Abbreviations: The abbreviations used in the Schemes of this supporting information are as defined in the instructions to authors of the Journal, 1999, **64**, 21A. The exceptions are: DHP = dihydropyran; TBAF = tetrabutylammonium fluoride; TPS = *tert*-butyldiphenylsilyl; CDI = 1,1'-thiocarbonyl diimidazolide.

2,4-Dimethoxybenzyl 4-Methoxyphenylacetate (7b). DCC (2.18 g, 10.5 mmol) was added at 0 °C to a solution of 4-methoxyphenylacetic acid (1.66 g, 10.0 mmol), 2,4-dimethoxybenzyl alcohol (1.68 g, 10.0 mmol) and DMAP (0.30 g, 2.50 mmol) in CH_2Cl_2 (50 mL). The reaction mixture was stirred overnight at room temperature after which the precipitate was by removed by filtration and the concentrated filtrate purified by flash chromatography on silica gel (hexane/EtOAc 3/1) to give **7b** in 100%yield. ^{1}H NMR ($CDCl_3$) δ 7.22-7.19 (m, 3 H), 6.85 (d, J = 8.7 Hz, 2 H), 6.46-6.44(m, 2 H), 5.11 (s, 2 H), 3.81 (s, 3 H), 3.79 (s, 3 H), 3.78 (s, 3 H), 3.58 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 172.2, 161.4, 159.1, 158.8, 131.5, 130.5, 126.5, 116.8, 114.1, 104.1, 98.7, 62.3, 55.6, 55.4, 40.6. Anal. Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37. Found: C, 68.14; H, 6.47.

2,4-Dimethoxybenzyl 2-(4-Methoxyphenyl)propanoate. Ester (**7b**) (1.17 g, 3.70 mmol) in THF (1 mL) was added dropwise to a solution of LDA (4.44 mmol) in THF (20 mL) at –78 °C. The resulting solution was stirred for 0.5 h before HMPA (4.0 mL) and MeI (0.25 mL, 4.07 mmol) were added successively. The reaction mixture was stirred for a further 1.5 h at –78 °C and then quenched with NH_4Cl solution. After routine aqueous work up, the crude product was purified by flash column chromatograph on silica gel (hexane/EtOAc 3/1) to afford the title compound (1.15 g, 94%). ^{1}H NMR δ 7.23 (d, J = 8.7 Hz, 2 H), 7.13 (d, J = 8.8 Hz, 1 H), 6.84 (d, J = 8.7 Hz, 2 H), 6.43-6.40 (m, 2 H), 5.09 (AB quart, J = 15.6, 12.1 Hz, 2 H), 3.80 (s, 3 H), 3.79 (s, 3 H), 3.74 (s, 3 H), 3.71 (q, J = 7.2 Hz, 1 H), 1.48 (d, J = 7.2 Hz, 3 H); ^{13}C NMR δ 174.9, 161.2, 158.9, 158.7, 132.9, 131.0, 128.7, 117.0, 114.0, 104.0, 98.6, 62.1, 55.4 (d), 44.8, 18.8. Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.08; H, 6.71. Found: C, 69.05; H, 6.75.

2,4-Dimethoxybenzyl 2-Phenylpropanoate was prepared from 2-phenylpropanoic acid analogously to **7a**.[1] ^{1}H NMR δ 7.31-7.24 (m, 5 H), 7.12 (d, J = 9.0 Hz, 1 H), 6.43-6.40 (m, 2 H), 5.09 (s, 2 H), 3.80 (s, 3 H), 3.74 (q, J = 7.2 Hz, 1 H), 3.72 (s, 3 H), 1.51 (d, J = 7.2 Hz, 3 H); ^{13}C NMR δ 174.7, 161.3, 159.0,

140.9, 131.1, 128.6, 127.7, 127.1, 117.0, 104.0, 98.6, 62.2, 55.5, 52.4, 45.7, 18.8. Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.00; H, 6.81.

2,4-Dimethoxybenzyl 3-(Diphenylphosphatoxy)-2,2-dimethyl-3-(4-fluorophenyl)propanoate (16b) was prepared from 2,4-dimethoxybenzyl 2-methylpropanoate[2] and 4-fluorobenzaldehyde by general protocol A. ^{1}H NMR δ 7.30-6.88 (m, 15 H), 6.45 (m, 2 H), 5.86 (d, J = 8.2 Hz, 2 H), 5.01 (AB quart, J = 54.1, 12.0 Hz, 2 H), 3.80 (s, 3 H), 3.77 (s, 3 H), 1.27 (s, 3 H), 1.08 (s, 3 H); ^{1}H NMR δ 174.7, 164.4, 161.4, 161.1, 159.1, 150.6 (t), 132.0, 131.5, 129.8, 129.7, 125.4, 125.2, 120.3, 120.2, 120.0 (d), 116.6, 115.6, 115.0, 114.7, 104.1, 98.6, 85.1, 85.0, 62.5, 55.5, 48.7, 48.6, 21.1, 20.6; ^{31}P NMR δ -12.23; ^{19}F NMR δ -40.99. Anal. Calcd for $C_{32}H_{32}FO_8P$: C, 64.64; H, 5.42. Found: C, 64.86; H, 5.49.

2,4-Dimethoxybenzyl 3-(Diphenylphosphatoxy)-2,2-dimethyl-3-(4-trifluoromethylphenyl)propanoate (16c) was prepared from 2,4-dimethoxybenzyl 2-methylpropanoate[2] and 4-trifluoromethylbenzaldehyde by general protocol A. ^{1}H NMR δ 7.42 (d, J = 8.4 Hz, 2 H), 7.32-7.14 (m, 11 H), 6.95 (d, J = 8.4 Hz, 2 H), 6.47-6.42 (m, 2 H), 5.93 (d, J = 8.4 Hz, 1 H), 5.05 (AB quart, J = 53.9, 11.9 Hz, 2 H), 3.80 (s, 3 H), 3.77 (s, 3 H), 1.31 (s, 3 H), 1.11 (s, 3 H); ^{13}C NMR δ 174.4, 161.5, 159.1, 150.5 (q), 140.2, 131.6, 130.7, 130.3, 129.8, 129.7, 129.4, 128.3, 125.5, 125.3, 124.8, 120.2, 120.1, 119.9, 119.8, 116.4, 115.5, 104.1, 98.6, 84.8, 84.7, 62.6, 55.4, 48.6, 48.5, 21.4, 20.3; ^{31}P NMR δ -12.17; ^{19}F NMR δ -6.01. Anal. Calcd for $C_{33}H_{32}F_3O_8P$: C, 61.49; H, 5.00. Found: C, 61.80; H, 5.06.

2,4-Dimethoxybenzyl 3-(Diphenylphosphatoxy)-2-methyl-2-(4-methoxyphenyl)-3-phenylpropanoate (16d) was prepared from 2,4-dimethoxybenzyl 2-(4-methoxyphenyl)propanoate and benzaldehyde by general protocol A. ^{1}H NMR δ 7.33-6.67 (m, 24 H), 6.43-6.35 (m, 3 H), 5.07 (AB quart, J = 16.2, 12.1 Hz), 5.40 (AB quart, J = 94.5, 11.9 Hz) (2 H), 3.79 (s), 3.77 (s), 3.74 (s), 3.72 (s), 3.71 (s), 3.69 (s) (9 H), 1.65 (s), 1.56 (s) (3 H); ^{13}C NMR δ 173.3, 161.3, 161.2, 159.0, 158.9, 150.8 (t), 136.1, 135.4, 131.3, 129.9, 129.7, 129.6, 129.4, 129.0, 128.7, 128.5, 128.2, 128.0, 127.6, 127.2, 125.2, 125.0, 120.4 (d), 120.1 (d), 116.6, 116.4, 113.4, 113.3, 103.9, 98.4, 85.5 (d), 85.1, 85.0, 62.8, 62.7, 55.4 (t), 17.6, 15.3; ^{31}P NMR δ -12.40, -12.71. Anal. Calcd for $C_{38}H_{37}O_9P.0.5H_2O$: C, 67.35; H, 5.65. Found: C, 67.40; H, 5.87.

2,4-Dimethoxybenzyl 3-(Diphenylphosphatoxy)-2-methyl-2,3-diphenylpropanoate (16e) was prepared from 2,4-dimethoxybenzyl 2-phenylpropanoate and benzaldehyde by general protocol A. ^{1}H NMR δ 7.42 -

6.76 (m, 20 H), 6.44-6.34 (m, 3 H), 5.07 (AB quart, J = 89.7, 12.1 Hz), 5.03 (AB quart, J = 16.2, 12.0 Hz) (2 H), 3.79 (s), 3.77 (s), 3.68 (s) (6 H), 1.67 (s), 1.58 (s) (3 H); ^{31}P NMR δ -12.52, -12.76; Anal. Calcd for $C_{37}H_{35}O_8P.0.5H_2O$: C, 68.62; H, 5.60. Found: C, 68.80; H, 5.72.

(1*H*)-2-Thioxo-1-pyridyl 3-(Diphenylphosphatoxy)-2,2-dimethyl-3-(4-fluorophenyl)-propanoate (17b) Application of general protocol D to **16b** gave the title compound. ^{1}H NMR δ 7.76 (dd, 1 H), 7.55 (dd, 1 H), 7.26-6.85 (m, 12 H), 6.35 (dt, 1 H), 5.94 (d, J = 8.3 Hz, 1 H), 1.35 (s, 6 H); ^{13}C NMR δ 175.6, 170.1, 164.5, 161.2, 150.5, 149.4, 138.4, 137.3, 136.8, 133.7, 129.8, 129.6, 125.7, 125.3, 121.1, 120.2 (d), 119.5 (d), 115.2, 114.9, 112.6, 84.0, 83.9, 48.5, 48.4, 22.9, 17.5; ^{31}P NMR δ -11.76; ^{19}F NMR δ -39.46. Anal. Calcd for $C_{28}H_{25}FO_6NPS$: C, 60.72; H, 4.55. Found: C, 60.92; H, 4.60.

