SUPPORTING INFORMATION

“Canopy Catalysts” for Alkyne Metathesis: Molybdenum Alkylidyne Complexes with a Tripodal Ligand Framework

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SUPPORTING CRYSTALLOGRAPHIC INFORMATION

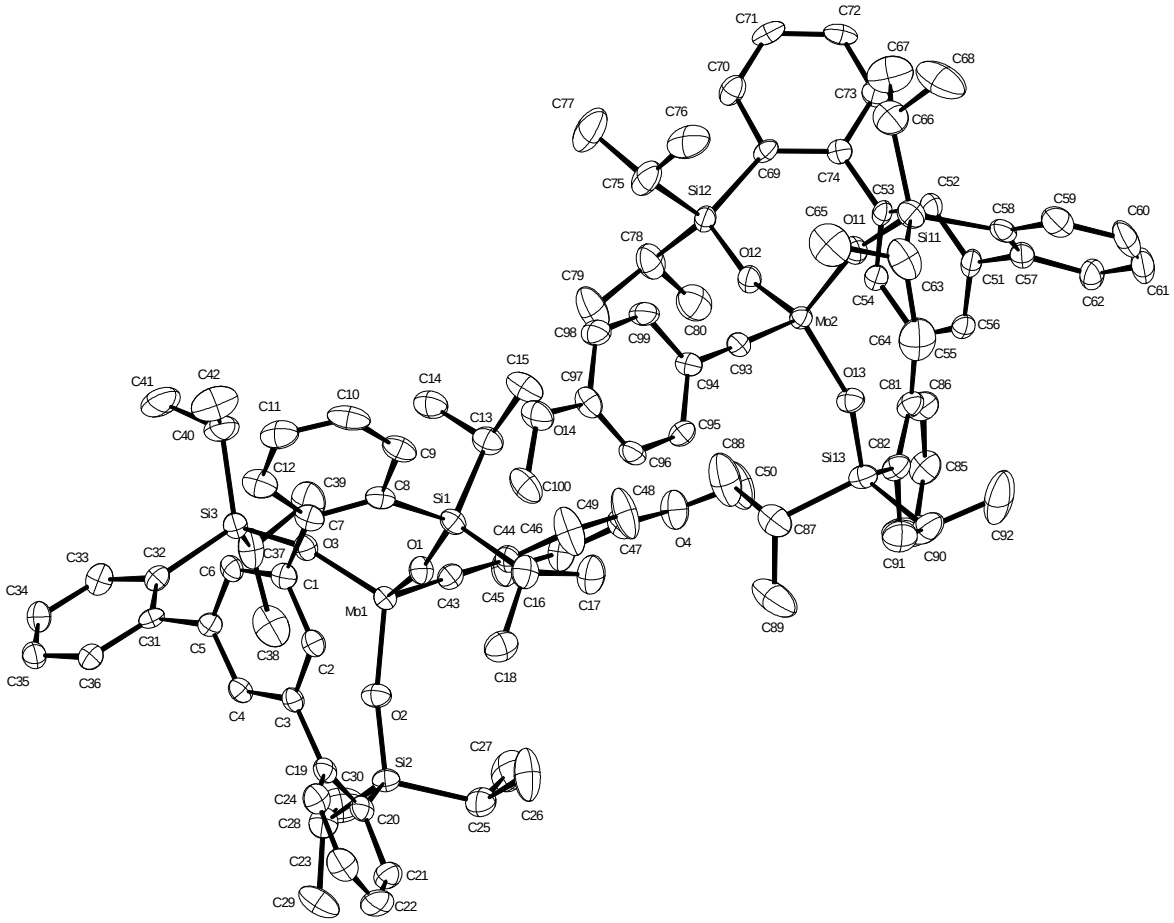


Figure S1. Structure of complex **1d** in the solid state, showing the two independent molecules in the unit cell; hydrogen atoms omitted for clarity

X-ray Crystal Structure Analysis of Complex 1d: $C_{50}\,H_{64}\,Mo\,O_4\,Si_3$, M_r = 909.22 g · mol^{-1}, yellow prism, crystal size 0.19 x 0.08 x 0.07 mm^3, monoclinic, space group $P2_1$ [4], a = 11.3831(10) Å, b = 40.159(3) Å, c = 11.6138(12) Å, β = 91.474(7)°, V = 5307.3(8) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.138 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.352 mm^{-1}, analytical absorption correction (T_{min} = 0.95, T_{max} = 0.98), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Mo-anode X-ray source, 2.674 < θ < 32.069°, 128378 measured reflections, 33802 independent reflections, 22677 reflections with $I > 2\sigma(I)$, R_{int} = 0.0889, 1071 parameters, S = 1.027, residual electron density +0.4 (0.97 Å from H28) / –0.9 (0.76 Å from Mo2) e · Å^{-3}, absolute structure parameter = –0.002(13). The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.056 [$I > 2\sigma(I)$], wR_2 = 0.122. **CCDC-1987911**

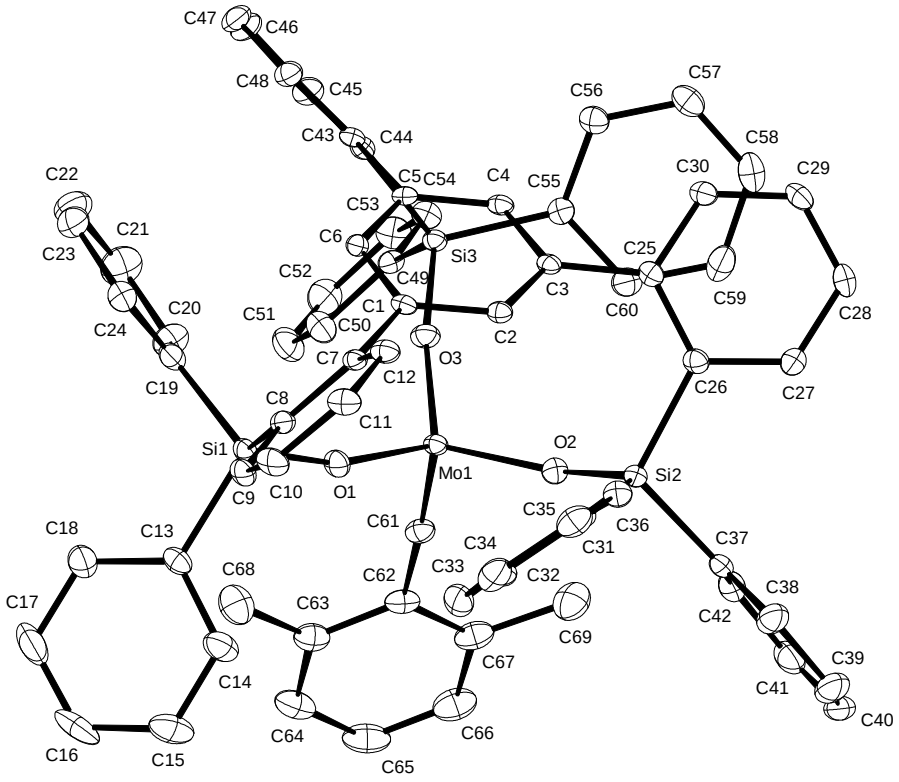


Figure S2. Structure of complex **1e** in the solid state; hydrogen atoms omitted for clarity

X-ray Crystal Structure Analysis of Complex 1e: $C_{69}\,H_{54}\,Mo\,O_3\,Si_3$, M_r = 1111.33 g · mol^{-1}, yellow block, crystal size 0.110 x 0.097 x 0.011 mm^3, triclinic, space group $P\bar{1}$ [2], a = 13.9667(5) Å, b = 14.1087(5) Å, c = 16.4977(6) Å, α = 83.661(2)°, β = 72.572(2)°, γ = 61.763(2)°, V = 2730.67(18) Å^3, T = 100(2) K, Z = 2, D_{calc} = 1.352 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.356 mm^{-1}, analytical absorption correction (T_{min} = 0.97, T_{max} = 1.00), Bruker-AXS Kappa Mach3 diffractometer with APEX-II detector and IμS micro focus X-ray source, 1.295 < θ < 30.514°, 86764 measured reflections, 16547 independent reflections, 12420 reflections with $I > 2\sigma(I)$, R_{int} = 0.0577. S = 1.041, 687 parameters, residual electron density +0.6 (0.92 Å from C61) / –0.9 (0.58 Å from Mo1) e · Å^{-3}. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.040 [$I > 2\sigma(I)$], wR_2 = 0.097. **CCDC-1987913**

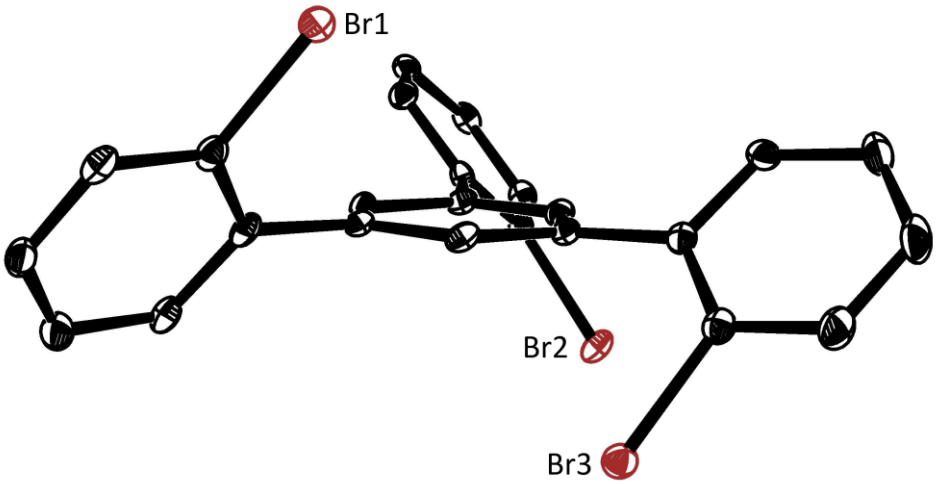


Figure S3. Structure of compound **8a** in the solid state; hydrogen atoms omitted for clarity

X-ray Crystal Structure Analysis of Compound 8a: $C_{24}H_{15}Br_3$, M_r = 543.09 g · mol^{-1}, light green prism, crystal size 0.208 x 0.174 x 0.100 mm^3, triclinic, space group $P\bar{1}$ [2], a = 9.9442(4) Å, b = 10.9266(4) Å, c = 11.1792(4) Å, α = 111.2510(10)°, β = 99.0800(10)°, γ = 112.6310(10)°, V = 980.54(6) Å^3, T = 100(2) K, Z = 2, D_{calc} = 1.839 g · cm^3, λ = 1.54178 Å, μ(*Cu-K*$_\alpha$) = 7.663 mm^{-1}, analytical absorption correction (T_{min} = 0.36, T_{max} = 0.56), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Cu-anode X-ray source, 4.522 < θ < 63.667°, 18480 measured reflections, 3076 independent reflections, 3053 reflections with $I > 2\sigma(I)$, R_{int} = 0.0392, 244 parameters, S = 1.138, residual electron density +0.4 (0.99 Å from Br1) / –0.5 (0.98 Å from C16) e · Å^{-3}. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.023 [$I > 2\sigma(I)$], wR_2 = 0.060. **CCDC-1987908**

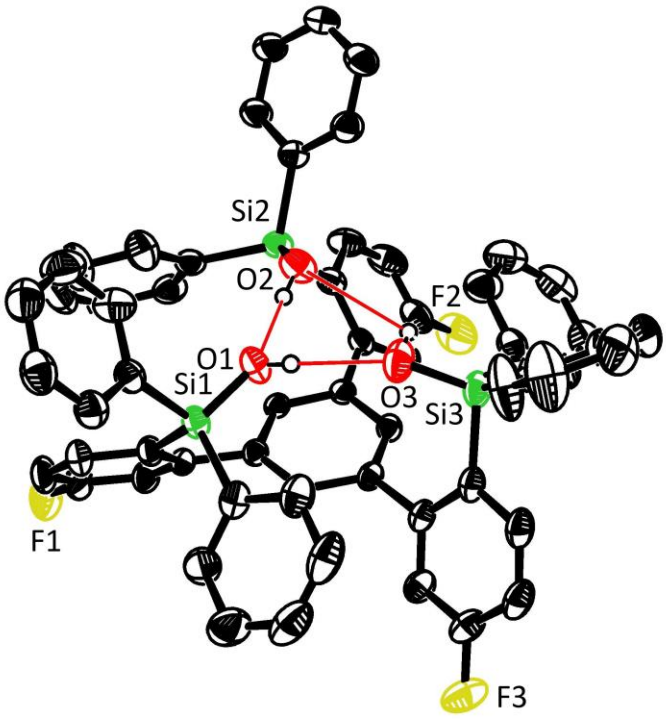


Figure S4. Structure of compound **11b** in the solid state; hydrogen atoms (except for –OH) omitted for clarity

X-ray Crystal Structure Analysis of Compound 11b: $C_{60}H_{45}F_3O_3Si_3$, M_r = 955.23 g · mol^{-1}, colourless prism, crystal size 0.203 x 0.074 x 0.050 mm^3, triclinic, space group $P\bar{1}$ [2], a = 13.4432(5) Å, b = 13.9609(5) Å, c = 15.6464(6) Å, α = 94.388(2)°, β = 101.719(2)°, γ = 117.6550(10)°, V = 2496.95(16) Å^3, T = 200(2) K, Z = 2, D_{calc} = 1.271 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.152 mm^{-1}, analytical absorption correction (T_{min} = 0.98, T_{max} = 0.99), Bruker-AXS Kappa Mach3 diffractometer with APEX-II detector and IμS micro focus X-ray source, 2.812 < θ < 30.842°, 77584 measured reflections, 15632 independent reflections, 11148 reflections with $I > 2\sigma(I)$, R_{int} = 0.0293. S = 1.028, 633 parameters, residual electron density +0.4 (0.83 Å from Si3) / –0.4 (0.72 Å from Si3) e · Å^{-3}. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.046 [$I > 2\sigma(I)$], wR_2 = 0.129. **CCDC-1987910**

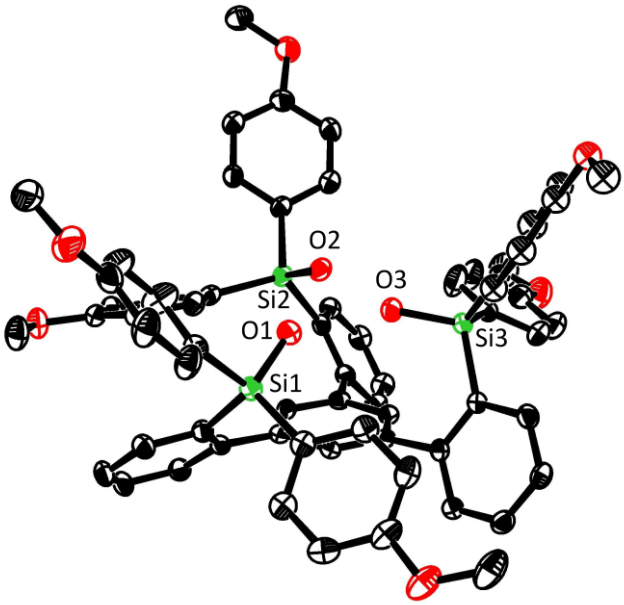


Figure S5. Structure of one of the two independent molecules of compound **11c** in unit cell, which shows the "upward-inward" orientation of the three –OH groups; hydrogen atoms omitted for clarity, disorder of one of the phenyl rings not shown

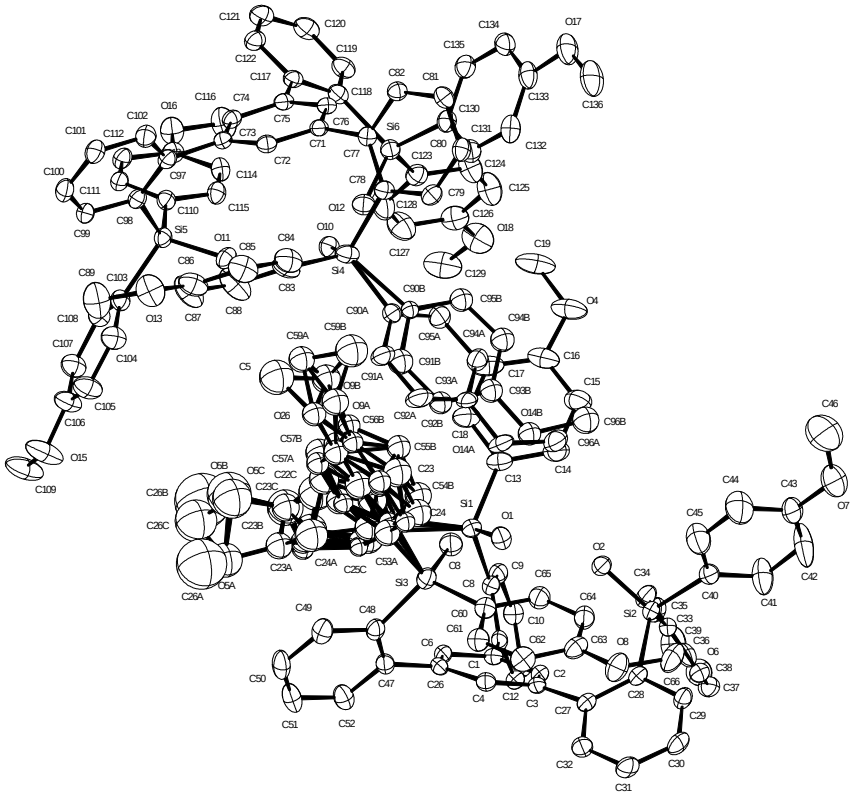


Figure S6. Structure of compound **11c** in the solid state, showing the two independent moleculesin the unit cell; hydrogen atoms omitted for clarity

X-ray Crystal Structure Analysis of Compound 11c: $C_{66}H_{60}O_9Si_3$, M_r = 1081.41 g · mol^{-1}, colourless prism, crystal size 0.21 x 0.20 x 0.10 mm^3, triclinic, space group $P\bar{1}$ [2], a = 14.3600(8) Å, b = 20.7942(18) Å, c = 23.1783(16) Å, α = 64.756(8)°, β = 77.870(5)°, γ = 78.137(7)°, V = 6067.6(9) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.184 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*α) = 0.133 mm^{-1}, analytical absorption correction (T_{min} = 0.98, T_{max} = 0.99), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Mo-anode X-ray source, 2.605 < θ < 27.500°, 76645 measured reflections, 27319 independent reflections, 18846 reflections with $I > 2\sigma(I)$, R_{int} = 0.0470, 1448 parameters, S = 1.030, residual electron density +1.7 (1.38 Å from O7) / –0.6 (0.71 Å from O5B) e · Å^{-3}. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.067 [$I > 2\sigma(I)$], wR_2 = 0.193. **CCDC-1987912**

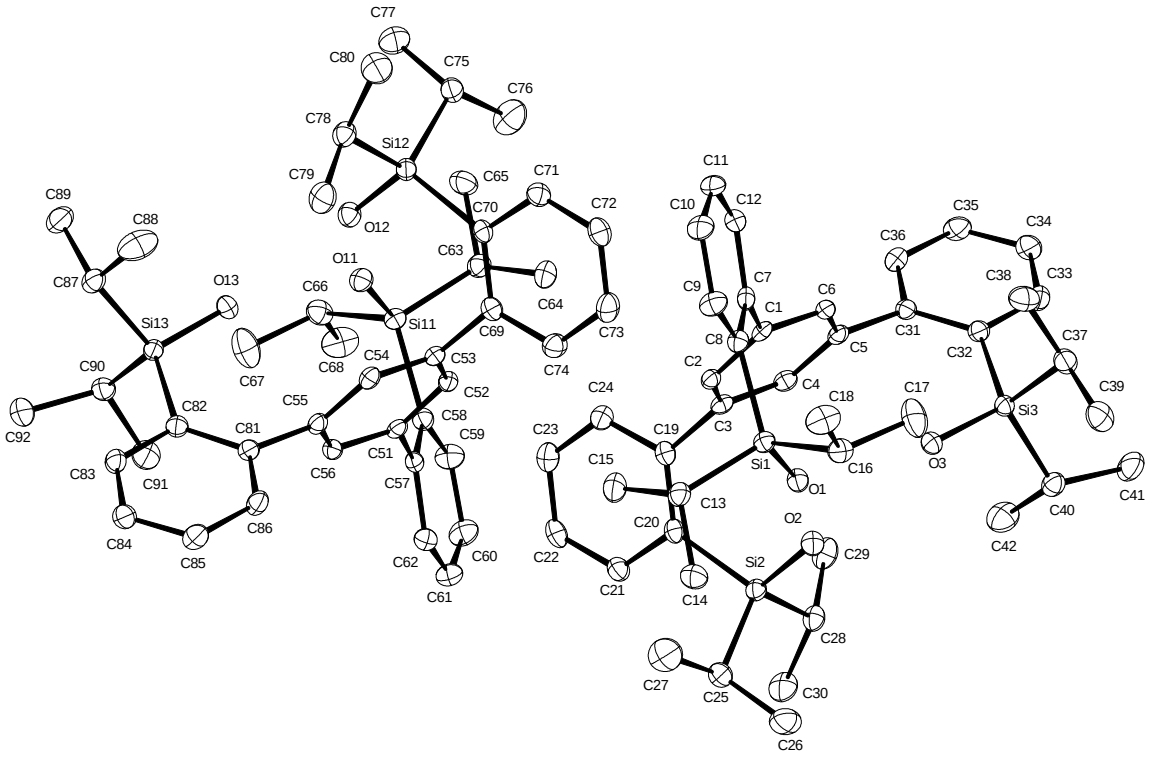


Figure S7. Structure of compound **11e** comprising two independent molecules in the unit cell, both of which show the "upward-inward" orientation of the three –OH groups; hydrogen atoms omitted for clarity

X-ray Crystal Structure Analysis of Compound 11e: $C_{42}H_{60}O_3Si_3$, M_r = 697.17 g · mol^{-1}, colourless block, crystal size 0.13 x 0.10 x 0.08 mm^3, monoclinic, space group $P2_1/c$ [14], a = 22.679(3) Å, b = 9.0827(6) Å, c = 39.202(6) Å, β = 90.474(11)°, V = 8074.9(16) Å^3, T = 100(2) K, Z = 8, D_{calc} = 1.147 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*α) = 0.153 mm^{-1}, analytical absorption correction (T_{min} = 0.98, T_{max} = 0.99), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Mo-anode X-ray source, 2.627 < θ < 33.100°, 161750 measured reflections, 30637 independent reflections, 14249 reflections with $I > 2\sigma(I)$, R_{int} = 0.1451, 913 parameters, S = 1.012, residual electron density +0.5 (0.83 Å from C90) / -0.4 (0.80 Å from Si12) e · Å^{-3}. The

structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.057 [$I > 2\sigma(I)$], wR_2 = 0.147. **CCDC-1987914**

