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Supporting Information

A Strategy to Control the Reactivation of Frustrated Lewis Pairs from Shelf-Stable Carbene Borane Complexes

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[1] General Considerations

All manipulations were conducted under a nitrogen atmosphere by using standard Schlenk or dry box techniques unless otherwise noted. ^{1}H, ^{11}B ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker AVANCE III 400, JEOL AL-400, and Bruker AVANCE III 600 spectrometers at 25 °C unless otherwise noted. The chemical shifts in the ^{1}H NMR spectra were recorded relative to Me_4Si or residual protonated solvent (C_6D_5H (δ7.16), $CHCl_3$ (7.26), or $CHDCl_2$ (5.32)). The chemical shifts in the ^{13}C spectra were recorded relative to Me_4Si or deuterated solvent (C_6D_6 (δ128.06), $CDCl_3$ (77.16), or CD_2Cl_2 (53.84)). The chemical shifts in the ^{31}P NMR spectra were recorded relative to 85% H_3PO_4 as an external standard. The chemical shifts in the ^{11}B NMR spectra were recorded relative to BF_3. The chemical shifts in the ^{19}F NMR spectra were recorded relative to α,α,α-trifluorotoluene (δ –65.64). Assignment of the resonances in ^{1}H and ^{13}C NMR spectra was based on ^{1}H-^{1}H COSY, HMQC and HMBC experiments. High resolution mass spectrometry (HRMS) and elementary analyses were performed at Instrumental Analysis Center, Faculty of Engineering, Osaka University. ESI-MS analyses were performed with a Bruker Daltonics micrOTOF mass spectrometer. X-ray crystal data were collected with a Rigaku RAXIS-RAPID imaging Plate diffractometer.

[2] Materials

Benzene-d_6 was distilled from sodium benzophenone ketyl prior to use. 1,2-Dichloroethane and C_6H_5Br were distilled over CaH_2 prior to use. CD_2Cl_2 was distilled over CaH_2 and stored in the presence of molecular sieves (4 Å). C_6D_5Br was degassed by a freeze-pump-thaw technique prior to use. All commercially available reagents including super dehydrated solvents (toluene, hexane, THF and CH_2Cl_2) were employed as received. $NHCP^{dipp}$ was furnished by the known procedures.[S1] Metrical data for the solid state structures are available from Cambridge Crystallographic Data Centre: CCDC 1053782 (**1a**), 1053783 (**2a**), 1053784 (**2b**), 1053785 (**2c**), 1053786 (**4a**), 1053787 (**4b**), 1053788 (**7**).

[3] Synthesis of Imidazoles, PoxIm·HOTf (1), and PoxIm (2)

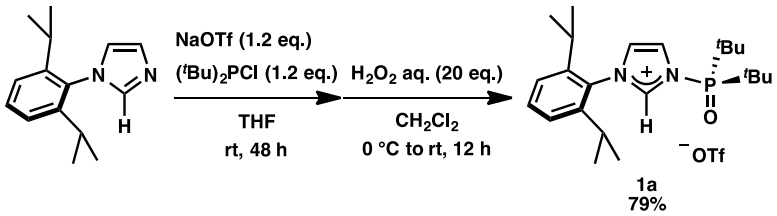
・Synthesis of 1-(2,6-diisopropylphenyl)imidazole and 1-(2,4,6-trimethylphenyl)-imidazole[S2]

The target compounds were prepared by the literature procedures.[S2]

・Synthesis of 1-(3,5-di-*tert*-butylphenyl)imidazole

The literature procedure[S2] was followed with 3,5-di-*tert*-butylaniline (10.0 g, 49.0 mmol) to give 1-(3,5-di-*tert*-butylphenyl)imidazole (2.5 g, 9.8 mmol, 20%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83 (s, 1H, Im-*H*), 7.44 (t, *J* = 1.6 Hz, 1H, Ar-*H*), 7.27 (s, 1H, Im-*H*), 7.20 (s, 1H, Im-*H*), 7.19 (d, *J* = 1.6 Hz, 2H, Ar-*H*), 1.36 (s, 18H, ^{t}Bu-*H*). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 152.6, 136.9, 135.7, 129.9, 121.5, 118.6, 116.3, 34.9, 31.2.

- **Synthesis of PoxIm^{dipp}·HOTf (1a)**



To a solution of 1-(2,6-diisopropylphenyl)imidazole (5.0 g, 22.0 mmol) and NaOTf (4.5 g, 26.0 mmol, 1.2 equiv) in THF (10 mL) was added dropwise P(^{t}Bu)$_2$Cl (4.8 g, 26.0 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature for 48 h. After removal of the all volatiles *in vacuo*, the resulting solid was dissolved into CH_2Cl_2 (150 mL) followed by addition of H_2O_2 aq. (35% aq., 43.0 g, 440.0 mmol, 20 equiv) very slowly at 0 °C (*Caution! Exothermic process*). The reaction mixture was stirred vigorously for overnight, and then neutralized with saturated $NaHCO_3$ aq. The organic layer was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resultant solid was washed with ether, giving **1a** as a white solid (9.3 g, 17.3 mmol, 79%). A single crystal suitable for X-ray diffraction analysis was prepared by recrystallization from CH_2Cl_2/hexane at –20 °C (Figure S1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.81 (brs, 1H, Im-*H*), 8.64 (brs, 1H, Im-*H*), 7.82 (brs, 1H, Im-*H*), 7.58 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 7.34 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 2.19 (sept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 1.42 (d, $^3J_{H,P}$ = 16.4 Hz, 18H, ^{t}Bu-*H*), 1.21 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.14 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 144.9, 140.1, 132.6, 129.7, 128.8 (brs), 125.8, 125.0, 120.9 (q, $^1J_{C,F}$ = 318.0 Hz), 38.3 (d, $^1J_{C,P}$ = 59.0 Hz), 29.1, 26.0, 24.5, 23.7. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ 77.1 (s). **HRMS** (FAB$^+$): m/z Calcd for $C_{23}H_{38}N_2OP$: ([M–OTf]$^+$) 389.2716, found 389.2717. X-ray data for **1a·CH$_2$Cl$_2$**: *M* = 623.54, colorless, monoclinic, *P2$_1$/c* (#14), *a* = 10.7550(3) Å, *b* = 22.0653(5) Å, *c* = 13.3666(3) Å, α = 90.0000°, β = 91.7560(12)°, γ = 90.0000°, *V* = 3170.57(11) Å^3, *Z* = 4, *Dcalcd* = 1.306 g/cm^3, *T* = –150 °C, R_1 (wR_2) = 0.0825 (0.2941).

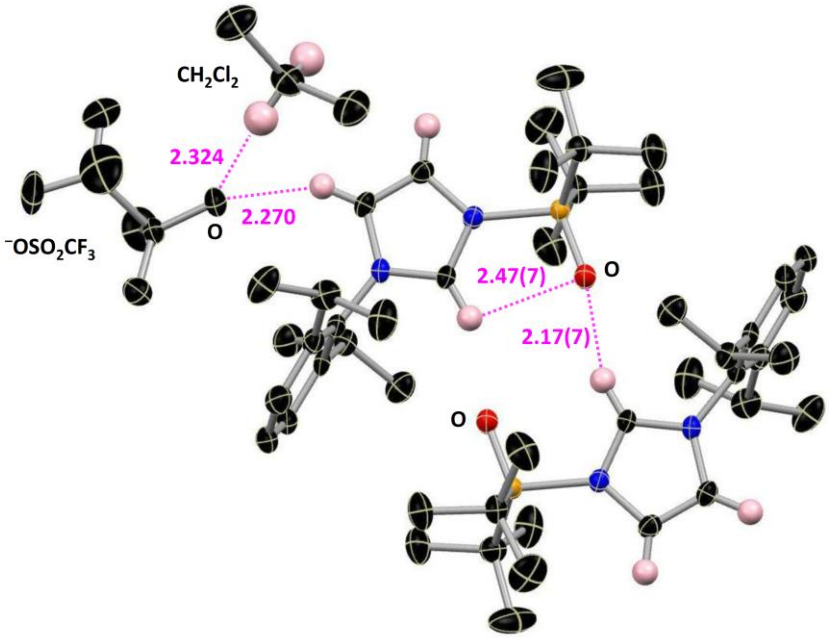
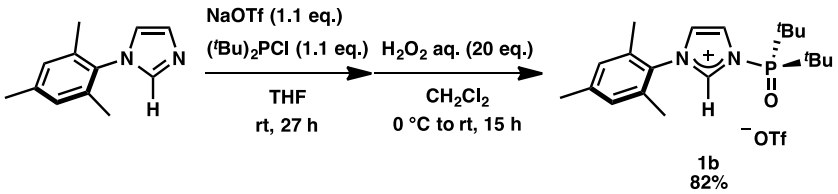


Figure S1. Molecular structure of **1a·CH_2Cl_2**. Inter- and intra-atomic distances between C2–H and O (Å) are shown.

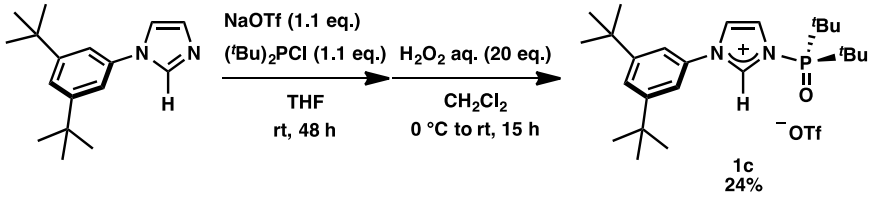
· Synthesis of $PoxIm^{mes}$·HOTf (1b)



To a solution of 1-(2,4,6-trimethylphenyl)imidazole (1.9 g, 10.0 mmol) and NaOTf (1.9 g, 11.0 mmol, 1.1 equiv) in THF (10 mL) was added dropwise $P(^tBu)_2Cl$ (2.0 g, 11.0 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature for 27 h. After removal of the all volatiles *in vacuo*, the resulting solid was dissolved into CH_2Cl_2 (20 mL) followed by addition of H_2O_2 aq. (35% aq., 19.4 g, 200.0 mmol, 20 equiv) very slowly at 0 °C (*Caution! Exothermic process*). The reaction mixture was stirred vigorously for overnight, and then neutralized with saturated $NaHCO_3$ aq. The organic layer was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resultant solid was washed with ether, giving **1b** as a white solid (4.1 g, 8.2 mmol, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.20 (brs, Im-*H*), 8.38 (brs, 1H, Im-*H*), 7.71 (brs, 1H, Im-*H*), 7.01 (s, 2H, Ar-*H*), 2.31 (s, 3H, Ar-CH_3), 1.99 (s,

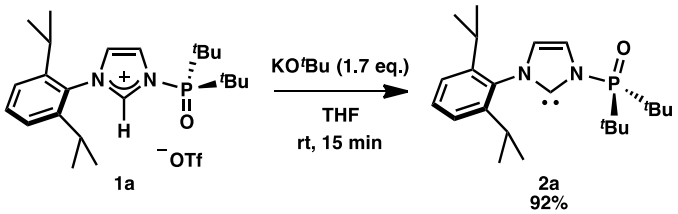
6H, Ar-CH_3), 1.33 (d, $^3J_{H,P}$ = 16.4 Hz, 18H, ^{t}Bu-*H*). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 142.0, 140.1, 133.7, 130.1, 130.0, 127.1, 125.3, 120.7 (q, $^1J_{C,F}$ = 318.0 Hz), 37.4 (d, $^1J_{C,P}$ = 60.0 Hz), 25.2, 20.7, 16.8. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ 75.8 (s). **HRMS** (FAB$^+$): m/z Calcd for $C_{20}H_{32}N_2OP$: ([M–OTf]$^+$) 347.2247, found 347.2251.

- **Synthesis of PoxIm^{dtbp}·HOTf (1c)**



To a solution of 1-(3,5-di-*tert*-butylphenyl)imidazole (1.0 g, 4.0 mmol) and NaOTf (0.69 g, 4.4 mmol, 1.1 equiv) in THF (5 mL) was added dropwise P(^{t}Bu)$_2$Cl (0.80 g, 4.4 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature for 48 h. After removal of the all volatiles *in vacuo*, the resulting solid was dissolved into CH_2Cl_2 (10 mL) followed by addition of H_2O_2 aq. (35% aq., 7.8 g, 80.0 mmol, 20 equiv) very slowly at 0 °C (*Caution! Exothermic process*). The reaction mixture was stirred vigorously for overnight, and then neutralized with saturated $NaHCO_3$ aq. The organic layer was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resultant solid was washed with ether, giving **1c** as a white solid (0.54 g, 0.95 mmol, 24%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.98 (brs, 1H, Im-*H*), 8.48 (brs, 1H, Im-*H*), 8.20 (brs, 1H, Im-*H*), 7.67 (s, 1H, Ar-*H*), 7.30 (d, *J* = 1.2 Hz, 2H, Ar-*H*), 1.47 (d, $^3J_{H,P}$ = 16.8 Hz, 18H, ^{t}Bu-*H*), 1.38 (s, 18H, ^{t}Bu-*H*). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 153.6, 136.4 (brs), 133.3, 125.1 (brs), 124.7, 124.6, 120.2 (q, $^1J_{C,F}$ = 319.0 Hz), 116.5, 34.5 (d, $^1J_{C,P}$ = 60.0 Hz), 34.8, 30.7, 25.5. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ 77.1 (s). **HRMS** (FAB$^+$): m/z Calcd for $C_{25}H_{42}N_2OP$: ([M–OTf]$^+$) 417.3029, found 417.3034.

- **Synthesis of PoxIm^{dipp} (2a)**



To a suspension of **1a** (0.80 g, 1.5 mmol) in THF (20 mL) was added KO^{t}Bu (0.28 g, 2.5 mmol, 1.7 equiv). The reaction mixture was stirred at room temperature for 15 min. The solvent was removed *in vacuo*, and the product was extracted with toluene and filtered through a Celite pad. The filtrate was concentrated *in vacuo* to give **2a** as a white solid (0.54 g, 1.38 mmol, 92%). A single crystal suitable for X-ray diffraction analysis was prepared by recrystallization from THF/hexane at –30 °C (Figure S2). **^{1}H NMR** (400 MHz, C_6D_6): δ 7.81 (t, J = 1.6 Hz, 1H, Im-*H*), 7.25 (t, J = 7.6 Hz, 1H, Ar-*H*), 7.12 (d, J = 7.6 Hz, 2H, Ar-*H*), 6.43 (s, 1H, Im-*H*), 2.66 (sept, J = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 1.40 (d, $^3J_{H,P}$ = 14.8 Hz, 18H, ^{t}Bu-*H*), 1.17 (d, J = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 1.09 (d, J = 6.8 Hz, 6H, CH(C*H*$_3)_2$). **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6): δ 222.1 (d, $^2J_{C,P}$ = 25.0 Hz, N*C*N), 146.0, 138.3, 129.2, 123.7, 123.1 (d, $J_{C,P}$ = 4.0 Hz), 121.2 (d, $J_{C,P}$ = 4.0 Hz), 37.6 (d, $^1J_{C,P}$ = 70.0 Hz), 28.6, 26.7, 24.6, 23.4. **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ 61.4 (s). X-ray data for **2a**: M = 388.53, colorless, monoclinic, $P2_1/c$ (#14), a = 11.2747(2) Å, b = 12.0947(3) Å, c = 17.3210(4) Å, α = 90.0000°, β = 100.6379(8)°, γ = 90.0000°, V = 2321.38(8) Å^3, Z = 4, $Dcalcd$ = 1.112 g/cm^3, T = –150 °C, R_1 (wR_2) = 0.0427 (0.1075).

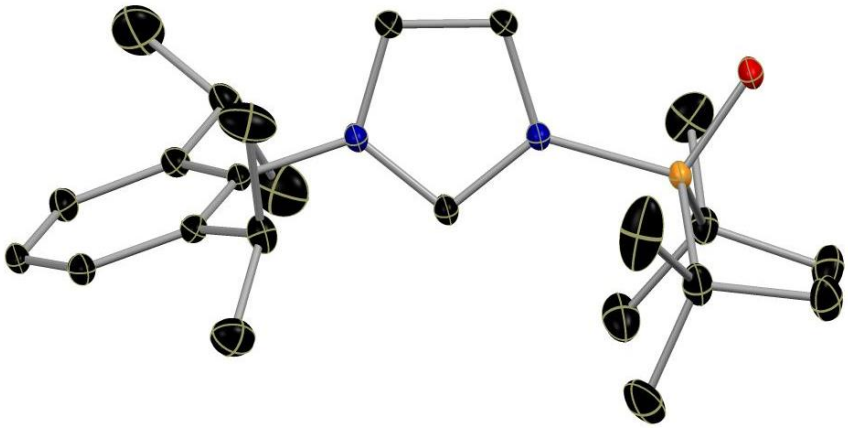
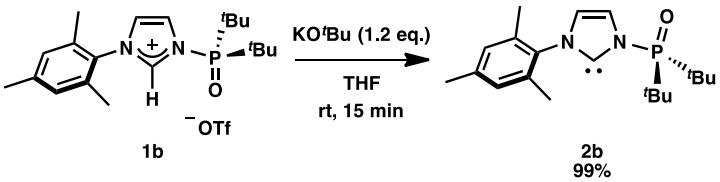


Figure S2. Molecular structure of **2a**.

- **Synthesis of PoxIm^{mes} (2b)**



To a suspension of **1b** (1.5 g, 3.0 mmol) in THF (70 mL) was added KO^{t}Bu (0.40 g, 3.6 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature for 15 min. The solvent was removed *in vacuo*, and the product was extracted with toluene and filtered through a Celite pad. The filtrate was concentrated *in vacuo* to give **2b** as a white solid (1.0 g, 2.97 mmol, 99%). A single crystal suitable for X-ray diffraction analysis was prepared by recrystallization from THF/hexane at –30 °C (Figure S3). **^{1}H NMR** (400 MHz, C_6D_6): δ 7.82 (s, 1H, Im-*H*), 6.73 (s, 2H, Ar-*H*), 6.27 (s, 1H, Im-*H*), 2.12 (s, 3H, Ar-CH_3), 1.96 (s, 6H, Ar-CH_3), 1.40 (d, $^3J_{H,P}$ = 14.8 Hz, 18H, ^{t}Bu-*H*). **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6): δ 221.9 (d, $^2J_{C,P}$ = 25.0 Hz, N*C*N), 138.6, 137.6, 125.1, 129.1, 123.1 (d, $J_{C,P}$ = 5.0 Hz), 119.8 (d, $J_{C,P}$ = 3.0 Hz), 37.5 (d, $^1J_{C,P}$ = 70.0 Hz), 26.8, 21.0, 18.0. **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ 61.2 (s). X-ray data for **2b**: *M* = 346.44, colorless, monoclinic, *C2* (#5), *a* = 26.1162(12) Å, *b* = 8.2562(5) Å, *c* = 9.7993(6) Å, α = 90°, β = 107.022(3)°, γ = 90°, *V* = 2020.4(2) Å^3, *Z* = 4, *Dcalcd* = 1.139 g/cm^3, *T* = –150 °C, R_1 (wR_2) = 0.0530 (0.1603).

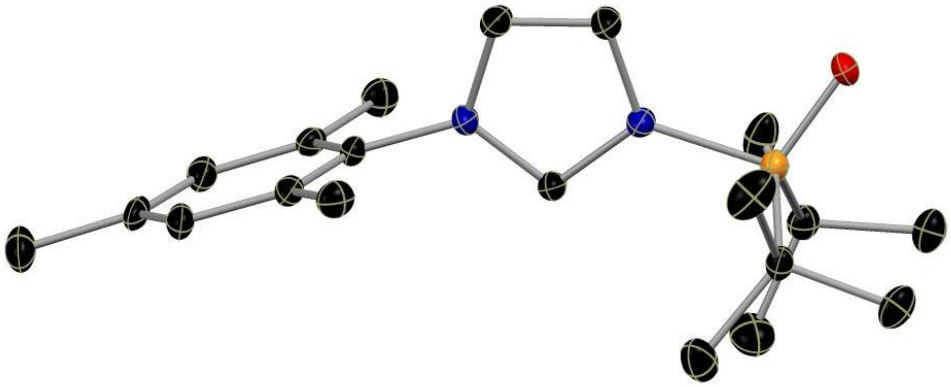
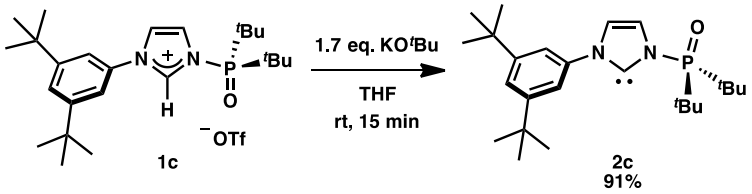


Figure S3. Molecular structure of **2b**.

- **Synthesis of PoxIm^{dtbp} (2c)**

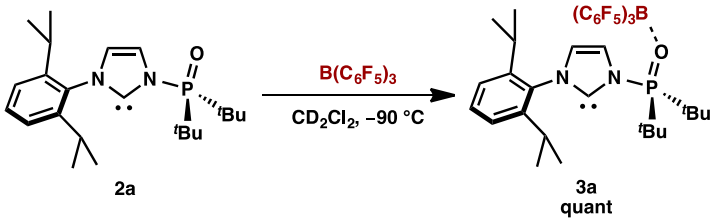


To a suspension of **1c** (378.0 mg, 0.67 mmol) in THF (15 mL) was added KO^{t}Bu (127.0 mg, 1.13 mmol, 1.7 equiv). The reaction mixture was stirred at room temperature for 15 min. The solvent was removed *in vacuo*, and the product was extracted with toluene and filtered through a Celite pad. The filtrate was concentrated *in*

vacuo to give **2c** as a white solid (253.0 mg, 0.61 mmol, 91%). A single crystal suitable for X-ray diffraction analysis was prepared by recrystallization from THF/hexane at –30 °C (Figure S4). **^{1}H NMR** (400 MHz, C_6D_6): δ 7.87 (s, 1H, Im-*H*), 7.76 (d, J = 1.6 Hz, 2H, Ar-*H*), 7.46 (s, 1H, Ar-*H*), 6.94 (s, 1H, Im-*H*), 1.40 (d, $^{3}J_{H,P}$ = 14.8 Hz, 18H, ^{t}Bu-*H*), 1.27 (s, 18H, ^{t}Bu-*H*). **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6): δ 220.9 (d, $^{2}J_{C,P}$ = 25.0 Hz, N*C*N), 152.3, 142.3, 124.0 (d, $J_{C,P}$ = 5.0 Hz), 121.0, 117.5 (d, $J_{C,P}$ = 4.0 Hz), 116.7, 37.5 (d, $^{1}J_{C,P}$ = 69.0 Hz), 35.1, 31.5, 26.8. **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ 61.9 (s). X-ray data for **2c**: M = 416.57, colorless, orthorhombic, $P2_12_12_1$ (#19), a = 10.46137(19) Å, b = 15.2109(3) Å, c = 15.7785(3) Å, α = 90°, β = 90°, γ = 90°, V = 2510.79(8) Å^3, Z = 4, $Dcalcd$ = 1.102 g/cm^3, T = –150 °C, R_1 (wR_2) = 0.0318 (0.0777).

Figure S4. Molecular structure of **2c**.

[4] Reaction of 2a with $B(C_6F_5)_3$ at –90 °C Giving 3a



A solution of **2a** (38.9 mg, 0.10 mmol) in CD_2Cl_2 (0.5 mL) was cooled to –80 °C. A solution of $B(C_6F_5)_3$ (51.2 mg, 0.10 mmol) and α,α,α-trifluorotoluene (10.7 mg, 0.073 mmol; internal standard) was also cooled to –80 °C. Two solutions were mixed at –80 °C and the resulting mixture was transferred into a J.Young NMR tube. The quantitative formation of **3a** was confirmed by ^{1}H, ^{11}B, ^{19}F, and ^{31}P NMR at –90 °C

(Figure S5–9). Then, the reaction mixture was allowed to warm to room temperature to give **4a** in 72% yield. **^{1}H NMR of 3a** (600 MHz, CD_2Cl_2, –90 °C, Figure S5): δ 7.43 (m, 1H, Ar-*H*), 7.25 (d, J = 7.8 Hz, 2H, Ar-*H*), 7.05 (s, 1H, Im-*H*), 6.94 (s, 1H, Im-*H*), 2.26 (brs, 2H, C*H*$(CH_3)_2$), 1.25 (brs, 18H, ^{t}Bu-*H*), 1.11 (brs, 6H, CH(C*H*$_3)_2$), 0.97 (brs, 6H, CH(C*H*$_3)_2$). **^{11}B NMR of 3a** (193 MHz, CD_2Cl_2, –90 °C, Figure S6): δ –3.0 (s). **^{13}C{^{1}H} NMR of 3a** (151 MHz, CD_2Cl_2, –90 °C, Figure S7): The following resonances are assigned to **3a**; δ 219.5 (d, $^{2}J_{C,P}$ = 30.2 Hz, N*C*N), 123.3, 122.8, 122.1, 38.8 (d, $^{1}J_{C,P}$ = 60.4 Hz), 27.7, 25.6, 23.7, 22.5. **^{19}F NMR of 3a** (565 MHz, CD_2Cl_2, –90 °C, Figure S8): δ –129.6, –134.6, –156.6, –159.1, –164.0, –164.7. **^{31}P{^{1}H} NMR of 3a** (243 MHz, CD_2Cl_2, –90 °C, Figure S9): δ 79.2 (s).

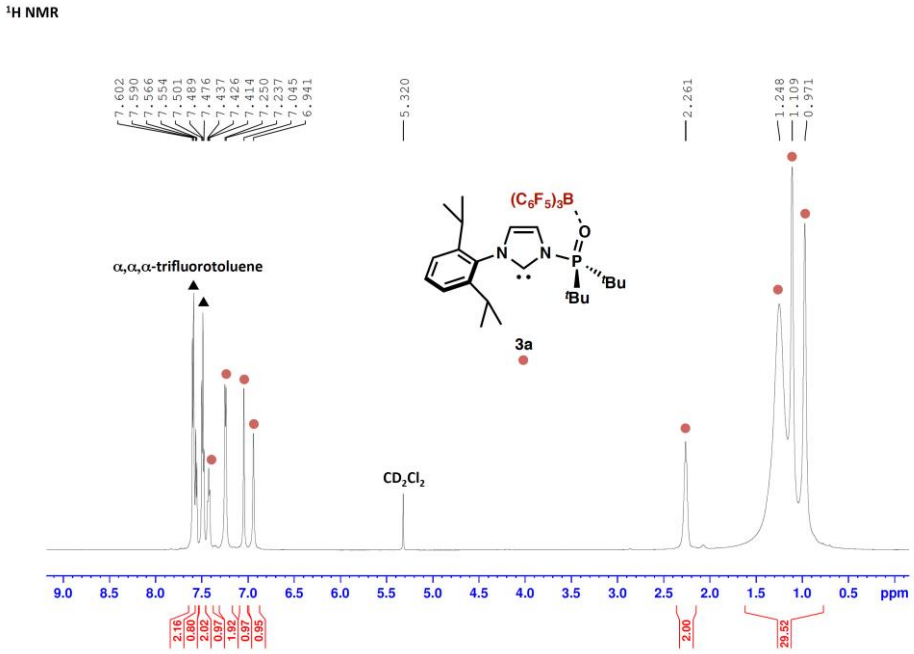


Figure S5. ^{1}H NMR spectrum for **3a**.

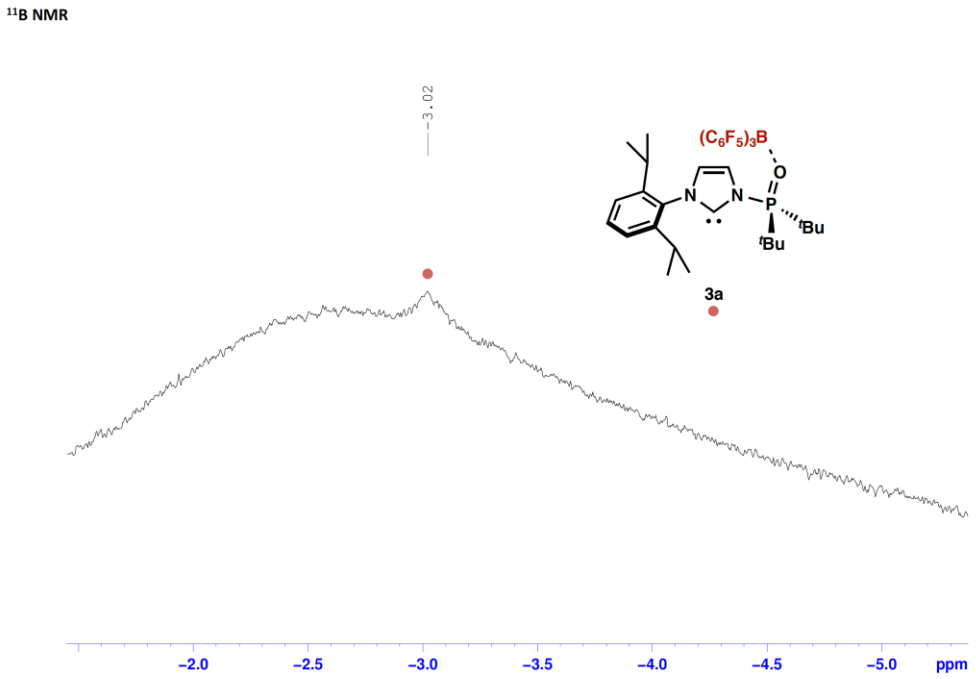


Figure S6. ^{11}B NMR spectrum for **3a**.

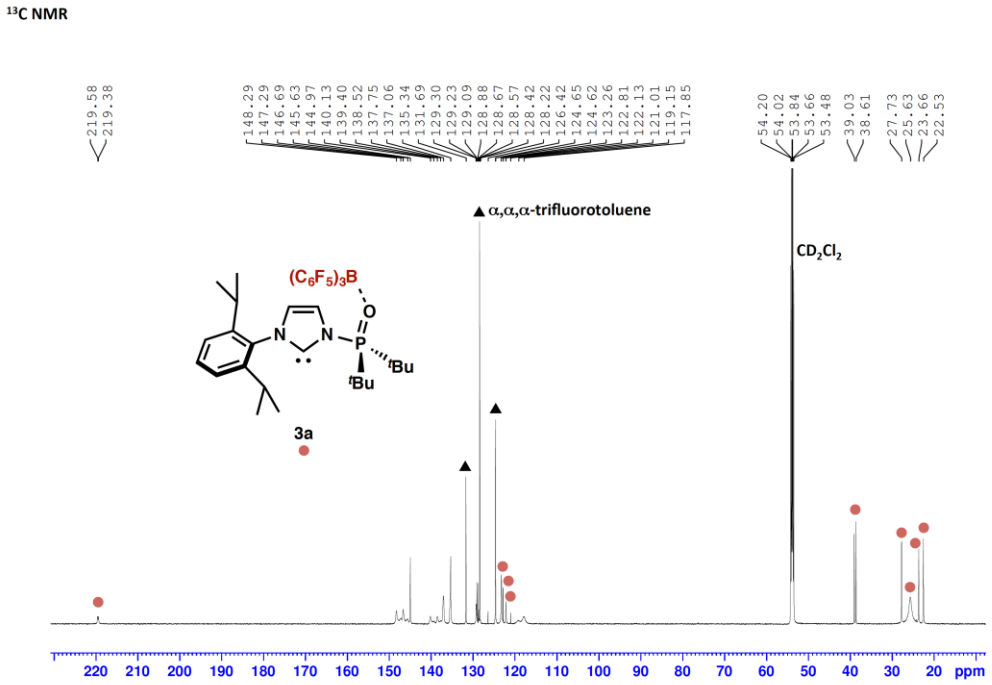


Figure S7. ^{13}C NMR spectrum for **3a**.

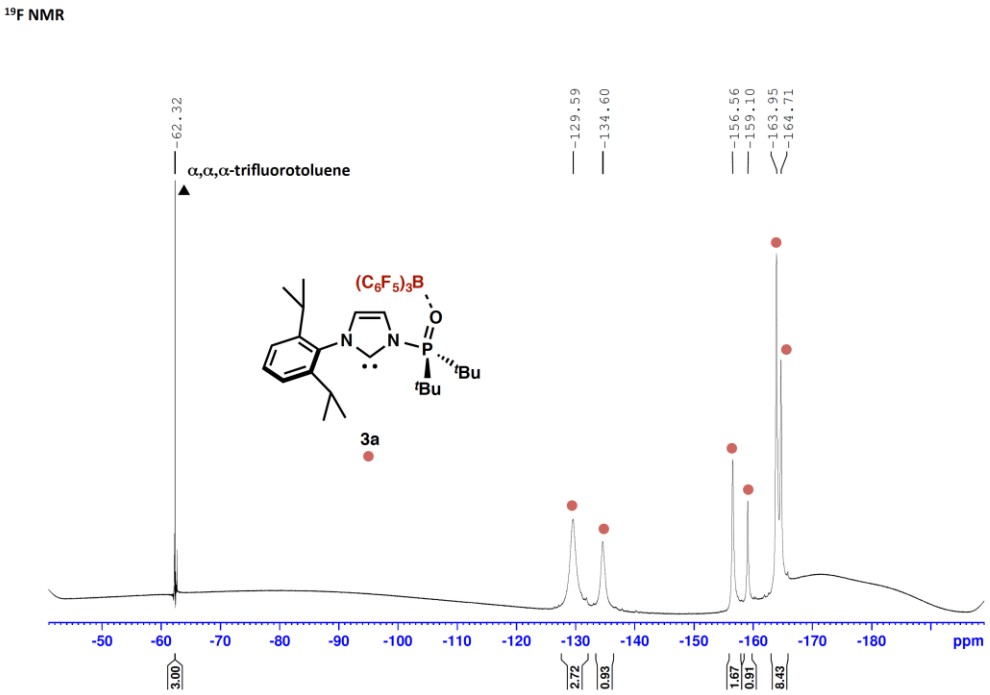


Figure S8. ^{19}F NMR spectrum for **3a**.

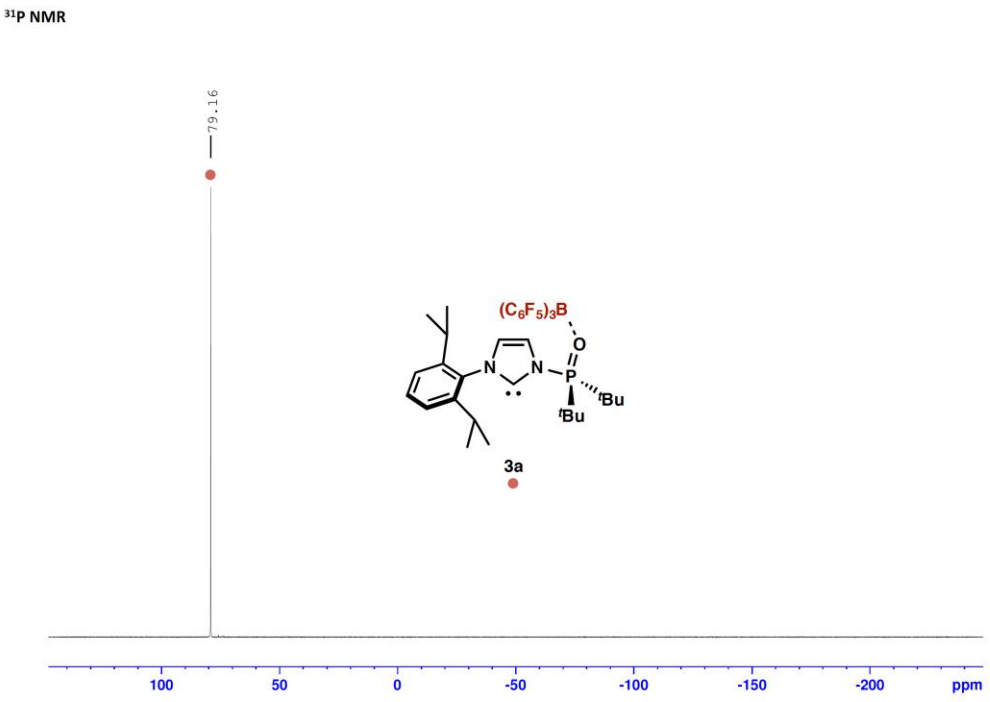
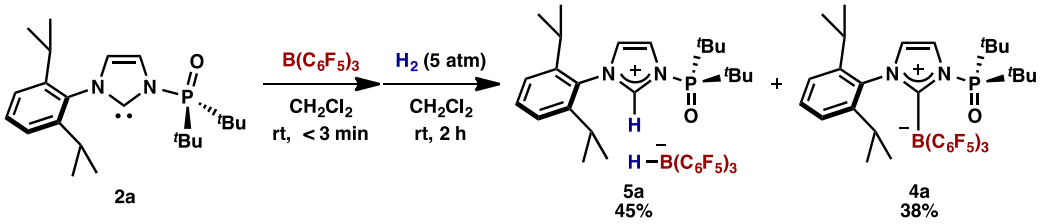


Figure S9. ^{31}P NMR spectrum for **3a**.

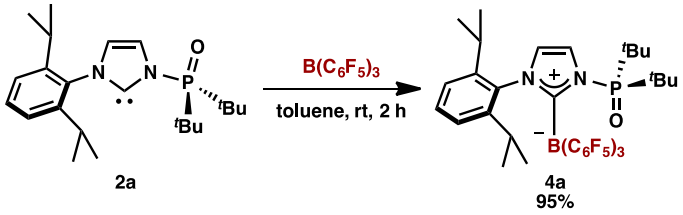
[5] Reaction of 2a, $B(C_6F_5)_3$, and H_2 at Room Temperature



To a solution of **2a** (7.8 mg, 20.0 μmol) in CH_2Cl_2 (1 mL) was added $B(C_6F_5)_3$ (10.2 mg, 20.0 μmol). The resulting mixture was transferred into an autoclave reactor, and H_2 (5 atm) was pressurized followed by stirring for 2 h at room temperature. Then, all volatiles were removed *in vacuo* to give a white solid including **5a** (9.0 μmol, 45%) and **4a** (7.6 μmol, 38%), which was calculated by NMR analyses with triphenylphosphine oxide (2.8 mg, 10.0 μmol) as an internal standard.

[6] Synthesis of B-Pox (4)

- **Synthesis of B-Pox^{dipp} (4a)**



To a solution of **2a** (77.7 mg, 0.20 mmol) in toluene (10 mL) was added $B(C_6F_5)_3$ (102.4 mg, 0.20 mmol), and the reaction mixture was stirred for 2 h at room temperature. Then, the solvent was removed *in vacuo*, and the resulting solid was washed with hexane, and dried *in vacuo* to give **4a** as a white solid (170.3 mg, 0.19 mmol, 95%). A single crystal suitable for X-ray diffraction analysis was prepared by recrystallization from THF/hexane at –30 °C (Figure S10). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.45 (m, 1H, Im-*H*), 7.30 (t, J = 7.6 Hz, 1H, Ar-*H*), 7.20 (dd, J = 7.6, 1.2 Hz, 1H, Ar-*H*), 7.13 (s, 1H, Im-*H*), 6.90 (dd, J = 7.6, 1.2 Hz, 1H, Ar-*H*), 2.94 (brs, 1H, C*H*$(CH_3)_2$), 2.47 (sept, J = 6.8 Hz, 1H, C*H*$(CH_3)_2$), 1.45 (d, $^3J_{H,P}$ = 16.0 Hz, 9H, ^{t}Bu-*H*), 1.30 (d, J = 6.0 Hz, 3H, CH(C*H*$_3)_2$), 1.09 (d, J = 6.8 Hz, 3H, CH(C*H*$_3)_2$), 1.09 (d, $^3J_{H,P}$ = 16.0 Hz, 9H, ^{t}Bu-*H*), 0.98 (d, J = 6.8 Hz, 3H, CH(C*H*$_3)_2$), 0.90 (d, J = 6.8 Hz, 3H, CH(C*H*$_3)_2$). **^{11}B NMR** (128 MHz, CD_2Cl_2): δ –14.5 (s). **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 148.2, 145.7, 134.5, 131.4, 128.1 (d, $J_{C,P}$ = 5.0 Hz), 123.9, 123.6, 122.0 (d, $J_{C,P}$ = 6.0 Hz), 43.3 (d, $^1J_{C,P}$ = 57.0 Hz), 41.1 (d, $^1J_{C,P}$ = 60.0 Hz), 29.1, 29.0, 28.0

(apparent d, J = 21.0 Hz, *C*H(CH$_3$)$_2$), 27.4, 27.4, 27.2, 21.2 (two CH(*C*H$_3$)$_2$ groups are overlapped). Resonances for N*C*N and C_6F_5 could not be identified. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ –115.7, –126.6, –131.2, –131.4, –133.8, –138.5, –162.9 (t, $^3J_{F,F}$ = 18.8 Hz), –163.7 (t, $^3J_{F,F}$ = 18.8 Hz), –165.3 (t, $^3J_{F,F}$ = 18.8 Hz), –167.7, –169.0 (t, $^3J_{F,F}$ = 18.8 Hz), –169.4, –171.0 (t, $^3J_{F,F}$ = 20.7 Hz), –172.5, –172.7. **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 76.0 (s). **Anal. Calcd for $C_{41}H_{37}BF_{15}N_2OP$:** C, 54.69; H, 4.14; N, 3.11. Found: C, 54.64; H, 4.02; N, 3.11. X-ray data for **4a**: M = 900.50, colorless, monoclinic, $P2_1/n$ (#14), a = 11.2697(4) Å, b = 19.5340(7) Å, c = 18.1441(6) Å, α = 90°, β = 96.396(2)°, γ = 90°, V = 3969.4(2) Å^3, Z = 4, $Dcalcd$ = 1.507 g/cm^3, T = –150 °C, R_1 (wR_2) = 0.0447 (0.1060).

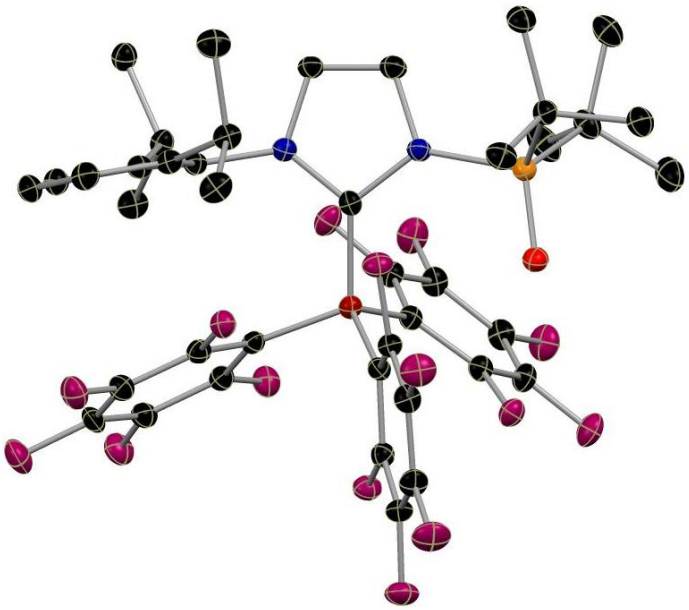
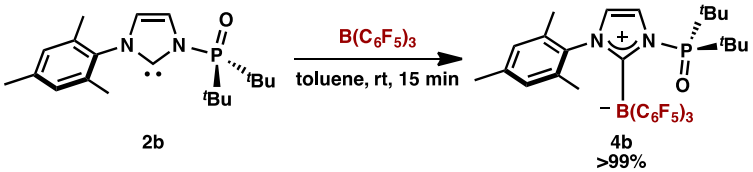


Figure S10. Molecular structure of **4a**.

- **Synthesis of B-Pox^{mes} (4b)**



2b 4b >99%

To a solution of **2b** (243.0 mg, 0.70 mmol) in toluene (20 mL) was added $B(C_6F_5)_3$ (358.0 mg, 0.70 mmol), and the reaction mixture was stirred for 15 minutes at room temperature. Then, the solvent was removed *in vacuo*, and the resulting solid was

washed with hexane, and dried *in vacuo* to give **4b** as a white solid (600.2 mg, 0.70 mmol, >99%). A single crystal suitable for X-ray diffraction analysis was prepared by recrystallization from THF/hexane at –30 °C (Figure S11). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.47 (t, J = 2.4 Hz, 1H, Im-*H*), 7.07 (s, 1H, Ar-*H*), 6.87 (s, 1H, Ar-*H*), 6.55 (s, 1H, Im-*H*), 2.21 (s, 3H, Ar-CH_3), 1.98 (s, 3H, Ar-CH_3), 1.96 (s, 3H, Ar-CH_3), 1.46 (d, $^{3}J_{H,P}$ = 15.6 Hz, 9H, ^{t}Bu-*H*), 1.10 (d, $^{3}J_{H,P}$ = 15.6 Hz, 9H, ^{t}Bu-*H*). **^{11}B NMR** (128 MHz, CD_2Cl_2): δ –14.7 (s). **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 140.6, 136.8, 135.1, 134.3, 129.5, 129.1, 126.5 (d, $J_{C,P}$ = 5.0 Hz), 123.3 (d, $J_{C,P}$ = 6.0 Hz), 43.0 (d, $^{1}J_{C,P}$ = 60.0 Hz), 41.2 (d, $^{1}J_{C,P}$ = 60.0 Hz), 29.2, 27.2, 20.6, 18.6–18.2 (apparent m, Ar-*C*H$_3$). Resonances for N*C*N and C_6F_5 could not be identified. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ –119.8 (br), –124.5, –128.8, –131.2 (m), –134.3 (m), –139.0 (m), –163.2 (t, $^{3}J_{F,F}$ = 18.8 Hz), –163.7 (t, $^{3}J_{F,F}$ = 18.8 Hz), –165.4 (t, $^{3}J_{F,F}$ = 18.8 Hz), –168.7, –169.4, –169.6, –171.0, –172.2, –172.2. **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 75.6 (s). **Anal. Calcd for $C_{38}H_{31}BF_{15}N_2OP$:** C, 53.17; H, 3.64; N, 3.26. Found: C, 53.17; H, 3.56; N, 3.10. X-ray data for **4b**: M = 858.44, colorless, monoclinic, $P2_1/n$ (#14), a = 11.5471(2) Å, b = 25.2133(5) Å, c = 13.4051(3) Å, α = 90°, β = 99.2440(10)°, γ = 90°, V = 3852.09(12) Å^3, Z = 4, $Dcalcd$ = 1.480 g/cm^3, T = –150 °C, R_1 (wR_2) = 0.0913 (0.3062). *Note; SQUEEZE/PLATON was used in structural refinement for **4b**.*

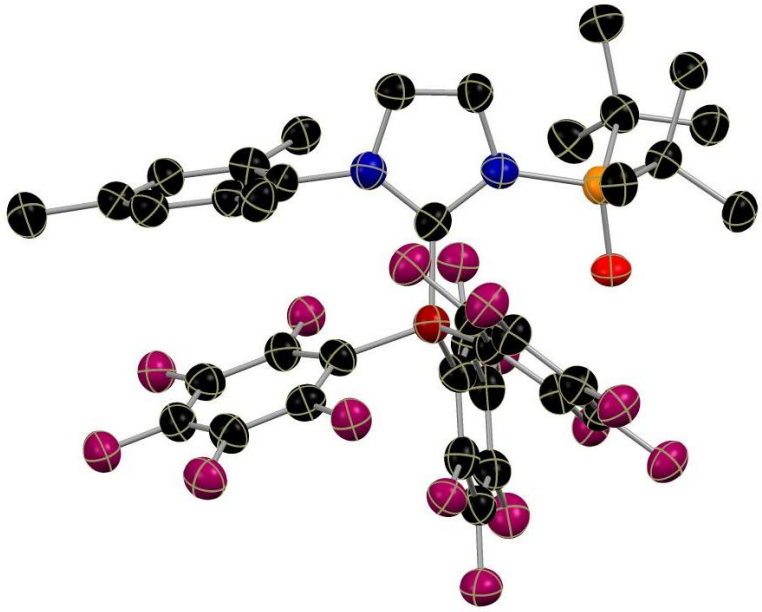
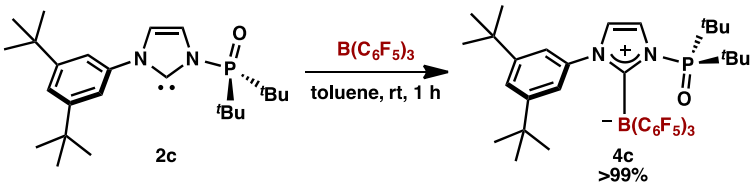


Figure S11. Molecular Structure of **4b**.

