

Molybdenum Disubstituted Alkylidene Complexes

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General considerations. Unless otherwise noted, all manipulations were carried out using standard Schlenk or glovebox techniques under a N₂ atmosphere. THF, Et₂O, hexanes, benzene, toluene, and acetonitrile were dried and deoxygenated by passage through activated alumina in a solvent purification system from JC Meyer Solvent Systems followed by storage over 4 Å molecular sieves. Non-halogenated and non-nitrile containing solvents were tested with a standard solution of purple sodium benzophenone ketyl in THF to confirm effective oxygen and moisture removal prior to use. Pentafluorophenol (C₆F₅OH), 2,4,6-trimethylphenol (MesOH), α -methylstyrene, 2,2'-bipyridine (bipy) and trimethylchlorosilane (TMSCl) were purchased from commercial suppliers and purified according to literature procedures prior to use. Sodium pyrrolide (NaN₄C₄H₄),¹ lithium-hexamethylterphenoxide (LiOHMT = LiO-2,6-(2,4,6-Me₃C₆H₂)₂C₆H₃),² Mo(NAr)(CHCMe₃)(OR_{F6})₂³ and Mo(NAr)(CHMe₂Ph)(OR_{F6})₂³ (OR_{F6} = OC(CH₃)(CF₃)₂) were prepared according to literature procedures. Elemental analyses were performed by Midwest Microlab, LLC, Indianapolis, IN. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc., degassed, and dried over activated 4 Å molecular sieves for at least 24 h prior to use. NMR spectra were recorded on Bruker Avance 600 MHz and Bruker Avance 300 MHz spectrometers. ¹H and ¹³C chemical shifts are reported in ppm relative to tetramethylsilane using residual solvent as an internal standard. ¹⁹F chemical shifts are reported in ppm relative to fluorobenzene as an external standard.

Mo(NAr)(CMePh)(OMes)₂ (1). α -Methylstyrene (0.014 g, 0.12 mmol) was added to a solution of Mo(NAr)(CHCMe₃)(OR_{F6})₂ (0.042 g, 0.060 mmol) in benzene (5 mL) and the vessel was sealed in a 50 mL Schlenk flask with Teflon stopper. The reaction was subjected to three freeze-pump-thaw cycles prior to being heated to 60 °C for 5 hours. Every 1 hour, the Teflon stopper was opened to vacuum (10⁻² mbar) briefly prior to continuing heating. After 5 h, the volatiles were removed *in vacuo*. The dark red residue was extracted with pentane (3 x 1 mL) and extract was filtered through Celite. Volatiles were again removed *in vacuo* prior to dissolving the residue in benzene (2 mL) and adding 2,4,6-trimethylphenol (0.016 g, 0.12 mmol) as a benzene (0.5 mL) solution. The reaction was stirred 1 h prior to removing volatiles *in vacuo*. The red residue was dissolved in minimal pentane (~0.3 mL) and the solution was left at -30 °C overnight during which time red plates grew. The crystals were rinsed with chilled pentane (-30 °C, 0.3 mL) and dried *in vacuo*: yield 0.029 g (74 %). A single crystal suitable for XRD was obtained by cooling a saturated pentane solution to -30 °C: ¹H NMR (600 MHz, C₆D₆) δ 7.3-7.4 (m, 3H), 7.0 – 6.9 (m, 5H), 6.8 (s, 4H), 3.5 (dq, *J* = 13.7, 6.8 Hz, 2H), 3.0 (s, 3H), 2.3 (s, 12H), 2.2 (s, 6H), 1.0 (d, *J* = 6.8 Hz, 12H); ¹³C{¹H} NMR (151 MHz, C₆D₆) δ 263.1, 159.7, 153.6, 147.3, 146.0, 130.3, 129.3, 128.6, 128.4, 127.6, 126.4, 126.2, 123.4, 29.1, 23.5, 20.8, 17.4, 16.9. Anal. Calcd. for C₃₈H₄₇MoNO₂ (+ 1 C₇H₈): C, 73.25; H, 7.51; N, 1.90. Found: C, 73.58; H, 7.77; N, 1.98.

[Mo(NAr)(CMePh)(OC₆F₅)₂]₂ (2). α -Methylstyrene (0.466 g, 3.95 mmol) was added to a solution of Mo(NAr)(CHMe₂Ph)(OR_{F6})₂ (0.604 g, 0.789 mmol) in Et₂O (7 mL). The solution was stirred for 5 minutes and a solution of pentafluorophenol (0.312 g, 1.66 mmol) in Et₂O (2 mL) was added dropwise. After 4 hours, the yellow precipitate was filtered off, washed with Et₂O (4 x 1 mL), and dried *in vacuo*: yield 0.572 g (95 %). [Mo(NAr)(CMePh)(OC₆F₅)₂]₂ is not soluble enough in CD₂Cl₂ or CDCl₃ to acquire NMR data readily. Anal. Calcd. for C₃₂H₂₅F₁₀MoNO₂: C, 51.84; H, 3.40; N, 1.89. Found: C, 51.81; H, 3.75; N, 1.62.

Mo(NAr)(CMePh)(OC₆F₅)₂(THF)_x (2(THF)_x; x = 1 or 2). [Mo(NAr)(CMePh)(OC₆F₅)₂]₂ (0.007 g, 0.0094 mmol) was dissolved in THF-*d*₈ (0.6 mL) to give an orange solution: ¹H NMR

(600 MHz, THF-*d*₈, -40 °C) δ 7.4 (d, *J* = 7.7 Hz, 2H), 7.3 (t, *J* = 7.7 Hz, 2H), 7.2 (s, 3H), 7.1 (t, *J* = 7.3 Hz, 1H), 3.8 (hept, *J* = 6.1, 5.6 Hz, 2H), 3.7 (s, 2H), 3.6 (s, 3H), 1.7 (s, 2H), 1.1 (dd, *J* = 10.1, 7.0 Hz, 12H); $^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, THF-*d*₈, -40 °C) Major Isomer: δ -157.5 (d, *J* = 21.7 Hz), -158.3 (d, *J* = 21.9 Hz), -164.8 (t, *J* = 21.7 Hz), -165.1 (t, *J* = 21.7 Hz), -172.2 (d, *J* = 22.9 Hz), -172.3 (dd, *J* = 45.6, 23.5 Hz); $^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, THF-*d*₈, 22 °C) δ -156.2, -157.1, -163.7, -163.9, -170.8, -171.1; $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, THF-*d*₈, -40 °C) δ 310.7, 152.3, 148.2, 144.5, 142.6, 142.0, 141.7 (t, *J* = 13.0 Hz), 141.0, 140.5, 139.8, 139.4, 138.1, 137.8, 134.6 (d, *J* = 14.6 Hz), 133.0, 130.3, 128.9, 127.1, 124.5, 68.1, 29.0, 25.9 (M=CMePh), 24.9, 24.7, 24.4, 22.5.

Mo(NAr)(CMePh)(OC₆F₅)₂(MeCN) (2(MeCN)). Solid [Mo(NAr)(CMePh)(OC₆F₅)₂]₂ (0.007 g, 0.0094 mmol) was dissolved in CD₃CN (0.6 mL) in order to give an orange solution. Single crystals of 2(MeCN) suitable for XRD were obtained through addition of MeCN (0.5 mL) to solid 2 (0.020 g) to produce an orange solution that was filtered through Celite and chilled at -30 °C for 12 h: ^1H NMR (600 MHz, CD₃CN) Major Isomer: δ 7.4 – 7.3 (m, 3H), 7.2 (dd, *J* = 8.9, 6.7 Hz, 2H), 7.2 (s, 2H), 7.1 (d, *J* = 1.6 Hz, 1H), 3.7 (s, 3H), 3.7 (hept, *J* = 6.7 Hz, 2H), 1.0 (d, *J* = 4.5 Hz, 6H), 1.0 (d, *J* = 4.6 Hz, 6H), 1.0 (s, 3H); $^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, CD₃CN) δ -163.5 (d, *J* = 19.5 Hz), -164.2 (d, *J* = 19.5 Hz), -169.2 (t, *J* = 20.4 Hz), -169.8 (t, *J* = 20.7 Hz), -177.0 (t, *J* = 21.3 Hz), -177.7 (t, *J* = 21.3 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD₃CN) δ Selected resonances of major Isomer: δ 316.8, 151.8, 149.9, 148.3, 142.3 (m), 140.7 (m), 139.7 (m), 138.0 (m), 130.1, 129.3, 128.9, 126.8, 124.2, 29.1, 28.7, 28.5, 25.3, 24.8, 24.4, 24.4, 23.6. Selected resonances of the minor isomer 1: ^1H NMR (600 MHz, CD₃CN) δ 4.05 (hept, *J* = 6.5 Hz, 2H), 3.98 (s, 3H), 0.99 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD₃CN) δ 354.9, 37.4. Selected resonances of the minor isomer 2: ^1H NMR (600 MHz, CD₃CN) δ 3.57 (hept, *J* = 6.5 Hz, 2H), 3.45 (s, 3H), 0.98 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD₃CN) δ 294.9, 19.5.

Note: Orange crystals of 2(MeCN) readily lose MeCN under vacuum (10⁻² mbar, 10 minutes) and collapse to a yellow powder. For this reason, consistent elemental analyses for 2(MeCN) could not be obtained.

Mo(NAr)(CMePh)(OC₆F₅)₂(bipy) (2(bipy)). A solution of 2,2'-Bipyridine (0.004 g, 0.027 mmol) in THF (1 mL) was added dropwise to a solution of [Mo(NAr)(CMePh)(OC₆F₅)₂]₂ (0.020 g, 0.026 mmol) in THF (1 mL). The reaction was stirred for 30 minutes prior to removing volatiles *in vacuo*. The orange residue was dissolved in minimal Et₂O (0.5 mL). Pentane (1 mL) was added and the solution filtered rapidly through Celite. The filtrate was cooled to -30 °C for 12 h during which time orange crystals formed. The product was filtered off, washed with pentane (1 mL), and dried *in vacuo*: yield 0.022 g (98 %). A crystal suitable for XRD was obtained by vapor diffusion of Et₂O into a concentrated dichloromethane solution: ^1H NMR (600 MHz, C₆D₆) δ 9.52 (d, *J* = 5.0 Hz, 1H), 8.57 (d, *J* = 5.4 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.8 Hz, 2H), 6.94 – 6.84 (m, 1H), 6.85 (t, *J* = 7.3 Hz, 1H), 6.74 (m, *J* = 7.7 Hz, 5H), 6.62 (d, *J* = 14.6, 8.3 Hz, 1H), 6.57 – 6.53 (m, 1H), 6.42 (td, *J* = 6.4, 5.7, 1.1 Hz, 1H), 4.70 (s, 1H), 4.15 (s, 3H), 2.68 (s, 1H), 1.44 – 1.31 (m, 3H), 1.26 (d, *J* = 7.0 Hz, 3H), 0.56 – 0.42 (m, 3H), -0.09 – -0.22 (m, 3H); $^{19}\text{F}\{^1\text{H}\}$ NMR (564 MHz, C₆D₆) δ -160.63 (dt, *J* = 17.6, 8.6 Hz), -160.76 (dq, *J* = 16.9, 7.7 Hz), -168.16 (t, *J* = 21.5 Hz), -168.94 (t, *J* = 21.5 Hz), -176.16 (tt, *J* = 23.5, 7.7 Hz), -178.04 (tt, *J* = 22.3, 8.0 Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C₆D₆) δ 316.9, 158.0, 157.9, 153.9, 152.5, 150.4, 150.0, 149.6, 147.9, 143.1, 142.4, 141.5, 140.8, 140.0, 139.8, 138.9, 138.1, 137.2, 134.1 (t, *J* = 15.0 Hz), 132.5 (q, *J* = 16.7, 15.2 Hz), 131.0 (t, *J* = 13.2 Hz), 128.4, 127.6, 127.3, 127.1, 126.1, 126.0, 125.8, 123.8, 122.4, 121.4, 120.5, 34.5, 28.0, 27.7, 25.1, 24.3, 22.3. Anal. Calcd. for C₄₂H₃₃F₁₀MoN₃O₂ (+ 1 C₄H₈O): C, 56.97; H, 4.26; N, 4.33. Found: C, 57.22; H, 4.16; N, 4.30.

Mo(NAr)(CMePh)(Cl)₂(bipy) (3(bipy)). Chlorotrimethylsilane (0.091 g, 0.838 mmol) was added to a stirred suspension of Mo(NAr)(CMePh)(OC₆F₅)₂(bipy) (0.188 g, 0.209 mmol) in Et₂O (6 mL). The reaction was stirred for 12 h during which time an orange solid precipitated. The product was collected on a frit, washed with Et₂O (4 x 1 mL) and dried *in vacuo*: yield 0.112 g (89%). A crystal suitable for XRD was obtained through layering a concentrated dichloromethane solution with Et₂O: ¹H NMR (600 MHz, CD₂Cl₂, -20 °C) δ 9.4 (d, *J* = 4.2 Hz, 1H), 8.8 (d, *J* = 4.6 Hz, 1H), 8.3 (d, *J* = 8.0 Hz, 1H), 8.2 (d, *J* = 8.0 Hz, 2H), 8.1 – 8.0 (m, 1H), 7.7 – 7.7 (m, 1H), 7.7 – 7.6 (m, 1H), 7.3 (d, *J* = 7.3 Hz, 2H), 7.1 (t, *J* = 7.8 Hz, 2H), 6.9 (dt, *J* = 13.0, 7.1 Hz, 4H), 6.6 (d, *J* = 7.1 Hz, 1H), 4.5 (dt, *J* = 13.2, 6.1 Hz, 1H), 4.1 (s, 2H), 2.7 (dd, *J* = 13.0, 6.2 Hz, 1H), 1.2 (d, *J* = 6.3 Hz, 3H), 1.0 (d, *J* = 6.4 Hz, 3H), 0.3 (d, *J* = 6.4 Hz, 3H), -0.1 (d, *J* = 6.4 Hz, 3H); ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, -20 °C) δ 324.2, 159.2, 157.2, 154.4, 152.5, 151.7, 149.2, 148.9, 148.4, 141.0, 139.7, 128.6, 127.8, 127.5, 127.3, 127.0, 126.7, 125.4, 123.8, 123.5, 122.9, 122.5, 38.9, 27.9, 27.5, 25.0, 24.6, 24.1, 22.1. Anal. Calcd. for C₃₀H₃₃Cl₂MoN₃ (+1 CH₂Cl₂): C, 54.17; H, 5.13; N, 6.11. Found: C, 54.10; H, 5.21; N, 5.72.

Mo(NAr)(CMePh)(Cl)(OHMT) (4). A stirred suspension of Mo(NAr)(CMePh)(Cl)₂(bipy) (0.121 g, 0.202 mmol) in Et₂O (5 mL) was cooled to -30 °C before adding a -30 °C solution of LiOHMT (0.081 g, 0.242 mmol) and ZnCl₂•dioxane (0.047 g, 0.209 mmol) in THF (3 mL). The suspension was stirred for 12 hours at 22 °C to yield a ruby red solution and a colorless precipitate. All volatiles were removed from the mixture *in vacuo*, and the residue was extracted with pentane (3 mL). The extract was filtered through Celite and volatiles were removed *in vacuo* to afford a ruby red oil. The oil was dissolved in benzene (0.5 mL) and lyophilized to yield a red foam that aided manipulation: yield 0.307 g (73%). Anal. Calcd. for C₄₄H₅₀ClMoNO: C, 71.39; H, 6.81; N, 1.89. Found: C, 70.96; H, 6.44; N, 1.67.

Mo(NAr)(CMePh)(Cl)(OHMT)(MeCN) (4(MeCN)). Mo(NAr)(CMePh)(Cl)(OHMT) (0.010 g, 0.014 mmol) was added to CD₃CN (0.5 mL) to produce a yellow solution. A crystal suitable for XRD was obtained by cooling a concentrated solution of a toluene:MeCN:pentane (1:1:2) mixture at -30 °C for 24 h: ¹H NMR (600 MHz, C₆D₆) δ 7.1 (d, *J* = 7.7 Hz, 2H), 7.0 – 6.9 (m, 10H), 6.8 (s, 2H), 6.7 (tt, *J* = 14.7, 2.4 Hz, 1H), 3.7 (hept, *J* = 6.3, 5.7 Hz, 2H), 3.0 (s, 3H), 2.5 (s, 6H), 2.4 (s, 6H), 2.3 (s, 6H), 1.3 (d, *J* = 6.8 Hz, 6H), 1.2 (d, *J* = 6.7 Hz, 6H), 0.6 (s, 3H); ¹³C{¹H} NMR (151 MHz, C₆D₆) δ 296.8, 160.1, 152.9, 148.6, 146.8, 137.2, 137.1, 136.8, 136.2, 131.8, 129.8, 128.9, 128.5, 128.4, 127.8, 126.1, 123.3, 121.7, 118.4, 38.9, 28.5, 24.0, 23.9, 22.1, 21.2, 21.2, 21.0, 0.4. ¹H NMR (600 MHz, CD₃CN) Major Isomer: δ 7.2 – 7.2 (m, 2H), 7.1 – 7.0 (s, 5H), 7.0 – 7.0 (m, 1H), 7.0 – 7.0 (s, 1H), 7.0 – 6.9 (m, 2H), 6.9 – 6.8 (m, 2H), 6.8 (s, 1H), 6.8 (s, 1H), 3.4 (s, 1H), 3.2 (dq, *J* = 13.4, 6.8 Hz, 1H), 2.6 (s, 3H), 2.2 (s, 6H), 2.2 (s, 6H), 2.1 (s, 3H), 2.0 (s, 3H), 1.9 (s, 3H), 1.0 (d, *J* = 5.6 Hz, 6H), 0.9 (d, *J* = 6.8 Hz, 3H), 0.9 (d, *J* = 6.8 Hz, 3H); ¹³C{¹H} NMR (151 MHz, CD₃CN) Major Isomer: δ 323.6, 161.7, 152.0, 150.5, 138.0, 137.8, 137.5, 137.4, 137.1, 137.0, 131.4, 131.3, 130.4, 130.2, 129.8, 129.6, 129.4, 129.0, 128.7, 128.6, 128.4, 128.2, 128.1, 127.1, 126.9, 126.1, 125.7, 123.7, 121.1, 28.4, 28.3, 27.7, 26.9, 24.9, 23.6, 23.1, 21.6, 21.3, 21.1, 21.1, 21.0, 20.7, 20.4. Selected resonances of the minor isomer: ¹H NMR (600 MHz, CD₃CN) δ 6.8 (s), 6.7 (s), 2.8 (s), 2.3 (s), 2.3 (s), 1.0 (bs); ¹³C{¹H} NMR (151 MHz, CD₃CN) 160.8, 151.2, 147.6, 135.1, 129.1, 25.0, 23.0.

