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Supporting Information

Using Ylide Functionalization to Stabilize Boron Cations

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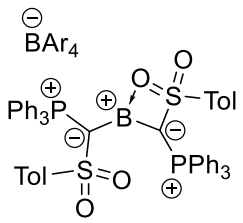
1. Experimental Details

General procedure

All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Solvents were dried over sodium or potassium (or over P_4O_{10}, CH_2Cl_2 and $CHCl_3$) and distilled prior to use. ^{1}H, ^{11}B, $^{11}B\{^{1}H\}$, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR spectra were recorded on Avance-500, Avance-400 or Avance-250 spectrometers at 22 °C if not stated otherwise. All values of the chemical shift are in ppm regarding the δ-scale. All spin-spin coupling constants (J) are printed in Hertz (Hz). To display multiplicities and signal forms correctly the following abbreviations were used: s = singlet, d = doublet, t = triplet, q= quartet, sep= septet, m = multiplet, br = broad signal. Signal assignment was supported by DEPT, HSQC and HMBC experiments. Elemental analyses were performed on an Elementarvario MICRO-cube elemental analyzer. All reagents were purchased from Sigma-Aldrich, ABCR, Rockwood Lithium or Acros Organics and used without further purification, unless otherwise noted. Phenylamine, diethylamine and pyrrole were distilled prior to use. YNa, Y_2BH **1**,[1] trityl salts[2] and NaBArCl[3] were prepared according to literature procedures.

Preparation of 2a-c



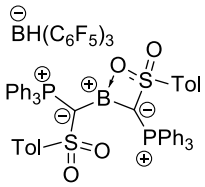
2a-c

Borane **1** (30 mg, 0.034 mmol) and a trityl salt (**2a**: $[Ph_3C]BAr^{Cl}$: 32 mg, 0.038; **2b**: $[Ph_3C]BAr^{F}$: 42mg, 0.038 mmol; mmol; **2c**: $[Ph_3C][B(C_6F_5)_4]$: 35 mg, 0.038 mmol) were dissolved in $CDCl_3$ (BAr^{F} and BAr^{Cl}) or C_6D_6 ($B(C_6F_5)_4$) and heated for 3 days at 60 °C. Thereby, conversion to the borenium cation was observed as indicated by the disappearance of the sharp signal for borane **1** at 23.8 ppm in the ^{31}P NMR spectrumg and the appearance of a broad singlet at 12.5 ppm. In the ^{1}H NMR spectrum the broad signal at ~5 ppm for the BH moiety disappeared, while a sharp singlet at 5.47 ppm for triphenylmethane appeared (see NMR-Spectra in Figure 1-3). Conversion to **2** was found to be greater than ~80% in case of all three trityl salts.

Purification of the resulting borenium salts proved to be difficult. Due to the large, non-interacting anions necessary for successful synthesis of the borenium cation (smaller, less unreactive anions like BF_4^-, PF_6^- or triflate produced no borenium cations) all salts formed highly viscous oils and showed no tendency to solidify or crystallize from any common organic solvent. Purification was possibly by anion exchange to PF_6^- and subsequent crystallization (see below). Pure **2a** could then be obtained by a second anion exchange from the PF_6 salt. To this end, a pure sample of **2d** (50 mg, 0.049 mmol) was suspended in 0.7 ml of CD_2Cl_2 and $NaBAr^{Cl}$ (30 mg 0.049 mmol) was added and stirred for 20 min. The precipitate of $NaPF_6$ was subsequently filtered off and NMR spectra were recorded of the resulting solution.

^{1}H NMR: (500.1 MHz, CD_2Cl_2): δ = 2.34 (s, 6H, CH_3), 6.91-6.97 (m, 4H, C$H_{STol,\ ortho}$), 6.98-6.99 (m, 4H, C$H_{BAr,\ para}$), 7.00-7.04 (m, 4H, C$H_{STol,\ meta}$), 7.05-7.07 (m, 8H, C$H_{BAr,\ ortho}$)7.46-7.52 (m, 12H, C$H_{PPh,\ meta}$), 7.59-7.66 (m, 18H, C$H_{PPh,\ ortho}$ and C$H_{PPh,\ para}$) ^{13}C{^{1}H} NMR: (125.8 MHz, CD_2Cl_2): δ = 21.7, (s, CH$_3$), 57.9 (br d, $^{1}J_{CP}$ = 106.7 Hz, PCS) 123.0 (d, $^{1}J_{CP}$ = 94.0 Hz, $C_{PPh,\ ipso}$), 123.4 (s, CH$_{BAr,\ para}$), 126.9 (s, CH$_{STol,\ ortho}$), 129.5 (d, $^{3}J_{CP}$ = 13.0 Hz, CH$_{PPh,\ meta}$) 129.9 (s, CH$_{STol,\ meta}$), 133.3 (q, $^{2}J_{CB}$ = 4.3 Hz, $C_{BAr,\ meta}$) , 133.5 (q, $^{4}J_{CB}$ = 1.5 Hz, CH$_{BAr,\ ortho}$); 134.0 (d, $^{4}J_{CP}$ = 3.0 Hz, CH$_{PPh,\ para}$), 134.4 (d, $^{2}J_{CP}$ = 10.5 Hz, CH$_{PPh,\ ortho}$), 138.6 (v.br $C_{STol,\ para}$), 144.8 (br, $C_{STol,\ ipso}$), 165.1 (q, ^{1}J$_{CB}$ = 49.3 Hz, CH$_{BAr,\ ipso}$) ^{31}P{^{1}H} NMR: (202.5 MHz, , CD_2Cl_2): δ = 12.5 (br) ^{11}B{^{1}H} NMR: (160.5 MHz, CD_2Cl_2): –6.9 (s, BAr^{Cl}), 40.5 (br, CBC).

Preparation of 2d

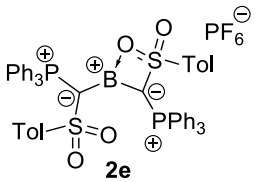


2d

Borane **1** (50 mg, 0.057 mmol) and $B(C_6F_5)_3$ (30 mg, 0.059 mmol) were dissolved in 0.6 ml of dry $CDCl_3$. The solution was heated to 50 °C for 16 h and NMR spectra were recorded (see NMR spectra in Figure 4-6). The conversion accoring to the ^{31}P{^{1}H} and ^{1}H NMR spectra was found to be greater than 80 %. Purification of this compound failed due to the same problems described for **2a-c**.

^{1}H NMR: (500.1 MHz, $CDCl_3$): δ = 2.30 (s, 6H, CH_3), 3.78 (q, $^{1}J_{HB}$ = 87.0 Hz, HB), 6.86-6.93 (m, 4H, C$H_{STol,\ ortho}$) 6.93-7.00 (m, 4H, C$H_{STol,\ meta}$), 7.45-7.52 (m, 12H, C$H_{PPh,\ meta}$), 7.59-7.69 (m, 18H, C$H_{PPh,\ ortho}$ and C$H_{PPh,\ para}$) ^{13}C{^{1}H}-NMR: (125.8 MHz, $CDCl_3$): δ = 21.4, (s, CH$_3$), 57.9 (br d, $^{1}J_{CP}$ = 106.7 Hz, PCS), 122.7 (d, $^{1}J_{CP}$ = 94.0 Hz, $C_{PPh,\ ipso}$), 126.6 (s, CH$_{STol,\ ortho}$), 129.2 (d, $^{3}J_{CP}$ = 13.0 Hz, CH$_{PPh,\ meta}$) 129.4 (s, CH$_{STol,\ meta}$), 133.7 (d, $^{4}J_{CP}$ = 2.9 Hz, CH$_{PPh,\ para}$), 134.1 (d, $^{2}J_{CP}$ = 10.5 Hz, CH$_{PPh,\ ortho}$) ^{19}F{^{1}H} NMR (470.6 MHz, $CDCl_3$): -167.1-166.9 (m, 3F, BPh$F_{5,meta}$), –164.3 (t, $^{3}J_{FF}$ = 20.4 Hz, 3F, BPh$F_{5,para}$), –133.2 (d, $^{3}J_{FF}$ = 21.7 Hz, 6F, BPh$F_{5,ortho}$) ^{31}P{^{1}H} NMR: (202.5 MHz, , $CDCl_3$): δ = 12.5 (br) ^{11}B{^{1}H} NMR (160.5 MHz, $CDCl_3$): –25.5 (s, B_{Ar}), 39.8 (br, CBC).

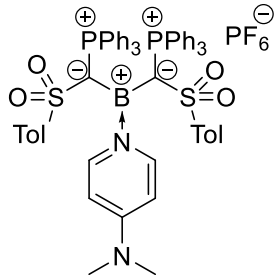
Preparation of 2e



Borane **1** (210 mg, 0.24 mmol) and $[Ph_3C]BAr^F$ (252 mg, 0.23 mmol) were dissolved in 6 ml dry $CHCl_3$. The solution was heated to 50 °C for 16 h and the cooled to RT. Subsequently, tetrabutylammonium hexafluorophosphate (103 mg, 0.27 mmol) was added to the deep blue solution. The solution was stirred for 5 min. Then, 2 ml hexane were added, the mixture stirred for further 5 min and then filtered to remove the precipitate formed. The solution was storred at –30 °C for 5 days, upon which small colourless crystals of borenium salt **2e** formed. The supernant solution was removed via syringe and the crystals were washed 3 times with 0.5 ml of a 3:1 $CHCl_3$:hexane mixture. After drying *in vacuo* **2e** was obtained as colorless solid (150 mg, 0.15 mmol, 61%). Crystals suitable for X-ray diffraction analysis were obtained by very slow evaporation of a saturated DCM solution of **2e.**

^{1}H NMR: (400.1 MHz, CD_2Cl_2): δ = 2.36 (s, 6H, CH_3), 6.99-7.05 (m, 4H, C$H_{STol,\ ortho}$), 7.05-7.11 (m, 4H, C$H_{STol,\ meta}$), 7.47-7.55 (m, 12H, C$H_{PPh,\ meta}$), 7.60-7.69 (m, 18H, C$H_{PPh,\ ortho}$ and C$H_{PPh,\ para}$) ^{13}C{^{1}H} NMR: (125.8 MHz, CD_2Cl_2): δ = 21.7, (s, CH$_3$), 123.0 (d, $^1J_{CP}$ = 94.0 Hz, $C_{PPh,\ ipso}$), 127.0 (s, CH$_{STol,\ ortho}$), 129.5 (d, $^3J_{CP}$ = 13.0 Hz, CH$_{PPh,\ meta}$) 130.0 (s, CH$_{STol,\ meta}$), 133.9 (d, $^4J_{CP}$ = 3.0 Hz, CH$_{PPh,\ para}$), 134.5 (d, $^2J_{CP}$ = 10.5 Hz, CH$_{PPh,\ ortho}$) ^{31}P{^{1}H} NMR: (162.0 MHz, , CD_2Cl_2): δ = 12.5 (br), –144.3 (sep, $^1J_{PF}$ = 710.6 Hz, PF_6^-). Due to the low solubility of **2e** in CD_2Cl_2 (<5 mg/ml) and the fluxional behavior in solution no ^{11}B NMR signal as well as some of the ^{13}C NMR signals of the quaternary carbon atoms could not be detected. Anal. Calcd. for $C_{52}H_{44}O_4BF_6P_3S_2$: C, 61.55; H, 4.37; S 6.32. Found: C, 61.46; H, 4.35; S, 6.17.

Preparation of 3a

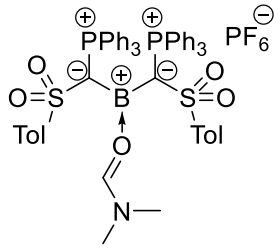


Borenium cation **2e** (20.0 mg, 0.02 mmol) and 4-dimethylaminopyridine (3.00 mg , 0.025 mmol) were suspended in 2 ml of DCM and stirred for 10 min, upon which all solids dissolved. The solution was layered with 4 ml of benzene and stored at RT for 2 days, resulting in the formation of a colorless precipitate. The supernatant solution was removed and the solid was washed twice with 0.5 ml of benzene. Drying *in vacuo* gave **3b** as a colorless solid (20 mg, 0.017 mmol, 90%). Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a solution of **3a** in DCM at –30 °C.

^{1}H NMR: (500.1 MHz, CD_2Cl_2): δ = 2.29 (s, 6H, ArCH_3), 2.98 (s, 6H, NCH_3), 5.75-5.80 (m, 2H, C$H_{DMAP,\ meta}$), 6.84-6.88 (m, 4H, C$H_{STol,\ meta}$), 7.01-7.06 (m, 4H, C$H_{STol,\ ortho}$), 7.33-7.38 (m, 12H, C$H_{PPh,\ meta}$), 7.38-7.41 (m, 2H, C$H_{DMAP,\ ortho}$), 7.48-7.56 (m, 18H, C$H_{PPh,\ ortho}$ and C$H_{PPh,\ para}$) ^{13}C{^{1}H} NMR: (125.8 MHz, CD_2Cl_2): δ = 21.3, (s, ArCH$_3$), 40.0, (s, NCH$_3$), 69.1 (br d, $^1J_{CP}$ = 82.2 Hz, PCS), 106.1 (s, CH$_{DMAP,\ meta}$), 125.9 (s, CH$_{STol,\ ortho}$), 126.8 (d, $^1J_{CP}$ = 92.4 Hz, $C_{PPh,\ ipso}$), 128.7 (d, $^3J_{CP}$ = 12.4 Hz, CH$_{PPh,\ meta}$) 129.0 (s, CH$_{STol,\ meta}$), 132.5 (d, $^4J_{CP}$ = 2.8 Hz,

*C*H$_{PPh,\ para}$), 135.4 (d, $^2J_{CP}$ = 9.7 Hz, *C*H$_{PPh,\ ortho}$), 141.4 (s, *C*$_{STol,\ para}$), 143.6 (s, *C*H$_{DMAP,\ ortho}$), 145.7 (s, *C*$_{STol,\ ipso}$), 156.3 (s, *C*$_{DMAP,\ para}$). ^{31}P{^{1}H} NMR: (202.5 MHz, CD_2Cl_2): δ = 21.0 (s), –144.3 (sep, $^1J_{PF}$ = 710.6 Hz, PF_6^-). ^{11}B{^{1}H} NMR: (160.5 MHz, CD_2Cl_2): 46.3 (br).

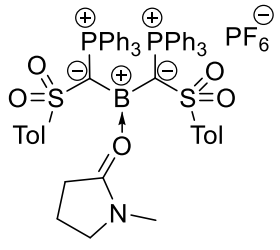
Preparation of 3b



Borenium cation **2e** (10 mg, 0.019 mmol) and DMF (30 mg, 0.4 mmol) were dissolved in 0.7 ml of CD_2Cl_2. NMR spectra of the resulting solution were recorded, showing clean formation of the Lewis base adduct. At RT the DMF adduct of the boron cation is in equilibrium with **2e**. However, due to the large excess of DMF used, only the adduct can be observed under these conditions. Any attempts to purify or recrystallize the product or evaporation of the solvent led to the re-liberation of the coordinated DMF and reformation of borenium salt **2e**. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of **2e** in DCM with a 20-fold excess of DMF at –30 °C.

^{1}H NMR: (250.1 MHz, CD_2Cl_2): δ = 2.31 (s, 6H, C*H*$_3$), 6.90-6.98 (m, 4H, C*H*$_{STol,\ meta}$), 7.04-7.12 (m, 4H, C*H*$_{STol,\ ortho}$), 7.41-7.53 (m, 12H, C*H*$_{PPh,\ meta}$), 7.54-7.68 (m, 18H, C*H*$_{PPh,\ ortho}$ and C*H*$_{PPh,\ para}$) ^{31}P{^{1}H} NMR: (101.2 MHz, CD_2Cl_2): δ = 19.5 (s), –144.4 (sep, $^1J_{PF}$ = 710.6 Hz, PF_6^-). Due to presumably rapid exchange on the NMR timescale, the signals for bound DMF could not be observed. The DMF-adduct could also be produced by dissolving borenium **2e** in d$_7$-DMF: ^{1}H NMR: (400.1 MHz, d$_7$-DMF): δ = 2.37 (s, 6H, C*H*$_3$), 7.07-7.11 (m, 4H, C*H*$_{STol,\ meta}$), 7.13-7.17 (m, 4H, C*H*$_{STol,\ ortho}$), 7.55-7.63 (m, 12H, C*H*$_{PPh,\ meta}$), 7.69-7.78 (m, 18H, C*H*$_{PPh,\ ortho}$ and C*H*$_{PPh,\ para}$) ^{31}P{^{1}H} NMR: (162.0 MHz, d$_7$-DMF): δ = 20.3 (s), –144.1 (sep, $^1J_{PF}$ = 708.8 Hz, PF_6^-).

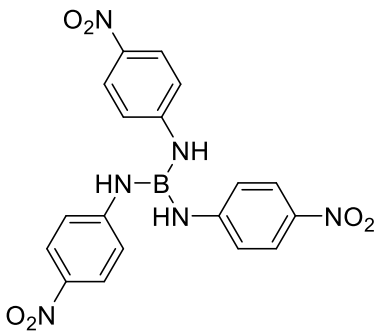
Preparation of 3c



Borenium cation **2e** (10 mg, 0.019 mmol) and 1-methyl-2-pyrrolidinone (10 mg, 0.1 mmol) were dissolved in 0.7 ml of CD_2Cl_2. NMR spectra of the resulting solution were recorded. At RT the NMP adduct of the boron cation is in equilibrium with **2e** forming an approx. 1:1 ratio of **2e** and **3c**. Any attempts to purify or recrystallize the product or evaporation of the solvent led to the re-liberation of the coordinated NMP and reformation of the borenium salt **2e**. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a solution of **2e** in DCM using a 10-fold excess of NMP at –30 °C.

$^{31}P\{^{1}H\}$ NMR: (101.2 MHz, , CD_2Cl_2): δ = 20.7 (br), 12.6 (br), –144.4 (sep, $^{1}J_{PF}$ = 710.6 Hz, PF_6^-). In the ^{1}H NMR spectrum the signals for **2e** and **3c** overlap and are somewhat broadened. Thus, the signals could not be assigned to either species.

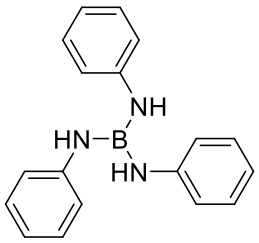
Preparation of 4a



Borenium **2e** (30 mg, 0.030 mmol) and $NaBAr^F$ (28 mg, 0.030 mmol) were added to 0.7 ml of CD_2Cl_2 and stirred for 30 min. The formed suspension was filtered directly into a Y-Joung-NMR-tube to remove $NaPF_6$. Subsequently, 4-nitroaniline (12 mg, 0.06 mmol) was added and the solution was heated to 50 °C for 16 h, during which a yellow crystalline solid precipitated. The precipitate was filtered of, washed twice with 0.2 ml of DCM and dried in a vacuum, thus giving **4a** as a yellow solid (8.5 mg, 0.02 mmol, 67%). Crystals suitable for X-ray diffraction analysis were obtained directly from the reaction mixture after cooling.

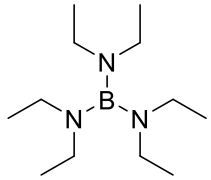
^{1}H NMR (250.1 MHz, CD_3CN): δ = 6.28 (s, 3H, N*H*), 7.07-7.15 (m, 6H, CH_{ortho}), 7.99-8.06 (m, 6H, CH_{meta}) $^{13}C\{^{1}H\}$ NMR (62.9 MHz, CD_3CN): δ = 119.9 (*C*H_{ortho}), 126.2 (*C*H_{meta}) 142.0 (O_2NC) 152.1 (HN*C*). $^{11}B\{^{1}H\}$ NMR (80.3MHz, CD_3CN): δ = 24.5 (br).

Preparation of 4b



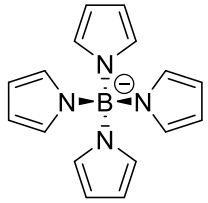
Borenium cation **2e** (20 mg, 0.020 mmol) and $NaBAr^F$ (18 mg , 0.020 mmol) were added to 0.7 ml of CD_2Cl_2 and stirred for 30 min. The suspension was filtered directly into a *J*-Young NMR tube to remove $NaPF_6$ and subsequently aniline (75 µl, 0.8 mmol) was added. The solution was kept at RT for 6 h, then NMR spectra of the reaction were recorded, showing the clean formation of **4b** together with a 1:1 mixture of the phosphonium salt $[Ph_3PCH_2SO_2Tol]^+$ (δ_P = 16.9 ppm) and ylide $[Ph_3PCHSO_2Tol]$ (δ_P = 14.1 ppm). The NMR data of **4b** (e.g. δ_B = 23.7 ppm) are in accordance with literature reports: U. Braun, T. Habereder, H. Nöth, H. Piotrowski, M. Warchhold, *Eur. J. Inorg. Chem*. **2002**, 1132.

Preparation 4c



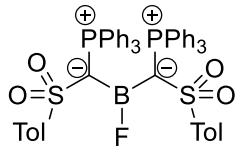
Borenium cation **2e** (10 mg, 0.010 mmol) and $NaBAr^F$ (9 mg , 0.010 mmol) were added to 0.7 ml of $CDCl_3$ and stirred for 30 min. The suspension was filtered directly into a *J*-Young NMR tube to remove $NaPF_6$ and subsequently diethylamine (10 µl, 0.1 mmol) was added. The solution was heated to 70 °C for 72h and then NMR spectra of the reaction mixture were recorded, showing the clean formation of **4c** together with the phosphonium salt $[Ph_3PCH_2SO_2Tol]^+$ and ylide $[Ph_3PCHSO_2Tol]$. The NMR data of **4c** (e.g. δ_B = 28.8 ppm) are in accordance with literature reports: H. Nöth, H. Vahrenkamp, *Eur. J. Inorg. Chem.* **1966**, 1049.

Preparation 4d



Borenium cation **2e** (20 mg, 0.020 mmol) and $NaBAr^F$ (18 mg, 0.020 mmol) were added to 0.7 ml of $CDCl_3$ and stirred for 30 min. The suspension was filtered directly into a *J*-Young NMR tube to remove $NaPF_6$ and subsequently pyrrole (7 µl, 0.1 mmol) was added. The solution was heated to 70 °C for 72h and then NMR spectra of the reaction mixture were recorded, showing the clean formation of **4c** together with the phosphonium salt $[Ph_3PCH_2SO_2Tol]^+$ and little amounts of ylide $[Ph_3PCHSO_2Tol]$. The NMR data of **4d** (e.g. δ_B = 1.0 ppm) are in accordance with literature reports: H. Fußstetter, H. Nöth, B. Wrackmeyer, W. McFarlane, *Eur. J. Inorg. Chem.* **1966**, 1049.

Preparation of 5 from 2e



Borenium cation **2e** (10 mg, 0.010 mmol) and anhydrous KF (2 mg, 0.034 mmol) were added to 0.7 ml of CD_3CN. The suspension was sonicated for 6 hours, and then heated to 85 °C for 3 days. ^1H, $^{19}F\{^1H\}$, $^{31}P\{^1H\}$ NMR spectra were recorded, showing the clean formation of **5** and KPF_6. The NMR signals were identical to the fully characterized compound **5**, which can also be obtained from the metalated ylide $[Ph_3PCSO_2Tol]Na$ and $BF_3{\cdot}Et_2O$ (see below).

^1H NMR: (250.1 MHz, CD_3CN): δ = 2.18 (s, 6H, CH_3), 6.85-6.93 (m, 4H, C$H_{STol,\ meta}$), 7.34-7.47 (m, 16H, C$H_{PPh,\ meta}$ and C$H_{STol,\ ortho}$) 7.47-7.61 (m, 18 H, C$H_{PPh,\ para}$ and C$H_{PPh,\ ortho}$) $^{31}P\{^1H\}$ NMR: (101.3 MHz, CD_3CN): δ = 21.7 (d, $^3J_{PF}$ = 4.7 Hz), –144.3 (sep, $^1J_{PF}$ = 706.2 Hz, PF_6^-) $^{19}F\{^1H\}$ NMR (235.4 MHz, CD_3CN): –44.8 (br), –71.8 (d, $^1J_{FP}$ = 706.2 Hz, PF_6^-)

Preparation of 4 from the metalated ylide $[Ph_3PCSO_2Tol]Na$

[Ph_3PCSO_2Tol]Na (1 g, 2.21 mmol) was dissolved in 20 ml THF. Subsequently, $BF_3{\cdot}Et_2O$ (500 mg, 0.44 ml, 3.52 mmol) was added. The solution was stirred for 3 hours, upon which a colourless solid precipicated. The solid was filtered, dried in vacuo and then dissolved in 20 ml DCM. The remaining solids were filtered off and the solution was reduced to about 8 ml in a vacuum. 20 ml of toluene were added and the solution was kept at –78 °C for 2 days. The resulting crystals were filtered off and washed with a small amount of toluene. After drying for 18h in a vacuum the product was obtained as colourless crystalline solid (280 mg, 0.31 mmol, 28%).

^{1}H NMR: (500.1 MHz, CD_2Cl_2): δ = 2.19 (s, 6H, CH_3), 6.75-6.80 (m, 4H, C$H_{STol,\ meta}$), 7.34-7.39 (m, 12H, C$H_{PPh,\ meta}$), 7.39-7.43 (m, 4H, C$H_{STol,\ ortho}$), 7.50-7.55 (m, 6H, C$H_{PPh,\ para}$), 7.63-7.72 (m, 12H, C$H_{PPh,\ ortho}$) ^{13}C{^{1}H} NMR: (125.8 MHz, CD_2Cl_2): δ = 21.3, (s, CH$_3$), 56.8 (br, PCS), 126.7 (s, CH$_{STol,\ ortho}$), 127.3 (d, $^1J_{CP}$ = 90.9 Hz, $C_{PPh,\ ipso}$), 128.1 (s, CH$_{STol,\ meta}$), 128.5 (m, CH$_{PPh,\ meta}$), 132.1 (m, CH$_{PPh,\ para}$), 134.8 (m, CH$_{PPh,\ ortho}$), 139.9 (s, $C_{STol,\ para}$), 144.8 (d, $^3J_{CP}$ = 3.5 Hz, $C_{STol,\ ipso}$) ^{31}P{^{1}H} NMR: (202.5 MHz, , CD_2Cl_2): δ = 21.5 (d, $^3J_{PF}$ = 5.0 Hz) ^{11}B{^{1}H} NMR (160.5 MHz, CD_2Cl_2): –41.5 (br) ^{19}F{^{1}H} NMR (470.6 MHz, CD_2Cl_2): –44.8 (br). Anal. Calcd. for $C_{52}H_{44}O_4BFP_2S_2$: C, 70.72; H, 4.99; S 6.97. Found: C, 70.44; H, 5.22; S, 6.75.