(1*H*)-2-Thioxo-1-pyridyl 3-(Diphenylphosphatoxy)-2,2-dimethyl-3-(4-trifluoromethylphenylpropanoate (17c) Application of general protocol D to **16c** gave the title compound. ^{1}H NMR δ 7.78 (dd, 1 H), 7.55-7.04 (m, 14 H), 6.87 (d, 2 H), 6.36 (dt, 1 H), 6.02 (d, J = 8.5 Hz, 1 H), 1.38 (s, 3 H), 1.37 (s, 3 H); ^{13}C NMR δ 175.6, 170.0, 150.0 (t), 138.3, 138.1, 136.8, 133.7, 131.2, 130.7, 129.8, 129.6, 128.4, 125.8, 125.4, 124.9, 120.2 (d), 119.9, 119.5, 119.4, 112.6, 83.8, 83.7, 48.4, 48.3, 22.9, 17.5; ^{31}P NMR δ -11.83; ^{19}F NMR δ 9.80. No further characterization was attempted on this hydrolytically and photolytically unstable compound.

(1*H*)-2-Thioxo-1-pyridyl 3-(Diphenylphosphatoxy)-2-methyl-2-(4-methoxyphenyl)-3-phenylpropanoate (17d) Application of general protocol D to **16d** gave the title compound. ^{1}H NMR δ 7.59-6.81 (m, 22 H), 6.38 (d, J = 7.5 Hz), 6.29 (d, 7.6 Hz) (1 H), 3.79 (s), 3.75 (s) (3 H), 1.95 (s), 1.87 (s) (3 H); ^{13}C NMR δ 175.6, 170.2, 159.6, 159.5, 150.5 (t) 137.9, 137.8, 137.3, 134.4, 134.2, 133.2, 130.4, 129.8, 129.6, 129.1, 129.0, 128.8, 128.4, 128.2, 127.6, 127.5, 127.4, 126.9, 125.4, 125.2, 120.4, 120.2, 120.1, 120.0, 119.9, 113.9, 113.5, 112.9, 112.6, 84.9 (d), 55.3, 14.8, 14.3; ^{31}P NMR δ -12.69. No further characterization was attempted on this hydrolytically and photolytically unstable compound.

(1*H*)-2-Thioxo-1-pyridyl 3-(Diphenylphosphatoxy)-2-methyl-2,3-diphenylpropanoate (17e) Application of general protocol D to **16e** gave the title compound. ^{1}H NMR δ 7.59-7.81 (m, 23H), 6.44 (m, 1 H), 6.41 (d, J = 7.2 Hz), 6.32 (d, J = 7.6 Hz) (1 H), 2.02 (s), 1.92 (s) (3 H); ^{13}C NMR δ 175.6, 169.9, 150.4 (t), 150.3 (t), 137.8, 137.6, 135.6, 134.9, 134.2, 134.0, 133.4, 134.3, 133.3, 129.7, 129.6, 129.1,

128.9, 128.6, 128.4, 127.9, 127.6, 127.4, 127.3, 125.3, 125.1, 120.3, 120.1, 120.0 (d), 119.9, 119.8, 119.7 (d), 112.8, 112.6, 84.8, 84.7, 55.9, 55.8, 55.6, 55.5, 20.3, 14.6; ^{31}P NMR δ -12.65, -12.77. Anal. Calcd for $C_{33}H_{28}NO_6PS$: C, 66.32; H, 4.72. Found: C, 66.05; H, 4.80.

***cis/trans*-2,2,4-Trimethyl-3-(4-fluorophenyl)tetrahydrofuran (18b).** Application of general protocol C to **17b** gave the title compound. ^{1}H NMR δ *trans*- 7.18 (dd, *J* = 8.7, 5.5 Hz, 2 H), 7.01 (d, *J* = 8.7 Hz, 2 H), 4.12 (t, *J* = 8.0 Hz, 1 H), 3.48 (dd, *J* = 9.1, 8.3 Hz, 1 H), 2.73 (m, 1 H), 2.59 (d, *J* = 11.5 Hz, 1 H), 1.29 (s, 3 H), 0.95 (d, *J* = 6.3 Hz, 3 H), 0.83 (s, 3 H); *cis*- 7.18 (dd, *J* = 8.7, 5.5 Hz, 2 H), 7.01 (t, *J* = 8.7 Hz, 2 H), 4.18 (t, *J* = 9.0 Hz, 1 H), 3.59 (t, *J* = 9.0 Hz, 1 H), 3.07 (m, 1 H), 2.89 (d, *J* = 7.5 Hz, 1 H), 1.32 (s, 3 H), 1.00 (s, 3 H), 0.66 (d, *J* = 6.9 Hz, 3 H); ^{13}C NMR δ 163.7, 160.5, 134.4 (d), 131.7, 131.6, 130.2, 130.1, 115.5, 115.2, 115.1, 114.8, 83.3, 73.0, 72.6, 62.5, 58.2, 38.3, 37.5, 31.1, 28.4, 25.6, 24.4, 15.6, 14.4; ^{19}F NMR δ -44.00 (*trans*-), -44.76 (*cis*-). Anal. Calcd for $C_{13}H_{17}FO1/2H_2O$: C, 71.86; H, 8.35. Found: C, 71.64; H, 8.08.

***cis/trans*-2,2,4-Trimethyl-3-(4-trifluoromethylphenyl)tetrahydrofuran (18c).** Application of general protocol C to **17c** gave the title compound. *trans*- ^{1}H NMR δ 7.58 (d, *J* = 8.2 Hz, 2 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 4.16 (t, *J* = 7.8 Hz, 1 H), 3.51 (t, *J* = 8.7 Hz, 1 H), 2.84 (m, 1 H), 2.68 (d, *J* = 11.4 Hz, 1 H), 1.32 (s, 3 H), 0.97 (d, *J* = 6.3 Hz, 3 H), 0.85 (s, 3 H); ^{13}C NMR δ 142.9, 129.1, 125.4, 83.4, 77.4, 72.6, 63.0, 38.2, 28.4, 24.4, 15.5; *cis*- ^{1}H NMR δ 7.58 (d, *J* = 9.5 Hz, 2 H), 7.24 (d, *J* = 9.5 Hz, 2 H), 4.21 (t, *J* = 8.9 Hz, 1 H), 3.62 (t, *J* = 8.9 Hz, 1 H), 3.13 (m, 1 H), 2.97 (d, *J* = 7.7 Hz, 1 H), 1.37 (s, 3 H), 1.01 (s, 3 H), 0.66 (d, *J* = 6.9 Hz, 3 H); ^{19}F NMR δ 10.0 (*trans*-), 10.10 (*cis*-). Anal. Calcd for $C_{14}H_{17}F_3O$: C, 65.10; H, 6.63. Found: C, 65.02; H, 6.78.

2-(Diethylphosphatoxy)-1-phenyl-5-pentanol (42) and 1-(Diethylphosphatoxy)-1-phenyl-5-pentanol (43). Application of general protocol G to **29** followed by chromatography on silica gel gave **42** and **43** in 25 and 15% yields respectively. **42:** ^{1}H NMR δ 7.30-7.20 (m, 5 H), 4.64 (m, 1 H), 4.01 (m, 2 H), 3.84 (m, 2 H), 3.62 (m, 2 H), 2.98 (dd, *J* = 13.8, 6.6 Hz, 1 H), 2.89 (dd, *J* = 13.8, 5.3 Hz, 1 H), 2.32 (br. s, 1 H), 1.70 (m, 4 H), 1.28 (dt, *J* = 7.1, 0.9 Hz, 3 H), 1.20 (dt, *J* = 7.0, 0.9 Hz, 3 H); ^{13}C NMR δ 137.4, 129.8, 128.6, 80.0, 79.9, 63.8 (q), 62.5, 41.9, 31.5 (d), 28.1, 16.3 (d); ^{31}P NMR δ -0.96. Anal. Calcd for $C_{15}H_{25}O_5P.0.5H_2O$: C, 55.38; H, 8.05. Found: C, 55.78; H, 8.06. **43:** ^{1}H NMR δ 7.33-7.26 (m, 5 H), 5.25

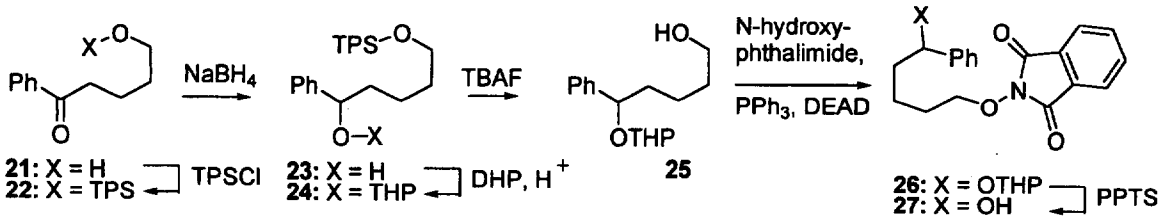
(dd, J = 13.6, 7.6 Hz, 1 H), 4.01 (m, 2 H), 3.82 (m, 2 H), 3.58 (t, J = 6.3 Hz, 2 H), 2.38 (br. s, 1 H), 2.01 (m, 1 H), 1.82 (m, 1 H), 1.55 (m, 2 H), 1.42 (m, 2 H), 1.23 (dt, J = 7.0, 0.8 Hz, 3 H), 1.09 (dt, J = 7.0, 0.8 Hz, 3 H); ^{13}C NMR δ 140.7, 128.6, 128.4, 126.6, 80.7, 80.6, 63.8 (t), 62.5, 37.9, 37.8, 32.3, 21.6, 16.1 (t); ^{31}P NMR δ -1.06. Anal. Calcd for $C_{15}H_{25}O_5P.0.5H_2O$: C, 55.38; H, 8.05. Found: C, 55.56; H, 8.16.

