Table 6. Anisotropic Displacement Parameters (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C27	0.050(4)	0.046(4)	0.059(5)	0.005(4)	0.001(4)	0.001(3)
C28	0.052(5)	0.072(6)	0.071(5)	0.003(5)	0.002(4)	0.005(4)
C29	0.074(6)	0.058(5)	0.098(7)	0.011(5)	-0.010(5)	0.003(4)
C30	0.088(7)	0.088(8)	0.077(7)	0.022(6)	-0.002(5)	-0.030(6)
C31	0.100(7)	0.103(8)	0.065(6)	-0.003(6)	0.027(5)	-0.026(6)
C32	0.074(6)	0.071(6)	0.068(5)	-0.008(5)	0.009(5)	-0.020(4)
C33	0.105(7)	0.084(7)	0.116(7)	0.020(6)	0.061(6)	-0.002(6)
C34	0.063(5)	0.089(7)	0.056(5)	0.003(4)	0.021(4)	-0.005(5)
C35	0.087(6)	0.086(6)	0.088(6)	-0.003(5)	0.053(5)	-0.012(6)
C36	0.122(8)	0.082(7)	0.121(8)	-0.003(6)	0.084(7)	0.007(6)
C37	0.101(8)	0.139(11)	0.105(8)	-0.008(7)	0.057(7)	0.024(7)
C38	0.077(7)	0.145(11)	0.133(9)	-0.019(8)	0.059(6)	-0.012(7)
C39	0.084(7)	0.114(8)	0.088(6)	-0.001(6)	0.046(5)	-0.014(6)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$$

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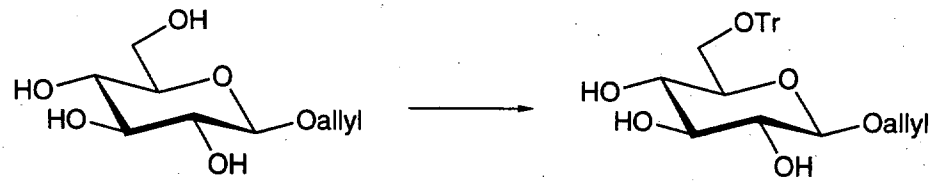
Table 7. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H5O	0.0782	0.1654	0.0806	0.122
H2	-0.0141	-0.0319	0.1962	0.074
H3	0.0278	-0.2389	0.1134	0.064
H4	-0.1130	-0.0579	0.0034	0.064
H5	0.0366	-0.0384	-0.0812	0.072
H6	0.2003	0.0373	0.0589	0.075
H8	0.4192	-0.1459	0.2755	0.111
H9A	0.4311	-0.0992	0.5309	0.126
H9B	0.5582	-0.0361	0.5747	0.126
H9C	0.5514	-0.1455	0.5112	0.126
H10A	0.3018	0.0953	0.4187	0.532
H10B	0.3597	0.1620	0.3459	0.532
H10C	0.4240	0.1644	0.4665	0.532
H11A	0.6035	0.0759	0.3179	0.611
H11B	0.6615	-0.0335	0.3749	0.611
H11C	0.6684	0.0759	0.4384	0.611
H12A	-0.0621	-0.0865	0.3275	0.268
H12B	0.0668	-0.0292	0.3810	0.268
H14	0.2139	-0.1220	0.5199	0.161
H15	0.2482	-0.2269	0.6645	0.177
H16	0.0948	-0.3302	0.6885	0.196
H17	-0.0882	-0.3404	0.5601	0.190
H18	-0.1210	-0.2343	0.4147	0.152
H19A	-0.0586	-0.3240	0.2238	0.083
H19B	-0.1279	-0.3663	0.1110	0.083
H21	-0.1641	-0.4589	0.2925	0.106
H22	-0.3327	-0.4951	0.3485	0.157
H23	-0.5145	-0.4110	0.2771	0.155
H24	-0.5339	-0.2820	0.1512	0.150
H25	-0.3645	-0.2380	0.0988	0.128
H26A	-0.2808	-0.1278	-0.1060	0.077
H26B	-0.2722	-0.2214	-0.1834	0.077
H28	-0.2682	0.0538	-0.1561	0.083

Table 7. Derived Parameters for Hydrogen Atoms (continued)

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H29	-0.2315	0.1857	-0.2666	0.103
H30	-0.1480	0.1292	-0.3914	0.109
H31	-0.0954	-0.0502	-0.4041	0.106
H32	-0.1321	-0.1784	-0.2936	0.089
H33A	0.2721	-0.0823	-0.0455	0.115
H33B	0.1648	-0.1216	-0.1442	0.115
H35	0.1730	-0.3586	-0.0673	0.097
H36	0.2898	-0.5080	-0.0775	0.118
H37	0.4762	-0.4834	-0.1148	0.131
H38	0.5471	-0.3099	-0.1220	0.135
H39	0.4327	-0.1582	-0.1015	0.110

2-Propenyl 6-*O*-(Triphenylmethyl)-β-D-glucopyranoside (35).



- **35**

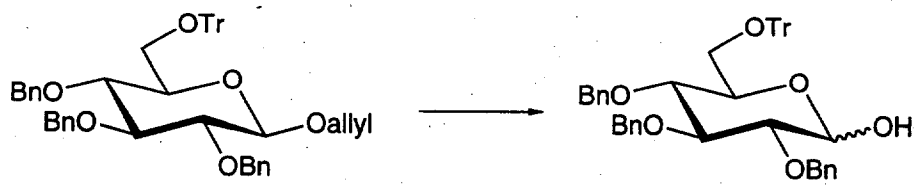
Dry pyridine (20 mL) was added to a dry 50 mL round-bottomed flask charged with 2-propenyl-β-D-glucopyranoside[56] (2.60 g, 11.8 mmol), Ph_3CCl (5.70 g, 20.4 mmol), and DMAP (180 mg, 1.47 mmol). The resulting mixture was heated at 80 °C for 8 h, cooled to room temperature, and evaporated. The residue was dissolved in CH_2Cl_2 (30 mL) and washed with cold (4 °C) hydrochloric acid (0.5 M, 2 x 20 mL), saturated aqueous $NaHCO_3$ (20 mL) and brine (20 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (4 x 20 cm), using 3:7 EtOAc-hexane and then EtOAc, gave **35** (3.73 g, 68%) as a pure (^1H NMR, 400 MHz) solid: FTIR (CH_2Cl_2 cast) 3388 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.27-3.52 (m, 6 H), 3.67 (br s, 1 H), 4.00 (br s, 1 H), 4.17 (dd, *J* = 12.2, 5.8 Hz, 1 H), 4.32 (d, *J* = 7.1 Hz, 1 H), 4.38 (dd, *J* = 12.2, 4.5 Hz, 1 H), 4.72 (br s, 1 H), 5.20 (d, *J* = 10.6 Hz, 1 H), 5.33 (d, *J* = 17.2 Hz, 1 H), 5.91-6.05 (m, 1 H), 7.16-7.38 (m, 9 H), 7.38-7.58 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 64.1 (t'), 70.1 (t'), 71.5 (d'), 73.5 (d'), 74.5 (d'), 76.4 (d'), 86.8 (s'), 101.4 (d'), 118.1 (t'), 127.1 (d'), 127.9 (d'), 128.7 (d'), 134.0 (d'), 143.8 (s'); exact mass *m/z* calcd for $C_{28}H_{30}O_6$ 462.20425, found 462.20517.

2-Propenyl 2,3,4-Tris-*O*-(phenylmethyl)-6-*O*-(triphenylmethyl)-β-D-glucopyranose (36).

35 **36**

Triol **35** (17.2 g, 37.2 mmol), powdered NaOH (30 g, 0.75 mol), and BnCl (200 mL, 1.74 mol) were heated at 120 °C with mechanical stirring for 1 h. Another portion of powdered NaOH (30 g, 0.75 mol) was then added and stirring and heating were continued for 36 h. The mixture was cooled, diluted with water (200 mL), and extracted with Et_2O (4 x 200 mL). The combined organic extracts were washed with brine (200 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (8 x 24 cm), using 1:10 EtOAc-hexane, gave **36** (23.8 g, 87%) as a pure (^{1}H NMR, 400 MHz) solid: FTIR (CH_2Cl_2 cast) unexceptional; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.27 (dd, *J* = 9.3, 3.6 Hz, 1 H), 3.37-3.47 (m, 1 H), 3.54-3.68 (m, 3 H), 3.76-3.89 (m, 1 H), 4.28 (dd, *J* = 10.6, 4.6 Hz, 1 H), 4.40 (d, *J* = 9.3 Hz, 1 H), 4.48-4.60 (m, 2 H), 4.73 (d, *J* = 9.6 Hz, 1 H), 4.76-4.86 (m, 2 H), 4.94 (d, *J* = 9.9 Hz, 1 H), 5.05 (d, *J* = 9.9 Hz, 1 H), 5.27 (d, *J* = 9.6 Hz, 1 H), 5.43 (d, *J* = 16.6 Hz, 1 H), 6.00-6.13 (m, 1 H), 6.84-6.97 (m, 2 H), 7.10-7.48 (m, 22 H), 7.48-7.66 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 62.5 (t'), 70.1 (t'), 74.7 (d'), 75.0 (t'), 75.0 (t'), 76.0 (t')1, 78.0 (d'), 82.6 (d'), 84.8 (d'), 86.4 (s'), 102.8 (d'), 117.4 (t'), 127.0 (d'), 127.3 (d'), 127.7 (d'), 127.8 (d'), 127.9 (d'), 128.1 (d'), 128.2 (d'), 128.2 (d'), 128.4 (d'), 128.9 (d'), 134.2 (d'), 137.9 (s'), 138.6 (s'), 144.0 (s'); mass (FAB) *m/z* calcd for $C_{49}H_{48}NaO_6$ (M + Na) 755.3, found 755.3.

2,3,4-Tris-*O*-(phenylmethyl)-6-*O*-(triphenylmethyl)-D-glucopyranose (37).

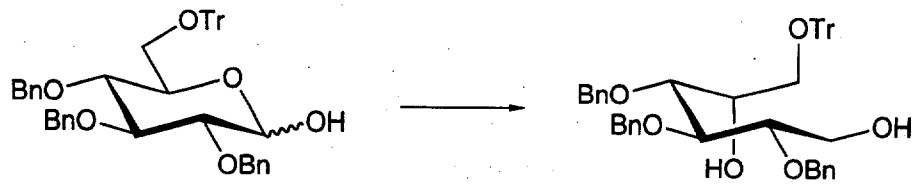


36 **37**

DMSO (60.0 mL) was added in one portion to a stirred suspension of **36** (16.7 g, 22.8 mmol) and *t*-BuOK (10.0 g, 89.1

mmol). The mixture was stirred to dissolve the solids and was then heated at 100 °C for 1 h with continued stirring. The resulting solution was cooled to room temperature, poured into water (200 mL), and extracted with Et_2O (4 x 50 mL). The combined organic extracts were washed with water (1 x 40 mL) and evaporated. The solid residue was dissolved in 10:1 acetone-water (50 mL), and HgO (8.38 g, 38.7 mmol) was added (stirring). A solution of $HgCl_2$ (10.5 g, 38.7 mmol) in 10:1 acetone-water (20 mL) was added dropwise, and stirring was continued for 4 h. The mixture was filtered through a pad (5 x 4 cm) of Celite, using acetone (100 mL) as a rinse. The combined filtrates were evaporated and the residue was dissolved in Et_2O (200 mL), washed with 20% aqueous NaI (1 x 200 mL) and brine (100 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (8 x 25 cm), using 2:8 EtOAc-hexane, gave **37** (14.0 g, 88%) as a pure (^1H NMR, 300 MHz), gummy solid, which was a mixture of epimers: FTIR (CH_2Cl_2 cast) 3439 (br) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.92 (br s, 0.66 H), 3.14 (br d, *J* = 5.3 Hz, 0.34 H), 3.23 (dd, *J* = 3.3, 3.3 Hz, 0.34 H), 3.26 (dd, *J* = 3.3, 3.3 Hz, 0.66 H), 3.43-3.75 (m, 2.66 H), 3.75-3.87 (m, 1 H), 3.95 (dd, *J* = 9.0, 9.0 Hz, 0.66 H), 4.06 (br d, *J* = 10.5 Hz, 0.66 H), 4.36 (d, *J* = 10.5, 1 H), 4.66-4.96 (m, 5 H), 5.02 (d, *J* = 11.3 Hz, 0.34 H), 5.39 (dd, *J* = 2.8, 2.8 Hz, 0.66 H), 6.83-6.93 (m, 2 H), 7.12-7.42 (m, 22 H), 7.42-7.53 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 62.3 (t'), 62.6 (t'), 70.6 (d'), 73.3 (t'), 74.8 (t'), 74.9 (t'), 75.9 (t'), 75.9 (t'), 77.8 (d'), 80.5 (d'), 81.9 (d'), 83.4 (d'), 84.6 (d'), 86.3 (s'), 86.6 (s'), 91.2 (d'), 97.6 (d'), 126.9 (d'), 127.5 (d'), 127.6 (d'), 127.7 (d'), 127.8 (d'), 127.9 (d'), 128.1 (d'), 128.1 (d'), 128.1 (d'), 128.4 (d'), 128.4 (d'), 128.5 (d'), 128.8 (d'), 137.9 (s'), 138.0 (s'), 138.5 (s'), 138.6 (s'), 143.8 (s'), 143.9 (s'); mass (FAB) *m/z* calcd for $C_{46}H_{44}NaO_6$ (M + Na) 715.3, found 715.2. Anal. calcd for $C_{46}H_{44}O_6$: C, 79.73; H, 6.41. Found: C, 79.49; H, 6.50.

