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Electronic Supplementary Information for

Dinitrogen-derived (diarylboryl)diazenido Complexes with Differing Coordination to the Thallium Cation

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I. General Information

All manipulations were carried out under a dry and oxygen free argon or dinitrogen atmosphere using Schlenk techniques and a Jacomex glove box. The water and oxygen levels were kept at less than 1.0 ppm and 0.5 ppm respectively. Glassware was oven- or flame-dried before use. Solvents were pre-dried (toluene and *n*-pentane by passing through a Puresolv MD 7 solvent purification machine), degassed by freeze-pump-thaw cycles, dried with molecular sieves and stored in the glove box. C_6D_6 and C_6D_5Cl (purchased from Eurisotop) was degassed by freeze-pump-thaw cycles, dried with molecular sieves and stored in the glove box. ^{1}H, ^{13}C, ^{11}B, ^{19}F , and ^{31}P NMR spectra were recorded in C_6D_6 or C_6D_5Cl using NMR tubes equipped with J. Young valves on a Bruker Avance III 400 spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and were referenced to the residual solvent resonance as the internal standard for ^{1}H and ^{13}C NMR experiments. ^{11}B and ^{31}P NMR spectra were calibrated according to the IUPAC recommendation.[S1] Data are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet), coupling constant (Hz), assignment and integration. Infrared (IR) spectra were recorded in the glove box on an Agilent Cary 630 FT-IR spectrophotometer equipped with ATR or transmission modules and are reported in wavenumbers (cm^{-1}) with (s) indicating strong absorption. Elemental analyses were performed on samples sealed in tin capsules under dinitrogen by the Analytical Service of the Laboratoire de Chimie de Coordination; results are the average of two independent measurements. *trans*-$[W(L)_2(N_2)_2]$ (L = dppe, **1^{Ph}**;[S2] L = depe, **1^{Et}**[S3]), $B(Cl)(R)_2$ (R = C_6F_5,[S4] mesityl {Mes}[S5]) and $TlBAr^F_4$ (Ar^F = 3,5-$(CF_3)_2C_6H_3$)[S6] were prepared according to reported procedures. Unless otherwise noted, other reagents were purchased from commercial suppliers and used without further purification.

II. Syntheses and Characterization of New Compounds

II.1. Synthesis and characterization of the complex [W(Cl){N_2BMes_2}(dppe)$_2$] (2^{Ph})

In a glove box, the dinitrogen complex *trans*-$[W(dppe)_2(N_2)_2]$ (**1^{Ph}**, 31 mg, 30 µmol) was weighed in a 4-mL glass vial and dissolved in C_6D_6 (0.5 mL). Dimesityl(chloro)borane (26 mg, 90 µmol, 3 equiv) was added at room temperature to the orange C_6D_6 solution of **1^{Ph}** in one portion. The mixture was then transferred to an NMR tube equipped with a J. Young valve and was irradiated at 365 nm for 18 days. A conversion of ca. 40% to the boryldiazenido-chloro complex was recorded according to ^{31}P NMR analysis. Single crystals spontaneously grew in the NMR tube upon standing at room temperature for a few days. They were recovered by decantation and submitted to X-ray diffraction and IR spectroscopy analyses.

Yellow crystals, isolated yield 30% (11 mg, 9 µmol). The collected amount of crystals were not sufficient to perform other analyses than X-ray diffraction and IR spectroscopy; NMR spectra were recorded from the crude mixture that contains **1^{Ph}** and $B(Cl)Mes_2$. **^{1}H NMR** (400 MHz, C_6D_6) δ = 7.55–7.44 (m, 8H, **Ar**), 7.25–7.15 (m, overlaps with signals of **1^{Ph}**, 12 H, **Ar**), 6.92 (t, *J* = 7.2 Hz, 4H, **Ar**), 6.89–6.81 (m, 16H, **Ar**), 6.79 (s, overlaps with signals of $B(Cl)Mes_2$, *m*-**Ar**, 4H), 2.70–2.53 (m, 8H, P-C**H$_2$**-C**H$_2$**-P), 2.25 (s, 6H, *p*-Ar-C**H$_3$**), 1.97 (s, 12H, *o*-Ar-C**H$_3$**). **^{11}B NMR** (128 MHz, C_6D_6) δ = 70.7 ($B(Cl)Mes_2$). **^{13}C NMR** (101 MHz, C_6D_6) δ = 134.0 (td, *J* = 38.1, 4.9 Hz, **Ar**), 133.1–132.5 (m, *o*-**Ar^{Mes}**), 129.1 (s, *p*-**Ar^{Mes}**), 30.6–29.9

(m, P-**C**H_2-**C**H_2-P), 22.9 (s, *p*-Ar-**C**H_3), 21.1 (s *o*-Ar-**C**H_3). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6) δ 37.2 ($^1J_{WP}$ = 292.8 Hz). **IR** (ATR) ν/cm^{-1} = 3054, 2916, 1948, 1602, 1433, 1395, 1235, 1197, 1093, 846, 809, 742.

II.2. General procedure for the synthesis of complexes [W(Cl){$N_2B(Ar)_2$}{$R_2P(CH_2)_2PR_2$}$_2$] ({Ar,R} = {Mes,Et}, 2^{Et}; {Ar,R} = {C_6F_5,Ph}, 3^{Ph}; {Ar,R} = {C_6F_5,Et}, 3^{Et}).

In a glove box, the dinitrogen complex *trans*-[W{$R_2P(CH_2)_2PR_2$}$_2$(N_2)$_2$] (**1^R** with R = Ph or Et, 30 µmol) is weighed in a 4-mL glass vial and dissolved in C_6D_6 (0.5 mL). The diaryl(chloro)borane (30 µmol, 1 equiv) is added at room temperature to the orange C_6D_6 solution of **1^R** in one portion. The solution is then stirred vigorously for 5 min, time during which color change (from orange to either red or green) and gas evolution (N_2) are observed. The mixture is then transferred to an NMR tube equipped with a J. Young valve and analyzed by NMR spectroscopy to check for the complete formation of the *trans*-chloro boryldiazenido complex **2^{Et}**, **3^{Ph}** or **3^{Et}**. Back to the glove box, the mixture is transferred from the NMR tube to a 4-mL glass vial. The NMR tube is rinsed with a minimal amount of toluene that is next added to the reaction solution in the vial. The latter is layered with pentane (3 mL) and the resulting mixture is kept at – 40 °C over few days, affording crystals of **2^{Et}**, **3^{Ph}** or **3^{Et}**. After removal of the supernatant, part of the crystalline material is submitted to an X-ray diffraction analysis. The rest is washed with pentane (2 × 1 mL) and dried under vacuum, affording **2^{Ph}**, **2^{Et}**, **3^{Ph}** or **3^{Et}** as a pure compound.

II.3. Characterization of the complexes [W(Cl){$N_2B(Ar)_2$}{$R_2P(CH_2)_2PR_2$}$_2$] ({Ar,R} = {Mes,Et}, 2^{Et}; {Ar,R} = {C_6F_5,Ph}, 3^{Ph}; {Ar,R} = {C_6F_5,Et}, 3^{Et}).

II.3.1 [W(Cl){N_2BMes_2}(depe)$_2$] (2^{Et})

Yellow crystals, isolated yield 68% (18 mg, 20 µmol). **^{1}H NMR** (400 MHz, C_6D_6) δ = 6.78 (s, *m*-Ar, 4H), 2.45 (s, 12H, *o*-Ar-C**H_3**), 2.23 (s, 6H, *p*-Ar-C**H_3**), 2.18 – 2.04 (m, 8H, CH_3-C**H_2**-), 1.84 – 1.64 (m, 8H, CH_3-C**H_2**-), 1.47 (t, *J* = 7.3 Hz, 8H, P-C**H_2**-C**H_2**-P), 1.04 – 0.93 (m, 24H, C**H_3**-CH_2-). **^{11}B NMR** (128 MHz, C_6D_6) no signal could be detected. **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6) δ 35.6 ($^1J_{WP}$ = 143.2 Hz). **^{13}C NMR** (101 MHz, C_6D_6) δ = 145.0 (*ipso*-**Ar**^{Mes}), 140.5 (*o*-**Ar**^{Mes}), 135.3 (*p*-**Ar**^{Mes}), 127.9 (*m*-**Ar**^{Mes}), 24.6 (q, $^1J_{CP}$ = 9.3 Hz, P-**C**H_2-**C**H_2-P), 23.9 (*o*-Ar-**C**H_3), 21.3 (*p*-Ar-**C**H_3), 18.6 (dquint., $^1J_{CP}$ = 47.0, $^3J_{CP}$ = 5.9 Hz, CH_3-**C**H_2-), 9.1 (d, $^2J_{CP}$ = 50.7 Hz, **C**H_3-CH_2-). **IR** (ATR) ν/cm^{-1} = 2933, 2900, 2875, 1604, 1449, 1413, 1241, 1197, 1141, 1027, 831, 807, 728, 663. **Elem. Anal.** Calcd. for $C_{38}H_{70}BClN_2P_4W$: C, 50.21; H, 7.76; N, 3.08; Found: C, 50.48; H, 6.96; N, 3.09.

II.3.2 [W(Cl){$N_2B(C_6F_5)_2$}(dppe)$_2$] (3^{Ph})

Yellow crystals, isolated yield 71% (29 mg, 21 µmol). **^{1}H NMR** (400 MHz, C_6D_6) δ = 7.41 – 7.33 (m, 8H, Ar), 7.25 – 7.18 (m, 8H, Ar), 6.96 – 6.89 (m, 12H, Ar), 6.82 (t, J_{HH} = 7.5 Hz, 12H, Ar), 2.58 – 1.36 (m, 8H P-C**H_2**-C**H_2**-P). **^{11}B NMR** (128 MHz, C_6D_6) no signal could be detected. **^{19}F NMR** (377 MHz, C_6D_6) δ = – 132.4 (dd, J_{FF} = 26.4, J_{FF} = 9.0 Hz, 4F_{ortho}), –156.7 (t, J_{FF} = 20.9 Hz, 2F_{para}), –163.2 - –163.5 (m, 4F_{meta}). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6) δ = 34.6 (J_{WP} = 285 Hz). **IR** (ATR) ν/cm^{-1} = 3051, 1642, 1510, 1465, 1432, 1381, 1296, 1082, 965, 805, 738, 693. **Elem. Anal.** Calcd. for $C_{64}H_{48}BClF_{10}N_2P_4W$: C, 55.34; H, 3.48; N, 2.02; Found: C, 55.44; H, 3.07; N, 2.02.

II.3.1 [W(Cl){$N_2B(C_6F_5)_2$}(depe)$_2$] (3^{Et})

Green crystals, isolated yield 81% (24 mg, 24 µmol). **^{1}H NMR** (400 MHz, C_6D_6) δ = 1.95 –1.70 (m, 16H, CH_3-C**H_2**-), 1.43 – 1.22 (m, 8H, P-C**H_2**-C**H_2**-P), 1.03 (m, $^{3}J_{HH}$ = $^{3}J_{HP}$ = 9.8 Hz, 12H, C**H_3**-CH_2-), 0.91 (m, $^{3}J_{HH}$ = $^{3}J_{HP}$ = 9.8 Hz, 12H, C**H_3**-CH_2-). **^{11}B NMR** (128 MHz, C_6D_6) δ = 21.8. **^{19}F NMR** (377 MHz, C_6D_6) δ = –133.4 (dd, J_{FF} = 25.9, J_{FF} = 9.8 Hz, 4F$_{ortho}$), –157.1 (t, J_{FF} = 20.4 Hz, 2F$_{para}$), –163.7 (ddd, J_{FF} = 26.2, 20.3, 9.4 Hz, 4F$_{meta}$). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6) δ = 33.3 (J_{PW} = 282.5 Hz). **IR** (ATR) ν/cm^{-1} = 2961, 2938, 2904, 2881, 1642, 1511, 1463, 1378, 1290, 1117, 1080, 1030, 965, 846, 736, 695. **Elem. Anal.** Calcd. for $C_{32}H_{48}BClF_{10}N_2P_4W$: C, 38.25; H, 4.82; N, 2.79; Found: C, 38.64; H, 4.85; N, 2.73.

II.4. General procedure for the reaction of compounds 2^{Et}, 3^{Ph} and 3^{Et} with TlBAr$^{F}_4$

Caution: Thallium compounds are notoriously highly toxic, even by skin contact. Proper protective and disposal measures have to be taken by the experimenter.

In a glove box, the *trans*-chloro boryldiazenido complex (56 µmol) is weighed in a 4-mL glass vial and dissolved in C_6D_6 or C_6D_5Cl (0.5 mL). TlBAr$^{F}_4$ (56 µmol, 1.0 equiv) is added at room temperature to the solution in one portion. The resulting mixture is then stirred vigorously for 5 min, then transferred to an NMR tube equipped with a J. Young valve and analyzed by NMR spectroscopy to check for the complete conversion of the starting complex. The reaction of **3^{Et}** with TlBAr$^{F}_4$ did not show signs of adduct formation according to NMR analysis. The mixture is transferred in the glove box from the NMR tube to a 4-mL glass vial. The NMR tube was rinsed with a minimal amount of toluene. Then pentane (2 mL) was added and the resulting mixture was kept at –40 °C over few days, affording crystals of the thallium adduct. After removal of the supernatant, part of the crystals are submitted to an X-ray diffraction analysis, while the rest is washed with pentane (2 × 1 mL) and dryed under vacuum, to give [**2^{Et}·Tl**]BAr$^{F}_4$ or [**3^{Ph}·Tl**]BAr$^{F}_4$ as a pure compound.

II.5. Characterization of the complexes [Tl(W{Cl}{$N_2B(R)_2$}{L}$_2$)]BAr$^{F}_4$ ({R,L} = {Mes,depe} or {C_6F_5,dppe}) ([2^{Et}·Tl]BAr$^{F}_4$ and [3^{Ph}·Tl]BAr$^{F}_4$).

*II.5.1 [W(Cl)(NN(Tl){B(Mes)$_2$})(depe)$_2$]BAr$^{F}_4$ ([**2^{Et}·Tl**]BAr$^{F}_4$)*

Orange crystals, isolated yield 53% (33 mg, 29 µmol). **^{1}H NMR** (400 MHz, C_6D_5Cl) δ = 8.31–8.19 (m, 8H, *o*-Ar^{F}), 7.62 (s, 4H, *p*-Ar^{F}), 6.69 (s, 4H, *m*-Ar^{Mes}), 2.14 (s, 6H, *o*-C**H_3**), 2.06 (s, 12H, *p*-C**H_3**), 1.95 (m, 5H, CH_3-C**H_2**-), 1.76 (m, 5H, CH_3-C**H_2**-), 1.70–1.48 (m, 12H, P-C**H_2**-C**H_2**-P + CH_3-C**H_2**-P), 1.38 (m, 5H, CH_3-C**H_2**-P), 0.94 (d, *J* = 5.9 Hz, 24H, C**H_3**-CH_2-).**^{11}B NMR** (128 MHz, C_6D_5Cl) δ = –5.90 (BAr$^{F}_4$). **^{13}C NMR** (101 MHz, C_6D_5Cl) δ = 167.4 (q, J_{CB} = 49.8 Hz, *ipso*-Ar^{F}), 147.0 (s, *ipso*-Ar^{Mes}), 144.4 (s, *m*-Ar^{Mes}), 143.7 (s, *o*-Ar^{Mes}), 140.2 (s, *o*-Ar^{F}), 134.7 (s, *m*-Ar^{Mes}), 131.3 (s, C_{IV}-Ar^{F}), 128.5 (s, *o*-Ar^{F}), 122.7 (s, J_{CF} = 3.8 Hz, *p*-Ar^{F}), 27.9 (s, *o*- **C**H_3), 25.9 (s, *p*- **C**H_3), 23.5 (t, J_{CP} = 12.8 Hz, P-**C**H_2-**C**H_2-P). **IR** (ATR) ν/cm^{-1} = 2974, 1608, 1352, 1274, 1115, 885, 837, 743, 713, 682. **^{19}F NMR** (377 MHz, C_6D_5Cl) δ = –61.9 (s, CF_3). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_5Cl) δ = 31.3 (J_{PW} = 137.4 Hz). **Elem. Anal.** Calcd. for $C_{70}H_{82}B2ClF_{24}N_2P_4TlW$: C, 42.54; H, 4.18; N, 1.42; Found: C, 42.36; H, 3.95; N, 0.95.

*II.5.2 [W(ClTl){$N_2B(C_6F_5)_2$}(dppe)$_2$]BAr$^{F}_4$ ([**3^{Ph}·Tl**]BAr$^{F}_4$)*

Yellow crystals, isolated yield 50% (44 mg, 28 µmol). **^{1}H NMR** (400 MHz, C_6D_6) δ = 8.40 (m, 8H, *o*-Ar^{F}), 7.68 (s, 4H, *p*-Ar^{F}), 7.35 (m, 8H, *m*-Ar), 6.99–6.97 (m, 4H, *p*-Ar), 6.95 (s, 8H, *o*-Ar), 6.91–6.87 (m, 4H, *p*-Ar), 6.85 (m, 8H, *m*-Ar), 6.79 (m, 8H, *o*-Ar), 2.59 – 2.41 (m, 8H, P-C**H_2**-C**H_2**-P). **^{11}B NMR** (128 MHz,

C_6D_6) δ 23.5, – 5.9. **^{13}C NMR** (101 MHz, C_6D_6) δ = 162.8 (q, J_{CB} = 49.5 Hz, *ipso*-Ar^F), 135.5 (s, *o*-Ar^F), 133.8 (dt, J_{CP} = 21.9, 2.2 Hz, *m*-Ph), 130.3 (s, *o*-Ph), 129.6 (s, *p*-Ph), 128.6 (s, *p*-Ph), 127.9 (s, *o*-Ph),126.6 (C_{IV}-Ar^F), 123.9 (C_{IV}-Ar^F), 118.0 (m, *p*-Ar^F), 31.6 (quint, J_{CP} = 9.7 Hz, P-**C**H_2-**C**H_2-P). **IR** (ATR) ν/cm^{-1} = 3056, 1643, 1513, 1469, 1434, 1353, 1275, 1120, 967, 885, 838, 807, 741. **^{19}F NMR** (377 MHz, C_6D_6) δ = –62.0 (s, CF_3), –132.4 (dd, J_{FF} = 26.0, 9.1 Hz, $4F_{ortho}$), –155.7 (t, J_{FF} = 20.8 Hz, $2F_{para}$), –162.8 - –163.1 (m, $4F_{meta}$). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6) δ 35.9 (J_{WP} = 145 Hz). **Elem. Anal.** Calcd. for $C_{96}H_{60}B_2ClF_{34}N_2P_4TlW$ • 0.2 C_6D_6: C, 47.20; H, 2.44; N, 1.13; Found: C, 47.75; H, 3.05; N, 0.97.

III. Spectroscopic Data of New Compounds

III.1. $[W(Cl)\{N_2BMes_2\}(dppe)_2]$ (2^{Ph}) in the reaction mixture.

Figure S1. ^1H NMR (400 MHz, C_6D_6).

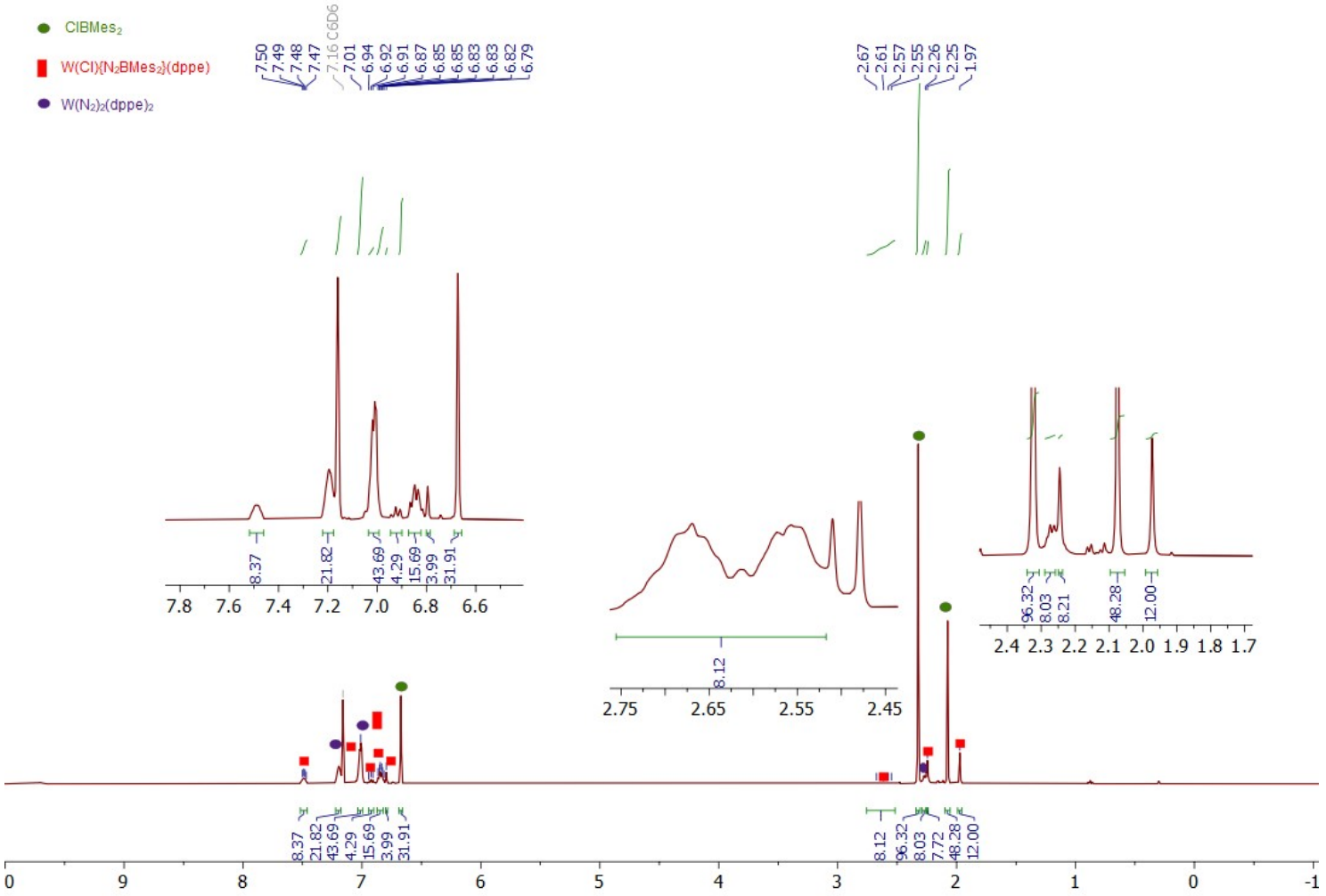


Figure S2. ^{11}B NMR (128 MHz, C_6D_6).

