Electronic Supplementary Information

Insertion of CO_2 into the Carbon-Boron Bond of a Boronic Ester Ligand

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1. General procedures. $RuHCl(CO)(PPh_3)_3$,[1] diazafluorene,[2] $Mes_2nacnacH$[3] were prepared from literature methods. All operations were performed using Schlenk techniques under dinitrogen or in a dinitrogen-filled glovebox. All glassware was either flame-dried or dried overnight in a 180 °C oven prior to use except for J. Young NMR tubes which were dried overnight in a 60 °C oven. Grade 4.0 carbon dioxide was purchased from Linde. THF, Et_2O, and toluene were distilled from Na/benzophenone under dinitrogen. Pentane, hexanes, C_6D_6, and toluene-d_8 were distilled from sodium under dinitrogen. C_6D_5Br was degassed using three freeze-pump-thaw cycles and dried over 3 Å molecular sieves. All solvents were then stored over 3 Å molecular sieves prior to use. HBpin and HBcat were purchased from Aldrich and used as received unless otherwise stated. IR spectra were collected on a Perkin-Elmer Spectrum One FT-IR spectrometer. ^1H, ^{31}P, ^{13}C, and ^{11}B NMR spectra were recorded on a Varian 400 MHz, Agilent DD2 500 MHz, or Agilent DD2 600 MHz spectrometer. All chemical shifts are reported in ppm relative the residual protio-solvent peaks (for C_6D_5Br these are the *meta-H* at 7.28 ppm and the *ipso-C* at 122.4 ppm), ^{31}P NMR signals are referenced externally using 85% H_3PO_4, and ^{11}B NMR signals are referenced externally using $BF_3(OEt_2)$. Elemental analyses were performed by ANALEST at the University of Toronto.

2. Synthesis of Compounds 1a–3b.

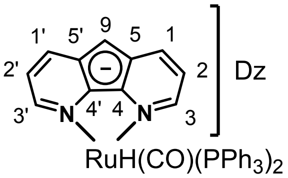

Chart S1. Labeling scheme for NMR assignments of Ru compounds.

Synthesis of 1a: Diazafluorene (60 mg, 0.36 mmol) was added to a suspension of NaH (25 mg, 1.0 mmol) in THF (5 mL). The mixture was stirred for 90 min after which it was filtered and slowly added to a suspension of $RuHCl(CO)(PPh_3)_3$ (352 mg, 0.37 mmol) in THF (30 mL) over a period of ca. 20 min. The purple mixture was stirred at room temperature for 12 h and the solvent was removed under reduced pressure. The residue was extracted with toluene (50 mL), filtered through Celite and volatiles were removed in *vacuo*. THF (15 mL) was added to dissolve the product and pentane (50 mL) was layered on top. After cooling to –25 °C; the purple precipitate that separated was collected on a fritted funnel and washed with Et_2O (3 x 2 mL). The powder on the frit was then dissolved in THF, filtered, and the THF was removed. The residue was suspended in pentane (15 mL) and collected on a fritted funnel, where it was washed with pentane (10 mL) and dried *in vacuo*. (174 mg, 0.212 mmol, 59%). ^{1}H NMR (500 MHz, Benzene-d_6) δ 7.96 (d, J = 4.6 Hz, 1H, Dz-$C_{(3)}H$), 7.73 (d, J = 8.0 Hz, 1H, Dz-$C_{(1)}H$), 7.62 (d, J = 8.1 Hz, 1H, Dz-$C_{(1')}H$), 7.41–7.32 (m, 12H, PPh$_3$-*H*), 7.03 (dd, J = 4.7, 1.0 Hz, 1H, Dz-$C_{(3')}H$), 6.91–6.80 (m, 18H, PPh$_3$-*H*), 6.69 (dd, J = 8.2, 4.6 Hz, 1H, Dz-$C_{(2)}H$), 6.47 (s, 1H, Dz-$C_{(9)}H$), 6.20 (dd, J = 8.1, 4.7 Hz, 1H, Dz-$C_{(2')}H$), –11.54 (t, J = 19.7 Hz, 1H, Ru-*H*).^{13}C NMR (126 MHz, Benzene-d_6) δ 206.65 (Ru-*C*O, observed only via HMBC cross peak with Ru-*H*) 140.28 (Dz-$C_{(4')}$), 140.10 (Dz-$C_{(4)}$), 136.22 (Dz-$C_{(3)}H$), 136.09 (Dz-$C_{(3')}H$) 133.77 (t, J = 5.9 Hz, PPh$_3$), 133.62 (t, J = 21.3 Hz, PPh$_3$), 129.47 (PPh$_3$) 127.91 (PPh$_3$), 127.47 (Dz-$C_{(5')}$), 127.09 (Dz-$C_{(5)}$), 125.14 (Dz-$C_{(1)}H$), 124.86 (Dz-$C_{(1')}H$) , 117.58 (Dz-$C_{(2')}H$), 117.50 (Dz-$C_{(2)}H$), 81.71 (Dz-$C_{(9)}H$). ^{31}P NMR (202 MHz, Benzene-d_6) δ 48.56. Anal. Calcd for $C_{48}H_{38}N_2OP_2Ru$: C, 70.15; H, 4.66; N, 3.41. Found: C, 70.03; H, 4.68; N, 3.27. IR (nujol mull): ν(CO) 1918 cm^{-1}.

Synthesis of 2a: To **1a** (100 mg, 0.12 mmol) dissolved/suspended in toluene (4 mL) was added a solution of pinacolborane (140 mg, 1.1 mmol) dissolved in toluene (4 mL), The resulting purple mixture was heated to 100 °C in a bomb sealed with a Teflon stopcock for 24 h, causing a colour change to pink. Volatiles were removed under reduced pressure. The residue was dissolved in toluene and the solution was concentrated until precipitate began to form. Pentane (5 mL) was layered on top and the mixture cooled to –25 °C for two days. The precipitate was collected on a frit and washed minimally with cold toluene and thoroughly with pentane. After drying under vacuum a pink powder was obtained (72 mg, 0.076 mmol, 63%). Single crystals for X-Ray analysis were grown by diluting a C_6D_6 solution with hexanes and cooling to –25 °C. The analytical sample was recrystallized an additional time. ^{1}H NMR (500 MHz, Benzene-d_6) δ 8.56 (d, J = 7.9 Hz, 1H, Dz-$C_{(1)}H$), 8.45 (d, J = 8.0 Hz, 1H, Dz-$C_{(1')}H$), 7.91 (d, J = 4.7 Hz, 1H, Dz-$C_{(3)}H$), 7.36–7.31 (m, 12H, PPh$_3$), 6.92 (dd, J = 4.9, 1.0 Hz, 1H, Dz-$C_{(3')}H$), 6.86 (t, J = 7.2 Hz, 6H, PPh$_3$), 6.81 (t, J = 7.2 Hz, 12H, PPh$_3$), 6.76 (dd, J = 8.1, 4.7 Hz, 1H, Dz-$C_{(2)}H$), 6.26 (dd, J = 8.1, 4.9 Hz, 1H, Dz-$C_{(2')}H$), 1.36 (s, 12H, pin-CH_3), –11.68 (t, J = 19.8 Hz, 1H, Ru-*H*). ^{13}C NMR (126 MHz, Benzene-d_6) δ 206.31 (Ru-*C*O, observed only via HMBC cross peak with Ru-*H*) 144.95 (Dz-$C_{(4')}$), 144.69 (Dz-$C_{(4)}$), 138.26 (Dz-$C_{(3)}H$), 138.14 (Dz-$C_{(3')}H$), 135.25 (Dz-$C_{(5')}$) , 134.73 (Dz-$C_{(5)}$) ,133.71 (t, J = 5.9 Hz, PPh$_3$), 133.54 (t, J = 21.3 Hz, PPh$_3$), 129.51 (PPh$_3$), 128.46 (Dz-$C_{(1)}H$), 128.27 (overlapped with solvent signal, Dz-$C_{(1')}H$), 127.97 (t, J = 4.7 Hz, PPh$_3$), 119.09 (Dz-$C_{(2')}H$), 118.89 (Dz-$C_{(2)}H$), 81.33(pin*C*-O), 25.55 (pinCH_3). We didn't observe a signal due to Dz-$C_{(9)}$ due to broadening caused by the bound quadrupolar ^{11}B nucleus.[4] ^{31}P NMR (202 MHz, Benzene-d_6) δ 48.47. ^{11}B NMR (128 MHz, Benzene-d_6, 25 °C) δ 31.30. Anal. Calcd for $C_{54}H_{49}N_2O_3BP_2 \cdot 0.5(C_7H_8)$: Note: the ratio of **2a**

to toluene was determined by integration of the ^{1}H NMR spectrum C, 69.49; H, 5.38; N, 2.82. Found: C, 69.63; H, 5.29; N, 2.79. IR (nujol mull): ν(CO) 1936 cm^{-1}.

Synthesis of 3a: 2a (60 mg, 0.060 mmol) was dissolved in toluene (6 mL) and Et_2O (6 mL). The solution was transferred to a Schlenk flask capped with a rubber septum. CO_2 gas (4.5 mL, 0.18 mmol) was syringed into the flask above the solution. The flask was sealed with tape and left in the glovebox freezer (–25 °C) for 16h, which brought about a colour change from pink to orange. Removal of volatiles yielded a brown oil which solidified upon standing. Pentane (3 mL) was added and the mixture was triturated. The pentane was decanted off and the orange solid was washed again with pentane. Drying *in vacuo* yielded **3a** (40 mg, 0.040 mmol, 64%). Single crystals were grown by layering hexanes over a toluene/Et_2O solution. ^{1}H NMR (600 MHz, Benzene-d_6) δ 8.61 (d, J = 7.9 Hz, 1H, Dz-$C_{(1)}H$), 8.51 (d, J = 8.0 Hz, 1H, Dz-$C_{(1')}H$), 7.91 (d, J = 4.8 Hz, 1H, Dz-$C_{(3)}H$), 7.33 – 7.26 (m, 12H, PPh_3), 6.96 (d, J = 4.9 Hz, 1H, Dz-$C_{(3')}H$), 6.85 (t, J = 7.2 Hz, 6H, PPh_3), 6.79 (t, J = 7.5 Hz, 12H, PPh_3), 6.67 (dd, J = 8.1, 4.8 Hz, 1H, Dz-$C_{(2)}H$), 6.17 (dd, J = 8.0, 5.0 Hz, 1H, Dz-$C_{(2')}H$), 1.19 (s, 12H, pinCH_3), –11.79 (t, J = 19.3 Hz, 1H, Ru-H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 205.82 (Ru-CO), 162.29 (C=O), 145.69 (Dz-$C_{(4')}$), 145.37 (Dz-$C_{(4)}$), 141.19 (overlapped Dz-$C_{(3)}H$ and $C_{(3')}H$) ,133.54 (t, J = 6.0 Hz, PPh_3), 132.78 (t, J = 21.6 Hz, PPh_3), 131.21 (Dz-$C_{(5')}$), 130.63 (Dz-$C_{(5)}H$), 129.95 (PPh_3), 128.20 (t, J = 4.7 Hz, PPh_3), 127.71 (Dz-$C_{(1)}H$), 127.54 (Dz-$C_{(1')}H$), 121.66 (Dz-$C_{(2')}H$), 121.32(Dz-$C_{(2)}H$), 88.00 (Dz-$C_{(9)}$), 83.40 (pin-CO), 24.91 (pin-CH_3) . ^{31}P NMR (243 MHz, Benzene-d_6) δ 48.19. ^{11}B NMR (128 MHz, Benzene-d_6) δ 23.06. Anal. Calcd for $C_{55}H_{49}BN_2O_5P_2Ru$: C, 66.60; H, 4.98; N, 2.82. Found: C, 66.21; H, 5.09; N, 2.85. IR (nujol mull): ν(CO) 1942 cm^{-1}, 1647 cm^{-1}.

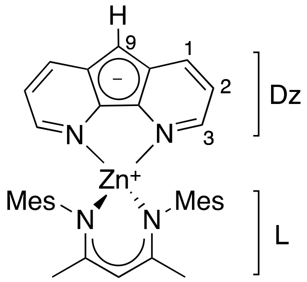

Chart S2. Labeling scheme for NMR assignments of Zn compounds.

Synthesis of EtZn(Mes$_2$nacnac): A solution of $ZnEt_2$ (1.0 M in hexanes, 0.36 mL, 0.36 mmol) was dissolved in toluene (1 mL) and added dropwise to a stirring solution of Mes$_2$nacnacH (0.0986 g, 0.295 mmol) in toluene (1.5 mL) over 1 minute. The solution was allowed to stir for at least 3 hours, until the reaction had reached completion as determined by ^{1}H NMR spectroscopy, after which the solvent was removed *in vacuo* to yield EtZn(Mes$_2$nacnac) as an off-white solid in quantitative yield (0.129 g). The crude product was used without further purification, however the compound can be purified by recrystallization from hexanes in the freezer if desired. ^{1}H NMR (400 MHz, Benzene-d_6, 25 °C) δ 6.82 (s, 4H, *m*-Mes *CH*), 4.98 (s, 1H, L-*CH*), 2.15 (s, 6H, *p*-Mes *CH*$_3$), 2.14 (s, 12H, *o*-Mes *CH*$_3$), 1.64 (s, 6H, L-*CH*$_3$), 1.03 (t, *J* = 8.1 Hz, 3H, Zn-CH$_2$*CH*$_3$), 0.30 (q, *J* = 8.1 Hz, 2H, Zn-*CH*$_2$CH$_3$). ^{13}C{^{1}H} NMR (101 MHz, Benzene-d_6, 25 °C) δ 167.00 (L-*C*), 145.74 (*i*-Mes *C*), 133.78 (*p*-Mes *C*), 130.87 (*o*-Mes *C*), 129.45 (*m*-Mes *CH*), 95.67 (L-*CH*), 22.53 (L-C*CH*$_3$), 20.98 (*p*-Mes *CH*$_3$), 18.71 (*o*-Mes *CH*$_3$), 12.19 (Zn-CH$_2$*CH*$_3$), -2.83 (Zn-*CH*$_2$CH$_3$). Anal. Calcd for $C_{25}H_{34}N_2Zn$: C, 70.17; H, 8.01; N, 6.55. Found: C, 70.16; H, 7.74; N, 6.68.

Synthesis of 1b: A solution of EtZn(Mes$_2$nacnac) (0.2103 g, 0.4914 mmol) in toluene (4 mL) was added dropwise to a stirring solution of 4,5-diazafluorene (0.0773 g, 0.460 mmol) in toluene (2 mL) over 2 minutes. The solution was stirred at room temperature for 3 days after which the solvent was removed *in vacuo* to obtain the crude complex **1b** as a purple solid. The crude solid was dissolved in a minimum amount of hexanes (2-4 mL) and the solution was cooled in the freezer (-35 °C) overnight causing purple crystals to form. The crystalline product was collected by vacuum filtration and washed with hexanes, then dried under vacuum yielding pure complex **1b** as a dark purple crystalline solid (0.242 g, 0.428 mmol, 87% yield). Single crystals suitable for X-ray crystallography were obtained by slow evaporation at -35 °C of a saturated solution of the complex in hexanes with toluene added (10:1 hexanes to toluene). ^{1}H NMR (500 MHz, Benzene-d_6, 25 °C) δ 7.88 (d, *J* = 4.6 Hz, 2H, Dz-$C_{(3)}H$), 7.82 (d, *J* = 8.3 Hz, 2H, Dz-$C_{(1)}H$), 6.90 (dd, *J* = 8.3, 4.6 Hz, Dz-$C_{(2)}H$), 6.40 (s, 4H, *m*-Mes *CH*), 6.27 (s, 1H, Dz-$C_{(9)}H$), 5.00 (s, 1H, L-*CH*), 2.22 (s, 12H, *o*-Mes *CH*$_3$), 1.77 (s, 6H, *p*-Mes *CH*$_3$), 1.70 (s, 6H, L-*CH*$_3$). ^{13}C{^{1}H} NMR (126 MHz, Benzene-d_6, 25 °C) δ 168.81 (L-*C)*, 144.22 (*i*-Mes *C*), 135.48 (Dz-N-*C*), 133.77 (*p*-Mes *C*), 131.07 (Dz-$C_{(3)}H$), 130.80 (*o*-Mes *C*), 129.30 (*m*-Mes *CH*), 128.95 (Dz-$\mathrm{C}_{(9)}$-*C*), 128.39 (Dz-$C_{(1)}H$), 118.13 (Dz-$C_{(2)}H$), 94.51 (L-*CH*), 81.52 (Dz-$C_{(9)}H$), 23.02 (L-*CH*$_3$), 20.63 (*p*-Mes *CH*$_3$), 18.46 (*o*-Mes *CH*$_3$). Anal. Calcd for $C_{34}H_{36}N_4Zn$: C, 72.14; H, 6.41; N, 9.90. Found: C, 72.36; H, 6.88; N, 9.98.

