Further studies on silatropic carbonyl ene cyclisations: β-crotyl(diphenyl)silyloxy aldehyde substrates; synthesis of 2-deoxy-2-*C*-phenylhexoses

Jeremy Robertson,* Stuart P. Green, Michael J. Hall, Andrew J. Tyrrell and William P. Unsworth

Electronic Supplementary Information

Experimental procedures and characterisation data for compounds **5**, **6**, **9** (and intermediates), **11** (and intermediates), **15**, **20**–**24**, **31**/**32** & **43**/**44**, **37**/**38** & **49**/**50**, **39**/**40** & **51**/**52**.

Ethyl 3-(allyldiphenylsilanyloxy)butyrate (5)

To a solution of allyldiphenylsilane[i] (1.10 g, 4.9 mmol) and ester **4** (633 mg, 4.8 mmol) in dichloromethane (10 mL) was added tris(pentafluorophenyl)borane (128 mg, 0.24 mmol) and the reaction mixture was heated at reflux for 2 h. The mixture was allowed to cool and then poured into water (10 mL) and ether (10 mL). The aqueous layer was extracted with ether (2 × 20 mL) and the combined organic extracts were washed with brine (10 mL) and then dried over magnesium sulphate. The solvent was removed *in vacuo* and the resulting oil was purified by column chromatography (petrol/ether, 25:1) to give the *title compound* (**5**, 1.49 g, 88%) as a colourless oil. R_f 0.27 (petrol/ether, 10:1); ν_{max}/cm^{-1} (film) 3070m, 2976m, 2930m, 1736s, 1630m, 1590w, 1446w, 1429s, 1378s, 1303s, 1260m, 1185s, 1158s, 1117s, 1080s, 1031s, 1006s, 932w, 899m, 773s, 737s, 701s, 674w, 595s; δ_H (400 MHz; $CDCl_3$) 1.21 (3 H, d, *J* 5.8, C*H*$_3$CHO), 1.22 (3 H, t, *J* 7.1, CH$_2$C*H*$_3$), 2.21 (2 H, ddd, *J* 7.8, 1.5, 1.0, SiCH$_2$), 2.41 (1 H, dd, *J* 14.8, 5.6) and 2.59 (1 H, dd, *J* 14.8, 7.4, CH$_2$CO), 4.00–4.11 (2 H, m, C*H*$_2$CH$_3$), 4.43 (1 H, dqd, *J* 7.4, 5.8, 5.6, CH$_3$C*H*O), 4.89 (1 H, ddt, *J* 10.1, 1.9, 1.0) and 4.94 (1 H, ddt, *J* 17.0, 1.9, 1.5, =CH$_2$), 5.82 (1 H, ddt, *J* 17.0, 10.1, 7.8, C*H*=CH$_2$), 7.35–7.45 (6 H, m) and 7.59–7.62 (4 H, m, 2 × Ph); δ_C (100 MHz; $CDCl_3$) 14.1 (q), 22.2 (t), 23.7 (q), 44.6 (t), 60.3 (t), 66.7 (d), 115.1 (t), 127.7 (d), 129.8 (d), 133.2 (s), 133.7 (d), 134.8 (d), 171.4 (s); *m/z* (CI^+) 372 (MNH_4^+, 6%), 355 (MH^+, 2), 313 (100), 277 (30), 244 (13), 216 (14), 199 (13); HRMS (CI^+) 355.1724 (MH^+. $C_{21}H_{27}O_3Si$ requires 355.1729).

Ethyl 3-[(*Z*-but-2-enyl)diphenylsilanyloxy]butyrate (en route to 9)

To a solution of (*Z*-but-2-enyl)diphenylsilane[ii] (481 mg, 2.02 mmol) and ester **4** (264 mg, 2.0 mmol) in dichloromethane (10 mL) was added tris(pentafluorophenyl)borane (162 mg, 0.32 mmol) and the reaction mixture was heated at reflux for 2 h. The mixture was allowed to cool and then poured into water (10 mL) and ether (10 mL). The aqueous layer was extracted with ether (2 × 20 mL) and the combined organic extracts were washed with brine (10 mL) and then dried over magnesium sulphate. The solvent was removed *in vacuo* and the resulting oil was purified by column chromatography (petrol/ether, 25:1) to give the *title compound* (526 mg, 71%) as a colourless oil. R_f 0.37 (petrol/ether, 10:1); ν_{max}/cm^{-1} (film) 3070s, 3016s, 2975s, 2929s, 1736s, 1650m, 1591m, 1446m, 1429s, 1384s, 1378s, 1303s, 1260s, 1185s, 1116s br, 1030s, 997s, 951m, 900w, 855w, 782s, 738s, 700s, 644m, 554s; δ_H (400 MHz; $CDCl_3$) 1.21 (3 H, d, *J* 6.4, C*H*$_3$CHO), 1.22 (3 H, t, *J* 7.0, CH$_2$C*H*$_3$), 1.33 (3 H, d, *J* 6.5, =CHC*H*$_3$), 2.13 (2 H, d, *J* 6.9, SiCH$_2$), 2.41 (1 H, dd, *J* 14.8, 5.6) and 2.58 (1 H, dd, *J* 14.8, 7.2, CH$_2$CO), 4.06 (2 H, q, *J* 7.0, C*H*$_2$CH$_3$), 4.42 (1 H, dqd, *J* 7.2, 6.4, 5.6, CH$_3$C*H*O), 5.32–5.43 (1 H, m) and 5.45–5.53 (1 H, m, CH=CH), 7.29–7.43 (6 H, m) and 7.55–7.63 (4 H, m, 2 × Ph); δ_C (100 MHz; $CDCl_3$) 12.6 (q), 14.1 (q), 15.6 (t), 23.7 (q), 44.6 (t), 60.3 (t), 66.7 (d), 123.5 (d), 124.0 (d), 127.7 (d), 129.8 (d), 134.5 (d), 135.0 (s), 171.4 (s); *m/z* (CI^+) 386 (MNH_4^+, 2%), 369 (MH^+, 1), 313 (100), 219 (8), 244 (7), 227 (6), 199 (11); HRMS (CI^+) 386.2147 (MNH_4^+. $C_{22}H_{32}NO_3Si$ requires 386.2151).

