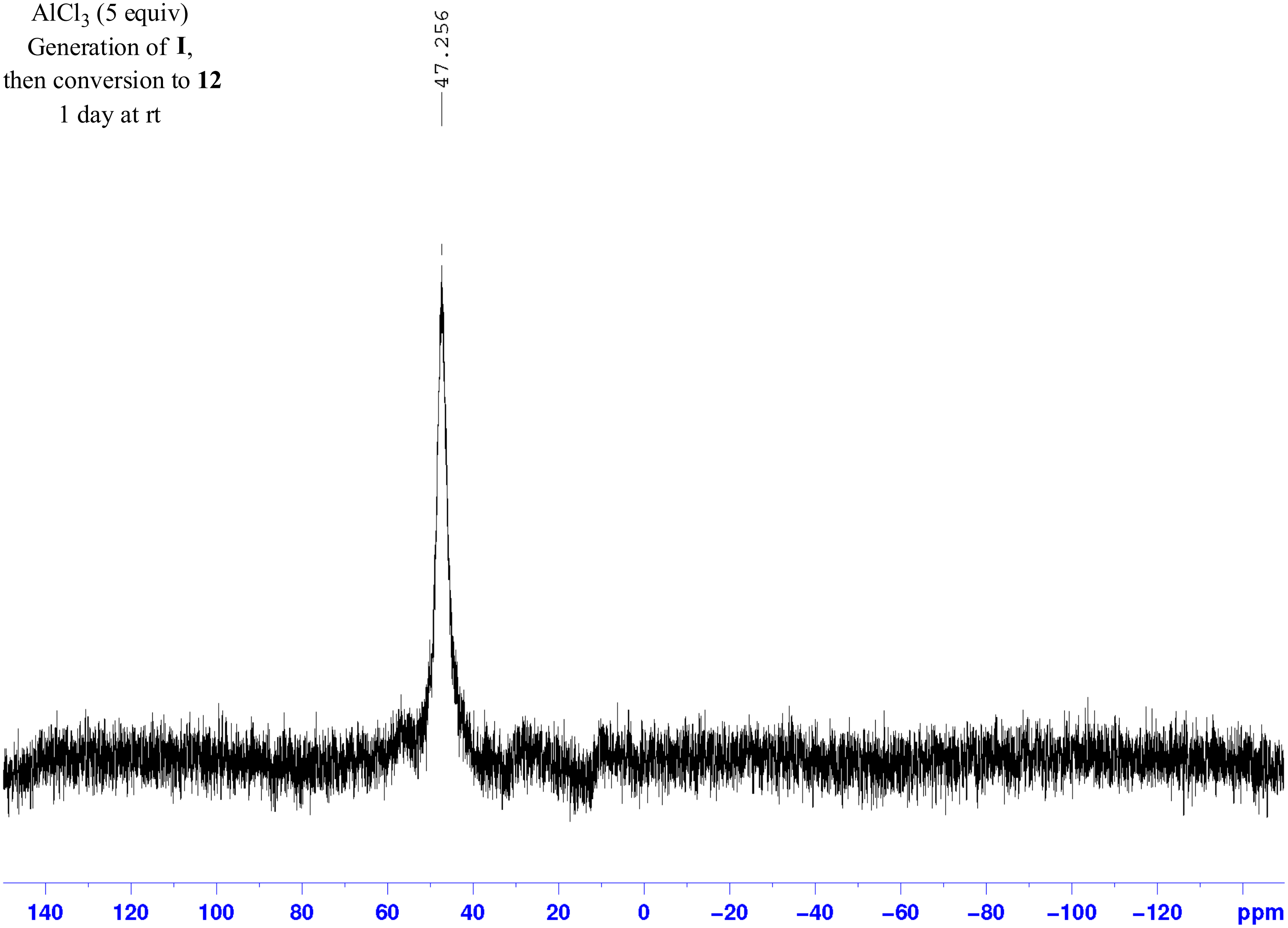
$^{13}C\{^1H\}$ NMR (101 MHz), $CH_2Cl_2$

Activation of **2a** with $AlCl_3$ (5 equiv) Generation of **I** 1 h at rt



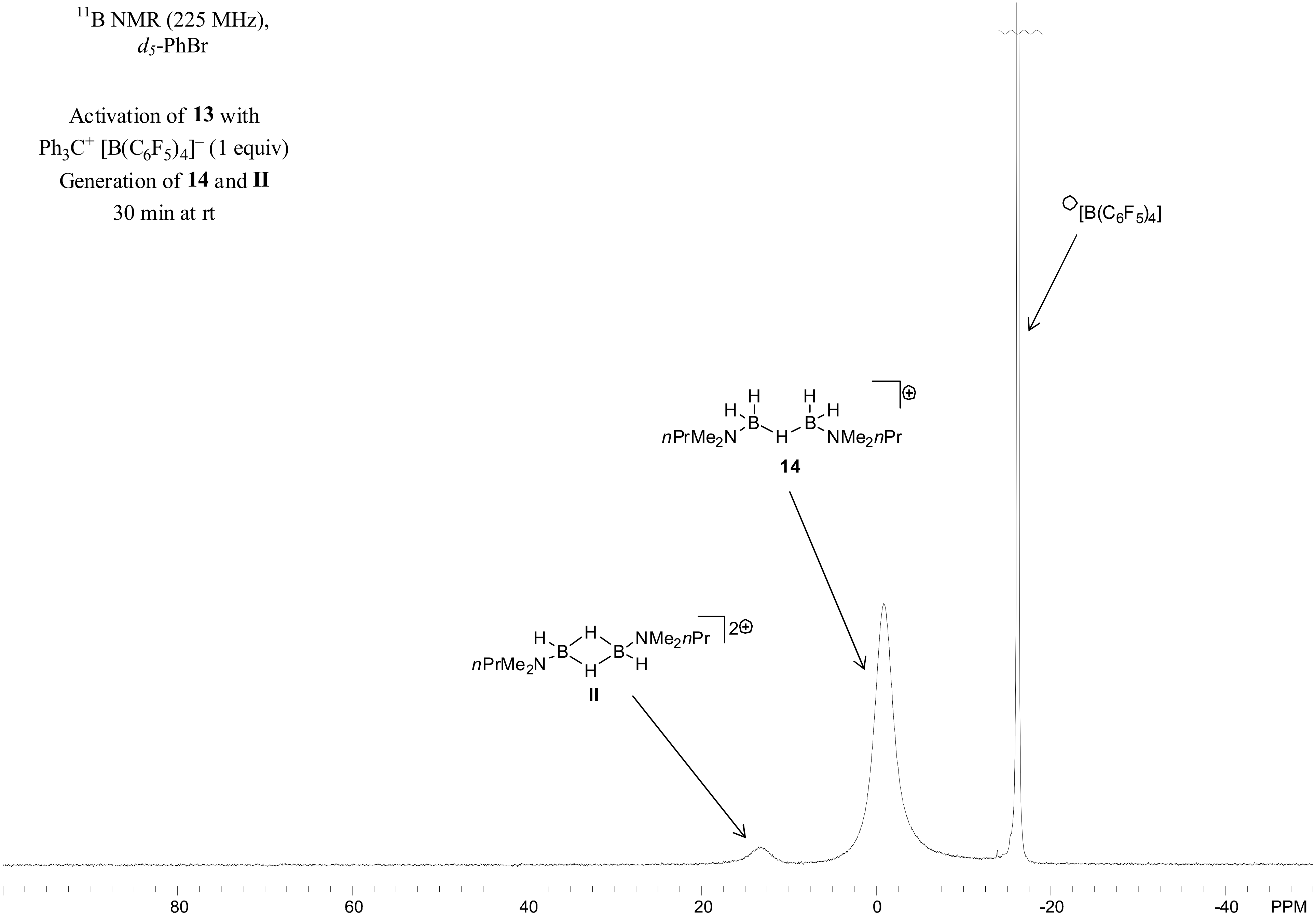
$^{11}B$ NMR (96 MHz),
$CH_2Cl_2$

Activation of **2a** with
$AlCl_3$ (5 equiv)
Generation of **I**,
then conversion to **12**
1 day at rt



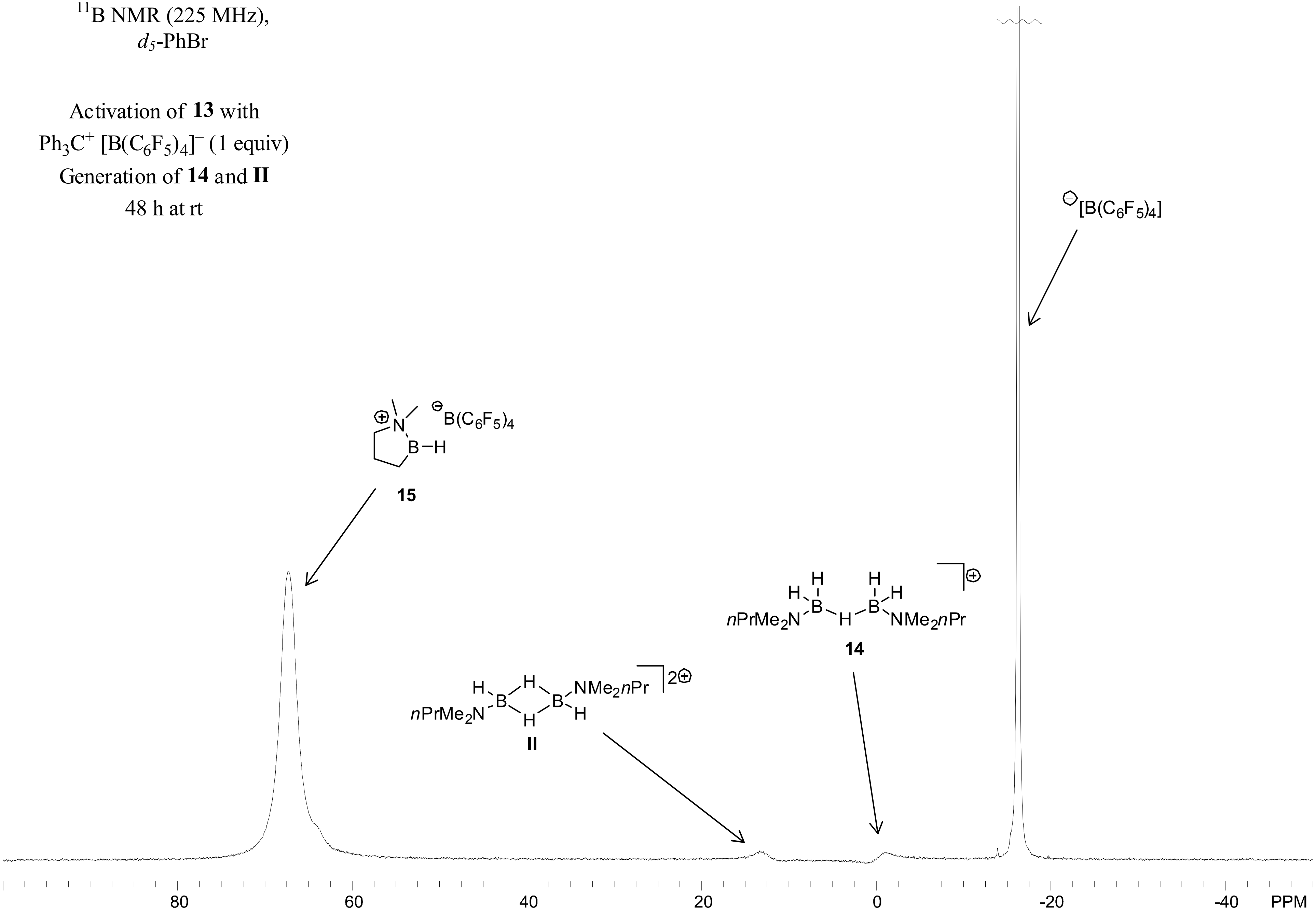
$^{11}$B NMR (225 MHz),
*d*$_5$-PhBr

Activation of **13** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
Generation of **14** and **II**
30 min at rt



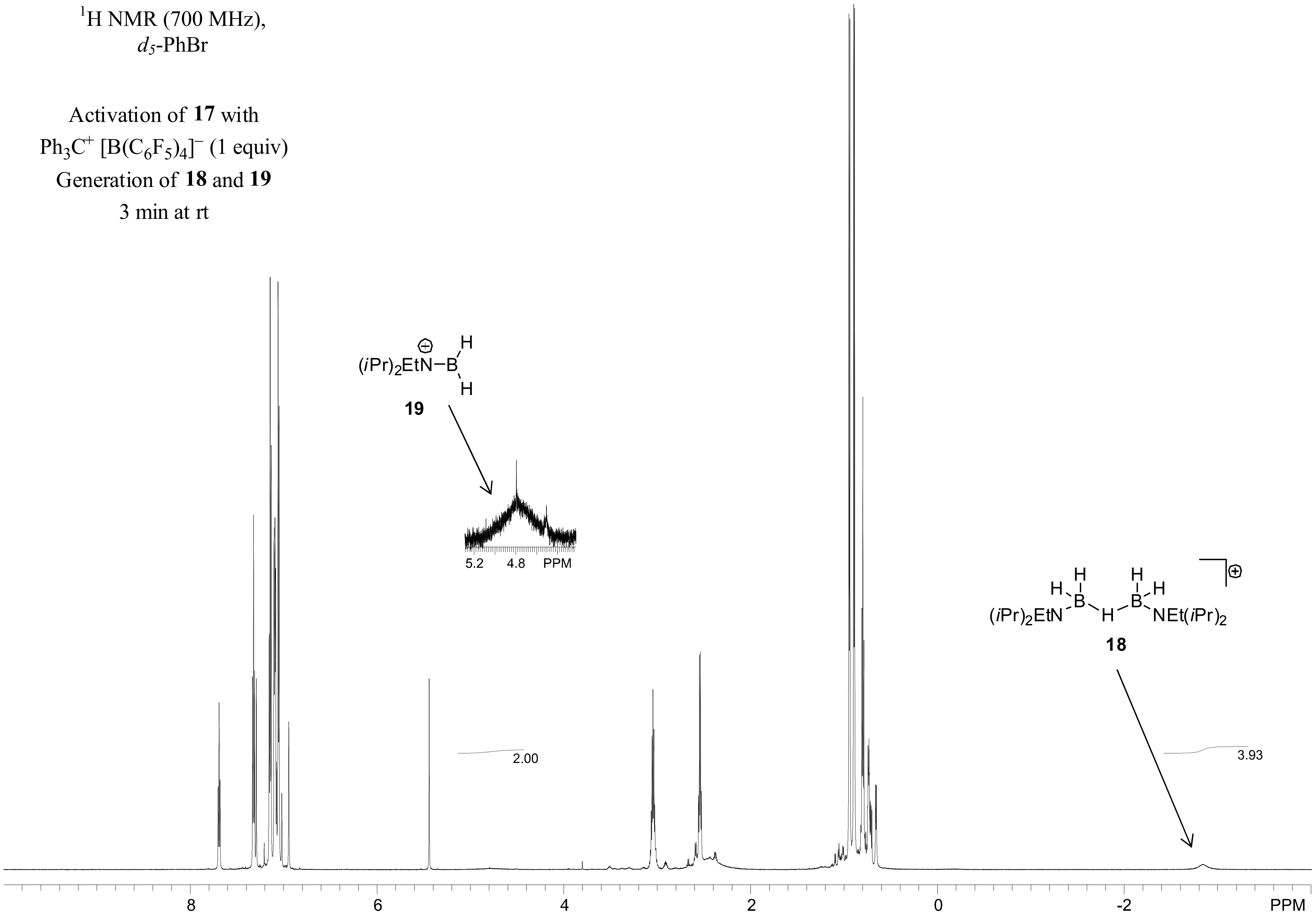
$^{11}$B NMR (225 MHz),
$d_5$-PhBr

Activation of **13** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
Generation of **14** and **II**
48 h at rt



