Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPLEMENTARY INFORMATION

Catalytic Study of Water Dispersed Gold Nanoparticles for Hydrolytic Oxidation of Diorganosilanes - *en route* Formation of Pickering Catalyst and Synthesis of Tetraorganodisiloxane-1,3-diols

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General Information

The solvents such as acetonitrile, diethyl ether, chloroform, *n*-hexane were dried by standard methods. Glassware was dried in an oven at 110–120 ˚C and further flame-dried under vacuum prior to use. 2,4,6,8-Tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, lithium aluminium hydride and azobisisobutyronitrile (AIBN) were purchased from Sigma Aldrich and used as procured. ^{1}H and ^{29}Si NMR spectra were recorded in $CDCl_3$ or CD_3OD on a Bruker AVANCE III 500 MHz NMR spectrometer and the chemical shifts are quoted relative to Me_4Si. IR spectra were recorded on a Nicolet Protege 460 ESP spectrophotometer using KBr optics. Electrospray ionization (ESI) mass spectra were recorded on a micro TOF-Q II 10262 mass spectrometer in positive ion mode using an internal standard. The UV-Vis spectra of AuNPs were obtained using a Perkin Elmer UV/Vis/NIR Lambda 1050 spectrophotometer. High resolution transmission electron microscopy (HRTEM) and TEM studies were carried out using a carbon coated copper grid on a Philips CM 20 electron microscope operating at 100 kV and JEOL JEM-1400 operating at 120 KV, a +/- 70 degrees tilted computer control stage, respectively. Zeta potential and DLS measurements of aqueous dispersion of AuNPs were performed on Malvern Zetasizer Na. FESEM studies were carried out on a FEI Quanta 200 F SEM. ^{1}H NMR titrations for receptor-anion binding studies were performed using the stock solutions of **1, 2** (5×10^{-3} M) and Bu_4NCl (2×10^{-5} M) in $CDCl_3$. Binding constants were calculated by a non-linear fitting using Bindfit (http://www.supramolecular.org) and NMR fitting for 2:1 model was done using the Nelder-Mead method.

For crystallographic studies, Intensity data of **1**, **2** and **3** was collected on a Bruker APEX-III CCD, using graphite monochromated Mo-Kα radiation (λ=0.71073 Å). Cell parameters, data reduction and absorption corrections were performed using Bruker SAINT, using SAINT and SADABS.[1] The crystal was kept at a steady T= 273 K during data collection. The structure was solved with the ShelXT 2014/5 (Sheldrick 2014)[2] solution program and by Olex2 1.3-dev (Dolomanov *et al*., 2009)[3] as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015)[4] using full matrix least squares minimisation on F^2. Their site occupancy factors and U_{iso} values were refined as free variables. All hydrogen atoms were placed in geometrically calculated positions using a riding model while the -OH hydrogen atoms were located by the difference Fourier map and refined with bond length restraints and fixed U*ij*. Graphics were created using the diamond program.[5]

References

1 (a) SAINT, Bruker (2003), Bruker AXS Inc., Madison Wisconsin, USA; (b) SADABS, Bruker (2002), Bruker AXS Inc., Madison Wisconsin, USA.

2 G. M. Sheldrick, ShelXT-Integrated space-group and crystal structure determination, *Acta Cryst*., 2015, A71, 3-8.

3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.* 2009, **42**, 339-341.

4 (a) SHELXL-2018/3 (Sheldrick, 2018); (b) G. M. Sheldrick, A Short History of ShelX. *Acta Cryst*., 2008, A64, 339-341; (c) G. M. Sheldrick, Crystal structure refinement with ShelXT, *Acta Cryst*., 2015, C71, 3-8.

5 B. Klaus, DIAMOND, Version 1.2c, University of Bonn, Germany, 1999.

Synthetic methods

Synthesis of $[RSCH_2CH_2SiMeO]_4$; $R=CH_2CH(OH)CH_2OH$. The reaction between 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane $[CH=CH_2SiMeO]_4$ (1.994 g, 2.0 mL, 5.7 mmol) and 3-mercaptopropane-1,2-diol (2.50 g, 2 mL, 23 mmol) was performed in acetonitrile using 2,2′-azobisisobutyronitrile (AIBN, 10 wt%) as a free radical catalyst. The mixture was heated at 70 ˚C for nearly 18 h. The title compound was obtained as an oily liquid after repeated washing with acetonitrile (yield: 85%).

