

# SUPPORTING INFORMATION

## Practical New Silyloxy-Based Alkyne Metathesis Catalysts with Optimized Activity- and Selectivity Profiles

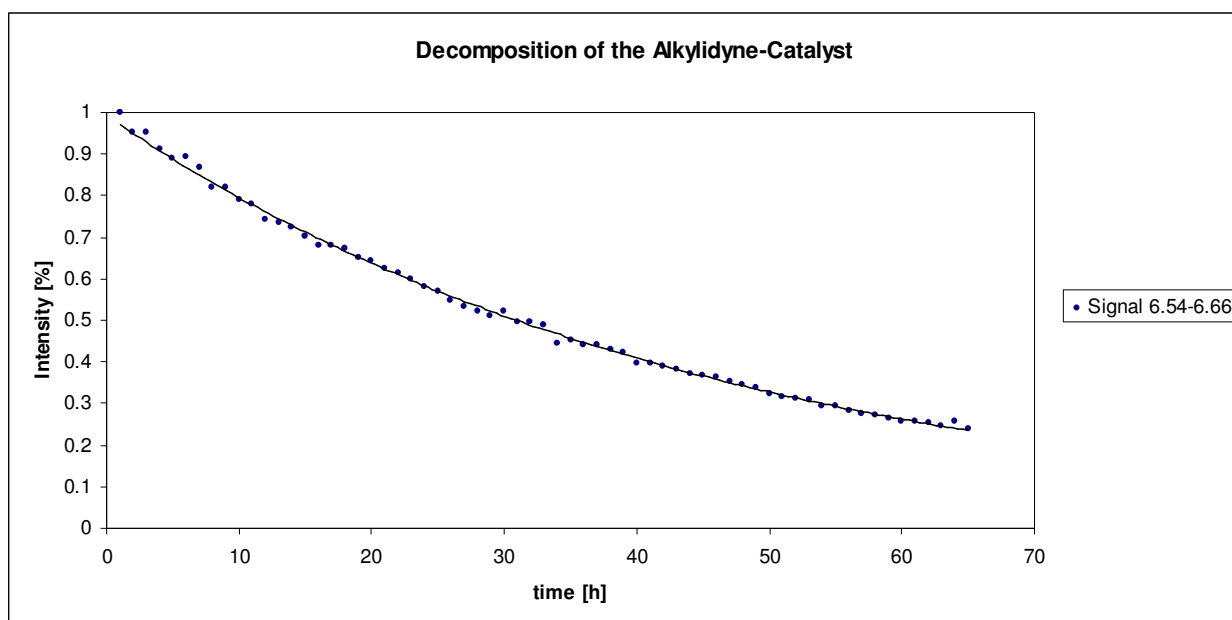
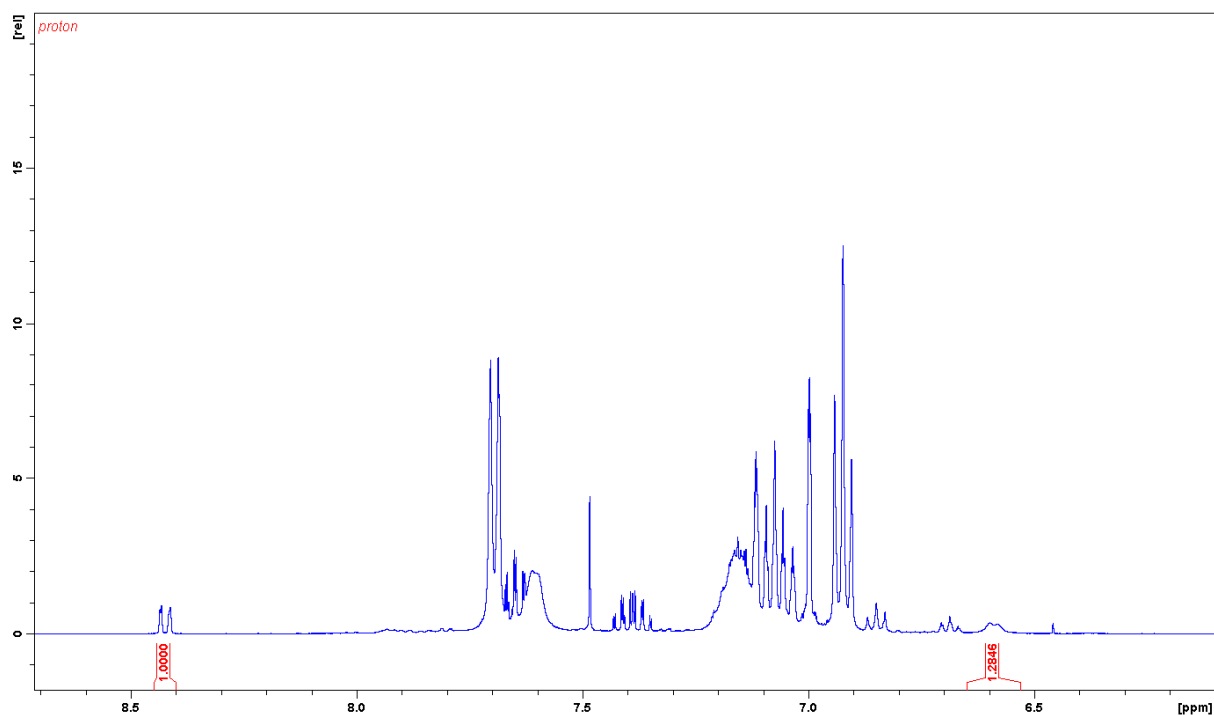
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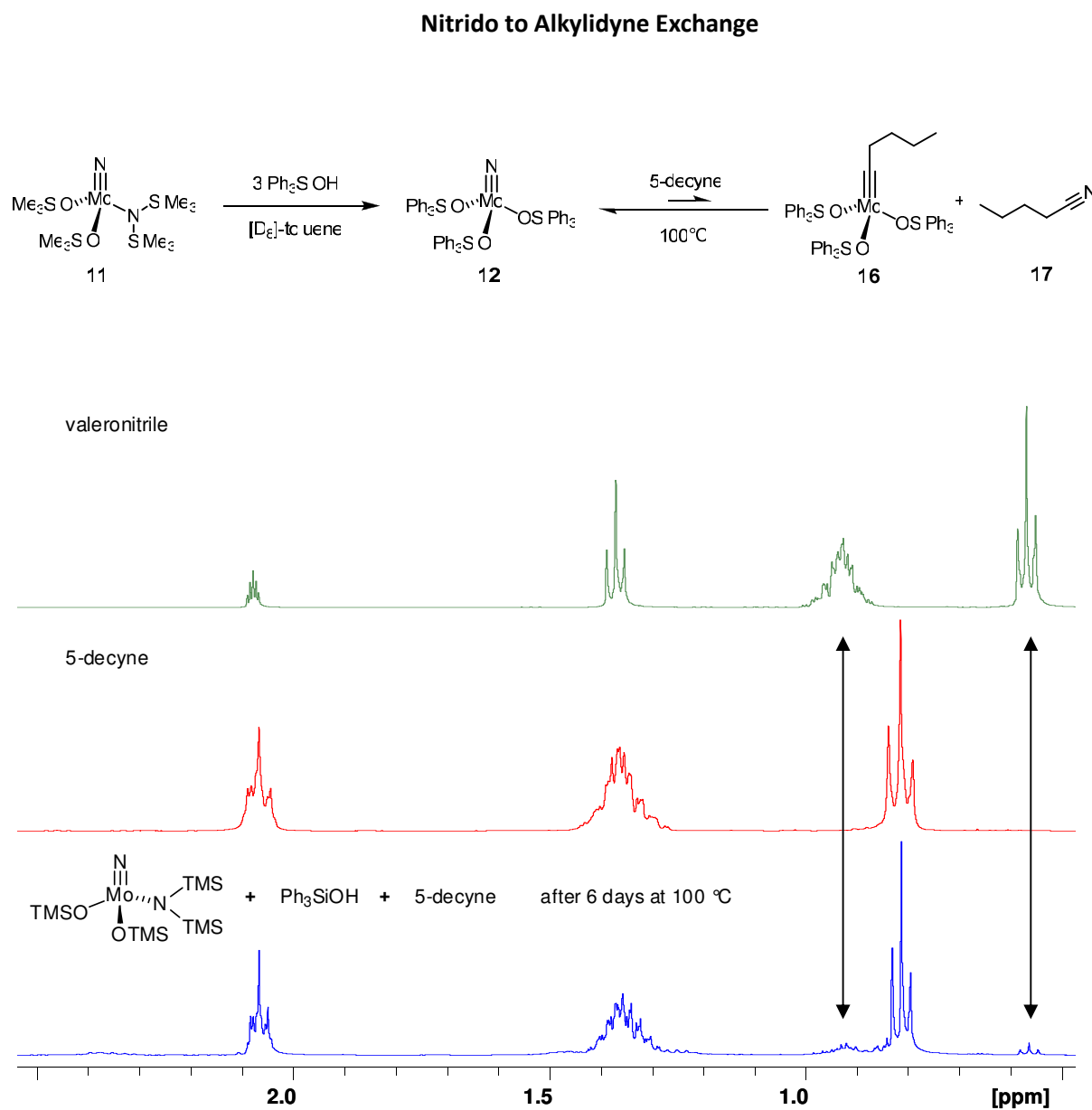
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Determination of the Half-Lifetime of  $[\text{Mo}(\equiv\text{CPh})(\text{OSiPh}_3)_3(\text{Et}_2\text{O})] (24 \cdot \text{Et}_2\text{O})$ 

**Figure S-1.** Decomposition of complex **24**·Et<sub>2</sub>O in [D<sub>8</sub>]-toluene solution at ambient temperature as monitored by <sup>1</sup>H NMR, revealing a half-lifetime of ca. 30 h. The data were recorded by integrating the signal of the *ortho* protons of the benzylidene phenyl ring ( $\delta_{\text{H}} = 6.54\text{--}6.66$  ppm) against a well separated signal of phenanthrene ( $\delta_{\text{H}} = 8.41\text{--}8.43$  ppm) used as the internal standard (top: spectrum of the mixture at time = zero).



**Figure S-2.** Aliphatic region of the <sup>1</sup>H NMR spectra of authentic valeronitrile (**17**, top) and 5-decyne (middle) in [D<sub>8</sub>]-toluene in comparison with the spectrum of a mixture of **11**, Ph<sub>3</sub>SiOH (3 equiv.) and 5-decyne (2 equiv.) after heating for 6 d to 100°C in the same solvent (bottom). The formation of small amounts of **17** was independently confirmed by GC/MS analysis of the reaction mixture.

## Screening

**Table S-1.** Metathesis of 1-phenyl-1-propyne to toluene in toluene at 80°C catalyzed by complex **15** (10 mol%) activated by different metal salts (12 mol%)

Metal Salt	Yield (% GC)		
	1 h	3 h	19 h
MgCl <sub>2</sub>	0	0	65
MnCl <sub>2</sub>	39	56	64
FeCl <sub>2</sub>	46	56	68
FeCl <sub>3</sub>	61	75	80
CoCl <sub>2</sub>	6	52	61
NiCl <sub>2</sub>	0	0	66
CuCl <sub>2</sub>	57	58	66
ZnCl <sub>2</sub>	53	60	73

**Table S-2.** Metathesis of 1-phenyl-1-propyne to toluene catalyzed by complex **24**·Et<sub>2</sub>O (1 mol%) in toluene (0.2 M) at ambient temperature in the presence of molecular sieves of different specifications (2 mg per μmol of released 2-butyne).

Additive	Yield (GC)	
	1 h	3 h
---	48%	49%
MS 3 Å, pellets	50%	53%
MS 4 Å, pellets	73%	89%
MS 5 Å, pellets	76%	95%
MS 5 Å, powder	> 99%	> 99%

**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<sub>2</sub>O, 1,4-dioxane (Mg/anthracene), CH<sub>2</sub>Cl<sub>2</sub>, DME, MeCN (CaH<sub>2</sub>), hexane, toluene (Na/K), MeOH (Mg). Flash chromatography (FC): Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on Bruker DPX 300, AMX 300, AV 400, and AVIII 600 spectrometer in the solvents indicated; chemical shifts ( $\delta$ ) 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<sub>3</sub>:  $\delta_c \equiv 77.0$  ppm; residual CHCl<sub>3</sub> in CDCl<sub>3</sub>:  $\delta_H \equiv 7.26$  ppm; CD<sub>2</sub>Cl<sub>2</sub>:  $\delta_c \equiv 53.8$  ppm; residual <sup>1</sup>H:  $\delta_H \equiv 5.32$  ppm; [D<sub>8</sub>]-toluene:  $\delta_c \equiv 20.7$  ppm; residual D<sub>5</sub>C<sub>6</sub>CD<sub>2</sub>H:  $\delta_H \equiv 2.09$  ppm). IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ( $\tilde{\nu}$ ) in cm<sup>-1</sup>. 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). Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received, unless stated otherwise.

1,10-Phenanthroline was purified and dried by two subsequent sublimations of the commercial sample (Aldrich,  $\geq 99\%$ ) under vacuum ( $10^{-3}$  mbar).

The molecular sieves used in this investigation were dried for 24 h at 280°C (sand bath) under vacuum prior to use and were stored and transferred under Ar.