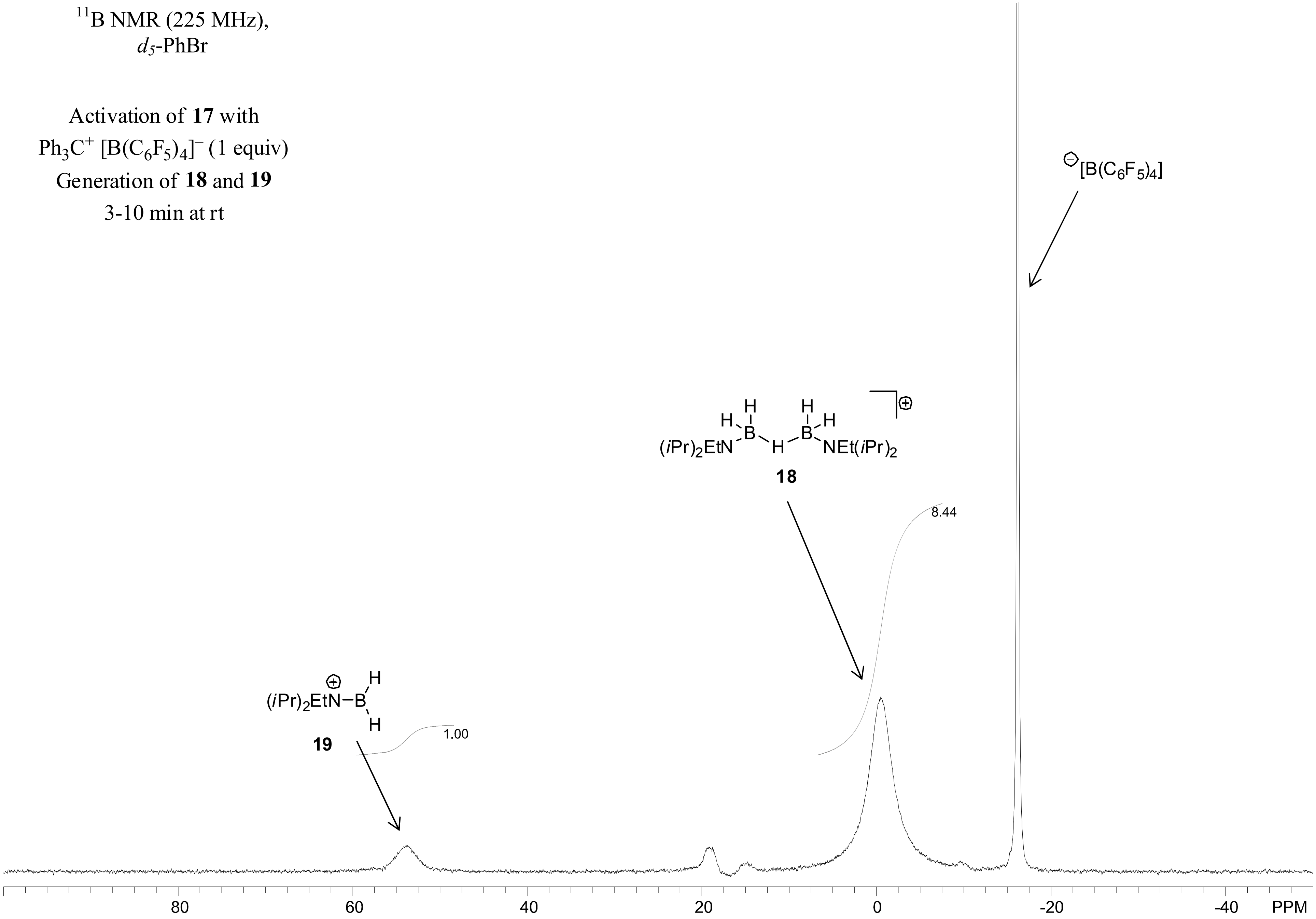
$^{1}$H NMR (700 MHz),
$d_5$-PhBr

Activation of **17** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
Generation of **18** and **19**
3 min at rt



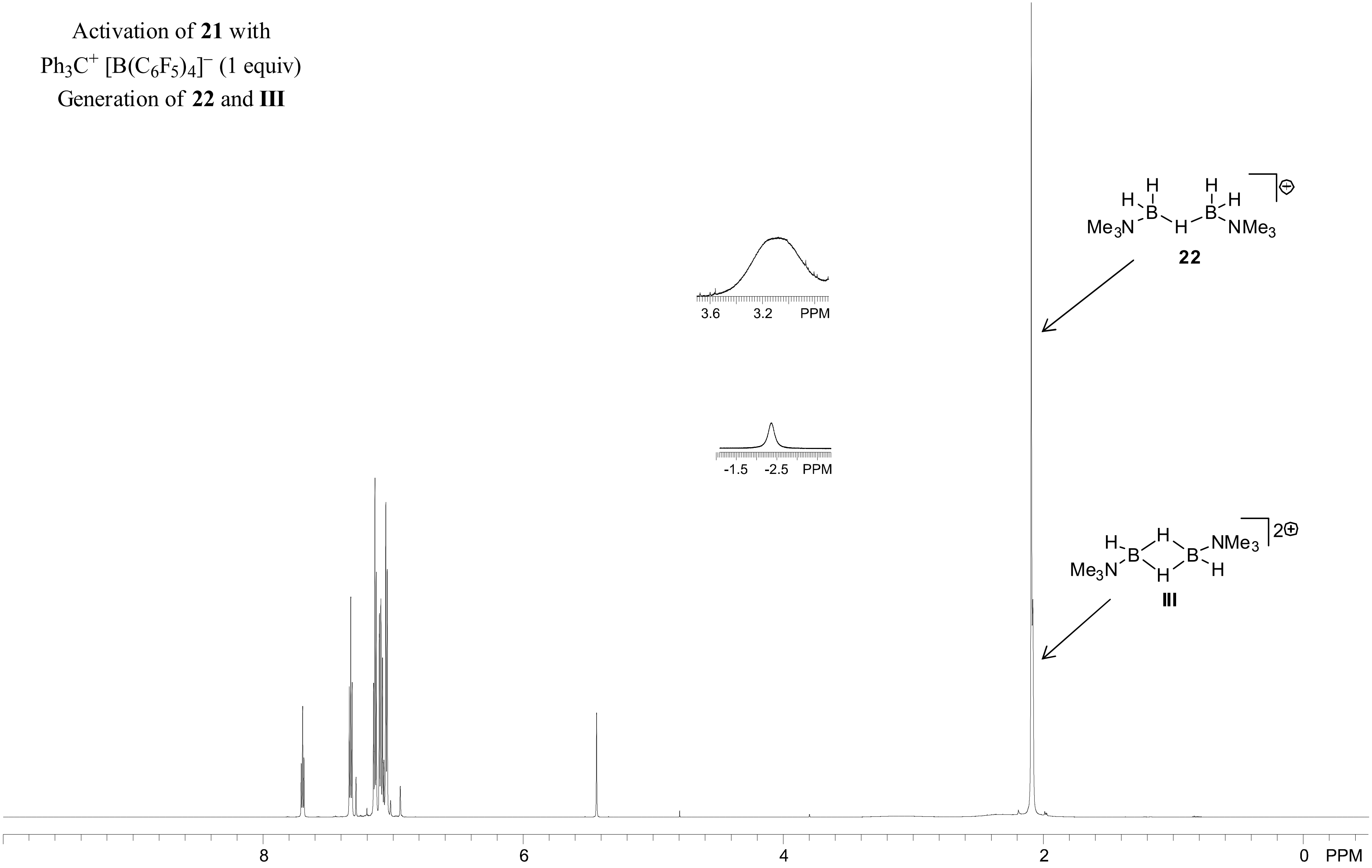
$^{11}$B NMR (225 MHz),
*$d_5$*-PhBr

Activation of **17** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
Generation of **18** and **19**
3-10 min at rt



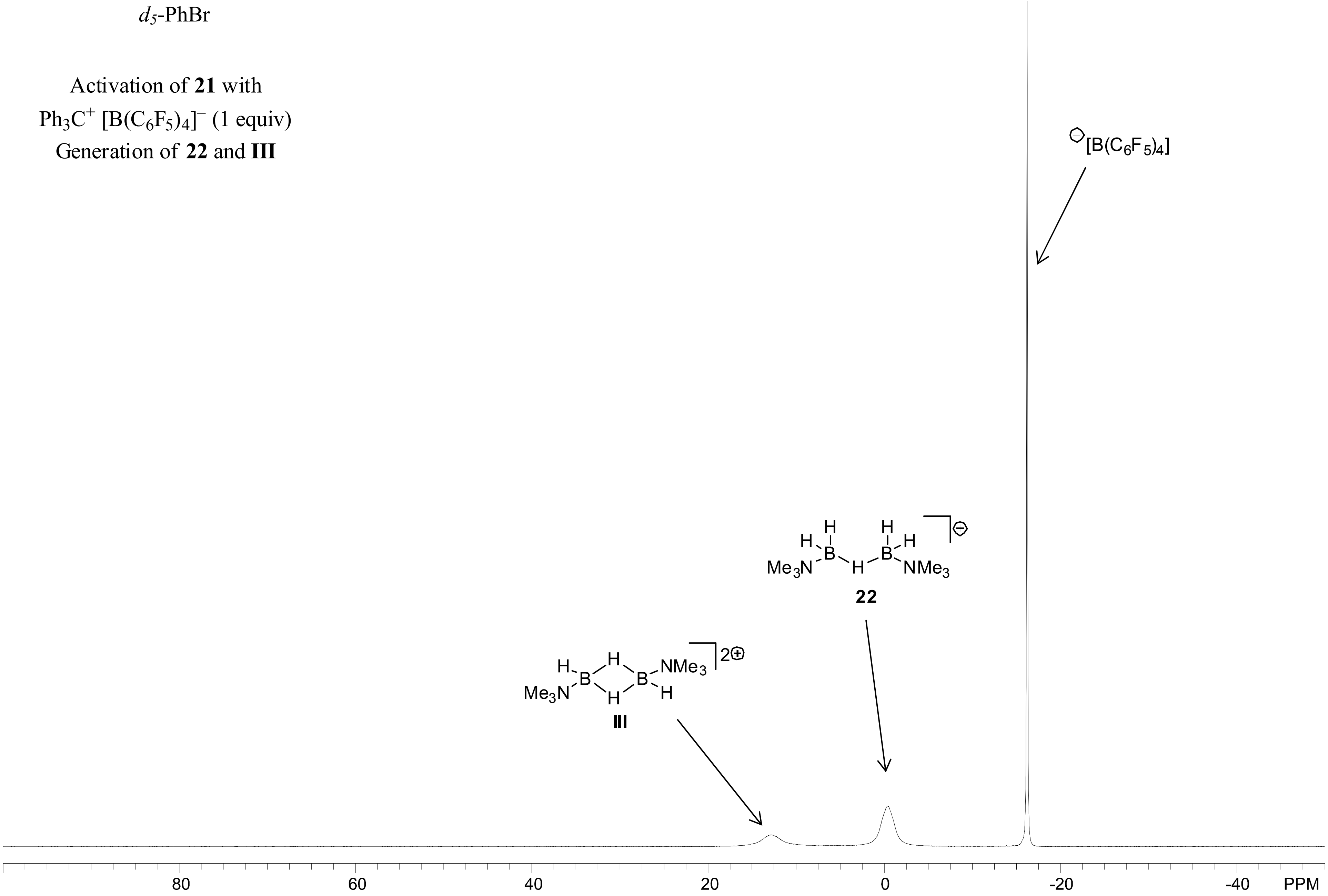
$^1$H NMR (700 MHz),
$d_5$-PhBr

Activation of **21** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
Generation of **22** and **III**



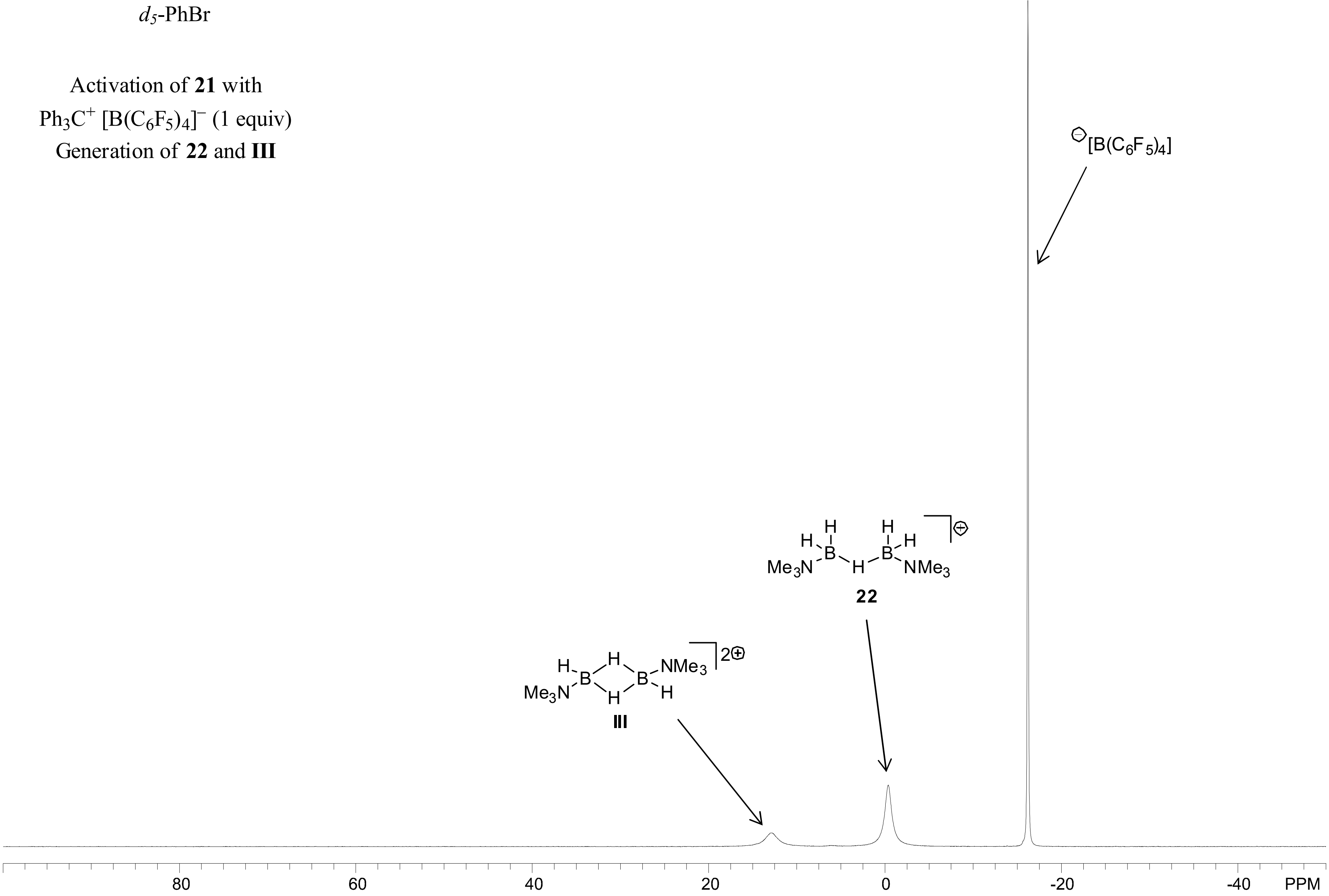
$^{11}$B NMR (225 MHz),
$d_5$-PhBr

Activation of **21** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
Generation of **22** and **III**



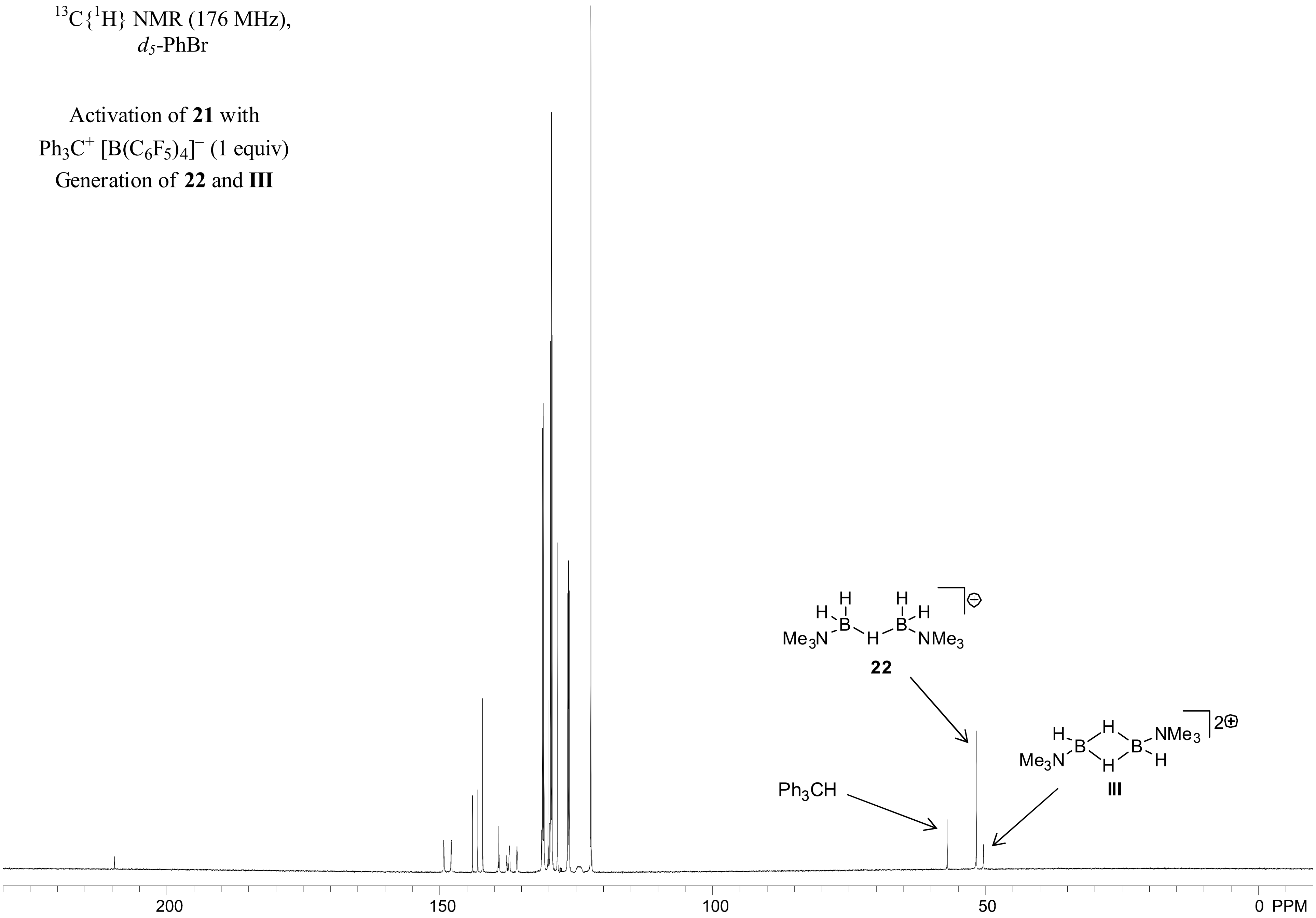
$^{11}$B{$^{1}$H} NMR (225 MHz),
$d_5$-PhBr