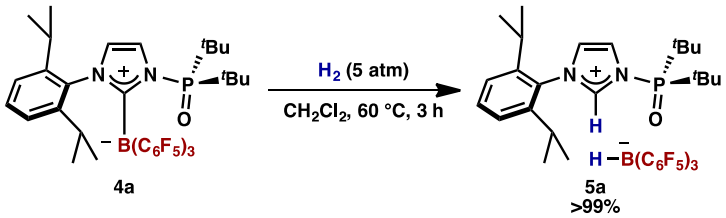
• **Synthesis of B-Pox^{dtbp} (4c)**



To a solution of **2c** (45.0 mg, 0.11 mmol) in toluene (10 mL) was added $B(C_6F_5)_3$ (55.3 mg, 0.11 mmol), and the reaction mixture was stirred for 1 h at room temperature. Then, the solvent was removed *in vacuo*, and the resulting solid was washed with hexane, and dried *in vacuo* to give **4c** as a white solid (98.8 mg, 0.11 mmol, >99%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.44–7.43 (m, 1H, Im-*H*), 7.40 (s, 1H, Ar-*H*), 7.17 (brm, 2H, Im-*H* and Ar-*H*), 6.96 (s, 1H, Ar-*H*), 1.50 (d, $^3J_{H,P}$ = 15.6 Hz, 9H, ^{t}Bu-*H*), 1.27 (s, 9H, ^{t}Bu-*H*), 1.19 (s, 9H, C ^{t}Bu-*H*), 1.09 (d, $^3J_{H,P}$ = 15.6 Hz, 9H, ^{t}Bu-*H*). **^{11}B NMR** (128 MHz, CD_2Cl_2): δ –15.5 (s). **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 152.6, 152.0, 138.8, 127.5 (d, $J_{C,P}$ = 5.0 Hz), 125.0, 121.6 (d, $J_{C,P}$ = 7.0 Hz), 121.4, 120.3, 42.3 (d, $^1J_{C,P}$ = 58.0 Hz), 41.2 (d, $^1J_{C,P}$ = 61.0 Hz), 35.3, 35.2, 31.2, 28.5, 27.4. Resonances for N*C*N and C_6F_5 were not identified. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ –124.5, –126.4 (br), –128.4, –132.3, –135.1 (br), –136.7 (br), –163.4 (two Ar-*F* are overlapped), –165.1, –167.7, –168.1, –170.1, –170.8, –171.6 (two Ar-*F* are overlapped). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 74.5 (s). **Anal. Calcd for $C_{43}H_{41}BF_{15}N_2OP$:** C, 55.62; H, 4.45; N, 3.02. Found: C, 55.46; H, 4.42; N, 3.01.

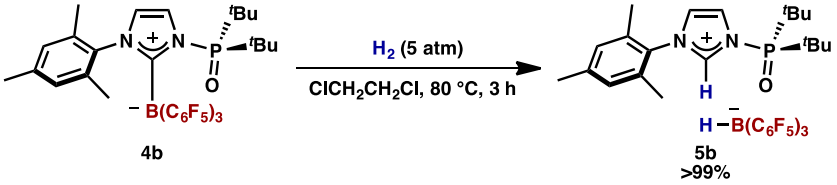
[7] Heterolytic Cleavage of H_2 with PoxIm

• **Isolation of 5**

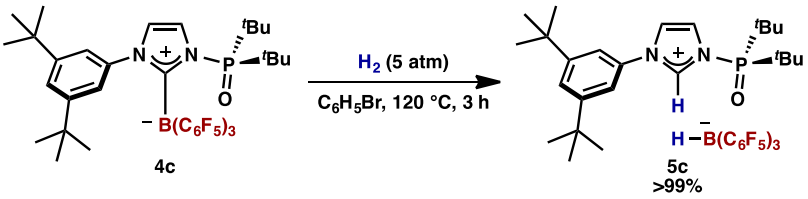


5a (autoclave experiment): A solution of **4a** (93.5 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) was stirred under H_2 (5 atm) at 60 ˚C for 3 h. Then, the solvent was removed *in vacuo* to give **5a** as a white solid (93.7 mg, 0.10 mmol, >99%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.79 (s, 1H, Im-*H*), 7.77 (s, 1H, Im-*H*), 7.66 (t, *J* = 7.6 Hz, Ar-*H*), 7.62 (s, 1H, Im-*H*), 7.41 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 3.60 (1:1:1:1 q, $^1J_{H,B}$ = 91 Hz, *H*B$(C_6F_5)_3$,

1H), 2.17 (sept, J = 6.8 Hz, 2H, C*H*(CH_3)$_2$), 1.21 (d, $^3J_{H,P}$ = 16.8 Hz, 18H, ^{t}Bu-*H*), 1.20 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.17 (d, J = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). **^{11}B NMR** (128 MHz, CD_2Cl_2): δ –25.4 (d, $^1J_{H,B}$ = 91 Hz, H*B*(C_6F_5)$_3$). **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 148.6 (dm, $^1J_{C,F}$ = 234 Hz), 145.2, 142.0 (N*C*HN), 138.2 (dm, $^1J_{C,F}$ = 242 Hz), 136.8 (dm, $^1J_{C,F}$ = 243 Hz), 133.3, 129.7, 128.1, 125.5, 123.3, 38.5 (d, $^1J_{C,P}$ = 59.0 Hz), 29.6, 25.8, 24.5, 23.6. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ –137.1 (d, $^3J_{F,F}$ = 22.6 Hz, 6F, Ar-*F*), –167.8 (t, $^3J_{F,F}$ = 20.7 Hz, 3F, Ar-*F*), –170.8 (m, 6F, Ar-*F*). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 77.6 (s). **ESI-MS** (pos): m/z Calcd for $C_{23}H_{38}N_2OP$ $[M–HBAr_3]^+$ 389.2716, found 389.2765; (neg): m/z Calcd for $C_{18}HBF_{15}$ $[M–Im]^-$ 512.9937, found 512.9778. **Anal. Calcd for $C_{41}H_{39}BF_{15}N_2OP$:** C, 54.56; H, 4.36; N, 3.10. Found: C, 54.71; H, 4.42; N, 3.04.

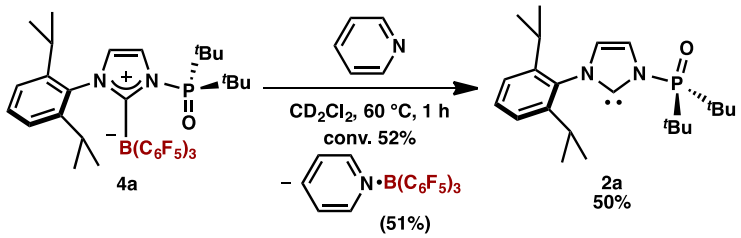


5b (autoclave experiment): A solution of **4b** (135.0 mg, 0.16 mmol) in 1,2-dichloroethane (10 mL) was stirred under H_2 (5 atm) at 80 ˚C for 3 h. Then, the solvent was removed *in vacuo* to give **5b** as a white solid (133.9 mg, 0.16 mmol, >99%). Recrystallization from THF/hexane gave a crystal of **5b**·(THF)$_{0.4}$, of which formula was confirmed by ^{1}H NMR analysis. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.91 (s, 1H, NC*H*N), 7.75 (s, 1H, Im-*H*), 7.56 (s, 1H, Im-*H*), 7.10 (s, 2H, Ar-*H*), 3.58 (1:1:1:1 q, $^1J_{H,B}$ = 86 Hz, 1H, *H*B(C_6F_5)$_3$), 2.37 (s, 3H, Ar-C*H*$_3$), 2.01 (s, 6H, Ar-C*H*$_3$), 1.39 (d, $^3J_{H,P}$ = 16.8 Hz, 18H, ^{t}Bu-*H*). **^{11}B NMR** (128 MHz, CD_2Cl_2): δ –25.4 (d, $^1J_{H,B}$ = 86 Hz, H*B*(C_6F_5)$_3$). **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 148.6 (dm, $^1J_{C,F}$ = 236 Hz), 143.2, 141.1 (N*C*HN), 138.2 (dm, $^1J_{C,F}$ = 241 Hz), 136.8 (dm, $^1J_{C,F}$ = 237 Hz), 134.0, 130.6, 130.0, 127.1, 123.5, 38.5 (d, $^1J_{C,P}$ = 60.0 Hz), 25.9, 21.2, 17.3. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ –137.1 (d, $^3J_{F,F}$ = 18.8 Hz, 6F, Ar-*F*), –167.7 (t, $^3J_{F,F}$ = 18.8 Hz, 3F, Ar-*F*), –170.7 (m, 6F, Ar-*F*). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 77.1 (s). **ESI-MS** (pos): m/z Calcd for $C_{20}H_{32}N_2OP$ $[M–HBAr_3]^+$ 347.2247, found 347.2235; (neg): m/z Calcd for $C_{18}HBF_{15}$ $[M–Im]^-$ 512.9937, found 512.9641. **Anal. Calcd for $C_{38}H_{33}BF_{15}N_2OP$·$(C_4H_8O)_{0.4}$:** C, 53.48; H, 4.10; N, 3.15. Found: C, 53.70; H, 4.22; N, 3.07.



5c (autoclave experiment): A solution of **4c** (154.4 mg, 0.166 mmol) in C_6H_5Br (10 mL) was stirred under H_2 (5 atm) at 120 ˚C for 3 h. Then, the solvent was removed *in vacuo* to give **5c** as a white solid (153.0 mg, 0.164 mmol, >99%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 9.03 (d, J = 1.6 Hz, 1H, NC*H*N), 7.89 (s, 1H, Im-*H* or Ar-*H*), 7.74 (t, J = 1.6 Hz, 1H, Im-*H* or Ar-*H*), 7.67 (s, 1H, Im-*H* or Ar-*H*), 7.28 (d, J = 1.6 Hz, 2H, Ar-*H*), 3.59 (1:1:1:1 q, $^1J_{H,B}$ = 91 Hz, *H*B(C_6F_5)$_3$, 1H), 1.42 (d, $^3J_{H,P}$ = 16.8 Hz, 18H, ^{t}Bu-*H*), 1.37 (s, 18H, ^{t}Bu-*H*). **^{11}B NMR** (128 MHz, CD_2Cl_2): δ –25.4 (d, $^1J_{H,B}$ = 91 Hz, H*B*(C_6F_5)$_3$). **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 155.2, 148.5 (dm, $^1J_{C,F}$ = 229 Hz), 138.3 (N*C*HN), 138.2 (dm, $^1J_{C,F}$ = 224 Hz), 137.0 (dm, $^1J_{C,F}$ = 233 Hz), 133.8, 126.6, 125.5, 123.4, 117.1, 38.6 (d, $^1J_{C,P}$ = 59.0 Hz), 35.7, 31.3, 26.1. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ –137.1 (d, $^3J_{F,F}$ = 21.8 Hz, 6F, Ar-*F*), –167.7 (t, $^3J_{F,F}$ = 24.4 Hz, 3F, Ar-*F*), –170.6 (m, 6F, Ar-*F*). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 77.4 (s). **ESI-MS** (pos): m/z Calcd for $C_{25}H_{42}N_2OP$ $[M–HBAr_3]^+$ 417.3029, found 417.3013; (neg): m/z Calcd for $C_{18}HBF_{15}$ $[M–Im]^-$ 512.9937, found 512.9659. **Anal. Calcd for $C_{43}H_{43}BF_{15}N_2OP$:** C, 54.50; H, 4.66; N, 3.01. Found: C, 54.80; H, 4.66; N, 3.00.

- **Reaction with Pyridine**



Scheme S1. Reaction of **4a** with pyridine. NMR yields are given.

To a solution of **4a** (9.0 mg, 0.010 mmol) in CD_2Cl_2 (0.5 mL) was added pyridine (0.79 mg, 0.010 mmol), and the resulting mixture was heated at 60 °C. The conversion of **4a**, and yields of **2a** and [pyridine-B(C_6F_5)$_3$] were determined by ^{1}H and ^{31}P NMR after 1 h. The same reaction was conducted at 30 °C, which regenerated **2a** in 2% after 2 h. This result also shows the existence of thermal decomplexation process.

[8] Variable Temperature NMR Experiments

A J.Young NMR tube was charged with **4c** (9.3 mg, 0.010 mmol) and C_6D_5Br (0.5 mL). Then, ^{1}H, ^{19}F, and ^{31}P NMR were recorded at 30 ˚C followed by raising temperature to 90 ˚C, and NMR measurements were conducted at every 10 ˚C. After that, the reaction mixture was allowed to cool to 30 ˚C, and NMR measurements were conducted again. These results are shown in Figure S12–14.

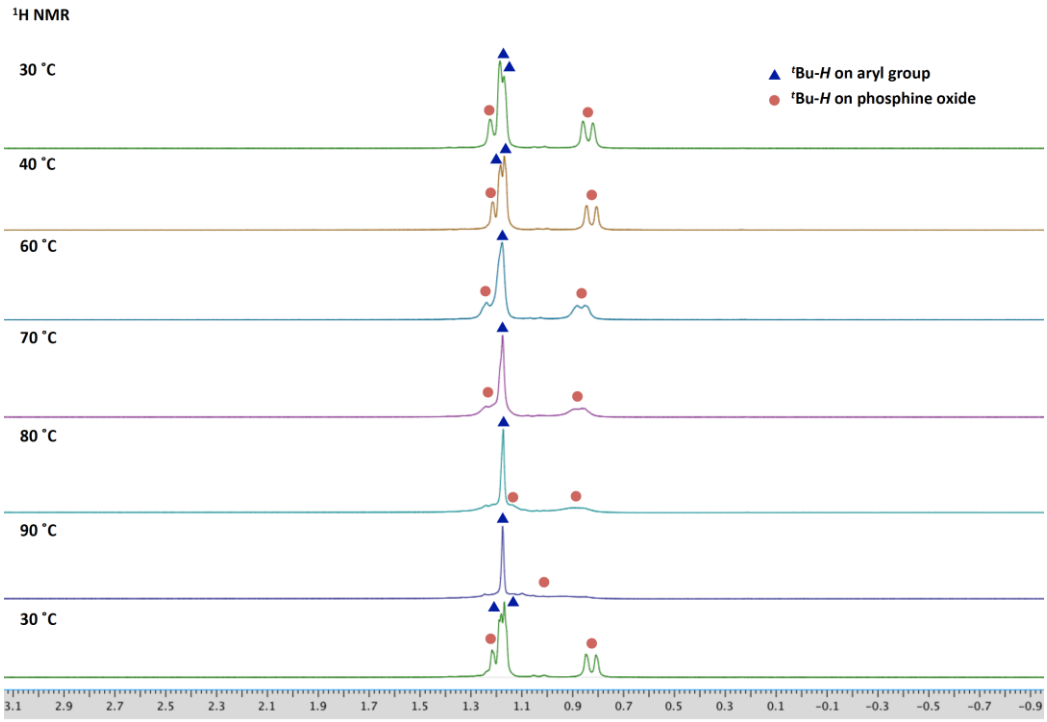


Figure S12. Variable-temperature ^{1}H NMR using **4c** in C_6D_5Br.

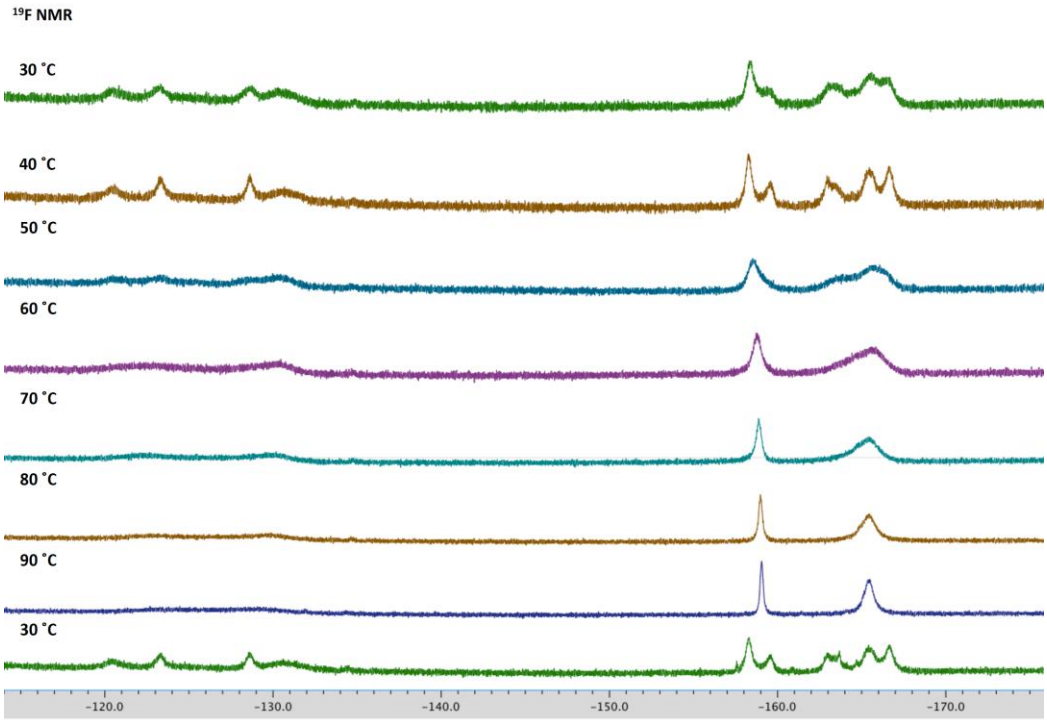


Figure S13. Variable-temperature ^{19}F NMR using **4c** in C_6D_5Br.

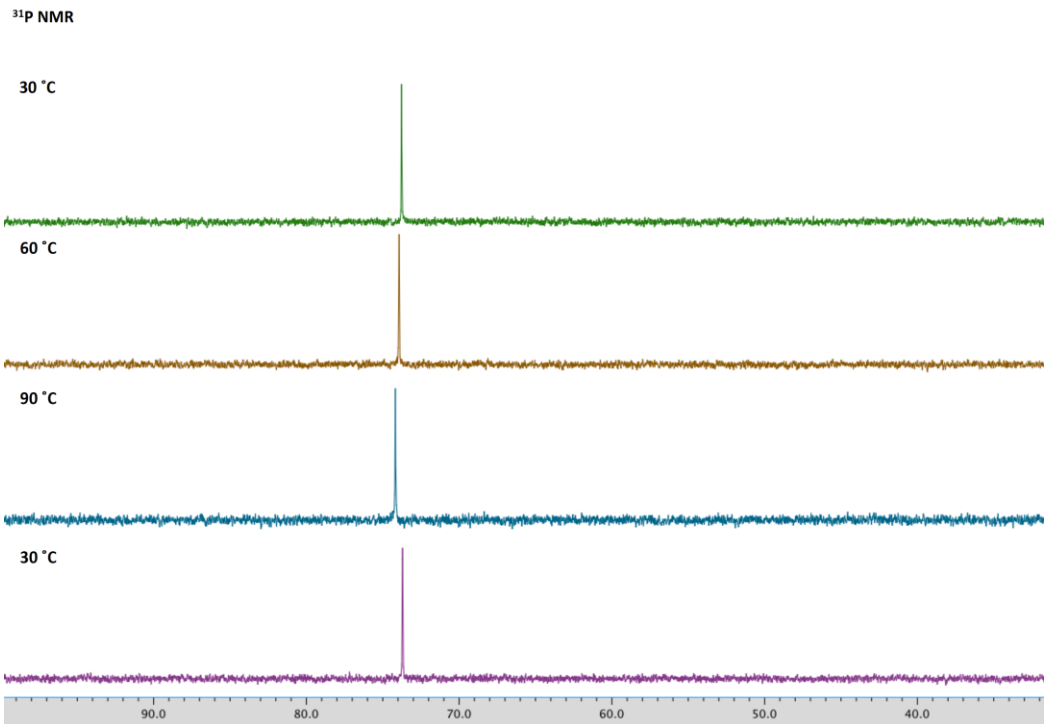
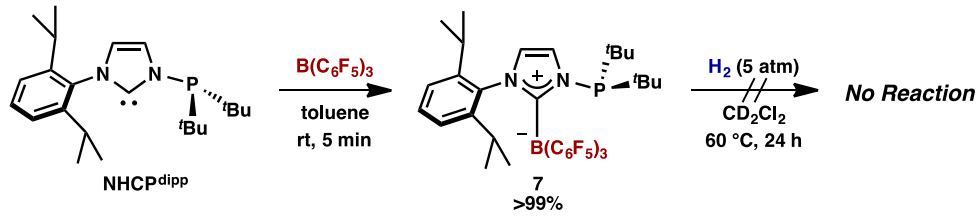
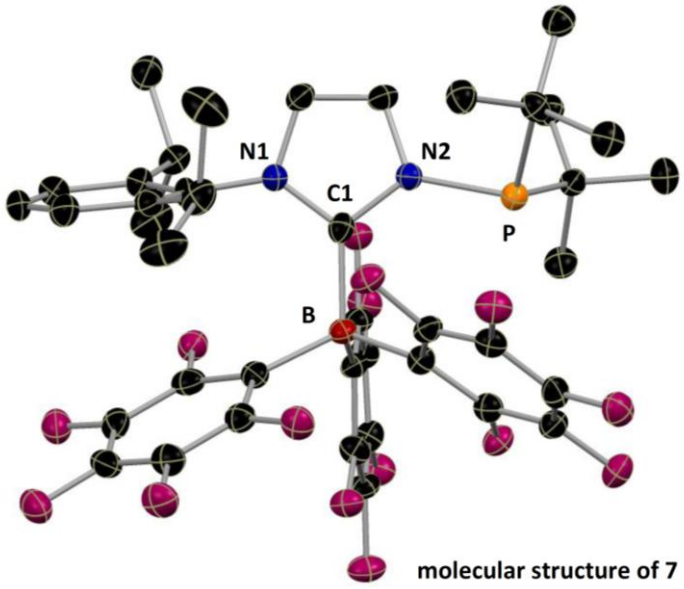


Figure S14. Variable-temperature ^{31}P NMR using **4c** in C_6D_5Br.

[9] Comparison with NHCP

- **Synthesis of [NHCP^{dipp}-B(C_6F_5)$_3$] (7) and Reaction with H_2**





Scheme S2. Reaction of **7** with H_2. Isolated yield is given. The crystal structure of **7** with ellipsoids set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angle (°):C1–B 1.678(8), N2–P 1.779(2), ∠C1-N2-P 128.7(3). Interatomic distance between B and P is 3.564(6) Å.

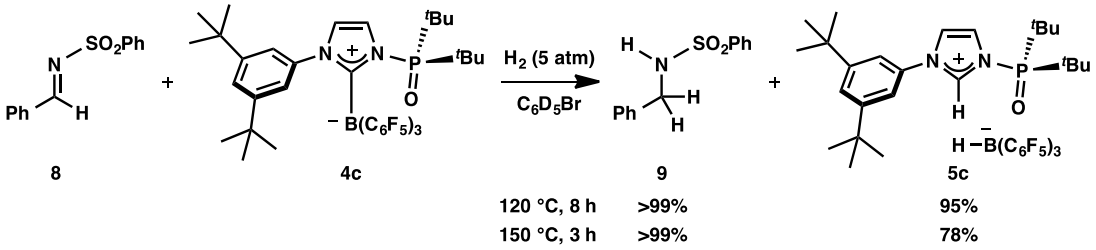
To a solution of NHCP^{dipp} (37.5 mg, 0.10 mmol) in toluene (5 mL) was added B(C_6F_5)$_3$ (51.0 mg, 0.10 mmol), and the reaction mixture was stirred for 5 minutes at room temperature. Then, the solvent was removed *in vacuo*, and the resulting solid was washed with hexane, and dried *in vacuo* to give **7** as a white solid (90.6 mg, 0.10 mmol, >99%). A single crystal suitable for X-ray diffraction analysis was prepared by recrystallization from THF/hexane at –30 °C. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.60 (s, 1H, Im-*H*), 7.29 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 7.24 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 7.09 (s, 1H, Im-*H*), 6.80 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 2.84 (m, 2H, C*H*(CH_3)$_2$), 1.24–1.18 (m, 15H, CH(CH_3)$_2$ and ^{t}Bu-*H*), 1.08 (d, $^3J_{H,P}$ = 12.8 Hz, 9H, ^{t}Bu-*H*), 0.97 (d, *J* = 6.8 Hz, 3H, CH(CH_3)$_2$), 0.71 (d, *J* = 6.8 Hz, 3H, CH(CH_3)$_2$). **^{11}B NMR** (128 MHz, CD_2Cl_2): δ –15.8 (s). **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 147.9, 145.9, 134.9, 131.0, 127.5, 127.2,

124.8, 122.2, 36.9 (d, $^{1}J_{C,P}$ = 70.0 Hz), 36.5 (d, $^{1}J_{C,P}$ = 70.0 Hz), 29.4 (d, $^{2}J_{C,P}$ = 20.0 Hz), 28.9 (d, $^{2}J_{C,P}$ = 20.0 Hz), 28.6, 27.3, 26.3, 22.1, 20.6. Resonances for N*C*N and C_6F_5 could not be identified. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ −114.4 (1F), −123.0 (1F), −131.5 (1F), −133.5 (1F), −134.2 (1F), −137.1 (1F), −162.8 (1F), −163.5 (1F), −163.8 (1F), −168.3 (1F), −169.2 (1F), −169.4 (1F), −169.7 (1F), −170.7 (2F). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 119.0. X-ray data for **7**: *M* = 884.50, colorless, monoclinic, *P2₁/c* (#14), *a* = 9.8387(3) Å, *b* = 17.9881(6) Å, *c* = 22.6266(7) Å, α = 90°, β = 103.864(2)°, γ = 90°, *V* = 3887.8(2) Å^3, *Z* = 4, *Dcalcd* = 1.511 g/cm^3, *T* = −150 °C, R_1 (wR_2) = 0.0857 (0.2582).

A solution of **7** (2.2 mg, 2.5 μmol) in CD_2Cl_2 (0.5 mL) was heated at 60 ˚C under H_2 (5 atm) for 24 h. Then, NMR analysis was conducted. No reaction was observed in NMR.

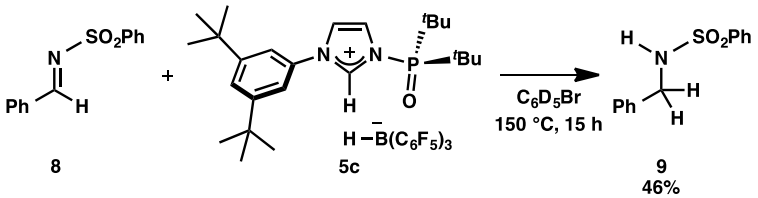
[10] Hydrogenation of *N*-benzylidenebenzenesulfonamide (8)

- **Reaction of 8 with 4c under H_2**



A solution of **4c** (9.3 mg, 0.01 mmol), *N*-benzylidenebenzenesulfonamide (**8**) (2.5 mg, 0.01 mmol), and 1,2-dichloroethane (1.3 mg, 0.013 mmol, internal standard) in C_6D_5Br (0.5 mL) was heated at 120 ˚C (or 150 ˚C) under H_2 (5 atm) for 8 h. The yields of **9** and **5c** were determined by ^{1}H NMR. Spectroscopic data of **9** was identified to that previously reported.

- **Reaction of 8 with 5c**



A solution of **5c** (9.3 mg, 0.01 mmol), **8** (2.5 mg, 0.01 mmol), and 1,2-dichloroethane (1.3 mg, 0.013 mmol, internal standard) in C_6D_5Br (0.5 mL) was

heated at 150 ˚C for 15 h. The yield of **9** and H_2 was determined by ^{1}H NMR (Figure S15).

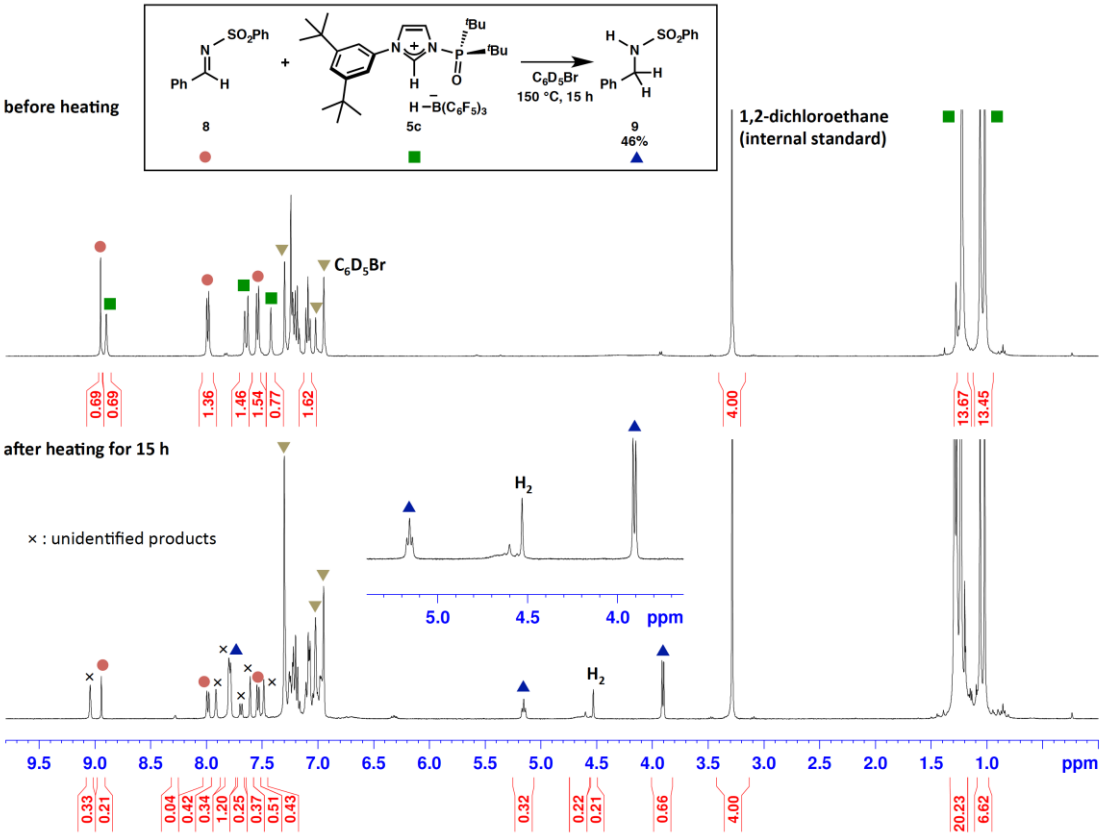


Figure S15. ^{1}H NMR results for the reaction of **8** with **5c**.

[11] Theoretical Study

General considerations. All calculations were performed with the Gaussian 09, Revision A.02[S3] of programs with the hybrid B3LYP[S4] or M06-2X[S5] functions. The 6-31G++(d,p) basis set was used for compounds **2a–c** (including conformers A and B, and their TS state), and 6-311G(d,p) for **4a–c** (including State I–IV of **4c**), **6c**, and **6c'**. The geometry optimizations were performed without any symmetry constraint followed by analytical frequency calculations to confirm that a minimum or a transition state had been reached. The gas-phase Gibbs energies were calculated at 298.15 K or 393.00 K and 1 atm from the harmonic approximation for frequencies. These calculations involve a certain margin error.

Calculation of %V_{bur}. The %V_{bur} values were calculated with the crystallographic data (*vide supra*) and DFT-optimized structural parameters (*vide infra*) by using the

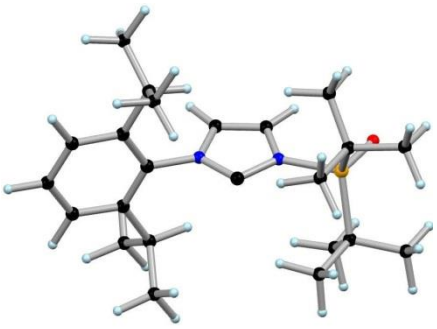
Samb*V*ca program (https://www.molnac.unisa.it/OMtools/sambvca.php).[S6] The following parameters were employed: sphere radius, 3.00 Å; distance for the metal-ligand bond, 2.00 Å; H atoms are omitted; Bondi radius, 1.17.

Optimized structure and Cartesian coordinates (x, y, z) for 2a in the conformation A (Table S1):

298.15 K

E:-1424.347978

G:-1424.411981



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N	2.992436	0.439044	4.347688
C	1.924971	1.286576	4.247343
C	4.215577	1.114830	4.449594
C	3.928353	2.437520	4.413796
C	2.879747	-0.999391	4.345412
C	2.715216	-1.671439	5.573965
C	2.610541	-3.068694	5.543240
C	2.669983	-3.769951	4.340975
C	2.835924	-3.081945	3.141015
C	2.945729	-1.685015	3.115038
C	2.625404	-0.932469	6.905746
C	3.696475	-1.408508	7.906723
C	1.210794	-1.047346	7.509024
C	3.104227	-0.960565	1.781616
C	1.823419	-1.079784	0.930948
C	4.338706	-1.448958	0.998533
C	0.640663	4.161782	5.741386
C	-0.489275	3.116964	5.798751
C	1.607946	3.941688	6.929235
C	0.055754	5.588754	5.839632
C	0.860404	4.094854	2.526280
C	-0.310630	3.104095	2.393256
C	1.957042	3.742651	1.493034
C	0.376739	5.537839	2.256423
H	5.157647	0.596172	4.535996
H	4.552106	3.316019	4.459145
H	2.477332	-3.614727	6.472453
H	2.585119	-4.853077	4.338980
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H	2.809341	0.127721	6.713853
H	3.253937	0.101390	1.992612
H	5.253456	-1.348980	1.592199
H	4.462535	-0.860193	0.082824
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H	1.542017	3.873858	0.486702
H	-0.028880	2.094828	2.704870
H	-0.620815	3.070383	1.341283
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H	-0.446731	5.828683	2.914694
H	1.187153	6.262068	2.373913
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H	-0.123367	2.106273	5.600052

H	-0.931043	3.137390	6.802947
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H	2.004870	2.922908	6.945493
H	-1.179762	3.418110	2.977048
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H	4.704284	-1.310975	7.489580
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H	3.649414	-0.810415	8.823566
H	1.144209	-0.469856	8.438187
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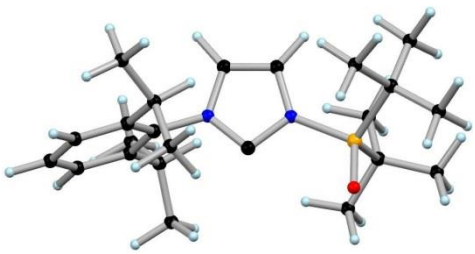
Optimized structure and Cartesian coordinates (x, y, z) for 2a in the conformation B (Table S2):

298.15 K

E:-1424.333312

G:-1424.396492



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C	0.669681	0.111345	-1.704222
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C	2.574172	-0.135366	-0.100610
C	3.311826	1.045244	0.118007
C	4.675015	0.914309	0.416876
C	5.277163	-0.339319	0.494971
C	4.523846	-1.491179	0.276336
C	3.157811	-1.417002	-0.027148
C	2.663939	2.426254	0.090137
C	3.424796	3.421346	-0.806564
C	2.500469	2.977420	1.521935
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C	1.971612	-3.297877	1.160587
C	3.030500	-3.727804	-1.112596
C	-3.662687	-1.045165	-0.513919
C	-4.186246	-0.422929	-1.822770
C	-2.866331	-2.335167	-0.819666
C	-4.873348	-1.429210	0.372661
C	-3.007794	1.878516	0.617818
C	-2.786874	2.625525	-0.711266
C	-2.094122	2.489988	1.706071
C	-4.478402	2.021639	1.066976
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H	-1.425544	0.273601	-2.356018
H	5.270835	1.803663	0.598362
H	6.334669	-0.419604	0.731030
H	5.003945	-2.461965	0.348411
H	1.660079	2.316588	-0.329148
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H	-3.393218	-0.145413	-2.521677
H	-4.814573	-1.163014	-2.333386
H	-4.546690	-1.867390	1.317702
H	-5.481296	-2.165169	-0.167270
H	-5.514203	-0.572521	0.597527
H	-3.542574	-3.064688	-1.281342
H	-2.037707	-2.161976	-1.510976
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H	3.542297	3.034727	-1.824601
H	4.423873	3.643508	-0.416034
H	2.878502	4.369452	-0.863833
H	1.993258	3.949136	1.502514
H	1.910859	2.292272	2.138224
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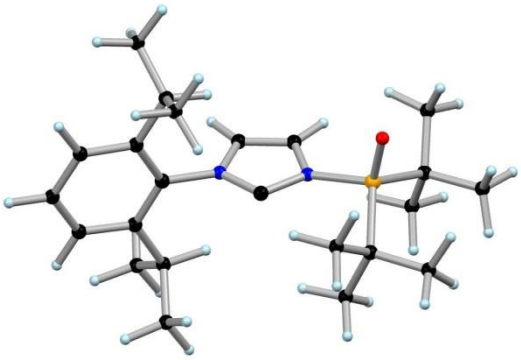
Optimized structure and Cartesian coordinates (x, y, z) for 2a in TS (Table S3):

298.15 K

E:-1424.328621

G:-1424.388870



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C	-0.600118	-0.697079	-1.814393
C	2.511250	-0.028990	-0.156248
C	3.121596	1.222933	-0.372151
C	4.459220	1.370720	0.019368
C	5.158920	0.316954	0.603110
C	4.530613	-0.910020	0.806204
C	3.195916	-1.113517	0.430029
C	2.373354	2.404340	-0.982742
C	3.055035	2.920869	-2.265183
C	2.192813	3.539484	0.045433
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C	2.252842	-2.652131	2.197177
C	3.329872	-3.638867	0.114810
C	-3.845073	-0.346679	-1.234927
C	-3.567945	0.854794	-2.159959
C	-3.807207	-1.691821	-2.009049
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C	-2.712288	0.851865	1.541185
C	-2.166001	2.209501	1.062035
C	-1.902925	0.344175	2.761949
C	-4.174202	1.031852	2.015992
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H	-1.264786	-0.971471	-2.611588
H	4.957442	2.324298	-0.128924
H	6.194344	0.452818	0.902897
H	5.084525	-1.721924	1.267556
H	1.373632	2.061229	-1.261739
H	1.553189	-2.454443	0.189816
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H	2.772506	-4.572446	0.248083

H	4.296420	-3.759389	0.616533
H	1.728457	-3.598424	2.370264
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H	-4.152752	1.604807	2.949992
H	-4.782676	1.597315	1.307871
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H	-3.686979	1.805452	-1.631741
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H	-2.837814	-1.947395	-2.435734
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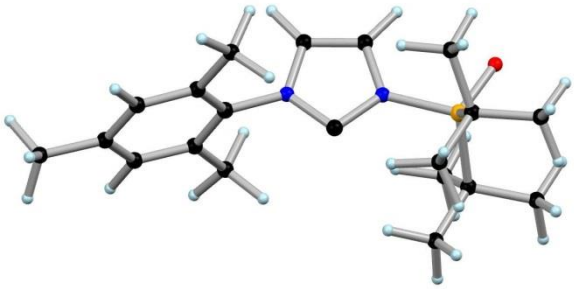
H	4.053186	3.323066	-2.059521
H	2.460352	3.724708	-2.713487
H	1.605022	4.356874	-0.387800
H	1.674088	3.179930	0.939309
H	3.158609	3.951763	0.358814

Optimized structure and Cartesian coordinates (x, y, z) for 2b in the conformation A (Table S4):

298.15 K

E: -1306.491316

G: -1306.550855



P	7.036657	0.526084	27.470091
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N	5.811291	3.932052	28.830906
C	5.948185	2.589011	29.037471
C	6.794462	3.234982	26.980654
C	6.317543	4.345452	27.590446
C	5.419452	-0.444010	27.438573
C	5.723980	-1.840135	26.850076
C	4.707902	-0.580478	28.797365
C	4.504754	0.318861	26.450531
C	8.306253	0.057135	28.783728
C	8.950822	-1.279957	28.353676
C	7.758401	-0.050918	30.218798
C	9.384173	1.165925	28.724186
C	5.211294	4.831018	29.783625
C	6.025552	5.449117	30.746844
C	5.421692	6.329299	31.652853
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C	3.270584	5.955880	30.650492
C	3.828120	5.067657	29.722897
C	7.505802	5.160309	30.823340
C	3.427534	7.580043	32.587527
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H	7.267200	3.079750	26.023961
H	6.289393	5.374638	27.267434
H	6.311897	-2.458075	27.534794
H	4.775409	-2.361456	26.673832

H	6.259303	-1.768476	25.899487
H	3.709049	-1.001430	28.626449
H	5.235806	-1.261754	29.469433
H	4.597944	0.383892	29.300382
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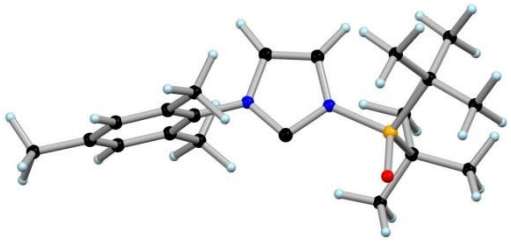
H	4.201268	1.291365	26.847347
H	4.993751	0.470995	25.484192
H	9.800101	-1.489173	29.015172
H	8.256412	-2.120510	28.440868
H	9.318066	-1.237473	27.324768
H	8.606105	-0.151309	30.908319
H	7.180463	0.832210	30.503754
H	7.127293	-0.933400	30.350802
H	9.000120	2.124442	29.083462
H	10.219812	0.874451	29.371471
H	9.768743	1.299933	27.709187
H	6.041349	6.810702	32.406092
H	2.199799	6.143834	30.616028
H	7.687039	4.101603	31.037604
H	7.974848	5.755418	31.611192
H	8.013381	5.386132	29.879258
H	3.970430	7.601478	33.537492
H	3.440537	8.598928	32.180017
H	2.384126	7.326091	32.798331
H	3.294241	4.566910	27.680260
H	2.983237	3.285052	28.845762
H	1.920613	4.704443	28.790072

Optimized structure and Cartesian coordinates (x, y, z) for 2b in the conformation B (Table S5):

298.15 K

E: -1306.476403

G: -1306.535186



P	2.374496	-0.091410	-0.587413
O	2.259125	-0.391341	-2.048843
N	0.806057	-0.196091	0.233720
N	-1.324815	-0.155748	0.469037
C	-0.363119	-0.045420	-0.496365
C	0.547408	-0.377484	1.604701
C	-0.797916	-0.358334	1.747702
C	3.463425	-1.409546	0.238102
C	4.640054	-1.653377	-0.739683
C	4.039469	-1.069083	1.626320
C	2.628773	-2.709769	0.310016
C	2.897613	1.696428	-0.294048
C	4.367146	1.875356	-0.733437
C	2.717253	2.177302	1.158389
C	1.995669	2.537023	-1.228562
C	-2.737023	-0.083268	0.192213
C	-3.406654	-1.239799	-0.240523
C	-4.780859	-1.148242	-0.490790
C	-5.486622	0.048891	-0.323019
C	-4.779827	1.181596	0.095798
C	-3.404703	1.140864	0.356713
C	-2.666393	-2.537848	-0.455700
C	-6.976573	0.110756	-0.570548
C	-2.662069	2.388853	0.771471
H	1.312014	-0.503028	2.351796
H	-1.415246	-0.474025	2.625803
H	5.306347	-0.789998	-0.814484
H	5.232531	-2.498177	-0.368072
H	4.277202	-1.891123	-1.741482

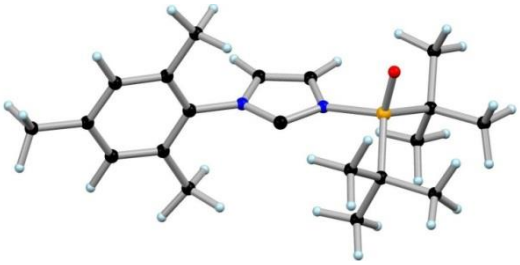
H	4.649083	-1.914762	1.967646
H	4.690991	-0.191433	1.600220
H	3.274727	-0.901907	2.388826
H	3.288513	-3.535231	0.603382
H	1.820021	-2.650537	1.042509
H	2.192705	-2.954132	-0.662923
H	4.609570	2.944941	-0.730280
H	5.070394	1.380947	-0.056277
H	4.532439	1.498257	-1.746786
H	3.023260	3.228799	1.220697
H	1.674246	2.119365	1.480349
H	3.330523	1.618874	1.871035
H	0.936210	2.427481	-0.981263
H	2.269057	3.594040	-1.121273
H	2.123169	2.242375	-2.272482
H	-5.309891	-2.035418	-0.831611
H	-5.306931	2.125695	0.213804
H	-1.904878	-2.426446	-1.234680
H	-3.356947	-3.330581	-0.755277
H	-2.148301	-2.863683	0.453206
H	-7.276713	-0.571304	-1.372203
H	-7.538045	-0.174309	0.328324
H	-7.293716	1.120679	-0.847846
H	-2.194806	2.279284	1.756551
H	-1.861140	2.619645	0.060980
H	-3.340504	3.244893	0.814340