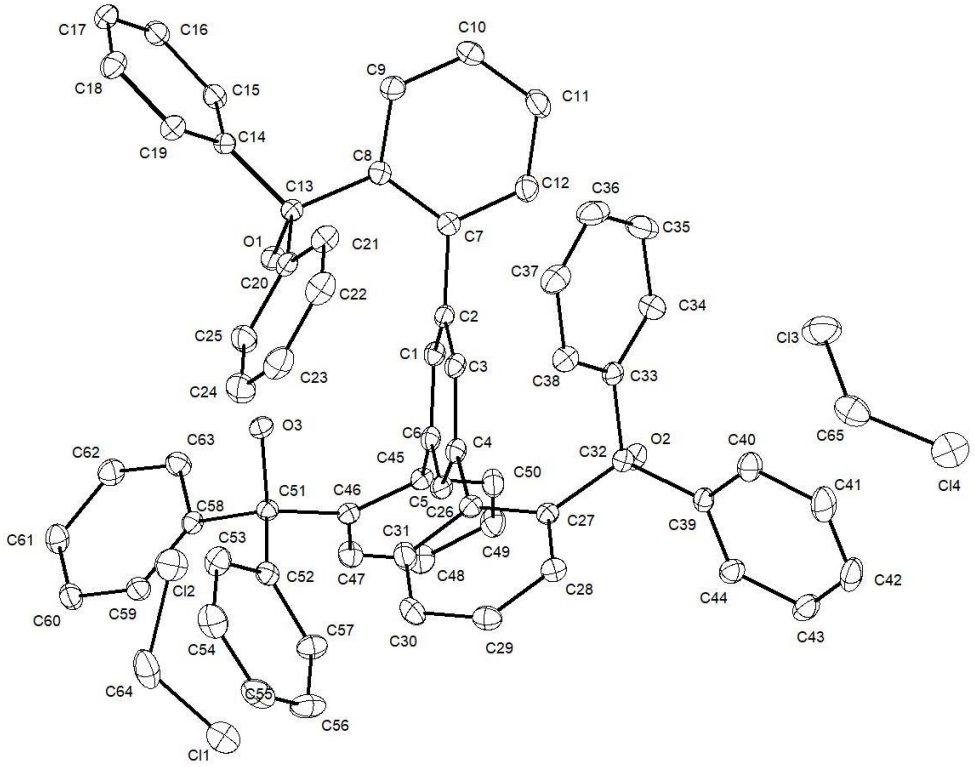


Figure S8. Structure of compound **12** in the solid state; hydrogen atoms omitted for clarity

X-ray Crystal Structure Analysis of Compound 12: $C_{65}H_{52}Cl_4O_3$, M_r = 1022.86 g · mol^{-1}, colourless block, crystal size 0.154 x 0.141 x 0.104 mm^3, triclinic, space group $P\bar{1}$ [2], a = 13.1915(14) Å, b = 13.5990(15) Å, c = 14.5650(15) Å, α = 88.176(5)°, β = 82.096(4)°, γ = 86.176(5)°, V = 2581.6(5) Å^3, T = 100(2) K, Z = 2, D_{calc} = 1.316 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.278 mm^{-1}, analytical absorption correction (T_{min} = 0.97, T_{max} = 0.98), Bruker-AXS Kappa Mach3 diffractometer with APEX-II detector and IμS micro focus X-ray source, 2.097 < θ < 30.508°, 85349 measured reflections, 15745 independent reflections, 12687 reflections with $I > 2\sigma(I)$, R_{int} = 0.0324. S = 1.026, 667 parameters, residual electron density +0.6 (0.82 Å from Cl2) / –0.9 (0.64 Å from Cl1) e · Å^{-3}. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.045 [$I > 2\sigma(I)$], wR_2 = 0.126. **CCDC-1987909**

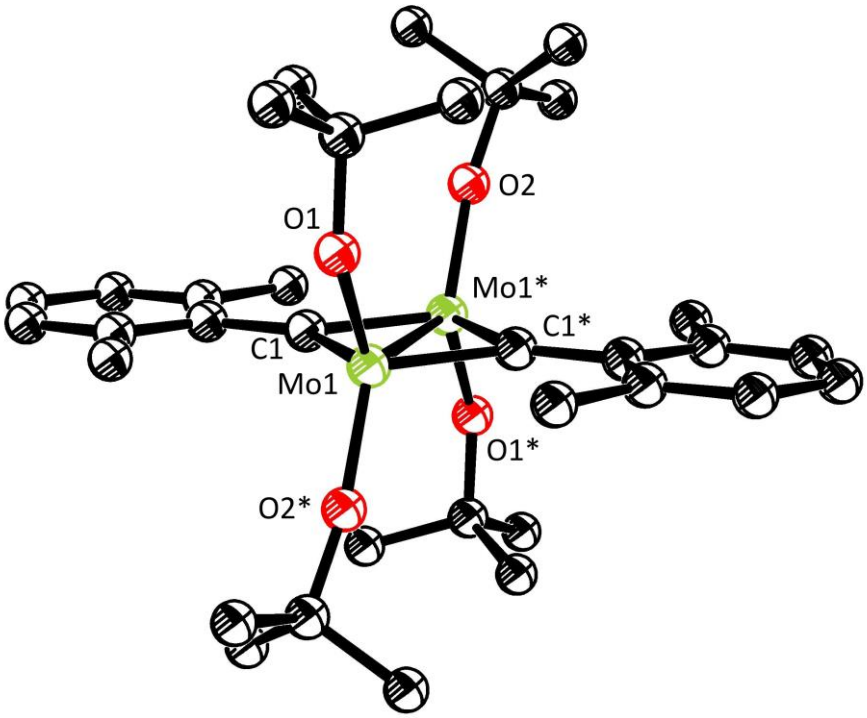


Figure S9. Structure of complex **15b** in the solid state, which was formed as a byproduct during the preparation of complex **14b**; hydrogen atoms omitted for clarity

X-ray Crystal Structure Analysis of Complex 15b: $C_{34}H_{54}Mo_2O_4$, M_r = 718.65 g · mol^{-1}, red needle, crystal size 0.06 x 0.03 x 0.01 mm^3, monoclinic, space group $P2_1/c$ [14], a = 9.096(4) Å, b = 16.677(16) Å, c = 11.573(11) Å, β = 105.59(6)°, V = 1691(2) Å^3, T = 100(2) K, Z = 2, D_{calc} = 1.411 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.775 mm^{-1}, analytical absorption correction (T_{min} = 0.96, T_{max} = 0.99), Bruker AXS Enraf-Nonius KappaCCD diffractometer with a FR591 rotating Mo-anode X-ray source, 2.626 < θ < 30.521°, 23980 measured reflections, 5156 independent reflections, 2934 reflections with $I > 2\sigma(I)$, R_{int} = 0.2246, 189 parameters, S = 1.022, residual electron density +1.0 (0.54 Å from N1) / –1.4 (0.74 Å from Mo1) e · Å^{-3}. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.067 [$I > 2\sigma(I)$], wR_2 = 0.171. **CCDC-1987917**

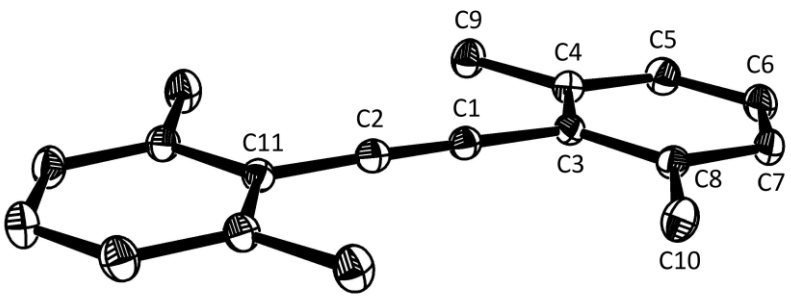


Figure S10. Structure of 1,2-bis(2,6-dimethylphenyl)ethyne in the solid state, which was formed as a byproduct during the preparation of complex **14b**; hydrogen atoms omitted for clarity

X-ray Crystal Structure Analysis of 1,2-Bis(2,6-dimethylphenyl)ethyne: $C_{18}H_{18}$, M_r = 234.32 g · mol^{-1}, light yellow needle, crystal size 0.120 x 0.045 x 0.031 mm^3, monoclinic, space group $P2_1/c$ [14], a = 5.6223(2) Å, b = 12.6521(5) Å, c = 18.5302(8) Å, β = 92.518(2)°, V = 1316.85(9) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.182 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.066 mm^{-1}, analytical absorption correction (T_{min} = 0.94, T_{max} = 0.98), Bruker-AXS Kappa Mach3 diffractometer with APEX-II detector and IμS micro focus X-ray source, 1.950 < θ < 31.447°, 44365 measured reflections, 4340 independent reflections, 3127 reflections with $I > 2\sigma(I)$, R_{int} = 0.0658, 167 parameters, S = 1.040, residual electron density +0.4 (0.70 Å from C11) / –0.3 (0.11 Å from H10B) e · Å^{-3}. The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 to R_1 = 0.050 [$I > 2\sigma(I)$], wR_2 = 0.153. **CCDC-1987915**

GENERAL

Unless stated otherwise, all reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O, 1,4-dioxane (Mg/anthracene), CH_2Cl_2, DME, MeCN (CaH_2), *n*-pentane, benzene, toluene (Na/K). Flash chromatography on silica gel (FC): Merck silica gel 60 (230–400 mesh). NMR: Spectra were acquired on Bruker AvanceIII 300, 400, 500 MHz and an Avance Neo 600 MHz NMR spectrometers in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C \equiv 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm; CD_2Cl_2: $\delta_C \equiv 53.8$ ppm; residual 1H: $\delta_H \equiv 5.32$ ppm; [D_8]-toluene: $\delta_C \equiv 20.7$ ppm; residual $D_5C_6CD_2H$: $\delta_H = 2.09$ ppm). IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or Mat 95 (Finnigan). Elemental analysis: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received, unless stated otherwise. Compounds **2a,**[1] **2b**,[2] and **13b**[2] were prepared as described in the literature. The molecular sieves used in this investigation were dried for 24 h at 150°C (sand bath) under vacuum prior to use and were stored and transferred under argon atmosphere.

^{95}Mo NMR spectra were acquired with the aring pulse sequence to minimize acoustic ringing from the NMR probe. The π/2 pulse was calibrated for a 2 M Na_2MoO_4 in D_2O and had a typical length of 22.5 µs at a power of 85W. Chemical shifts were referenced indirectly to the ^{1}H chemical shift of the solvent.[3] For broad signals high sample amount (>40 mg) were necessary. Dependent on the line width of the signal, 8000 to 150000 FID containing 8192 complex data points were averaged to obtain a reasonable signal-to-noise ratio. The acquisition time of a single FID was around 150 ms. The data was Fourier-transformed with zero-filling to 8192 data points and with a line broadening lb = 20 Hz, unless noted otherwise.

Data acquired on the AVneo 600 MHz NMR spectrometer was acquired with a Bruker BBO CryoProbe, which significantly reduced the measurement time of most of the spectra, especially the 1D ^{13}C NMR data.

Diffusion coefficients were obtained from a double stimulated echo sequence with bipolar gradient pulses, convection compensation, longitudinal eddy current delay (LED) and three spoiler gradients (Bruker sequence: dstebpgp3s). The gradient pulse strength G was incremented from 2% to 98% of the maximum G_{max} with a squared gradient ramp in 60 steps. The diffusion time (Δ) used was 71 ms and the length of a gradient pulse gradient pulse (δ/2) of the encoding gradient was 1.3 ms. The maximum gradient strength G_{max} of the NMR probe (PA BBO 400S1 BBF-H-D-05 Z PLUS) was 53.5 $G \cdot cm^{-1}$. Diffusion coefficients were obtained by averaging three diffusion coefficients obtained from fitting the signal decay of three different resonance integrals to the Stejskal-Tanner equation (I) in the Bruker TOPSPIN T1T2 relaxation module.

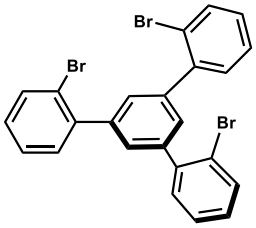
$$I(G) = I_0 e^{-D(\gamma G\delta)^2(\Delta-\delta/3)} \quad \text{(I)}$$

Diffusion values were predicted using an EXCEL spreadsheet Stokes−Einstein Gierer-Wirtz Estimation (SEGWE) method.[4]

EXPERIMENTAL DATA

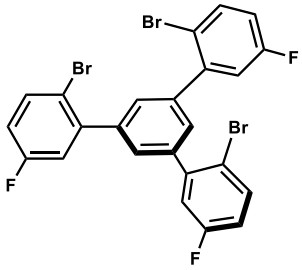
Preparation of the Ligands

1,3,4-Tris-2'-bromophenylbenzene (8a)



A two-necked, round-bottomed flask was equipped with a magnetic stir bar and a gas inlet connected to an argon-vacuum manifold. The flame-dried flask was filled with argon and charged with a solution of 2-bromoacetophenone (20.0 g, 100 mmol) in EtOH (164 mL). The flask was cooled to 0°C, connected to a bubbler containing aqueous KOH solution and silicon tetrachloride (34.5 mL, 301 mmol) was added dropwise over 1 min. The resulting yellow mixture was stirred for 1.5 h at 0°C and then allowed to warm to ambient temperature. After 24 h, the mixture was again cooled to 0°C and the reaction quenched with water (800 mL). The orange-yellow slurry obtained was extracted with $CHCl_3$ (3 x 250 mL). The combined extracts were dried over $MgSO_4$, filtered and concentrated in vacuo. The red syrup obtained was triturated with hexanes (100 mL) and filtered with suction to give the title compound as a yellow flaky solid (16 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (dd, *J* = 8.0, 1.2 Hz, 3H), 7.50 (s, 3H), 7.46 (dd, *J* = 7.6, 1.7 Hz, 3H), 7.38 (td, J = 7.5, 1.2 Hz, 3H), 7.22 (ddd, *J* = 8.0, 7.4, 1.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9, 140.4, 133.2, 131.5, 129.6, 128.9, 127.4, 122.7. The analytical and spectroscopic data are in agreement with those reported in the literature.[5]

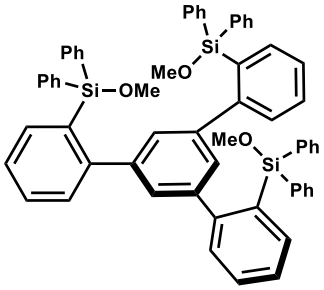
2,2''-Dibromo-5'-(2-bromo-5-fluorophenyl)-5,5''-difluoro-1,1':3',1''-terphenyl (8b)[6]



A two-necked, round-bottomed flask was equipped with a magnetic stir bar, a reflux condenser and a gas inlet connected to an argon-vacuum manifold. The flame-dried flask was filled with argon and charged with 2-bromo-5-fluoroacetophenone (1.00 g, 4.60 mmol). Trifluoromethanesulfonic acid (0.041 mL, 0.460 mmol) was added dropwise to the neat stirred solution at 23°C. The mixture was heated with stirring to 140°C for 6 h in a microwave oven. The black mixture was allowed to cool to ambient temperature, the reaction was quenched by adding water (20 mL) and mixture extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 95:5) to give the title compound as a yellow solid (0.50 g, 55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (dd, *J* = 8.8, 5.3 Hz, 3H), 7.48 (s, 3H), 7.18 (dd, *J* = 9.0, 3.1 Hz, 3H), 6.98 (ddd, *J* = 8.7, 7.8, 3.0 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –115.0. ^{13}C NMR (100 MHz, $CDCl_3$): δ =162.0 (d, *J* = 248.0 Hz), 143.4 (d, *J* = 8.0 Hz), 134.6 (d, *J* = 8.1 Hz), 118.6 (d, *J* = 23.0 Hz), 117.0 (d, *J* = 3.2 Hz), 116.5 (d, *J* = 22.2 Hz). IR (film): $\tilde{\nu}$ 3067, 2921, 2854, 1876, 1748, 1573, 1594, 1471, 1429, 1405, 1380, 1330, 1256, 1284, 1175, 1195, 1117, 1089, 1069, 1030, 950, 907, 871, 811, 732, 759, 705, 716, 651, 666, 602, 628, 592, 526, 460, 436,419 cm^{-1}. HRMS-ESI (m/z): calculated for $C_{24}H_{12}Br_3F_3Na^+$ $[M+Na]^+$, 593.84416; found, 593.84402. The analytical and spectroscopic data are in agreement with those reported in the literature.[6]

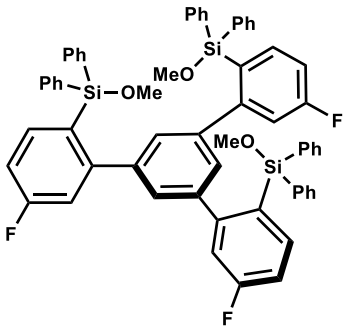
CAUTION: **This and other experiments described below require pyrophoric materials (*tert*-butyllithium) which must be handled and disposed with great care! Likewise, quenching of the reactions can be dangerous. Especially when carried out on large scale, the use of either isopropanol in heptanes (2 M) or of dry CO_2 as quenching agent is recommended.**

(5'-(2-(Methoxydiphenylsilyl)phenyl)-[1,1':3',1''-terphenyl]-2,2''-diyl)bis(methoxydiphenylsilane) (9a)



A three-necked, round-bottomed flask was equipped with a magnetic stir bar and a gas inlet connected to an argon-vacuum manifold. The flame-dried flask was filled with argon and charged with 1,3,4-tris-2'-bromophenylbenzene (**8a**) (4.00 g, 7.37 mmol). Et_2O (90 mL) was added and the stirred suspension was cooled to −125°C. A solution of *tert*-butyllithium (28.3 mL, 45.3 mmol, 1.7 M in *n*-pentane) was added over 10 min while the suspension was stirring. The mixture was allowed to warm to ambient temperature and stirring was continued for 1.5 h. The obtained brown suspension was again cooled to −125°C and a solution of diphenyldimethoxysilane (5.17 mL, 22.1 mmol) in Et_2O (30 mL) was added dropwise over 15 min. The reaction mixture was allowed to warm to ambient temperature and stirred for 12 h. The reaction was carefully quenched with water and the mixture was transferred into a separation funnel. The organic phase was separated and the aqueous solution was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Hexanes (50 mL) was added to precipitate the title compound as a white solid (7.53 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 (dd, *J* = 7.4, 1.4 Hz, 3H), 7.38 (td, *J* = 7.5, 1.5 Hz, 3H), 7.35 (dd, *J* = 7.6, 1.3 Hz, 12H), 7.30 (td, *J* = 7.4, 1.3 Hz, 3H), 7.24 (tt, *J* = 7.4, 1.4 Hz, 6H), 7.14 (t, *J* = 7.5, 7.1 Hz, 12H), 6.98 (dd, *J* = 7.6, 1.3 Hz, 3H), 6.95 (s, 3H), 3.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 149.6, 141.5, 137.3, 135.2, 135.1, 131.6, 130.9, 129.6, 129.4, 129.2, 127.5, 125.7, 50.9. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = −11.6. IR (film): $\tilde{\nu}$ 3045, 2930, 2830, 1582, 1557, 1471, 1427, 1409, 1263, 1183, 1108, 1082, 998, 877, 830, 760, 735, 697, 621, 499, 477, 411 cm^{-1}. HRMS-ESI (m/z): calc'd. for $C_{36}H_{54}O_3Si_3Na^+$ $[M+Na]^+$, 965.32730; found, 965.32862.

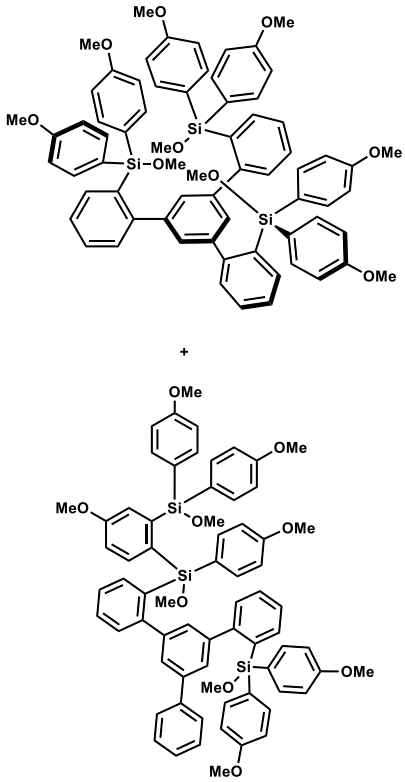
(5,5''-Difluoro-5'-(5-fluoro-2-(methoxydiphenylsilyl)phenyl)-[1,1':3',1''-terphenyl]-2,2''-diyl)bis-(methoxydiphenylsilane) (9b)



A three-necked, round-bottomed flask was equipped with a magnetic stir bar and a gas inlet connected to an argon-vacuum manifold. The flame-dried flask was filled with argon and charged with 2,2''-dibromo-5'-(2-bromo-5-fluorophenyl)-5,5''-difluoro-1,1':3',1''-terphenyl (**8b**) (0.50 g, 0.837 mmol). Et_2O (23 mL) was added and the stirred suspension was cooled to –125°C. A solution of *tert*-butyllithium (3.00 mL, 5.15 mmol, 1.7 M in *n*-pentane) was added over 10 min while the suspension was stirring. The mixture was allowed to warm to ambient temperature and stirring was continued for 1.5 h. The obtained brown suspension was again cooled to −125°C and a solution of diphenyldimethoxysilan (0.57 mL, 2.51 mmol) in Et_2O (8 mL) was added dropwise over 15 min. The reaction mixture was allowed to warm to ambient temperature and stirred for 12 h. The reaction was carefully quenched with water and the resulting mixture was transferred into a separation funnel. The organic phase was separated and the aqueous solution was extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried over $MgSO_4$,

filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 95:5) to give the title compound as a white solid (0.80 g, 86%). ^{1}H NMR (500 MHz, C_6D_6): δ =7.64 (dd, *J* = 8.4, 6.6 Hz, 3H), 7.50 – 7.45 (m, 12H), 7.17 (s, 3H), 7.13 – 7.09 (m, 6H), 7.09 – 7.04 (m, 12H), 7.02 (dd, *J* = 10.2, 2.6 Hz, 3H), 6.83 (td, *J* = 8.5, 2.6 Hz, 3H), 3.00 (s, 9H). ^{19}F NMR (470 MHz, C_6D_6): δ = −111.0. ^{13}C NMR (126 MHz, C_6D_6): δ = 164.1 (d, *J* = 249.9 Hz), 152.3 (d, *J* = 7.5 Hz), 140.7 (d, *J* = 1.8 Hz), 140.0 (d, *J* = 7.9 Hz), 118.1 (d, *J* = 20.1 Hz), 112.9 (d, *J* = 19.2 Hz). ^{29}Si NMR (99 MHz, C_6D_6): δ = −11.5. IR (film): *ṽ* 3068, 3011, 2933, 2833, 1568, 1588, 1473, 1427, 1376, 1329, 1276, 1224, 1172, 1082, 1108, 1055, 1029, 998, 952, 870, 894, 820, 772, 736, 698, 687, 618, 633, 643, 569, 495, 442, 421 cm^{-1}. HRMS-ESI (m/z): calculated for $C_{63}H_{51}F_3O_3Si_3Na^+$ [M+Na]$^+$, 1019.29904; found, 1019.29849.

