Supplementary Information

Grafting a Homogeneous Transition Metal Catalyst onto a silicon AFM Probe: a Promising Strategy for Chemically Constructive Nanolithography

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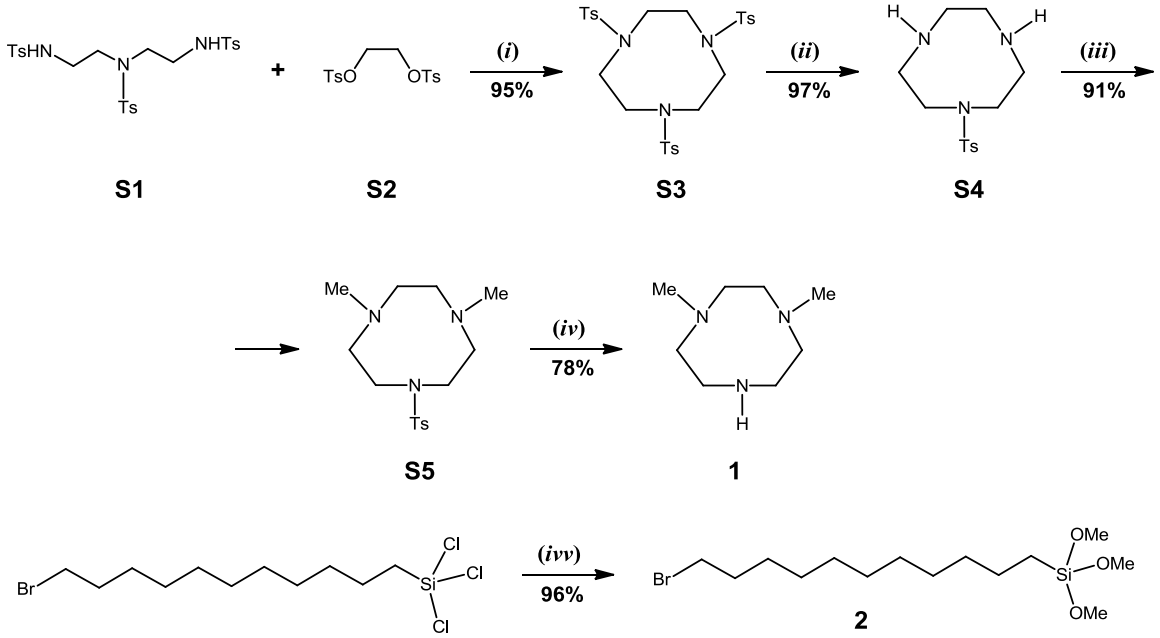
General information on synthesis

All synthetic manipulations were carried out under argon atmosphere using Schlenck techniques unless otherwise stated. For synthetic use commercial acetonitrile, methanol, hexane, pyridine, and Et*N*i*Pr*$_2$ were distilled over CaH_2 and stored under Ar. Reagent grade DMF was dried by vigorous stirring with CaH_2 at room temperature overnight and distilled under reduced pressure. All other solvents were degassed and purified using BRAUN MB-SPS800 solvent purification system. Milli-Q water was prepared using Direct-Q 3 (Merck Millipore) apparatus. 10-undecenyltrichlorosilane and 11-bromoundecyltrichlorosilane were purchased from ABCR and Fluorochem, respectively. All other commercial reagents were used as received. Anhydrous manganese(II) triflate was synthesized according to the published procedure.[1] 1,3-dimethyl-1,3,7-triazacyclononane (compound **1**) was prepared using slightly modified literature methods.[2]

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC400 spectrometer and referenced to the residual signals of deuterated solvents. ESI and HR-ESI mass spectra were obtained using Bruker Esquire 6000 and QStar Elite (Applied Biosystems SCIEX) spectrometers, respectively. The XPS spectra were recorded under ultrahigh vacuum in normal emission geometry with a 125 mm radius hemispherical analyzer (Omicron EA125) using an Al Kα source. Contact angle measurements with millipore water and hexadecane were made using a DSA 10 MK2 goniometer from Krüss GmbH.

Synthesis of 1,3-dimethyl-1,3,7-triazacyclononane (1) and 11-bromoundecyl-trimethoxysilane (2)



(*i*) - Cs_2CO_3, DMF, 25°C, 24h; (*ii*) - 30% HBr/AcOH, PhOH, 90°C, 72h; (*iii*) - HCHO, HCOOH, 115°C, 15h; (*iv*) - 97% H_2SO_4, 120°C, 36h; (*ivv*) MeOH, Et*N*i*Pr*$_2$, hexane, -40°C.

