Supporting Information

for

Hydrogen bonding molecular capsule versus 3D

Network of Tripodal Organopolysilanols

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1. Experimental Procedures and Spectral Data

       All reactions were performed under an argon atmosphere unless otherwise specified. The ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature using the JEOL JNM-ECP 500, JNM-ECS 400 and JNM-ECA 400 spectrometers. The low resolution EI mass spectra were measured on a JEOL JMS-AX505H mass spectrometer and the MALDI-TOF mass spectra were measured on a SHIMAZU AXIMA-CFR mass spectrometer using angiotensin II and Insulin $^\beta$ for accurate mass calibration. The high resolution mass spectra (ESI) were recorded on a JEOL JMS-T100LC mass spectrometer using reserpine for accurate mass calibration. Melting points were determined using a Yanaco MP-S3. HPLC (GPC) purification was performed using a Japan analytical industry LC-908. The commercially available solvents and reagents were purchased from Sigma-Aldrich, Wako, TCI and KANTO. Tetrahydrofuran (THF), Hexane and Benzene were distilled from sodium benzophenone ketyl. Methanol was distilled from magnesium methoxide, and toluene was distilled from lithium aluminum hydride (LAH). Diphenylchlorosilane and diisopropylchlorosilane were synthesized from trichlorosilane and the corresponding Grinard reagent according to the literature methods.[1] 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (**1**) was also prepared according to the reported procedure.[2]

1-1. Synthesis of 1,3,5-tris(dimethylsilyl)methyl-2,4,6-triethylbenzene (**2a**)
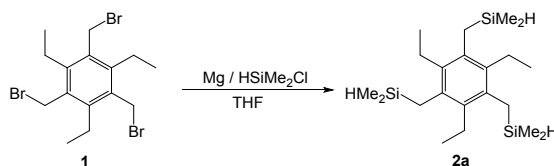
A solution of dimethylchlorosilane (2.60 mL, 23.4 mmol) in anhydrous THF (10 mL) and magnesium (0.559 g, 23.0 mmol) had added to it 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (**1**) (3.00 g, 6.80 mmol) in anhydrous THF (40 mL) dropwise over 1 hour with cooling in an ice-salt bath. The resulting mixture was stirred for 3 hours at room temperature and then quenched with saturated NH$_4$Cl aqueous solution extracted with CHCl$_3$. After the organic layer was dried over magnesium sulfate, the solvent was evaporated. The crude product was purified by silica gel column chromatography with hexane as the eluent and recrystallized with hot methanol to yield 2.43 g of a white solid of **2a** (94.3%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 0.03 (d, J = 3.7 Hz, 18H, SiCH$_3$), 1.13 (t, J = 7.5 Hz, 9H, Ar-CH$_2$-C<u>H$_3$</u>), 2.19 (d, J = 3.7 Hz, 6H, Ar-CH$_2$-Si), 2.52 (q, J = 7.5 Hz, 6H, Ar-<u>CH$_2$</u>-CH$_3$), 4.00 (m, 3H, SiH) ppm.

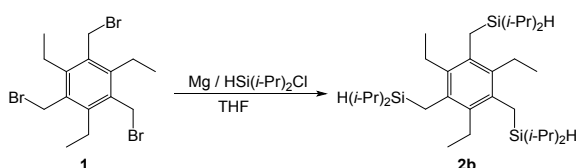^{13}C NMR (125 MHz, CDCl$_3$): δ -3.78 (Si-CH$_3$), 13.8 (CH$_3$), 17.0 (CH$_2$), 24.1 (CH$_2$), 133.3 (C), 134.5 (C) ppm.

^{29}Si NMR (80 MHz, CDCl$_3$): δ -13.2 (SiH) ppm.

LRMS (MALDI-TOF): m/z calcd for C$_{21}$H$_{42}$Si$_3$ [M$^+$] 378, found 378.

IR (KBr): ṽ = 2961 (s), 2927 (m), 2871 (w), 2119 (s, Si-H), 1559 (vw), 1452 (w), 1410 (w), 1251 (m), 1166 (m), 1078 (vw), 886 (s), 858 (m), 835 (m), 780 (w), 758 (w), 710 (w), 665 (w), 627 (w) cm^{-1}.

M.p. 58 ºC.

1-2. Synthesis of 1,3,5-tris(diisopropylsilyl)methyl-2,4,6-triethylbenzene (2b)

The reaction of diisopropylchlorosilane (3.65 mL, 21.4 mmol) and magnesium (0.559 g, 23.0 mmol) in anhydrous THF (10 mL) and 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (**1**) (3.00 g, 6.80 mmol) in anhydrous THF (40 mL) was performed as described previously. The crude product was recrystallized with hot methanol to yield 1.70 g of a white solid of **2b** (45.7%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 0.91 (d, J = 6.3 Hz, 18H, SiCH(C$\underline{H}_3$)$_2$), 0.92-1.00 (m, 6H, SiC$\underline{H}$(CH$_3$)$_2$), 1.03 (d, J = 6.3 Hz, 18H, SiCH(C$\underline{H}_3$)$_2$), 1.39 (t, J = 7.5 Hz, 9H, Ar-CH$_2$-C$\underline{H}_3$), 2.14 (d, J = 4.1 Hz, 6H, Ar-CH$_2$-Si), 2.60 (q, J = 7.5 Hz, 6H, Ar-C$\underline{H}_2$-CH$_3$), 3.58 (m, 3H, Si-H) ppm.

^{13}C NMR (125 MHz, CDCl$_3$): δ 10.9 (CH$_3$), 12.3 (CH), 13.6 (CH$_2$), 19.0 (CH$_3$), 19.2 (CH$_3$), 24.1 (CH$_2$), 133.6 (C), 135.1 (C) ppm.
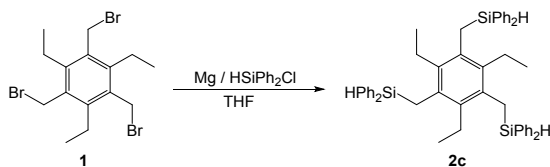
^{29}Si NMR (80 MHz, CDCl$_3$): δ 5.9 (SiH) ppm.

HRMS (ESI): m/z calcd for C$_{33}$H$_{67}$Si$_3$ [M+H$^+$] 547.4551, found 547.4513; calcd for C$_{33}$H$_{66}$KSi$_3$ [M+K$^+$] 585.4109, found 585.4154.

IR (KBr): ṽ = 2938 (s), 2864 (s), 2095 (s, Si-H), 1558 (vw), 1463 (m), 1413 (w), 1380 (w), 1240 (w), 1170 (m), 1074 (w), 1004 (m), 877 (s), 795 (s), 725 (m), 691 (m), 647 (w) cm^{-1}.

M.p. 65 ºC.

1-3. Synthesis of 1,3,5-tris(diphenylsilyl)methyl-2,4,6-trietylbenzene (2c)

The reaction of diphenylchlorosilane (4.93 mL, 25.2 mmol) and magnesium (0.5590 g, 23.0 mmol) in anhydrous THF (10 mL) and 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (**1**) (3.00 g, 6.80 mmol) in anhydrous THF (40 mL) was performed as described above. The crude product was recrystallized with hexane to yield 3.50 g of a white solid of **2c** (68.5%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 1.02 (t, J = 7.4 Hz, 9H, Ar-CH$_2$-<u>CH$_3$</u>), 2.20 (q, J = 7.4 Hz, 6H, Ar-<u>CH$_2$</u>-CH$_3$), 2.58 (d, J = 3.6 Hz, 6H, Ar-CH$_2$-Si), 4.73 (t, J = 3.6 Hz, 3H, SiH), 7.34 (t, J = 7.1 Hz, 12H, SiPh (*m*)), 7.39 (t, J = 7.3 Hz, 6H, SiPh (*p*)), 7.48 (d, J = 6.7 Hz, 12H, SiPh (*o*)) ppm.

^{13}C NMR (125 MHz, CDCl$_3$): δ 13.4 (CH$_3$), 16.1 (CH$_2$), 24.1 (CH$_2$), 128.0 (*m*-CH), 129.6 (*p*-CH), 132.5 (C), 134.4 (*ipso*-C), 135.2 (*o*-CH), 136.1 (C) ppm.

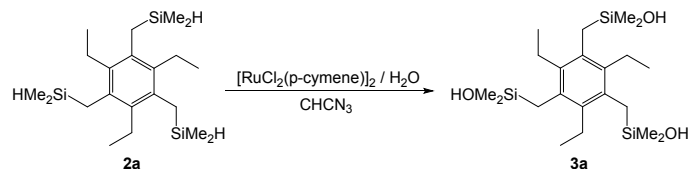^{29}Si NMR (80 MHz, CDCl$_3$): δ -16.1 (SiH) ppm.

HRMS (ESI): m/z calcd for C$_{51}$H$_{54}$NaSi$_3$ [M+Na$^+$] 789.3380, found 789.3294.

IR (KBr): ṽ = 3067 (w), 3047 (w), 2967 (m), 2925 (m), 2871 (w), 2128 (m, Si-H), 1559 (vw), 1484 (w), 1427 (m), 1162 (m), 1113 (m), 872 (s), 800 (s), 725 (m), 701 (s), 610 (vw), 541 (vw), 474 (m), 430 (w) cm^{-1}.

M.p. 119 ℃.

1-4. Synthesis of 1,3,5-tris(dimethylhydroxysilyl)methyl-2,4,6-triethylbenzene (**3a**)

According to the reported procedure,[3] the mixture of 1,3,5-tris(dimethylsilyl)methyl-2,4,6-triethylbenzene (**2a**) (300 mg, 0.792 mmol), RuCl$_2$(*p*-cymene)]$_2$ (15.0 mg, 24.5 μmol) and H$_2$O (0.214 mL, 11.9 mmol) in acetonitrile (5 mL) was stirred for 2 hours at 80 ℃. The reaction mixture was purified by silica gel flush column chromatography with ethyl acetate:hexane (1:4) to yield 293 mg of a white solid of **3a** (86.6%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 0.13 (s, 18H, SiMe), 1.09 (t, J = 7.4 Hz, 9H, Ar-CH$_2$-<u>CH$_3$</u>), 1.98 (br, 3H, SiOH), 2.26 (s, 6H, Ar-CH$_2$-Si), 2.58 (q, J = 7.4 Hz, 6H, Ar-<u>CH$_2$</u>-CH$_3$), 4.41 (SiOH, Acetone-d_6) ppm.

^{13}C NMR (125 MHz, CDCl$_3$): δ 0.99 (Si-CH$_3$), 13.7 (CH$_3$), 21.1 (CH$_2$), 24.2 (CH$_2$), 132.7 (C), 135.0 (C) ppm.

^{29}Si NMR (80 MHz, Acetone-d_6): δ 12.2 (SiOH) ppm.

HRMS (ESI): m/z calcd for C$_{21}$H$_{42}$NaO$_3$Si$_3$ [M+Na$^+$] 449.2339, found 449.2338.

IR (KBr): ṽ = 3171 (brs, SiO-H), 2964 (s), 2927 (s), 2873 (m), 1560 (w), 1412 (m), 1254 (s), 1161

(m), 1117 (m), 1078 (m), 875 (s), 770 (m), 730 (w), 642 (w) cm^{-1}.

M.p. 186 ºC.

1-5. Synthesis of 1,3,5-tris(diisopropylhydroxysilyl)methyl-2,4,6-triethylbenzene (3b)
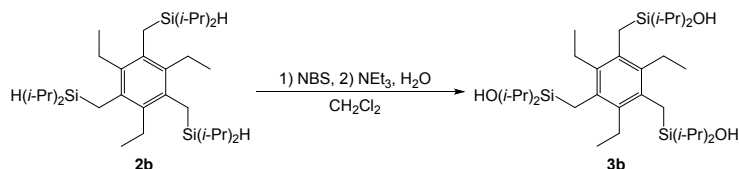
The mixture of 1,3,5-tris(diisopropylsilyl)methyl-2,4,6-triethylbenzene (**2b**) (220 mg, 0.403 mmol), N-bromosuccinimide (NBS) (237 mg, 1.33 mmol) in CH$_2$Cl$_2$ (10 mL) was stirred for 2 hours at room temperature. Then triethylamine (0.300 mL, 2.15 mmol) and H$_2$O (32.6 μL, 1.81 mmol) were added and strried for 2 additional hours. The solvent remained in vacuo. The resulting mixture was extracted with hexane (15 mL) and filtered. The filterate was evaporated to yield a yellow solid. The crude product was recrystallized with benzene to yield 235 mg of a white solid of **3b** (98.0%).

^{1}H NMR (500 MHz, CDCl$_3$): δ 0.94 (d, J = 5.6 Hz, 18H, SiCH(C$\underline{H_3}$)$_2$), 0.97-1.01 (m, 6H, SiC$\underline{H}$(CH$_3$)$_2$), 1.04 (d, J = 6.3 Hz, 18H, Si(CH(C$\underline{H_3}$)$_2$), 1.10 (t, J = 7.4 Hz, 9H, Ar-CH$_2$-C$\underline{H_3}$), 1.66 (br, SiOH), 2.21 (s, 6H, Ph-CH$_2$-Si), 2.65 (q, J = 7.4 Hz, 6H, Ph-C$\underline{H_2}$-CH$_3$), 4.13 (SiOH, Acetone-d_6) ppm.

^{13}C NMR (125 MHz, CDCl$_3$): δ 13.5 (CH$_3$), 13.6 (CH), 15.4 (CH$_2$), 17.4 (CH$_3$)×2, 24.2 (CH$_2$), 132.9 (C), 135.6 (C) ppm.

^{29}Si NMR (80 MHz, CDCl$_3$): δ 13.1 (SiOH) ppm.

HRMS (ESI): m/z calcd for C$_{33}$H$_{67}$O$_3$Si$_3$ [M+H$^+$] 595.4398, found 595.4430; calcd for C$_{33}$H$_{66}$NaO$_3$Si$_3$ [M+Na$^+$] 617.4217, found 617.4193; calcd for C$_{33}$H$_{66}$KO$_3$Si$_3$ [M+K$^+$] 633.3957, found 633.3938.

IR (KBr): ṽ = 3453 (brm, SiO-H), 2943 (s), 2867 (m), 1558 (vw), 1464 (m), 1411 (w), 1377 (vw), 1243 (w), 1151 (m), 1068 (w), 990 (w), 880 (m), 847 (m), 810 (s), 727 (m), 662 (m), 456 (w) cm^{-1}.

