SUPPORTING INFORMATION

Supplementary Information (16 pages)

Host-Guest Chemistry in a Urea Matrix: The Catalytic and Selective Oxidation of Triorganosilanes to the Corresponding Silanols by Methyltrioxorhenium (MTO) and the Urea/Hydrogen Peroxide Adduct (UHP)

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We report herein the synthetic details and characteristic spectral data of the silanes **1a-c,f,h**, silanols **2a-d,f-h**, and disiloxanes **3a-c, g, h**. The general catalytic oxidation procedures with MTO/UHP, MTO/85% H_2O_2, Re_2O_7/85% H_2O_2, Ti(O*i*Pr)$_4$/*L*-DET/*t*BuOOH, VO(acac)$_2$/*t*BuOOH, MoO_2(acac)$_2$/*t*BuOOH, Mn(salen)/[O], the analytical protocol for the determination of the conversions, product distributions, and the enantiomeric excess of silanol **2h** are described.

General Aspects: ^{1}H- and ^{13}C-NMR spectra were measured on a Bruker AC 200 (^{1}H-NMR: 200 MHz, ^{13}C-NMR: 50 MHz) and AC 250 (^{1}H-NMR: 250 MHz, ^{13}C-NMR: 63 MHz) with deuterochloroform or deuterodichloromethane as internal standards. ^{29}Si-NMR spectra were measured on a Bruker AMX 400 (^{29}Si-NMR: 400 MHz) with tetramethylsilane (TMS) as external standard. IR spectra were obtained on a Perkin-Elmer 1420 Ratio Recording Spectrophotometer. For TLC runs, precoated silica-gel foils 60 F_{254} (5 x 10 cm) from Merck were used. Spots were visualized by irradiation under a UV lamp or by treatment with phosphomolybdic acid test spray. Column-chromatographic purifications were performed on silica gel (32-63 μm) from Woelm, Erlangen. Melting points were measured on a Büchi B-545 melting point apparatus and have not been corrected. The high-performance-liquid-chromatography (HPLC) analytical system consisted of Kontron (Eching/München) HPLC pumps (models T-414 or 322), a Kontron HPLC detector (model 430), or a UVIKON® HPLC detector (model 720LC micro), and a polarimetric detector (CHIRALYSER® 1.6 by IBZ Messtechnik, Hannover) run by the data system 450 MT/EMS. The conversions of silane **1h** were determined by HPLC analysis on the commercially available LiChrosorb Diol column (250 x 4.6 mm, Knauer). The enantiomeric excesses of silanol **2h** were determined by HPLC analysis on the commercially available column Chiralcel OD-H (Daicel Chemical Industries, Exton, PA) and the sense of optical rotation determined by the

CHIRALYSER® detector. For GC analysis of the silanes **1a-f**, the silanols **2a-f**, and the disiloxanes **3a-e** a gas chromatograph from Carlo Erba (model HRGC 5160 Mega Series) with a Shimadzu C-R6A Chromatopac integrator or on-line computer (Chrom-Card for Windows 1.19; CE Instruments) was used. The conversions of the silanes **1d,e**, and the yields of the silanols **2a-e** and the disiloxanes **3a-e** were determined on a fused-silica capillary column [SE 54 (30 m), Ø 0.25 mm or HP-5 (30 m), Ø 0.25 mm].

Materials: Solvents and commercially available chemicals were purified by standard procedures. Tetrahydrofuran (THF) was destilled immediately before use from a potassium-benzophenone mixture under an argon-gas atmosphere. Commercially available Re_2O_7, $VO(acac)_2$, $Ti(OiPr)_4$, $MoO_2(acac)_2$, and the Jacobsen catalyst (*S*,*S*)-(-)-N,N'-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminocyclohexanemanganese(III) chloride were employed as obtained. Dimethyldioxirane,[39] methyltrioxorhenium,[20] and methyl(oxo)bis(η^2-peroxo)rhenium(VIII)-hydrate[21] were prepared according to literature procedures. The silanes **1c-e,g**, the silanol **2e**, and the disiloxanes **3d,e** were commercially available and used as received. H_2O_2 was employed as the urea adduct (UHP), as a 85% aqueous solution, or as a 10.4 M solution in ethyl ether, the latter prepared by extraction of aqueous 85% H_2O_2 with ethyl ether (20 mL). Iodosobenzene was prepared by hydrolysis of the corresponding diacetate with aqueous NaOH.[40] *t*-BuOOH was employed as a 70% aqueous solution or as a 3.64 M solution in dichloromethane, the latter prepared was by extraction of aqueous 70% *t*-BuOOH with CH_2Cl_2 (3 x 20 mL).

CAUTION! Concentrated solutions of hydrogen peroxide are potentially dangerous and should be handled with care !

Dimethylethylsilane (1a)[22a]

To a slurry of 2.78 g (73.2 mmol) of lithium aluminum hydride in abs. 1,4-dioxane (25 mL) was added dropwise at 0 °C a solution of 5.00 g (40.8 mmol) of chlorodimethylethylsilane in 1,4-dioxane (5 mL). The reaction mixture was stirred at ca. 20 °C for 12 h. The dimethylethylsilane was then removed by distillation over a short Vigreux column to yield 2.82 g (78%; lit.[22a] 92%) of a colorless oil (bp 44-46 °C; lit.[22a] bp 48 °C).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.06 (d, *J* = 3.7 Hz, 6 H, $SiCH_3$), 0.56 (ddq, *J* = 7.9 Hz, 3.1 Hz, 0.8 Hz, 2 H, $SiCH_2$), 0.97 (dt, *J* = 8.2 Hz, 0.6 Hz, 3 H, CH_3), 3.82 (nonet, *J* = 3.5 Hz, 1 H, SiH).