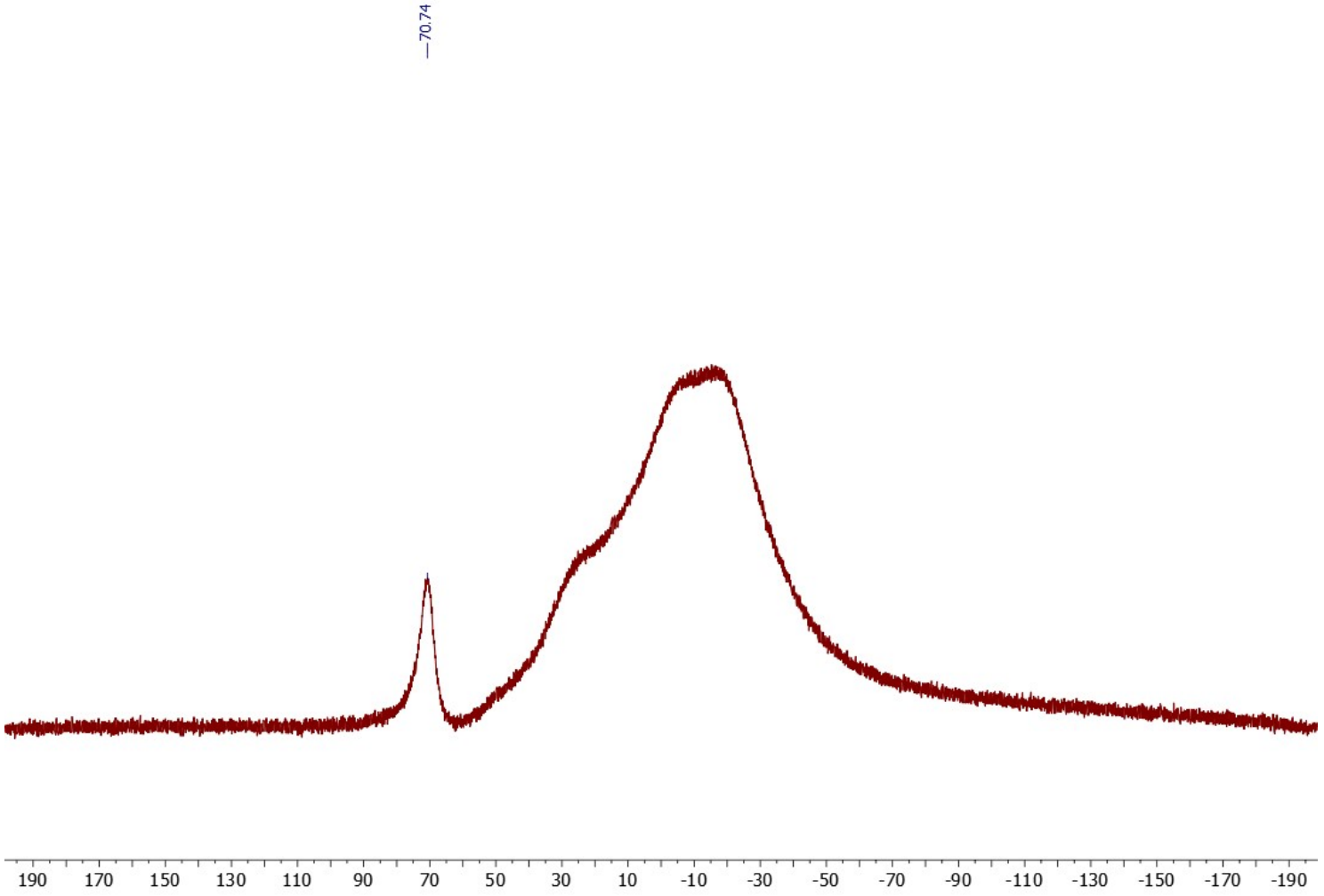


Figure S3. $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6).

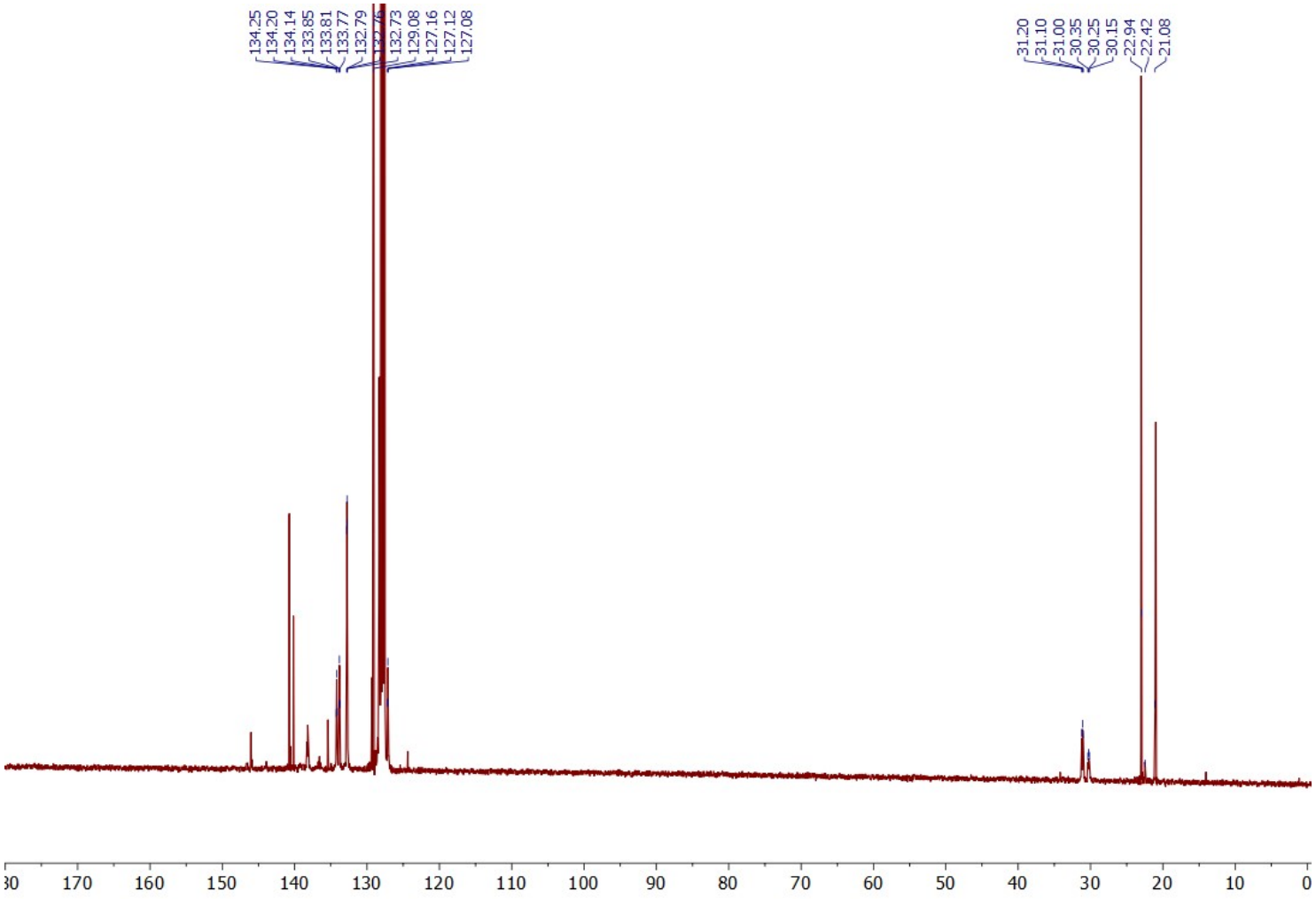


Figure S4. ^{31}P NMR (162 MHz, C_6D_6).

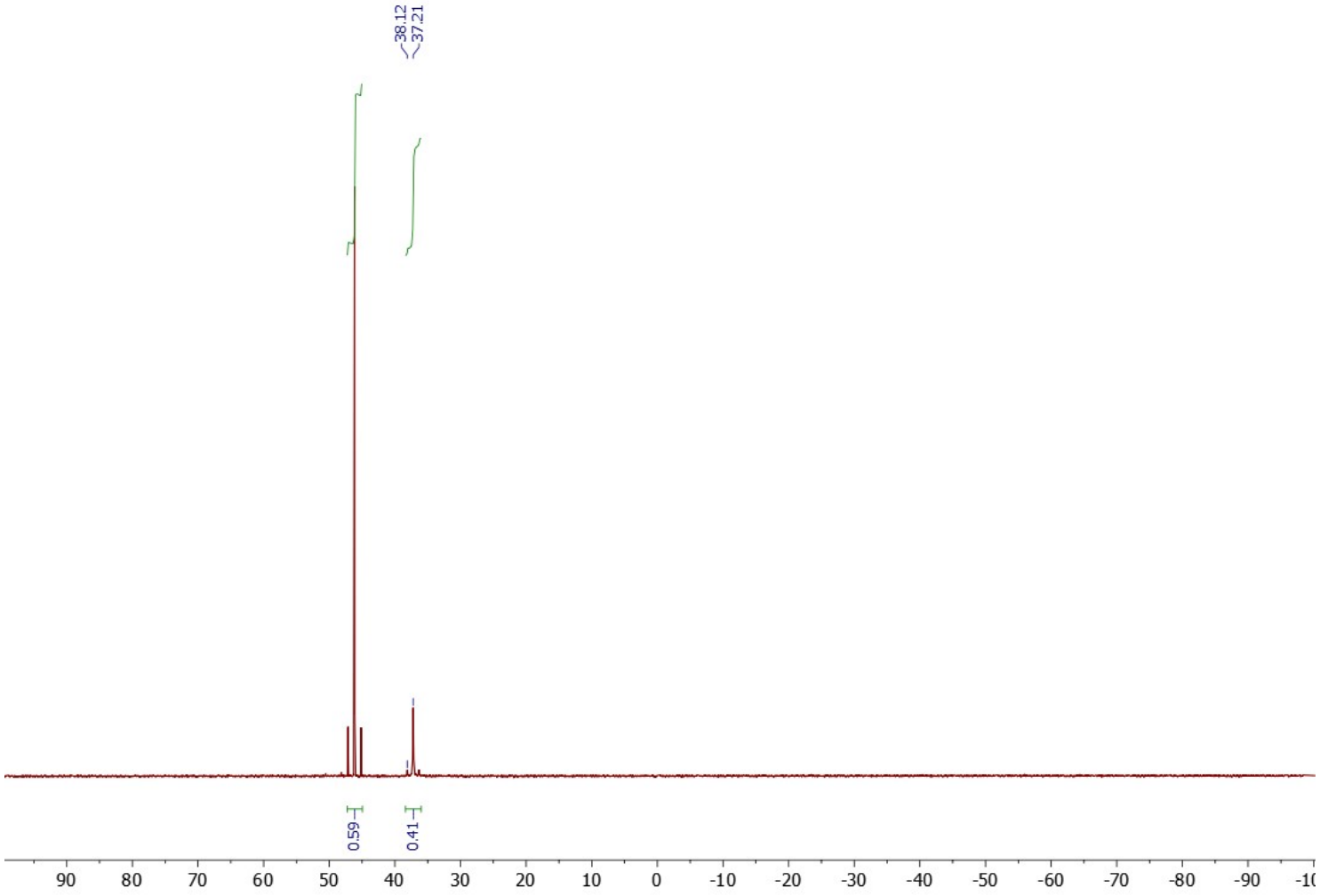
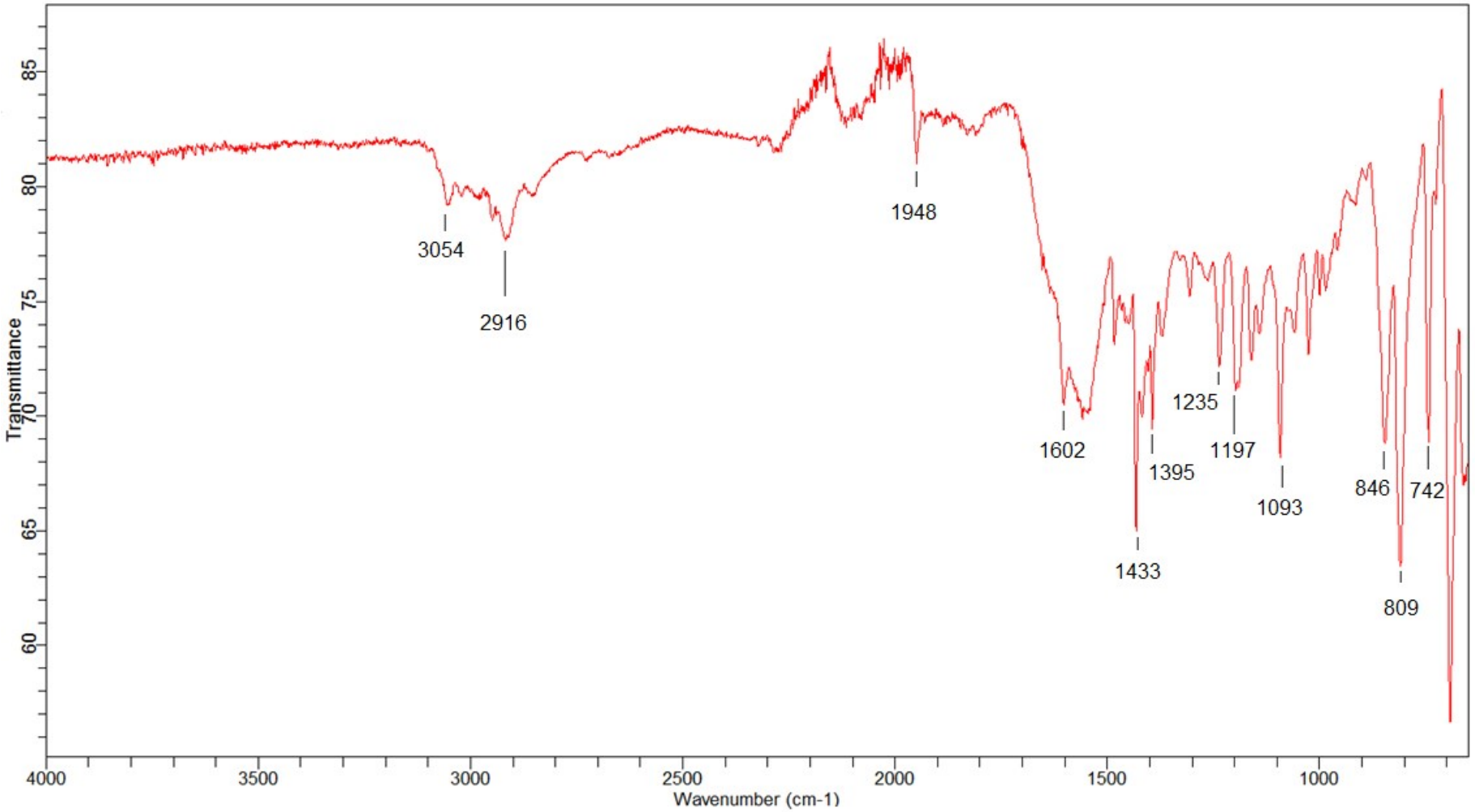


Figure S5. FT-IR (ATR, 400–4000 cm^{-1} range) of crystalline [W(Cl){N_2BMes_2}$(dppe)_2$] (**2^{Ph}**).



III.2. [W(Cl){N_2BMes_2}(depe)$_2$] (2^{Et})

Figure S6. ^{1}H NMR (400 MHz, C_6D_6).

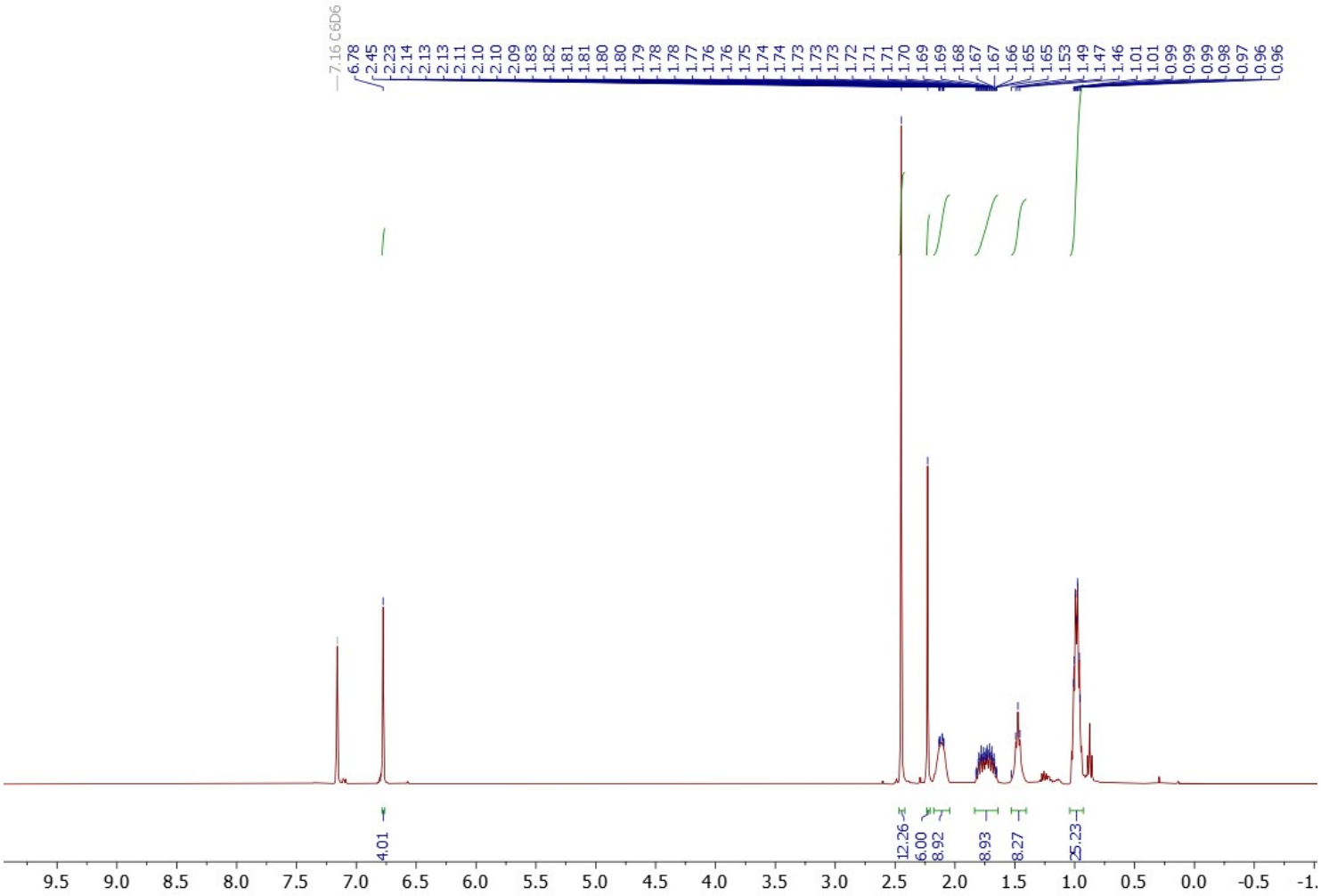


Figure S7. ^{11}B NMR (128 MHz, C_6D_6).

