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Synthesis of supramolecular cyclosiloxane ligands

Błażej Gierczyk* and Grzegorz Schroeder

Faculty of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland. Fax: +48 61 8291 505;
e-mail: hanuman@amu.edu.pl, schroede@amu.edu.pl

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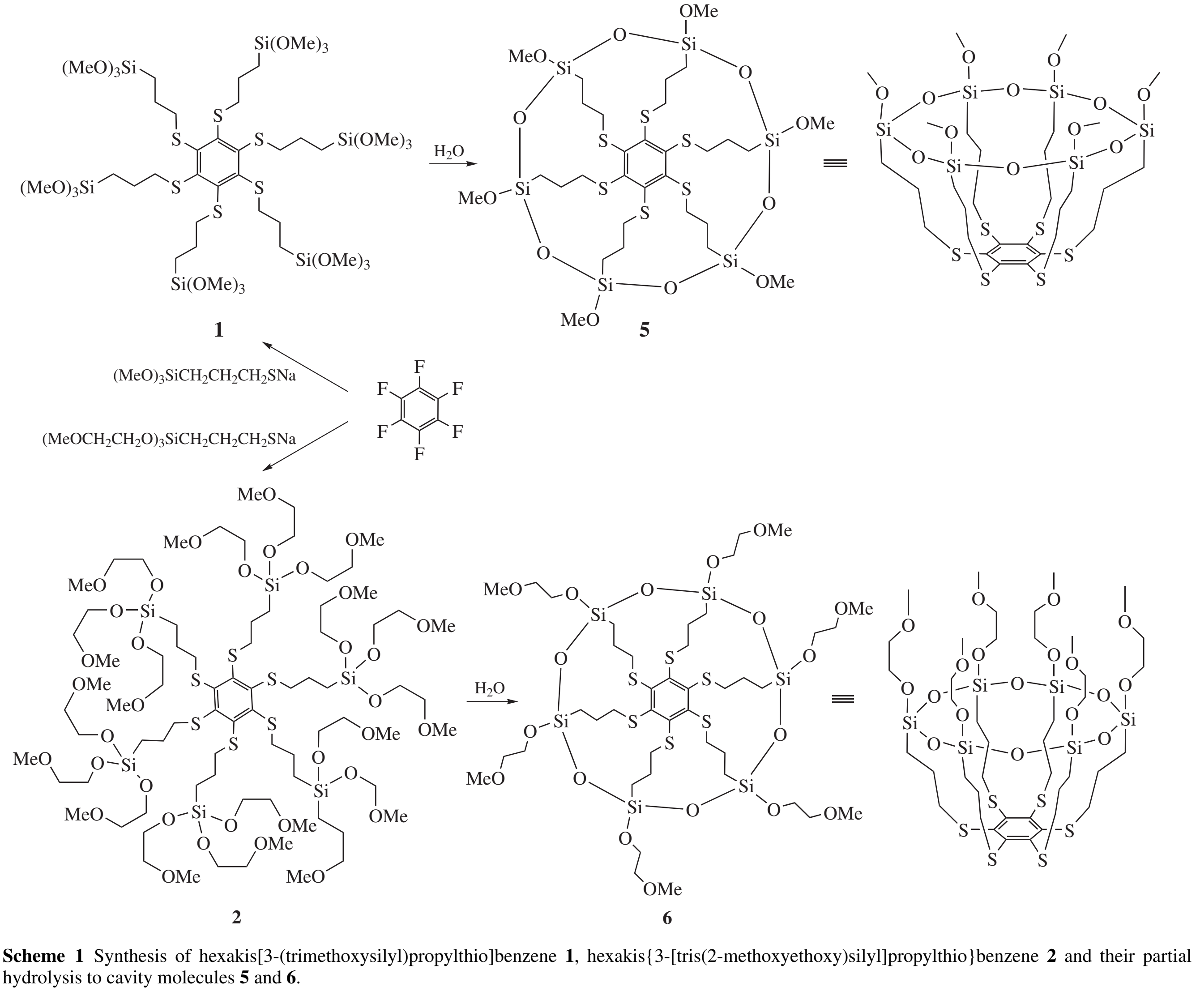
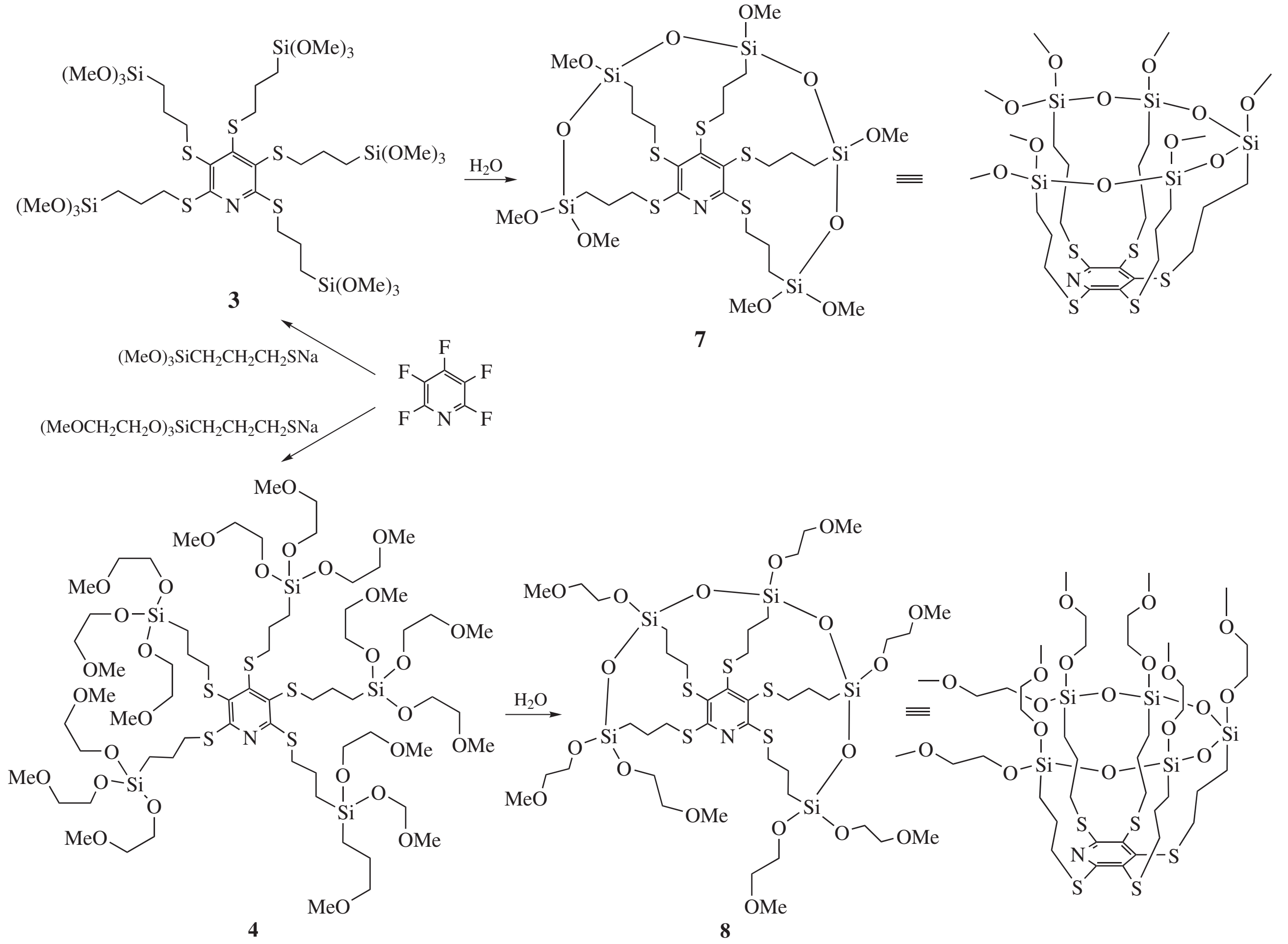
The synthesis and properties of new polypodand ligands based on benzene or pyridine molecules, as well as their calix-shape derivatives, formed by the partial hydrolysis of pre-organized supramolecules are presented.