Synthesis of 2b: Complex **1b** (0.290 g, 0.512 mmol) and pinacolborane (0.290 g, 2.27 mmol) were transferred to a Teflon-sealed bomb with THF (5 mL). The sealed bomb was heated to 100 °C for 36 h, which brought about a subtle colour change from dark purple to pink. Volatiles were removed *in vacuo*; pentane (5 mL) and toluene (0.5 mL) were added, the mixture was filtered through Celite and cooled to -25 °C for 6 h. The pink crystals that formed were collected on a frit, and were washed with several drops each of cold toluene and cold ether, after which they were washed thoroughly with cold pentane and dried under vacuum, which yielded analytically pure **2b**·(toluene)$_{1/2}$(pentane)$_{1/3}$ (0.156 g, 0.205 mmol, 46% yield). Anal. Calcd for $C_{40}H_{47}N_4O_2BZn\cdot 1/2(C_7H_8)\cdot 1/3(C_5H_{12})$ C, 71.18; H, 7.27; N, 7.35. Found C, 71.09, H, 7.60, N, 7.33 (note that the ratio of **2b** to toluene and pentane was determined by integration of the ^{1}H NMR spectrum of the sample used for EA). Concentration and recrystallization of the filtrate yielded a second crop of crystals (0.121 g, 0.159 mmol, total yield 71%). ^{1}H NMR (600 MHz, Benzene-*d*$_6$, 25 °C) δ 8.68 (dd, *J* = 8.4, 1.2, 2H, Dz-*C$_{(1)}$H*), 7.86 (dd, *J* = 4.8, 1.2, 2H, Dz-*C$_{(3)}$H*), 6.93 (dd, *J* = 8.4, 4.8, 2H, Dz-*C$_{(2)}$H*), 6.44 (s, 4H, *m*-Mes *CH*), 4.98 (s, 1H, L-*CH*), 2.17 (s, 12H, *o*-Mes *CH$_3$*), 1.80 (s, 6H, *p*-Mes *CH$_3$*), 1.68 (s, 6H, L-*CH$_3$*), 1.26 (s, 12H, Pin-*CH$_3$*). ^{1}H NMR (500 MHz, Bromobenzene-*d*$_5$, 25 °C) δ 8.42 (d, *J* = 8.5, 2H, Dz-*C$_{(1)}$H*), 7.94 (d, *J* = 4.5, 2H, Dz-*C$_{(3)}$H*), 6.99 (dd, *J* = 8.5, 4.5, 2H, Dz-*C$_{(2)}$H*), 6.40 (s, 4H, *m*-Mes *CH*), 4.98 (s, 1H, L-*CH*), 2.15 (s, 12H, *o*-Mes *CH$_3$*), 1.75 (s, 6H, *p*-Mes *CH$_3$*), 1.68 (s, 6H, L-*CH$_3$*), 1.21 (s, 12H, Pin-*CH$_3$*). ^{13}C{^{1}H} NMR (151 MHz, Benzene-*d*$_6$, 25 °C) δ 168.81 (L-*C*), 144.14 (*i*-Mes *C*), 139.54 (Dz-N-*C*), 136.67 (Dz-C$_{(9)}$*C*), 133.85 (*p*-Mes *C*), 133.00 (Dz-*C$_{(3)}$H*), 131.90 (Dz-*C$_{(1)}$H*), 130.81 (*o*-Mes *C*), 129.29 (*m*-Mes *CH*), 119.49 (Dz-*C$_{(2)}$H*), 94.53 (L-*CH*), 81.44 (Pin-*C*), 25.35 (Pin-*CH$_3$*), 22.99 (L-*CH$_3$*), 20.65 (*p*-Mes *CH$_3$*), 18.40 (*o*-Mes *CH$_3$*). We didn't observe a signal due to Dz-*C$_{(9)}$* due to broadening caused by the bound quadrupolar ^{11}B nucleus.[4] ^{13}C{^{1}H} NMR (126 MHz, Bromobenzene-*d*$_5$, 25 °C) δ 168.58 (L-*C*), 143.87 (*i*-Mes *C*), 139.04 (Dz-N-*C*), 136.03 (Dz-C$_{(9)}$*C*), 133.45 (*p*-Mes *C*), 133.02 (Dz-*C$_{(3)}$H*), 131.42 (Dz-*C$_{(1)}$H*), 130.58 (*o*-Mes *C*), 128.98 (*m*-Mes *CH*), 119.29 (Dz-*C$_{(2)}$H*), 94.46 (L-*CH*), 81.16 (Pin-*C*), 25.28 (Pin-*CH$_3$*), 23.08 (L-*CH$_3$*), 20.67 (*p*-Mes *CH$_3$*), 18.39 (*o*-Mes *CH$_3$*). ^{11}B NMR (128 MHz, Benzene-*d*$_6$, 25 °C) δ 31.40.

Synthesis of 3b: A solution of Complex **2b** (15 mg, 0.022 mmol) in bromobenzene (3 mL) in a 50 mL Schlenk bomb was frozen in liquid nitrogen and the headspace was evacuated. After thawing, the solution was allowed to warm to room temperature at which point the bomb was opened and 1 atm CO_2 gas was added. The bomb was then sealed and allowed to sit at room temperature for 4 hours causing a colour change from dark pink to orange. Volatiles were removed *in vacuo* and the orange residue was washed with cold pentane (2 mL). Drying under vacuum yielded an orange powder (12 mg, 75%), crude **3b**. X-ray quality crystals of **3b** were grown from a toluene/pentane solution stored at -25 °C. IR (nujol mull): ν(CO) 1626 cm^{-1}. ^{1}H NMR (400 MHz, Bromobenzene-*d*$_5$, 25 °C) δ 8.45 (d, *J* = 8.1, 2H, Dz-*C$_{(1)}$H*), 7.95 (d, *J* = 4.8, 2H, Dz-*C$_{(3)}$H*), 7.01 (dd, *J* = 8.4, 4.6, 2H, Dz-*C$_{(2)}$H*), 6.44

(s, 4H, *m*-Mes *CH*), 4.98 (s, 1H, L-*CH*), 2.11 (s, 12H, *o*-Mes CH_3), 1.78 (s, 6H, *p*-Mes CH_3), 1.67 (s, 6H, L-CH_3), 1.16 (s, 12H, Pin-CH_3). $^{13}C\{^1H\}$ NMR (101 MHz, Bromobenzene-d_5, 25 °C) δ 168.90 (L-*C*), 161.52 ($C_{(9)}$-CO_2-B), 143.67 (*i*-Mes *C*), 139.66 (Dz-N-*C*), 135.33 (Dz-$C_{(3)}H$), 133.83 (*p*-Mes *C*), 131.85 (Dz-$C_{(9)}C$), 131.18 (Dz-$C_{(1)}H$), 130.54 (*o*-Mes *C*), 129.10 (*m*-Mes *CH*), 121.58 (Dz-$C_{(2)}H$), 94.61 (L-*CH*), 87.68 (Dz-$C_{(9)}$), 82.77 (Pin-*C*), 24.80 (Pin-CH_3), 23.08 (L-CH_3), 20.66 (*p*-Mes CH_3), 18.36 (*o*-Mes CH_3) ^{11}B NMR (193 MHz, C_6D_5Br, 25 °C) δ 22.53.

We noticed that **3a** is much more robust with respect to hydrolysis by trace moisture in bromobenzene compared to all other solvents. Therefore, to obtain the analytically pure sample of **3a**, a modified work-up method was used: **2b** (45.1 mg, 0.0652 mmol) was dissolved in bromobenzene (3 mL) in a 50 mL bomb sealed with a Teflon screw cap. The solution was frozen in liquid nitrogen and the headspace was evacuated. The frozen solution was thawed and allowed to warm to room temperature at which time 1 atm CO_2 was admitted. The pink solution gradually turned orange and was kept under CO_2 for 3 h. The orange solution was filtered through Celite and volatiles were removed *in vacuo* leaving **3b·PhBr** as a waxy orange solid (39.1 mg, 0.0438 mmol, 67 %). Anal. Calcd for $C_{41}H_{47}N_4O_4BZn\cdot(C_6H_5Br)$ C, 63.21; H, 5.87; N, 6.27. Found C, 63.21; H, 5.74; N, 6.02. In order to establish the residual solvent content in the sample to corroborate with the elemental analysis (EA) results, a portion of the solid was dissolved in C_6D_6 for ^1H NMR experiment and the remaining portion was analyzed with elemental analysis. Although **3b** is highly prone to hydrolysis in solvents other than bromobenzene, in order to establish the PhBr content in the EA sample, we cannot use PhBr-d_5 as the NMR solvent. Therefore, C_6D_6 was used as the NMR solvent ONLY to establish the **3b** to PhBr ratio. Consequently, a small amount of the hydrolysis products of **3b** can also be seen in the ^1H NMR spectrum (see Figure S28). These hydrolysis products include pinBOBpin and [Zn(Mes_2nacnac)(L–COOH)].

3. Regeneration of 2a: **3a** (3.4 mg, 3.4 x 10^{-3} mmol, 1 eq) and pinacolborane (8.8 mg, 6.9 x 10^{-2} mmol, 20 eq) were dissolved in C_6D_6 in a thick-walled J. Young NMR tube which was heated in an oil bath preheated to 110 °C. After 8 h of heating, the ratio of **2a** : **3a** was 0.9 : 1.

4. Catalytic experiments: Into a vial was weighed the desired catalyst (0.0065 mmol), borane (0.65 mmol) and hexamethylbenzene (2-10 mg). The reagents were transferred to a Teflon sealed 50 mL glass bomb using bromobenzene-d_5 (0.6 mL). The solution was degassed through one freeze-pump-thaw cycle using liquid nitrogen, then it was refrozen in a -70 °C dry ice/isopropanol bath. The bomb was opened a flow of CO_2 for 10 minutes, then it was sealed and allowed to warm to room temperature before heating at the desired catalysis temperature. The bomb was cooled after the desired amount of time and a portion of the reaction mixture was transferred to a J. Young NMR tube for analysis by ^{1}H NMR spectroscopy (delay time extended to 10 sec for quantitative integration). The hexamethylbenzene standard peak (2.05 ppm) was used to quantify the amounts of each reduction product present in the sample (for HBPin: CH_3OBPin at 3.48 ppm, $CH_2(OBPin)_2$ at 5.34 ppm and HCO_2BPin at 8.35 ppm; for HBCat: CH_3OBCat at 3.6 ppm).

5. X-ray Crystallography The X-ray diffraction data were collected on a Bruker Kappa Apex II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 K controlled by an Oxford Cryostream 700 series low-temperature system and processed with the Bruker Apex 2 software package.[5] The structures were solved by direct methods and refined using SHELX-2013 and SHELX-2014 software packages.[6,7] All non-hydrogen atoms were refined anisotropically, except for the carbon atoms of the disordered pin moiety of **3a**. The hydrides were located directly from the difference Fourier map and the atomic coordinates of the hydride were refined freely, while all other hydrogen atoms were calculated using the riding model. The disordered pin moieties in **2b**, **3a**, and **3b** were modeled successfully with two sets of atomic coordinates. The occupancies of the atoms involved in the disordered portions are refined freely with least square refinements. No restraints were used. The diffuse residual electron density from disordered solvents in the lattices of **2a**, **2b**, and **3b** was removed with the SQUEEZE function of PLATON,[8] and these removed solvent molecules were not included in the formula or the refinement due to unknown identity. Selected crystallographic data of are listed in Table 1S.

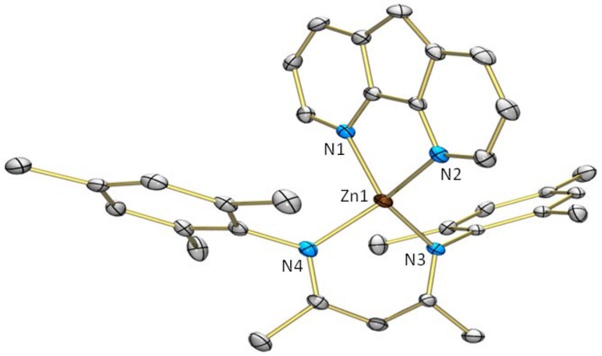

Figure S1. Molecular structure of **1b**. H atoms omitted for clarity. Ellipsoids shown at 30% probability.

The solid state structure of **1b** (Figure S1) features a ZnN_4 core with distorted tetrahedral geometry. The diazafluorenyl ligand chelates Zn1 with an N1-Zn1-N2 bite angle of 88°, which is larger than the N3-Zn1-N4 bite angle of 100° formed by the nacnac chelate. Diazafluorenyl and the plane containing N3-Zn1-N4 are nearly perpendicular (dihedral angle = 88°). Notably, the Zn-N bonds made by diazafluorenyl have statistically different lengths: Zn1-N1 is 2.060(2) and Zn1-N2 is 2.103(2). This lack of symmetry in the solid state (likely resulting from lattice packing effects) contrasts with the symmetric solution-state structure suggested by the NMR data. Both Zn-N-(diazafluorenyl) bonds are longer than the Zn-N-(nacnac) bonds of 1.959(2) for Zn1-N3 and 1.952(2) for Zn1-N4.

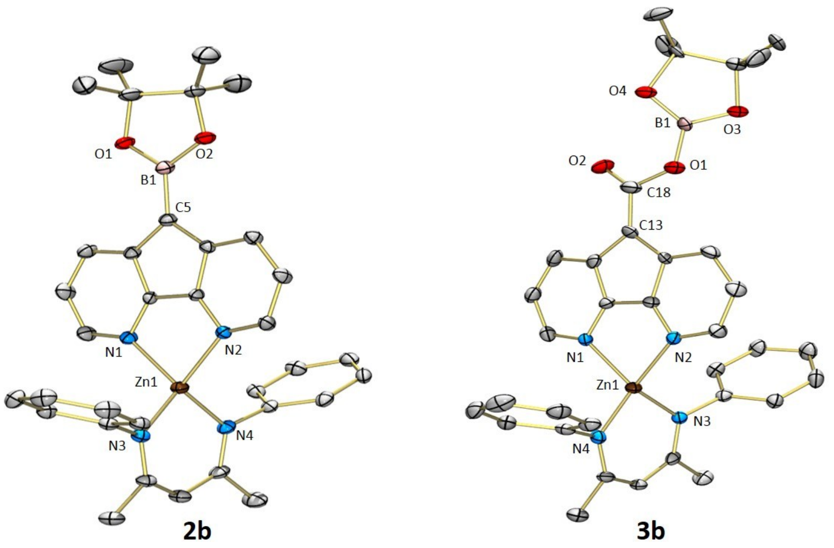

Figure S2. Molecular structures of **2b**, and **3b**. Ellipsoids shown at 30% probability. Hydrogen atoms except for hydrides omitted for clarity. Mesityl methyl groups removed for clarity. Only one disordered component shown. Co-crystallized molecules removed for clarity.

Table 1S. Selected crystallographic data.

	1b	**2a**	**2b**	**3a**	**3b**
Formula	$C_{34}H_{36}N_4Zn$	$C_{63}H_{66}BN_2O_3P_2Ru$	$C_{45}H_{50}BN_4O_2Zn$	$C_{55}H_{49}BN_2O_5P_2Ru$	$C_{49}H_{53}BN_4O_2Zn$
FW	566.04	1072.99	691.99	991.78	736.00
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
space group	C2/c	P-1	P-1	P 4_1	Pbca
a (Å)	21.3090(19)	12.4687(13)	14.4273(7)	10.4711(4)	15.0418(7)
b (Å)	10.0652(9)	15.7310(16)	14.5211(10)	10.4711(4)	21.3952(11)
c (Å)	29.168(3)	17.5343(19)	21.5927(15)	44.073(4)	28.2235(14)

α (deg)	90	67.020(4)	100.551(2)	90	90
β (deg)	108.052(4)	80.866(5)	91.968(2)	90	90
γ (deg)	90	70.636(4)	102.418(2)	90	90
V (Å^3)	5947.9(10)	2985.5(6)	4330.3(5)	4832.4(5)	9083.0(8)
Z	8	2	4	4	8
D_c (g·cm^{-3})	1.264	1.194	1.061	1.363	1.076
μ (mm^{-1})	0.854	0.360	0.600	0.441	0.579
no. of refln collected	25438	48173	64351	33106	34255
no. of indept refln	6770	13690	19613	10940	10394
GOF on F^2	1.002	0.953	0.883	1.072	0.984
R [I> 2σ(I)]	R_1 = 0.0434	R_1 = 0.0506 [a]	R_1 = 0.0554	R_1 = 0.0780	R_1 = 0.0737
	wR_2 = 0.0882	wR_2 = 0.1013 [b]	wR_2 = 0.1088	wR_2 = 0.1662	wR_2 = 0.1949
R (all data)	R_1 = 0.0821	R_1 = 0.1001	R_1 = 0.1285	R_1 = 0.1088	R_1 = 0.1450
	wR_2 = 0.0990	wR_2 = 0.1129	wR_2 = 0.1250	wR_2 = 0.1791	wR_2 = 0.2156

[a] $R_1 = \Sigma(F_o - F_c)/\Sigma F_o$ [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$

6. Computations All calculations were performed using Gaussian 09 program[9] at the B3LYP[10,11] level. The SDD basis set and effective core potential were used on Ru, while 6-31G* basis set was used on all other elements. All structures were optimized in the gas phase first and the solvation correction was performed using self-consistent reaction field by means of the PCM method using toluene as the solvent. Vibrational frequency analyses were performed on all optimized structures to obtain thermodynamic data and to confirm that the optimized structures of **2a** and **3a** have no imaginary frequency, while the transition state structure has one imaginary frequency.