Activation of **21** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
Generation of **22** and **III**



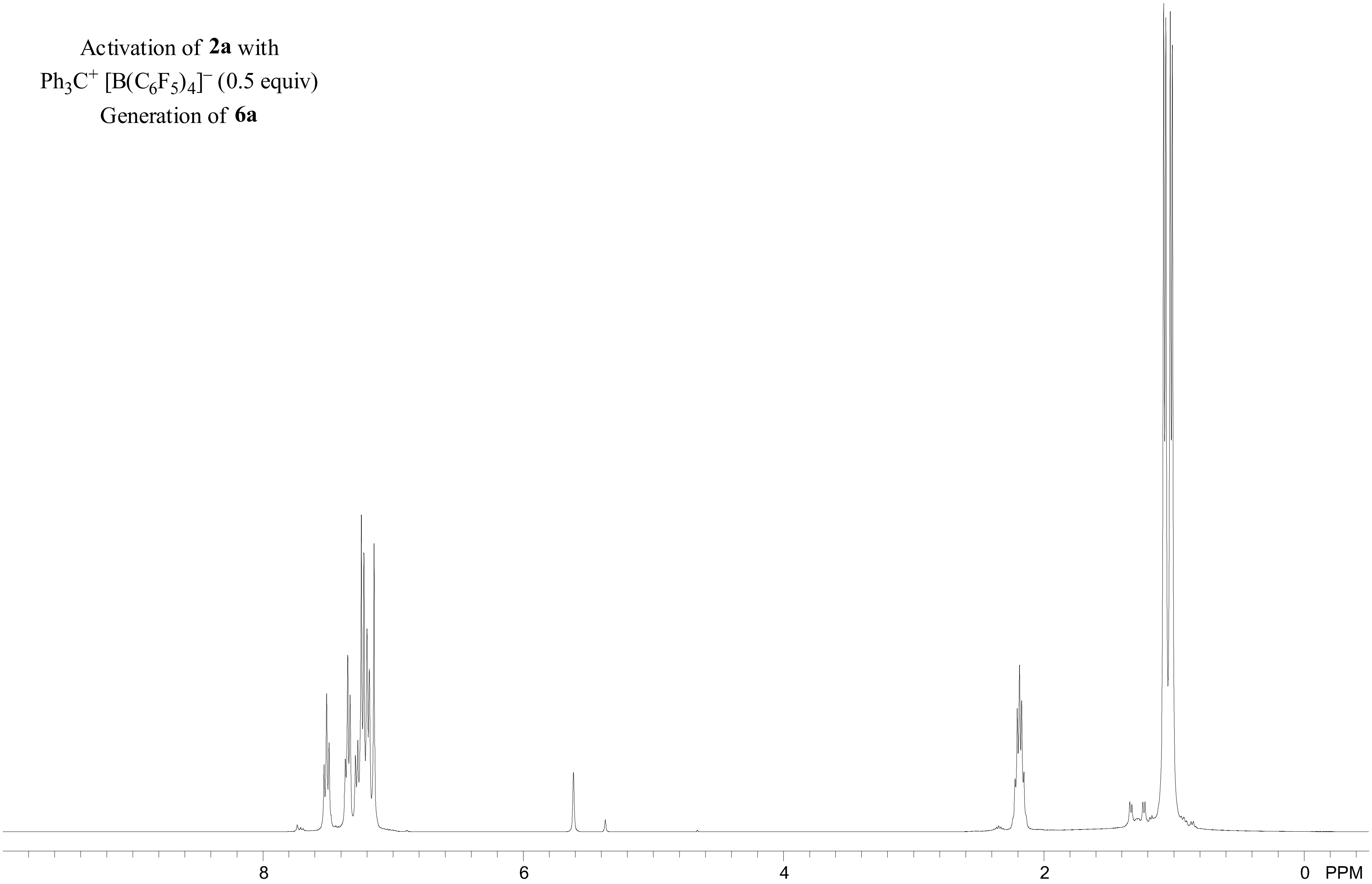
$^{13}C\{^{1}H\}$ NMR (176 MHz),
$d_5$-PhBr

Activation of **21** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
Generation of **22** and **III**



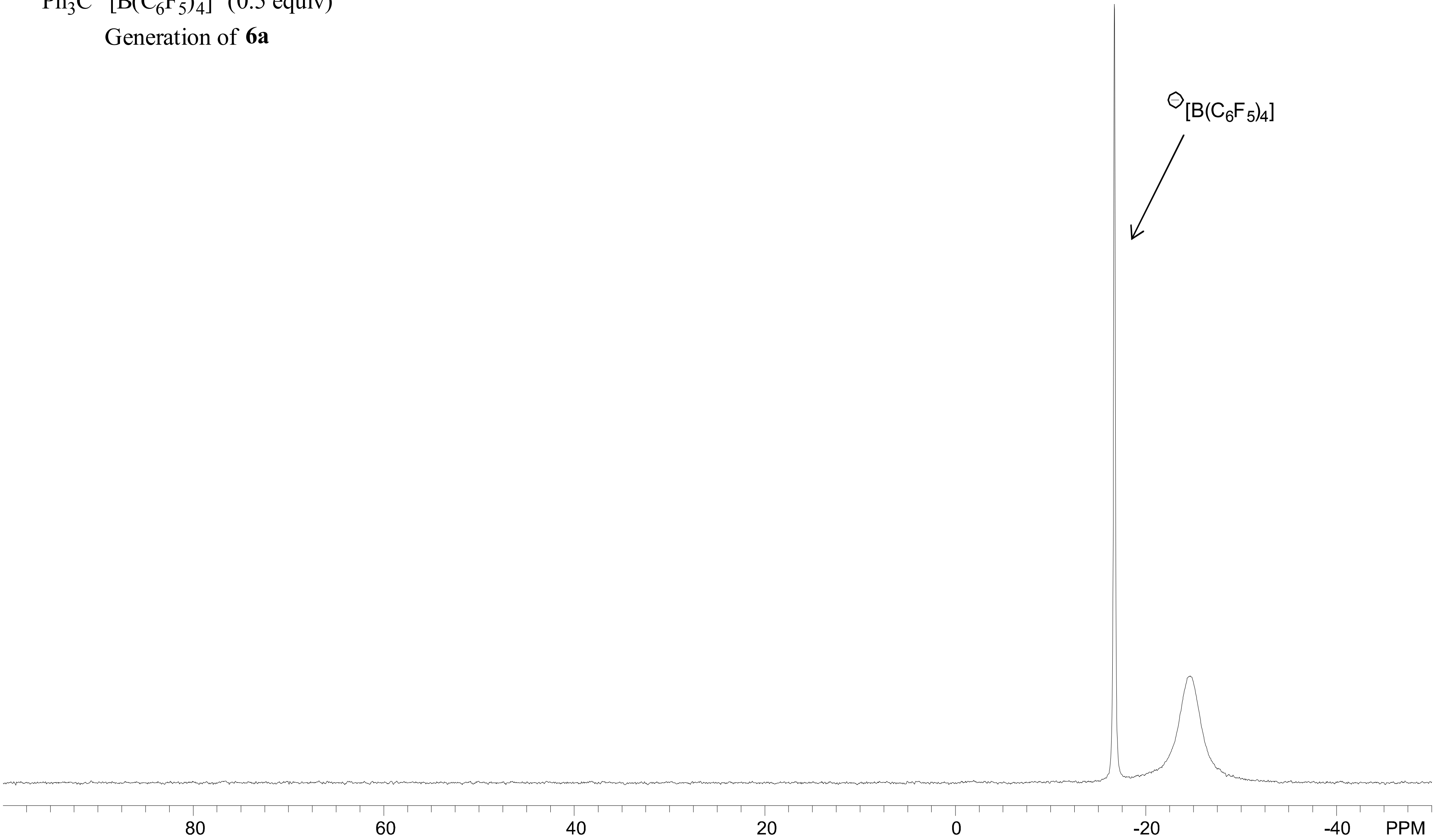
$^1$H NMR (400 MHz),
$CD_2Cl_2$

Activation of **2a** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (0.5 equiv)
Generation of **6a**



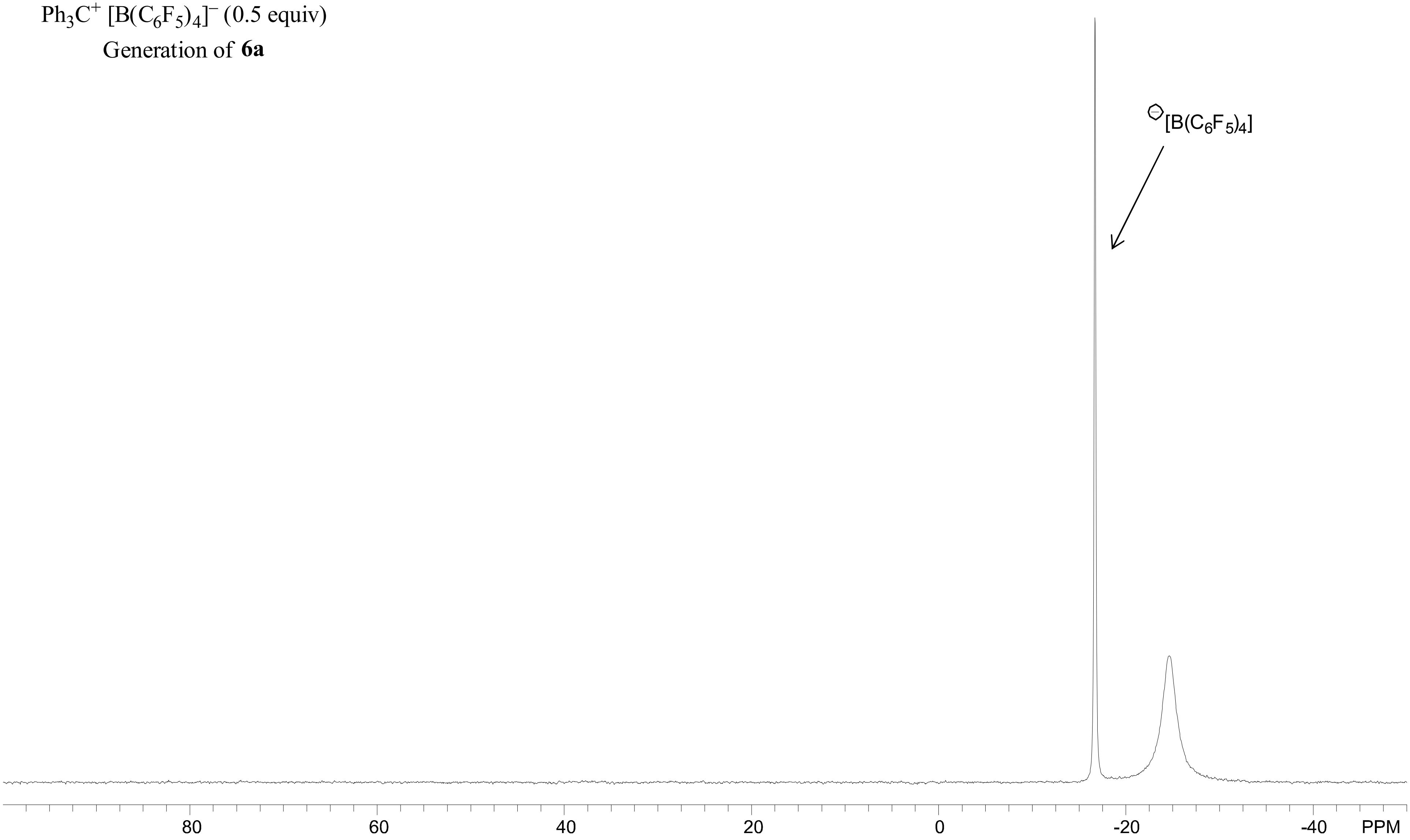
$^{11}$B NMR (128 MHz),
$CD_2Cl_2$

Activation of **2a** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (0.5 equiv)
Generation of **6a**



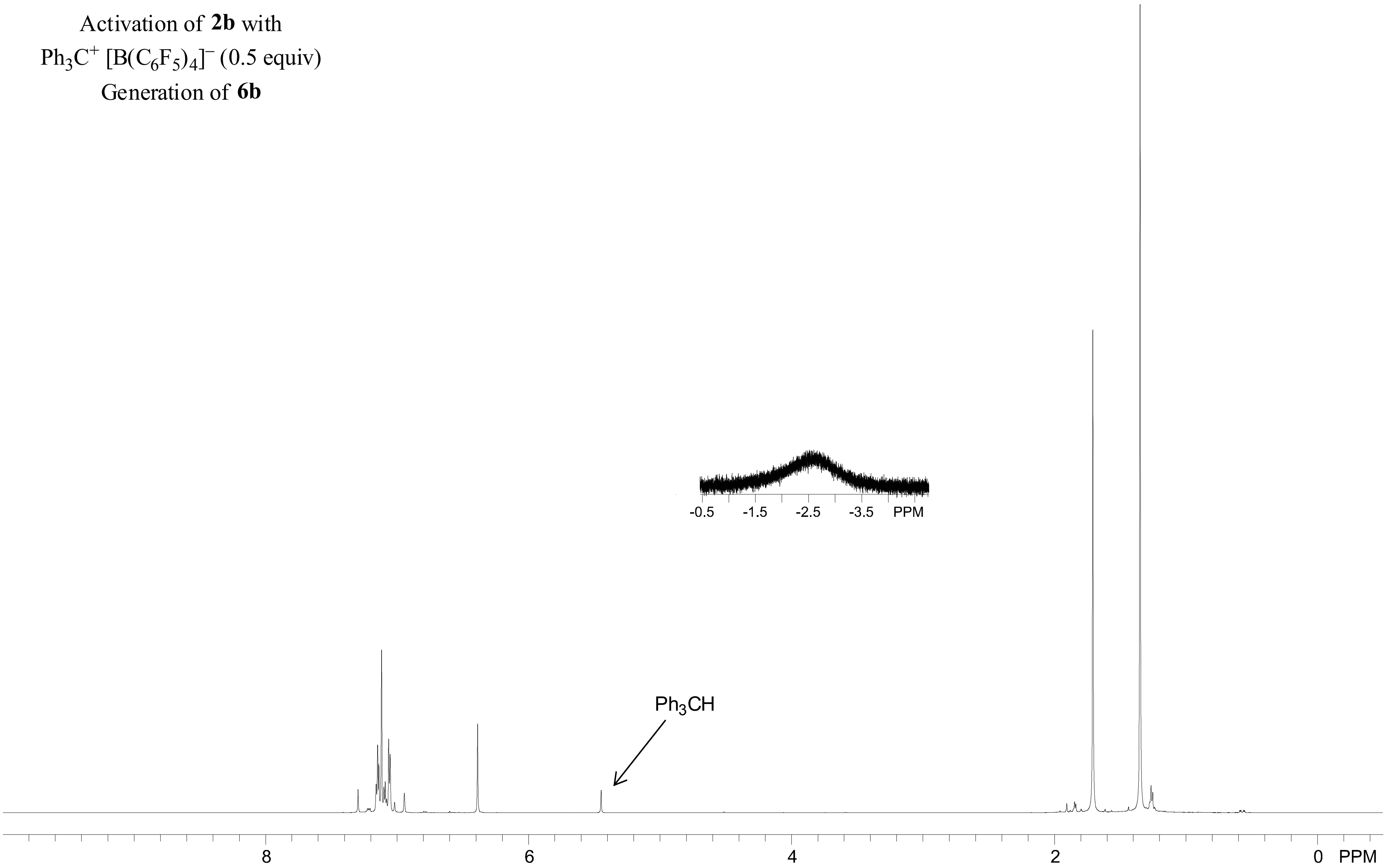
$^{11}B\{^1H\}$ NMR (128 MHz),
$CD_2Cl_2$

