Supporting Information

**Origin and Use of Hydroxyl Group Tolerance in Cationic Molybdenum Imido Alkyldene N-Heterocyclic Carbene Catalysts**

*Roman Schowner, Iris Elser, Mathis Benedikter, Mohasin Momin, Wolfgang Frey, Tanja Schneck, Laura Stöhr, and Michael R. Buchmeiser*

anie_201913322_sm_miscellaneous_information.pdf
# Table of Contents

General Information........................................................................................................... 3  
Experimental Procedures................................................................................................... 3  
Synthesis of Organometallic Complexes............................................................................ 4  
NMR Spectra of Organometallic Complexes...................................................................... 12  
NMR Spectra of Organic Compounds............................................................................... 51  
NMR Spectra of Stability Experiments .............................................................................. 57  
Single Crystal X-Ray Analyses ......................................................................................... 74  
High Resolution Mass Spectra (ESI) ................................................................................ 81  
References ......................................................................................................................... 81
General Information

All reactions were performed under the exclusion of air and moisture by standard Schlenk techniques unless noted otherwise. Reactions involving metal complexes were performed in a nitrogen-filled glove box (MBAura Labmaster 130). Glassware was stored at 120 °C overnight and cooled in an evacuated antechamber. 1H and 13C NMR spectra were recorded on a Bruker Avance III 400 spectrometer at 400 and 100 MHz, respectively. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from residual solvent protons (CDCl3: 7.26 ppm, CD2Cl2: 3.32 ppm) as reference.[1] Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, br = broad, m = multiplet), coupling constants (Hz) and integration. Elemental analyses were carried out at the Institute of Inorganic Chemistry, University of Stuttgart, Germany. High-resolution mass spectra were recorded at the Institute of Organic Chemistry, University of Stuttgart, Germany. CHCl3, diethyl ether, toluene and pentane were dried by using an MBAura SPS-800 solvent purification system with alumina drying columns and stored over 4 Å Linde type molecular sieves. THF, benzene and DME were distilled from Na prior to use and stored over 4 Å Linde type molecular sieves and Selexsorb®. Deuterated solvents were filtered over activated alumina and stored over 4 Å Linde type molecular sieves inside the glove box. Reagents prepared according to the literature: 6-hydroxy-1,10-undecadieno,[2] DFTOH,[3] IMes,[4] IMesCl,[5] 1,3,5-trimethylpyrazole (TMP),[5] NaB[Ph][4]+, silver pentafluorobenzoate,[7] LiAl(OC(CF3)2),[8] LiOC(CF3)3,[8] Li2O2C(CF3)3,[9] Li2O2C(CF3)2,[9] prepared by treating the corresponding alcohol or acid with n-BuLi (in hexane) in diethyl ether at -35 °C. TiOCl2(2,6-(CF3)2-C6H4) was prepared by treating the corresponding acid with 1 equiv. Thallium ethoxide in diethyl ether at -35 °C. 2-Allyloxyethanol (98%, Sigma Aldrich), 2-PrOH (99%, Acros), 4-penten-1-ol (99%, Sigma Aldrich), 5-hexen-1-ol (99%, TCI), 7-octene-1-ol (99%, TCI), allyl alcohol (99+, Alfa Aesar), 1,6-hepadiene-4-ol (97%, Acros), 2-exo-norborn-5-enemethanol (98+, Sigma Aldrich), 2-exo-3-exo-norborn-5-enemethanol (97%, Sigma Aldrich), 2-endo-3-exo-norborn-5-enemethanol (98%, Sigma Aldrich), 1-hexene (99%, Acros), allyltrimethylsilane (99%, Acros), dodecan (99%, Acros) and cyclooctane (99%, Sigma Aldrich) were used as received. The following metal complexes were published earlier and prepared according to the literature procedures: Compounds 1,[10] 2c,[10] 4a,[11] 4b,[11] 4c,[12] 5d,[13] 7,[14] 8,[15] 9a,[14] 9b,[15] 9c,[15] 9d,[16] and SF9[17].

Experimental Procedures

General Procedure HM, CM: A catalyst stock solution was prepared (15 mg/mL in CH2Cl2 or 2-PrOH). The appropriate amount of substrate (cat: substrate = 1:4000, approximately 30-80 mg) and internal standard (2-4 drops, dodecan or cyclooctane) were dissolved in the appropriate amount of solvent (3 M solution of substrate in CH2Cl2 or 2-PrOH). A sample for GC-MS was withdrawn. Then, the catalyst solution (15 mg/mL, 1 equiv.) was added and the vials were closed with a cap which was pierced with a cannula for ethylene removal. The reaction mixtures were stirred at room temperature for two hours and were then analyzed via GC-MS.

General Procedure ROMP: The NBE-derivative (200 equiv., approx. 70 mg) was dissolved in 2-PrOH (0.3 mL) and 3 (1 equiv.) was dissolved in 2-PrOH (0.3 mL). The catalyst solution was added to the NBE-derivative solution and the mixture was stirred at room temperature for four hours. Then, the suspension was dropped into n-pentane and the resulting precipitated colorless polymer was separated via centrifuge and dried in vacuo overnight. All polymers were insoluble and were therefore not be subjected to further analysis.

General Procedure ADMET: The monomers M1 and M2 (100 equiv., approx. 40-70 mg) used for the ADMET polymerization were pre-dried and distilled under N2 atmosphere. Catalyst 1 was added (1 equiv.) at room temperature. The ADMET polymerization was carried out at a temperature of 80 °C in bulk for four days. By applying a high vacuum (20 mbar), volatile by-products (ethylene) were removed and the reaction equilibrated directed to the side of the products (polymers). After the indicated time period, the polymerization was terminated by precipitation in methanol. The suspension was centrifuged and decanted. The resulting polymer was dried in vacuo.

Poly(M1): 1H NMR (400 MHz, 100 °C, C2D2Cl4) δ = 5.41 (br s, 2H, CH), 3.55 (br s, 1H, CHOH), 1.99 (br s, 4H, CH2), 1.59 - 1.24 (m, 9H, CH2, OH). 13C NMR (100 MHz, 100 °C, C2D2Cl4) δ = 130.7, 72.0, 37.3, 32.7, 25.8.

Poly(M2): 1H NMR (400 MHz, CDCl3) δ = 7.53 - 7.46 (m, 4H, ArH), 7.45 - 7.30 (m, 6H, ArH), 5.82 - 5.72 (m, 2H, CH), 2.13 - 1.96 (m, 4H, CH2), 1.63 - 0.78 (br s, 8H, CH2). 13C NMR (100 MHz, CDCl3) δ = 138.8, 135.0, 129.3, 127.9, 114.9, 37.8, 26.8, 23.4, 12.3.

General Procedure ROCM: A catalyst stock solution was prepared (15 mg/mL in CHCl3). The appropriate amount of 2-endo,3-endo-norborn-5-ene-2,3-dimethanol (100 equiv., approximately 80 mg), cross partner (1000 equiv.) and internal standard (2-4 drops, dodecan) were dissolved in the appropriate amount of CHCl3 (0.3 M solution of 2-endo, 3-endo-norborn-5-ene-2,3-dimethanol). A sample for GC-MS was withdrawn. Then, the catalyst solution (15 mg/mL, 1 equiv.) was added and the vials were closed with a cap which was pierced with a cannula for ethylene removal. The reaction mixtures were stirred at room temperature for 2 hours and were then analyzed via GC-MS. The solutions were filtered over silica and purified via semi-preparative HPLC (ethyl acetate : heptane 1:10) to afford the pure mono- or di-subststituted products (mixtures of cis and trans).

(3,5-bis[3-(trimethylsilyl)prop-1-en-1-yl]cyclopentane-1,2-diyl)dimethanol: 1H NMR (400 MHz, CDCl3) δ = 5.45 - 5.23 (m, 4H, 3.71 (br s, 4H), 2.67 (m, 2H), 2.44 (br s, 2H), 2.35 (m, 2H), 1.98 (m, 2H), 1.41 (m, 4H), 1.29 (m, 1H), -0.01 (s, 18H). 13C NMR (100 MHz, CDCl3) δ = 130.4, 127.3, 61.9, 48.3, 44.2, 38.4, 23.0, -1.8.
SUPPORTING INFORMATION

(3-(3-trimethylsilyl)prop-1-en-1-yl)-5-vinylcyclopentane-1,2-diyldimethanol: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 5.87 (m, 1H), 5.44 (m, 1H), 5.25 (m, 1H), 3.71 (m, 4H), 2.72 (m, 2H), 2.59 (s, 2H), 2.39 (m, 2H), 2.00 (m, 2H), 1.44-1.29 (m, 4H), -0.01 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 142.3, 131.9, 129.3, 116.9, 63.6, 63.4, 50.1, 49.8, 46.7, 45.8, 39.1, 24.7, -0.01.

(3,5-bis(hex-1-en-1-yl)cyclopentane-1,2-diyldimethanol: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 5.48 - 5.38 (m, 4H), 3.71 - 3.65 (m, 4H), 2.72 - 2.65 (m, 2H), 2.48 (s, 2H), 2.40 - 2.33 (m, 2H), 2.02 - 1.95 (m, 5H), 1.38 - 1.31 (m, 9H), 0.89 (t, $^3$J$_{CH}$ = 7.1 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 131.8, 131.5, 61.8, 48.2, 43.8, 37.6, 32.4, 31.9, 22.4, 14.1.

(3-(hex-1-en-1-yl)-5-vinylcyclopentane-1,2-diyldimethanol: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 5.91 - 5.83 (m, 1H), 5.49 - 5.39 (m, 2H), 5.06 - 4.99 (m, 2H), 3.74 - 3.65 (m, 4H), 2.75 - 2.69 (m, 2H), 2.53 (s, 2H), 2.46 - 2.35 (m, 2H), 2.05 - 1.97 (m, 3H), 1.44 - 1.28 (m, 6H), 0.80 (t, $^3$J$_{CH}$ = 7.1 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 140.5, 131.7, 115.1, 61.7, 61.6, 48.2, 48.0, 44.9, 43.7, 37.0, 32.4, 31.9, 22.4, 14.11, 1.17.

**Synthesis of Organometallic Complexes**

Scheme S1. Synthesis of 3d and 4d from previously not reported precursors.