Ethyl 3-[(but-3-enyl)diphenylsilanyloxy]butyrate (en route to 11)

To a solution of (but-3-enyl)diphenylsilane[iii] (1.19 g, 5.0 mmol) and ester **4** (661 mg, 5.0 mmol) in dichloromethane (5 mL) was added tris(pentafluorophenyl)borane (128 mg, 0.25 mmol) and the reaction mixture was heated at reflux for 1 h. The mixture was allowed to cool and then partitioned between water (10 mL) and ether (20 mL). The aqueous layer was extracted with ether (2 × 10 mL) and the combined organic extracts were washed with brine (10 mL) and then dried over magnesium sulphate. The solvent was removed *in vacuo* and the resulting oil was purified by column chromatography (petrol/ether, 25:1) to give the *title compound* (1.62 g, 88%) as a colourless oil (Found: C, 71.3; H, 7.8. $C_{22}H_{28}O_3Si$ requires C, 71.7; H, 7.7%); R_f 0.30 (petrol/ether, 10:1); ν_{max}/cm^{-1} (film) 3070m, 2977s, 2913m, 1737s, 1639w, 1590w, 1429s, 1378m, 1303m, 1260w, 1185s, 1116s, 1080s, 1031m, 997s, 909w, 768w, 739s, 701s; δ_H (400 MHz; $CDCl_3$) 1.20 (3 H, d, *J* 5.2, C*H*$_3$CHO), 1.23 (3 H, t, *J* 7.1, CH$_2$C*H*$_3$), 1.26–1.30 (2 H, m, SiCH$_2$), 2.11–2.17 (2 H, m, C*H*$_2$CH=), 2.42 (1 H, dd, *J* 14.7, 5.4) and 2.58 (1 H, dd, *J* 14.7, 7.4, CH$_2$CO), 4.03–4.11 (2 H, m, C*H*$_2$CH$_3$), 4.38–4.42 (1 H, m, CH$_3$C*H*O), 4.91 (1 H, dd, *J* 10.1, 1.6) and 5.01 (1 H, dd, *J* 17.1, 1.6, =CH$_2$), 5.86–5.96 (1 H, m, C*H*=CH$_2$), 7.37–7.44 (6 H, m) and 7.59–7.62 (4 H, m, 2 × Ph); δ_C (100 MHz; $CDCl_3$) 13.2 (t), 14.2 (q), 23.7 (q), 27.0 (t), 44.6 (t), 60.3 (t), 66.6 (d), 112.9 (t), 127.8 (d), 129.8 (d), 135.1 (s), 135.8 (d), 141.1 (d), 171.4 (s); *m/z* (CI^+) 369 (MH^+, 4%), 313 (68), 291 (100), 244 (18), 227 (22), 216 (19), 199 (39), 183 (22), 115 (48), 99 (21); HRMS (CI^+) 369.1897 (MH^+. $C_{22}H_{29}O_3Si$ requires 369.1886).

Ethyl 3-[(*E*-but-2-enyl)diphenylsilanyloxy]butyrate (en route to 11)

(1,5-Cyclooctadiene)bis(methyldiphenylphosphine)iridium(I) hexafluorophosphate (32 mg, 0.038 mmol) was dissolved

in dichloromethane (5 mL). The catalyst was activated by bubbling hydrogen slowly through the solution at –78 °C until a colour change was observed from deep red to colourless (few minutes). The remaining hydrogen in the vessel was purged with argon and the solution added by cannula to a cooled (–78 °C) solution of ethyl 3-(but-3-enyldiphenylsilanyloxy)butyrate (1.41 g, 3.83 mmol) in dichloromethane (15 mL). The reaction mixture was warmed to 0 °C and stirred for 20 min. The solvent was removed *in vacuo* then the residue was triturated with ether (30 mL) and the extract filtered through a plug of silica gel and concentrated *in vacuo* to give the *title compound* (1.39 g, 99%) as a colourless oil that was used without further purification. R_f 0.36 (petrol/ether, 10:1); ν_{max}/cm^{-1} (film) 3070w, 2977m, 2931m, 1736s, 1590w, 1429m, 1378m, 1303m, 1530w, 1185s, 1117s, 1081s, 1032m, 1006s, 965w, 798w, 764m, 737m, 701s; δ_H (400 MHz; $CDCl_3$) 1.20 (3 H, d, *J* 6.1, C*H*$_3$CHO), 1.21 (3 H, t, *J* 7.1, CH$_2$C*H*$_3$), 1.59 (3 H, d, *J* 7.0, C*H*$_3$CH=), 2.11 (2 H, d, *J* 6.2, SiCH$_2$), 2.41 (1 H, dd, *J* 14.8, 5.8) and 2.58 (1 H, dd, *J* 14.8, 7.2, CH$_2$CO), 4.05 (2 H, q, *J* 7.1, C*H*$_2$CH$_3$), 4.42 (1 H, dqd, *J* 7.2, 6.1, 5.8, CH$_3$C*H*O), 5.30–5.46 (2 H, m, CH=CH), 7.35–7.44 (6 H, m) and 7.57–7.61 (4 H, m, 2 × Ph); δ_C (100 MHz; $CDCl_3$) 14.1 (q), 18.1 (q), 20.1 (t), 23.7 (q), 44.6 (t), 60.3 (t), 66.6 (d), 124.8 (d), 125.6 (d), 127.7 (d), 129.8 (d), 134.8 (d), 135.1 (s), 171.4 (s); *m/z* (CI^+) 386 (MNH_4^+, 3%), 369 (MH^+, 3), 313 (100), 291 (31), 244 (8), 216 (8), 199 (10); HRMS (CI^+) 369.1885 (MH^+. $C_{22}H_{29}O_3Si$ requires 369.1886).

General reduction procedure, used to prepare aldehydes 6, 9 and 11

To a solution of the ethyl ester (1.12–2.5 mmol) in dichloromethane (10 mL) at –78 °C was added DIBAL (1 M in hexane, 1.1 eq) dropwise and the resulting solution was stirred for 1 h. A saturated solution of tartaric acid in methanol (5 mL) was added and the mixture was poured into water (10 mL) and ether (20 mL). The aqueous layer was extracted with ether (2 × 20 mL) and the combined organic extracts were washed with brine (20 mL) and dried over magnesium sulphate. The solvent was removed *in vacuo* and the resulting oil was purified by column chromatography (petrol/ether, 20:1).