Activation of **2a** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (0.5 equiv)
Generation of **6a**



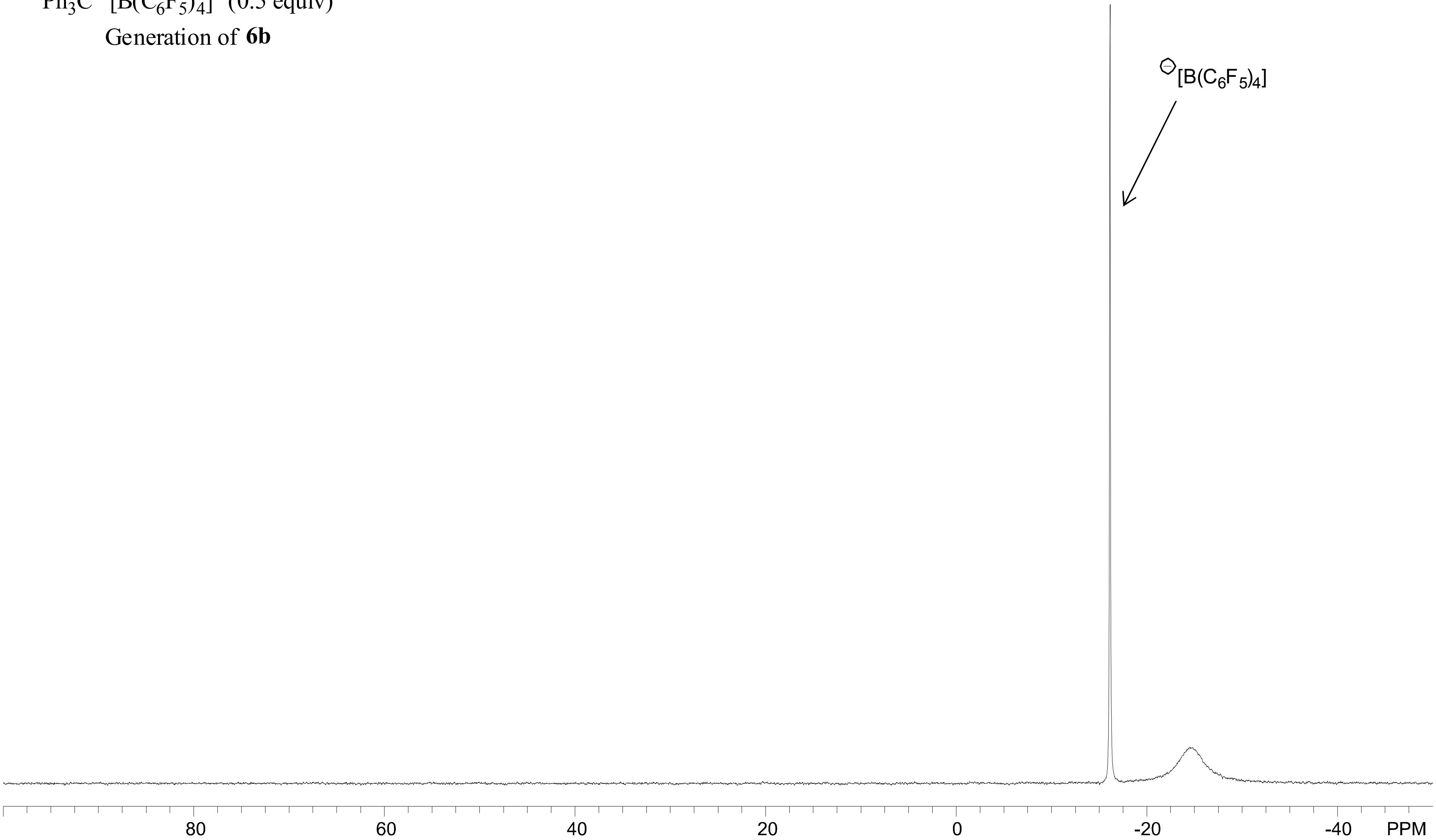
$^1$H NMR (700 MHz),
$d_5$-PhBr

Activation of **2b** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (0.5 equiv)
Generation of **6b**



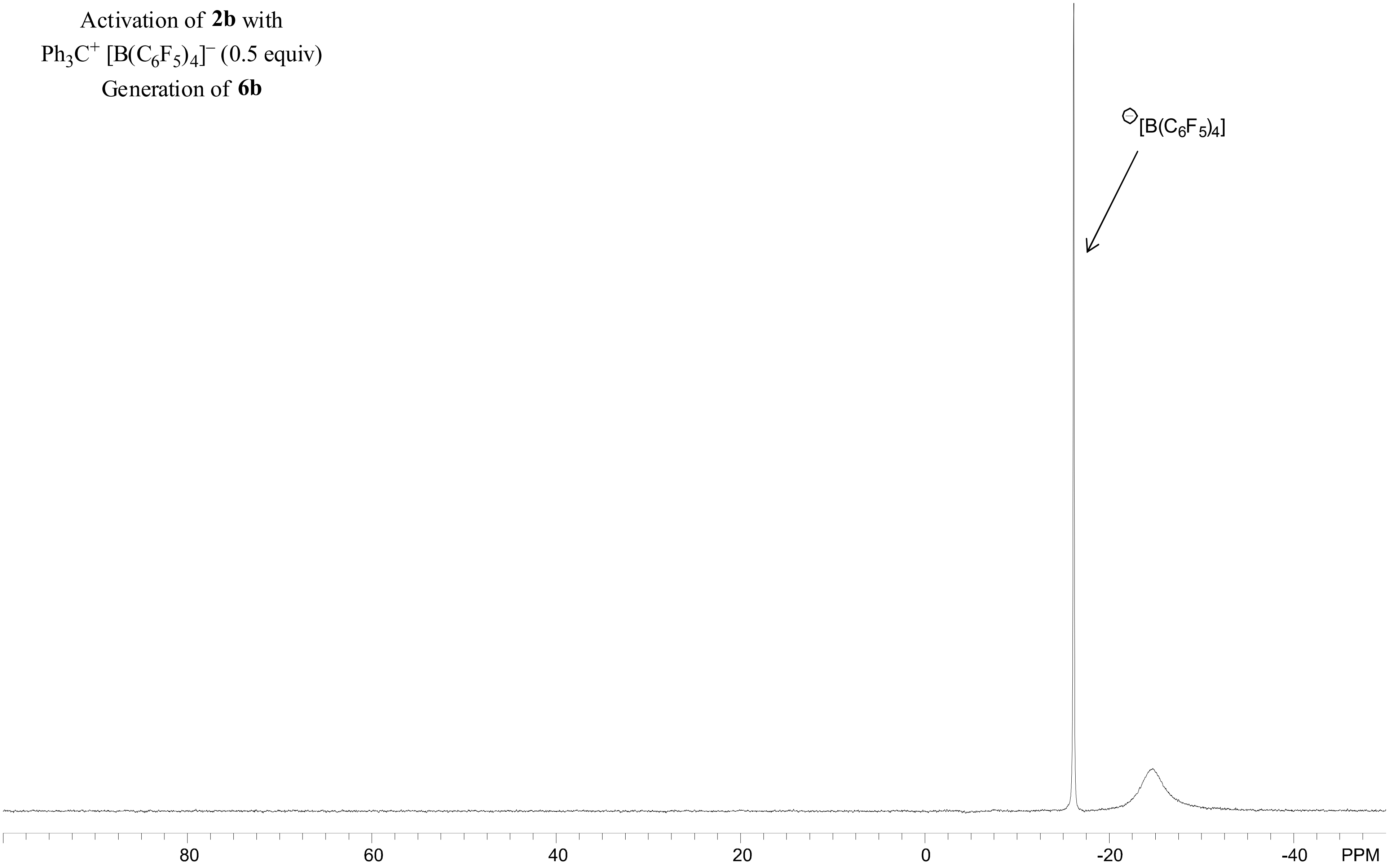
$^{11}$B NMR (225 MHz),
$d_5$-PhBr

Activation of **2b** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (0.5 equiv)
Generation of **6b**

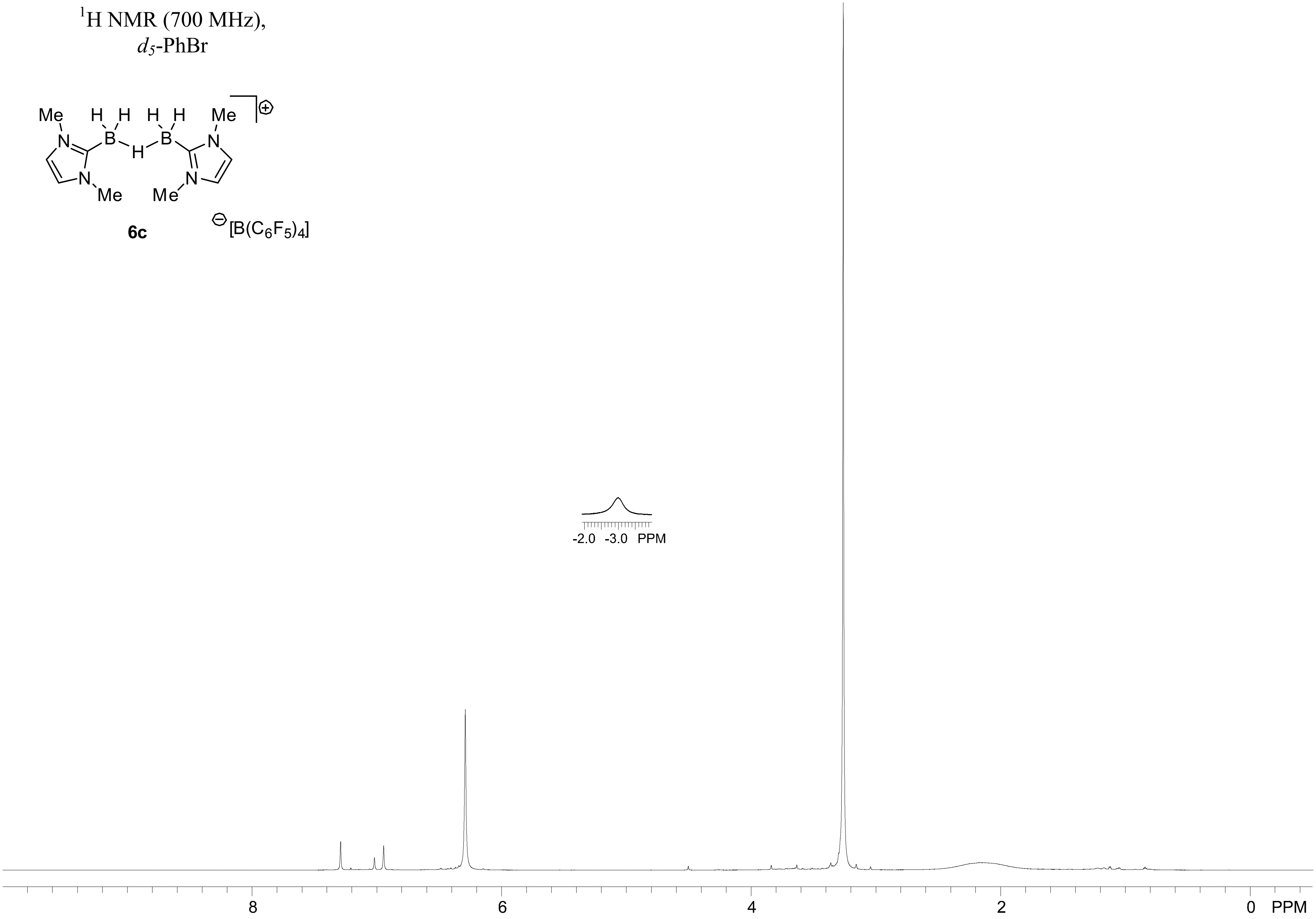


$^{11}B\{^{1}H\}$ NMR (225 MHz),
$d_5$-PhBr

Activation of **2b** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (0.5 equiv)
Generation of **6b**