**[Mo(N(2,6-Pr-C$_6$H$_5$))(CHCMe$_2$Ph)(DFTO)(THF)][B(ArF)$_2$]**, 2a

[Mo(N(2,6-Pr-C$_6$H$_5$))(CHCMe$_2$Ph)(Me$_2$pyr)(THF)][B(ArF)$_2$]$^{10}$ (71.1 mg, 0.0472 mmol, 1 equiv) was dissolved in 3 mL THF and cooled to -35 °C. To the cold solution solid DFTOH (20.1 mg, 0.0472 mmol, 1 equiv) was added as a solid. The red solution turned yellow and was stirred at room temperature for 30 min. All volatiles were removed in vacuo. The dark residue was washed with 5 mL of pentane. The crude product was recrystallized from 2 mL of a 1:1 mixture of diethyl ether and pentane at -35 °C. The product precipitated as a crystalline yellow solid (61 mg, 73%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 13.09 (s, $^3$J$_{CH}$ = 118.4 Hz, 1H, Mo=CH), 7.72 (br m, 8H, $\sigma$-Ar-B(ArF)$_2$), 7.56 (br s, 4H, $\sigma$-Ar-B(ArF)$_2$), 7.45 (br m, 1H, Ar), 7.40 (m, 3H, Ar), 7.31 (m, 2H, Ar), 7.23 (m, 3H, Ar), 7.15 (m, 2H, Ar), 3.62 (m, 4H, THF), 3.48 (m, 4H, THF), 3.09 (m, $^3$J$_{CH}$ = 6.8 Hz, 2H, CH=Pr), 1.82 (m, 8H, THF), 1.76 (s, 6H, C$_5$H$_5$Me$_2$Ph), 1.15 (d, $^3$J$_{CH}$ = 13.2 Hz, 12H, CH$_2$-Pr). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 298.9 (Mo=CH), 162.3 (q, $^1$J$_{CF}$ = 49.8 Hz, $\alpha$-Ar-B(ArF)$_2$), 160.4 ($\alpha$-Ar-DFTO), 151.9 ($\pi$-Ar-imido), 146.9 ($\pi$-Ar-MeC$_6$Ph), 144.9 (m-Or-Imido), 135.4 (br m, $\sigma$-Ar-B(ArF)$_2$), 134.1 ($\pi$-CoF$_3$), 130.9 (Ar-DFTO), 129.9 (Ar-DFTO), 129.4 (q, $^1$J$_{CF}$ = 30.9 Hz, 2.5 Hz, m-Ar-B(ArF)$_2$), 128.7 (Ar-Imido), 125.8 (Ar-MeC$_6$Ph), 125.13 (q, $^1$J$_{CF}$ = 272.4 Hz, CF$_3$-B(ArF)$_2$), 125.08 (Ar-MeC$_6$Ph), 122.3 (Ar-DFTO), 118.0 (m, $^3$J$_{CH}$ = 3.9 Hz, $\alpha$-Ar-B(ArF)$_2$), 80.8 (OCH$_2$-THF), 57.7 (C$_5$H$_5$Me$_2$Ph), 30.3 (MeC$_6$Ph), 28.9 (CH$_2$-Pr), 26.3 (CH$_3$-THF), 24.7 (CH$_2$-Pr), Resonances of fluorinated aromatic carbons were not observed. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ = -62.90 (br s, 24F, B(ArF)$_2$), -134.40 (d, $^2$J$_{FF}$ = 25.2 Hz, 2F, DFTO), -138.92 (d, $^2$J$_{FF}$ = 25.2 Hz, 2F, DFTO), -151.36 (m, 1F, p-F-DFTO), -153.14 (m, 1F, p-F-DFTO), -159.61 (m, 2F, DFTO), -160.78 (m, 2F, DFTO). Elemental analysis (%) calcd. for C$_{30}$H$_{23}$F$_{12}$MnO$_{12}$: C, 52.33; H, 3.29; N, 0.76. Found: C, 52.29; H, 3.41; N, 0.84.

**[Mo(N(2,6-Pr-C$_6$H$_5$))(CHCMe$_2$Ph)(Me$_2$pyr)(TMP)][B(ArF)$_2$]**, 2b

[Mo(N(2,6-Pr-C$_6$H$_5$))(CHCMe$_2$Ph)(Me$_2$pyr)(THF)][B(ArF)$_2$]$^{10}$ (65 mg, 0.0433 mmol, 1 equiv) was dissolved in 3 mL CHCl$_3$. At room temperature, 1,3,5-trimethylpyrazole (24 mg, 0.22 mmol, 5 equiv) was added as a solid and the mixture was stirred for 15 mins. The color changed from dark red to yellow. All volatiles were removed in vacuo and the dark yellow residue was washed with 10 mL pentane to obtain a yellow solid (61 mg, 96%). The product can be recrystallized from diethyl ether/pentane. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 14.08 (br s, 1H, Mo=CH), 7.73 (br m, 8H, $\sigma$-Ar-B(ArF)$_2$), 7.55 (br s, 4H, $\sigma$-Ar-B(ArF)$_2$), 7.38 - 7.28 (m, 5H, Ar), 7.27 - 7.22 (m, 1H, Ar), 7.18 (d, $^3$J$_{CH}$ = 7.7 Hz, 2H, m-Ar-imido), 6.24 (br s, 1H, CH-pyr), 6.19 (br s, 1H, CH-TMP), 5.80 (br s, 1H, CH-pyr), 3.88 -
SUPPORTING INFORMATION

[47x119]A cold (124.7 MHz, ipso-Ar(Me)) solid was filtered off and washed with pentane to yield the product as a yellow solid. Yield: 184 mg, 87%. 

[50x569]SUPPORTING INFORMATION

[47x231]At room temperature solid NaB(Ar[Mo(C2H5)2(p-MeS)]p)suspension. The pentane was removed in vacuo and the oily product was triturated with pentane until a yellow solid formed. Yield: 184 mg, 87%. 

[47x524]C NMR (376 MHz, CDCl3) δ = -62.34 (s, 24F, B(Ar2)2). Elemental analysis (%) calcd. for C35H36B2F32MoN6: C, 53.89; H, 4.04; N, 3.81. Found: C, 53.62; H, 4.17; N, 3.91. HR-MS ESI calcd. for C35H36B2F32MoN6+: 609.2848. Found: 609.2848.

[47x164]It was quickly dissolved in 2 mL CHCl3 and a few drops of acetonitrile. The resulting solution was stirred overnight, and the solvent was removed in vacuo. The residue was triturated with pentane to give a yellow suspension. The pentane was decanted, and the residue dried in vacuo. CHCl3 was added and the resulting suspension was filtered through a pad of celite. The solvent was removed, and the residue was triturated with pentane, yielding the product as a yellow solid. Yield: 85 mg (81%). 

[50x501]3C NMR (101 MHz, CDCl3) δ = 135.2 (s, 1JC = 212.0 Hz, Mo=CH), 7.70 (br m, 8H, o-Ar(B(Ar2))2), 7.51 (br s, 4H, p-Ar(B(Ar2))2), 7.19 (d, 1JC = 8.1 Hz, 1H, m-Ar-Imido), 7.15 (s, 2H, CH=CH-NHC), 7.07 (t, 1JCH = 8.1 Hz, 1H, p-Ar-Imido), 6.99 (br s, 2H, m-Ar-Imido), 6.63 (br s, 2H, m-Ar-Imido), 2.26 (s, 6H, Me-Mes), 2.05 (s, 6H, Me-Mes), 1.96 (br s, 6H, Me-Mes), 0.88 (s, 9H, tBu). 

[47x210]C NMR (376 MHz, CDCl3) δ = -62.46 (s, 24F, B(Ar2)2), -73.63 (s, 3F, OTf). Elemental analysis (%) calcd. for C60H62B2F22MoN6O6S: C, 47.52; H, 3.01; N, 2.56. Found: C, 47.48; H, 3.23; N, 2.73.

[47x164]The mixture was stirred at room temperature for 30 min. Subsequently all solids were filtered off and the filtrate was reduced to dryness. The oily product was dissolved in 1 mL CHCl3 and filtered once more. The CHCl3 was removed in vacuo and the oily product was triturated with pentane until a yellow solid formed. Yield: 184 mg, 87%. 

[47x243]To a solution of [Mo(N-2,6-Cl2-C6H4)(CHCMe3)(Mes)(OTf)]2(B(Ar2))2 3a a solution of [Mo(N-2,6-Cl2-C6H4)(CHCMe3)(Mes)(OTf)]2(B(Ar2))2 3a (100 mg, 0.061 mmol, 1 equiv.) in 2 mL CHCl3 was quickly added to a solution of LiOC(F3)2 (14.7 mg, 0.061 mmol, 1 equiv.) in 2 mL of CHCl3 and a few drops of acetonitrile. The resulting solution was stirred overnight, and the solvent was removed in vacuo. The residue was triturated with pentane to give a yellow suspension. The pentane was decanted, and the residue dried in vacuo. CHCl3 was added and the resulting suspension was filtered through a pad of celite. The solvent was removed, and the residue was triturated with pentane, yielding the product as a yellow solid. Yield: 85 mg (81%). 

[50x501]1H NMR (400 MHz, CDCl3) δ = 135.2 (s, 1JC = 120.2 Hz, Mo=CH), 7.70 (br m, 8H, o-Ar(B(Ar2))2), 7.51 (br s, 4H, p-Ar(B(Ar2))2), 7.19 (d, 1JC = 8.1 Hz, 1H, m-Ar-Imido), 7.15 (s, 2H, CH=CH-NHC), 7.07 (t, 1JCH = 8.1 Hz, 1H, p-Ar-Imido), 6.99 (br s, 2H, m-Ar-Imido), 6.63 (br s, 2H, m-Ar-Imido), 2.26 (s, 6H, Me-Mes), 2.05 (s, 6H, Me-Mes), 1.96 (br s, 6H, Me-Mes), 0.88 (s, 9H, tBu). 

[47x210]C NMR (376 MHz, CDCl3) δ = -62.46 (s, 24F, B(Ar2)2), -73.63 (s, 3F, OTf). Elemental analysis (%) calcd. for C60H62B2F22MoN6O6S: C, 47.52; H, 3.01; N, 2.56. Found: C, 47.48; H, 3.23; N, 2.73.

[47x119]A cold (-35 °C) solution of iMesCl2 (261 mg, 0.70 mmol) in 8 mL of toluene was added to a cold (-35 °C) solution of Mo(N-2,6-Cl2-C6H4)(CHCMe3)(DME)(OTf)2 (500 mg, 0.70 mmol, 1 equiv.) in 25 mL of toluene. The mixture was stirred at room temperature for four hours during which time a yellow solid precipitated. The suspension was filtered and the solid was washed with 2 mL of toluene and 2 mL of pentane to yield the product as a yellow solid. Yield: 455 mg (65%). 

[47x501]1H NMR (400 MHz, CDCl3) δ = -12.95 (s, 1JC = 120.0 Hz, Mo=CH), 7.27 (br m, 1H, p-Ar-Imido), 7.14 (br m, 2H, m-Ar-Imido), 7.01 (br s, 2H, m-Ar-Imido), 6.73 (br s, 2H, m-Ar-Imido), 2.24 (br s, 6H, Mes), 2.11 (br s, 6H, Mes), 2.09 (br s, 6H, Mes), 1.14 (s, 9H, tBu). 

[47x145]C NMR (101 MHz, CDCl3) δ = 329.5.
SUPPORTING INFORMATION

[Equations and text from the document]
Supporting Information

Mo(N(2,6-$t$-F-C$_6$H$_4$)C$_5$(DMED) 4d-p1 (0.131 g, 0.25 mmol, 1 equiv.) was dissolved in 15 mL THF and cooled to -30 °C. Neopentylmagnesium chloride (1.21 M in diethyl ether, 0.4 mL, 0.50 mmol, 2 equiv.) was added dropwise to the stirring solution. The reaction mixture was stirred overnight at room temperature and filtered through celite. The solvent was removed in vacuo and the yellow-orange solid was recrystalized from pentane (0.14 g, 92% yield). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ = 7.38 (m, 4H, o-Ar-CMePh), 7.22 (m, 4H, m-Ar-CMePh), 7.08 (m, 2H, p-Ar-CMePh), 6.97 (m, 2H, p-Ar-Imido), 6.82 (m, 4H, m-Ar-Imido), 1.97 (s, 4H, Ch$_2$), 1.40 (s, 12H, Me). $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$): $\delta$ = 156.6 (d, $^1$JC$_{CF}$ = 252.1 Hz, o-Ar-Imido), 151.2 (ipso-Ar-CMePh), 135.2 (m, ipso-Ar-Imido), 128.7 (Ar-CMePh), 126.3 (Ar-CMePh), 126.3 (Ar-Imido), 111.4 (m, Ar-Imido), 83.4 (CH$_3$), 41.2 (CMePh), 32.2 (CMe$_2$). $^{33}$F NMR (376 MHz, CD$_2$Cl$_2$): $\delta$ = -119.52 (m, 4F, Imido). Elemental analysis (%): C, 62.34; H, 5.23; N, 4.54. Found: C, 62.37; H, 5.39; N, 4.44.