^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.09 (d, *J* = 3.6 Hz, 6 H, $SiCH_3$), 0.60 (ddq, *J* = 7.9 Hz, 3.1 Hz, 1.1 Hz, 2 H, $SiCH_2$), 1.00 (t, *J* = 7.8 Hz, 3 H, CH_3), 3.85 (nonet, *J* = 3.5 Hz, 1 H, SiH).

^{13}C NMR (63 MHz, $CDCl_3$): δ = -4.9 (q, 2 C, $SiCH_3$), 6.0 (t, $SiCH_2$), 7.8 (q, CH_3).

^{29}Si NMR (400 MHz, $CDCl_3$): δ = -10.75 (s).

Dimethyl-*n*-propylsilane (1b)[22b]

To a slurry of 0.800 g (21.1 mmol) of lithium aluminum hydride in abs. ethyl ether (5 mL) was added dropwise at 0 °C a solution of 5.00 g (36.6 mmol) of chlorodimethyl-*n*-propylsilane in ethyl ether (11 mL). The reaction mixture was stirred at ca. 20 °C for 12 h and then slowly poured on 2 M sulfuric acid (20 mL). The two phases were separated and the aqueous layer was extracted with ether (2 x 10 mL). The ether solution was washed with sat. brine (10 mL) and dried over anhydr. Na_2SO_4. Distillation yielded 1.58 g (32%) of a colorless oil (bp 71-72 °C; lit.[22b] bp 73-74 °C) as a 75 : 25 mixture of the silane **1b** and ethyl ether.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.04 (d, J = 3.7 Hz, 6 H, $SiCH_3$), 0.52 - 0.62 (m, 2 H, $SiCH_2$), 0.95 (t, J = 7.2 Hz, 3 H, CH_3), 1.28 - 1.45 (m, 2 H, CH_2), 3.83 (nonet, J = 3.6 Hz, 1 H, SiH).
^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.09 (d, J = 3.7 Hz, 6 H, $SiCH_3$), 0.51 - 0.67 (m, 2 H, $SiCH_2$), 0.99 (t, J = 7.2 Hz, 3 H, CH_3), 1.32 - 1.49 (m, 2 H, CH_2), 3.87 (septet, J = 3.5 Hz, 1 H, SiH).
^{13}C NMR (63 MHz, $CDCl_3$): δ = -4.4 (q, 2 C, $SiCH_3$), 15.3 (t, $SiCH_2$), 16.7 (t, CH_2), 17.8 (q, CH_3).
^{29}Si NMR (400 MHz, $CDCl_3$): δ = -13.46 (s).

***tert*-Butyldimethylsilane (1c)**

^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.06 (d, J = 3.6 Hz, 6 H, $SiCH_3$), 0.94 (s, 9 H, CH_3), 3.66 (septet, J = 3.6 Hz, 1 H, SiH).

Triisopropylsilane (1f)

To a slurry of 0.320 g (8.43 mmol) of lithium aluminum hydride in abs. ethyl ether (2 mL) was added dropwise at 0 °C a solution of 1.62 g (8.40 mmol) of chlorotriisopropylsilane in ethyl ether (10 mL) and pentane (2 mL). The reaction mixture was stirred at ca. 20 °C for 2 h, then slowly hydrolyzed with water and neutralized with dilute aqueous HCl solution. The two phases were separated and the aqueous layer extracted with ether (3 x 10 mL). The combined organic phases were washed with water (10 mL) and dried over Na_2SO_4. After removal of the solvent (20 °C/50 mbar), the crude product was purified by distillation at reduced pressure to yield 0.775 g (58%) of a colorless oil (bp 60 °C/10 Torr; lit.[41] bp 60 °C/10 Torr).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.07 (s, 21 H, SiC$\underline{H}(CH_3)_2$ and SiCH(C$\underline{H}_3)_2$), 3.31 (br. s, 1 H, SiH).
^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.2 (d, 3 C, Si$\underline{C}$H$(CH_3)_2$), 19.4 (q, 6 C, SiCH($\underline{C}H_3)_2$).

Dimethoxymethylphenylsilane[42]

To a solution of 32.6 mL (0.200 mol) of dichloromethylphenylsilane in pentane (100 mL) were added dropwise 30.7 mL (0.220 mol) of triethylamine. The subsequent slow addition of a solution of 12.8 g (0.400 mol) methanol in pentane (200 mL) was accompanied by a strong evolution of HCl gas. After stirring at ambient temperature for 23 h, the solvent was removed under reduced pressure (20 °C/50 mbar) and the colorless residue was suspended in ethyl ether and the solid material removed by filtration. The filtrate was concentrated and purified by distillation at reduced pressure to yield 13.2 g (36%) of a colorless liquid (bp 84-85 °C/10 mbar; lit.[42] bp 202 °C).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.37 (s, 3 H, $SiCH_3$), 3.57 (s, 6 H, OCH_3), 7.35 - 7.71 (m, 5 H, aryl H).
^{13}C NMR (50 MHz, $CDCl_3$): δ = -5.2 (q, $SiCH_3$), 50.5 (q, 2 C, OCH_3), 127.9 (d), 130.2 (d, 2 C), 134.0 (d).

