Combination of Redox-Active Ligand and Lewis Acid for Dioxygen Reduction with π-Bound Molybdenum-Quinonoid Complexes

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I. Experimental Details

II. Nuclear Magnetic Resonance Spectra

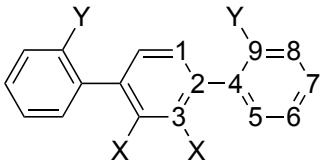
I. Experimental Details

General considerations:

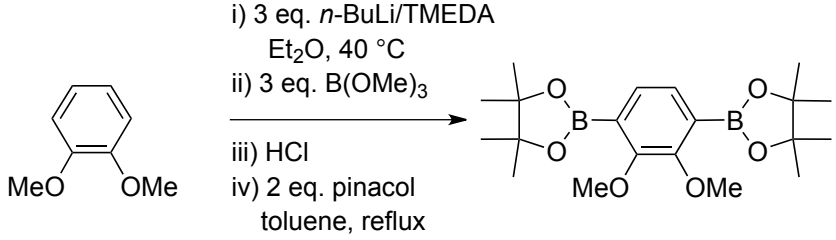
Unless indicated otherwise, reactions performed under inert atmosphere were carried out in oven-dried glassware in a glovebox under a nitrogen atmosphere purified by circulation through RCI-DRI 13X-0408 Molecular Seives 13X, 4x8 Mesh Beads and BASF PuriStar® Catalyst R3-11G, 5x3 mm (Research Catalysts, Inc.). Solvents for all reactions were purified by Grubbs' method.[1] C_6D_6 was purchased from Cambridge Isotope Laboratories and vacuum distilled from sodium benzophenone ketyl. CD_3CN, CD_2Cl_2, and $CDCl_3$ were also purchased from Cambridge Isotope Laboratories and distilled from CaH_2 prior to use. Alumina and Celite were activated by heating under vacuum at 200 °C for 24 hours. ^1H, ^{19}F, and ^{31}P NMR spectra were recorded on Varian Mercury 300 MHz spectrometers at ambient temperature, unless denoted otherwise. ^{13}C NMR spectra were recorded on a Varian INOVA-500 MHz spectrometer. ^1H and ^{13}C NMR chemical shifts are reported with respect to internal solvent: 7.16 ppm and 128.06 ppm for C_6D_6, 1.94 ppm and 118.26 for CD_3CN, 5.32 ppm and 53.84 ppm for CD_2Cl_2, and 7.26 ppm and 77.16 ppm for $CDCl_3$, respectively. ^{19}F and ^{31}P NMR chemical shifts are reported with respect to an external standard of C_6F_6 (-164.9 ppm) and 85% H_3PO_4 (0.0 ppm).

Powder and thin film ATR-IR measurements were obtained by placing a powder or drop of solution of the complex on the surface of a Bruker APLHA ATR-IR spectrometer probe and allowing the solent to evaporate (Platinum Sampling Module, diamond, OPUS software package) at 2 cm^{-1} resolution. Solution IR spectra were recorded on a Thermo-Fisher Scientific Nicolet 6700 FTIR spectrometer using a CaF_2 plate solution cell. Fast atom bombardment-mass spectrometry (FAB-MS) analysis was performed with a JEOL JMS-600H high resolution mass spectrometer. Gas chromatography-mass spectrometry (GC-MS) analysis was performed upon filtering the sample through a plug of silica gel. Electrochemical measurements were recorded with a Pine Instrument Company AFCBP1 bipotentiostat using the AfterMath software package. Cyclic voltammograms were recorded on ca. 2 mM solutions of the relevant complex in the glovebox at 20 °C with an auxiliary Pt-coil electrode, a Ag/Ag^+ reference electrode (0.01 M $AgNO_3$, 0.1 M [^{n}Bu4N$^+$][PF_6^-] in MeCN), and a 3.0 mm glassy carbon electrode disc (BASI). The electrolyte solution was 0.1 M [^{n}Bu4N$^+$][PF_6^-] in THF. All reported values are referenced to an internal ferrocene/ferrocenium couple. Elemental analysis was conducted by Robertson Microlit Labs (Ledgewood, NJ).

Unless otherwise noted all chemical reagents were purchased from commercial sources and used without further purification. Pinacol, 2-bromoiodobenzene, $HNpic_2$ ($HNpic_2$ = di(2-picolyl)amine), and *para*-trifluoromethylphenylboronic acid were purchased from Alfa Aesar. Veratrole and TMEDA were purchased from Alfa Aesar and distilled from CaH_2 prior to use. $B(OMe)_3$ was purchased from Alfa Aesar and distilled from sodium prior to use. Chlorodiisopropylphosphine and $Cu(MeCN)_4OTf$ were purchased from Sigma Aldrich. Me_2SiCl_2, Et_2SiCl_2, $^iPr_2SiCl_2$, and $(ClMe_2Si)_2$ were purchased from Sigma Aldrich and distilled from CaH_2 prior to use. $(ClEt_2Si)_2O$ was prepared by hydrolysis of Et_2SiCl_2 followed by fractional distillation. Assignments of NMR spectra are given corresponding to the following numbering scheme:

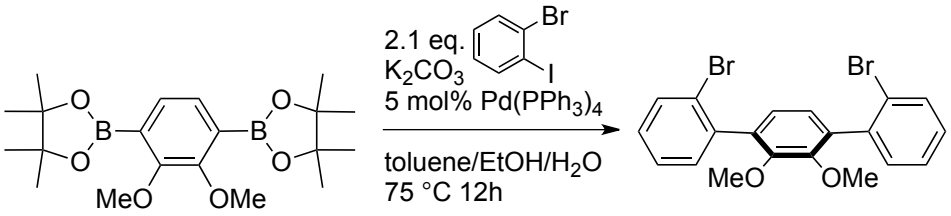


Synthesis of 2,3-dimethoxyphenylene-1,4-bis(pinacolato)boronic ester



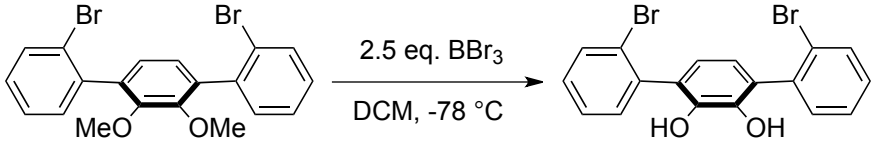
Adapted from the literature.[2] On the Schlenk line, veratrole (10.0 mL, 78.5 mmol) and TMEDA (20.0 mL, 133 mmol) were added via syringe under a counter-flow of N_2 to a 1000 mL Schlenk bomb charged with Et_2O (500 mL) and a large stir bar and fitted with a rubber septum. The bomb was cooled toca. 4 °C using an ice bath, and under a counter-flow of N_2 *n*BuLi (100 mL, 2.5 M, 250 mmol) was added via Teflon cannula transfer. The ice bath was removed, the bomb was sealed with a screw-in Teflon stopper and heated to 40 °C (CAUTION: *Always* use a blast shield and all necessary personal protective equipment when heating/manipulating pyrophorics in a sealed vessel.) for 4 hours with *vigorous* stirring (Note: large amounts of precipitate form during this stage, and if adequate stirring is not maintained the final yield will be significantly diminished). The reaction was removed from heat and once again cooled to ca. 4 °C using an ice bath and the Teflon stopper replaced with a rubber septum. $B(OMe)_3$ (29.0 mL, 260 mmol) was then added via syringe under counterflow of N_2 with vigorous stirring. After complete addition, the bomb was once again sealed with the screw-in Teflon stopper, and the reaction allowed to warm to room temperature over the course of 12 hours with stirring. The bomb was again cooled to ca. 4 °C using an ice bath, opened to air, and the mixture quenched with the slow addition of HCl (6 M, 500 mL, 3 mol). All further manipulations were performed in air. Upon complete addition of HCl, the mixture was transferred to a 2L separatory funnel and the layers separated. The aqueous layer was washed with Et_2O (2 x 200 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated via rotary evaporation. The residue was combined with pinacol (19 g, 160 mmol) and toluene (50 mL) in a 500 mL round bottom flask charged with a stir bar and equipped with a Dean-Stark trap. The mixture was then refluxed for 4 hours with stirring. After cooling to room temperature, all volatiles were removed by rotary evaporation and the residue was recrystallized from hot hexanes (ca. 200 mL) at -30 °C to afford approximately 10 g of the desired product as off-white powder/microcrystalline solid. Concentration of the filtrate followed by recrystallization from pentane can afford approximately another 5 g of desired product. Total isolated yield is 15.449 g (50.5%). The obtained product displayed a ^1H NMR spectrum matching that previously reported in literature.[2] ^1H NMR (300 MHz, d_6-acetone), δ(ppm): 7.31 (s, 2H, Ar-C*H*), 3.80 (s, 6H, OCH_3), 1.34 (s, 24H, C(CH_3)$_2$).

Synthesis of 1,4-bis(2-bromophenyl)-2,3-dimethoxybenzene



Suzuki coupling conditions were adapted from a previously published procedure.[3] 2,3-dimethoxyphenylene-1,4-bis(pinacolato)boronic ester (15.4993 g, 39.7 mmol), K_2CO_3 (26 g, 190 mmol), toluene (340 mL), H_2O (185 mL), EtOH (185 mL) were combined in a 1000 mL Schlenk bomb with screw-in Teflon stopper. The mixture was degassed by three freeze-pump-thaw cycles, and 2-bromoiodobenzene (10.7 mL, 83.3 mmol) and $Pd(PPh_3)_4$ (1.744 g, 1.51 mmol) were added under a counter-flow of N_2. The mixture was again degassed by a freeze-pump-thaw cycle, and the Schlenk tube was placed in an oil bath and heated to 80°C. After stirring for 12 h, the mixture was allowed to cool to room temperature, and further manipulations were performed in air. The volatiles removed via rotary evaporation. H_2O (250 mL) and DCM (250 mL) were added and the mixture transferred to a 1L separatory funnel with vigorous mixing. The layers were separated and the aqueous layer washed with DCM (2 x 100 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated via rotary evaporation. The residue was dissolved in hot MeOH (100 mL), filtered, and cooled to -30 °C in a freezer. After 12 hours the resulting white precipitate was collected on a glass frit, rinsing with minimal cold MeOH and dried under vacuum to afford the desired product (10.3468 g, 58.1%). ^{1}H NMR (300 MHz, $CDCl_3$), δ(ppm): 7.70 (d, 8.0 Hz, 2 H, Ar-C*H*), 7.39 (d, 5.5 Hz, 4 H, Ar-C*H*), 7.25 (m, 2 H, Ar-C*H*), 6.99 (s, 2 H, Ar-C$_1$*H*), 3.70 (s, 6 H, OC*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$), δ(ppm): 150.58 (s, Ar-*C*H), 139.44 (s, Ar-C*H*), 135.88 (s, Ar-C*H*), 132.74 (s, Ar-C*H*), 131.56 (s, Ar-C*H*), 129.07 (s, Ar-C*H*), 127.10 (s, Ar-C*H*), 125.33 (s, Ar-C*H*), 123.92 (s, Ar-C*H*), 60.97 (s, OC*H*$_3$). MS (m/z): calcd, 447.9496 $[M]^+$; found, 447.9483 (FAB^+, $[M]^+$).

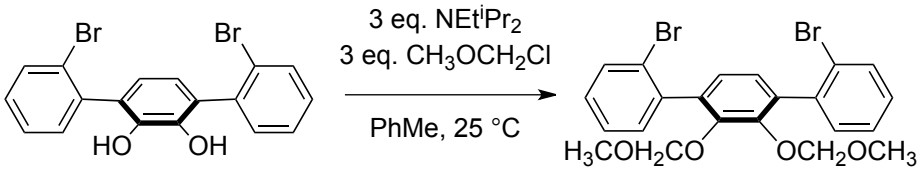
Synthesis of 1,4-bis(2-bromophenyl)-2,3-dihydroxybenzene (1^{Br})



In a Schlenk flask under N_2 counterflow, 1,4-di(2-bromophenyl)-2,3-dimethoxybenzene (8.4322 g, 18.8 mmol) was dissolved in DCM (50 mL) with stirring. The flask was fitted with a septum and chilled to -78 °C in a dry ice/acetone bath. BBr_3 (4.5 mL neat, 1 mmol) was added to the flask drop-wise via syringe over 5 min. The reaction was allowed to warm to room temperature over 12 h. After cooling with an ice/water bath, the reaction was then quenched by *slow* dropwise addition of H_2O until bubbling ceased. Further manipulations performed in air. The reaction mixture was further diluted with H_2O (50 mL). The mixture was transferred to a separatory funnel, mixed well, and the layers separated. The aqueous layer was washed with DCM (2 x 25 mL). The combined organics were dried with $MgSO_4$, filtered, and concentrated via rotary evaporation to yield the desired product as a tan powder (7.389 g, 93.5%). ^{1}H NMR (300 MHz, $CDCl_3$),

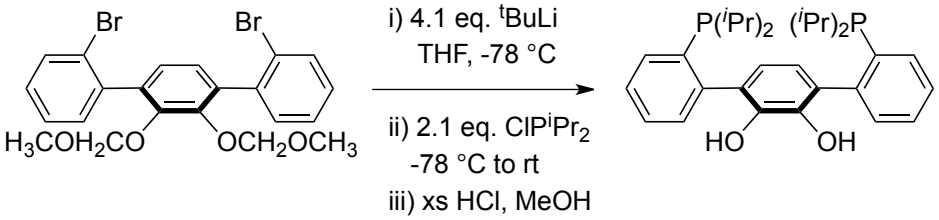
δ(ppm): 7.75 (d, 2 H, Ar-C*H*), 7.46 (s, 2 H, Ar-C*H*), 7.44 (s, 2 H, Ar-C*H*), 7.34-7.27 (m, 2 H, Ar-C*H*), 6.84 (s, 2 H, Ar-C$_1$*H*), 5.34 (br, 2 H, O*H*). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ(ppm): 140.9 (s, Ar-C*H*), 138.1 (s, Ar-C*H*), 133.2 (s, Ar-C*H*), 132.1 (s, Ar-C*H*), 129.7 (s, Ar-C*H*), 127.9 (s, Ar-C*H*), 127.7 (s, Ar-C*H*), 124.0 (s, Ar-C*H*), 121.9 (s, Ar-C*H*). MS (m/z): calcd, 419.9184 $[M]^+$; found, 419.9180 (FAB^+, $[M]^+$).

Synthesis of 1,4-bis(2-bromophenyl)-2,3-di(methoxymethylether)benzene



A Schlenk flask was charged with 1,4-di(2-bromophenyl)-2,3-dihydroxybenzene (6.0973 g, 14.5 mmol) dissolved in PhMe (100 mL). Under N_2 counter-flow, a 2.1 M solution of chloromethyl methyl ether in toluene (21.0 mL, 44.1 mmol)[4] was added to the stirred reaction mixture, followed by N,N-diisopropylethylamine (7.8 mL, 43.7 mmol). The reaction was allowed to stir for 12 hours at room temperature under N_2. The volatiles were removed under rotary evaporation, and further manipulations were performed in air. The residue was dissolved in H_2O (150 mL) and DCM (150 mL) and transferred to a separatory funnel. The layers were separated and the aqueous layer washed with DCM (2 x 50 mL). The combined organic extracts were dried with $MgSO_4$, filtered and concentrated under rotary evaporation to yield the desired product as a white powder (6.9031 g, 93.6%). ^{1}H NMR (300 MHz, $CDCl_3$), δ(ppm): 7.68 (d, 2 H, Ar-C*H*), 7.51-7.34 (m, 4 H, Ar-C*H*), 7.25-7.19 (m, 2 H, Ar-C*H*), 7.07 (s, 2 H, Ar-C$_1$*H*), 5.01-4.85 (br, 4 H, C*H*$_2$OCH$_3$), 2.93 (s, 6 H, CH$_2$OC*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ(ppm): 147.8 (s, Ar-C*H*), 139.4 (s, Ar-C*H*), 136.6 (s, Ar-C*H*), 132.6 (s, Ar-C*H*), 132.3 (s, Ar-C*H*), 129.0 (s, Ar-C*H*), 127.0 (s, Ar-C*H*), 126.0 (s, Ar-C*H*), 124.2 (s, Ar-C*H*), 99.2 (s, Ar-C*H*), 56.7 (s, Ar-C*H*). MS (m/z): calcd, 507.9708 $[M]^+$; found, 507.9713 (FAB^+, $[M]^+$).

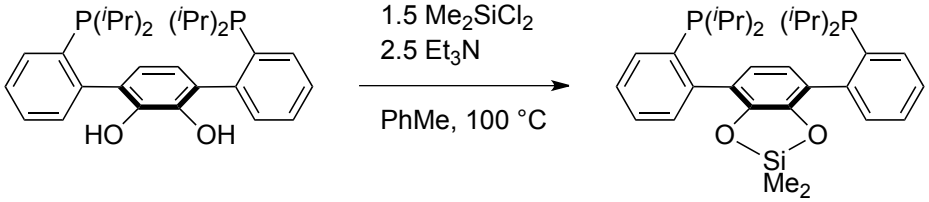
Synthesis of 1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-catechol (1a)



A Schlenk tube was charged with 1,4-di(2-bromophenyl)-2,3-di(methoxymethylether)benzene (6.9031 g, 13.6 mmol), THF (60 mL), and a stir bar. The reaction mixture was cooled to -78 °C with the use of a dry ice/acetone bath. Under a counter-flow of N_2, a 1.7 M solution of ^{t}BuLi (33.0 mL, 56.1 mmol) in pentanes was added via syringe drop-wise. A light yellow color appeared in seconds, and as the reaction was allowed to stir for 30 minutes at -78 °C, a pale orange color evolved. After stirring for 1 hour at -78 °C, chlorodiisopropylphosphine (4.60 mL, 28.6 mmol) was added to the reaction mixture via syringe under a counter-flow of N_2, inducing a light

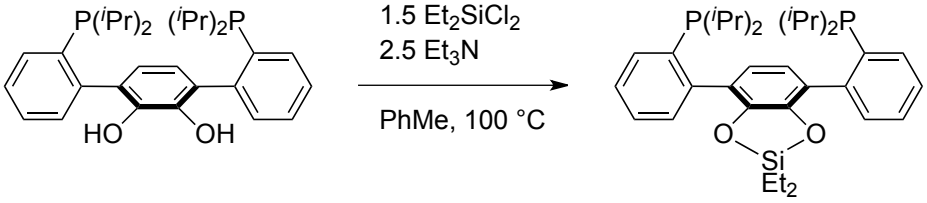
yellow color. After stirring for 1 hour at -78 °C, the reaction was removed from the dry ice/acetone bath and allowed to warm to room temperature. After stirring for 2 hours at room temperature the volatiles were removed under reduced pressure. To the residue was added degassed MeOH (60 mL) and HCl (12 M, 10 mL). The mixture was then heated to 60 °C for 4 hours. After cooling to room temperature, the volatiles were again removed under reduced pressure. All further manipulations were performed under an N_2 atmosphere in a water-tolerant nitrogen-filled glove box. The residue was treated with DCM (100 mL) and saturated aqueous K_2CO_3 (100 mL) and transferred to a separatory funnel with vigorous mixing. The layers were separated and the organics washed with saturated aqueous NH_4Cl (100 mL). The layers were again separated and the aqueous layer washed with DCM (2 x 50 mL). The combined organics were dried with $MgSO_4$, filtered, and concentrated under vacuum to afford an off-white powder. Trituration with MeOH (25 mL) afforded a white precipitate that was collected on a glass frit. The solid was washed with Et_2O (25 mL) and MeCN (25 mL), and then dried under vacuum to yield the desired product in 81.3% yield (5.4627 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ(ppm): 7.57 – 7.50 (m, 2 H, Ar-C*H*), 7.45 – 7.36 (m, 6 H, Ar-C*H*), 6.80 (s, 2 H, Ar-C$_1$*H*), 6.56, (br, 2 H, Ar-C$_3$O*H*), 2.24 (br, 2 H, PC*H*$(CH_3)_2$), 2.02 (br, 2 H, PC*H*$(CH_3)_2$), 1.20 – 0.80 (br, 24 H, PCH$(CH_3)_2$). ^{31}P{^{1}H} (121 MHz, $CDCl_3$), δ(ppm): 3.06 (br), 2.17 (br), -1.56 (s), -29.16 (s). ^{13}C{^{1}H} (126 MHz, $CDCl_3$) d: 146.25 (d), 141.00 (s), 134.00 (d), 131.99 (s), 131.67 (s), 130.02 (s), 128.90 (s), 126.97 (s), 123.95 (s), 25.04 (br), 22.47 (br), 20.00 (br), 18.97 (br). MS (m/z): calcd, 493.2425 $[M-H]^+$; found, 493.2438 (FAB^+, $[M-H]^+$).

Synthesis of dimethyl-(1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-catechol)silane (1b)



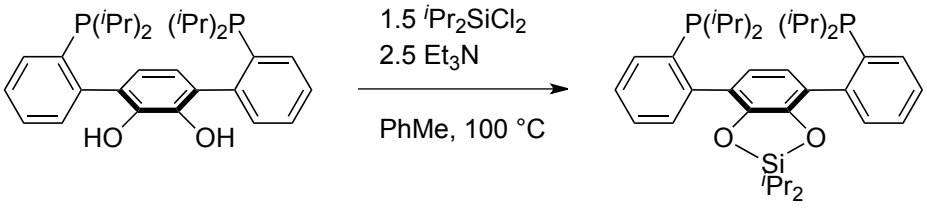
Diphosphine **1a** (2.5003 g, 5.06 mmol), Me_2SiCl_2 (0.835 g, 6.47 mmol), and Et_3N (1.2033 g, 11.9 mmol) were combined with PhMe (20 mL) in a Schlenk bomb charged with a stir bar and a screw-in Teflon stopper. The bomb was removed from the glove box and heated to 100 °C in an oil bath for 12 hours generating a white precipitate. After cooling to room temperature, the bomb was taken back into the glove box and the white precipitate filtered on celite, washing with additional PhMe. The filtrate was then concentrated *in vacuo* to yield the desired compound **1b** as a white powder in 97.5% yield (2.7152 g). ^{1}H NMR (300 MHz, C_6D_6), δ(ppm): 7.40 (m, 4 H, Ar-C*H*), 7.14 (m, 4 H, Ar-C*H*), 6.94 (s, 2 H, Ar-C$_1$*H*), 1.90 (m, 4 H, PC*H*$(CH_3)_2$), 0.99 (m, 24 H, PCH$(CH_3)_2$), 0.17 (s, 6 H, SiC*H*$_3$). ^{31}P{^{1}H} (121 MHz, C_6D_6), δ(ppm): -1.24 (s). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6), δ(ppm): 146.55 (s), 146.31 (s), 145.87 (s), 136.32 (d), 132.53 (d), 131.23 (d), 128.66 (s), 126.89 (s), 123.45 (d), 24.66 (br), 20.68 (s), 20.52 (s), 19.73 (br), -0.02 (s, Si*C*H$_3$). Compound hydrolyzed under FAB-MS conditions, only mass consistent with **1a** observed.

Synthesis of diethyl-(1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-catechol)silane (1c)



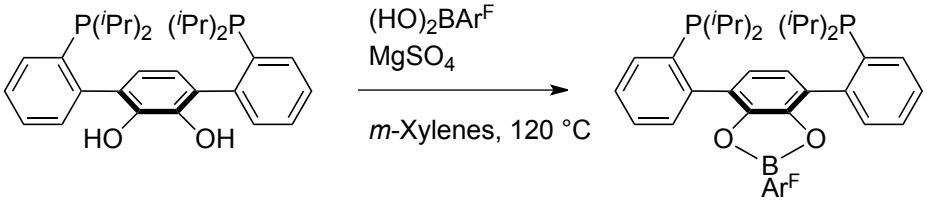
Compound **1c** was prepared analogously to above using diphosphine **1a** (0.1555 g, 0.314 mmol), Et_2SiCl_2 (0.0715 g, 0.455 mmol), and Et_3N (0.1031 g, 1.02 mmol) in PhMe (10 mL). The desired compound **1c** was isolated as a white powder in 98.5% yield (0.1793 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ(ppm): 7.55 (m, 2 H, Ar-C*H*), 7.36 (m, 6 H, Ar-C*H*), 6.75 (s, 2 H, Ar-C_1*H*), 2.03 (m, 4 H, PC*H*$(CH_3)_2$), 0.97 (m, 4 H, PCH(C*H*$_3)_2$ and SiC*H*$_2$C*H*$_3$). ^{31}P{^{1}H} (121 MHz, $CDCl_3$), δ(ppm): -2.06 (br), -2.73 (br). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ(ppm): 146.15 (s), 145.85 (s), 145.61 (s), 135.77 (d), 132.41 (s), 131.14 (s), 123.22 (s), 126.73 (d), 123.15 (s), 24.36 (d, PC*H*$(CH_3)_2$), 20.29 (s, PCH(C*H*$_3)_2$), 20.14 (s, PCH(C*H*$_3)_2$), 19.67 (d, PCH(C*H*$_3)_2$), 6.72 (s, SiCH$_2$C*H*$_3$), 5.49 (s, SiC*H*$_2$CH$_3$). MS (m/z): calcd, 579.2977 $[M+H]^+$; found, 579.2980 (FAB^+, $[M+H]^+$).

Synthesis of diisopropyl-(1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-catechol)silane (1d)



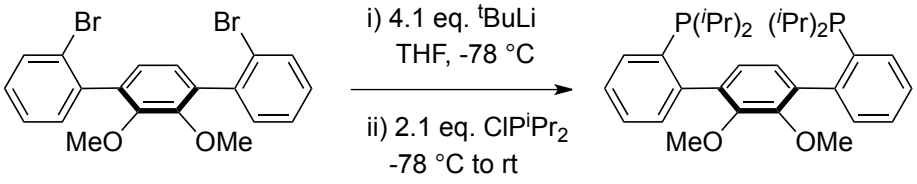
Compound **1d** was prepared analogously to above using diphosphine **1a** (0.1518 g, 0.307 mmol), ^{i}Pr$_2$SiCl$_2$ (0.0976 g, 0.527 mmol), and Et_3N (0.0942 g, 0.931 mmol) in PhMe (10 mL). The desired compound **1d** was isolated as a white powder in 96.7% yield (0.1799 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ(ppm): 7.58 (m, 2 H, Ar-C*H*), 7.38 (m, 6 H, Ar-C*H*), 6.76 (s, 2 H, Ar-C_1*H*), 2.03 (m, 4 H, PC*H*$(CH_3)_2$), 1.05 (m, 42 H, PCH(C*H*$_3)_2$ and SiC*H*$(CH_3)_2$). ^{31}P{^{1}H} (121 MHz, $CDCl_3$), δ(ppm): -2.61 (br), -2.98 (br). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ(ppm): 146.62 (s), 145.89 (s), 145.66 (s), 135.67 (d), 132.39 (s), 131.42 (s), 128.05 (s), 126.57 (m), 123.32 (s), 24.46 (d, PC*H*$(CH_3)_2$), 20.31 (s, PCH(C*H*$_3)_2$), 20.17 (s, PCH(C*H*$_3)_2$), 19.78 (d, PCH(C*H*$_3)_2$), 16.04 (s, SiCH(C*H*$_3)_2$), 13.02 (s, SiC*H*$(CH_3)_2$). MS (m/z): calcd, 607.3290 $[M+H]^+$; found, 607.3290 (FAB^+, $[M+H]^+$).

Synthesis of 4-(trifluoromethyl)phenyl-(1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-catechol)borane (1e)



In the wet glove box under an atmosphere of N_2, **1a** (1.53 g, 3.09 mmol) and *p*(F_3C)$C_6H_4B(OH)_2$ (0.5876 g, 3.09 mmol), and $MgSO_4$ (0.4 g, 3.3 mmol) were combined in a Schlenk tube with *m*-xylenes (10 mL). The reaction was heated to 120 °C for 2.5 hours. The volatiles were removed under vacuum, the residue washed with Et_2O (10 mL), and the product extracted with C_6H_6 (15 mL), filtered through Celite, and concentrated under vacuum to yield 0.9 g (44.8%) of the desired product as an off-white solid. ^{1}H NMR (300 MHz, C_6D_6), δ(ppm): 7.80 (m, 2 H, Ar-C*H*), 7.52 (m, 2 H, Ar-C*H*), 7.37 (m, 2 H, Ar-C*H*), 7.24 (m, 2 H, Ar-C*H*), 7.20 (s, 2 H, Ar-C_1*H*), 1.92 (m, 4 H, PC*H*(CH_3)$_2$), 0.98 (m, 24 H, PCH(C*H*$_3$)$_2$). ^{31}P{^{1}H} (121 MHz, C_6D_6), δ(ppm): -1.54 (s). ^{19}F NMR (282 MHz, C_6D_6 , 25 °C), δ(ppm): -61.52 (s). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6), δ(ppm): 146.01 (s), 145.02 (s), 144.78 (s), 136.57 (s), 136.39 (s), 135.78 (s), 133.74 (q, *C*F_3), 132.79 (s), 131.12 (s), 128.88 (s), 127.62 (s), 125.40 (d), 124.85 (m), 24.70 (d, PC*H*(CH_3)$_2$), 20.45 (s, PCH(C*H*$_3$)$_2$), 20.29 (s, PCH(C*H*$_3$)$_2$), 19.75 (d, PCH(C*H*$_3$)$_2$). MS (m/z): calcd, 649.2784 $[M+H]^+$; found, 649.2794 (FAB^+, $[M+H]^+$).