2. NMR spectra

2.1 NMR spectra of the reaction mixtures of the formation of 2a-d

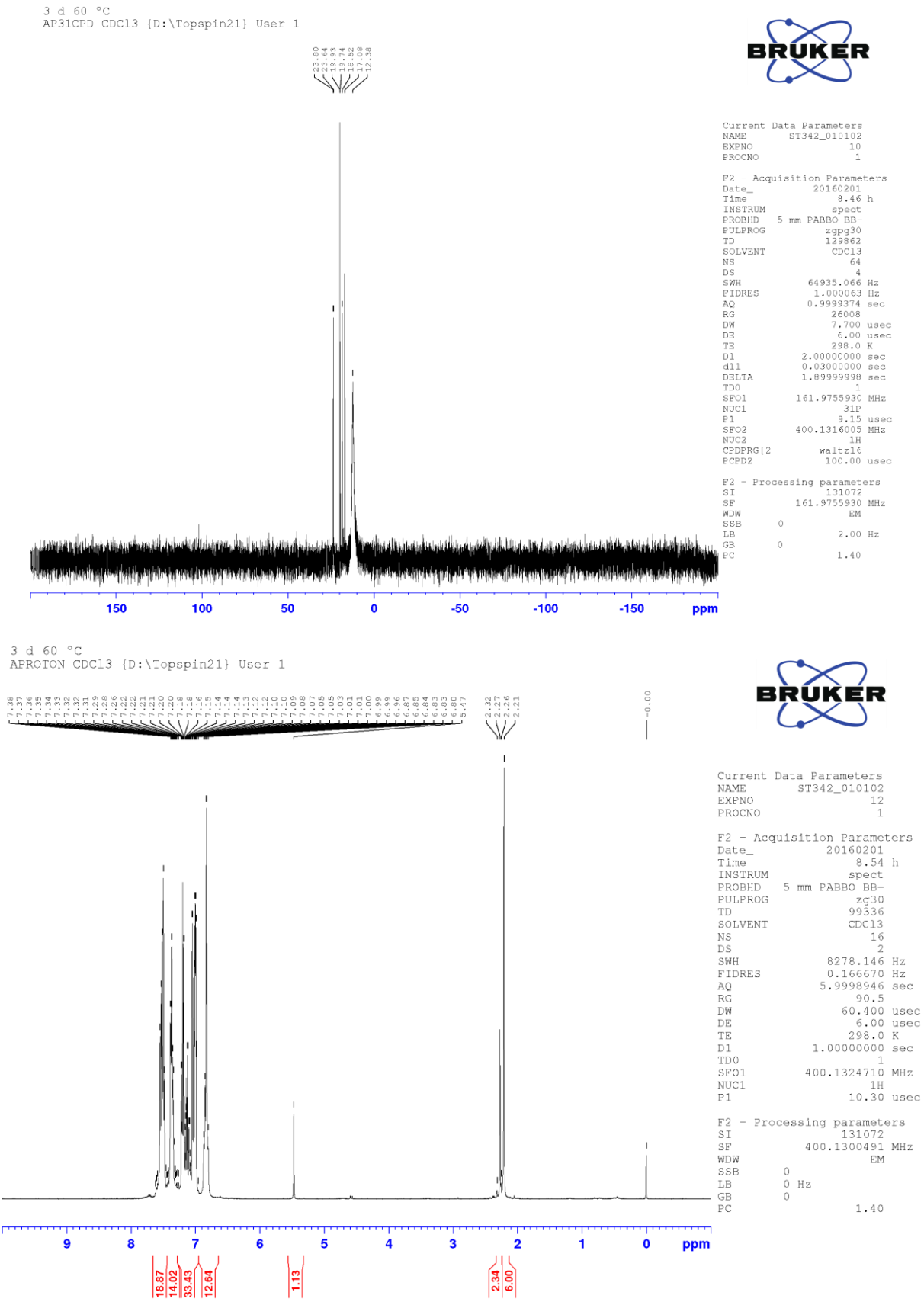


Figure S1. $^{31}P\{^{1}H\}$ NMR and ^{1}H NMR spectra of **2a**

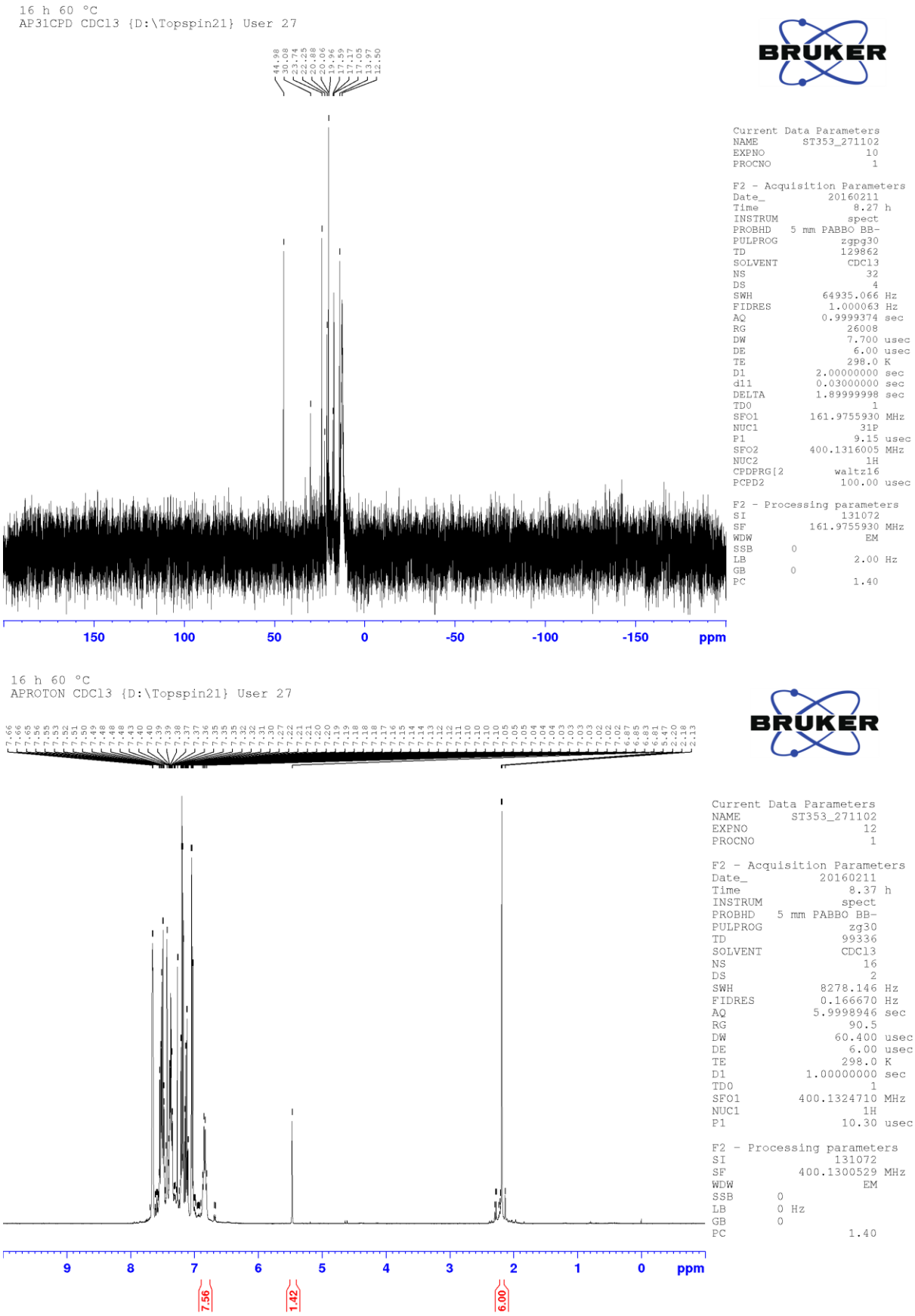


Figure S2. $^{31}P\{^{1}H\}$ NMR and ^{1}H NMR spectra of **2b**

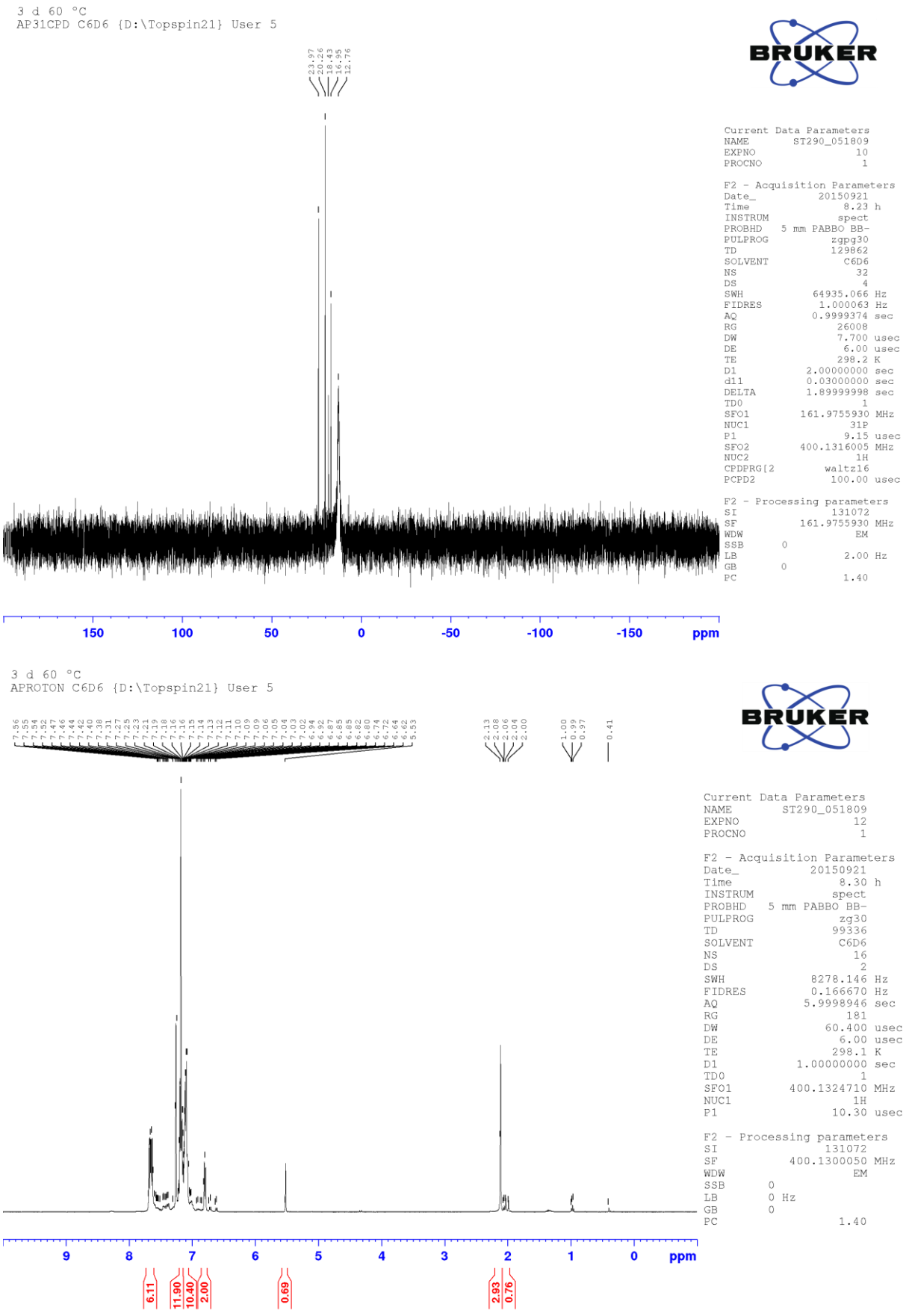


Figure S3. $^{31}P\{^{1}H\}$ NMR and ^{1}H NMR spectra of **2c**

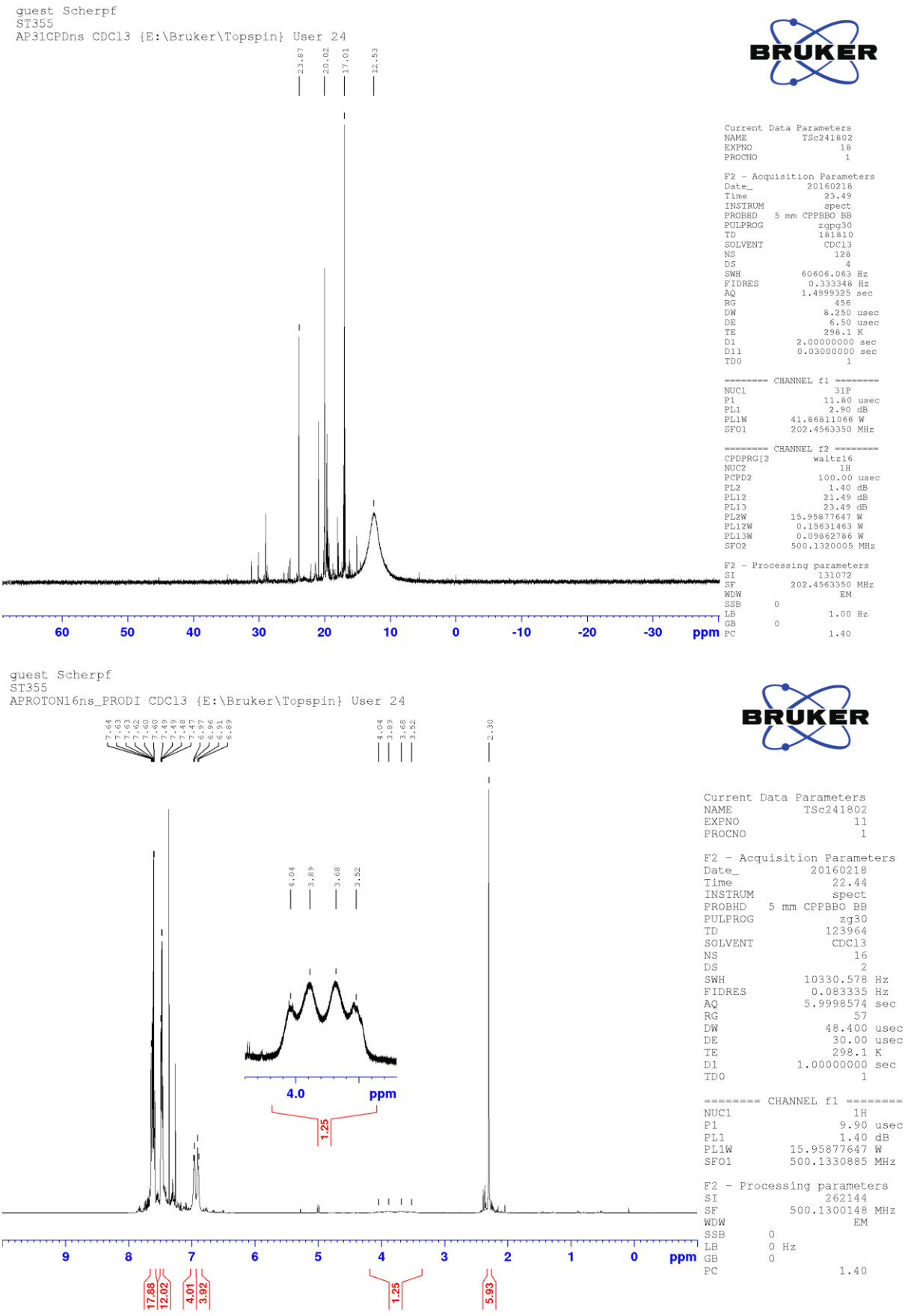


Figure S4. $^{31}P\{^{1}H\}$ NMR and ^{1}H NMR spectra of **2d**

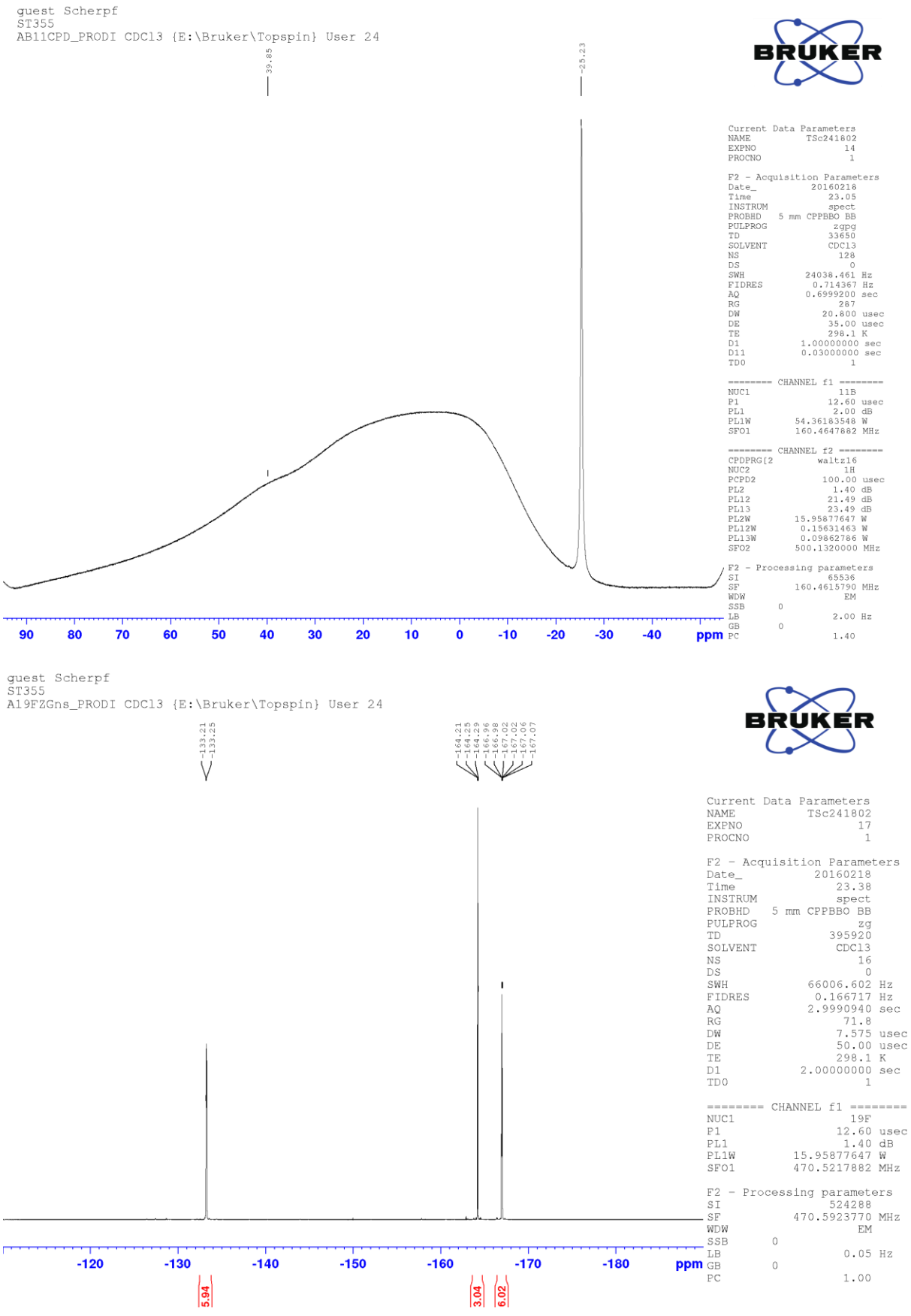


Figure S5. $^{11}B\{^{1}H\}$ NMR and $^{19}F\{^{1}H\}$ NMR spectra of **2d**

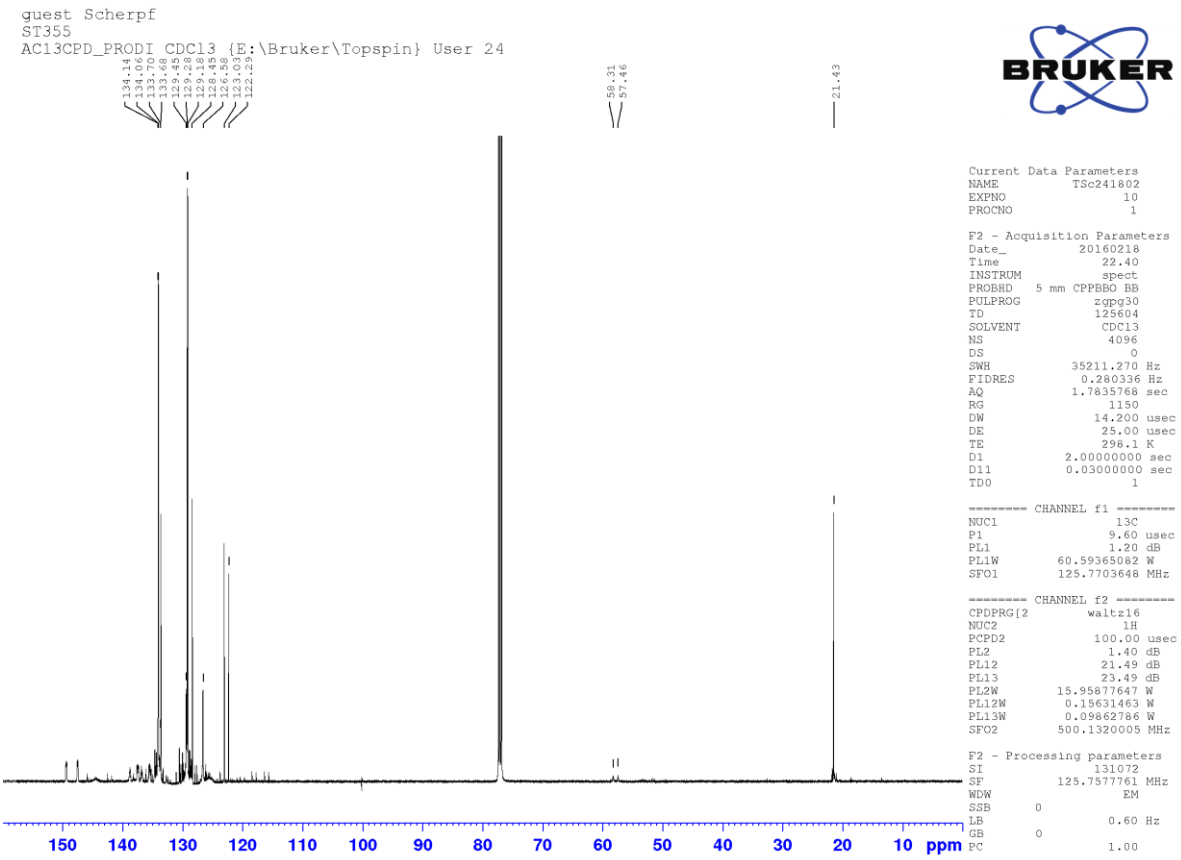


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **2d**.

2.2 NMR spectra of the isolated compounds

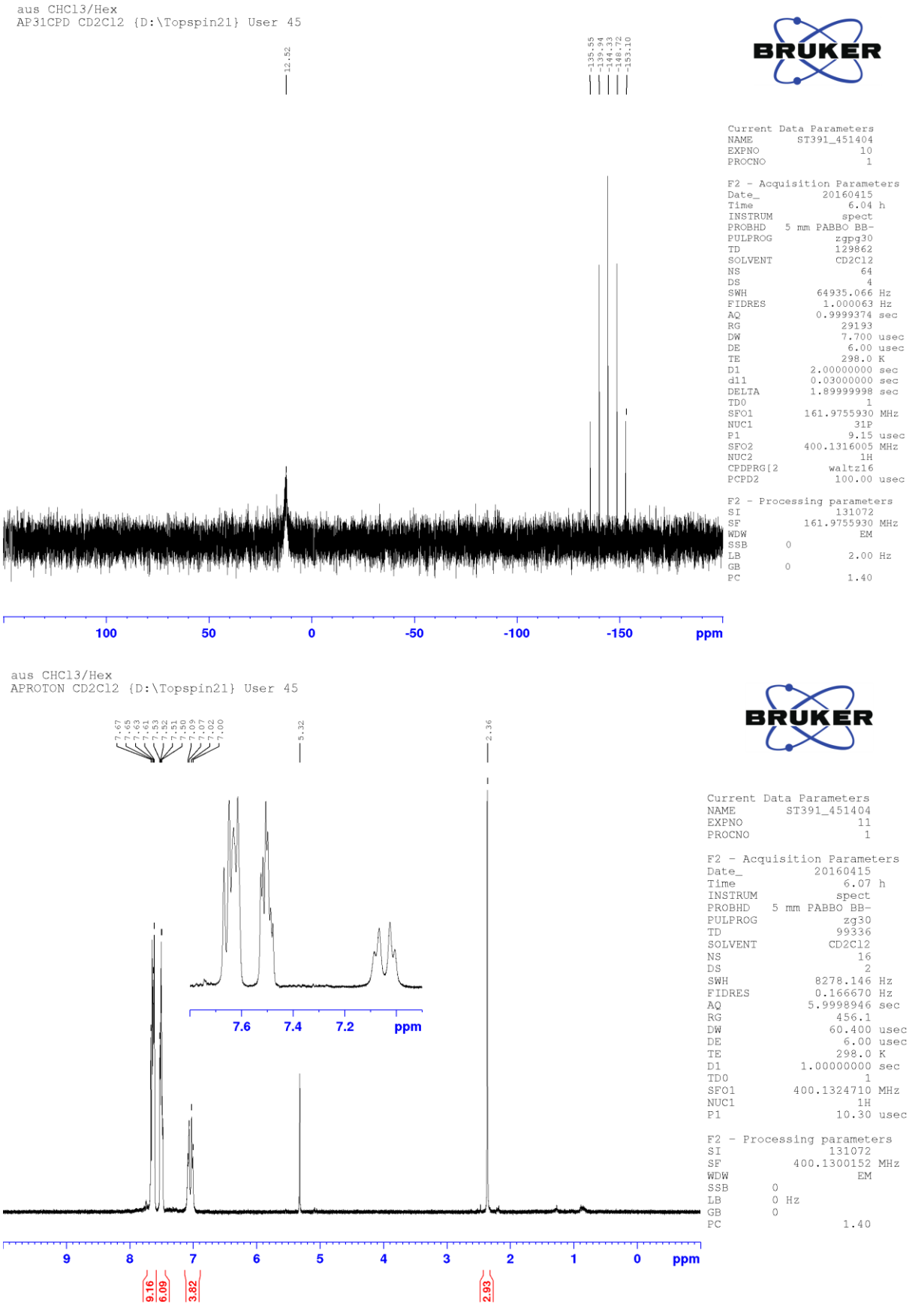


Figure S7. $^{31}P\{^{1}H\}$ NMR and ^{1}H NMR spectra of **2e**.

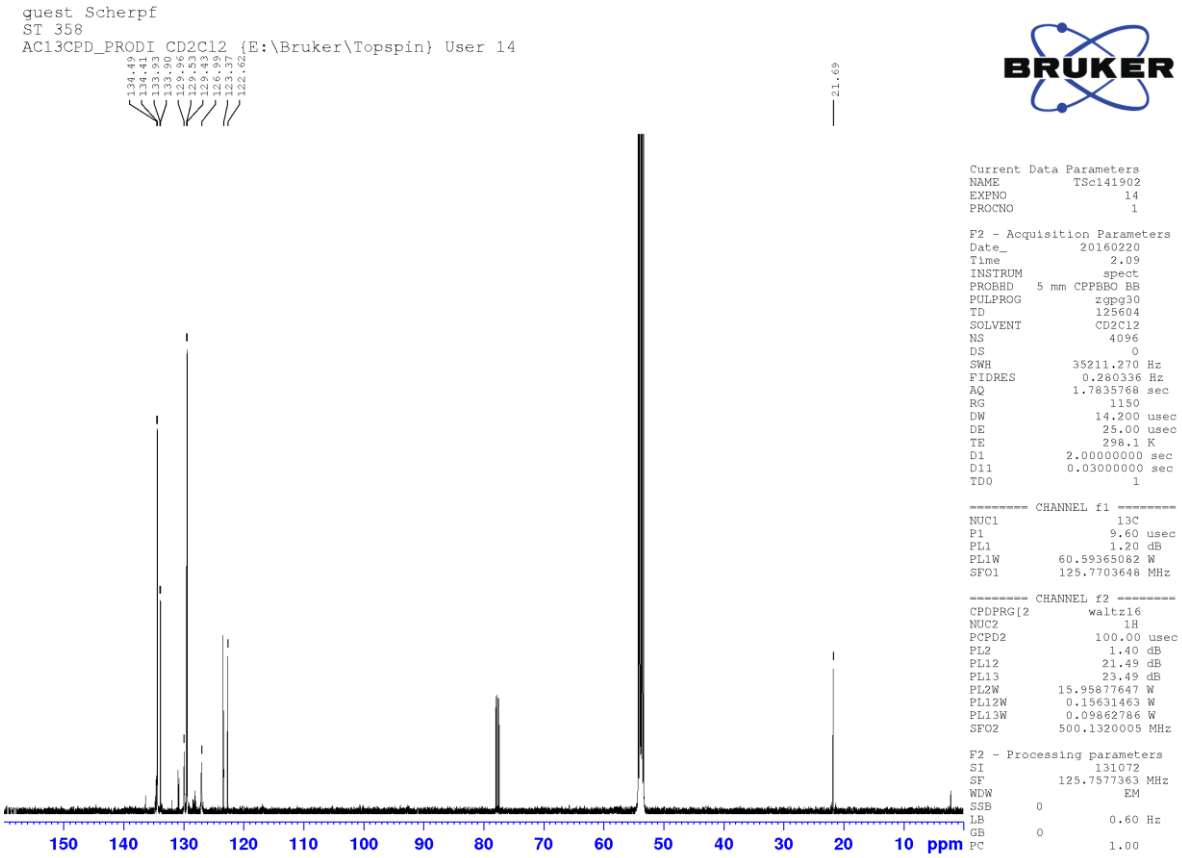


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **2e**.