**Abbreviations:** phen = 1,10-phenanthroline; dme = 1,2-dimethoxyethane;

## Preparation of the Catalysts

**[(Me<sub>3</sub>SiO)<sub>2</sub>((Me<sub>3</sub>Si)<sub>2</sub>N)Mo≡N] (11).** Me<sub>3</sub>SiCl (51 mL, 400 mmol) was added to a suspension of Na<sub>2</sub>MoO<sub>4</sub> (20.59 g, 100 mmol) in DME (700 mL) under Ar and the mixture was vigorously stirred under reflux for 16 h. After evaporation of the solvents, the light blue residue was suspended in hexane (600 mL). Commercial LiN(SiMe<sub>3</sub>)<sub>2</sub> (33.47 g, 200 mmol) was added in portions to the suspension and the mixture was stirred at room temperature for 2 h. For work-up, the suspension was filtered through a pad of Celite under Ar, the filtrate was evaporated and the residue purified by distillation in high vacuum to give complex **11** as a pale yellow liquid (29.9 g, 67%). B. p. = 57-58 °C ( $1.8 \cdot 10^{-2}$  mbar); <sup>1</sup>H NMR (300 MHz, [D<sub>8</sub>]-toluene, -20 °C):  $\delta$  = 0.54 (s, 9H), 0.34 (s, 18H), 0.25 (s, 9H); <sup>13</sup>C NMR (75 MHz, [D<sub>8</sub>]-toluene, -20 °C):  $\delta$  = 4.4, 2.5, 1.2; IR (film):  $\tilde{\nu}$  = 1056 (Mo≡N) cm<sup>-1</sup>. The spectroscopic data are in agreement with those reported in the literature.<sup>1</sup>

**[Mo(≡N)(OSiPh<sub>3</sub>)<sub>3</sub> · phen] (15).** Ph<sub>3</sub>SiOH (16.58 g, 60.0 mmol) was added to a solution of [Mo(≡N)(OTMS)<sub>2</sub>(N(TMS)<sub>2</sub>)] (**11**) (8.97 g, 20.0 mmol) in toluene (200 mL) under Ar and the resulting solution stirred for 30 min at ambient temperature before it was transferred via canula into a flask containing 1,10-phenanthroline (doubly sublimed, 3.60 g, 20.0 mmol). A pale-yellow precipitate started to form after a few minutes from the resulting yellow solution. After 30 min, the solvent was evaporated and the residue was dried in vacuo ( $10^{-3}$  mbar) for 1 h at ambient temperature to remove residual silanol impurities and then at 60°C. The resulting solid was suspended in hot (105°C) toluene (500 mL), insoluble residues were removed by filtration of the hot suspension, and the filtrate was allowed to reach ambient temperature. After 2 d, the greenish solution was decanted from the yellow crystals (14.44 g), which were dried in vacuo. The greenish mother liquor was evaporated; recrystallization of the remaining material from toluene (200 mL) as described above gave another crop of product (2.95 g). A third round of recrystallization gave yet another crop of product (1.59 g). Overall, 18.98 g (82 %) of complex **15** were obtained in form of yellow crystals, which contained ½ equivalent of toluene per Mo according to the X-ray structure analysis. Depending on the degree of drying, however, the amount of toluene in the crystals can vary slightly. The crystals can be stored in air for extended periods of time (> 1 year) without any signs of decomposition. Their catalytic activity after activation with MnCl<sub>2</sub> (see below) is also unchanged after this period of time. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 9.20 (dd, *J* = 5.0, 1.6 Hz, 1H), 8.98 (dd, *J* = 4.5, 1.6 Hz, 1H), 8.24 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.89-7.85 (m, 6H), 7.83 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.59 (dd, *J* = 8.2, 4.5 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 7.31-7.25 (m, 3H), 7.14-7.10 (m, 6H), 7.10-7.05 (m, 18H), 6.98 (dd, *J* = 8.1, 5.0 Hz, 1H), 6.91-6.85 (m, 12H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 156.2, 147.7, 142.2, 141.5, 139.0, 138.0, 137.7, 137.2, 136.1, 135.2, 134.9, 129.6, 129.5, 129.0, 128.3, 127.9, 127.6, 127.4, 127.1, 127.1, 124.3, 124.2; IR (ATR): 3044, 3021, 1588, 1518, 1495, 1483, 1426, 1341, 1298, 1262, 1222, 1188, 1113, 1104, 1056, 1028, 1011, 998, 942, 893, 865, 840, 768, 740, 727, 708, 697 cm<sup>-1</sup>; MS (ESI<sup>+</sup>): *m/z* (%): 1118 (100)

<sup>1</sup> Chiu, H.-T.; Chuang, S.-H.; Lee, G.-H.; Peng, S.-M. *Adv. Mater.* **1998**, *10*, 1475.

$[M+H^+]$ , 1043 (10); HRMS (ESI<sup>+</sup>):  $m/z$ : calcd for  $C_{66}H_{54}MoN_3O_3Si_3$   $[M+H^+]$ : 1118.2513, found: 1118.2523; elemental analysis (%) calcd for  $[2(C_{66}H_{53}MoN_3O_3Si_3) \cdot (C_7H_8)]$ : C 71.81, H 4.94, N 3.61; found: C 72.28, H 4.98, N 3.83.



**Figure S-3.** Crystals of the air-stable complex **15**.

**[NMe<sub>4</sub>][Mo(CO)<sub>5</sub>(COPh) (20)]**.<sup>2</sup> PhLi (1.8 M in Bu<sub>2</sub>O, 11.2 mL, 20.0 mmol) was added dropwise to a solution of Mo(CO)<sub>6</sub> (5.28 g, 20.0 mmol) in boiling Et<sub>2</sub>O (300 mL) and reflux was continued for 30 min once the addition was complete. The mixture was allowed to reach ambient temperature before all volatile materials were distilled off. The residue was dissolved in water and a solution of Me<sub>4</sub>NBr (4.60 g, 30.0 mmol) in water (10 mL) was added. After stirring for 15 min, the resulting orange-red precipitate was filtered off, washed with Et<sub>2</sub>O (20 mL) and dried in vacuo. For further purification, the material was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and the product was precipitated by slow addition of Et<sub>2</sub>O (100 mL). This procedure was repeated one more time to give complex **20** as an orange solid (4.28 g, 52%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.44-7.41 (m, 2H), 7.36-7.30 (m, 2H), 7.23 (tt,  $J = 7.2, 1.4$  Hz, 1H), 3.21 (s, 12H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 211.6, 156.2, 128.3, 127.9, 125.0, 56.5.

**[Mo(≡CPh)Br<sub>3</sub>(dme)] (22)**.<sup>3</sup> A cold (−78°C) solution of oxalyl bromide (0.19 mL, 2.02 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added to a solution of complex **20** (830 mg, 2.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) at −78°C. After stirring for 15 min at this temperature, the mixture was allowed to warm until a sudden color change from orange-brown to yellow was observed (at about −15°C). At this point, the mixture was immediately cooled to −78°C and quickly filtered under Ar at this temperature. The resulting pale yellow filtrate (a brown color indicates partial decomposition, leading to impurities that are difficult to remove at a later stage) was treated with dme (1.04 mL, 10.0 mmol) at −78°C before a pre-cooled (−78°C) solution of Br<sub>2</sub> (0.11 mL, 2.02 mmol) in

<sup>2</sup> (a) Fischer, E. O.; Maasboel, A.; *Chem. Ber.* **1967**, *100*, 2445. (b) Fischer, E. O.; Maasboel, A. *Ger. Offen.* **1966**, DE 1214233 (CAN **65**:12474).

<sup>3</sup> (a) Mayr, A.; McDermott, G. A.; Dorries, A. M. *Organometallics* **1985**, *4*, 608. (b) Mayr, A.; McDermott, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 548. (c) Poli, R.; Smith, K. M. *Science of Synthesis* **2003**, *2*, 283-332.

CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was slowly introduced at this temperature. After stirring for 15 min, the mixture was allowed to reach ambient temperature over the course of 30 min, causing a color change from green to orange-brown. After an additional 15 min, the solvent was distilled off and the residue washed with pentanes (30 mL). The remaining material was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and the product precipitated with pentanes (100 mL). The solid was collected under Ar and dried in vacuo to give complex **22** as a red-brown solid (904 mg, 88%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.55-7.48 (m, 4H), 7.21 (tt, *J* = 7.2, 1.6 Hz, 1H), 4.06 (br s, 2H), 4.04 (br s, 2H), 3.95 (s, 3H), 3.91 (s, 3H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 330.7, 140.4, 131.9, 131.7, 77.6, 71.1, 69.4, 58.0.

**[Mo(≡CPh)(OSiPh<sub>3</sub>)<sub>3</sub>(Et<sub>2</sub>O)] (24·Et<sub>2</sub>O).** A solution of Ph<sub>3</sub>SiOK (3.47 g, 11.0 mmol) in toluene (30 mL) was added to a solution of Mo(≡CPh)Br<sub>3</sub>(dme) (**22**) (1.42 g, 2.76 mmol) in toluene (45 mL) and the resulting mixture was stirred for 1 h at ambient temperature. After filtration under Ar, the filtrate was evaporated and the residue triturated with Et<sub>2</sub>O (50 mL), causing the formation of **24·Et<sub>2</sub>O** as a lilac solid, which was washed with Et<sub>2</sub>O (50 mL) and dried in vacuo (2.74 g, 92 %). <sup>1</sup>H NMR (400 MHz, [D<sub>8</sub>]-toluene): δ = 7.71 (dd, *J* = 8.0, 1.3 Hz, 18 H); 7.08 (tt, *J* = 7.4, 1.4 Hz, 9H); 6.93 (t, *J* = 7.6 Hz, 18H); 6.84 (t, *J* = 7.7 Hz, 2H); 6.68 (tt, *J* = 7.4, 1.2 Hz, 1H); 6.56 (d, *J* = 7.6 Hz, 2H); 3.29 (q, *J* = 7.0 Hz, 4H); 1.12 (t, *J* = 7.0 Hz, 6H); <sup>13</sup>C NMR (100 MHz, [D<sub>8</sub>]-toluene): δ = 282.6, 145.7, 140.4, 138.2, 137.4, 131.2, 130.8, 129.7, 128.8, 128.4, 128.1, 127.5, 126.3, 66.6, 16.2; elemental analysis (%) calcd for C<sub>65</sub>H<sub>60</sub>MoO<sub>4</sub>Si<sub>3</sub>: C 71.93, H 5.57; found: C 71.11, H 5.26.

**[Mo(≡CtBu)(OSiPh<sub>3</sub>)<sub>3</sub>(MeCN)] (19·MeCN).** Mo(≡CMe<sub>3</sub>)Cl<sub>3</sub>(dme) (**18**) (50 mg, 0.14 mmol)<sup>4</sup> was added in portions to a solution of Ph<sub>3</sub>SiOLi (118 mg, 0.42 mmol) in Et<sub>2</sub>O (1 mL) at -40 °C. After stirring for 1 h, the reaction was allowed to reach ambient temperature and stirring was continued for one more hour. The resulting red mixture was filtered and acetonitrile (1 mL) was added. Precipitated materials were filtered off, the filtrate was concentrated to ca. ½ of its volume and then cooled to -40 °C, causing precipitation of complex **19·MeCN** in form of red crystals (123 mg, 85%). Characteristic data: <sup>1</sup>H-NMR (300 MHz, [D<sub>8</sub>]-toluene): δ = 7.83 (dd, *J* = 7.7, 1.3 Hz, 18 H); 7.21-7.10 (m, 27H), 0.56 (s, 3H), 0.38 (s, 9H); <sup>13</sup>C-NMR (75 MHz, [D<sub>8</sub>]-toluene): δ = 323.5, 136.9, 135.9, 130.1, 128.2, 127.9, 54.9, 29.4, 1.4; elemental analysis (%) calcd for C<sub>61</sub>H<sub>57</sub>MoNO<sub>3</sub>Si<sub>3</sub>: C 70.97, H 5.57, N 1.36; found: C 71.24, H 5.20, N 1.50.

**[Mo(≡CPh)(OSiPh<sub>3</sub>)<sub>3</sub>(phen)] (25).** A solution of Ph<sub>3</sub>SiOK (2.49 g, 7.92 mmol) in toluene (25 mL) was added to a solution of Mo(≡CPh)Br<sub>3</sub>(dme) (**22**) (1.02 g, 1.98 mmol) in toluene (25 mL). After stirring for 1 h, the mixture was filtered and the filtrate added to a solution of 1,10-phenanthroline (doubly sublimed, 357 mg, 1.98 mmol) in Et<sub>2</sub>O (50 mL), causing an immediate color change to violet and finally almost black. After stirring for 1 h, the solvents were evaporated and the residue washed with Et<sub>2</sub>O (3 x 100 mL) before being dried in vacuo to give complex **24** as a violet solid (1.90 g, 81%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 9.26 (dd, *J* = 4.6, 1.6 Hz, 1H), 9.14 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.90 (dd, *J* = 5.0, 1.8 Hz, 1H), 8.33 (dd, *J* = 8.2, 1.6 Hz, 1H), 8.30 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.89 (dd, *J* = 8.0, 1.3 Hz, 4H), 7.82 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.66-7.58 (m, 2H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.49-7.43 (m, 6H), 7.41-7.37 (m, 3H), 7.28 (tt, *J* = 7.6, 1.3 Hz, 6H), 7.19 (tt, *J* = 7.4, 1.4 Hz, 2H), 7.06 (tt, *J* = 7.4, 1.3 Hz, 4H), 7.03 (dd, *J* = 8.0, 1.4 Hz, 8H), 6.96-6.92 (m, 4H), 6.86 (tt, *J* = 7.4, 1.2 Hz, 1H), 6.80 (t, *J* = 7.9 Hz, 8H), 6.31 (dd, *J* = 8.4, 1.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 292.3, 155.5, 150.5, 147.5, 143.7, 143.2, 142.7, 139.4, 138.9, 138.2, 137.2, 136.3, 136.1, 135.8, 135.5, 135.3, 131.2, 130.3, 130.2, 130.0, 129.7, 129.4, 129.2, 128.7, 128.6, 128.1, 127.8, 127.3, 127.2, 127.1, 127.0, 126.7, 125.6, 124.3, 124.0, 123.4; IR (film): ν = 3065, 3047, 3022, 1958, 1895, 1823, 1649, 1625, 1587, 1566, 1516, 1483, 1427, 1381, 1342, 1302, 1260, 1221, 1186, 1141, 1110, 1031, 1017, 998, 927, 867,

<sup>4</sup> (a) McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5987. (b) McCullough, L. G.; Schrock, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 4067.