2,3,4-Tris-*O*-(phenylmethyl)-6-*O*-(triphenylmethyl)-D-glucitol (38).

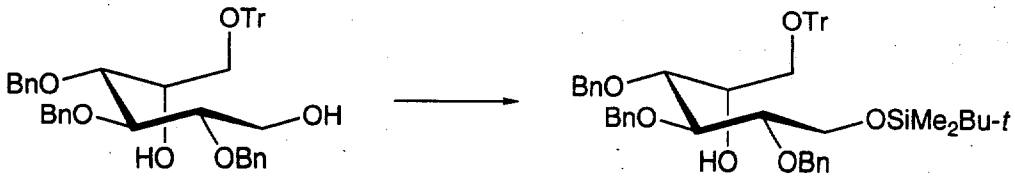


37 **38**

$LiAlH_4$ (2.42 g, 63.8 mmol) was added in five portions to a stirred and cooled (0 °C) solution of **37** (16.9 g, 24.4 mmol) in THF (300 mL). The cold bath was removed, stirring was continued for 4 h, and the mixture was then cooled to 0 °C. Water (1.0 mL), 15% aqueous NaOH (1.0 mL), and water (1.0 mL) were added sequentially with stirring. The cold bath was removed, stirring was continued for 30 min, and the mixture was then filtered through a pad (8 x 3 cm) of Celite, using Et_2O (500 mL) as a rinse. Evaporation of the combined filtrates, and flash chromatography of the residue over silica gel (8 x 25 cm), using 3:7 EtOAc-hexane, gave **38** (16.2 g, 95%) as a pure (^1H NMR, 400 MHz) solid: $[\alpha]_D$ = 3.10 (*c* 2.03, CH_2Cl_2); FTIR (CH_2Cl_2 cast) 3457 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.09 (t, *J* = 5.8 Hz, 1 H), 3.09 (d, *J* = 5.4 Hz, 1 H), 3.32 (dd, *J* = 9.6, 4.6 Hz, 1 H), 3.37 (dd, *J* = 9.6, 4.0 Hz, 1 H), 3.53-3.61 (m, 1 H), 3.66-3.75 (m, 1 H), 3.76-3.84 (m, 2 H), 3.87 (dd, *J* = 6.6, 2.6 Hz, 1 H), 4.03-4.11 (m, 1 H), 4.42 (d, *J* = 12.0 Hz, 1 H), 4.45 (d, *J* = 12.0 Hz, 1 H), 4.53 (d, *J* = 13.0 Hz, 1 H), 4.61 (d, *J* = 13.4 Hz, 1 H), 4.66 (d, *J* = 13.4 Hz, 1 H), 4.68 (d, *J* = 13.0 Hz, 1 H), 7.07-7.16 (m, 2 H), 7.20-7.38 (m, 22 H), 7.40-7.51 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 61.9 (t'), 64.7 (t'), 70.7 (d'), 72.9 (t'), 73.0 (t'), 74.4 (t'), 77.0 (d'), 79.3 (d'), 79.5 (d'), 86.7 (s'), 127.1 (d'), 127.3 (d'), 127.8 (d'), 127.8 (d'), 127.85 (d'), 127.90 (d'), 127.94 (d'), 128.2 (d'), 128.2 (d'), 128.3 (d'), 128.3 (d'), 128.4 (d'), 128.4 (d'), 128.5 (d'), 128.7 (d'), 128.85 (d'), 128.87 (d'), 129.1 (d'), 137.6 (s'), 137.8 (s'), 138.2 (s'), 143.8 (s'); mass (FAB) *m/z* calcd for $C_{46}H_{46}NaO_6$ (M + Na) 717.3, found 717.2.

1-*O*-[(1,1-Dimethylethyl)dimethylsilyl]-2,3,4-tris-*O*-

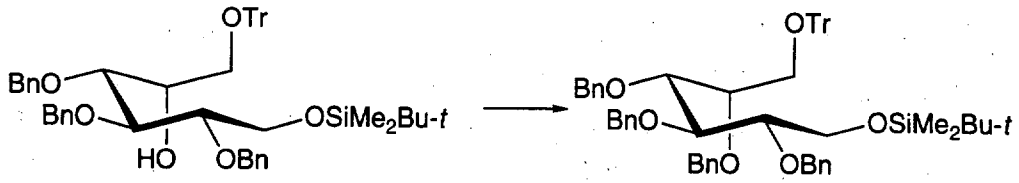
(phenylmethyl)-6-*O*-(triphenylmethyl)-D-glucitol (39).



38 **39**

Et_3N (5.13 mL, 36.8 mmol) was added in one portion to a stirred solution of **38** (16.1 g, 23.2 mmol), DMAP (710 mg, 5.81 mmol), and *t*-$BuMe_2SiCl$ (5.44 g, 36.1 mmol) in CH_2Cl_2 (500 mL). Stirring was continued for 16 h, CH_2Cl_2 (200 mL) was added, and the mixture was washed with brine (2 x 200 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (8 x 25 cm), using 1:10 EtOAc-hexane, gave **39** (18.3 g, 95%) as a pure (^1H NMR, 300 MHz), gummy solid: $[\alpha]_D$ = 3.35 (*c* 1.55, CH_2Cl_2); FTIR (CH_2Cl_2 cast) unexceptional; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.02 (s, 6 H), 0.90 (s, 9 H), 3.11 (dd, *J* = 4.9, 1.2 Hz, 1 H), 3.27-3.42 (m, 2 H), 3.67-3.84 (m, 4 H), 3.84-3.93 (m, 1 H), 3.98-4.10 (m, 1 H), 4.44 (d, *J* = 11.4 Hz, 1 H), 4.47 (d, *J* = 11.4 Hz, 1 H), 4.54 (d, *J* = 11.0 Hz, 1 H), 4.63 (d, *J* = 11.2 Hz, 2 H), 4.73 (d, *J* = 11.0 Hz, 1 H), 7.04-7.16 (m, 2 H), 7.16-7.40 (m, 22 H), 7.40-7.56 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -5.39 (q'), -5.35 (q'), 18.2 (s'), 25.9 (q'), 63.2 (t'), 64.9 (t'), 71.1 (d'), 73.0 (t'), 73.2 (t'), 74.1 (t'), 77.2 (d'), 78.3 (d'), 79.8 (d'), 86.6 (s'), 127.0 (d'), 127.5 (d'), 127.7 (d'), 127.8 (d'), 127.95 (d'), 128.03 (d'), 128.17 (d'), 128.19 (d'), 128.3 (d'), 128.4 (d'), 128.8 (d'), 138.09 (s'), 138.12 (s'), 138.6 (s'), 144.0 (s'); mass (FAB) *m/z* calcd for $C_{52}H_{60}NaO_6Si$ (M + Na) 831.4, found 831.4. Anal. Calcd for $C_{52}H_{60}O_6Si$: C, 77.19; H, 7.48. Found: C, 77.08; H, 7.58.

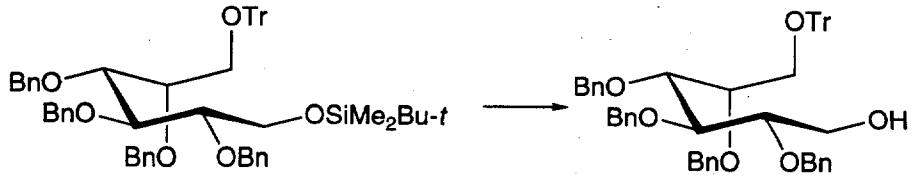
1-*O*-[(1,1-Dimethylethyl)dimethylsilyl]-2,3,4,5-tetrakis-*O*-(phenylmethyl)-6-*O*-(triphenylmethyl)-D-glucitol (40).



39 **40**

NaH (80% dispersion in oil, 1.48 g, 49.3 mmol) was added in six portions to a stirred and cooled (0 °C) solution of **39** (18.2 g, 22.5 mmol) in THF (400 mL). The resulting mixture was stirred for 30 min and then BnBr (5.88 mL, 49.4 mmol) was added neat in one portion. The cold bath was removed and the mixture was stirred for 1 h and then refluxed for 14 h. The resulting mixture was cooled (0 °C) and quenched with MeOH (60 mL), diluted with brine (200 mL), and extracted with Et_2O (3 x 500 mL). The combined organic extracts were washed with brine (1 x 150 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (8 x 25 cm), using 1:20 EtOAc-hexane, gave **40** (19.2 g, 94%) as a pure (^{1}H NMR, 300 MHz), thick syrup: $[\alpha]_D$ = -3.23 (*c* 3.5, CH_2Cl_2); FTIR (CH_2Cl_2 cast) unexceptional; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.07 (s, 3 H), 0.08 (s, 3 H), 0.96 (s, 9 H), 3.47 (dd, *J* = 10.2, 5.1 Hz, 1 H), 3.66 (dd, *J* = 10.0, 2.6 Hz, 1 H), 3.71-3.84 (m, 3 H) 3.87-3.96 (m, 2 H), 4.17 (dd, *J* = 5.5, 5.5 Hz, 1 H), 4.47 (d, *J* = 11.5 Hz, 1 H), 4.61-4.73 (m, 5 H), 4.78 (d, *J* = 11.5 Hz, 1 H), 4.81 (d, *J* = 11.7 Hz, 1 H), 7.10-7.20 (m, 2 H), 7.20-7.46 (m, 27 H), 7.51-7.64 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -5.4 (q'), 18.2 (s'), 26.0 (q'), 63.2 (t'), 64.0 (t'), 72.2 (t'), 73.2 (t'), 73.8 (t'), 74.5 (t'), 78.6 (d'), 79.6 (d'), 80.7 (d'), 86.8 (s'), 126.9 (d'), 127.2 (d'), 127.3 (d'), 127.3 (d'), 127.8 (d'), 127.9 (d'), 128.05 (d'), 128.12 (d'), 128.16 (d'), 128.23 (d'), 128.9 (d'), 138.7 (s'), 138.79 (s'), 138.84 (s'), 139.0 (s'), 144.1 (s'); mass (FAB) *m/z* calcd for $C_{59}H_{66}NaO_6Si$ (M + Na) 921.5, found 921.4.

2,3,4,5-Tetrakis-*O*-(phenylmethyl)-6-*O*-(triphenylmethyl)-D-glucitol (41).



40 **41**

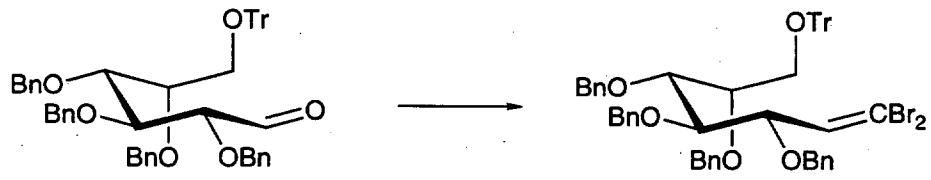
TBAF (21.6 mL, 1 M in THF, 21.6 mmol) was added in one portion to a stirred solution of **40** (19.1 g, 21.3 mmol) in THF (410 mL). Stirring was continued for 4 h, the mixture was diluted with Et_2O (200 mL), and washed with water (1 x 150 mL). The aqueous phase was extracted with Et_2O (2 x 100 mL) and the combined organic extracts were washed with brine (1 x 150 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (8 x 20 cm), using 2:8 EtOAc-hexane, gave **41** (16.2 g, 97%) as a pure (^1H NMR, 400 MHz) solid: $[\alpha]_D$ = -9.08 (*c* 9.08, CH_2Cl_2); FTIR (CH_2Cl_2 cast) 3457 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.08 (br s, 1 H), 3.42 (dd, *J* = 10.2, 5.3 Hz, 1 H), 3.57 (dd, *J* = 10.2, 2.9 Hz, 2 H), 3.65 (ddd, *J* = 4.9, 4.9, 4.9 Hz, 1 H), 3.68-3.77 (m, 1 H), 3.83-3.89 (m, 2 H), 4.05 (dd, *J* = 4.9, 4.9 Hz, 1 H), 4.43 (d, *J* = 11.4 Hz, 1 H), 4.54-4.64 (m, 6 H), 4.74 (d, *J* = 11.4 Hz, 1 H), 7.05-7.14 (m, 2 H), 7.18-7.40 (m, 26 H), 7.40-7.54 (m, 7 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 61.8 (t'), 63.0 (t'), 72.0 (t'), 72.3 (t'), 73.5 (t'), 74.3 (t'), 78.3 (d'), 78.96 (d'), 79.04 (d'), 79.07 (d'), 86.8 (s'), 126.8 (d'), 127.2 (d'), 127.41 (d'), 127.46 (d'), 127.6 (d'), 127.71 (d'), 127.74 (d'), 128.0 (d'), 128.1 (d'), 128.2 (d'), 128.6 (d'), 129.0 (d'), 138.17 (s'), 138.21 (s'), 138.4 (s'), 143.8 (s'); exact mass *m/z* calcd for $C_{34}H_{37}O_6$ (M - Ph_3C) 541.25903, found 541.25931. Anal. Calcd for $C_{53}H_{52}O_6$: C, 81.08; H, 6.68. Found: C, 81.06; H, 6.72.

