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A general synthesis of five, six and seven-membered silasultones via dehydrative cyclisation

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Abstract—Five, six and seven-membered silasultones can be conveniently prepared in good yield by dehydrative cyclisation of siloxane disulphonic acids. The siloxanes are prepared by protodesilylation of the corresponding phenylsilane sulphonic acids. The sulphonate group is introduced either by free-radical sulphonation of vinyl silanes, or by S_N2 sulphite displacement of a long chain alkyl chloride.

1. Introduction

Silasultones are alicyclic structures containing the –Si–O–SO_2– molecular fragment. Silasultones have potential as monomers in polymer chemistry and are the cyclic equivalents of useful aliphatic reagents and catalysts such as trimethylsilyl trifluoromethanesulphonate.[1] However, the silasultones as a class of compounds has been little explored, and synthetic routes to them are severely limited. Pre-existing methods for the preparation of silasultones include only the formal insertion of SO_3 into silacyclobutanes,[2a–f] or the rearrangement of 1-silacyclopent-3-enes and 3-silabicyclo[3.2.1]hexanes mediated by Me_3SiOSO_2-Cl.[2g] The former method is restricted to the preparation of six-membered silasultones from silacyclobutanes† since attempted SO_3 insertion into larger non-strained sila-rings results in competitive attack at *exo*-Si–C bonds.[1c] The latter method generally results in mixtures of compounds, and necessarily leaves a(n) (unwanted) pendant alkene chain in the silasultone product. Herein, we describe the first general synthetic approach to silasultones of ring sizes of 5–7.‡

Keywords: Silasultone; Cyclisation; Siloxane; Protodesilylation; Sulphonation.
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† It seems reasonable to assume that the insertion of SO_3 into silacyclopropanes would yield 5-membered silasultones. To date, however, this approach has not been demonstrated.
‡ Two isolated examples in the patent literature make reference to the synthesis of a six-membered silasultone via dehydration of a disulphonic acid siloxane. Only one example is given in each case, the generality and scope is not demonstrated, limited experimental details are available and no characterising spectroscopic data is given. See: Ryan, J. W. (Dow Corning Corporation, U.S.A.) September 6th, **1966**, Patent no.: CA742243 and Hager, R.; Wolferseder, J.; Deubzer, B. (Wacker-Chemie, Gmbh) October 24th, **1991**, Patent no.: DE4135170.

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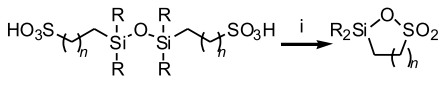
2. Results and discussion

Silasultones **1–6** were prepared by dehydrative cyclisation of disulphonic acid siloxanes (**7–12**) via vacuum sublimation (Scheme 1). This method provides the silasultones **1–6** in good-to-moderate yields (ca. 65–45%). It was found to be superior to attempted dehydrative cyclisation of the disulphonic acids by azeotropic removal of water in refluxing toluene which consistently generated a mixture of silasultones and the corresponding unreacted diacids even after extended heating (48 h).

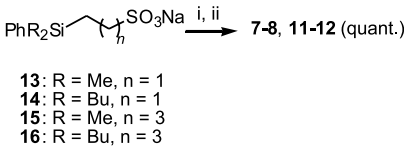
With the exception of disulphonic acids **9** and **10**, the diacids **7–8**, **11–12** were prepared by *ipso*-protodesilylation of the corresponding phenylsilanes **13–16** followed by treatment with a strong acid ion-exchange resin to ensure complete protonation of the sulphonates. This two-step procedure delivered the disulphonic acids in essentially quantitative yields (Scheme 2). Aqueous hydrochloric acid was a sufficiently acidic medium for *ipso*-protodesilylation of methylsilanes **13** and **15**, but the more sterically hindered butylsilanes **14** and **16** required the use of a more powerful acidic medium: aqueous hydrobromic acid was employed. Presumably this is a reflection of the increased steric clash



7: R = Me, n = 1
8: R = Bu, n = 1
9: R = Me, n = 2
10: R = Bu, n = 2
11: R = Me, n = 3
12: R = Bu, n = 3

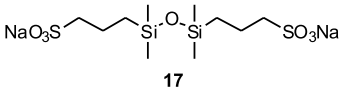
1: R = Me, n = 1 (67%)
2: R = Bu, n = 1 (67%)
3: R = Me, n = 2 (65%)
4: R = Bu, n = 2 (46%)
5: R = Me, n = 3 (48%)
6: R = Bu, n = 3 (45%)

Scheme 1. Reagents and conditions: (i) 0.02 mmHg, up to 250 °C.



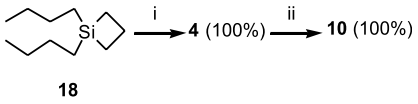
Scheme 2. Reagents and conditions: (i) aq. HX (X=Cl: **13**, **15**; X=Br **14**, **16**), reflux 24–36 h; (ii) Proton exchange resin, MeOH, H_2O.

between the butyl groups and the phenyl ring in the Wheland intermediate as the phenyl group undergoes *ipso*-protonation. Methylsiloxane **9**[1b] was prepared by Dowex-H mediated acid exchange of disodium disulphonate **17** obtained directly from a sulphonation reaction (vide infra). Butylsiloxane **10**[1b] was most conveniently prepared by hydrolysis of silasultone **4**, which can be obtained directly by sulphur trioxide insertion[1a] into butylsilacyclobutane **18**[3] using trimethylsilylchlorosulphonate (Scheme 3). Silasultone **4** formed in this manner is not pure, but hydrolysis to diacid **10** followed by diethyl ether washes removes the impurities and subsequent dehydrative cyclisation delivers pure **4**.

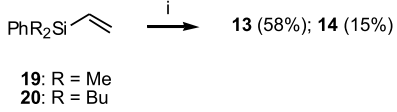


Two distinct methods were employed for the preparation of phenylsilanes **13**–**16**. Free-radical sulphonation of vinylsilanes **19** and **20** allowed access to silanes **13** and **14**. For the preparation of phenylsilanes **15** and **16**, S_N2 displacement of an appropriate alkylchloride with sulphite anion was employed. Vinyl silanes **19** and **20** were prepared by the Grignard reactions of phenylmagnesium bromide with chlorodimethylvinylsilane and double addition of butylmagnesium bromide to dichlorophenylvinylsilane,[4] respectively. Using a modified method of Weinreb,[5] regioselective free-radical sulphonation of dimethylvinylsilane **19** in a methanol/water mixture proceeded smoothly to give sodium sulphonate **13** in good yield (58%) (Scheme 4).[§] Under identical conditions, dibutylvinylsilane **20** failed to undergo sulphonation and starting material was recovered along with diphenyltetrabutylsiloxane (from vinyl protodesilylation). Attempts to perform this sulphonation instead under microwave conditions or sonication failed. Sulphonation in an *n*-propanol/water mixture proceeded to some degree giving a 15% isolated yield of sodium salt **14**. Clearly, the extra lipophilicity of the dibutyl substrate is problematic under the aqueous regime required for sodium hydrogen sulphite solubility. As a solution to this problem, we set about preparing a water-soluble dibutylvinylsilane substrate for the sulphonation reaction. We chose to functionalise the phenyl substituent since it is to be ultimately eliminated from the substrate during the protodesilylation reaction after the crucial free-radical sulphonation step. Accordingly, addition of the Grignard reagent of tertiary amine, (4-bromobenzyl)dimethylamine (**21**),[6] to dibutylmethoxyvinylsilane (**22**) gave phenylsilane **23** (81%) (Scheme 5). Quaternisation with methyliodide gave ammonium salt **24**

[§] In an initial approach to the preparation of silasultones, the direct extrusion of benzene via intramolecular *ipso*-protodesilylation of the acid of sodium sulphonate **13** was explored. After much experimentation only 2% of the desired silasutone **1** could be isolated by sublimation.