Note: Yellow crystals of 4(MeCN) readily lose MeCN under vacuum (10⁻² mbar, 10 minutes) and turn red. For this reason elemental analysis for 4(MeCN) could not be obtained.

Mo(NAr)(CMePh)(OHMT)(NC₄H₄) (5). A chilled (−30 °C) solution of Mo(NAr)(CMePh)(Cl)(OHMT) (0.100 g, 0.135 mmol) in Et₂O (4 mL) was added to a suspension of sodium pyrrolide (0.013 g, 0.135 mmol) in Et₂O (3 mL) that had been cooled to −30 °C. The reaction was stirred 2 hours during which time an orange/red solution was obtained along with a precipitate. Volatiles were removed *in vacuo* and the residue was extracted into pentane (3 x 1 mL). The extract was filtered through Celite and the volatiles removed from the filtrate *in vacuo* to afford the product as an orange/red foam: yield 0.060 g (72%). A crystal suitable for XRD was obtained through slow evaporation of a concentrated heptane solution into silicon grease at −30 °C: ¹H NMR (600 MHz, C₆D₆) δ 7.4 (d, *J* = 7.4 Hz, 2H), 7.2 - 7.0 (m, 10H), 7.0 (s, 2H), 6.9 (t, *J* = 7.3 Hz, 1H), 6.57 (t, *J* = 1.7 Hz, 2H), 6.40 (t, *J* = 1.7 Hz, 2H), 3.3 (hept, *J* = 6.6 Hz, 2H), 2.7 (s, 3H), 2.5 (s, 6H), 2.3 (s, 6H), 2.2 (s, 6H), 1.1 (d, *J* = 6.8 Hz, 6H), 1.0 (d, *J* = 6.7 Hz, 6H); ¹³C{¹H} NMR (151 MHz, C₆D₆) δ 290.6, 159.2, 152.6, 148.5, 146.7, 137.4, 137.1, 136.9, 136.4, 132.1, 130.0, 128.8, 128.8, 128.6, 127.7, 126.8, 123.2, 122.7, 110.6, 28.7, 24.0, 23.5, 21.2, 20.9, 20.6, 20.2. Anal. Calcd. for C₄₈H₅₄MoN₂O: C, 74.78; H, 7.06; N, 3.63. Found: C, 74.60; H, 7.05; N, 3.62.

Spectroscopic Data

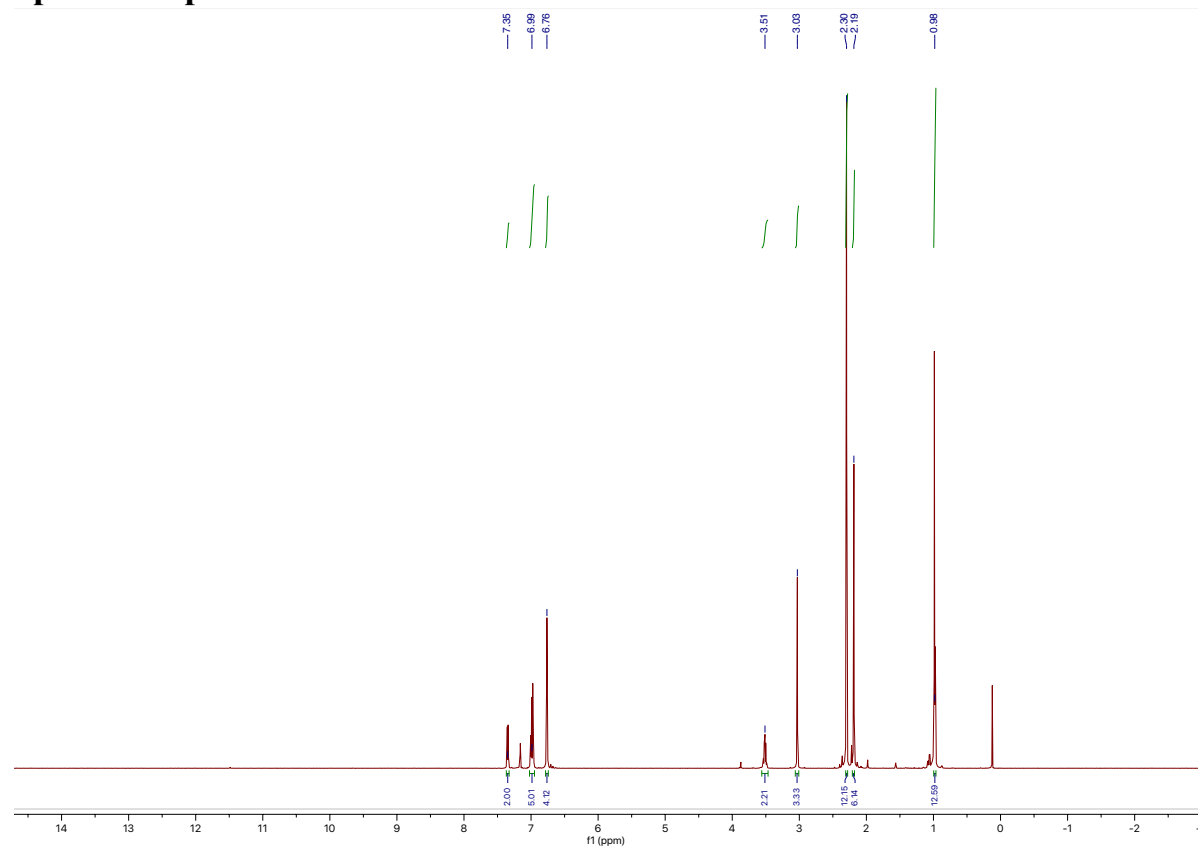
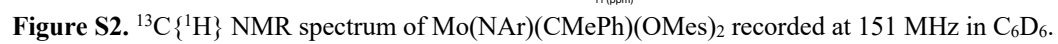


Figure S1. ¹H NMR spectrum of Mo(NAr)(CMePh)(OMes)₂ recorded at 600 MHz in C₆D₆.



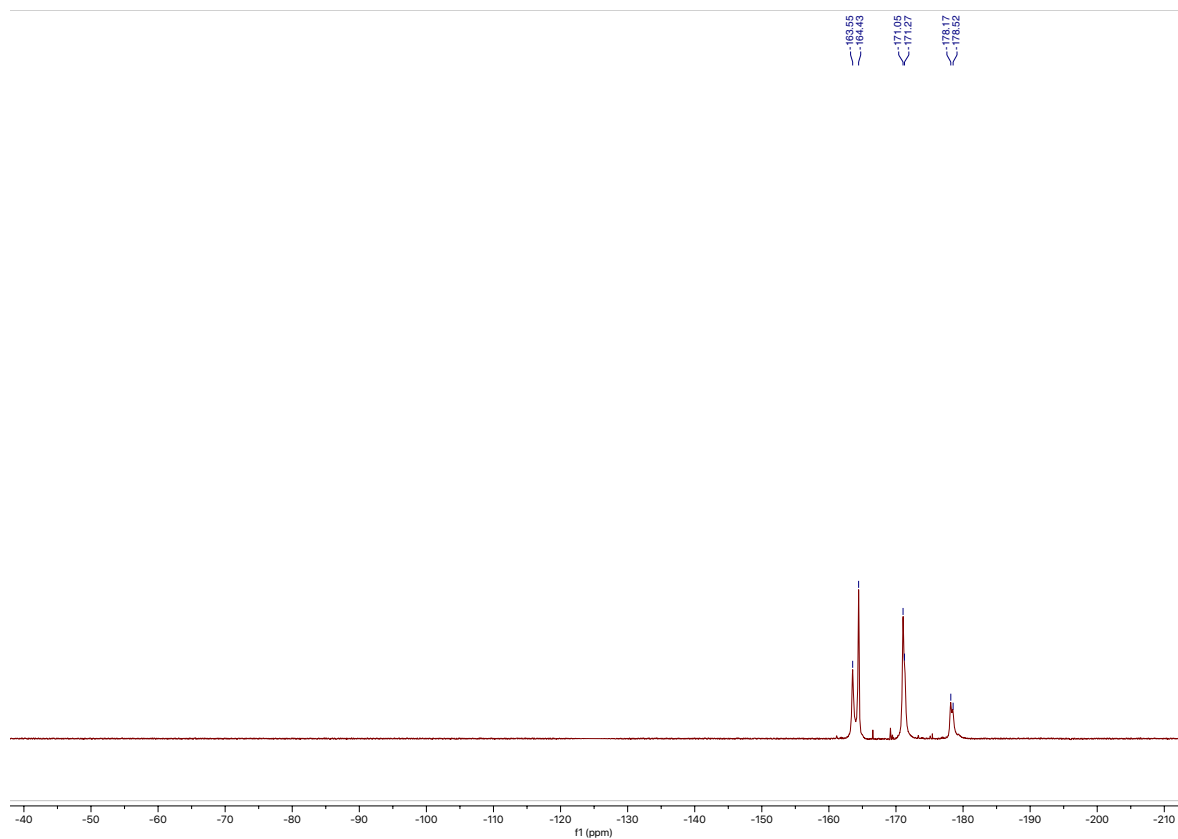


Figure S4. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{THF})_x$ recorded at 565 MHz in $\text{THF-}d_8$ at 22 °C.

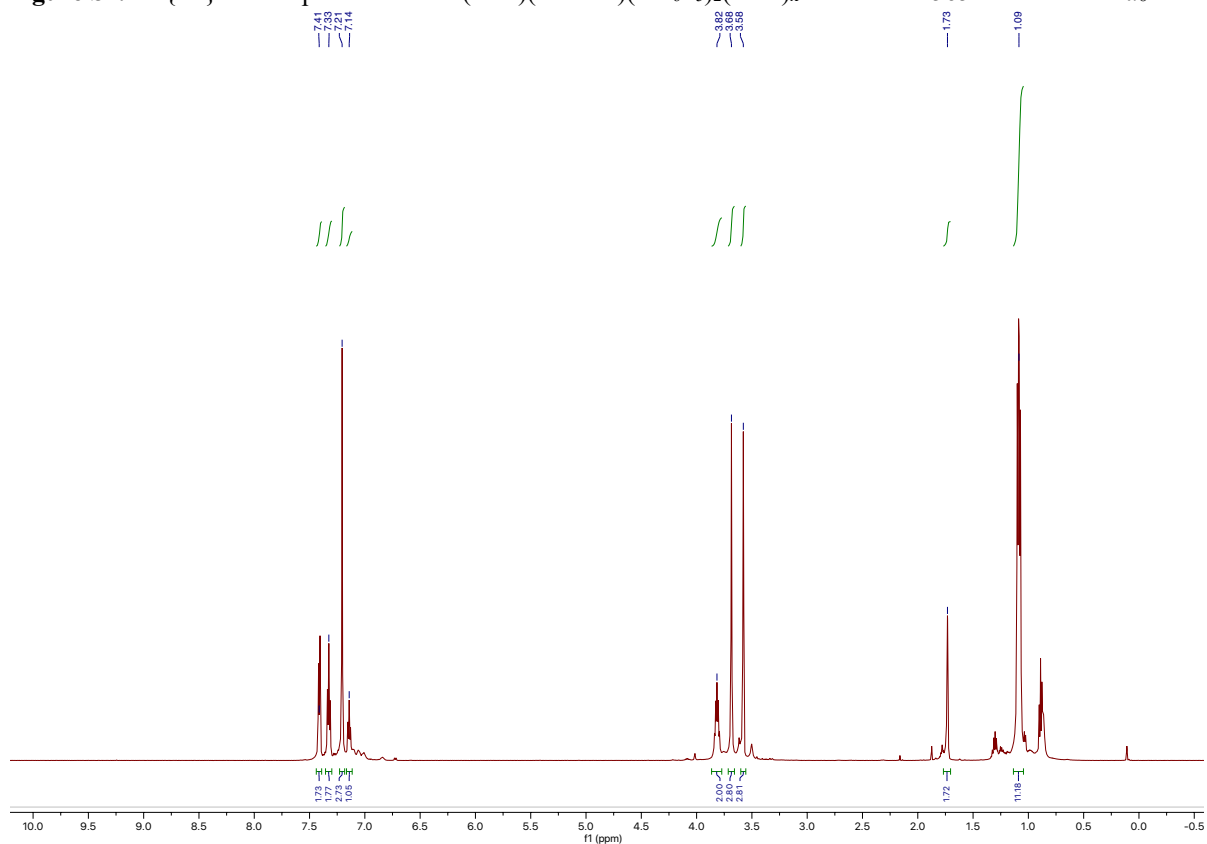


Figure S5. ^1H NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{THF})_x$ recorded at 600 MHz in $\text{THF-}d_8$ at -40 °C.

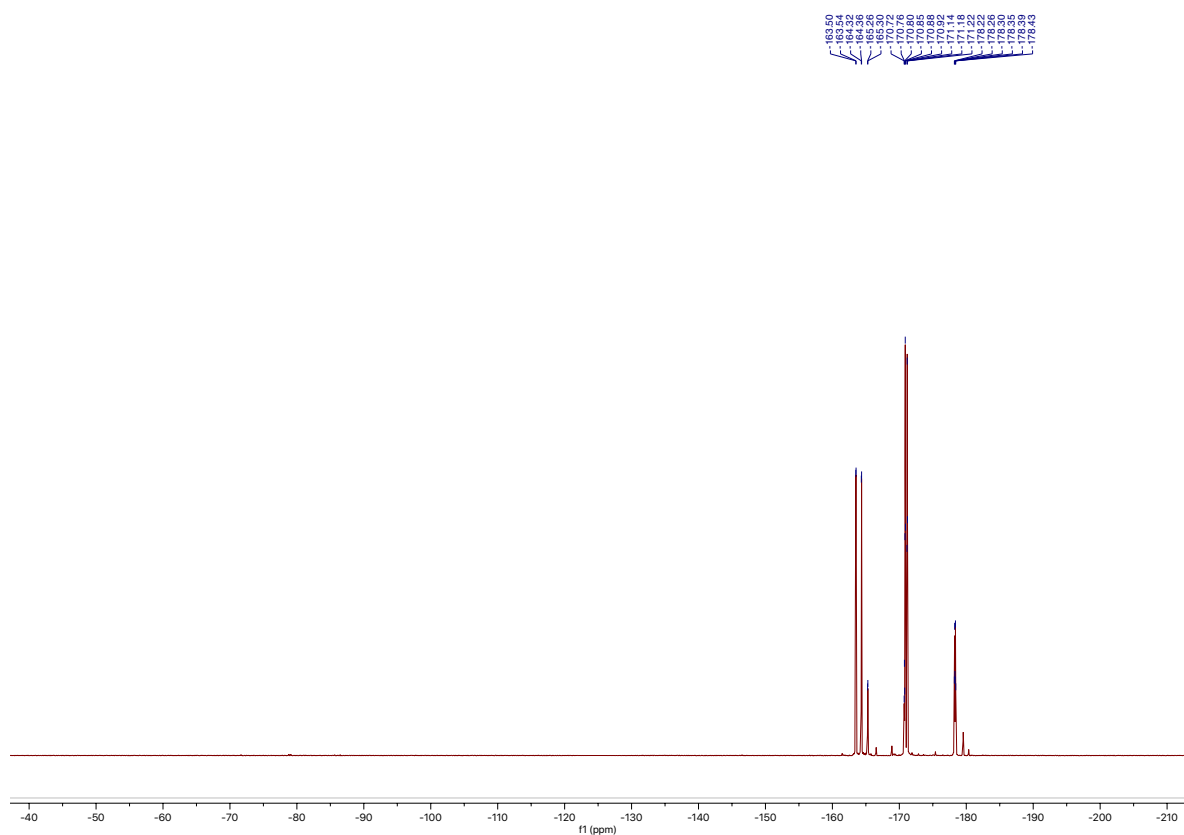


Figure S6. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{THF})_x$ recorded at 565 MHz in $\text{THF}-d_8$ at -40°C .

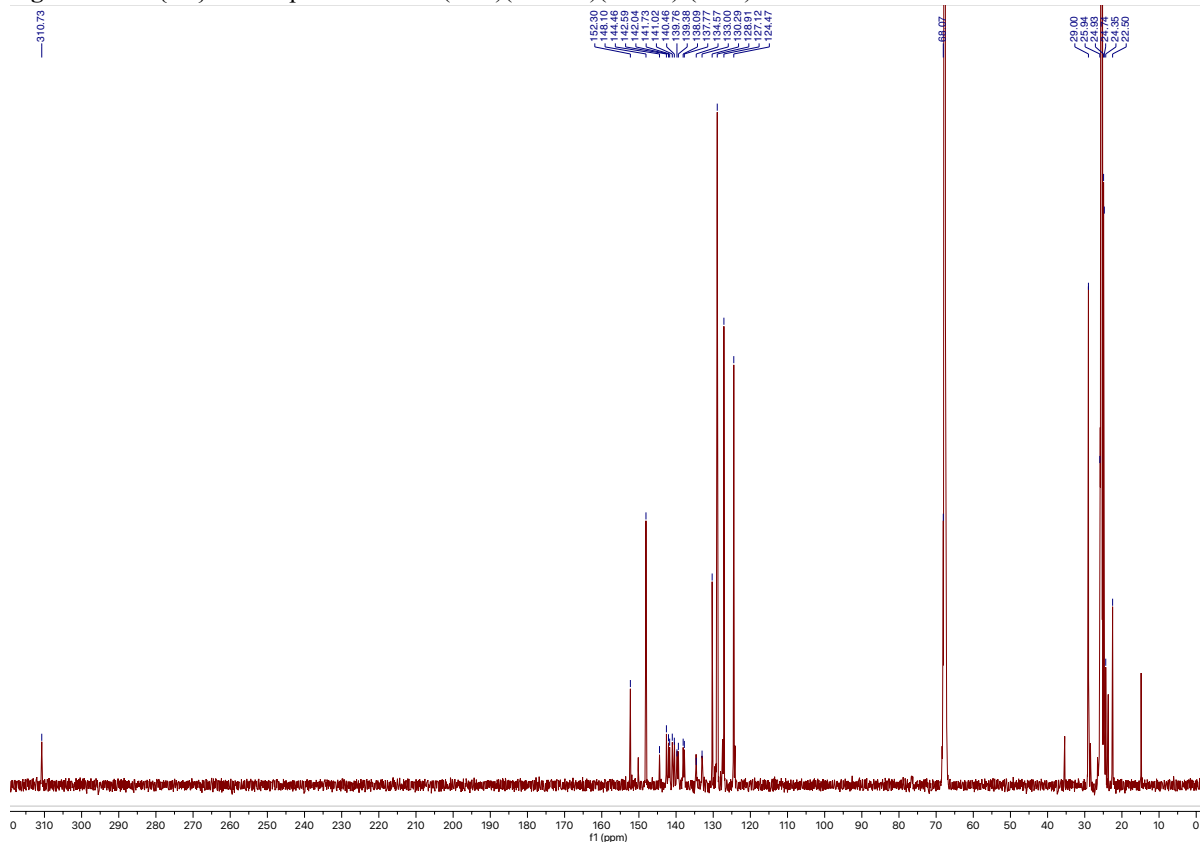


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{THF})_x$ recorded at 151 MHz in $\text{THF}-d_8$ at -40°C .