ESI-MS (+ve mode, m/z): 799.1596 (obs.)/ 799.1624 (calcd) $[M + Na]^+$. ^1H NMR (CD_3OD): δ 0.00-0.04 (m, 3H, SiCH_3), 0.74-0.79 (t, 2H, SiCH_2), 2.41-2.57 (m, 4H, SCH_2), 3.55 (m, 1H, CHOH), 3.36-3.42 (d, CH_2OH). ^{13}C {^1H} NMR: δ 72.99 (*C*HOH), δ 66.26 (*C*H_2OH), δ 36.36, 28.30 (S*C*H_2), δ 19.15 (Si*C*H_2), δ 0.00 (Si*C*H_3) ^{29}Si {^1H} NMR: δ -21.25, -21.32, -21.41. IR (KBr, cm^{-1}): 3359 (*v* OH), 1056 (*v* SiO), 1260 (*v* SiMe).

Synthesis of AuNPs. To a sonicated solution of $HAuCl_4.3H_2O$ (4.0 mg, 0.01 mmol) and $[RSCH_2CH_2SiMeO]_4$; R = $CH_2CH(OH)CH_2OH$ (7.7 mg, 0.01 mmol) in Milli-Q water (25.0 mL), sodium borohydride (0.70 mg, 0.06 mmol) was added in increments. A gradual colour change of the solution from yellow to wine red was observed within 4–5 h. The solution was left for equilibration for 24 h at room temperature and used for analysis. The stock solution contains 4.0 x 10^{-4}M AuNPs.

Synthesis of tetraorganodisiloxanes-1,3-diols, 1–3. In a typical procedure, methylphenylsilane (1.0 mL, 8.2 mmol) was added to the aqueous dispersion of AuNPs (2.0 mL) at 25 and 80 °C separately. After completion of the reaction, the viscous mass was dissolved in chloroform, treated with charcoal and dried over sodium sulphate. The solvent was stripped off and the disiloxane-1,3-diol, **1** was isolated as a crystalline solid. A similar procedure was followed for the synthesis of $[Me(cyclo\text{-}Hex)SiOH]_2O$, **2** by using the appropriate diorganosilanes. Compound **3** was obtained from the hydrolytic oxidation of $(HPh_2Si)_2O$ under similar conditions.

$(MePhSiOH)_2O$, 1. M.p. 95-96 ˚C, yield = 75%. ^1H NMR ($CDCl_3$): δ 7.26-7.40 (m, 5H, Si*Ph*), 2.62 (br, Si*OH*), 0.42-0.43 (s, 3H, Si*Me*). $^{29}Si\{^1H\}$ NMR: δ -22.8 (*Si*O). IR (KBr, cm^{-1}): 3410 (*v* OH), 3070 (*v* CH, aromatic), 2961 (*v* CH, aliphatic), 1260 (*v* SiMe), 1045 (*v* SiO). ESI-MS (+ve mode): m/z obs.(cald): 313.0720 (313.0687), $[M + Na]^+$.

$[Me(cyclo\text{-}Hex)SiOH]_2O$, 2. M.p. 69-70 ˚C, yield = 65%. ^1H NMR ($CDCl_3$): δ 2.24 (br, Si*OH*) 1.40-1.46, 1.84 (br, 10H, Si-*cyclo-Hex*), 0.87-0.90 (br, 1H, Si-C*H*), 0.33 (br, 3H, Si*Me*). $^{29}Si\{^1H\}$ NMR: δ -12.4 (*Si*O). IR (KBr, cm^{-1}): 3304 (*v* OH), 2921, 2849 (*v* CH, aliphatic), 1256 (*v* SiMe), 1034 (*v* SiO). ESI-MS: m/z = (+ve mode, m/z): 325.1636 (obs.)/ 325.1626 (calcd) $[M + Na]^+$.

$(Ph_2SiOH)_2O$, 3. M.p. 110-112 ˚C, yield = 75%. ^1H NMR ($CDCl_3$): δ 3.12 (br, Si*OH*), 7.62-7.32 (m, 20H, *Ph*). $^{29}Si\{^1H\}$ NMR: δ -36.0 (*Si*O). IR (KBr, cm^{-1}): 3223 (*v* OH), 3050, 3019 (*v* CH, aromatic), 1075 (*v* SiO). ESI-MS: m/z = (+ve mode, m/z): 437.0983 (obs.)/ 437.1000 (calcd) $[M + Na]^+$.