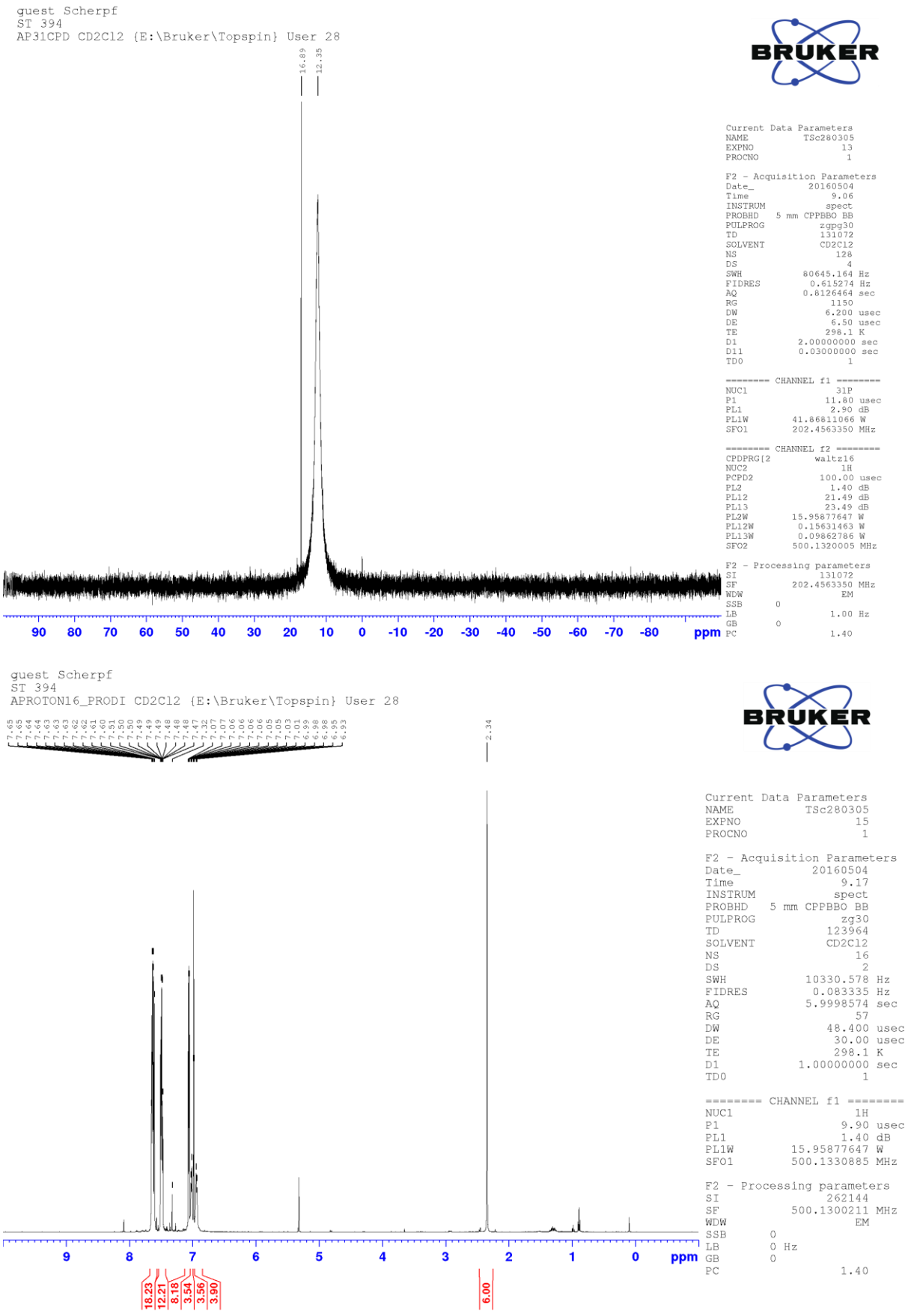
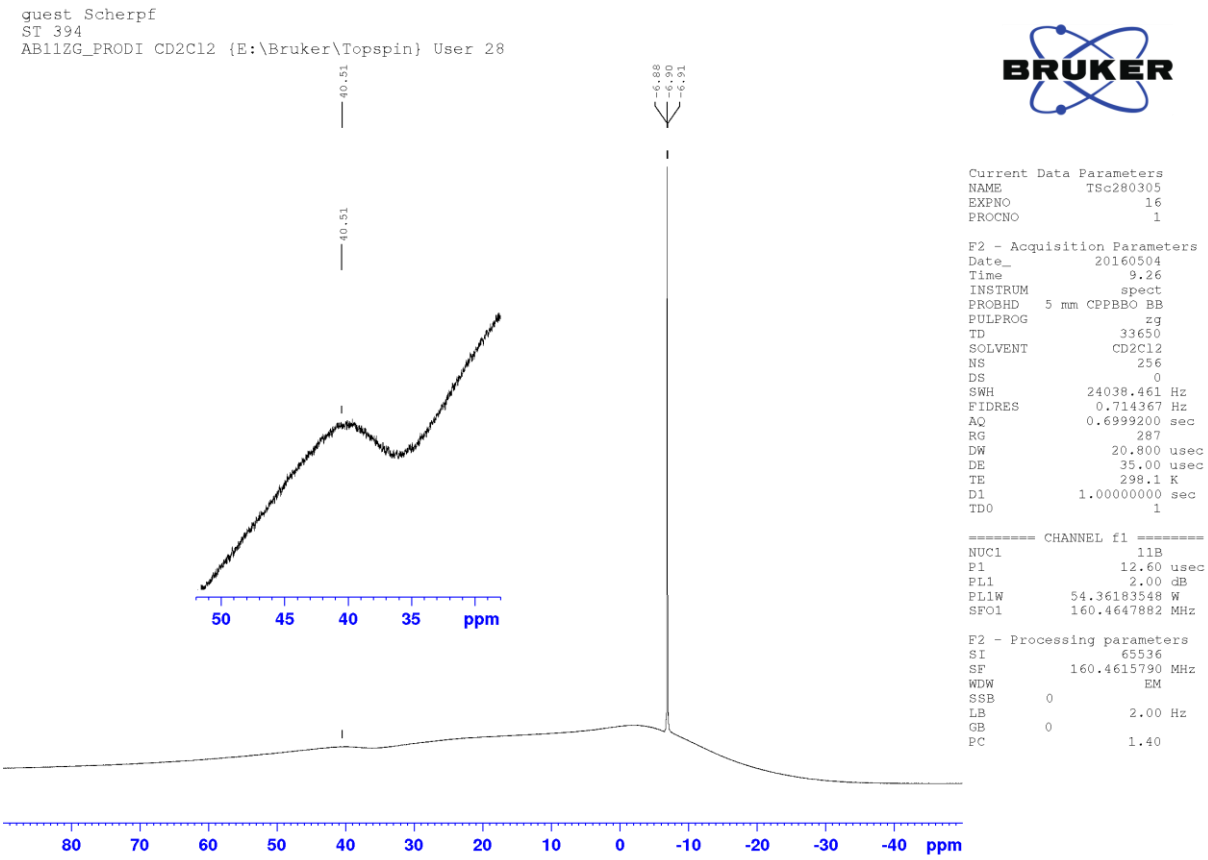


Figure S9. $^{31}P\{^{1}H\}$ NMR and ^{1}H NMR spectra of **2a**.



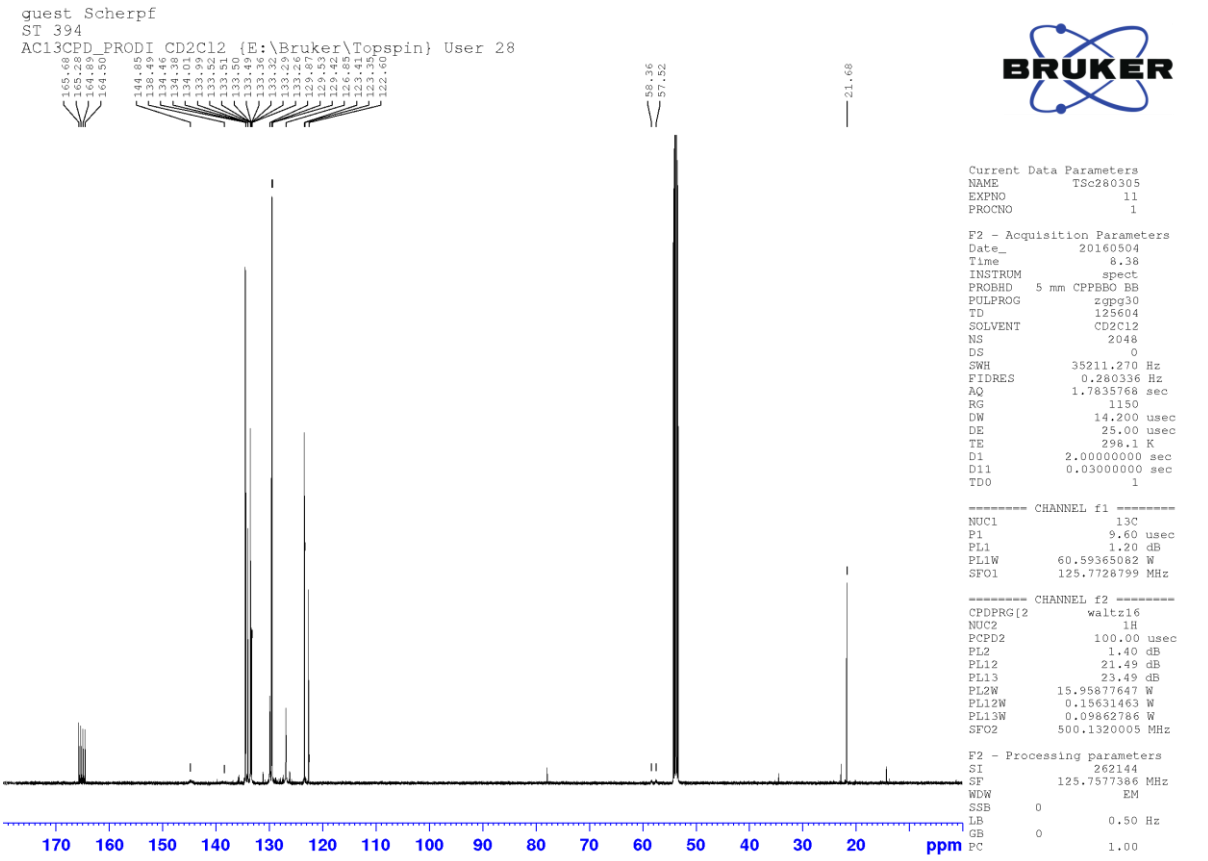
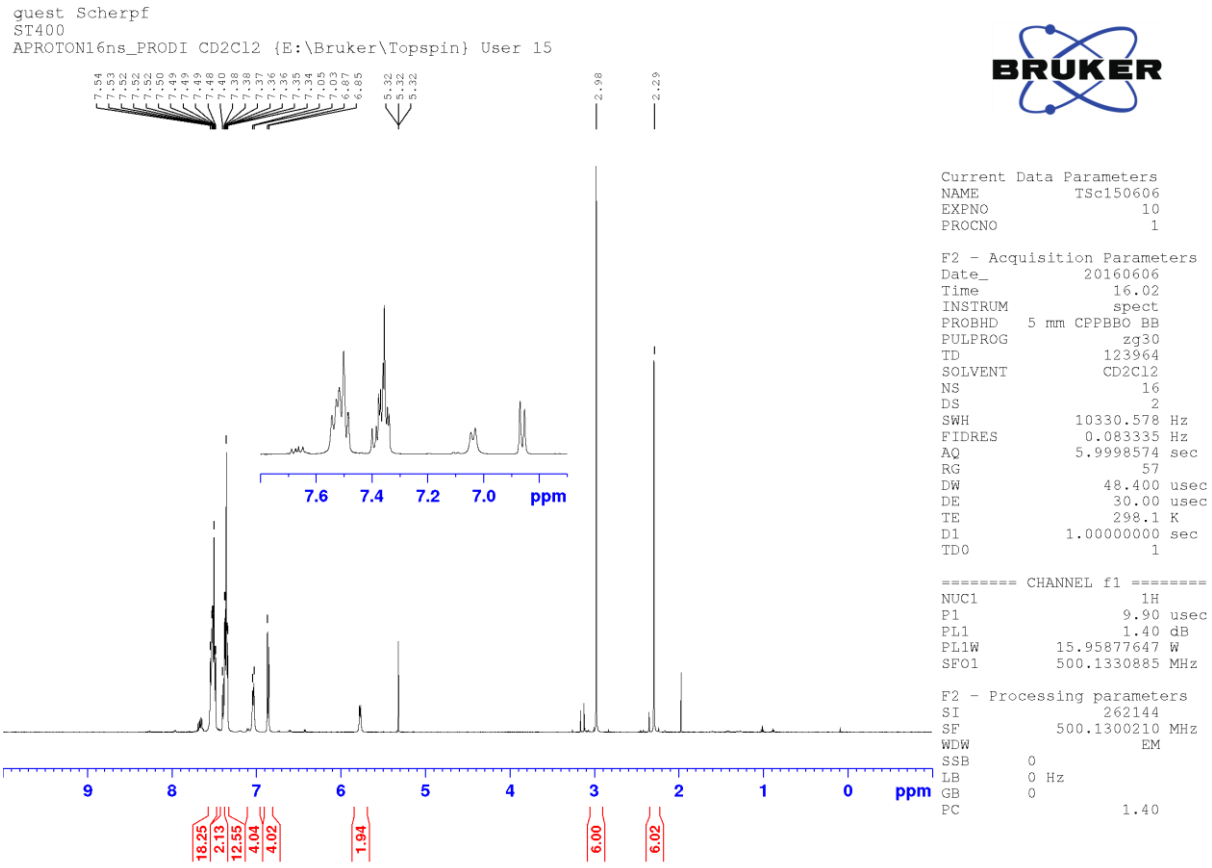


Figure S10. $^{11}B\{^{1}H\}$ NMR and $^{13}C\{^{1}H\}$ NMR spectra of **2a**.



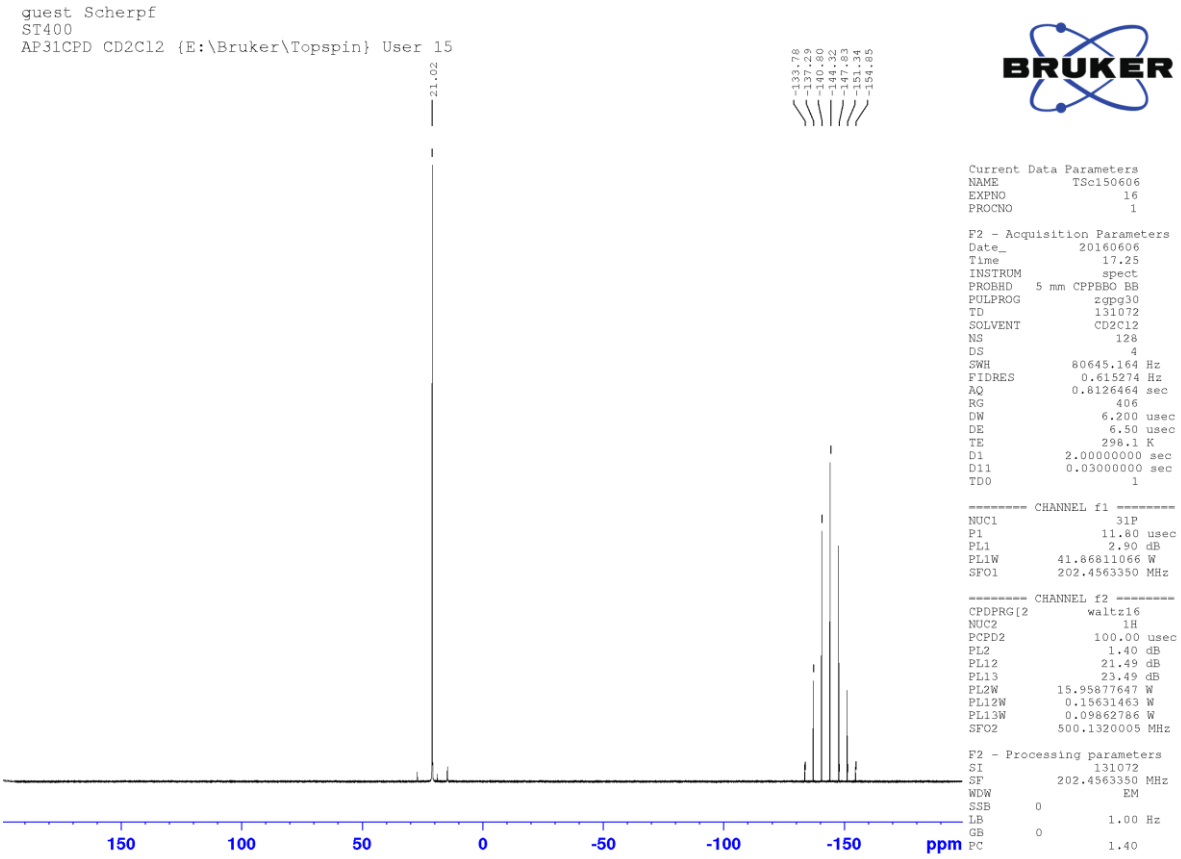
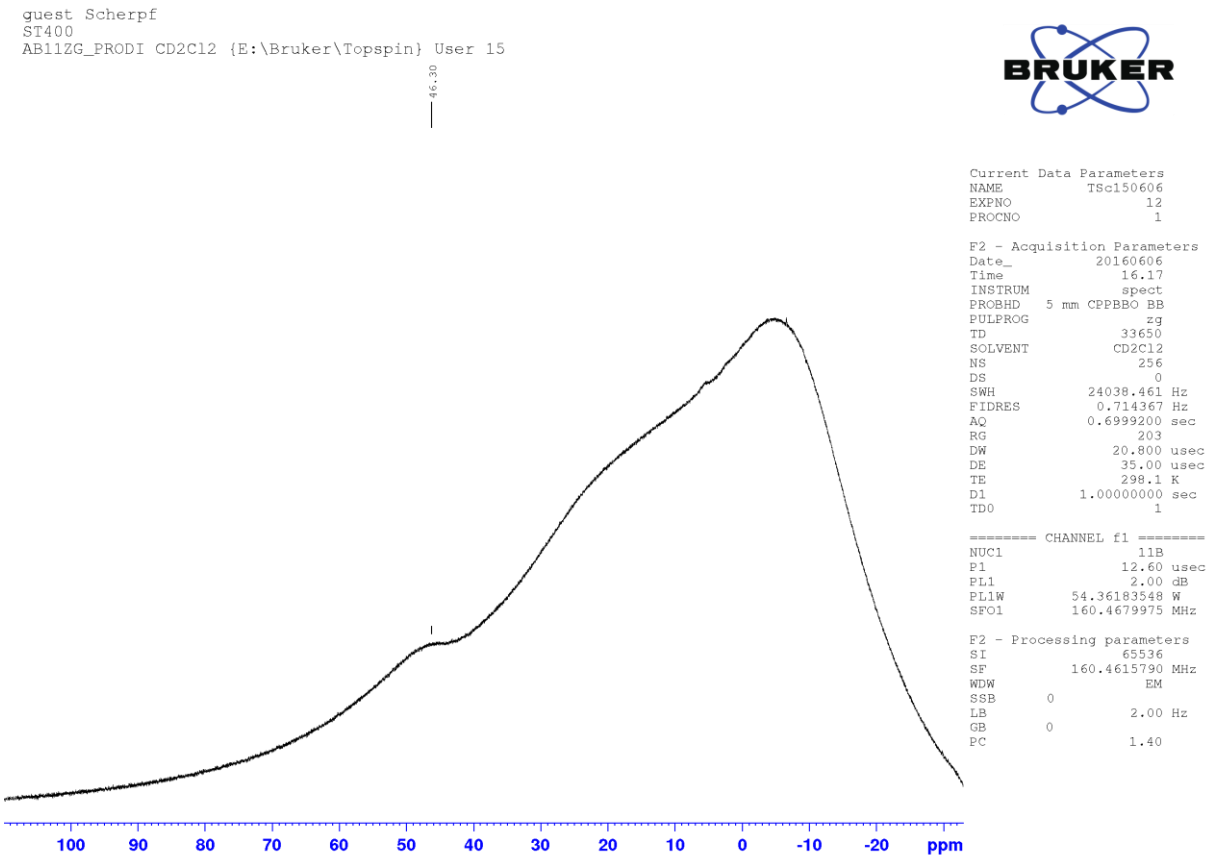


Figure S11. ^{1}H NMR and ^{31}P{^{1}H} NMR spectra of **3a.**



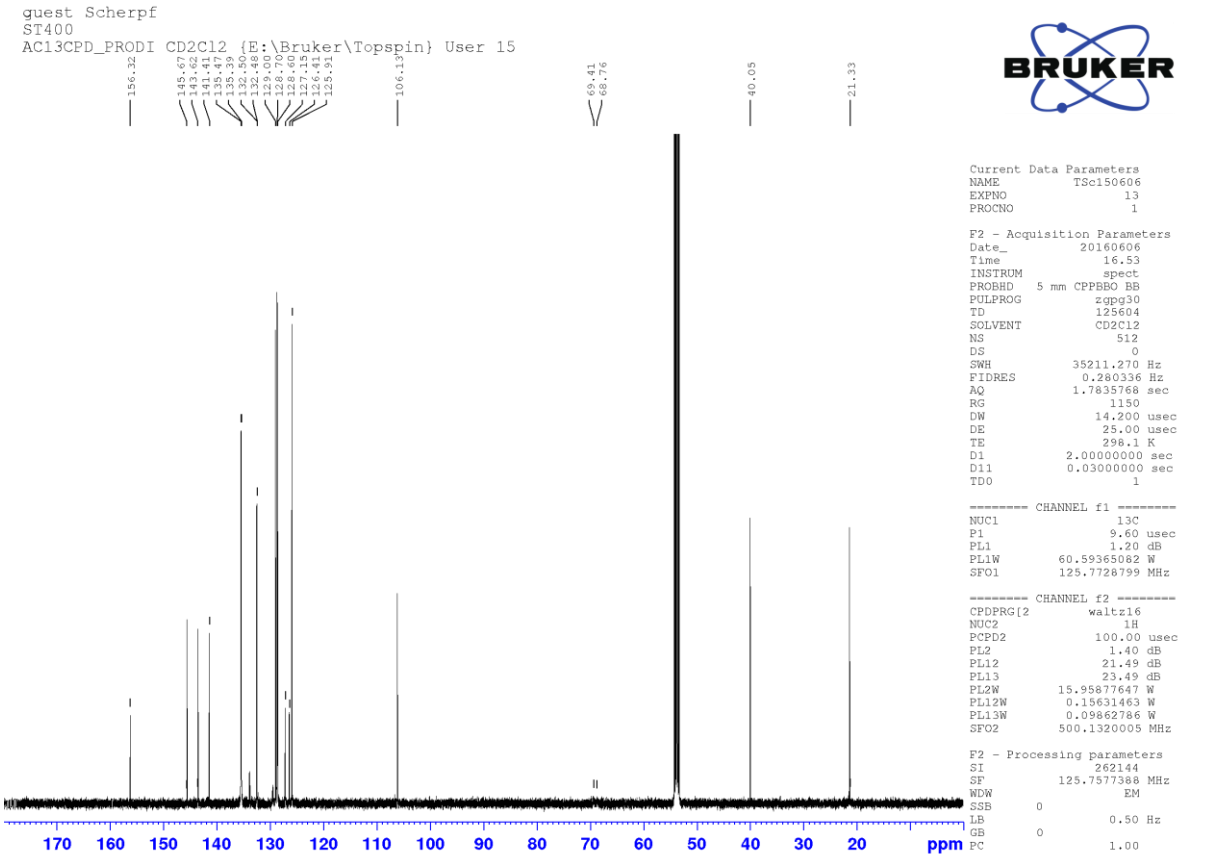


Figure S12. $^{11}B\{^1H\}$ NMR and $^{13}C\{^1H\}$ NMR spectra of **3a**

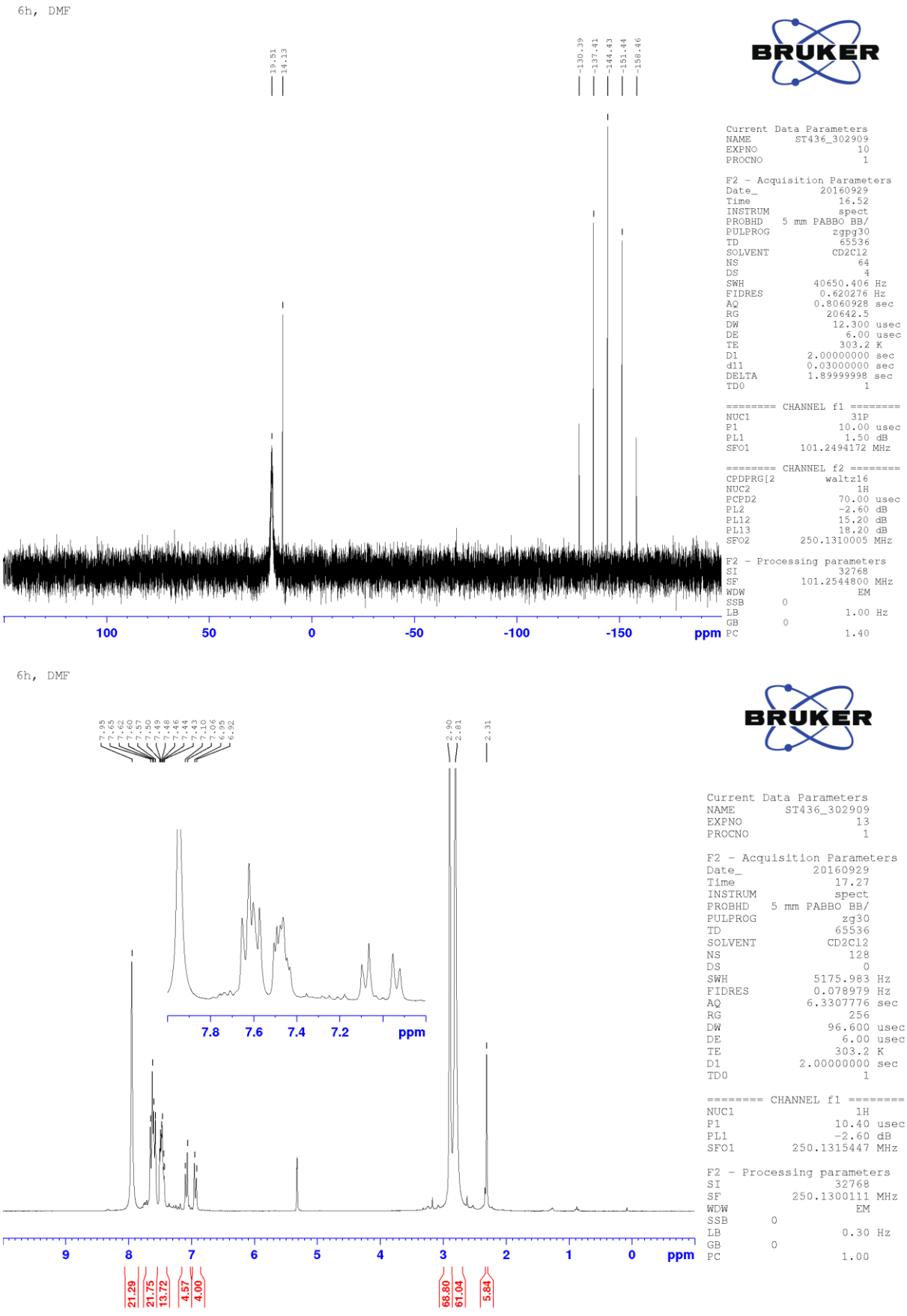


Figure S13. $^{31}P\{^{1}H\}$ NMR and ^{1}H NMR spectra of **3b**.

