**SUPPORTING INFORMATION**

**Facile and Chemoselective Rhodium-Catalysed Intramolecular Hydroacylation of \(\alpha,\alpha\)-Disubstituted 4-Alkylidenecyclopropanals**

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**General.** Otherwise noted, all reactions were carried out in flame-dried glassware under dry nitrogen atmosphere. The solvents were purified either with the solvent purification system Pure Solv MD-6 (THF, Et\(_2\)O, CH\(_2\)Cl\(_2\), benzene, toluene, hexane) or by distillation over the drying agents indicated and were transferred under N\(_2\): 1,2-DCE (CaH\(_2\)), acetone (Na\(_2\)SO\(_4\)). Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on a Bruker DRX 500 spectrometer in CDCl\(_3\); chemical shifts (\(\delta\)) are given in ppm relative TMS and were converted to the TMS scale using the solvent signals as references (CDCl\(_3\): \(\delta\)C = 77.0 ppm; residual CHCl\(_3\) in CDCl\(_3\): \(\delta\)H = 7.24 ppm). IR: PerkinElmer Spectrum 100 FT-IR spectrometer, wavenumbers (\(\tilde{\nu}\)) in cm\(^{-1}\). HRMS at the University of Liverpool: VG7070E (CI), micromass LCT mass spectrometer (ES+), except for compounds 2, 4a, 5, 7, 10, and 15d whose HMRS spectra were obtained from the EPSRC National Mass Spectrometry Service Centre at Swansea. Melting points: Griffin melting point apparatus (not corrected). Elemental analyses: University of Liverpool. All commercially available compounds were used as received. Compounds 16 and 22 are known compounds and were prepared according to literature.\(^1\)

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**Preparation of compound 1**

\[ \text{Ph-CO}_2\text{Me} \xrightarrow{a} \text{Ph-CO}_2\text{Me} \xrightarrow{b} \text{Ph-CO}_2\text{Me} \xrightarrow{c} \text{Ph-CH}_2\text{OH} \xrightarrow{d} \text{Ph-CHO} \]

\( ^a \) 1) NaH, methyl phenylacetate, DMF, 2) 16, Pd\(_2\)(dba)\(_3\), dppe, DMF, THF, 60 °C, 86%.  \( ^b \) LiHMDS, methylallyl bromide, THF, -78 °C to r.t., 89%.  \( ^c \) LiAlH\(_4\), Et\(_2\)O, r.t., 84%.  \( ^d \) (COCl)\(_2\), DMSO, Et\(_3\)N, CH\(_2\)Cl\(_2\), -78 °C, 94%.

**Compound 17.** Under N\(_2\), methyl phenylacetate (1.27 mL, 8.82 mmol) was added at 0 °C to a suspension of sodium hydride (336 mg, 8.40 mmol) in DMF (16 mL) and the mixture was stirred at room temperature for 40 minutes. In another flask, tosylate 16 (1 g, 4.20 mmol) was added to a suspension of tris(dibenzylideneacetone)dipalladium (115 mg, 0.126 mmol) and dppe (100 mg, 0.252 mmol) in THF (24 mL) and the mixture was stirred at room temperature for 30 minutes. The palladium complex was cannulated to the enolate and the resulting mixture was stirred at 60 °C for 3 hours. The mixture was quenched with water (25 mL) and extracted with Et\(_2\)O (3 \( \times \) 20 mL). The organic layers were dried over Na\(_2\)SO\(_4\), filtered and concentrated. Purification by flash chromatography (PE/Et\(_2\)O, 50/1) gave 17 as a pale yellow oil (778 mg, 86%). 1H NMR (500 MHz, CDCl\(_3\)): \( \delta \) = 7.40–7.25 (m, 5H), 5.80–5.71 (m, 1H), 3.77 (t, \( J \) = 7.7 Hz, 2H), 3.68 (s, 3H), 3.09–2.93 (m, 1H), 2.76–2.63 (m, 1H), 1.14–0.98 (m, 3H), 0.97–0.88 (m, 1H); 13C NMR (125 MHz, CDCl\(_3\)): \( \delta \) = 174.1, 138.9, 128.5 (2C), 128.0 (2C), 127.2, 124.0, 114.8, 51.9, 51.4, 35.8, 2.3, 1.9; IR (neat): \( \nu \sim \) 3030, 2980, 2951, 2845, 1734, 1602, 1495, 1435, 1266, 1223, 1157, 836, 729, 697 cm\(^{-1}\); MS (CI): \( m/z \) (rel. intensity): 234 (100), 217 (17); HRMS (CI) calcd for (C\(_{14}\)H\(_{16}\)O\(_2\) + NH\(_4\))^+: 234.14940; found: 234.14907; elemental analysis (%) calcd for C\(_{14}\)H\(_{16}\)O\(_2\): C 77.75, H 7.46; found: C 77.86, H 7.48.

**Compound 18.** LiHMDS (1M in THF, 0.90 mL, 0.90 mmol) was added dropwise via syringe to 17 (150 mg, 0.69 mmol) in 5 mL THF at -78 °C under N\(_2\). After stirring at that temperature for 1h, methylallyl bromide (91 \( \mu \)L, 0.90 mmol) was added via microsyringe. The mixture was allowed to slowly warm to room temperature overnight. The mixture was then quenched with a saturated solution of NH\(_4\)Cl (5 mL) and extracted with EtOAc (3 \( \times \) 10 mL). The organic layers were dried over Na\(_2\)SO\(_4\), filtered and concentrated. Purification by flash chromatography (PE/EtOAC, 30/1) gave 18 as a colourless oil (167 mg, 89%). 1H NMR (500 MHz, CDCl\(_3\)): \( \delta \) = 7.31–7.23 (m, 4H), 7.23–7.18 (m, 1H), 5.57–5.49 (m, 1H), 4.82–4.80 (m, 1H), 2.97–2.93 (m, 2H), 2.88 (d, \( J \) = 13.7 Hz, 1H), 2.74 (d, \( J \) = 13.7 Hz, 1H), 1.40 (s, 3H), 1.01–0.90 (m, 2H), 0.89–0.80 (m, 1H), 0.80–0.72 (m, 1H); 13C NMR (125 MHz, CDCl\(_3\)): \( \delta \) = 176.1, 142.5, 141.8, 128.2 (2C), 126.7, 126.6 (2C), 125.5, 115.2, 113.1, 53.8, 51.9, 42.5, 37.0, 23.8, 2.7, 1.9; IR (neat): \( \nu \) = 3058, 3023, 2980, 2951, 2845, 1734, 1602, 1495, 1435, 1266, 1223, 1157, 836, 729, 697 cm\(^{-1}\); MS (ES\(^+\)): \( m/z \) (rel. intensity): 293 (100); HRMS (ES\(^+\)) calcd for (C\(_{18}\)H\(_{22}\)O\(_2\) + Na\(^+\)): 293.1517; found: 293.1518; elemental analysis calcd (%) for C\(_{18}\)H\(_{22}\)O\(_2\): C 79.96, H 8.20; found: C 80.04, H 8.47.
**Compound 19.** Under N\textsubscript{2}, ester 18 (154 mg, 0.57 mmol) in Et\textsubscript{2}O (2.8 mL) was added to a suspension of lithium aluminium hydride (11 mg, 0.285 mmol) in Et\textsubscript{2}O (4 mL) at 0 °C. After stirring for 20 minutes at room temperature, lithium aluminium hydride (11 mg, 0.285 mmol) was added at 0 °C. After stirring for another 30 minutes at room temperature, a saturated aqueous solution of Na\textsubscript{2}SO\textsubscript{4} was added dropwise, first at 0 °C then at room temperature, until a white precipitate appeared. The mixture was filtered through a pad of celite and concentrated. Purification by flash chromatography (PE/EtOAc, 30/1 \rightarrow 15/1) afforded 19 as a colourless oil (116 mg, 84%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta = 7.37–7.34 \) (m, 2H), 7.33–7.28 (m, 2H), 7.21–7.16 (m, 1H), 5.69–5.63 (m, 1H), 4.77–4.74 (m, 1H), 4.62–4.59 (m, 1H), 3.85 (d, \(J = 6.7 \) Hz, 2H), 2.72 (dd, \(J = 14.1, J = 6.7, J = 1.4 \) Hz, 1H), 2.63 (dd, \(J = 14.1, J = 7.7, J = 1.1 \) Hz, 1H), 2.47 (s, 2H), 1.43 (t, \(J = 6.7 \) Hz, 1H (OH)), 1.30 (s, 3H), 1.04–0.98 (m, 2H), 0.97–0.92 (m, 2H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta = 144.1, 143.1, 128.2 \) (2C), 127.0 (2C), 126.0, 124.6, 114.5, 114.2, 67.4, 46.2, 44.8, 38.3, 24.5, 2.8, 1.8; IR (neat): \(\tilde{\nu} = 3436 \) (br), 3055, 2978, 2922, 1498, 1445, 1375, 1024, 964, 937, 764, 697 cm\textsuperscript{-1}; MS (ES\textsuperscript{+}): \(m/z\) (rel. intensity): 265 (100); HRMS (ES\textsuperscript{+}) calcd for (C\textsubscript{17}H\textsubscript{22}O + Na\textsuperscript{+}): 265.1568; found: 265.1560; elemental analysis calcd (%) for C\textsubscript{17}H\textsubscript{22}O: C 84.25, H 9.15; found: C 84.43, H 8.90.

**Compound 1.** Under N\textsubscript{2}, dimethyl sulfoxide (0.18 mL, 2.60 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (0.5 mL) was added to a solution of oxalyl chloride (0.11 mL, 1.30 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (5 mL) at –78 °C. After 10 minutes stirring at –78 °C, a solution of 19 (243 mg, 1 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (1 mL) was added. After 20 minutes stirring at –78 °C, triethylamine (0.70 mL, 5 mmol) was added rapidly and the mixture was stirred at room temperature during 20 minutes. A saturated solution of NH\textsubscript{4}Cl (10 mL) was added to the reaction mixture which was then extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 \times 10 mL). The organic layers were dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated. Purification by flash chromatography PE/EtOAc, 80/1 gave 1 as colourless oil (225 mg, 94%). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta = 9.54 \) (s, 1H), 7.37–7.32 (m, 2H), 7.29–7.21 (m, 3H), 5.65–5.59 (m, 1H), 4.81–4.78 (m, 1H), 4.62–4.58 (m, 1H), 2.89 (d, \(J = 7.2 \) Hz, 2H), 2.74 (d, \(J = 14.2 \) Hz, 1H), 2.67 (d, \(J = 14.4 \) Hz, 1H), 1.37 (s, 3H), 1.04–0.94 (m, 2H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta = 202.3, 141.3, 138.6, 128.6 \) (2C), 127.9 (2C), 127.3, 126.0, 115.3, 112.5, 57.6, 41.0, 34.8, 24.3, 2.8, 2.0; IR (neat): \(\tilde{\nu} = 3057, 2979, 2709, 1721, 1643, 1544, 1495, 1446, 1377, 1091, 1030, 1002, 967, 930, 894, 759, 697 \) cm\textsuperscript{-1}; MS (CI): \(m/z\) (rel. intensity): 259 (17), 258 (100), 242 (12), 241 (69), 173 (14); elemental analysis calcd (%) for C\textsubscript{17}H\textsubscript{20}O: C 84.16, H 9.83; found: C 83.20, H 8.44.
Preparation of compound 3a

a NaHMDS, MeI, THF, r.t., 79%. b LiAlH4, Et2O, r.t., 95%. c (COCl)2, DMSO, Et3N, CH2Cl2, –78 °C, 91%.

Compound 20. Under N2, NaHMDS (407 mg, 2.22 mmol) was added as solid in one portion to a solution of 17 (320 mg, 1.48 mmol) in THF (15 mL) at 0 °C. The mixture was stirred at room temperature during 1 hour. Then iodomethane (0.55 mL, 8.88 mmol) was added via syringe and the mixture was stirred for another 4 hours at room temperature. The reaction mixture was quenched with a saturated solution of NH4Cl (10 mL) and extracted with EtOAc (310 mL). The organic layers were dried over Na2SO4, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 60/1) gave 20 as a colourless oil (270 mg, 79%). 

$\delta$H NMR (500 MHz, CDCl3): $\delta$ = 7.32–7.31 (m, 4H), 7.24–7.20 (m, 1H), 5.62-5.56 (m, 1H), 3.64 (s, 3H), 2.94 (dd, $J$ = 13.2 Hz, $J$ = 7.2 Hz, 1H), 2.77 (dd, $J$ = 13.2 Hz, $J$ = 7.6 Hz, 1H), 1.52 (s, 3H), 1.06–0.98 (m, 2H), 0.95–0.84 (m, 2H); 13C NMR (125 MHz, CDCl3): $\delta$ = 176.5, 143.5, 128.3 (2C), 126.7, 126.0 (2C), 125.6, 113.4, 52.1, 50.5, 41.6, 22.7, 2.8, 1.7; IR (neat): $\nu$ ~ = 3053, 3023, 2980, 2950, 1729, 1601, 1497, 1446, 1434, 1377, 1268, 1227, 1203, 1147, 1120, 1074, 1031, 986, 968, 935, 857, 810, 764, 732, 697 cm$^{-1}$; MS (ES+): m/z (rel. intensity): 253 (100); HRMS (ES+) calcd for (C15H18O2 + Na)$^+$: 253.1204; found: 253.1194; elemental analysis (%)
calcd for C15H18O2: C 78.23, H 7.88; found: C 77.32, H 7.74.

Compound 21. This compound was prepared from 20 (117 mg, 0.508 mmol) according to the procedure described for the preparation of 19. Colourless oil (81 mg, 79%). 

$\delta$H NMR (500 MHz, CDCl3): $\delta$ = 7.37 (d, $J$ = 7.1 Hz, 2H), 7.33 (t, $J$ = 7.1 Hz, 2H), 7.20 (t, $J$ = 7.1 Hz, 1H), 5.61–5.53 (m, 1H), 3.76 (d, $J$ = 10.8 Hz, 1H), 3.60 (dd, $J$ = 10.8 Hz, $J$ = 4.7 Hz, 1H), 2.63 (dd, $J$ = 13.9 Hz, $J$ = 6.5 Hz, 1H), 2.47 (dd, $J$ = 13.9 Hz, $J$ = 7.9 Hz, 1H), 1.33 (s, 3H), 1.30–1.22 (br s, 1H), 1.04–0.82 (m, 4H); 13C NMR (125 MHz, CDCl3): $\delta$ = 144.8, 128.4 (2C), 126.7 (2C), 126.2, 124.5, 113.9, 71.8, 43.9, 40.9, 21.9, 2.8, 1.7; IR (neat): $\nu$ = 3367 (br), 3053, 2977, 2926, 2871, 1601, 1497, 1445, 1373, 1296, 1156 1024, 966, 935, 830, 760, 709, 690 cm$^{-1}$; MS (CI): m/z (rel. intensity): 221 (15), 220 (100), 185 (5); HRMS (CI) calcd for (C14H18O + NH4)$^+$: 220.1696; found: 220.1692.