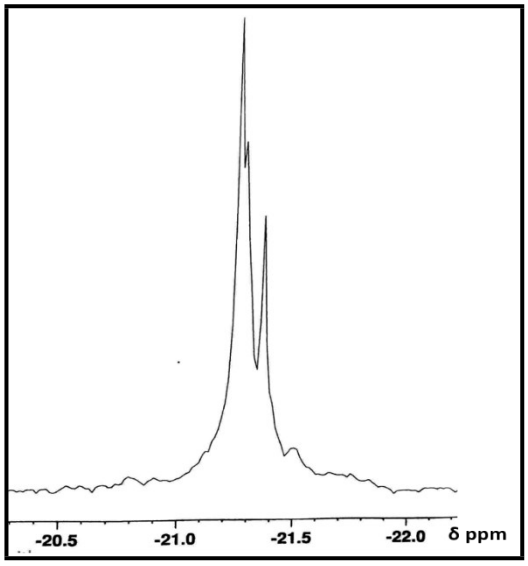


Figure S1. ^{29}Si NMR spectrum of Si^{gly}.

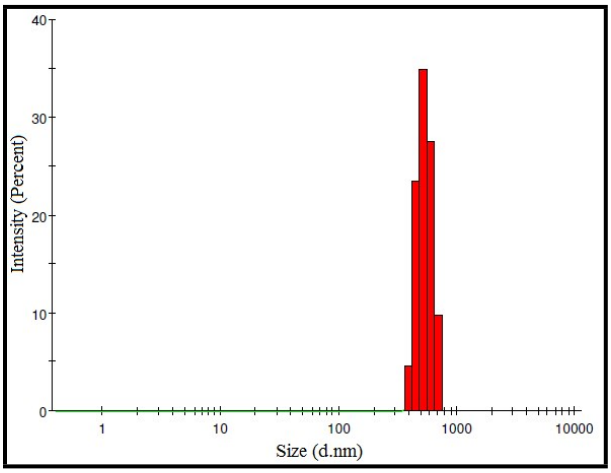


Figure S2. DLS profile of Si^{gly} in aqueous medium.

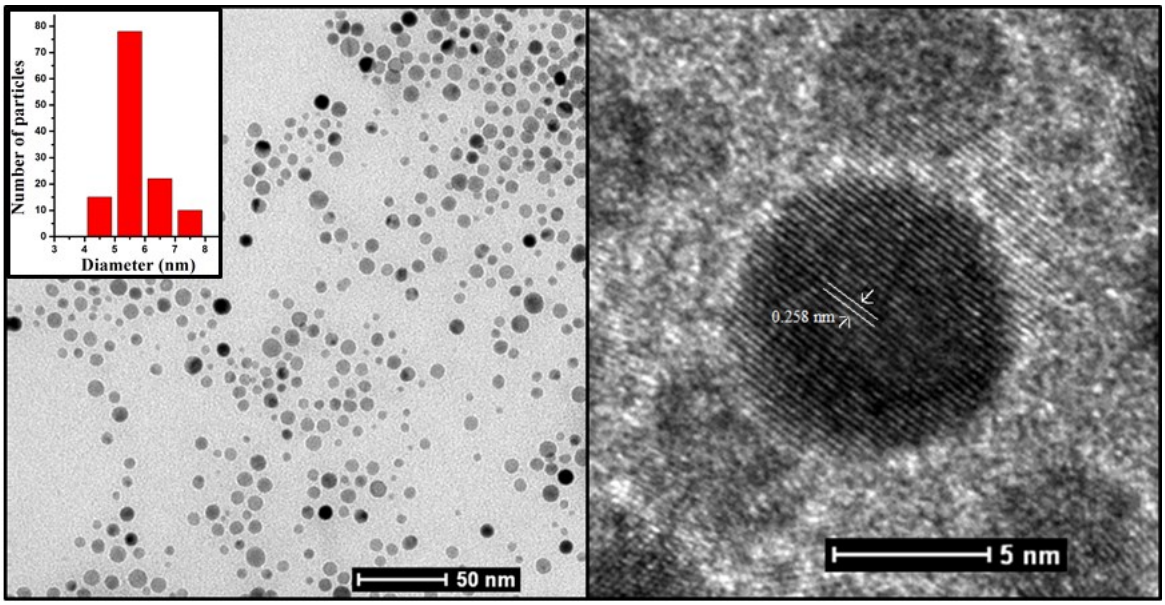


Figure S3. HRTEM micrograph of Au@Si^{gly} with lattice fringes.