3-(Allyldiphenylsilanyloxy)butyraldehyde (6)

On a 2.5 mmol scale the general procedure gave the *title compound* (**6**, 570 mg, 74%) as a colourless oil. R_f 0.20 (petrol/ether, 10:1); ν_{max}/cm^{-1} (film) 3071m, 3000m, 2973s, 2913m, 2827m, 2726w, 1727s, 1630s, 1590m, 1487w, 1428s, 1378s, 1262w, 1188m, 1153s, 1116s, 1024s, 997s, 931m, 901s, 769s, 737s, 701s, 595s; δ_H (400 MHz; $CDCl_3$) 1.25 (3 H, d, *J* 6.2, CH$_3$), 2.22 (2 H, ddd, *J* 7.9, 1.6, 1.0, SiCH$_2$), 2.51 (1 H, ddd, *J* 16.0, 5.2, 1.9) and 2.63 (1 H, ddd, *J* 16.0, 6.6, 2.6, CH$_2$CO), 4.48 (1 H, dqd, *J* 6.6, 6.2, 5.2, CH$_3$C*H*), 4.90–4.94 (1 H, m) and 4.94–4.99 (1 H, m, =CH$_2$), 5.82 (1 H, ddt, *J* 17.0, 10.0, 7.9, C*H*=CH$_2$), 7.38–7.47 (6 H, m) and 7.59–7.63 (4 H, m, 2 × Ph), 9.75 (1 H, dd, *J* 2.6, 1.9, CHO); δ_C (100 MHz; $CDCl_3$) 22.2 (t), 24.0 (q), 52.7 (t), 65.3 (d), 115.3 (t), 127.9 (d), 130.1 (d), 132.8 (d), 134.3 (s), 134.4 (s), 134.8 (d), 201.8 (d); *m/z* (CI^+) 328 (MNH_4^+, 53%), 311 (MH^+, 14), 286 (18), 269 (100), 258 (16), 216 (87), 198 (40), 183 (20), 155 (16); HRMS (CI^+) 311.1463 (MH^+. $C_{19}H_{23}O_2Si$ requires 311.1467).

3-[(*Z*-But-2-enyl)diphenylsilanyloxy]butyraldehyde (9)

On a 1.12 mmol scale the general procedure gave the *title compound* (**9**, 350 mg, 96%) as a colourless oil. R_f 0.30 (petrol/ether, 10:1); ν_{max}/cm^{-1} (film) 3070s, 3016s, 2927s, 2828m, 2726m, 1727s, 1649w, 1590m, 1487m, 1446m, 1429m, 1394s, 1377s, 1364s, 1262w, 1218w, 1117s br, 1025s, 996s, 902w, 781s, 739s, 700s, 644s, 534s; δ_H (400 MHz; $CDCl_3$) 1.26 (3 H, d, *J* 7.3, C*H*$_3$CHO), 1.43 (3 H, d, *J* 6.4, C*H*$_3$CH=), 2.14 (2 H, d, *J* 8.0, SiCH$_2$), 2.50 (1 H, ddd, *J* 16.1, 5.3, 2.0) and 2.63 (1 H, ddd, *J* 16.1, 6.6, 3.0, CH$_2$CO), 4.46 (1 H, qdd, *J* 7.3, 6.6, 5.3, CH$_3$C*H*O), 5.31–5.52 (2 H, m, CH=CH), 7.32–7.44 (6 H, m) and 7.57–7.63 (4 H, m, 2 × Ph), 9.75 (1 H, dd, *J* 3.0, 2.0, CHO); δ_C (100 MHz; $CDCl_3$) 12.7 (q), 15.6 (t), 24.0 (q), 52.8 (t), 65.4 (d), 123.8 (d), 127.7 (d), 127.9 (d), 130.1 (d), 134.5 (s), 134.8 (d), 201.8 (d); *m/z* (CI^+) 342 (MNH_4^+, 11%), 325 (MH^+, 4), 269 (100), 216 (48), 199 (20), 183 (8), 88 (13), 70 (28); HRMS (CI^+) 342.1875 (MNH_4^+. $C_{20}H_{28}NO_2Si$ requires 342.1889).

3-[(*E*-But-2-enyl)diphenylsilanyloxy]butyraldehyde (11)

On a 2.05 mmol scale the general procedure gave the *title compound* (**11**, 523 mg, 79%) as a colourless oil (Found: C, 73.6; H, 7.7. $C_{20}H_{24}O_2Si$ requires C, 74.0; H 7.5%); R_f 0.29 (petrol/ether, 10:1); ν_{max}/cm^{-1} (film) 3070m, 3015m, 2971m, 2931m, 2728w, 1727s, 1590w, 1487w, 1452w, 1429s, 1377m, 1307w, 1262w, 1218w, 1116s br, 1024s, 998m, 966m, 907w, 799m, 763m, 738s, 701s; δ_H (400 MHz; $CDCl_3$) 1.25 (3 H, d, *J* 6.2, C*H*$_3$CHO), 1.61 (3 H, d, *J* 5.8, C*H*$_3$CH=), 2.13 (2 H, d, *J* 7.1, SiCH$_2$), 2.51 (1 H, ddd, *J* 16.0, 5.2, 1.7) and 2.62 (1 H, ddd, *J* 16.0, 6.6, 2.6, CH$_2$CO), 4.48 (1 H, dqd, *J* 6.6, 6.2, 5.2, CH$_3$C*H*O), 5.32–5.47 (2 H, m, CH=CH), 7.38–7.47 (6 H, m) and 7.58–7.62 (4 H, m, 2 × Ph), 9.76 (1 H, dd, *J* 2.6, 1.7, CHO); δ_C (100 MHz; $CDCl_3$) 18.1 (q), 20.1 (t), 23.9 (q), 52.8 (t), 65.3 (d), 124.6 (d), 125.9 (d), 127.8 (d), 130.0 (d), 134.7 (s), 134.8 (d), 201.8 (d); *m/z* (CI^+) 342 (MNH_4^+, 10%), 325 (MH^+, 5), 269 (100), 225 (6), 216 (10), 198 (22), 183 (12); HRMS (CI^+) 342.1876 (MNH_4^+. $C_{20}H_{28}NO_2Si$ requires 342.1889).

2-Allyldimethylsilanyloxy-3,3-dimethylbutyronitrile (15)

To a solution of sodium hydrogen sulphite (17 g) in water (50 mL) at 0 °C was added pivalaldehyde (4.85 mL, 45.0 mmol) and the mixture was stirred for 30 min. A solution of potassium cyanide (11.6 g, 179 mmol) in water (250 mL) was added dropwise over 30 min and the resulting mixture was stirred at RT for 2 h. The reaction mixture was extracted with ether (3 × 125 mL) and the combined organic extracts were washed successively with hydrochloric acid (125 mL, 5.0 M) and brine (250 mL) and were then dried over magnesium sulphate. The solvent was removed *in vacuo* to yield 2-hydroxy-3,3-dimethylbutyronitrile[iv] (4.52 g, 89 %) as a colourless waxy solid. [mp 41–42 °C; δ_H (400 MHz; $CDCl_3$) 1.06 (9 H, s, C(CH$_3$)$_3$), 3.39 (1 H, br s, OH), 4.11 (1 H, s, C*H*CN); δ_C (100 MHz; $CDCl_3$) 24.9 (q), 35.4 (s), 70.4 (d), 119.3 (s)]. To a stirred solution of this crude cyanohydrin (4.52 g, 40 mmol), DMAP (0.24 g, 2.00 mmol) and triethylamine (22.4 mL, 160 mmol) in anhydrous DMF (300 mL) was added allylchlorodimethylsilane (9.93 mL,