Podands make a large and important group of supramolecuar ligands. Their properties could be designed *via* changing the length, structure and flexibility of complexing arms (especially the number of donor atoms and the hydrophobicity) or the character and geometry of the 'clipping' centre (an atom or group to which the arms are connected).[1] This class of ligands is especially interesting and important for industry, nanotechnology and laboratory applications because of low cost, simple and fast synthesis and high versatility. Previously, we described methods of synthesis of di- and tri(oxaalkyl) phosphates, tri(oxaalkyl) borates, bis(oxaalkyl) sulfates and di- and tri(oxaalkyl) silicon podands. NMR, FTIR and calorimetric methods have been used to study metal cation complexation. These ligands form cation channels or cavities. In the FTIR spectra of these complexes, the fast fluctuation of the cation was indicated by a characteristic continuous absorption.[2–6] In the reaction of perfluoroarenes with sodium tris(alcoxysilyl)alkyl thiolate, interesting new octopus-like polypodands could be obtained. Their partial hydrolysis followed by spontaneous Si–O–Si bond formation produces a cavity molecule of ionophore character.



Scheme 1 Synthesis of hexakis[3-(trimethoxysilyl)propylthio]benzene **1**, hexakis{3-[tris(2-methoxyethoxy)silyl]propylthio}benzene **2** and their partial hydrolysis to cavity molecules **5** and **6**.



Scheme 2 Synthesis of pentakis[3-(trimethoxysilyl)propylthio]pyridine **3** and pentakis{3-[tris(2-methoxyethoxy)silyl]propylthio}pyridine **4** and their partial hydrolysis to cavity molecules **7** and **8**.

The octopus-like polypodands were obtained in the reaction of sodium thiolates with perfluoroarenes.† The structures of ligands obtained are presented in Schemes 1 and 2; ^{1}H, ^{13}C and ^{29}Si NMR data of the ligands are collected in Tables 1 and 2 and in a footnote.‡ For all compounds, no ^{19}F NMR signal of the C–F fluorine atom was detected (only a weak line of the F$^-$ ion occurred in the spectra of some samples). Elemental analysis results of the calix-like compounds obtained are not satisfactory (errors of 0.2–0.6%). It is probably caused by solvent encapsulation or the complexation of sodium fluoride.‡ In the IR spectra of compounds **1**–**4**, the absence of absorption characteristic of C–F and S–H bonds was confirmed. Hydrolysis and cyclization during the formation of **5**, **6** caused a decrease in Si–O–C (1090 and 820 cm^{-1}) and SiOC–H (2840 cm^{-1}) bands and the appearance

Table 1 ^{1}H NMR chemical shifts for compounds **1**–**8**.

Compound	^{1}H NMR, δ/ppm					
	$\mathrm{SCH_2}$	$\mathrm{CH_2}\mathit{CH}_2\mathrm{CH_2}$	$\mathrm{CH_2Si}$	OMe	$\mathrm{SiOCH_2}$	$\mathrm{C}\mathit{H}_2\mathrm{OMe}$
1	2.65 (t, 12H)	1.74 (q,[a] 12H)	0.75 (t, 12H)	3.60 (s, 54H)	—	—
2	2.63 (t, 12H)	1.74 (q, 12H)	0.75 (t, 12H)	3.25 (s, 54H)	3.71 (m, 36H)	3.48 (m, 36H)
3	2.71 (t, 4H), 2.62 (t, 6H)	1.73 (m, 10H)	0.76 (t, 10H)	3.58[b] (s, 45H)	—	—
4	2.70 (t, 4H), 2.63 (t, 6H)	1.74 (m, 10H)	0.75 (t, 10H)	3.26 (s, 45H)	3.72 (m, 30H)	3.48 (m, 30H)
5	2.70 (br., 12H)	1.70 (br., 12H)	0.65 (br., 12H)	3.60 (br., 18H)	—	—
6	2.70 (br. t, 12H)	1.70 (br., 12H)	0.65 (br., 12H)	3.28 (s, 18H)	3.65 (m, 12H)	3.45 (m, 12H)
7	2.70 (br., 4H), 2.60 (br., 6H)	1.70 (br., 10H)	0.64[b] (br., 10H)	3.28[b] (br. s, 21H)	—	—
8	2.70 (br., 4H), 2.60 (br., 6H)	1.70 (br., 10H)	0.66[b] (br., 10H)	3.27 (s, 12H), 3.25 (br. s, 9H)	3.66; m, 14 H	3.43; m, 14H