Optimized geometry of the transition state (enthalpy -3412.720647 Hartree):

Ru	20.017733000	19.708052000	4.819948000
P	18.205201000	18.517994000	3.742129000
P	21.673132000	21.114758000	5.893119000
O	18.698536000	19.268187000	7.487372000
O	25.460928000	18.720784000	0.244943000
O	25.792037000	16.761278000	1.415455000
N	20.932943000	20.122061000	2.849529000
N	21.460644000	17.908049000	4.621840000
B	24.862538000	17.666197000	0.922548000
C	20.818343000	21.092897000	1.927252000
H	20.111823000	21.886655000	2.142349000
C	21.576628000	21.083512000	0.748171000
H	21.445073000	21.898897000	0.043882000
C	22.485183000	20.053264000	0.470554000
H	23.072958000	20.051379000	-0.441830000

C	22.611736000	19.033871000	1.415375000
C	23.376949000	17.744386000	1.483257000
C	23.035628000	17.221857000	2.847344000
C	23.421208000	16.108458000	3.596546000
H	24.171763000	15.414981000	3.230922000
C	22.808020000	15.927226000	4.842711000
H	23.074533000	15.077028000	5.463161000
C	21.841784000	16.826217000	5.321123000
H	21.367675000	16.675682000	6.284740000
C	22.067814000	18.052596000	3.432924000
C	21.809473000	19.150578000	2.558970000
C	19.219441000	19.420731000	6.453499000
C	18.099818000	18.703368000	1.909477000
C	17.122244000	19.523561000	1.323125000
H	16.379262000	20.016752000	1.941288000
C	17.090683000	19.705501000	-0.061132000
H	16.324208000	20.339825000	-0.499259000
C	18.028999000	19.070487000	-0.877044000
H	17.996478000	19.208851000	-1.954707000
C	19.007493000	18.256481000	-0.302807000
H	19.752949000	17.746003000	-0.904675000
C	19.048102000	18.079099000	1.080735000
H	19.829793000	17.439126000	1.476288000
C	16.505727000	18.996504000	4.311376000
C	15.428210000	18.107789000	4.154312000
H	15.594127000	17.123266000	3.728576000
C	14.141651000	18.475505000	4.546615000
H	13.321112000	17.773971000	4.421991000
C	13.908654000	19.737201000	5.099275000
H	12.906188000	20.020783000	5.408604000
C	14.969651000	20.628991000	5.254664000
H	14.798893000	21.611538000	5.686612000
C	16.259844000	20.261120000	4.864854000
H	17.083168000	20.954830000	4.993197000
C	18.186939000	16.687377000	4.050313000
C	18.293358000	16.246247000	5.381558000
H	18.397473000	16.964680000	6.187928000
C	18.245689000	14.887442000	5.689231000
H	18.322337000	14.568840000	6.725625000
C	18.103689000	13.941158000	4.671413000
H	18.075915000	12.881290000	4.909687000
C	17.995317000	14.366522000	3.348418000
H	17.883625000	13.641249000	2.547246000
C	18.028942000	15.729245000	3.038471000
H	17.933512000	16.035533000	2.003560000
C	22.871361000	20.240859000	7.010337000
C	24.241182000	20.544215000	7.057614000
H	24.656109000	21.298236000	6.398005000
C	25.087046000	19.883085000	7.951847000
H	26.145382000	20.129420000	7.968400000
C	24.577905000	18.917805000	8.820387000
H	25.236901000	18.405626000	9.516138000
C	23.214807000	18.616229000	8.791057000
H	22.805266000	17.870289000	9.467009000
C	22.370949000	19.266946000	7.891172000
H	21.314604000	19.021984000	7.886533000
C	21.000958000	22.425841000	7.020454000
C	19.694027000	22.906947000	6.854906000
H	19.064724000	22.479382000	6.082300000
C	19.199352000	23.920878000	7.678861000
H	18.182577000	24.277951000	7.538697000
C	20.001729000	24.464623000	8.681799000
H	19.614532000	25.248758000	9.326885000
C	21.304867000	23.992593000	8.856002000
H	21.936561000	24.408427000	9.636391000
C	21.801608000	22.982796000	8.032450000
H	22.814666000	22.624398000	8.183984000
C	22.762153000	22.069291000	4.744395000

C	22.610801000	23.451934000	4.564736000
H	21.884283000	24.001426000	5.154486000
C	23.396386000	24.134891000	3.632459000
H	23.269600000	25.207222000	3.508988000
C	24.337684000	23.447178000	2.866195000
H	24.944442000	23.979523000	2.138730000
C	24.495379000	22.069128000	3.035339000
H	25.210861000	21.517489000	2.431613000
C	23.714524000	21.386945000	3.967383000
H	23.849399000	20.316849000	4.089061000
C	26.701248000	17.643610000	-1.519767000
H	26.320191000	18.398538000	-2.215629000
H	26.005671000	16.801656000	-1.532868000
H	27.683034000	17.313047000	-1.877163000
C	27.717074000	19.485079000	-0.151013000
H	27.702900000	20.032856000	0.794921000
H	27.393557000	20.169309000	-0.942668000
H	28.750243000	19.187012000	-0.365195000
C	26.790875000	18.268794000	-0.119098000
C	27.923021000	16.003292000	0.569388000
H	28.058605000	15.318966000	1.413974000
H	28.916584000	16.301804000	0.213489000
H	27.413292000	15.457546000	-0.227308000
C	27.748473000	17.844952000	2.267437000
H	27.750941000	17.104656000	3.074199000
H	27.174444000	18.712492000	2.608567000
H	28.782293000	18.159310000	2.085757000
C	27.108102000	17.216395000	1.020397000
H	19.135125000	21.028394000	4.635398000
C	22.811044000	16.749114000	0.283531000
O	21.641378000	16.374255000	0.299813000
O	23.773029000	16.557065000	-0.505906000

Optimized geometry of **2** (enthalpy -3224.174648 Hartree):

Ru	20.027269000	19.744948000	4.866605000
P	18.283890000	18.543887000	3.710939000
P	21.575685000	21.197904000	6.012482000
O	18.619830000	19.222708000	7.476351000
O	25.075864000	18.052112000	-0.355424000
O	25.438910000	16.258355000	1.037772000
N	21.012232000	20.186606000	2.935469000
N	21.535036000	17.990019000	4.756978000
B	24.701999000	17.421174000	0.829123000
C	20.906402000	21.133902000	1.995384000
H	20.172160000	21.914143000	2.163279000
C	21.715764000	21.116915000	0.838400000
H	21.583157000	21.913311000	0.111726000
C	22.664888000	20.120228000	0.615449000
H	23.280082000	20.128031000	-0.280113000
C	22.808616000	19.104254000	1.584240000
C	23.632372000	17.936495000	1.766446000
C	23.229392000	17.365515000	3.027247000
C	23.601856000	16.253775000	3.813035000
H	24.382768000	15.573648000	3.484805000
C	22.941285000	16.054637000	5.022941000
H	23.204495000	15.210133000	5.653872000
C	21.922391000	16.926924000	5.470543000
H	21.421712000	16.757178000	6.418028000
C	22.185041000	18.167433000	3.589282000
C	21.930595000	19.228839000	2.707642000
C	19.172850000	19.412043000	6.464837000
C	18.210417000	18.775967000	1.878788000
C	17.212047000	19.555251000	1.276349000
H	16.429584000	20.001151000	1.881246000
C	17.209636000	19.761011000	-0.105407000
H	16.426380000	20.365632000	-0.555274000
C	18.201482000	19.190445000	-0.902863000

H	18.198162000	19.350128000	-1.977854000
C	19.201428000	18.414399000	-0.311931000
H	19.985424000	17.973045000	-0.920617000
C	19.209640000	18.211071000	1.067334000
H	19.999176000	17.611820000	1.509270000
C	16.558770000	18.976868000	4.249678000
C	15.512007000	18.044180000	4.160223000
H	15.708292000	17.038336000	3.804243000
C	14.213682000	18.394037000	4.532520000
H	13.418511000	17.656502000	4.462170000
C	13.936921000	19.682066000	4.994892000
H	12.925662000	19.952172000	5.287354000
C	14.967660000	20.618095000	5.083774000
H	14.764347000	21.622054000	5.447044000
C	16.269005000	20.267418000	4.718232000
H	17.070273000	20.993175000	4.801342000
C	18.285118000	16.699844000	3.918605000
C	18.552634000	16.175665000	5.194015000
H	18.791995000	16.843685000	6.014005000
C	18.507228000	14.800962000	5.424998000
H	18.715125000	14.416664000	6.420061000
C	18.206269000	13.922865000	4.382221000
H	18.179763000	12.851138000	4.560045000
C	17.940494000	14.430456000	3.110329000
H	17.702958000	13.756470000	2.291479000
C	17.973737000	15.807950000	2.880116000
H	17.755605000	16.183379000	1.886354000
C	22.788675000	20.363238000	7.143410000
C	24.142657000	20.722818000	7.224558000
H	24.539572000	21.501398000	6.582698000
C	24.995490000	20.086759000	8.130457000
H	26.042121000	20.376506000	8.173521000
C	24.508044000	19.090995000	8.976586000
H	25.172348000	18.598097000	9.681344000
C	23.159970000	18.732616000	8.912356000
H	22.767708000	17.960283000	9.568695000
C	22.310230000	19.357909000	8.000522000
H	21.266017000	19.067209000	7.965136000
C	20.793398000	22.427235000	7.164738000
C	19.482286000	22.874401000	6.944595000
H	18.915235000	22.465872000	6.115601000
C	18.904304000	23.828939000	7.784825000
H	17.885559000	24.159620000	7.600353000
C	19.625722000	24.346749000	8.860524000
H	19.173455000	25.084123000	9.518470000
C	20.931816000	23.908547000	9.089945000
H	21.501508000	24.304063000	9.926730000
C	21.512007000	22.958659000	8.249288000
H	22.526710000	22.626909000	8.444282000
C	22.637308000	22.261494000	4.937128000
C	22.433047000	23.645516000	4.837727000
H	21.667400000	24.127534000	5.436451000
C	23.214375000	24.417196000	3.974039000
H	23.043928000	25.488854000	3.911298000
C	24.209130000	23.818245000	3.201290000
H	24.816608000	24.419706000	2.530223000
C	24.418444000	22.440075000	3.291406000
H	25.181663000	21.959557000	2.686090000
C	23.637476000	21.666247000	4.148718000
H	23.807522000	20.595547000	4.198196000
C	25.052203000	16.385553000	-2.081417000
H	24.525550000	17.110119000	-2.711023000
H	24.301672000	15.782647000	-1.560506000
H	25.638311000	15.726333000	-2.731416000
C	26.981202000	17.973354000	-1.838937000
H	27.535138000	18.631714000	-1.165840000
H	26.482733000	18.599042000	-2.587081000
H	27.694903000	17.325283000	-2.361517000

C	25.938305000	17.148446000	-1.084234000
C	26.771143000	14.778107000	-0.330837000
H	27.136610000	14.221090000	0.538495000
H	27.532532000	14.715190000	-1.117413000
H	25.861450000	14.287254000	-0.684604000
C	27.753724000	16.821673000	0.745416000
H	27.961914000	16.252170000	1.656930000
H	27.589077000	17.865501000	1.030905000
H	28.636480000	16.771807000	0.098304000
C	26.508771000	16.231463000	0.064929000
H	19.126331000	21.050841000	4.640899000

Optimized geometry of **3** (enthalpy -3412.76698 Hartree):

Ru	20.028742000	19.747927000	4.869938000
P	18.271899000	18.583029000	3.696889000
P	21.592212000	21.175117000	6.033567000
O	18.622043000	19.206072000	7.475337000
O	26.115226000	15.542172000	-0.926375000
O	26.634768000	14.435332000	1.023701000
N	21.033219000	20.200082000	2.951895000
N	21.494553000	17.963577000	4.729889000
B	25.964146000	15.487802000	0.435769000
C	20.947477000	21.164396000	2.025683000
H	20.221165000	21.950073000	2.201780000
C	21.764237000	21.158331000	0.875920000
H	21.647291000	21.968497000	0.162262000
C	22.702531000	20.152831000	0.641034000
H	23.328281000	20.154266000	-0.245143000
C	22.815475000	19.124847000	1.596544000
C	23.601187000	17.929385000	1.769142000
C	23.186921000	17.322014000	3.011834000
C	23.518035000	16.184549000	3.776429000
H	24.283410000	15.490468000	3.446631000
C	22.832260000	15.980468000	4.972480000
H	23.061744000	15.114059000	5.586191000
C	21.835741000	16.871814000	5.424639000
H	21.311407000	16.695734000	6.357766000
C	22.165097000	18.145777000	3.576349000
C	21.940913000	19.236402000	2.714544000
C	19.174374000	19.405550000	6.465650000
C	18.230437000	18.821370000	1.865118000
C	17.255496000	19.624774000	1.255491000
H	16.473252000	20.080147000	1.853517000
C	17.276854000	19.842710000	-0.124147000
H	16.511539000	20.465807000	-0.579531000
C	18.269538000	19.261255000	-0.912747000
H	18.284611000	19.430254000	-1.986108000
C	19.247409000	18.462536000	-0.315096000
H	20.031926000	18.012754000	-0.916855000
C	19.231934000	18.247517000	1.062514000
H	20.004563000	17.630351000	1.509662000
C	16.546253000	19.039369000	4.209733000
C	15.477230000	18.151498000	3.999885000
H	15.660239000	17.174217000	3.565090000
C	14.176132000	18.509793000	4.351549000
H	13.362736000	17.808184000	4.186558000
C	13.919727000	19.761568000	4.915780000
H	12.906001000	20.037985000	5.193352000
C	14.972426000	20.652455000	5.124565000
H	14.783854000	21.627122000	5.566807000
C	16.276792000	20.293827000	4.775913000
H	17.094126000	20.985406000	4.946183000
C	18.233497000	16.738913000	3.913811000
C	18.381490000	16.224799000	5.213519000
H	18.541564000	16.897020000	6.049719000
C	18.309583000	14.852763000	5.451528000
H	18.422847000	14.477571000	6.465204000