68.0 mmol). The reaction mixture was heated at 60 °C for 6 h then cooled to RT and partitioned between water (200 mL) and ether (100 mL). The aqueous layer was extracted with ether (3 × 50 mL) and the combined organic layers were washed successively with brine (100 mL) and water (100 mL) and were then dried over magnesium sulphate. The solvent was removed *in vacuo* and the residue purified by column chromatography (petrol/ether, 15:1) to afford the *title compound* (**15**, 7.0 g, 83%) as a colourless oil. R_f 0.44 (petrol/ether, 10:1); ν_{max}/cm^{-1} (film) 3080m, 2966s, 2911m, 2875s, 2235w, 1632m, 1479m, 1466m, 1398m, 1368m, 1257s, 1195m, 1165s, 1108s, 1035s, 953m, 933m, 886s, 855s, 754m, 652m, 576m; δ_H (400 MHz; $CDCl_3$) 0.22 (3 H, s) and 0.23 (3 H, s, $Si(CH_3)_2$), 1.02 (9 H, s, $C(CH_3)_3$), 1.64–1.78 (2 H, m, $SiCH_2$), 4.03 (1 H, s, CHCN), 4.88–5.00 (2 H, m, $=CH_2$), 5.72–5.87 (1 H, m, C*H*=CH_2); δ_C (100 MHz; $CDCl_3$) –2.6 (q), –2.5 (q), 24.0 (t), 24.9 (q), 35.9 (s), 71.0 (d), 114.6 (t), 119.1 (s), 132.9 (d); *m/z* (CI^+) 229 (MNH_4^+, 100%), 212 (MH^+, 18), 187 (74), 170 (44), 143 (82), 128 (34), 91 (18), 75 (19), 74 (33); HRMS (CI^+) 229.1738 (MNH_4^+. $C_{11}H_{25}N_2OSi$ requires 229.1736).

General Procedure for DIBAL reduction of nitriles 15–19

To a stirred solution of silylcyanohydrin (**15**–**19**) in anhydrous dichloromethane (*ca.* 10 mL $mmol^{-1}$ of nitrile) at –78 °C was added DIBAL (1.5 eq., 1.0 M solution in dichloromethane) and the mixture was stirred for 1 h. A saturated solution of tartaric acid in methanol (5 mL $mmol^{-1}$ of nitrile) was added and the mixture was stirred for a further 30 min. The mixture was then warmed to RT and partitioned between water (15 mL $mmol^{-1}$) and ether (30 mL $mmol^{-1}$). The aqueous layer was extracted with ether (2 × 20 mL $mmol^{-1}$) and the combined organic layers were washed successively with saturated aqueous tartaric acid solution (20 mL $mmol^{-1}$) and brine (15 mL $mmol^{-1}$) and then dried over magnesium sulphate. The solvent was removed *in vacuo* to afford the crude product (**20**–**24**).

2-(*E*-4-Hydroxybut-2-enyl)dimethylsilanyloxy-3,3-dimethylbutyronitrile (20)

Following the general procedure for DIBAL reduction, silylcyanohydrin **19** (56 mg, 0.21 mmol) afforded the *title compound* (**20**, 23 mg, 46%) as a colourless oil following purification by column chromatography (petrol/ether, 5:1). R_f 0.12 (petrol/ether, 2:1); ν_{max}/cm^{-1} (film) 3399br, 2963s, 2891m, 2232w, 1659w, 1370s, 1257s, 1104m, 843m, 804m; δ_H (400 MHz; $CDCl_3$) 0.21 (3 H, s) and 0.24 (3 H, s, $Si(CH_3)_2$), 1.02 (9 H, s, $C(CH_3)_3$), 1.52 (1 H, br s, OH), 1.68 (2 H, d, *J* 8.0, $SiCH_2$), 4.02 (1 H, s, CHCN), 4.08 (2 H, d, *J* 6.0, C*H*$_2$OH), 5.60 (1 H, dt, *J* 15.0, 6.0) and 5.70 (1 H, dt, *J* 15.0, 8.0, CH=CH); δ_C (100 MHz; $CDCl_3$) –2.5 (q), –2.5 (q), 22.3 (t), 24.9 (q), 35.9 (s), 63.9 (t), 71.1 (d), 119.2 (s), 127.6 (d), 129.4 (d); *m/z* (FI^+) 241 (M^+, 8%), 220 (18), 192 (100), 146 (35), 75 (20), 57 (44); HRMS (FI^+) 241.1500 (M^+. $C_{12}H_{23}NO_2Si$ requires 241.1493).

2-(*E*-3-Triethoxysilylprop-2-enyl)dimethylsilanyloxy-3,3-dimethylbutyraldehyde (21)

Following the general procedure for DIBAL reduction, silylcyanohydrin **16** (60.6 mg, 0.16 mmol) afforded the *title compound* (**21**, 8.6 mg, 14%) as a colourless oil following purification by column chromatography (petrol/ether, 10:1). R_f 0.22 (petrol/ether, 10:1); ν_{max}/cm^{-1} (film) 2972m, 1734m, 1606m, 1392w, 1258m, 1077s; δ_H (400 MHz; $CDCl_3$) 0.14 (6 H, s, $Si(CH_3)_2$), 0.97 (9 H, s, $C(CH_3)_3$), 1.23 (9 H, t, *J* 7.0, 3 × CH_2CH_3), 1.72–1.90 (2 H, m, $SiCH_2$), 3.55 (1 H, d, *J* 2.5, CHCO), 3.81 (6 H, q, *J* 7.0, 3 × C*H*$_2$CH$_3$), 5.30 (1 H, d, *J* 18.5, =CHSi), 6.43 (1 H, dt, *J* 18.5, 8.0, CH_2CH=), 9.62 (1 H, d, *J* 2.5, CHO); δ_C (100 MHz; $CDCl_3$) –2.0 (q), –1.8 (q), 18.3 (q), 25.7 (q), 28.9 (t), 35.7 (s), 58.4 (t), 84.5 (d), 118.7 (d), 149.1 (d), 204.1 (d); *m/z* (ES^+) 435 (MNH_4^+·MeCN, 100%).

