Supplementary Material for Organic & Biomolecular Chemistry

Supporting Information

An efficient method for synthesising unsymmetrical silaketals: substrates for ring-closing, including macrocycle-closing, metathesis

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General Experimental Background

All non-aqueous reactions were performed under an atmosphere of nitrogen. Water-sensitive reactions were performed in oven-dried glassware, cooled under nitrogen before use, or flame-dried, and cooled, under vacuum if stated. Solvents were removed under reduced pressure using either a Büchi rotary evaporator and a Vacuubrand PC2001 Vario diaphragm pump, or a Genevac HT-4 evaporation system. Solvents were distilled before use when necessary and possible according to scale. Dichloromethane was freshly distilled from calcium hydride. Triethylamine was purified by refluxing with potassium hydroxide and potassium carbonate, followed by distillation under nitrogen, and was stored over potassium hydroxide. Ether refers to diethyl ether and petrol refers to petroleum spirit (b.p. 40-60 °C). Commercially available starting materials were obtained from Sigma–Aldrich or Alfa Aesar.

Flash column chromatography was carried out using silica (35-70 μm particles), with crude reaction mixtures loaded in dichloromethane or the initial solvent system, or pre-absorbed. Flash column chromatography was carried out using either hand pumps or compressed air, by a variation of the procedure described by Still, Kahn and Mitra.[1] Thin layer chromatography was carried out on commercially available pre-coated glass or aluminium plates (Merck silica 2 8 8 0 Kieselgel 60F254). Analytical HPLC was performed using either a Thermo Hypersil–Keystone achiral column (250 × 4.6 mm 8 l Hyperprep HSC18), an XTerra® analytical HPLC column, a Jupiter® analytical coloumn or an Ultron chiral column (150 × 4.6 mm ES-OVM) with a Dionex P580 pump and a PDA-100 UV detector at wavelengths between 200 and 250 nm. The purity of fluorous-tagged products which were purified by Fluorous-Solid Phase Extraction (F-SPE) alone was determined using the Jupiter® column eluting with either 75→95% MeCN–water or 90→95% MeCN–water. The purities of fluorous-tagged products which were purified by F-SPE followed by a filtration through Florisil was determined as >95% by analytical HPLC for initial products and was later determined as >95% by 500 MHz ^{1}H NMR spectroscopy, unless otherwise stated. Preparative HPLC was conducted with a Waters 2525 binary gradient pump with detection by a Micromass ZQ mass spectrometer; a Jupiter® semi-preparative HPLC column (19 × 50 mm) was used. Fluorous-Solid Phase Extraction (F-SPE) was carried out using pre-packed Fluoro*Flash*® cartridges purchased from Fluorous Technologies Inc. Cartridges were washed extensively with *N*,*N*-dimethylformamide, tetrahydrofuran and methanol and were

pre-conditioned with 8:2 methanol–water. Crude reaction mixtures were loaded onto cartridges using either *N*,*N*,-dimethylformamide or tetrahydrofuran and eluted using 8:2 methanol–water (a fluorophobic eluent) followed by methanol (a fluorophilic solvent) using compressed air in a manner similar to that described by Curran.[2,3]

Proton and carbon NMR spectra were recorded on a Bruker Avance 500, Avance DPX300 or DRX500 spectrophotometer with an internal deuterium lock. Carbon NMR spectra were recorded with composite pulse decoupling using the waltz 16 pulse sequence. DEPT, COSY, HMQC, HMBC, TOCSY or NOESY pulse sequences were used to aid the assignment of spectra. Chemical shifts are quoted in parts per million downfield of tetramethylsilane, and coupling constants (*J*) are given in Hz. NMR spectra were recorded at 300 K unless otherwise stated.

Infra-red spectra were recorded using a Perkin–Elmer Spectrum One FT-IR spectrophotometer. Spectra of solids and foams were recorded using solid state golden gate probes whilst spectra of oils were performed neat on sodium chloride discs. Melting points were recorded on a Reichert hot stage microscope and are uncorrected. Nominal mass spectrometry was routinely performed on a Waters-Micromass ZMD spectrometer using electrospray (+) ionization. Nominal and accurate mass spectrometry using electrospray ionisation was carried out by staff in the School of Chemistry using either a Micromass LCT-KA111 or Bruker MicroTOF mass spectrometer. Field Desorption ionisation mass spectra were acquired on a Waters-Micromass GCT premier spectrometer equipped with a Linden LIFDI probe. Optical activity measurements were recorded at room temperature unless otherwise stated; units for $[\alpha]_D$ are 10^{-1} deg cm^2 g^{-1} and are omitted.

General Procedures

A. Allyl ether formation in *N*,*N*-dimethylformamide

Sodium hydride (1.5 eq. of a 60% dispersion in mineral oil) was added to a stirred solution of the alcohol (1 eq.) in *N*,*N*-dimethylformamide (0.25 M) at 0 °C. The suspension was allowed to warm to room temperature and stirred for 30 mins, until effervescence ceased, cooled to 0 °C and allyl bromide added (5 eq.). The reaction mixture was allowed to warm and stirred until completion was indicated by TLC (often around 16 h), cooled to 0 °C and quenched with saturated aqueous ammonium chloride solution (0.25 × reaction volume), diluted with ether (10 × reaction volume) and washed with brine (2 × reaction volume, three times), dried ($MgSO_4$) and the solvent removed under reduced pressure to give a crude product.

B. Zemplén deacylation

Sodium methoxide (0.1 eq.) was added to a stirred solution of the ester (1 eq.) in methanol (0.25 M) and the reaction mixture stirred at room temperature until completion was indicated by TLC. The solvent was removed under reduced pressure to give a crude product.

C. Di*iso*propylsilyl ether formation

Chlorodi*iso*propyl silane (1.2 eq.) was added to a solution of the alcohol (1 eq.) and triethylamine (1.5 eq.) in dichloromethane (0.5 M) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred until completion was indicated by TLC (often 15 mins). The reaction mixture was cooled to 0 °C, the reaction was quenched with methanol (*ca*.5 eq.) and the solvent removed under reduced pressure. The reaction mixture was suspended in pentane and filtered, washing with pentane. The solvent was removed under reduced pressure to give a crude product, which was used without further purification.

D. Silaketal formation using di*iso*propylsilyl ethers

N-Bromosuccinimide (3 eq.) was added to a stirred solution of the silyl ether (3.5 eq.) in dichloromethane (0.2 M) at 0 °C. The reaction mixture was allowed to warm to room temperature, stirred for 15 mins and cooled to 0 °C. The alcohol (1 eq.) and the *N*,*N*-dimethylaminopyridine (0.5 eq.) were added as a solution in triethylamine (15 eq.), rinsing the vessel containing the alcohol with dichloromethane (reaction volume) and adding this wash to the reaction mixture. The suspension was allowed to warm to room temperature and was stirred until completion was indicated by TLC.

E. Olefin metathesis using Grubbs' catalysts

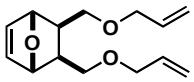
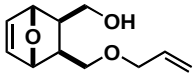
The olefin metathesis catalyst **10** (3 mol%) was added portionwise to a stirred solution of the substrate (1 eq.) in refluxing dichloromethane (1-4 mM) and the reaction mixture was stired at reflux until completion was indicated by TLC with additional catalyst added, if necessary, periodically. The reaction mixture was then cooled to room temperature and tris(hydroxymethyl)phosphine (86 eq. relative to the catalyst) added, stirred for a minimum of 15 mins and triethylamine (*ca*. 10 eq.) added, stirred for a minimum of 15 mins and

silica (5 × amount of phosphine) added and the reaction mixture stirred for a minimum of 15 mins. The reaction mixture was filtered through a pad of Celite, washing with ethyl acetate, and the solvent removed under reduced pressure to give the crude product.

F. Desilylation using hydrogen fluoride–pyridine complex in tetrahydrofuran

Hydrogen fluoride–pyridine complex (70% as hydrogen fluoride, resulting in a final concentration of 5%) was added to a stirred solution of the silyl ether (1 eq.) in 1:1 tetrahydrofuran–pyridine (1 mL) and the reaction mixture stirred at room temperature until completion was indicated by TLC (often less than 1 h). Excess hydrogen fluoride was quenched with methoxytrimethylsilane (10 × hydrogen fluoride–pyridine complex), the reaction mixture stirred for 1 h and solvent removed under reduced pressure to give a crude product.

Synthesis of starting materials for the preparation of the di*iso*propylsilyl ethers 13

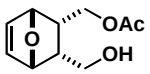



(1*R, 2*R**, 3*S**, 4*S**)-2-allyloxymethyl-3-hydroxymethyl-7-oxabicyclo[2.2.1]hept-5-ene**

By general procedure A, (1*R**,2*R**,3*S**,4*S**)-(3-hydroxymethyl-7-oxa-bicyclo[2.2.1]hept-5-en-2-yl)-methanol[4] (2.0 g, 12.82 mmol) and allyl bromide (2.2 eq.), gave a crude product after 16 h. The crude product was purified by flash chromatography, eluting with 1:1 petrol–EtOAc, to give (1*R**, 2*R**, 3*S**, 4*S**)-2-allyloxymethyl-3-hydroxymethyl-7-oxabicyclo[2.2.1]hept-5-ene (0.64 g, 25%) as a colourless oil, R_f 0.26 (1:1 petrol–EtOAc); ν_{max}/cm^{-1} 3412, 2939, 2924, 2868, 1643 and 1465; δ_H (500 MHz, $CDCl_3$) 6.40 (1H, d, *J* 6.0, 5-H or 6-H), 6.38 (1H, d, *J* 6.0, 5-H or 6-H), 5.91 (1H, ddt, *J* 16.7, 10.7 and 5.6, *allyl* 2-H), 5.29 (1H, d, *J* 16.7, *allyl* 3-H_a), 5.22 (1H, d, *J* 10.7, *allyl* 3-H_b), 4.74 (1H, s, 1-H), 4.72 (1H, s, 4-H), 4.04 (1H, dd, *J* 13.3 and 5.6, *allyl* 1-H_a), 4.00 (1H, dd, *J* 13.3 and 5.6, *allyl* 1-H_b), 3.81 (1H, dd, *J* 11.1 and 8.1, 2-CCH_a), 3.68-3.62 (2H, m, 2-CCH_b and 3-CCH_a), 3.57 (1H, dd, *J* 9.4 and 7.5, 3-CCH_b), 3.20 (1H, br s, OH), 2.02-2.00 (1H, m, 3-H) and 1.94-1.92 (1H, m, 2-H); δ_C (75 MHz, $CDCl_3$) 136.4, 135.9 (5-C and 6-C), 134.4 (*allyl* 2-C), 118.3 (*allyl* 3-C), 81.7 (4-C), 81.5 (1-C), 72.7 (*allyl* 1-C), 71.0 (3-C*C*H_2O), 62.8 (2-C*C*H_2O), 43.2 (2-C) and 40.5 (3-C); *m/z* (ES+) 197 (100%, MNa^+). (Found: MNa^+ 219.0998, $C_{11}H_{16}O_3$ requires *MNa*, 219.0997).

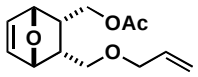
Also obtained was (1*R**,5*R**,4*S**,6*S**)-5,6-bis-allyloxymethyl-7-oxa-bicyclo[2.2.1]hept-2-ene (0.71 g, 23%) as a colourless oil, R_f 0.80 (1:1 petrol–EtOAc); ν_{max}/cm^{-1} 2924, 2961, 2854, 1465, 1372 and 1091; δ_H (300 MHz, $CDCl_3$) 6.35 (2H, app s, 2-H), 5.92 (2H, ddt, *J* 17.3, 10.3 and 5.7, *allyl* 2-H), 5.31 (2H, dd, *J* 17.3 and 1.6, *allyl* 3-H_a), 5.19 (2H, dd, *J* 10.3 and 1.6, allyl 3-H_b), 4.86 (2H, app s, 1-H), 4.12 (2H, dd, *J* 14.2 and 7.1, 5-CH_a), 3.99 (2H, dd, *J* 14.2 and 5.6, 5-CH_b), 3.66 (2H, dd, *J* 9.2 and 4.2, *allyl* 1-H_a), 3.57 (2H, dd, *J* 9.2 and 4.2, *allyl* 1-H_b) and 3.35 (2H, dd, *J* 7.1 and 5.6, 5-H); δ_C (75 MHz, $CDCl_3$) 135.9 (2-C), 135.1 (*allyl* 2-C), 117.6 (*allyl* 3-C), 81.1 (1-C), 72.6 (*allyl* 1-C), 70.0 (5-C*C*H_2) and 40.3 (5-C); *m/z* (ES+) 235 (100%, $[M-H]^+$).

(1*R, 2*S**, 3*R**, 4*S**)-2-Acetoxymethyl-3-hydroxymethyl-7-oxabicyclo[2.2.1]hept-5-ene**



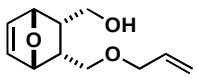
Acetic anhydride (1.3 mL, 12.8 mmol) was added to a stirred solution of (1*R**,2*S**,3*R**,4*S**)-(3-hydroxymethyl-7-oxa-bicyclo[2.2.1]hept-5-en-2-yl)-methanol[5] (200 mg, 1.28 mmol) and cerium chloride (47.6 mg, 0.13 mmol) in tetrahydrofuran (4 mL). The reaction mixture was stirred at room temperature for 16 hours, diluted with ethyl acetate (20 mL) and washed with saturated aqueous sodium bicarbonate solution (2 × 10 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to give a crude product which was purified by flash chromatography, eluting with 1:1 petrol–EtOAc, to give (1*R**, 2*S**, 3*R**, 4*S**)-2-acetoxymethyl-3-hydroxymethyl-7-oxabicyclo[2.2.1]hept-5-ene (65 mg, 0.33 mmol, 26%) as a colourless oil, R_f 0.11 (petrol–EtOAc); ν_{max}/cm^{-1} 3428, 3081, 3005, 2936 and 1736; δ_H (500 MHz, $CDCl_3$)

6.49 (1H, dd, *J* 5.9 and 2.1, 6-H), 6.45 (1H, dd, *J* 5.9 and 2.1, 5-H), 5.05-5.01 (1H, m, 1-H), 4.99-4.94 (1H, m, 4-H), 3.98 (1H, app dd, *J* 11.3 and 5.9, 2-CH_A), 3.67 (1H, app. dd, *J* 10.8 and 9.2, 3-CH_A), 3.49 (1H, app dd, *J* 10.5 and 5.9, 2-CH_B), 3.32-3.23 (1H, m, 3-CH_B), 2.71-2.56 (2H, m, 2-H and 3-H), 2.15 (1H, br s, OH) and 2.08 (3H, s, OAc); δ_C (75 MHz, $CDCl_3$) 171.3 (C=O), 135.9 (5-C), 135.3 (6-C), 80.9 (4-C), 80.7 (1-C), 63.8 (2-CCH_2), 61.9 (3-CCH_2), 43.9 (3-C), 40.1 (2-C) and 21.4 (OAc); *m/z* (ES+) 221.1 (100%, MNa^+). (Found: MNa^+ 221.0784, $C_{10}H_{14}NaO_4$ requires 221.0790)



(1*R,2*S**,3*R**,4*S**)-2-Acetoxymethyl-3-allyloxymethyl-7-oxa-bicyclo[2.2.1]hept-5-ene**