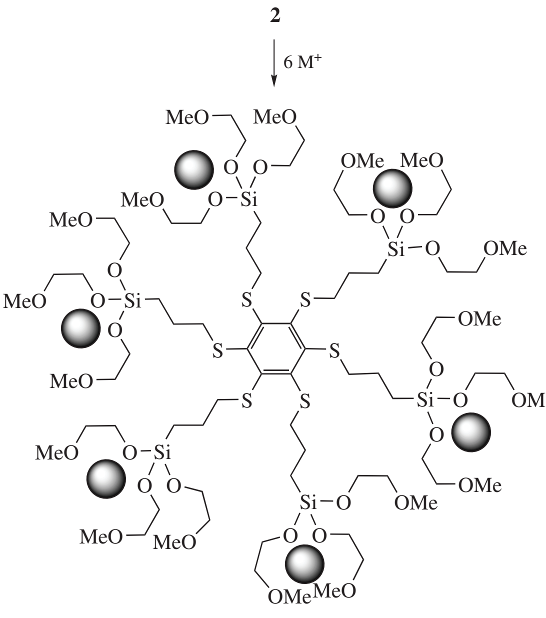
[a]q – quintet. [b]Partly resolved into two lines.

Table 2 ^{13}C NMR chemical shifts for compounds **1**–**8**.

Compound	^{13}C NMR, δ/ppm					
	$\mathrm{SCH_2}$	$\mathrm{CH_2}\mathit{CH}_2\mathrm{CH_2}$	$\mathrm{SiCH_2}$	$\mathrm{SiOCH_2}$	$\mathrm{CH_2}\mathit{CH}_2\mathrm{OMe}$	OMe	'core' carbons
1	35.82	28.27	8.35	—	—	51.40	148.32
2	35.82	28.30	9.39	61.72	73.69	58.43	148.30
3	33.19, 35.70, 35.78	28.28, 27.93	8.35, 8.29	—	—	51.40, 51.25	169.23, 159.11, 130.89
4	33.18, 35.70, 35.76	28.25, 27.90	9.27, 9.31	61.68, 61.79	73.68	58.44	169.23, 159.12, 130.90
5	35.71	28.23	8.18	—	—	51.23	147.02
6	35.68	28.22	9.21	61.77	73.72	58.70	147.19
7	31.95, 33.73, 33.84	27.27, 26.63	7.78, 8.03	—	—	51.18, 51.23	167.76, 159.00, 130.67
8	31.98, 33.71, 33.84	27.20, 26.59	8.64, 8.99	61.72, 61.84	73.12, 73.99	58.11, 58.61	167.72, 159.01, 130.67

of strong bands at 1060 and 890 cm^{-1}, characteristic of Si–O–Si compounds.

Partial hydrolysis of compounds **1**–**4** produces calix-like molecules. Unfortunately, the tendency to vitrification of products precludes obtaining them in crystalline form and *ipso facto* their X-ray analysis. Additionally, the presence of some impurities in the synthesized samples makes it difficult to confirm their structures. Therefore, structures **5**–**8**, presented in Schemes 1 and 2 are only propositions (*e.g.*, for **5** and **6** the formation of isomers containing two six-membered trisiloxane rings with a benzene ring between them is possible). Although the formation of oligomers and some non-organized species during hydrolysis is possible, the preferable intramolecular cyclization could be clearly confirmed by ESI-MS measurements;[‡] the signals corresponding to the proposed structures are the major ones in the spectra. Preorganisation of an octopus-like molecule before hydrolysis is probably caused by metal ions existing in solution as impurities.



Scheme 3 Complexation of M$^+$ ions by octopus-like Si podands.