Mo(N(2,6-$t$-F-C$_6$H$_4$)C$_5$(H)Mo=CH)(OTf)$_2$ (4d-p3) (0.080 g, 0.11 mmol, 1 equiv.) was dissolved in 5 mL benzene and a solution of 1.3-bis{[2,4,6-trimethoxyphenyl]imidazol-2-ylidene}(0.052 mmol, 1 equiv.) was added dropwise. The reaction mixture was stirred for 3 h at room temperature. The solvent was removed in vacuo. The yellow solid was recrystalized from a mixture of dichloromethane and pentane to yield a yellow crystalline solid (0.070 g, 67% yield). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ = 13.12 (s, $^1$JC$_{CH}$ = 123.4 Hz, 1H, Mo=CH), 7.26 (m, 3H, Ar), 7.22 (m, 1H, Ar), 7.13 (s, 2H, CH=CH-NHC), 7.20 (m, 2H, Ar), 6.83 (m, 2H, Ar), 6.73 (br s, 2H, m-Ar-Mes), 6.63 (br s, 2H, m-Ar-Mes), 2.15 (s, 6H, Me-Mes), 2.03 (s, 6H, Me-Mes), 2.00 (s, 6H, Me-Mes), 1.71 (s, 3H, CMe$_2$), 1.69 (s, 3H, CMe$_2$). $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$): $\delta$ = 320.4 (Mo=CH), 184.0 (NCN-NHC), 160.2 (d, $^1$JC$_{CF}$ = 258.8 Hz, o-Ar-Imido), 148.1 (ipso-Ar-CMePh), 141.0 (ipso-Ar-CMePh), 136.0 (Ar-Mes), 135.3 (Ar-Mes), 135.1 (Ar-Mes), 134.0 (m, Ar-Imido), 131.2 (m, Ar-Mes), 129.7 (m, Ar-Imido), 128.8 (Ar-CMePh), 127.0 (Ar-CMePh), 125.98 (CH=CH-NHC), 125.96 (Ar-CMePh), 119.5 (q, $^1$JC$_{CF}$ = 318.8 Hz, OTf), 111.8 (dd, $^1$JC$_{CF}$ = 19.9, 3.1 Hz, m-Ar-Imido), 56.5 (CMe$_2$), 35.1 (CMe$_2$), 27.9 (CMe$_2$), 21.4 (p-Me-Mes), 18.49 (o-Me-Mes), 18.44 (o-Me-Mes). $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$): $\delta$ = -75.77 (br s, 3F, OTf), -77.02 (br s, 3F, OTf), -109.53 (br s, 2F, Imido). Elemental analysis (%): calcd for C$_{58}$H$_{63}$FeMoN$_{10}$O$_{12}$S: C, 48.91; H, 4.10; N, 4.39. Found: C, 48.65; H, 4.21; N, 4.41.

Mo(N(2,6-$t$-F-C$_6$H$_4$)C$_5$(H)Mo=CH)(Mes)(CF$_3$)(OTf)(MeCN) (4d-p4) (0.050 g, 0.052 mmol, 1 equiv.) was dissolved in 4 mL dichloromethane and cooled to -30 °C for about 30 min. Then Ag(CH$_3$CN)$_2$B(Ar$^+$)$_2$ (0.057 mg, 0.052 mmol, 1 equiv.) was added in small portions as a solid and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was filtered through a pad of celite and CH$_2$Cl$_2$ was removed in vacuo. The residue was evaporation to give a yellow solid. The product was recrystalized from a mixture of CH$_2$Cl$_2$/Et$_2$O (pentane) to yield a yellow solid (0.080 g, 89% yield). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ = 13.26 (s, $^1$JC$_{CH}$ = 124.0 Hz, 1H, Mo=CH), 7.73 (br m, 8H, o-Ar-B(Ar$^+$)$_2$), 7.56 (br s, 4H, p-Ar-B(Ar$^+$)$_2$), 7.33 (s, 2H, CH=CH-NHC), 7.30 (m, 1H, Ar), 7.22 (m, 2H, Ar), 7.15 (m, 1H, Ar), 7.07 (m, 2H, Ar), 6.95 (s, 2H, m-Ar-Mes), 6.88 (br s, 2H, Ar), 6.70 – 6.35 (br s, 2H, m-Ar-Mes), 2.22 (s, 6H, Me-Mes), 2.05 (s, 12H, Me-Mes), 1.87 (s, 3H, Me), 1.78 (s, 3H, Me), 1.10 (s, 3H, CH$_3$). $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$): $\delta$ = 328.6 (Mo=CH), 182.8 (NCN-NHC), 162.1 (q, $^1$JC$_{CF}$ = 50.0 Hz, o-Ar-B(Ar$^+$)$_2$), 144.2 (ipso-Ar-CMePh), 141.5 (ipso-Ar-Mes), 135.9 (Ar-Mes), 135.2 (br m, o-Ar-B(Ar$^+$)$_2$), 134.8 (Ar-Mes), 134.4 (Ar-Mes), 132.7 (m, Ar-Imido), 130.6 (m, Ar-Imido), 130.1 (Ar-Imido), 129.8 (br, Ar-Imido), 129.2 (q, $^1$JC$_{CF}$ = 31.2 Hz, $^1$JC$_{CH}$ = 2.9 Hz, m-Ar-B(Ar$^+$)$_2$), 129.0 (Ar-CMePh), 127.5 (Ar-CMePh), 126.4 (CH=CH-NHC), 125.8 (Ar-CMePh), 125.8 (Ar-CMePh), 119.5 (q, $^1$JC$_{CF}$ = 272.4 Hz, CF$_3$-B(Ar$^+$)_2), 119.5 (q, $^1$JC$_{CF}$ = 318.5 Hz, OTf), 117.9 (sept, $^1$JC$_{CF}$ = 3.6 Hz, p-Ar-B(Ar$^+$)$_2$), 112.3 (dd, $^1$JC$_{CF}$ = 19.5, 3.1 Hz, Ar-Imido), 56.5 (CMe$_2$), 28.5 (CMe$_2$), 27.8 (CMe$_2$), 21.3 (p-Me-Mes), 18.1 (o-Me-Mes), 3.0 (MeCN). $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$): $\delta$ = -82.76 (s, 24F, B(Ar$^+$)$_2$), -76.28 (s, 3F, OTf), -111.14 (br s, 2F, Imido). Elemental analysis (%): calcd for C$_{58}$H$_{63}$FeMoN$_{10}$O$_{12}$S: C, 50.48; H, 3.18; N, 3.27. Found: C, 50.52; H, 3.23; N, 3.32.
Mo(N(2,6-Me₂-C₆H₃)CHMePh)(Imes)[OTf]⁺[3] (70.7 mg, 0.0744 mmol, 1 equiv) was dissolved in 5 mL CH₂Cl₂. At room temperature solid NaB(ArF)₃ (66 mg, 0.0744 mmol, 1 equiv) was added. The mixture was stirred for 30 min. Subsequently all solids were filtered off over celite and the filtrate was reduced to dryness. The oily product was dissolved in 1 mL CH₂Cl₂ and filtered once more. The CH₂Cl₂ was removed in vacuo and the oily product was triturated with pentane until a yellow solid formed. Yield: 103 mg, 83%. ²H NMR (400 MHz, CDCl₃) δ = 13.03 (s, 1H, ¹JC = 120.7 Hz, Mo=CH), 7.70 (br m, 8H, o-Ar-B(ArF)₃), 7.51 (br s, 4H, p-Ar-B(ArF)₃), 7.34 (s, 2H, CH=CH=CH=H), 7.07 (m, 3H, Ar), 7.00 (m, 2H, Ar), 6.95 (m, 2H, Ar), 6.87 (br s, 2H, Ar-Mes), 6.78 (m, 3H, Ar), 2.31 (s, 6H, Me-Mes), 2.08 (br s, 3H, Me-Imido), 1.85 (br s, 9H, Me-Mes overlapping with Me-Imido). 1.10 (s, 3H, CMe₃), 0.98 (s, 3H, CMe₃Ph). ¹³C NMR (101 MHz, CDCl₃) δ = 321.5 (Mo=CH), 179.9 (NNC-NHC), 161.9 (q, ¹JC = 50.0 Hz, ipso-Ar-B(ArF)₃), 154.3 (ipso-Ar-Imido), 145.5 (ipso-Ar-CMePh), 142.4 (ipso-Ar-Mes), 135.4 (Ar-Mes), 135.3 (Br-Mes), 135.0 (m-Ar-Mes), 129.1 (q, ¹JC = 31.1 Hz, ipso-Ar-B(ArF)₃), 128.3 (Ar-CMePh), 128.2 (br, Ar-Imido), 127.2 (Ar-CMePh), 126.3 (CH=CH-NHC), 126.2 (Ar-CMePh), 124.5 (q, ¹JC = 272.4 Hz, CF₃-B(ArF)₃), 119.9 (q, ¹JC = 320.0 Hz, OTf), 117.6 (sept, ¹JC = 3.6 Hz, p-Br-Ar(BF₄)₂). 58.1 (CMe₃Ph), 30.5 (CMe₃Ph), 26.2 (CMe₃Ph), 21.1 (p-Me-Mes), 19.5 (Me-Imido), 17.9 (p-Me-Mes), 17.4 (o-Me-Mes). ¹⁹F NMR (376 MHz, CDCl₃) δ = -62.42 (s, 24F, B(ArF)₃), -73.22 (s, 3F, OTf). Elemental analysis (%) calcld. for CsH₁₇BF₃MeN₃O₇S: C, 51.97; H, 3.45; N, 2.53. Found: C, 51.94; H, 3.68; N, 2.46.