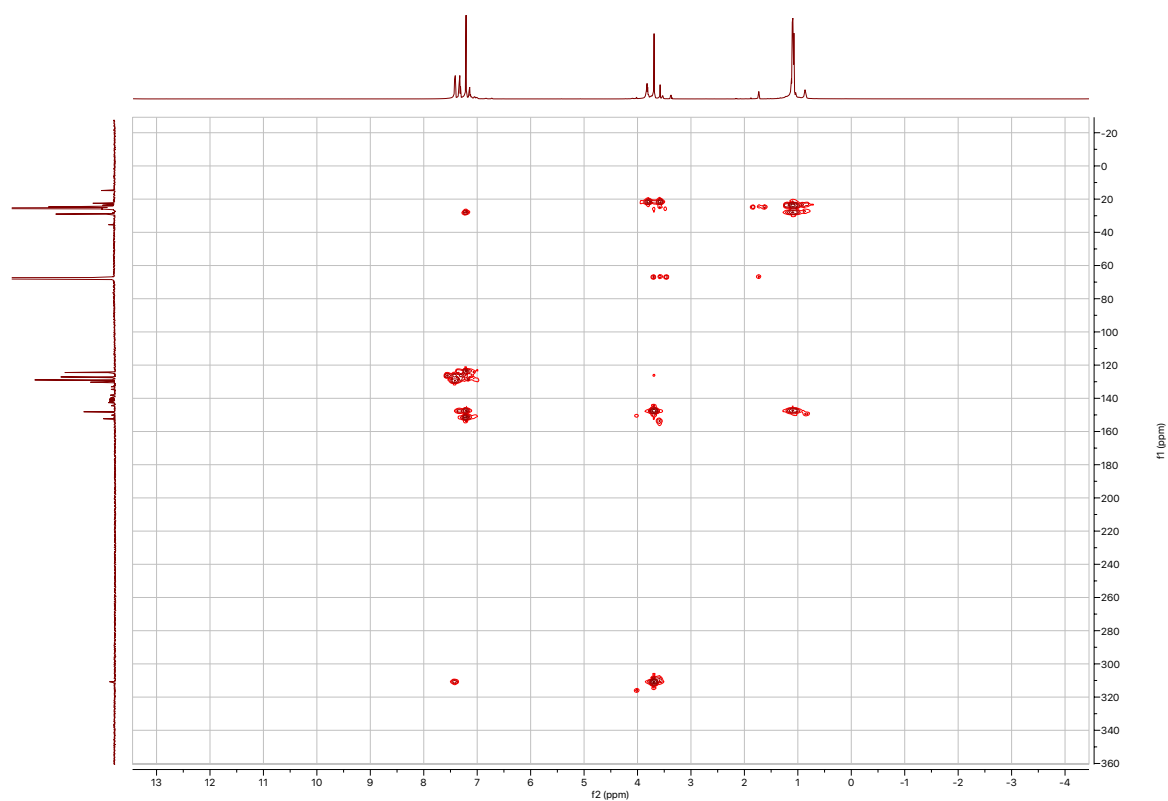


Figure S8. ^{13}C , ^1H -HMBC NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{THF})_x$ recorded at 600 MHz in $\text{THF}-d_8$ at -40°C .

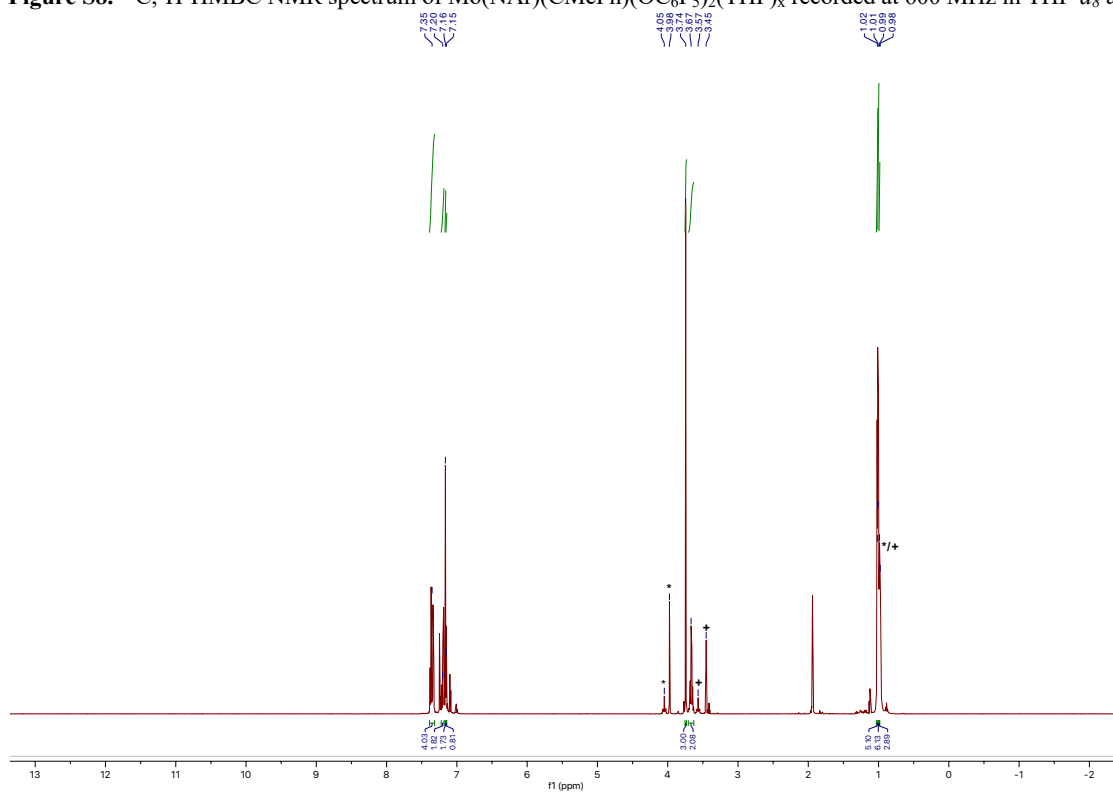


Figure S9. ^1H NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{MeCN})$ recorded at 600 MHz in CD_3CN . The asterisk (*) and plus (+) symbols denote resonances for isomers 1 and 2, respectively, which are proposed to be $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{MeCN})_2$ complexes.

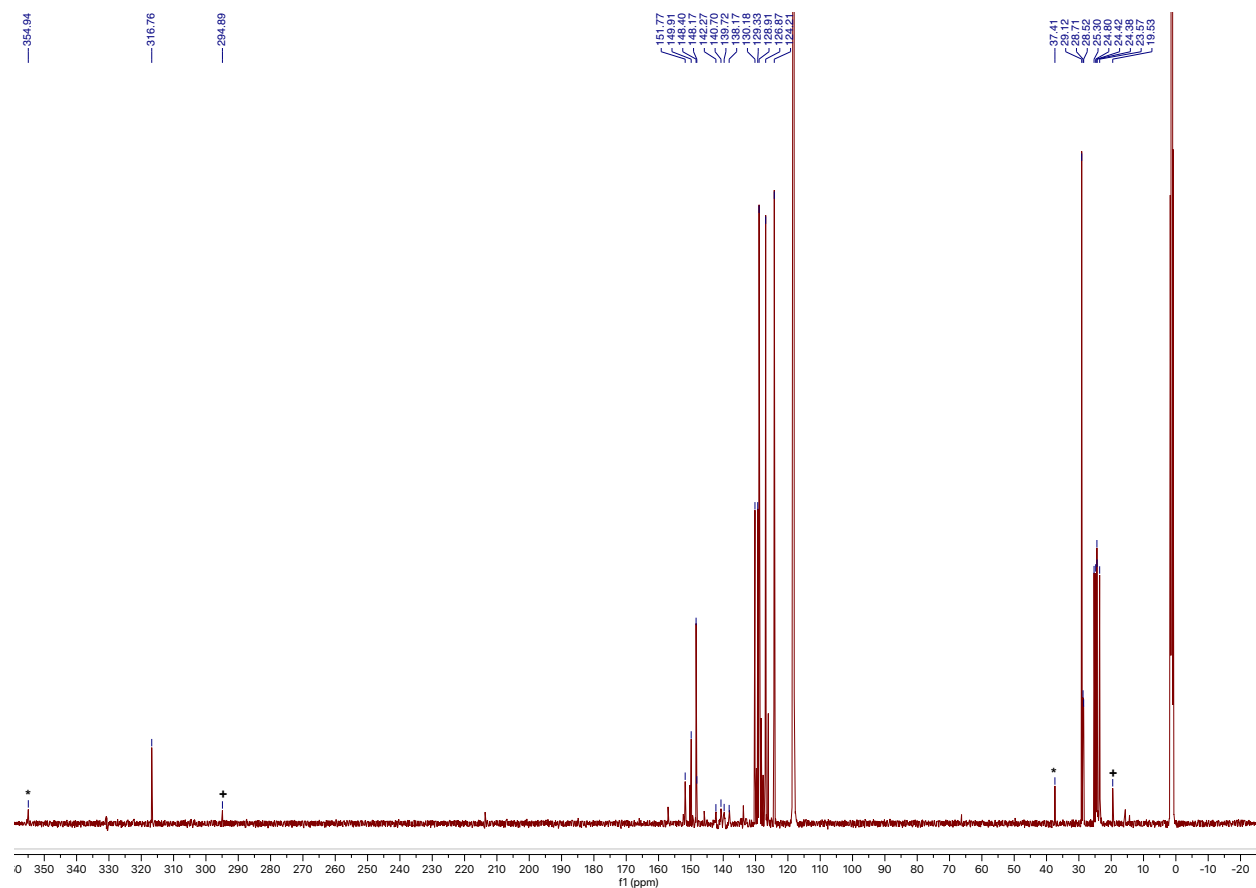


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{MeCN})$ recorded at 151 MHz in CD_3CN . The asterisk (*) and plus (+) symbols denotes resonances for isomers 1 and 2, respectively, which are proposed to be $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{MeCN})_2$ complexes.

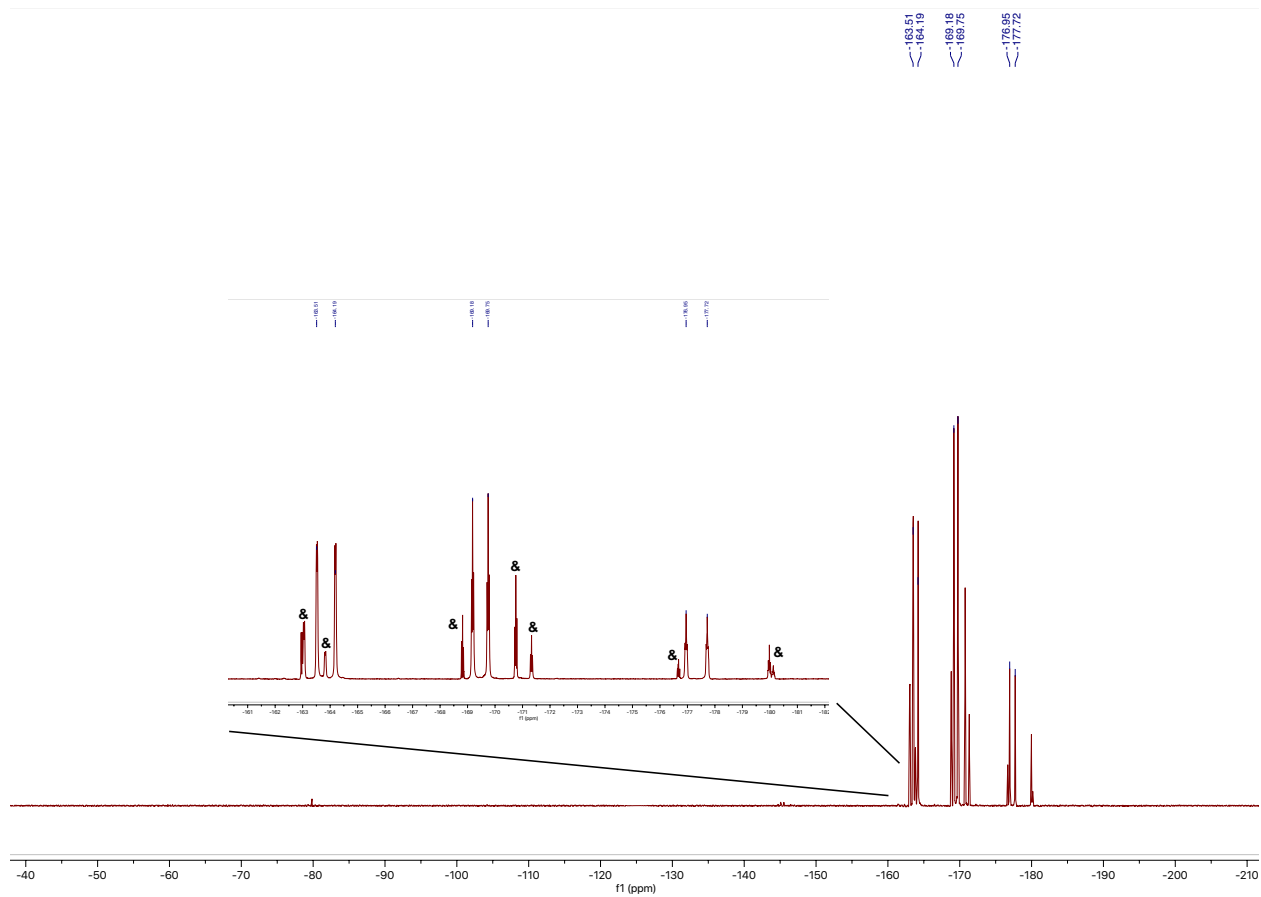


Figure S11. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{MeCN})$ recorded at 564 MHz in CD_3CN . The ampersand (&) denotes resonances for isomers 1 and 2, which are proposed to be $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{MeCN})_2$ complexes.



Figure S12. ^1H , ^1H -COSY NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{MeCN})$ recorded at 600 MHz in CD_3CN .

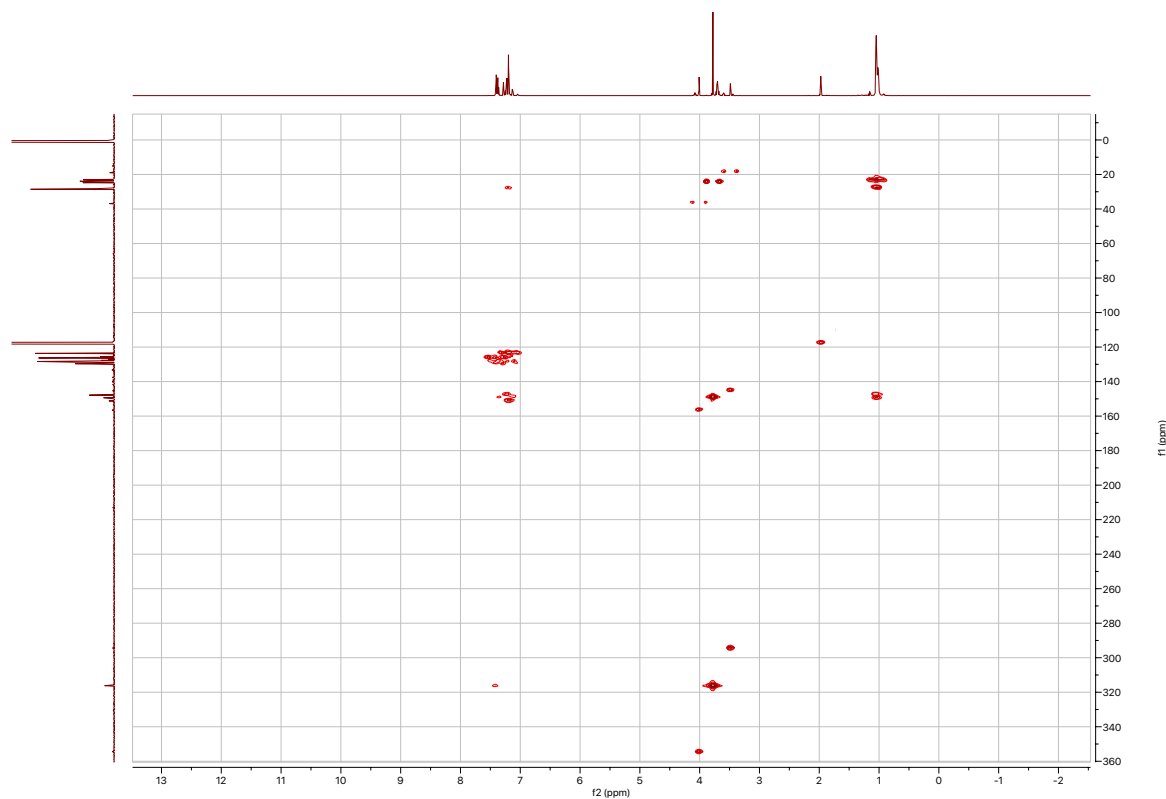


Figure S13. ^{13}C , ^1H -HMBC NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{MeCN})$ recorded at 151 MHz in CD_3CN .