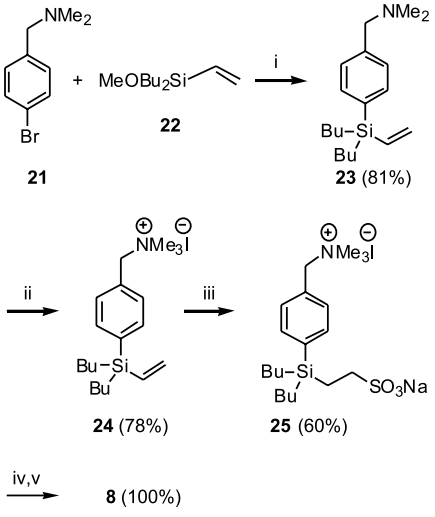
Scheme 3. Reagents and conditions: (i) Me_3SiOSO_2Cl, CH_2Cl_2, −78→−20 °C, 16 h; (ii) H_2O, 20 °C, 1 h.



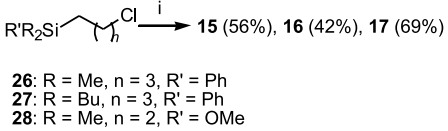
Scheme 4. Reagents and conditions: (i) $NaHSO_3$, cat. $PhCO_3{}^tBu$, H_2O, $R'OH$ (R'=Me: **19**; R'=Pr: **20**), reflux, 72 h.

(78%). Subsequent free-radical sulphonation using the original conditions gave the new sulphonate salt **25** in a pleasing 60% yield. Protodesilylation with aqueous HBr, followed by treatment with Dowex-H furnished the disulphonic acid **8** in quantitative yield.

For the longer chain sulphonates **15**–**17**, the sulphonate groups were introduced by nucleophilic displacement of chlorides **26**–**28**, respectively, with sodium sulphite (Scheme 6). Chloride **26** was prepared by the addition of Negishi's 1-chloro-4-lithiobutane reagent[7] to chlorodimethylphenylsilane. Dibutyl chloride **27** was obtained in good yield (85%) by the reaction of the alkyllithium with dibutylphenylsilyl triflate **29**. The latter was prepared by the action of triflic acid on dibutyldiphenylsilane[8] applying Matyjaszewski's method for the preparation of dimethylphenylsilyl triflate.[9] Commercially available methoxysilane **28** underwent smooth substitution reaction with sodium



Scheme 5. Reagents and conditions: (i) Mg, THF, reflux, 72 h; (ii) MeI, EtOH, 20 °C, 48 h; (iii) $NaHSO_3$, cat. $PhCO_3{}^tBu$, H_2O, MeOH, reflux, 72 h; (iv) aq. HBr, reflux, 32 h; (v) proton exchange resin, MeOH, H_2O.



Scheme 6. Reagents and conditions: (i) Na_2SO_3.

sulphite in refluxing water to give the disulphonate salt **17** directly (69%). The corresponding reaction of dimethylsilane **26** required the addition of a co-solvent (ethanol) for reasonable yields (56%). The more lipophilic dibutylsilane **27** gave only poor yields (ca. 14%) under these conditions, but the application of microwave irradiation (150 °C, 11250 mmHg, 1.5 h) gave the desired product in moderate yield (42%).

3. Conclusion

In conclusion we have shown that silasultones **1–6** can be prepared by a dehydrative cyclisation of the corresponding disulphonic acid siloxanes. In general, the latter compounds can be approached synthetically by *ipso*-protodesilylation of the corresponding phenylsilanes. The phenylsilanes can either be prepared by free-radical sulphonation of vinylsilanes or sulphite displacement of alkylchlorides as appropriate. These procedures allow for a general method for the synthesis of silasultones.

4. Experimental

4.1. General

Dichlorocyclobutasilane,[10] dichlorophenylvinylsilane,[4] bromobenzyldimethylamine (**21**),[6] 4-chloro-1-iodobutane[11] and dibutyldiphenylsilane[9] were prepared according to the published procedures. Trimethylsilylchlorosulfonate was distilled immediately before use. *N*′,*N*′,*N*,*N*-Tetramethylethane-1,2-diamine was dried over NaOH pellets and distilled immediately before use. DOWEX®50WX4-400 was activated using aqueous hydrochloric acid (1 M) and washed with water immediately before use. All other chemicals were used as received.

All reactions were performed under N_2 in dry solvents unless used in combination with water. Et_2O and THF were distilled from sodium and potassium, respectively, in the presence of benzophenone. EtOH, used during the synthesis of ammonium iodide **24**, was dried over sodium and distilled.

4.2. General procedure for silasultone formation

Disulphonic siloxane was placed in a sublimation apparatus under reduced pressure (0.02 mmHg) and gradually heated to 250 °C. The sublimed product was collected under N_2.

4.2.1. 3,3-Dimethyl-3-sila-1,3-propanesultone (1). Following the general procedure, silasultone **1** (0.11 g, 0.69 mmol, 67%) was obtained from disulphonic diacid **7** (0.18 g, 0.51 mmol) as a white solid: mp 95–105 °C; IR (CH_2Cl_2) ν_{max} 1344, 1257, 1172, 1070 cm^{-1}; ^1H NMR (270 MHz; $CDCl_3$) δ 3.35–3.27 (m, 2H, –C$H_2$$CH_2$Si), 1.53–1.44 (m, 2H, –CH_2Si), 0.51 (s, 6H, H_3C–Si) ppm; ^{13}C NMR (68 MHz; $CDCl_3$) δ 47.4 (–C$H_2$$CH_2$Si), 11.8 (–C$H_2$Si), −0.1 ($H_3C$–Si) ppm; ^{29}Si NMR (99 MHz; $CDCl_3$) δ 32.9 ppm; MS (CI^+) *m*/*z* 184 $[M+NH_4]^+$; HRMS (CI^+) *m*/*z* calculated for $C_4H_{14}NO_3SiS$ $[M+NH_4]^+$ 184.0464, found 184.0466; MS (EI^+) *m*/*z* 151 $[M-CH_3]^{+\cdot}$; HRMS (EI^+) *m*/*z* calculated for $C_3H_7O_3SiS$ $[M-CH_3]^{+\cdot}$ 150.9885, found 150.9893.

4.2.2. 3,3-Dibutyl-3-sila-1,3-propanesultone (2). Following the general procedure, silasultone **2** (97 mg, 0.58 mmol, 67%) was obtained from disulphonic diacid **8** (0.15 g, 0.29 mmol) as a colourless oil: IR (CH_2Cl_2) ν_{max} 1344, 1170, 1082 cm^{-1}; ^1H NMR (270 MHz; $CDCl_3$) δ 3.28 (t, 2H, ^3J=7.9 Hz, O_3SCH_2–), 1.46 (t, 2H, ^3J=7.9 Hz, $O_3SCH_2CH_2$–), 1.50–1.18 (m, 8H, alk), 0.96–0.77 (m, 10H, alk) ppm; ^{13}C NMR (68 MHz; $CDCl_3$) δ 47.5 (O_3SCH_2–), 26.0, 24.3, 13.7, 13.7, 7.7 ($O_3SCH_2CH_2$–) ppm; ^{29}Si NMR (99 MHz; $CDCl_3$) δ 34.8 ppm; MS (CI^+) *m*/*z* 268 $[M+NH_4]^+$; HRMS (CI^+) *m*/*z* calculated for $C_{10}H_{26}NO_3SiS$ $[M+NH_4]^+$ 268.1403, found 268.1407; MS (EI^+) *m*/*z* 193 $[M-C_4H_9]^{+\cdot}$; HRMS (EI^+) *m*/*z* calculated for $C_6H_{13}O_3SiS$ $[M-C_4H_9]^{+\cdot}$ 193.0355, found 193.0364.

4.2.3. 4,4-Dimethyl-4-sila-1,4-butanesultone (3). Following the general procedure, silasultone **3** (0.20 g, 1.11 mmol, 65%) was obtained from disulphonic diacid **9** (0.32 g, 0.86 mmol) as a white solid: mp ~40–50 °C; IR (CH_2Cl_2) ν_{max} 1349, 1257, 1169 cm^{-1}; ^1H NMR (270 MHz; $CDCl_3$) δ 3.10–3.00 (m, 2H, O_3SCH_2–), 2.30–2.15 (m, 2H, –CH_2–), 0.85–0.75 (m, 2H, –CH_2Si), 0.33 (s, 6H, H_3C–Si) ppm; ^{13}C NMR (68 MHz; $CDCl_3$) δ 50.7 (O_3SCH_2–), 19.0 (–CH_2–), 11.0 (–CH_2Si), −1.0 (H_3C–Si) ppm; ^{29}Si NMR (99 MHz; $CDCl_3$) δ 37.9 ppm; MS (CI^+) *m*/*z* 198 $[M+NH_4]^+$; HRMS (CI^+) *m*/*z* calculated for $C_5H_{16}NO_3SiS$ $[M+NH_4]^+$ 198.0620, found 198.0617; MS (EI^+) *m*/*z* 165 $[M-CH_3]^{+\cdot}$; HRMS (EI^+) *m*/*z* calculated for $C_4H_9O_3SiS$ $[M-CH_3]^{+\cdot}$ 165.0042, found 165.0044.