C	18.100285000	13.965691000	4.393573000
H	18.052973000	12.895787000	4.577663000
C	17.950270000	14.463176000	3.099553000
H	17.782260000	13.783219000	2.268566000
C	18.010029000	15.838862000	2.860680000
H	17.879716000	16.204638000	1.848332000
C	22.814398000	20.318522000	7.135816000
C	24.159772000	20.704854000	7.241328000
H	24.542838000	21.518142000	6.634992000
C	25.021446000	20.050070000	8.124842000
H	26.061073000	20.360557000	8.186922000
C	24.551560000	19.008050000	8.924198000
H	25.223052000	18.499962000	9.611032000
C	23.212429000	18.622772000	8.836196000
H	22.834478000	17.814209000	9.456206000
C	22.353673000	19.267591000	7.946407000
H	21.316545000	18.955412000	7.890879000
C	20.817648000	22.386924000	7.209244000
C	19.513126000	22.854518000	6.991004000
H	18.945774000	22.470404000	6.150605000
C	18.942055000	23.799148000	7.846833000
H	17.928835000	24.146642000	7.662970000
C	19.663446000	24.285878000	8.937049000
H	19.216553000	25.015560000	9.607064000
C	20.962357000	23.826546000	9.165076000
H	21.531865000	24.197757000	10.012995000
C	21.536111000	22.886961000	8.308450000
H	22.545412000	22.539156000	8.502640000
C	22.644889000	22.254723000	4.965439000
C	22.416953000	23.634900000	4.864144000
H	21.640727000	24.104083000	5.459500000
C	23.188818000	24.419445000	4.003515000
H	23.000186000	25.487941000	3.939475000
C	24.197851000	23.837741000	3.236079000
H	24.798165000	24.449251000	2.567800000
C	24.431461000	22.463529000	3.328387000
H	25.207155000	21.996793000	2.728171000
C	23.659511000	21.677043000	4.182403000
H	23.850059000	20.609812000	4.235183000
C	25.669266000	13.351082000	-1.791672000
H	25.090313000	13.833804000	-2.585059000
H	24.983802000	13.110862000	-0.972377000
H	26.082220000	12.415483000	-2.184119000
C	27.711263000	14.631062000	-2.494105000
H	28.421140000	15.419623000	-2.234484000
H	27.125298000	14.976987000	-3.351711000
H	28.271135000	13.739811000	-2.801241000
C	26.773400000	14.313251000	-1.330460000
C	27.542133000	12.341826000	0.222861000
H	28.016658000	12.128517000	1.186440000
H	28.133463000	11.854573000	-0.561235000
H	26.544141000	11.897147000	0.234689000
C	28.881891000	14.464128000	0.187815000
H	29.220422000	14.270124000	1.210510000
H	28.862311000	15.548440000	0.038907000
H	29.610596000	14.030907000	-0.505694000
C	27.485463000	13.853122000	0.003542000
H	19.145943000	21.068528000	4.662799000
C	24.593939000	17.497036000	0.829703000
O	24.922272000	18.069015000	-0.196746000
O	25.207444000	16.305220000	1.233238000

Optimized geometry of CO_2 (enthalpy -188.566928 Hartree):

C	1.776638000	5.876532000	1.316820000
O	2.328477000	5.749700000	2.339730000
O	1.224799000	6.003364000	0.293909000

7. NMR Spectra

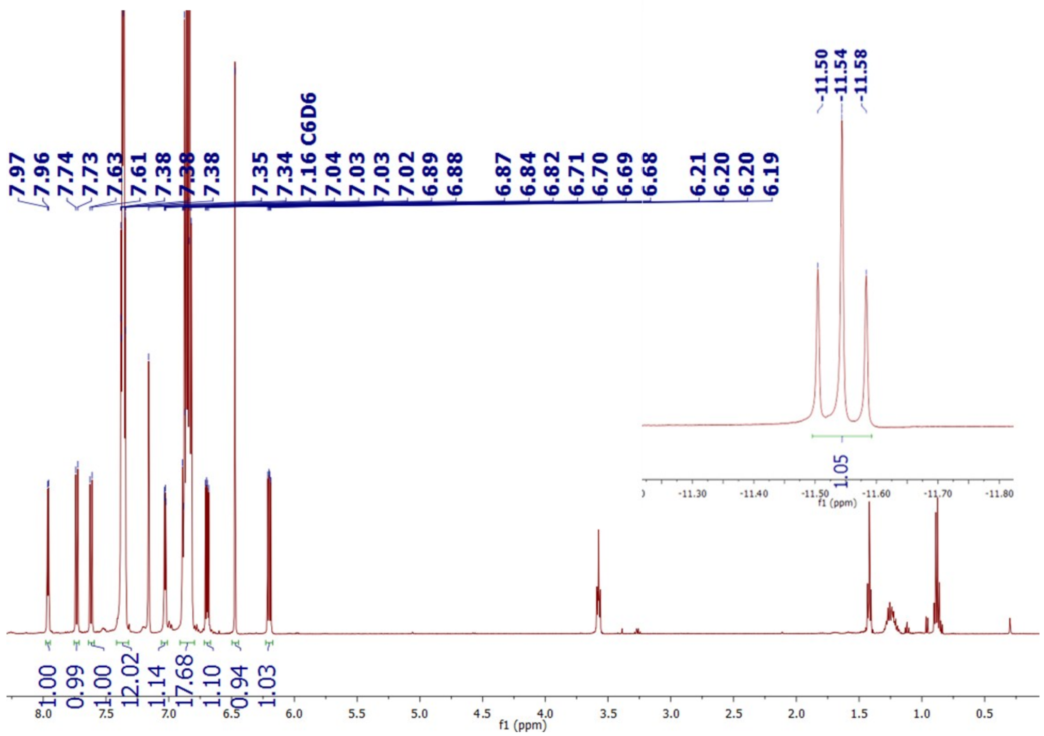

Figure S3 ^{1}H NMR Spectrum (500 MHz, 25 °C) of **1a** in C_6D_6 Note: spectrum contains residual THF at 3.58 and 1.42, and pentane at 1.26 and 0.87.

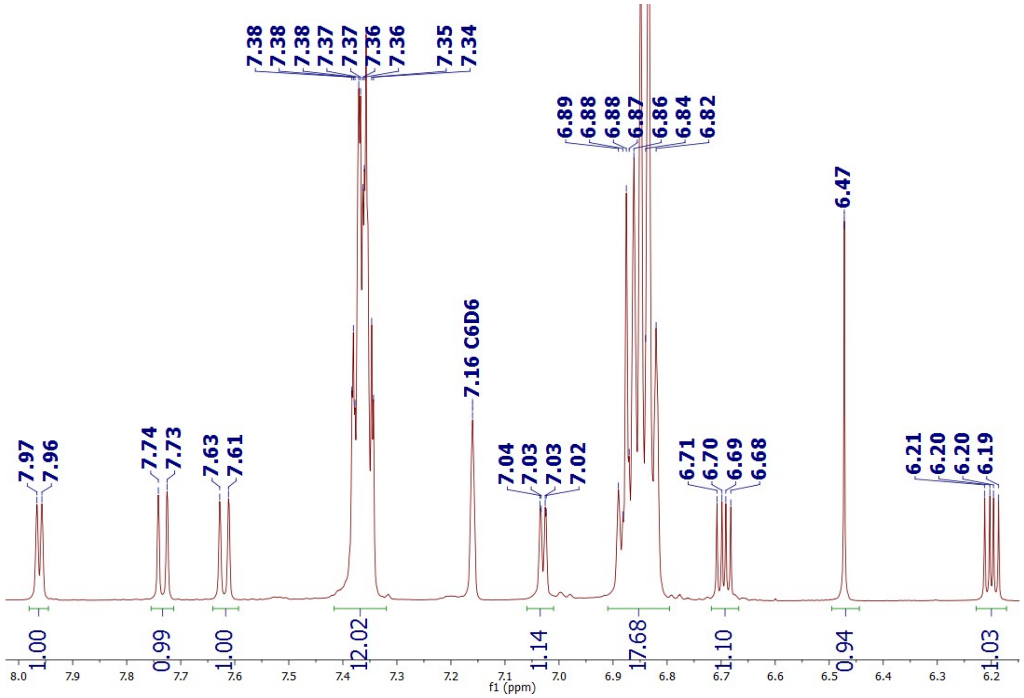

Figure S4. Expansion of aromatic region of ^{1}H NMR spectrum (500 MHz, 25 °C) of **1a** in C_6D_6

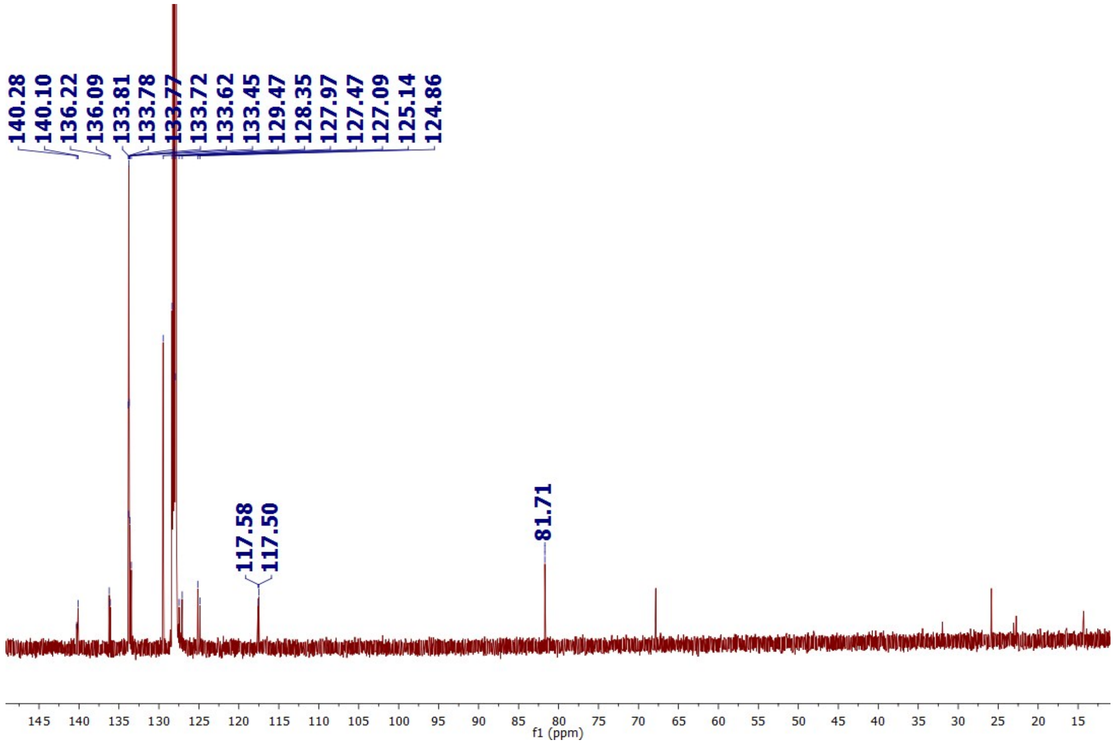

Figure S5. ^{13}C NMR Spectrum (126 MHz, 25 °C) of **1a** in C_6D_6 Note: spectrum contains residual THF at 67.83 and 25.84.

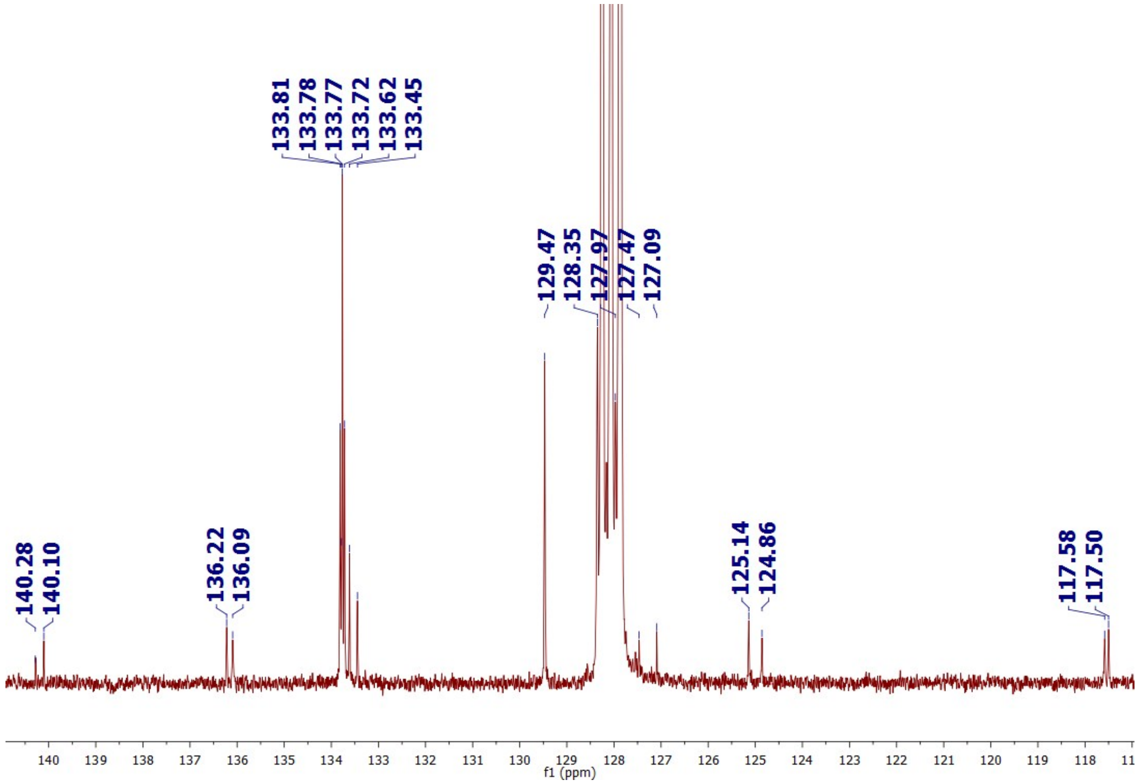

Figure S6 Expansion of aromatic region of ^{13}C NMR spectrum (126 MHz, 25 °C) of **1a** in C_6D_6

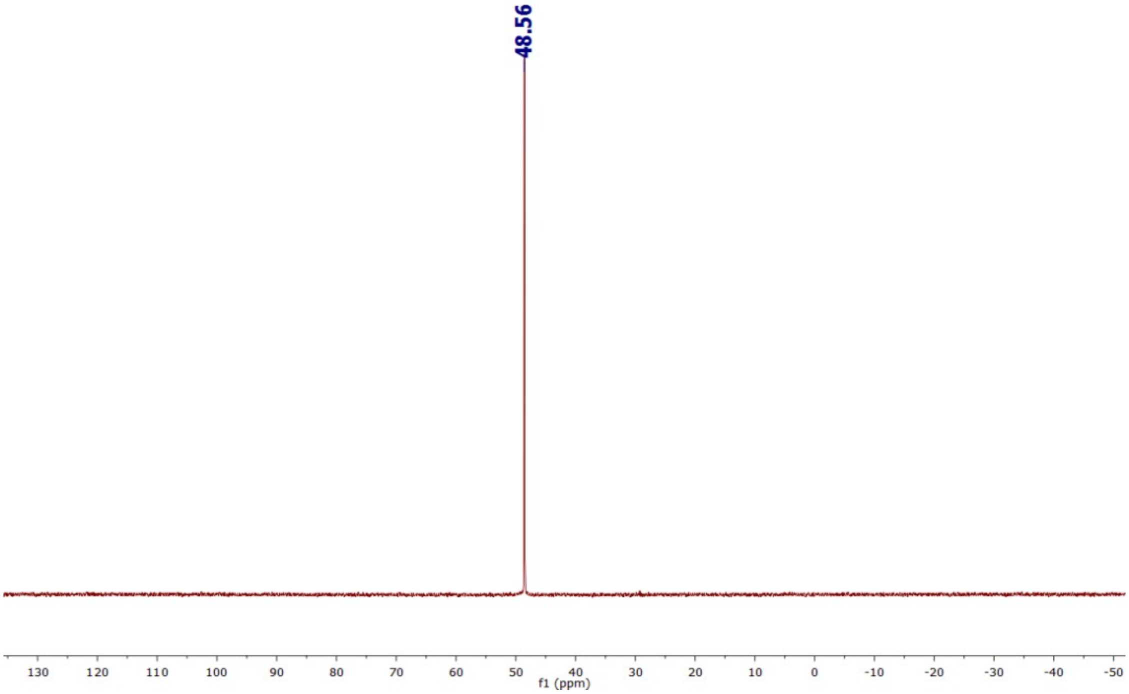

Figure S7. ^{31}P NMR Spectrum (202 MHz, 25 °C) of **1a** in C_6D_6

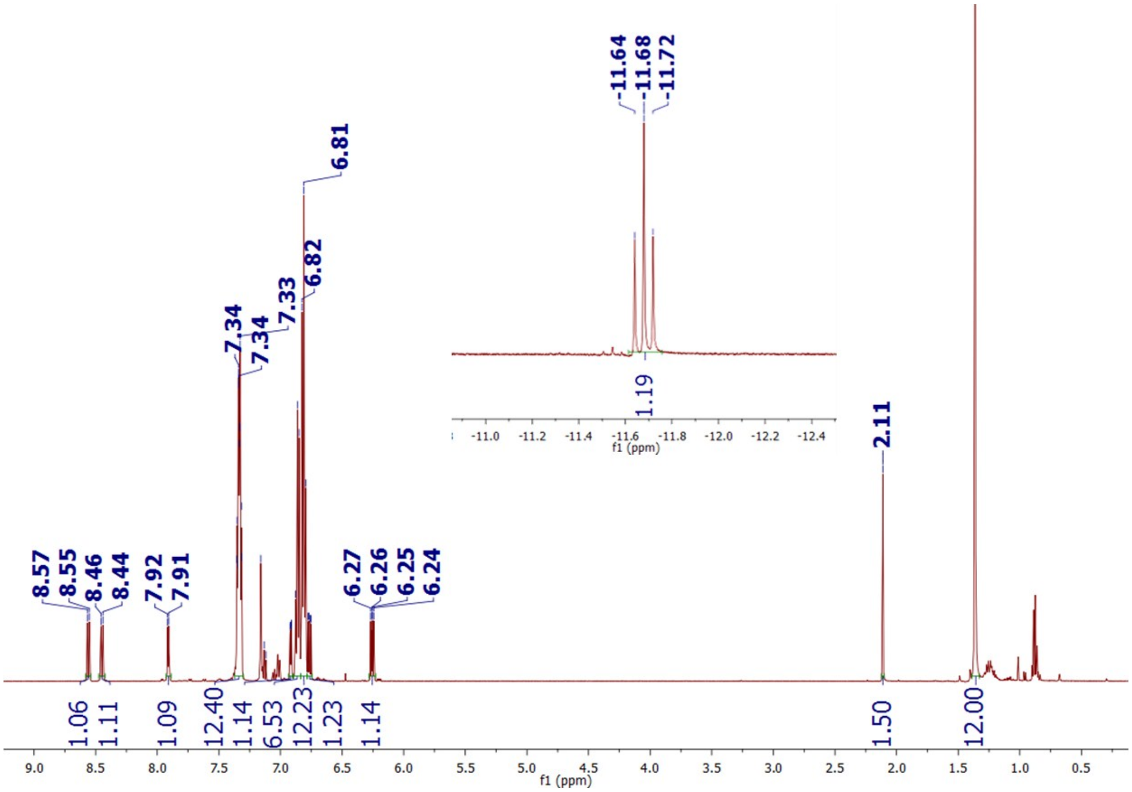

Figure S8. ^{1}H NMR Spectrum (500 MHz, 25 °C) of **2a** in C_6D_6 Note: spectrum contains pentane at 1.26 and 0.87.