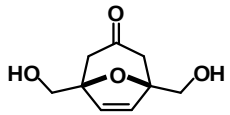
Silver oxide (2.62 g, 11.3 mmol, 2 eq.) was added to a stirred solution of (1*R**, 2*S**, 3*R**, 4*S**)-2-acetoxymethyl-3-hydroxymethyl-7-oxabicyclo[2.2.1]hept-5-ene (1.12 g, 5.65 mmol) in allyl bromide (20 mL) and the suspension was stirred in the dark for 3 days. The reaction mixture was filtered through Celite, washing with EtOAc, and the filtrate was concentrated under reduced pressure to give a crude product which was purified by flash chromatography, eluting with 85:15 petrol–EtOAc, to give (1*R**,2*S**,3*R**,4*S**)-2-acetoxymethyl-3-allyloxymethyl-7-oxa-bicyclo[2.2.1]hept-5-ene (714 mg, 53%) as a colourless oil, R_f 0.43 (7:3 petrol–EtOAc); ν_{max}/cm^{-1} 3079, 3000, 2937, 2863, 1732, 1645, 1428, 1367, 1238 and 1080; δ_H (500 MHz, $CDCl_3$) 6.50 (1H, d, *J* 7.3, 5-H), 6.48 (1H, d, *J* 7.3, 6-H), 5.91 (1H, ddt, *J* 17.2, 10.4 and 5.7, *allyl* 2-H), 5.30 (1H, dd, *J* 17.2 and 1.5, *allyl* 3-H_a), 5.24 (1H, dd, *J* 10.4 and 1.2, *allyl* 3-H_b), 5.05 (1H, d, *J* 4.2, 4-H), 5.00 (1H, d, *J* 4.1, 1-H), 4.03 (1H, dd, *J* 10.6 and 5.7, 2-CCH_a), 3.97 (1H, dd, *J* 12.8 and 5.7, *allyl* 1-H_a), 3.93 (1H, dd, *J* 12.8 and 5.7, *allyl* 1-H_b), 3.66 (1H, app t, *J* 10.6, 2-CCH_b), 3.27 (1H, dd, *J* 9.2 and 6.5, 3-CCH_b), 3.06 (1H, dd, *J* 9.2, 3-CCH_b), 2.76-2.64 (2H, m, 2-H and 3-H) and 2.11 (3H, s, Ac); δ_C (75 MHz, $CDCl_3$) 171.3, 136.0, 135.2, 134.9, 117.7, 81.0, 80.7, 72.6, 69.1, 63.9, 41.3, 39.9 and 21.3; *m/z* (ES+) 261 (100%, MNa^+). (Found: MNa^+ 261.1095, $C_{13}H_{18}O_4$ requires *MNa*, 261.1097)



(1*R,2*S**,3*R**,4*S**)-(3-Allyloxymethyl-7-oxa-bicyclo[2.2.1]hept-5-en-2-yl)-methanol**

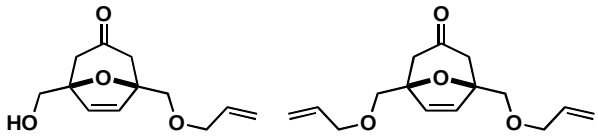
By general procedure B, (1*R**,2*S**,3*R**,4*S**)-2-acetoxymethyl-3-allyloxymethyl-7-oxa-bicyclo[2.2.1]hept-5-ene (710 mg, 2.98 mmol) gave a crude product after 19 h. The crude product was purified by flash chromatography, eluting with 6:4 petrol–EtOAc, to give (1*R**,2*S**,3*R**,4*S**)-(3-allyloxymethyl-7-oxa-bicyclo[2.2.1]hept-5-en-2-yl)-methanol (455 mg, 78%) as a colourless oil, R_f 0.20 (1:1 petrol–EtOAc); ν_{max}/cm^{-1} 3428, 3079, 3008, 2933 and 2866; δ_H (500 MHz, $CDCl_3$) 6.39 (1H, dd, *J* 6.0 and 2.6, 5-H), 6.33 (1H, dd, *J* 6.0 and 2.6, 6-H), 5.86 (1H, ddt, *J* 17.1, 10.7 and 5.6, *allyl* 2-H), 5.26 (1H, app dq, *J* 17.3 and 1.5, *allyl* 3-H_a), 5.20 (1H, app dq, *J* 10.3 and 1.5, *allyl* 3-H_b), 4.91-4.88 (2H, m, 1-H and 4-H), 3.95 (1H, app ddt, *J* 14.1, 5.8 and 1.5, *allyl* 1-H_a), 3.94 (1H, app ddt, *J* 14.1, 5.8 and 1.5, *allyl* 3-H_b), 3.45-3.39 (1H, m, 3-CCH_a), 3.35 (1H, dd, *J* 9.4 and 6.0, 2-CCH_a), 3.31 (1H, dd, *J* 11.1 and 9.4, 2-CCH_a), 3.15 (1H, t, *J* 9.4, OH), 3.06-3.00 (1H, m, 3-CCH_b), 2.73 (1H, ddt, *J* 9.8, 5.6 and 4.5, 3-H) and 2.65 (1H, ddt, *J* 9.4, 5.3 and 4.5, 2-

H); δ_C (75 MHz, $CDCl_3$) 135.5 (5-C), 135.2 (6-C), 134.1 (*allyl* 2-C), 118.5 (*allyl* 3-C), 80.8 (1-C), 80.6 (4-C), 72.7 (*allyl* 1-C), 69.3 (3-C*C*H_2), 61.3 (2-C*C*H_2), 44.8 (3-C) and 41.6 (2-C); *m/z* (ES+) 219 (100%, MNa^+). (Found: MNa^+ 219.0992, $C_{11}H_{16}O_3$ requires 219.0997)



(1*R, 5*S**)-1,5-Bis-hydroxymethyl-8-oxa-bicyclo[3.2.1]oct-6-en-3-one**

(1*R**, 5*S**)-1,5-Bis-(*tert*-butydimethylsilyloxymethyl)-8-oxa-bicyclo[3.2.1]oct-6-en-3-one[6] (5.07 g, 12.3 mmol) was dissolved in 13:7:3 acetic acid–water–THF (230 mL) and stirred at room temperature for 18 h. The solvent was removed under reduced pressure and the resulting residue azeotroped with toluene (5 × 100 mL) and dichloromethane (2 × 100 mL) to give a crude product which was purified by recrystallisation from chloroform to give (1*R**, 5*S**)-1,5-bis-hydroxymethyl-8-oxa-bicyclo[3.2.1]oct-6-en-3-one (1.56 g, 8.48 mmol, 69%) as colourless needles, m.p. 134.8-135.3 °C (from chloroform), R_f 0.18 (50:50 petrol–EtOAc); (Found: C, 58.4; H, 6.60%; $C_9H_{12}O_4$ requires: C, 58.7; H, 6.57%); ν_{max}/cm^{-1} (solid) 3429, 2956, 2870 and 1689; δ_H (300 MHz, CD_3OD) 6.01 (2 H, s, H-6 and H-7), 3.65 (4 H, s, CH_2-O), 2.48 (2 H, d, *J* 16.9, H-2_A and H-4_A), 2.19 (2 H, d, *J* 16.8, H-2_B and H-4_B); δ_C (75 MHz, CD_3OD) 208.9 (C-3), 131.1 (C-6 and C-7), 89.3 (C-1 and C-5), 65.6 (CH_2O) and 47.5 (C-2 and C-4); *m/z* (CI) 202.1 ($[M + NH_4]^+$, 100%).



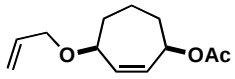
(1*R, 5*S**)-1-Allyloxymethyl-5-hydroxymethyl-8-oxa-bicyclo[3.2.1]oct-6-en-3-one**

Sodium hydride (120 mg of a 60% dispersion in mineral oil, 2.99 mmol, 1.1 eq.) was added to a stirred solution of (1*R**, 5*S**)-1,5-bis-hydroxymethyl-8-oxa-bicyclo[3.2.1]oct-6-en-3-one (500 mg, 2.71 mmol) in *N*,*N*-dimethylformamide (6 mL) at 0 °C, the reaction mixture allowed to warm to room temperature and stirred for 30 mins. The reaction mixture was cooled to 0 °C, allyl bromide (282 μL, 3.26 mmol, 1.2 eq.) added dropwise and the reaction mixture allowed to warm to room temperature and stirred for 22 h. The reaction mixture was cooled to 0 °C, quenched with saturated aqueous ammonium chloride solution (6 mL), diluted with ether (60 mL), aqueous separated, organics washed with brine (4 × 30 mL) and water (30 mL). The combined aqueous fractions were extracted with ethyl acetate (100 mL), washed with brine (50 mL), organics combined, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (gradient elution: 9:1→8:2→7:3→6:4→1:1 petrol–EtOAc) to give (1*R**,5*S**)-1-allyloxymethyl-5-hydroxymethyl-8-oxa-bicyclo[3.2.1]oct-6-en-3-one (137 mg, 23%) as a pale yellow oil, R_f 0.17 (1:1 petrol–EtOAc); ν_{max}/cm^{-1} 3445, 3082, 3010, 2919, 2862, 1714, 1643, 1454, 1343, 1282, 1152 and 1056; δ_H (500 MHz, $CDCl_3$) 6.16 (1H, d, *J* 6.5, 6-H), 6.15 (1H, d, *J* 6.5, 7-H), 5.95 (1H, ddd, *J* 17.3, 10.4 and 5.8, *allyl* 2-H), 5.34 (1H, dd, *J* 17.3 and 1.5, *allyl* 3-H_a), 5.27 (1H, dd, *J* 10.4 and 1.5, *allyl* 3-H_b), 4.16 (1H, dd, *J* 13.0 and 5.8, *allyl* 1-H_a), 4.11 (1H, dd, *J* 13.0 and 5.8, *allyl* 1-H_b), 3.87 (1H, d, *J* 12.3, 5-CH_a),

3.85 (1H, d, *J* 12.3, 5-CCH$_b$), 3.74 (1H, d, *J* 10.4, 1-CCH$_a$), 3.70 (1H, d, *J* 10.4, 1-CCH$_b$), 2.81 (1H, d, *J* 16.4, 2-H$_a$), 2.66 (1H, d, *J* 16.2, 4-H$_a$), 2.41 (1H, d, *J* 16.4, 2-H$_b$), 2.35 (1H, d, *J* 16.2, 4-H$_b$) and 2.26 (1H, br s, OH); δ_C (75 MHz, $CDCl_3$) 206.2 (3-C), 135.4 (6-C), 134.7 (*allyl* 2-C), 134.6 (7-C), 118.2 (*allyl* 3-C), 88.3 (5-C), 87.1 (1-C), 73.1 (*allyl* 1-C), 72.3 (1-C*C*H$_2$), 65.3 (5-C*C*H$_2$), 47.3 (2-C) and 46.6 (4-C); *m/z* (ES+) 247 (100%, MNa$^+$). (Found: MNa$^+$ 247.0930, $C_{12}H_{16}O_4$ requires *MNa*, 247.0941).

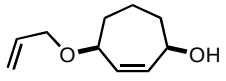
Also obtained was 1,5-bis-allyloxymethyl-8-oxa-bicyclo[3.2.1]oct-6-en-3-one (125 mg, 17%) as a colourless oil, R_f 0.72 (1:1 petrol–EtOAc); δ_H (500 MHz, $CDCl_3$) 6.16 (2H, s, 6-H), 5.94 (2H, dddd, *J* 17.3, 10.4, 5.9 and 5.6, *allyl* 2-H), 5.33 (2H, br dd, *J* 17.3 and 1.6, *allyl* 3-H$_a$), 5.25 (2H, br dd, *J* 10.4 and 1.6, *allyl* 3-H$_b$), 4.14 (2H, ddd, *J* 13.1, 5.6 and 1.2, *allyl* 1-H$_a$), 4.11 (2H, ddd, *J* 13.1, 5.9 and 1.2, *allyl* 1-H$_b$), 3.70 (2H, d, *J* 10.4, 1-CCH$_a$), 3.73 (2H, d, *J* 10.4, 1-CCH$_b$), 2.75 (2H, d, *J* 16.9, 2-H$_a$) and 2.42 (2H, d, *J* 16.9, 2-H$_b$); δ_C (75 MHz, $CDCl_3$) 206.8 (3-C), 134.8 (6-C), 134.7 (*allyl* 2-C), 117.9 (*allyl* 3-C), 87.1 (1-C), 73.1 (*allyl* 1-C), 72.5 (1-C*C*H$_2$) and 47.4 (2-C); *m/z* (ES+) 287 (100%, MNa$^+$). (Found: MNa$^+$ 287.1253, $C_{15}H_{20}O_4$ requires *MNa*, 287.1254).

(1*R*,4*S*)-4-(Allyloxy)cyclohept-2-enyl acetate



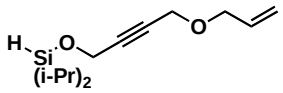
Silver oxide (4.58 g, 19.76 mmol, 2 eq.), was added to a rapidly stirred suspension of (1*R*,4*S*)-4-hydroxy-cyclohept-2-enyl acetate[7] (1.68 g, 9.88 mmol, 1 eq.), and 4 Å molecular sieves (500 mg) in allyl bromide (40 mL). The contents of the flask were protected from the light and the progress monitored by TLC. After 36 hours the reaction was complete. The suspension was filtered through celite and washed with EtOAc (3 × 50 mL). The organic filtrate was washed with brine (2 × 30 mL) and dried over magnesium sulfate. Concentration under reduced pressure gave a residue which was purified by flash chromatography, eluting with 8:2 petrol–EtOAc to afford (1*R*,4*S*)-4-(allyloxy)cyclohept-2-enyl acetate (1.30 g, 6.20 mmol, 63%) as a clear colourless oil, R_f 0.65 (8:2 petrol–EtOAc); $[\alpha]_D$ −20.0 (*c* 2.0 in $CHCl_3$); ν_{max}/cm^{-1} (film) 3080, 2935, 2860, 1738, 1647, 1445, 1371, 1243; δ_H (500 MHz; $CDCl_3$) 5.90 (1H, ddt, *J* 16.5, 10.5 and 5.5, 2$_{allyl}$-H), 5.82 (1H, br. d, *J* 12.2, 3-H), 5.66 (1H, br. d, *J* 12.2, 2-H), 5.35-5.30 (1H, m, 1-H), 5.28 (1H, dd, *J* 16.5 and 1.3, 3$_{allyl}$-H$_{trans}$), 5.18 (1H, dd, *J* 10.5 and 1.3, 3$_{allyl}$-H$_{cis}$), 4.05-3.95 (3H, m, 4-H and 1$_{allyl}$-H$_2$), 2.06 (3H, s, C=OC*H*$_3$), 2.04-1.98 (1H, m, 6-H$_A$), 1.95-1.91 (1H, m, 5-H$_A$), 1.84-1.80 (1H, m, 7-H$_A$), 1.76-1.67 (1H, m, 6-H$_B$), 1.59-1.52 (1H, m, 7-H$_B$), 1.51-1.45 (1H, m, 5-H$_B$); δ_C (75 MHz; $CDCl_3$) 135.6. 135.2, 132.5, 117.3, 78.9, 74.4, 70.0, 32.9 (2×C), 24.5, 21.7. *An ionisation technique was not found which identified the required mass ion.*

(1*R*,4*S*)-4-(allyloxy)cyclohept-2-enol



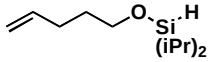
Sodium methoxide (33 mg, 0.62 mmo, 0.1 eq.), was added to a solution of (1*R*,4*S*)-4-(allyloxy)cyclohept-2-enyl acetate (1.30 g, 6.2 mmo, 1 eq.), in MeOH (50 mL), and the progress of the reaction monitored by TLC. After 24 hrs the reaction was concentrated under reduced pressure to afford a residue that was purified using flash chromatography, eluting with 8:2 petrol–EtOAc, to give (1*R*,4*S*)-4-(allyloxy)cyclohept-2-enol (880 mg, 5.4 mmol, 87 %), as a clear colourless oil, R_f 0.20 (8:2 petrol–EtOAc); ν_{max}/cm^{-1} (film) 3391, 3030, 2930, 2857, 1646 and 1445; δ_H (500 MHz; $CDCl_3$) 5.91 (1H, ddt, *J* 17.1, 10.7 and 5.6, 2_{allyl}-H), 5.85 (1H, dd, *J* 12.0 and 3.4, 2-H or 3-H), 5.81 (1H, dd, *J* 12.0 and 3.4, 2-H or 3-H), 5.28 (1H, dd, *J* 17.1 and 1.3, 3_{allyl}-H_A), 5.18 (1H, dd, *J* 10.7 and 1.3, 3_{allyl}-H_B), 4.31-4.26 (1H, m, 1-H or 4-H), 4.04 (1H, dd, *J* 12.8 and 5.6, 1_{allyl}-H_A), 3.97 (1H, dd, *J* 12.8 and 5.6, 1_{allyl}-H_B), 3.95-3.91 (1H, m, 1-H or 4-H), 1.86-1.73 (2H, m, 6-H_2) and 1.71-1.54 (4H, m, 5-H_2 and 7-H_2); δC (75 MHz; $CDCl_3$) 137.2, 135.1, 134.5, 117.4, 78.1, 71.4, 69.9, 36.2, 32.6 and 23.6. *An ionisation technique was not found which identified the required mass ion.*

Synthesis of di*iso*propylsilyl ethers



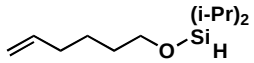
(4-(Allyloxy)but-2-ynyloxy)di*iso*propylsilane 13a

By general procedure C, 4-(allyloxy)but-2-yn-1-ol[8] (422 mg, 3.34 mmol) gave a crude product after 15 mins. The crude *silyl ether* **13a** (743 mg, 93%) was obtained as a pale yellow oil which was used without furher purification, R_f 0.83 (8:2 petrol–EtOAc); ν_{max}/cm^{-1} 3082, 2944, 2893, 2865, 2097, 2236, 1463, 1366, 1352, 1262, 1245, 1128, 1086, 1065 and 1001; δ_H (500 MHz, $CDCl_3$) 5.94 (1H, ddt, *J* 17.2, 10.4 and 5.8, *allyl* 2-H), 5.34 (1H, d, *J* 17.2, *allyl* 3-H_a), 5.24 (1H, d, *J* 10.4, *allyl* 3-H_b), 4.45 (2H, t, *J* 1.7, 1-H), 4.23 (3H, br s, 4-H and Si–H), 4.09 (2H, d, *J* 5.8, *allyl* 1-H) and 1.09-1.07 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 134.4 (*allyl* 2-C), 118.3 (*allyl* 3-C), 84.8 (2-C), 81.6 (3-C), 70.9 (*allyl* 1-C), 57.8 (4-C), 54.3 (1-C), 17.7 (^{i}Pr), 17.6 (^{i}Pr) and 12.7 (^{i}Pr); *m/z* (ES+) 263 (100%, MNa^+). (Found: MNa^+ 263.1435, $C_{13}H_{24}O_2Si$ requires *MNa*, 263.1438).