Compound 3a. This compound was prepared from 21 (50 mg, 0.25 mmol) according to the procedure described for the preparation of 1. Colourless oil (45 mg, 91%). 

$\delta$H NMR (500 MHz, CDCl3): $\delta$ = 9.56 (s, 1H), 7.39–7.36 (m, 2H), 7.31–7.25 (m, 3H), 5.61–5.55 (m, 1H), 2.80 (d, $J$ = 7.2 Hz, 2H), 1.44 (s, 3H), 1.08-0.98 (m, 2H); 13C NMR (125 MHz, CDCl3): $\delta$ = 202.4, 139.8, 128.7 (2C), 127.2 (3C), 125.9, 112.6, 54.4, 38.4, 19.0, 2.9, 1.7; IR (neat): $\nu$ = 3056, 2979, 2934, 2806, 2707, 1722, 1600, 1495, 1446, 1389, 1372, 1267, 1075, 1029, 967, 935, 837, 760, 733, 698 cm$^{-1}$; MS (CI): m/z (rel. intensity): 219 (12), 218 (100), 201 (3), 200 (1); HRMS (CI) calcd for (C14H16O + NH4)$^+$: 218.1539; found: 218.1539.
Preparation of compound 3b

\[ \text{22} \xrightarrow{a} \text{MeO}- \text{C} \xrightarrow{b} \text{CO}- \text{Me} \xrightarrow{c} \text{23} \xrightarrow{d} \text{24} \xrightarrow{e} \text{25} \xrightarrow{f} \text{3b} \]

a NaH, MeI, THF, r.t., 80%. b LiAlH\(_4\), Et\(_2\)O, r.t., 89%. c NaH, TBSCl, CH\(_2\)Cl\(_2\), r.t., 84%. d (COCl\(_2\)), DMSO, Et\(_3\)N, CH\(_2\)Cl\(_2\), -78 °C, 82%.

**Compound 23.** Under N\(_2\), \( \text{22} \) (300 mg, 1.51 mmol) in THF (4 mL) was added to a suspension of sodium hydride (44 mg, 1.82 mmol) in THF (12 mL) cooled at 0 °C. The mixture was stirred at room temperature for 1 hour, then iodomethane (141 \( \mu \)L, 2.27 mmol) was added and the mixture was stirred for another 40 minutes at room temperature. The mixture was quenched with brine (10 mL) and extracted with Et\(_2\)O (3 \( \times \) 10 mL). The organic layers were dried over Na\(_2\)SO\(_4\), filtered and concentrated. Purification by flash chromatography (PE/Et\(_2\)O, 40/1 \( \rightarrow \) 30/1) afforded 23 as a colourless oil (257 mg, 80%). 1H NMR (500 MHz, CDCl\(_3\)): \( \delta = 5.63–5.57 \) (m, 1H), 3.67 (s, 6H), 2.70 (d, \( J = 7.6 \) Hz, 2H), 1.35 (s, 3H), 1.06–1.01 (m, 2H), 0.98–0.92 (m, 2H); 13C NMR (125 MHz, CDCl\(_3\)): \( \delta = 172.5 \) (2C), 126.5, 112.0, 53.9, 52.4 (2C), 38.2, 19.8, 2.9, 1.7; IR (neat): \( \nu = 2985, 2954, 1731, 1454, 1434, 1377, 1287, 1242, 1202, 1159, 1110, 982, 936, 755 \) cm\(^{-1}\); MS (CI): \( m/z \) (rel. intensity): 232 (42), 230 (95), 215 (82), 213 (100), 164 (93), 147 (10); HRMS (CI) calcd for (C\(_{11}\)H\(_{16}\)O\(_4\) + H): 213.11268; found: 213.11277; elemental analysis (%) calcd for C\(_{11}\)H\(_{16}\)O\(_4\): C 62.25, H 7.60; found: C 62.32, H 7.63.

**Compound 24.** To a suspension of lithium aluminum hydride (67 mg, 1.77 mmol) in Et\(_2\)O (12 mL), a solution of 23 (250 mg, 1.18 mmol) in Et\(_2\)O (6 mL) was added at 0°C. The mixture was stirred during 20 minutes at room temperature then lithium aluminum hydride (67 mg, 1.77 mmol) was added at 0°C. After 30 minutes of stirring at room temperature, few drops of a saturated solution of Na\(_2\)SO\(_4\) was added until a white precipitate appeared. The mixture was filtered through a pad of celite and evaporated. Colourless oil (164 mg, 89%). 1H NMR (500 MHz, CDCl\(_3\)): \( \delta = 5.82–5.72 \) (m, 1H), 3.53 (d, \( J = 10.6 \) Hz, 2H), 3.47 (d, \( J = 10.6 \) Hz, 2H), 2.90 (s, 2H (OH)), 2.16 (d, \( J = 7.7 \) Hz, 2H), 1.09–0.94 (m, 4H), 0.81 (s, 3H); 13C NMR (125 MHz, CDCl\(_3\)): \( \delta = 124.6, 113.5, 70.2 \) (2C), 40.0, 36.4, 18.5, 2.8, 1.7; IR (neat): \( \nu = 3246 \) (br), 2962, 2936, 2877, 1470, 1429, 1387, 1367, 1295, 1251, 1223, 1156, 1096, 1044, 1018, 988, 964, 941, 887, 871, 807, 755, 715 \) cm\(^{-1}\); MS (CI): \( m/z \) (rel. intensity): 176 (24), 174 (100), 159 (16), 157 (43), 139 (14), 132 (13), 128 (16), 126 (23), 115 (17), 109 (16); HRMS (CI) calcd for (C\(_9\)H\(_{16}\)O\(_2\) + H): 157.12285; found: 157.12310; elemental analysis (%) calcd for C\(_9\)H\(_{16}\)O\(_2\): C 69.19, H 10.32; found: C 69.32, H 10.37.

**Compound 25.** Under N\(_2\), a solution of 24 (170 mg, 1.088 mmol) in THF (2 mL) was added to a suspension of sodium hydride (26 mg, 1.088 mmol) in THF (8 mL) cooled at 0 °C. The mixture was stirred at room temperature during 18 hours then \( \text{tert} \)-butyldimethylsilyl chloride (163 mg, 1.088 mmol) was added. The mixture was stirred at room temperature during 1 hour then quenched with water (10 mL) and extracted with Et\(_2\)O (3 \( \times \) 15 mL). The organic layers were washed with brine, dried over Na\(_2\)SO\(_4\), filtered and concentrated. Purification by flash chromatography (PE/Et\(_2\)O, 35/1 \( \rightarrow \) 30/1) gave 25 as a colourless oil (247 mg, 84%). 1H NMR
Compound 3b. This compound was prepared from 25 (210 mg, 0.78 mmol) according to the procedure described for the preparation of 1. Colourless oil (181 mg, 82%).

\[ \text{H NMR (500 MHz, CDCl}_3\) : } \delta = 9.57 (s, 1H), 5.68–5.62 (m, 1H), 3.67 (s, 6H), 3.23 (s, 2H), 2.68 (d, J = 7.5 Hz, 2H), 1.11–1.06 (m, 2H), 1.02–0.96 (m, 2H); 13C NMR (125 MHz, CDCl3): } \delta = 206.3, 171.4 (2C), 136.0, 129.8 (2C), 128.2 (2C), 126.9, 126.4, 59.1, 59.0, 52.3 (2C), 38.1, 34.5, 2.9, 2.0; IR (neat): } \tilde{\nu} = 3031, 2977, 2952, 1732, 1497, 1434, 1328, 1278, 1242, 1201, 1175, 1084, 1044, 1003, 953, 899, 862, 821, 780, 743, 700 cm\(^{-1}\); MS (ES\(^{+}\)) : } m/z (rel. intensity): 311 (100); HRMS (ES\(^{+}\)) calcd for (C\(_{17}\)H\(_{20}\)O\(_4\) + Na\(^{+}\)) : 311.1259; found: 311.1260; elemental analysis (%) calcd for C\(_{17}\)H\(_{20}\)O\(_4\): C 70.81, H 6.99; found: C 70.25, H 6.97.

Preparation of compound 3c

\[ \text{a NaH, BnBr, Bu}_4\text{NI, THF, r.t., 71%.} \quad \text{b LiAlH}_4, \text{Et}_2\text{O, r.t., 99%.} \quad \text{c TBSCl, Pyridine, CH}_2\text{Cl}_2, 40 ^\circ\text{C, 90%}. \quad \text{d (COCl)}_2, \text{DMSO, Et}_3\text{N, CH}_2\text{Cl}_2, -78 ^\circ\text{C, 95%.} \]

Compound 26. Under N\(_2\), a solution of ester 22 (200 mg, 1.01 mmol) in THF (3 mL) was added to a suspension of sodium hydride (29 mg, 1.21 mmol) in THF (3 mL) at 0 °C. The resulting mixture was stirred at room temperature during 2 hours then benzyl bromide (145 µL, 1.21 mmol) followed by tetrabutylammonium iodide (149 mg, 0.40 mmol) were added. The resulting mixture was stirred at room temperature during 14 hours. The mixture was quenched with a saturated solution of NH\(_4\)Cl (5 mL) and extracted with EtOAc (3 x 10 mL). The organic layers were dried over Na\(_2\)SO\(_4\), filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 60/1 \(\rightarrow\) 40/1) gave 26 as a colourless oil (445 mg, 71%).

\[ \text{H NMR (500 MHz, CDCl}_3\) : } \delta = 7.29–7.18 (m, 3H), 7.09–7.04 (m, 2H), 5.74–5.68 (m, 1H), 3.67 (s, 6H), 3.23 (s, 2H), 2.68 (d, J = 7.5 Hz, 2H), 1.11–1.06 (m, 2H), 1.02–0.96 (m, 2H); 13C NMR (125 MHz, CDCl3): } \delta = 171.4 (2C), 136.0, 129.8 (2C), 128.2 (2C), 126.9, 126.4, 59.1, 52.3 (2C), 38.1, 34.5, 2.9, 2.0; IR (neat): } \tilde{\nu} = 3031, 2977, 2952, 1732, 1497, 1434, 1328, 1278, 1242, 1201, 1175, 1084, 1044, 1003, 953, 899, 862, 821, 780, 743, 700 cm\(^{-1}\); MS (ES\(^{+}\)) : } m/z (rel. intensity): 311 (100); HRMS (ES\(^{+}\)) calcd for (C\(_{17}\)H\(_{20}\)O\(_4\) + Na\(^{+}\)) : 311.1259; found: 311.1260; elemental analysis (%) calcd for C\(_{17}\)H\(_{20}\)O\(_4\): C 70.81, H 6.99; found: C 70.25, H 6.97.
**Compound 27.** This compound was prepared from **26** (197 mg, 0.68 mmol) according to the procedure described for the preparation of **24**. Colourless oil (157 mg, 99%).

\[ \text{H NMR (500 MHz, CDCl}_3\] : \( \delta = 7.30–7.25 \text{ (m, 3H)}, 7.23–7.19 \text{ (m, 2H)}, 5.91–5.85 \text{ (m, 1H)}, 3.60 \text{ (d, } J = 10.7 \text{ Hz, 2H)}, 3.54 \text{ (d, } J = 10.7 \text{ Hz, 2H)}, 2.98 \text{ (s, 2H)}, 2.71 \text{ (s, 2H)}, 2.11 \text{ (d, } J = 7.5 \text{ Hz, 2H)}, 1.14–1.08 \text{ (m, 2H)}, 1.04–0.98 \text{ (m, 2H)}; \]

\[ \text{13C NMR (125 MHz, CDCl}_3\] : \( \delta = 137.6, 130.4 \text{ (2C), 128.0 (2C), 126.1, 124.9, 113.4, 67.8 (2C), 43.3, 37.4, 34.0, 2.9, 2.0} \]

IR (neat): \( \tilde{\nu} = 3349, 3058, 3028, 2978, 2923, 2876, 1603, 1496, 1453, 1323, 1211, 1089, 1064, 1027, 967, 933, 870, 797, 722, 701 \text{ cm}^{-1} \); MS (ES+): \( m/z \) (rel. intensity): 255 (100); HRMS (ES+) calcd for (C\textsubscript{13}H\textsubscript{30}O\textsubscript{2} + Na): 255.1361; found: 255.1366.

**Compound 28.** Under N\textsubscript{2}, pyridine (51 µL, 0.698 mmol) was added to a solution of **27** (135 mg, 0.582 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (4 mL) at room temperature. The mixture was stirred at room temperature during 2 hours before adding tert-butyldimethylsilyl chloride (85 mg, 0.564 mmol). The resulting mixture was stirred at 40 °C during 14 hours. The mixture was quenched with a saturated solution of NH\textsubscript{4}Cl (4 mL) and extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 × 10 mL). The organic layers were dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 70/1 \( \rightarrow \) 50/1) afforded **28** as a colourless oil (181 mg, 90%).

\[ \text{H NMR (500 MHz, CDCl}_3\] : \( \delta = 7.31–7.19 \text{ (m, 5H)}, 5.90–5.83 \text{ (m, 1H)}, 3.63–3.54 \text{ (m, 2H)}, 3.52–3.44 \text{ (m, 2H)}, 2.81 \text{ (d, } J = 12.7 \text{ Hz, 1H)}, 2.78–2.73 \text{ (m, 1H (OH))}, 2.67 \text{ (d, } J = 12.9 \text{ Hz, 1H)}, 2.15–2.03 \text{ (m, 2H)}, 1.14–1.08 \text{ (m, 2H)}, 1.04–0.98 \text{ (m, 2H)}, 0.94 \text{ (s, 9H)}, -0.09 \text{ (s, 6H)}; \]

\[ \text{13C NMR (125 MHz, CDCl}_3\] : \( \delta = 137.9, 130.6 \text{ (2C), 127.9 (2C), 126.0, 124.6, 113.6, 68.7, 68.1, 43.4, 37.3, 34.0, 25.8 (3C), 18.1, 2.8, 2.0, -5.6, -5.7} \]

IR (neat): \( \tilde{\nu} = 3454 \text{ (br), 3028, 2953, 2928, 2857, 1492, 1471, 1391, 1360, 1252, 1070, 1034, 1006, 967, 938, 834, 774, 723, 701, 669 cm}^{-1} \); MS (ES+): \( m/z \) (rel. intensity): 369 (100); HRMS (ES+) calcd for (C\textsubscript{21}H\textsubscript{34}O\textsubscript{2}Si + Na): 369.2226; found: 369.2236.

