

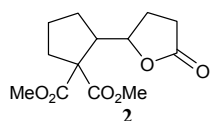
Synthesis of fused tricyclic γ -lactones mediated by manganese(III) acetate

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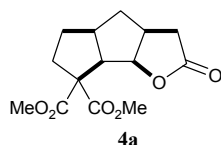
General Experimental Procedure.

Mn(OAc)₃•2HO (39.7 mg, 0.148 mmol) was added to a stirring solution of substrate (0.074 mmol) in acetonitrile (2 mL). The mixture was degassed and then heated under reflux under N₂ overnight. The cooled reaction mixture was partitioned between water (4 mL) and ether (4 mL) and the aqueous layer was washed with ether (5 × 4 mL). The combined organic layers were dried (MgSO₄), filtered and the solvent removed *in vacuo*. The resulting oil was purified by flash chromatography (petroleum ether: EtOAc, 1:1) to provide the product γ -lactones.

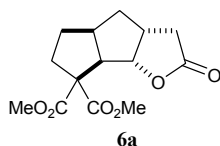


Diastereomer 1: isolated as a clear, colourless oil; R_f 0.4 (petroleum ether: EtOAc, 1:1); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1773, 1728; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 4.72 (1H, ddd, J 8.0, 6.6 and 4.4), 3.74 (3H, s), 3.73 (3H, s), 2.78 (1H, ddd, J 12.0, 7.0 and 4.4), 2.56-2.47 (3H, m), 2.30 (1H, td, J 13.0 and 6.6), 2.07-1.89 (4H, m) and 1.72-1.58 (2H, m); $\delta_{\text{C}}(125 \text{ MHz}; \text{CDCl}_3)$ 176.9, 172.7, 170.9, 80.1, 61.7, 52.8, 52.7, 50.4, 35.0, 28.8, 27.2, 25.5 and 22.6; m/z (EI) [Found: M^+ , 270.1101. C₁₃H₁₈O₆ requires M , 270.1103].

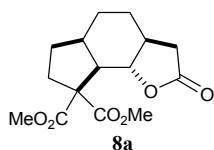
Diastereomer 2: isolated as a clear, colourless oil; R_f 0.3 (petroleum ether: EtOAc, 1:1); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1774, 1728; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 4.64 (1H, ddd, J 9.0, 7.8 and 6.2), 3.74 (6H, 2 × s), 2.90 (1H, q, J 9.0), 2.52-2.38 (3H, m), 2.34-2.18 (2H, m), 1.98-1.88 (2H, m), 1.83-1.75 (1H, m) and 1.63-1.46 (2H, m); $\delta_{\text{C}}(125 \text{ MHz}; \text{CDCl}_3)$ 176.2, 172.4, 171.3, 79.9, 62.1, 52.9, 52.7, 51.0, 35.5, 28.5, 26.9, 26.8, 22.7; m/z (EI) [Found: M^+ , 270.1107. C₁₃H₁₈O₆ requires M , 270.1103].



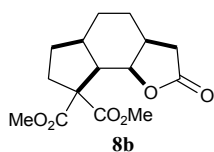
Isolated as a clear, colourless oil; R_f 0.3 (petroleum ether: EtOAc, 1:1); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1776, 1732; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 4.88 (1H, t, J 5.2), 3.77 (3H, s), 3.71 (3H, s), 3.39 (1H, dd, J 9.2 and 5.2), 2.87 (1H, dd, J 9.2 and 4.0), 2.83-2.74 (1H, m), 2.65 (1H, dd, J 17.0 and 7.0), 2.40-2.30 (3H, m), 2.18 (1H, dd, J 13.8 and 2.4), 1.73 (1H, ddd, J 13.0, 11.8, 9.2 and 7.2), 1.47-1.40 (1H, m) and 1.15 (1H, ddd, J 14.0, 9.8 and 8.4); $\delta_{\text{C}}(125 \text{ MHz}; \text{CDCl}_3)$ 175.6, 172.2, 170.6, 88.2, 63.3, 53.4, 53.1, 52.7, 44.0, 41.8, 38.9, 36.0, 33.8 and 30.3; m/z (EI) [Found: M^+ , 282.1112. C₁₄H₁₈O₆ requires M , 282.1103].



