Supporting Information

Samarium diiodide catalyzed diastereoselective pinacol couplings

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Procedure for synthesis of substrates for intramolecular pinacol couplings (Scheme 2)

2-oxo-1-(2-oxo-ethyl)-cyclohexanecarboxylic acid ethyl ester

A solution of acrolein (6 mL, 90 mmol) and triethylamine (0.85 mL, 6 mmol) in dry DMF (70 mL) was added to a solution of ethyl 2-oxocyclohexanecarboxylate (60 mmol). The mixture was stirred for 3 hrs at room temperature and quenched with water (10 mL). The organic layer was then extracted with ethyl acetate (50 mL) and washed twice with water (50 mL). The combined extracts were dried (MgSO_4) and evaporated under reduced pressure. The crude product was purified by flash chromatography (petroleum ether/ Et_2O = 8/2 to petroleum ether/ Et_2O = 6/4) to give a pale yellow oil (6.3g, 87%).

R_f : 0.55 (PE/ Et_2O = 2/8). δ_H (400 MHz; CDCl_3 ; TMS) 9.7 (s, 1H), 4.2 (br. q, 2H, J 7.1), 2.46-2.36 (m, 5H), 2.16 (ddd, 1H, J 5.5, 9.8, 14.5), 2.0 (m, 1H), 1.9 (ddd, 1H, J 5.7, 10, 14.3), 1.79 (m, 1H), 1.65 (td, 2H, J, 10.5, 1.8), 1.48 (td, 1H, J 12.9, 3.9), 1.28 (t, J 7.1, 3H); δ_C (100 MHz; CDCl_3 ; TMS) 208.1, 201.6, 172.1, 60.5, 60.2, 39.9, 37, 36.7, 27.8, 27.2, 22.7, 14.4; $\nu_{\text{max}}/\text{cm}^{-1}$ (neat) 2941, 2866, 2726, 1712, 1449; m/z (C.I.); 227 (100% $[\text{M}+\text{H}]$), 244 (88.43% $[\text{M}+\text{NH}_4]$; $\text{C}_{12}\text{H}_{18}\text{O}_4$ requires C, 63.7; H, 8.02% found: C, 63.76; H, 8.13%.

(3-acetyl-2-oxo-tetrahydrofuran-3-yl)acetaldehyde

An analogous procedure to that above was adopted. Crude product was purified by flash chromatography (petroleum ether/ Et_2O = 6/4 to petroleum ether/ Et_2O = 1/9) gave a pale yellow oil (9.8g, 90%).

R_f : 0.1 (petroleum ether/ Et₂O: 2/8). δ_H (400 MHz; CDCl₃; TMS) 9.76 (s, 1H), 4.34 (dt, 1H, J 3.6, 8.3), 4.19 (dd, 1H, 8.3, 16.3), 2.83 (ddd, 1H, 3.6, 7.3, 12), 2.5 (m, 2H), 2.37 (m, 1H), 2.33 (s, 3H), 2.2 (m, 1H), 2.07 (ddd, 1H, 4.2, 8.3, 12); δ_C (100 MHz; CDCl₃; TMS) 202.6, 200.0, 175.6, 66.4, 60.5, 39.3, 29.8, 26.3, 26.1; ν_{max}/cm^{-1} (neat): 2928, 2730, 1762, 1711, 1168, 1218; m/z (C.I.) 202 (100%, [M+NH₄]), 184 (17.5%, [M]) C₉H₁₂O₄ requires C, 58.69; H, 6.57% found: C, 58.31; H, 6.65%

2-acetyl-2-methyl-5-oxo-pentanoic acid ethyl ester

An analogous procedure to those above was adopted. The crude product was purified by flash chromatography (petroleum ether/Et₂O = 7/3 to petroleum ether/Et₂O = 5/5) to give a pale yellow oil (7.92g, 66%).

R_f ; (5/5 petroleum ether/ Et₂O): 0.3. δ_H (400 MHz; CDCl₃; TMS) 9.76 (t, 1H, J 1.2), 4.2 (br. q, J, 7.2, 2H), 2.44 (dddd, 1H, J 1.3, 3.6, 4.6, 6.3), 2.33 (ddd, 1H, J 1.9, 4.8, 6.3), 2.23 (m, 1H), 2.16 (s, 3H), 2.07 (m, 1H), 1.35 (d, 3H, J 1.6), 1.26 (t, 3H, J 7.2); δ_C (100 MHz; CDCl₃; TMS) 205.4, 201.2, 172.7, 61.8, 58.9, 39.4, 26.8, 26.4, 19.5, 14.3; ν_{max}/cm^{-1} (neat) 2984, 2941, 2729, 1712, 1256. 1190, 1107; m/z (C.I.) 228 (100%, [M+NH₄]), 201 (57.68 %, [M+H]⁺) C₉H₁₂O₄ requires C, 59.98; H, 8.05; O, 31.96% : found: C, 59.71; H, 7.98%

General procedure for SmI₂ catalyzed pinacol couplings

A Schlenk tube was charged with magnesium turnings (154 mg, 6.4 mmol). After vigorous stirring for 1 hr under argon, to activate the magnesium, a solution of 0.1M SmI₂ (10 mol %, 4 mL, 0.4) in THF, dimethyl dichlorosilane (0.05 mL, 0.4 mmol) and tetraglyme (0.09 mL, 0.4 mmol) were added successively to the magnesium. A mixture of aldehyde (1mmol), dimethyl dichlorosilane (0.1 mL, 0.8 mmol) and THF was then added dropwise *via* a syringe pump at such a rate as to retain the blue colour. After the addition, the mixture was filtered, quenched with Bu₄NF (1.0 M in THF, 10 mL) and

washed with brine (10 mL). The mixture was evaporated under reduced pressure and the product was extracted by continuous extraction with diethylether (200mL), overnight. The mixture was evaporated under reduced pressure and purified by flash chromatography to give the diol.