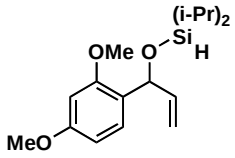
(Pent-4-enyloxy)di*iso*propylsilane 13b

By general procedure C, pent-4-en-1-ol (1.00 g, 11.6 mmol) gave a crude product after 30 mins. The crude *silyl ether* **13b** (2.27 g, >98%) was obtained as a pale yellow oil which was used without further purification, R_f 0.92 (9:1 petrol–EtOAc); ν_{max}/cm^{-1} 3079, 2942, 2894, 2866, 2090, 1642, 1463, 1385, 1100, 1066, 1037 and 1000; δ_H (500 MHz, $CDCl_3$) 5.86 (1H, ddt, *J* 17.1, 10.2 and 7.8, 4-H), 5.06 (1H, app q, *J* 171 and 1.8, 5-H_a), 4.99 (1H, br d, *J* 10.2, 5-H_b), 4.16 (1H, s, Si–H), 3.74 (2H, t, *J* 6.5, 1-H), 2.15 (2H, app q, *J* 7.8, 3-H), 1.70 (2H, tt, *J* 7.8 and 6.5, 2-H) and 1.08-1.00 (14H, m, ^{i}Pr); δ_C (125 MHz, $CDCl_3$) 138.4 (4-C), 114.6 (5-C), 65.0 (1-C), 31.8 (2-C), 29.9 (3-C), 17.3 (^{i}Pr) and 12.4 (^{i}Pr). *An ionisation technique was not found which identified the required mass ion.*

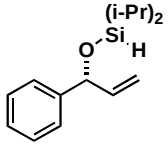


(hex-5-enyloxy)di*iso*propylsilane 13c

By general procedure C, hex-5-en-1-ol (300 mg, 3.0 mmol) gave a crude product after 40 mins. The crude *silyl ether* **13c** (536 mg, 83%) was obtained as a colourless oil and was used without further purification, R_f 0.84 (8:2 petrol–EtOAc); ν_{max}/cm^{-1} 3078, 2941, 2894, 2865, 2089, 1641, 1462, 1385, 1101, 1067 and 1000; δ_H (500 MHz, $CDCl_3$) 5.84 (1H, ddt, *J* 17.1, 10.2 and 7.1, 5-H), 5.04 (1H, dt, *J* 17.1 and 1.7, 6-H_a), 4.98 (1H, dt, *J* 10.2 and 1.7, 6-H_b), 4.16 (1H, s, Si–H), 3.73 (2H, t, *J* 6.5, 1-H), 2.10 (2H, td, *J* 7.2 and 7.1, 4-H), 1.62-1.57 (2H, m, 2-H), 1.49-1.46 (2H, m, 3-H) and 1.08-1.05 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 139.3 (5-C), 114.8 (6-C), 65.9 (1-C), 33.9 (4-C), 32.5 (2-C), 25.5 (3-C), 17.9 (^{i}Pr), 17.7 (^{i}Pr), 17.5 (^{i}Pr) and 12.8 (^{i}Pr). *An ionisation technique was not found which identified the required mass ion.*



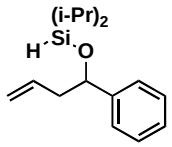
[1-(2',4'-Dimethoxy-phenyl)-allyloxy]-di*iso*propyl-silane 13d By general procedure C, 1-(2,4-dimethoxyphenyl)prop-2-en-1-ol[9] (300 mg, 1.54 mmol) gave a crude product after 1 h. The crude *silyl ether* **13d** (473 mg, >98%) was obtained as a colourless oil which was used without further purification, R_f 0.78 (8:2 petrol–EtOAc); ν_{max}/cm^{-1} 3081, 3000, 2943, 2890, 2865, 2097, 1613, 1590, 1504, 1463, 1290, 1256, 1208, 1157 and 1039; δ_H (500 MHz, $CDCl_3$) 7.93 (1H, d, *J* 8.4, 6′-H), 6.55 (1H, dd, *J* 8.4 and 2.3, 5′-H), 6.47 (1H, d, *J* 2.3, 3′-H), 6.00 (1H, ddd, *J* 17.1, 10.3 and 5.1, 2-H), 5.60 (1H, br d, *J* 5.1, 1-H), 5.32 (1H, app dt, *J* 17.1 and 1.5, 3-H_a), 5.08 (1H, dt, *J* 10.3 and 1.5, 3-H_b), 4.22 (1H, s, Si–H), 3.85 (6H, s, OMe), 1.11-1.06 (8H, m, ^{i}Pr) and 1.03-1.00 (6H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 160.3, 157.2 (2′-C and 4′-C), 140.9, 128.0, 124.6, 113.0 (3-C), 104.7, 98.5, 71.3 (1-C), 55.7 (OMe), 17.9, 17.8, 17.7, 17.5, 12.9, 12.8 (^{i}Pr) [two OMe-C's overlapping]; *m/z* (ES+) 331 (100%, MNa^+). (Found: MNa^+ 331.1698, $C_{17}H_{28}O_3Si$ requires *MNa*, 331.1700).



(*R*)-Di*iso*propyl-(1-phenyl-allyloxy)-silane (–)-13e

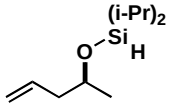
By general procedure C, (*R*)-1-phenylprop-2-en-1-ol (479 mg, 3.57 mmol) gave a crude product after 20 mins. The crude *silyl ether* **13e** (821 mg, 93%) was obtained as a colourless oil which was used without purification, R_f 0.86 (9:1 petrol–EtOAc); $[\alpha]_D$ –18.0 (*c* 1.0 in $CHCl_3$); ν_{max}/cm^{-1} 3085, 3065, 3029, 2097, 1492, 1462, 1124, 1087, 1059, 1029, 1001 and 920; δ_H (500 MHz, $CDCl_3$) 7.41-7.37 (4H, m, *meta*-Ph and *ortho*-Ph), 7.32-7.29 (1H, m, *para*-Ph), 6.00 (1H, ddd, *J* 17.0, 10.2 and 6.0, 2-H), 5.36 (1H, d, *J* 17.0, 3-H_a), 5.24 (1H, d, *J* 6.0, 1-H), 5.17 (1H, d, *J* 10.2, 3-H_b), 4.27 (1H, s, Si–H) and 1.13-1.00 (14H, m, ^{i}Pr); δ_C (75

MHz, $CDCl_3$) 143.6 (*ipso*-Ph), 141.4 (2-C), 128.6 (Ph), 127.6 (*para*-Ph), 126.6 (Ph), 114.4 (3-C), 78.5 (1-C), 17.9 (^{i}Pr), 17.8 (^{i}Pr), 17.7 (^{i}Pr), 17.5 (^{i}Pr) and 12.9 (^{i}Pr). *An ionisation technique was not found which identified the required mass ion.*



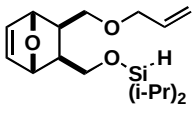
Di*iso*propyl(1-phenylbut-3-enyloxy)silane 13f

By general procedure C, 1-phenylbut-3-en-1-ol (224 mg, 1.51 mmol) gave a crude product after 15 mins. The crude *silyl ether* **13f** (421 mg, >98%) was obtained as a pale yellow oil which was used without further purification, R_f 0.89 (9:1 petrol–EtOAc); ν_{max}/cm^{-1} 3078, 3030, 2943, 2893, 2865, 2096, 1641, 1493, 1462, 1365, 1243, 1087, 1063 and 1001; δ_H (500 MHz, $CDCl_3$) 7.39-7.36 (4H, m, *ortho*-Ph and *meta*-Ph), 7.32-7.28 (1H, m, *para*-Ph), 5.83 (1H, dddd, *J* 18.7, 9.3, 7.1 and 5.9, 3-H), 5.08 (1H, d, *J* 18.7, 4-H_a), 5.06 (1H, d, *J* 9.3, 4-H_b), 4.78 (1H, app br t, *J* 7.0, 1-H), 4.23 (1H, s, Si–H), 2.59 (1H, app br dt, *J* 14.0 and 7.1, 2-H_a), 2.52 (1H, ddd, *J* 14.0, 6.9 and 5.9, 2-H_b) and 1.13-0.93 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 144.6 (*ipso*-Ph), 135.2 (3-C), 128.4 (*ortho*-Ph), 128.3 (*para*-Ph), 127.5 (*meta*-Ph), 117.5 (4-C), 77.5 (1-C), 45.3 (2-C), 18.0 (^{i}Pr), 17.8 (^{i}Pr), 17.7 (^{i}Pr), 17.6 (^{i}Pr), 17.5 (^{i}Pr), 13.8 (^{i}Pr), 13.7 (^{i}Pr), 13.0 (^{i}Pr) and 12.9 (^{i}Pr); *m/z* (ES+) 227 (100%, MNH_4^+). *An ionisation technique was not found which identified the required accurate mass ion.*



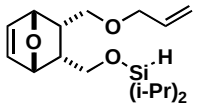
(+)-(2*S*)-di*iso*propyl(pent-4-en-2-yloxy)silane 13g

By general procedure C, (*S*)-pent-4-en-2-ol (258 mg, 3.0 mmol) gave a crude product after 40 mins. The crude *silyl ether* **13g** (221 mg, 37%) was obtained as a colourless oil and was used without further purification, R_f 0.69 (8:2 petrol–EtOAc); $[\alpha]_D$ + 3.6 (*c* 1.0 in $CHCl_3$); ν_{max}/cm^{-1} 3079, 2943, 2894, 2866, 2093, 1642, 1463, 1377, 1242, 1128, 1089, 1057, 1045 and 1001; δ_H (500 MHz, $CDCl_3$) 5.84 (1H, dddd, *J* 17.3, 10.1, 7.3 and 7.0, 4-H), 5.08 (1H, d, *J* 17.3, 5-H_a), 5.06 (1H, d, *J* 10.1, 5-H_b), 4.21 (1H, s, Si–H), 3.91 (1H, app qt, *J* 6.1 and 6.0, 2-H), 2.30 (1H, ddd, *J* 13.7, 7.0 and 5.8, 3-H_a), 2.22 (1H, ddd, *J* 13.7, 7.3 and 6.2, 3-H_b), 1.20 (3H, d, *J* 6.1, 1-H) and 1.08-1.04 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 135.7 (4-C), 117.2 (5-C), 71.1 (2-C), 44.3 (3-C), 23.2 (1-C), 17.9 (^{i}Pr), 17.8 (^{i}Pr), 17.7 (^{i}Pr), 17.6 (^{i}Pr), 17.5 (^{i}Pr), 13.6 (^{i}Pr) and 12.9 (^{i}Pr). *An ionisation technique was not found which identified the required mass ion.*



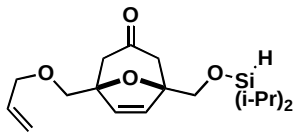
(1*R,2*R**,3*S**,4*S**)-(3-Allyloxymethyl-7-oxa-bicyclo[2.2.1]hept-5-en-2-ylmethoxy)-di*iso*propyl-silane 13h**

By general procedure C, (1*S**,2*S**,3*R**,4*R**)-(3-(allyloxymethyl)-7-oxabicyclo[2.2.1]hept-5-en-2-yl)methanol (305 mg, 1.55 mmol) gave a crude product after 10 mins. The crude *silyl ether* **13h** (475 mg, >98%) was obtained a colourless oil and was used without further purification, R_f 0.78 (8:2 petrol–EtOAc); ν_{max}/cm^{-1} 3080, 3010, 2943, 2892, 2865, 2090, 1463, 1384, 1310, 1113, 1085 and 1001; δ_H (500 MHz, $CDCl_3$) 6.40 (2H, s, 5-H and 6-H), 5.97 (1H, ddt, *J* 17.1, 10.5 and 5.7, *allyl* 2-H), 5.33 (1H, dd, *J* 17.1 and 1.4, *allyl* 3-H_a), 5.24 (1H, br d, *J* 10.5, *allyl* 3-H_b), 4.91 (1H, s, 1-H), 4.90 (1H, s, 4-H), 4.20 (1H, s, Si–H), 4.03 (2H, d, *J* 5.7, *allyl* 1-H), 3.88 (1H, dd, *J* 9.8 and 5.3, 2-CCH_a), 3.67 (1H, app t, *J* 9.8, 2-CCH_b), 3.60 (1H, dd, *J* 9.0 and 5.4, 3-CCH_a), 3.42 (1H, app t, *J* 9.0, 3-CCH_b), 1.96 (1H, ddd, *J* 9.0, 8.5 and 5.4, 3-H), 1.90 (1H, ddd, *J* 9.8, 8.5 and 5.3, 2-H) and 1.11-1.06 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 136.0, 135.9 (5-C and 6-C), 135.1 (*allyl* 2-C), 117.6 (*allyl* 3-C), 81.1 (4-C), 80.6 (1-C), 72.6 (*allyl* 1-C), 70.0 (3-C*C*H_2O), 65.2 (2-C*C*H_2O), 42.8 (2-C), 40.4 (3-C), 17.9 (^{i}Pr), 17.8 (^{i}Pr) and 12.8 (^{i}Pr); *m/z* (ES+) 333 (100%, MNa^+). (Found: MNa^+ 333.1868, $C_{17}H_{30}O_3Si$ requires *MNa*, 333.1856).