1-Phenyl-2,5-pentanediol (46) and 1-Phenyl-1,5-pentanediol (49) via Acetates 44, 45, 47 and 48. Application of general protocol G to **30** gave a complex mixture of the four monoacetates **44, 45, 47** and **48**. Chromatography on silica gel (eluent: hexane/EtOAc 10/1) enabled separation in to a mixture of the two primary alcohols **44** and **47** and a mixture of the two secondary alcohols **45** and **48**. Saponification of both mixtures led to mixtures of the diols **46**:[3] ^{1}H NMR δ 7.33-7.19 (m, 5 H), 3.82 (m, 1 H), 3.61 (m, 2 H), 3.05 (br. s, 2 H), 2.78 (dd, J = 13.5, 5.2 Hz, 1 H), 2.70 (dd, J = 13.5, 7.8 Hz, 1 H), 1.67 (m, 3 H), 1.51 (m, 1 H) and **49**:[4] ^{1}H NMR δ 7.35-7.26 (m, 5 H), 4.68 (dd, J = 7.5, 5.6 Hz, 1 H), 3.62 (t, J = 6.3 Hz, 2 H), 1.80 (m, 2 H), 1.57 (m, 3 H), 1.40 (m, 1H) whose spectral data agreed with the literature values. Key spectral data for the monoacetates were as follows: **44:** ^{1}H NMR δ 7.34-7.25 (m, 5 H), 5.10 (m, 1 H), 3.62 (br. t, 2 H), 2.90 (dd, J = 13.8, 6.4 Hz, 1 H), 2.81 (dd, J = 13.8, 6.1 Hz, 1 H), 2.05 (s, 3 H), 1.89-1.51 (m, 4 H). **45:** ^{1}H NMR δ 7.36-7.20 (m, 5 H), 4.10 (t, J = 6.5 Hz, 2 H), 3.84 (m, 1 H), 2.84 (dd, J = 13.5, 4.2 Hz, 1 H), 2.66 (dd, J = 13.5, 8.4 Hz, 1 H), 2.04 (s, 3 H), 1.88-1.50 (m, 4 H). **47:** 7.37-7.26 (m, 5 H), 5.72 (dd, J = 5.5, 4.8 Hz, 1 H), 3.60 (t, J = 4.8 Hz, 2 H), 2.06 (s, 3 H), 1.93 (m, 1 H), 1.79 (m, 1 H), 1.56 (m, 2 H), 1.39 (m, 1 H), 1.30 (m, 1 H). **48:** ^{1}H NMR δ 7.36-7.19 (m, 5 H), 4.68 (dd, J = 7.4, 5.7 Hz, 1 H), 4.04 (t, J = 6.6 Hz, 2 H), 2.02 (s, 3 H), 1.89-1.28 (m, 6 H).

2-Methyl-1-phenyl-2,5-pentanediol (52) and 2-Methyl-1-phenyl-1,5-pentanediol (55) via Acetates 50, 51, 53 and 54. Application of general protocol G to **33** gave a complex mixture of the four monoacetates **50, 51, 53** and **54**. Chromatography on silica gel (eluent: hexane/EtOAc 10/1) enabled separation in to a mixture of the two primary alcohols **50** and **53** and a mixture of the secondary and tertiary alcohols **51** and **54**. Saponification of both mixtures led to mixtures of the diols **52** and **55**. Separation by chromatography on silica gel (eluent: hexane/EtOAc 3/1 – 1/3) gave **52** ^{1}H NMR δ 7.30-7.18 (m, 5 H), 3.62 (m, 2 H), 2.76 (AB quart, J = 23.2, 13.2 Hz, 2 H), 1.71 (m, 2 H), 1.56 (m, 2 H), 1.13 (s, 3 H); ^{13}C NMR δ 137.6, 130.8, 128.3, 126.6, 72.9, 63.2, 48.4, 38.2, 26.8, 26.2 and the known diol **55**.[5] Key spectral data for the

monoacetates were as follows: **50:** ^{1}H NMR δ 7.30-7.20 (m, 5 H), 3.64 (br. t, 2 H), 3.12 (AB quart, J = 55.4, 13.7 Hz, 2 H), 2.09 (s, 3 H), 1.80-1.45 (m, 4 H), 1.40 (s, 3 H). **51:** ^{1}H NMR δ 7.30-7.20 (m, 5 H), 4.08 (t, J = 6.7 Hz, 2 H), 2.77 (AB quart, J = 20.5, 13.1 Hz, 2 H), 2.05 (s, 3 H), 1.81 (m, 2 H), 1.53 (m, 2 H), 1.16 (s, 3 H). **53:** ^{1}H NMR δ 7.31-7.25 (m, 5 H), 5.63 (d, J = 6.4 Hz), 5.54 (d, J = 7.6 Hz) (1 H), 3.60 (t, J = 5.2 Hz), 3.53 (t, J = 6.5 Hz) (2 H), 2.08 (s), 2.06 (s) (3 H), 1.96 (m), 1.62 (m), 1.49 (m), 1.38 (m), 1.15 (m) (5 H), 0.93 (d, J = 6.7 Hz), 0.78 (d, J = 6.8 Hz) (3 H). **54:** ^{1}H NMR δ 7.35-7.27 (m, 5 H), 4.45 (d, J = 7.5 Hz, 1 H), 4.07 (t, J = 5.5 Hz, 2 H), 2.06 (s, 3 H), 1.90-1.10 (m, 5 H), 0.78 (d, J = 6.7 Hz, 3 H).

1-Methyl-1-phenyl-2,5-pentanediol (58) and 1-Methyl-1-phenyl-1,5-pentanediol (61) via Acetates 56, 57, 59 and 60. Application of general protocol G to **36** gave a complex mixture of the four monoacetates **56**, **57**, **59** and **60**. Chromatography on silica gel (eluent: hexane/EtOAc 10/1) enabled separation in to a mixture of the two primary alcohols **56** and **59** and a mixture of the two secondary alcohols **57** and **60**. Saponification of both mixtures gave mixtures of diols **58** and **61**, which could be separated chromatographically. **58:** ^{1}H NMR δ 7.40-7.16 (m, 5 H), 3.62 (m, 1 H), 3.53 (m, 2 H), 2.74 (m, 1 H), 1.88-1.35 (m, 4 H), 1.30 (d, J = 7.0 Hz), 1.25 (d, J = 8.3 Hz) (3 H). ^{13}C NMR δ 144.8, 143.7, 128.5, 128.3, 128.2, 127.9, 126.6, 126.4, 76.4, 76.2, 62.7, 46.1, 45.9, 31.7, 30.8, 29.0, 28.9, 17.6, 17.0. Anal. Calcd for $C_{12}H_{18}O_2.H_2O$: C, 67.89; H, 9.50. Found: C, 67.40; H, 9.18. **61:**[4] ^{1}H NMR δ 7.45-7.20 (m, 5 H), 3.60 (t, J = 6.4 Hz, 2 H), 1.87 (m, 2 H), 1.56 (s, 3 H), 1.51 (m, 2 H), 1.30 (m, 2 H). Key spectral data for the monoacetates were as follows: **56:** ^{1}H NMR δ 7.32-7.17 (m, 5 H), 5.10 (m, 1 H), 3.55 (m, 2 H), 3.05-2.90 (m, 1 H), 2.08 (s), 2.01 (s) (3 H), 1.70-1.40 (m, 4 H), 1.27 (d, J = 6.7 Hz), 1.25 (d, J = 6.7 Hz) (3 H). **57:** ^{1}H NMR δ 7.34-7.17 (m, 5 H), 4.09 (t, J = 6.4 Hz), 4.03 (t, J = 6.6 Hz) (2 H), 3.67 (m, 1 H), 2.76 (m, 1 H), 2.04 (s), 2.00 (s) (3 H), 1.90-1.34 (m, 4 H), 1.32 (d, J = 7.0 H), 1.28 (d, J = 7.1 Hz) (3 H). **59:** ^{1}H NMR δ 7.34-7.20 (m, 5 H), 3.53 (dt, J = 6.5, 1.4 Hz, 2 H), 2.05 (s, 3 H), 2.03 (m, 2 H), 1.82 (s, 3 H), 1.47 (m, 2 H), 1.26 (m, 2 H); ^{13}C NMR δ 169.9, 145.0, 128.3, 127.0, 124.6, 84.1, 62.6, 42.3, 32.8, 25.0, 22.4, 20.1. Anal. Calcd for $C_{14}H_{20}O_3.1/4H_2O$: C, 69.83; H, 8.58. Found: C, 69.97; H, 8.49. **60:** ^{1}H NMR δ 7.44-7.22 (m, 5 H), 4.01 (t, J = 6.5 Hz, 2 H), 2.00 (s, 3 H), 1.82 (m, 2 H), 1.57 (s, 3 H), 1.52 (m, 2 H), 1.31 (m, 2 H).



