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An orbitally adapted push-pull template for N_2 activation and reduction to diazene-diide

David Specklin,[a] Marie-Christine Boegli,[a] Anaïs Coffinet,[a] Léon Escomel,[a] Laure Vendier,[a] Mary Grellier[a] and Antoine Simonneau*[a]

a LCC-CNRS, Université de Toulouse, CNRS, UPS, 205 route de Narbonne, BP44099, F-31077 Toulouse cedex 4, France.

E-mail: antoine.simonneau@lcc-toulouse.fr

Abstract: A Lewis superacidic bis(borane) $C_6F_4\{B(C_6F_5)_2\}_2$ was reacted with tungsten N_2-complexes $[W(N_2)_2(R_2PCH_2CH_2PR_2)_2]$ (R = Ph or Et), affording zwitterionic boryldiazenido W(II) complexes *trans*-$[W(L)(R_2PCH_2CH_2PR_2)_2(N_2\{B(C_6F_5)_2(C_6F_4B(C_6F_5)_3\})]$ (L = ø, N_2 or THF). Those compounds feature only one N-B linkage of covalent type, as a result of intramolecular boron-to-boron C_6F_5 transfer. Complex *trans*-$[W(THF)(Et_2PCH_2CH_2PEt_2)_2(N_2\{B(C_6F_5)_2C_6F_4B(C_6F_5)_3\})]$ (**5**) was shown to split H_2, leading to a seven-coordinate complex $[W(H)_2(Et_2PCH_2CH_2PEt_2)_2(N_2\{B(C_6F_5)_2\}_2C_6F_4)]$ (**7**). Interestingly, hydride storage at the metal triggers backward C_6F_5 transfer. This reverts the bis(boron) moiety to its bis(borane) state, now doubly binding the distal N, with structural parameters and DFT computations pointing to dative N→B bonding. By comparison with an N_2 complex $[W(H)_2(Et_2PCH_2CH_2PEt_2)_2(N_2\{B(C_6F_5)_3\}]$ (**10**) differing only by the Lewis acid (LA), namely $B(C_6F_5)_3$, coordinated to the distal N, we demonstrate that two-fold LA coordination imparts strong N_2 activation up to the diazene-diide (N_2^{2-}) state. To the best of our knowledge, this is the first example of a neutral LA coordination that induces reduction of N_2.

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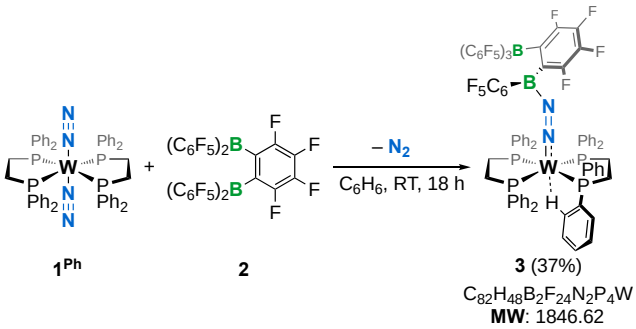
2 Experimental Procedures

2.1 General Considerations

All reactions were performed in flame- or oven-dried glassware with rigorous exclusion of air and moisture, using a nitrogen filled Jacomex glove box (O_2 < 0.5 ppm, H_2O < 1 ppm). Solvents used were pre-dried (*n*-pentane and tetrahydrofuran by passing through a Puresolv MD 7 solvent purification machine; benzene, fluorobenzene, hexamethyldisiloxane (HMDSO) and tetrahydropyran by distillation over CaH_2), degassed by freeze-pump-thaw cycles, dried over molecular sieves and stored in the glove box. C_6D_6, C_6D_5Cl and THF-d_8 (purchased from Eurisotop) were degassed by freeze-pump-thaw cycles, dried over molecular sieves and stored in the glove box. The W-dinitrogen complexes **1**^{R}, **9** and the isotopomer ^{15}N-**1**^{Et},[S1] and 1,2-[B(C_6F_5)$_2$]$_2$$C_6F_4$ (**2**) [S2] were prepared according to reported procedures from unpurified commercially available chemicals and stored in the glove box. ^{1}H, ^{11}B, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded using NMR tubes equipped with J. Young valves on a Bruker Avance III 400 spectrometer. Chemical shifts are in parts per million (ppm) downfield from tetramethylsilane and are referenced to the most upfield residual solvent resonance as the internal standard in ^{1}H NMR (C_6HD_5: δ reported = 7.16 ppm, C_6HD_4Cl: δ reported = 6.96 ppm, THF-d_8: δ reported = 1.72 ppm). ^{11}B, ^{15}N, ^{19}F and ^{31}P NMR spectra were calibrated according to the IUPAC recommendation using a unified chemical shift scale based on the proton resonance of tetramethylsilane as primary reference.[S3] Data are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, hept = heptuplet, m = multiplet), coupling constant (Hz), and integration. Infrared (IR) spectra were recorded in the glove box (O_2 < 0.5 ppm, H_2O < 1 ppm) 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. Raman spectra were measured on XploRA Raman microspectrometer (Horiba). Excitation was achieved with a 785 nm laser line focused on the sample with a microscope objective (x100, numerical aperture = 0.5). Elemental analyses were performed on samples sealed in tin capsules under Ar or N_2 by the Analytical Service of the Laboratoire de Chimie de Coordination; results are the average of two independent measurements.

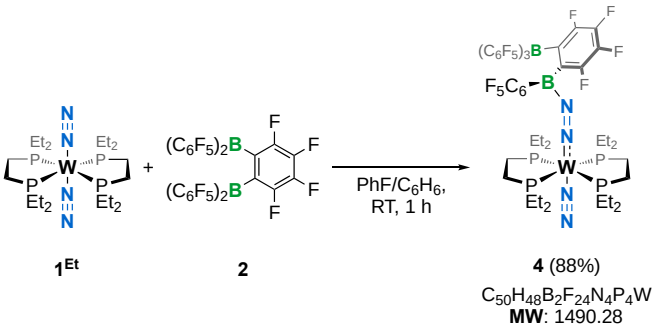
2.2 Preparation and Characterization of New Compounds

*2.2.1 Preparation of [W(dppe)$_2$(μ-N$_2$)B(C$_6$F$_5$)(C$_6$F$_4${B(C$_6$F$_5$)$_3$})] (**3**)*



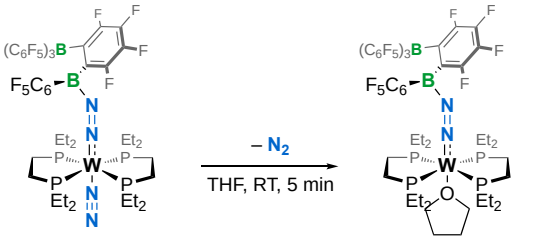
A solution of 1,2-[B(C_6F_5)$_2$]$_2$$C_6F_4$ (**2**, 25 mg, 30 μmol) in C_6H_6 (1 mL) was added to a deep orange solution of W(N_2)$_2$(dppe)$_2$ (**1**^{Ph}, 31 mg, 30 μmol, 1 equiv.) in C_6H_6 (3.5 mL) at room temperature, causing immediate gas (N_2) evolution and color change of the solution to dark red. The mixture was left standing for two days while dark red crystals of **2** precipitated out of the solution, the crystals were then recovered by decantation, washed with pentane (3 x 1.5 mL) and dried under vacuum (21 mg, 11 μmol, 37% yield). Crystals obtained in this manner were of sufficient quality for X-ray diffraction analyses (see section 4.2). The insolubility of **3** in non-polar deuterated solvents and its instability in polar ones precluded the collection of meaningful NMR data. **IR** (ATR) ν/cm^{-1} = 3056, 1642, 1552, 1511, 1458 (s), 1437, 1390, 1375, 1309, 1293, 1273, 1254, 1187, 1087(s), 1045, 1027, 976(s), 962, 911, 866, 845, 813, 787, 771, 749, 740(s), 692(s), 661. **Elem. Anal.** no satisfying elemental analyses could be obtained for this compound, probably due to its extreme sensitivity.

*2.2.2 Preparation of [W(N$_2$)(depe)$_2$(μ-N$_2$)B(C$_6$F$_5$)(C$_6$F$_4${B(C$_6$F$_5$)$_3$})] (**4**)*



A solution of 1,2-$[B(C_6F_5)_2]_2C_6F_4$ (**2**, 101 mg, 120 μmol) in PhF (1 mL) was added to a deep red solution of $W(N_2)_2(depe)_2$ (**1^{Et}**, 78 mg, 120 μmol) in PhF (1 mL) at room temperature to observe immediately a darkening of the solution. C_6H_6 (1 mL) was then added and the mixture was left standing 18 h while dark brown crystals of **4**•PhF precipitated out of the solution. The crystals were then recovered by decantation, washed with pentane (3 x 1.5 mL) and dried under vacuum (163 mg, 105 mmol, 88%). Crystals obtained in this manner were of sufficient quality for X-ray diffraction analyses (see section 4.3). The insolubility of **4** in apolar deuterated solvents and its instability in polar ones precluded the collection of meaningful NMR data. **^{15}N-4** was obtained similarly from **^{15}N-1^{Et}**. **IR** (ATR) ν/cm^{-1} = 2978, 2944, 2913, 2885, 2220, 1641, 1628, 1595, 1513, 1495, 1454(s), 1387, 1375, 1310, 1294, 1271, 1254, 1219, 1189, 1156, 1111, 1083(s), 1039, 1029, 973(s), 897, 869, 842, 806, 771, 749(s), 739, 729, 683(s), 662; **^{15}N-4** ν/cm^{-1} = 2974, 2942, 2914, 2882, 2220, 1667, 1641, 1595, 1513, 1493, 1454, 1375, 1307, 1293, 1271, 1218, 1109, 1083, 1039, 973, 867, 841, 806, 755, 687. **Elem. Anal.** calcd. for $C_{50}H_{48}B_2F_{24}N_2P_4W$•1.5$C_6H_5F$ (%): C, 43.36; H, 3.42; N, 3.43. Found: C, 43.19; H, 3.29; N, 2.00.

*2.2.3 Preparation of [W(THF)(depe)$_2$(μ-N$_2$)B(C$_6$F$_5$)(C$_6$F$_4${B(C$_6$F$_5$)$_3$})] (**5**)*

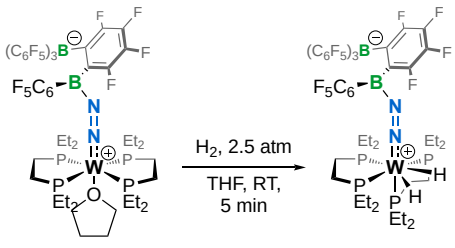


4 **5** (98%)

$C_{54}H_{56}B_2F_{24}N_2OP_4W$
MW: 1534.37

Solubilisation of **3**•PhF (37 mg, 23 μmol) in THF (1 mL) led to immediate gas (N_2) evolution. After 5 min at RT the solvent was removed under vacuum and the resulting oily residue triturated with pentane to yield **5** as a dark yellow powder recovered by decantation and dried under vacuum (35 mg, 23 μmol, 98%). Crystals suitable for analysis of **5** by X-ray diffraction were grown from a THF solution layered with HMDSO, but despite several attempts, the obtained structures were of too low resolution (see section 4.4). **^{15}N-5** was obtained similarly from **^{15}N-4**. **^{1}H NMR** (400 MHz, THF-d_8): δ 2.34–2.19 (m, 2H, PCH_2CH$_3$), 2.16–1.95 (m, 8H, PCH_2CH$_3$; PCH_2CH_2P), 1.91–1.65 (m, 10H, PCH_2CH$_3$; PCH_2CH_2P), 1.64–1.46 (m, 4H, PCH_2CH_2P), 1.38–1.10 (m, 21H, PCH$_2$CH_3), 0.88–0.75 (m, 3H, PCH$_2$CH_3) ppm. **^{11}B NMR** (128 MHz, THF-d_8): δ −15.05 (s, 1B, -*B*(C$_6$F$_5$)$_3$) ppm. **^{15}N-NMR** (41 MHz, C$_6$D$_6$): δ – 55.7, – 80.7. **^{19}F NMR** (376 MHz, THF-d_8): δ −122.40 (dd, *J* = 27.5, 14.7 Hz, 1F, *o*-C$_6$F$_5$ -B(C$_6$*F*$_5$)$_3$), −124.39 (dd, *J* = 23.1, 18.2 Hz, 1F, *o*-C$_6$F$_5$ -B(C$_6$*F*$_5$)$_3$), −126.44 (dd, *J* = 27.2, 18.5 Hz, 1F, -(C$_6$*F*$_4$B$_2$)-), −130.76 (dd, *J* = 27.0, 7.8 Hz, 1F, *o*-C$_6$F$_5$ -B(C$_6$*F*$_5$)N-), −131.33 (ddd, *J* = 27.4, 16.5, 10.4 Hz, 1F, -(C$_6$*F*$_4$B$_2$)-), −132.02 (d, *J* = 24.8 Hz, 1F, *o*-C$_6$F$_5$ -B(C$_6$*F*$_5$)$_3$), −132.31 – −132.71 (m, 1F, *o*-C$_6$F$_5$ -B(C$_6$*F*$_5$)$_3$), −133.36 (td, *J* = 25.3, 7.0 Hz, 1F, *o*-C$_6$F$_5$ -B(C$_6$*F*$_5$)$_3$), −133.87 – −134.22 (m, 2F, *o*-C$_6$F$_5$ -B(C$_6$*F*$_5$)$_3$; -B(C$_6$*F*$_5$)N-), −158.92 (t, *J* = 20.3 Hz, 1F, *p*-C$_6$F$_5$ -B(C$_6$*F*$_5$)N-), −164.39 (t, *J* = 20.1 Hz, 1F, *p*-C$_6$F$_5$ -B(C$_6$*F*$_5$)$_3$), −164.65 (t, *J* = 21.0 Hz, 1F, -(C$_6$*F*$_4$B$_2$)-), −164.93 (td, *J* = 22.8, 8.8 Hz, 1F, *m*-C$_6$F$_5$ -B(C$_6$*F*$_5$)N-), −165.42 (ddd, J = 29.9, 20.5, 9.3 Hz, 1F, *m*-C$_6$F$_5$ -B(C$_6$*F*$_5$)N-), −166.12 (t, *J* = 20.4 Hz, 1F, *p*-C$_6$F$_5$ -B(C$_6$*F*$_5$)$_3$), −166.36 (t, *J* = 20.2 Hz, 1F, *p*-C$_6$F$_5$ -B(C$_6$*F*$_5$)$_3$), −167.17 (td, *J* = 21.8, 8.7 Hz, 1F, *m*-C$_6$F$_5$ -B(C$_6$*F*$_5$)$_3$), −167.69 (dd, *J* = 27.0, 19.7 Hz, 1F, -(C$_6$*F*$_4$B$_2$)-), −168.12 (td, *J* = 22.3, 5.8 Hz, 1F, *m*-C$_6$F$_5$ -B(C$_6$*F*$_5$)$_3$), −168.89 – −169.11 (m, 1F, *m*-C$_6$F$_5$ -B(C$_6$*F*$_5$)$_3$), −169.09– −169.30 (m, 1F, *m*-C$_6$F$_5$ -B(C$_6$*F*$_5$)$_3$), −169.74 – −169.97 (m, 1F, *m*-C$_6$F$_5$ -B(C$_6$*F*$_5$)$_3$), −169.95 – −170.15 (m, 1F, *m*-C$_6$F$_5$ -B(C$_6$*F*$_5$)$_3$) ppm. **^{31}P{^{1}H} NMR** (162 MHz, THF-d_8): δ 38.6 (s, 2P, J_{WP} = 284.2 Hz), 33.8 (s, 2P, J_{WP} = 283.2 Hz). **IR** (ATR) ν/cm^{-1} = 2963, 2941, 2883, 1641, 1512, 1455, 1377, 1297, 1271, 1253, 1109, 1079, 1039, 973, 867, 841, 810, 771, 758, 739, 730, 685, 662; **^{15}N-5** ν/cm^{-1} = 2964, 2922, 2884, 1642, 1512, 1455, 1377, 1298, 1271, 1183, 1107, 1081, 1038, 973, 867, 825, 810, 771, 755, 749, 729, 686, 665. **Raman** cm^{-1} = 1648, 1486, 1461, 1419, 1364, 1318, 1239, 1218, 1201, 1136, 1047, 984, 950, 916, 850, 816, 775, 733, 678; **^{15}N-5** cm^{-1} = 1647, 1468, 1419, 1343, 1319, 1299, 1242, 1202, 1133, 1048, 996, 955, 915, 848, 819, 774, 732, 672. **Elem. Anal.** calcd. for $C_{54}H_{56}B_2F_{24}N_2OP_4W$ (%): C, 42.27; H, 3.68; N, 1.83. Found: C, 41.98; H, 3.69; N, 1.97.

*2.2.4 Spectroscopic characterization of [W(depe)$_2$(H)$_2$(μ-N$_2$)B(C$_6$F$_5$)(C$_6$F$_4${B(C$_6$F$_5$)$_3$})] (**6**)*

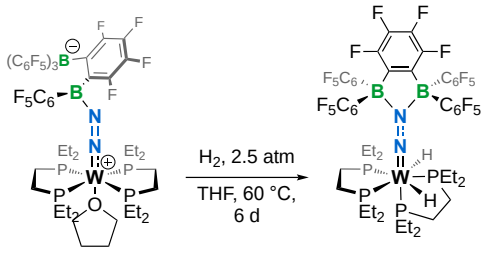


5 **6**

Complex **5** (12.2 mg, 8.0 μmol) was solubilized in THF-d_8 (0.5 mL) and transferred in a high pressure Young NMR tube. After 5 min at RT, H_2 was added (2.5 atm) and the mixture rapidly turned yellow from dark brown upon conversion to a mixture of two isomers of H_2 complex **6**. **^{1}H NMR** (400 MHz, THF-d_8): Owing to signal superposition, the two isomers could not be differentiated; δ 2.43 – 1.7 (m, PCH_2CH$_3$, PCH_2CH_2P), 1.70 – 1.42 (m, PCH_2CH$_3$, PCH$_2$CH_3), 1.34 – 1.03 (m, PCH$_2$CH_3), 1.03 – 0.91 (m, PCH$_2$CH_3), 0.90 – 0.78 (m, PCH$_2$CH_3); hydride signals are hidden under the phosphine's substituents (see section 5.4.2 and 5.4.3). **^{11}B NMR** (128 MHz, THF-d_8):

Both isomers = δ −15.09 (s, 1B, -*B*(C_6F_5)$_3$) ppm. **^{15}N-NMR** (41 MHz, C_6D_6): Min = δ – 60.5, – 97.3; Maj = δ – 63.1, – 100.4. **^{19}F NMR** (376 MHz, THF-d_8): Maj = δ −123.21 (br, 1F), −123.92 – −124.30 (m, 1F), −126.77 (br, 1F), −132.24 – −132.90 (m, 3F), −133.27 (dt, *J* = 24.2, 11.9 Hz, 1F), −133.43 – −133.65 (m, 1F), −134.24 – −134.46 (m, 1F), −134.51 – −134.78 (m, 1F), −156.62 (t, *J* = 19.7 Hz, 1F), −163.54 – −163.81 (m, 2F), −164.04 – −164.42 (m, 1F), −165.74 – −166.00 (m, 2F), −166.34 – −166.53 (m, 1F), −166.75 – −166.97 (m, 1F), −167.08 – −167.28 (m, 1F), −167.47 (td, *J* = 22.4, 21.8, 9.5 Hz, 1F), −168.45 (q, *J* = 25.8, 23.9 Hz, 2F), −168.89 (t, *J* = 22.0 Hz, 1F), −169.73 – −169.93 (m, 1F); Min = δ −123.89 – −124.44 (m, 1F), −125.76 (br, 1F), −128.37 (br, 1F), −131.87 (d, *J* = 23.7 Hz, 1F), −132.26 – −132.89 (m, 3F), −133.43 – −133.65 (m, 1F), −133.77 (dd, *J* = 26.1, 7.9 Hz, 1F), −135.25 – −135.67 (m, 1F), −156.67 (t, *J* = 20.1 Hz, 1F), −162.81 (t, *J* = 21.2 Hz, 1F), −163.54 – −163.76 (m, 1F), −164.06 – −164.41 (m, 1F), −165.51 – −165.73 (m, 2F), −165.75 – −166.02 (m, 1F), −166.06 – −166.58 (m, 1F), −166.77 – −166.99 (m, 1F), −167.92 – −168.21 (m, 1F), −169.17 (t, *J* = 21.6 Hz, 1F), −169.31 – −169.54 (m, 1F), −169.56 – −169.74 (m, 1F), −170.44 – −170.71 (m, 1F). **^{31}P{^{1}H} NMR** (162 MHz, THF-d_8): Maj = δ 49.02 – 47.97 (m, 2P), 46.53 – 45.80 (m, 1P), 7.24 (t, *J* = 22.2 Hz, 1P) ppm; Min = δ 50.93 (t, *J* = 20.7 Hz, 1P), 48.06 – 47.68 (m, 1P), 45.91 – 45.35 (m, 1P), 8.73 (t, *J* = 22.5 Hz, 1P) ppm.

*2.2.5 Preparation of [W(depe)$_2$(H)$_2$(μ-N$_2$)(1,2-{B(C$_6$F$_5$)$_2$}$_2$C$_6$F$_4$)] (**7**) from **5***

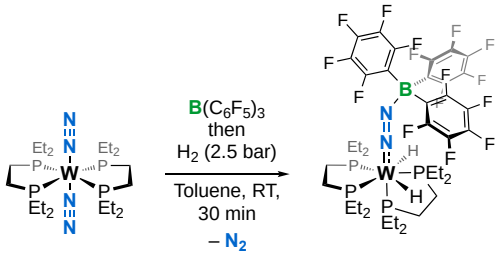


5

7
$C_{50}H_{50}B_2F_{24}N_2P_4W$
MW: 1453.47

Complex **5** (46 mg, 30 μmol) was solubilized in THF-d_8 (0.65 mL) and transferred in a high pressure Young NMR tube. After 5 min at RT, H_2 was added (2.5 atm) and the mixture rapidly turned yellow from dark brown upon conversion to complex **6**. After 6 days at 60 °C, NMR monitoring shows that **7** is the major component of the reaction mixture. Slow diffusion of HMDSO in the THF solution allowed for the deposition of **7** as bright yellow crystals (21 mg, 48%) that were suitable for an XRD analysis (see section 4.8). **^{15}N-7** was obtained by another approach, see 2.2.7.
^{1}H NMR (400 MHz, THF-d_8): δ 2.41 – 2.25 (m, 4H, PC*H*$_2$CH$_3$), 2.20 – 2.06 (m, 4H, PC*H*$_2$CH$_3$), 2.03 – 1.80 (m, 8H, PC*H*$_2$C*H*$_2$P), 1.68 – 1.54 (m, 7H, PC*H*$_2$CH$_3$, PCH$_2$C*H*$_3$), 1.38 – 1.14 (m, 15H, PCH$_2$C*H*$_3$), 1.05 (t, J = 7.5 Hz, 3H, PCH$_2$C*H*$_3$), 1.01 (t, J = 7.5 Hz, 3H, PCH$_2$C*H*$_3$); hydride signals are hidden under the phosphine's substituents (see section 5.4.4). **^{11}B NMR** (128 MHz, THF-d_8): δ −3.36 (br, 2B) ppm. **^{19}F NMR** (376 MHz, THF-d_8): −116.38 (s br, 1F, *o*-C_6F_5), −119.07 (s br, 1F, *o*-C_6F_5), −126.64 (s br, 1F, *o*-C_6F_5), −128.17 (s br, 1F, *o*-C_6F_5), −129.03 (s br, 2F, *o*-C_6F_5), −129.73 (s br, 1F, *o*-C_6F_5), −130.78 (s br, 1F, *o*-C_6F_5), −138.33 (d br, *J* = 36.3 Hz, 1F, *o*-C_6F_5), −139.60 (s br, 1F, *o*-C_6F_5), −162.36 (s br, 1F, *p*-C_6F_5), −163.52 (s br, 1F, *p*-C_6F_5), −163.89 (s br, 1F, *p*-C_6F_5), −164.08 (s br, 1F, *p*-C_6F_5), −165.96 (s br, 1F, *m*-C_6F_5), −166.14 (s br, 1F, *m*-C_6F_5), −166.58 (s br, 1F, *m*-C_6F_5), −166.75 (s br, 1F, *m*-C_6F_5), −166.97 (s br, 2F, *m*-C_6F_5), −167.40 (s br, 2F, *m*-C_6F_5), −167.75 (s br, 1F, *m*-C_6F_5), −168.82 (s br, 1F, *m*-C_6F_5) ppm. **^{31}P{^{1}H} NMR** (162 MHz, THF-d8): δ 44.24 (t, *J* = 13.7 Hz, J_{PW} = 76.5 Hz, 1P), 37.85 (br, 1P), 35.51 (br, 1P), -3.89 (t, *J* = 20.8 Hz, 1P). **IR** (ATR) ν/cm^{-1} = 2978, 2943, 2885, 1850, 1640, 1513, 1446, 1399, 1360, 1327, 1274, 1252, 1082, 1031, 971, 959, 860, 823, 795, 751, 734, 677. **Elem. Anal.** calcd. for $C_{50}H_{50}B_2F_{24}N_2P_4W$ (%): C, 41.01; H, 3.44; N, 1.91. Found: C, 41.35; H, 3.54; N, 1.96.

*2.2.6 Preparation of [W(depe)$_2$(H)$_2$(μ-N$_2$)B(C$_6$F$_5$)$_3$] (**10**)*



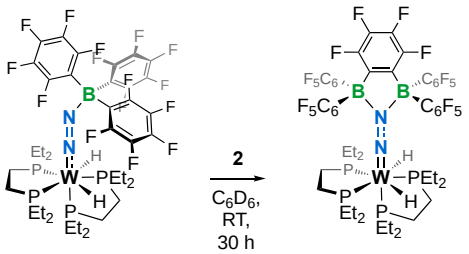
1^{Et}

10
$C_{38}H_{50}BF_{15}N_2P_4W$
MW: 1138,35

Toluene (2 mL) was added at room temperature to a vial containing **1^{Et}** (150 mg, 230 μmol) and B(C_6F_5)$_3$ (118 mg, 230 μmol, 1 equiv.). The reaction mixture was transferred to a Fisher-Porter vessel and placed under an H_2 atmosphere (2.5 bar). The dark maroon-purple solution was stirred for 30 min, time during which the mixture turned to a deep orange solution. This was concentrated under vacuum to 1 mL and layered with pentane. After 3 days at –30 °C, dark red-orange crystals of **10** precipitated. They were recovered by filtration, washed with pentane and dried under vacuum (212 mg, 81% yield, toluene solvate). **^{15}N-10** was obtained similarly from **^{15}N-1^{Et}**.
^{1}H NMR (400 MHz, C_6D_6): δ 1.88 - 1.73 (m, 2H), 1.73 - 1.53 (m, 4H), 1.53 - 1.32 (m, 5H), 1.32 - 1.08 (m, 6H), 1.08 - 0.86 (m, 16H), 0.86 - 0.76 (m, 3H), 0.76 - 0.57 (m, 6H), 0.40 (dt, *J* = 14.3, 7.5 Hz, 6H), –1.38 - –2.04 (m, 2H) ppm. **^{11}B NMR** (128 MHz, C_6D_6): δ – 9.7

ppm. **^{15}N-NMR** (41 MHz, C_6D_6): δ – 35.5, – 130.3. **^{19}F NMR** (376 MHz, C_6D_6): δ – 131.3 (dd, *J* = 25.7, 7.9 Hz, $2F_{ortho}$), – 160.3 (t, *J* = 20.7 Hz, $1F_{para}$), – 165.2 (m, $2F_{meta}$) ppm. **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6): δ 49.9 (br s,1P, $^{1}J_{P\text{-}W}$ = 182.7 Hz), 49.8 (br s, 2P, $^{1}J_{P\text{-}W}$ = 180.7 Hz), 15.7 (m, 1P) ppm. **IR (ATR)** ν/cm^{-1} = 2967, 2940, 1712(s), 1641, 1513(s), 1452(s), 1375, 1274, 1082(s), 1038, 973(s), 884, 872, 806, 755, 730, 703, 676, 660; **^{15}N-10** ν/cm^{-1} = 2967, 2939, 2906, 2879, 1778, 1659(s), 1640(s), 1513(s), 1452(s), 1425, 1374, 1273, 1245, 1125, 1098, 1083(s), 1037, 1026, 973(s), 882, 871, 817, 803, 768, 756, 730, 704, 675, 665. **Raman** cm^{-1} = 1827, 1714, 1641, 1513, 1464, 1418, 1374, 1322, 1277, 1236, 1191, 1132, 1083, 1041, 1002, 981, 956, 884, 833, 816, 806, 761, 740, 707, 675, 667; **^{15}N-10** cm^{-1} = 1826, 1664, 1640, 1514, 1463, 1416, 1374, 1347, 1276, 1258, 1235, 1131, 1082, 1041, 1004, 980, 900, 881, 837, 817, 804, 760, 739, 707, 676, 666. **Elem. Anal.** calcd. for $C_{38}H_{50}BF_{15}N_2P_4W{\cdot}0.4C_7H_8$ (%): C, 41.46; H, 4.58; N, 2.39. Found: C, 41.41; H, 4.68; N, 2.33.

*2.2.7 Preparation of [W(depe)$_2$(H)$_2$(μ-N$_2$)(1,2-{B(C$_6$F$_5$)$_2$}$_2$C$_6$F$_4$)] (**7**) from **10***



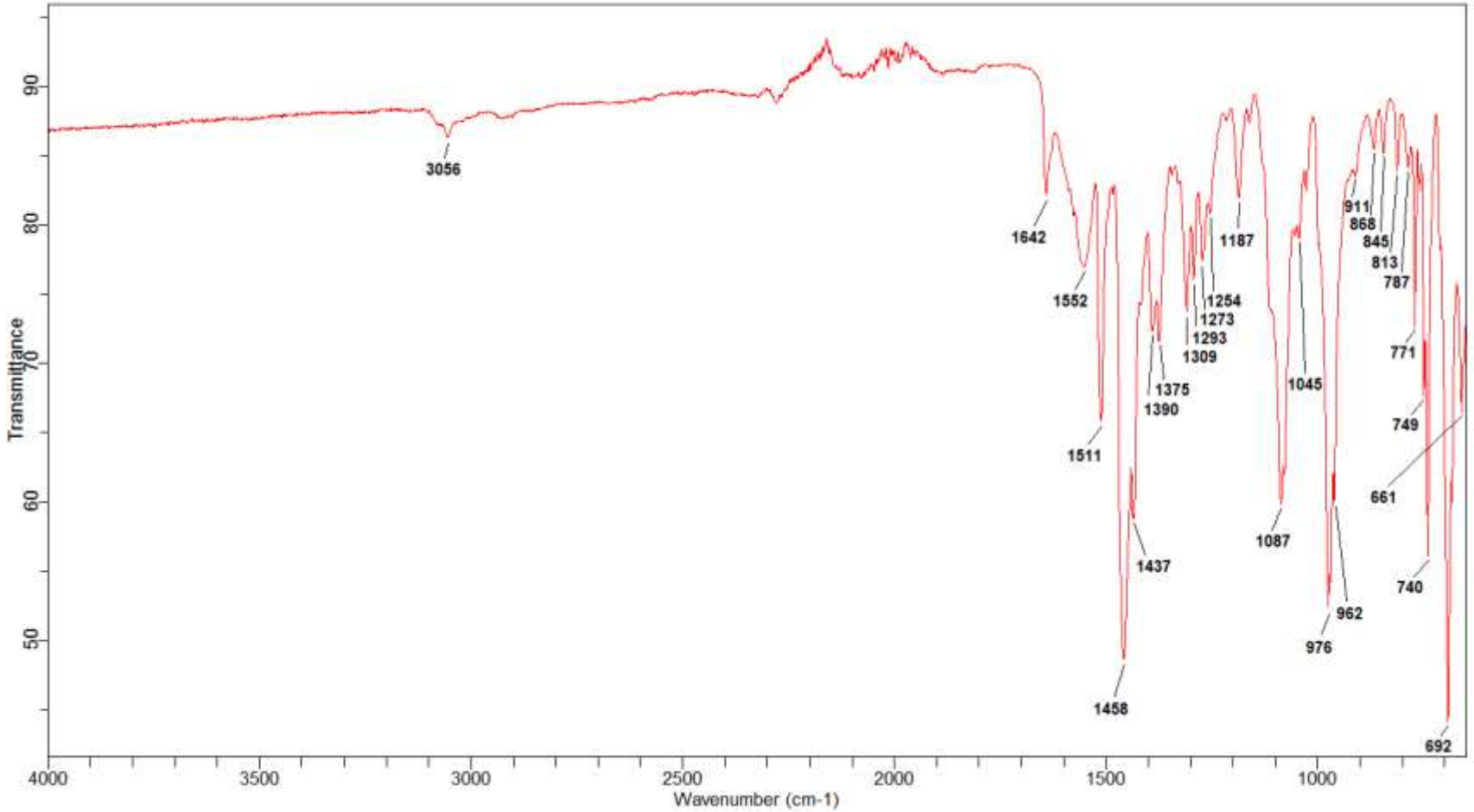
10 **7**

C_6D_6 (0.6 mL) was added to a J. Young-valved NMR tube containing [W(depe)$_2$(H)$_2$(μ-N$_2$)B(C$_6$F$_5$)$_3$] (**10**, 23 mg, 20 μmol) and 1,2-[B(C$_6$F$_5$)$_2$]$_2$C$_6$F$_4$ (**2**, 17 mg, 20 μmol, 1 equiv). The precipitation of a dense orange oil was observed and NMR analysis revealed the total consumption of **10** after 30 hours at room temperature. The light-yellow supernatant was separated by filtration, the oil washed with C_6D_6 (3 x 0.1 mL) and dissolved in $C_6D_4Cl_2$ (0.5 mL). The orange solution was then heated at 50 °C for 2 days, leading to the deposition of [W(depe)$_2$(H)$_2$(μ-N$_2$)(1,2-{B(C$_6$F$_5$)$_2$}$_2$C$_6$F$_4$)] as bright yellow crystals (18 mg, 63% yield). **^{15}N-7** was obtained similarly from **^{15}N-10**. Despite several hours of acquisition, no nitrogen resonances could be detected in the ^{15}N NMR spectra. **IR (ATR) ^{15}N-7** ν/cm^{-1} = 2965, 2940, 2883, 1849, 1640, 1513, 1484, 1446, 1383, 1338, 1323, 1274, 1252, 1083, 1038, 971, 960, 859, 789, 750, 734, 712, 693, 678. **Raman** cm^{-1} = 1899, 1855, 1645, 1466, 1417, 1387, 1328, 1276, 1258, 1244, 1153, 1086, 1068, 1041, 984, 887, 863, 826, 794, 775, 733, 693, 675; **^{15}N-7** cm^{-1} = 1899, 1854, 1645, 1466, 1417, 1388, 1326, 1275, 1258, 1241, 1154, 1087, 1068, 1040, 991, 888, 863, 827, 794, 775, 733, 693, 674.