Optimized structure and Cartesian coordinates (x, y, z) for 2b in TS (Table S6):

298.15 K

E: -1306.471899

G: -1306.528183



P	2.435916	0.041120	-0.557763
O	2.633812	-0.185456	-2.029253
N	0.858801	-0.581020	0.016511
N	-1.288400	-0.683944	0.149508
C	-0.285887	0.175145	-0.182137
C	0.532323	-1.884340	0.441464
C	-0.815335	-1.941703	0.530806
C	3.724241	-0.987307	0.401927
C	5.134526	-0.380554	0.195447
C	3.456671	-1.102372	1.915512
C	3.780019	-2.379761	-0.281930
C	2.389666	1.900960	-0.151995
C	3.813799	2.493805	-0.276719
C	1.828247	2.223877	1.245064
C	1.526036	2.573392	-1.249922
C	-2.685977	-0.339211	0.085868
C	-3.364738	-0.480127	-1.136031
C	-4.724431	-0.148646	-1.172457
C	-5.406204	0.310360	-0.039350
C	-4.690484	0.446252	1.155569
C	-3.329395	0.129243	1.242495
C	-2.649880	-0.953701	-2.378823
C	-6.882445	0.629786	-0.100325
C	-2.575990	0.312828	2.538633
H	1.250635	-2.653533	0.653285
H	-1.468009	-2.748737	0.826756
H	5.305426	0.506738	0.805132
H	5.875180	-1.129432	0.500069
H	5.324570	-0.134184	-0.852612

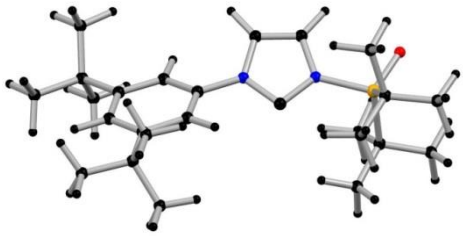
H	4.228149	-1.738837	2.366627
H	3.512145	-0.127497	2.408846
H	2.485059	-1.539418	2.154305
H	4.544618	-2.981474	0.223858
H	2.847274	-2.942048	-0.251824
H	4.056187	-2.273935	-1.333334
H	3.717703	3.584566	-0.323007
H	4.444897	2.264729	0.583888
H	4.321684	2.170051	-1.189462
H	1.879639	3.309024	1.399074
H	0.784495	1.918635	1.335191
H	2.406406	1.754712	2.047907
H	0.493017	2.229970	-1.209361
H	1.552720	3.657507	-1.081062
H	1.930704	2.366632	-2.244113
H	-5.261059	-0.248108	-2.113291
H	-5.199521	0.815284	2.043138
H	-1.842391	-0.267215	-2.653630
H	-3.344735	-1.025398	-3.219547
H	-2.190881	-1.937636	-2.232440
H	-7.168534	1.009062	-1.086284
H	-7.487590	-0.264916	0.093846
H	-7.159975	1.380511	0.645908
H	-2.136504	-0.626426	2.892290
H	-1.751575	1.023351	2.415639
H	-3.239968	0.690158	3.320704

Optimized structure and Cartesian coordinates (x, y, z) for 2c in the conformation A (Table S7):

298.15 K

E: -1502.927208

G: -1502.992350



P	11.240146	10.720692	5.161920
O	11.618904	9.872037	6.346209
N	9.754754	11.577737	5.574812
N	8.040635	12.858352	5.575467
C	9.087120	12.479520	4.776894
C	9.140981	11.406095	6.824599
H	9.534944	10.727675	7.564378
C	8.057751	12.216373	6.822302
H	7.293902	12.364102	7.568278
C	12.515600	12.080385	4.877219
C	13.903825	11.404908	4.804367
H	14.027348	10.808344	3.895991
H	14.083554	10.760949	5.669286
H	14.673223	12.186127	4.788573
C	12.464008	12.967307	6.144330
H	13.289559	13.687382	6.098371
H	12.579276	12.374777	7.056459
H	11.530055	13.532121	6.206081
C	12.278568	12.952208	3.630347
H	11.258606	13.344055	3.593994
H	12.475328	12.404783	2.704822
H	12.975200	13.799399	3.661017
C	10.772757	9.638679	3.689627
C	11.963857	8.696024	3.405650
H	12.285949	8.170146	4.308518
H	12.822501	9.229822	2.987907
H	11.652700	7.949722	2.664831
C	9.573278	8.789592	4.175001
H	9.339094	8.045205	3.404809
H	8.680414	9.401133	4.332177

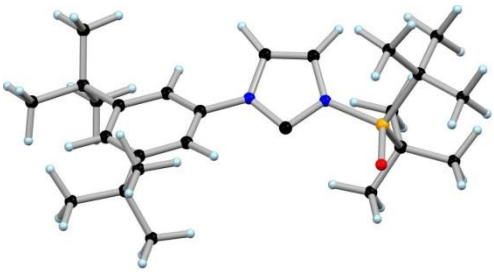
H	9.804215	8.260550	5.103728
C	10.377944	10.399021	2.410078
H	9.965350	9.679599	1.691595
H	11.237560	10.877061	1.934173
H	9.624218	11.165691	2.606913
C	7.053968	13.817012	5.180136
C	6.497565	14.674878	6.129921
H	6.846159	14.624886	7.155635
C	5.522992	15.612069	5.758248
C	5.141559	15.664590	4.408966
H	4.393588	16.383361	4.107197
C	5.698926	14.818403	3.435773
C	6.660043	13.885603	3.843862
H	7.124242	13.204453	3.141525
C	4.928492	16.550733	6.828071
C	6.058866	17.411247	7.444412
H	6.547194	18.022392	6.677796
H	6.828024	16.795035	7.919990
H	5.650935	18.083750	8.208019
C	4.261644	15.708593	7.943276
H	3.831884	16.364649	8.709075
H	4.978378	15.046277	8.438519
H	3.456637	15.087081	7.536404
C	3.863564	17.504393	6.251416
H	4.277588	18.161938	5.479649
H	3.473318	18.142199	7.051599
H	3.016234	16.959597	5.821426
C	5.287051	14.875646	1.950777
C	6.529836	15.203655	1.087296
H	7.316655	14.452716	1.204443
H	6.952381	16.175723	1.363827
H	6.255471	15.240563	0.026513
C	4.713628	13.503018	1.520949
H	4.418489	13.529152	0.465495
H	3.830393	13.244326	2.115149
H	5.446202	12.699644	1.642677
C	4.215304	15.948236	1.673945
H	4.568151	16.954252	1.925320
H	3.291372	15.757982	2.230787
H	3.963146	15.945379	0.608185

Optimized structure and Cartesian coordinates (x, y, z) for 2c in the conformation B (Table S8):

298.15 K

E: -1502.912775

G: -1502.976989



P	3.541999	0.446268	0.169732
O	3.417867	1.897114	0.513851
N	1.981877	-0.250238	-0.311343
N	-0.150703	-0.470504	-0.423791
C	0.810476	0.359920	0.092418
C	1.734610	-1.426352	-1.041343
H	2.504942	-2.057505	-1.449900
C	0.390638	-1.558117	-1.115391
H	-0.206661	-2.299568	-1.621693
C	4.662875	0.254912	-1.349791
C	5.836030	1.242813	-1.132601
H	6.484004	0.945173	-0.303957
H	5.469988	2.251793	-0.933203
H	6.448487	1.261971	-2.042153
C	3.852744	0.738851	-2.575396
H	4.530001	0.821776	-3.433942
H	3.412045	1.723612	-2.395184
H	3.049525	0.049603	-2.847640
C	5.242375	-1.148078	-1.615302

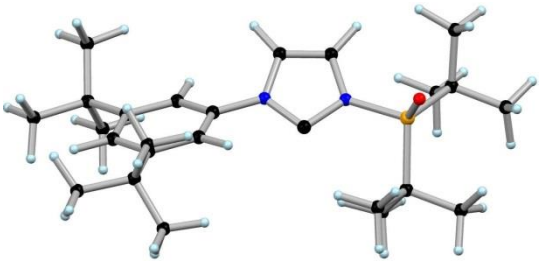
H	4.479751	-1.908541	-1.800602
H	5.877718	-1.495702	-0.796172
H	5.869468	-1.101551	-2.514095
C	4.024881	-0.577874	1.677340
C	5.484531	-0.253373	2.062968
H	5.646023	0.824480	2.155568
H	6.206650	-0.655681	1.345811
H	5.703087	-0.709646	3.035980
C	3.091033	-0.089547	2.810187
H	3.340380	-0.635522	3.728438
H	2.037489	-0.268650	2.578318
H	3.213366	0.980643	2.990615
C	3.851312	-2.097760	1.493782
H	4.137386	-2.598175	2.426966
H	4.483278	-2.506724	0.700517
H	2.813016	-2.367024	1.283215
C	-1.553192	-0.231264	-0.261107
C	-2.447059	-1.302039	-0.217776
H	-2.065882	-2.315785	-0.274291
C	-3.823093	-1.073951	-0.070545
C	-4.261546	0.253680	0.044571
H	-5.318443	0.445044	0.161066
C	-3.374864	1.343501	0.018290
C	-2.009366	1.081707	-0.143368
H	-1.274129	1.876455	-0.168981
C	-4.788688	-2.275958	-0.022840
C	-4.427636	-3.181186	1.180610
H	-4.509831	-2.629316	2.123077
H	-3.406392	-3.567926	1.108652
H	-5.107211	-4.040206	1.227625
C	-4.664226	-3.093387	-1.332005
H	-5.348081	-3.949977	-1.312214
H	-3.650922	-3.481145	-1.475976
H	-4.914096	-2.477882	-2.202960
C	-6.260955	-1.845519	0.129945
H	-6.431390	-1.293246	1.060122
H	-6.900669	-2.734218	0.153222
H	-6.593563	-1.221572	-0.706485
C	-3.848658	2.804427	0.155003
C	-3.187071	3.440733	1.402179
H	-2.095460	3.428478	1.335278
H	-3.472106	2.902647	2.312861
H	-3.506113	4.484168	1.509048
C	-3.433552	3.601592	-1.105943
H	-3.763251	4.643592	-1.020418
H	-3.887358	3.173741	-2.006745
H	-2.348696	3.605738	-1.245697
C	-5.377732	2.919217	0.311004
H	-5.737942	2.403753	1.207945
H	-5.910232	2.514178	-0.556559
H	-5.656348	3.974243	0.404599

Optimized structure and Cartesian coordinates (x, y, z) for 2c in TS (Table S9):

298.15 K

E: -1502.907363

G: -1502.969277



P	3.618240	0.290106	-0.357209
O	3.896066	1.149194	-1.557103
N	2.022405	-0.518588	-0.459551
N	-0.127835	-0.668438	-0.489227
C	0.878194	0.168946	-0.101222
C	1.700432	-1.743288	-1.076856

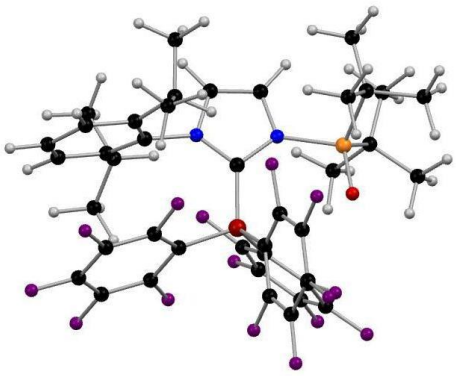
H	2.420487	-2.440651	-1.461128
C	0.352804	-1.837351	-1.084478
H	-0.289081	-2.606279	-1.483700
C	4.867963	-1.150825	-0.324552
C	6.275224	-0.613643	0.036655
H	6.390702	-0.419579	1.103173
H	6.523221	0.294285	-0.519501
H	7.011439	-1.379860	-0.233586
C	4.992934	-1.662379	-1.784797
H	5.733400	-2.470935	-1.804336
H	5.334761	-0.857884	-2.439634
H	4.070288	-2.051887	-2.214012
C	4.513859	-2.288320	0.653653
H	3.542222	-2.745743	0.457879
H	4.513614	-1.941228	1.691034
H	5.274369	-3.075151	0.574519
C	3.521812	1.340378	1.227818
C	4.939994	1.831162	1.607237
H	5.487212	2.227872	0.747498
H	5.541743	1.058107	2.088099
H	4.827539	2.646794	2.330573
C	2.692361	2.601519	0.874708
H	2.696400	3.262448	1.750826
H	1.663928	2.342807	0.626356
H	3.138065	3.137625	0.032753
C	2.899497	0.607354	2.430671
H	2.919455	1.280563	3.296876
H	3.458843	-0.292327	2.707447
H	1.860440	0.333830	2.239284
C	-1.516116	-0.372150	-0.303688
C	-2.410460	-1.397789	0.004384
H	-2.033131	-2.406423	0.134554
C	-3.775053	-1.123080	0.174209
C	-4.199826	0.207143	0.036008
H	-5.248026	0.434392	0.165711
C	-3.312592	1.254675	-0.263381
C	-1.958506	0.943346	-0.437720
H	-1.225650	1.704361	-0.676121
C	-4.742106	-2.273912	0.519832
C	-4.320668	-2.915181	1.864927
H	-4.351673	-2.179243	2.675521
H	-3.305786	-3.322398	1.822631
H	-4.999322	-3.736375	2.123529
C	-4.690684	-3.346642	-0.595595
H	-5.376171	-4.169823	-0.362990
H	-3.688315	-3.771516	-0.707319
H	-4.984119	-2.921609	-1.561546
C	-6.202168	-1.798410	0.654831
H	-6.320807	-1.062999	1.457610
H	-6.843653	-2.653044	0.894685
H	-6.575971	-1.356393	-0.274942
C	-3.775058	2.717720	-0.415800
C	-3.042332	3.597246	0.626891
H	-1.956480	3.559184	0.500469
H	-3.272136	3.268628	1.646336
H	-3.355364	4.643110	0.527091
C	-3.432627	3.220632	-1.839760
H	-3.753777	4.261701	-1.961096
H	-3.939720	2.617147	-2.600552
H	-2.358012	3.177851	-2.039728
C	-5.292310	2.884660	-0.201951
H	-5.600988	2.576853	0.802991
H	-5.874765	2.312134	-0.932009
H	-5.563192	3.939185	-0.320157

Optimized structure and Cartesian coordinates (x, y, z) for 4a (Table S10):

298.15 K

E: -3631.140425

G: -3631.228188



P	-0.303960	6.438875	2.572905
F	2.878600	4.197764	-0.086953
F	3.226135	5.616322	-2.306206
F	3.558418	8.333593	-2.150853
F	3.522046	9.536266	0.288447
F	3.247335	8.158100	2.481916
F	1.406582	4.891878	5.136407
F	1.862393	6.253443	7.380476
F	4.097205	7.823857	7.598994
F	5.811113	8.010447	5.487402
F	5.291496	6.708256	3.207099
F	3.524669	3.224575	4.765491
F	5.415159	1.403840	5.047394
F	7.262909	1.012836	3.065281
F	7.159285	2.584312	0.833680
F	5.357755	4.435999	0.560042
O	0.787075	7.245688	3.172319
N	1.338780	2.892362	2.167631
N	0.309892	4.793953	2.196606
C	1.537110	4.215567	2.440878
C	0.058782	2.666124	1.697055
C	-0.582038	3.847900	1.711241
C	2.144689	1.719601	2.488229
C	2.034722	1.205340	3.795191
C	2.814390	0.093314	4.111271
C	3.639364	-0.499103	3.162084
C	3.636157	-0.034843	1.854385
C	2.857738	1.062721	1.474385
C	1.058598	1.768262	4.816701
C	1.550502	1.662691	6.264761
C	-0.294896	1.048572	4.695363
C	2.688481	1.366844	-0.005288
C	4.008702	1.578853	-0.752138
C	1.900336	0.215420	-0.652311
C	-1.731162	6.211330	3.765817
C	-1.169376	5.801921	5.133278
C	-2.329688	7.626357	3.918007
C	-2.836574	5.206973	3.408970
C	-0.890359	7.109180	0.922448
C	-0.750563	8.641267	1.044634
C	-2.322276	6.756067	0.497814
C	0.069088	6.651212	-0.179913
C	3.110505	6.055293	1.336920
C	3.245381	7.446818	1.356910
C	3.393417	8.212200	0.199425
C	3.410630	7.606586	-1.046902
C	3.249776	6.231507	-1.122480
C	3.081799	5.520639	0.053767
C	3.261688	5.829130	4.033423
C	4.410926	6.591239	4.212488
C	4.705204	7.272353	5.385526
C	3.837100	7.176507	6.464476
C	2.704144	6.385846	6.350191
C	2.467756	5.720838	5.157554
C	4.268287	3.917319	2.629954
C	5.278401	3.720880	1.691891
C	6.271839	2.751330	1.814474
C	6.332118	1.955031	2.943485
C	5.392605	2.152645	3.943656
C	4.416331	3.117446	3.764764
B	3.034545	5.027956	2.630727
H	-0.259529	1.677167	1.407387
H	-1.587600	4.099491	1.419613

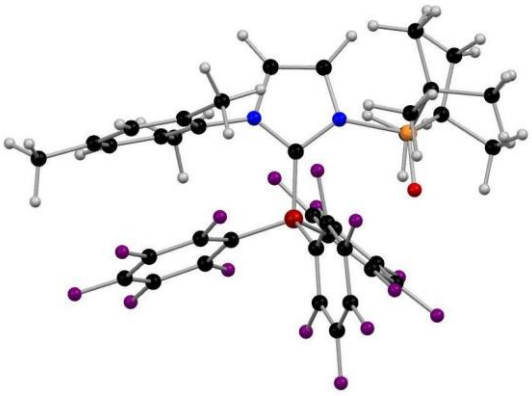
H	2.784523	-0.305406	5.119808
H	4.262256	-1.344587	3.437277
H	4.226178	-0.547792	1.100272
H	0.909664	2.827641	4.598984
H	2.584209	1.994389	6.368507
H	1.476612	0.634162	6.635160
H	0.920986	2.285748	6.907161
H	-0.173679	-0.021158	4.898276
H	-0.736307	1.153998	3.700441
H	-1.003788	1.454197	5.425311
H	2.089971	2.271469	-0.110684
H	4.650538	0.693722	-0.686371
H	4.564306	2.437090	-0.374639
H	3.802949	1.759209	-1.812032
H	0.946725	0.039722	-0.142624
H	2.470839	-0.718594	-0.614048
H	1.692753	0.443088	-1.702566
H	-0.806911	4.772157	5.123997
H	-1.986277	5.866039	5.861316
H	-0.359062	6.456000	5.460153
H	-3.034941	7.607104	4.755859
H	-2.881006	7.957157	3.034778
H	-1.553418	8.362473	4.148233
H	-3.281601	5.356312	2.423569
H	-3.638525	5.324390	4.146833
H	-2.479404	4.176246	3.486946
H	-1.447837	9.073610	1.766401
H	-0.963815	9.082198	0.064536
H	0.264504	8.917215	1.341922
H	-2.460100	5.685386	0.316340
H	-2.516982	7.262814	-0.454026
H	-3.082954	7.093547	1.204005
H	-0.260831	7.087183	-1.129697
H	0.104350	5.563563	-0.300648
H	1.072143	7.016552	0.024060

Optimized structure and Cartesian coordinates (x, y, z) for 4b (Table S11):

298.15 K

E: -3514.296369

G: -3514.380888



P	-3.036567	-0.633968	-1.137083
F	0.251861	2.507432	-1.161518
F	-0.880562	4.884612	-0.893469
F	-2.748477	5.293783	1.062704
F	-3.432025	3.234330	2.690097
F	-2.280109	0.908609	2.498447
F	-0.475710	-2.661872	0.080912
F	-1.140281	-4.451114	1.946826
F	-1.130096	-3.734225	4.583057
F	-0.470030	-1.189020	5.274718
F	0.107087	0.616520	3.385637
F	2.065609	-1.857436	0.786943
F	4.626761	-1.650082	1.353377
F	5.780905	0.787761	1.686674
F	4.238666	3.025861	1.487893
F	1.696055	2.877165	0.979288
O	-3.002151	-0.591768	0.342251
N	0.769698	-0.274659	-2.070452
N	-1.367957	-0.387249	-1.760972
C	-0.171915	-0.245465	-1.090553
C	0.188494	-0.374453	-3.320014

C	-1.139012	-0.441250	-3.130161
C	2.204772	-0.483757	-1.971226
C	2.642856	-1.807662	-1.877852
C	4.012211	-2.026838	-1.729314
C	4.925051	-0.980605	-1.714018
C	4.451933	0.310961	-1.944210
C	3.097940	0.589303	-2.092900
C	-3.623569	-2.295519	-1.769522
C	-2.949548	-3.399665	-0.943809
C	-5.130165	-2.334580	-1.435447
C	-3.406091	-2.615878	-3.253857
C	-4.027429	0.771674	-1.879948
C	-5.224629	0.977834	-0.926767
C	-4.531082	0.584421	-3.316888
C	-3.185911	2.048333	-1.810865
C	-0.840972	1.589616	0.709509
C	-1.846261	1.831925	1.647492
C	-2.483426	3.063629	1.771261
C	-2.140655	4.118624	0.945533
C	-1.182918	3.914725	-0.030341
C	-0.599598	2.667314	-0.131893
C	-0.314821	-0.912363	1.640615
C	-0.242988	-0.615853	2.993742
C	-0.521390	-1.536496	3.990664
C	-0.853508	-2.835420	3.642728
C	-0.867848	-3.193850	2.306218
C	-0.574686	-2.235489	1.354237
C	1.693129	0.488971	0.819122
C	2.336221	1.702145	1.048058
C	3.692130	1.821458	1.334816
C	4.476349	0.692635	1.447017
C	3.884734	-0.545134	1.275401
C	2.537010	-0.615063	0.976775
B	0.069419	0.216900	0.529714
H	0.790465	-0.410720	-4.211517
H	-1.935157	-0.530505	-3.845008
H	4.362598	-3.045886	-1.600007
H	5.158303	1.134229	-2.000114
H	-1.914243	-3.547865	-1.239933
H	-3.490593	-4.331852	-1.127949
H	-2.984001	-3.185846	0.125466
H	-5.481099	-3.355452	-1.604486
H	-5.728221	-1.675493	-2.063281
H	-5.309698	-2.089312	-0.386282
H	-3.824656	-1.875278	-3.935352
H	-3.906119	-3.566310	-3.461530
H	-2.348064	-2.755015	-3.481541
H	-5.947525	0.164056	-0.964206
H	-5.736840	1.895900	-1.227243
H	-4.883780	1.090297	0.103793
H	-3.720583	0.537343	-4.046849
H	-5.127272	1.465507	-3.570310
H	-5.173352	-0.285257	-3.444625
H	-3.777085	2.876544	-2.211115
H	-2.254162	1.990523	-2.378226
H	-2.959148	2.272139	-0.773427
C	6.381207	-1.216938	-1.420676
H	7.019512	-0.601964	-2.057262
H	6.591612	-0.952768	-0.380221
H	6.650264	-2.263973	-1.560711
C	2.670988	2.003208	-2.381712
H	2.546611	2.578313	-1.462384
H	3.435959	2.492816	-2.985232
H	1.724014	2.047600	-2.917825
C	1.718184	-2.998181	-1.908180
H	2.083673	-3.720429	-2.641007
H	1.694470	-3.483709	-0.932232
H	0.692802	-2.736522	-2.166670

Optimized structure and Cartesian coordinates (x, y, z) for 4c in State I (Table S12):

298.15 K

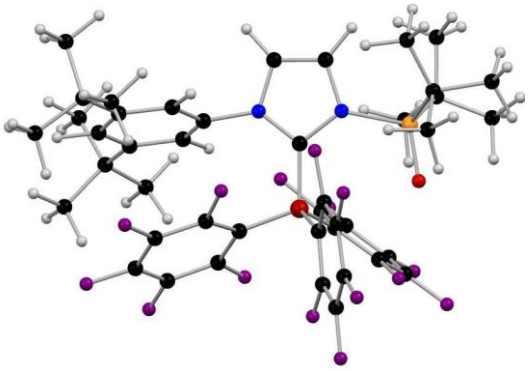
E: -3710.682586

G: -3710.773745

393.00 K

E: -3710.682586

G: -3710.828028



P	-3.101757	-0.515581	-1.030863
F	0.655088	2.276413	-1.070839
F	-0.278121	4.755222	-1.018682
F	-2.214680	5.450747	0.784576
F	-3.165986	3.577821	2.498132
F	-2.230940	1.140279	2.506334
F	-0.802294	-2.783996	0.156799
F	-1.589981	-4.478899	2.040440
F	-1.579460	-3.735862	4.662398
F	-0.745634	-1.239233	5.343503
F	0.025574	0.484860	3.449721
F	1.781409	-2.191774	0.673454
F	4.349509	-2.307804	1.271464
F	5.727647	-0.042339	1.893273
F	4.415789	2.340965	1.944369
F	1.871838	2.500717	1.375997
O	-3.136010	-0.074052	0.380636
N	0.741490	-0.713263	-1.894143
N	-1.399798	-0.701274	-1.588588
C	-0.203233	-0.453913	-0.955924
C	0.162718	-1.118882	-3.082853
C	-1.165120	-1.109773	-2.893678
C	2.194495	-0.698974	-1.849673
C	2.838138	-1.925730	-1.891570
C	4.233882	-1.973550	-1.909368
C	4.924681	-0.760497	-1.910549
C	4.282014	0.481845	-1.888934
C	2.888781	0.499670	-1.875548
C	-3.962509	-2.170854	-1.238965
C	-3.786063	-2.950014	0.078380
C	-5.466013	-1.866015	-1.384644
C	-3.506796	-3.059232	-2.400061
C	-3.737121	0.816829	-2.177511
C	-5.061852	1.332286	-1.573300
C	-3.939678	0.427725	-3.648247
C	-2.738238	1.978824	-2.090192
C	-0.689384	1.561847	0.730131
C	-1.692121	1.961527	1.612840
C	-2.208009	3.253035	1.632208
C	-1.726283	4.215073	0.762681
C	-0.739068	3.864730	-0.139708
C	-0.273749	2.564568	-0.134160
C	-0.505977	-1.011329	1.706969
C	-0.438135	-0.709265	3.062167
C	-0.804279	-1.592846	4.062218
C	-1.221870	-2.869184	3.720001
C	-1.231835	-3.240209	2.388496
C	-0.857192	-2.318514	1.424849
C	1.656345	0.155916	0.971201
C	2.400980	1.272637	1.334923
C	3.753178	1.221567	1.652488
C	4.425691	0.015929	1.633599
C	3.722652	-1.130653	1.313927
C	2.377957	-1.036209	1.012314
B	0.035442	0.084303	0.619683
H	0.765399	-1.364235	-3.939260
H	-1.954996	-1.363747	-3.573074

H	-2.824292	-3.451512	0.119167
H	-4.560261	-3.720797	0.117280
H	-3.893829	-2.302427	0.949409
H	-5.998915	-2.819643	-1.362589
H	-5.715528	-1.372909	-2.323642
H	-5.834175	-1.262173	-0.552451
H	-3.697035	-2.616632	-3.380900
H	-4.081396	-3.988384	-2.350080
H	-2.451132	-3.322570	-2.316748
H	-5.907274	0.678443	-1.776616
H	-5.278021	2.302128	-2.028980
H	-4.971665	1.476298	-0.494892
H	-2.993341	0.370825	-4.187358
H	-4.527225	1.216249	-4.126799
H	-4.484021	-0.508170	-3.784601
H	-3.097588	2.791899	-2.726917
H	-1.732780	1.709591	-2.422840
H	-2.688943	2.345948	-1.066008
H	2.240065	-2.826431	-1.851565
H	2.340484	1.426268	-1.862700
H	6.006583	-0.779756	-1.930504
C	5.093543	1.779662	-1.951553
C	4.977889	-3.310508	-1.970023
C	5.238323	-3.646339	-3.448700
H	5.772304	-4.597268	-3.531283
H	4.298161	-3.730999	-3.999856
H	5.842461	-2.869347	-3.923857
C	6.322745	-3.231925	-1.230211
H	7.032195	-2.573602	-1.735355
H	6.187501	-2.879115	-0.206049
H	6.776198	-4.225214	-1.196717
C	4.146946	-4.436936	-1.338078
H	3.842017	-4.177866	-0.321903
H	3.252765	-4.663101	-1.923113
H	4.743620	-5.350913	-1.298528
C	6.260521	1.751741	-0.951698
H	6.841059	2.672610	-1.048831
H	5.903271	1.692529	0.077005
H	6.940426	0.916036	-1.125516
C	5.656181	1.917688	-3.377202
H	6.230020	2.844063	-3.467059
H	6.315885	1.081579	-3.622522
H	4.847749	1.939916	-4.112208
C	4.229646	3.007824	-1.636830
H	3.452474	3.167638	-2.388011
H	3.749408	2.925272	-0.657727
H	4.860761	3.898999	-1.624327

Optimized structure and Cartesian coordinates (x, y, z) for 4c in State II (Table S13):

298.15 K

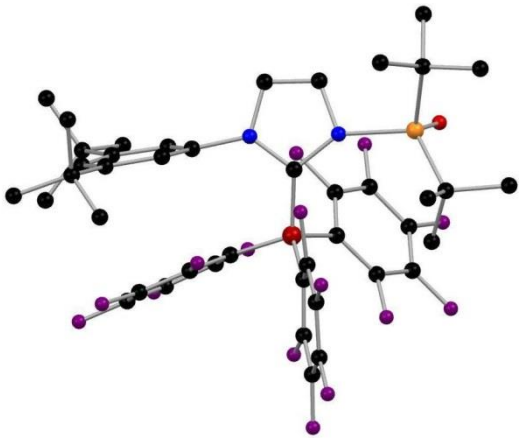
E: -3710.636521

G: -3710.726681

393.00 K

E: -3710.636521

G:-3710.780373



P	-3.566020	-0.708477	-1.861154
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F	-1.458296	3.840846	-3.101641
F	-3.237854	5.202935	-1.548541

F	-3.722389	4.336107	0.983644	C	-1.713867	3.435813	-1.861218
F	-2.549359	2.213001	1.934553	C	-1.081700	2.327648	-1.335038
F	-1.166793	-2.401413	0.821781	C	-0.925619	-0.254770	1.805956
F	-1.989659	-3.500516	3.090754	C	-0.873597	0.419149	3.021103
F	-2.022110	-2.045964	5.396480	C	-1.246797	-0.155202	4.226144
F	-1.203843	0.543471	5.356180	C	-1.653796	-1.479032	4.253404
F	-0.412630	1.671623	3.071689	C	-1.640860	-2.213882	3.080704
F	1.534225	-1.266993	1.722211	C	-1.249956	-1.598464	1.904643
F	3.957714	-0.657908	2.546462	C	1.143548	0.876675	0.766077
F	4.984510	1.822795	2.130854	C	1.740206	2.117388	0.554857
F	3.525136	3.650303	0.744375	C	3.009288	2.450374	1.011139
F	1.144374	3.087247	-0.149634	C	3.760843	1.526619	1.708078
O	-3.908213	0.581953	-2.507573	C	3.229292	0.269786	1.923909
N	0.485741	-0.881627	-1.675670	C	1.953333	-0.014958	1.474116
N	-1.686226	-0.761392	-1.760650	B	-0.435989	0.468964	0.419599
C	-0.589611	-0.526906	-0.938446	H	0.867454	-1.457699	-3.706116
C	0.130539	-1.204411	-2.965015	H	-1.834106	-1.208988	-3.872282
C	-1.201068	-1.099905	-3.020819	H	-4.462861	0.096364	1.663178
C	1.893769	-0.915716	-1.354053	H	-4.194080	1.167540	0.277955
C	2.408372	-2.047540	-0.760676	H	-2.895775	0.126734	0.883533
C	3.783107	-2.119962	-0.496917	H	-6.361851	-0.324776	0.516390
C	4.576241	-1.049407	-0.900407	H	-6.529558	-1.425976	-0.838263
C	4.063313	0.085001	-1.554043	H	-6.066508	0.267302	-1.118106
C	2.694618	0.139640	-1.780241	H	-4.813411	-3.082298	-0.071896
C	-4.449364	-0.918487	-0.222907	H	-4.701618	-2.221756	1.454662
C	-3.956865	0.190280	0.698671	H	-3.239323	-2.583440	0.542508
C	-5.946657	-0.593827	-0.458128	H	-5.678682	-2.939409	-1.821712
C	-4.280882	-2.286280	0.447023	H	-5.690115	-3.308304	-3.533079
C	-3.954365	-2.192988	-2.987254	H	-6.089277	-1.673733	-3.004357
C	-5.448584	-2.533811	-2.802010	H	-2.081003	-3.347532	-2.868987
C	-3.142994	-3.453540	-2.653112	H	-3.525805	-4.279071	-3.260054
C	-3.821664	-1.784093	-4.481142	H	-3.245416	-3.738315	-1.604608
C	-1.279533	1.825638	-0.048492	H	-2.937575	-2.220135	-4.949138
C	-2.178868	2.577354	0.699324	H	-3.809670	-0.699357	-4.610343
C	-2.838851	3.700434	0.216301	H	-4.679345	-2.163040	-5.037455
C	-2.609436	4.135643	-1.072829	H	1.731115	-2.843045	-0.475363

H	2.218357	0.990905	-2.250209
H	5.641796	-1.091692	-0.715975
C	5.012550	1.172512	-2.067258
C	4.358251	-3.377251	0.160580
C	4.313860	-4.519123	-0.869548
H	4.724834	-5.434313	-0.434552
H	3.287887	-4.724140	-1.185500
H	4.898887	-4.264637	-1.756901
C	5.807017	-3.170945	0.614723
H	6.480348	-2.999485	-0.228583
H	5.884188	-2.327743	1.306068
H	6.154191	-4.067287	1.133258
C	3.526501	-3.773620	1.392018
H	3.526467	-2.976922	2.136574
H	2.489013	-3.996844	1.136496
H	3.954370	-4.672534	1.843312
C	5.952822	1.669567	-0.957885
H	6.713027	2.322685	-1.394279
H	5.411286	2.252079	-0.212319
H	6.469233	0.855117	-0.446706
C	5.852563	0.561042	-3.203333
H	6.516473	1.318904	-3.627694
H	6.467965	-0.265709	-2.840468
H	5.208322	0.180916	-3.999991
C	4.249246	2.383907	-2.614148
H	3.647751	2.125967	-3.489258
H	3.592829	2.821523	-1.856314
H	4.962657	3.152833	-2.918596

Optimized structure and Cartesian coordinates (x, y, z) for 4c in State III (Table S14):

298.15 K

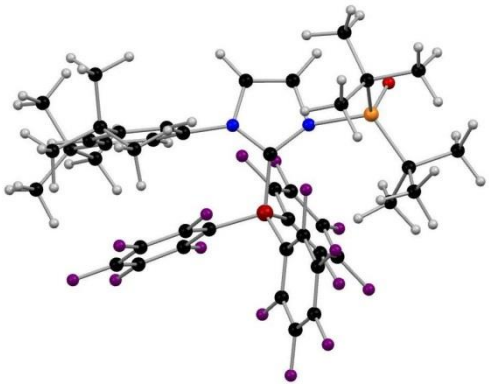
E: -3710.649047

G: -3710.741619

393.00 K

E: -3710.649047

G: -3710.796396



P	-3.482574	-1.338120	-1.958730
F	0.162812	1.931939	-2.090152
F	-0.791355	4.188245	-3.048722
F	-2.670331	5.600214	-1.665251
F	-3.578198	4.623300	0.706374
F	-2.721685	2.361498	1.655252
F	-1.692637	-2.141083	0.889170
F	-2.589819	-3.047870	3.217771
F	-2.465712	-1.466544	5.446086
F	-1.431847	1.036218	5.249081
F	-0.562515	1.957657	2.901187
F	1.122376	-1.510549	1.466546
F	3.578074	-1.304951	2.455481
F	4.874615	1.082581	2.431699
F	3.657927	3.254332	1.335733
F	1.258374	3.084216	0.300073
O	-3.952315	-0.764690	-3.247955
N	0.460729	-0.699862	-1.770702
N	-1.712406	-0.711653	-1.860682
C	-0.638557	-0.477414	-1.005702
C	0.125320	-0.924390	-3.087060
C	-1.212442	-0.901015	-3.151613
C	1.868105	-0.790443	-1.438127
C	2.337127	-2.008788	-0.985951
C	3.700184	-2.166782	-0.712325

C	4.538776	-1.082558	-0.964117	H	-6.392744	-1.519219	-1.650723
C	4.076404	0.142528	-1.467913	H	-5.922700	0.128893	-2.077994
C	2.713642	0.277429	-1.711247	H	-5.338424	-2.607800	0.385631
C	-4.607186	-0.778478	-0.583282	H	-5.343821	-1.160209	1.379877
C	-4.097622	0.582827	-0.128532	H	-3.834491	-2.006954	1.077748
C	-5.980696	-0.587868	-1.260970	H	-5.373335	-3.553556	-1.348646
C	-4.772743	-1.707916	0.624763	H	-4.765135	-4.759739	-2.472227
C	-3.335753	-3.196395	-2.129170	H	-5.304158	-3.189857	-3.086028
C	-4.793134	-3.687953	-2.259533	H	-1.584794	-3.590715	-0.897176
C	-2.618838	-3.926014	-0.995496	H	-2.604723	-4.992533	-1.238748
C	-2.639075	-3.534624	-3.457752	H	-3.110290	-3.808700	-0.031056
C	-1.207347	1.978878	-0.157612	H	-1.562879	-3.372068	-3.410734
C	-2.154134	2.756068	0.506386	H	-3.060245	-2.966616	-4.289183
C	-2.651258	3.958852	0.021079	H	-2.804359	-4.597399	-3.653775
C	-2.203540	4.454224	-1.187139	H	1.627192	-2.806980	-0.812853
C	-1.258731	3.729333	-1.890923	H	2.286507	1.200423	-2.076556
C	-0.795145	2.538416	-1.364405	H	5.598193	-1.187578	-0.770044
C	-1.191169	-0.013027	1.760234	C	5.068373	1.261016	-1.802459
C	-1.099496	0.734488	2.932288	C	4.235229	-3.511537	-0.212460
C	-1.523123	0.271540	4.165555	C	4.426731	-4.432347	-1.429878
C	-2.043392	-1.010180	4.273213	H	4.807371	-5.406473	-1.109997
C	-2.102043	-1.808377	3.147055	H	3.479840	-4.589258	-1.952920
C	-1.658966	-1.297067	1.938019	H	5.137931	-3.998395	-2.137160
C	1.033083	0.768208	0.833149	C	5.579225	-3.348429	0.509924
C	1.744519	1.961845	0.843572	H	6.374601	-3.031579	-0.168051
C	3.018538	2.085577	1.383296	H	5.500407	-2.623688	1.323743
C	3.643898	0.988229	1.941171	H	5.881215	-4.308665	0.933836
C	2.977665	-0.223896	1.955621	C	3.245882	-4.167122	0.764777
C	1.702761	-0.298561	1.429709	H	3.013982	-3.499673	1.596159
B	-0.541592	0.545811	0.366172	H	2.310214	-4.448339	0.277588
H	0.880760	-1.068715	-3.838913	H	3.686431	-5.082776	1.166417
H	-1.874144	-1.005058	-3.991222	C	6.008836	1.544424	-0.620466
H	-4.860254	1.068197	0.486691	H	6.768728	2.267118	-0.928855
H	-3.873970	1.235497	-0.976135	H	5.467899	1.975914	0.222195
H	-3.209636	0.463460	0.483585	H	6.526524	0.649162	-0.271853
H	-6.663426	-0.208802	-0.495418	C	5.902715	0.803412	-3.012291

H	6.603907	1.590068	-3.303493
H	6.477529	-0.096041	-2.778740
H	5.257828	0.582338	-3.866361
C	4.353439	2.568921	-2.160388
H	3.756370	2.472193	-3.070430
H	3.700734	2.905811	-1.349817
H	5.095978	3.350509	-2.334972

Optimized structure and Cartesian coordinates (x, y, z) for 4c in State IV (Table S15 and see the following discussions):

298.15 K

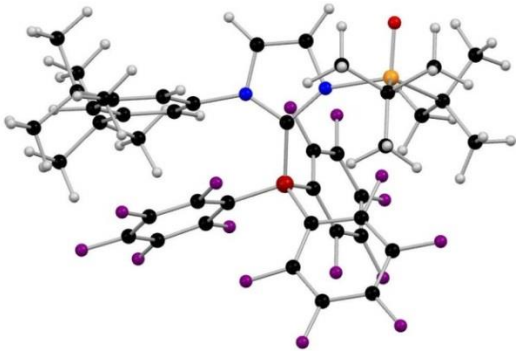
E: -3710.641036

G: -3710.732278

393.00 K

E: -3710.641035

G: -3710.786345



P	-3.120291	-1.842394	-2.247806
F	-0.071599	1.293723	-2.381139
F	-1.006813	3.548605	-3.326143
F	-2.465605	5.231599	-1.754772
F	-2.927763	4.558978	0.837573
F	-1.984429	2.325020	1.844666
F	-3.152158	-0.405657	0.040897
F	-5.116061	-0.671636	1.864201
F	-4.480115	-0.733474	4.516898
F	-1.881502	-0.494958	5.261908
F	0.007839	-0.148863	3.525845
F	1.039965	-1.909852	1.527398
F	3.447704	-1.769405	2.667422
F	4.719623	0.631458	2.875306
F	3.505580	2.876627	1.932105
F	1.190359	2.746859	0.705589
O	-3.022704	-2.409352	-3.623902
N	0.817684	-1.166286	-1.525514
N	-1.319972	-1.271911	-1.946153
C	-0.396265	-0.883052	-0.971613
C	0.687729	-1.644391	-2.807447
C	-0.619643	-1.700272	-3.072780
C	2.204855	-1.027513	-1.113199
C	2.867166	-2.172866	-0.701923
C	4.240102	-2.119627	-0.450921
C	4.891216	-0.903601	-0.662811
C	4.232259	0.252439	-1.095203
C	2.862171	0.171320	-1.339322
C	-4.411210	-0.449996	-2.371135
C	-3.712514	0.909745	-2.467534
C	-5.109515	-0.735985	-3.719097
C	-5.500942	-0.441100	-1.286177
C	-3.343471	-3.336880	-1.142419
C	-4.573466	-4.050258	-1.741649
C	-3.533393	-3.155075	0.356369
C	-2.098344	-4.207022	-1.388004
C	-1.050454	1.608162	-0.228834
C	-1.761306	2.530795	0.538811
C	-2.248023	3.733002	0.048038
C	-2.004825	4.086675	-1.267248
C	-1.257612	3.234455	-2.057153
C	-0.797381	2.040750	-1.525820
C	-1.478037	-0.283003	1.639879
C	-1.213546	-0.315330	3.010362
C	-2.204031	-0.472970	3.972735

C	-3.530600	-0.585988	3.603526
C	-3.846379	-0.547475	2.258892
C	-2.817636	-0.416712	1.348335
C	0.989633	0.391174	1.045460
C	1.661363	1.593885	1.203329
C	2.894200	1.695065	1.836914
C	3.513163	0.561163	2.324356
C	2.867399	-0.659110	2.210281
C	1.633226	-0.705984	1.601403
B	-0.491725	0.171516	0.383506
H	1.548953	-1.890192	-3.402247
H	-1.126959	-2.044117	-3.953299
H	-4.447464	1.647374	-2.802706
H	-2.896944	0.897165	-3.197256
H	-3.320451	1.231397	-1.506075
H	-5.843669	0.059022	-3.871991
H	-5.633884	-1.693308	-3.711245
H	-4.410276	-0.744132	-4.551189
H	-5.842052	-1.443400	-1.020324
H	-6.364085	0.090014	-1.695102
H	-5.200920	0.070227	-0.379635
H	-5.492492	-3.474660	-1.610397
H	-4.702148	-4.998713	-1.213368
H	-4.434808	-4.254027	-2.802807
H	-2.630898	-2.770251	0.831695
H	-3.728718	-4.141254	0.787341
H	-4.382426	-2.515362	0.596978
H	-1.204819	-3.764228	-0.940655
H	-1.926192	-4.369310	-2.452596
H	-2.267398	-5.176683	-0.911862
H	2.293530	-3.077588	-0.552109
H	2.287509	1.019928	-1.687049
H	5.958921	-0.852143	-0.491204
C	5.023971	1.538158	-1.349450
C	5.026855	-3.356405	-0.009394
C	5.747305	-3.933091	-1.240186
H	6.323585	-4.819071	-0.959076
H	5.028758	-4.219809	-2.012189
H	6.433581	-3.199567	-1.670675
C	6.070555	-2.987096	1.058124
H	6.854409	-2.339878	0.660614
H	5.603016	-2.482858	1.905448
H	6.556795	-3.895900	1.420978
C	4.100002	-4.429014	0.576753
H	3.500749	-4.024375	1.396038
H	3.427836	-4.842974	-0.178592
H	4.699296	-5.255721	0.964215
C	5.961503	1.841492	-0.169147
H	6.505334	2.768628	-0.366801
H	5.404770	1.972116	0.759661
H	6.701577	1.054424	-0.015136
C	5.864730	1.337660	-2.622437
H	6.442504	2.240881	-2.836852
H	6.562766	0.504900	-2.506533
H	5.223130	1.126517	-3.481473
C	4.100884	2.745820	-1.550636
H	3.483745	2.642801	-2.446469
H	3.444038	2.901307	-0.690669
H	4.706323	3.646451	-1.672970

Optimized structure and Cartesian coordinates (x, y, z) for 6c (Table S16):