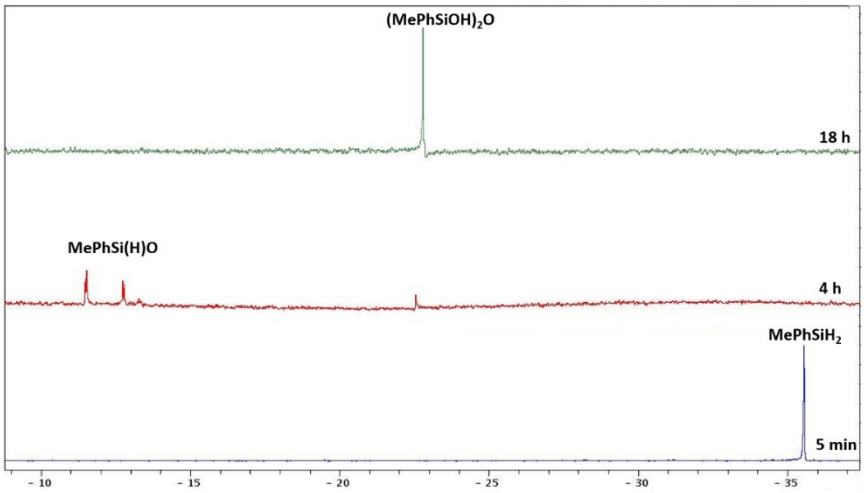


Figure S4. ^{29}Si NMR spectra of hydrolytic oxidation of $MePhSiH_2$ at different time interval.

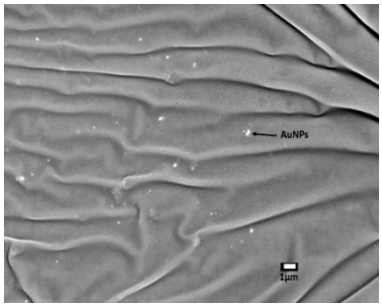


Figure S5. SEM micrograph of Pickering emulsion coated on a glass surface.

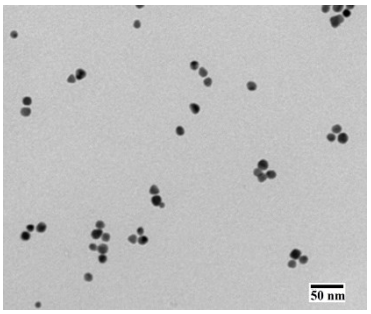


Figure S6. TEM micrograph of AuNPs after the catalytic cycle.

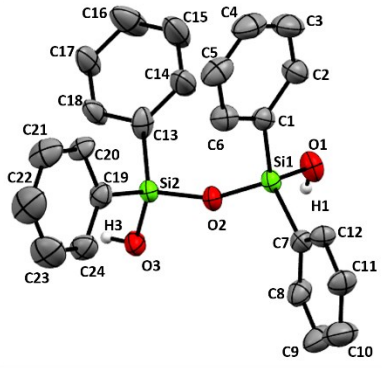


Figure S7. Crystal structure of $(Ph_2SiOH)_2O$ (**3**). Selected bond lengths (Å) and bond angles (˚) Si1-O1 1.6312(18), Si1-O2 1.6183(16), Si2-O2 1.6153(16), Si2-O3 1.6301(17), Si1-O2-Si2 156.86(12), O2-Si1-O1 106.83(9), O2-Si2-O3 105.63(9).

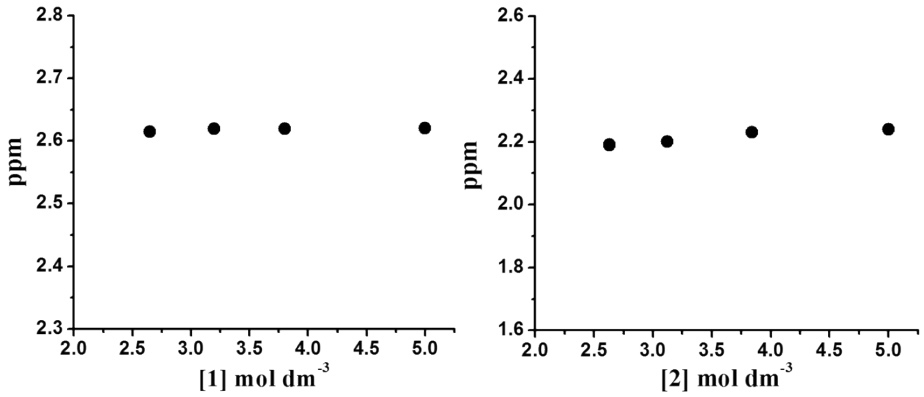


Figure S8. Plot of ^{1}H NMR (δ Si-OH) vs concentration (a) 5.0 × 10^{-3} (b) 3.8 × 10^{-3} (c) 3.1 × 10^{-3} (d), 2.6 × 10^{-3} mol dm^{-3} of **1** and **2** in $CDCl_3$.