2,3,4,5-Tetrakis-*O*-(phenylmethyl)-6-*O*-(triphenylmethyl)-D-glucose (42).

41 **42**

DMSO (1.05 mL, 14.8 mmol) was added dropwise to a stirred and cooled (-78 °C) solution of $(COCl)_2$ (0.96 mL, 11.0 mmol) in CH_2Cl_2 (40 mL). After 20 min, **41** (2.89 g, 3.69 mmol) in CH_2Cl_2 (12 mL) was added by syringe over 1 min. Stirring was continued for 30 min at -78 °C, and then Et_3N (4.11 mL, 29.5 mmol) was added dropwise over 2 min. The cold bath was removed and stirring was continued for 6 h. The solution was diluted with water (2 mL) and CH_2Cl_2 (50 mL), and the mixture was transferred to a separatory funnel. The organic phase was washed with brine (1 x 30 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (3 x 25 cm), using 1:10 to 2:8 EtOAc-hexane, gave **42** (2.56 g, 89%) as a pure (^{1}H NMR, 300 MHz) solid: $[\alpha]_D$ = -3.64 (*c* 0.44, CH_2Cl_2); FTIR (CH_2Cl_2 cast) 1728 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.36 (dd, *J* = 10.2, 4.2 Hz, 1 H), 3.73 (dd, *J* = 10.0, 2.4 Hz, 1 H), 3.83-3.91 (m, 1 H), 3.92 (d, *J* = 5.0 Hz, 1 H), 4.15-4.25 (m, 2 H), 4.36-4.62 (m, 6 H), 4.81 (d, *J* = 11.8 Hz, 1 H), 4.85 (d, *J* = 11.8 Hz, 1 H), 6.88-6.98 (m, 2 H), 7.10-7.29 (m, 18 H), 7.31-7.42 (m, 9 H), 7.44-7.54 (m, 6 H), 9.72 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 62.6 (t'), 72.2 (t'), 73.2 (t'), 73.4 (t'), 74.0 (t'), 76.8 (d'), 78.7 (d'), 70.0 (d'), 81.2 (d'), 86.9 (s'), 127.0 (d'), 127.27 (d'), 127.33 (d'), 127.5 (d'), 127.8 (d'), 128.0 (d'), 128.1 (d'), 128.4 (d'), 128.5 (d'), 128.8 (d'), 137.5 (s'), 137.7 (s'), 137.8 (s'), 138.5 (s'), 143.9 (s'), 200.8 (d'); mass (FAB) *m/z* calcd for $C_{53}H_{50}NaO_6$ (M + Na) 805.4, found 805.4. Anal. Calcd for $C_{53}H_{50}O_6$: C, 81.29; H,6.44. Found: C, 81.25; H, 6.24.

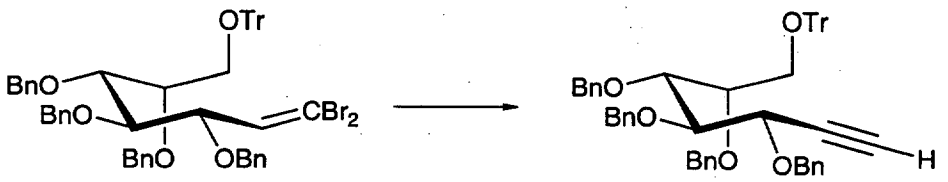
1,1-Dibromo-1,2-dideoxy-3,4,5,6-tetrakis-*O*-(phenylmethyl)-7-*O*-(triphenylmethyl)-D-*gluco*-hept-1-enitol (43).



42 **43**

A solution of CBr_4 (1.22 g, 3.68 mmol) in CH_2Cl_2 (20 mL) was added at a fast dropwise rate to a stirred and cooled (-20 °C) solution of Ph_3P (0.96 g, 3.66 mmol) in CH_2Cl_2 (20 mL). Stirring at -20 °C was continued for 15 min, and then a solution of **42** (1.44 g, 1.84 mmol) and Et_3N (0.26 mL, 1.87 mmol) in CH_2Cl_2 (20 mL) was added dropwise at -60 °C. The cold bath was removed, stirring was continued for 30 min, and the mixture was filtered through a pad (3 x 3 cm) of flash chromatography silica gel, using Et_2O (50 mL) as a rinse. Evaporation of the combined filtrates, and flash chromatography of the residue over silica gel (1.5 x 20 cm), using 1:9 EtOAc-hexane, gave **43** (1.31 g, 76%) as a pure (^1H NMR, 200 MHz), gummy solid: $[\alpha]_D$ = 6.02 (*c* 0.98 CH_2Cl_2); FTIR (CH_2Cl_2 cast) unexceptional; ^1H NMR ($CDCl_3$, 200 MHz) δ 3.46 (d, *J* = 4.0 Hz, 2 H), 3.69-3.86 (m, 2 H), 4.14 (dd, *J* = 5.1, 5.1 Hz, 1 H), 4.30 (dd, *J* = 7.9, 4.0 Hz, 1 H), 4.42 (d, *J* = 11.7 Hz, 1 H), 4.47 (d, *J* = 11.5 Hz, 1 H), 4.55-4.82 [m, 6 H, including doublet at δ 4.75 (*J* = 11.5 Hz, 1 H)], 6.66 (d, *J* = 7.9 Hz, 1 H), 7.05-7.18 (m, 2 H), 7.18-7.42 (m, 27 H), 7.42-7.59 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 63.1 (t'), 71.3 (t'), 72.4 (t'), 74.2 (t'), 75.0 (t'), 78.8 (d'), 79.5 (d'), 79.7 (d'), 86.8 (s'), 92.6 (s'), 127.0 (d'), 127.3 (d'), 127.4 (d'), 127.5 (d'), 127.6 (d'), 127.8 (d'), 128.0 (d'), 128.1 (d'), 128.18 (d'), 128.24 (d'), 128.3 (d'), 128.4 (d'), 128.9 (d'), 137.3 (d'), 137.6 (s'), 138.3 (s'), 138.6 (s'), 138.7 (s'), 144.0 (s'); mass (FAB) *m/z* calcd for $C_{54}H_{50}{}^{79}Br^{81}BrNaO_5$ (M + Na) 961.2, found 961.6.

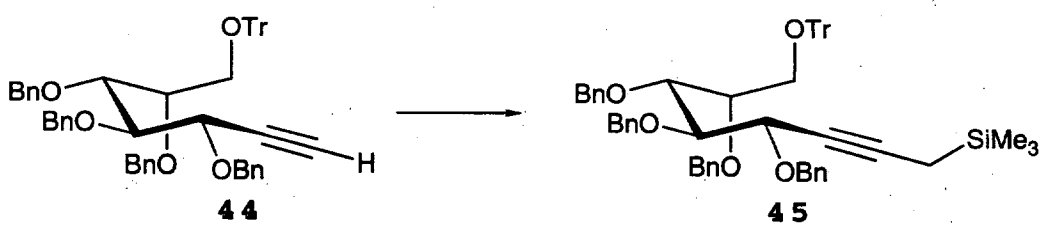
1,2-Dideoxy-3,4,5,6-tetrakis-*O*-(phenylmethyl)-7-*O*-(triphenylmethyl)-D-*gluco*-hept-1-ynitol (44).



43 **44**

n-BuLi (2.5 M in hexane, 1.17 mL, 2.93 mmol) was added dropwise to a stirred and cooled (-78 °C) solution of **43** (1.31 g, 1.40 mmol) in THF (50 mL). Stirring at -78 °C was continued for 2 h, and then water (2 mL) was added. The cold bath was removed, stirring was continued for 20 min, and the resulting mixture was diluted with Et_2O (20 mL) and washed with brine (2 x 10 mL). The organic extract was dried, and evaporated. Flash chromatography of the residue over silica gel (1.5 x 25 cm), using 2:8 EtOAc-hexane, gave **44** (0.844 g, 78%) as a pure (^1H NMR, 360 MHz) solid: FTIR (CH_2Cl_2 cast) 3283 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 2.65 (d, *J* = 2.0 Hz, 1 H), 3.28 (dd, *J* = 10.3, 4.6 Hz, 1 H), 3.67 (dd, *J* = 10.3, 2.5 Hz, 1 H), 3.84-3.92 (m, 1 H), 4.08 (dd, *J* = 7.4, 3.2 Hz, 1 H), 4.35 (d, *J* = 11.6 Hz, 1 H), 4.39 (dd, *J* = 7.4, 3.2 Hz, 1 H), 4.47-4.58 [m, 4 H, including doublet at δ 4.56 (*J* = 11.7 Hz, 1 H)], 4.62 (d, *J* = 11.0 Hz, 1 H), 4.74 (d, *J* = 11.7 Hz, 1 H), 4.87 (d, *J* = 11.5 Hz, 1 H), 4.93 (d, *J* = 11.6 Hz, 1 H), 6.96-7.07 (m, 2 H), 7.14-7.40 (m, 27 H), 7.46-7.53 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 62.5 (t'), 71.4 (t'), 71.5 (d'), 71.9 (t'), 74.6 (t'), 74.9 (t'), 76.4 (s'), 78.5 (d'), 78.7 (d'), 80.9 (s'), 81.1 (d'), 86.7 (s'), 127.0 (d'), 127.25 (d'), 127.34 (d'), 127.8 (d'), 128.01 (d'), 128.04 (d'), 128.11 (d'), 128.2 (d'), 128.3 (d'), 128.4 (d'), 128.9 (d'), 137.5 (s'), 138.5 (s'), 138.7 (s'), 139.0 (s'), 144.1 (s'); mass (FAB) *m/z* calcd for $C_{54}H_{50}O_5$ 779.0, found 778.9.

1,2,3-Trideoxy-4,5,6,7-tetrakis-*O*-(phenylmethyl)-1-(trimethylsilyl)-8-*O*-(triphenylmethyl)-D-*gluco*-oct-2-ynitol (45).