M.p. 130 ºC.

1-6. Synthesis of 1,3,5-tris(diphenylhydroxysilyl)methyl-2,4,6-triethylbenzene (3c)
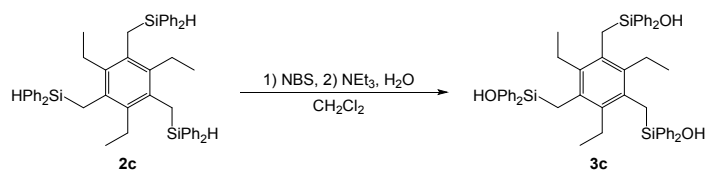
The reaction of 1,3,5-tris(diphenylsilyl)methyl-2,4,6-triethylbenzene (**2c**) (303 mg, 0.403 mmol) and

N-bromosuccinimide (NBS) (237 mg, 1.33 mmol) in CH_2Cl_2 (8 mL) was performed as described previously. The solvent was removed in vacuo. The resulting mixture was extended with ethyl acetate, then washed with water three times. The organic layer was dried with anhydrous magnesium sulfate, and then the solvent was evaporated. The resulting oily solid was extracted with diethylether and the solvent was removed in vacuo to yield 278 mg of a yellow solid of **3c** (86.4%).

^{1}H NMR (500 MHz, CDCl$_3$) : δ 0.95 (t, J = 7.4 Hz, 9H, Ar-CH$_2$-<u>CH$_3$</u>), 2.20 (q, J = 7.4 Hz, 6H, Ar-<u>CH$_2$</u>-CH$_3$), 2.66 (s, 6H, Ar-CH$_2$-Si), 3.26 (br, SiOH), 7.30 (t, J = 7.3 Hz, 12H, SiPh (*m*)), 7.37 (t, J = 7.3 Hz, 6H, SiPh (*p*)), 7.51 (d, J = 6.7 Hz, 12H, SiPh (*o*)), 4.67 (SiOH, Acetone-d_6) ppm.

^{13}C NMR (125 MHz, CDCl$_3$): δ 13.3 (CH$_3$), 18.9 (CH$_2$), 24.3 (CH$_2$), 127.9 (*m*-CH), 129.8 (*p*-CH), 132.1 (C), 134.0 (*o*-CH), 136.6 (C), 137.0 (*ipso*-C) ppm.

^{29}Si NMR (80 MHz, CDCl$_3$): δ -10.8 (SiOH) ppm.

HRMS (ESI): m/z calcd for $C_{51}H_{54}NaO_3Si_3$ [M+Na$^+$] 821.3278, found 821.3294.

IR (KBr): $\tilde{v}$ = 3401 (brm, SiO-H), 3068 (m), 3048 (m), 2960 (m), 2925 (m), 2870 (w), 1589 (w), 1485 (w), 1426 (m), 1167 (m), 1114 (s), 1075 (m), 853 (s), 729 (s), 699 (s), 630 (m), 557 (m), 479 (m), 450 (w) cm^{-1}.

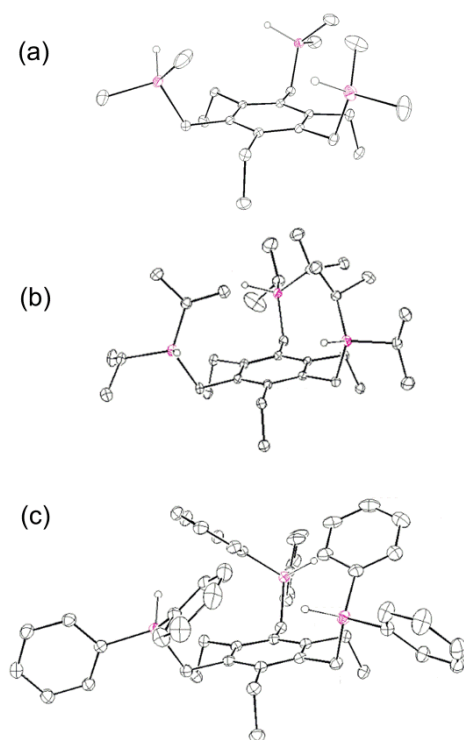M.p. 104 ºC.

2. Crystallographic Data

Figure S1 X-ray molecular structures of (a) **2a**, (b) **2b** and (c) **2c·0.5 hexane**. The thermal ellipsoids were scaled to 30% probability. One of the two independent molecules in (b) and a solvent molecule in (c) were omitted for clarity.

Table S1. Crystal data and data collection parameters of **2a**, **2b** and **2c**·0.5hexane

	2a	2b	2c·0.5hexane
Empirical formula	$C_{21}H_{42}Si_3$	$C_{33}H_{66}Si_3$	$C_{54}H_{61}Si_3$
Formula weight	378.82	547.13	794.3
Temperature (K)	120 (2)	120 (2)	120 (2)
Wavelength (Å)	0.7103	0.7103	0.7103
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P21/n	P21/c	P-1
a (Å)	8.5296 (13)	27.388 (3)	13.138 (3)
b (Å)	22.691 (3)	9.4848 (9)	14.093 (3)
c (Å)	13.414 (2)	27.972 (3)	14.255 (3)
α (deg)	90.00	90.00	70.500 (8)
β (deg)	105.992 (2)	93.236 (2)	84.236 (10)
γ (deg)	90.00	90.00	70.660 (8)
Volume (Å^3)	2495.7 (7)	7254.9 (13)	2347.5 (8)
Z	4	4	2
Density (calculated) (g/cm^3)	1.008	1.002	1.124

Absorption coefficient (mm^{-1})	0.192	0.149	0.135
F (000)	840	2448	854
Crystal size (mm)	0.36×0.25×0.12	0.20×0.15×0.10	0.30×0.30×0.16
Crystal color and habit	Colorless, Prism	Colorless, Platelet	Colorless, Block
Solvent system	MeOH	MeOH	Hexane
Diffractometer	Rigaku Mercury CCD	Rigaku Mercury CCD	Rigaku Mercury CCD
Theta range for Data collection (deg)	3.12 to 27.48	3.03 to 27.48	3.10 to 27.45
Indexes	-11 ≦ h ≦ 10	-35 ≦ h ≦ 32	-17 ≦ h ≦ 17
	-29 ≦ k ≦ 26	-11 ≦ k ≦ 11	-18 ≦ k ≦ 18
	-17 ≦ l ≦ 17	-36 ≦ l ≦ 36	-18 ≦ l ≦ 18
Reflections collected	19840	57106	37424
Independent reflections (Rint)	5674 (0.1054)	16329 (0.0480)	10655 (0.0859)
Completeness to theta (%)	99.2 %	98.1 %	99.3 %
Absorption correction	None	None	None
Solution method	SHELXS-97 (Sheldrick, 2008)	SHELXS-97 (Sheldrick, 2008)	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2 (SHELXS-97)	Full-matrix least-squares on F^2 (SHELXS-97)	Full-matrix least-squares on F^2 (SHELXS-97)
Data / restraints / parameters	5674 / 0 / 238	16329 / 1 / 703	10655 / 0 /530
Goodness of Fit Indicator	1.063	1.072	1.079
Final R indices [I>2sigma(I)]	R1 = 0.0523, wR2 = 0.1258	R1 = 0.0604, wR2 = 0.1535	R1 = 0.0605, wR2 = 0.1359
R indices (all data)	R1 = 0.0601, wR2 = 0.1325	R1 = 0.0780, wR2 = 0.1677	R1 = 0.0716, wR2 = 0.1435
Largest diff peak and hole (eÅ^{-3})	0.757 and -0.449	1.282 and -0.635	0.411 and -0.276

Table S2. Crystal data and data collection parameters of **3a, 3b** and **3c·H$_2$O**

	3a	**3b**	**3c·H$_2$O**
Empirical formula	C$_{21}$H$_{42}$O$_3$Si$_3$	C$_{33}$H$_{66}$O$_3$Si$_3$	C$_{51}$H$_{56}$O$_4$Si$_3$
Formula weight	426.82	595.13	817.23
Temperature (K)	120 (2)	120 (2)	120 (2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Cubic	Monoclinic	Orthorhombic
Space group	P213	P21/c	Pcan

a (Å)	17.538 (3)	17.093 (4)	19.2489 (17)
b (Å)	17.538 (3)	12.364 (3)	19.7912 (18)
c (Å)	17.538 (3)	19.610 (5)	23.545 (2)
α (deg)	90.00	90.00	90.00
β (deg)	90.00	112.776 (3)	90.00
γ (deg)	90.00	90.00	90.00
Volume (Å^3)	5394.4 (13)	V = 3821.4 (16)	8969.5 (14)
Z	8	4	8
Density (calculated) (g/cm^3)	1.051	1.034	1.210
Absorption coefficient (mm^{-1})	0.192	0.152	0.150
F (000)	1872	1320	3488
Crystal size (mm)	0.27×0.27×0.25	0.36 × 0.33 × 0.30	0.34×0.23×0.18
Crystal color and habit	Colorless, Prism	Colorless, Block	Colorless, Prism
Solvent system	Et$_2$O / Toluene	Benzene	Et$_2$O / Hexane
Diffractometer	Rigaku Mercury CCD	Rigaku Mercury CCD	Rigaku Mercury CCD
Theta range for Data collection (deg)	3.49 to 27.46	3.00 to 27.47	3.08 to 27.49
Indexes	$-22 \leqq h \leqq 21$	$-17 \leqq h \leqq 22$	$-24 \leqq h \leqq 24$
	$-22 \leqq k \leqq 21$	$-16 \leqq k \leqq 16$	$-25 \leqq k \leqq 20$
	$-22 \leqq l \leqq 22$	$-25 \leqq l \leqq 23$	$-30 \leqq l \leqq 20$
Reflections collected	43825	29167	70063
Independent reflections (Rint)	4127 (0.0758)	8565 (0.1250)	10228 (0.0830)
Completeness to theta (%)	99.5 %	98.1	99.5 %
Absorption correction	None	None	None
Solution method	SHELXS-97	SHELXS-97	SHELXS-97
	(Sheldrick, 2008)	(Sheldrick, 2008)	(Sheldrick, 2008)
Refinement method	Full-matrix	Full-matrix	Full-matrix
	least-squares on F^2	least-squares on F^2	least-squares on F^2
	(SHELXS-97)	(SHELXS-97)	(SHELXS-97)
Data / restraints / parameters	4127 / 0 / 169	8565 / 0 / 367	10228 / 12 / 534
Goodness of Fit Indicator	1.124	1.048	1.120
Final R indices [I>2sigma(I)]	R1 = 0.0513,	R_1 = 0.0549,	R1 = 0.0547,
	wR2 = 0.1203	wR_2 = 0.1482	wR2 = 0.1235
R indices (all data)	R1 = 0.0534,	R_1 = 0.0625,	R1 = 0.0649,
	wR2 = 0.1219	wR_2 = 0.1568	wR2 = 0.1290
Largest diff peak and hole (eÅ^{-3})	0.300 and -0.285	0.647 and -0.394	0.326 d -0.370

3. ^{1}H NMR titrations and Job's plots

3-1. ^{1}H NMR dilution experiments

The NMR experiments are only suitable for determining equilibrium constants in relatively simple systems. If there are more than two or three equilibrium constants, it is unlikely that the NMR experiments will give reliable association constants. In such circumstances, the uncertainties will be unacceptably large.

For incompletely condensed polyhedral silsesquioxane (POSS)-triol there existed a dynamic equilibrium between the single molecules and hydrogen-bonded dimers.

With decreasing concentrations of POSS-triol, the POSS-triol dimer gradually dissociated to form a single POSS-triol, which represented the SiOH single shift to the upfield.[4]

The ^{1}H NMR dilution experiments for **3a, 3b** and **3c** were investigated at three different concentrations, ca 5 mM, 2.5 mM and 1.25 mM for each compound. Stock solutions of **3a, 3b** and **3c** were prepared as follows. ca 1.2 mmol of **3a, 3b** and **3c** were placed in 2 mL volumetric flasks, which were then dissolved in Acetone-d_6. By adding one drop of tetramethylsilane (TMS) as the internal standard, these solutions were brought up to 2 mL total volume.

From the stock solutions, ca 400 μL of each solution of **3a, 3b** and **3c** was placed into 5 mL volumetric flasks using a microsyringe. The resulting solutions were diluted with Acetone-d_6 up to 5 mL, resulting in ca 5 mM solutions. Using a microsyringe, two-fold dilutions of the stock solution was placed in a NMR tube yielding ca 2.5 mM solution, while four-fold dilutions yielded ca 1.25 mM solution.
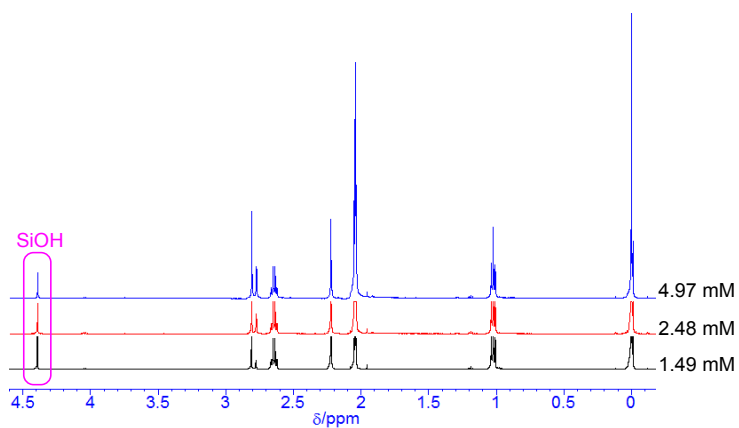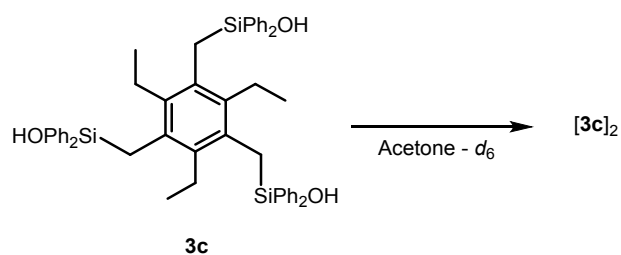