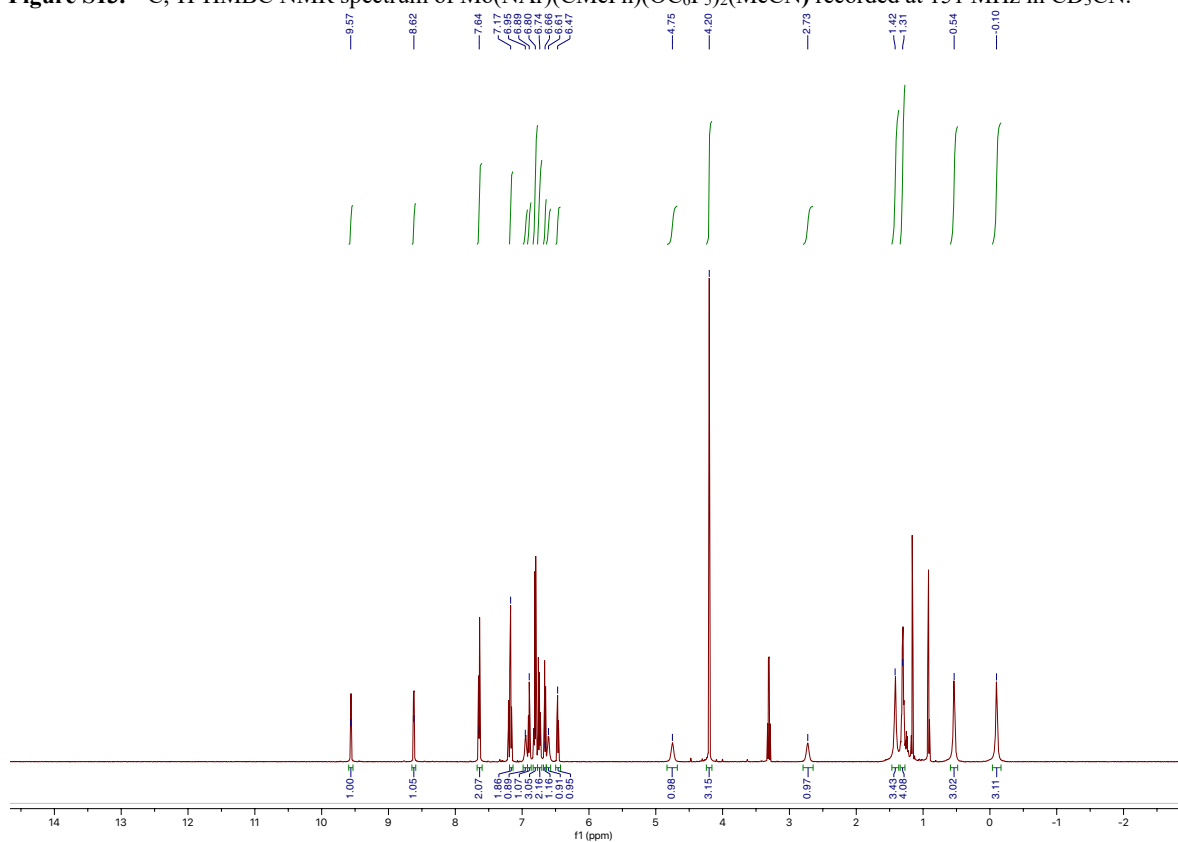


Figure S14. ^1H NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{bipy})$ recorded at 600 MHz in C_6D_6 .

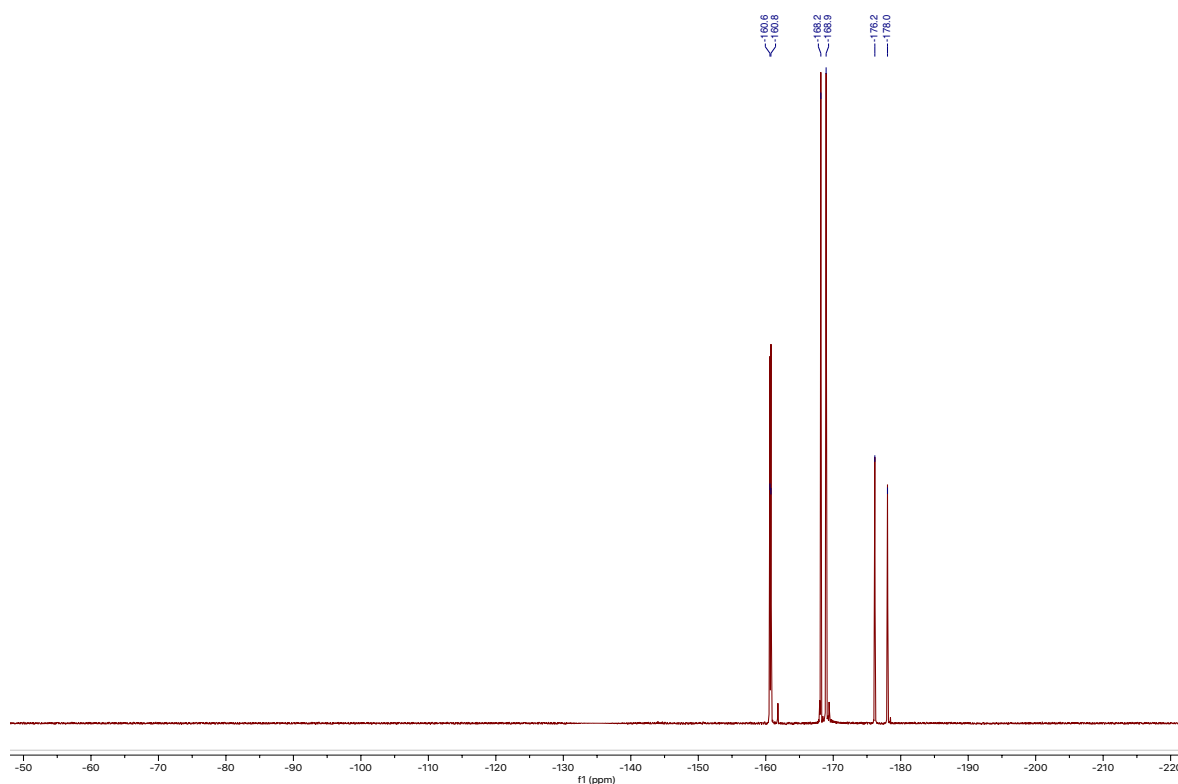


Figure S15. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{bipy})$ recorded at 565 MHz in C_6D_6 .

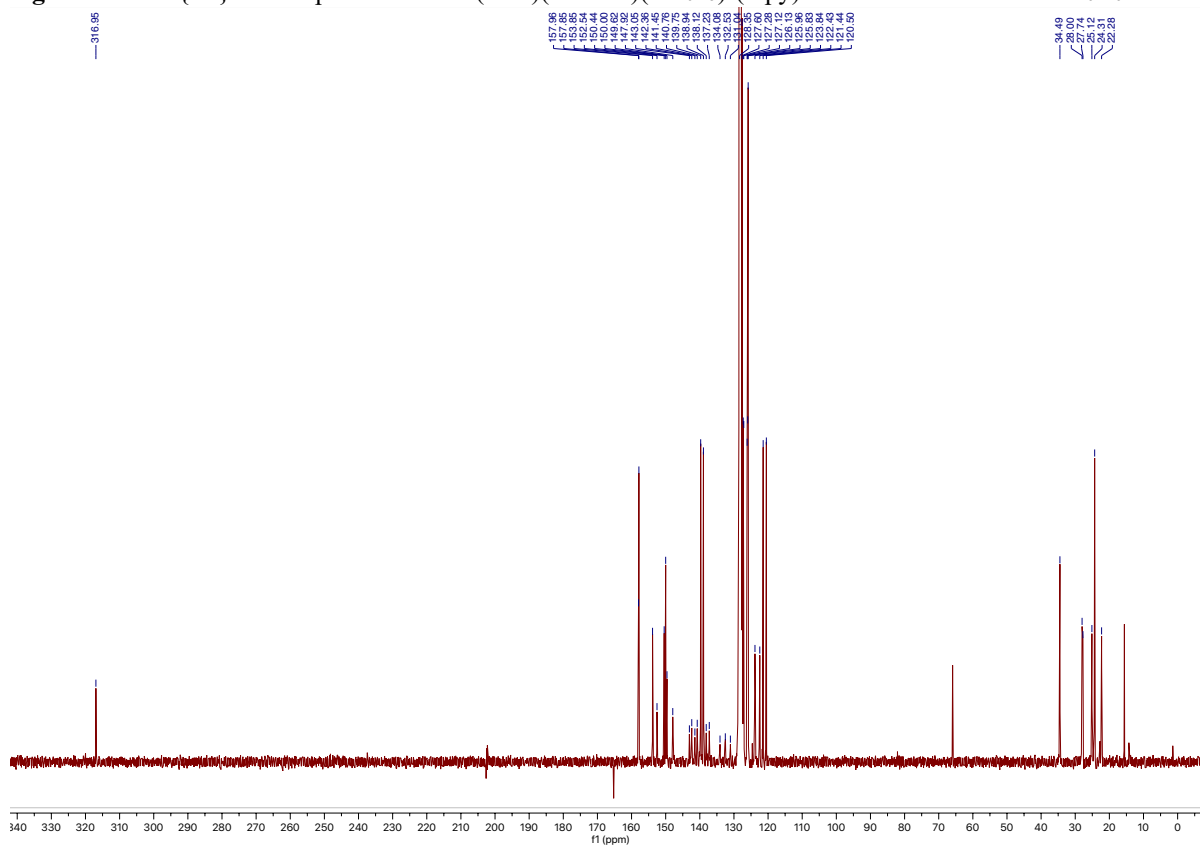


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{bipy})$ recorded at 151 MHz in C_6D_6 .

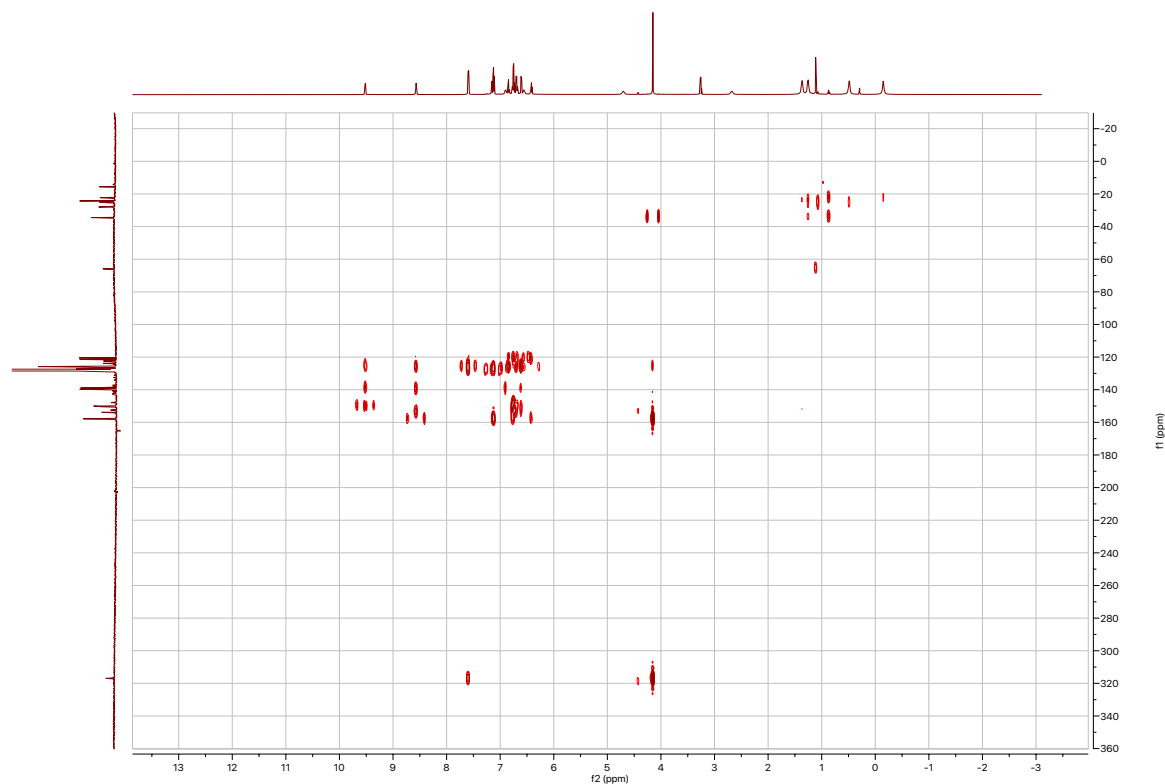


Figure S17. ^{13}C , ^1H -HMBC NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{bipy})$ recorded at 151 MHz in C_6D_6 .

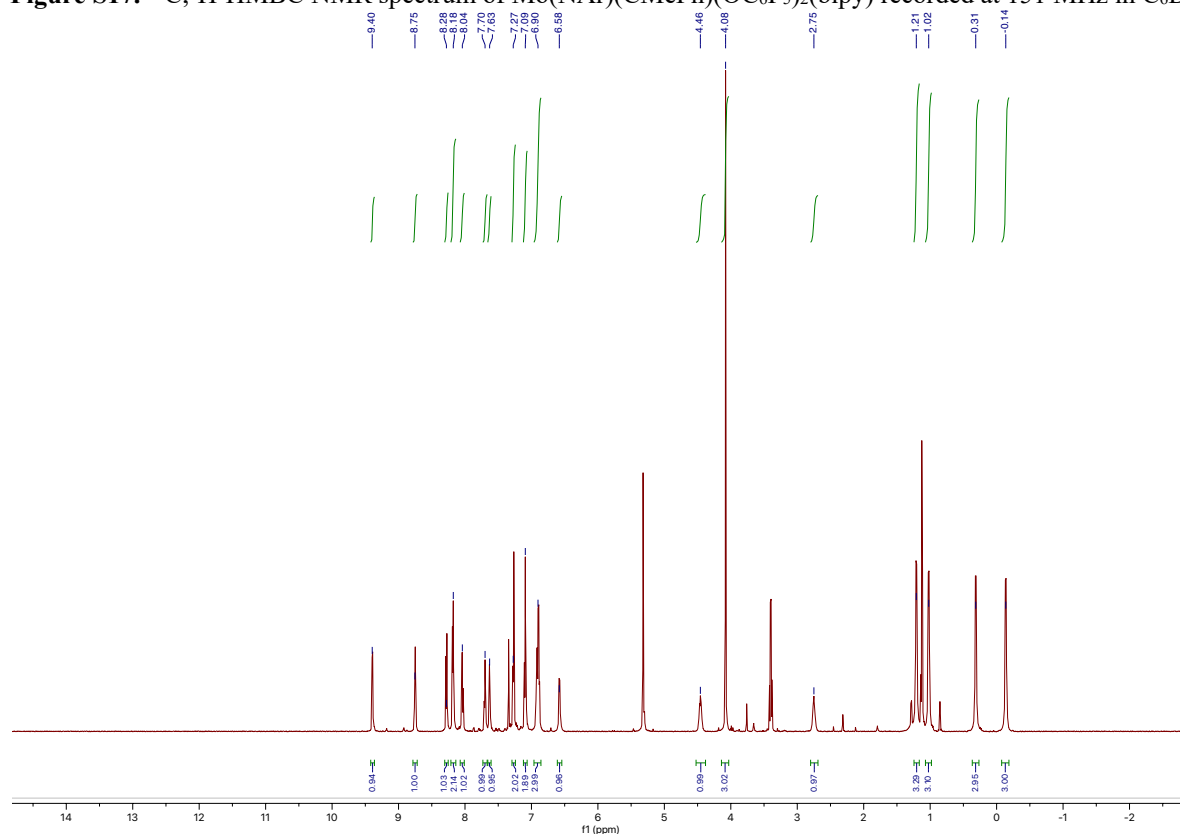


Figure S18. ^1H NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{Cl})_2(\text{bipy})$ recorded at 600 MHz in CD_2Cl_2 at -40°C .

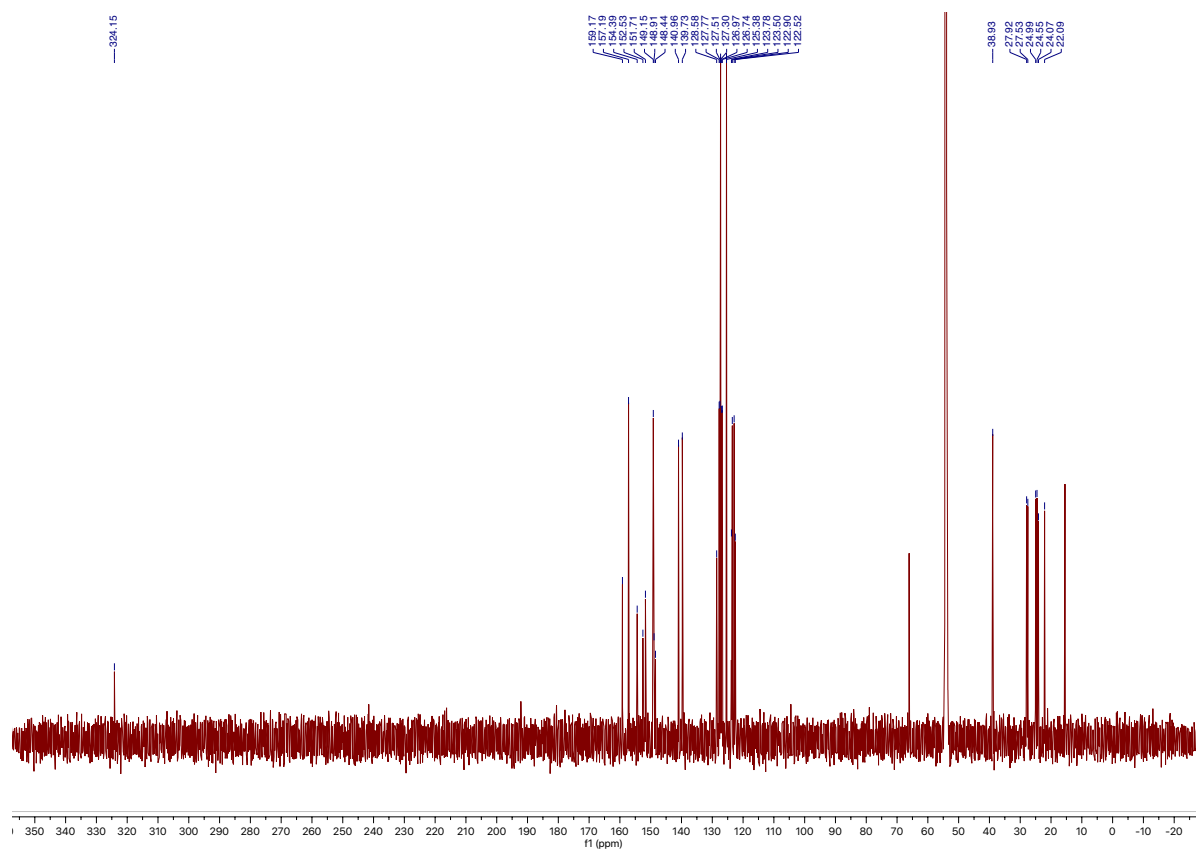


Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{Cl})_2(\text{bipy})$ recorded at 151 MHz in CD_2Cl_2 at -40°C .