298.15 K

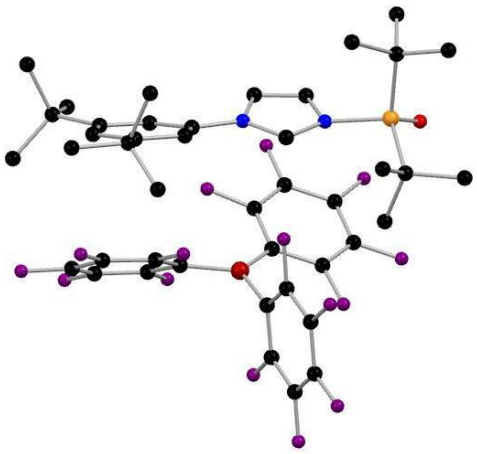
E: -3710.634666

G: -3710.728946

393.00 K

E: -3710.634666

G: -3710.784554



P	-3.858758	-2.034280	0.477675
F	0.762067	-0.744519	-2.446980
F	-0.925993	-2.072992	-3.981832
F	-3.459138	-1.192937	-4.317000
F	-4.269308	1.112058	-3.129496
F	-2.606446	2.490105	-1.620849
F	-0.858066	1.273927	1.935600
F	-1.889440	3.239615	3.424634
F	-2.057241	5.760529	2.436494
F	-1.198985	6.292179	-0.084224
F	-0.201504	4.287499	-1.609009
F	1.728690	1.531496	1.480563
F	4.399491	1.477993	1.528065
F	5.790563	1.534866	-0.791520
F	4.496436	1.444681	-3.163712
F	1.822420	1.477200	-3.238471
O	-4.703961	-2.118295	-0.748512
N	-0.048198	-2.135889	0.023667
N	-2.179261	-2.072800	-0.020077
C	-1.107527	-1.577625	0.677360
C	-0.445095	-2.966369	-1.025919
C	-1.789142	-2.919419	-1.061894
C	1.313855	-1.940621	0.420487
C	1.598105	-1.536123	1.714609
C	2.927103	-1.417685	2.139548
C	3.940276	-1.709585	1.228136
C	3.669173	-2.127208	-0.083230
C	2.341456	-2.219917	-0.482045
C	-4.118214	-0.451722	1.402429
C	-3.602988	0.665972	0.486794
C	-5.640557	-0.265172	1.547881
C	-3.431346	-0.371351	2.770321
C	-3.990968	-3.562582	1.527448
C	-5.281726	-3.501926	2.358481
C	-2.775507	-3.768338	2.439785
C	-4.102567	-4.749384	0.555408
C	-0.826663	0.945165	-1.928398
C	-2.137555	1.375435	-2.175045
C	-3.026987	0.679163	-2.971646
C	-2.618884	-0.496986	-3.579638
C	-1.317969	-0.941173	-3.406888
C	-0.455525	-0.227362	-2.598106
C	-0.496317	2.723953	0.110480
C	-0.596785	4.025820	-0.355841
C	-1.112363	5.059989	0.402453
C	-1.551310	4.788799	1.690192
C	-1.459687	3.502235	2.194111
C	-0.926278	2.493285	1.406301
C	1.656195	1.472910	-0.877744
C	2.416965	1.452802	-2.047123
C	3.799981	1.463459	-2.032601
C	4.468805	1.496068	-0.818122
C	3.754050	1.480884	0.366334
C	2.372215	1.494428	0.318464
B	0.101152	1.651147	-0.896783
H	0.243472	-3.500901	-1.655101
H	-2.502708	-3.375858	-1.728905
H	-3.799296	1.630403	0.965817
H	-4.129147	0.650860	-0.470730
H	-2.530380	0.572397	0.323283

H	-5.819586	0.749253	1.915148
H	-6.084321	-0.957607	2.262399
H	-6.144421	-0.380225	0.586583
H	-3.855933	-1.081760	3.482253
H	-3.593092	0.633605	3.173504
H	-2.357407	-0.533965	2.685352
H	-5.225223	-2.759283	3.155470
H	-5.437831	-4.477434	2.827377
H	-6.151936	-3.287878	1.733170
H	-1.867925	-3.945351	1.858850
H	-2.955417	-4.650726	3.061398
H	-2.591803	-2.920149	3.099981
H	-3.184975	-4.888298	-0.019314
H	-4.933617	-4.616296	-0.138346
H	-4.267154	-5.659376	1.139529
H	0.769568	-1.343428	2.383903
H	2.096527	-2.513217	-1.491125
H	4.972856	-1.647134	1.547427
C	4.816977	-2.582854	-0.992714
C	3.209867	-1.100507	3.613148
C	2.657240	-2.262983	4.458752
H	2.881700	-2.095324	5.515739
H	1.574047	-2.352766	4.351915
H	3.108386	-3.210832	4.154816
C	4.708720	-0.965404	3.899993
H	5.242257	-1.901775	3.717344
H	5.160367	-0.177936	3.292307
H	4.851600	-0.703521	4.950925
C	2.520438	0.204183	4.043431
H	2.971501	1.063577	3.546258
H	1.453650	0.202457	3.811086
H	2.632050	0.334136	5.123357
C	5.871596	-1.480013	-1.160990
H	6.766322	-1.893154	-1.634394
H	5.499984	-0.684964	-1.810008
H	6.170291	-1.037138	-0.208846
C	5.473271	-3.814275	-0.341367
H	6.260337	-4.206984	-0.990926
H	5.922548	-3.563354	0.621910
H	4.734919	-4.602366	-0.175431
C	4.328089	-2.977556	-2.390277
H	3.653958	-3.837157	-2.357004
H	3.813600	-2.147374	-2.883328
H	5.185485	-3.252288	-3.008900

Optimized structure and Cartesian coordinates (x, y, z) for 6c' (Table S17 and see the following discussions):

298.15 K

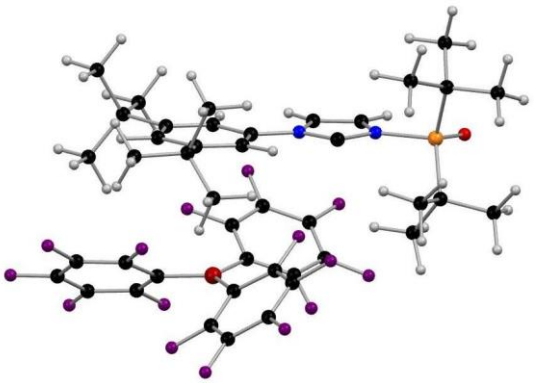
E: -3710.642369

G: -3710.736861

393.00 K

E: -3710.642369

G: -3710.792624



P	-5.367024	-0.567962	0.058089
F	1.949169	-2.355806	-0.812490
F	0.109315	-4.180196	-1.335062
F	-2.036546	-3.560940	-2.866878
F	-2.319994	-1.052359	-3.861260
F	-0.618041	0.860932	-3.155374
F	-0.969085	1.301240	-0.526957
F	-1.734393	3.799722	-0.076486

F	-0.024455	5.853480	-0.505035	C	1.658946	4.360234	-1.167523
F	2.495952	5.368866	-1.371793	C	0.366649	4.612385	-0.732399
F	3.308938	2.873917	-1.799510	C	-0.510659	3.559917	-0.533029
F	3.277310	1.572819	0.777356	C	-0.085679	2.265377	-0.769328
F	5.776725	0.880351	1.367329	C	3.202725	0.136107	-1.101176
F	7.130264	-0.837003	-0.235339	C	3.934081	-0.754824	-1.885184
F	5.917877	-1.920864	-2.401763	C	5.254794	-1.073913	-1.625377
F	3.366447	-1.334482	-2.942728	C	5.881999	-0.512092	-0.523040
O	-6.110093	-1.597224	-0.725176	C	5.192248	0.374962	0.286667
N	-1.767105	-1.453391	1.043446	C	3.884488	0.696172	-0.023925
N	-3.790725	-1.221316	0.426593	B	1.704321	0.486995	-1.406575
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C	-2.165448	-2.683927	0.507868	H	-4.137579	-3.206518	-0.366750
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C	-0.231856	0.090986	2.129031	H	-2.996083	0.397089	-1.520533
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C	1.731037	-1.901314	2.248142	H	-6.685151	0.417445	-2.274589
C	0.489533	-2.168788	1.676602	H	-5.318896	2.554209	0.495015
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C	-0.036240	-2.946226	-1.814722	H	0.284452	-3.155231	1.286089
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C	1.207851	1.958167	-1.193936	C	2.812691	-2.978580	2.382795
C	2.056186	3.052971	-1.380384	C	1.186717	1.733446	3.419658

C	0.221937	1.785733	4.618878	H	4.864657	-3.286073	1.740365
H	0.342012	2.730945	5.155778	H	3.890334	-2.320725	0.615475
H	-0.818001	1.705708	4.294933	H	4.493506	-1.601972	2.122018
H	0.425194	0.965971	5.312141	C	3.113302	-3.200020	3.875514
C	2.613669	1.930052	3.943081	H	3.877147	-3.973734	3.992476
H	2.863260	1.191612	4.709102	H	3.480020	-2.288436	4.351483
H	3.353053	1.866444	3.142399	H	2.213304	-3.520536	4.405682
H	2.696104	2.918298	4.401394	C	2.382245	-4.319741	1.778658
C	0.849741	2.888856	2.464408	H	1.501826	-4.722039	2.286731
H	1.512620	2.881223	1.595886	H	2.162559	-4.233489	0.712461
H	-0.184849	2.831447	2.117642	H	3.190742	-5.044611	1.897245
H	0.971559	3.844631	2.981677				
C	4.093379	-2.513759	1.671592				

A potential energy surface scan with respect to ∠C-N-P-O (°) in PoxIm 2a: The scan was conducted with B3LYP/6-31G++(d,p) level (gas-phase, 298.15 K, 1 atm) starting from the optimized structure of **2a** between ∠C-N-P-O = –180 to 0°, which gave a profile shown in Figure S16.

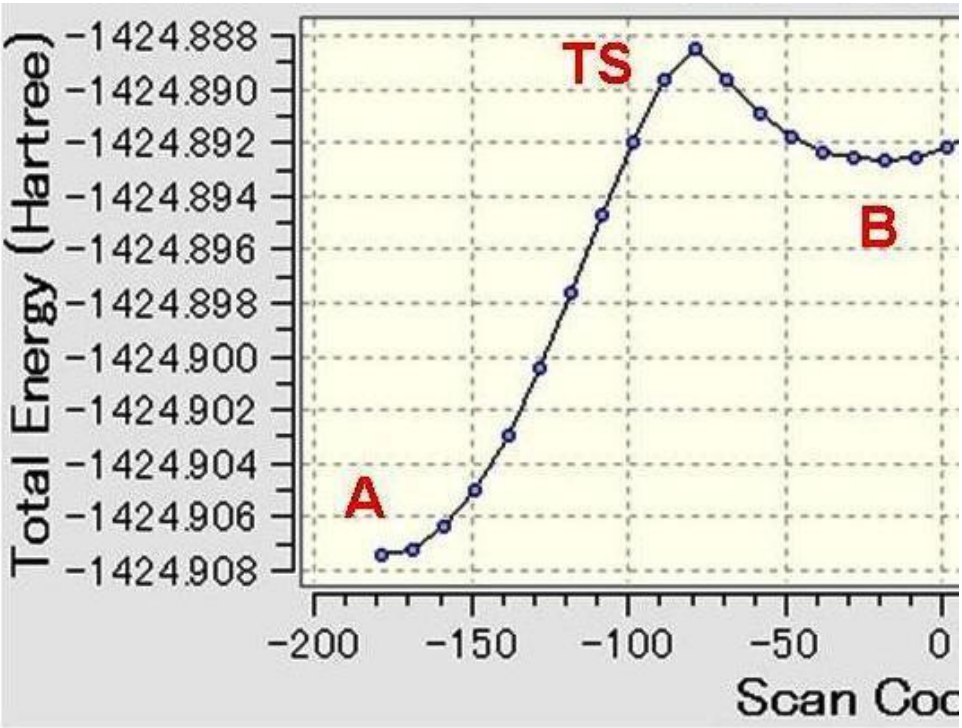

Figure S16. A potential energy surface scan with respect to ∠C-N-P-O (°) in **2a**

In particular, we focused on the results between ∠C-N-P-O = −180 to 0°, and the optimization of structures for TS and conformer B was further conducted, giving the results shown in Figure 2c where absolute values of angles are given. Similar calculations were conducted for both **2b** and **2c**.

A potential energy surface scan with respect to ∠C-N-P-O (°) in 4c: The scan was conducted with M06-2X/6-311G(d,p) level (gas-phase, 298.15 K, 1 atm) starting from the optimized structure of **4c**, which gave a profile shown in Figure S17.

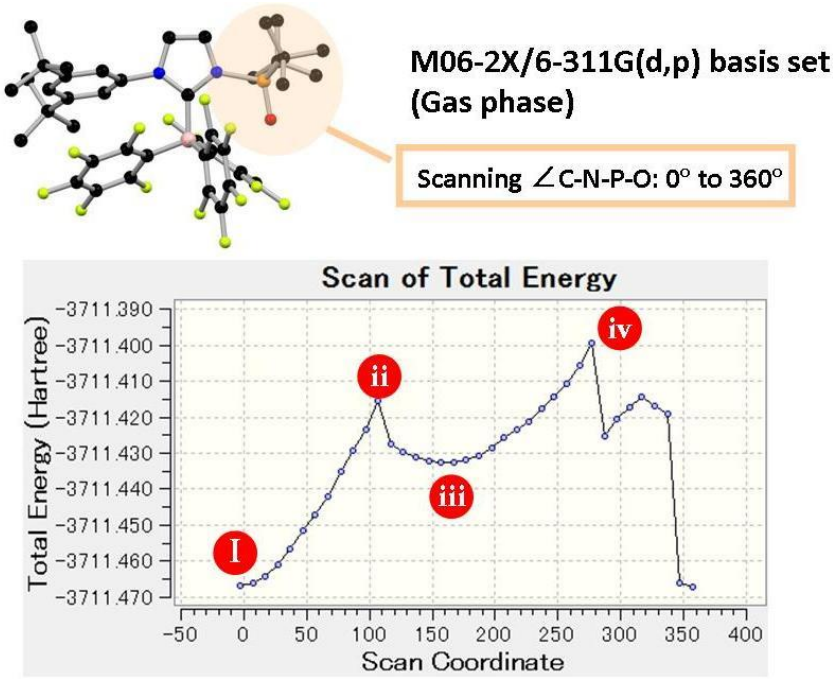

Figure S17. A potential energy surface scan with respect to ∠C-N-P-O (°) in **4c**

Then, the structures of States II–IV were optimized by using the structural parameters of States ii–iv as an initial coordinate (Table S12–15). Their relative energies are shown in Figure S18. In these calculations, States II and IV were optimized as TS states, and III was as a minimum energy state. From these calculations, it was found that State II is slightly higher energy state than IV. Compared to State III, the angle of ∠C-N-P-O (°) in State IV is found to be not much varied; however, increment of the strain is obviously found (Figure S18). Thus, we concluded that the rotation of the phosphine oxide moiety more than 160° would not be beneficial and dissociation process would occur dominantly. *Note: The result at 393.00 K is given in Figure 6c.*

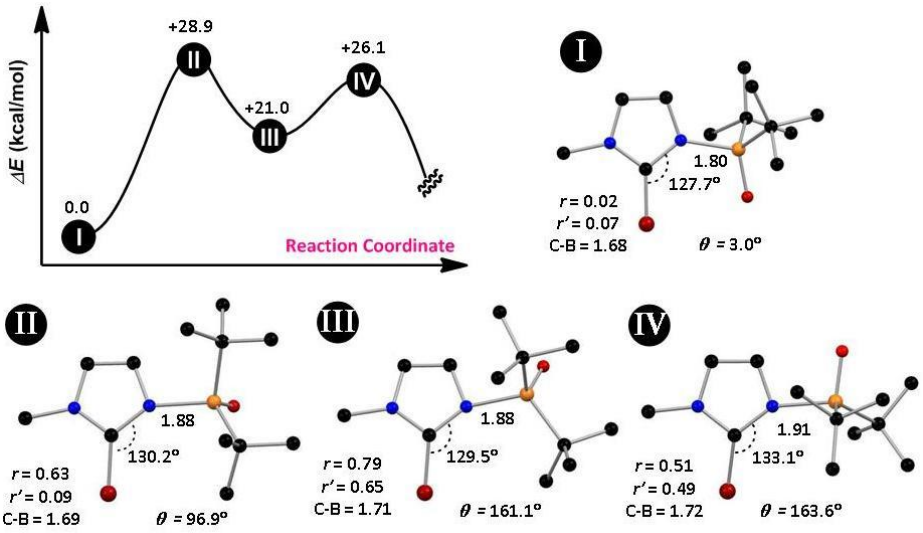

Figure S18. Comparison of energy in State I–IV (for detail, see Figure 6c)

A potential energy surface scan with respect to distance between C and B in State I of 4c: The scan was conducted with M06-2X/6-311G(d,p) level (gas-phase, 298.15 K, 1 atm) starting from the optimized structure of State I of **4c**, which gave a profile shown in Figure S19; however, any metastable state was not found.

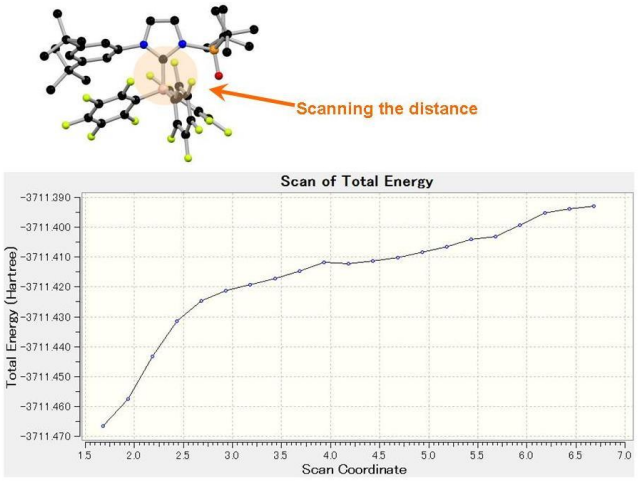

Figure S19. Energy scans vs B–C distances from state I of **4c**

A potential energy surface scan with respect to distance between C and B in State III of 4c: The scan was conducted with M06-2X/6-311G(d,p) level (gas-phase, 298.15 K, 1 atm) starting from the optimized structure of State III of **4c**, which gave a profile shown in Figure S20. Two minimum energy states were found, and their structures were optimized, giving compounds **6c** and **6c'** (Table S16 and S17).

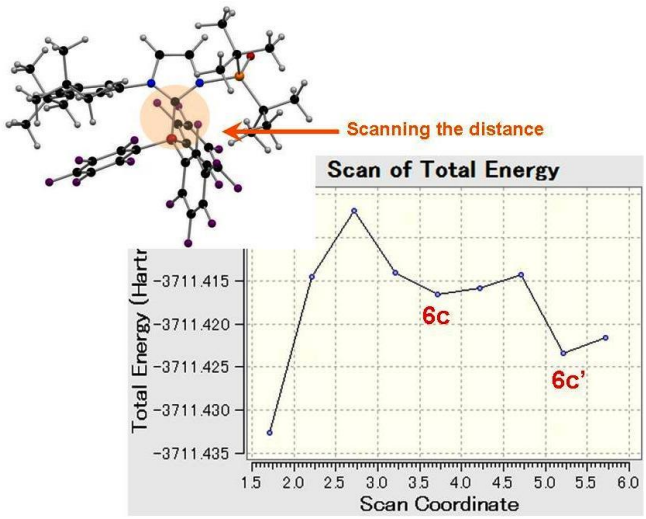

Figure S20. Energy scans vs B–C distances from state III of **4c**

In **6c**, hydrogen bonding interaction between C–H (^{t}Bu groups on *N*-aryl group) and F (C_6F_5 group) and π-π stacking interaction between aromatic rings on PoxIm and C_6F_5 groups are found to support the complexation (Figure S21). In addition, pre-organization of the carbene's lone pair and empty *p* orbital of $B(C_6F_5)_3$ is also confirmed (Figure S22), whereas the same tendency is not confirmed in **6c'**. Thus, we concluded that 6c would be regarded as the encountered complex comprised of **2c** and $B(C_6F_5)_3$. In **6c'**, a significant interaction between the 3,5-^{t}BuC_6H_3 ring and the *p* orbital of $B(C_6F_5)_3$ is found as a π-p interaction, which can be considered as "a pre-frustration state complex".

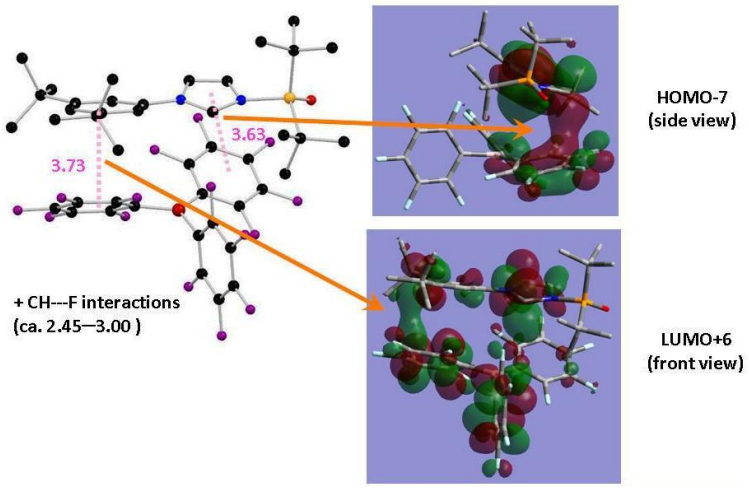

Figure S21. Interactions found in **6c**

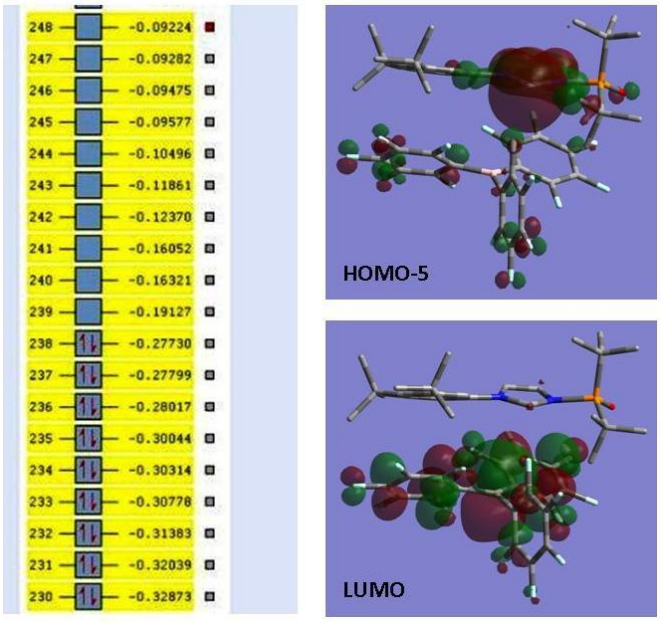

Figure S22. Selected MOs in **6c** and their relative energies (eV)

Natural population analysis for 4a: In order to estimate the interaction between O atom (phosphine oxide group) and B atom, second order perturbation theory analysis was conducted for **4a** with both STO-3G and M062X, which uncovered that there is no significant interaction between these atoms.

Summary of potential energy profiles for 4c and related compounds: In Figure S23, the detailed profiles (Δ*G* kcal/mol at 393.00 K, values for 298.15 K are in parenthesis) for **4c** (each states), **6c**, and **6c'** are given.

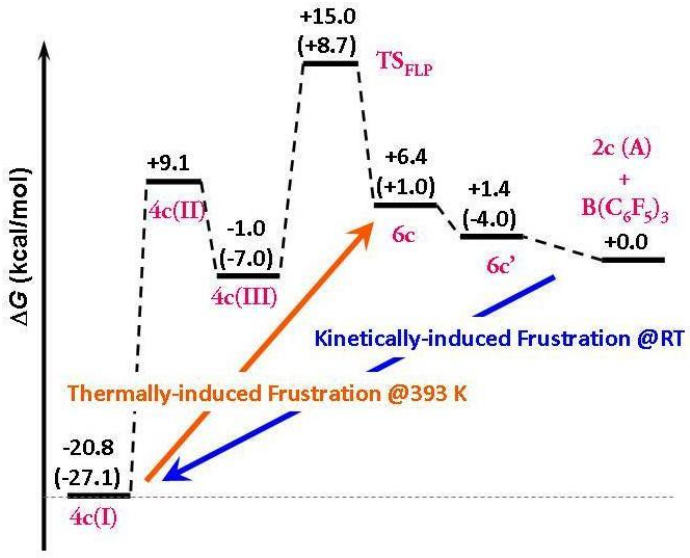

Figure S23. Summary of relative energies in this work

[12] References for Supporting Information

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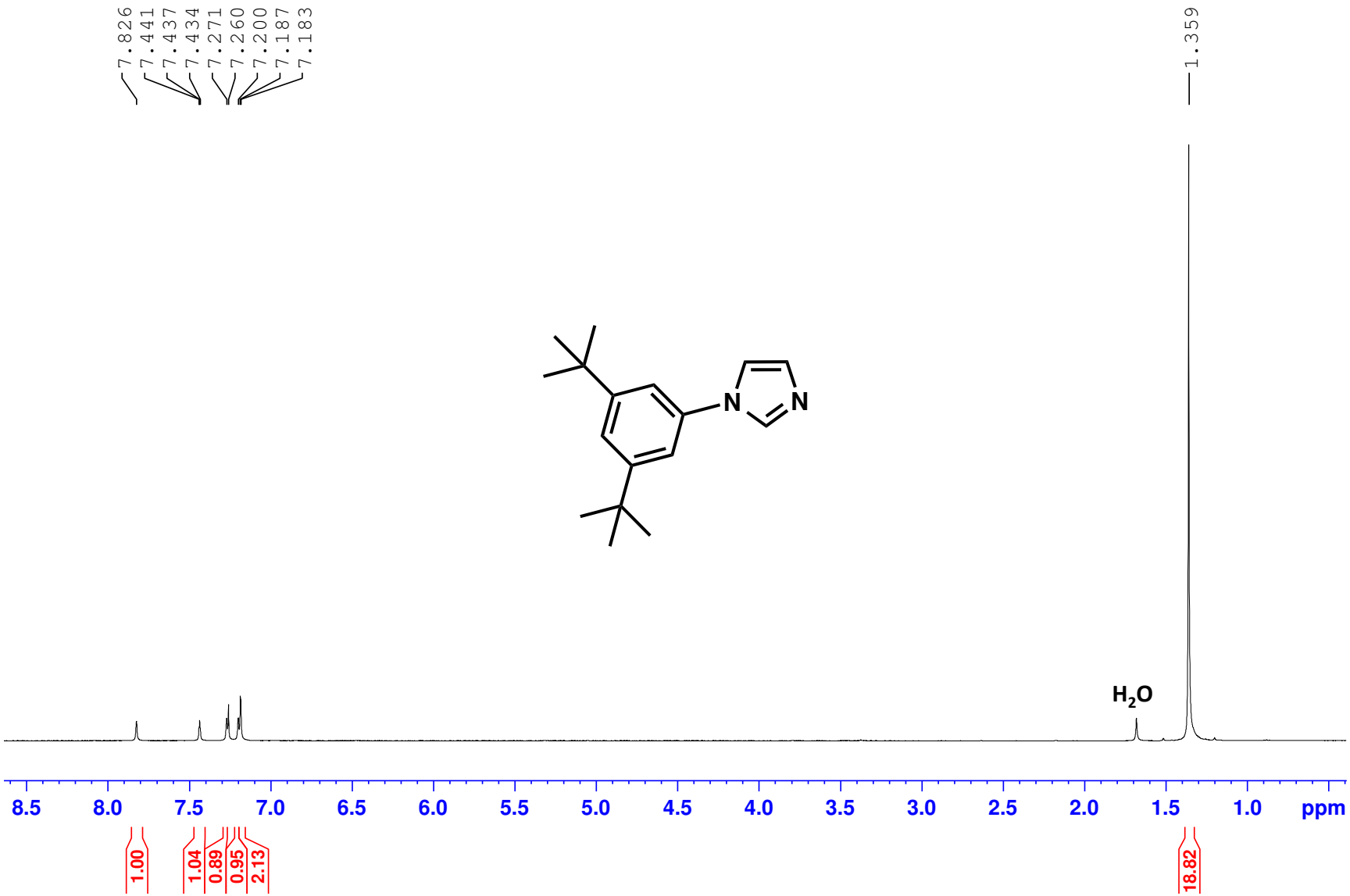
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3.5
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18.82