Methoxymethyl-α-naphthylphenylsilane[19a]

The Grignard reagent was prepared from 14.8 g (71.5 mmol) α-bromonaphthalene with 2.09 g (86.0 mmol) magnesium turnings in a solvent mixture, which contained ether (5 mL), toluene (10 mL), and tetrahydrofuran (5 mL). To this mixture was added a solution of 13.0 g (71.3 mmol) dimethoxymethylphenylsilane in tetrahydrofuran (10 mL). The reaction mixture was stirred under reflux for 13 h, cooled to ambient temperature (ca. 20 °C), and treated with saturated aqueous ammonium chloride (20 mL). The phases were separated and the aqueous phase was extracted with ether (2 x 20 mL). The ether solution was washed with water (2 x 20 mL), dried over Na_2SO_4, and the solvent removed at reduced pressure (20 °C/50 mbar). The crude product was purified by distillation to yield 13.5 g (68%; lit.[19a] 80%) of a pale yellow oil (bp 134-142 °C/0.034 mbar; lit.[19a] bp 143-146 °C/0.15 Torr), which crystallized overnight as colorless prisms (lit.[19a] mp 62.5-63.5 °C).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.82 (s, 3 H, $SiCH_3$), 3.61 (s, 3 H, $SiOCH_3$), 7.38 - 8.22 (m, 12 H, aryl H).

^{13}C NMR (63 MHz, $CDCl_3$): δ = -2.4 (q, $SiCH_3$), 51.2 (q, $SiOCH_3$), 125.0 (d), 125.5 (d), 126.1 (d), 127.9 (d, 2 C), 128.4 (d), 128.8 (d), 129.8 (d), 130.8 (d), 133.3 (s), 133.5 (s), 134.3 (d, 2 C), 135.2 (d), 136.2 (s), 137.0 (s).

Methyl-α-naphthylphenylsilane (1h)[19a]

To a slurry of 3.28 g (86.4 mmol) of lithium aluminum hydride in abs. ethyl ether (100 mL) was added dropwise at 0 °C a solution of 2.00 g (7.18 mmol) of methoxymethyl-α-naphthylphenylsilane in pentane (25 mL). The reaction mixture was stirred at ca. 20 °C for 22 h and then ethyl acetate slowly added until all excess lithium aluminum hydride had reacted. This mixture was then slowly added to conc. HCl (30 mL), water (500 mL), and ethyl ether (50 mL) in a separatory funnel. The aqueous phase was separated and extracted with pentane (100 mL) and ether (2 x 100 mL), followed by washing of the combined organic layers with water (100 mL), dried over Na_2SO_4, and the solvents removed (20 °C/50 mbar). The resulting pale yellow oil was purified by flash chromatography on silica gel (*n*-hexane as eluent) to yield 1.72 g (≥95%; lit.[19a] 68%) of a colorless oil.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.79 (d, *J* = 4.0 Hz, 3 H, $SiCH_3$), 5.39 (q, *J* = 4.0 Hz, 1 H, SiH), 7.32 - 8.17 (m, 12 H, aryl H).
^{13}C NMR (63 MHz, $CDCl_3$): δ = -4.5 (q, $SiCH_3$), 125.2 (d), 125.6 (d), 126.0 (d), 128.0 (d), 128.0 (d), 128.9 (d), 129.5 (d), 130.5 (d), 133.2 (s), 133.3 (s), 134.9 (d), 135.2 (s), 135.4 (d), 137.1 (s).
^{29}Si NMR (400 MHz, $CDCl_3$): δ = -19.88 (s).

(+)-Methyl-α-naphthylphenylsilane ((*S*)-1h)[19a]

To a solution of 10.0 g (35.9 mmol) of methoxymethyl-α-naphthylphenylsilane in toluene (10 mL) were added 5.66 g (36.2 mmol) of (-)-menthol and 131 mg (2.34 mmol) solid KOH. The reaction mixture was maintained at 140 °C for a total of 11 h, while the methanol-toluene azeotrope was distilled over a Vigreux column (bp 63.5 °C). After cooling to ambient temperature (ca. 20 °C), the catalyst was removed by passing the reaction mixture through a short column of silica gel with ethyl ether as eluent. The extract was concentrated (20 °C/50 mbar) to yield 14.7 g (≥95%) of a pale yellow oil. The sirupy mixture of diastereomers was diluted with twice its volume of pentane and chilled to -50°C. After several days, colorless needles crystallized, which were then recrystallized from pentane to afford 1.39 g (10%; lit.[19a] 22%) of (-)-menthoxymethyl-α-naphthylphenylsilane. To a slurry of 277 mg (7.30 mmol) of lithium aluminum hydride in abs. ethyl ether (2 mL) was added a solution of 772 mg (1.92 mmol) of (-)-menthoxymethyl-α-

naphthylphenylsilane in *n*-butyl ether (2 mL). The ethyl ether was removed by distillation until the temperature reached 80 °C. Heating at 80-90 °C was continued for 24 h, after which time the reaction mixture was cooled to ambient temperature (ca. 20 °C) and the excess lithium aluminum hydride slowly decomposed with water. Neutralisation with conc. HCl was followed by extraction with ethyl ether (3 x 10 mL) and drying of the organic phase over Na_2SO_4. The solvent was removed (20 °C/50 mbar) and the crude product purified by flash chromatography on silica gel (*n*-hexane as eluent) to yield 335 mg (70%; lit.[19a] 96%) of colorless prisms (mp 60-62 °C; lit.[19a] mp 60-62 °C). The optical purity was determined by HPLC analysis on a Chiracel OD-H column to be ≥98%.