836, 754, 739, 725, 696  $\text{cm}^{-1}$ ; analysis (%) calcd for  $\text{C}_{73}\text{H}_{58}\text{MoN}_2\text{O}_3\text{Si}_3$ : C 73.59, H 4.91, N 2.35; found: C 73.21, H 5.09, N 2.54.

**[NMe<sub>4</sub>][W(CO)<sub>5</sub>(COPh) (26)]**.<sup>2</sup> PhLi (1.8 M in  $\text{Bu}_2\text{O}$ , 5.6 mL, 10.0 mmol) was rapidly added to a solution of  $\text{W}(\text{CO})_6$  (3.52 g, 10.0 mmol) in boiling  $\text{Et}_2\text{O}$  (150 mL) and reflux was continued for 30 min once the addition was complete. The mixture was then allowed to reach ambient temperature before all volatile materials were distilled off. The residue was dissolved in water and a solution of  $\text{Me}_4\text{NBr}$  (2.30 g, 15.0 mmol) in water (5 mL) was added. After stirring for 15 min, the resulting orange-red precipitate was filtered off, washed with  $\text{Et}_2\text{O}$  (20 mL) and dried in vacuo. For further purification, the material was suspended in  $\text{CH}_2\text{Cl}_2$  (20 mL), insoluble materials were filtered off, and the product was precipitated upon slow addition of  $\text{Et}_2\text{O}$  (100 mL). The resulting solid was filtered off and dried in vacuo to give complex **26** as an orange solid (2.74 g, 55%). <sup>1</sup>H NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 7.46-7.43 (m, 2H), 7.35-7.31 (m, 2H), 7.25 (tt,  $J$  = 7.2, 1.4 Hz, 1H), 3.25 (s, 12H); <sup>13</sup>C NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  (ppm) = 203.7, 158.0, 128.6, 127.9, 125.5, 56.6.

**[W( $\equiv$ CPh)Br<sub>3</sub>(dme) (27)]**.<sup>3</sup> A solution of oxalyl bromide (0.18 mL, 2.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (4 mL) was added at  $-78^\circ\text{C}$  to a solution of complex **26** (1.01 g, 2.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL). After stirring for 15 min at this temperature, the mixture was allowed to warm until a sudden color change from orange-brown to yellow was observed (at about  $-15^\circ\text{C}$ ). At this point, the mixture was immediately cooled to  $-78^\circ\text{C}$  and quickly filtered under Ar at this temperature. The resulting pale yellow filtrate (a brown color indicates partial decomposition, leading to impurities that are difficult to remove at a later stage) was treated with dme (1.04 mL, 10.0 mmol) at  $-78^\circ\text{C}$  before a solution of  $\text{Br}_2$  (0.10 mL, 2.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (4 mL) was slowly introduced at this temperature. After stirring for 15 min, the mixture was allowed to reach ambient temperature over the course of 30 min. After an additional 15 min, the solvent was distilled off and the orange-brown residue washed with pentanes (30 mL) leaving a green solid behind. This material was dissolved in  $\text{CH}_2\text{Cl}_2$  (10 mL) and the product precipitated with pentanes (100 mL), which was collected under Ar and dried in vacuo to give complex **26** as a green solid (1.02 g, 85%). <sup>1</sup>H NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 7.66 (t,  $J$  = 7.9 Hz, 2H), 6.89 (d,  $J$  = 7.2 Hz, 2H), 6.73 (t,  $J$  = 7.5 Hz, 1H), 4.31 (s, 3H), 4.17-4.15 (m, 2H), 4.07-4.05 (m, 2H), 3.99 (s, 3H); <sup>13</sup>C NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 331.9, 138.1, 133.6, 132.8, 130.8, 128.7, 126.3, 79.8, 76.8, 70.6, 60.9.

**[K(phen)][W( $\equiv$ CPh)(OSiPh<sub>3</sub>)<sub>4</sub>] (29)**. A solution of  $\text{Ph}_3\text{SiOK}$  (289 mg, 0.92 mmol) in toluene (2.5 mL) was added to a solution of  $\text{W}(\equiv\text{CPh})\text{Br}_3(\text{dme})$  (**27**) (138 mg, 0.23 mmol) in toluene (2.5 mL). After stirring for 1 h, the mixture was filtered and the filtrate added to a solution of 1,10-phenanthroline (doubly sublimed, 41 mg, 0.23 mmol) in  $\text{Et}_2\text{O}$  (5 mL). After stirring for 1 h, the solvents were evaporated, and the residue was washed with  $\text{Et}_2\text{O}$  (3 x 10 mL) and dried in vacuo to give complex **29** as an orange solid (232 mg, 79%). <sup>1</sup>H NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 8.32 (d,  $J$  = 7.9 Hz, 2H), 7.89 (s, 2H), 7.64 (d,  $J$  = 6.9 Hz, 2H), 7.44 (dd,  $J$  = 8.0, 1.4 Hz, 24H), 7.40 (t,  $J$  = 7.5 Hz, 2H), 7.05 (tt,  $J$  = 7.5 1.3 Hz, 12H), 6.83 (t,  $J$  = 7.5 Hz, 25H), 6.66 (tt,  $J$  = 7.4 1.1 Hz, 1H), 5.81 (d,  $J$  = 7.2 Hz, 2H); <sup>13</sup>C NMR (150 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 262.9, 150.4, 147.0, 146.0, 139.2, 137.1, 136.4, 135.7, 135.4, 135.2, 133.5, 130.4, 129.3, 128.9, 128.5, 128.3, 128.2, 127.4, 127.3, 127.2, 127.1, 125.6, 125.1, 123.7.



## Alkyne Metathesis Reactions

**Representative Alkyne Metathesis Reaction using [Mo(≡N)(OSiPh<sub>3</sub>)<sub>3</sub>(phen)] Activated by MnCl<sub>2</sub> (Table 1, entry 1): 1,2-Diphenylethyne.** A suspension of [Mo(≡N)(OSiPh<sub>3</sub>)<sub>3</sub>(phen)]·½(toluene) (116.2 mg, 0.10 mmol), MnCl<sub>2</sub> (12.6 mg, 0.10 mmol) and powdered MS 5Å (1 g) in toluene (5 mL) was stirred at 80°C under Ar for 30 min before 1-propynyl benzene (1.00 mmol, 116.2 mg) was introduced and stirring was continued for 3h. The mixture was then allowed to reach ambient temperature before it was filtered through a short pad of silica. The filtrate was evaporated and the residue purified by flash chromatography (hexanes) to give 1,2-diphenylethyne as a white solid (88.2 mg, 99%). M. p. = 59-61°C; the spectroscopic properties were identical to those of a commercial sample.

**Representative Alkyne Metathesis Reaction using Complex [Mo(≡CPh)(OSiPh<sub>3</sub>)<sub>3</sub>(Et<sub>2</sub>O)] (24·Et<sub>2</sub>O) (Table 1, entry 2): 1,2-Bis(2-methoxyphenyl)ethyne.** A suspension containing 1-methoxy-2-(prop-1-yl)benzene (146 mg, 1 mmol), complex 24·Et<sub>2</sub>O (22 mg, 0.02 mmol, 2 mol%) and powdered MS 5Å (1 g) in toluene (5 mL) was stirred for 2 h at ambient temperature before the mixture was filtered through a short plug of silica. The filtrate was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 20:1) to give 1,2-bis(2-methoxyphenyl)ethyne as a colorless solid (115 mg, 97%). M. p. = 126–127°C; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.49 (ddd, *J* = 7.3, 1.6, 0.5 Hz, 2H), 7.33 (ddd, *J* = 7.9, 7.7, 1.9 Hz, 2H), 6.95 (td *J* = 7.9, 1.0 Hz, 4H), 3.92 (s, 6H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 160.3 (2xC), 133.7 (2xCH), 130.1 (2xCH), 120.8 (2xCH), 113.0 (2xC), 111.3 (2xCH), 90.1 (2xC), 56.2 (2xCH<sub>3</sub>); IR (film):  $\tilde{\nu}$  = 3105, 3033, 2998, 2963, 2937, 2833, 1945, 1903, 1863, 1598, 1574, 1498, 1464, 1456, 1432, 1274, 1241, 1184, 1162, 1115, 1047, 1020, 937, 750 cm<sup>-1</sup>; MS (EI) *m/z* (%): 238 [M<sup>+</sup>] (100), 237 (32), 223 (23), 221 (15), 207 (10), 195 (5), 178 (8), 165 (14), 152 (9), 131 (19), 111 (6), 97 (3), 89 (3); HRMS (ESI): *m/z*: calcd for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub> + Na: 261.0886; found: 261.0884.

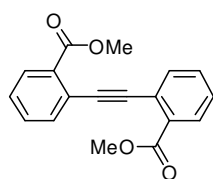
**Representative Alkyne Metathesis Reaction using [Mo(≡CPh)(OSiPh<sub>3</sub>)<sub>3</sub>(phen)] (25) Activated with MnCl<sub>2</sub> (Table 1, entry 13).** A solution containing [Mo(≡CPh)(OSiPh<sub>3</sub>)<sub>3</sub>(phen)] (25) (60 mg, 0.05 mmol, 5 mol%) and MnCl<sub>2</sub> (6.3 mg, 0.05 mmol) in toluene (1 mL) was stirred at 80°C for 30 min. After this activation phase, the mixture was allowed to reach ambient temperature before it was added to a suspension of pentadec-13-ynyl 3-cyanobenzoate (325 mg, 1.0 mmol) and powdered MS 5Å (1 g) in toluene (4 mL). The resulting mixture was stirred at ambient temperature for 2 h before it was filtered through a short plug of silica. The filtrate was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 20:1) to give the desired product as a colorless solid (265 mg, 89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.35 (td, *J* = 7.6, 1.2 Hz, 2 H); 7.22 (dt, *J* = 7.6, 1.2 Hz, 2H), 7.12-7.10 (m, 4H), 3.95 (t, *J* = 6.5 Hz, 4H), 2.13 (t, *J* = 7.1 Hz, 4H), 1.78 (quint., *J* = 8.0 Hz, 4H), 1.50-1.41 (m, 8H), 1.36-1.28 (m, 28H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 159.2, 134.9, 130.2, 130.1, 127.9, 124.2, 119.8, 118.8, 117.3, 113.1, 80.2, 68.4, 29.6, 29.5, 29.3, 29.1, 29.0, 28.8, 25.9, 18.7; IR (film):  $\tilde{\nu}$  = 3087, 2918, 2851, 2230, 1957, 1739, 1606, 1576, 1523, 1473, 1444, 1428, 1405, 1319, 1291, 1256, 1185, 1163, 1144, 1118, 1048, 1026, 999, 988, 904, 870, 834, 799, 782, 761, 738, 718, 698, 681 cm<sup>-1</sup>; MS (EI) *m/z* (%): 596 [M<sup>+</sup>] (100), 553 (6), 478 (7), 394 (6), 380 (11), 366 (17), 352 (15), 339 (47), 325 (73), 310 (15), 296 (13), 283 (8), 151 (6), 137 (11), 132 (9), 123 (18), 109 (34), 95 (66), 81 (67), 67 (49), 55 (68), 41 (21); HRMS (ESI): *m/z*: calcd for C<sub>40</sub>H<sub>56</sub>N<sub>2</sub>O<sub>2</sub> + Na : 619.4239; found: 619.4234.

**Gram-Scale Synthesis of 1,2-Bis(4-(trifluoromethyl)phenyl)ethyne with [Mo(≡CPh)(OSiPh<sub>3</sub>)<sub>3</sub>(phen)] (25) Activated with MnCl<sub>2</sub> (Table 1, entry 5).** A solution containing [Mo(≡CPh)(OSiPh<sub>3</sub>)<sub>3</sub>(phen)] (25) (387 mg, 0.33 mmol, 5 mol%) and MnCl<sub>2</sub> (41 mg, 0.33 mmol) in toluene (5 mL) was stirred at 80°C for 30 min. After

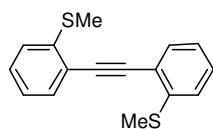
this activation phase, the mixture was allowed to reach ambient temperature before it was added to a suspension of 1-(prop1-ynyl)-4-(trifluoromethyl)benzene (1.20 g, 6.52 mmol) and powdered MS 5Å (6.5 g) in toluene (28 mL). The resulting mixture was stirred at ambient temperature for 3 h before it was filtered through a short plug of silica. The filtrate was evaporated and the residue purified by flash chromatography (hexanes) to give the desired product as a colorless solid (973 mg, 95%). <sup>1</sup>H NMR (300 MHz, [D<sub>8</sub>]-toluene): δ = 7.26–7.18 (m, 8H); <sup>13</sup>C NMR (75 MHz, [D<sub>8</sub>]-toluene): δ = 132.9, 131.6, 131.1, 127.3, 127.3, 126.3, 126.3, 126.2, 123.4, 91.2; <sup>19</sup>F NMR (300 MHz, [D<sub>8</sub>]-toluene): δ = –62.8; IR (film):  $\tilde{\nu}$  = 2929, 2635, 1934, 1808, 1689, 1636, 1613, 1569, 1523, 1406, 1312, 1171, 1133, 1104, 1062, 1016, 968, 838, 754, 738, 712, 701, 692 cm<sup>-1</sup>; MS (EI) *m/z* (%): 314 [M<sup>+</sup>] (100), 295 (18), 264 (9), 245 (5), 225 (7), 194 (2), 176 (3), 132 (2), 107 (2); HRMS (ESI): *m/z*: calcd for C<sub>16</sub>H<sub>8</sub>F<sub>6</sub> : 314.0530; found: 314.0530.