3 Spectroscopic Data of New Compounds

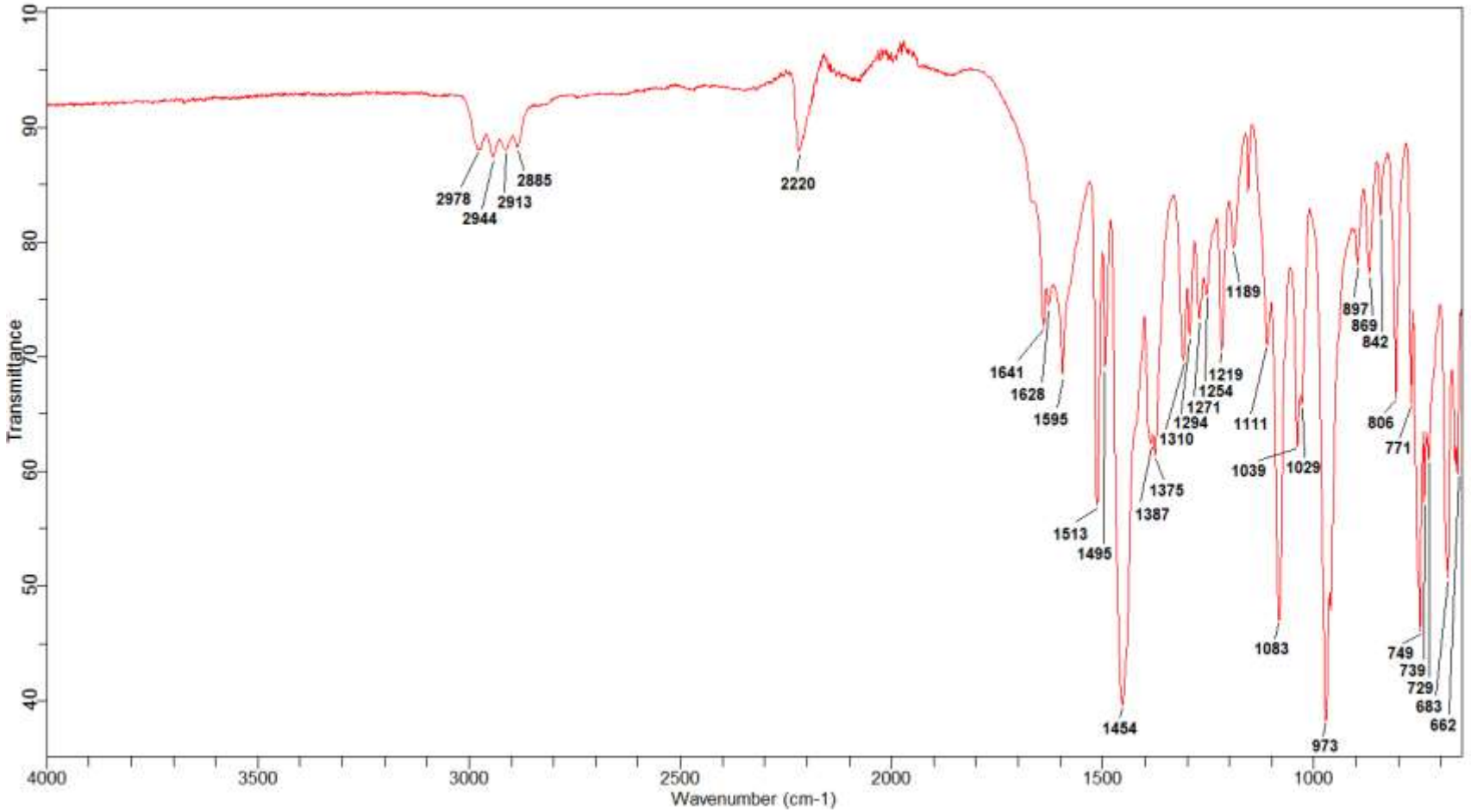
3.1 $[W(dppe)_2(\mu\text{-}N_2)B(C_6F_5)(C_6F_4\{B(C_6F_5)_3\})]$ (3)

3.1.1 ***Figure S1.*** *FT-IR (ATR) of* ***3****.*

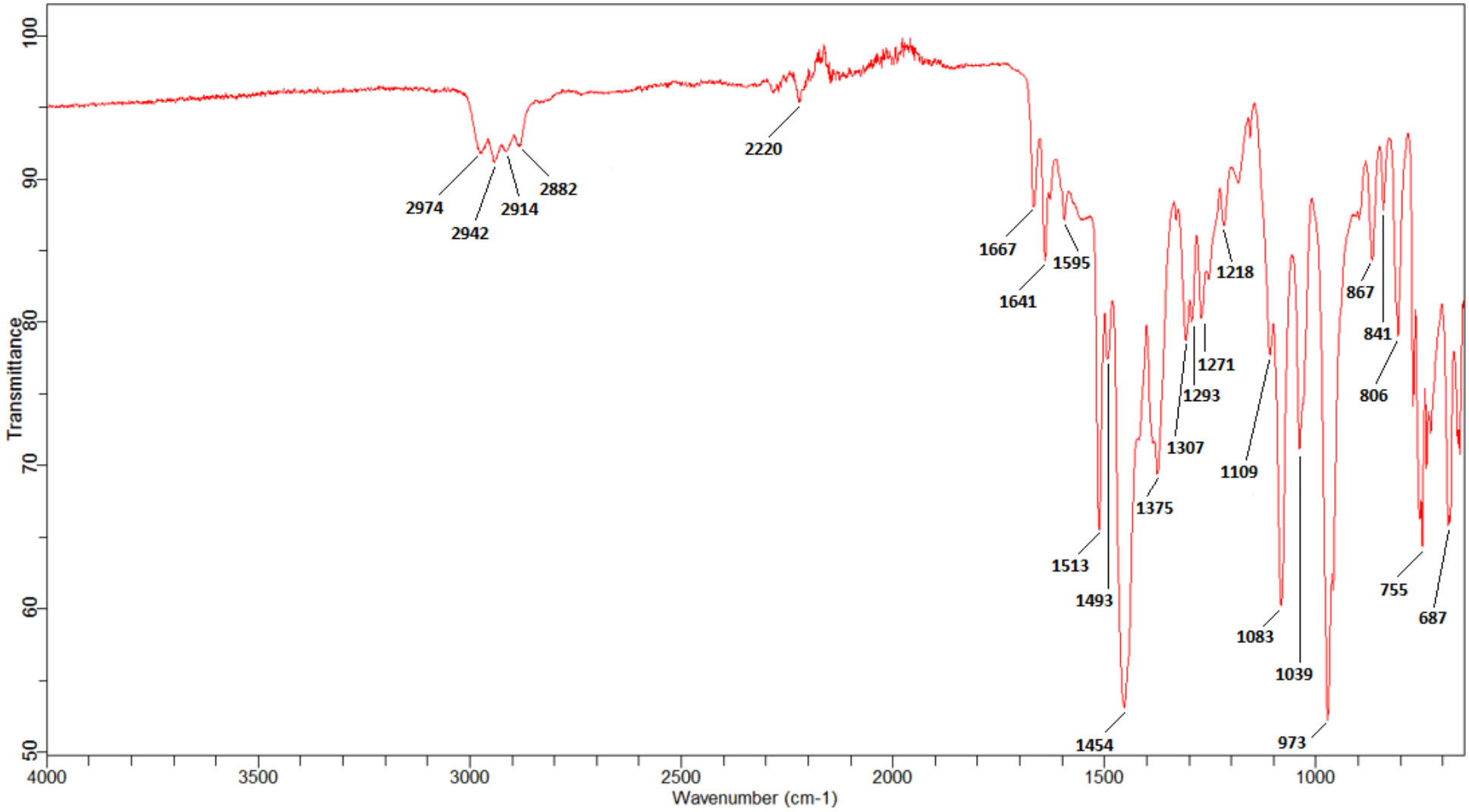


3.2 $[W(N_2)(depe)_2(\mu\text{-}N_2)B(C_6F_5)(C_6F_4\{B(C_6F_5)_3\})]$ (4)

3.2.1 ***Figure S2.*** *FT-IR (ATR) of* ***4****.*

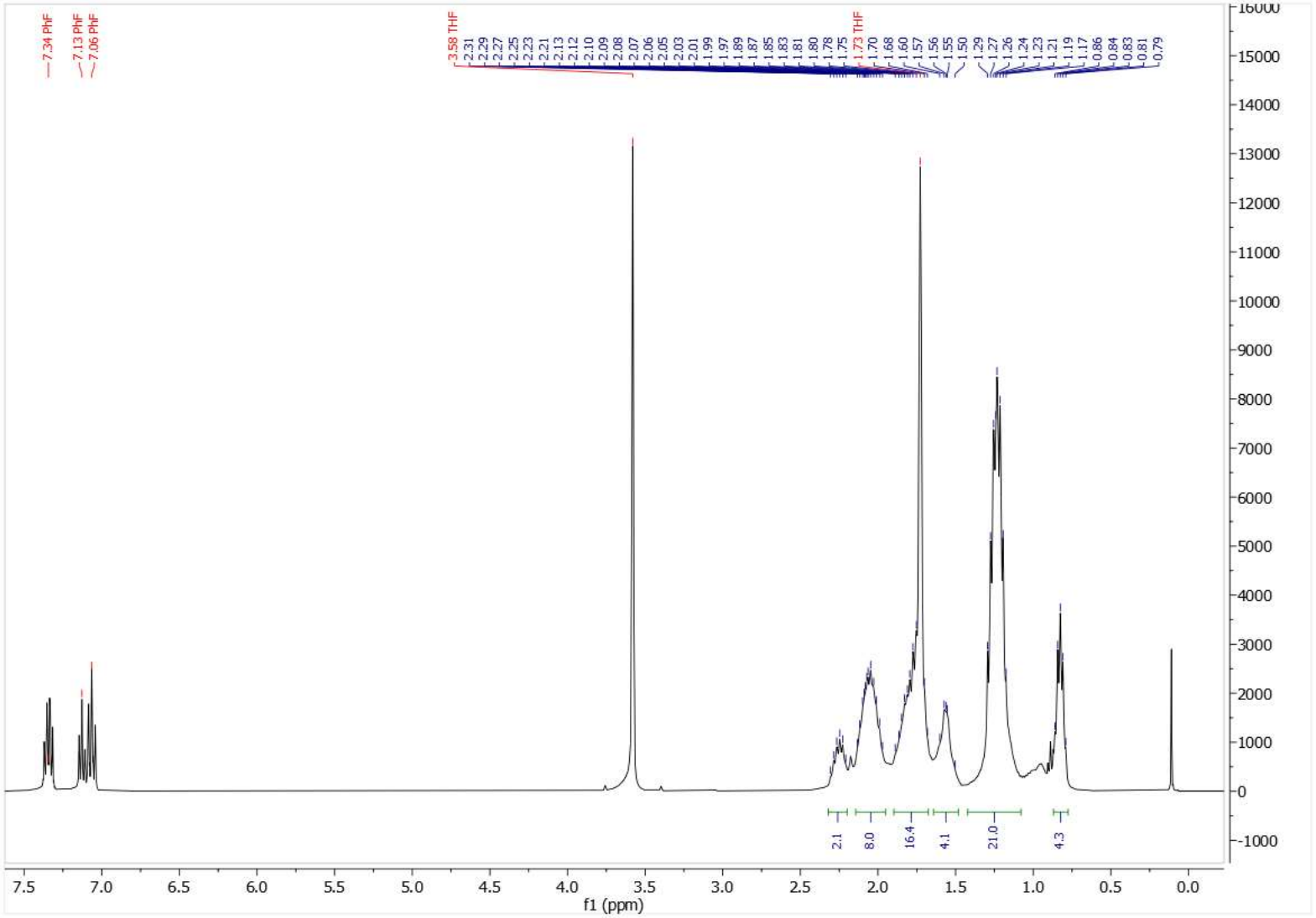


3.2.2 ***Figure S3.*** *FT-IR (ATR) of* ***^{15}N-4****.*

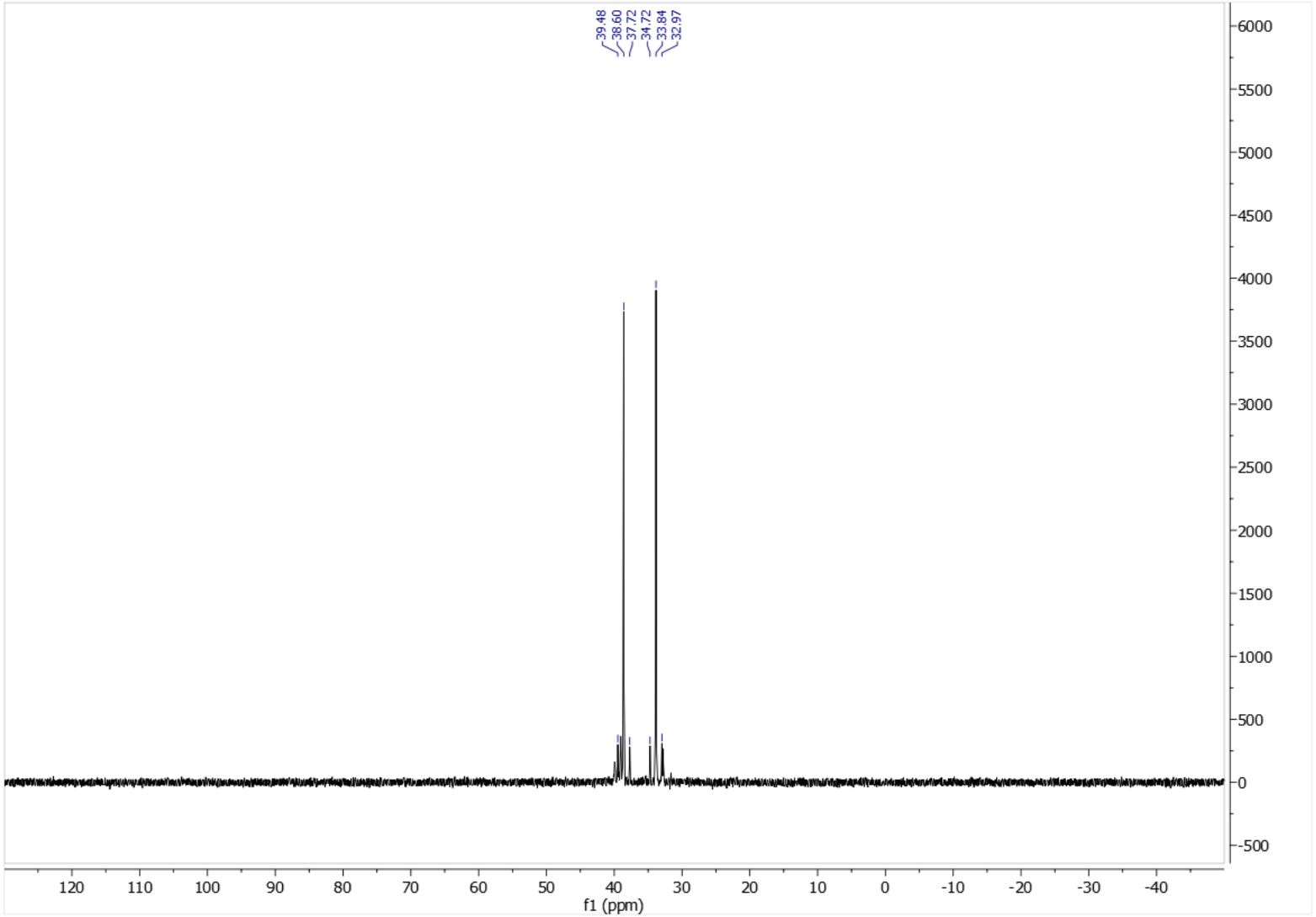


3.3 [W(THF)(depe)$_2$(μ-N$_2$)B(C$_6$F$_5$)(C$_6$F$_4${B(C$_6$F$_5$)$_3$})] (5)

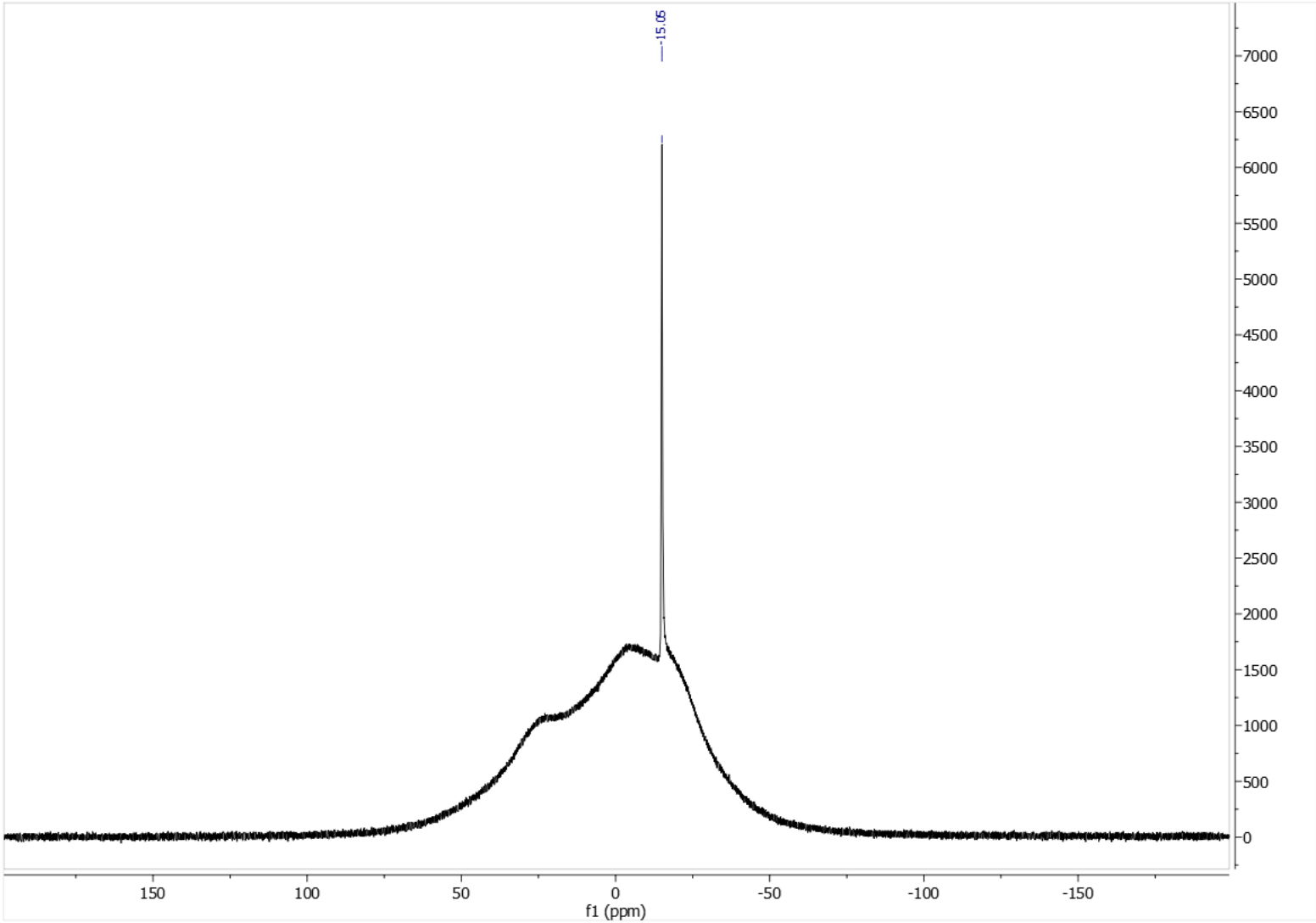
3.3.1 ***Figure S4****. ^{1}H NMR (400 MHz, THF-d$_8$) of* ***5****.*



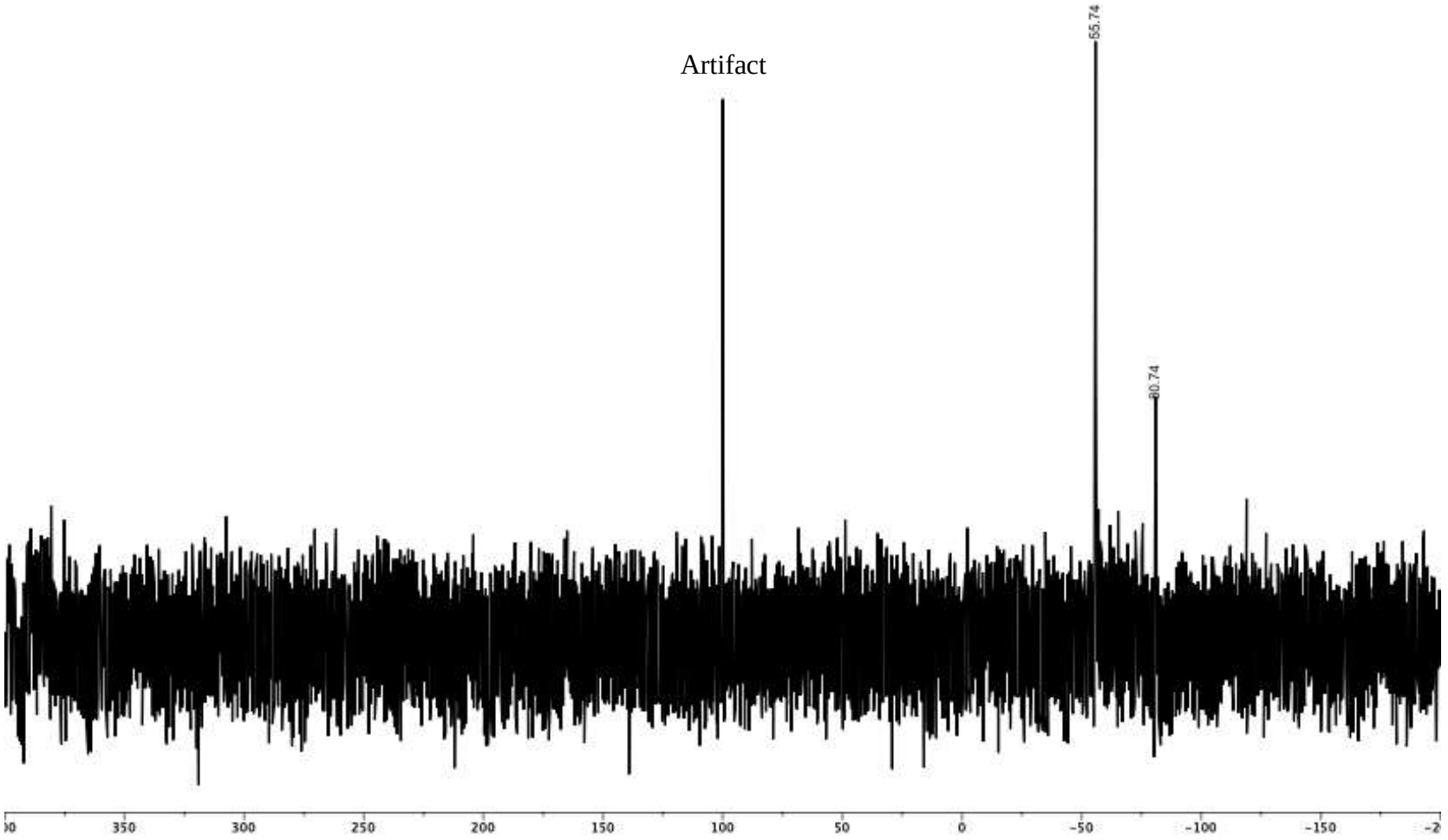
3.3.2 ***Figure S5.*** *$^{31}P\{^{1}H\}$ NMR (162 MHz, THF-d_8) of **5**.*



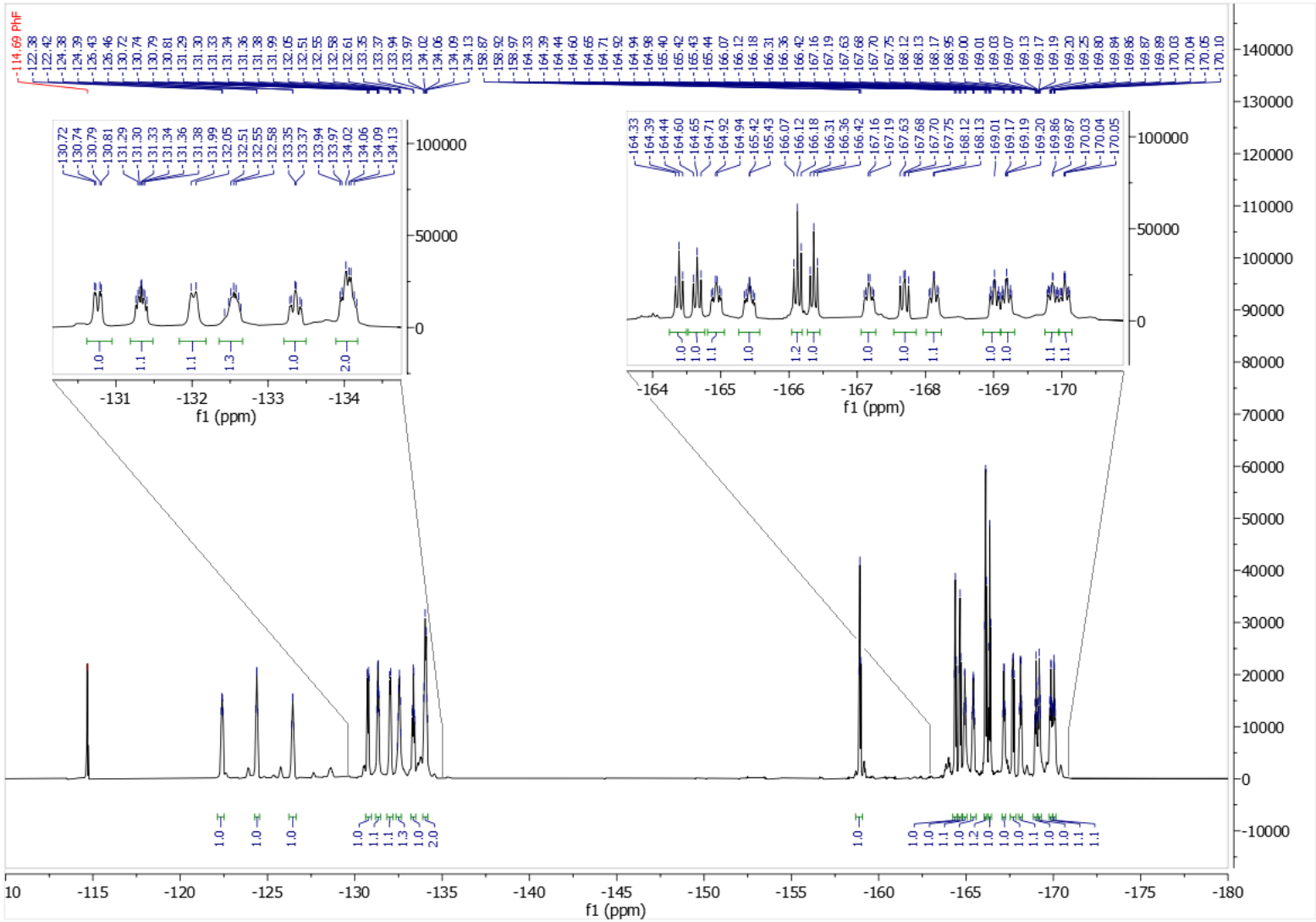
3.3.3 ***Figure S6.*** *^{11}B NMR (128 MHz, THF-d_8) of* ***5****.*



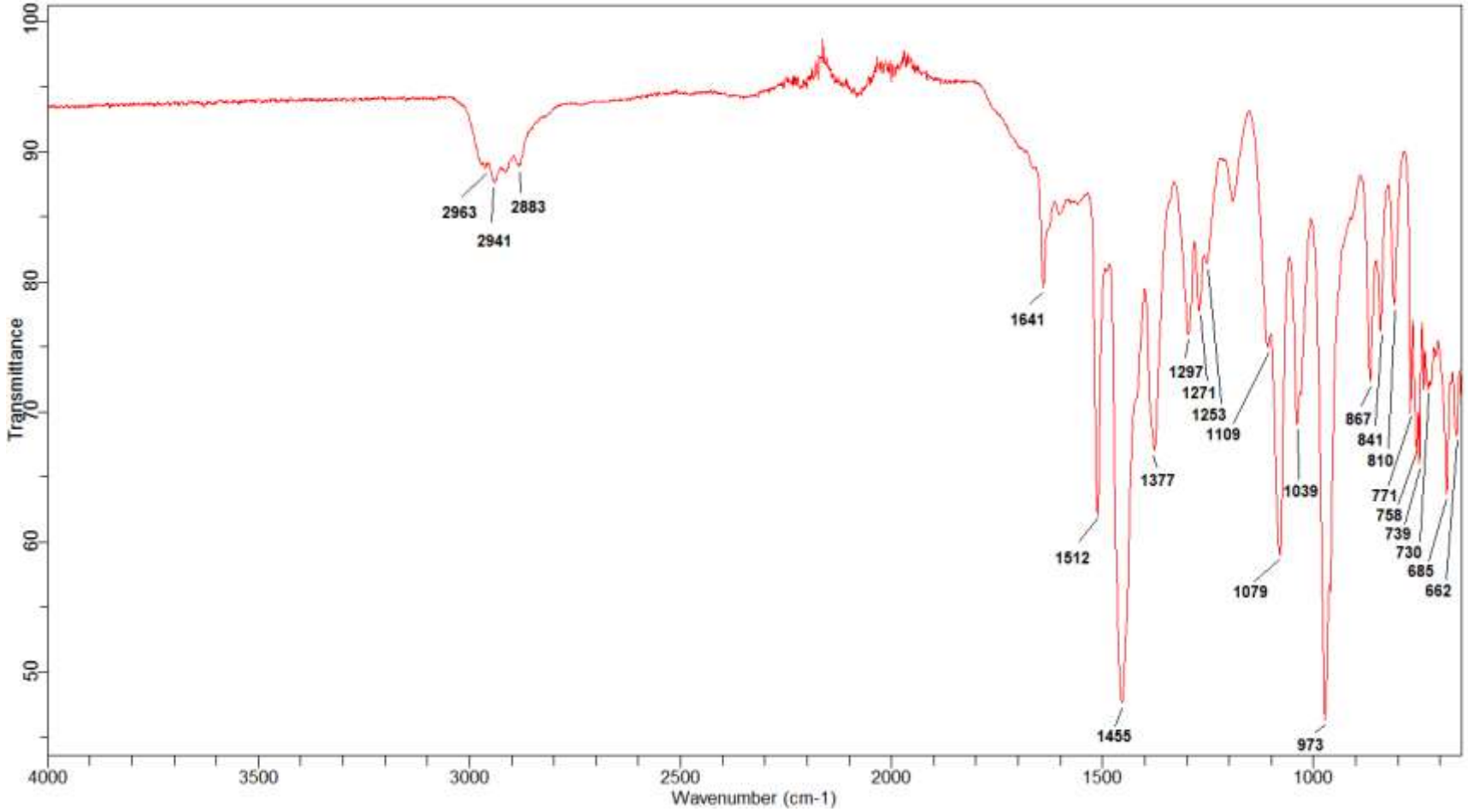
3.3.4 ***Figure S7.*** *^{15}N INVGATED ^{1}H NMR (41 MHz, C_6D_6) of* ***5****.*



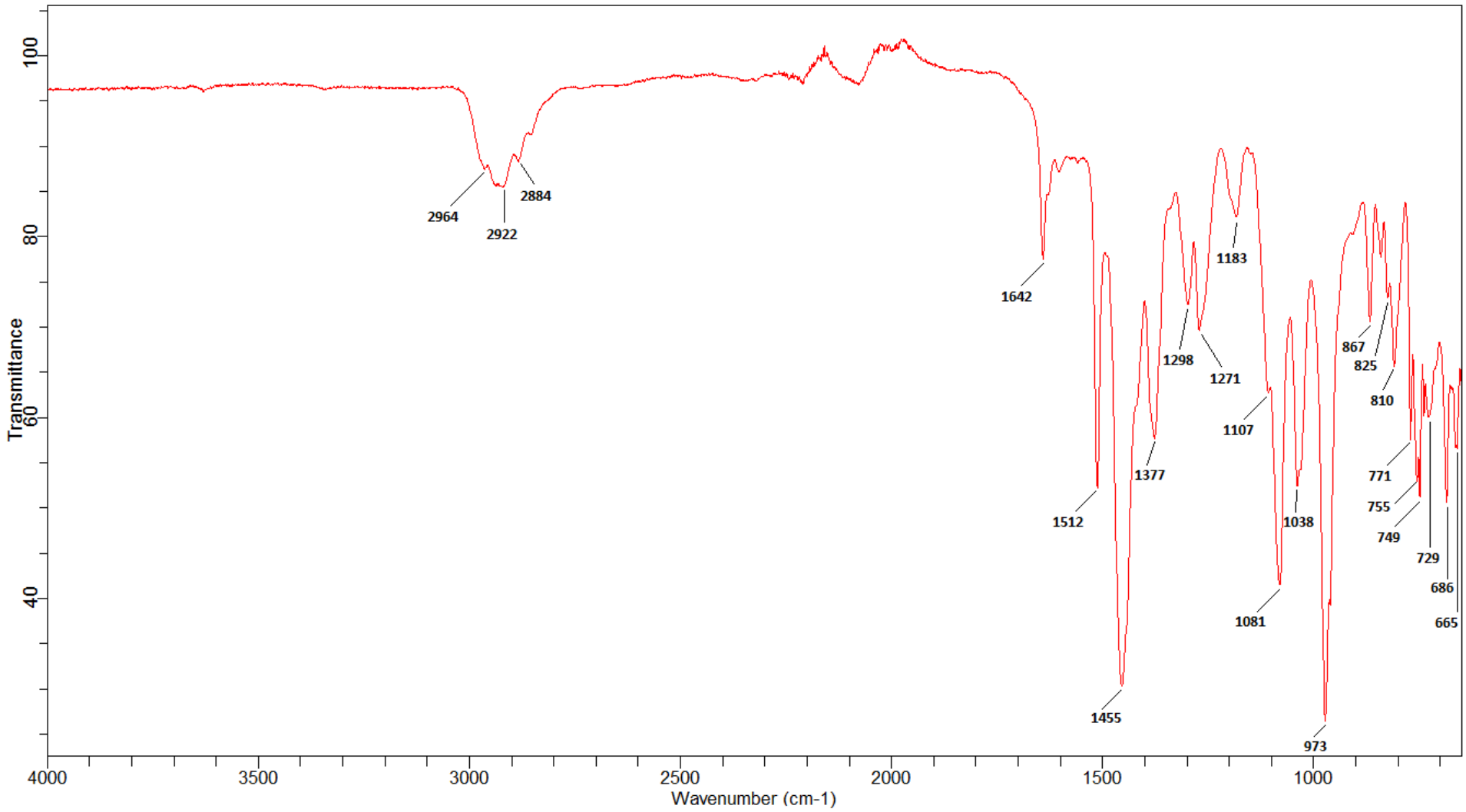
3.3.5 ***Figure S8.*** *^{19}F NMR (376 MHz, THF-d_8) of* ***5****.*