Synthesis of 1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-dimethoxybenzene (1f)

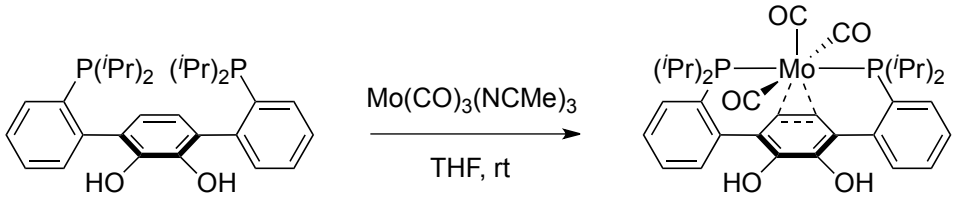


1^{Br}f **1f**

A Schlenk tube was charged with 1,4-di(2-bromophenyl)-2,3-di(methoxy)benzene (2.0449 g, 4.56 mmol), THF (30 mL), and a stir bar. The reaction mixture was cooled to -78 °C with the use of a dry ice/acetone bath. Under a counter-flow of N_2, a 1.7 M solution of ^{t}BuLi (11.0 mL, 18.7 mmol) in pentanes was added via syringe dropwise. A light yellow color appeared in seconds, and as the reaction was allowed to stir for 30 min at -78 °C, an orange color evolved. After stirring for 1 hour at -78 °C, chlorodiisopropylphosphine (1.55 mL, 9.74 mmol) was added to the reaction mixture via syringe under a counter-flow of N_2, inducing a light yellow color. After stirring for 1h at -78 °C, the reaction was removed from the dry ice/acetone bath and allowed to warm to room temperature. After stirring for 2 hours at room temperature the volatiles were removed under reduced pressure. Further manipulations were performed under an N_2 atmosphere in a wet glove box. The residue was treated with DCM (50 mL) and H_2O (50 mL) and transferred to a separatory funnel with vigorous mixing. The layers were

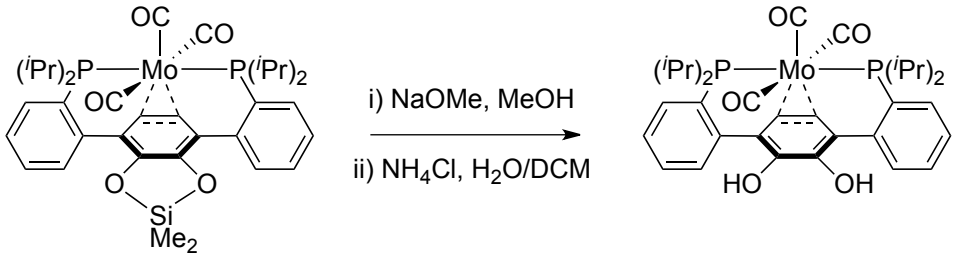
separated and the aqueous washed with DCM (2 x 25 mL). The combined organics were dried with $MgSO_4$, filtered, and concentrated under vacuum to an off-white powder. Trituration with MeOH (20 mL) afforded a white precipitate that was collected on a glass frit, and then dried under vacuum to yield the desired product in 60.3% (1.4385 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ(ppm): 7.42 (m, 2 H, Ar-C*H*), 7.12 (m, 6 H, Ar-C*H*), 7.00 (s, 2 H, Ar-C$_1$*H*), 3.56 (s, 6 H, OCH_3), 2.00 (m, 2 H, PC*H*(CH_3)$_2$), 1.79 (m, 2 H, PC*H*(CH_3)$_2$), 1.20 – 0.75 (m, 24H, PCH(CH_3)$_2$). ^{31}P{^{1}H} (121 MHz, $CDCl_3$), δ(ppm): -1.13 (s). ^{13}C{^{1}H} (126 MHz, $CDCl_3$), δ(ppm): 150.43 (s), 146.83 (d), 136.44 (m), 132.32 (s), 130.77 (s), 127.97 (s), 126.55 (s), 125.77 (s), 60.12 (s), 25.22 (br), 24.41 (br), 20.0-19.0 (m). MS (m/z): calcd, 523.2895 $[M+H]^+$; found, 523.2891 (FAB^+, $[M+H]^+$).

Synthesis of [1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-catechol] tricarbonylmolybdenum(0) (2a)



1a **2a**

From **1a**: $Mo(CO)_3(MeCN)_3$ (1.3010 g, 4.29 mmol) and **1a** (1.0494 g, 2.12 mmol) were combined with THF (20 mL) and stirred at room temperature for 72 hours, generating a dark brown solution. Upon completion of the reaction (a single major peak near 50 ppm by ^{31}P NMR), the volatiles were removed under reduced pressure and the residue then triturated with MeCN (15 mL). The resulting orange precipitate was collected on a glass frit and washed with minimal MeCN until the brown filtrate had lightened to pale orange. The remaining solid was then dried under vacuum to yield 0.6192 g (43.3%) of the desired product (spectroscopic features reported below).

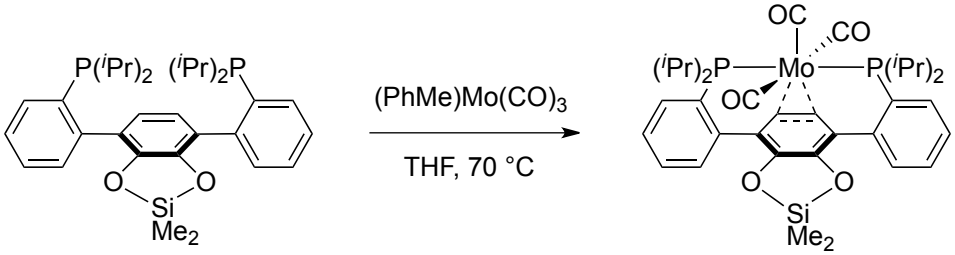


2b **2a**

From **2b**: In a wet glove box under N_2, NaOMe (0.3380 g, 6.25 mmol) was added to a stirred suspension of **2b** (1.5179 g, 2.08 mmol) in MeOH (15 mL) in a 100 mL round bottom flask, and the solution rapidly became homogeneous. After stirring for 1 hour at

room temperature, the volatiles were removed under reduced pressure. The residue was then treated with a saturated aqueous NH_4Cl solution (50 mL) and DCM (50 mL) and transferred to a separatory funnel and thoroughly mixed. The layers were separated and the aqueous layer washed with DCM (2 x 25 mL). The combine organics were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting orange powder was transferred to a dry glove box and residual H_2O/MeOH removed by triturating the powder in dry MeCN, collecting the solid on a glass frit, washing with additional dry MeCN, and finally drying under vacuum to yield 1.3072 g (93.3%) of the desired product. Crystals suitable for X-ray diffraction were grown from slow evaporation of a saturated C_6H_6 solution. ^{1}H NMR (300 MHz, C_6D_6 , 25 °C), δ(ppm): 7.55 (m, 4 H, Ar-C*H*), 7.12 (m, 4 H, Ar-C*H*), 5.73 (t, J_{PH} = 4 Hz, 2 H, Ar-C_1*H*), 5.26 (s, 2 H, Ar-C_1O*H*), 2.66 (m, PC*H*(CH_3)$_2$), 2.54 (m, PC*H*(CH_3)$_2$). 1.62 (m, 6H, PCH(C*H*$_3$)$_2$), 1.20 (m, 12H, PCH(C*H*$_3$)$_2$), 0.92 (m, 6 H, PCH(C*H*$_3$)$_2$). ^{31}P NMR (121 MHz, C_6D_6 , 25 °C), δ(ppm): 50.62 (s). ^{13}C NMR (125 MHz, C_6D_6 , 75 °C), δ(ppm): 224.00 (t, Mo-*C*O), 214.23 (t, Mo-*C*O), 212.48 (t, Mo-*C*O), 144.34 (t, Ar-*C*$_4$), 141.67 (s, Ar-*C*$_3$), 132.77 (t, Ar-*C*$_9$), 131.96 (s, Ar-*C*$_5$), 130.06 (s, Ar-*C*$_8$), 129.21 (s, Ar-*C*$_7$), 127.65 (s, Ar-*C*$_2$), 122.25 (t, Ar-*C*$_6$), 87.58 (s, Ar-*C*$_1$), 35.92 (t, P*C*H(CH_3)$_2$), 32.39 (t, P*C*H(CH_3)$_2$), 20.82 (m, PCH(*C*H$_3$)$_2$), 20.02 (s, PCH(*C*H$_3$)$_2$), 19.67 (m, PCH(*C*H$_3$)$_2$), 19.57 (m, PCH(*C*H$_3$)$_2$). IR (DCM), ν_{CO} (cm^{-1}): 1959.3, 1843.2 (br). λ_{max} (THF, nm), ε ($M^{-1}cm^{-1}$): 478, 3.9x10^3; 355, 8.2x10^3; 285, 3.3x10^4. Anal. Calcd for [**2a**], $C_{33}H_{40}MoO_5P_2$: C, 58.76; H, 5.98. Found: C, 59.01; H, 5.72.

Synthesis of [dimethyl-(1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-catechol)silane]tricarbonylmolybdenum(0) (2b)

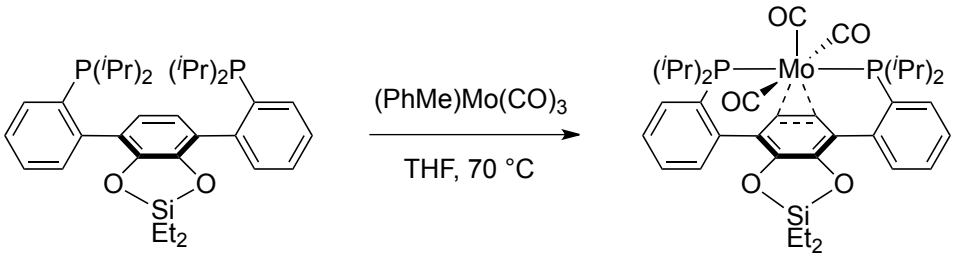


1b **2b**

Diphosphine **1b** (2.204 g, 4.00 mmol) and (PhMe)Mo(CO)$_3$ (1.314 g, 4.83 mmol) were combined in THF (10 mL) and added to a Schlenk tube charged with a stir bar and fitted with a screw-in Teflon stopper. The sealed vessel was removed from the glove box and heated to 70 °C with stirring in an oil bath for 3 hours. After complete conversion (a single peak at 52 ppm by ^{31}P NMR), the Schlenk tube was returned to the glove box and the volatiles were removed under reduced pressure. The residue was triturated with MeCN (10 mL), and the resulting orange precipitate was collected on a glass frit, washing with minimal additional MeCN until the filtrate was a pale orange. The orange powder was then dried under vacuum to yield 2.7561 g (94.2%) of the desired product. Crystals suitable for X-ray diffraction were grown from cooling of a saturated MeCN solution at -35 °C. ^{1}H NMR (300 MHz, C_6D_6 , 25 °C), δ(ppm): 7.92 (d, 2 H, Ar-C*H*), 7.55 (d, 2 H, Ar-C*H*), 7.25 (t, 2 H, Ar-C*H*), 7.10 (t, 2 H, Ar-C*H*), 5.69 (t, J_{PH} = 4 Hz, 2 H, Ar-C_1*H*), 2.67 (m, PC*H*(CH_3)$_2$), 2.44 (m, PC*H*(CH_3)$_2$). 1.60 (m, 6H, PCH(C*H*$_3$)$_2$), 1.25

(m, 6H, PCH(CH_3)$_2$), 1.13 (m, 6H, PCH(CH_3)$_2$), 0.87 (m, 6 H, PCH(CH_3)$_2$), 0.58 (s, 3H, MeCN CH_3) 0.08 (s, 3 H, SiCH_3), -0.16 (s, 3 H, SiCH_3). ^{31}P NMR (121 MHz, C_6D_6 , 25 °C), δ(ppm): 51.37 (s). ^{13}C NMR (125 MHz, C_6D_6 , 25 °C), δ(ppm): 223.96 (t, Mo-*C*O), 214.11 (t, Mo-*C*O), 212.85 (t, Mo-*C*O), 146.48 (s, Ar-C_3), 144.58 (t, Ar-C_4), 131.45 (t, Ar-C_9), 131.27 (s, Ar-C_5), 131.17 (t, Ar-C_8), 128.73 (s, Ar-C_7), 127.31 (t, Ar-C_2), 120.99 (t Ar-C_6), 115.96 (s, MeCN N*C*CH$_3$), 85.12 (s, Ar-C_1), 35.66 (t, P*C*H(CH$_3$)$_2$), 32.39 (t, P*C*H(CH$_3$)$_2$), 20.57 (t, PCH(*C*H$_3$)$_2$), 19.67 (t, PCH(*C*H$_3$)$_2$), 19.60 (t, PCH(*C*H$_3$)$_2$), 19.40 (m, PCH(*C*H$_3$)$_2$), 0.16 (s, MeCN NC*C*H$_3$), -0.88 (s, Si*C*H$_3$), -1.04 (s, Si*C*H$_3$). IR (powder), ν_{CO} (cm^{-1}): 1956, 1838, 1800 (br). IR (DCM), ν_{CO} (cm^{-1}): 1959.3, 1843, 1835. Anal. Calcd for [**2b**•MeCN], $C_{37}H_{47}MoNO_5P_2$: C, 57.58; H, 6.24; N, 1.81. Found: C, 57.25; H, 5.87; N, 1.80.

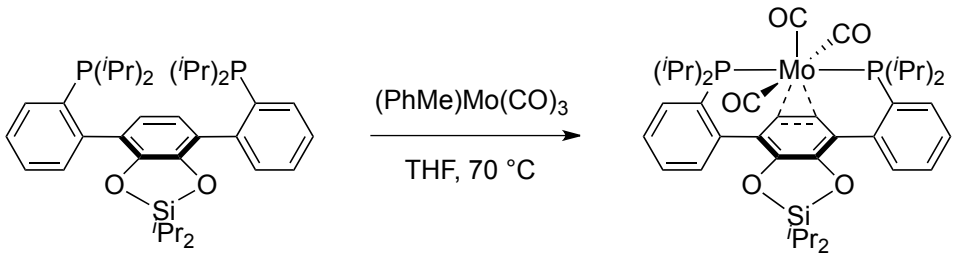
Synthesis of [diethyl-(1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-catechol)silane]tricarbonylmolybdenum(0) (2c)



1c **2c**

Compound **2c** was prepared analogously to **2b** using diphosphine **1c** (0.1577 g, 0.272 mmol) and (PhMe)Mo(CO)$_3$ (0.1120 g, 0.412 mmol) in THF (8 mL). The desired compound **2c** was isolated as an orange powder in 79.2% yield (0.1638 g). ^{1}H NMR (300 MHz, C_6D_6 , 25 °C), δ(ppm): 8.01 (d, 2 H, Ar-C*H*), 7.60 (d, 2 H, Ar-C*H*), 7.30 (t, 2 H, Ar-C*H*), 7.14 (t, 2 H, Ar-C*H*), 5.78 (t, J_{PH} = 4 Hz, 2 H, Ar-C_1H), 2.72 (m, PC*H*(CH$_3$)$_2$), 2.49 (m, PC*H*(CH$_3$)$_2$). 1.66 (m, 6H, PCH(CH_3)$_2$), 1.30 (m, 6H, PCH(CH_3)$_2$), 1.21 (m, 6H, PCH(CH_3)$_2$), 0.94 (m, 9 H, PCH(CH_3)$_2$ and SiCH_2CH$_3$), 0.62 (m, 5 H, SiCH$_2$CH_3 and SiCH_2CH$_3$). ^{31}P NMR (121 MHz, C_6D_6 , 25 °C), δ(ppm): 51.47 (s). ^{13}C NMR (125 MHz, C_6D_6 , 25 °C), δ(ppm): 223.92 (t, Mo-*C*O), 214.07 (t, Mo-*C*O), 212.59 (t, Mo-*C*O), 146.84 (s, Ar-C_3), 144.67 (t, Ar-C_4), 131.56 (t, Ar-C_9), 131.32 (s, Ar-C_5), 131.14 (t, Ar-C_8), 128.76 (s, Ar-C_7), 127.28 (t, Ar-C_2), 120.97 (t, Ar-C_6), 85.14 (s, Ar-C_1), 35.65 (t, P*C*H(CH$_3$)$_2$), 31.38 (t, P*C*H(CH$_3$)$_2$), 20.59 (t, PCH(*C*H$_3$)$_2$), 19.68 (t, PCH(*C*H$_3$)$_2$), 19.56 (t, PCH(*C*H$_3$)$_2$), 19.39 (m, PCH(*C*H$_3$)$_2$), 6.21 (s, SiCH$_2$*C*H$_3$), 5.92 (s, SiCH$_2$*C*H$_3$), 5.64 (s, Si*C*H$_2$CH$_3$), 5.05 (s, Si*C*H$_2$CH$_3$). IR (film), ν_{CO} (cm^{-1}): 1957, 1840, 1819. Anal. Calcd for [**2c**], $C_{37}H_{47}MoO_5P_2Si$: C, 58.57; H, 6.38. Found: C, 59.02; H, 6.51.

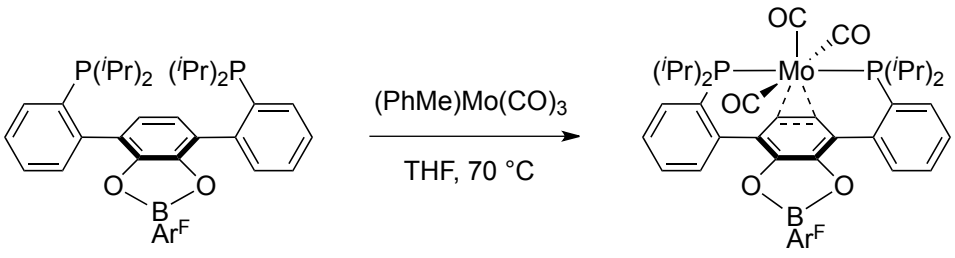
Synthesis of [diisopropyl-(1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-catechol)silane]tricarbonylmolybdenum(0) (2d)



1d **2d**

Compound **2d** was prepared analogously to **2b** using diphosphine **1d** (0.1829 g, 0.301 mmol) and (PhMe)Mo(CO)$_3$ (0.1260 g, 0.463 mmol) in THF (8 mL). The desired compound **2d** was isolated as an orange powder in 78.5% yield (0.1862 g). ^{1}H NMR (300 MHz, C_6D_6 , 25 °C), δ(ppm): 8.03 (d, 2 H, Ar-C*H*), 7.59 (d, 2 H, Ar-C*H*), 7.29 (t, 2 H, Ar-C*H*), 7.12 (t, 2 H, Ar-C*H*), 5.79 (t, J_{PH} = 4 Hz, Ar-C$_1$*H*), 2.71 (m, PC*H*(CH$_3$)$_2$), 2.47 (m, PC*H*(CH$_3$)$_2$). 1.66 (m, 6H, PCH(C*H*$_3$)$_2$), 1.30 (m, 6H, PCH(C*H*$_3$)$_2$), 1.21 (m, 6H, PCH(C*H*$_3$)$_2$), 1.07 (m, 6 H, SiCH(C*H*$_3$)$_2$), 0.93 (m, 8 H, PCH(C*H*$_3$)$_2$ and SiC*H*(CH$_3$)$_2$), 0.79 (m, 6 H, SiCH(C*H*$_3$)$_2$. ^{31}P NMR (121 MHz, C_6D_6 , 25 °C), δ(ppm): 51.69 (s). ^{13}C NMR (125 MHz, C_6D_6 , 25 °C), δ(ppm): 223.84 (t, Mo-*C*O), 214.02 (t, Mo-*C*O), 212.30 (t, Mo-*C*O), 146.92 (s, Ar-*C*$_3$), 144.68 (t, Ar-*C*$_4$), 131.66 (t, Ar-*C*$_9$), 131.36 (s, Ar-*C*$_5$), 130.98 (t, Ar-*C*$_8$), 128.82 (s, Ar-*C*$_7$), 127.25 (t, Ar-*C*$_2$), 120.76 (t, Ar-*C*$_6$), 84.98 (s, Ar-*C*$_1$), 35.65 (t, P*C*H(CH$_3$)$_2$), 31.72 (t, P*C*H(CH$_3$)$_2$), 20.61 (t, PCH(*C*H$_3$)$_2$), 19.69 (t, PCH(*C*H$_3$)$_2$), 19.51 (t, PCH(*C*H$_3$)$_2$), 19.36 (m, PCH(*C*H$_3$)$_2$), 16.34 (s, SiCH(*C*H$_3$)$_2$), 15.85 (s, SiCH(*C*H$_3$)$_2$), 13.45 (s, Si*C*H(CH$_3$)$_2$), 12.76 (s, Si*C*H(CH$_3$)$_2$). IR (powder), ν_{CO} (cm^{-1}): 1953, 1836, 1812. Anal. Calcd for [**2d**], $C_{39}H_{52}MoO_5P_2Si$: C, 59.53; H, 6.66. Found: C, 59.22; H, 6.51.

Synthesis of [4-(trifluoromethyl)phenyl-(1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-catechol)borane]tricarbonylmolybdenum(0) (2e)

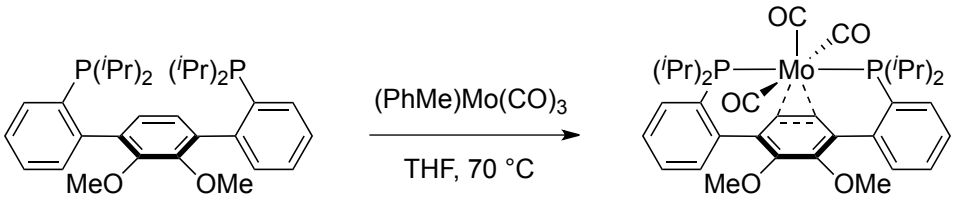


1e Ar^F = *p*(CF$_3$)C$_6$H$_4$ **2e**

Compound **2e** was prepared analogously to **2b** using diphosphine **1e** (0.4090 g, 0.631 mmol) and (PhMe)Mo(CO)$_3$ (0.2345 g, 0.862 mmol) in THF (10 mL). The desired compound **2e** was isolated as a red powder in 76.6% yield (0.4010 g). ^{1}H NMR (300 MHz, C_6D_6 , 25 °C), δ(ppm): 7.96 (m, 2 H, Ar-C*H*), 7.69 (d, 2 H, BAr-C*H*), 7.62 (d, 2 H,

Ar-C*H*), 7.41 (t, 2 H, Ar-C*H*), 7.23 (m, 4 H, BAr-C*H* and Ar-C*H*), 5.80 (t, J_{PH} = 4 Hz, 2 H, quinonoid Ar-C*H*), 2.73 (m, 2 H, PC*H*(CH_3)$_2$), 2.45 (m, 2 H, PC*H*(CH_3)$_2$). 1.63 (m, 6H, PCH(C*H*$_3$)$_2$), 1.29 (m, 6 H, PCH(C*H*$_3$)$_2$), 1.10 (m, 6 H, PCH(C*H*$_3$)$_2$), 0.86 (m, 6 H, PCH(C*H*$_3$)$_2$). ^{31}P NMR (121 MHz, C_6D_6 , 25 °C), δ(ppm): 51.49 (s). ^{19}F NMR (282 MHz, C_6D_6 , 25 °C), δ(ppm): -61.68 (s). ^{13}C NMR (125 MHz, C_6D_6 , 25 °C), δ(ppm): 221.97 (t, Mo-*C*O), 213.90 (t, Mo-*C*O), 213.15 (t, Mo-*C*O), 146.13 (s, Ar-C_3), 143.08 (t, Ar-C_4), 135.89 (m, BAr-*C*), 134.00 (q, BAr-*C*F$_3$), 131.58 (m, BAr-*C*), 131.21 (t, Ar-C_9), 130.94 (m, Ar-C_5 and Ar-C_8), 129. 28 (br, Ar-C_7), 124.82 (t, Ar-C_2), 121.80 (t, Ar-C_6), 84.01 (s, Ar-C_1), 35.54 (t, P*C*H(CH_3)$_2$), 31.70 (t, P*C*H(CH_3)$_2$), 20.35 (br, CH(*C*H$_3$)$_2$), 19.53 (br, PCH(*C*H$_3$)$_2$), 19.37 (br, PCH(*C*H$_3$)$_2$). IR (powder), ν_{CO} (cm^{-1}): 1956, 1839 (br). Anal. Calcd for [**2e**] $C_{40}H_{42}BF_3MoO_5P_2$: C, 57.99; H, 5.11. Found: C, 57.50; H, 5.14.

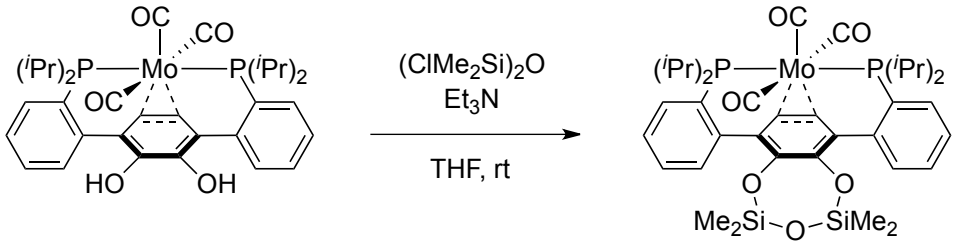
Synthesis of [1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-dimethoxybenzene]tricarbonylmolybdenum(0) (2f)



1f **2f**

Compound **2f** was prepared analogously to **2b** using diphosphine **1f** (0.6007 g, 1.15 mmol) and (PhMe)Mo(CO)$_3$ (0.3988 g, 1.47 mmol) in THF (15 mL). The desired compound **2f** was isolated as an orange powder in 78.7% yield (0.6354 g). ^{1}H NMR (300 MHz, C_6D_6 , 25 °C), δ(ppm): 7.78 (m, 2 H, Ar-C*H*), 7.54 (d, 2 H, Ar-C*H*), 7.24 (t, 2 H, Ar-C*H*), 7.16 (t, 2 H, Ar-C*H*), 5.81 (t, J_{PH} = 4 Hz, 2 H, Ar-C$_1$*H*), 2.64 (m, 2 H, PC*H*(CH_3)$_2$), 2.40 (m, 2 H, PC*H*(CH_3)$_2$). 1.68 (m, 6 H, PCH(C*H*$_3$)$_2$), 1.23 (m, 12 H, PCH(C*H*$_3$)$_2$), 0.91 (m, 6 H, PCH(C*H*$_3$)$_2$). ^{31}P NMR (121 MHz, C_6D_6 , 25 °C), δ(ppm): 50.09 (s). ^{13}C NMR (125 MHz, C_6D_6 , 25 °C), δ(ppm): 222.76 (t, Mo-*C*O), 213.66 (t, Mo-*C*O), 213.62 (t, Mo-*C*O), 150.05 (s, Ar-C_3), 145.13 (t, Ar-C_4), 132.33 (t, Ar-C_9), 131.16 (s, Ar-C_5), 131.05 (t, Ar-C_8), 120.89 (t, Ar-C_6), 128.67 (s, Ar-C_7), 127.66 (t, Ar-C_2), 87.21 (s, Ar-C_1), 60.53 (s, quinonoid Ar-O*C*H$_3$), 36.42 (t, P*C*H(CH_3)$_2$), 33.08 (t, P*C*H(CH_3)$_2$), 21.26 (t, PCH(*C*H$_3$)$_2$), 20.04 (s, PCH(*C*H$_3$)$_2$), 19.59 (t, PCH(*C*H$_3$)$_2$), 19.47 (t, PCH(*C*H$_3$)$_2$). IR (powder), ν_{CO} (cm^{-1}): 1954, 1824 (br). Anal. Calcd for [**2f**], $C_{35}H_{44}MoO_5P_2$: C, 59.83; H, 6.31. Found: C, 60.12; H, 6.21.

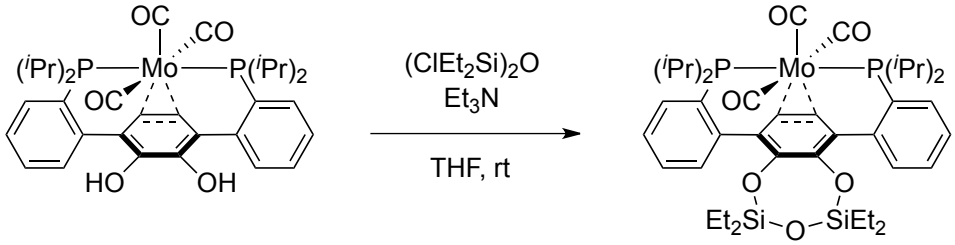
Synthesis of [tetramethyl-1,3-(1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-catechol)disiloxane]tricarbonylmolybdenum(0) (2h)



2a **2h**

Compound **2a** (0.0785 g, 0.116 mmol), $(ClMe_2Si)_2O$ (0.0404 g, 0.199 mmol), and Et_3N (0.0643 g, 0.635 mmol) were combined in THF (5 mL) and stirred for 12 hours at room temperature, developing a precipitate over this time. The mixture was then filtered through a pad of celite, washing with additional THF. The filtrate was then concentrated *in vacuo* and triturated with MeCN (5 mL). The resulting orange precipitate was collected on a pad of celite, dissolved in C_6H_6, filtered through celite, and concentrated under reduced pressure. The resulting residue is a mixture of **2h** and **2b** in ca. 8:1 ratio, respectively. Recrystallization twice via vapor diffusion of pentane into a saturated C_6H_6 solution of the residue, collecting the filtrate, yields the desired compound (0.0187g, 20.0%). ^{1}H NMR (300 MHz, C_6D_6 , 25 °C), δ(ppm): 7.77 (d, 2 H, Ar-C*H*), 7.57 (d, 2 H, Ar-C*H*), 7.22 (t, 2 H, Ar-C*H*), 7.16 (m, 2 H, Ar-C*H*), 5.88 (t, J_{PH} = 4 Hz, 2 H, Ar-C_1*H*), 2.67 (m, 2 H, PC*H*$(CH_3)_2$), 2.44 (m, 2 H, PC*H*$(CH_3)_2$). 1.66 (m, 6 H, PCH(C*H*$_3)_2$), 1.23 (m, 12 H, PCH(C*H*$_3)_2$), 0.93 (m, 6H, PCH(C*H*$_3)_2$), 0.30 (s, 3 H, SiC*H*$_3$), 0.05 (s, 3 H, SiC*H*$_3$). ^{31}P NMR (121 MHz, C_6D_6 , 25 °C), δ(ppm): 50.05 (s). ^{13}C NMR (121 MHz, C_6D_6 , 25 °C), δ(ppm): 223.83 (t, Mo-*C*O), 214.20 (t, Mo-*C*O), 213.02 (t, Mo-*C*O), 145.64 (t, Ar-C_4), 142.53 (s, Ar-C_3), 132.24 (t, Ar-C_9), 131.26 (s, Ar-C_5), 130.89 (t, Ar-C_8), 127.23 (t, Ar-C_2), 127.20 (t, Ar-C_6), 87.50 (s, Ar-C_1), 35.72 (t, P*C*H$(CH_3)_2$), 32.51 (t, P*C*H$(CH_3)_2$), 21.02 (t, PCH(*C*H$_3)_2$), 19.96 (s, PCH(*C*H$_3)_2$), 19.40 (t, PCH(*C*H$_3)_2$), -0.31 (s, Si*C*H$_3$), -0.47 (s, Si*C*H$_3$). IR (powder), ν_{CO} (cm^{-1}): 1956, 1838, 1800 (br).