The following compounds were prepared analogously:

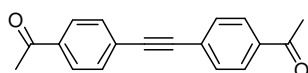
**Dimethyl 2,2'-(ethin-1,2-diyl)dibenzoate.** Yellow solid. M. p. = 83–84°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.97–8.00 (m, 2H), 7.73 (ddd, *J* = 7.7, 1.2, 0.4 Hz, 2H), 7.51 (dt, *J* = 7.6, 1.4 Hz, 2H), 7.39 (dt, *J* = 7.7, 1.3 Hz, 2H), 3.96 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 166.6, 134.3, 131.8, 131.7, 130.4, 128.1, 123.8, 93.1, 52.2; IR (ATR)  $\tilde{\nu}$  = 2950, 1725, 1714, 1595, 1567, 1491, 1448, 1431, 1292, 1250, 1189, 1128, 1077, 1041, 963, 755, 699 cm<sup>-1</sup>; MS (EI) *m/z* (%): 294 (11) [M<sup>+</sup>], 280 (18), 279 (100), 265 (5), 264 (24), 248 (20), 220 (16), 176 (5), 163 (8), 132 (10), 102 (7), 88 (9); HRMS (ESI): *m/z*: calcd for C<sub>18</sub>H<sub>14</sub>O<sub>4</sub> + Na: 317.0784; found: 317.0785. The analytical and spectroscopic data are in agreement with those reported in the literature.<sup>5</sup>



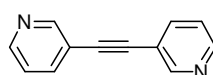
**1,2-Bis(2-(methylthio)phenyl)ethyne.** Pale yellow solid. M. p. = 123–124°C; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 7.52 (ddd, *J* = 7.9, 1.5, 0.5 Hz, 2H), 7.34 (ddd, *J* = 8.1, 7.4, 1.5 Hz, 2H), 7.22 (dd, *J* = 8.1, 0.7 Hz, 2H), 7.14 (td, *J* = 7.4, 1.2, Hz, 2H), 2.52 (s, 6H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 142.2 (2xC), 132.8 (2xCH), 129.4 (2xCH), 124.6 (2xCH), 124.5 (2xCH), 121.4 (2xC), 93.4 (2xC), 15.3 (2xCH<sub>3</sub>); IR (film):  $\tilde{\nu}$  = 3086, 3053, 3011, 2915, 2854, 2830, 1954, 1909, 1868, 1827, 1781, 1584, 1555, 1470, 1432, 1279, 1245, 1125, 1074, 1036, 972, 954 cm<sup>-1</sup>; MS (EI) *m/z* (%): 270 [M<sup>+</sup>] (16), 255 (53), 241 (17), 240 (100), 221 (19), 208 (6), 195 (5), 163 (5), 120 (15); HRMS (EI): *m/z*: calcd for C<sub>16</sub>H<sub>14</sub>S<sub>2</sub>: 270.0537; found: 270.0535. The analytical and spectroscopic data are in agreement with those reported in the literature.<sup>5</sup>



**1,1'-(4,4'-(Ethin-1,2-diyl)bis(4,1-phenylen))diethanone.** Pale yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.96 (d, *J* = 8.5 Hz, 4H), 7.63 (d, *J* = 8.5 Hz, 4H), 2.61 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) = 197.2, 136.6, 131.8, 128.3, 127.4, 91.6, 26.6; IR (film):  $\tilde{\nu}$  = 3338, 1673, 1601, 1555, 1423, 1402, 1354, 1288, 1264, 1179, 1112, 1078, 1028, 1013, 978, 959, 852, 833, 688 cm<sup>-1</sup>; MS (EI) *m/z* (%): 262 [M<sup>+</sup>] (54), 247 (100), 219 (6), 204 (15), 189 (5), 176 (23), 150 (8), 116 (12), 102 (9), 88 (6), 75 (4), 43 (16); HRMS (EI): *m/z*: calcd for C<sub>18</sub>H<sub>14</sub>O<sub>2</sub> : 262.0994; found: 262.0994.



**1,2-Di(pyridin-3-yl)ethyne.** Pale yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.79 (br s, 2H); 8.58 (d, *J* = 4.0 Hz, 2H), 7.83 (dt, *J* = 7.8, 1.8 Hz, 2H), 7.31 (dd, *J* = 7.8, 5.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 152.4, 149.2, 138.7, 123.3, 119.9, 89.3; IR (film): 3029, 2924, 1987, 1952, 1916 1881, 1771, 1727, 1558, 1480, 1410, 1328, 1295, 1254, 1187, 1127, 1097, 1040, 1018, 959, 926, 882, 850, 809, 701 cm<sup>-1</sup>; MS (EI) *m/z* (%): 180 (100) [M<sup>+</sup>], 153 (7), 152 (6), 127 (11), 126 (5), 100 (6), 99(5), 76 (5), 74 (12), 63 (5); HRMS (EI): *m/z*: calcd for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub> [M<sup>+</sup>]: 180.0687, found: 180.0686. The analytical and spectroscopic data are in agreement with those reported in the literature.<sup>5</sup>



<sup>5</sup> Bindl, M.; Stade, R.; Heilmann, E. K.; Picot, A.; Goddard, R.; Fürstner, A. *J. Am. Chem. Soc.* **2009**, *131*, 9468.

**1,2-Di(thiophene-2-yl)ethyne.** Pale yellow solid. M. p. = 98–99°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 7.35 (dd,  $J$  = 5.2, 1.1 Hz, 2H), 7.29 (dd,  $J$  = 3.6, 1.1 Hz, 2H), 7.04 (dd,  $J$  = 5.2, 3.6 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 132.5 (2xCH), 128.2 (2xCH), 127.6 (2xCH), 123.1 (2xC), 86.4 (2xC); IR (film):  $\tilde{\nu}$  = 3100, 3082, 1791, 1723, 1651, 1596, 1432, 1406, 1195, 1098, 1040, 1028, 849, 824, 692  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 192 (9), 191 (13), 190 (100), 158 (8), 145 (13), 114 (9), 95 (8), 69 (6), 45 (5); HRMS (EI):  $m/z$ : calcd for  $\text{C}_{10}\text{H}_6\text{S}_2$ : 189.9911; found: 189.9912. The analytical and spectroscopic data are in agreement with those reported in the literature.<sup>5</sup>

**Hex-3-yn-1,6-diyl bis(4-methylbenzolsulfonate).** Colorless solid. M. p. = 83–84°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.77–7.80 (m, 4H), 7.34–7.36 (m, 4H), 4.01 (t,  $J$  = 7.0 Hz, 4H), 2.44–2.47 (m, 10H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 145.0, 132.9, 129.9, 127.9, 76.8, 67.7, 21.6, 19.6; IR (film):  $\tilde{\nu}$  = 2955, 2920, 1597, 1453, 1352, 1293, 1190, 1170, 1096, 969, 898, 841, 813, 761, 662  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  (%): 423 (5), 422 (21) [ $M^+$ ], 251 (11), 250 (10), 186 (6), 156 (8), 155 (86), 139 (21), 92 (9), 91 (100), 90 (7), 79 (10), 78 (62), 77 (9), 66 (7), 65 (47); HRMS (ESI): calcd ( $m/z$ ) for [ $\text{C}_{20}\text{H}_{22}\text{O}_6\text{S}_2 + \text{Na}^+$ ]: 445.0750; found: 445.0750. The analytical and spectroscopic data are in agreement with those reported in the literature.<sup>5</sup>

**Representative Example of a Ring Closing Alkyne Metathesis using [Mo( $\equiv\text{N}$ )(OSiPh<sub>3</sub>)<sub>3</sub>(phen)] (15) (Table 2,**

**entry 3).** A suspension of [Mo( $\equiv\text{N}$ )(OSiPh<sub>3</sub>)<sub>3</sub>(phen)]·0.5 toluene (**15**) (116.2 mg, 0.10 mmol) and MnCl<sub>2</sub> (12.6 mg, 0.10 mmol) in toluene (15 mL) was stirred at 80°C for 30 min before a solution of bis(pent-3-ynyl) butandioate (250 mg, 1.00 mmol) in toluene (35 mL) was introduced and stirring continued at 80°C for 24 h. After reaching ambient temperature, the mixture was filtered through a short pad of silica and the filtrate was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 4:1) furnished 1,6-dioxacyclododec-9-yn-2,5-dione as a colorless oil (179 mg, 91%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 4.21–4.14 (m, 4H), 2.61 (s, 4H), 2.44–2.37 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 171.9 (2xC), 79.0 (2xC), 61.6 (2xCH<sub>2</sub>), 30.2 (2xCH<sub>2</sub>), 19.7 (2xCH<sub>2</sub>); IR (film):  $\tilde{\nu}$  = 2965, 2915, 2840, 1729, 1458, 1421, 1383, 1353, 1336, 1267, 1251, 1158, 1053, 1030, 1000, 952, 837  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 166 (1), 101 (14), 78 (100), 66 (59), 65 (16), 55 (7), 40 (12), 28 (7); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_4 + \text{Na}$ : 219.0628; found: 219.0627. The analytical and spectroscopic data are in accordance with those reported in the literature.<sup>6</sup>

**1,8-Dioxacyclotetradec-11-yn-2,7-dione (Table 2, entry 4). Method A using Complex 24·Et<sub>2</sub>O:**

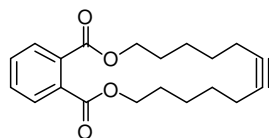
A mixture containing bis(pent-3-ynyl) hexandioate (135 mg, 485  $\mu\text{mol}$ ), complex **24**·OEt<sub>2</sub> (10.5 mg, 9.67  $\mu\text{mol}$ , 2 mol%) and powdered MS 5Å (970 mg) in toluene (24 mL) was stirred at ambient temperature for 24 h. For work up, the suspension was filtered through a short pad of silica, the filtrate was evaporated, and the residue purified by flash chromatography (hexanes/EtOAc, 20:1) to give 1,8-dioxacyclotetradec-11-yn-2,7-dione as a colorless solid (100 mg, 92%).

**Method B using Complex 15:** A suspension of [Mo( $\equiv\text{N}$ )(OSiPh<sub>3</sub>)<sub>3</sub>(phen)]·0.5 toluene (**15**) (1.16 g, 1.0 mmol) and MnCl<sub>2</sub> (126 mg, 1.0 mmol) in toluene (150 mL) was stirred at 80°C for 30 min before a solution of bis(pent-3-ynyl) hexanedioate (2.78 g, 10.0 mmol) in toluene (350 mL) was introduced and stirring continued at 80°C for 24 h. After reaching ambient temperature, the mixture was filtered through a short pad of silica and the filtrate was evaporated. Purification of the residue by flash chromatography (hexanes/EtOAc, 5:1) furnished the title compound as a colorless solid (1.90 g, 85%). M. p. = 109–110°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 4.13–4.06 (m, 4H), 2.53–2.47 (m, 4H), 2.39–2.30 (m, 4H), 1.76–1.67 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 173.2 (2xC), 78.2 (2xC), 62.8 (2xCH<sub>2</sub>), 35.2 (2xCH<sub>2</sub>), 25.4 (2xCH<sub>2</sub>), 19.4 (2xCH<sub>2</sub>); IR (film)  $\tilde{\nu}$  = 2995, 2954, 2937, 2918, 2901, 2872, 1721, 1458, 1425, 1384, 1341, 1272, 1236, 1167, 1140,

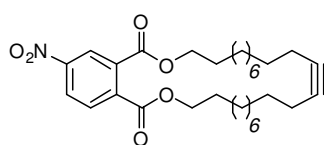
<sup>6</sup> Fürstner, A.; Guth, O.; Rumbo, A.; Seidel, G. *J. Am. Chem. Soc.* **1999**, *121*, 11108.

1080, 1065, 1021, 981, 931, 843, 824, 699  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 129 (3), 111 (8), 78 (100), 66 (20), 55 (15), 41 (8); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{12}\text{H}_{16}\text{O}_4 + \text{Na}$ : 247.0941; found: 247.0938. The analytical and spectroscopic data are in accordance with those reported in the literature.<sup>6</sup>

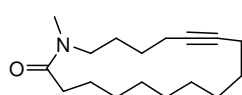
The following compounds were prepared analogously:



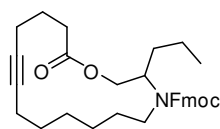
Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 7.72 (dd,  $J$  = 5.7, 3.3 Hz, 2H), 7.55 (dd,  $J$  = 5.7, 3.3 Hz, 2H), 4.32 (t,  $J$  = 6.0 Hz, 4H), 2.21–2.14 (m, 4H), 1.82–1.73 (m, 4H), 1.60–1.47 (m, 8H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 168.0 (2xC), 132.8 (2xC), 131.3 (2xCH), 129.1 (2xCH), 80.9 (2xC), 66.7 (2xCH<sub>2</sub>), 28.7 (2xCH<sub>2</sub>), 28.5 (2xCH<sub>2</sub>), 26.3 (2xCH<sub>2</sub>), 18.9 (2xCH<sub>2</sub>); IR (film):  $\tilde{\nu}$  = 2928, 2859, 1720, 1600, 1579, 1488, 1460, 1447, 1433, 1385, 1269, 1122, 1070, 1039, 957, 734, 703  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 328 [ $M^+$ ] (8), 180 (9), 162 (30), 149 (100), 133 (17), 122 (18), 121 (26), 119 (14), 108 (43), 107 (18), 105 (15), 95 (11), 94 (24), 93 (44), 91 (29), 81 (19), 80 (28), 79 (34), 77 (13), 67 (19), 55 (13); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{24}\text{O}_4 + \text{Na}$ : 351.1567; found: 351.1567; elemental analysis (%) calcd for  $\text{C}_{20}\text{H}_{24}\text{O}_4$ : C 73.15, H 7.37; found: C 73.26, H 7.28. The analytical and spectroscopic data are in accordance with those reported in the literature.<sup>5</sup>