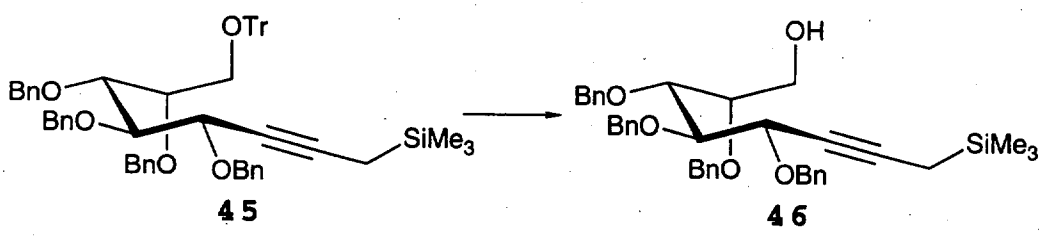


44 **45**

n-BuLi (2.5 M in hexane, 0.29 mL, 0.725 mmol) was added

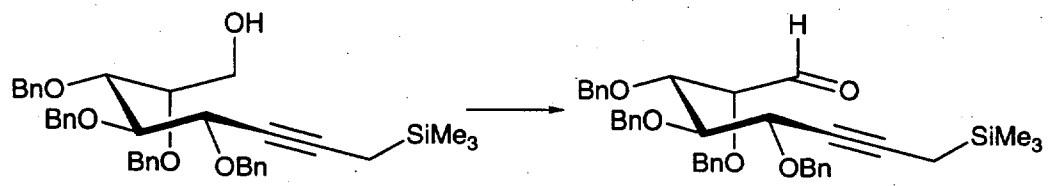
dropwise to a stirred and cooled (-78 °C) solution of **44** (0.509 g, 0.654 mmol) in THF (20 mL). Stirring at -78 °C was continued for 1 h, and then $Me_3SiCH_2OSO_2CF_3$ (0.17 mL, 0.850 mmol) and HMPA (0.40 mL, 2.30 mmol) were added rapidly, each in one portion. The cold bath was removed and stirring was continued for 10 h. The mixture was diluted with Et_2O (20 mL) and washed with brine (1 x 20 mL). The aqueous phase was extracted with Et_2O (2 x 20 mL) and the combined organic extracts were dried and evaporated. Flash chromatography of the residue over silica gel (1.5 x 20 cm), using 1:10 EtOAc-hexane, gave **45** (0.441 g, 78%) as a pure (^{1}H NMR, 300 MHz) solid: FTIR (CH_2Cl_2 cast) unexceptional; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.27 (s, 9 H), 1.73 (dd, *J* = 1.9, 1.9 Hz, 2 H), 3.36 (dd, *J* = 10.2, 4.4 Hz, 1 H), 3.74 (dd, *J* = 10.2, 2.0 Hz, 1 H), 3.92-4.01 (m, 1 H), 4.13 (dd, *J* = 7.6, 3.5 Hz, 1 H), 4.38 (d, *J* = 11.7 Hz, 1 H), 4.47 (dd, *J* = 7.6, 2.8 Hz, 1 H), 4.52-4.67 [m, 4 H, including doublet at δ 4.56 (*J* = 11.0 Hz, 1 H)], 4.71 (d, *J* = 11.0 Hz, 1 H), 4.81 (d, *J* = 11.7 Hz, 1 H), 4.95 (d, *J* = 11.6 Hz, 1 H), 5.04 (d, *J* = 11.7 Hz, 1 H), 7.02-7.12 (m, 2 H), 7.20-7.50 (m, 27 H), 7.50-7.62 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -1.8 (q'), 7.4 (t'), 62.7 (t'), 71.0 (t'), 71.9 (s'), 72.4 (d'), 74.68 (t'), 74.72 (t'), 75.9 (t'), 78.5 (d'), 79.1 (d'), 81.8 (d'), 86.7 (s'), 87.0 (s'), 126.9 (d'), 127.1 (d'), 127.19 (d'), 127.21 (d'), 127.23 (d'), 127.6 (d'), 127.7 (d'), 127.8 (d'), 127.99 (d'), 128.02 (d'), 128.1 (d'), 128.2 (d'), 128.25 (d'), 128.33 (d'), 128.9 (d'), 138.2 (s'), 138.7 (s'), 138.9 (s'), 139.3 (s'), 144.2 (s'); exact mass *m/z* calcd for $C_{32}H_{37}O_4Si$ (M - H - Ph_3C - OBn) 513.24609, found 513.24569.

1,2,3-Trideoxy-4,6,5,7-tetrakis-*O*-(phenylmethyl)-1-(trimethylsilyl)-D-*gluco*-oct-2-ynitol (46).



CSA (12.0 mg, 0.052 mmol) in MeOH (2 mL) was added in one portion to a stirred solution of **45** (0.409 g, 0.473 mmol) in CH_2Cl_2 (20 mL). Stirring was continued for 24 h, Et_3N (1 mL) was added, and the solution was evaporated. Flash chromatography of the residue over silica gel (1.5 x 20 cm), using 2:8 EtOAc-hexane, gave **46** (0.276 g, 94%) as a pure (^1H NMR, 300 MHz), thick syrup: FTIR (CH_2Cl_2 cast) 3474, 2212 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.19 (s, 9 H), 1.62 (dd, *J* = 2.3, 2.3 Hz, 2 H), 2.08 (br s, 1 H), 3.73-3.86 (m, 2 H), 3.87-3.97 (m, 2 H), 4.21-4.28 (m, 1 H), 4.37 (d, *J* = 11.5 Hz, 1 H), 4.48-4.68 (m, 4 H), 4.79 (d, *J* = 2.5 Hz, 2 H), 4.90 (dd, *J* = 11.5, 2.5 Hz, 1 H), 5.00 (dd, *J* = 11.7, 2.2 Hz, 1 H), 7.19-7.44 (m, 20 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -1.8 (q'), 7.4 (t'), 60.3 (t'), 71.1 (t'), 71.4 (t'), 72.1 (d'), 74.7 (t'), 75.2 (t'), 75.4 (s'), 79.2 (d'), 79.3 (d'), 81.6 (d'), 87.2 (s'), 127.4 (d'), 127.55 (d'), 127.58 (d'), 127.66 (d'), 127.69 (d'), 128.01 (d'), 128.05 (d'), 128.12 (d'), 128.2 (d'), 128.3 (d'), 128.39 (d'), 128.44 (d'), 138.0 (s'), 138.3 (s'), 138.5 (s'), 138.9 (s'); exact mass *m/z* calcd for $C_{25}H_{31}O_4Si$ (M - H - Bn - OBn) 423.19916, found 423.19960.

6,7,8-Trideoxy-2,3,4,5-tetrakis-*O*-(phenylmethyl)-8-(trimethylsilyl)-L-*gulo*-oct-6-ynose (27).

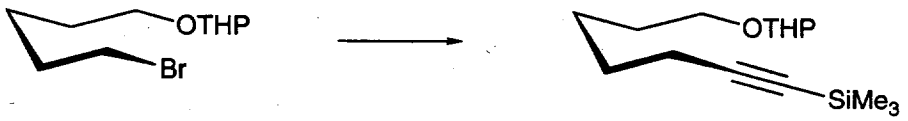


46 **27**

DMSO (0.14 mL, 1.97 mmol) was added dropwise to a stirred and cooled solution (-78 °C) of $(COCl)_2$ (0.13 mL, 1.49 mmol) in CH_2Cl_2 (10 mL). After 20 min, **46** (0.302 g, 0.486 mmol) in CH_2Cl_2 (5 mL) was added by syringe over 1 min. Stirring was continued for 30 min at -78 °C, and then Et_3N (0.54 mL, 3.86 mmol) was added dropwise over 2 min. After a further 30 min, the cold bath was

removed and stirring was continued for 6 h. The mixture was diluted with water (2 mL) and CH_2Cl_2 (15 mL), and transferred to a separatory funnel. The organic phase was washed with brine (20 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (1.5 x 15 cm), using 1:10 to 2:8 EtOAc-hexane, gave **27** (0.253 g, 84%) as a pure (^{1}H NMR, 360 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 2213, 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 0.17 (s, 9 H), 1.58 (d, *J* = 2.1 Hz, 2 H), 3.89 (dd, *J* = 6.9, 3.5 Hz, 1 H), 4.08 (dd, *J* = 4.3, 1.6 Hz, 1 H), 4.29 (d, *J* = 11.4 Hz, 1 H), 4.31 (dd, *J* = 4.3, 4.3 Hz, 1 H), 4.49-4.70 (m, 6 H), 4.87 (d, *J* = 11.4 Hz, 1 H), 4.94 (d, *J* = 11.2 Hz, 1 H), 7.23-7.38 (m, 20 H), 9.69 (d, *J* = 1.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -1.8 (q'), 7.4 (t'), 71.0 (t'), 71.8 (d'), 72.4 (t'), 74.6 (t'), 75.0 (t'), 75.1 (s'), 80.9 (d'), 81.5 (d'), 83.9 (d'), 87.2 (s'), 127.6 (d'), 127.7 (d'), 127.8 (d'), 127.9 (d'), 128.1 (d'), 128.2 (d'), 128.3 (d'), 128.39 (d'), 128.43 (d'), 137.5 (s'), 137.9 (s'), 138.4 (s'), 201.3 (d'); exact mass *m/z* calcd for $C_{39}H_{44}O_5Si$ 620.29578, found 620.29554.

Trimethyl[7-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-heptynyl]silane (48).



47 **48**

n-BuLi (2.5 M in hexane, 2.52 mL, 6.30 mmol) was added dropwise to a stirred and cooled (-78 °C) solution of trimethylsilylacetylene (0.647 g, 6.60 mmol) in THF (20 mL). Stirring at -78 °C was continued for 15 min, and then a mixture of **47** (1.51 g, 6.01 mmol) and HMPA (1.5 mL, 8.63 mmol) was added in one portion. The cold bath was removed and stirring was continued for 15 h. The mixture was then quenched with saturated aqueous NH_4Cl (20 mL) at -78 °C, and extracted with hexane (3 x 20 mL). The combined organic extracts were washed with water (15 mL) and

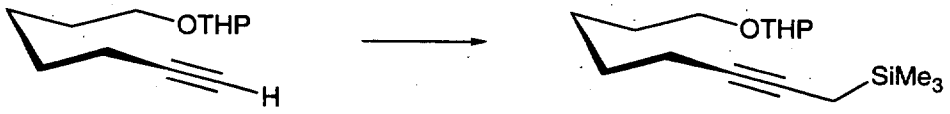
brine (20 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (2 x 25 cm), using 1:10 EtOAc-hexane, gave **48** [0.975 g, 94% after correction for recovered **47** (35%)] as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 2175 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz), δ 0.11 (s, 9 H), 1.35-1.90 (m, 12 H), 2.21 (t, *J* = 6.8 Hz, 2 H), 3.38 (dt, *J* = 9.6, 6.2 Hz, 1 H), 3.42-3.54 (m, 1 H), 3.72 (dt, *J* = 9.6, 6.2 Hz, 1 H), 3.77-3.90 (m, 1 H), 4.56 (dd, *J* = 3.6, 3.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 0.2 (q'), 19.6 (t'), 19.8 (t'), 25.5 (t'), 28.5 (t'), 29.3 (t'), 30.8 (t'), 62.2 (t'), 67.4 (t'), 84.4 (s'), 98.8 (d'), 107.4 (s'); exact mass *m/z* calcd for $C_{15}H_{28}O_2Si$ 268.18585, found 268.18529.

2-(6-Heptynyloxy)tetrahydro-2*H*-pyran (49).

48 **49**

K_2CO_3 (0.677 g, 4.90 mmol) was added in one portion to a stirred and cooled (0 °C) solution of **48** (1.31 g, 4.89 mmol) in 2:1 MeOH-THF (51 mL). The resulting mixture was stirred for 5 h, the cold bath was removed, and stirring was continued for 12 h. The mixture was then filtered through a pad (2 x 3 cm) of Celite, using Et_2O (50 mL) as a rinse. Evaporation of the combined filtrates, and flash chromatography of the residue over silica gel (2.5 x 20 cm), using 1:10 EtOAc-hexane, gave **49** (0.905 g, 94%) as a pure (^{1}H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 3296, 2117 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.36-1.87 (m, 12 H), 1.91 (t, *J* = 2.5 Hz, 1 H), 2.17 (td, *J* = 6.6, 2.5 Hz, 2 H), 3.37 (dt, *J* = 9.6, 6.2 Hz, 1 H), 3.41-3.55 (m, 1 H), 3.72 (dt, *J* = 9.6, 6.2 Hz, 1 H), 3.76-3.92 (m, 1 H), 4.54 (d, *J* = 3.6, 3.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 18.4 (t'), 19.7 (t'), 25.46 (t'), 25.52 (t'), 28.3 (t'), 29.3 (t'), 30.8 (t'), 62.3 (t'), 67.4 (t'), 68.2 (d'), 84.5 (s'), 98.9 (d'); exact mass *m/z* calcd for $C_{12}H_{19}O_2$ (M - 1) 195.13850, found 195.13841.

Trimethyl[8-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-octynyl]silane (50).[57]



49 **50**

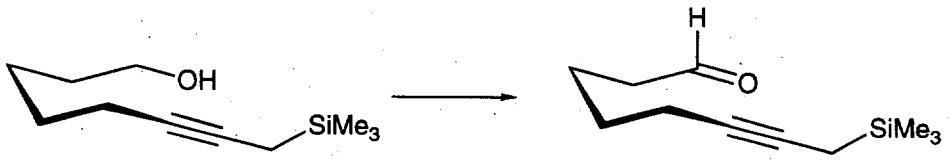
n-BuLi (2.5 M in hexane, 0.40 mL, 1.00 mmol) was added dropwise to a stirred and cooled (-78 °C) solution of **49** (0.200 g, 1.00 mmol) in THF (15 mL). Stirring at -78 °C was continued for 20 min, and then $Me_3SiCH_2OSO_2CF_3$ (0.237 g, 1.00 mmol) was added in one portion, followed immediately by HMPA (0.3 mL), which was also added rapidly in one portion. The cold bath was removed and stirring was continued for 18 h. The resulting mixture was poured into water (25 mL) and extracted with hexane (3 x 25 mL). The combined organic extracts were dried and evaporated. Flash chromatography of the residue over silica gel (1 x 20 cm), using 1:20 EtOAc-hexane, gave **50** [0.215 g, 91% after correction for recovered **49** (18%)] as a pure (^{1}H NMR, 400 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 2940, 2868, 1352 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.07 (s, 9 H), 1.35-1.63 [m, including triplet (2 H) at δ 1.38, J = 2.6 Hz, 12 H], 1.64-1.73 (m, 1 H), 1.75-1.86 (m, 1 H), 2.13 (tt, J = 6.5, 2.4 Hz, 2 H), 3.36 (dt, J = 9.6, 6.8 Hz, 1 H), 3.43-3.51 (m, 1 H), 3.71 (dt, J = 9.6, 6.8 Hz, 1 H), 3.80-3.88 (m, 1 H), 4.55 (dd, J = 3.6, 3.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -2.1 (q'), 6.9 (t'), 18.9 (t'), 19.6 (t'), 25.5 (t'), 29.31 (t'), 29.34 (t'), 30.8 (t'), 62.2 (t'), 67.5 (t'), 77.4 (s'), 78.7 (s'), 98.8 (d'); exact mass *m/z* calcd for $C_{16}H_{30}O_2Si$ 282.20151, found 282.20168.