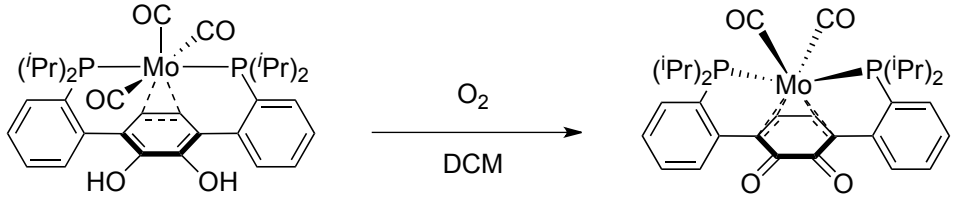
Synthesis of [tetraethyl-1,3-(1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-catechol)disiloxane]tricarbonylmolybdenum(0) (2i)



2a **2i**

Compound **2a** (0.1961 g, 0.291 mmol), $(ClEt_2Si)_2O$ (0.0768 g, 0.296 mmol), and Et_3N (0.1414 g, 1.40 mmol) were combined in THF (5 mL) and stirred for 12 hours at room temperature, developing a precipitate over this time. The mixture was then filtered through a pad of celite, washing with additional THF. The filtrate was then concentrated *in vacuo* and triturated with MeCN (5 mL). The resulting orange precipitate was collected on a pad of celite, dissolved in C_6H_6, filtered through celite, and concentrated under reduced pressure. The resulting residue is a mixture of **2i**, **2c**, and **2a** in ca. 7:2:1 ratio, respectively. Recrystallization four times from hot pentane yields the desired compound (0.0165 g, 6.7%). ^{1}H NMR (300 MHz, C_6D_6 , 25 °C), δ(ppm): 7.77 (d, 2 H, Ar-C*H*), 7.57 (d, 2 H, Ar-C*H*), 7.24 (t, 2 H, Ar-C*H*), 7.16 (m, 2 H, Ar-C*H*), 5.88 (t, J_{PH} = 4 Hz, 2 H, Ar-C_1H), 2.68 (m, 2 H, PC*H*$(CH_3)_2$), 2.45 (m, 2 H, PC*H*$(CH_3)_2$). 1.67 (m, 6 H, PCH(C*H*$_3)_2$), 1.24 (m, 12 H, PCH(C*H*$_3)_2$), 1.12 (t, J^3 = 8 Hz, 6 H, $SiCH_2CH_3$), 0.95 (m, 6H, PCH(C*H*$_3)_2$), 0.77 (m, 10 H, $SiCH_2CH_3$ and $SiCH_2CH_3$), 0.57 (m, 4 H, $SiCH_2CH_3$). ^{31}P NMR (121 MHz, C_6D_6 , 25 °C), δ(ppm): 59.96 (s). ^{13}C NMR (121 MHz, C_6D_6 , 25 °C), δ(ppm): 223.88 (t, Mo-*C*O), 214.28 (t, Mo-*C*O), 212.80 (t, Mo-*C*O), 145.68 (t, Ar-C_4), 142.74 (s, Ar-C_3), 132.30 (t, Ar-C_9), 131.28 (d, Ar-C_5), 131.13 (t, Ar-C_8), 127.27 (m, Ar-C_2), 127.21 (t, Ar-C_6), 88.15 (s, Ar-C_1), 35.73 (m, P*C*H$(CH_3)_2$), 32.52 (m, P*C*H$(CH_3)_2$), 21.07 (m, PCH(*C*H$_3)_2$), 19.95 (m, PCH(*C*H$_3)_2$), 19.59 (m, PCH(*C*H$_3)_2$), 19.41 (m, PCH(*C*H$_3)_2$), 6.64 (s, $SiCH_2CH_3$), 6.49 (s, $SiCH_2CH_3$), 6.42 (s, $SiCH_2CH_3$), 6.24 (s, $SiCH_2CH_3$). IR (film), ν_{CO} (cm^{-1}): 1956, 1840, 1816.

Synthesis of [1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-quinone]dicarbonylmolybdenum(0) (3)



2a **3**

A solution of **2a** (0.0215 g, 0.0319 mmol) in THF (0.6 mL) was added to a J. Young style NMR tube and degassed via three freeze-pump-thaw cycles. An atmosphere of O_2 was then added to the headspace and the tube inverted for 60 seconds. ^{31}P NMR spectroscopy revealed complete conversion to a new species at approximately 72 ppm. The volatiles were removed under vacuum, and the residue was dissolved in MeCN (2 mL) and then the volatiles removed under vacuum, repeating this multiple times to remove the H_2O side product. Finally, the residue was triturated with Hexanes and the volatiles removed under vacuum to afford the desired product in 96.4% yield (0.0198 g, 0.0307 mmol). Refluxing the compound in PhMe for an hour and then allowing the solution to cool to room temperature formed crystals suitable for X-ray diffraction. ^{1}H NMR (300 MHz, CD_3CN , 25 °C), δ(ppm): 7.43-7.68 (m, 8 H, Ar-C*H*), 5.09 (s, 2 H, C_1H), 3.11 (m, 2 H, PC*H*$(CH_3)_2$). 2.93 (m, 2 H, PC*H*$(CH_3)_2$), 1.10-1.34 (m, 18 H, PCH(C*H*$_3)_2$), 0.82-0.92 (m, 6 H, PCH(C*H*$_3)_2$). ^{31}P NMR (121 MHz, CD_3CN , 25 °C), δ(ppm): 72.43 (s). ^{13}C NMR

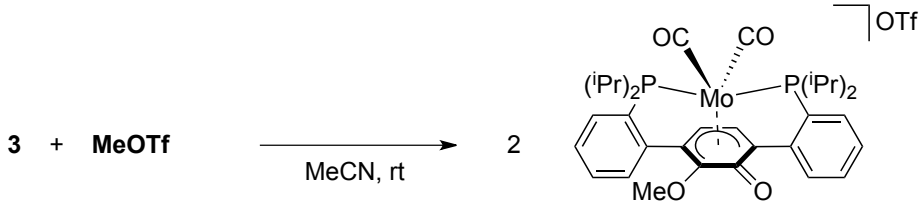
(126 MHz, CD_3CN , 25 °C), δ(ppm): 246.34 (t, 20 Hz, Mo-*C*O), 222.58 (t, 18 Hz, Mo-*C*O), 173.31 (s, quinonoid Ar-*C*O), 138.02 (m), 135.81 (m), 134.51 (s), 134.12 (s), 132.62 (t), 132.10 (t), 130.02 (t), 100.58 (s, quinonoid Ar-*C*H), 65.30 (s, O*C*H_3), 29.58 (m, P*C*H(CH_3)$_2$), 28.98 (s, P*C*H(CH_3)$_2$), 19.03 (s, PCH(*C*H_3)$_2$), 18.30 (t, PCH(*C*H_3)$_2$), 18.12 (s, PCH(*C*H_3)$_2$), 18.04 (s, PCH(*C*H_3)$_2$). IR (THF), ν_{CO} (cm^{-1}): 1875, 1605. Anal. Calcd for [**3**], $C_{32}H_{38}MoO_4P_2$: C, 59.63; H, 5.94. Found: C, 60.11; H, 6.04.

Synthesis of [1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-dimethoxybenzene]dicarbonylmolybdenum(II) trifluoromethanesulfonate ([5^{2+}][OTf^-]$_2$)

2f **[5^{2+}](OTf)$_2$**

To a stirred suspension of **2f** (0.0400 g, 0.0569 mmol) in MeCN (2 mL) was added a solution of AgOTf (0.0331 g, 0.129 mmol) in MeCN (2 mL). Upon addition the reaction became a purple heterogeneous mixture, which was stirred at room temperature until the purple color dissipated (approximately 20 min), resulting in a yellow/brown heterogeneous mixture. The solution was then filtered through celite, and the filtrate was evaporated under reduced pressure. The resulting residue was freed of excess MeCN by trituration with hexanes (3 mL), followed by evaporation under reduced pressure to yield the desired product as a tan solid (0.0505 g, 91.2%). ^{1}H NMR (300 MHz, CD_3CN , 25 °C), δ(ppm): 7.70-8.00 (m, 8 H, Ar-C*H*), 6.80 (s, 2 H, Ar-C$_1$*H*), 3.42 (m, 2 H, PC*H*(CH_3)$_2$). 3.18 (m, 2 H, PC*H*(CH_3)$_2$), 1.35 (m, 18 H, PCH(C*H*$_3$)$_2$), 1.18 (m, 6 H, PCH(C*H*$_3$)$_2$). ^{31}P NMR (121 MHz, CD_3CN , 25 °C), δ(ppm): 72.43 (s). ^{19}F NMR (282 MHz, CD_3CN , 25 °C), δ(ppm): -79.19 (s). ^{13}C NMR (126 MHz, CD_3CN , 25 °C), δ(ppm): 222.65 (t, Mo-*C*O), 222.58 (t, Mo-*C*O), 141.31 (s, quinonoid Ar-*C*O), 138.02 (m), 135.81 (m), 134.51 (s), 134.12 (s), 132.62 (t), 132.10 (t), 130.02 (t), 100.58 (s, quinonoid Ar-*C*H), 65.30 (s, O*C*H_3), 29.58 (m, P*C*H(CH_3)$_2$), 28.98 (s, P*C*H(CH_3)$_2$), 19.03 (s, PCH(*C*H_3)$_2$), 18.30 (t, PCH(*C*H_3)$_2$), 18.12 (s, PCH(*C*H_3)$_2$), 18.04 (s, PCH(*C*H_3)$_2$). IR (MeCN), ν_{CO} (cm^{-1}): 2019, 1961. λ_{max} (MeCN, nm), ε ($M^{-1}cm^{-1}$): 430, 5.0x10^2; 350, 2.0x10^3; 290, 6.4x10^3. Anal. Calcd for [**5^{2+}**][OTf^-]$_2$, $C_{36}H_{44}F_6MoO_{10}P_2S_2$: C, 44.45; H, 4.56. Found: C, 44.23; H, 4.39.

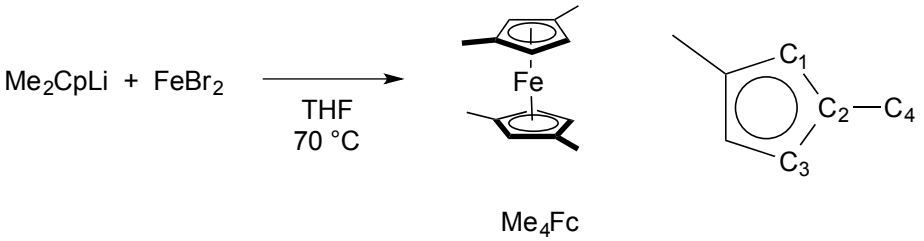
Synthesis of [1,4-bis(2-(diisopropylphosphino)phenyl)-2,3-methylsemiquinonate]dicarbonylmolybdenum(II) trifluoromethanesulfonate ([6$^+$][OTf$^-$])



[6$^+$][OTf$^-$]

To a solution of **3** (0.0205 g, 0.0318 mmol) in MeCN (2 mL) was added MeOTf (5 μL, 0.0442 mmol). The mixture was stirred for 5 minutes and the volatiles were removed under vacuum. The residue was triturated with C_6H_6 and the precipitate collected on a pad of celite, washing with additional C_6H_6. The solid was dissolved in MeCN, filtered through celite, and concentrated under reduced pressure. Excess MeCN was removed by triturating in hexanes followed by removal volatiles under vacuum. The desired compound was isolated as a pale yellow powder (0.0159 g, 0.0197 mmol, 61.8%). ^{1}H NMR (300 MHz, CD_3CN , 25 °C), δ(ppm): 7.60-7.80 (m, 8 H, Ar-C*H*), 5.89 (dd, J_{HP} = 5.7 Hz, 1.2 Hz, 1 H, Ar-C$_1$*H*), 5.71 (dd, J_{HP} = 5.7 Hz, 2.4 Hz, 1 H, Ar-C$_1$*H'*), 3.92 (s, 3 H, OC*H*$_3$), 3.41 (m, 2 H, PC*H*(CH$_3$)$_2$), 3.17 (m, 2 H, PC*H*(CH$_3$)$_2$), 1.20-1.45 (m, 18 H, PCH(C*H*$_3$)$_2$), 0.93-1.10 (m, 6 H, PCH(C*H*$_3$)$_2$). ^{31}P NMR (121 MHz, CD_3CN , 25 °C), δ(ppm): 78.19 (d, $J_{PP'}$ = 18 Hz), 65.44 (d, $J_{PP'}$ = 18 Hz). ^{19}F NMR (282 MHz, CD_3CN , 25 °C), δ(ppm): -77.09 (s). ^{13}C NMR (126 MHz, CD_3CN , 25 °C), δ(ppm): 233.60 (dd, J_{CP} = 23.0 Hz, 21.5 Hz, Mo-*C*O), 228.62 (dd, J_{CP} = 23.0 Hz, 21.5 Hz, Mo-*C*O), 163.51 (s, quinonoid Ar-*C*=O), 143.03 (d, Ar-*C),* 142.68 (d, Ar-*C*), 141.17 (d, Ar-*C*), 135.24 (m, O$_3$S-*C*F$_3$), 133.50 (m, Ar-*C*), 133.04 (m, Ar-*C*), 130.84 (m, Ar-*C*), 129.99 (m, Ar-*C*), 129.28 (m, Ar-*C*), 128.06 (m, Ar-*C*), 124.13 (m, Ar-*C*), 123.31 (s, Ar-*C*), 120.76 (s, Ar-*C*), 99.23 (m, quinonoid Ar-*C*H), 129.99 (m, Ar-*C*), 83.47 (m, quinonoid Ar-*C*H), 62.11 (m, O*C*H$_3$), 30.31 (s, P*C*H(CH$_3$)$_2$), 30.12 (s, P*C*H(CH$_3$)$_2$), 27.70 (m, P*C*H(CH$_3$)$_2$), 26.70 (m, P*C*H(CH$_3$)$_2$), 18.46 (m, PCH(*C*H$_3$)$_2$), 18.46 (m, PCH(*C*H$_3$)$_2$), 18.04 (m, PCH(*C*H$_3$)$_2$), 17.73 (m, PCH(*C*H$_3$)$_2$), 17.46 (m, PCH(*C*H$_3$)$_2$). IR (film), ν_{CO} (cm^{-1}): 1979, 1907, 1615.

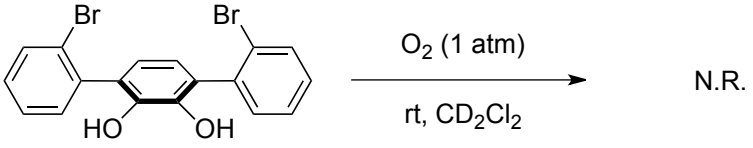
Synthesis of bis(1,3-dimethylcyclopentadienyl)iron(II) (Me$_4$Fc)



Me$_4$Fc

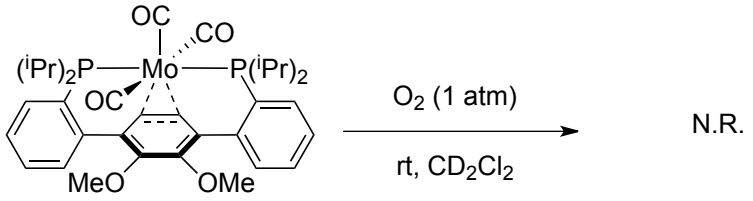
In a schlenk tube, $FeBr_2$ (1.0828 g, 5.02 mmol) and 1,3-dimethylcyclopentadienyl lithium (1.0438 g, 10.4 mmol) were combined in THF (30 mL) and heated to 70 °C for 3 hours, and the resulting brown/orange suspension was then concentrated under reduced pressure. The red-brown residue was extracted with Et_2O (50 mL), filtered through alumina and concentrated under reduced pressure to yield the desired product as a red-orange oil (0.4038 g, 33.2%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C), δ(ppm): 3.73 (s, 4 H), 3.66 (s, 2 H), 1.86 (s, 12 H). ^{13}C NMR (126 MHz, C_6D_6, 25 °C), δ(ppm): 83.17 (s, C_2), 71.86 (s, C_1), 70.03 (s, C_3), 14.34 (s, C_4). ESI-MS (m/z, relative abundance): 242.2 $[M]^+$, 100%; 227.2 $[M\text{-}CH_3]^+$, 12%. MS (m/z): calcd, 242.0785 $[M]^+$; found, 242.0764 (FAB^+, $[M]^+$).

Control Reactions with O_2



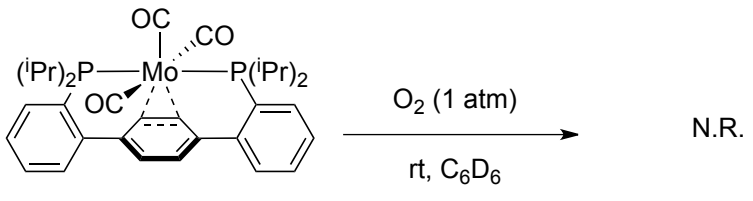
1^{Br}

1^{Br}: An NMR solution of **1^{Br}** (0.0214 g, mmol) in CD_2Cl_2 (0.5 mL) prepared on the bench top was added to a J. Young style NMR tube and degassed via three freeze-pump-thaw cycles. An atmosphere of O_2 was added to the headspace and the reaction monitored by ^{1}H NMR spectroscopy. There was no observed reaction over the course of 24 hours.



2f

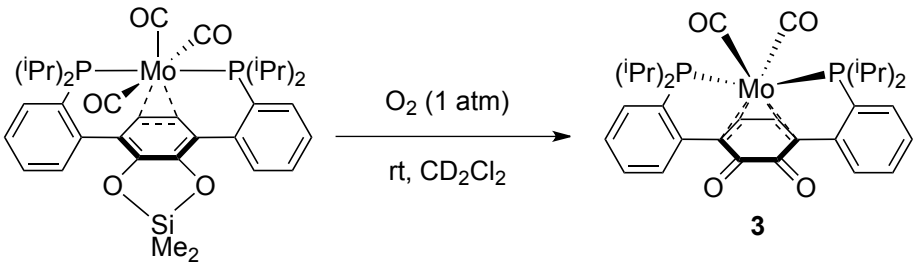
2f: In the glove box, a solution of **2f** (0.0198 g, mmol) in CD_2Cl_2 (0.6 mL) was added to a J. Young style NMR tube. On the Schlenk line, the solution was degassed via three freeze-pump-thaw cycles and an atmosphere of O_2 was added to the headspace. The reaction was then monitored by ^{1}H and ^{31}P NMR spectroscopy. There was no observed reaction over the course of 24 hours.



2g

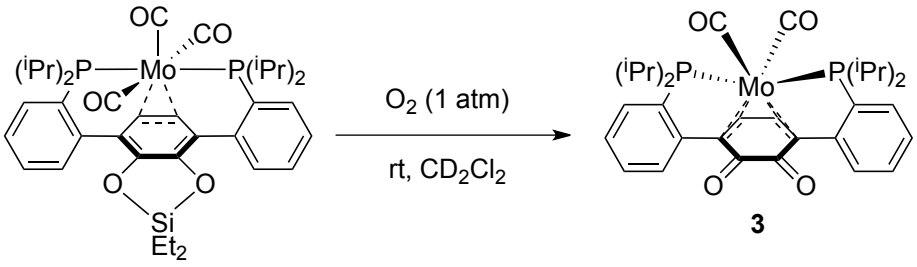
2g: In the glove box, a solution of **2g** (0.0225 g, mmol) in C_6D_6 (0.6 mL) was added to a J. Young style NMR tube. On the Schlenk line, the solution was degassed via three freeze-pump-thaw cycles and an atmosphere of O_2 was added to the headspace. The reaction was then monitored by ^1H and ^{31}P NMR spectroscopy. There was no observed reaction over the course of 24 hours.

Reactions with O_2



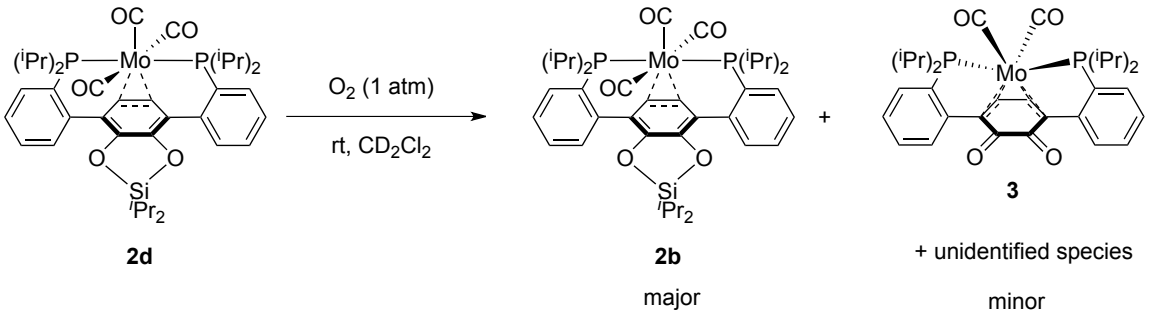
2b

2b: A solution of **2b** (0.0232 g, 0.0317 mmol) in CD_2Cl_2 (0.6 mL) in a J. Young style NMR tube was degassed via three freeze-pump-thaw cycles. An atmosphere of O_2 was then added to the headspace, and the tube continuously inverted, monitoring the reaction over time by ^1H and ^{31}P NMR spectroscopy. After 1.5 hours at room temperature, the reaction exhibited a roughly 1:1:1 mixture of unconverted **2b**, product **3**, as well as an intermediate species identified as **2h** (confirmed by independent synthesis, *vida supra*). After 3 hours the reaction had gone to completion with **2b** fully converted to **3** and a mixture of Me_2Si-containing products. An aliquant of the reaction mixture diluted in DCM was filtered through silica gel and submitted to gas chromatography-mass spectrometry (GC-MS) analysis, which revealed the Me_2Si-containing products to be cyclooligomers of dimethylsiloxane (i.e. $(Me_2SiO)_n$ where n = 3, 4, 5, 6).

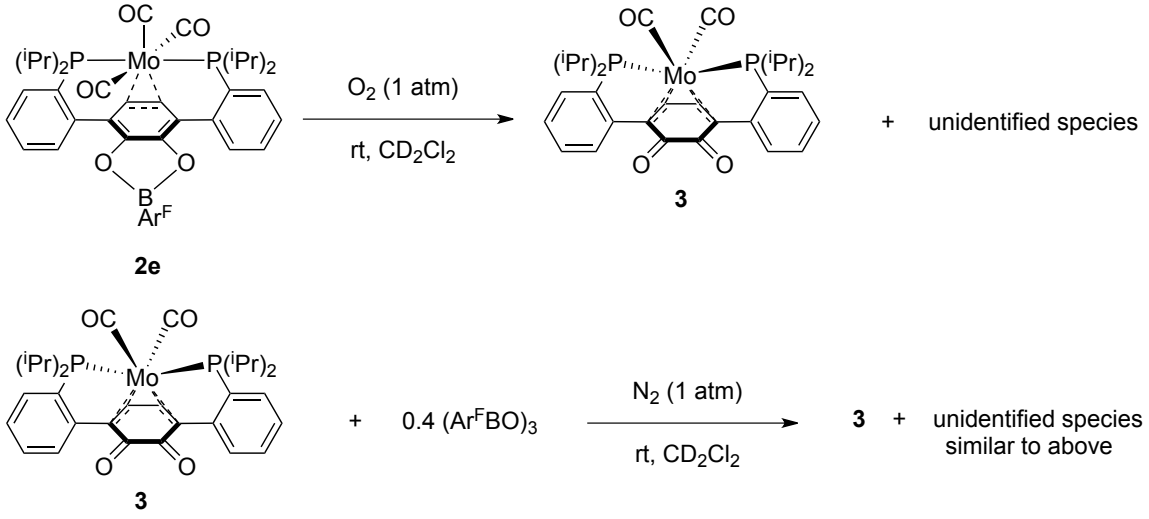


2c

2c: The above procedure was repeated with **2c** (0.0211 g, mmol) in CD_2Cl_2 (0.6 mL). After 8 hours at room temperature, **2c** had converted to a 1:1 mixture of **3** and **2i**. After 48 hours at room temperature, **2i** had fully converted to **3**.



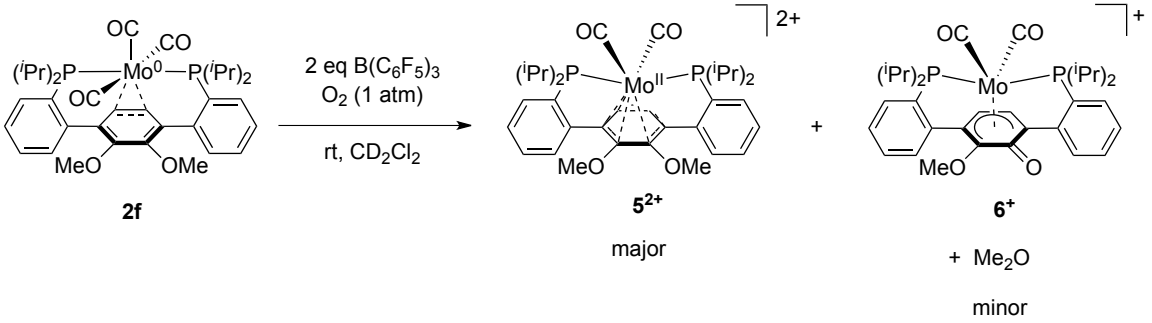
2d: The above procedure was repeated with **2d** (0.0241 g, mmol) in CD_2Cl_2 (0.6 mL) and monitored by ^{1}H and ^{31}P NMR spectroscopy. After 5 days at room temperature, **3** had formed in ca. 15% along with ca. 35% unidentified species.



2e: The above procedure was repeated with **2e** (0.0201 g, 0.0243 mmol) in CD_2Cl_2 (0.6 mL) and monitored by ^{1}H, ^{19}F, and ^{31}P NMR spectroscopy. After 36 hours, **2e** had converted to a mixture of species comprised mainly of **3** (ca. 80% relative integration by ^{31}P NMR) and other unidentified products. Additionally, the ^{19}F NMR revealed two clusters of broad peaks grouped around -59.5 ppm and -61.5 ppm.

To better understand the unidentified mixture of species, a solution of **3** (0.0202 g, 0.0313 mmol) and $(Ar^FBO)_3$ (0.0063 g, 0.0122 mmol, independently synthesized, Ar^F = *p*-$CF_3C_6H_4$)[5] in CD_2Cl_2 (0.6 mL) was monitored by ^{1}H, ^{19}F, and ^{31}P NMR spectroscopy. After one hour at room temperature, the mixture exhibited spectra that were qualitatively similar to the product of **2e** with O_2. Notably, by ^{31}P NMR spectroscopy, broad peaks were observed ca. 1.5 ppm upfield of **3**, with a relative ratio of 1:4 (unknown species : **3**), and by ^{19}F NMR, two sets of broad peaks were observed, grouped around -59.5 ppm and -61.5 ppm. Based on these results, it is plausible that in the reaction of **2e** with O_2 "$Ar^FB{=}O$" or some other reactive B-O species may be transiently generated (analogous to $Me_2Si{=}O$ in reaction of **2b** with O_2), which could then react further by cyclization or oligomerization. The reaction of **3** with $(Ar^FBO)_3$ suggests that **3** may form a Lewis acid-

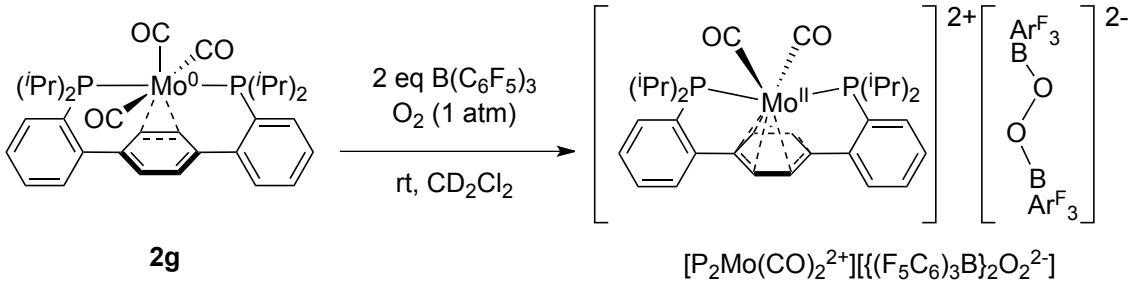
base adduct with $(Ar^FBO)_3$, possibly prohibiting cyclization of "Ar^FBO" into the otherwise thermodynamic sink $(Ar^FBO)_3$ and instead favoring higher oligomers.



2f with $B(C_6F_5)_3$: A solution of **2f** (0.0210 g, 0.0299 mmol) and $B(C_6F_5)_3$ (0.0301 g, 0.0588 mmol) were combined in CD_2Cl_2 (0.6 mL) and added to a J. Young style NMR tube. The solution was degassed via three freeze-pump-thaw cycles and an atmosphere of O_2 was added to the headspace. The reaction was followed by ^1H, ^{19}F, and ^{31}P NMR spectroscopy. After 30 minutes the color of the solution had changed from orange to dark brown to deep purple with no signals observable by ^{31}P NMR spectroscopy and only broad resonances observable by ^1H NMR spectroscopy. After ca. 2 hours a large number of purple crystals had formed in the tube suitable for x-ray diffraction. If unperturbed, over the course of another 4-5 hours the purple color faded to yield a pale yellow solution with non-crystalline yellow precipitate. ^{31}P and ^1H NMR spectroscopy revealed two new diamagnetic products, a major symmetric species assigned as $\mathbf{5}^{2+}$ and a minor asymmetric species assigned as $\mathbf{6}^{+}$. These assignments were confirmed by removal of the volatiles under vacuum and reconstituting the residue in CD_3CN (0.6 mL) and comparing the NMR spectra to those of the independently synthesized [$\mathbf{5}^{2+}$][OTf$^-$]$_2$ and [$\mathbf{6}^{+}$][OTf$^-$].

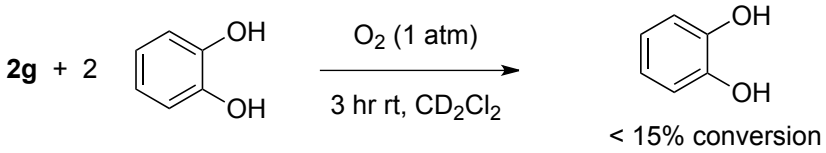
The above reaction with O_2 was repeated with **2f** (0.0221g, 0.0315 mmol) and $B(C_6F_5)_3$ (0.0332 g, 0.0648 mmol) in CD_2Cl_2 (0.6 mL). After approximately 24 hours, the volatiles were vacuum transferred to a second J. Young style NMR tube and the formation of Me_2O was confirmed (δ = 3.27 ppm)[6] in addition to small amounts of MeOH and H_2O. The solution was then submitted to GC-MS and the Me_2O eluted at 1.45 min with two major peaks at 45.1 and 46.1 m/z.

The reaction was repeated as above with **2f** (0.0197 g, 0.0280 mmol) and $B(C_6F_5)_3$ (0.0302 g, 0.0590) in CD_2Cl_2 (0.6 mL). Instead of natural abundance O_2, 98% $^{18}O_2$. After 3 days, the volatiles were vacuum transferred to a second J. Young style NMR tube and the formation of Me_2O confirmed. The solution was submitted to GC-MS, and the Me_2O observed at 1.45 min with major peaks at 47.1 and 48.2 m/z consistent with $Me_2{}^{18}O$, as well as minor peaks at 45.1 and 46.1 m/z consistent with $Me_2{}^{16}O$. Relative ratio of $^{18}O/^{16}O$ estimated at 3:1.