White solid. M. p. = 81–82°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.60 (d,  $J$  = 2.2 Hz, 1H), 8.37 (dd,  $J$  = 8.4, 2.2 Hz, 1H), 7.85 (d,  $J$  = 8.4 Hz, 1H), 4.35–4.30 (m, 4H), 2.15 (br s, 4H), 1.74 (sext,  $J$  = 7.1 Hz, 4H), 1.45–1.29 (m, 28H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.3 (C), 165.2 (C), 148.8 (C), 138.2 (C), 133.2 (C), 130.1 (CH), 125.8 (CH), 124.4 (CH), 80.6 (2xC), 66.7 (2xCH<sub>2</sub>), 29.6 (2xCH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 29.3 (2xCH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 28.5 (CH<sub>2</sub>), 28.4 (CH<sub>2</sub>), 28.4 (CH<sub>2</sub>), 28.4 (CH<sub>2</sub>), 25.8 (CH<sub>2</sub>), 25.7 (CH<sub>2</sub>), 18.5 (2xCH<sub>2</sub>); IR (film):  $\tilde{\nu}$  = 3108, 3077, 3046, 2918, 2851, 1741, 1720, 1613, 1548, 1532, 1468, 1354, 1298, 1272, 1241, 1136, 1061, 997, 962, 932, 861, 835, 733, 725  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 496 (19), 195 (37), 194 (32), 192 (33), 191 (11), 180 (13), 179 (19), 178 (69), 177 (15), 164 (22), 149 (22), 148 (11), 136 (12), 135 (30), 123 (12), 122 (14), 121 (43), 111 (23), 110 (16), 109 (29), 108 (14), 107 (29), 105 (11), 97 (15), 96 (28), 95 (64), 94 (26), 93 (46), 91 (19), 83 (38), 82 (30), 81 (84), 80 (42), 79 (54), 69 (92), 68 (25), 67 (84), 57 (20), 56 (11), 55 (100), 54 (24), 43 (30), 41 (61); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{30}\text{H}_{43}\text{NO}_6 + \text{Na}$ : 536.2982; found: 536.2989. The analytical and spectroscopic data are in accordance with those reported in the literature.<sup>5</sup>



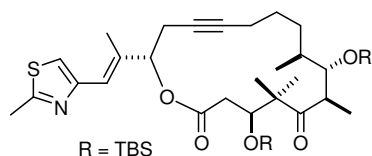
Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , rotamers):  $\delta$  = 3.43 (t,  $J$  = 7.0 Hz, 1H), 3.27 ( $J$  = 7.6 Hz, 1H), 2.99 (s, 1H), 2.91 (s, 2H), 2.32–2.36 (m, 2H), 2.15–2.23 (m, 4H), 1.56–1.77 (m, 4H), 1.28–1.52 (m, 14H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , rotamers):  $\delta$  = 173.0, 172.7, 80.9, 79.6, 49.8, 46.6, 35.3, 33.4, 33.0, 31.1, 29.4, 28.6, 28.5, 28.0, 28.0, 27.9, 27.9, 27.7, 27.5, 27.4, 27.1, 26.8, 26.8, 26.6, 26.2, 25.0, 23.9, 18.9, 18.7, 18.5, 18.4; IR (film)  $\tilde{\nu}$  = 2926, 2855, 1643, 1459, 1437, 1401, 1333, 1273, 1170, 1091  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  (%): 263 (20) [ $M^+$ ], 262 (15), 248 (20), 124 (17), 111 (23), 110 (14), 93 (10), 91 (10), 86 (16), 81 (10), 79 (19), 73 (13), 70 (86), 67 (16), 58 (18), 57 (17), 55 (27), 44 (100), 41 (29), 40 (16); HRMS (ESI): calcd for  $[\text{C}_{17}\text{H}_{29}\text{NO} + \text{Na}^+]$ : 286.2141; found: 286.2139. The analytical and spectral data are in agreement with those reported in the literature.<sup>7</sup>



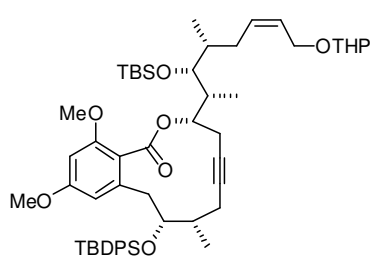
Colorless oil.  $^1\text{H}$  NMR (rotamers, 400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.76 (d,  $J$  = 7.4 Hz, 2H), 7.61–7.53 (m, 2H), 7.42–7.28 (m, 4H), 4.72–4.49 (m, 2H), 4.34–4.24 (m, 2H), 3.88–3.79 (m, 1.5H), 3.41 (br s, 0.5H), 3.02–2.91 (m, 1H), 2.65–2.40 (m, 2H), 2.28–2.15 (m, 3H), 2.13–2.01 (m, 1H), 1.83–1.70 (m, 2H), 1.64–0.77 (m, 14.5H), 0.70 (br s, 1.5H);  $^{13}\text{C}$  NMR (rotamers, 150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 173.3 (C), 173.2 (C), 156.8 (C), 156.4 (C), 144.1 (C), 144.0 (C), 143.9 (C), 141.4 (C),

<sup>7</sup> Fürstner, A.; Mathes, C.; Lehmann, C. W. *Chem. Eur. J.* **2001**, *7*, 5299.

141.3 (C), 127.6 (CH), 127.5 (CH), 127.1 (CH), 127.0 (CH), 124.6 (CH), 119.9 (CH), 119.8 (CH), 82.7 (C), 79.6 (C), 79.4 (C), 66.5 (CH<sub>2</sub>), 66.2 (CH<sub>2</sub>), 63.4 (CH<sub>2</sub>), 47.5 (CH), 47.3 (CH), 34.9 (CH<sub>2</sub>), 34.6 (CH<sub>2</sub>), 34.5 (CH<sub>2</sub>), 32.4 (CH<sub>2</sub>), 32.3 (CH<sub>2</sub>), 28.4 (CH<sub>2</sub>), 28.2 (CH<sub>2</sub>), 26.7 (CH<sub>2</sub>), 26.6 (CH<sub>2</sub>), 23.5 (CH<sub>2</sub>), 23.4 (CH<sub>2</sub>), 19.5 (CH<sub>2</sub>), 18.2 (CH<sub>2</sub>), 17.7 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>), 13.8 (CH<sub>3</sub>); IR (film):  $\tilde{\nu}$  = 3065, 3043, 3020, 2931, 2859, 1734, 1688, 1450, 1410, 1386, 1328, 1312, 1292, 1268, 1241, 1222, 1155, 1135, 1054, 1010, 758, 737 cm<sup>-1</sup>; MS (EI) *m/z* (%): 236 (3), 180 (4), 179 (36), 178 (100), 165 (2); HRMS (ESI): *m/z*: calcd for C<sub>32</sub>H<sub>39</sub>NO<sub>4</sub> + Na: 524.2771; found: 524.2776. The analytical and spectroscopic data are in accordance with those reported in the literature.<sup>6</sup>

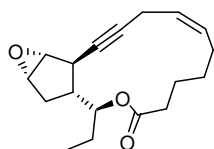


Amorphous solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.96 (s, 1H), 6.55 (br s, 1H), 5.33 (dd, *J* = 7.3, 3.1 Hz, 1H), 4.70 (dd, *J* = 6.4, 5.0 Hz, 1H), 3.93 (dd, *J* = 6.8, 1.9 Hz, 1H), 3.24 (quin, *J* = 6.9 Hz, 1H), 2.78 (dq, *J* = 17.2, 2.8 Hz, 1H), 2.71 (s, 3H), 2.69–2.63 (m, 2H), 2.57 (dd, *J* = 15.3, 5.0 Hz, 1H), 2.27–2.21 (m, 1H), 2.18 (d, *J* = 1.2 Hz, 3H), 2.13–2.07 (m, 1H), 1.78–1.71 (m, 1H), 1.59–1.53 (m, 1H), 1.30–1.20 (m, 2H), 1.41–1.34 (m, 1H), 1.16 (d, *J* = 7.0 Hz, 3H), 1.14 (s, 3H), 1.10 (s, 3H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.91 (s, 9H), 0.86 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  = 216.7 (C), 170.1 (C), 164.9 (C), 152.3 (C), 136.9 (C), 120.4 (CH), 116.8 (CH), 82.2 (C), 78.0 (CH), 76.7 (CH), 76.3 (C), 72.6 (CH), 54.5 (C), 44.4 (CH), 41.6 (CH<sub>2</sub>), 38.9 (CH), 29.5 (CH<sub>2</sub>), 26.2 (3xCH<sub>3</sub>), 26.1 (3xCH<sub>3</sub>), 25.9 (CH<sub>2</sub>), 24.1 (CH<sub>2</sub>), 20.9 (CH<sub>3</sub>), 20.5 (CH<sub>3</sub>), 19.3 (C), 18.6 (CH<sub>3</sub>), 18.5 (CH<sub>2</sub>), 18.3 (C), 17.0 (2xCH<sub>3</sub>), 15.0 (CH<sub>3</sub>), -3.2 (CH<sub>3</sub>), -3.7 (CH<sub>3</sub>), -4.0 (CH<sub>3</sub>), -4.1 (CH<sub>3</sub>); IR (film):  $\tilde{\nu}$  = 2952, 2929, 2894, 2856, 1739, 1702, 1505, 1472, 1463, 1385, 1361, 1254, 1182, 1152, 1097, 1085, 1039, 1018, 1007, 988, 836, 775 cm<sup>-1</sup>; MS (EI) *m/z* (%): 703 [M<sup>+</sup>] (5), 648 (23), 647 (47), 646 (97), 604 (11), 446 (14), 445 (33), 444 (100), 402 (22), 344 (15), 270 (38), 195 (12), 185 (18), 178 (12), 151 (21), 143 (13), 115 (13), 101 (12), 75 (45), 73 (51); HRMS (ESI): *m/z*: calcd for C<sub>38</sub>H<sub>65</sub>NO<sub>5</sub>SSi<sub>2</sub> + Na: 726.4014; found: 726.4015. The analytical and spectroscopic data are in accordance with those reported in the literature.<sup>7</sup>

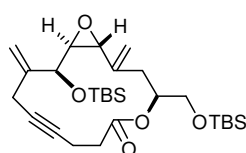


Amorphous solid. <sup>1</sup>H NMR (two diastereomers at the THP acetal, 400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.75–7.67 (m, 2H), 7.62–7.54 (m, 2H), 7.42–7.27 (m, 6H), 6.39 (d, *J* = 2.8 Hz, 1H), 6.28 (d, *J* = 2.8 Hz, 1H), 5.67–5.52 (m, 2H), 5.52–5.41 (m, 1H), 4.66–4.59 (m, 1H), 4.28–4.18 (m, 1H), 4.09–3.94 (m, 2H), 3.93–3.81 (m, 2H), 3.75 (s, 3H), 3.60 (s, 3H), 3.54–3.45 (m, 2H), 2.55–2.41 (m, 3H), 2.25–2.14 (m, 1H), 1.91–1.65 (m, 8H), 1.65–1.44 (m, 5H), 1.00–0.84 (m, 26H), 0.05 (s, 6H); <sup>13</sup>C NMR (two diastereomers at the THP acetal, 75 MHz, CDCl<sub>3</sub>):  $\delta$  = 167.1 (C), 160.5 (C), 157.5 (C), 139.0 (C), 136.0 (2xCH), 135.8 (2xCH), 134.5 (C), 134.0 (C), 132.4 (CH), 129.5 (CH), 129.4 (CH), 127.5 (2xCH), 127.4 (2xCH), 127.0 and 126.9 (CH), 118.1 (C), 107.5 (CH), 97.9 and 97.8 (CH), 97.0 (CH), 79.0 (C), 77.2 (CH), 76.4 (CH), 76.3 (CH), 74.5 (C), 62.8 (CH<sub>2</sub>), 62.2 and 62.1 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 55.3 (CH<sub>3</sub>), 40.7 and 40.7 (CH), 38.9 (CH<sub>2</sub>), 37.9 (CH), 36.0 (CH), 30.7 and 30.6 (CH<sub>2</sub>), 30.1 and 30.1 (CH<sub>2</sub>), 26.8 (3xCH<sub>3</sub>), 26.2 (3xCH<sub>3</sub>), 25.5 and 25.5 (CH<sub>2</sub>), 23.7 (CH<sub>2</sub>), 22.2 (CH<sub>2</sub>), 19.5 (CH<sub>2</sub>), 19.4 (C), 18.4 (C), 16.9 (CH<sub>3</sub>), 16.9 (CH<sub>3</sub>), 11.3 (CH<sub>3</sub>), -3.8 (CH<sub>3</sub>), -3.7 (CH<sub>3</sub>); IR (film):  $\tilde{\nu}$  = 3052, 2961, 2928, 2857, 1729, 1604, 1588, 1463, 1427, 1342, 1264, 1202, 1158, 1104, 1079, 1050, 1025, 908, 835 cm<sup>-1</sup>; MS (EI) *m/z* (%): 855 (14), 854 (30), 853 (46), 769 (11), 642 (14), 641 (28), 528 (11), 527 (26), 243 (11), 225 (19), 199 (13), 135 (13), 85 (100), 73 (24); HRMS (ESI): *m/z*: calcd for C<sub>54</sub>H<sub>78</sub>O<sub>8</sub>Si<sub>2</sub> + Na: 933.5132; found: 933.5127; elemental analysis (%) calcd for C<sub>54</sub>H<sub>78</sub>O<sub>8</sub>Si<sub>2</sub>: C 71.17, H 8.63; found: C 71.06, H 8.62. The analytical and spectroscopic data are in accordance with those reported in the literature.<sup>8</sup>

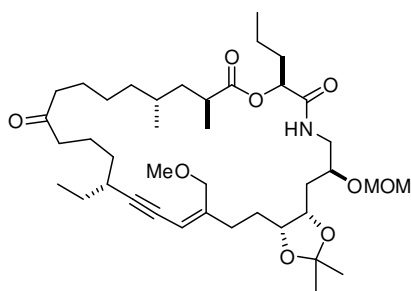
<sup>8</sup> Bindl, M.; Jean, L.; Herrmann, J.; Müller, R.; Fürstner, A. *Chem. Eur. J.* **2009**, *15*, 12310.