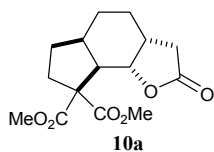
Isolated as a white crystalline solid; mp 88 – 90 °C (from petroleum ether: EtOAc); R_f 0.4 (petroleum ether: EtOAc, 1:1); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1777, 1731; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 4.50 (1H, dd, J 6.2 and 2.0), 3.74 (3H, s), 3.72 (3H, s), 3.33 (1H, dd, J 7.8 and 2.0), 3.02-2.93 (1H, m), 2.90-2.81 (1H, m), 2.67 (1H, dd, J 15.2 and 8.4), 2.31 (1H, dd, J 15.2, and 2.6); 2.15 (2H, dd, J 9.0 and 6.0), 1.87 (1H, ddd, J 13.2, 8.0 and 2.8), 1.85-1.72 (2H, m) and 1.46-1.38 (1H, m); $\delta_{\text{C}}(125 \text{ MHz}; \text{CDCl}_3)$ 176.4, 171.4, 170.8, 88.7, 64.1, 56.0, 53.0, 52.8, 43.7, 40.2, 38.5, 35.1, 34.1 and 30.3; m/z (EI) [Found: M^+ , 282.1108. $\text{C}_{14}\text{H}_{18}\text{O}_6$ requires M , 282.1103].



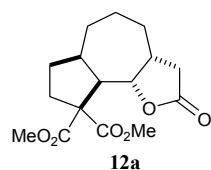
Isolated as a clear, colourless oil; R_f 0.5 (petroleum ether: EtOAc, 1:1); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1783, 1731; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 3.74 (3H, s), 3.73 (1H, t, J 11.0), 3.72 (3H, s), 2.95 (1H, dd, J 11.0 and 6.0), 2.82 (1H, ddd, J 15.0, 10.6 and 4.4), 2.63-2.53 (1H, m), 2.48 (1H, dd, J 16.0 and 6.6), 2.20-2.11 (2H, m), 2.01-1.90 (1H, m), 1.82 (1H, dq, J 12.6 and 3.0), 1.75-1.60 (4H, m) and 1.48-1.35 (1H, m); $\delta_{\text{C}}(125 \text{ MHz}; \text{CDCl}_3)$ 175.5, 172.6, 170.7, 81.2, 62.6, 53.1, 52.8, 50.1, 43.5, 39.8, 35.3, 30.4, 27.1, 26.1, 23.7; m/z (ESI) [Found: $(M + \text{Na})^+$, 319.1165. $\text{C}_{15}\text{H}_{20}\text{O}_6\text{Na}$ requires M , 319.1158].



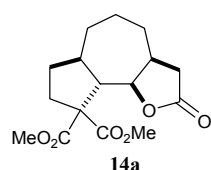
Isolated as a clear, colourless oil; R_f 0.4 (petroleum ether: EtOAc, 1:1); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1779, 1733; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 4.80 (1H, t, J 4.5), 3.74 (3H, s), 3.72 (3H, s), 2.88 (1H, dd, J 8.0 and 4.0), 2.76 (1H, ddd, J 14.6, 10.0 and 4.4), 2.72 (1H, dd, J 17.0 and 7.8), 2.50-2.44 (1H, m), 2.44-2.34 (1H, m), 2.19 (1H, d, J 17.0), 2.09 (1H, ddd, J 14.6, 8.0 and 7.0), 1.78-1.68 (2H, m) and 1.64-1.35 (4H, m); $\delta_{\text{C}}(125 \text{ MHz}; \text{CDCl}_3)$ 176.7, 172.8, 170.1, 78.9, 64.1, 53.1, 52.7, 45.1, 37.9, 36.5, 34.4, 32.5, 25.8, 23.8 and 23.5; m/z (ESI) [Found: $(M + \text{Na})^+$, 319.1161. $\text{C}_{15}\text{H}_{20}\text{O}_6\text{Na}$ requires M , 319.1158].



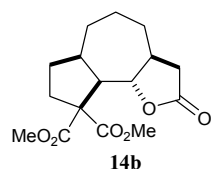
Isolated as a clear, colourless oil; R_f 0.5 (petroleum ether: EtOAc, 1:1); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1777, 1727; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 4.78 (1H, dd, J 2.8 and 3.8), 3.74 (3H, s), 3.73 (3H, s), 2.95 (1H, dd, J 8.0 and 3.8), 2.66 (1H, dd, J 17.0 and 8.0), 2.50 (1H, ddd, J 14.0, 8.0 and 6.0), 2.52-2.42 (1H, m), 2.31-2.22 (1H, m), 2.24 (1H, dd, J 17.0 and 8.8), 2.12 (1H, ddd, J 14.0, 8.8 and 6.0), 1.94 (1H, ddd, J 13.1, 8.9, 8.5 and 6.6), 1.77-1.69 (1H, m), 1.64-1.57 (1H, m), 1.56 (1H, ddd, J 17.9, 8.5, 6.4 and 4.5) and 1.25-1.05 (2H, m); $\delta_{\text{C}}(125 \text{ MHz}; \text{CDCl}_3)$ 176.4, 172.1, 171.7, 79.1, 62.1, 53.0, 52.8, 47.1, 36.9, 36.0, 33.9, 33.0, 29.7, 26.4 and 26.0; m/z (ESI) [Found: $(M + \text{H})^+$, 297.1344. $\text{C}_{15}\text{H}_{21}\text{O}_6$ requires M , 297.1338].