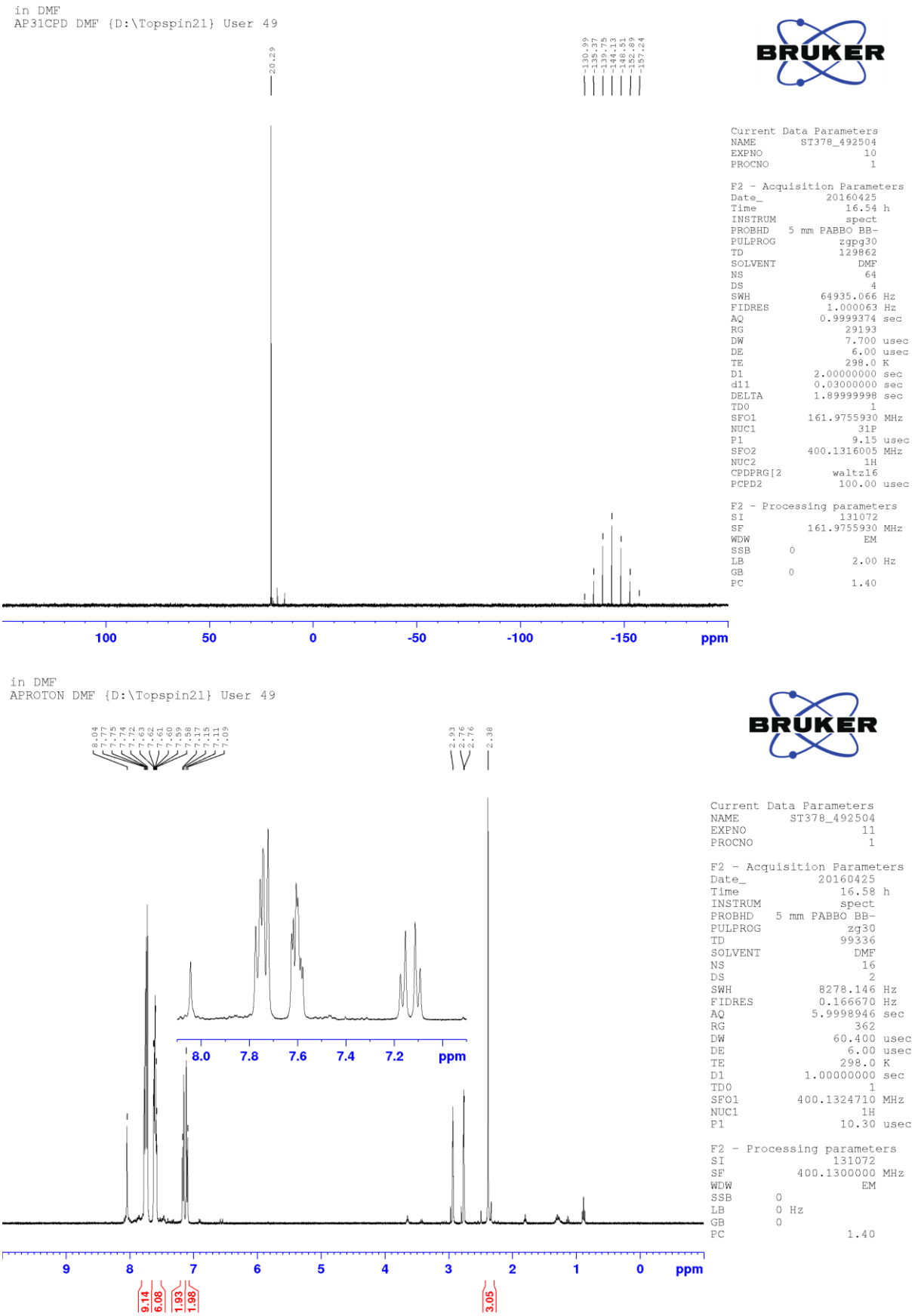


Figure S14. $^{31}P\{^{1}H\}$ NMR and ^{1}H NMR spectra of **3b** in d7-DMF.

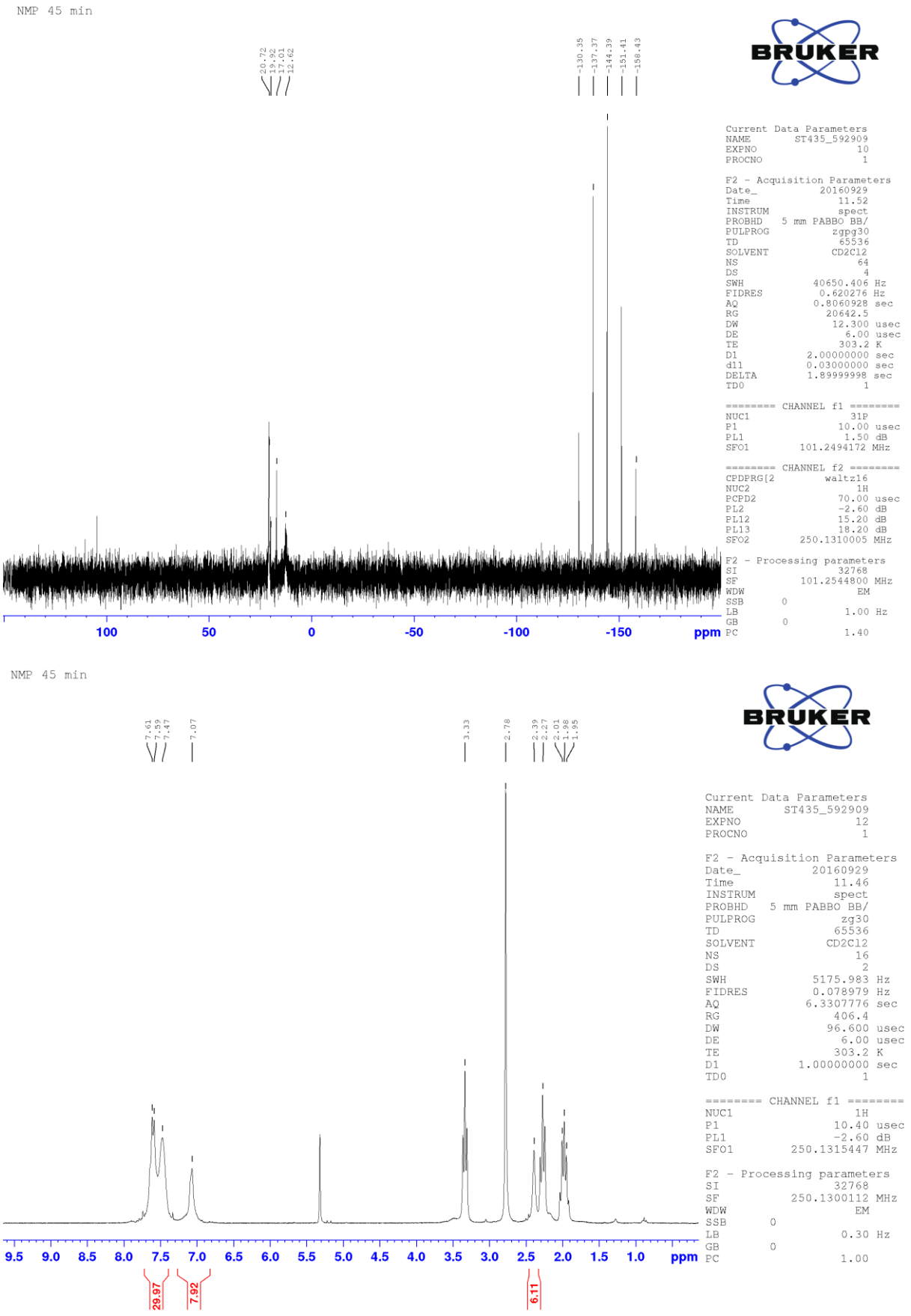


Figure S15. $^{31}P\{^{1}H\}$ NMR and ^{1}H NMR spectra of **3c**.

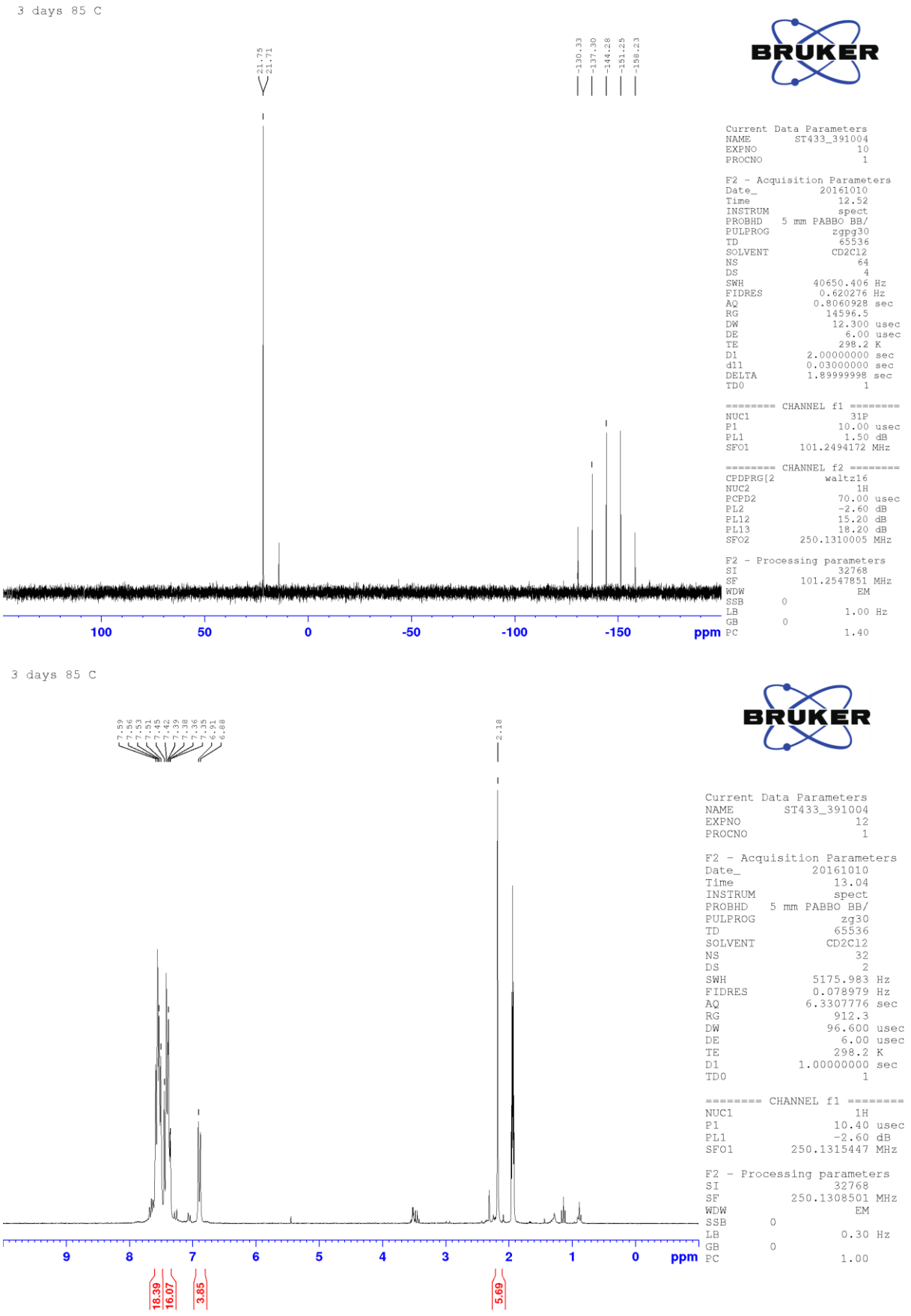


Figure S16. $^{31}P\{^{1}H\}$ NMR and ^{1}H NMR spectra of the reaction of **2e** and KF to **5**.

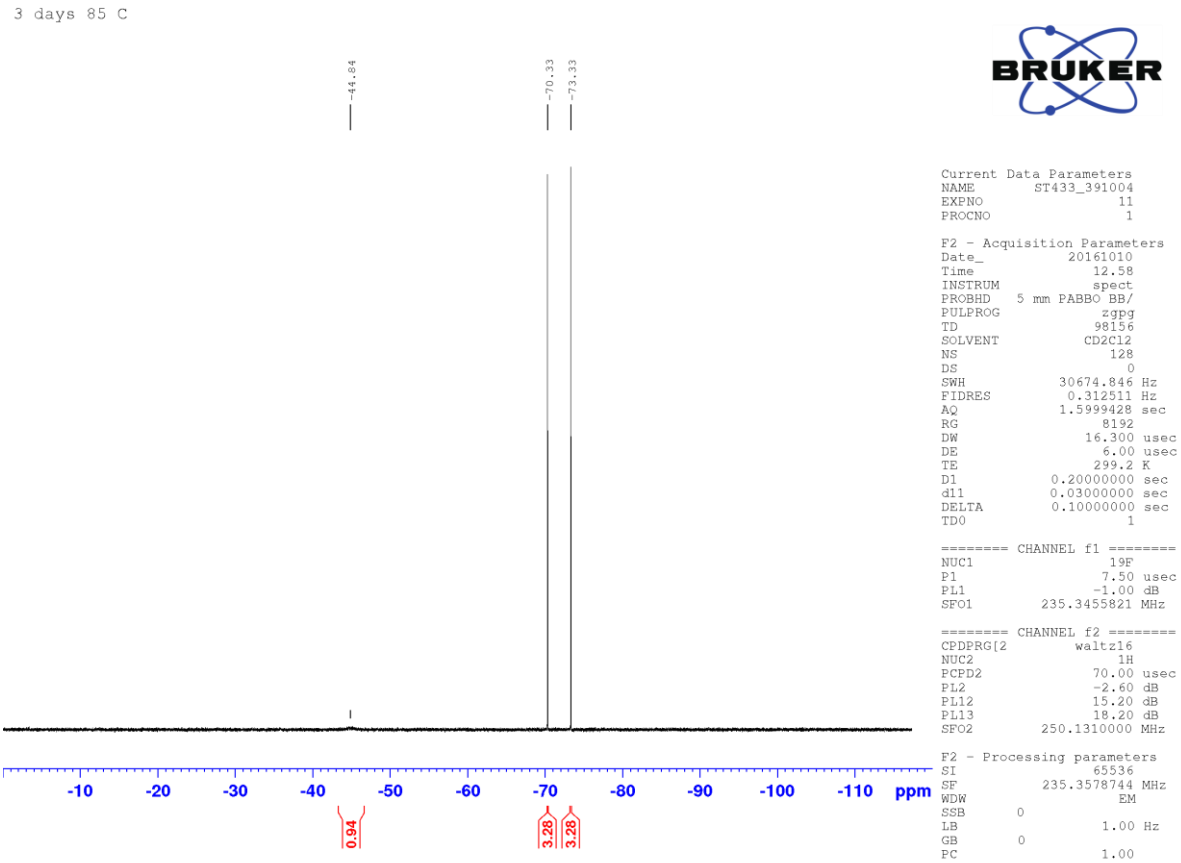


Figure S17. $^{19}F\{^{1}H\}$ NMR of the reaction of **2e** and KF to **5**.

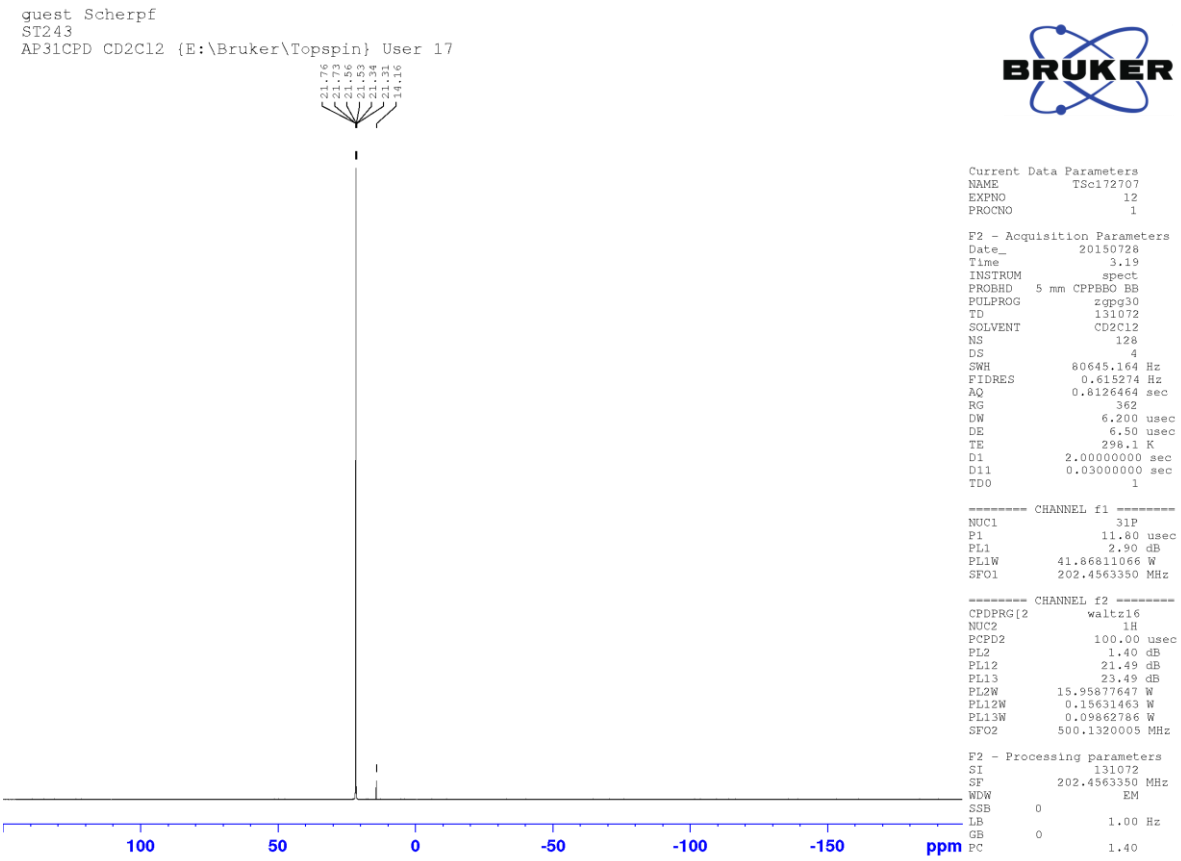
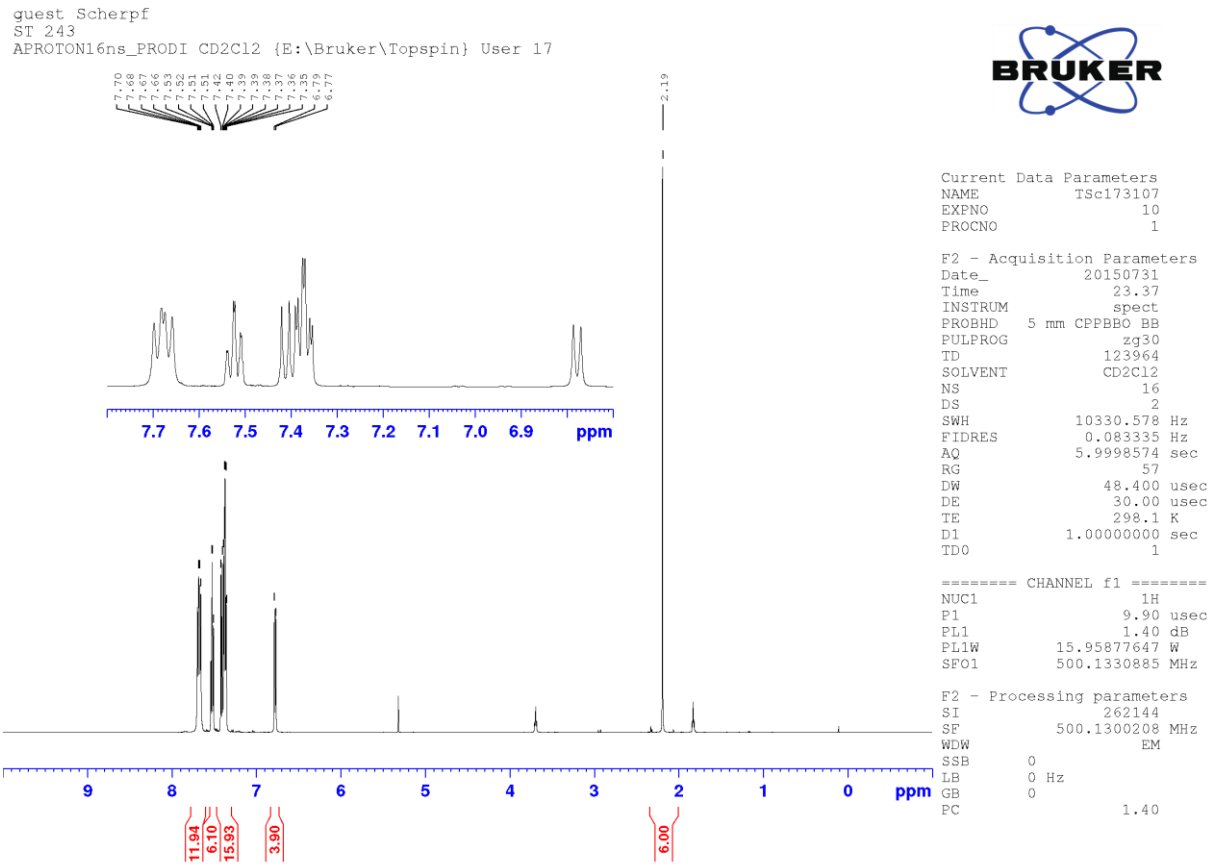


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of **5**.



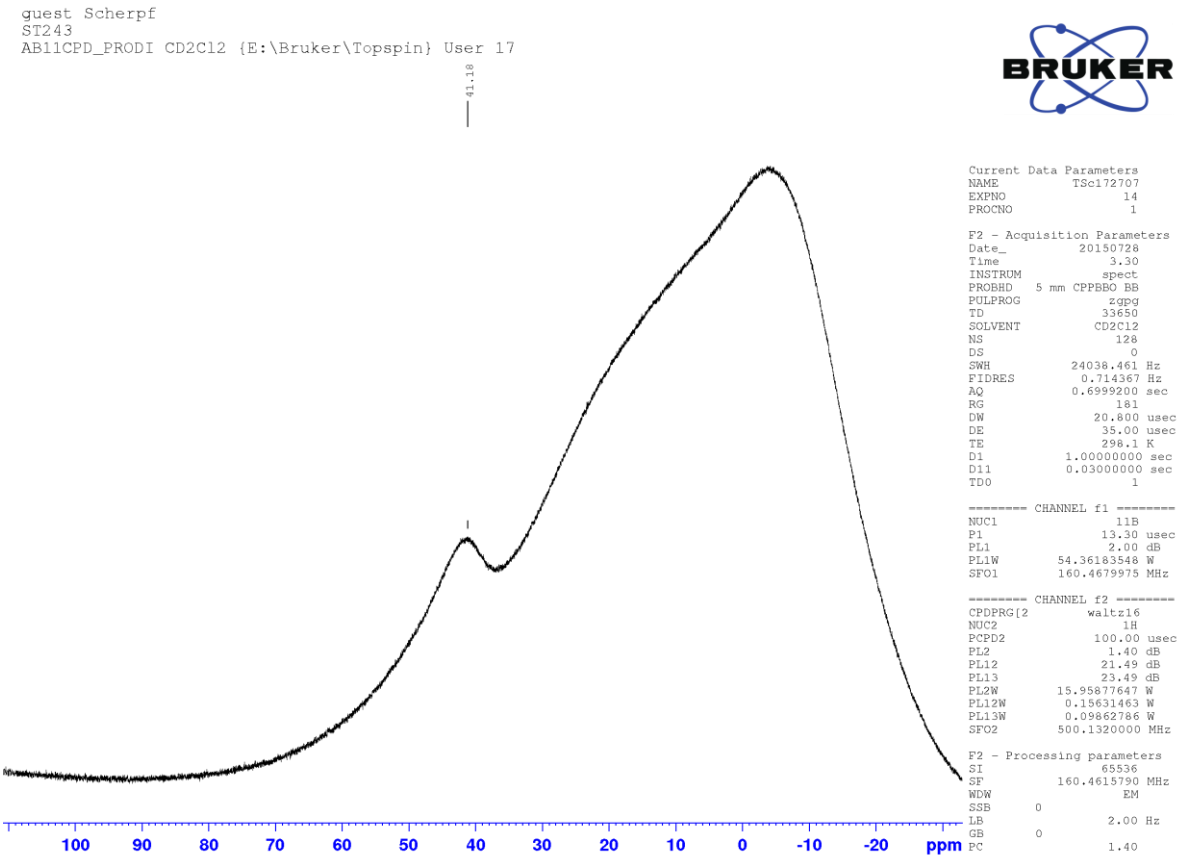
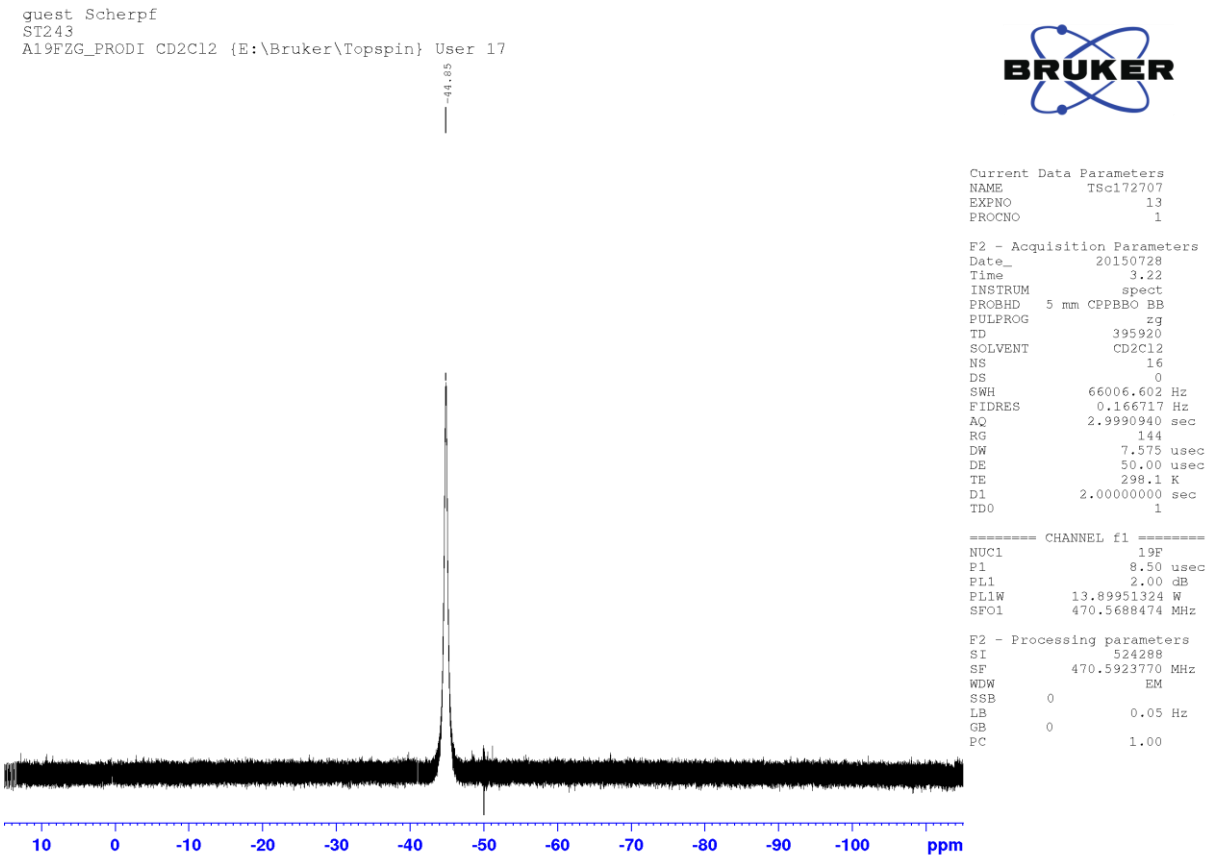


Figure S19. ^{1}H and $^{11}B\{^{1}H\}$ NMR spectrum of **5**.