4.2.4. 4,4-Dibutyl-4-sila-1,4-butanesultone (4).[1a,b] Following the general procedure, silasultone **4** (95 mg, 0.36 mmol, 46%) was obtained from disulphonic diacid **10** (0.21 g, 0.39 mmol) as a colourless oil: IR (CH_2Cl_2) ν_{max} 1344, 1172, 1076 cm^{-1}; ^1H NMR (270 MHz; $CDCl_3$) δ 3.13–3.05 (m, 2H, O_3SCH_2–), 2.37–2.23 (m, 2H, $O_3SCH_2CH_2$–), 1.50–1.20 (m, 8H, alk), 1.00–0.75 (m, 12H, alk and $O_3SCH_2CH_2CH_2$–) ppm; ^{13}C NMR (68 MHz; $CDCl_3$) δ 50.9 (O_3SCH_2–), 26.1, 24.3, 19.3 ($O_3SCH_2CH_2$–), 13.7, 13.5, 8.3 ($O_3SCH_2CH_2CH_2$–) ppm; ^{29}Si NMR (99 MHz; $CDCl_3$) δ 36.1 ppm; MS (CI^+) *m*/*z* 282 $[M+NH_4]^+$; HRMS (CI^+) *m*/*z* calculated for $C_{11}H_{28}NO_3SiS$ $[M+NH_4]^+$ 282.1559, found 282.1559; MS (EI^+) *m*/*z* 207 $[M-C_4H_9]^{+\cdot}$; HRMS (EI^+) *m*/*z* calculated for $C_7H_{15}O_3SiS$ $[M-C_4H_9]^{+\cdot}$ 207.0511, found 207.0518. *Alternative synthesis of silasultone* **4**: to neat silacyclobutane **18** (2.0 g, 7.56 mmol) at −20 °C, trimethylsilylchlorosulfonate (1.17 mL, 7.56 mmol) was added dropwise over 10 min. The light orange mixture was allowed to warm to room temperature, stirred for 6 h at room temperature and the volatiles were removed under reduced pressure (0.02 mmHg) at 60–80 °C for 30 min to leave silasultone **4** (2.0 g, 7.56 mmol, 100%) as a colourless oil: data as reported above.

4.2.5. 5,5-Dimethyl-5-sila-1,5-pentanesultone (5). Following the general method, silasultone **5** (80 mg, 0.41 mmol, 48%) was obtained from disulphonic diacid **11** (0.18 g, 0.43 mmol) as a colourless oil: IR (CH_2Cl_2) ν_{max} 1351, 1257, 1171, 1070 cm^{-1}; ^1H NMR (270 MHz; $CDCl_3$)

δ 3.28–3.18 (m, 2H, O_3SCH_2–), 2.05–1.91 (m, 2H, $O_3SCH_2CH_2$–), 1.88–1.76 (m, 2H, –CH_2CH_2Si), 1.11–1.00 (m, 2H, –CH_2Si), 0.33 (s, 6H, H_3C–Si) ppm; ^{13}C NMR (68 MHz; $CDCl_3$) δ 53.6 (O_3SCH_2–), 26.0 ($O_3SCH_2CH_2$–), 21.6 (–CH_2CH_2Si), 16.7 (–CH_2Si), −1.2 (CH_3Si) ppm; ^{29}Si NMR (99 MHz; $CDCl_3$) δ 29.7 ppm; MS (CI^+) *m/z* 212 $[M+NH_4]^+$; HRMS (CI^+) *m/z* calculated for $C_6H_{14}NO_3SiS$ $[M+NH_4]^+$ 212.0777, found 212.0783; MS (EI^+) *m/z* 179 $[M-CH_3]^+$; HRMS (EI^+) *m/z* calculated for $C_5H_{11}O_3SiS$ $[M-CH_3]^+$ 179.0198, found 179.0206.

4.2.6. 5,5-Dibutyl-5-sila-1,5-pentanesultone (6). Following the general method, silasultone **6** (52 mg, 0.19 mmol, 45%) was obtained from disulphonic diacid **12** (0.12 g, 0.21 mmol) as a colourless oil: IR (CH_2Cl_2) ν_{max} 1376, 1160 cm^{-1}; ^1H NMR (270 MHz; $CDCl_3$) δ 3.27–3.17 (m, 2H, O_3SCH_2–), 2.04–1.90 (m, 2H, $O_3SCH_2CH_2$–), 1.90–1.75 (m, 2H, $O_3SCH_2CH_2CH_2$–), 1.44–1.26 (m, 8H, alk), 1.08–0.97 (m, 2H, $O_3SCH_2CH_2CH_2CH_2$–), 0.93–0.69 (m, 10H, alk) ppm; ^{13}C NMR (68 MHz; $CDCl_3$) δ 53.7 (O_3SCH_2–), 26.3, 26.0 ($O_3SCH_2CH_2$–), 24.7, 22.1 ($O_3SCH_2CH_2CH_2$–), 14.2 ($O_3SCH_2CH_2CH_2CH_2$–), 13.7, 13.6 ppm; ^{29}Si NMR (99 MHz; $CDCl_3$) δ 27.7 ppm; MS (CI^+) *m/z* 296 $[M+NH_4]^+$; HRMS (CI^+) *m/z* calculated for $C_{12}H_{30}NO_3SiS$ $[M+NH_4]^+$ 296.1716, found 296.1705; MS (EI^+) *m/z* 221 $[M-C_4H_9]^{+\cdot}$; HRMS (EI^+) *m/z* calculated for $C_8H_{17}O_3SiS$ $[M-C_4H_9]^{+\cdot}$ 221.0668, found 221.0677.

4.3. General procedure for the formation of disulphonic acids

(A) A solution of arylsilane (1/50, w/v) in an aqueous solution of HCl (12 M) (**13**, **15**) or HBr (12 M) (**14**, **16**) was heated at reflux. After 24 h (**13**, **15**) or 32 h (**14**, **16**) the mixture was allowed to cool to room temperature and concentrated. The resulting di-sodium salts were extracted with PrOH and the resultant liquor was concentrated to dryness. (B) A solution of the sodium salt (typically ~10% w/v) in MeOH:H_2O (1:1) was passed through a DOWEX®50WX4-400 proton exchange resin packed column (typically ~100 times as much mass of wet resin as sodium salt) at room temperature. The column was eluted further with MeOH:H_2O (1:1) (typically ~10 times as much volume as sodium salt solution) and H_2O (typically ~10 times as much volume as sodium salt solution). The eluate was concentrated to afford quantitatively the expected acid as a pale yellow oil. Chemical shifts of the protons from the sulphonic acid groups are not reported since they range variously and unpredictably between 13 and 7 ppm irrespective of the solvent or the sulphonic acid. These compounds also displayed two very broad, intense absorbances in their IR spectra at 3600–2500 and 2000–1500 wavenumbers.

4.3.1. 3,3,5,5-Tetramethyl-4-oxa-3,5-disilaheptane-1,7-disulphonic diacid (7). Following the general procedure above (Part A and Part B) using sodium sulphonate **13** (1.23 g, 4.62 mmol) gave disulphonic diacid **7** (0.84 g, 2.22 mmol, 96%) as a pale yellow oil: ^1H NMR (270 MHz; DMSO-d_6) δ 2.65–2.53 (m, 4H, HO_3SCH_2–), 0.93–0.80 (m, 4H, –CH_2Si), 0.03 (s, 12H, H_3C–Si) ppm; ^{13}C NMR (68 MHz; DMSO-d_6) δ 46.7 (HO_3SCH_2–), 13.5 (–CH_2Si), 0.7 (H_3C–Si) ppm; ^1H NMR (270 MHz; $CDCl_3$) δ 3.16–3.02 (m, 4H), 1.13–1.02 (m, 4H), 0.13 (s, 12H) ppm; MS (CI^+) *m/z* 350 $[M-H_2O+NH_4]^+$; HRMS (CI^+) *m/z* calculated for $C_8H_{24}NO_6Si_2S_2$ $[M-H_2O+NH_4]^+$ 350.0584, found 350.0579.