(1*R,2*S**,3*R**,4*S**)-(3-Allyloxymethyl-7-oxa-bicyclo[2.2.1]hept-5-en-2-ylmethoxy)-diisopropyl-silane 13i**

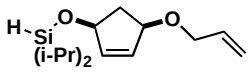
By general procedure C, (1*R**,2*S**,3*R**,4*S**)-(3-(allyloxymethyl)-7-oxabicyclo[2.2.1]hept-5-en-2-yl)methanol (92 mg, 0.47 mmol) gave a crude product after 10 mins. The crude *silyl ether* **13i** (124 mg, 85%) was obtained as a colourless oil which was used without further purification, R_f 0.49 (9:1 petrol–EtOAc); ν_{max}/cm^{-1} 3079, 3012, 2941, 2890, 2864, 2089, 1646, 1462, 1337, 1127, 1083 and 1001; δ_H (500 MHz, $CDCl_3$) 6.48 (1H, dd, *J* 5.9 and 1.8, 5-H or 6-H), 6.45 (1H, dd, *J* 5.9 and 1.4, 5-H or 6-H), 5.91 (1H, ddt, *J* 17.2, 10.4 and 5.6, *allyl* 2-H), 5.28 (1H, dd, *J* 17.2 and 1.7, *allyl* 3-H_a), 5.21 (1H, dd, *J* 10.4 and 1.3, *allyl* 3-H_b), 5.02 (2H, br s, 1-H and 4-H), 4.13 (1H, s, Si–H), 3.95 (1H, br dd, *J* 12.8 and 5.6, *allyl* 1-H_a), 3.91 (1H, br dd, *J* 12.8 and 5.6, *allyl* 1-H_a), 3.65 (1H, dd, *J* 10.1 and 5.6, 2-CCH_a), 3.29 (1H, dd, *J* 9.2 and 5.9, 3-CCH_a), 3.26 (1H, app t, *J* 10.1, 2-CCH_b), 3.02 (1H, app t, *J* 9.2, 3-CCH_b), 2.66-2.62 (2H, m, 2-H and 3-H) and 1.08-1.02 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 135.6 (5-C or 6-C), 135.5 (*allyl* 2-C), 135.1 (5-C or 6-C), 117.5 (*allyl* 3-C), 81.1 (1-C and 4-C), 72.5 (*allyl* 1-C), 69.5 (3-C*C*H_2O), 65.1 (2-C*C*H_2O), 43.5 (2-C), 41.0 (3-C), 17.9 (^{i}Pr), 17.7 (^{i}Pr), 12.8 (^{i}Pr) and 12.7 (^{i}Pr); *m/z* (ES+) 333 (100%, MNa^+). (Found: MNa^+ 333.1855, $C_{17}H_{30}O_3Si$ requires *MNa*, 333.1856).



(1*R,5*S**)-1-Allyloxymethyl-5-di*iso*propylsilanyloxymethyl-8-oxa-bicyclo[3.2.1]oct-6-en-3-one 13j**

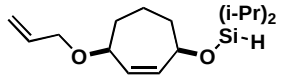
By general procedure C, (1*S**,5*R**)-1-(allyloxymethyl)-5-(hydroxymethyl)-8-oxabicyclo[3.2.1]oct-6-en-3-one (87 mg, 0.388 mmol) gave a crude product after 10 mins. The *silyl ether* **13j** (132 mg, >98%), a

colourless oil, was used without further purification, R_f 0.42 (9:1 petrol–EtOAc); ν_{max}/cm^{-1} 3081, 2944, 2866, 2096, 1722, 1463, 1341, 1159, 1099, 1064 and 1001; δ_H (500 MHz, $CDCl_3$) 6.20 (1H, d, *J* 5.9, 7-H), 6.13 (1H, d, *J* 5.9, 6-H), 5.95 (1H, app dddd, *J* 17.2, 10.3, 5.8 and 5.6, *allyl* 2-C), 5.33 (1H, br dd, *J* 17.2 and 1.5, *allyl* 3-H_a), 5.25 (1H, br dd, *J* 10.3 and 1.1, *allyl* 3-H_b), 4.23 (1H, s, Si–H), 4.16 (1H, br dd, *J* 13.2 and 5.8, *allyl* 1-H_a), 4.11 (1H, br dd, *J* 13.2 and 5.6, *allyl* 1-H_b), 3.97 (1H, d, *J* 10.3, 5-CCH_a), 3.95 (1H, d, *J* 10.3, 5-CCH_b), 3.72 (1H, d, *J* 10.5, 1-CCH_a), 3.69 (1H, d, *J* 10.5, 1-CCH_b), 2.76 (1H, d, *J* 16.3, 2-H_a), 2.63 (1H, d, *J* 16.3, 4-H_a), 2.48 (1H, d, *J* 16.3, 4-H_b), 2.41 (1H, d, *J* 16.3, 2-H_b) and 1.08-1.06 (14H, m, ^{i}Pr); δ_C (75 MHZ, $CDCl_3$) 206.6 (3-C), 134.6 (7-C), 134.4 (*allyl* 2-C), 134.0 (6-C), 117.4 (*allyl* 3-C), 87.4 (5-C), 86.6 (1-C), 72.6 (*allyl* 1-C), 72.0 (1-C*C*H_2O), 68.2 (5-C*C*H_2O), 47.0 (2-C), 46.9 (4-C), 17.4 (^{i}Pr), 17.3 (^{i}Pr) and 12.4 (^{i}Pr); *m/z* (ES+) 361 (100%, MNa^+). (Found: MNa^+ 361.1800, $C_{18}H_{30}O_4Si$ requires *MNa*, 361.1806).



(1*R,4*S**)-(4-Allyloxy-cyclopent-2-enyloxy)-di*iso*propyl-silane 13k**

By general procedure C, (1*R**,4*S**)-4-(allyloxy)cyclopent-2-enol[10] (169 mg, 1.21 mmol) gave a crude product after 10 mins. The crude *silyl ether* **13k** (311 mg, >98%) was obtained as a pale yellow oil which was used without further purification, R_f 0.74 (petrol–EtOAc); ν_{max}/cm^{-1} 3064, 2943, 2893, 2865, 2091, 1647, 1463, 1368, 1124, 1082, 1042 and 1000; δ_H (500 MHz, $CDCl_3$) 6.01 (1H, br d, *J* 5.5, 2-H), 6.00 (1H, br d, *J* 5.5, 3-H), 5.95 (1H, dddd, *J* 17.2, 10.4, 5.6 and 4.3, *allyl* 2-H), 5.33 (1H, dd, *J* 17.2 and 1.6, *allyl* 3-H_a), 5.21 (1H, dd, *J* 10.4 and 1.3, *allyl* 3-H_b), 4.74 (1H, br app t, *J* 6.0, 1-H), 4.44 (1H, br app t, *J* 6.0, 4-H), 4.25 (1H, s, Si–H), 4.07 (1H, br d, *J* 12.9, *allyl* 1-H_a), 4.04 (1H, br d, *J* 12.9, *allyl* 1-H_b), 2.77 (1H, dt, *J* 13.3 and 7.2, 5-H_a), 1.68 (1H, dt, *J* 13.3 and 5.5, 5-H_b) and 1.09-0.95 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 137.3 (3-C), 135.6 (*allyl* 2-C), 133.6 (2-C), 117.2 (*allyl* 3-C), 81.6 (4-C), 77.6 (1-C), 69.8 (*allyl* 1-C), 41.4 (5-C), 17.7 (^{i}Pr), 17.5 (^{i}Pr), 13.6 (^{i}Pr) and 12.8 (^{i}Pr); *m/z* (ES+) 277 (100%, MNa^+). (Found: MNa^+ 277.1592, $C_{14}H_{26}O_2Si$ requires *MNa*, 277.1594).

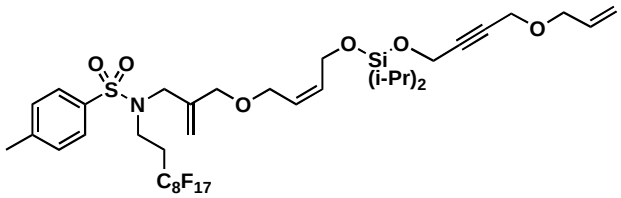


(1*R*,4*S*)-(4-Allyloxy-cyclohept-2-enyloxy)-di*iso*propyl-silane 13l

By general procedure C, (1*R*,4*S*)-4-(allyloxy)cyclohept-2-enol (131 mg, 0.78 mmol) gave a crude product after 30 mins. The crude *silyl ether* **13l** (232 mg, >98%) was obtained as a colourless oil and was used without further purification, R_f 0.74 (9:1 petrol–EtOAc); $[\alpha]_D$ –12.0 (*c* 1.0 in $CHCl_3$); ν_{max}/cm^{-1} 3081, 3016, 2940, 2893, 2865, 2093, 1647, 1463, 1425, 1391, 1366, 1300, 1243, 1254, 1083, 1061 and 1001; δ_H (500 MHz, $CDCl_3$) 5.95 (1H, dddd, *J* 17.2, 10.4, 5.6 and 5.4, *allyl* 2-H), 5.77 (1H, br d, *J* 12.2, 2-H), 5.73 (1H, br d, *J* 12.2, 3-H), 5.31 (1H, app dq, *J* 17.2 and 1.4, *allyl* 3-H_a), 5.19 (1H, app dq, *J* 10.4 and 1.4, *allyl* 3-H_b), 4.30 (1H, br d, *J* 9.9, 1-H), 4.20 (1H, s, Si–H), 4.05 (1H, app ddt, *J* 12.8, 5.4 and 1.4, *allyl* 1-H_a), 4.00 (1H, app ddt, *J* 12.8, 5.6 and 1.4, *allyl* 1-H_b), 3.94 (1H, br d, *J* 10.8, 4-H), 2.03-1.99 (1H, m, 6-H_a), 1.93-1.89 (1H, m, 7-H_a), 1.86-1.82 (1H, m, 5-H_a), 1.67-1.64 (1H, m, 6-H_b), 1.59-1.54 (1H, m, 5-H_b), 1.50-1.45 (1H, m, 7-

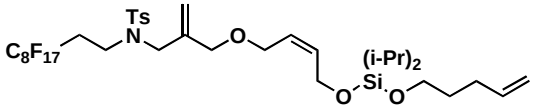
H_b) and 1.09-0.95 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 137.6 (2-C), 135.4 (*allyl* 2-C), 133.8 (3-C), 117.0 (*allyl* 3-C), 79.3 (4-C), 75.3 (1-C), 69.8 (*allyl* 1-C), 36.5 (7-C), 32.9 (5-C), 25.1 (6-C), 17.7 (^{i}Pr), 17.7 (^{i}Pr), 17.6 (^{i}Pr), 17.5 (^{i}Pr), 13.7 (^{i}Pr), 13.0 (^{i}Pr) and 12.8 (^{i}Pr); *m/z* (ES+) 283 (100%, MNa^+). (Found: MNa^+ 283.2081, $C_{16}H_{31}OSi$ requires *MNa*, 283.2088)

Synthesis of fluorous-tagged silaketals



***N*-(2-{4′-[(4″-Allyloxy-but-2″-ynyloxy)-di*iso*propyl-silanyloxy]-but-2′-enyloxymethyl}-allyl)-*N*-(3‴,3‴,4‴,4‴,5‴,5‴,6‴,6‴,7‴,7‴,8‴,8‴,9‴,9‴,10‴,10‴,10‴-heptadecafluoro-decyl)-4''''-methyl-benzenesulfonamide 7a**

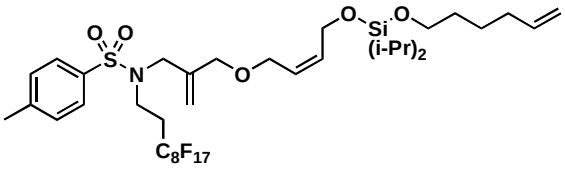
By general procedure D, the alcohol[11] **6** (60 mg, 79 μmol), the silyl ether **13a** (3.5 eq.), *N*-bromosuccinimide (3 eq.) at 0.1 M **6** gave a cude product after 30 mins. The crude product was purified by Fluorous-Solid Phase Extraction (loading with ≤ 400 μL DMF) to give the *silaketal* **7a** (74 mg, >94%, 98% purity) as a colourless oil, R_f 0.73 (9:1 petrol–EtOAc); δ_H (500 MHz, $CDCl_3$) 7.75 (2H, d, *J* 8.1, 2‴′-H), 7.38 (2H, d, *J* 8.1, 3‴′-H), 5.94 (1H, ddd, *J* 17.2, 10.4 and 5.7, *allyloxy* 2-H), 5.80-5.76 (1H, m, 3′-H), 5.66-5.61 (1H, m, 2′-H), 5.34 (1H, dd, *J* 17.2 and 1.5, *allyloxy* 3-H), 5.32 (1H, s, 3-H), 5.25 (1H, dd, *J* 10.4 and 1.0, *allyloxy* 3-H), 4.51 (2H, t, *J* 1.6, 1″-H), 4.43 (2H, d, *J* 5.8, 4′-H), 4.23 (2H, t, *J* 1.6, 4″-H), 4.10-4.09 (4H, m, 1′-H and *allyloxy* 1-H), 3.95 (2H, s, 2-CCH_2O), 3.82 (2H, s, 2-H), 3.43-3.40 (2H, m, *decyl* 1-H), 2.48 (3H, s, 4‴′-CH_3), 2.46-2.35 (2H, m, *decyl* 2-H) and 1.10 (14H, s, ^{i}Pr); δ_C (75 MHZ, $CDCl_3$), 144.3 (4‴′-C), 141.1 (2-C), 136.1 (1‴′-C), 134.4 (*allyloxy* 2-C), 132.6 (3′-C), 130.3 (3‴′-C), 127.6 (2‴′-C), 127.3 (2′-C), 118.2 (*allyloxy* 3-C), 117.2 (3-C), 85.0 (2″-C), 81.1 (3″-C), 70.9 (*allyloxy* 1-C), 70.8 (2-C*C*H_2O), 66.7 (1′-C), 59.7 (4′-C), 57.8 (4″-C), 52.0 (1-C), 51.7 (1″-C), 40.8 (*decyl* 1-C), 30.9 (t, $^2J_{C-F}$ 26.2, *decyl* 2-C), 21.9 (4‴′-C*C*H_3), 17.6 (^{i}Pr) and 12.5 (^{i}Pr).



***N*-(2-{4′-[(pen-4″-enyloxy)-di*iso*propyl-silanyloxy]-but-2′-enyloxymethyl}-allyl)-*N*-(3‴,3‴,4‴,4‴,5‴,5‴,6‴,6‴,7‴,7‴,8‴,8‴,9‴,9‴,10‴,10‴,10‴-heptadecafluoro-decyl)-4''''-methyl-benzenesulfonamide 7b**

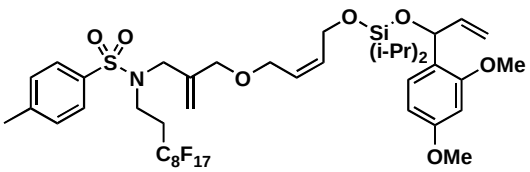
By general procedure D, the alcohol[11] **6** (200 mg, 0.264 mmol), the silyl ether **13b** (3.5 eq.), *N*-bromosuccinimide (3 eq.) at 0.1 M **6** gave a cude product after 14 h. The crude product was purified by Fluorous-Solid Phase Extraction (loading with ≤ 400 μL DMF) to give the *silaketal* **7b** (252 mg, >98%, 98% purity), R_f 0.46 (9:1 petrol–EtOAc); ν_{max}/cm^{-1} 3080, 3030, 2945, 2869, 1642, 1599, 1463, 1351, 1242, 1160, 1086 and 1017; δ_H (500 MHz, $CDCl_3$) 7.75 (2H, d, *J* 8.2, 2‴′-H), 7.38 (2H, d, *J* 8.2, 3‴′-H), 5.88 (1H, ddt, *J* 17.1, 10.2 and 7.2, 4″-H), 5.78 (1H, dt, *J* 11.3 and 5.9, 3′-H), 5.62 (1H, dt, *J* 11.3 and 6.4, 2′-H), 5.32 (1H, s, 3-H_a), 5.18 (1H, s, 3-H_b), 5.07 (1H, dd, *J* 17.1 and 1.5, 5″-H_a), 5.01 (1H, br d, *J* 10.2, 5″-H_b), 4.40 (2H, d, *J* 5.9, 4′-H), 4.09 (2H, d, *J* 6.4, 1′-H), 3.95 (2H, s, 2-CCH_2O), 3.83 (2H, s, 1-H), 3.79 (2H, t, *J* 6.5, 1″-H),

3.44-3.41 (2H, m, 1′′′-H), 2.46-2.43 (5H, m, 4′′′′-CCH_3 and 2′′′-H), 2.18 (2H, app q, *J* 7.2, 3′′-H), 1.70 (2H, tt, *J* 7.2 and 6.5, 2′′-H) and 1.09-1.03 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 144.3 (4′′′′-C), 141.1 (2-C), 138.8 (3′′-C), 136.1 (1′′′′-C), 132.9 (3′-C), 130.3 (3′′′′-C), 127.6 (2′′′′-C), 127.0 (2′-C), 117.2 (3-C), 115.0 (5′′-C), 70.9 (2-C*C*H_2O), 66.7 (1′-C), 62.7 (1′′-C), 59.5 (4′-C), 52.0 (1-C), 40.7 (1′′′-C), 32.3 (2′′-C), 30.9 (t, $^{2}J_{C–F}$ 21.4, 2′′′-C), 30.4 (3′′-C), 21.9 (4′′′′-C*C*H_3), 17.7 (^{i}Pr) and 12.5 (^{i}Pr); *m/z* (ES+) 978 (100%, MNa^+). (Found: MNa^+ 978.2491, $C_{36}H_{46}F_{17}NO_5SSi$ requires *MNa*, 978.2487).