**Compound 3c.** This compound was prepared from **28** (166 mg, 0.48 mmol) according to the procedure described for the preparation of **1**. Colourless oil (157 mg, 95%).

\[ \text{H NMR (500 MHz, CDCl}_3\] : \( \delta = 9.64 \text{ (s, 1H)}, 7.26–7.22 \text{ (m, 2H)}, 7.21–7.18 \text{ (m, 1H)}, 7.15–7.12 \text{ (m, 2H)}, 5.76–5.71 \text{ (m, 1H)}, 3.62 \text{ (d, } J = 10.1 \text{ Hz, 1H)}, 3.55 \text{ (d, } J = 10.1 \text{ Hz, 1H)}, 2.98 \text{ (d, } J = 13.9 \text{ Hz, 1H)}, 2.87 \text{ (d, } J = 13.9 \text{ Hz, 1H)}, 2.37 \text{ (d, } J = 7.1 \text{ Hz, 2H)}, 1.10–1.05 \text{ (m, 2H)}, 1.00–0.95 \text{ (m, 2H)}, 0.90 \text{ (s, 9H)}, 0.04 \text{ (s, 3H)}, 0.03 \text{ (s, 3H)}; \]

\[ \text{13C NMR (125 MHz, CDCl}_3\] : \( \delta = 206.0, 136.7, 130.3 \text{ (2C), 128.1 (2C), 126.4, 125.8, 112.3, 62.8, 56.0, 35.8, 32.7, 25.8 (3C), 18.1, 2.9, 2.1, -5.6 \text{ (2C)}} \]

IR (neat): \( \tilde{\nu} = 3053, 3028, 2954, 2929, 2857, 2714, 1726, 1603, 1496, 1471, 1390, 1360, 1252, 1095, 1031, 1006, 968, 937, 835, 775, 723, 700, 669 \text{ cm}^{-1} \); MS (ES+): \( m/z \) (rel. intensity): 367 (100); HRMS (ES+) calcd for (C\textsubscript{21}H\textsubscript{32}O\textsubscript{2}Si + Na): 367.2069; found: 367.2075; elemental analysis (%) calcd for C\textsubscript{21}H\textsubscript{32}O\textsubscript{2}Si: C 73.20, H 9.36; found: C 72.12, H 9.42.
Preparation of compound 3d

![Diagram](image)

* Preparation of compound 3d

\[ \text{NaH, BnBr, Bu₄NI, DMF, r.t., 63%} \]

\[ \text{(COCl)₂, DMSO, Et₃N, CH₂Cl₂, -78 °C, 86%}. \]

**Compound 29.** Under N₂, a solution of 24 (153 mg, 0.979 mmol) in DMF (0.4 mL) was added to a suspension of sodium hydride (24 mg, 0.979 mmol) in DMF (1 mL). The resulting mixture was stirred at room temperature for 2 hours. Then, benzyl bromide (117 µL, 0.979 mmol) followed by tetrabutylammonium iodide (217 mg, 0.588 mmol) were added. The mixture was stirred at room temperature for 16 hours. The mixture was quenched with water (10 mL) and extracted with Et₂O (3 × 15 mL). The organic layer was dried over MgSO₄, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 40/1 → 10/1) afforded 29 as a colourless oil (152 mg, 63%).

\[ \begin{align*}
\text{δ} & = 7.37–7.26 \text{ (m, 5H)}, 5.78–5.71 \text{ (m, 1H)}, 4.49 \text{ (s, 2H)}, 3.50 \text{ (s, 2H)}, 3.39 \text{ (d,} \ J = 9.1 \text{ Hz, 1H)}, 3.33 \text{ (d,} \ J = 8.8 \text{ Hz, 1H)}, 2.73–2.50 \text{ (m, 1H (OH))}, 2.29–2.17 \text{ (m, 2H), 1.10–1.03 \text{ (m, 2H), 1.00–0.93 \text{ (m, 2H), 0.85 \text{ (s, 3H)}};} \\
\text{ν} & = 3434 \text{ (br), 3031, 2977, 2946, 1497, 1454, 1406, 1362, 1307, 1292, 1249, 1206, 1095, 1075, 1028, 967, 936, 902, 801, 734, 696 \text{ cm}^{-1};} \\
\text{MS (ES⁺):} \ m/z \ \text{(rel. intensity): 267 (100); HRMS (ES⁺) calcd for} \ (C₁₆H₂₂O₂ + Na)^⁺: 269.1517; \text{ found: 269.1508; elemental analysis (%) calcd for} \ C₁₆H₂₂O₂: C 78.01, H 9.00; \text{ found: C 77.17, H 9.40.}
\end{align*} \]

**Compound 3d.** This compound was prepared from 29 (166 mg, 0.67 mmol) according to the procedure described for the preparation of 1. Colourless oil (141 mg, 86%).

\[ \begin{align*}
\text{δ} & = 9.58 \text{ (s, 1H)}, 7.35–7.31 \text{ (m, 2H)}, 7.29–7.25 \text{ (m, 3H)}, 5.67–5.61 \text{ (m, 1H)}, 4.48 \text{ (s, 2H)}, 3.53 \text{ (d,} \ J = 9.3 \text{ Hz, 1H)}, 3.43 \text{ (d,} \ J = 9.2 \text{ Hz, 1H)}, 2.44 \text{ (dd,} \ J = 13.8 \text{ Hz,} \ J = 7.6 \text{ Hz, 1H)}, 2.38 \text{ (dd,} \ J = 13.8 \text{ Hz,} \ J = 7.6 \text{ Hz, 1H)}, 1.06 \text{ (s, 3H)}, 1.07–1.02 \text{ (m, 2H), 0.98–0.93 \text{ (m, 2H);} } \\
\text{ν} & = 3027, 2979, 2857, 2704, 1726, 1492, 1454, 1406, 1361, 1305, 1257, 1205, 1093, 1028, 967, 934, 900, 798, 735, 697 \text{ cm}^{-1}; \text{ MS (ES⁺):} \ m/z \ \text{(rel. intensity): 267 (100); HRMS (ES⁺) calcd for} \ (C₁₆H₂₀O₂ + Na)^⁺: 267.1361; \text{ found: 267.1359.}
\end{align*} \]
**Preparation of compound 3e**

![Diagram of compound 3e]

a Pyridine, pivaloyl chloride, CH$_2$Cl$_2$, reflux, 85%. b (COCl)$_2$, DMSO, Et$_3$N, CH$_2$Cl$_2$, -78 °C, 94%.

**Compound 30.** Under N$_2$, pyridine (42 µL, 0.518 mmol) was added to a solution of 24 (140 mg, 0.896 mmol) in CH$_2$Cl$_2$ (14 mL). The resulting mixture was stirred at room temperature during 2 hours. Then, pivaloyl chloride (111 µL, 0.905 mmol) was added and the mixture was stirred under reflux for 14 hours. The mixture was quenched with brine (10 mL) and extracted with Et$_2$O (3 × 15 mL). The organic layer was dried over MgSO$_4$, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 50/1 → 25/1 → 10/1) afforded 30 as a colourless oil (183 mg, 85%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 5.80–5.70 (m, 1H), 3.95 (d, $J = 11.2$ Hz, 1H), 3.90 (d, $J = 11.2$ Hz, 1H), 3.30 (d, $J = 11.5$ Hz, 1H), 3.26 (d, $J = 11.6$ Hz, 1H), 2.65–2.35 (m, 1H (OH)), 2.16 (dd, $J = 13.6$ Hz, $J = 7.9$ Hz, 1H), 2.10 (dd, $J = 13.5$ Hz, $J = 7.6$ Hz, 1H), 1.19 (s, 9H), 1.09–1.02 (m, 2H), 1.00–0.93 (m, 2H), 0.86 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 179.4, 125.2, 112.9, 67.5, 66.9, 40.2, 39.0, 36.5, 27.2 (3C), 18.6, 2.8, 1.7; IR (neat): $\tilde{\nu}$ = 3452 (br), 2976, 2937, 2876, 1728, 1481, 1462, 1398, 1366, 1284, 1155, 1096, 1034, 986, 968, 937, 890, 793, 771, 750, 714 cm$^{-1}$; MS (ES+): m/z (rel. intensity): 263 (100); HRMS (ES+) calcd for (C$_{14}$H$_{24}$O$_3$ + Na)$^+$: 263.1623; found: 263.1617.

**Compound 3e.** This compound was prepared from 30 (207 mg, 0.86 mmol) according to the procedure described for the preparation of 1. Colourless oil (194 mg, 94%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 9.54 (s, 1H), 5.68–5.61 (m, 1H), 4.14 (d, $J = 11.3$ Hz, 1H), 4.05 (d, $J = 11.1$ Hz, 1H), 2.39 (d, $J = 7.7$ Hz, 2H), 1.14 (s, 9H), 1.07 (s, 3H), 1.08–1.03 (m, 2H), 0.98–0.93 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 203.6, 178.0, 126.7, 111.3, 66.2, 50.3, 38.8, 34.9, 27.0 (3C), 16.3, 2.9, 1.8; IR (neat): $\tilde{\nu}$ = 2978, 2937, 2906, 2871, 2709, 1728, 1481, 1461, 1398, 1366, 1282, 1144, 1036, 993, 936, 872, 787, 769, 718 cm$^{-1}$; MS (ES+): m/z (rel. intensity): 261 (100); HRMS (ES+) calcd for (C$_{14}$H$_{22}$O$_3$ + Na)$^+$: 261.1467; found: 261.1468.

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Preparation of compound 5

\[ \text{CO}_2\text{Et} \quad \text{a} \quad \text{CO}_2\text{Et} \quad \text{b} \quad \text{HO} \quad \text{HO} \]

\[ \text{16} \quad \text{31} \quad \text{5} \]

\( ^{a} 1) \text{NaH, DMF, 2) Pd}_2(\text{dba})_3, \text{dppe, 16, THF, r.t., 99%).}^{b} \text{LiAlH}_4, \text{Et}_2\text{O, r.t., 70%}. \)

**Compound 31.** This compound was prepared from 16 (200 mg, 0.84 mmol) and commercially available 2-ethoxycarbonylcyclopentanone according to the procedure described for the preparation of 17. Colourless oil (184 mg, 99%).

\(^1\text{H NMR (500 MHz, CDCl}_3\):} ^{\delta} 5.68–5.61 (m, 1H), 4.14 (q, \( J = 7.2 \text{ Hz, 2H} \)), 2.76 (dd, \( J = 13.7 \text{ Hz, } J = 7.0 \text{ Hz, 1H} \)), 2.49 (dd, \( J = 13.7 \text{ Hz, } J = 7.5 \text{ Hz, 1H} \)), 2.46–2.34 (m, 2H), 2.29–2.17 (m, 1H), 2.04–1.82 (m, 3H), 1.23 (t, \( J = 7.2 \text{ Hz, 3H} \)), 1.09–1.03 (m, 2H), 1.01–0.95 (m, 2H); \(^{13}\text{C NMR (125 MHz, CDCl}_3\):} ^{\delta} 214.8, 171.0, 126.1, 112.5, 61.2, 60.3, 38.0, 35.7, 32.0, 19.4, 13.9, 2.8, 1.8; IR (neat): \( {\tilde{\nu}} = 2980, 2906, 1749, 1718, 1448, 1406, 1366, 1278, 1223, 1146, 1117, 1094, 1028, 965, 934, 921, 861, 788, 761, 722 \text{ cm}^{-1} \); MS (ES+): \( m/z \) (rel. intensity): 245 (100); HRMS (ES+) calcd for (C\(_{13}\)H\(_{18}\)O\(_3\) + Na\(^+\)): 245.1154; found: 245.1157; elemental analysis (%): calcd for C\(_{13}\)H\(_{18}\)O\(_3\): C 70.24, H 8.16; found: C 70.33, H 8.29.

**Compound 5.** This compound was prepared from 31 (64 mg, 0.29 mmol) according to the procedure described for the preparation of 19, using 2 equivalents of lithium aluminium hydride. White solid (37 mg, 70%). m.p.: 53–55°C; \(^1\text{H NMR (500 MHz, CDCl}_3\):} ^{\delta} 5.90–5.80 (m, 1H), 4.05 (m, 1H), 3.61 (d, \( J = 10.3 \text{ Hz, 1H} \)), 3.34 (d, \( J = 10.9 \text{ Hz, 1H} \)), 2.51 (dd, \( J = 14.2 \text{ Hz, } J = 7.8 \text{ Hz, 1H} \)), 2.29–2.24 (n, \( 1\text{H (OH)} \)), 2.20 (dd, \( J = 14.2 \text{ Hz, } J = 7.1 \text{ Hz, 1H} \)), 2.06–1.94 (m, 2H), 1.79–1.68 (m, 1H), 1.66–1.584 (m, 1H), 1.582–1.47 (m, 2H), 1.27–1.17 (m, 1H), 1.11–1.05 (m, 2H), 1.04–0.97 (m, 2H); \(^{13}\text{C NMR (125 MHz, CDCl}_3\):} ^{\delta} 124.2, 114.9, 79.4, 68.9, 49.4, 32.3, 31.1, 30.4, 19.6, 2.9, 1.8; IR (neat): \( {\tilde{\nu}} = 3320, 3038, 2962, 2922, 2901, 2871, 2860, 1467, 1440, 1356, 1319, 1254, 1202, 1136, 1090, 1048, 1036, 1017, 962, 948, 929, 905, 878, 850, 792, 766, 719 \text{ cm}^{-1} \); MS (CI): \( m/z \) (rel. intensity): 201 (11), 200 (100), 183 (31), 165 (31), 158 (12), 147 (38), 141 (22); HRMS (CI) calcd for (C\(_{11}\)H\(_{18}\)O\(_2\) + NH\(_3\)\(^+\)): 200.1645; found: 200.1643; elemental analysis (%): calcd for C\(_{11}\)H\(_{18}\)O\(_2\): C 72.49, H 9.95; found: C 71.99, H 9.90.
Preparation of compound 8

\[
\begin{align*}
\text{MeO}_2\text{C}-&\text{CO}_2\text{Me} \quad a \\
\text{MeO}_2\text{C}-&\text{CO}_2\text{Me} \quad b
\end{align*}
\]

a 1) NaH, DMF; 2) Pd\(_2\)(dba)\(_3\), dppe, 16, THF, r.t., 71%. b LiAlH\(_4\), Et\(_2\)O, r.t., 95%. c (COCl)\(_2\), DMSO, ET\(_3\)N, CH\(_2\)Cl\(_2\), -78 °C, full conversion.