2-(*E*-Cinnamyl)dimethylsilanyloxy-3,3-dimethylbutyraldehyde (22)

Following the general procedure for DIBAL reduction, silylcyanohydrin **17** (53.0 mg, 0.19 mmol) afforded the *title compound* (**22**, 15 mg, 30%) as a colourless oil following purification by column chromatography (petrol/ether, 30:1). R_f 0.34 (petrol/ether, 10:1); ν_{max}/cm^{-1} (film) 3060w, 3024m, 2959s, 2873m, 1733s, 1642m, 1600w, 1496m, 1479m, 1448m, 1397m, 1366m, 1254s, 1100s, 963m, 834s, 750s, 694s; δ_H (400 MHz; $CDCl_3$) 0.17 (6 H, s, $Si(CH_3)_2$), 0.99 (9 H, s, $C(CH_3)_3$), 1.80 (2 H, dd, *J* 7.5, 2.5, $SiCH_2$), 3.58 (1 H, d, *J* 3.0, CHCO), 6.18–6.33 (2 H, m, CH=CH), 7.28–7.33 (5 H, m, Ph), 9.65 (1 H, d, *J* 3.0, CHO); δ_C (100 MHz; $CDCl_3$) –2.4 (q), –1.9 (q), 23.9 (t), 25.7 (q), 35.7 (s), 84.5 (d), 125.6 (d), 125.8 (d), 126.5 (d), 128.5 (d), 129.6 (d), 138.2 (s), 204.3 (d); *m/z* (CI^+) 308 (MNH_4^+, 71%), 291 (MH^+, 39), 173 (100), 131 (45), 70 (39); HRMS (CI^+) 308.2031 (MNH_4^+. $C_{17}H_{30}NO_2Si$ requires 308.2046).

2-(*E*-4-Nitrocinnamyl)dimethylsilanyloxy-3,3-dimethylbutyraldehyde (23)

Following the general procedure for DIBAL reduction, silylcyanohydrin **18** (120 mg, 0.36 mmol) afforded the *title compound* (**23**, 80 mg, 66%) as a brown oil which was sufficiently pure to use directly in the next reaction. ν_{max}/cm^{-1} (film) 3404w, 2961m, 1732s, 1638m, 1595s, 1516s, 1397w, 1341s, 1256m, 1147m, 1108s, 969w, 875m, 842s, 748m; δ_H (400 MHz; $CDCl_3$) 0.19 (6 H, s, $Si(CH_3)_2$), 0.98 (9 H, s, $C(CH_3)_3$), 1.82–1.92 (2 H, m, $SiCH_2$), 3.60 (1 H, d, *J* 2.5, CHCO), 6.34 (1 H, d, *J* 16.0, =C*H*Ar), 6.48 (1 H, dt, *J* 16.0, 8.0, CH_2CH=), 7.40 (2 H, d, *J* 8.5) and 8.15 (2 H, d, *J* 8.5, Ar), 9.65 (1 H, d, *J* 2.5, CHO); δ_C (100 MHz; $CDCl_3$) –1.7 (q), –1.6 (q), 25.0 (t), 25.8 (q), 35.7 (s), 84.7 (d), 124.1 (d), 125.8 (d), 127.7 (d), 132.1 (d), 144.6 (s), 146.1 (s), 203.8 (d); *m/z* (CI^+) 353 (MNH_4^+, 13%), 298 (13), 295 (7), 224 (41), 149 (100), 94 (26); HRMS (CI^+) 353.1909 (MNH_4^+. $C_{17}H_{29}N_2O_4Si$ requires 353.1897).

2-Allyldimethylsilanyloxy-3,3-dimethylbutyraldehyde (24)

Following the general procedure for DIBAL reduction, silylcyanohydrin **15** (500 mg, 2.38 mmol) afforded the *title compound* (**24**, 320 mg, 64%) as a colourless oil which was sufficiently pure to use directly in the next reaction. R_f 0.57 (petrol/ether, 10:1); ν_{max}/cm^{-1} (film) 2960s, 1734s, 1632m, 1366m, 1256m, 1100m, 898m; δ_H (400 MHz; $CDCl_3$) 0.10 (6 H, s, $Si(CH_3)_2$), 0.94 (9 H, s, $C(CH_3)_3$), 1.61 (2 H, d, *J* 8.0, $SiCH_2$), 3.51 (1 H, d, *J* 3.0, CHCO), 4.77–4.97 (2 H, m, $=CH_2$), 5.67–5.87 (1 H, m,

C*H*=CH_2), 9.60 (1 H, d, *J* 3.0, CHO); δ_C (100 MHz; $CDCl_3$) –2.2 (q), –2.0 (q), 24.6 (t), 25.7 (q), 35.6 (s), 84.4 (d), 114.1 (t), 133.5 (d), 204.3 (d); *m/z* (CI^+) 232 (MNH_4^+, 6%), 185 (6), 173 (100), 131 (29), 87 (44); HRMS (CI^+) 232.1726 (MNH_4^+. $C_{11}H_{26}NO_2Si$ requires 232.1733).

(2*R*)- and (2*S*)-2-Allyldiphenylsilanyloxy-2-[(2*R*,6*S*)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl]acetonitrile (31) and (32)