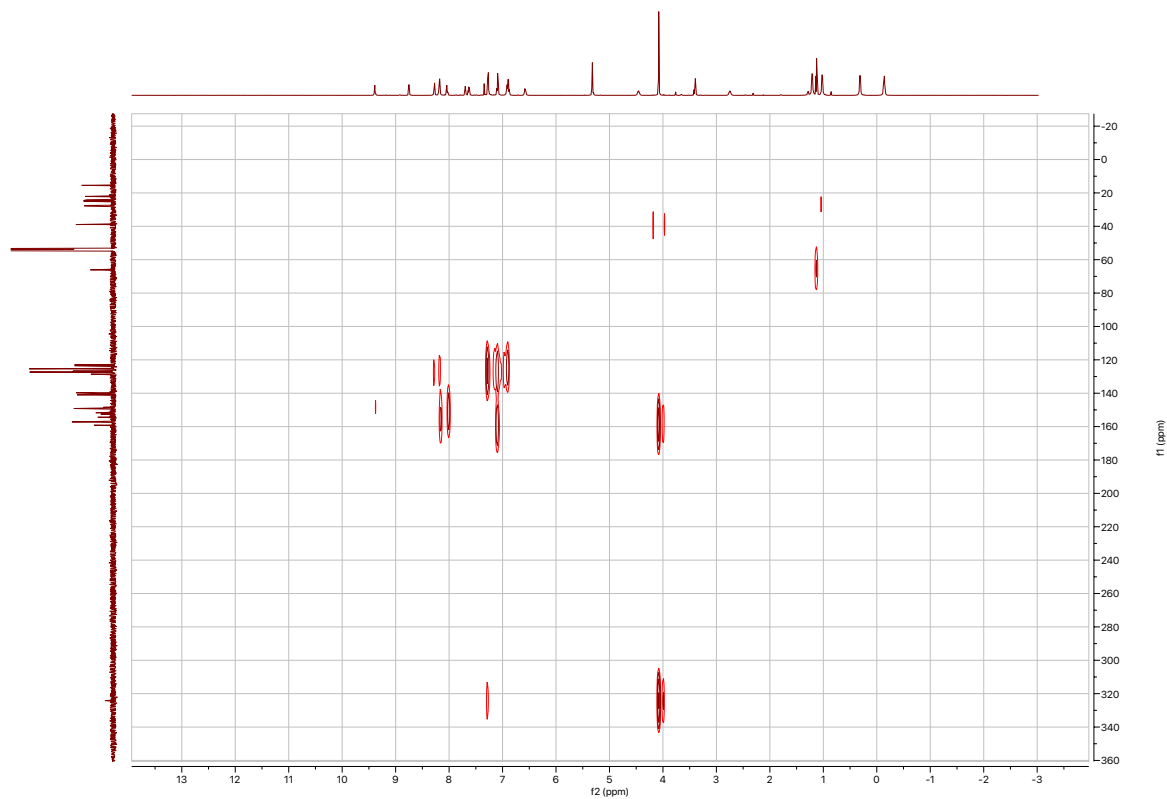


Figure S20. $^{13}\text{C},^1\text{H}$ -HMBC NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{Cl})_2(\text{bipy})$ recorded at 151 MHz in CD_2Cl_2 at -40°C .

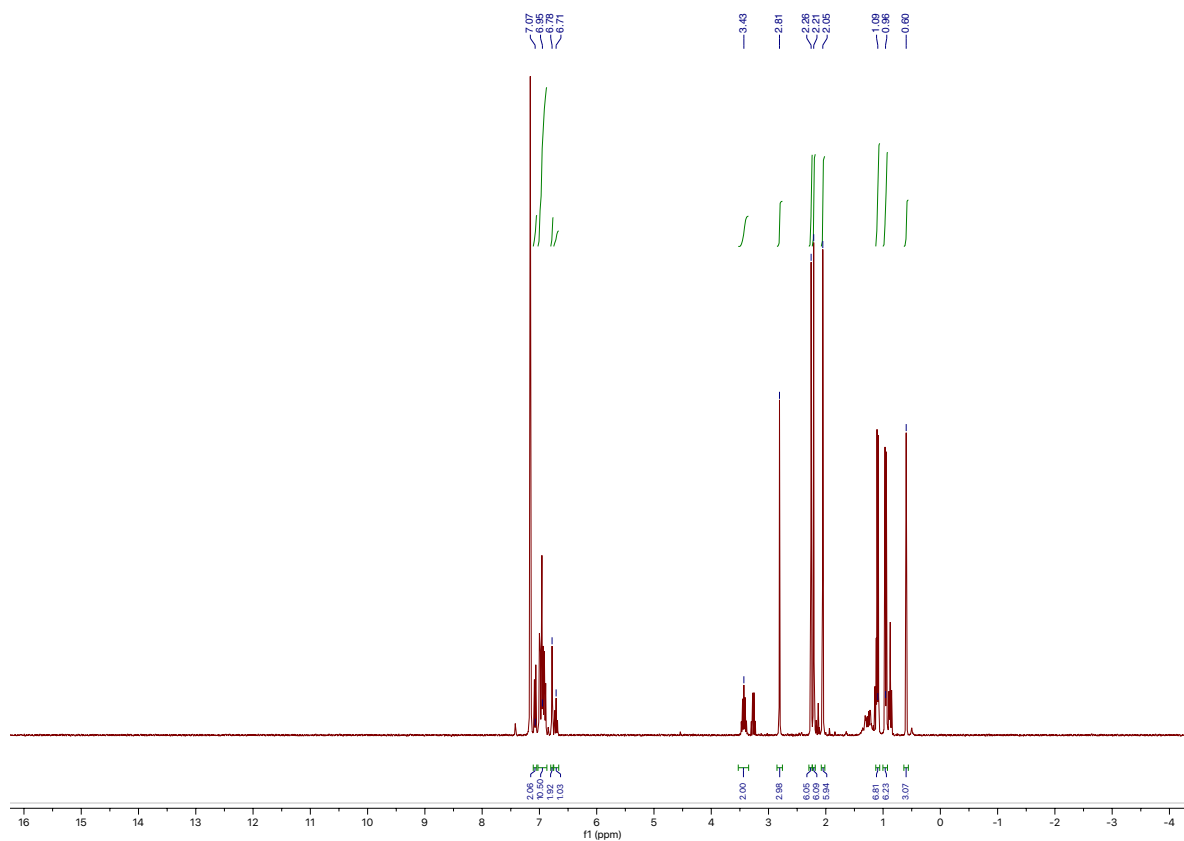


Figure S21. ¹H NMR spectrum of Mo(NAr)(CMePh)(Cl)(OHMT)(MeCN) recorded at 600 MHz in C₆D₆.

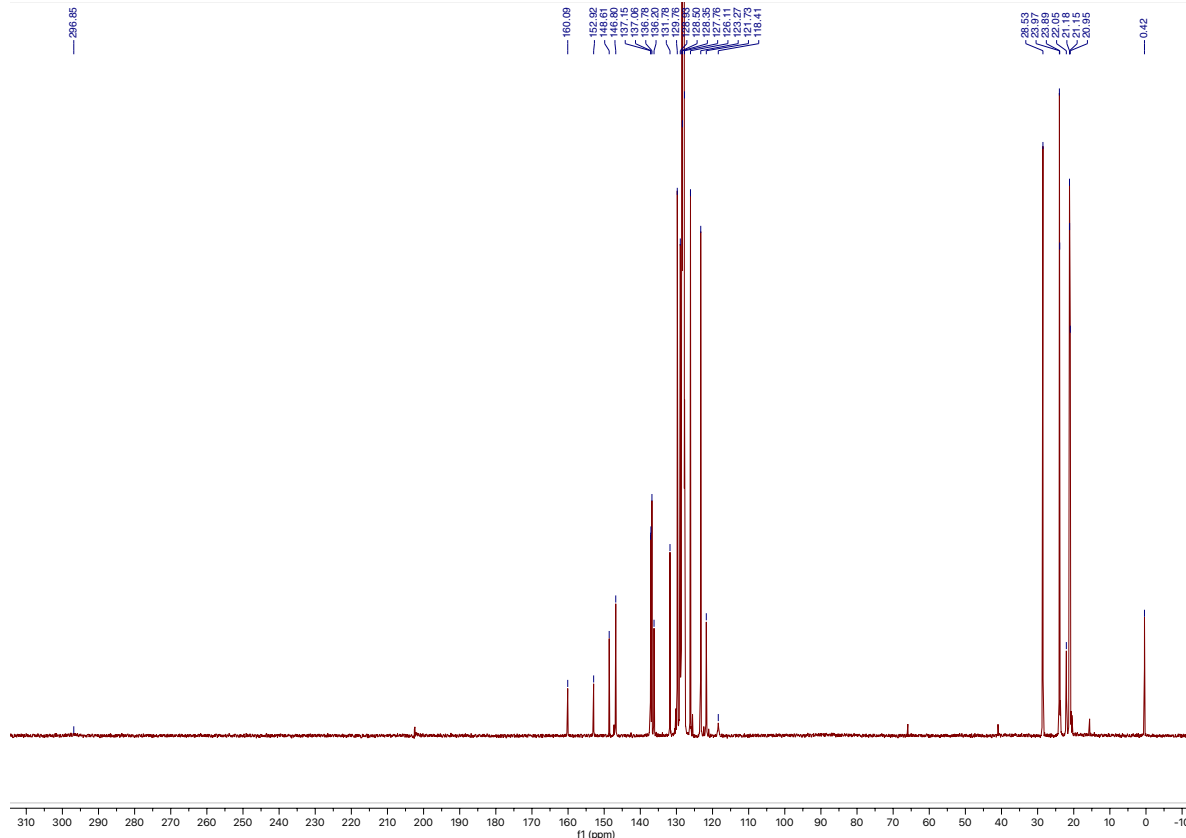


Figure S22. ¹³C{¹H} NMR spectrum of Mo(NAr)(CMePh)(Cl)(OHMT)(MeCN) recorded at 151 MHz in C₆D₆.

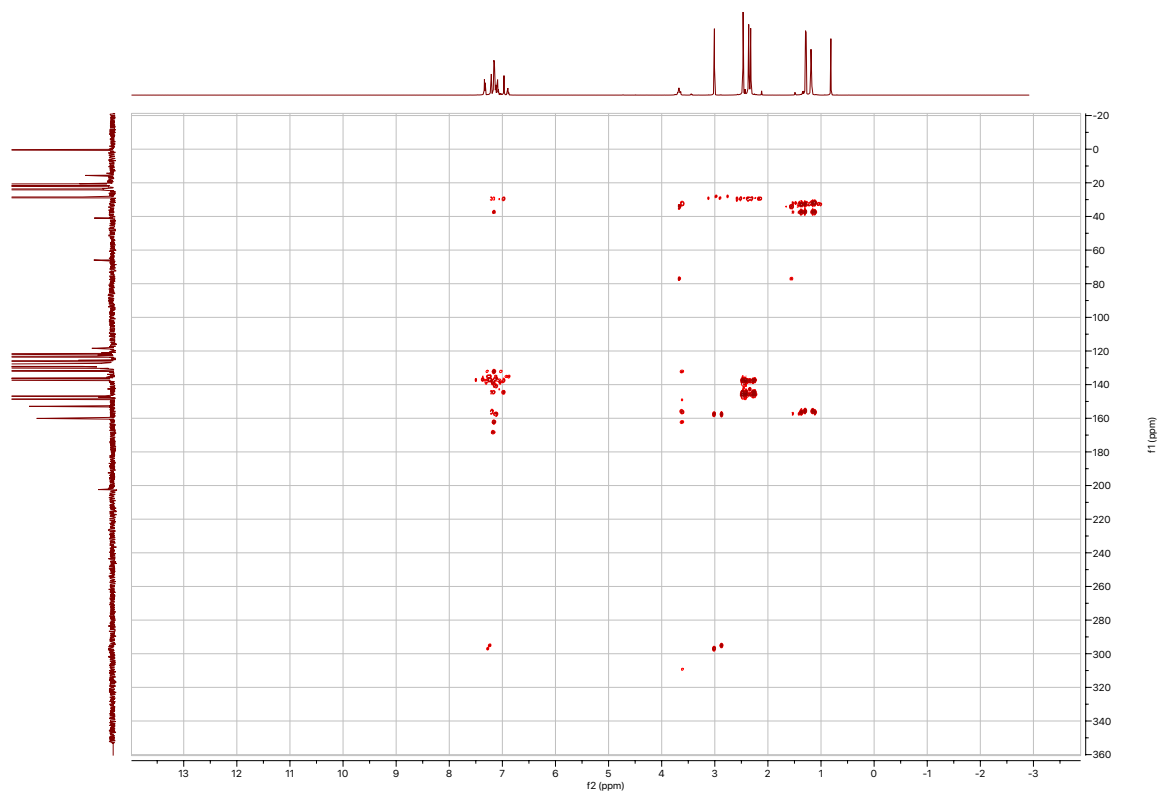


Figure S23. $^{13}\text{C}, ^1\text{H}$ -HMBC NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{Cl})(\text{OHMT})(\text{MeCN})$ recorded at 151 MHz in C_6D_6 .

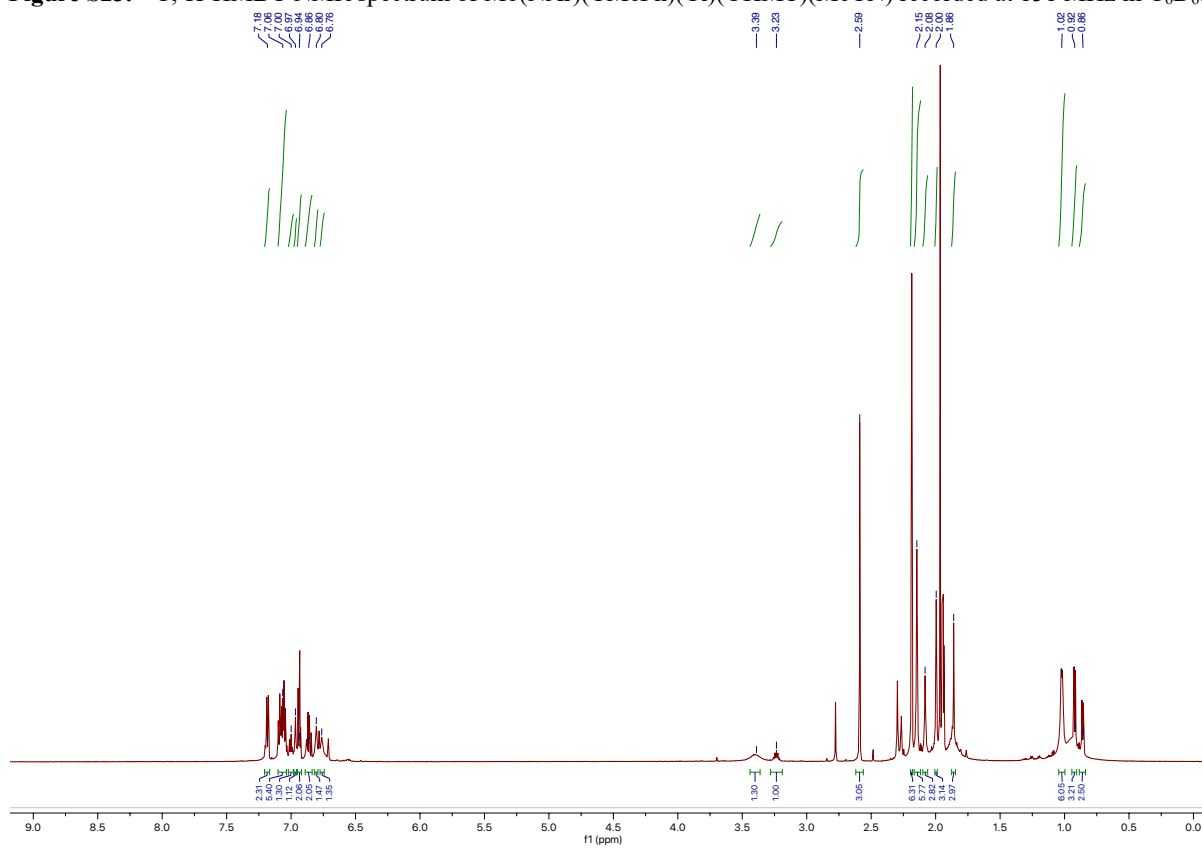


Figure S24. ^1H NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{Cl})(\text{OHMT})(\text{MeCN})$ recorded at 600 MHz in CD_3CN .

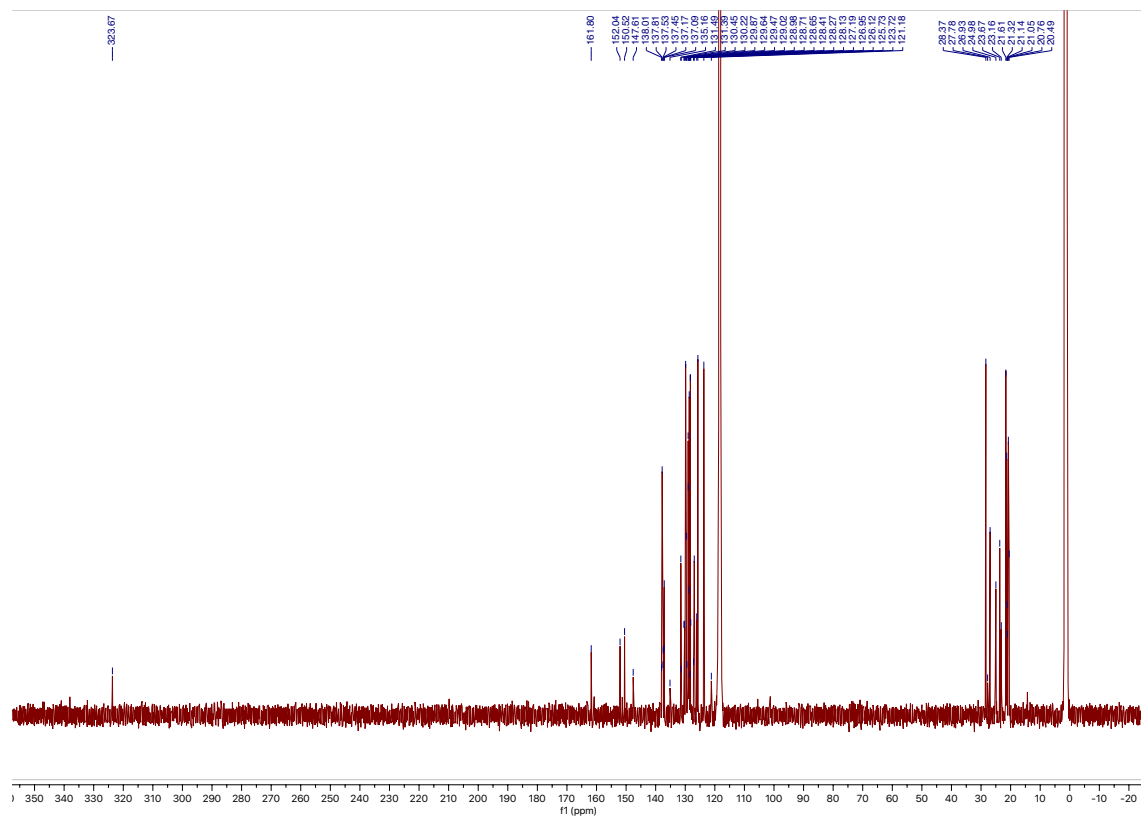


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{Cl})(\text{OHMT})(\text{MeCN})$ recorded at 151 MHz in CD_3CN .