SUPPORTING INFORMATION

|[Mo(N(2,6-Me₂-C₆H₃)CHMePh)(Imes)[OC(F)CF₃]][B(ArF)₃], 5b|[Mo(N(2,6-Me₂-C₆H₃)CHMePh)(Imes)[OTf]][B(ArF)₃], 5a|[Mo(N(2,6-Me₂-C₆H₃)CHMePh)(Imes)[Cl]][B(ArF)₃], 6b|[Mo(N(2,6-Me₂-C₆H₃)CH₂OCH₂CH₂OH)(Imes)[OTf]][B(ArF)₃], 6a|
|17C NMR (101 MHz, CDCl₃) δ = 305 mg. | Yield: 77% (305 mg). | Yield: 400 MHz, CDCl₃ δ = 12.69 (s, 1H, Mo=CH), 7.72 (br m, 8H, o-Br-Ar(BF₄)₂), 7.56 (br s, 4H, p-Br-Ar(BF₄)₂), 7.47 (s, 2H, CH=CH-NHC), 7.12 (t, ¹JC = 7.6 Hz, 1H, p-Br-Ar), 7.09 (s, 2H, m-Ar-Mes), 7.03 - 6.98 (m, 4H, Ar-CMePh), 6.95 (d, ¹JC = 7.6 Hz, 2H, m-Ar-Mes), 6.85 (br m, 3H, overlapping signals of p-Br-Ar-CMePh and m-Ar-Mes), 2.33 (s, 6H, Me-Mes), 2.07 (s, 6H, Me-Mes), 1.91 (s, 6H, Me-Mes), 1.91 (br s, 6H, Me-Imido), 1.24 (s, 3H, CMe₃Ph), 0.95 (s, 3H, CMe₃Ph). ¹³C NMR (101 MHz, CDCl₃) δ = 315.6 (Mo=CH), 180.0 (NNC-NHC), 162.3 (q, ¹JC = 50.1 Hz, ipso-Ar-B(ArF)₃), 156.1 (ipso-Ar-Imido), 145.6 (ipso-Ar-CMePh), 142.5 (ipso-Ar-Mes), 135.5 (Ar-Mes), 134.5 (m-Ar-Mes), 134.2 (Ar-Mes), 131.2 (p-Ar-B(ArF)₃), 129.4 (q, ¹JC = 31.2 Hz, Ar-Me-B(ArF)₃), 128.7 (Ar-Imido), 128.6 (Ar-CMePh), 127.5 (Ar-CMePh), 127.2 (Ar-CMePh), 126.3 (CH=CH-NHC), 125.2 (q, ¹JC = 272.5 Hz, CF₃-B(ArF)₃), 121.1 (q, ¹JC = 292.9 Hz, OC(F)CF₃), 118.0 (br m, p-Ar-B(ArF)₃), 84.7 (m, O(CF)₃), 57.4 (CMe₃Ph), 31.3 (CMe₃Ph), 27.9 (CMe₃Ph), 21.3 (p-Me-Mes), 19.7 (Me-Imido), 18.1 (o-Me-Mes). ¹⁹F NMR (367 MHz, CDCl₃) δ = -62.69 (s, 24F, B(ArF)₃), -73.3 (s, 9F, OC(F)CF₃). Elemental analysis (%) calcld. for CsH₁₇BF₃MeN₃O₇S: C, 51.48; H, 3.28; N, 2.40. Found: C, 51.48; H, 3.57; N, 2.71.

Mo(N(2,6-Me₂-C₆H₃)CHMePh)(Imes)[OTf](CF₃CO₂O), 10

Mo(N(2,6-Me₂-C₆H₃)CHMePh)(Imes)[OTf][Cl] (111 mg, 0.123 mmol, 1 equiv) was dissolved in 5 mL CH₂Cl₂ and cooled to -35 °C. To the cold solution solid silver pentfluoroazobenzene (40 mg, 0.123 mmol, 1 equiv) was added. The mixture was stirred for one hour in the dark. All solids were filtered off and the filtrate was reduced to dryness. The oily residue was redissolved in 1 mL CH₂Cl₂ and filtered once more. All volatiles were removed in vacuo. The residue was triturated with 5 mL pentane until a pale yellow solid precipitated. Yield: 82 mg, 69%. ¹⁹F NMR (400 MHz, CDCl₃) δ = 13.59 (s, ¹JC = 123.11 Hz, 1H, Mo=CH), 7.18 (m, 2H, Ar-CMePh), 7.15 - 7.00 (m, 7H, overlapping ArH), 6.82 (br s, 2H, m-Ar-Mes), 2.35 (s, 6H, Me-Mes), 2.18 (br s, 6H, Me-Mes), 1.89 (br s, 6H, Me-Mes), 1.66 (s, 3H, CMe₃Ph), 1.64 (s, 3H, CMe₃Ph), 1.10 (s, 9H, tBu). ¹³C NMR (101 MHz, CDCl₃) δ = 317.2 (Mo=CH), 188.4 (NNC-NHC), 174.4 (CO₂Carboxylate), 149.4 (ipso-Ar-CMePh), 140.0 (ipso-Ar-Mes), 130.0 (br, m-Ar-Mes), 129.5 (br, m-Ar-Mes), 128.2 (CH=CH-NHC), 128.1 (CH=CH-NHC).
The suspension was stirred for 30 min.

Subsequently all solvents were filtered off and the filtrate was reduced to dryness. The oily product was dissolved in 1 mL CHCl₃ and filtered once more. The CHCl₃ was removed in vacuo and the dark oil (pure by NMR) was triturated with pentane until a pale yellow solid formed. Yield: 86 mg, 93%. 

**¹H NMR** (400 MHz, CDCl₃) δ = 13.06 (s, 2JCH = 118.55 Hz, 1H, MeOH), 7.71 (br m, 7H, o-Ar(2)H₃), 7.51 (br s, 4H, p-Ar(6)H₃), 7.25 (m, 5H, overlapping resonances of Ph, solvent and CH=CH-NHC), 7.12 (m, 2H, Ar-C=C=Ph), 7.06 (br s, 2H, m-Ar-Ph), 6.86 (br s, 2H, m-Ar-Ph), 2.28 (s, 6H, Me-Ph), 2.11 (s, 6H, Me-Ph), 1.90 (s, 6H, Me-Ph), 1.45 (s, 3H, CMe₃), 1.40 (s, 3H, CMe₃), 0.87 (N-Bu). 

**¹C NMR** (101 MHz, CDCl₃) δ = 315.4 (Mo=CH), 182.2 (NCC-HNC), 180.0 (CO-carboxylate), 162.1 (q, 2JCH = 49.8 Hz, ipso-Ar(2)H₃), 148.5 (ipso-Ar-C=C=Ph), 146.9 (br m, carboxylate), 145.8 (br m, carboxylate), 144.3 (br m, carboxylate), 141.9 (ipso-Ar-Ph), 139.5 (br m, carboxylate), 136.9 (br m, carboxylate), 135.5 (Ar-Ph), 135.0 (br m, o-Ar(2)H₃), 134.8 (Ar-Ph), 134.5 (Ar-Ph), 130.7 (m-Ar-Ph), 130.5 (m-Ar-Ph), 129.0 (q, 2JCH = 31.5 Hz, 3JCH = 2.7 Hz, m-Ar(6)H₃), 128.7 (Ar-C=C=Ph), 127.2 (p-Ar(2)H₃), 126.3 (CH=CH-NHC), 126.01 (Ar-C=C=Ph), 124.7 (q, 2JCH = 272.5 Hz, CF₂-Ar(4)H₃), 117.6 (sept, 6JCH = 3.8 Hz, p-b-Br(5)H₂), 105.9 (br m, carboxylate), 79.1 (N(1)-Me), 55.3 (CMe₃), 32.5 (CMe₃), 30.0 (N-Me), 29.5 (CMe₂), 21.1 (p-Me-Ph), 17.7 (o-Me-Ph). 

**¹F NMR** (376 MHz, CDCl₃) δ = -62.46 (s, 24F, Br₂Ar₂), -134.69 (m, 2F, C=Fs), -141.37 (m, 1F, C=Fs), -158.72 (m, 2F, C=Fs). 

**Elemental analysis** (% calcd. for C₇₀H₅₁Br₂F₁₀Mo₃N₇O₁₆S: C, 53.58; H, 4.71; N, 4.36. Found: C, 53.52; H, 4.71; N, 4.48.

---

**SUPPORTING INFORMATION**

[S9](image)
was triturated with pentane to yield a yellow solid. The pentane was decanted and the solid was dried in vacuo. The compound was recrystallized from a mixture of CH₂Cl₂ diethyl ether and pentane to yield the product as yellow crystals. Yield: 71 mg (57%). ¹H NMR (400 MHz, CDCl₃) δ = 12.75 (s, 1JCH = 118.9 Hz, 1H, CH=CH), 7.70 (br m, 8H, o-Br-B(ArF₃)), 7.50 (br m, 4H, p-Br-B(ArF₃)), 7.34 (s, 2H, CH=CH-NHC), 7.23 (m, 2H, m-Br-Imido), 7.15 (m, 2H, m-Br-Imido), 6.91 (br s, 2H, m-Br-Mes), 6.81 (br s, 2H, m-Br-Mes), 2.17 (s, 6H, Me-Mes), 2.08 (s, 6H, Me-Mes), 2.00 (s, 6H, Me-Mes), 1.14 (s, 9H, tBu). ¹³C NMR (101 MHz, CDCl₃) δ = 321.2 (Mo=CH), 183.7 (NCN-NHC), 180.0 (CO₂), 161.9 (q, 1JCF = 49.8 Hz, ipso-B(ArF₃)), 148.8 (ipso-B(ArImido), 148.7 (br m, carboxylate), 146.0 (br m, carboxylate), 141.5 (ipso-B(ArF₃)), 139.5 (br m, carboxylate), 136.9 (br m, carboxylate), 135.7 (Ar-Mes), 134.9 (br m, o-Br-B(ArF₃)), 134.4 (Ar-Mes), 134.2 (Ar-Mes), 130.6 (Ar-Imido), 130.4 (m-Br-Mes), 129.9 (m-Br-Mes), 129.0 (q, 1JCF = 31.5 Hz, 1JCH = 2.7 Hz, m-Br-B(ArF₃)), 128.3 (Ar-Imido), 125.6 (CH=CH-NHC), 124.7 (q, 1JCF = 272.5 Hz, CF₂-B(ArF₃)), 117.6 (sept, 1JCH = 3.8 Hz, p-Br-B(ArF₃)), 105.1 (br m, carboxylate), 50.3 (CMes), 30.6 (CMes), 21.2 (p-Mes), 18.1 (m-Mes), 17.9 (o-Mes-Mes). ¹⁹F NMR (376 MHz, CDCl₃) δ = -62.45 (s, 24F, B(ArF₃)), -134.52 (m, 2F, CsF), -140.55 (m, 1F, p-CsF), -158.35 (m, 2F, CsF). **Elemental analysis (%)** calcd. for C₂₁H₂₅Cl₂F₂₀Mo₅Oₑ₆C: 50.02; H: 2.90; N: 2.46. Found: C: 50.08; H: 2.97; N: 2.48.

[SUPPORTING INFORMATION]
SUPPORTING INFORMATION

59.22 (s, 6F; ArCF_3), -75.48 (s, 36F; OC(CF_3)_3).