General Procedure for the Preparation of Silanols 2a-d,f,h

Procedure A: To a solution of the silane **1** (1.35-6.80 mmol) in dichloromethane (5 mL) were added dropwise at 0 °C a solution (0.058-0.100 M) of dimethyldioxirane (DMD) in acetone (0.88-1.40 equiv.). The reaction mixture was stirred at 0 °C for 0.5-1.5 h, the solvent removed (20 °C/100 mbar), and the crude product was purified by Kugelrohr distillation or flash chromatography over silica gel.

Procedure B: To a solution of the chlorosilane (3.39-4.15 mmol) in *n*-hexane or ethyl ether were added 15% NaOH (5 mL). After stirring at ambient temperature for 10 min, the phases were separated and the aqueous phase extracted with ethyl ether (2 x 5 mL). The organic phase was washed with water (5 mL) and sat. brine (5 mL), dried over Na_2SO_4, and the solvent removed (20 °C/50 mbar). The crude product was purified by Kugelrohr distillation or recrystallisation.

Dimethylethylsilanol (2a)

A sample of 0.600 g (6.80 mmol) of dimethylethylsilane (**1a**) was oxidized for 0.5 h with 81.0 mL (5.99 mmol) of a DMD solution (0.074 M in acetone) according to *Procedure A*. Kugelrohr distillation of the crude product afforded 0.476 g (73%) of a colorless liquid (bp 120 °C; lit.[9a] bp 120 °C/774 Torr) as a 23.5 : 76.5 mixture of the silanol **2a** and the corresponding disiloxane **3a**.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.12 (s, 6 H, $SiCH_3$), 0.58 (q, *J* = 7.9 Hz, 2 H, $SiCH_2$), 0.96 (t, *J* = 8.2 Hz, 3 H, CH_3), 1.57 (br. s, 1 H, OH).
^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.12 (s, 6 H, $SiCH_3$), 0.57 (q, *J* = 7.6 Hz, 2 H, $SiCH_2$), 0.98 (t, *J* = 7.9 Hz, 3 H, CH_3), 1.98 (br. s, 1 H, OH).

^{13}C NMR (63 MHz, $CDCl_3$): δ = -0.8 (q, 2 C, $SiCH_3$), 6.8 (t, $SiCH_2$), 9.6 (q, CH_3).
^{29}Si NMR (400 MHz, $CDCl_3$): δ = 19.33 (s).

Dimethyl-*n*-propylsilanol (2b)

A sample of 0.660 g (4.89 mmol) of dimethyl-*n*-propylsilane (**1b**; 75.3 : 24.7 mixture of the silane and ethyl ether) was oxidized for 0.5 h with 78.0 mL (4.68 mmol) of a DMD solution (0.060 M in acetone) according to *Procedure A*. Kugelrohr distillation of the crude product afforded 0.359 g (63%) of a colorless liquid (bp 160 °C; lit.[9a] bp 137-139 °C/740 Torr) as a 92.4 : 7.6 mixture of the silanol **2b** and the corresponding disiloxane **3b**.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.11 (s, 6 H, $SiCH_3$), 0.56 - 0.62 (m, 2 H, $SiCH_2$), 0.95 (t, *J* = 6.9 Hz, 3 H, CH_3), 1.24 - 1.47 (m, 2 H, CH_2), 1.63 (br. s, 1 H, OH).
^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.12 (s, 6 H, $SiCH_3$), 0.51 - 0.67 (m, 2 H, $SiCH_2$), 0.99 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.32 - 1.49 (m, 2 H, CH_2), 1.89 (br. s, 1 H, OH).
^{13}C NMR (63 MHz, $CDCl_3$): δ = -0.2 (q, 2 C, $SiCH_3$), 16.7 (t, $SiCH_2$), 18.0 (t, CH_2), 20.4 (q, CH_3).
^{29}Si NMR (400 MHz, $CDCl_3$): δ = 18.14 (s).

***tert*-Butyldimethylsilanol (2c)**

A sample of 0.370 g (3.18 mmol) of *tert*-butyldimethylsilane (**1c**) was oxidized for 0.5 h with 35.0 mL (3.50 mmol) of a DMD solution (0.100 M in acetone) according to *Procedure A*. Kugelrohr distillation of the crude product afforded 0.251 g (60%) of colorless needles (bp 100 °C/35 Torr; lit.[43] bp 139 °C/739 Torr).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.08 (s, 6 H, $SiCH_3$), 0.89 (s, 9 H, CH_3), 1.69 (br. s, 1 H, OH).
^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.10 (s, 6 H, $SiCH_3$), 0.93 (s, 9 H, CH_3), 1.97 (br. s, 1 H, OH).
^{13}C NMR (63 MHz, $CDCl_3$): δ = -3.6 (q, 2 C, $SiCH_3$), 18.0 (s, $Si\underline{C}(CH_3)_3$), 25.6 (q, 3 C, $SiC(\underline{C}H_3)_3$).
^{29}Si NMR (400 MHz, $CDCl_3$): δ = 20.49 (s).