5-(*tert*-Butyldiphenylsiloxy)-1-phenyl-1-pentanone (22). TPSCl (1.75 ml, 6.67 mmol) in CH_2Cl_2 (5.0 mL) was added to a solution of **21**[6] (1.08 g, 6.07 mmol), DMAP (0.06 g, 0.486 mmol) and NEt_3 (0.97 mL, 6.98 mmol) in CH_2Cl_2 (15 mL) at room temperature and the resulting reaction mixture was stirred overnight at room temperature before CH_2Cl_2 (50 mL) was added. The CH_2Cl_2 layer was washed with saturated NH_4Cl solution, water and brine, then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (hexane/EtOAc 10:1) gave **22** (2.02 g, 80%) as an oil. ^{1}H NMR δ 7.94 (d, 2 H), 7.68 (dd, 4 H), 7.47-7.37 (m, 9 H), 3.72 (t, J = 6.2 Hz, 2 H), 2.96 (t, J = 7.5 Hz, 2 H), 1.86 (m, 2 H), 1.66 (m, 2 h), 1.06 (s, 9 H); ^{13}C NMR δ 200.5, 137.2, 135.8, 134.2, 133.1, 129.8, 128.7, 128.2, 127.8, 63.7, 38.5, 32.2, 27.1, 20.9, 19.4. Anal. Calcd for $C_{27}H_{32}O_2Si$: C, 77.84, H, 7.74. Found: C, 77.57; H, 7.82.

5-(*tert*-Butyldiphenylsiloxy)-1-phenyl-1-pentanol (23). $NaBH_4$ (29 mg, 0.75 mmol) was added at room temperature to a solution of **22** (0.208 g, 0.5 mmol) in methanol (2.5 mL) and the resulting reaction mixture was stirred for 30 min before saturated NH_4Cl solution (10 mL) was added. The resulting mixture was extracted with EtOAc and the combined extracts were washed with water and brine, then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (hexane/EtOAc 5:1) gave **23** (0.195 g, 94%) as a colorless oil. ^{1}H NMR δ 7.72 (m, 4 H), 7.49-7.31 (m, 11 H), 4.66 (t, J = 6.7 Hz, 2 H), 3.70 (t, J = 6.2 Hz, 2 H), 2.03 (br. s, 1 H), 1.79 (m, 2 H), 1.64 (m, 2 H), 1.44 (m, 2 H), 1.10 (s, 9 H); ^{13}C NMR δ 145.0, 135.7, 134.2, 129.7, 128.6, 127.8, 127.6, 126.1, 74.7, 63.9, 38.9, 32.5, 27.0, 22.2, 19.4. Anal. Calcd for $C_{27}H_{34}O_2Si.1/4H_2O$: C, 76.64; H, 8.22. Found: C, 76.75; H, 8.25.

5-(*tert*-Butyldiphenylsiloxy)-1-phenyl-1-(2-tetrahydropyranyloxy)pentane (24). PPTS (0.11 g, 40 mol%, 0.44 mmol) was added at room temperature to a solution of **23** (0.459 g, 1.10 mmol) and dihydropyran (0.20 mL, 2.20 mmol) in CH_2Cl_2 (10 mL). The resulting reaction mixture was stirred at room temperature overnight before it was diluted with EtOAc (50 mL). The organic layer was washed

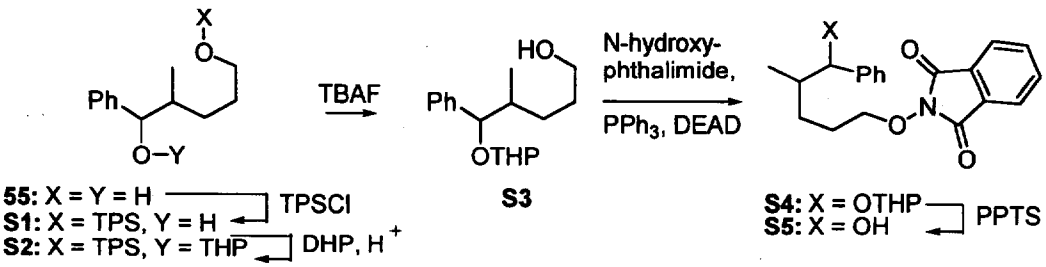
subsequently with saturated $NaHCO_3$ solution, water and brine, then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (hexane/EtOAc 5/1) gave **24** (0.528 g, 96%) as a colorless oil. ^{1}H NMR δ 7.70 (m, 4 H), 7.46-7.30 (m, 11 H), 4.88 (t, J = 3.3 Hz), 4.47 (t, J = 3.4 Hz) (1 H), 4.73 (dd, J = 7.8, 5.4 Hz), 4.61 (t, J = 6.4 Hz) (1 H), 4.00 (m), 3.58 (m), 3.34 (m) (2 H), 3.70 (t, J = 6.1 Hz), 3.68 (t, J = 6.4 Hz) (2 H), 1.90 (m, 2 H), 1.76 (m, 2 H), 1.67-1.44 (m, 8 H), 1.16 (s, 9 H); ^{13}C NMR δ 143.8, 142.8, 135.7, 134.2, 129.7, 128.5, 128.2, 127.8, 127.1 (d), 126.6, 98.2, 95.2, 79.1, 77.2, 64.0, 63.9, 62.4, 62.0, 38.3, 37.2, 32.7, 30.9, 27.0, 25.8, 25.6, 22.7, 22.0, 19.6, 19.4. Anal. Calcd for $C_{32}H_{42}O_3Si$: C, 76.45; H, 8.42. Found: C, 76.77; H, 8.59.

1-Phenyl-1-(2-tetrahydropyranyloxy)-5-pentanol (25). TBAF (2.024 mL, 2.024 mmol) was added dropwise at room temperature to a solution of **24** (0.508 g, 1.012 mmol) in THF (12 mL). The resulting reaction mixture was stirred at room temperature for 2 h before it was diluted with EtOAc (50 mL). The organic layer was washed subsequently with saturated NH_4Cl solution, water and brine, then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (hexane/EtOAc 1/1) gave **25** (0.261 g, 98%) as a colorless oil. ^{1}H NMR δ 7.36-7.21 (m, 5 H), 4.82 (t, J = 5.2 Hz), 4.38 (t, J = 4.2 Hz), (1 H), 4.67 (dd, J = 7.8, 5.7 Hz), 4.55 (t, J = 6.4 Hz) (1 H), 3.91 (m), 3.48 (m), 3.25 (m) (2 H), 3.56 (t, J = 6.4 Hz), 3.53 (t, J = 6.5 Hz) (2 H), 2.34 (s, 1 H), 1.82 (m, 2 H), 1.71 (m, 2 H), 1.61-1.34 (m, 8 H); ^{13}C NMR δ 143.5, 142.4, 128.4, 128.1, 127.5, 127.0, 126.9, 126.5, 98.0, 95.6, 79.0, 77.2, 62.6, 62.5, 61.9, 38.0, 36.9, 32.7, 32.6, 30.8, 30.7, 25.5, 25.4, 22.2, 21.7, 19.7, 19.2. Anal. Calcd for $C_{16}H_{24}O_3.1/4\ H_2O$: C, 71.48; H, 9.18. Found: C, 71.82; H, 9.14.

1-Phenyl-5-(*N*-phthalimidoxy)-1-(2-tetrahydropyranyloxy)pentane (26). Application of general protocol F to **25** gave **26** quantitatively. ^{1}H NMR δ 7.79 (dd, 2 H), 7.70 (dd, 2 H), 7.36 –7.19 (m, 5 H), 4.83 (t, J = 3.3 Hz), 4.37 (t, J = 3.6 Hz) (1 H), 4.68 (dd, J = 7.8, 5.4 Hz), 4.58 (t, J = 6.4 Hz) (1 H), 4.16 (t, J = 6.8 Hz), 4.14 (t, J = 6.8 Hz) (2 H), 3.91 (m), 3.48 (m), 3.26 (m) (2 H), 1.91-1.68 (m, 6 H), 1.58-1.39 (m, 6 H); ^{13}C NMR δ 163.6, 143.4, 142.4, 125.0, 134.5, 129.0, 128.4, 128.2, 127.5, 127.0, 126.5, 124.1, 123.5, 98.1, 95.3, 78.7, 78.4 (d), 76.9, 62.4, 62.0, 38.0, 36.7, 30.8, 28.2, 25.6, 25.5, 22.2, 21.5, 19.6, 19.3.

1-Phenyl-5-(*N*-phthalimidoxy)-1-pentanol (27). PPTS (44.7 mg, 0.18 mmol) was added at room temperature to a solution of **26** (0.368 g, 0.9 mmol) in ethanol (14 mL). The resulting reaction mixture was

heated to 55°-60 °C for 4 h before it was cooled to room temperature and the solvent was removed under vacuum. The residue was taken up in EtOAc (75 mL) and washed subsequently with saturated $NaHCO_3$ solution, water and brine, then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (hexane/EtOAc 1/1) gave **27** (0.28 g, 96%) as a white solid (mp 66-67 °C). ^{1}H NMR δ 7.79 (dd, 2 H), 7.71 (dd, 2 H), 7.35-7.21 (m, 5 H), 4.68 (dd, J = 7.5, 5.4 Hz, 1 H), 4.16 (t, J = 6.5 Hz, 2 H), 2.43 (br. s, 1 H), 1.80 (m, 4 H), 1.60-1.47 (m, 2 H); ^{13}C NMR δ 163.8, 144.9, 134.6, 129.0, 128.5, 127.5, 126.0, 123.6, 78.4, 74.2, 38.7, 28.0, 22.0; Anal. Calcd for $C_{19}H_{29}NO_4$: C, 70.14; H, 5.88. Found: 70.78; H, 6.03.