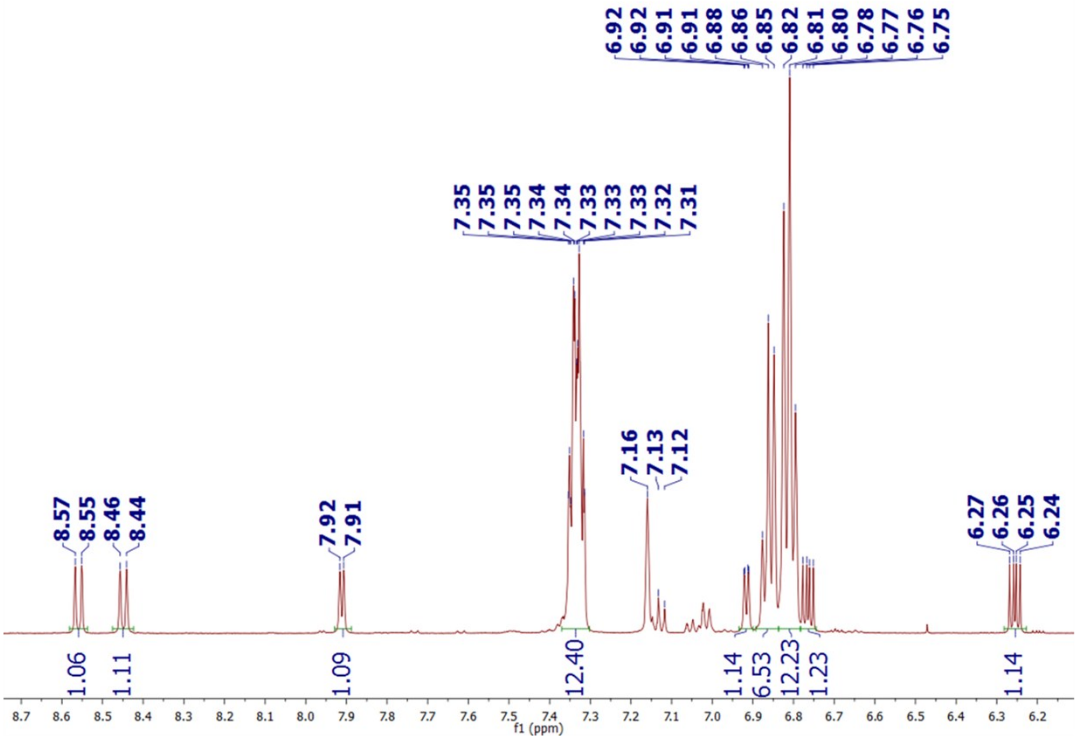

Figure S9. Expansion of aromatic region of ^{1}H NMR Spectrum (500 MHz, 25 °C) of **2a** in C_6D_6

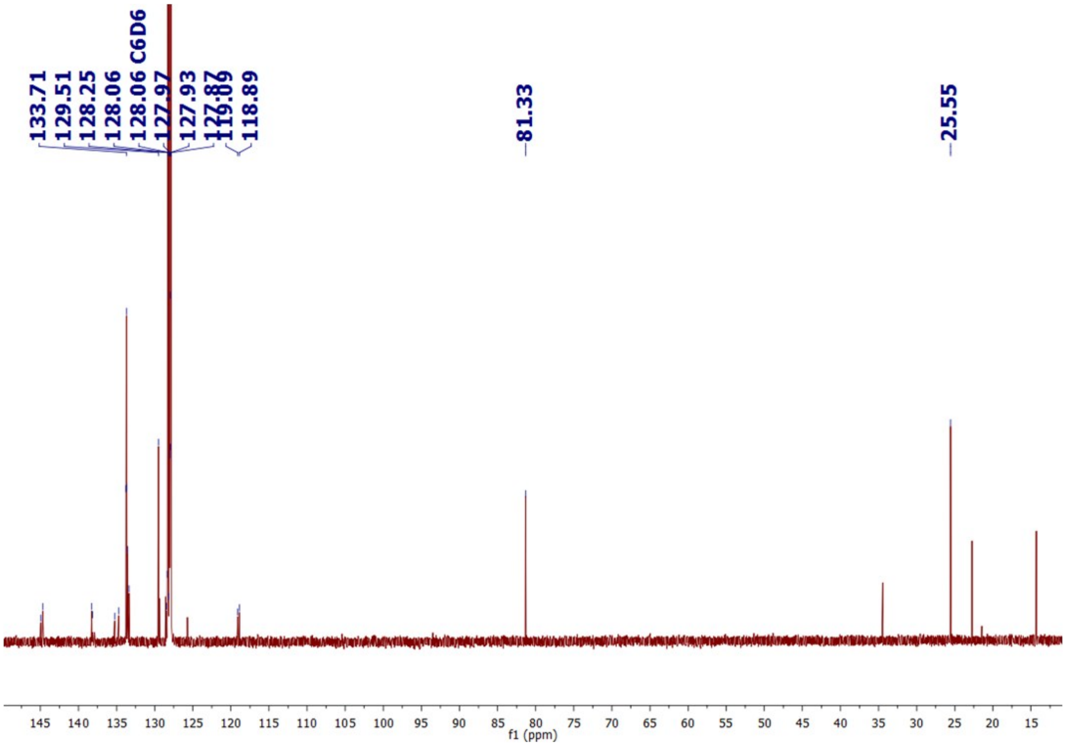

Figure S10. ^{13}C NMR Spectrum (126 MHz, 25 °C) of **2a** in C_6D_6 Note: spectrum contains pentane at 34.45, 22.73, and 14.30.

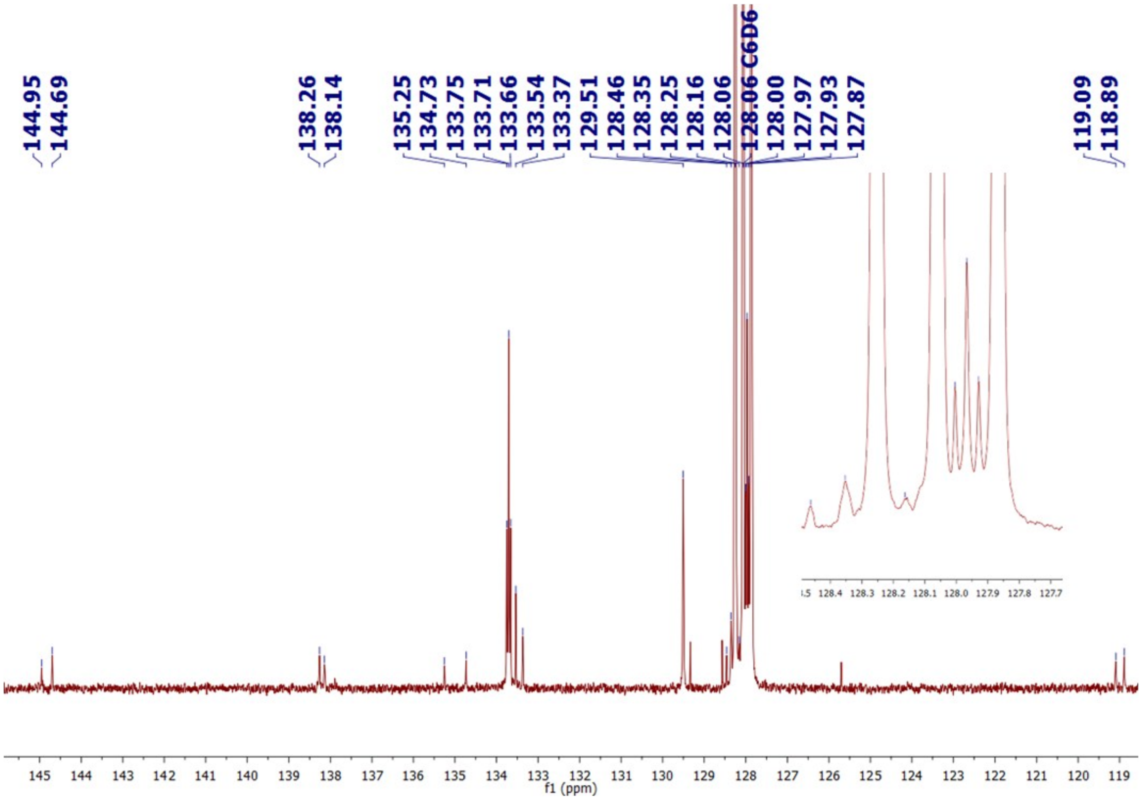

Figure S11. Expansion of aromatic region of ^{13}C NMR Spectrum (126 MHz, 25 °C) of **2a** in C_6D_6

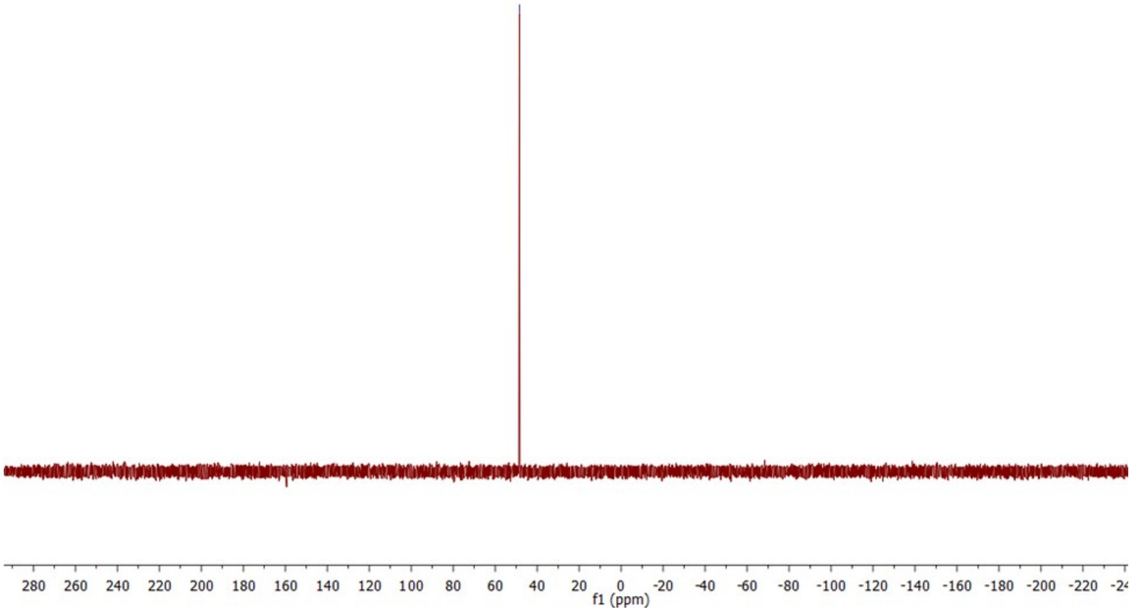

Figure S12. ^{31}P NMR Spectrum (202 MHz, 25 °C) of **2a** in C_6D_6

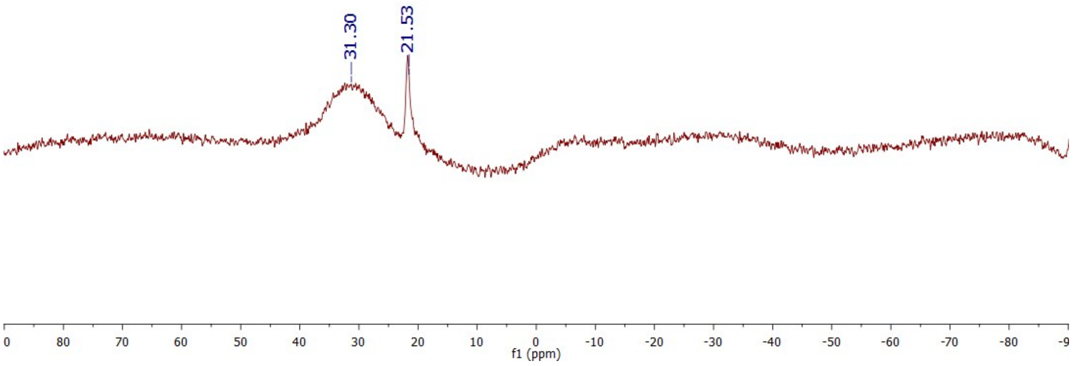

Figure S13. ^{11}B NMR Spectrum (128 MHz, 25 °C) of **2a** in C_6D_6. Note: spectrum contains a peak at 21.53 due to pinBOBpin.