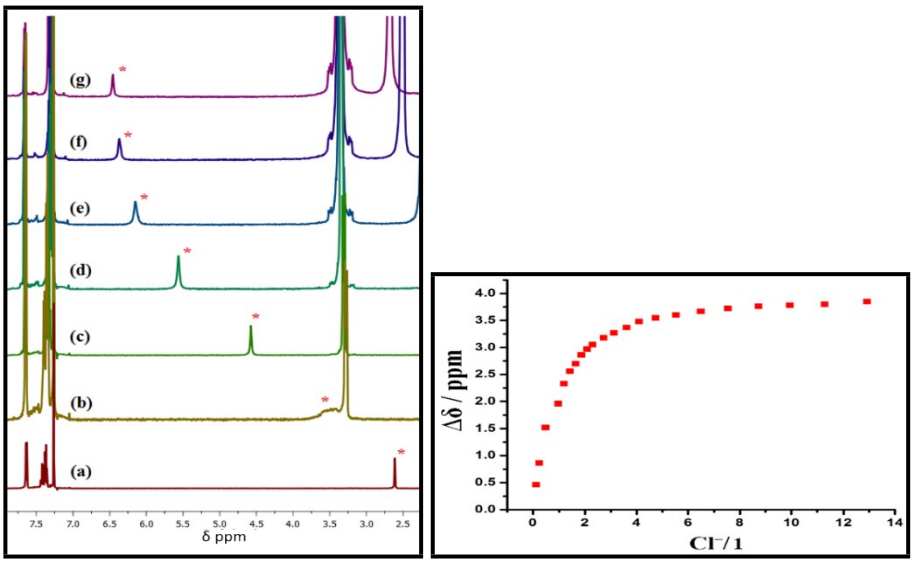


Figure S9. ^{1}H NMR spectra of **1** in the (a) absence and (b-g) presence of 0.12, 0.99, 2.24, 4.73, 12.13 and 22.09 equivalent of Cl^- in $CDCl_3$ (left). Changes in δ Si-OH groups and the best fitting curve for a 2:1 complexation model (right). [**1**] = 5.0 × 10^{-3} mol dm^{-3}. * ^{1}H NMR signal of Si-OH groups.

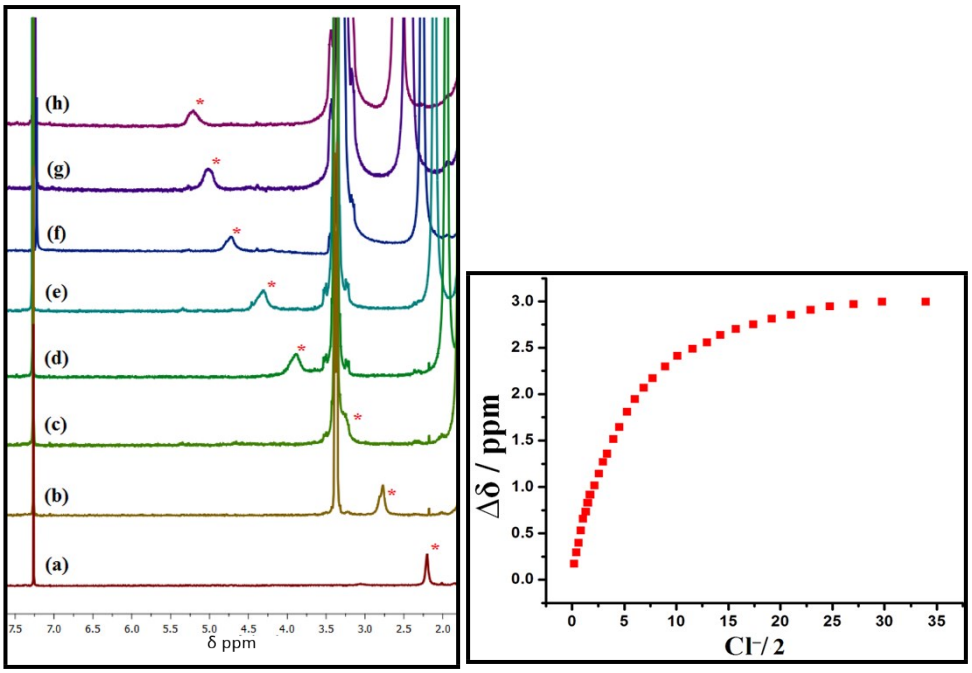


Figure S10. ^{1}H NMR spectra of **2** in the (a) absence and (b-h) presence of 0.22, 1.34, 5.83, 10.66, 14.59, 33.67 and 85.8 equivalent of Cl^- in $CDCl_3$ (left). Changes in δ Si-OH groups and the best fitting curve for a 2:1 complexation model (right). [**2**] = 5.0×10^{-3} mol dm^{-3}. * ^{1}H NMR signal of Si-OH groups.