Synthesis of TsN(CH$_2$CH$_2$NHTs)$_2$ (S1). A solution of HN(CH$_2$CH$_2$NH$_2$)$_2$ (4.3 mL, 40.0 mmol) in pyridine (10 mL) was added dropwise to a solution of TsCl (22.9 g, 120.0 mmol) in pyridine (80 mL) over a 15 min period at room temperature. An exothermic reaction took place and the color of reaction mixture turned orange. Reaction mixture was stirred at 60°C during 1 h and then cooled to room temperature. Addition of the solution to an Erlenmeyer flask containing water (400 mL) under vigorous stirring induced the formation of a very abundant white precipitate. The suspension was stirred overnight, cooled to 0°C and filtered. The precipitate was thoroughly washed with ice-cooled water (10×50 mL), ethanol (2×50 mL), and dried *in vacuo* at 70°C to give 20.5 g (90.5%) of **S1** as a white powder.

S1: ^{1}H NMR (400.1 MHz, DMSO-d_6) δ 7.65 (d, J = 8.1 Hz, 4H), 7.54 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.1 Hz, 4H), 7.37 (d, J = 8.3 Hz, 2H), 3.01 (m, 4H), 2.80 (m, 4H), 2.40 (s, 6H), 2.39 (s, 3H); ^{13}C {^{1}H} NMR (100.6 MHz, DMSO-d_6) δ 129.9, 129.7, 126.8, 126.5, 48.4, 41.6, 21.0. ESI-MS: *m/z* 566.1 [M+H]$^+$, 588.1 [M+Na]$^+$.

Synthesis of TsOCH$_2$CH$_2$OTs (S2). A solution of TsCl (7.62 g, 40 mmol) in CH$_2$Cl$_2$ (50 mL) was added dropwise under stirring over a 30 min period to a solution of HOCH$_2$CH$_2$OH (1.12 mL, 20.0 mmol) and Et$_3$N (11.2 mL, 80.0 mmol) in CH$_2$Cl$_2$ (100 mL) cooled to 0°C. The reaction mixture was stirred for additional 20 min at 0°C and then placed into the freezer at *ca.* –15°C during 6 days, the time after which ^{1}H NMR analysis showed more than 85% conversion of TsCl. The precipitate of [Et$_3$NH]Cl was filtered off and the filtrate was washed with 2M HCl (50 mL), water (3×50 mL), and saturated NaHCO$_3$ (2×50 mL). The resulting solution was dried over MgSO$_4$ and evaporated to give white crystals. The crude product was dissolved in a minimum amount of warm chloroform (25-30 mL at *ca.* 50°C), the solution was filtered through Celite and Et$_2$O (40 mL) was added dropwise at room temperature to induce the crystallization of **S2**. The supernatant was removed, the precipitate was washed with ether (40 mL) and dried to give **S2** (5.54 g, 75%) as white crystals.

S2: ^{1}H NMR (400.1 MHz, CDCl$_3$) δ 7.73 (d, J = 8.0 Hz, 4H), 7.33 (d, J = 8.0 Hz, 4H), 4.18 (s, 4H), 2.46 (s, 6H); ^{13}C {^{1}H} NMR (100.6 MHz, CDCl$_3$) δ 130.0, 128.0, 66.7, 21.7; ESI-MS: *m/z* 393.0 [M+Na]$^+$.

Synthesis of Ts$_3$-tacn (S3). Solid Cs$_2$CO$_3$ (9.12 g, 28.0 mmol) was introduced into 250 mL two-necked flask and dried at 60°C under vacuum during 1 h. After cooling to room temperature solid **S1** (7.35 g, 13.0 mmol) and DMF (80 mL) were added and the resulting suspension was vigorously stirred at room temperature for 1.5 h. A solution of **S2** (4.8 g, 13.0 mmol) in DMF (30 mL) was then added dropwise over a 1 h period. The reaction mixture was stirred at room temperature for 2 days and then slowly added to an Erlenmeyer flask containing water (400 mL) under vigorous stirring. This induced the formation of an abundant white precipitate. The suspension was stirred during 1 h and then the precipitate was filtered off. The resulting powder was suspended in H$_2$O/DMF 1:1 mixture (200 mL) and stirred overnight. The solid was collected by filtration, thoroughly washed with water (5×50 mL) and dried under vacuum. The crude **S3** was dissolved in CH$_2$Cl$_2$ (20 mL) and the solution was filtered through Celite. The slow addition of ethanol (100

mL) at room temperature induced the crystallization of the desired product, which was completed at –20°C to give after drying 7.3 g (95%) of pure **S3** as white powder.