**Compound 32.** Under N\(_2\), at room temperature, a solution of 22 (470 mg, 2.37 mmol) was added to a suspension of sodium hydride (56 mg, 2.37 mmol) in DMF (8 mL). The mixture was stirred at room temperature during 1 hour. In another flask, under N\(_2\), 16 (564 mg, 2.37 mmol) was added to a solution of tris(dibenzylideneacetone)dipalladium (66 mg, 0.071 mmol) and dppe (28 mg, 0.071 mmol) in THF (15 mL) at room temperature. The resulting mixture was stirred at room temperature during 30 minutes before being cannulated to the enolate. The resulting mixture was stirred during 48 hours at room temperature. The mixture was quenched with water (15 mL) and extracted with Et\(_2\)O (3 × 20 mL). The organic layers were dried over Na\(_2\)SO\(_4\), filtered and concentrated. Purification by flash chromatography (PE/Et\(_2\)O, 50/1 → 20/1) gave 32 as a colourless oil (445 mg, 71%). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 5.65–5.57\) (m, 2H), 3.65 (s, 6H), 2.75 (d, \(J = 7.8\) Hz, 4H), 1.07–1.00 (m, 4H), 0.96–0.90 (m, 4H); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 171.6\) (2C), 126.2 (2C), 111.9 (2C), 58.0, 52.3 (2C), 35.0 (2C), 2.9 (2C), 1.7 (2C); IR (neat): \(\tilde{\nu} = 3053, 2982, 2953, 2841, 1732, 1436, 1411, 1307, 1281, 1245, 1198, 1180, 1109, 1071, 1000, 969, 947, 931, 861, 826, 794, 756, 733\) cm\(^{-1}\); MS (ES+): \(m/z\) (rel. intensity): 287 (100); HRMS (ES+) calcd for (C\(_{15}\)H\(_{20}\)O\(_4\) + Na): 287.1259; found: 287.1266; elemental analysis (%) calcd for: C 68.16, H 7.63; found: C 68.15, H 7.69.

**Compound 8.** This compound was prepared from 32 (286 mg, 1.08 mmol) according to the procedure described for the preparation of 24. White solid (214 mg, 95%). m.p.: 39–41°C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 5.86–5.78\) (m, 2H), 3.59 (s, 4H), 2.20 (d, \(J = 7.9\) Hz, 4H), 2.11–1.96 (m, 2H), 1.11–1.06 (m, 4H), 1.03–0.97 (m, 4H); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 124.7\) (2C), 113.5 (2C), 68.6 (2C), 43.4, 33.9 (2C), 2.9 (2C), 1.8 (2C); IR (neat): \(\tilde{\nu} = 3346\) (br), 3051, 2978, 2923 1464, 1438, 1408, 1312, 1211, 1091, 1025, 965, 933, 871, 785, 748, 717 cm\(^{-1}\); MS (ES+): \(m/z\) (rel. intensity): 231 (100); HRMS (ES+) calcd for (C\(_{13}\)H\(_{20}\)O\(_2\) + Na): 231.1361; found: 231.1364; elemental analysis (%) calcd for: C 74.96, H 9.68; found: C 75.09, H 9.82.
Preparation of compound 11

\[ \text{a TBSCI, DMAP, Et₃N, CH₂Cl₂, r.t., 83%}. \text{ b (COCl)}₂, \text{DMSO, Et₃N, CH₂Cl₂, -78 °C, 97%}. \]

**Compound 33.** 4-(dimethylamino)pyridine (6 mg, 0.049 mmol) followed by triethylamine (70 µL, 0.504 mmol) and t-butyldimethylsilyl chloride (72 mg, 0.480 mmol) were added to a solution of 8 (100 mg, 0.480 mmol) in CH₂Cl₂ (2 mL) at 0 °C. The resulting mixture was stirred at room temperature for 16 hours. The mixture was quenched with a saturated solution of NH₄Cl (4 mL) then extracted with CH₂Cl₂ (3 \times 5 mL). The organic layers were dried over Na₂SO₄, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 10/1 \(\rightarrow\) 5/1) afforded 33 as a colourless oil (129 mg, 83%). \(^1\)H NMR (500 MHz, CDCl₃): \(\delta = 5.81–5.75 \) (m, 2H), 3.55 (s, 2H), 3.53 (d, \(J = 6.3 \) Hz, 2H), 2.72 (t, \(J = 5.9 \) Hz, 1H), 2.23–2.13 (m, 4H), 1.09–1.03 (m, 4H), 1.01–0.94 (m, 4H), 0.88 (s, 9H), 0.04 (s, 6H); \(^13\)C NMR (125 MHz, CDCl₃): \(\delta = 124.2 \) (2C), 113.8 (2C), 69.2, 68.9, 43.2, 34.0 (2C), 25.8 (3C), 18.1, 2.8 (2C), 1.8 (2C), -5.7 (2C); IR (neat): \(\tilde{\nu} = 3463 \) (br); MS (ES+): \(m/z\) (rel. intensity): 345 (100); HRMS (ES+) calcd for (C₁₉H₃₄O₂Si + Na)\(^+\): 345.2226; found: 345.2223; elemental analysis (%) calcd for C₁₉H₃₄O₂Si: C 70.75, H 10.62; found: C 70.45, H 10.60.

**Compound 11.** This compound was prepared from 33 (30 mg, 0.093 mmol) according to the procedure described for the preparation of 1. Colourless oil (29 mg, 97%). \(^1\)H NMR (500 MHz, CDCl₃): \(\delta = 9.57 \) (s, 1H), 5.71–5.65 (m, 2H), 3.67 (s, 2H), 2.49–2.37 (m, 4H), 1.08–1.01 (m, 4H), 0.99–0.92 (m, 4H), 0.85 (s, 9H), 0.00 (s, 6H); \(^13\)C NMR (125 MHz, CDCl₃): \(\delta = 206.3, 125.3 \) (2C), 112.5 (2C), 64.0, 55.5, 32.3 (2C), 25.7 (3C), 18.1, 2.8 (2C), 1.9 (2C), -5.7 (2C); IR (neat): \(\tilde{\nu} = 3054, 2981, 2954, 2929, 2896, 2857, 2704, 1725, 1472, 1438, 1410, 1386, 1362, 1252, 1100, 1006, 967, 934, 836, 815, 776, 670 \) cm\(^{-1}\); MS (ES+): \(m/z\) (rel. intensity): 343 (100); HRMS (ES+) calcd for (C₁₉H₃₂O₂Si + Na)\(^+\): 343.2069; found: 343.2073.
Preparation of compound 14a

\[ \begin{align*}
\text{Ph} - \text{COMe} \quad \xrightarrow{\text{a}} \quad \text{Ph} - \text{COMe} \\
\text{Ph} - \text{CHO} \quad \xrightarrow{\text{b}} \quad \text{Ph} - \text{CH} \\
\text{Ph} - \text{CH} \quad \xrightarrow{\text{c}} \quad \text{Ph} - \text{CHO}
\end{align*} \]

\text{a} \ NaHMDS, allyl bromide, THF, -78 °C to r.t., 74%. \text{b} \ LiAlH}_4, \text{Et}_2\text{O}, \text{r.t.}, 97%. \text{c} \ \text{(COCl)}_2, \text{DMSO, Et}_3\text{N, CH}_2\text{Cl}_2, -78 °C, 89%.

**Compound 34.** Under N\textsubscript{2}, NaHMDS (188 mg, 1.023 mmol) was added as solid in one portion to a solution of 17 (170 mg, 0.787 mmol) in THF (5 ml) at -78 °C. The mixture was stirred for 1.5 hour at -78 °C then allyl bromide (89 µL, 1.023 mmol) and tetrabutylammonium iodide (116 mg, 0.315 mmol) were added. The mixture was slowly warmed at room temperature overnight. The mixture was quenched with a saturated solution of NH\textsubscript{4}Cl (5 mL) and extracted with EtOAc (3 × 10 mL). The organic layers were dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 30/1) gave 34 as a colourless oil (150 mg, 74%). 1H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta = 7.33-7.27 \) (m, 2H), 7.26–7.20 (m, 3H), 5.57 (ddt, \( J = 17.2 \) Hz, 10.5 Hz, 7.1 Hz, 1H), 5.51–5.47 (m, 1H), 5.04–5.01 (m, 1H), 5.01–4.97 (m, 1H), 3.62 (s, 3H), 2.93 (dd, \( J = 13.7 \) Hz, \( J = 7.7 \) Hz, 1H), 2.85 (dd, \( J = 13.7 \) Hz, \( J = 7.0 \) Hz, 1H), 2.79 (dd, \( J = 13.9 \) Hz, 7.9 Hz, 1H), 2.75 (dd, \( J = 13.9 \) Hz, 7.0 Hz, 1H), 1.05–0.94 (m, 2H), 0.92–0.85 (m, 1H), 0.85–0.77 (m, 1H); 13C NMR (125 MHz, CDCl\textsubscript{3}): \( \delta = 175.7, 142.0, 133.6, 128.2 \) (2C), 126.7, 126.5 (2C), 125.6, 113.8, 54.2, 51.9, 39.1, 37.2, 2.8, 1.9; IR (neat): \( \tilde{\nu} = 2980, 2950, 1729, 1640, 1600, 1581, 1498, 1445, 1320, 1301, 1268, 1206, 1138, 1108, 1088, 1035, 996, 916, 889, 847, 811, 763, 729, 698 \) cm\textsuperscript{-1}; MS (ES+): \( m/z \) (rel. intensity): 295 (16), 280 (19), 279 (100); HRMS (ES+) calcd for (C\textsubscript{17}H\textsubscript{20}O\textsubscript{2} + Na)\textsuperscript{+}: 279.1361; found: 279.1362; Elemental analysis calcd (%): C 79.65, H 7.86; found: C 79.59, H 7.87.

**Compound 35.** This compound was prepared from 34 following the procedure described for the preparation of 19. Colourless oil (217 mg, 97%). 1H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta = 7.41–7.29 \) (m, 3H), 7.23–7.18 (m, 2H), 5.74–5.57 (m, 2H), 5.07 (d, \( J = 16.9 \) Hz, 1H), 5.01 (d, \( J = 10.2 \) Hz, 1H), 3.78 (s, 2H), 2.64 (dd, \( J = 13.8 \) Hz, \( J = 7.4 \) Hz, 1H), 2.59–2.53 (m, 2H), 2.48 (dd, \( J = 13.3 \) Hz, \( J = 7.3 \) Hz, 1H), 1.48–1.30 (s, 1H), 1.06–0.98 (m, 2H), 0.97–0.87 (m, 2H); 13C NMR (125 MHz, CDCl\textsubscript{3}): \( \delta = 143.6, 134.6, 128.3 \) (2C), 126.9 (2C), 126.2, 124.7, 117.6, 113.7, 68.1, 46.5, 39.7, 37.7, 2.8, 1.9; IR (neat): \( \tilde{\nu} = 3403 \) (br), 3057, 2977, 2925, 1638, 1498, 1446, 1413, 1043, 997, 963, 697 cm\textsuperscript{-1}; MS (CI): \( m/z \) (rel. intensity): 246 (100); HRMS (CI) calcd for (C\textsubscript{14}H\textsubscript{16}O + NH\textsubscript{4})\textsuperscript{+}: 246.1852; found: 246.1855.

**Compound 14a.** Under N\textsubscript{2}, dimethyl sulfoxide (29 µL, 0.410 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (0.5 mL) was added to a solution of oxalyl chloride (18 µL, 0.205 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (1.9 mL) at -78 °C. After 10 minutes stirring at -78 °C, a solution of 35 (36 mg, 0.158 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (0.7 mL) was added. After 20 minutes stirring at -78 °C, triethylamine (0.11 mL, 0.788 mmol) was added rapidly and the mixture was stirred at room temperature during 15 minutes. A saturated solution of NH\textsubscript{4}Cl (4 mL) was added to the reaction mixture which was then extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 × 5 mL). The organic layers were dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated. Purification by flash chromatography PE/EtOAc, 80/1) gave 1 as a colourless oil (32 mg, 89%). 1H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta = 9.53 \) (s, 1H), 7.39–7.32 (m, 2H), 7.30–7.25 (m, 1H), 7.24–7.19 (m, 2H), 5.61–5.50 (m, 2H), 5.02 (d, \( J = 16.2 \) Hz, 1H), 5.01 (d, \( J = 12.9 \) Hz, 1H), 2.85 (dd, \( J = 14.2 \) Hz, \( J = 12.2 \) Hz, 1H), 2.59–2.53 (m, 2H), 2.48 (dd, \( J = 13.3 \) Hz, \( J = 12.2 \) Hz, 1H), 1.48–1.30 (s, 1H), 1.06–0.98 (m, 2H), 0.97–0.87 (m, 2H); 13C NMR (125 MHz, CDCl\textsubscript{3}): \( \delta = 143.6, 134.6, 128.3 \) (2C), 126.9 (2C), 126.2, 124.7, 117.6, 113.7, 68.1, 46.5, 39.7, 37.7, 2.8, 1.9; IR (neat): \( \tilde{\nu} = 3403 \) (br), 3057, 2977, 2925, 1638, 1498, 1446, 1413, 1043, 997, 963, 697 cm\textsuperscript{-1}; MS (CI): \( m/z \) (rel. intensity): 246 (100); HRMS (CI) calcd for (C\textsubscript{14}H\textsubscript{16}O + NH\textsubscript{4})\textsuperscript{+}: 246.1852; found: 246.1855.
$J = 7.7 \text{ Hz}, 1\text{H}$), 2.79 (dd, $J = 14.2 \text{ Hz}, J = 7.0\text{ Hz}, 1\text{H}$), 2.69 (d, $J = 7.5 \text{ Hz}, 2\text{H}$), 1.07–0.96 (m, 2H), 0.93–0.81 (m, 2H); $^{13}\text{C NMR (125 MHz, CDCl}_3): \delta = 202.3, 138.3, 133.1, 128.7 (2\text{C}), 127.7 (2\text{C}), 127.3, 126.1, 118.6, 112.2, 57.7, 37.1, 34.8, 2.9, 2.0; \text{IR (neat): } \tilde{\nu} = 3057, 2980, 2921, 2804, 2709, 1722, 1640, 1599, 1580, 1496, 1446, 997, 967, 918, 875, 842, 759, 738, 698 \text{ cm}^{-1}; \text{MS (ES+): } m/z (\text{rel. intensity}): 249 (100); \text{HRMS (ES+) calcd for (C}_{16}\text{H}_{18}\text{O} + \text{Na})^+: 249.1255; \text{found: 249.1258.}

### Preparation of compound 14c

![Image](image_url)  

* KHMDS, 3,3-dimethylallyl bromide, THF, -78 °C to r.t., 82%.  
  