5-(*tert*-Butyldiphenylsiloxy)-2-methyl-1-phenyl-1-pentanol (S1). **55**[5] was silylated by the same procedure described for **22**. 100%. ^{1}H NMR δ 7.70-7.64 (m, 4 H), 7.43-7.26 (m, 11 H), 4.51 (d, J = 5.9 Hz), 4.44 (d, J = 6.8 Hz) (1 H), 3.68 (t, J = 6.4 Hz), 3.62 (t, J = 6.4 Hz), (2 H), 1.90-1.40 (m, 5 H), 1.06 (s), 1.03 (s) (9 H), 0.93 (d, J = 6.7 Hz), 0.76 (d, J = 6.8 Hz) (3 H); ^{13}N MR δ 143.9, 143.6, 135.8, 135.0, 134.3, 129.8, 126.6, 79.1, 78.4, 64.4, 64.2, 40.2, 40.1, 30.4, 30.2, 29.4, 28.6, 27.1, 26.8, 19.4, 15.8, 14.7. Anal. Calcd for $C_{28}H_{36}O_2Si$: C, 77.73; H, 8.39. Found: C, 77.84; H, 8.34.

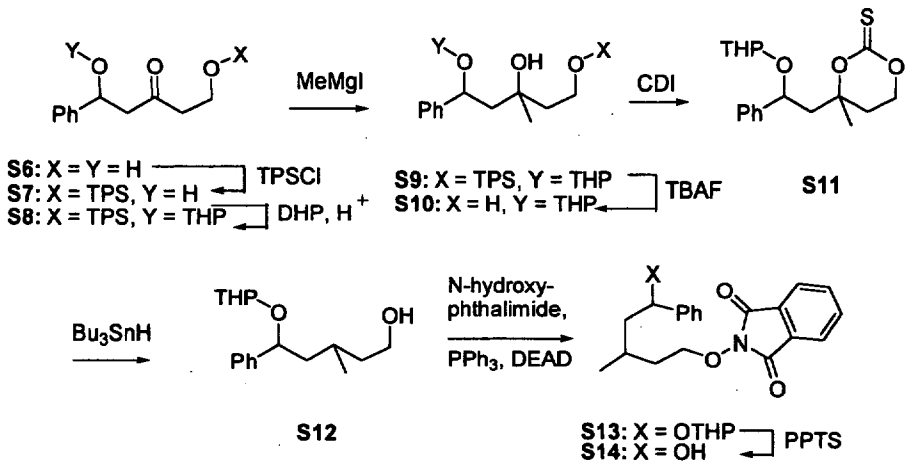
5-(*tert*-Butyldiphenylsiloxy)-2-methyl-1-phenyl-1-(2-tetrahydropyranyloxy)pentane (S2). Same procedure as for **24**. 60%. ^{1}H NMR δ 7.70-7.62 (m, 4 H), 7.41-7.23 (m, 11 H), 4.78 (br s), 4.40 (m) (1 H), 4.47 (d, J = 6.8 Hz), 4.42 (d, J = 7.4 Hz), 4.32 (d, J = 6.3 Hz), 4.26 (d, J = 7.1 Hz) (1 H), 3.94 (m), 3.46 (m), 3.21 (m) (2 H), 3.69 (t, J = 6.5 Hz), 3.66 (t, J = 6.2 Hz), 3.58 (t, J = 6.4 Hz) (2 H), 2.02-1.37 (m, 5 H), 1.06 (s), 1.03 (s), 1.02 (s) (9 H), 0.92 (d, J = 6.7 Hz), 0.72 (d, J =6.6 Hz), 0.70 (d, J = 6.7 Hz) (3 H); ^{13}C NMR δ 142.7, 142.5, 141.6, 141.5, 141.3, 135.8, 134.3, 129.7, 128.2, 127.9, 127.8, 127.5, 127.0, 126.9 (d), 99.5, 99.2, 95.1, 84.3, 84.0, 81.7, 81.3, 64.6, 64.3, 62.2, 62.1, 62.0, 39.8, 39.5, 39.2, 31.0, 30.7, 30.4, 30.3,

29.4 (d), 29.1, 27.1, 25.8, 25.7, 19.5, 19.4, 16.0, 15.8, 15.6, 15.4. Anal. Calcd for $C_{33}H_{44}O_3Si$: C, 76.70; H, 8.58. Found: C, 76.53; H, 8.65.

2-Methyl-1-phenyl-1-(2-tetrahydropyranyloxy)-5-pentanol (S3). Same procedure as for **25**. 95%. ^{1}H NMR δ 7.34-7.22 (m, 5 H), 4.78(t, *J* = 3.3 Hz), 4.37 (t, *J* = 3.3 Hz), 4.33 (t, *J* = 3.6 Hz) (1 H), 4.50 (d, *J* = 6.5 Hz), 4.42 (d, *J* = 7.6 Hz), 4.32 (d, *J* = 6.4 Hz), 4.26 (d, *J* = 7.1 Hz) (1 H), 3.92 (m), 3.42 (m), 3.18 (m) (2 H), 3.62 (m), 3.53 (m) (2 H), 1.94-1.41 (m, 5 H), 1.01 (d, *J* = 6.7 Hz), 0.94 (d, *J* = 6.7 Hz), 0.72 (d, J = 6.8 Hz) (3 H); ^{13}C NMR δ 142.6, 142.3, 141.1, 128.2, 128.0, 127.8, 127.6, 127.5, 127.3, 127.0, 99.5, 99.3, 95.7, 95.6, 84.3, 83.9, 81.8, 81.1, 63.3, 63.2, 62.9, 62.6, 62.1 (d), 39.7, 39.3, 39.2, 31.0, 30.7, 30.6 (d), 30.5, 30.3, 29.1, 28.8, 28.7, 25.7, 25.6, 19.9, 19.7, 19.3, 16.2, 15.8, 15.7, 15.5. Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 73.07; H, 9.56.

2-Methyl-1-phenyl-1-(2-tetrahydropyranyloxy)-5-(*N*-phthalimidoxy)pentane (S4). Application of general protocol F to **S3** gave **S4** in 77% yield. ^{1}H NMR δ 7.85-7.80 (m, 2 H), 7.75-7.72 (m, 2 H), 7.31-7.21 (m, 5 H), 4.79 (t, *J* = 3.2 Hz), 4.37 (m) (1 H), 4.50 (d, *J* = 6.5 Hz), 4.42 (d, *J* = 7.6 Hz), 4.36 (d, *J* = 6.4 Hz), 4.26 (d, *J*= 7.0 Hz) (1 H), 4.19 (m), 4.10 (m) (2 H), 3.93 (m), 3.46 (m), 3.21 (m) (2 H), 2.00-1.10 (m, 5 H), 1.03 (d, *J* = 6.7 Hz), 0.95 (d, *J* = 6.7 Hz), 0.75 (d, *J* = 6.8 Hz) (3 H); ^{13}C NMR δ 163.8, 142.2, 142.3, 141.2, 141.1, 134.6, 129.1, 128.2, 128.0 (d), 127.8, 127.6, 127.4, 127.3, 127.0 (d), 123.6, 99.5, 99.4, 95.2 (d), 84.3, 83.8, 81.5, 81.0, 79.1, 79.0, 78.9, 78.8, 62.4, 62.2, 62.0, 39.7, 39.5, 39.3, 30.9, 30.7, 29.0, 28.8, 28.6, 28.5, 26.1, 26.0, 25.8, 25.6, 19.5, 19.3, 16.1, 15.6, 15.3. Anal. Calcd for $C_{25}H_{29}NO_5$: C, 70.90; H, 6.90. Found: C, 70.38; H, 6.92.

2-Methyl-1-phenyl-5-(*N*-phthalimidoxy)-1-pentanol (S5). Same procedure as for **27**. 83%. ^{1}H NMR δ 7.83-7.80 (m, 2 H), 7.75-7.72 (m, 2 H), 7.32-7.24 (m, 5 H), 4.61 (d, *J* = 5.3 Hz), 4.42 (d, *J* = 7.2 Hz) (1 H), 4.20 (m), 4.15 (t, *J* = 6.6 Hz) (2 H), 2.20 (br. s, 1 H), 1.87 (m, 2 H), 1.80-1.58 (m), 1.46-1.22 (m) (3 H), 0.93 (d, *J* = 6.7 Hz), 0.76 (d, *J* = 6.8 Hz) (3 H); ^{13}C NMR δ 163.9, 143.6, 134.6, 129.1, 128.4, 128.3, 127.6, 127.4, 126.9, 126.5, 123.7, 79.0 (d), 78.8, 40.0 (d), 29.1, 28.4, 26.1, 25.7, 16.0, 14.4. Anal. Calcd for $C_{20}H_{21}NO_4.1/4H_2O$: C: 68.95; H, 6.22. Found: C, 68.63; H, 6.05.



5-(*tert*-Butyldiphenylsiloxy)-1-hydroxy-1-phenyl-3-pentanone (S7). Prepared from **S6**[7] by the same procedure as employed for **22**. 41%. ^{1}H NMR δ 7.66 (dd, 4 H), 7.44-7.26 (m, 11 H), 5.18 (dd, J = 8.0, 4.3 Hz, 1 H), 3.96 (t, J = 6.1 Hz, 2 H), 2.92 (dd, J = 23.2, 17.7 Hz, 1 H), 2.90 (d, J = 1.6 Hz, 1 H), 2.65 (t, J = 6.1 Hz, 2 H), 1.05 (s, 9 H); ^{13}C NMR δ 210.6, 142.9, 135.7, 133.4, 130.0, 128.7, 127.9, 127.8, 125.8, 70.0, 59.7, 46.3, 27.0. Anal. Calcd for $C_{27}H_{32}O_3Si$: C, 74.96; H, 7.46. Found: C, 74.49; H, 7.44.