S3: ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 6H), 7.32 (d, *J* = 8.0 Hz, 6H), 3.42 (s, 12H), 2.43 (s, 9H); ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 129.9, 127.5, 51.9, 21.6; ESI-MS: *m/z* 614.0 $[M+Na]^+$.

Synthesis of H_2Ts-tacn (S4). A 250 mL Schlenck tube was charged with **S3** (7.8 g, 13.2 mmol), phenol (9.4 g, 100.0 mmol) and a 30% solution of HBr in AcOH (110 mL). The suspension was slowly warmed to 90°C under stirring over a *ca.* 1 h period. At 70°C a strong gas evolution took place and all solid was completely dissolved. (**Caution**: temperature should be increased very carefully after 60-70°C to avoid a brisk reaction. Highly corrosive vapors, gaseous HBr should be trapped with flask filled with water under positive Ar pressure). Gas evolution ceased after heating at 90°C for 2-3 h and a white precipitate of the product H_2Ts-tacn×2HBr appeared. The reaction mixture was stirred at 90°C for 3 days, then cooled to room temperature and left to stand overnight. The precipitate was filtered off, washed with ether (3×20 mL), and dissolved in 1.5 M aqueous NaOH to give a rose solution, which was extracted with $CHCl_3$ (4×15 mL). Combined extracts were dried over $MgSO_4$, concentrated to *ca.* 10 mL, filtered through Celite and dried to give 3.65 g (97%) of **S4** as a pale yellow oil.

S4: ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.19 (m, 4H), 3.08 (m, 4H), 2.90 (s, 4H), 2.41 (s, 3H), 2.13 (br s, 2H); ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 129.7, 127.3, 54.0, 49.6, 49.5, 21.5 ; ESI-MS: *m/z* 284.0 $[M+H]^+$.

Synthesis of Me_2Ts-tacn (S5). Compound **S4** (3.65 g, 12.85 mmol) was mixed with water (3 mL). The resulting suspension was cooled to 0°C and 37% HCHO (10 mL) was added dropwise under stirring until all solid dissolved (20 min). Then 97% HCOOH (10 mL) was added dropwise over a 10 min period and the reaction mixture was stirred for 30 min at 0°C, allowed to reach room temperature and then heated to reflux for 15 h (bath temperature 110°C). After cooling to room temperature 33% HCl (6 mL) was added to the reaction mixture and the volatiles were removed *in vacuo*. The residue was dissolved in 1.5 M aqueous NaOH (20 mL) and the resulting suspension was extracted with $CHCl_3$ (4×15 mL). The combined extracts were concentrated to *ca.* 10 mL, dried over $MgSO_4$, filtered through Celite and evaporated to dryness to give 3.73 g (91%) of **S5** as a pale yellow solid.

S5: ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.23 (m, 4H), 2.90 (m, 4H), 2.69 (s, 4H), 2.41 (s, 3H), 2.39 (s, 6H); ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 129.7, 127.1, 57.2, 56.7, 51.2, 46.1, 21.5; ESI-MS: *m/z* 312.0 $[M+H]^+$.

Synthesis of Me_2H-tacn (1). Compound **S5** (3.7 g, 12.0 mmol) was added gradually with ice cooling to 97% H_2SO_4 (15 mL) in a 50 mL one-necked flask. The flask was flushed with Ar for 30 min and the mixture was heated at 120°C for 36 h. The resulting dark brown solution was cooled to room temperature and poured into an Erlenmeyer flask containing crushed ice. An aqueous 12 M

solution of NaOH was added slowly with ice cooling until the pH of the solution became >12. The resulting dark brown suspension of partially precipitated Na_2SO_4 was extracted with $CHCl_3$ (5×40 mL). The combined extracts were concentrated to *ca.* 15 mL, dried over $MgSO_4$, filtered through Celite, and evaporated to give crude **1** as a yellow liquid, which was further purified by short-path vacuum distillation using Hickman apparatus (0.1-0.2 mm, 50-60°C) to give 1.3 g (68%) of pure **1** as a colorless oil.

1: ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 3.01 (br s, 1H), 2.66 (m, 4H), 2.52 (m, 4H), 2.50 (s, 4H), 2.39 (s, 6H); ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 53.7, 51.8, 45.3, 45.0; ESI-MS: *m/z* 158.1 $[M+H]^+$.