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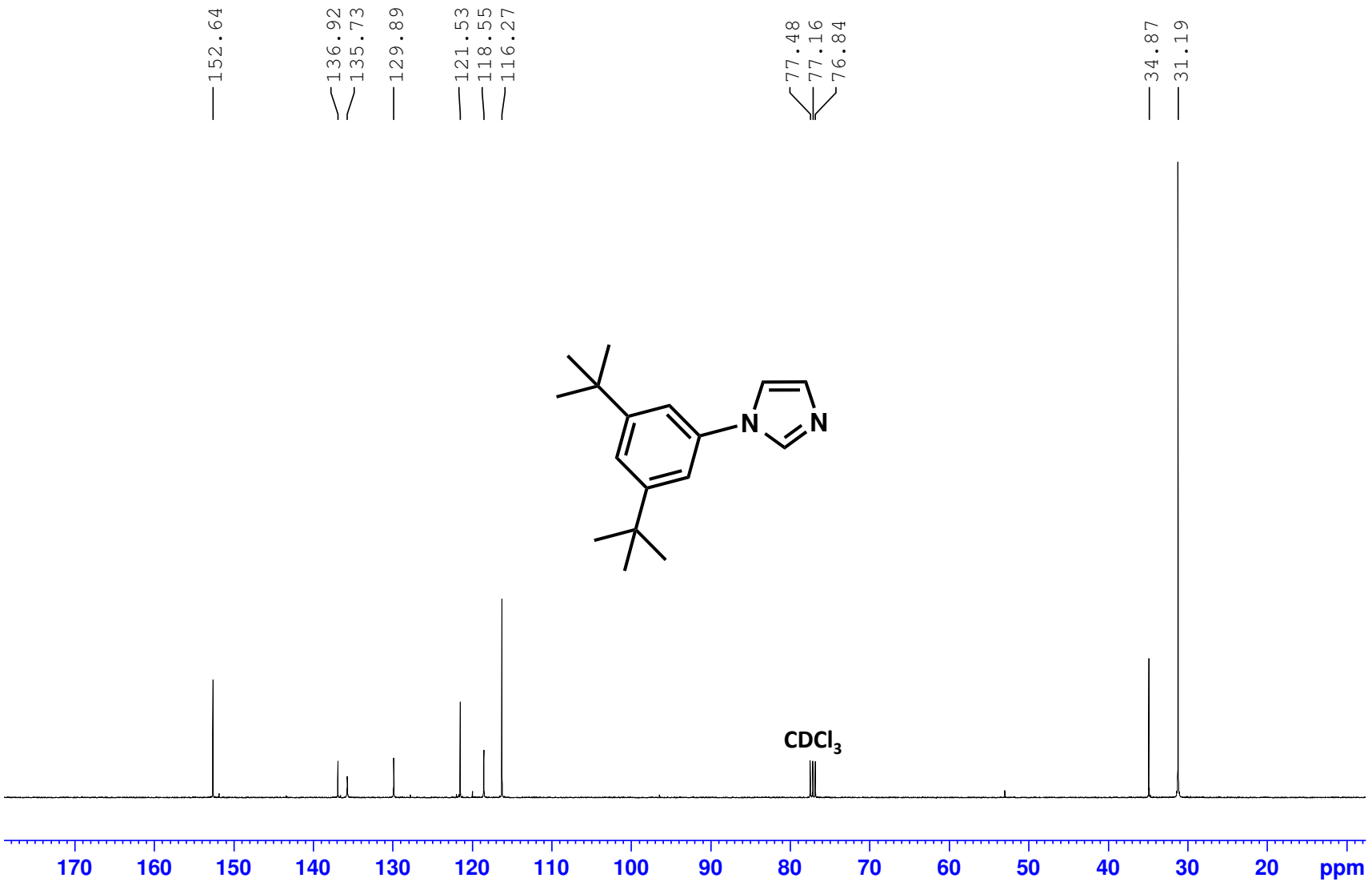
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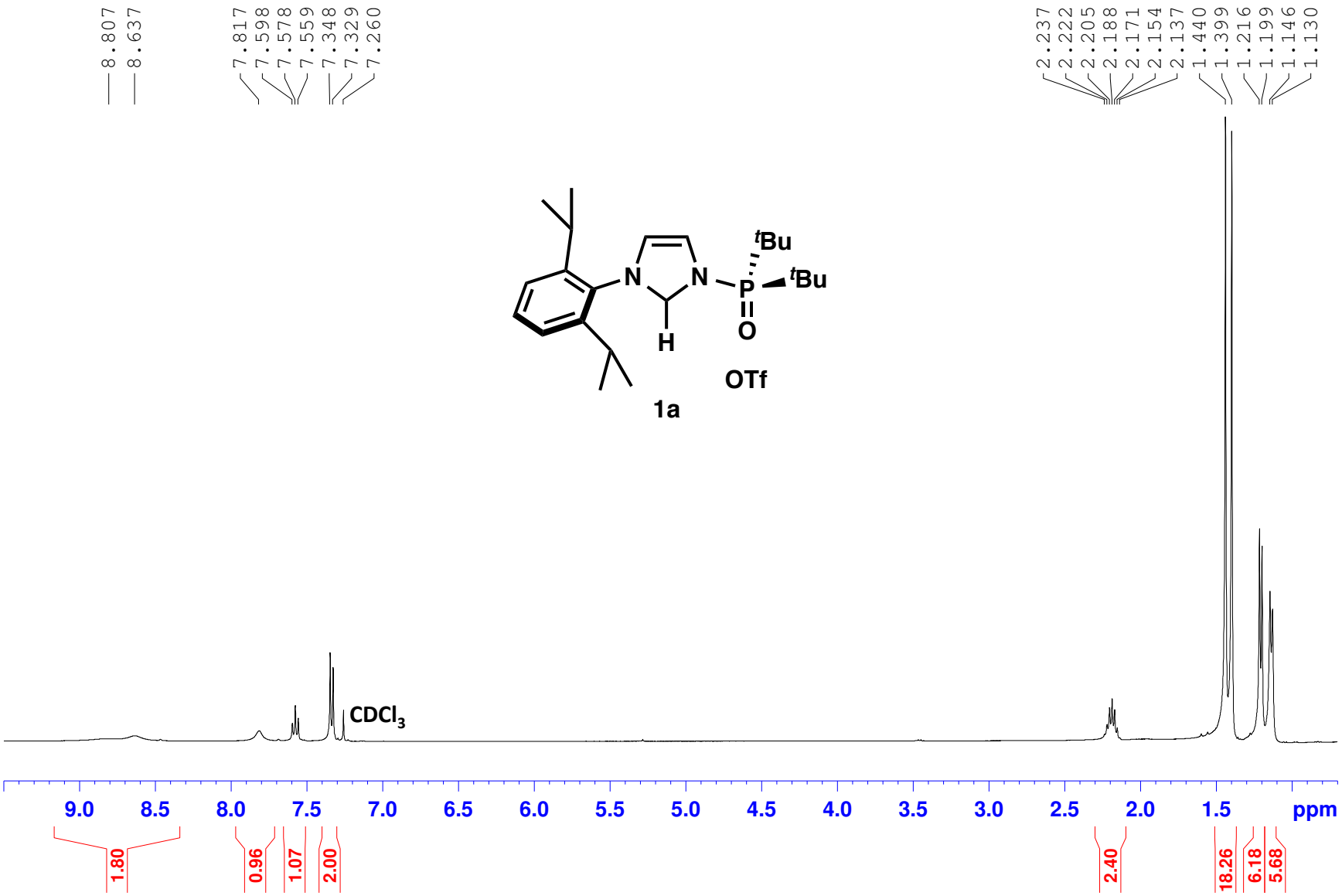
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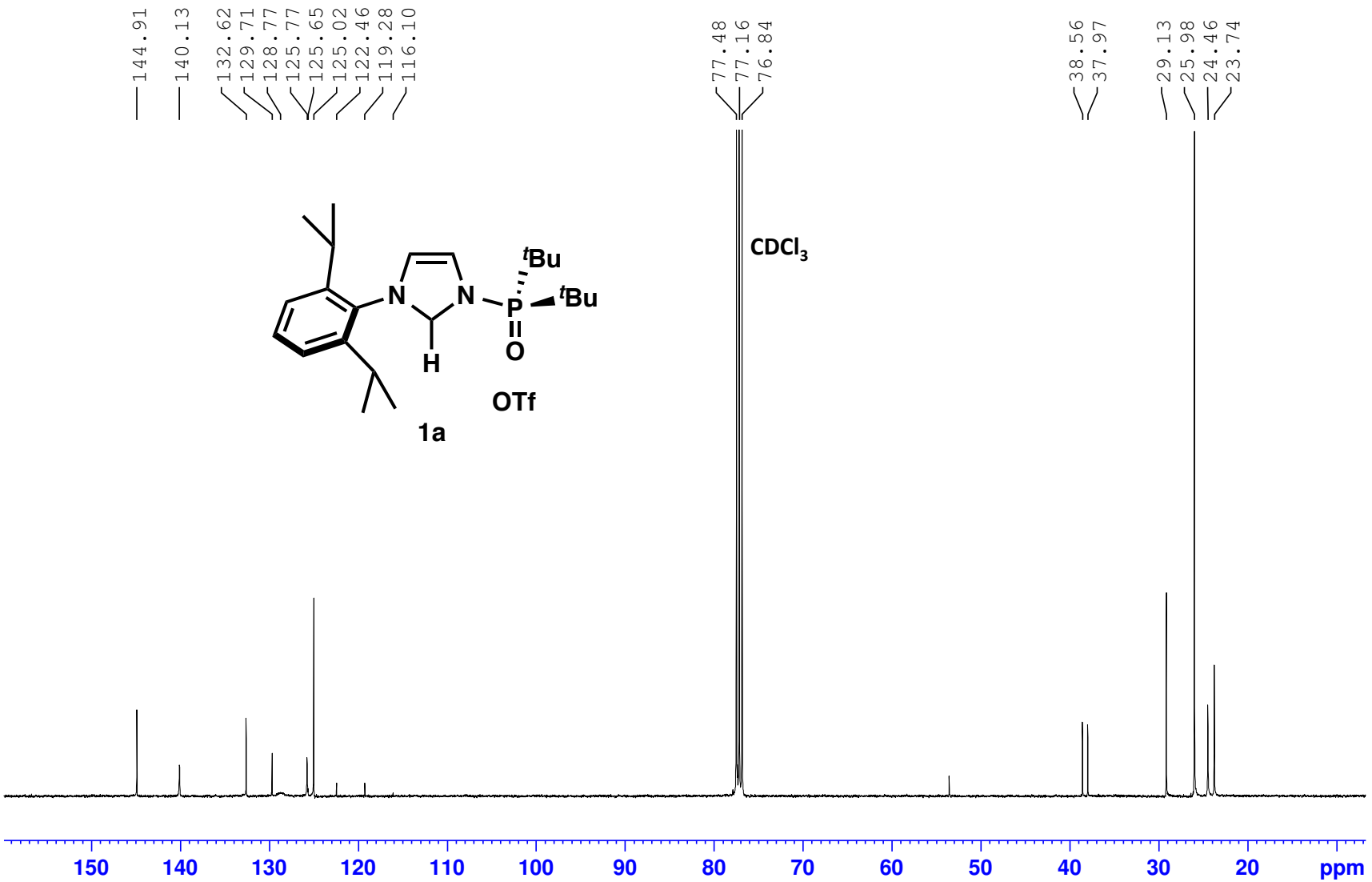
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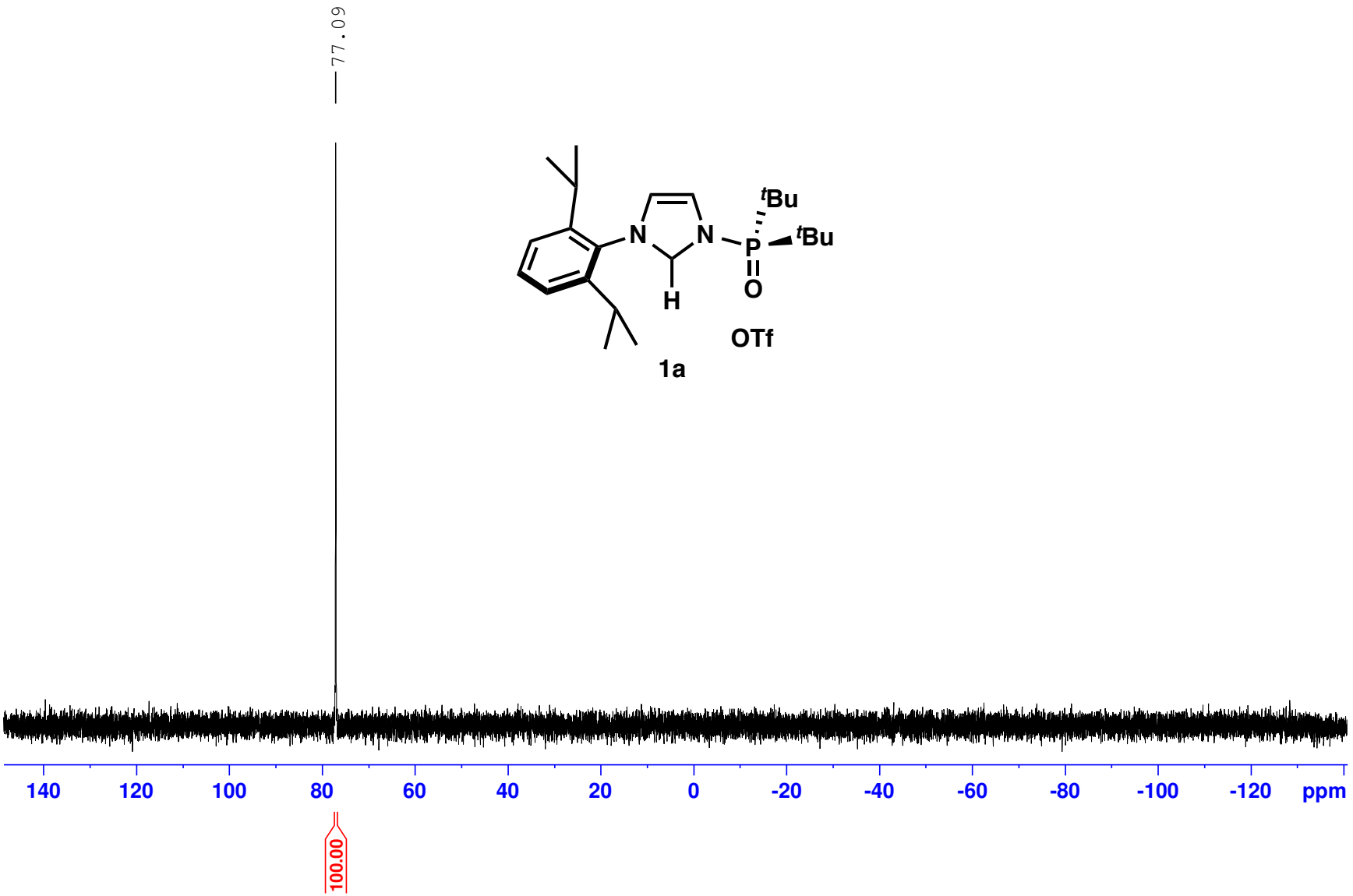
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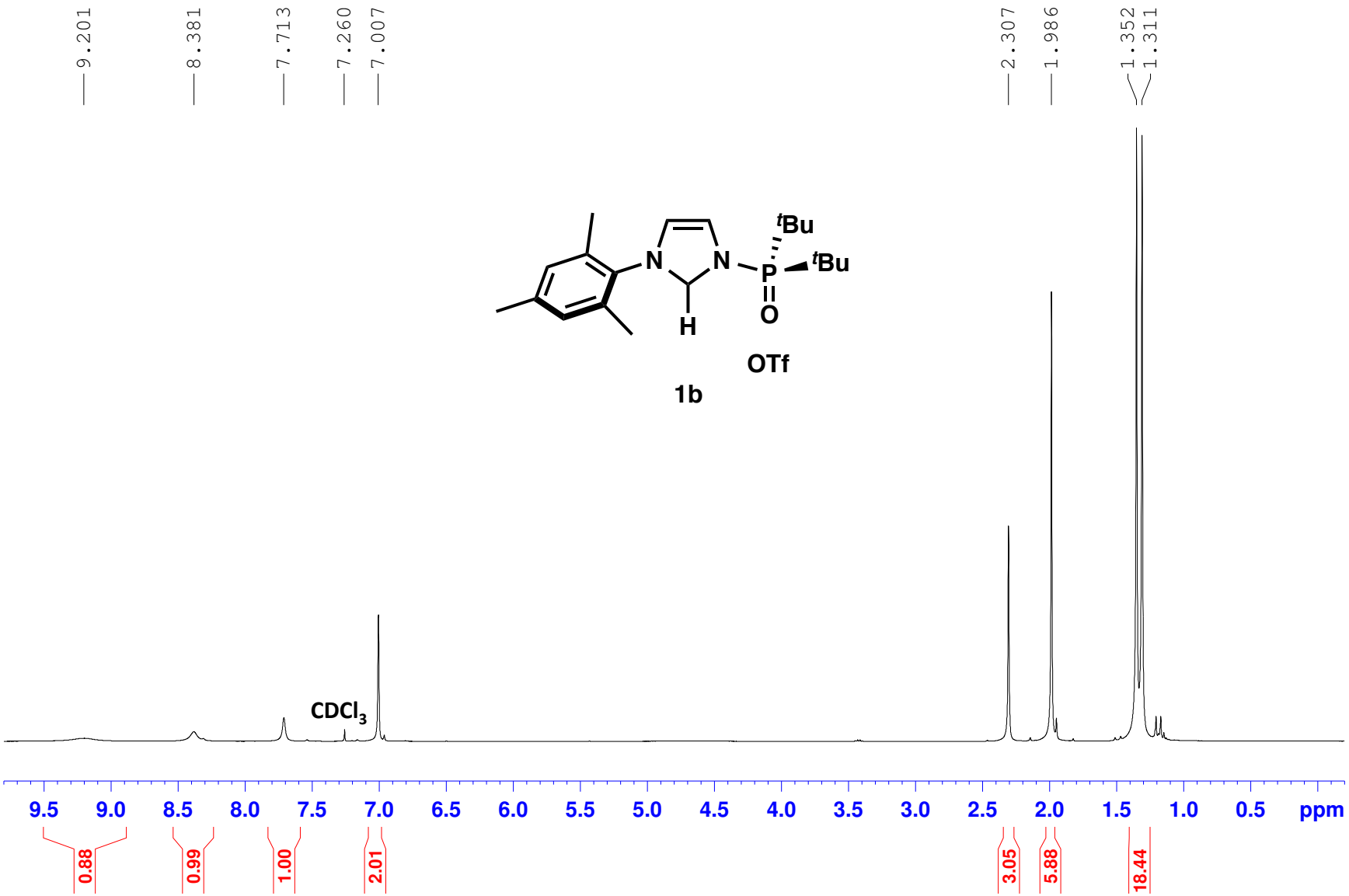
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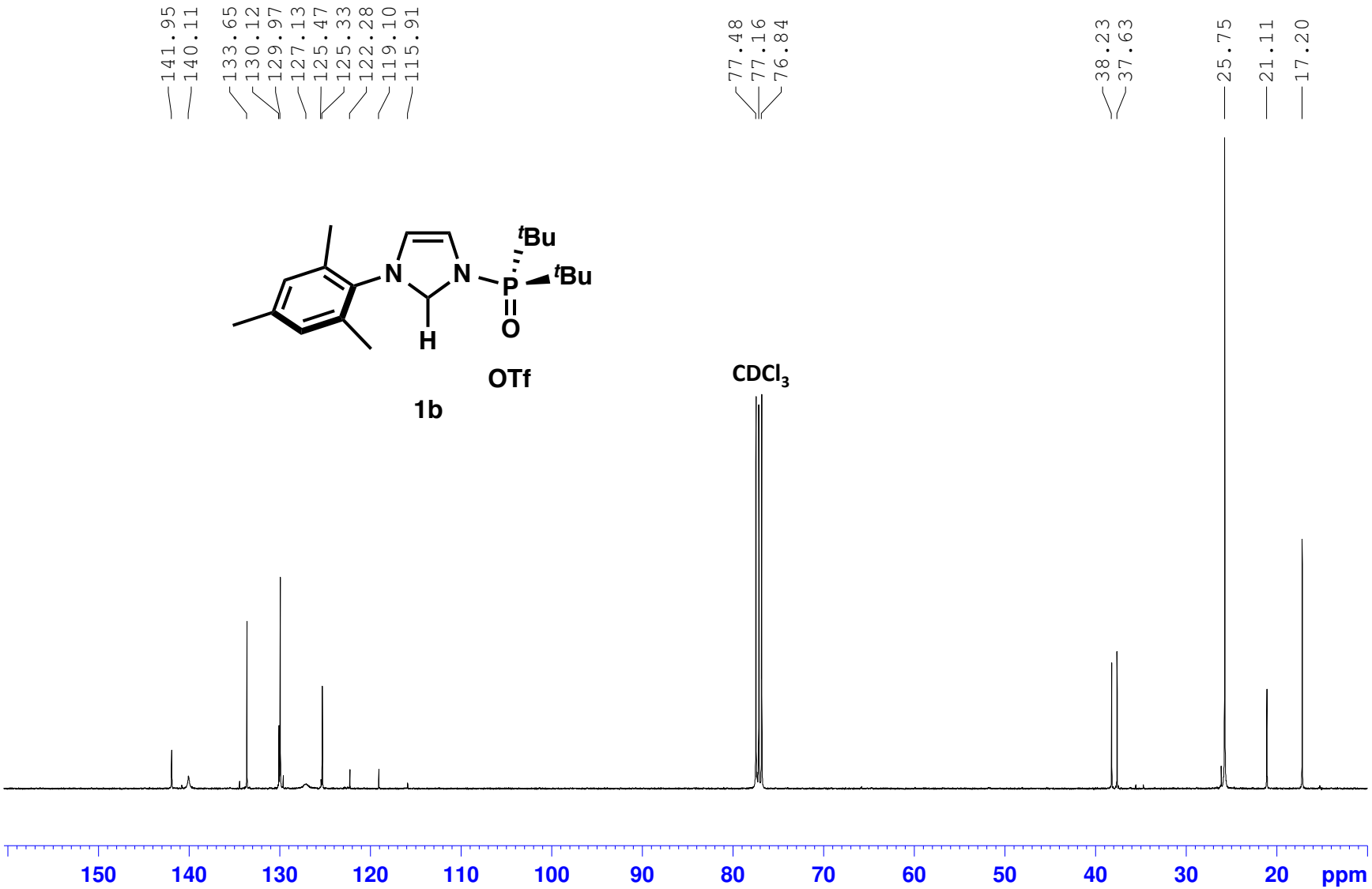
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P
O
H
OTf
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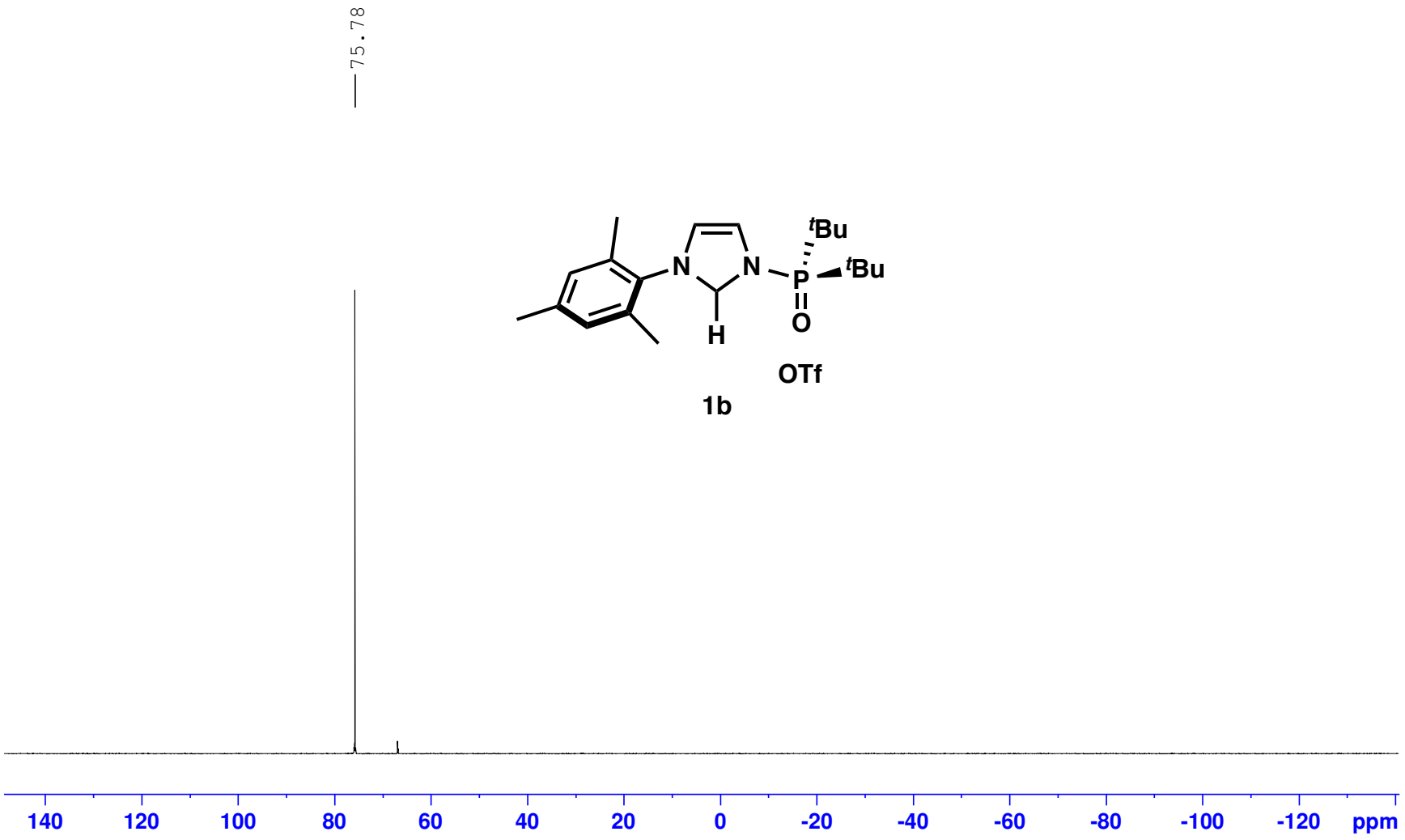
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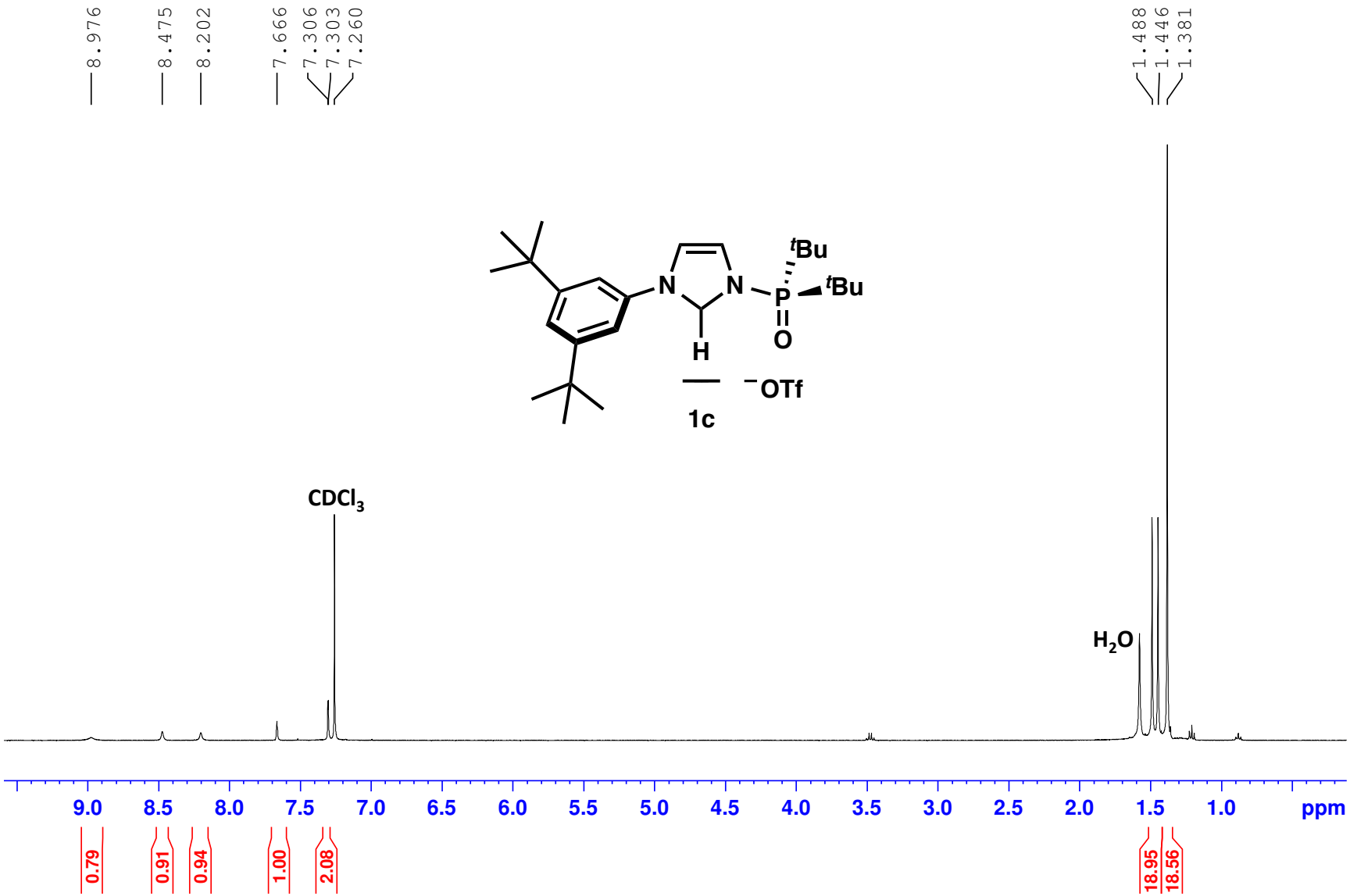
^{31}P NMR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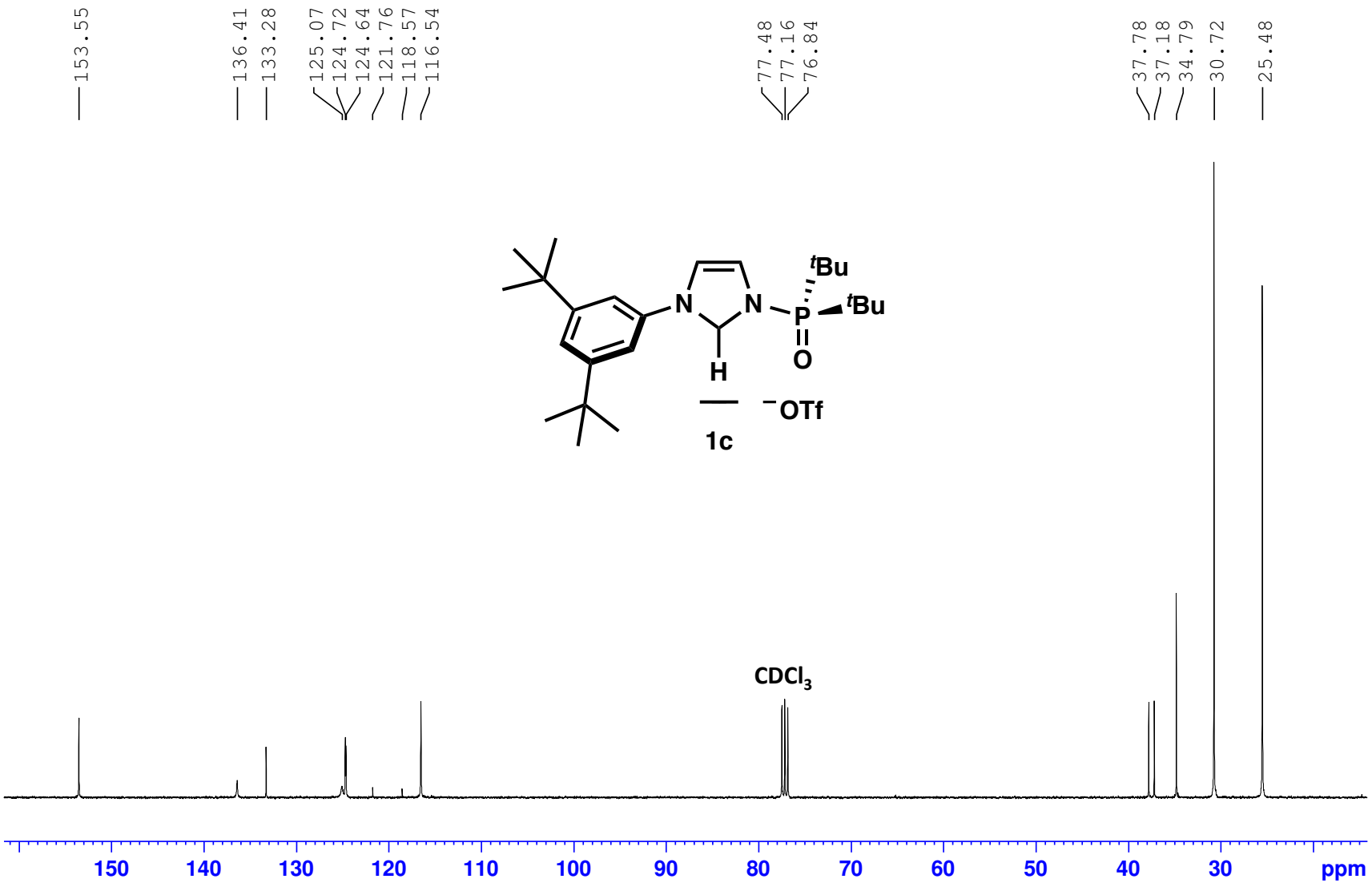
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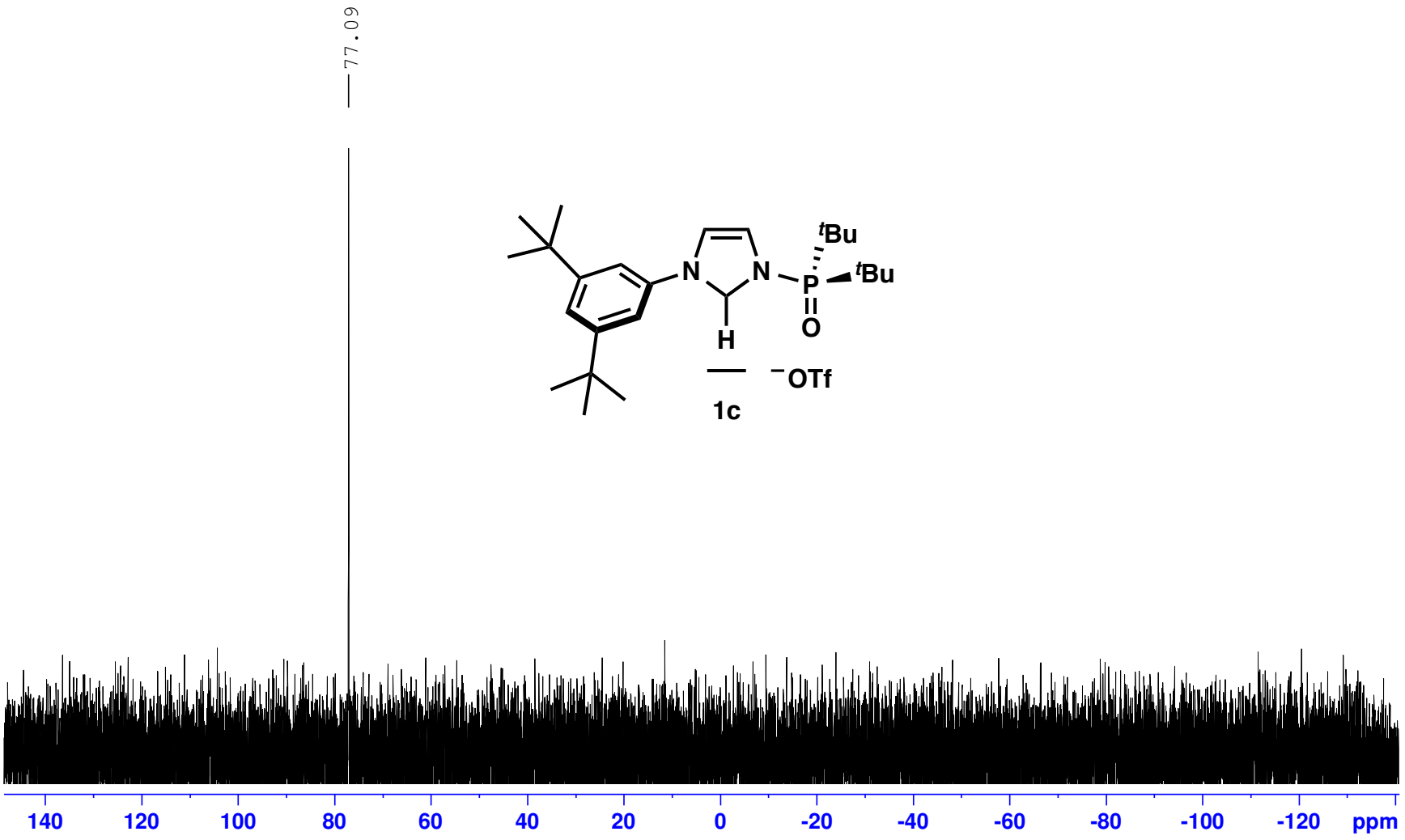
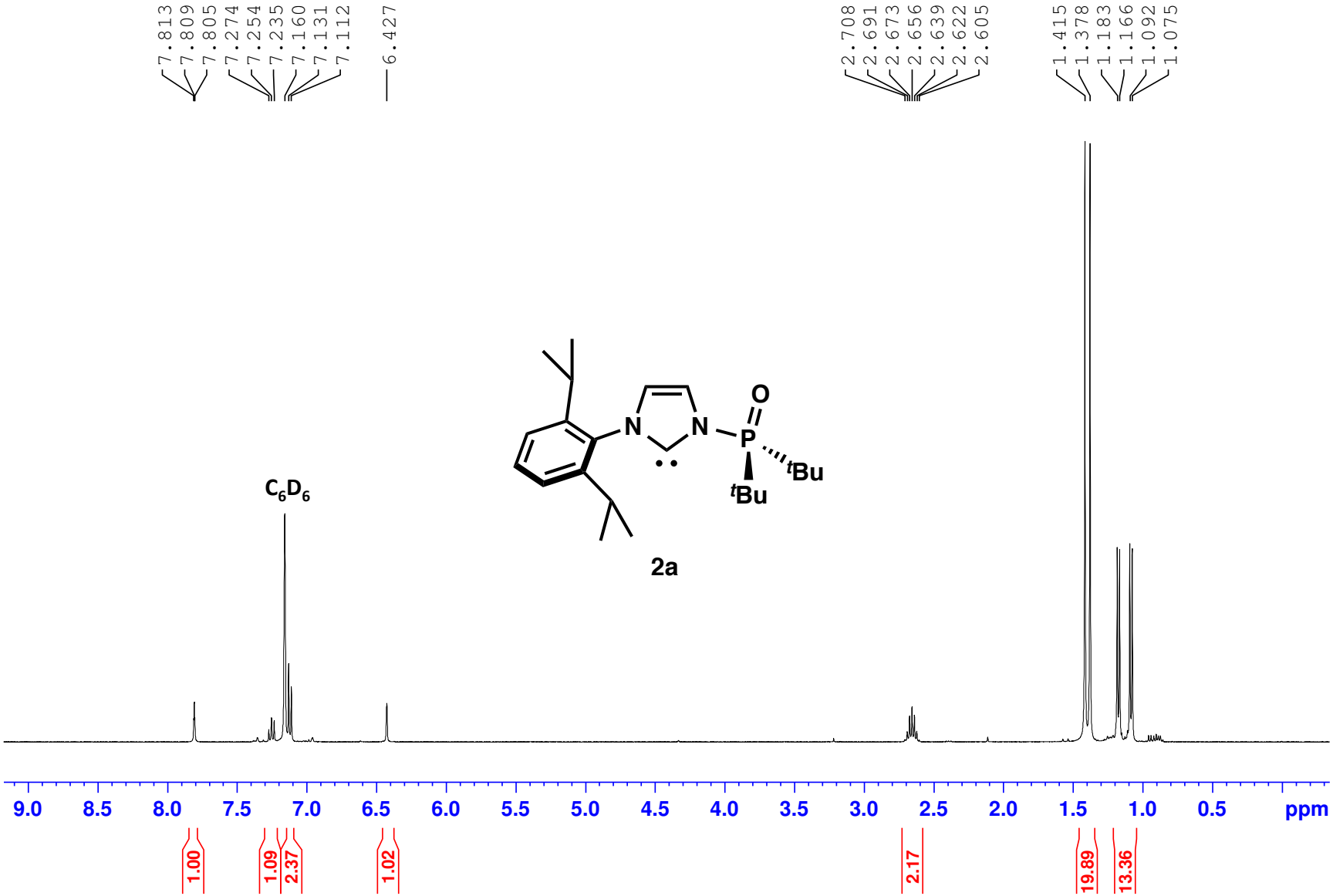
30
ppm

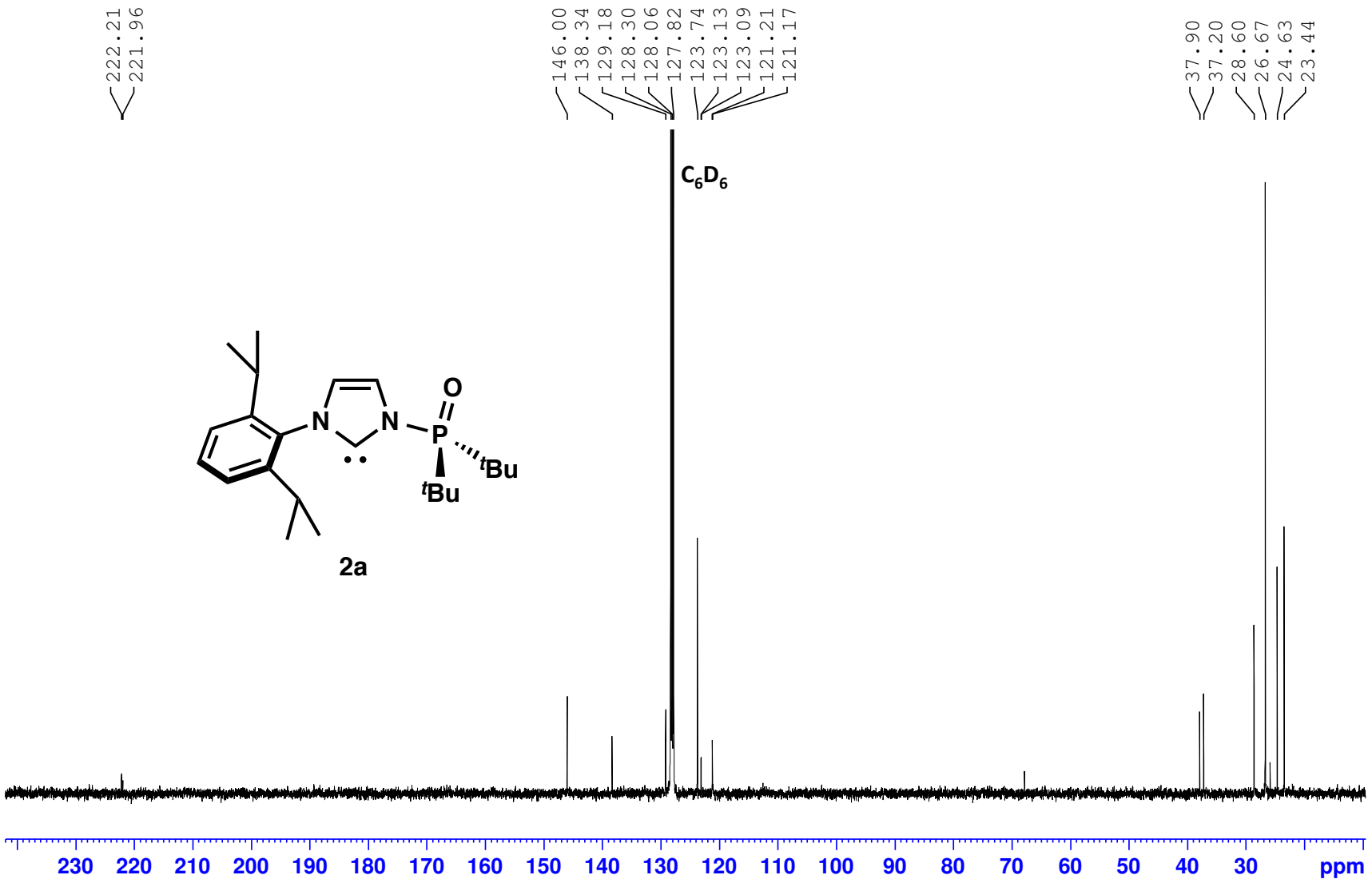
^{13}C NMR


77.09
tBu
tBu
N
N
P
O
H
OTf
1c
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm

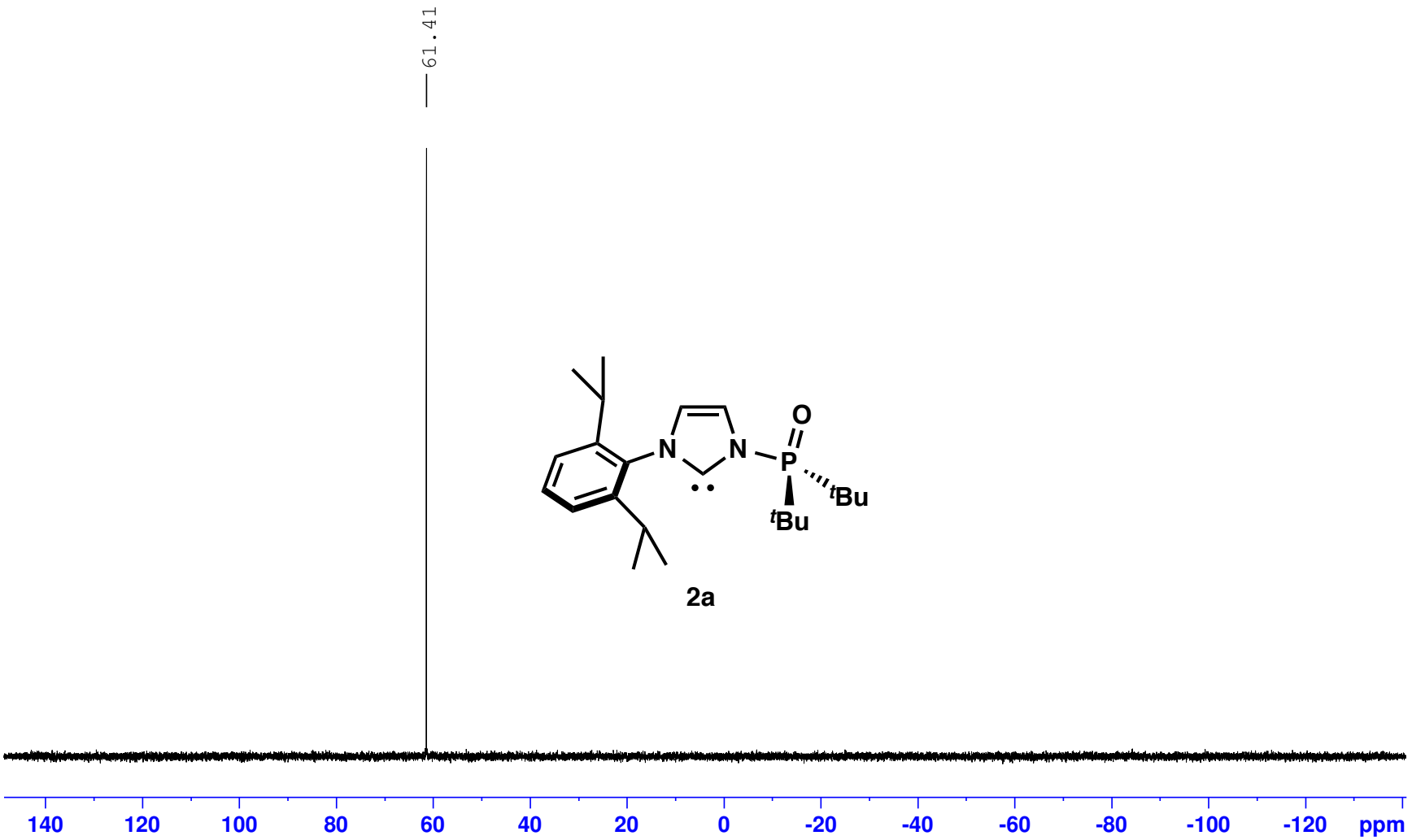
^{31}P NMR


7.813
7.809
7.805
7.274
7.254
7.235
7.160
7.131
7.112
6.427
2.708
2.691
2.673
2.656
2.639
2.622
2.605
1.415
1.378
1.183
1.166
1.092
1.075
C6D6
N
N
O
P
tBu
tBu
2a
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.09
2.37
1.02
2.17
19.89
13.36

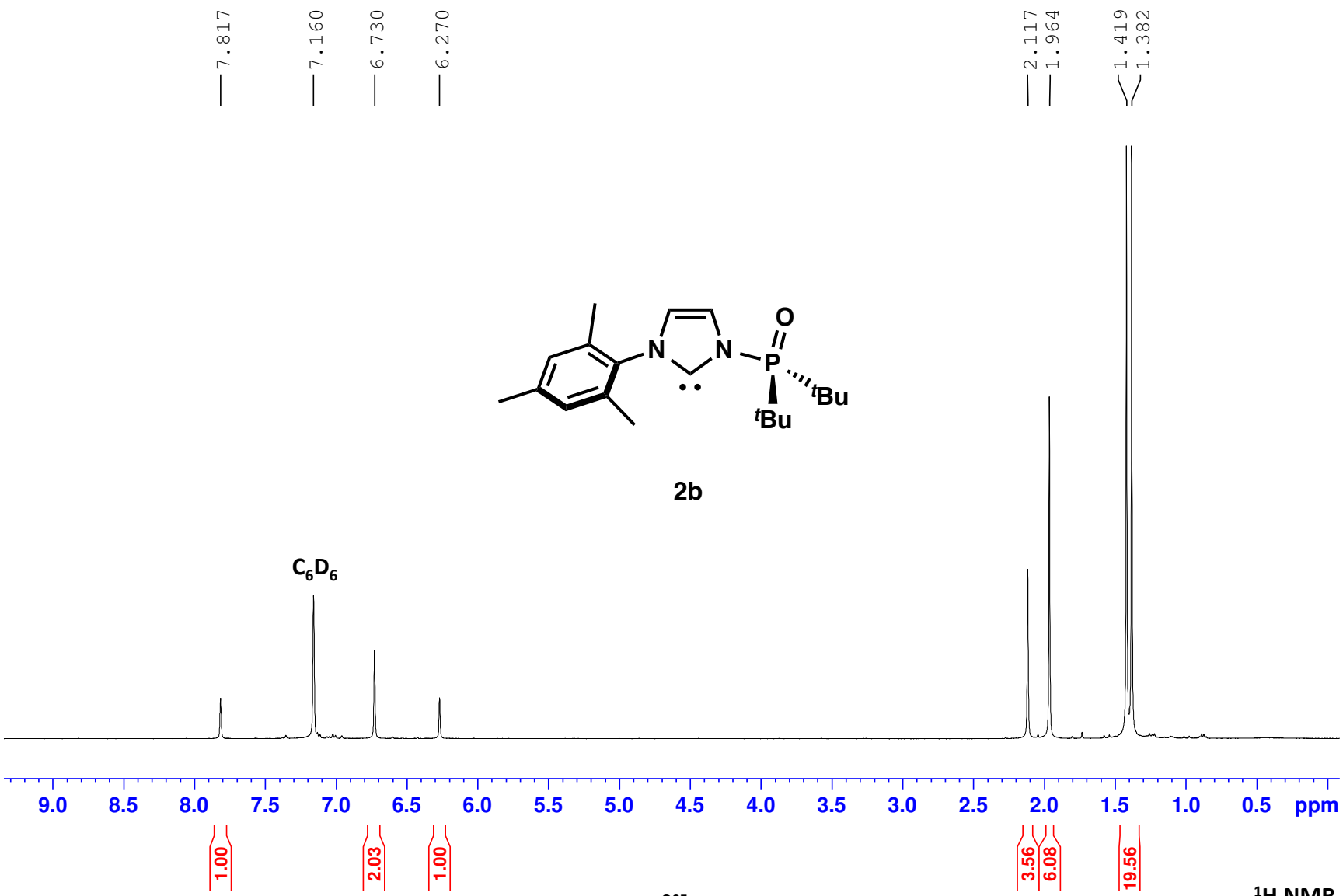
^{1}H NMR


222.21
221.96
146.00
138.34
129.18
128.30
128.06
127.82
123.74
123.13
123.09
121.21
121.17
37.90
37.20
28.60
26.67
24.63
23.44
C6D6
O
N
N
P
tBu
tBu
2a
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

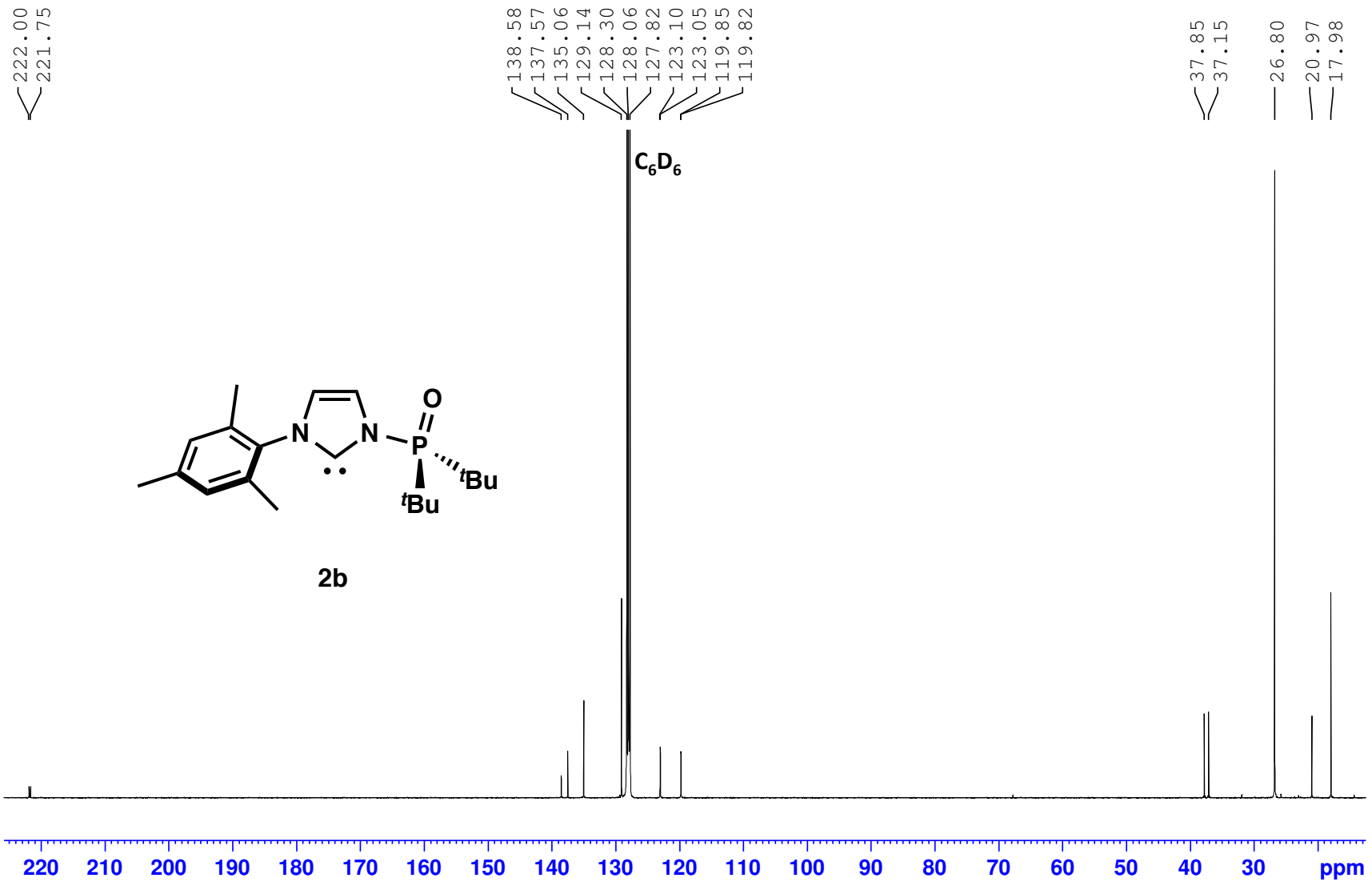
^{13}C NMR


61.41
O
N
N
P
tBu
tBu
2a
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm

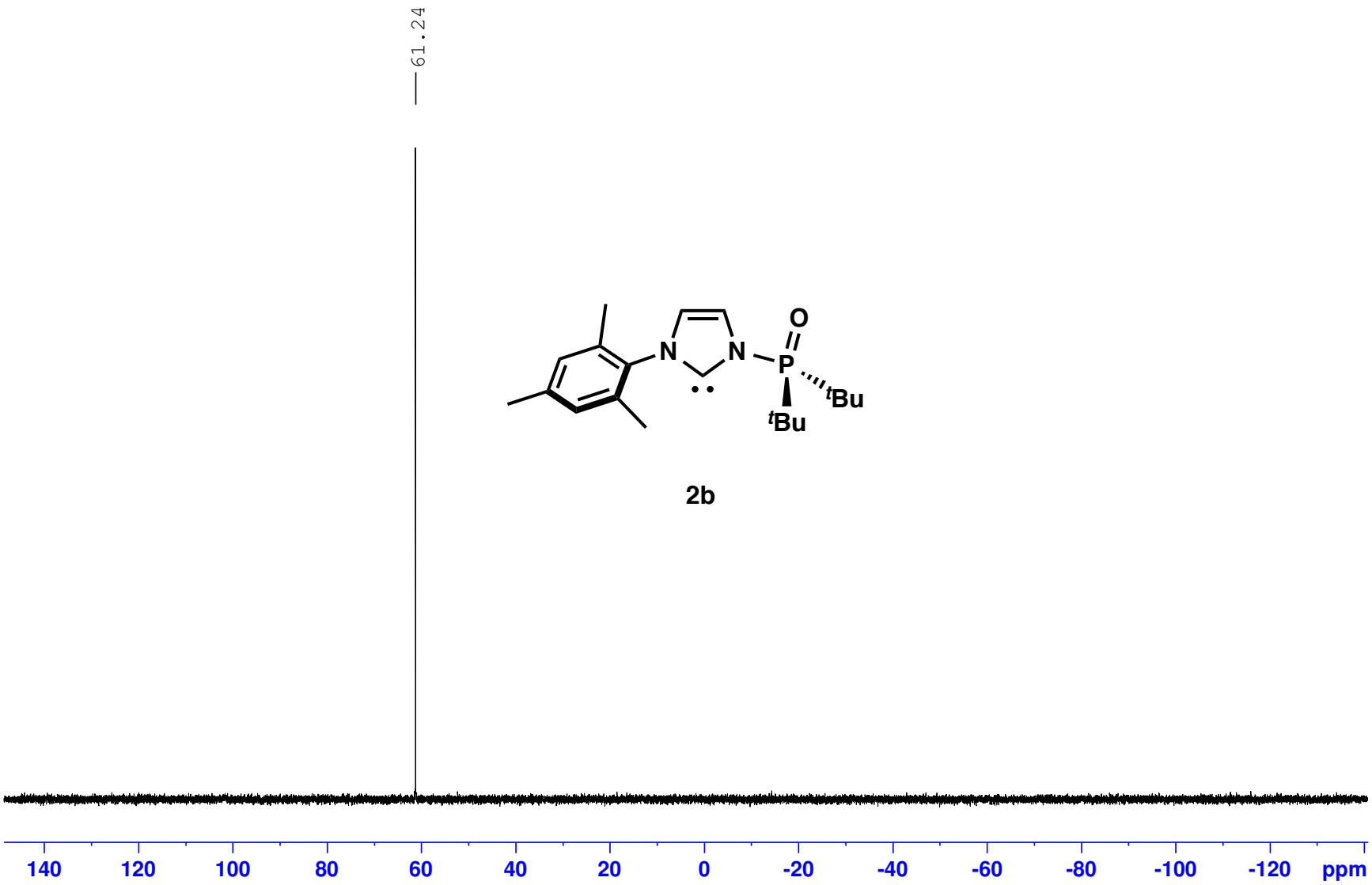
^{31}P NMR


7.817
7.160
6.730
6.270
2.117
1.964
1.419
1.382
O
N
N
P
tBu
tBu
2b
C6D6
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.03
1.00
3.56
6.08
19.56

^{1}H NMR

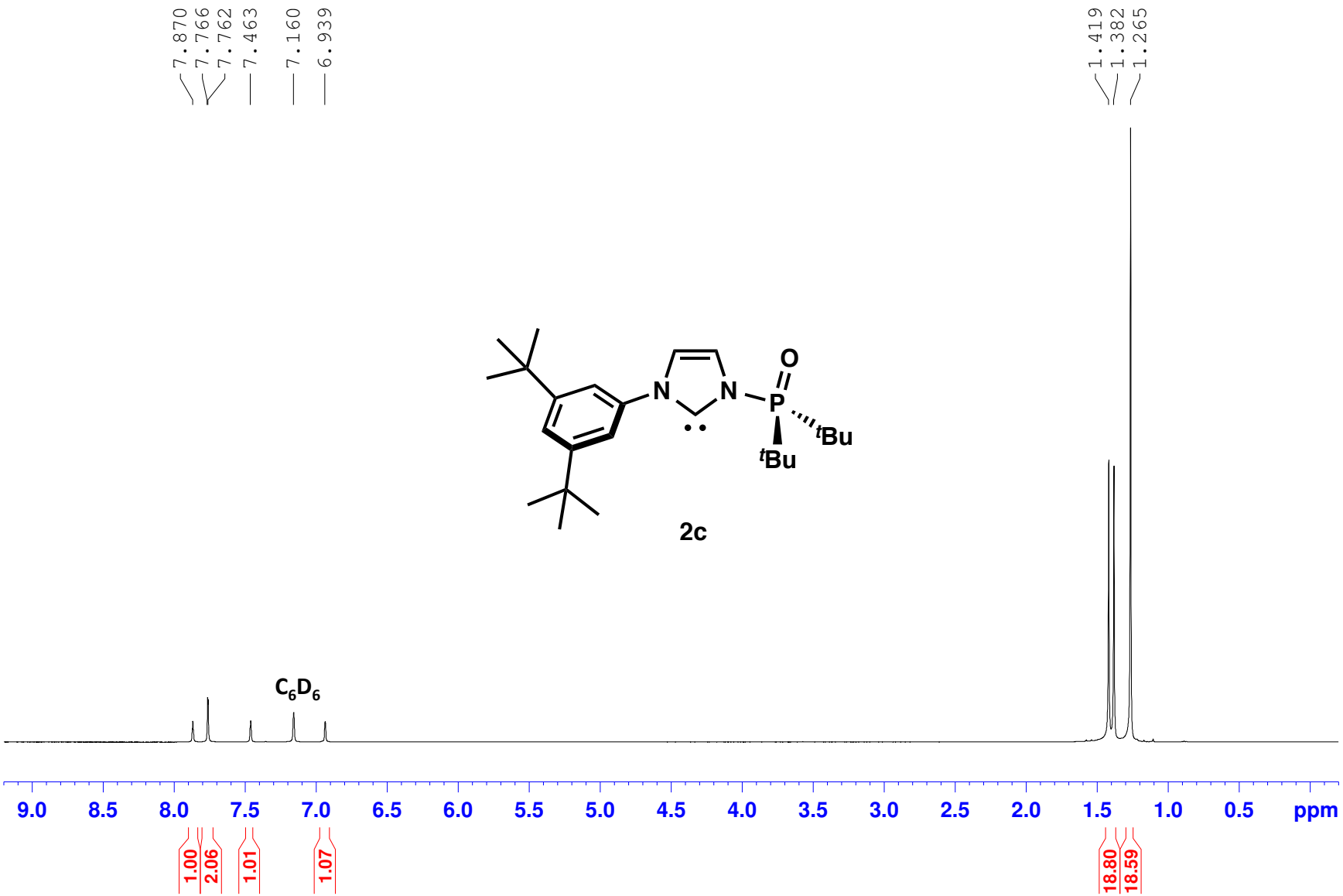

222.00
221.75
138.58
137.57
135.06
129.14
128.30
128.06
127.82
123.10
123.05
119.85
119.82
37.85
37.15
26.80
20.97
17.98
C6D6
O
N
N
P
tBu
tBu
2b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