Isolated as a clear, colourless oil; R_f 0.5 (petroleum ether: EtOAc, 1:1); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1778, 1728; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 4.96 (1H, dd, J 12.3 and 8.3), 3.76 (3H, s), 3.758 (3H, s), 3.13 (1H, dd, J 12.3 and 10.1), 2.78-2.70 (1H, m), 2.64 (1H, dd, J 17.6 and 9.3), 2.34 (1H, ddd, 13.3, 7.2 and 5.1), 2.32-2.25 (1H, m), 2.29 (1H, dd, J 17.6 and 10.0), 2.10 (1H, ddd, J 13.5, 9.4 and 6.8), 1.86 (1H, dddd, J 12.9, 8.0, 6.8 and 5.0), 1.85-1.80 (1H, m), 1.75-1.58 (5H, m), 1.54-1.48 (1H, m); $\delta_{\text{C}}(125 \text{ MHz}; \text{CDCl}_3)$ 175.5, 172.8, 171.7, 79.8, 63.8, 52.9, 52.8, 47.1, 38.9, 36.5, 34.9, 34.1, 32.6, 28.1, 27.7 and 24.1; m/z (ESI) [Found: $(\text{M} + \text{Na})^+$, 333.1298. $\text{C}_{16}\text{H}_{22}\text{O}_6\text{Na}$ requires M , 333.1314].



Isolated as a clear, colourless oil; R_f 0.5 (petroleum ether: EtOAc, 1:1); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1778, 1725; $\delta_{\text{H}}(500 \text{ MHz}; \text{C}_6\text{D}_6)$ 4.75 (1H, dd, J 10.5 and 6.5), 3.63 (3H, s), 3.62 (3H, s), 2.96 (1H, t, J 10.0), 2.53 (1H, ddd, J 12.8, 7.0 and 5.1), 2.42 (1H, ddd, 12.8, 9.5 and 6.5), 2.18 (1H, dd, J 16.7 and 8.4), 1.80-1.73 (1H, m), 1.74 (1H, dd, J 16.7 and 3.0), 1.71-1.67 (1H, m), 1.61-1.56 (1H, m), 1.49-1.42 (2H, m), 1.24-1.14 (1H, m), 1.15-1.04 (2H, m), 0.86-0.76 (2H, m); $\delta_{\text{C}}(125 \text{ MHz}; \text{CDCl}_3)$ 176.1, 172.4, 171.6, 81.9, 63.8, 53.8, 52.8, 52.6, 41.8, 39.6, 67.7, 65.6, 35.3, 32.2, 30.3 and 28.2; m/z (ESI) [Found: $(\text{M} + \text{H})^+$, 311.1486. $\text{C}_{16}\text{H}_{23}\text{O}_6$ requires M , 311.1495].



Isolated as a clear, colourless oil; R_f 0.5 (petroleum ether: EtOAc, 1:1); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1780, 1726; $\delta_{\text{H}}(500 \text{ MHz}; \text{C}_6\text{D}_6)$ 4.91 (1H, dd, J 10.5 and 9.7), 3.67 (3H, s), 3.58 (3H, s), 2.91 (1H, t, J 10.6), 2.563 (1H, ddd, J 12.4, 6.4 and 5.1), 2.35 (1H, ddd, 12.4, 10.4 and 6.8), 2.08 (1H, dd, J 16.9 and 8.1), 1.99-1.91 (1H, m), 1.81 (1H, dddd, J 13.1, 8.2, 6.7 and 5.0), 1.61 (1H, dd, J 16.9 and 12.2), 1.52-1.43 (2H, m), 1.42-1.34 (1H, m), 1.31-1.26 (1H, m), 1.25-1.19 (2H, m), 0.88-0.79 (1H, m), 0.73 (1H, dddd, J 15.0, 13.0, 11.3 and 3.6); $\delta_{\text{C}}(125 \text{ MHz}; \text{CDCl}_3)$ 175.4, 172.4, 171.8, 84.4, 62.9, 54.9, 52.9, 52.4, 42.9, 41.1, 36.9, 36.2, 33.3, 32.8, 32.2, 29.1; m/z (ESI) [Found: $(\text{M} + \text{Na})^+$, 333.1301. $\text{C}_{16}\text{H}_{22}\text{O}_6\text{Na}$ requires M , 333.1314].