Dimethylphenylsilanol (2d)[15]

A sample of 0.330 g (2.42 mmol) of dimethylphenylsilane (**1d**) was oxidized for 0.5 h with 50.0 mL (2.90 mmol) of a DMD solution (0.058 M in acetone) according to *Procedure A*. Kugelrohr distillation of the crude product afforded 0.341 g (92%%; lit.[15] ≥98%) of a colorless oil (bp 150 °C/40 Torr; lit.[44] bp 100 °C/10 Torr).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.33 (s, 6 H, $SiCH_3$), 1.54 (br. s, 1 H, OH), 7.30 - 7.42 (m, 3 H, aryl H), 7.50 - 7.57 (m, 2 H, aryl H).
^{13}C NMR (63 MHz, $CDCl_3$): δ = 0.8 (q, 2 x C, $SiCH_3$), 127.7, 129.2, 133.0 (3 x d, 5 C), 139.8 (s).
^{29}Si NMR (400 MHz, $CDCl_3$): δ = -1.12 (s).

Triisopropylsilanol (2f)

A sample of 0.800 g (4.15 mmol) of chlorotriisopropylsilane was hydrolyzed according to *Procedure B* in 5 mL ethyl ether. Kugelrohr distillation of the crude product afforded 0.680 g (94%) of the product as a colorless liquid (bp 180 °C; lit.[45] bp 196 °C/750 Torr).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.01 (d, J = 0.9 Hz, 21 H, SiCH and CH_3), 1.87 (br. s, 1 H, OH).
^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.3 (d, 3 C, Si<u>C</u>H$(CH_3)_2$), 17.7 (q, 6 C, SiCH(<u>C</u>$H_3)_2$).

Triphenylsilanol (2g)

A sample of 1.00 g (3.39 mmol) of chlorotriphenylsilane in 5 mL *n*-hexane and 5 mL ethyl ether was processed according to *Procedure B* for 10 min. Recrystallisation [PE (30-50)/ethyl ether] of the crude product afforded 0.779 g (83%) of colorless polycrystalline powder (mp 148-150 °C; lit.[46] mp 151 °C).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.04 (br. s, 1 H, SiOH), 7.34 - 7.50 (m, 9 H, aryl H), 7.62 - 7.67 (m, 6 H, aryl H).
^{13}C NMR (63 MHz, $CDCl_3$): δ = 127.9, 130.1, 135.0 (3 x d, 5 C), 135.1 (s, 1 C).

Methyl-α-naphthylphenylsilanol (2h)

A sample of 0.500 g (2.01 mmol) of methyl-α-naphthylphenylsilane (**1h**) was oxidized for 1.0 h with 27.5 mL (2.23 mmol) of a DMD solution (0.081 M in acetone) according to *Procedure A*. The crude product was purified by flash chromatography over silica gel (2 : 1 *n*-hexane : ethyl ether, $R_f = 0.45$) to yield 0.546 g (≥98%) of pale beige amorphous powder (mp 70-71 °C; lit.[47] mp 73-74 °C).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.82 (s, 3 H, $SiCH_3$), 2.42 (br. s, 1 H, OH), 7.33 - 7.51, 7.61 - 7.66, 7.79 - 7.95, 8.11 - 8.14 (4 x m, 12 H, aryl H).
^{13}C NMR (63 MHz, $CDCl_3$): δ = 0.0 (q, $SiCH_3$), 125.0 (d), 125.5 (d), 126.0 (d), 128.0 (d), 128.4 (d), 128.9 (d), 129.9 (d), 130.8 (d), 133.4 (s), 133.9 (d), 134.6 (d), 134.8 (s), 136.7 (s), 137.6 (s).
^{29}Si NMR (400 MHz, $CDCl_3$): δ = -0.78 (s).

(+)-Methyl-α-naphthylphenylsilanol [(*R*)-2h]

A sample of 0.335 g (1.35 mmol) of (+)-methyl-α-naphthylphenylsilane [(*S*)-**1h**] was oxidized for 1.5 h with 21.9 mL (1.89 mmol) of a DMD solution (0.086 M in acetone) according to *Procedure A*. The crude product was purified by flash chromatography over silica gel (2 : 1 *n*-hexane : ethyl ether, $R_f = 0.45$) to yield 0.346 g (97%; lit.[15] ≥98%) of a colorless oil.

General Procedure for the Preparation of Disiloxanes 3a-c,g[23a]

To a solution of the chlorosilane (4.08 - 8.16 mmol) in acetonitrile (1.3 - 2.5 mL) and water (0.25 - 0.50 mL) were added ca. 1.1 equiv. sodium iodide. The reaction mixture was stirred at ambient temperature for 18 - 24 h. Two layers separated and the color of the reaction mixture turned to orange. Saturated sodium thiosulfate solution (5 mL) and ethyl ether (5 mL) were added, the two phases separated and the aqueous phase extracted with ether or pentane (2 x 5 mL). The combined organic phase was washed with water (5 mL) and sat. brine (5 mL), dried over Na_2SO_4, and the solvent removed (20 °C/50 mbar). The crude product was purified by Kugelrohr distillation or recrystallisation.