Synthesis of Br(CH$_2$)$_{11}$Si(OMe)$_3$ (2). A solution of $Br(CH_2)_{11}SiCl_3$ (1.1 g, 3.0 mmol) in hexane (30 mL) was cooled to –40°C and MeOH (0.38 mL, 9.3 mmol) was added dropwise under vigorous stirring followed by Et*i*Pr$_2$N (1.55 mL, 9.1 mmol) to produce an abundant white precipitate. The reaction mixture was slowly warmed up to room temperature and stirred overnight. The solution was filtered and the precipitate was washed with hexane (30 mL). Combined extracts were evaporated under vacuum to a give pale-yellow oil which was further purified by short-path vacuum distillation using Hickman apparatus (0.1-0.2 mm, 140-160°C) to give 1.02 g (96%) of **2** as a colorless oil.

2: ^{1}H NMR (400.1 MHz, C_6D_6) δ 3.46 (s, 9H), 2.97 (t, *J* = 6.9 Hz, 2H), 1.61-1.46 (m, 4H), 1.40-1.31 (m, 2H), 1.30-1.00 (m, 12H), 0.72 (t, *J* = 8.2 Hz, 2H); ^{13}C {^{1}H} NMR (100.6 MHz, C_6D_6) δ 50.2, 33.6, 33.4, 32.9, 29.85, 29.80, 29.65, 29.60, 28.9, 28.3, 23.1, 9.8.