Table S1. Summary of crystallographic data of 1-3.

crystal data	**1**	**2**	**3**
empirical formula	$C_{14}H_{18}O_3Si_2$	$C_{14}H_{30}O_3Si_2$	$C_{24}H_{22}O_3Si_2$
formula weight	290.46	302.56	414.59
temperature(K)	273	273	273
wavelength (Å)	0.71073	0.71073	0.71073
crystal system	Monoclinic	Monoclinic	Triclinic
space group	$P2_1$	$P2_1/n$	$P\bar{1}$
a [Å]	11.226(2)	12.8568(7)	13.4751(8)
b [Å]	6.4276(13)	6.6114(3)	14.2528(9)
c [Å]	11.494(2)	21.7760(11)	20.2962(14)
α [°]	90	90	98.906(2)
β [°]	99.141(6)	102.749(2)	99.541(2)
γ [°]	90	90	113.364(2)
volume ($Å^3$)	818.8(3)	1805.36(16)	3422.6(4)
Z	2	4	6
$D_{calcd.}$ [mg m^{-3}]	1.178	1.113	1.207
μ [mm^{-1}]	0.217	0.199	0.177
F(000)	308	664	1308
crystal size [mm]	0.60 x 0.23 x 0.12	0.928 x 0.428 x 0.326	0.132 x 0.106 x 0.098
θ range [°]	1.837 to 28.279	3.227 to 26.997	1.700 to 25.50
reflections collected	12756	31060	55779
independent reflections	4029 [R(int) = 0.0836]	3941 [R(int) = 0.0521]	12754 [R(int) = 0.0427]
completeness to theta %	99.9	99.6	100.0
data / restraints / parameters	4029 / 213 / 213	3941 / 311 / 290	12754 / 104 / 1009
goodness-of-fit on F^2	1.201	1.080	1.043
final R indices [I>2sigma(I)]	R1 = 0.0582, wR2 = 0.1363	R1 = 0.0479, wR2 = 0.1212	R1 = 0.0479, wR2 = 0.1257
R indices (all data)	R1 = 0.0877, wR2 = 0.1546	R1 = 0.0684, wR2 = 0.1388	R1 = 0.0687, wR2 = 0.1452
largest diff. peak and hole $eÅ^{-3}$	0.327 and -0.338	0.226 and -0.171	0.302 and -0.333

Table S2. Selected bond lengths [Å] and angles [°] for 1.

Si(1)-O(1)	1.637(3)	Si(2)-O(2)	1.618(4)
Si(1)-O(2)	1.610(4)	Si(2)-O(3)	1.629(3)
Si(1)-C(7)	1.848(6)	Si(2)-C(8)	1.827(5)
Si(1)-C(1)	1.857(5)	Si(2)-C(9)	1.886(4)
		Si(2)-C(9A)	1.861(10)
O(2)-Si(1)-O(1)	110.74(19)	O(2)-Si(2)-O(3)	111.07(19)
O(2)-Si(1)-C(7)	110.6(3)	O(2)-Si(2)-C(8)	108.0(2)
O(1)-Si(1)-C(7)	105.3(2)	O(3)-Si(2)-C(8)	108.1(2)
O(2)-Si(1)-C(1)	106.40(19)	O(2)-Si(2)-C(9)	106.5(5)
O(1)-Si(1)-C(1)	109.86(19)	O(3)-Si(2)-C(9)	110.6(4)
C(7)-Si(1)-C(1)	114.0(2)	C(8)-Si(2)-C(9)	112.6(4)
Si(1)-O(2)-Si(2)	148.3(2)	O(2)-Si(2)-C(9A)	109.3(5)
C(8)-Si(2)-C(9A)	112.7(5)	O(3)-Si(2)-C(9A)	107.7(5)

D-H…A	d(D-H)	d(H..A)	<DHA	d(D..A)
O1-H1…O3(#1)	0.82(4)	1.969(4)	159.83(3)	2.753(5)
O3-H3A…O1(#2)	0.797(3)	1.914(3)	170.05(3)	2.702(4)

Symmetry transformations used to generate equivalent atoms:

#1 x, y-1, z

#2 -x+1, y+1/2, -z+2

Table S3. Selected bond lengths [Å] and angles [°] for 2.

