Supporting Information

Transformation of CO_2 and Isocyanate Mediated by *N*-Borane-Substituted Cyclic Phosphine Imides (BCPIs) *via* λ^5-Oxazaphosphetanes

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[1] General considerations

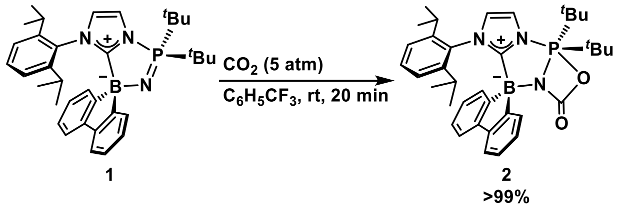
Unless otherwise noted, all manipulations were conducted under a nitrogen atmosphere using standard Schlenk line or grove box (GB) techniques. ^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker AVANCE III 400 or JEOL JNM-ECS400 spectrometers at 25 °C. The chemical shifts in the ^{1}H NMR spectra were recorded relative to Me_4Si or residual protonated solvent ($CDHCl_2$ (δ 5.32), C_6D_5H (δ 7.16)). The chemical shifts in the ^{11}B NMR spectra were recorded relative to $BF_3 \cdot OEt_2$. The chemical shifts in the ^{13}C spectra were recorded relative to Me_4Si or deuterated solvent (CD_2Cl_2 (δ 53.84), C_6D_6 (δ 128.06)). The chemical shifts in the ^{19}F NMR spectra were recorded relative to α,α,α-trifluorotoluene (δ −65.64). The chemical shifts in the ^{31}P NMR spectra were recorded relative to 85% H_3PO_4 as an external standard. Assignment of the resonances in ^{1}H and ^{13}C NMR spectra was based on ^{1}H−^{1}H COSY, HMQC, HSQC, and HMBC experiments. High resolution mass spectrometry (HRMS) and elementary analyses were performed at the Instrumental Analysis Center, Faculty of Engineering, Osaka University; however, for some compounds, these analyses were precluded due to their instability under the measurement conditions. A single-crystal X-ray diffraction analysis was carried out using the Rigaku XtaLAB Synergy equipping with the HyPix-6000HE detector.

For identification of NMR resonances, Dipp-*H*/*C*, B^{f}-*H*/*C*, Im-*H*/*C* and Ts-*H*/*C* are used for the identification of H and C atoms in 2,6-diisopropylphenyl (Dipp), 9-borafluonyl (B^{f}), imidazole (Im) and *p*-toluenesulfonyl (Ts) moieties.

[2] Materials

All commercially available reagents including super-dehydrated solvents (*n*-hexane, THF and CH_2Cl_2), were purchased from Sigma Aldrich, TCI, and Wako Pure Chemical Industries, and used as received. α,α,α-Trifluorotoluene was distilled over CaH_2 prior to use. CD_2Cl_2 was degassed by several freeze-pump-thaw cycles and stored inside GB over molecular sieves (4 Å). Molecular sieves (4 Å) were activated by heating *in vacuo* (ca. 0.2 mmHg) for 3 days. *N*-Borane-substituted cyclic phosphine imide **1**[S1] and $HB(C_6F_5)_2$[S2] were prepared *via* the previously reported procedures. Metrical data for the solid-state structures are available from Cambridge Crystallographic Data Centre: CCDC 2240798 (**2**), 2240797 ((**4**)$_2$), 2240796 (**5**), 2378677 (**6a**), 2378678 (**6b**), 2378679 (**8b**).

[3] Synthesis of 2



A solution of **1** (220.2 mg, 0.40 mmol) in α,α,α-trifluorotoluene (25 mL) was transferred into the autoclave reactor, and then, CO_2 (5 atm) was pressurized followed by stirring at room temperature for 20 min. After all volatiles were removed *in vacuo,* to afford **2** as a white solid (235.0 mg, 0.40 mmol, >99%). A single crystal suitable for X-ray diffraction analysis was prepared by recrystallization from CH_2Cl_2/*n*-hexane at −30 °C (Figure S1). **^{1}H NMR** (400 MHz, CD_2Cl_2, −50 °C): δ 7.45 (s, 1H, Im-*H*), 7.29 (d, 2H, $J_{H,H}$ = 6.9 Hz, B^f-*H*), 7.26 (d, 2H, $J_{H,H}$ = 6.0 Hz, B^f-*H*), 7.10 (t, 1H, $J_{H,H}$ = 6.9 Hz, *p*-Dipp-*H*), 7.02-6.97 (m, 5H, B^f-*H* and Im-*H*), 6.78 (d, 2H, $J_{H,H}$ = 6.9 Hz, *m*-Dipp-*H*), 2.11 (brs, 2H, C*H*(CH$_3$)$_2$), 1.62 (d, 18H, $^3J_{H,P}$ = 19.2 Hz, C(C*H*$_3$)$_3$), 0.83 (d, 6H, $J_{H,H}$ = 5.0 Hz, CH(C*H*$_3$)$_2$), 0.56 (d, 6H, $J_{H,H}$ = 4.1 Hz, CH(C*H*$_3$)$_2$). **^{13}C {^{1}H} NMR** (100 MHz, CD_2Cl_2, −50 °C): δ 172.5 (brs, Im-*C*), 154.6 (s, *C*=O), 151.2 (brs, B^f-*C*), 149.4 (s, B^f-*C*), 145.0 (s, *o*-Dipp-*C*), 131.8 (s, *ipso*-Dipp-*C*), 130.7 (s, B^f-*C*), 129.9 (s, *p*-Dipp-*C*), 126.2 (s, B^f-*C*), 126.0 (s, Im-*C*), 124.0 (s, Im-*C*), 122.8 (s, *m*-Dipp-*C*), 118.4 (s, B^f-*C*), 41.9 (d, $^1J_{C,P}$ = 86.0 Hz, *C*(CH$_3$)$_2$), 29.1 (s, C(*C*H$_3$)$_3$), 28.2 (s, *C*H(CH$_3$)$_2$), 26.2 (s, CH(*C*H$_3$)$_2$), 21.5 (s, CH(*C*H$_3$)$_2$). **^{31}P {^{1}H} NMR** (162 MHz, CD_2Cl_2, −50 °C): δ −18.5 (s). **^{11}B NMR** (128 MHz, CD_2Cl_2, −50 °C): δ −10.3 (s). **Crystal Data** for $C_{36}H_{45}BN_3O_2P \bullet CH_2Cl_2$ (M = 678.45 g/mol): monoclinic, space group $P2_1/c$ (#14), a = 12.6693(3) Å, b = 19.5252(3) Å, c = 16.0002(4) Å, α = 90°, β = 107.512(2)°, γ = 90°, V = 3774.54(15) Å^3, Z = 4, T = 173.15 K, μ(Cu Kα) = 2.213 mm^{-1}, *Dcalc* = 1.194 g/cm^3, 28175 reflections measured ($7.352° \leq 2\theta \leq 136.492°$), 6898 unique ($R_{int}$ = 0.0558, R_{sigma} = 0.0441) which were used in all calculations. The final R_1 was 0.0716 ($I \geq 2\sigma(I)$) and wR_2 was 0.1998 (all data).

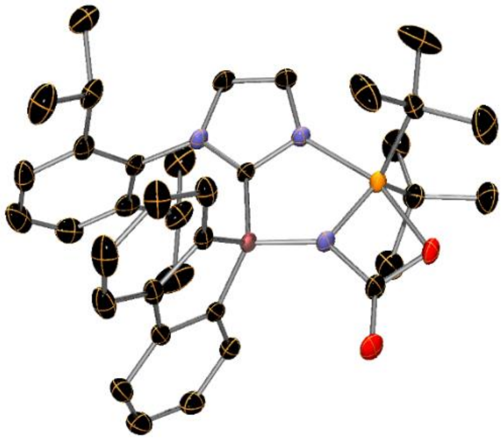
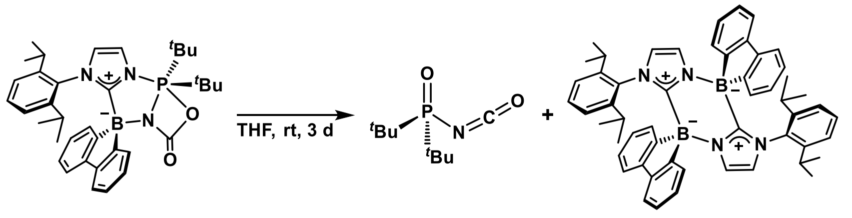


Figure S1. Molecular structure of **2** with ellipsoids set at 30% probability; H atoms and solvated CH_2Cl_2 are omitted for clarity.

[4] Conversion of 2 to 3 and (4)$_2$



2

3 **69%**

(4)$_2$ **47%**

Compound **2** (190.2 mg, 0.32 mmol) was dissolved in THF (10 mL), and the reaction mixture was allowed to stand at room temperature for 3 days. The precipitation of crystals of **(4)$_2$** was confirmed from this solution (a single crystal of **(4)$_2$** was independently prepared by following this method; Figure S2). The supernatant was then removed and all volatiles were removed *in vacuo*. The resultant solid was washed with *n*-hexane followed by removal of all volatiles *in vacuo* to afford **(4)$_2$** as a white solid (114.2 mg, 0.15 mmol, 47% based on the loading amount of **2**). On the other hand, removal of all volatiles from the supernatant *in vacuo*. Subsequently, the residue was extracted with *n*-hexane to afford **3** as a colorless oil (44.5 mg, 0.22 mmol, 69%).

Identification of **3**: **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 1.29 (d, 18H, $^3J_{H,P}$ = 15.8 Hz, $C(CH_3)_3$). **^{13}C {^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 127.1 (s, N=*C*=O), 37.5 (d, $^1J_{C,P}$ = 77.9 Hz, $C(CH_3)_3$), 26.3 (d, $^2J_{C,P}$ = 4.8 Hz, $C(CH_3)_3$). **^{31}P {^{1}H} NMR** (162 MHz, CD_2Cl_2): δ60.0 (s). **HRMS** (CI$^+$): m/z Calcd for $C_9H_{19}NO_2P$: ([M+H]$^+$) 204.1148, found 204.1156.

Identification of **(4)$_2$**: **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.40 (d, 2H, $J_{H,H}$ = 6.2 Hz, B^f-*H*), 7.37 (d, 2H, $J_{H,H}$ = 6.2 Hz, B^f-*H*), 7.11 (t, 4H, $J_{H,H}$ = 3.2 Hz, B^f-*H*), 7.05 (t, 1H, $J_{H,H}$ = 7.9 Hz, *p*-Dipp-*H*), 6.77 (d, 2H, $J_{H,H}$ = 7.7 Hz, *m*-Dipp-*H*), 6.63 (s, 1H, Im-*H*), 6.13 (s, 1H, Im-*H*), 2.24 (sept, 2H, $J_{H,H}$ = 6.6 Hz, $CH(CH_3)_2$), 0.74 (d, 12H, $J_{H,H}$ = 6.7 Hz, $CH(CH_3)_2$). **^{13}C {^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 149.9 (s, B^f-*C*), 146.4 (s, *o*-Dipp-*C*), 133.9 (s, *ipso*-Dipp-*C*), 130.8 (s, B^f-*C*), 129.8 (s, *p*-Dipp-*C*), 127.2 (s, B^f-*C*), 125.5 (s, Im-*C*), 122.9 (s, *m*-Dipp-*C*), 121.9 (s, Im-*C*), 119.3 (s, B^f-*C*), 28.9 (s, $CH(CH_3)_2$), 27.0 (s, $CH(CH_3)_2$), 21.7 (s, $CH(CH_3)_2$). Resonances for the carbon atoms connected to the boron atom were not observed. **^{11}B NMR** (128 MHz, CD_2Cl_2): δ –5.5 (brs). **Crystal Data** for $C_{54}H_{54}B_2N_4 \cdot (THF)_2$ (M = 924.84 g/mol): monoclinic, space group $P2_1/c$ (#14), a = 12.7952(3) Å, b = 19.5207(4) Å, c = 20.9941(4) Å, α = 90°, β = 95.160(2)°, γ = 90°, V = 5222.47(19) Å^3, Z = 4, T = 123.15 K, μ(Cu Kα) = 0.536 mm^{-1}, *Dcalc* = 1.176 g/cm^3, 9444 reflections measured (8.286° $\leq 2\theta \leq$ 136.494°), 9444 unique (R_{int} = ?, R_{sigma} = 0.0360) which were used in all calculations. The final R_1 was 0.0793 ($I \geq 2\sigma(I)$) and wR_2 was 0.2258 (all data).

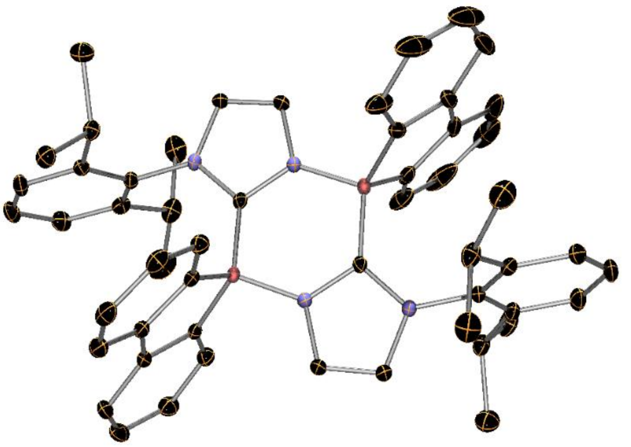
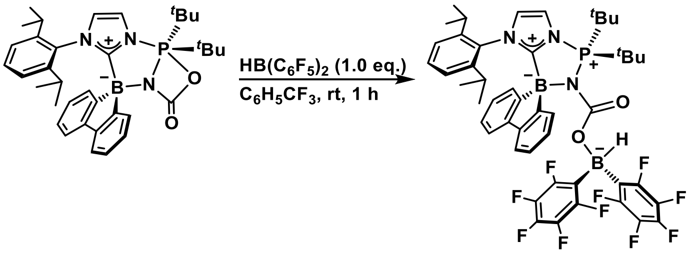


Figure S2. Molecular structure of **(4)**$_2$ with ellipsoids set at 30% probability; H atoms and solvated THF are omitted for clarity.

[5] Synthesis of 5



2

5
97%

To a suspension of **2** (224.6 mg, 0.38 mmol) in α,α,α-trifluorotoluene (25 mL) was added $HB(C_6F_5)_2$ (130.9 mg, 0.38 mmol, 1.0 equiv.), followed by stirring at room temperature for 1 h. After all volatiles were removed *in vacuo,* the resultant solid was washed with *n*-hexane to afford **5** as a white solid (347.3 mg, 0.37 mmol, 97%). A single crystal suitable for X-ray diffraction analysis was prepared by recrystallization from CH_2Cl_2/*n*-hexane at −30 °C (Figure S3). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.62 (s, 1H, Im-*H*), 7.24 (s, 1H, Im-*H*), 7.19 (d, 2H, $J_{H,H}$ = 6.4 Hz, B^f-*H*), 7.16 (t, 1H, *p*-Dipp-*H*), 7.09 (d, 2H, $J_{H,H}$ = 7.3 Hz, B^f-*H*), 6.97-6.91 (m, 4H, B^f-*H*), 6.86 (d, 2H, $J_{H,H}$ = 7.8 Hz, *m*-Dipp-*H*), 3.68 (brs, 1H, B-*H*), 2.14 (sept, 2H, $J_{H,H}$ = 6.5 Hz, C*H*$(CH_3)_2$), 1.77 (d, 18H, $^3J_{H,P}$ = 19.2 Hz, C(C*H*$_3$)$_3$), 0.89 (d, 6H, $J_{H,H}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 0.65 (d, 6H, $J_{H,H}$ = 6.4 Hz, CH(C*H*$_3$)$_2$). **^{13}C {^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 161.8 (s, *C*=O), 150.6 (s, B^f-*C*), 147.6 (brd, $^1J_{C,F}$ = 231.0 Hz, *o*-*C*$_6$F$_5$), 145.1 (s, *o*-Dipp-*C*), 138.8 (brd, $^1J_{C,F}$ = 251.2 Hz, *p*-*C*$_6$F$_5$), 136.6 (brd, $^1J_{C,F}$ = 244.5 Hz, *m*-*C*$_6$F$_5$), 131.4 (s, *p*-Dipp-*C*), 131.1 (s, *ipso*-Dipp-*C*), 130.5 (s, B^f-*C*), 129.8 (s, Im-*C*), 127.2 (s, B^f-*C*), 126.4 (s, B^f-*C*), 123.9 (s, *m*-Dipp-*C*), 121.8 (s, Im-*C*), 118.8 (s, B^f-*C*), 43.8 (d, $^2J_{C,P}$ = 51.0 Hz, *C*(CH$_3$)$_3$), 29.1 (s, C(*C*H$_3$)$_3$), 28.9 (s, *C*H(CH$_3$)$_2$), 26.4 (s, CH(*C*H$_3$)$_2$), 21.9 (s, CH(*C*H$_3$)$_2$). Resonances for the carbon atoms connected to the boron atom were not observed. **^{19}F NMR** (376 MHz, CD_2Cl_2): δ −135.6 (s, 2F, *o*-C$_6$*F*$_5$), −163.2 (s, 1F, *p*-C$_6$*F*$_5$),

−167.1 (s, 2F, *m*-C_6F_5). **^{31}P {^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 59.9 (s). **^{11}B NMR** (128 MHz, CD_2Cl_2): δ −6.4 (brs). **Crystal Data** for $C_{48}H_{46}B_2F_{10}N_3O_2P{\bullet}CH_2Cl_2$ (M = 1024.39 g/mol): triclinic, space group P-1 (#2), a = 10.5399(5) Å, b = 11.4428(6) Å, c = 21.6413(9) Å, α = 85.586(4)°, β = 85.395(4)°, γ = 69.910(4)°, V = 2439.9(2) Å^3, Z = 2, T = 123.15 K, μ(Cu Kα) = 2.212 mm^{-1}, *Dcalc* = 1.394 g/cm^3, 29927 reflections measured (8.208° ≤ 2θ ≤ 136.494°), 8887 unique (R_{int} = 0.0948, R_{sigma} = 0.0752) which were used in all calculations. The final R_1 was 0.0721 (I ≥ 2σ(I)) and wR_2 was 0.1892 (all data).

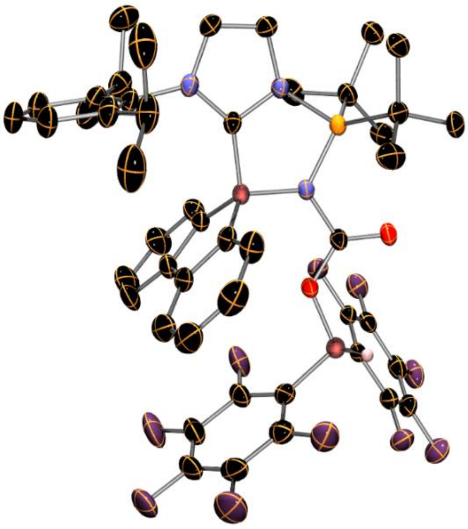
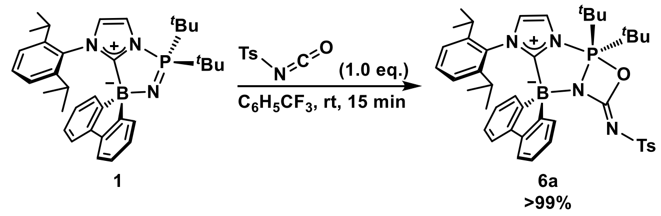


Figure S3. Molecular structure of **5** with ellipsoids set at 30% probability; H atoms connected to the carbon atoms and solvated CH_2Cl_2 are omitted for clarity.