(5'-(2-(Methoxybis(4-methoxyphenyl)silyl)phenyl)-[1,1':3',1''-terphenyl]-2,2''-diyl)bis(methoxybis(4-methoxyphenyl)silane) (9c)

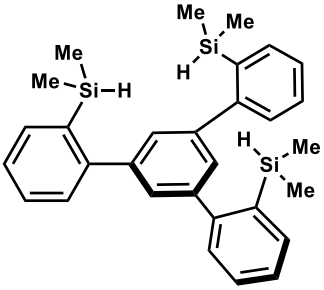


A three-necked, round-bottomed flask was equipped with a magnetic stir bar and a gas inlet connected to an argon-vacuum manifold. The flame-dried flask was filled with argon and charged with 1,3,4-tris-2'-bromophenylbenzene (**8a**) (1.63 g, 3.00 mmol). Diethyl ether (60 mL) was added and the stirred suspension was cooled to −125°C. A solution of *tert*-butyllithium (10.9 mL, 18.5 mmol, 1.7 M in pentane) was added over 10 min while the suspension was stirring. The mixture was allowed to warm to ambient temperature and stirring was continued for 1.5 h. The obtained brown suspension was again cooled to −125°C and a solution of dimethoxybis(4-methoxyphenyl)silane (4.30 g, 14.1 mmol)[1] in diethyl ether (5 mL) was added dropwise over 15 min. The reaction mixture was allowed to warm to ambient temperature. After stirring for 8 h, the mixture was carefully quenched with water and was transferred into a separation funnel. The organic phase was separated and the aqueous solution extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by high-performance liquid chromatography with MeCN as the eluent to afford compound **9c** as a white solid (400 mg, 12%) as well as a constitutional isomer **S1** (1.63 g, 47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 – 7.62 (m, 3H), 7.37 (td, *J* = 7.5, 1.6 Hz, 3H), 7.31 (dd, *J* = 7.4, 1.3 Hz, 3H), 7.27 – 7.23 (m, 12H), 6.99 – 6.95 (m, 3H), 6.92 (s, 3H), 6.70 – 6.64 (m, 12H), 3.71 (s, 18H), 3.00 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 160.7, 149.8, 141.6, 137.3, 136.9, 132.6, 131.0, 129.6, 129.3, 126.4, 125.7, 113.3, 55.0, 50.8. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = −11.3. IR (film): *ṽ* 2932, 2832, 1592, 1562, 1501, 1461, 1440, 1398, 1276, 1244, 1178, 1027, 815, 797, 719, 689, 649, 629, 609, 531, 463 cm^{-1}. HRMS-ESI (*m/z*): calcd. for $C_{69}H_{66}O_9Si_3Na^+$ [M+Na]$^+$, 1145.39069; found, 1145.39091.

Data of the constitutional isomer **S1**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (ddd, *J* = 7.4, 1.6, 0.7 Hz, 1H), 7.60 (dd, *J* = 7.0, 1.9 Hz, 1H), 7.41 (tdd, *J* = 7.4, 1.4, 0.6 Hz, 1H), 7.38 – 7.30 (m, 7H), 7.30 – 7.22 (m, 6H), 7.22 – 7.15 (m, 4H), 7.10 (t, *J* = 7.6 Hz, 2H), 7.04 – 7.02 (m, 1H), 6.97 (td, *J* = 1.7, 0.7 Hz, 1H), 6.83 – 6.76 (m, 7H), 6.72 – 6.69 (m, 2H), 6.68 – 6.64 (m, 3H), 6.59 – 6.56 (m, 1H), 6.55 (dd, *J* = 2.7, 0.6 Hz, 1H), 6.54 – 6.53 (m, 0H), 6.51 (s, 3H), 3.82 (d, *J* = 0.4 Hz, 3H), 3.76 – 3.75 (m, 6H), 3.74 (d, *J* = 0.4 Hz, 3H), 3.69 (s,

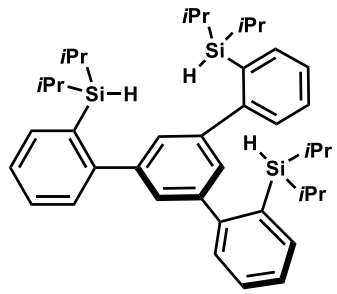
3H), 3.59 (d, *J* = 0.5 Hz, 3H), 3.36 (d, *J* = 0.7 Hz, 3H), 2.92 (s, 3H), 2.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 160.8, 160.7, 160.7, 160.5, 160.4, 160.3, 158.9, 149.8, 148.8, 143.8, 143.7, 142.8, 140.2, 139.2, 138.3, 137.9, 137.6, 137.3, 137.0, 137.0, 137.0, 137.0, 136.9, 136.8, 136.8, 136.5, 135.3, 133.2, 130.1, 129.8, 129.5, 129.1, 129.0, 129.0, 129.0, 128.4, 128.3, 128.2, 128.2, 128.1, 126.8, 126.7, 126.6, 126.4, 126.3, 126.3, 126.0, 125.7, 125.6, 125.6, 125.3, 123.2, 113.4, 113.4, 113.4, 113.2, 113.0, 113.0, 112.7, 77.3, 77.0, 76.8, 72.8, 54.9, 54.9, 54.9, 54.9, 54.9, 54.8, 54.8, 54.8, 54.8, 54.8, 54.8, 54.8, 54.6, 54.6, 54.6, 54.6, 51.0, 51.0, 51.0, 50.8, 50.8, 50.6, 49.5, 27.0, 27.0, 27.0, 27.0, 27.0, 27.0, 27.0, 27.0, 21.5. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = –11.1, –11.3, –11.7. HRMS-ESI (m/z): calcd. for $C_{69}H_{66}O_9Si_3Na^+$ $[M+Na]^+$, 1145.39069; found, 1145.39080.

(5'-(2-(Dimethylsilyl)phenyl)-[1,1':3',1''-terphenyl]-2,2''-diyl)bis(dimethylsilane) (10d)



A two-necked, round-bottomed flask was equipped with a magnetic stir bar and a gas inlet connected to an argon-vacuum manifold. The flame-dried flask was filled with argon and charged with 1,3,4-tris-2'-bromophenylbenzene (**8a**) (1.00 g, 1.84 mmol) and Et_2O (39 mL). The resulting mixture was cooled to −125°C. A solution of *tert*-butyllithium (7.08 mL, 11.3 mmol, 1.7 M in *n*-pentane) was added dropwise and the resulting mixture was allowed to warm to ambient temperature. After stirring at ambient temperature for 1 h, the mixture was cooled to −125°C and dimethylchlorosilane (1.29 mL, 11.1 mmol) was added dropwise. The mixture was allowed to warm to ambient temperature and stirred overnight. The reaction was carefully quenched with water and the solvent was removed *in vacuo*. The residue was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 4:1) to give the title compound as a pale yellow foam (807 mg, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): 7.55 – 7.50 (m, 3H), 7.36 – 7.30 (m, 3H), 7.28 – 7.24 (m, 8H), 7.16 (s, 3H), 4.34 (hept, *J* = 3.8 Hz, 3H), 0.05 (d, *J* = 3.8 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.94, 143.03, 135.84, 135.03, 129.41, 129.11, 128.81, 126.44, - 2.80. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = –19.1. IR (film): ṽ 3051, 2956, 2117, 1583, 1558, 1468, 1409, 1247, 1124, 1100, 1063, 893, 833, 967, 707, 524, 426, 448 cm^{-1}. HRMS-ESI (m/z): calculated for $C_{30}H_{36}Si_3$ $[M]^{\cdot+}$,480.21229; found, 480.21249.

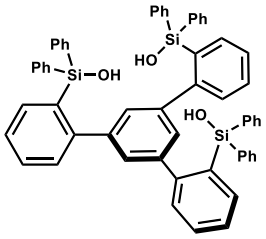
5'-(2-(Diisopropylsilyl)phenyl)-[1,1':3',1''-terphenyl]-2,2''-diyl)bis(diisopropylsilane) (10e)



A two-necked, round-bottomed flask was equipped with a magnetic stir bar and a gas inlet connected to an argon-vacuum manifold. The flame-dried flask was filled with argon and charged with 1,3,4-tris-2'-bromophenylbenzene (**8a**) (1.50 g, 2.57 mmol) and Et_2O (58 mL). The resulting mixture was cooled to −125°C and a solution of *tert*-butyllithium (10.6 mL, 17.0 mmol, 1.7 M in *n*-pentane) was added dropwise. The reaction mixture was allowed to warm to ambient temperature and stirring continued for 1 h. After cooling to −125°C, diisopropylchlorosilane (2.92 mL, 16.6 mmol) was added dropwise and the resulting mixture was allowed to warm to ambient temperature while stirring overnight. The reaction was carefully quenched with water, the solvent was removed *in vacuo*, and the residue was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 4:1) to give the title compound as a pale yellow foam (1.50 g, 81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (ddd, *J* = 7.3, 1.5, 0.6 Hz, 3H), 7.41 (td, *J* = 7.7, 7.1, 1.5 Hz, 3H), 7.36 (ddd, *J* = 7.7, 1.5, 0.6 Hz, 3H), 7.32 (td, *J* = 7.3, 1.5 Hz, 3H), 7.20 (s, 3H), 3.87 (t, *J* = 3.7 Hz, 3H), 1.07 (heptd, *J* = 7.2, 3.7 Hz, 6H), 0.95 (d, *J* = 7.2 Hz, 18H), 0.89 (d, *J* = 7.3 Hz, 18H). ^{13}C

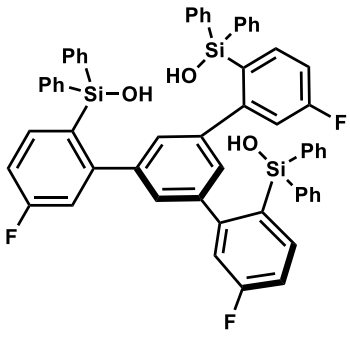
NMR (126 MHz, $CDCl_3$): δ = 149.7, 142.6, 135.8, 129.6, 129.4, 128.7, 125.9, 77.2, 77.0, 76.7, 19.2, 18.9, 11.6. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = 2.1. IR (film): ῦ 3051, 2939, 2889, 2862, 2132, 1583, 1557, 1461, 1409, 1383, 1364, 1259, 1122, 1098, 1065, 1001, 919, 877, 811, 773, 734, 686, 656, 631, 603, 527, 481, 458 cm^{-1}. HRMS-ESI (m/z): calculated for $C_{42}H_{61}Si_3$ $[M+H]^+$, 649.40756; found, 649.40680.

Ligand 11a



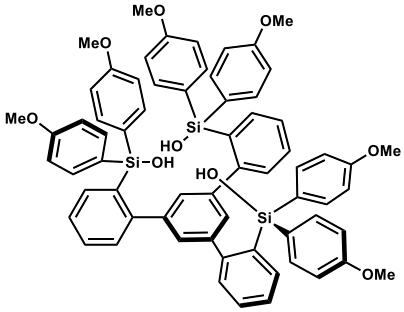
A two-necked, round-bottomed flask was equipped with a magnetic stir bar and a dropping funnel. The flask was charged with compound **9a** (4.97 g, 5.27 mmol) and THF (120 mL). The solution was cooled to 0°C before concentrated aqueous HCl (39.5 mL, 474 mmol) was added dropwise. The mixture was allowed to warm to ambient temperature and stirring was continued for 1 h. After cooling to 0°C, the mixture was carefully neutralized by dropwise addition of saturated aqueous $NaHCO_3$ solution. The organic phase was separated and the aqueous solution extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were washed with water (200 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the title compound as a white solid (4.74 g, quant.). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.55 – 7.51 (m, 12H), 7.48 – 7.43 (m, 3H), 7.30 – 7.22 (m, 12H), 7.21 – 7.13 (m, 12H), 6.92 – 6.87 (m, 6H), 4.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 149.0, 143.8, 137.5, 137.0, 134.6, 133.9, 130.1, 129.7, 129.4, 128.6, 127.9, 126.0. IR (film): *ῦ* 3046, 1582, 1471, 1427, 1263, 1204, 1112, 1087, 997, 900, 824, 762, 735, 698, 622, 471, 411 cm^{-1}. HRMS-ESI (*m/z*): calcd. for $C_{60}H_{48}O_3Si_3Na^+$ $[M+Na]^+$, 923.28035; found, 923.28182.

Ligand 11b



A two-necked, round-bottomed flask was equipped with a magnetic stir bar and a dropping funnel. The flask was charged with compound **9b** (200 mg, 0.201 mmol) and THF (3 mL). The solution was cooled to 0°C before concentrated aqueous HCl (0.5 mL, 6.02 mmol) was added dropwise. The mixture was allowed to warm to ambient temperature and stirring was continued for 1.5 h. After cooling to 0°C, the mixture was carefully neutralized by adding saturated aqueous $NaHCO_3$ solution. The organic phase was separated and the aqueous solution was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with water (20 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the title compound as a white solid (150 mg, 78%). ^1H NMR (500 MHz, $[D_7]$-DMF): δ = 7.49 (dd, *J* = 8.5, 6.6 Hz, 3H), 7.49 – 7.45 (m, 12H), 7.38 – 7.33 (m, 6H), 7.32 – 7.26 (m, 12H), 7.20 (td, *J* = 8.9, 8.4, 2.6 Hz, 3H), 6.88 (s, 3H), 6.69 (dd, *J* = 10.2, 2.6 Hz, 3H), 6.65 (s, 3H). ^{19}F NMR (470 MHz, $[D_7]$-DMF): δ = −112.6. ^{13}C NMR (126 MHz, $[D_7]$-DMF): δ = 163.5 (d, *J* = 248.4 Hz), 151.8 (d, *J* = 7.4 Hz), 141.3, 139.3 (d, *J* = 8.1 Hz), 137.7, 134.5, 130.7 (d, *J* = 3.4 Hz), 129.5, 128.8, 127.7, 116.9 (d, *J* = 20.2 Hz), 112.9 (d, *J* = 19.4 Hz). ^{29}Si NMR (99 MHz, $[D_7]$-DMF): δ = -16.0. IR (film): *ῦ* 3407, 3067, 3018, 1737, 1588, 1569, 1475, 1428, 1380, 1329, 1307, 1276, 1262, 1249, 1228, 1186, 1174, 1112, 1091, 1054, 1028, 998, 954, 918, 872, 860, 814, 762, 740, 700, 660, 641, 634, 614, 573, 493, 416 cm^{-1}. HRMS-ESI (m/z): calculated for $C_{60}H_{44}F_3O_3Si_3^-$ $[M-H]^-$, 953.25559; found, 953.25501.

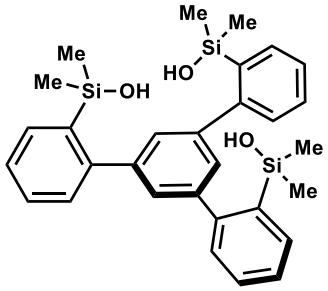
Ligand 11c



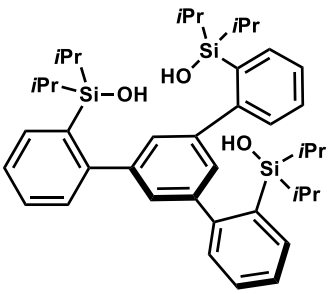
A two-necked, round-bottomed flask was equipped with a magnetic stir bar and a dropping funnel. The flask was charged with compound **8a** (400 mg, 2.22 mmol) and THF (7.6 mL). The resulting solution was cooled to 0°C before concentrated aqueous HCl (2.60 mL, 31.2 mmol) was added dropwise. The mixture was allowed to warm to ambient temperature and stirring was continued for 1 h. After cooling to 0°C, the solution was carefully neutralized by dropwise addition of saturated aqueous $NaHCO_3$. The organic phase was separated and the aqueous solution was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with water (50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the title compound as a white solid (380 mg, 99%). Colorless crystals suitable for single-crystal X-ray diffraction were grown by storing a concentrated toluene solution at 5°C for three days. M. p. = 250–253°C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 – 7.45 (m, 3H), 7.45 – 7.42 (m, 12H), 7.28 – 7.25 (m, 6H), 6.92 (d, *J* = 7.0 Hz, 6H), 6.72 – 6.68 (m, 12H), 3.74 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 160.7, 148.9, 143.5, 137.3, 136.0, 134.7, 129.7, 129.3, 128.5, 128.3, 125.7, 113.4, 54.9. The analytical and spectroscopic data are in agreement with those reported in the literature.[1]

Ligand 11d

A one-neck round bottomed flask equipped with a stir bar was charged with compound **10d** (1.00 g, 2.08 mmol) and CH_2Cl_2 (28 mL). The resulting mixture was cooled to 0°C. *m*CPBA (1.54 g, 6.86 mmol, 77% w/w) was added portionwise and the resulting mixture stirred at ambient temperature for 4 h. The mixture was diluted with CH_2Cl_2 (370 mL), carefully transferred to a separation funnel, and washed with sat. $NaHCO_3$ (3 x 150 mL) and brine (3 x 100 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the title compound as a pale colorless fluffy solid (1.03 g, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.4 Hz, 3H), 7.43 – 7.34 (m, 6H), 7.33 – 7.28 (m, 6H), 3.30 (s, 3H), 0.31 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.9, 143.8, 137.9, 134.2, 129.6, 128.9, 127.9, 126.4, 2.1. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = 6.9. IR (film): ṽ 3262, 3050, 2898, 1699, 1558, 1409, 1430, 1408, 1252, 1161, 1126, 1065, 830, 778, 759, 694, 664, 623, 580, 530, 460, 440 cm^{-1}. HRMS-ESI (m/z): calculated for $C_{30}H_{35}O_3Si_3^-$[M-H]$^-$, 527.18996; found, 527.19076.



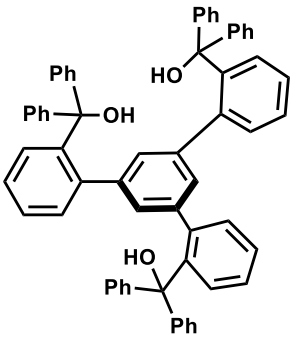
Ligand 11e



A round bottomed flask equipped with a stir bar was charged with compound **10e** (843 mg, 1.30 mmol) and THF (14 mL). *m*CPBA (1.75 g, 7.79 mmol, 77% *w/w*) was added portionwise and the resulting mixture was stirred at ambient temperature overnight before it was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 4:1) to give the title compound as a white powdery solid (786 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (dd, *J* = 7.4, 1.6 Hz, 3H), 7.40 – 7.29 (m, 6H), 7.29 – 7.25 (m, 3H), 7.21 (s, 3H), 2.97 (s, 3H), 1.12 (ddt, *J* = 13.5, 8.4, 6.5 Hz, 6H), 0.99 (d, *J* = 7.2 Hz, 18H), 0.95 (d, *J* = 7.4 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.3, 143.6, 135.0, 134.3, 130.2, 128.5,

127.7, 126.0, 18.1, 17.9, 14.1. ^{29}Si NMR (99 MHz, $CDCl_3$): δ = 7.7. IR (film): ṽ 3473, 3044, 2943, 2864, 2182, 2021, 1966, 1583, 1557, 1462, 1410, 1381, 1363, 1259, 1242, 1023, 1088, 1064, 997, 950, 919, 884, 760, 740, 738, 720, 653, 633, 495, 467 cm^{-1}. HRMS-ESI (m/z): calculated for $C_{42}H_{59}O_3Si_3^-$[M-H]$^-$, 695.37776; found, 695.37766.

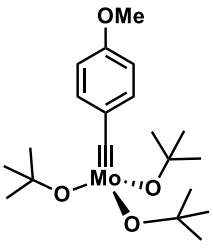
Ligand 12



A two-necked, round-bottomed flask was equipped with a magnetic stir bar and a gas inlet connected to an argon-vacuum manifold. The flame-dried flask was filled with argon and charged with compound **8a** (2.00 g, 3.86 mmol). Et_2O (78 mL) was added and the resulting bright yellow mixture was cooled to –125°C. A solution of *tert*-butyllithium (14.2 mL, 22.6 mmol, 1.6 M in *n*-pentane) was added over 10 min and the mixture was allowed to warm to ambient temperature. After stirring for another 1 h, the heterogeneous dark brown mixture was again cooled to –125°C. A solution of benzophenone (2.01 g, 11.0 mmol) in Et_2O (10 mL) was added and the resulting mixture was allowed to warm to ambient temperature while stirring overnight. The reaction was carefully quenched with water and the solution transferred into a separation funnel. The organic phase was separated and the aqueous solution was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by trituration with ice-cold MeOH (3 x 20 mL) to afford the title compound as a pale pink powdery solid (2.46 g, 78%). ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.25 (m, 8H), 7.21 (m, 4H), 7.18 (m, 4H), 7.12 (m, 12H), 7.04 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 4H), 6.95 (d, *J* = 7.7 Hz, 4H), 6.91 (d, *J* = 7.4 Hz, 2H), 6.59 (d, *J* = 7.9 Hz, 2H), 6.45 (d, *J* = 7.9 Hz, 1H), 6.04 (d, *J* = 7.5 Hz, 1H), 5.62 (d, *J* = 1.6 Hz, 2H), 3.25 (s, 2H), 2.81 (s, 1H). ^{13}C NMR (151 MHz, CD_2Cl_2): δ = 147.6, 147.5, 147.1, 144.4, 143.9, 141.2, 140.7, 139.3, 139.2, 133.8, 132.5, 129.9, 129.6, 129.4, 129.2, 128.2, 127.9, 127.9, 127.8, 127.6, 127.4, 127.3, 127.1, 127.0, 126.8, 126.3, 126.1, 126.0, 83.0, 82.9. IR (film): *ṽ* 3537, 3057, 1980, 1587, 147, 1445, 1414, 1317, 1262, 1154, 1014, 896, 750, 728, 706, 636, 583, 508, 446, 416 cm^{-1}. HRMS-ESI (m/z): calculated for $C_{63}H_{48}O_3Na^+$ [M+Na]$^+$, 875.34956; found, 875.34907.