^{13}C NMR

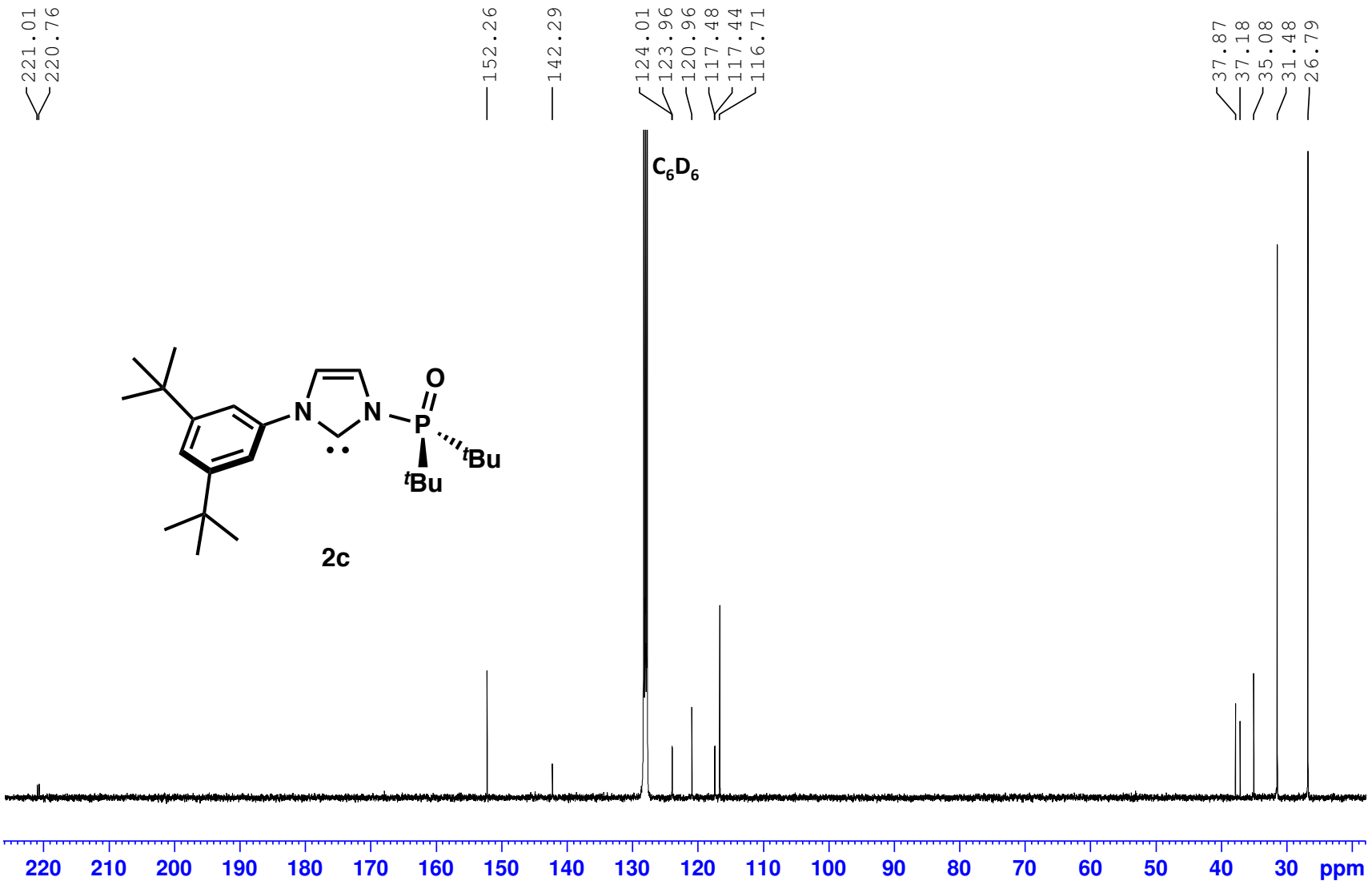


2b

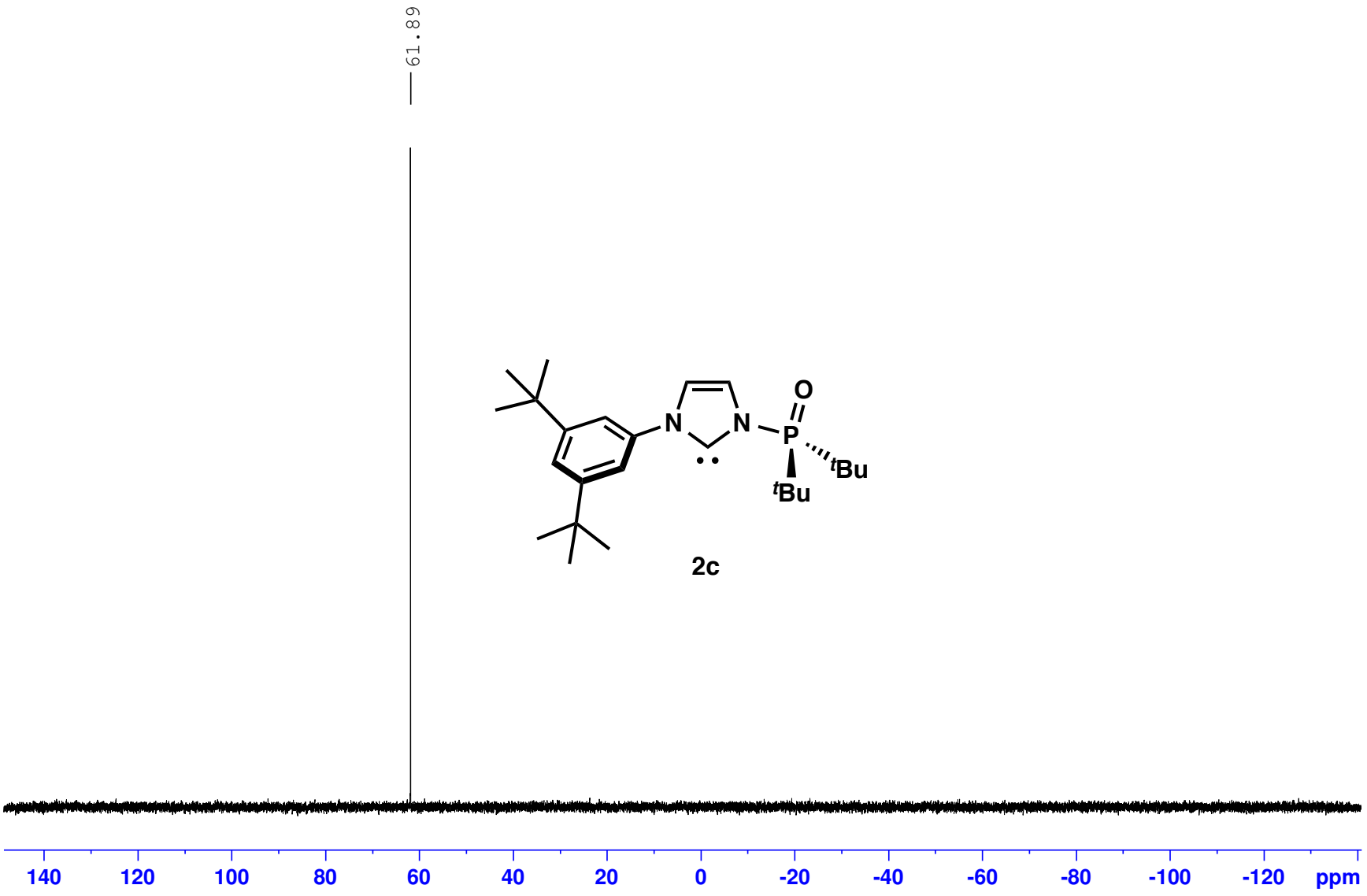
^{31}P NMR


7.870
7.766
7.762
7.463
7.160
6.939
1.419
1.382
1.265
O
N
N
P
tBu
tBu
2c
C6D6
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.06
1.01
1.07
18.80
18.59

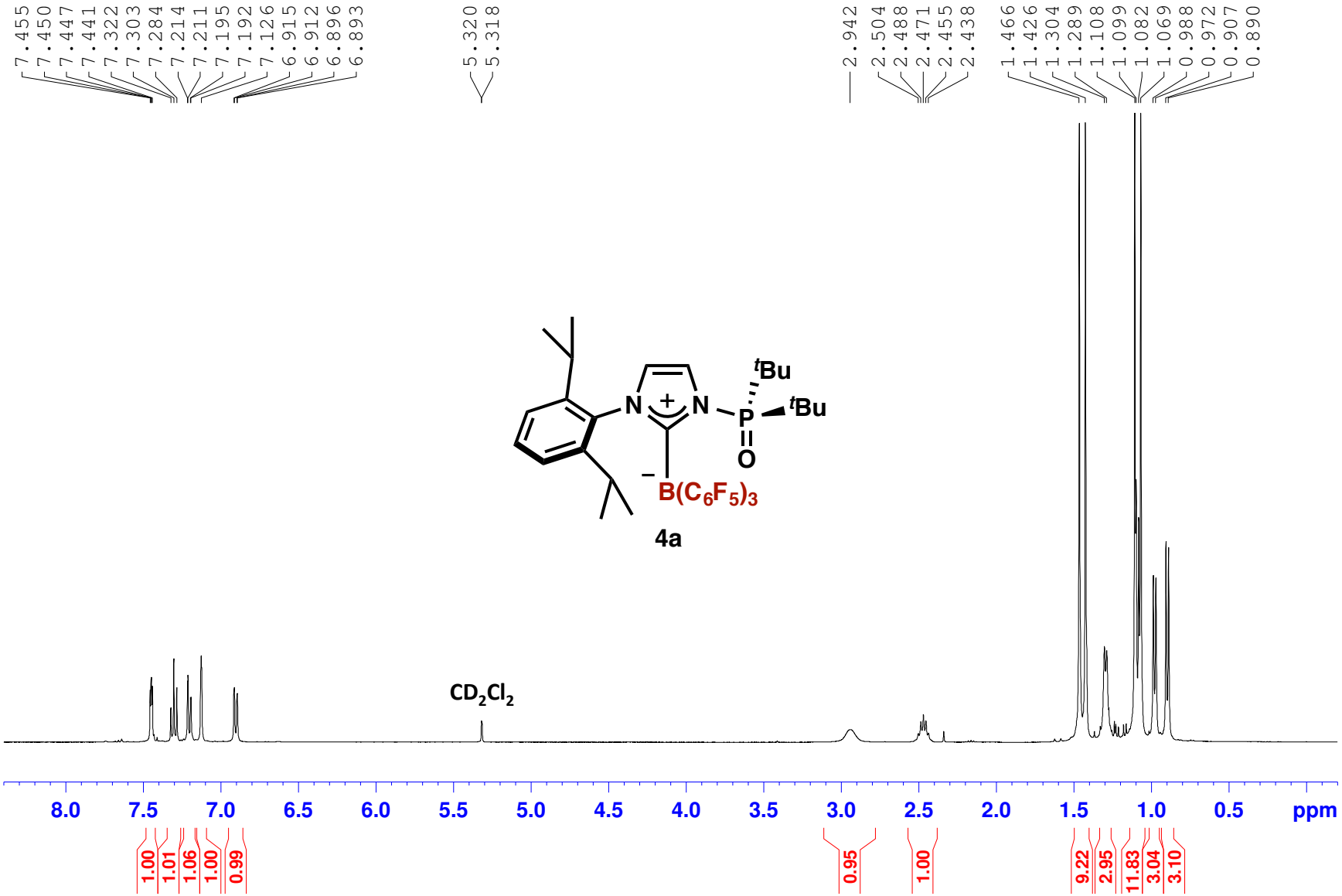
^{1}H NMR


221.01
220.76
152.26
142.29
124.01
123.96
120.96
117.48
117.44
116.71
37.87
37.18
35.08
31.48
26.79
C6D6
O
N
N
P
tBu
tBu
2c
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

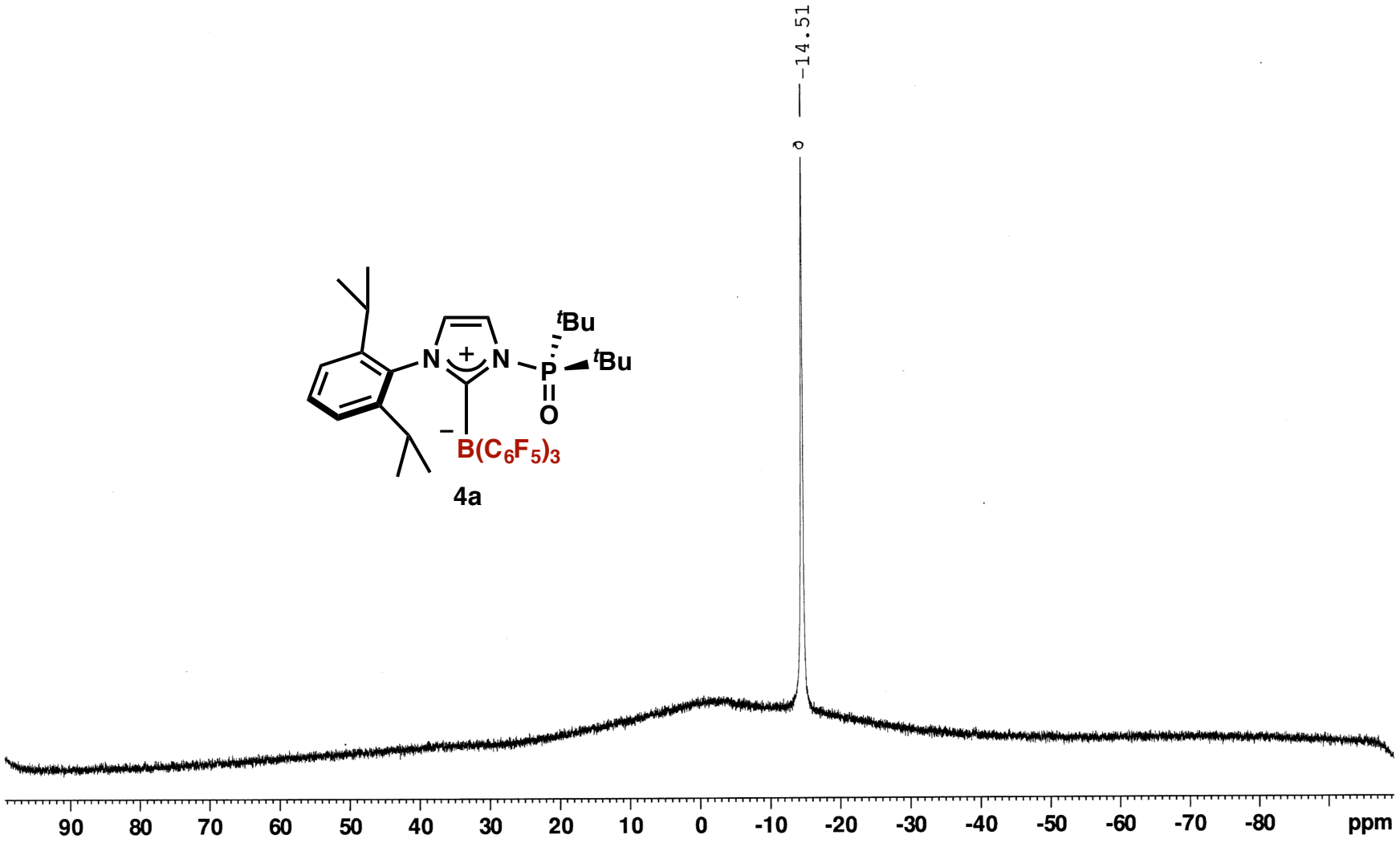
^{13}C NMR


61.89
O
N
N
P
tBu
tBu
2c
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm

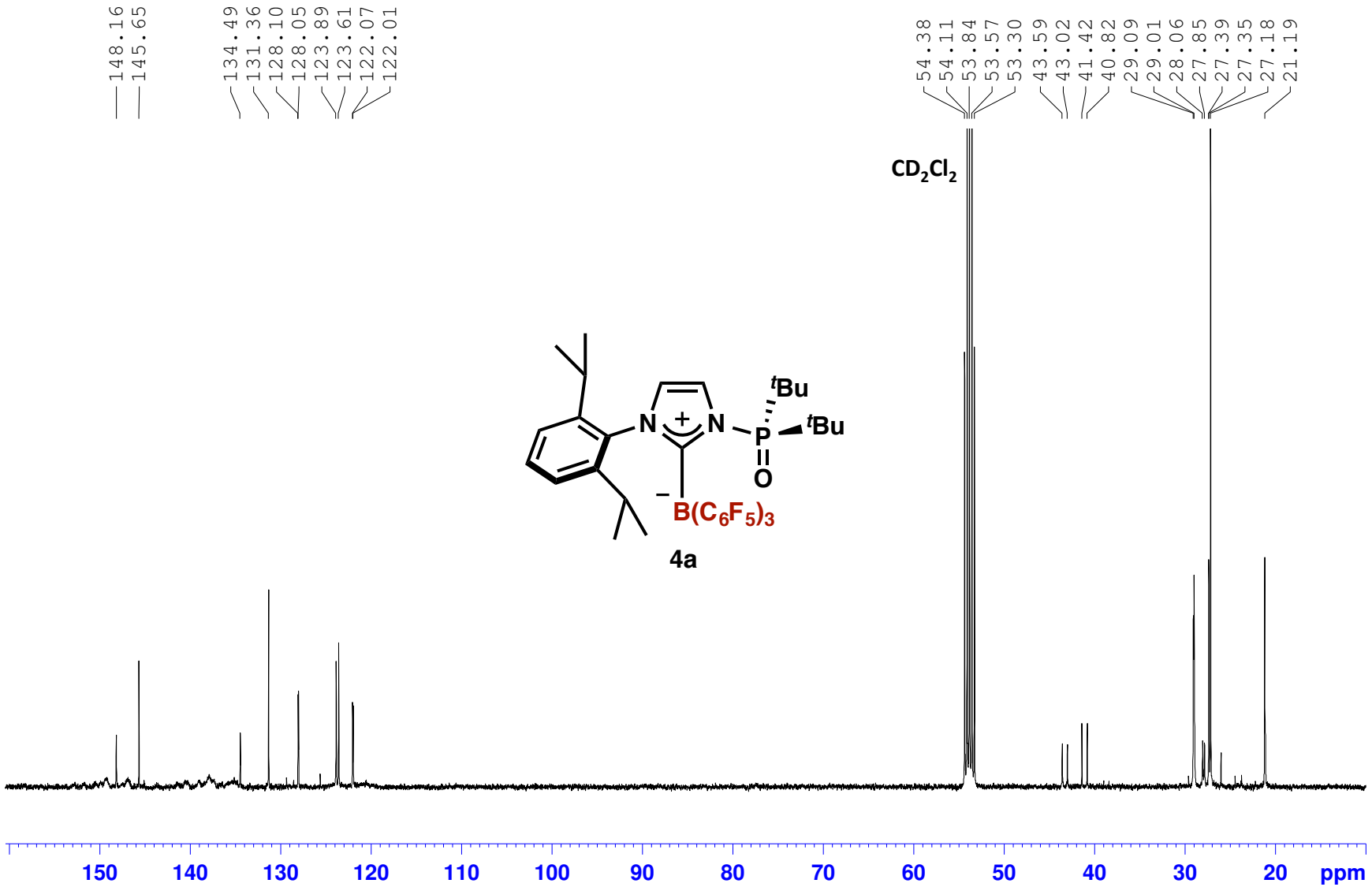
^{31}P NMR


7.455
7.450
7.447
7.441
7.322
7.303
7.284
7.214
7.211
7.195
7.192
7.126
6.915
6.912
6.896
6.893
5.320
5.318
2.942
2.504
2.488
2.471
2.455
2.438
1.466
1.426
1.304
1.289
1.108
1.099
1.082
1.069
0.988
0.972
0.907
0.890
tBu
tBu
N
N
P
O
B(C6F5)3
4a
CD2Cl2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.01
1.06
1.00
0.99
0.95
1.00
9.22
2.95
11.83
3.04
3.10

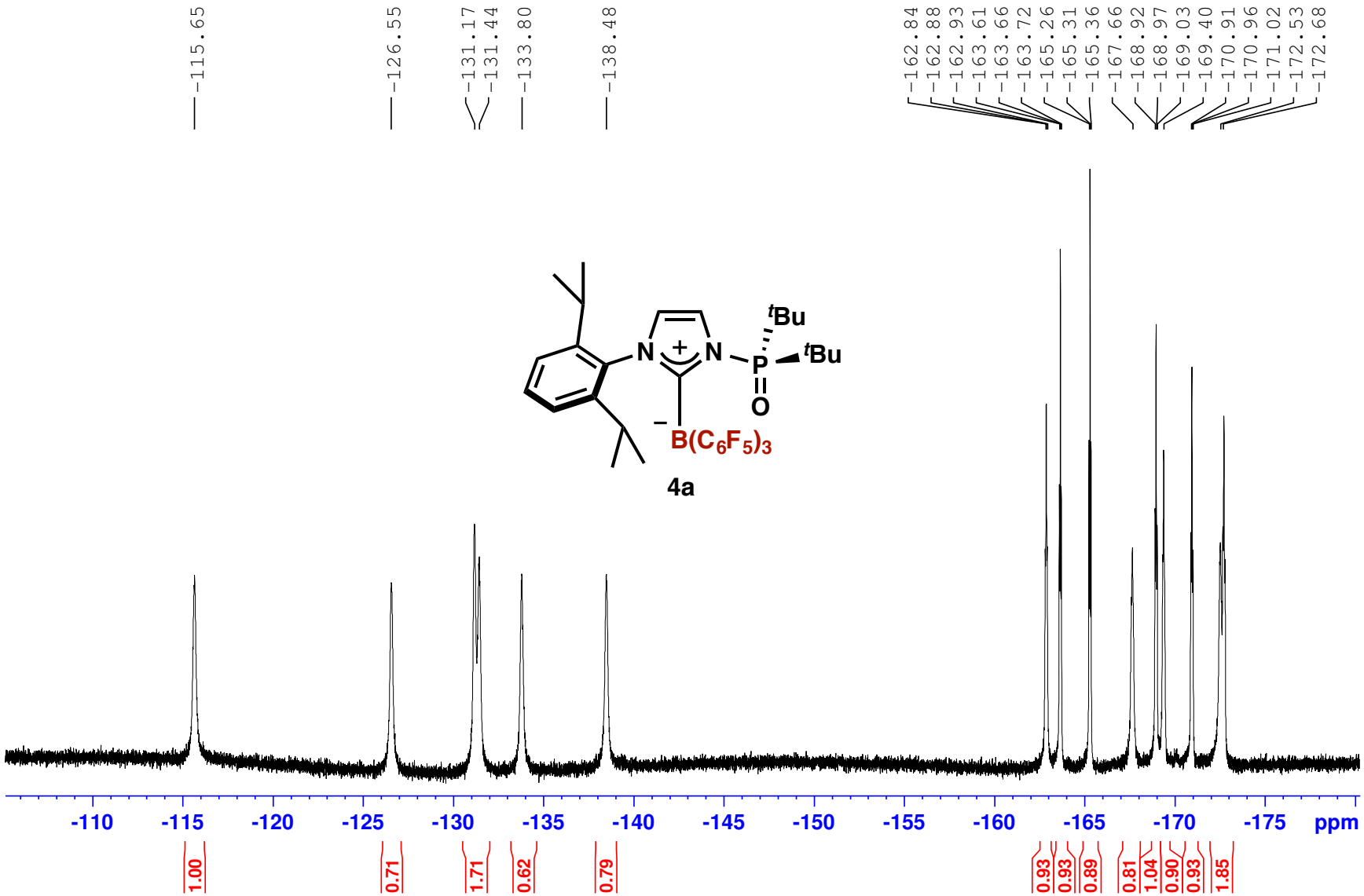
^{1}H NMR


-14.51
tBu
tBu
N
N
P
O
B(C6F5)3
4a
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm

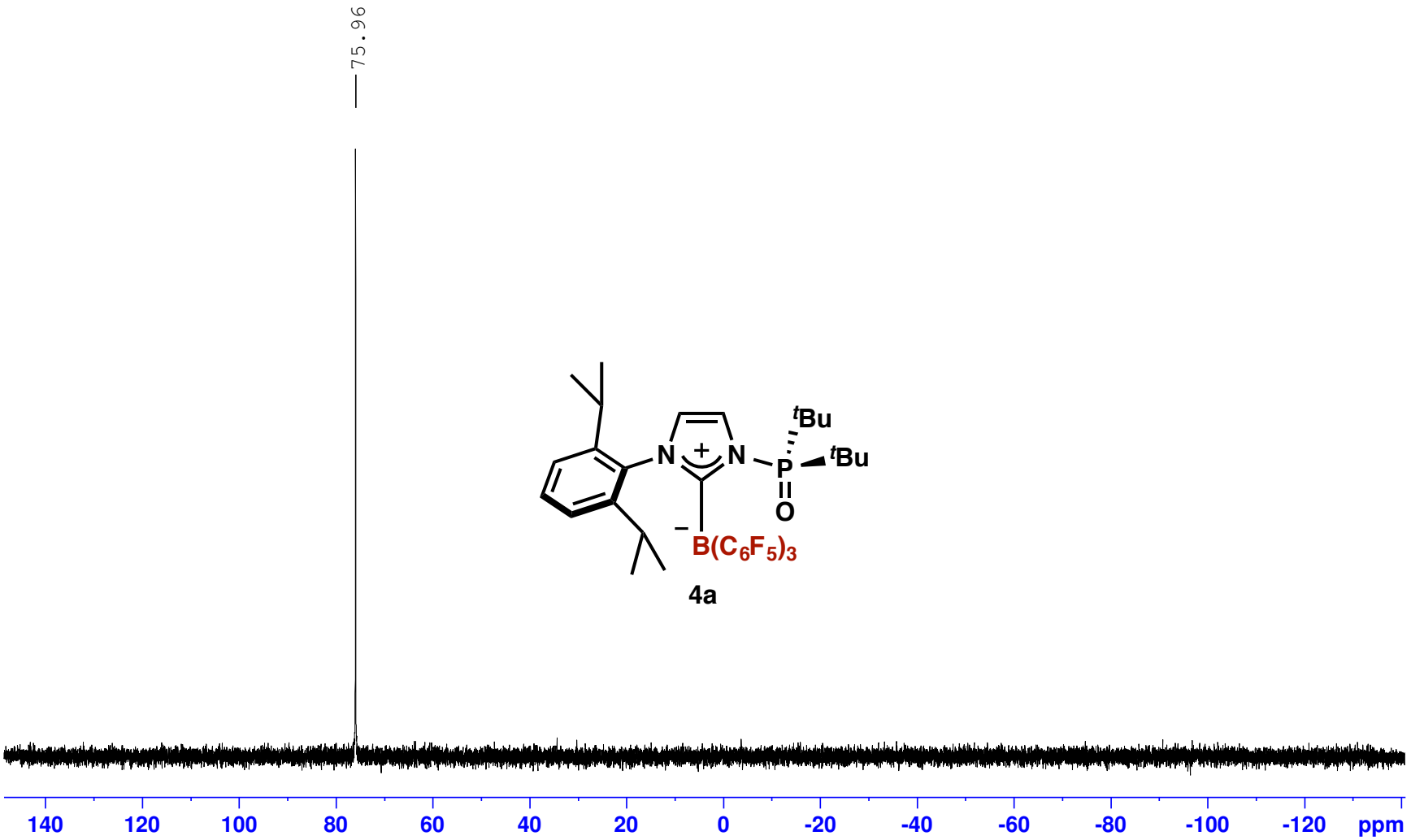
^{11}B NMR


148.16
145.65
134.49
131.36
128.10
128.05
123.89
123.61
122.07
122.01
54.38
54.11
53.84
53.57
53.30
43.59
43.02
41.42
40.82
29.09
29.01
28.06
27.85
27.39
27.35
27.18
21.19
CD2Cl2
tBu
tBu
N
N
P
O
B(C6F5)3
4a
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

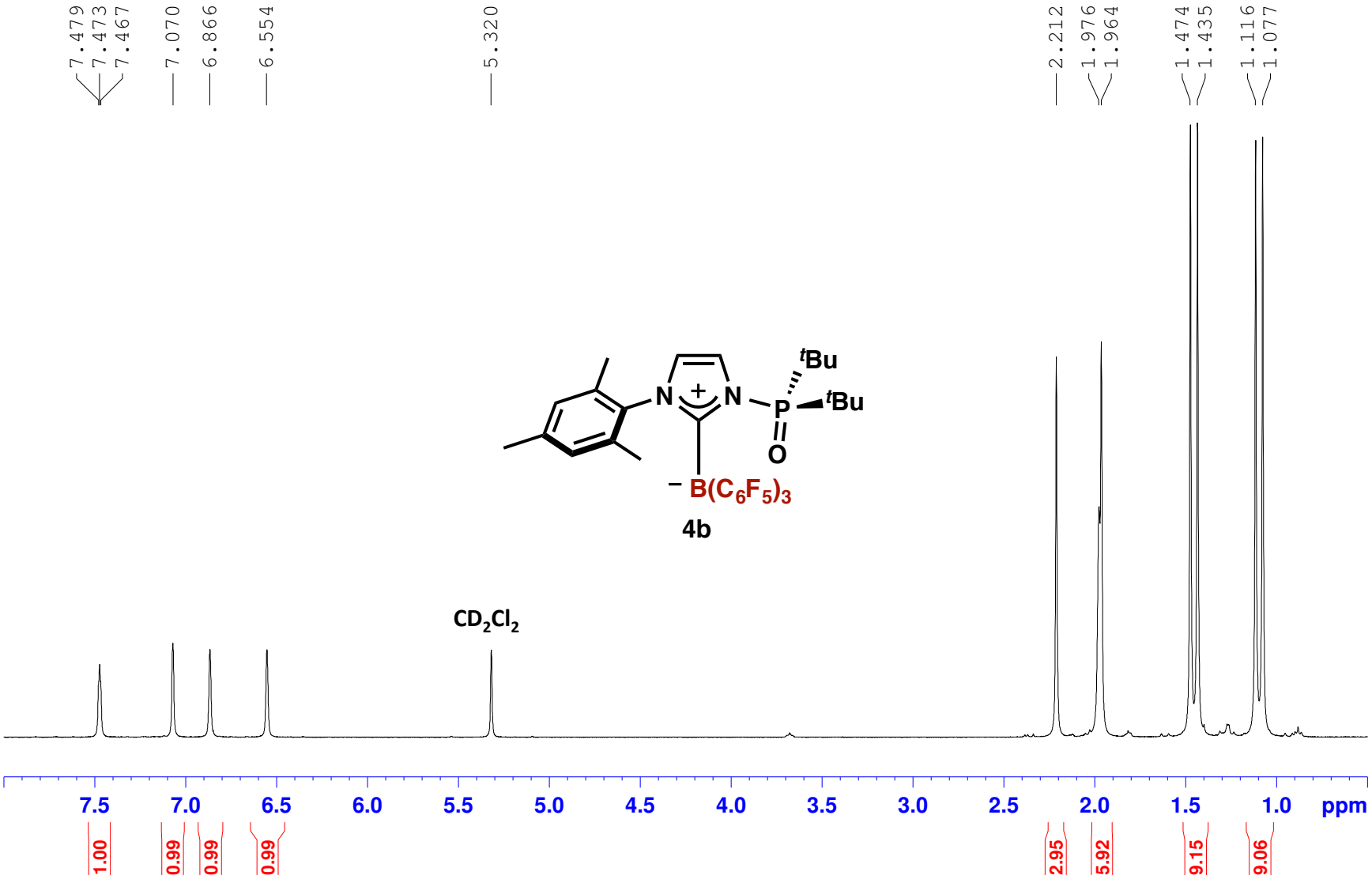
^{13}C NMR


-115.65
-126.55
-131.17
-131.44
-133.80
-138.48
-162.84
-162.88
-162.93
-163.61
-163.66
-163.72
-165.26
-165.31
-165.36
-167.66
-168.92
-168.97
-169.03
-169.40
-170.91
-170.96
-171.02
-172.53
-172.68
tBu
tBu
P
O
N
N
+
−
B(C6F5)3
4a
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
ppm
1.00
0.71
1.71
0.62
0.79
0.93
0.93
0.89
0.81
1.04
0.90
0.93
1.85

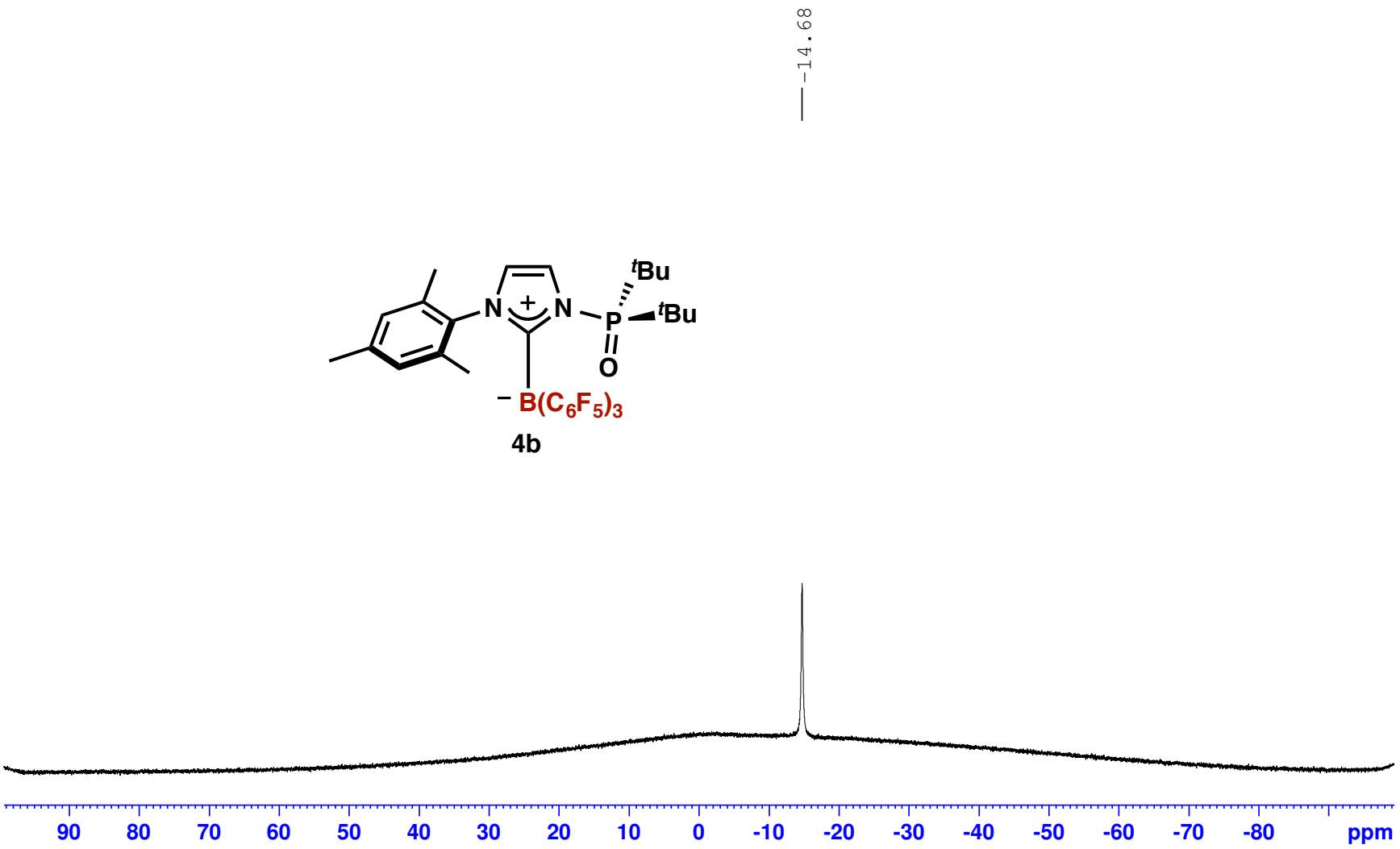
^{19}F NMR


75.96
tBu
tBu
N
N
P
O
B(C6F5)3
4a
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm

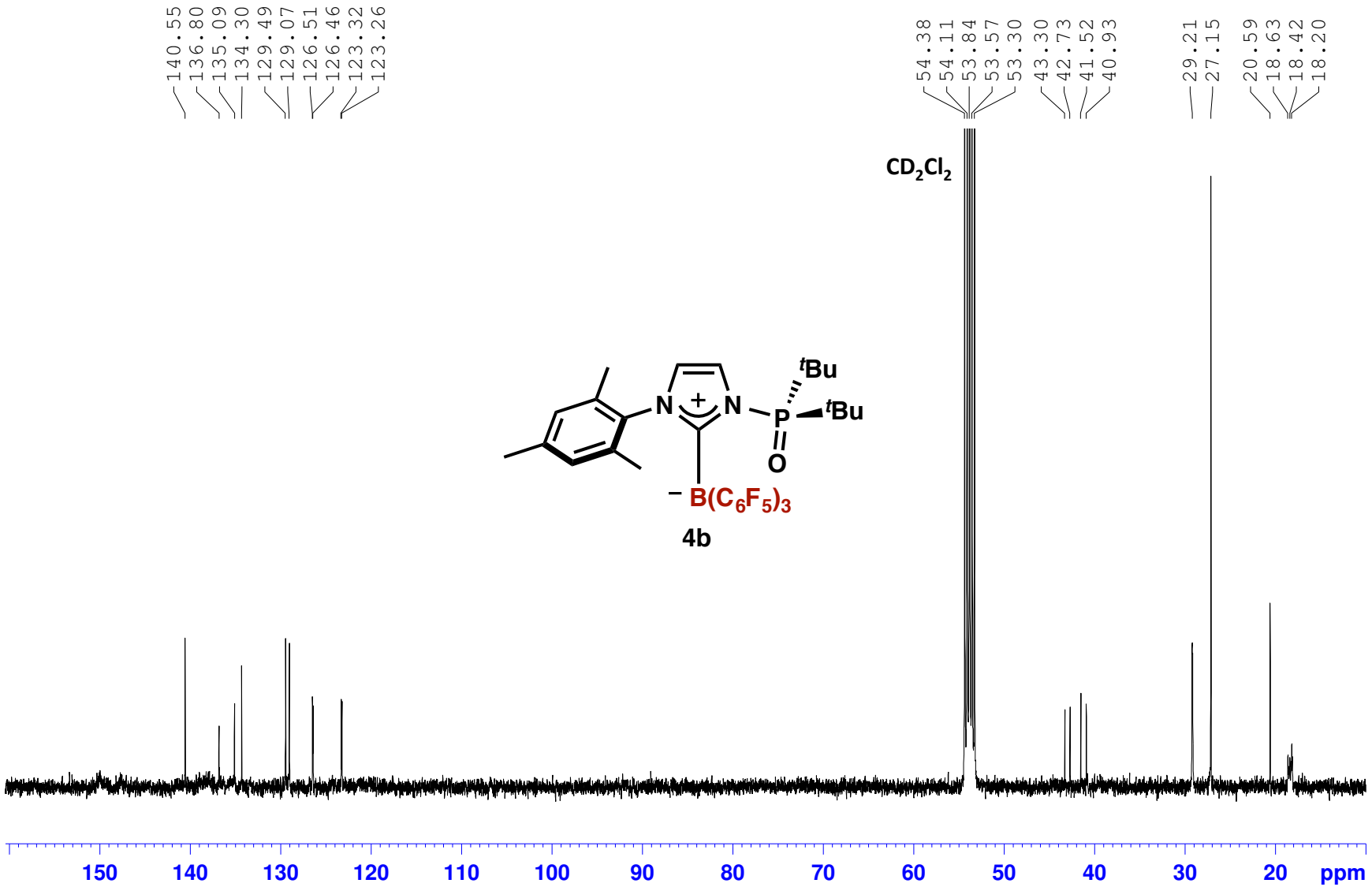
^{31}P NMR


7.479
7.473
7.467
7.070
6.866
6.554
5.320
2.212
1.976
1.964
1.474
1.435
1.116
1.077
tBu
tBu
N
N
P
O
− B(C6F5)3
4b
CD2Cl2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
0.99
0.99
0.99
2.95
5.92
9.15
9.06

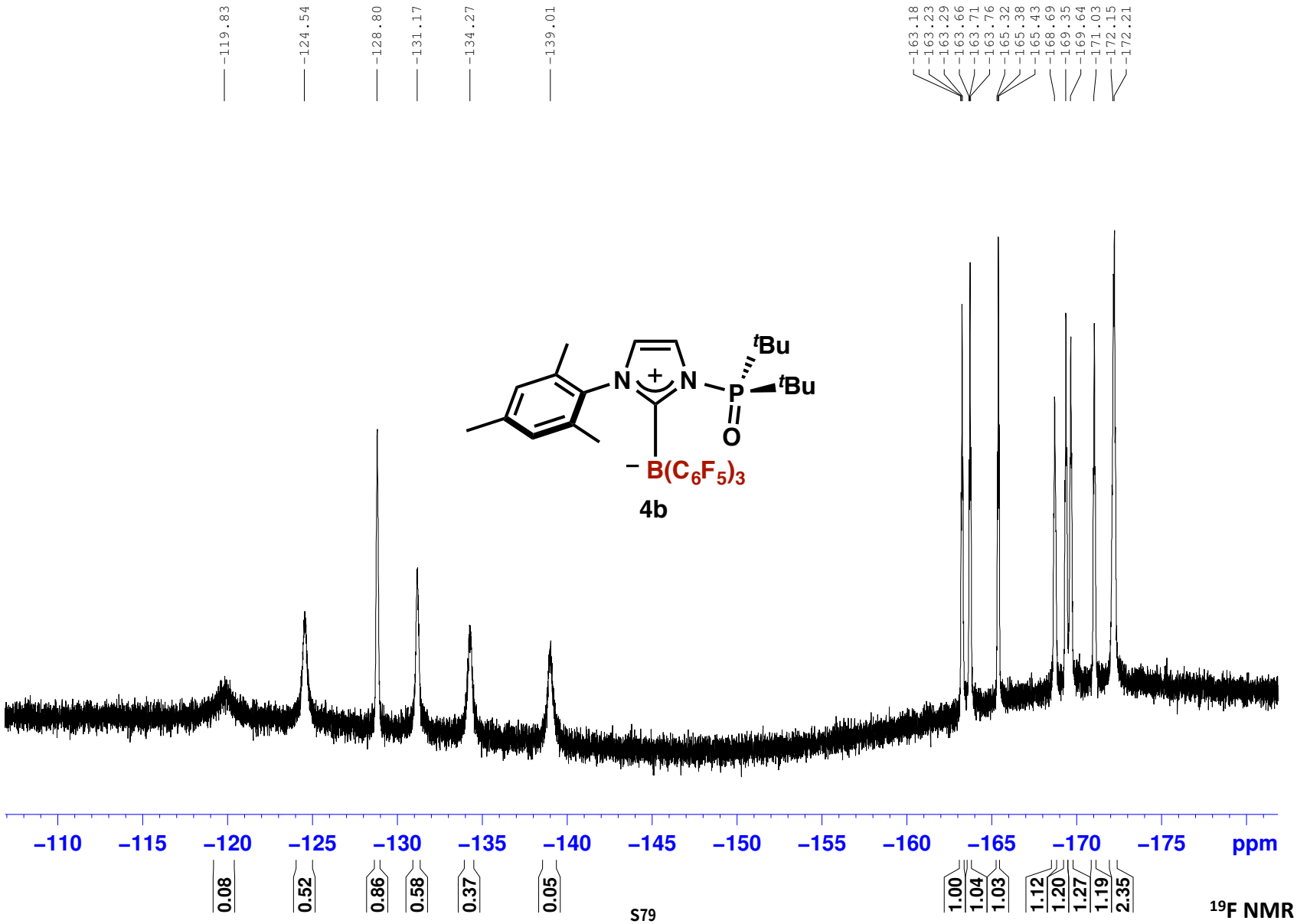
^{1}H NMR


-14.68
tBu
tBu
N
N
P
O
B(C6F5)3
4b
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm

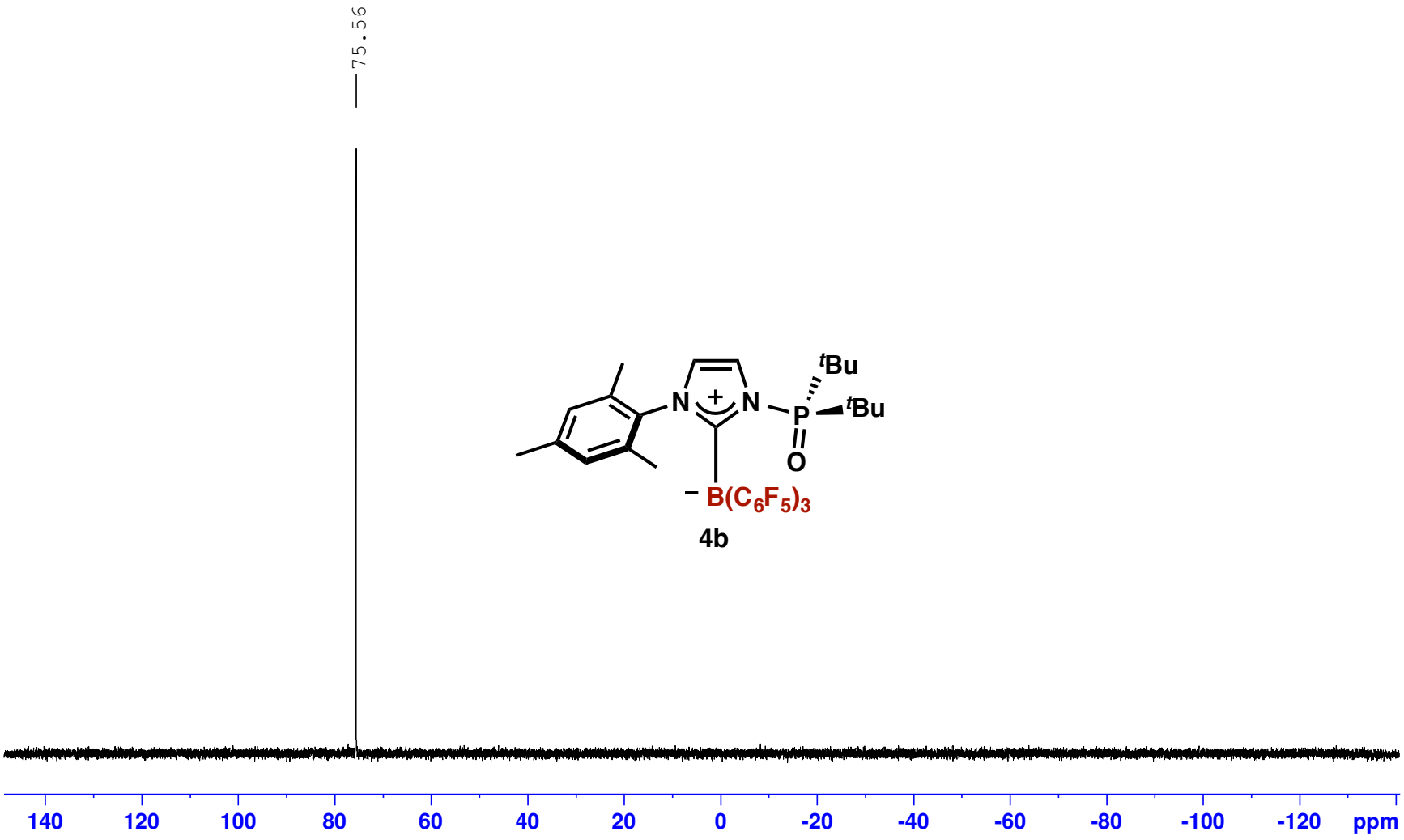
^{11}B NMR


140.55
136.80
135.09
134.30
129.49
129.07
126.51
126.46
123.32
123.26
54.38
54.11
53.84
53.57
53.30
43.30
42.73
41.52
40.93
29.21
27.15
20.59
18.63
18.42
18.20
CD2Cl2
tBu
tBu
N
N
P
O
− B(C6F5)3
4b
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