[6] Synthesis of 6a



To a suspension of **1** (164.9 mg, 0.30 mmol) in α,α,α-trifluorotoluene (20 mL) was added *p*-toluenesulfonyl isocyanate (59.2 mg, 0.30 mmol, 1.0 equiv.), followed by stirring at room temperature for 15 min. After all volatiles were removed *in vacuo,* the resultant solid was washed with *n*-hexane to afford **6a** as a white solid (223.7 mg, 0.30 mmol, >99%). A single crystal suitable for X-ray diffraction analysis was prepared by recrystallization from CH_2Cl_2/*n*-hexane at room temperature (Figure S4). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.462 (d, 2H, $J_{\mathrm{H,H}}$ = 7.8 Hz, Ts-C_6H_4), 7.456 (s, 1H, Im-*H*), 7.35 (d, 2H, $J_{\mathrm{H,H}}$ = 7.8 Hz, B$^{\mathrm{f}}$-*H*), 7.21 (d, 2H, $J_{\mathrm{H,H}}$ = 6.9 Hz, B$^{\mathrm{f}}$-*H*), 7.15-7.07 (m, 5H, *p*-Dipp-*H,* Ts-C_6H_4, B$^{\mathrm{f}}$-*H*), 7.03-7.00 (m, 3H, B$^{\mathrm{f}}$-*H,* Im-*H*), 6.81 (d, 2H, $J_{\mathrm{H,H}}$ = 7.8 Hz, *m*-Dipp-*H*), 2.36 (s, 3H, Ts-CH_3), 2.09 (sept, 2H, $J_{\mathrm{H,H}}$ = 6.7 Hz, $CH(CH_3)_2$), 1.51 (d, 18H,

$^{3}J_{\mathrm{H,P}}$ = 19.7 Hz, C(CH_3)$_3$), 0.84 (d, 6H, $J_{\mathrm{H,H}}$ = 6.4 Hz, CH(CH_3)$_2$), 0.62 (d, 6H, $J_{\mathrm{H,H}}$ = 6.9 Hz, CH(CH_3)$_2$). **^{13}C {^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 175.2 (brs, Im-*C*), 160.5 (s, *C*=N), 150.4 (s, B^{f}-*C*), 150.1 (brs, B^{f}-*C*), 145.4 (s, *o*-Dipp-*C*), 142.0 (s, Ts-C_6H_4), 141.1 (s, Ts-C_6H_4), 132.0 (s, *ipso*-Dipp-*C*), 130.9 (s, B^{f}-*C*), 130.7 (s, *p*-Dipp-*C*), 128.9 (s, Ts-C_6H_4), 127.5 (s, Ts-C_6H_4), 127.2 (s, Im-*C*), 127.1 (s, B^{f}-*C*), 126.6 (s, B^{f}-*C*), 123.5 (s, Im-*C*), 123.4 (s, *m*-Dipp-*C*), 119.2 (s, B^{f}-*C*), 43.0 (d, $^{1}J_{\mathrm{C,P}}$ = 77.9 Hz, *C*(CH$_3$)$_3$), 29.5 (s, *C*H(CH$_3$)$_2$), 28.8 (s, C(*C*H$_3$)$_3$), 26.5 (s, CH(*C*H$_3$)$_3$), 21.9 (s, CH(*C*H$_3$)$_3$), 21.5 (s, Ts-*C*H$_3$). **^{31}P {^{1}H} NMR** (162 MHz, CD_2Cl_2): δ –2.8 (s). **^{11}B NMR** (128 MHz, CD_2Cl_2): δ –10.5 (brs). **Crystal Data** for $C_{43}H_{52}BN_4O_3PS{\bullet}CH_2Cl_2$ (M =831.65 g/mol): monoclinic, space group $P2_1/c$ (#14), a = 9.24486(14) Å, b = 19.6073(3) Å, c = 24.3636(4) Å, α = 90°, β = 93.1494(14)°, γ = 90°, V = 4409.64(11) Å^3, Z = 4, T = 123.15 K, μ(Cu Kα) = 2.446 mm^{-1}, *Dcalc* = 1.253 g/cm^3, 28396 reflections measured (7.268° ≤ 2θ ≤ 136.502°), 8046 unique (R_{int} = 0.0488, R_{sigma} = 0.0401) which were used in all calculations. The final R_1 was 0.0409 (I ≥ 2σ(I)) and wR_2 was 0.1318 (all data).

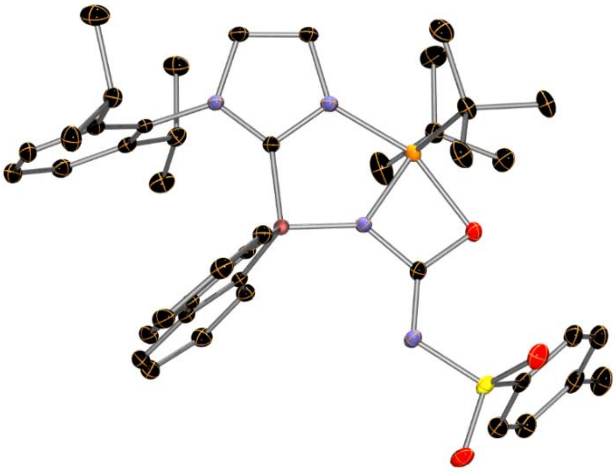
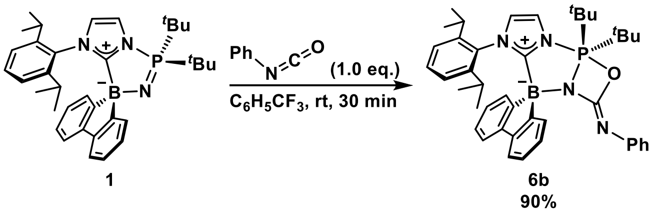


Figure S4. Molecular structure of **6a** with ellipsoids set at 30% probability; H atoms and solvated CH_2Cl_2 are omitted for clarity.

[7] Synthesis of 6b



To a suspension of **1** (165.2 mg, 0.30 mmol) in α,α,α-trifluorotoluene (15 mL) was added phenyl isocyanate (35.8 mg, 0.30 mmol, 1.0 equiv.), followed by stirring at room temperature for 30 min. After all volatiles were removed *in vacuo,* the resultant solid was washed with *n*-hexane to afford **6b** as a white solid (181.6 mg, 0.27 mmol, 90%). A single crystal suitable for X-ray diffraction analysis was prepared by recrystallization from CH_2Cl_2/*n*-hexane at –30 ºC (Figure S5). **^{1}H NMR** (400 MHz, CD_2Cl_2, –50 ºC): δ 7.46 (s, 1H, Im-*H*), 7.34 (d, 2H, $J_{\mathrm{H,H}}$ = 6.0 Hz, B$^{\mathrm{f}}$-*H*), 7.27 (d, 2H, $J_{\mathrm{H,H}}$ = 6.4 Hz, B$^{\mathrm{f}}$-*H*), 7.10 (t, 1H, $J_{\mathrm{H,H}}$ = 7.8 Hz, *p*-Dipp-*H*), 7.09-7.05 (m, 2H, *m*-$\mathrm{C_6}H_5$), 7.02-6.99 (m, 4H, B$^{\mathrm{f}}$-*H*), 6.97 (s, 1H, Im-*H*), 6.82 (t, 1H, $J_{\mathrm{H,H}}$ = 7.3 Hz, *p*-$\mathrm{C_6}H_5$), 6.79 (d, 2H, $J_{\mathrm{H,H}}$ = 6.9 Hz, *o*-$\mathrm{C_6}H_5$), 6.77 (d, 2H, $J_{\mathrm{H,H}}$ = 7.8 Hz, *m*-Dipp-*H*), 2.07 (sept, 2H, $J_{\mathrm{H,H}}$ = 6.5 Hz, $\mathrm{C}H(\mathrm{CH_3})_2$), 1.62 (d, 18H, $^3J_{\mathrm{H,P}}$ = 19.2 Hz, $\mathrm{C}H(\mathrm{CH_3})_2$), 0.82 (d, 6H, $J_{\mathrm{H,H}}$ = 6.4 Hz, $\mathrm{CH(C}H_3)_2$), 0.56 (d, 6H, $J_{\mathrm{H,H}}$ = 6.9 Hz, $\mathrm{CH(C}H_3)_2$). **^{13}C {^{1}H} NMR** (100 MHz, CD_2Cl_2, –50 ºC): δ 173.1 (brs, Im-*C*), 152.0 (brs, B$^{\mathrm{f}}$-*C*), 149.9 (d, $^2J_{\mathrm{C,P}}$ = 5.4 Hz, *C*=N), 149.4 (s, B$^{\mathrm{f}}$-*C*), 148.4 (s, *ipso*-$C_6\mathrm{H_5}$), 145.0 (s, *o*-Dipp-*C*), 131.9 (s, *ipso*-Dipp-*C*), 130.7 (s, B$^{\mathrm{f}}$-*C*), 129.8 (s, *p*-Dipp-*C*), 128.1 (s, *m*-$C_6\mathrm{H_5}$), 126.1 (s, B$^{\mathrm{f}}$-*C*), 126.0 (s, B$^{\mathrm{f}}$-*C*), 125.9 (s, Im-*C*), 123.6 (s, Im-*C*), 123.3 (s, *m*-$C_6\mathrm{H_5}$), 122.6 (s, *m*-Dipp-*C*), 121.3 (s, *p*-$C_6\mathrm{H_5}$), 118.3 (s, B$^{\mathrm{f}}$-*C*), 42.3 (d, $^2J_{\mathrm{C,P}}$ = 86.0 Hz, $C(\mathrm{CH_3})_3$), 29.3 (s, $\mathrm{C(}C\mathrm{H_3)_3}$), 28.2 (s, $C\mathrm{H(CH_3)_2}$), 26.2 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 21.5 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$). **^{31}P {^{1}H} NMR** (162 MHz, CD_2Cl_2, –50 ºC): δ –10.8 (s). **^{11}B NMR** (128 MHz, CD_2Cl_2, –50 ºC): δ –10.0 (brs). **Crystal Data** for $C_{42}H_{50}BN_4OP \bullet 2CH_2Cl_2$ (M = 838.49 g/mol): monoclinic, space group $P2_1/c$ (#14), a = 9.90590(10) Å, b = 19.1588(2) Å, c = 23.6340(2) Å, α = 90°, β = 93.5180(10)°, γ = 90°, V = 4476.93(8) Å^3, Z = 4, T = 193.15 K, μ(Cu Kα) = 3.026 mm^{-1}, $Dcalc$ = 1.244 g/cm^3, 34450 reflections measured (7.496° ≤ 2θ ≤ 136.5°), 8160 unique (R_{int} = 0.0377, R_{sigma} = 0.0287) which were used in all calculations. The final R_1 was 0.0548 (I ≥ 2u(I)) and wR_2 was 0.1545 (all data).

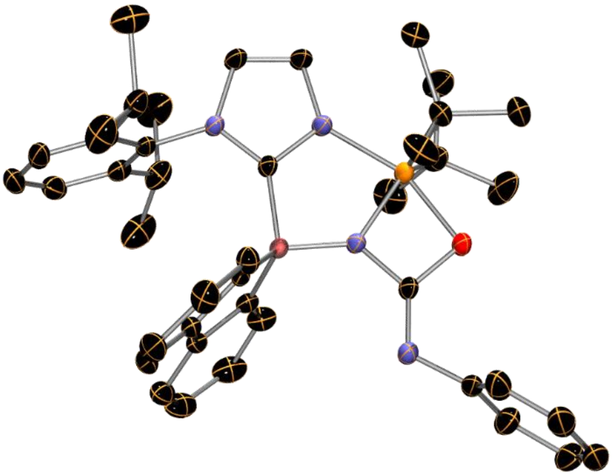
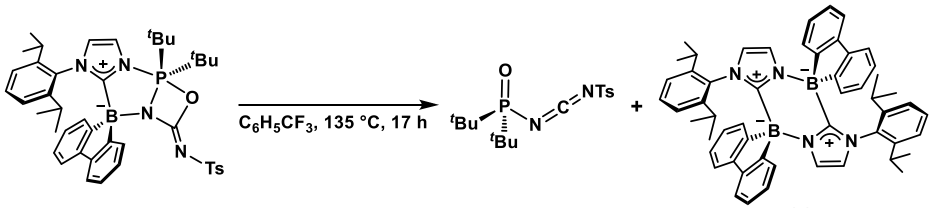


Figure S5. Molecular structure of **6b** with ellipsoids set at 30% probability; H atoms and solvated CH_2Cl_2 are omitted for clarity.

[8] Conversion of 6a to 7a and $(4)_2$

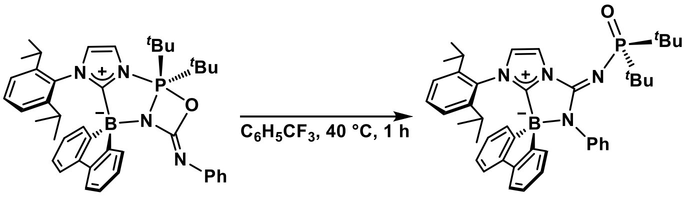


6a **7a** 97% **$(4)_2$** 46%

Compound **6a** (288.0 mg, 0.39 mmol) was dissolved in α,α,α-trifluorotoluene (30 mL), and the reaction mixture was stirred at 135 ºC for 17 h. Then, all volatiles were removed *in vacuo*, and the resultant mixture was separated into supernatant and residue with *n*-hexane. The supernatant liquid was concentrated *in vacuo* to afford **7a** as a white solid (136.4 mg, 0.38 mmol, 97%). Also, the resultant solid was concentrated *in vacuo* to afford **$(4)_2$** as a white solid (144.0 mg, 0.18 mmol, 46% based on the loading amount of **6a**).

Identification of **7a**: **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.74 (d, 2H, $J_{H,H}$ = 8.2 Hz, Ts-C_6H_4), 7.24 (d, 2H, $J_{H,H}$ = 8.2 Hz, Ts-C_6H_4), 2.39 (s, 3H, Ts-CH_3), 1.30 (d, 18H, $^3J_{H,P}$ = 17.7 Hz, $C(CH_3)_3$). **^{13}C {^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 143.5 (s, Ts-C_6H_4), 141.7 (s, Ts-C_6H_4), 129.4 (s, Ts-C_6H_4), 125.8 (s, Ts-C_6H_4), 38.9 (d, $^1J_{C,P}$ = 77.4 Hz, $C(CH_3)_3$), 26.1 (s, $C(CH_3)_3$), 21.5 (s, Ts-CH_3). The resonance for the carbon atom of carbodiimide was not observed. **^{31}P {^{1}H} NMR** (162 MHz, CD_2Cl_2): δ45.3 (s). **HRMS** (EI$^+$): m/z Calcd for $C_{16}H_{25}N_2O_3PS$: 356.1323, found 356.1334.

[9] Synthesis of 8b from 6b



6b **8b** 85%

Compound **6b** (134.0 mg, 0.20 mmol) was dissolved in α,α,α-trifluorotoluene (12 mL), and the reaction mixture was then stirred at 40 ºC for 1 h. After all volatiles were removed *in vacuo*, **8b** was afforded as a white solid (111.5 mg, 0.17 mmol, 85%). A single crystal suitable for X-ray diffraction analysis was prepared by recrystallization from CH_2Cl_2/*n*-hexane at –30 ºC (Figure S6). **^{1}H NMR** (400 MHz, CD_2Cl_2, –50 ºC): δ 9.66 (s, 1H, Im-*H*), 7.29 (d, 2H, $J_{H,H}$ = 6.9 Hz, B^f-*H*), 7.22 (d, 2H, $J_{H,H}$ = 6.4 Hz, B^f-*H*), 7.19 (t, 1H, $J_{H,H}$ = 7.8 Hz, *p*-Dipp-*H*), 7.06-7.02 (m, 4H, B^f-*H*, *m*-C_6H_5), 7.00-6.97 (m, 6H, B^f-*H*, *o,p*-C_6H_5, Im-*H*), 6.89 (d, 2H, $J_{H,H}$ = 7.8 Hz, *m*-Dipp-*H*), 2.17 (sept, 2H, $J_{H,H}$ = 6.3 Hz, $CH(CH_3)_2$), 1.15 (d, 18H, $^3J_{H,P}$ = 14.2 Hz, $C(CH_3)_3$), 0.90 (d, 6H, $J_{H,H}$ = 6.9 Hz, $CH(CH_3)_2$), 0.54 (d, 6H, $J_{H,H}$ = 6.9 Hz, $CH(CH_3)_2$). **^{13}C {^{1}H} NMR** (100 MHz,

CD_2Cl_2, –50 ºC): δ 170.0 (brs, Im-*C*), 149.5 (s, B^f-*C*), 148.9 (brs, B^f-*C*), 145.7 (d, $^2J_{C,P}$ = 6.7 Hz, N=*C*), 144.9 (s, *o*-Dipp-*C*), 141.2 (s, *o*-C_6H_5), 131.0 (s, *ipso*-Dipp-*C*), 130.5 (s, B^f-*C*), 130.3 (s, *p*-Dipp-*C*), 127.8 (s, *m*-C_6H_5), 126.9 (s, B^f-*C*), 126.7 (s, *o*-C_6H_5), 126.5 (s, B^f-*C*), 126.4 (s, Im-*C*), 125.1 (s, *p*-C_6H_5), 123.2 (s, *m*-Dipp-*C*), 119.4 (s, Im-*C*), 119.0 (s, B^f-*C*), 36.1 (d, $^1J_{C,P}$ = 88.7 Hz, *C*(CH_3)$_3$), 28.0 (s, *C*H(CH_3)$_2$), 26.5 (s, C(*C*H_3)$_3$), 26.0 (s, CH(*C*H_3)$_2$), 21.5 (s, CH(*C*H_3)$_2$). **^{31}P {^{1}H} NMR** (162 MHz, CD_2Cl_2, –50 ºC): δ 45.4 (s). **^{11}B NMR** (128 MHz, CD_2Cl_2, –50 ºC): δ –4.2 (brs). **Crystal Data** for $C_{42}H_{50}BN_4OP$ (M = 668.64 g/mol): triclinic, space group *P*-1 (#2), a = 9.9881(3) Å, b = 13.2977(5) Å, c = 15.5488(6) Å, α = 102.478(3)°, β = 94.349(3)°, γ = 100.379(3)°, V = 1969.19(13) Å^3, Z = 2, T = 193.15 K, μ(Cu Kα) = 0.886 mm^{-1}, $Dcalc$ = 1.128 g/cm^3, 22010 reflections measured (6.952° ≤ 2θ ≤ 136.496°), 7179 unique (R_{int} = 0.0496, R_{sigma} = 0.0499) which were used in all calculations. The final R_1 was 0.0500 (I ≥ 2u(I)) and wR_2 was 0.1236 (all data).