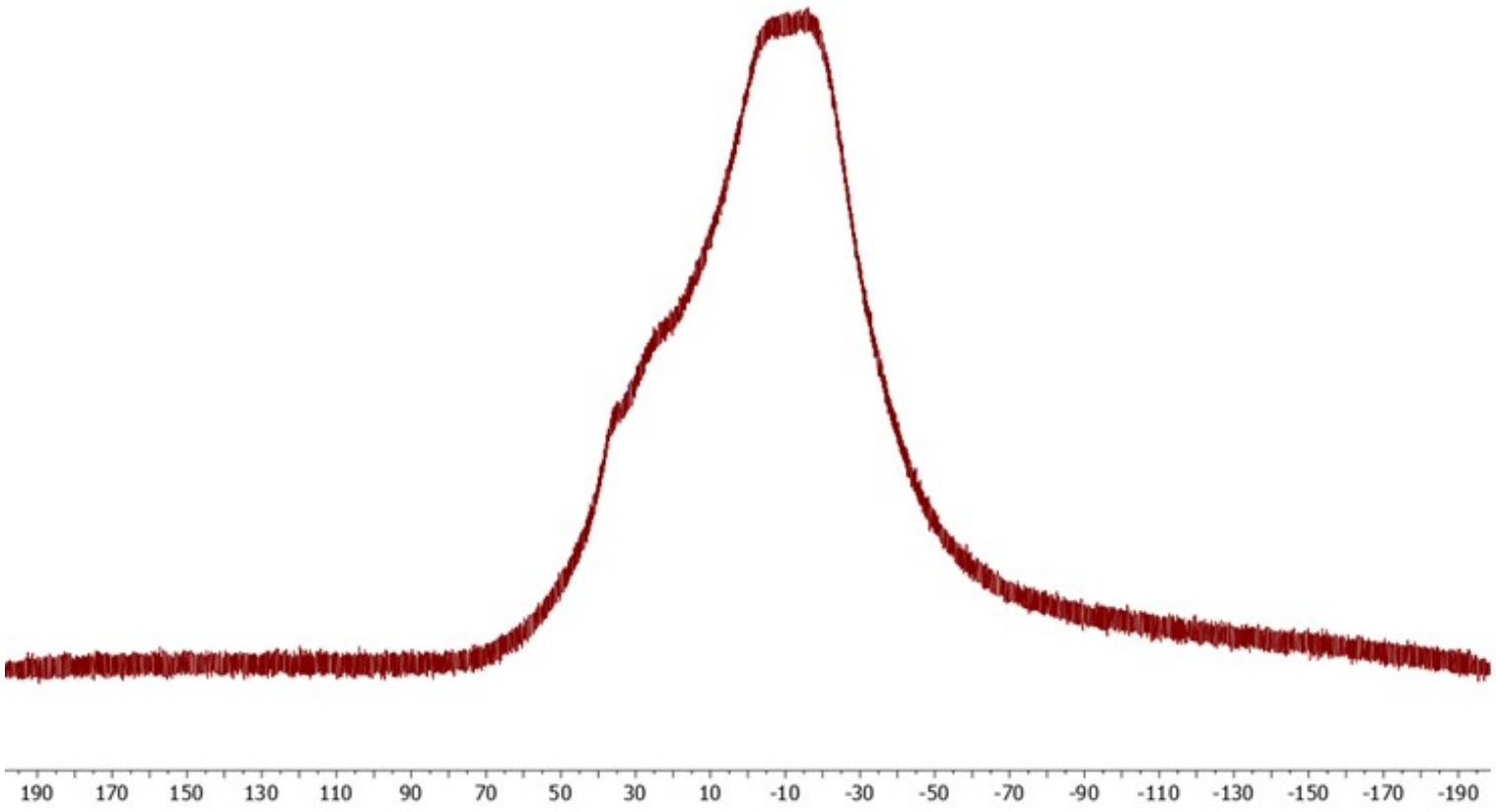


Figure S8. $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6).

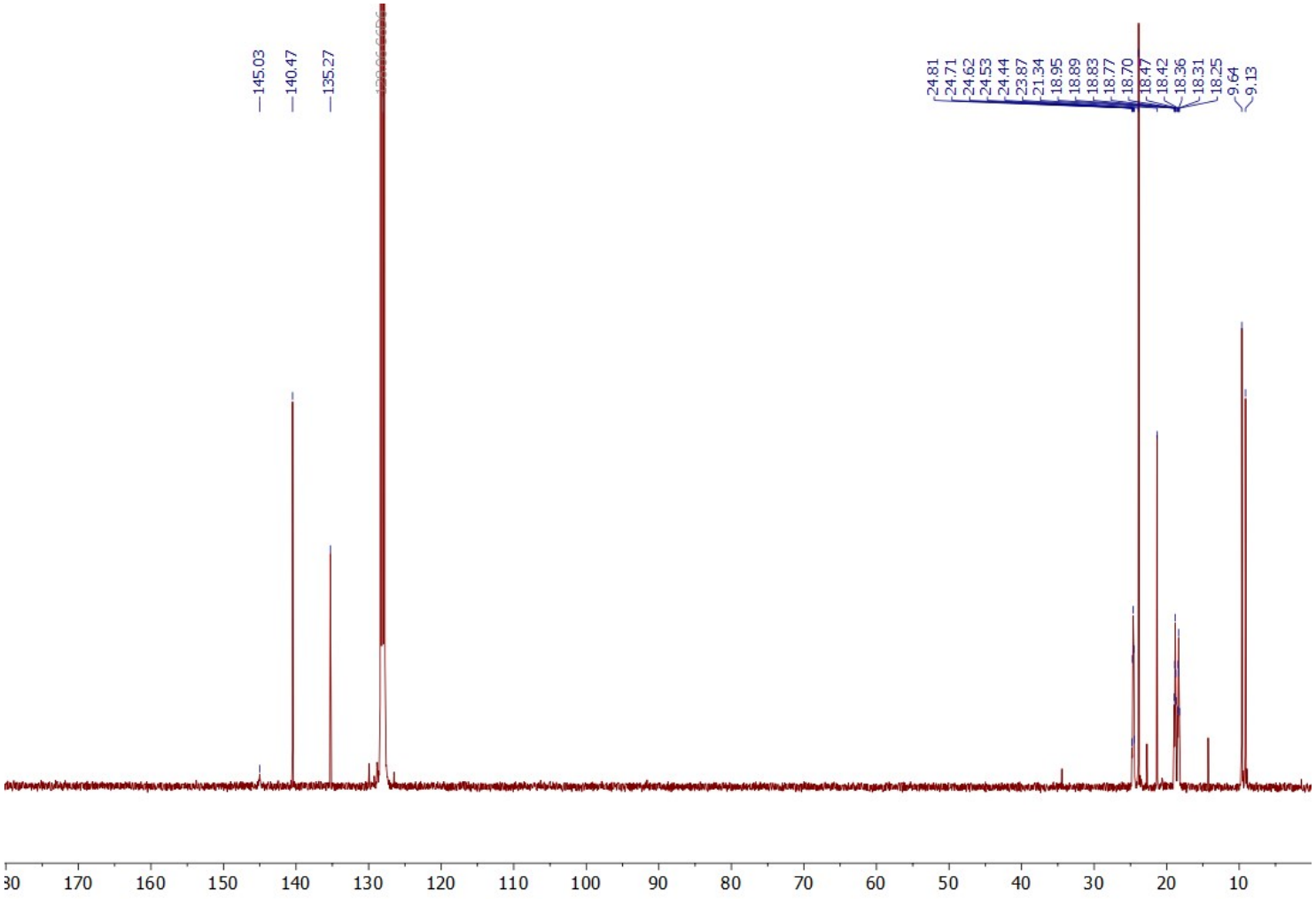


Figure S9. ^{31}P NMR (162 MHz, C_6D_6).

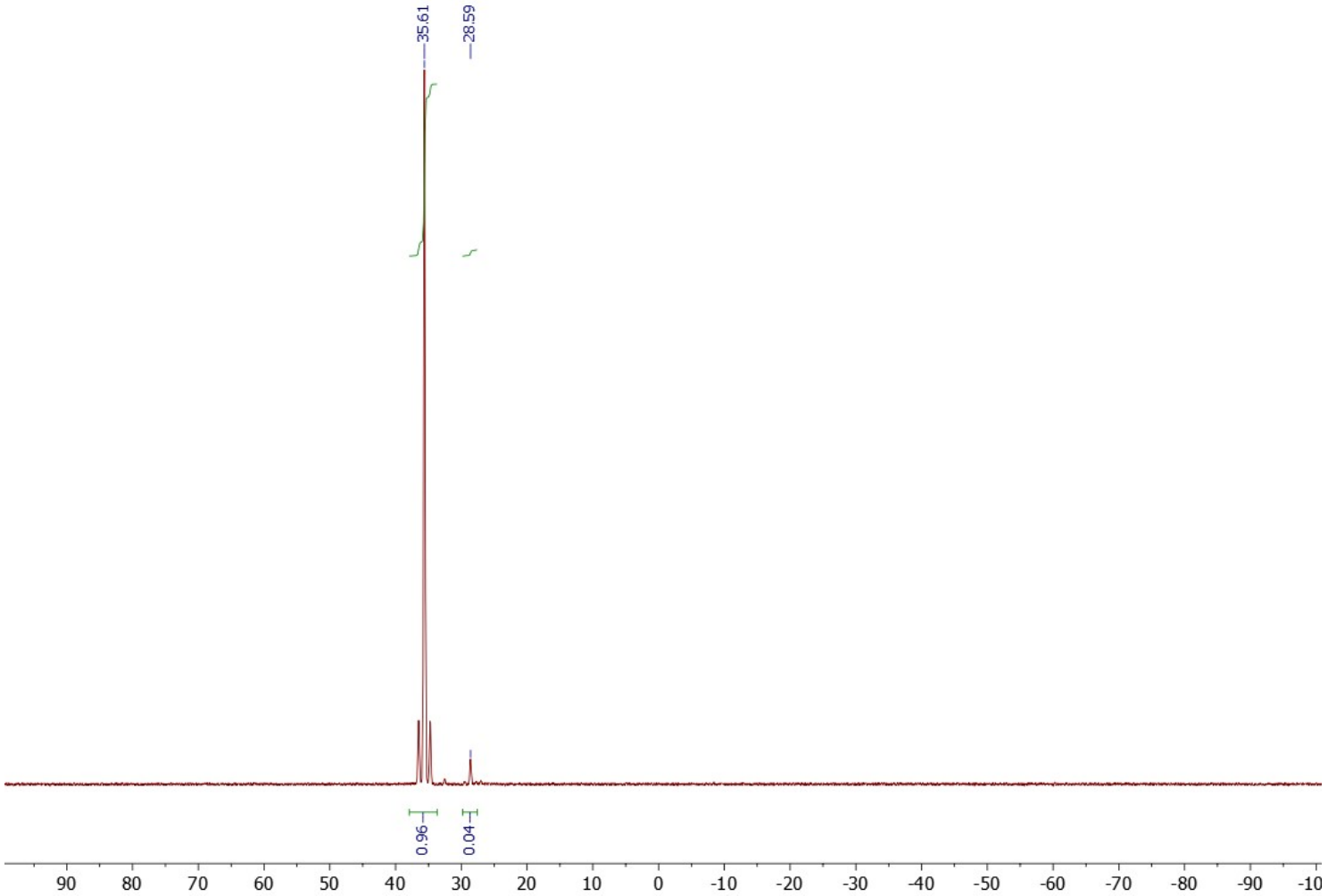
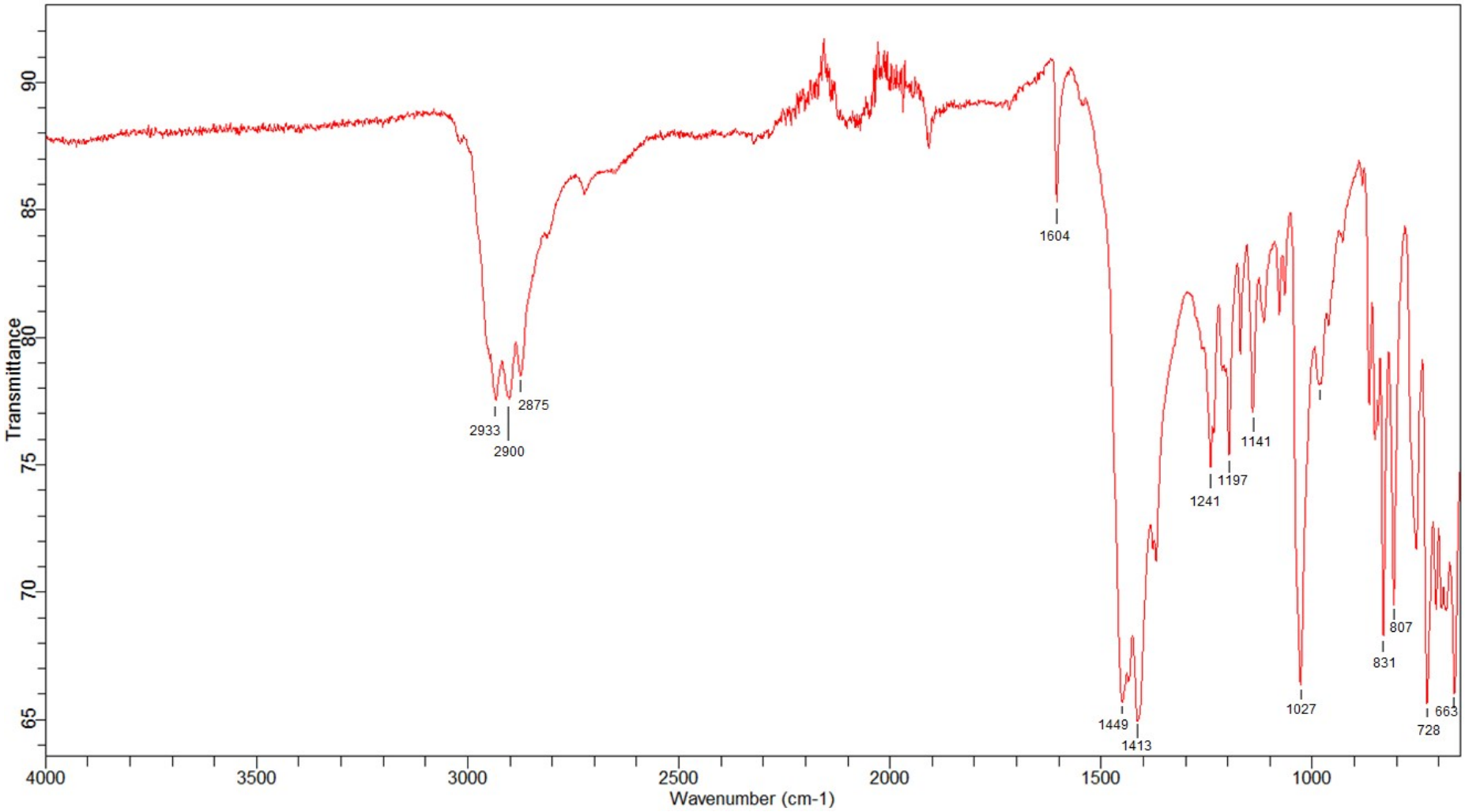


Figure S10. FT-IR (ATR, 400–4000 cm^{-1} range).



III.3. $[W(Cl)\{N_2B(C_6F_5)_2\}(dppe)_2]$ (3^{Ph})

Figure S11. ^1H NMR (400 MHz, C_6D_6).

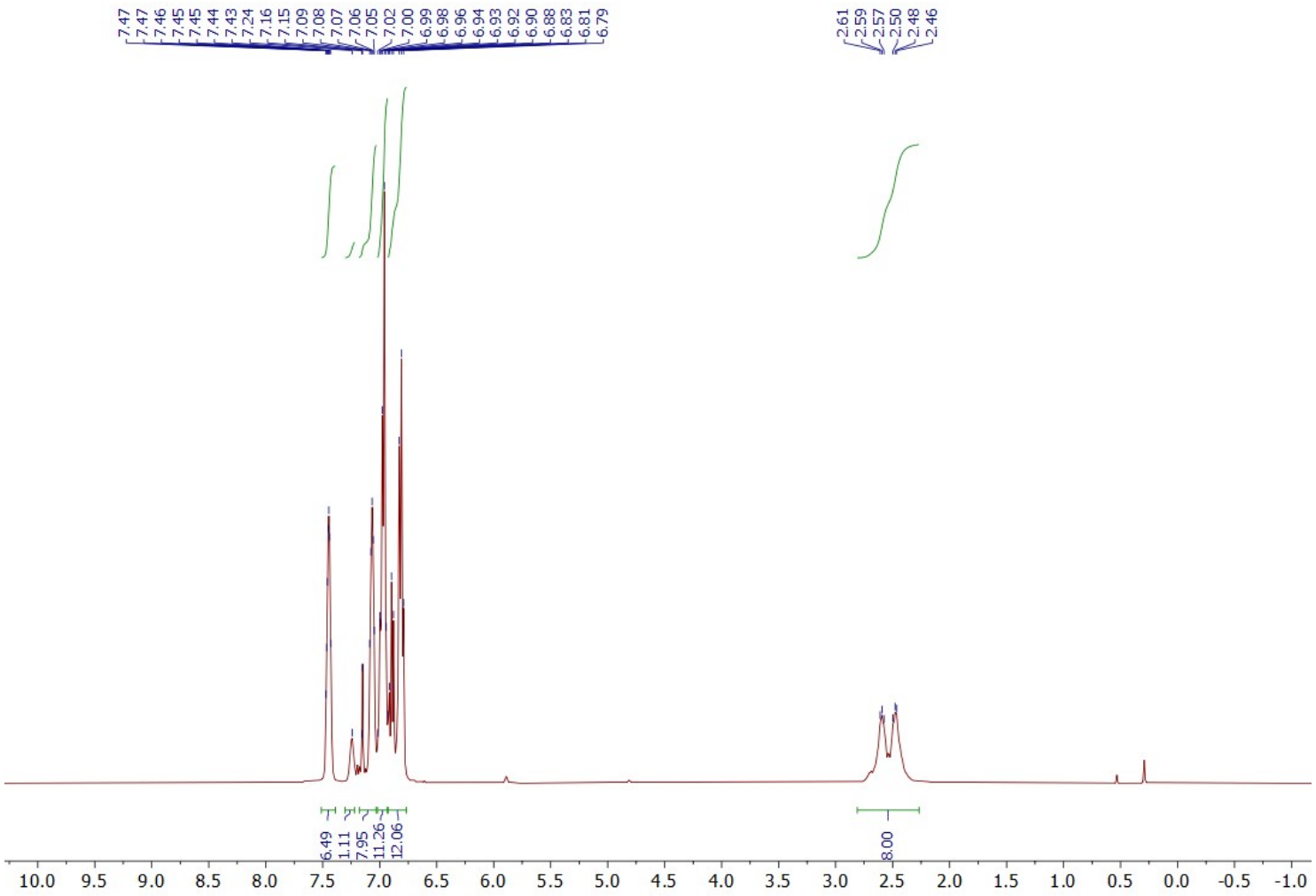


Figure S12. ^{11}B NMR (128 MHz, C_6D_6).