4.3.2. 3,3,5,5-Tetrabutyl-4-oxa-3,5-disilaheptane-1,7-disulphonic diacid (8). Following the general procedure above (Part A and Part B) using sodium sulphonate **14** (0.46 g, 1.31 mmol) or {2-[dibutyl-(*p*-trimethylammoniumiodide)-benzyl]-silyl}ethane sulfonate (**25**) (0.72 g, 1.31 mmol) gave disulphonic diacid **8** (0.34 g, 0.66 mmol, 100%) as a pale yellow oil: ^1H NMR (270 MHz; DMSO-d_6) δ 2.61–2.38 (m, 4H, HO_3SCH_2–), 1.35–1.17 (m, 16H, alk), 0.93–0.75 (m, 16H, alk and $HO_3SCH_2CH_2$–), 0.61–0.41 (m, 8H, alk) ppm; ^{13}C NMR (68 MHz; DMSO-d_6) δ 46.7 (HO_3SCH_2–), 26.4, 25.4, 15.1, 14.1, 11.0 ($HO_3SCH_2CH_2$–) ppm; ^1H NMR (270 MHz; $CDCl_3$) δ 2.96–2.75 (m, 4H), 1.45–1.16 (m, 16H), 1.09–0.92 (m, 4H), 0.92–0.76 (m, 12H), 0.66–0.45 (m, 8H) ppm; MS (CI^+) *m/z* 518 $[M-H_2O+NH_4]^+$; HRMS (CI^+) *m/z* calculated for $C_{20}H_{48}NO_6Si_2S_2$ $[M-H_2O+NH_4]^+$ 518.2462, found 518.2462.

4.3.3. 4,4,6,6-Tetramethyl-5-oxa-4,6-disilanonane-1,9-disulphonic diacid (9).[1b] Following the general procedure above (Part B only) using disodium disulfonate **17** (1.54 g, 3.64 mmol), gave disulphonic diacid **9** (1.38 g, 3.64 mmol, 100%) as a pale yellow oil: ^1H NMR (270 MHz; DMSO-d_6) δ 2.69 (br t, 4H, $^3J=7.6$ Hz, HO_3SCH_2–), 1.70–1.55 (m, 4H, –CH_2–), 0.55 (br t, 4H, $^3J=8.5$ Hz, –CH_2Si), 0.01 (s, 12H, H_3C–Si) ppm; ^{13}C NMR (68 MHz; DMSO-d_6) δ 54.9 (HO_3SCH_2–), 19.0 (–CH_2–), 17.4 (–CH_2Si), 0.8 (H_3C–Si) ppm; ^1H NMR (270 MHz; $CDCl_3$) δ 3.08–2.88 (m, 4H), 1.83–1.65 (m, 4H), 0.60–0.46 (m, 4H), −0.04 (s, 12H); MS (CI^+) *m/z* 378 $[M-H_2O+NH_4]^+$; HRMS (CI^+) *m/z* calculated for $C_{10}H_{28}O_6Si_2S_2$ $[M-H_2O+NH_4]^+$ 378.0897 found 378.0899.

4.3.4. 4,4,6,6-Tetrabutyl-5-oxa-4,6-disilanonane-1,9-disulphonic diacid (10).[1b] To silasultone **4** (2.0 g, 7.56 mmol) at room temperature was added H_2O (10 mL). The resulting solution was stirred for 1 h, and washed with Et_2O (3× 10 mL). The resulting mixture was dissolved in MeOH and concentrated to give disulphonic diacid **10** (2.1 g, 3.78 mmol, 100%) as an orange oil: ^1H NMR (270 MHz; DMSO-d_6) δ 2.66 (br t, 4H, $^3J=7.6$ Hz, HO_3SCH_2–), 1.73–1.54 (m, 4H, $HO_3SCH_2CH_2$–), 1.37–1.16 (m, 20H, alk and $HO_3SCH_2CH_2CH_2$–), 0.94–0.78 (m, 12H, alk), 0.65–0.40 (m, 8H, alk) ppm; ^{13}C NMR (68 MHz; DMSO-d_6) δ 55.3 (HO_3SCH_2–), 26.6, 25.4, 19.0 ($HO_3SCH_2CH_2$–), 15.4, 15.1 ($HO_3SCH_2CH_2CH_2$–), 14.1(H_3C–) ppm; ^1H NMR (270 MHz; $CDCl_3$) δ 3.01–2.83 (m, 4H), 1.91–1.66 (m, 4H), 1.52–1.18 (m, 20H), 1.02–0.71 (m, 12H), 0.70–0.45 (m, 8H) ppm; MS (CI^+) *m/z* 546 $[M-H_2O+NH_4]^+$, 281 $[M-C_{11}H_{25}O_4SSi]^+$; HRMS (CI^+) *m/z* calculated for $C_{22}H_{52}O_6NSi_2S_2$ $[M-H_2O+NH_4]^+$ 546.2775, found 546.2780.

4.3.5. 5,5,7,7-Tetramethyl-6-oxa-5,7-disilaundecane-1,11-disulphonic diacid (11). Following the general procedure above (Part A and Part B) using sodium sulphonate **15** (1.21 g, 4.11 mmol) gave disulphonic diacid

11 (0.84 g, 2.05 mmol, 100%) as a pale yellow oil: ^{1}H NMR (270 MHz; DMSO-d_6) δ 2.60–2.45 (m, 4H, HO_3SCH_2–), 1.71–1.49 (m, 4H, $HO_3SCH_2CH_2$–), 1.38–1.24 (m, 4H, –CH_2CH_2Si), 0.56–0.36 (m, 4H, –CH_2Si), 0.00 (s, 12H, H_3C–Si) ppm; ^{13}C NMR (68 MHz; DMSO-d_6) δ 51.9 (HO_3SCH_2–), 28.8 ($HO_3SCH_2CH_2$–), 22.8 (–CH_2CH_2Si), 18.4 (–CH_2Si), 1.0 (H_3C–Si) ppm; ^{1}H NMR (270 MHz; $CDCl_3$) δ 3.02–2.88 (m, 4H), 1.85–1.70 (m, 4H), 1.54–1.33 (m, 4H), 0.55–0.45 (m, 4H), 0.03 (s, 12H) ppm; MS (CI^+) m/z 406 $[M-H_2O+NH_4]^+$; HRMS (CI^+) m/z calculated for $C_{12}H_{32}NO_6Si_2S_2$ $[M-H_2O+NH_4]^+$ 406.1210, found 406.1201.

4.3.6. 5,5,7,7-Tetrabutyl-6-oxa-5,7-disilaundecane-1,11-disulphonic diacid (12). Following the general procedure above (Part A and Part B) using sodium sulphonate **16** (0.16 g, 0.42 mmol) gave disulphonic diacid **12** (0.12 g, 0.21 mmol, 100%) as a pale yellow oil: ^{1}H NMR (270 MHz; DMSO-d_6) δ 2.62–2.50 (m, 4H, HO_3SCH_2–), 1.68–1.55 (m, 4H, $HO_3SCH_2CH_2$–), 1.48–1.12 (m, 20H, alk and $HO_3SCH_2CH_2CH_2$–), 0.98–0.72 (m, 12H, alk), 0.63–0.35 (m, 12H, alk and $HO_3SCH_2CH_2CH_2CH_2$–) ppm; ^{13}C NMR (68 MHz; DMSO-d_6) δ 51.7 (HO_3SCH_2–), 29.0 ($HO_3SCH_2CH_2$–), 26.6, 25.6, 22.6 ($HO_3SCH_2CH_2CH_2$–), 15.7 ($HO_3SCH_2CH_2CH_2CH_2$–), 15.4, 14.2 (H_3C–) ppm; ^{1}H NMR (270 MHz; $CDCl_3$) δ 3.02–2.88 (m, 4H), 1.89–1.60 (m, 4H), 1.58–1.11 (m, 20H), 0.98–0.71 (m, 12H), 0.67–0.35 (m, 12H) ppm; MS (CI^+) m/z 574 $[M-H_2O+NH_4]^+$; HRMS (CI^+) m/z calculated for $C_{24}H_{56}NO_6Si_2S_2$ $[M-H_2O+NH_4]^+$ 574.3088, found 574.3090.

