Supporting Information for

An approach to hyperolactone C and analogues using late stage conjugate addition on an oxonium ylide-derived spirofuranone

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Synthesis and Characterisation Data

(±)-9-Methyl-2-phenyl-9-vinyl-1,7-dioxaspiro[4.4]nonane-4,6-dione 16¹



PhLi (80 μ L, 1.7 M in Bu₂O, 0.136 mmol) was added dropwise to a solution of spirofuranone **2** (21 mg, 0.108 mmol) in THF (1 mL) at –78 °C. After 40 min, H₂O (10 μ L) was added and the mixture stirred at –78 °C for 10 min and then warmed to rt. The mixture was diluted with CH₂Cl₂ (5 mL), dried over Na₂SO₄ and concentrated under reduced pressure. Purification of the residue by column chromatography (EtOAc/petrol, 1/6) gave dihydrohyperolactone C **16**¹ (17 mg, 57%) as a colourless oil. The relative configuration was assigned by ¹H and ¹³C NMR data comparison with the dihydrohyperolactones reported in ref. 1.

 R_{f} : 0.18 (EtOAc/petrol, 1/9); ¹H NMR (400 MHz, CDCl₃): 7.55-7.51 (m, 2H, Ar), 7.44-7.38 (m, 2H, Ar), 7.38-7.32 (m, 1H, Ar), 5.99 (dd, *J* = 17.4, *J* = 10.8, 1H, CH=CH₂), 5.42-5.37 (m, 2H, CH=CH₂), 5.34 (dd, *J* = 9.9, *J* = 6.6, 1H, Ar-CHCH₂), 4.66 (d, *J* = 8.7, 1H, OCH_aH_b), 4.02 (d, *J* = 8.7, 1H, OCH_aH_b), 2.94 (dd, *J* = 18.6, *J* = 6.6, 1H, Ar-CHCH_aH_b), 2.67 (dd, *J* = 18.6, *J* = 9.9, 1H, Ar-CHCH_aH_b), 1.38 (s, 3H, CH₃); ¹³C NMR (101 MHz, CDCl₃): 208.4 (C=O), 170.6 (O-C=O), 139.8 (Ar), 135.7 (CH=CH₂), 128.9 (Ar), 128.7 (Ar), 126.2 (Ar), 119.4 (CH=CH₂), 90.6 (C(O)CC(O₂)), 78.6 (Ar-CHCH₂), 73.7 (OCH₂), 48.6 (CCH₃), 45.0 (Ar-CHCH₂), 18.7 (CH₃); IR (neat): 2974 w, 2914 w, 1787 s, 1749 s, 1169 m, 1103 s, 1001 m, 699 m cm⁻¹; HRMS (ESI): [M+Na]⁺ found 295.0930, C₁₆H₁₆O₄Na requires 295.0941.

¹ D. M. Hodgson and S. Man, *Chem. Eur. J.*, 2011, **17**, 9731. [Note, the sense of asymmetric induction here (Ph addition *syn* to the lactone carbonyl) contrasts with that observed in the conjugate reduction of hyperolactone C using L-selectride (see: K. C. Nicolaou, T. R. Wu, D. Sarlah, D. M. Shaw, E. Rowcliffe and D. R. Burton, *J. Am. Chem. Soc.*, 2008, **130**, 11114)].

Cis-bis[(R)-1,1'-bi-2-naphtholphosphate]-bis[acetate]dirhodium(II)



If the symmetry elements of the *cis* and *trans* isomers of the complex are considered, it is seen that the C₂ axes perpendicular to the Rh-Rh bond bisect the angle between the ligands for the *cis* isomer, and pass through the ligands for the trans isomer. The result for the ¹H NMR spectrum is that for the *cis* isomer, there would be 2 sets of signals expected for at least some of the binaphthol protons, whereas for the *trans* isomer only one set would be expected. Inspection of the data indicates 2 sets of signals [eg, C(4)H δ = 7.84, 2H rather than 4H], leading to the *cis* assignment.²

Reduction and lactonisation of aldehydes 14/14-diast



To a solution of aldehydes **14/14-diast** (32 mg, 0.12 mmol) in THF (1.2 mL) cooled to 0 °C, was added glacial AcOH (120 μ L), followed by NaBH₃CN (15 mg, 0.24 mmol). After stirring for 4 h at rt, H₂O (4 mL) was added and the mixture was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with aq. sat. NaHCO₃ (15 mL) and brine (15 mL), dried (Na₂SO₄) and concentrated. The residue was dissolved in CH₂Cl₂ (3.6 mL) and MeSO₃H (8 μ L, 0.12 mmol) was added. After stirring for 3.5 h, the mixture was concentrated. Purification of the residue by column chromatography (EtOAc/petrol, 1/4) gave a mixture of spirolactone **12** and **12-diast** (20 mg, 85%). Ers determined by HPLC, as described in General Procedure for asymmetric catalysis in main paper experimental part.

² For another example of cis ligand orientation, in Rh(OAc)₂(OCOCF₃)₂ arising from ligand exchange in Rh₂(OAc)₄, and discussion of the origin, see: Y. Lou, T. P. Remarchuk and E. J. Corey, *J. Am. Chem. Soc.*, 2005, **127**, 14223. For other examples, see: R. Hrdina, L. Guénée, D. Moraleda and J. Lacour, *Organometallics*, 2013, **32**, 473.





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¹³C NMR (101 MHz, CDCl₃)



³¹P NMR (162 MHz, CDCI₃)



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HPLC Data

HPLC data for spirolactone 12/12-diast

a) From **11** using cat $Rh_2(OAc)_4$

b) From **10** using cat $Rh_2(R-BNP)_4$



HPLC data for α,β -unsaturated aldehyde 15

a) From **10** using cat Rh₂(OAc)₄

b) From 10 using cat Rh₂(*R*-BNP)₄