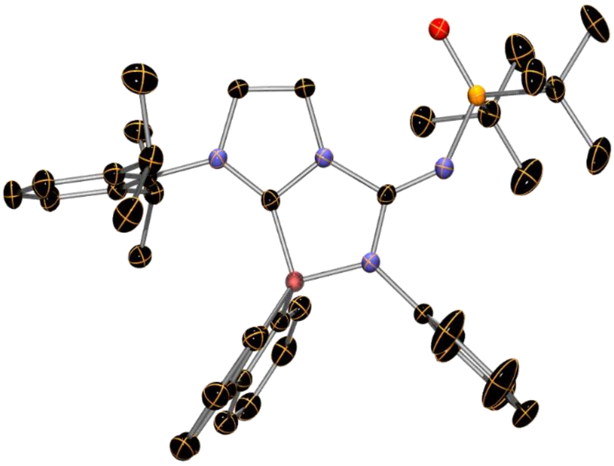
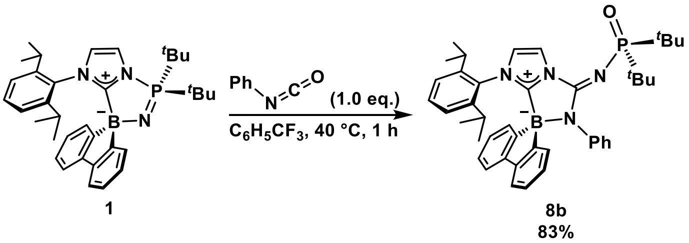


Figure S6. Molecular structure of **8b** with ellipsoids set at 30% probability; H atoms are omitted for clarity.

[10] Synthesis of 8b from 1



To a suspension of **1** (165.2 mg, 0.30 mmol) in α,α,α-trifluorotoluene (15 mL) was added phenyl isocyanate (35.9 mg, 0.30 mmol, 1.0 equiv.), followed by stirring at 40 ºC for 1 h. After all volatiles were removed *in vacuo*, the resultant solid was washed with *n*-hexane to afford **8b** as a white solid (170.5 mg, 0.25 mmol, 83%).

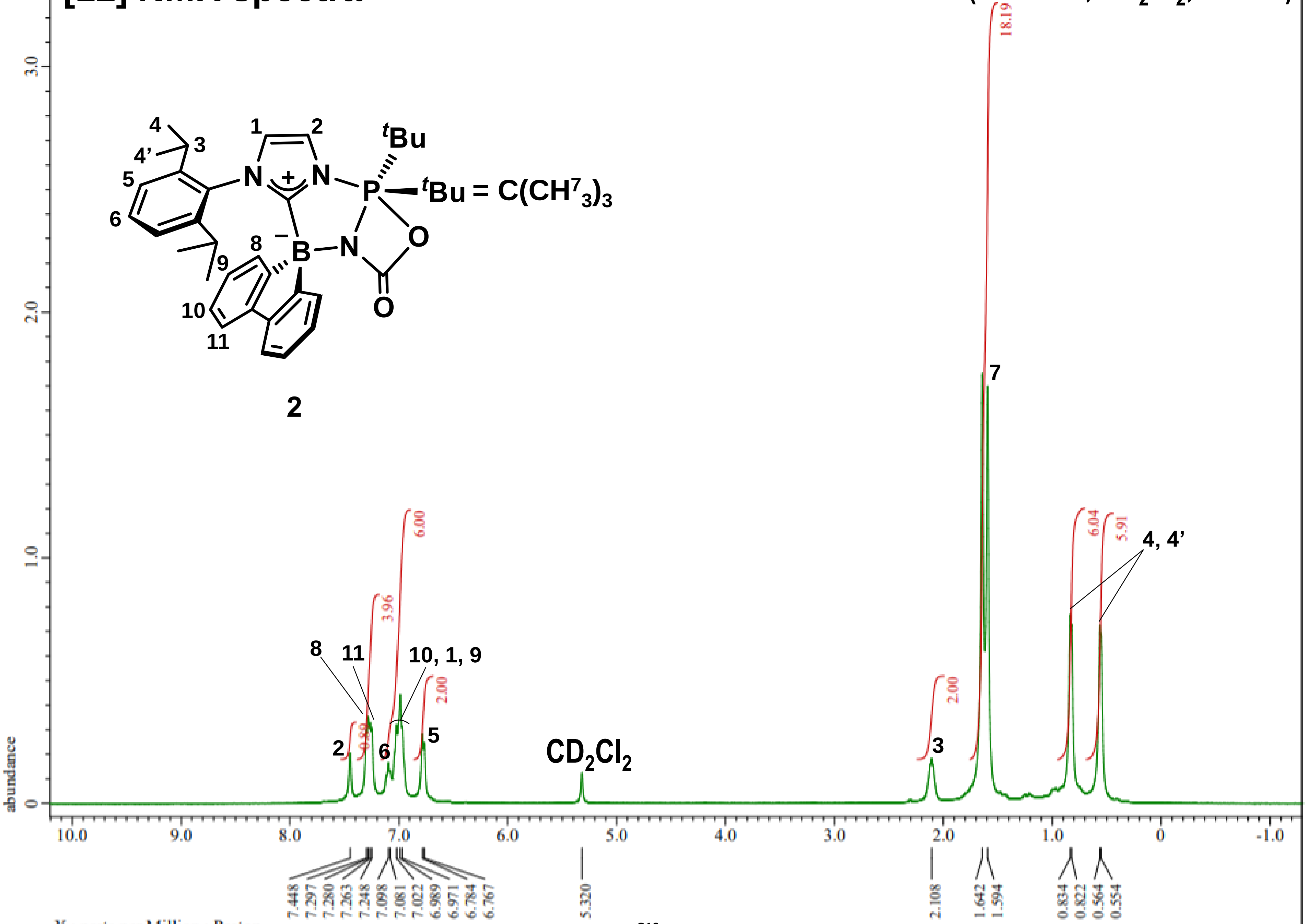
[11] References

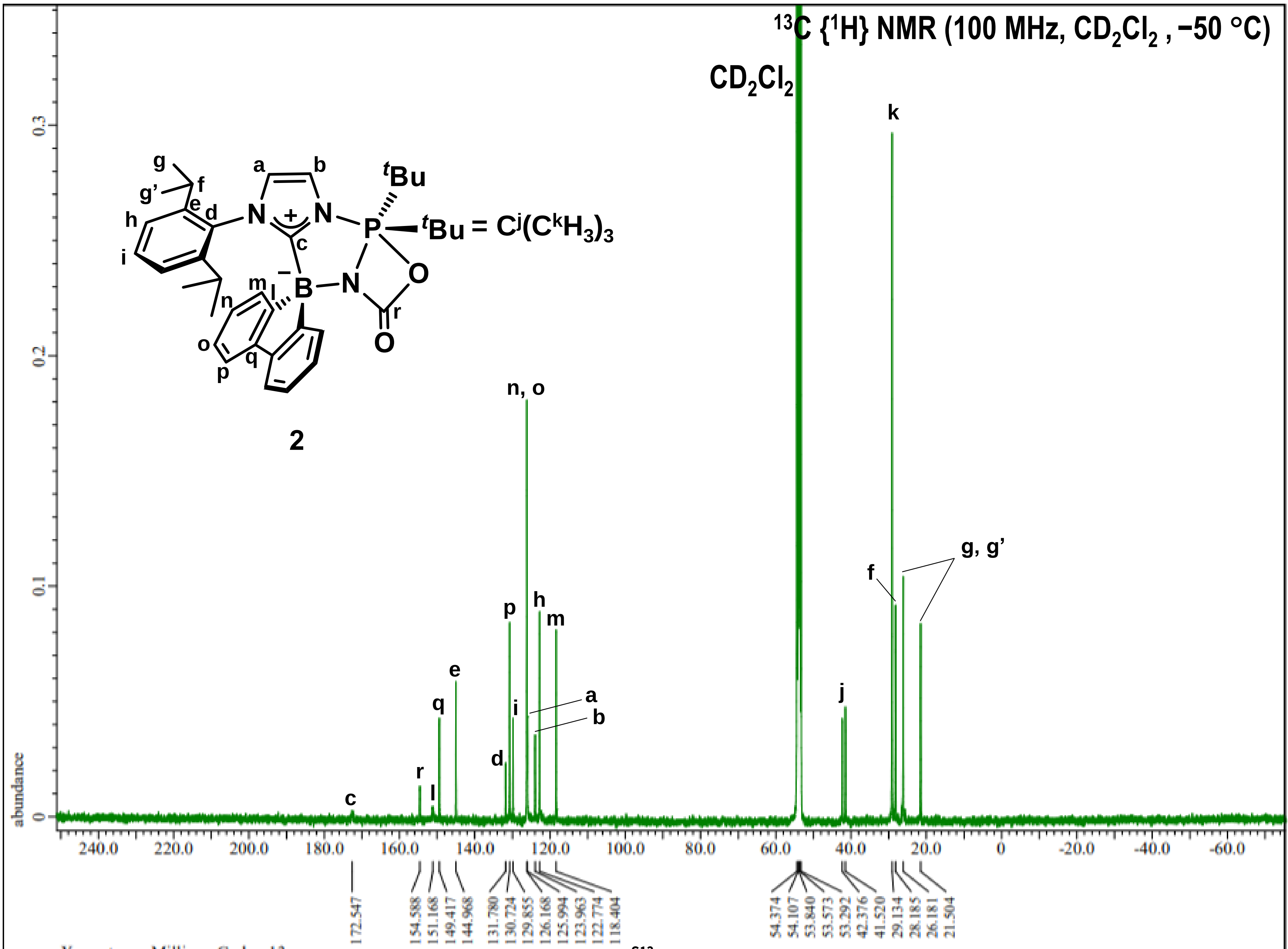
S1) Nagai, S.; Hinogami, T.; Ogoshi, S.; Hoshimoto, Y. *Bull. Chem. Soc. Jpn.* **2023**, *96*, 1346.

S2) a) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345; b) Patrick, E. A.; Piers, W. E. *Chem. Commun.* **2020**, *56*, 841.

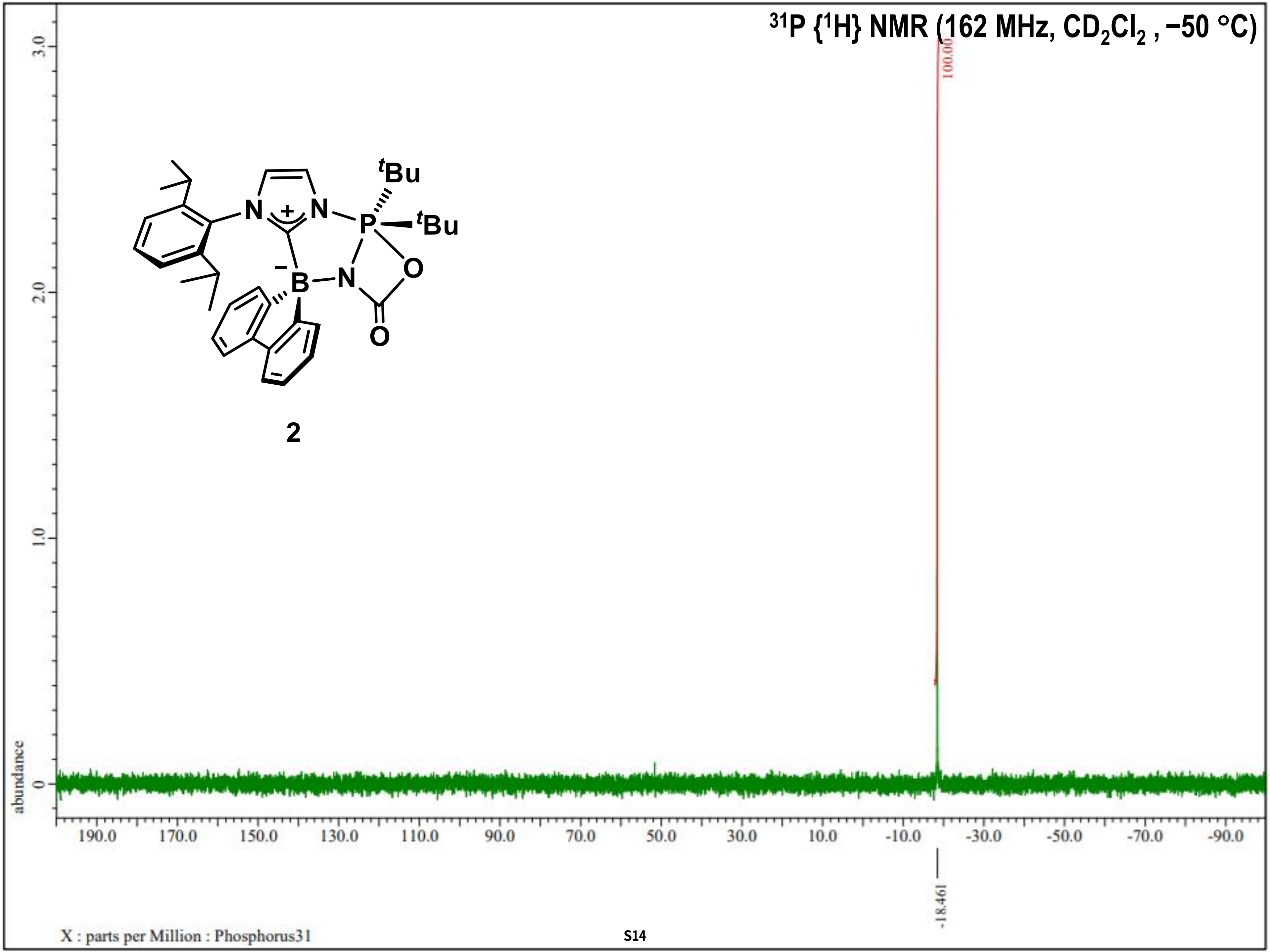
[12] NMR spectra

^{1}H NMR (400 MHz, CD_2Cl_2, −50 °C)

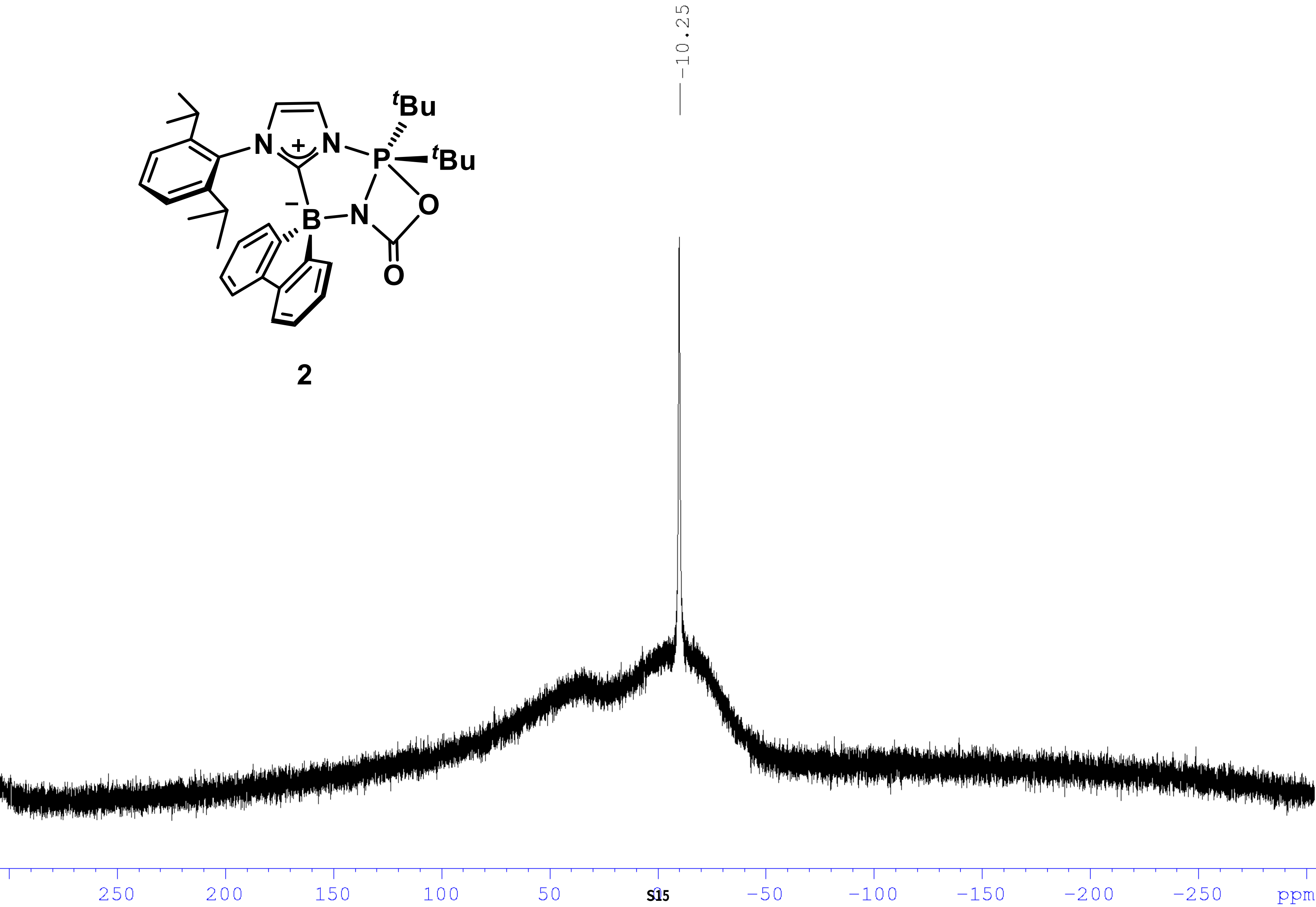



13C {1H} NMR (100 MHz, CD2Cl2 , −50 °C)
CD2Cl2
k
n, o
g, g'
f
p
h
m
e
q
i
a
b
j
d
r
l
c
tBu
tBu = Cj(CkH3)3
0,3
0,2
0,1
0
abundance
240.0
220.0
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0
-20.0
-40.0
-60.0
172.547
154.588
151.168
149.417
144.968
131.780
130.724
129.855
126.168
125.994
123.963
122.774
118.404
54.374
54.107
53.840
53.573
53.292
42.376
41.520
29.134
28.185
26.181
21.504
X : parts per Million : Carbon13