Preparation of the Complexes

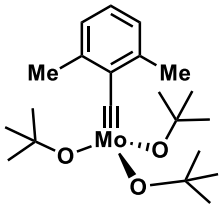
Complex 14a



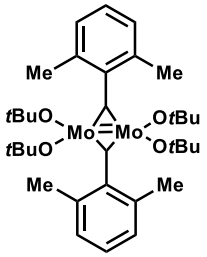
A 250 mL Schlenk flask was equipped with a magnetic stir bar and was flame dried under vacuum. The flask was filled with argon and charged with Mo(≡CAr)Br_3(dme) (**13a**, Ar = 4-methoxyphenyl) (3.02 g, 5.55 mmol) and THF (62 mL). A solution of NaOtBu (1.62 g, 16.5 mmol) in THF (15 mL) was added dropwise at ambient temperature and stirring was continued for 14 h before the solvent was removed *in vacuo* to obtain a dark brown solid. A second, flame dried 250 mL Schlenk flask was equipped with a magnetic stir bar and a Celite® (2 cm) packed argon frit. The dark brown solid was suspended in *n*-pentane (4 x 20 mL) and was filtered through the Celite® pad. The resulting filtrate was concentrated and the residue dried under vacuum (10^{-3} mbar) to give complex **14a** as a brown sticky solid (2.00 g, 83%) free of any residual THF. ^{1}H NMR (400 MHz, $C_6D_5CD_3$): δ = 7.44 – 7.35 (m, 2H), 6.77 – 6.49 (m, 2H), 3.26 (s, 3H), 1.51 (s, 27H). ^{13}C NMR (101 MHz, $C_6D_5CD_3$): δ = 276.0, 158.2, 140.4, 130.8, 113.1, 79.5, 54.2, 32.4. ^{95}Mo NMR (26 MHz, 60°C, $C_6D_5CD_3$): δ = 79.6. IR (film): *ṽ* 2969, 1595, 1502, 1466, 1358,

1281, 1244, 1166, 1037, 933, 827, 785, 585, 562, 503, 480 cm^{-1}. HRMS-EI (m/z): calculated for $C_{20}H_{34}MoO_4^+$ $[M]^+$, 436.15122; found, 436.15181. The analytical and spectroscopic data are in agreement with those reported in the literature.[1]

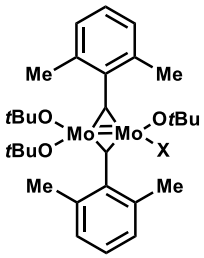
Complexes 14b and 15b



A 250 mL Schlenk flask was equipped with a magnetic stir bar and was flame dried under vacuum. The flask was filled with argon and charged with Mo(≡CAr)Br_3(dme) (**13b**, Ar = 2,6-dimethylphenyl) (1.05 g, 1.93 mmol)[2] and THF (21 mL). A solution of NaOtBu (563 mg, 5.74 mmol) in THF (5 mL) was added dropwise at 23°C and stirring was continued for 14 h before the solvent was removed *in vacuo* to obtain a dark brown solid. A second, flame dried 250 mL Schlenk flask was equipped with a magnetic stir bar and a Celite® (2 cm) packed argon frit. The dark brown solid was suspended in *n*-pentane (4 x 15 mL) and was filtered through the Celite® pad. The resulting filtrate was concentrated and the residue dried under vacuum (10^{-3} mbar) to give complex **14b** as a brown solid containing 1,2-bis(2,6-dimethylphenyl)ethyne and dinuclear complex **15b** (769 mg, 92%). The mixture was dissolved in minimum of *n*-pentane (20 mL) and filtered via cannula into a flame dried 50 mL Schlenk flask under Ar. The brown/purple solution was stored for 6 h on dry ice (–85°C) to give red/purple crystals. The brown supernatant solution was filtered off via cannula and the solvent of this solution was removed *in vacuo* to give pure complex **14b**. ^{1}H NMR (400 MHz, C_6D_6): δ = 6.90 (dd, *J* = 7.3, 0.8 Hz, 2H), 6.80 (dd, *J* = 8.2, 6.8 Hz, 2H), 2.86 (s, 6H), 1.44 (s, 27H). ^{13}C NMR (101 MHz, C_6D_6): δ = 297.1, 145.5, 139.4, 127.4, 127.1, 78.7, 33.2, 32.3. IR (film): $\tilde{\nu}$ 2969, 2923, 1461, 1359, 1383, 1236, 1162, 1099, 1025, 946, 895, 765, 788, 732, 640, 575, 591, 475, 412 cm^{-1}. Elemental analysis (%) calculated for $C_{21}H_{36}MoO_3$: C 58.32, H 8.39, Mo 22.19; found: C 58.32, H 8.66, Mo 21.77. HRMS: not detectable (decomp.).



and

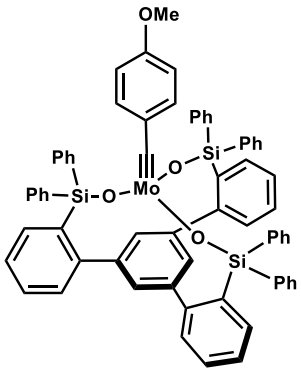


The remaining red/purple crystals were redissolved in Et_2O (5 mL) and the concentrated Et_2O solution was filtered via cannula into a 10 mL Schlenk flask. This solution was cooled from ambient temperature to –75°C over 10 h to give red crystals suitable for single-crystal X-ray diffraction. NMR spectroscopy confirmed the dinuclear complex **15b** but it was also observed that a chemically very similar unsymmetric complex was also present in solution. Also free *tert*-butanol as well as 1,2-bis(2,6-dimethylphenyl)ethyne were present in solution. Symmetric dinuclear complex **15b**: ^{1}H NMR (600 MHz, $C_6D_5CD_3$): δ = 7.18 (m, 4H), 7.02 (m, 2H), 2.98 (s, 12H), 0.98 (s, 36H). ^{13}C NMR (151 MHz, $C_6D_5CD_3$): δ = 341.3, 151.4, 131.9, 128.6, 126.6, 80.8, 31.9, 24.7. HRMS was not detectable (decomposition observed). Unsymmetric dinuclear complex: ^{1}H NMR (400 MHz, $C_6D_5CD_3$): δ = 7.18 (m, 4H), 7.05 (t, *J* = 7.3 Hz, 2H), 3.38 (s, 12H), 1.06 (s, 9H), 1.06 (s, 9H), 0.42 (s, 9H) . ^{13}C NMR (151 MHz, $C_6D_5CD_3$): δ = 339.5, 146.0, 134.1, 129.2, 127.0, 81.4, 81.0, 79.4, 32.1, 31.8, 30.9, 26.2. HRMS: not detectable (decomp.).

Complex 1a

A 250 mL Schlenk flask was equipped with a magnetic stir bar and was flame dried under vacuum. The flask was filled with argon and charged with ligand **11a** (968 mg, 1.07 mmol), which was azeotropically dried with benzene (3 x 5 mL) to remove residual water. Then toluene (81 mL) was added and the mixture

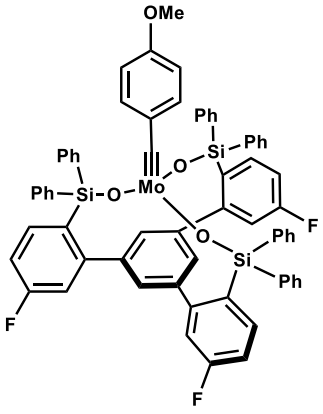
was vigorously stirred for 10 min to obtain a clear solution. A solution of complex **14a** (467 mg, 1.07 mmol) in toluene (16 mL) was added dropwise under vigorous stirring at 23°C. After stirring for an additional 1 h, the solvent was removed *in vacuo* to give a yellow powder (1.14 g, 95%, mixture of monomer **1a** and dimer [**1a**]$_2$), which was used in the next step.



A 10 mL Schlenk flask was equipped with a magnetic stir bar and was flame dried under vacuum. The flask was filled with argon and then charged with complex [**1a**]$_2$ (94.0 mg, 42.2 µmol) and $C_6D_5CD_3$ (2 mL). The resulting yellow suspension was vigorously stirred at 60°C for 1 h to give an orange solution containing only monomeric complex **1a** which showed the following analytical and spectral data: ^{1}H NMR (400 MHz, $C_6D_5CD_3$): δ = 7.86 – 7.77 (m, 12H), 7.78 – 7.69 (m, 3H), 7.25 (s, 3H), 7.13 – 7.00 (m, 24H), 6.87 (dd, *J* = 6.3, 2.5 Hz, 3H), 6.21 (d, *J* = 8.8 Hz, 2H), 6.13 (d, *J* = 8.6 Hz, 2H), 3.05 (s, 3H). ^{13}C NMR (101 MHz, $C_6D_5CD_3$): δ = 310.4, 158.7, 149.1, 143.6, 140.6, 137.7, 137.0, 137.0, 135.0, 134.6, 130.1, 130.0, 129.6, 129.3, 128.9, 128.8, 128.0, 127.7, 125.8, 112.1, 53.9. ^{29}Si NMR (79 MHz, C_6D_6): δ = −9.9. ^{95}Mo NMR (26 MHz, 60°C, $C_6D_5CD_3$): δ = 421.8. ^{1}H-DOSY NMR ($C_6D_5CD_3$): $D_{exp.}$ = $5.557 \cdot 10^{-10}$ m^2/s^{-2}. HRMS-ESI (*m/z*): calculated for $C_{68}H_{53}MoO_4Si_3^+$ $[M+H]^+$, 1115.23002; found, 1115.23153; Elemental analysis (%) calculated for $C_{68}H_{52}MoO_4Si_3$: C 73.36, H 4.71, Mo 8.62, Si 7.57; found: C 71.10, H 4.92, Mo 8.31, Si 7.51.

Complex 1b

A 100 mL Schlenk flask was equipped with a magnetic stir bar and was flame dried under vacuum. The flask was filled with argon and charged with ligand **11b** (571 mg, 0.598 mmol), which was azeotropically dried with benzene (3 x 5 mL) to remove residual water. Toluene (45 mL) was added and the mixture vigorously stirred for 10 min to obtain a clear solution. A solution of complex **14a** (260 mg, 0.598 mmol) in toluene (9 mL) was added dropwise to the vigorously stirred solution at 23°C. After stirring for 1 h, the solvent was removed *in vacuo* to give a bright yellow powder (350 mg, 50%, mixture of monomer **1b** and dimer [**1b**]$_2$), which was used in the next step.

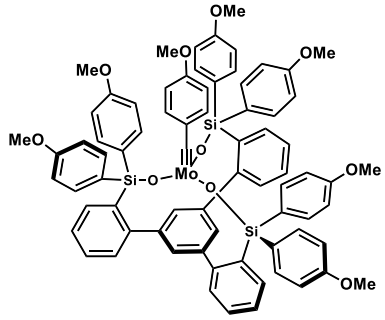


A 10 mL Schlenk flask was equipped with a magnetic stir bar and was flame dried under vacuum. The flask was filled with argon and charged with the crude mixture of **1b**/[**1b**]$_2$ (70.0 mg, 59.9 µmol) and $C_6D_5CD_3$ (1 mL) to give a yellow suspension. The mixture was vigorously stirred at 60°C for 3 h to give an orange solution containing only monomeric complex **1b**. ^{1}H NMR (400 MHz, $C_6D_5CD_3$): δ = 7.74 (d, *J* = 7.1 Hz, 12H), 7.56 (dd, *J* = 8.3, 6.5 Hz, 3H), 7.18 – 7.01 (m, 21H), 6.74 (td, *J* = 8.5, 2.6 Hz, 3H), 6.57 (dd, *J* = 10.1, 2.5 Hz, 3H), 6.24 (d, *J* = 8.5 Hz, 2H), 6.14 (d, *J* = 8.6 Hz, 2H), 3.05 (s, 3H). ^{13}C NMR (101 MHz, $C_6D_5CD_3$): δ = 311.4, 164.0 (d, *J* = 250.2 Hz), 158.9, 151.3 (d, *J* = 7.5 Hz), 142.4, 140.6, 139.3 (d, *J* = 8.1 Hz), 137.4, 134.4, 130.7 (d, *J* = 3.4 Hz), 130.0, 129.5, 128.9, 127.8, 117.0 (d, *J* = 20.3 Hz), 112.8 (d, *J* = 19.5 Hz), 112.2, 53.9. ^{19}F NMR (376 MHz, $C_6D_5CD_3$): δ = −111.2. ^{29}Si NMR (79 MHz, $C_6D_5CD_3$): δ = −9.8. ^{95}Mo NMR (26 MHz, 60°C, $C_6D_5CD_3$): δ = 433.6. IR (film): $\tilde{\nu}$ 1590, 1569, 1505, 1474, 1247, 1428, 1172, 1112, 1030, 995, 871, 826, 762, 740, 697, 635, 493, 461, 422 cm^{-1}. HRMS-APPI (m/z): calculated for $C_{68}H_{49}F_3MoO_4Si_3^+$ $[M]^+$, 1168.19478; found, 1168.19393. Elemental analysis (%)

calculated for $C_{68}H_{49}F_3MoO_4Si_3$: C 69.97, H 4.23, F 4.88, Mo 8.22, Si 7.22; found: C 67.87, H 4.59, F 4.69, Mo 7.91, Si 6.95.

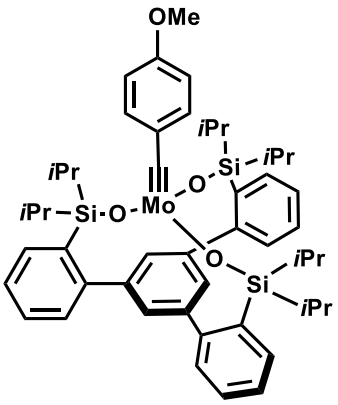
Complex 1c

A 50 mL Schlenk flask was equipped with a magnetic stir bar and flame dried under vaccum. The flask was filled with argon and charged with ligand **11c** (329 mg, 0.304 mmol), which was azeotropically dried with benzene (3 x 5 mL) to remove residual water. Toluene (23 mL) was added and the resulting mixture vigorously stirred for 10 min to obtain a clear solution. A solution of complex **14a** (132 mg, 0.304 mmol) in toluene (5 mL) was added dropwise and stirring was continued for 1 h. The solvent was removed *in vacuo* to give a yellow powder (299 mg, 76%, mixture of monomer **16b** and dimer [**16b**]$_2$), which was used in the next step.



A 10 mL Schlenk flask was equipped with a magnetic stir bar and flame dried under vacuum. The flask was filled with argon and charged with the crude mixture of [**1c**]$_2$/**1c** (60.0 mg, 46.4 µmol) and $C_6D_5CD_3$ (1 mL). The resulting yellow suspension was vigorously stirred at 60°C for 1 h to give an orange solution containing only monomeric complex **1c**. ^{1}H NMR (400 MHz, $C_6D_5CD_3$): δ = 7.85 (dd, *J* = 6.9, 1.9 Hz, 3H), 7.81 – 7.73 (m, 9H), 7.36 (s, 3H), 7.15 (dd, *J* = 7.1, 1.8 Hz, 3H), 7.13 – 7.08 (m, 3H), 6.97 – 6.93 (m, 3H), 6.73 – 6.58 (m, 12H), 6.28 – 6.23 (m, 3H), 6.20 – 6.10 (m, 3H), 3.31 (s, 18H), 3.06 (s, 3H). ^{13}C NMR (101 MHz, $C_6D_5CD_3$): δ = 309.3, 161.0, 158.5, 149.3, 143.6, 140.7, 136.2, 136.1, 130.2, 130.0, 129.4, 129.1, 128.9, 125.6, 113.6, 112.0, 53.9, 53.9. ^{29}Si NMR (79 MHz, C_6D_6): δ = −9.1. ^{95}Mo NMR (26 MHz, 60°C, $C_6D_5CD_3$): δ = 414.3. ^{1}H-DOSY NMR ($C_6D_5CD_3$): $D_{exp.}$ = 5.557·10^{-10} m^2/s^{-2}. IR (film): $\tilde{\nu}$ 2834, 1592, 1563, 1501, 1461, 1439, 1409, 1397, 1277, 1244, 1179, 1113, 1063, 1030, 994, 868, 820, 796, 759, 731, 692, 647, 622, 530, 502, 464, 426, 408 cm^{-1}. HRMS-APPI (*m/z*): calculated for $C_{74}H_{64}MoO_{10}Si_3^+$ $[M+H]^+$, 1294.28559; found, 1294.28623. Elemental analysis (%) calculated for $C_{74}H_{64}MoO_{10}Si_3$: C 68.71, H 4.99, Mo 7.42, Si 6.51; found: C 68.37, H 5.12, Mo 7.33, Si 6.41.

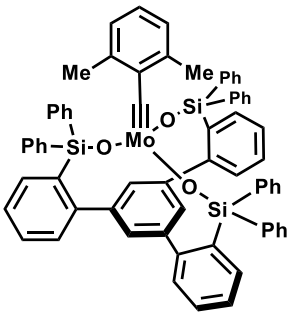
Complex 1d



A 50 mL Schlenk flask was equipped with a magnetic stir bar and was flame dried under vacuum. The flask was filled with argon and charged with ligand **11e** (264 mg, 0.379 mmol), which was azeotropically dried with benzene (3 x 5 mL) to remove residual water. Toluene (28 mL) was added and the mixture vigorously stirred for 10 min to obtain a clear solution. Then a solution of complex **14a** (158 mg, 0.365 mmol) in toluene (6 mL) was added dropwise at 23°C and stirring continued for 3 h. The solvent was removed *in vacuo* to give a yellow/orange powder containing only monomeric complex **1d** (340 mg, 99%). Yellow crystals suitable for single-crystal X-ray diffraction were grown from a concentrated Et_2O solution at –30°C. ^{1}H NMR (400 MHz, $C_6D_5CD_3$): δ = 7.45 – 7.38 (m, 6H), 7.28 – 7.21 (m, 3H), 7.17 (td, *J* = 6.6, 5.6, 3.7 Hz, 6H), 7.13 – 7.06 (m, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 3.16 (s, 3H), 1.29 (hept, *J* = 7.1 Hz, 6H), 1.24 (d, *J* = 6.8 Hz, 18H), 1.11 (d, *J* = 7.1 Hz, 18H). ^{13}C NMR (101 MHz, $C_6D_5CD_3$): δ = 303.3, 158.7, 149.6, 143.6, 140.9, 135.0, 133.8, 130.8, 129.6, 128.3 (t, *J* = 23.8 Hz), 127.6, 125.9, 112.7, 54.1, 18.1, 17.7, 15.0. ^{29}Si NMR (79 MHz, $C_6D_5CD_3$): δ = 10.2. ^{95}Mo NMR (26 MHz, 60°C, $C_6D_5CD_3$): δ = 358.0. ^{1}H-DOSY NMR ($C_6D_5CD_3$): $D_{predicted.}$ = 6.08·10^{-10} m^2/s^{-2}; $D_{exp.}$ = 6.80·10^{-10} m^2/s^{-2}. IR

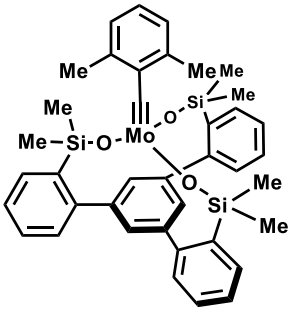
(film): $\tilde{\nu}$ 2941, 2862, 1591, 1503, 1462, 1408, 1259, 1243, 1171, 1088, 1017, 919, 875, 799, 757, 738, 722, 671, 651, 627, 518, 471 cm^{-1}. HRMS-ESI (m/z): calculated for $C_{50}H_{65}MoO_4Si_3^+$ $[M+H]^+$, 911.32392; found, 911.32409. Elemental analysis (%) calculated for $C_{50}H_{64}MoO_4Si_3$: C 66.05, H 7.09, Mo 10.55, Si 9.27; found: C 62.02, H 6.82, Mo 9.93, Si 8.72.

Complex 1e



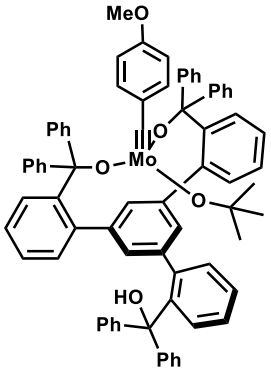
A 100 mL Schlenk flask was equipped with a magnetic stir bar and flame dried under vacuum. The flask was filled with argon and charged with ligand **11a** (388 mg, 0.431 mmol), which was azeotropically dried with benzene (3 x 5 mL) to remove residual water. Toluene (32 mL) was added and the mixture vigorously stirred for 10 min to obtain a clear solution. Then a solution of complex **14b** (192 mg, 0.444 mmol) in toluene (6 mL) was added dropwise and stirring was continued for 6 h at ambient temperature. The solvent was removed *in vacuo* and the yellow/orange solid was washed with *n*-pentane (3 x 5 mL) and Et_2O (3 x 5 mL) to give a yellow/orange powder containing only the monomeric complex **1e** (312 mg, 65%). Yellow crystals suitable for single-crystal X-ray diffraction were grown from a concentrated Et_2O solution at –20°C. ^{1}H NMR (400 MHz, $C_6D_5CD_3$): δ = 7.81 – 7.76 (m, 12H), 7.76 – 7.72 (m, 3H), 7.23 (s, 3H), 7.13 – 7.00 (m, 24H), 6.87 – 6.81 (m, 3H), 6.37 (s, 3H), 1.95 (s, 6H). ^{13}C NMR (101 MHz, $C_6D_5CD_3$): δ = 312.2, 149.2, 144.8, 143.8, 138.6, 137.5, 137.1, 134.8, 134.6, 130.1, 129.7, 129.4, 128.7, 127.6, 127.2, 125.8, 125.6, 19.7. ^{29}Si NMR (79 MHz, $C_6D_5CD_3$): δ = −9.4. ^{95}Mo NMR (26 MHz, 60°C, $C_6D_5CD_3$): δ = 466.8. ^{1}H-DOSY NMR ($C_6D_5CD_3$): $D_{predicted.}$ = $5.56 \cdot 10^{-10}$ m^2/s^{-2}; $D_{exp.}$ = $5.56 \cdot 10^{-10}$ m^2/s^{-2}. IR (film): $\tilde{\nu}$ 1428, 1112, 1086, 1020, 1032, 997, 875, 849, 736, 772, 443, 413 cm^{-1}. HRMS-ESI (m/z): calculated for $C_{69}H_{55}MoO_3Si_3^+$ $[M+H]^+$, 1113.25076; found, 1113.25104. Elemental analysis (%) calculated for $C_{69}H_{54}MoO_3Si_3$: C 74.57, H 4.90, Mo 8.63; found: C 74.45, H 5.06, Mo 9.13.