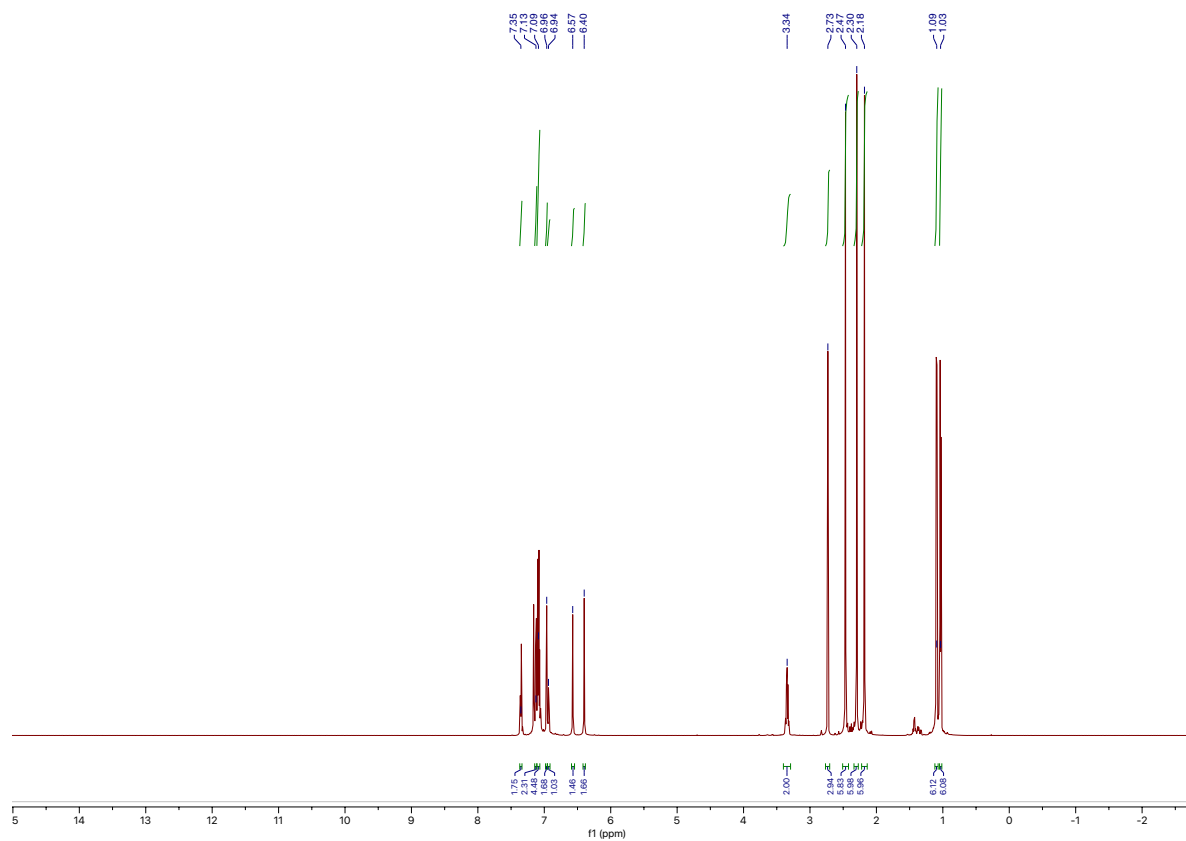


Figure S26. ^1H NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OHMT})(\text{NC}_4\text{H}_4)$ recorded at 600 MHz in C_6D_6 .

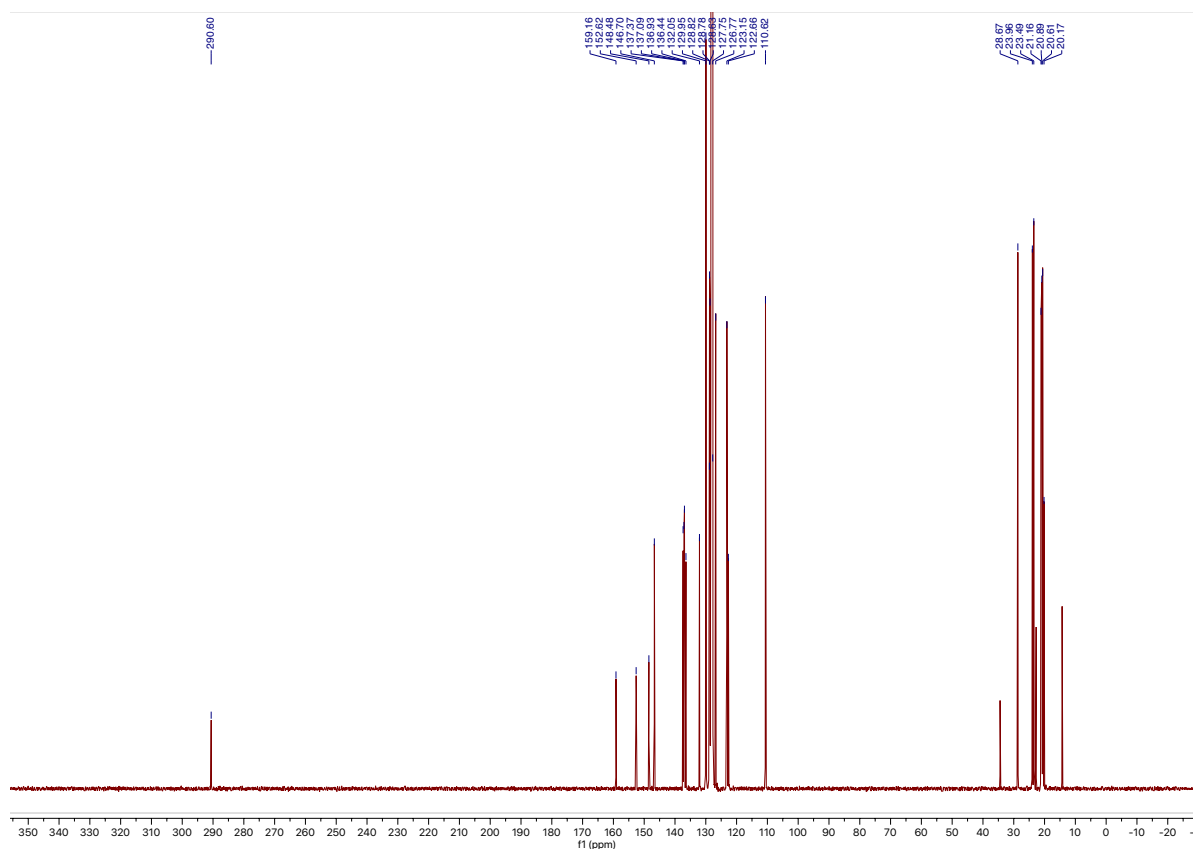


Figure S27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OHMT})(\text{NC}_4\text{H}_4)$ recorded at 151 MHz in C_6D_6 .

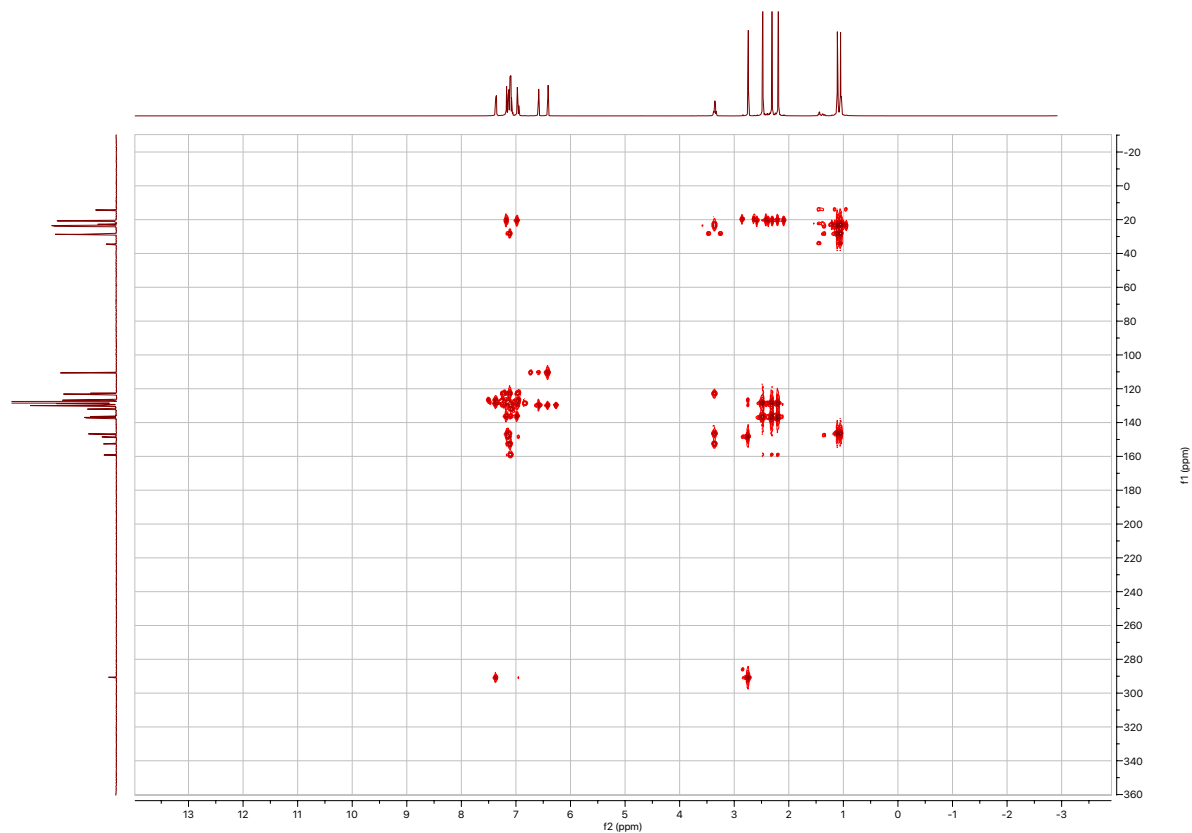
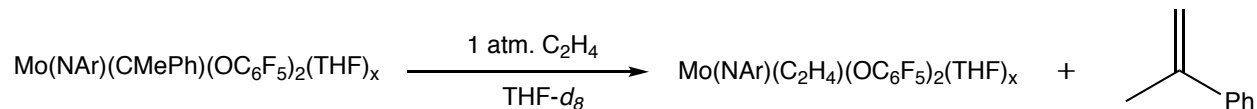


Figure S28. $^{13}\text{C}, ^1\text{H}$ -HMBC NMR spectrum of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OHMT})(\text{NC}_4\text{H}_4)$ recorded at 151 MHz in C_6D_6 .

Preliminary studies of reactions of disubstituted alkylidene complexes with olefins.

Reaction of $2(\text{THF})_x$ with ethylene.



$[\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2]$ (0.007 g, 0.0094 mmol) was dissolved in $\text{THF-}d_8$ (0.6 mL) to give an orange solution of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{THF})_x$ that was freeze-pump-thawed three times prior to addition of 1 atm of ethylene. After 2 hours, the volatiles were removed from the dark green solution *in vacuo* (10^{-2} mbar, 10 minutes) prior to dissolving the residue in $\text{THF-}d_8$ and collecting NMR spectra. Crystallization of what is proposed to be $\text{Mo}(\text{NAr})(\text{C}_2\text{H}_4)(\text{OC}_6\text{F}_5)_2(\text{THF})_x$ was hindered by its gradual decomposition in the absence of ethylene to unidentified products. ^1H NMR (600 MHz, $\text{THF-}d_8$) δ 7.1 (dd, $J = 8.9, 6.2$ Hz, 1H), 7.1 – 7.1 (m, 2H), 3.6 (s, 4H), 2.6 – 2.6 (m, 2H), 2.2 – 2.1 (m, 2H), 1.7 (s, 4H), 1.1 (d, $J = 6.8$ Hz, 12H). $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, $\text{THF-}d_8$) δ –159.9 – –160.4 (m), –168.3 (t, $J = 21.1$ Hz), –177.5 (ddd, $J = 29.5, 21.3, 7.2$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, $\text{THF-}d_8$) δ 153.5, 149.5, 145.4, 143.3, 141.7, 140.7 – 139.6 (m), 138.6 (t, $J = 13.8$ Hz), 134.0 (t, $J = 12.6$ Hz), 132.4 (t, $J = 16.2$ Hz), 129.8, 129.1, 128.6, 126.2, 124.1, 68.4, 64.0, 28.7, 26.5, 24.9.

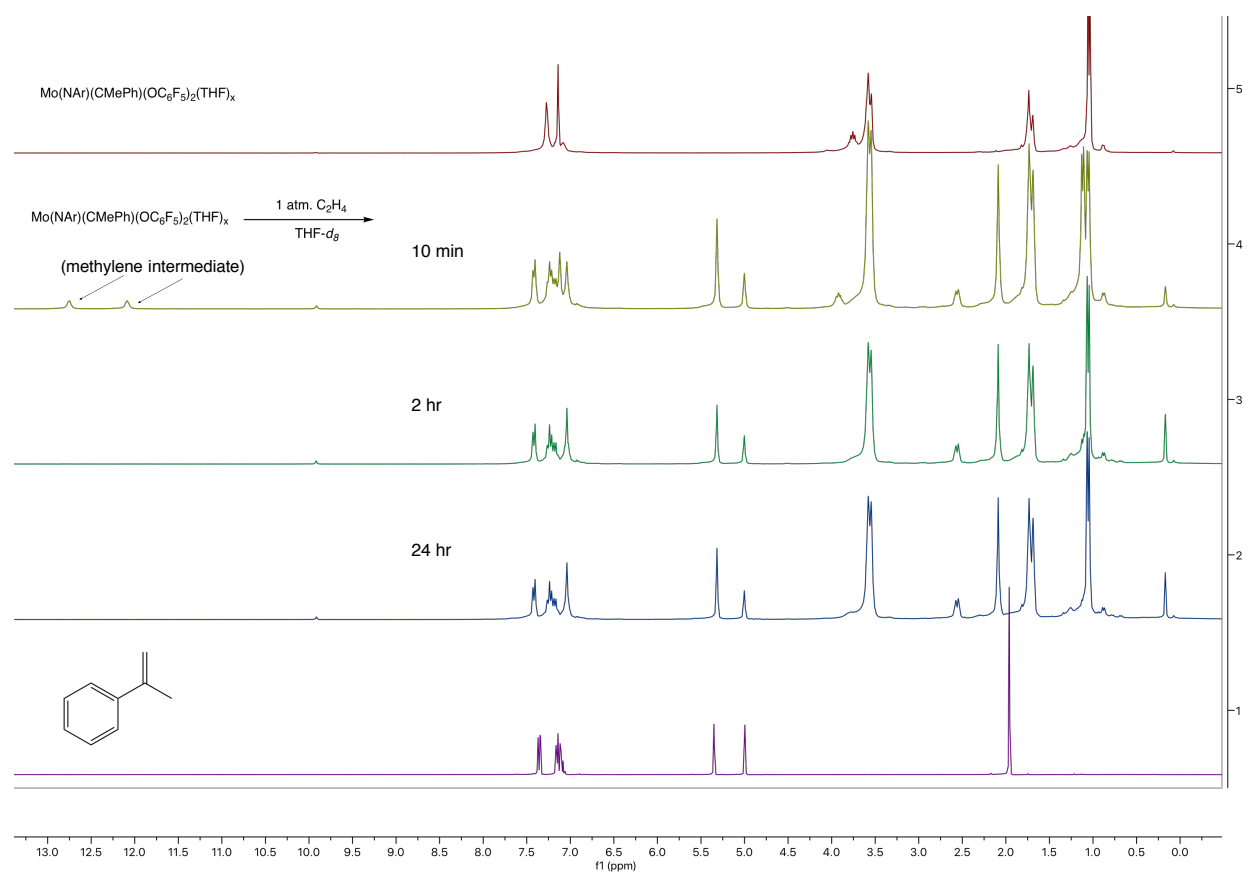


Figure S29. ^1H NMR spectra monitoring the progress of the reaction of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{THF})_x$ with 1 atm ethylene. Spectrum 5 is pure $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{THF})_x$, spectra 2-4 track the reaction over 24 hours with time of collection inlayed. Spectrum 1 is pure α -methylstyrene. All spectra were recorded at 300 MHz in $\text{THF-}d_8$ at 22 $^\circ\text{C}$.