8-(Trimethylsilyl)-6-octyn-1-ol (51).[57]

50 **51**

TsOH.H_2O (20.0 mg, 0.105 mmol) was added to a stirred solution of **50** (0.860 g, 3.05 mmol) in 3:1 MeOH-H_2O (200 mL), and the mixture was refluxed for 3 h, cooled, and concentrated. The resulting aqueous mixture was extracted with Et_2O (3 x 30 mL), and the combined organic extracts were washed with saturated aqueous $NaHCO_3$ (20 mL), water (20 mL) and brine (20 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (2 x 20 cm), using 2:8 EtOAc-hexane, gave **51** (0.560 g, 93%) as a pure (^1H NMR, 200 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 3334 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 0.04 (s, 9 H), 1.28-1.63 [m, including triplet (2 H) at δ 1.36, J = 2.6 Hz, 8 H], 2.01 (br s, 1 H), 2.11 (tt, J = 6.2, 2.2 Hz, 2 H), 3.57 (t, J = 6.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -2.1 (q'), 6.9 (t'), 18.8 (t'), 24.9 (t'), 29.2 (t'), 32.3 (t'), 62.7 (t'), 77.5 (s'), 78.6 (s'); exact mass *m/z* calcd for $C_{11}H_{22}OSi$ 198.14400, found 198.14457.

8-(Trimethylsilyl)-6-octynal (28).

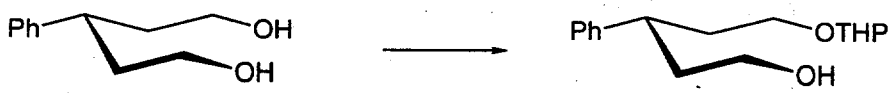


51 **28**

DMSO (0.067 mL, 0.95 mmol) was added to a stirred and cooled (-78 °C) solution of $(COCl)_2$ (0.063 mL, 0.72 mmol) in CH_2Cl_2 (10 mL). Stirring at -78 °C was continued for 20 min, and then a solution of **51** (47.4 mg, 0.24 mmol) in CH_2Cl_2 (2 mL) was added by syringe over 1 min. Stirring was continued for 30 min at -78 °C, and then Et_3N (0.28 mL, 1.98 mmol) was added dropwise over 2 min. The cold bath was removed, and the mixture was stirred for 3 h, diluted with water (1 mL) and CH_2Cl_2 (10 mL), and transferred to a separatory funnel. The organic phase was washed with brine (10 mL), dried, and evaporated. Flash chromatography of the residue

over silica gel (1 x 15 cm), using 1:10 EtOAc-hexane, gave **28** (37.5 mg, 80%) as a pure (^{1}H NMR, 300 MHz), colorless oil: FTIR (CH_2Cl_2, cast) 2718, 1727 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.07 (s, 9 H), 1.39 (t, *J* = 2.5 Hz, 2 H), 1.48 (tt, *J* = 7.5, 7.5 Hz, 2 H), 1.72 (tt, *J* = 7.5, 7.5 Hz, 2 H), 2.15 (tt, *J* = 7.5, 2.5 Hz, 2 H), 2.42 (tt, *J* = 7.5, 1.8 Hz, 2 H), 9.74 (t, *J* = 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -2.1 (q'), 6.9 (t'), 18.7 (t'), 21.2 (t'), 28.7 (t'), 43.4 (t'), 77.9 (s'), 78.0 (s'), 202.4 (d'); exact mass *m/z* calcd for $C_{11}H_{20}OSi$ 196.12834, found 196.12779.

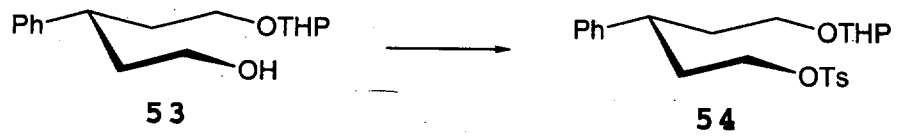
3-Phenyl-5-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-pentanol (53).



52 **53**

3,4-Dihydro-2*H*-pyran (2.48 mL, 27.8 mmol) and $TsOH.H_2O$ (30.0 mg, 0.174 mmol) were added to a stirred solution of **52**[58] (5.00 g, 27.8 mmol) in Et_2O (300 mL). Stirring was continued for 24 h, and the solution was washed with saturated aqueous $NaHCO_3$ (50 mL), water (50 mL) and brine (50 mL), dried and evaporated. Flash chromatography of the residue over silica gel (3 x 25 cm), using 3:7 EtOAc-hexane, gave **53** [3.10 g, 66% after correction for recovered diol (36%)] as a colorless oil that was a mixture of two diastereoisomers (^{1}H NMR, 300 MHz): FTIR (CH_2Cl_2 cast) 3424 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.39-2.09 (m, 11 H), 2.78-2.98 (m, 1 H), 3.09-3.32 (m, 1 H), 3.32-3.70 (m, 4 H), 3.70-3.87 (m, 1 H), 4.41 (d, *J* = 3.6, 3.6 Hz, 0.5 H), 4.47 (dd, *J* = 3.6, 3.6 Hz, 0.5 H), 7.00-7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 19.4 (t'), 19.7 (t'), 25.4 (t'), 30.6 (t'), 30.7 (t'), 36.48 (t'), 36.50 (t'), 38.9 (d'), 39.2 (d'), 39.5 (t'), 39.6 (t'), 60.7 (t'), 62.0 (t'), 62.4 (t'), 65.6 (t'), 98.6 (d'), 99.2 (d'), 126.2 (d'), 127.6 (d'), 128.4 (d'), 144.5 (s'); exact mass *m/z* calcd for $C_{16}H_{24}O_3$ 264.17255, found 264.17227.

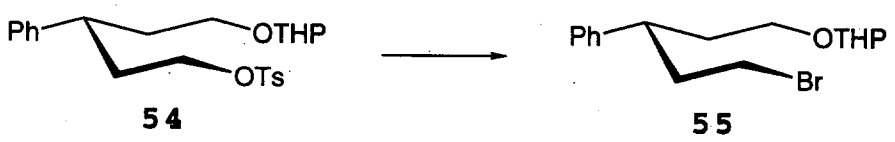
3-Phenyl-5-[(tetrahydro-2*H*-pyran-2-yl)oxy]pentyl 4-Methylbenzenesulfonate (54).



53 **54**

Alcohol **53** (3.10 g, 11.7 mmol) was added to a stirred solution of TsCl (3.13 g, 16.4 mmol), pyridine (3.80 mL, 47.0 mmol) and DMAP (0.360 g, 2.94 mmol) in CH_2Cl_2 (200 mL). Stirring was continued for 12 h, and the mixture was quenched with water (50 mL), and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with brine (40 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (3 x 25 cm), using 3:7 EtOAc-hexane, gave **54** (3.10 g, 63%) as a colorless oil that was a mixture of two diastereoisomers (^{1}H NMR, 300 MHz): FTIR (CH_2Cl_2 cast) 1362, 1176 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.40-2.00 (m, 9 H), 2.00-2.16 (m, 1 H), 2.44 (s, 3 H), 2.72-2.90 (m, 1 H), 3.02-3.23 (m, 1 H), 3.33-3.47 (m, 1 H), 3.47-3.64 (m, 1 H), 3.64-3.86 (m, 2 H), 3.86-3.99 (m, 1 H), 4.38 (dd, J = 3.2, 3.2 Hz, 0.5 H), 4.46 (dd, J = 3.2, 3.2 Hz, 0.5 H), 6.96-7.05 (m, 2 H), 7.11-7.27 (m, 3 H), 7.29 (d, J = 7.9 Hz, 2 H), 7.71 (d, J = 7.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 19.5 (t'), 19.7 (t'), 21.6 (q'), 25.5 (t'), 30.7 (t'), 30.7 (t'), 35.7 (t'), 38.9 (t'), 36.4 (t'), 38.6 (d'), 38.7 (d'), 62.1 (t'), 62.4 (t'), 65.29 (t'), 65.31 (t'), 68.66 (t'), 68.72 (t'), 98.7 (d'), 99.1 (d'), 126.6 (d'), 127.6 (d'), 127.9 (d'), 128.6 (d'), 129.8 (d'), 133.2 (s'), 142.9 (s'), 144.6 (s'); exact mass *m/z* calcd for $C_{23}H_{30}O_5S$ 418.18140, found 418.18123.

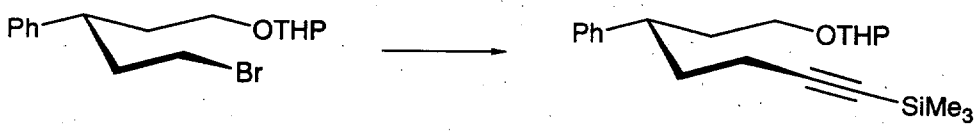
2-[(5-Bromo-3-phenylpentyl)oxy]tetrahydro-2*H*-pyran (55).



54 **55**

A solution of **54** (2.60 g, 6.22 mmol) and LiBr (5.40 g, 6.23 mmol) in acetone was refluxed for 2 h, cooled and evaporated. The residue was diluted with water (40 mL), and extracted with Et_2O (4 x 30 mL). The combined organic extracts were washed with brine (30 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (2 x 35 cm), using 2:8 EtOAc-hexane, gave **55** (1.93 g, 95%) as a colorless oil that was a mixture of two diastereoisomers (^{1}H NMR, 300 MHz): FTIR (CH_2Cl_2 cast) unexceptional; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.40-1.62 (m, 4 H), 1.62-1.74 (m, 1 H), 1.74-2.06 (m, 3 H), 2.06-2.40 (m, 2 H), 2.89-3.05 (m, 1 H), 3.05-3.35 (m, 3 H), 3.35-3.50 (m, 1 H), 3.54-3.71 (m, 1 H), 3.71-3.87 (m, 1 H), 4.44 (dd, *J* = 3.5, 3.5 Hz, 0.5 H), 4.50 (dd, *J* = 3.5, 3.5 Hz, 0.5 H), 7.10-7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 19.5 (t'), 19.7 (t'), 25.46 (t'), 25.48 (t'), 30.68 (t'), 30.74 (t'), 31.8 (t'), 36.25 (t'), 36.31 (t'), 39.67 (t'), 39.76 (t'), 41.0 (d'), 41.2 (d'), 62.1 (t'), 62.3 (t'), 65.42 (t'), 65.44 (t'), 98.7 (d'), 99.1 (d'), 126.6 (d'), 127.7 (d'), 128.6 (d'), 143.08 (s'), 143.13 (s'); exact mass *m/z* calcd for $C_{16}H_{23}{}^{81}BrO_2$ 328.08609, found 328.08641.

Trimethyl[5-phenyl-7-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-heptynyl]silane (56).

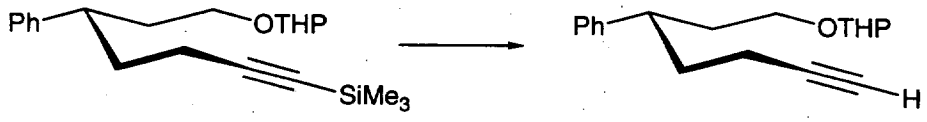


55 **56**

n-BuLi (2.5 M in hexane, 1.13 mL, 2.83 mmol) was added to a stirred and cooled (-78 °C) solution of trimethylsilylacetylene (0.43 mL, 2.83 mmol) in THF (10 mL). Stirring at -78 °C was continued for 1.5 h, and then **55** (0.396 g, 1.21 mmol) and HMPA (0.5 mL, 2.9 mmol) were added rapidly, each in one portion. The cold bath was removed and stirring was continued for 10 h. The mixture was quenched with water (5 mL) at -78 °C, and extracted with hexane (3 x 10 mL). The combined organic extracts were

washed with water (10 mL) and brine (10 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (1 x 20 cm), using 1:10 EtOAc-hexane, gave **56** (0.377 g, 81%) as a colorless oil that was a mixture of two diastereoisomers (^{1}H NMR, 300 MHz): FTIR (CH_2Cl_2 cast) 2174 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.17 (s, 9 H), 1.37-2.15 (m, 12 H), 2.76-2.94 (m, 1 H), 3.10-3.27 (m, 1 H), 3.34-3.48 (m, 1 H), 3.52-3.69 (m, 1 H), 3.69-3.85 (m, 1 H), 4.43 (dd, *J* = 3.4, 3.4 Hz, 0.5 H), 4.49 (dd, *J* = 3.4, 3.4 Hz, 0.5 H), 7.10-7.30 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 0.2 (q'), 18.0 (t'), 19.5 (t'), 19.6 (t'), 25.5 (t'), 30.69 (t'), 30.74 (t'), 35.65 (t'), 35.75 (t'), 36.3 (t'), 36.4 (t'), 41.5 (d'), 41.6 (d'), 62.0 (t'), 62.3 (t'), 65.6 (t'), 84.6 (s'), 98.5 (d'), 99.1 (d'), 107.2 (s'), 126.3 (d'), 127.7 (d'), 128.4 (d'), 143.9 (s'); exact mass *m/z* calcd for $C_{21}H_{32}O_2Si$ 344.21716, found 344.21734.