All the diols were analysed by GC (SE-30) 60 to 260°C 10°C/min.

Characterisation of products from intramolecular pinacol couplings

(5S, 10S*, 11R*)-5,11-dihydroxy-octahydro-indene carboxylic acid ethyl ester*

R_f : (petroleum ether/ Et₂O 8/2) 0.21. The data are consistent with the literature:¹ δ_H (400 MHz; CDCl₃; TMS) 4.2 (br.s, 1H), 4.18, (br q, 2H, J 7.1), 4.06 (br. s, 1H), 2.25 (ddd, 1H, J 4.0, 8.9, 17), 2.14 (ddd, 1H, J 4.1, 8.9, 12.9), 1.99 (br. td, 1H, J 13.8, 8.3), 1.80 (m, 1H), 1.72-1.59 (m, 5H), 1.50 (m, 1H, H₉), 1.39 (dt, 2H, J 3.0, 13.8), 1.27 (t, 3H, J 7.1); δ_C (100 MHz; CDCl₃; TMS) 177.0, 79.7, 74.5, 61.2, 54.1, 33.3, 31.7, 31.3, 29.7, 22.8, 22.6, 14.4; ν_{max}/cm^{-1} , 3432.1, 2938.1, 2864.4, 1721.9, 1449.0, 1368.6, 1231.0; m/z (C.I.) 246 (11.31% [M+NH₄]), 229 (100% [M+H]), 228 (.18% [M]); C₁₂H₂₀O₄ requires: C, 63.14; H, 8.83; O, 28.03%, found: C, 63.43; H, 8.65%.

(2R, 8S*, 9S*)-2,9-dihydroxy-9-methyloxa-spiro[4,4]non-1-one*

R_f : (petroleum ether/ Et₂O 8/2) 0.21. δ_H (400 MHz; CDCl₃; TMS) 4.34 (t, 1H, J 7.8), 4.31 (ddd, 1H, J 6.4, 8.4, 9.0), 4.25 (ddd, 1H, J 6.4, 8.4, 9.0), 2.80 (ddd, 1H, J 6.4, 8.1, 13.7), 2.74 (br. s, 1H), 2.45 (br. s, 1H), 2.2 (dddd, 1H, J 5.8, 8.5, 8.9, 13.2), 2.09 (ddd, 1H, J 6.5, 8.0, 13.3), 2.02 (ddd, 1H, J 5.9, 8.9, 13.2), 1.93 (ddd, 1H, J 5.8, 10.8, 13.2), 1.71 (ddd, J 5.9, 10.8, 13.0, 1H); δ_C (100 MHz; CDCl₃; TMS) 181.0, 80.0, 77.8, 66.7, 55.6,

¹ Molander, G. A., Kenny, C. *J. Am. Chem. Soc.* **1989**, *111*, 8236-8246.

32.4, 31.4, 30.0, 21.1 other isomer 182.7, 80.0, 78.9, 67.4, 56.6, 31.8, 31.6, 31.0, 23.0;
 $\nu_{\max}/\text{cm}^{-1}$ (nujol): 3389, 1746, 1720; m/z (C.I.) 204 (100% $[\text{M}+\text{NH}_4]$), 187 (16.77% $[\text{M}+\text{H}]$); $\text{C}_{12}\text{H}_{20}\text{O}_4$ requires C 58.05; H 7.58; O 34.37 %; found: C 58.41, H 7.72 %

(5R, 8R*, 9S*)-5,9-dihydroxy-8,9-dimethyl-cyclopentanecarboxylic acid ethyl ester*

The data are consistent with the literature:¹ δ_{H} (400 MHz; CDCl_3 ; TMS) 4 (ddd, 1H, J 2.3, 7.1, 9.4, H_5), 3.94 (dd, 2H, J 7.1, 13.7), 3.34 (br. s, 1H), 3.05 (br. s, 1H), 2.02 (m, 1H), 1.93 (m, 1H), 1.61-1.47 (m, 2H), 1.16 (s, 3H), 1.13 (t, 3H, J 7.1), 1.01 (s, 3H); δ_{C} (100 MHz; CDCl_3 ; TMS) 176.5, 79.7, 77.9, 60.3, 54.8, 32.0, 29.5, 21.4, 18.4, 13.8 minor diastereomer, 177.1, 80.6, 77.3, 60.7, 53.1, 31.9, 29.4, 22.0 21.8, 13.7; $\nu_{\max}/\text{cm}^{-1}$ 3458, 2978, 2879, 1716; m/z (C.I.) 220 (100% $[\text{M}+\text{NH}_4]$), 202 (36.39% $[\text{M}]$); $\text{C}_{10}\text{H}_{18}\text{O}_4$ require: C, 59.39; H, 8.97; O, 31.64%; found: C, 59.2, H, 8.9%.