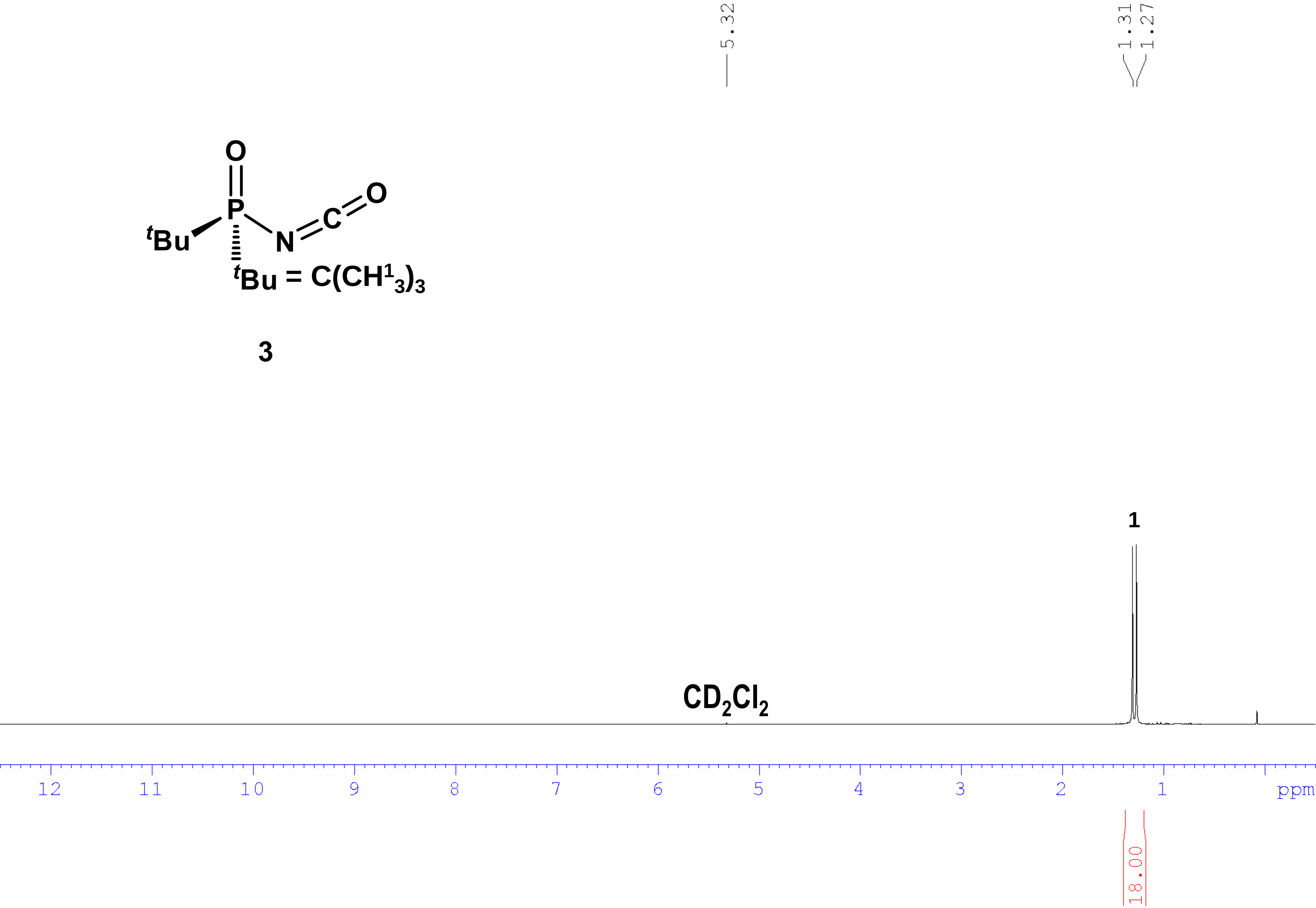
2


^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2 , −50 °C)
100.00
-18.461
2
N
N
+
P
tBu
tBu
O
N
B
−
O
3.0
2.0
1.0
0
abundance
190.0
170.0
150.0
130.0
110.0
90.0
70.0
50.0
30.0
10.0
-10.0
-30.0
-50.0
-70.0
-90.0
X : parts per Million : Phosphorus31

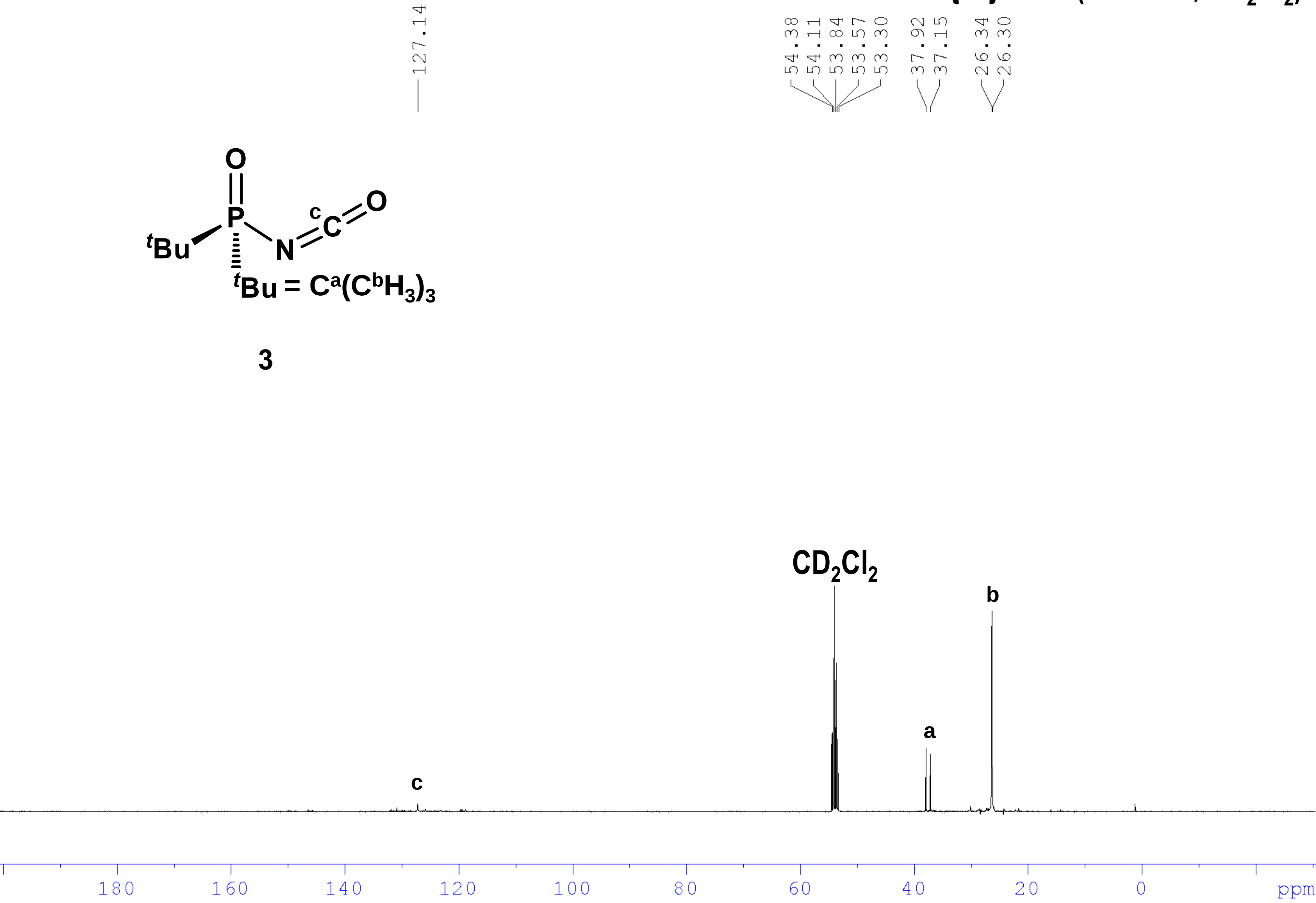
^{11}B NMR (128 MHz, CD_2Cl_2 , −50 °C)



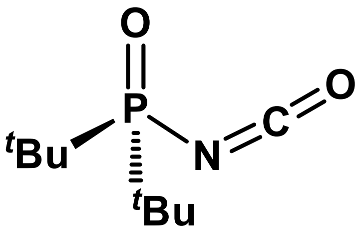
^{1}H NMR (400 MHz, CD_2Cl_2)



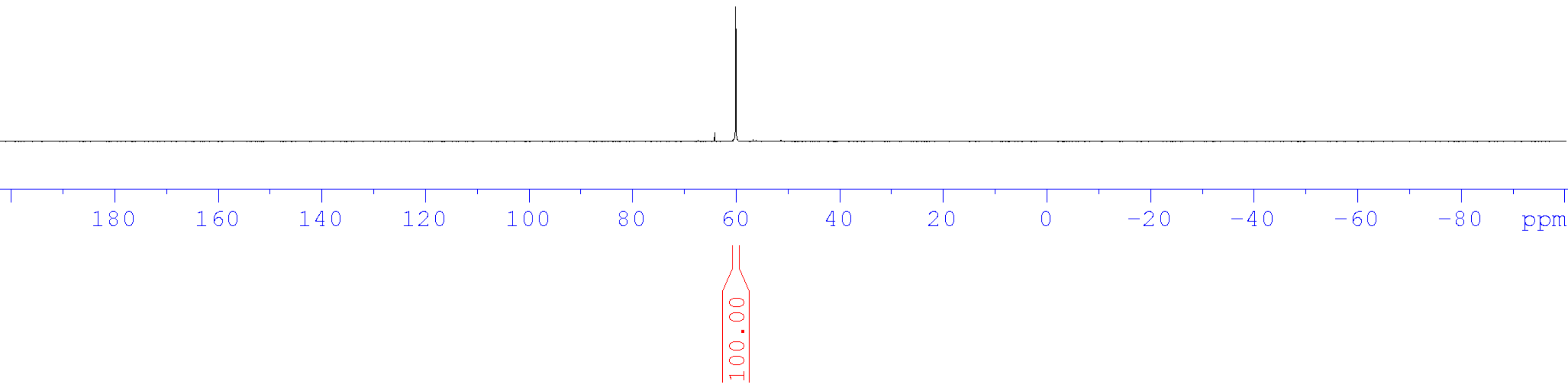
$^{13}C\ \{^1H\}$ NMR (100 MHz, CD_2Cl_2)



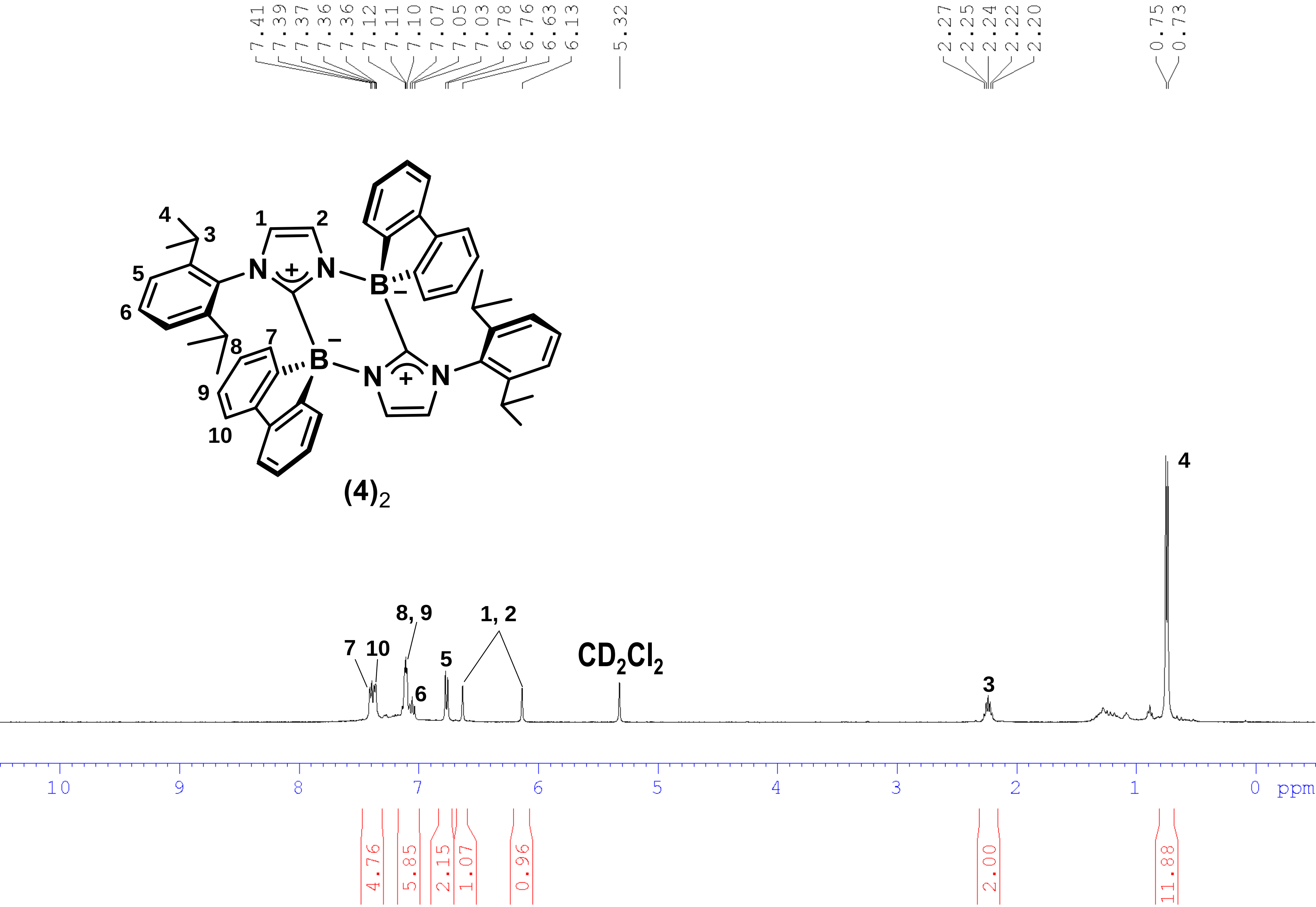
^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2)



3

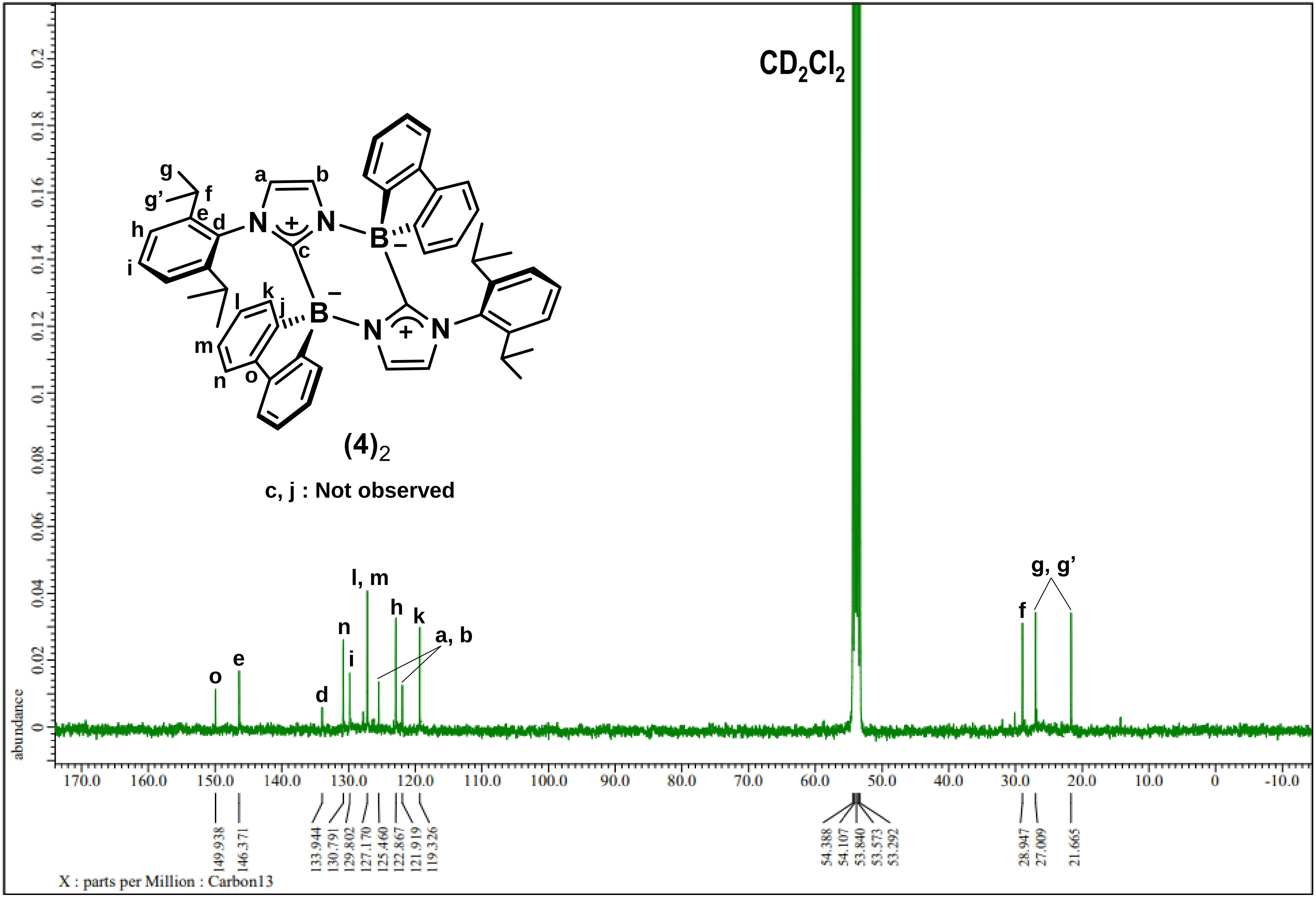


^1H NMR (400 MHz, CD_2Cl_2)