**Elemental analysis (%) calcd. for C_{66}H_{56}AlF_{42}MoN_3O_6: C, 41.55; H, 2.96; N, 2.20.**

**Found: C, 41.56; H, 2.97; N, 2.34.**

\[
\text{Mo(N-Ad)(CHCMe}_2\text{Ph)(5-iPr)(Cl)}^{19}\text{)}\rightleftharpoons [19] (58 \text{ mg, 0.096 mmol, 1 equiv) was dissolved in 3 mL CH}_2\text{Cl}_2\text{ and cooled to -35 °C. To this solution solid LiAl(OC(CF}_3)_3\text{)4 (93.6 mg, 0.096 mmol, 1 equiv) was added and the solution was stirred for 15 min at room temperature. All solids were filtered off and solid Tl(2,6-(CF}_3\text{-C}_6\text{H}_3\text{CO}_2\text{) (47 mg, 0.1 mmol, 1.05 equiv) was added to the filtrate. The mixture was stirred under the exclusion of light for one hour. Subsequently the reaction mixture was filtered and reduced to dryness. The residue was triturated with \text{n-pentane until a pale yellow solid precipitated. The product can be recrystallized from chloroform. Yield: 142 mg, 84%.)}
\]

**1H NMR** (400 MHz, CDCl_3) \(\delta = 13.80 \text{ (s, } J_{CH} = 116.4 \text{ Hz, } 1\text{H, Mo=CH)}, 8.05 \text{ (d, } J_{HH} = 8.0 \text{ Hz, } 2\text{H, } m\text{-Ar}), 7.89 \text{ (t, } J_{HH} = 8.0 \text{ Hz, } 1\text{H, } p\text{-Ar}), 7.41 \text{ (s, } 2\text{H, Ar}), 7.30 \text{ (m, } 1\text{H, Ar}), 7.28 \text{ (s, } 2\text{H, Ar}), 4.21 \text{ (sept, } J_{HH} = 6.6 \text{ Hz, } 2\text{H, } CH\text{-iPr}), 2.14 \text{ (br m, } 9\text{H, Ad}), 2.09 \text{ (s, } 3\text{H, CMeoPh)}, 1.70 \text{ (br m, } 6\text{H, Ad}), 1.67 \text{ (s, } 3\text{H, CMeoPh)}, 1.33 \text{ (d, } J_{HH} = 6.6 \text{ Hz, } 6\text{H, } C\text{-iPr}), 1.27 \text{ (d, } J_{HH} = 6.6 \text{ Hz, } 6\text{H, } C\text{-iPr})

**13C NMR** (101 MHz, CDCl_3) \(\delta = 308.7 \text{ (Mo=CH), 188.5 (NCN-NHC), 175.5 (CO}_2\text{), 146.0 (ipso-CMe}_2\text{Ph), 132.7 (p-Ar-carboxylate), 131.0 (q, } J_{CF} = 4.1 \text{ Hz, } m\text{-Ar-carboxylate), 129.7 (Ar-CMe}_2\text{Ph), 128.8 (q, } J_{CF} = 32.8 \text{ Hz, o-Ar-carboxylate), 128.0 (Ar-CMe}_2\text{Ph), 126.2 (Ar-CMe}_2\text{Ph), 123.5 (q, } J_{CF} = 274.4 \text{ Hz, } C\text{-f-carboxylate), 121.8 (q, } J_{CF} = 292.4 \text{ Hz, } OC(CF}_3\text{)), 120.6 (CH=CH-NHC), 80.1 (N-Ad), 55.1 (CH-iPr), 54.6 (CMe}_2\text{Ph), 44.7 (CH=Ad), 35.8 (CH=Ad), 31.9 (CH-Ad), 30.0 (CMe}_2\text{Ph), 29.6 (CMe}_2\text{Ph), 23.9 (CH=Ad), 23.7 (CH=Ad), 19\text{F NMR} (376 MHz, CDCl_3) \delta = -59.53 \text{ (s, } 6\text{F, CF}_3\text{-carboxylate), -75.75 \text{ (s, } 36\text{F, } OC(CF}_3\text{)).}

**Elemental analysis (%) calcd. for C_{54}H_{46}AlF_{42}MoN_3O_6 \times CHCl_3: C, 35.25; H, 2.58; N, 2.24.**

**Found: C, 35.17; H, 2.56; N, 2.35.**
**Figure S1.** $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 2a.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ = 13.09, 7.72, 7.56, 7.40, 7.40, 7.31, 7.23, 7.15, 3.62, 3.48, 3.10, 1.82, 1.76, 1.15.

**Figure S2.** $^{19}$F NMR (375 MHz, 25 °C, CD$_2$Cl$_2$) of 2a.

$^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ = -62.90, -138.40, -138.92, -151.36, -153.14, -159.61, -160.78.

NMR Spectra of Organometallic Complexes
Figure S3. $^{13}$C NMR (100 MHz, 25 °C, CD$_2$Cl$_2$) of 2a.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 14.08, 7.73, 7.55, 7.31, 7.24, 7.19, 7.17, 6.24, 6.19, 5.96, 3.73, 2.96, 2.55, 1.75, 1.59, 1.20.

Figure S4. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 2b.
Figure S5. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of 2b.

Figure S6. $^{13}$C NMR (100 MHz, 25 °C, CDCl$_3$) of 2b.
Figure S7. Variable temperature $^1$H NMR (400 MHz, CDCl$_3$) of 2b, alkylidene and aromatic region.

Figure S8. Variable temperature $^1$H NMR (400 MHz, CDCl$_3$) of 2b, expansion.
**Figure S9.** $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 3a.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 12.59, 7.72, 7.52, 7.39, 7.27, 7.26, 7.25, 7.21, 7.17, 6.97, 6.82, 2.20, 2.02, 1.08.

**Figure S10.** $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of 3a.

$^{19}$F NMR (375 MHz, CDCl$_3$) δ = -62.41, -73.72.
**Figure S11.** $^{13}$C NMR (100 MHz, 25 °C, CDCl$_3$) of 3a.

$^{1}$H NMR (400 MHz, CDCl$_3$) δ = 13.52, 7.70, 7.52, 7.19, 7.15, 7.07, 6.99, 6.63, 2.26, 2.05, 1.99, 1.96, 0.88.

**Figure S12.** $^{1}$H NMR (400 MHz, 25 °C, CDCl$_3$) of 3b.
Figure S13. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of 3b.

Figure S14. $^{13}$C NMR (100 MHz, 25 °C, CDCl$_3$) of 3b.
Figure S15. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 3c.

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 336.5, 207.0, 161.8, 168.6, 140.5, 136.3, 135.8, 134.9, 131.5, 131.1, 129.8, 128.3, 117.7, 52.6, 51.4, 29.7, 20.9, 18.5, 18.3.

Figure S16. $^{13}$C NMR (100 MHz, 25 °C, CDCl$_3$) of 3c.
Figure S17. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of 3c.

Figure S18. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 3d-p1.
$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ = 329.5, 165.5, 149.6, 142.0, 136.9, 156.6, 132.7, 131.0, 130.6, 129.5, 128.3, 127.9, 122.1, 119.7, 50.7, 31.3, 21.4, 18.9, 18.8.

Figure S19. $^{13}$C NMR (100 MHz, 25 °C, CD$_2$Cl$_2$) of 3d-p1.

$^{19}$F NMR (375 MHz, CD$_2$Cl$_2$) δ = -75.05, -76.58.

Figure S20. $^{19}$F NMR (375 MHz, 25 °C, CD$_2$Cl$_2$) of 3d-p1.
Figure S21. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 3d.

$^1$C NMR (101 MHz, CDCl$_3$) δ = 33.4, 181.4, 161.9, 149.5, 143.2, 136.2, 135.0, 132.2, 131.1, 131.0, 130.2, 129.1, 128.6, 122.9, 120.6, 117.5, 52.2, 30.1, 21.2, 18.3, 17.9.

Figure S22. $^{13}$C NMR (100 MHz, 25 °C, CDCl$_3$) of 3d.
Figure S23. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of 3d.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta = 13.28, 7.72, 7.52, 7.49, 7.43, 7.32, 7.23, 7.14, 7.04, 6.97, 6.66, 2.23, 2.08, 1.92, 1.80, 1.79, 1.01.$

Figure S24. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 4c.
$^{13}$C NMR (100 MHz, CDCl$_3$) δ = 308.0, 182.2, 161.6, 149.4, 143.0, 141.5, 134.3, 134.9, 134.5, 134.2, 132.3, 131.0, 130.6, 129.8, 129.5, 128.8, 127.3, 126.2, 125.7, 124.7, 122.8, 117.6, 58.0, 29.1, 28.7, 26.9, 18.1, 18.0, 2.3.

$^{19}$F NMR (375 MHz, CDCl$_3$) δ = -59.24, -62.41, -75.62.
Figure S27. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 4d-p1.

$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ = 159.0, 157.0, 155.5, 129.2, 112.0, 72.0, 64.7.

Figure S28. $^{13}$C NMR (100 MHz, 25 °C, CD$_2$Cl$_2$) of 4d-p1.
Figure S29. $^{19}$F NMR (375 MHz, 25 °C, CD$_2$Cl$_2$) of 4d-p1.

Figure S30. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 4d-p2.
$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) $\delta = 157.8, 155.4, 151.2, 135.2, 128.7, 126.3, 126.3, 125.1, 111.4, 93.4, 41.2, 32.2.

Figure S31. $^{13}$C NMR (100 MHz, 25 °C, CD$_2$Cl$_2$) of 4d-p2.

$^{19}$F NMR (375 MHz, CD$_2$Cl$_2$) $\delta = -119.52$.

Figure S32. $^{19}$F NMR (375 MHz, 25 °C, CD$_2$Cl$_2$) of 4d-p2.
Figure S33. $^1$H NMR (400 MHz, 25°C, CD$_2$Cl$_2$) of 4d-p3.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ = 14.74, 13.89, 7.47, 7.39, 7.19, 7.08, 6.98, 6.67, 6.82, 4.19, 4.11, 4.00, 3.88, 3.67, 3.60, 3.56, 1.83, 1.62, 1.50.

Figure S34. $^{13}$C NMR (100 MHz, 25°C, CD$_2$Cl$_2$) of 4d-p3.

$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ = 336.0, 327.1, 162.4, 162.1, 159.8, 159.6, 148.5, 147.0, 133.3, 131.3, 131.0, 129.0, 128.5, 127.7, 127.3, 126.9, 120.0, 119.8, 112.7, 112.5, 79.0, 77.1, 75.9, 70.9, 65.7, 63.2, 61.7, 58.8, 58.0, 29.9, 29.6, 29.2
Figure S35. $^{19}$F NMR (375 MHz, 25 °C, CD$_2$Cl$_2$) of 4d-p3.

Figure S36. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 4d-p4.
**Figure S37.** $^{13}$C NMR (100 MHz, 25 °C, CD$_2$Cl$_2$) of 4d-p4.

**Figure S38.** $^{19}$F NMR (375 MHz, 25 °C, CD$_2$Cl$_2$) of 4d-p4.
Figure S39. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 4d.

Figure S40. $^{13}$C NMR (100 MHz, 25 °C, CD$_2$Cl$_2$) of 4d.
**Supporting Information**

Figure S41. $^{19}$F NMR (375 MHz, CDCl$_2$) of 4d.

Figure S42. $^1$H NMR (400 MHz, CDCl$_3$) 5a.
Figure S43. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of 5a.

Figure S44. $^{13}$C NMR (100 MHz, 25 °C, CDCl$_3$) of 5a.
**Figure S45.** $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 5b.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ = 12.69, 7.72, 7.56, 7.47, 7.12, 7.09, 7.00, 6.99, 6.96, 6.85, 2.33, 2.07, 1.91, 1.24, 0.95.