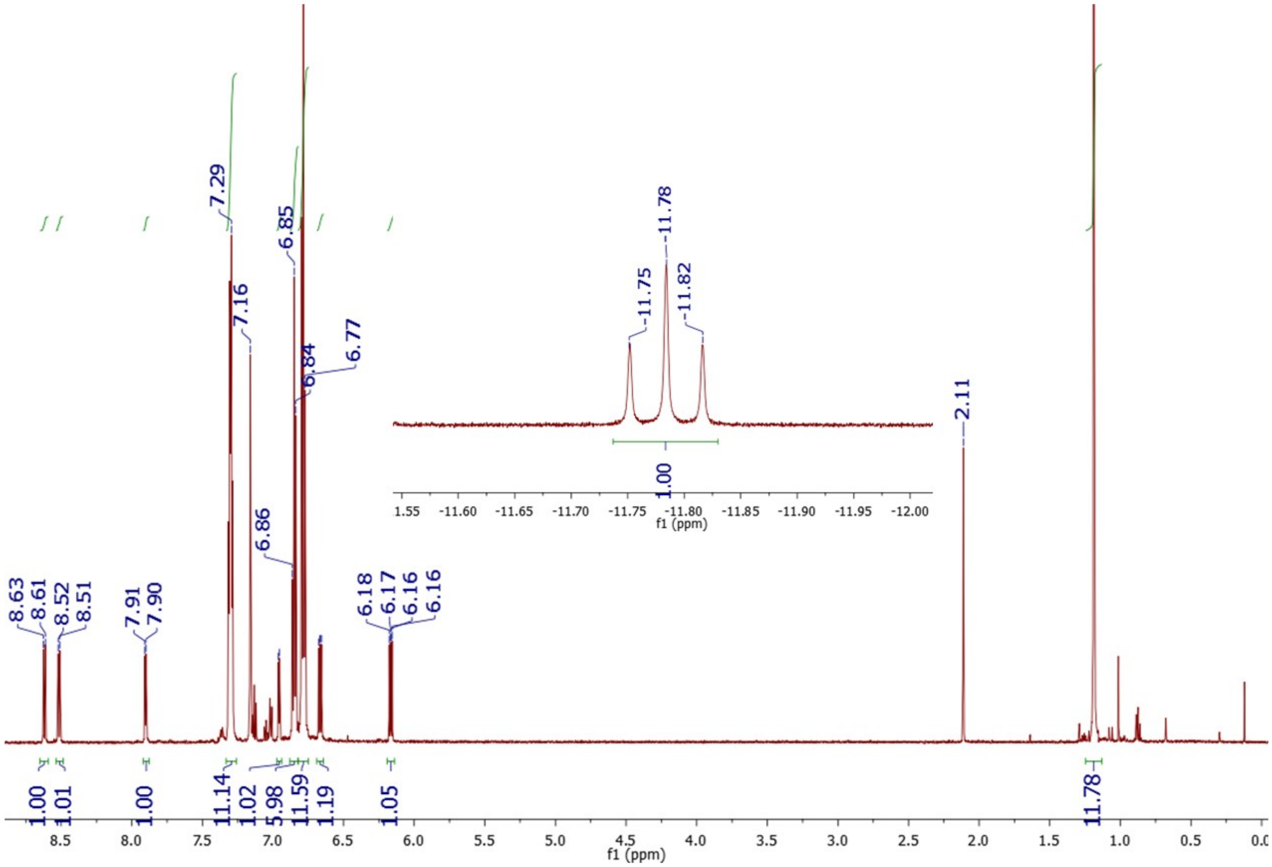

Figure S14. ^{1}H NMR Spectrum (600 MHz, 25 °C) of **3a** in C_6D_6

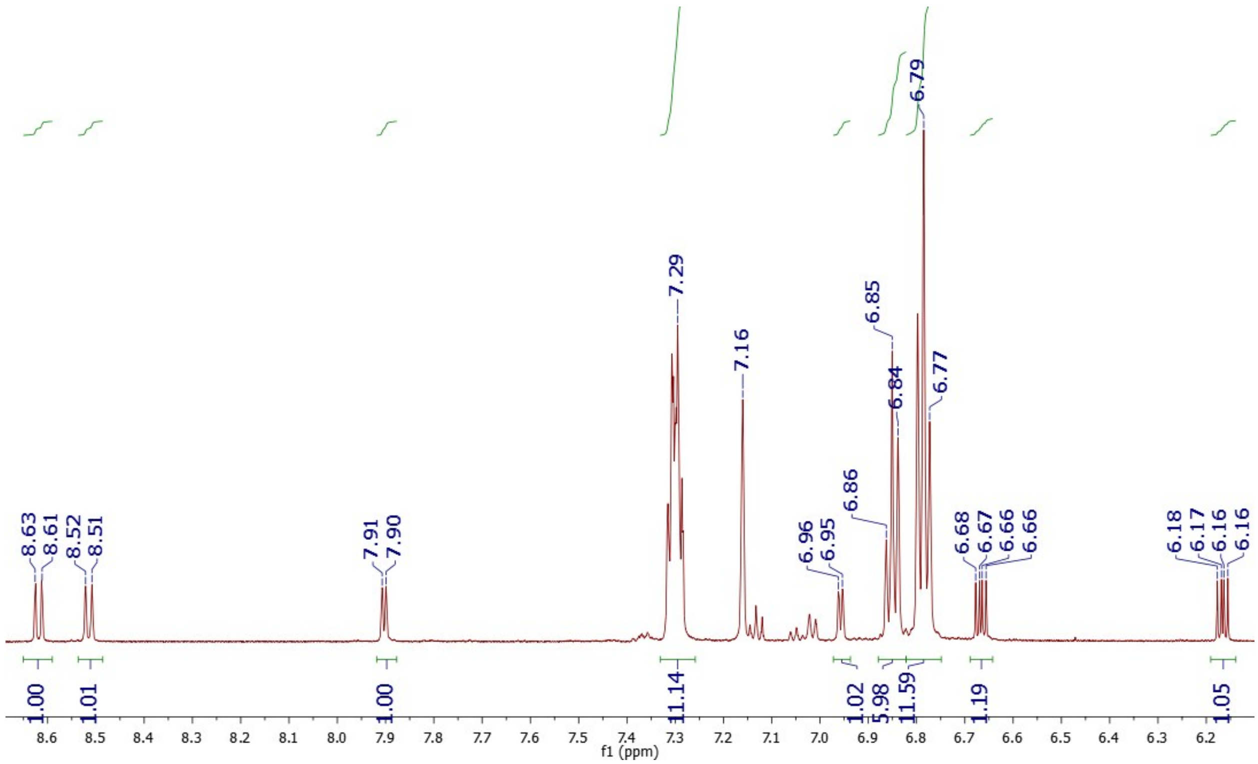

Figure S15. Expansion of aromatic region of ^{1}H NMR Spectrum (600 MHz, 25 °C) of **3a** in C_6D_6.

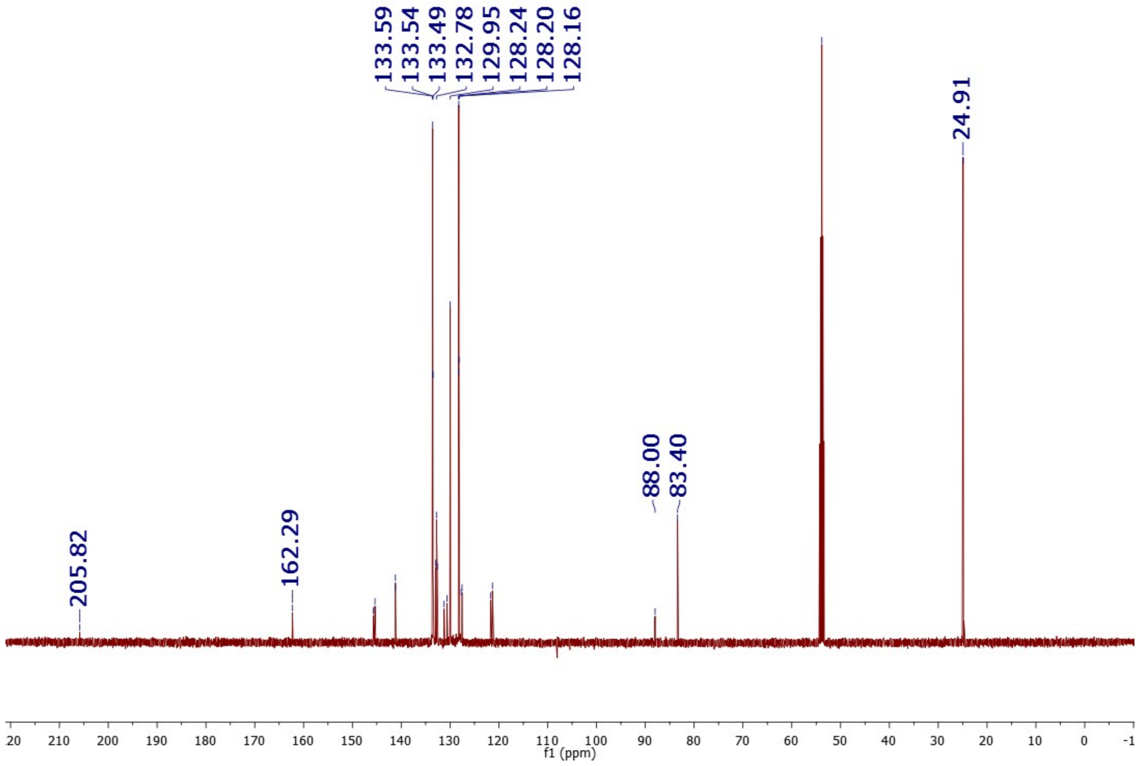

Figure S16. ^{13}C NMR Spectrum (126 MHz, 25 °C) of **3a** in CD_2Cl_2

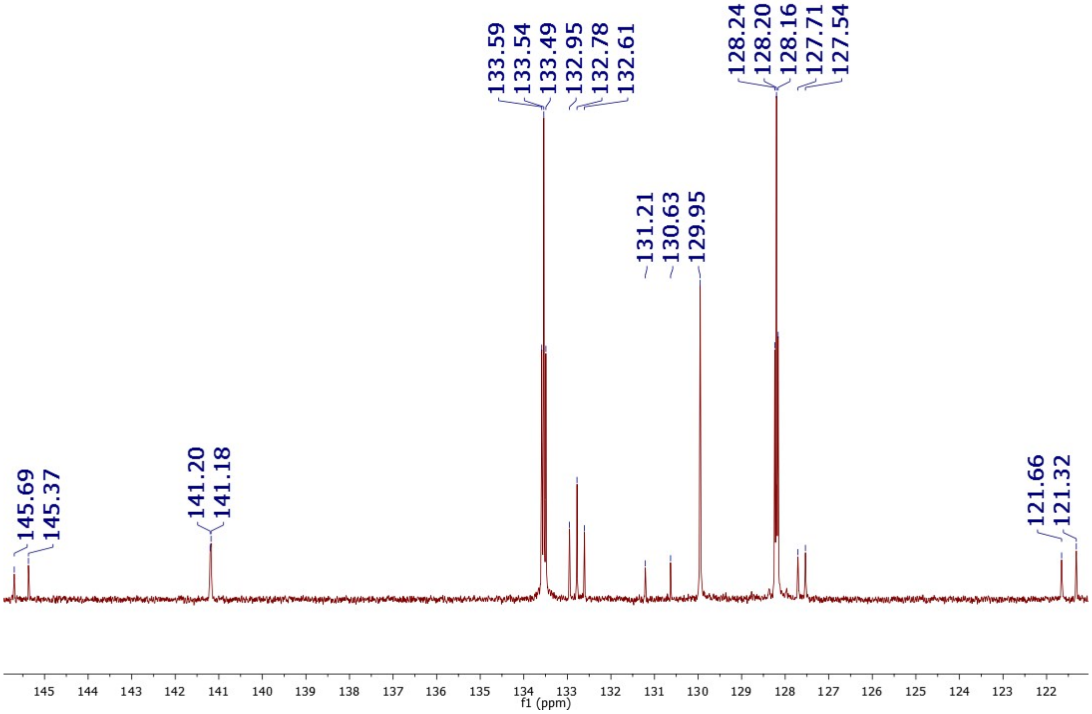

Figure S17. Expansion of the aromatic region of ^{13}C NMR Spectrum (126 MHz, 25 °C) of **3a** in CD_2Cl_2

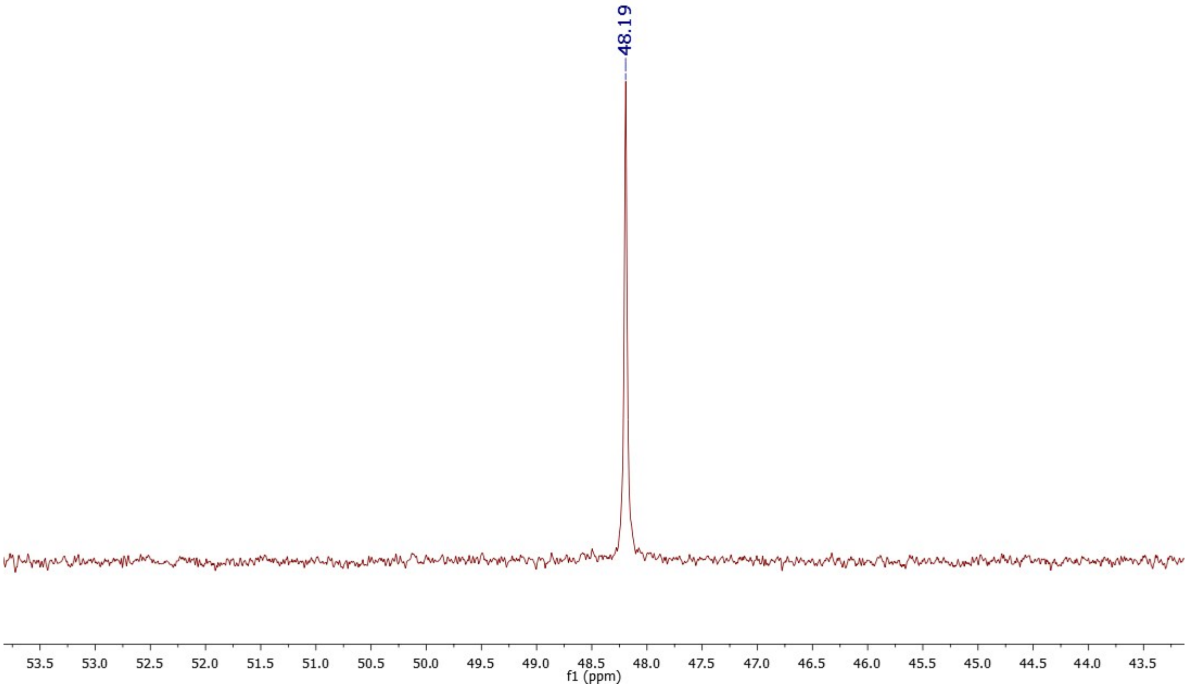

Figure S18 ^{31}P NMR Spectrum (243 MHz, 25 °C) of **3a** in C_6D_6.

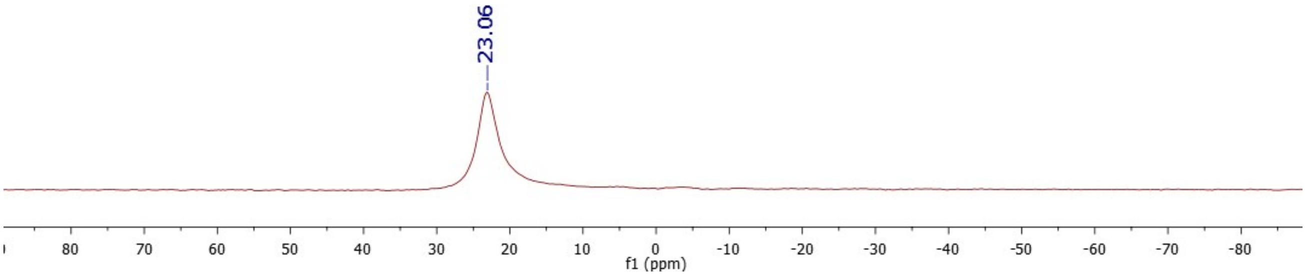

Figure S19. ^{11}B NMR Spectrum (128 MHz, 25 °C) of **3a** in C_6D_6.

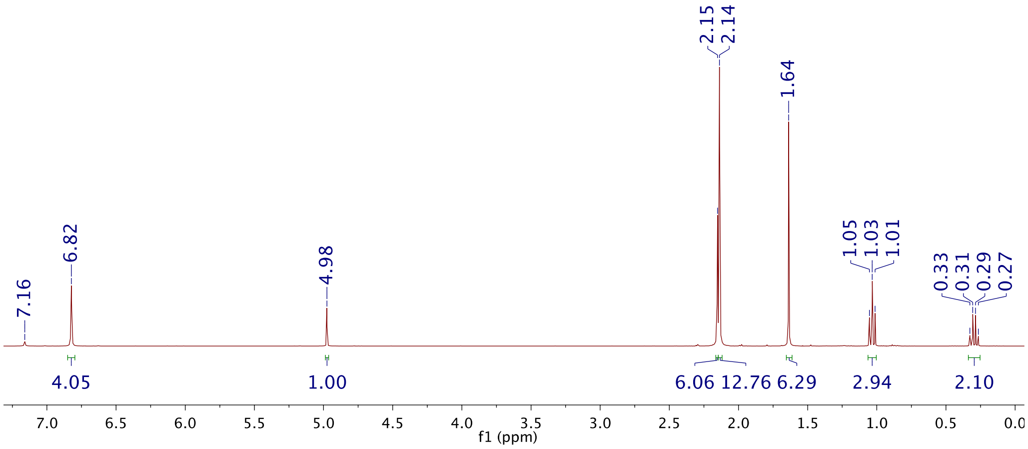

Figure S20. ^{1}H NMR Spectrum (400 MHz, C_6D_6, 25 °C) of (Mes$_2$nacnac)ZnEt.