5-(*tert*-Butyldiphenylsiloxy)-1-phenyl-1-(2-tetrahydropyranyloxy)-3-pentanone (S8). Same procedure as for **24**. 95%. ^{1}H NMR δ 7.68 (m, 4 H), 7.44-7.26 (m, 11 H), 5.27 (dd, J = 8.8, 4.6 Hz), 5.11 (dd, J = 8.8, 4.1 Hz) (1 H), 4.91 (t, J = 3.2 Hz), 4.43 (t, J = 3.3 Hz) (1 H), 3.97 (d, J = 6.4 Hz), 3.94 (t, J = 6.4 Hz) (2 H), 3.88 (m), 3.48 (m), 3.24 (dt, J = 11.3, 5.0 Hz) (2 H), 3.13 (ddd, J = 16.5, 8.8, 4.2 Hz, 1 H), 3.73 (m, 2 H), 2.64 (m, 1 H), 1.82-1.37 (m, 6 H), 1.04 (s, 9 H); ^{13}C NMR δ 207.5, 207.3, 143.0, 141.2, 135.7, 133.6, 129.9, 128.7, 128.5, 128.0, 127.9, 127.5, 126.5, 99.4, 75.7, 73.1, 62.2, 62.1, 59.6, 51.9, 51.7, 46.9, 46.7, 30.7, 30.6, 27.0, 25.6, 25.5, 19.4, 19.3. Anal. Calcd for $C_{32}H_{40}O_4Si$: C, 74.38; H, 7.80. Found: C, 74.31; H, 7.76.

5-(*tert*-Butyldiphenylsiloxy)-3-methyl-1-phenyl-1-(2-tetrahydropyranyloxy)-3-pentanol (S9). Same procedure as for **25**. 2 Isomers 92%. Anal. Calcd for $C_{33}H_{44}O_4Si$: C, 74.39; H, 8.32. Found: C, 74.53; H, 8.50. **Isomer 1:** ^{1}H NMR δ 7.77-7.68 (m, 4 H), 7.45-7.28 (m, 11 H), 5.20 (dd, J = 10.9, 2.5 Hz), 5.14 (dd, J = 10.7, 2.4 Hz) (1 H), 4.42 (t, J = 2.6 Hz), 4.38 (t, J = 8.7 Hz) (2 H), 4.04 (m, 1 H), 3.94 (m, 2 H), 3.52 (m, 1 H), 2.16 (m, 2 H), 1.88 (m, 2 H), 1.78 (m, 2 H), 1.67 (m, 1H), 1.53 (m, 3 H), 1.45 (s), 1.31 (s) (3 H), 1.11

(s), 1.05 (s) (9 H); ^{13}C NMR δ 142.3, 142.2, 135.6, 133.8, 133.7, 129.8, 129.7, 128.6, 127.8, 127.7, 126.8, 96.4, 96.2, 94.7, 75.6, 75.4, 72.0, 71.9, 63.8, 63.7, 63.0, 61.4, 60.7, 49.2, 49.0, 45.3, 42.9, 30.9, 28.3, 27.0, 26.9, 26.8, 25.6, 25.4, 20.3, 20.2, 19.8, 19.2. **Isomer 2:** ^{1}H NMR δ 7.74 (m, 4 H), 7.48-7.28 (m, 11 H), 4.94-4.82 (m, 2 H), 4.15 (m, 1 H), 3.94 (m, 2 H), 3.52 (m, 1 H), 3.21 (m, 1 H), 2.22 (m, 1 H), 1.99-1.63 (m, 5 H), 1.51 (m, 4 H), 1.35 (s), 1.30 (s) (3 H), 1.12 (s), 1.08 (s) (9 H); ^{13}C NMR δ 144.2, 144.0, 135.6, 133.4, 133.2, 129.9, 129.8, 128.2, 127.8 (d), 27.3, 127.2, 126.6, 99.4 (d), 79.0, 78.8, 71.9, 62.2, 61.4, 60.9, 49.4, 44.4, 43.0, 30.8, 28.0, 27.3, 26.9, 25.3, 19.3, 19.1.

3-Methyl-1-phenyl-1-(2-tetrahydropyranyloxy)-3,5-pentandiol (S10). Same procedure as for **25**. 89%. ^{1}H NMR δ 7.28 (m, 5 H), 5.21 (dd, J = 11.0, 2.2 Hz), 5.18 (dd, J = 7.8, 2.2 Hz) (1 H), 4.58 (s), 4.46 (s) (1 H), 4.34 (m), 3.98(m) (1 H), 3.83 (m, 1 H), 3.82 (br. s), 3.70 (br.s) (1 H), 3.47 (m, 1 H), 2.24 (dd, J = 14.8, 11.5 Hz), 2.07 (dd, J = 14.8, 11.2 Hz) (1 H), 1.75-1.46 (m, 9 H), 1.46 (s), 1.30 (s) (3 H); ^{13}C NMR δ 141.8, 141.6, 128.7, 128.0, 127.9, 126.7, 96.9, 96.7, 76.0, 75.5, 74.2, 73.6, 64.2, 59.9, 59.5, 49.8, 48.5, 44.1, 41.2, 31.0, 29.8, 27.9, 26.3, 25.2, 20.4.

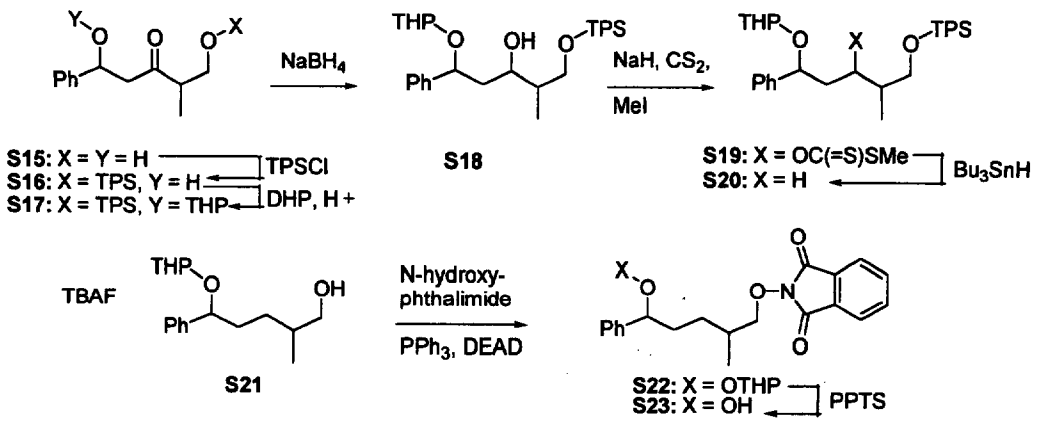
4-Methyl-4-[2-phenyl-2-(2-tetrahydropyranyloxy)ethyl]-1,3-dioxan-2-thione (S11). 1,1'-Thiocarbonyl diimidazole (0.10 g, 0.562 mmol) and DMAP (0.137 g, 1.12 mmol) were added successively to a solution of **S10** (0.11 g, 0.374 mmol) in dry CH_3CN (10 mL) at 0°C. The resulting reaction mixture was then heated to reflux for 5 h before it was cooled down and diluted with EtOAc (50 mL) and saturated NH_4Cl solution (10 mL). The water layer was extracted with EtOAc. The combined extracts were washed subsequently with HCl soluton (0.5 N), water, saturated $NaHCO_3$ solution, water and brine, then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (hexane/EtOAc 1/1) gave **S11** (0.0812 g, 65%) as a colorless oil. ^{1}H NMR δ 7.36-7.26 (m, 5 H), 4.93 (dd, J = 9.4, 3.2 Hz, 1 H), 4.47 (m, 2 H), 4.21 (m, 1 H), 3.88 (m, 1 H), 2.62 (m, 1 H), 2.35 (m), 2.08(m) (3 H), 1.86-1.36 (m, 6 H), 1.68 (s), 1.59 (s) (3 H); ^{13}C NMR δ 190.8, 141.5, 128.9, 128.2, 126.8, 126.6, 97.5, 97.1, 86.3, 74.0, 73.2, 66.9, 66.4, 65.1, 64.6, 48.6, 47.7, 31.8, 31.4, 31.2, 30.0, 27.0, 25.4, 21.3, 20.9.

3-Methyl-1-phenyl-1-(2-tetrahydropyranyloxy)-5-pentanol (S12). n-Bu_3SnH (0.205 mL, 0.765 mmol) and AIBN (0.128 mmol) in degassed PhH (2.0 mL) were added to a refluxing solution of **S11** (0.0856 g, 0.255 mmol) in PhH (8.0 mL) over 15 min. The resulting reaction mixture was heated to reflux for a further

3 h before it was cooled to room temperature and a solution of CH_3ONa in CH_3OH (2.0 mL, 1.0 M) and THF (2.0 mL) were added. The mixture was stirred overnight before it was diluted with saturated NH_4Cl solution (15 mL) and EtOAc (50 mL). The water layer was extracted with EtOAc and the combined extracts were washed subsequently with water, and brine, then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (hexane/EtOAc gradient eluent 9/1 to 1/1) gave **S12** (0.050 g, 71%) as a colorless oil. ^{1}H NMR δ 7.37-7.21 (m, 5 H), 4.81 (m, 1 H), 4.37 (dd, J = 4.5, 2.8 Hz), 4.33 (dd, J = 5.4, 2.7 Hz) (1 H), 3.93 (m, 1 H), 3.70 (m, 2 H), 3.46 (m, 1 H), 2.00-1.25 (m, 10 H), 1.02-0.90 (m, 3 H).