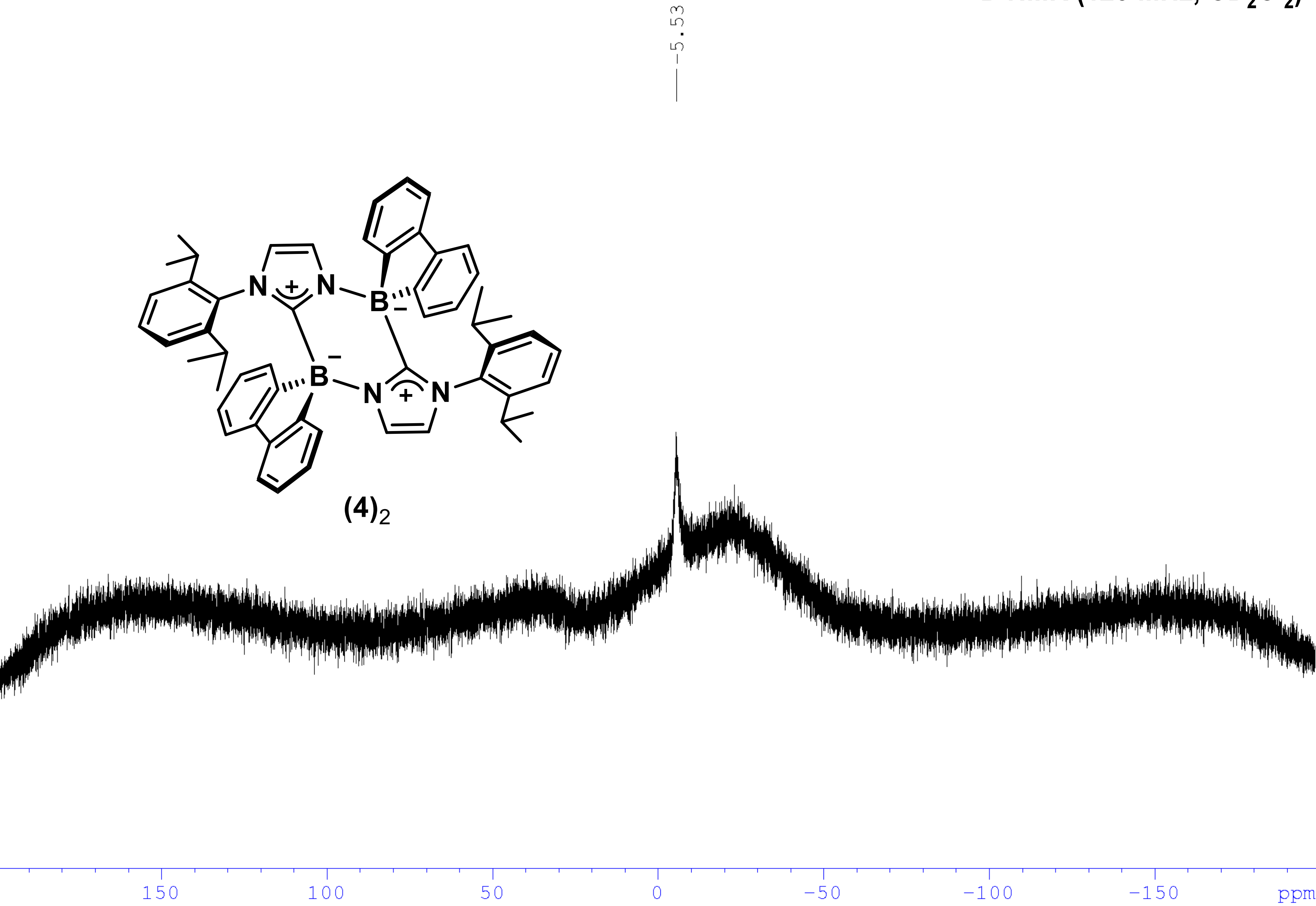


(4)$_2$

^{13}C {^{1}H} NMR (100 MHz, CD_2Cl_2)

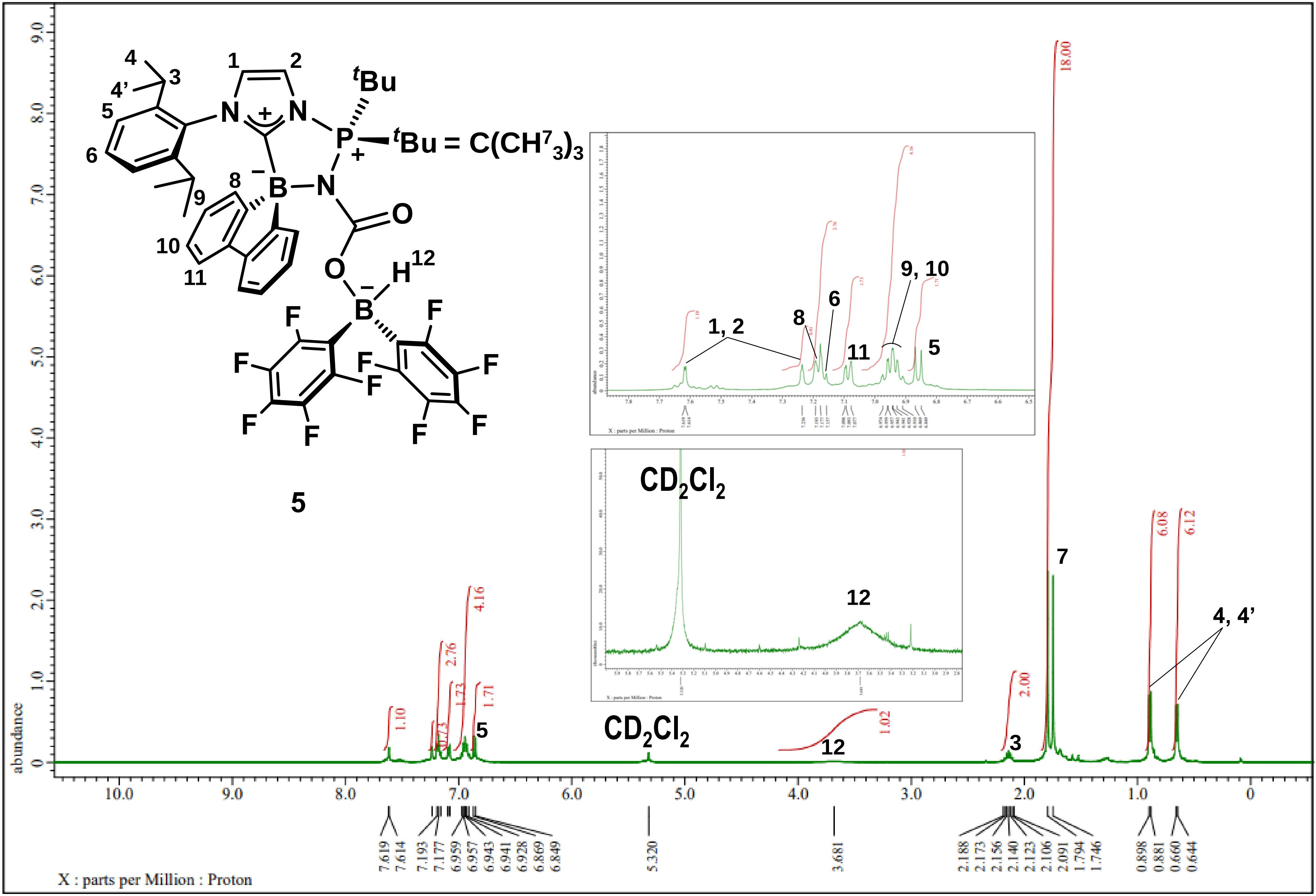


^{11}B NMR (128 MHz, CD_2Cl_2)

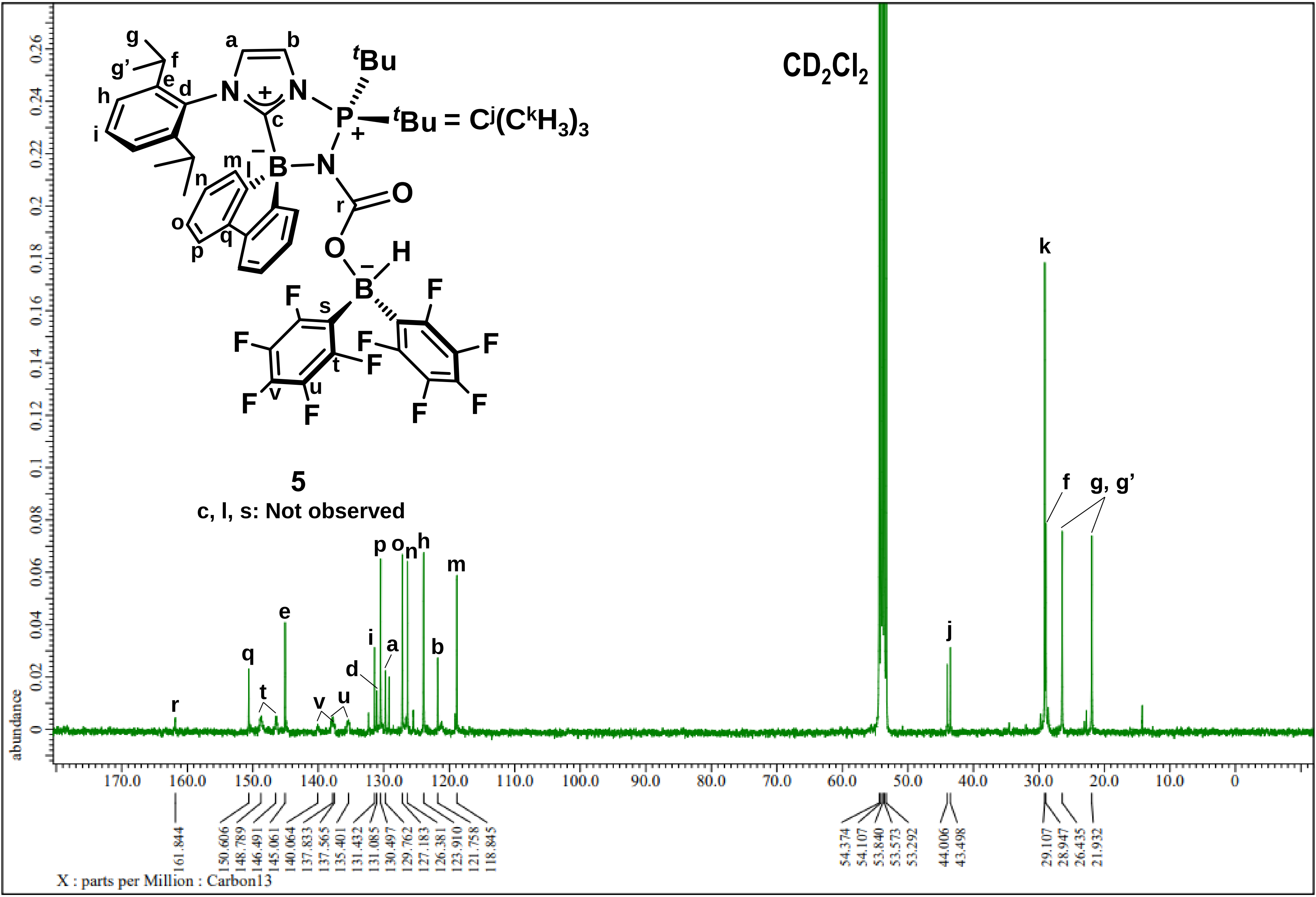


(4)$_2$

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



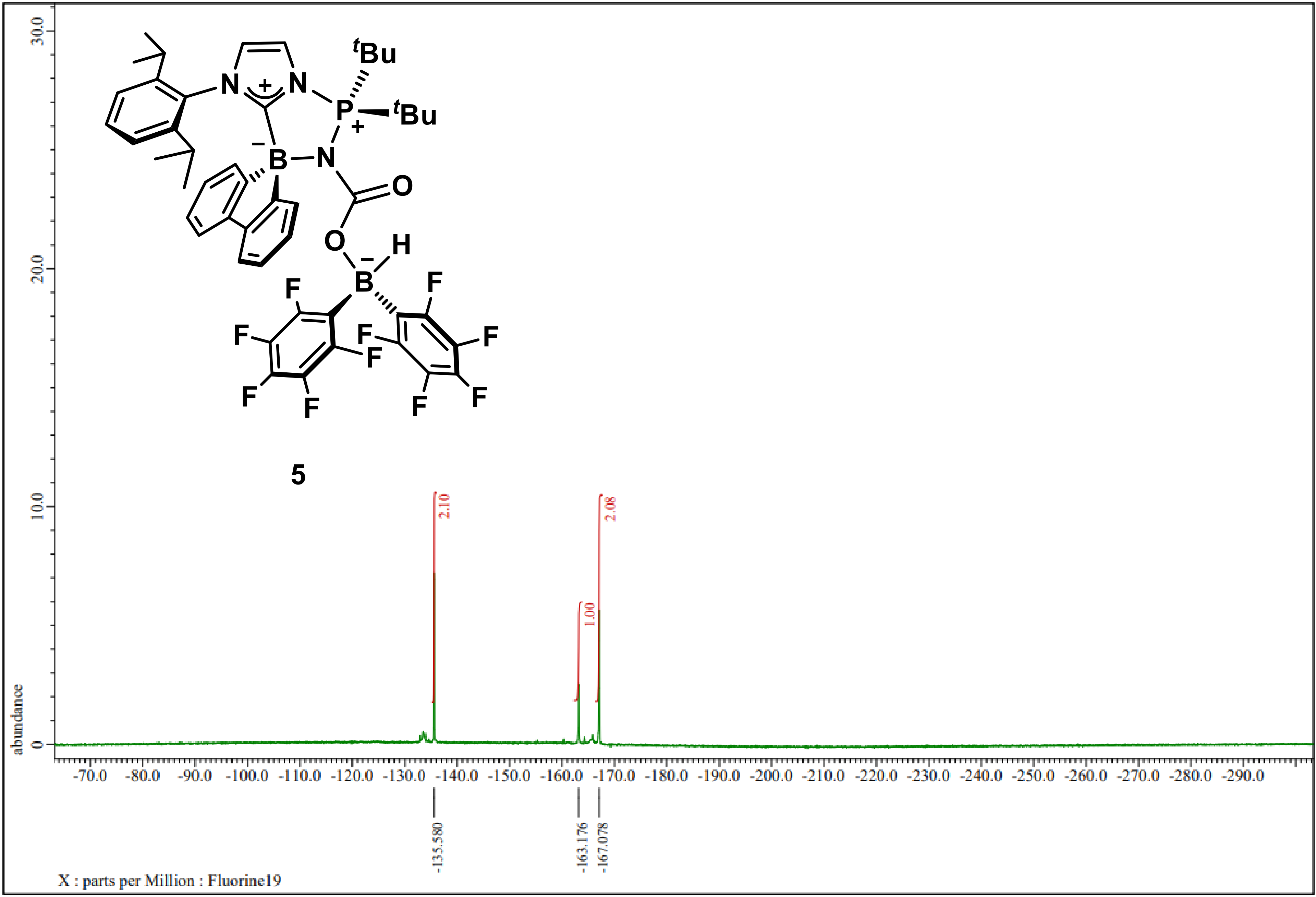
$^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2)



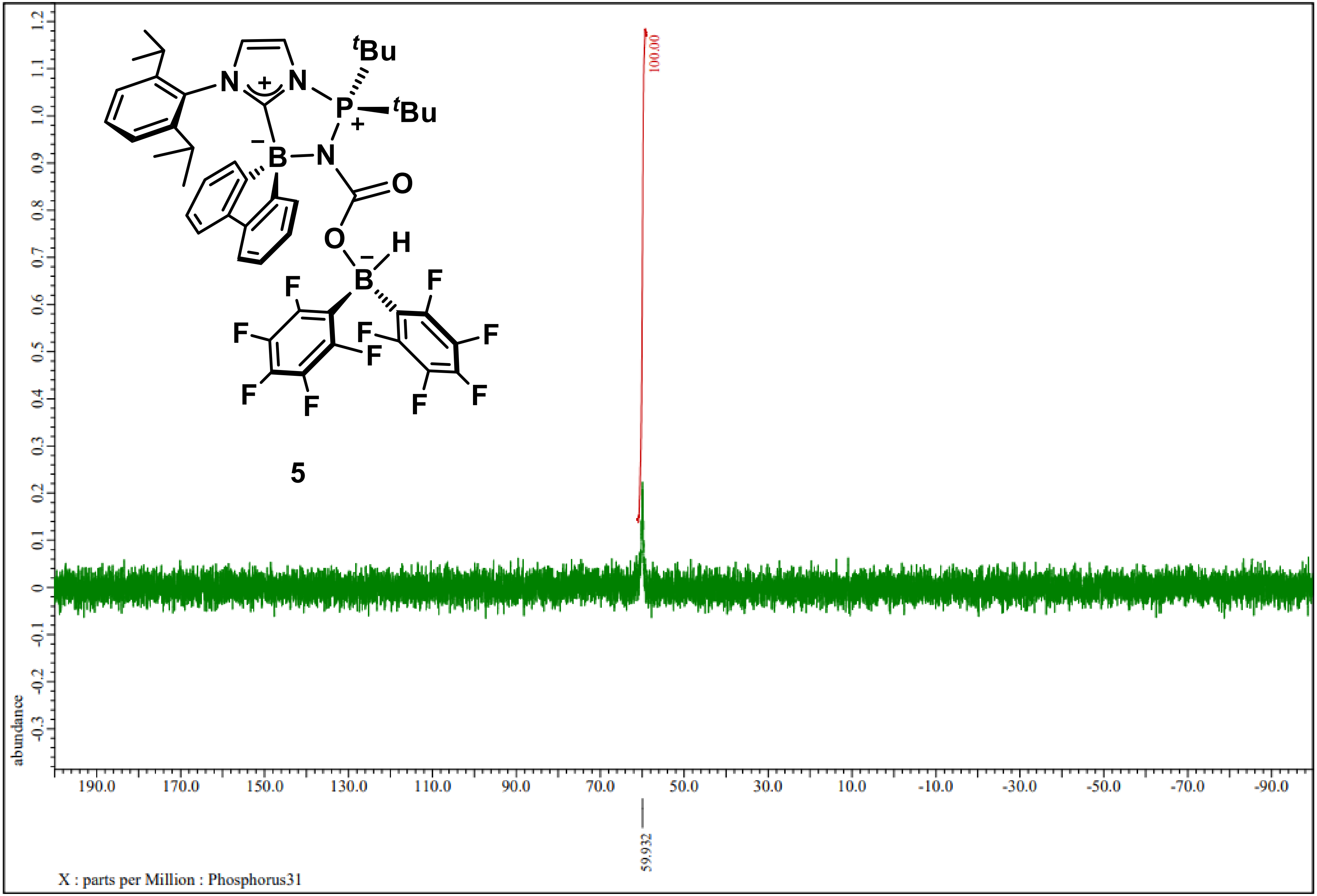
5

c, l, s: Not observed

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

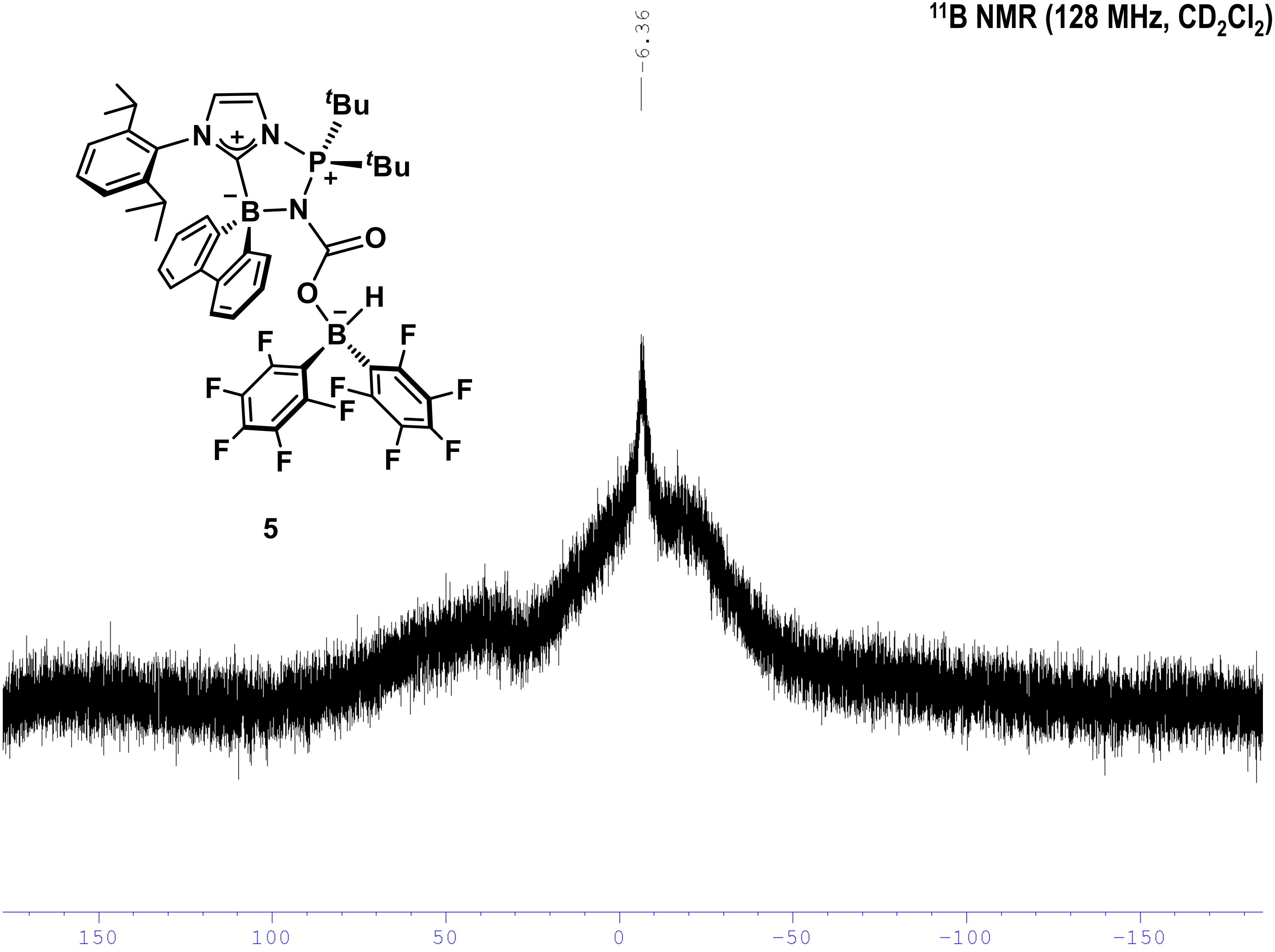


^{31}P {^1H} NMR (162 MHz, CD_2Cl_2)