Complex 1f



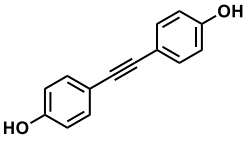
A 250 mL Schlenk flask was equipped with a magnetic stir bar and flame dried under vacuum. The flask was filled with argon and charged with ligand **11d** (468 mg, 0.885 mmol), which was azeotropically dried with benzene (3 x 5 mL) to remove residual water. Toluene (70 mL) was added and the mixture was vigorously stirred for 10 min to obtain a clear solution. Then a solution of complex **14b** (403 mg, 0.932 mmol) in toluene (14 mL) was added dropwise and stirring was continued for 4 h at ambient temperature. The solvent was removed *in vacuo* and the crude solid was extracted with *n*-pentane (5 x 5 mL) to give a yellow/orange powder containing monomeric complex **1f** and a minor (oligomeric) impurity (550 mg, 84%). ^{1}H NMR (400 MHz, $C_6D_5CD_3$): δ 7.44 (s, 3H), 7.43 – 7.40 (m, 3H), 7.25 – 7.13 (m, 9H), 6.77 (d, *J* = 7.5 Hz, 2H), 6.71 – 6.62 (m, 1H), 2.63 (s, 6H), 0.41 (s, 18H). ^{13}C NMR (101 MHz, $C_6D_5CD_3$): δ = 304.7, 148.4, 145.0, 144.2, 138.4, 138.0, 134.2, 130.1, 128.7, 127.9, 127.1, 126.4, 126.3, 20.3, 3.0. ^{29}Si NMR (79 MHz, $C_6D_5CD_3$): δ = 9.4. ^{95}Mo NMR (26 MHz, 60°C, $C_6D_5CD_3$): δ = 421.8. ^{1}H-DOSY NMR ($C_6D_5CD_3$): $D_{predicted.}$ = $6.69 \cdot 10^{-10}$ m^2/s^{-2}; $D_{exp.}$ = $7.09 \cdot 10^{-10}$ m^2/s^{-2}. IR (film): $\tilde{\nu}$ 2964, 2037, 1259, 1124, 1094, 1020, 987, 886, 877, 832, 806, 781, 759, 743, 728, 695, 653, 633, 605, 592, 581, 562, 529, 518, 509, 493, 474, 463, 454, 430, 412 cm^{-1}. HRMS-ESI (m/z): calculated for $C_{39}H_{43}MoO_3Si_3^+$ $[M+H]^+$, 741.15686; found, 741.15690.

Complex 16



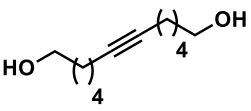
A 50 mL Schlenk flask was equipped with a magnetic stir bar and flame dried under vacuum. The flask was filled with argon and charged with ligand **12** (153 mg, 0.179 mmol), which was azeotropically dried with benzene (3 x 5 mL) to remove residual water. Toluene (13 mL) was added and the mixture vigorously stirred for 10 min to obtain a clear solution. A solution of complex **14a** (86.0 mg, 0.198 mmol) in toluene (3 mL) was added dropwise and stirring continued for 14 h. The solvent was removed *in vacuo* and the brown residue was washed with *n*-pentane (3 x 5 mL) to give complex **16** as a bright brown powder (156 mg, 82%). ^{1}H NMR (600 MHz, $C_6D_5CD_3$): 7.71 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.57 (dd, *J* = 8.4, 1.3 Hz, 4H), 7.38 (dd, *J* = 8.4, 1.3 Hz, 4H), 7.32 – 7.29 (m, 4H), 7.28 (td, *J* = 7.4, 1.3 Hz, 1H), 7.11 (dd, *J* = 8.4, 7.0 Hz, 4H), 7.04 – 7.00 (m, 9H), 6.97 – 6.89 (m, 8H), 6.89 – 6.84 (m, 5H), 6.75 (t, *J* = 1.7 Hz, 1H), 6.71 (d, *J* = 1.7 Hz, 2H), 6.66 (dd, *J* = 7.6, 1.5 Hz, 2H), 6.36 – 6.27 (m, 2H), 5.46 – 5.40 (m, 2H), 3.66 (s, 1H), 3.09 (s, 3H), 1.46 (s, 9H). ^{13}C NMR (151 MHz, $C_6D_5CD_3$): δ = 287.1, 158.3, 149.3, 149.0, 148.7, 145.2, 144.9, 144.5, 141.2, 141.1, 139.2, 138.8, 133.9, 132.5, 131.0, 130.8, 130.0, 129.3, 128.7, 128.5, 127.7, 127.6, 127.5, 127.5, 127.5, 127.4, 127.0, 126.7, 126.5, 126.1, 126.1, 125.7, 112.1, 94.2, 83.6, 82.7, 53.9, 32.8. ^{95}Mo NMR (26 MHz, 60°C, $C_6D_5CD_3$): δ = 118.3. ^{1}H-DOSY NMR ($C_6D_5CD_3$): $D_{predicted.}$ = 5.50·10^{-10} m^2/s^{-2}; $D_{exp.}$ = 5.58·10^{-10} m^2/s^{-2}. IR (film): $\tilde{\nu}$ 3533, 3058, 2968, 1593, 1503, 1445, 1360, 1283, 1243, 1168, 1040, 1013, 922, 908, 828, 804, 787, 755, 729, 696, 637, 607, 591, 515, 498, 454, 430, 412 cm^{-1}. HRMS-ESI (m/z): calculated for $C_{75}H_{62}MoO_5Na^+$ [M+Na]$^+$, 1163.35435; found, 1163.35514. Elemental analysis (%) calculated for $C_{75}H_{62}MoO_5$: C 79.07, H 5.49, Mo 8.42; found: C 79.25, H 5.66, Mo 8.12.

Representative Procedure for Alkyne Homo-Metathesis. 4,4'-(Ethyne-1,2-diyl)diphenol (20b).



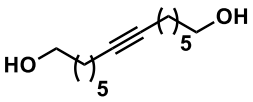
4-(Prop-1-yn-1-yl)phenol (33.0 mg, 25.0 µmol) was added to a stirred suspension of complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) and powdered molecular sieves 5Å (250 mg) in toluene (1.25 mL) at 60°C under argon atmosphere. The mixture was stirred for 14 h at this temperature before it was filtered through a short pad of Celite® which was carefully rinsed with ethyl acetate (20 mL). The combined filtrates were evaporated and the residue was purified by flash chromatography on silica gel (hexanes/toluene/EA, 6:2:2) to give the title compound as a white solid (24.3 mg, 93%). ^{1}H NMR (400 MHz, CD_3CN): δ = 7.39 – 7.31 (m, 4H), 7.27 (s, 2H), 6.85 – 6.77 (m, 4H). ^{13}C NMR (101 MHz, CD_3CN): δ = 158.1, 133.8, 116.5, 115.6, 88.4. The analytical and spectroscopic data are in agreement with those reported in the literature.[7]

Dodec-6-yne-1,12-diol (21a)



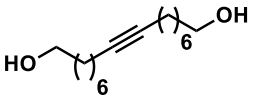
Prepared analogously with either complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) or complex **1f** (9.72 mg, 12.5 µmol, 5 mol%) at 23°C; colorless oil (16.0 mg, 69%; 18.0 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.64 – 3.54 (m, 4H), 2.14 – 2.03 (m, 4H), 1.58 – 1.33 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 80.2, 62.9, 32.3, 28.8, 24.9, 18.7.The analytical and spectroscopic data are in agreement with those reported in the literature.[8]

Tetradec-7-yne-1,14-diol (21b)



Prepared analogously with either complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) or complex **1f** (9.7 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (18.0 mg, 66%; 20.1 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.58 (t, *J* = 6.6 Hz, 4H), 2.09 (td, *J* = 5.9, 5.0, 2.0 Hz, 4H), 1.58 – 1.26 (m, 16 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 80.2, 62.9, 32.7, 29.0, 28.6, 25.3, 18.7.The analytical and spectroscopic data are in agreement with those reported in the literature.[7]

Hexadec-8-yne-1,16-diol (21c)

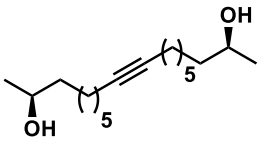


Prepared analogously with either complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) or complex **1f** (9.7 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (25.0 mg, 83%; 28.0 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ =3.57 (t, *J* = 6.6 Hz, 4H), 2.19 – 1.96 (m, 4H), 1.62 – 1.13 (m, 20H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 80.2, 63.0, 32.7, 29.0, 28.9, 28.8, 25.7, 18.7. The analytical and spectroscopic data are in agreement with those reported in the literature.[9]

Octadec-9-yne-1,18-diol (21d)

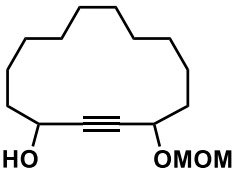
Prepared analogously with either complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) or complex **1f** (9.7 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (32.2 mg, 91%; 30.7 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.63 (t, *J* = 6.6 Hz, 4H), 2.19 – 2.06 (m, 4H), 1.61 – 1.42 (m, 8H), 1.37 – 1.27 (m, 16H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 80.4, 63.2, 32.9, 29.5, 29.3, 29.2, 28.9, 25.8, 18.9. IR (film): $\tilde{\nu}$ 3260, 2930, 2851, 1460, 1414, 1052, 1023, 995, 725, 420 cm^{-1}. HRMS-ESI (*m/z*): calcd. for $C_{18}H_{34}O_{32}$ $[M]^+$, 283.263155; found, 283.26328.

(2S,17S)-octadec-9-yne-2,17-diol (22)



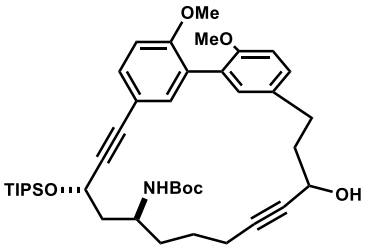
Prepared analogously with complex **1f** (9.2 mg, 12.5 µmol, 5 mol%) at 23°C; pale yellow oil (33.1 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83 – 3.70 (m, 2H), 2.18 – 2.08 (m, 4H), 1.66 (s, 2H), 1.53 – 1.24 (m, 20H), 1.17 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 80.3, 68.2, 39.4, 29.3, 29.2, 28.9, 25.8, 23.6, 18.8. The analytical and spectroscopic data are in agreement with those reported in the literature.[7]

4-(Methoxymethoxy)cyclotetradec-2-yn-1-ol (23)



To a stirred suspension of 15-(methoxymethoxy)octadeca-2,16-diyn-4-ol (9.60 mg, 29.8 µmol) and powdered molecular sieves 5Å (200 mg) in toluene (13 mL) at 110°C was added a solution of complex **1f** (2.2 mg, 3.0 µmol, 10 mol%) in toluene (2.0 mL) under argon atmosphere. The mixture was stirred for 2 h at this temperature before it was cooled to ambient temperatures and filtered through a short pad of Celite® and rinsed with ethyl acetate (20 mL). The filtrate was evaporated and the residue was purified by flash chromatography on silica gel (hexanes/*t*-butyl methyl ether 8:2 to 7:3) to give the title compound as an oil (5.4 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 (dd, *J* = 6.8, 5.0 Hz, 1H), 4.60 (dd, *J* = 6.8, 1.6 Hz, 1H), 4.55 – 4.35 (m, 2H), 3.38 (d, *J* = 0.7 Hz, 3H), 1.79 – 1.62 (m, 4H), 1.57 – 1.25 (m, 16H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 94.3, 87.1, 87.1, 84.1, 83.9, 66.3, 66.2, 63.1, 63.0, 55.8, 37.2, 37.1, 35.1, 35.0, 26.6, 26.5, 25.9, 25.9, 25.8, 25.8, 23.9, 23.8, 22.5, 22.4, 22.3, 22.3. The analytical and spectroscopic data are in agreement with those reported in the literature.[7]

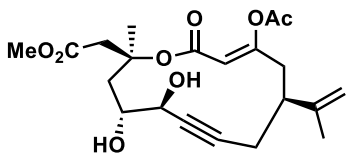
Compound (24)



To a stirred suspension of diyne (17.3 mg, 23.2 µmol) and powdered molecular sieves 5Å (200 mg) in toluene (10 mL) at 80°C was added a solution of complex **1f** (3.4 mg, 4.6 µmol, 20 mol%) in toluene (2.0 mL) under argon atmosphere. The mixture was stirred for 3 h at this temperature before it was cooled to ambient temperatures and filtered through a short pad of Celite® and rinsed with ethyl acetate (20 mL). The filtrate was evaporated and the residue was purified by flash chromatography on silica gel (hexanes/*t*-butyl methyl ether 6:4 to 7:3) to give the title compound as an oil (10.5 mg, 66%). ^{1}H NMR (mixture of conformers 400 MHz, $CDCl_3$): δ = 7.39 – 7.27 (m, 2H), 7.21 – 7.13 (m, 1H), 7.07 (d, *J* = 2.3 Hz, 1H), 6.93 – 6.83 (m, 2H), 5.17 – 5.08 (m, 1H), 4.90 – 4.81 (m, 1H), 4.71 (ddd, *J* = 19.1, 10.5, 3.4 Hz, 1H), 4.51 (d, *J* = 8.2 Hz, 1H), 4.07 (ddd, *J* = 16.1, 9.9, 4.0 Hz, 1H), 3.93 (d, *J* = 20.6 Hz, 1H), 3.79 (dd, *J* = 14.1, 2.8 Hz, 7H), 3.65 (q, *J* = 2.0 Hz, 1H), 2.93 – 2.65 (m, 2H), 2.42 – 2.16 (m, 1H), 2.17 – 1.88 (m, 2H), 1.88 – 1.53 (m, 2H), 1.41 (d, *J* = 9.3 Hz, 9H), 1.22 – 0.95 (m, 18H). The analytical and spectroscopic data are in agreement with those reported in the literature.[7]

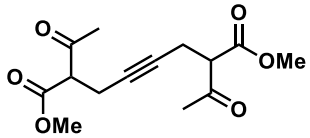
Compound 25.

Diyne (50.0 mg, 83.1 µmol) was added to a stirred suspension of complex **1a** (27.8 mg, 24.9 µmol, 30 mol%) and powdered molecular sieves 5Å (20 mg) in toluene (42 mL) at 110°C under Ar. The mixture was stirred for 45 min at this temperature before it was filtered through a short pad of Celite®, which was carefully rinsed with ethyl acetate(100 mL). The combined filtrates were evaporated and the residue was purified by flash chromatography on silica (hexanes/ethyl acetate,3:1).



Zinc dust (217 mg, 332 µmol) was added to a solution of this compound in HOAc/THF/H_2O (0.3 mL, 3:1:1). The suspension was vigorously stirred for 3 h at room temperature before all insoluble materials were filtered off through a pad of Celite. The filtrate was diluted with sat. aq. $NaHCO_3$ (10 mL), the aqueous phase was extracted with ethyl acetate (3 x 20 mL), the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash chromatography on silica (hexanes/ethyl acetate, 2:1 to 1:1) to afford the title compound as a colorless oil (23.0 mg, 68% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.61 (s, 1H), 4.82 (p, *J* = 1.6 Hz, 1H), 4.78 – 4.73 (m, 1H), 4.58 (q, *J* = 2.3 Hz, 1H), 4.18 – 4.11 (m, 1H), 3.84 – 3.77 (m, 1H), 3.75 (d, *J* = 1.7 Hz, 1H), 3.72 (s, 3H), 3.42 (dd, *J* = 14.4, 5.0 Hz, 1H), 3.06 (d, *J* = 14.6 Hz, 1H), 2.74 – 2.69 (m, 1H), 2.67 (d, *J* = 1.9 Hz, 1H), 2.63 (d, *J* = 1.4 Hz, 1H), 2.48 (tt, *J* = 9.0, 4.6 Hz, 1H), 2.39 (dd, *J* = 4.1, 1.7 Hz, 1H), 2.34 (dd, *J* = 4.1, 1.7 Hz, 1H), 2.30 (dd, *J* = 8.8, 3.0 Hz, 1H), 2.11 (s, 3H), 2.05 (dd, *J* = 16.2, 8.4 Hz, 1H), 1.71 (s, 3H), 1.69 (t, *J* = 1.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.9, 168.1, 165.1, 163.2, 144.9, 114.2, 112.9, 85.7, 83.2, 81.4, 71.6, 67.3, 52.4, 44.7, 42.6, 40.1, 33.6, 25.8, 24.0, 21.2, 20.1. The analytical and spectroscopic data are in agreement with those reported in the literature.[10]

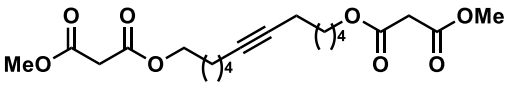
Dimethyl 2,7-diacetyloct-4-ynedioate (26)



Prepared analogously with catalyst **1a** (27.8 mg, 0.025 mmol, 10 mol%) at 90°C; colorless oil (28.0 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.75 (s, 3H), 3.65 – 3.56 (m, 1H), 2.67 – 2.61 (m, 2H), 2.27 (s, 3H). ^{13}C NMR (101 MHz,

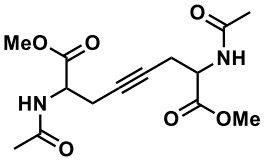
$CDCl_3$): δ = 201.4, 168.8, 78.4, 58.5, 52.8, 29.6, 17.9. IR (film): $\tilde{\nu}$ 2956, 2163, 2002, 1745, 1719, 1435, 1361, 1266, 1226, 1151, 1004, 904, 510, 424 cm^{-1}. HRMS-ESI (m/z): calculated for $C_{14}H_{18}O_6Na^+$ $[M+Na]^+$, 305.09956; found, 305.09970.

_O_,_O_'-(Dodec-6-yne-1,12-diyl) dimethyl dimalonate (27)



Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (45.3 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.11 (t, *J* = 6.7 Hz, 4H), 3.71 (s, 6H), 3.35 (s, 4H), 2.19 – 2.05 (m, 4H), 1.72 – 1.59 (m, 4H), 1.44 (ddt, *J* = 15.0, 8.0, 4.3 Hz, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.1, 166.6, 80.1, 65.6, 52.5, 41.4, 28.7, 28.0, 25.1, 18.7. The analytical and spectroscopic data are in agreement with those reported in the literature.[7]

Dimethyl 2,7-diacetamidooct-4-ynedioate (28)

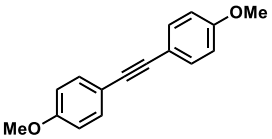


Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (26.2 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (d, *J* = 9.1 Hz, 2H), 6.57 (d, *J* = 8.5 Hz, 2H), 4.88 (dt, *J* = 9.1, 3.7 Hz, 2H), 4.79 (dt, *J* = 7.8, 3.9 Hz, 2H), 3.80 – 3.76 (m, 13H), 2.64 (dtd, *J* = 17.4, 4.5, 2.8 Hz, 8H), 2.12 – 2.11 (m, 13H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.6, 171.5, 170.4, 170.4, 78.6, 78.0, 52.9, 50.7, 50.4, 23.5, 23.2, 23.2, 22.9. The analytical and spectroscopic data are in agreement with those reported in the literature.[7]

Di-*tert*-butyl (1,10-bis(phenylsulfonyl)dec-5-yne-1,10-diyl)dicarbamate (29)

Prepared analogously with either complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (62 mg, 76%). ^{1}H NMR (Diastereomer 1, 600 MHz, C_6D_6): δ = 8.15 – 8.10 (m, 4H), 7.09 – 7.03 (m, 6H), 6.38 (d, *J* = 10.7 Hz, 2H), 5.19 (td, *J* = 10.4, 5.1 Hz, 2H), 2.52 – 2.37 (m, 1H), 2.13 – 2.02 (m, 4H), 1.97 – 1.90 (m, 3H), 1.52 – 1.34 (m, 4H), 1.15 (s, 18H). ^{1}H NMR (Diastereomer 2, 600 MHz, C_6D_6): δ = 8.08 (dt, *J* = 7.4, 1.9 Hz, 4H), 6.99 (td, *J* = 5.8, 5.1, 2.9 Hz, 6H), 5.30 (d, *J* = 10.8 Hz, 2H), 5.13 (td, *J* = 10.9, 3.5 Hz, 2H), 2.52 – 2.46 (m, 1H), 1.93 (td, *J* = 5.1, 3.9, 2.1 Hz, 4H), 1.85 (d, *J* = 4.2 Hz, 1H), 1.30 – 1.21 (m, 4H), 1.16 (s, 18H). ^{13}C NMR (Diastereomer 1, 151 MHz, C_6D_6): δ = 154.3, 138.1, 133.1, 129.7, 128.5, 80.3, 79.4, 71.2, 27.7, 26.4, 24.4, 18.3. ^{13}C NMR (Diastereomer 2, 151 MHz, C_6D_6): δ = 153.9, 138.1, 133.0, 129.5, 128.6, 80.0, 79.5, 70.7, 27.7, 25.4, 24.5, 17.9. IR (film): $\tilde{\nu}$ 3339, 2977, 2933, 1718, 1514, 1447, 1393, 1367, 1307, 1284, 1242, 1164, 1138, 1081, 1048, 1025, 999, 864, 812, 776, 754, 732, 715, 687, 592, 545, 517, 498, 428 cm^{-1}. HRMS-ESI (m/z): calcd. for $C_{32}H_{44}N_2O_8S_2Na$ $[M+Na]^+$, 671.243131; found, 671.243520.

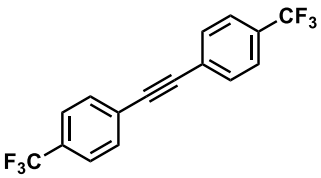
1,2-Bis(4-methoxyphenyl)ethyne (20a)



Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (27.3 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.8 Hz, 3H), 6.87 (d, *J* = 8.8 Hz, 4H), 3.82 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.5, 133.0, 115.9, 114.1, 88.1, 55.4. The analytical and spectroscopic data are in

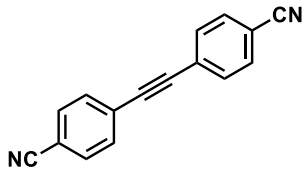
agreement with those reported in the literature.[11]

1,2-Bis(4-(trifluoromethyl)phenyl)ethyne (20c)



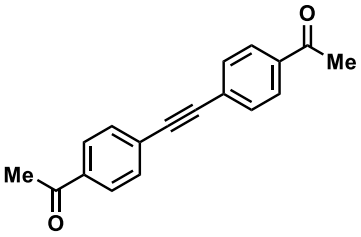
Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 60°C; white solid (35.5 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 – 7.59 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 132.1, 131.1, 130.8, 130.5, 130.2, 128.0, 126.5, 125.6, 125.5, 125.5, 125.3, 122.6, 119.9, 90.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −62.9. The analytical and spectroscopic data are in agreement with those reported in the literature.[12]

4,4'-(Ethyne-1,2-diyl)dibenzonitrile (20d)



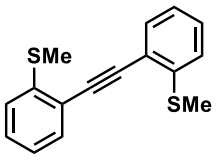
Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 60°C ; white solid (22.0 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 132.7, 132.6, 127.5, 118.7, 112.9, 92.0. The analytical and spectroscopic data are in agreement with those reported in the literature.[12]

1,1'-(Ethyne-1,2-diylbis(4,1-phenylene))bis(ethan-1-one) (20e).