2-[(3-Phenyl-6-heptynyl)oxy]tetrahydro-2*H*-pyran (57).



56 **57**

K_2CO_3 (0.154 g, 1.11 mmol) was added in one portion to a stirred and cooled (0 °C) solution of **56** (0.381 g, 1.11 mmol) in 2:1 MeOH-THF (15 mL), and stirring at 0 °C was continued for 6 h. The cold bath was removed, stirring was continued for 12 h, and the mixture was then filtered through a pad (1 x 2 cm) of Celite, using Et_2O (20 mL) as a rinse. Evaporation of the combined filtrates, and flash chromatography of the residue over silica gel (1.5 x 15 cm), using 1:10 EtOAc-hexane, gave **57** (0.284 g, 94%) as a colorless oil that was a mixture of two diastereoisomers (^{1}H NMR, 300 MHz): FTIR (CH_2Cl_2 cast) 3296, 2116 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.45-2.16 (m, 13 H), 2.82-2.96 (m, 1 H), 3.18-3.32 (m, 1 H), 3.41-3.52 (m, 1 H), 3.60-3.74 (m, 1 H), 3.74-3.90 (m, 1 H), 4.47 (dd, *J* = 3.3, 3.3 Hz, 0.5 H), 4.53 (dd, *J* = 3.3, 3.3 Hz, 0.5 H), 7.12-7.41 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 16.46 (t'), 16.49

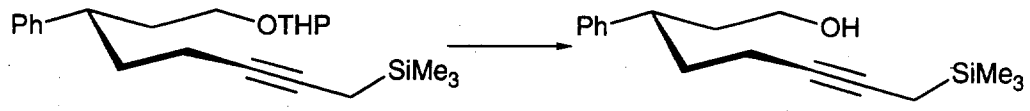
(t'), 19.5 (t'), 19.6 (t'), 25.4 (t'), 30.6 (t'), 30.7 (t'), 35.5 (t'), 35.6 (t'), 36.3 (t'), 36.4 (t'), 41.4 (d'), 41.6 (d'), 62.0 (t'), 62.2 (t'), 65.55 (t'), 65.59 (t'), 68.39 (d'), 68.42 (d'), 84.2 (s'), 98.6 (d'), 99.0 (d'), 126.3 (d'), 127.7 (d'), 128.4 (d'), 143.8 (s'), 143.9 (s'); exact mass *m/z* calcd for $C_{18}H_{24}O_2$ 272.17764, found 272.17726.

Trimethyl[6-phenyl-8-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-octynyl]silane (58).

57 **58**

n-BuLi (2.5 M in hexane, 1.20 mL, 3.00 mmol) was added to a stirred and cooled (-78 °C) solution of **57** (0.652 g, 2.40 mmol) in THF (15 mL). Stirring at -78 °C was continued for 1.5 h, and then $Me_3SiCH_2OSO_2CF_3$ (0.60 mL, 3.00 mmol) and HMPA (0.5 mL) were added rapidly, each in one portion. The cold bath was removed and stirring was continued for 10 h. The mixture was poured into water (25 mL) and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic extracts were dried and evaporated. Flash chromatography of the residue over silica gel (1.5 x 20 cm), using 1:10 EtOAc-hexane, gave **58** (0.791 g, 92%) as a colorless oil that was a mixture of two diastereoisomers (^{1}H NMR, 300 MHz): FTIR (CH_2Cl_2 cast) unexceptional; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.10 (s, 9 H), 1.38-2.11 (m, 14 H), 2.76-2.94 (m, 1 H), 3.11-3.26 (m, 1 H), 3.35-3.48 (m, 1 H), 3.53-3.69 (m, 1 H), 3.70-3.86 (m, 1 H), 4.43 (dd, *J* = 3.4, 3.4 Hz, 0.5 H), 4.49 (dd, *J* = 3.4, 3.4 Hz, 0.5 H), 7.03-7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -2.0 (q'), 7.0 (t'), 17.1 (t'), 19.5 (t'), 19.7 (t'), 25.5 (t'), 30.7 (t'), 30.8 (t'), 36.3 (t'), 36.4 (t'), 36.7 (t'), 36.8 (t'), 41.5 (d'), 41.7 (d'), 62.0 (t'), 62.3 (t'), 65.8 (t'), 77.5 (t'), 77.6 (s'), 78.4 (s'), 78.5 (s'), 98.6 (d'), 99.1 (d'), 126.2 (d'), 127.2 (d'), 128.4 (d'), 144.3 (s'), 144.4 (s'); exact mass *m/z* calcd for $C_{22}H_{34}O_2Si$ 358.23282, found 358.23321.

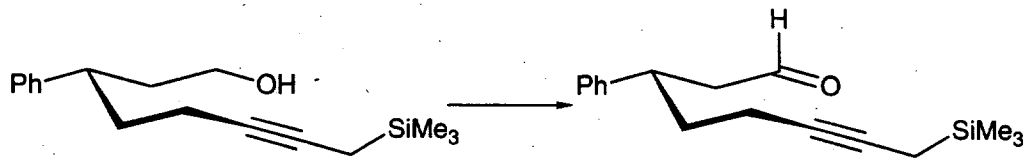
3-Phenyl-8-(trimethylsilyl)-6-octyn-1-ol (59).



58 **59**

$TsOH.H_2O$ (30.0 mg, 0.158 mmol) was added to a stirred solution of **58** (0.685 g, 1.91 mmol) in 3:1 MeOH-H_2O (150 mL), and the mixture was refluxed for 4 h, cooled, and concentrated. The resulting aqueous mixture was extracted with Et_2O (3 x 20 mL), and the combined organic extracts were washed with saturated aqueous $NaHCO_3$ (20 mL), water (20 mL), and brine (20 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using 2:8 EtOAc-hexane, gave **59** (0.469 g, 89%) as a pure (^1H NMR, 300 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 3332 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.10 (s, 9 H), 1.16 (t, J = 5.0 Hz, 1 H), 1.43 (t, J = 2.3 Hz, 2 H), 1.65-2.12 (m, 6 H), 2.87 (dddd, J = 4.7, 4.7, 4.7, 4.7 Hz, 1 H), 3.40-3.60 (m, 2 H), 7.12-7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -2.0 (q'), 7.0 (t'), 17.0 (t'), 36.6 (t'), 39.3 (t'), 41.4 (d'), 61.2 (t'), 77.8 (s'), 78.3 (s'), 126.4 (d'), 127.7 (d'), 128.5 (d'), 144.2 (s'); exact mass *m/z* calcd for $C_{17}H_{26}OSi$ 274.17529, found 274.17522.

3-Phenyl-8-(trimethylsilyl)-6-octynal (29).

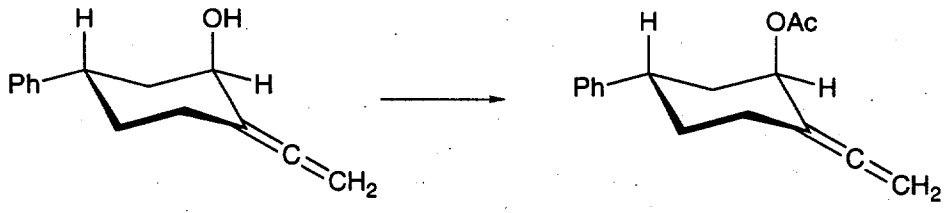


59 **29**

DMSO (0.19 mL, 2.67 mmol) was added to a stirred and cooled (-78 °C) solution of $(COCl)_2$ (0.19 mL, 2.18 mmol) in CH_2Cl_2 (25 mL). Stirring at -78 °C was continued for 20 min, and then a solution of **59** (0.147 g, 0.536 mmol) in CH_2Cl_2 (2 mL) was added by

syringe over 1 min. Stirring was continued for 30 min at -78 °C, and then Et_3N (0.76 mL, 5.45 mmol) was added. The cold bath was removed, and the mixture was stirred for 3 h, diluted with water (1 mL) and CH_2Cl_2 (10 mL), and transferred to a separatory funnel. The organic phase was washed with brine (10 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (2 x 15 cm), using (1:10 EtOAc-hexane, gave **29** (0.132 g, 90%) as a pure (^1H NMR, 300 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 1725 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.12 (s, 9 H), 1.43 (t, J = 2.4 Hz, 2 H), 1.67-2.15 (m, 4 H), 2.63-2.81 (m, 2 H), 3.30-3.43 (m, 1 H), 7.15-7.37 (m, 5 H), 9.66 (t, J = 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -2.0 (q'), 7.0 (t'), 16.9 (t'), 36.2 (t'), 39.0 (d'), 50.1 (t'), 77.7 (s'), 78.4 (s'), 126.8 (d'), 127.6 (d'), 128.8 (d'), 143.0 (s'), 201.7 (d'); exact mass m/z calcd for $C_{17}H_{24}OSi$ 272.15964, found 272.15907.

Derivatization of 28a: *Trans*-2-Ethenylidene-5-phenyl-1-cyclohexyl Acetate.

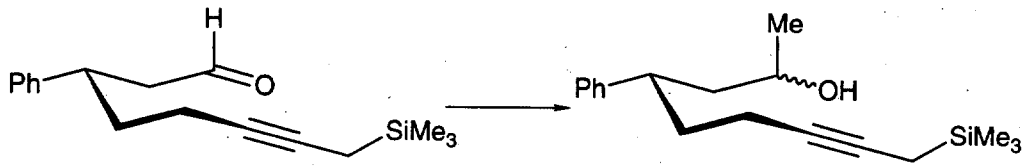


28a -

Ac_2O (0.014 mL, 0.15 mmol), Et_3N (0.025 mL, 0.18 mmol), and DMAP (0.5 mg, 0.004 mmol) were added to a stirred solution of **28a** (8.0 mg, 0.040 mmol) in CH_2Cl_2 (3 mL). Stirring was continued for 1 h and the mixture was then filtered through a pad (1.5 x 1 cm) of flash chromatography silica gel, using CH_2Cl_2 (20 mL) as a rinse. Evaporation of the combined filtrates, and flash chromatography of the residue over silica gel (1 x 10 cm), using 1:10 EtOAc-hexane, gave the derived acetate (8.5 mg, 88%) as a pure (^1H NMR, 300 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 1962, 1738, 1234 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.66 (dddd, J = 13.0,

13.0, 13.0, 4.1 Hz, 1 H), 1.84 (ddd, J = 13.6, 13.0, 2.8 Hz, 1 H), 1.95-2.08 (m, 1 H), 2.08-2.23 [m, including singlet at δ 2.12 (3 H), 4 H], 2.34 (ddd, J = 13.0, 3.4, 3.4 Hz, 1 H), 2.47 (ddd, J = 13.6, 4.1, 4.1 Hz, 1 H), 3.02 (dddd, J = 13.0, 13.0, 3.4, 3.4 Hz, 1 H), 4.75 (d, J = 4.1 Hz, 2 H), 5.57 (dd, J = 2.8, 2.8 Hz, 1 H), 7.16-7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 21.5 (q'), 27.0 (t'), 33.9 (t') 37.9 (d'), 38.6 (t'), 72.2 (d'), 74.8 (t'), 98.6 (s'), 126.4 (d'), 126.9 (d'), 128.6 (d'), 147.8 (s'), 170.1 (s'), 205.1 (s'); exact mass m/z calcd for $C_{16}H_{18}O_2$ 242.13068, found 242.13060.

4-Phenyl-9-(trimethylsilyl)-7-nonyn-2-ol (60).

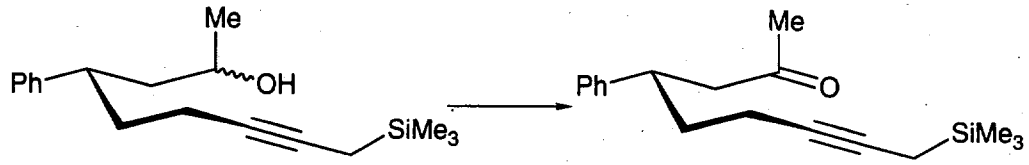


29 **60**

A solution of **29** (46.6 mg, 0.171 mmol) in Et_2O (3 mL) was added dropwise to a stirred and cooled (0 °C) solution of MeMgBr (0.36 mmol) in Et_2O (15 mL). The cold bath was removed and stirring was continued for 2 h. The mixture was quenched with saturated aqueous NH_4Cl solution (5 mL) at 0 °C and extracted with Et_2O (3 x 25 mL). The combined organic extracts were washed with brine (10 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (1.5 x 15 cm), using 2:8 EtOAc-hexane, gave **60** (44.6 mg, 90%) as a pure (^{1}H NMR, 400 MHz), colorless oil, which was a 1:1 mixture of diastereoisomers (^{1}H NMR, 400 MHz): FTIR (CH_2Cl_2 cast) 3347 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.10 (s, 9 H), 1.12 (d, J = 5.9 Hz, 3 H), 1.39 (br s, 1 H), 1.43 (t, J = 2.5 Hz, 2 H), 1.64-2.08 (m, 6 H), 2.97 (dddd, J = 4.9, 4.9, 4.9, 4.9 Hz, 1 H), 3.43-3.56 (m, 1 H), 7.15-7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -2.0 (q'), 7.0 (t'), 16.9 (t'), 17.1 (t'), 23.2 (q'), 24.3 (q'), 36.7 (t'), 37.0 (t'), 41.4 (d'), 42.0 (d'), 46.0 (t'), 46.1 (t'), 65.7 (d'), 66.6 (d'), 77.7 (s'), 77.8 (s'), 78.3 (s'),

78.4 (s'), 126.3 (d'), 126.4 (d'), 127.6 (d'), 127.8 (d'), 128.5 (d'), 128.6 (d'), 144.3 (s'), 144.4 (s'); exact mass *m/z* calcd for $C_{18}H_{28}OSi$ 288.19095, found 288.19067.