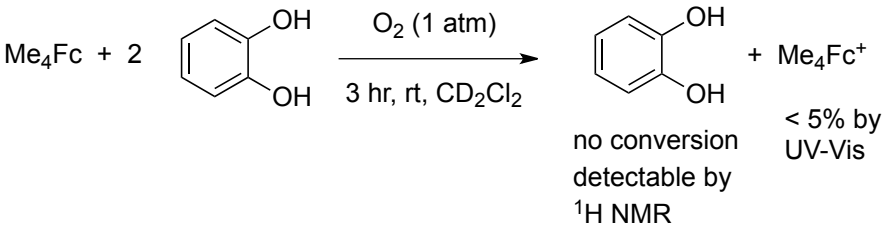


2g $[P_2Mo(CO)_2^{2+}][\{(F_5C_6)_3B\}_2O_2^{2-}]$

2g with $B(C_6F_5)_3$: A solution of **2g** (0.0186 g, 0.0289 mmol) and $B(C_6F_5)_3$ (0.0329 g, 0.0643 mmol) were combined in CD_2Cl_2 (0.6 mL) and added to a J. Young style NMR tube. The solution was degassed via three freeze-pump-thaw cycles and an atmosphere of O_2 was added to the headspace. The reaction was followed by ^1H, ^{19}F, and ^{31}P NMR spectroscopy. After 45 minutes the color of the solution had changed from orange to dark brown to purple with loss of signal by ^{31}P NMR spectroscopy and broadening of resonances by ^1H NMR spectroscopy. By ^{19}F NMR spectroscopy, generation of $[((F_5C_6)_3B)_2O_2^{2-}]$ can be observed. After 36 hours at room temperature, ^{31}P and ^1H NMR spectroscopy reveal formation of $[P_2Mo(CO)_2]^{2+}$.



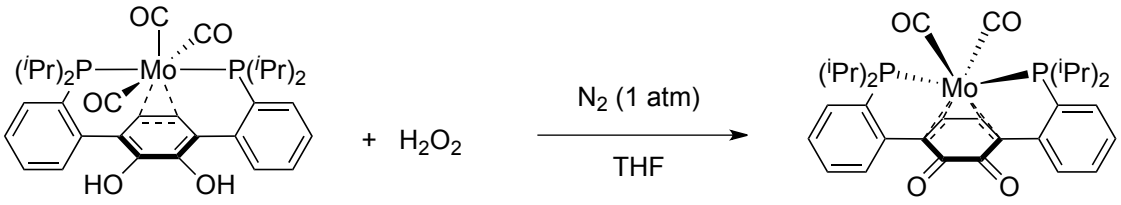
2g with catechol: A solution of **2g** (0.0203 g, 0.0315 mmol) and catechol (0.0073 g, 0.0663 mmol) in CD_2Cl_2 (0.6 mL) in a J. Young style NMR tube was degassed via three freeze-pump-thaw cycles. An atmosphere of O_2 was then added to the headspace, and the tube continuously inverted, monitoring the reaction over time by ^1H and ^{31}P NMR spectroscopy. Conversion of catechol was determined via ^1H NMR integration using the residual PhMe from synthesis of **2g** as internal standard.



Me_4Fc with catechol: A solution of Me_4Fc (0.0106 g, 0.0438 mmol) and catechol (0.0107 g, 0.0972 mmol) with diglyme (0.0022g, 0.0164 mmol) used as internal standard in CD_2Cl_2 (0.6 mL) in a J. Young style NMR tube was degassed via three freeze-pump-thaw cycles. An atmosphere of O_2 was then added to the headspace, and the tube continuously inverted, monitoring the reaction over time by ^1H and ^{31}P NMR spectroscopy. After 3 hours, the volatiles were removed under vacuum. The residue was diluted in THF (3 mL), and an aliquot (0.15 mL) was then further diluted with additional THF (2.85 mL, total

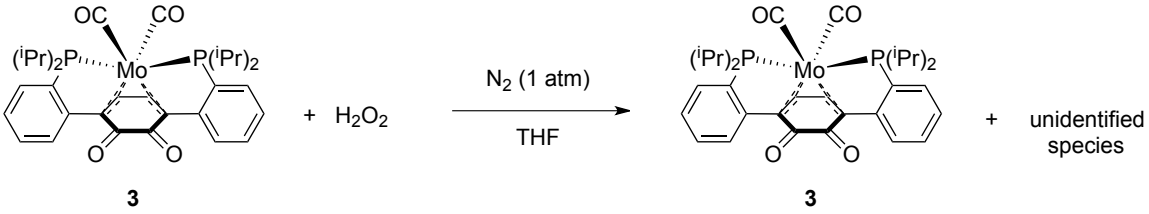
volume 3.0 mL). Quantification of Me_4Fc oxidation was determined by UV-vis analysis of this diluted solution and comparison to a similarly diluted solution of Me_4Fc (0.0106 g, 0.0438 mmol) after oxidation with Ag(OTf) (0.0118 g, 0.0459 mmol) and filtering to remove the Ag^0 precipitates.

Reactions with H_2O_2



2a **3**

2a: In a wet glove box under an N_2 atmosphere, **2a** (0.0213 g, 0.0316 mmol) in THF (2 mL) was stirred in a 20 mL vial. An aqueous solution of H_2O_2 (3.3 M, 12 μL, 0.0396 mmol) was added to the solution and the mixture stirred for 1 hour at room temperature. The volatiles were then removed under reduced pressure, and the residue was taken up in CD_2Cl_2 (0.6 mL) to reveal quantitative conversion from **2a** to **3**.



3: As above, to a stirred solution of **3** (0.0198 g, 0.0307 mmol) and 1,3,5-trimethoxybenzene (0.0039 g, 0.0315 mmol) in THF (2 mL) in a 20 mL vial was added an aqueous solution of H_2O_2 (3.3 M, 12 μL, 0.0396 mmol). The mixture was stirred for 1 hour at room temperature. The volatiles were then removed under reduced pressure, and the residue was taken up in CD_2Cl_2 (0.6 mL) to reveal approximately 80% of **3** remained, along with approximately 20% conversion to unidentified species by ^1H (relative integration of central arene C-H to internal standard trimethoxybenzene aryl C-H) and ^{31}P (relative integration of peak at 71 ppm corresponding to **3** to group of signals at ca. 58 ppm corresponding to unidentified species) NMR spectroscopy.

Quantification of O_2 consumed and CO released in conversion of 2a to 3

In a Schlenk flask charged with a stir bar, 0.0504 g (0.0747 mmol) of **2a** was dissolved in $CHCl_3$ (12 mL). The solution was degassed by three freeze-pump-thaw cycles. The

reaction vessel was then exposed to 5.01 eq of O_2 (0.377 mmol) via calibrated gas bulb and stirred *vigorously* for 5 hours at room temperature. After 5 hours the solution was frozen and the gas in the Schlenk flask was pumped through a liquid nitrogen cooled trap and collected in a calibrated volume (31.2 mL) using a Toepler pump. After 20 minutes (ca. 25 cycles of the Toepler pump) the Schlenk flask was sealed and thawed. Upon thawing the solution was re-frozen and the aforementioned Toepler pump process was repeated. After three of the described freeze-Toepler pump-thaw cycles, the pressure of gas collected was found to be 246.6 mm Hg (0.414 mmol, 5.51 eq after confirming quantitative conversion of **2a** to **3** by ^{1}H and ^{31}P NMR spectroscopy). The gas was then exposed to a degassed solution of NaOH (0.75 g, 18.8 mmol) and pyrogallol (0.5 g, 3.96 mmol) in H_2O (20 mL) in a second Schlenk flask, and the solution was stirred *vigorously* for 4 hours to consume the excess O_2. After 4 hours, the aqueous solution was frozen and the gas in the Schlenk flask was pumped through a liquid nitrogen cooled trap and collected in a calibrated bulb (31.2 mL) using three of the aforementioned freeze-Toepler pump-thaw cycles and the pressure of gas measured. Using the Toepler pump, the gas was then pumped through a CuO filled tube. The tube was heated and kept between 300 and 350 °C. After 1 hour of pumping the gas through the CuO tube, the pressure of gas was again measured. By subtracting the two measurements, the total pressure of gas consumed in the CuO tube was found to be 47.5 mm Hg (0.0797 mmol, 1.06 eq). Performing the experiment described above in triplicate, it was found that reaction of **3** with approximately 5 equivalents of O_2 generated 0.48 ± 0.02 equivalents of gas, and the amount of non-O_2 gas consumed in the CuO tube was found to be 1.05 ± 0.05. This data is consistent with a stoichiometry of **2a** consuming 0.5 equivalents of O_2 and releasing 1 equivalent of CO.

To further support this stoichiometry and confirm the identity of the gas being released in the reaction as CO, the Toepler pump experiment was repeated as mentioned above using 0.0492 g (0.0729 mmol) of **2a** with the following modification: after consuming the excess O_2 in the NaOH/pyrogallol solution (rather than burning the gas in the CuO tube) the remaining gas was exposed to a solution of $HN(pic)_2$ (0.0524 g, 0.263 mmol) and $Cu(MeCN)_4OTf$ (0.0954 g, 0.253 mmol) in MeCN (12 mL) and the mixture stirred *vigorously* for 4 hours. After 4 hours the gas remaining was measured, and the total gas consumed by the Cu^{I} solution was found to be 0.98 eq. IR data of the resulting Cu^{I} solution revealed a band at 2091 cm^{-1} consistent with formation of the previously reported $HNpic_2Cu(CO)BArF_{20}$,[7] and identical to the band observed by independently exposing a mixture of $Cu(MeCN)_4OTf$ and $HN(pic)_2$ to excess CO in MeCN.

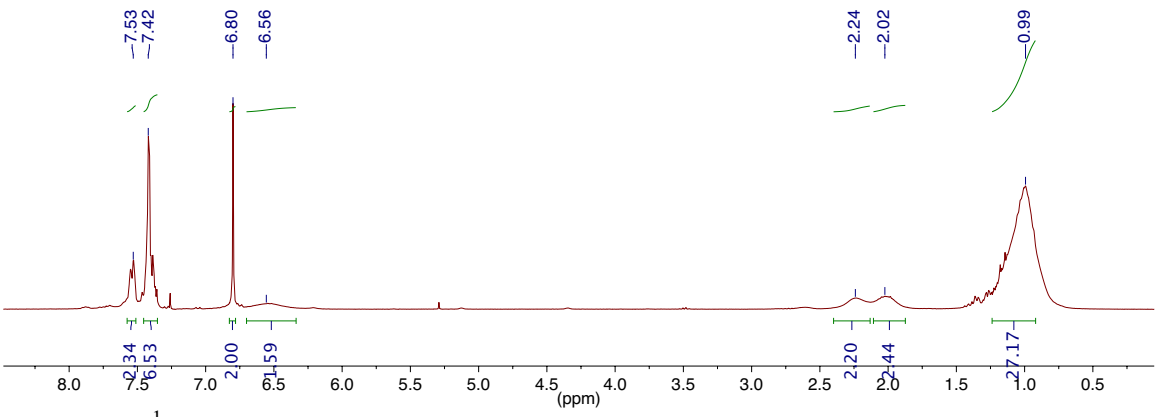


Figure S1. ^{1}H NMR spectrum of **1a** in $CDCl_3$ at 25 °C.

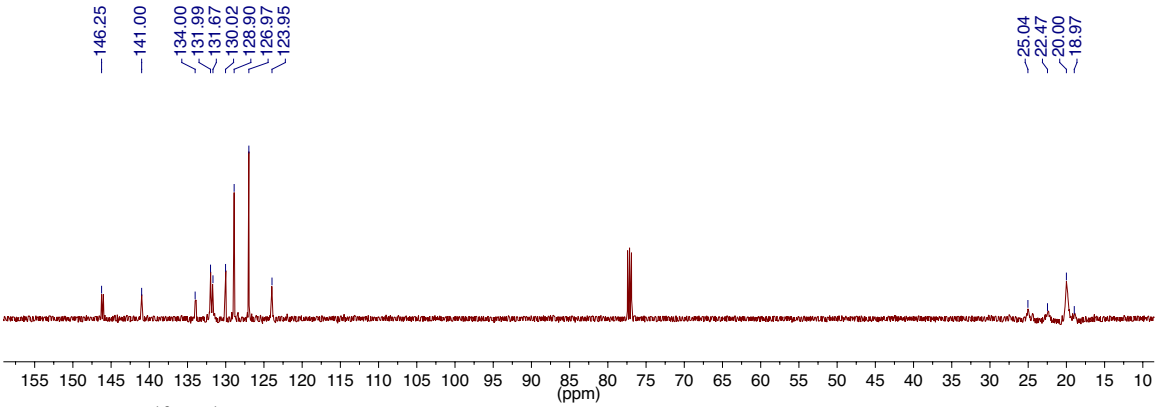


Figure S2. ^{13}C{^{1}H} NMR spectrum of **1a** in $CDCl_3$ at 25 °C.

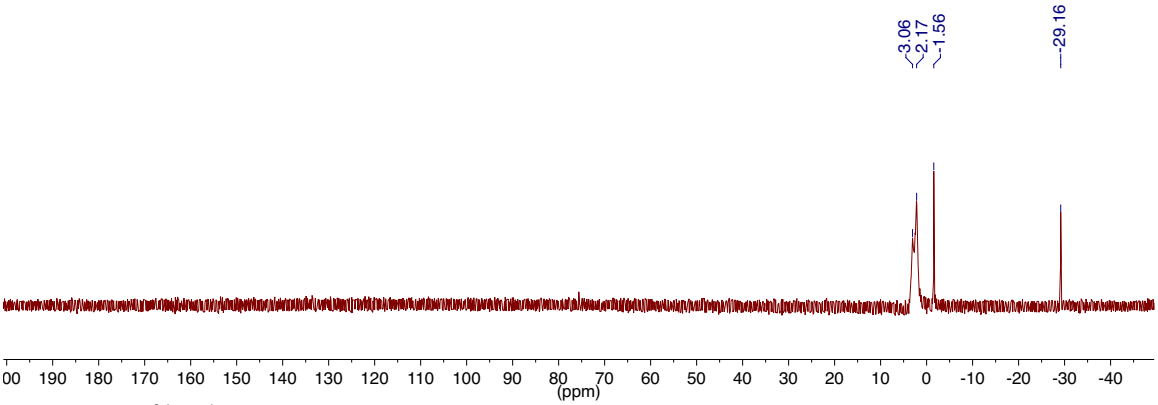


Figure S3. ^{31}P{^{1}H} NMR spectrum of **1a** in $CDCl_3$ at 25 °C.

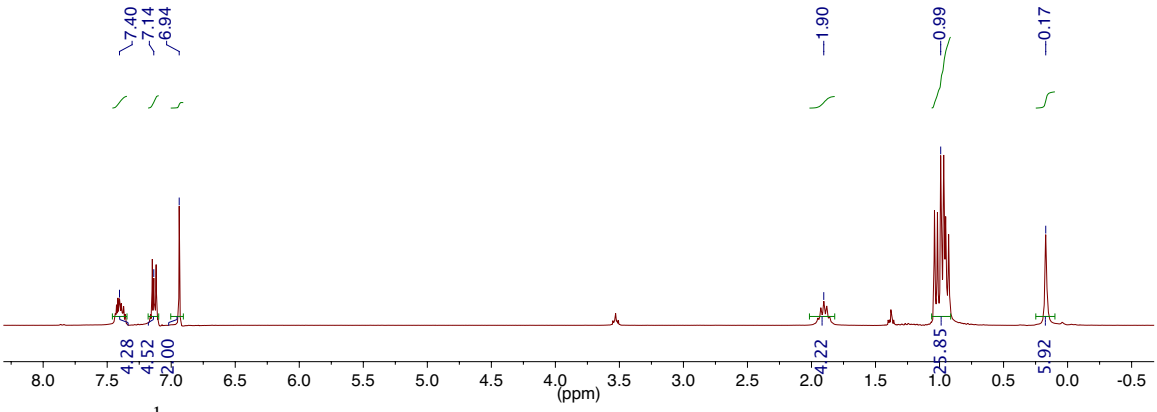


Figure S4. ^{1}H NMR spectrum of **1b** in C_6D_6 at 25 °C.

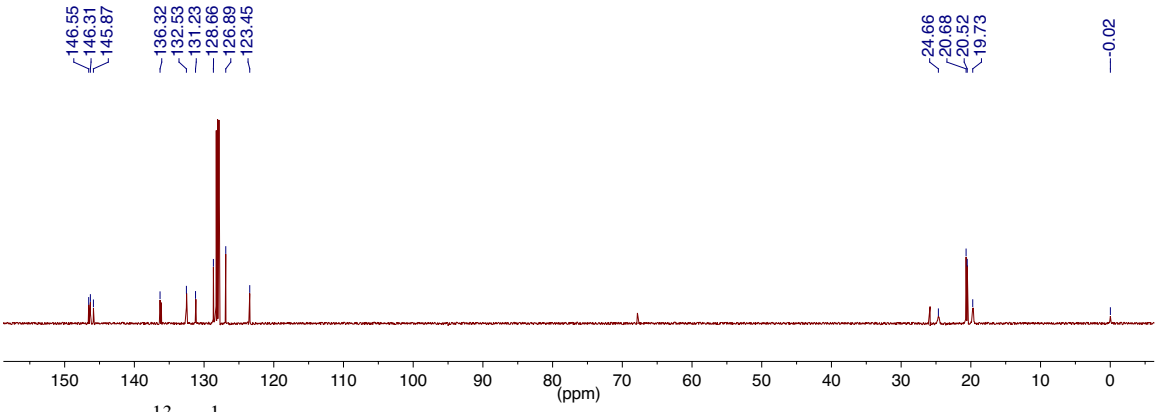


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **1b** in C_6D_6 at 25 °C.

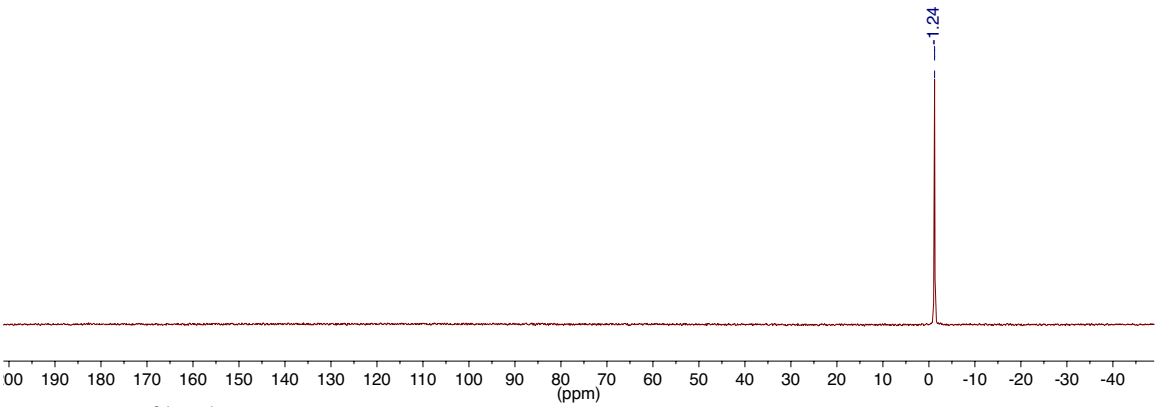


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **1b** in C_6D_6 at 25 °C.

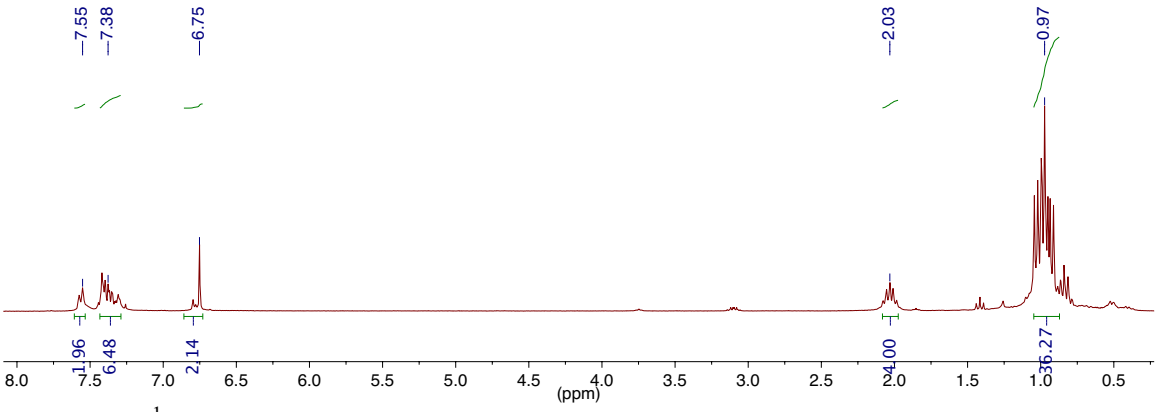


Figure S7. ^{1}H NMR spectrum of **1c** in $CDCl_3$ at 25 °C.

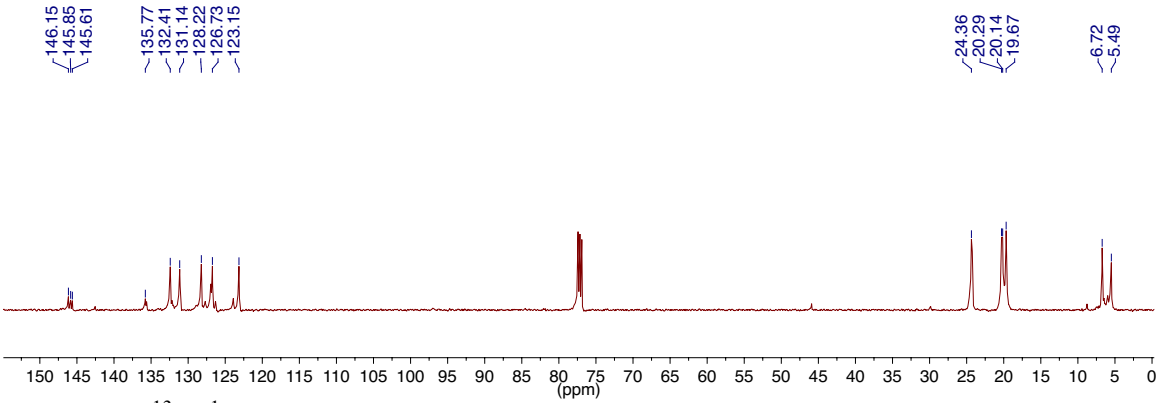


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **1c** in $CDCl_3$ at 25 °C.

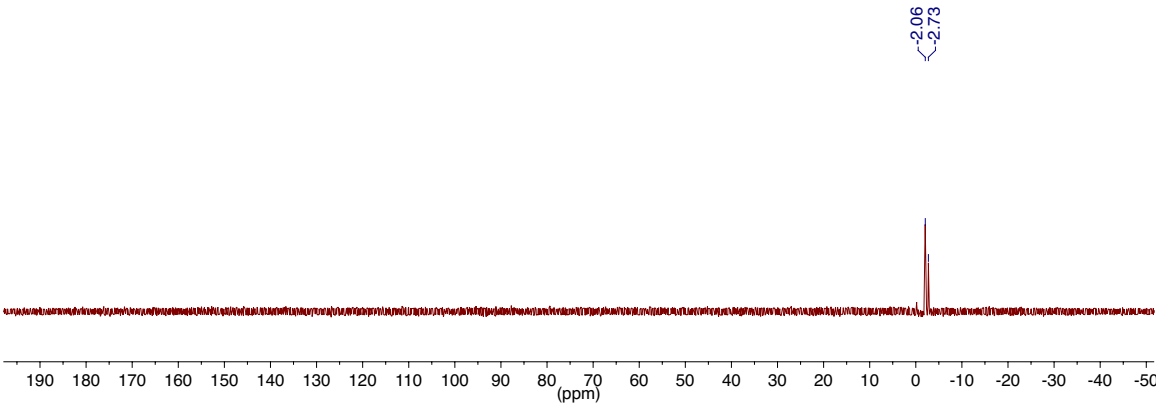


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of **1c** in $CDCl_3$ at 25 °C.

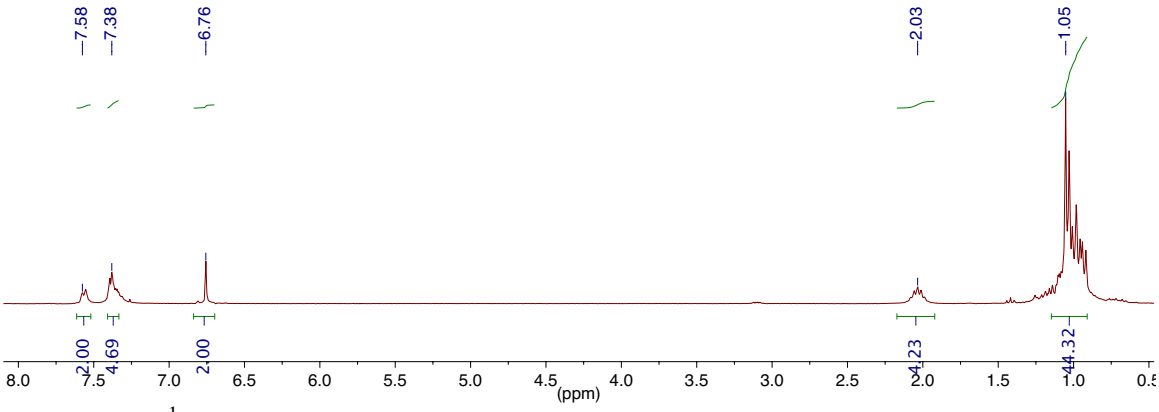


Figure S10. ^{1}H NMR spectrum of **1d** in $CDCl_3$ at 25 °C.

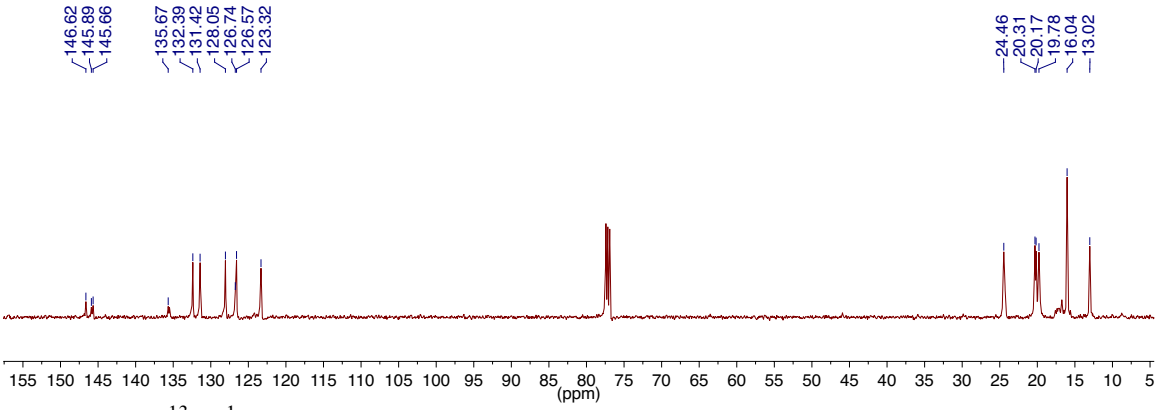


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **1d** in $CDCl_3$ at 25 °C.

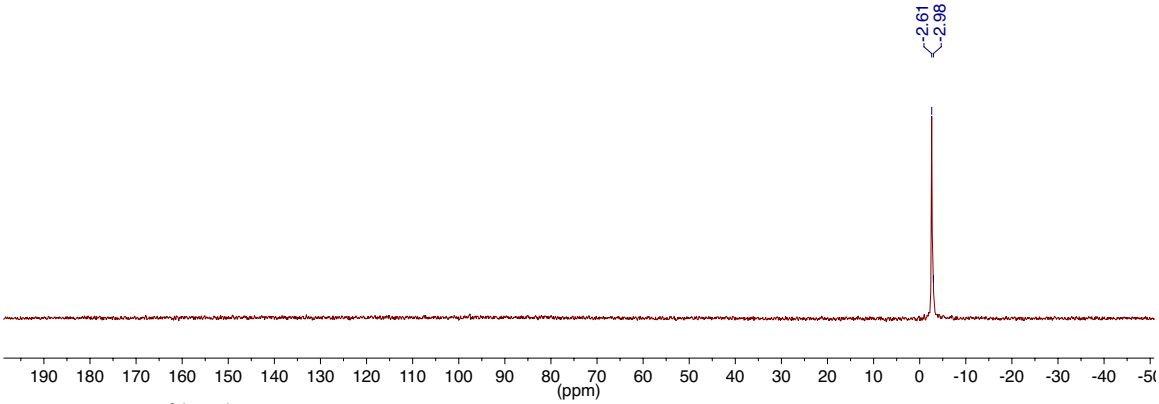


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of **1d** in $CDCl_3$ at 25 °C.

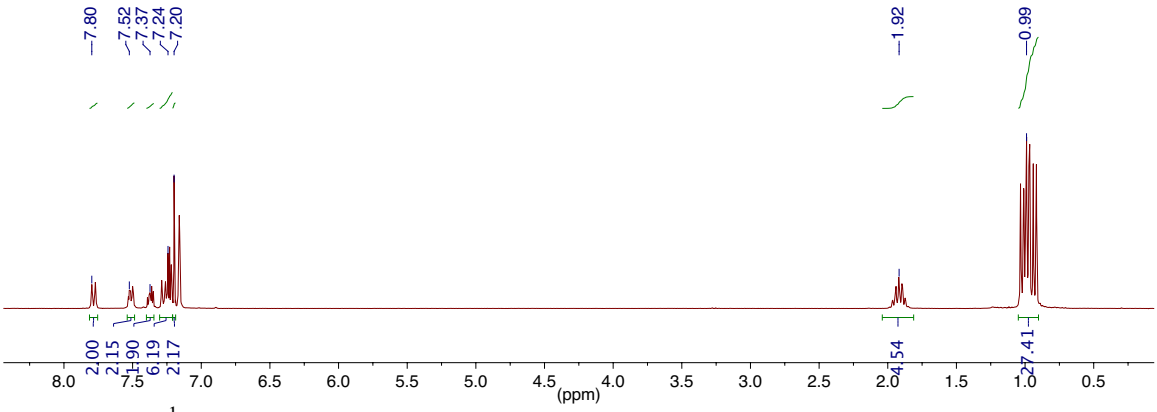


Figure S13. ^{1}H NMR spectrum of **1e** in C_6D_6 at 25 °C.

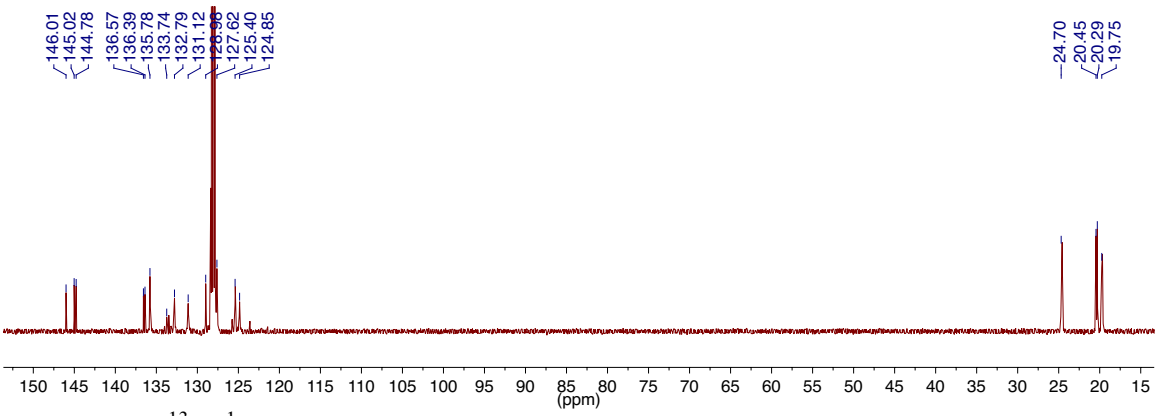


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **1e** in C_6D_6 at 25 °C.