3a

3b
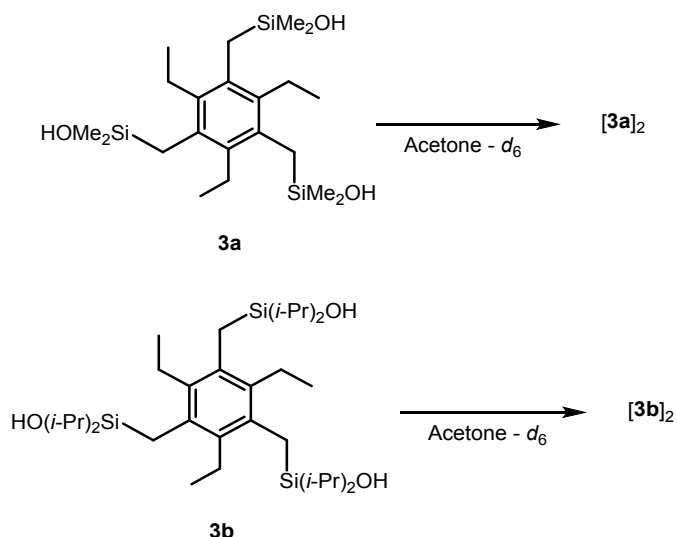
Figure S2 ¹H NMR spectrum of **3a** (500 MHz, Acetone-d_6).
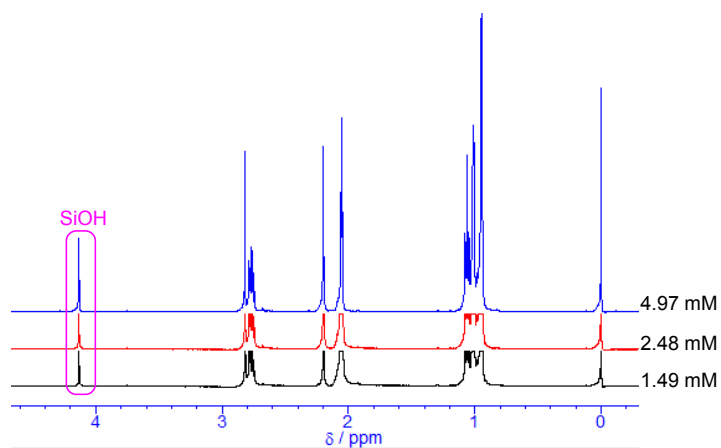
Top; 4.97 mM, middle; 2.48 mM, bottom; 1.49 mM

Figure S3 ¹H NMR spectrum of **3b** (500 MHz, Acetone-d_6).
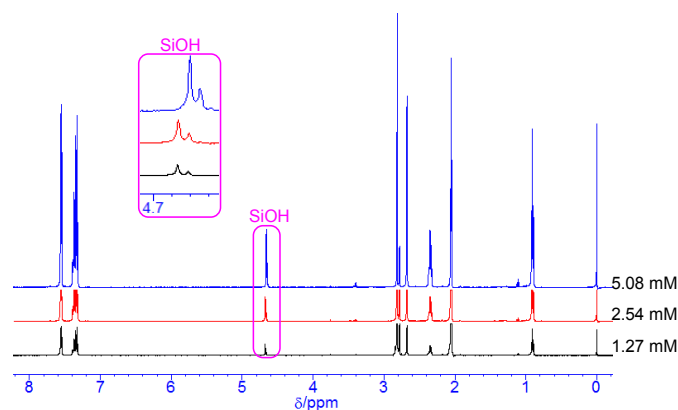
Top; 4.97 mM, middle; 2.48 mM, bottom; 1.49 mM

Figure S4 ^{1}H NMR spectrum of **3c** (500 MHz, Acetone-d_6).

Top; 5.08 mM, middle; 2.54 mM, bottom; 1.27 mM

The dilutions of **3a**, **3b** and **3c** caused virtually no shift ($\Delta\delta \leqq 0.002$ ppm for **3a**, 0.0018 ppm for **3b**, and 0.010 ppm for **3c**) indicating that intermolecular dimerization is negligible, at least in our experimental condition range in Acetone-d_6 (see Figure S2, S3, and S4). Therefore, NMR titrations and Job's plots were carried out in less than 5 mM solution of **3a**, **3b** and **3c** as follows.

3-2. ^{1}H NMR titrations and Job's plots

  5 mM stock solutions of **3a-c** ([H]) and anion ([G]) were prepared separately after a two-fold dilution. For the ^{1}H NMR titrations, 5 mM stock solutions of **3a, 3b** and **3c** and 100-400 mM stock solutions of a one-fold dilution were used. For Job's plots[5] both the 5 mM stock solutions were used. When succesive studies of ^{1}H NMR titrations and Job's plots were not performed at once, a different stock solution was prepared for each experiment.

  The ^{1}H-NMR titrations were carried out by adding aliquots of the anion as their n-butylammonium salts to a NMR tube using a microsyringe. After each addition, spectra were recorded and SiOH resonance was monitored for calculating the associaton constants by the WinEQNMR[6]. Anion from 7.0 to 66.5 equivalents were added.

  In order to determine the association stoichiometry, the NMR samples were prepared with different proportions of **3a**, **3b** and **3c** and anion solution so that the total concentration ([H] + [G]) for each sample was 5 mM. TMS was used as an external reference. Each NMR sample was run at room temperature. The resonance of SiOH was shifted downfield as the mole fraction of the anion was decreased. The Job's plots[5] plotting $\Delta\delta$ [H]/([H] + [G]) with mole fraction [H]/([H] + [G]), indicated an 1 : 1 stoichiometry.

For the titrations and Job's plot of 3a and the chloride anion
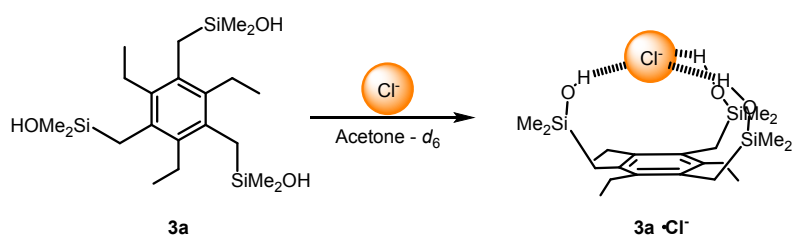
3a (47.7 mg, 0.112 mmol) was placed in a 2 mL volumetric flask, and was then dissolved in Acetone-d_6. By adding one drop of TMS as the internal standard, the solution came to 2 mL total volume. From the stock solution, 450 μL of solution **3a** was placed in a 5 mL volumetric flask using a microsyringe. The resulting solution was diluted with Acetone-d_6 up to 5 mL, yielding a 5.03 mM host solution.

Tetrabutylammoniumchloride (TBACl) (166 mg, 0.598 mmol) was placed in a 2 mL volumetric flask, and was then dissolved in Acetone-d_6 up to 2 mL total volume, yielding a 299 mM guest solution.

After 500 μL of the host solution (5.03 mM) was added to a NMR tube, the ^{1}H NMR spectra was recorded. The host solution was titrated by adding incremental amounts of the 299 mM guest solution shown in Table S3. The gradual downshift of the SiOH resonance was monitored as shown in Figure S5. The association constant K_a = 35.2 M^{-1} was obtained by titration curve fitting using the WinEQNMR program shown in Figure S6.

As shown in Table S4, the NMR samples with different proportions of **3a** ([H]) and chloride anions ([G]) were prepared for the total concentration of ([H]+[G]) to be 5 mM. The ^{1}H NMR spectra were recorded and the change in ^{1}H NMR SiOH resonances with the mole fraction of [G] is listed in Table S4. The Job's plot is shown in Figure S7. The maximum appears at a mole fraction of 0.5 indicating an 1 : 1 stoichiometry.

Table S3 Added amounts of TBACl to **3a** and chemical shift changes of SiOH resonance

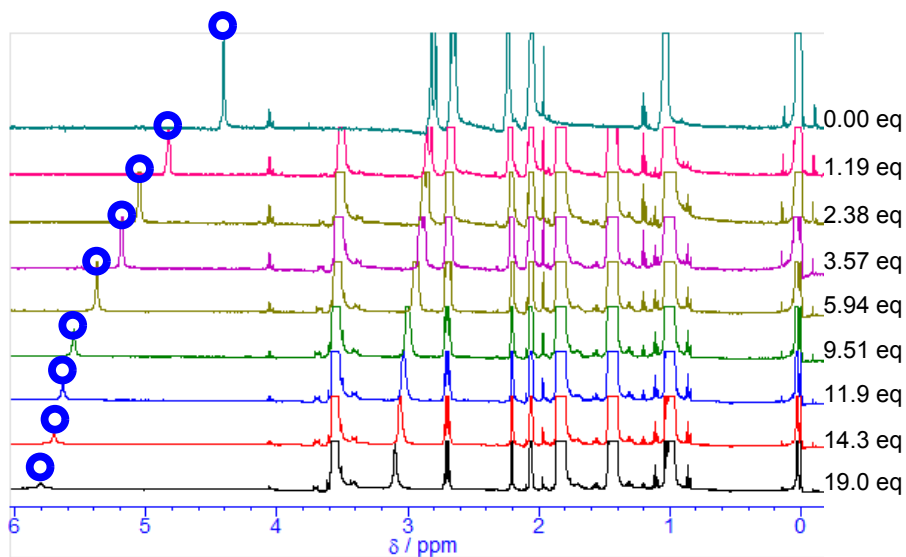| TOTAL Guest (μL)	eq	δ (ppm)	$\Delta\delta$ (ppm)
0	0	4.4058	0.0000
10	1.19	4.8281	0.4223
20	2.38	5.0489	0.6431
30	3.57	5.1836	0.7778
50	5.94	5.3751	0.9693
80	9.51	5.5528	1.1470
100	11.9	5.6362	1.2304
120	14.3	5.7030	1.2972
160	19.0	5.8047	1.3989

Figure S5 ¹H NMR titration spectra of **3a** with TBACl.

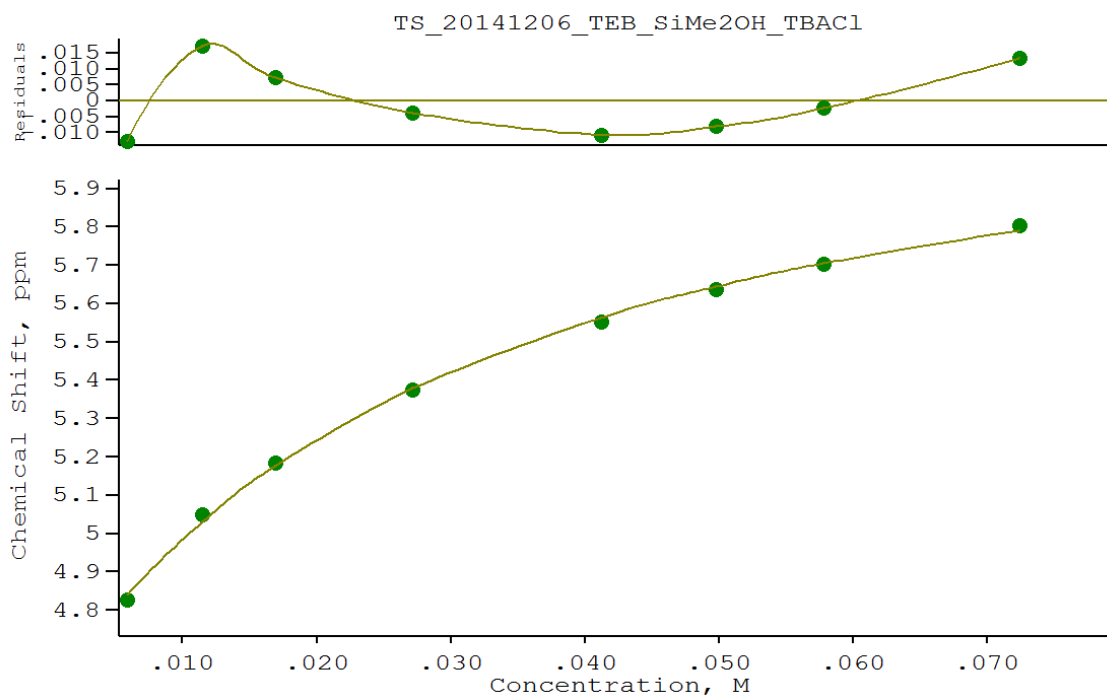The SiOH chemical shifts are marked with circles.

Figure S6 Determination of K_a using SiOH resonance by WinEQNMR for **3a** and TBACl. The concentration of TBACl is given on the X-axis.

Calculation for the titration of 3a with TBACl.

Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes

Program run at 16:40:58   on 03/19/2015

TS_20141206_TEB_SiMe2OH_TBACl

Equilibrium constants are floating point numbers

NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
1	1	3.51744E+01	1.000E+00	3.747E+00	6.366E+01	K11
2	1	4.58115E+00	4.410E-02	2.722E-02	1.029E+01	SHIFT_H
3	1	6.28407E+00	5.800E-02	5.335E-02	3.332E+01	SHIFT_HG

0RMS ERROR = 1.34E-02   MAX ERROR = 1.73E-02 AT OBS.NO.   2

RESIDUALS SQUARED = 8.96E-04

RFACTOR =   0.1959 PERCENT

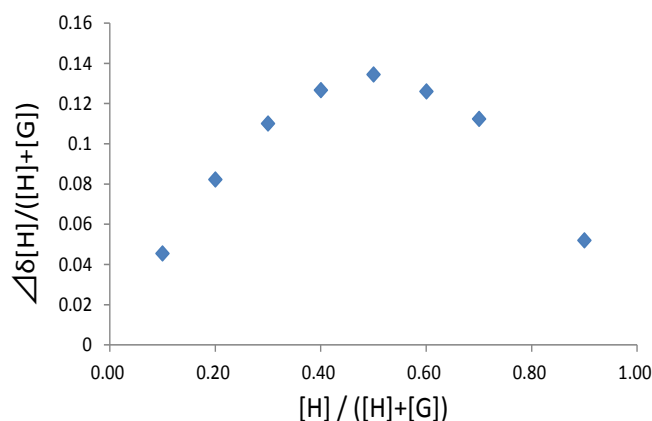| NO.	A	EXPT. DEL	CALC. DEL	RESIDUAL	% DEV	WEIGHT	Cl-receptor	pH
1	1	4.8281E+00	4.8409E+00	-1.2835E-02	-2.6583E-01	1.0000E+00	5.8600E-03	
							4.9300E-03	0.0000E+00
2	1	5.0489E+00	5.0316E+00	1.7269E-02	3.4204E-01	1.0000E+00	1.1490E-02	
							4.8400E-03	0.0000E+00
3	1	5.1836E+00	5.1763E+00	7.3233E-03	1.4128E-01	1.0000E+00	1.6910E-02	
							4.7400E-03	0.0000E+00
4	1	5.3751E+00	5.3789E+00	-3.8362E-03	-7.1369E-02	1.0000E+00	2.7170E-02	
							4.5700E-03	0.0000E+00
5	1	5.5528E+00	5.5635E+00	-1.0730E-02	-1.9323E-01	1.0000E+00	4.1220E-02	
							4.3400E-03	0.0000E+00
6	1	5.6362E+00	5.6443E+00	-8.1449E-03	-1.4451E-01	1.0000E+00	4.9800E-02	
							4.1900E-03	0.0000E+00
7	1	5.7030E+00	5.7054E+00	-2.3613E-03	-4.1404E-02	1.0000E+00	5.7840E-02	
							4.0600E-03	0.0000E+00
8	1	5.8047E+00	5.7914E+00	1.3316E-02	2.2939E-01	1.0000E+00	7.2440E-02	
							3.8100E-03	0.0000E+00

TOLERANCE ON SUM OF SQUARES   0.0100

TOLERANCE ON EIGEN VALUES   0.0001

CONVERGANCE AFTER   10   ITERATIONS

Table S4 Data for Job's plot of **3a** with TBACl

Host (μL)	Guest (μL)	[H]/([H]+[G])	δ (ppm)	$\Delta\delta$ [H]/([H]+[G])
50	450	0.1	4.8565	0.0454
100	400	0.2	4.8135	0.0822
150	350	0.3	4.7695	0.1101
200	300	0.4	4.7191	0.1266
250	250	0.5	4.6715	0.1344
300	200	0.6	4.6129	0.1260
350	150	0.7	4.5633	0.1123
450	50	0.9	4.4607	0.0519
500	0	1	4.4030	0.0000

Figure S7 Job's plot of **3a** with TBACl

For the titrations and Job's plot of 3a and the bromide anion
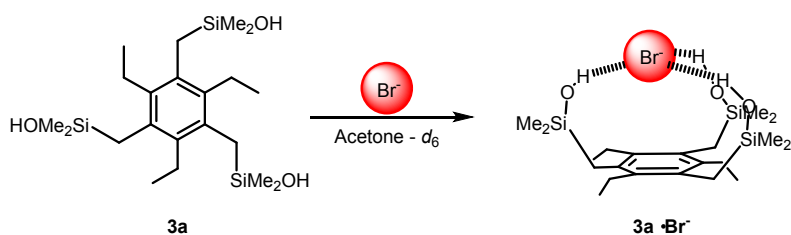
3a (58.1 mg, 0.136 mmol) was placed in a 2 mL volumetric flask, and was then dissolved in Acetone-d_6. By adding a drop of TMS as the internal standard, the solution came to 2 mL total volume.

From the stock solution, 370 μL of solution **3a** was placed in a 5 mL volumetric flask using a microsyringe. The resulting host solution was diluted with Acetone-d_6 up to 5 mL, yielding a 5.00 mM host solution.

Tetrabutylammonium Bromide (TBABr) (300 mg, 0.930 mmol) was placed in a 2 mL volumetric flask, and was then dissolved in Acetone-d_6 up to 2 mL, yielding a 465 mM guest solution.

From the resulting guest solution, 54.0 μL was placed in a 5 mL volumetric flask using a microsyringe, and was then dissolved in Acetone-d_6 up to 5 mL, yielding 5.00 mM of guest solution.

After 500 μL of the host solution (5.00 mM) was added to a NMR tube,the ^{1}H NMR spectra was recorded. The host solution was titrated by adding an incremental amount of the 465 mM guest solution as shown in Table S5. The gradual downshift of the SiOH resonance was monitored as shown in Figure S8. The association constant K_a = 6.94 was obtained by titration curve fitting using the WinEQNMR program shown in Figure S9.

As shown in Table S6, the NMR samples with different proportions of **3a** ([H])and the bromide anion ([G]) were prepared for a total concentration of ([H]+[G]) to be 5 mM. The ^{1}H NMR spectra were recorded and the change in the ^{1}H NMR SiOH resonances with a mole fraction of [G] is listed in Table S6. The Job's plot is shown in Figure S10. The maximum appears at a mole fraction of 0.5 indicating an 1 : 1 stoichiometry.

Table S5 Added amounts of TBABr to **3a** and chemical shift changes of SiOH resonance

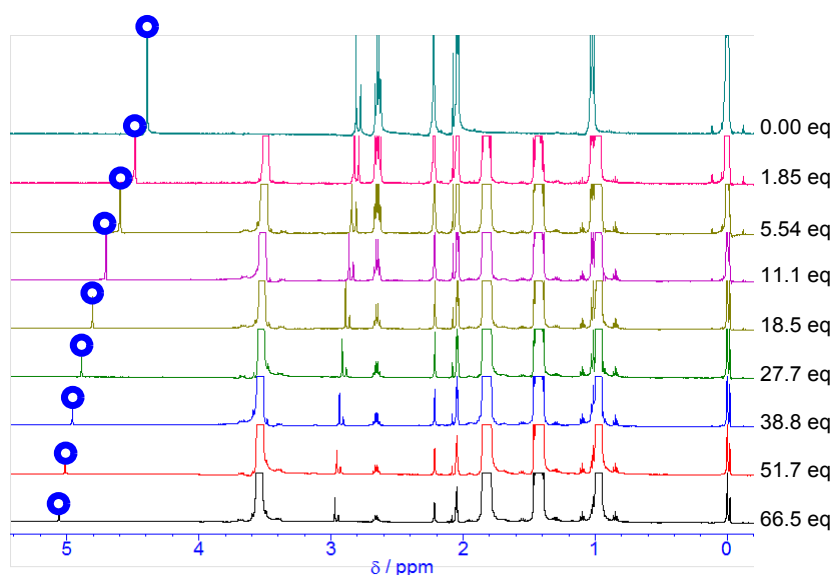| TOTAL Guest (μL)	eq	δ (ppm)	Δδ (ppm)
0	0	4.4058	0.0000
10	1.19	4.8281	0.4223
20	2.38	5.0489	0.6431
30	3.57	5.1836	0.7778
50	5.94	5.3751	0.9693
80	9.51	5.5528	1.1470
100	11.9	5.6362	1.2304
120	14.3	5.7030	1.2972
160	19.0	5.8047	1.3989

Figure S8 ^{1}H NMR titration spectra of **3a** with TBABr.
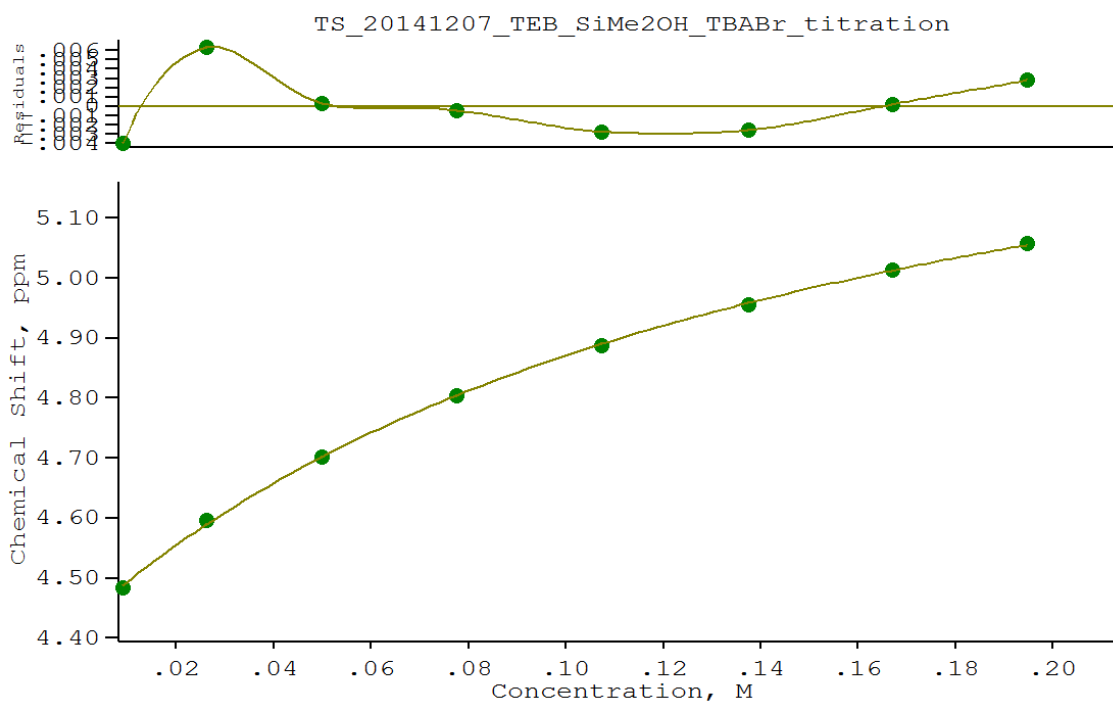
The SiOH chemical shifts are marked with circles.

Figure S9 Determination of K_a using SiOH resonance by WinEQNMR for **3a** and TBABr. The concentration of TBABr is given on the X-axis.

Calculation for the titration of 3a with TBABr

Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes

Program run at 16:42:34   on 03/19/2015

  TS_20141207_TEB_SiMe2OH_TBABr_titration

  Equilibrium constants are floating point numbers

NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
1	1	6.93826E+00	5.000E-02	3.684E-01	7.587E+01	K11
2	1	4.42307E+00	4.400E-02	5.120E-03	6.035E+00	SHIFT_H
3	1	5.52666E+00	5.100E-02	2.581E-02	5.279E+01	SHIFT_HG

0RMS ERROR = 3.95E-03   MAX ERROR = 6.32E-03 AT OBS.NO.   2

  RESIDUALS SQUARED = 7.81E-05

  RFACTOR =   0.0649 PERCENT

NO. A	EXPT. DEL	CALC. DEL	RESIDUAL	% DEV	WEIGHT	Cl-TBABr
						pH
1 1	4.4832E+00	4.4872E+00	-4.0088E-03	-8.9418E-02	1.0000E+00	9.1200E-03
4.9400E-03	0.0000E+00					
2 1	4.5963E+00	4.5900E+00	6.3171E-03	1.3744E-01	1.0000E+00	2.6330E-02
4.7500E-03	0.0000E+00					
3 1	4.7026E+00	4.7022E+00	3.5524E-04	7.5542E-03	1.0000E+00	4.9840E-02
4.5000E-03	0.0000E+00					
4 1	4.8043E+00	4.8047E+00	-4.1866E-04	-8.7143E-03	1.0000E+00	7.7520E-02
4.2000E-03	0.0000E+00					
5 1	4.8877E+00	4.8904E+00	-2.7156E-03	-5.5560E-02	1.0000E+00	1.0734E-01
3.8700E-03	0.0000E+00					
6 1	4.9564E+00	4.9589E+00	-2.5415E-03	-5.1278E-02	1.0000E+00	1.3757E-01
3.5500E-03	0.0000E+00					
7 1	5.0132E+00	5.0130E+00	2.1124E-04	4.2137E-03	1.0000E+00	1.6697E-01
3.2300E-03	0.0000E+00					
8 1	5.0581E+00	5.0553E+00	2.8100E-03	5.5554E-02	1.0000E+00	1.9471E-01
2.9300E-03	0.0000E+00					

TOLERANCE ON SUM OF SQUARES   0.0100

TOLERANCE ON EIGEN VALUES   0.0001

CONVERGANCE AFTER   5   ITERATIONS

Table S6 Data for Job's plot of **3a** with TBABr

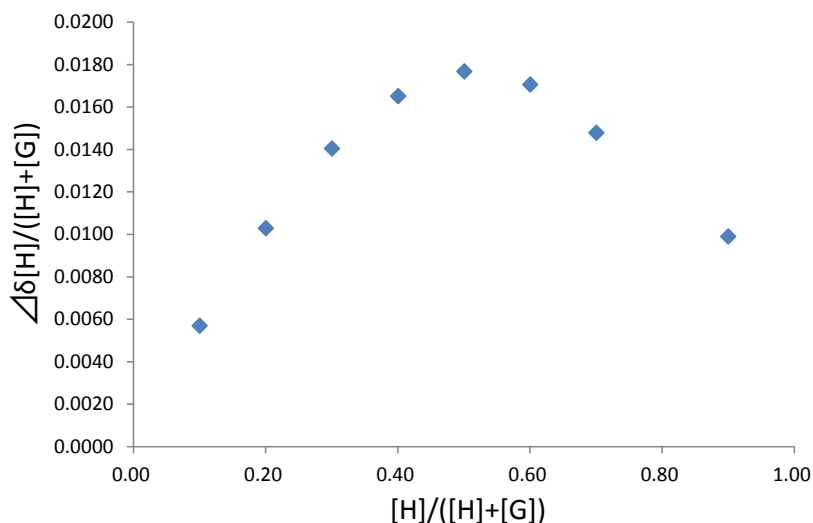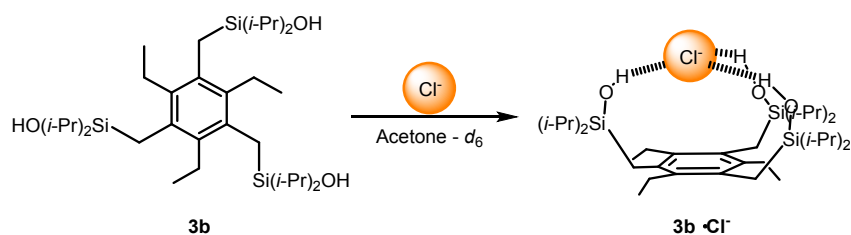| Host (μL)	Guest (μL)	[H]/([H]+[G])	δ (ppm)	Δδ [H]/([H]+[G])
50	450	0.1	4.4580	0.0057
100	400	0.2	4.4525	0.0103
150	350	0.3	4.4479	0.0140
200	300	0.4	4.4424	0.0165
250	250	0.5	4.4365	0.0177
300	200	0.6	4.4296	0.0171
350	150	0.7	4.4223	0.0148
450	50	0.9	4.4122	0.0099
500	0	1	4.4012	0.0000

Figure S10 Job's plot of **3a** with TBABr

For the titrations and Job's plot of 3b and the chloride anion

3a (56.3 mg, 0.103 mmol) was placed in a 2 mL volumetric flask, and was then dissolved in Acetone-d_6. By adding a drop of TMS as the internal standard, the solution came to 2 mL total volume. From the stock solution, 480 μL of solution **3b** was placed in a 5 mL volumetric flask using a microsyringe. The resulting host solution was diluted with Acetone-d_6 up to 5 mL, yielding a 4.94 mM host solution.