### Compound 36.

This compound was prepared from 17 (119 mg, 0.551 mmol) according to the procedure described for the preparation of 18 and using 3,3-dimethylallyl bromide. Colourless oil (128 mg, 82%). $^1\text{H NMR (500 MHz, CDCl}_3): \delta = 7.29 (t, J = 7.7 \text{ Hz}, 1\text{H}), 7.26–7.18 (m, 4\text{H}), 5.53–5.45 (m, 1\text{H}), 4.94 (t, J = 6.7 \text{ Hz}, 1\text{H}), 3.61 (s, 3\text{H}), 2.91 (dd, J = 13.3 \text{ Hz}, J = 7.7 \text{ Hz}, 1\text{H}), 2.83 (dd, J = 13.5 \text{ Hz}, J = 6.5 \text{ Hz}, 1\text{H}), 2.76 (dd, J = 14.3 \text{ Hz}, J = 7.6 \text{ Hz}, 1\text{H}), 2.64 (dd, J = 14.3 \text{ Hz}, J = 6.4 \text{ Hz}, 1\text{H}), 1.63 (s, 3\text{H}), 1.47 (s, 3\text{H}), 1.02–0.91 (m, 2\text{H}), 0.88–0.80 (m, 1\text{H}), 0.80–0.73 (m, 1\text{H}); $^{13}\text{C NMR (125 MHz, CDCl}_3): \delta = 176.2, 142.4, 134.4, 128.1 (2\text{C}), 126.63 (2\text{C}), 125.59, 125.4, 119.0, 113.1, 54.5, 51.9, 37.5, 33.3, 26.0, 17.8, 2.8, 1.7; \text{IR (neat): } \tilde{\nu} = 3290, 2916, 1730, 1601, 1498, 1446, 1377, 1311, 1268, 1202, 1069, 1031, 1002, 852, 765, 737, 697 \text{ cm}^{-1}; \text{MS (ES+): } m/z (\text{rel. intensity}): 307 (100); \text{HRMS (ES+) calcd for (C}_{19}\text{H}_{24}\text{O}_{2} + \text{Na})^+: 307.1674; \text{found: 307.1685; elemental analysis calcd (\%)} \text{for C}_{19}\text{H}_{24}\text{O}_{2}: \text{ C 80.28, H 8.45; found: C 79.92, H 8.77.}

### Compound 37.

This compound was prepared from 36 (119 mg, 0.419 mmol) according to the procedure described for the preparation of 19. Colourless oil (101 mg, 94%). $^1\text{H NMR (500 MHz, CDCl}_3): \delta = 7.39–7.29 (m, 4\text{H}), 7.22–7.17 (m, 1\text{H}), 5.63–5.57 (m, 1\text{H}), 5.04–4.98 (m, 1\text{H}), 3.77 (d, J = 6.0 \text{ Hz}, 2\text{H}), 2.64 (ddquint, J = 13.9 \text{ Hz}, J = 7.2 \text{ Hz}, J = 1.3 \text{ Hz}, 1\text{H}), 2.56 (ddquint, J = 13.9 \text{ Hz}, J = 7.3 \text{ Hz}, J = 1.3 \text{ Hz}, 1\text{H}), 2.47 (dd, J = 14.6 \text{ Hz}, J = 7.3 \text{ Hz}, 1\text{H}), 2.40 (dd, J = 14.6 \text{ Hz}, J = 7.3 \text{ Hz}, 1\text{H}), 1.63 (s, 3\text{H}), 1.57 (s, 3\text{H}), 1.30 (t, J = 6.0 \text{ Hz}, 1\text{H}), 1.03–0.96 (m, 2\text{H}), 0.96–0.87 (m, 2\text{H}); $^{13}\text{C NMR (125 MHz, CDCl}_3): \delta = 144.1, 133.8, 128.7 (2\text{C}), 127.1 (2\text{C}), 126.0, 124.4, 120.0, 114.1, 68.5, 47.0, 38.0, 33.9, 26.0, 17.9, 2.8, 1.8; \text{IR (neat): } \tilde{\nu} = 3432 (br), 3054, 2978, 2914, 1601, 1498, 1445, 1376, 1028, 965, 936, 760, 697 \text{ cm}^{-1}; \text{MS (ES+): } m/z (\text{rel. intensity}): 279 (100); \text{HRMS (ES+) calcd for (C}_{19}\text{H}_{24}\text{O} + \text{Na})^+: 279.1725; \text{found: 279.1729; elemental analysis calcd (\%)} \text{for C}_{19}\text{H}_{24}\text{O}: \text{ C 84.38, H 9.38; found: C 84.50, H 9.79.}

### Compound 14c.

This compound was prepared from 37 (89 mg, 0.348 mmol) according to the procedure described for the preparation of 1. Colourless oil (79 mg, 90%). $^1\text{H NMR (500 MHz, CDCl}_3): \delta = 9.53 (s, 1\text{H}), 7.38–7.32 (m, 2\text{H}), 7.29–7.19 (m, 3\text{H}), 5.56–5.50 (m, 1\text{H}), 4.99–4.92 (m, 1\text{H}), 2.83 (dd, J = 14.1 \text{ Hz}, J = 7.6 \text{ Hz}, 1\text{H}), 2.76 (J = 14.1 \text{ Hz}, J = 6.9 \text{ Hz}, 1\text{H}), 2.67 (dd, J = 15.0 \text{ Hz}, J = 7.5 \text{ Hz}, 2\text{H}).
1H), 2.58 (dd, J = 15.0 Hz, J = 6.9 Hz, 1H), 1.62 (s, 3H), 1.49 (s, 3H), 1.04–0.93 (m, 2H),
0.89–0.76 (m, 2H); 13C NMR (125 MHz, CDCl3): δ = 202.8, 138.8, 134.7, 128.6 (2C), 127.8
(2C), 127.2, 125.7, 118.3, 112.6, 58.2, 35.2, 31.1, 26.1, 18.0, 3.0, 1.9; IR (neat): ν = 3055,
2980, 2916, 2707, 1722, 1599, 1466, 1377, 1088, 1030, 1002, 967, 932, 880, 858, 759,
698 cm⁻¹; MS (ES⁺): m/z (rel. intensity): 277 (100); HRMS (ES⁺) calcd for (C₁₈H₂₄O₇ + Na)⁺:
277.1568; found: 277.1566.

Preparation of compound 14d

CO₂Me
MeO₂C
MeO₂C

22

a

b

38

39

C

14d

c

a NaH, allyl bromide, Bu₄NI, THF, 0 °C to r.t., 76%. b LiCl, DMSO, water, 150 °C, 66%. c 1) LiAlH₄, Et₂O, r.t.
2) (COCl)₂, DMSO, Et₃N, CH₂Cl₂, -78 °C, 59%.

Compound 38. Under N₂, A solution of 22 (500 mg, 2.52 mmol) in THF (7 mL) was added
to a suspension of sodium hydride (61 mg, 2.55 mmol) in THF (7 mL) at
0°C. The resulting mixture was stirred at room temperature during 40
minutes then cooled down at 0°C. Allyl bromide (0.22 mL, 2.55 mmol)
followed by tetrabutylammonium iodide (186 mg, 0.50 mmol) were added
and the mixture was stirred at room temperature for 1 hour. The mixture was quenched with
brine (10 mL) and extracted with EtOAc (3 × 15 mL). The organic layers were dried over
Na₂SO₄, filtered and evaporated. Purification by flash chromatography (PE/EtOAc, 40/1)
gave 38 as colourless oil (396 mg, 66%). ¹H NMR (500 MHz, CDCl₃): δ = 5.71–5.61 (m,
1H), 5.60–5.54 (m, 1H), 5.07–5.04 (m, 2H), 3.68 (s, 6H), 2.75 (d, J = 7.4 Hz, 2H), 2.60 (d, J = 7.4 Hz, 2H), 1.07–1.02 (m, 2H), 0.98–0.93 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ =
171.4 (2C), 132.5, 126.5, 118.9, 111.7, 57.9, 52.3 (2C), 36.9, 34.9, 2.9, 1.8; IR (neat): ν =
3078, 3048, 2982, 2954, 2841, 1731, 1642, 1436, 1284, 1198, 1142, 1082, 1043, 996,
968, 921, 859, 823, 756, 721 cm⁻¹; MS (CI): m/z (rel. intensity): 257 (10), 256 (84), 240 (12),
239 (100); HRMS (CI) calcd for (C₁₃H₁₈O₄ + H)⁺: 239.1278; found: 239.1275; elemental
analysis (%) calcd for C₁₃H₁₈O₄: C 65.53, H 7.61; found: C 65.52, H 7.62.

Compound 39. Lithium chloride (149 mg, 3.51 mmol) was added to a solution of 38 (380 mg,
1.60 mmol) in DMSO (11 mL). Water (100 µL) was added then the mixture
was stirred at 150 °C (oil bath temperature) during 6 hours. At room
temperature, the mixture was partitioned between brine (10 mL) and Et₂O
and extracted with Et₂O (3 × 10 mL). The organic layers were dried over
Na₂SO₄, filtered and concentrated. Purification by flash chromatography (pentane/Et₂O,
50/1) gave 39 as a colourless oil (188 mg, 66%); ¹H NMR (500 MHz, CDCl₃): δ = 5.77–5.64
(m, 2H), 5.02 (dd, J = 17.2 Hz, J = 1.8 Hz, 1H), 4.99 (d, J = 11.0 Hz, 1H), 3.62 (s, 3H), 2.62–
2.54 (m, 1H), 2.51–2.42 (m, 1H), 2.39–2.29 (m, 2H), 2.27–2.20 (m, 1H), 1.05–0.94 (m, 4H);
¹³C NMR (125 MHz, CDCl₃): δ = 175.6, 135.4, 123.9, 116.7, 114.7, 51.4, 45.2, 35.8, 33.8,
2.5 1.9; IR (neat): ν = 3078, 3053, 2982, 2951, 2911, 2846, 1736, 1642, 1436, 1370, 1340,
1262, 1232, 1164, 1120, 1067, 1046, 995, 964, 916, 857, 834, 754, 718 cm⁻¹; MS (CI): m/z
(rel. intensity): 198 (100), 181 (73), 121 (26); HRMS (CI) calcd for (C₁₁H₁₆O₂ + H)⁺:
181.12285; found: 181.12233; elemental analysis (%) calcd for C₁₁H₁₆O₂: C 73.30, H 8.95;
found: C 73.25, H 8.99;
Compound 14d. This compound was prepared from 39 (160 mg, 0.89 mmol) according to the procedure described for the preparation of 19. The crude alcohol was then oxidised according to the procedure described for the preparation of 1. Colourless oil (79 mg, 59% over two steps). 1H NMR (500 MHz, CDCl3): \( \delta = 9.64 \) (s, 1H), 5.79 (d, \( J = 17.3 \) Hz, 1H), 5.06 (d, \( J = 17.5 \) Hz, 1H), 5.01 (d, \( J = 10.4 \) Hz, 1H), 2.55–2.63 (m, 1H), 2.48–2.55 (m, 1H), 2.46–2.36 (m, 2H), 2.30–2.22 (m, 1H), 1.07–0.98 (m, 4H); 13C NMR (125 MHz, CDCl3): \( \delta = 174.8, 141.1, 128.4 \) (2C), 126.8 (2C), 126.5, 125.3, 113.1, 104.6, 87.7, 68.9, 46.8, 38.1, 26.0, 2.8, 1.9, 0.0 (3C); IR (neat): \( \tilde{\nu} = 3078, 3048, 2981, 2922, 2849, 2718, 1725, 1641, 1440, 1393, 1070, 994, 966, 915, 835, 776, 749, 719 \); MS (Cl): m/z (rel. intensity): 168 (100), 152 (21), 150 (22), 135 (17), 133 (14); HRMS (Cl) calcd for \((C_{10}H_{14}O + NH_4)^+\): 168.1384; found: 168.1386.

Preparation of compound 14e

\[ \text{Ph} \quad \text{CO}_2\text{Me} \quad \xrightarrow{a} \quad \text{Ph} \quad \text{CO}_2\text{Me} \quad \xrightarrow{b} \quad \text{Ph} \quad \text{CHO} \quad \xrightarrow{c} \quad \text{Ph} \quad \text{CHO} \]

This compound was prepared from 17 (233 mg, 1.08 mmol) according to the procedure described for the preparation of 18 and using 3-bromo-1-(trimethylsilyl)-1-propyne. Colourless oil (271 mg, 77%). 1H NMR (500 MHz, CDCl3): \( \delta = 7.33–7.27 \) (m, 2H), 7.26–7.21 (m, 3H), 5.48 (tq, \( J = 7.3 \) Hz, \( J = 2.0 \) Hz, 1H), 3.66 (s, 3H), 3.14–3.01 (m, 2H), 2.93 (d, \( J = 16.5 \) Hz, 1H), 2.80 (d, \( J = 16.7 \) Hz, 1H), 1.08–0.92 (m, 4H), 0.08 (s, 9H); 13C NMR (125 MHz, CDCl3): \( \delta = 174.8, 141.1, 128.2 \) (2C), 127.1, 126.7, 126.3 (2C), 112.5, 103.6, 87.5, 54.0, 52.2, 37.2, 26.9, 2.9, 2.0, 0.0 (3C); IR (neat): \( \tilde{\nu} = 3078, 3048, 2981, 2922, 2849, 2718, 1725, 1641, 1440, 1393, 1070, 994, 966, 915, 835, 776, 749, 719 \); MS (Cl): m/z (rel. intensity): 168 (100), 152 (21), 150 (22), 135 (17), 133 (14); HRMS (Cl) calcd for \((C_{10}H_{14}O + NH_4)^+\): 168.1384; found: 168.1386.

Compound 40. This compound was prepared from 40 (255 mg, 0.782 mmol) according to the procedure described for the preparation of 19. Colourless oil (224 mg, 96%). 1H NMR (500 MHz, CDCl3): \( \delta = 7.39–7.29 \) (m, 4H), 7.26–7.19 (m, 1H), 5.54–5.44 (m, 1H), 5.95–5.83 (m, 2H), 2.79–2.71 (m, 2H), 2.68–2.58 (m, 2H), 1.59–1.44 (m, 1H (OH)), 1.03–0.94 (m, 3H), 0.94–0.85 (m, 1H), 0.11 (s, 9H); 13C NMR (125 MHz, CDCl3): \( \delta = 142.6, 128.4 \) (2C), 126.8 (2C), 126.5, 125.3, 113.1, 104.6, 87.7, 68.9, 46.8, 38.1, 26.0, 2.8, 1.9, 0.0 (3C); IR (neat): \( \tilde{\nu} = 3436, 3055, 2958, 2173, 1741, 1602, 1499, 1445, 1249, 1080, 1025, 838, 759, 696 \) cm\(^{-1}\); MS (ES+): m/z (rel. intensity): 321 (100); HRMS (ES+) calcd for \((C_{19}H_{26}OSi + Na)^+\): 321.1651; found: 321.1661; elemental analysis calcd (%) for \(C_{17}H_{26}O_2Si\): C 73.62, H 7.98; found: C 72.79, H 8.21.