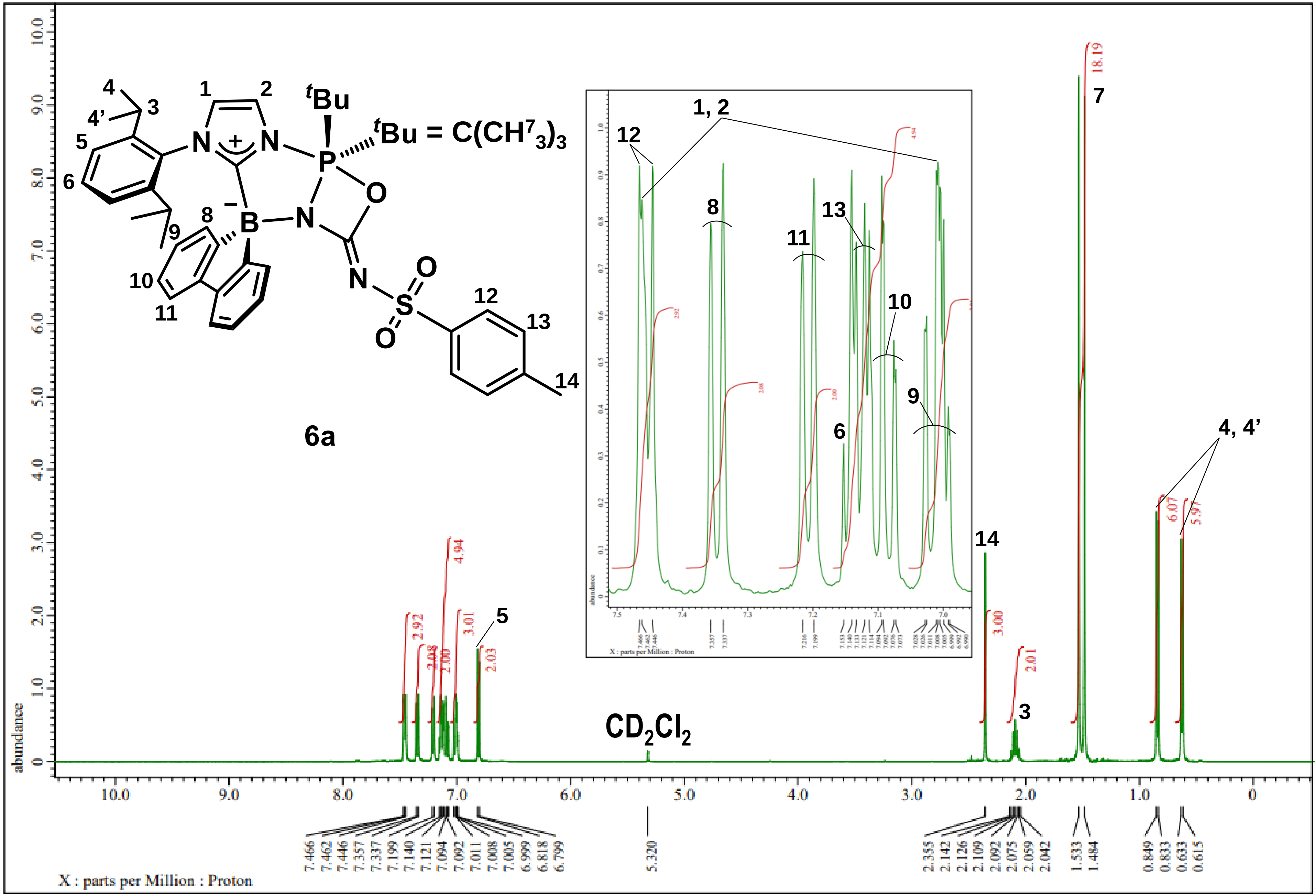


5

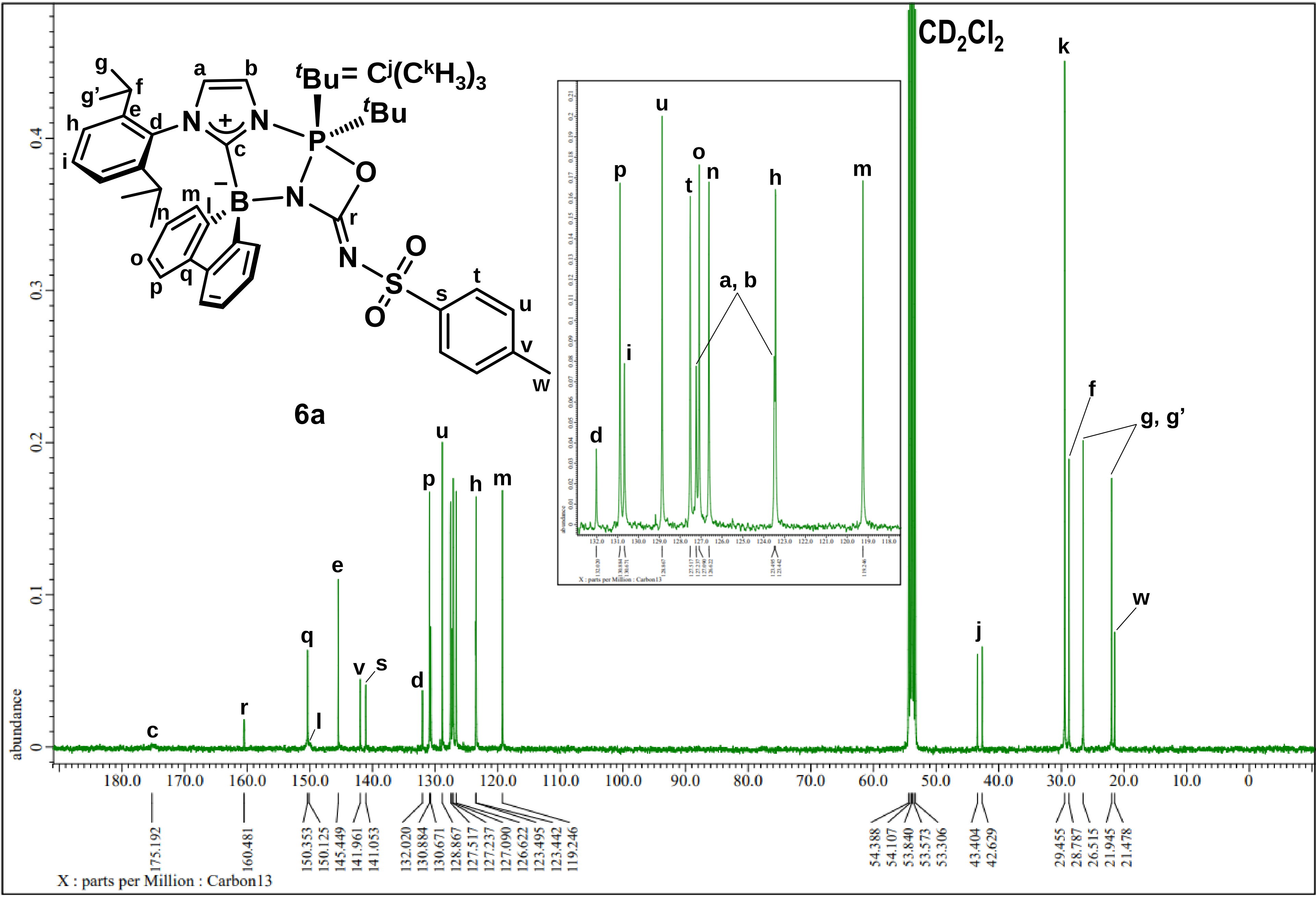
^{11}B NMR (128 MHz, CD_2Cl_2)



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

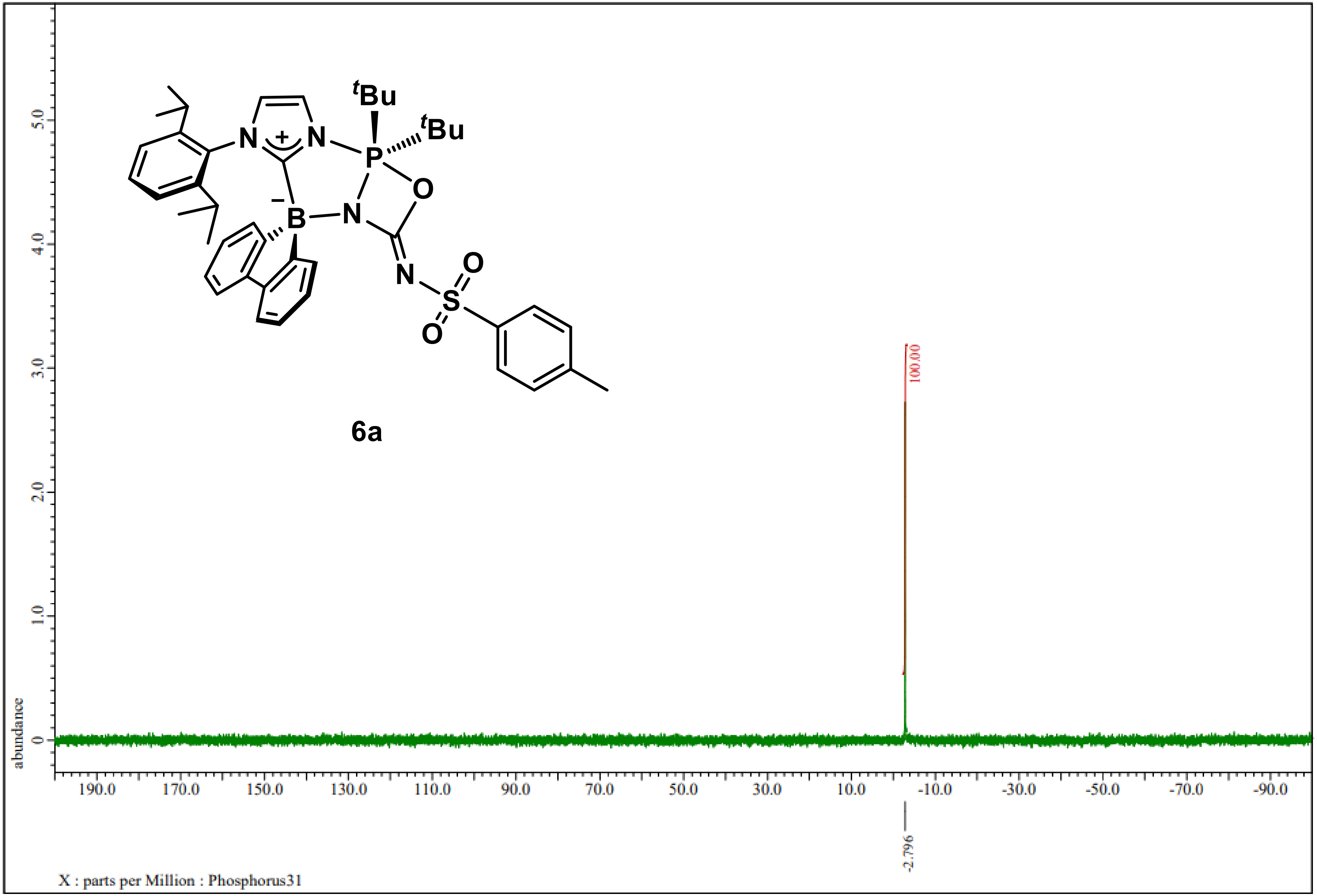


$^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2)



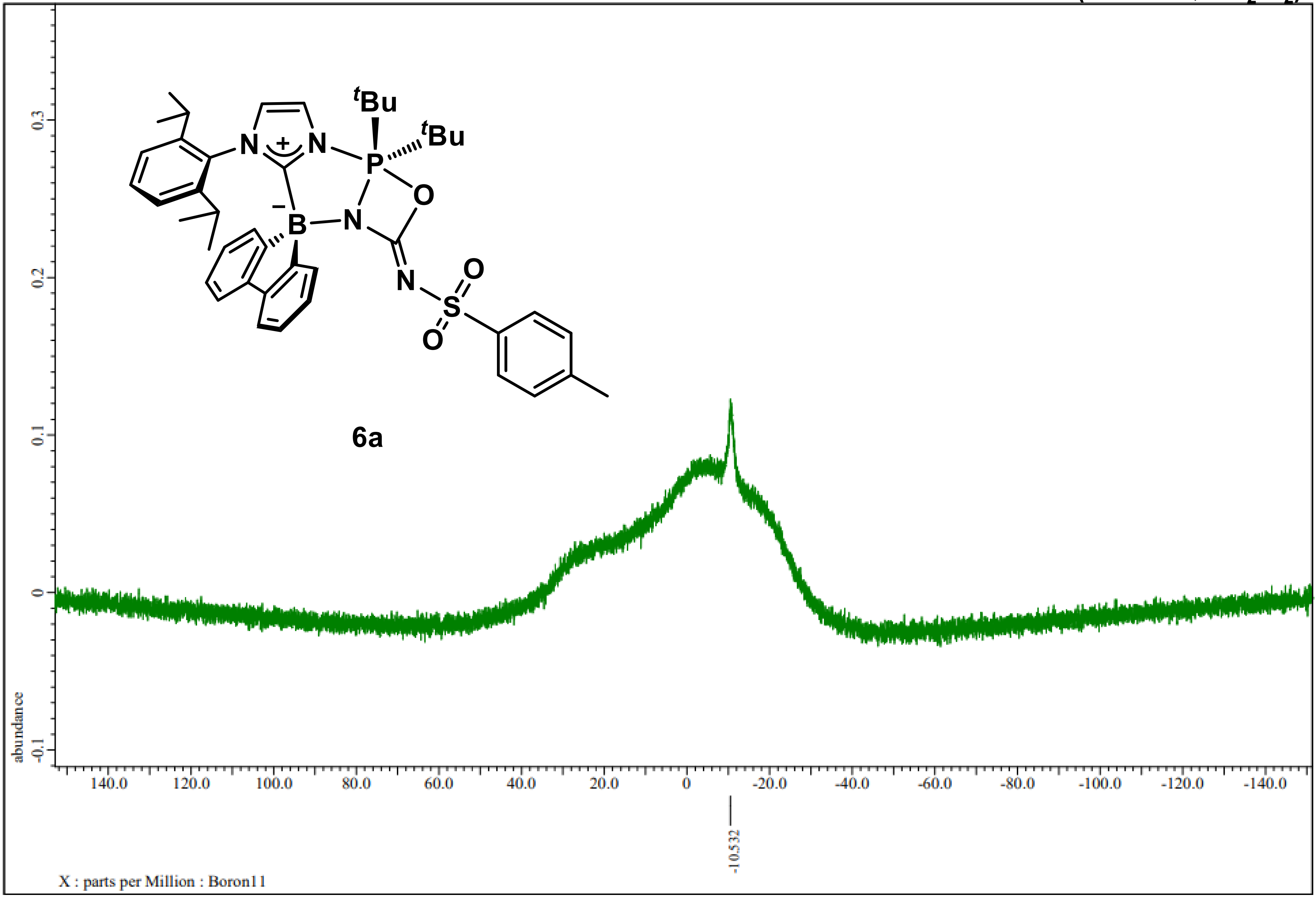
6a

^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2)



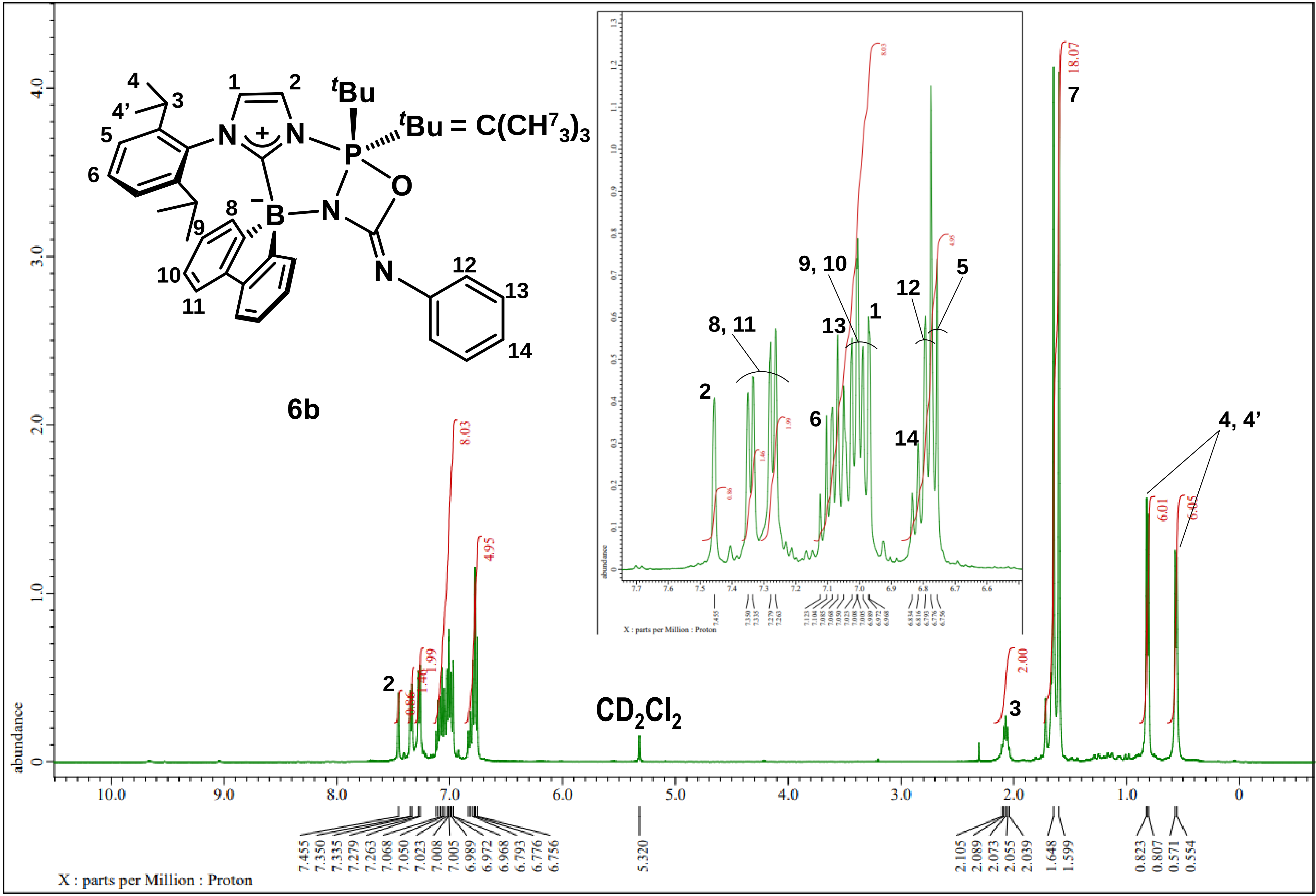
6a

^{11}B NMR (128 MHz, CD$_2$Cl$_2$)