TBACl (77.2 mg, 0.278 mmol) was placed in a 2 mL volumetric flask, and was then dissolved in Acetone-d_6 up to 2 mL, yielding a 139 mM guest solution. After 500 μL of host solution (4.94 mM) was added to a NMR tube, the ^{1}H NMR spectra was recorded. The host solution was titrated by adding an incremental amount of the 139 mM guest solution as shown in Table S7. The gradual downshift of the SiOH resonance was monitored as shown in Figure S11. The association constant $K_a = 73.0$ M^{-1} was obtained by titration curve fitting using the WinEQNMR program shown in Figure S12. For Job's plots, different stock solutions were prepared as follows.

3b (82.7 mg, 0.151 mmol) was placed in a 2 mL volumetric flask, and was then dissolved in Acetone-d_6. By adding a drop of TMS as the internal standard, the solution came to 2 mL total volume.

From the stock solution, 330 μL of solution **3b** was placed in a 5 mL volumetric flask using a

microsyringe. The resulting host solution was diluted with Acetone-d_6 up to 5 mL, yielding a 4.99 mM host solution.

TBACl (51.3 mg, 0.185 mmol) was placed in a 2 mL volumetric flask, and was then dissolved in Acetone-d_6 up to 2 mL. From the resulting guest solution, 27.0 μL of solution was placed in a 5 mL volumetric flask using a microsyringe, and was then dissolved in Acetone-d_6 up to 2 mL, yielding 4.98 mM of guest solution.

As shown in Table S8, the NMR samples with different proportions of **3b** ([H]) and the chloride anion ([G]) were prepared for the total concentration of ([H]+[G]) to be 5 mM. The ^{1}H NMR spectra were recorded and the change in the ^{1}H NMR SiOH resonances with a mole fraction of [G] is listed in Table S8. The Job's plot is shown in Figure S13. The maximum appears at a mole fraction of 0.5 indicating an 1 : 1 stoichiometry.

Table S7 Added amounts of TBACl to **3b** and chemical shift changes of SiOH resonance

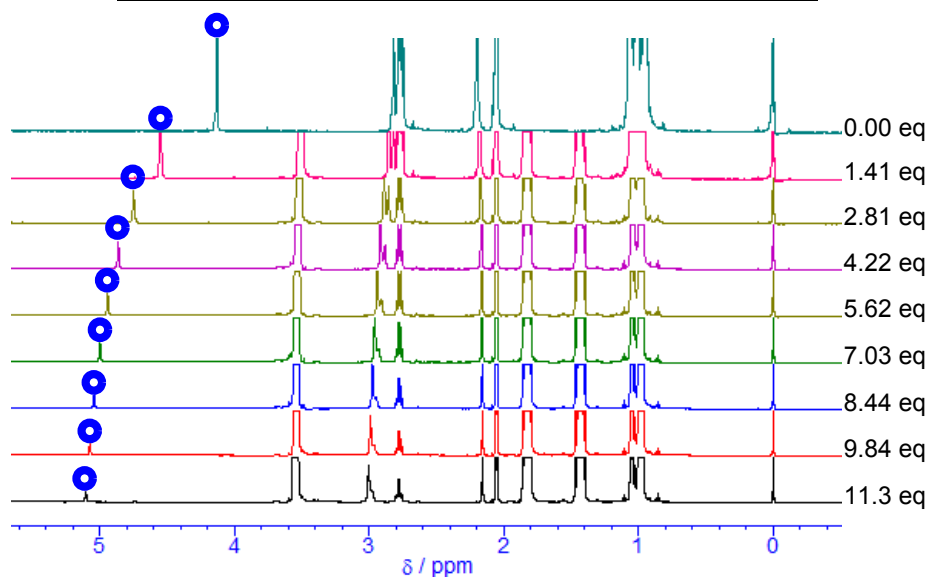| TOTAL Guest (μL)	eq	δ (ppm)	$\Delta\delta$ (ppm)
0	0	4.1328	0.0000
25	1.41	4.5533	0.4205
50	2.81	4.7530	0.6202
75	4.22	4.8648	0.7320
100	5.62	4.9436	0.8108
125	7.03	5.0004	0.8676
150	8.44	5.0425	0.9097
175	9.84	5.0764	0.9436
200	11.3	5.1048	0.9720

Figure S11 ^{1}H NMR titration spectra of **3b** with TBACl.

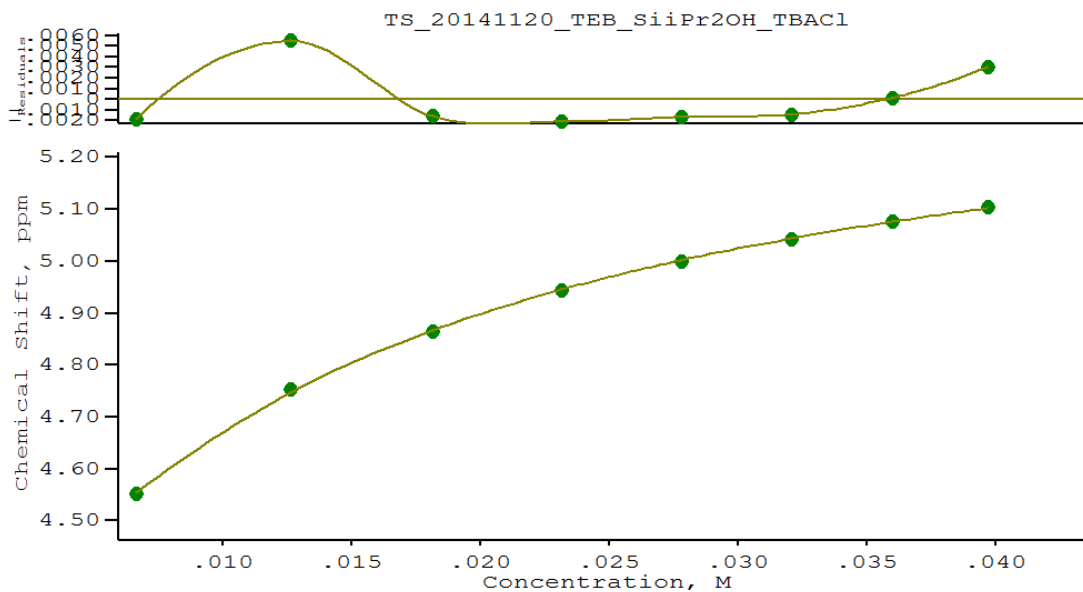The SiOH chemical shifts are marked with circles.

Figure S12 Determination of K_a using SiOH resonance by WinEQNMR for **3b** and TBACl. The concentration of TBACl is given on the X-axis.

Calculation for the titration of 3b with TBACl

Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes

Program run at 13:00:27   on 11/21/2014

  TS_20141120_TEB_SiiPr2OH_TBACl

  Equilibrium constants are floating point numbers

NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
1	1	7.30049E+01	5.000E-01	3.791E+00	1.288E+02	K11
2	1	4.21703E+00	4.100E-02	1.281E-02	2.390E+01	SHIFT_H
3	1	5.42783E+00	5.100E-02	1.464E-02	5.565E+01	SHIFT_HG

0RMS ERROR = 3.31E-03   MAX ERROR = 5.51E-03 AT OBS.NO.   2

 RESIDUALS SQUARED = 5.47E-05

 RFACTOR =   0.0531 PERCENT

NO.	A	EXPT. DEL	CALC. DEL	RESIDUAL	% DEV	WEIGHT	Cl-receptor	pH
1	1	4.5533E+00	4.5551E+00	-1.8311E-03	-4.0214E-02	1.0000E+00	6.6100E-03	4.7000E-03

0.0000E+00

2 1   4.7530E+00   4.7475E+00   5.5113E-03   1.1595E-01   1.0000E+00   1.2630E-02   4.4900E-03   0.0000E+00

3 1   4.8648E+00   4.8664E+00 -1.5860E-03 -3.2601E-02   1.0000E+00   1.8120E-02   4.2900E-03
0.0000E+00

4 1   4.9436E+00   4.9457E+00 -2.1138E-03 -4.2759E-02   1.0000E+00   2.3150E-02   4.1200E-03
0.0000E+00

5 1   5.0004E+00   5.0021E+00 -1.6727E-03 -3.3452E-02   1.0000E+00   2.7780E-02   3.9500E-03
0.0000E+00

6 1   5.0425E+00   5.0439E+00 -1.4272E-03 -2.8303E-02   1.0000E+00   3.2050E-02   3.8000E-03
0.0000E+00

7 1   5.0764E+00   5.0762E+00   1.7405E-04   3.4285E-03   1.0000E+00   3.6010E-02   3.6600E-03   0.0000E+00

8 1   5.1048E+00   5.1018E+00   3.0165E-03   5.9091E-02   1.0000E+00   3.9680E-02   3.5300E-03   0.0000E+00

TOLERANCE ON SUM OF SQUARES   0.0100

TOLERANCE ON EIGEN VALUES   0.0001

CONVERGANCE AFTER   4   ITERATIONS

Table S8 Data for Job's plot of **3b** with TBACl

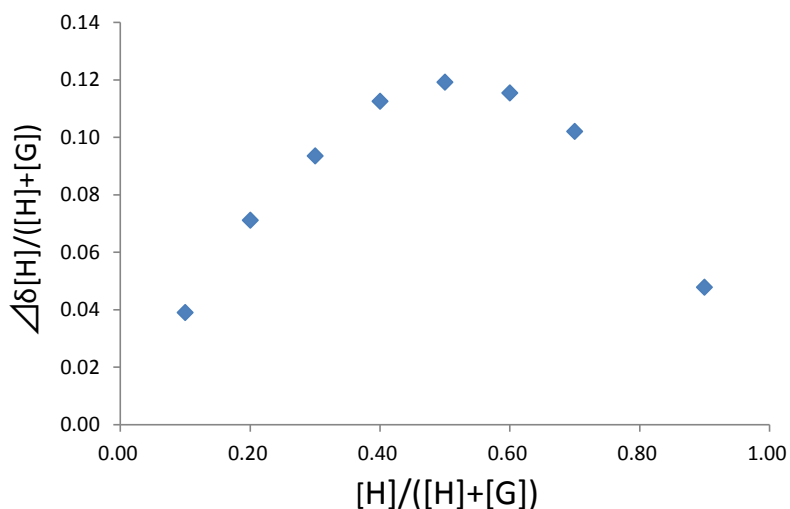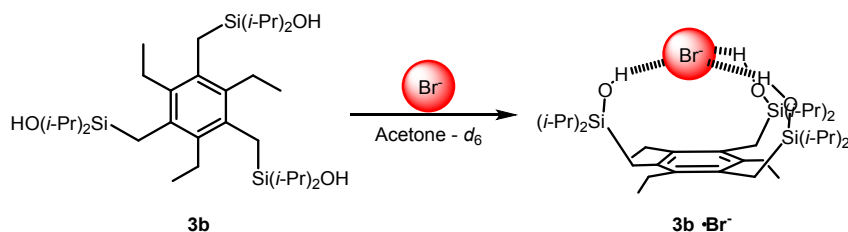| Host (μL)	Guest (μL)	[H]/([H]+[G])	δ (ppm)	Δδ [H]/([H]+[G])
50	450	0.1	4.5185	0.0390
100	400	0.2	4.4846	0.0711
150	350	0.3	4.4406	0.0935
200	300	0.4	4.4104	0.1126
250	250	0.5	4.3673	0.1191
300	200	0.6	4.3215	0.1155
350	150	0.7	4.2748	0.1020
450	50	0.9	4.1822	0.0478
500	0	1	4.1291	0.0000

Figure S13 Job's plot of **3b** with TBACl

For the titrations and Job's plot of 3b and the Bromide ion

3b (63.2 mg, 0.116 mmol) was placed in a 2 mL volumetric flask, and was then dissolved in Acetone-d_6. By adding TMS as the internal standard, the solution came to 2 mL total volume. From the stock solution, 430 μL of solution **3b** was placed in a 5 mL volumetric flask using a microsyringe. The resulting host solution was diluted with Acetone-d_6 up to 5 mL, yielding a 4.97 mM host solution.

TBABr (2.7 mg, 0.672 mmol) was placed in a 2mL volumetric flask, and was then dissolved in Acetone-d_6 up to 2 mL, yielding a 336 mM guest solution.

From the resulting guest solution, 74 μL of solution was placed in a 5 mL volumetric flask using a microsyringe, and was then dissolved in Acetone-d_6 up to 5 mL, yielding 4.97 mM of guest solution.

After 500 μL of the host solution (4.97 mM) was added to a NMR tube, the ^{1}H NMR spectra was recorded. The host solution was titrated by adding an incremental amount of the 336 mM guest solution as shown in Table S9.

The gradual downshift of the SiOH resonance was monitored as shown in Figure S14. The association constant K_a = 9.61 M^{-1} was obtained by titration curve fitting using the WinEQNMR program shown in Figure S15.

As shown in Table S10, the NMR samples with different proportions of **3b** ([H]) and the bromide anion ([G]) were prepared for the total concentration of ([H]+[G]) to be 5 mM. The ^{1}H NMR spectra were recorded and the change in the ^{1}H NMR SiOH resonances with a mole fraction of [G] is listed in Table S10.

The Job's plot is shown in Figure S16. The maximum appears at a mole fraction of 0.5 indicating an 1 : 1 stoichiometry.