**Figure S46.** $^{19}$F NMR (375 MHz, 25 °C, CD$_2$Cl$_2$) of 5b.

$^{19}$F NMR (375 MHz, CD$_2$Cl$_2$) δ = -62.98, -73.34.
**Figure S47.** $^{13}$C NMR (100 MHz, 25 °C, CD$_2$Cl$_2$) of 5b.

**Figure S48.** $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 6.

$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ = 315.6, 180.1, 162.3, 156.1, 146.5, 142.5, 135.4, 134.2, 131.2, 131.1, 130.3, 129.3, 128.7, 128.6, 127.5, 127.2, 126.3, 125.1, 124.2, 118.0, 84.4, 57.4, 31.3, 27.9, 21.3, 19.7, 16.1.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 13.38, 7.95, 7.70, 7.51, 7.16, 7.15, 6.99, 6.97, 6.67, 5.11, 4.21, 3.83, 3.67, 2.27, 1.98, 1.86.
$^{19}$F NMR (375 MHz, CDCl$_3$) δ = -62.39, -76.70.

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 309.5, 209.7, 180.4, 151.6, 155.2, 141.5, 135.7, 135.0, 131.3, 130.0, 129.9, 129.2, 128.9, 128.7, 126.0, 126.0, 125.3, 117.6, 82.3, 71.5, 63.6, 21.1, 19.5, 17.8, 17.5.

$^{13}$C NMR (100 MHz, 25 °C, CDCl$_3$) of 6.

Figure S49. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of 6.

Figure S50. $^{13}$C NMR (100 MHz, 25 °C, CDCl$_3$) of 6.
Figure S51. \(^1\)H NMR (400 MHz, 25 °C, CDCl\(_3\)) of 10.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 13.09, 7.18, 7.06, 6.62, 2.35, 2.18, 1.89, 1.66, 1.64, 1.10.\)

Figure S52. \(^{13}\)C NMR (100 MHz, 25 °C, CDCl\(_3\)) of 10.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 317.2, 182.4, 174.4, 149.4, 140.0, 130.0, 129.6, 128.2, 126.1, 125.0, 76.4, 53.00, 33.0, 29.7, 29.7, 21.2, 18.5, 18.3.\)
$^{19}$F NMR (375 MHz, CDCl$_3$) $\delta$ = -77.38, -136.57, -149.92, -162.69.

Figure S53. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of 10.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 13.06, 7.71, 7.51, 7.25, 7.12, 7.06, 6.86, 2.28, 2.11, 1.90, 1.45, 1.40, 0.87.

Figure S54. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 11.
$^{19}F$ NMR (375 MHz, CDCl$_3$) $\delta$ = 82.46, -134.69, -141.37, -158.72.

$^{13}C$ NMR (100 MHz, 25 °C, CDCl$_3$) of 11.

$^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ = 315.4, 162.2, 180.0, 162.1, 148.5, 147.2, 145.9, 141.9, 139.5, 136.9, 135.5, 135.0, 134.8, 134.5, 130.7, 130.5, 128.3, 128.7, 127.2, 126.3, 126.1, 126.0, 123.3, 120.6, 117.6, 79.1, 55.3, 32.5, 30.0, 29.5, 21.1, 17.7.
Figure S57. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 12.

Figure S58. $^{19}$F NMR (375 MHz, 25 °C, CD$_2$Cl$_2$) of 12.
Figure S59. $^{13}$C NMR (100 MHz, 25 °C, CD$_2$Cl$_2$) of 12.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ = 13.01, 7.40, 7.20, 7.10, 7.01, 6.87, 6.78, 6.49, 2.27, 2.20, 2.08, 1.99, 1.58, 1.37.

Figure S60. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 13.
**SUPPORTING INFORMATION**

Figure S61. $^{19}$F NMR (375 MHz, CD$_2$Cl$_2$) of 13.

$^{13}$C NMR (191 MHz, CD$_2$Cl$_2$) δ = 313.5, 183.6, 180.5, 154.3, 149.1, 146.7, 146.6, 144.1, 143.1, 139.9, 137.5, 137.9, 134.7, 134.8, 133.2, 124.3, 123.6, 121.8, 56.7, 53.0, 25.9, 21.3, 18.1, 18.0.

**Figure S62.** $^{13}$C NMR (100 MHz, 25 °C, CD$_2$Cl$_2$) of 13.
Figure S63. $^1$H NMR (400 MHz, CDCl$_3$) of 14.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 12.75, 7.70, 7.50, 7.34, 7.23, 7.15, 6.91, 6.81, 2.17, 2.00, 2.00, 1.14.

Figure S64. $^{13}$C NMR (100 MHz, CDCl$_3$) of 14.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ = 321.2, 183.7, 160.0, 161.9, 148.8, 148.7, 146.0, 141.5, 139.5, 136.9, 135.7, 134.9, 134.4, 134.2, 130.6, 130.4, 129.1, 129.0, 129.3, 125.6, 124.7, 117.6, 105.1, 50.3, 39.6, 21.2, 19.1, 17.9.
Figure S65. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of 14.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ = 12.91, 8.02, 7.88, 7.43, 7.34, 7.52, 7.24, 7.06, 6.82, 2.20, 2.06, 2.04, 1.09.

Figure S66. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 15a.
$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ = 321.5, 166.3, 163.7, 149.9, 142.0, 136.1, 155.3, 134.7, 152.7, 131.1, 131.0, 131.0, 130.1, 128.7, 51.0, 30.3, 21.4, 18.4, 10.2.

$^{19}$F NMR (375 MHz, CD$_2$Cl$_2$) δ = -59.15, -76.75.

Figure S67. $^{13}$C NMR (100 MHz, 25 °C, CD$_2$Cl$_2$) of 15a.

Figure S68. $^{19}$F NMR (375 MHz, 25 °C, CD$_2$Cl$_2$) of 15a.
Figure S69. $^1$H NMR (400 MHz, CD$_2$Cl$_2$) of 15b.

$^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ = -59.14, -62.87.

Figure S70. $^{19}$F NMR (375 MHz, CD$_2$Cl$_2$) of 15b.
Figure S71. $^{13}$C NMR (100 MHz, 25 °C, CD$_2$Cl$_2$) of 15b.

$^{1}$H NMR (400 MHz, CDCl$_3$) δ = 13.09, 8.00, 7.85, 7.34, 7.28, 7.17, 7.03, 6.83, 4.07, 3.95, 2.32, 2.29, 2.14, 1.85, 1.65, 1.53, 1.45, 1.34, 1.24.

Figure S72. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 17a.
**Figure S73.** $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of 17a.

$^{19}$F NMR (375 MHz, CDCl$_3$) $\delta = -59.22, -75.48$.

**Figure S74.** $^{13}$C NMR (100 MHz, 25 °C, CDCl$_3$) of 17a.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 311.4, 207.6, 187.0, 147.4, 140.8, 136.6, 135.6, 134.5, 132.1, 131.0, 130.8, 128.8, 127.2, 126.4, 82.0, 55.7, 41.1, 35.0, 32.8, 29.5, 29.3, 21.1$. 

$\delta_{ppm}$ range: 310 to 30.
**Figure S75.** $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 17b.

**Figure S76.** $^{13}$C NMR (100 MHz, 25 °C, CD$_2$Cl$_2$) of 17b.
$^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ = -59.53, -75.75.

Figure S77. $^{19}$F NMR (375 MHz, 25 °C, CD$_2$Cl$_2$) of 17b.
Figure S78. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of (3,5-bis(3-(trimethylsilyl)prop-1-en-1-yl)cyclopentane-1,2-diyl)dimethanol.

Figure S79. $^{13}$C NMR (100 MHz, 25 °C, CDCl$_3$) of (3,5-bis(3-(trimethylsilyl)prop-1-en-1-yl)cyclopentane-1,2-diyl)dimethanol.
Figure S80. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of (3-(3-(trimethylsilyl)prop-1-en-1-yl)-5-vinylcyclopentane-1,2-diyl)dimethanol.

Figure S81. $^{13}$C NMR (100 MHz, 25 °C, CDCl$_3$) of (3-(3-(trimethylsilyl)prop-1-en-1-yl)-5-vinylcyclopentane-1,2-diyl)dimethanol.
Figure S82. $^1$H NMR (400 MHz, 25 °C, CDCl₃) of (3,5-bis(hex-1-en-1-yl)cyclopentane-1,2-diyl)dimethanol.

Figure S83. $^{13}$C NMR (100 MHz, 25 °C, CDCl₃) of (3,5-bis(hex-1-en-1-yl)cyclopentane-1,2-diyl)dimethanol.
Figure S84. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of (3-(hex-1-en-1-yl)-5-vinylcyclopentane-1,2-diyl)dimethanol.

Figure S85. $^{13}$C NMR (100 MHz, 25 °C, CDCl$_3$) of (3-(hex-1-en-1-yl)-5-vinylcyclopentane-1,2-diyl)dimethanol.
Figure S86. $^1$H NMR (400 MHz, 100 °C, C$_2$D$_4$Cl$_2$) of poly(M1).

Figure S87. $^{13}$C NMR (100 MHz, 100 °C, C$_2$D$_4$Cl$_2$) of poly(M1).
Figure S88. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of poly(M2).

Figure S89. $^{13}$C NMR (100 MHz, 25 °C, CDCl$_3$) of poly(M2).
Figure S90. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 3a and 3a in the presence of 2-PrOH.

Figure S91. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of pure 3a and 3a in the presence of 2-PrOH.
Figure S92. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 3a in the presence of 1 equiv. 2-PrOH.

Figure S93. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 3a after 12 h in air containing 2 equiv. H$_2$O and superimposed spectra (expansion) of the alkylidene region of pure 3a (red) and 3a after 12 h in air (blue).
Figure S94. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of pure 3a and 3a after 12 h in air.

Figure S95. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 3c after 12 h in air containing 2 equiv. H$_2$O and superimposed spectra (expansion) of the alkylidene region of pure 3c (blue) and 3a after 12 h in air (red).
Figure S96. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of pure 3c and 3c after 12 h in air.

Figure S97. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 3d after 12 h in air.
Figure S98. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 3d (bottom) and 3d after 12 h in air (top).

Figure S99. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of pure 3d and 3d after 12 h in air.
Figure S100. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 4a after 24 h in air containing 0.5 equiv. H$_2$O and superimposed spectra (expansion) of the alkylidene region of pure 4a (blue) and 4a with 0.5 equiv. H$_2$O (red).

Figure S101. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 4a (bottom), 4a after 12 (middle) and 24 h in air (top).
Figure S102. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of 4a (bottom), 4a after 12 h (middle) and 24 h in air (top).

Figure S103. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 4b after 12 h in air containing ~1.5 - 2 equiv. H$_2$O.
Figure S104. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of pure 4b (bottom) and 4b after 12 h in air (top).

Figure S105. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of pure 4b (bottom), 4c (middle) and 4b after 12 h in air (top).
Figure S106. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of pure 4d (bottom) and 4d after 12 h in air (top).

Figure S107. $^{19}$F NMR (375 MHz, 25 °C, CD$_2$Cl$_2$) of pure 4d (bottom) and 4d after 12 h in air (top).
Figure S108. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) superimposed spectra of pure 5a (blue) and 5a after 24 h in air (red).

Figure S109. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of pure 5a (red, bottom) and after 24 h in air (blue, top).
Figure S110. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 7 after 12 h in air.