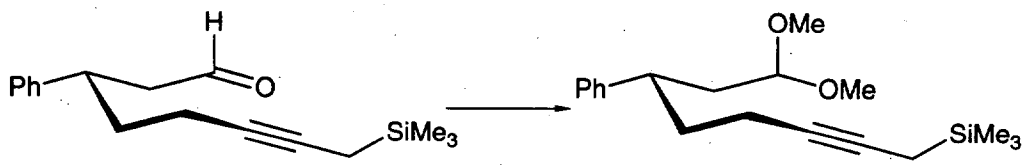
4-Phenyl-9-(trimethylsilyl)-7-nonyn-2-one (30).



60 **30**

A solution of alcohols **60** (0.140 g, 0.486 mmol) in CH_2Cl_2 (4 mL) was added to a stirred mixture of PCC (1.63 g, 7.56 mmol) and powdered molecular sieves (3Å, 3.1 g) in CH_2Cl_2 (20 mL). The mixture was stirred for 25 min, diluted with Et_2O (20 mL), and filtered through a pad (2 x 2 cm) of flash chromatograhy silica gel, using Et_2O (30 mL) as a rinse. Evaporation of the combined filtrates, and flash chromatography of the residue over silica gel (1 x 15 cm), using 1:10 EtOAc-hexane, gave **30** (0.126 g, 90%) as a pure (^{1}H NMR, 300 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 1717 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.10 (s, 9 H), 1.42 (t, *J* = 2.4 Hz, 2 H), 1.61-2.10 [m, including singlet at δ 2.01 (3 H), 7 H], 2.71 (dd, *J* = 16.5, 7.6 Hz, 1 H), 2.76 (dd, *J* = 16.5, 7.6 Hz, 1 H), 3.22-3.35 (m, 1 H), 7.10-7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -2.0 (q'), 7.0 (t'), 17.0 (t'), 30.4 (d'), 36.1 (t'), 40.3 (d'), 50.5 (t'), 77.9 (s'), 78.0 (s'), 126.6 (d'), 127.6 (d'), 128.5 (d'), 143.5 (s'), 207.5 (s'); exact mass *m/z* calcd for $C_{18}H_{26}OSi$ 286.17529, found 286.17498.

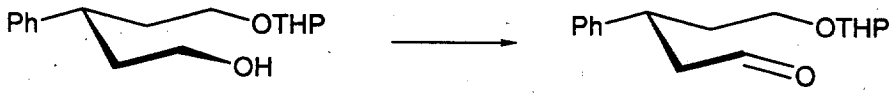
(8,8-Dimethoxy-6-phenyl-2-octynyl)trimethylsilane (31).



29 **31**

$YbCl_3.6H_2O$ (0.560 g, 1.45 mmol) and $CH(OMe)_3$ (2.62 mL, 23.9 mmol) were added to a stirred solution of **29** (0.178 g, 0.654 mmol) in MeOH (1.5 mL). Stirring was continued for 10 h, and the mixture was diluted with Et_2O (5 mL) and filtered through a pad (2 x 2 cm) of flash chromatograhy silica gel, using Et_2O (20 mL) as a rinse. Evaporation of the combined filtrates, and flash chromatography of the residue over silica gel (1.5 x 15 cm), using 1:10 EtOAc-hexane, gave **31** (0.160 g, 77%) as a pure (^1H NMR, 300 MHz), colorless oil: FTIR (CH_2Cl_2 cast) unexceptional; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.12 (s, 9 H), 1.42 (t, *J* = 2.5 Hz, 2 H), 1.64-2.09 (m, 6 H), 2.86 (dddd, *J* = 4.9, 4.9, 4.9, 4.9 Hz, 1 H), 3.22 (s, 3 H), 3.27 (s, 3 H), 4.07 (dd, *J* = 7.6, 3.7 Hz, 1 H), 7.13-7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -2.0 (q'), 7.0 (t'), 17.0 (t'), 36.6 (t'), 39.3 (t'), 40.6 (d'), 52.6 (q'), 52.7 (q'), 77.7 (s'), 78.3 (s'), 102.8 (d'), 126.3 (d'), 127.7 (d'), 128.5 (d'),, 144.1 (s'); exact mass *m/z* calcd for $C_{19}H_{30}O_2Si$ 318.20151, found 318.20148.

3-Phenyl-5-[(tetrahydro-2*H*-pyran-2-yl)oxy]pentanal (61).

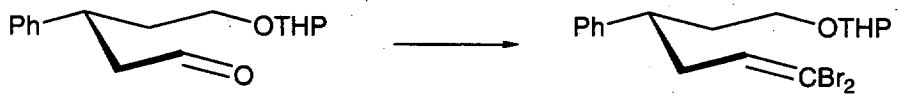


53 **61**

A solution of **53** (0.154 g, 0.583 mmol) in CH_2Cl_2 (4 mL) was added to a stirred mixture of PCC (1.32 g, 6.12 mmol) and powdered molecular sieves (3Å, 1.90 g) in CH_2Cl_2 (25 mL). The mixture was stirred for 35 min, diluted with Et_2O (20 mL), and filtered through a pad (2 x 2 cm) of flash chromatography silica gel, using Et_2O (30 mL) as a rinse. Evaporation of the combined filtrates, and flash chromatography of the residue over silica gel (1 x 15 cm), using 1:10 EtOAc-hexane, gave **61** (0.125 g, 82%) as a colorless oil that was a mixture of two diastereoisomers (^1H NMR, 300 MHz): FTIR

(CH_2Cl_2 cast) 2723, 1724 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.42-2.07 (m, 8 H), 2.75 (dd, *J* = 7.4, 1.9 Hz, 2 H), 3.11-3.22 (m, 1 H), 3.32-3.53 (m, 2 H), 3.55-3.86 (m, 2 H), 4.43 (dd, *J* = 3.6, 3.6 Hz, 0.5 H), 4.49 (dd, *J* = 3.6, 3.6 Hz, 0.5 H), 7.10-7.30 (m, 5 H), 9.66 (t, *J* = 1.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 19.4 (t'), 19.6 (t'), 25.3 (t'), 30.56 (t'), 30.63 (t'), 36.2 (t'), 36.3 (t'), 36.8 (d'), 36.9 (d'), 50.2 (t'), 50.3 (t'), 62.0 (t'), 62.3 (t'), 64.9 (t'), 65.0 (t'), 98.5 (d'), 99.1 (d'), 126.6 (d'), 127.4 (d'), 128.6 (d'), 143.16 (s'), 143.22 (s'), 201.5 (d'), 201.6 (d'); exact mass *m/z* calcd for $C_{16}H_{22}O_3$ 262.15689, found 262.15621.

2-[(6,6-Dibromo-3-phenyl-5-hexenyl)oxy]tetrahydro-2*H*-pyran (62).

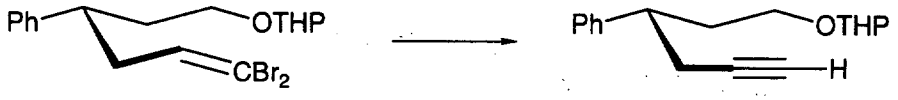


61 **62**

A solution of CBr_4 (2.78 g, 8.40 mmol) in CH_2Cl_2 (75 mL) was added at a fast dropwise rate to a stirred and cooled (-20 °C) solution of Ph_3P (2.20 g, 8.40 mmol) in CH_2Cl_2 (75 mL). Stirring at -20 °C was continued for 15 min, and then a solution of **61** (1.10 g, 4.20 mmol) and Et_3N (0.59 mL, 4.20 mmol) in CH_2Cl_2 (40 mL) was added dropwise at -60 °C. The cold bath was removed, stirring was continued for 30 min, and the mixture was filtered through a pad (2 x 3 cm) of flash chromatography silica gel, using Et_2O (50 mL) as a rinse. Evaporation of the combined filtrates, and flash chromatography of the residue over silica gel (1.5 x 25 cm), using 1:20 EtOAc-hexane, gave **62** (1.34 g, 76%) as a colorless oil that was a mixture of two diastereoisomers (^1H NMR, 300 MHz): FTIR (CH_2Cl_2 cast) unexceptional; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.42-2.10 (m, 8 H), 2.30-2.57 (m, 2 H), 2.82-2.97 (m, 1 H), 3.11-3.31 (m, 1 H), 3.36-3.50 (m, 1 H), 3.53-3.86 (m, 2 H), 4.42 (dd, *J* = 3.2, 3.2 Hz, 0.5 H), 4.49 (dd, *J* = 3.2, 32.2 Hz, 0.5 H), 6.26 (t, *J* = 7.1 Hz, 1 H), 7.10-7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 19.5

(t'), 19.7 (t'), 25.4 (t'), 30.66 (t'), 30.71 (t'), 35.7 (t'), 35.8 (t'), 40.05 (t'), 40.14 (t'), 41.3 (d'), 41.5 (d'), 62.1 (t'), 62.4 (t'), 65.30 (t'), 65.34 (t'), 89.4 (s'), 89.5 (s'), 98.7 (d'), 99.1 (d'), 126.6 (d'), 126.7 (d'), 127.5 (d'), 128.5 (d'), 128.6 (d'), 136.88 (d'), 136.93 (d'), 143.4 (s'), 143.5 (s'); exact mass *m/z* calcd for $C_{17}H_{22}{}^{81}Br_2O_2$ 419.99457, found 419.99404.

2-[(3-Phenyl-5-hexynyl)oxy]tetrahydro-2*H*-pyran (63).

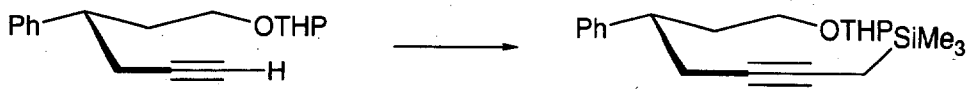


62 **63**

n-BuLi (2.5 M in hexane, 0.88 mL, 2.20 mmol) was added dropwise to a stirred and cooled (-78 °C) solution of **62** (0.440 g, 1.05 mmol) in THF (30 mL). Stirring at -78 °C was continued for 2 h, and then water (1.0 mL) was added. The cold bath was removed, stirring was continued for 30 min, and the mixture was diluted with Et_2O (20 mL) and washed with brine (20 mL). The organic extract was dried and evaporated. Flash chromatography of the residue over silica gel (1.5 x 15 cm), using 1:20 EtOAc-hexane, gave **63** (0.255 g, 94%) as a colorless oil that was a mixture of two diastereoisomers (^{1}H NMR, 300 MHz): FTIR (CH_2Cl_2 cast) 3290, 2117 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.40-2.03 (m, 8 H), 2.14-2.27 (m, 1 H), 2.46-2.56 (m, 2 H), 2.92-3.08 (m, 1 H), 3.16-3.34 (m, 1 H), 3.35-3.48 (m, 1 H), 3.57-3.86 (m, 2 H), 4.44 (dd, *J* = 3.3, 3.3 Hz, 0.5 H), 4.53 (dd, *J* = 3.3, 3.3 Hz, 0.5 H), 7.13-7.38 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 19.4 (t'), 19.6 (t'), 25.4 (t'), 26.1 (t'), 26.3 (t'), 30.6 (t'), 30.6 (t'), 34.7 (t'), 34.8 (t'), 41.2 (d'), 41.4 (d'), 61.8 (t'), 62.2 (t'), 65.2 (t'), 65.3 (t'), 69.8 (d'), 82.6 (s'), 98.4 (d'), 98.9 (d'), 126.5 (d'), 127.5 (d'), 128.3 (d') 128.4 (d'), 143.5 (s'); exact mass *m/z* calcd for $C_{17}H_{22}O_2$ 258.16199, found 258.16187.

Trimethyl[5-phenyl-7-[(tetrahydro-2*H*-pyran-2-yl)oxy]-

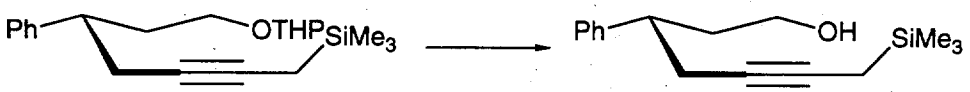
2-heptynyl]silane (64).