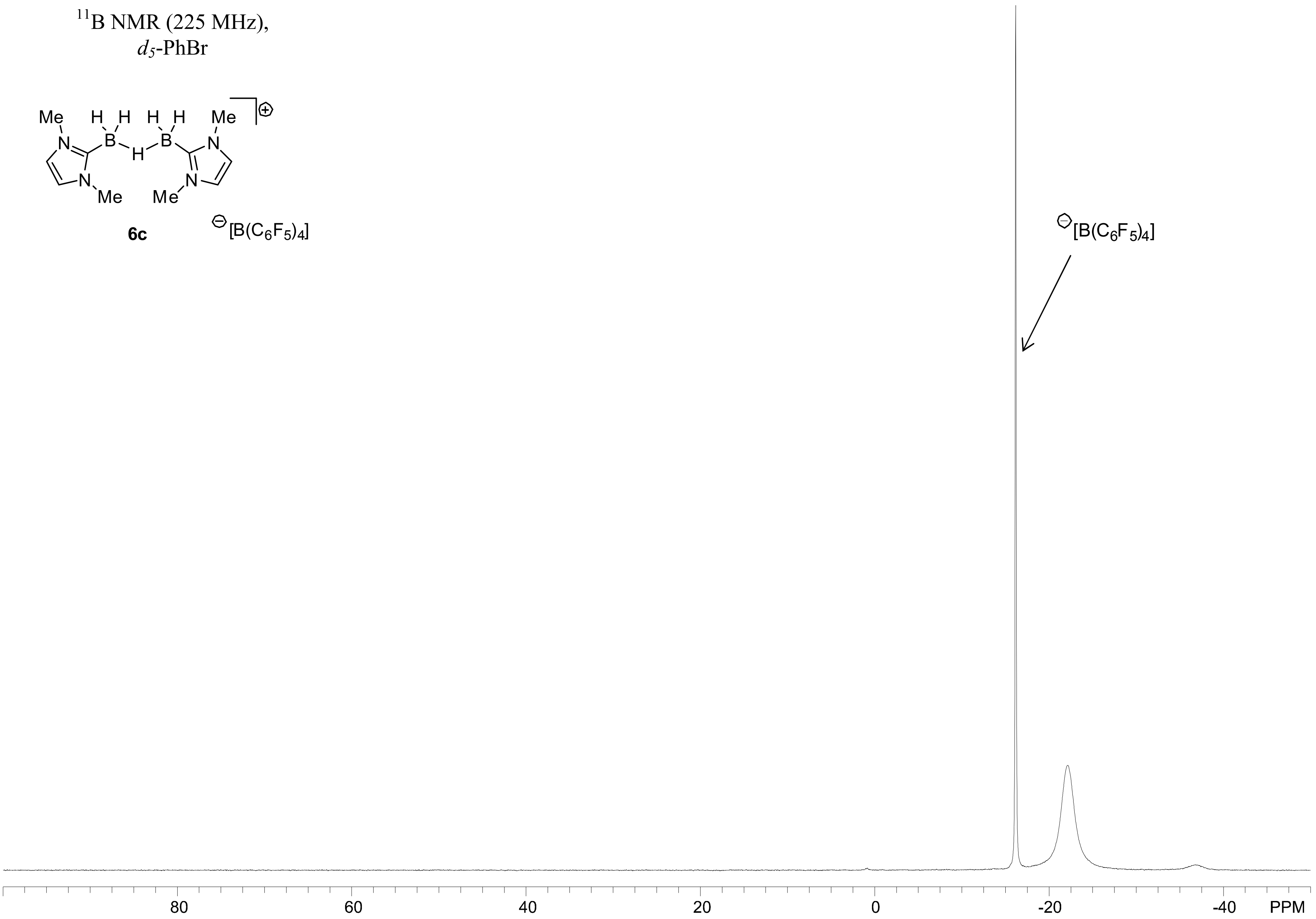


$^1$H NMR (700 MHz),
*$d_5$*-PhBr



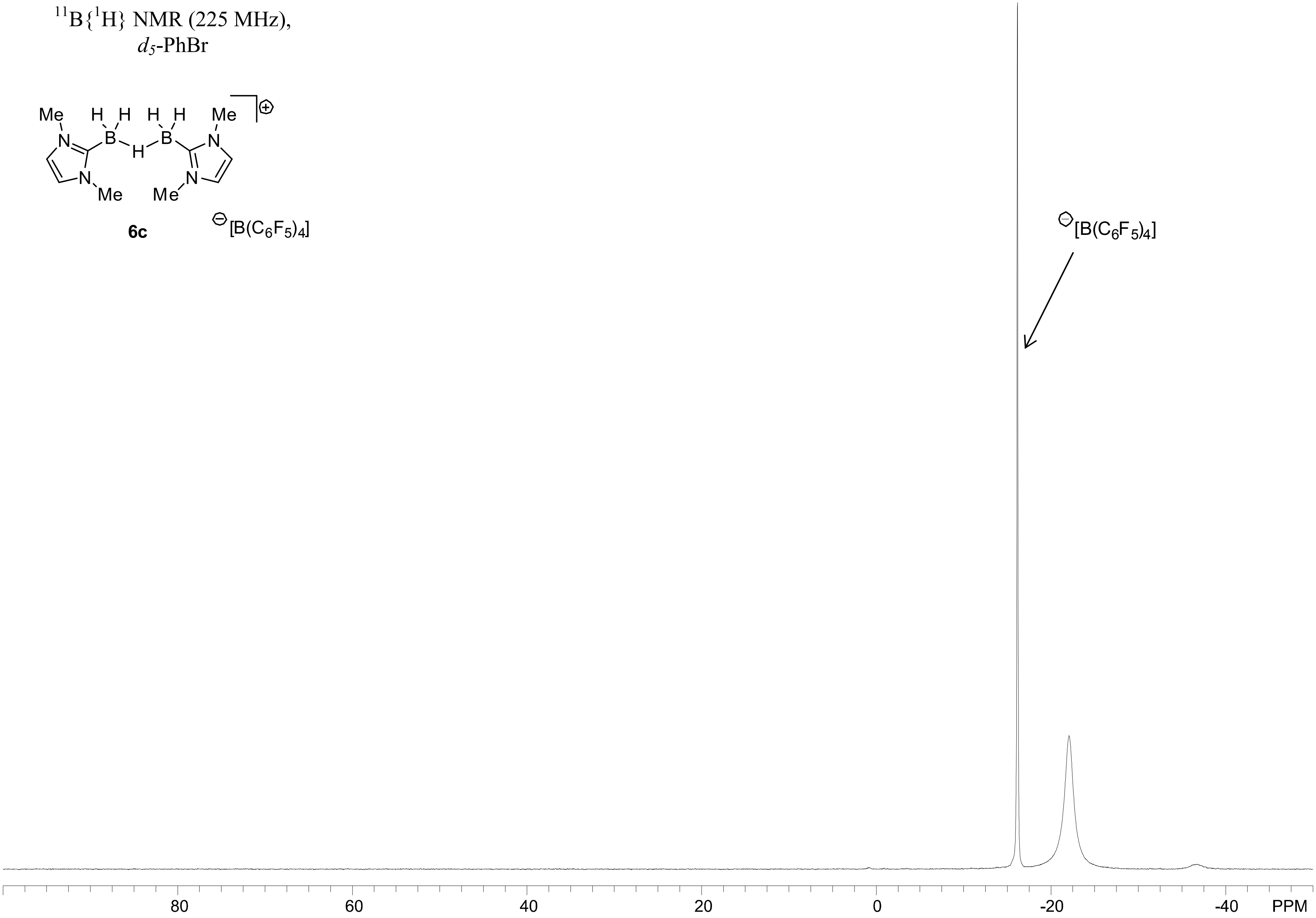
**6c**

$^{11}$B NMR (225 MHz),
$d_5$-PhBr



**6c**

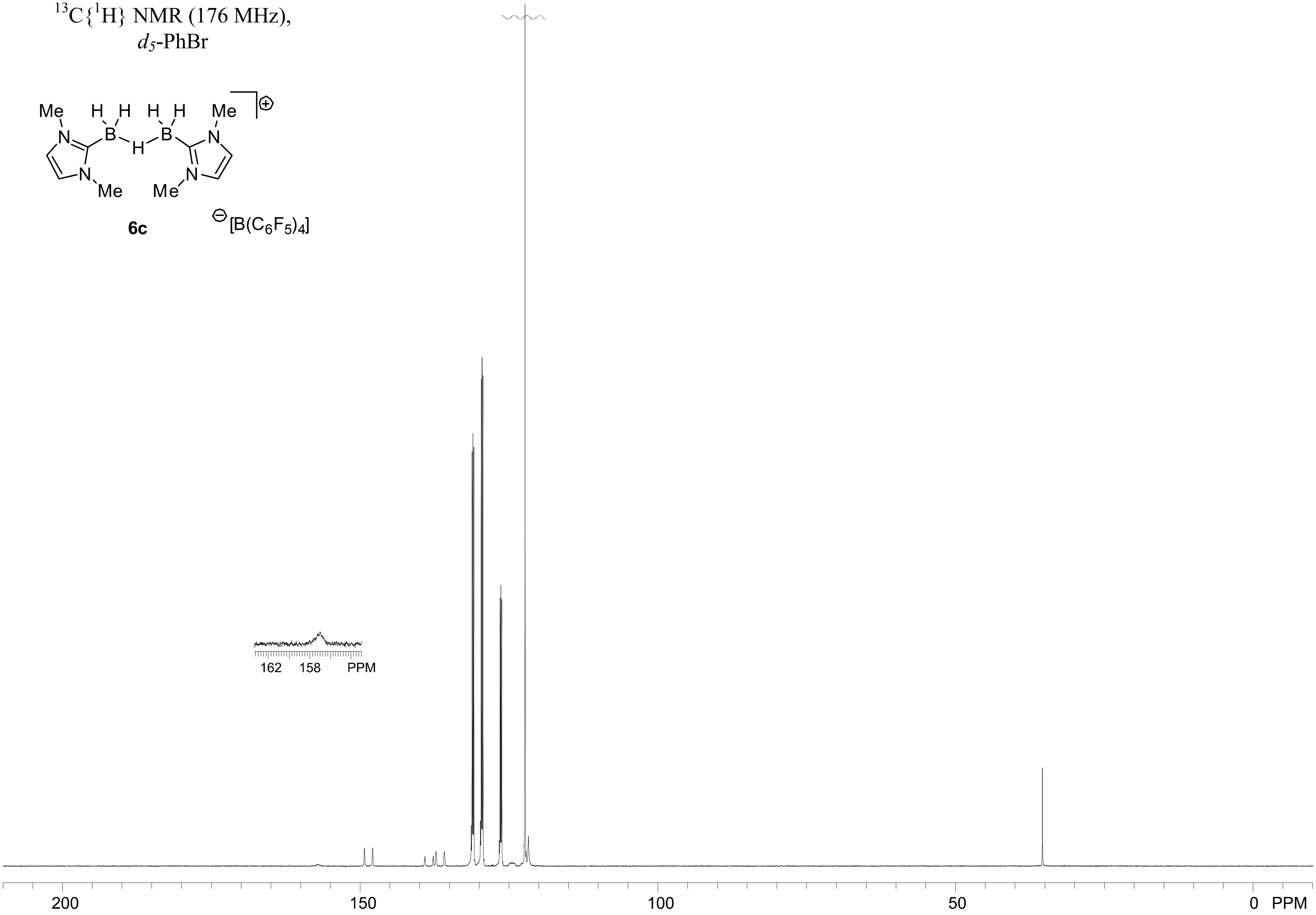
$^{11}B\{^1H\}$ NMR (225 MHz),
$d_5$-PhBr



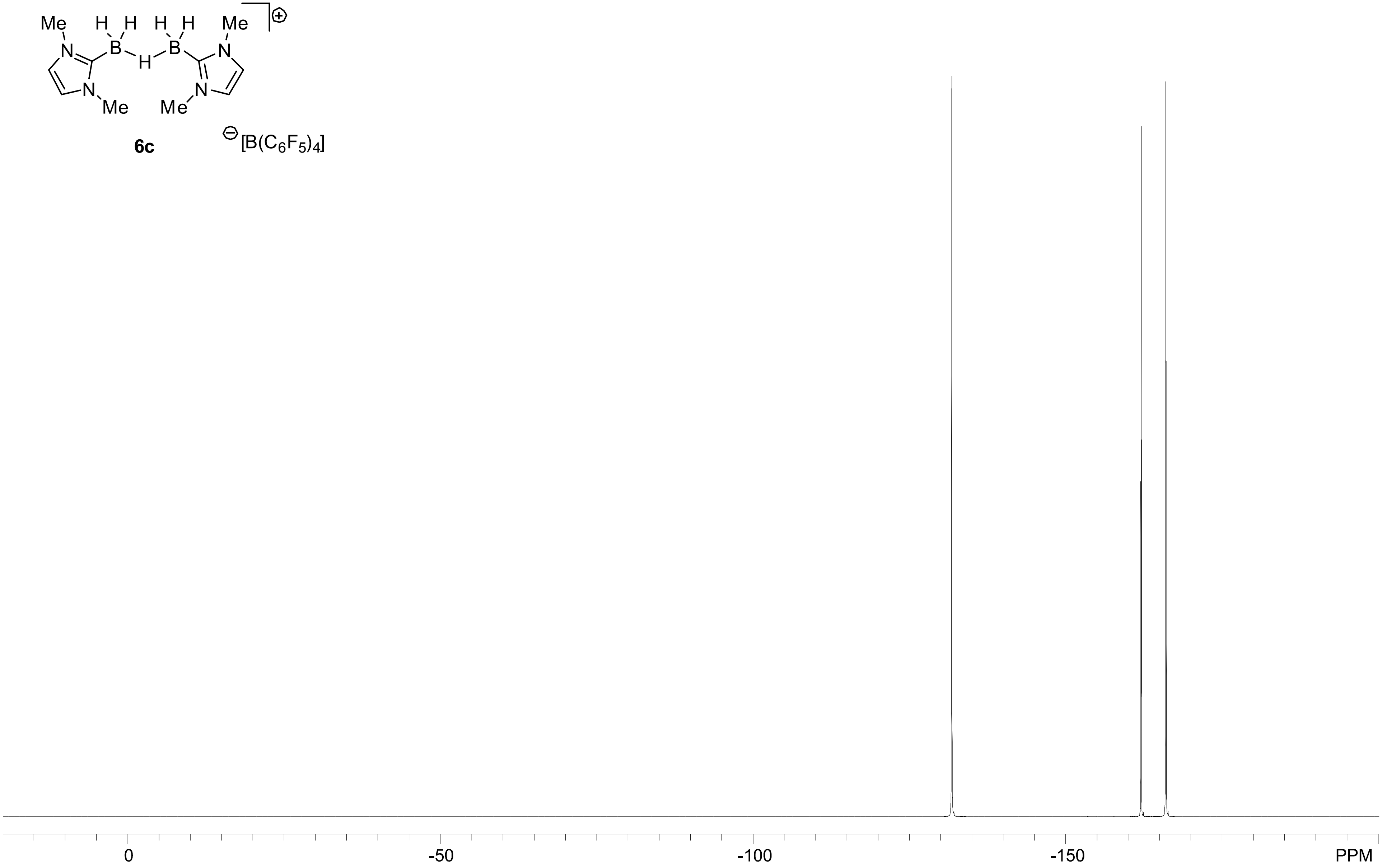
**6c** $^{\ominus}[B(C_6F_5)_4]$

$^{13}C\{^{1}H\}$ NMR (176 MHz),
$d_5$-PhBr

**6c**



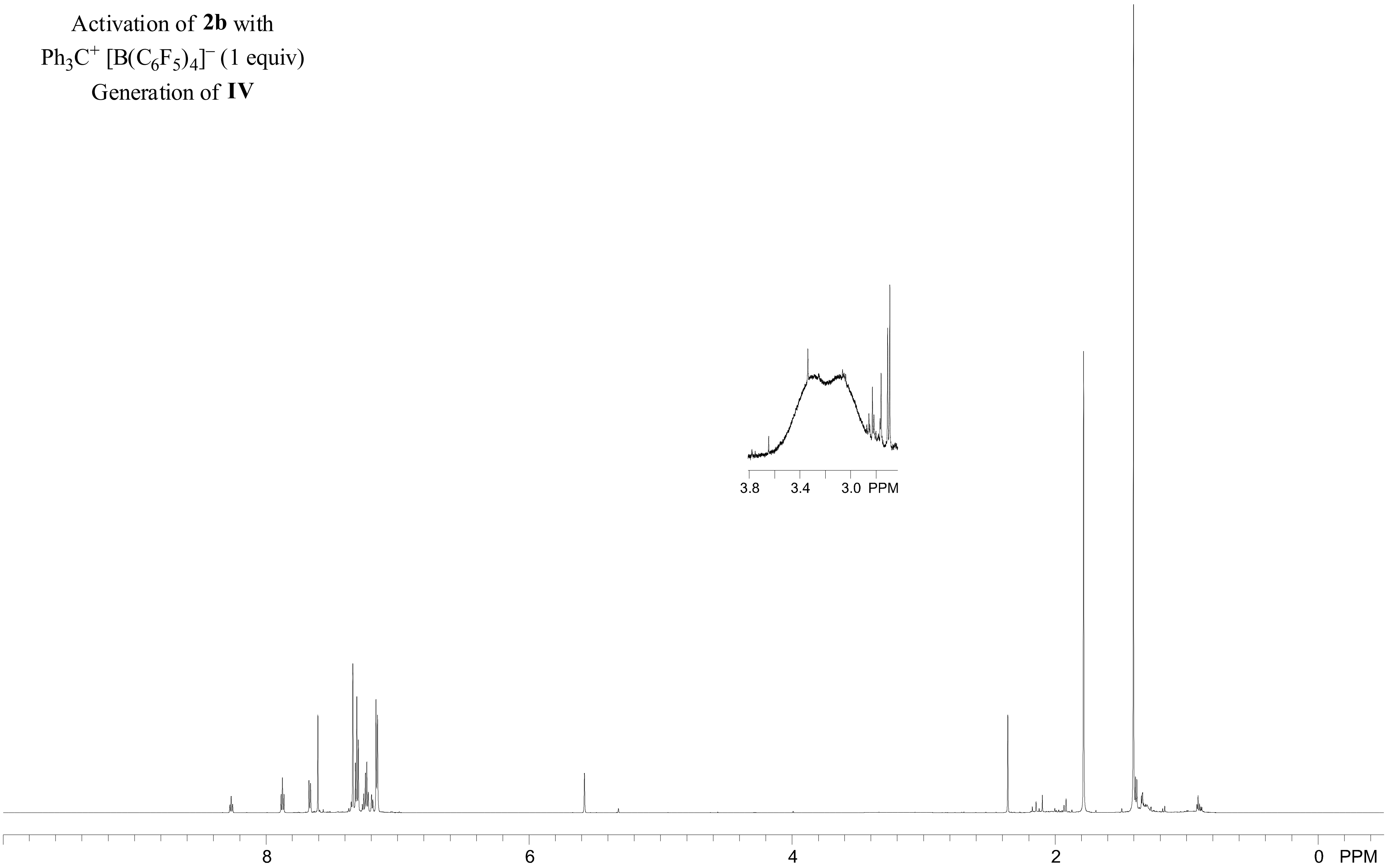
$^{19}$F NMR (471 MHz),
*$d_5$*-PhBr



**6c**

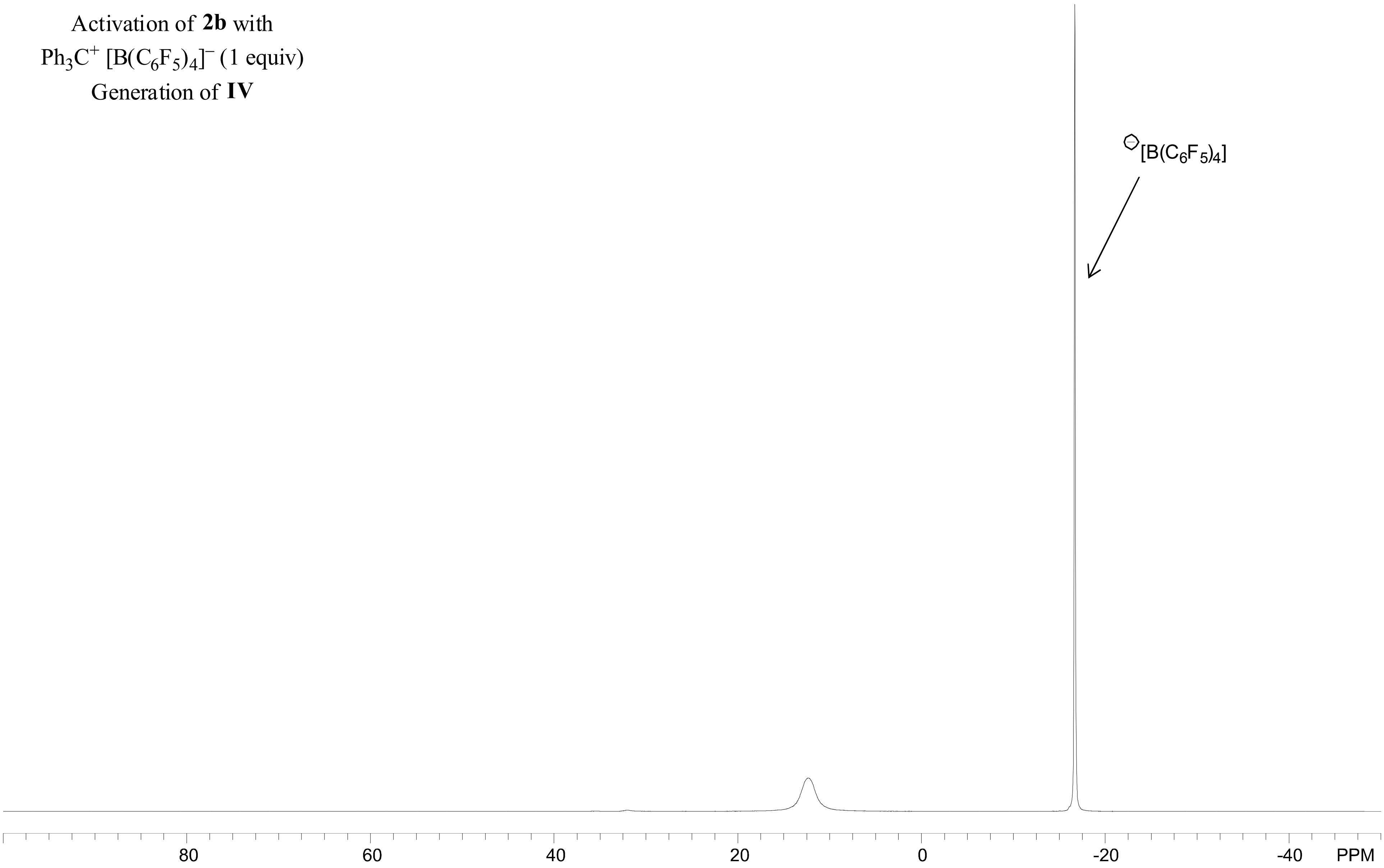
$^1$H NMR (700 MHz),
$CD_2Cl_2$

Activation of **2b** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
Generation of **IV**