4.3.7. Sodium 2-(dimethylphenylsilyl)ethanesulfonate (13). An aqueous solution of HCl (3.3 mL, 12 M, 40 mmol) and then a solution of vinylsilane **19** (3.6 mL, 20 mmol) in MeOH (8 mL) followed by *t*-butylbenzoic peroxide (0.25 mL, 1.3 mmol) were added dropwise to a solution of Na_2SO_3 (5.0 g, 40 mmol) in H_2O (4 mL) over 10 min. The resulting biphasic suspension was heated at reflux. After 72 h, the mixture was allowed to cool to room temperature, washed with Et_2O (3×15 mL), and concentrated to dryness. The resulting salts were extracted with EtOH (5×20 mL) and the resultant liquor was concentrated to dryness to afford sodium sulfonate **13** (3.1 g, 11.6 mmol, 58%) as a white solid: mp 185–187 °C (decomp.); IR (DRIFTS) ν_{max} 1191 cm^{-1}; ^{1}H NMR (270 MHz; DMSO-d_6) δ 7.56–7.42 (m, 2H, Ar), 7.42–7.30 (m, 3H, Ar), 2.42–2.30 (m, 2H, NaO_3SCH_2–), 1.13–1.02 (m, 2H, –CH_2Si), 0.23 (s, 6H, H_3C–Si) ppm; ^{13}C NMR (68 MHz; DMSO-d_6) δ 138.8, 133.9, 129.6, 128.4, 40.9 (NaO_3SCH_2–), 11.6 (–CH_2Si), −2.7 (H_3C–Si) ppm; MS (FAB^-) m/z 243 $[M-Na]^-$. Sodium salt **13** could be converted to the corresponding monosulphonic acid (a yellow oil) using Part B of the general procedure above: ^{1}H NMR (270 MHz; DMSO-d_6) δ 7.53–7.42 (m, 2H, Ar), 7.40–7.29 (m, 3H, Ar), 2.93–2.78 (m, 2H, HO_3SCH_2–), 1.34–1.09 (m, 2H, –CH_2Si), 0.27 (s, 6H, H_3C–Si) ppm; ^{13}C NMR (68 MHz; DMSO-d_6) δ 138.4, 133.9, 129.7, 128.4, 47.3 (HO_3SCH_2–), 11.1 (–CH_2Si), −2.8 ppm (H_3C–Si); MS (CI^+) m/z 184 $[M-C_6H_6+NH_4]^+$. *ipso*-Desilylation–cyclisation was attempted: the sulphonic acid (22 g, 90 mmol) was heated to 250 °C in a short-path distillation apparatus under high vacuum (~0.02 mmHg) for 72 h and then allowed to cool to room temperature. From the receiving flask under N_2, silasultone **1** (0.27 g, 1.6 mmol, 2%) was collected as a white solid. Data as reported above.

4.3.8. Sodium 2-(dibutylphenylsilyl)ethanesulfonate (14). An aqueous solution of HCl (20 mL, 12 M, 244 mmol), a solution of vinylsilane **20** (20 g, 81 mmol) in PrOH (50 mL) followed by *t*-butyl benzoic peroxide (1.5 mL, 8 mmol) were added dropwise to a solution of Na_2SO_3 (31 g, 244 mmol) in H_2O (24 mL) over 10 min. The resulting biphasic suspension was heated at reflux. After 120 h, the mixture was allowed to cool to room temperature, washed with Et_2O (3×40 mL), and concentrated to dryness. The resulting salts were extracted with PrOH (5×10 mL) and the resultant liquor was concentrated to dryness to afford sodium sulfonate **14** (4.3 g, 12.2 mmol, 15%) as a white solid: mp 280 °C (decomp.); IR (DRIFTS) ν_{max} 1190 cm^{-1}; ^{1}H NMR (270 MHz; DMSO-d_6) δ 7.49–7.41 (m, 2H, Ar), 7.41–7.31 (m, 3H, Ar), 2.42–2.28 (m, 2H, NaO_3SCH_2–), 1.35–1.18 (m, 8H, alk), 1.18–1.06 (m, 2H, $NaO_3SCH_2CH_2$–), 0.91–0.69 (m, 10H, alk) ppm; ^{13}C NMR (68 MHz; DMSO-d_6) δ 137.3, 134.5, 129.7, 128.5, 47.0 (NaO_3SCH_2–), 26.8, 26.3, 14.3 (H_3C–), 12.2, 8.5 ($NaO_3SCH_2CH_2$–) ppm; MS (FAB^-) m/z 327 $[M-Na]^-$.

4.3.9. Sodium 4-(dimethylphenylsilanyl)butane-1-sulfonate (15). A vigorously stirred biphasic suspension of Na_2SO_3 (6.6 g, 44.9 mmol), chlorobutylsilane **26** (2.4 g, 10.5 mmol) and NaI (0.8 g, 5.2 mmol) in H_2O (25 mL) and EtOH (15 mL) was heated at reflux. After 72 h, the mixture was allowed to cool to room temperature, extracted with Et_2O (3×30 mL) and the aqueous was concentrated to dryness. The resulting salts were extracted with EtOH (5×30 mL) and the resultant liquor was concentrated. The resulting salts were washed with acetone (3×10 mL) and dried under vacuum to afford sodium sulfonate **15** (1.6 g, 5.9 mmol, 56%) as a white solid: mp 186–190 °C (decomp.); IR (DRIFTS) ν_{max} 1193 cm^{-1}; ^{1}H NMR (270 MHz; DMSO-d_6) δ 7.54–7.41 (m, 2H, Ar), 7.41–7.28 (m, 3H, Ar), 2.48–2.35 (m, 2H, NaO_3SCH_2–), 1.68–1.49 (m, 2H, $NaO_3SCH_2CH_2$–), 1.38–1.20 (m, 2H, –CH_2CH_2Si), 0.76–0.61 (m, 2H, –CH_2Si), 0.22 (s, 6H, H_3C–Si) ppm; ^{13}C NMR (68 MHz; DMSO-d_6) δ 139.4, 133.9, 129.4, 128.3, 51.7 (NaO_3SCH_2–), 29.4 ($NaO_3SCH_2CH_2$–), 23.5 (–CH_2CH_2Si), 15.6 (–CH_2Si), −2.4 (H_3C–Si) ppm; MS (FAB^-) m/z 271 $[M-Na]^-$.

4.3.10. Sodium 4-(dibutylphenylsilanyl)butane-1-sulfonate (16). A biphasic suspension of Na_2SO_3 (0.7 g, 5.6 mmol), (4-chlorobutyl)silane **27** (0.32 g, 1 mmol) in H_2O (1.5 mL) and EtOH (1.5 mL) was heated at 150 °C at 11,250 mmHg for 60 min using a microwave reactor. After cooling, the biphasic suspension was washed with Et_2O (3×5 mL) and the aqueous layer was concentrated to dryness. The resulting salts were extracted with EtOH (3×10 mL) and PrOH (3×10 mL) and the resultant combined liquors were concentrated to dryness to afford sodium sulfonate **16** (0.16 g, 0.42 mmol, 42%) as a white solid: mp 240–245 °C (decomp); IR (DRIFTS) ν_{max} 1190 cm^{-1}; ^{1}H NMR (270 MHz; DMSO-d_6) δ 7.48–7.39 (m, 2H, Ar), 7.37–7.27 (m, 3H, Ar), 2.52–2.39 (m, 2H, NaO_3SCH_2–), 1.71–1.53 (m, 2H, $NaO_3SCH_2CH_2$–), 1.39–1.12 (m, 10H, alk and $NaO_3SCH_2CH_2CH_2$–), 0.90–0.65 (m, 12H, alk and $NaO_3SCH_2CH_2CH_2CH_2$–) ppm; ^{13}C NMR (68 MHz; DMSO-d_6)

δ 137.8, 134.4, 129.5, 128.4, 51.9 (NaO_3SCH_2–), 29.7 ($NaO_3SCH_2CH_2$–), 26.8, 26.3, 23.6 ($NaO_3SCH_2CH_2CH_2$–), 14.3 (H_3C–), 12.6 ($NaO_3SCH_2CH_2CH_2CH_2$–), 12.3 ppm; MS (FAB$^-$) *m/z* 355 $[M-Na]^-$.