***N*-(2-{4′-[(hex-5′′-enyloxy)-di*iso*propyl-silanyloxy]-but-2′-enyloxymethyl}-allyl)-*N*-(3′′′,3′′′,4′′′,4′′′,5′′′,5′′′,6′′′,6′′′,7′′′,7′′′,8′′′,8′′′,9′′′,9′′′,10′′′,10′′′,10′′′-heptadecafluoro-decyl)-4′′′′-methyl-benzenesulfonamide 7c**

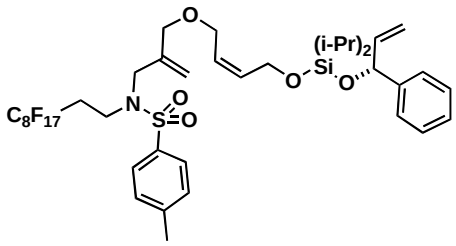
By general procedure D, the alcohol[11] **6** (150 mg, 0.198 mmol), the silyl ether **13c** (3.5 eq.), *N*-bromosuccinimide (3 eq.) and *N*,*N*-dimethylaminopyridine (0.1 eq.) gave a crude product after 12 h. The crude product was purified by Fluorous-Solid Phase Extraction (2 g cartridge, loading with ≤ 400 μL DMF) to give the *silaketal* **7c** (179 mg, 93%, 88% purity) as a colourless oil, R_f 0.87 (7:3 petrol–EtOAc), ν_{max}/cm^{-1} 3079, 3027, 2944, 2869, 1657, 1641, 1599, 1495, 1463, 1350, 1242, 1212, 1163, 1089 and 1067; δ_H (500 MHz, $CDCl_3$) 7.77 (2H, d, *J* 8.3, 2′′′′-H), 7.34 (2H, d, *J* 8.3, 3′′′′-H), 5.87-5.83 (1H, m, 5′′-H), 5.78-5.75 (1H, m, 3′-H), 5.63-5.60 (1H, m, 2′-H), 5.31 (1H, s, 3-H_a), 5.17 (1H, s, 3-H_b), 5.05 (1H, d, *J* 17.1, 6′′-H_a), 4.98 (1H, d, *J* 9.9, 6′′-H_b), 4.39 (2H, d, *J* 5.0, 4′-H), 4.08 (2H, d, *J*, 5.6, 1′-H), 3.95 (2H, s, 2-CCH_2O), 3.78 (2H, t, *J* 6.4, 1′′-H), 3.43-3.41 (2H, m, 1′′′-H), 2.49-2.41 (5H, m, 4′′′′-CCH_3 and 2′′′-H), 2.13-2.10 (2H, m, 4′′-H), 1.62-1.61 (2H, m, 2′′-H), 1.52-1.49 (2H, m, 3′′-H) and 1.09-1.08 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 144.3 (4′′′′-C), 141.1 (2-C), 139.3 (5′′-C), 136.1 (1′′′′-C), 133.0 (3′-C), 130.3 (3′′′′-C), 127.6 (2′′′′-C), 127.0 (2′-C), 117.2 (3-C), 114.8 (6′′-C), 70.9 (2-C*C*H_2O), 66.7 (1′-C), 63.2 (1′′-C), 59.5 (4′-C), 52.0 (1-C), 40.8 (1′′′-C), 33.9 (4′′-C), 32.6 (2′′-C), 30.9 (t, $^{2}J_{C–F}$ 21.7, 2′′′-C), 25.5 (3′′-C), 21.9 (4′′′′-C*C*H_3), 17.8 (^{i}Pr), 17.6 (^{i}Pr), 17.5 (^{i}Pr), 17.4 (^{i}Pr) and 12.5 (^{i}Pr); *m/z* (ES+) 1026 (100%, MNa^+). (Found: MNa^+ 1026.2491, $C_{40}H_{46}F_{17}NO_5SSi$ requires *MNa*, 1026.2487).



***N*-[2-(4′-{[1′′-(2′′′,4′′′-Dimethoxy-phenyl)-allyloxy]-di*iso*propyl-silanyloxy}-but-2′-enyloxymethyl)-allyl]-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-decyl)-4′′′′-methyl-benzenesulfonamide 7d**

By general procedure D, the alcohol[11] **6** (150 mg, 0.198 mmol), the silyl ether **13d** (3.5 eq.), *N*-bromosuccinimide (3 eq.) and *N*,*N*-dimethylaminopyridine (0.1 eq.) gave a crude product after 12 h. The

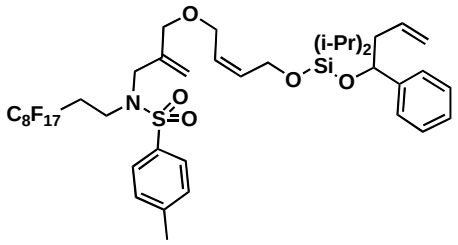
crude product was purified by Fluorous-Solid Phase Extraction (2 g cartridge, loading with ≤ 400 μL DMF). The organic fraction was filtered through a short pad of Florisil, eluting with 9:1 petrol–EtOAc, to give the *silaketal* **7d** (47 mg, 56%) as a colourless oil, R_f 0.53 (8:2 petrol–EtOAc); ν_{max}/cm^{-1} 3082, 2945, 2868, 1640, 1614, 1588, 1504, 1463, 1352, 1330, 1289, 1242 and 921; δ_H (500 MHz, $CDCl_3$) 7.74 (2H, d, *J* 8.1, 2‴′-H), 7.42 (1H, d, *J* 8.5, 6‴-H), 7.36 (2H, d *J* 8.1, 3‴′-H), 6.53 (1H, dd, *J* 8.5 and 2.3, 5‴-H), 6.45 (1H, d, *J* 2.3, 3‴-H), 5.98 (1H, ddd, *J* 17.0, 10.3 and 5.9, 5″-H), 5.75 (1H, br d, *J* 5.1, 1″-H), 5.68-5.63 (1H, m, 2′-H), 5.55-5.50 (1H, m, 3′-H), 5.31 (1H, app dt, *J* 17.0 and 1.7, 3″-H_a), 5.28 (1H, s, 3-H_a), 5.15 (1H, s, 3-H_b), 5.01 (1H, app dt, *J* 10.3 and 1.7, 3″-H_b), 4.25 (1H, dd, *J* 13.5 and 5.9, 1′-H_a), 4.18 (1H, dd, *J* 13.5 and 6.0, 1′-H_b), 3.95 (2H, d, *J* 5.9, 4′-H), 3.88 (2H, s, 2-CC*H*$_2$O), 3.82 (6H, s, OMe), 3.80 (2H, s, 1-H), 3.42-3.39 (2H, m, *decyl* 1-H), 2.46-2.38 (5H, m, 4‴′-CCH_3 and *decyl* 2-H), 1.09-1.07 (7H, m, ^{i}Pr) and 1.02-0.99 (7H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 160.2 (4‴-C), 156.8 (2‴-C), 144.3 (4‴′-C), 141.2 (2″-C), 141.1 (2-C), 136.1 (1‴′-C), 132.9 (2′-C), 130.3 (3‴′-C), 127.7 (2‴′-C and 6‴-C), 126.8 (3′-C), 125.0 (1‴-C), 117.1 (3-C), 112.4 (3″-C), 104.9 (5‴-C), 98.4 (3‴-C), 70.8 (2-C*C*H$_2$O), 68.8 (1″-C), 66.7 (4′-C), 59.6 (1′-C), 55.7 (2 × OMe), 51.9 (1-C), 40.8 (*decyl* 1-C), 31.0 (t, $^2J_{C-F}$ 21.8, *decyl* 2-C), 21.9 (4‴′-C*C*H$_3$), 17.8 (^{i}Pr), 17.6 (^{i}Pr), 12.7 (^{i}Pr) and 12.6 (^{i}Pr); *m/z* (ES+) 1086 (MNa^+). (Found: MNa^+ 1086.2664, $C_{42}H_{50}F_{17}NO_7SSi$ requires *MNa*, 1086.2698).



(1″*R*)-*N*-(2-{(*Z*)-4′-[Di*iso*propyl-(1″-phenyl-allyloxy)-silanyloxy]-but-2′-enyloxymethyl}-allyl)-*N*-(3‴,3‴,4‴,4‴,5‴,5‴,6‴,6‴,7‴,7‴,8‴,8‴,9‴,9‴,10‴,10‴,10‴-heptadecafluoro-decyl)-4‴′-methyl-benzenesulfonamide (+)-7e

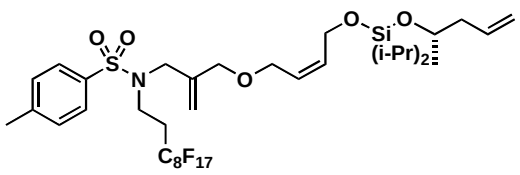
By general procedure D, the alcohol[11] **6** (200 mg, 0.264 mmol), the silyl ether **13e** (3.5 eq.), *N*-bromosuccinimide (3 eq.) and *N*,*N*-dimethylaminopyridine (0.1 eq.) in dichloromethane (0.1 M) gave a crude product after 10 h. The crude product was purified by Fluorous-Solid Phase Extraction (2 g cartridge, loading with ≤ 400 μL DMF) to give the *silaketal* **7e** (147 mg, 55%, 93% purity) as a colourless oil, R_f 0.76 (8:2 petrol–EtOAc); $[\alpha]_D$ +11.2 (*c* 1.0 in $CHCl_3$); ν_{max}/cm^{-1} 3065, 3027, 2946, 2928, 2868, 1657, 1599, 1463, 1352, 1243, 1209, 1160 and 1053; δ_H (500 MHz, $CDCl_3$) 7.73 (2H, d, *J* 8.2, 2‴′-H), 7.40-7.33 (6H, m, *ortho*-Ph, *meta*-Ph and 3‴′-H), 7.27 (1H, t, *J* 7.2, *para*-Ph), 5.99 (1H, ddd, *J* 17.0, 10.5 and 10.3, 2″-H), 5.65 (1H, dt, *J* 11.3 and 5.8, 3′-H), 5.53 (1H, dt, *J* 11.3 and 6.3, 2′-H), 5.36 (1H, d, *J* 10.5, 3″-H_a), 5.35 (1H, d, *J* 17.0, 3″-H_b), 5.28 (1H, s, 3-H_a), 5.15 (1H, s, 3-H_b), 5.10 (1H, d, *J* 10.3, 1″-H), 4.24 (1H, dd, *J* 13.4 and 5.8, 4′-H_a), 4.18 (1H, dd, *J* 13.4 and 5.8, 4′-H_b), 3.94 (2H, d, *J* 6.3, 1′-H), 3.88 (2H, s, 2-CCH_2O), 3.80 (2H, s, 1-H), 3.42-3.39 (2H, m, 1‴-H), 2.46-2.38 (5H, m, 2‴-H and 4‴′-CCH_3) and 1.10-0.98 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 144.3, 143.9, 141.8, 141.1, 136.1, 132.8, 130.3, 128.7, 128.6, 127.6, 127.5, 126.9, 126.8,

126.4, 117.1, 113.7, 75.9, 70.8, 66.7, 59.6, 52.0, 40.8, 31.0, 21.9, 17.7, 17.6, 17.5 and 12.7; *m/z* (ES+) 1026 (100%, MNa^+). (Found: MNa^+ 1026.2496, $C_{40}H_{46}F_{17}NO_5SSi$ requires *MNa*, 1026.2487)



***N*-(2-{(*Z*)-4′-[Di*iso*propyl-(1″-phenyl-but-3″-enyloxy)-silanyloxy]-but-2′-enyloxymethyl}-allyl)-*N*-(3‴,3‴,4‴,4‴,5‴,5‴,6‴,6‴,7‴,7‴,8‴,8‴,9‴,9‴,10‴,10‴,10‴-heptadecafluoro-decyl)-4⁗-methyl-benzenesulfonamide 7f**

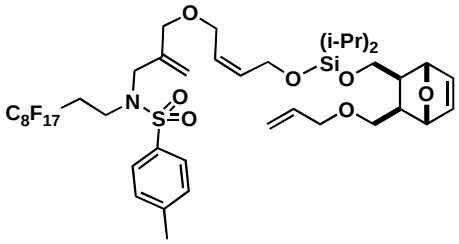
By general procedure D, the alcohol[11] **6** (168 mg, 0.22 mmol), the silyl ether **13f** (5.5 eq.), *N*-bromosuccinimide (5 eq.) and *N*,*N*-dimethylaminopyridine (0.5 eq.) in dichloromethane (0.1 M) gave a crude product after 14 h. The crude product was purified by Fluorous-Solid Phase Extraction (5 g cartridge, loading with ≤ 1 mL DMF) to give the *silaketal* **7f** (222 mg, >98%, 76% purity), R_f 0.86 (8:2 petrol–EtOAc); ν_{max}/cm^{-1} 3061, 3018, 2947, 2935, 2858, 1655, 1590, 1465, 1357, 1245, 1201, 1165 and 1053; δ_H (500 MHz, $CDCl_3$) 7.73 (2H, d, *J* 8.2, 2⁗-H), 7.37-7.33 (6H, m, 3⁗-H, *ortho*-Ph and *meta*-Ph), 7.25 (1H, t, *J* 6.5, *para*-Ph), 5.76 (1H, ddt, *J* 15.9, 11.5 and 6.2, 3″-H), 5.61 (1H, dt, *J* 11.4 and 5.6, 3′-H), 5.52 (1H, dt, *J* 11.4 and 6.5, 2′-H), 5.28 (1H, s, 3-H_a), 5.15 (1H, s, 3-H_b), 5.02 (1H, d, *J* 15.9, 4″-H_a), 5.01 (1H, d, *J* 11.5, 4″-H_b), 4.91 (1H, t, *J* 6.2, 1″-H), 4.20 (1H, dd, *J* 13.6 and 5.6, 4′-H_a), 4.09 (1H, dd, *J* 13.6 and 5.6, 4′-H_b), 3.93 (2H, d, *J* 6.5, 1′-H), 3.89 (2H, s, 2-CCH_2O), 3.80 (2H, s, 1-H), 3.42-3.39 (2H, m, 1‴-H), 2.56 (1H, app dt, *J* 13.9 and 6.2, 2″-H_a), 2.50 (1H, app dt, *J* 13.9 and 6.2, 2″-H_b), 2.47-2.38 (5H, m, 2‴-H and 4⁗-CCH_3) and 1.10-.095 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 144.9, 144.3, 141.1, 136.2, 135.0, 132.9, 130.3, 128.4, 127.7, 127.5, 126.8, 126.5, 117.5, 117.0, 74.9, 70.8, 66.7, 59.6, 51.9, 45.6, 40.8, 31.1, 21.9, 17.8, 17.7, 17.6, 17.5, 17.4 and 12.7; *m/z* (ES+) 1040 (100%, MNa^+). (Found: MNa^+ 1040.2641, $C_{41}H_{48}F_{17}NO_5SSi$ requires *MNa*, 1040.2643)



(2″*S*)-*N*-(2-{4′-[(pent-4″-en-2″-yloxy)-di*iso*propyl-silanyloxy]-but-2′-enyloxymethyl}-allyl)-*N*-(3‴,3‴,4‴,4‴,5‴,5‴,6‴,6‴,7‴,7‴,8‴,8‴,9‴,9‴,10‴,10‴,10‴-heptadecafluoro-decyl)-4⁗⁗-methyl-benzenesulfonamide 7g

By general procedure D, the alcohol[11] **6** (150 mg, 0.198 mmol), the silyl ether **13e** (3.5 eq.), *N*-bromosuccinimide (3 eq.) and *N*,*N*-dimethylaminopyridine (0.1 eq.) gave a crude product after 12 h. The crude product was purified by Fluorous-Solid Phase Extraction (2 g cartridge, loading with ≤ 400 μL DMF) to give the *silaketal* **7e** (182 mg, 96%, 85% purity), R_f 0.86 (7:3 petrol–EtOAc); ν_{max}/cm^{-1} 3078, 3027, 2945,