63 **64**

n-BuLi (2.5 M in hexane, 0.50 mL, 1.25 mmol) was added dropwise to a stirred and cooled (-78 °C) solution of **63** (0.255 g, 0.988 mmol) in THF (18 mL). Stirring at -78 °C was continued for 1 h, and then $Me_3SiCH_2OSO_2CF_3$ (0.25 mL, 1.25 mmol) and HMPA (0.50 mL, 2.88 mmol) were added rapidly, each in one portion. The cold bath was removed and stirring was continued for 10 h. The mixture was diluted with Et_2O (20 mL) and washed with brine (20 mL). The aqueous phase was extracted with Et_2O (2 x 20 mL) and the combined organic extracts were dried and evaporated. Flash chromatography of the residue over silica gel (1.5 x 15 cm), using 1:20 EtOAc-hexane, gave **64** (0.292 g, 86%) as a colorless oil that was a mixture of two diastereoisomers (^{1}H NMR, 300 MHz): FTIR (CH_2Cl_2 cast) unexceptional; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.03 (s, 9 H), 1.38 (t, *J* = 2.6 Hz, 2 H), 1.43-1.97 (m, 7 H), 2.12-2.26 (m, 1 H), 2.42-2.52 (m, 2 H), 2.84-2.98 (m, 1 H), 3.15-3.32 (m, 1 H), 3.35-3.48 (m, 1 H), 3.56-3.86 (m, 2 H), 4.45 (dd, *J* = 3.4, 3.4 Hz, 0.5 H), 4.52 (dd, *J* = 3.4, 3.4 Hz, 0.5 H), 7.14-7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -2.1 (q'), 7.0 (t'), 19.4 (t'), 19.6 (t'), 25.5 (t'), 26.7 (t'), 26.9 (t'), 30.68 (t'), 30.74 (t'), 35.08 (t'), 35.10 (t'), 42.1 (d'), 42.3 (d'), 61.9 (t'), 62.2 (t'), 65.5 (t'), 65.6 (t'), 76.9 (s'), 78.9 (s'), 98.5 (d'), 98.9 (d'), 126.3 (d'), 126.47 (d'), 127.49 (d'), 127.6 (d'), 128.3 (d'), 128.4 (d'), 144.3 (s'); exact mass *m/z* calcd for $C_{21}H_{32}O_2Si$ 344.21716, found 344.21696.

3-Phenyl-7-(trimethylsilyl)-5-heptyn-1-ol (65).



64 **65**

TsOH.H_2O (12.0 mg, 0.063 mmol) was added to a stirred solution of **64** (0.292 g, 0.848 mmol) in 3:1 MeOH-H_2O (80 mL), and the mixture was refluxed for 3.5 h, cooled, and concentrated. The resulting aqueous mixture was extracted with Et_2O (3 x 20 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (20 mL), water (20 mL) and brine (20 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (1.5 x 15 cm), using 2:8 EtOAc-hexane, gave **65** (0.216 g, 98%) as a pure (^1H NMR, 300 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 3332 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.04 (s, 9 H), 1.38 (t, *J* = 2.6 Hz, 2 H), 1.47 (br s, 1 H), 1.79-1.93 (m, 1 H), 2.05-2.19 (m, 1 H), 2.38-2.57 (m, 2 H), 2.83-2.96 (m, 1 H), 3.44-3.64 (m, 2 H), 7.13-7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -2.1 (q'), 7.0 (t'), 26.7 (t'), 38.1 (t'), 42.1 (d'), 61.1 (t'), 76.8 (s'), 79.1 (s'), 126.5 (d'), 127.5 (d'), 128.4 (d'), 144.2 (s'); exact mass *m/z* calcd for $C_{16}H_{24}OSi$ 260.15964, found 260.15939.

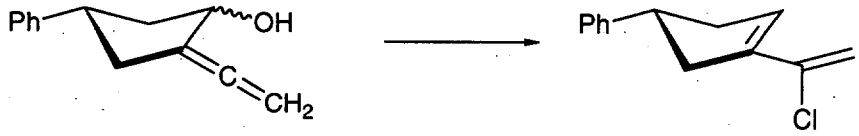
3-Phenyl-7-(trimethylsilyl)-5-heptynal (32).

65 **32**

A solution of **65** (0.165 g, 0.635 mmol) in CH_2Cl_2 (5 mL) was added to a stirred mixture of PCC (1.43 g, 6.63 mmol) and powdered molecular sieves (3Å, 2.20 g) in CH_2Cl_2 (30 mL). The mixture was stirred for 30 min, diluted with Et_2O (20 mL), and filtered through a pad (2 x 2 cm) of flash chromatograhy silica gel, using Et_2O (30 mL) as a rinse. Evaporation of the combined filtrates, and flash chromatography of the residue over silica gel (1 x 15 cm), using 1:10 EtOAc-hexane, gave **32** (0.148 g, 90%) as a pure (^1H NMR, 300 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 2722, 2220, 1724 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.06 (s, 9 H), 1.42 (t, *J* = 2.7 Hz, 2 H), 2.47 (ddt, *J* = 16.6, 6.0, 2.7 Hz, 1 H), 2.56 (ddt, *J* = 16.6, 5.8, 2.7 Hz, 1 H), 2.77 (ddd, *J* = 17.2, 8.2, 1.8 Hz, 1 H), 3.02 (ddd, *J*

= 17.2, 6.2, 1.8 Hz, 1 H), 3.39 (br dddd, J = 8.2, 6.2, 6.0, 5.8 Hz, 1 H), 7.16-7.37 (m, 5 H), 9.72 (t, J = 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -2.0 (q'), 7.0 (t'), 26.6 (t'), 39.6 (d'), 48.8 (t'), 75.9 (s'), 80.3 (s'), 126.9 (d'), 127.3 (d'), 128.6 (d'), 143.1 (s'), 201.5 (d'); exact mass m/z calcd for $C_{16}H_{21}OSi$ (M - H) 257.13617, found 257.13608.

1-(1-Chloroethenyl)-4-phenylcyclopentene (32b).



32a **32b**

A solution of alcohols **32a** (15.0 mg, 0.081 mmol) in CH_2Cl_2 (2.0 mL) was added to a stirred suspension of $ZnCl_2$ (12.0 mg, 0.088 mmol) in CH_2Cl_2 (20 mL). Stirring was continued for 24 h, and the resulting solution was filtered through a pad (2 x 2 cm) of flash chromatography silica gel, using Et_2O (30 mL) as a rinse. Evaporation of the solvent, and flash chromatography of the residue over silica gel (1.5 x 10 cm), using hexane, gave **32b** (7.5 mg, 45%) as a pure (^1H NMR, 360 MHz), colorless oil, identified by its ^1H NMR spectrum.

(7,7-Dimethoxy-5-phenyl-2-heptynyl)trimethylsilane (33).

32 **33**

$YbCl_3.6H_2O$ (0.30 g, 0.77 mmol) and $CH(OMe)_3$ (1.60 mL, 14.6 mmol) was added to a stirred solution of **32** (0.102 g, 0.395 mmol) in MeOH (1 mL). Stirring was continued for 10 h, and the mixture was diluted with Et_2O (5 mL) and filtered through a pad (2 x 2 cm) of flash chromatograhy silica gel, using Et_2O (20 mL) as a rinse.

Evaporation of the combined filtrates, and flash chromatography of the residue over silica gel (1.5 x 15 cm), using 1:20 EtOAc-hexane, gave **33** (0.103 g, 86%) as a pure (^{1}H NMR, 300 MHz), colorless oil: FTIR (CH_2Cl_2 cast) unexceptional; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.03 (s, 9 H), 1.38 (t, *J* = 2.6 Hz, 2 H), 1.85 (ddd, *J* = 14.3, 9.8, 3.8 Hz, 1 H), 2.22 (ddd, *J* = 14.3, 7.8, 4.8 Hz, 1 H), 2.37-2.55 (m, 2 H), 2.82-2.94 (m, 1 H), 3.22 (s, 3 H), 3.28 (s, 3 H), 4.15 (dd, *J* = 7.8, 3.8 Hz, 1 H), 7.15-7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -2.1 (q'), 7.0 (t'), 26.7 (t'), 37.7 (t'), 41.2 (d'), 52.4 (q'), 52.5 (q'), 76.6 (s'), 79.1 (s'), 102.6 (d'), 126.5 (d'), 127.5 (d'), 128.4 (d'), 144.1 (s'); exact mass *m/z* calcd for $C_{17}H_{25}O_2Si$ (M - CH_3) 289.16238, found 289.16295.

4-Phenyl-8-(trimethylsilyl)-6-octyn-2-ol (66).

32 **66**

A solution of **32** (120 mg, 0.465 mmol) in Et_2O (5 mL) was added dropwise to a stirred and cooled (0 °C) solution of commercial MeMgBr (3.0 M in Et_2O, 0.31 mL, 0.93 mmol) in Et_2O (35 mL). The cold bath was removed, and stirring was continued for 2 h. The mixture was then recooled to 0 °C, quenched with saturated aqueous NH_4Cl (15 mL), and extracted with Et_2O (3 x 25 mL). The combined organic extracts were washed with brine (20 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (1.5 x 15 cm), using 2:8 EtOAc-hexane, gave **66** (115 mg, 90%) as a colorless oil that was a 1:1 mixture of two diastereoisomers (^{1}H NMR, 300 MHz): FTIR (CH_2Cl_2 cast) 3356 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.04 (s, 9 H), 1.12 (d, *J* = 6.1 Hz, 1.5 H), 1.17 (d, *J* = 6.1 Hz, 1.5 H), 1.39 (dd, *J* = 2.6, 2.6 Hz, 1 H), 1.40 (dd, *J* = 2.6, 2.6 Hz, 1 H), 1.60-2.04 (m, 3 H), 2.33-2.56 (m, 2 H), 2.78-2.92 (m, 0.5 H), 2.94-3.08 (m, 0.5 H), 3.45-3.60 (m, 0.5 H), 3.67-3.82 (m, 0.5 H), 7.14-7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ

-2.1 (q'), 7.0 (t'), 23.4 (q'), 24.4 (q'), 26.7 (t'), 27.2 (t'), 42.0 (d'), 42.5 (d'), 44.7 (t'), 44.7 (t'), 65.6 (d'), 66.4 (d'), 76.8 (s'), 76.9 (s'), 79.0 (s'), 79.2 (s'), 126.4 (d'), 126.5 (d'), 127.4 (d'), 127.6 (d'), 128.4 (d'), 128.5 (d'), 144.3 (s'), 144.6 (s'); exact mass *m/z* calcd for $C_{17}H_{26}OSi$ 274.17529, found 274.17552.

4-Phenyl-8-(trimethylsilyl)-6-octyn-2-one (34).

66 **34**

A solution of alcohols **66** (71.6 mg, 0.261 mmol) in CH_2Cl_2 (2 mL) was added to a stirred mixture of PCC (0.880 g, 4.08 mmol) and powdered molecular sieves (3Å, 1.76 g) in CH_2Cl_2 (18 mL). The mixture was stirred for 30 min, diluted with Et_2O (10 mL), and filtered through a pad (2 x 1.5 cm) of flash chromatograhy silica gel, using Et_2O (20 mL) as a rinse. Evaporation of the combined filtrates, and flash chromatography of the residue over silica gel (1 x 15 cm), using 1:20 EtOAc-hexane, gave **34** (65.3 mg, 92%) as a pure (^1H NMR, 300 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 1717 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.05 (s, 9 H), 1.42 (t, *J* = 2.5 Hz, 2 H), 2.02 (s, 3 H), 2.44 (ddt, *J* = 15.4, 7.0, 2.5 Hz, 1 H), 2.53 (ddt, *J* = 15.4, 6.0, 2.5 Hz, 1 H), 2.79 (dd, *J* = 16.6, 8.1 Hz, 1 H), 3.00 (dd, *J* = 16.6, 6.5 Hz, 1 H), 3.35 (dddd, *J* = 8.1, 7.0, 6.5, 6.0 Hz, 1 H), 7.16-7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ -2.0 (q'), 7.0 (t'), 26.3 (t'), 30.5 (q'), 40.3 (d'), 48.7 (t'), 76.2 (s'), 79.8 (s'), 126.6 (d'), 127.4 (d'), 128.4 (d'), 143.7 (s'), 207.4 (s'); exact mass *m/z* calcd for $C_{17}H_{24}OSi$ 272.15964, found 272.15931.

References

(56) Timell, T. E. *Can. J. Chem.* **1964**, *42*, 1456-1472.

(57) Pornet, J.; Damour, D.; Miginiac, L. *Tetrahedron* **1986**, *42*,

2017-2024.

(58) (a) Cope, A. C.; Cotter, R. J. *J. Org. Chem.* **1964**, 29, 3467-3469. (b) Irwin, A. J.; Jones, J. B. *J. Am. Chem. Soc.* **1977**, *99*, 556-561.