4.3.11. Disodium 4,4,6,6-tetramethyl-5-oxa-4,6-disilanonane-1,9-disulfonate (17). A vigorously stirred biphasic suspension of Na_2SO_3 (25.2 g, 200 mmol), (3-chloropropyl)methoxydimethylsilane **28** (6.68 g, 40.0 mmol) in H_2O (135 mL) was heated at reflux. After 96 h, the mixture was allowed to cool to room temperature, extracted with Et_2O (3×100 mL) and the aqueous was concentrated to dryness under vacuum. The resulting salts were extracted with EtOH (5×100 mL) and the resultant liquor was concentrated to dryness under vacuum to afford disodium disulfonate **17** (5.83 g, 13.8 mmol, 69%) as a white solid: mp>350 °C; IR (DRIFTS) ν_{max} 1213, 1184 cm^{-1}; ^1H NMR (270 MHz; D_2O) δ 3.11–2.96 (m, 4H, NaO_3SCH_2–), 2.00–1.84 (m, 4H, –CH_2–), 0.88–0.74 (m, 4H, –CH_2Si), 0.26 (s, 12H, H_3C–Si) ppm; ^{13}C NMR (68 MHz; D_2O) δ 54.4 (NaO_3SCH_2–), 18.6 (–CH_2–), 16.3 (–CH_2Si), −1.00 (H_3C–Si) ppm; ^1H NMR (270 MHz; DMSO-d_6) δ 2.47–2.41 (m, 4H), 1.70–1.55 (m, 4H), 0.51–0.44 (m, 4H), −0.02 (s, 12H) ppm; ^{13}C NMR (68 MHz; DMSO-d_6) δ 55.4, 19.5, 18.0, 1.0 ppm; MS (FAB$^-$) *m/z* 399 $[M-Na]^-$, 319 $[M-SO_3Na]^-$.

4.3.12. Dibutylsilacyclobutane (18).[3] To a stirred suspension of Mg (1.54 g, 63.3 mmol) in Et_2O (20 mL) at room temperature was added dropwise a solution of 4-bromobutane (6.8 mL, 63.3 mmol) in Et_2O (10 mL) over 30 min so as to maintain a gentle reflux. After a further 3 h at room temperature, the solution of Grignard reagent was decanted from the remaining Mg and added dropwise to a solution of dichlorocyclobutasilane[10] (2.5 mL, 21.1 mmol) in Et_2O (18 mL) at room temperature over 30 min. The resulting mixture was stirred at room temperature for 48 h, aqueous NH_4Cl solution (40 mL) was added, the layers were separated and the aqueous layer was extracted with Et_2O (3×40 mL). The combined organics were dried over $MgSO_4$, concentrated and distilled under reduced pressure to afford silane **18** (3.4 g, 18.3 mmol, 87%) as a colourless oil: bp 104–108 °C/4 mmHg (lit.[1e] 63 °C/0.3 mmHg); IR (neat) ν_{max} 2929, 2872, 2858, 2798 cm^{-1}; ^1H NMR (270 MHz; $CDCl_3$) δ 2.05 (quintuplet, 2H, ^3J=8.3 Hz, $Si(CH_2)_2CH_2$), 1.50–1.22 (m, 8H, –$CH_2CH_2CH_3$), 0.95 (t, 4H, ^3J=8.3 Hz, $Si(CH_2)_2CH_2$), 0.90 (t, 6H, ^3J=6.9 Hz, –CH_3), 0.80–0.61 (m, 4H, –$CH_2CH_2CH_2CH_3$) ppm; ^{13}C NMR (68 MHz; $CDCl_3$) δ 26.5, 26.1, 18.5 ($Si(CH_2)_2CH_2$), 14.9 ($Si(CH_2)_2CH_2$), 13.9 (–CH_3), 12.2 ppm; MS (CI$^+$) *m/z* 202 $[M+NH_4]^+$.

4.3.13. Dimethylphenylvinylsilane (19). To a suspension of Mg (4.0 g, 165 mmol) and a crystal of iodine in Et_2O (20 mL) at room temperature, bromobenzene (1.2 mL, 11.5 mmol) was added dropwise over 20 min until decolouration was observed. The remaining bromobenzene (4.6 mL, 43.5 mmol) was added dropwise over 1 h to maintain a gentle reflux. After a further 1 h at room temperature, the solution of Grignard reagent was decanted from the remaining Mg and added dropwise over 1 h to a solution of chlorodimethylvinylsilane (7.1 mL, 50 mmol) in Et_2O (40 mL) at room temperature. After a further 16 h, aqueous NH_4Cl solution (40 mL) was added. The layers were separated and the aqueous layer was extracted with Et_2O (3×20 mL). The organics were combined, dried over $MgSO_4$, concentrated and distilled under reduced pressure to give silane **19** (6.1 g, 2.3 mmol, 75%) as a colourless oil: bp 90–93 °C/40 mmHg (lit.[12] 82 °C/20 mmHg); IR (neat) ν_{max} 1592, 1249 cm^{-1}; ^1H NMR (270 MHz; $CDCl_3$) δ 7.68–7.55 (m, 2H, Ar), 7.50–7.37 (m, 3H, Ar), 6.60 (dd, 1H, ^3J=14.5, 20.0 Hz, Si–C*H*=$CH_{cis}H_{trans}$), 6.13 (dd, 1H, ^2J=3.9 Hz, ^3J=14.5 Hz, Si–CH=$CH_{cis}H_{trans}$), 5.83 (dd, 1H, ^2J=3.9 Hz, ^3J=20.0 Hz, Si–CH=$CH_{cis}H_{trans}$), 0.43 (s, 6H, H_3C–Si) ppm; ^{13}C NMR (68 MHz; $CDCl_3$) δ 138.6, 138.1, 134.0, 133.0, 129.1, 127.9, −2.8 (H_3C–Si) ppm; ^1H NMR (270 MHz; DMSO-d_6) δ 7.54–7.47 (m, 2H), 7.38–7.31 (m, 3H), 6.29 (dd, 1H, ^3J=14.5, 20.0 Hz), 6.04 (dd, 1H, ^2J=3.9 Hz, ^3J=14.5 Hz), 5.74 (dd, 1H, ^2J=3.9 Hz, ^3J=20.0 Hz), 0.32 (s, 6H); ^{13}C NMR (68 MHz; DMSO-d_6) δ 138.4, 138.2, 134.1, 133.4, 129.6, 128.3, -2.5 ppm; MS (CI$^+$) *m/z* 180 $[M+NH_4]^+$, 163 $[M+H]^+$.

4.3.14. Dibutylphenylvinylsilane (20). To a stirred suspension of Mg (7.3 g, 300 mmol) in Et_2O (60 mL) at room temperature, a solution of 4-bromobutane (16.1 mL, 150 mmol) in Et_2O (16 mL) was added dropwise over 1.5 h to maintain a gentle reflux. After a further 3 h at room temperature, the solution of Grignard reagent was decanted from the remaining Mg and added dropwise over 30 min to a solution of dichlorophenylvinylsilane[4] (10.2 mL, 50 mmol) in Et_2O (20 mL) at room temperature. After 48 h at room temperature, a saturated aqueous NH_4Cl solution (100 mL) was added. The layers were separated, and the aqueous layer was extracted with Et_2O (3×100 mL). The organics were combined, dried over $MgSO_4$, concentrated and the residual oil was distilled under vacuum to afford silane **20** (10.5 g, 42 mmol, 85%) as a colourless oil: bp 120–125 °C/4 mmHg; IR (neat) ν_{max} 1593 cm^{-1}; ^1H NMR (270 MHz; $CDCl_3$) δ 7.75–7.51 (m, 2H, Ar), 7.51–7.35 (m, 3H, Ar), 6.37 (dd, 1H, ^3J=14.8, 19.9 Hz, Si–C*H*=$CH_{cis}H_{trans}$), 6.19 (dd, 1H, ^2J=4.4 Hz, ^3J=14.8 Hz, Si–CH=$CH_{cis}H_{trans}$), 5.83 (dd, 1H, ^2J=4.4 Hz, ^3J=19.9 Hz, Si–CH=$CH_{cis}H_{trans}$), 1.53–1.28 (m, 8H, alk), 1.10–0.81 (m, 10H, alk) ppm; ^{13}C NMR (68 MHz; $CDCl_3$) δ 136.0, 134.4, 133.7, 133.7, 128.9, 127.7, 26.7, 26.0, 13.7 (H_3C–), 12.2 ppm; MS (EI$^+$) *m/z* 246 $[M]^{+\cdot}$, 189 $[M-C_4H_9]^{+\cdot}$; HRMS (EI$^+$) *m/z* calculated for $C_{16}H_{26}Si$ $[M]^{+\cdot}$ 246.1804, found 246.1792.