3-Methyl-1-phenyl-5-(*N*-phthalimidoxy)-1-(2-tetrahydropyranyloxy)pentane (S13). Application of general protocol F to **S12** gave **S13** in 43% yield. ^{1}H NMR δ 7.84 (m, 2 H), 7.74 (m, 2 H), 7.38-7.19 (m, 5 H), 4.81 (m, 1 H), 4.63 (m), 4.40 (m) (1 H), 4.22 (m, 2 H), 3.94 (m), 3.23 (m) (1 H), 3.49 (m, 1 H), 1.95-1.33 (m, 10 H), 1.07-0.98 (m, 3 H); ^{13}C NMR δ 163.8, 144.2, 143.5, 142.3, 135.1, 134.6, 129.2, 128.6, 128.3, 127.7, 127.6, 127.3, 127.2, 127.0, 126.9, 126.6, 124.3, 123.7, 99.1, 98.5, 95.5, 95.4, 77.9, 77.8, 77.1, 77.0, 75.4, 75.0, 62.7, 62.5, 62.2, 62.1, 46.3, 45.8, 45.4, 44.6, 35.6, 35.5, 35.2, 34.8, 30.9, 30.8, 29.9, 26.9, 26.8, 25.7, 25.6, 20.2, 20.1, 19.8, 19.6, 19.4. Anal. Calcd for $C_{25}H_{29}NO_5$: C, 70.90; H, 6.90. Found: C, 71.00; H, 6.86.

3-Methyl-1-phenyl-5-(*N*-phthalimidoxy)-1-pentanol (S14). Same procedure as for **27**. 85%. ^{1}H NMR δ 7.84 (m, 2 H), 7.75 (m, 2 H), 7.38-7.25 (m, 5 H), 4.82 (m, 1 H), 4.26 (m, 2 H), 2.27 (br. s 1 H), 2.17-1.85 (m, 2 H), 1.83-1.45 (m, 3 H), 1.08 (d, J = 6.6 Hz), 1.03 (d, J = 6.5 Hz) (3 H); ^{13}C NMR δ 163.9, 145.7, 145.0, 134.6, 129.0, 128.6 (d), 127.6, 127.5, 126.0, 125.8, 123.7, 77.0, 76.9, 72.3, 46.8, 46.7, 35.6, 34.7, 29.9, 26.8, 26.7, 20.4, 19.8. Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24. Found: C, 70.82; H, 6.42.



5-(*tert*-Butyldiphenylsiloxy)-1-hydroxy-4-methyl-1-phenyl-3-pentanone (S16). Prepared from **S15**[7] by the same procedure as employed for **22**. 42%. ^{1}H NMR δ 7.66 (m, 4 H), 7.45-7.25 (m, 11 H), 5.20 (m, 1 H), 3.84 (t, J = 10.0 Hz, 1 H), 3.71 (dd, J = 10.0, 5.2 Hz, 1 H), 2.96 (m, 2 H), 2.82 (m, 1 H), 1.07 (s), 1.06 (s), (9 H), 1.03 (d, J = 3.0 Hz, 3 H); ^{13}C NMR δ 214.5, 214.4, 143.0, 135.7, 133.2, 130.0, 128.6, 128.0, 127.7, 125.9, 125.8, 70.0 (d), 66.3, 66.1, 51.4, 50.9, 49.4, 49.2, 27.0. Anal. Calcd for $C_{28}H_{34}O_3Si$: C, 75.29; H, 7.67. Found: C, 75.16; H, 7.69.

5-(*tert*-Butyldiphenylsiloxy)-4-methyl-1-phenyl-1-(2-tetrahydropyranyloxy)-3-pentanone (S17). Same procedure as for **24**. 93%. ^{1}H NMR δ 7.65 (m, 4 H), 7.43-7.26 (m, 11 H), 5.29 (m), 5.15 (dd, J = 8.9, 4.1 Hz), 5.13 (dd, J = 8.5, 4.4 Hz) (1 H), 4.94 (dd, J = 7.5, 3.5 Hz), 4.44 (dd, J = 7.2, 3.5 Hz) (1 H), 3.89 (m), 3.21 (m) (3 H), 3.68 (m, 1 H), 3.50 (m, 1 H), 2.76 (m, 2 H), 1.83-1.36 (m, 6 H), 1.10-1.00 (m, 12 H); ^{13}C NMR δ 211.0, 210.5, 143.3, 143.2, 141.4 (d), 135.7, 133.4, 129.9, 128.6, 128.4, 127.9, 127.4, 127.2, 126.5, 126.4, 99.7, 99.5, 94.5, 77.6, 77.2, 76.8, 75.8, 75.6, 72.9, 72.7, 65.9, 62.2, 62.1, 61.8, 51.2, 50.8, 50.6, 50.4, 49.8, 49.5, 49.4, 30.7, 30.6, 26.9, 25.6, 25.5, 19.3, 19.1, 12.8. Anal. Calcd for $C_{33}H_{42}O_4Si$: C, 74.68; H, 7.98. Found: C, 74.72; H, 8.03.

5-(*tert*-Butyldiphenylsiloxy)-4-methyl-1-phenyl-1-(2-tetrahydropyranyloxy)-3-pentanol (S18). Same procedure as for **23**. 2 Isomers 89%. Anal. Calcd for $C_{33}H_{44}O_4Si.1/4H_2O$: C, 73.77; H, 8.35. Found: C, 73.87; H, 8.35. **Isomer 1:** ^{1}H NMR δ 7.68 (m, 4 H), 7.44-7.29 (m, 11 H), 5.01 (m, 1 H), 4.47 (br. s, 1 H), 4.09-3.90 (m, 2 H), 3.75-3.58 (m, 2 H), 3.54 (m, 1 H), 2.14-1.57 (m, 9 H), 1.07 (s, 9 H), 0.94 (d, J = 6.9 Hz, 3 H); ^{13}C NMR δ 141.8, 135.8, 133.9, 133.8, 129.8, 128.6, 127.9, 127.8, 127.1, 95.3, 77.8, 73.4, 71.7, 66.9,

66.7, 62.5, 42.9, 42.0, 41.1, 30.6, 27.0, 25.5, 19.6, 19.4, 13.1, 11.0. **Isomer 2:** ^{1}H NMR δ 7.68 (m, 4 H), 7.46-7.26 (m, 11 H), 5.18-4.80 (m), 4.46 (m), 4.07 (m), 3.85-3.50 (m), 3.27 (m) (7 H), 2.18-1.43 (m, 9 H), 1.07 (m, 9 H), 0.98-0.84 (m, 3 H).

***O*-[5-(*tert*-Butyldiphenylsiloxy)-4-methyl-1-phenyl-1-(2-tetrahydropyranyloxy)-3-pentyl]-*S*-methyl Dithiocarbonate (S19).** NaH (0.123 g, 60% in paraffin, 3.073 mmol) was added at room temperature to a solution of **S18** (0.545 g, 1.024 mmol) in THF (12 mL). The reaction mixture was stirred at room temperature for 1.5 h before CS_2 (0.184 mL, 3.073 mmol) was added. Then CH_3I (0.255 mL, 4.10 mmol) was added over 1 h. The resulting reaction mixture was stirred at room temperature for 20 h. before it was quenched by addition of saturated NH_4Cl solution (10 mL) dropwise and then EtOAc (60 mL). The water layer was extracted with EtOAc and the combined extracts were washed subsequently with water and brine, then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (hexane/EtOAc 5/1) gave **S19** (0.588 g, 92%) as a colorless oil. ^{1}H NMR δ 7.64 (m, 4 H), 7.42-7.25 (m, 11 H), 5.94 (m), 5.83 (dt, J = 10.1, 3.4 Hz) (1 H), 4.82 (m, 1 H), 4.39 (m, 1 H), 3.94 (m, 1 H), 3.58 (ddd, J = 20.1, 10.0, 6.8 Hz, 1 H), 3.51 (m, 2 H), 2.51 (s), 2.48 (s) (3 H), 2.44 (m), 2.33-2.05 (m) (2 H), 1.88 (m), 1.57 (m), 1.29 (m) (7 H), 1.04 (s), 0.97 (s) (9 H), 0.96-0.86 (m, 3 H); ^{13}C NMR δ 214.7 (d), 141.3, 141.0, 135.8, 133.8, 133.7, 133.6 (d), 129.7, 128.7, 128.0, 127.8, 127.6, 127.4, 95.3, 95.0, 82.9, 82.0, 74.3, 74.0, 65.5, 65.2, 62.6, 62.3, 38.8, 38.4, 38.0, 37.4, 30.8, 29.9, 27.0, 26.9, 25.7, 19.6, 19.3, 18.8, 11.8.