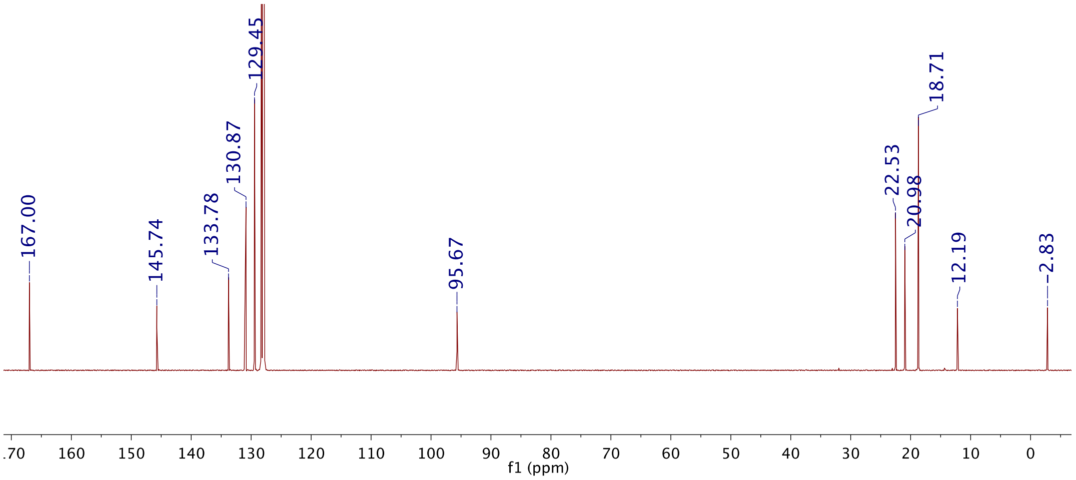

Figure S21. ^{13}C{^{1}H} NMR Spectrum (101 MHz, C_6D_6, 25 °C) of complex (Mes$_2$nacnac)ZnEt.

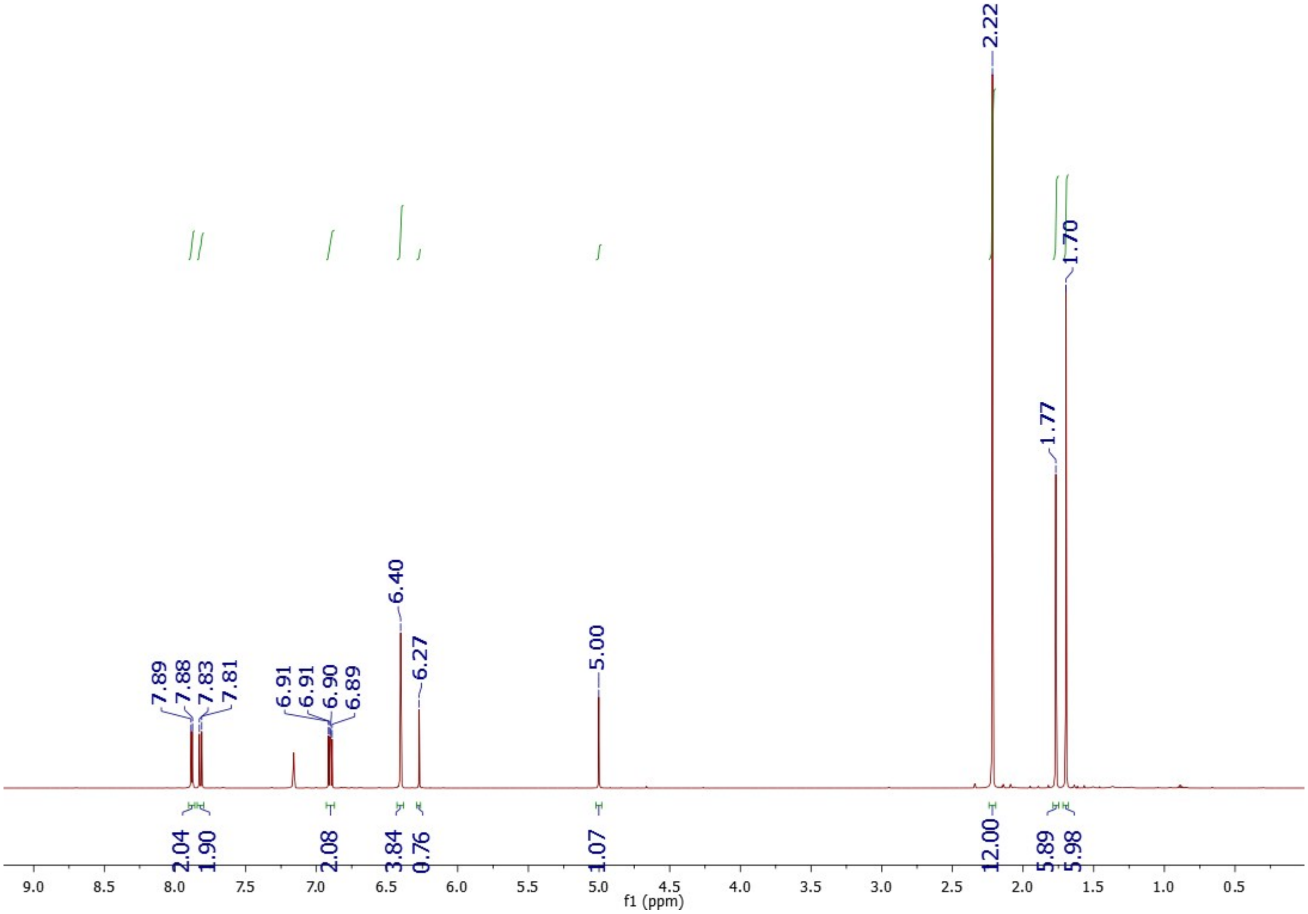

Figure S22. ^{1}H NMR Spectrum (500 MHz, C_6D_6, 25 °C) of complex **1b**.

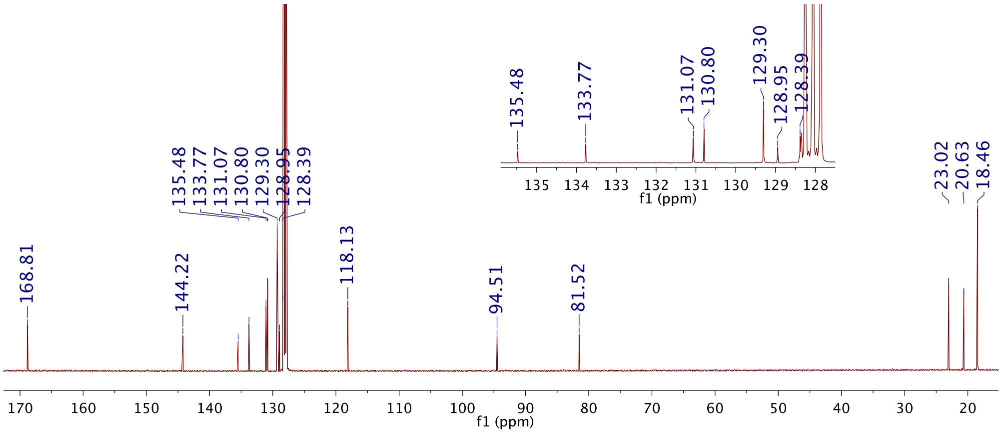

Figure S23. $^{13}C\{^{1}H\}$ NMR Spectrum (126 MHz, C_6D_6, 25 °C) of complex **1b**.

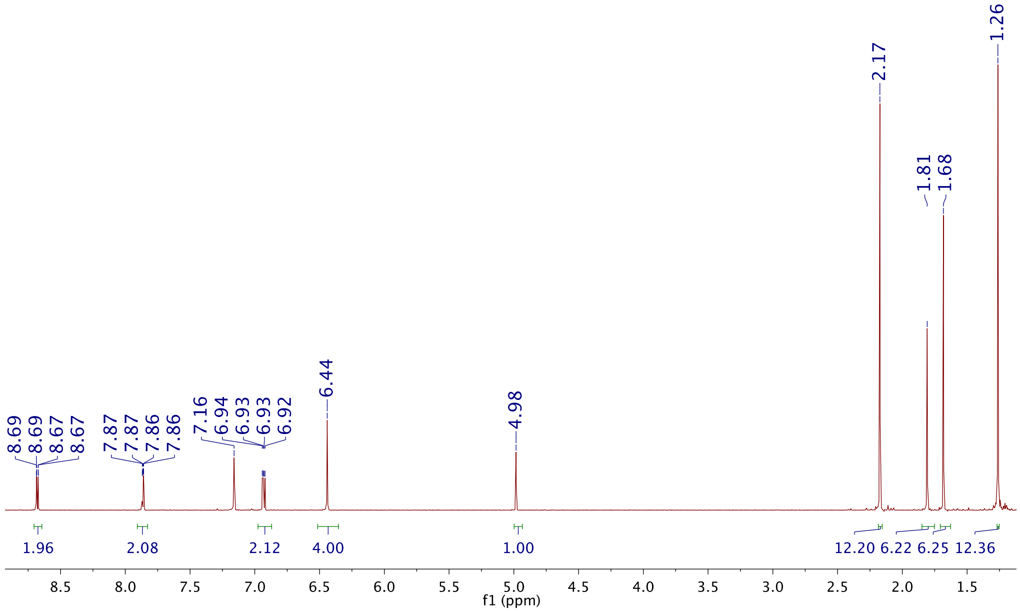

Figure S24. ^{1}H NMR Spectrum (600 MHz, C_6D_6, 25 °C) of complex **2b**.

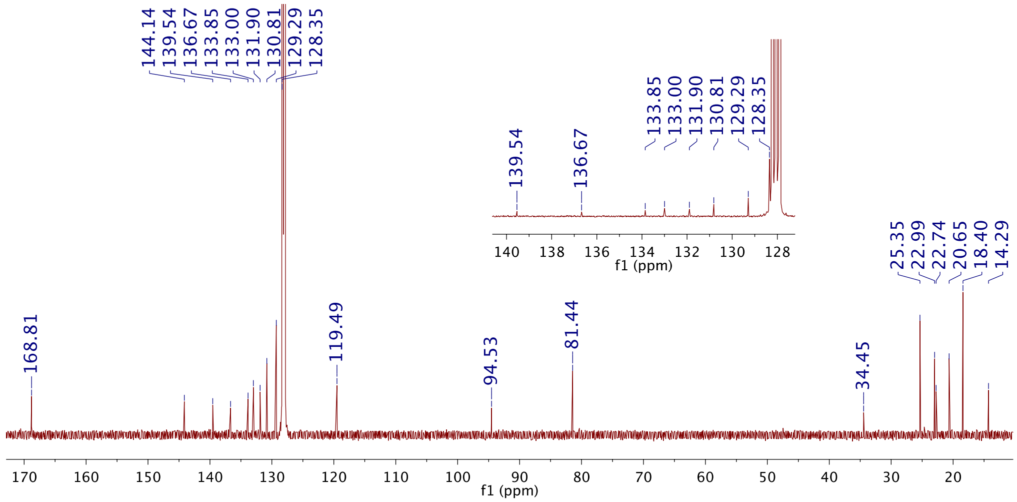

Figure S25. $^{13}C\{^1H\}$ NMR Spectrum (151 MHz, C_6D_6, 25 °C) of complex **2b** (sample contains trace *n*-pentane at 14.25, 22.72 and 34.45 ppm).

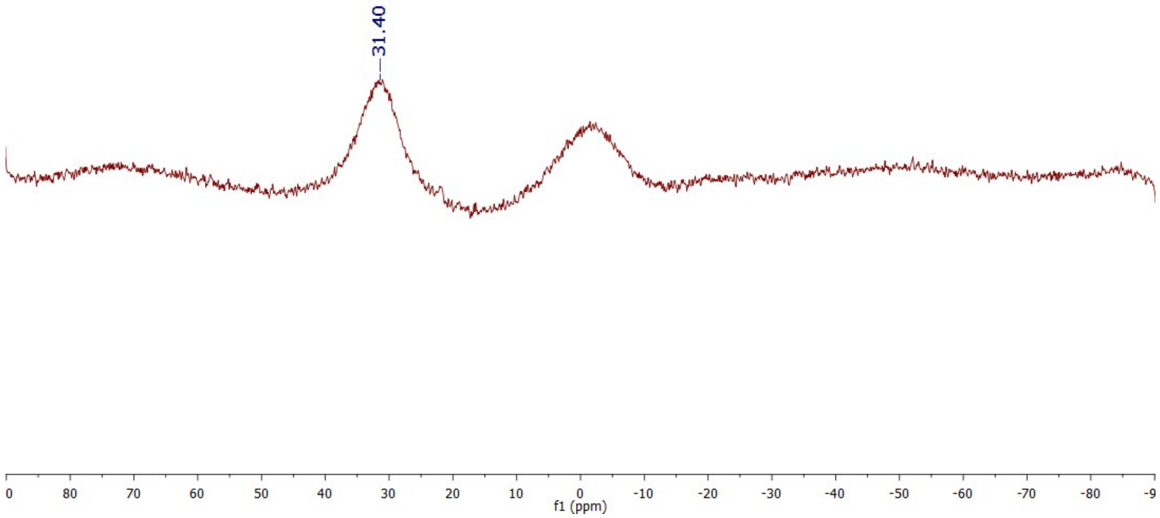

Figure 26. ^{11}B NMR Spectrum (128 MHz, 25 °C) of **2b** in C_6D_6. Note: spectrum contains a broad borosilicate peak at 0ppm.

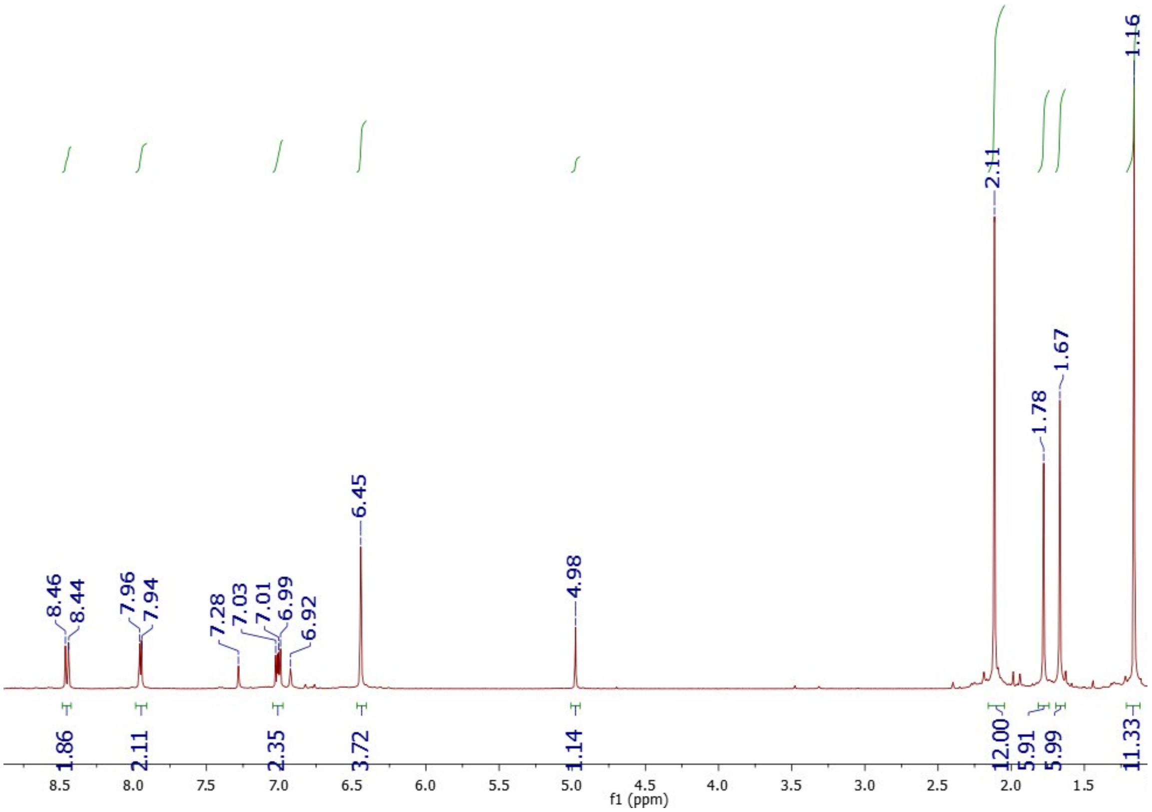

Figure S27. ^{1}H NMR Spectrum (400 MHz, C_6D_5Br, 25 °C) of complex **3b**.