Ethyldimethyldisiloxane (3a)

Samples of 1.00 g (8.15 mmol) of chlorodimethylethylsilane and 1.40 g (9.34 mmol) NaI were processed for 18 h according to the *General Procedure* in 2.5 mL acetonitrile and 0.50 mL water. After Kugelrohr distillation, 0.342 g (44%) of a colorless liquid were isolated (bp 120 °C; lit.[48] bp 151 °C/750 Torr).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.02 (s, 12 H, $SiCH_3$), 0.47 (q, *J* = 7.8 Hz, 4 H, $SiCH_2$), 0.91 (t, *J* = 7.9 Hz, 6 H, CH_3).
^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.08 (s, 12 H, $SiCH_3$), 0.53 (dq, *J* = 8.1 Hz, 1.0 Hz, 4 H, $SiCH_2$), 0.96 (t, *J* = 7.7 Hz, 6 H, CH_3).
^{13}C NMR (63 MHz, $CDCl_3$): δ = -0.3 (q, 2 C, $SiCH_3$), 6.8 (t, $SiCH_2$), 10.0 (q, CH_3).
^{29}Si NMR (400 MHz, $CDCl_3$): δ = 8.44 (s).

Dimethyl-*n*-propyldisiloxane (3b)

Samples of 1.00 g (7.32 mmol) of chlorodimethyl-*n*-propylsilane and 1.15 g (7.67 mmol) NaI were processed for 22 h according to the *General Procedure* in 2.5 mL acetonitrile and 0.50 mL water. After Kugelrohr distillation, 0.342 g (43%) of a colorless liquid was isolated (bp 115 °C/10 Torr; lit.[22b] bp 66 °C/11 Torr).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.02 (s, 12 H, $SiCH_3$), 0.47 - 0.53 (m, 4 H, $SiCH_2$), 0.94 (t, *J* = 7.2 Hz, 6 H, CH_3), 1.26 - 1.34 (m, 4 H, CH_2).
^{1}H NMR (200 MHz, CD_2Cl_2): δ = 0.06 (s, 12 H, $SiCH_3$), 0.51 - 0.67 (m, 4 H, $SiCH_2$), 0.98 (t, *J* = 7.2 Hz, 6 H, CH_3), 1.32 - 1.49 (m, 4 H, CH_2).
^{13}C NMR (63 MHz, $CDCl_3$): δ = 0.4 (q, 2 C, $SiCH_3$), 16.8 (t, $SiCH_2$), 18.1 (t, CH_2), 21.1 (q, CH_3).
^{29}Si NMR (400 MHz, $CDCl_3$): δ = 7.17 (s).

***tert*-Butyldimethyldisiloxane (3c)**

Samples of 1.23 g (8.16 mmol) of *tert*-butylchlorodimethylsilane and 1.40 g (9.34 mmol) NaI were processed for 24 h according to the *General Procedure* in 2.5 mL acetonitrile and 0.50 mL water. After Kugelrohr distillation, 0.676 g (67%) of a colorless liquid were isolated (bp 175 °C; lit.[49] bp 191 - 193 °C).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.01 (s, 12 H, $SiCH_3$), 0.86 (s, 18 H, CH_3).

^{13}C NMR (63 MHz, $CDCl_3$): δ = -2.9 (q, 4 C, $SiCH_3$), 18.1 (s, 2 C, $Si\underline{C}(CH_3)_3$), 25.7 (q, 6 C, $SiC(\underline{C}H_3)_3$).
^{29}Si NMR (400 MHz, $CDCl_3$): δ = 10.09 (s).

Triphenyldisiloxane (3g)

Samples of 1.20 g (4.08 mmol) of chlorotriphenylsilane and 0.700 g (4.67 mmol) NaI were processed for 24 h according to the *General Procedure* in 1.3 mL acetonitrile and 0.25 mL water. Recrystallisation of the crude product from ethyl acetate afforded 0.304 g (28%) of colorless polycrystalline powder (mp 229 - 230 °C; lit.[50] mp 224 - 227 °C).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.22 - 7.50 (m, 30 H, aryl H).
^{13}C NMR (63 MHz, $CDCl_3$): δ = 127.7, 129.8, 135.2 (3 x d, 5 C), 135.4 (s, 1 C).

Methyl-α-naphthylphenyldisiloxane (3h)[23b]

To a sample of 500 mg (2.01 mmol) of methyl-α-naphthylphenylsilane (**1h**) were added 20.5 mg (90.0 μmol) benzyltriethylammonium chloride, 1 mL of 50% sodium hydroxide, and 1 mL chloroform. The reaction mixture was heated to 65 °C for 30 min and to 100 °C for a further 1.5 h. Subsequently, the mixture was cooled, acidified with concentrated HCl, and the product extracted into pentane (3 x 10 mL). The organic layer was dried over Na_2SO_4 and concentrated (20 °C/50 mbar). The crude product was purified by flash chromatography on silica gel (*n*-hexane; 8 : 2 *n*-hexane / ethyl ether) to yield 520 mg (≥95%; lit.[23b] 96%) of a colorless resin.

R_f [8 : 2 *n*-hexane / ethyl ether] = 0.69.
^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.59 (s, 6 H, $SiCH_3$), 7.00 - 7.45, 7.62 - 7.90 (2 x m, 24 H, aryl H).
^{13}C NMR (63 MHz, $CDCl_3$): δ = 0.6 (q, 2 C, $SiCH_3$), 124.9 (d), 125.3 (d), 125.6 (d), 127.8 (d), 128.6 (d), 128.8 (d), 129.5 (d), 130.5 (d), 133.3 (s), 133.9 (d), 134.7 (d), 135.0 (s), 136.6 (s), 138.2 (s).
^{29}Si NMR (400 MHz, $CDCl_3$): δ = -8.36 (s).