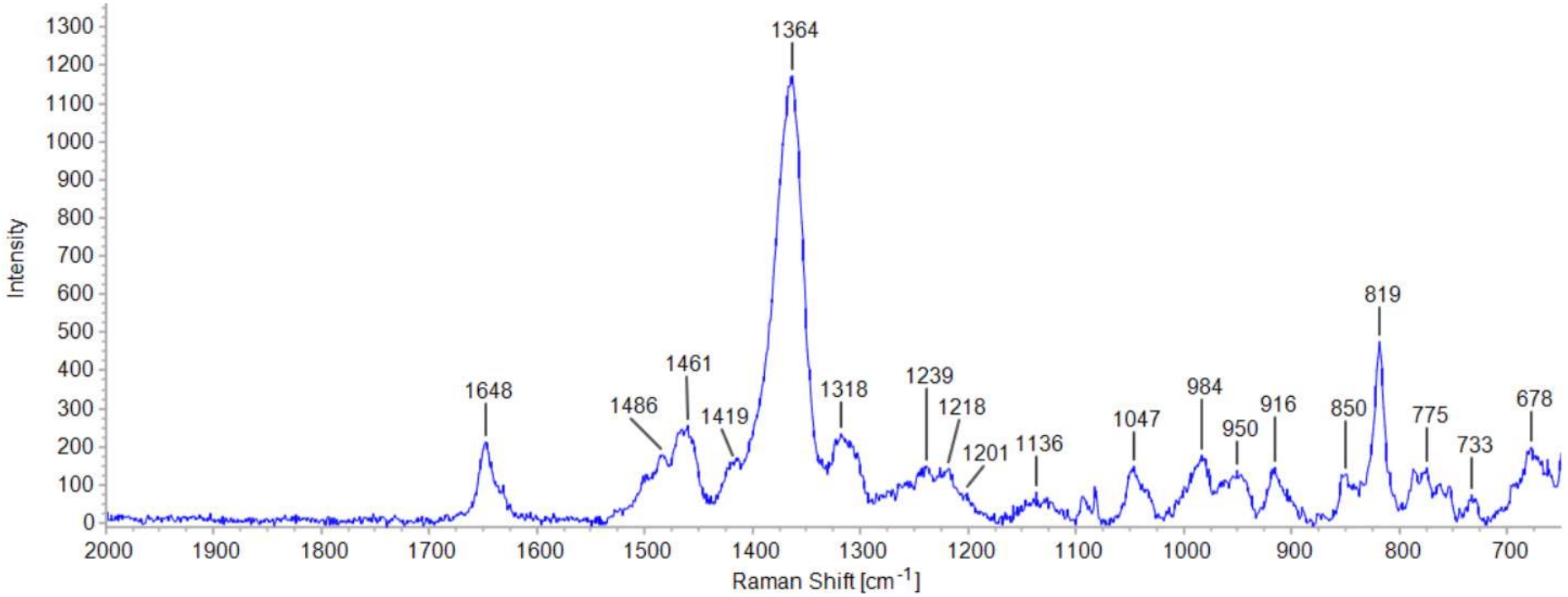
3.3.6 ***Figure S9.*** *FT-IR (ATR) of* ***5****.*



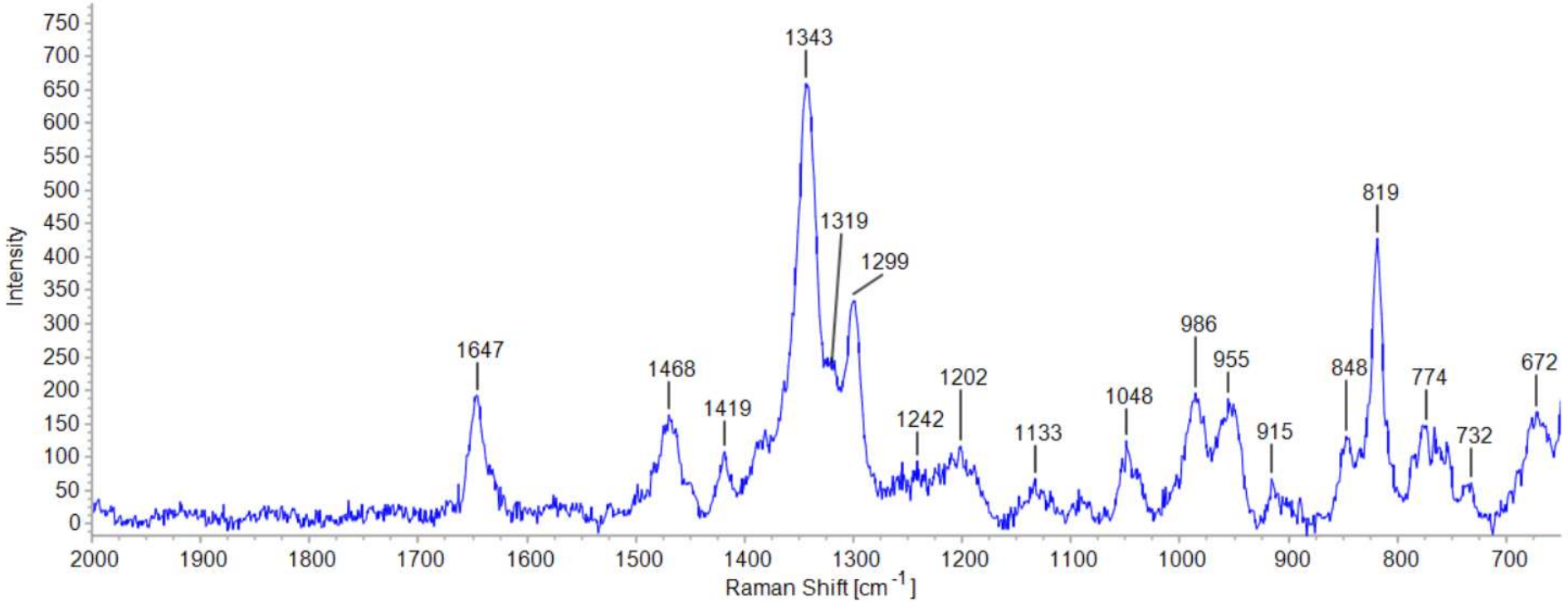
3.3.7 ***Figure S10.*** *FT-IR (ATR) of* ***^{15}N-5****.*



3.3.8 ***Figure S11.*** *Raman spectrum of* ***5****.*

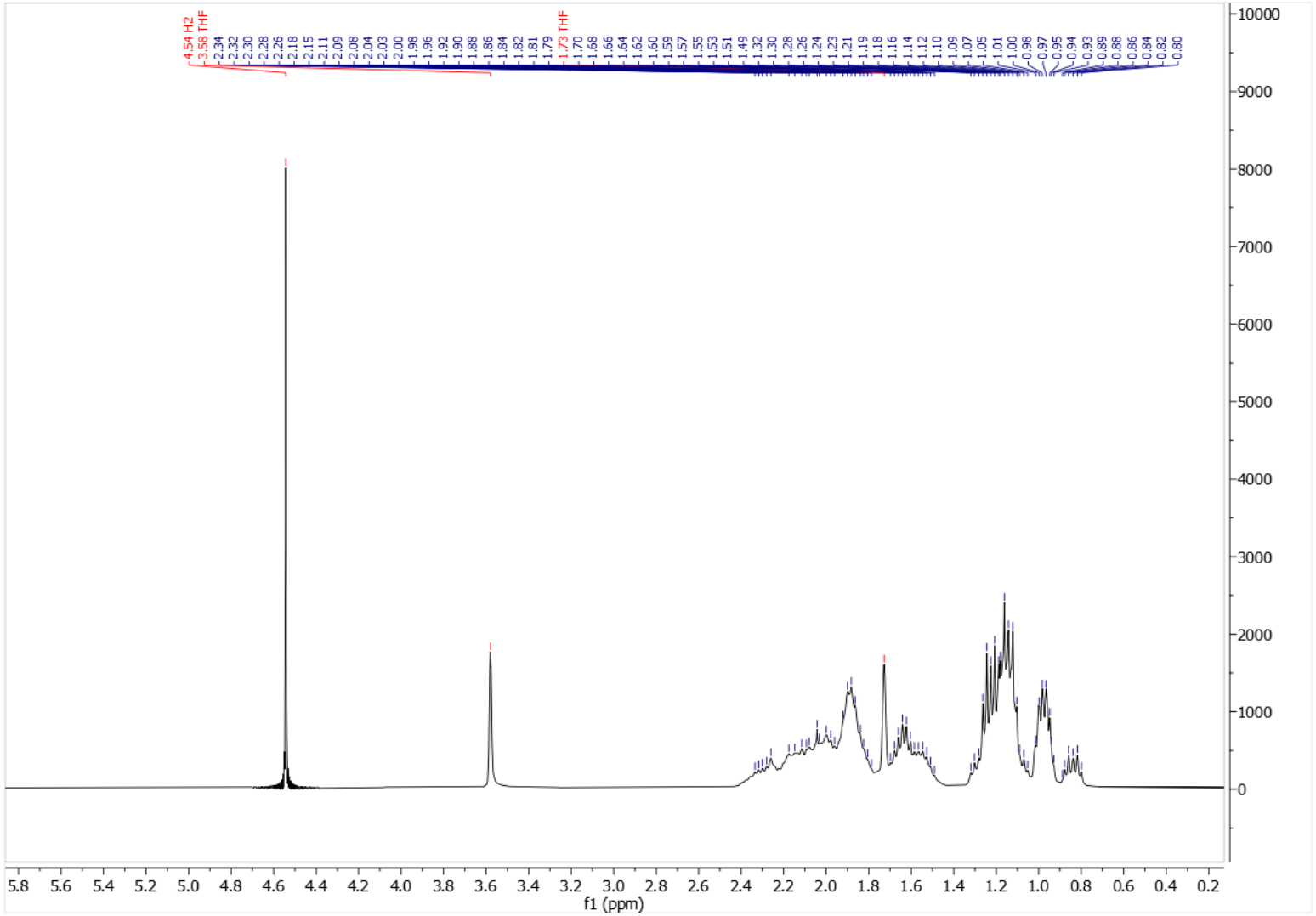


3.3.9 ***Figure S12.*** *Raman spectrum of* ***^{15}N-5****.*

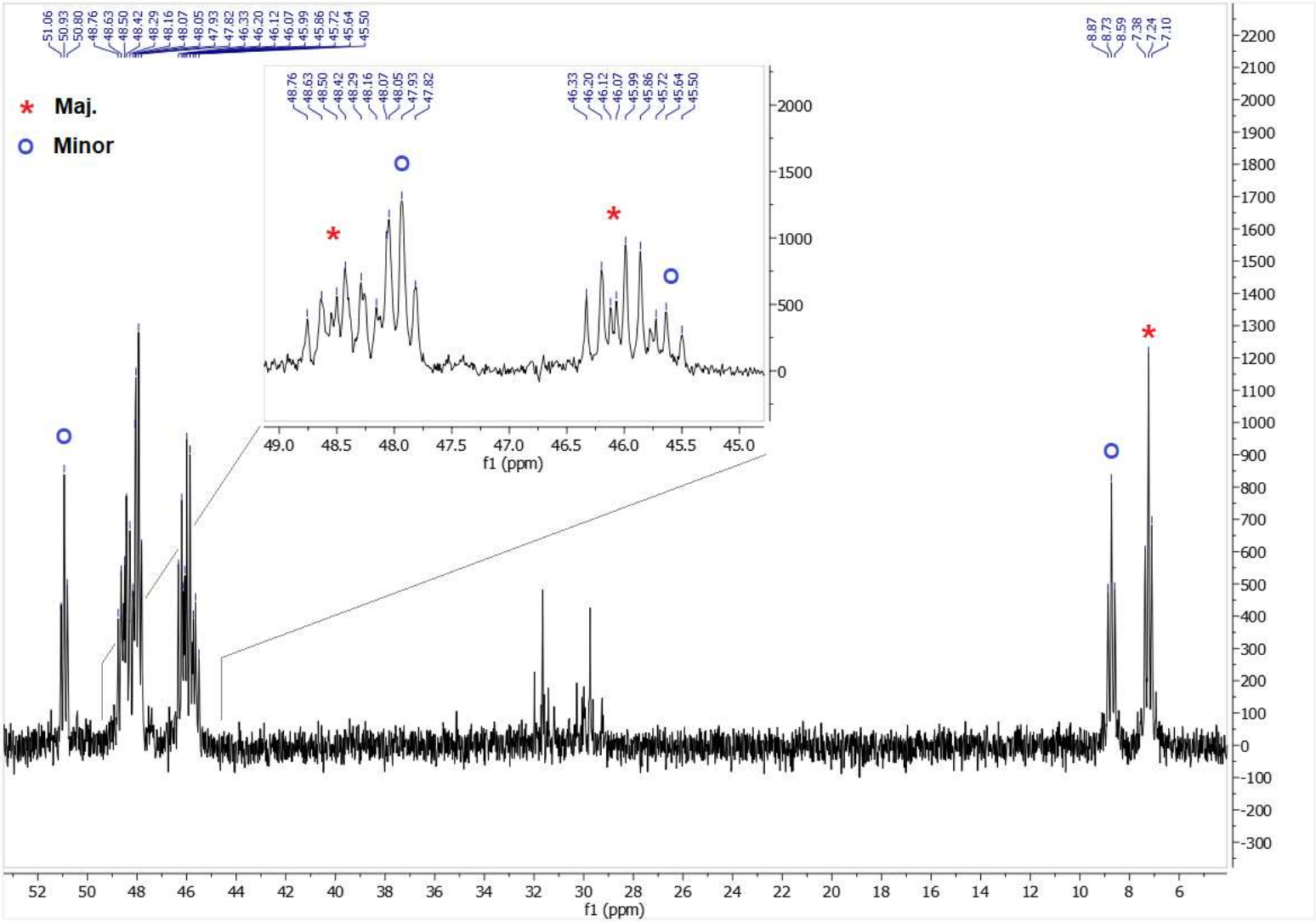


3.4 $[W(depe)_2(H)_2(\mu\text{-}N_2)B(C_6F_5)(C_6F_4\{B(C_6F_5)_3\})]$ (6)

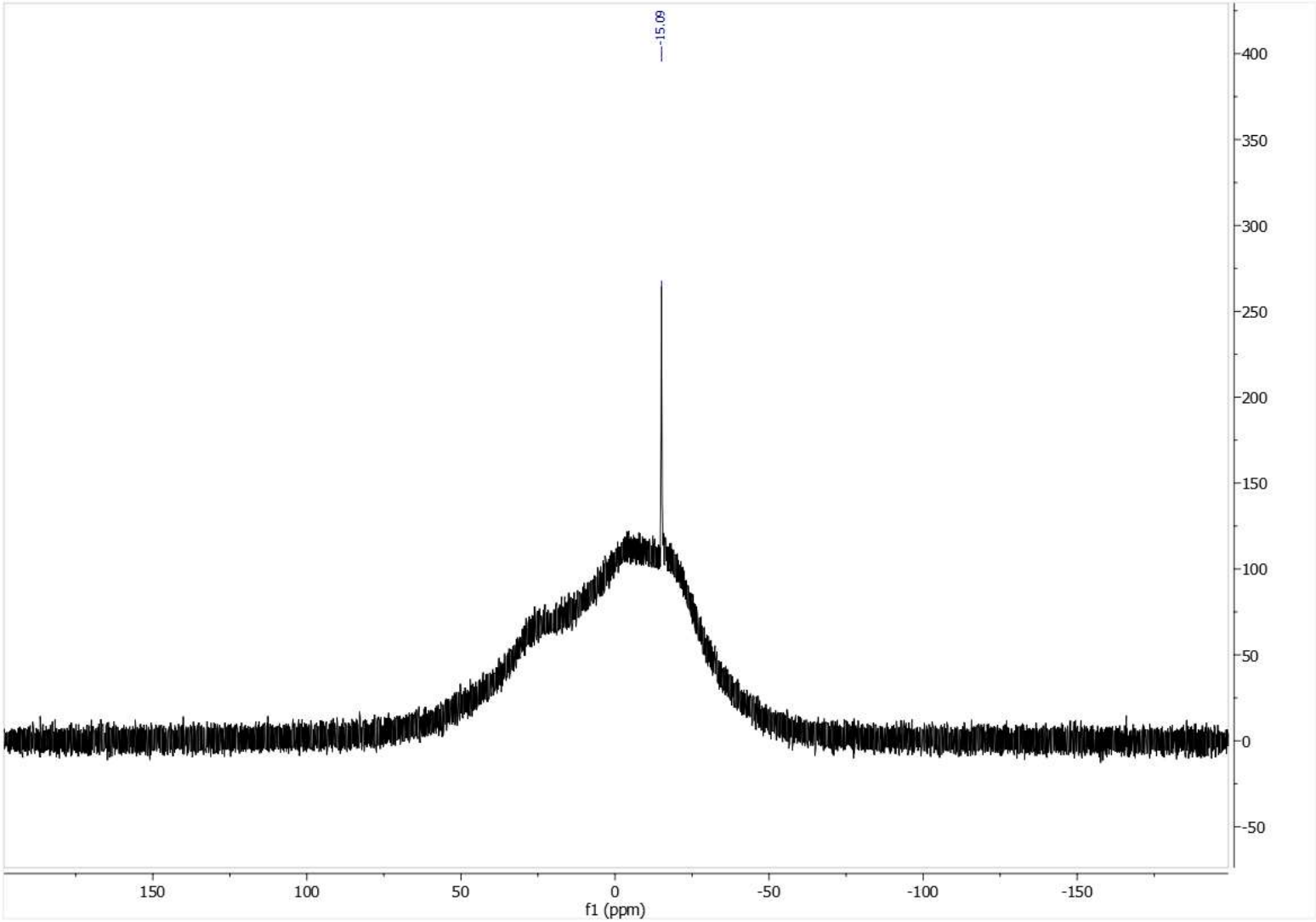
3.4.1 ***Figure S13.*** *^1H NMR (400 MHz, THF-d_8) of* ***6*** *isomers.*



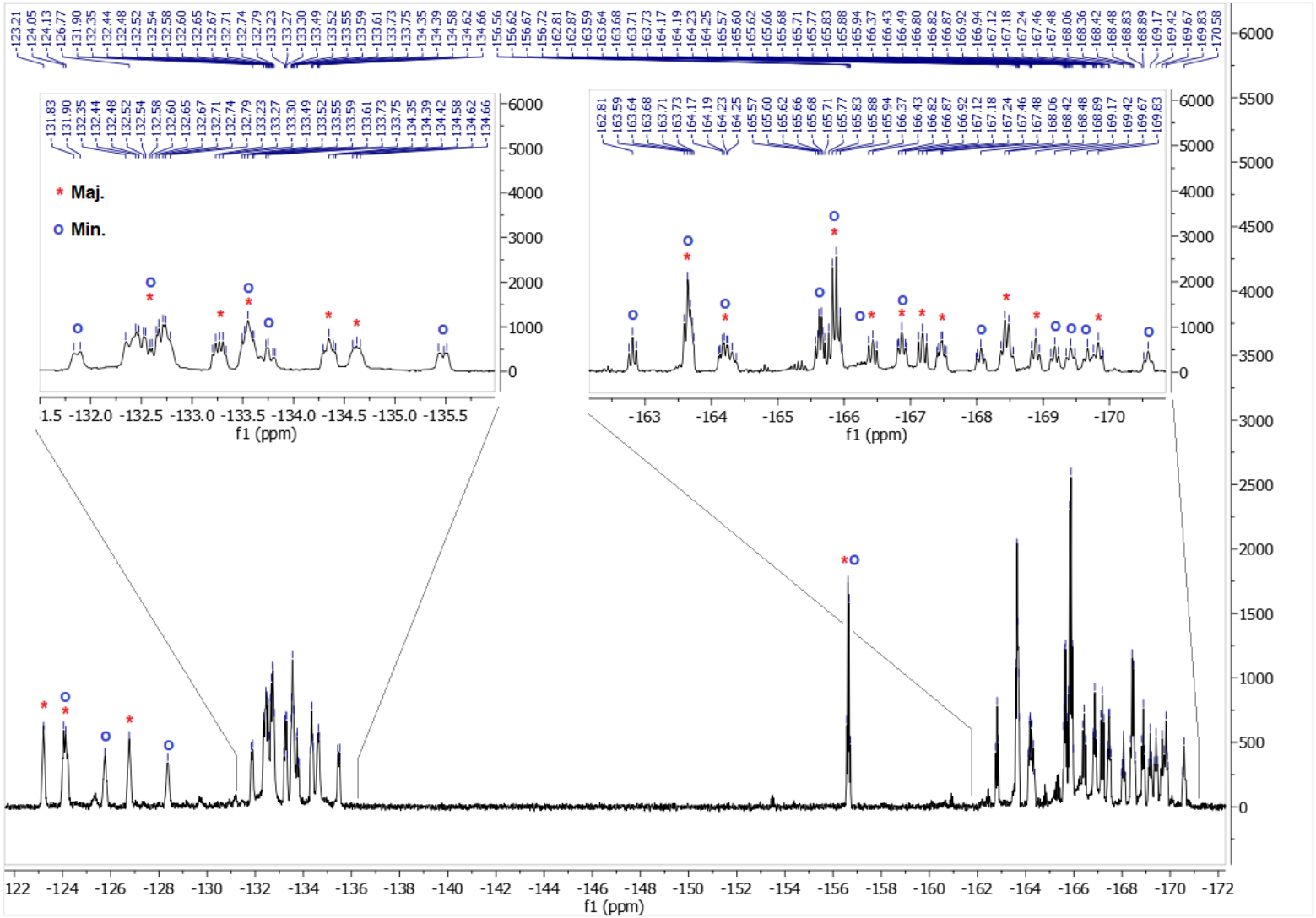
3.4.2 ***Figure S14.*** *$^{31}P\{^{1}H\}$ NMR (162 MHz, THF-d_8) of **6** isomers.*



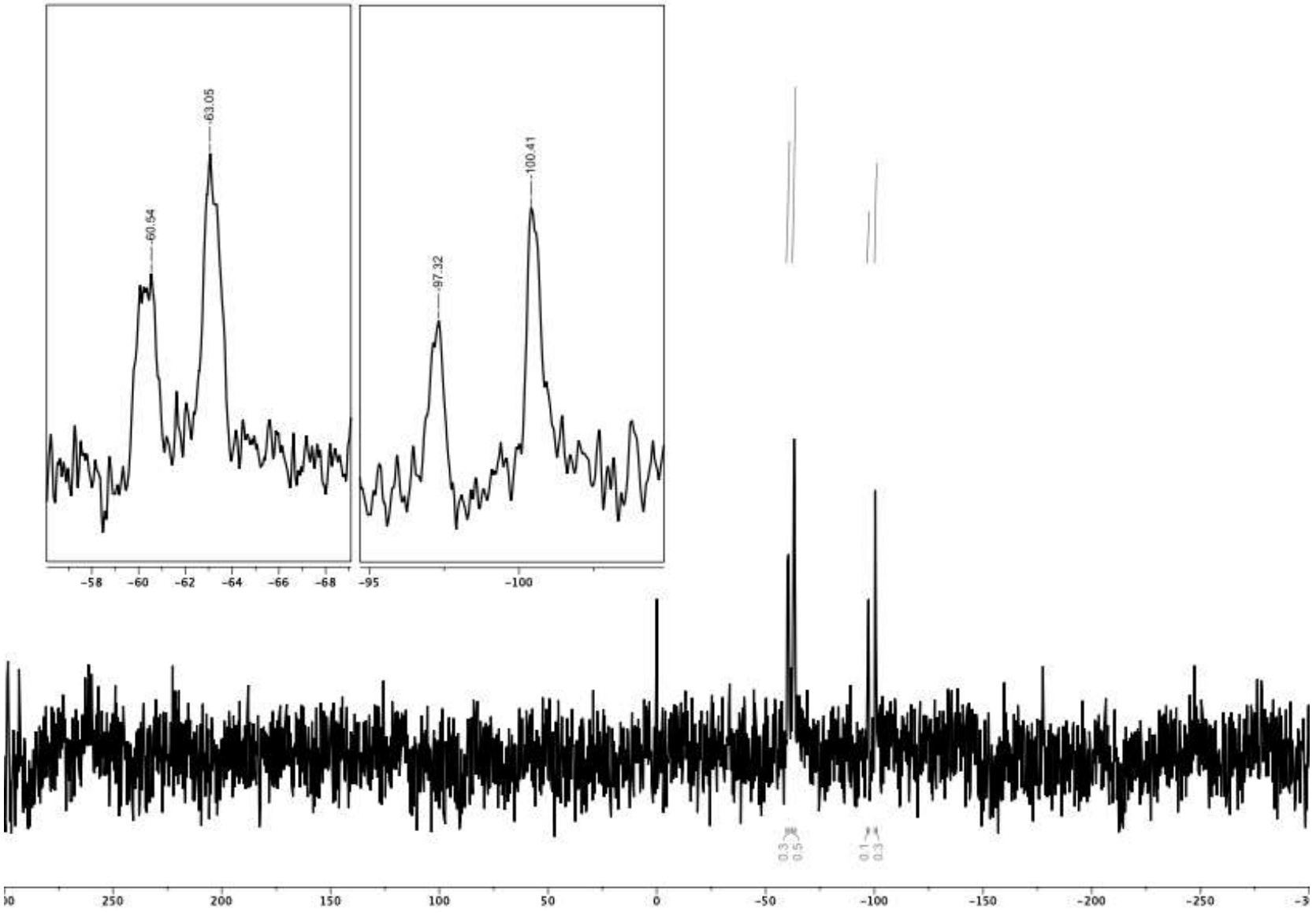
3.4.3 ***Figure S15.*** *^{11}B NMR (128 MHz, THF-d_8) of* ***6*** *isomers.*



3.4.4 ***Figure S16.*** *^{19}F NMR (376 MHz, THF-d_8) of **6** isomers.*

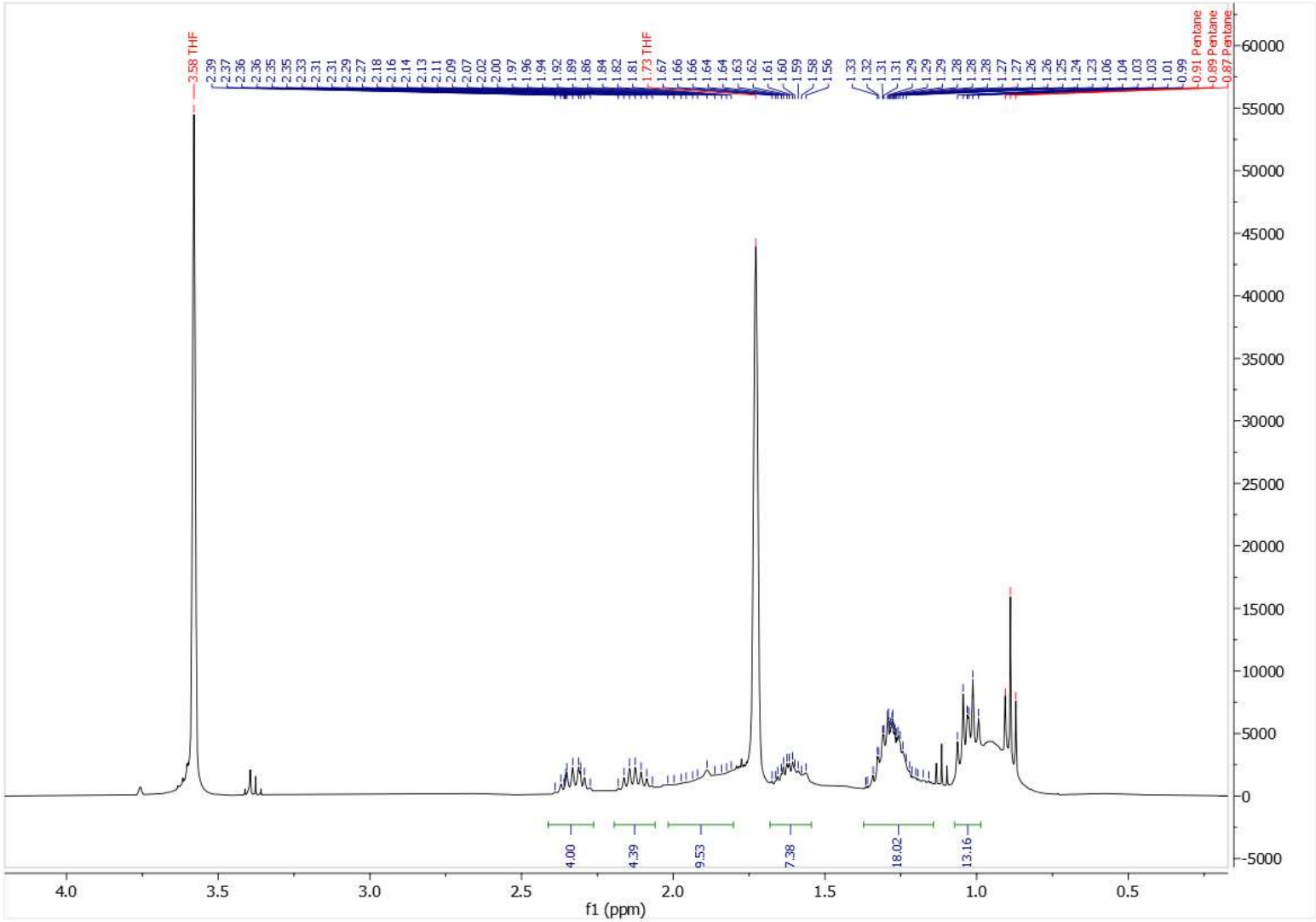


3.4.5 ***Figure S17.*** *^{15}N INVGATED ^{1}H NMR (41 MHz, THF-d_8) of **6** isomers.*

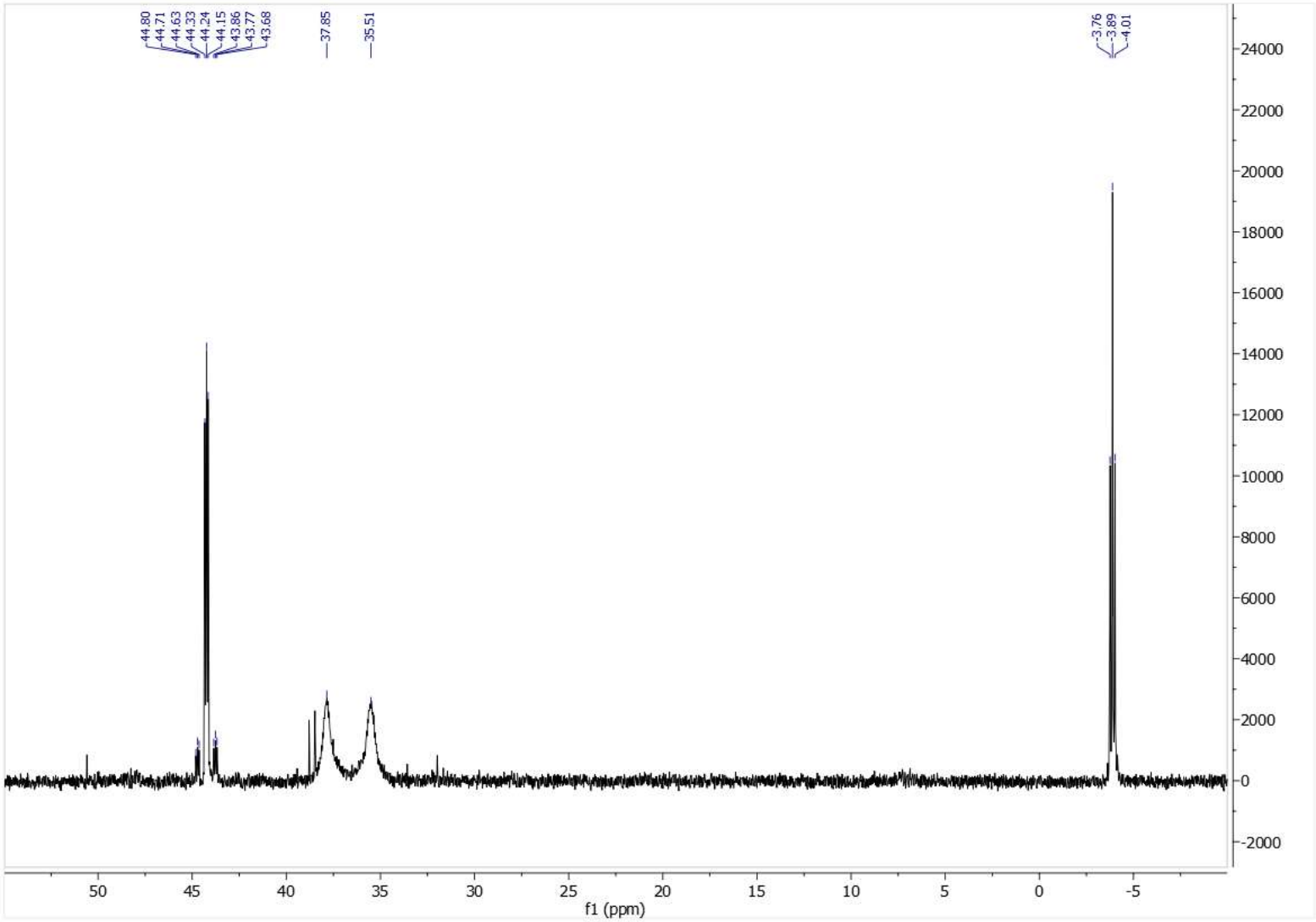


3.5 II. 6. [W(depe)$_2$(H)$_2$(μ-N$_2$)(1,2-{B(C$_6$F$_5$)$_2$}$_2$C$_6$F$_4$)] (7)

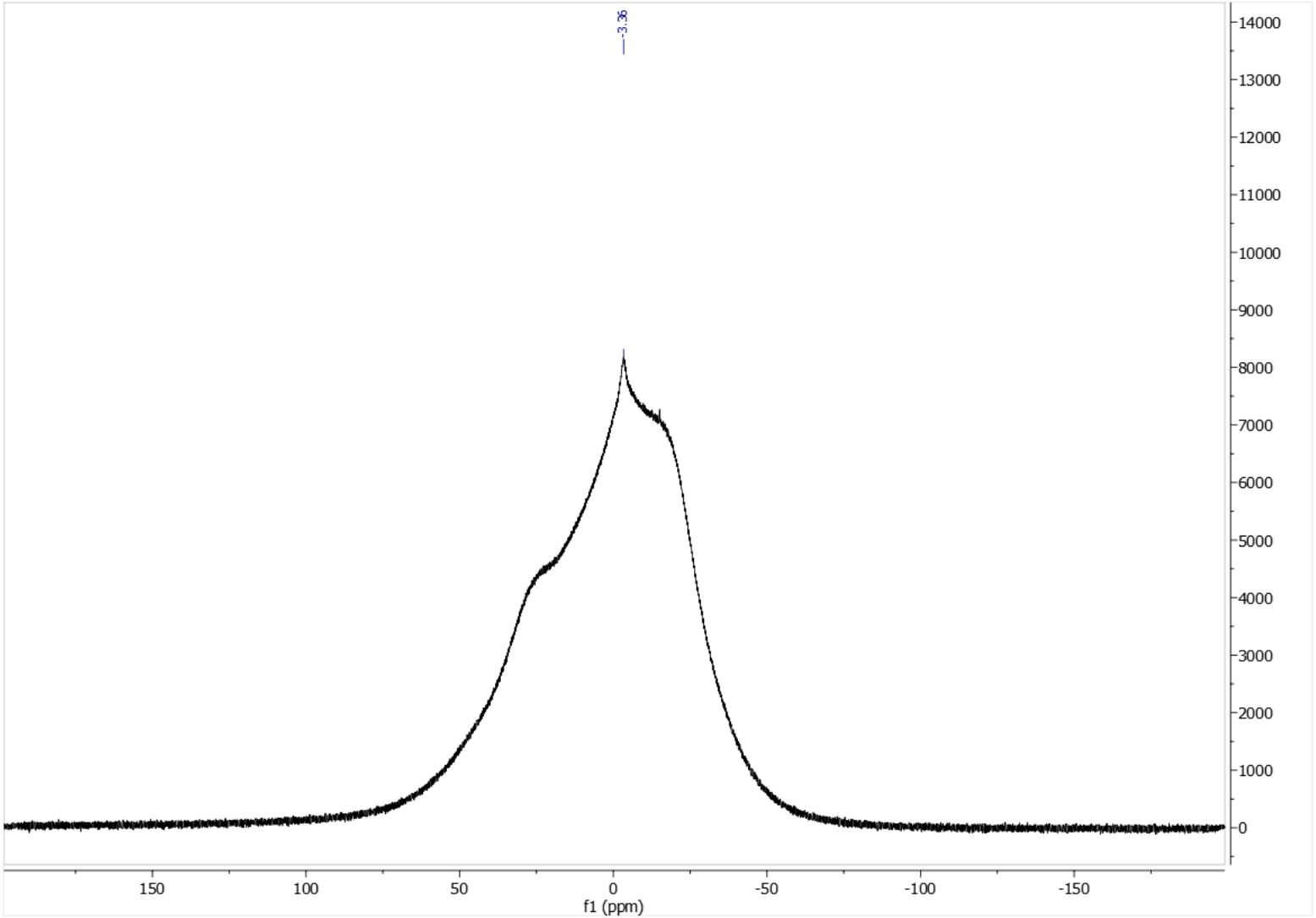
3.5.1 ***Figure S18****. ^{1}H NMR (400 MHz, THF-d$_8$) of* ***7****.*