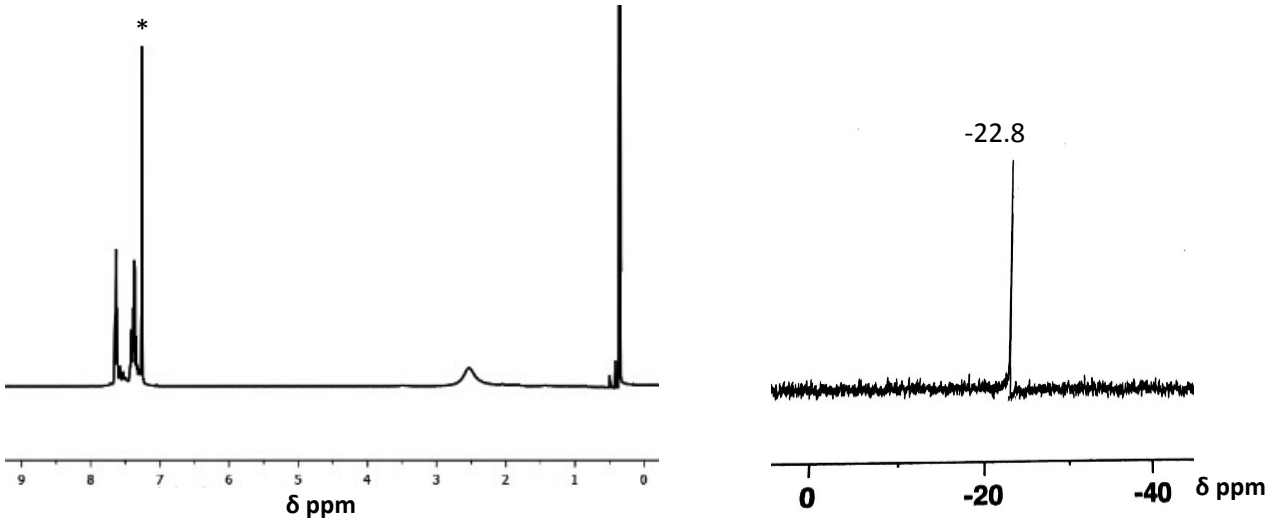
Si(1)-O(1)	1.6355(16)	Si(2)-O(2)	1.6145(17)
Si(1)-O(2)	1.6188(17)	Si(2)-O(3)	1.6387(16)
Si(1)-C(7)	1.848(3)	Si(2)-C(5_1)	1.866(5)
Si(1)-C(1)	1.854(2)	Si(2)-C(8)	1.840(3)
O(2)-Si(1)-O(1)	109.88(10)	O(2)-Si(2)-O(3)	110.33(9)
O(2)-Si(1)-C(7)	109.62(12)	O(2)-Si(2)-C(8)	107.64(12)
O(1)-Si(1)-C(7)	105.58(11)	O(3)-Si(2)-C(8)	106.98(12)
O(2)-Si(1)-C(1)	106.94(10)	O(2)-Si(2)-C(5_1)	101.63(17)
O(1)-Si(1)-C(1)	111.38(10)	O(3)-Si(2)-C(5_1)	109.11(17)
C(7)-Si(1)-C(1)	113.45(13)	C(8)-Si(2)-C(5_1)	120.9(2)
Si(1)-O(2)-Si(2)	147.87(12)		

D-H…A	d(D-H)	d(H..A)	<DHA	d(D..A)
O1-H1…O3(#1)	0.854(2)	1.947(2)	165.19(2)	2.782(3)
O3-H3…O1(#2)	0.856(2)	1.921(2)	171.83(2)	2.771(3)