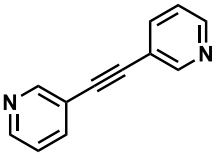
Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (32.0 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.6 Hz, 4H), 7.64 (d, *J* = 8.6 Hz, 4H), 2.63 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.2, 136.6, 131.8, 128.3, 127.5, 91.7, 26.7. The analytical and spectroscopic data are in agreement with those reported in the literature.[12]

1,2-Bis(2-(methylthio)phenyl)ethyne (30)



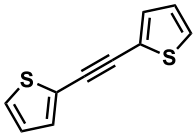
Prepared analogously with complex **1f** (9.7 mg, 12.5 µmol, 5 mol%) at 90°C; white solid (31.0 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 – 7.53 (m, 2H), 7.33 – 7.28 (m, 2H), 7.21 – 7.18 (m, 2H), 7.14 – 7.10 (m, 2H), 2.52 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.6, 132.6, 128.9, 124.2, 121.4, 92.2, 77.2, 15.3. The analytical and spectroscopic data are in agreement with those reported in the literature.[12]

1,2-Di(pyridin-3-yl)ethyne (31)



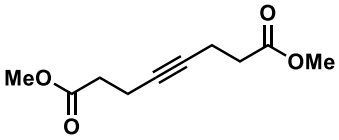
Prepared analogously with either complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) or complex **1f** (9.7 mg, 12.5 µmol, 5 mol%) at 90°C; pale yellow solid (14.0 mg, 62%; 17.0 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 – 8.77 (m, 2H), 8.67 – 8.55 (m, 2H), 7.87 (dt, *J* = 6.1 Hz, 2H), 7.35 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.8, 148.6, 138.96, 123.3, 119.8, 89.2. The analytical and spectroscopic data are in agreement with those reported in the literature.[12]

1,2-Di(thiophen-2-yl)ethyne (32)



Prepared analogously with either complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) or complex **1f** (9.7 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (22.3 mg, 94%; 20.2 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.27 (m, 4H), 7.02 (dd, *J* = 5.2, 3.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 132.1, 127.6, 127.1, 122.9, 86.2. The analytical and spectroscopic data are in agreement with those reported in the literature.[12]

Dimethyl oct-4-ynedioate (33)

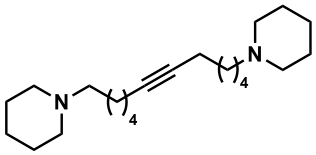


Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C; colorless oil (28.0 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.63 (s, 6H), 2.56 – 2.27 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.5, 77.9, 50.7, 32.7, 13.7. The analytical and spectroscopic data are in agreement with those reported in the literature.[12]

***N*^{1},*N*^{12}-Dibutyldodec-6-yne-1,12-diamine (34)**

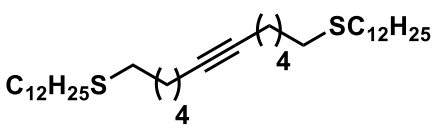
N-Butyloct-6-yn-1-amine (45.3 mg, 25.0 µmol) was added to a stirred suspension of complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) and powdered molecular sieves 5Å (250 mg) in toluene (1.25 mL) at 60°C under argon atmosphere. After stirring for 12 h, the mixture was filtered through a short pad of Celite®, which was rinsed with MeOH (20 mL). The combined filtrates were evaporated and the residue was dissolved in $CHCl_3$ (1 mL). Ethyl acetate (20 mL) was added to precipitate the product. The supernatant solution was decanted and the remaining solid was dissolved in CH_2Cl_2 (10 mL). The organic layer was washed with sat. aq. $NaHCO_3$ (10 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the title compound as a beige solid (38.6 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.59 (td, *J* = 7.3, 1.9 Hz, 8H), 2.18 – 2.09 (m, 4H), 1.55 – 1.29 (m, 20H), 0.90 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 80.3, 50.1, 49.9, 32.4, 29.8, 29.2, 26.8, 20.7, 18.9, 14.2. IR (film): $\tilde{\nu}$ 3260, 2930, 2851, 1460, 1414, 1052, 1023, 995, 725, 420 cm^{-1}. HRMS-ESI (m/z): calcd. for $C_{20}H_{40}N_2$ $[M+H]^+$,309.32642; found,309.32602. The analytical and spectroscopic data are in agreement with those reported in the literature.[7]

1,12-Di(piperidin-1-yl)dodec-6-yne (35)



Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (36.7 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ =2.42 – 2.31 (m, 8H), 2.32 – 2.24 (m, 4H), 2.16 – 2.07 (m, 4H), 1.57 (p, *J* = 5.6 Hz, 8H), 1.49 – 1.33 (m, 16H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 80.3, 59.5, 54.7, 29.2, 27.1, 26.5, 26.0, 24.6, 18.8. The analytical and spectroscopic data are in agreement with those reported in the literature.[7]

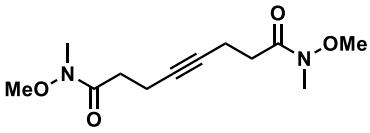
1,10-Bis(dodecylthio)dec-5-yne (36)



Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (64.0 mg, 95%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.46 – 2.42 (m, 8H), 2.10 – 2.06 (m, 4H),1.54 – 1.46 (m, 16H), 1.30 – 1.18 (m, 32H), 0.83 – 0.79 (m, 6H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 80.5, 32.6, 32.5,

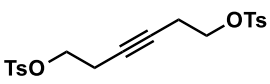
32.5, 30.7, 30.4, 30.3, 30.2, 30.1, 30.0, 29.9, 29.9, 29.5, 29.4, 28.7, 23.3, 19.2, 14.5. The analytical and spectroscopic data are in agreement with those reported in the literature.[7]

N^1,N^8-Dimethoxy-N^1,N^8-dimethyloct-4-ynediamide (37)



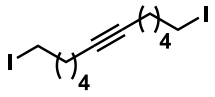
Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (16.7 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.69 (s, 6H), 3.18 (s, 6H), 2.63 (t, *J* = 7.3 Hz, 4H), 2.47 (dd, *J* = 8.7, 6.7 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.9, 79.6, 61.4, 32.3, 31.7, 14.4. The analytical and spectroscopic data are in agreement with those reported in the literature.[7]

Hex-3-yne-1,6-diyl bis(4-methylbenzenesulfonate) (38)



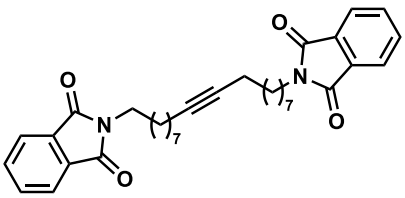
Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (43.8 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 – 7.75 (m, 4H), 7.35 (d, *J* = 8.0 Hz, 4H), 4.04 – 3.97 (m, 4H), 2.45 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 145.1, 133.0, 130.0, 128.1, 76.9, 67.9, 21.8, 19.8. The analytical and spectroscopic data are in agreement with those reported in the literature.[12]

1,12-Diiodododec-6-yne (39)



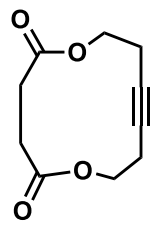
Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C; pale orange oil (43.0 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.21 (t, *J* = 7.0 Hz, 4H), 2.17 (m, 4H), 1.85 (m, 4H), 1.50 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 80.1, 33.1, 29.7, 27.9, 18.6, 6.9. IR (film): ṽ 2931, 2855, 1606, 1509, 1456, 1428, 1368, 1347, 1333, 1290, 1246, 1202, 1164, 1120, 1077, 1032, 891, 832, 805, 765, 723, 593, 532, 503 cm^{-1}. HRMS-CI (m/z): calculated for $C_{12}H_{21}I_2^+$ $[M+H]^+$, 418.97272; found, 418.97282.

2,2'-(Octadec-9-yne-1,18-diyl)bis(isoindoline-1,3-dione) (40)



Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (60.0 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (dt, *J* = 7.2, 3.6 Hz, 4H), 7.68 (dd, *J* = 5.4, 3.0 Hz, 4H), 3.65 (t, *J* = 7.3 Hz, 4H), 2.14 – 2.05 (m, 4H), 1.64 (t, *J* = 7.2 Hz, 4H), 1.43 (t, *J* = 7.3 Hz, 4H), 1.34 – 1.25 (m, 16H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.5, 133.9, 132.3, 123.2, 80.3, 38.1, 29.2, 29.1, 28.9, 28.7, 26.9, 18.8. The analytical and spectroscopic data are in agreement with those reported in the literature.[7]

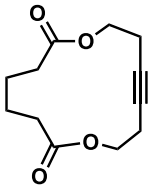
Representative Procedure for Ring Closing Alkyne Metathesis. 1,6-Dioxacyclododec-9-yne-2,5-dione (41a)



Di(pent-3-yn-1-yl) succinate (25.0 mg, 0.100 mmol) was added to a stirred suspension of complex **1a** (5.57 mg, 0.5 µmol, 5 mol%) and powdered molecular sieves 5Å (200 mg) in toluene (50 mL) at 60°C under argon atmosphere. The mixture was stirred for 14 h at this temperature before it was filtered through a short pad of Celite® which was carefully rinsed with ethyl acetate (20 mL). The combined filtrates were evaporated and the residue was purified by flash chromatography on silica gel (hexanes/*t*-butyl methyl ether 6:4 to 1:4) to give the title compound as a white

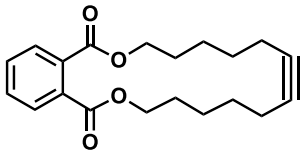
solid (18.6 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.34 – 4.16 (m, 4H), 2.69 (s, 4H), 2.58 – 2.34 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.8, 78.9, 61.5, 30.1, 19.8. The analytical and spectroscopic data are in agreement with those reported in the literature.[12]

1,8-Dioxacyclotetradec-11-yne-2,7-dione (41b)



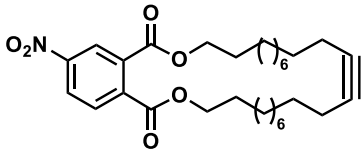
Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (19.1 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.18 – 4.10 (m, 4H), 2.56 – 2.49 (m, 4H), 2.39 (ddt, *J* = 6.0, 3.8, 1.8 Hz, 4H), 1.79 – 1.69 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.3, 78.1, 62.7, 35.1, 25.2, 19.3. The analytical and spectroscopic data are in agreement with those reported in the literature.[12]

Compound 42



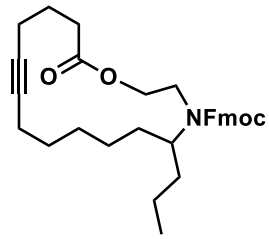
Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (32.1 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.77 – 7.69 (m, 2H), 7.58 – 7.49 (m, 2H), 4.35 (t, *J* = 6.1 Hz, 4H), 2.24 – 2.15 (m, 4H), 1.79 (dq, *J* = 9.0, 5.8 Hz, 4H), 1.64 – 1.45 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.9, 132.4, 131.1, 129.0, 80.8, 66.5, 28.5, 28.2, 26.0, 18.8. The analytical and spectroscopic data are in agreement with those reported in the literature.[12]

Compound 43



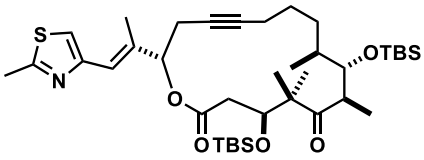
Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 60°C; white solid (51.4 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (d, *J* = 2.3 Hz, 1H), 8.38 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 4.33 (td, *J* = 7.0, 4.7 Hz, 4H), 2.17 (h, *J* = 2.1 Hz, 4H), 1.75 (h, *J* = 7.2 Hz, 4H), 1.48 – 1.28 (m, 28H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.5, 165.4, 148.9, 138.4, 133.4, 130.3, 126.0, 124.6, 80.7, 66.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.3, 29.3, 26.0, 25.9, 18.7. The analytical and spectroscopic data are in agreement with those reported in the literature.[12]

Compound 45



Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C ; white solid (26.8 mg, 99%). ^{1}H NMR (rotamers, 400 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 7.7, 2.2 Hz, 2H), 7.63 – 7.53 (m, 2H), 7.45 – 7.27 (m, 4H), 4.73 – 4.49 (m, 2H), 4.22 (q, *J* = 5.2 Hz, 2H), 3.92 – 3.66 (m, 1H), 3.42 (s, 0H), 2.99 (s, 1H), 2.70 – 2.35 (m, 1H), 2.32 – 2.13 (m, 3H), 2.13 – 2.01 (m, 1H), 1.86 – 1.69 (m, 2H), 1.61 – 0.77 (m, 14H), 0.70 (s, 2H). ^{13}C NMR (rotamers, 101 MHz, $CDCl_3$): δ = 173.5, 173.4, 144.3, 144.2, 144.1, 141.6, 141.6, 127.8, 127.8, 127.7, 127.3, 127.2, 127.2, 127.1, 124.8, 124.7, 120.1, 120.1, 120.0, 120.0, 79.8, 79.6, 77.4, 66.6, 66.4, 63.6, 47.8, 47.5, 35.1, 34.8, 34.7, 32.6, 32.5, 28.6, 28.4, 26.9, 26.8, 23.7, 23.6, 19.7, 18.4, 17.9, 14.2, 14.0. The analytical and spectroscopic data are in

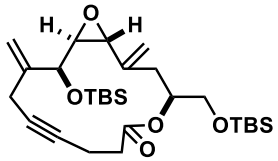
agreement with those reported in the literature.[12,13]



Compound 47

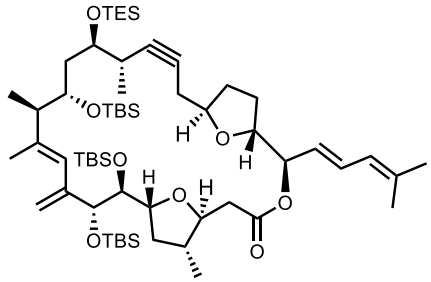
Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 60°C; white solid (5.30 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.96 (s, 1H), 6.55 (s, 1H), 5.34 (dd, *J* = 7.3, 3.4 Hz, 1H), 4.70 (dd, *J* = 6.4, 4.8 Hz, 1H), 3.94 (dd, *J* = 6.6, 1.9 Hz, 1H), 3.31 – 3.12 (m, 1H), 2.83 – 2.74 (m, 1H), 2.71 (s, 3H), 2.71 – 2.53 (m, 3H), 2.18 (d, *J* = 1.3 Hz, 3H), 2.39 – 1.94 (m, 3H), 1.81 – 1.35 (m, 1H), 1.17 (s, 3H), 1.15 (s, 3H), 1.11 (s, 3H), 0.95 – 0.94 (m, 3H), 0.92 (s, 9H), 0.87 (s, 9H), 0.10 (s, 6H), 0.09 (s, 3H), 0.07 (d, *J* = 2.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 216.7, 170.2, 164.9, 152.6, 137.0, 120.7, 116.9, 82.3, 78.2, 77.4, 76.5, 72.8, 54.7, 53.5, 44.6, 41.8, 39.1, 29.9, 26.4, 26.2, 26.1, 24.3, 21.2, 20.7, 19.4, 18.8, 18.7, 18.5, 17.1, 15.2, −3.1, −3.6, −3.9, −3.9. The analytical and spectroscopic data are in agreement with those reported in the literature.[14]

Compound 49.



Prepared analogously with complex **1a** (13.9 mg, 12.5 µmol, 5 mol%) at 23°C; white solid (4.42 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.19 (p, *J* = 1.1 Hz, 1H), 5.14 (d, *J* = 1.2 Hz, 1H), 5.12 – 5.06 (m, 1H), 5.05 (t, *J* = 1.5 Hz, 1H), 5.01 (p, *J* = 1.2 Hz, 1H), 4.12 (d, *J* = 4.8 Hz, 1H), 3.71 (dd, *J* = 10.4, 5.0 Hz, 1H), 3.60 (dd, *J* = 10.4, 5.7 Hz, 1H), 3.31 (dd, *J* = 2.1, 0.8 Hz, 1H), 3.19 (d, *J* = 17.6 Hz, 1H), 3.14 (dd, *J* = 4.8, 2.1 Hz, 1H), 2.93 (d, *J* = 17.6 Hz, 1H), 2.55 – 2.32 (m, 6H), 0.91 (s, 9H), 0.89 (s, 9H), 0.14 (s, 3H), 0.05 (d, *J* = 0.8 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.7, 143.9, 141.2, 114.2, 114.1, 80.4, 78.8, 74.9, 72.6, 64.5, 62.7, 57.0, 34.3, 34.1, 26.0, 25.9, 22.7, 18.4, 18.4, 15.3, –4.7, –4.9, –5.3, –5.3. The analytical and spectroscopic data are in agreement with those reported in the literature.[15]

Compound 50.



To a stirred suspension of diyne 50 (8.1 mg, 7.3 µmol) and powdered molecular sieves 5Å (30 mg) in toluene (3.5 mL) at 80°C was added a solution of complex **1f** (1.8 mg, 2.2 µmol, 30 mol%) in toluene (1.0 mL) under argon atmosphere. The mixture was stirred for 5 h at this temperature before it was filtered through a short pad of Celite® and rinsed with ethyl acetate (10 mL). The filtrate was evaporated and the residue was purified by flash chromatography on silica gel (hexanes/*t*-butyl methyl ether 97:3 to 9:1) to give the title compound as an oil (6.3 mg, 81%). ^{1}H NMR (600 MHz, C_6D_6, broad signals due to slowly equilibrating conformers): δ = 6.65 (m, 1H), 6.48 (s, 1H), 5.77 (m, 1H), 5.48 (m, 1H), 5.43 (m, 1H), 5.10 (s, 1H), 5.04 (s, 1H), 4.26 (bs, 1H), 4.15 (s, 1H), 4.12 (m, 1H), 4.10 (m, 1H), 4.03 (m, 1H), 4.00 (m, 1H), 3.80 (d, *J* = 7 Hz, 1H), 3.58 (bs, 1H), 2.86 (m, 1H), 2.82 (m, 1H), 2.73 (bs, 1H), 2.57 (m, 1H), 2.53 (m, 1H), 2.40 (m, 1H), 2.33 (d, *J* = 13 Hz, 1H), 2.18 (m, 1H), 2.13 (m, 3H), 2.07 (m, 1H), 2.06 (m, 1H), 1.83 (m, 1H), 1.60 (m, 1H), 1.57 (m, 1H), 1.54 (s, 3H), 1.48 (s, 3H), 1.45 (m, 3H), 1.43 (m, 1H), 1.34 (m, 3H), 1.29 (s, 9H), 1.13 (m, 1H), 1.07 (m, 9H), 1.05 (s, 9H), 1.01 (s, 9H), 0.82 (m, 3H), 0.70 (q, *J* = 8 Hz, 6H), 0.49 (s, 3H), 0.43 (s, 3H), 0.25 (s, 3H), 0.22 (s, 3H), 0.13 (s, 3H), 0.12 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, broad signals due to slowly equilibrating rotamer): δ = 169.2,

147.3, 140.9, 137.2, 132.1, 129.4, 126.0, 125.0, 115.0, 83.8, 83.1, 81.4, 80.3, 80.0, 79.4, 77.8, 76.3, 73.9, 72.6, 47.7, 38.8, 37.8, 33.0, 31.3, 27.8, 27.0, 26.9, 26.3, 26.0, 19.2, 18.7, 18.4, 18.3, 17.6, 16.4, 16.3, 14.4, 7.3, 5.6, –3.8, –3.9, –4.3, –4.3. The analytical and spectroscopic data are in agreement with those reported in the literature.[16]

Stability of Solid $[1a]_2$ in Air

In solid form, the complex is only moderately air-sensitive, showing a half-lifetime at ambient temperature of approximately 8 h (Figure S-11).

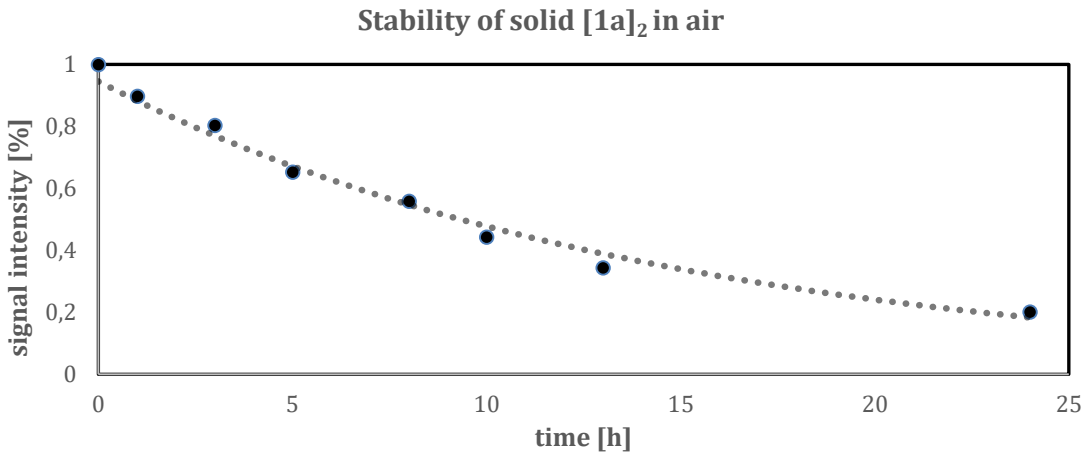


Figure S-11. Stability of solid [**16a**]$_2$ in air at ambient temperature as determined by ^{1}H NMR in C_6D_6; the signals of the *ortho*-protons of the *p*-methoxybenzylidyne group were integrated against the signal of the free ligand. The humidity of the air was ≈ 60%.

Diffusion NMR Studies

Table S-1. Measured and predicted diffusion coefficients (*D*) of the different complexes.