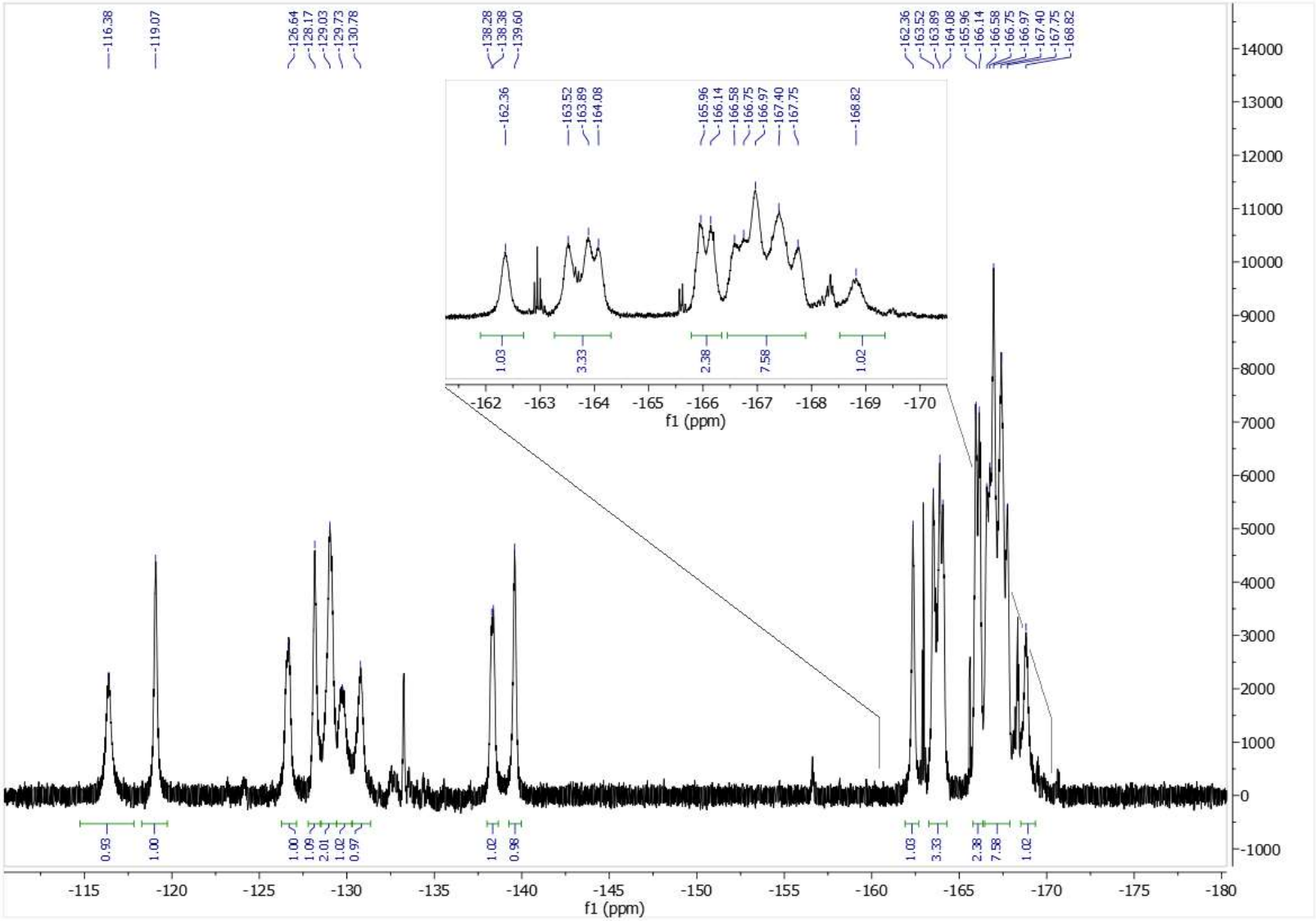
3.5.2 ***Figure S19***. *$^{31}P\{^{1}H\}$ NMR (162 MHz, THF-d_8) of **7**.*



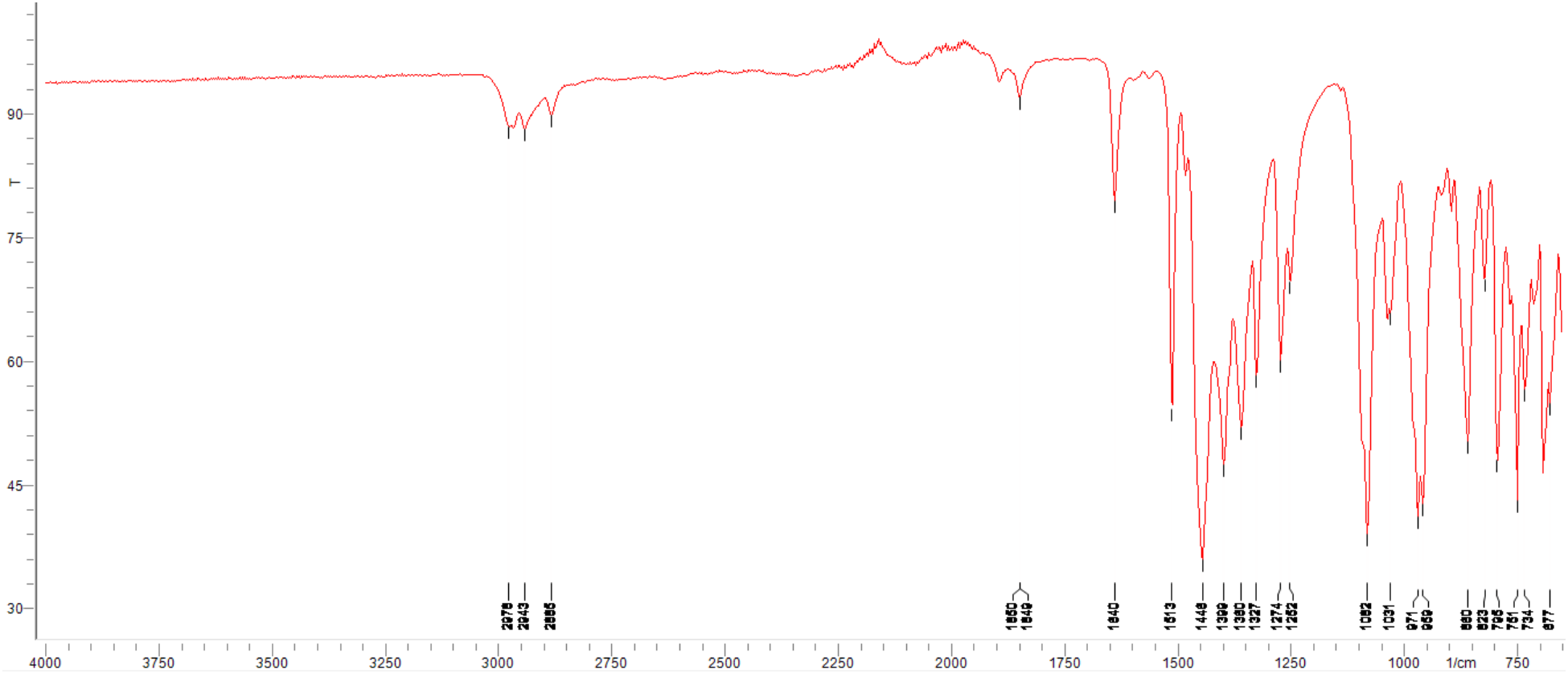
3.5.3 ***Figure S20***. *^{11}B NMR (128 MHz, THF-d$_8$) of **7**.*



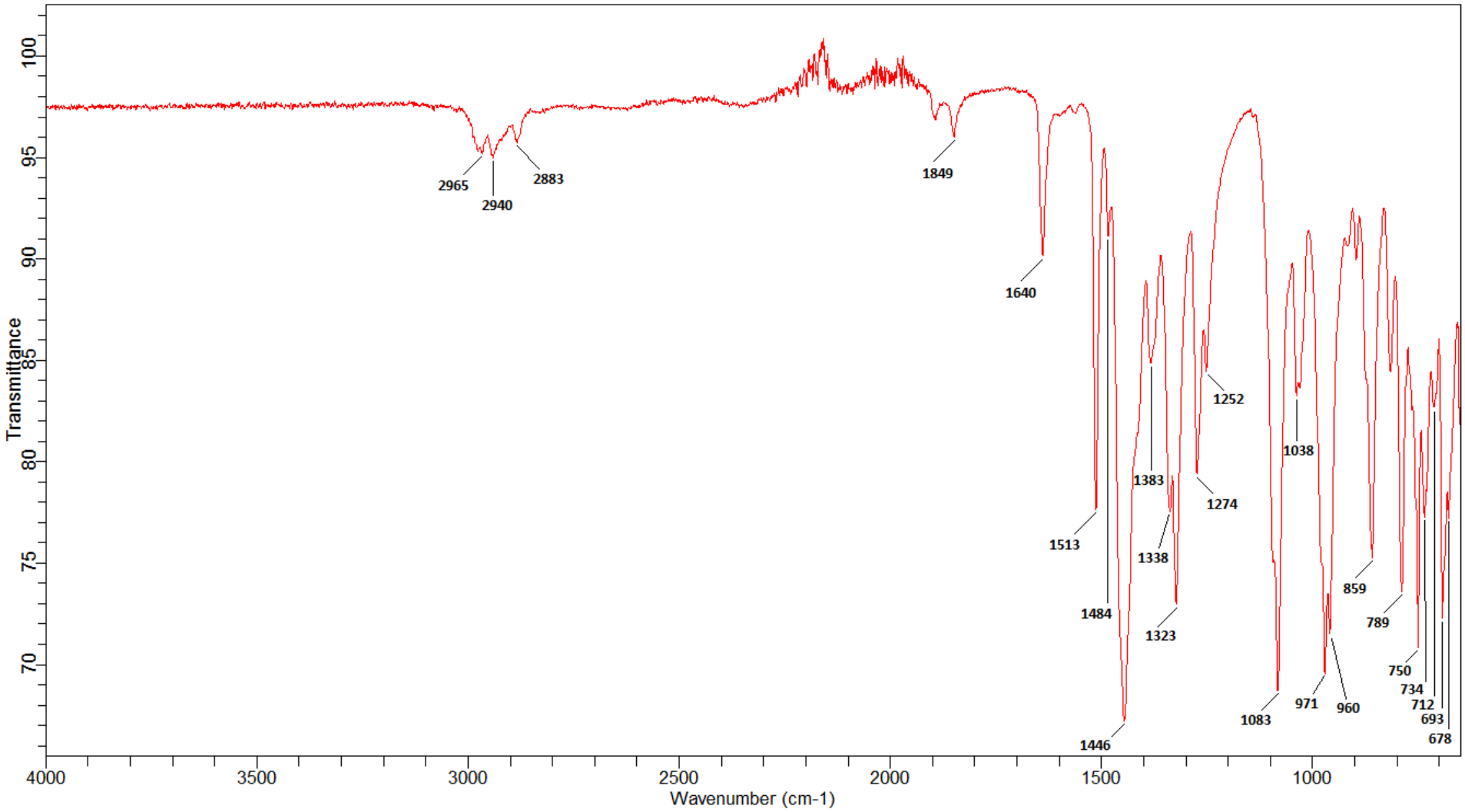
3.5.4 ***Figure S21.*** *^{19}F NMR (376 MHz, THF-d_8) of **7**.*



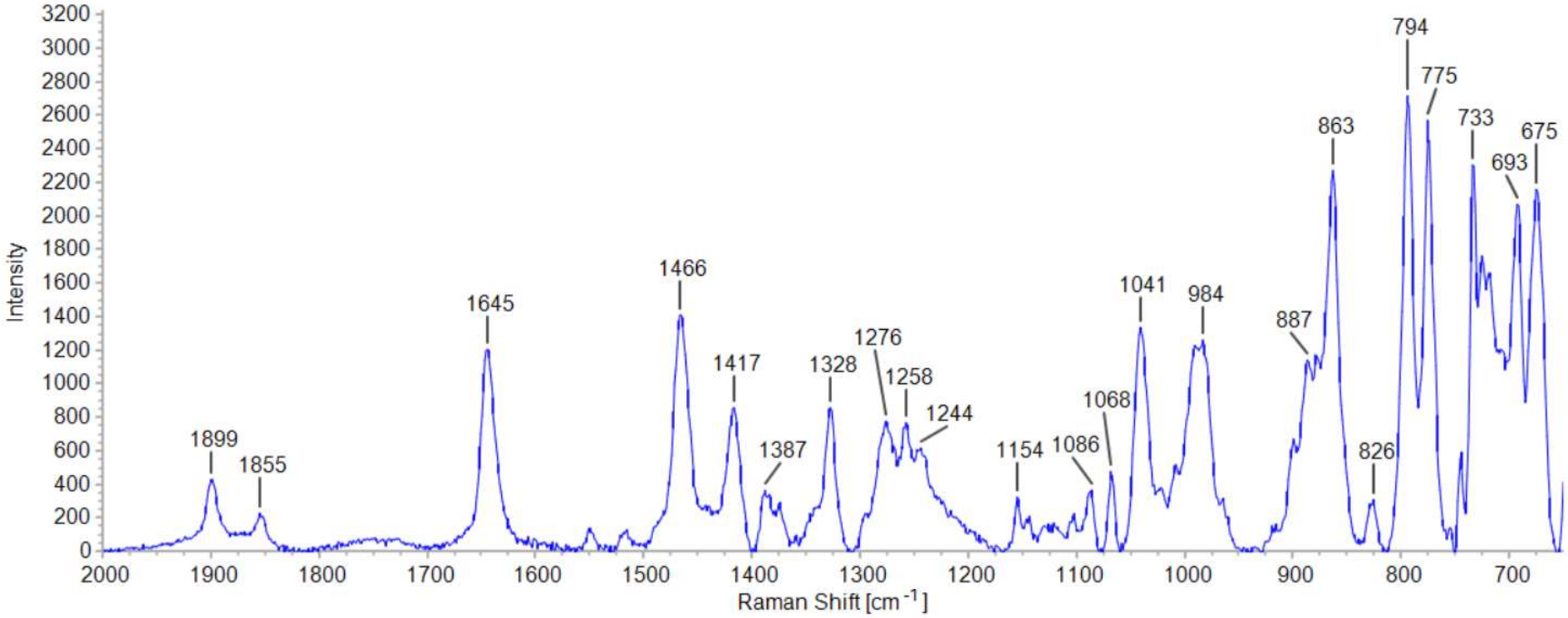
3.5.5 ***Figure S22.*** *FT-IR (ATR) of* ***7****.*



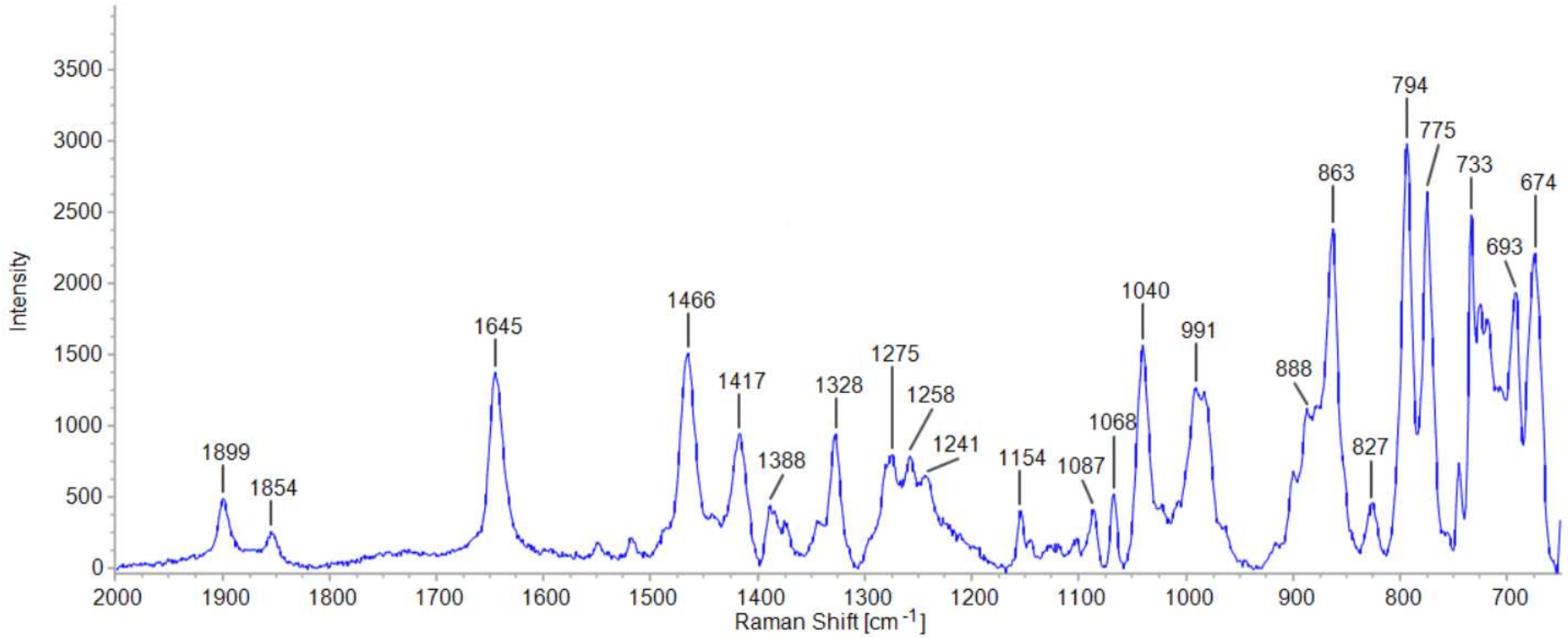
3.5.6 ***Figure S23.*** *FT-IR (ATR) of* ***^{15}N-7****.*



3.5.7 ***Figure S24.*** *Raman spectrum of* ***7****.*

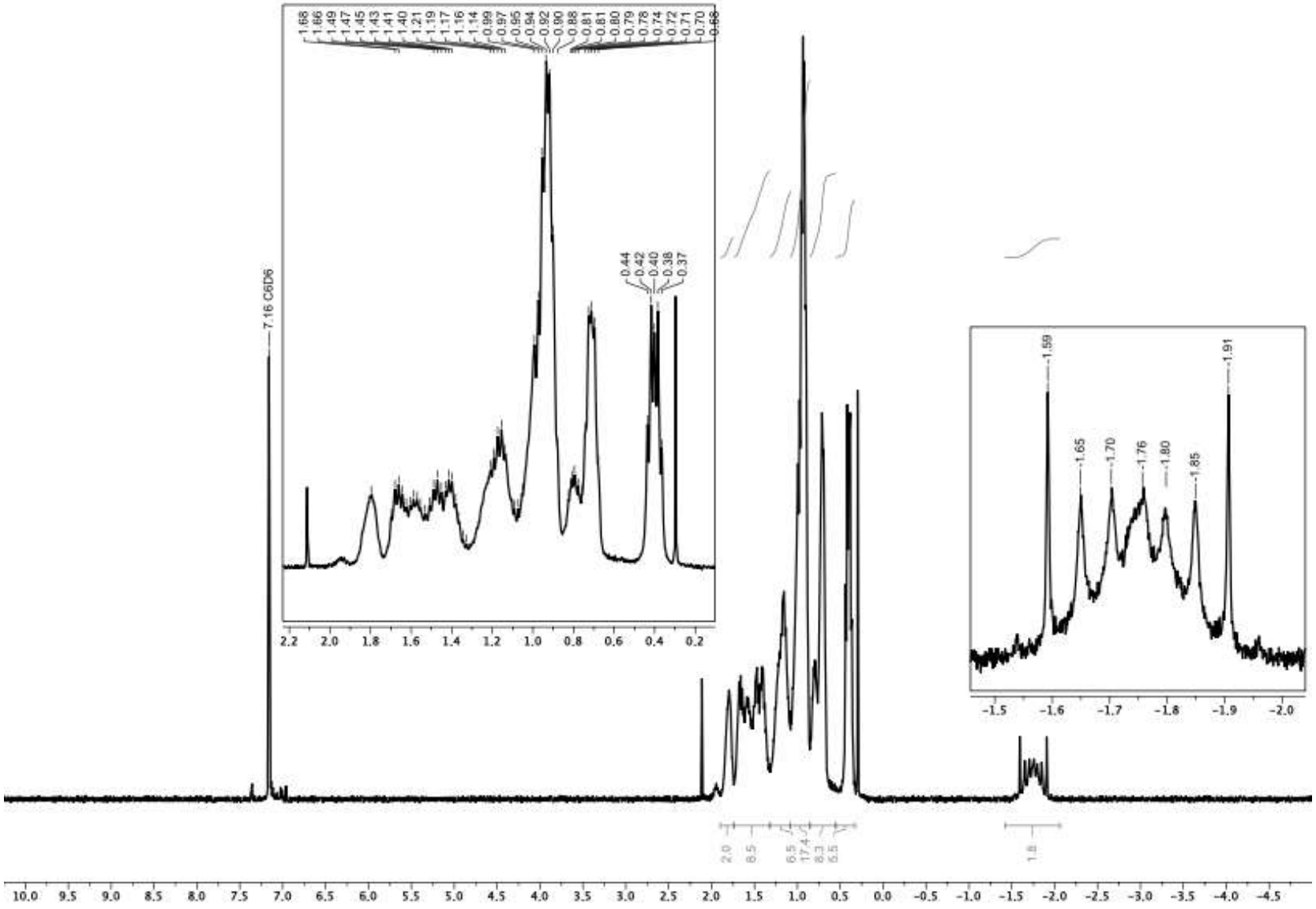


3.5.8 ***Figure S25.*** *Raman spectrum of* ***^{15}N-7****.*

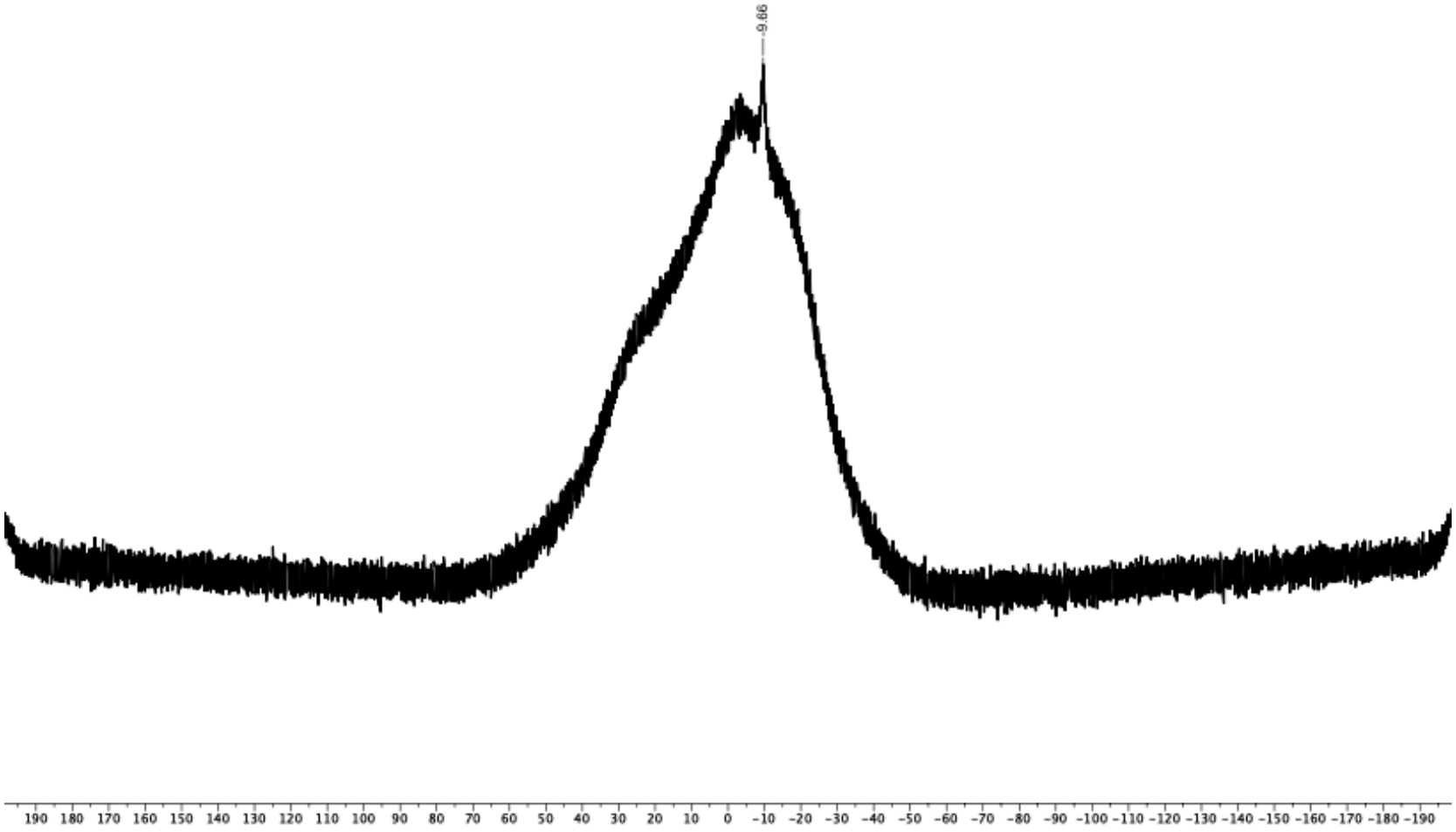


3.6 [W(depe)$_2$(H)$_2$(μ-N$_2$)B(C$_6$F$_5$)$_3$] (10)

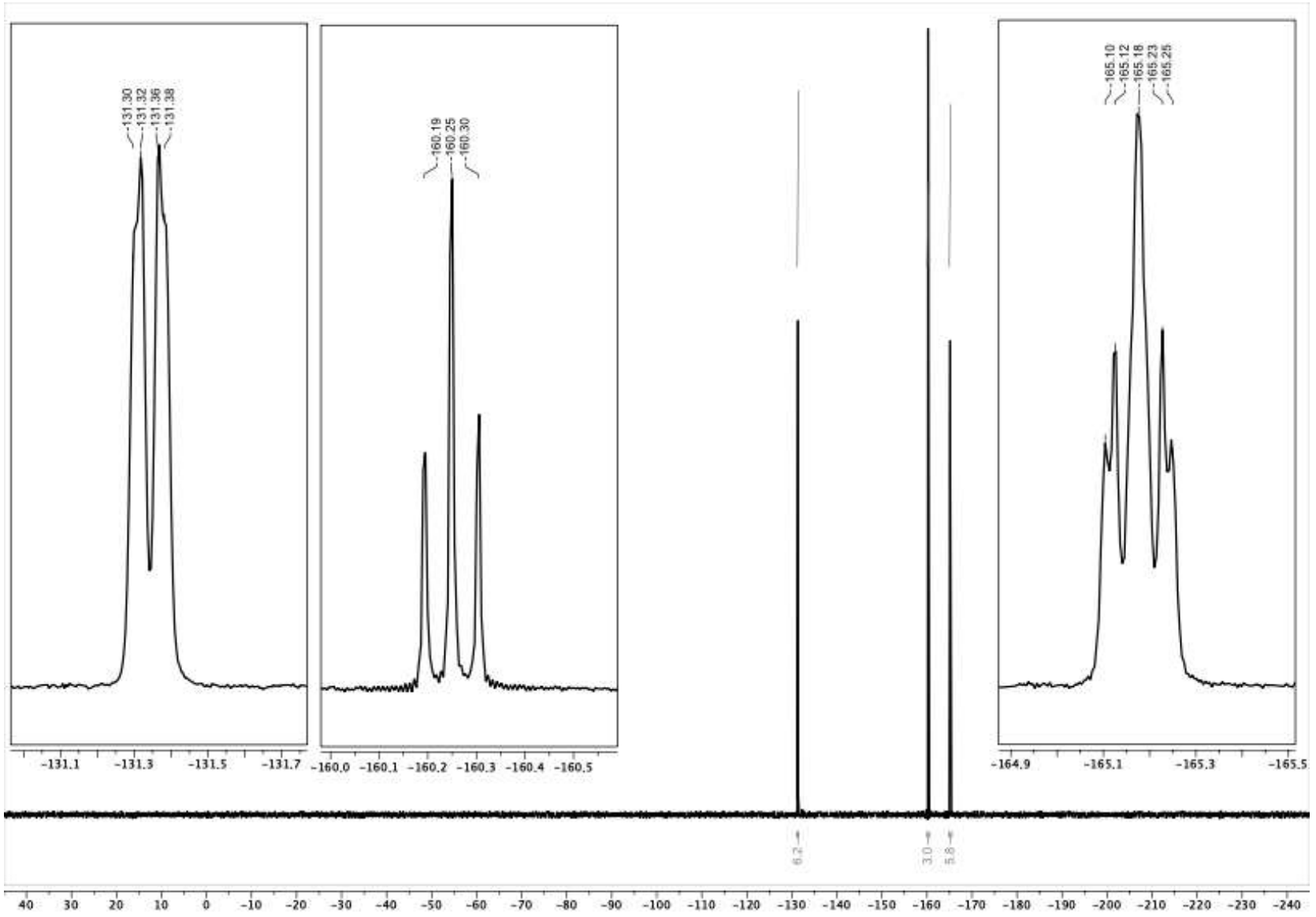
3.6.1 ***Figure S26.*** *^{1}H NMR (400 MHz, C$_6$D$_6$) of* ***10****.*



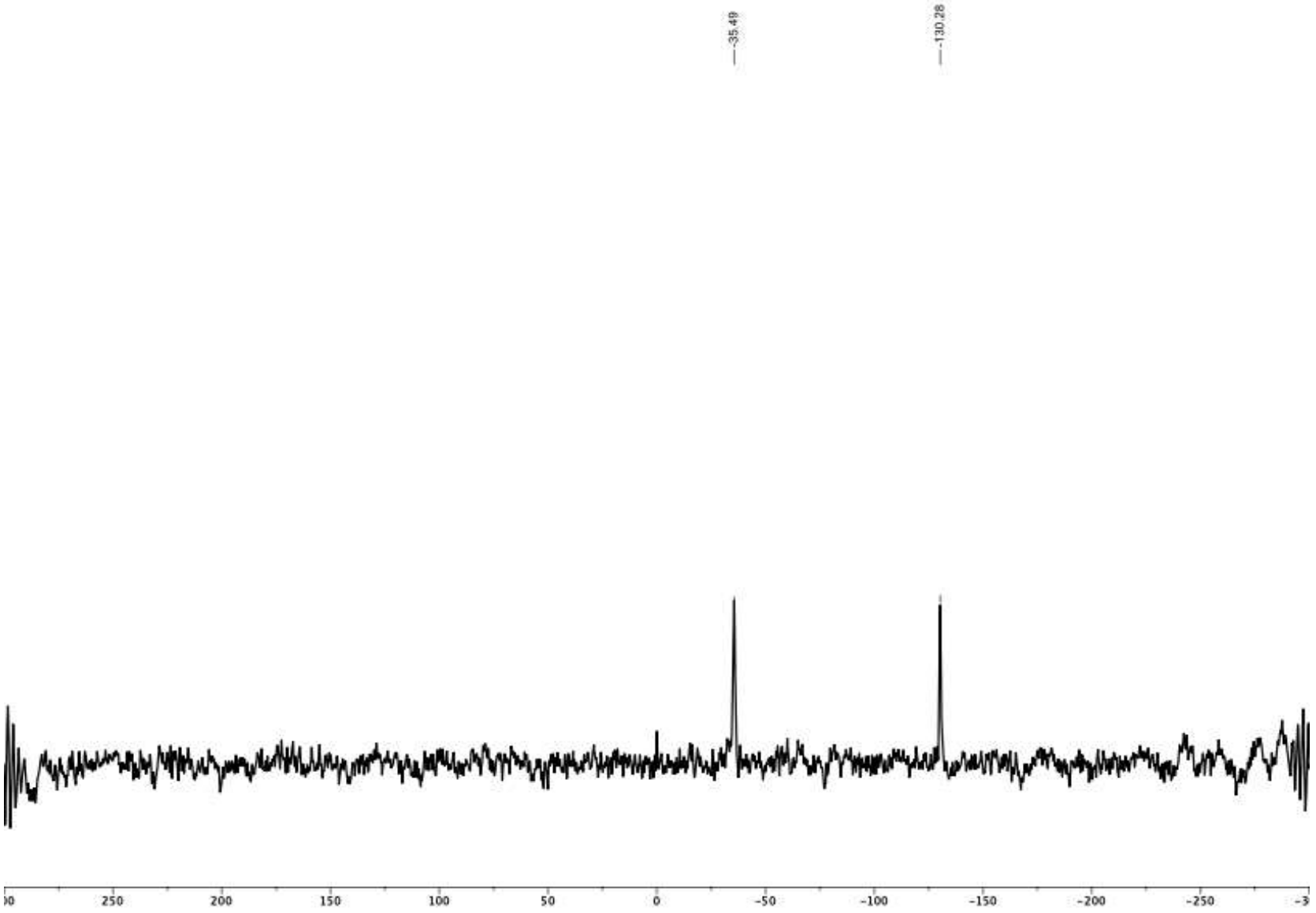
3.6.2 ***Figure S27.*** *^{11}B NMR (128 MHz, C_6D_6) of* ***10****.*