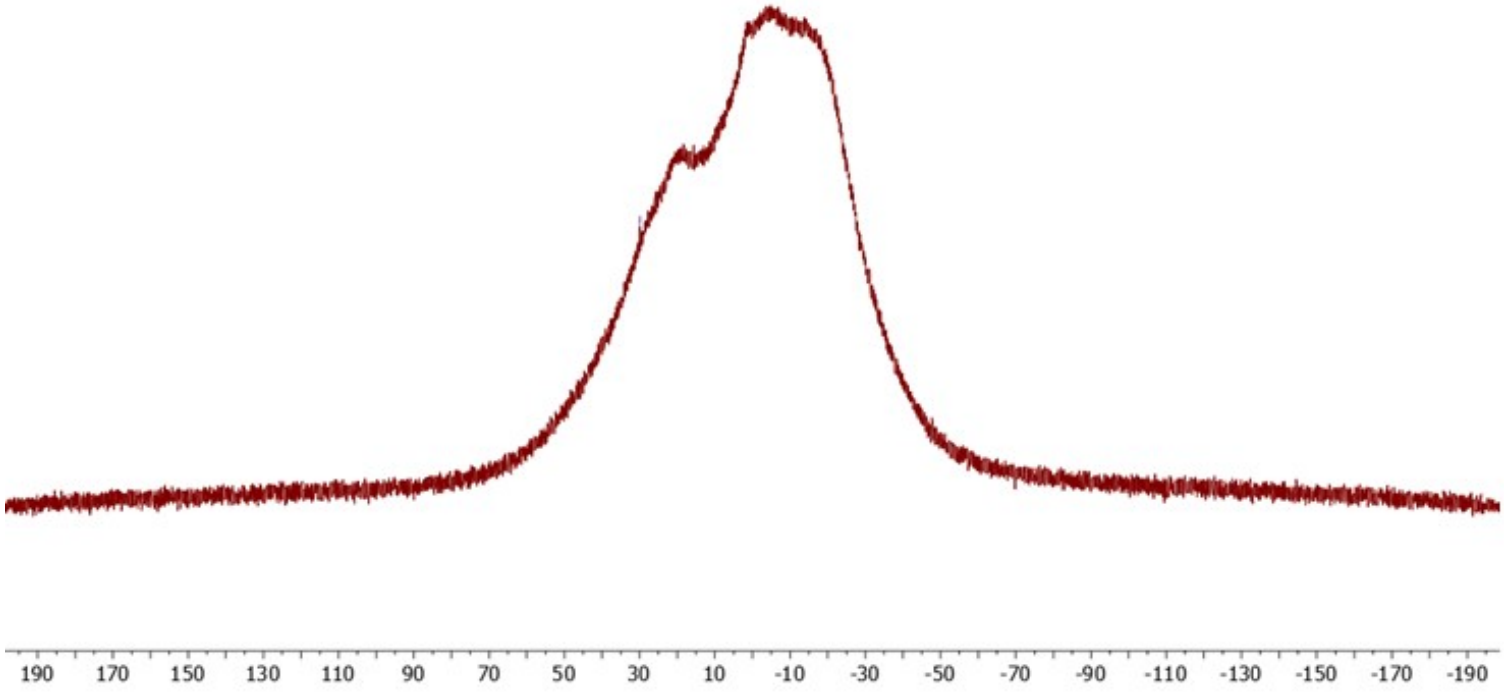


Figure S13. ^{19}F NMR (376 MHz, C_6D_6).

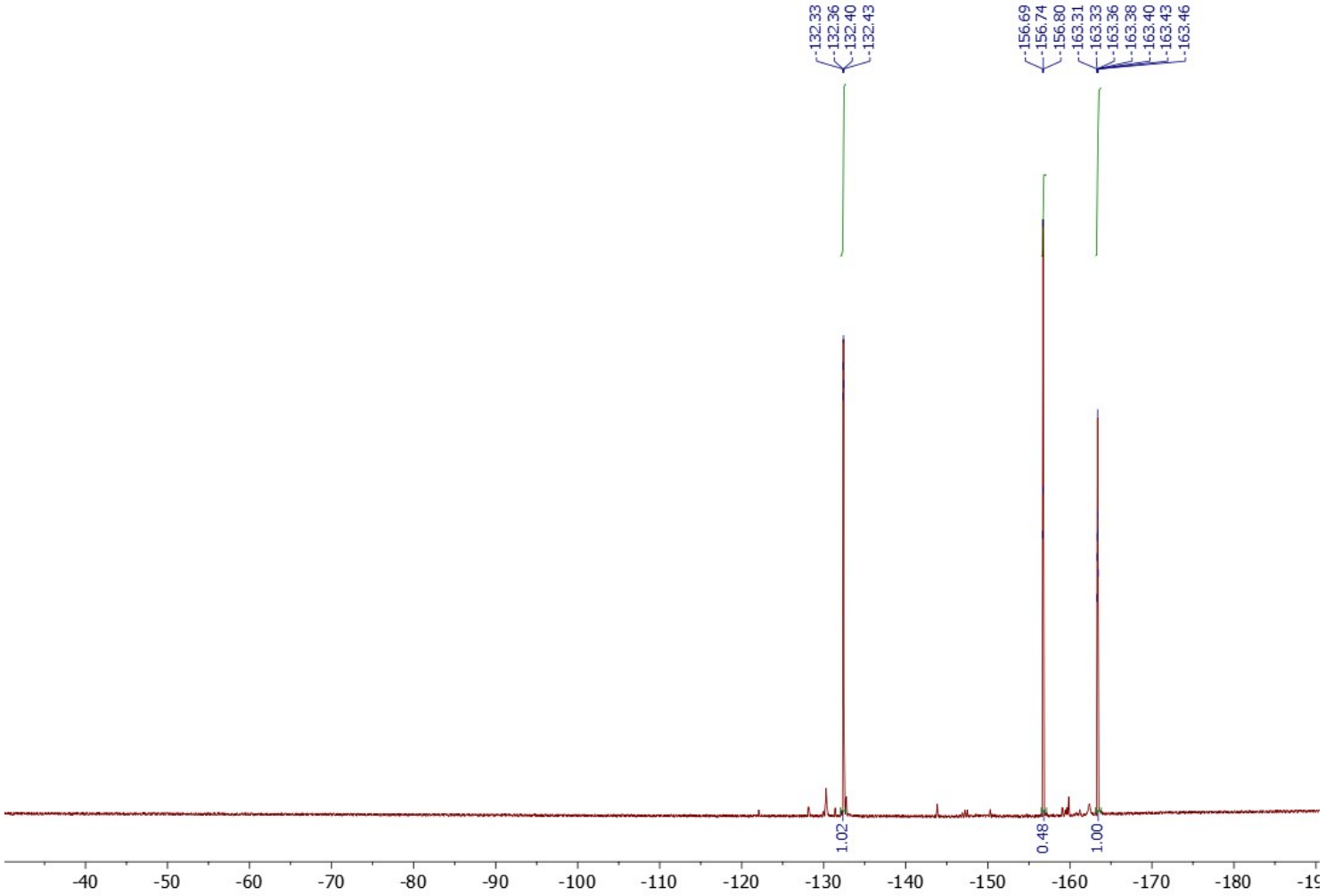


Figure S14. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6)

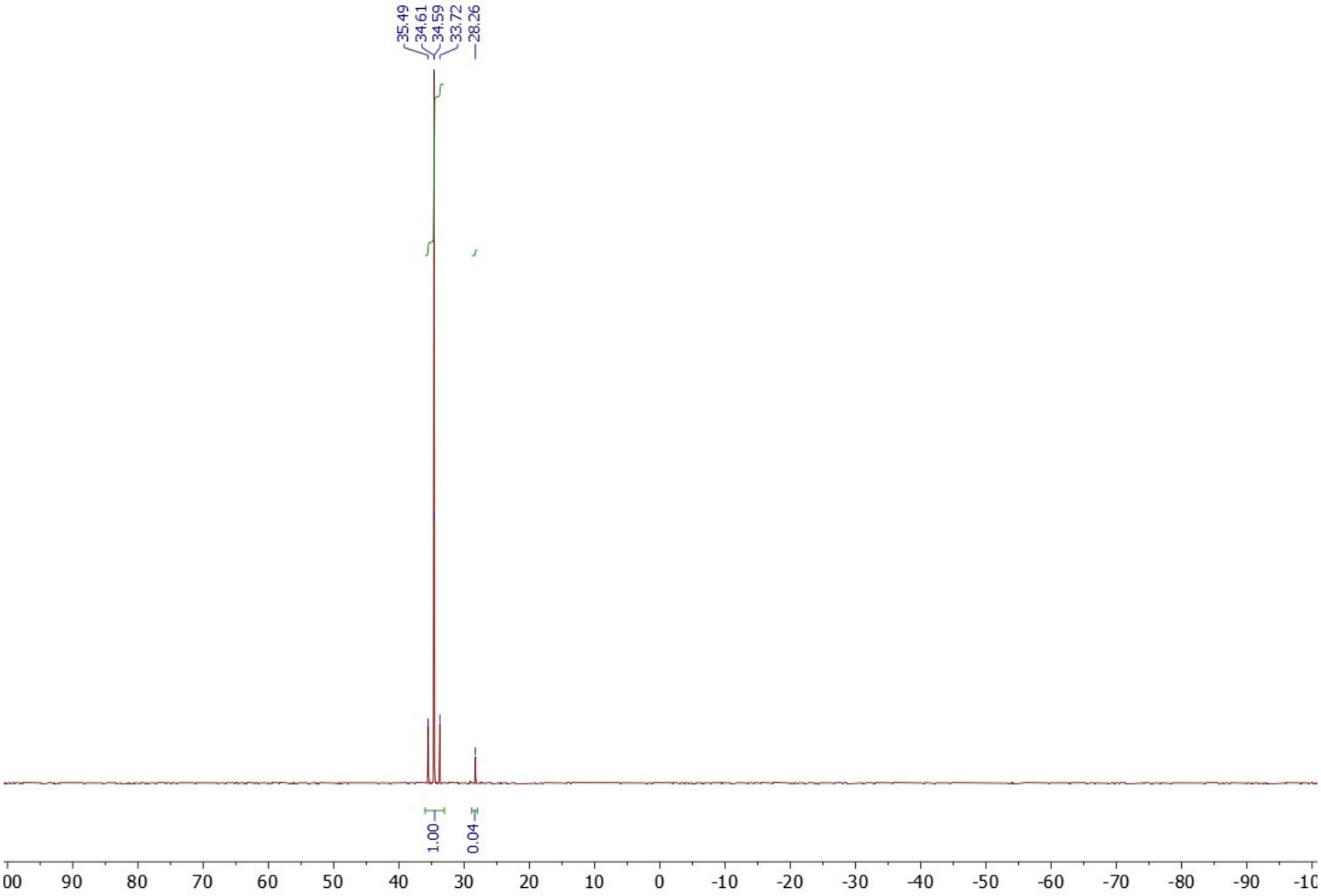
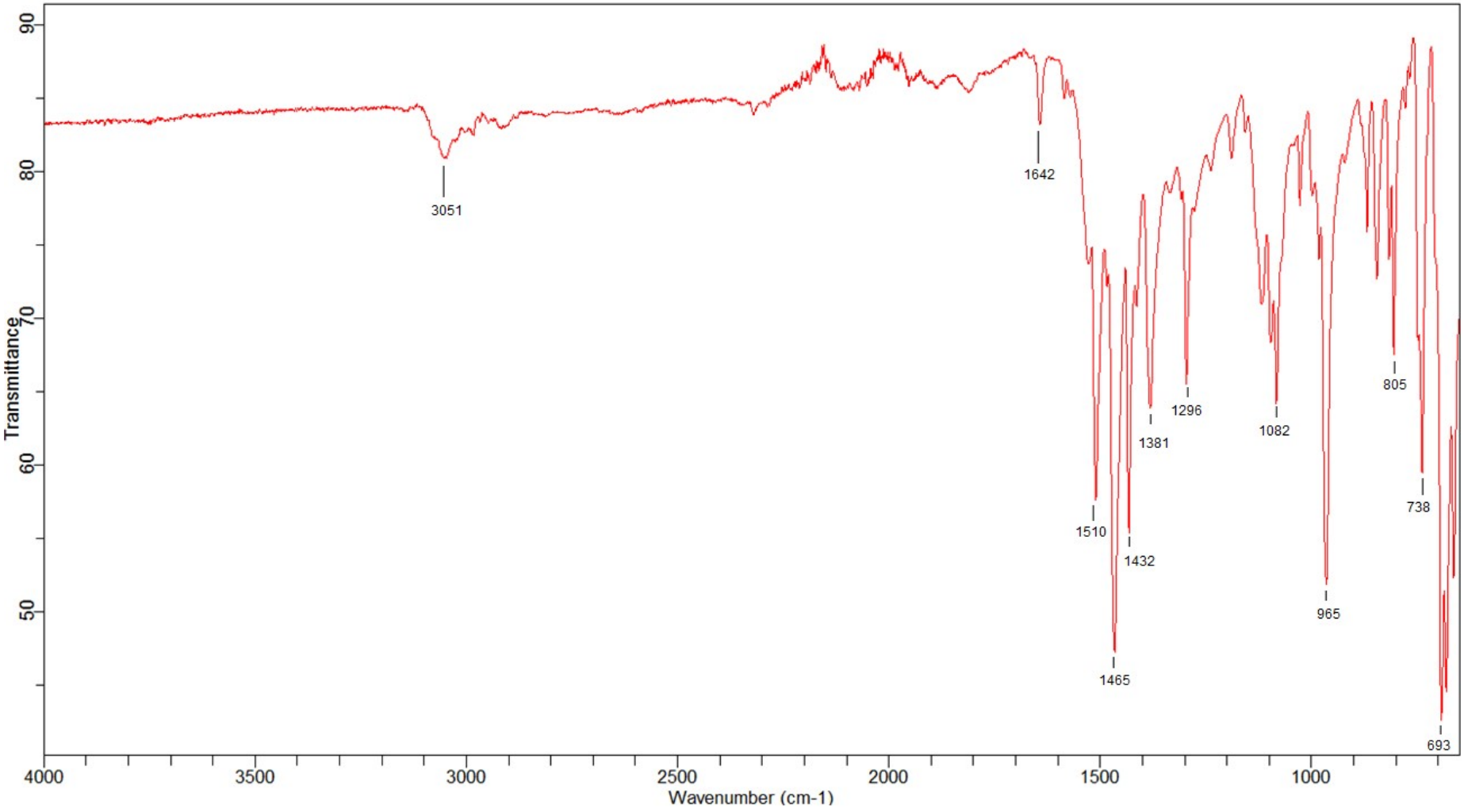


Figure S15. FT-IR (ATR, 400–4000 cm^{-1} range).



III.4. $[W(Cl)\{N_2B(C_6F_5)_2\}(depe)_2]$ (3^{Et})

Figure S16. ^1H NMR (400 MHz, C_6D_6).

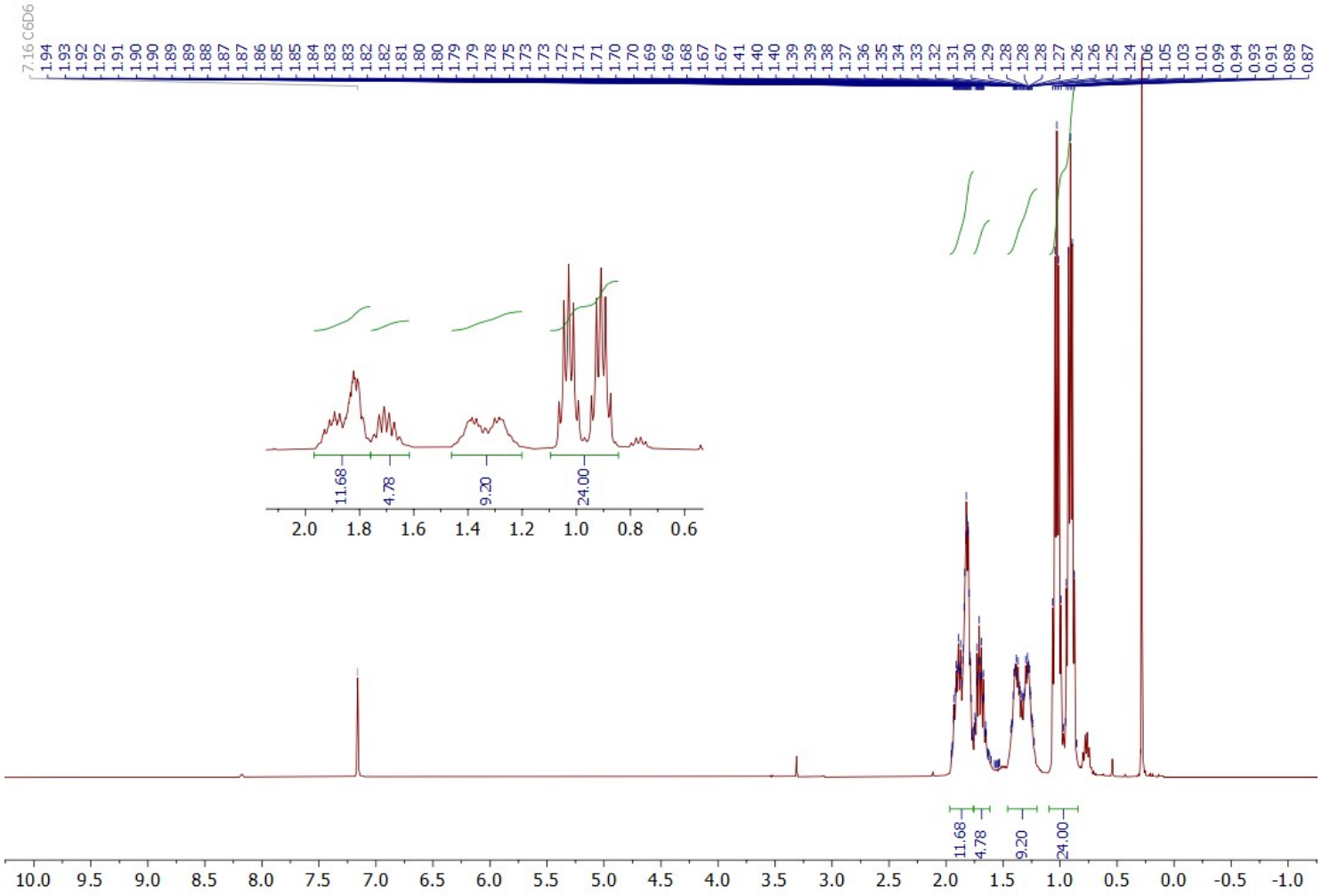


Figure S17. ^{11}B NMR (128 MHz, C_6D_6).

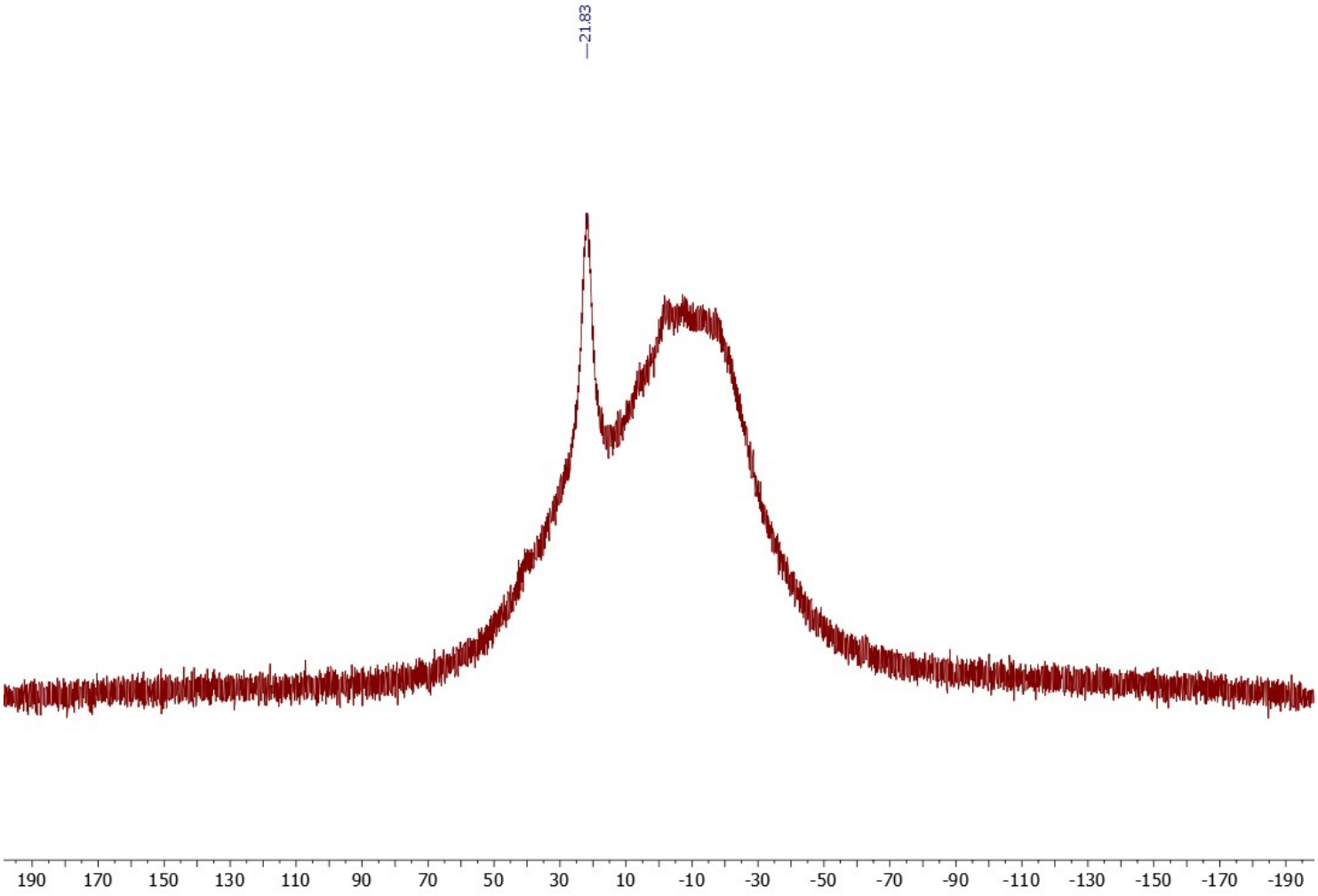


Figure S18. ^{19}F NMR (376 MHz, C_6D_6).