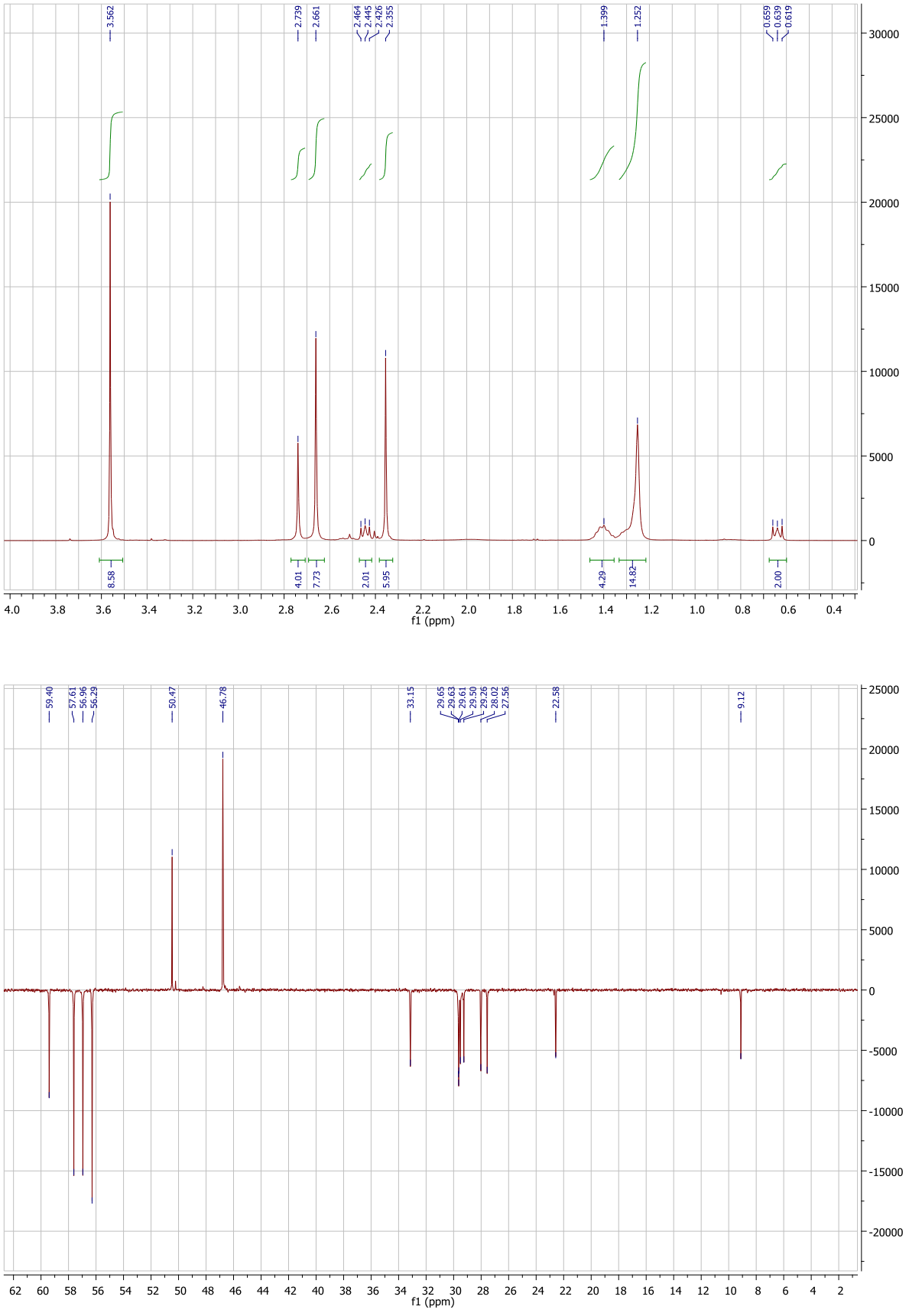


Figure S1. ^{1}H ($CDCl_3$, 400.1 MHz) (**a**) and ^{13}C {^{1}H} DEPT 135 ($CDCl_3$, 100.6 MHz) (**b**) NMR spectra of 1,3-dimethyl-7-(11-trimethoxysilylundecyl)-1,3,7-triazacyclononane (**3**).

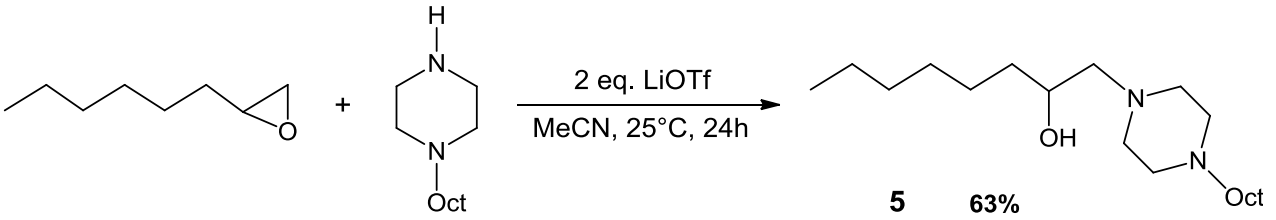
Grafting of 3 onto the amorphous silica and epoxidation of 1-octene catalyzed by the resulting heterogeneous catalyst

Preparation of heterogeneous version of manganese catalyst with tacn-type ligand **3** was carried out using slightly modified procedure for immobilization of the similar ligand obtained *in situ* from secondary amine **1** and (3-glycidyloxypropyl)trimethoxysilane.[4]

Preparation of silica supported compound 3 (SiO_2-3). A solution of ligand **3** (45 mg, 1.05 mmol) in toluene (5 mL) was added at room temperature to Schlenck tube containing amorphous silica (120 mg, Acros, 0.060-0.200 mm, 60Å) dried prior to use under vacuum for 15 hours at 90°C. The resulting suspension was heated at 90°C for 15 hours with gentle stirring. After cooling, the solid was filtered off using Pasteur pipette plugged with a glass wool, washed portionwise with CH_2Cl_2 (25×2 mL) and dried under vacuum at room temperature to give **SiO_2-3** as a white powder (160 mg) appearing heavier than the initial unmodified silica. The ligand loading in **SiO_2-3** was roughly estimated by mass difference to be 0.7-0.8 mmol/g, which is consistent with literature data (0.57 mmol/g).[4]

Complexation of SiO_2-3 with manganese(II) triflate and epoxidation of 1-octene catalyzed by the resulting catalyst. Silica supported ligand **SiO_2-3** (20 mg) was suspended in the mixture of methanol (1 mL) and water (0.25 mL), $Mn(OTf)_2$ (10 mg, 0.03 mmol) was then added and the suspension was stirred at room temperature for one hour. The resulting slightly rose solid was filtered off using a Pasteur pipette plugged with a glass wool, washed with methanol (1 mL), dried under argon flow, and added to a solution of 1-octene (157 μL, 1.0 mmol) in MeCN (2 mL). The reaction mixture was cooled to 0°C and non-stabilized 30% solution of H_2O_2 in water (410 μL, 4.0 mmol) was added dropwise over a 20 min period. The vigorously stirred reaction mixture was allowed to slowly reach room temperature over a 2 h period, and finally MnO_2 was added to destroy the excess of H_2O_2. A TLC of the solution on silica using PE/EtOAc mixture (95:5) as an eluant revealed 1,2-epoxyoctane to be a major product (Rf 0.95). The reaction mixture was diluted with water (3 mL) and the product was extracted with CH_2Cl_2 (3×1 mL). The combined extracts were dried over $MgSO_4$ and carefully evaporated under vacuum. An ^1H NMR analysis of the crude product showed a 1:3.8 alkene/epoxide ratio. Column chromatography on silica using PE/EtOAc mixture (95:5) afforded pure 1,2-epoxyoctane (70 mg, 55%).