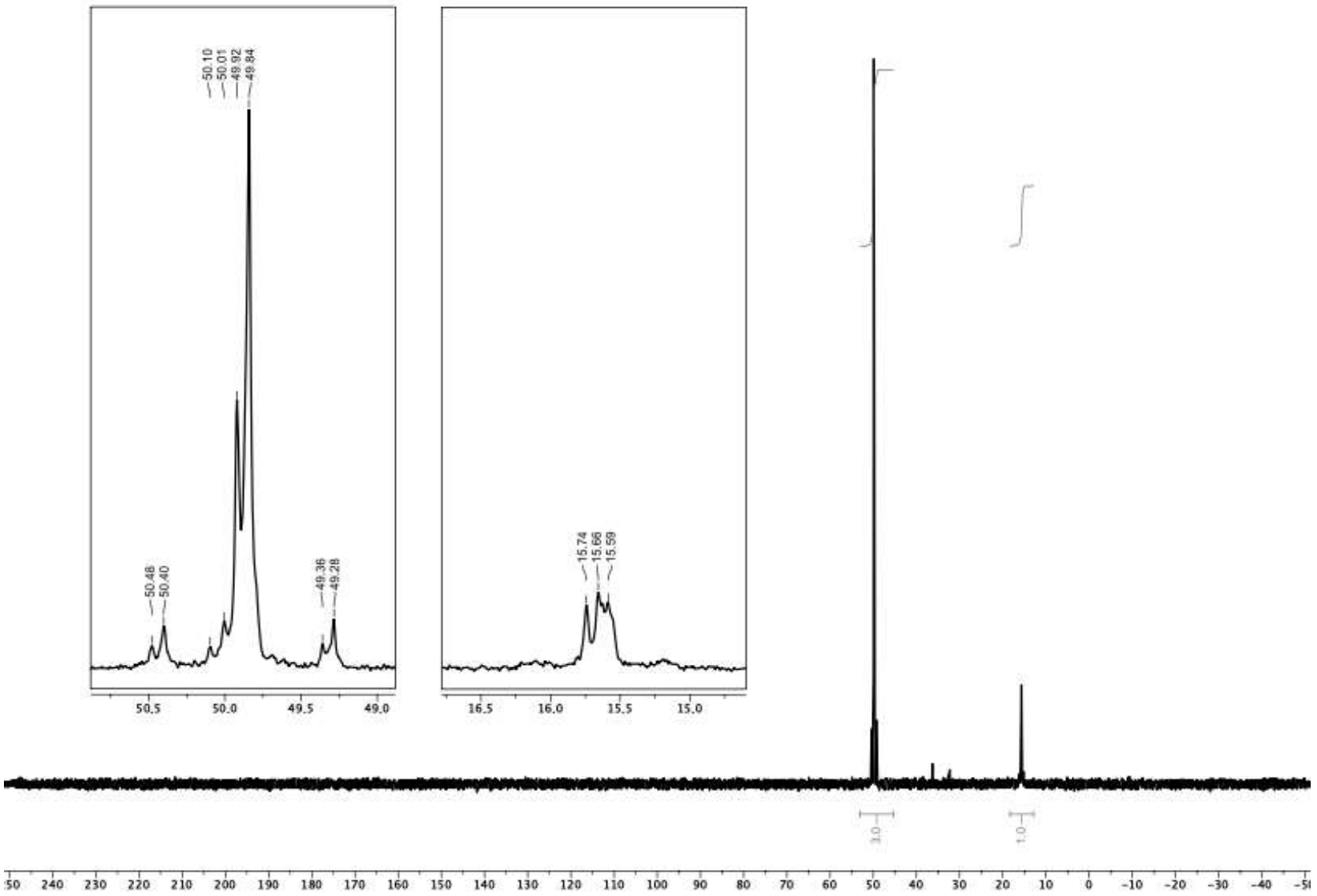
3.6.3 ***Figure S28.*** *^{19}F NMR (376 MHz, C_6D_6) of* ***10****.*



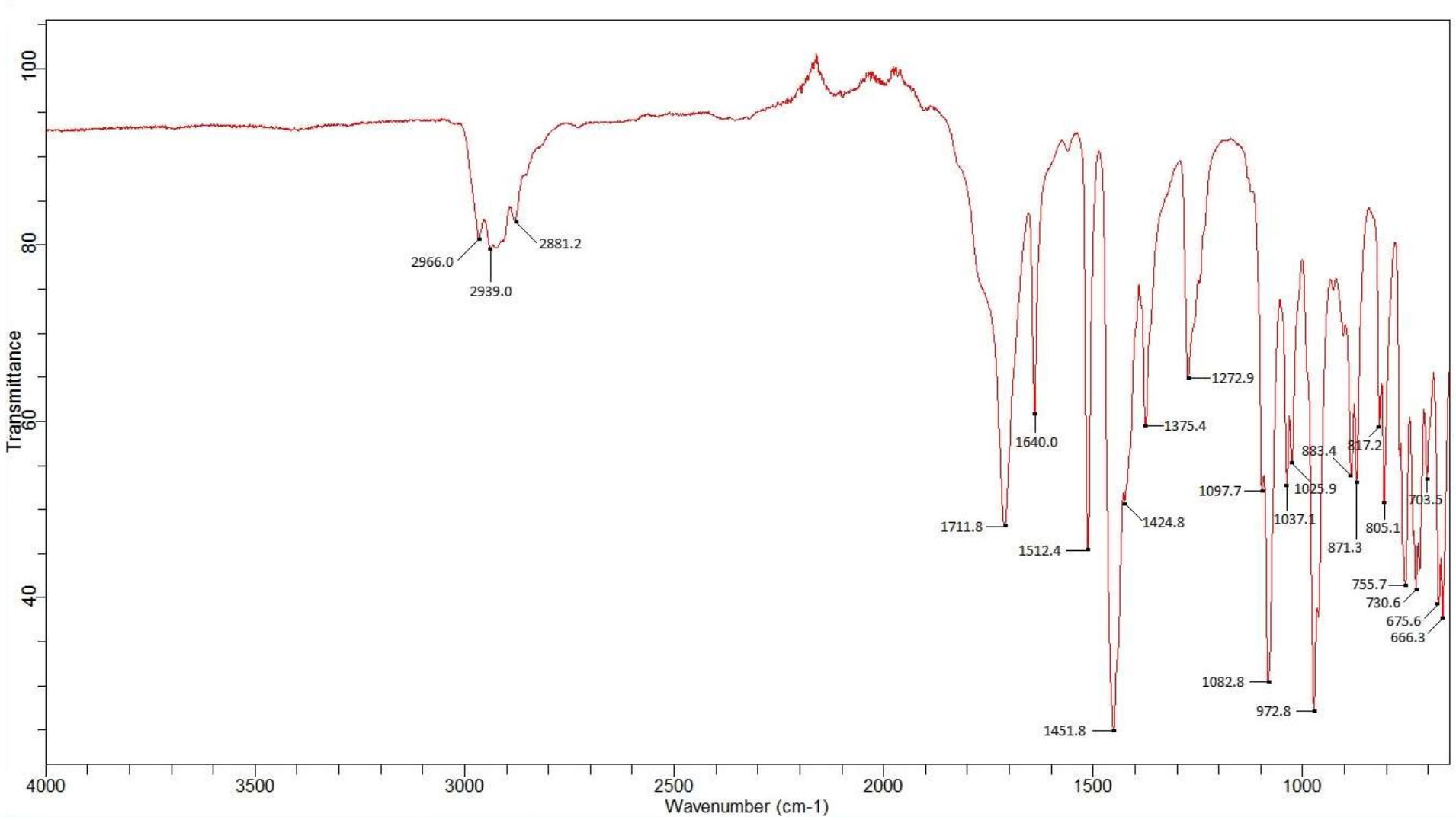
3.6.4 ***Figure S29.*** *^{15}N INVGATED ^{1}H NMR (41 MHz, C_6D_6) of* ***10****.*



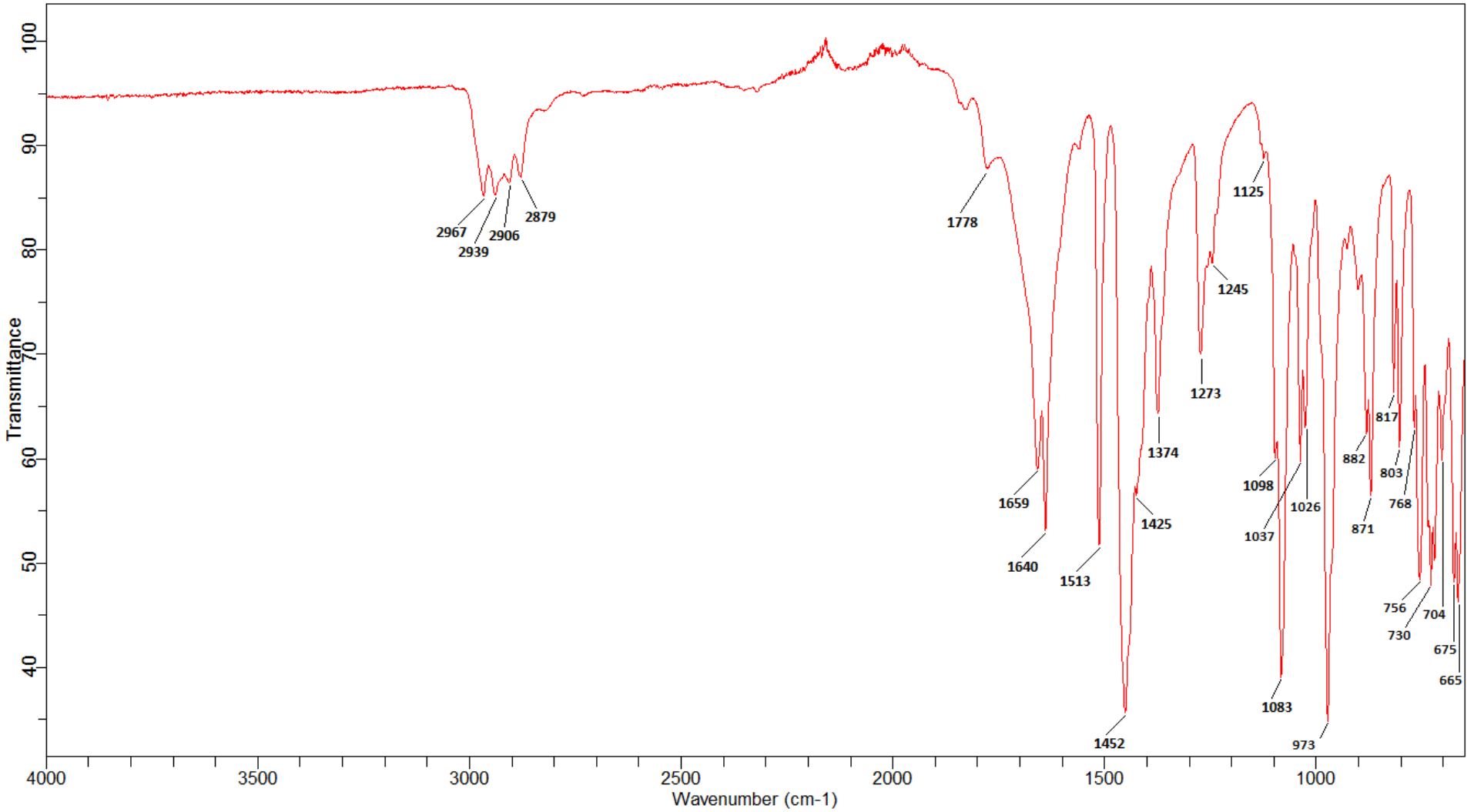
3.6.5 ***Figure S30.*** *$^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6) of **10**.*



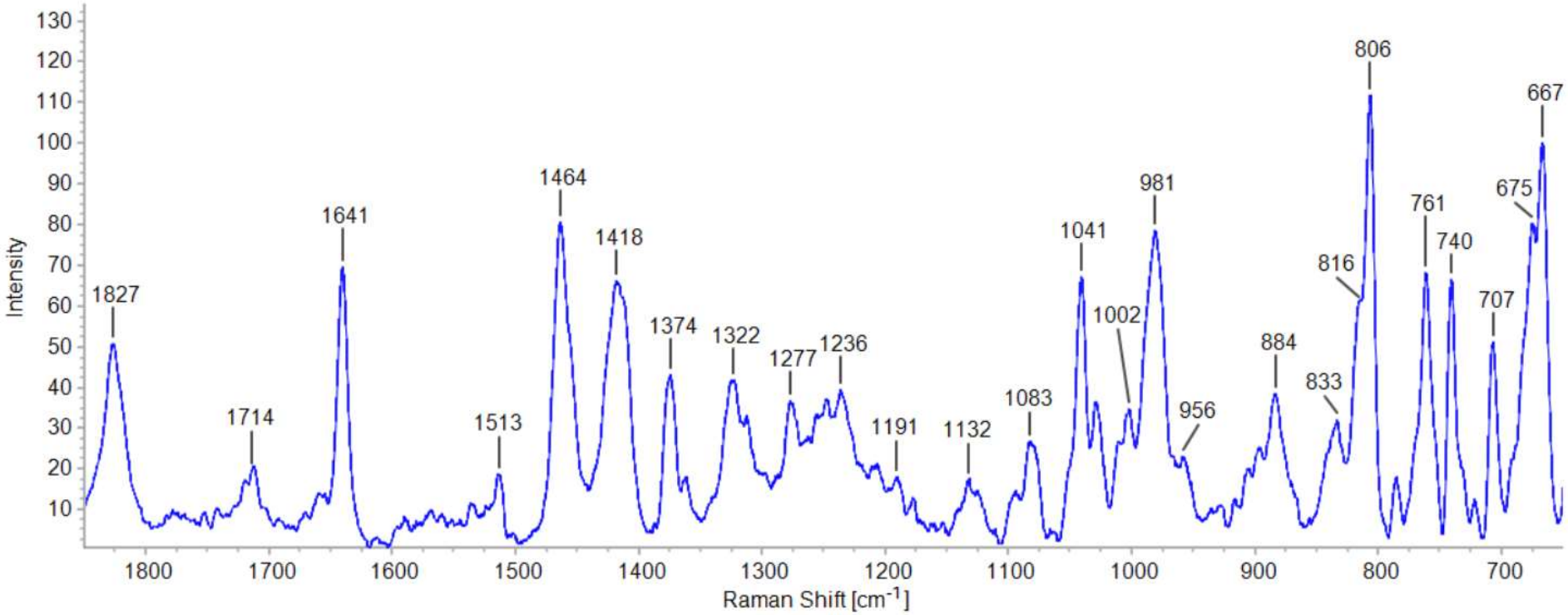
3.6.6 ***Figure S31.*** *FT-IR (ATR) of* ***10****.*



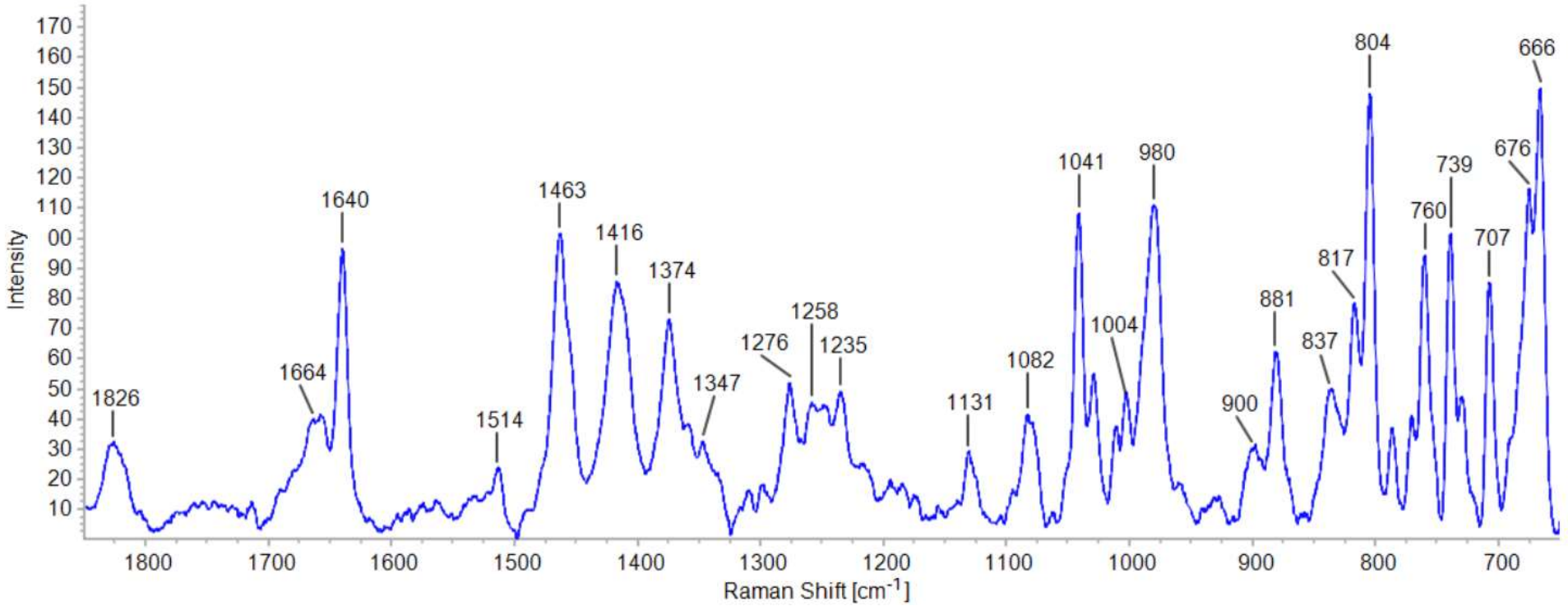
3.6.7 ***Figure S32.*** *FT-IR (ATR) of* ***^{15}N-10****.*



3.6.8 ***Figure S33.*** *Raman spectra of* ***10.***



3.6.9 ***Figure S34.*** *Raman spectra of* ***^{15}N-10***



4 Crystallographic data

4.1 Data collection and refinement

Data for compounds **3**, **4**, **5**, **7** and **10** were collected at low temperature (100 K) on a Bruker Kappa Apex II diffractometer using a Mo-Kα radiation (l = 0.71073Å) micro-source and equipped with an Oxford Cryosystems Cryostream Cooler Device. The structures have been solved by Direct Methods and refined by means of least-squares procedures using the SHELXS97[S4] program included in the softwares package WinGX version 1.63[S5] or with the aid of the software package Crystal.[S6] The Atomic Scattering Factors were taken from International tables for X-Ray Crystallography.[S7] 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[S8] 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 2115061-2115063, 2115066 and 2285830.

4.2 X-Ray diffraction analysis of 3.

Figure S35. X-ray crystal structure of **3**, hydrogen atoms omitted for clarity. Ellipsoids at the 30% probability level.

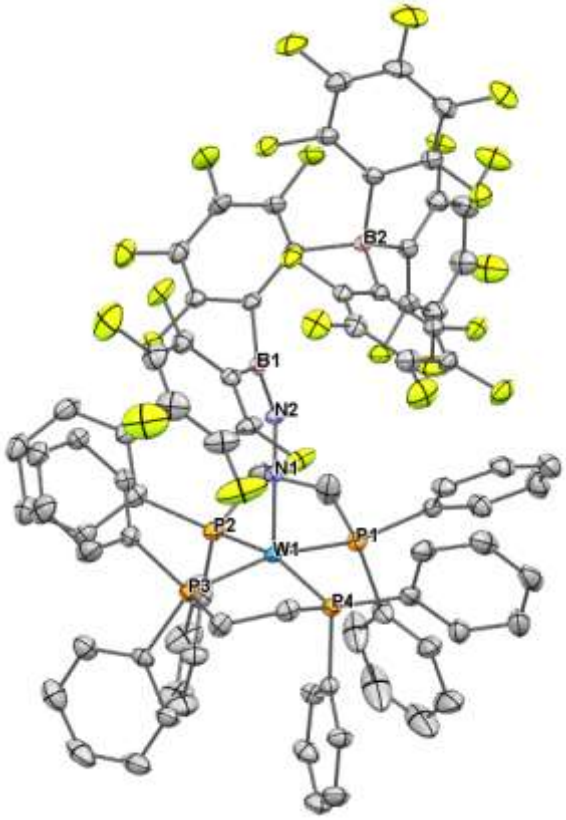


Table S1. Crystallographic data for **3**.

Chemical formula	$C_{82}H_{48}B_2F_{24}N_2P_4W$
M_r	1846.57
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	200 K
a, b, c (Å)	13.6255 (5), 28.1927 (11), 22.8261 (9)
β (°)	101.761 (1)
V (Å^3)	8584.3 (6)
Z	4
Radiation type	Mo *K*α radiation, λ = 0.71073 Å
μ (mm^{-1})	1.51
Crystal size (mm)	0.15 × 0.12 × 0.02
Data collection	
Diffractometer	Bruker Kappa APEX II diffractometer
Absorption correction	multi-scan DENZO/SCALEPACK (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.652, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	192193, 14618, 12352
R_{int}	0.067
θ_{max} (°)	24.7
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.093, 1.12
No. of reflections	14618
No. of parameters	1036
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.87, –0.85

4.3 X-Ray diffraction analysis of **4**.

Figure S36. X-ray crystal structure of **4**, hydrogen atoms omitted for clarity. Ellipsoids at the 30% probability level.

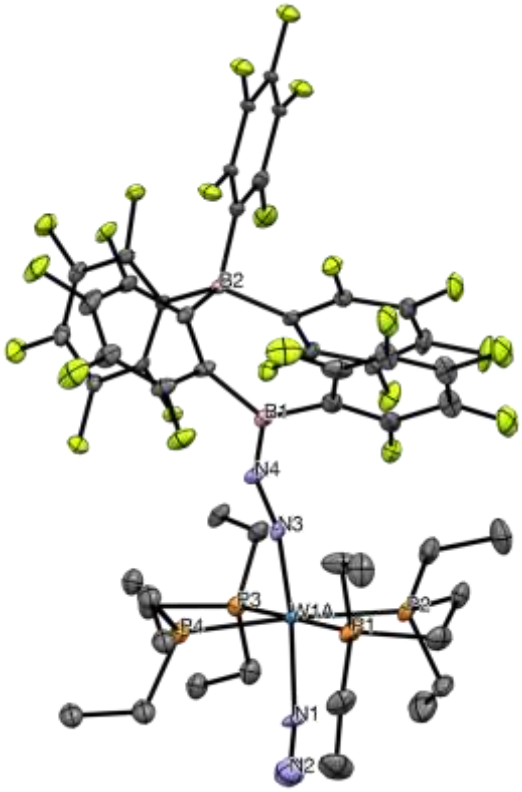


Table S2. Crystallographic data for **4**.

Chemical formula	$C_{50}H_{48}B_2F_{24}N_4P_4W \cdot C_7H_8 \cdot 0.5(C_6H_6)$
M_r	1621.46
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	110 K
a, b, c (Å)	12.833 (3), 24.785 (5), 19.899 (4)
β (°)	91.015 (7)
V (Å^3)	6328 (2)
Z	4
Radiation type	Mo *K*α radiation, λ = 0.71073 Å
μ (mm^{-1})	2.04
Crystal size (mm)	0.17 × 0.12 × 0.04
Data collection	
Diffractometer	Bruker Kappa APEX II diffractometer
Absorption correction	multi-scan DENZO/SCALEPACK (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.669, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	123400, 12924, 10277
R_{int}	0.100
θ_{max} (°)	26.4
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.063, 0.144, 1.13
No. of reflections	12923
No. of parameters	829
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.12, –1.83

4.4 X-Ray diffraction analysis of 5.

Figure S37. X-ray crystal structure of **5**, hydrogen atoms omitted for clarity. Ellipsoids at the 30% probability level.

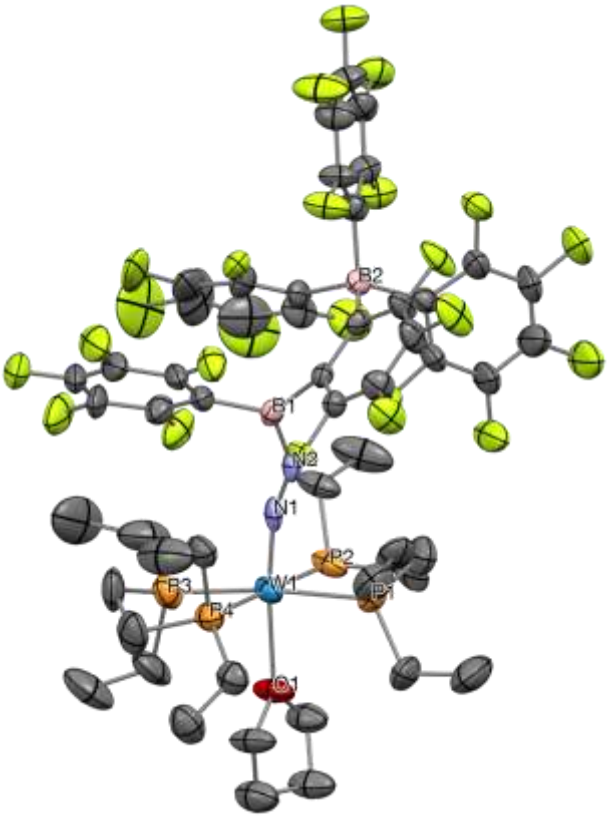


Table S3. Crystallographic data for **4**.

Chemical formula	$C_{54}H_{56}B_2F_{24}N_2OP_4W$
M_r	1534.27
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	133 K
a, b, c (Å)	15.1504(9), 23.4318(15), 19.2226(11)
β (°)	93.953(2)
V (Å^3)	6807.8(7)
Z	4
Radiation type	Mo *K*α radiation, λ = 0.71073 Å
μ (mm^{-1})	1.91
Crystal size (mm)	
Data collection	
Diffractometer	Bruker Kappa APEX II diffractometer
Absorption correction	multi-scan DENZO/SCALEPACK (Otwinowski & Minor, 1997)
T_{min}, T_{max}	
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	99634, 7122, 5695
R_{int}	0.107
θ_{max} (°)	20.8
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.082, 0.220, 1.10
No. of reflections	7122
No. of parameters	796
H-atom treatement	H atoms parameters constrained
$\Delta\rho_{max}$ (e Å^{-3})	0.032

4.5 X-Ray diffraction analysis of **7**.

Figure S38. X-ray crystal structure of **7**, hydrogen atoms except those bound to tungsten omitted for clarity. Ellipsoids at the 30% probability level.

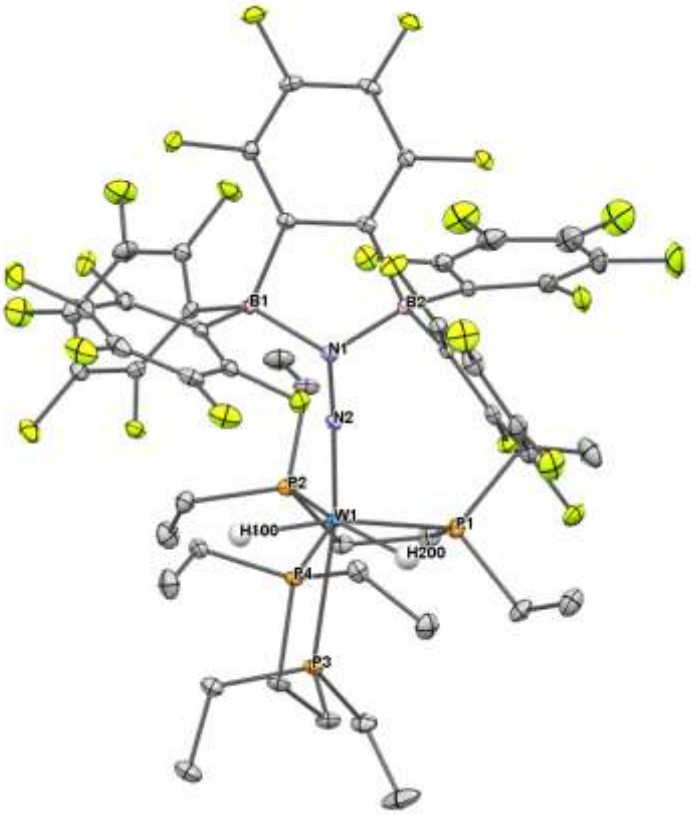


Table S4. Crystallographic data for **7**.

Chemical formula	$C_{50}H_{50}B_2F_{24}N_2P_4W$
M_r	1464.27
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	133 K
a, b, c (Å)	20.1462 (11), 11.8225 (6), 22.9963 (12)
β (°)	92.163 (2)
V (Å^3)	5473.3 (5)
Z	4
Radiation type	Mo *K*α radiation, λ = 0.71073 Å
μ (mm^{-1})	2.35
Crystal size (mm)	0.18 × 0.15 × 0.03
Data collection	
Diffractometer	Bruker Kappa APEX II diffractometer
Absorption correction	multi-scan DENZO/SCALEPACK (Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.633, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	235655, 11190, 10270
R_{int}	0.064
θ_{max} (°)	26.4
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.022, 0.054, 1.09
No. of reflections	11190
No. of parameters	764
H-atom treatement	mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.45, –0.58

4.6 X-Ray diffraction analysis of **10**.

Figure S39. X-ray crystal structure of **10**, hydrogen atoms except those bound to tungsten omitted for clarity. Ellipsoids at the 30% probability level.

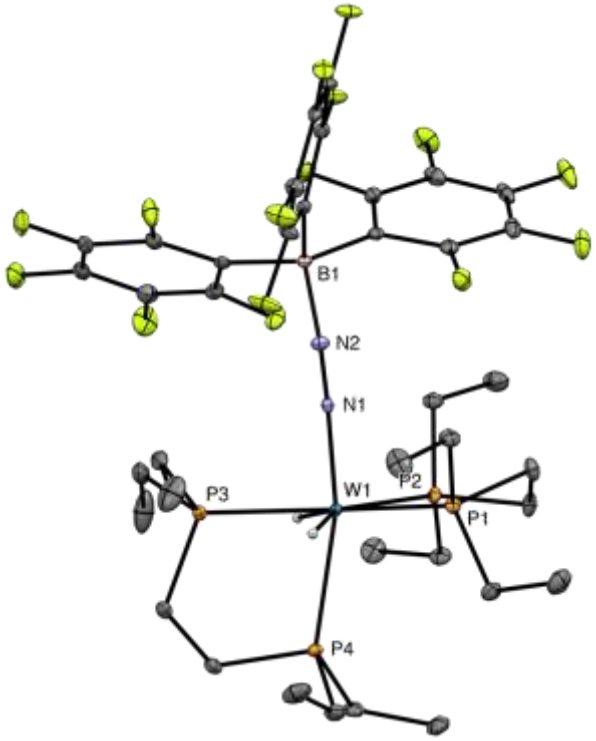


Table S5. Crystallographic data for **7**.