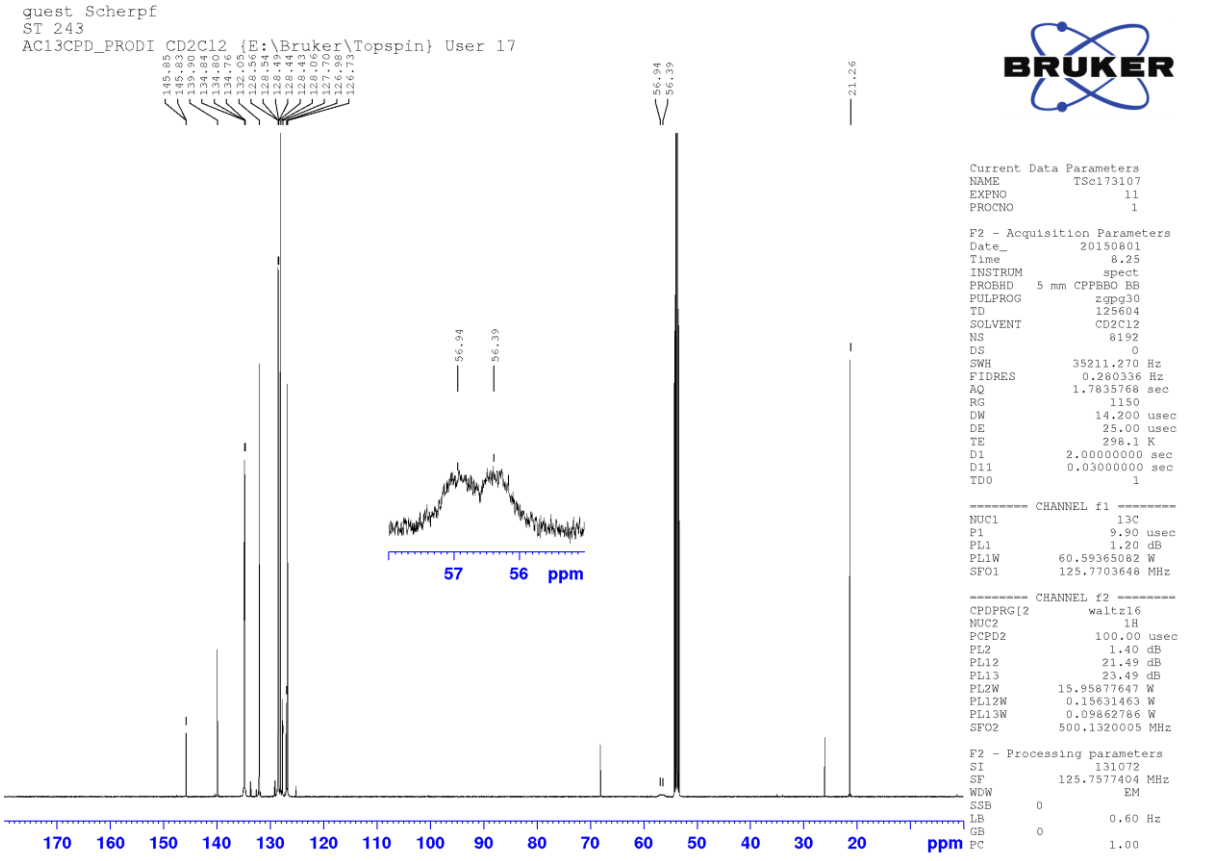
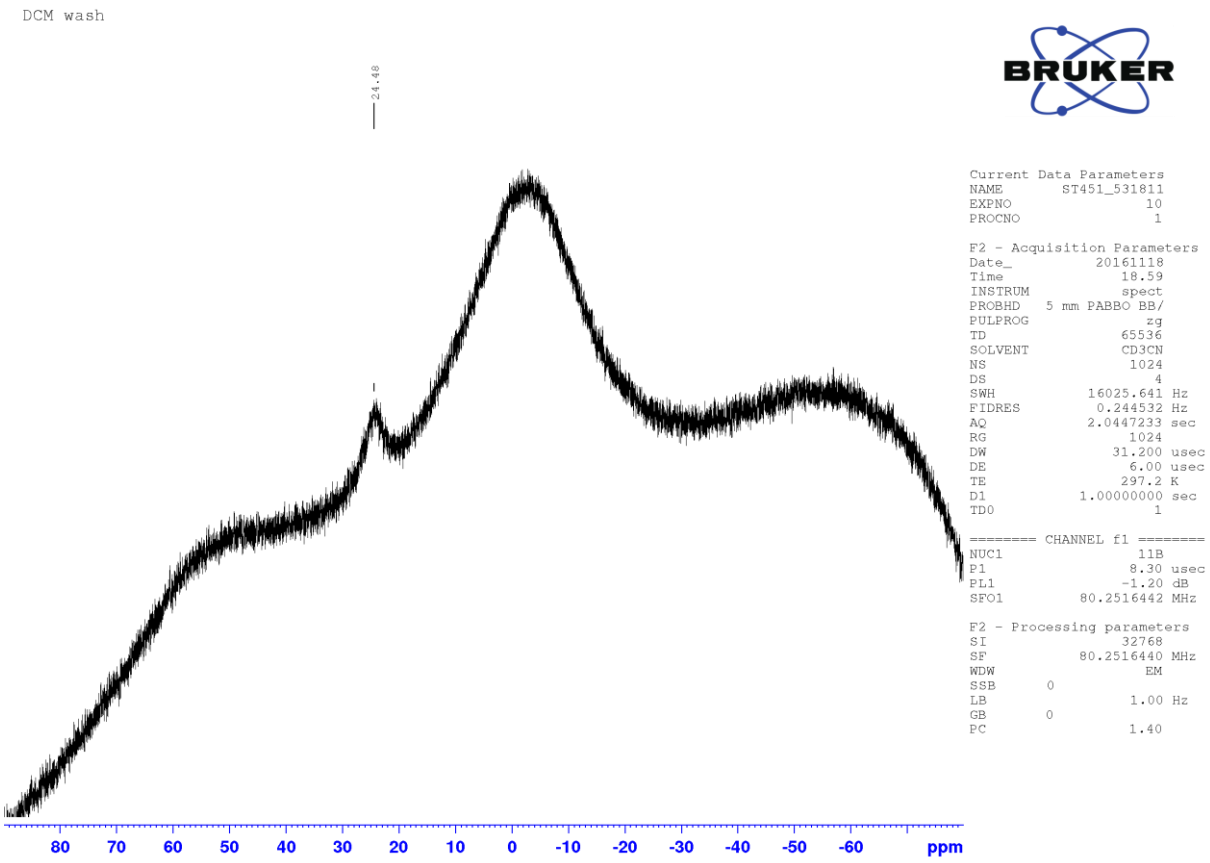


Figure S20. $^{19}F\{^{1}H\}$ NMR and $^{13}C\{^{1}H\}$ NMR spectra of **5**.



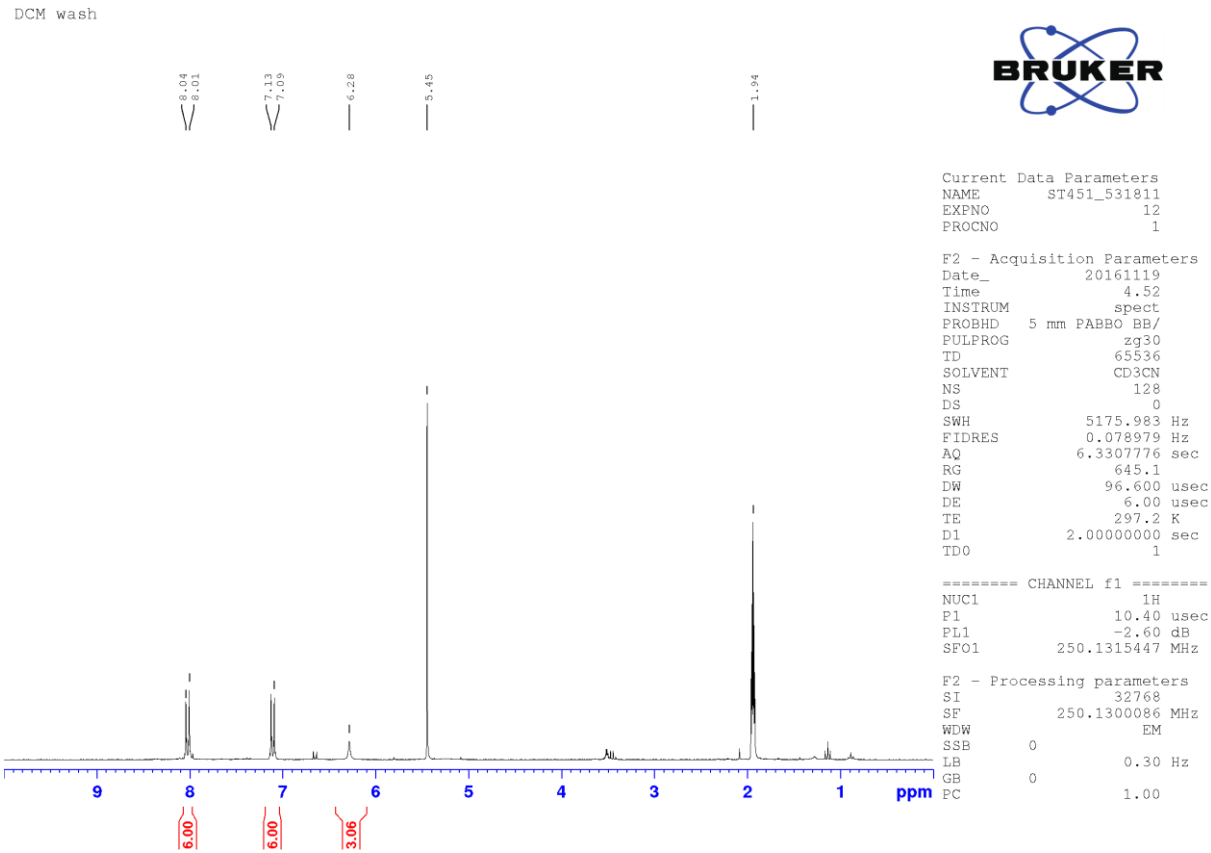


Figure S21. $^{11}B\{^{1}H\}$ NMR and ^{1}H NMR of **4a**.

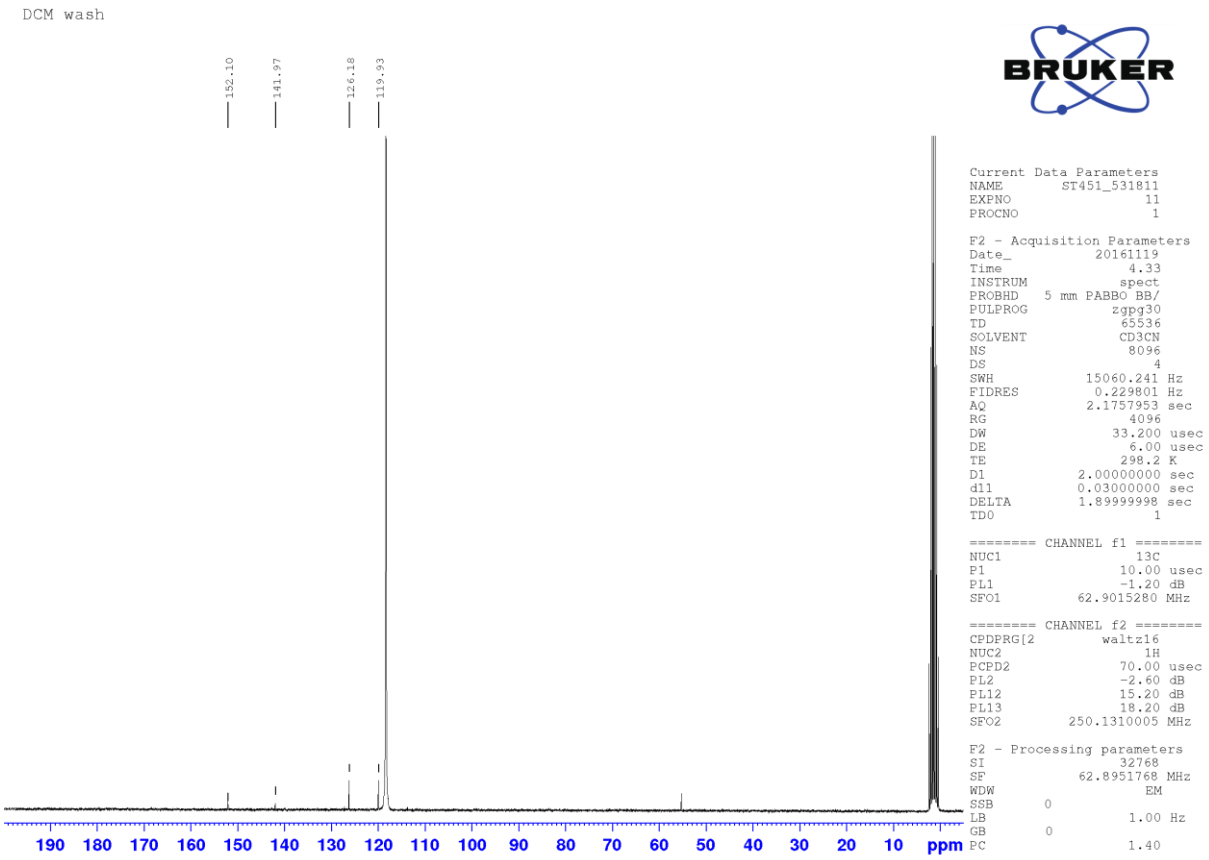


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **4a**.

2.3 $^{11}B\{^{1}H\}$ NMR of aminoboranes 4b-d

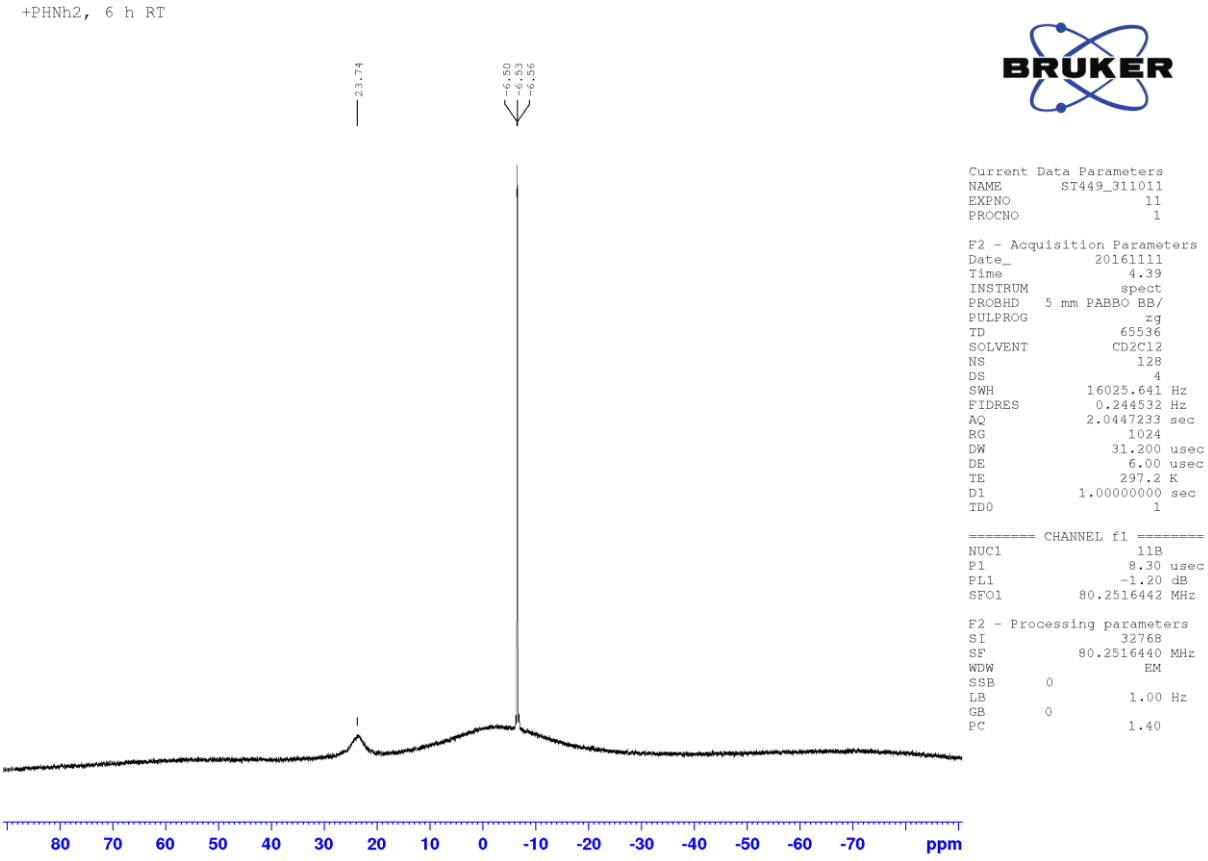


Figure S23. $^{11}B\{^{1}H\}$ NMR of **4b**.

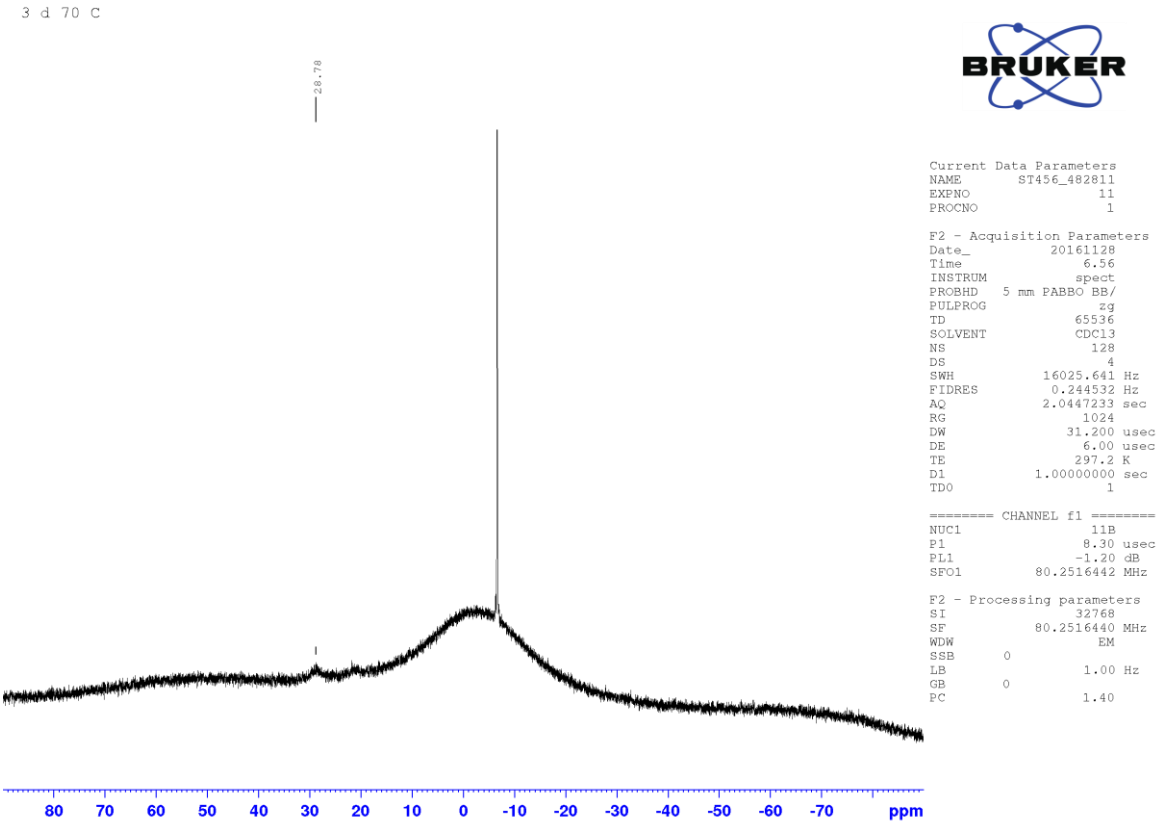


Figure S24. $^{11}B\{^{1}H\}$ NMR **4c**.

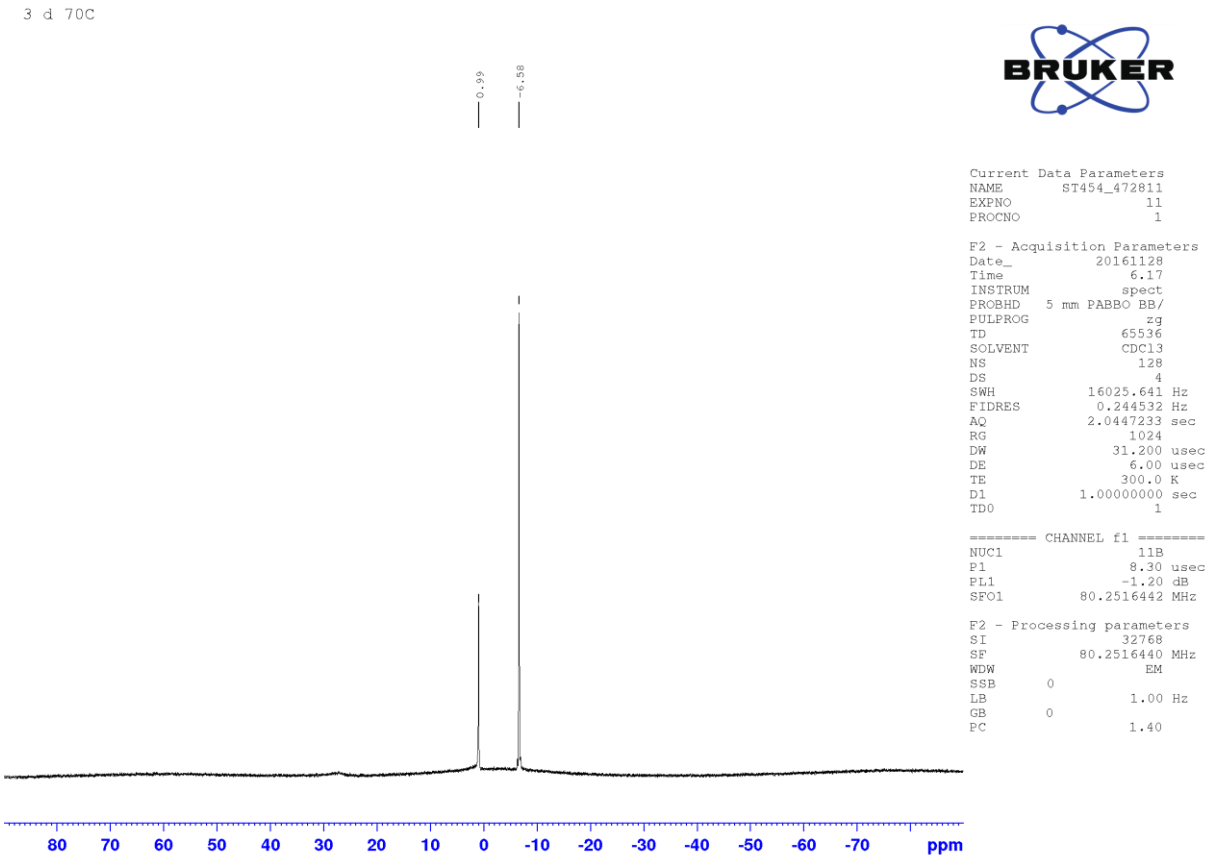


Figure S25. $^{11}B\{^{1}H\}$ NMR **4d**.

2.4 $^{31}P\{^{1}H\}$ and ^{1}H VT NMR spectra of 2e

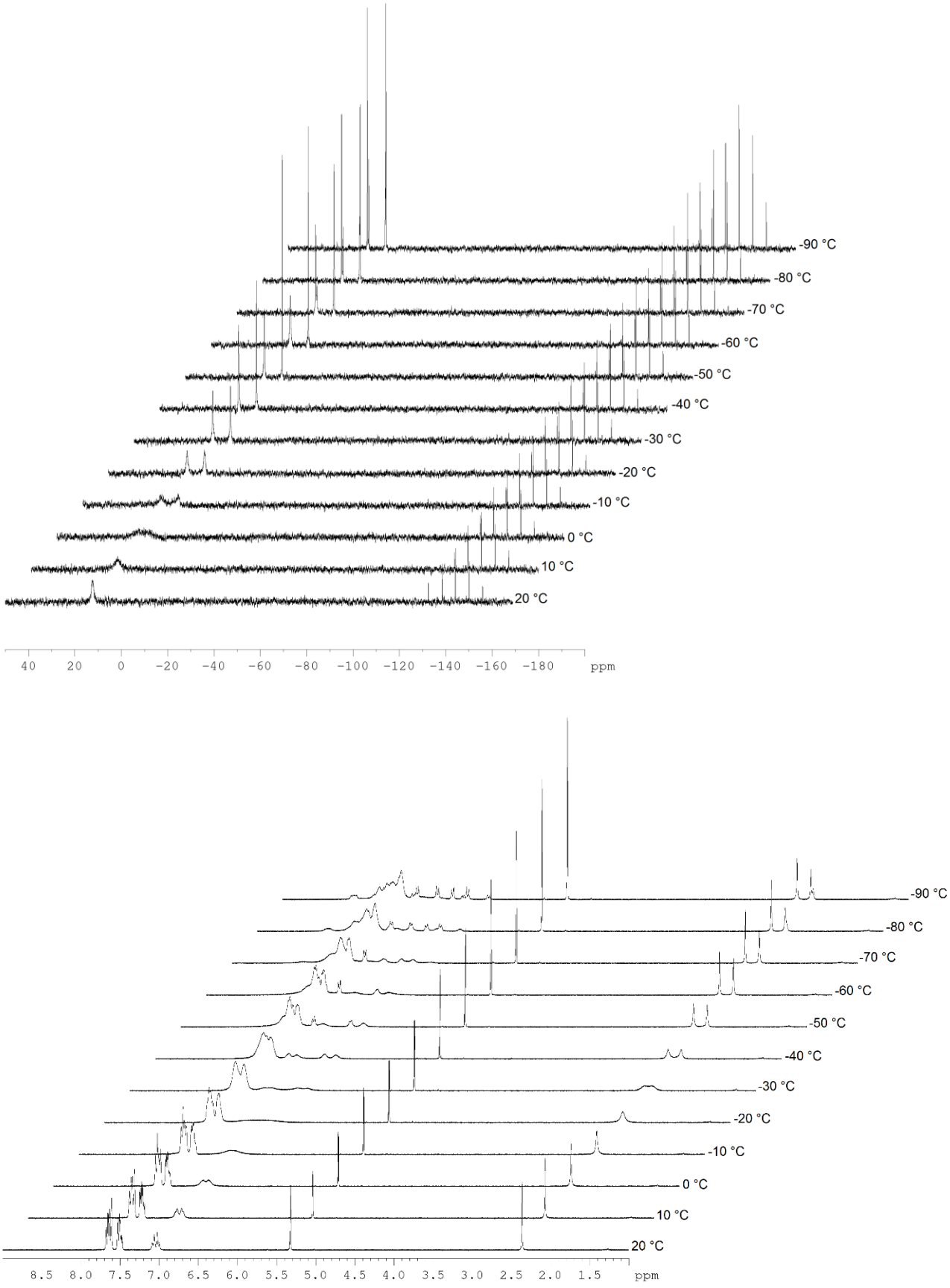


Figure S26. $^{31}P\{^{1}H\}$ VT NMR and ^{1}H VT NMR spectra of **2e**.

4. Crystal Structure Determination

Data collection of all compounds was conducted with a Bruker D8 APEX2-CCD (**2e**, **3b** and **5**) or an Oxford XCalibur (Sapphire2) (**3a**) or an Oxford SuperNova (Cu-µsource, Atlas) (**3c** and **4a**). The structures were solved using direct methods, refined with the Shelx software package[4] and expanded using Fourier techniques. The crystals of all compounds were mounted in an inert oil (perfluoropolyalkylether). Crystal structure determinations were effected at 100 K or 170 K. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1520039-1520044. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk].

Table S1. Data collection and structure refinement details for compounds **2e, 3a** and **3b**.

Compound	**2e**	**3a**	**3b**
CCDC No.	CCDC 1520042	CCDC 1520043	CCDC 1520044
Formula	$C_{52}H_{44}BF_6O_4P_3S_2$	$C_{59}H_{54}BF_6N_2O_4P_3S_2$	$C_{55}H_{51}BNO_5P_2S_2 \cdot PF_6 \cdot$ 0.91 DMF · 0.1 DCM
Formula weight [g·mol^{-1}]	1014.71	1136.88	1161.90
Temperature [K]	100(2)	170(2)	100(2)
Wave length [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	Triclinic
Space group	*P*2/n (13)	*P*2$_1$/c (14)	*P-1* (2)
a [Å]	11.5223(7)	14.7651(10)	10.6672(6)
b [Å]	15.3614(9)	15.0417(9)	13.5510(8)
c [Å]	13.3922(9)	28.7918(19)	20.9364(12)
α [°]	90	90	102.584(2)
β [°]	90.017(3)	96.079(7)°.	102.1356(19)
γ [°]	90	90	101.9592(19)
Volume [Å^3]	2370.4(3)	6358.5(7)	2784.3(3)
Z	2	4	2
Calc. density [Mg·m^{-3}]	1.422	1.188	1.386
µ ($Mo_{K\alpha}$) [mm^{-1}]	0.284	0.220	0.264
F(000)	1048	2360	1208
Crystal dimensions [mm]	0.206 x 0.192 x 0.066	0.70 x 0.40 x 0.30	0.23 x 0.18 x 0.05
Theta range [°]	1.521 to 29.984	2.981 to 26.999	2.406 to 28.998
Index ranges	$-15 \le h \le 16$	$-18 \le k \le 18$	$-14 \le h \le 14$
	$-19 \le k \le 21$	$-19 \le k \le 19$	$-18 \le k \le 18$
	$-15 \le l \le 18$	$-36 \le k \le 36$	$-28 \le l \le 28$
Reflections collected	17224	101049	44673
Independent reflections	6126 [R(int) = 0.0417]	13854 [R(int) = 0.0824]	14703 [R(int) = 0.0497]
Data/Restraints/Parameter	6126 / 45 / 351	13854 / 583 / 728	14703 / 274 / 801
Goodness-of-fit on F^2	1.039	1.016	1.015
Final R indices [I>2sigma(I)]	*R*1 = 0.0412 w*R*2 = 0.0875	*R*1 = 0.0597 w*R*2 = 0.1417	*R*1 = 0.0513 w*R*2 = 0.1062
R indices (all data)	*R*1 = 0.0545 w*R*2 = 0.0969	*R*1 = 0.0873 w*R*2 = 0.1630	*R*1 = 0.0942 w*R*2 = 0.1238
Largest diff. peak and	0.464 and –0.360	0.567 and –0.509	0.533 and –0.431

hole

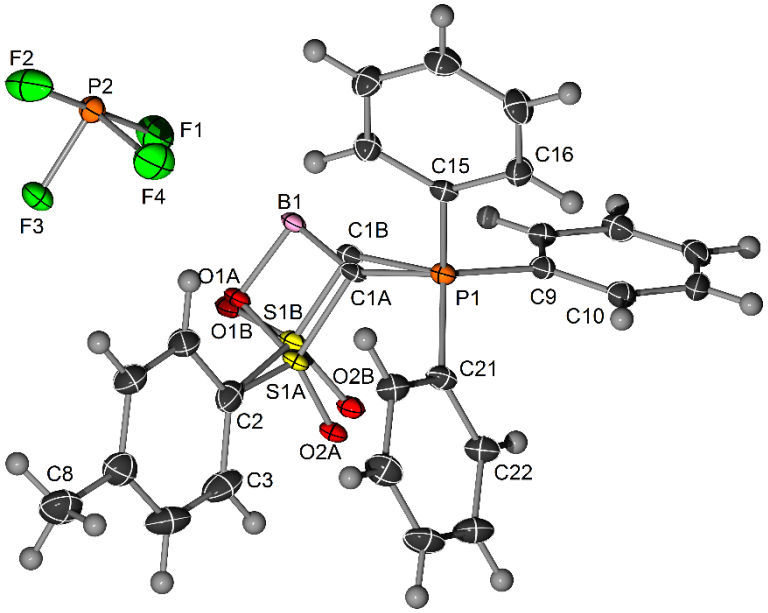


Figure S27. ORTEP Plot of complex **2e**. Ellipsoids are drawn at the 50% probability level.