General Procedure for the MTO-Catalyzed Oxidation of Silanes 1a-h

To a solution of MTO (1-20 mol%) in dichloromethane, dichloromethane-d_2, deuterochloroform, or methanol (0.2 - 0.6 mL) were added 1.00-10.0 equiv. of the oxidant, and in some cases the additives urea (0.1-10.0 equiv.), tetramethylurea (1.0 equiv.), amylose (44.5-445 wt-%), or silica

gel (135 wt-%); the resulting mixture was stirred for 10 min before addition of the substrate. After stirring at ambient temperature for 6-24 h, the reaction mixture was filtered over ca. 1 g silica gel and the filtrate submitted to GC or HPLC analysis. The quantitative product data are given in Tables 1 and 2.

In a preparative-scale experiment, 347 mg (3.69 mmol) UHP were added to a solution of 9.2 mg (36.8 μmol) MTO in 6.6 mL CH_2Cl_2. After stirring at ambient temperature for ca. 10 min, 502 mg (3.69 mmol) of silane **1d** were added and the reaction mixture stirred for a further 8 h. Work-up by filtration through a short column of silica gel and subsequent flash chromatography over silica gel (4 : 1 *n*-hexane : ethyl ether) gave 487 mg (87%) of silanol **2d**.

General Procedure for the Stoichiometric Oxidation of Silanes 1d and (*S*)-1h with the Rhenium Monoperoxo Complex A

To a solution of MTO (1.25 equiv.) in dichloromethane or deuterochloroform (0.6 mL) was added the silane (80.2-100 μmol) and 0.8 equiv. of 30% aqueous H_2O_2. After stirring at ambient temperature for 45 min to 24 h, the reaction mixture was filtered over ca. 1 g silica gel and the filtrate submitted to GC or HPLC analysis.

General Procedure for the Stoichiometric Oxidation of Silanes 1d and (*S*)-1h with the Rhenium Diperoxo Complex B

To a solution of the diperoxo complex $CH_3ReO(O_2)_2 \cdot H_2O$ (0.5 equiv.) in dichloromethane (0.2-0.3 mL) was added the silane (97.0-117 μmol). After stirring at ambient temperature for 45 min to 2 h, the reaction mixture was filtered over ca. 1 g silica gel and the filtrate submitted to GC or HPLC analysis.

Procedure for the Oxidation of Silane 1d Catalyzed by Re_2O_7/85% H_2O_2

To a suspension of Re_2O_7 (1 mol%) in dichloromethane (0.6 mL) were added the oxygen source 85% H_2O_2 (1.00 equiv.) and the silane **1d** (330 μmol). After stirring at ambient temperature for 24 h, the reaction mixture was filtered over ca. 1 g silica gel and the filtrate submitted to GC analysis. The quantitative product data are given in Table 3.

General Procedure for the Oxidation of Silanes 1d and (*S*)-1h Catalyzed by Ti(O*i*Pr)$_4$/*L*-DET/*t*-BuOOH

To a solution of the silane (0.10-0.33 mmol) in dichloromethane (0.2-0.4 mL) were added a solution of Ti(O*i*Pr)$_4$ in CH_2Cl_2 (10 mol%; 165 mM solution) and a solution of diethyl *L*-tartrate in ethyl ether (11-12 mol%; 363 mM solution). To this solution were administered 1.00-10.0 equiv. of the oxidant *t*BuOOH as a solution in CH_2Cl_2 (3.64 M) and the reaction mixture stirred for 8-42 h. After filtration over ca. 1 g silica gel, the filtrate was submitted to GC or HPLC analysis. The quantitative product data for silane **1d** are given in Table 3.

General Procedure for the Oxidation of Silanes 1d and (*S*)-1h Catalyzed by VO(acac)$_2$/*t*-BuOOH

To a solution of VO(acac)$_2$ in CH_2Cl_2 (1.0-10 mol%; 16.5-31.8 mM solution) were added the silane (0.10-0.33 mmol) and 1.00-10.0 equiv. of *t*BuOOH as a solution in CH_2Cl_2 (3.64 M). The reaction mixture was stirred for 10-24 h and, after filtration over ca. 1 g silica gel, the filtrate was submitted to GC or HPLC analysis. The quantitative product data for silane **1d** are given in Table 3.

General Procedure for the Oxidation of Silanes 1d and (*S*)-1h Catalyzed by MoO$_2$(acac)$_2$/*t*-BuOOH

To a solution of MoO$_2$(acac)$_2$ (1-10 mol%) in CH_2Cl_2 (0.5 mL) were added the silane (0.10-0.33 mmol) and 1.00-10.0 equiv. of the oxidant *t*BuOOH as a solution in CH_2Cl_2 (3.64 M). The reaction mixture was stirred for 8-24 h and, after filtration over ca. 1 g silica gel, the filtrate was submitted to GC or HPLC analysis. The quantitative product data for silane **1d** are given in Table 3.

General Procedure for the Oxidation of Silanes 1d and (*S*)-1h Catalyzed by the Jacobsen Catalyst (*S*,*S*)-(-)-N,N'-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-diamino-cyclohexanemanganese(III) Chloride

PhIO as Oxygen Source

To a solution of the silane (50.3-330 μmol) in dichloromethane (0.5 mL) was added the Mn(salen) catalyst (7.4 mol%). To this solution was then added at 0 °C iodosobenzene (1.0 equiv.) as the oxygen source and the reaction mixture was stirred for 15-35 min. After filtration over ca. 1 g

silica gel, the filtrate was submitted to GC or HPLC analysis. The quantitative product data for silane **1d** are given in Table 3.