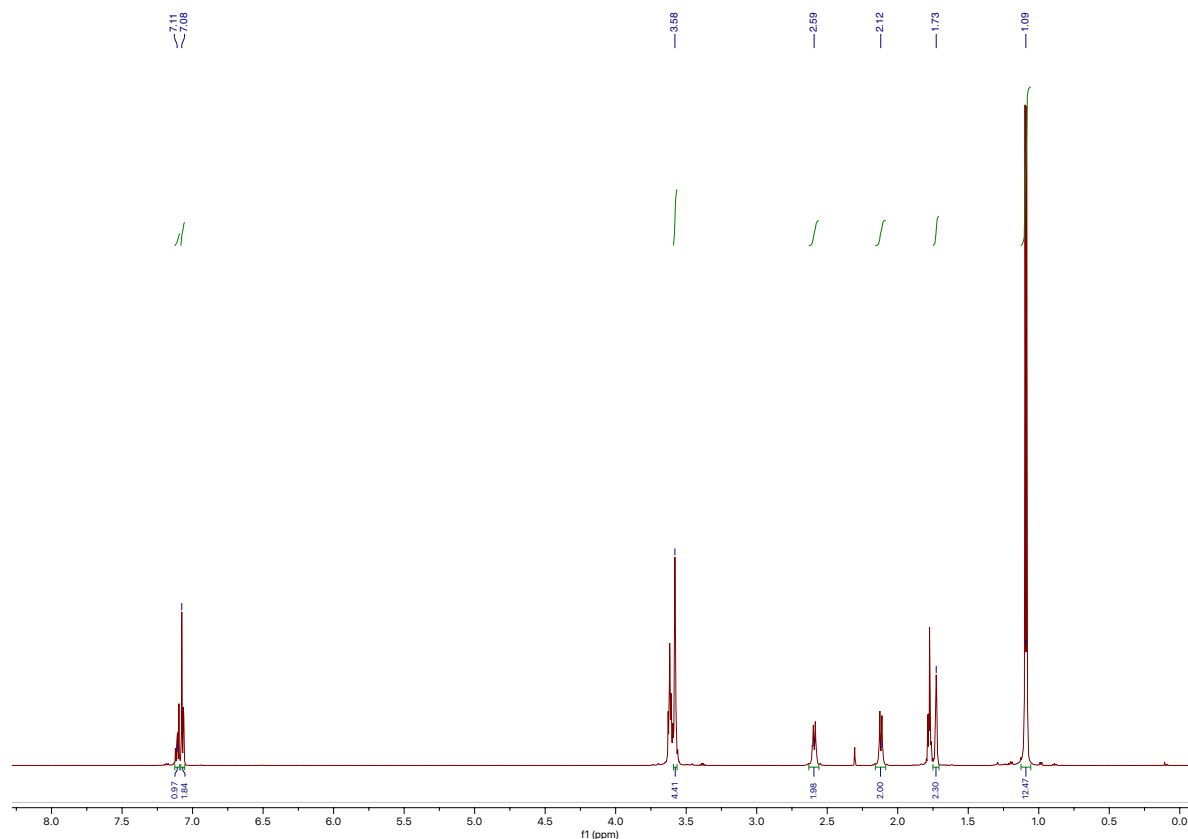


Figure S30. ¹H NMR spectrum of Mo(NAr)(C₂H₄)(OC₆F₅)₂(THF)_x recorded at 600 MHz in THF-*d*₈.

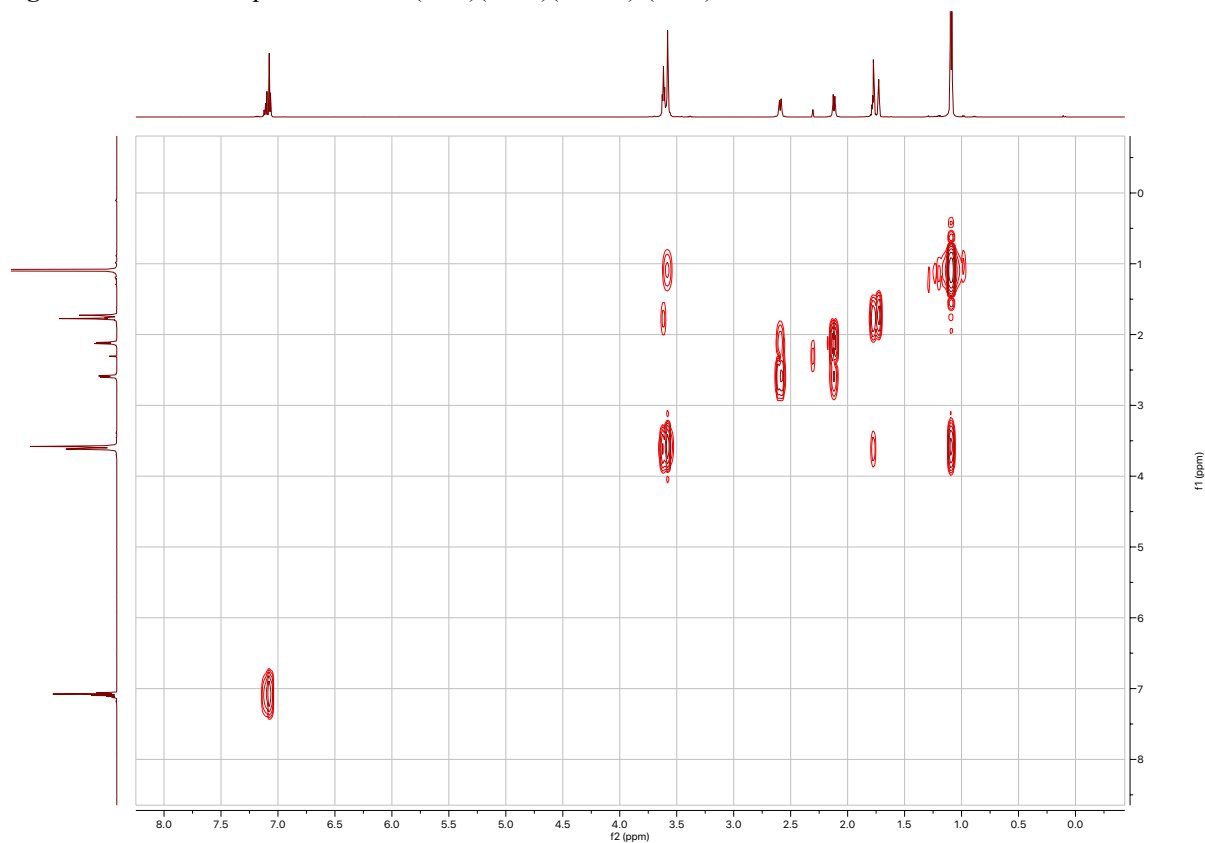


Figure S31. ¹H, ¹H-COSY NMR spectrum of Mo(NAr)(C₂H₄)(OC₆F₅)₂(THF)_x recorded at 600 MHz in THF-*d*₈.

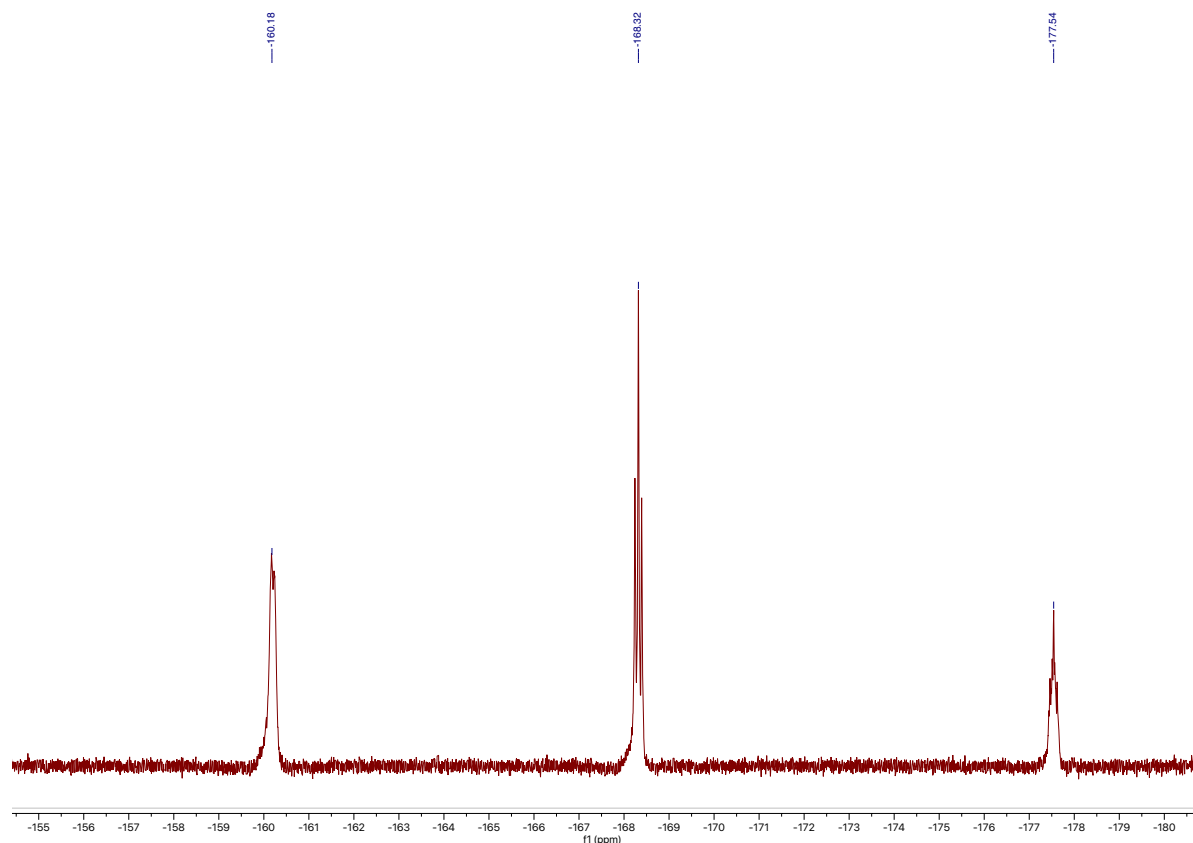


Figure S32. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $\text{Mo}(\text{NAr})(\text{C}_2\text{H}_4)(\text{OC}_6\text{F}_5)_2(\text{THF})_x$ recorded at 282 MHz in $\text{THF}-d_8$.

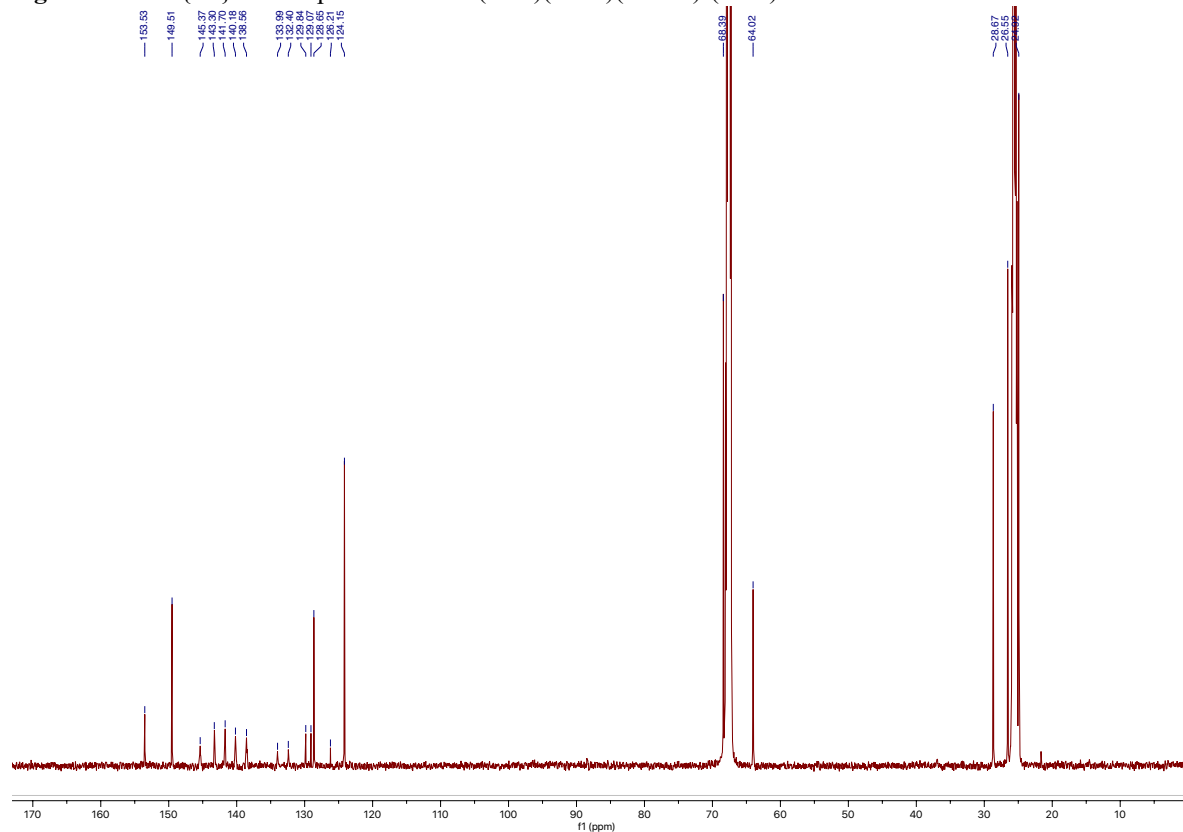


Figure S33. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Mo}(\text{NAr})(\text{C}_2\text{H}_4)(\text{OC}_6\text{F}_5)_2(\text{THF})_x$ recorded at 151 MHz in $\text{THF}-d_8$.

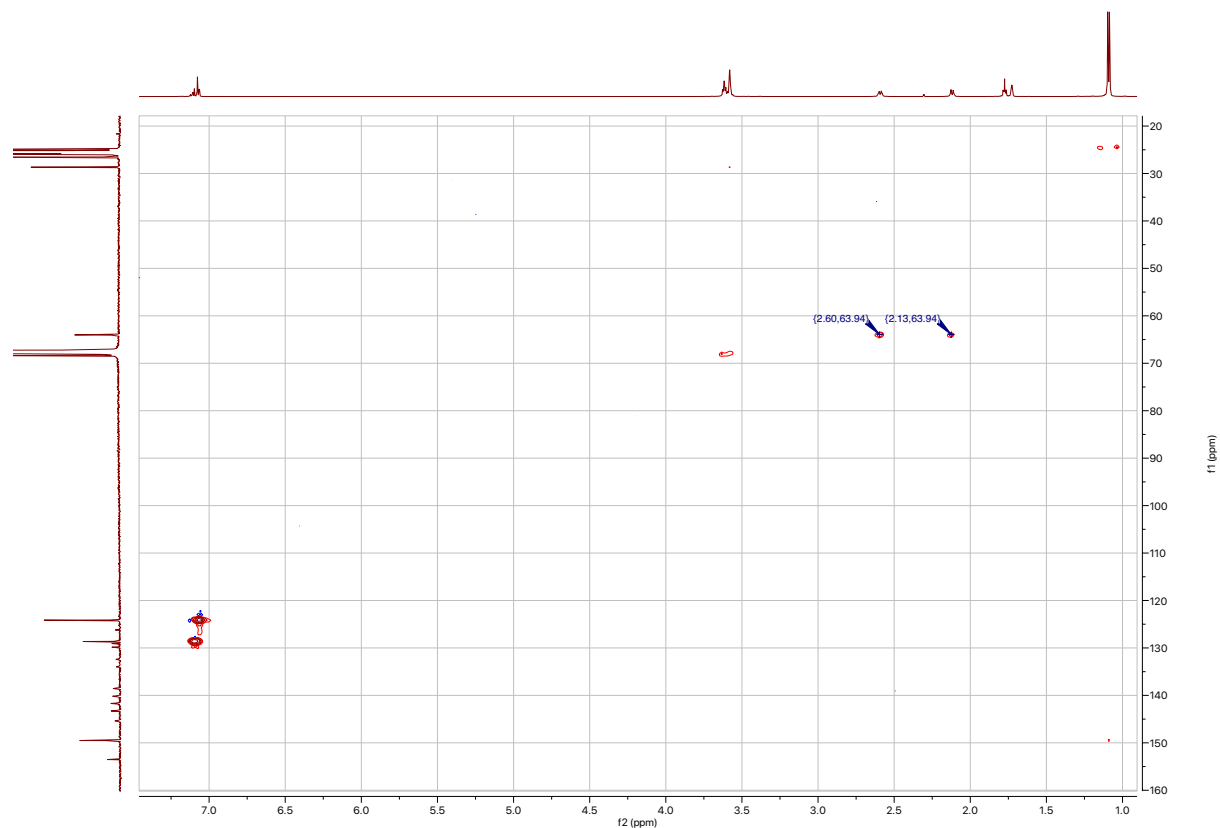
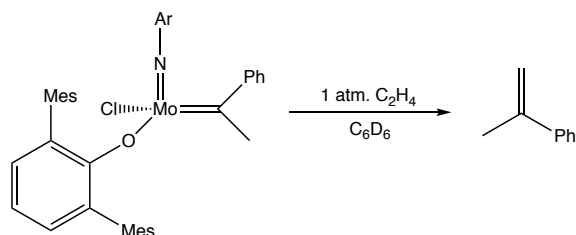


Figure S34. ^{13}C , ^1H -HSQC NMR spectrum of $\text{Mo}(\text{NAr})(\text{C}_2\text{H}_4)(\text{OC}_6\text{F}_5)_2(\text{THF})_x$ recorded at 151 MHz in $\text{THF}-d_8$.

Reaction of 4(MeCN) with ethylene



Mo(NAr)(CMePh)(Cl)(OHMT)(MeCN) (0.007 g, 0.0094 mmol) was dissolved in C₆D₆ (0.6 mL) and the solution was freeze-pump-thawed three times before addition of 1 atm of ethylene. α -Methylstyrene was observed by ¹H NMR after 10 minutes.