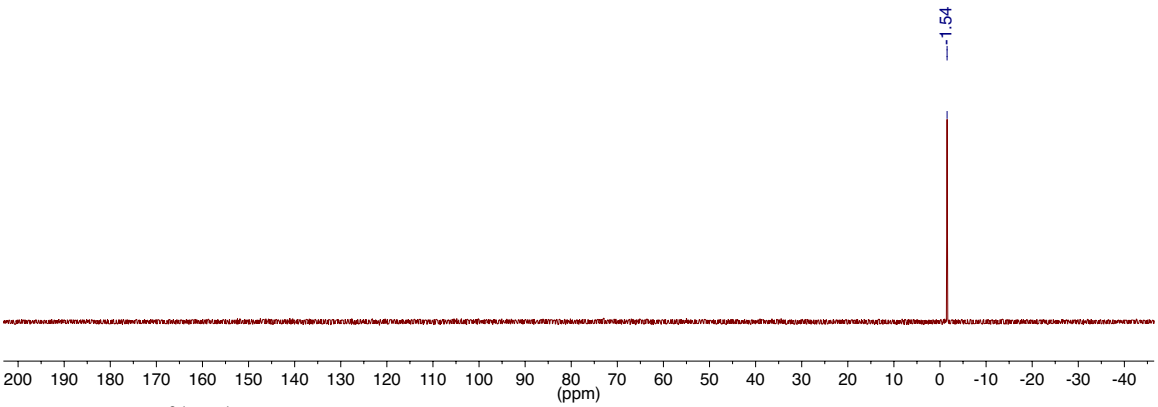


Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum of **1e** in C_6D_6 at 25 °C.

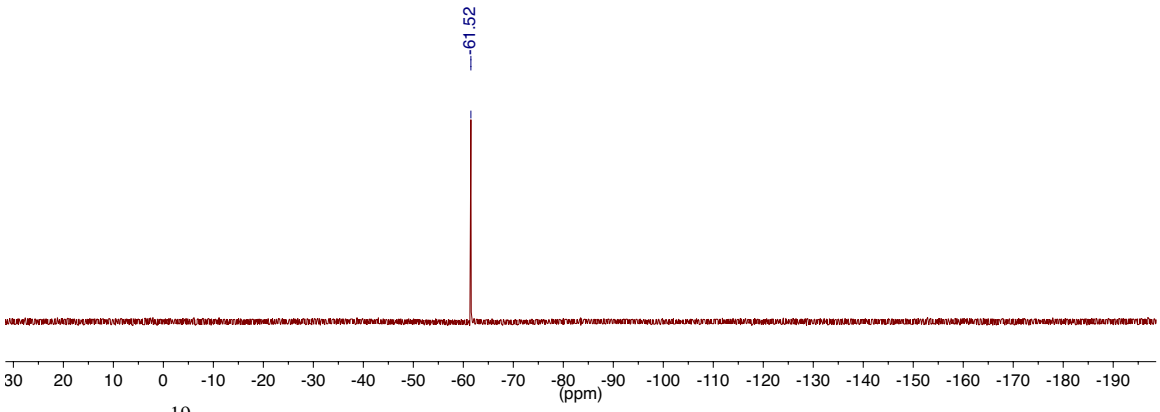


Figure S16. ^{19}F NMR spectrum of **1e** in C_6D_6 at 25 °C.

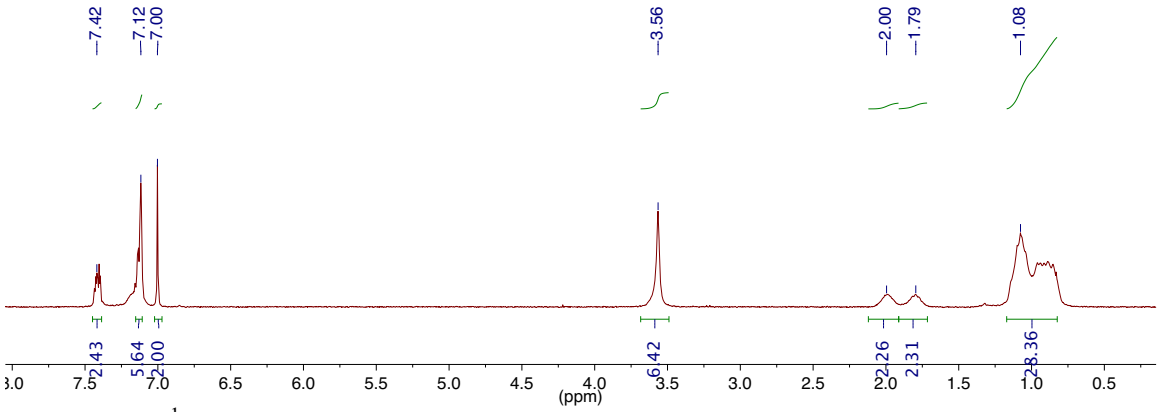


Figure S17. ^{1}H NMR spectrum of **1f** in $CDCl_3$ at 25 °C.

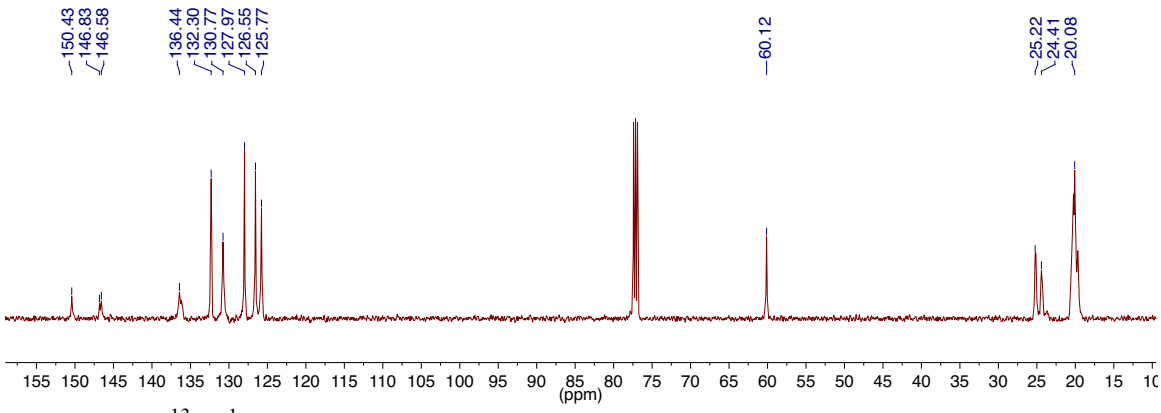


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **1f** in $CDCl_3$ at 25 °C.

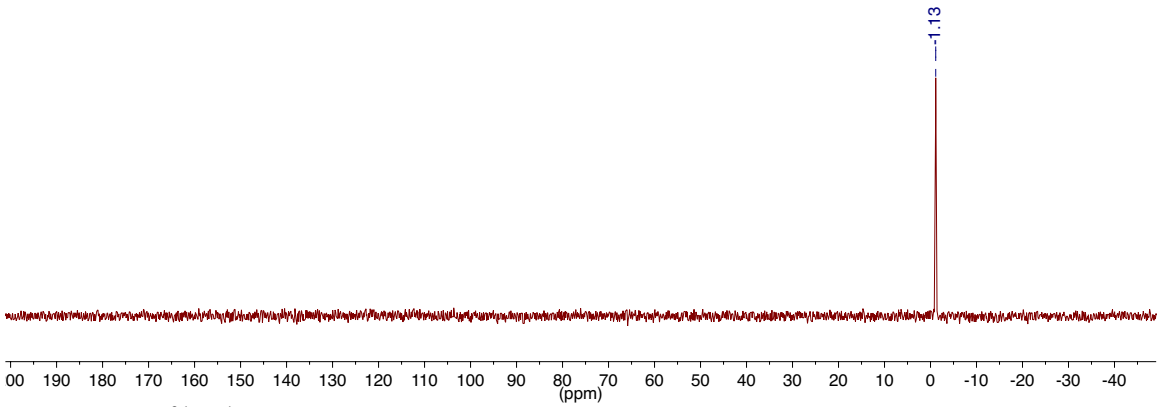


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of **1f** in $CDCl_3$ at 25 °C.

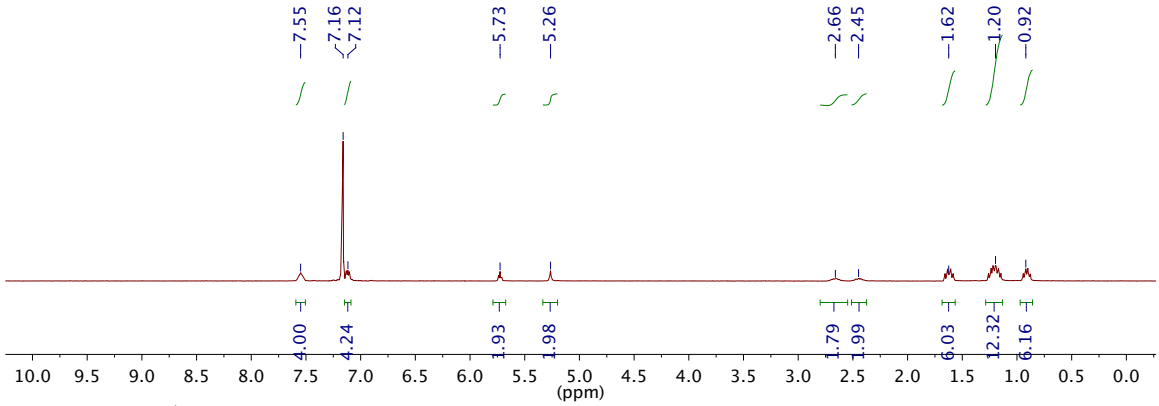


Figure S20. ^{1}H NMR spectrum of **2a** in C_6D_6.

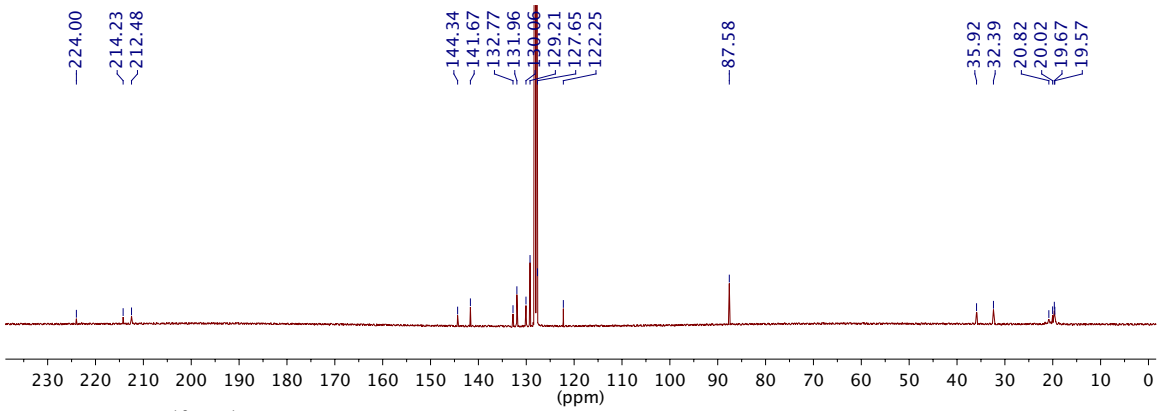


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6 at 75 °C.

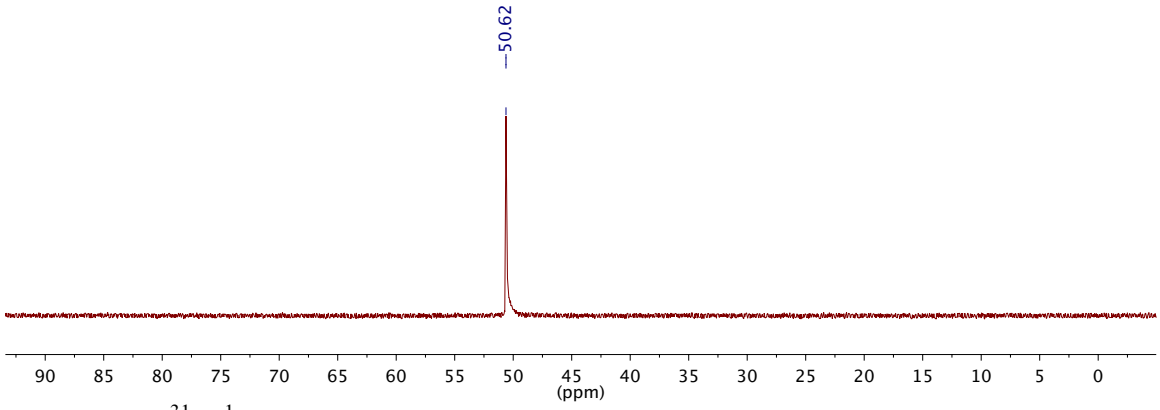


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6.

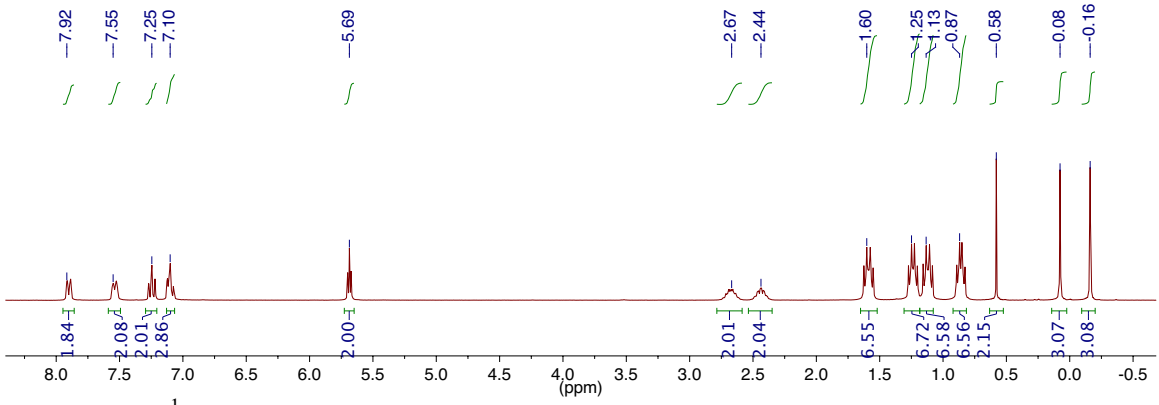


Figure S23. ^{1}H NMR spectrum of **2b** in C_6D_6 at 25 °C.

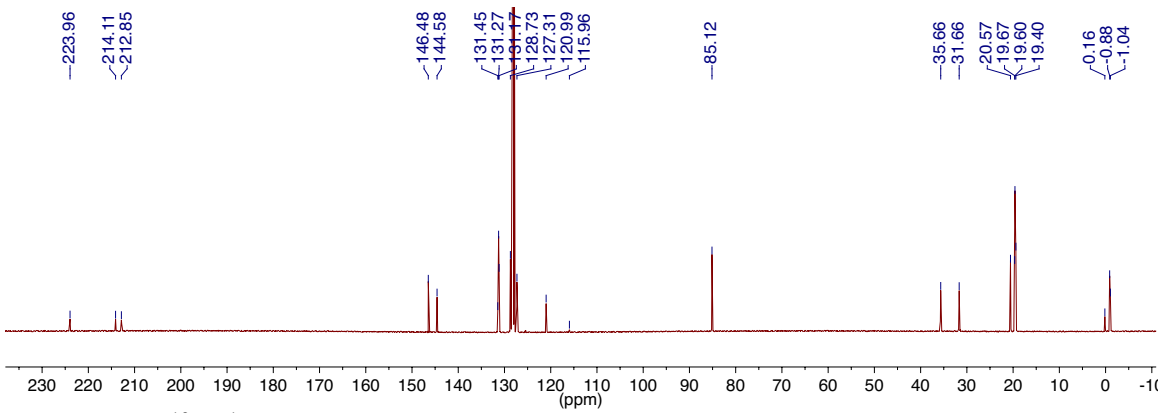


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in C_6D_6 at 25 °C.

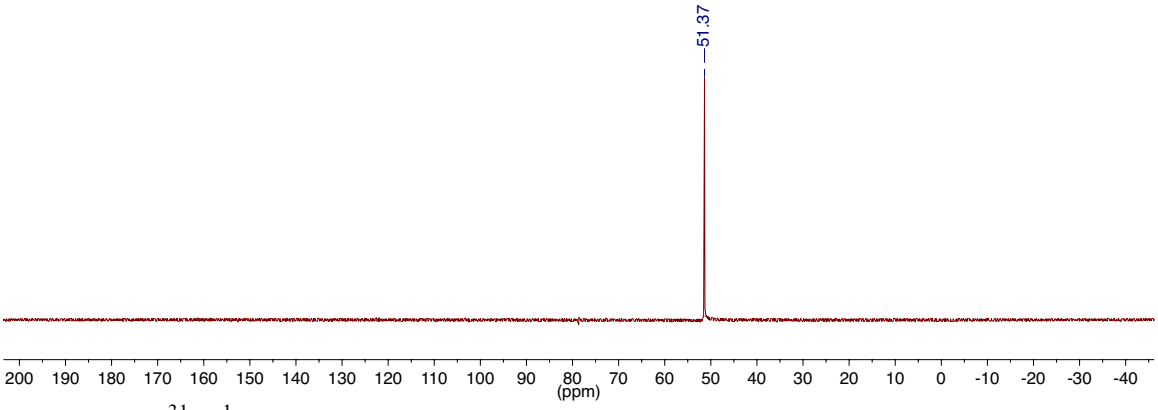


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum of **2b** in C_6D_6 at 25 °C.

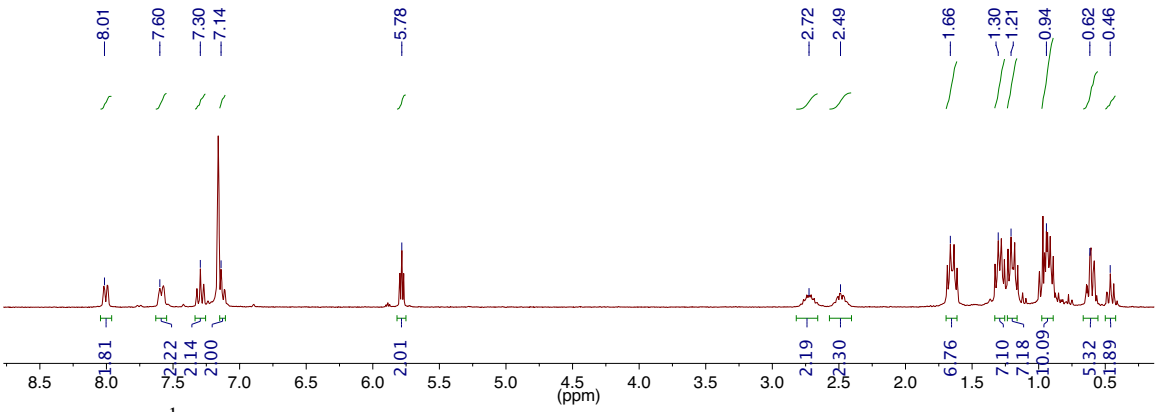


Figure S26. ^{1}H NMR spectrum of **2c** in C_6D_6 at 25 °C.

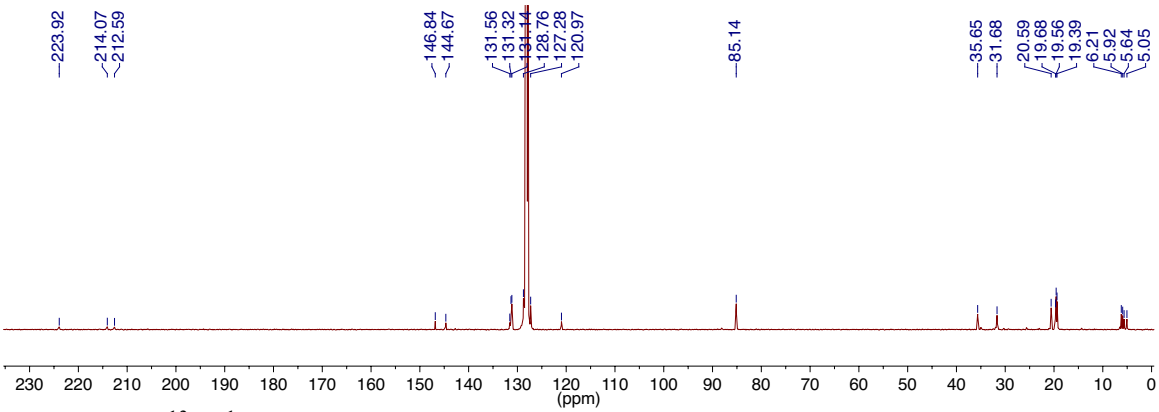


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of **2c** in C_6D_6 at 25 °C.

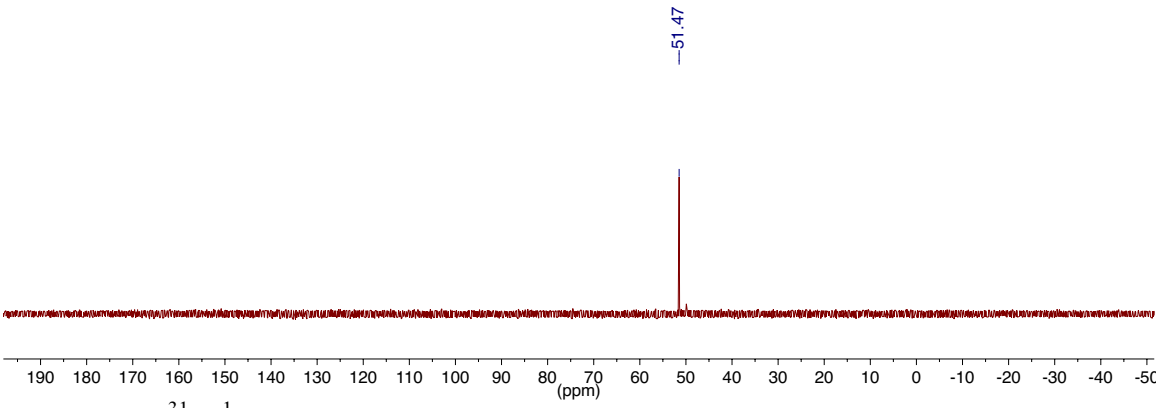


Figure S28. $^{31}P\{^{1}H\}$ NMR spectrum of **2c** in C_6D_6 at 25 °C.

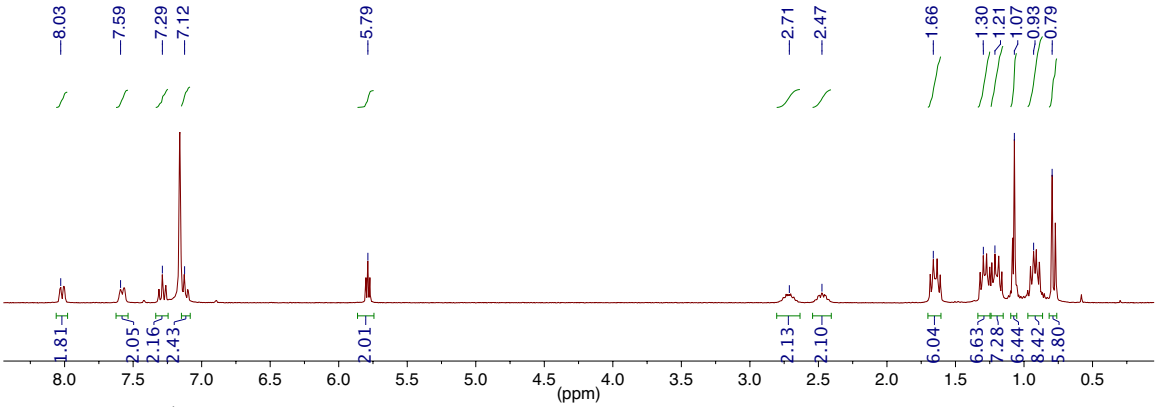


Figure S29. ^{1}H NMR spectrum of **2d** in C_6D_6 at 25 °C.

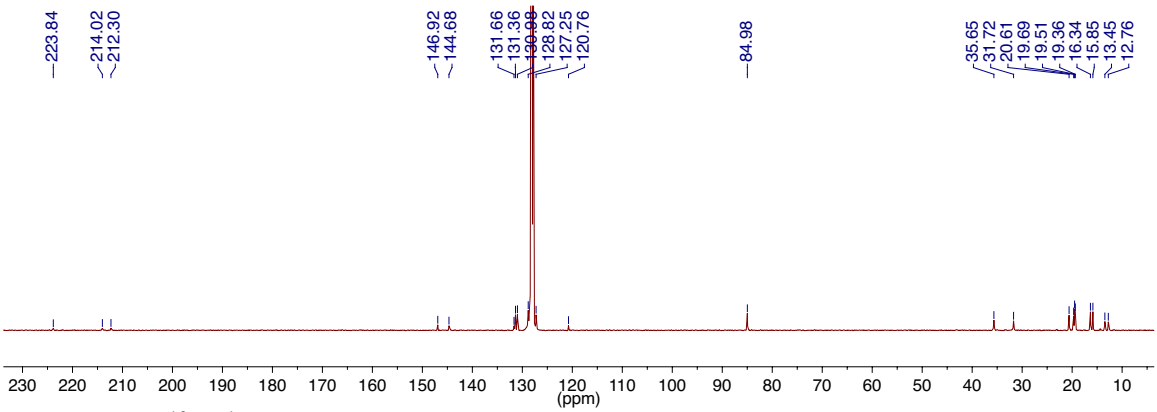


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of **2d** in C_6D_6 at 25 °C.

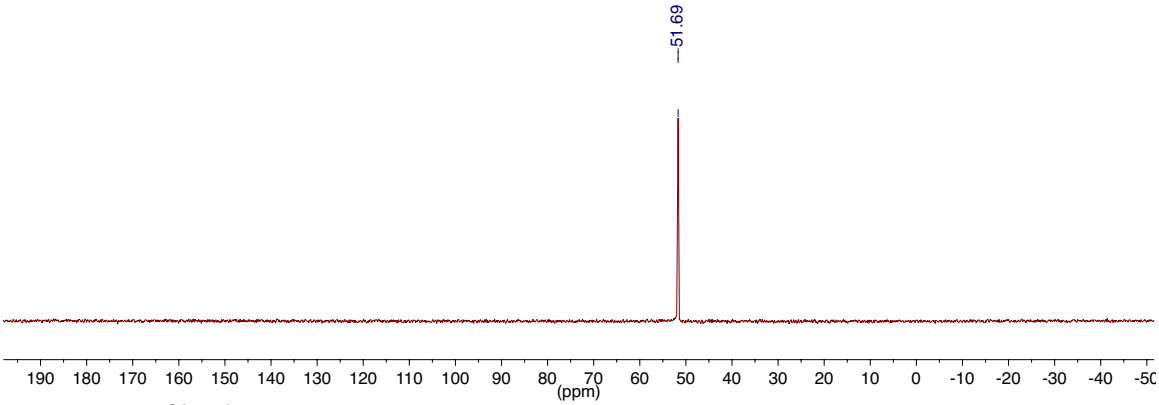


Figure S31. $^{31}P\{^{1}H\}$ NMR spectrum of **2d** in C_6D_6 at 25 °C.

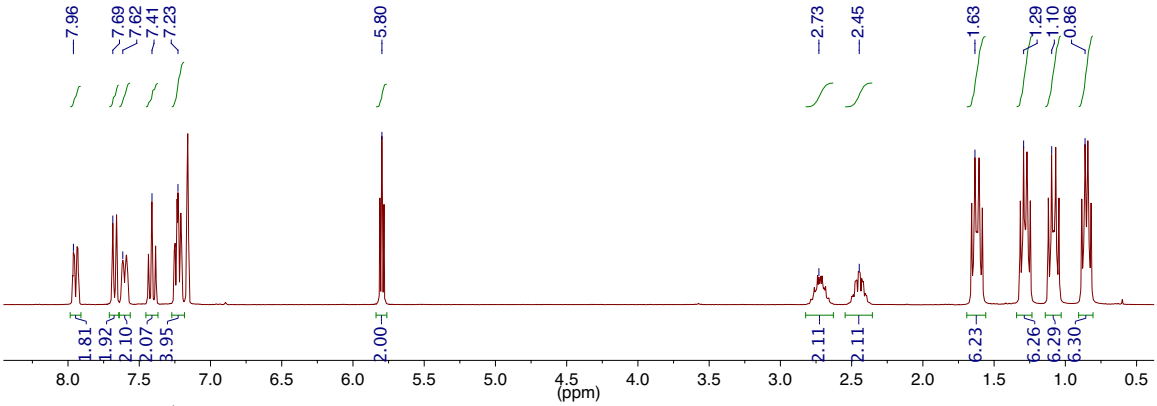


Figure S32. ^{1}H NMR spectrum of **2e** in C_6D_6 at 25 °C.

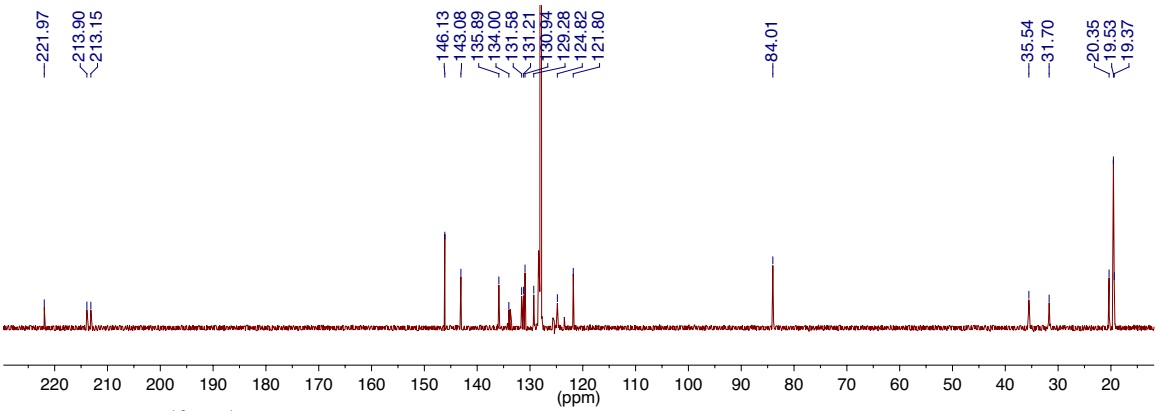


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of **2e** in C_6D_6 at 25 °C.