NaOCl as Oxygen Source

To a solution of silane **1d** (330 μmol) in dichloromethane (0.5 mL) was added the Mn(salen) catalyst (7.4 mol%). To this solution was then administered at ambient temperature bleach (13% aqueous solution buffered with Na_2HPO_4 to pH 11.3; 2.0 equiv.) and the reaction mixture was stirred for 24 h. After filtration over ca. 1 g silica gel, the filtrate was submitted to GC analysis.

30% Hydrogen Peroxide as Oxygen Source

To a solution of silane **1d** (330 μmol) in acetonitrile (0.5 mL) was added the Mn(salen) catalyst (7.4 mol%). To this solution was then administered at ambient temperature 30% aqueous H_2O_2 (6.0 equiv.) and the reaction mixture was stirred for 24 h. After filtration over ca. 1 g silica gel, the filtrate was submitted to GC analysis.

Determination of Conversions, Yields, and Enantiomeric Excesses

The conversions of the silanes **1a-c,f,g** were determined by ^{1}H-NMR spectroscopy, those of the silanes **1d,e** by GC analysis on a fused-silica SE-54 or HP-5 capillary column, and that of silane **1h** by HPLC analysis on a LiChrosorb Diol column. Product ratios of the silanols **2a-f** and the disiloxanes **3a-e** were determined by GC analysis, those of the silanol **2g** and disiloxane **3g** by TLC, and those of silanol **2h** and disiloxane **3h** by HPLC analysis.

Table 4: GC[a] and HPLC[b] Retention Times of Silanes **1c-f,h**, Silanols **2a-f,h**, and Disiloxanes **3a-e,h**

silane 1	t_R [min]	silanol 2	t_R [min]	standard	t_R [min]	disiloxane 3	t_R [min]
		2a[c]	9.03	toluene[c]	12.39	**3a**[c]	16.44
		2b[d]	10.62	ethylbenzene[d]	13.15	**3b**[d]	17.21
1c[e]	7.91	**2c**[e]	14.16	toluene[e]	17.78	**3c**[e]	28.02
1d[f]	3.28	**2d**[f]	6.08	hexadecane[f]	10.95	**3d**[f]	11.68
1d[g]	3.45	**2d**[g]	6.74	hexadecane[g]	11.64	**3d**[g]	12.32
1e[h]	2.83	**2e**[h]	5.35	dodecane[h]	8.77	**3e**[h]	9.92
1f[f]	9.19	**2f**[f]	11.69				
1h[i]	7.85	**2h**[i]	33.34	dimethyl-isophthalate[i]	13.08	**3h**[i]	10.75
1h[j]	12.29	**2h**[j]	32.81 (-) 35.24 (+)			**3h**[j]	12.29

[a] GC analysis of silanes **1c-f**, silanols **2a-f**, and disiloxanes **3a-e** on a 'fused-silica' SE 54 capillary column, N_2 as carrier gas. [b] HPLC analysis of silane **1h**, silanol **2h**, and disiloxane **3h** on a LiChrosorb Diol column; the enantiomer ratios of silanol **2h** were determined on a Chiralcel OD-H column. [c] GC conditions: $T_{Inj.}$ = 240 °C, $T_{Det.}$ = 250 °C, N_2 flow rate = 0.3 kg/cm^2; 35 °C (10 min) → 30 °C/min → 100 °C (1 min) → 30 °C/min → 160 °C (2 min) → 30 °C/min → 240 °C. [d] GC conditions: $T_{Inj.}$ = 240 °C, $T_{Det.}$ = 250 °C, N_2 flow rate = 0.3 kg/cm^2; 40 °C (7 min) → 30 °C/min → 100 °C (2 min) → 30 °C/min → 150 °C (5 min) → 30 °C/min → 240 °C. [e] GC conditions: $T_{Inj.}$ = 240 °C, $T_{Det.}$ = 250 °C, N_2 flow rate = 0.3 kg/cm^2; 35 °C (18 min) → 30 °C/min → 240 °C (5 min). [f] GC conditions: $T_{Inj.}$ = 240 °C, $T_{Det.}$ = 250 °C, N_2 flow rate = 1.0 kg/cm^2; 80 °C (4 min) → 30 °C/min → 130 °C (1 min) → 30 °C/min → 240 °C (1 min). [g] GC analysis on a 'fused-silica' HP-5 capillary column, N_2 as carrier gas; GC conditions: $T_{Inj.}$ = 240 °C, $T_{Det.}$ = 250 °C, N_2 flow rate = 1.4 kg/cm^2; 80 °C (5 min) → 30 °C/min → 130 °C (1 min) → 30 °C/min → 240 °C (2 min). [h] GC conditions: $T_{Inj.}$ = 190 °C, $T_{Det.}$ = 200 °C, N_2 flow rate = 1.0 kg/cm^2; 40 °C (3 min) → 30 °C/min → 100 °C (1 min) → 30 °C/min → 160 °C (2 min). [i] HPLC conditions: LiChrosorb Diol column, 9:1 *n*-hexane/MTB as eluent, flow rate: 0.4 mL/min (20 min) → 0.6 mL/min^2 → 1.0 mL/min (14 min), UV-metric (220 nm) detection. [j] HPLC conditions: Chiralcel column, 9:1 *n*-hexane/2-propanol as eluent, flow rate 0.4 mL/min, UV-metric (220 nm) and polarometric detection.

Additional References

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