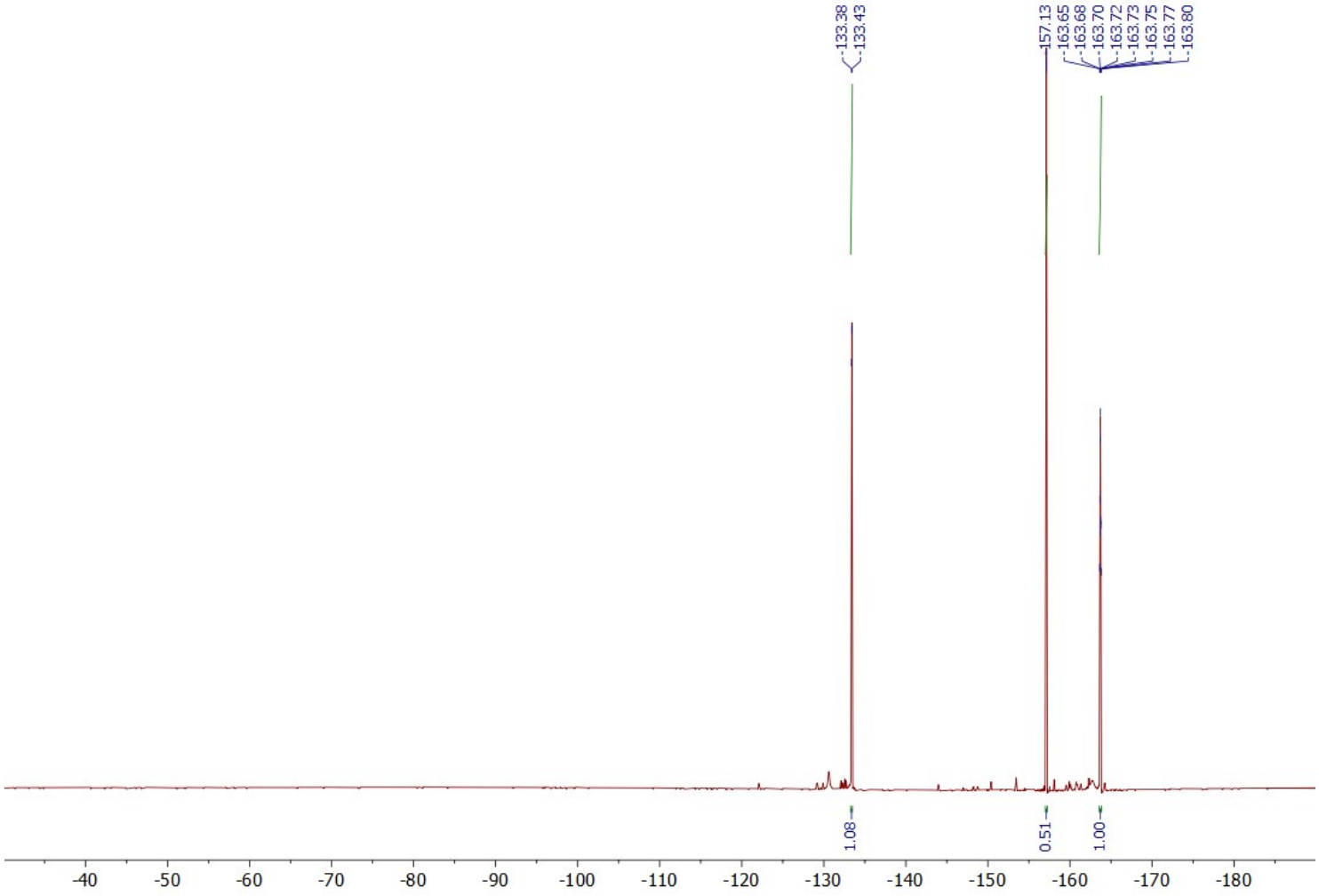


Figure S19. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6).

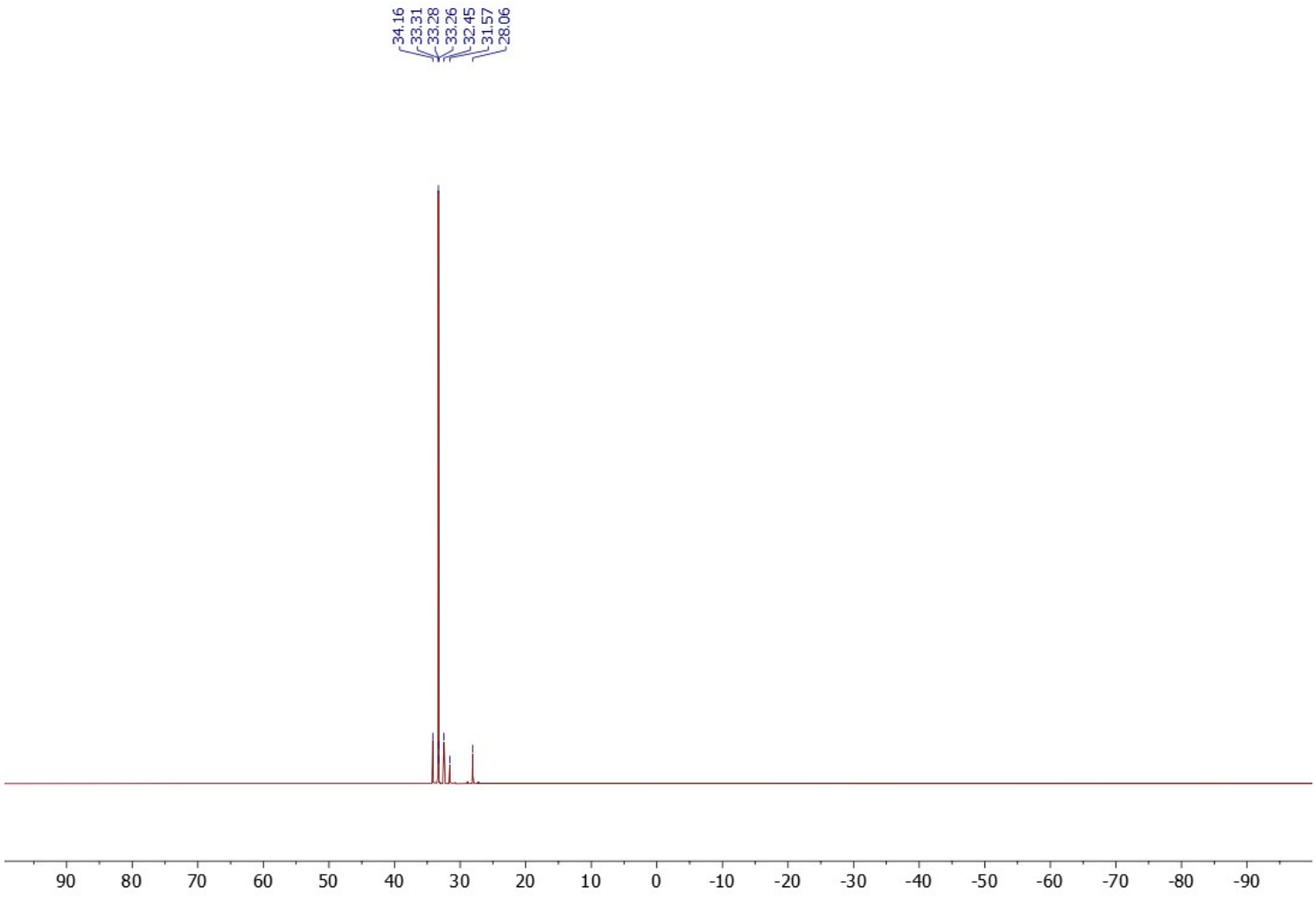
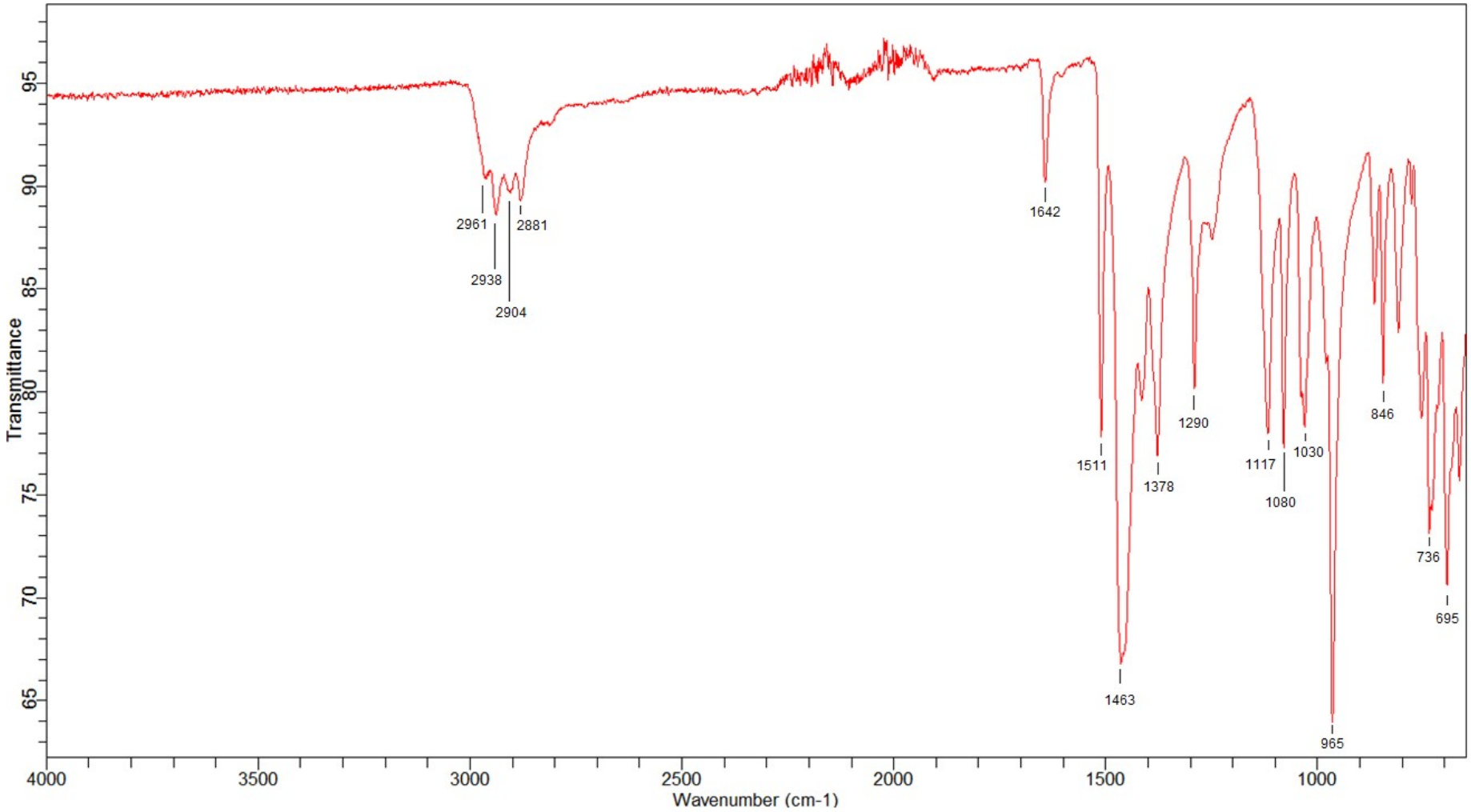


Figure S20. FT-IR (ATR, 400–4000 cm^{-1} range).



III.1. [W(Cl)(NN(Tl){B(Mes)$_2$})(depe)$_2$] ([2^{Et}·Tl]BAr$^F{}_4$)

Figure S21. ^{1}H NMR (400 MHz, C_6D_5Cl).

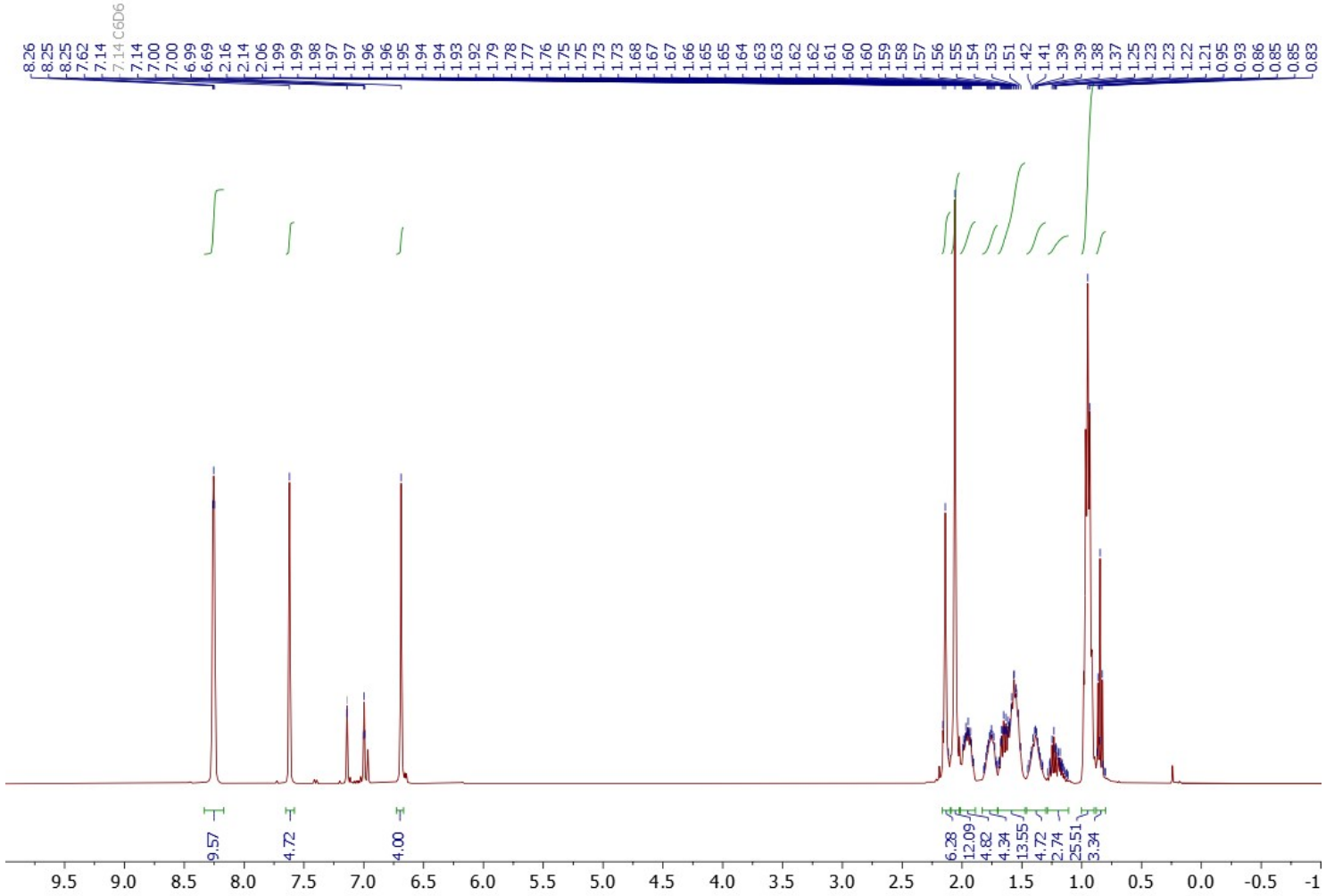


Figure S22. ^{11}B NMR (128 MHz, C_6D_5Cl).

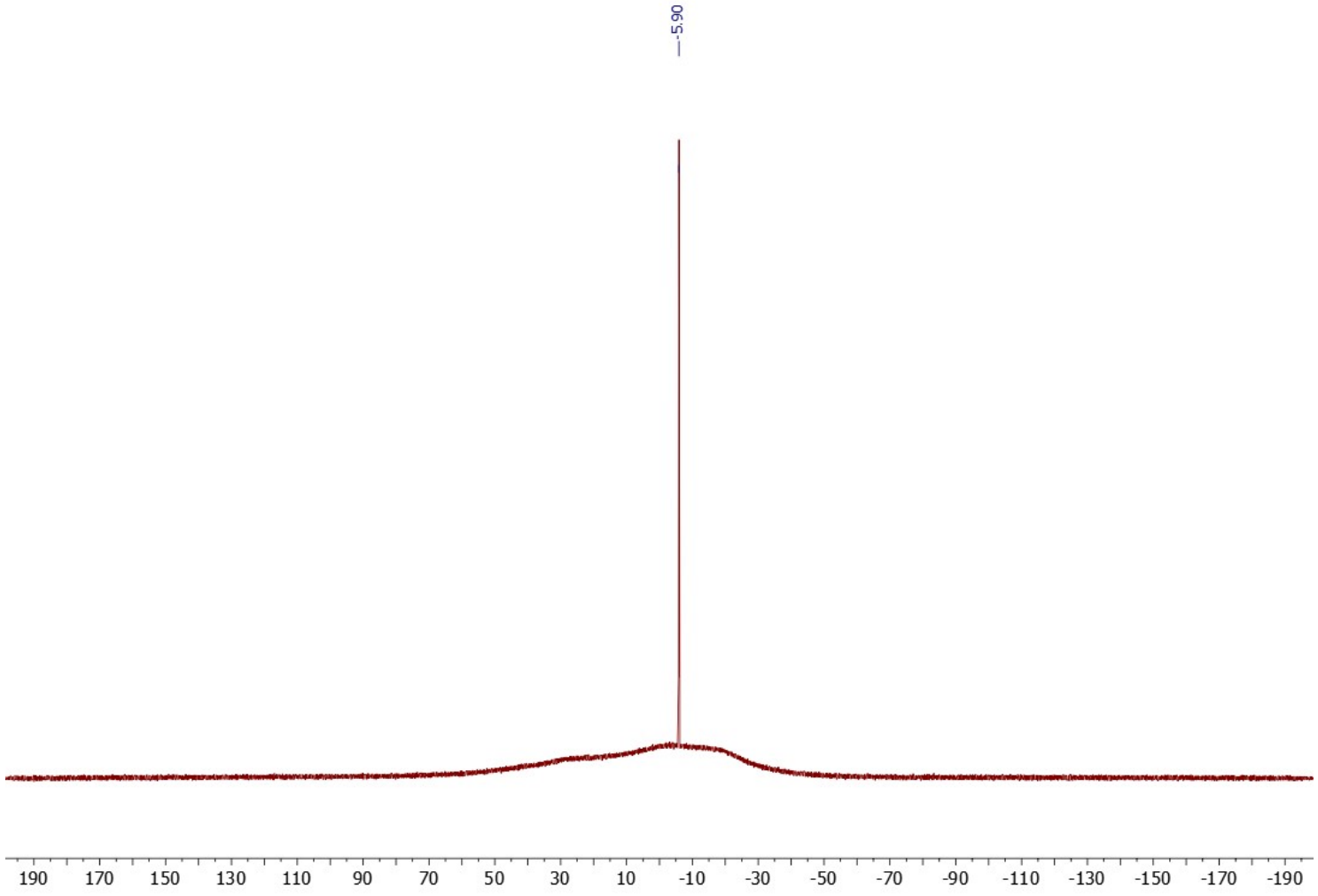


Figure S23. $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_5Cl).