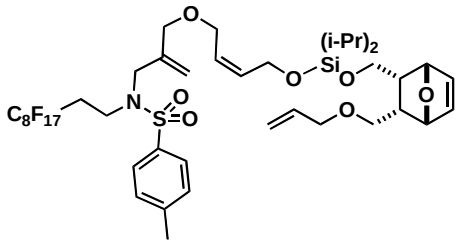
2869, 1642, 1599, 1463, 1396, 1351, 1243, 1209, 1089 and 1059; δ_H (500 MHz, $CDCl_3$) 7.75 (2H, d, *J* 8.0, 2′′′-H), 7.37 (2H, d, *J* 8.0, 3′′′-H), 5.92-5.83 (1H, m, 4′′-H), 5.78-5.75 (1H, m, 3′-H), 5.63-5.59 (1H, m, 2′-H), 5.31 (1H, s, 3-H_a), 5.17 (1H, s, 3-H_b), 5.09 (1H, d, *J* 15.5, 5′′-H_a), 5.08 (1H, d, *J* 10.1, 5′′-H_b), 4.39 (2H, d, *J* 5.6, 4′-H), 4.11-4.08 (3H, m, 1′-H and 2′′-H), 3.95 (2H, s, 2-CCH_2O), 3.83 (2H, s, 1-H), 3.44-3.41 (2H, m, 1′′′-H), 2.49 (3H, s, 4′′′′-CCH_3), 2.45-2.43 (2H, m, 2′′′-H), 2.35-2.31 (1H, m, 3′′-H_a), 2.28-2.24 (1H, m, 3′′-H_b), 1.22 (3H, d, *J* 6.7, 1′′-H) and 1.08-1.07 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 144.3 (4′′′′-C), 141.1 (2-C), 136.1 (1′′′′-C), 135.6 (4′′-C), 133.0 (3′-C), 130.3 (3′′′′-C), 127.7 (2′′′′-C), 126.9 (2′-C), 117.2 (3-C), 117.1 (5′′-C), 70.9 (2-*C*CH_2O), 68.6 (2′′-C), 66.8 (1′-C), 59.5 (4′-C), 52.0 (1-C), 44.6 (3′′-C), 40.8 (1′′′-C), 31.1 (t, $^2J_{C-F}$ 21.2, 2′′′-C), 23.6 (1′′-C), 21.9 (4′′′′-*C*CH_3), 17.8 (^{i}Pr), 17.7 (^{i}Pr), 17.6 (^{i}Pr), 17.5 (^{i}Pr), 12.8 (^{i}Pr) and 12.7 (^{i}Pr); *m/z* (ES+) 978 (100%, MNa^+). (Found: MNa^+ 978.2519, $C_{36}H_{46}F_{17}NO_5SSi$ requires *MNa*, 978.2498).



(1′′*R,2′′*R**,3′′*S**,4′′*S**)-*N*-(2-{(Z)-4′-[(3′′-Allyloxymethyl-7′′-oxa-bicyclo[2.2.1]hept-5′′-en-2′′-ylmethoxy)-di*iso*propyl-silanyloxy]-but-2′-enyloxymethyl}-allyl)-*N*-(3′′′,3′′′,4′′′,4′′′,5′′′,5′′′,6′′′,6′′′,7′′′,7′′′,8′′′,8′′′,9′′′,9′′′,10′′′,10′′′,10′′′-heptadecafluoro-decyl)-4′′′′-methyl-benzenesulfonamide 7h**

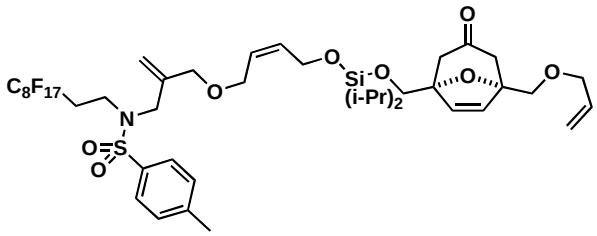
By general procedure D, the alcohol[11] **6** (318 mg, 0.42 mmol), the silyl ether **13h** (3.5 eq.), *N*-bromosuccinimide (3 eq.) and *N*,*N*-dimethylaminopyridine (0.1 eq.) gave a crude product after 14 h. The crude product was purified by Fluorous-Solid Phase Extraction (5 g cartridge, loading with ≤ 1 mL DMF) and the fluorous fraction was filtered through a pad of Florisil eluting with 9:1 petrol–EtOAc to give the *silaketal* **7h** (244 mg, 54%) as a colourless oil, R_f 0.73 (7:3 petrol–EtOAc); ν_{max}/cm^{-1} 3081, 2945, 2868, 1657, 1599, 1463, 1349, 1242, 1207, 1155, 1116 and 1061; δ_H (500 MHz, $CDCl_3$) 7.73 (2H, d, *J* 8.5, 2′′′′-H), 7.36 (2H, d, *J* 8.5, 3′′′′-H), 6.39 (1H, d, *J* 7.4, 5′′-H), 6.38 (1H, d, *J* 7.4, 6′′-H), 5.95 (1H, ddd, *J* 17.2, 10.4 and 5.4, *allyl* 2-H), 5.75 (1H, dt, *J* 11.3 and 5.8, 3′-H), 5.61 (1H, dt, *J* 11.3 and 6.2, 2′-H), 5.30 (1H, dd, *J* 17.2 and 1.4, *allyl* 3-H_a), 5.29 (1H, s, 3-H_a), 5.21 (1H, br d, *J* 10.4, *allyl* 3-H_b), 5.15 (1H, s, 3-H_b), 4.93 (1H, s, 4′′-H), 4.87 (1H, s, 1′′-H), 4.38 (2H, d, *J* 5.8, 4′-H), 4.07 (2H, d, *J* 6.2, 1′-H), 4.01 (2H, d, *J* 5.4, *allyl* 1-H), 3.94-3.91 (3H, m, 2-CCH_2O and 2′′-CCH_a), 3.81 (2H, s, 1-H), 3.67 (1H, app t, *J* 9.8, 2′′-CCH_b), 3.59 (1H, dd, *J* 8.9 and 5.5, 3′′-CCH_a), 3.42-3.38 (3H, m, 1′′′-H and 3′′-CCH_b), 2.47 (3H, s, 4′′′′-CCH_3), 2.44-2.40 (2H, m, 2′′′-H), 1.92 (1H, ddd, *J* 8.9, 8.5 and 5.5, 3′′-H), 1.89 (1H, ddd, *J* 9.8, 8.5 and 5.6, 2′′-H) and 1.08-1.04 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 144.3 (4′′′-C), 141.1 (2-C), 136.1 (1′′′′-C), 136.0 (5′′-C), 135.9 (6′′-C), 135.1 (*allyl* 2-C), 132.8 (3′-C), 130.3 (3′′′′-C), 127.6 (2′′′′-C), 127.2 (2′-C), 117.5 (*allyl* 3-C), 117.2 (3-C), 81.1 (1′′-C), 80.6 (4′′-C), 72.6 (*allyl* 1-C), 70.9 (1′-C), 70.0 (3′′-*C*CH_2O), 66.8 (*allyl* 1-C), 62.5 (2′′-*C*CH_2O),

59.6 (4′-C), 52.0 (1-C), 42.8 (3′′-C), 40.8 (1′′′-C), 40.4 (2′′-C), 31.0 (t, $^{2}J_{C–F}$ 21.5, 2′′′-C), 21.9 (4′′′′-C*C*H$_3$), 17.7 (^{i}Pr) and 12.4 (^{i}Pr); *m/z* (ES+) 1088 (100%, MNa$^+$). (Found: 1088.2892, $C_{42}H_{52}F_{17}NO_7SSi$ requires *MNa*, 1088.2855).



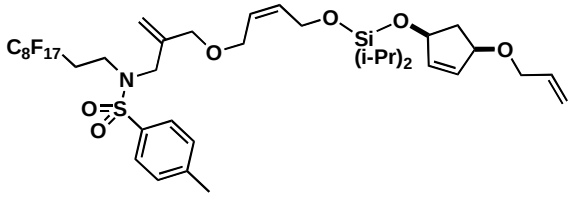
(1′′*R,2′′*S**,3′′*R**,4′′*S**)-*N*-(2-{(Z)-4′-[(3′′-Allyloxymethyl-7′′-oxa-bicyclo[2.2.1]hept-5′′-en-2′′-ylmethoxy)-di*iso*propyl-silanyloxy]-but-2′-enyloxymethyl}-allyl)-*N*-(3′′′,3′′′,4′′′,4′′′,5′′′,5′′′,6′′′,6′′′,7′′′,7′′′,8′′′,8′′′,9′′′,9′′′,10′′′,10′′′,10′′′-heptadecafluoro-decyl)-4′′′′-methyl-benzenesulfonamide 7i**

By general procedure D, the alcohol[11] **6** (76 mg, 0.10 mmol), the silyl ether **13i** (3.5 eq.), *N*-bromosuccinimide (3 eq.) and *N*,*N*-dimethylaminopyridine (0.1 eq.) gave a crude product after 14 h. The crude product was purified by Fluorous-Solid Phase Extraction (5 g cartridge, loading with ≤ 1 mL DMF) and the fluorous fraction was filtered through a pad of Florisil eluting with 9:1 petrol–EtOAc to give the *silaketal* **7i** (63 mg, 59%) as a colourless oil, R_f 0.50 (7:3 petrol–EtOAc); ν_{max}/cm^{-1} 3081, 3010, 2945, 2862, 1651, 1599, 1492, 1465, 1455, 1401, 1347, 1336 and 1242; δ_H (500 MHz, $CDCl_3$) 7.72 (2H, d, *J* 8.2, 2′′′′-H), 7.34 (2H, d, *J* 8.2, 3′′′′-H), 6.48 (1H, dd, *J* 5.9 and 1.4, 6′′-H), 6.44 (1H, dd, *J* 5.9 and 1.4, 5′′-H), 5.89 (1H, dddd, *J* 17.3, 10.4, 5.6 and 4.1, *allyl* 2-H), 5.73 (1H, dt, *J* 11.3 and 5.8, 3′-H), 5.62 (1H, dt, *J* 11.3 and 6.1, 2′-H), 5.89 (1H, dddd, *J* 17.3, 10.4, 5.6 and 4.1, *allyl* 2-H), 5.73 (1H, dt, *J* 11.3 and 5.8, 3′-H), 5.62 (1H, dt, *J* 11.3 and 6.1, 2′-H), 5.30 (1H, s, 3-H$_a$), 5.27 (1H, app dq, *J* 17.3 and 1.5, *allyl* 3-H$_a$), 5.20 (1H, app dq, *J* 10.4 and 1.4, *allyl* 3-H$_b$), 5.16 (1H, s, 3-H$_b$), 5.02 (1H, br d, *J* 3.1, 1′′-H), 5.01 (1H, br d, *J* 3.3, 4′′-H), 4.37 (2H, d, *J* 5.8, 4′-H), 4.07 (2H, d, *J* 6.1, 1′-H), 3.96 (2H, s, 2-CCH$_2$O), 3.92 (1H, br dd, *J* 12.9 and 4.1, *allyl* 1-H$_a$), 3.90 (1H, br dd, *J* 12.9 and 5.7, *allyl* 1-H$_b$), 3.81 (2H, s, 1-H), 3.70 (1H, dd, *J* 9.9 and 5.6, 2′′-CCH$_a$), 3.41-3.38 (2H, m, 1′′′-H), 3.32-3.27 (2H, m, 2′′-CCH$_b$ and 3′′-CCH$_a$), 3.02 (1H, app t, *J* 9.2, 3′′-CCH$_b$), 2.65-2.60 (2H, m, 2′′-H and 3′′-H), 2.46 (3H, s, 4′′′′-CCH$_3$), 2.43-2.40 (2H, m, 2′′′-H) and 1.04-1.01 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 144.3 (4′′′′-C), 141.1 (2-C), 136.1 (1′-C), 135.6, 135.5 (5′′-C and 6′′-C), 135.0 (*allyl* 2-C), 132.7 (3′-C), 130.3 (3′′′′-C), 127.6 (2′′′′-C), 127.2 (2′-C), 117.4 (*allyl* 3-C), 117.2 (3-C), 81.2, 81.1 (1′′-C and 4′′-C), 72.5 (*allyl* 1-C), 70.9 (2-C*C*H$_2$O), 69.5 (3′′-C*C*H$_2$O), 66.8 (1′-C), 62.3 (2′′-C*C*H$_2$O), 59.6 (4′-C), 52.0 (1-C), 43.6 (2′′-C), 41.0 (3′′-C), 40.8 (2′′′-C), 31.0 (t, $^{2}J_{C–F}$ 21.0, 1′′′-C), 21.9 (4′′′′-C*C*H$_3$), 17.7 (^{i}Pr), 17.5 (^{i}Pr), 17.4 (^{i}Pr), 12.8 (^{i}Pr) and 12.4 (^{i}Pr); *m/z* (ES+) 1088 (100%, MNa$^+$). (Found: MNa$^+$ 1088.2863, $C_{42}H_{52}F_{17}O_7SSi$ requires *MNa*, 1088.2855).



(1*R,5*S**)-*N*-(2-{(Z)-4′-[(-5-Allyloxymethyl-3-oxo-8-oxa-bicyclo[3.2.1]oct-6-en-1-ylmethoxy)-di*iso*propyl-silanyloxy]-but-2′-enyloxymethyl}-allyl)-*N*-(3‴,3‴,4‴,4‴,5‴,5‴,6‴,6‴,7‴,7‴,8‴,8‴,9‴,9‴,10‴,10‴,10‴-heptadecafluoro-decyl)-4‴′-methyl-benzenesulfonamide 7j**

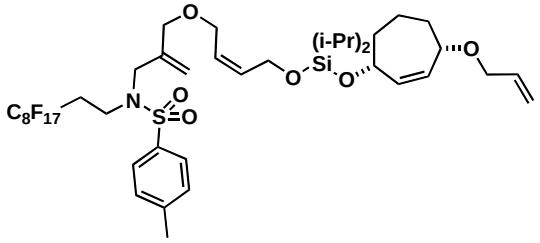
By general procedure D, the alcohol[11] **6** (73 mg, 0.096 mmol), the silyl ether **13j** (3.5 eq.), *N*-bromosuccinimide (3 eq.) and *N*,*N*-dimethylaminopyridine (0.1 eq.) gave a crude product after 14 h. The crude product purified by Fluorous-Solid Phase Extraction (2 g cartridge, loading with ≤ 400 μL DMF). The fluorous fraction was filtered through a pad of Florisil eluting with 9:1 petrol–EtOAc to give the *silaketal* **7j** (34 mg, 32%) as a colourless oil, R_f 0.79 (7:3 petrol–EtOAc); ν_{max}/cm^{-1} 3082, 3021, 2927, 2862, 1715, 1657, 1599, 1495, 1463, 1451, 1401, 1344, 1243, 1212, 1160 and 1061; δ_H (500 MHz, $CDCl_3$) 7.73 (2H, d, *J* 8.2, 2‴′-H), 7.36 (2H, d, *J* 8.2, 3‴′-H), 6.21 (1H, d, *J* 5.9, 2″-H), 6.10 (1H, d, *J* 5.9, 3″-H), 5.92 (1H, ddt, *J* 17.2, 10.4 and 5.0, *allyl* 2-H), 5.76-5.72 (1H, m, 3′-H), 5.64-5.59 (1H, m, 2′-H), 5.30 (1H, br dd, *J* 17.2 and 1.5, *allyl* 3-H_a), 5.29 (1H, s, 3-H_a), 5.22 (1H, br dd, *J* 10.4 and 1.2, *allyl* 3-H_b), 5.15 (1H, s, 3-H_b), 4.40 (2H, d, *J* 6.0, 4′-H), 4.11-4.09 (2H, m, *allyl* 1-H), 4.06 (2H, d, *J* 6.1, 1′-H), 3.99 (2H, s, 1″-CCH_2), 3.94 (2H, s, 2-CCH_2), 3.80 (2H, s, 1-H), 3.68 (1H, d, *J* 10.5, 5″-CH_a), 3.65 (1H, d, *J* 10.5, 5″-CCH_b), 3.41-3.38 (2H, m, 1‴-H), 2.74 (1H, d, *J* 16.3, 4″-H_a), 2.63 (1H, d, *J* 16.3, 2″-H_a), 2.94 (1H, d, *J* 16.3, 2″-H_b), 2.47-2.43 (5H, m, 4‴′-CCH_3 and 2‴-H), 2.39 (1H, d, *J* 16.3, 4″-H_b) and 1.07 (14H, s, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 207.1 (3″-C), 144.3 (4‴′-C), 141.1 (2-C), 136.1 (1‴′-C), 135.0 (7″-C), 134.8 (*allyl* 2-C), 134.3 (6″-C), 132.7 (3′-C), 130.3 (3‴′-C), 127.6 (2‴′-C), 127.3 (2′-C), 117.8 (*allyl* 3-C), 117.2 (3-C), 87.7 (1″-C), 87.0 (5″-C), 73.0 (*allyl* 1-C), 72.5 (5″-CCH_2O), 70.9 (2-CCH_2O), 66.8 (1′-C), 66.1 (1″-CCH_2), 59.6 (4′-C), 52.0 (1-C), 47.4 (4″-C), 47.3 (2″-C), 40.8 (1‴-C), 31.0 (t, $^2J_{C-F}$ 21.1, 2‴-C), 21.9 (4‴′-CCH_3), 17.6 (^{i}Pr) and 12.4 (^{i}Pr); *m/z* (ES+) 1116 (100%, MNa^+). (Found: MNa^+ 1116.2835, $C_{43}H_{52}F_{17}NO_8SSi$ requires *MNa* 1116.2804).