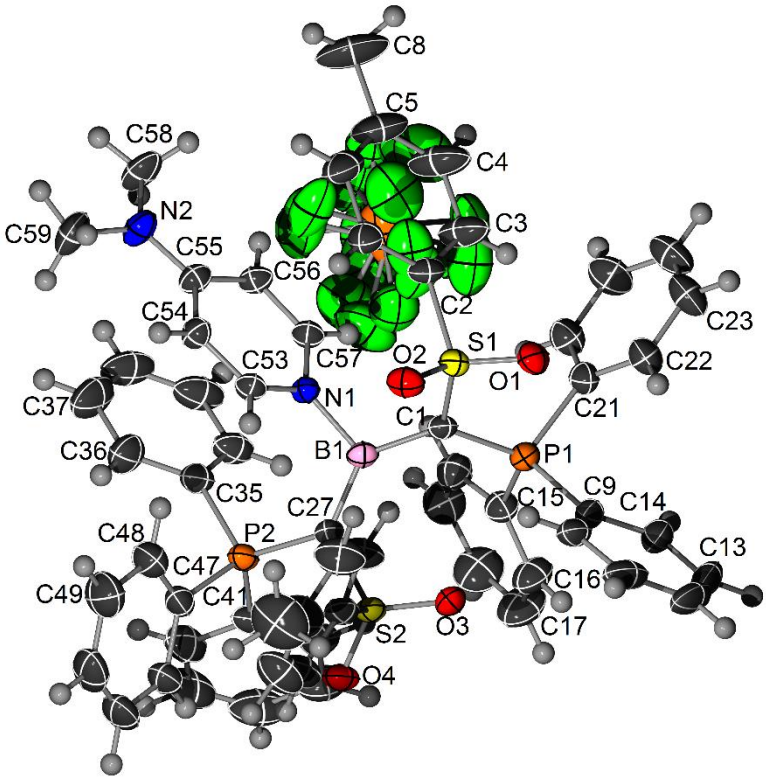


Figure S28. ORTEP Plot of complex **3a**. Ellipsoids are drawn at the 50% probability level.

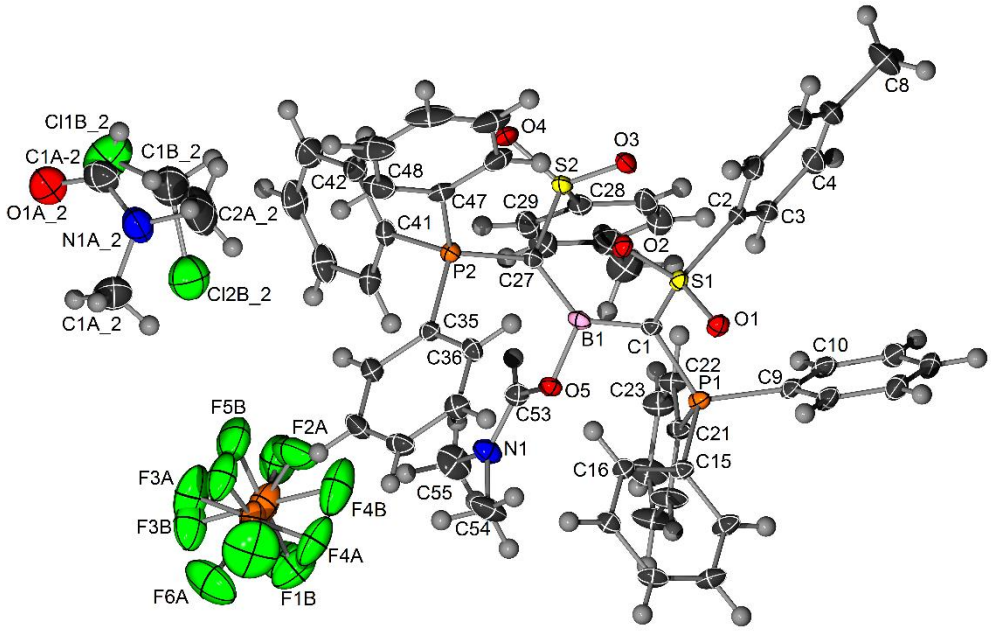


Figure S29. ORTEP Plot of complex **3b**. Ellipsoids are drawn at the 50% probability level. One DMF and one DCM solvent molecule are disordered over one position with occupation factors of 0.91 and 0.1. This disorder as well as the disordered PF_6 were refined using the PART keyword together with free variables.

Table S2. Data collection and structure refinement details for compounds **3c**, **4a** and **5**.

Compound	**3c**	**4a**	**5**
CCDC No.	CCDC 1520039	CCDC 1520040	CCDC 1520041
Formula	$C_{60}H_{59}BCl_6F_6NO_5P_3S_2$	$C_{18}H_{15}BN_6O_6$	$C_{52}H_{44}BFO_4P_2S_2$
Formula weight [g·mol^{-1}]	1368.62	422.17	888.74
Temperature [K]	100(2)	100(2)	100(2)
Wave length [Å]	1.54178	1.54184	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P-1* (2)	*P-1* (2)	*P-1* (2)
a [Å]	12.8258(4)	6.70382(19)	10.6603(4)
b [Å]	14.4919(3)	11.1662(3)	11.8096(5)
c [Å]	19.6214(4)	15.6334(4)	17.8344(7)
α [°]	90.1189(18)	84.573(2)	81.2250(10)
β [°]	100.383(2)	84.256(2)	89.5540(10)
γ [°]	95.098(2)	87.562(2)	79.6300(10)
Volume [Å^3]	3572.51(15)	1158.51(6)	2182.27(15)
Z	2	2	2
Calc. density [Mg·m^{-3}]	1.272	1.210	1.353
μ ($Mo_{K\alpha}$) [mm^{-1}]	3.873	0.782	0.247
F(000)	1408	436	928
Crystal dimensions [mm]	0.31 x 0.18 x 0.05	0.277 x 0.146 x 0.076	0.22 x 0.18 x 0.15
Theta range [°]	3.518 to 74.994	3.979 to 74.959	1.77 to 25.00
Index ranges	$-15 \le k \le 14$	$-8 \le k \le 8$	$-12 \le k \le 12$

	–18 ≤ k ≤ 18 –24 ≤ k ≤ 24	–13 ≤ k ≤ 13 –19 ≤ k ≤ 19	–14 ≤ k ≤ 14 –21 ≤ k ≤ 21
Reflections collected	54395	23374	26609
Independent reflections	14402 [R(int) = 0.0625]	4767 [R(int) = 0.0278]	7687 [R(int) = 0.0273]
Data/Restraints/Parameter	14402 / 268 / 853	4767 / 0 / 301	7687 / 0 / 561
Goodness-of-fit on F^2	1.053	1.068	1.003
Final R indices [I>2sigma(I)]	*R*1 = 0.0653 w*R*2 = 0.1817	R1 = 0.0512 wR2 = 0.1376	R1 = 0.0319 wR2 = 0.0767
R indices (all data)	*R*1 = 0.0791 w*R*2 = 0.1977	R1 = 0.0588 wR2=0.1447	R1 = 0.0423 wR2 = 0.0818
Largest diff. peak and hole	1.068 and -0.513	0.371 and -0.320	0.362 and -0.404

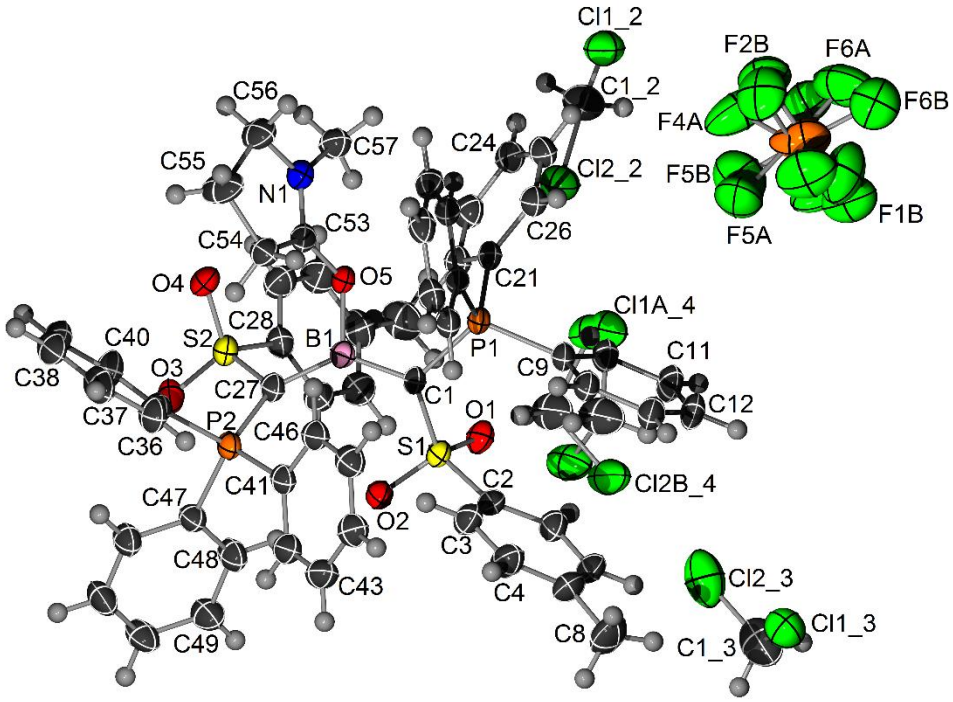


Figure S30.: ORTEP Plot of complex **3c**. Ellipsoids are drawn at the 50% probability level.

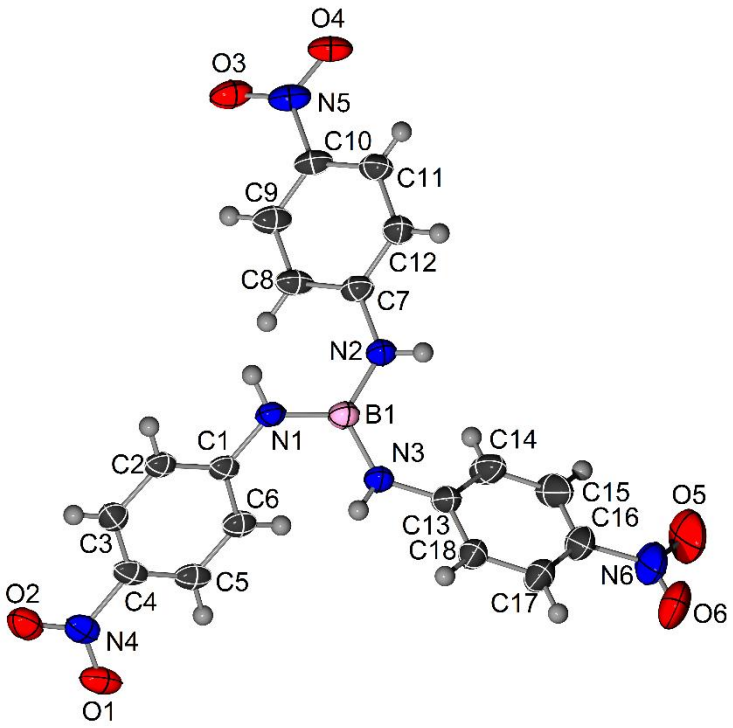


Figure S31. ORTEP Plot of complex **4a**. Ellipsoids are drawn at the 50% probability level.

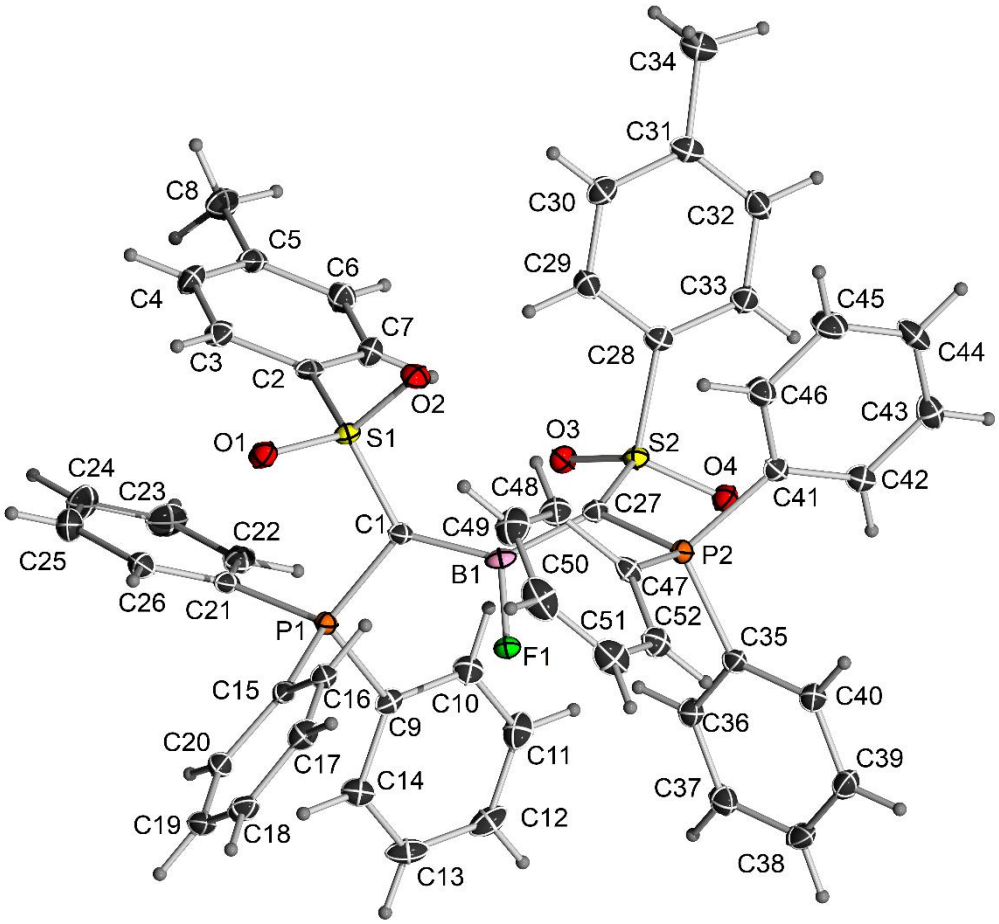


Figure S32. ORTEP Plot of complex **5**. Ellipsoids are drawn at the 50% probability level.

4. Thermogravimetric analysis of 2e

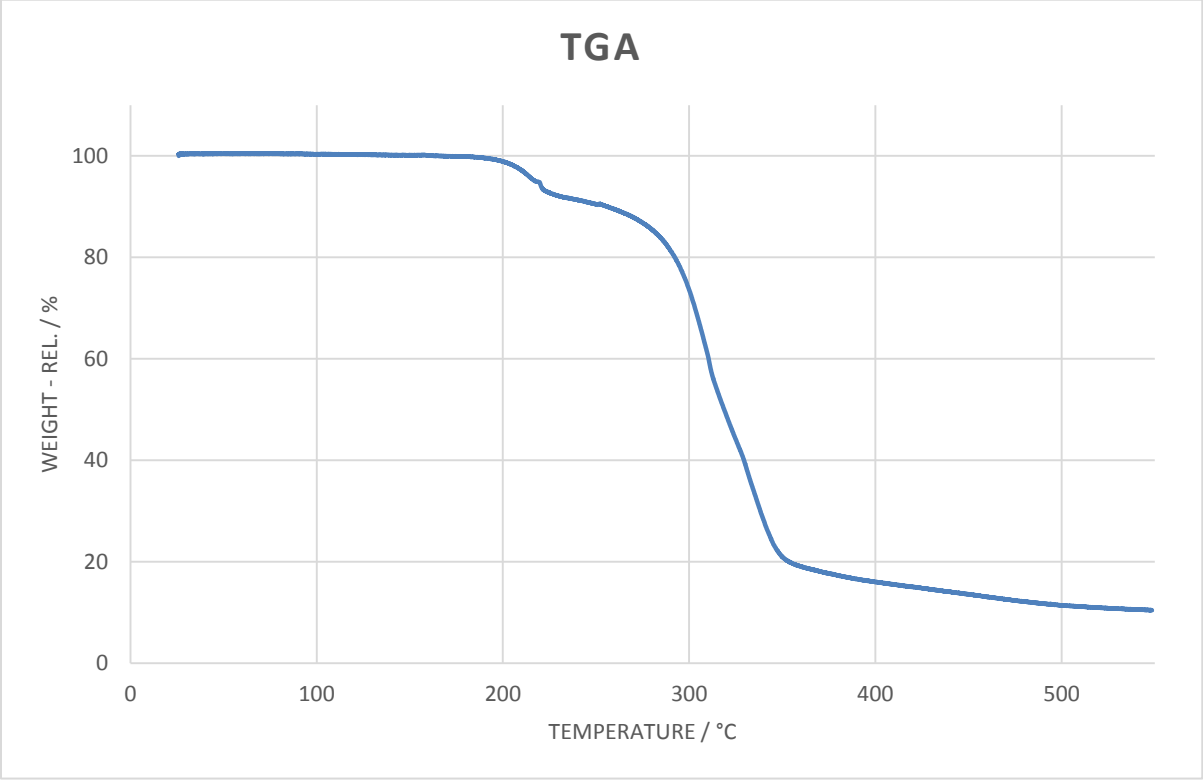


Figure S33. TGA of compound **2e**. Gas: N_2. Heating rate: 3 °C/s

5. Computational Studies

Methods.

All calculations were performed without symmetry restrictions. Starting coordinates were obtained with Chem3DUltra 10.0 or directly from the crystal structure analyses. All calculations were done with the Gaussian09 (Revision D.01) program package[5] using Density-Functional Theory (DFT) with the dispersion corrected M062X functional.[6] Geometry optimizations on the real systems were performed with 6-31G(d) basis set followed by a single-point calculation with the 6-311+G(d,p) basis set. In case of the hydrogen-substituted model system the later was also employed for energy-optimization. Harmonic vibrational frequency analyses were performed on the same levels of theory as used for the energy optimizations. In case of the real systems, thermal corrections obtained from the calculations with the smaller basis set were used for the correction of the SCF energies of the single-point calculations. Natural bond orbital (NBO) analyses were performed with the energy-optimized structures using the NBO 5.0 program.[7]

The vibrational frequency analyses showed no imaginary frequencies for the ground states and one imaginary frequency for the transition state. Thereby, the frequency corresponds to the expected translational motion of the transition state. An intrinsic reaction coordinate (IRC) calculation[8] was carried out to ensure the connectivity of the reported minima and transition state for the dynamic behaviour of **2**. Table S3 gives the energies of all calculated compounds, Table S4-S15 the Cartesian coordinates of all optimized compounds. Figure S34 and S35 show the structures of the compounds.

Table S3. Calculated energies [in kJ/mol] of the optimized structures [M062x/6-311+g(d,p)].

Compounds	SCF energy	Enthalpy	Free Energy	ΔH	ΔG
Potential isomers of boron cation **2**					
Xray *syn*-**2**^{Ph}	-9802500,44	-9800313,42	-9800676,94		
anti-**2**^{Ph}	-9802494,33	-9800307,60	-9800679,61	5,82	-2,67
cis(PPh_3)-**2**^{Ph}	-9802474,74	-9800287,06	-9800643,50	26,36	33,44
Borinium isomer	-9802430,47	-9800242,81	-9800606,26	70,61	70,68
borinium	-9802449,59	-9800261,66	-9800627,99	51,77	48,95
2^{Ph}-TS	-9802405,08	-9800221,51	-9800579,47	91,91	97,48
Adduct formation					
DMF	-652359,42	-652067,37	-652162,30		
DMF adduct	-10454912,19	-10452423,55	-10452815,43	-42,76	23,81
Pyridine	-651748,43	-651498,57	-651584,11		
Pyridine adduct	-10454326,54	-10451881,94	-10452263,48	-69,95	-2,42
Acetone	-507034,82	-506795,04	-506886,97		
Acetone adduct	-10309524,03	-10307090,03	-10307476,12	18,43	87,79

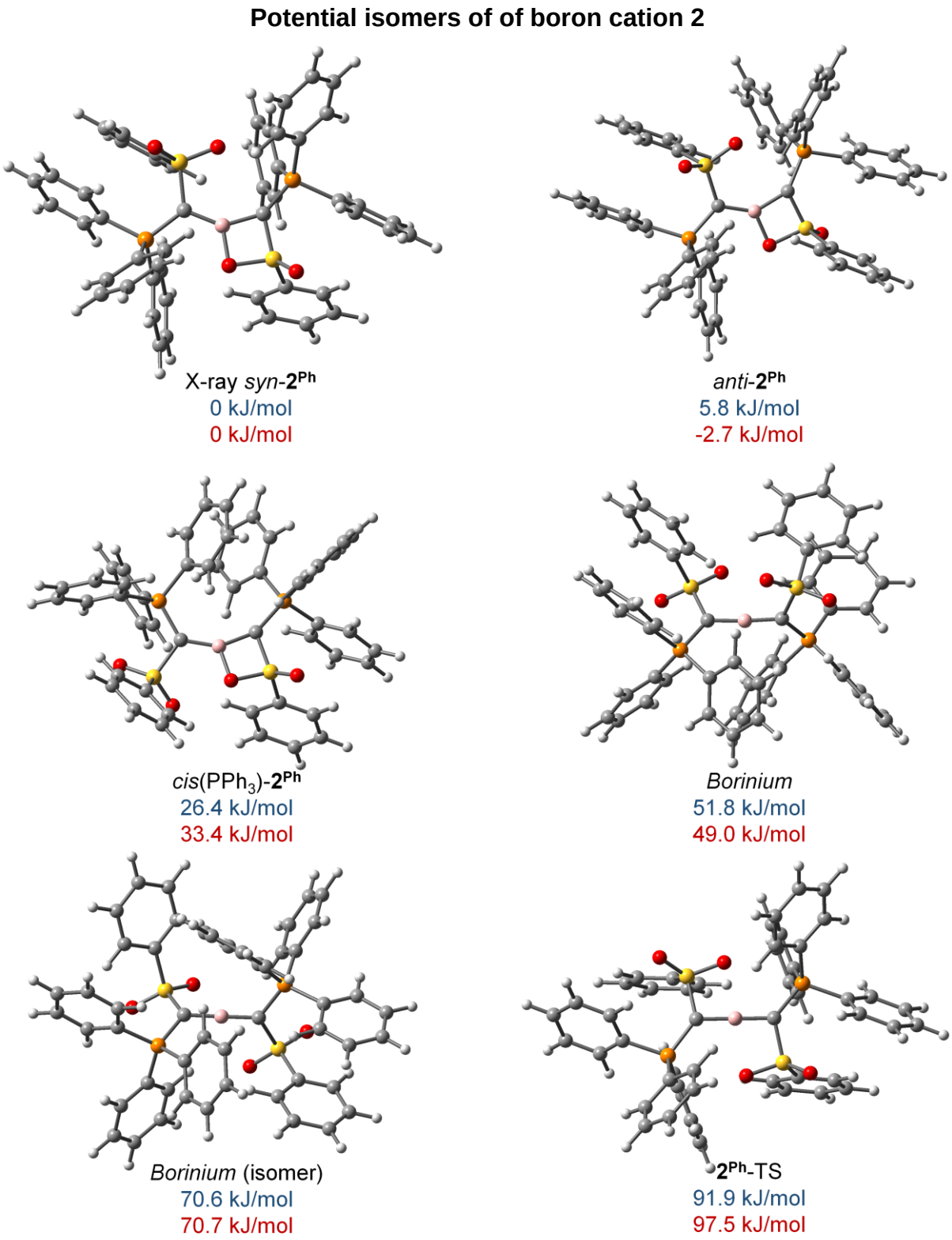


Figure S34. Displays of the energy-optimized structures of the different isomers of $\mathbf{2^{Ph}}$ and transition state $\mathbf{2^{Ph}}$-TS (enthalpies are given in blue, free energies in red; M062X/6-311+G(d,p)).

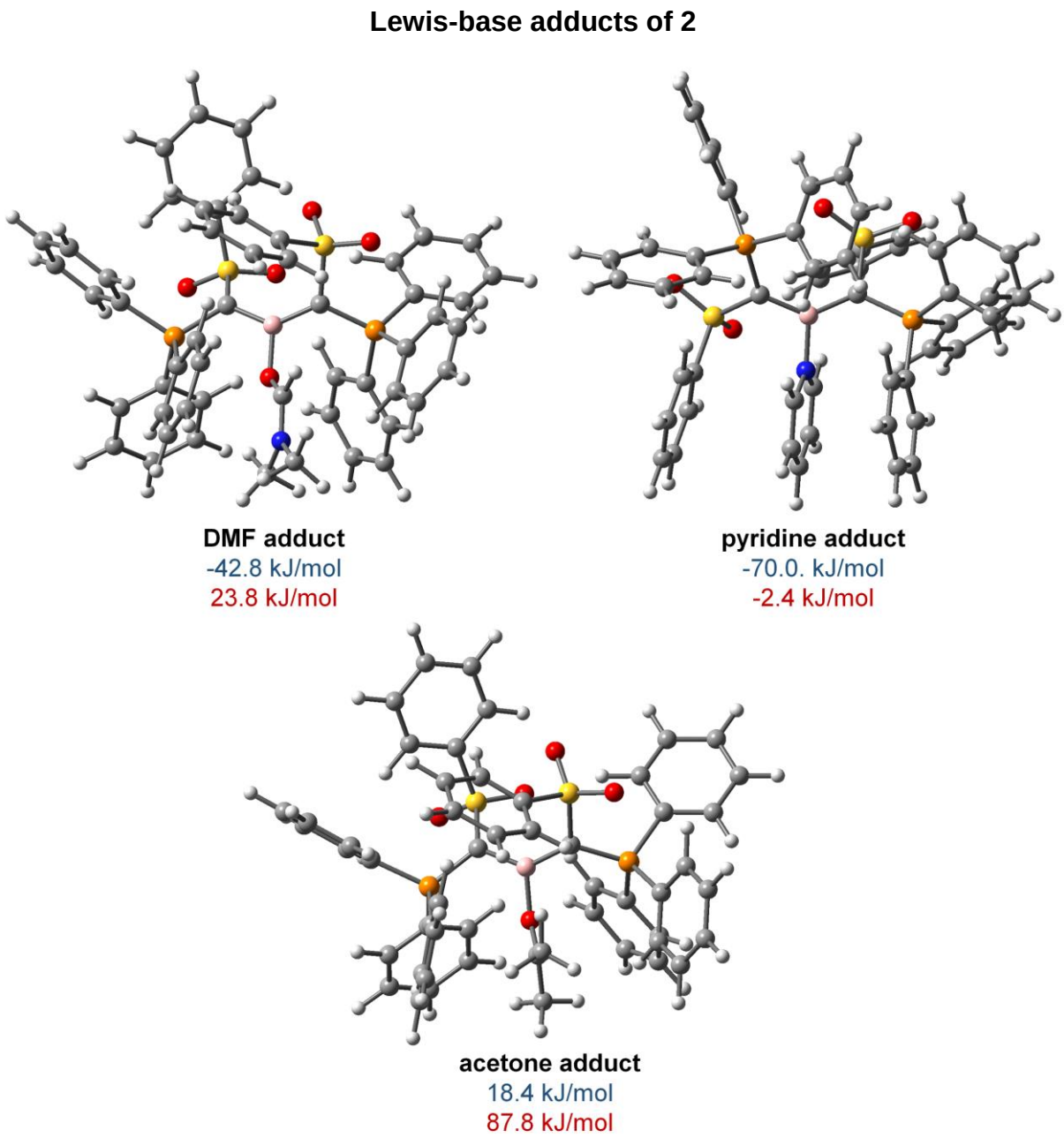


Figure S35. Displays of the energy-optimized structures of the different Lewis base adducts of (enthalpies are given in blue, free energies in red; M062X/6-311+G(d,p)).