4.3.15. Dibutylmethoxyvinylsilane (22). To a stirred suspension of Mg (5.8 g, 240 mmol) in Et_2O (50 mL) at room temperature, a solution of 4-bromobutane (19.8 mL, 184 mmol) in Et_2O (25 mL) was added dropwise over 1.5 h. After a further 3 h at room temperature, the solution of Grignard reagent was decanted from the remaining Mg and added dropwise over 30 min to a solution of trimethoxyvinylsilane (12.2 mL, 80 mmol) in Et_2O (20 mL) at room temperature. The resulting beige suspension was stirred for a further 18 h at room temperature. The salts were filtered off and washed with petroleum ether (3×20 mL), the filtrate concentrated, petroleum ether (60 mL) was added and the resulting salts were filtered off and washed repeatedly with petroleum ether (3×20 mL). The combined filtrates were concentrated and distilled under reduced pressure to afford methoxysilane **22** (2.5 g, 12.2 mmol, 72%) as a colourless oil: bp 80–82 °C/4 mmHg; IR (neat) ν_{max} 1593 cm^{-1}; ^1H

NMR (270 MHz; $CDCl_3$) δ 6.06 (m, 1H), 6.04 (m, 1H), 5.77 (m, 1H), 3.44 (s, 3H, H_3C–O), 1.41–1.20 (m, 8H, alk), 0.96–0.76 (m, 6H, alk), 0.76–0.58 (m, 4H, alk) ppm; ^{13}C NMR (68 MHz; $CDCl_3$) δ 135.3, 133.9, 50.8 (H_3C–O), 26.5, 25.2, 13.8, 12.8 ppm; MS (CI^+) *m/z* 218 $[M+NH_4]^+$, 201 $[M+H]^+$, 186 $[M-MeOH+NH_4]^+$; HRMS (CI^+) *m/z* calculated for $C_{11}H_{28}NOSi$ $[M+NH_4]^+$ 218.1940, found 218.1942.

4.3.16. [4-(Dibutylvinylsilyl)benzyl]dimethylamine (23). To a suspension of Mg (2.3 g, 96.0 mmol) in THF (60 mL) under reflux, (4-bromobenzyl)dimethylamine (**21**)[6] (10.3 g, 48.0 mmol) was added dropwise over 2 h. After a further 30 min under reflux, methoxysilane **22** (4.8 g, 24.0 mmol) was added dropwise over 1 h. After a further 72 h at reflux, the reaction mixture was allowed to cool to room temperature and saturated aqueous NH_4Cl solution (60 mL) was added. The layers were separated and the aqueous layer was extracted with Et_2O (3×60 mL). The organics were combined, dried over $MgSO_4$, concentrated, and the volatiles were removed under reduced pressure (4 mmHg) to leave amine **23** (5.9 g, 19.4 mmol, 81%) as a yellow oil: IR (neat) ν_{max} 1601 cm^{-1}; ^1H NMR (270 MHz; $CDCl_3$) δ 7.47 (d, 2H, ^3J=6.8 Hz, Ar), 7.27 (d, 2H, ^3J=6.8 Hz, Ar), 6.27 (dd, 1H, ^3J=10.6, 19.8 Hz, Si–C*H*=CH$_{cis}$H$_{trans}$), 6.12 (dd, 1H, ^2J=4.3 Hz, ^3J=10.6 Hz, Si–CH=CH$_{cis}$*H*$_{trans}$), 5.76 (dd, 1H, ^2J=4.3 Hz, ^3J=19.8 Hz, Si–CH=C*H*$_{cis}$H$_{trans}$), 3.41 (s, 2H, ArC*H*$_2$–), 2.22 (s, 6H, –N(C*H*$_3$)$_2$), 1.42–1.20 (m, 8H, alk), 0.95–0.78 (m, 10H, alk) ppm; ^{13}C NMR (68 MHz; $CDCl_3$) δ 139.5, 136.2, 135.3, 134.5, 133.7, 128.6, 64.5 (Ar*C*H$_2$–), 45.5 (–N(*C*H$_3$)$_2$), 26.7, 26.0, 13.8, 12.3 ppm; MS (CI^+) *m/z* 304 $[M+H]^+$; HRMS (CI^+) *m/z* calculated for $C_{19}H_{34}NSi$ $[M+H]^+$ 304.2461, found 304.2470.

4.3.17. [4-(Dibutylvinylsilyl)benzyl]trimethylammonium iodide (24). To a solution of amine **23** (5.8 g, 19.1 mmol) in EtOH (40 mL) at 0 °C, MeI (1.3 mL, 20.0 mmol) was added dropwise over 30 min. The solution was allowed to warm to room temperature and stirred for 48 h. To the resulting mixture was added Et_2O (60 mL) and the precipitate obtained was filtered off and washed with Et_2O (2× 30 mL). The residue was dried under vacuum for 4 h to give ammonium iodide **24** (6.7 g, 15.0 mmol, 78%) as a white solid: mp 195–196 °C (decomp.); IR (DRIFTS) ν_{max} 1591 cm^{-1}; ^1H NMR (270 MHz; DMSO-d_6) δ 7.61 (d, 2H, ^3J=7.8 Hz, Ar), 7.55 (d, 2H, ^3J=7.8 Hz, Ar), 6.25 (dd, 1H, ^3J=10.6, 19.8 Hz, Si–C*H*=CH$_{cis}$H$_{trans}$), 6.12 (dd, 1H, ^2J=4.4 Hz, ^3J=10.6 Hz, Si–CH=CH$_{cis}$*H*$_{trans}$), 5.76 (dd, 1H, ^2J=4.4 Hz, ^3J=19.8 Hz, Si–CH=C*H*$_{cis}$H$_{trans}$), 4.57 (s, 2H, ArC*H*$_2$–), 3.05 (s, 9H, –N^+(C*H*$_3$)$_3$), 1.40–1.13 (m, 8H, alk), 0.94–0.70 (m, 10H, alk) ppm; ^{13}C NMR (68 MHz; DMSO-d_6) δ 139.5, 135.8, 135.1, 135.1, 132.7, 129.6, 68.1 (Ar*C*H$_2$–), 52.4 (–N^+(*C*H$_3$)$_3$), 26.5, 26.0, 14.2, 11.9 ppm; MS (FAB^+) *m/z* 318 $[M-I]^+$; HRMS (FAB^+) *m/z* calculated for $C_{20}H_{36}NSi$ $[M-I]^+$ 318.2617, found 318.2633.