Compound 41. This compound was prepared from 41 (127 mg, 0. 426 mmol) according to the procedure described for the preparation of 1. The crude material was purified by flash chromatography (PE only \( \rightarrow \) PE/EtOAc = 30/1). However, an unidentified small impurity was still visible by NMR. Further purification was not attempted. Colourless oil (107 mg, 85%). 1H NMR (500 MHz, CDCl3): \( \delta = 7.33–7.27 \) (m, 2H), 7.26–7.21 (m, 3H), 5.48 (tq, \( J = 7.3 \) Hz, \( J = 2.0 \) Hz, 1H), 5.06 (d, \( J = 17.3 \) Hz, 1H), 5.01 (d, \( J = 10.4 \) Hz, 1H), 2.55–2.63 (m, 1H), 2.48–2.55 (m, 1H), 2.46–2.36 (m, 2H), 2.30–2.22 (m, 1H), 1.07–0.98 (m, 4H); 13C NMR (125 MHz, CDCl3): \( \delta = 204.5, 136.5, 124.6, 117.1, 115.4, 51.7, 32.2, 31.2, 2.7, 2.3 \); IR (neat): \( \tilde{\nu} = 3078, 3048, 2981, 2922, 2849, 2718, 1725, 1641, 1440, 1413, 1393, 1070, 994, 966, 915, 835, 776, 749, 719 \); MS (Cl): m/z (rel. intensity): 168 (100), 152 (21), 150 (22), 135 (17), 133 (14); HRMS (Cl) calcd for \((C_{10}H_{14}O + NH_4)^+\): 168.1384; found: 168.13860.
9.58 (s, 1H), 7.39–7.33 (m, 2H), 7.32–7.20 (m, 2H), 5.55 (tq quint,
\(J = 7.4 \text{ Hz}, J = 2.0 \text{ Hz}, 1H\),
3.05–2.93 (m, 2H), 2.83 (d, \(J = 17.0 \text{ Hz}, 1H\), 2.72 (d, \(J = 17.2 \text{ Hz}, 1H\), 1.09–0.91 (m, 4H),
0.06 (s, 9H); ^13C NMR (125 MHz, CDCl₃): δ = 200.9, 137.5, 125.7 (2C), 127.6, 127.5 (2C),
127.0, 111.9, 102.7, 88.5, 57.3, 34.9, 24.5, 3.0, 2.0, -0.1 (3C); IR (neat): ν = 2959, 2702,
2178, 1725, 1496, 1447, 1249, 107, 838, 758, 697 cm⁻¹; HRMS (ES+) calcd for (C₁₉H₂₄OSi + Na⁺): 319.1494; found: 319.1496.

**Preparation of compound 14f**

![Diagram]

**Compound 42.** Under N₂, a solution of LDA (1.80 mmol), prepared from 0.72 mL of a 2.5 M
of nBuLi and 0.25 mL of diisopropylamine in THF (3.60 mL) at 0°C, was added
to a solution of 17 (150 mg, 0.694 mmol) in THF (3.30 mL) at -78°C. The
resulting solution was stirred at -78°C for 1.5 hour then 4-bromo-1-butyne (0.16
mL, 1.80 mmol) was slowly added. The mixture was stirred at -78°C for another
30 minutes before being quenched with few drops of methanol and allowed to
warm at room temperature. The mixture was diluted with a saturated solution of NH₄Cl (5
mL) and extracted with EtOAc (3 × 10 mL). The organic layers were dried over Na₂SO₄,
filtered and concentrated. Purification by flash chromatography (PE/EtOAc, 200/1 → 175/1 → 150/1) afforded 35 as a colourless oil (136 mg, 73%). ^1H NMR (500 MHz, CDCl₃): δ = 7.33–7.28 (m, 2H), 7.26–7.21 (m, 3H), 5.53–5.46 (m, 1H ), 3.64 (s, 3H), 3.10–3.01 (m, 2H),
2.88 (dq, \(J = 16.3 \text{ Hz}, J = 2.5 \text{ Hz}, 1H\), 2.75 (dq, \(J = 16.3 \text{ Hz}, J = 2.5 \text{ Hz}, 1H\), 1.71 (t, \(J = 2.5 \text{ Hz}, 3H\),
1.05–0.91 (m, 3H), 0.91–0.84 (m, 1H); ^13C NMR (100 MHz, CDCl₃): δ = 175.1, 141.3, 128.2 (2C), 126.9, 126.34 (2C), 126.31, 112.7, 78.1, 75.1, 54.0, 52.2, 37.4, 25.6, 3.5, 2.9, 1.8; IR (neat): ν = 3053, 3023, 2981, 2951, 2921, 2851, 1731, 1601, 1580, 1498, 1436, 1322, 1307, 1270, 1070, 1002, 964, 910, 849, 764, 731, 698 cm⁻¹; MS (ES+): m/z (rel. intensity): 291 (100); HRMS (ES+) calcd for (C₁₈H₂₀O₂ + Na)+: 291.1361; found: 291.1357; elemental analysis (%) calcd for C₁₈H₂₀O₂: C 80.56, H 7.51; found: C 80.85, H 7.59.

**Compound 43.** This compound was prepared from 42 (83 mg, 0.310 mmol) according to the
procedure described for the preparation of 19. Colourless oil (63 mg, 84%). ^1H NMR (400 MHz, CDCl₃): δ = 7.43–7.28 (m, 4H), 7.23–7.15 (m, 1H), 5.55–5.45 (m, 1H), 3.87 (d, \(J = 5.8 \text{ Hz}, 2H\), 2.75–2.65 (m, 2H), 2.63–2.57 (m, 1H), 2.56 (dq, \(J = 16.4 \text{ Hz}, J = 2.6 \text{ Hz}, 1H\), 1.75 (t, \(J = 2.6 \text{ Hz}, 3H\), 1.60–1.56 (m, 1H
(OH)), 1.03–0.90 (m, 3H), 0.89–0.82 (m, 1H); ^13C NMR (100 MHz, CDCl₃): δ = 143.0, 128.3 (2C), 126.9 (2C), 126.3, 125.0, 113.3, 78.2, 76.1, 68.9, 46.7, 38.4, 24.9, 3.5, 2.8, 1.8; IR (neat): ν = 2412, 3084, 3048, 2978, 2918, 1602, 1580, 1498, 1445, 1378, 1075, 1028, 966, 937, 860, 846, 761, 698 cm⁻¹; MS (ES+): m/z (rel. intensity): 263 (100); HRMS (ES+) calcd for (C₁₇H₂₀O + Na⁺): 263.1412; found: 263.1410.
**Compound 14f.** This compound was prepared from 43 (32 mg, 0.133 mmol) according to the procedure described for the preparation of 1. Colourless oil (29 mg, 91%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 9.57 (s, 1H), 7.39–7.32 (m, 2H), 7.30–7.26 (m, 1H), 7.24–7.21 (m, 2H), 5.57–5.49 (m, 1H), 2.99–2.88 (m, 2H), 2.79 (dq, $J$ = 16.8 Hz, $J$ = 2.6 Hz, 1H), 2.67 (dq, $J$ = 16.8 Hz, $J$ = 2.6 Hz, 1H), 1.70 (t, $J$ = 2.6 Hz, 3H), 1.06-0.82 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 201.4, 137.8, 128.7 (2C), 127.5 (2C), 127.4, 126.5, 112.0, 79.0, 74.4, 57.4, 35.3, 23.2, 3.5, 2.9, 1.9; IR (neat): $\tilde{\nu}$ = 3055, 2980, 2919, 2854, 2800, 2712, 1723, 1599, 1580, 1496, 1446, 1384, 1317, 1257, 1231, 1090, 1070, 1002, 967, 933, 910, 874, 837, 759, 733, 698 cm$^{-1}$; MS (ES+): $m/z$ (rel. intensity): 261 (100); HRMS (ES+) calcd for (C$_{17}$H$_{18}$O + Na)$^+$: 261.1255; found: 261.1257.
Representative procedure for rhodium-catalysed rearrangement

A Teflon-screw Schlenk flask equipped with a small stirring bar was charged with [Rh(nbd)2]BF4 (3.4 mg, 0.0091 mmol), BINAP (5.7 mg, 0.0091 mmol), and acetone (1.8 mL) under N2 before bubbling H2 (3.8 mL, 0.153 mmol) via syringe and sealing the flask under N2. After stirring for 1h at room temperature, this solution was added to aldehyde 1a (20.8 mg, 0.091 mmol) in acetone (0.83 mL) was added under N2 and the flask was again sealed. After stirring for 4 h at room temperature, the mixture was allowed to cool before evaporation. Purification by flash chromatography (PE/EtOAc: 250/1) gave ketone 2 (15.6 mg, 75%).

Compounds 4a–4e, 12, and 15c–15e were obtained according to this procedure using purified aldehydes as starting material and the catalyst loadings specified in the manuscript. Compounds 7, 10, 15a and 15b were obtained from crude aldehydes and after treating this crude material with the active catalyst prepared according to this general and representative procedure. Compound 15f was obtained according to this general procedure, except that BINAP was replaced with dpff.

**Compound 2.** White solid (25 mg, 89%). m.p.: 41–43 °C; 1H NMR (500 MHz, CDCl3): δ = 7.32–7.16 (m, 5H), 5.83–5.73 (m, 1H), 5.64–5.56 (m, 1H), 4.76–4.71 (m, 1H), 4.54–4.49 (m, 1H), 3.15–3.06 (m, 1H), 3.00–2.91 (m, 1H), 2.70 (d, J = 13.6 Hz, 1H), 2.59 (dd, J = 15.0 Hz, J = 7.5 Hz, 1H), 2.53 (d, J = 13.6 Hz, 1H), 2.36–2.21 (m, 3H), 1.06 (s, 1H); 13C NMR (125 MHz, CDCl3): δ = 212.2, 143.2, 140.6, 130.3, 128.4 (2C), 127.0, 126.9, 115.0, 61.8, 44.9, 37.9, 29.1, 27.1, 23.9; IR (neat): ν ~ = 3069, 3022, 2947, 2918, 2851, 1702, 1641, 1597, 1580, 1497, 1445, 1375, 1343, 1308, 1267, 1196, 1139, 1032, 963, 893, 793, 770, 728, 698, 661 cm⁻¹; MS (ES+): m/z (rel. intensity): 263 (100); HRMS (ES+) calcd for (C17H20O + Na)⁺: 263.1412; found: 263.1408.

**Compound 4a.** Colourless oil (25.2 mg, 85%). 1H NMR (500 MHz, CDCl3): δ = 7.33–7.28 (m, 2H), 7.24–2.20 (m, 3H), 5.85–5.77 (m, 1H), 5.68–5.61 (m, 1H), 3.09 (dd, J = 15.4 Hz, J = 5.9 Hz, 1H), 2.98 (ddd, J = 12.2 Hz, J = 9.5 Hz, J = 6.9 Hz, 1H), 2.47–2.38 (m, 2H), 2.32–2.24 (m, 2H); 13C NMR (125 MHz, CDCl3): δ = 213.6, 143.5, 130.3, 128.6 (2C), 127.0, 126.7, 126.1 (2C), 58.6, 38.7, 34.7, 26.7, 26.4; IR (neat): ν = 3053, 3022, 2969, 2928, 2851, 1706, 1600, 1580, 1495, 1445, 1375, 1343, 1308, 1267, 1196, 1139, 1032, 963, 893, 793, 770, 728, 698, 661 cm⁻¹; MS (CI): m/z (rel. intensity) 219 (13), 218 (100), 201 (9), 200 (3); HRMS (CI) calcd for (C14H16O + NH4)⁺: 218.1539; found: 218.1542; elemental analysis (%) calcd for C14H16O: C 83.96 H 8.05; found: C 83.17, H 8.17.

**Compound 4b.** Colourless oil (17.8 mg, 87%). 1H NMR (500 MHz, CDCl3): δ = 5.73–5.65 (m, 1H), 3.65 (d, J = 9.3 Hz, 1H), 3.37 (d, J = 9.3 Hz, 1H), 3.03 (td, J = 11.2 Hz, J = 5.3 Hz, 1H), 3.00–2.93 (m, 1H), 2.56–2.49 (m, 1H), 2.44–2.21 (m, 2H), 1.91 (dd, J = 15.9 Hz, J = 7.7 Hz, 1H), 1.00 (s, 3H), 0.84 (s, 9H), -0.01 (s, 3H), -0.03 (s, 3H); 13C NMR (125 MHz, CDCl3): δ = 217.4, 129.0, 126.7, 70.1, 56.0, 39.9, 31.5, 27.6, 25.8 (3C), 19.9, 18.2, -5.86 (2C); IR (neat): ν = 2954, 2929, 2896, 2857, 1706, 1464, 1383, 1362, 1211, 1251, 1203, 1089, 1006, 939, 907, 834, 774, 734, 657 cm⁻¹; MS (CI): m/z (rel. intensity) 271 (12), 269 (100); HRMS (CI) calcd for (C15H28O2Si + H): 269.19368; found: 255.19400; elemental analysis (%) calcd for C15H28O2Si: C 67.11, H 10.51; found: C 68.00, H 10.70.
**Compound 4c.** Colourless oil (23.4 mg, 93%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.24–7.16 (m, 3H), 7.06 (d, $J$ = 7.2 Hz, 2H), 5.70–5.61 (m, 1H), 5.53 (dt, $J$ = 11.4 Hz, 3.8 Hz, 1H), 3.65 (d, $J$ = 9.2 Hz, 1H), 3.46 (d, $J$ = 9.2 Hz, 1H), 2.87 (s, 2H), 2.69 (dd, $J$ = 11.3 Hz, $J$ = 7.9 Hz, $J$ = 6.0 Hz, 1H), 2.62 (dd, $J$ = 15.6 Hz, $J$ = 6.5 Hz, 1H), 2.55 (ddd, $J$ = 11.3 Hz, $J$ = 7.7 Hz, $J$ = 6.0 Hz, 1H), 2.36–2.23 (m, 2H), 2.16 (dd, $J$ = 15.6 Hz, $J$ = 6.3 Hz, 1H), 0.87 (s, 9H), 0.00 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 216.6, 137.5, 130.2 (2C), 129.2, 128.0 (2C), 126.3 (2C), 66.5, 60.4, 40.0, 39.9, 27.7, 27.4, 25.8 (3C), 18.2, -5.6, -5.7; IR (neat): $\tilde{\nu}$ = 3026, 2952, 2928, 2856, 1702, 1603, 1495, 1471, 1411, 1388, 1361, 1311, 1251, 1195, 1095, 1031, 1022, 1004, 939, 900, 834, 775, 733, 701, 667 cm$^{-1}$; MS (ES+): $m/z$ (rel. intensity): 367 (100); HRMS (ES+) calcd for (C$_{21}$H$_{32}$O$_2$Si + Na)$^+$: 367.2069; found: 367.2066; elemental analysis (%) calcd for C$_{21}$H$_{32}$O$_2$Si: C 73.20, H 9.36; found: C 72.98, H 9.30.