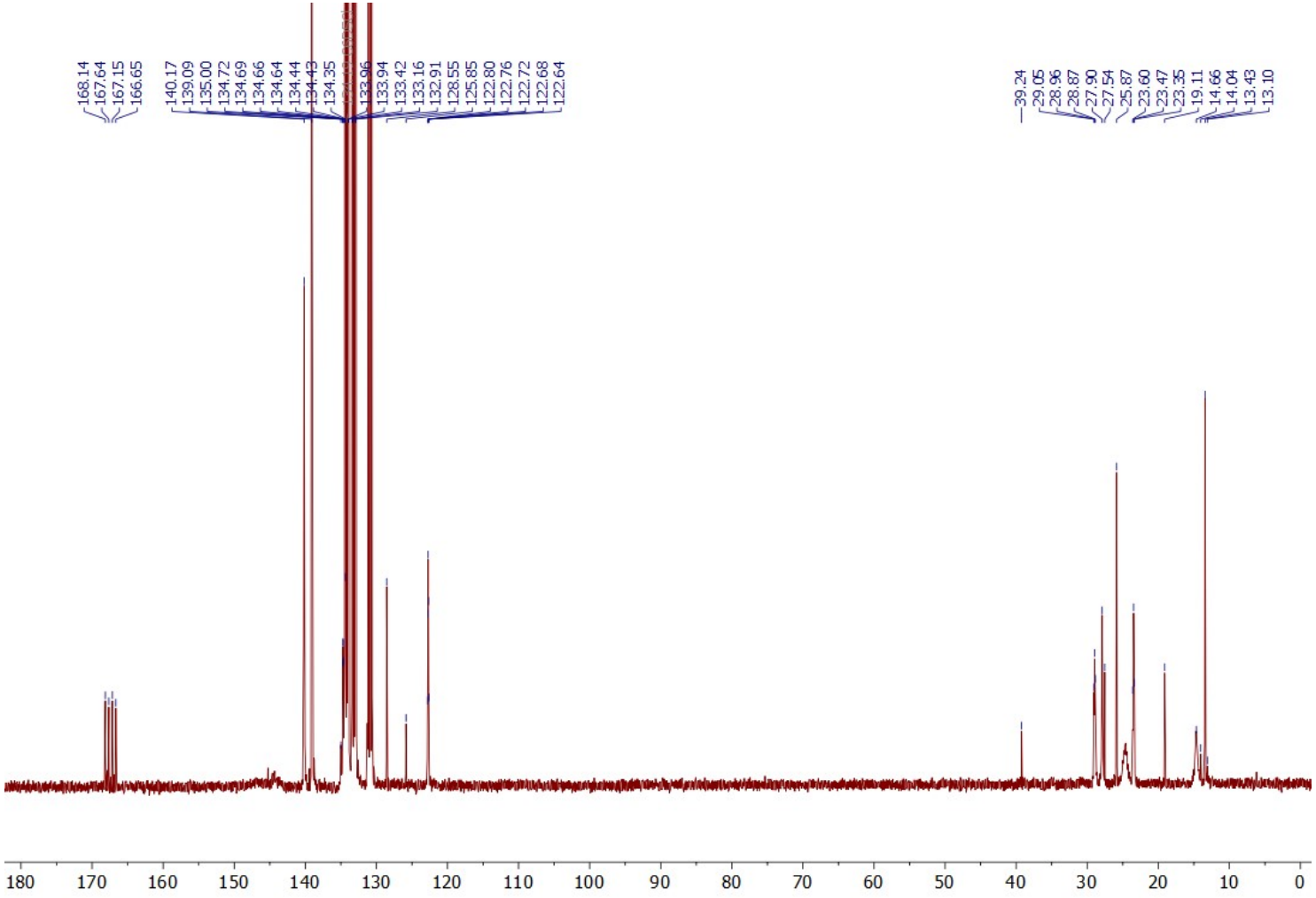


Figure S24. ^{19}F NMR (376 MHz, C_6D_6).

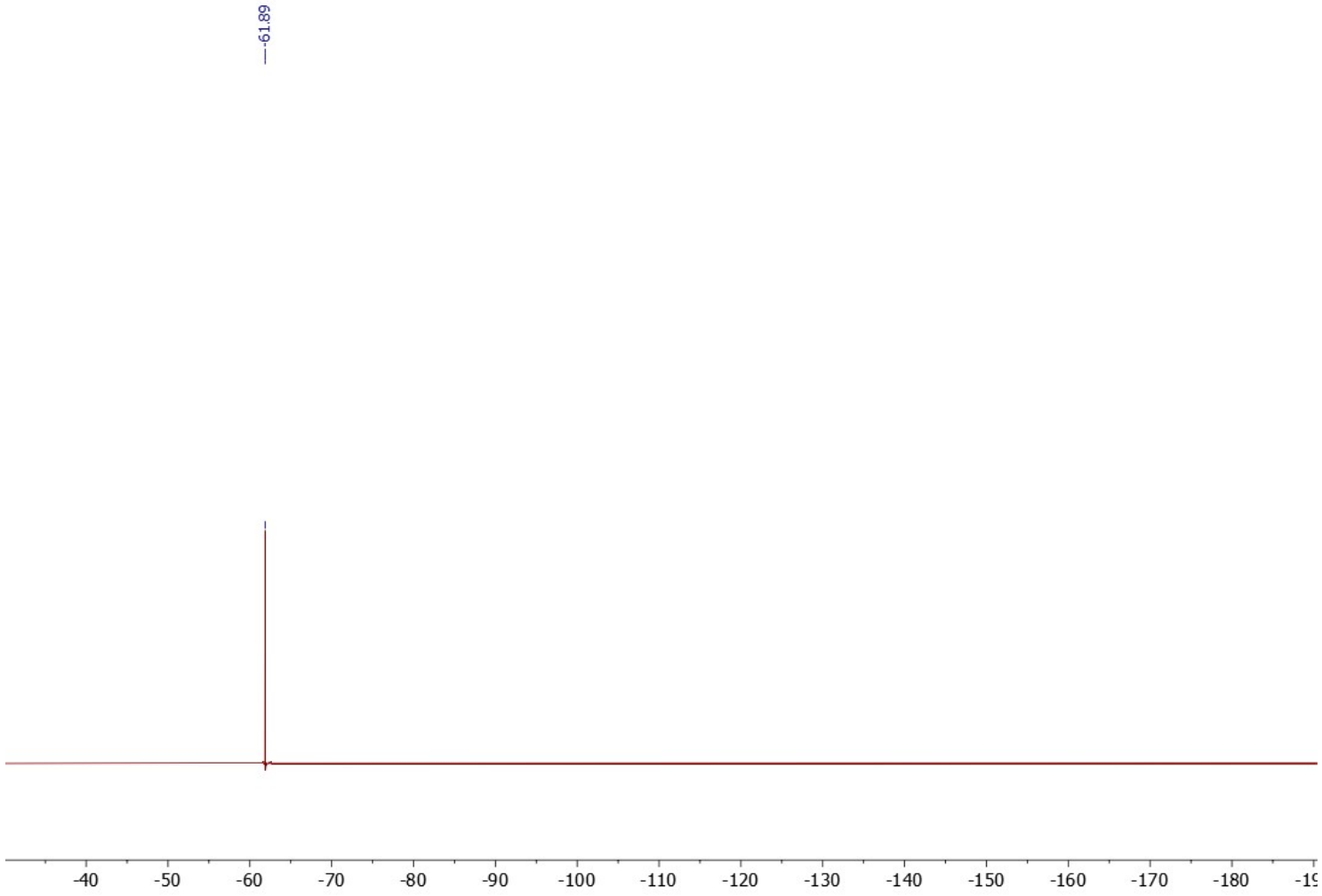


Figure S25. ^{31}P NMR (162 MHz, C_6D_5Cl).

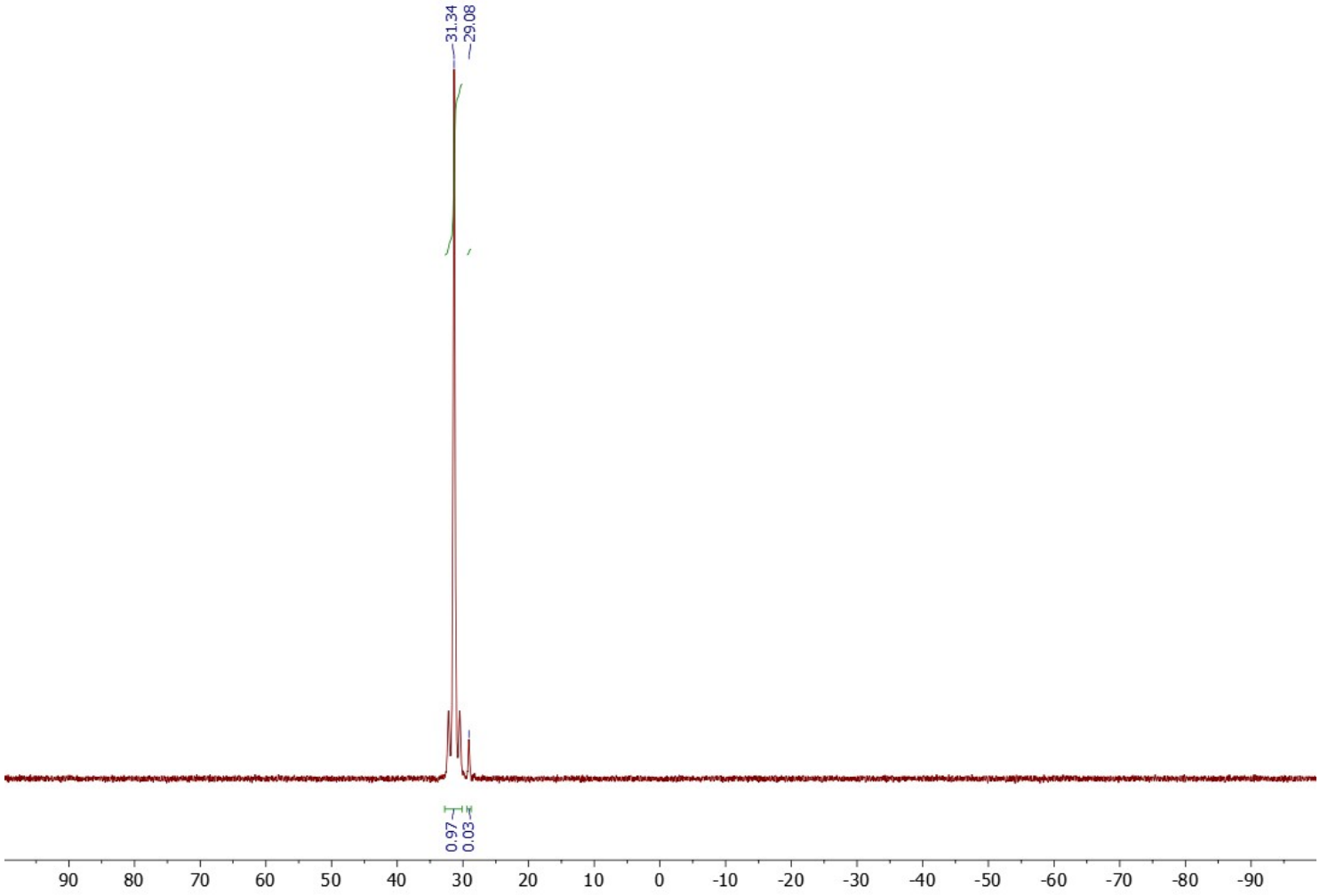
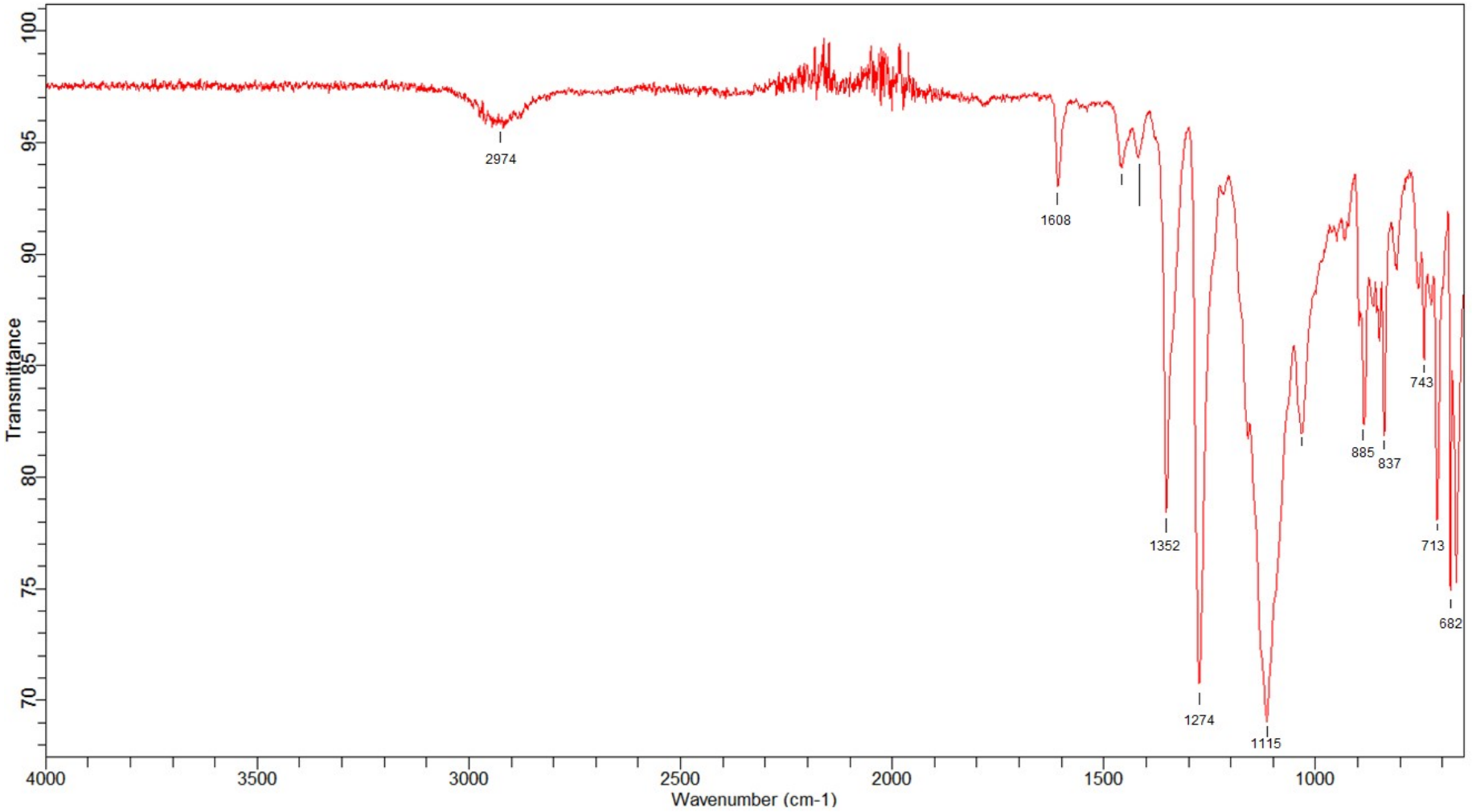


Figure S26. FT-IR (ATR, 400–4000 cm^{-1} range).



III.2. [W(ClTl){$N_2B(C_6F_5)_2$}$(dppe)_2$] ([3^{Ph}·Tl]BAr^F_4)

Figure S27. ^{1}H NMR (400 MHz, C_6D_6).

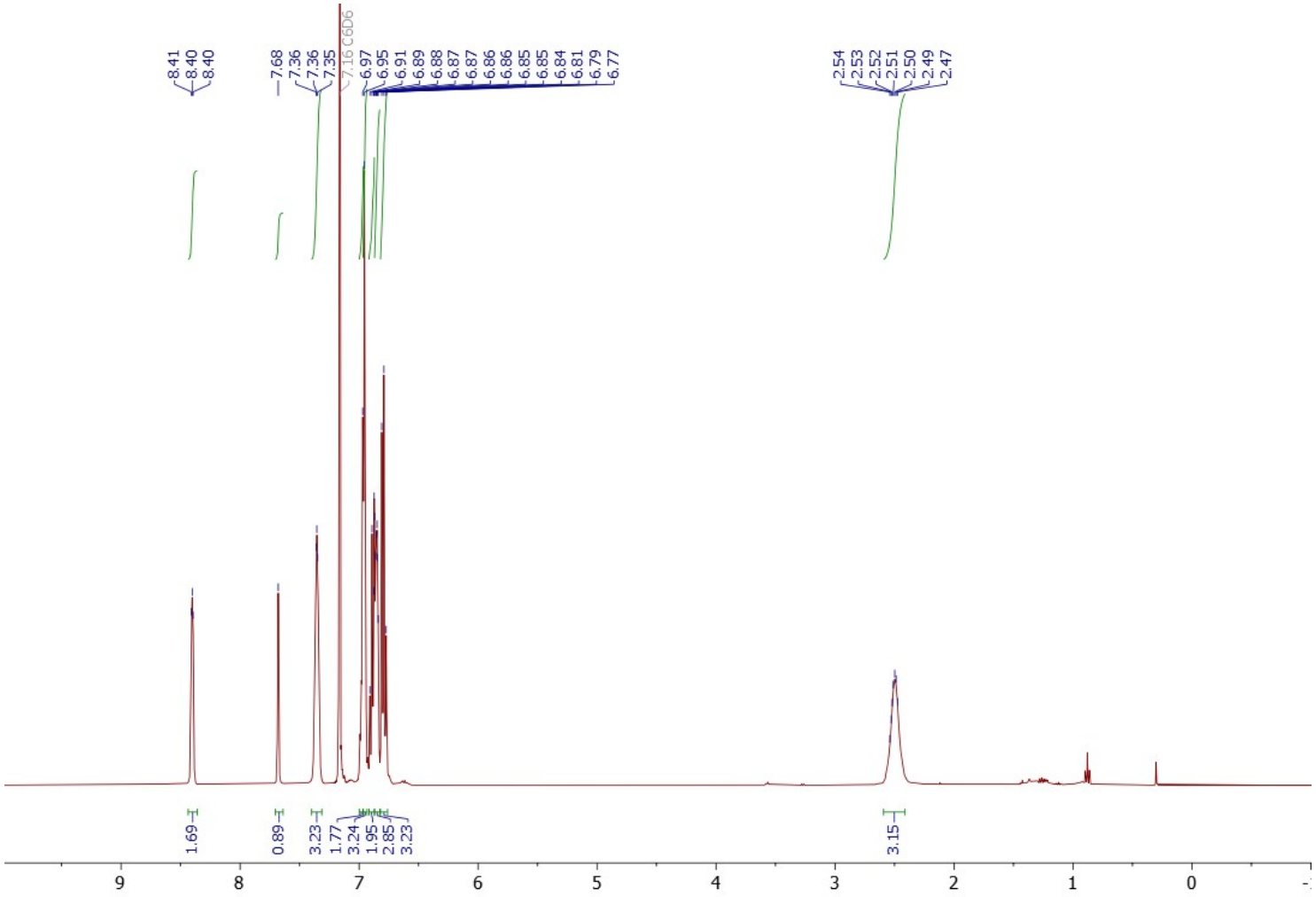


Figure S28. ^{1}H NMR (400 MHz, C_6D_5Cl).

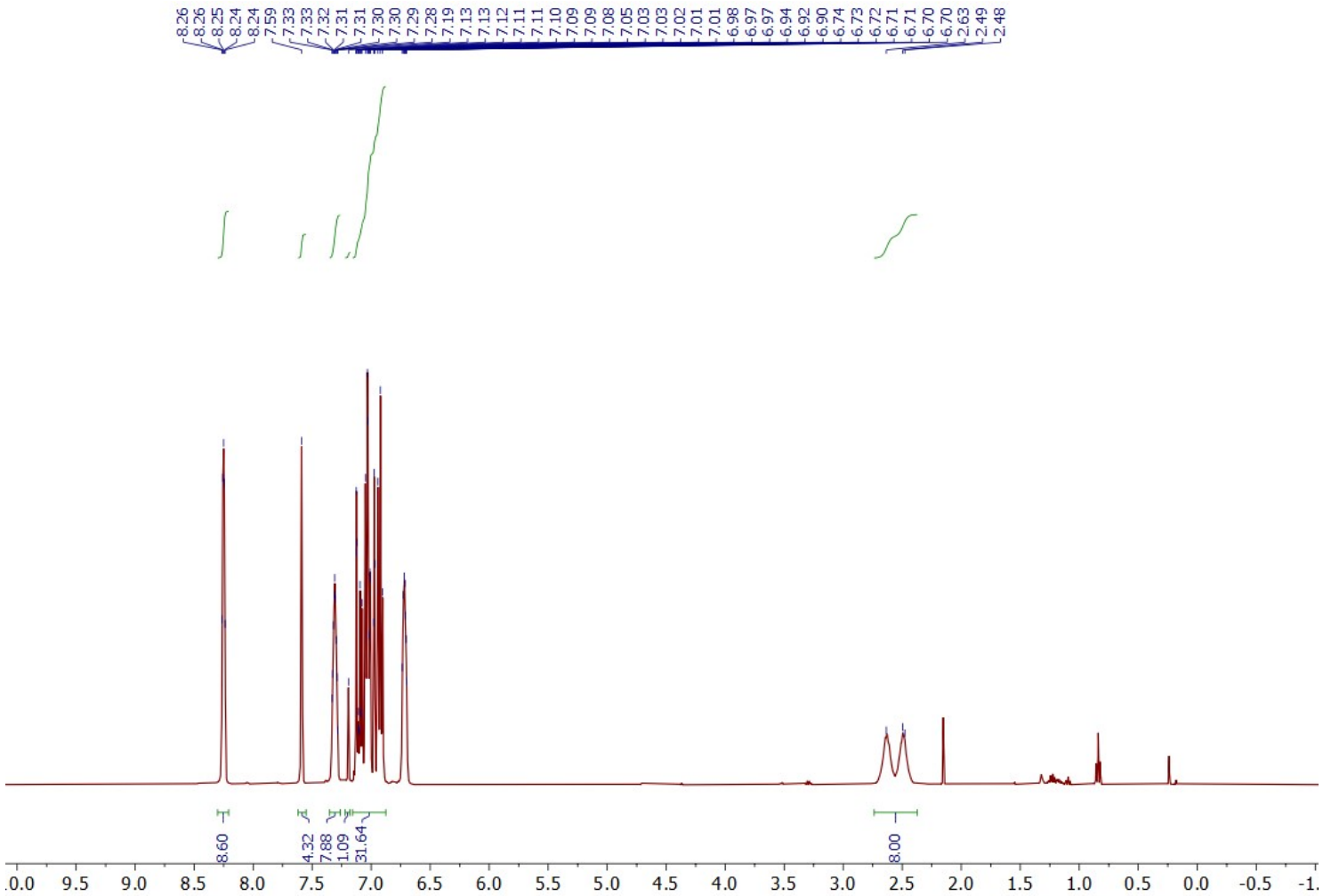


Figure S29. ^{11}B NMR (128 MHz, C_6D_6).