Synthesis of *N*-octylpiperazine (4), its reaction with 1,2-epoxyoctane under homogeneous conditions, and the calculations simulating the addition of 4 to the model of SAM epoxide chain



4 **5** **63%**

Monoalkylation of piperazine with n-OctBr. 1-bromooctane (172 µL, 1.0 mmol) was added to the suspension of piperazine (0.86 g, 10 mmol) and K_2CO_3 (1.38 g, 10 mmol) in MeCN (5 mL) and the reaction mixture was vigorously stirred at 60°C for 24 h. The resulting white suspension was diluted with water (50 mL) at room temperature and chloroform (10 mL) was added. The aqueous layer was discarded and the organic layer was extracted with water (5×40 mL) to remove excess of piperazine, dried over $MgSO_4$ and evaporated *in vacuo* to give a slightly yellow liquid. The crude product was purified by short-path vacuum distillation using Hickman apparatus (0.1-0.2 mm, 50-60°C) to give 172 mg (87%) of pure *N*-octylpiperazine (**4**) as a colorless oil.

4: ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 2.81 (t, *J* = 4.9 Hz, 4H), 2.40-2.24 (m, 4H), 2.21 (t, *J* = 7.8 Hz, 2H), 1.64 (br s, 1H), 1.40 (br qv, *J* = 7 Hz, 2H), 1.24-1.15 (m, 10H), 0.80 (t, *J* = 6.8 Hz, 3H); ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 59.5, 54.7, 46.1, 31.8, 29.5, 29.2, 27.6, 26.7, 22.6, 14.0; ESI-MS: *m/z* 199.2 $[M+H]^+$.

Addition of *N*-octylpiperazine (4) to 1,2-epoxyoctane. A solution of 1,2-epoxyoctane (38 µL, 0.25 mmol), LiOTf (78 mg, 0.5 mmol) and N-octylpiperazine (**4**) (60 µL, 0.25 mmol) in MeCN (1 mL) was stirred at room temperature for 24 h. Then water (2 mL) was added and the product was extracted with CH_2Cl_2 (3×1 mL). Combined extracts were dried over $MgSO_4$. The volatiles were evaporated under vacuum to give a colorless oil, which was purified by flash chromatography on silica (elution with petroleum ether / EtOAc mixture from 10:1 to 5:1) to give compound **5** (51 mg, 63%) as colorless crystals.

5: ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 3.68-3.61 (m, 1H), 3.51 (br. s, 1H), 2.79-2.63 (m, 2H), 2.58-2.35 (m, 5H), 2.33-2.21 (m, 5H), 1.52-1.37 (m, 4H), 1.34-1.22 (m, 18H), 0.87 (t, *J* = 7.0 Hz, 6H); ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$) δ 66.1, 64.2, 58.9, 53.4, 35.0, 31.9, 31.8, 29.6, 29.5, 29.3, 27.6, 26.9, 25.6, 22.7, 22.6, 14.1; ESI-MS: *m/z* 327.3 $[M+H]^+$; HRMS (ESI) 327.3375 $[M+H]^+$ Calculated for $[M+H]^+$ 327.3370.