Figure S111. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of pure 7 (bottom) and 7 after 12 h in air (top).
Figure S112. $^{19}$F NMR (375 MHz, 25 °C, CD$_2$Cl$_2$) of pure 7 (bottom) and after 12 h in air (top).

Figure S113. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 8 after 12 h in air.
Figure S114. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of pure 8 and 8 after 12 h in air.

Figure S115. $^{19}$F NMR (375 MHz, 25 °C, CDCl$_3$) of pure 8 (bottom) and after 12 h in air (top).
Figure S116. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 11 after 5 days in air.

Figure S117. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 13 after 5 days in air.
Figure S118. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 15a after 5 days in air.

Figure S119. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 17a after 5 days in air.
Figure S120. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 5c after treatment with 4-penten-1-ol, expansion of the alkylidene region.

Figure S121. $^1$H NMR (400 MHz, 25 °C, CD$_2$Cl$_2$) of 5c after treatment with 4-penten-1-ol (bottom) and pyrrole (top).
Figure S122. $^1$H NMR (400 MHz, 25 °C, CDCl$_3$) of 11 in the presence of 10 equiv. 10-undecenoic acid.
X-ray Analysis: Single crystal X-ray measurements were carried out on a Bruker Kappa APEXII Duo diffractometer with Mo-Kα radiation at the Institute of Organic Chemistry, University of Stuttgart. CCDC 1946042 (3a), 1946041 (4aH2O), 1959263 (4d), 1959261 (5d), 1959260 (5d-MeCN), 1960403 (6) and 1959262 (15b) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Comment on checkcif: The B level alert in the analysis of compound 4aH2O stems from the water molecules; one hydrogen of each water molecule lacks a classic acceptor for hydrogen bonding (here a carbon). This is routinely indicated by the software.

Figure S123. Single crystal X-ray structure of [Mo(N(2,6-Cl2-C6H3))(CHCMe3)(IMes)(OTf)][B(ArF)4]. Relevant bond lengths [pm] and angles [°]: Mo-N3 = 173.4, Mo-C28 = 186.7, Mo-O2 = 217.9, Mo-C1 = 218.2, Mo-O1 = 226.9, Mo-S = 280.2, N3-Mo-C28 = 104.81, N3-Mo-O2 = 136.15, C28-Mo-O2 = 115.56, N3-Mo-C1 = 99.87, C28-Mo-C1 = 101.72, O2-Mo-C1 = 88.45, N3-Mo-O1 = 98.45, C28-Mo-O1 = 94.12, O2-Mo-O1 = 63.52, C1-Mo-O1 = 151.75, C22-N3-Mo = 160.5, C29-C28-Mo = 144.3. Thermal ellipsoids are set at a 50% probability level. One CH2Cl2 molecule, the anion and hydrogens omitted for clarity.

Table S1. Crystal data and structure refinement for [Mo(N(2,6-Cl2-C6H3))(CHCMe3)(IMes)(OTf)][B(ArF)4].

| Empirical formula | C65 H49 B Cl2 F27 Mo N3 O3 S |
|-------------------|--------------------------------|
| Formula weight    | 1642.78 g/mol                  |
| Temperature       | 130(2) K                       |
| Wavelength        | 0.71073 Å                      |
| Crystal system    | monoclinic                     |
| Space-group       | P 2_1/n                        |
| Cell parameters   | a = 18.9245(17) Å, b = 16.5339(15) Å, c = 22.735(2) Å |
|                   | α = γ = 90 °, β = 94.994(3) ° |
| Cell volume       | 7086.6(11) Å^3                |
| Z                 | 4                              |
| Calc. density     | 1.540 g/cm^3                   |
| Absorption coefficient | 0.407 mm^-1                 |
| F(000)            | 3296                           |
| Crystal size      | 0.520 x 0.314 x 0.116 mm       |
| Theta range for data collection | 1.638 to 28.259 ° |
| Limiting indices  | -25<=h<=25, -21<=k<=22, -30<=l<=30 |
| Reflections collected / unique | 73512 / 17461 [R(int) = 0.0573] |
| Completeness to theta = 25.242 | 99.9%                            |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7457 and 0.6847 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 17461 / 36 / 938 |
| Goodness-of-fit on F^2 | 1.027                        |
| Final R indices [I>2σ(I)] | R1 = 0.0623, wR2 = 0.1496 |
| R indices (all data) | R1 = 0.1154, wR2 = 0.1656 |
| Largest diff. peak and hole | 1.828 and -0.775 e Å^3 |
Figure S124. Single crystal X-ray structure of [Mo(N-2,6-F2-C6H3)(CHCMe2Ph)(IMes)(OTf)(MeCN)][B(ArF)4]. 4d. Relevant bond lengths [pm] and angles [°]: Mo-N3 = 173.1, Mo-C28 = 187.1, Mo-O1 = 208.9, Mo-N4 = 217.2, Mo-C1 = 218.3; N3-Mo-C28 = 102.03, N3-Mo-O1 = 151.93, C28-Mo-O1 = 105.03, N3-Mo-C1 = 97.06, C28-Mo-C1 = 102.72, N4-Mo-C1 = 160.29, N3-Mo-O1 = 151.93, C28-Mo-O1 = 105.03, N4-Mo-O1 = 81.88, C1-Mo-O1 = 84.21, C22-N3-Mo = 166.38, C29-C28-Mo = 143.56. The anion and hydrogens omitted for clarity. Thermal ellipsoids are set at a 50% probability level.

Table S2. Crystal data and structure refinement for [Mo(N-2,6-F2-C6H3)(CHCMe2Ph)(IMes)(OTf)(MeCN)][B(ArF)4].

| Property                              | Value                                      |
|---------------------------------------|--------------------------------------------|
| Empirical formula                     | C72 H54 B F29 Mo N4 O3 S                   |
| Formula weight                        | 1713.00 g/mol                              |
| Temperature                           | 135(2) K                                   |
| Wavelength                            | 0.71073 Å                                  |
| Crystal system                        | Triclinic                                  |
| Space-group                           | P1bar                                      |
| Cell parameters                       | a = 12.7917(5) Å, b = 18.1854(7) Å, c = 18.6054(8) Å |
|                                       | α = 64.059(2) °, γ = 73.654(2) °, β = 70.333(2) ° |
| Cell volume                           | 3618.6(3) Å                               |
| Z                                      | 2                                          |
| Calc. density                         | 1.572 g/cm³                                |
| Absorption coefficient                | 0.335 mm⁻¹                                 |
| F(000)                                | 1724                                       |
| Crystal size                          | 0.643 x 0.470 x 0.461 mm                   |
| Theta range for data collection       | 1.712 to 33.254 °                         |
| Limiting indices                      | -19<≤h<≤17, -28<≤k<≤21, -28<≤l<≤28         |
| Reflections collected / unique        | 109223 / 27676 [R(int) = 0.0317]            |
| Completeness to theta = 25.242        | 100%                                       |
| Absorption correction                 | Semi-empirical from equivalents            |
| Max. and min. transmission            | 0.7465 and 0.7150                          |
| Refinement method                     | Full-matrix least-squares on F²            |
| Data / restraints / parameters         | 27676 / 168 / 1084                         |
| Goodness-of-fit on F²                 | 1.046                                      |
| Final R indices [I>2σ(I)]             | R1 = 0.0399, wR2 = 0.0969                  |
| R indices (all data)                  | R1 = 0.0640, wR2 = 0.1065                  |
| Largest diff. peak and hole           | 0.672 and -0.590 e.A⁻³                   |
Figure S125. Single crystal X-ray structure of [Mo(N-2-tBu-C6H4)2(CHCMe2Ph)(IMes)(OTf)(H2O)]2[B(ArF)4]. Relevant bond lengths [pm] and angles [°]: Mo-N3 = 173.2, Mo-C32 = 191.8, Mo-O2W = 219.2, Mo-O1W = 232.11, N3-Mo-C32 = 99.47, N3-Mo-O2W = 99.39, C32-Mo-O2W = 88.23, N3-Mo-C1 = 95.05, C32-Mo-C1 = 96.37, O2W-Mo-C1 = 163.92, N3-Mo-O1 = 172.82, C32-Mo-O1 = 87.69, O2W-Mo-O1 = 81.21, C1-Mo-O1W = 83.58, N3-Mo-O1W = 99.06, C32-Mo-O1W = 142.38, C22-N3-Mo = 172.02. Thermal ellipsoids are set at a 50% probability level. One CH2Cl2 molecule, anion and hydrogens were omitted for clarity.

Table S3. Crystal data and structure refinement for [Mo(N-2-tBu-C6H4)2(CHCMe2Ph)(IMes)(OTf)(H2O)]2[B(ArF)4].

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Empirical formula               | C75 H67 B Cl2 F27 Mo N3 O5 S               |
| Formula weight                  | 1813.03 g/mol                              |
| Temperature                     | 130(2) K                                   |
| Wavelength                      | 0.71073 Å                                  |
| Crystal system                  | Triclinic                                  |
| Space group                     | P 1                                       |
| Cell parameters                 | a = 15.4478(14) Å, b = 16.3148(15) Å, c = 17.2214(16) Å |
|                                | α = 96.014(5) °, γ = 97.988(4) °, β = 110.634(5) ° |
| Cell volume                     | 3966.7(6) Å³                              |
| Z                               | 2                                         |
| Calc. density                   | 1.518 g/cm³                                |
| Absorption coefficient          | 0.374 mm⁻¹                                 |
| F(000)                          | 1836                                      |
| Crystal size                    | 0.42 x 0.39 x 0.28 mm                      |
| Theta range for data collection | 1.53 to 30.52 °                            |
| Limiting indices                | -22<=h<=22, -23<=k<=23, -24<=l<=24         |
| Reflections collected / unique  | 85852 / 24106 [R(int) = 0.0363]             |
| Completeness to theta           | 30.52                                     |
| Absorption correction           | Semi-empirical from equivalents            |
| Max. and min. transmission      | 0.7461 and 0.7168                          |
| Refinement method               | Full-matrix least-squares on F²            |
| Data / restraints / parameters   | 24106 / 116 / 1083                         |
| Goodness-of-fit on F²            | 1.038                                      |
| Final R indices [I>2σ(I)]       | R1 = 0.0452, wR2 = 0.1149                  |
| R indices (all data)            | R1 = 0.0702, wR2 = 0.1246                  |
| Largest diff. peak and hole     | 1.075 and -0.840 e.Å³                      |
SUPPORTING INFORMATION

Figure S126. Single crystal X-ray structure of [Mo(N-2,6-Me2-C6H4)(CHCH2O(CH2)2OH)(IMes)(OTf)][B(ArF)4]. Selected bond lengths [pm] and angles [°]: Mo-N3 = 171.8, Mo-C30 = 192.2, Mo-O4 = 217.7, Mo-O1 = 218.9, Mo-C1 = 220.5, Mo-O5 = 229.3, N3-Mo-C30 = 98.63, N3-Mo-O4 = 94.36, C30-Mo-O4 = 97.11, N3-Mo-O1 = 117.38, C30-Mo-O1 = 143.97, O4-Mo-O1 = 79.88, N3-Mo-C1 = 96.24, C30-Mo-C1 = 95.16, O4-Mo-C1 = 162.38, O1-Mo-C1 = 82.75, N3-Mo-O5 = 157.22, C30-Mo-O5 = 64.87, O4-Mo-O5 = 73.49, O1-Mo-O5 = 80.10, C1-Mo-O5 = 100.64, C22-N3-Mo = 168.47. Thermal ellipsoids are set at a 50% probability level.