$C_{38}H_{50}BF_{15}N_2P_4W$	
M_r = 1138.35	D_x = 1.712 Mg m^{-3}
Monoclinic, $P2_1/c$	
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 10.96920 (3) Å	Cell parameters from 9782 reflections
b = 20.06390 (4) Å	θ = 3–28°
c = 20.47910 (4) Å	μ = 2.86 mm^{-1}
β = 101.510 (3)°	T = 110 K
V = 4416.50 (5) Å^3	Block, yellow
Z = 4	0.15 × 0.10 × 0.04 mm
F(000) = 2264	
Data Collection	
Bruker Kappa Apex2 diffractometer	9836 reflections with I > 2.0σ(I)
Radiation source: Mo micro focus	R_{int} = 0.056
Graphite monochromator	θ_{max} = 28.4°, θ_{min} = 1.4°
φ & ω scans	h = −14 14
Absorption correction: multi-scan SADABS (Siemens, 1996)	k = −26 26
T_{min} = 0.83, T_{max} = 0.89	l = −27 26
95890 measured reflections	Standard reflections: 0
11037 independent reflections	
Refinement	
Refinement on F^2	
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.020	H atoms treated by a mixture of independent and constrained refinement
$wR(F2)$ = 0.047	Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.01P)^2 + 5.38P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$
S = 0.99	$(\Delta/\sigma)_{max}$ = 0.005
11030 reflections	$\Delta\rho_{max}$ = 0.67 e Å−3
557 parameters	$\Delta\rho_{min}$ = −0.54 e Å−3
0 restraints	Extinction correction: None

5 DFT Calculations

5.1 Methods

5.1.1 Thermodynamics of H_2 oxidative addition and NMR chemical shifts

DFT calculations employing the B3PW91 functional[S9] were performed with the Gaussian16 series of programs, B.01 version.[S10] The tungsten atoms were represented by the relativistic effective core potential (RECP) from the Stuttgart group and their associated basis set,[S11,12] augmented by polarization functions (αf = 0.823, W; αd = 0.387 P).[S13] The remaining atoms (C, B, N, F, Si, O, H) were represented by 6-31G(d,p) basis sets.[S14] Full optimizations of geometry without any constraint were performed. Calculations of harmonic vibrational frequencies were performed to determine the nature of each extremum. The contributions to the Gibbs free energy were taken at T = 298 K and with P = 1 atm within the harmonic oscillator and rigid rotator approximations. To compute chemical shielding tensors, the gauge including atomic orbital (GIAO) method has been adopted. Chemical shifts are calculated as $\delta = \sigma^{TMS} - \sigma^{complex}$ where σ^{TMS} and $\sigma^{complex}$ are the isotropic chemical shieldings of H atoms in tetramethylsilane (TMS) and in a transition metal complex, respectively. The average calculated isotropic shielding in TMS is 31.7 ppm for ^{1}H.[S15]

*5.1.2 IR frequencies calculations, Kohn-Sham orbitals and NBO analysis of **7** and **10***

The DFT calculations were carried out with the Gaussian16 series of programs, B.01 version,[S10] using the B3PW91 functional in combination with the 6-31G(d,p) basis set and Grimme's DFT-D3 London-dispersion correction with Becke-Johnson damping (D3BJ).[S16] Calculated Infra-red values were corrected with a scaling factor = 0.958. Natural Bond Orbital[S17] analyses – NBO – (Wiberg indexes, NPA charges, pNBO, and pNLMO) were performed with the NBO program version 6.0.[S18]

5.2 Thermodynamics of H_2 oxidative addition

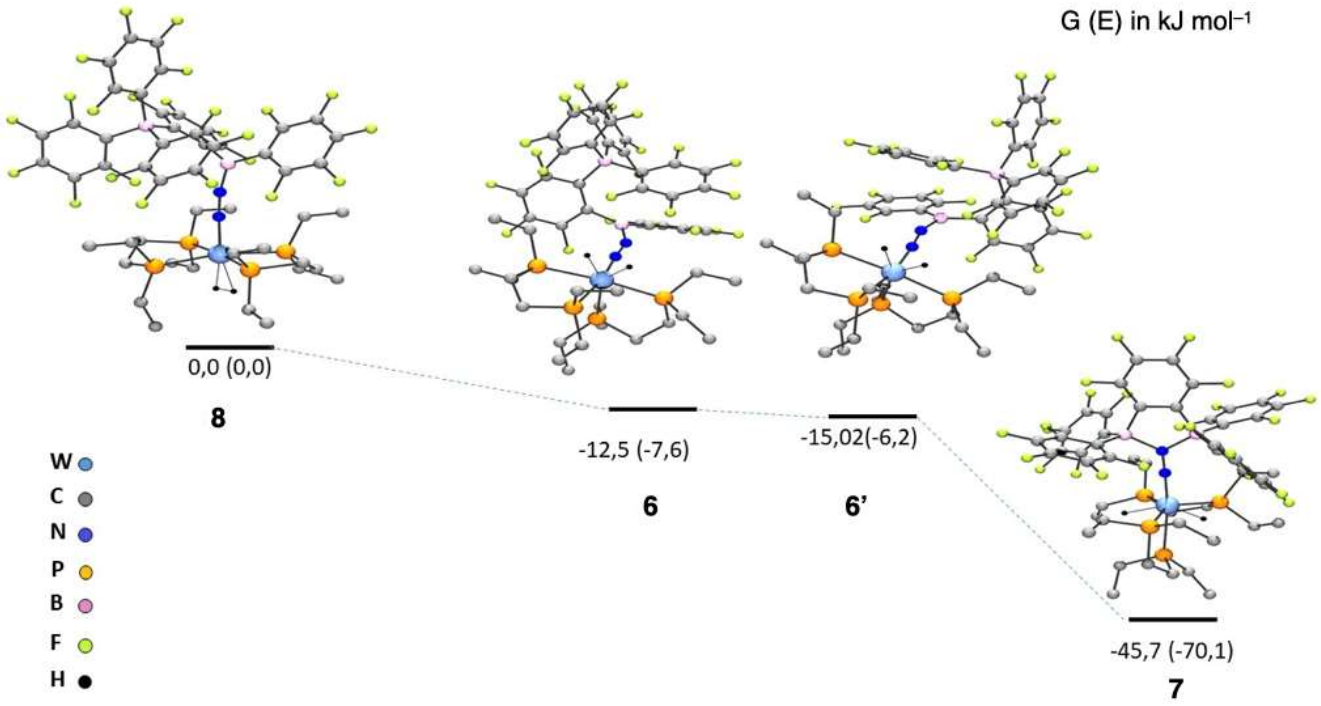
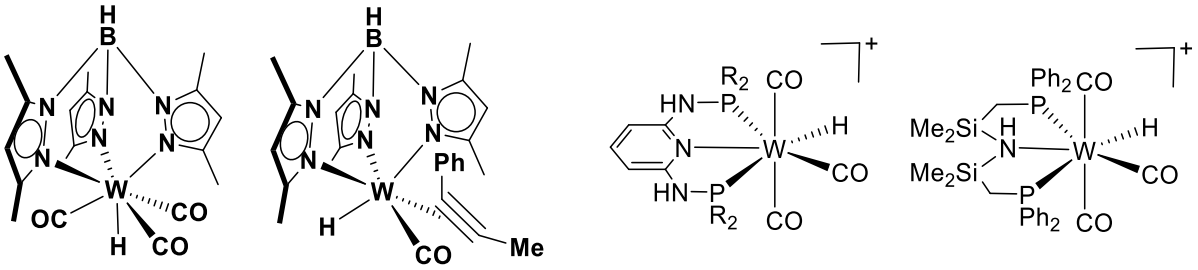


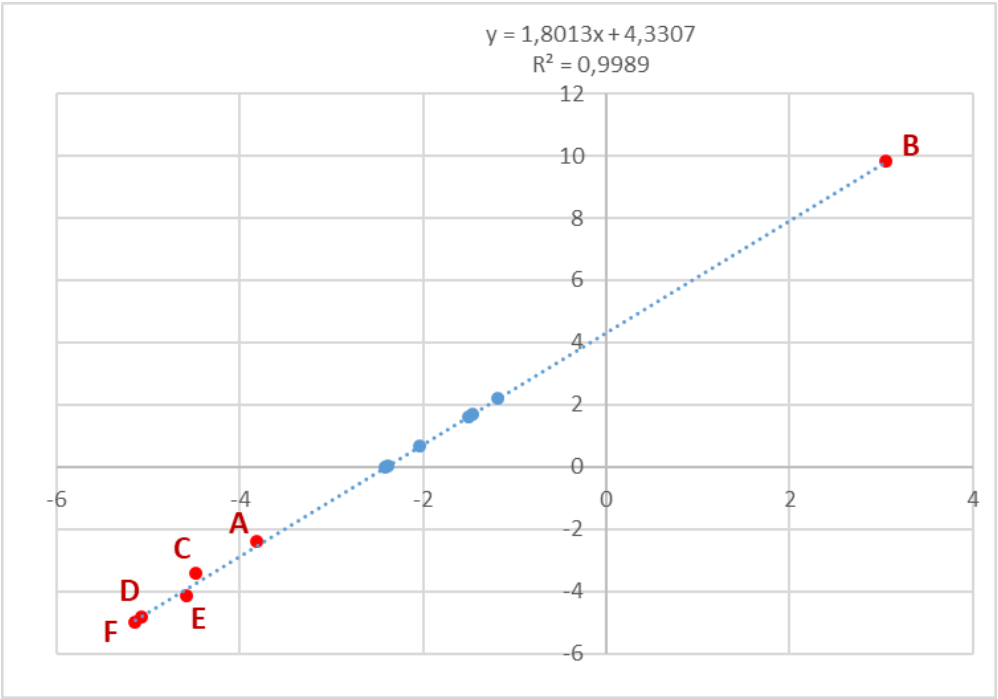
Figure S40. Possible intermediates in the **5** + H_2 ⟶ **7** reaction and their relative energies.

5.3 Chemical shift estimations

The structures of the literature-known tungsten-hydride complexes **A-F**[S19] have been optimized using their X-ray diffraction structures as the starting point.

Chart S1. Known W–H species used as basis for ^{1}H-NMR chemical shift prediction of the W-bound protons in **6** and **7**.





Plot S1. **Red series**: computed W–H chemical shifts plotted against the experimental values for complexes **A**–**F**. **Blue dotted line**: linear regression of the red series. **Blue series**: computed W–H chemical shifts plotted against the estimated values (extracted from the linear regression curve equation 1.8013 × ∂_{calc} + 4.3307) for complexes **6**–**7**.

Table S6. Isotropic chemical shieldings tensor (σ) and chemical shift (∂) values: ∂_{est} (ppm) are calculated using the equation ∂_{est} = 1.8013 × ∂_{calc} + 4.3307; $\partial_{calc} = \sigma^{TMS} - \sigma^{complex} = 31.7 - \sigma^{complex}$.

	$\sigma^{complex}$ (Ha)	δ_{calc} (ppm)	δ_{est} (ppm)	$\sigma^{complex}$ (Hb)	δ_{calc} (ppm)	δ_{est} (ppm)
6	33.16 (H84)	-1.46	1.70	34.08 (H85)	-2.38	0.04
6'	33.74 (H85)	-2.04	0.66	34.11 (H84)	-2.41	-0.01
7	32.89 (H71)	-1.19	2.19	33.21 (H85)	-1.51	1.61
	$\sigma^{complex}$ (Ha)	δ_{calc} (ppm)	δ_{exp} (ppm)			
A	35.51 (H52)	-3.81	-2.42			
B	28.65 (H65)	+3.05	+9.8			
C	36.18 (H2)	-4.48	-4.83			
D	36.76 (H4)	-5.06	-4.16			
E	36.27 (H4)	-4.57	-3.43			
F	36.84 (H80)	-5.14	-5.02			

5.4 Coordinates of optimized geometries used for chemical shift estimations (B3PW91, 6-31G)

*5.4.1 Compound **8** (E = -4582.518956 Ha)*

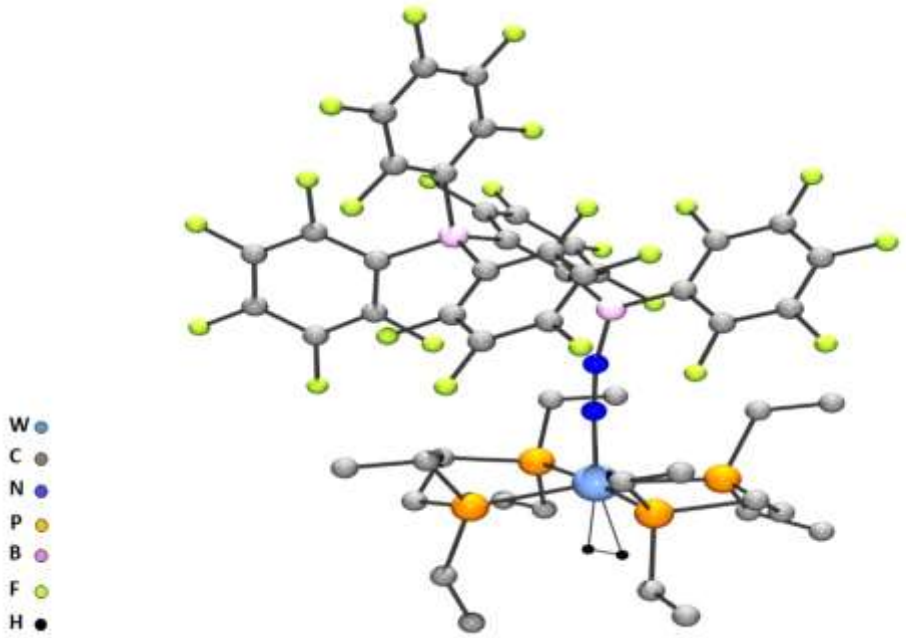


Figure S41. Optimized structure for **8,** hydrogen atoms except those bound to tungsten omitted for clarity.

C	7.438127	1.220960	-0.901398	C	-2.775888	2.641389	-3.878797	F	5.482309	-5.135809	-0.202034
C	6.788351	0.380421	-1.797758	C	-5.612969	0.412994	-2.882283	F	5.702278	-2.524824	-0.121150
C	5.544109	-0.135820	-1.459346	C	-6.046824	1.285915	-4.057163	C	2.509657	0.252405	-1.253477
C	4.884115	0.120737	-0.255087	P	-2.878722	-2.630745	-1.496978	C	1.899707	-0.345483	-2.359072
C	5.570493	0.982625	0.598529	C	-1.288970	-2.431845	-2.447807	C	1.289838	0.363670	-3.390781
C	6.822040	1.523097	0.304465	C	-0.761764	-3.626019	-3.238756	C	1.302717	1.751087	-3.381133
B	3.361695	-0.489513	-0.033375	C	-4.044772	-3.280937	-2.810288	C	1.931785	2.403099	-2.330782
C	2.702335	-0.194951	1.459420	C	-5.478914	-3.540586	-2.357580	C	2.513896	1.651691	-1.312852
C	1.470296	0.437584	1.767346	C	-2.631957	-4.162831	-0.435767	F	0.685243	-0.286449	-4.397861
C	1.022552	0.442256	3.088413	C	-2.038941	-3.788126	0.915082	F	1.869793	-1.681455	-2.512372
C	1.705803	-0.141650	4.140306	P	-2.954941	-2.353254	1.697874	F	0.715096	2.444260	-4.362824
C	2.919569	-0.750698	3.857844	C	-1.798861	-1.966503	3.110554	F	1.958619	3.740870	-2.296129
C	3.380361	-0.758826	2.546023	C	-2.392626	-1.137003	4.244096	F	3.123639	2.362950	-0.349563
F	-0.155719	1.059288	3.392337	C	-4.421467	-3.172379	2.534176	H	-6.983586	0.909090	-4.481957
B	0.440014	1.216527	0.841216	C	-4.138610	-4.335593	3.481986	H	-5.353146	-0.933871	-0.204456
N	-0.668024	0.520371	0.342958	C	0.424359	2.796854	0.703615	H	-6.073834	-3.944894	-3.183083
N	-1.738200	0.045514	0.123635	C	-0.429436	3.471904	-0.174641	H	-6.416758	0.346525	-2.137791
W	-3.453187	-0.650986	-0.061625	C	-0.508025	4.851694	-0.283970	H	-5.432098	-0.612541	-3.221878
P	-4.484499	1.205278	1.241024	C	0.312311	5.639803	0.515422	H	-6.220553	2.324893	-3.761529
C	-3.244869	2.304914	2.099503	C	1.189386	5.025787	1.402299	H	-5.302892	1.284191	-4.858322
C	-3.749364	3.421566	3.008811	C	1.238694	3.635613	1.481819	H	-5.971455	-2.625326	-2.016149
F	1.210477	-0.126914	5.385633	F	-1.250154	2.777165	-0.989308	H	-4.024261	-2.550972	-3.628093
F	3.622245	-1.326780	4.836817	F	-1.364530	5.417366	-1.141382	H	-7.558025	1.465749	3.595258
F	4.563862	-1.369130	2.360174	F	0.253493	6.965040	0.435530	H	-5.090875	-3.491992	1.725699
F	4.971514	-0.945755	-2.372323	F	2.102622	3.136030	2.359849	H	-5.069222	-4.688341	3.939296
F	5.043874	1.370497	1.771678	F	1.975672	5.773889	2.173896	H	-7.482073	2.085759	1.948251
F	7.363631	0.079376	-2.968789	C	3.339195	-2.154409	-0.126307	H	-3.690547	-5.187789	2.963043
F	7.427332	2.344086	1.171543	C	2.127400	-2.842350	-0.075186	H	-4.945889	-2.365236	3.058655
F	8.635275	1.733868	-1.199955	C	1.994804	-4.222741	-0.119114	H	-5.525475	-4.269419	-1.541897
C	-5.805064	0.804043	2.514478	C	3.131883	-5.017016	-0.169216	H	-6.344591	1.953414	-0.149491
C	-6.876662	1.848644	2.827854	C	4.370410	-4.394699	-0.175062	H	-3.616668	-4.630164	-0.314571
C	-5.362130	2.390426	0.068446	C	4.451782	-3.001221	-0.144782	H	-3.603357	-4.203703	-3.202877
C	-4.556664	2.569053	-1.215720	F	0.777725	-4.803540	-0.116335	H	-6.278486	-0.117252	2.155715
P	-4.074225	0.891646	-1.916632	F	3.029287	-6.348435	-0.206042	H	-6.453152	2.782833	3.202291
C	-2.799010	1.253390	-3.238359	F	0.962028	-2.148656	0.002936	H	-3.464649	-4.048670	4.294353

H	-2.941688	0.473745	-3.997166	H	-3.621829	3.100625	-1.016880	H	-0.546029	-2.112112	-1.714310
H	-5.112279	3.157098	-1.953370	H	-1.836378	1.047327	-2.763717	H	0.153055	-3.322470	-3.755017
H	-1.995124	-4.880259	-0.961829	H	-1.456693	-1.573993	-3.107035	H	-2.575335	1.635151	2.645724
H	-5.255171	0.523481	3.420663	H	-4.263345	3.028637	3.890629	H	-0.955349	-1.439880	2.653977
H	-3.714175	2.893763	-4.378820	H	-0.499112	-4.463428	-2.586915	H	-2.640306	2.713794	1.283899
H	-5.543331	3.352195	0.559931	H	-2.560594	3.417693	-3.141389	H	-4.430327	4.106969	2.494377
H	-1.975420	2.681090	-4.623267	H	-1.407514	-2.917113	3.491092	H	-2.902197	4.015025	3.367938
H	-2.015101	-4.646669	1.594274	H	-2.859179	-0.222221	3.868602	H	-5.084936	-1.659919	0.103990
H	-3.148322	-1.693830	4.807356	H	-1.006527	-3.449907	0.790872				
H	-1.467189	-3.980670	-3.996267	H	-1.605007	-0.837654	4.940753				

*5.4.2 Compound **6** (E = -4582.521840 Ha)*

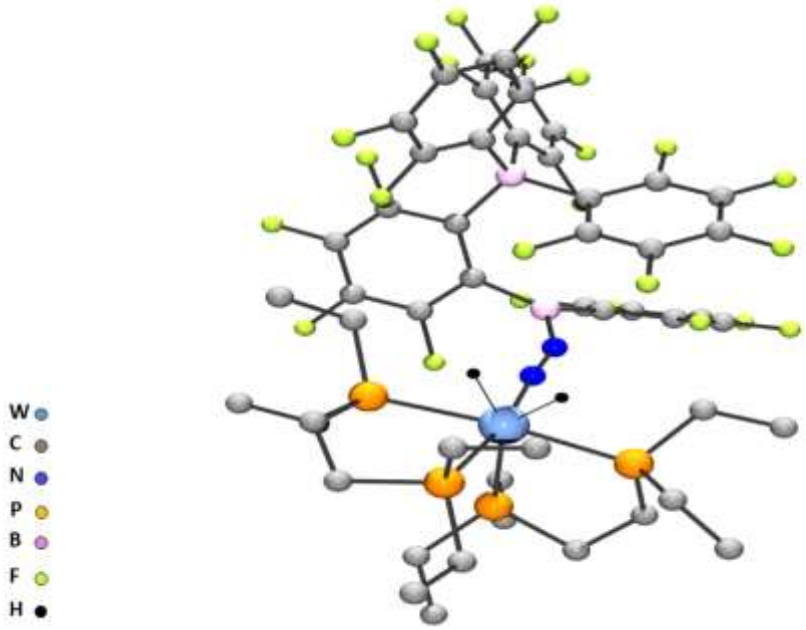


Figure S42. Optimized structure for **6,** hydrogen atoms except those bound to tungsten omitted for clarity.

C	-4.352476	-2.498304	1.920065	F	-2.382684	6.793010	-0.243421	F	-8.269133	-1.224943	-1.219088
C	-3.508313	-2.288254	0.824785	F	-1.143514	5.620995	1.884796	F	-8.436909	1.433382	-1.821938
C	-2.755111	-3.406159	0.480252	F	-0.387495	3.067611	1.764906	F	-6.243978	3.032397	-1.438351
C	-2.830932	-4.634515	1.133072	F	-1.862151	-3.362724	-0.531924	F	-3.985722	2.004338	-0.485915
C	-3.696177	-4.789323	2.205247	F	-2.062231	-5.661245	0.736714	N	0.590831	1.073145	-0.045493
C	-4.467147	-3.703094	2.603736	F	-3.782568	-5.957930	2.848465	N	1.617637	0.450322	0.038959
B	-3.390445	-0.758964	0.180058	F	-5.304878	-3.827669	3.639806	W	3.252837	-0.366597	0.199665
C	-2.479910	-0.667367	-1.207660	F	-5.122695	-1.492729	2.370259	P	5.321256	-1.950257	0.395625
C	-2.887764	-1.488547	-2.264954	C	-2.691227	0.046277	1.454715	C	7.106787	-1.381237	0.454429
C	-2.275874	-1.537029	-3.512574	C	-3.308167	0.966838	2.309892	C	8.192457	-2.455675	0.436371
C	-1.189929	-0.710927	-3.759705	C	-2.723580	1.448918	3.480839	P	3.970639	1.490686	1.736143
C	-0.775159	0.127476	-2.739625	C	-1.468246	0.998279	3.864302	C	5.294520	1.124501	3.016315
C	-1.381424	0.192962	-1.485004	C	-0.823311	0.063035	3.069734	C	6.242659	2.250179	3.423752
F	-3.921064	-2.332276	-2.108084	C	-1.434739	-0.379246	1.902983	P	4.445944	1.278599	-1.437609
F	-2.709781	-2.371470	-4.461871	F	-3.366192	2.338807	4.244297	C	5.657115	0.742924	-2.772289
F	-0.554128	-0.738347	-4.942102	F	-4.541358	1.427436	2.070522	C	6.825379	1.674742	-3.096213
F	0.287410	0.937797	-3.022064	F	-0.751854	-1.309824	1.206167	P	2.691311	-2.088262	-1.593853
B	-0.699762	1.300275	-0.570261	F	0.392046	-0.389326	3.427936	C	2.797560	-1.598388	-3.397153
C	-1.213641	2.794082	-0.449110	F	-0.884140	1.461279	4.974399	C	2.355297	-2.602043	-4.460107
C	-1.857879	3.441252	-1.510170	C	-4.872748	-0.183007	-0.295116	C	2.556246	2.167657	2.724087
C	-2.251312	4.774812	-1.459429	C	-6.017972	-0.949910	-0.526324	C	2.828623	3.334619	3.669526
C	-2.014463	5.516037	-0.307737	C	-7.210597	-0.428245	-1.027572	C	4.597432	2.971967	0.777990
C	-1.379549	4.916342	0.775047	C	-7.301621	0.920368	-1.339113	C	5.419822	2.510940	-0.419318
C	-0.992756	3.585462	0.681519	C	-6.188211	1.726988	-1.143240	C	3.201533	2.334925	-2.338723
F	-2.104082	2.796715	-2.653339	C	-5.023672	1.159075	-0.642895	C	3.705318	3.470130	-3.225279
F	-2.845831	5.348092	-2.506021	F	-6.044515	-2.270261	-0.286688	C	1.018980	-2.885539	-1.393497

C	0.859535	-4.343527	-1.825276	H	1.527272	-5.012962	-1.274497	H	4.563201	-1.928528	3.382672
C	3.893548	-3.516595	-1.446070	H	3.510222	-4.158141	-0.646121	H	4.313537	4.195382	-2.675579
C	5.309664	-3.054800	-1.119384	H	6.037355	-0.238888	-2.473243	H	5.728077	3.354273	-1.045357
C	5.205457	-3.220700	1.760412	H	5.046931	0.574236	-3.666619	H	2.527674	2.710378	-1.560848
C	5.342254	-2.666610	3.174848	H	-0.162178	-4.657734	-1.600190	H	5.862417	0.272574	2.636385
H	2.595549	-1.859047	0.762750	H	5.955243	-3.996474	1.567038	H	3.708882	3.523812	0.450344
H	3.070156	-0.711198	1.871589	H	2.195588	-0.687024	-3.478684	H	4.738951	0.750435	3.884500
H	2.878858	-3.559701	-4.378511	H	7.496543	1.802350	-2.242002	H	6.878816	2.568414	2.591439
H	2.562793	-2.201077	-5.457808	H	6.491444	2.666481	-3.409917	H	5.173178	3.645542	1.419054
H	3.876330	-4.112584	-2.364030	H	7.225481	-0.699598	-0.396334	H	6.907108	1.907740	4.224261
H	8.150983	-3.067147	-0.469545	H	0.312058	-2.240052	-1.924063	H	5.712256	3.130615	3.794875
H	5.970849	-3.913655	-0.958073	H	4.219171	-3.679679	1.638431	H	1.795703	2.437695	1.986544
H	1.281234	-2.790688	-4.410087	H	7.204108	-0.759469	1.351102	H	2.142510	1.310114	3.263356
H	1.033904	-4.496260	-2.892761	H	4.294856	3.101718	-4.069891	H	3.256211	4.200754	3.153903
H	5.731520	-2.473518	-1.948178	H	0.776290	-2.774693	-0.335135	H	3.500847	3.056987	4.486812
H	8.117931	-3.125247	1.297993	H	6.318254	-2.198918	3.342357	H	1.886409	3.659306	4.121683
H	7.418630	1.254287	-3.914990	H	2.593103	1.633306	-2.915897	H	5.238354	-3.474151	3.906289
H	9.184177	-1.992640	0.470776	H	2.852129	4.014973	-3.642172				
H	3.841289	-1.305365	-3.558607	H	6.331681	2.000391	-0.087478				

*5.4.3 Compound **6'** (E = -4582.521326 Ha)*

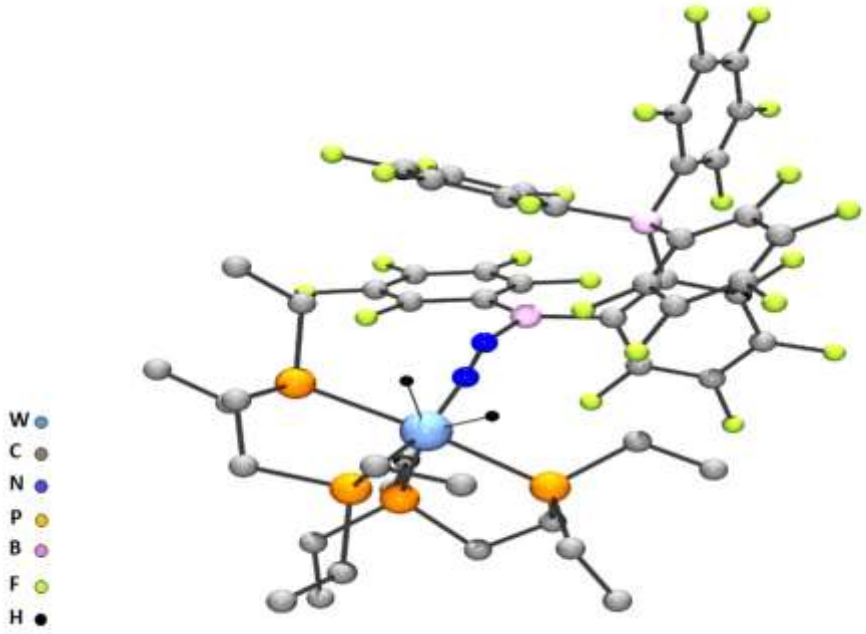


Figure S43. Optimized structure for **6',** hydrogen atoms except those bound to tungsten omitted for clarity.

C	-3.753430	-3.503948	-0.580303	F	-0.069835	0.937388	3.369331	F	-4.198933	-5.823541	-0.805333
C	-2.896810	-2.401387	-0.528238	B	-0.792252	1.299298	0.857179	F	-5.079528	-3.373493	-0.446168
C	-1.547300	-2.740913	-0.632178	C	-1.030939	2.862974	0.940550	C	-4.958329	-0.582698	-0.348413
C	-1.067357	-4.030347	-0.814271	C	-2.025645	3.430230	1.754748	C	-5.584980	-0.874296	-1.562445
C	-1.962615	-5.089786	-0.877532	C	-2.210714	4.804624	1.883888	C	-6.929057	-0.642383	-1.826117
C	-3.317385	-4.818335	-0.760142	C	-1.385695	5.680157	1.188914	C	-7.723730	-0.071910	-0.838657
B	-3.327802	-0.824333	-0.213180	C	-0.379618	5.169410	0.375634	C	-7.149806	0.253552	0.381870
C	-2.710678	-0.587136	1.312592	C	-0.223491	3.794802	0.272909	C	-5.795207	0.003769	0.599394
C	-3.225737	-1.411512	2.319451	F	-2.844554	2.666948	2.471588	F	-7.462744	-0.958387	-3.012994
C	-2.737551	-1.471774	3.620480	F	-3.167541	5.287362	2.674721	F	-4.871970	-1.425412	-2.563910
C	-1.659186	-0.673956	3.975069	F	-1.546682	6.994362	1.307049	F	-5.329841	0.387861	1.799731
C	-1.138394	0.162859	3.003998	F	0.432752	5.999575	-0.286017	F	-7.898722	0.817185	1.338233
C	-1.625588	0.242470	1.700210	F	0.788931	3.390002	-0.521350	F	-9.019742	0.164293	-1.064526
F	-4.258128	-2.231484	2.059894	F	-0.609857	-1.773395	-0.565262	C	-2.724034	0.259579	-1.316629
F	-3.277232	-2.300712	4.519538	F	0.256879	-4.269024	-0.911409	C	-2.079252	-0.022987	-2.525409
F	-1.133041	-0.729322	5.206807	F	-1.524110	-6.341990	-1.043017	C	-1.693138	0.953826	-3.439174

C	-1.962080	2.292138	-3.189701	C	1.908661	1.591784	-3.125113	H	7.013409	-1.021622	0.149658
C	-2.643313	2.628367	-2.029550	C	2.044177	1.885994	-4.618990	H	1.413326	2.416840	-2.604741
C	-3.013987	1.618150	-1.144730	C	4.644570	0.480676	-3.372677	H	4.076287	-2.646648	-3.142193
F	-1.789804	-1.276955	-2.899901	C	5.807360	-0.207469	-2.662784	H	6.544186	-2.706238	0.183646
F	-1.042978	0.611431	-4.563101	C	4.894136	-2.942379	-2.476907	H	4.437274	3.971822	2.760701
F	-1.561981	3.234963	-4.050654	C	4.511774	-4.212619	-1.724378	H	1.274517	0.714305	-2.973581
F	-2.925020	3.909910	-1.763477	H	2.616305	-0.988670	-1.872199	H	5.304408	-4.544282	-1.045351
F	-3.709570	2.022449	-0.067965	H	2.415271	-2.009256	-0.577295	H	2.806392	2.937587	1.120141
N	0.390584	0.869839	0.236332	H	4.840814	3.553881	-3.784341	H	2.774502	4.132168	3.321483
N	1.420950	0.291740	0.059217	H	4.832816	4.824756	-2.562964	H	5.250985	-0.597793	3.021787
W	3.066539	-0.453661	-0.287379	H	5.005967	1.245410	-4.067729	H	3.597861	-4.060525	-1.144711
P	5.201392	-1.451498	-1.393214	H	8.314030	-1.423479	-1.994552	H	3.820910	2.916284	4.044175
C	6.789922	-1.881040	-0.493102	H	6.464882	-0.704279	-3.384761	H	4.501817	0.688053	3.968981
C	8.005223	-2.246325	-1.343565	H	3.308847	4.251997	-3.235708	H	2.148152	1.929775	2.372056
P	2.837593	-1.894316	1.773286	H	2.675698	2.751922	-4.829966	H	4.894837	-3.111087	1.380817
C	4.006911	-3.351624	1.969903	H	6.417203	0.526214	-2.120414	H	2.212431	-0.254174	3.438170
C	4.418275	-3.772201	3.380101	H	7.815297	-3.120518	-1.972921	H	3.512573	-4.177758	1.446064
P	4.201142	1.020657	1.540641	H	7.705985	2.475544	2.302212	H	5.005752	-2.996755	3.881870
C	5.893910	1.808559	1.329842	H	8.857353	-2.489620	-0.700242	H	3.215482	-1.489772	4.191594
C	6.770200	1.974465	2.571633	H	5.219437	2.682375	-1.395204	H	5.043793	-4.670139	3.333191
P	3.451903	1.230168	-2.142452	H	2.448782	1.030088	-5.167150	H	3.561707	-4.004393	4.016786
C	4.218896	2.902393	-1.785486	H	4.069238	-0.242934	-3.959506	H	0.453822	-1.788035	1.840547
C	4.301626	3.931985	-2.910340	H	6.416922	1.205912	0.580093	H	1.009538	-3.277577	1.131655
C	1.145770	-2.621105	1.995786	H	5.706784	2.781532	0.862172	H	0.955622	-2.706360	4.177888
C	0.837202	-3.349716	3.300950	H	1.050208	2.087505	-5.026593	H	1.456265	-4.241202	3.436388
C	3.116125	-0.858578	3.303607	H	5.781852	-3.103469	-3.099476	H	-0.205360	-3.682084	3.288715
C	4.349436	0.019362	3.115629	H	3.642753	3.314419	-0.950382	H	4.324559	-5.027508	-2.430558
C	3.072061	2.419151	2.045942	H	7.035258	1.010998	3.016039				
C	3.564022	3.406758	3.100223	H	6.286440	2.576866	3.343796				

*5.4.4 Compound **7** (E = -4582.545643 Ha)*

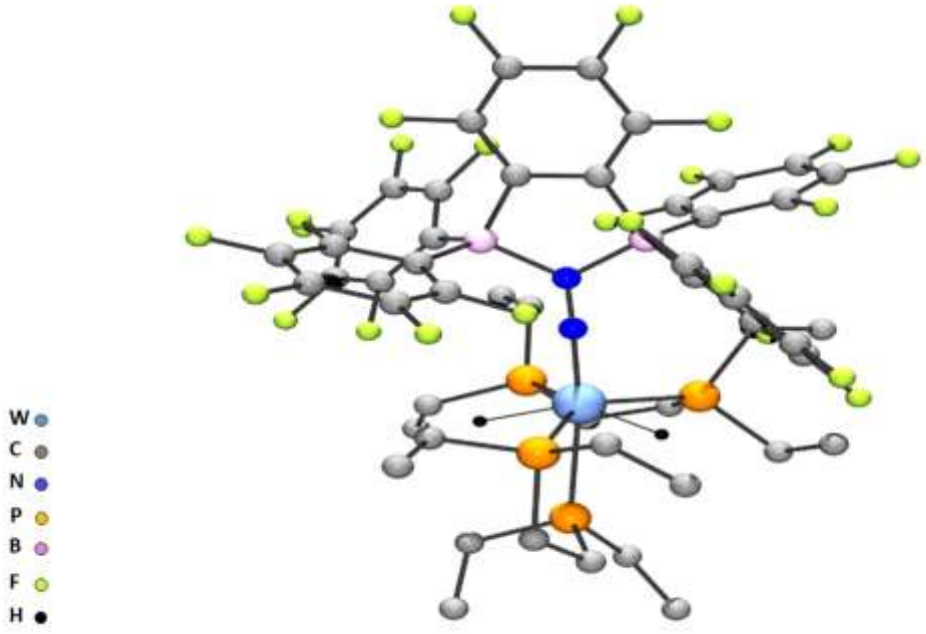


Figure S44. Optimized structure for **7,** hydrogen atoms except those bound to tungsten omitted for clarity.