**Compound 4d.** Colourless oil (15.3 mg, 77%). $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ = 7.22-7.17 (m, 4H), 7.10-7.08 (m, 1H), 5.58-5.49 (m, 1H), 5.38-5.30 (m, 1H), 4.24 (d, $J$ = 12.0 Hz, 1H), 4.17 (d, $J$ = 12.0 Hz, 1H), 3.52 (d, $J$ = 8.6 Hz, 1H), 2.97-2.91 (m, 1H), 2.88 (dt, $J$ = 11.6 Hz, 8.2 Hz, 1H), 2.42 (dt, $J$ = 11.5 Hz, 5.7 Hz, 1H), 2.04-1.96 (m, 2H), 1.75 (dd, $J$ = 15.7 Hz, $J$ = 7.8 Hz, 1H), 1.09 (s, 3H); $^{13}$C NMR (125 MHz, C$_6$D$_6$): $\delta$ = 214.4, 138.9, 129.6, 128.6 (2C), 127.73, 127.66 (2C), 126.7, 77.6, 73.4, 54.9, 39.7, 32.2, 27.7, 20.6; IR (neat): $\tilde{\nu}$ = 3064, 3023, 2967, 2928, 2901, 1494, 1454, 1371, 1312, 1252, 1205, 1100, 1097, 776, 737, 698 cm$^{-1}$; MS (ES+): $m/z$ (rel. intensity): 267 (100); HRMS (ES+) calcd for (C$_{16}$H$_{20}$O$_2$ + Na)$^+$: 267.1361; found: 267.1356; elemental analysis (%) calcd for C$_{16}$H$_{20}$O$_2$: C 78.65, H 8.25; found: C 77.99, H 8.41.

**Compound 4e.** Colourless oil (5.4 mg, 54%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 5.74-5.60 (m, 2H), 4.06 (d, $J$ = 10.7 Hz, 1H), 4.03 (d, $J$ = 10.7 Hz, 1H), 2.91 (ddd, $J$ = 15.2 Hz, $J$ = 10.0 Hz, $J$ = 5.2 Hz, 1H), 2.69-2.62 (m, 2H), 2.45-2.363 (m, 1H), 2.356-2.58 (m, 2H), 2.11 (dd, $J$ = 15.6 Hz, $J$ = 6.5 Hz, 1H), 1.16 (s, 9H), 1.12 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 214.6, 178.1, 129.8, 125.9, 69.8, 53.7, 39.0, 32.0, 29.7, 27.3, 27.1 (3C), 20.5; IR (neat): $\tilde{\nu}$ = 3023, 2967, 2928, 2901, 1494, 1454, 1371, 1312, 1252, 1205, 1100, 1097, 776, 737, 698 cm$^{-1}$; MS (ES+): $m/z$ (rel. intensity): HRMS (ES+) calcd for (C$_{14}$H$_{22}$O$_3$ + Na)$^+$: 261.1467; found: 261.1356; elemental analysis (%) calcd for C$_{14}$H$_{22}$O$_3$: C 78.65, H 8.25; found: C 77.99, H 8.41.

**Compound 12.** Colourless oil (34.5 mg, 88%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 5.69–5.61 (m, 2H), 5.59–5.52 (m, 1H), 3.64 (d, $J$ = 9.6 Hz, 1H), 3.55 (d, $J$ = 9.6 Hz, 1H), 2.82–2.75 (m, 1H), 2.74–2.64 (m, 2H), 2.45–2.37 (m, 2H), 2.35–2.28 (m, 2H), 2.21 (dd, $J$ = 15.7 Hz, $J$ = 6.7 Hz, 1H), 1.06–1.01 (m, 2H), 0.99–0.90 (m, 2H), 0.85 (s, 9H), -0.01 (s, 3H), -0.02 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 216.6, 129.2, 126.7, 124.9, 113.4, 66.9, 59.8, 39.9, 36.1, 28.4, 27.5, 25.8 (3C), 18.1, 2.8, 1.8, -5.65, -5.69; IR (neat): $\tilde{\nu}$ = 3018, 2953, 2929, 2856, 1703, 1464, 1440, 1408, 1386, 1361, 1312, 1251, 1197, 1095, 1005, 960, 938, 902, 834, 775, 667 cm$^{-1}$; MS (ES+): $m/z$ (rel. intensity): 343 (100); HRMS (ES+) calcd for (C$_{19}$H$_{32}$O$_2$Si + Na)$^+$: 343.2069; found: 343.2067; elemental analysis (%) calcd for C$_{19}$H$_{32}$O$_2$Si: C 71.19, H 10.06; found: C 71.30, H 10.30.
### Compound 15a

This compound was obtained from crude aldehyde obtained according to the procedure and aqueous work up described for the preparation of compound 9. Colourless oil (15.6 mg, 75% over two steps). $^1$H NMR (500 MHz, CDCl₃): $\delta$ = 7.34–7.28 (m, 2H), 7.23–7.18 (m, 3H), 5.81–5.73 (m, 1H), 5.66–5.59 (m, 1H), 5.39–5.28 (m, 1H), 4.94 (d, $J$ = 17.0 Hz, 1H), 4.97 (d, $J$ = 9.0 Hz, 1H), 3.07 (dd, $J$ = 15.4 Hz, 5.5 Hz, 1H), 2.98–2.91 (m, 1H), 2.78 (dd, $J$ = 14.2 Hz, 5.9 Hz, 1H), 2.54 (dd, $J$ = 14.5 Hz, 12.2 Hz, 1H), 2.53 (t, $J$ = 14.3 Hz, 1H), 2.35–2.25 (m, 3H); $^{13}$C NMR (125 MHz, CDCl₃): $\delta$ = 121.4, 140.3, 134.3, 130.4, 128.5, 126.9, 126.8, 117.8, 61.8, 42.2, 38.3, 29.8, 26.7; IR (neat): $\tilde{\nu}$ = 3063, 3022, 2972, 2856, 1705, 1638, 1598, 1578, 1495, 1472, 1445, 1345, 1308, 1196, 1134, 1090, 1075, 1035, 998, 948, 913, 840, 785, 761, 727, 698, 673 cm⁻¹; MS (CI): $m/z$ (rel. intensity): 245 (16), 244 (100), 228 (10), 227 (70); HRMS (CI) calcd for (C₁₆H₁₈O + H)⁺: 227.1430; found: 227.1433; elemental analysis (%) calcd for C₁₄H₁₈O: C 84.91, H 8.02; found: C 84.96, H 8.18.

### Compound 15c

Colourless oil (17.2 mg, 75%). $^1$H NMR (500 MHz, CDCl₃): $\delta$ = 7.31–7.27 (m, 2H), 7.23–7.16 (m, 3H), 5.81–5.71 (m, 1H), 5.66–5.57 (m, 1H), 4.76–4.67 (m, 1H), 2.98 (dd, $J$ = 15.3 Hz, $J$ = 5.8 Hz, 1H), 2.91 (dt, $J$ = 16.4 Hz, 8.1 Hz, 1H), 2.58 (dd, $J$ = 14.8 Hz, 6.6 Hz, 1H), 2.52 (dd, $J$ = 15.0 Hz, 8.7 Hz, 1H), 2.49 (dd, $J$ = 15.3 Hz, 6.9 Hz), 2.39–2.32 (m, 1H), 2.31–2.22 (m, 2H), 1.58 (s, 3H), 1.44 (s, 3H); $^{13}$C NMR (125 MHz, CDCl₃): $\delta$ = 213.0, 140.8, 134.3, 130.3, 128.3 (2C), 127.09, 127.05 (2C), 126.7, 119.8, 62.3, 38.6, 36.1, 30.1, 26.7, 25.9, 17.8; IR (neat): $\tilde{\nu}$ = 3084, 3053, 3022, 2967, 2914, 2851, 1706, 1599, 1580, 1496, 1445, 1376, 1345, 1308, 1195, 1140, 1110, 1031, 1002, 981, 948, 899, 844, 774, 751, 724, 698, 681, 667 cm⁻¹; MS (ES⁺): $m/z$ (rel. intensity): 277 (100); HRMS (ES⁺) calcd for (C₁₈H₂₂O₂ + Na)⁺: 277.1568; found: 277.1568; elemental analysis (%) calcd for C₁₈H₂₂O₂: C 84.99, H 8.72; found: C 84.94, H 8.71.

### Compound 15d

Colourless oil (99% conversion was obtained when the reaction was performed in NMR tube). $^1$H NMR (500 MHz, CDCl₃): $\delta$ = 5.80–5.65 (m, 3H), 5.018 (dq, $J$ = 17.1 Hz, $J$ = 1.6 Hz, 1H), 5.017–4.98 (m, 1H), 2.91–2.83 (m, 1H), 2.68 (ddd, $J$ = 15.1 Hz, $J$ = 11.3 Hz, $J$ = 3.9 Hz, 1H), 2.53 (dd, $J$ = 6.5 Hz, $J$ = 3.7 Hz, 1H), 2.52–2.43 (m, 2H), 2.37–2.29 (m, 1H), 2.23–2.15 (m, 1H), 2.12–2.00 (m, 2H); $^{13}$C NMR (125 MHz, CDCl₃): $\delta$ = 214.0, 136.0, 129.5, 128.8, 116.8, 50.3, 42.2, 35.1, 30.1, 24.1; IR (neat): $\tilde{\nu}$ = 3073, 3018, 2916, 2851, 1706, 1641, 1436, 1373, 1259, 1219, 1194, 991, 913 cm⁻¹; MS (EI): $m/z$ (rel. intensity): 150 (6), 96 (48), 95 (27), 81 (24), 79 (53), 67 (44), 65 (18), 53 (44), 51 (21), 41 (59), 39 (100); HRMS (CI) calcd for (C₁₀H₁₄O)⁺: 150.1030; found: 150.1037.

### Compound 15e

Colourless oil (14 mg, 58%): 7.33–7.28 (m, 2H), 7.26–7.24 (m, 1H), 7.22–7.19 (m, 1H), 5.88–5.80 (m, 1H), 5.65 (dt, $J$ = 11.4 Hz, 4.2 Hz, 1H), 3.12 (ddqint, $J$ = 15.4 Hz, 6.1 Hz, 1.6 Hz, 1H), 2.94 (dt, $J$ = 12.4 Hz, 8.2 Hz, 1H), 2.84 (dd, $J$ = 17.2 Hz, $J$ = 1.1 Hz, 1H), 2.80 (dd, $J$ = 15.5 Hz, 7.0 Hz, 1H), 2.63 (d, $J$ = 17.2 Hz, 1H), 2.40 (dt, $J$ = 12.4 Hz, 5.6 Hz, 1H), 2.31–2.22 (m, 2H) 0.03 (s, 9H); $^{13}$C NMR (125 MHz, CDCl₃): $\delta$ = 211.4, 139.7, 130.9, 128.3 (2C), 127.2, 127.0 (2C), 126.7, 104.1, 87.7, 61.2, 38.8, 30.4, 29.7, 26.5, 0.0; IR (neat): $\tilde{\nu}$ = 3058, 3024, 2958, 2901, 2851, 2177, 1709, 1598, 1497, 1472, 1446, 1308, 1249, 1199, 1142, 1051, 1037, 1025, 1001, 976, 943, 842, 759, 729, 698, 670 cm⁻¹; MS (ES⁺): $m/z$ (rel. intensity): 319 (100); HRMS (ES⁺) calcd for (C₁₃H₂₂O⁺ + Na)⁺: 319.1494; found: 319.1487; elemental analysis (%) calcd for C₁₃H₂₂O⁺: C 76.97, H 8.16; found: C 71.11, H 8.46.
**Compound 15f.** Colourless oil (7.5 mg, 75%). 7.33–7.28 (m, 2H), 7.26–7.20 (m, 3H), 5.87–5.79 (m, 1H), 5.64 (dt, $J = 11.4$ Hz, $J = 4.3$ Hz, 1H), 3.13–3.06 (m, 1H), 2.92 (dt, $J = 12.5$ Hz, $J = 8.0$ Hz, 1H), 2.81 (dd, $J = 15.5$ Hz, $J = 6.8$ Hz, 1H), 2.75–2.69 (m, 1H), 2.60 (dq, $J = 16.9$ Hz, $J = 2.6$ Hz, 1H), 2.40 (dt, $J = 12.5$ Hz, $J = 5.8$ Hz, 1H), 2.28–2.21 (m, 2H), 1.66 (t, $J = 2.6$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 211.9$, 140.1, 130.6, 128.3 (2C), 127.1, 126.9 (2C), 126.8, 78.4, 75.7, 61.3, 38.9, 30.5, 28.7, 26.5, 3.5; IR (neat): $\tilde{\nu} = 3053, 3023, 2920, 2853, 1702, 1598, 1578, 1497, 1446, 1308, 1196, 1142, 1037, 758, 698, 670$ cm$^{-1}$; HRMS (ES+) calcd for (C$_{17}$H$_{18}$O + Na)$^+$: 261.1255; found: 261.1264.
Oxidation of diol 5 and hydroacylation of 1,3-keto-aldehyde 6

\[ \text{HO} \quad \text{a} \quad \text{HO} \rightarrow \begin{cases} \text{O} \quad \text{CHO} \quad \text{b} \quad \text{O} \end{cases} \]

\( ^a \) Dess-Martin periodinane, NaHCO\(_3\), CH\(_2\)Cl\(_2\), 0 °C, full conversion. \( ^b \) 10 mol% [Rh(BINAP)]BF\(_4\), acetone, 60 °C. 80% over two steps.