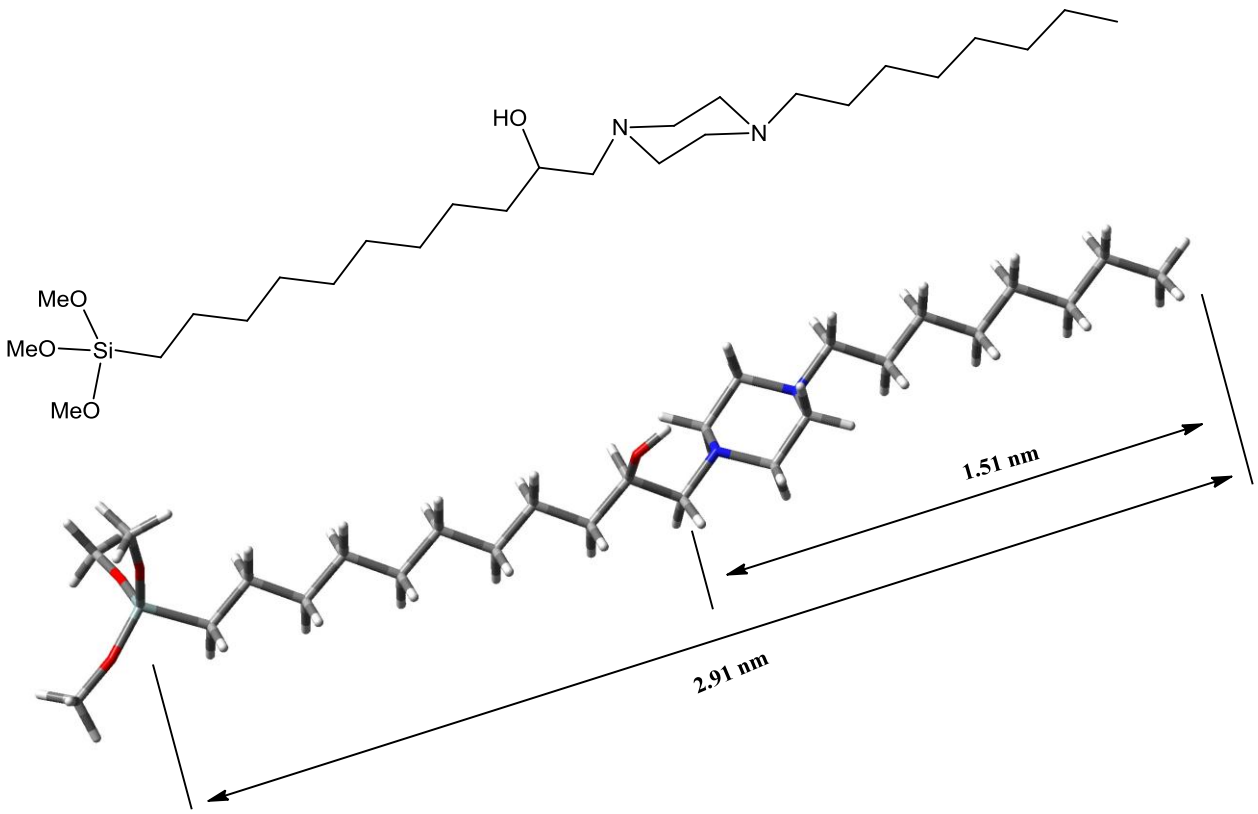


Figure S2. Semi-empirical calculations (PM3, Gaussian 2009) of a model simulating the reaction between *N*-octylpiperazine (**4**) and 11,10-epoxyundecyltrimethoxysilane (model of the 10-undecenyltrichlorosilane SAM chain after the epoxidation).

AFM images of silicon wafer with immobilized 3/Mn(II) pre-catalyst

A piece of silicon wafer (*ca.* 5×10 mm) was sonicated for 10 min successively in hexane, acetone, and Milli-Q water (20 mL of each solvent). Then it was treated in piranha solution (25 mL of 3:7 mixture of 30% H_2O_2 and 97% H_2SO_4; **Caution:** Pirahna solution is a highly corrosive liquid, which reacts violently with organic compounds) at 115°C for 40 min, washed thoroughly with Milli-Q water and dried over a strong stream of Ar. Immediately after drying the wafer was immersed into a 5 mM solution of ligand **3** in toluene (2 mL) and kept for 3 days at room temperature without stirring. The resulting wafer was sonicated in toluene for 10 min and then immersed into a 1 mM stock solution of manganese(II) triflate (1 mL) in anhydrous methanol for 1.5 h. Then the sample was washed with methanol, Milli-Q water and dried over a stream of argon. An AFM image of the surface (Figure **S3**) shows a good level of surface coverage with immobilized **3** and formation of some aggregates having 8-10 nm height.