$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 5.56 (dt,  $J$  = 10.6, 7.0 Hz, 1 H), 5.51 (ddd,  $J$  = 10.6, 8.3, 6.8 Hz, 1 H), 4.75 (ddd,  $J$  = 10.7, 8.4, 2.9 Hz, 1 H), 3.50 (t,  $J$  = 2.5 Hz, 1 H), 3.46 (d,  $J$  = 2.5 Hz, 1 H), 2.92 (ddd,  $J$  = 17.2, 6.8, 2.0 Hz, 1 H), 2.83 (dt,  $J$  = 5.4, 2.0 Hz, 1 H), 2.75 (ddd,  $J$  = 17.1, 7.1, 2.6 Hz, 1 H), 2.54 (tt,  $J$  = 10.6, 5.8 Hz, 1 H), 2.41 (dt,  $J$  = 15.2, 7.2 Hz, 1 H), 2.27 (dt,  $J$  = 15.2, 7.4 Hz, 1 H), 2.21 (ddt,  $J$  = 12.9, 8.3, 7.7 Hz, 1 H), 2.07 (ddd,  $J$  = 14.8, 10.6, 2.4 Hz, 1 H), 1.99 (dq,  $J$  = 13.0, 6.8 Hz, 1 H), 1.71 (m, 2 H), 1.66 (dd,  $J$  = 14.8, 6.0, 1 H), 1.61 (ddq,  $J$  = 14.4, 7.4, 2.8 Hz, 1 H), 1.48 (qi,  $J$  = 7.4 Hz, 2 H), 1.37 (ddq,  $J$  = 14.4, 8.4, 7.4 Hz, 1 H), 0.82 (t,  $J$  = 7.4 Hz, 3 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 173.2, 133.0, 123.8, 81.4, 79.6, 78.9, 62.8, 59.8, 53.1, 36.7, 34.3, 30.2, 27.5, 27.4, 25.7, 24.9, 16.4, 9.0; IR (film):  $\tilde{\nu}$  = 3021, 2962, 2930, 2855, 1726, 1459, 1441, 1380, 1350, 1330, 1266, 1251, 1228, 1211, 1185, 1165, 1153, 1091, 1059, 1032, 1011, 942, 842, 799  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 288 (2) [ $\text{M}^+$ ], 270 (2), 259 (10), 241 (10), 213 (11), 201 (20), 187 (32), 157 (31), 143 (100), 129 (73), 115 (40), 103 (18), 91 (76), 79 (35), 65 (22), 55 (30), 41 (36); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{24}\text{O}_3\text{Na}$  311.1617 [ $\text{M}+\text{Na}$ ] $^+$ , found: 311.1618.



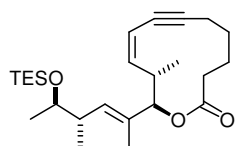
Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.04 (3 H, s), 0.04 (3 H, s), 0.07 (3 H, s), 0.14 (3 H, s), 0.88 (9 H, s), 0.92 (9 H, s), 2.41–2.58 (6 H, m), 2.83 (1 H, dd,  $J$  = 2.1, 7.0 Hz), 2.97 (1 H, d,  $J$  = 17.6), 3.12 (1 H, d,  $J$  = 17.6 Hz), 3.64 (1 H, d,  $J$  = 1.4 Hz), 3.65 (2 H, d,  $J$  = 6.0 Hz), 3.97 (1 H, d,  $J$  = 7.0 Hz), 4.98 (1 H, s), 5.01 (1 H, s), 5.12 (1 H, dq,  $J$  = 3.7, 6.1 Hz), 5.19 (1 H, s), 5.21 (1 H, s) ppm;  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -5.3 ( $\text{CH}_3$ ), -5.1 ( $\text{CH}_3$ ), -4.6 ( $\text{CH}_3$ ), 15.6 ( $\text{CH}_2$ ), 18.1 (C), 18.3 (C), 23.5 ( $\text{CH}_2$ ), 25.7 ( $\text{CH}_3$ ), 25.8 ( $\text{CH}_3$ ), 34.4 ( $\text{CH}_2$ ), 34.6 ( $\text{CH}_2$ ), 57.6 (CH), 63.0 ( $\text{CH}_2$ ), 64.0 (CH), 73.1 (CH), 75.9 (CH), 78.8 (C), 79.8 (C), 113.7 ( $\text{CH}_2$ ), 114.6 ( $\text{CH}_2$ ), 140.4 (C), 143.2 (C), 171.5 (C) ppm; IR (film):  $\tilde{\nu}$  = 2955, 2929, 2857, 1740, 1649, 1472, 1463, 1432, 1389, 1361, 1251, 1152, 1102, 1055, 1005, 971, 906, 833, 775, 669  $\text{cm}^{-1}$ ; MS (EI):  $m/z$  (%): 463 (12), 331 (22), 169 (11), 147 (10), 117 (11), 89 (11), 75 (53), 73 (100); HRMS (ESI+):  $m/z$ : calcd for  $\text{C}_{28}\text{H}_{48}\text{O}_5\text{Si}_2\text{Na}$  543.2929; found: 543.2932 ([ $\text{M}+\text{Na}$ ] $^+$ ). The analytical and spectroscopic data are in accordance with those reported in the literature.<sup>9</sup>



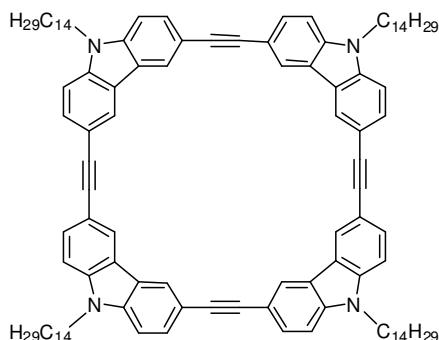
Pale yellow liquid.  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 6.17 (br dd,  $J$  = 6.4, 4.4 Hz, 1H), 5.66 (m, 1H), 5.24 (dd,  $J$  = 7.7, 5.0 Hz, 1H), 4.55 (d,  $J$  = 6.7 Hz, 1H), 4.53 (d,  $J$  = 6.7 Hz, 1H), 4.37 (d,  $J$  = 11.9 Hz, 1H), 4.34 (d,  $J$  = 11.9 Hz, 1H), 4.18 (m, 1H), 3.97 (m, 1H), 3.88 (m, 1H), 3.55 (ddd,  $J$  = 14.0, 7.2, 3.2 Hz, 1H), 3.41 (dt,  $J$  = 13.9, 4.5 Hz, 1H), 3.26 (s, 3H), 3.17 (s, 3H), 2.58 (m, 1H), 2.52 (m, 1H), 2.30 (m, 1H), 2.25 (m, 1H), 2.22 (m, 1H), 2.18 (m, 1H), 2.15 (m, 1H), 2.09 (m, 1H), 1.85 (m, 3H), 1.73–1.52 (m, 8H), 1.49 (m, 1H), 1.44–1.21 (m, 10H), 1.41 (s, 3H), 1.27 (s, 3H), 1.13 (d,  $J$  = 6.9 Hz, 3H), 1.08 (m, 1H), 0.98 (t,  $J$  = 7.4 Hz, 3H), 0.83 (d,  $J$  = 6.9 Hz, 3H), 0.81 (t,  $J$  = 7.4 Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 209.0, 175.7, 169.8, 149.9, 109.0, 107.7, 97.4, 96.5, 79.7, 77.2, 74.8, 74.5, 74.3, 71.9, 57.9, 55.4, 42.8, 42.6, 41.9, 41.2, 37.7, 36.9, 34.6, 34.3, 33.3, 30.7, 30.5, 28.8, 28.4, 26.7, 26.1, 24.2, 23.0, 19.9, 18.7, 17.2, 13.8, 12.1; IR (film):  $\tilde{\nu}$  = 3445, 3342, 2960, 2930, 2874, 2822, 2209, 1739, 1710, 1691, 1525, 1459, 1406, 1378, 1218, 1153, 1099, 1034, 918, 863; MS (ESI+): 728 [ $\text{M}^+\text{Na}$ ]; HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{40}\text{H}_{68}\text{NO}_9$ : 706.4889 (M+H); found: 706.4891 (M+H). The analytical and spectroscopic data are in accordance with those reported in the literature.<sup>10</sup>

<sup>9</sup> Fürstner, A.; Flügge, S.; Larionov, O.; Takahashi, Y.; Kubota, T.; Kobayashi, J. *Chem. Eur. J.* **2009**, *15*, 4011.

<sup>10</sup> Fürstner, A.; Bonnekessel, M.; Blank, J. T.; Radkowski, K.; Seidel, G.; Lacombe, F.; Gabor, B.; Mynott, R. *Chem. Eur. J.* **2007**, *13*, 8762.



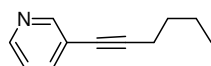
Yellow oil (1.18 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 5.52 (dd,  $J$  = 10.6, 20.0 Hz, 1H), 5.46 (d,  $J$  = 10.7 Hz, 1H), 5.31 (d,  $J$  = 9.8 Hz, 1H), 5.17 (d,  $J$  = 4.2 Hz, 1H), 3.74 (dq,  $J$  = 3.6, 6.2 Hz, 1H), 3.30 (dq,  $J$  = 4.1, 6.9, 9.4 Hz, 1H), 2.69 (ddd,  $J$  = 2.5, 12.0, 17.3 Hz, 1H), 2.40–2.49 (m, 1H, overlap), 2.33–2.42 (m, 1H, overlap), 2.22 (dd,  $J$  = 10.2, 17.3 Hz, 1H), 2.00–2.13 (m, 1H), 1.79–1.93 (m, 1H), 1.62 (d,  $J$  = 1.3 Hz, 1H, overlap), 1.58–1.69 (m, 2H, overlap), 1.05 (d,  $J$  = 6.1 Hz, 3H), 0.91–1.00 (m, 15H), 0.57 (q,  $J$  = 7.9 Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 172.7 (C), 143.9 (CH), 133.6 (CH), 129.9 (C), 110.8 (CH), 94.9 (C), 82.1 (CH), 79.3 (C), 71.4 (CH), 39.5 (CH), 37.1 (CH), 32.3 ( $\text{CH}_2$ ), 26.5 ( $\text{CH}_2$ ), 23.9 ( $\text{CH}_2$ ), 20.9 ( $\text{CH}_3$ ), 18.7 ( $\text{CH}_2$ ), 17.2 ( $\text{CH}_3$ ), 16.1 ( $\text{CH}_3$ ), 14.5 ( $\text{CH}_3$ ), 6.9 ( $3\times\text{CH}_3$ ), 5.0 ( $3\times\text{CH}_2$ ); IR (film):  $\tilde{\nu}$  = 2958, 2932, 2875, 1730, 1455, 1416, 1376, 1344, 1260, 1241, 1194, 1152, 1130, 1100, 1088, 1028, 1006, 973, 909, 803, 767, 726, 699  $\text{cm}^{-1}$ ; HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{25}\text{H}_{42}\text{O}_3\text{Si}$  + Na: 441.2795; found 441.2789.



Colorless solid. M. p. = 220–224°C (ref.<sup>11</sup> 222–224°C).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  (ppm) = 8.43 (s, 2H), 7.72 (dd,  $J$  = 8.3, 1.1 Hz, 2H), 7.40 (d,  $J$  = 8.4 Hz, 2H), 4.32 (t,  $J$  = 6.8 Hz, 2H), 1.91 (quint.,  $J$  = 6.8 Hz, 2H), 1.44–1.25 (m, 22H), 0.88 (t,  $J$  = 6.5 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  (ppm) = 140.2, 129.3, 124.0, 122.7, 114.5, 108.9, 89.0, 31.9, 29.7, 29.67, 29.64, 29.60, 29.55, 29.50, 29.4, 29.0, 27.3, 22.7, 14.1. The analytical and spectroscopic data are in accordance with those reported in the literature.<sup>11</sup>

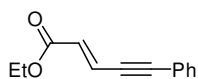
**Representative Alkyne Cross Metathesis Reaction using  $[\text{Mo}(\equiv\text{CPh})(\text{OSiPh}_3)_3(\text{Et}_2\text{O})]$  (**24**· $\text{Et}_2\text{O}$ ) (Table 3, entry 1).**

A mixture containing 3-(propyn-1-yl)-pyridine (117 mg, 1.00 mmol), 5-decyne (346 mg, 2.50 mmol), complex **24**· $\text{Et}_2\text{O}$  (10.5 mg, 9.67  $\mu\text{mol}$ , 2 mol%) and powdered MS 5 Å (1.0 g) in toluene (5 mL) was stirred at ambient temperature for 4 h. For work up, the suspension was filtered through a short pad of



silica, the filtrate was evaporated, and the residue purified by flash chromatography (hexanes/ $\text{EtOAc}$ , 20:1) to give 3-(hex-1-yn-1-yl)-pyridine as a pale yellow oil (103 mg, 65%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 8.61 (d,  $J$  = 1.5 Hz, 1H), 8.46 (dd,  $J$  = 4.9, 1.6 Hz, 1H), 7.66 (dt,  $J$  = 7.9, 1.9 Hz, 1H), 7.19 (ddd,  $J$  = 7.9, 4.9, 0.8 Hz, 1H), 2.42 (t,  $J$  = 7.0 Hz, 2H), 1.63–1.56 (m, 2H), 1.52–1.43 (m, 2H), 0.95 (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 152.3, 147.8, 138.4, 127.8, 122.8, 121.2, 94.0, 30.6, 22.0, 19.1, 13.6; IR (film):  $\tilde{\nu}$  = 3030, 2957, 2932, 2872, 2229, 1584, 1558, 1475, 1429, 1406, 1379, 1363, 1328, 1301, 1263, 1185, 1118, 1101, 1023, 1007, 949, 923, 889, 802, 747, 704  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 159 [ $\text{M}^+$ ] (52), 144 (100), 130 (46), 116 (45), 103 (25), 89 (32), 77 (13), 63 (39), 51 (14), 41 (15), 39 (15), 27 (17); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{11}\text{H}_{13}\text{N}$ : 159.1048; found: 159.1048.