The ^{23}Na NMR spectra of the mixtures of compounds **1**–**8** with NaClO$_4$ (1:2 L/M$^+$ molar ratio)[‡] have confirmed the complexing properties of the ligands. Compounds **1**–**4** due to the presence of five or six ions binding areas could form complexes of higher stoichiometry (up to 1:5 or 1:6, respectively; Scheme 3). Low values of complexation induced shifts (CIS) for compounds **1** and **3** result from the structure of the ligand arms. The Si–O group oxygen atoms are relatively ineffective as donors and, consequently, Na$^+$ ion binding constants are low. Compounds **2** and **4** form much stronger complexes with the ions due to the presence of ether oxygen atoms in their structure.

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References

1 E. Weber, in *Encyclopædia of Supramolecular Chemistry*, eds. J. L. Atwood and J. W. Steed, Marcel Dekker Inc., New York, 2004, vol. 2, p. 1106.
2 B. Łęska, R. Pankiewicz, G. Schroeder, B. Gierczyk and H. Maciejewski, *Catal. Commun.*, 2007, **9**, 821.
3 B. Łęska, B. Gierczyk, K. Eitner, V. Rybachenko and G. Schroeder, *Supramol. Chem.*, 2004, **16**, 303.
4 B. Gierczyk, B. Łęska, B. Brzezinski and G. Schroeder, *Supramol. Chem.*, 2002, **14**, 497.
5 G. Schroeder, B. Gierczyk, B. Łęska, G. Wojciechowski, R. Pankiewicz, B. Brzezinski and F. Bartl, *J. Mol. Struct.*, 2002, **9**, 607.
6 B. Gierczyk, G. Schroeder, G. Wojciechowski, B. Różalski, B. Brzezinski and G. Zundel, *Phys. Chem. Chem. Phys.*, 1999, **1**, 4897.

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[†] The NMR spectra were recorded at 293 K on a Varian Gemini 300 spectrometer using standard sequences and parameters. The ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR measurements were carried out in [^{2}H$_8$]THF, while the ^{23}Na NMR spectra were measured in [^{2}H$_3$]acetonitrile. For ^{1}H and ^{29}Si NMR spectra internal tetramethylsilane, for ^{19}F – internal CFCl$_3$ and for ^{23}Na NMR external 1 M solution of NaCl in D$_2$O were used as standards. Because of poor solubility, in all cases saturated samples were used. For ESI-MS spectra, a Waters/Micromass (Manchester, UK) ZQ mass spectrometer equipped with a Harvard Apparatus syringe pump was used. The sample solutions were prepared in acetonitrile at a concentration of 5×10^{-5} mol dm^{-3}. The samples were infused into the ESI source at a flow rate of 40 µl min^{-1}. The ESI source potentials were 3 kV on capillary, 0.5 kV on lens, 4 V on extractor and 40 V as cone voltage. The source and desolvation temperatures were 120 and 300 °C, respectively. Nitrogen was used as a nebulizing and desolvation gas at flow rates of 100 and 300 dm^3 h^{-1}, respectively. Elemental analysis was performed on a Vario EL III (Elementar, USA) analyser.

All compounds used for synthesis were dried and deoxygenated by standard procedures.

General method of synthesis of hexakis/pentakis 3-trialkoxysilylpropylthio benzene/pyridine **1**–**4**. To 0.06 mol of 3-(trialkoxysilyl)propanethiol dissolved in anhydrous THF (50 ml), 0.07 mol of NaH was added. The suspension was vigorously mixed for 25 min (until hydrogen release had stopped) and then 0.01 mol of hexafluorobenzene (or 0.012 mol of pentafluoropyridine) in anhydrous THF (10 ml) was added dropwise. After 24 h, the sodium fluoride precipitate was separated by centrifugation and the solvent was evaporated in a vacuum. The glassy residue was dried in a vacuum at 325 K. The yields of octopus-like compounds were above 95%, purity > 85% (NMR).

General procedure of the partial hydrolysis of compounds **1**–**4**. To 0.01 mol of hexakis[3-(trialkoxysilyl)propylthio]benzene or pentakis-[3-(trialkoxysilyl)propylthio]pyridine dissolved in 100 ml THF, a mixture of water (0.06 or 0.05 mol, respectively) in 100 ml THF was added. The solution was vigorously stirred for 10 h and the solvent was evaporated in a vacuum. The compounds were obtained as glassy solids. After evaporation, further dissolution was very difficult. The yield of the compounds was above 95%, purity > 80% (NMR, MS).