C	-1.568056	3.314417	-4.324488	C	-1.284327	1.433622	-2.861180	C	-0.514413	3.309173	1.058737
C	-1.897149	4.076270	-3.211160	C	-1.596417	2.145395	-1.704652	C	-1.182333	4.331648	3.116987
C	2.412791	3.516536	-3.629310	C	4.100248	3.011996	-0.928967	C	-1.598038	2.435963	1.017150
C	-1.255046	1.974746	-4.142063	C	-4.499982	1.479184	-0.550259	C	-2.286122	3.489646	3.133332
C	-1.909842	3.488991	-1.946684	C	-5.714580	0.834279	-0.742180	C	-3.317745	0.775761	-0.357400
C	1.799425	2.521121	-2.646410	C	-0.288551	4.245299	2.058569	C	-2.474736	2.572947	2.098738
C	3.395646	4.132769	-0.172029	C	4.067060	0.756391	-2.818435	C	-5.747599	-0.557265	-0.752977

C	1.982868	-2.439462	-4.427717
C	1.571840	-1.601835	-3.220152
C	4.281692	-0.727425	-2.541520
C	-3.349589	-0.627100	-0.365716
C	-4.568591	-1.265667	-0.559725
C	7.096782	1.289139	1.162655
C	6.229170	0.357331	0.317203
C	1.872852	2.436742	3.867314
C	-1.941331	-2.612355	-2.365796
C	1.006917	1.197707	3.660334
C	-1.408570	-2.453296	-1.081619
C	-1.596740	-3.660247	-3.221139
C	4.627585	0.388118	2.826697
C	4.422401	-3.841735	-2.261534
C	3.255119	-3.267497	-1.459003
C	-2.186562	-1.993784	1.487198
C	-2.141979	-1.258635	2.669583
C	3.508937	-0.284281	3.609248
C	-0.482076	-3.433601	-0.723612
C	-0.682326	-4.617075	-2.803156
C	5.164127	-2.094529	1.408696
C	-2.578481	-1.711938	3.910120
C	-2.708808	-3.283208	1.662167
C	-0.128095	-4.505541	-1.534696
C	1.088736	-1.784744	3.352748
C	6.367657	-2.315963	2.321399
C	-3.094807	-2.994398	4.022829
C	-3.154060	-3.785616	2.883364
C	0.843775	-1.909672	4.853814
H	1.631488	3.892705	-4.296905
H	2.849437	4.381575	-3.122901
H	3.187698	3.068694	-4.260126
H	2.659895	4.651344	-0.790743
H	1.052437	2.997445	-2.011239
H	4.131525	4.872861	0.159371
H	1.276419	1.724299	-3.180829
H	4.615752	3.406227	-1.812644
H	3.549514	0.880931	-3.774715
H	5.021579	1.285241	-2.911860
H	2.868517	3.758438	0.706403
H	4.861674	2.556466	-0.291812
H	1.351483	-0.572675	-3.514845
H	1.206805	-2.369786	-5.196603
H	2.919395	-2.098925	-4.881891
H	4.558434	-1.257551	-3.458266
H	5.947058	0.859966	-0.610472
H	7.962361	1.620536	0.579562
H	6.554884	2.185362	1.479328
H	2.227764	2.845605	2.917389
H	2.426899	1.477861	1.014863
H	0.641919	-1.976272	-2.785610
H	5.093645	-0.883382	-1.826036
H	1.286609	3.220593	4.355474
H	2.089137	-3.498137	-4.175827
H	0.112185	1.447737	3.089284
H	6.811626	-0.521662	0.018412
H	4.449589	1.463277	2.731848
H	2.740278	2.240920	4.505746
H	4.249644	-3.804695	-3.339736
H	7.477860	0.795979	2.060684
H	5.364361	-3.322009	-2.058101
H	0.678635	0.796732	4.624498
H	2.355747	-3.865121	-1.619867
H	2.275296	-1.686632	0.784943
H	5.594973	0.246780	3.317642
H	4.566734	-4.892977	-1.991350
H	3.454672	-3.330913	-0.388242
H	5.362839	-2.513237	0.415942
H	3.407711	0.155735	4.606058
H	7.260212	-1.790790	1.966858
H	0.174227	-1.951944	2.782107
H	4.281463	-2.620566	1.785394
H	3.732137	-1.346487	3.756106
H	6.171767	-1.989708	3.346947
H	1.792783	-2.548056	3.000855
H	0.024286	-1.269538	5.187823
H	6.614755	-3.381802	2.363344
H	1.732667	-1.669886	5.447402
H	0.561580	-2.939670	5.094775
N	-0.966978	0.020219	-0.038206
N	0.279249	0.002686	0.034801
B	-1.845686	1.411715	-0.241407
B	-1.938941	-1.325117	-0.016298
F	-1.527228	3.864329	-5.540724
F	-2.196063	5.370308	-3.360196
F	-2.239607	4.319261	-0.946897
F	-0.876500	1.223894	-5.187004
F	-4.510148	2.828175	-0.547673
F	-6.845042	1.528504	-0.921142
F	0.794346	5.038847	2.027777
F	0.398796	3.301985	0.061242
F	-0.963682	5.190893	4.116062
F	-0.912462	0.140187	-2.785603
F	-3.151822	3.556033	4.148170
F	-6.909581	-1.193352	-0.946294
F	-3.563838	1.807501	2.216371
F	-2.839050	-1.756819	-2.861117
F	-2.135758	-3.748651	-4.440115
F	-4.651693	-2.611706	-0.582703
F	-1.604298	-0.021358	2.673936
F	-2.467952	-0.932770	4.996313
F	-0.325710	-5.619501	-3.609728
F	0.101971	-3.408728	0.491852
F	-2.810666	-4.141919	0.636784
F	0.764259	-5.421268	-1.118074
F	-3.508727	-3.462287	5.201729
F	-3.634488	-5.029561	2.967126
P	2.990476	1.628542	-1.528971
P	2.755098	-1.492555	-1.787938
P	4.641293	-0.320013	1.102713
P	1.840620	-0.195486	2.740505
W	2.108203	-0.053506	0.250495

*5.4.5 Compound **A** (E = -1345.722637 Ha)*

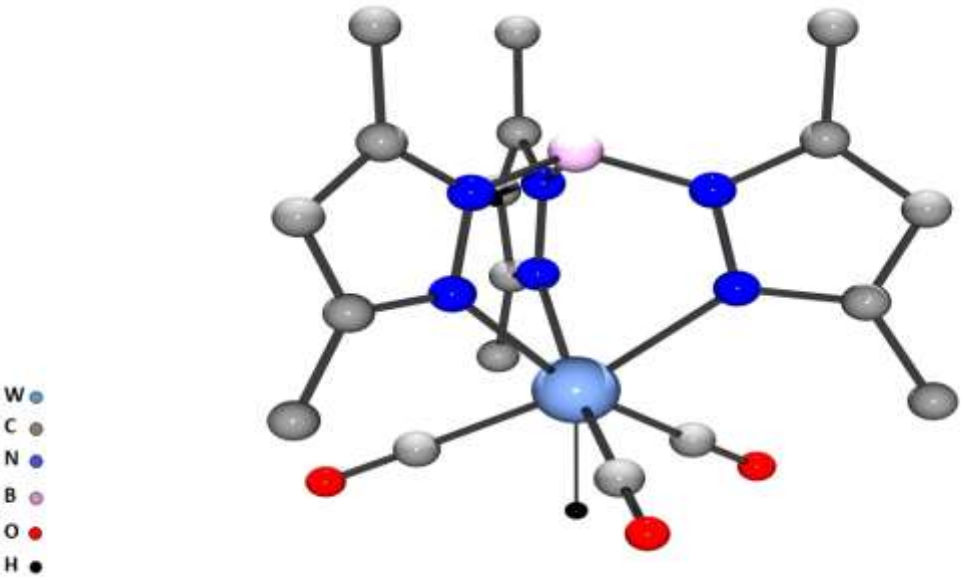


Figure S45. Optimized structure for **A,** hydrogen atoms except those bound to tungsten omitted for clarity.

C	0.104573	-0.844891	2.929469	H	-1.807525	-1.782887	-3.125401
N	0.253344	-0.473940	1.645194	H	1.588242	4.568454	-1.132473
N	1.589756	-0.401463	1.395688	H	4.095675	3.614664	-0.899375
C	2.288941	-0.722677	2.508781	H	4.213247	2.345344	0.327073
C	1.370059	-1.010810	3.505701	H	4.212909	1.917806	-1.385340
W	-1.212302	0.000536	-0.000405	H	-1.061296	4.678368	-1.168292
C	-2.130340	0.488019	-1.697321	H	-1.815155	3.163558	-1.683327
O	-2.653813	0.774886	-2.696609	H	-1.802377	3.604343	0.025478
B	2.107269	-0.000383	0.000112	H	1.585733	-1.304132	4.522843
N	1.590739	1.409044	-0.350305	H	4.093580	-1.031080	3.580973
N	0.254479	1.661917	-0.412415	H	4.212251	-1.455070	1.867683
C	0.106319	2.959686	-0.733397	H	4.211240	0.240691	2.357074
C	1.372069	3.541012	-0.877978	H	-1.064010	-1.325526	4.635325
C	2.290492	2.533174	-0.628934	H	-1.817465	-0.123737	3.578794
C	3.781464	2.599791	-0.645964	H	-1.803987	-1.824709	3.108560
C	-1.216620	3.631283	-0.897247	H	3.303658	-0.000885	0.000283
C	3.779882	-0.741179	2.575755	H	-2.919256	0.002813	-0.001919
C	-1.218737	-1.038207	3.592488				
N	0.253655	-1.188585	-1.232417				
N	1.590008	-1.008311	-1.045163				
C	2.289306	-1.812488	-1.879013				
C	1.370510	-2.532817	-2.626113				
C	0.104982	-2.116504	-2.194684				
C	3.780240	-1.860848	-1.928730				
C	-1.218281	-2.595527	-2.692327				
C	-2.131332	1.226665	1.269380				
O	-2.655369	1.948618	2.017093				
C	-2.133388	-1.711360	0.425746				
O	-2.658816	-2.719236	0.676674				
H	1.586281	-3.267678	-3.388058				
H	4.094041	-2.586572	-2.682239				
H	4.212236	-0.890633	-2.193305				
H	4.211845	-2.161988	-0.969041				
H	-1.063414	-3.350537	-3.466900				
H	-1.813164	-3.047063	-1.894059				

*5.4.6 Compound **B** (E = -1466.741397 Ha)*

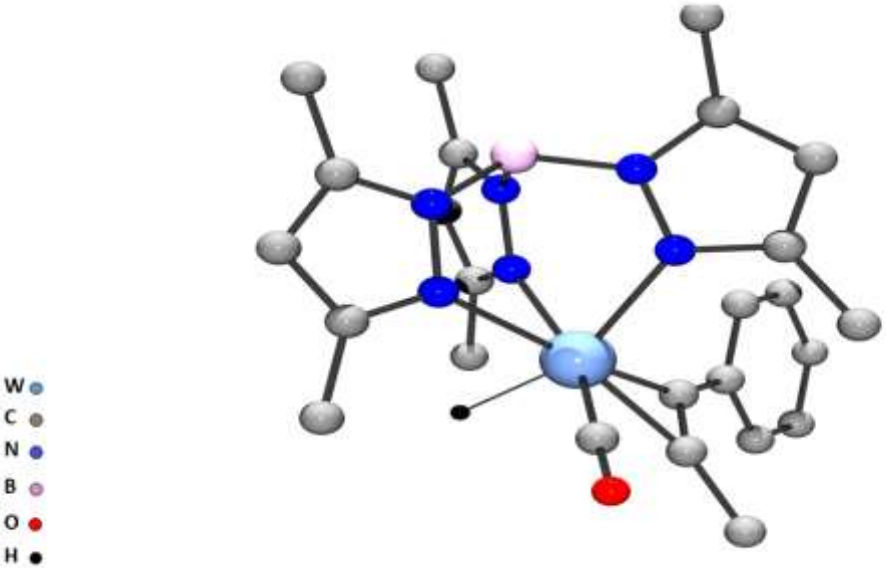


Figure S46. Optimized structure for **B,** hydrogen atoms except those bound to tungsten omitted for clarity.

C	5.638583	0.874023	-0.286406	H	2.207541	-3.971907	0.618449
C	4.584531	-0.027890	-0.397519	H	3.651483	-2.947315	0.857442
C	3.281189	0.340788	-0.017110	H	2.064556	1.924291	0.776780
C	3.069914	1.636050	0.486002	H	3.951833	3.522818	1.014969
C	4.130396	2.528160	0.615226	H	6.241539	2.853739	0.318490
C	5.416313	2.153046	0.225059	H	6.637804	0.576561	-0.593433
C	2.174846	-0.600588	-0.116741	H	4.760585	-1.023878	-0.794004
C	1.989710	-1.918830	-0.004411	H	-5.062439	-1.424275	-1.855466
C	2.793903	-3.147086	0.204592	H	-1.505094	-2.746756	-2.597231
W	0.198982	-0.976411	-0.325719	H	-3.223856	-3.139303	-2.862975
C	-0.114560	-2.875404	0.032701	H	-2.390872	-3.697112	-1.404648
O	-0.263778	-4.021039	0.232587	H	-5.195402	1.282085	0.745553
N	-0.027435	1.159573	-1.038828	H	-6.056058	0.810079	-0.726803
N	-0.963186	1.990981	-0.499443	H	-4.876059	2.127305	-0.770400
C	-0.940689	3.189803	-1.130238	H	-0.766148	0.281242	4.857634
C	0.042472	3.126608	-2.103395	H	1.729789	-1.480475	2.910875
C	0.582875	1.833964	-2.027281	H	0.396678	-2.609313	2.660692
B	-2.038813	1.413551	0.439614	H	0.673951	-1.904515	4.268249
N	-1.386360	0.857904	1.715726	H	-2.433484	2.386304	4.543333
N	-0.553201	-0.211078	1.622624	H	-3.510666	2.138981	3.161294
C	-0.214539	-0.566483	2.877365	H	-2.156926	3.263071	3.031117
C	-0.839931	0.302331	3.779920	H	0.329032	3.910895	-2.789283
C	-1.584431	1.185976	3.011808	H	1.450813	0.182100	-3.060757
C	1.640753	1.245923	-2.897669	H	2.634587	1.345497	-2.450674
C	0.695765	-1.703280	3.194274	H	1.651718	1.760975	-3.862332
C	-1.851857	4.322157	-0.788885	H	-1.801044	4.581591	0.273043
C	-2.468960	2.303415	3.454835	H	-1.567515	5.204295	-1.367058
N	-2.035920	-0.815010	-0.752179	H	-2.897119	4.091513	-1.019560
N	-2.749392	0.252158	-0.293149	H	0.109647	-1.295785	-2.022433
C	-4.042172	0.141669	-0.672942				
C	-4.163979	-1.032104	-1.401213				
C	-2.885735	-1.603356	-1.434110				
C	-2.477416	-2.866782	-2.112365				
C	-5.093352	1.146527	-0.335613				
H	-2.832262	2.263813	0.726096				
H	3.189675	-3.485030	-0.761070				

*5.4.7 Compound **C** (E = -1704.654681 Ha)*

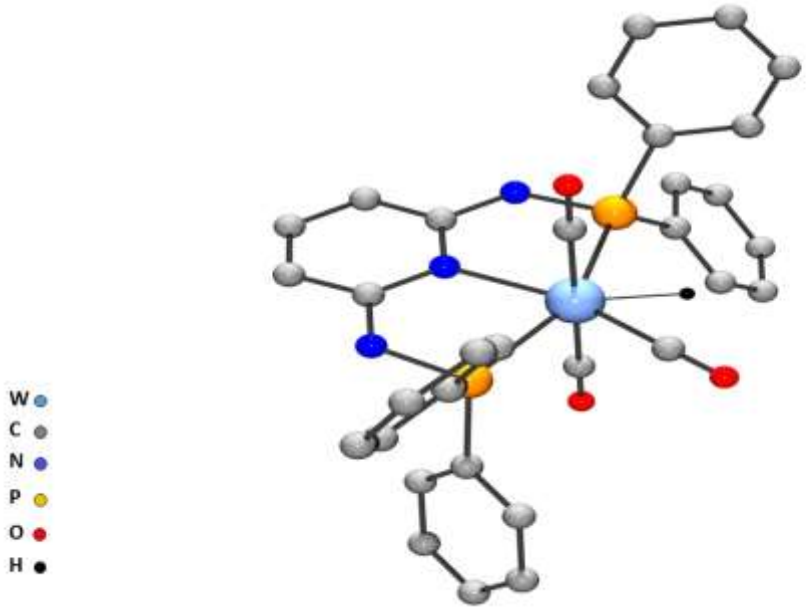


Figure S47. Optimized structure for **C,** hydrogen atoms except those bound to tungsten omitted for clarity.

W	-0.032459	0.030146	-0.380804	C	3.436373	-2.485000	0.821571
H	-1.012298	-0.201844	-1.793931	H	2.908177	-2.380969	1.764982
P	2.420158	0.069181	0.170277	C	-3.508809	-1.486976	-0.314018
P	-2.454855	-0.054189	0.137777	C	-3.082551	-2.424658	-1.259553
N	-0.046503	0.056315	1.895049	H	-2.119495	-2.311123	-1.745814
N	2.292594	0.170491	1.898336	C	-3.900912	-3.505108	-1.588978
H	3.134127	0.284583	2.447701	H	-3.565074	-4.227949	-2.326206
N	-2.384803	-0.075976	1.873570	C	-5.140896	-3.655201	-0.973437
H	-3.234978	-0.134982	2.417446	H	-5.774590	-4.499668	-1.227530
C	1.113447	0.133496	2.602012	C	-5.576474	-2.715169	-0.037224
C	1.139105	0.167146	3.999444	H	-6.548809	-2.823985	0.433713
H	2.086563	0.233610	4.521732	C	-4.770344	-1.628834	0.284716
C	-0.062841	0.103216	4.686302	H	-5.138861	-0.885036	0.987284
H	-0.069146	0.122860	5.771649	C	-3.533216	1.388215	-0.223178
C	-1.256591	0.010682	3.988289	C	-4.279878	1.405267	-1.408599
H	-2.209377	-0.043658	4.502218	H	-4.275616	0.546950	-2.074740
C	-1.215429	-0.005983	2.590987	C	-5.046005	2.523099	-1.729495
C	3.577904	1.421175	-0.276824	H	-5.624559	2.532202	-2.648311
C	3.129060	2.547295	-0.974640	C	-5.077535	3.621003	-0.869911
H	2.096980	2.616195	-1.297884	H	-5.680612	4.488677	-1.120135
C	4.012375	3.585759	-1.265697	C	-4.337556	3.604371	0.311446
H	3.659114	4.453583	-1.814167	H	-4.362321	4.457128	0.983270
C	5.341777	3.506857	-0.856873	C	-3.559925	2.494261	0.634213
H	6.028130	4.317330	-1.083616	H	-2.980222	2.491183	1.552815
C	5.796563	2.382988	-0.164947	C	-0.247813	2.058859	-0.388206
H	6.835109	2.316233	0.145103	O	-0.388898	3.205314	-0.404570
C	4.923148	1.337524	0.117256	C	0.120410	-2.008802	-0.321590
H	5.294616	0.452135	0.626820	O	0.207235	-3.158762	-0.289319
C	3.416347	-1.447770	-0.117240	C	0.613840	0.142845	-2.274909
C	4.093075	-1.595683	-1.336003	O	0.984290	0.214522	-3.368718
H	4.093735	-0.793090	-2.068643				
C	4.784512	-2.773841	-1.606611				
H	5.308337	-2.884193	-2.551316				
C	4.810636	-3.803028	-0.665330				
H	5.355191	-4.718280	-0.877272				
C	4.139586	-3.656703	0.547548				
H	4.159956	-4.455768	1.282572				

*5.4.8 Compound **D** (E = -1252.420032 Ha)*

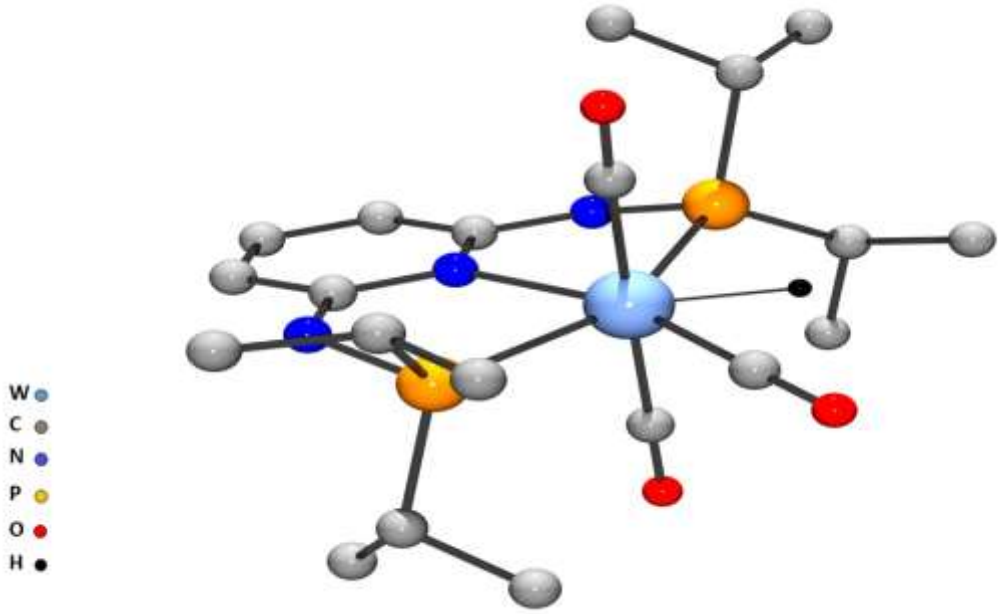


Figure S48. Optimized structure for **D,** hydrogen atoms except those bound to tungsten omitted for clarity.

W	0.026768	-0.592057	0.045141	H	-4.602101	0.034138	-0.862736
C	-0.015080	-0.553676	2.081171	C	-3.363880	0.773442	-2.461248
O	-0.069260	-0.601795	3.236249	C	-3.559118	-1.638452	-1.729548
H	0.961843	-2.046897	0.195158	H	-5.027528	0.666742	2.840222
C	-0.673141	-2.469459	0.094120	H	-4.202940	1.900845	1.904213
O	-1.054544	-3.562935	0.109808	H	-5.302179	0.749843	1.105712
C	0.018961	-0.706133	-1.991942	H	-4.263528	-1.724712	2.852957
O	-0.024995	-0.800839	-3.143713	H	-4.646625	-1.817561	1.137248
P	-2.397098	0.131666	0.127263	H	-3.042511	-2.302766	1.722102
N	-2.130765	1.849687	0.148751	H	-4.350790	-1.819098	-2.463873
H	-2.928841	2.469602	0.175039	H	-2.605940	-1.871512	-2.211914
C	-0.933850	2.457104	-0.146627	H	-3.707424	-2.345428	-0.909894
N	0.175803	1.673733	-0.212159	H	-4.077592	0.543934	-3.259224
C	1.364454	2.273636	-0.506389	H	-3.496379	1.825041	-2.195019
C	1.472863	3.648091	-0.732362	H	-2.360419	0.650105	-2.878428
C	0.328980	4.427398	-0.651757	H	5.287884	0.137044	2.653439
C	-0.889942	3.839302	-0.355289	H	5.317535	-0.898454	1.230996
H	-1.799139	4.426085	-0.290653	H	5.251242	0.866319	1.054088
H	0.388188	5.497840	-0.822186	H	3.155513	1.152730	3.521361
H	2.438189	4.084269	-0.962588	H	3.245104	2.134817	2.056783
N	2.480838	1.471610	-0.582976	H	1.747086	1.292941	2.471718
H	3.354809	1.962074	-0.721076	H	4.560252	-3.027601	-1.192137
P	2.475417	-0.151433	0.048103	H	4.012128	-2.645125	0.440144
C	-3.379303	-0.127966	1.708176	H	2.836274	-3.064198	-0.817404
C	-3.609943	-0.172204	-1.284283	H	4.176400	-1.338682	-3.132975
C	3.669097	-1.065242	-1.063743	H	2.454548	-1.529738	-2.814237
C	3.356386	-0.013738	1.714904	H	3.171409	0.089701	-2.860978
C	4.885529	0.016467	1.642237				
C	2.835978	1.210572	2.476501				
H	3.037913	-0.922546	2.242383				
H	4.632491	-0.572586	-0.879436				
C	3.770906	-2.529185	-0.620893				
C	3.337476	-0.944928	-2.549780				
C	-4.536555	0.859246	1.880671				
C	-3.851276	-1.578301	1.849714				
H	-2.632471	0.075048	2.484373				

*5.4.9 Compound **E** (E = -1409.587756 Ha)*

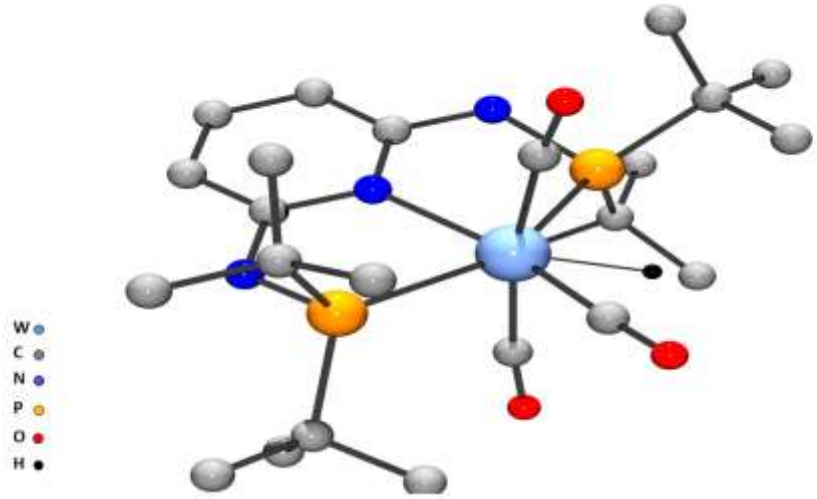


Figure S49. Optimized structure for **E,** hydrogen atoms except those bound to tungsten omitted for clarity.

W	0.027166	-0.578715	-0.020168	H	-5.601983	0.080088	1.095110
C	0.119785	-0.805201	1.996541	H	-4.071097	-1.415702	3.046999
O	0.151272	-1.086101	3.121035	H	-4.127407	-2.004974	1.387181
H	0.997245	-1.992877	-0.252902	H	-2.571295	-1.843034	2.224656
C	-0.597310	-2.477652	0.062642	H	-3.903279	-2.286138	-2.658554
O	-0.925935	-3.584570	0.151600	H	-2.230026	-2.134882	-2.132433
C	-0.020039	-0.708672	-2.051506	H	-3.492458	-2.583158	-0.971672
O	-0.020124	-0.945347	-3.185824	H	-3.567293	-0.055321	-3.675012
P	-2.472896	0.079734	-0.053649	H	-3.515162	1.413095	-2.696368
N	-2.233655	1.784035	-0.323875	H	-2.055912	0.446273	-2.923343
H	-3.045330	2.382161	-0.402496	H	5.647193	-1.327007	1.867452
C	-1.063800	2.445550	-0.040098	H	5.398824	-1.380928	0.128069
N	0.066178	1.704591	0.131894	H	5.517592	0.181237	0.973189
C	1.219805	2.369396	0.427474	H	3.885536	-0.821913	3.463927
C	1.273664	3.760650	0.556780	H	3.849408	0.783690	2.735220
C	0.112877	4.492812	0.364690	H	2.348957	-0.118223	2.972629
C	-1.070598	3.841250	0.059562	H	3.957917	-0.987670	-3.352510
H	-1.994221	4.388937	-0.089835	H	4.119389	-1.828203	-1.812270
H	0.130920	5.574587	0.454260	H	2.515731	-1.572080	-2.522948
H	2.213832	4.245289	0.794478	H	2.899381	1.226713	-3.511246
N	2.364001	1.626829	0.603106	H	1.491482	1.002118	-2.480168
H	3.200163	2.174171	0.758088	H	2.672982	2.256587	-2.095672
P	2.507578	-0.010459	0.019519	H	3.863240	-2.890012	2.092256
C	-3.451286	0.072651	1.609926	H	2.178263	-2.497133	1.747166
C	-3.549584	-0.464854	-1.567335	H	3.297045	-2.864794	0.422579
C	3.410705	0.243204	-1.664480	H	5.089732	1.231189	-2.560655
C	3.624036	-0.888940	1.335549	H	4.835686	1.750273	-0.904444
C	5.128081	-0.837298	1.035850	H	5.581920	0.177032	-1.245233
C	3.397391	-0.211276	2.695906	H	-3.016980	0.745059	3.607857
C	3.201756	-2.366519	1.393129	H	-1.568866	0.669202	2.613389
C	4.810116	0.874707	-1.562811	H	-2.725334	1.985179	2.385423
C	3.497249	-1.118634	-2.366822	H	-5.541942	-0.545534	-2.336063
C	2.555010	1.235986	-2.471264	H	-5.470842	-0.992043	-0.637904
C	-4.848716	0.712091	1.560696	H	-5.362249	0.716746	-1.124295
C	-3.552926	-1.383686	2.081919				
C	-2.628739	0.916549	2.597809				
C	-5.063681	-0.302542	-1.380333				
C	-3.133143	0.391528	-2.773533				
C	-3.262935	-1.951097	-1.834966				
H	-5.171242	0.889381	2.592970				
H	-4.853702	1.688313	1.063186				

*5.4.10 Compound **F** (E = -2219.506031 Ha)*

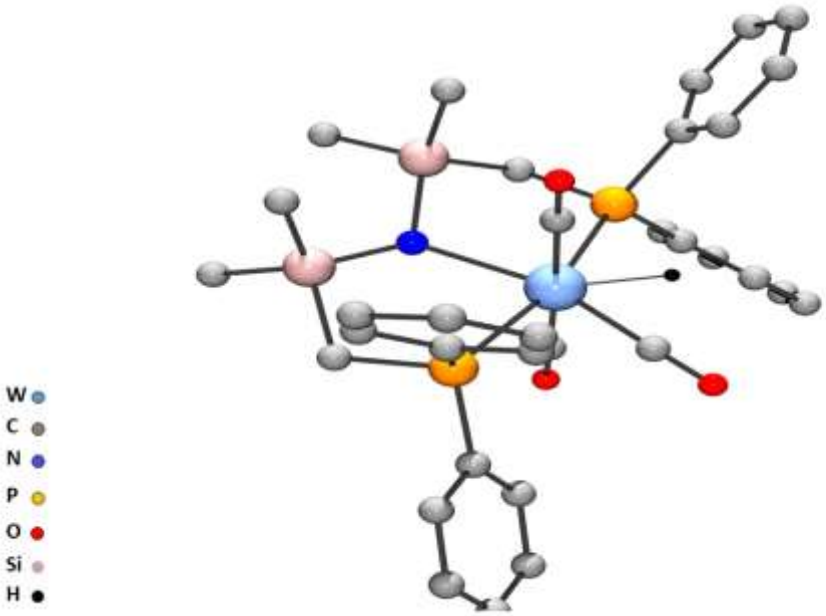
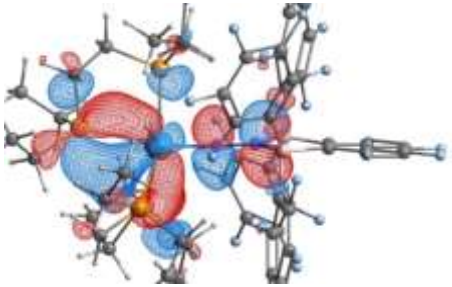
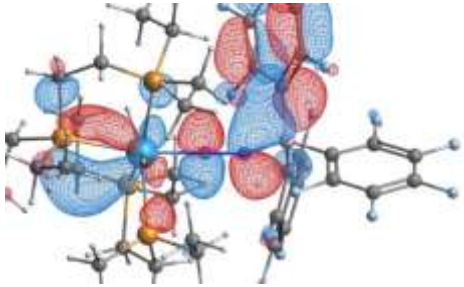
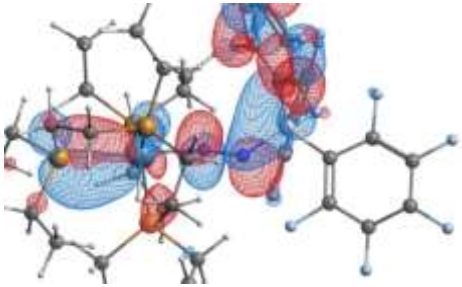
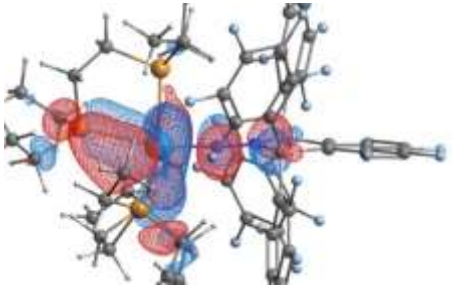
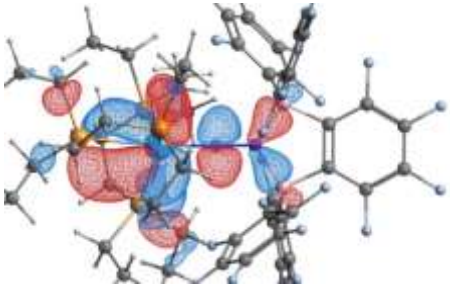
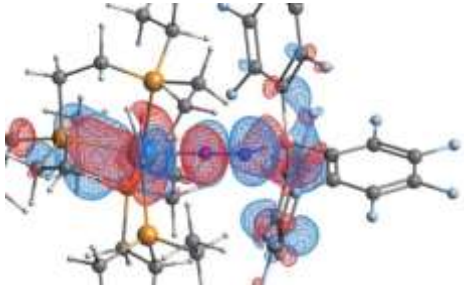
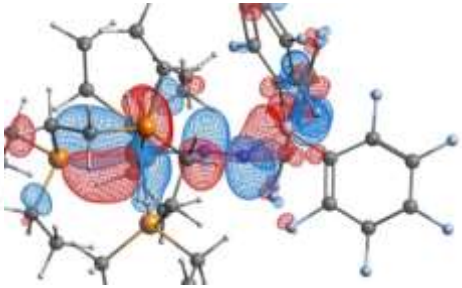
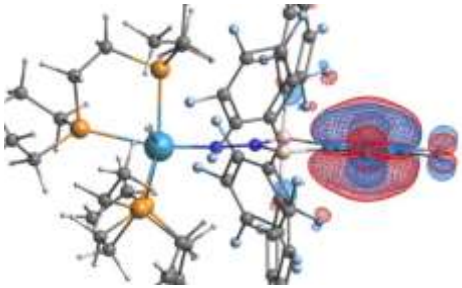
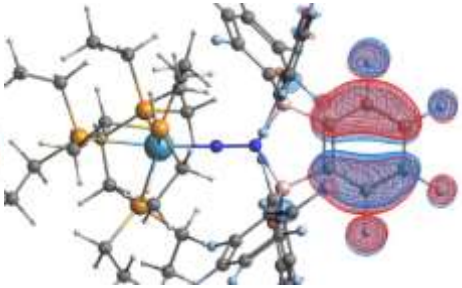
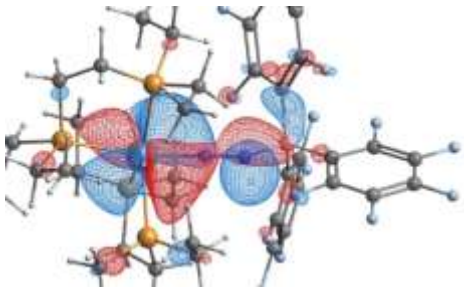
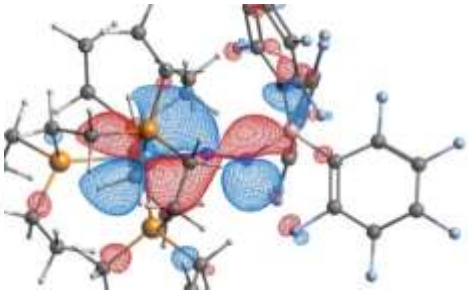