Table S4. Cartesian coordinates of *syn*-**2**^{Ph}.

Atom type	x	y	z
S	1.328750184	-1.8492662361	0.7040415465
C	-3.090526604	3.7240796833	-2.9635889683
C	1.9543967635	-2.4735990585	-0.8503581745
C	1.2527404987	-2.1829676104	-2.018524307
C	1.7428295589	-2.654689197	-3.2309108788
C	2.9141540532	-3.4142868964	-3.2621597273
C	3.5907739872	-3.7126184354	-2.0826540603
C	3.1095992977	-3.2438949595	-0.8610269153
C	2.4672004704	2.0394669154	-0.8956337611

C	2.6041369102	3.4123791255	-0.6846946804
C	2.351376294	4.3016821444	-1.7282604574
C	1.981102532	3.8239957496	-2.9821460738
C	1.8336266546	2.452232472	-3.1929411185
C	2.0550449236	1.561117143	-2.1480904344
C	3.2082365436	1.7053869819	1.9333938534
C	4.4210186459	2.4073924492	1.9735888546
C	2.37330637	1.6781587618	3.0500762352
C	2.7422602702	2.3681156607	4.2029135161
C	3.9379088315	3.0785591366	4.2377848287
O	-0.077403755	-2.2805333172	0.7973030172
O	2.2681509735	-2.2835901436	1.7400673107
S	-1.7061762313	1.929679488	0.9553788081
O	-0.1034132927	2.0365629127	0.9088302826
O	-2.3709422909	2.6105485341	2.0505522784
C	-2.2103063807	2.7039430582	-0.5630619054
C	-1.2900066929	2.8729296451	-1.5958687831
C	-3.5558367178	3.0386987271	-0.6962384842
P	-2.6824375293	-0.953042059	0.5351680322
C	-4.2794709733	-0.083736201	0.466854357
C	-5.0729590794	-0.0335408509	-0.681873422
C	-4.7053322443	0.5518719969	1.6423823155
C	5.8216598254	-1.01607824	-1.5942472118
C	6.42946733	-1.7507916588	-0.579938286
C	5.9366827658	-1.6884440743	0.7226279681
C	4.8309698305	-0.8976822105	1.0133622152
C	4.2121076245	-0.1675364307	-0.0102992432
C	-2.3747734076	-1.6988869088	-1.084889316
C	-2.2770661041	-0.8475567084	-2.1931567741
C	-1.4976576251	0.2579820601	0.9053417128
C	-1.8653805574	-2.7589679714	-3.6050191652
C	4.7796046945	3.0971963896	3.1245991471
C	-2.0320510809	-1.3820981209	-3.4543457029
C	-2.9035037886	-2.2188744087	1.8003065125
C	-3.9969537164	-3.0845995147	1.677428748
C	-1.7444194878	3.3949916417	-2.8019817215
C	-4.2281114991	-4.0411276764	2.6583979788
C	-3.3814873872	-4.1188421196	3.7637316178
C	-2.3047854254	-3.2450131033	3.8900466493
C	-5.9028123799	1.258285701	1.6536488142
C	4.7143995125	-0.2208676164	-1.3135157236
C	-6.2746017432	0.6719674957	-0.6607781912
C	-6.685542262	1.3215159359	0.5002773526
C	-2.0582573306	-2.2910235914	2.9070580874
C	-2.187111752	-3.0739037697	-1.2324247189
B	-0.0044599206	0.5566532993	0.7718970162
C	-1.9322933997	-3.5995261914	-2.4966890681
C	-3.9918119168	3.5488317225	-1.9153382584
C	1.2936868185	-0.12570532	0.5647880291
P	2.7509582955	0.8179627764	0.4231235974
H	0.3386807157	-1.5939943834	-1.9722705995
H	1.2060691383	-2.4380949131	-4.1498187055
H	4.4976617928	-4.3083320105	-2.1096663052
H	3.6200843798	-3.4539158423	0.0733135238
H	2.8895576137	3.7908794346	0.2916759355
H	2.4479130012	5.3688697672	-1.558615767
H	1.8024620521	4.5205497755	-3.7956315773
H	1.5368717084	2.0772382059	-4.1676952577
H	1.9049041808	0.4939323722	-2.3002756669
H	5.0842424403	2.4055650808	1.1112529585
H	1.4511380373	1.1061237469	3.0233477805
H	2.0957261429	2.3451577331	5.0736787382
H	4.2228343169	3.6141540623	5.1376864976
H	-0.2437503402	2.6225449664	-1.4514738307
H	-4.2428685605	2.9083350023	0.1354298223

H	-4.7626839329	-0.5411149902	-1.5894093513
H	-4.0996828399	0.5014509316	2.5438877068
H	6.2095663515	-1.0565370881	-2.6067649506
H	7.2950915104	-2.3672022617	-0.8018397671
H	6.4129909283	-2.2555375736	1.5155297958
H	4.4384122546	-0.8639654088	2.0247074854
H	-2.3951474129	0.2286039837	-2.0737708595
H	-1.6739282081	-3.1762353107	-4.5888844169
H	5.7175234564	3.6415369983	3.1586905781
H	-1.9699561031	-0.7248489474	-4.3159106225
H	-4.6680830718	-3.0082362181	0.8243036821
H	-1.0396576972	3.5514970131	-3.6125089329
H	-5.0706966068	-4.7181470701	2.5658118425
H	-3.5659574131	-4.8630316646	4.5318904938
H	-1.6490639832	-3.3090695586	4.751743418
H	-6.2257981464	1.7539245141	2.5629918165
H	4.2571931775	0.3559583065	-2.1099082277
H	-6.890984882	0.7076205939	-1.553188539
H	-7.6228851847	1.8686753278	0.5124464156
H	-1.2115738299	-1.6177336262	2.9831868058
H	-2.2087590809	-3.7226500637	-0.362597077
H	-1.7768055115	-4.6668424856	-2.6124596172
H	-5.0364419426	3.813685511	-2.040414319
H	3.2945810495	-3.7798302788	-4.2108340842
H	-3.4366243843	4.128639361	-3.9092539724

Table S5. Cartesian coordinates of *trans*-**2**$^{\mathbf{Ph}}$.

Atom type	x	y	z
S	1.2265924566	-1.7375783741	0.6762504963
C	1.8686423255	-2.4467772792	-0.8344696015
C	1.240713353	-2.1430835273	-2.0399373639
C	1.7375642121	-2.6983660421	-3.2131416036
C	2.843398696	-3.5490974737	-3.16938008
C	3.4485467563	-3.8541843011	-1.9532644772
C	2.9597660831	-3.3032217105	-0.7699984384
C	2.577945795	2.3333189077	-0.4607098882
C	3.058865425	3.5647083808	-0.012171265
C	2.9415229524	4.6904585954	-0.8238072645
C	2.3456852509	4.5910325576	-2.0769060917
C	1.8532241141	3.3650358195	-2.5216886428
C	1.9620982241	2.2389592907	-1.71588525
C	3.2045694183	1.2672553328	2.2269795234
C	4.4568009532	1.8397683721	2.4882891074
C	2.3250848867	1.0007549836	3.2762528362
C	2.6816254303	1.3345793875	4.5806799166
C	3.9137674723	1.928401809	4.8360844614
O	-0.1751984849	-2.1782038635	0.7832072793
O	2.164407618	-2.0945554434	1.747036893
S	-1.8674973735	1.9731176249	0.3544603899
O	-0.2682572232	2.1388768805	0.3738691182
P	-2.7581972741	-0.9386895425	0.2659048419
C	-4.3661677196	-0.1027959306	0.1089480739
C	-5.1283963319	-0.1143281312	-1.0600258662
C	-4.8264939425	0.5863310244	1.23953036
C	5.4063020156	-0.9603446327	-1.991027598
C	6.1707891205	-1.7383140952	-1.1236511757
C	5.9052136556	-1.7302289858	0.2432740408
C	4.8739648307	-0.9453005271	0.7506930536
C	4.1144421877	-0.1546164276	-0.1187234822
C	-2.4024007288	-1.8226911999	-1.2689491293
C	-2.2980739446	-1.0656505117	-2.4431310112

C	-1.6009305309	0.3237569118	0.5358732032
C	-1.7931005682	-3.0789971726	-3.6703128894
C	4.8040524253	2.1769502039	3.7911095136
C	-2.0043282057	-1.7002726242	-3.6459362141
C	-2.9886857609	-2.0748838432	1.6496078386
C	-4.0375817562	-2.9984420736	1.5777104782
C	-4.2835876094	-3.8437900435	2.6534393144
C	-3.4977832506	-3.7523902938	3.801278478
C	-2.4664212068	-2.8195663056	3.8761589228
C	-6.0267989603	1.2846032303	1.1859832553
C	4.3818123202	-0.1642937947	-1.4918308567
C	-6.3359593663	0.579411274	-1.1022078959
C	-6.7801803647	1.2834648628	0.0128912084
C	-2.2055846352	-1.9780498611	2.7992566294
C	-2.1724091776	-3.1988059885	-1.2889167801
B	-0.1071695042	0.6642461234	0.4516899506
C	-1.8665941842	-3.8229696512	-2.4954347918
C	1.2072407088	-0.0211929559	0.4491919586
P	2.7296728749	0.8243318121	0.5342274424
H	0.3769793339	-1.4814998526	-2.0551386442
H	1.2588762887	-2.4710832322	-4.1608719456
H	4.3065820768	-4.5182848206	-1.9223335872
H	3.4163275837	-3.5156873897	0.1909919483
H	3.5063133594	3.6577915179	0.9715041716
H	3.3111124492	5.6471961449	-0.4700406688
H	2.2548144269	5.4711453366	-2.7053087978
H	1.3738475876	3.289611414	-3.4920867279
H	1.5500949556	1.2884498086	-2.0465475016
H	5.1628302031	2.0077046651	1.678080493
H	1.3829521726	0.5014307757	3.0684117787
H	2.0027456431	1.1168653079	5.3987480847
H	4.1910647163	2.1856459546	5.8533422364
H	-4.7912311962	-0.6626050418	-1.9335053911
H	-4.2525418522	0.5680622625	2.1643716378
H	5.6101852921	-0.9684568703	-3.0566584068
H	6.9760024792	-2.3522596784	-1.5152149896
H	6.4973443046	-2.339057982	0.9187664205
H	4.6477606172	-0.963265231	1.8118787242
H	-2.4394585864	0.0138330788	-2.4136574252
H	-1.5590219141	-3.5730338225	-4.6082663467
H	5.7722220286	2.6226785829	3.9938640359
H	-1.935710782	-1.1195610133	-4.5602574866
H	-4.663625282	-3.0534557199	0.6894685272
H	-5.0909176339	-4.5664176941	2.5994261851
H	-3.6931756531	-4.4104985685	4.6418765458
H	-1.8559412857	-2.7540203125	4.7705199455
H	-6.3762582858	1.8213721225	2.0621879647
H	3.7999929975	0.4501522876	-2.171572492
H	-6.9285359435	0.568347164	-2.0109149622
H	-7.7203467774	1.8240372466	-0.0276575469
H	-1.3895956216	-1.263704363	2.8327587612
H	-2.1991094342	-3.7698002348	-0.3662390681
H	-1.6752091417	-4.8905528555	-2.5140742715
H	3.2307218551	-3.9779584521	-4.0883330475
C	-2.3888900114	2.8681547579	1.7969287538
C	-3.4585423226	3.748526631	1.6785899374
C	-1.7502726256	2.6217679215	3.0110302976
C	-3.8958318546	4.4121906281	2.8228167635
H	-3.9272742262	3.9032626485	0.7124138181
C	-2.1961356829	3.2958086686	4.1402668862
H	-0.9189008072	1.9244022019	3.0649823309
C	-3.2676250965	4.1860159196	4.0446882272
H	-4.7253684082	5.1079609632	2.7558487523
H	-1.7095377765	3.1294858722	5.095278944
H	-3.6127455802	4.7070340983	4.9318251754

O	-2.5581617875	2.5361235161	-0.7945911774

Table S6. Cartesian coordinates of *cis*(PPh_3)-**2^{Ph}**.

Atom type	x	y	z
S	2.5970505843	0.8774930517	-0.2910667282
C	-2.9600595824	4.452016433	-1.6070329791
C	3.5290224691	1.3595635114	1.1500144478
C	3.1055163284	2.4484753338	1.9055094862
C	3.8304283327	2.7914153235	3.043430089
C	4.9552260488	2.0528434081	3.406062613
C	5.3714938982	0.9731541648	2.6287624994
C	4.6600116224	0.6197415049	1.4869731229
C	0.6881608088	-3.1029103101	0.5640273046
C	0.2691921248	-4.2831821956	-0.0580070909
C	-0.465675492	-5.2262007217	0.6535510604
C	-0.7925310374	-5.0015720406	1.987857692
C	-0.3898350033	-3.8227710365	2.6090930175
C	0.3449811055	-2.8733365396	1.9028772166
C	1.7184532155	-2.2098607859	-2.0771722257
C	2.1180814797	-3.4206822892	-2.655537967
C	1.2871209888	-1.1604776517	-2.892709277
C	1.2221515798	-1.3334578028	-4.2726136604
C	1.58371281	-2.5528862367	-4.8421047581
O	1.8829444877	2.0632572112	-0.7751037553
O	3.5265587759	0.1876823954	-1.1968782468
S	-1.4591935703	1.5347537827	1.4965652178
O	0.1275258027	1.576937189	1.3478944069
O	-2.0287018326	1.8795838	2.7882097578
C	-2.0098428283	2.7145806951	0.2930421312
C	-1.284647443	2.8636869658	-0.8897922948
C	-3.1822104827	3.4134734927	0.5583323182
P	-2.7758444073	-1.0577835706	0.8283289201
C	-4.1487394126	0.0189630204	0.3115712319
C	-4.2547748279	0.395278577	-1.0332058512
C	-5.0269376828	0.5513638756	1.2614338911
C	5.0097911351	-3.0972334955	1.9899658759
C	6.0662242647	-3.079727697	1.082687384
C	5.8350996402	-2.7551298935	-0.2530005505
C	4.5509145367	-2.439766975	-0.6852918803
C	3.4883690475	-2.4596215065	0.2244487572
C	-2.5196096819	-2.3235985171	-0.4353144823
C	-1.7498864365	-1.9973532414	-1.5594373923
C	-1.3636837682	-0.0743846604	0.9813417085
C	-2.256514182	-4.1505734959	-2.5207339415
C	2.0346805567	-3.5953084331	-4.0338128221
C	-1.6170911342	-2.9143298738	-2.59757765
C	-3.3111801049	-1.7817381575	2.3994599372
C	-4.531881948	-2.4658300755	2.4928273543
C	-1.7764590265	3.7497378318	-1.8409940059
C	-4.9516685609	-2.9664511511	3.7193558201
C	-4.1723595458	-2.7633219154	4.8588447076
C	-2.9801293423	-2.05038323	4.7747407666
C	-6.0221893707	1.4397782925	0.8579815861
C	3.7214600093	-2.7918310955	1.5624732024
C	-5.2452950461	1.2868297652	-1.4249447395
C	-6.1329606298	1.8031815966	-0.4806412862
C	-2.5468054918	-1.5576441554	3.5456362865
C	-3.1328702002	-3.5759295076	-0.346537062
B	0.145600313	0.1967221048	0.7888327979
C	-3.006143414	-4.4823337798	-1.395859115
C	-3.6573880015	4.2905813839	-0.4126055984

C	1.41073797	-0.3224782108	0.2012811623
P	1.8136830117	-1.9447224956	-0.280002451
H	2.2345443305	3.014632981	1.5933231061
H	3.5214775513	3.6419443463	3.6421683015
H	6.2584783109	0.41125317	2.9035991743
H	4.9862134288	-0.1984345968	0.8514747352
H	0.4918834771	-4.4648152357	-1.1030963259
H	-0.7864671717	-6.1370633813	0.1579661611
H	-1.3583131	-5.7424470473	2.5438232417
H	-0.6448252126	-3.64116095	3.6479020575
H	0.6619765907	-1.9585814896	2.3963743216
H	2.5175010648	-4.2200921375	-2.0359246576
H	1.0248347948	-0.2032424022	-2.4497259798
H	0.9030516852	-0.5102676155	-4.9034827639
H	1.5357911652	-2.6848420995	-5.918410395
H	-0.3362760795	2.3500930593	-1.0391381759
H	-3.6967045695	3.2803307834	1.5040464165
H	-3.5705014815	-0.0116086885	-1.77250918
H	-4.9369637127	0.2793977056	2.3088784825
H	5.1857097616	-3.3499285797	3.0303255603
H	7.0711653246	-3.3189840074	1.4159651394
H	6.6582329935	-2.733037298	-0.9594347846
H	4.3823715837	-2.139041719	-1.7133638781
H	-1.2419709869	-1.0363762216	-1.6112151218
H	-2.1599211347	-4.8601709051	-3.3364927983
H	2.3430191843	-4.53626236	-4.4775861581
H	-1.0067540053	-2.6648056642	-3.4602980013
H	-5.1679002786	-2.5820493038	1.6184992625
H	-1.2222518419	3.9060156147	-2.7602427239
H	-5.8940195547	-3.4992883012	3.7906909626
H	-4.5084744755	-3.1457503052	5.8172636466
H	-2.3896456079	-1.8667595392	5.6664300135
H	-6.709125426	1.8452959477	1.5936722365
H	2.9052416117	-2.8101379225	2.2776018663
H	-5.327690708	1.5764447143	-2.4672724408
H	-6.9116149514	2.4925880374	-0.7918204283
H	-1.6259724653	-0.9856865169	3.4742546852
H	-3.6888241827	-3.8591268934	0.5402912325
H	-3.4880526056	-5.4523189281	-1.3267314672
H	-4.5684002101	4.8507399828	-0.2293157847
H	5.517510729	2.3278507522	4.2928670046
H	-3.3312922853	5.1429132477	-2.3572828621

Table S7. Cartesian coordinates of the *borinium* structure.

Atom type	x	y	z
S	1.9159548513	0.9617371101	1.5709002832
P	2.3461798963	-1.4838676659	-0.2544252896
O	2.6824526811	0.2384923693	2.5871725573
C	1.3490078145	-0.1680611788	0.3539161922
S	-1.290714406	1.7021542446	-1.833503728
P	-2.6980825671	-0.1685875968	0.2041368195
O	0.739155995	1.7421711998	1.9744767332
O	0.0860623965	1.7643361373	-2.3429035228
O	-2.4024436868	1.4676692423	-2.754862462
C	-1.2686044492	0.4381136413	-0.609984989
B	0.0283706075	0.0898720801	-0.1229307183
C	-1.6354454567	3.2200597438	-0.9700465078
C	-0.6451222566	3.7809806779	-0.1683146883
C	-2.8985053011	3.7892429139	-1.0987484733
C	-0.9340579227	4.9516199242	0.5237381799
H	0.3299030658	3.3122827736	-0.0794018309

C	-3.1724015626	4.9621055591	-0.400235732
H	-3.6374861093	3.3220611336	-1.7414371223
C	-2.1934012884	5.5397360772	0.4056892413
H	-0.1740852483	5.4040609824	1.1519779337
H	-4.149679523	5.4252191458	-0.4895640525
H	-2.4120273174	6.4559642023	0.9455316571
C	-3.5311069677	1.1803919764	1.0621302716
C	-4.8900808979	1.4477440117	0.880388556
C	-2.7391787949	2.0095427847	1.872800792
C	-5.4664607859	2.5342998752	1.5340579895
H	-5.4922370493	0.8267835952	0.2246941994
C	-3.3297962027	3.0835301263	2.5260740584
H	-1.6678613517	1.8342158918	1.9729302382
C	-4.6906528133	3.3433925079	2.3586826724
H	-6.5209114305	2.7478125032	1.3939008254
H	-2.7211504675	3.7295731425	3.1500400487
H	-5.1441835673	4.1894114362	2.8656656125
C	-3.8561069047	-1.0740729543	-0.8449789214
C	-4.9319631062	-1.7179555795	-0.2155332558
C	-3.644135804	-1.2270135735	-2.2158241356
C	-5.8117392541	-2.4844393663	-0.968009629
H	-5.0759863624	-1.6270291369	0.8591118039
C	-4.5293988794	-2.0055113366	-2.9596874162
H	-2.8129286597	-0.7259932758	-2.6976736882
C	-5.6101249505	-2.6258012824	-2.34173306
H	-6.6482341559	-2.9777146177	-0.48443653
H	-4.3740092949	-2.1183380467	-4.0276411792
H	-6.2978298261	-3.2268710566	-2.9280145841
C	-2.0974793522	-1.4110672645	1.380477028
C	-1.6115432211	-2.6109241208	0.8383243534
C	-2.1228700552	-1.2158926568	2.7605722341
C	-1.1614797861	-3.6138173861	1.6860220936
H	-1.5995014058	-2.762040741	-0.2401330412
C	-1.6735055664	-2.2328112009	3.6041268263
H	-2.4993910581	-0.2881057385	3.1798904033
C	-1.2035198149	-3.427915012	3.0695007286
H	-0.7858025011	-4.5436557134	1.2701943178
H	-1.7018111219	-2.0882905639	4.678954003
H	-0.8675219684	-4.2214797042	3.7298414969
C	3.0733728186	2.04283294	0.7419827628
C	4.1386467915	2.5200397375	1.5021575787
C	2.911983768	2.3813956889	-0.5995111508
C	5.0656871136	3.3640862893	0.8989465698
H	4.2421495175	2.2146912964	2.5385762606
C	3.8568048643	3.2156723703	-1.191241662
H	2.0798836606	1.993415703	-1.183508695
C	4.928310019	3.7046241013	-0.445697195
H	5.9000302862	3.7479851105	1.4770429171
H	3.7525994925	3.4802733278	-2.2383047901
H	5.6601590895	4.3542450169	-0.9154154872
C	1.3363721944	-2.30765263	-1.5093431356
C	1.0596678477	-3.6740853956	-1.3986358486
C	0.7622519377	-1.5505276688	-2.5415370801
C	0.2025243709	-4.2795816856	-2.3143701268
H	1.5009337188	-4.2594507264	-0.5973711846
C	-0.0929745849	-2.165810263	-3.4497402116
H	0.9526496689	-0.4820969945	-2.6283147121
C	-0.3768277552	-3.5261469004	-3.3332354878
H	-0.0133674306	-5.3395885541	-2.2294022668
H	-0.5386626995	-1.5755414326	-4.2443570201
H	-1.0488857097	-4.0010958063	-4.0410012527
C	2.7744038243	-2.6661916381	1.0344247436
C	3.8194676506	-3.5715172276	0.8077717001
C	2.0389623588	-2.7093857274	2.2200904907
C	4.117619276	-4.528498758	1.7704953452

H	4.3999186685	-3.5222429337	-0.1102673073
C	2.351797406	-3.6664383025	3.1810631186
H	1.2475677857	-1.9881667989	2.3985935278
C	3.3844615834	-4.5728691555	2.956603834
H	4.9269607053	-5.2308094758	1.6016898286
H	1.7964397023	-3.690546954	4.1131210732
H	3.6282515373	-5.3128347602	3.712301185
C	3.8914821017	-0.871747149	-0.9576768843
C	4.878717496	-0.4234004564	-0.0689464987
C	4.0582647413	-0.7241042486	-2.3371095618
C	6.0192890432	0.192582253	-0.5693404527
H	4.7435344218	-0.5365969972	1.0049971155
C	5.2103798794	-0.1156928266	-2.8271322103
H	3.3027935297	-1.0849184674	-3.0276991406
C	6.1823651758	0.3491806047	-1.9453960754
H	6.7784423666	0.5546298151	0.1160193439
H	5.3458133416	-0.005073366	-3.8978032783
H	7.0752175898	0.8308868054	-2.3312302719

Table S8. Cartesian coordinates of the *borinium* structure (isomer).

Atom type	x	y	z
S	-2.239830468	-1.1372969736	1.7960684692
P	-2.4359832809	1.23775752	-0.0843281573
O	-3.4958504699	-0.5046900835	2.2000457454
C	-1.4855740237	-0.0574383935	0.6249742826
S	2.116145559	1.0451372268	1.8396221542
P	2.3616124637	-1.1646822474	-0.2197548895
O	-1.2095099313	-1.5005641012	2.7664032705
O	1.0201084278	1.6415720727	2.6025209715
O	3.1733766104	0.2834638533	2.504426624
C	1.368482407	0.0104713033	0.6277040331
B	-0.0575469285	-0.0118913451	0.6224121446
C	2.9151003193	2.3469077973	0.9149064727
C	4.2675905652	2.5777991357	1.1327258303
C	2.1667942188	3.1110415333	0.0220121201
C	4.8881368659	3.612548711	0.4350866545
H	4.8123222596	1.9508909212	1.8312476929
C	2.8011004492	4.1322665787	-0.6750851981
H	1.1096129179	2.9031346034	-0.1308413138
C	4.1584756987	4.3841450401	-0.4652745165
H	5.9428945408	3.811904328	0.594737836
H	2.234586128	4.7383896489	-1.3751951515
H	4.6467669156	5.1890494956	-1.00590363
C	3.8745182268	-0.3816297867	-0.803239313
C	5.1239251912	-0.7655555495	-0.3129625901
C	3.7599296446	0.7001695255	-1.689460925
C	6.2642990234	-0.0892010789	-0.7417986266
H	5.2058368379	-1.5716424264	0.4093505702
C	4.9026770916	1.3619049722	-2.1167327125
H	2.7788252329	1.0420360725	-2.0146324553
C	6.1545776826	0.9620475828	-1.6465935945
H	7.2369650138	-0.3839185355	-0.3625340317
H	4.8167602163	2.2029896823	-2.7967311835
H	7.046504992	1.4849589168	-1.9771808291
C	2.7206854962	-2.6043880745	0.8038861009
C	3.465829425	-3.6560257474	0.2530075035
C	2.1841881008	-2.7055602649	2.0897620756
C	3.6919243145	-4.8020308883	1.0041516942
H	3.8634612158	-3.580660358	-0.7569945274
C	2.4106787068	-3.8646532127	2.82996886
H	1.5968981277	-1.8956727282	2.5114000668

C	3.1640730496	-4.9038956178	2.2922923576
H	4.2731632532	-5.6168522443	0.5856041342
H	1.9996197877	-3.9461410954	3.8305207448
H	3.3408440768	-5.8014360224	2.8763572647
C	1.3758130894	-1.7669657842	-1.616752368
C	0.213367434	-2.4735324956	-1.2870490263
C	1.6795593758	-1.5043127442	-2.9543299265
C	-0.6769141951	-2.8626494728	-2.2810893658
H	0.001237758	-2.7245330164	-0.2515935822
C	0.7939338855	-1.9136440407	-3.9502356887
H	2.5992168866	-0.9942889619	-3.2231805611
C	-0.3878637733	-2.5725985075	-3.6148075451
H	-1.5832974874	-3.3960974972	-2.007579777
H	1.031462913	-1.7197620169	-4.9914900271
H	-1.0739913207	-2.8800888771	-4.3976974839
C	-2.6566068815	-2.6433489326	0.9214217925
C	-1.844026933	-3.7610984426	1.0959662437
C	-3.7977018184	-2.6867384099	0.1243578115
C	-2.1671712182	-4.9399713176	0.427475693
H	-0.9870148077	-3.7034559135	1.7612810946
C	-4.1102237759	-3.8704566093	-0.5379603053
H	-4.4484991182	-1.8220311219	0.0501617175
C	-3.295282535	-4.9928060538	-0.3903714899
H	-1.547271261	-5.820721544	0.5592978828
H	-5.001720353	-3.918807646	-1.1551940878
H	-3.549300282	-5.9165872604	-0.9006145313
C	-1.3811665409	1.9745440977	-1.3692171552
C	-1.293650477	3.3660699517	-1.4839894998
C	-0.636434935	1.1540464452	-2.2292123311
C	-0.4690291225	3.9328786772	-2.4531902537
H	-1.8526960476	4.0081867165	-0.8108018257
C	0.1843619522	1.7299835117	-3.1938014255
H	-0.6890856723	0.0702323925	-2.1454314506
C	0.2724842676	3.1172967596	-3.3038310783
H	-0.406503263	5.0130639493	-2.538128085
H	0.7512094101	1.0886678594	-3.8618616135
H	0.914918983	3.5617690798	-4.0576649872
C	-2.8378551164	2.5220869686	1.1140116166
C	-3.8408562344	3.4583642171	0.8252514019
C	-2.0915113327	2.6162535917	2.2916516959
C	-4.0932740067	4.48985778	1.7214701058
H	-4.4237398716	3.379336715	-0.0893585782
C	-2.35549448	3.654898529	3.1813008652
H	-1.3086473474	1.8975887279	2.5177821011
C	-3.3511997422	4.5852927085	2.8991862653
H	-4.8715500865	5.2141131284	1.5051318383
H	-1.7792900804	3.7280851174	4.097238815
H	-3.5547346886	5.3889159594	3.5996615943
C	-3.974639226	0.642999089	-0.8278225235
C	-5.1558186849	0.6350982864	-0.075359588
C	-3.9504636273	0.0874870997	-2.111580513
C	-6.3091144496	0.0757480358	-0.6176975206
H	-5.1624873676	1.0291366552	0.9355330358
C	-5.1063399058	-0.4770404291	-2.6409560716
H	-3.0368086951	0.093858138	-2.6989155104
C	-6.2838910024	-0.4817691477	-1.8952514976
H	-7.2247475705	0.0670198612	-0.0359750584
H	-5.0897371615	-0.9056989271	-3.6375362623
H	-7.1859884106	-0.9184626248	-2.3120260044

Table S9. Cartesian coordinates of **2^{Ph}**-TS.