The anion, hydrogens and one Pr2O molecule coordinating to the hydrogen on O4 were omitted for clarity.

Table S4. Crystal data and structure refinement for [Mo(N-2,6-Me2-C6H4)(CHCH2O(CH2)2OH)(IMes)(OTf)][B(ArF)4].

| Crystal data | Value |
|--------------|-------|
| Empirical formula | C72 H67 B F27 Mo N3 O6 S |
| Formula weight | 1722.09 g/mol |
| Temperature | 130(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space-group | P1 |
| Cell parameters | a = 13.3310(6) Å, b = 17.3449(7) Å, c = 18.1979(9) Å, α = 78.865(2) °, γ = 88.528(2) °, β = 88.052(2) ° |
| Cell volume | 4125.4(3) Å³ |
| Z | 2 |
| Calc. density | 1.386 g/cm³ |
| Absorption coefficient | 0.293 mm⁻¹ |
| F(000) | 1748 |
| Crystal size | 0.264 x 0.223 x 0.060 mm |
| Theta range for data collection | 1.486 to 26.491 ° |
| Limiting indices | -16<≤h<≤16, -21<≤k<≤21, -22<≤l<≤22 |
| Reflections collected / unique | 75808 / 16980 [R(int) = 0.0309] |
| Completeness to theta = 25.242 | 100% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7454 and 0.7030 |
| Refinement method | Full-matrix least-squares on F² |
| Data / restraints / parameters | 16980 / 72 / 1086 |
| Goodness-of-fit on F² | 1.033 |
| Final R indices [I>2σ(I)] | R1 = 0.0366, wR2 = 0.0915 |
| R indices (all data) | R1 = 0.0487, wR2 = 0.0958 |
| Largest diff. peak and hole | 0.824 and -0.637 e Å⁻³ |
Figure S127. Single crystal X-ray structure of [Mo(N-2,6-Cl2-C6H3)(CHCMe3)(IMes)(2,6-(CF3)2-C6H3)][B(ArF)4]15b. Selected bond lengths [pm] and angles [°]: Mo-N3 = 172.5, Mo-C37 = 184.1, Mo-O2 = 218.6, Mo-C1 = 219.1, Mo-C28 = 255.3, N3-Mo-C37 = 103.4, N3-Mo-O2 = 142.33, C37-Mo-C1 = 101.58, C37-Mo-C1 = 101.41, O2-Mo-O1 = 89.29, C37-Mo-O1 = 95.22, O2-Mo-O1 = 59.42, C1-Mo-O1 = 148.17, C22-N3-Mo = 165.1, C38-C37-Mo = 145.9. Thermal ellipsoids are set at a 50% probability level. The B(ArF)4 anion and hydrogens except for H on C37 were omitted for clarity.

Table S5. Crystal data and structure refinement for [Mo(N-2,6-Cl2-C6H3)(CHCMe3)(IMes)(2,6-(CF3)2-C6H3)][B(ArF)4].

| Property                      | Value                                      |
|-------------------------------|--------------------------------------------|
| Empirical formula             | C73 H52 B Cl2 F30 Mo N3 O2                |
| Formula weight                | 1750.83 g/mol                              |
| Temperature                   | 130(2) K                                   |
| Wavelength                    | 0.71073 Å                                  |
| Crystal system                | Triclinic                                  |
| Space group                   | P1                                          |
| Cell parameters               |                                             |
| a                             | 9.4743(4) Å                                |
| b                             | 19.9174(8) Å                               |
| c                             | 20.9981(9) Å                               |
| α                             | 105.326(2) °                               |
| γ                             | 102.824(2) °                               |
| β                             | 98.096(3) °                                |
| Cell volume                   | 3641.4(3) Å                                |
| Z                             | 2                                          |
| Calc. density                 | 1.597 g/cm³                                |
| Absorption coefficient        | 0.379 mm⁻¹                                 |
| F(000)                        | 1756                                       |
| Crystal size                  | 0.35 x 0.33 x 0.08 mm                      |
| Theta range for data collection | 1.72 to 25.00 °                           |
| Limiting indices              | -11<=h<=9, -23<=k<=23, -24<=l<=24          |
| Reflections collected / unique | 46897 / 12462 [R(int) = 0.0405]             |
| Completeness to theta = 25.00 | 97.1%                                      |
| Absorption correction         | Numerical                                  |
| Max. and min. transmission    | 0.9978 and 0.7912                           |
| Refinement method             | Full-matrix least-squares on F²            |
| Data / restraints / parameters | 12462 / 6 / 1018                           |
| Goodness-of-fit on F²         | 1.047                                      |
| Final R indices (R > 2σ)      | R1 = 0.0627, wR2 = 0.1452                  |
| R indices (all data)          | R1 = 0.0952, wR2 = 0.1603                  |
| Largest diff. peak and hole   | 2.036 and -0.713 e.A⁻³                    |
Figure S128. Single crystal X-ray structure of 5d. Relevant bond lengths [pm] and angles [°]: Mo-N3 = 172.5, Mo-C36 = 187.2, Mo-O1 = 193.9, Mo-C1 = 214.6; N3-Mo-C36 = 103.63, N3-Mo-O1 = 121.42, C36-Mo-O1 = 105.79, N3-Mo-C1 = 101.63, C36-Mo-C1 = 101.46, O1-Mo-C1 = 120.12, Mo-C36-H36 = 96, C37-C36-Mo = 144.8, C28-N3-Mo = 167.1. Thermal ellipsoids are set at a 50% probability level. All hydrogen atoms except for H at C36 and B(ArF)₄ anion are omitted for clarity. z' = 0.84. Mo adopts a distorted tetrahedral geometry.²⁰

Table S6. Crystal data and structure refinement for [Mo(N-2,6-Me₂-C₆H₃)(CHCMe₂Ph)(IMes)(OC₆F₅)]·[B(ArF)₄].

| Property                          | Value                                      |
|----------------------------------|--------------------------------------------|
| Empirical formula                | C₇₇H₅₇B₂F₂₉MoN₃O                          |
| Formula weight                   | 1698.01 g/mol                              |
| Temperature                      | 130(2) K                                   |
| Wavelength                       | 0.71073 Å                                  |
| Crystal system                   | monoclinic                                 |
| Space-group                      | P 2₁/n                                     |
| Cell parameters                  | a = 19.4445(10) Å, b = 18.7532(10) Å, c = 21.3407(11) Å |
|                                  | α = γ = 90°, β = 103.348(3)°              |
| Cell volume                      | 7571.6(7) Å                                |
| Z                                | 4                                          |
| Calc. density                    | 1.490 g/cm³                                |
| Absorption coefficient           | 0.291 mm⁻¹                                 |
| F(000)                           | 3424                                       |
| Crystal size                     | 0.52 x 0.47 x 0.36 mm                      |
| Theta range for data collection  | 1.46 to 28.35 °                            |
| Limiting indices                 | -25°≤h≤25, -24≤k≤24, -28≤l≤28              |
| Reflections collected / unique   | 83780 / 18768 [R(int) = 0.0490]            |
| Completeness to theta            | 28.35                                      |
| Absorption correction            | Numerical                                  |
| Max. and min. transmission       | 0.9873 and 0.8519                          |
| Refinement method                | Full-matrix least-squares on F²            |
| Data / restraints / parameters    | 18768 / 246 / 1106                         |
| Goodness-of-fit on F²             | 1.042                                      |
| Final R indices [I>2σ(I)]        | R1 = 0.0551, wR2 = 0.1322                  |
| R indices (all data)             | R1 = 0.1210, wR2 = 0.1575                  |
| Largest diff. peak and hole      | 1.022 and -0.554 e.A⁻³                    |
Figure S129. Single crystal X-ray structure of 5d-MeCN. Relevant bond lengths [pm] and angles [°]: Mo-N3 = 174.3, Mo-C36 = 189.2, Mo-O1 = 200.03, Mo-N4 = 220.0, Mo-C1 = 221.0; N3-Mo1-C36 = 105.46, N3-Mo1-O1 = 140.04, C36-Mo1-O1 = 112.52, N3-Mo1-N4 = 86.05, C36-Mo1-N4 = 90.36, O1-Mo1-N4 = 81.53, N3-Mo1-C1 = 100.51, C36-Mo1-C1 = 101.71, O1-Mo1-C1 = 164.04, C28-N3-Mo = 156.5, C37-C36-Mo = 142.6, Mo-C36-H36 = 101.0. Thermal ellipsoids are set at a 50% probability level. All hydrogen atoms except for H at C36 and B(ArF4)4 anion are omitted for clarity. The acetonitrile adduct of 5d adopts a geometry intermediate between trigonal bipyramidal and square pyramidal with $t_5 = 0.4$.\[20]\]

Table S7. Crystal data and structure refinement for [Mo(N(2,6-Me2-C6H3)(CHCMesPh))(IMes)(OC6F5)(MeCN)][B(ArF4)].

| Property                                  | Value                  |
|-------------------------------------------|------------------------|
| Empirical formula                         | C79 H60 B F29 Mo N4 O  |
| Formula weight                            | 1739.06 g/mol          |
| Temperature                               | 130(2) K               |
| Wavelength                                | 0.71073 Å              |
| Crystal system                            | monoclinic             |
| Space-group                               | $P 2_1/n$              |
| Cell parameters                           | $a = 12.7337(7)$ Å, $b = 37.442(2)$ Å, $c = 16.5162(9)$ Å |
|                                           | $\alpha = \gamma = 90 \degree$, $\beta = 100.906(3) \degree$ |
| Cell volume                               | 7732.2(7) Å$^3$       |
| Z                                         | 4                      |
| Calc. density                             | 1.494 g/cm$^3$         |
| Absorption coefficient                    | 0.287 mm$^{-1}$        |
| F(000)                                    | 3512                   |
| Crystal size                              | 0.30 x 0.23 x 0.13 mm |
| Theta range for data collection           | 1.66 to 28.33 °        |
| Limiting indices                          | -16<=h<=16, -49<=k<=49, -22<=l<=21 |
| Reflections collected / unique            | 90866 / 19024 [R(int) = 0.0391] |
| Completeness to theta                     | 28.33 98.8%            |
| Absorption correction                     | Numerical              |
| Max. and min. transmission                | 0.9877 and 0.9142      |
| Refinement method                         | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters             | 19024 / 172 / 1052     |
| Goodness-of-fit on F$^2$                  | 1.049                  |
| Final R indices [I>2σ(I)]                 | R1 = 0.0523, wR2 = 0.1189 |
| R indices (all data)                      | R1 = 0.0751, wR2 = 0.1264 |
| Largest diff. peak and hole               | 0.982 and -0.802 eÅ$^{-3}$ |
**Figure S130:** High resolution mass spectrum of 2b. Found (top) and calculated (bottom) isotope distribution of the molecular ion peak.

**References**

[1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* 2010, 29, 2176-2179.

[2] J. Zhao, D. Wang, B. Autenrieth, M. R. Buchmeiser, *Macromol. Rapid Commun.* 2015, 36, 190-194.