Complex	MW [g mol^{-1}]	$D_{predicted}$ [10^{-10} m^{2}s^{-1}]	$D_{exp.}$ [10^{-10} m^2 s^{-1}]		Conc. [M]	Δ
1a	1113.33	5.55 ±1.6	5.56	±0.11	0.16	0.1%
[1a]$_2$	2226.66	4.11 ±1.0	3.30	±0.03	0.16	-19.7%
[1a·MeCN**]**	1154.38	5.43 ±1.6	5.46	±0.02	0.016	0.5%
1b	1293.48	5.2 ±1.5	4.76	±0.06	0.16	-8.5%
[1b]$_2$	2586.97	3.86 ±1.1	2.96	±0.05	0.16	-23.3%
1d	909.27	6.08 ±1.6	6.80	±0.31	0.006	11.8%
1e	1111.4	5.56 ±1.6	5.56	±0.04	0.006	0.0%
1f	738.98	6.69 ±1.6	7.09	±0.45	0.006	6.0%
2a	1041.31	5.72 ±1.7	6.02	±0.12	0.006	5.2%
[2a]$_2$	2082.62	4.23 ±1.2	4.18	±0.04	0.16	-1.3%
[2a·MeCN**]**	1082.36	5.6251 ±1.6	5.87	±0.22	0.016	4.3%
2b	1039.34	5.73 ±1.6	6.16	±0.05	0.016	7.4%
[2b·MeCN**]**	1080.39	5.63 ±1.6	6.04	±0.09	0.016	7.3%
16	1039.28	5.50 ±1.6	5.58	±0.18	0.006	1.5%

^{95}Mo NMR Experiments

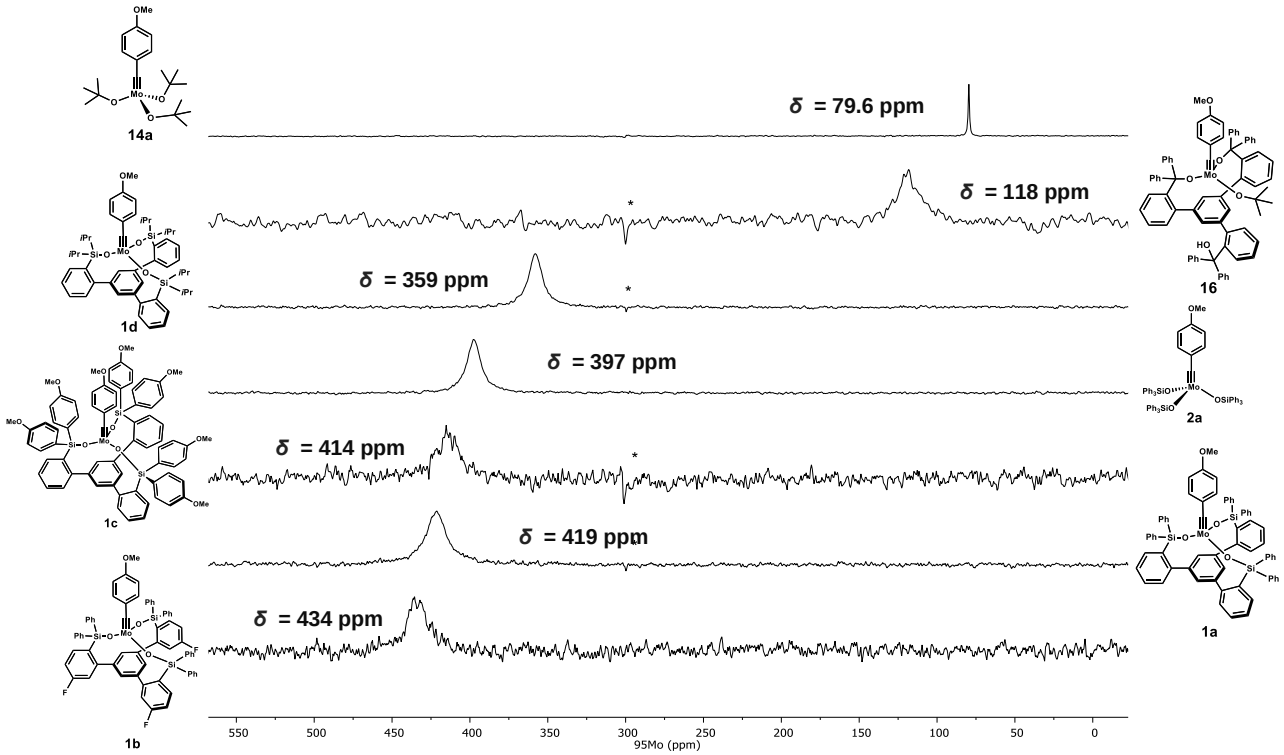


Figure S-12. ^{95}Mo-NMR spectra of different complexes (all in monomeric form). *Indicates artifacts at the pulse-offset; All spectra were recorded at 60°C.

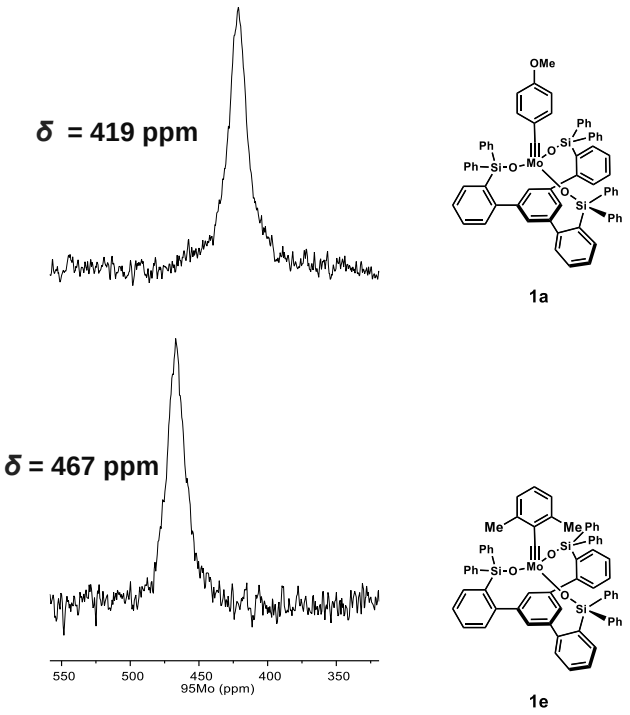


Figure S-13. ^{95}Mo-NMR spectra of the monomeric canopy complexes **1a** and **1e** differing only in the aryl substituent on the alkylidyne; All spectra were recorded at 60°C.

Exchange NMR Experiments

A flame dried *J. Young* NMR tube was filled with argon, charged with a stock solution of complex [**1a**]$_2$ (12.1 µmol, 0.60 mL, 20.2 mM in [D$_8$]-toluene) and a ^{1}H-NMR spectrum was recorded at 25°C. The solution was stirred at 60°C until full conversion to monomeric complex **1a** was observed. Then 3-hexyne (6.9 µL, 61 µmol) was added and the resulting mixture monitored by ROESY NMR spectroscopy. Metallatetrahedrane **18** exchanges with 3-hexyne as well as with the corresponding propylidyne complex **1a'**.

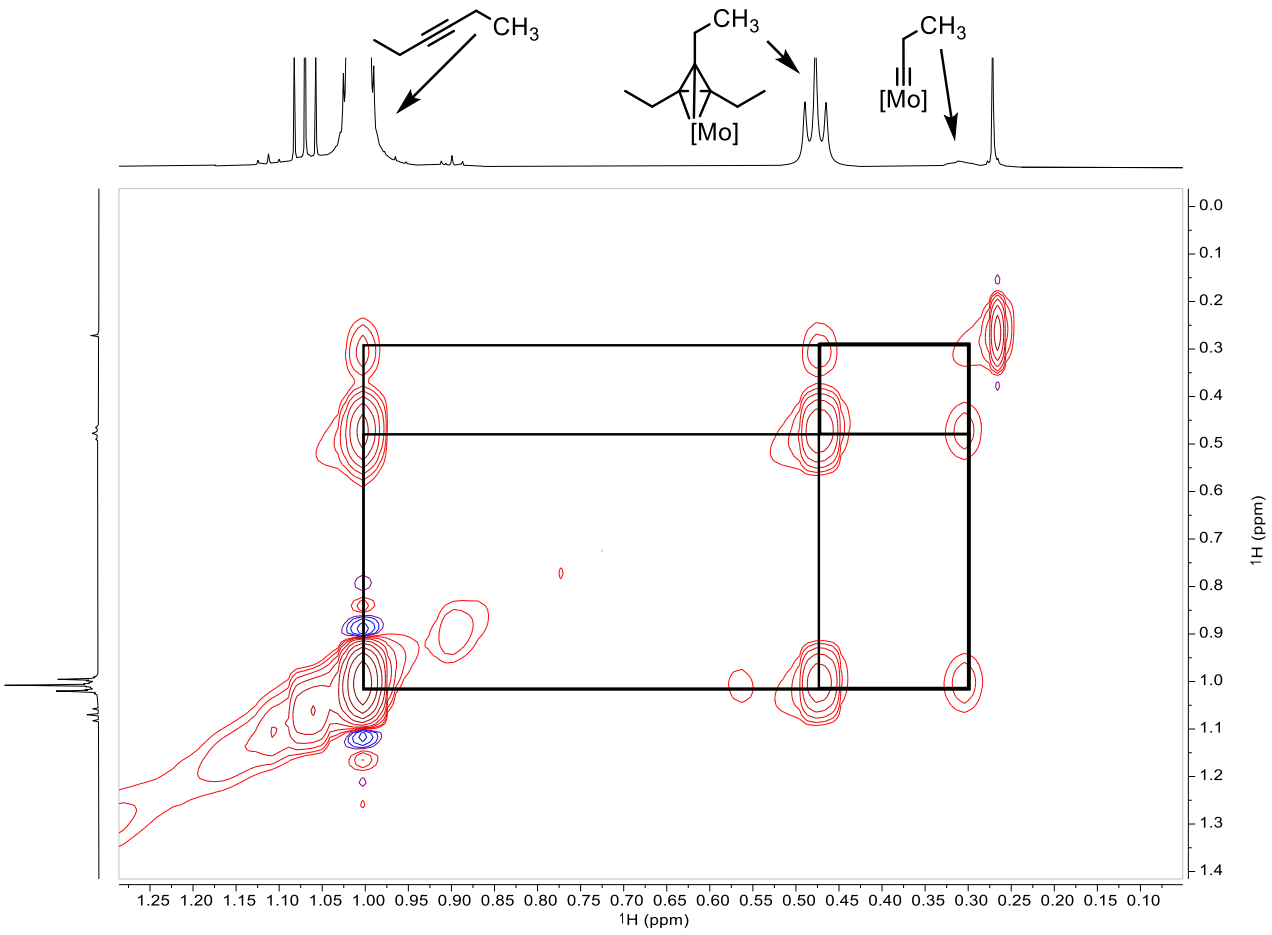
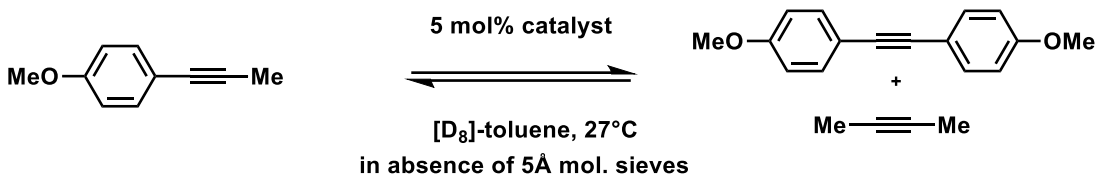


Figure S-14. EASY-ROESY experiment acquired at room temperature showing the interconversion of species in the mixture. The spin-lock time used for this experiment was 300 ms.[17]

Equilibration Kinetic Data



A flame dried *J. Young* NMR tube was filled with argon, charged with a stock solution of the respective complex (3.0 µmol, 0.5 mL, 5.0 µM in [D8]-toluene, 5 mol%) and a ^{1}H-NMR spectrum was recorded at 27°C (dimeric complexes were heated to 60°C until full conversion to monomeric complex was observed). Then a solution of 1-methoxy-4-(prop-1yn-1-yl)benzene **(19)** (100 µL, 60 µmol, 0.6 M in [D8]-toluene) was added and the conversion of the substrate to 1,3-bis(4-methoxyphenyl)-2-propa-1,2-diyne (**20a**) and 2-butyne was monitored by ^{1}H-NMR spectroscopy at 27°C.

The data was corrected for relaxation effects as the relaxation time of 2-butyne is significantly longer due to its high symmetry and small size. Therefore two measurements were compared after the reaction: One with the standard data set and one with a longer delay (30s). Correction factor: 1-methoxy-4-(prop-1yn-1-yl)benzene = 1.023; 2-butyne = 1.127; 1,3-bis(4-methoxyphenyl)-2-propa-1,2-diyne = 1.028.

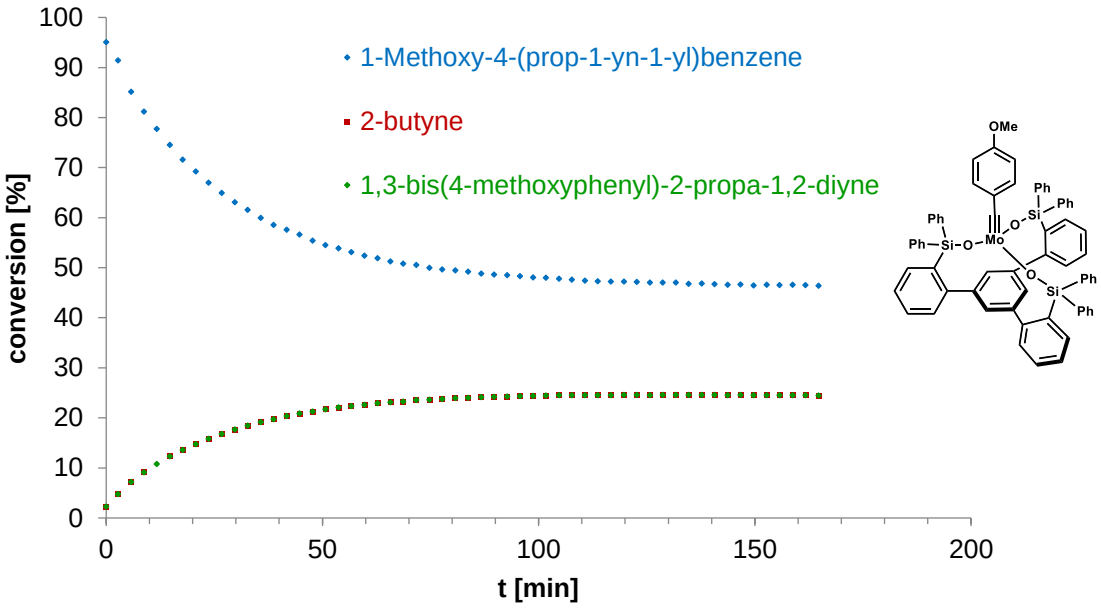


Figure S-15. Benchmarking Experiment: Consumption of 1-methoxy-4-(prop-1yn-1-yl)benzene and generation of 1,3-bis(4-methoxyphenyl)-2-propa-1,2-diyne and 2-butyne in [D8]-toluene, 27°C, 5 mol% of **1a**.

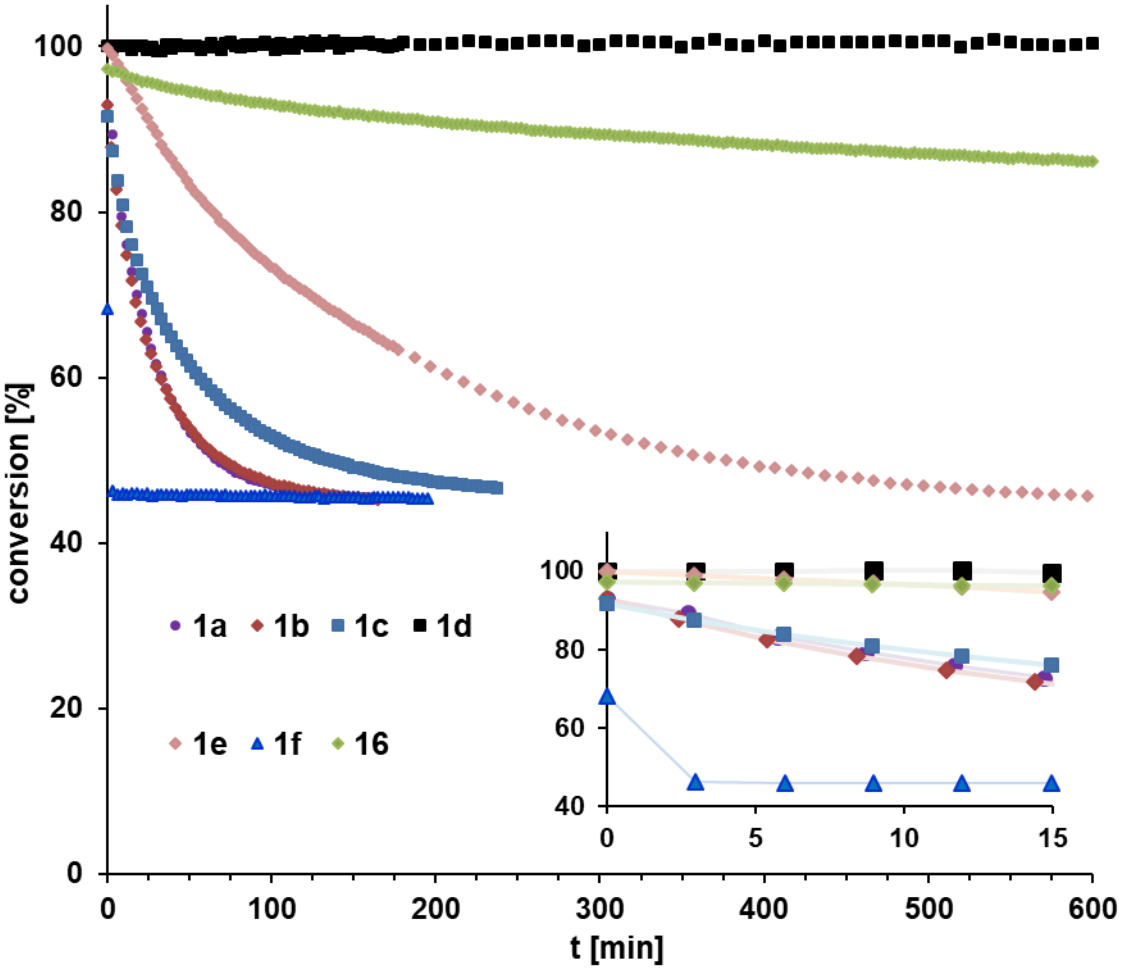
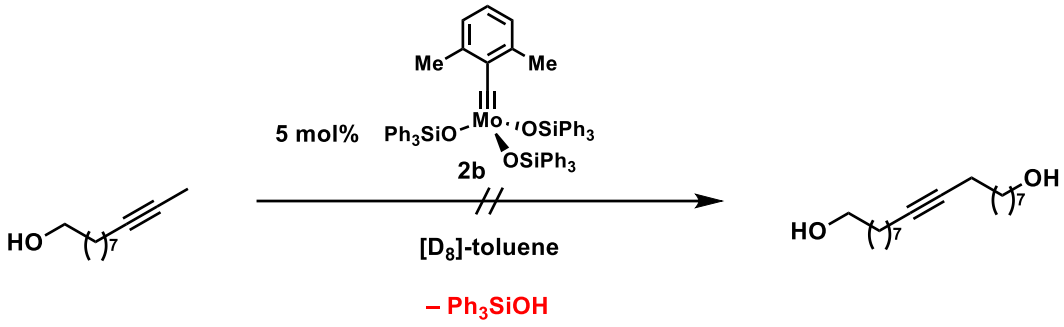


Figure S-16. Benchmarking Experiment: Consumption of 1-methoxy-4-(prop-1yn-1-yl)benzene in [D_8]-toluene, 27°C, 5 mol% of different monomeric catalysts.

Stability Test: Primary Alcohols

A flame dried *J. Young* NMR tube was filled with argon, charged with a stock solution of the catalyst **2b** (3.0 µmol, 0.5 mL, 5.0 µM in [D_8]-toluene, 5 mol%) and a ^{1}H-NMR spectrum was recorded at 27°C. Then undec-9-yn-1-ol (10.4 mg, 0.06 mmol) was added and a ^{1}H-NMR spectrum was recorded. Instantaneous hydrolysis and formation of free ligand was observed, but no alkylidene signal in the range between 10-20 ppm (not shown). We noticed in the ^{1}H-NMR spectrum that the free ligand shifts in presence of undec-9-yn-1-ol, likely due to hydrogen bonding interactions.

The hydrolysis of the silanolate ligands was equally fast when EtOH (10 equiv.) was used.



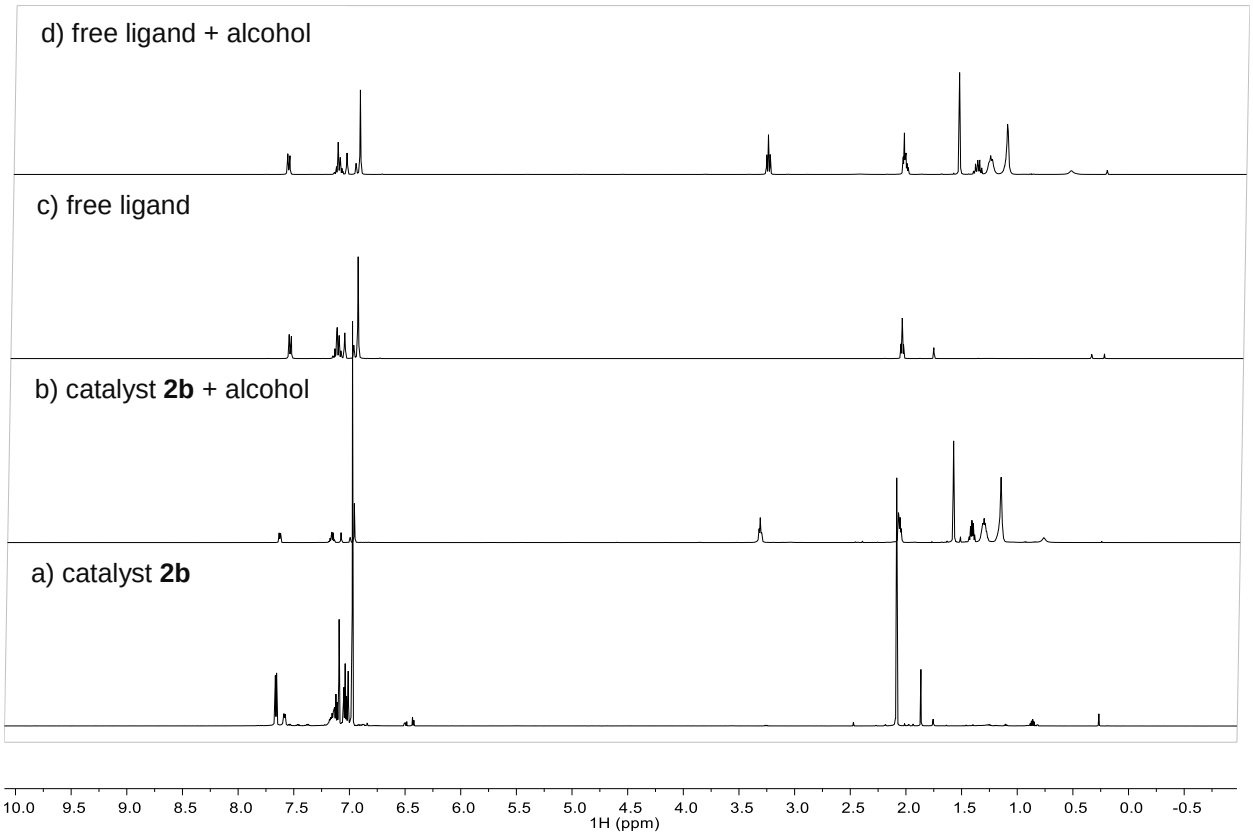


Figure S-17. Tolerance test for primary alcohols in [D_8]-toluene at 25°C: a) catalyst **2b** b) hydrolysis of catalyst **2b** upon addition of undec-9-yn-1-ol c) free ligand d) free ligand (1.0 equiv.) and undec-9-yn-1-ol (3.0 equiv.).