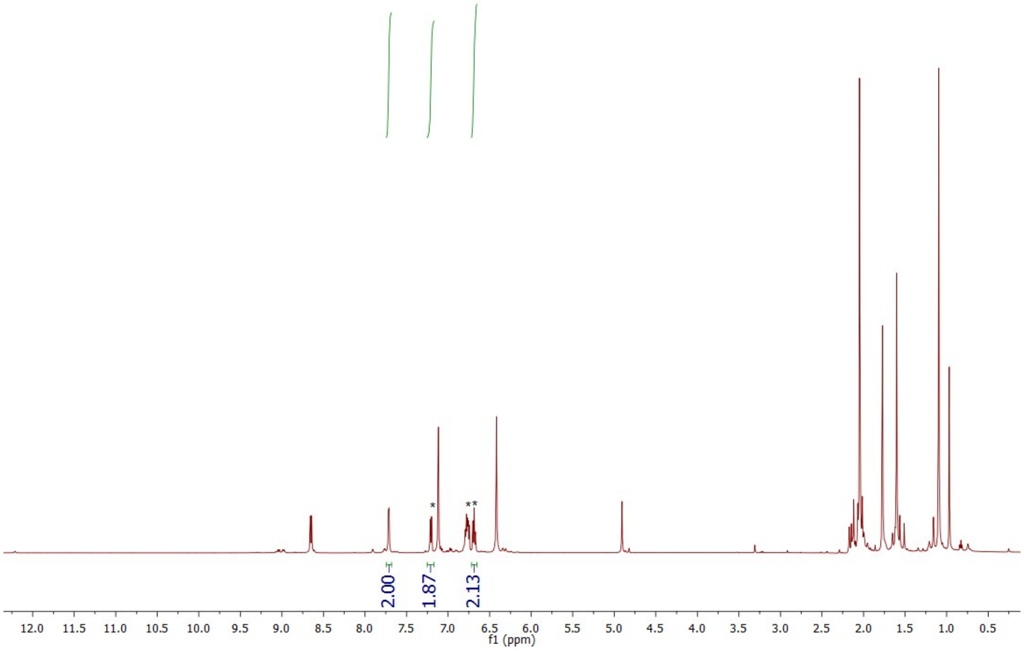

Figure S28. ^{1}H NMR Spectrum (500 MHz, C_6D_6, 25 °C) of elemental analysis sample of **3b**·(PhBr). Bromobenzene resonances are marked with an asterisk.

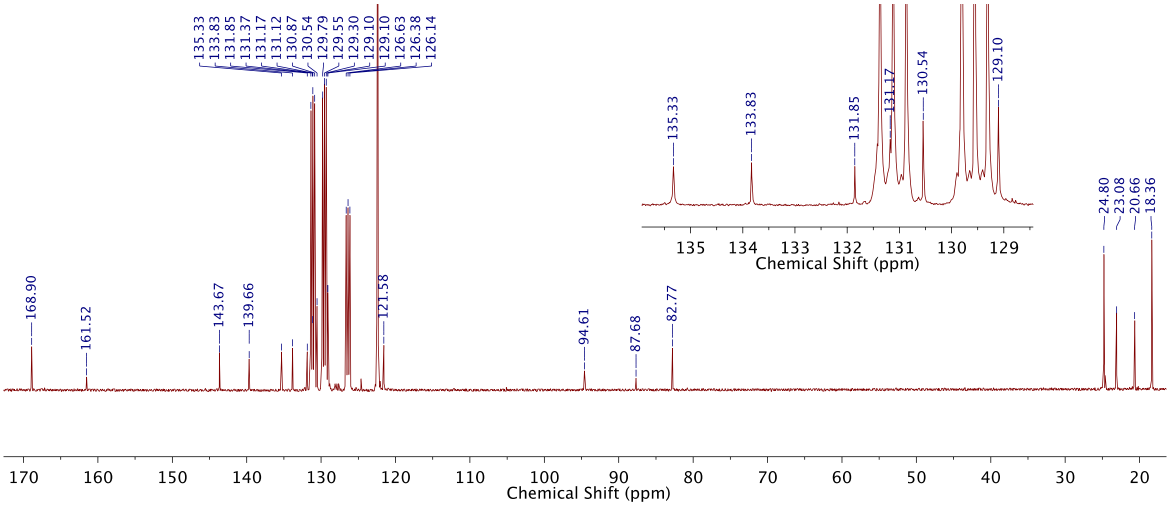

Figure S29. $^{13}C\{^1H\}$ NMR Spectrum (101 MHz, C_6D_5Br, 25 °C) of complex **3b**.

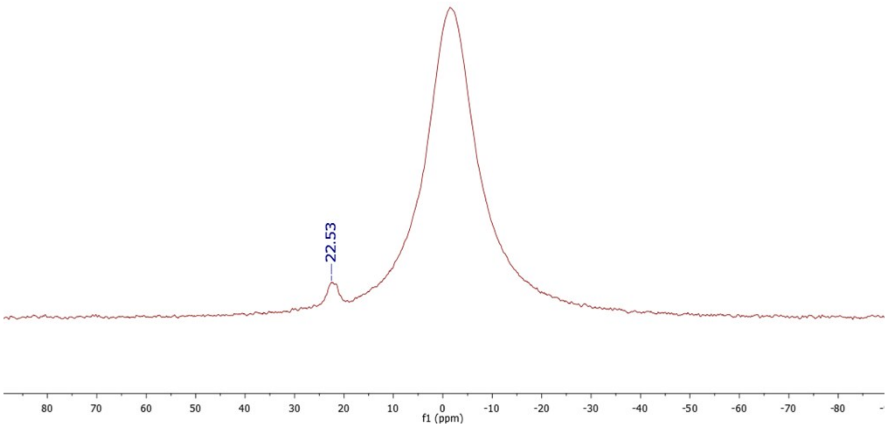

Figure S30. ^{11}B NMR Spectrum (193 MHz, 25 °C) of **3b** in C_6D_5Br. Note: spectrum contains a broad borosilicate peak.

8. IR Spectra

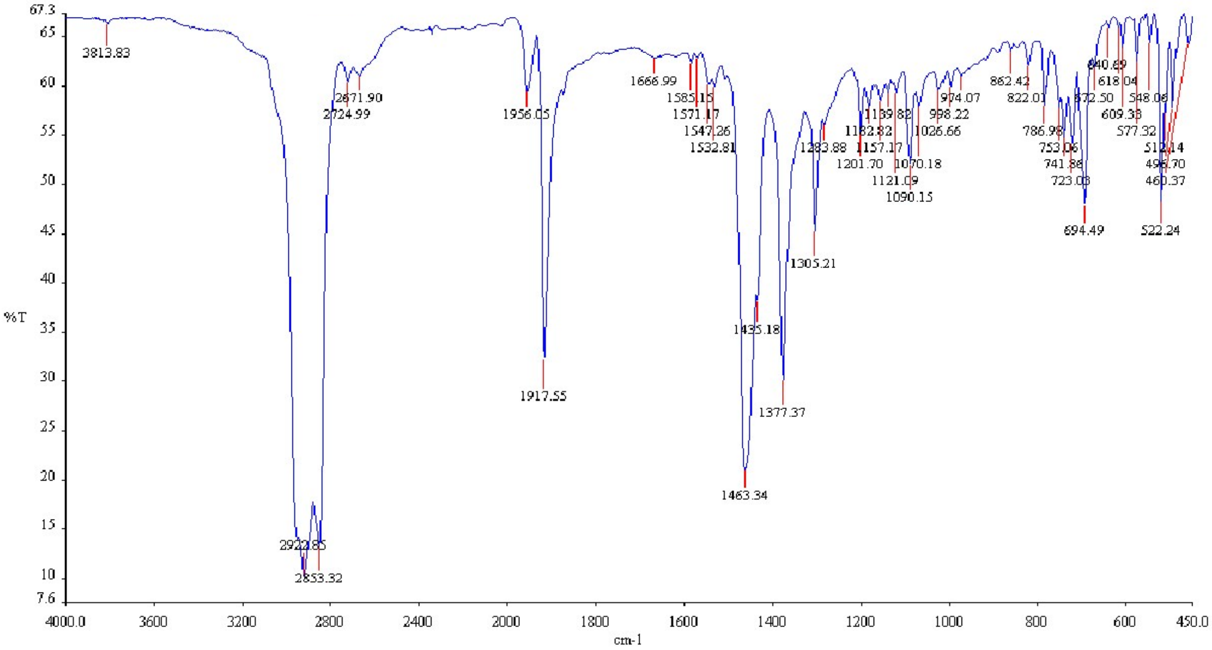

Figure S31. FT-IR Spectrum of **1a** as a nujol mull.

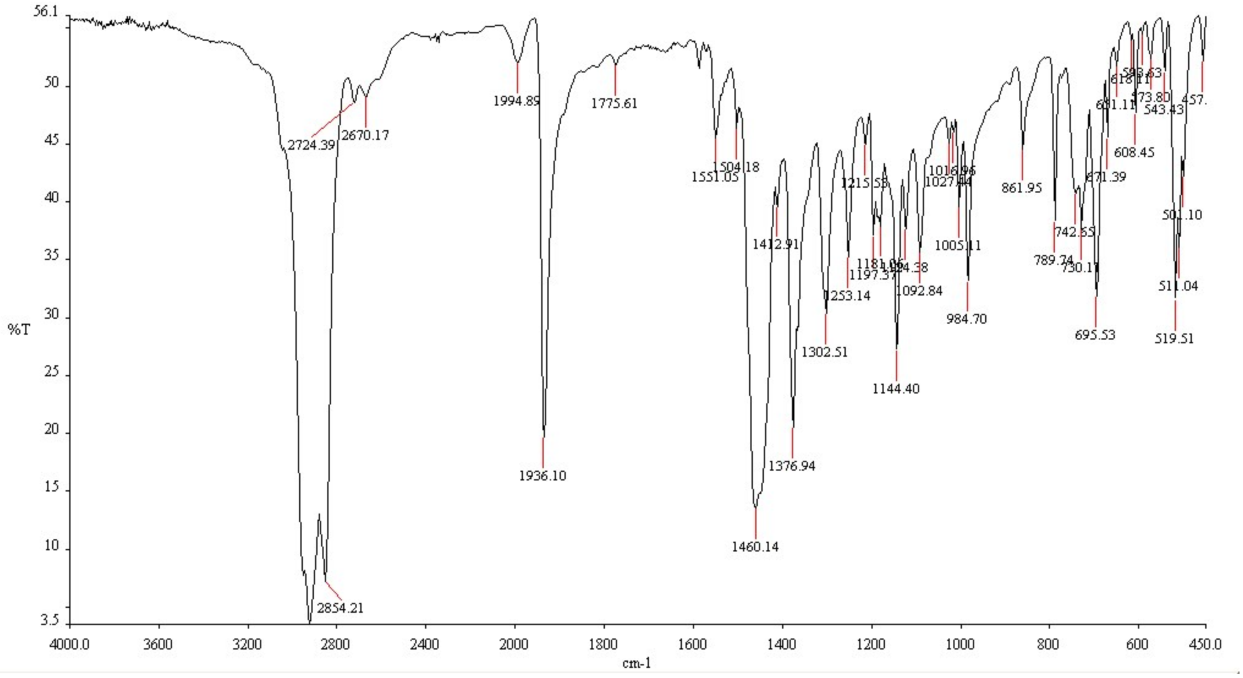

Figure S32. FT-IR spectrum of **2a** as a nujol mull.

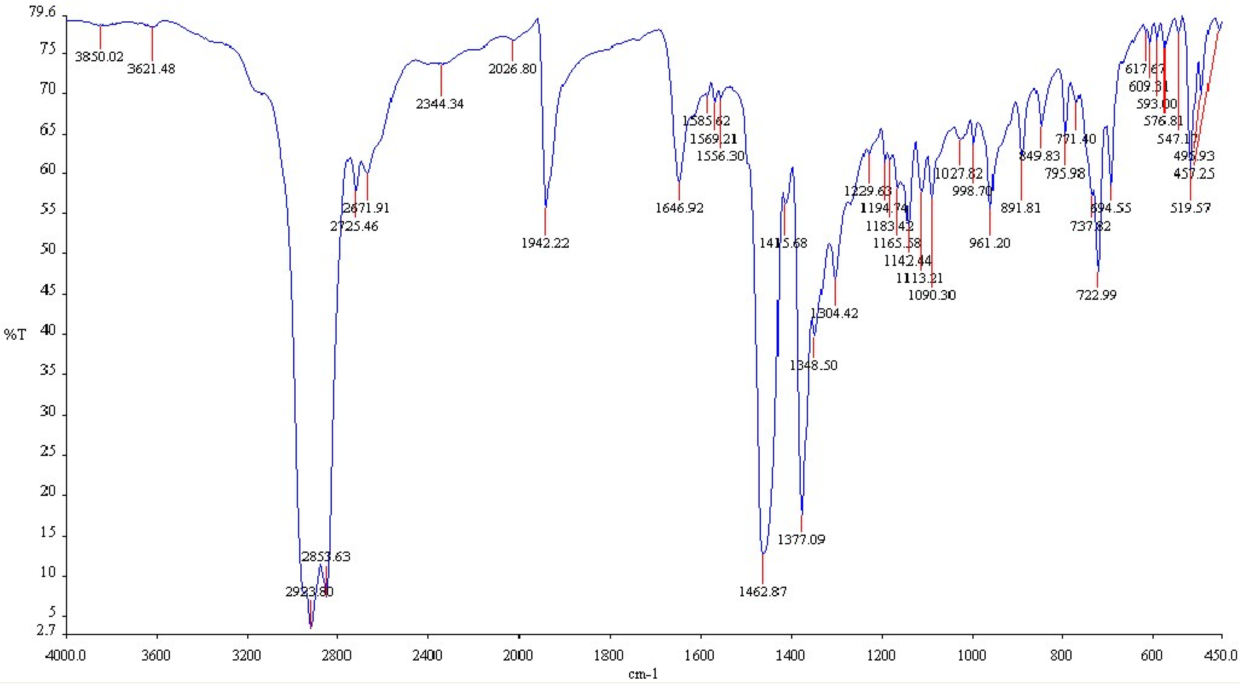

Figure S33. FT-IR spectrum of **3a** as a nujol mull.

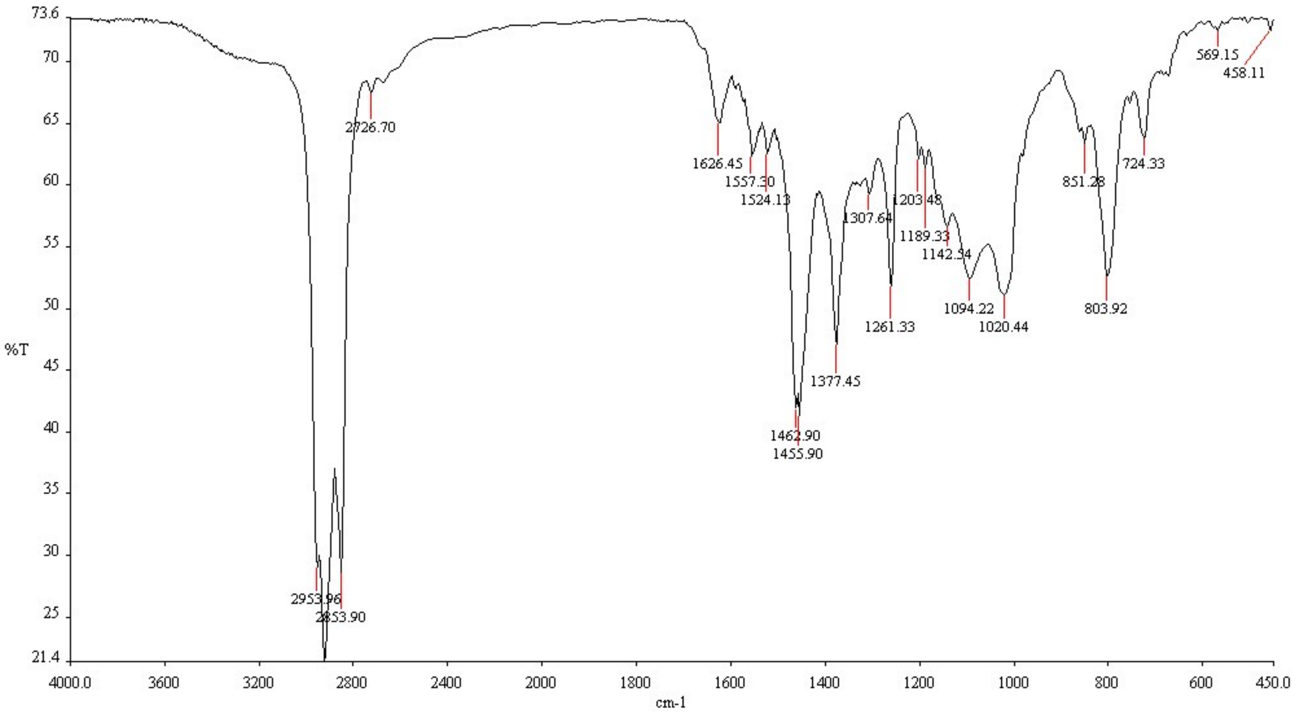

Figure S34 FT-IR spectrum of **3b** as a nujol mull.

9. References:

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