Table S9 Added amounts of TBABr to **3b** and chemical shift changes of SiOH resonance

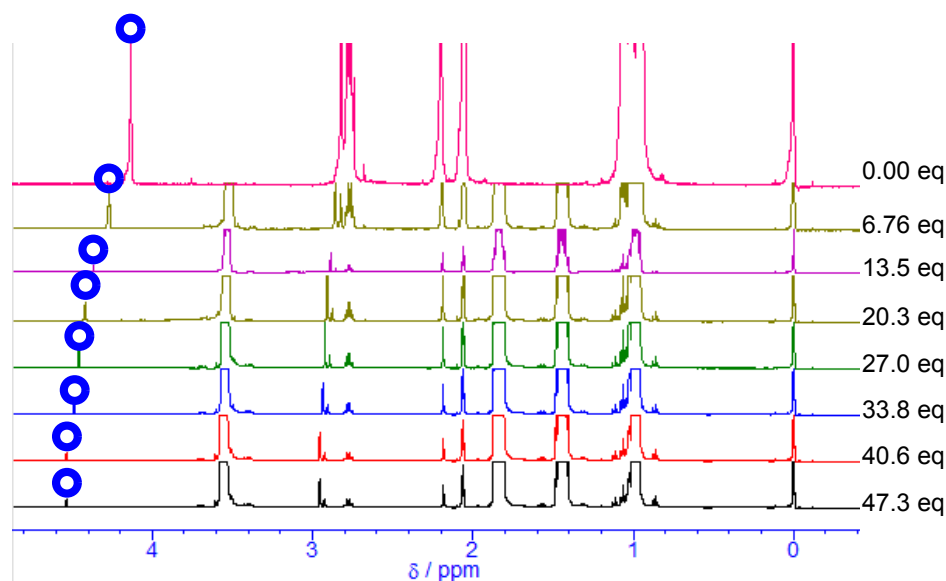| TOTAL Guest (µL)	eq	δ (ppm)	Δδ (ppm)
0	0	4.1337	0.0000
50	6.76	4.2674	0.1337
100	13.5	4.3655	0.2318
150	20.3	4.4195	0.2858
200	27.0	4.4589	0.3252
250	33.8	4.4891	0.3554
300	40.6	4.5130	0.3793
350	47.3	4.5331	0.3994

Figure S14 ^{1}H NMR titration spectra of **3b** with TBABr.

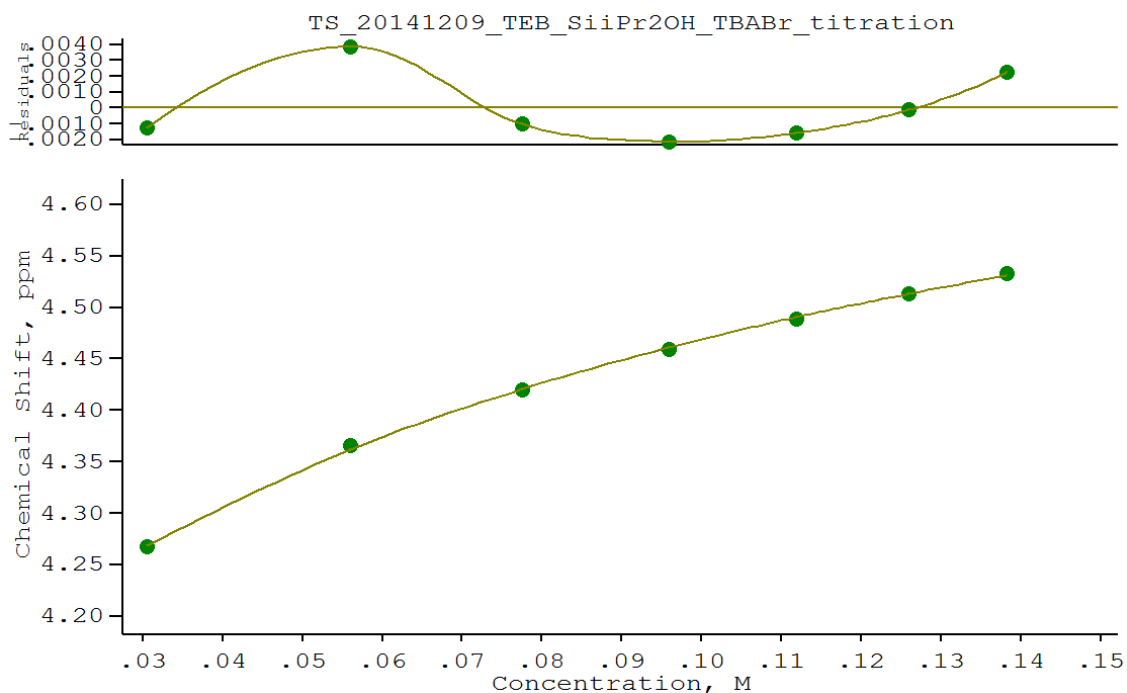The SiOH chemical shifts are marked with circles.

Figure S15 Determination of K_a using SiOH resonance by WinEQNMR for **3b** and TBABr. The concentration of TBABr is given on the X-axis.

Calculation for the titration of 3b with TBABr

Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes

Program run at 16:39:19   on 03/19/2015

  TS_20141209_TEB_SiiPr2OH_TBABr_titration

  Equilibrium constants are floating point numbers

NO. A   PARAMETER   DELTA   ERROR   CONDITION   DESCRIPTION

   1   1   9.61408E+00 5.000E-02 1.141E+00 4.120E+02 K11

   2   1   4.10104E+00 4.100E-02 1.293E-02 5.138E+01 SHIFT_H

   3   1   4.85751E+00 4.500E-02 3.182E-02 1.997E+02 SHIFT_HG

0RMS ERROR = 2.72E-03   MAX ERROR = 3.88E-03 AT OBS.NO.   2

 RESIDUALS SQUARED = 2.96E-05

 RFACTOR =   0.0463 PERCENT

 NO. A   EXPT. DEL   CALC. DEL   RESIDUAL   % DEV   WEIGHT   Br-

receptor   pH

  1 1   4.2674E+00   4.2687E+00 -1.2546E-03 -2.9399E-02   1.0000E+00   3.0530E-02
4.5200E-03   0.0000E+00

  2 1   4.3655E+00   4.3616E+00   3.8757E-03   8.8781E-02   1.0000E+00   5.5960E-02
4.1400E-03   0.0000E+00

  3 1   4.4195E+00   4.4205E+00 -1.0233E-03 -2.3154E-02   1.0000E+00   7.7490E-02
3.8200E-03   0.0000E+00

  4 1   4.4589E+00   4.4610E+00 -2.1257E-03 -4.7674E-02   1.0000E+00   9.5940E-02
3.5500E-03   0.0000E+00

  5 1   4.4891E+00   4.4907E+00 -1.5645E-03 -3.4851E-02   1.0000E+00   1.1193E-01
3.3100E-03   0.0000E+00

  6 1   4.5130E+00   4.5131E+00 -1.3018E-04 -2.8845E-03   1.0000E+00   1.2592E-01
3.1000E-03   0.0000E+00

  7 1   4.5331E+00   4.5309E+00   2.2268E-03   4.9124E-02   1.0000E+00   1.3826E-01
2.9200E-03   0.0000E+00

TOLERANCE ON SUM OF SQUARES   0.0100
TOLERANCE ON EIGEN VALUES   0.0001

CONVERGANCE AFTER   4   ITERATIONS

Table S10 Data for Job's plot of **3b** with TBABr

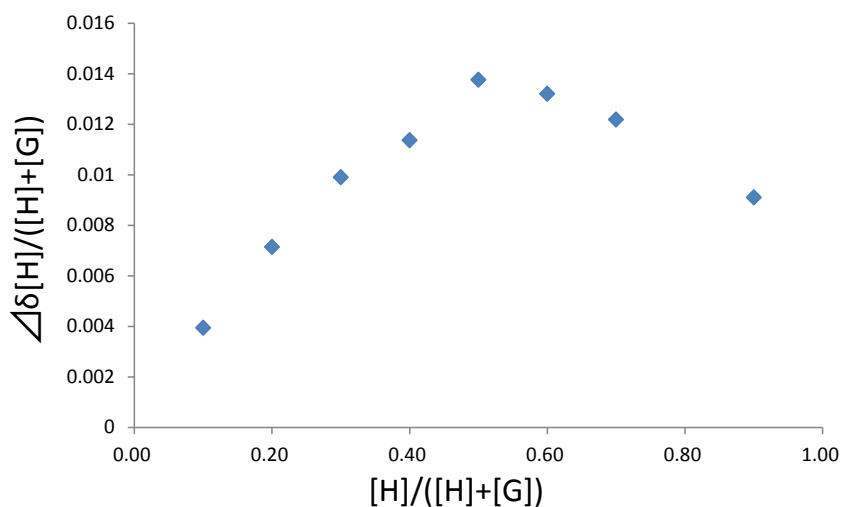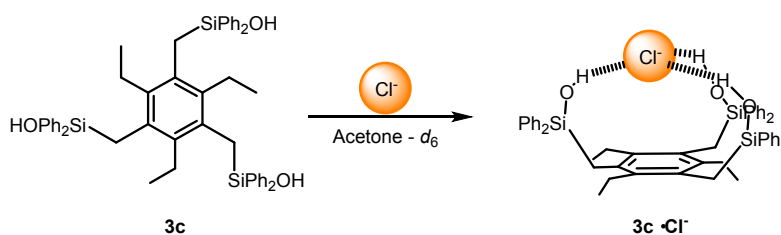| Host (μL)	Guest (μL)	[H]/([H]+[G])	δ (ppm)	Δδ [H]/([H]+[G])
50	450	0.1	4.1685	0.0039
100	400	0.2	4.1648	0.0071
150	350	0.3	4.1621	0.0099
200	300	0.4	4.1575	0.0114
250	250	0.5	4.1566	0.0137
300	200	0.6	4.1511	0.0132
350	150	0.7	4.1465	0.0122
450	50	0.9	4.1392	0.0091
500	0	1	4.1291	0.0000

Figure S16 Job's plot of **3b** with TBABr

For the titrations and Job's plot of 3c and the chloride ion

3c (96.9 mg, 0.121 mmol) was placed in a 2 mL volumetric flask, and was then dissolved in Acetone-d_6. By adding a drop of TMS as the internal standard, the solution came to 2 mL total volume. From the stock solution, 400 μL of solution **3c** was placed in a 5 mL volumetric flask using a microsyringe. The resulting host solution was diluted with Acetone-d_6 up to 5 mL, yielding a 4.85 mM host solution.

TBACl (79.0 mg, 0.284 mmol) was placed in a 2 mL volumetric flask, and was then dissolved in Acetone-d_6 up to 2 mL, yielding a 142 mM guest solution.

After 500 μL of the host solution (4.85 mM) was added to a NMR tube, the ^{1}H NMR spectra was recorded. The host solution was titrated by adding an incremental amount of the 142 mM guest solution as shown in Table S11.

The gradual downshift of the SiOH resonance was monitored as shown in Figure S17. The association constant K_a = 6829 M^{-1} was obtained by titration curve fitting using the WinEQNMR program shown in Figure S18.

For Job's plots, different stock solutions were prepared as follows.

3c (7.99 mg, 0.01 mmol) was placed in a 2 mL volumetric flask, and was then diluted in Acetone-d_6. By adding a drop of TMS as the internal standard, the solution volume was 2 mL, yielding a 5.0 mM

host solution.

TBACl (6.95 mg, 0.025 mmol) was placed in a 5 mL volumetric flask, and was then dissolved in Acetone-d_6 up to 2 mL, yielding a 5.0 mM guest solution.

As shown in Table S12, the NMR samples with different proportions of **3c** ([H]) and the chloride anion ([G]) were prepared for the total concentration of ([H]+[G]) to be 5 mM. The ^{1}H NMR spectra were recorded and the change in ^{1}H NMR SiOH resonances with a mole fraction [G] is listed in Table S12.

The Job's plot is shown in Figure S19. The maximum appears at a mole fraction of 0.5 indicating an 1 : 1 stoichiometry.

Table S11 Added amounts of TBACl to **3c** and chemical shift changes of SiOH resonance

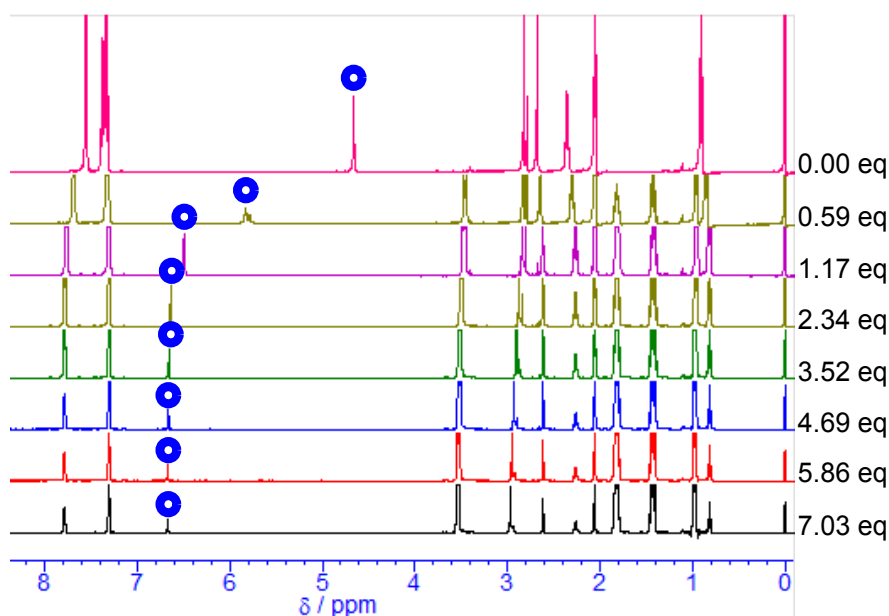| TOTAL Guest (µL)	eq	δ (ppm)	Δδ (ppm)
0	0	4.6660	0.0000
10	0.59	5.8304	1.1644
20	1.17	6.4946	1.8286
40	2.34	6.6458	1.9798
60	3.52	6.6650	1.9990
80	4.69	6.6723	2.0063
100	5.86	6.6761	2.0101
120	7.03	6.6763	2.0103

Figure S17 ^{1}H NMR titration spectra of **3c** with TBACl.
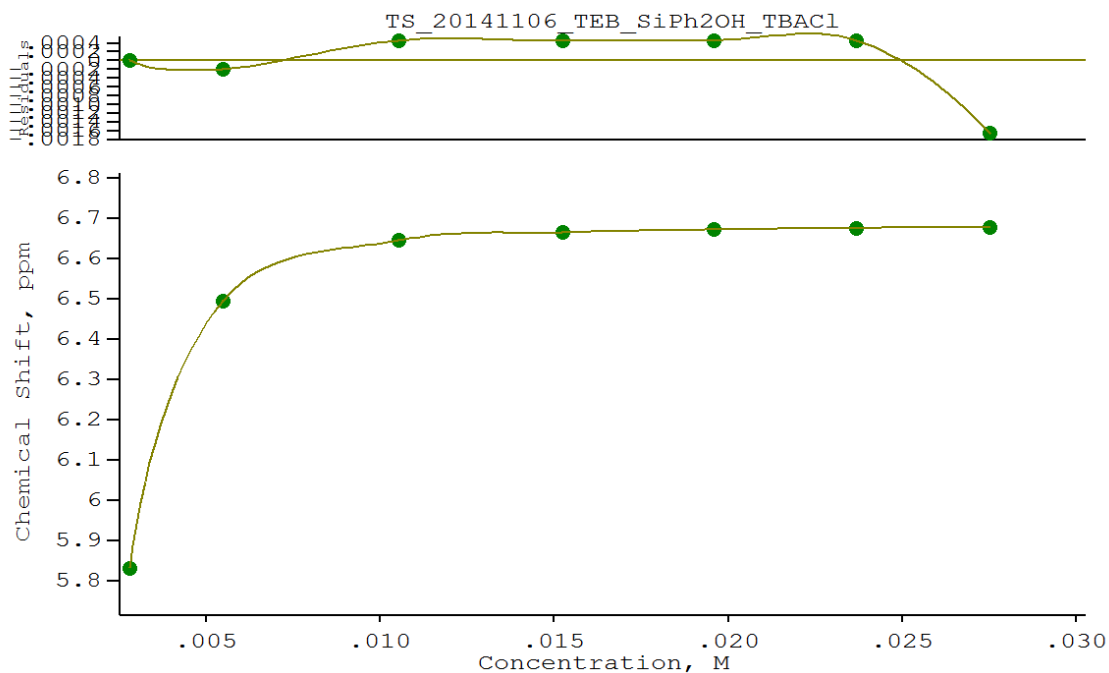
The SiOH chemical shifts are marked with circles.