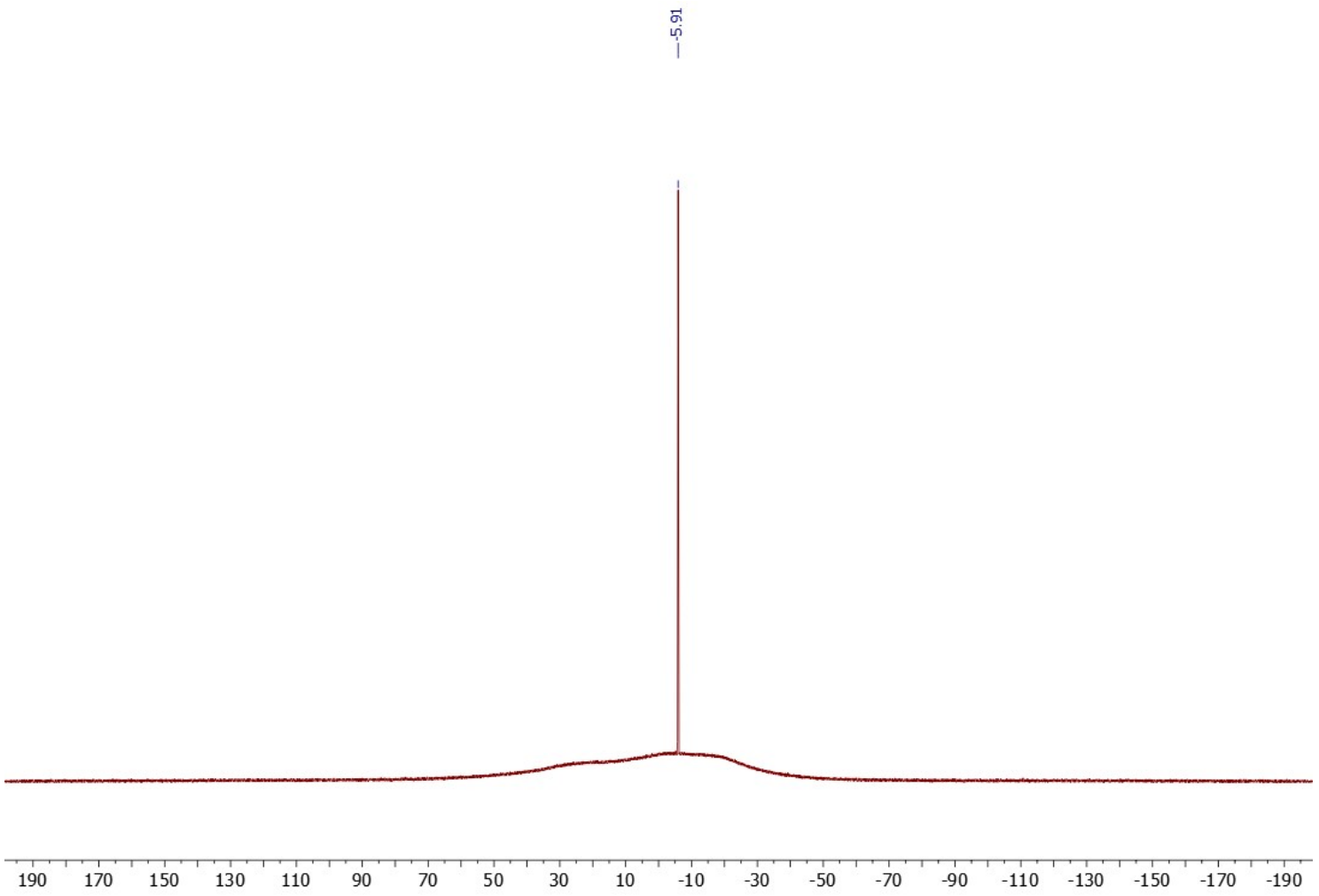


Figure S30. $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6).

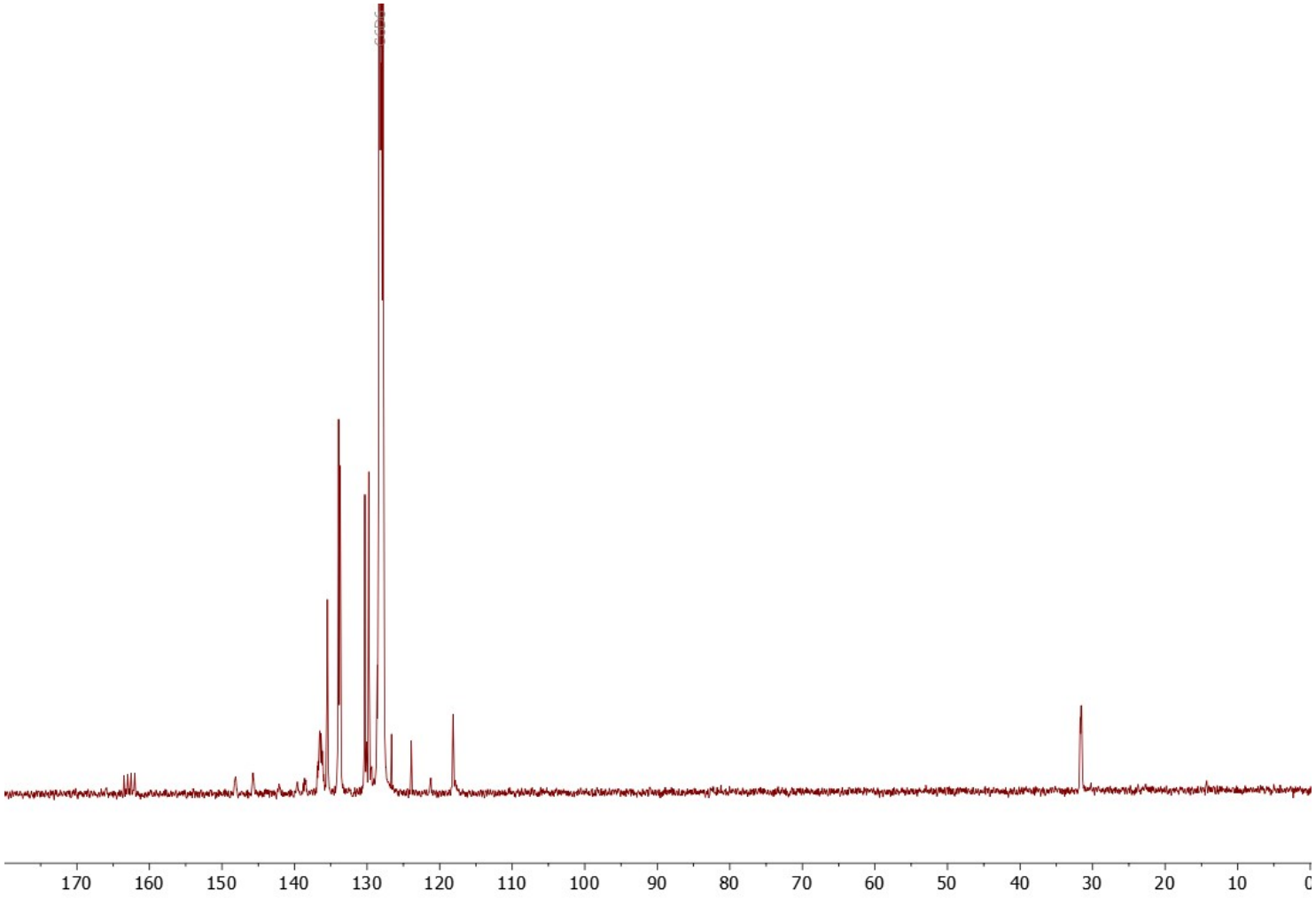


Figure S31. ^{19}F NMR (376 MHz, C_6D_6).

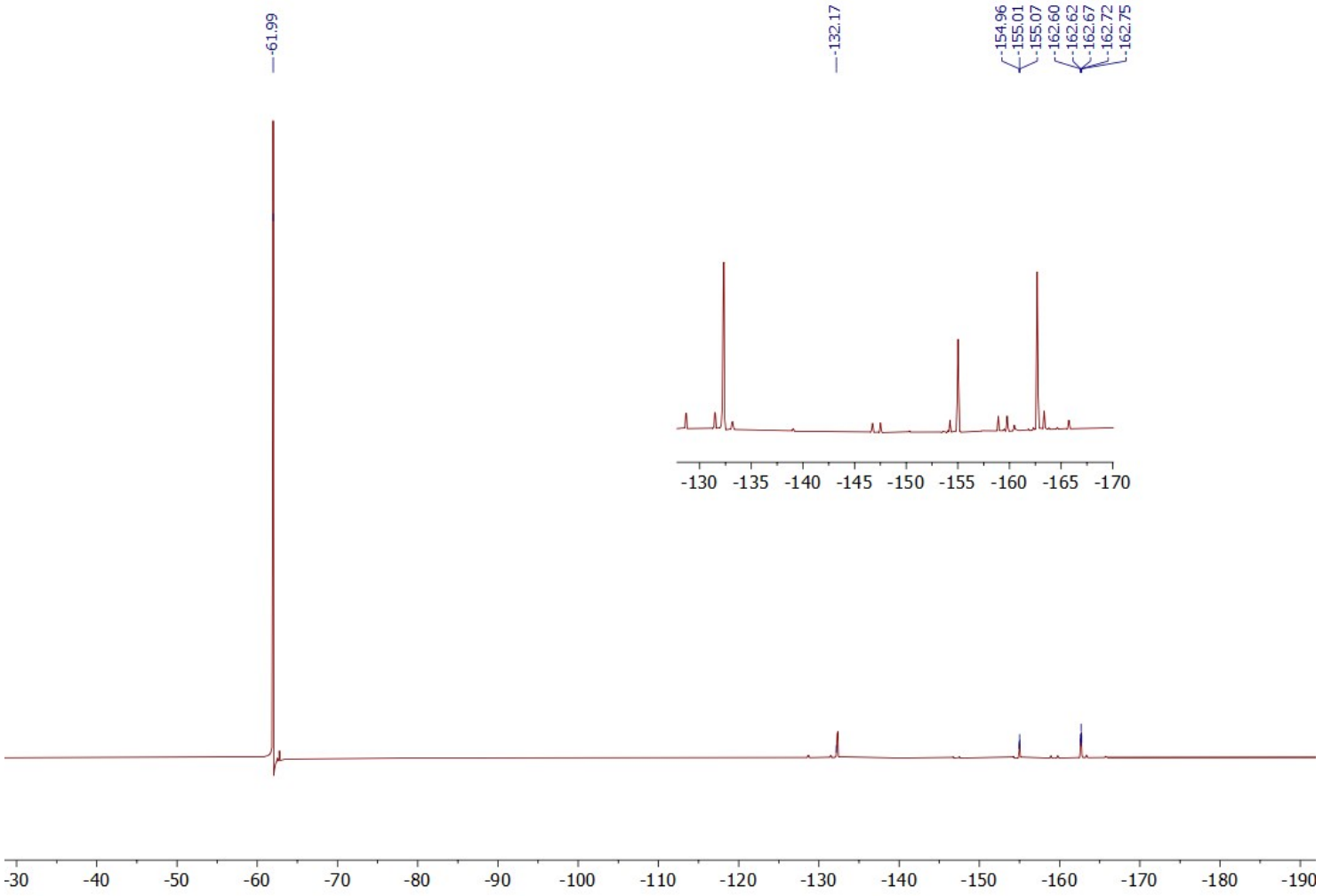


Figure S32. ^{31}P NMR (162 MHz, C_6D_6).

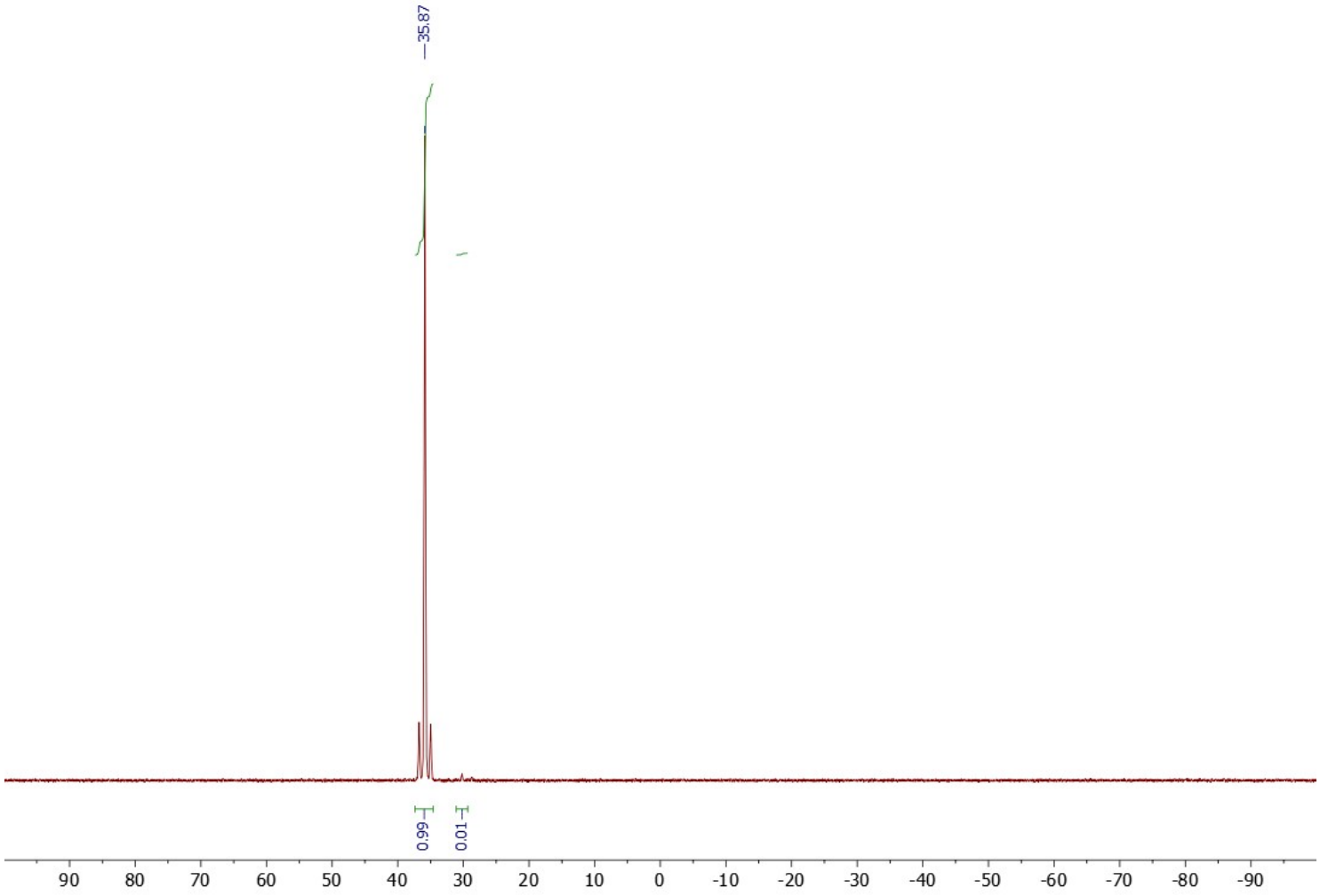
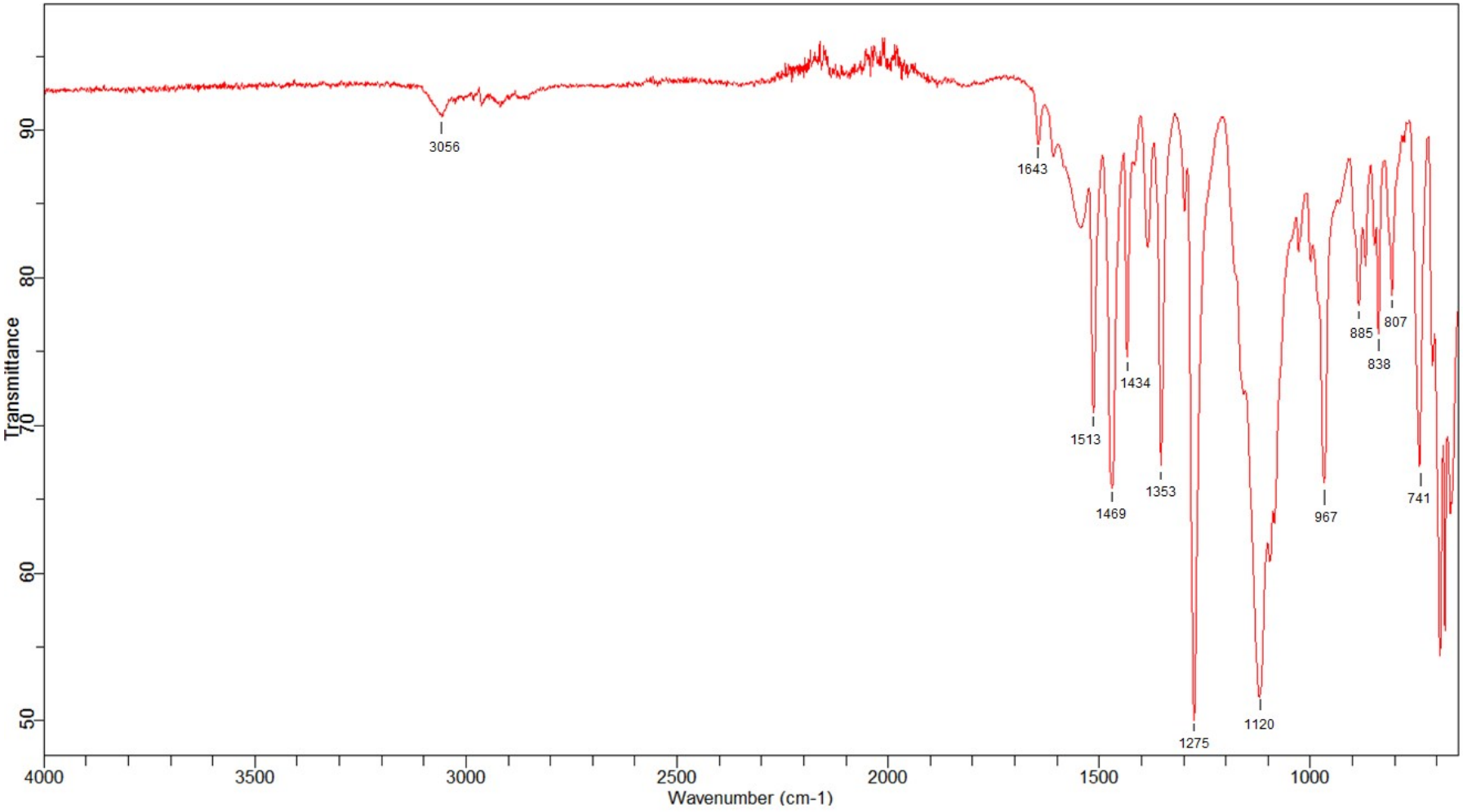


Figure S33. FT-IR (ATR, 400–4000 cm^{-1} range).



IV. Crystallographic data

IV.1. Data collection and refinement

Data for compounds **2^{Ph}**, **2^{Et}**, **3^{Ph}**, **3^{Et}**, [**2^{Et}·Tl**]BAr^F_4 and [**3^{Ph}·Tl**]BAr^F_4 were collected at low temperature (100 K) on a Bruker Kappa Apex II diffractometer using a Mo-Ka radiation (l = 0.71073Å) micro-source and equipped with an Oxford Cryosystems Cooler Device. The structures have been solved by Direct Methods and refined by means of least-squares procedures using the SHELXS97[S7] program included in the softwares package WinGX version 1.63[S8] or with the aid of the software package Crystal[S9]. The Atomic Scattering Factors were taken from International tables for X-Ray Crystallography[S10]. Hydrogen atoms were placed geometrically and refined using a riding model. All non-hydrogens atoms were anisotropically refined. Drawing of molecules in the following figures were performed with the program Mercury[S11] with 30% probability displacement ellipsoids for non-hydrogen atoms. The crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 2114361–2114366 and 2122445.

IV.1. X-Ray analysis of 2^{Ph}

Figure S34. X-ray crystal structure of $\mathbf{2^{Ph}}$, with ellipsoids set at the 30% probability level; hydrogen atoms omitted for clarity.