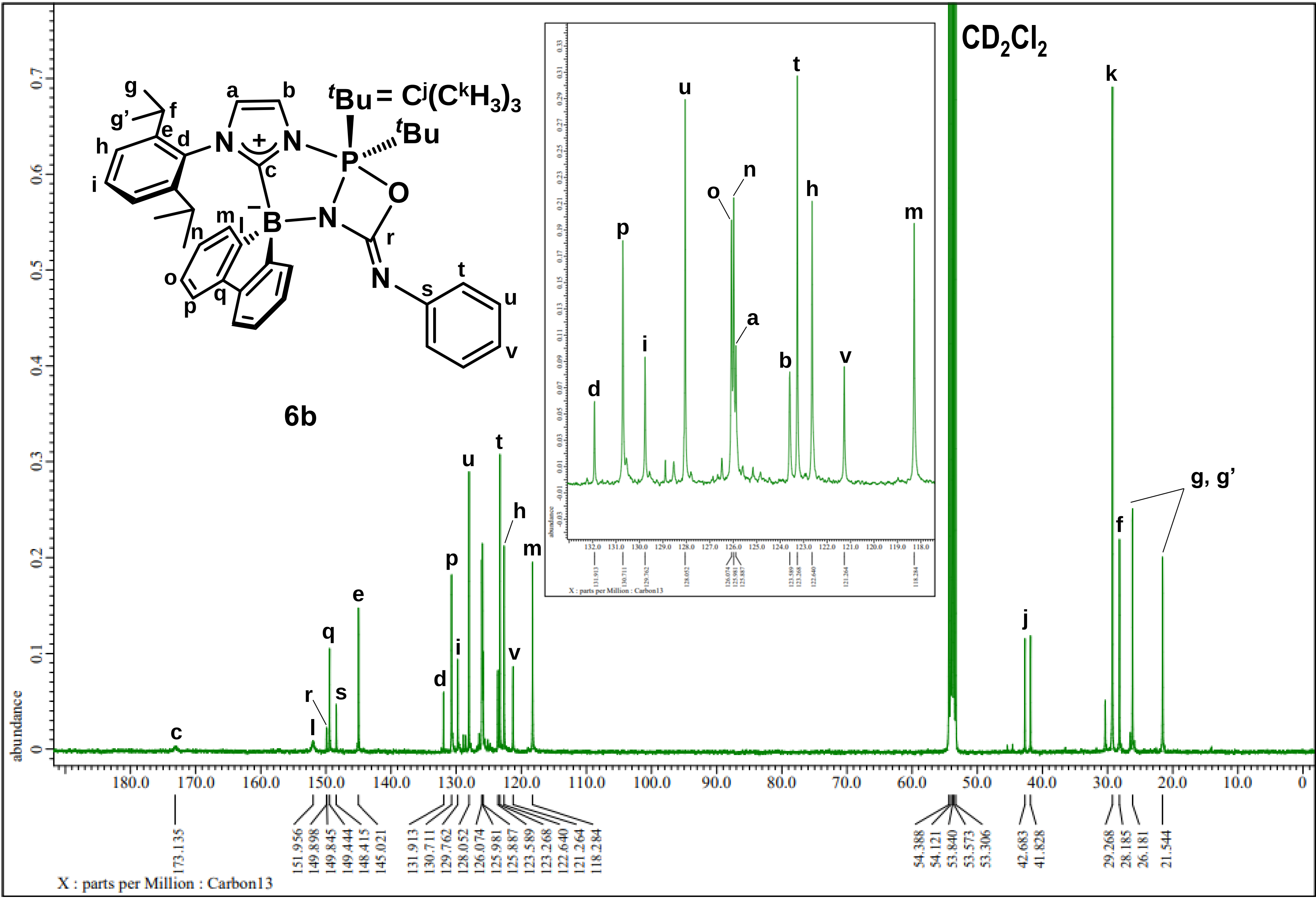


6a

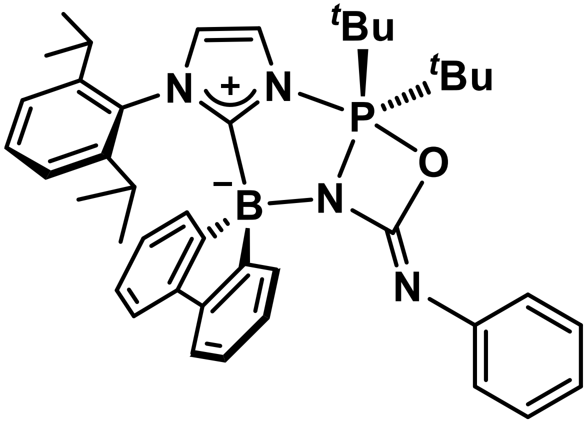
^1H NMR (400 MHz, CD_2Cl_2, −50 °C)



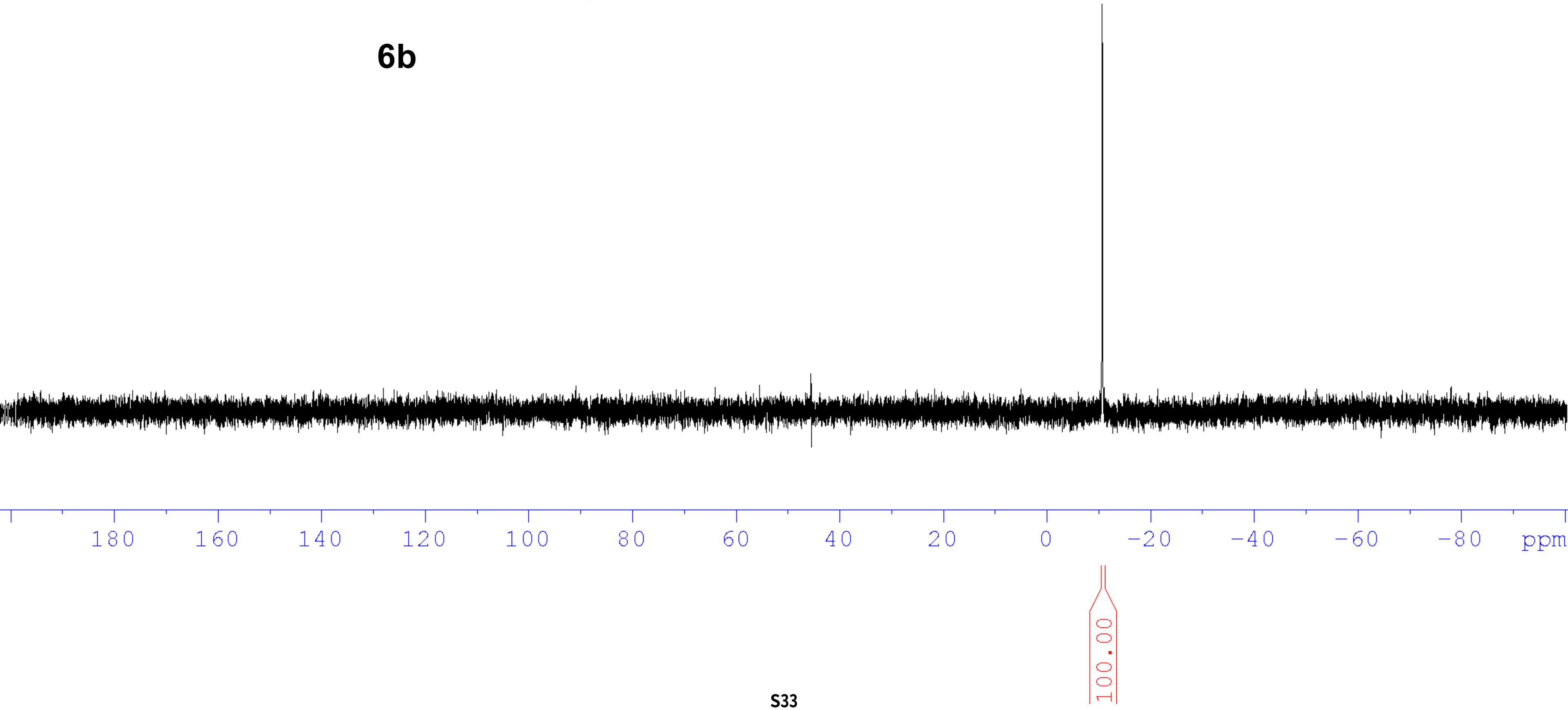
$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2, −50 °C)



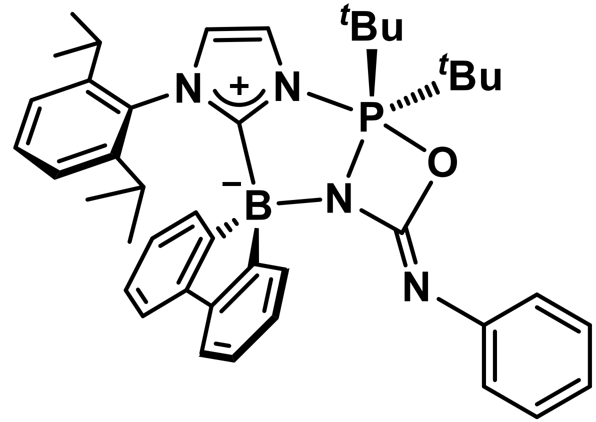
^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2, −50 ºC)



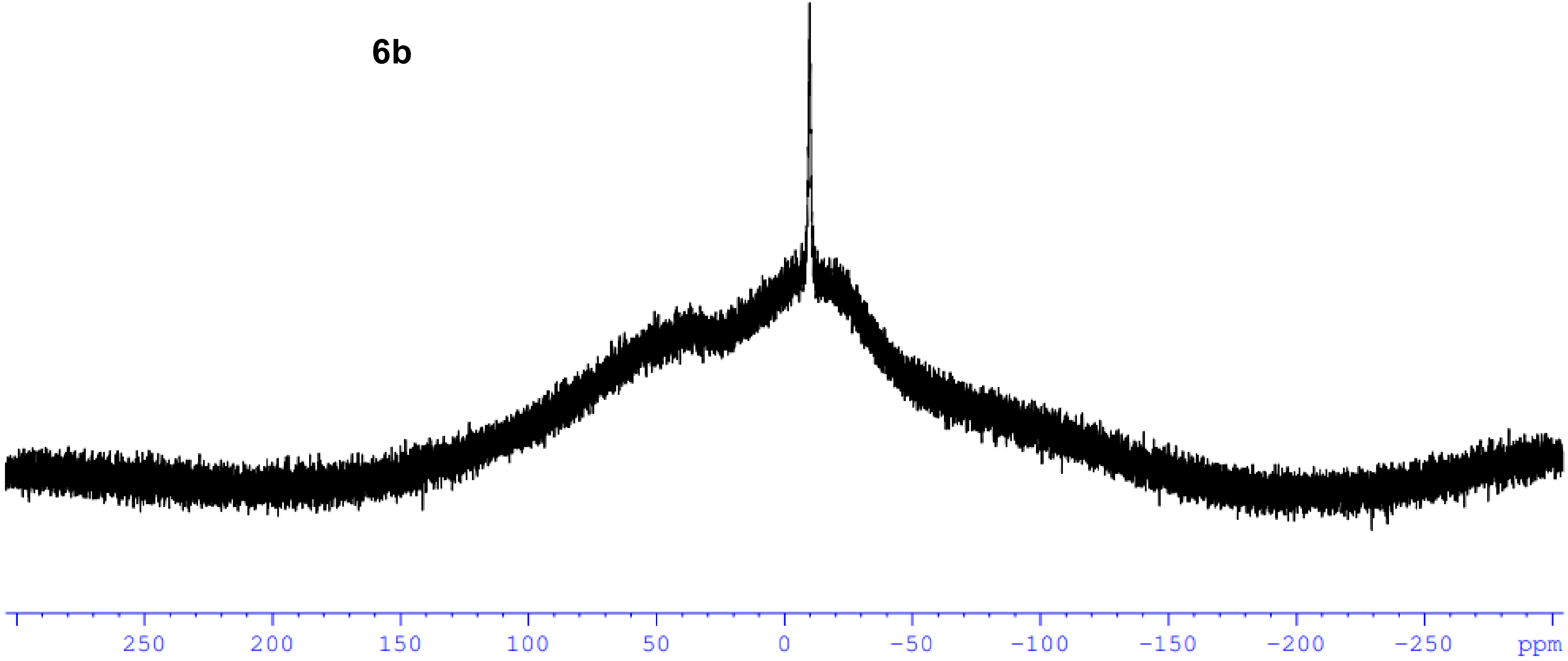
6b



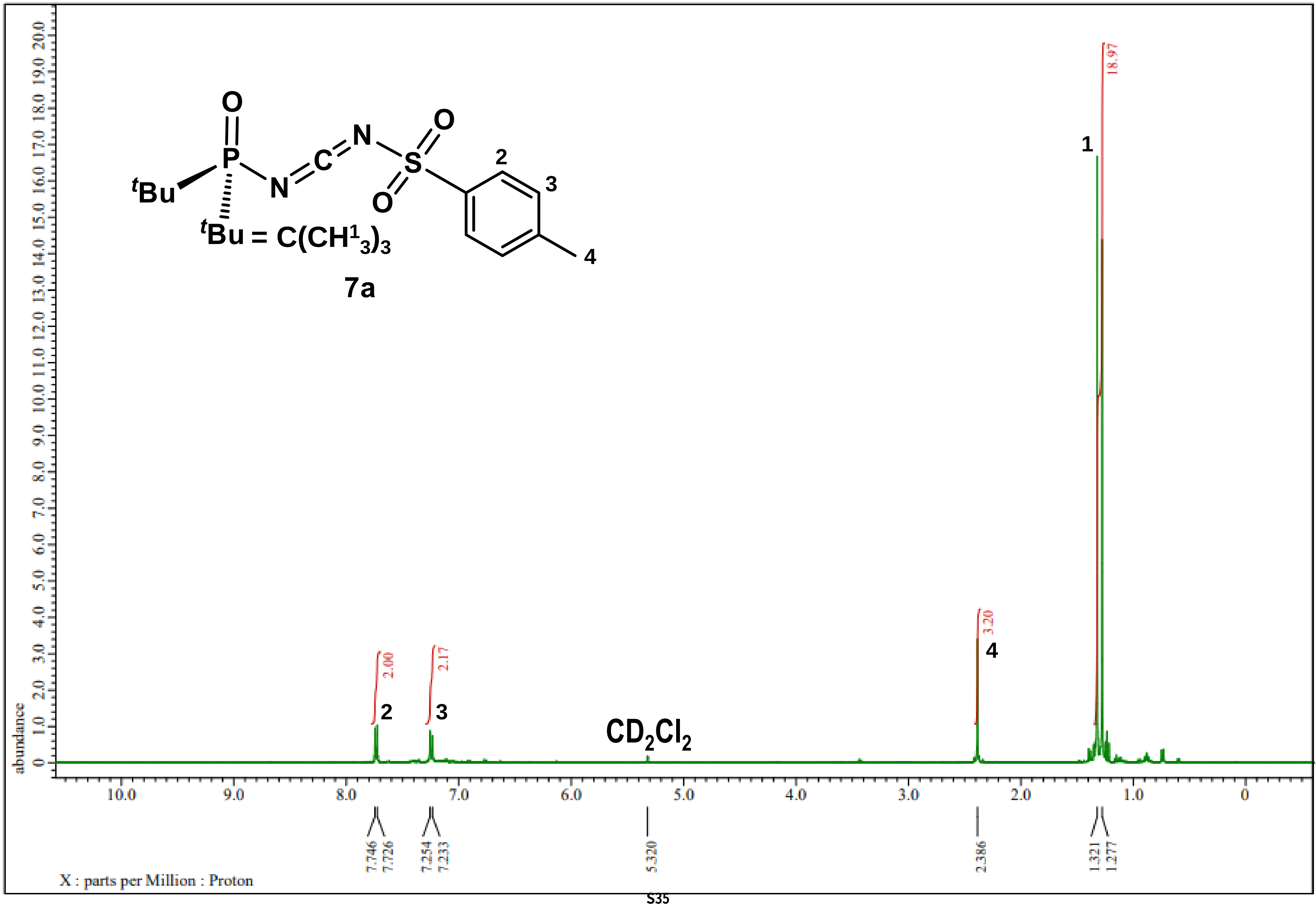
^{11}B NMR (128 MHz, CD$_2$Cl$_2$, −50 ºC)