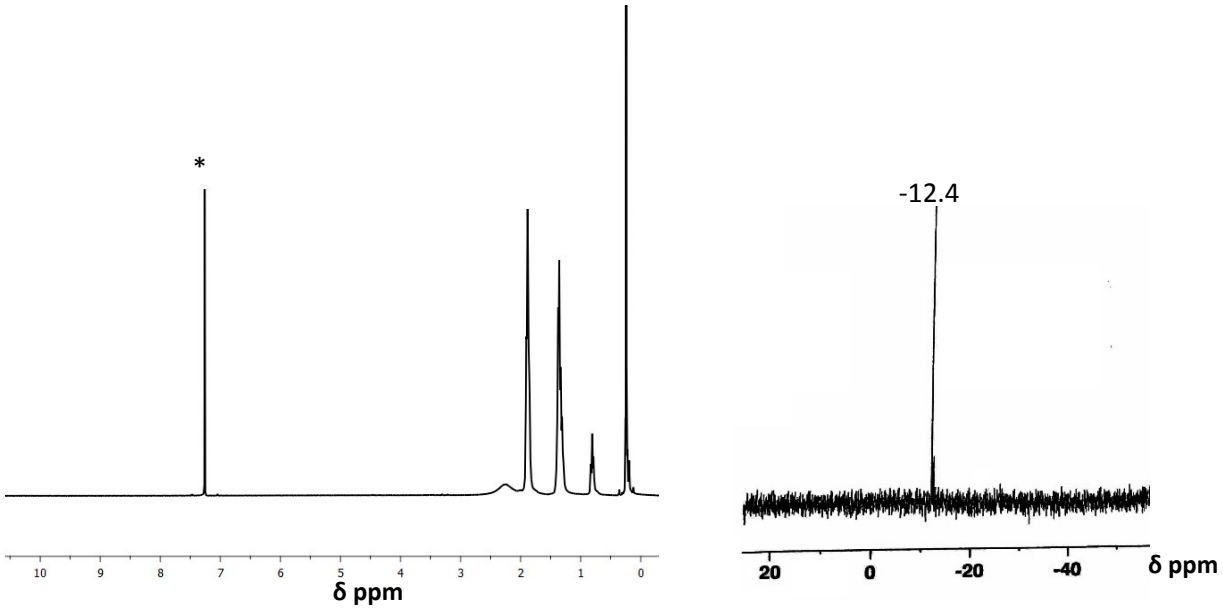
Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2, y+1/2, -z+3/2 #2 x, y-1, z

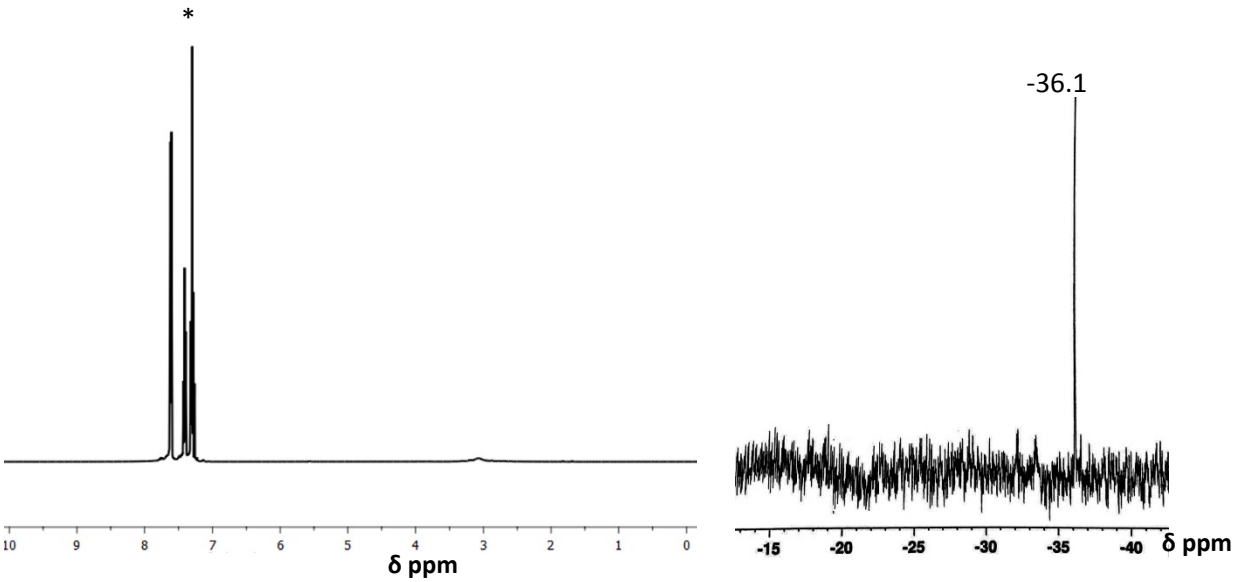
Supplementary figures



^{1}H and ^{29}Si NMR of $(MePhSiOH)_2O$ (**1**). * $CDCl_3$ signal.



^{1}H and ^{29}Si NMR of $[Me(cyclo\text{-}Hex)SiOH]_2O$ (**2**). * $CDCl_3$ signal.



^{1}H and ^{29}Si NMR of $(Ph_2SiOH)_2O$ (**3**). * $CDCl_3$ signal