Water Resistance Tests

A flame dried *J. Young* NMR tube was filled with argon, charged with a stock solution of the catalyst **2b** (3.0 µmol, 0.5 mL, 5.0 µM in [D8]-toluene) and a ^{1}H-NMR spectrum was recorded at 27°C. Then water (0.5 µL, 30.0 µmol) was added and a ^{1}H-NMR spectrum was recorded. Complete hydrolysis after 5 min and formation of free ligand was observed, but no alkylidene signal in the range between 10-20 ppm (not shown).

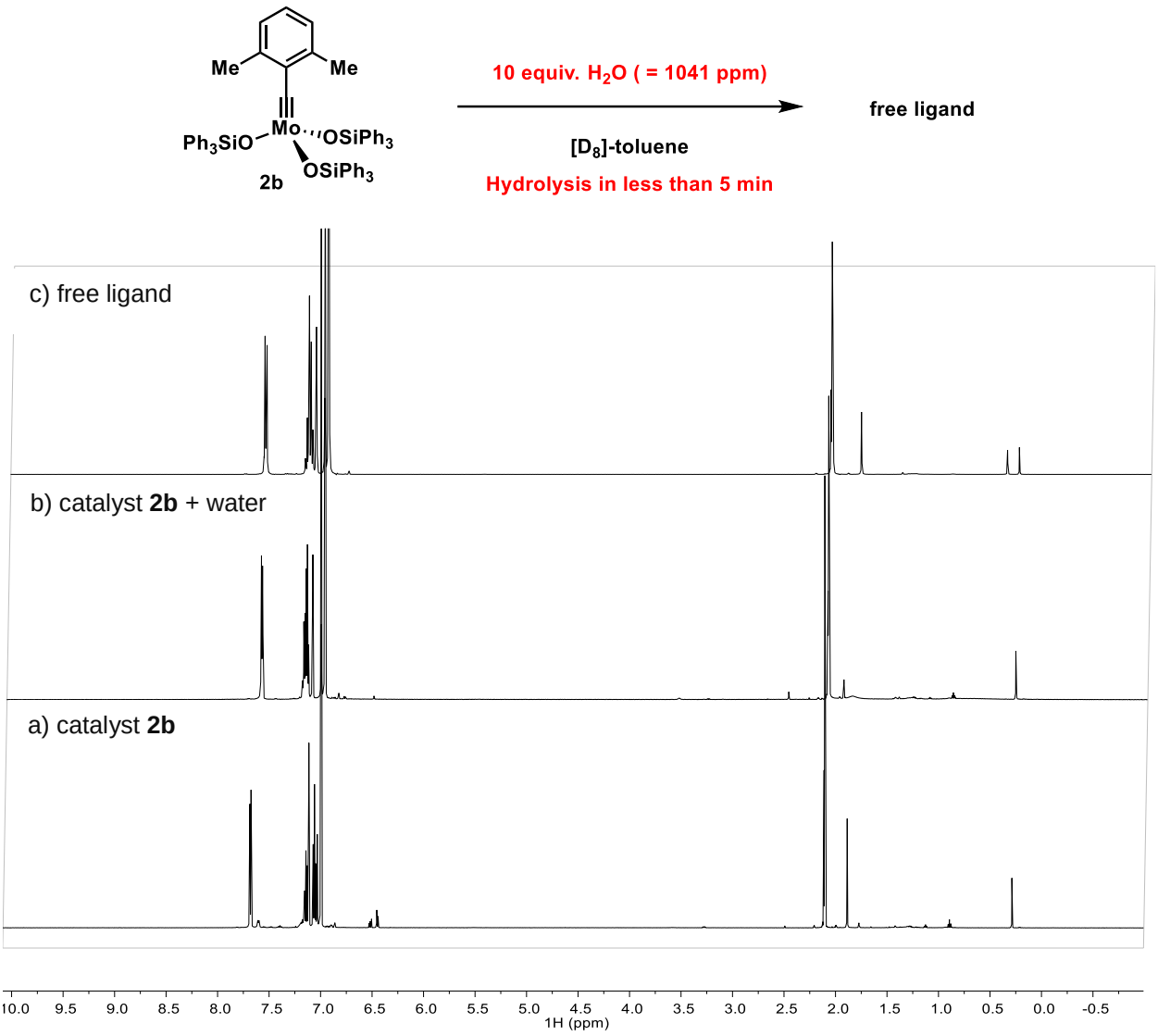


Figure S-18. Water resistance test in [D8]-toluene at 25°C: a) catalyst **2b** b) hydrolysis of catalyst **2b** upon addition of water c) free ligand.

A flame dried *J. Young* NMR tube was filled with argon, charged with a stock solution of the catalyst **1e** (3.0 µmol, 0.5 mL, 5.0 µM in [D_8]-toluene) and a ^{1}H-NMR spectrum was recorded at 27°C. Then water (0.5 µL, 30.0 µmol) was added and a ^{1}H-NMR spectrum was recorded every 10 mins. Complete hydrolysis after 9 h and formation of free ligand was observed, but no alkylidene signal in the range between 10-20 ppm (not shown). The tripodal catalyst **1e** proofed to be significant more water resistant. The NMR measurement starts at roughly 78%, since water had to be added and the NMR tube needed to be shimmed again.

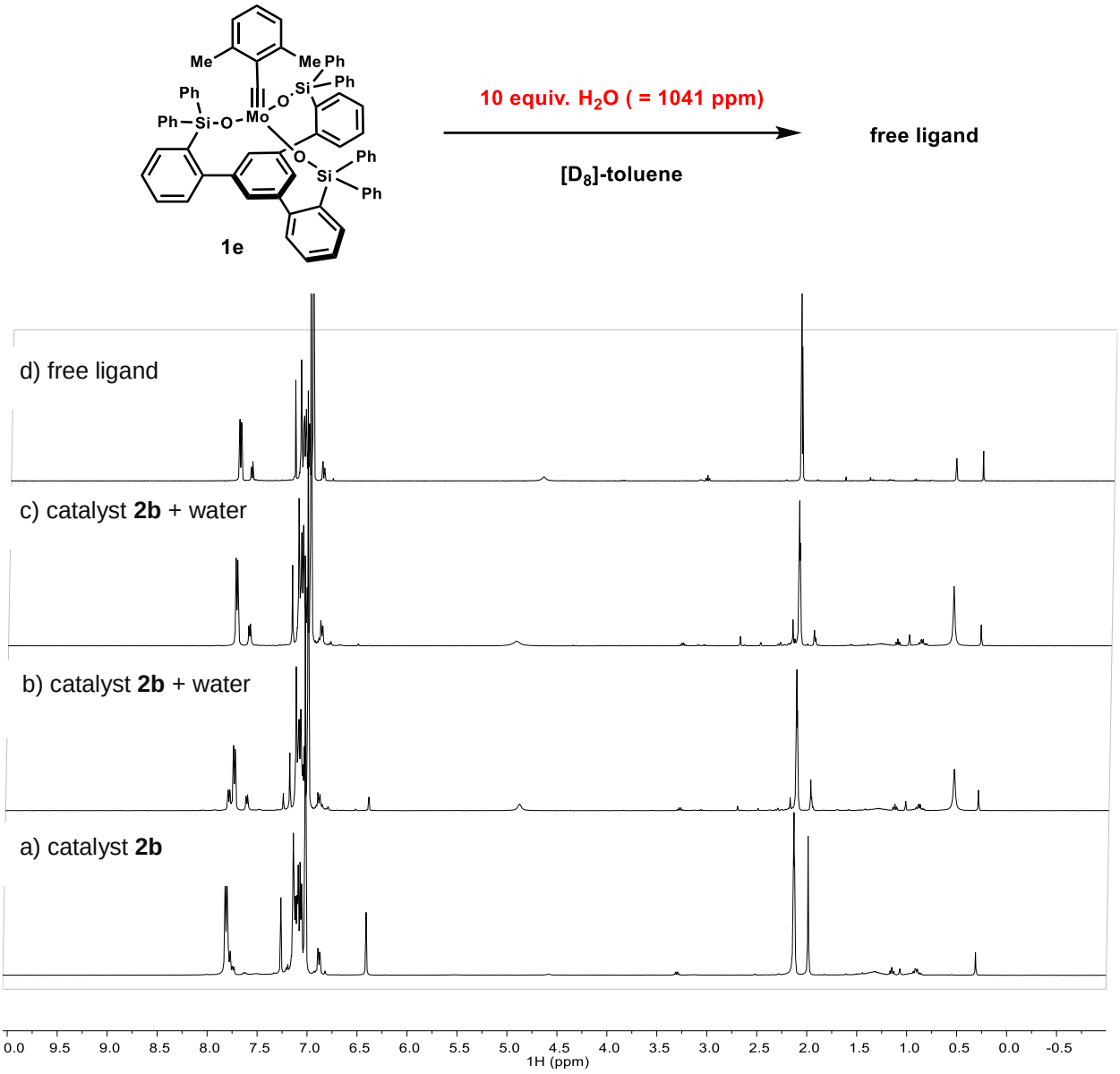


Figure S-19. Water resistance test in [D_8]-toluene at 25°C: a) catalyst **2b** b) hydrolysis of catalyst **2b** after 4h c) hydrolysis of catalyst **2b** after 15h d) free ligand.

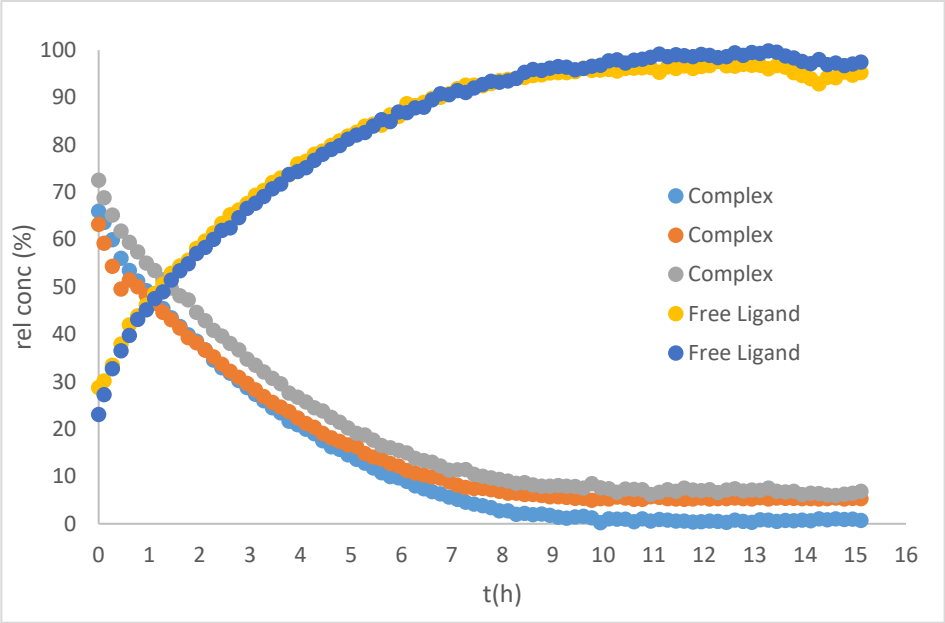
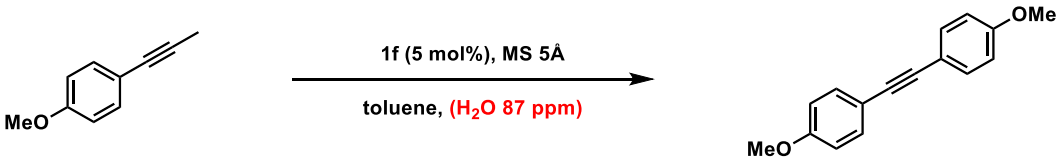


Figure S-20. Decay of catalyst **1e** over time as monitored by ^{1}H-NMR spectroscopy.

Alkyne Metathesis in the Presence of Molecular Sieves in *a priori* Technical Grade Solvent



Methoxy-4-(prop-1-yn-1-yl)benzene (36.5 mg, 25.0 µmol) was added to a stirred suspension of powdered molecular sieves (5Å, 250 mg) in technical grade toluene (1.25 mL) at 23°C under argon atmosphere. The mixture was stirred for 4 h at this temperature before catalyst **1e** (9.2 mg, 12.5 µmol, 5 mol%) was added. This suspension was stirred for additional 14 h before it was filtered through a short pad of Celite® which was carefully rinsed with ethyl acetate (20 mL). The combined filtrates were evaporated to give 1,3-bis(4-methoxyphenyl)-2-propa-1,2 diyne (96%, NMR yield).

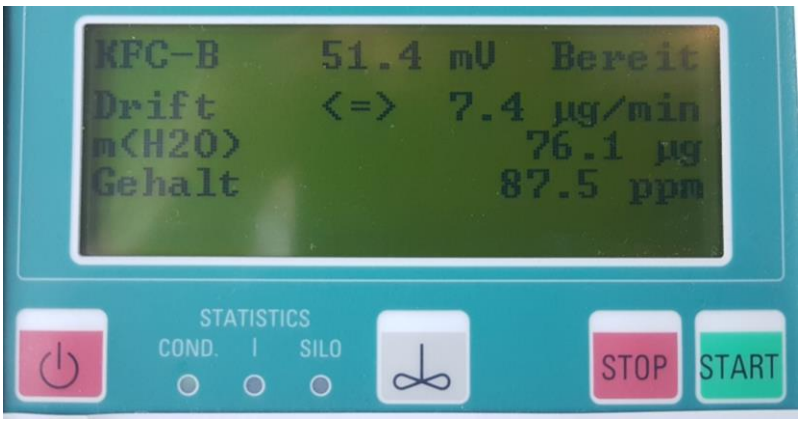
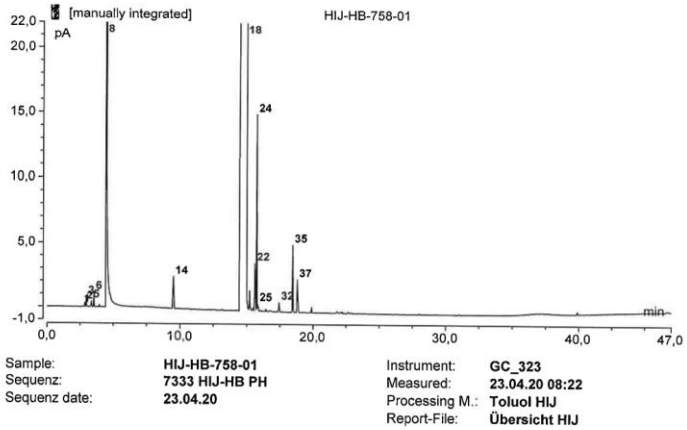


Figure S-21. Karl Fischer Titration of used technical grade toluene reveals a water content of 87.5 ppm.

Alkyne Metathesis in the Presence of Molecular Sieves in Toluene Contaminated with Ethanol



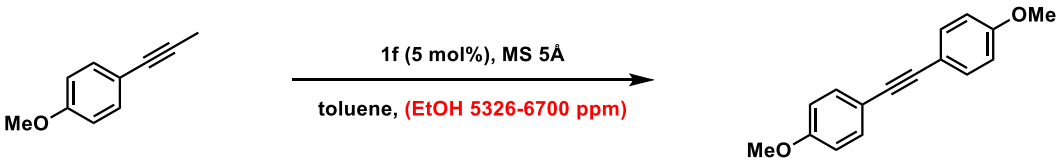
No.	Ret.Time min	area-% %	Peak Name
8	4,44	0,192	MG:46 Ethanol
14	9,51	0,003	MG:78 Benzol
18	14,94	99,762	MG:92 Toluol
19	15,22	0,002	
22	15,61	0,005	
23	15,66	0,001	
24	15,75	0,017	MG:112 Ethylcyclohexan
35	18,46	0,006	MG:106 Ethylbenzol
37	18,81	0,004	MG:106 Xylol

39 peaks out of 48 (total area percentage= 0,01 %) are below threshold.

Instrument parameters:

Column:	59,5 m	DB-1701 0,25/0,5df G/733
Temperature:	220 / 30, 7 min iso 6/min 240, 5min iso / 350	
Gas:	1,10 bar	H2
Sample size:	1,0 µL	

Figure S-22. Determination of ethanol content in toluene by GC-MS.



Ethanol-containing toluene (1.25 mL, 5326-6700 ppm EtOH) was added to powdered molecular sieves (5Å, 250 mg) and catalyst **1e** (9.2 mg, 12.5 µmol, 5 mol%) at 23°C under argon atmosphere. The mixture was stirred for 1 h at this temperature before methoxy-4-(prop-1-yn-1-yl)benzene (36.5 mg, 25.0 µmol) was introduced. This suspension was stirred for additional 14 h before it was filtered through a short pad of Celite® which was carefully rinsed with ethyl acetate (20 mL). The combined filtrates were evaporated to give 1,3-bis(4-methoxyphenyl)-2-propa-1,2 diyne (98%, NMR yield).

Temperature Stability

A flame dried *J. Young* NMR tube was filled with argon, charged with a stock solution of complex **[1a]$_2$** (3.0 μmol, 0.5 mL, 5.0 μM in [D_8]-toluene) and a ^{1}H-NMR spectrum was recorded at 27°C. The solution was stirred at 60°C for 1h to form monomeric complex **1a** quantitatively.

The temperature stability of the monomeric complex was monitored for 7 days at 25°C by NMR spectroscopy: neither decomposition nor reversion to **[1a]$_2$** was observed.

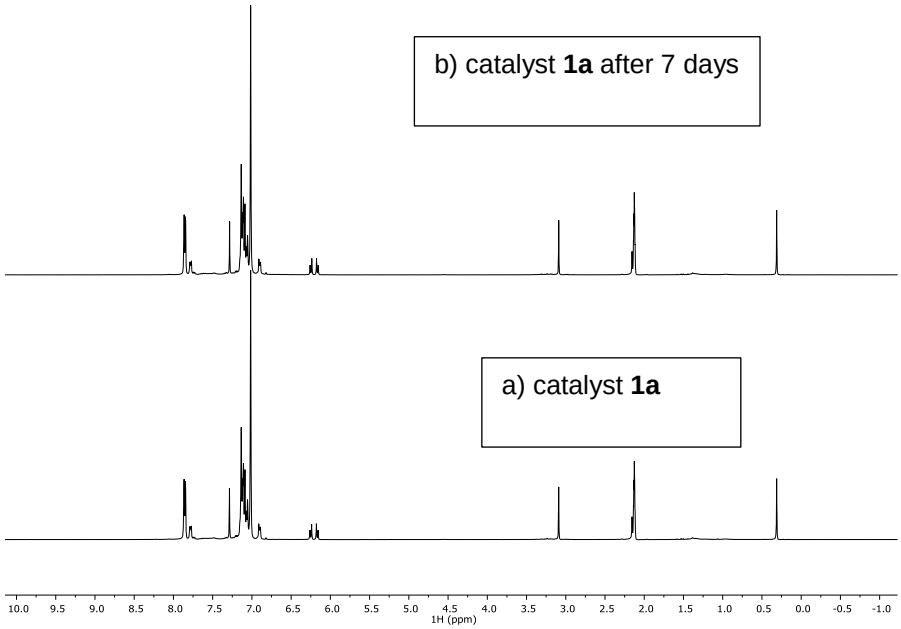


Figure S-23. Temperature stability test of catalyst **1a** in [D_8]-toluene at 25°C: a) catalyst **1a** b) catalyst **1a** after 7 days.

The temperature stability of monomeric catalyst was also monitored for 12 h at 60°C by NMR spectroscopy. Also in this case, neither decomposition nor reversion to **[1a]$_2$** was observed.

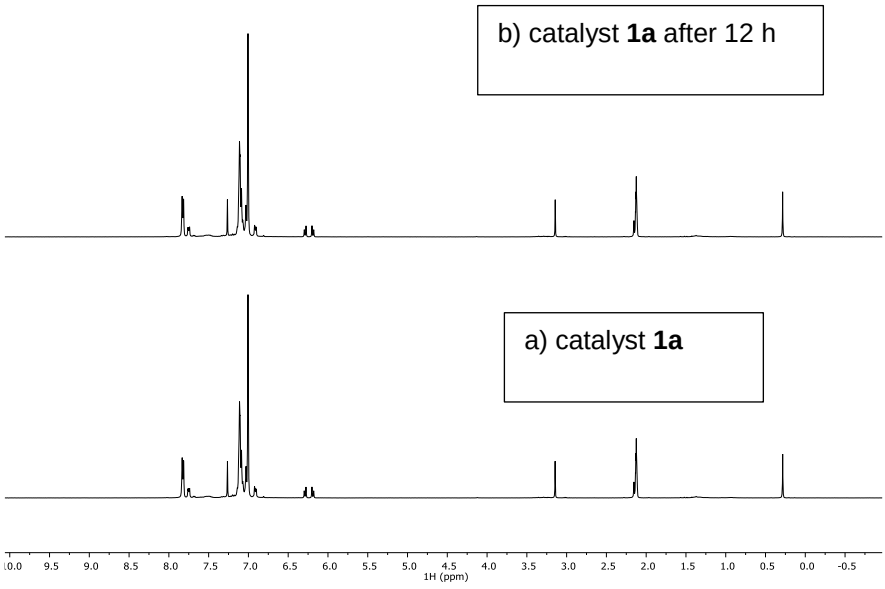


Figure S-24. Temperature stability test of catalyst **1a** in [D_8]-toluene at 60°C: a) catalyst **1a** b) catalyst **1a** after 12 h.

COMPUTATIONAL DETAILS

All geometry optimizations were performed with the Gaussian09 package[18] with the PBE0 functional.[19] Mo was represented by the quasi-relativistic effective core potential (RECP) from the Stuttgart group and the associated basis sets.[20,21,22] The remaining atoms (H, C, O, Si) were represented by a double-ζ Def2-SVP basis set.[23] NMR calculations were performed within the GIAO framework using ADF 2014[24] with the PBE0 functional and Slater-type basis sets of double-ζ quality (DZ). Relativistic effects were treated by the 2 component zeroth order regular approximation (ZORA).[25] Analysis of scalar-relativistic natural localized molecular orbitals were done with the NBO 6.0 program.[26] Calculated NMR shielding tensors were analyzed using these scalar-relativistic NLMO.[27,28] The 3D representation of the calculated shielding tensors were obtained as polar plots[29] of functions $\sum_{ij} r_i \sigma_{ij} r_j$.

Results of Natural Chemical Shielding (NCS) Analysis

Table S-2. Metal alkylidynes **1e** and **2b**. All values are reported in ppm.

	σ_{xx}	σ_{dia}	σ_{para}	components of σ_{para}			
				σ(M-C)	σ(C-C)	π(M-C)	π(M-C)'
alkylidyne **1e** (σ_{11})	-234	248	-481	-269	-159	-62	0
alkylidyne **1e** (σ_{22})	-219	243	-462	-247	-134	0	-67
alkylidyne **1e** (σ_{33})	113	278	-166	-3	0	-46	-48
alkylidyne **2b** (σ_{11})	-227	249	-476	-269	-149	-62	0
alkylidyne **2b** (σ_{22})	-201	245	-446	-242	-135	0	-57
alkylidyne **2b** (σ_{33})	138	281	-143	-2	0	-37	-34

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