(1″*S,4″*R**)-*N*-(2-{(*Z*)-4′-[(4″-Allyloxy-cyclopent-2″-enyloxy)-di*iso*propyl-silanyloxy]-but-2′-enyloxymethyl}-allyl)-*N*-(3‴,3‴,4‴,4‴,5‴,5‴,6‴,6‴,7‴,7‴,8‴,8‴,9‴,9‴,10‴,10‴,10‴-heptadecafluoro-decyl)-*N*-4‴′-methyl-benzenesulfonamide 7k**

By general procedure D, the alcohol[11] **6** (81 mg, 0.108 mmol), the silyl ether **13k** (3.5 eq.), *N*-bromosuccinimide (3 eq.) and *N*,*N*-dimethylaminopyridine (0.1 eq.) in dichloromethane (0.2 M) gave a crude

product after 2 h. The crude product was purified by Fluorous-Solid Phase Extraction (2 g cartridge, loading with ≤ 400 μL DMF) and the fluorous fraction filtered through a short pad of Florisil eluting with 9:1 petrol–EtOAc to give the *silaketal* **7k** (70 mg, 64%) as a colourless oil, R_f 0.63 (8:2 petrol–EtOAc); ν_{max}/cm^{-1} 3060, 2945, 2895, 2868, 1598, 1464, 1363, 1350, 1242, 1213, 1163, 1088 and 1017; δ_H (500 MHz, $CDCl_3$) 7.73 (2H, d, *J* 8.2, 2′′′′-H), 7.36 (2H, d, *J* 8.2, 3′′′′-H), 6.00-5.92 (3H, m, *allyl* 2-H, 2′′-H and 3′′-H), 5.75 (1H, dtt, *J* 11.3, 5.9 and 1.4, 3′-H), 5.61 (1H, dtt, *J* 11.3, 6.2 and 1.6, 2′-H), 5.31 (1H, dd, *J* 17.0 and 1.6, *allyl* 3-H_a), 5.30 (1H, s, 3-H_a), 5.20 (1H, dd, *J* 10.3 and 1.2, *allyl* 3-H_b), 5.16 (1H, s, 3-H_b), 4.86 (1H, app br t, *J* 5.8, 4′′-H), 4.42 (1H, app br t, *J* 5.7, 1′′-H), 4.39 (2H, d, *J* 5.9, 4′-H), 4.06 (2H, d, *J* 6.2, 1′-H), 4.05 (2H, br d, *J* 5.6, *allyl* 1-H), 3.93 (2H, s, 2-CCH_2O), 3.81 (2H, s, 1-H), 3.42-3.38 (2H, m, 1′′′-H), 2.75 (1H, dt, *J* 13.3 and 7.2, 5′′-H_a), 2.47 (3H, s, 4′′′′-CCH_3), 2.44-2.37 (2H, m, 2′′′-H), 1.66 (1H, dt, *J* 13.3 and 5.5, 5′′-H_b) and 1.07-1.04 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 144.3 (4′′′′-C), 141.1 (2-C), 137.5 (2′′-C), 136.2 (*allyl* 2-C), 135.6 (1′′′′-C), 133.5 (3′′-C), 132.8 (3′-C), 130.3 (3′′′′-C), 127.6 (2′′′′-C), 127.1 (2′-C), 117.2 (3-C), 117.1 (*allyl* 3-C), 81.7 (1′′-C), 74.9 (4′′-C), 70.9 (2-CCH_2O), 69.9 (1′-C), 66.8 (*allyl* 1-C), 59.6 (4′-C), 51.9 (1-C), 41.8 (5′′-C), 40.8 (1′′′-C), 31.0 (t, $^2J_{C-F}$ 23.2, 2′′′-C), 21.9 (4′′′′-CCH_3), 17.7 (^{i}Pr), 17.6 (^{i}Pr), 17.5 (^{i}Pr) and 12.6 (^{i}Pr); *m/z* (ES+) 1032 (100%, MNa^+). (Found: MNa^+ 1032.2672, $C_{38}H_{45}F_{17}NO_6SSi$ requires *MNa*, 1032.2598).

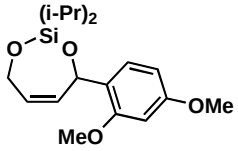


(1′′*R*,4′′*S*)-*N*-(2-{(*Z*)-4′-[(4′′-Allyloxy-cyclohept-2′′-enyloxy)-di*iso*propyl-silanyloxy]-but-2′-enyloxymethyl}-allyl)-*N*-(3′′′,3′′′,4′′′,4′′′,5′′′,5′′′,6′′′,6′′′,7′′′,7′′′,8′′′,8′′′,9′′′,9′′′,10′′′,10′′′,10′′′-heptadecafluoro-decyl)-4′′′′-methyl-benzenesulfonamide (+)-7l

By general procedure D, the alcohol[11] **6** (43 mg, 0.057 mmol), the silyl ether **13l** (3.5 eq.), *N*-bromosuccinimide (3 eq.) and *N*,*N*-dimethylaminopyridine (0.3 eq.) in dichloromethane (0.1 M) gave a crude product after 12 h. The crude product was purified by Flurous-Solid Phase Extraction (2 g cartridge, loading with ≤ 400 μL DMF) to give the *silaketal* **7l** (56 mg, 95%, >80% purity as estimated using 500 MHz ^{1}H NMR spectroscopy) as a colourless oil, R_f 0.43 (9:1 petrol–EtOAc), $[\alpha]_D$ +3.6 (*c* 1.0 in $CHCl_3$); ν_{max}/cm^{-1} 3076, 3027, 2929, 2868, 1656, 1599, 1495, 1463, 1393, 1351, 1242, 1212, 1157, 1061 and 1017; δ_H (500 MHz, $CDCl_3$) 7.73 (2H, d, *J* 8.2, 2′′′′-H), 7.36 (2H, d, *J* 8.2, 3′′′′-H), 5.97 (1H, dddd, *J* 17.2, 10.4, 5.5 and 5.2, *allyl* 2-H), 5.78 (1H, br d, *J* 12.1, 2′′-H), 5.78-5.71 (2H, m, 3′-H and 3′′-H), 5.61 (1H, dt, *J* 11.3 and 6.4, 2′-H), 5.30 (1H, dd, 17.2 and 1.6, *allyl* 3-H_a), 5.29 (1H, s, 3-H_a), 5.19 (1H, dd, *J* 10.4 and 1.4, *allyl* 3-H_b), 5.16 (1H, s, 3-H_b), 4.47 (1H, app br d, *J* 10.2, 1′′-H), 4.37 (2H, d, *J* 5.3, 4′-H), 4.06 (2H, d, *J* 6.4, 1′-H), 4.06-4.04 (1H, m, *allyl* 2-H_a), 4.00-3.97 (2H, m, 4′′-H and *allyl* 2-H_b), 3.93 (2H, s, 2-CCH_2), 3.81 (2H, s, 1-H), 3.42-3.38 (2H, m, 1′′′-H), 2.47-2.37 (5H, m, 4′′′′-CCH_3 and 1′′′-H), 2.03-1.99 (1H, m, 6-H_a), 1.93-1.89 (1H,

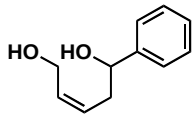
m, 5-H_a), 1.84-1.81 (1H, m, 7-H_a), 1.68-1.58 (2H, m, 6-H_b and 7-H_b), 1.46 (1H, app q, *J* 12.5, 5-H_b) and 1.07-1.02 (14H, m, ^{i}Pr); δ_C (75 MHz, $CDCl_3$) 144.3, 141.1, 137.9, 136.2, 135.3, 133.8, 132.8, 130.3, 127.6, 127.1, 117.1, 117.0, 79.2, 72.6, 70.9, 69.8, 66.8, 59.6, 52.0, 40.8, 36.9, 32.8, 31.1, 30.1, 25.1, 21.9, 17.7, 17.6, 17.5 and 12.6; *m/z* (ES+) 1060 (100%, MNa^+). (Found: MNa^+ 1060.2942, $C_{41}H_{52}F_{17}NO_6SSi$ requires *MNa*, 1060.2905)

Synthesis of metathesis products



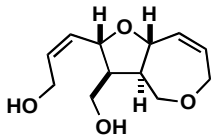
4-(2',4'-Dimethoxy-phenyl)-2,2-di*iso*propyl-4,7-dihydro-[1,3,2]dioxasilepine 9

By general procedure E, the silaketal **7d** (45 mg, 0.042 mmol) and **8** (3 × 3 mol%) gave a crude product after 7.5 h. The crude product was purified by flash chromatography (gradient elution: 3:97→5:95→7:93→9:1 petrol−EtOAc) to give the *silaketal* **9** (10 mg, 71%) as a colourless oil, R_f 0.72 (8:2 petrol–EtOAc); δ_H (500 MHz, $CDCl_3$) 7.74 (1H, dd, *J* 8.2 and 1.6, 3′-H), 7.41-7.33 (2H, m, 5′-H and 6′-H), 5.77 (1H, br s, 4-H), 4.65 (1H, br d, *J* 10.1, 6-H), 4.46 (1H, br d, *J* 10.1, 5-H), 3.45-3.36 (2H, m, 7-H) and 1.28-1.05 (14H, m, ^{i}Pr); δ_C (125 MHz, $CDCl_3$) 144.5 (Ph), 141.6 (Ph), 135.7 (Ph), 130.4 (5-H), 127.5 (6-H), 126.3 (Ph), 120.3 (Ph), 110.7 (Ph), 76.1 (4-C), 75.7 (7-C), 56.1 (OMe), 43.9 (OMe), 17.7 (^{i}Pr), 17.6 (^{i}Pr) and 12.4 (^{i}Pr); *m/z* (ES+) 337 (100%, MH^+). (Found: MH^+ 337.1828, $C_{18}H_{28}O_4Si$ requires *MH*, 337.1830).



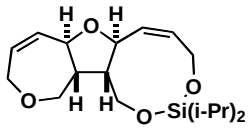
(*Z*)-5-phenylpent-2-ene-1,5-diol 14

By general procedure E, the silaketal **7f** (210 mg, 0.206 mmol) and **8** (5 × 3 mol%) gave a crude product after 7 days. The crude product was purified by Fluorous-Solid Phase Extraction (2 g cartridge, loading with ≤ 200 μL THF) and the organic fraction was subjected to general procedure F for 1 h to give a crude product. The crude product was purified by flash chromatography (gradient elution: 7:3→6:4→1:1 petrol–EtOAc) to give the *diol* **14** (7.1 mg, 19%) as a colourless film, R_f 0.32 (6:4 EtOAc–petrol), ν_{max}/cm^{-1} 3337, 3060, 3026, 2923, 2873, 1493, 1452, 1418, 1358, 1311, 1240, 1201, 1094, 1072, 1024 and 1001; δ_H (500 MHz, $CDCl_3$) 7.39-7.38 (4H, m, *ortho*-Ph and *meta*-Ph), 7.34-7.29 (1H, m, *para*-Ph), 5.89 (1H, br d, *J* 10.9, 2-H), 5.65 (1H, br dt, *J* 10.9 and 7.6, 3-H), 4.77 (1H, dd, *J* 7.8 and 4.7, 5-H), 4.16 (1H, dd, *J* 12.3 and 7.2, 1-H_a), 4.06 (1H, dd, *J* 12.3 and 6.9, 1-H_b), 2.68-2.62 (1H, m, 4-H_a) and 2.56-2.50 (1H, m, 4-H_b); δ_C (125 MHz, $CDCl_3$) 144.3 (*ipso*-Ph), 132.1 (2-C), 129.2 (3-C), 128.9 (*ortho*-Ph), 128.1 (*para*-Ph), 126.1 (*meta*-Ph), 73.5 (5-C), 58.1 (1-C) and 37.6 (4-C).



(2′*R,3′*R**,3′a*S**,8′a*S**)-(*Z*)-3-(3′-Hydroxymethyl-2′,3′,3′a,4′,6′,8′a-hexahydro-furo[3,2-*c*]oxepin-2-yl)-propenol 15**

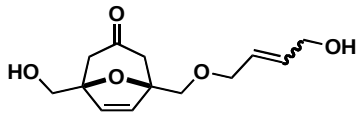
By general procedure E, the silaketal **7h** (66 mg, 0.062 mmol) and **8** (3 × 3 mol%) gave a crude product after 24 h. The crude product was purified by Fluorous-Solid Phase Extraction (2 g cartridge, loading with ≤ 200 μL THF) and the organic fraction was subjected to general procedure F for 1 h to give a crude product. The crude product was purified by preparative HPLC to give the *diol* **15** (3 mg, 21%) as a colourless film, R_f 0.30 (EtOAc); ν_{max}/cm^{-1} 3368, 3010, 2924, 2873, 1456, 1418, 1390, 1305, 1240, 1201, 1179, 1124, 1086, 1072 and 1035; δ_H (500 MHz, CD_3OD) 6.05 (1H, dd, *J* 11.2 and 1.4, 7′-H), 5.85 (1H, ddd, *J* 11.1, 7.0 and 6.3, 2-H), 5.78-5.74 (2H, m, 3-H and 8′-H), 4.79 (1H, dd, *J* 8.4 and 5.4, 2′-H), 4.66 (1H, app dt, *J* 10.4 and 1.4, 8′a-H), 4.33 (1H, ddd, *J* 12.9, 7.0 and 1.2, 1-H_a), 4.22-4.17 (3H, m, 1-H_b and 6′-H), 4.07 (1H, dd, *J* 11.5 and 5.8, 4-H_a), 3.83-3.76 (3H, m, 4-H_b and 3′-CCH_2), 2.61 (1H, ddd, *J* 10.4, 10.4 and 5.8, 3′a-H), 2.31 (1H, ddd, *J* 10.2, 7.8 and 5.4, 3′-H) and 2.18 (2H, br s, OH); δ_C (125 MHz, $CDCl_3$) 134.1 (7′-C), 134.0 (8′-C), 130.6 (2-C), 129.2 (3-C), 82.1 (8′a-C), 78.6 (2′-C), 68.9 (4-C), 68.0 (6′-C), 62.1 (3′-C*C*H_2O), 58.8 (1-C), 49.5 (3′a-C) and 47.6 (3′-C).