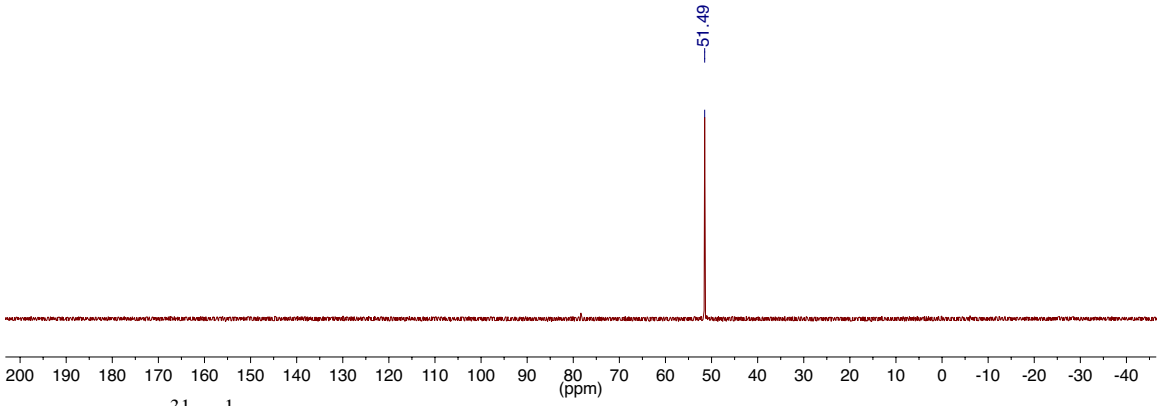


Figure S34. $^{31}P\{^{1}H\}$ NMR spectrum of **2e** in C_6D_6 at 25 °C.

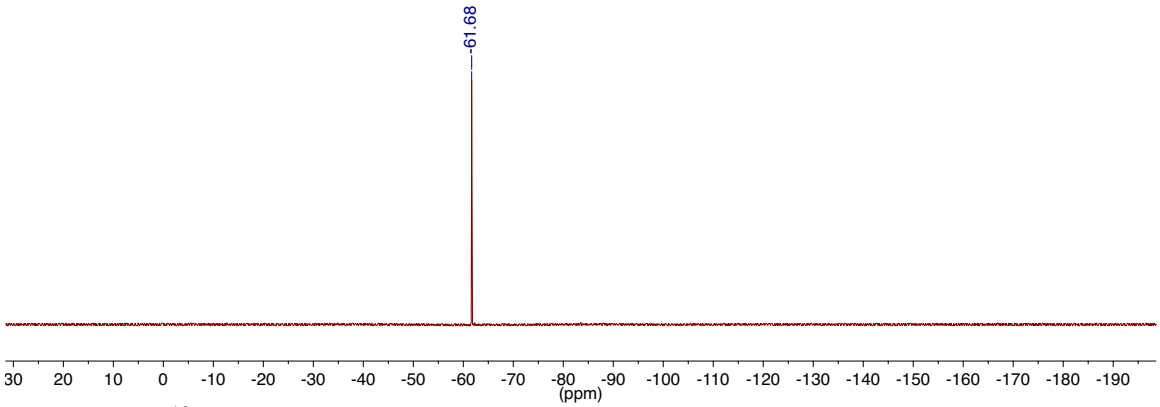


Figure S35. ^{19}F NMR spectrum of **2e** in C_6D_6 at 25 °C.

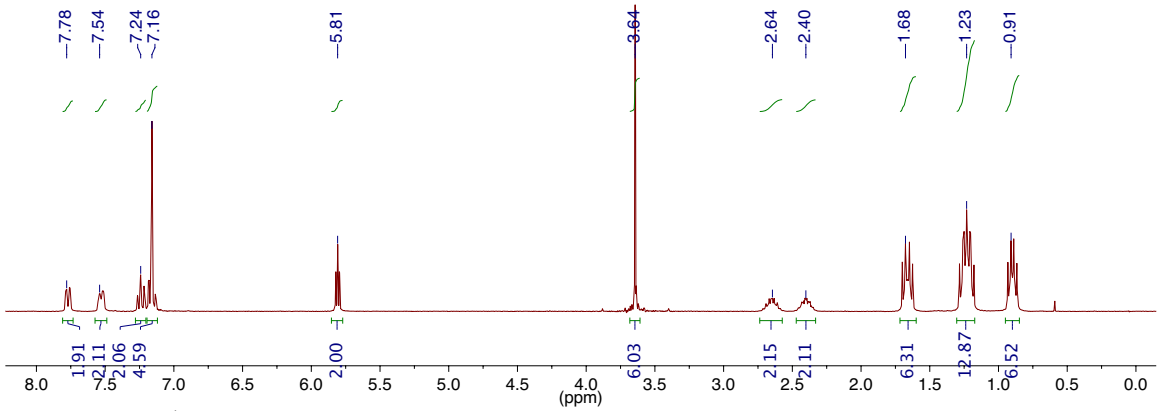


Figure S36. ^{1}H NMR spectrum of **2f** in C_6D_6 at 25 °C.

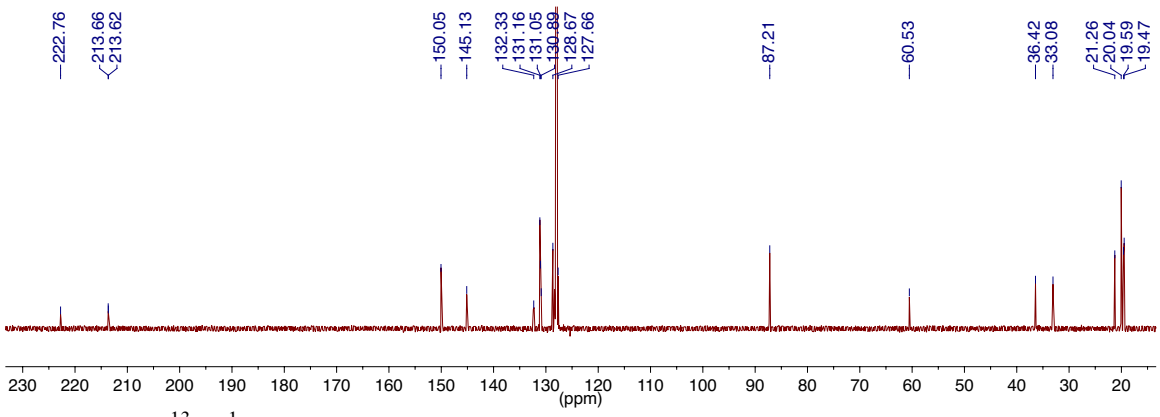


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum of **2f** in C_6D_6 at 25 °C. Solvent peaks off scale.

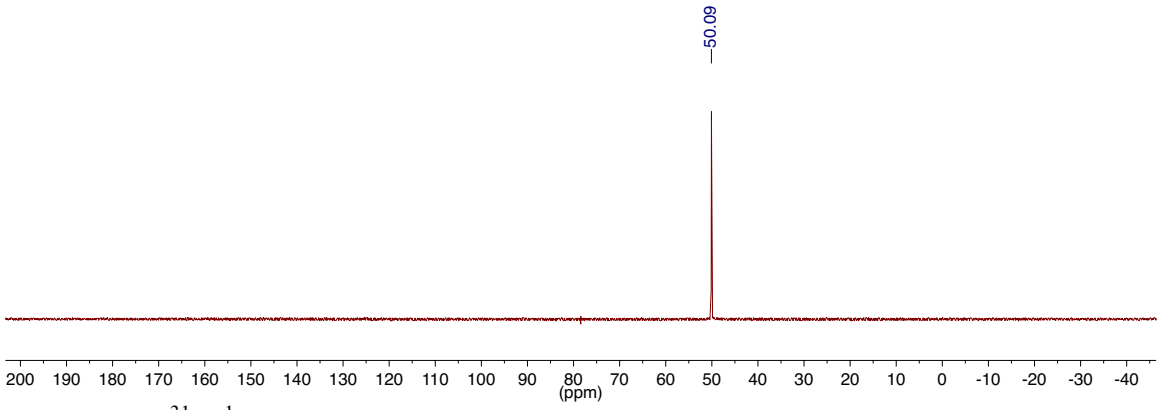


Figure S38. $^{31}P\{^{1}H\}$ NMR spectrum of **2f** in C_6D_6 at 25 °C.

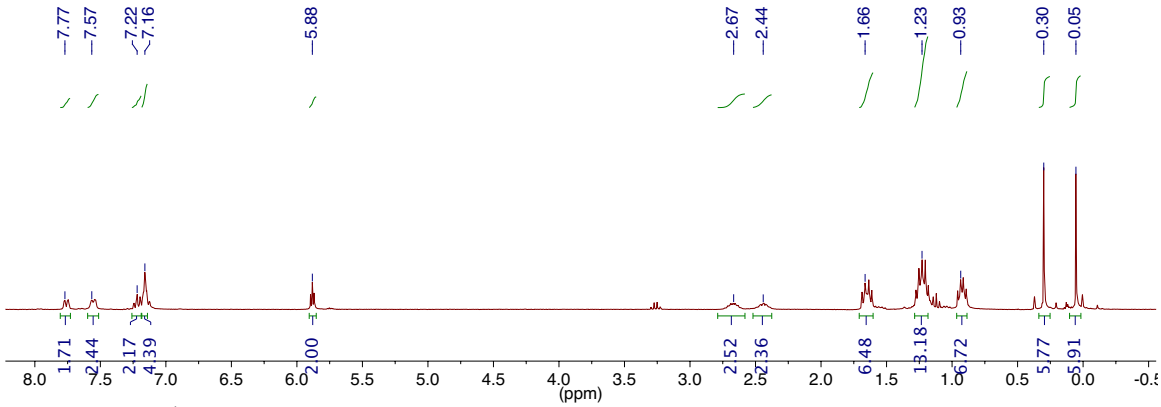


Figure S39. ^{1}H NMR spectrum of **2h** in C_6D_6 at 25 °C.

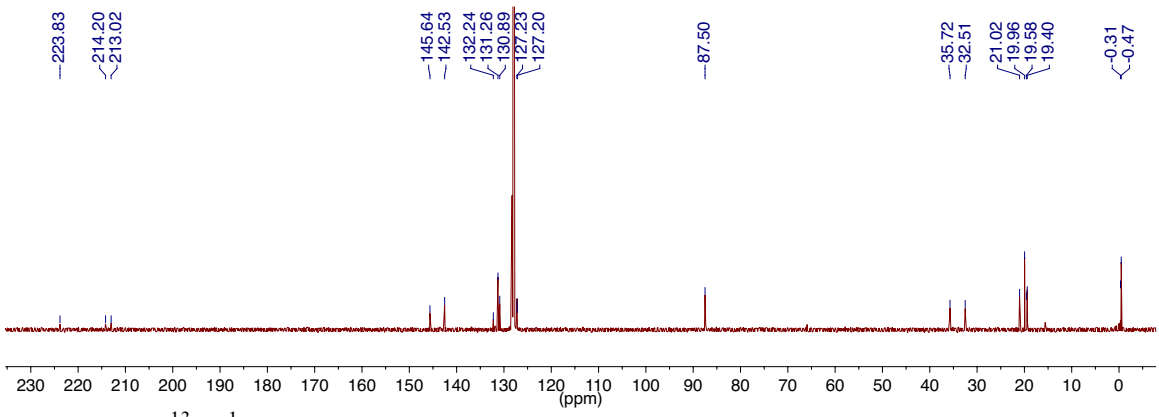


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of **2h** in C_6D_6 at 25 °C. Solvent peaks off scale

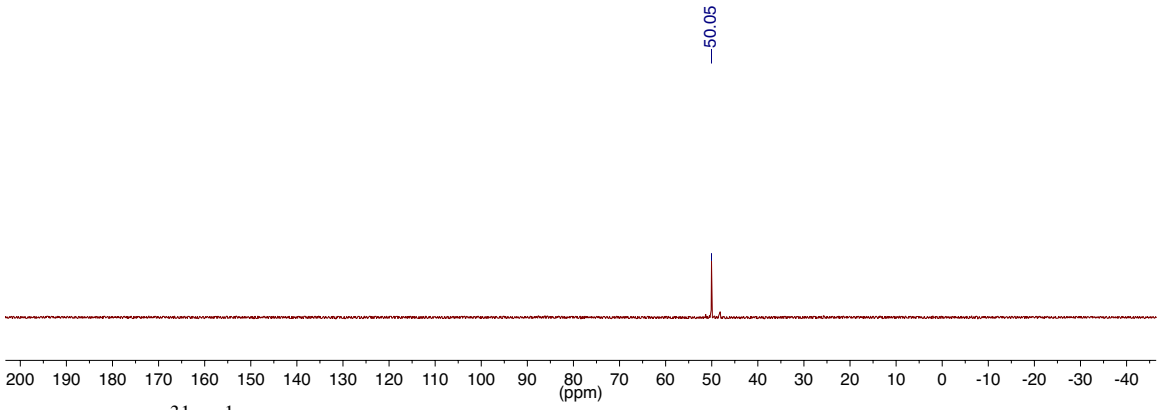


Figure S41. $^{31}P\{^{1}H\}$ NMR spectrum of **2h** in C_6D_6 at 25 °C.

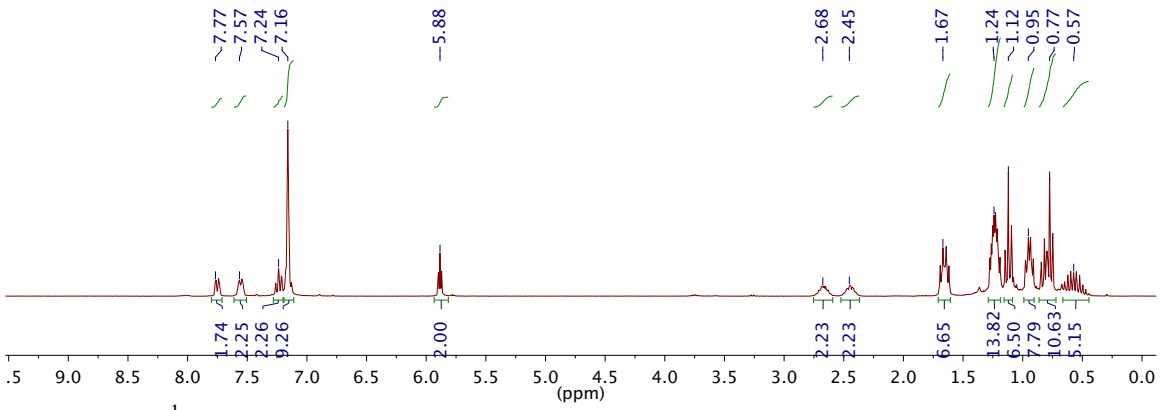


Figure S42. ^{1}H NMR spectrum of **2i** in C_6D_6 at 25 °C.

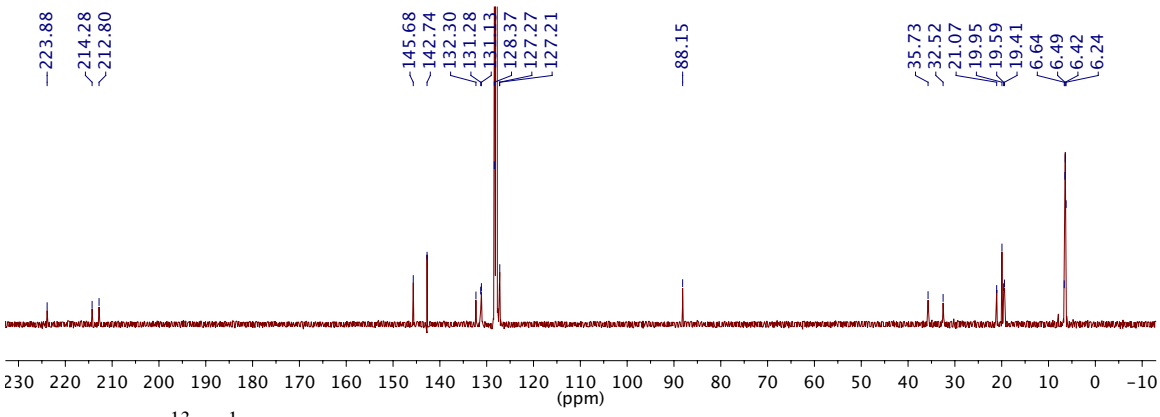


Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum of **2i** in C_6D_6 at 25 °C. Solvent peaks off scale

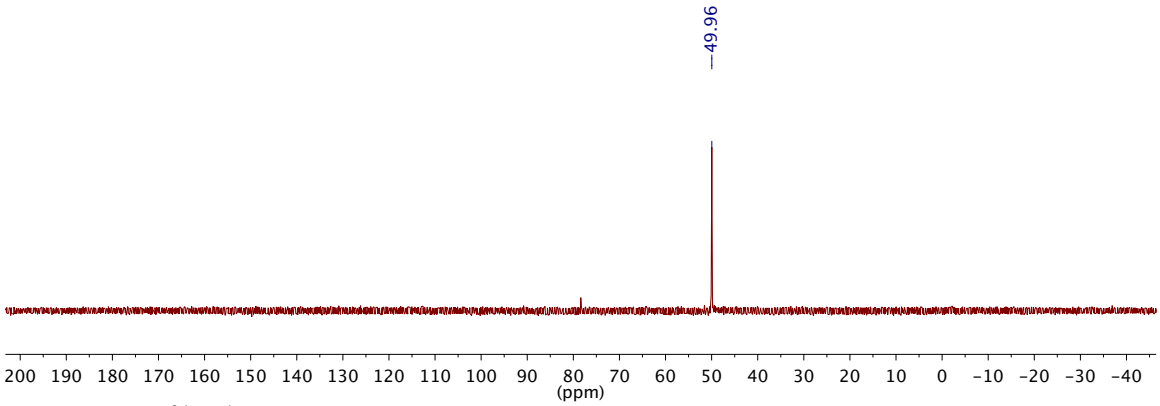


Figure S44. $^{31}P\{^{1}H\}$ NMR spectrum of **2i** in C_6D_6 at 25 °C.

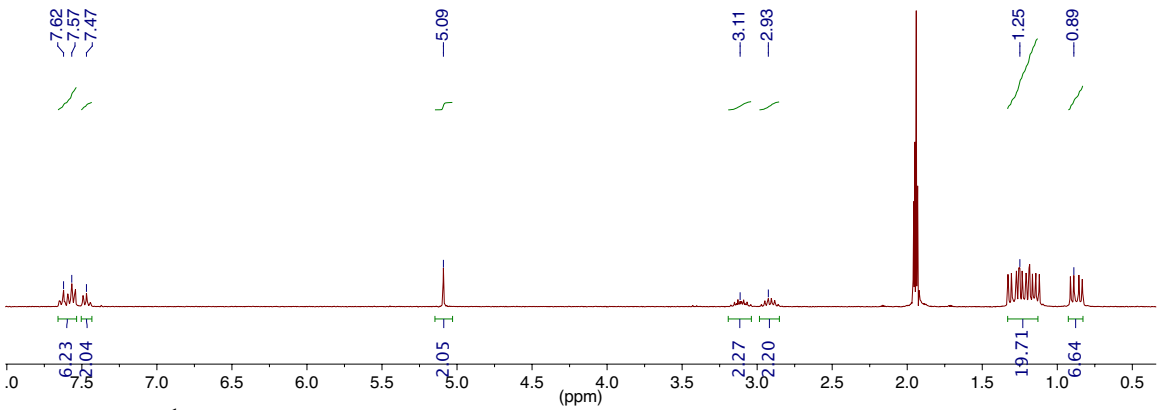


Figure S45. ^{1}H NMR spectrum of **3** in CD_3CN at 25 °C.

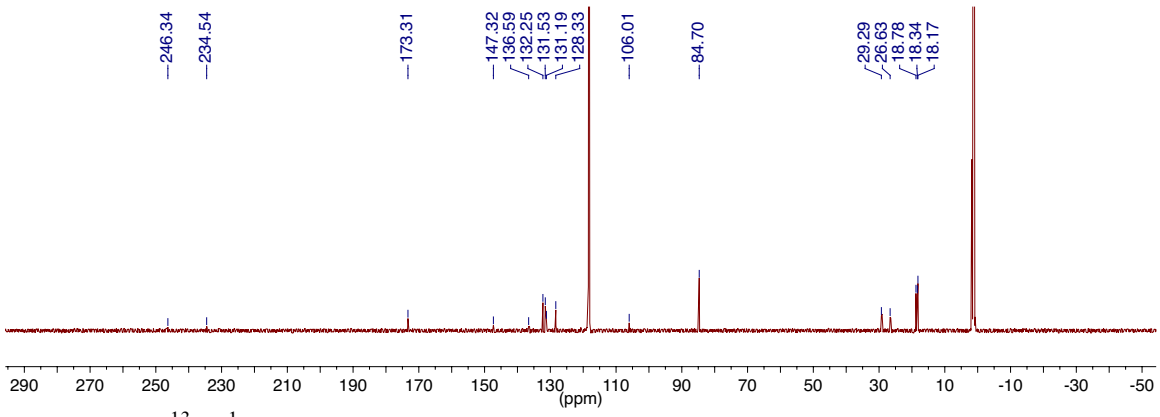


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in CD_3CN at 25 °C. Solvent peaks off scale.

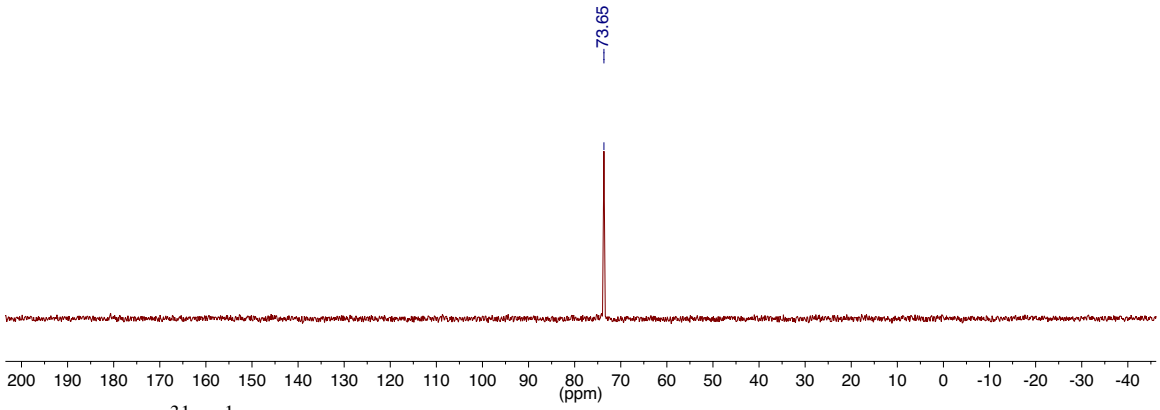


Figure S47. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in CD_3CN at 25 °C.

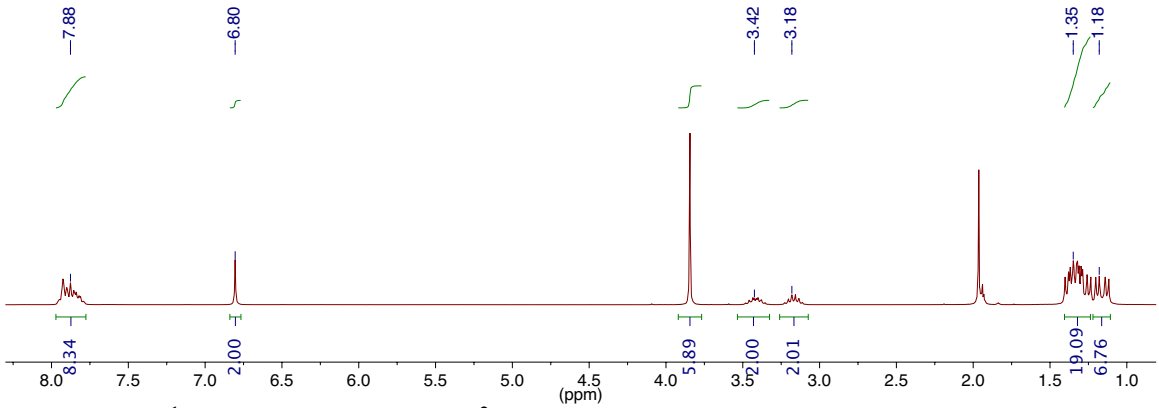


Figure S48. ^{1}H NMR spectrum of $[\mathbf{5}^{2+}][OTf^-]_2$ in CD_3CN at 25 °C.

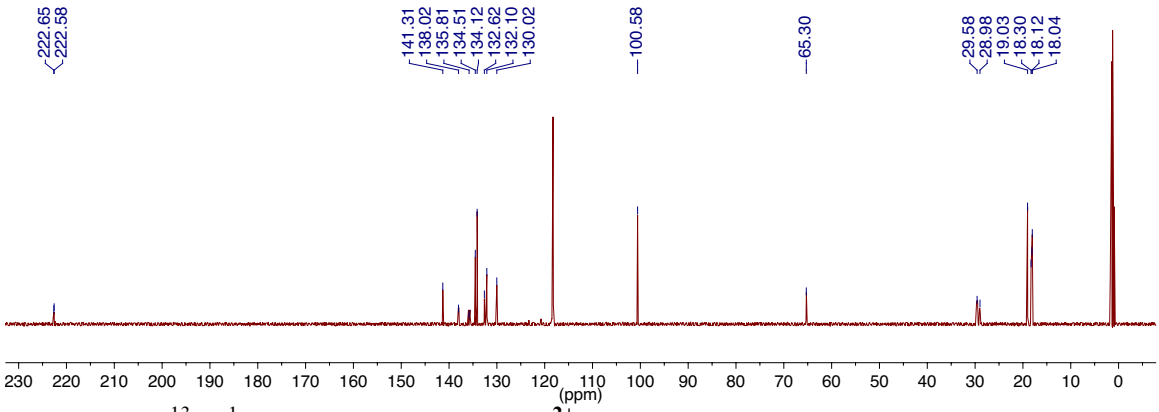


Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum of $[\mathbf{5}^{2+}][OTf^-]_2$ in CD_3CN at 25 °C.

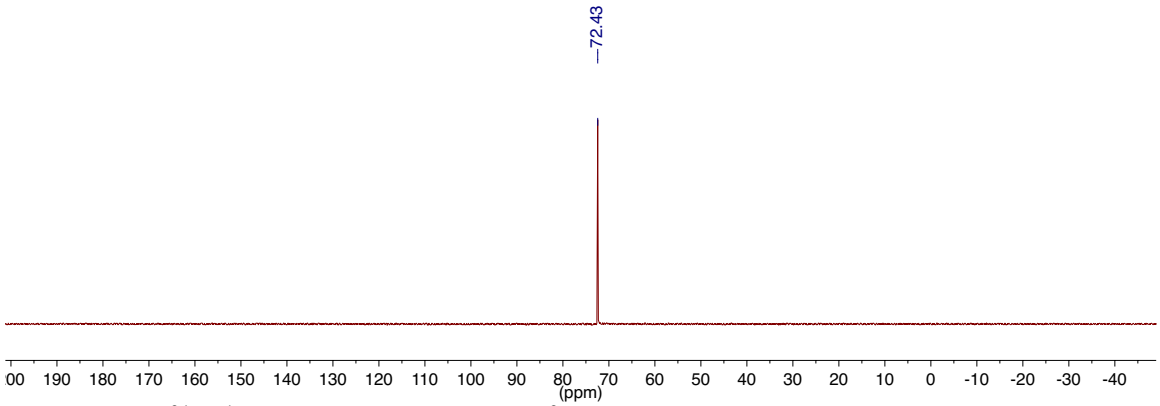


Figure S50. $^{31}P\{^{1}H\}$ NMR spectrum of $[\mathbf{5}^{2+}][OTf^-]_2$ in CD_3CN at 25 °C.

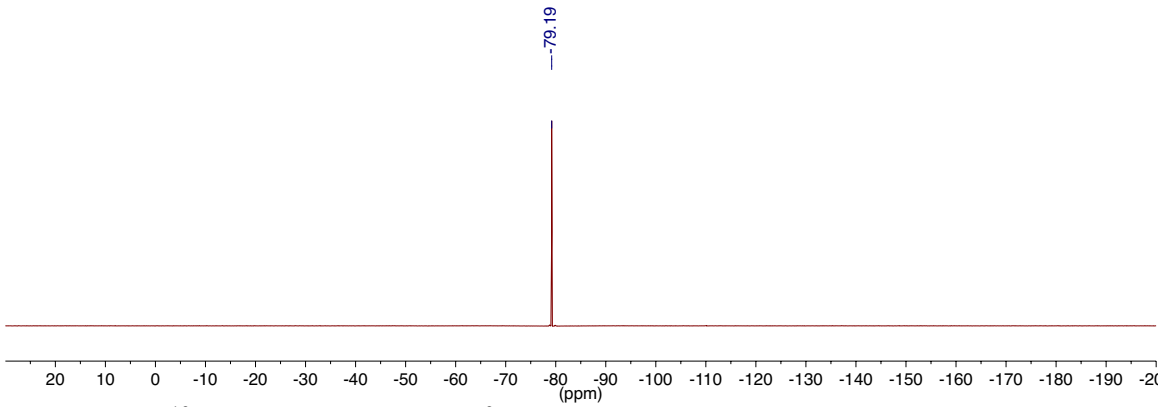


Figure S51. ^{19}F NMR spectrum of $[\mathbf{5}^{2+}][OTf^-]_2$ in CD_3CN at 25 °C.

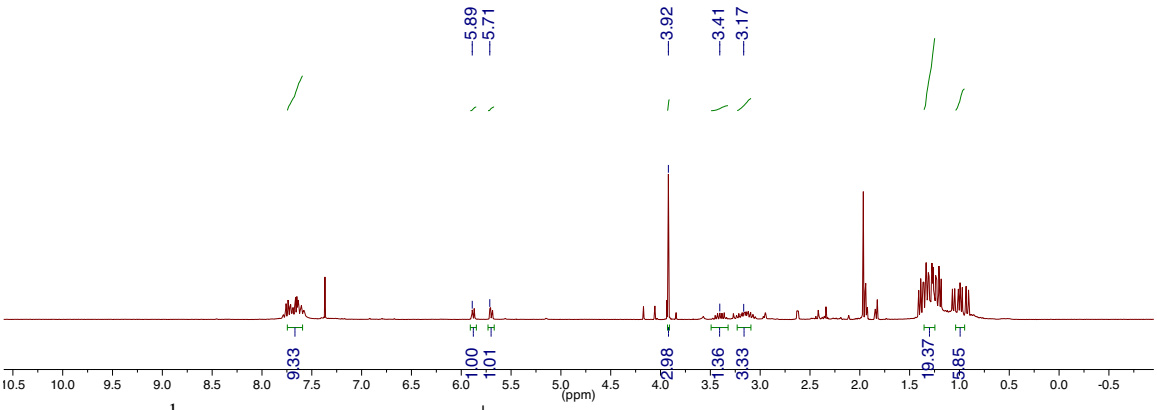


Figure S52. ^{1}H NMR spectrum of [**6**$^{+}$][OTf^{-}] in CD_3CN at 25 °C.