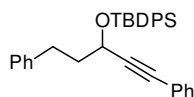
**(E)-Ethyl-5-phenylpent-2-en-4-ynoate.** Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.49–7.47 (m,



2H), 7.37–7.32 (m, 3H), 7.00 (d,  $J$  = 15.8 Hz, 1H), 6.33 (d,  $J$  = 15.8 Hz, 1H), 4.25 (q,  $J$  = 7.2 Hz, 2H), 1.31 (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 165.9, 131.9, 130.0, 129.3, 128.4, 125.0, 122.2, 98.2, 86.3, 60.7, 14.2; IR (film):  $\tilde{\nu}$  = 3064, 2982, 2938, 2905, 2199, 1709, 1617, 1594, 1490, 1465, 1443, 1392, 1367, 1311, 1293, 1250, 1164, 1113, 1095, 1069, 1036, 996, 956, 916, 859, 812, 754, 717, 687  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 200 [ $\text{M}^+$ ] (100), 185 (2), 172 (78), 155 (74), 144 (27), 127 (77), 115 (49), 101 (15), 87 (7), 77 (52), 63 (19), 51 (19), 39 (5), 29 (18); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{13}\text{H}_{12}\text{O}_2$  + Na: 223.0735; found: 223.0729.

<sup>11</sup> Zhang, W.; Cho, H. M.; Moore, J. S. *Org. Synth.* **2007**, *84*, 177.

**1,5-Diphenyl-3-(*tert*-butyldiphenylsilyloxy)-1-pentyne.** Colorless solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 7.82-7.80 (m, 2H), 7.75-7.72 (m, 2H), 7.50-7.34 (m, 6H), 7.29-7.15 (m, 10H), 4.63 (t,  $J = 6.1$  Hz, 1H), 2.87-2.82 (m, 2H), 2.13-2.07 (m, 2H), 1.13 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 141.8, 136.1, 135.9, 133.8, 133.7, 131.5, 129.7, 129.5, 128.4, 128.3, 128.1, 128.0, 127.6, 127.4, 125.8, 123.0, 90.4, 85.3, 63.8, 40.1, 31.3, 27.0, 19.4; IR (film):  $\tilde{\nu}$  = 3070, 3026, 2931, 2892, 2857, 1599, 1589, 1489, 1472, 1454, 1443, 1390, 1361, 1341, 1258, 1170, 1156, 1105, 1084, 1050, 1029, 1007, 998, 979, 938, 908, 843, 821, 798, 755, 734, 698, 689  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 474 [ $\text{M}^+$ ] (3), 417 (23), 369 (2), 339 (100), 313 (4), 283 (62), 223 (4), 199 (20), 181 (5), 135 (3), 91 (12), 77 (3); HRMS (ESI):  $m/z$ : calcd for  $\text{C}_{33}\text{H}_{34}\text{OSi}$ : 474.2379; found: 474.2379.





## Supplementary Crystallographic Information

### Crystal Structure Analysis of Complex [15·½(toluene)]

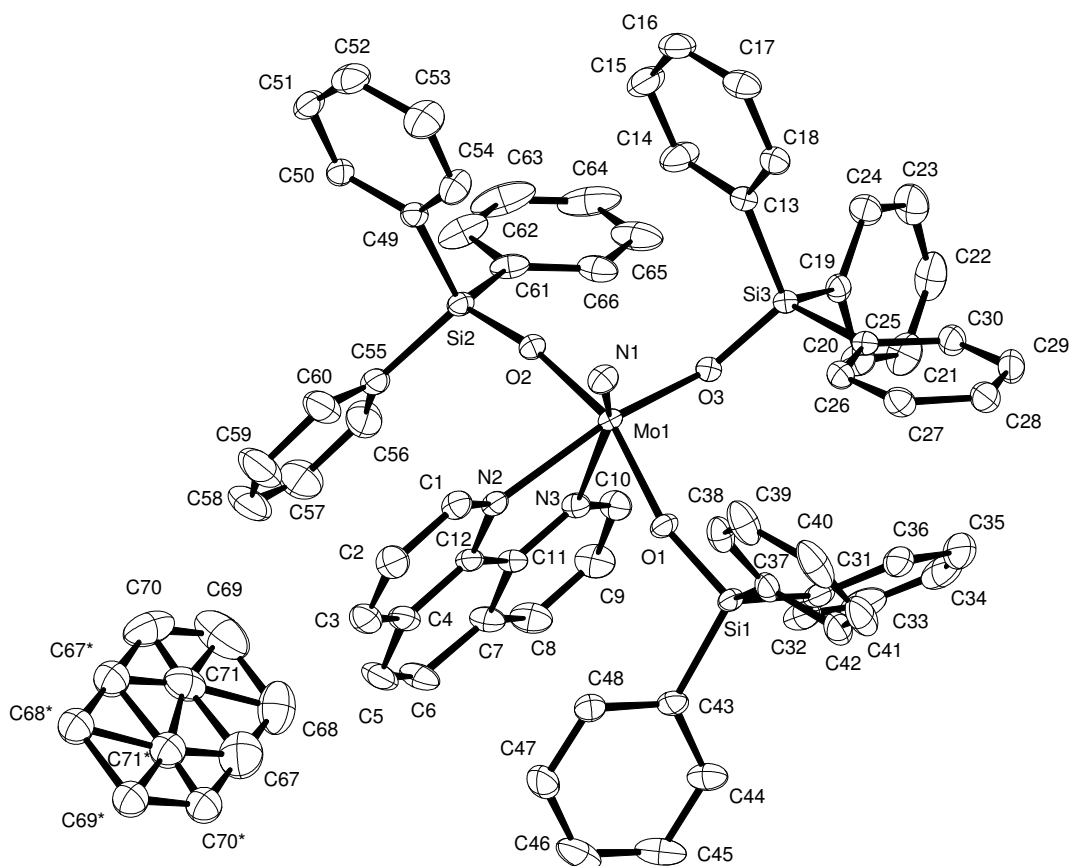


Figure S1. The crystal structure of **15**·½ toluene). The toluene molecule is disordered about a center of symmetry. The structure is shown with 50% probability ellipsoids. Hydrogen atoms omitted for clarity.

**Crystal Data for 15**·½(toluene):  $2[\text{C}_{66}\text{H}_{53}\text{MoN}_3\text{O}_3\text{Si}_3] \cdot [\text{C}_7\text{H}_8]$ ,  $\text{C}_{139}\text{H}_{118}\text{Mo}_2\text{N}_6\text{O}_6\text{Si}_6$ ,  $M_r = 2328.81 \text{ g} \cdot \text{mol}^{-1}$ , colorless block from toluene at  $80^\circ\text{C}$ , crystal size  $0.094 \times 0.043 \times 0.026 \text{ mm}$ , monoclinic, space group  $P2_1/n$ ,  $a = 9.8913(13) \text{ \AA}$ ,  $b = 42.226(6) \text{ \AA}$ ,  $c = 14.1812(18) \text{ \AA}$ ,  $\beta = 101.691(2)^\circ$ ,  $V = 5800.2(13) \text{ \AA}^3$ ,  $T = 100(1) \text{ K}$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.333 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 0.339 \text{ mm}^{-1}$ , Gaussian absorption correction ( $T_{\text{min}} = 0.98$ ,  $T_{\text{max}} = 0.99$ ), Bruker-AXS Smart APEX-II diffractometer,  $2.80^\circ < \theta < 30.10^\circ$ , 139390 measured reflections, 17002 independent reflections, 14274 reflections with  $I > 2\sigma(I)$ . Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.038$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.091$ , 730 parameters, H atoms were not calculated for the disordered solute toluene, otherwise H atoms calculated and refined using a riding model,  $S = 1.114$ , residual electron density  $+0.8 / -0.8 \text{ e} \cdot \text{\AA}^{-3}$ . CCDC 775727.

### Crystal Structure Analysis of Complex [19·(MeCN)]

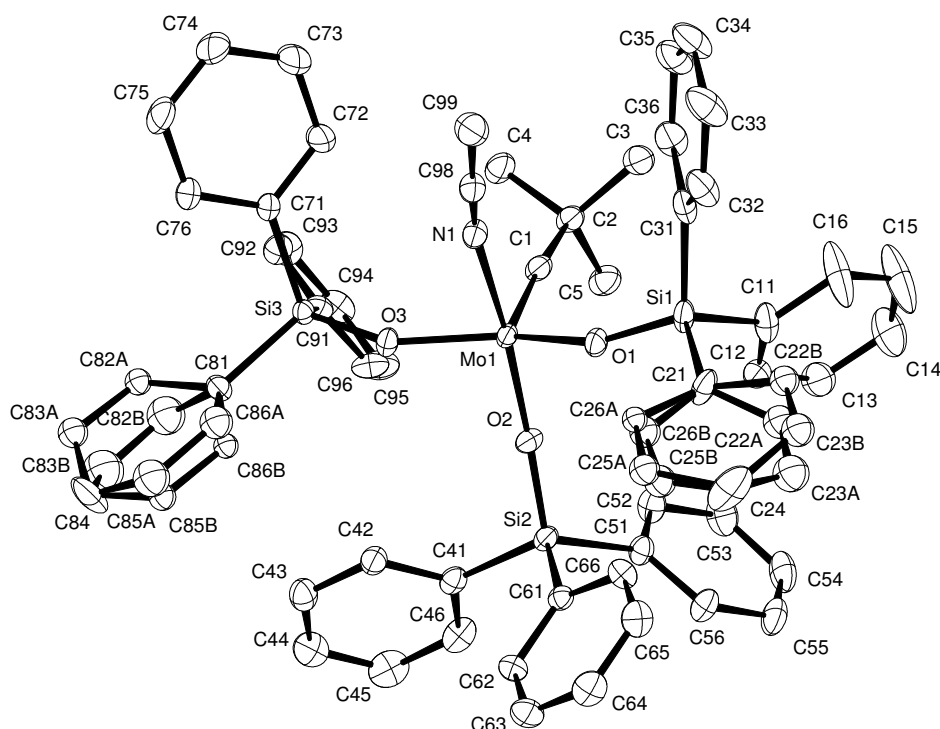


Figure S1. The crystal structure of **19**·(MeCN). One phenyl group attached to Si1 and one phenyl group attached to Si3 are disordered over two positions. The structure is shown with 50% probability ellipsoids. Hydrogen atoms omitted for clarity.

**Crystal Data for 19**·(MeCN):  $[C_{61}H_{57}MoNO_3Si_3]$ ,  $M_r = 1032.29 \text{ g} \cdot \text{mol}^{-1}$ , red-orange block, crystal size  $0.08 \times 0.07 \times 0.03 \text{ mm}$ , monoclinic, space group  $P2_1/c$ ,  $a = 9.386(3) \text{ \AA}$ ,  $b = 39.315(3) \text{ \AA}$ ,  $c = 14.803(2) \text{ \AA}$ ,  $\beta = 106.1450(10)^\circ$ ,  $V = 5247(2) \text{ \AA}^3$ ,  $T = 100(1) \text{ K}$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.307 \text{ g} \cdot \text{cm}^{-3}$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(Mo-K\alpha) = 0.365 \text{ mm}^{-1}$ , Semi-empirical absorption correction ( $T_{\text{min}} = 0.70$ ,  $T_{\text{max}} = 0.74$ ), Bruker-AXS Smart APEX-II diffractometer,  $3.90^\circ < \theta < 31.56^\circ$ , 151498 measured reflections, 16762 independent reflections, 15765 reflections with  $I > 2\sigma(I)$ . Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.038 [I > 2\sigma(I)]$ ,  $wR_2 = 0.127$ , 618 parameters. Two of the phenyl groups on two of the triphenylsilylanolate ligands are rotationally disordered in two positions about the C-Si bond. All four half-rings were restrained to be planar with a standard uncertainty of 0.1. The disorder, together with the small size of the crystal (thickness ca. 30 microns), contributed to difficulty in integrating reflections at high diffraction angles. At low angles several reflections were hidden by the beamstop due to the relatively long b axis length. Both these factors resulted in a coverage of only 96% to the maximum theta value of  $31.56^\circ$ . H atoms were refined using a riding model,  $S = 1.161$ , residual electron density  $+1.2 / -1.2 \text{ e} \cdot \text{\AA}^{-3}$ . CCDC 775728.

### Crystal Structure Analysis of Complex [23·(toluene)]

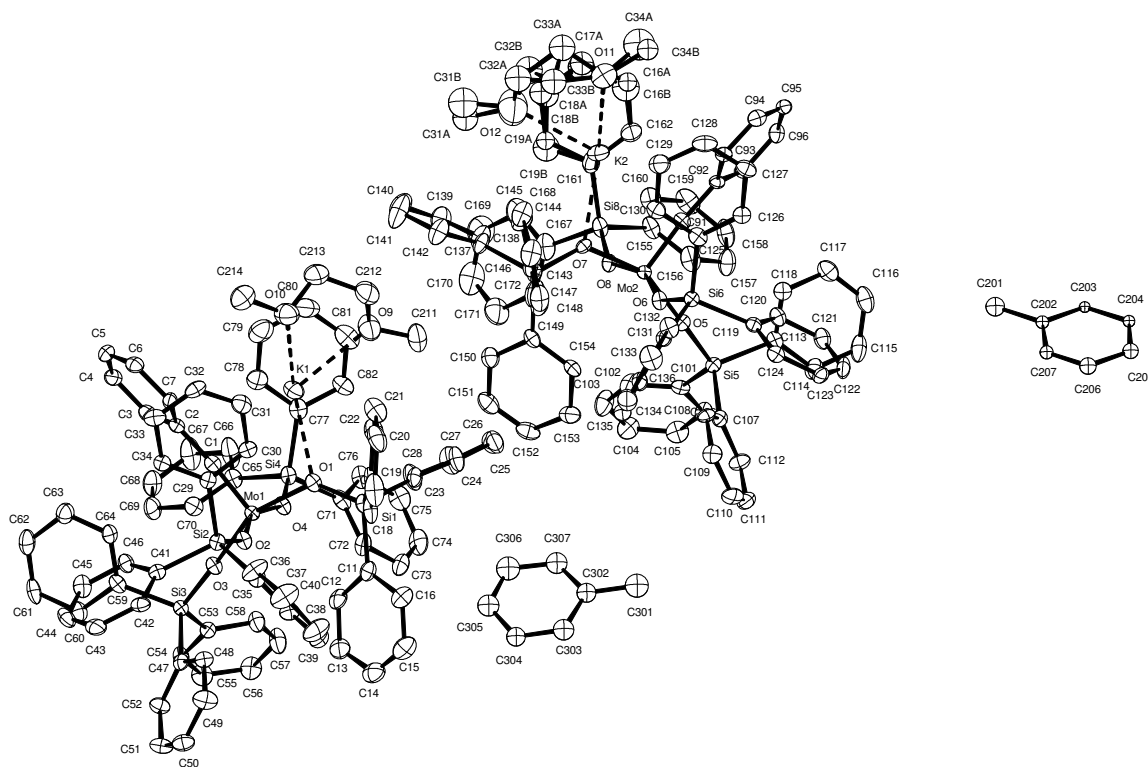


Figure S3. The crystal structure of **23**·(toluene). The structure is shown with 50% probability ellipsoids. Hydrogen atoms omitted for clarity.