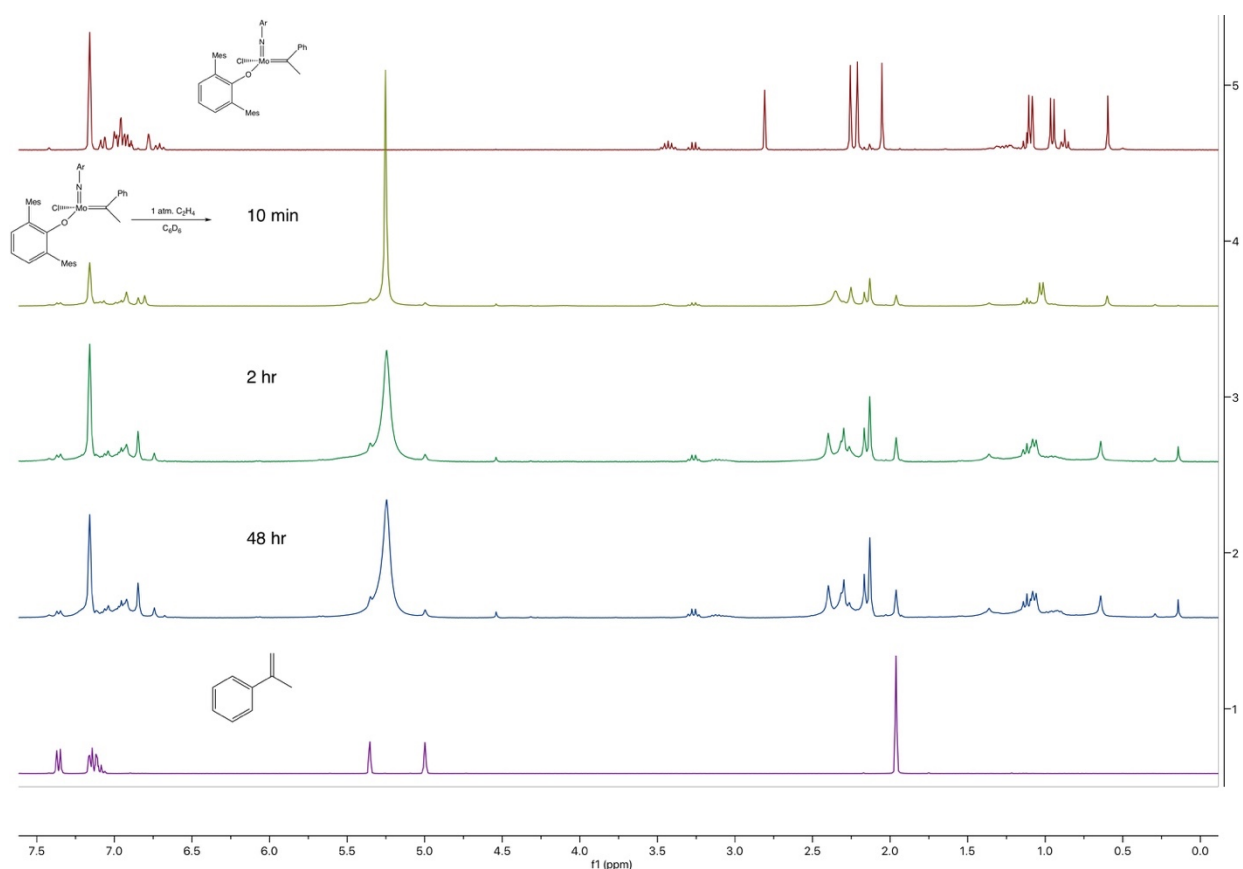
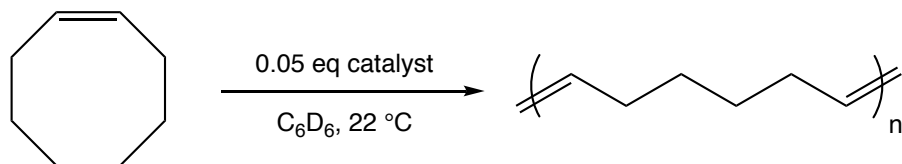


Figure S35. ¹H NMR spectra monitoring the progress of the reaction of Mo(NAr)(CMePh)(Cl)(OHMT)(MeCN) with 1 atm of ethylene. Spectrum 5 is pure Mo(NAr)(CMePh)(Cl)(OHMT)(MeCN), spectra 2-4 track the reaction progress over 48 hours. Spectrum 1 is pure α -methylstyrene. All spectra were recorded at 300 MHz in C₆D₆ at 22 °C.

Ring-opening polymerization of cyclooctene



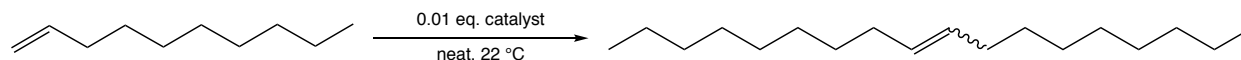
Polymerization with $\text{Mo}(\text{NAr})(\text{CMePh})(\text{Cl})(\text{OHMT})(\text{MeCN})$ as the initiator. A C_6D_6 (0.1 mL) solution of $\text{Mo}(\text{NAr})(\text{CMePh})(\text{Cl})(\text{OHMT})(\text{MeCN})$ (0.001 g, 0.0014 mmol) in C_6D_6 (0.1 mL) was added cyclooctene (2.52 μL , 0.022 mmol) via microsyringe. The reaction was stirred in an open vial at 22 °C. Aliquots were taken periodically that were diluted with C_6D_6 (0.5 mL) prior to collecting ^1H NMR spectra. Conversion was estimated by integration of the olefin proton resonance of cyclooctene (m, 5.69-5.61 ppm) and polycyclooctene (m, 5.51-5.45 ppm).

Polymerization with $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{THF})_x$ as the initiator. $[\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2]_2$ (0.001 g, 0.0013 mmol) was dissolved in $\text{THF-}d_8$ (100 μL) and diluted with C_6D_6 (900 μL) prior to adding cyclooctene (2.39 μL , 0.026 mmol) via microsyringe. The reaction was stirred in an open vial at 22 °C. Aliquots were taken periodically that were diluted with C_6D_6 (0.5 mL) prior to collecting ^1H NMR spectra. Conversion was estimated by integration of the olefin proton resonance of cyclooctene (m, 5.69-5.61 ppm) and polycyclooctene (m, 5.51-5.45 ppm).

Table S1. Conversion of cyclooctene to polycyclooctene.

Initiator/Conversion (%)	20 minutes	2 hours
$\text{Mo}(\text{NAr})(\text{CMePh})(\text{Cl})(\text{OHMT})(\text{MeCN})$	>99	>99
$\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{THF})_x$	97	>99

Homocoupling of 1-decene



Homocoupling with $\text{Mo}(\text{NAr})(\text{CMePh})(\text{Cl})(\text{OHMT})(\text{MeCN})$ as the initiator. 1-Decene (118 μL , 0.60 mmol) was added via microsyringe to $\text{Mo}(\text{NAr})(\text{CMePh})(\text{Cl})(\text{OHMT})(\text{MeCN})$ (0.005 g, 0.006 mmol) at 22 °C. The reaction was stirred in an open vial. Aliquots were removed periodically and diluted with 0.5 mL CDCl_3 prior to collecting ^1H NMR spectra. Conversion was estimated by integration of the olefin proton resonance of 1-decene (m, 5.86-5.78) and 9-octadecene (m, 5.39-5.32). The Z/E ratio was estimated by integration of the olefin proton resonance of E-9-octadecene (m, 5.39-5.37) and Z-9-octadecene (m, 5.37-5.32).

Homocoupling with $\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{THF})_x$ as the initiator. $[\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2]_2$ (0.005 g, 0.007 mmol) was dissolved in $\text{THF-}d_8$ (100 μL) prior to adding 1-decene (133 μL , 0.70 mmol) via microsyringe. The reaction was stirred in an open vial. Aliquots were removed periodically and diluted with 0.5 mL CDCl_3 prior to collecting ^1H NMR spectra. Conversion was estimated by integration of the olefin proton resonance of 1-decene (m, 5.86-5.78) and 9-octadecene (m, 5.39-5.32). The Z/E ratio was estimated by integration of the olefin proton resonance of E-9-octadecene (m, 5.39-5.37) and Z-9-octadecene (m, 5.37-5.32).

Table S2. Conversion of 1-decene to 9-octadecene and Z/E ratio of the product.

Initiator/Conversion, %	20 minutes	2 hours	24 hours	Final Z/E
$\text{Mo}(\text{NAr})(\text{CMePh})(\text{Cl})(\text{OHMT})(\text{MeCN})$	86	91	91	37/63
$\text{Mo}(\text{NAr})(\text{CMePh})(\text{OC}_6\text{F}_5)_2(\text{THF})_x$	32	48	>99	23/77

X-Ray Crystallography

General Considerations. Diffraction data were collected on a Bruker-AXS Apex II diffractometer with an Apex II CCD detector using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) from a fine-focus sealed tube source. Data were collected at 100 K by performing 0.5° ω -scans, integrated using SAINT¹, and absorption corrected using SADABS². The structure was solved by direct methods using SHELXT³ and refined against F^2 on all data by full-matrix least squares with SHELXL-2018/3⁴ following established refinement strategies.⁵ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Crystal and data quality details, as well as a summary of the residual refinement values, are listed in the accompanying table.

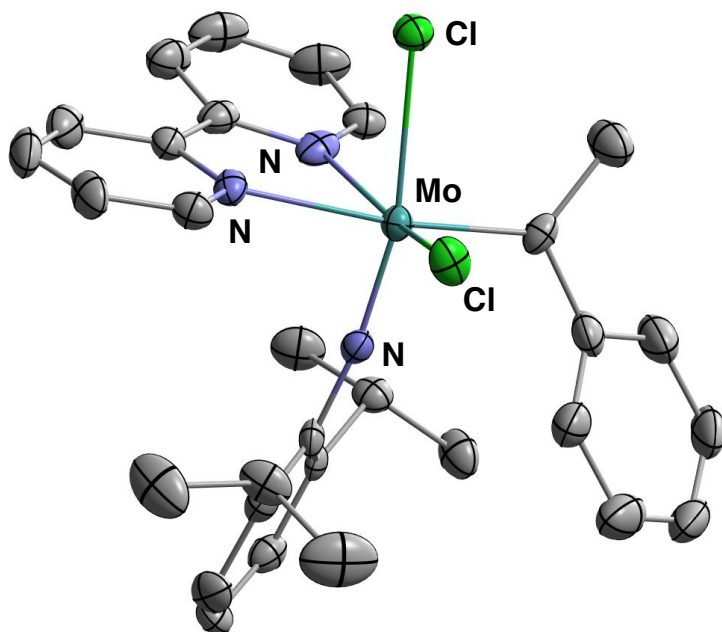


Figure S36. Thermal ellipsoid plot (50%) of Mo(NAr)(CMePh)(Cl)₂(bipy). Unlabeled gray ellipsoids correspond to carbon. Solvent molecules and hydrogen atoms have been omitted for clarity.

Table S3. Crystal data and structure refinement for Mo(NAr)(CMePh)(OMes)₂ (**1**).

Identification code	rrs8jt	
Empirical formula	C ₃₈ H ₄₇ MoNO ₂	
Formula weight	645.70 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	
Unit cell dimensions	$a = 17.3459(4)$ Å	$\alpha = 90^\circ$
	$b = 10.2404(3)$ Å	$\beta = 91.4203(11)^\circ$
	$c = 18.9524(5)$ Å	$\gamma = 90^\circ$
Volume	3365.46(15) Å ³	
Z	4	
Density (calculated)	1.274 mg/m ³	
Absorption coefficient	0.422 mm ⁻¹	
$F(000)$	1360	
Crystal size	0.295 x 0.290 x 0.092 mm ³	
θ range for data collection	2.150 to 30.996°	
Index ranges	$-25 \leq h \leq 25, -14 \leq k \leq 14, -27 \leq l \leq 27$	
Reflections collected	108793	
Independent reflections	10720 [$R_{\text{int}} = 0.0364$]	
Completeness to $\theta = 25.242^\circ$	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10720 / 0 / 390	
Goodness-of-fit on F^2	1.031	
Final R indices [$I > 2\sigma_1$]	$R_1 = 0.0248, wR_2 = 0.0613$	
R indices (all data, 0.69 Å)	$R_1 = 0.0309, wR_2 = 0.0648$	
Largest diff. peak and hole	0.530 and -0.459 e/Å ³	

Table S4. Crystal data and structure refinement for Mo(NAr)(CMePh)(OC₆F₅)₂(MeCN) (2(MeCN)).

Identification code	rrs17jt	
Empirical formula	C ₃₉ H ₄₀ F ₁₀ MoN ₂ O ₂	
Formula weight	854.67 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	$a = 10.2161(3)$ Å	$\alpha = 90^\circ$
	$b = 18.5134(5)$ Å	$\beta = 99.2977(12)^\circ$
	$c = 20.5418(5)$ Å	$\gamma = 90^\circ$
Volume	3834.12(18) Å ³	
Z	4	
Density (calculated)	1.481 mg/m ³	
Absorption coefficient	0.427 mm ⁻¹	
$F(000)$	1744	
Crystal size	0.339 x 0.157 x 0.120 mm ³	
θ range for data collection	2.009 to 27.876°	
Index ranges	$-13 \leq h \leq 13, -24 \leq k \leq 24, -27 \leq l \leq 27$	
Reflections collected	127521	
Independent reflections	9151 [$R_{\text{int}} = 0.0551$]	
Completeness to $\theta = 25.242^\circ$	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9151 / 1660 / 799	
Goodness-of-fit on F^2	1.307	
Final R indices [$I > 2\sigma_1$]	$R_1 = 0.0575, wR_2 = 0.1237$	
R indices (all data, 0.76 Å)	$R_1 = 0.0658, wR_2 = 0.1271$	
Largest diff. peak and hole	0.919 and -1.396 e/Å ³	

Note: Compound rrs17jt crystallizes in the monoclinic centrosymmetric space group P2₁/n with one molecule of rrs17jt and one molecule of pentane per asymmetric unit.

Both perfluorophenoxide ligands as well as the alkylidene ligand and the pentane solvent molecule each exhibited disorder that was modeled over two positions; all disorder ratios were refined freely, and the correlated disorder of the alkylidene ligand and one perfluorophenoxide ligand were refined on the same free variable. All disorders were refined with the help of similarity restraints on 1,2- and 1,3- distances as well as similarity and rigid bond restraints for anisotropic displacement parameters. Flatness restraints were used on two minor-component phenyl rings, isotropic approximation restraints were applied to the anisotropic displacement parameters of two poorly-behaved carbon atoms within the disordered pentane molecule, and the anisotropic displacement parameters of two nearly-overlapping positions of a disordered phenoxide oxygen were constrained to be equivalent.

Table S5. Crystal data and structure refinement for Mo(NAr)(CMePh)(OC₆F₅)₂(bipy) (**2**(bipy)).

Identification code	rrs12jt_sq	
Empirical formula	C ₄₂ H ₃₃ F ₁₀ MoN ₃ O ₂	
Formula weight	897.65 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	$a = 12.6221(4)$ Å	$\alpha = 72.5631(13)^\circ$
	$b = 18.1804(5)$ Å	$\beta = 82.1978(13)^\circ$
	$c = 19.4797(5)$ Å	$\gamma = 74.6797(13)^\circ$
Volume	4105.4(2) Å ³	
Z	4	
Density (calculated)	1.452 mg/m ³	
Absorption coefficient	0.404 mm ⁻¹	
$F(000)$	1816	
Crystal size	0.329 x 0.122 x 0.062 mm ³	
θ range for data collection	1.098 to 29.130°	
Index ranges	$-17 \leq h \leq 17, -24 \leq k \leq 24, -26 \leq l \leq 26$	
Reflections collected	151607	
Independent reflections	22083 [$R_{\text{int}} = 0.0515$]	
Completeness to $\theta = 25.242^\circ$	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22083 / 0 / 1055	
Goodness-of-fit on F^2	1.019	
Final R indices [$I > 2\sigma_1$]	$R1 = 0.0300, wR2 = 0.0678$	
R indices (all data, 0.73 Å)	$R1 = 0.0479, wR2 = 0.0757$	
Largest diff. peak and hole	0.571 and -0.523 e/Å ³	

Table S6. Crystal data and structure refinement for Mo(NAr)(CMePh)(Cl)₂(bipy) (**3**(bipy)).

Identification code	rrs11jt	
Empirical formula	C ₆₇ H ₇₄ Cl ₄ Mo ₂ N ₆	
Formula weight	1297.00 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Fdd2	
Unit cell dimensions	$a = 31.8856(12)$ Å	$\alpha = 90^\circ$
	$b = 37.8599(14)$ Å	$\beta = 90^\circ$
	$c = 10.3398(4)$ Å	$\gamma = 90^\circ$
Volume	12482.1(8) Å ³	
Z	8	
Density (calculated)	1.380 mg/m ³	
Absorption coefficient	0.618 mm ⁻¹	
$F(000)$	5360	
Crystal size	0.335 x 0.028 x 0.020 mm ³	
θ range for data collection	1.670 to 28.278°	
Index ranges	$-42 \leq h \leq 28, -50 \leq k \leq 49, -12 \leq l \leq 13$	
Reflections collected	30976	
Independent reflections	7306 [$R_{\text{int}} = 0.0793$]	
Completeness to $\theta = 25.242^\circ$	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7306 / 325 / 433	
Goodness-of-fit on F^2	1.020	
Final R indices [$I > 2\sigma_1$]	$R_1 = 0.0516, wR_2 = 0.0943$	
R indices (all data, 0.75 Å)	$R_1 = 0.0804, wR_2 = 0.1044$	
Absolute structure parameter	-0.05(3)	
Largest diff. peak and hole	0.692 and -0.758 e/Å ³	

Table S7. Crystal data and structure refinement for Mo(NAr)(CMePh)(Cl)(OHMT)(MeCN) (4(MeCN)).

Identification code	rrs15jt	
Empirical formula	C _{51.50} H ₆₀ ClMoN ₃ O	
Formula weight	868.41 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	$a = 8.8880(2)$ Å	$\alpha = 90^\circ$
	$b = 17.1281(4)$ Å	$\beta = 97.9340(12)^\circ$
	$c = 30.3238(7)$ Å	$\gamma = 90^\circ$
Volume	4572.14(18) Å ³	
Z	4	
Density (calculated)	1.262 mg/m ³	
Absorption coefficient	0.385 mm ⁻¹	
$F(000)$	1828	
Crystal size	0.205 x 0.135 x 0.130 mm ³	
θ range for data collection	1.803 to 29.130°	
Index ranges	$-12 \leq h \leq 12, -23 \leq k \leq 23, -41 \leq l \leq 41$	
Reflections collected	114788	
Independent reflections	12310 [$R_{\text{int}} = 0.0851$]	
Completeness to $\theta = 25.242^\circ$	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12310 / 415 / 603	
Goodness-of-fit on F^2	1.025	
Final R indices [$I > 2\sigma_1$]	$R_1 = 0.0405, wR_2 = 0.0923$	
R indices (all data, 0.73 Å)	$R_1 = 0.0593, wR_2 = 0.1010$	
Largest diff. peak and hole	0.487 and -0.802 e/Å ³	

Table S8. Crystal data and structure refinement for Mo(NAr)(CMePh)(OHMT)(NC₄H₄) (**5**).

Identification code	rrs16jt	
Empirical formula	C ₄₈ H ₅₄ MoN ₂ O	
Formula weight	770.87 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	$a = 9.0923(2)$ Å	$\alpha = 90^\circ$
	$b = 20.8485(6)$ Å	$\beta = 96.8195(13)^\circ$
	$c = 21.7949(6)$ Å	$\gamma = 90^\circ$
Volume	4102.23(19) Å ³	
Z	4	
Density (calculated)	1.248 mg/m ³	
Absorption coefficient	0.357 mm ⁻¹	
$F(000)$	1624	
Crystal size	0.199 x 0.140 x 0.040 mm ³	
θ range for data collection	1.882 to 26.372°	
Index ranges	$-11 \leq h \leq 11, -26 \leq k \leq 26, -27 \leq l \leq 27$	
Reflections collected	53660	
Independent reflections	8406 [$R_{\text{int}} = 0.0830$]	
Completeness to $\theta = 25.242^\circ$	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8406 / 0 / 480	
Goodness-of-fit on F^2	1.022	
Final R indices [$I > 2\sigma_1$]	$R_1 = 0.0375, wR_2 = 0.0785$	
R indices (all data, 0.80 Å)	$R_1 = 0.0594, wR_2 = 0.0880$	
Largest diff. peak and hole	0.458 and -0.423 e/Å ³	

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