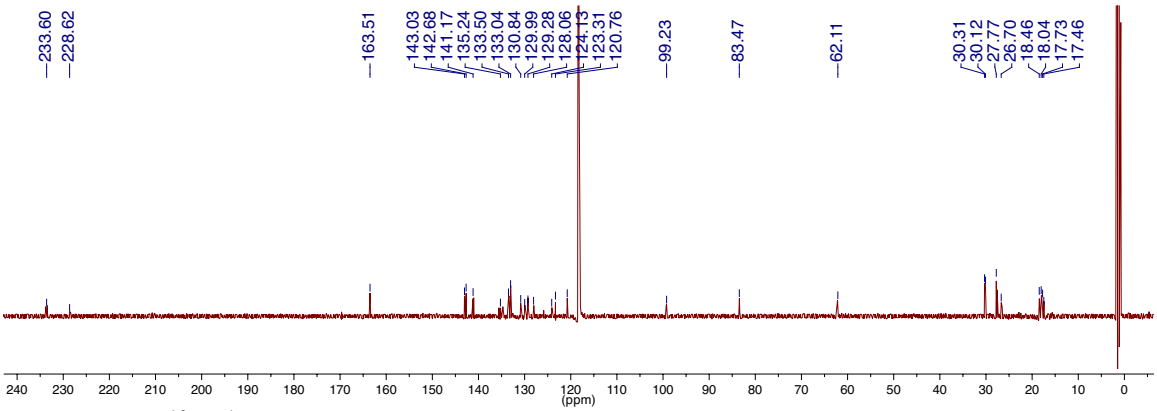


Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum of [**6**$^{+}$][OTf^{-}] in CD_3CN at 25 °C.

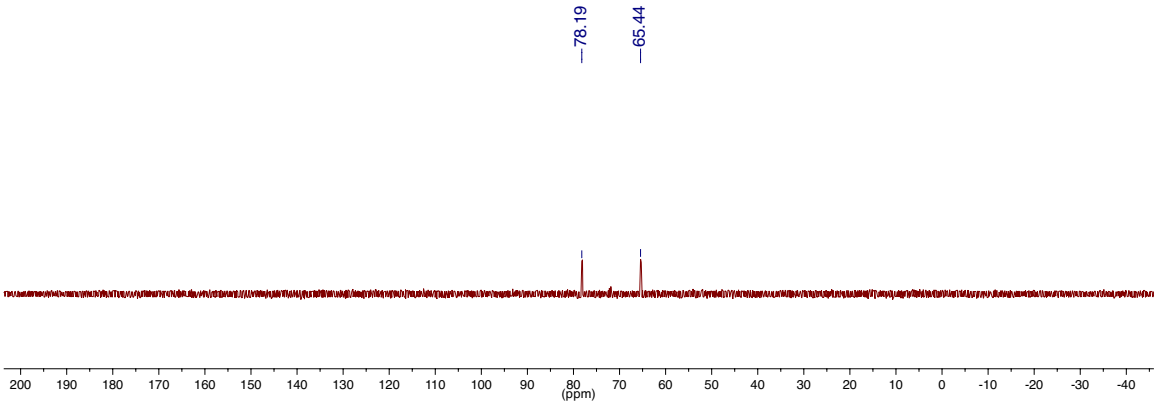


Figure S54. $^{31}P\{^{1}H\}$ NMR spectrum of [**6**$^{+}$][OTf^{-}] in CD_3CN at 25 °C.

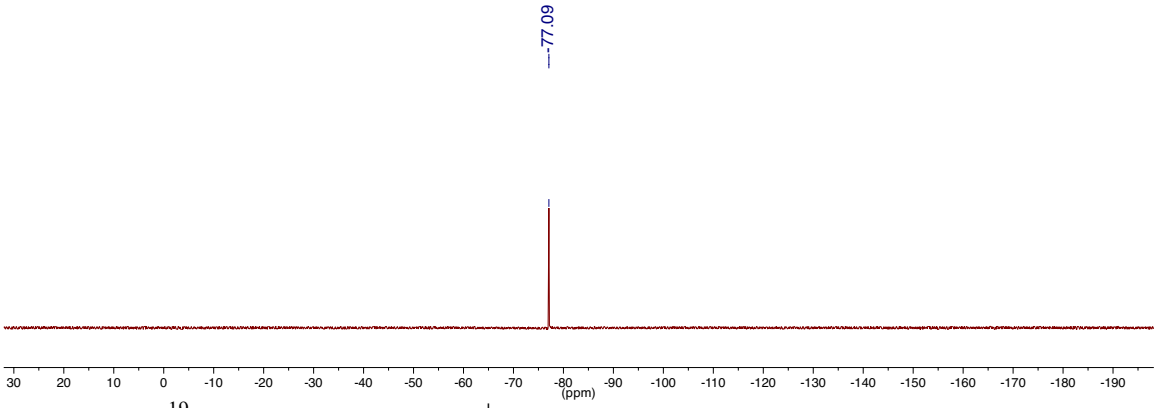


Figure S55. ^{19}F NMR spectrum of [**6**$^{+}$][OTf^{-}] in CD_3CN at 25 °C.

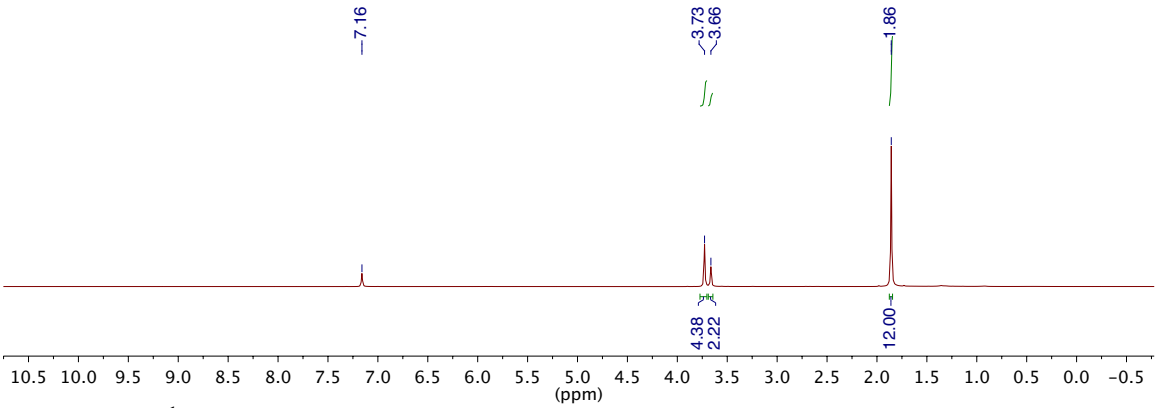


Figure S56. ^{1}H NMR spectrum of Me_4Fc in C_6D_6 at 25 °C.

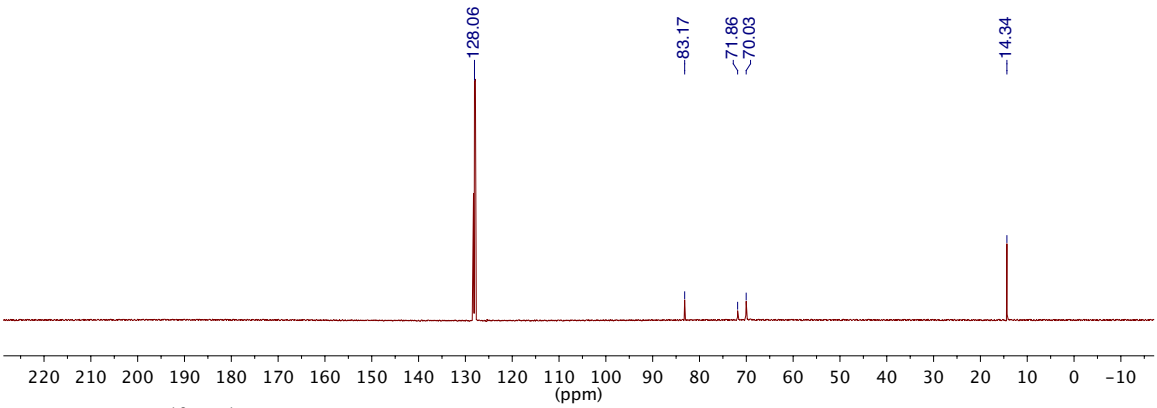


Figure S57. $^{13}C\{^{1}H\}$ NMR spectrum of Me_4Fc in C_6D_6 at 25 °C.

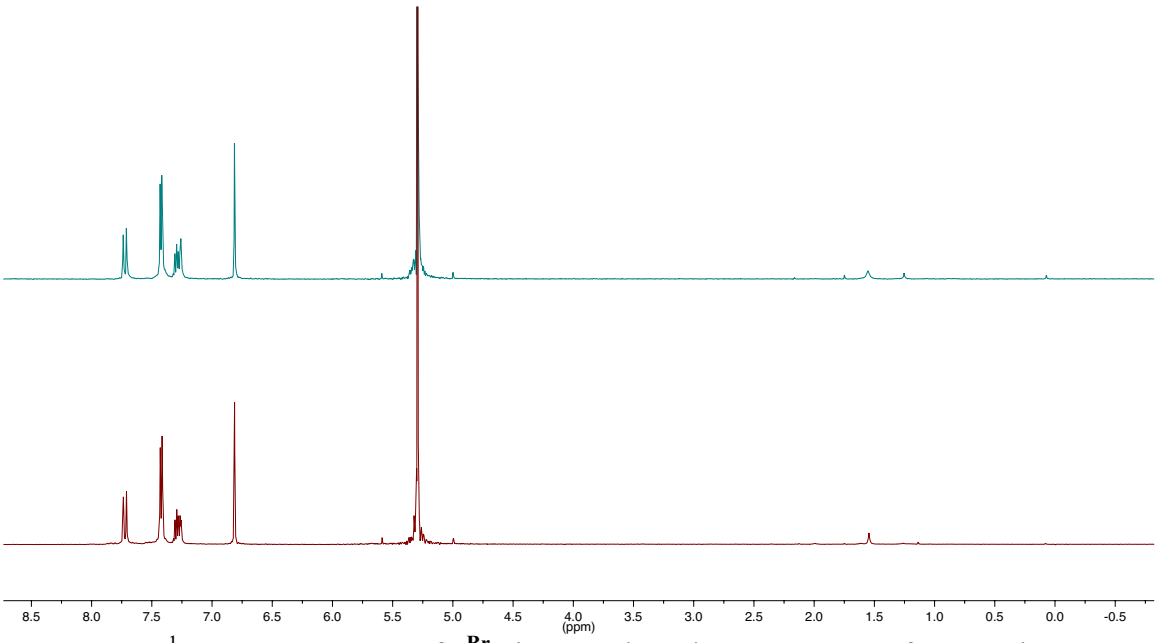


Figure S58. ^{1}H NMR spectrum of **1^{Br}a** in CD_2Cl_2 under O_2 at 25 °C after 10 minutes (bottom) and 24 hours (top). Solvent peak off scale.

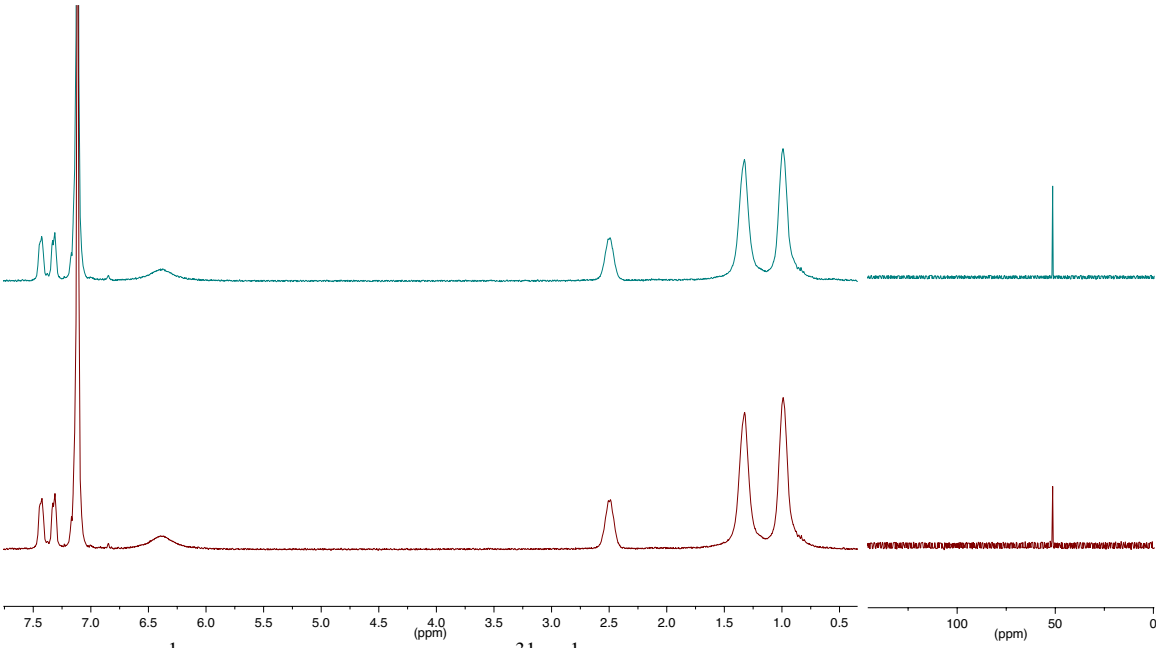


Figure S59. ^{1}H NMR spectra (left) and ^{31}P{^{1}H} NMR spectra (right) of **2g** in C_6D_6 under O_2 at 25 °C after 10 minutes (bottom) and 24 hours (top). Solvent peak off scale.

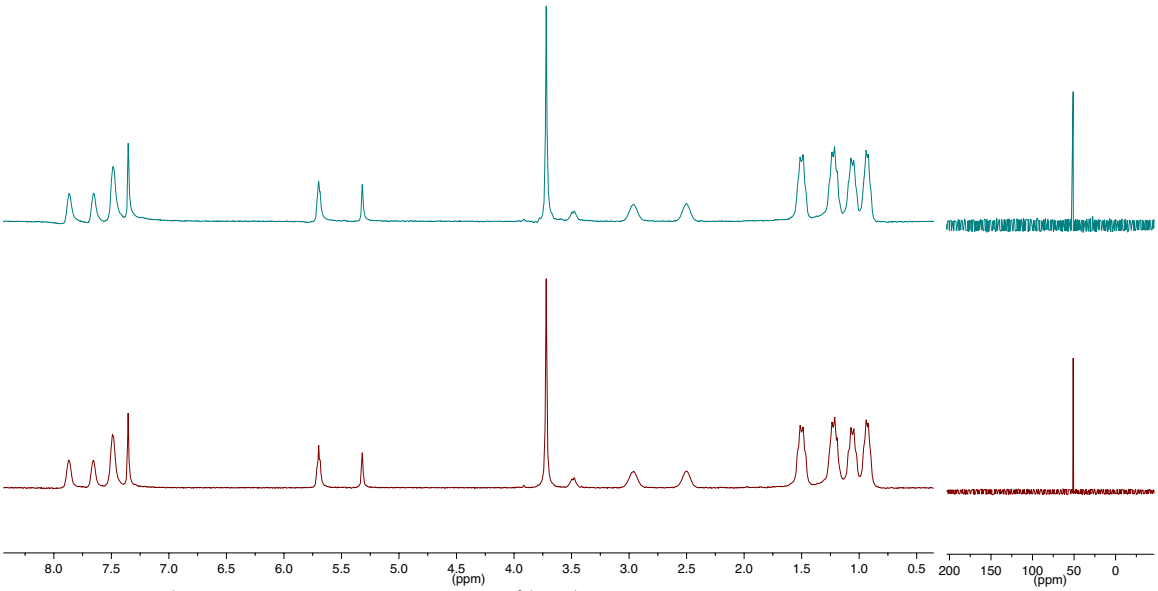


Figure S60. ^{1}H NMR spectra (left) and $^{31}P\{^{1}H\}$ NMR spectra (right) of **2f** in CD_2Cl_2 under O_2 at 25 °C after 10 minutes (bottom) and 24 hours (top).

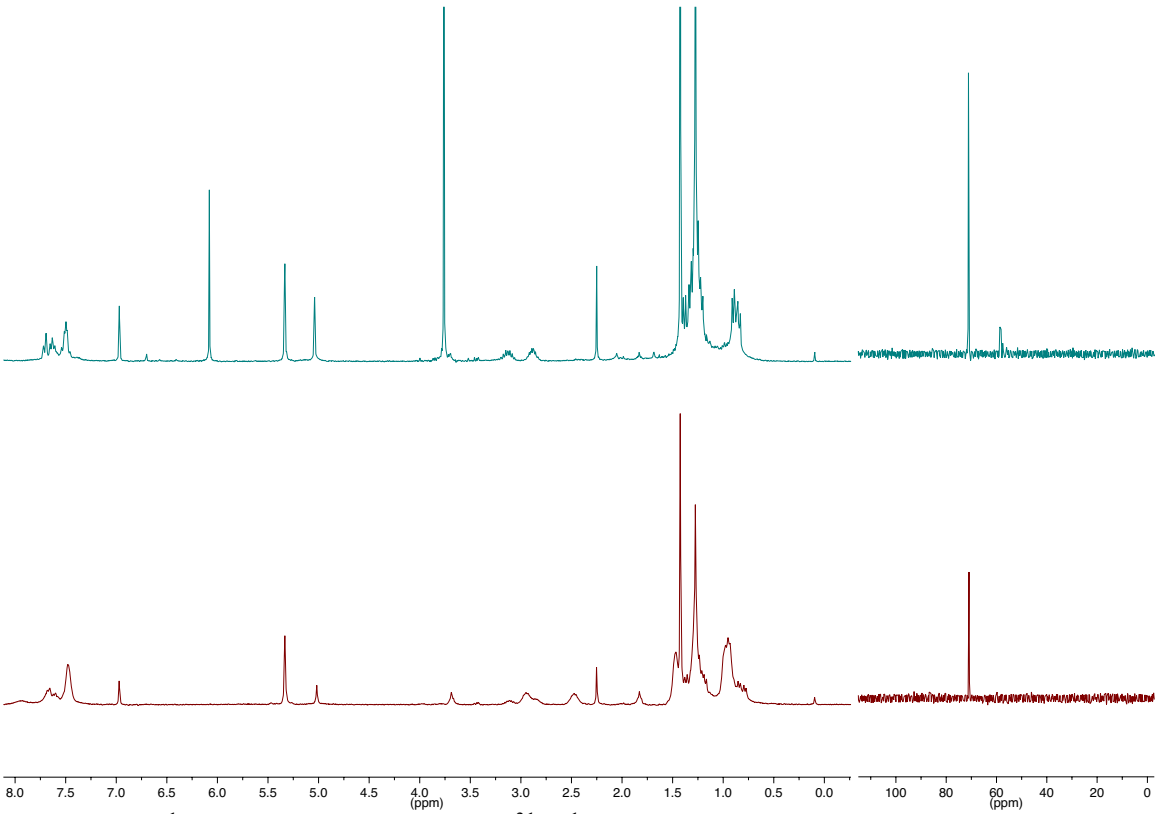


Figure S61. ^{1}H NMR spectra (left) and $^{31}P\{^{1}H\}$ NMR spectra (right) of **2a** + H_2O_2 after 1 hour (bottom) and **3** + H_2O_2 after 1 hour (top) in CD_2Cl_2 at 25 °C.

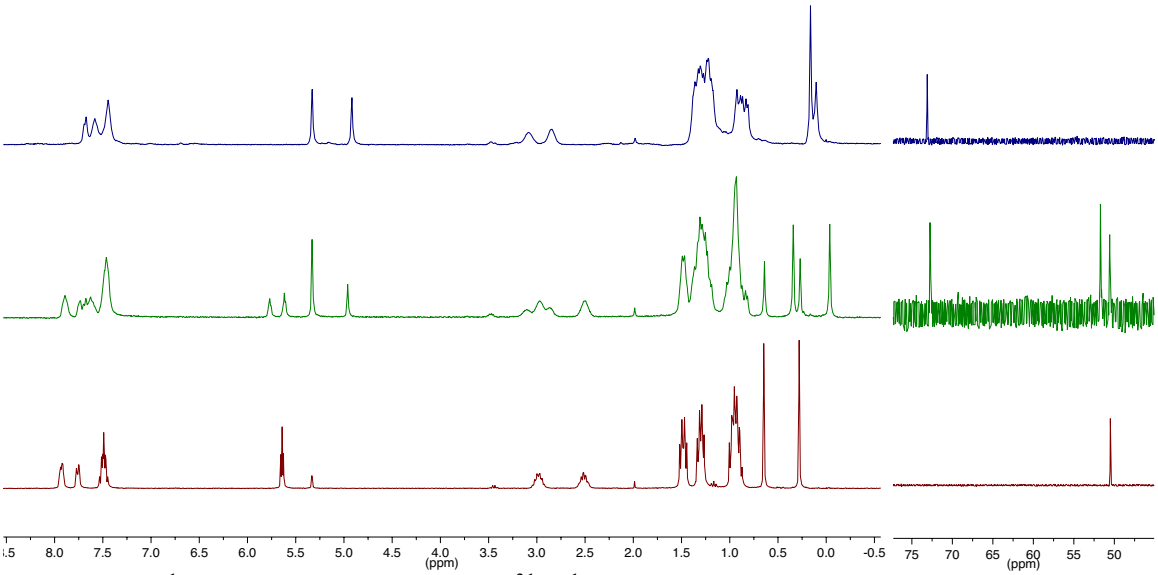


Figure S62. ^{1}H NMR spectra (left) and ^{31}P{^{1}H} NMR spectra (right) of **2b** under N_2 (bottom) and under O_2 after 1.5 hours (middle) and after 3 hours (top) in CD_2Cl_2 at 25 °C.

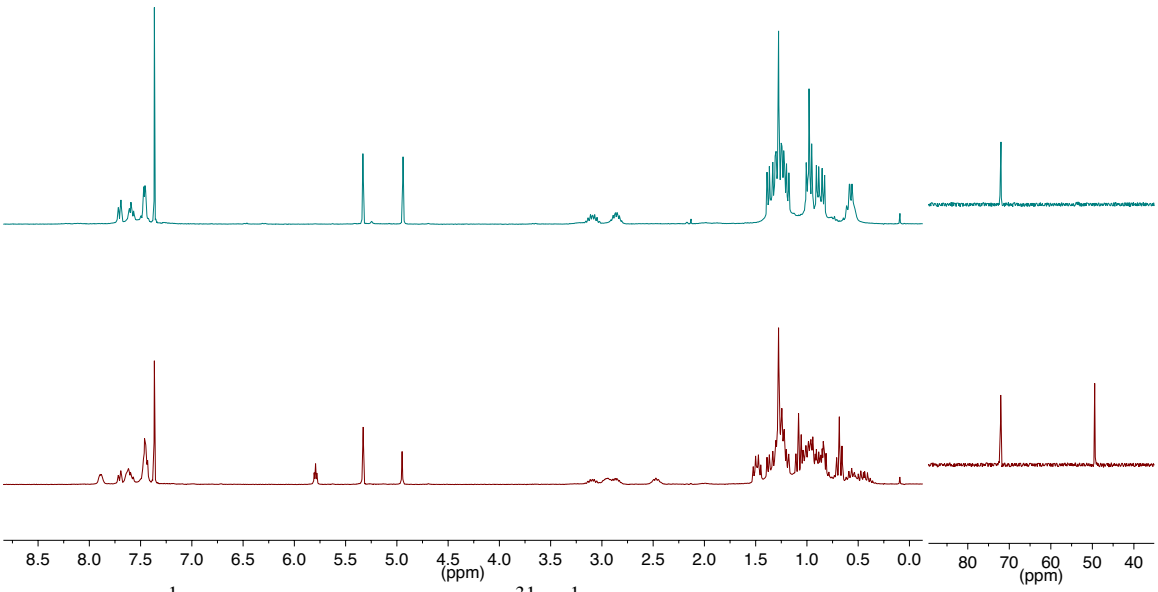


Figure S63. ^{1}H NMR spectra (left) and ^{31}P{^{1}H} NMR spectra (right) of **2c** under O_2 for 8 hours (bottom) and 48 hours (top) in CD_2Cl_2 at 25 °C.

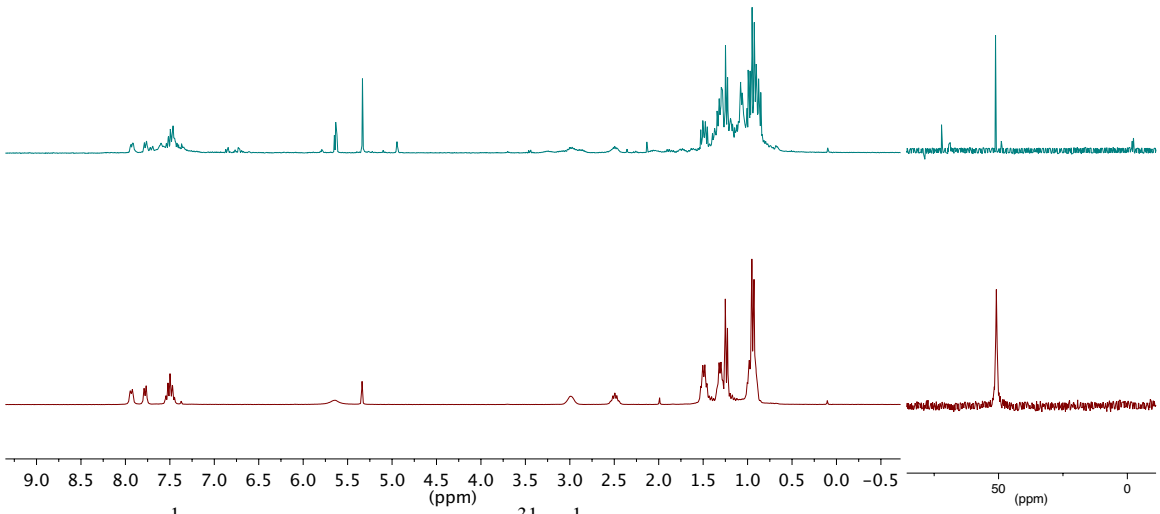


Figure S64. ^{1}H NMR spectra (left) and $^{31}P\{^{1}H\}$ NMR spectra (right) of **2d** under O_2 for 10 minutes (bottom) and 5 days (top) in CD_2Cl_2 at 25 °C.

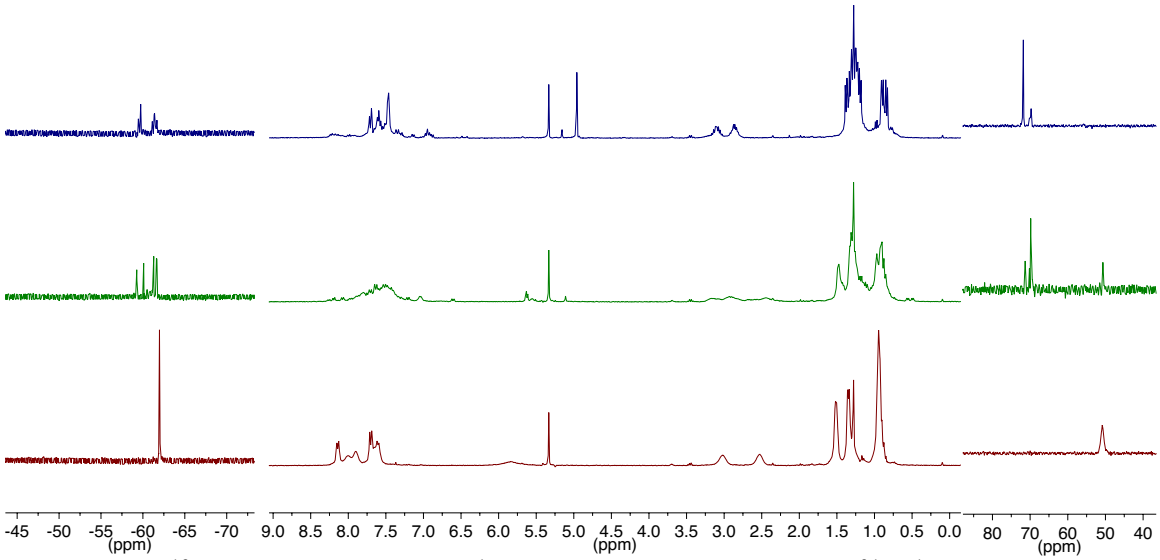


Figure S65. ^{19}F NMR spectra (left), ^{1}H NMR spectra (center) and $^{31}P\{^{1}H\}$ NMR spectra (right) of **2e** under O_2 after 10 minutes (bottom), 6 hours (middle), and 36 hours (top) in CD_2Cl_2 at 25 °C.

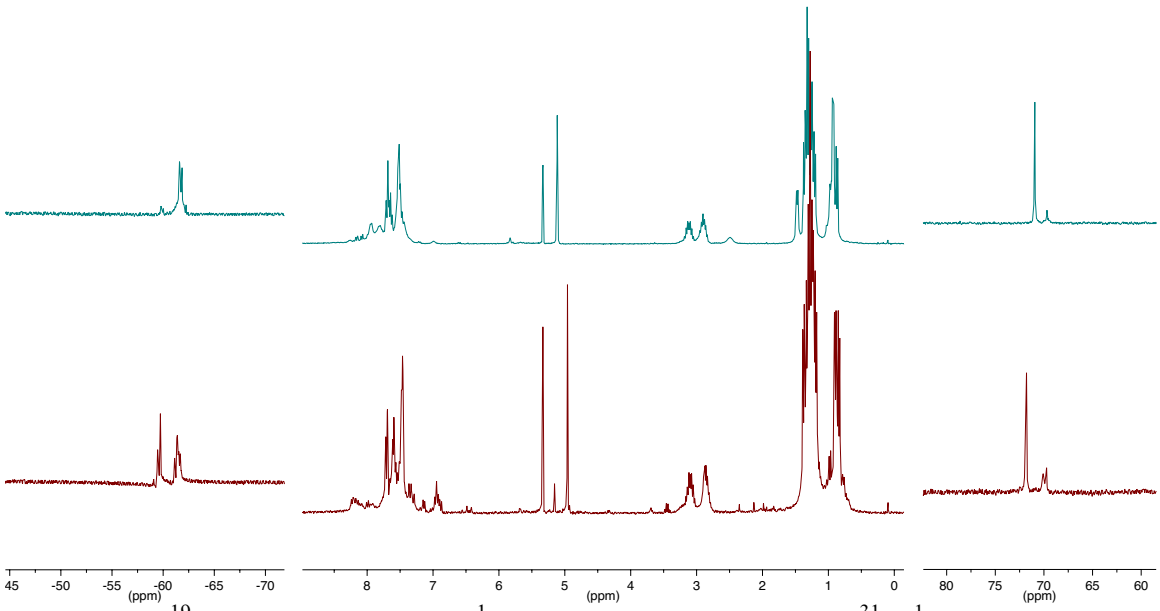


Figure S66. ^{19}F NMR spectra (left), ^{1}H NMR spectra (center) and $^{31}P\{^{1}H\}$ NMR spectra (right) of **2e** under O_2 (bottom) and **3** + (p-$CF_3C_6H_4BO)_3$ under N_2 (top) in CD_2Cl_2 at 25 °C.