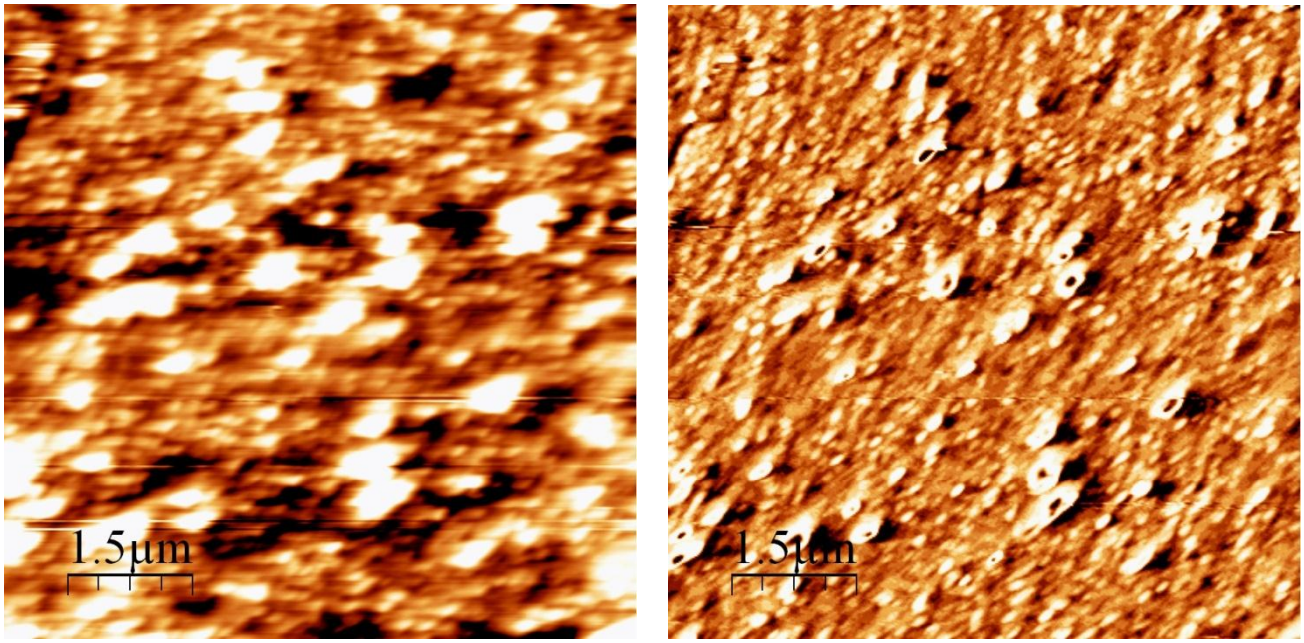


Figure S3. AFM tapping image (MeCN, 25°C, 10 µm/s, Z colour scale 6 nm) of silicon wafer with immobilized **3**/Mn(II) pre-catalyst in topography (left) and phase (right).

Preparation and characterization of SAM of 10-undecenyltrichlorosilane

Two pieces of silicon wafer (*ca.* 5×10 mm) were sonicated for 10 min successively in hexane, acetone, and Milli-Q water (20 mL of each solvent). Then the samples were treated in piranha solution (25 mL of 3:7 mixture of 30% H_2O_2 and 97% H_2SO_4; **Caution:** Pirahna solution is a highly corrosive liquid which reacts violently with organic compounds) at 115°C for 40 min, washed thoroughly with Milli-Q water and dried over strong stream of Ar. Immediately after drying the wafers were immersed into a freshly prepared 0.1 volume % of 10-undecenyltrichlorosilane in toluene (18 µL of silane in 18 mL of toluene) in a wide-neck 50 mL Erlenmeyer flask capped with a rubber septum under argon atmosphere. After incubation in silane solution for 40 min with gentle stirring the resulting wafers were washed with toluene and 95% ethanol, then sonicated successively in toluene, ethanol and Milli-Q water (15 min in each solvent) and dried by a stream of argon. The SAM formed was characterized by contact angle measurement with Milli-Q water (98.4±0.6°) and hexadecane (12.0±0.7°) giving values very close to literature data.[5] Characterization of the sample with AFM (Figure 1b,c) shows the formation of well-ordered SAM having low roughness and high homogenity in phase image.

Schematic representation of the home-built AFM liquid cell

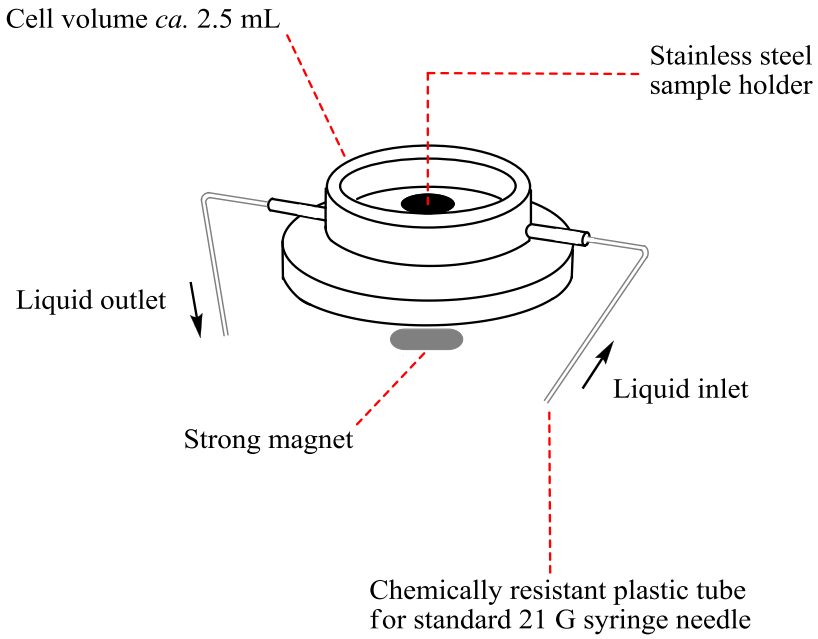


Figure S4

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