Figure S18 Determination of K_a using SiOH resonance by WinEQNMR for **3c** and TBACl. The concentration of TBACl is given on the X-axis.

Calculation for the titration of 3c with TBACl

Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes

Program run at 16:34:42   on 03/19/2015

   TS_20141106_TEB_SiPh2OH_TBACl

   Equilibrium constants are floating point numbers

NO. A   PARAMETER   DELTA   ERROR   CONDITION   DESCRIPTION

   1   1   6.82924E+03 3.000E+01 6.805E+01 2.647E+00 K11

   2   1   4.78256E+00 4.700E-02 2.572E-03 1.577E+00 SHIFT_H

   3   1   6.68910E+00 6.700E-02 5.388E-04 1.937E+00 SHIFT_HG

0RMS ERROR = 9.48E-04   MAX ERROR = 1.64E-03 AT OBS.NO.   7

 RESIDUALS SQUARED = 3.59E-06

 RFACTOR =   0.0110 PERCENT

   NO. A   EXPT. DEL   CALC. DEL   RESIDUAL   % DEV   WEIGHT   Cl-

receptor   pH

   1 1   5.8304E+00   5.8304E+00   1.9550E-05   3.3532E-04   1.0000E+00   2.7900E-03
4.7500E-03   0.0000E+00

   2 1   6.4946E+00   6.4948E+00   -1.9646E-04   -3.0249E-03   1.0000E+00   5.4700E-03
4.6600E-03   0.0000E+00

   3 1   6.6458E+00   6.6453E+00   4.6349E-04   6.9741E-03   1.0000E+00   1.0530E-02
4.4900E-03   0.0000E+00

   4 1   6.6650E+00   6.6646E+00   4.4918E-04   6.7394E-03   1.0000E+00   1.5230E-02
4.3300E-03   0.0000E+00

   5 1   6.6723E+00   6.6718E+00   4.6778E-04   7.0107E-03   1.0000E+00   1.9600E-02
4.1800E-03   0.0000E+00

   6 1   6.6761E+00   6.6756E+00   4.6062E-04   6.8996E-03   1.0000E+00   2.3690E-02
4.0400E-03   0.0000E+00

   7 1   6.6763E+00   6.6779E+00   -1.6446E-03   -2.4634E-02   1.0000E+00   2.7510E-02
3.9100E-03   0.0000E+00

TOLERANCE ON SUM OF SQUARES   0.0100
TOLERANCE ON EIGEN VALUES   0.0001
CONVERGANCE AFTER   2   ITERATIONS

Table S12 Data for Job's plot of **3c** with TBACl

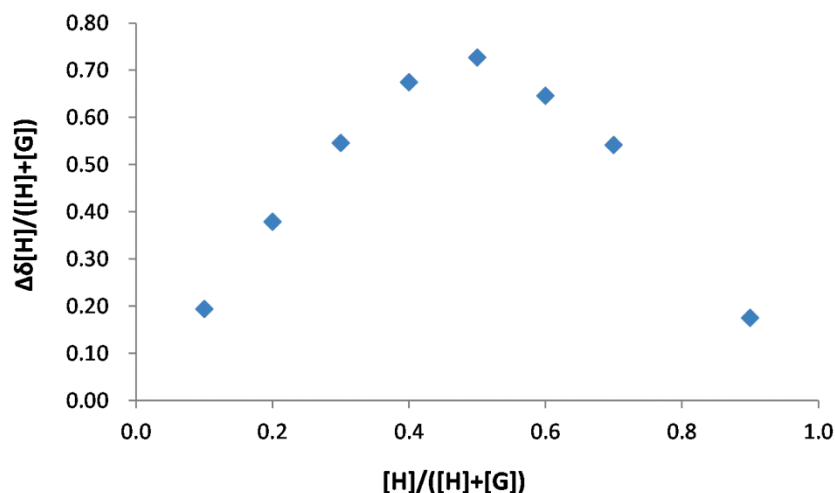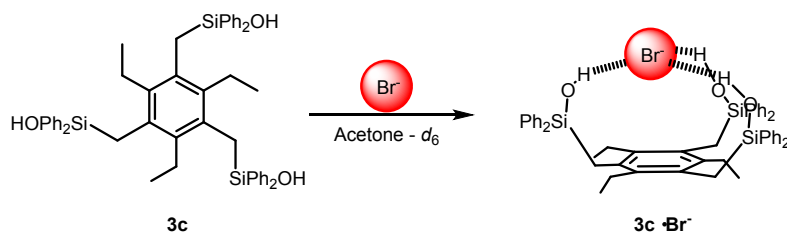| Host (μL)	Guest (μL)	[H]/([H]+[G])	δ (ppm)	$\Delta\delta$ [H]/([H]+[G])
500	0	1	4.6599	0.0000
50	450	0.1	6.5989	0.1939
100	400	0.2	6.5538	0.3788
150	350	0.3	6.4794	0.5459
200	300	0.4	6.3454	0.6742
250	250	0.5	6.1137	0.7269
300	200	0.6	5.7358	0.6455
350	150	0.7	5.4330	0.5412
450	50	0.9	4.8545	0.1751

Figure S19 Job's plot of **3c** with TBACl

For the titrations and Job's plot of 3c and the Bromide ion

3c (102 mg, 0.127 mmol) was placed in a 2 mL volumetric flask, and was then dissolved in Acetone-d_6. By adding TMS as the internal standard, the solution came to 2 mL total volume. From the stock solution, 400 μL of solution **3c** was placed in a 5 mL volumetric flask using a microsyringe. The resulting host solution was diluted with Acetone-d_6 up to 5 mL, yielding a 5.08 mM host solution.

TBABr (160 mg, 0.945 mmol) was placed in a 2 mL volumetric flask, and was then dissolved in Acetone-d_6 up to 2 mL, yielding 99.0 mM of guest solution. From the resulting guest solution, 200 μL of solution was placed in a 5 mL volumetric flask using a microsyringe, and was then dissolved in Acetone-d_6 up to 5 mL, yielding 4.95 mM of guest solution.

After 500 μL of the host solution (5.08 mM) was added to a NMR tube, the ^{1}H NMR spectra was recorded. The host solution was titrated by adding an incremental amount of 99 mM guest solution as shown in Table S13.

The gradual downfield of SiOH resonance was monitored as shown in Figure S20. The association constant 94.4 M^{-1} was obtained by titration curve fitting using the WinEQNMR program shown in Figure S21.

As shown in Table S14, the NMR samples with different proportions of **3c** ([*H*]) and the bromide anion ([*G*]) were prepared for the total concentration of ([*H*]+[*G*]) to be 5 mM.

The ^{1}H NMR spectra were recorded and the change in the ^{1}H NMR SiOH resonances with a mole fraction of [*G*] is listed in Table S14. The Job's plot is shown in Figure S22. The maximum appears at a mole fraction of 0.5 indicating an 1 : 1 stoichiometry.

Table S13 Added amounts of TBABr to **3c** and chemical shift changes of SiOH resonance

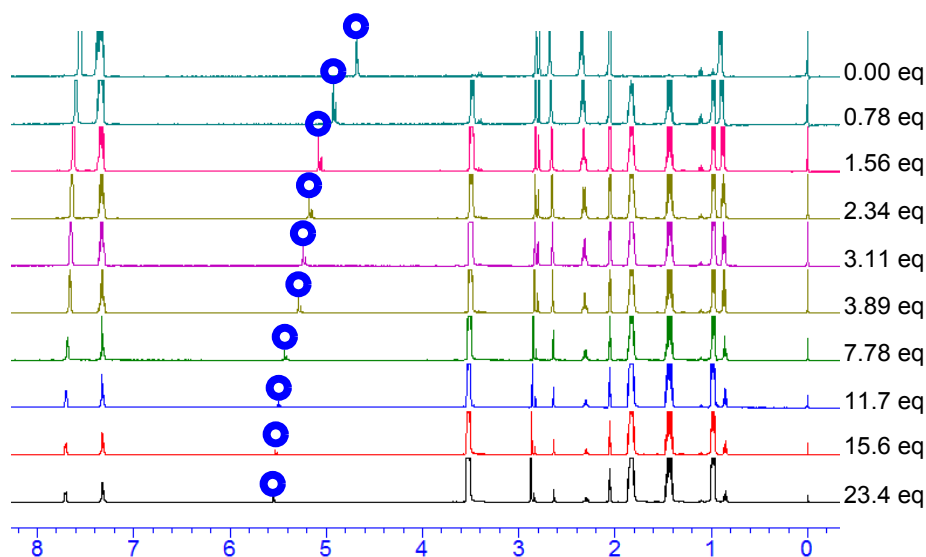| TOTAL Guest (μL)	eq	δ (ppm)	Δδ (ppm)
0	0	4.6843	0.0000
20	0.78	4.9280	0.2437
40	1.56	5.0791	0.3948
60	2.34	5.1781	0.4938
80	3.11	5.2422	0.5579
100	3.89	5.2908	0.6065
200	7.78	5.4319	0.7476
300	11.7	5.4969	0.8126
400	15.6	5.5299	0.8456
500	19.5	5.5510	0.8667
600	23.4	5.5528	0.8685

Figure S20 ^{1}H NMR titration spectra of **3c** with TBABr.
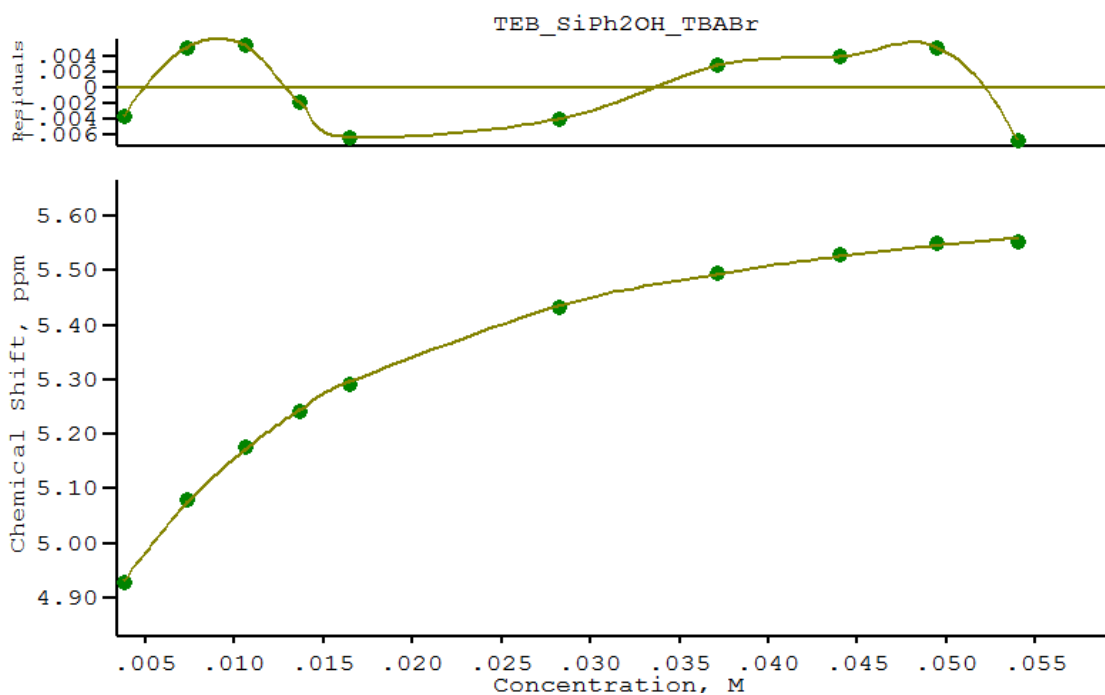The SiOH chemical shifts are marked with circles.

Figure S21 Determination of K_a using SiOH resonance by WinEQNMR for **3c** and TBABr. The concentration of TBABr is given on the X-axis.