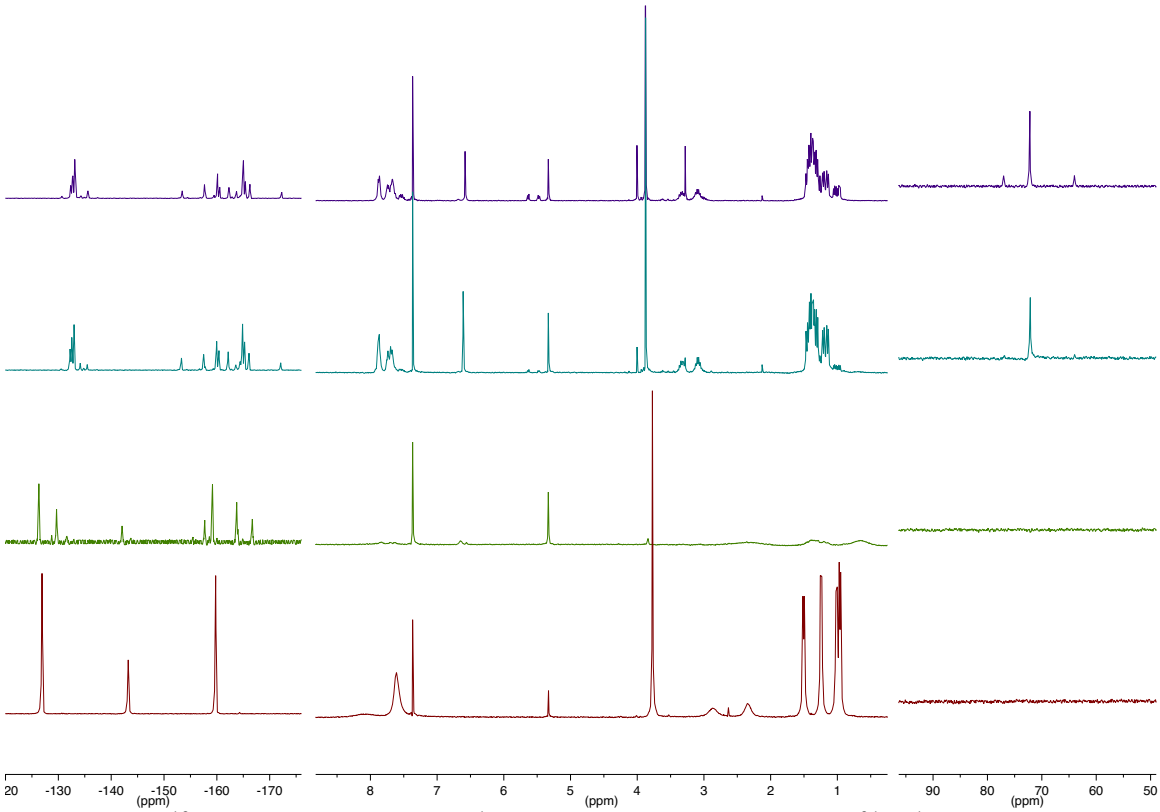


Figure S67. ^{19}F NMR spectra (left), ^{1}H NMR spectra (center) and $^{31}P\{^{1}H\}$ NMR spectra (right) of **2f** and 2 equivalents $B(C_6F_5)_3$ under N_2 (maroon), under O_2 for 10 minutes (green), 7 hours (teal), and 24 hours (purple) in CD_2Cl_2 at 25 °C.

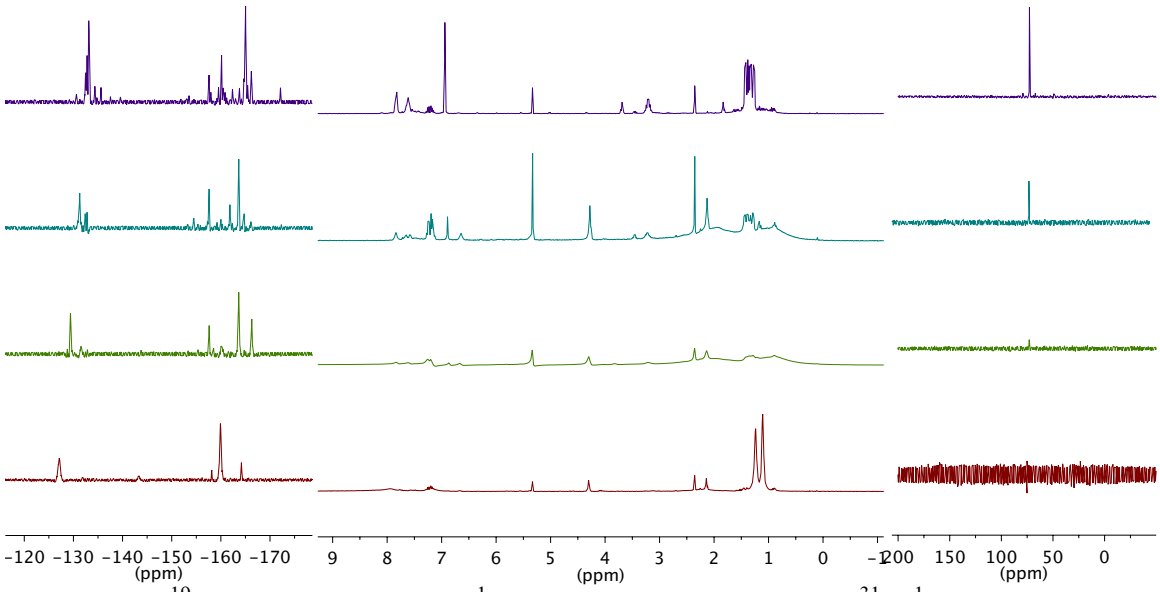


Figure S68. ^{19}F NMR spectra (left), ^{1}H NMR spectra (center) and $^{31}P\{^{1}H\}$ NMR spectra (right) of **2g** and 2 equivalents $B(C_6F_5)_3$ under N_2 (maroon), under O_2 for 15 minutes (green), 12 hours (teal), and 36 hours (purple) in CD_2Cl_2 at 25 °C.

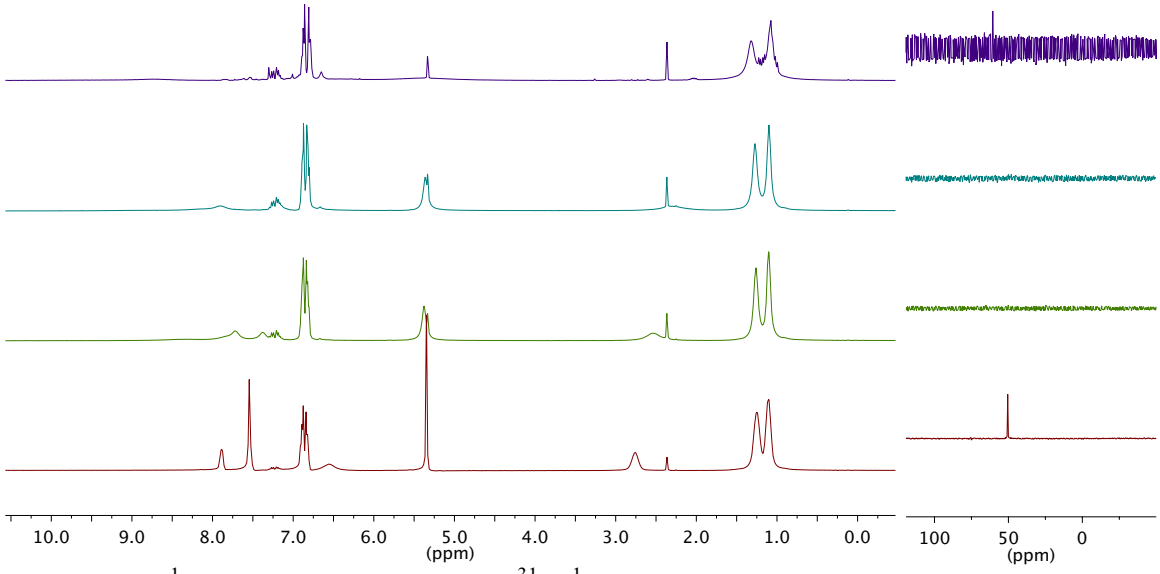


Figure S69. ^{1}H NMR spectra (left) and $^{31}P\{^{1}H\}$ NMR spectra (right) of **2g** and catechol under N_2 (maroon), under O_2 for 10 minutes (green), 3 hours (teal), and 36 hours (purple) in CD_2Cl_2 at 25 °C.

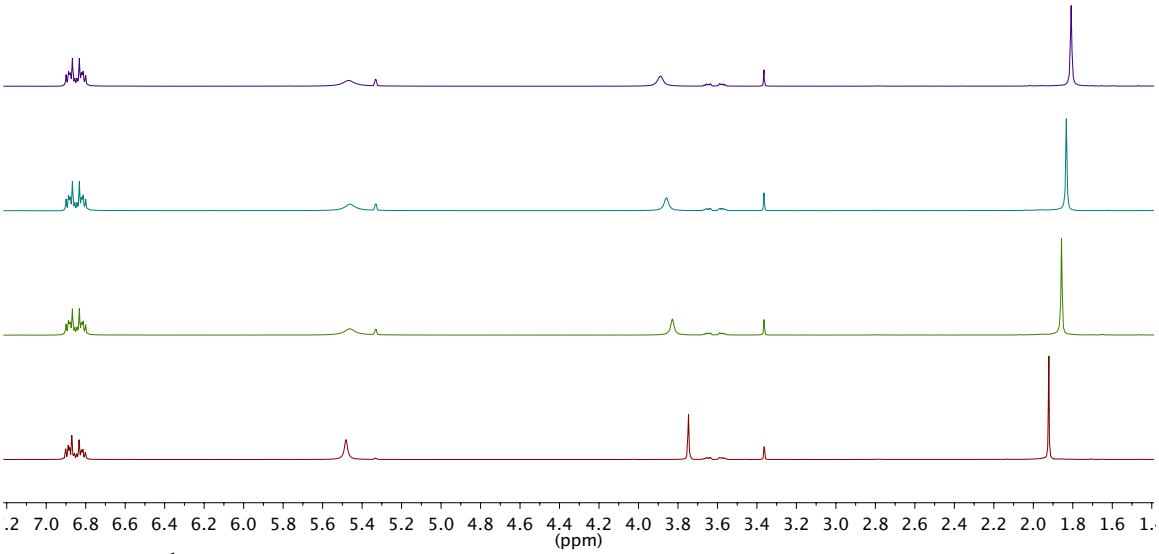


Figure S70. ^{1}H NMR spectra of Me_4Fc and catechol under N_2 (maroon), under O_2 for 10 minutes (green), 90 minutes (teal), and 3 hours (purple) in CD_2Cl_2 at 25 °C.

III. Ultraviolet-Visible Spectroscopy

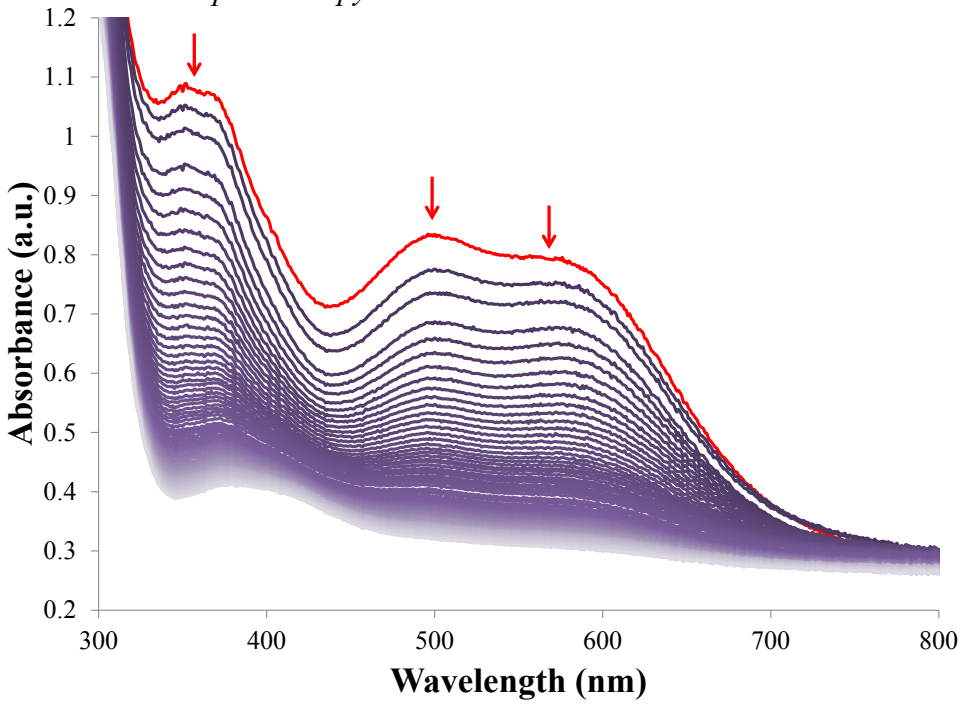


Figure S71. Reaction of **2e** with 2 AgOTf in THF. The red trace represents the first data point after mixing. New band with λ_{max} = 575 nm assigned to intermediate [**4**$^{+}$][OTf^{-}]. Traces taken every 30 seconds. After 20 minutes all of the major bands have diminished, consistent with formation of [**5**$^{2+}$][OTf^{-}]$_2$. (Note: traces shifted up ca. 0.3 a.u. with respect to baseline due to formation of Ag^0 precipitate).

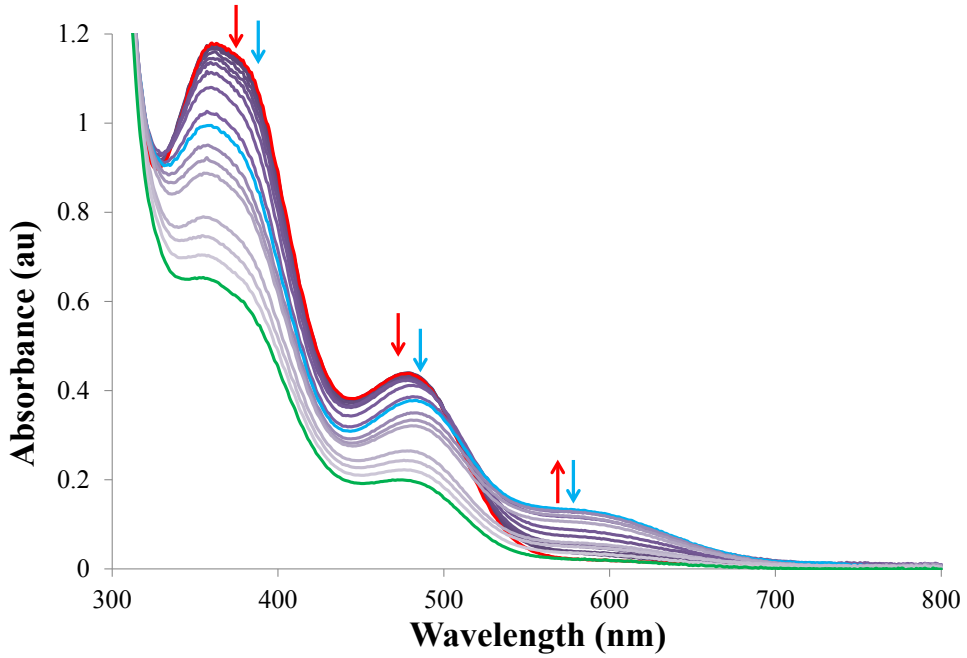


Figure S72. Reaction of **2e** and $B(C_6F_5)_3$ with O_2 in DCM. The red trace represents the first data point 30 seconds after mixing. Over time (red arrow), a new band with λ_{max} =

575 nm assigned to $[\mathbf{4}^{+}]_2[\{(F_5C_6)_3B\}_2O_2^{2-}]_2$ increases to a maximum at approximately 60 minutes (blue trace), and diminishes again (blue arrow) over the course of another 600 minutes (green trace). Over the course of the reaction, the bands with λ_{max} = 390 nm and 480 nm corresponding to **2e** have been halved, consistent with a **2e**:$B(C_6F_5)_3$ stoichiometry of 1:2. (Note: time between traces varies)

IV. Cyclic Voltammetry

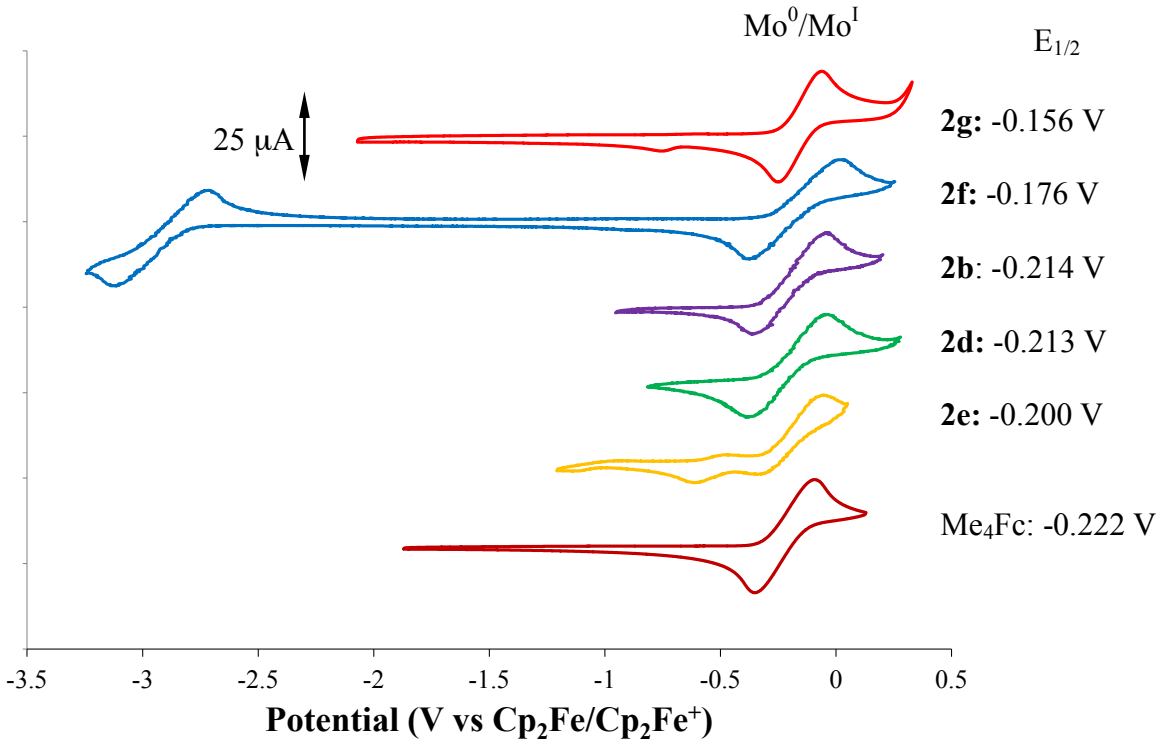


Figure S73. Cyclic voltammograms of compounds **2b**, **2d**, **2e**, **2f** , **2g**, and Me_4Fc taken in 0.1 M $[^nBu_4N^+][PF_6^-]$ in THF with a glassy carbon working electrode at 250 mV/s. Potentials reported with respect to the Cp_2Fe/Cp_2Fe^+ couple.

V. Crystallographic Information

CCDC 1026539-1026542 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Refinement Details

In each case, crystals were mounted on a glass fiber or nylon loop using Paratone oil, then placed on the diffractometer under a nitrogen stream. Low temperature (100 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_α = 0.71073 Å) or a Bruker PHOTON100 CMOS based diffractometer (Mo micro-focus sealed X-ray tube, K_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEXII software.[8] Absorption corrections were applied using SADABS.[9] Space groups were determined on the basis of systematic absences and intensity statistics and the structures were solved by direct methods using XS[10], by intrinsic phasing using XT (incorporated into SHELXTL), or by charge flipping using Olex2[11] and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in the idealized positions and refined using a riding model. The structure was refined (weighed least squares refinement on F^2) to convergence. Graphical representation of structures with 50% probability thermal ellipsoids was generated using Diamond visualization software.[12]

Table 1. Crystal and refinement data for **2a**•2.25C_6H_6, **2b**•NCMe, **3**, and $[\mathbf{4}^+]_2[[(F_5C_6)_3B]_2O_2^{2-}]$•2$CH_2Cl_2$.

Compound	**2a**•2.25C_6H_6	**2b**•NCMe	**3**	$[\mathbf{4}^+]_2[[(F_5C_6)_3B]_2O_2^{2-}]$•2$CH_2Cl_2$
CCDC	1026539	1026540	1026541	1026542
empirical formula	$C_{93}H_{107}Mo_2O_{10}P_4$	$C_{37}H_{47}MoNO_5P_2Si$	$C_{32}H_{38}MoO_4P_2$	$C_{108}H_{92}B_2Cl_4F_{30}Mo_2O_{12}P_4$
formula wt	1700.55	771.73	644.50 g/mol	2631.00 g/mol
T (K)	100	100	100	100
a, Å	11.9691(7)	11.4020(4)	11.6649(8)	12.511(1)
b, Å	16.935(1)	17.1733(7)	16.1870(8)	15.145(1)
c, Å	22.841(1)	19.0484(7)	16.4201(8)	15.613(1)
α, deg	106.621(3)	90	90	64.704(3)
β, deg	91.522(3)	102.399(1)	108.193(3)	81.599(3)
γ, deg	109.707(3)	90	90	85.342(3)
V, $Å^3$	4137.5(4)	3642.9(2)	2945.4(3)	2645.5(4)
Z	2	4	4	1
cryst syst	Triclinic	Monoclinic	Monoclinic	Triclinic
space group	P-1	$P2_1/c$	$P2_1/c$	P-1
d_{calc}, g/cm^3	1.365	1.407	1.453	1.651
θ range, deg	1.84-30.00	2.18-33.14	2.27-37.78	1.45-27.48
μ , mm^{-1}	0.440	0.523	0.590	0.514
abs cor	Semi-empirical	Semi-empirical	Semi-empirical	Semi-empirical
GOF	1.633	0.990	0.830	0.901
R_1[a], wR_2[b] (I > 2sig(I))	0.0506, 0.2015	0.0486, 0.1523	0.0356, 0.1189	0.0576, 0.1453
Diffractometer	APEXII	PHOTON100	APEXII	APEXII

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

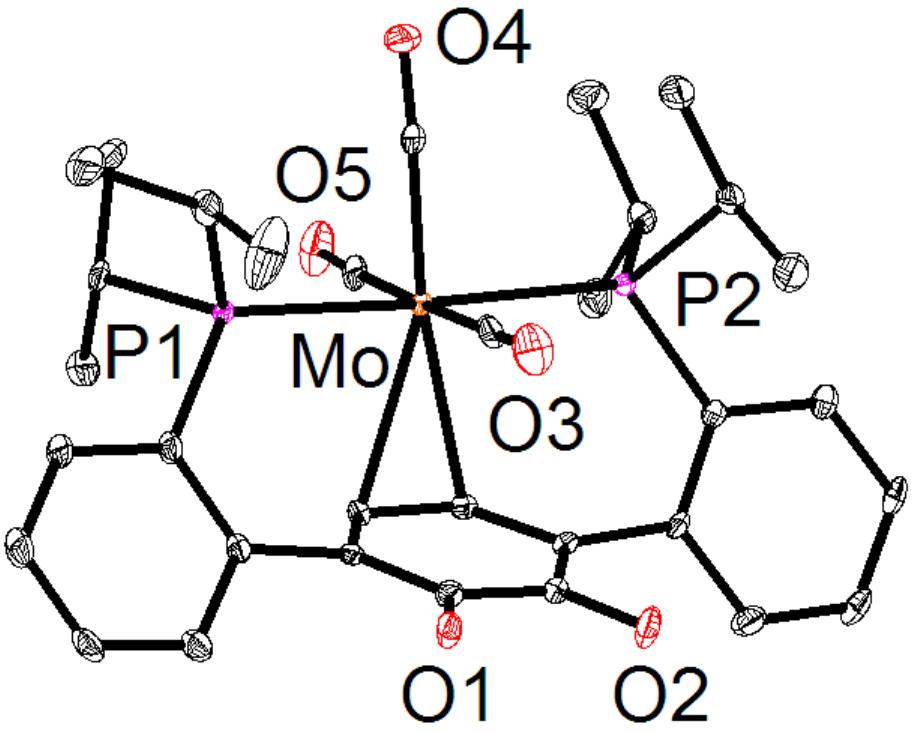


Figure S74. Structural drawing of **2a** with 50% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity. Carbon atoms are shown in black.

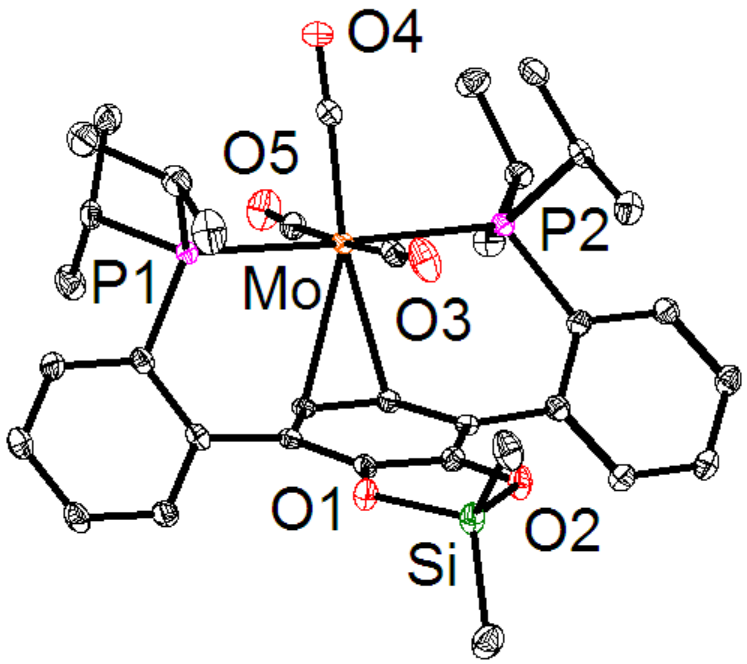


Figure S75. Structural drawing of **2b** with 50% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity. Carbon atoms are shown in black.

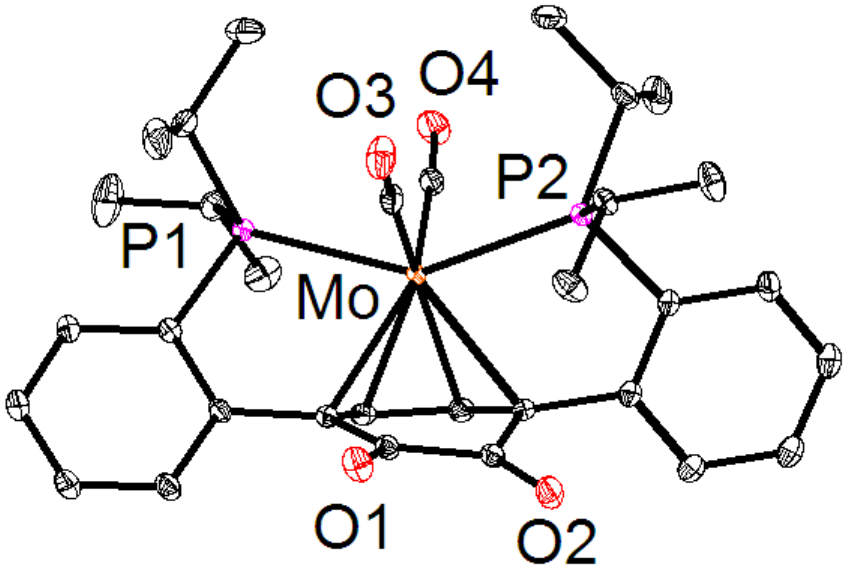


Figure S76. Structural drawing of **3** with 50% probability ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity. Carbon atoms are shown in black.

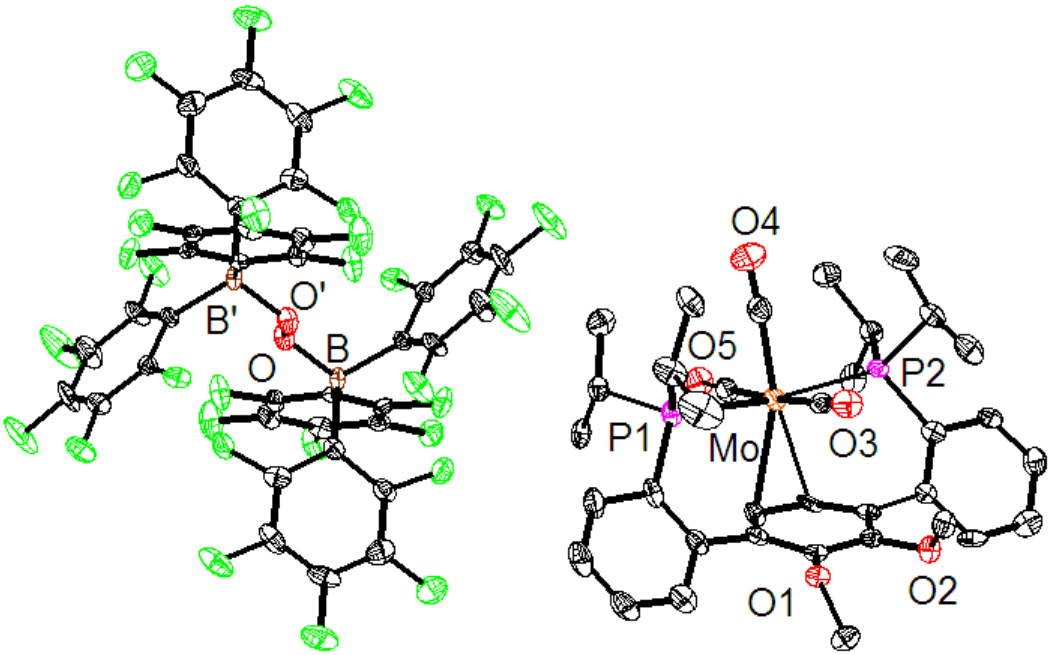


Figure S77. Structural drawing of $[\mathbf{4}^{+}]_2[[(F_5C_6)_3B]_2O_2^{2-}]$ with 50% probability ellipsoids. Hydrogen atoms, solvent molecules, and second Mo compound are omitted for clarity. Carbon and fluorine atoms are shown in black and green, respectively.

Special Refinement Details for $\mathbf{4}^{+}$: A ligand isopropyl group and the DCM solvent molecule were positionally disordered. Both were satisfactorily modeled as approximately 50:50 mixtures using "PART" cards in SHELX

VI. References

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