To a stirred solution of cyanohydrins **29** and **30** (1.60 g, 6.93 mmol) in anhydrous DMF (53 mL) were added successively DMAP (45 mg, 0.37 mmol), triethylamine (3.92 mL, 38.7 mmol), and a freshly prepared solution of allylchlorodiphenylsilane (theor. 3.02 g, 11.7 mmol) in THF (45 mL) *via* cannula. The reaction mixture was heated at 60 °C for 6 h, then cooled to RT and partitioned between water (100 mL) and ether (50 mL). The aqueous component was extracted with ether (3 × 50 mL) and the combined organic layers were washed successively with brine (100 mL) and water (60 mL) and then dried over magnesium sulphate. The solvent was removed *in vacuo* and the residue purified by column chromatography (petrol/ether, 9:1) to afford the *title compounds* (**31** and **32**, 3:2 ratio, 2.52 g, 80%) as a colourless oil. R_f 0.56 (petrol/ether, 1:1); ν_{max} (film)/cm^{-1} 3072w, 2998w, 1631w, 1590w, 1429m, 1376w, 1119s, 1037m, 992w, 877w, 849w, 813w, 768w, 737m, 700s; δ_H (400 MHz; $CDCl_3$) 1.27 (3 H, s, CH_3, **31**), 1.29 (3 H, s, CH_3, **32**), 1.29 (3 H, s, CH_3, **31**), 1.30 (3 H, s, CCH_3, **32**), 2.19 (2 H, d, *J* 8.0, $SiCH_2$, **31**), 2.23–2.37 (2 H, m, $SiCH_2$, **32**), 3.15 (3 H, s, OCH_3, **31**), 3.21 (3 H, s, OCH_3, **32**), 3.28 (3 H, s, OCH_3, **31**), 3.32 (3 H, s, OCH_3, **32**), 3.47 (1 H, t, *J* 11.0, C*H*H′, **32**), 3.68 (1 H, dd, *J* 11.0, 3.0, CH*H*′, **32**), 3.71 (1 H, dd, *J* 11.0, 3.0, C*H*H′, **31**), 3.85 (1 H, t, *J* 11.0, CH*H*′, **31**), 4.01 (1 H, app. dd, *J* 5.5, 3.0, C*H*CH(OSi), **31**), 4.16 (1 H, app. dd, *J* 8.0, 3.0, C*H*CH(OSi), **32**), 4.34 (1 H, d, *J* 8.0, CH(OSi), **32**), 4.49 (1 H, d, *J* 5.5, CH(OSi), **31**), 4.93–5.07 (4 H, m, 2 × =CH_2, **31**/**32**), 5.74–5.93 (2 H, m, 2 × C*H*=CH_2, **31**/**32**), 7.31–7.53 (12 H, m) and 7.57–7.67 (8 H, m, 4 × Ph, **31**/**32**); δ_C (100 MHz; $CDCl_3$) 17.4–17.5 (4 × q), 21.3 (t), 23.0 (t), 48.1–48.3 (4 × q), 59.3 (t), 60.4 (t), 63.3 and 63.4 (2 × d), 67.8 (d), 68.2 (d), 98.1 and 98.2 (2 × s), 99.6 and 99.7 (2 × s), 115.2 (t), 116.3 (t), 116.9 and 117.7 (2 × s), 127.7–153.0 (overlapping); *m/z* (FI^+) 453 (M^+, 5%), 412 (100), 380 (10); HRMS (FI^+) 453.1979 (M^+. $C_{25}H_{31}NO_5Si$ requires 453.1966).

(2*R*)- and (2*S*)-2-(*E*-Cinnamyl)diphenylsilyloxy-2-[(2*R*,6*S*)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl]acetonitrile (43) and (44)

To a stirred, degassed solution of silylcyanohydrins **31** and **32** (180 mg, 0.40 mmol) and styrene (0.046 mL, 0.40 mmol) in dichloromethane (7 mL) at RT was added Grubbs' second generation catalyst (26 mg, 0.030 mmol). The reaction mixture was heated at reflux for 18 h then cooled to RT. The solvent was removed *in vacuo* and the residue purified by column chromatography (petrol/ether, 9:1) to afford the *title compounds* (**43** and **44**, 3:2 ratio, 107 mg, 51%) as a colourless oil. R_f 0.29 (petrol/ether, 2:1); ν_{max} (film)/cm^{-1} 3023m, 1591w, 1429m, 1376m, 1120s, 1037m, 964m, 878m, 850m, 701s; δ_H (400 MHz; $CDCl_3$) 1.30 (3 H, s, CH_3, **43**), 1.32 (3 H, s, CH_3, **44**), 1.32 (3 H, s, CH_3, **43**), 1.33 (3 H, s, CH_3, **44**), 2.35 (2 H, d, *J* 7.5, $SiCH_2$, **43**), 2.40–2.57 (2 H, m, $SiCH_2$, **44**), 3.14 (3 H, s, OCH_3, **43**), 3.20 (3 H, s, OCH_3, **44**), 3.29 (3 H, s, OCH_3, **43**), 3.34 (3 H, s, OCH_3, **44**), 3.50 (1 H, t, *J* 11.0, C*H*H′, **44**), 3.72 (2 H, dd, *J* 11.0, 3.0, 2 × CH*H*′, **43**/**44**), 3.88 (1 H, t, *J* 11.0, C*H*H′, **43**), 4.05 (1 H, ddd, *J* 11.0, 5.5, 3.0, C*H*CH(OSi), **43**), 4.21 (1 H, ddd, *J* 11.0, 8.0, 3.0, C*H*CH(OSi), **44**), 4.41 (1 H, d, *J* 8.0, CH(OSi), **44**), 4.54 (1 H, d, *J* 5.5, CH(OSi), **43**), 6.18–6.45 (4 H, m, 2 × CH=CH, **43**/**44**), 7.16–7.23 (2 H, m), 7.24–7.33 (8 H, m), 7.39–7.57 (12 H, m) and 7.62–7.76 (8 H, m, 6 × Ph, **43**/**44**); δ_C (100 MHz; $CDCl_3$) 17.4, 17.5, 17.5 and 17.6 (4 × q), 20.8 and 22.4 (2 × t), 48.1–48.3 (4 × q), 59.3 and 60.5 (2 × t), 63.4 and 63.4 (2 × d), 67.9 and 68.3 (2 × d), 98.2 and 98.2 (2 × s), 99.7 and 99.8 (2 × s), 116.9 and 117.7 (2 × s), 123.6–135.1 (overlapping); *m/z* (FI^+) 316 ($C_{21}H_{20}OSi^+$, PhCH=$CHCH_2Si(OH)Ph_2$, 100%), 302 (25); HRMS (FI^+) 316.1291 ($C_{21}H_{20}OSi$ requires 316.1277).

Typical dibenzylation procedure, used to prepare 37/38 and 49/50

To a stirred suspension of sodium hydride (0.166 g, 60% suspension in mineral oil, 4.15 mmol) in DMF (2.8 mL) at 0 °C was added a solution of the diol (**35**/**36** or **47**/**48**, 0.95 mmol) in DMF (2.8 mL). The mixture was stirred for 1 h then tetrabutylammonium iodide (23 mg, 0.058 mmol) was added, followed by dropwise addition of benzyl bromide (0.28 mL, 2.35 mmol). The mixture was allowed to reach RT, stirred for a further 16 h, partitioned between water (20 mL) and dichloromethane (50 mL) and the aqueous layer extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with brine (3 × 50 mL) and dried over magnesium sulphate. The residue was concentrated *in vacuo* and purified by column chromatography (petrol/ether, 9:1) to afford the benzyl ethers **37**/**38** or **49**/**50**.