$^{11}$B NMR (225 MHz),
$CD_2Cl_2$

Activation of **2b** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
Generation of **IV**

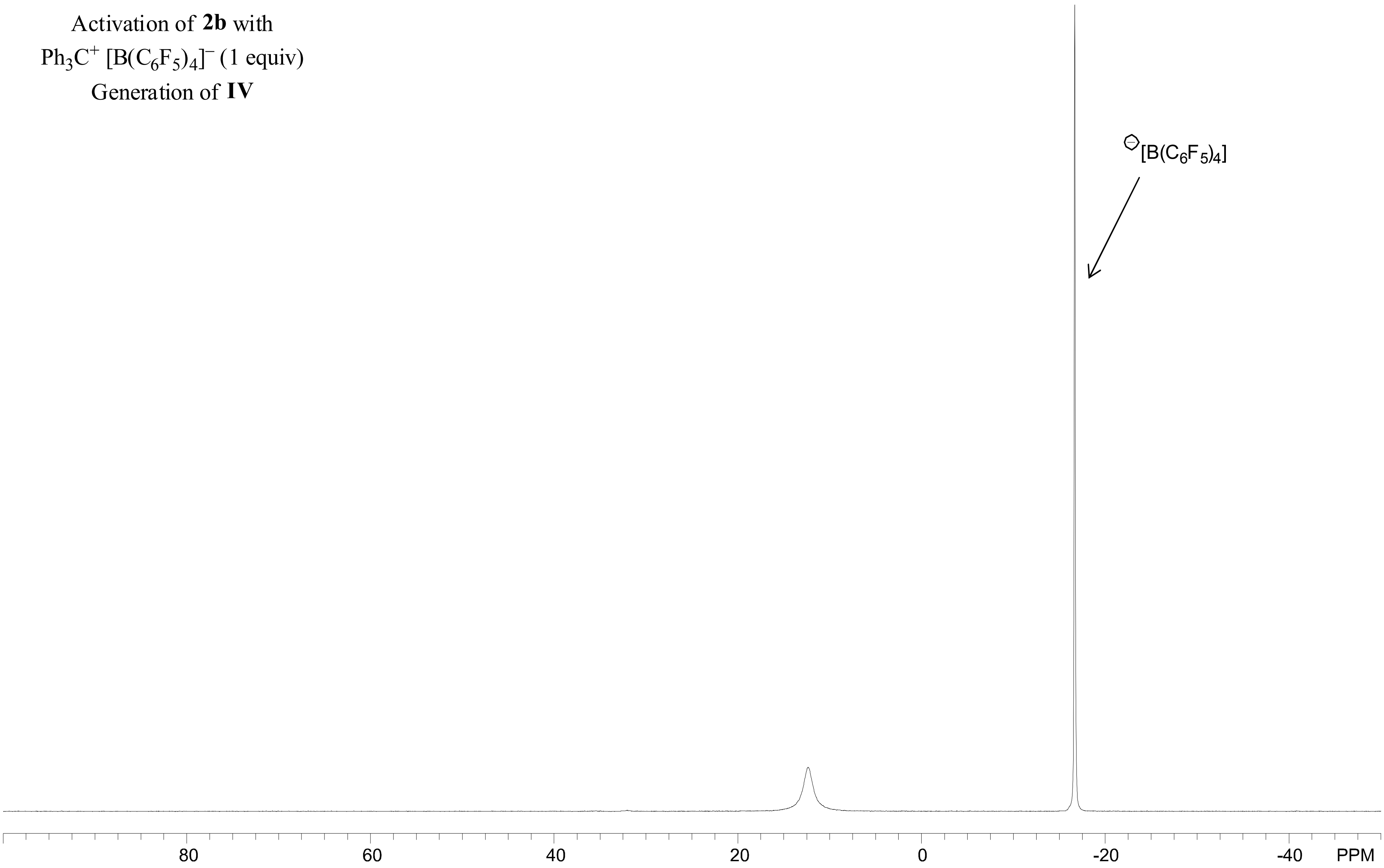


$^{11}B\{^1H\}$ NMR (225 MHz), $CD_2Cl_2$

Activation of **2b** with

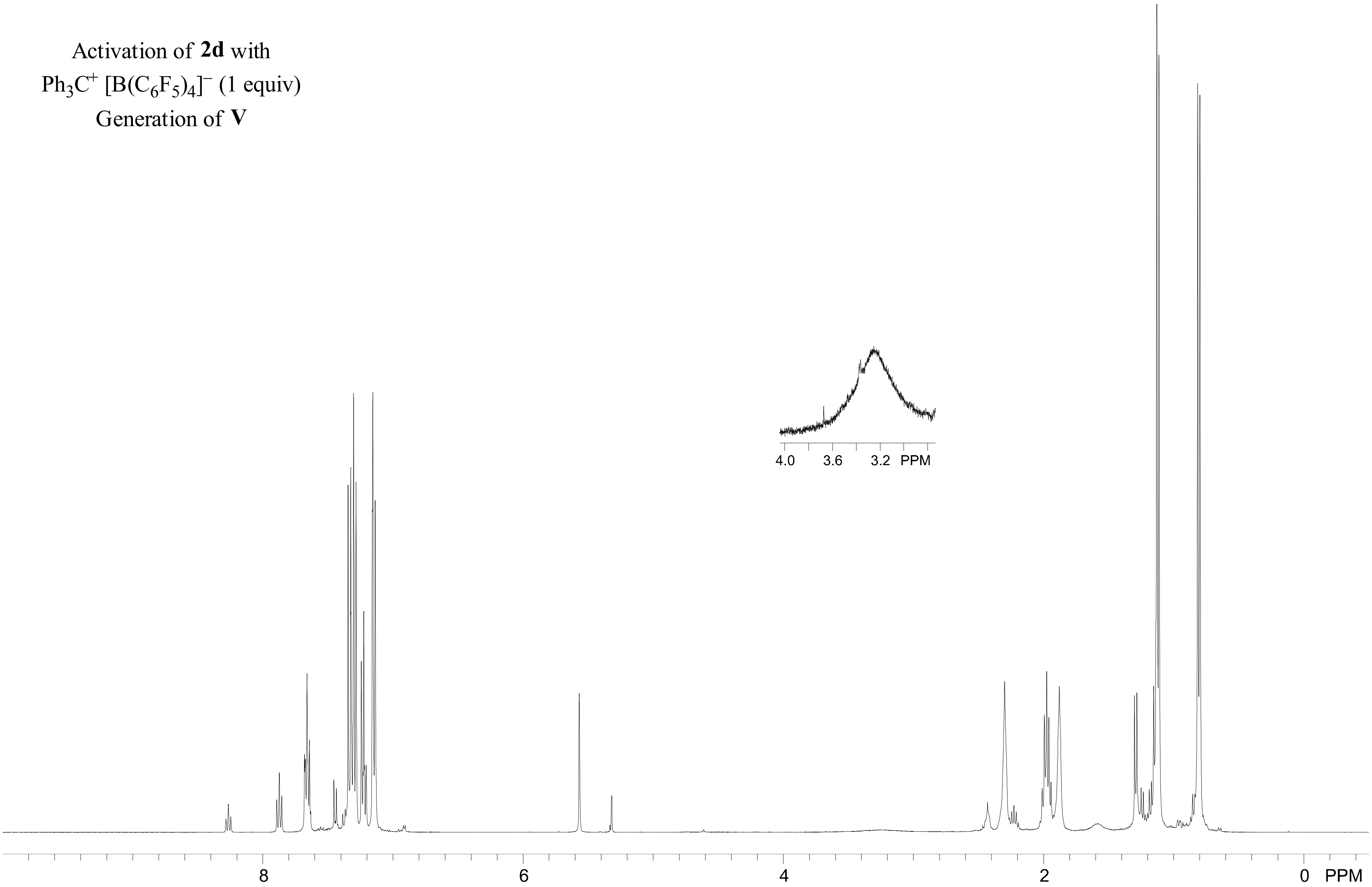
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)

Generation of **IV**



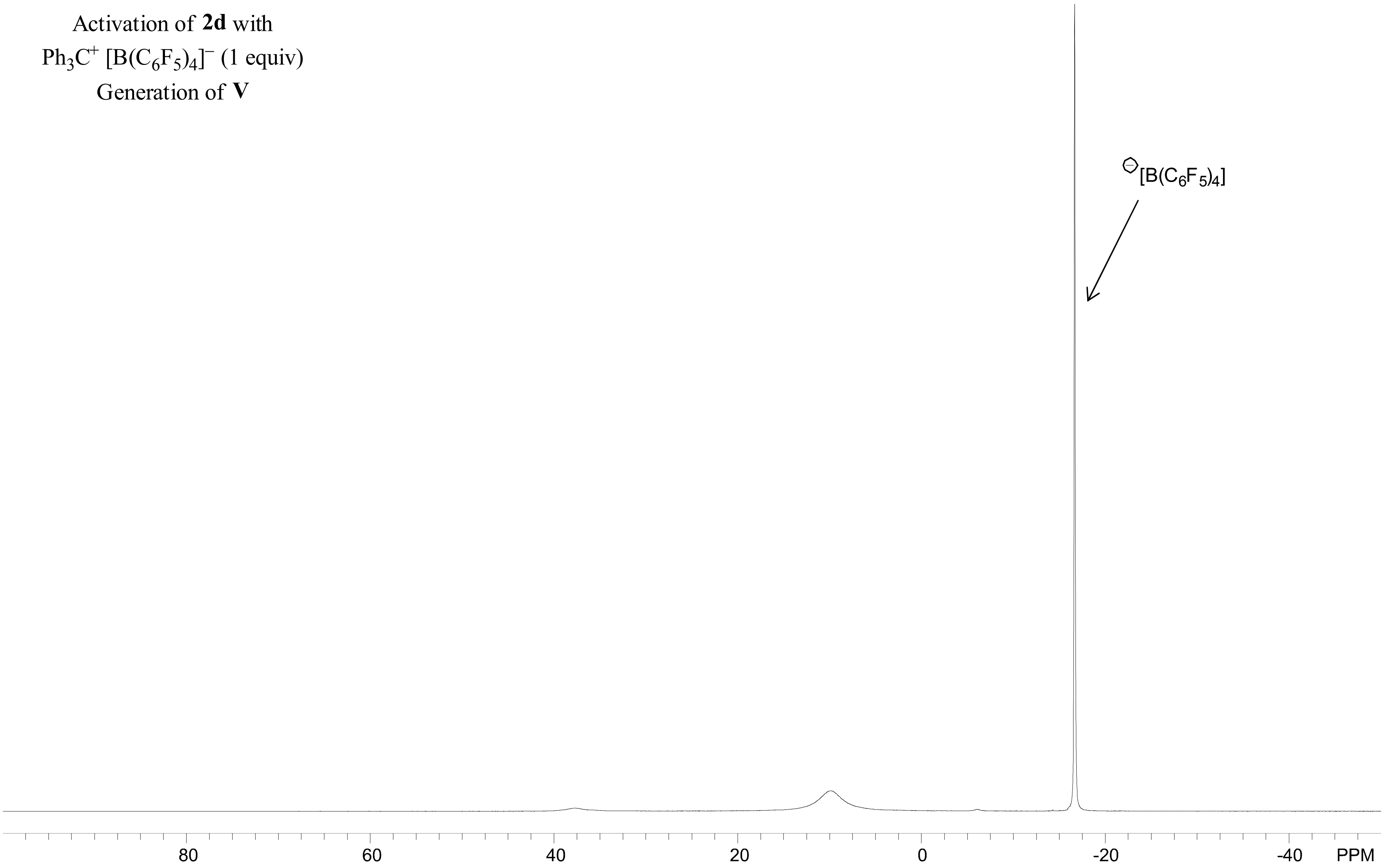
$^{1}H$ NMR (400 MHz),
$CD_2Cl_2$

Activation of **2d** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
Generation of **V**



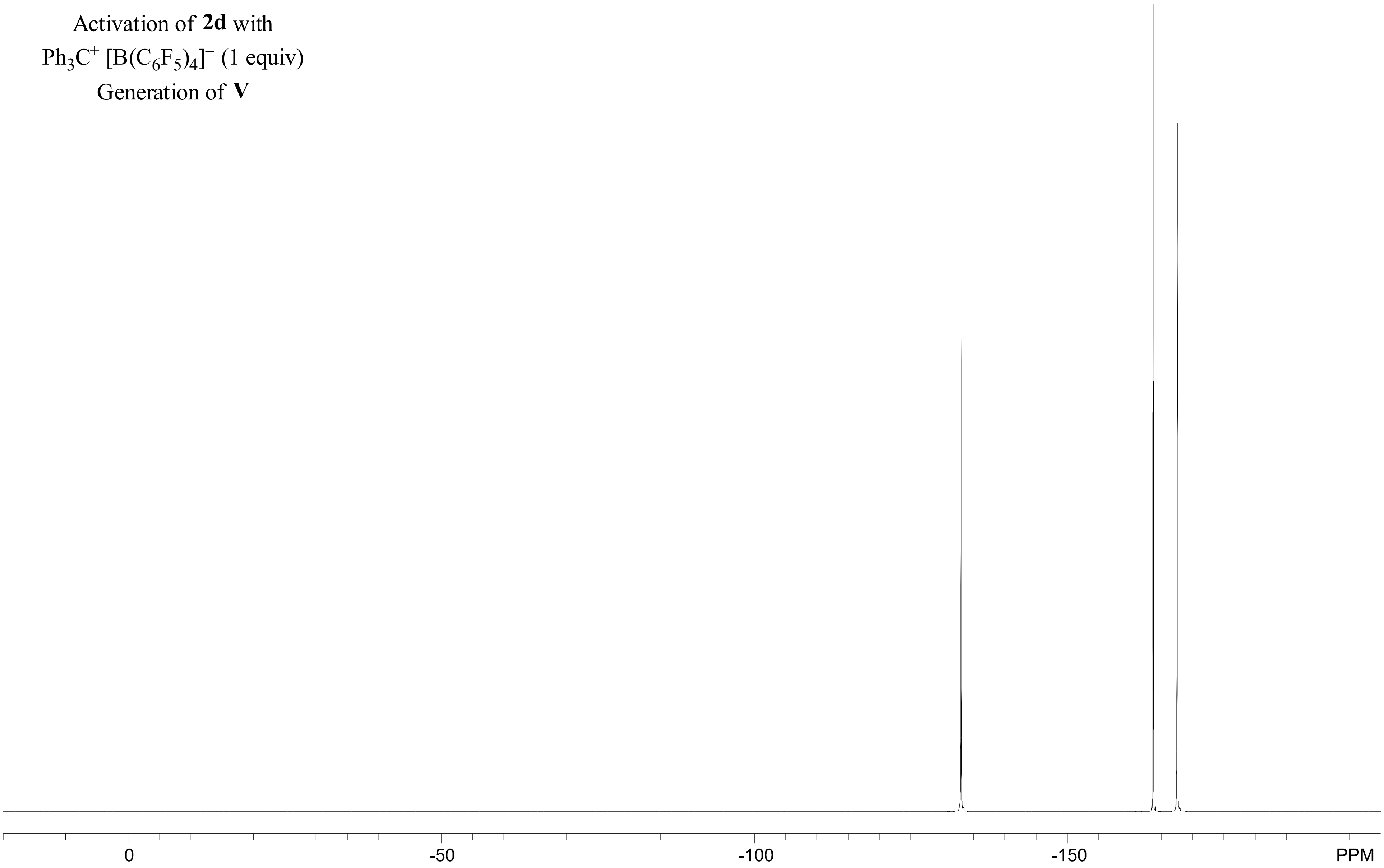
$^{11}B\{^1H\}$ NMR (225 MHz),
$CD_2Cl_2$