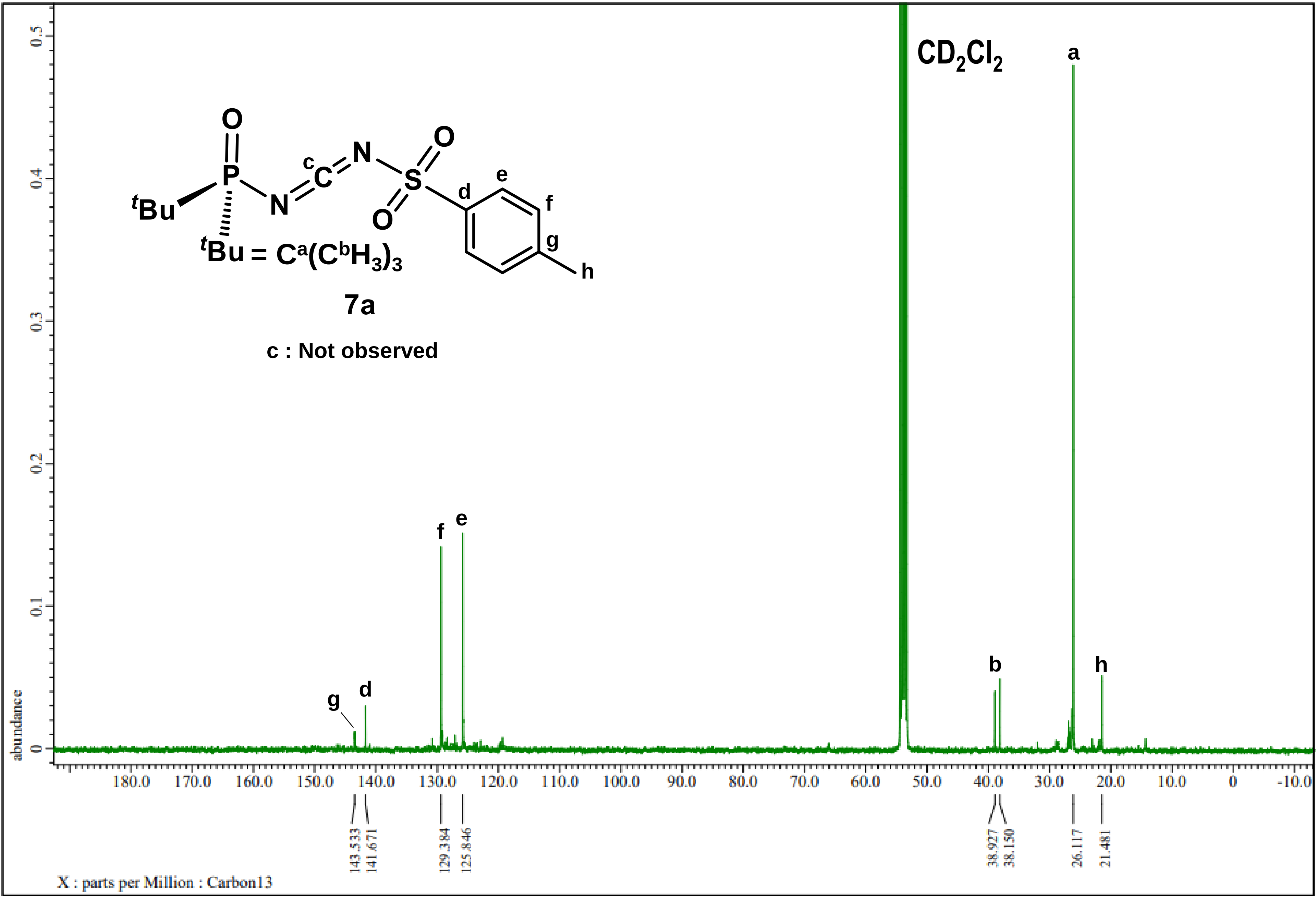
6b



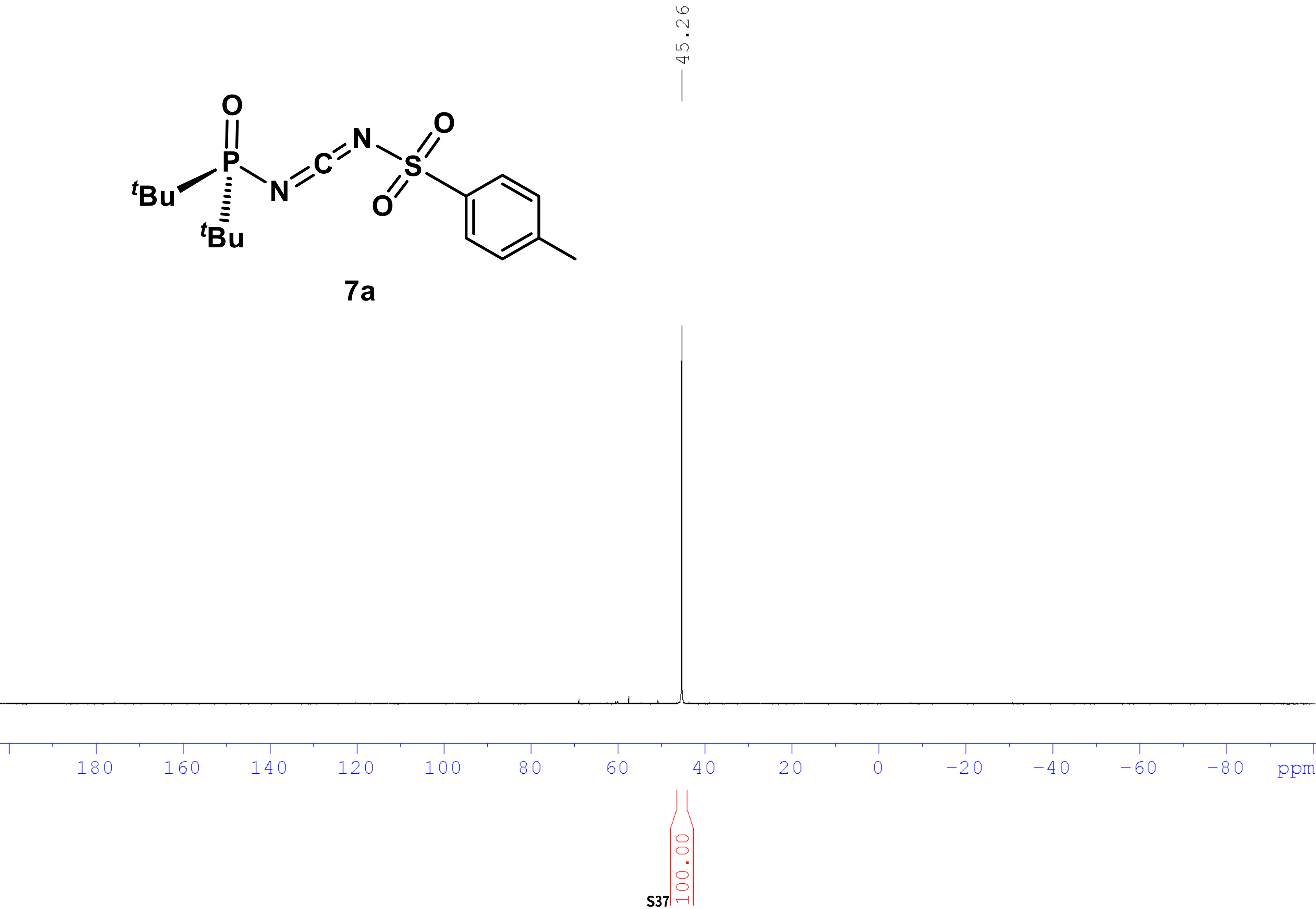
^{1}H NMR (400 MHz, CD_2Cl_2)



^{13}C {^{1}H} NMR (100 MHz, CD$_2$Cl$_2$)

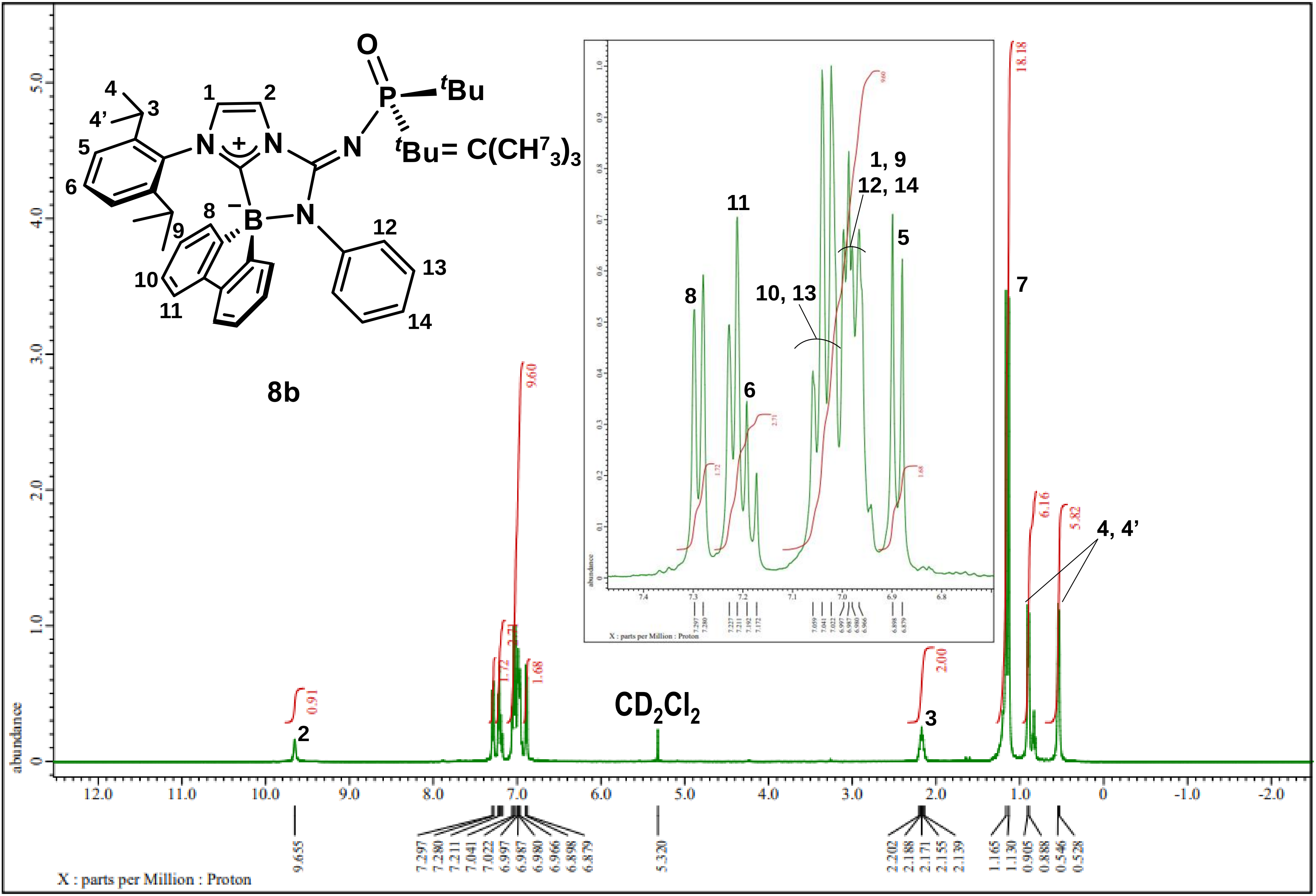


^{31}P {^{1}H} NMR (162 MHz, CD$_2$Cl$_2$)

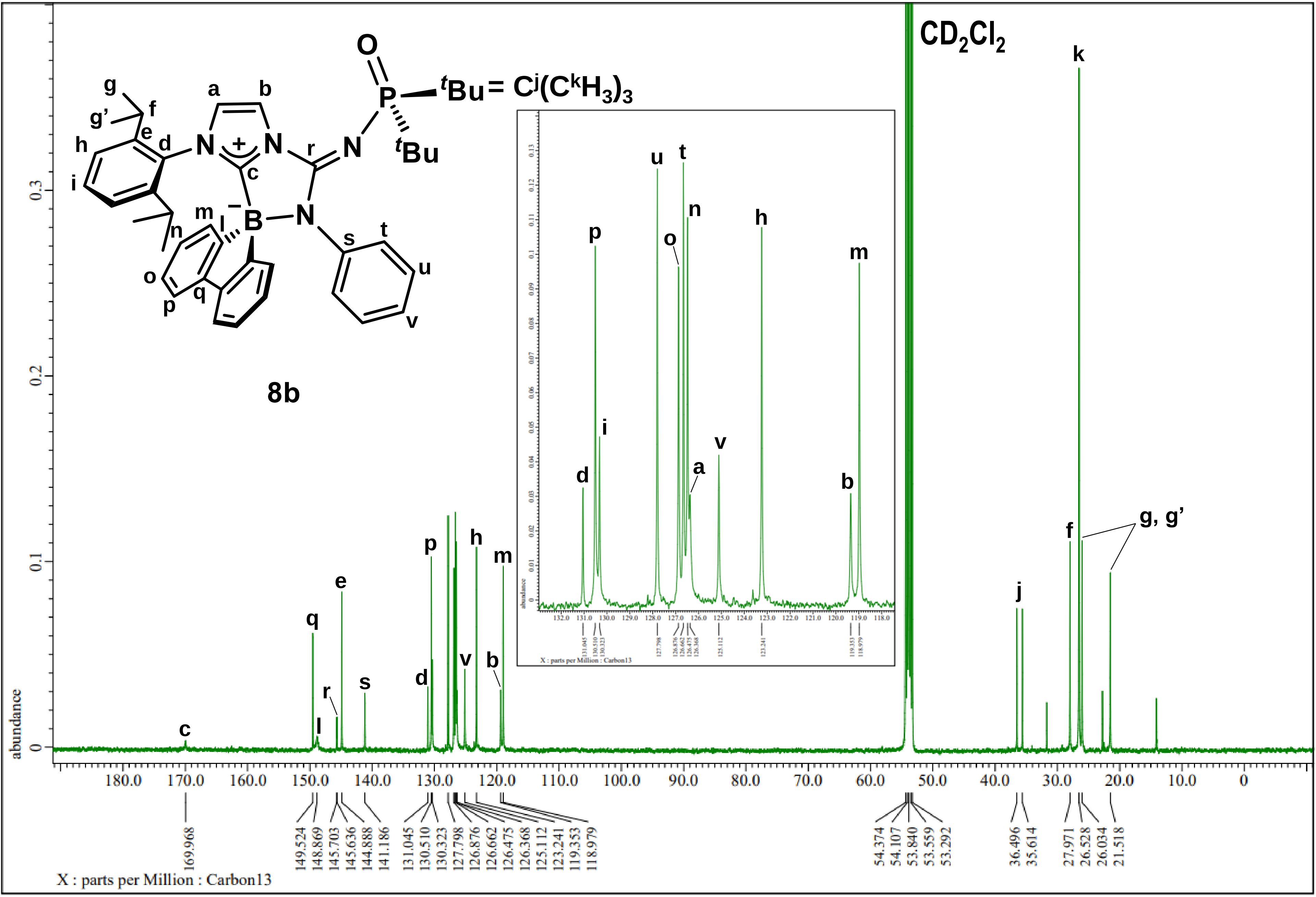


7a

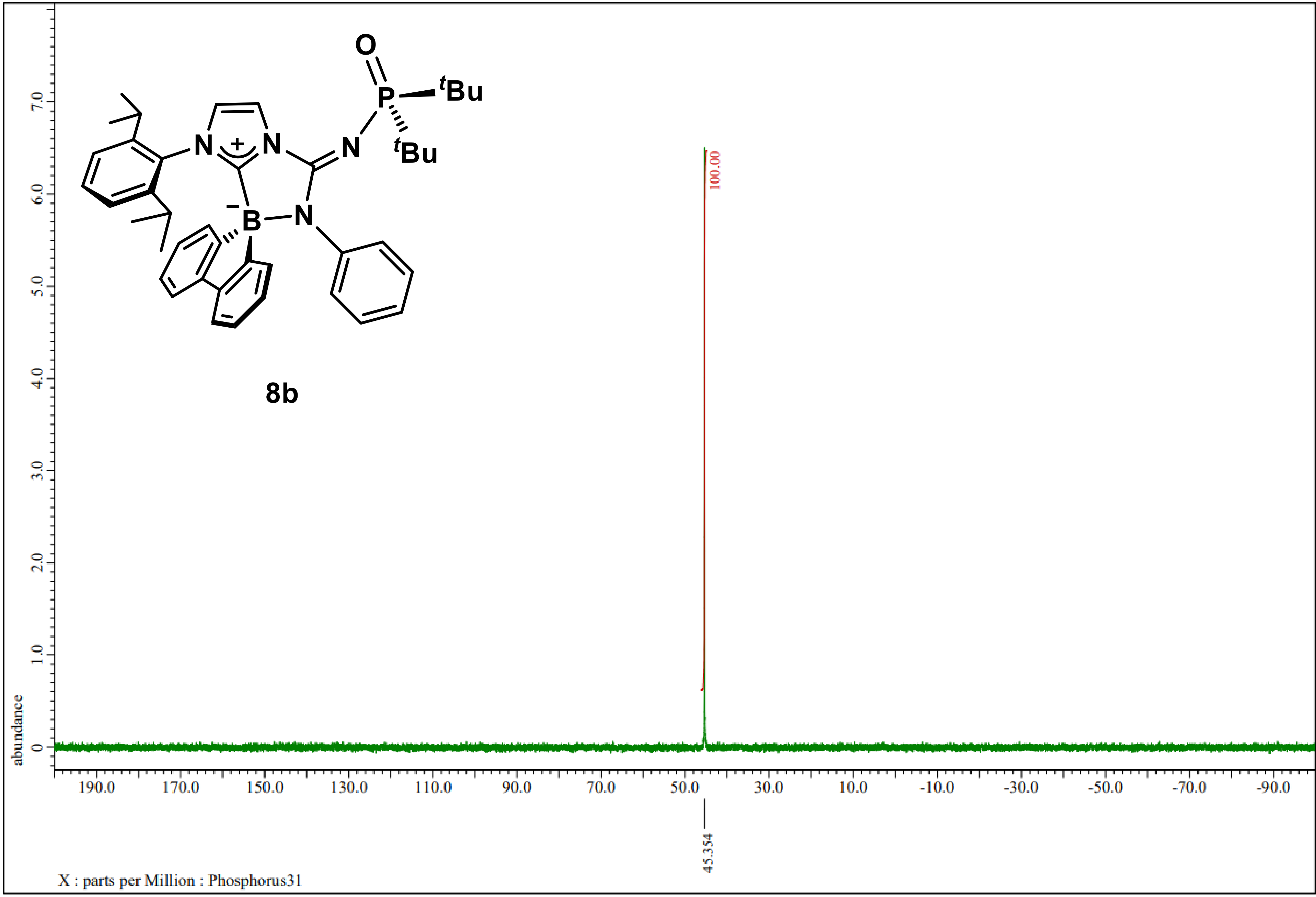
^{1}H NMR (400 MHz, CD_2Cl_2, −50 °C)



^{13}C {^{1}H} NMR (100 MHz, CD$_2$Cl$_2$, −50 ºC)

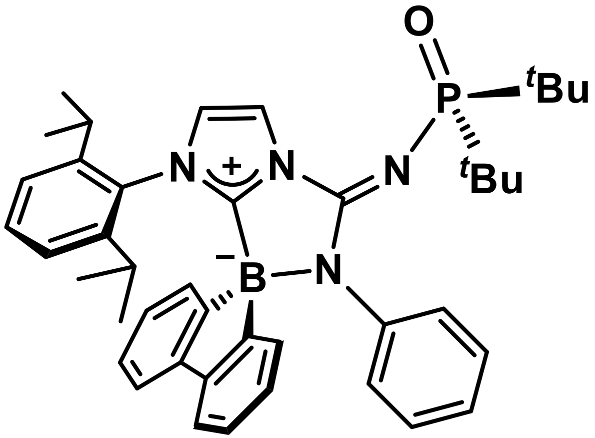

8b

$^{31}P\ \{^1H\}$ NMR (162 MHz, CD_2Cl_2, − 50 ºC)



8b

^{11}B NMR (128 MHz, CD$_2$Cl$_2$, −50 ºC)



8b