(1*R,2*S**,8*S**,10*R**)-15,15-Di*iso*propyl-4,9,14,16-tetraoxa-15-sila-tricyclo[8.7.0.02,8]heptadeca-6,11-diene 16**

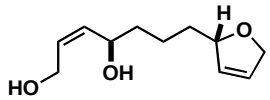
By general procedure E, the silaketal **7h** (70 mg, 0.066 mmol) and **8** (4 × 3 mol%) gave a crude product after 1.1 days. The crude product was purified by Fluorous-Solid Phase Extraction (2 g cartridge, loading with ≤ 200 μL THF) and the organic fraction was purified by column chromatography on Florisil (gradient elution: 1%→3%→5% EtOAc in petrol) to give the *silaketal* **16** (5.1 mg, 23%) as a colourless oil, R_f 0.25 (9:1 petrol–EtOAc); ν_{max}/cm^{-1} 3076, 3060, 3027, 2928, 2852, 1601, 1583, 1493, 1366, 1245, 1179 and 1127; δ_H (500 MHz, $CDCl_3$) 6.09 (1H, dd, *J* 11.1 and 1.4, 7-H), 5.83-5.78 (2H, m, 11-H and 12-H), 5.76-5.72 (1H, m, 6-H), 5.06 (1H, app t, *J* 7.5, 10-H), 4.62-4.56 (2H, m, 5-H_a and 13-H_a), 4.24 (1H, dd, *J* 13.8 and 5.3, 13-H_b), 4.20-4.19 (2H, m, 5-H_b and 8-H), 3.98 (1H, dd, *J* 11.2 and 6.2, 3-H_a), 3.92-3.89 (2H, m, 17-H), 3.80 (1H, app t, *J* 11.2, 3-H_b), 2.60 (1H, dddd, *J* 11.4, 11.2, 6.2 and 4.5, 2-H), 2.30 (1H, dddd, *J* 11.2, 7.5, 4.5 and 1.8, 1-H) and 1.12-1.02 (14H, m, ^{i}Pr); δ_C (125 MHz, $CDCl_3$) 135.2 (11-C), 133.7 (7-C), 129.4 (6-C), 129.0 (12-C), 82.2 (8-C), 79.9 (10-C), 68.5 (3-C), 67.9 (5-C), 62.1 (17-C), 59.8 (13-C), 48.3 (1-C), 47.3 (2-C), 18.0 (^{i}Pr), 17.9 (^{i}Pr), 17.8 (^{i}Pr), 12.4 (^{i}Pr) and 12.3 (^{i}Pr).

Also obtained was (2′*R**,3′*R**,3′a*S**,8′a*S**)-(*Z*)-3-(3′-Hydroxymethyl-2′,3′,3′a,4′,6′,8′a-hexahydro-furo[3,2-*c*]oxepin-2-yl)-propenol **15** (1.2 mg, 8%), with physical properties identical to that obtained previsouly.



(1*R,5*S**)-(2′*E*)- and (1*R**,5*S**)-(2′*Z*)-1-({4′-Hydroxybut-2′-enyloxy}methyl)-5-(hydroxymethyl)-8-oxabicyclo[3.2.1]oct-6-en-3-one 17**

By general procedure E, the silaketal **7j** (85 mg, 0.0668 mmol) and **8** (2 × 3 mol%) gave a crude product after 7 h. The crude product was purified by Fluorous-Solid Phase Extraction (2 g cartridge, loading with ≤ 200 μL THF) and the organic fraction was subjected to general procedure F and gave a crude product after 1 h. The crude product was purified by preparative HPLC to give the *diol* **17** (8.9 mg, 35%; *E*:*Z* 55:45) as a colourless film, R_f 0.64 (8:2 $CHCl_3$–MeOH); ν_{max}/cm^{-1} 3399, 3076, 3016, 2921, 2857, 1712, 1596, 1456, 1407, 1366, 1333, 1249, 1226, 1091, 1061 and 1033; δ_H (500 MHz, CD_3OD) 6.19 (1H, d, *J* 6.0, 6-H), 6.18 (1H, d, *J* 6.0, 7-H), 5.90 (1H, ddt, *J* 15.6, 5.1 and 1.2, 2′-H_E), 5.85-5.77 (2H, m, 2′-H_Z and 3′-H_Z), 5.67 (1H, ddt, *J* 11.2, 6.3 and 1.4, 3′-H_Z), 3.79 (1H, d, *J* 10.2, 5-CCH_a), 3.76 (1H, d, *J* 10.2, 5-CCH_b), 3.73 (1H, d, *J* 10.6, 1-CCH_a), 3.71 (1H, d, *J* 10.6, 1-CCH_b), 2.66 (1H, d, *J* 16.3, 4-H_{aZ}), 2.63 (1H, d, *J* 16.3, 2-H_{aE}) and 2.35-2.31 (4H, m, 4-H_{aE}, 2-H_{aZ}, 4-H_b and 2-H_b); δ_C (125 MHz, CD_3OD) 207.8 (3-C), 134.7 (6-C), 134.5 (7-C_Z), 134.4 (7-C_E), 133.0 (2′-C_E), 132.6 (2′-C_Z), 127.4 (3′-C_Z), 126.9 (3′-C_E), 88.1 (5-C), 87.0 (1-C_E), 86.9 (1-C_Z), 72.2 (1-CC_Z), 72.1 (1-CC_E), 71.7 (1′-C_E), 67.1 (1′-C_Z), 64.5 (5-C*C*), 61.9 (4′-C_E), 57.8 (4′-C_Z), 46.4 (4-C_Z), 46.3 (2-C_E and 4-C_E) and 46.2 (2-C_Z); *m/z* (ES+) 278 (100%, MNa^+). (Found: MNa^+ 278.1113, $C_{13}H_{19}O_5$ requires *MNa*, 278.1125)



(4*R*,2′*S*,2*Z*)-7-(2′,5′-dihydrofuran-2′-yl)hept-2-ene-1,4-diol 18

By general procedure E, the silaketal **7l** (54 mg, 0.052 mmol) and **8** (8 × 3 mol%) gave a crude product after 13 days. The crude product was purified by Fluorous-Solid Phase Extraction (2 g cartridge, loading with ≤ 200 μL THF) and the organic fraction was subjected to general procedure F for 1 h to give a crude product. The crude product was purified by flash chromatography on Florisil (gradient elution: petrol→1:1→6:4 EtOAc–petrol) to give the *diol* **18** (2.1 mg, 20%) as a colourless film, R_f 0.13 (8:2 EtOAc–petrol); ν_{max}/cm^{-1} 3368, 3021, 2950, 2919, 2850, 1596, 1577, 1494, 1449, 1374, 1327, 1314, 1240, 1212, 1157, 1103 and 1070; $[\alpha]_D$ +19.2 (*c* 0.5 in MeOH); δ_H (500 MHz, CD_3OD) 5.96 (1H, br d, *J* 6.3, 3′-H), 5.87 (1H, br d, *J* 6.3, 4′-H), 5.64 (1H, ddd, *J* 11.2, 7.1 and 6.0, 2-H), 5.47 (1H, ddd, *J* 11.2, 8.7 and 6.2, 3-H), 4.85-4.82 (1H, m, 2′-H), 4.65 (1H, br d, *J* 12.7, 5′-H_a), 4.60 (1H, br d, *J* 12.7, 5′-H_b), 4.40 (1H, dt, *J* 8.7 and 5.9, 4-H), 4.23 (1H, ddd, *J* 13.3, 7.0 and 1.5, 1-H_a), 4.13 (1H, ddd, *J* 13.3, 6.0 and 1.5, 1-H_b) and 1.64-1.32 (6H, m, 5-H, 6-H and 7-

H); δ_C (125 MHz, CD_3OD) 134.4 (3-C), 130.1 (2-C), 129.6 (4′-C), 126.3 (3′-C), 86.5 (2′-C), 74.9 (5′-C), 67.2 (4-C), 57.9 (1-C), 37.6 (5-C), 35.9 (7-C) and 21.1 (6-C); *m/z* (ES+) 221 (100%). (Found: MNa^+ 221.1149, $C_{11}H_{18}O_3$ requires *MNa*, 221.1148).

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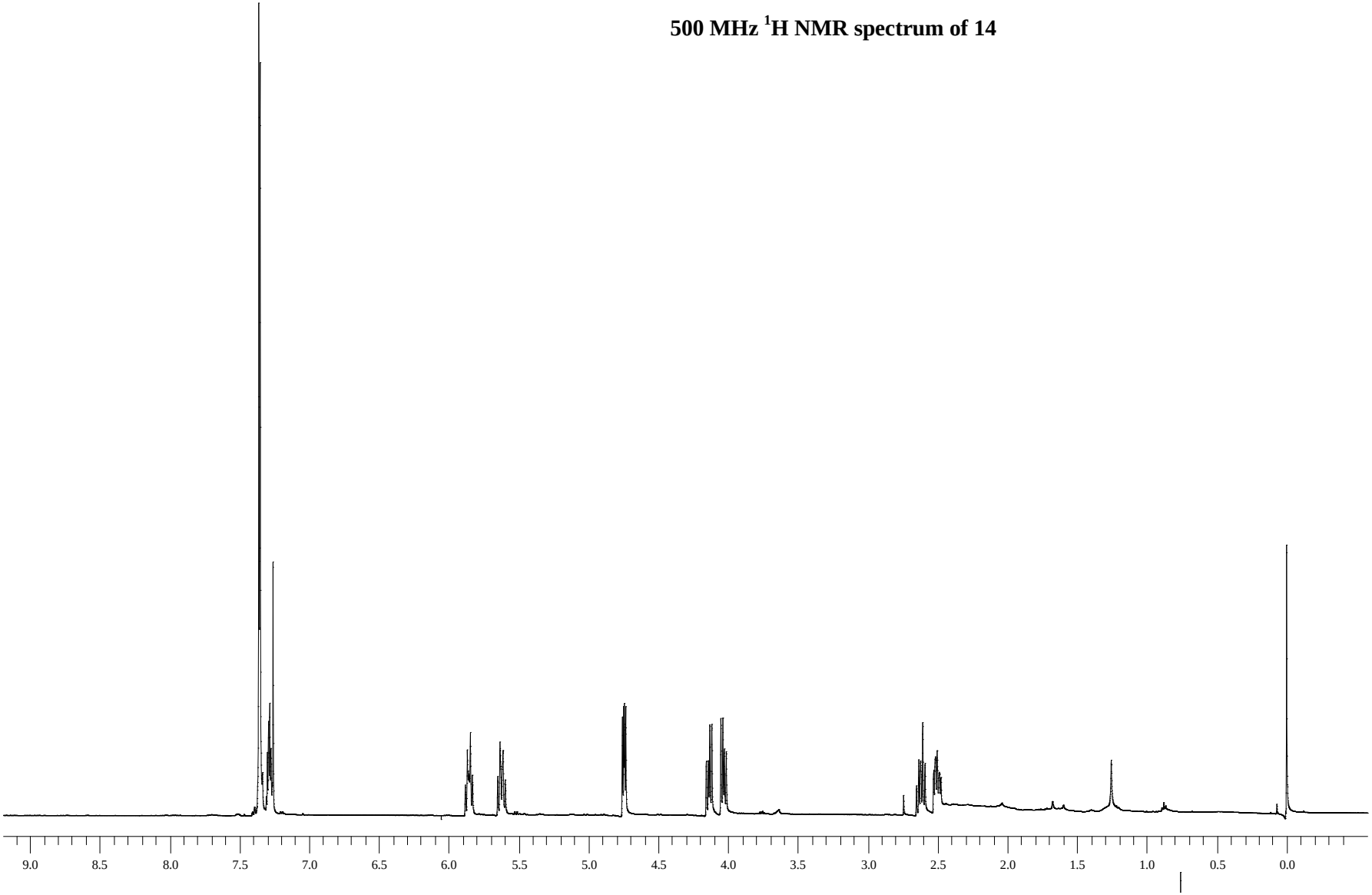
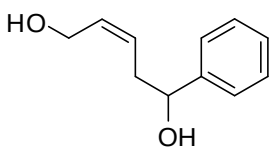
500 MHz ^{1}H NMR spectrum of 14



125 MHz ^{13}C NMR of 14



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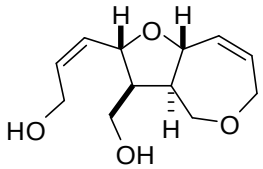

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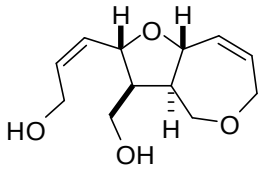

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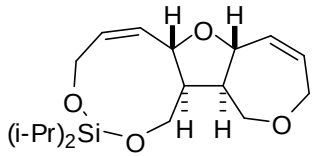

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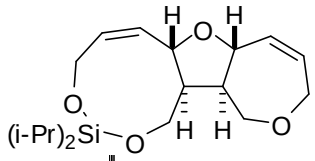
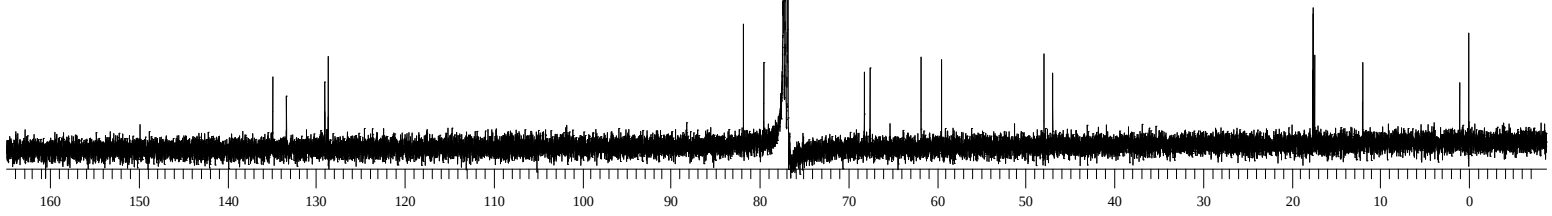
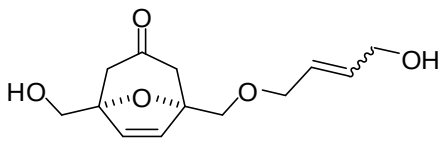
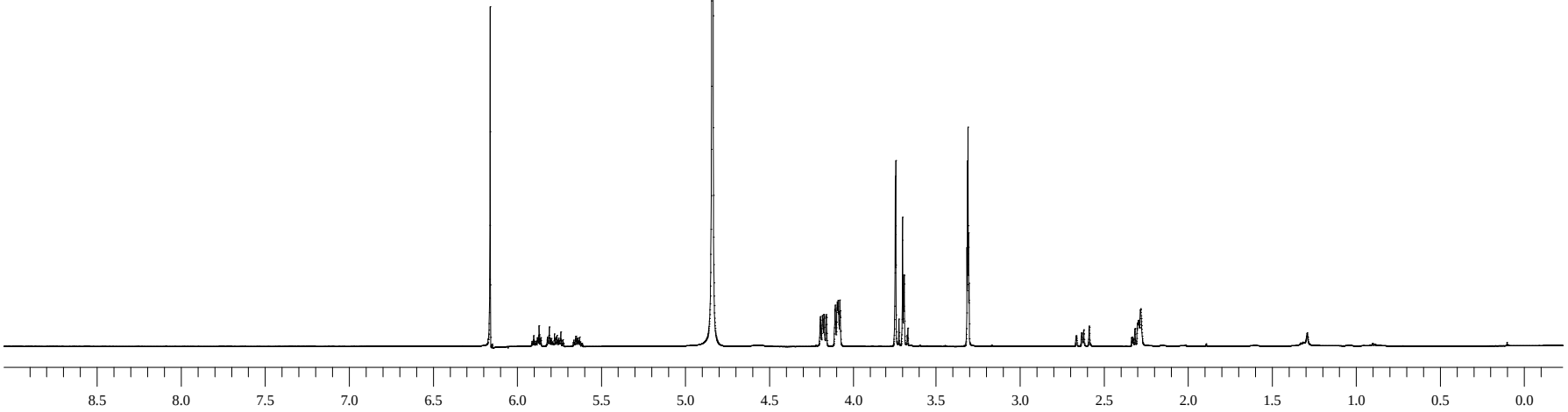




500 MHz ^{1}H NMR of 17





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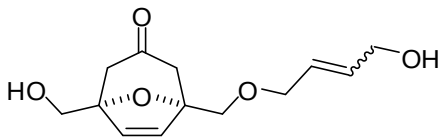
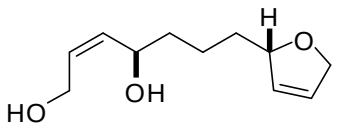


500 MHz ^{1}H NMR of 18



125 MHz ^{13}C NMR of 18