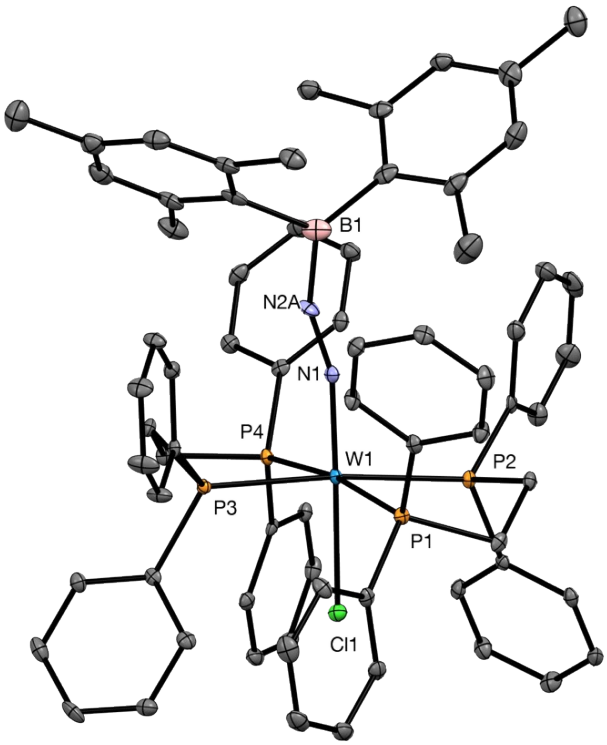


Table S1. Crystallographic data for $\mathbf{2^{Ph}}$.

Crystal Data	
Chemical formula	$C_{70}H_{70}BClN_2P_4W$
M_r	1293.26
Crystal system, space group	Triclinic, P-1
Temperature (K)	100 K
a, b, c (Å)	13.5795 (6), 18.9959 (8), 24.5911 (10)
α, β, γ (°)	85.873 (1), 78.351 (1), 89.176 (1)
V (Å^3)	6196.6 (5)
Z	4
Radiation type	Mo *K*α radiation, λ = 0.71073 Å
μ (mm^{-1})	2.05
Crystal size (mm)	0.15 × 0.08 × 0.02
Data collection	
Diffractometer	Bruker Kappa APEX II diffractometer
Absorption correction	Multi-scan [c.f. r.h. blessing, acta cryst. (1995), a51, 33-38]
T_{min}, T_{max}	0.668, 0.746
No. of measured, independent and observed [I > 2σ(I)] reflections	138108, 21899, 16338
Rint	0.092
θ_{max} (°)	25.0
Refinement	
R[F^2 > 2σ(F^2)], wR(F^2), S	0.031, 0.060, 0.96
No. of reflections	21899
No. of parameters	1438
H-atom treatement	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.65, –0.96

IV.2. X-Ray analysis of 2^{Et}

Figure S35. X-ray crystal structure of $\mathbf{2^{Et}}$, with ellipsoids set at the 30% probability level; hydrogen atoms omitted for clarity.

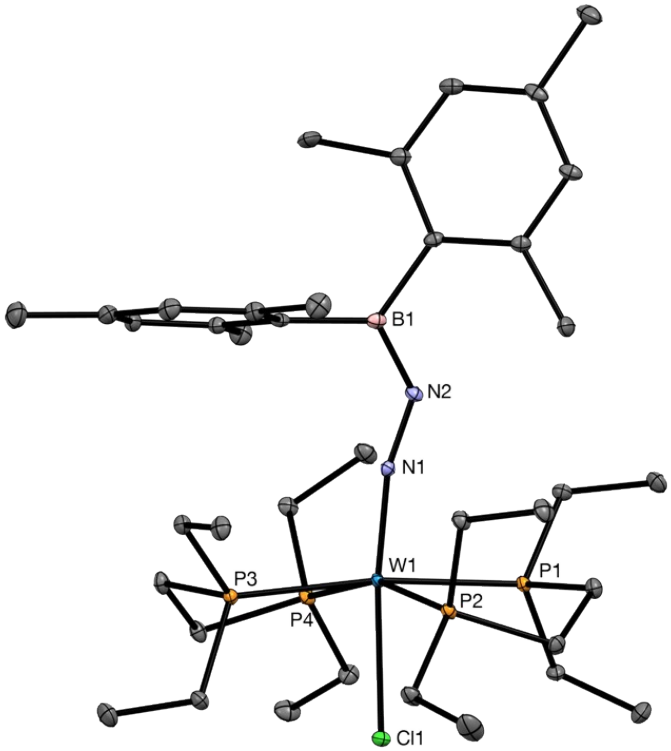


Table S2. Crystallographic data for $\mathbf{2^{Et}}$.

Crystal data	
Chemical formula	$C_{32}H_{69}BClN_2P_4W$
M_r	907.99
Crystal system, space group	Monoclinic, *C*2/c
Temperature (K)	100 K
a, b, c (Å)	31.524 (2), 13.0407 (8), 21.6455 (14)
α, β, γ (°)	91.897 (3)
V (Å^3)	8893.6 (10)
Z	8
Radiation type	Mo *K*α radiation, λ = 0.71073 Å
μ (mm^{-1})	2.82
Crystal size (mm)	0.18 × 0.10 × 0.03
Data collection	
Diffractometer	Bruker Kappa APEX II diffractometer
Absorption correction	multi-scan *SADABS* (Siemens, 1996)
T_{min}, T_{max}	0.82, 0.92
No. of measured, independent and observed [I > 2σ(I)] reflections	149547, 16194, 12199
Rint	0.102
θ_{max} (°)	33.2
Refinement	
R[F^2 > 2σ(F^2)], wR(F^2), S	0.035, 0.073, 0.98
No. of reflections	16186
No. of parameters	424
H-atom treatement	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.47, –2.29

IV.3. X-Ray analysis of 3^{Ph}

Figure S36. X-ray crystal structure of $\mathbf{3^{Ph}}$, with ellipsoids set at the 30% probability level; hydrogen atoms omitted for clarity.

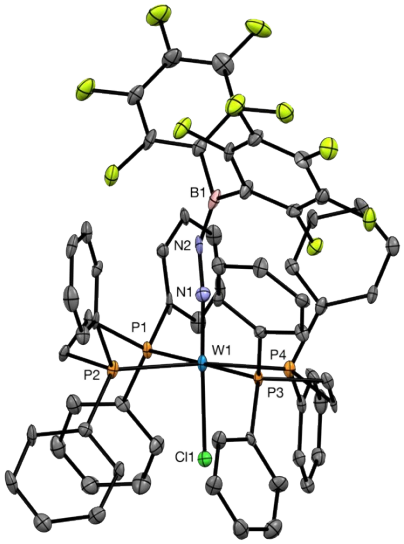


Table S3. Crystallographic data for $\mathbf{3^{Et}}$.

Crystal data	
$C_{79}H_{61}BCl_2F_{10}N_2OP_4W$	
M_r = 1633.73	D_x = 1.564 Mg m^{-3}
Monoclinic, *C*2/*c*	Melting point:
Hall symbol: -C 2yc	Mo *K*α radiation, λ = 0.71073 Å
a = 31.319 (5) Å	Cell parameters from 32.49 reflections
b = 23.807 (4) Å	θ = 2.6–20.0°
c = 19.028 (4) Å	μ = 1.91 mm^{-1}
β = 102.001 (5)°	*T* = 103 K
V = 13877 (4) Å^3	Platelet, light yellow
Z = 8	0.11 × 0.08 × 0.02 mm
F(000) = 6560	
Data collection	
Bruker Kappa Apex2 diffractometer	6361 reflections with $I > 2\sigma(I)$
Radiation source: ?	R_{int} = 0.329
Graphite monochromator	θ_{max} = 24.7°, θ_{min} = 1.1°
φ & ω scans	*h* = −36 36
Absorption correction: multi-scan *SADABS* (Siemens, 1996)	*k* = −26 28
T_{min} = 0.542, T_{max} = 0.745	*l* = −22 22
113592 measured reflections	
11810 independent reflections	
Refinement	
Refinement on F^2	
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.077	H-atom parameters constrained
$wR(F^2)$ = 0.220	$w = 1/[\sigma^2(F_o^2) + (0.0941P)^2 + 124.3535P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.05	$(\Delta/\sigma)_{max}$ = 0.001
11810 reflections	$\Delta\rho_{max}$ = 2.87 e Å^{-3}
886 parameters	$\Delta\rho_{min}$ = −2.83 e Å^{-3}
37 restraints	Extinction correction: none

IV.4. X-Ray analysis of 3^{Et}

Figure S37. X-ray crystal structure of $\mathbf{3^{Et}}$, with ellipsoids set at the 30% probability level; hydrogen atoms omitted for clarity.

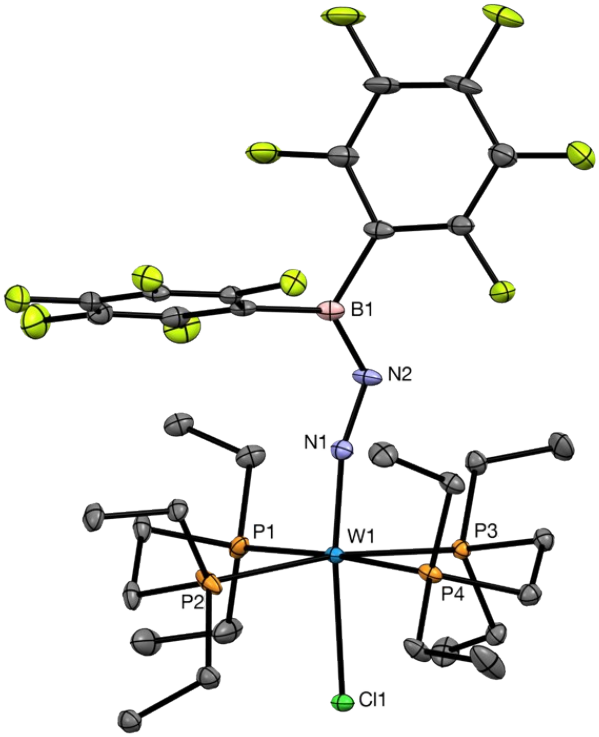


Table S4. Crystallographic data for $\mathbf{3^{Et}}$.

Crystal data	
Chemical formula	$C_{32}H_{48}BClF_{10}N_2P_4W$
M_r	1004.71
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	110 K
a, b, c (Å)	11.8464 (4), 13.1720 (3), 27.4046 (4)
α, β, γ (°)	99.148 (3)
V (Å^3)	4221.84 (19)
Z	4
Radiation type	Mo *K*α radiation, λ = 0.71073 Å
μ (mm^{-1})	3.02
Crystal size (mm)	0.10 × 0.05 × 0.02
Data collection	
Diffractometer	Bruker Kappa APEX II diffractometer
Absorption correction	multi-scan c.f. r.h. blessing, acta cryst. (1995), a51, 33-38
T_{min}, T_{max}	0.665, 0.746
No. of measured, independent and observed [I > 2σ(I)] reflections	188070, 21208, 16637
Rint	0.066
θ_{max} (°)	25.7
Refinement	
R[F^2 > 2σ(F^2)], wR(F^2), S	0.028, 0.067, 1.05
No. of reflections	7963
No. of parameters	472
H-atom treatement	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.57, –1.22

IV.5. X-Ray analysis of $[WCl_2(depe)_2]BAr^F{}_4$

Figure S38. X-ray crystal structure of $[WCl_2(depe)_2]BAr^F{}_4$, with ellipsoids set at the 30% probability level; hydrogen atoms omitted for clarity.

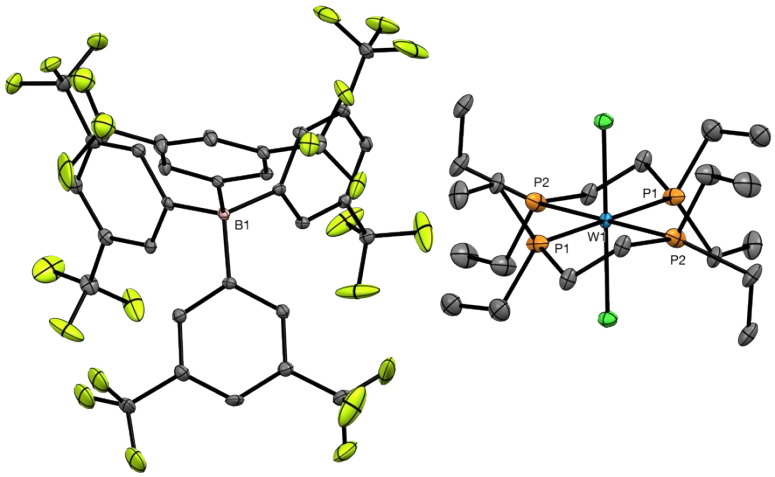


Table S5. Crystallographic data for $[WCl_2(depe)_2]BAr^F{}_4$.

Crystal data	
$C_{32}H_{12}BF_{24}\cdot C_{20}H_{48}Cl_2P_4W$	$F(000)$ = 1622
M_r = 1530.43	
Triclinic, P -1	D_x = 1.508 Mg m^{-3}
Hall symbol: -P 1	
a = 12.8472 (1) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
b = 14.4461 (1) Å	Cell parameters from 9988 reflections
c = 19.3710 (1) Å	θ = 2.5–29.3°
α = 108.898 (4)°	μ = 1.99 mm^{-1}
β = 94.296 (5)°	T = 110 K
γ = 94.608 (5)°	Plate, orange
V = 3370.84 (9) Å^3	0.16 × 0.11 × 0.03 mm
Z = 2	
Data collection	
Bruker Kappa APEX II diffractometer	9236 reflections with $I > 2\sigma(I)$
Radiation source: Mo micro-focus	R_{int} = 0.056
Graphite monochromator	θ_{max} = 24.7°, θ_{min} = 1.1°
ω–φ scans	h = −15 15
Absorption correction: multi-scan [c.f. r.h. blessing, acta cryst. (1995), a51, 33-38]	k = −16 16
T_{min} = 0.657, T_{max} = 0.747	l = −22 22
66473 measured reflections	Standard reflections: 0
11372 independent reflections	
Refinement	
Refinement on F^2	
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.041	H-atom parameters constrained
$wR(F^2)$ = 0.121	$w = 1/[\sigma^2(F_o^2) + (0.0654P)^2 + 12.3648P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.06	$(\Delta/\sigma)_{max}$ = 0.039
11372 reflections	$\Delta\rho_{max}$ = 1.66 e Å^{-3}
769 parameters	$\Delta\rho_{min}$ = −1.04 e Å^{-3}
9 restraints	Extinction correction: none

IV.6. X-Ray analysis of [3^{Ph}·Tl]BAr^F_4

Figure S39. X-ray crystal structure of [3^{Ph}·Tl]BAr^F_4, with ellipsoids set at the 30% probability level; hydrogen atoms omitted for clarity.

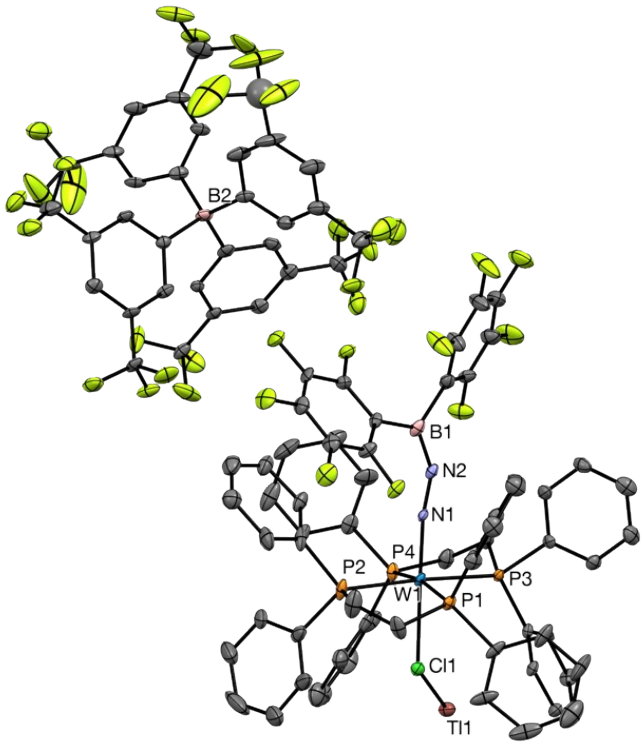


Table S6. Crystallographic data for [3^{Ph}·Tl]BAr^F_4.

Crystal data	
Chemical formula	$C_{105}H_{69}B_2ClF_{34}N_2P_4TlW$
M_r	2573.84
Crystal system, space group	Triclinic, P-1
Temperature (K)	100 K
a, b, c (Å)	16.7376 (8), 17.7790 (11), 20.2892 (17)
α, β, γ (°)	93.001 (5), 96.278(6), 92.960(4)
V (Å^3)	5983.2 (7)
Z	2
Radiation type	Mo *K*α radiation, λ = 0.71073 Å
μ (mm^{-1})	2.48
Crystal size (mm)	0.15 × 0.11 × 0.02
Data collection	
Diffractometer	Bruker Kappa APEX II diffractometer
Absorption correction	multi-scan *SADABS* (Siemens, 1996)
T_{min}, T_{max}	0.86, 0.95
No. of measured, independent and observed [I > 2σ(I)] reflections	20983, 20983, 14076
Rint	0.000
θ_{max} (°)	25.0
Refinement	
R[F^2 > 2σ(F^2)], wR(F^2), S	0.05, 0.055, 1.09
No. of reflections	12643
No. of parameters	1346
H-atom treatement	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.19, –1.16

IV.7. X-Ray analysis of [2^{Et}·Tl]BAr^F_4

Figure S40. X-ray crystal structure of [2^{Et}·Tl]BAr^F_4, with ellipsoids set at the 30% probability level; hydrogen atoms omitted for clarity.

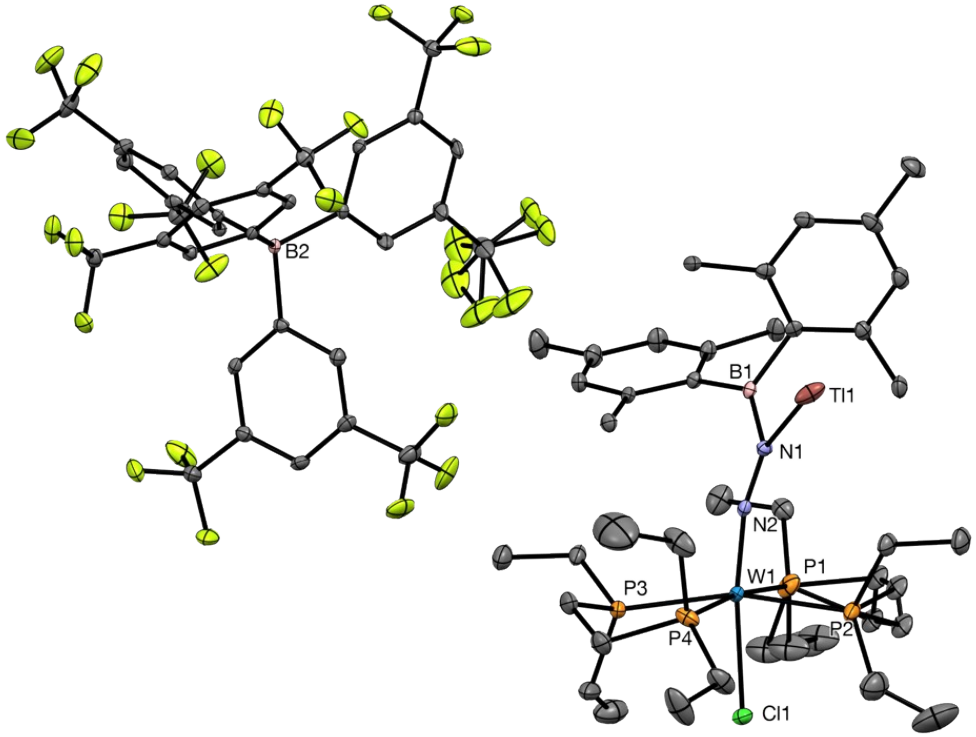


Table S7. Crystallographic data for [2^{Et}·Tl]BAr^F_4.

Crystal data	
Chemical formula	$C_{70}H_{82}B_2ClF_{24}N_2P_4TlW$
M_r	1976.58
Crystal system, space group	Monoclinic, P $2_1/c$
Temperature (K)	110 K
a, b, c (Å)	19.4938 (4), 20.5553 (5), 19.9296 (4)
α, β, γ (°)	106.853 (3)
V (Å^3)	7642.85 (14)
Z	4
Radiation type	Mo *K*α radiation, λ = 0.71073 Å
μ (mm^{-1})	3.829
Crystal size (mm)	0.12 × 0.12 × 0.14
Data collection	
Diffractometer	Bruker Kappa APEX II diffractometer
Absorption correction	multi-scan *SADABS* (Siemens, 1996)
T_{min}, T_{max}	0.56, 0.63
No. of measured, independent and observed [I > -3σ(I)] reflections	214287, 23419, 14999
Rint	0.0883
θ_{max} (°)	30.57
Refinement	
R[F^2 > 2σ(F^2)], wR(F^2), S	0.061, 0.117, 0.99
No. of reflections	9384
No. of parameters	940
H-atom treatement	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	6.89, –6.22

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