(1*R*,2*S*)- and (1*S*,2*R*)-1,2-Bis(benzyloxy)-1-[(2*R*,5*R*,6*R*)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl]pent-4-ene (37) and (38)

Pale yellow oil (**37** and **38**, 3:2 ratio, 264 mg, 65% on a 0.891 mmol scale). R_f 0.63 (petrol/ether, 1:1); ν_{max} (film)/cm^{-1} 3065m, 2947s, 1497m, 1455m, 1211w, 1122s, 949w, 916w, 879m, 736m, 698s; δ_H (400 MHz; $CDCl_3$) 1.29 (3 H, s, CH_3, **37**), 1.30 (6 H, s, 2 × CH_3, **38**), 1.33 (3 H, s, CH_3, **37**), 2.32–2.58 (4 H, m, 2 × CH_2CH=, **37**/**38**), 3.21 (3 H, s, OCH_3, **38**), 3.25 (3 H, s, OCH_3, **37**), 3.29 (3 H, s, OCH_3, **38**), 3.30 (3 H, s, OCH_3, **37**), 3.50–3.56 (3 H, m, C*H*(OBn)C*H*(OBn) and C*H*H′, **37**), 3.60–3.70 (3 H, m, C*H*(OBn)C*H*(OBn) and C*H*H′, **38**), 3.70 (1 H, t, *J* 11.3, CH*H*′, **37**), 3.90 (1 H, t, *J* 11.2, CH*H*′, **38**), 4.19 (1 H, dt, *J* 11.2, 3.5, C*H*(O)CH_2O, **38**), 4.22 (1 H, ddd, *J* 11.3, 6.2, 3.1, C*H*(O)CH_2O, **37**), 4.55 (1 H, d, *J* 11.7, C*H*HPh, **37**), 4.59 (1 H, d, *J* 11.5) and 4.65 (1 H, d, *J* 11.5, CH_2Ph, **38**), 4.69 (1 H, d, *J* 11.2, C*H*H′Ph, **38**), 4.69 (1 H, d, *J* 11.7, CH*H*′Ph, **37**), 4.80 (1 H, d, *J* 11.2, CH*H*′Ph, **38**), 4.82 (2 H, s, CH_2Ph, **37**), 5.01–5.14 (4 H, m, 2 × =CH_2, **37**/**38**), 5.73–5.89 (2 H, m, 2 × C*H*=CH_2, **37**/**38**), 7.26–7.41 (20 H, m, 2 × Ph, **37**/**38**); δ_C (100 MHz; $CDCl_3$); 17.6 (q), 17.6 (q), 17.9 (q), 17.9 (q), 34.5 (t), 35.1 (t), 48.0 (q), 48.0 (q), 48.1 (q), 48.2 (q), 60.7 (2 × t), 67.8 (d), 69.1 (d), 72.0 (2 × t), 74.2 (t), 74.6 (t), 78.3 and 78.9 (2 × d), 78.9 and 81.0 (2 × d), 97.9 (2 × s), 99.1 (s), 99.2 (s), 117.1 (t), 117.4 (t), 127.4–128.3 (overlapping), 134.8 (d), 135.1 (d), 138.2 (s), 138.6 (2 × s), 138.7 (s); *m/z* (ESI^+) 515 (MNH_4^+·MeCN,

100%), 479 (MNa^+, 10%); HRMS (ESI^+) 479.2390 (MNa^+. $C_{27}H_{36}NaO_6$ requires 479.2404).

(1*R*,2*S*,3*S*)- and (1*S*,2*R*,3*R*)-1,2-Bis(benzyloxy)-1-[(2*R*,5*R*,6*R*)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl]-3-phenylpent-4-ene (49) and (50)

Pale yellow oil (**49** and **50**, 3:2 ratio, 70 mg, 66% on a 0.199 mmol scale). R_f 0.71 (petrol/ether, 1:1); ν_{max} (film)/cm^{-1} 3063w, 3029m, 2475s, 2832m, 1637w, 1602w, 1496m, 1454s, 1374s, 1261w, 1211m, 1121s, 949w, 917w, 878m, 735m, 699s; δ_H (400 MHz; $CDCl_3$) 1.29 (3 H, s, 2 × CH_3, **49**/**50**), 1.31 (3 H, s, CH_3, **49**), 1.37 (3 H, s, CH_3, **50**), 3.16 (3 H, s, OCH_3, **49**), 3.24 (3 H, s, OCH_3, **50**), 3.29 (3 H, s, OCH_3, **49**), 3.34 (3 H, s, OCH_3, **50**), 3.48–3.51 (1 H, m, C*H*(OBn)CH(O), **50**), 3.60–3.80 (6 H, m, 2 × C*H*PhC*H*(OBn) and C*H*H′, **49**/**50**), 3.86 (1 H, dd, *J* 6.8, 5.5, C*H*(OBn)CH(O), **49**), 3.94–4.00 (2 H, m, 2 × CH*H*′, **49**/**50**), 4.14–4.19 (1 H, m, C*H*(O)CH_2O, **49**), 4.23 (1 H, ddd, *J* 11.1, 5.4, 3.0, C*H*(O)CH_2O, **50**), 4.52–4.77 (8 H, 4 × C*H*$_2$Ph, **49**/**50**), 5.01–5.08 (4 H, m, =CH_2, **49**/**50**), 6.12–6.21 (2 H, m, 2 × C*H*=CH_2, **49**/**50**), 7.08–7.45 (30 H, m, 6 × Ph, **49**/**50**); δ_C (100 MHz; $CDCl_3$) 17.6–18.0 (4 × q), 48.0 (2 × q), 48.3 (2 × q), 52.0 (d), 52.5 (d), 60.3 (2 × t), 68.4 (d), 68.5 (d), 73.5 (t), 74.2 (t), 74.4 (t), 74.6 (t), 78.7 (d), 81.3 (2 × d), 82.6 (d), 97.9 and 98.0 (2 × s), 99.2 and 99.3 (2 × s), 116.0 (t), 116.2 (t), 126.6–129.2 (overlapping), 138.7 (2 × s), 138.9 (2 × s), 139.6 (d), 139.7 (d), 141.0 (2 × s); *m*/*z* (ESI^+) 591 (MNH_4^+·CH_3CN, 100%).

Typical ozonolysis procedure, used to prepare aldehydes 39/40 and 51/52

Ozone was bubbled through a solution of the alkene (**37**/**38** or **49**/**50**, 0.081 mmol) in dichloromethane (5 mL) at −78 °C until a blue colour persisted. Oxygen was then bubbled through the solution until the blue colour dissipated. Dimethy sulphide (0.50 mL, 9.52 mmol) was then added, the mixture was warmed to RT and stirring continued for 5 h. The solution was concentrated *in vacuo* and then purified by column chromatography (petrol/ether, 2:1) to afford the aldehydes **39**/**40** or **51**/**52**.