**Crystal Data for 23**·(toluene):  $[\text{C}_{83}\text{H}_{75}\text{KMoO}_6\text{Si}_4] \cdot [\text{C}_7\text{H}_8]$ ,  $\text{C}_{173}\text{H}_{147.50}\text{K}_2\text{Mo}_2\text{O}_{12}\text{Si}_8$ ,  $M_r = 2913.21 \text{ g} \cdot \text{mol}^{-1}$ , orange prism, crystal size 0.04 x 0.02 x 0.02 mm, orthorhombic, space group  $Pca2$ ,  $a = 27.432(3) \text{ \AA}$ ,  $b = 13.8339(16) \text{ \AA}$ ,  $c = 40.197(5) \text{ \AA}$ ,  $V = 15254(3) \text{ \AA}^3$ ,  $T = 100(1) \text{ K}$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.268 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 0.342 \text{ mm}^{-1}$ , Gaussian absorption correction ( $T_{\text{min}} = 0.99$ ,  $T_{\text{max}} = 1.00$ ), Bruker-AXS Smart APEX-II diffractometer,  $1.79^\circ < \theta < 27.48^\circ$ , 180484 measured reflections, 34531 independent reflections, 24753 reflections with  $I > 2\sigma(I)$ . Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.054 [I > 2\sigma(I)]$ ,  $wR_2 = 0.195$ , 1763 parameters, absolute structure parameter = 0.04(3), H atoms riding. One of the two independent molecules in the asymmetric unit is disordered in the region around the potassium atom. In particular, the 1,2-dimethoxyethane and the phenyl group associated with the potassium cation were poorly resolved. Hydrogen atoms were not calculated for the disordered 1,2-dimethoxyethane ligand. The crystal contains one toluene molecule per molybdenum complex.  $S = 1.064$ , residual electron density  $+1.5 / -1.1 \text{ \AA}^{-3}$ . CCDC 775730.

## Crystal Structure Analysis of Complex 25

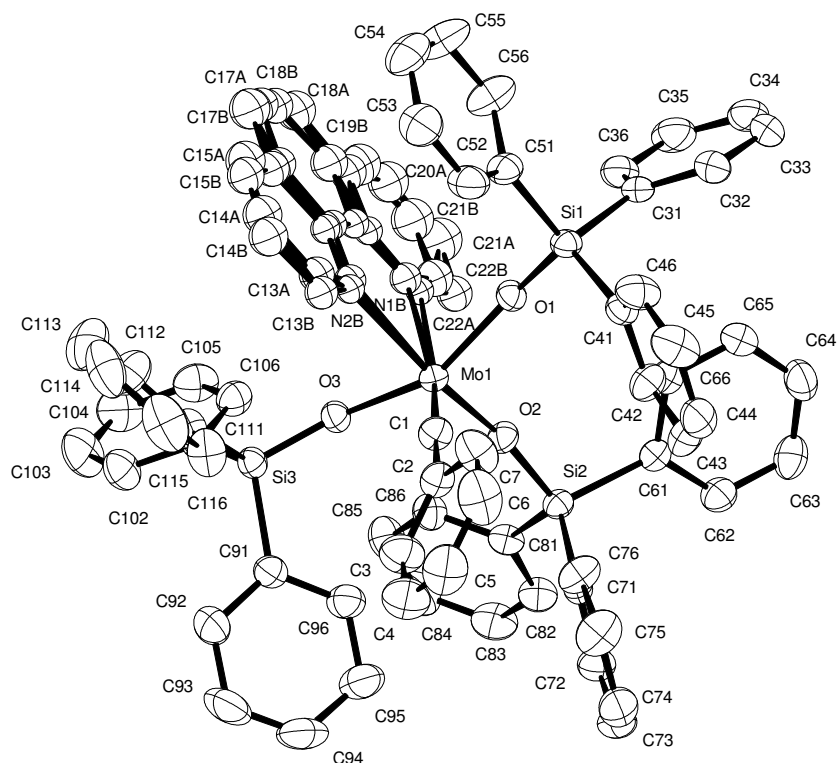


Figure S4. The crystal structure of **25**. The 1,10-phenanthroline ligand is disordered over two positions that are displaced by  $7(1)^\circ$  at the Mo atom in the equatorial plane defined by the 1,10-phenanthroline molecule, C1 of the benzylidene and O2 of one of the triphenylsilyloxy ligands. The structure is shown with 50% probability ellipsoids. Hydrogen atoms omitted for clarity.

**Crystal Data for 25:**  $[\text{C}_{73}\text{H}_{58}\text{MoN}_2\text{Si}_3\text{O}_3]$ ,  $M_r = 1191.42 \text{ g} \cdot \text{mol}^{-1}$ , violet plate, crystal size  $0.14 \times 0.12 \times 0.01 \text{ mm}$ , monoclinic, space group  $P2_1/c$ ,  $a = 18.6264(3) \text{ \AA}$ ,  $b = 19.7080(2) \text{ \AA}$ ,  $c = 16.8011(3) \text{ \AA}$ ,  $\beta = 102.7010(10)^\circ$ ,  $V = 6016.59(16) \text{ \AA}^3$ ,  $T = 200(1) \text{ K}$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.315 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 0.329 \text{ mm}^{-1}$ , Gaussian absorption correction ( $T_{\text{min}} = 0.96$ ,  $T_{\text{max}} = 1.00$ ), Bruker AXS Enraf-Nonius KappaCCD diffractometer,  $2.94^\circ < \theta < 32.09^\circ$ , 86289 measured reflections, 20954 independent reflections, 12198 reflections with  $I > 2\sigma(I)$ . Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.058 [I > 2\sigma(I)]$ ,  $wR_2 = 0.132$ , 725 parameters. It was examined whether the observed exact half occupancy of the disordered 1,10-phenanthroline ligand was the result of superposition of two independent molecules in a unit cell with a volume that is twice as large, but there is no indication in the diffraction frames that this occurs. H atoms riding,  $S = 1.012$ , residual electron density  $+0.6 / -0.8 \text{ \AA}^{-3}$ . CCDC 775729.

### Crystal Structure Analysis of Complex [28·2(toluene)]

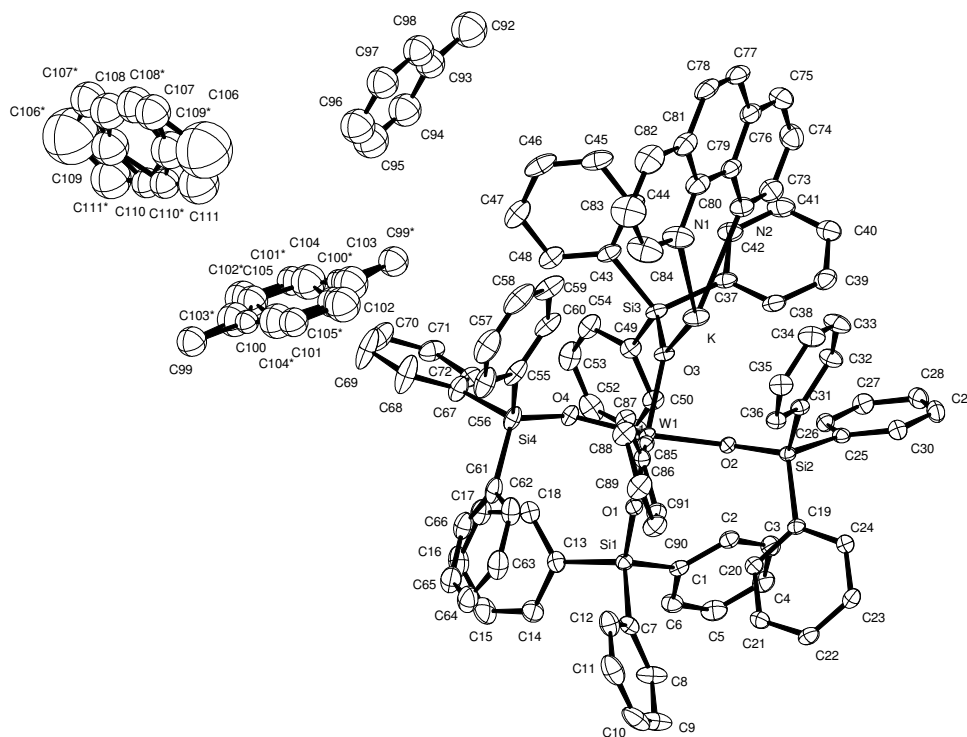


Figure S5. The crystal structure of **28**·(2 toluene). One of the toluene molecules is disordered about a center of symmetry in the crystal, the other about a 2-fold axis of symmetry. The structure is shown with 50% probability ellipsoids. Hydrogen atoms omitted for clarity.

**Crystal Data for 28·2(toluene):**  $[\text{C}_{91}\text{H}_{68}\text{KN}_2\text{O}_4\text{Si}_4\text{W}] \cdot 2[\text{C}_7\text{H}_8]$ ,  $\text{C}_{210}\text{H}_{168}\text{K}_2\text{N}_4\text{O}_8\text{Si}_8\text{W}_2$ ,  $M_r = 3546.10 \text{ g}\cdot\text{mol}^{-1}$ , red prism, crystal size  $0.034 \times 0.034 \times 0.010 \text{ mm}$ , monoclinic, space group  $C2/c$ ,  $a = 52.109(5) \text{ \AA}$ ,  $b = 14.7343(13) \text{ \AA}$ ,  $c = 25.228(2) \text{ \AA}$ ,  $\beta = 118.315(2)^\circ$ ,  $V = 17052(3) \text{ \AA}^3$ ,  $T = 100(1) \text{ K}$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.381 \text{ g}\cdot\text{cm}^{-3}$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 1.516 \text{ mm}^{-1}$ , Gaussian absorption correction ( $T_{\text{min}} = 0.95$ ,  $T_{\text{max}} = 0.99$ ), Bruker-AXS Smart APEX-II diffractometer,  $5.12^\circ < \theta < 28.58^\circ$ , 266743 measured reflections, 21016 independent reflections, 17798 reflections with  $I > 2\sigma(I)$ . Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.029 [I > 2\sigma(I)]$ ,  $wR_2 = 0.072$ , 1010 parameters, H atoms riding. Only 96% of the data were collected as a consequence of the shadow of the beamstop cutting off reflections at small theta values due to the long  $a$  axis. Reflections were measured with a high redundancy in order to increase the signal-to-noise ratio of the diffracted intensities because of the very small size of the crystal (thickness 10 microns).

## INTENSITY STATISTICS FOR DATASET 28-2(toluene):

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	R(int)	Rsigma
Inf - 2.05	1116	1167	95.6	12.48	76.8	67.53	0.0259	0.0100
2.05 - 1.63	1104	1104	100.0	16.62	59.0	72.12	0.0279	0.0098
1.63 - 1.42	1147	1147	100.0	16.93	48.1	65.89	0.0343	0.0109
1.42 - 1.29	1125	1125	100.0	16.17	40.1	56.41	0.0386	0.0128
1.29 - 1.19	1215	1215	100.0	15.14	32.4	46.94	0.0465	0.0153
1.19 - 1.12	1150	1150	100.0	14.37	28.2	40.72	0.0508	0.0175
1.12 - 1.06	1189	1189	100.0	13.73	24.9	35.88	0.0581	0.0200
1.06 - 1.01	1290	1290	100.0	13.08	23.4	33.44	0.0636	0.0221
1.01 - 0.97	1207	1207	100.0	12.59	20.5	28.89	0.0717	0.0252
0.97 - 0.93	1411	1411	100.0	12.13	18.7	26.08	0.0793	0.0282
0.93 - 0.90	1255	1255	100.0	11.67	16.6	22.93	0.0871	0.0321
0.90 - 0.87	1394	1394	100.0	11.36	14.9	20.76	0.0968	0.0363
0.87 - 0.84	1634	1634	100.0	11.00	14.2	19.40	0.1034	0.0393
0.84 - 0.82	1212	1212	100.0	10.58	13.0	17.40	0.1156	0.0440
0.82 - 0.80	1343	1343	100.0	10.39	11.9	15.98	0.1266	0.0487
0.80 - 0.78	1478	1478	100.0	10.04	10.5	14.06	0.1414	0.0560
0.78 - 0.76	1556	1669	93.2	7.50	9.6	11.47	0.1543	0.0817
0.76 - 0.74	88	611	14.4	0.15	4.5	2.53	0.3619	0.3681
0.84 - 0.74	6246	6882	90.8	8.78	11.3	14.69	0.1300	0.0572
Inf - 0.74	21914	22601	97.0	12.11	25.6	33.14	0.0542	0.0223

The crystal contains disordered and non-disordered toluene. H atoms on the methyl group of one toluene molecule disordered about a crystallographic 2-fold axis of symmetry were not calculated. The C atoms of disordered toluene molecules were refined with isotropic atomic displacement parameters.  $S = 1.063$ , residual electron density  $+1.3 / -1.0 \text{ e } \text{\AA}^{-3}$ . CCDC 775731.