Atom type	x	y	z
S	-1.2279949289	-2.187143555	-0.3870684685
C	2.4281943434	3.261989285	3.3541695613
C	-1.6659871824	-2.3917093555	1.3262148711
C	-0.7631313227	-1.9722980538	2.3008349964
C	-1.152282104	-2.0230893731	3.6346604787
C	-2.4298493445	-2.4729864314	3.9737277794
C	-3.3180820079	-2.8914845263	2.9840160117
C	-2.9379648365	-2.8595191224	1.6435427644
C	-2.7735487583	1.5694451425	0.7889849574
C	-2.6962455745	2.9565500599	0.6466121727
C	-2.5742813982	3.7590868327	1.7789005646
C	-2.5257315721	3.1821636923	3.045366877
C	-2.5898361295	1.7955148649	3.1876797192
C	-2.708075359	0.9862675355	2.0625451196
C	-3.1261341204	1.4631783811	-2.1402672202
C	-4.3279352691	2.176696531	-2.2317488466
C	-2.2054801644	1.4887891974	-3.1870718363
C	-2.4835396195	2.2419451224	-4.3243481426
C	-3.6710964648	2.9622915601	-4.4126444161
O	0.2622684509	-2.256705219	-0.4811863549
O	-2.0284259678	-3.1244351938	-1.1616372702
S	1.2161643152	2.0595124031	-0.8443559461
O	-0.2744298073	2.1073006155	-0.9474164563
O	2.0140684702	2.8117868975	-1.8017431798
C	1.6580464035	2.6221191317	0.7857380394
C	0.7577704721	2.4184190141	1.8292720875
C	2.9305255452	3.146533268	0.9937329686
P	2.8299603411	-0.6000999198	-0.5476948372
C	4.2704833116	0.4959409584	-0.6047199518
C	5.1811155932	0.5935257608	0.4521859068
C	4.4683687141	1.2384226812	-1.7760803676
C	-6.2742518991	-1.3476068937	0.6646055326
C	-6.4548929835	-2.3362749632	-0.2997407665
C	-5.5641137797	-2.4481249991	-1.3665898746
C	-4.4825852249	-1.5803530383	-1.4637545439
C	-4.2818727691	-0.6070669581	-0.4763594476
C	2.7658084521	-1.3632450418	1.0962161723
C	2.7031027912	-0.523756189	2.2176778335
C	1.3948353054	0.3447676688	-0.8679416876
C	2.5232404299	-2.4618806966	3.6433276551
C	-4.5947229964	2.9302432537	-3.3679106434
C	2.5874600111	-1.0765399543	3.4888356075
C	3.1114058129	-1.879370095	-1.7900113363
C	4.3132416961	-2.596280598	-1.7313801277
C	1.1500904459	2.7504132068	3.1211586945
C	4.5774910026	-3.5732974059	-2.6829477088
C	3.6512741617	-3.8256347828	-3.6948943071
C	2.4636573585	-3.1027536141	-3.7580923326
C	5.5499719434	2.1067325979	-1.8674068972
C	-5.1897952569	-0.4787020933	0.5795840778
C	6.2656144147	1.4603806923	0.3487341227
C	6.4435556435	2.2226839803	-0.8033429473
C	2.1881502567	-2.125861729	-2.8053402054
C	2.6883754806	-2.7490428259	1.2507786809
B	-0.0060667012	-0.0869006843	-0.8325017931
C	2.5690699037	-3.293755765	2.5275278776
C	3.3138115717	3.4615782883	2.2961237376
C	-1.4068730058	-0.5160356598	-0.7725172457
P	-2.8413821308	0.475727439	-0.6560251809
H	0.2213541038	-1.6112878201	2.0145016636
H	-0.4567739128	-1.7105269055	4.4075207831
H	-4.3067232431	-3.2490027048	3.2527842453

H	-3.6105821867	-3.1865787727	0.8547916321
H	-2.7019064904	3.4052248954	-0.3415156051
H	-2.5089944507	4.8361979937	1.6677690228
H	-2.4342322135	3.8135303676	3.9238602635
H	-2.5497488049	1.3400023216	4.1723533921
H	-2.7593323356	-0.0939695266	2.1810155674
H	-5.0535936182	2.1385769514	-1.4219928356
H	-1.2798203205	0.9285790424	-3.1115186821
H	-1.7685219499	2.2670736375	-5.139620137
H	-3.8826677639	3.5487915004	-5.3009288213
H	-0.2272331688	2.0050269769	1.6282597373
H	3.6010582405	3.2992511519	0.1519676954
H	5.0500600071	0.0021190254	1.3521672392
H	3.7681601594	1.1583856647	-2.6019206254
H	-6.9783532369	-1.2486754505	1.4842213587
H	-7.2984414469	-3.0154211764	-0.2268303094
H	-5.7088969428	-3.2114178003	-2.1234536231
H	-3.7845112009	-1.6769531797	-2.2896297371
H	2.7544901168	0.5570725255	2.104763692
H	2.4337952027	-2.8930144992	4.6357343476
H	-5.5235619945	3.4857443757	-3.442052455
H	2.5494873884	-0.4229597838	4.3549024224
H	5.0408762876	-2.3877536319	-0.9498405035
H	0.4566242037	2.6084859129	3.9443818906
H	5.5063518338	-4.1320517081	-2.6401505967
H	3.860852845	-4.5869166961	-4.4394212224
H	1.7466034601	-3.2998141992	-4.547744658
H	5.69264247	2.6926541003	-2.7689405099
H	-5.0566097985	0.2896038083	1.333819651
H	6.9718608646	1.53676655	1.1689151295
H	7.2871479205	2.9015994647	-0.8778766755
H	1.2624505044	-1.5622372267	-2.8477408194
H	2.6919284514	-3.3966787271	0.3799845475
H	2.5037203999	-4.3699705498	2.646992146
H	4.3028755585	3.8679646746	2.4806991067
H	-2.7312983825	-2.5060931993	5.0160252154
H	2.732121481	3.5149602918	4.3651025394

Table S10. Cartesian coordinates of DMF.

Atom type	x	y	z
N	-3.188474063	-1.4793007435	0.1280230641
O	-0.9132514906	-1.3030126868	0.3071850798
C	-2.032114289	-1.0519038695	0.7037296744
C	-3.1456009058	-2.3052913209	-1.0594014063
C	-4.4848172117	-1.1364200888	0.6616438592
H	-2.221240626	-0.4314715934	1.6000744596
H	-3.6294876686	-3.2709974872	-0.8727519842
H	-2.1000339601	-2.4644515604	-1.3217692128
H	-3.6624266851	-1.8104790219	-1.8898471597
H	-4.3623904254	-0.5133083508	1.5509188844
H	-5.0430003379	-2.0378299498	0.9415754738
H	-5.0759323368	-0.5798813271	-0.0754587324

Table S11. Cartesian coordinates of the DMF adduct.

Atom type	x	y	z
S	-0.3332547697	6.6368961853	7.8618704823
P	2.2799079989	7.1346897481	6.6340458402

O	0.5751297553	7.1387650523	8.9106143352
N	3.3356017368	3.4530106327	4.0710992568
C	0.6962444292	6.4060089572	6.4641926002
B	0.5369573016	5.1621161109	5.6241522507
S	-1.9802001253	5.4454145009	4.3644332494
P	-0.9002333867	2.7788826297	4.82489975
O	-1.0805779238	5.3942707871	8.0981212058
C	-1.5480559383	7.9297493368	7.6221779687
O	-2.7474896676	6.0689584456	5.440972013
C	-1.122025205	9.2446830295	7.4408759522
O	-2.6831485337	4.5903890501	3.3935073791
C	-2.071532214	10.2467556396	7.2770484697
O	1.8438547678	4.4579574538	5.4090988932
C	-3.4303900721	9.9339205833	7.3191389495
C	-3.8403379513	8.6217615534	7.5363651217
C	-2.8977438184	7.6081785113	7.6916630133
C	2.2838913076	8.9168555526	6.9770977129
C	2.09977696	9.8177535015	5.9222531769
C	1.9841412041	11.1788472078	6.186311427
C	2.0614690436	11.6432497395	7.4979035509
C	2.2572062097	10.7475887244	8.5475160367
C	2.3644707881	9.3837137532	8.2943338153
C	3.3791345672	6.361795509	7.8597065904
C	3.048455014	5.1021781969	8.3630641121
C	3.91522966	4.4577052115	9.2412121472
C	5.1028165918	5.0737246606	9.629929486
C	5.4268310577	6.3383630762	9.142403857
C	4.5673942608	6.9845045547	8.2582666772
C	3.1306103558	6.9365795198	5.0207649886
C	2.4155391451	7.140449945	3.8324126359
C	3.0385218075	6.9493766987	2.6006994933
C	4.3761298666	6.5589150195	2.5405467635
C	5.0887805191	6.3538128369	3.7191242951
C	4.4690541164	6.5373146315	4.9553081826
C	-0.6329112942	4.5038831969	4.9468168028
C	-1.2491353292	6.7983977382	3.4481690162
C	-0.7430204733	6.5585420458	2.1731427329
C	-0.2041216563	7.6227725606	1.4552615617
C	-0.1631077975	8.8994732994	2.0211756608
C	-0.6823243208	9.1217808645	3.2957084029
C	-1.2417470717	8.067290343	4.0168904946
C	0.3096358231	1.9523990044	5.917115936
C	0.4687904407	2.4895596042	7.2042578721
C	1.3003053244	1.8560400022	8.1210378894
C	1.9681759949	0.6815018252	7.7743670333
C	1.7750593499	0.1219533291	6.5150124514
C	0.9373126721	0.7472010895	5.590171814
C	-0.7494993879	2.1044965886	3.1352465713
C	-1.8791028324	2.0457933884	2.3105919014
C	-1.7504791889	1.6546947479	0.9801603047
C	-0.5024378649	1.3286042245	0.4571671015
C	0.6283186055	1.3945222733	1.2685025151
C	0.5049473996	1.7839619925	2.5982942221
C	-2.4973244192	2.2717833563	5.5099863998
C	-3.0738123649	1.0481230698	5.1548129005
C	-4.2399324543	0.6306181543	5.7864799712
C	-4.8183066796	1.4238125215	6.7757551235
C	-4.2262549773	2.6287191783	7.1439413663
C	-3.0592105636	3.0599045898	6.5194063751
C	2.2191789265	4.1021612866	4.243750169
C	4.1603926205	3.0370673859	5.2075259452
C	3.788701822	3.0818063419	2.7358798023
H	-4.1702525224	10.7179915504	7.1924788657
H	0.2552446038	9.7258862806	1.4548275149
H	-0.0670034873	9.4893119009	7.4394173829

H	-1.7479930769	11.2728397668	7.1319034666
H	-4.8970829555	8.3804767798	7.5783919321
H	-3.193883634	6.5770275724	7.8384845005
H	2.032218714	9.464997822	4.8975464171
H	1.8379807182	11.87603885	5.367588887
H	1.9700923285	12.7052708046	7.7025440218
H	2.3107722265	11.1082111061	9.5692425973
H	2.4634909963	8.6811363739	9.1145424911
H	2.1075763952	4.6387053993	8.077626486
H	3.6553829617	3.480011006	9.6350206442
H	5.7716136328	4.5741386663	10.3235197926
H	6.3441381904	6.8257941384	9.4560110903
H	4.8191577451	7.9743691173	7.884870691
H	1.3670589047	7.4294743768	3.8659535052
H	2.4717525473	7.1175887948	1.6905498379
H	4.8618937477	6.4255804672	1.5783841554
H	6.1336671742	6.059217876	3.6822657254
H	5.0340625709	6.3593517338	5.8645266264
H	-0.8102188441	5.5601275563	1.7470869476
H	0.166247619	7.4642007781	0.4466019055
H	-0.6699043256	10.1175695608	3.7290159473
H	-1.6839494988	8.2195485859	4.9968333259
H	-0.0700471604	3.389940499	7.5026573836
H	1.402261112	2.2717555202	9.1193243349
H	2.610521854	0.1862503183	8.4958834339
H	2.2556103664	-0.8156577024	6.2538057665
H	0.7600015179	0.2723294064	4.6309743875
H	-2.8489370212	2.332142568	2.7018387995
H	-2.6327227234	1.6119395392	0.3502649519
H	-0.409890373	1.0220860656	-0.5797745154
H	1.6028343899	1.1287651703	0.8692189924
H	1.3901973111	1.8097132732	3.2273441321
H	-2.6202418997	0.4232567284	4.3903108381
H	-4.696032334	-0.313232158	5.5064701198
H	-5.730312931	1.0965544281	7.2647499257
H	-4.6713435649	3.2406474589	7.9213819427
H	-2.595466229	3.9985517971	6.8155760779
H	1.6046670039	4.3463775249	3.3751185356
H	4.0193672588	1.9646908214	5.3751608475
H	3.8620619105	3.5890194732	6.0989296107
H	5.2058409656	3.2445652679	4.9706088226
H	3.0482161151	3.3912897642	1.9961180552
H	3.9238729815	1.9974047882	2.6887321873
H	4.7394793661	3.579862474	2.5292660455

Table S12. Cartesian coordinates of pyridine.

Atom type	x	y	z
C	3.013124944	0.5199052053	0.0000803707
C	4.4036968903	0.5376203197	0.0004647204
C	5.0501748429	1.7712790306	-0.00010811
C	3.0785927998	2.9097094668	-0.001516666
C	2.3332960967	1.7330311872	-0.0009114626
H	2.4702050493	-0.4204834393	0.0005571321
H	4.9797901306	-0.3815219003	0.0012560979
H	6.1369786596	1.8214687284	0.000183363
H	2.5786680693	3.8760158305	-0.0022760897
H	1.2492567879	1.7725469418	-0.0012497655
N	4.4126068797	2.9436345993	-0.0011325903

Table S13. Cartesian coordinates of the pyridine adduct.

Atom type	x	y	z
S	3.9507839882	3.6573206006	7.5836809901
S	2.5368846553	4.7331290848	3.133885566
P	6.3533397053	2.3655987448	6.643822991
P	1.4036414222	2.5564532092	4.7901362755
O	2.5048255352	3.6008854085	7.3571831009
O	4.5205984824	3.0245606665	8.7825513669
O	1.0882583204	4.9334598994	3.0371468977
O	3.3796172074	5.8792999738	3.5216367464
N	5.3264716717	3.6248574667	3.694662234
C	4.7987677911	3.0301678825	6.1840377328
C	2.8392335207	3.4256135893	4.252222197
C	7.2574658344	1.789382547	5.1660167419
C	6.8004064526	0.6005764418	4.5778276572
C	7.4696330435	0.0571545911	3.4876309718
C	8.6068146365	0.6885357535	2.9833013351
C	9.0683381067	1.862408505	3.5704128236
C	8.3985323438	2.414681396	4.6631537412
C	7.376752148	3.5576434796	7.562687553
C	7.7359930649	4.7686579703	6.9581063089
C	8.4370817413	5.7304674377	7.6746713471
C	8.7649372711	5.4979054411	9.0093109771
C	8.3856682892	4.307857931	9.6236018863
C	7.6898794457	3.3374487648	8.9064854504
C	6.315367384	0.840287966	7.6341617318
C	7.5417753549	0.2038469276	7.8750898853
C	7.5831045547	-0.9629766689	8.6263835385
C	6.3998175249	-1.5047281342	9.1301384134
C	5.1829583405	-0.8836487826	8.8722918711
C	5.1327231058	0.2902297052	8.1219162449
C	4.4191551297	5.3843534557	7.6882142634
C	5.0931841882	5.8244410848	8.820235391
C	5.4844562363	7.1612806276	8.8889742657
C	5.2036013762	8.0292945529	7.8376453735
C	4.5167621496	7.5714881958	6.7111574873
C	4.1130056957	6.2427947307	6.6340276211
C	0.12923113	3.4775643212	5.6919789816
C	0.326664688	4.8078657542	6.0593168507
C	-0.6912754503	5.5023074722	6.7030425662
C	-1.9002699554	4.8712004563	6.9847497739
C	-2.1026171548	3.544025901	6.6123826461
C	-1.0934890839	2.8486110908	5.9549491403
C	0.4669719323	1.8524939998	3.370327219
C	-0.5396582557	2.6194448711	2.7665404346
C	-1.2049732273	2.1408177212	1.6425252411
C	-0.8861994948	0.8934694123	1.1125285357
C	0.0914928754	0.1134142373	1.7234714683
C	0.7614633363	0.5863073566	2.8488816426
C	1.9322879803	1.1005173344	5.7465593087
C	1.2927172299	0.76217679	6.9397231612
C	1.5597439212	-0.4642940151	7.5487565253
C	2.4637446032	-1.3517078513	6.9742454822
C	3.1526250424	-0.9905315518	5.8167039384
C	2.8962878278	0.2347821168	5.2127757946
C	3.1264896893	4.2800861077	1.4975223222

C	2.7558054862	3.0630383842	0.9283491881
C	3.2270415624	2.7409994339	-0.3399106039
C	4.0441491416	3.6363128038	-1.0323890407
C	4.3851586663	4.8596196815	-0.4609992876
C	3.9260034974	5.1892736211	0.8134946065
C	5.517406554	2.7773265464	2.6682582402
C	6.4479735342	3.0411391797	1.6796876608
C	7.1619222137	4.2345106713	1.7383728302
C	6.9308989659	5.1221732516	2.7858367344
C	6.0047914685	4.784217095	3.7579029467
B	4.2435227501	3.3040861854	4.8045806527
H	5.9365479635	0.0898256057	4.9991237472
H	7.1195335466	-0.8703987849	3.0456652224
H	9.1416173151	0.2542824443	2.1443584512
H	9.9642317764	2.3451106645	3.1926003458
H	8.7891236577	3.3111727683	5.1337641344
H	7.4533043526	4.9708102246	5.9290137187
H	8.7088091602	6.6674634227	7.1997368999
H	9.3052360404	6.2517174874	9.5732388663
H	8.6227214174	4.1338759001	10.668040776
H	7.3670901037	2.4264260842	9.3990961027
H	8.4646369555	0.6236107007	7.4799676545
H	8.5338865565	-1.4487640114	8.8191388906
H	6.4311591122	-2.4132084787	9.7233084254
H	4.2614861165	-1.3024175119	9.263794182
H	4.1811914589	0.7761897726	7.9348759535
H	5.3138142784	5.123988269	9.6191346452
H	6.0136347982	7.5200663609	9.7662608014
H	4.2820915152	8.2473247536	5.8946572197
H	3.5755535623	5.8897630394	5.7568901666
H	1.2727204014	5.2938219801	5.8470501578
H	-0.53811219	6.5383894778	6.9851844606
H	-2.6910154474	5.4169654024	7.4896892648
H	-3.047487724	3.0537512689	6.8221033864
H	-1.2635386302	1.8219634889	5.6383048282
H	-0.7867062421	3.5973015662	3.1609778464
H	-1.9754534741	2.7496122156	1.1812074724
H	-1.4083857205	0.524259109	0.2354948784
H	0.326181245	-0.8727134758	1.3355316819
H	1.4985358129	-0.0519134865	3.3206006067
H	0.594805912	1.4553902253	7.3970232542
H	1.0492411379	-0.7243692324	8.4703663322
H	2.6512081239	-2.3160644093	7.4360920217
H	3.8870910849	-1.6657146933	5.3875655732
H	3.4333108975	0.515395543	4.3094613116
H	2.1127169017	2.3745682567	1.4699492162
H	2.94378561	1.7967606214	-0.7943130542
H	5.0043664892	5.5629803217	-1.0092587684
H	4.1805617026	6.133290553	1.2841460725
H	4.8933977762	1.8911034284	2.6651653158
H	6.5852602979	2.3324181413	0.8722142165
H	7.8846092345	4.4769033487	0.9656574868
H	7.4498166676	6.0710452354	2.8508199514
H	5.7530077805	5.4321222888	4.5913321058
H	4.4012215212	3.3840861697	-2.026065854
H	5.5123613113	9.06836245	7.8965164332

Table S14. Cartesian coordinates of acetone.

Atom type	x	y	z
C	-2.2312878939	0.4930667345	0.0001206331
C	-3.7462863234	0.4458826118	0.0000251243
H	-4.1082695081	-0.0962250353	0.8801041134
H	-4.1454261668	1.4602877443	0.0013510405
H	-4.108019937	-0.0936942443	-0.8817236402
C	-1.5166310207	-0.8436074713	-0.0001428523
H	-1.8054705279	-1.4271311822	-0.8807863131
H	-0.4383200976	-0.6836746405	-0.0007588254
H	-1.8044362151	-1.4268291275	0.8810423325
O	-1.6258635197	1.5399189705	0.0007683872

Table S15. Cartesian coordinates of the acetone adduct.

Atom type	x	y	z
S	-1.5631448012	1.4536979005	-1.5185291577
P	-2.5187779679	-0.8676359862	-0.0060071998
O	-2.7237149478	0.8887734579	-2.2311439377
C	-1.2253914402	0.2912744787	-0.2445337234
B	0.2132515	-0.1200266146	-0.0243620701
S	1.5061259399	2.1662169275	1.0035352301
P	3.064760287	0.1877338403	-0.4736260135
O	-0.3267492601	1.7102069897	-2.2674519497
C	-2.1051045851	3.0320268512	-0.8741772288
O	0.9115359469	3.2412258234	0.2122180782
C	-3.3274945851	3.1154066483	-0.2089666443
O	2.8774890562	2.3345149553	1.5112002377
C	-3.7393446549	4.3435124612	0.2949520183
O	0.3918206276	-1.6306757933	-0.1647604962
C	-2.9449999495	5.4758668367	0.1101250874
C	-1.7485553427	5.3846569254	-0.5950142254
C	-1.3209196217	4.1573425664	-1.0972551867
C	-4.1825638216	-0.1805336231	0.2593059359
C	-4.5631797314	0.2803497139	1.52441659
C	-5.8029670146	0.8882824922	1.6979191459
C	-6.6680300001	1.0303200131	0.6155420994
C	-6.2963996138	0.558741862	-0.6420185912
C	-5.0567315383	-0.0441020263	-0.8262514259
C	-2.7035368608	-2.128426237	-1.3066043195
C	-1.7387483216	-2.2287958083	-2.3104730047
C	-1.839913846	-3.2302991819	-3.2725653068
C	-2.9107792857	-4.1201913731	-3.2459830135
C	-3.8900046252	-4.0070080767	-2.260054549
C	-3.7902471598	-3.012465168	-1.2922792966
C	-2.136609172	-1.774856211	1.5388923431
C	-1.7704262438	-1.0437894299	2.6778469257
C	-1.6280715038	-1.6887286746	3.9046696465
C	-1.809762604	-3.0672973262	4.0004399896
C	-2.1200766391	-3.8060745477	2.8599399819
C	-2.2911916814	-3.1636446357	1.6344257817
C	1.4936831697	0.6197317305	0.1833293142
C	0.442005015	1.9808935982	2.4315266785
C	0.9228746568	1.3043106105	3.5496153118
C	0.1204610992	1.2289792859	4.6849287237
C	-1.1428815276	1.8245175332	4.6883850939

C	-1.6041820153	2.5062254103	3.5627579349
C	-0.8050713331	2.5972091703	2.4237955349
C	2.8202177701	-1.0357527557	-1.80848206
C	1.7448194342	-0.8273081947	-2.6842439614
C	1.5856207277	-1.6482240806	-3.795867266
C	2.4977491583	-2.6700281744	-4.0546419428
C	3.5950846923	-2.8459396745	-3.2166005715
C	3.7681553607	-2.0220408053	-2.1049582317
C	4.2449010124	-0.4882920823	0.7401292445
C	5.0394141502	0.3837729408	1.4961228369
C	5.8707294919	-0.1216232399	2.4921419425
C	5.9150494567	-1.4893531125	2.748984999
C	5.1199559581	-2.3614415772	2.0087894303
C	4.2876808663	-1.8612420418	1.0121450514
C	3.8443979688	1.5756998811	-1.3363582346
C	5.2330601678	1.6500174771	-1.4775817633
C	5.7896795747	2.6615347966	-2.253186185
C	4.9642944025	3.5829976371	-2.8936553702
C	3.580378185	3.4878857412	-2.7719514355
C	3.0091681551	2.4814940993	-1.9993822561
C	0.795695581	-2.5157582603	0.6199769529
H	-3.2690457427	6.4339942103	0.5041003156
H	-1.7595022175	1.774667374	5.5809368416
H	-3.9595278199	2.2423939914	-0.1029650699
H	-4.688615446	4.4175818243	0.8164004759
H	-1.1392512343	6.2681384837	-0.7527598409
H	-0.3844753784	4.0595024662	-1.6310590317
H	-3.8988007559	0.1813034349	2.3759996785
H	-6.0926231529	1.2473085866	2.6800647758
H	-7.6338126217	1.5063972308	0.7521881388
H	-6.9669954491	0.6714303709	-1.4872342452
H	-4.7514199172	-0.3695124814	-1.8142218685
H	-0.9212469612	-1.5152549141	-2.3475596801
H	-1.0872225962	-3.3053042458	-4.0512216318
H	-2.9923324467	-4.8943535512	-4.0022553418
H	-4.7355863276	-4.6868461076	-2.2497294563
H	-4.5626248278	-2.9182339805	-0.532260311
H	-1.5999886175	0.0285503747	2.607436543
H	-1.3661780768	-1.1067638057	4.7819815524
H	-1.7027050734	-3.5655680723	4.9588200628
H	-2.2498102003	-4.881805266	2.9244789269
H	-2.5572378847	-3.7479650714	0.7593078516
H	1.9270250163	0.887006663	3.5352540817
H	0.4888424674	0.7289203704	5.5756952869
H	-2.5781560986	2.9860160871	3.571456153
H	-1.1240994477	3.1564386783	1.5494607755
H	1.046170079	-0.0064541852	-2.5228710974
H	0.7567356126	-1.4658273656	-4.4739237415
H	2.3727279687	-3.3060426661	-4.9253657411
H	4.332866875	-3.611174933	-3.4350786773
H	4.6546819381	-2.1419564734	-1.4910014186
H	4.9888466539	1.4521362331	1.3181046803
H	6.4845491347	0.5610963395	3.0702308731
H	6.5691394568	-1.8767901903	3.5234836258
H	5.1562244053	-3.4297167377	2.1987215818
H	3.6802067916	-2.5529176812	0.4338477114
H	5.8803206246	0.9277781264	-0.9888523335
H	6.8676718619	2.7287266179	-2.3563937142
H	5.4020950719	4.37320471	-3.4951947165

H	2.9375402007	4.1991498435	-3.2797153463
H	1.9271493541	2.4075504786	-1.9119506699
C	1.1423701154	-2.267519052	2.0373770616
H	1.1121178484	-1.2093307601	2.2958246508
H	0.4211655878	-2.8330885569	2.6434161709
H	2.1317454741	-2.6870691757	2.2467439476
C	0.9085511149	-3.878121378	0.0288468536
H	1.0223195162	-4.650816352	0.7891487353
H	0.0404611967	-4.0696208776	-0.6095252906
H	1.7903322008	-3.8733397475	-0.6291303805

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