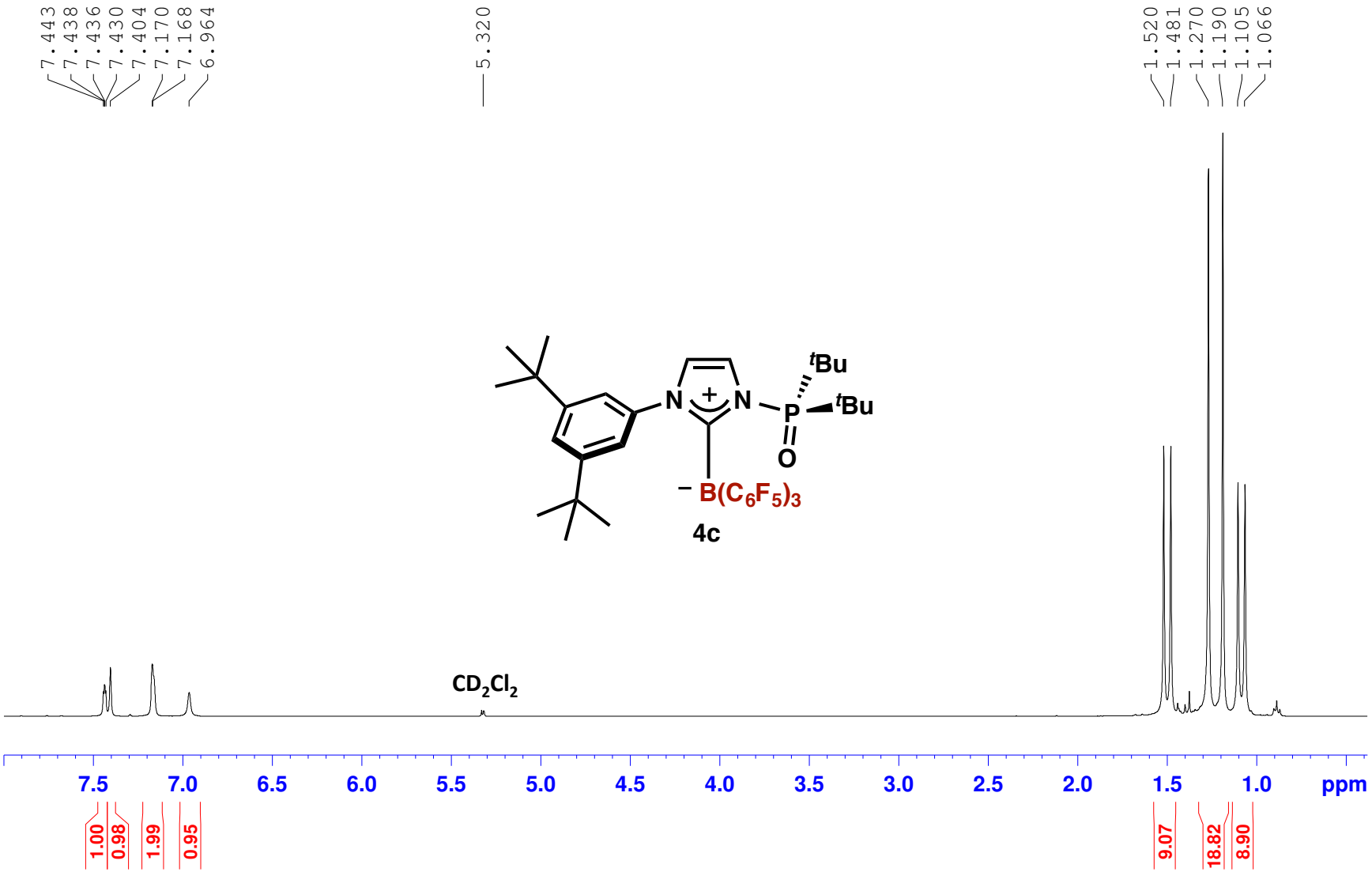
^{13}C NMR


-119.83
-124.54
-128.80
-131.17
-134.27
-139.01
-163.18
-163.23
-163.29
-163.66
-163.71
-163.76
-165.32
-165.38
-165.43
-168.69
-169.35
-169.64
-171.03
-172.15
-172.21
tBu
tBu
N
N
P
O
− B(C6F5)3
4b
−110
−115
−120
−125
−130
−135
−140
−145
−150
−155
−160
−165
−170
−175
ppm
0.08
0.52
0.86
0.58
0.37
0.05
1.00
1.04
1.03
1.12
1.20
1.27
1.19
2.35

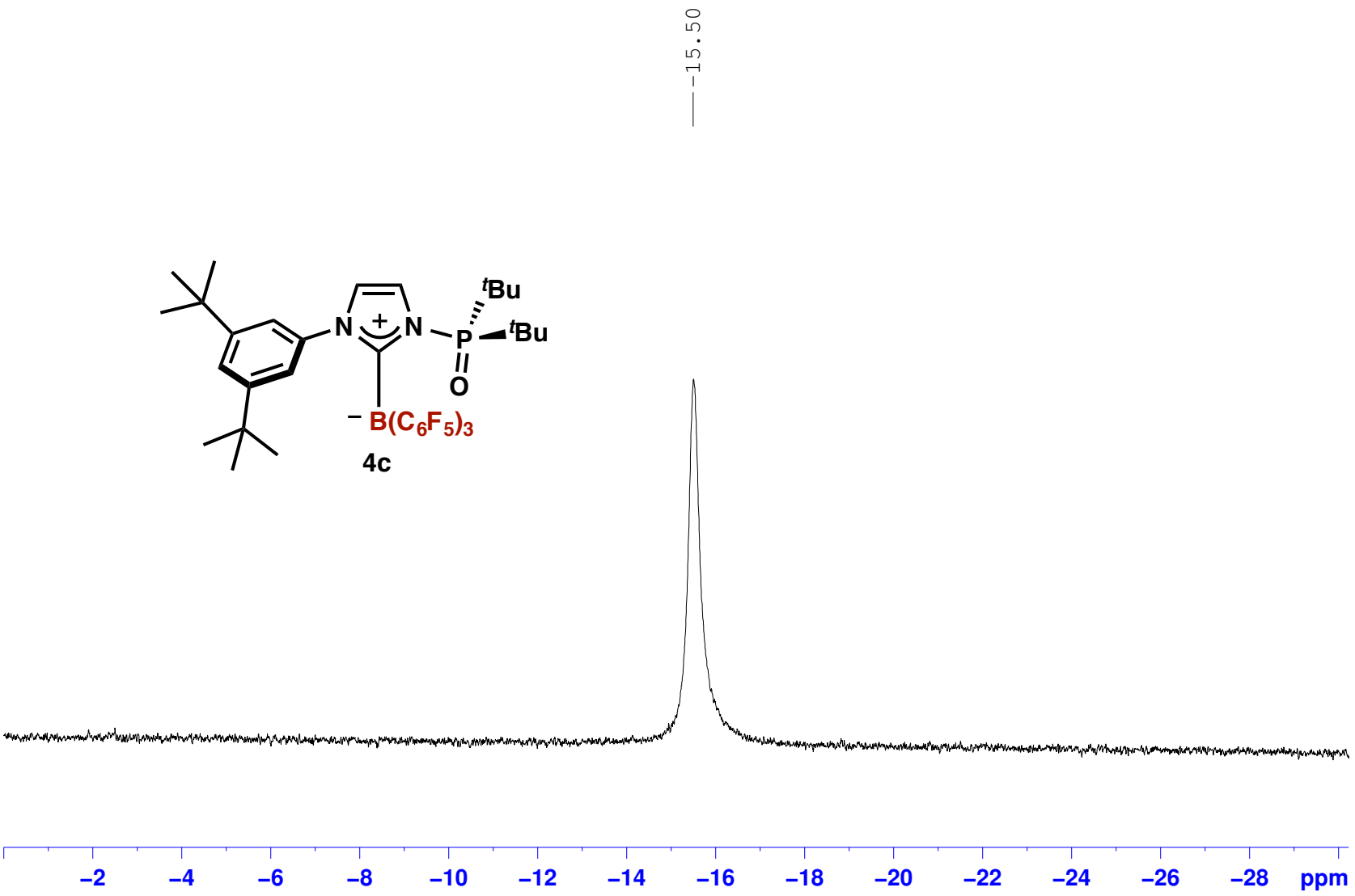
^{19}F NMR


75.56
tBu
tBu
N
N
P
O
− B(C6F5)3
4b
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm

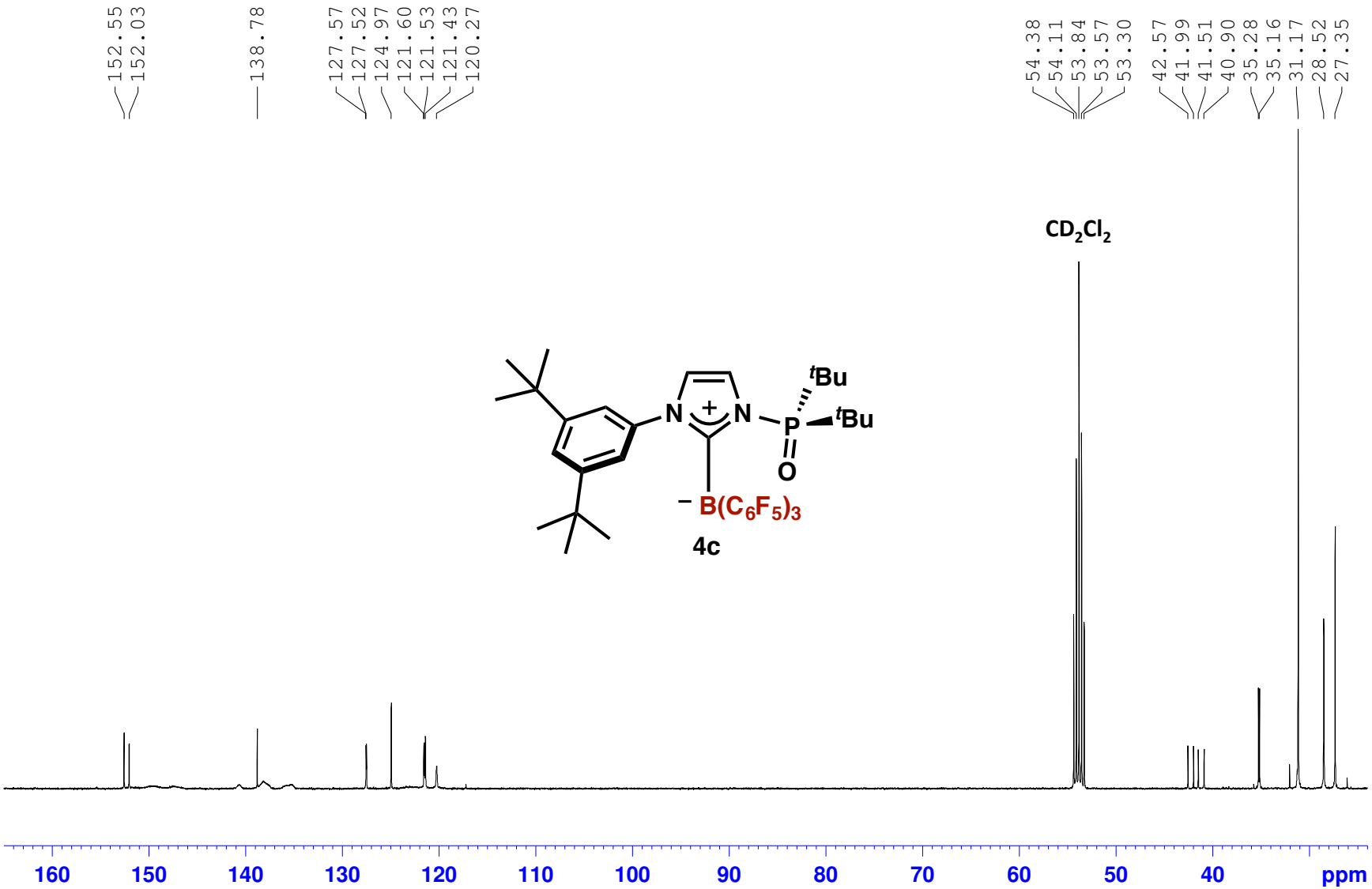
^{31}P NMR


7.443
7.438
7.436
7.430
7.404
7.170
7.168
6.964
5.320
1.520
1.481
1.270
1.190
1.105
1.066
tBu
tBu
N
N
P
O
B(C6F5)3
4c
CD2Cl2
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
0.98
1.99
0.95
9.07
18.82
8.90

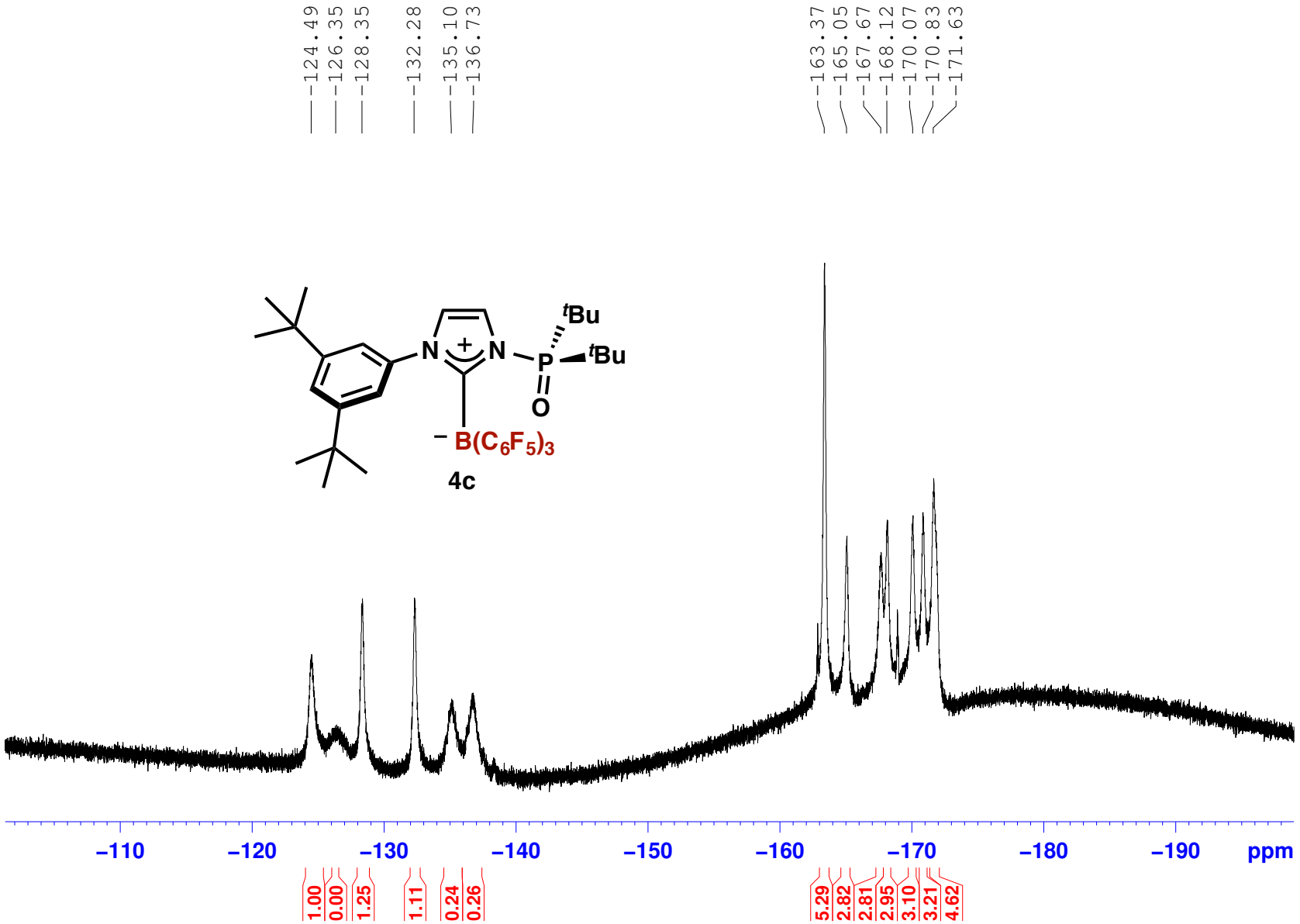
^{1}H NMR



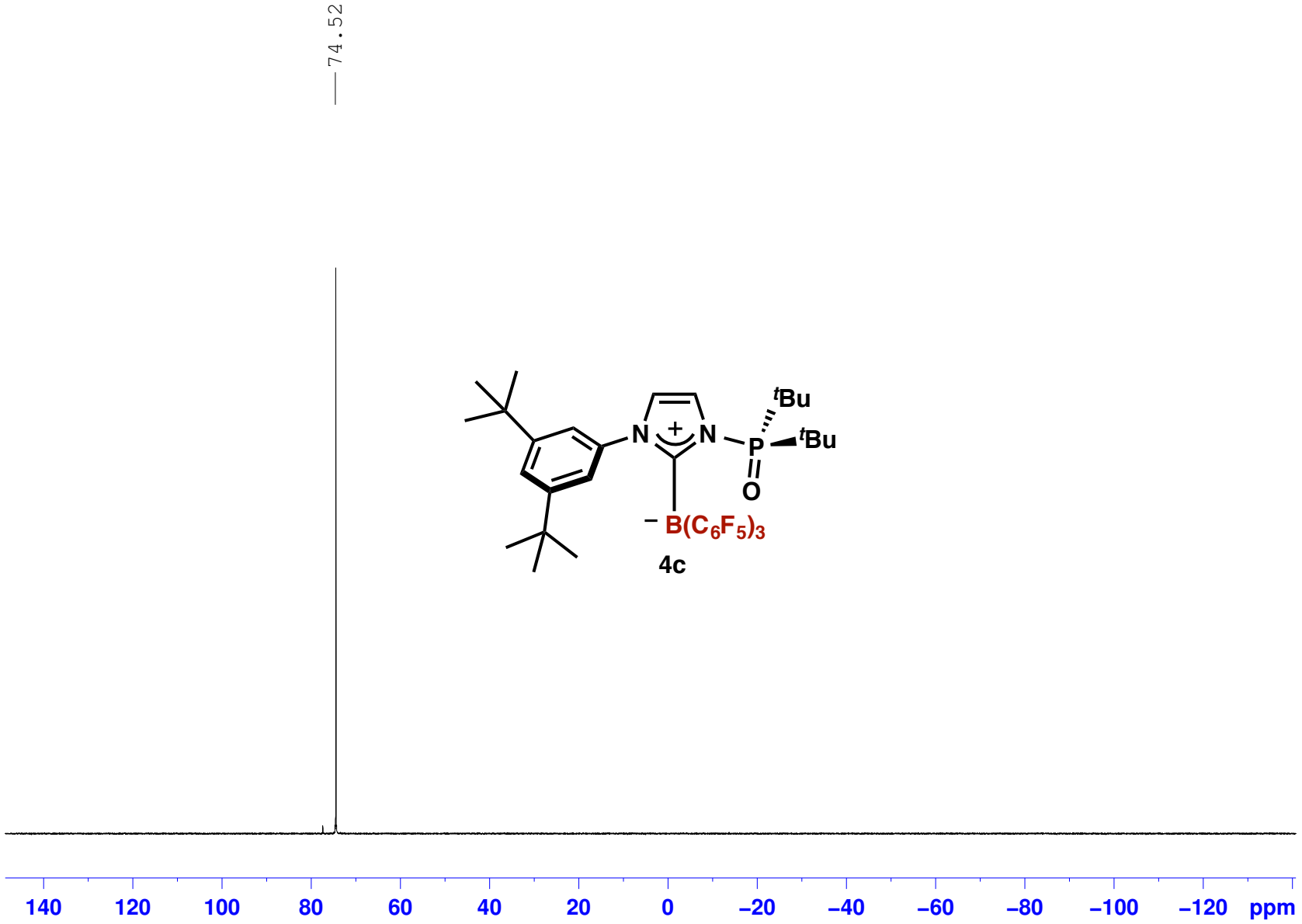
^{11}B NMR


152.55
152.03
138.78
127.57
127.52
124.97
121.60
121.53
121.43
120.27
54.38
54.11
53.84
53.57
53.30
42.57
41.99
41.51
40.90
35.28
35.16
31.17
28.52
27.35
CD2Cl2
tBu
tBu
N
N
P
O
B(C6F5)3
4c
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

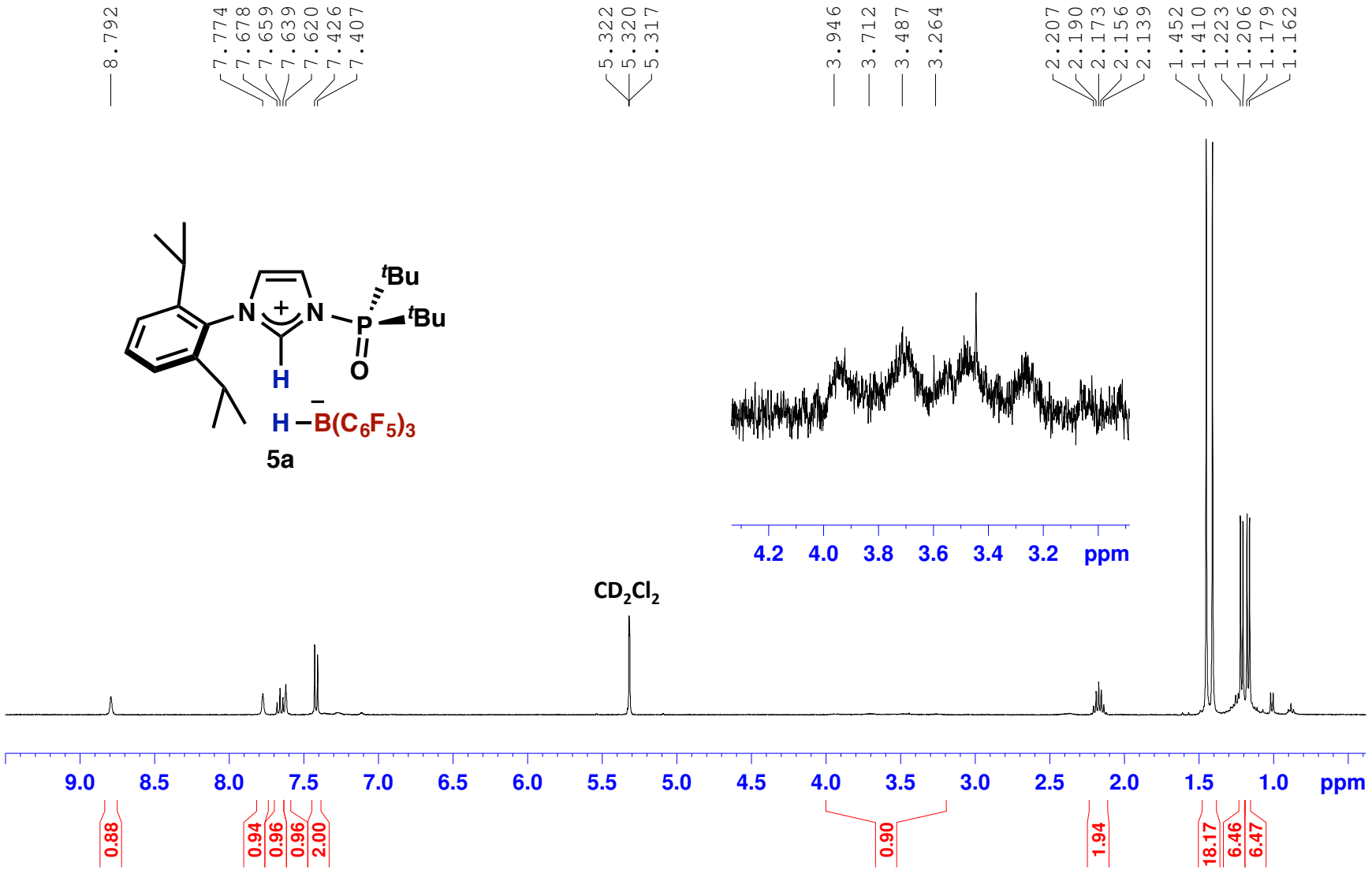
^{13}C NMR


-124.49
-126.35
-128.35
-132.28
-135.10
-136.73
-163.37
-165.05
-167.67
-168.12
-170.07
-170.83
-171.63
tBu
tBu
N
N
P
O
B(C6F5)3
4c
−110
−120
−130
−140
−150
−160
−170
−180
−190
ppm
1.00
0.00
1.25
1.11
0.24
0.26
5.29
2.82
2.81
2.95
3.10
3.21
4.62

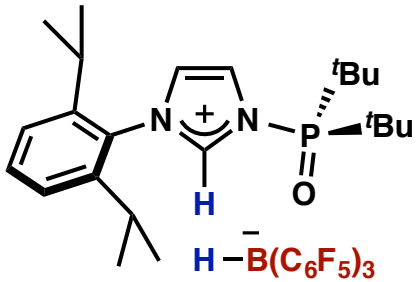
^{19}F NMR


74.52
tBu
tBu
N
N
P
O
B(C6F5)3
4c
140
120
100
80
60
40
20
0
−20
−40
−60
−80
−100
−120
ppm

^{31}P NMR

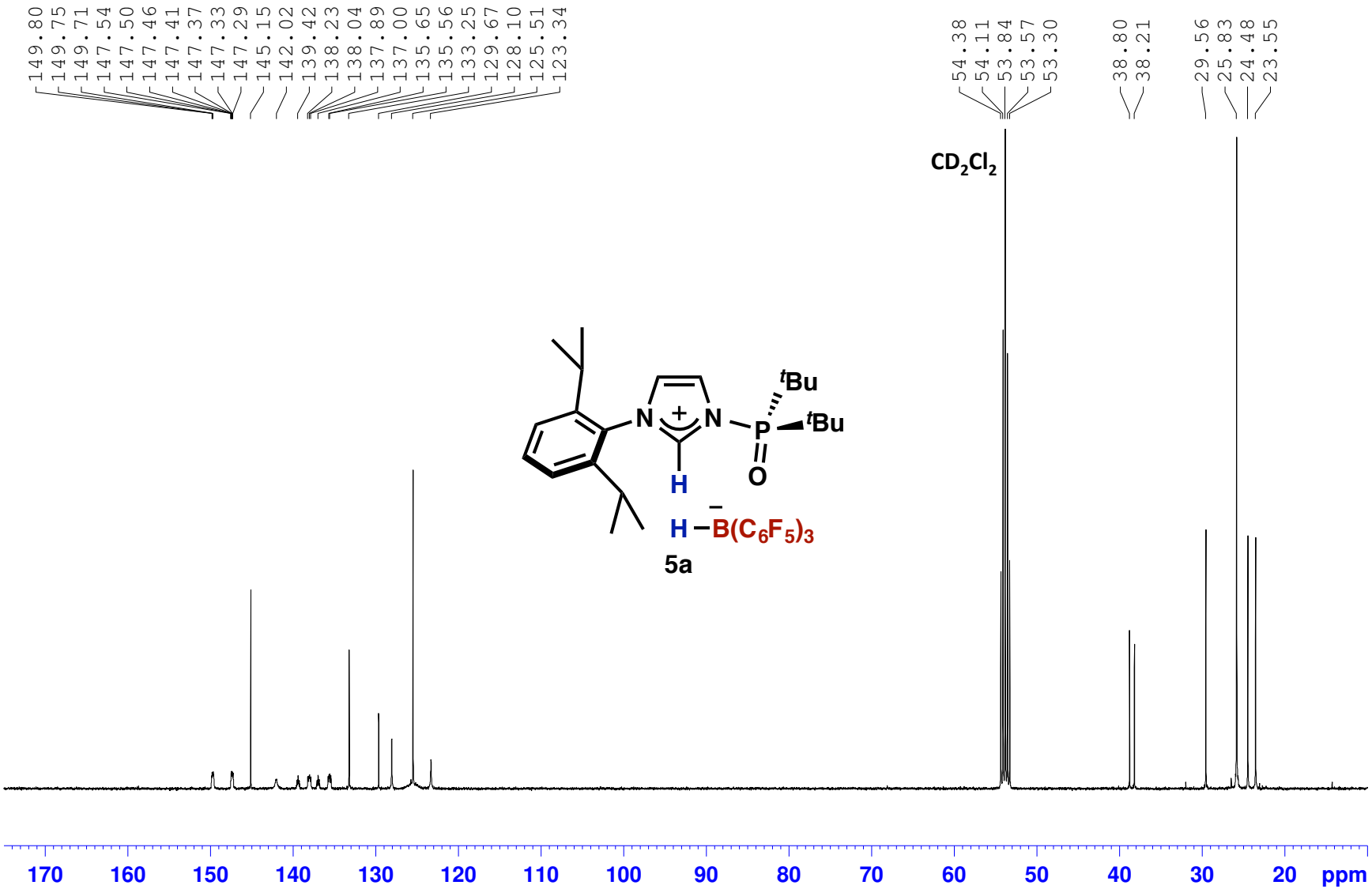

8.792
7.774
7.678
7.659
7.639
7.620
7.426
7.407
5.322
5.320
5.317
3.946
3.712
3.487
3.264
2.207
2.190
2.173
2.156
2.139
1.452
1.410
1.223
1.206
1.179
1.162
tBu
tBu
N
N
P
O
H
H–B(C6F5)3
5a
CD2Cl2
4.2
4.0
3.8
3.6
3.4
3.2
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.88
0.94
0.96
0.96
2.00
0.90
1.94
18.17
6.46
6.47

^{1}H NMR

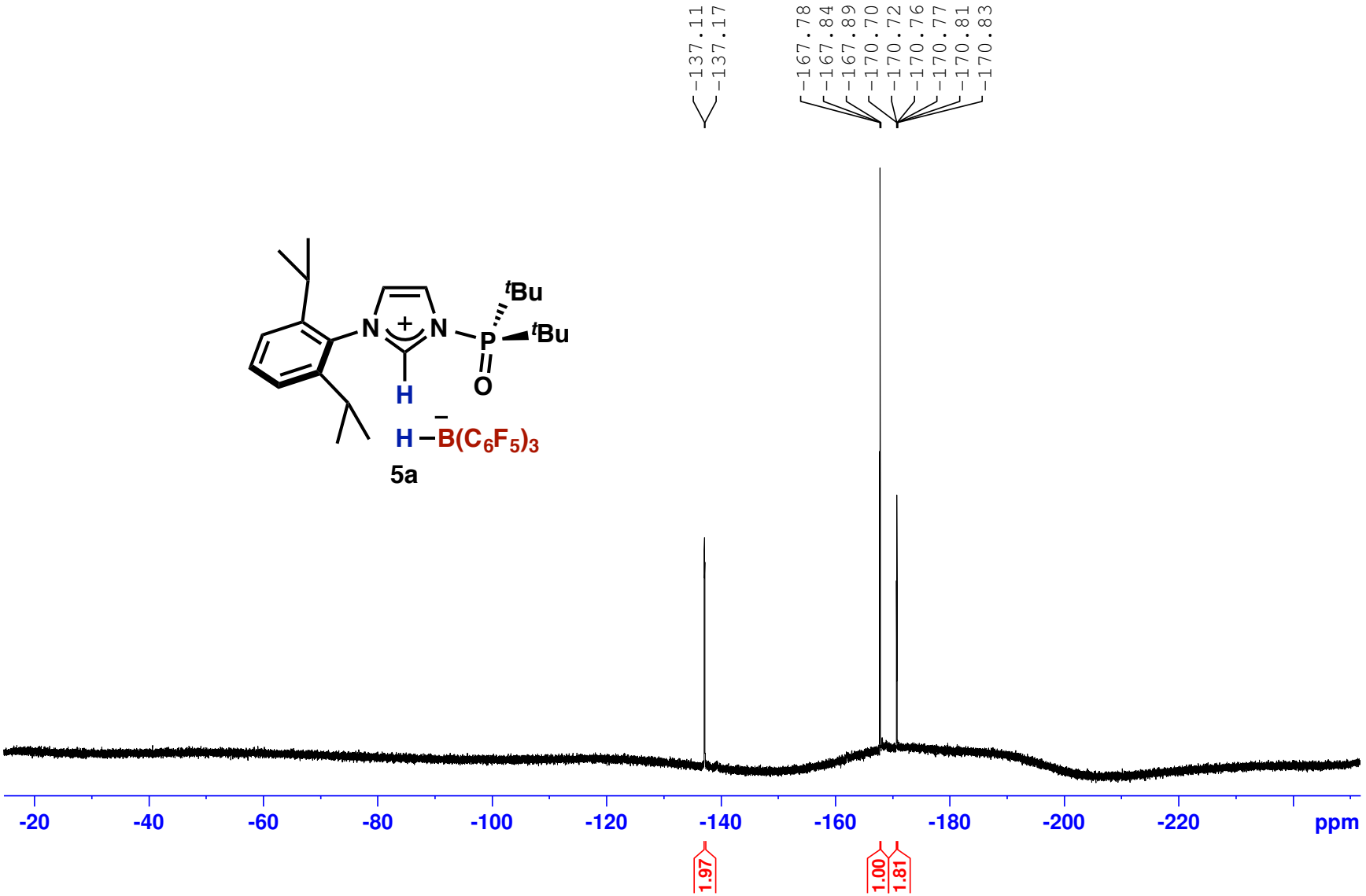


5a

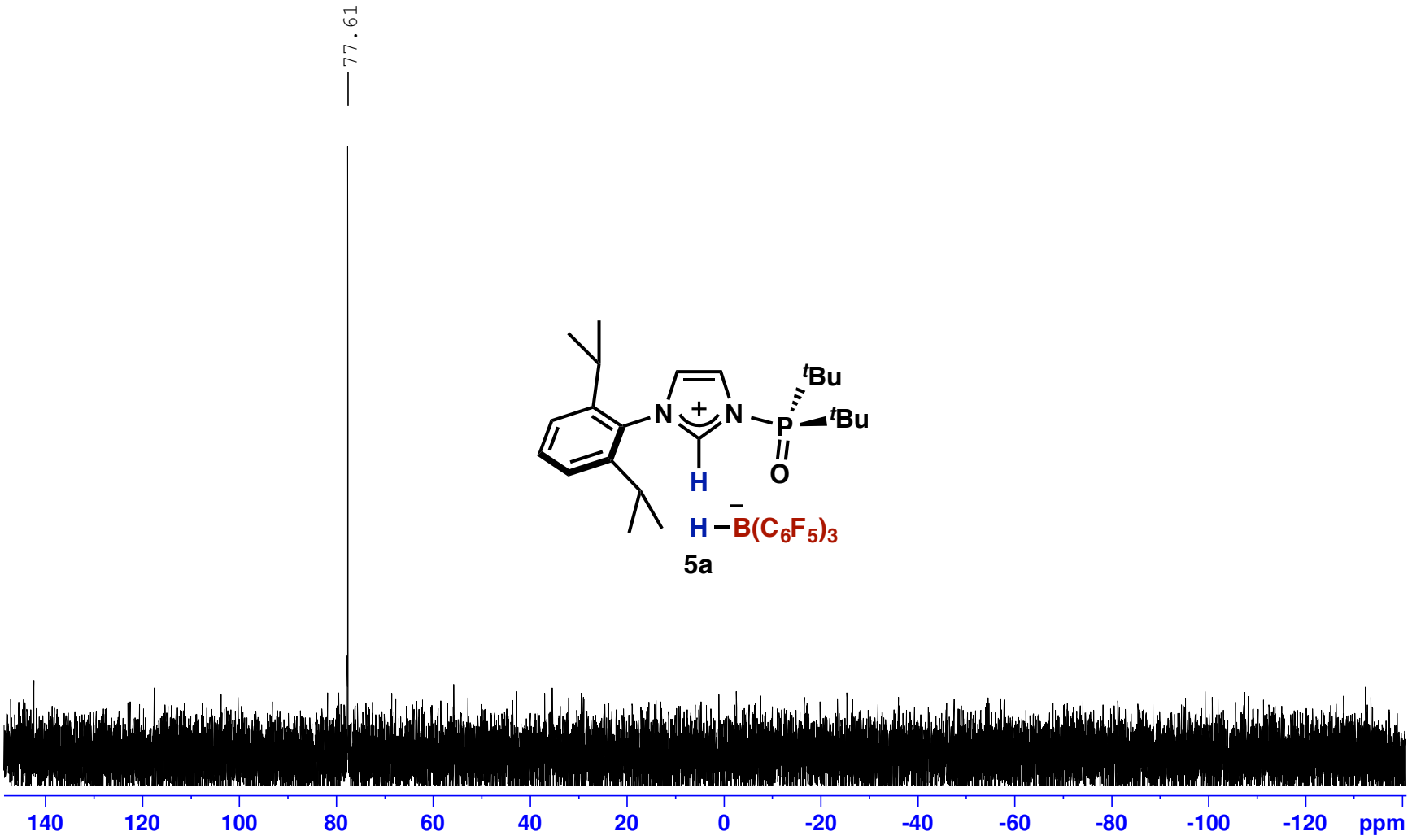
^{11}B NMR


149.80
149.75
149.71
147.54
147.50
147.46
147.41
147.37
147.33
147.29
145.15
142.02
139.42
138.23
138.04
137.89
137.00
135.65
135.56
133.25
129.67
128.10
125.51
123.34
54.38
54.11
53.84
53.57
53.30
38.80
38.21
29.56
25.83
24.48
23.55
CD2Cl2
tBu
tBu
N
N
P
O
H
H –B(C6F5)3
5a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

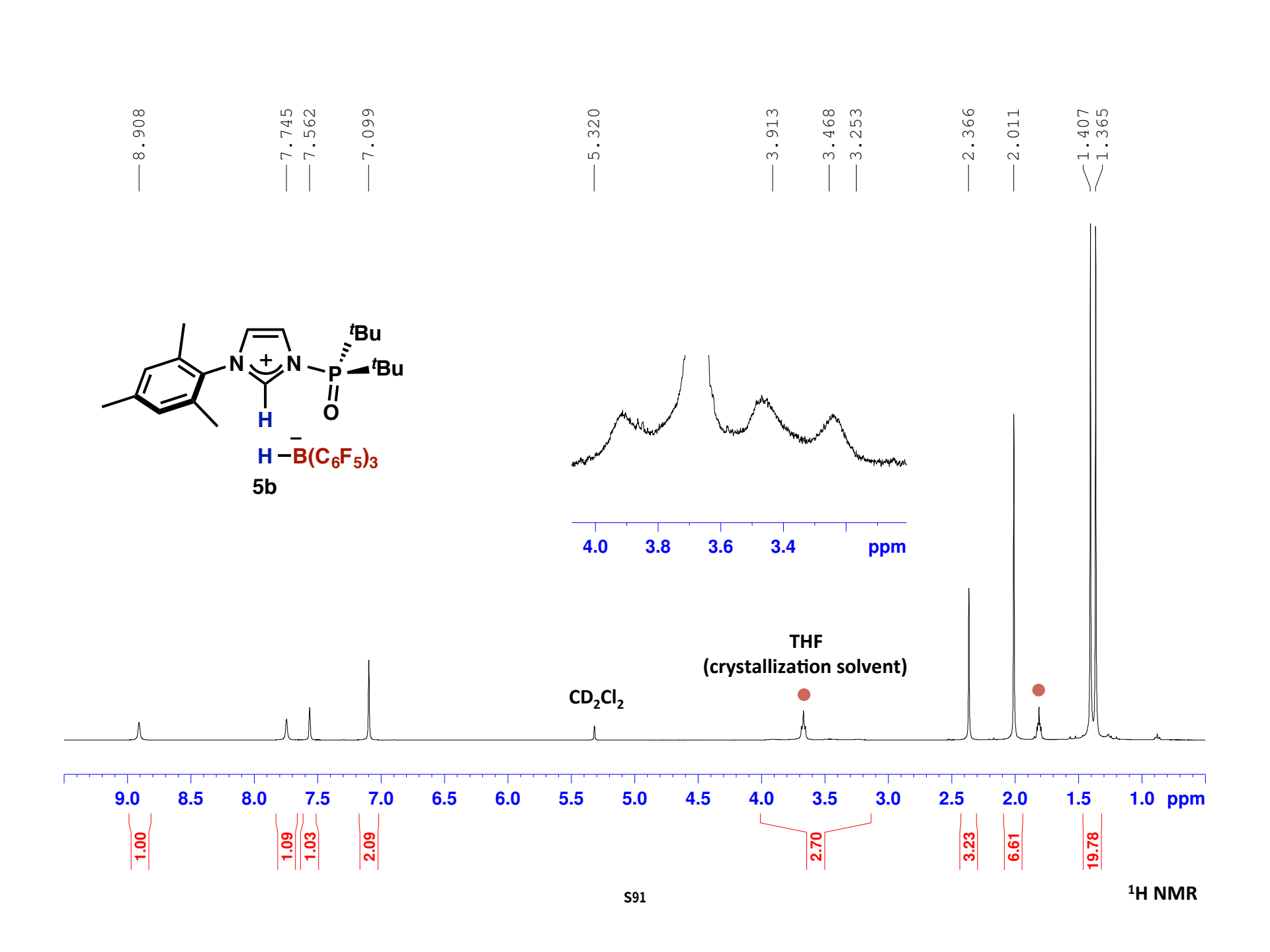
^{13}C NMR


-137.11
-137.17
-167.78
-167.84
-167.89
-170.70
-170.72
-170.76
-170.77
-170.81
-170.83
tBu
tBu
N
N
P
O
H
H –B(C6F5)3
5a
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
ppm
1.97
1.00
1.81

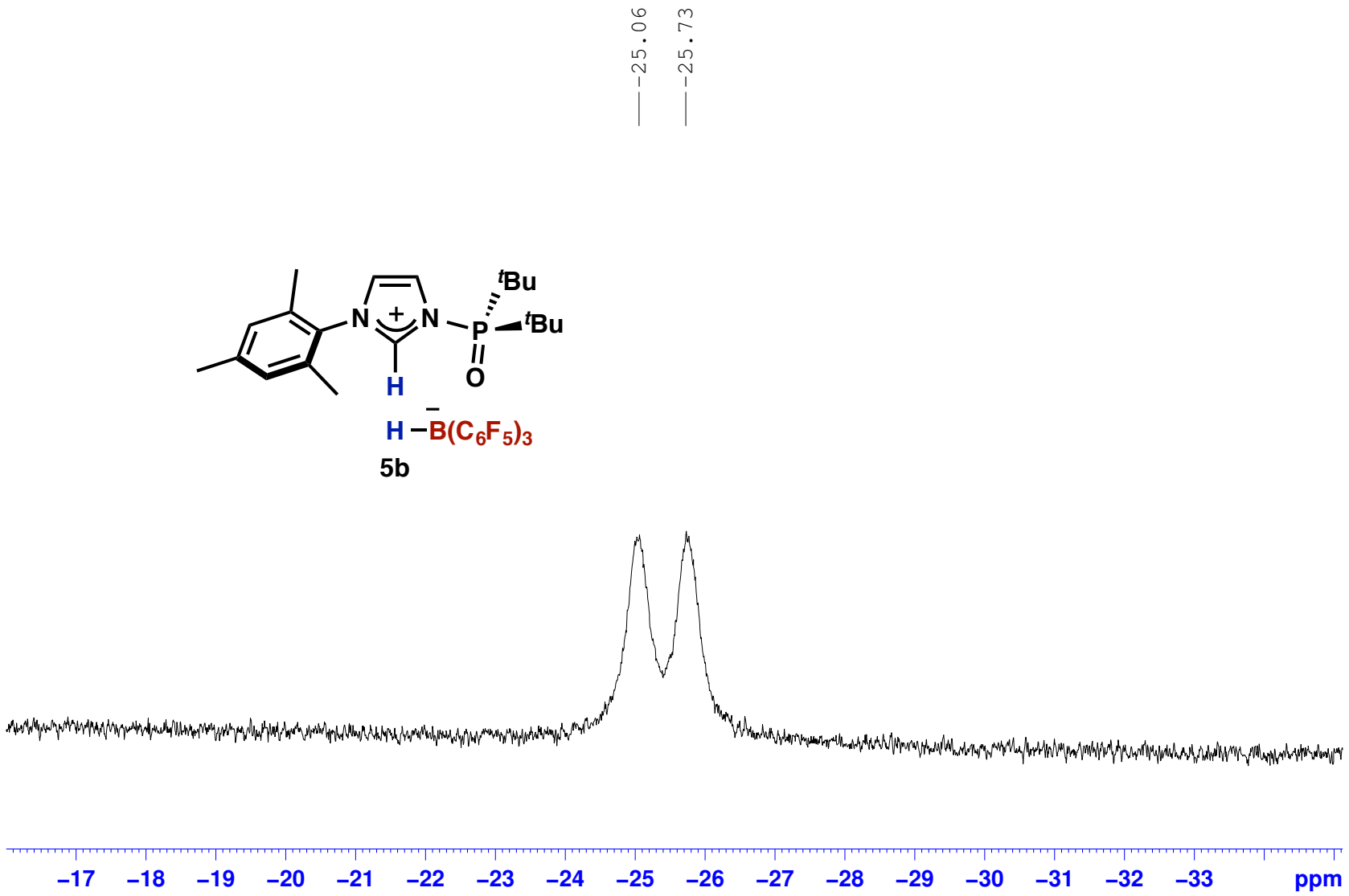
^{19}F NMR


77.61
tBu
tBu
N
N
P
O
H
H –B(C6F5)3
5a
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm

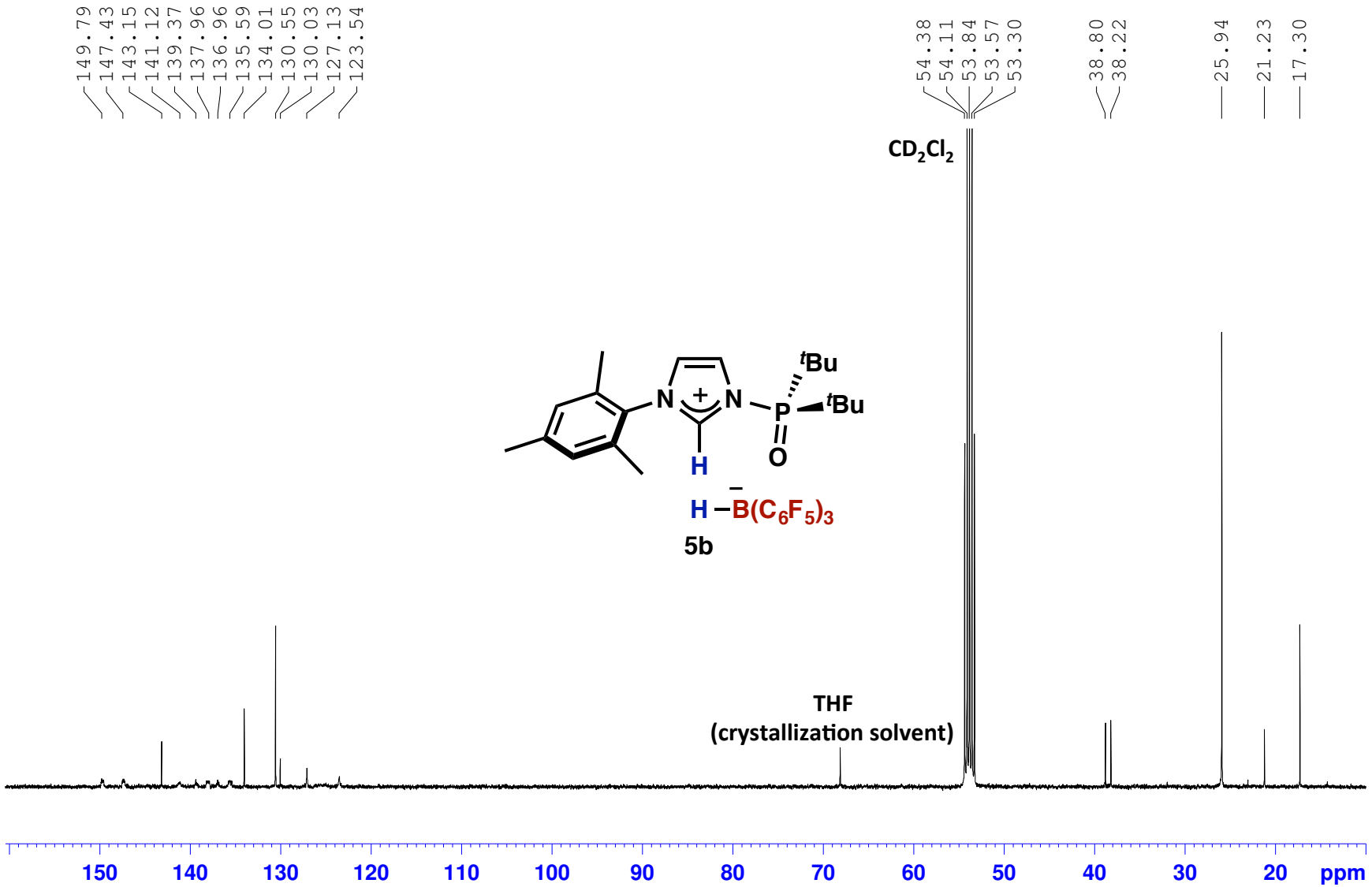
^{31}P NMR


8.908
7.745
7.562
7.099
5.320
3.913
3.468
3.253
2.366
2.011
1.407
1.365
tBu
tBu
N
N
P
O
H
H –B(C6F5)3
5b
4.0
3.8
3.6
3.4
ppm
THF
(crystallization solvent)
CD2Cl2
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.09
1.03
2.09
2.70
3.23
6.61
19.78

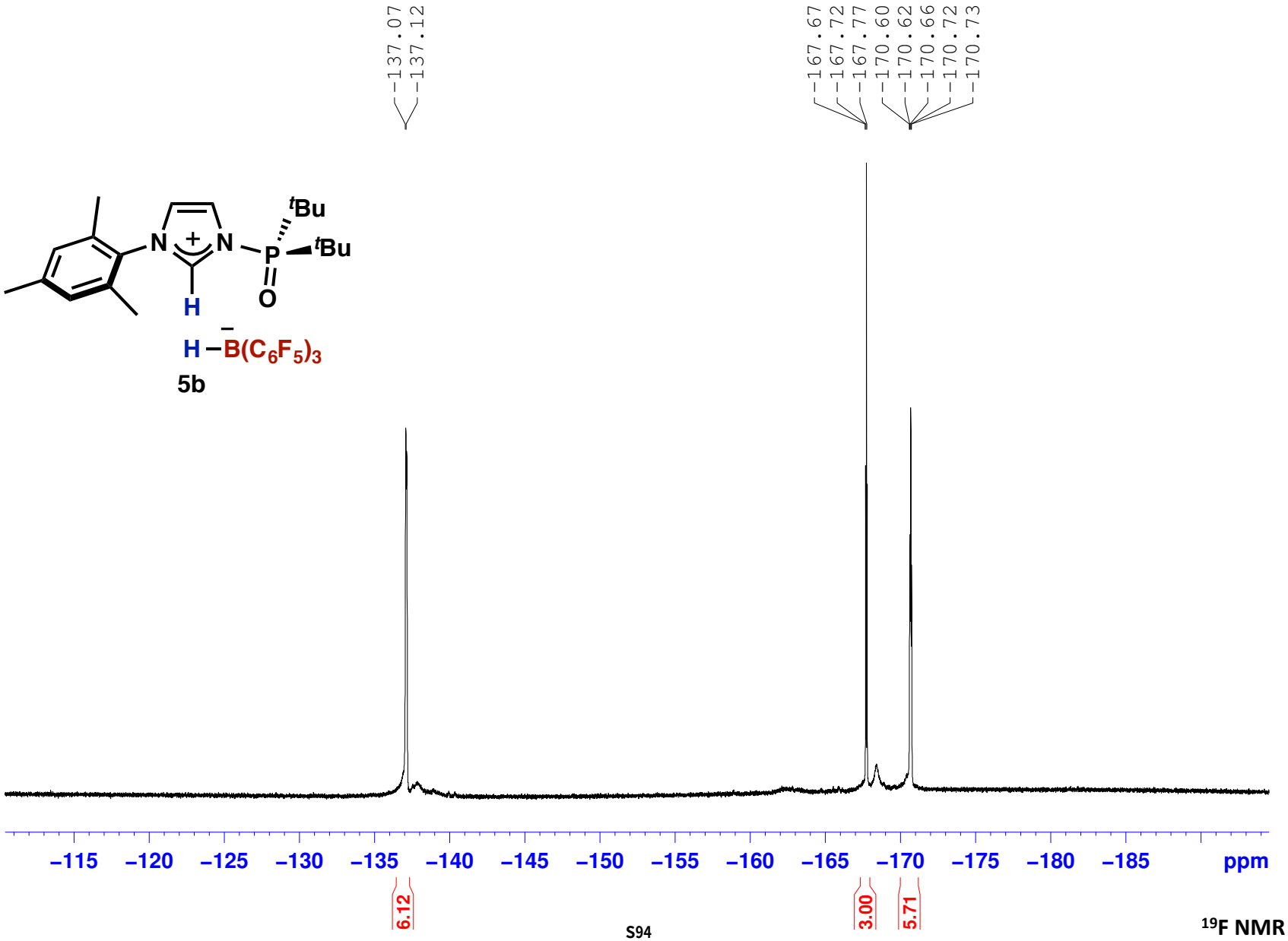
^{1}H NMR


-25.06
-25.73
tBu
tBu
N
N
P
O
H
H –B(C6F5)3
5b
–17
–18
–19
–20
–21
–22
–23
–24
–25
–26
–27
–28
–29
–30
–31
–32
–33
ppm

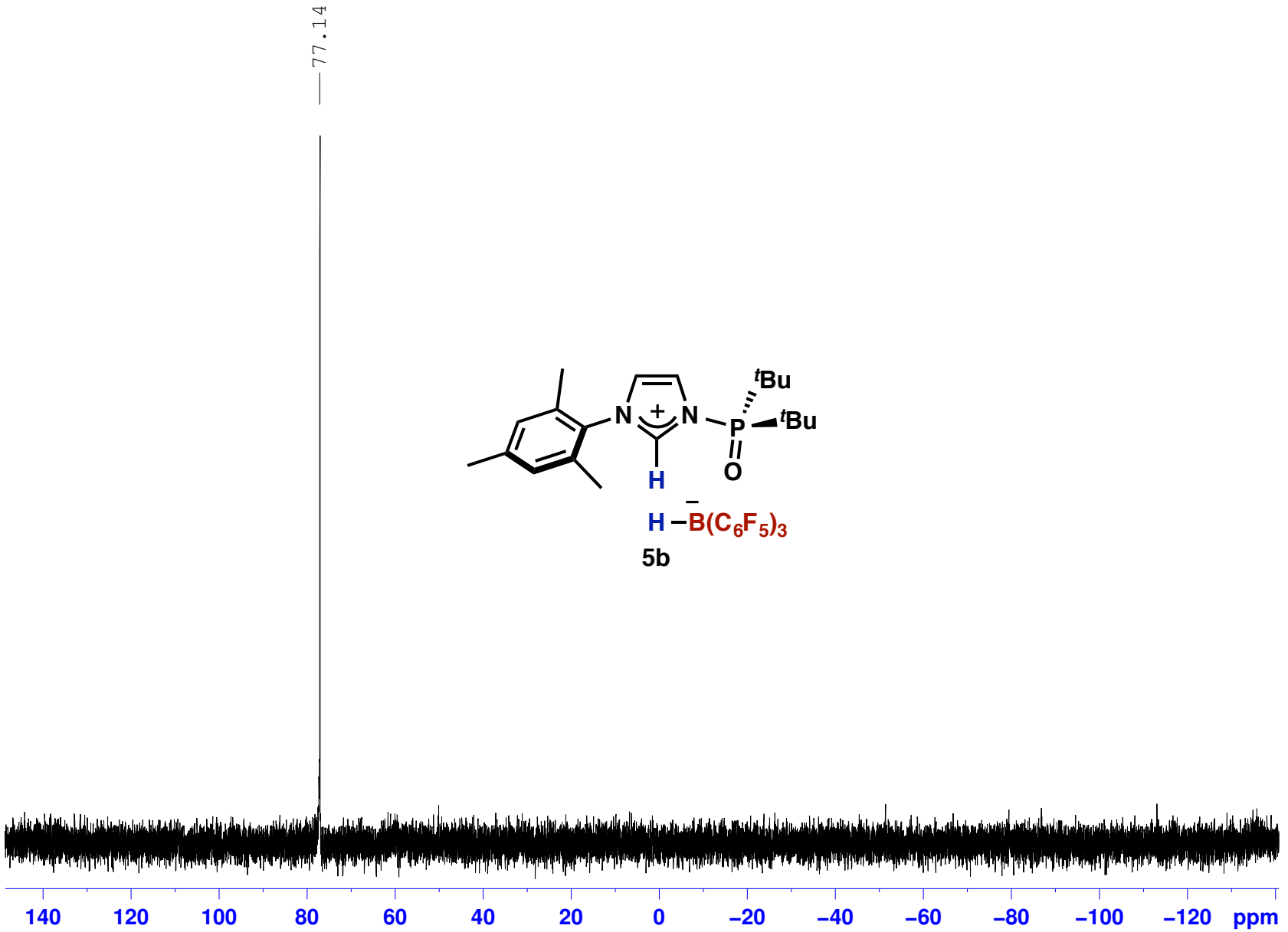
^{11}B NMR

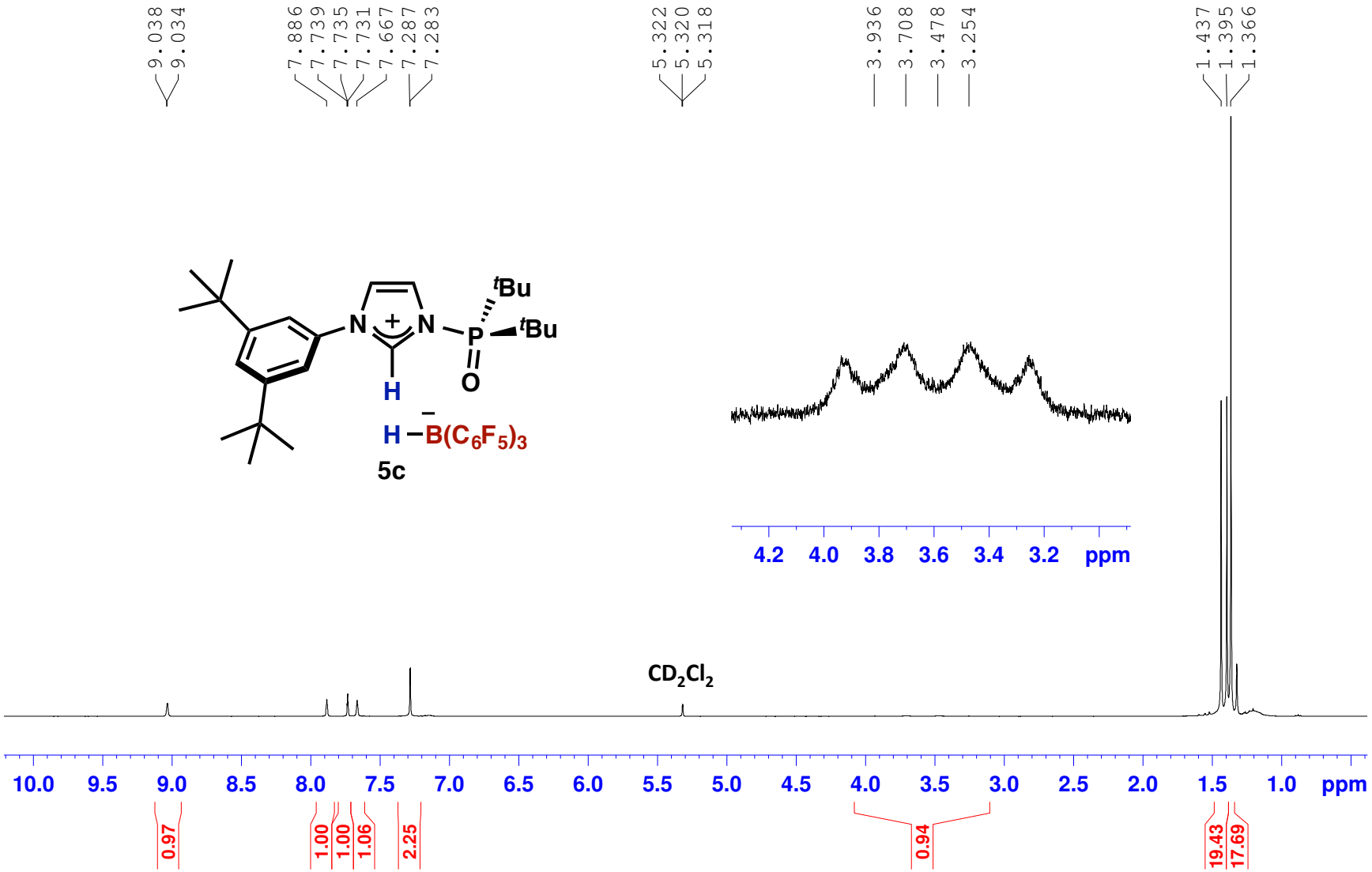

149.79
147.43
143.15
141.12
139.37
137.96
136.96
135.59
134.01
130.55
130.03
127.13
123.54
54.38
54.11
53.84
53.57
53.30
38.80
38.22
25.94
21.23
17.30
CD2Cl2
tBu
tBu
N
N
P
O
H
H –B(C6F5)3
5b
THF
(crystallization solvent)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

^{13}C NMR

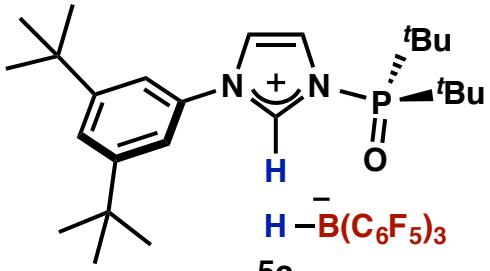

-137.07
-137.12
-167.67
-167.72
-167.77
-170.60
-170.62
-170.66
-170.72
-170.73
tBu
tBu
N
N
P
O
H
H–B(C6F5)3
5b
–115
–120
–125
–130
–135
–140
–145
–150
–155
–160
–165
–170
–175
–180
–185
ppm
6.12
3.00
5.71

^{19}F NMR


77.14
tBu
tBu
N
N
P
O
H
H – B(C6F5)3
5b
140
120
100
80
60
40
20
0
–20
–40
–60
–80
–100
–120
ppm
31P NMR


9.038
9.034
7.886
7.739
7.735
7.731
7.667
7.287
7.283
5.322
5.320
5.318
3.936
3.708
3.478
3.254
1.437
1.395
1.366
tBu
tBu
N
N
P
O
H
H–B(C6F5)3
5c
4.2
4.0
3.8
3.6
3.4
3.2
ppm
CD2Cl2
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.97
1.00
1.00
1.06
2.25
0.94
19.43
17.69

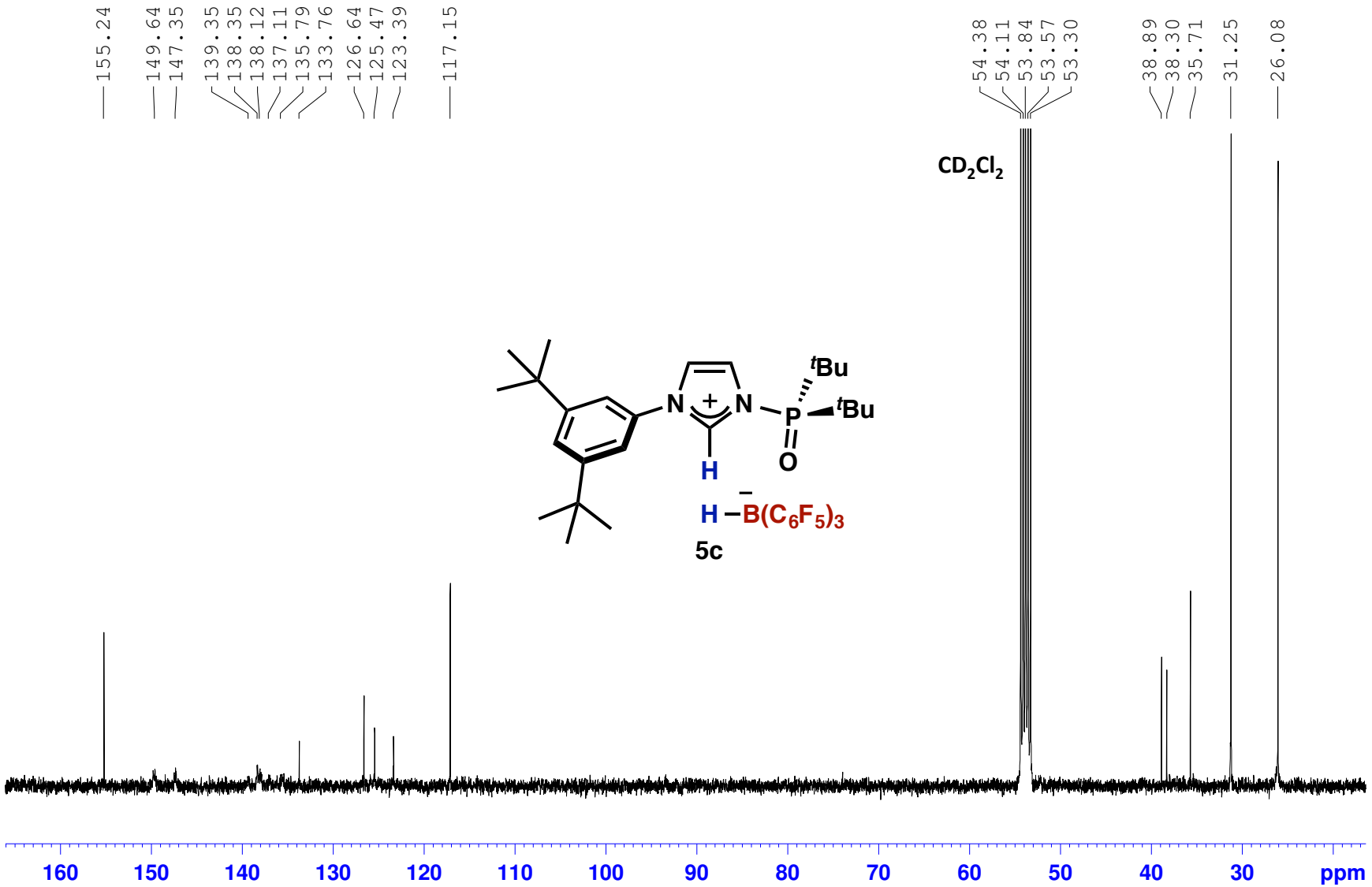
^{1}H NMR


tBu
tBu
N
N
P
O
H
H –B(C6F5)3

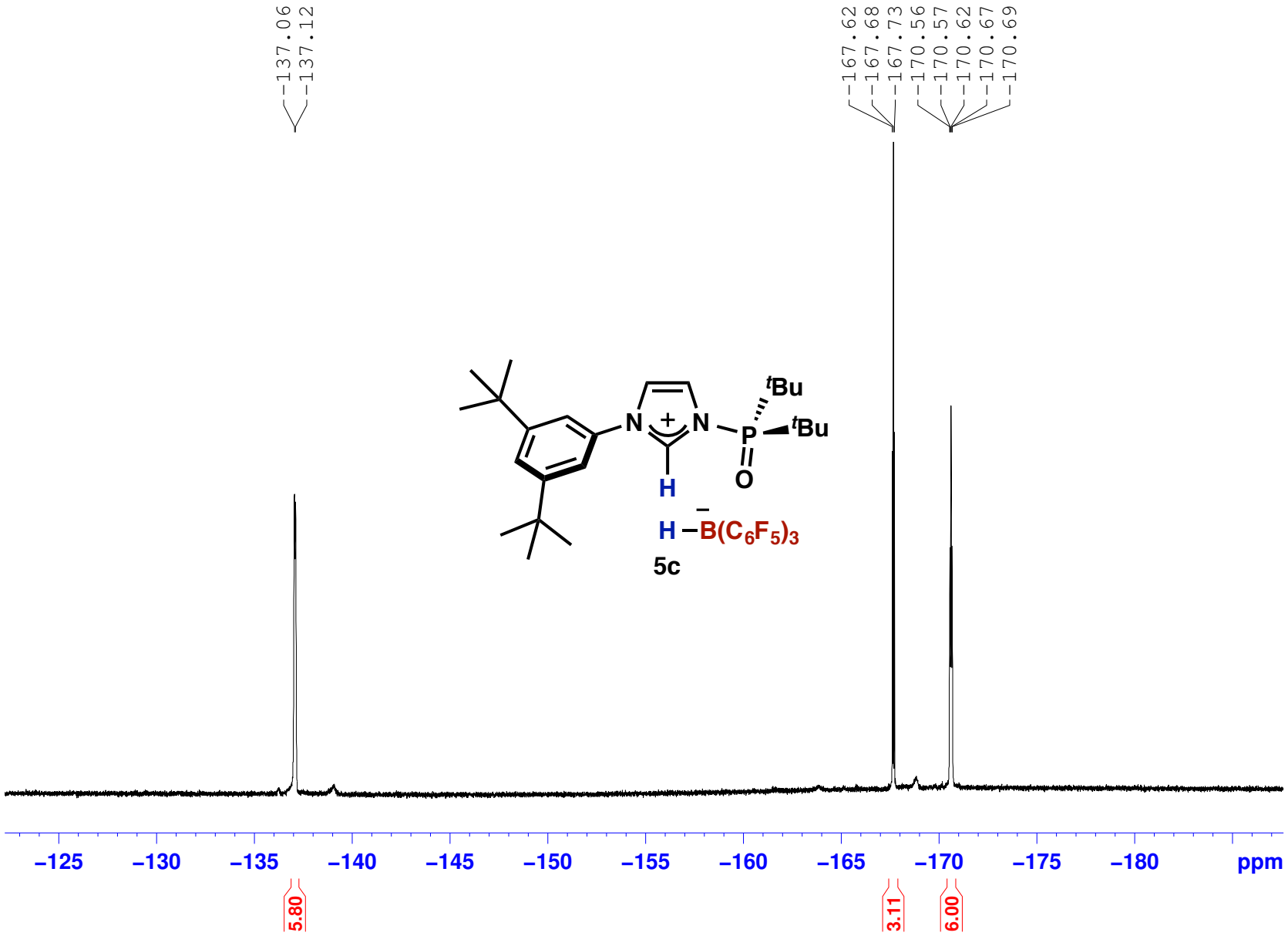
5c

−25.04
−25.75
−15 −16 −17 −18 −19 −20 −21 −22 −23 −24 −25 −26 −27 −28 −29 −30 −31 −32 −33 −34 −35 ppm

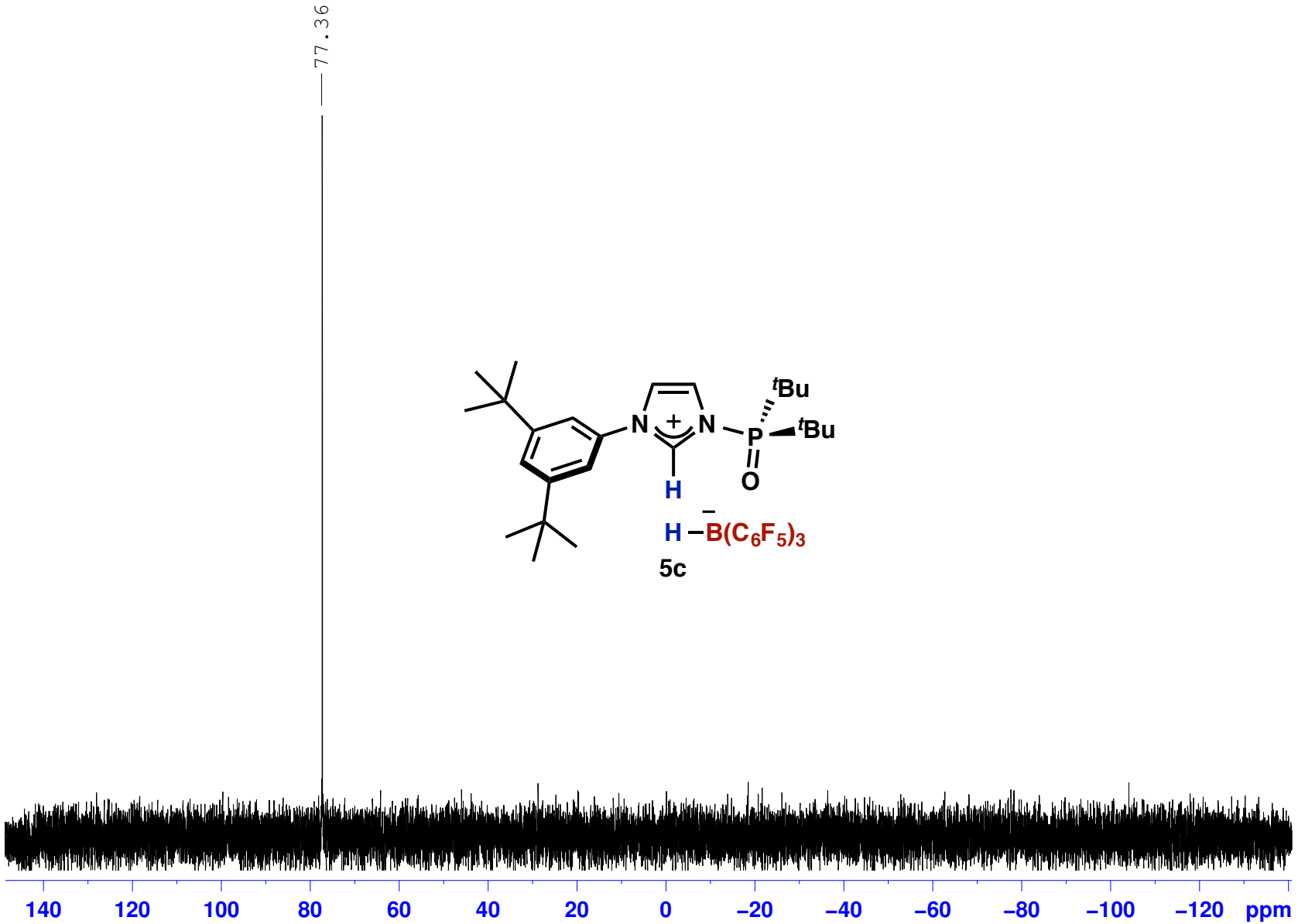
^{11}B NMR


155.24
149.64
147.35
139.35
138.35
138.12
137.11
135.79
133.76
126.64
125.47
123.39
117.15
54.38
54.11
53.84
53.57
53.30
38.89
38.30
35.71
31.25
26.08
CD2Cl2
tBu
tBu
N
N
P
O
H
H –B(C6F5)3
5c
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

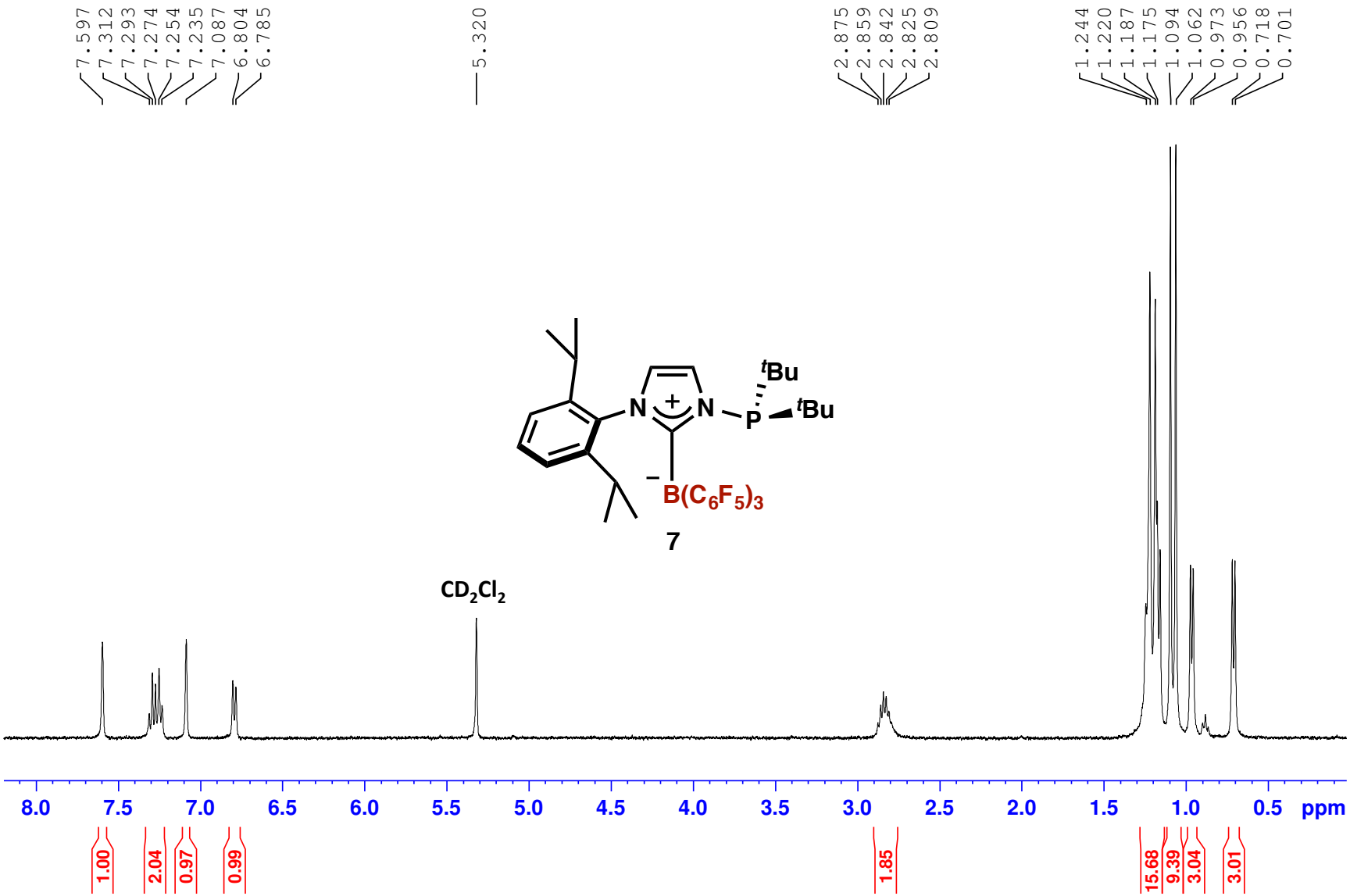
^{13}C NMR


-137.06
-137.12
-167.62
-167.68
-167.73
-170.56
-170.57
-170.62
-170.67
-170.69
tBu
tBu
N
N
P
O
H
H –B(C6F5)3
5c
–125
–130
–135
–140
–145
–150
–155
–160
–165
–170
–175
–180
ppm
5.80
3.11
6.00

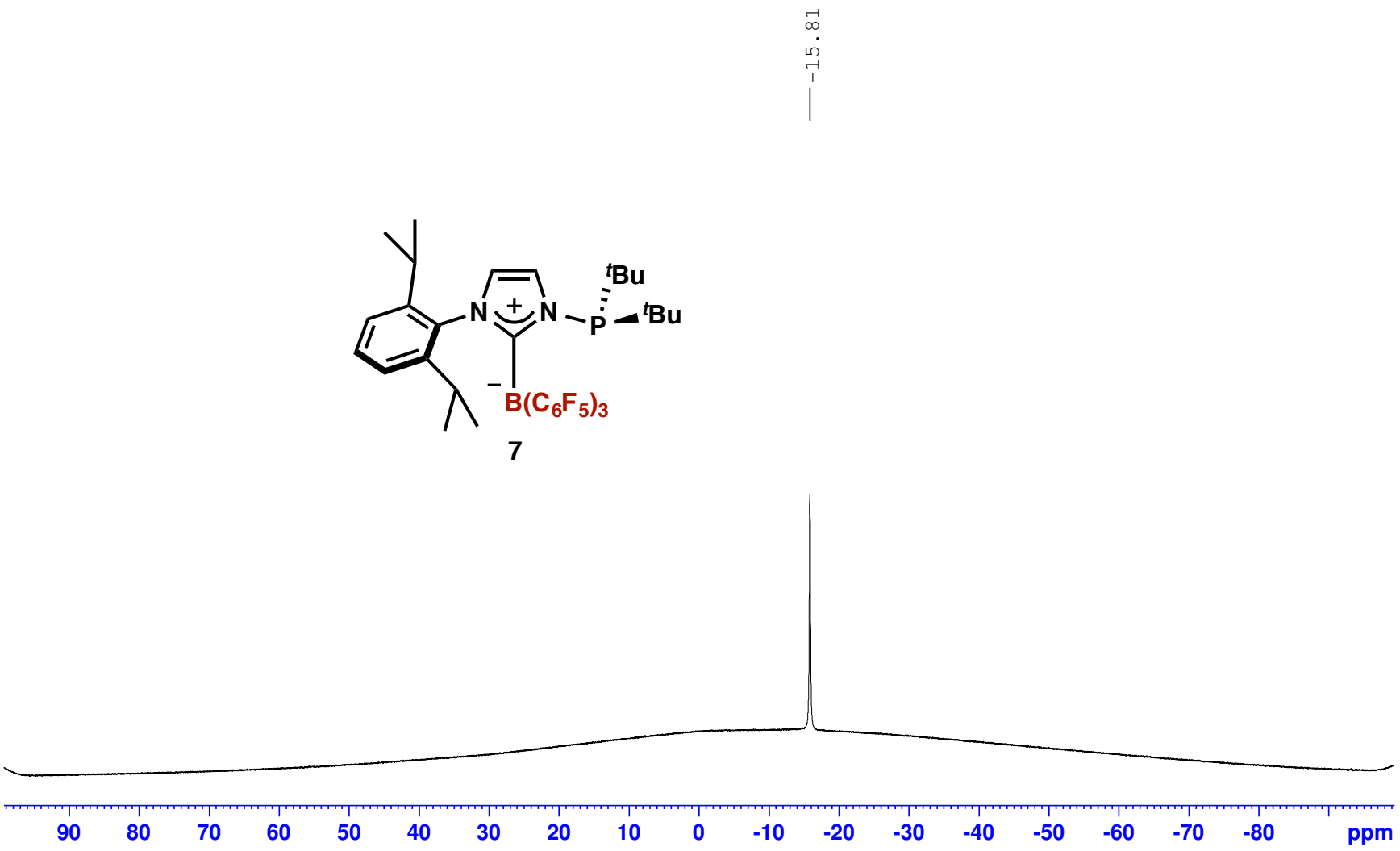
^{19}F NMR


77.36
tBu
tBu
N
N
P
O
H
H –B(C6F5)3
5c
140
120
100
80
60
40
20
0
–20
–40
–60
–80
–100
–120
ppm

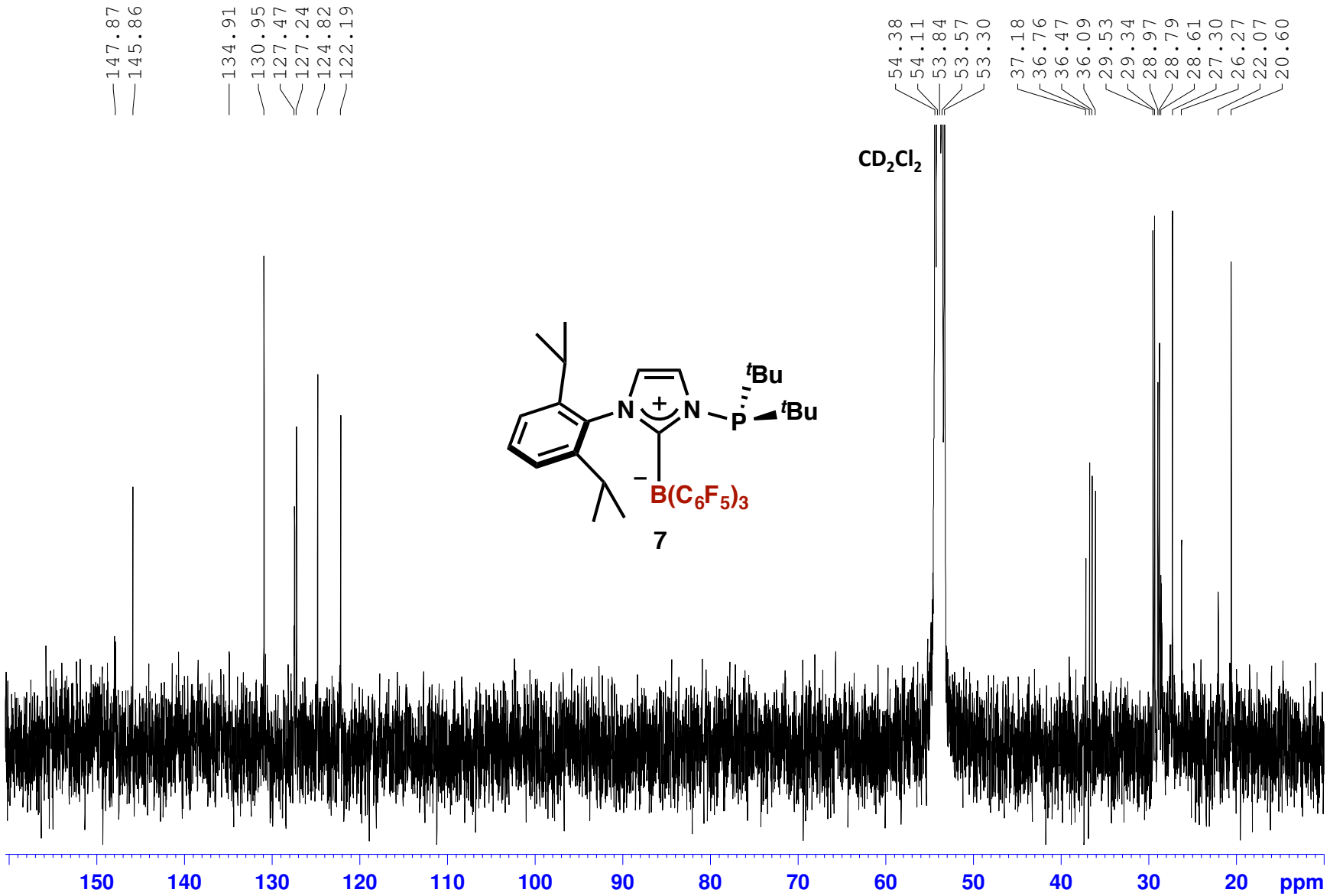
^{31}P NMR

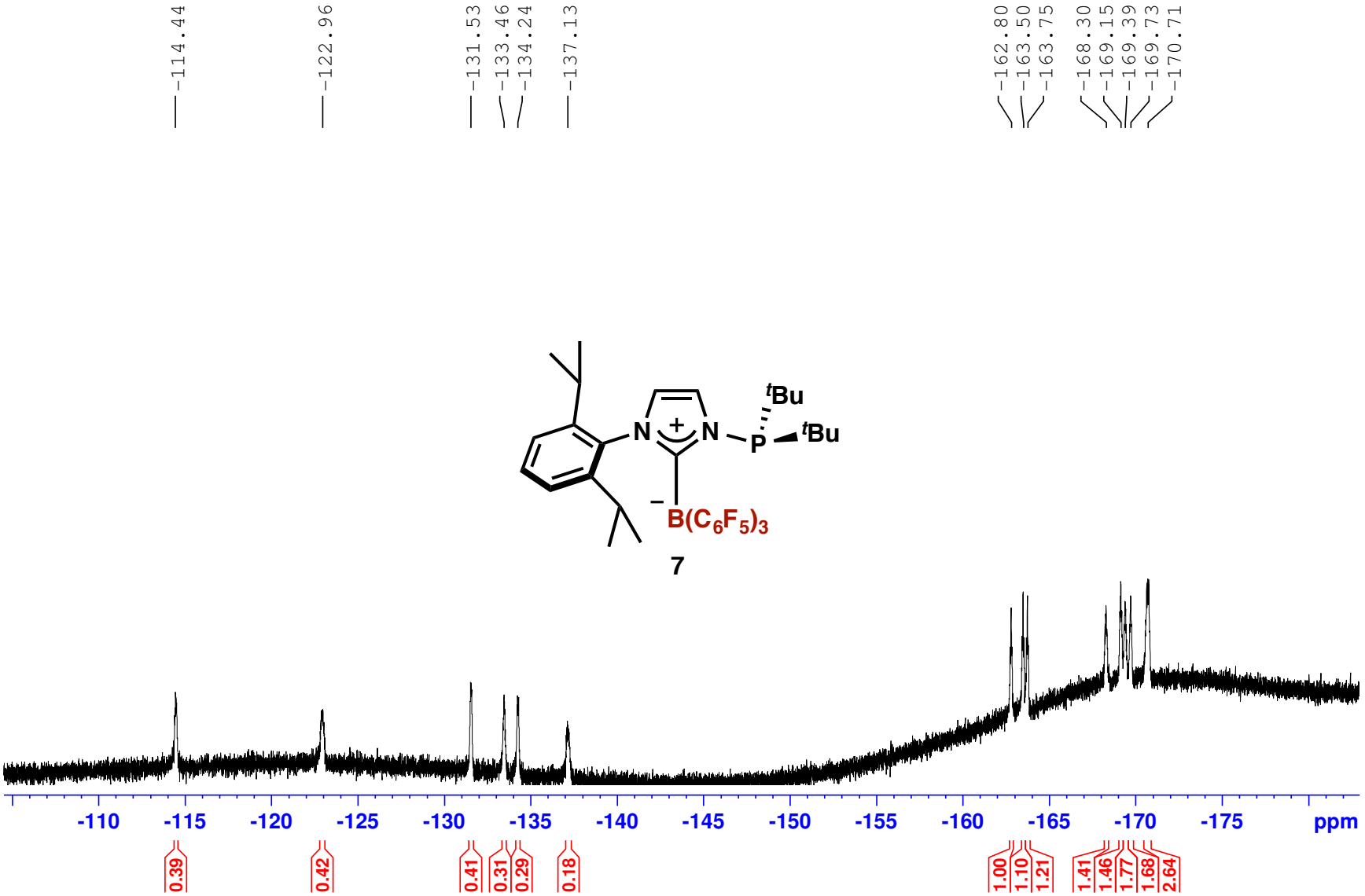

7.597
7.312
7.293
7.274
7.254
7.235
7.087
6.804
6.785
5.320
2.875
2.859
2.842
2.825
2.809
1.244
1.220
1.187
1.175
1.094
1.062
0.973
0.956
0.718
0.701
tBu
tBu
N
N
P
B(C6F5)3
7
CD2Cl2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
2.04
0.97
0.99
1.85
15.68
9.39
3.04
3.01

^{1}H NMR


-15.81
tBu
tBu
N
N
P
B(C6F5)3
7
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
ppm

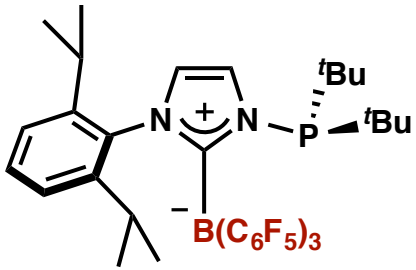
^{11}B NMR


147.87
145.86
134.91
130.95
127.47
127.24
124.82
122.19
54.38
54.11
53.84
53.57
53.30
37.18
36.76
36.47
36.09
29.53
29.34
28.97
28.79
28.61
27.30
26.27
22.07
20.60
CD2Cl2
tBu
tBu
N
N
P
B(C6F5)3
7
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm
13C NMR

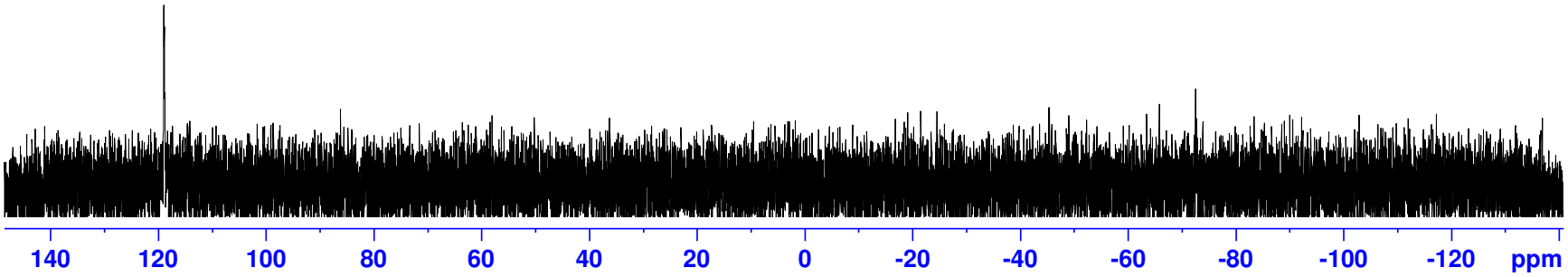

-114.44
-122.96
-131.53
-133.46
-134.24
-137.13
-162.80
-163.50
-163.75
-168.30
-169.15
-169.39
-169.73
-170.71
tBu
tBu
N
N
P
B(C6F5)3
7
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
ppm
0.39
0.42
0.41
0.31
0.29
0.18
1.00
1.10
1.21
1.41
1.46
1.77
1.68
2.64

^{19}F NMR

118.99



7



^{31}P NMR