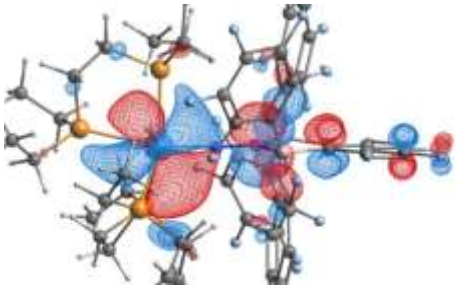
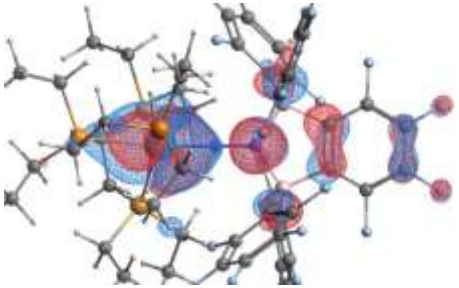
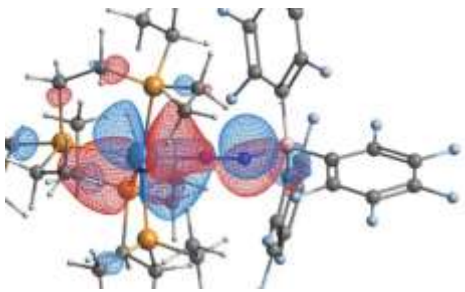
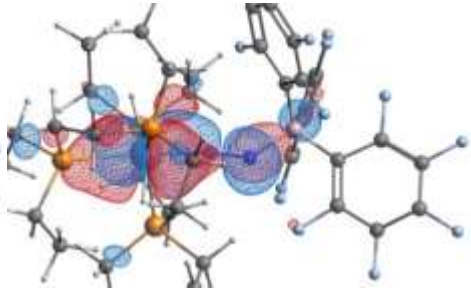
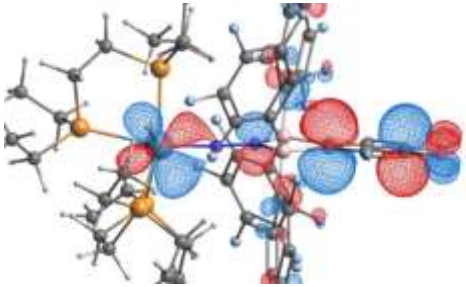
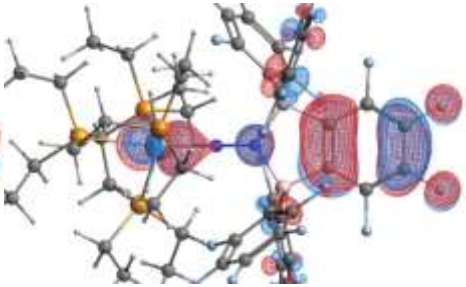
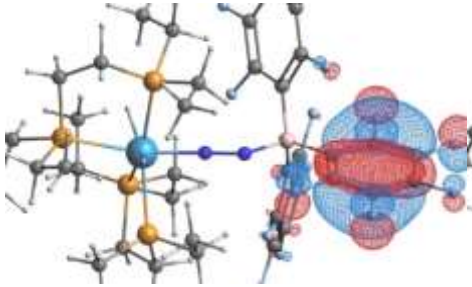
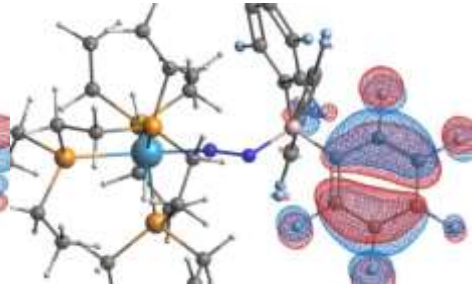
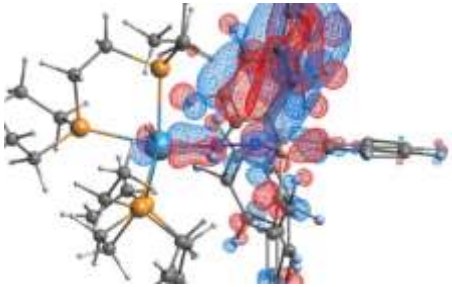
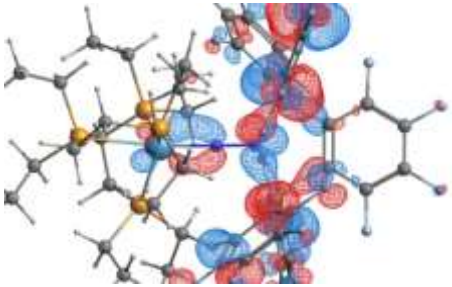
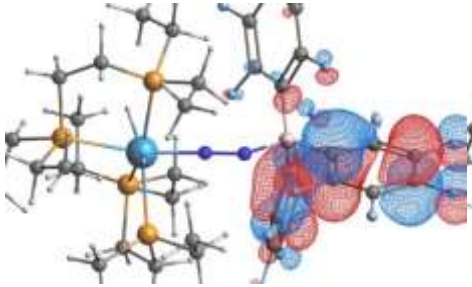
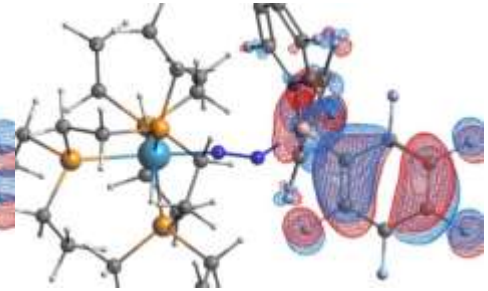
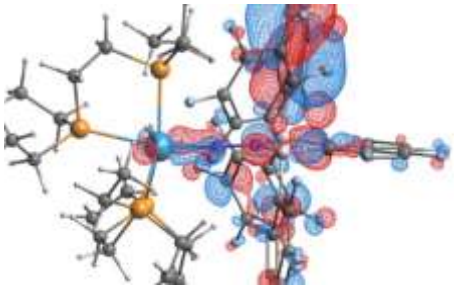
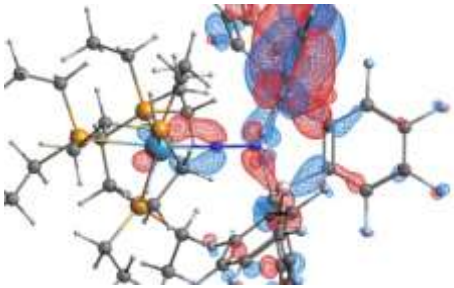
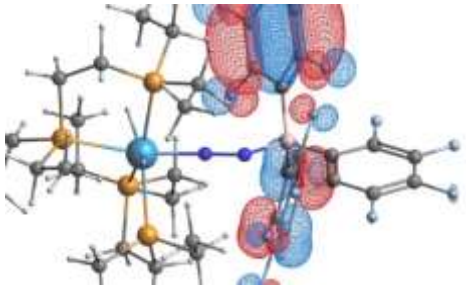
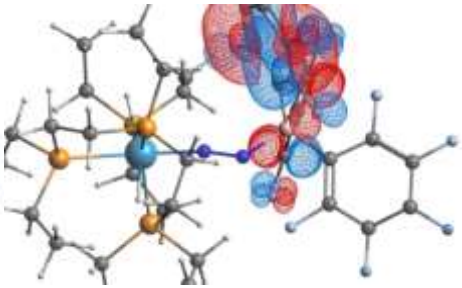
Figure S50. Optimized structure for **F,** hydrogen atoms except those bound to tungsten omitted for clarity.

C	2.930421	2.992758	-0.517042	C	-5.072401	-1.987932	3.222363	H	3.984078	-0.916434	4.409274
C	3.521928	1.766505	-0.195206	C	-5.635950	-1.732458	1.971299	H	2.770650	0.383244	2.710851
C	4.902795	1.709988	0.041966	C	-4.879950	-1.120476	0.976394	H	5.375963	0.769449	0.307737
C	5.675533	2.864460	-0.050775	C	-1.767452	-2.978946	-3.534563	H	6.743873	2.811493	0.137187
C	5.080613	4.083327	-0.375799	C	1.604340	-2.058980	-4.152653	H	5.685181	4.983083	-0.441416
C	3.708527	4.145825	-0.608476	C	1.822482	-3.497699	-1.420347	H	3.237247	5.092977	-0.853453
P	2.522719	0.210442	-0.165417	H	-2.584169	2.532437	1.520140	H	1.862841	3.058759	-0.691104
C	3.441342	-0.831741	1.048100	H	-3.806872	4.662173	1.376789	H	-0.981808	0.968499	1.416958
C	4.225890	-1.929320	0.678698	H	-5.398061	5.070484	-0.488702				
C	4.910498	-2.664770	1.647410	H	-5.765768	3.312190	-2.203305				
C	4.823660	-2.305894	2.989731	H	-4.566062	1.173599	-2.065791				
C	4.050954	-1.206196	3.364883	H	-1.968627	-0.720708	2.691576				
C	3.361677	-0.474714	2.402864	H	-3.312620	-1.806132	4.452048				
W	-0.036703	0.307704	0.137555	H	-5.664908	-2.464137	3.997888				
N	-0.059745	-1.141445	-1.785437	H	-6.668716	-2.003351	1.772629				
Si	1.545537	-1.862306	-2.285036	H	-5.346057	-0.901018	0.019539				
C	2.807293	-0.533448	-1.833717	H	-2.839852	-0.154165	-2.486771				
C	0.520195	1.623390	1.512519	H	-3.919989	-1.278863	-1.648468				
O	0.826034	2.399833	2.320607	H	-1.638159	-2.275878	-4.363417				
P	-2.571067	0.098390	-0.093163	H	-2.778606	-3.394948	-3.613475				
C	-2.912681	-0.852278	-1.643576	H	-1.070779	-3.810483	-3.679418				
Si	-1.576802	-2.170459	-1.849682	H	-0.803969	-4.138068	-0.501848				
C	-1.659633	-3.458998	-0.499099	H	-2.555415	-4.065059	-0.680271				
C	0.208496	-1.292584	1.380931	H	-1.755058	-3.032500	0.501139				
O	0.368089	-2.182971	2.100842	H	-0.234062	-0.433152	-2.504820				
C	-0.300795	1.850357	-1.159919	H	0.954213	-2.856188	-4.521505				
O	-0.475185	2.711611	-1.915117	H	2.628180	-2.308994	-4.454183				
C	-3.478001	1.699474	-0.267523	H	1.335725	-1.133330	-4.673915				
C	-3.278236	2.693998	0.699809	H	1.729980	-3.435794	-0.332945				
C	-3.969692	3.899424	0.621174	H	2.833634	-3.853482	-1.647342				
C	-4.863378	4.127514	-0.425406	H	1.132424	-4.264043	-1.786954				
C	-5.068797	3.142410	-1.387897	H	3.845255	-0.862952	-1.951295				
C	-4.382560	1.930484	-1.309479	H	2.669873	0.300358	-2.534417				
C	-3.544476	-0.767470	1.219021	H	4.319386	-2.220659	-0.361966				
C	-2.991964	-1.011226	2.479959	H	5.516119	-3.514924	1.347318				
C	-3.753707	-1.621031	3.477156	H	5.358823	-2.877558	3.742001				

5.5 Frontier Kohn-Sham Orbitals of 7 and 10

Table S7. Comparison of the frontier orbitals of **7** and **10**, rendered with Avogadro.[S20]

	7		**10**	
LUMO+1				
LUMO				
HOMO				

HOMO–1				
HOMO–2				
HOMO–3				
HOMO–4				

5.6 Coordinates of optimized geometries of 7 and 10 with dispersion (6-31G(d,p)-D3BJ)

*5.6.1 Compound **7***

C	-1.001058000	3.358179000	-4.303759000	H	3.019532000	3.451223000	0.906373000
C	-1.368699000	4.143055000	-3.218124000	H	4.954855000	2.326621000	-0.253721000
C	2.558598000	3.350059000	-3.518530000	H	1.435252000	-0.622585000	-3.436478000
C	-0.860666000	1.990960000	-4.121463000	H	1.144965000	-2.518285000	-5.017076000
C	-1.578994000	3.549196000	-1.976008000	H	2.870304000	-2.334035000	-4.689797000
C	1.904023000	2.334391000	-2.591098000	H	4.544261000	-1.500263000	-3.248287000
C	3.488050000	3.881350000	0.020541000	H	5.866312000	0.549417000	-0.465142000
C	-1.074080000	1.445327000	-2.861983000	H	7.620261000	1.668203000	0.842760000
C	-1.413581000	2.182542000	-1.734079000	H	6.073571000	2.137734000	1.550888000
C	4.159824000	2.808961000	-0.821839000	H	2.272828000	2.619813000	2.988518000
C	-4.403820000	1.709982000	-0.698098000	H	2.399398000	1.377341000	1.097715000
C	-5.639935000	1.128053000	-0.945949000	H	0.569367000	-1.910039000	-2.666104000
C	-0.026061000	4.102133000	2.069639000	H	5.046680000	-1.128436000	-1.604843000
C	4.134170000	0.544480000	-2.648526000	H	1.289165000	3.094353000	4.367893000
C	-0.326068000	3.230797000	1.033772000	H	1.941487000	-3.630903000	-3.914776000
C	-0.907717000	4.207294000	3.136116000	H	0.028340000	1.452558000	3.004404000
C	-1.481242000	2.460948000	0.963476000	H	6.744780000	-0.660462000	0.440104000
C	-2.079813000	3.462862000	3.121481000	H	4.271001000	1.209340000	2.945060000
C	-3.274558000	0.940366000	-0.469275000	H	2.617216000	1.963403000	4.601614000
C	-2.351486000	2.624033000	2.041835000	H	4.162503000	-3.936316000	-3.099555000
C	-5.742273000	-0.260968000	-0.978666000	H	7.070603000	0.916512000	2.341554000
C	1.906930000	-2.586462000	-4.234858000	H	5.208622000	-3.513119000	-1.741501000
C	1.540628000	-1.653170000	-3.090171000	H	0.414987000	0.734211000	4.565884000
C	4.269223000	-0.940992000	-2.349800000	H	2.165285000	-3.943126000	-1.529021000
C	-3.374594000	-0.457426000	-0.502353000	H	2.110503000	-1.771408000	0.838148000
C	-4.610715000	-1.034121000	-0.751609000	H	5.347251000	-0.083766000	3.500386000
C	6.739235000	1.288835000	1.369288000	H	4.352737000	-5.055525000	-1.751134000
C	6.067592000	0.193062000	0.546913000	H	3.182530000	-3.473128000	-0.206395000
C	1.818203000	2.253706000	3.912959000	H	5.167455000	-2.642060000	0.461090000
C	-1.922014000	-2.467493000	-2.445379000	H	3.102056000	-0.166506000	4.700234000
C	0.847926000	1.113386000	3.635918000	H	6.945201000	-1.985436000	2.212042000
C	-1.467104000	-2.342080000	-1.131165000	H	-0.129787000	-1.967121000	2.610508000
C	-1.516395000	-3.491887000	-3.300775000	H	3.995010000	-2.797030000	1.751621000
C	4.404860000	0.125730000	2.987362000	H	3.397104000	-1.622588000	3.759786000
C	4.265135000	-3.996811000	-2.013582000	H	5.750823000	-2.322124000	3.469933000
C	3.070435000	-3.389173000	-1.286873000	H	1.431891000	-2.656771000	2.928813000
C	-2.343270000	-1.856444000	1.378157000	H	-0.374840000	-1.277463000	5.021469000
C	-2.300150000	-1.120868000	2.556634000	H	6.311219000	-3.618318000	2.415876000
C	3.230709000	-0.543239000	3.681768000	H	1.264154000	-1.851588000	5.373427000
C	-0.581966000	-3.337380000	-0.722998000	H	-0.006174000	-2.992026000	4.923147000
C	-0.651591000	-4.472021000	-2.835007000	N	-1.007777000	0.066988000	-0.079016000
C	4.911424000	-2.275907000	1.460704000	N	0.228879000	-0.005273000	0.027311000
C	-2.804217000	-1.547536000	3.778324000	B	-1.779856000	1.480953000	-0.299993000
C	-2.925965000	-3.119465000	1.527013000	B	-2.013718000	-1.209821000	-0.101152000
C	-0.201443000	-4.406214000	-1.523540000	F	-0.737551000	3.916220000	-5.489006000
C	0.746068000	-1.864438000	3.249556000	F	-1.505496000	5.462913000	-3.373406000
C	6.041335000	-2.558293000	2.442674000	F	-1.924298000	4.391028000	-0.992413000
C	-3.376217000	-2.807622000	3.872438000	F	-0.420336000	1.218626000	-5.126383000
C	-3.430559000	-3.600015000	2.732646000	F	-4.334123000	3.056412000	-0.680704000
C	0.393507000	-1.993033000	4.724348000	F	-6.727500000	1.878244000	-1.160272000
H	1.830506000	3.682857000	-4.263713000	F	1.115157000	4.808922000	2.072729000
H	2.896894000	4.235605000	-2.974375000	F	0.577243000	3.187878000	0.030695000
H	3.415365000	2.937411000	-4.061602000	F	-0.608688000	4.987003000	4.179490000
H	2.705452000	4.406970000	-0.529170000	F	-0.816236000	0.128666000	-2.765861000
H	1.106381000	2.786330000	-2.005172000	F	-2.929714000	3.550196000	4.147324000
H	4.228218000	4.619522000	0.344588000	F	-6.927599000	-0.831624000	-1.226210000
H	1.445976000	1.526691000	-3.164645000	F	-3.503428000	1.951713000	2.114489000
H	4.623337000	3.240709000	-1.715696000	F	-2.785489000	-1.596863000	-2.971607000
H	3.670508000	0.683483000	-3.629381000	F	-1.946999000	-3.537144000	-4.564124000
H	5.110834000	1.036622000	-2.690964000	F	-4.754638000	-2.373723000	-0.796107000

F	-1.678930000	0.073881000	2.581431000
F	-2.696232000	-0.771510000	4.866606000
F	-0.236111000	-5.453974000	-3.639001000
F	-0.080439000	-3.336838000	0.528037000
F	-3.023642000	-3.967642000	0.493219000
F	0.619196000	-5.364219000	-1.057889000
F	-3.849021000	-3.255559000	5.036492000
F	-3.965004000	-4.822083000	2.803803000
P	3.033300000	1.456206000	-1.419171000
P	2.683704000	-1.602331000	-1.638540000
P	4.449432000	-0.483963000	1.233358000
P	1.623568000	-0.316353000	2.743659000
W	2.033069000	-0.132595000	0.313006000

*5.6.2 Compound **10***

W	-2.061879000	0.189679000	0.179400000
P	-2.254204000	-1.592453000	-1.555225000
P	-1.673648000	2.590973000	0.484699000
P	-4.445663000	0.974864000	0.294911000
P	-2.196637000	-1.861593000	1.554763000
F	6.634024000	-0.441785000	3.903308000
F	3.409038000	4.941115000	-0.474529000
F	7.132880000	-0.090256000	1.239775000
F	3.488210000	-2.709087000	-4.036136000
F	2.030475000	-0.257075000	3.119326000
F	4.056743000	-0.521811000	4.791006000
F	1.422519000	-4.827692000	-0.362016000
F	2.422318000	-4.948488000	-2.909680000
F	1.181273000	2.766114000	-4.017075000
F	5.094751000	0.169224000	-0.486816000
F	3.556487000	-0.418095000	-2.705555000
N	-0.204444000	0.057798000	0.376838000
F	3.418277000	2.691332000	0.928899000
F	1.114077000	0.521352000	-2.605562000
F	2.312397000	5.021369000	-2.974706000
F	1.485156000	-2.555275000	0.997398000
N	0.918447000	0.071805000	0.751200000
C	-3.530384000	-1.525071000	-2.905828000
C	-3.273721000	3.506205000	0.787635000
C	-0.695464000	-1.841529000	-2.526428000
C	-2.591293000	-3.261974000	-0.792880000
C	3.465470000	-0.034381000	1.212339000
C	2.461424000	-3.804592000	-2.223921000
C	1.978723000	-2.524807000	-0.257442000
C	-3.338036000	-0.350203000	-3.857288000
C	-4.428515000	2.835314000	0.051388000
C	5.623030000	-0.312134000	3.041409000
C	2.996975000	-2.657310000	-2.794541000
C	-0.651842000	-3.015955000	-3.494195000
C	2.999891000	-1.461581000	-2.079773000
C	3.262304000	-0.214988000	2.578076000
C	2.889482000	3.833391000	-1.012294000
C	1.953509000	-3.738255000	-0.934182000
C	-1.832216000	-3.368324000	0.522109000
C	-1.243751000	-1.041836000	4.089433000
C	-1.510600000	3.534442000	-2.218497000
C	-3.813632000	-3.563024000	3.237595000
C	-0.950216000	-1.969603000	2.918720000
C	-3.803926000	-2.300500000	2.384445000
C	1.766117000	2.728318000	-2.813722000
B	2.314132000	0.055122000	0.063327000
C	2.336710000	3.879138000	-2.285450000
C	-0.551192000	3.023144000	1.902791000
C	1.759622000	1.564643000	-2.056138000
C	-5.470389000	0.798526000	1.848046000
C	-1.193975000	2.969951000	3.281152000
C	2.353155000	1.445062000	-0.800551000
C	2.441406000	-1.330817000	-0.808636000
C	-0.854535000	3.579746000	-0.849172000
C	-4.825848000	1.304112000	3.131531000
C	-5.741370000	0.508657000	-0.961199000
C	5.873636000	-0.133747000	1.685361000
C	-6.312650000	-0.886745000	-0.725884000
C	4.309583000	-0.352250000	3.487855000
C	2.885744000	2.634137000	-0.301580000
C	4.800637000	-0.004282000	0.813728000
H	-3.494082000	-2.477369000	-3.446391000
H	-4.504794000	-1.476453000	-2.417647000
H	-3.447038000	3.491331000	1.865835000
H	-3.158873000	4.552242000	0.484631000
H	0.105530000	-1.902654000	-1.788880000
H	-0.538768000	-0.892744000	-3.041250000
H	-2.322530000	-4.060954000	-1.490049000
H	-3.673084000	-3.324758000	-0.625055000
H	-4.159210000	-0.296456000	-4.579009000
H	-2.406200000	-0.440256000	-4.422814000
H	-3.293874000	0.594652000	-3.307646000
H	-4.326639000	2.980984000	-1.029521000
H	-5.395317000	3.253038000	0.355645000
H	0.286885000	-2.999336000	-4.055790000
H	-0.694087000	-3.978051000	-2.975078000
H	-1.467097000	-2.987843000	-4.223752000
H	-0.751853000	-3.371596000	0.355311000
H	-2.078884000	-4.284630000	1.066678000
H	-0.443852000	-1.109170000	4.831993000
H	-2.188293000	-1.282425000	4.588577000
H	-1.292325000	-0.006558000	3.745532000
H	-0.905164000	4.074999000	-2.951060000
H	-1.615300000	2.501220000	-2.558883000
H	-2.505703000	3.991891000	-2.203688000
H	-4.798826000	-3.714916000	3.690511000
H	-3.084154000	-3.504560000	4.050074000
H	-3.585208000	-4.456196000	2.649105000
H	-0.882178000	-3.014934000	3.239331000
H	0.005047000	-1.698669000	2.465874000
H	-4.063822000	-1.424169000	2.984987000
H	-4.548498000	-2.355677000	1.582486000
H	0.262389000	2.292049000	1.830937000
H	-0.116769000	4.010230000	1.711629000
H	-5.692485000	-0.268134000	1.938639000
H	-6.424459000	1.308181000	1.663995000
H	-0.427719000	3.012663000	4.060585000
H	-1.754830000	2.041641000	3.415879000
H	-1.878572000	3.808053000	3.444508000
H	0.162054000	3.183772000	-0.891912000
H	-0.782755000	4.609551000	-0.478591000
H	-5.431366000	1.028768000	4.001088000
H	-3.824882000	0.883870000	3.260228000
H	-4.729339000	2.392824000	3.133979000
H	-5.250363000	0.577788000	-1.936079000
H	-6.539511000	1.260134000	-0.943210000
H	-6.878607000	-1.236944000	-1.594696000
H	-5.516053000	-1.612877000	-0.528593000

H	-6.988804000	-0.901819000	0.133089000	H	-2.199343000	0.928562000	-1.407519000
H	-2.288557000	0.632026000	1.857420000				

5.7 Visualization of pertinent pre-orthogonal Natural Localized Molecular Orbitals and Natural Bond Orbitals (pNLMOs and pNBOs)

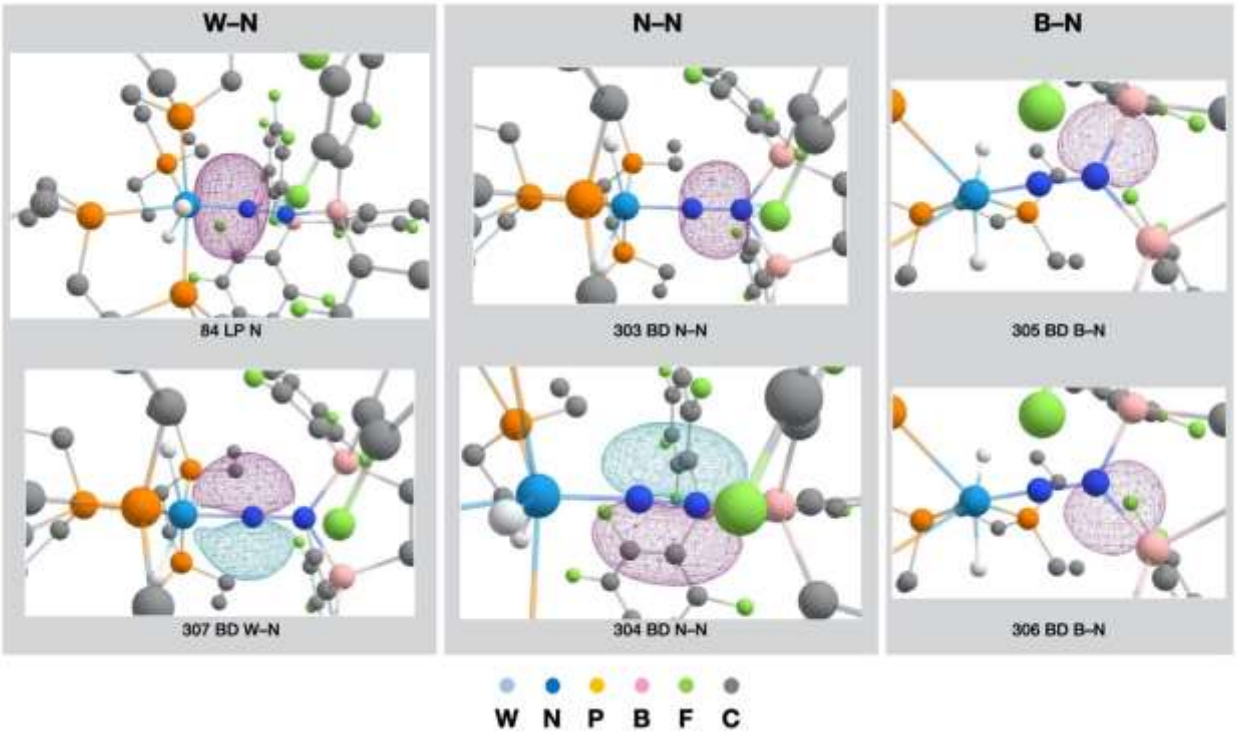


Figure S51. Depiction of key pNLMOs involved in the bonding of the N_2 unit of **7**.

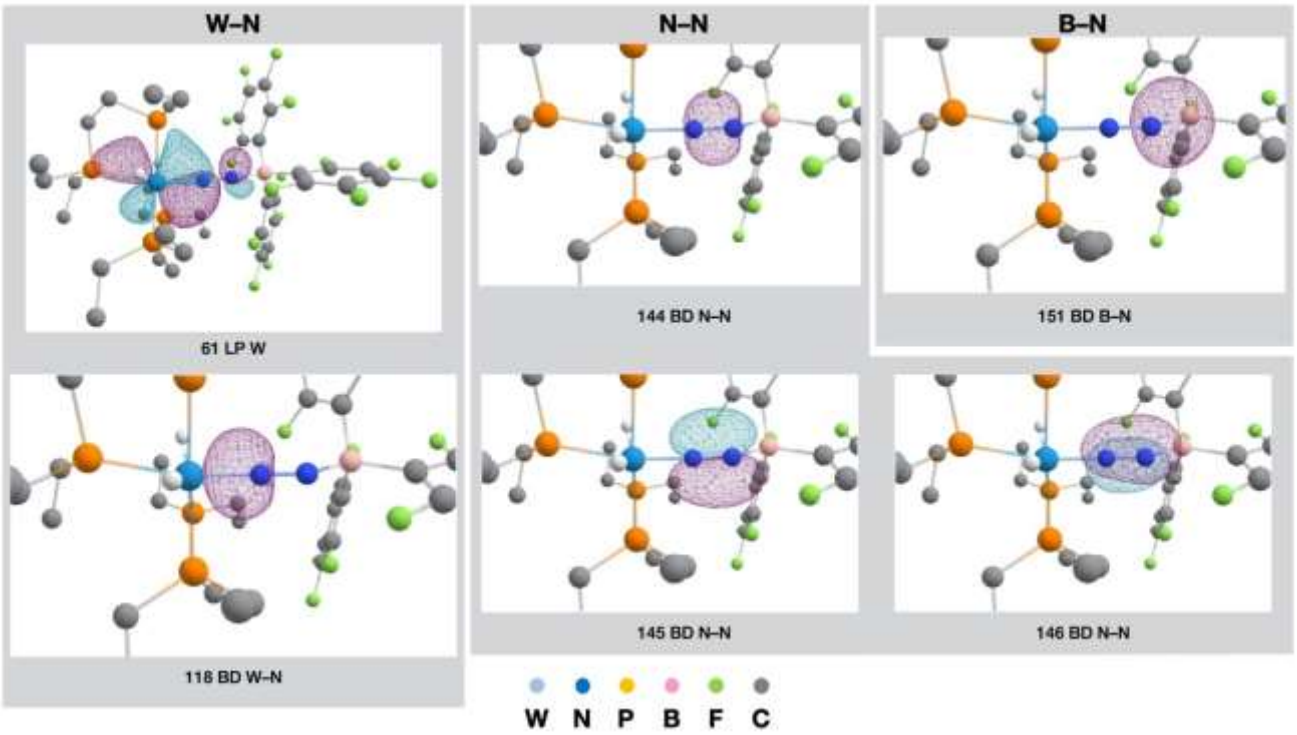


Figure S52. Depiction of key pNLMOs involved in the bonding of the N_2 unit of **10**.

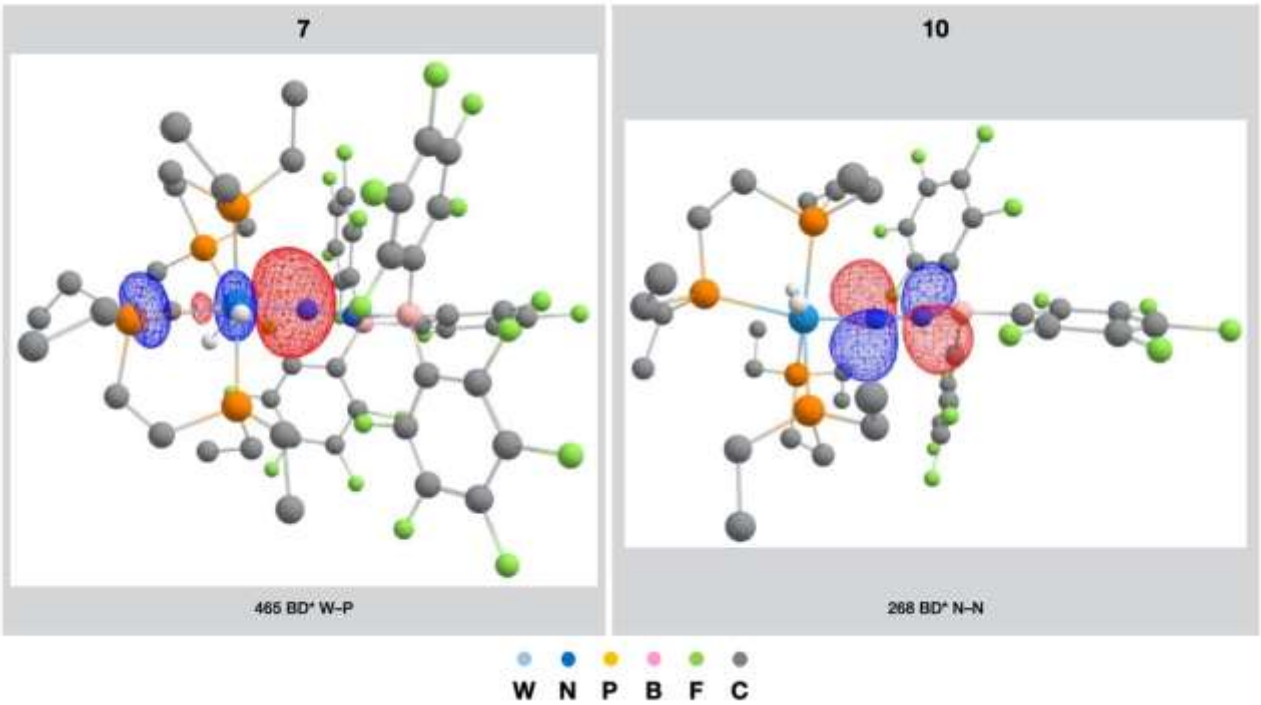


Figure S53. Depiction of key pNBOs for **7** and **10** involved in the stabilization of the lone pairs according to second-order perturbation theory.

Table S7. Key parameters issued by NBO analysis on **7** to explain the W–N–N–B bonding. LP = one-center valence lone pair, BD = two-center bond (Lewis NBO), BD* = two-center antibond (non-Lewis NBO), NHO = Natural Hybrid Orbital.

NBO Atom A(–Atom B)				NHO atom A						NHO atom B					
Number	**e^- occupancy**	**Type**	**Localization P–W–N_α–N_β–B**	**% of NBO on NHO (atom A)**	**%s**	**%p**	**%d**	**%f**	**NHO**	**% of NBO on NHO (atom B)**	**%s**	**%p**	**%d**	**%f**	**NHO**
84	1.61460	LP	N_α	100 (N_α)	55	45	0	n.a.	$sp^{0.81}$	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
303	1.98579	BD	N_α–N_β	50 (N_α)	44	56	0	n.a.	$sp^{1.25}$	50 (N_β)	29	71	0	n.a.	$sp^{2.42}$
304	1.96622	BD	N_α–N_β	41 (N_α)	0	100	0	n.a.	p	59 (N_β)	0	100	0	n.a.	p
305	1.91295	BD	N_β–B	77 (N_β)	35	65	0	n.a.	$sp^{1.85}$	23 (B)	20	80	0	n.a.	$sp^{3.98}$
306	1.91926	BD	N_β–B'	77 (N_β)	36	64	0	n.a.	$sp^{1.80}$	23 (B')	21	79	0	n.a.	$sp^{3.87}$
307	1.94215	BD	W–N_α	39 (W)	2	0	98	0	d	61 (N_α)	0	100	0	n.a.	p
465	0.44703	BD*	P–W	25 (P)	39	60	0	n.a.	$sp^{1.54}$	75	24	0	76	0	$sd^{3.16}$

Table S8. Key parameters issued by NBO analysis on **10** to explain the W–N–N–B bonding. LP = one-center valence lone pair, BD = two-center bond (Lewis NBO), BD* = two-center antibond (non-Lewis NBO), NHO = Natural Hybrid Orbital.

NBO Atom A(–Atom B)				NHO atom A						NHO atom B					
Number	**e^- occupancy**	**Type**	**Localization P–W–N_α–N_β–B**	**% of NBO on NHO (atom A)**	**%s**	**%p**	**%d**	**%f**	**NHO**	**% of NBO on NHO (atom B)**	**%s**	**%p**	**%d**	**%f**	**NHO**
61	1.40277	LP	W	100 (W)	1	0	99	0	d	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
118	1.93903	BD	W–N_α	22 (W)	28	0	72	0	$sd^{2.55}$	78 (N_α)	59	41	0	n.a.	$sp^{0.69}$
144	1.96622	BD	N_α–N_β	51 (N_α)	39	61	0	n.a.	$sp^{1.54}$	49 (N_β)	37	63	0	n.a.	$sp^{1.70}$
145	1.97116	BD	N_α–N_β	44 (N_α)	0	100	0	n.a.	p	56 (N_β)	2	98	0	n.a.	p
146	1.96743	BD	N_α–N_β	40 (N_α)	1	99	0	n.a.	p	60 (N_β)	3	97	0	n.a.	p
151	1.97095	BD	N_β–B	76 (N_β)	58	42	0	n.a.	$sp^{0.72}$	24 (B)	21	79	0	n.a.	$sp^{3.79}$
268	0.52117	BD*	N_α–N_β	56 (N_α)	0	100	0	n.a.	p	44	2	98	0	n.a.	p

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