Calculation for titration of 3c with TBABr

Calculations by WinEQNMR2 Version 2.00 by Michael J. Hynes

Program run at 20:45:23   on 10/03/2014

  TEB_SiPh2OH_TBABr

  Equilibrium constants are floating point numbers

NO. A   PARAMETER   DELTA   ERROR   CONDITION   DESCRIPTION

   1   1   9.43872E+01 2.000E+00 4.769E+00 2.824E+01 K11

   2   1   4.72155E+00 4.700E-02 1.146E-02 8.478E+00 SHIFT_H

   3   1   5.72955E+00 5.600E-02 9.437E-03 1.158E+01 SHIFT_HG

0RMS ERROR = 5.58E-03   MAX ERROR = 6.71E-03 AT OBS.NO. 10

 RESIDUALS SQUARED = 2.18E-04

 RFACTOR =   0.0876 PERCENT

NO. A   EXPT. DEL   CALC. DEL   RESIDUAL   % DEV   WEIGHT   Br-   TEB
pH

   1 1   4.9280E+00   4.9315E+00 -3.5057E-03 -7.1139E-02   1.0000E+00   3.8100E-03   4.8900E-03
0.0000E+00

   2 1   5.0791E+00   5.0740E+00   5.0697E-03   9.9816E-02   1.0000E+00   7.3300E-03   4.7100E-03
0.0000E+00

   3 1   5.1781E+00   5.1728E+00   5.3229E-03   1.0280E-01   1.0000E+00   1.0600E-02   4.5400E-03
0.0000E+00

   4 1   5.2422E+00   5.2440E+00 -1.8210E-03 -3.4738E-02   1.0000E+00   1.3650E-02   4.3800E-03
0.0000E+00

   5 1   5.2908E+00   5.2970E+00 -6.2346E-03 -1.1784E-01   1.0000E+00   1.6490E-02   4.2400E-03
0.0000E+00

   6 1   5.4319E+00   5.4358E+00 -3.8981E-03 -7.1764E-02   1.0000E+00   2.8270E-02   3.6300E-03
0.0000E+00

   7 1   5.4969E+00   5.4941E+00   2.7981E-03   5.0903E-02   1.0000E+00   3.7110E-02   3.1800E-03
0.0000E+00

   8 1   5.5299E+00   5.5260E+00   3.9248E-03   7.0975E-02   1.0000E+00   4.3980E-02   2.8200E-03
0.0000E+00

   9 1   5.5510E+00   5.5459E+00   5.1093E-03   9.2043E-02   1.0000E+00   4.9480E-02   2.5400E-03
0.0000E+00

   10 1   5.5528E+00   5.5595E+00 -6.7086E-03 -1.2082E-01   1.0000E+00   5.3970E-02   2.3100E-03
0.0000E+00

   TOLERANCE ON SUM OF SQUARES   0.0100

   TOLERANCE ON EIGEN VALUES   0.0001

   CONVERGANCE AFTER   5   ITERATIONS

Table S14 Data for Job's plot **3c** with TBABr

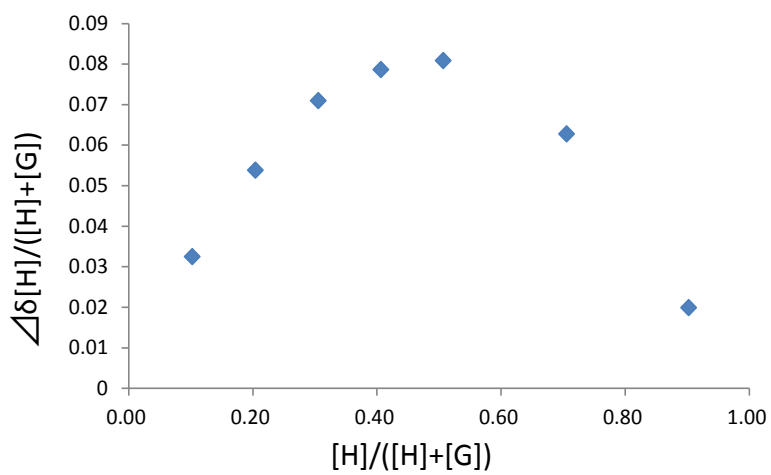| Host (μL)	Guest (μL)	[H]/([H]+[G])	δ (ppm)	$\Delta\delta$ [H]/([H]+[G])
50	450	0.1	5.0004	0.0324
100	400	0.2	4.9472	0.0537
150	350	0.3	4.9161	0.0709
200	300	0.4	4.8776	0.0786
250	250	0.5	4.8437	0.0808
300	200	0.6	4.7429	0.0355
350	150	0.7	4.7731	0.0627
450	50	0.9	4.7063	0.0199
500	0	1	4.6843	0.0000

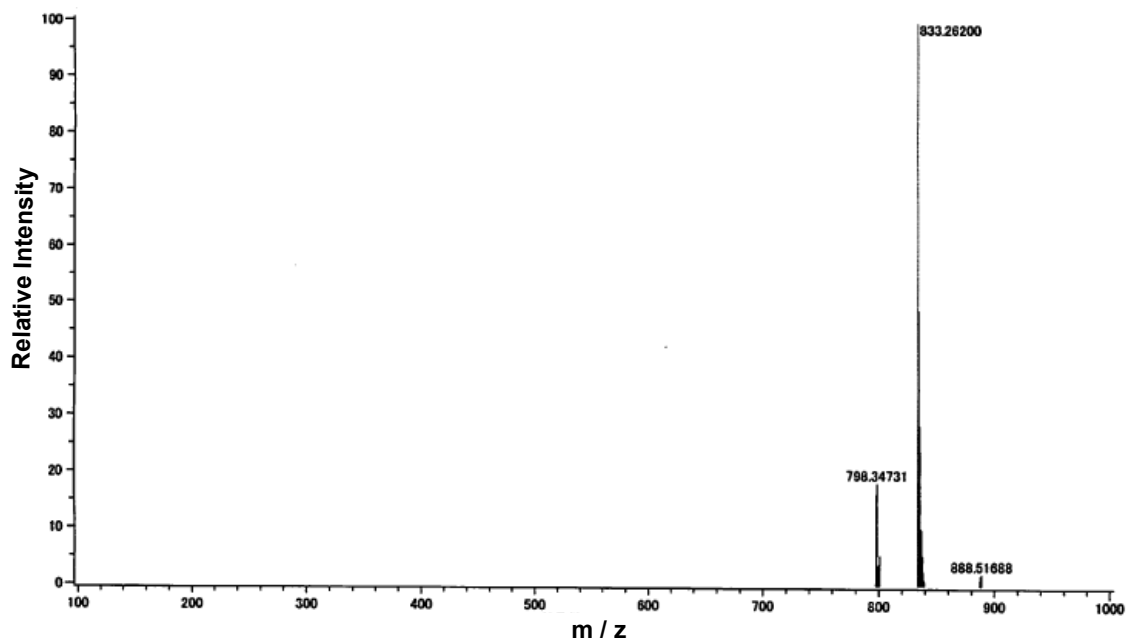Figure S22 Job's plot of **3c** with TBABr

4. ESI Mass Spectral Data
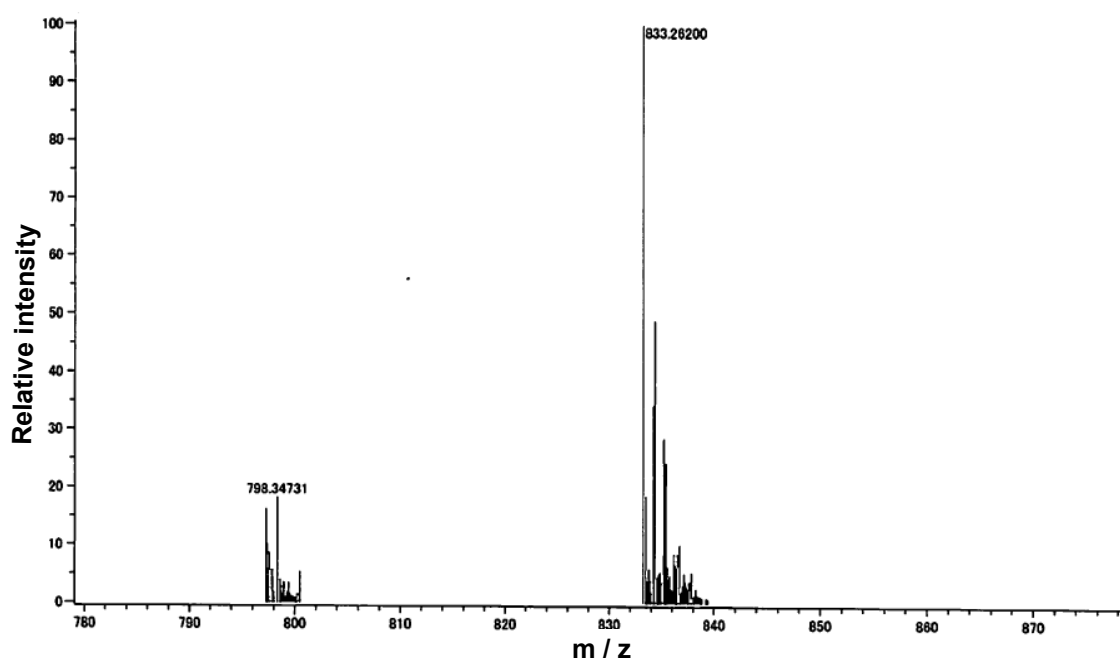

Figure S23 ESI-MS (negative ion mode) of **3c** · Cl⁻
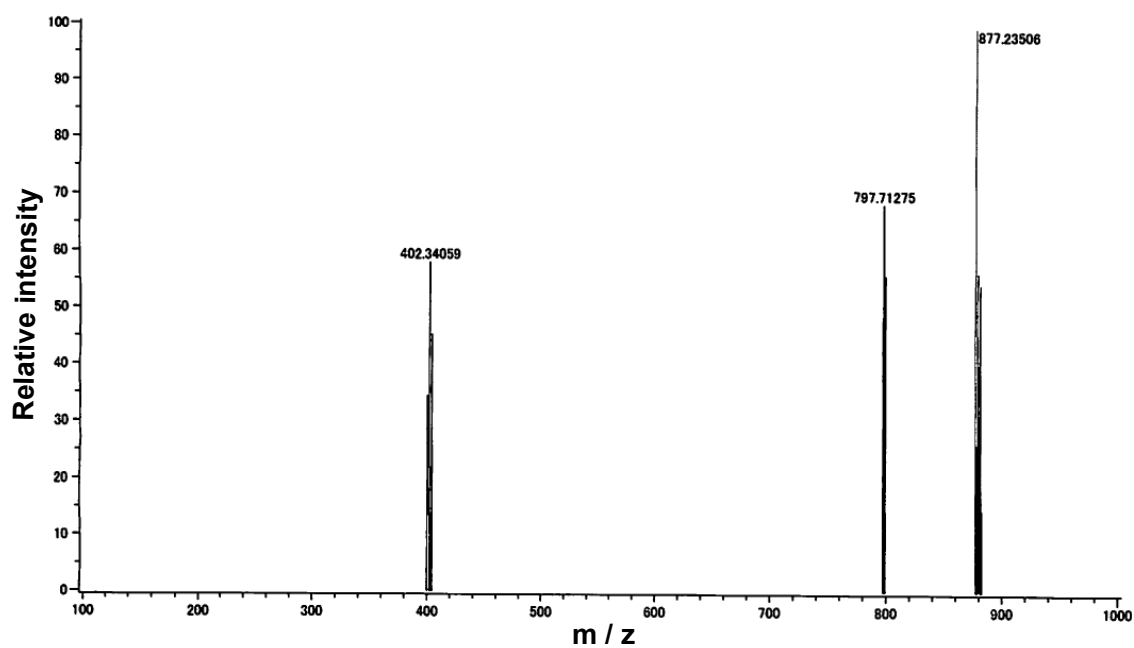
Figure S24 ESI-MS of **3c** · Cl⁻ in Selected Range
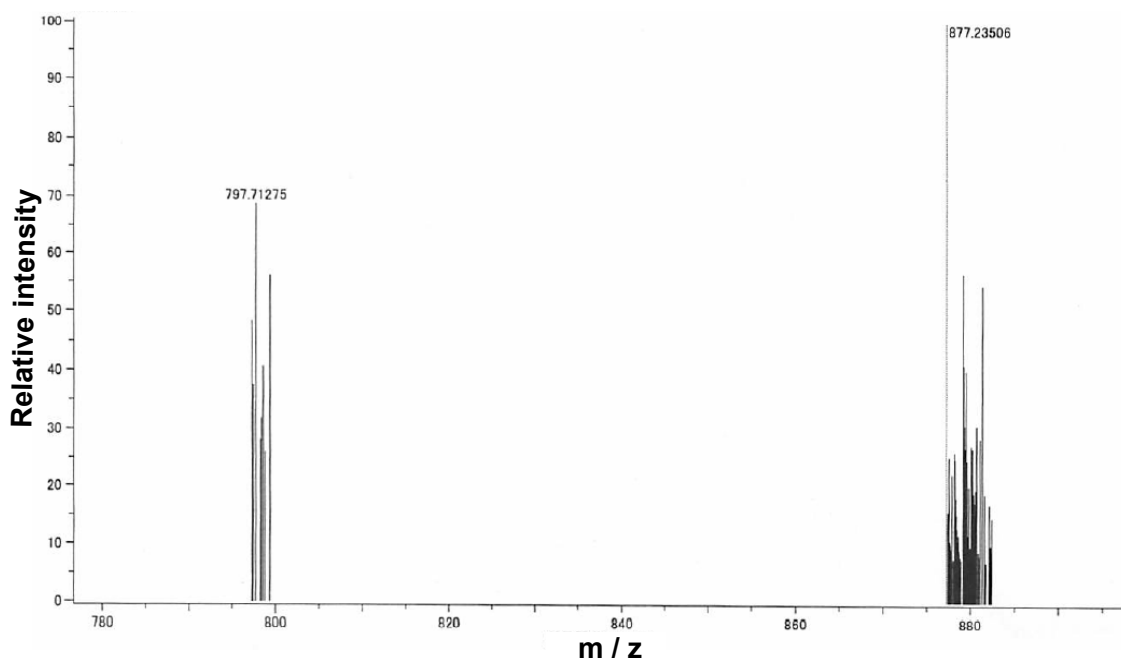

Figure S25 ESI-MS (negative ion mode) of **3c** · Br⁻

Figure S26 ESI-MS of **3c** ⋅ Br⁻ in Selected Range

5. Supporting References

1) Y. Kawakami, Y. Sakuma, T. Wakuda, T. Nakai, M. Sirasaka, Y. Kabe, *Organometallics* **2010**, *29*, 3281.

2) C. Walsdorff, W. Saak, S. Pohl, *J. Chem. Res. (M)*, **1996**, 1601.

3) M. Lee, S. Ko, S. Chang, *J. Am. Chem. Soc*., **2000**, *122*, 12011.

4) H. Liu, S. Kondo, R. Tanaka, H. Oku, M. Unno, *J. Organomet. Chem*., **2008**, *693*, 1301.

5) For details of numerical calculations being available in ESI: M. A. Saeed, F. R. Fronczek and M. A. Hossain, *Chem. Commun*., **2009**, 6409.

6) M. J. Hynes, *J. Chem., Soc., Dolton Trans.*, **1993**, 311.