Activation of **2d** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
Generation of **V**



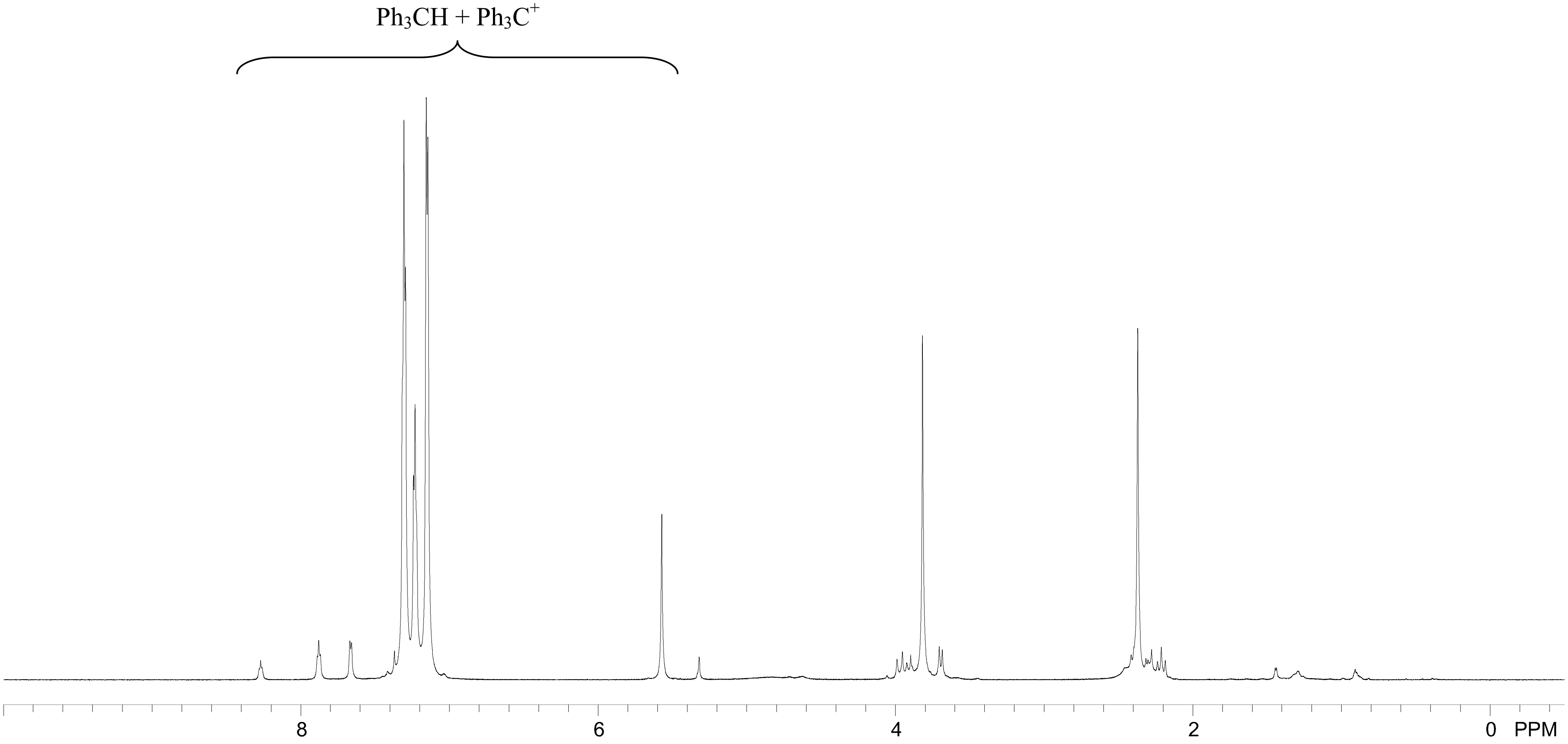
$^{19}$F NMR (376 MHz),
$CD_2Cl_2$

Activation of **2d** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
Generation of **V**



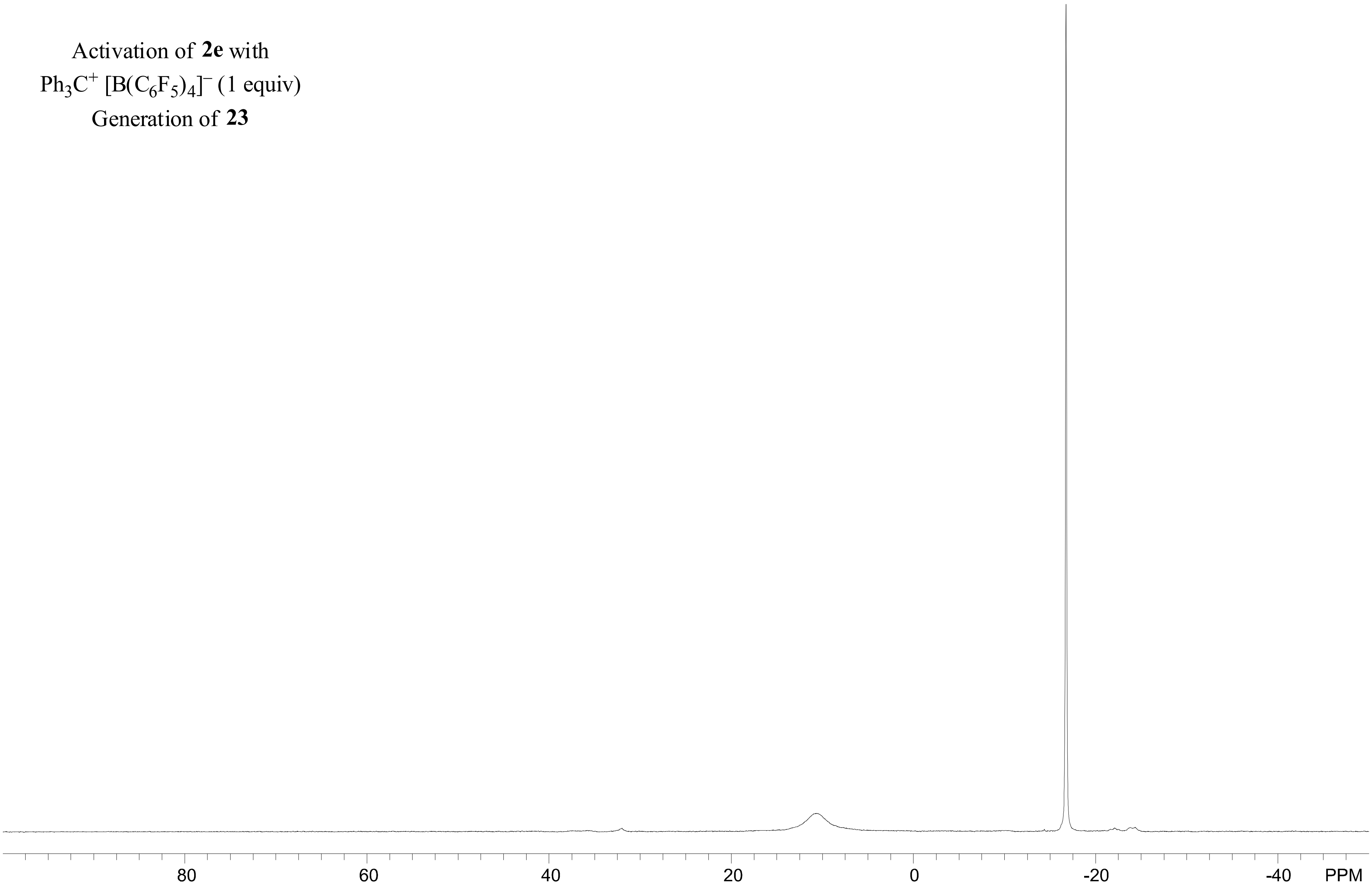
$^1$H NMR (700 MHz),
$CD_2Cl_2$

Activation of **2e** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
Generation of **23**



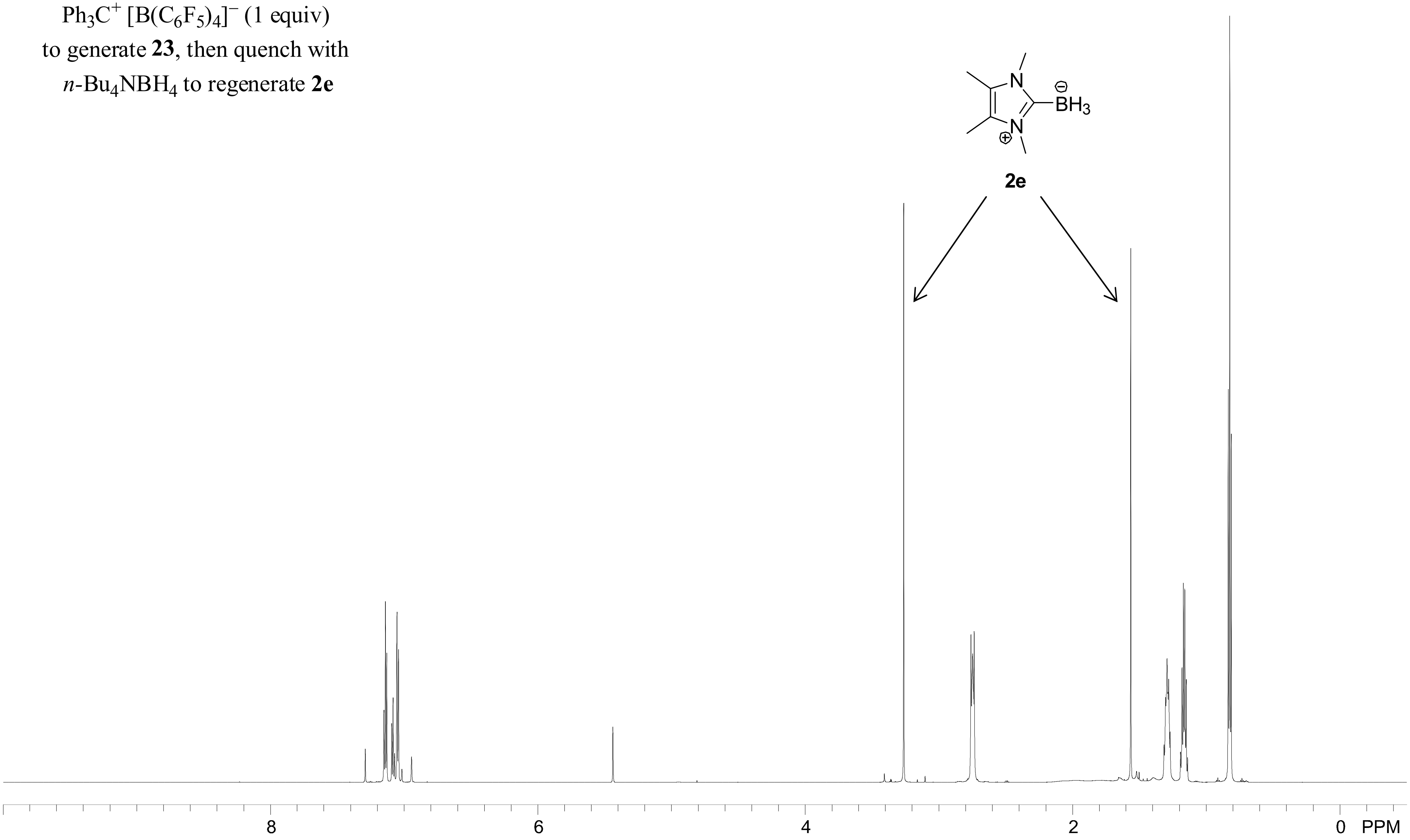
$^{11}$B NMR (225 MHz),
$CD_2Cl_2$

Activation of **2e** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
Generation of **23**



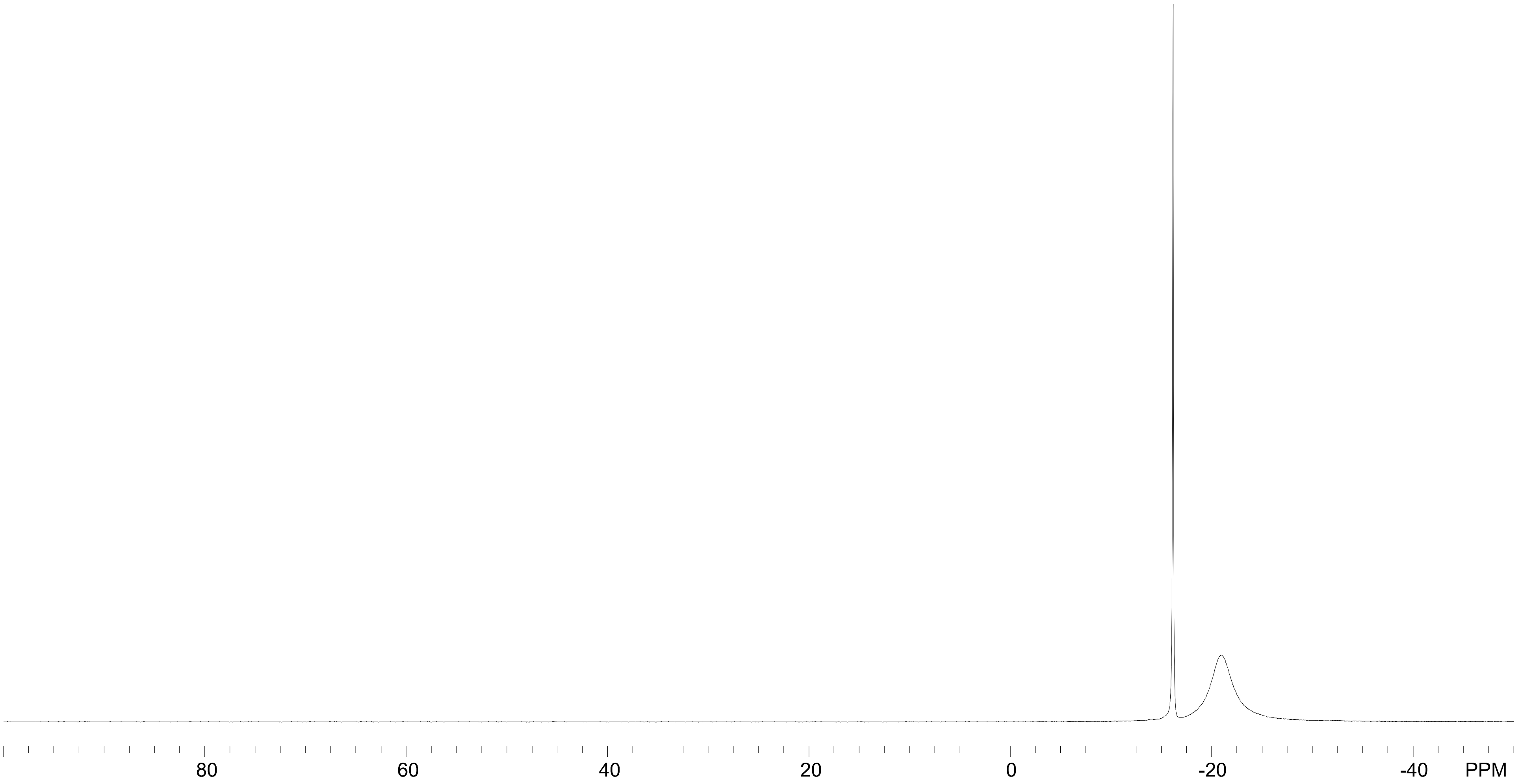
$^{1}$H NMR (700 MHz),
$d_5$-PhBr

Activation of **2e** with
Ph$_3$C$^+$ [B(C$_6$F$_5$)$_4$]$^-$ (1 equiv)
to generate **23**, then quench with
*n*-Bu$_4$NBH$_4$ to regenerate **2e**