Compound 7. Under N\(_2\), 5 (14 mg, 0.0768 mmol) was added to a suspension of Dess Martin periodinane (137 mg, 0.323 mmol) and NaHCO\(_3\) (84 mg, 0.999 mmol) in CH\(_2\)Cl\(_2\) (1 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 2 hours. The mixture was filtered through deactivated neutral alumina and rinsed with a mixture PE/Et\(_2\)O (2:1). The filtrate was evaporated and the filtration was repeated. Crude compound 6 was obtained as colourless oil [\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 5.58–5.50 \) (m, 1H), 2.76 (dd, \( J = 14.0 \) Hz, 7.6 Hz, 1H), 2.55 (dd, \( J = 14.1 \) Hz, 7.1 Hz, 1H), 2.48 (dd, \( J = 11.7 \) Hz, 5.9 Hz, 1H), 2.53–2.17 (m, 2H), 1.98–1.76 (m, 3H), 1.09–1.03 (m, 2H), 1.02–0.94 (m, 2H)]. This crude material was not further purified due to its inherent instability. Instead, a solution of [Rh(BINAP)]BF\(_4\) (0.00768 mmol) in 1.5 mL acetone prepared according to the general procedure was added under N\(_2\) to crude ketoaldehyde 6. After 12 h at 60 °C and purification by flash chromatography (PE/Et\(_2\)O = 70/1 → 50/1 → 30/1), spirobisketone 7 was obtained as colourless oil (10.8 mg, 80%). [\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 5.72–5.64 \) (m, 1H), 5.63–5.56 (m, 1H), 3.28 (dt, \( J = 11.7 \) Hz, \( J = 11.6 \) Hz, 4.9 Hz, 1H), 2.42–2.35 (m, 2H), 2.33–2.23 (m, 1H), 2.08–2.04 (m, 1H), 2.03 (dd, \( J = 15.6 \) Hz, 8.0 Hz, 1H), 1.89–1.75 (m, 2H); [\(^13\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 215.6, 210.0, 130.2, 125.5, 69.5, 39.1, 38.2, 33.2, 30.7, 27.3, 19.3; IR (neat): \( \tilde{\nu} = 3018, 2961, 2854, 1736, 1699, 1626, 1608, 1442, 1405, 1349, 1312, 1274, 1199, 1147, 1089, 1044, 1011, 951, 916, 860, 824, 774, 693, 662 \) cm\(^{-1}\); MS (CI): \( m/z \) (rel. intensity): 196 (100), 179 (12), 151 (10); HRMS (CI) calcd for (C\(_{11}H_{14}O_2 + H)^+\): 179.1067; found: 179.1069.]
Oxidation of diol 8 and hydroacylation of 1,3-keto-aldehyde 9

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{OH} & \quad \text{OH} \\
\text{8} & \quad \text{9} & \quad \text{10}
\end{align*}
\]

\( ^a \text{(COCl)}_2, \text{DMSO, Et}_3\text{N, CH}_2\text{Cl}_2, -78 \text{ °C, full conversion.} \)

\( ^b \text{10 mol\% [Rh(BINAP)]BF}_4, \text{acetone, r.t., 82\% over two steps} \)

**Compound 10.** Under N\(_2\), dimethyl sulfoxide (30 µL, 0.425 mmol) was added to a solution of oxalyl chloride (18 µL, 0.210 mmol) in CH\(_2\)Cl\(_2\) (1.5 mL) at -78 °C. After 10 minutes stirring at -78 °C, a solution of alcohol 8 (21 mg, 0.103 mmol) in CH\(_2\)Cl\(_2\) (0.6 mL) was added. After 20 minutes stirring at -78°C, triethylamine (0.12 mL, 0.83 mmol) was added rapidly and the mixture was stirred at room temperature during 30 minutes. The mixture was quenched with a saturated aqueous solution of CuSO\(_4\) (4 mL) and extracted with CH\(_2\)Cl\(_2\) (3 × 5 mL). The organic layers were concentrated before being dissolved in CH\(_2\)Cl\(_2\) (5 mL) and washed with water (2 x 3 mL). The organic layer was dried over Na\(_2\)SO\(_4\), filtered and concentrated, affording 9 as colourless oil. This aqueous work up\(^2\) was repeated until no Me\(_2\)S was visible by NMR \( ^{1}\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 9.71 \text{ (s, 2H), 5.73–5.62 \text{ (m, 2H), 2.70 (d, } J = 7.2 \text{ Hz, 4H), 1.10–1.03 \text{ (m, 4H), 1.01–0.93 \text{ (m, 4H);} \)} \)

\( ^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 201.5 \text{ (2C), 127.2 (2C), 110.9 (2C), 65.5, 33.2 (2C), 3.0 (2C), 2.1 (2C)] \). This crude material was not further purified due to its inherent instability. Instead, a solution of [Rh(BINAP)]BF\(_4\) (0.01 mmol) in 2 mL acetone prepared according to the general procedure was added under N\(_2\) to crude bisaldehyde 9. After stirring at room temperature for 12h, evaporation of volatiles and purification by flash chromatography gave 10. Colourless oil (16.7 mg, 82%). \( ^{1}\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 5.73–5.59 \text{ (m, 4H), 3.23 (td, } J = 11.4 \text{ Hz, } J = 5.5 \text{ Hz, 2H), 3.20–3.14 \text{ (m, 2H), 2.48–2.40 \text{ (m, 2H), 2.35 (dt, } J = 11.4 \text{ Hz, } J = 5.1 \text{ Hz, 2H), 2.33–2.23 \text{ (m, 2H), 2.18 (dd, } J = 15.7 \text{ Hz, } J = 7.5 \text{ Hz, 2H); } \)

\( ^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 209.6 \text{ (2C), 130.2 (2C), 126.1 (2C), 75.6, 38.5 \text{ (2C), 28.5 (2C), 27.4 (2C); IR (neat): } \nu = 3023, 2973, 2896, 2856, 1709, 1691, 1469, 1440, 1382, 1349, 1311, 1195, 1140, 1112, 1076, 1043, 980, 934, 902, 836, 794, 746, 669 \text{ cm}^{-1}; \text{ MS (Cl): } m/z \text{ (rel. intensity): } 222 \text{ (100), 205 (32); HRMS (Cl) caled for } (\text{C}_{13}\text{H}_{16}\text{O}_{2} + \text{H}) \text{: 205.1223; found: 205.1223; elemental analysis (% caled for } \text{C}_{13}\text{H}_{16}\text{O}_{2}: \text{ C } 76.44, \text{ H } 7.90; \text{ found: C 75.49, H 7.81.} \)

Preparation of compound 14b and hydroacylation to obtain 15b

![Chemical Structure](image)

a LiHMDS, crotyl chloride, THF, -78 °C to r.t., 83%. b LiAlH4, Et2O, r.t., 94%. c (COCl)2, DMSO, Et3N, CH2Cl2, -78 °C, CuSO4 aqueous work up, full conversion. d 10 mol% [Rh(BINAP)]BF4, acetone, r.t., 70% over two steps

**Compound 44.** This compound was prepared from 17 (152 mg, 0.698 mmol) according to the procedure described for the preparation of 18 and using crotyl chloride (E/Z = 6:1). This compound was obtained as an inseparable mixture of stereoisomers (E/Z = 5:1 (determined by 1H NMR)). Colourless oil (157 mg, 83%).

1H NMR (500 MHz, CDCl3): δ = 7.32–7.26 (m, 2H), 7.26–7.19 (m, 3H), 5.52–5.36 (m, 2H), 5.23–5.14 (m, 1H), 3.61 (s, 3H), 2.89 (dd, J = 13.8 Hz, J = 7.7 Hz, 1H), 2.82 (dd, J = 14.1 Hz, J = 6.9 Hz, 1H), 2.72 (dd, J = 13.7 Hz, J = 7.6 Hz, 1H), 2.64 (dd, J = 13.8 Hz, J = 6.7 Hz, 1H), 1.59 (dd, J = 6.6 Hz, J = 0.9 Hz, 3H), 1.02–0.92 (m, 2H), 0.89–0.82 (m, 1H), 0.82–0.74 (m, 1H);

13C NMR (125 MHz, CDCl3): δ = 175.9, 142.3, 129.0, 128.18 (2C), 126.63, 126.57 (2C), 125.8, 125.4, 112.97, 54.4, 51.9, 37.8, 37.2, 18.1, 2.75, 1.79; Additional signals for the minor isomer: 1H NMR (500 MHz, CDCl3): δ = 2.93 (dd, J = 14.1 Hz, J = 7.8 Hz, 1H), 1.47 (d, J = 6.6 Hz, 3H);

13C NMR (125 MHz, CDCl3): δ = 175.9, 142.3, 129.0, 128.18 (2C), 126.63, 126.57 (2C), 125.8, 125.4, 112.97, 54.4, 51.9, 37.8, 37.2, 18.1, 2.75, 1.79; Additional signals for the minor isomer: 1H NMR (500 MHz, CDCl3): δ = 2.93 (dd, J = 14.1 Hz, J = 7.8 Hz, 1H), 1.47 (d, J = 6.6 Hz, 3H);

IR (neat): ν ~ = 3024, 2981, 2949, 1730, 1600, 1498, 1439, 1260, 1201, 1130, 1092, 1068, 1036, 1002, 967, 934, 919, 847, 763, 736, 697 cm⁻¹;

MS (ES+): m/z (rel. intensity): 293 (100); HRMS (ES+) calcd for (C18H22O2 + Na)+: 293.1517; found: 293.1525; elemental analysis calcd (%) for C 18H22O2: C 79.96, H 8.20; found: C 80.41, H 8.46.

**Compound 45.** This compound was prepared from 44 (122 mg, 0.452 mmol) according to the procedure described for the preparation of 19. This compound was obtained as an inseparable mixture of stereoisomers (E/Z = 5:1 (determined by 1H NMR)). Colourless oil (103 mg, 94%).

1H NMR (500 MHz, CDCl3): δ = 7.40–7.29 (m, 4H), 7.23–7.17 (m, 1H), 5.66–5.56 (m, 1H), 5.54–5.44 (m, 1H), 5.34–5.24 (m, 1H), 4.98 (dd, J = 13.8 Hz, J = 7.2 Hz, 1H), 3.78 (s, 2H), 2.61 (dd, J = 13.9 Hz, J = 7.5 Hz, 1H), 2.54 (dd, J = 13.8 Hz, J = 7.2 Hz, 1H), 2.49 (dd, J = 13.8 Hz, J = 7.2 Hz, 1H), 2.41 (dd, J = 14.1 Hz, J = 7.2 Hz, 1H), 1.61 (dd, J = 6.0 Hz, J = 1.0 Hz, 3H), 1.41–1.31 (m, 1H (OH)), 1.05–0.96 (m, 2H), 0.96–0.86 (m, 2H);

13C NMR (125 MHz, CDCl3): δ = 143.9, 128.3 (2C), 128.1, 127.0 (2C), 126.8, 126.0, 124.4, 113.9, 68.26, 46.6, 38.4, 37.8, 18.0, 2.7, 1.8;

Additional signals for the minor isomer: 1H NMR (500 MHz, CDCl3): δ = 2.67 (dd, J = 13.9 Hz, J = 7.2 Hz, 1H), 1.58 (d, J = 6.8 Hz, 3H);

13C NMR (125 MHz, CDCl3): δ = 126.2, 126.1, 124.6, 114.0, 68.32, 46.8, 32.6, 12.9, 2.8; IR (neat): ν = 3413 (br), 3024, 2978, 2917, 1601, 1498, 1445, 1027, 967, 937, 759, 697 cm⁻¹;

MS (ES+): m/z (rel. intensity): 265 (100); HRMS (ES+) calcd for (C17H22O + Na)+: 265.1568; found: 265.1569; elemental analysis calcd (%) for C17H22O: C 84.25, H 9.15; found: C 83.94, H 9.48.
**Compound 15b.** Aldehyde 14b prepared from 45 (23.5 mg, 0.093 mmol) according to the procedure described for the preparation of 9 was not further purified due to its inherent instability \[^1H\ NMR (500 MHz, CDCl\textsubscript{3}): \delta = 9.52 (s, 1H), 7.40–7.32 (m, 2H), 7.31–7.17 (m, 3H), 5.62–5.39 (m, 2H), 5.26–5.14 (m, 1H), 2.90–2.56 (m, 4H), 1.58 (d, J = 6.5 Hz, 3H), 1.05–0.94 (m, 2H), 0.92-0.78 (m, 2H);\]^\[1\] Additional signal for the minor isomer: \[^1H\ NMR (500 MHz, CDCl\textsubscript{3}): \delta = 1.48 (d, J = 6.5 Hz, 3H)]. Instead, a solution of [Rh(BINAP)]BF\textsubscript{4} (0.0093 mmol) in 1.9 mL acetone prepared according to the general procedure was added under N\textsubscript{2} to the crude aldehyde. After stirring at room temperature for 12h, evaporation of volatiles and purification by flash chromatography gave 15b as inseparable mixture of stereoisomers (E/Z = 4:1, ratio determined by \[^1H\ NMR\]). Colourless oil (16.3 mg, 70%). \[^1H\ NMR (500 MHz, CDCl\textsubscript{3}): \delta = 7.33–7.27 (m, 2H), 7.24–7.16 (m, 3H), 5.81–5.71 (m, 1H), 5.66–5.57 (m, 1H), 5.39 (dq, J = 15.1 Hz, J = 6.5 Hz, 1H), 5.03–4.92 (m, 1H), 3.05–2.92 (m, 1H), 2.92 (dt, J = 11.9 Hz, J = 8.2 Hz, 1H), 2.67–2.58 (m, 1H), 2.49 (dd, J = 15.3 Hz, J = 7.0 Hz, 1H), 2.43 (dd, J = 14.1 Hz, J = 8.6 Hz, 1H), 2.37–2.301 (m, 1H), 2.297–2.22 (m, 2H), 1.54 (d, J = 6.3 Hz, 3H); \[^13C\ NMR (125 MHz, CDCl\textsubscript{3}): \delta = 212.8, 140.7, 130.2, 128.4 (2C), 128.3, 126.96, 126.92 (2C), 126.9, 126.7, 62.1, 41.2, 38.6, 30.04, 26.7, 17.96; Additional signals for the minor isomer: \[^1H\ NMR (500 MHz, CDCl\textsubscript{3}): 5.49 (dqt, J = 11.0 Hz, J = 6.8 Hz, J = 1.5 Hz, 1H), 1.46 (d, J = 6.8 Hz, 3H); \[^13C\ NMR (125 MHz, CDCl\textsubscript{3}): \delta = 140.5, 130.5, 127.04, 126.8, 125.9, 38.4, 34.7, 30.05, 26.8, 17.97; IR (neat): \tilde{\nu} = 3058, 3022, 2916, 2854, 1706, 1598, 1578, 1495, 1467, 1445, 1377, 1345, 1308, 1196, 1142, 1074, 1036,1002, 970, 912, 770, 753, 728, 698, 665 \text{cm}^{-1}; MS (ES\textsuperscript{+}): m/z (rel. intensity): 263 (100); HRMS (ES\textsuperscript{+}) calcd for (C\textsubscript{17}H\textsubscript{20}O + Na\textsuperscript{+}): 263.1412; found: 263.1410.]
Compound 4c – COSY1
Compound 4c – COSY2
Compound 15c – COSY1
Compound 15c – COSY2
Compound 15c – HSQC