4.3.18. Sodium {2-[dibutyl-(*p*-trimethylammonium iodide)benzyl]silyl}ethane sulfonate (25). To a solution of Na_2SO_3 (6.1 g, 48.7 mmol) in H_2O (9 mL), an aqueous solution of HCl (4.1 mL, 12 M, 48.7 mmol) was added dropwise over 10 min. A solution of vinylsilane **24** (6.6 g, 14.8 mmol) in MeOH (9 mL) was added dropwise over 5 min followed by *t*-butylbenzoic peroxide (250 μL, 0.4 mmol). The resulting mixture was heated at reflux. After 72 h, the mixture was allowed to cool to room temperature, washed with Et_2O, and concentrated to dryness. The resulting salts were extracted with EtOH (5×20 mL) and the resultant liquor was concentrated to dryness to afford sodium sulfonate **25** (4.8 g, 8.9 mmol, 60%) as a white solid: mp >350 °C; IR (DRIFTS) υ_{max} 1193 cm^{-1}; ^1H NMR (270 MHz; DMSO-d_6) δ 7.72–7.50 (m, 4H, Ar), 4.56 (s, 2H, ArC*H*$_2$–), 3.03 (s, 9H, –N^+(C*H*$_3$)$_3$), 2.43–2.30 (m, 2H, NaO_3SCH_2–), 1.41–1.21 (m, 8H, alk), 1.22–1.13 (m, 2H, $NaO_3SCH_2CH_2$–), 0.93–0.69 (m, 10H, alk) ppm; ^{13}C NMR (68 MHz; DMSO-d_6) δ 139.9, 134.8, 132.7, 129.4, 68.1 (Ar*C*H$_2$–), 52.4 (–N^+(*C*H$_3$)$_3$), 46.8 (NaO_3SCH_2–), 26.5, 26.0, 14.1 (H_3CCH_2–), 11.8, 8.1 ($NaO_3SCH_2CH_2$–) ppm; MS (FAB^+) *m/z* 422 $[M-I]^+$; HRMS (FAB^+) *m/z* calculated for $C_{20}H_{37}NO_3NaSiS$ $[M-I]^+$ 422.2179, found 422.2161.

4.3.19. Dimethyl(4-chlorobutyl)phenylsilane (26). To a solution of *t*-BuLi (39.5 mL, 1.55 M in pentane, 60.8 mmol) in Et_2O (20 mL) at −78 °C, 1-chloro-4-iodobutane[11] (3.8 mL, 30.4 mmol) was added dropwise over 5 min, and the solution was stirred for a further 1 h. A solution of chlorodimethylphenylsilane (4.2 mL, 25.3 mmol) in Et_2O (20 mL) was added dropwise over a 10 min period. The resulting solution was allowed to warm to room temperature and stirred for 16 h. Aqueous NH_4Cl solution (40 mL) was added and the layers were separated. The aqueous layer was extracted with Et_2O (3×40 mL) and the combined organics were washed with brine (60 mL), dried over $MgSO_4$, concentrated and distilled to afford (4-chlorobutyl)silane **26** (4.9 g, 21.5 mmol, 85%) as a colourless oil: bp 138–140 °C/4 mmHg (lit.[13] bp 87–89 °C/1 mmHg); ^1H NMR (270 MHz; $CDCl_3$) δ 7.63–7.47 (m, 2H, Ar), 7.46–7.32 (m, 3H, Ar), 3.54 (t, 2H, ^3J=6.7 Hz, ClC*H*$_2$–), 1.81 (quintuplet, 2H, ^3J=6.7 Hz, $ClCH_2CH_2$–), 1.58–1.40 (m, 2H, –C*H*$_2$-CH_2Si), 0.86–0.72 (m, 2H, –C*H*$_2$Si), 0.31 (s, 6H, H_3C–Si) ppm; ^{13}C NMR (68 MHz; $CDCl_3$) δ 139.2, 133.6, 129.0, 127.9, 44.7, 36.2, 21.3, 15.1, −3.0 ppm; ^1H NMR (270 MHz; DMSO-d_6) δ 7.57–7.40 (m, 2H), 7.40–7.24 (m, 3H), 3.55 (t, 2H, ^3J=6.6 Hz), 1.68 (quintuplet, 2H, ^3J=6.6 Hz), 1.51–1.24 (m, 2H), 0.78–0.62 (m, 2H), 0.21 (s, 6H) ppm; ^{13}C NMR (68 MHz; DMSO-d_6) δ 139.1, 133.8, 129.4, 128.3, 45.4, 36.1, 21.2, 14.8, −2.5 ppm; MS (CI^+) *m/z* 246 and 244 $[M+NH_4]^+$; MS (EI^+) *m/z* 213 and 211 $[M-CH_3]^{+\cdot}$, 135 $[M-C_4H_8Cl]^{+\cdot}$, 172 and 170 $[M-C_4H_8]^{+\cdot}$, 157 and 155 $[M-C_5H_{11}]^{+\cdot}$.

4.3.20. Dibutyl(4-chlorobutyl)phenylsilane (27). To a solution of *t*-BuLi (43.8 mL, 1.60 M in pentane, 70.0 mmol) in Et_2O (20 mL) at −78 °C, 1-chloro-4-iodobutane[11] (4.25 mL, 35.0 mmol) was added dropwise over 5 min. After a further 1 h, silylsulfonate **29** (11.7 g, 31.8 mmol) was added dropwise over 10 min. The solution was allowed to warm to −20 °C and *N*′,*N*′,*N*,*N*-tetramethylethane-1,2-diamine (10.4 mL, 70.0 mmol) was added dropwise over 5 min. The solution was allowed to warm to room temperature and stirred for a further 32 h. Aqueous NH_4Cl solution (60 mL) was added, the layers were separated and the aqueous layer was extracted with Et_2O (3×60 mL). The combined organics were washed with an aqueous HCl solution (3×150 mL, 2 M), brine (150 mL),

dried over $MgSO_4$ and concentrated to afford (4-chlorobutyl)silane **27** (9.3 g, 30 mmol, 94%) as a light yellow oil: IR (neat) ν_{max} 3068, 3049, 2956, 2924, 2858 cm^{-1}; ^1H NMR (270 MHz; $CDCl_3$) δ 7.52–7.44 (m, 2H, Ar), 7.40–7.31 (m, 3H, Ar), 3.52 (t, 2H, $^3J=7.0$ Hz, $ClCH_2$–), 1.79 (quintuplet, 2H, $^3J=7.0$ Hz, $ClCH_2CH_2$–), 1.54–1.40 (m, 2H, $ClCH_2CH_2CH_2$–), 1.40–1.15 (m, 8H, alk), 0.99–0.72 (m, 12H, alk and $ClCH_2CH_2CH_2CH_2$–) ppm; ^{13}C NMR (68 MHz; $CDCl_3$) δ 137.7, 134.1, 128.8, 127.8, 44.6 ($ClCH_2$–), 36.4 ($ClCH_2CH_2$–), 26.8, 26.1, 21.2 ($ClCH_2CH_2CH_2$–), 13.8, 12.1, 11.8 ($ClCH_2CH_2CH_2CH_2$–) ppm; MS (CI^+) *m/z* 330 and 328 $[M+NH_4]^+$; HRMS (CI^+) *m/z* calculated for $C_{18}H_{35}NSi^{35}Cl$ $[M+NH_4]^+$ 328.2227, found 328.2226; HRMS (CI^+) *m/z* calculated for $C_{18}H_{35}NSi^{37}Cl$ $[M+NH_4]^+$ 330.2198, found 330.2211.

4.3.21. Dibutylphenylsilyl trifluoromethanesulfonate (29). To stirred neat dibutyldiphenylsilane[8] (10.9 mL, 35.0 mmol) at −20 °C, trifluoromethylsulphonic acid (2.81 mL, 31.8 mmol) was added dropwise over 10 min. The resulting mixture was allowed to warm to room temperature and stirred for a further 4 h to afford silylsulfonate **29** (11.7 g, 31.8 mmol, 100%) as a light orange oil: ^1H NMR (270 MHz; $CDCl_3$) δ 7.76–7.66 (m, 2H, Ar), 7.66–7.45 (m, 3H, Ar), 1.63–1.37 (m, 8H, alk), 1.10–0.98 (m, 10H, alk) ppm; ^{13}C NMR (68 MHz; $CDCl_3$) δ 135.0, 133.8, 131.6, 128.4, 118.6 (q, $^1J_{CF}=318$ Hz, CF_3), 26.2, 24.4, 13.5, 13.3 ppm; MS (EI^+) *m/z* 368 $[M]^{+\cdot}$, 311 $[M-C_4H_9]^{+\cdot}$, 181 $[M-C_4H_9\text{-}F_3CSO_3+F]^{+\cdot}$, HRMS ($EI^+$) calculated for $C_{15}H_{23}O_3F_3SSi$ $[M]^{+\cdot}$ 368.1089, found 368.1095.

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