[‡] For **1**: ^{29}Si NMR, δ: –60.29. Found (%): C, 40.62; H, 7.31; S, 15.40. Calc. for $C_{42}H_{90}O_{18}S_6Si_6$ (%): C, 40.55; H, 7.29; S, 15.46. ^{23}Na NMR for **1** + NaClO$_4$, δ: –6.32.

For **2**: ^{29}Si NMR, δ: –61.92. Found (%): C, 46.03; H, 8.09; S, 9.36. Calc. for $C_{78}H_{162}O_{36}S_6Si_6$ (%): C, 45.99; H, 8.02; S, 9.44. ^{23}Na NMR for **2** + NaClO$_4$, δ: –6.24.

For **3**: ^{29}Si NMR, δ: –59.99, –60.11, –60.56. Found (%): C, 40.08; H, 7.27; N, 1.30; S, 15.22. Calc. for $C_{35}H_{75}NO_{15}S_5Si_5$ (%): C, 40.01; H, 7.19; N, 1.33; S, 15.26. ^{23}Na NMR for **3** + NaClO$_4$, δ: –6.32.

For **4**: ^{29}Si NMR, δ: –60.09, –61.17. Found (%): C, 46.02; H, 8.19; N, 0.77; S, 9.20. Calc. for $C_{65}H_{135}NO_{30}S_5Si_5$ (%): C, 45.62; H, 7.95; N, 0.82; S, 9.37. ^{23}Na NMR for **4** + NaClO$_4$, δ: –6.23.

For **5**: ^{29}Si NMR, δ: –68.78. Found (%): C, 37.50; H, 5.77; S, 19.51. Calc. for $C_{30}H_{54}O_{12}S_6Si_6$ (%): C, 37.24; H, 5.62; S, 19.88. ^{23}Na NMR for **5** + NaClO$_4$, δ: –6.28. MS (ESI), *m/z*: 504.0 $[C_{30}H_{54}S_6O_{12}Si_6Na_2]^{2+}$ = [L + 2Na$^+$].

For **6**: ^{29}Si NMR, δ: –69.56. Found (%): C, 41.33; H, 6.71; S, 15.34. Calc. for $C_{42}H_{78}O_{18}S_6Si_6$ (%): C, 40.95; H, 6.38; S, 15.62. ^{23}Na NMR for **6** + NaClO$_4$, δ: –6.20. MS (ESI), *m/z*: 638.0 $[C_{42}H_{78}O_{18}S_6Si_6Na_2]^{2+}$ = [L + 2Na$^+$].

For **7**: ^{29}Si NMR, δ: –67.90, –68.01. Found (%): C, 37.47; H, 6.00; N, 1.58; S, 18.45. Calc. for $C_{27}H_{51}NO_{11}S_5Si_5$ (%): C, 37.43; H, 5.93; N, 1.62; S, 18.50. ^{23}Na NMR for **7** + NaClO$_4$, δ: –6.29. MS (ESI), *m/z*: 455.5 $[C_{27}H_{51}NO_{11}S_5Si_5Na_2]^{2+}$ = [L + 2Na$^+$], 444.5 $[C_{27}H_{52}NO_{11}S_5Si_5Na]^{2+}$ = [L + Na$^+$ + H$^+$].

For **8**: ^{29}Si NMR, δ: –68.20, –69.01. Found (%): C, 42.15; H, 7.00; N, 1.09; S, 13.49. Calc. for $C_{41}H_{79}NO_{18}S_5Si_5$ (%): C, 41.92; H, 6.78; N, 1.19; S, 13.65. ^{23}Na NMR for **8** + NaClO$_4$, δ: –6.20. MS (ESI), *m/z*: 609.5 $[C_{41}H_{79}NO_{18}S_5Si_5Na_2]^{2+}$ = [L + 2Na$^+$], 598.5 $[C_{41}H_{80}NO_{18}S_5Si_5Na]^{2+}$ = [L + Na$^+$ + H$^+$].