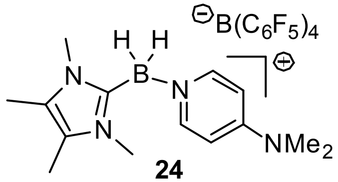


$^{11}$B NMR (225 MHz),
$d_5$-PhBr

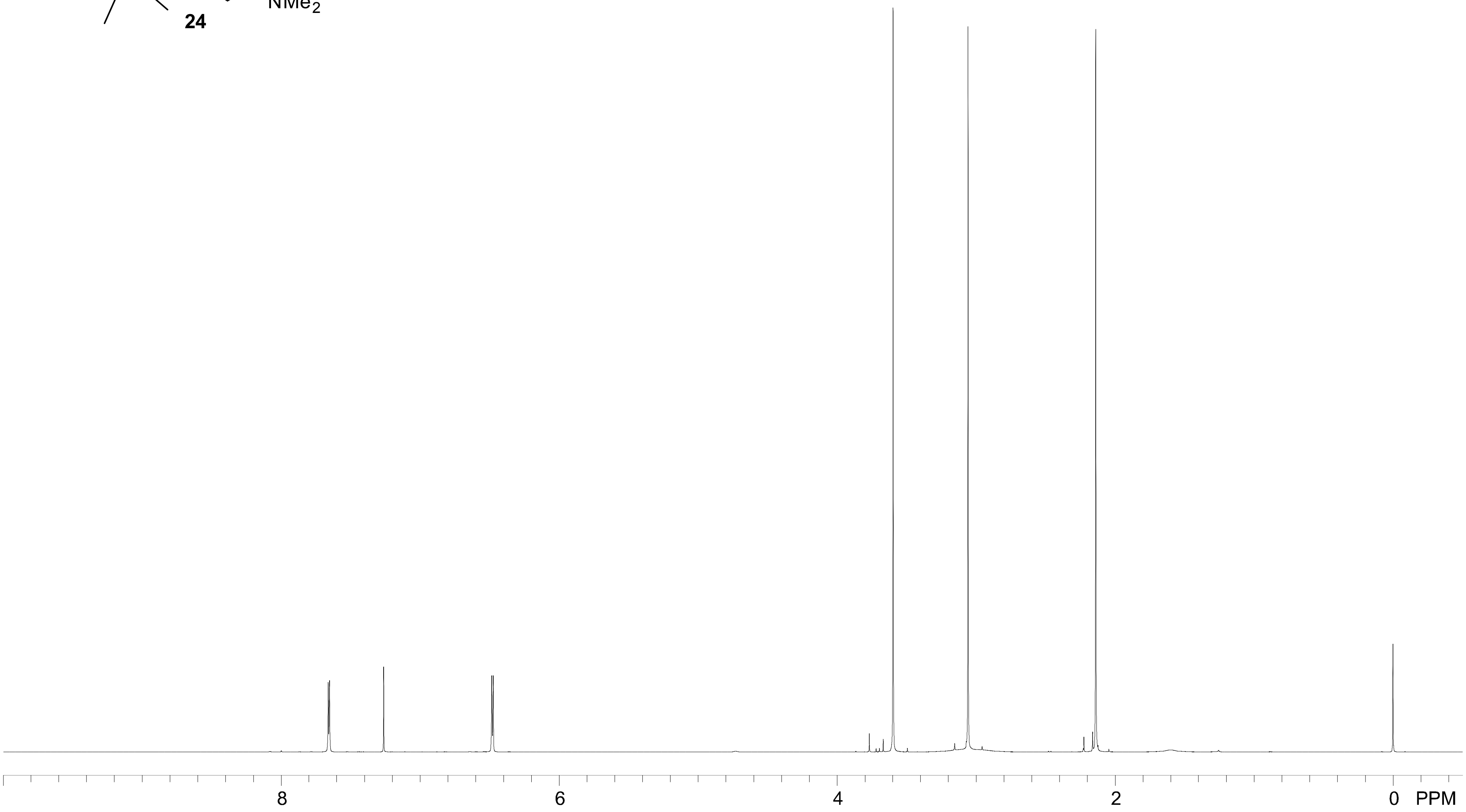
Activation of **2e** with
$Ph_3C^+ [B(C_6F_5)_4]^-$ (1 equiv)
to generate **23**, then quench with
**2e** (1 equiv) to generate **6e**



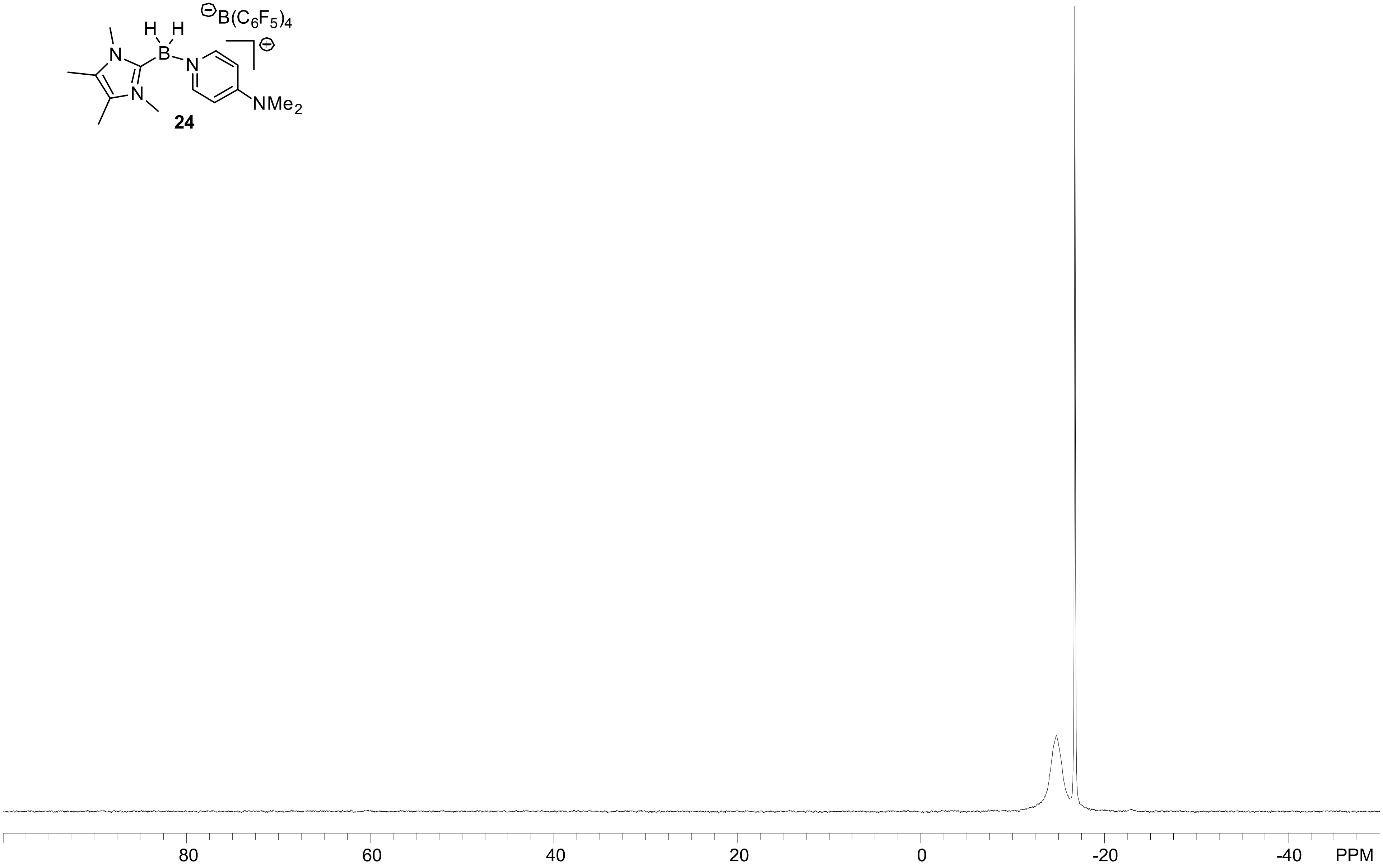
$^1$H NMR (700 MHz),
$CDCl_3$



**24**

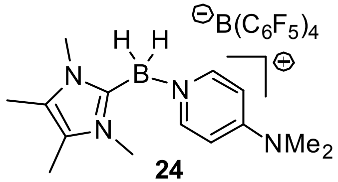


$^{11}$B NMR (225 MHz), CDCl$_3$

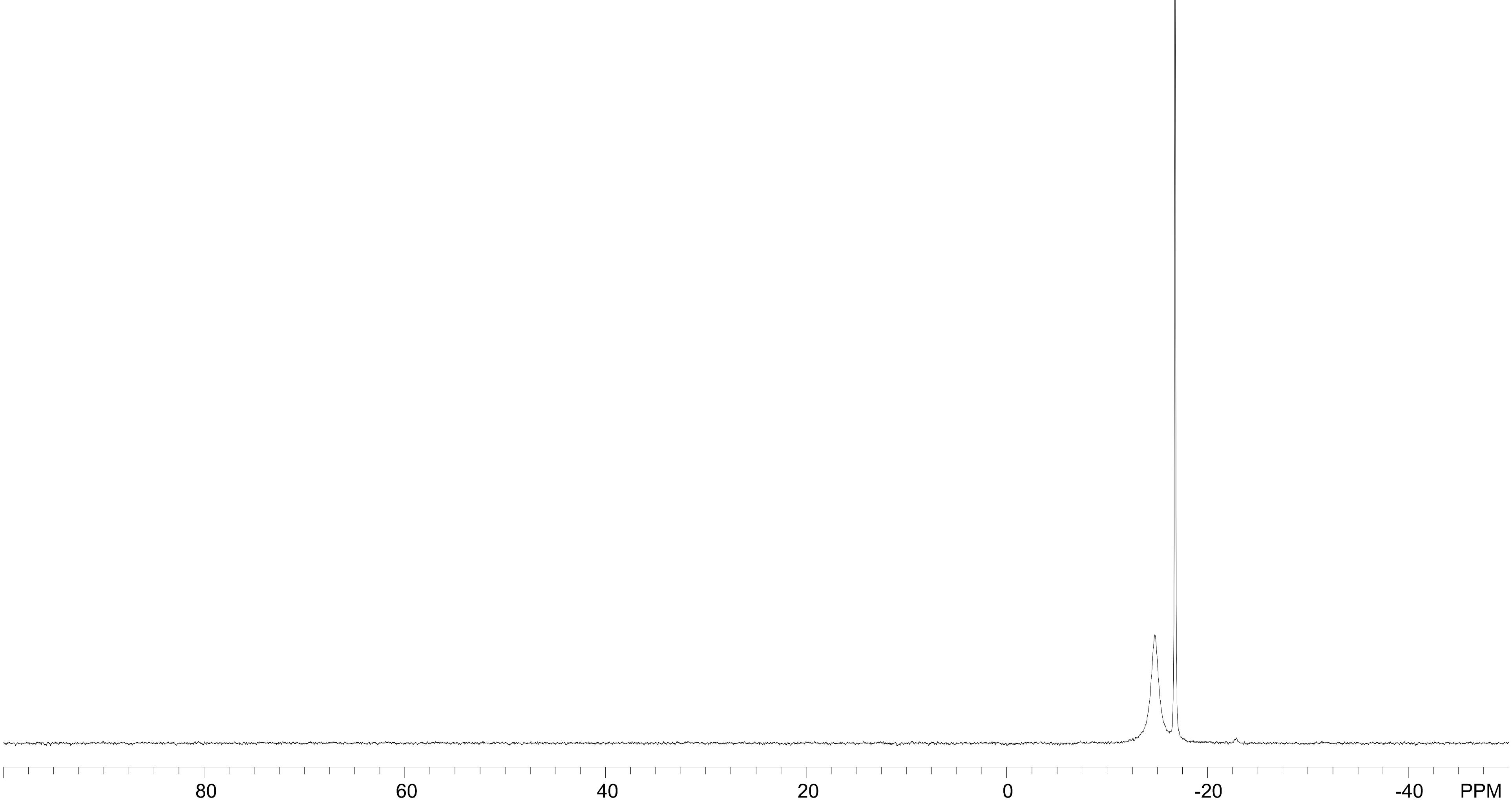


**24**

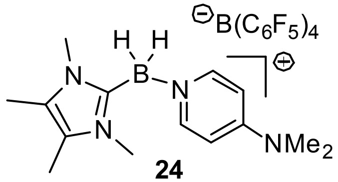
$^{11}B\{^1H\}$ NMR (225 MHz),
$CDCl_3$



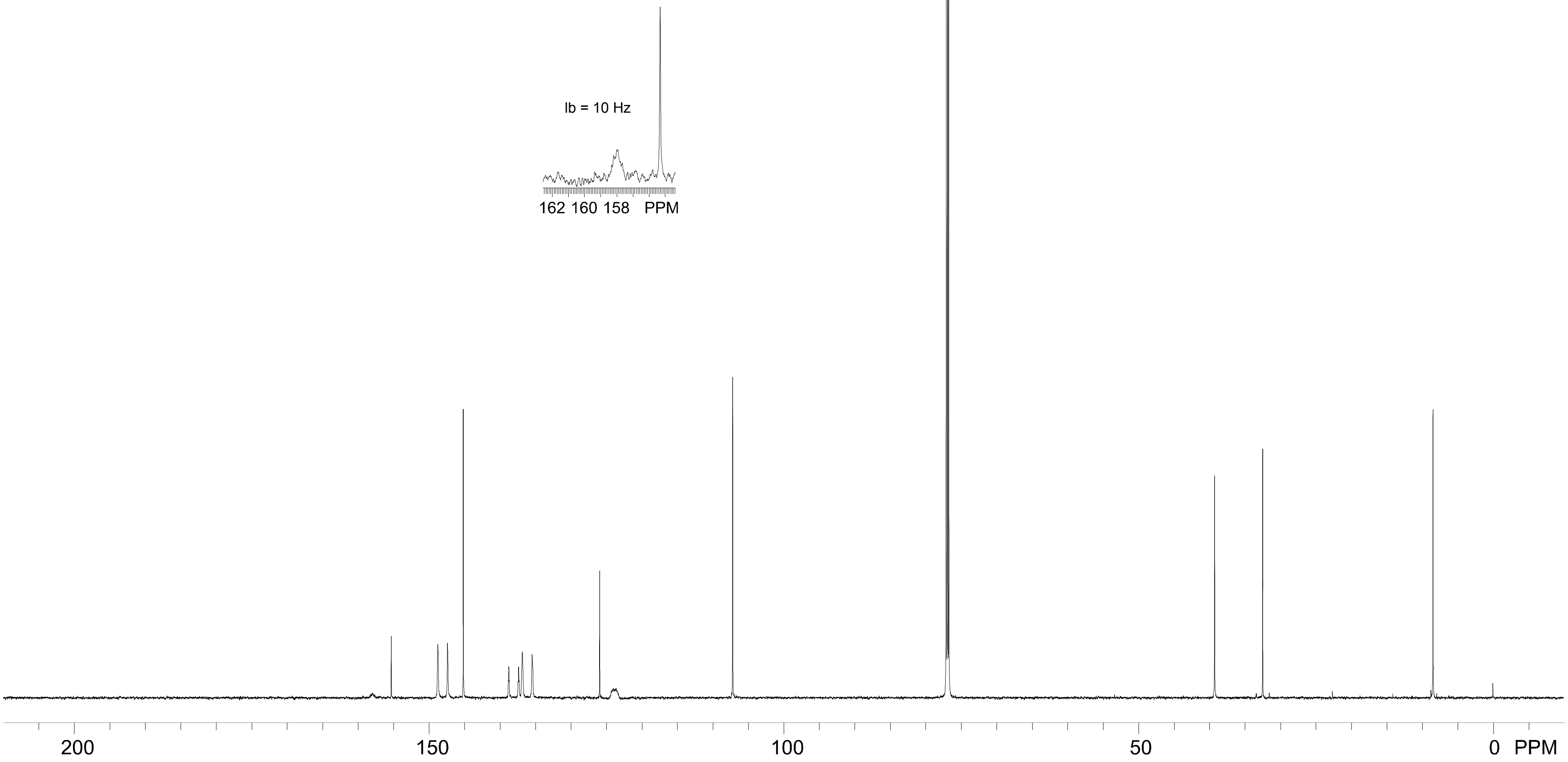
**24**



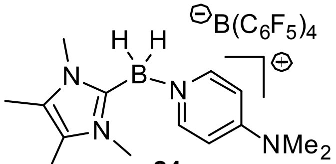
$^{13}C\{^{1}H\}$ NMR (176 MHz), $CDCl_3$



**24**



$^{19}$F NMR (471 MHz),
CDCl$_3$



**24**