5-(*tert*-Butyldiphenylsiloxy)-4-methyl-1-phenyl-1-(2-tetrahydropyranyloxy)pentane (S20). AIBN (32.3 mg, 0.180 mmol) was added to a solution of **S19** (0.5605 g, 0.901 mmol) and n-Bu_3SnH (0.363 mL, 1.352 mmol) in PhH (10.0 mL) at room temperature and the resulting reaction mixture was brought to reflux for 2 h. After cooling the solvent was removed under vacuum and the residue was dissolved in methanol (4 mL) and treated with $NaBH_4$ (51.4 mg, 1.352 mmol) at room temperature. After 5 min the methanol was removed under vacuum and the residue was partitioned between EtOAc and saturated NH_4Cl solution. The aqueous layer was extracted with EtOAc and the combined extracts were washed subsequently with water and brine, then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (hexane/EtOAc 100/0 then 10/1) gave **S20**, a mixture of 2 isomers (0.44 g, 95%) as a colorless oil. Anal. Calcd for $C_{33}H_{44}O_3Si.1/4H_2O$: C, 76.03; H, 8.60. Found: C, 75.77; H, 8.61. **Isomer 1:** ^{1}H NMR δ 7.69 (m,

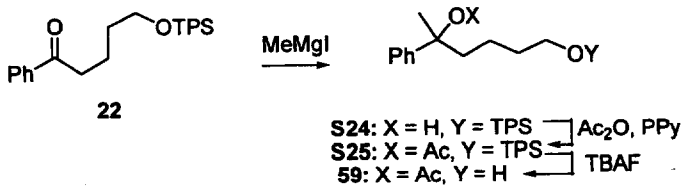
4 H), 7.44-7.26 (m, 11 H), 4.68 (t, J = 7.2 Hz, 1 H), 4.44 (t, J = 3.3 Hz, 1 H), 3.98 (m, 1 H), 3.50 (m, 3 H), 2.01-1.35 (m, 9 H), 1.08(s), 1.06 (s) (9 H), 0.95 (d, J = 6.6 Hz), 0.93 (d, J = 5.1 Hz) (3 H); ^{13}C NMR δ 142.8, 135.8, 134.2, 129.6, 128.5, 127.7, 127.6, 127.2, 95.3, 77.6, 69.0, 62.4, 35.9, 30.9, 29.7, 27.0, 25.8, 19.7, 19.5, 16.9. **Isomer 2:** ^{1}H NMR δ 7.69 (m, 4 H), 7.44-7.26 (m,11 H), 4.84 (dd, J = 5.7, 2.8 Hz), 4.42 (t, J = 3.6 Hz) (1 H), 4.66 (t, J = 7.0 Hz), 4.54 (dt, J = 6.4, 2.4 Hz) (1 H), 4.33 (t, J = 6.7 Hz), 3.93 (m) (1 H), 3.59-3.42 (m), 3.28 (m) (3 H), 1.95-1.30 (m, 9 H), 1.07 (s, 9 H), 1.02-0.90 (m, 3 H).

4-Methyl-1-phenyl-1-(2-tetrahydropyranyloxy)-5-pentanol (S21). Same procedure as for **25**. 2 Isomers 76%. Anal Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 72.84; H, 9.66. **Isomer 1:** ^{1}H NMR δ 7.35-7.25 (m, 5 H), 4.66 (m, 1 H), 4.37 (t, J = 3.0 Hz, 1 H), 3.93 (m, 1 H), 3.44 (m, 3 H), 1.95-1.32 (m), 1.09 (m) (9 H), 0.90 (d, J = 6.7 Hz), 0.88 (d, J = 6.5 Hz) (3 H); ^{13}C NMR δ 142.7, 142.5, 128.5, 127.6, 127.1, 127.0, 96.0, 95.7, 77.8, 77.6, 63.0, 62.8, 35.9, 35.8, 35.7, 31.0, 29.4, 29.3, 25.7, 20.0, 19.9, 16.8. **Isomer 2:** ^{1}H NMR δ 7.37-7.21 (m, 5 H), 4.82 (t, J = 3.3 Hz), 4.37 (t, J = 3.2 Hz) (1 H), 4.67 (m), 4.56 (m) (1 H), 3.93 (m), 3.55-3.34 (m), 3.26 (dt, J = 11.2, 4.7 Hz) (4 H), 1.95-1.00 (m, 9 H), 0.92-0.86 (m, 3 H); ^{13}C NMR δ 143.7, 143.6, 142.7, 128.5, 128.3, 127.6, 127.1, 127.0, 126.7, 126.6, 98.3, 98.2, 96.0, 95.7, 79.4, 79.3, 77.8, 68.2, 63.0, 62.9, 62.1, 35.9 (d), 35.8, 35.7, 34.6 (d), 31.0, 30.8, 29.4, 29.3, 28.9, 28.0, 25.7, 25.6, 20.0 (d), 19.4, 17.7, 16.7.

4-Methyl-1-phenyl-5-(*N*-phthalimidoxy)-1-(2-tetrahydropyranyloxy)pentane (S22). Application of general protocol F to **S21** gave **S22** in 83% yield. ^{1}H NMR δ 7.82 (m, 2 H), 7.73 (m, 2 H), 7.38-7.24 (m, 5 H), 4.85 (m), 4.39 (t, J = 3.2 Hz) (1 H), 4.67 (m), 4.58 (dt, J = 10.8, 6.1 Hz) (1 H), 4.05 (m, 1 H), 3.93 (m), 3.50 (m), 3.27 (dt, J = 11.1, 4.5 Hz) (3 H), 1.98-1.39 (m, 6 H), 1.09 (d, J = 6.8 Hz), 1.06 (d, J = 7.5 Hz), 1.05 (d, J = 6.7 Hz), 1.04 (d, J =7.0 Hz) (3 H); ^{13}C NMR δ 163.7, 143.6, 143.5, 142.6, 142.5, 134.6, 129.2, 128.5, 128.3, 127.6, 127.1, 126.7, 126.6, 123.6, 98.2, 95.4, 83.6, 83.5, 79.1, 79.0, 62.5, 62.1, 35.7, 35.5, 34.4, 34.2, 32.6, 30.8, 29.7, 29.0, 25.7, 25.6, 19.7, 19.4, 16.9, 16.8. Anal. Calcd for $C_{25}H_{29}NO_5$: C, 70.90; H, 6.90. Found: C, 71.06; H, 7.10.

4-Methyl-1-phenyl-5-(*N*-phthalimidoxy)-1-pentanol (S23). Same procedure as for **27**. 83%. ^{1}H NMR δ 7.81 (m, 2 H), 7.73 (m, 2 H), 7.37-7.24 (m, 5 H), 4.69 (br.q), 4.00 (m, 2 H), 2.40 (br s), 2.32 (br s) (1 H), 1.97 (m), 1.88 (m), 1.63 (m), 1.46 (m), 1.25 (m) (5 H), 1.04 (d, J = 6.8 Hz, 3 H); ^{13}C NMR δ 163.8, 145.0,

134.6, 129.1, 128.6, 127.6, 126.0 (d), 123.6, 83.4 (d), 74.9, 74.4, 36.4, 36.3, 32.6, 32.3, 29.4, 29.2, 16.8, 16.7. Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24. Found: C, 71.21; H, 6.65.



5-(*tert*-Butyldiphenylsiloxy)-1-methyl-1-phenyl-1-pentanol (S24). MeMgBr (0.424 mL, 3.0 M in Et_2O, 1.27 mmol) was added dropwise at 0 °C to a solution of **22** (0.352 g, 0.847 mmol) in THF (6.0 mL). The reaction mixture was stirred at this temperature for 30 min before EtOAc (50 mL) and HCl (0.5 N, 10 mL) was added to quench the reaction. The water layer was extracted with EtOAc and the combined extracts were washed subsequently with saturated $NaHCO_3$ solution, water and brine, then dried (Na_2SO_4) and concentrated to dryness. Column chromatography on silica gel (hexane/EtOAc 5/1) gave **S24** (0.25 g, 71%) as a colorless oil. ^{1}H NMR δ 7.64 (dd, 4 H), 7.45-7.24 (m, 4 H), 3.62 (t, J = 6.4 Hz, 2 H), 1.79 (M, 2 H), 1.68 (br. s, 1 H), 1.55 (s, 3 H), 1.32 (m, 2 H), 1.28 (m, 2 H), 1.03 (s, 9 H); ^{13}C NMR δ 148.1, 135.8, 134.2, 129.7, 128.3, 127.8, 126.7, 125.0, 74.9, 63.9, 44.0, 32.9, 30.3, 27.0, 20.5, 19.4. Anal. Calcd for $C_{28}H_{36}O_2Si$: C, 77.73; H, 8.39. Found: C, 77.25; H, 8.45.

1-Acetoxy-5-(*tert*-butyldiphenylsiloxy)-1-methyl-1-phenylpentane (S25). Same procedure as for **33**. 97%. ^{1}H NMR δ 7.66 (dd, 4 H), 7.44-7.26 (m, 11 H), 3.64 (t, J = 6.2 Hz, 2 H), 2.07 (s, 3 H), 2.00 (m, 2 H), 1.85 (s, 3 H), 1.52 (m, 2 H), 1.30 (m, 2 H), 1.05 (s, 9 H); ^{13}C NMR δ 169.8, 145.2, 135.8, 134.2, 129.7, 128.3, 127.8, 127.0, 124.7, 84.2, 63.7, 42.5, 32.8, 27.0, 25.0, 22.4, 20.3, 19.4. Anal. Calcd for $C_{30}H_{38}O_3Si$: C, 75.90; H, 8.07. Found: C, 75.74; H, 8.16.

1-Acetoxy-1-methyl-1-phenyl-5-pentanol (59) was prepared from **S25**, by the protocol outlined for **25**, in 86% yield. The bulk sample obtained in this manner was identical with the sample described above, obtained from the rearrangement of **36**.

References

(1) Newcomb, M.; Horner, J. H.; Whitted, P. O.; Crich, D.; Huang, X.; Yao, Q.; Zipse, H. *J. Am. Chem. Soc.* **1999**, *121*, 0000.

(2) Choi, S.-Y.; Crich, D.; Horner, J. H.; Huang, X.; Newcomb, M.; Whitted, P. O. *Tetrahedron* **1999**, *59*, 3317.

(3) Matsumoto, K.; Yokoo, T.; Oshima, K.; Utimoto, K.; Rahman, N. A. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1694.

(4) Ramon, D. J.; Yus, M. *Tetrahedron* **1992**, *48*, 3585.

(5) Bertocchio, R.; Longeray, R.; Dreux, J. *Bull. Soc. Chim. Fr.* **1964**, 60.

(6) Descotes, G.; Soula, J.-C. *Bull. Soc. Chim. Fr.* **1964**, 2636.

(7) Martin, V. A.; Murray, D. H.; Pratt, N. E.; Zhao, Y.-B.; Albizati, K. F. *J. Am. Chem. Soc.* **1990**, *112*, 6965.