(3*S*,4*R*)- and (3*R*,4*S*)-3,4-Bis(benzyloxy)-4-[(2*R*,5*R*,6*R*)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl]butanal (39) and (40)

Pale yellow oil (**39** and **40**, 3:2 ratio, 232 mg, 89% on a 0.570 mmol scale). R_f 0.37 (**40**) and 0.30 (**39**) (petrol/ether, 1:1); ν_{max} (film)/cm^{-1} 2948m, 1742s, 1497w, 1455m, 1374m, 1211s, 1123s, 951m, 738w, 699m; δ_H (400 MHz; $CDCl_3$); 1.29 (3 H, s, CH_3, **40**), 1.30 (3 H, s, CH_3, **40**), 1.30 (3 H, s, CH_3, **39**), 1.33 (3 H, s, CH_3, **39**), 2.62–2.80 (3 H, m, C*H*H′CO, **39** and CH_2CO, **40**), 2.92 (1 H, dd, *J* 17.3, 4.5, CH*H*′CO, **39**), 3.22 (3 H, s, OCH_3, **40**), 3.26 (3 H, s, OCH_3, **39**) 3.28 (3 H, s, OCH_3, **40**), 3.28 (3 H, s, OCH_3, **39**), 3.43 (1 H, dd, *J* 11.4, 3.1, C*H*H′O, **39**), 3.54 (1 H, dd, *J* 5.8, 4.5, C*H*(OBn)CH(O), **39**), 3.63 (1 H, t, *J* 4.7, C*H*(OBn)CH(O), **40**), 3.70 (1 H, dd, *J* 11.3, 3.3, C*H*H′O, **40**), 3.75 (1 H, t, *J* 11.4, CH*H*′O, **39**), 3.89 (1 H, t, *J* 11.3, CH*H*′O, **40**), 4.09 (1 H, dt, *J* 7.5, 4.5, C*H*(OBn)CH_2, **39**), 4.16–4.25 (3 H, m, C*H*(O)CH_2, **39** and C*H*(OBn)CH_2 and C*H*(O)CH_2, **40**), 4.51 (1 H, d, *J* 11.8) and 4.54 (1 H, d, *J* 11.8, C*H*$_2$Ph, **39**), 4.58 (1 H, d, *J* 11.4, C*H*H′Ph, **40**), 4.61 (1 H, d, *J* 11.6, C*H*H′Ph, **39**) 4.62 (1 H, d, *J* 11.4, CH*H*′Ph, **40**), 4.63 (1 H, d, *J* 11.2, C*H*H′Ph, **40**), 4.73 (1 H, d, *J* 11.6, CH*H*′Ph, **39**), 4.74 (1 H, d, *J* 11.2, CH*H*′Ph, **40**), 7.24–7.38 (20 H, m, 2 × Ph, **39**/**40**), 9.67 (1 H, d, *J* 1.0, CHO, **39**), 9.70 (1 H, dd, *J* 2.5, 1.3, CHO, **40**); δ_C (100 MHz; $CDCl_3$); 17.6 (2 × q), 17.9 (2 × q), 44.8 (t), 45.2 (t), 48.0 (2 × q), 48.2 (2 × q), 60.1 (t), 60.7 (t), 68.0 (d), 68.5 (d), 72.4 (t), 72.5 (t), 73.2 (d), 74.0 (t), 74.1 (t), 74.6 (d), 77.9 (d), 80.6 (d), 97.9 (s), 98.0 (s), 99.2 (s), 99.3 (s), 127.7–128.4 (overlapping), 137.7 (s), 137.8 (s), 137.8 (s), 138.0 (s), 200.7 (d), 200.9 (d); *m*/*z* (ESI^+) 549 (MNH_4^+·CH_3CN·MeOH, 100%), 513 (MNa^+·MeOH, 60%); HRMS (ESI^+) 513.2452 (MNa^+·MeOH. $C_{27}H_{38}NaO_8$ requires: 513.2459).

(2*S*,3*S*,4*R*)- and (2*R*,3*R*,4*S*)-3,4-Bis(benzyloxy)-4-[(2*R*,5*R*,6*R*)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxan-2-yl]-2-phenylbutanal (51) and (52)

Colourless oil (**51** and **52**, 3:2 ratio, 57 mg, 81% on a 0.132 mmol scale). R_f 0.48 (petrol/ether, 1:1); ν_{max} (film)/cm^{-1} 2948m, 2833w, 1723s, 1602w, 1496w, 1496m, 1454m, 1267w, 1120s, 951w, 878m, 737m, 700s; δ_H (400 MHz; $CDCl_3$) 1.29 (6 H, s, 2 × CH_3, **51**/**52**), 1.30 (6 H, s, 2 × CH_3, **51**/**52**), 3.20 (3 H, s, OCH_3, **51**), 3.24 (3 H, s, OCH_3, **52**), 3.27 (3 H, s, OCH_3, **51**), 3.31 (3 H, s, OCH_3, **52**), 3.31–4.15 (10 H, m, C*H*Ph, C*H*(OBn)C*H*(O)C*H*$_2$, **51**/**52**), 4.22–4.28 (2 H, m, C*H*(OBn)CHPh, **51**/**52**), 4.30–4.36 (2 H, m) and 4.53–4.70 (6 H, m, 4 × C*H*$_2$Ph, **51**/**52**), 7.02–7.40 (30 H, m, Ph, **51**/**52**), 9.65 (1 H, d, *J* 1.4, CHO, **51**), 9.69 (1 H, d, *J* 1.9, CHO, **52**); δ_C (100 MHz; $CDCl_3$) 17.6–17.9 (4 × q), 48.0–48.3 (4 × q), 60.1 (t), 60.3 (t), 60.1, 60.5, 68.4, 68.9, 77.8, 78.2, 79.7, 79.8 (8 × d), 74.0–74.4 (4 × t), 97.8–99.2 (4 × s), 127.6–130.7 (overlapping), 133.8 (2 × s), 137.9–138.2 (4 × s), 199.2 and 199.7 (2 × d); *m*/*z* (ESI^+) 593 (MNH_4^+·CH_3CN, 60%), 449 (20), 242 (20); HRMS (ESI^+) 557.2499 (MNa^+. $C_{32}H_{38}NaO_7$ requires 557.2510).

i J. Robertson, M. J. Hall, P. M. Stafford and S. P. Green, *Org. Biomol. Chem.* 2003, **1**, 3758–3767.

ii J. Robertson, P. M. Stafford and S. J. Bell, *J. Org. Chem.* 2005, **70**, 7133–7148.

iii(a) K. Kahle, P. J. Murphy, J. Scott and R. Tamagni, *J. Chem. Soc., Perkin Trans. 1* 1997, 997–999; (b) C. Kim, S. K. Choi, E. Park and I. Jung, *J. Korean Chem. Soc.* 1997, **41**, 88–97.

ivL. Meerpoel and G. Hoornaert, G. *Synthesis* 1990, 905–908 and references therein.