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Gold-catalysed cyclic ether formation from diols

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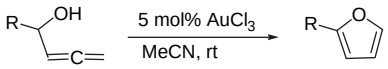
ABSTRACT

Gold(I) and (III) salts have been found to be highly effective at the catalysis of ether formation from alcohols. Intramolecular ether formation of a 1,5-diol was also achieved, with a stereoselectivity that indicates that an S_N1 mechanism predominates. In an attempt to form a seven-membered ring, a stable 14-membered dimer product was also formed. Attempts to control the diastereoselectivity of the reaction using a chiral anionic counterion did not give products with a high de.

1. Introduction

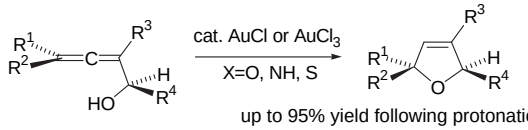
Gold salts and complexes can catalyse a variety of transformations, such as cycloadditions, isomerisations, hydroaminations or nucleophilic cyclisation of allenes.[1–5] Their soft, carbophilic Lewis acid character is capable of activating carbon–carbon double and triple bonds, leading to the formation of C–C, C–O, C–N and C–S bonds. In the specific arena of C–O bond formation reactions, Hashmi et al. described the use of gold(III)chloride in the cycloisomerisation of allenic alcohols to furans (Scheme 1).[2a]



Scheme 1. Gold(III) catalysed formation of furans from allenes.

Using chiral allenes as substrates, gold(I) or gold(III) chloride catalyse the *endo*-cycloisomerisation of **1** to the corresponding five-membered heterocycles with complete axis-to-centre chirality transfer (Scheme 2).[3,4] Gold salts catalyse the reaction by co-ordinating to an allenic double bond as a Lewis acid, resulting in increased electrophilicity of the terminal carbon atom.

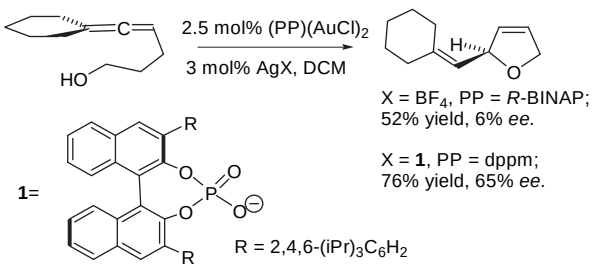
This axis-to-centre chirality transfer gold-catalysed *endo*-cycloisomerization was applied in the first enantioselective syntheses of the natural products β-carboline alkaloids (−)-isochrysotricine and (−)-isocyclocapitelline.[4] The cyclisation was



Scheme 2. Formation of 2,5-dihydrofurans by gold-catalysed cyclisation.

catalysed by as little as 0.05 mol % gold(III) chloride in THF, giving a key 2,5-dihydrofuran intermediate in a yield of 97% yield with a high level of stereochemical control (96% de, >98% ee).

It has also been found that high enantioselectivity may be achieved with the use of a chiral counterion in a gold-catalysed reaction. Toste et al.[5] carried out two sets of hydroalkoxylation reactions of an allene to test how chiral counterions mediate asymmetric gold reactions (Scheme 3); one catalysed by chiral phosphine-substituted gold catalysts $L(AuCl)_2$ and $AgBF_4$ and the other catalysed by $dppm(AuCl)_2$ and chiral silver phosphates AgX.



Scheme 3. Use of a chiral counterion in gold-catalysed reactions.

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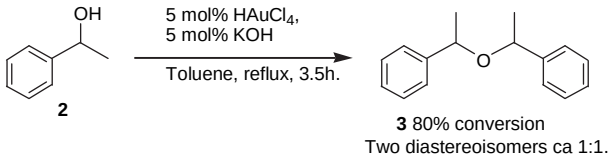
The hydroalkoxylation catalysed by chiral counterions[6] was more enantioselective (65% ee in DCM, up to 97% ee in benzene).

In this paper, we describe the use of gold catalysts for the cyclisation of diols under mild conditions.

2. Results and discussion

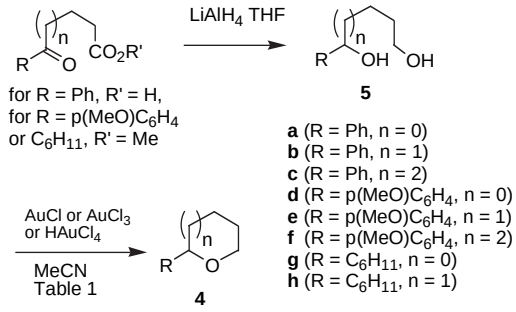
During the course of our ongoing studies on alcohol dehydrogenation,[7] we screened a series of organometallic complexes for the oxidation of 1-phenylethanol **2** to acetophenone. In the case of gold salts, including AuCl and $AuCl_3$, a new product was observed. This was identified from its characteristic methine proton quartet resonances in the ^{1}H NMR spectrum, as the known ether **3**,[8] formed as a diastereoisomeric mixture by the condensation of two molecules of the alcohol (Scheme 4). Some studies into this reaction permitted its optimisation to give a product in 80% conversion (5 mol % $HAuCl_4$, 5 mol % KOH, toluene, reflux, 3.5 h). A survey of the literature revealed that this condensation has been reported to be promoted by a Pd(II)/AgOTf catalyst,[8a] and TfOH.[8b] The closely related intramolecular cyclisation of 1,5-dihydroxy-1,5-diphenylpentane[9] has also been achieved using a range of acids,[9a] and $PtCl_2$/$AgSbF_6$.[9b] However we were aware of no similar reaction catalysed by a gold salt. Since this represented a potentially mild alternative to some relatively strong acids, we elected to study this reaction in more detail.



Scheme 4. Gold-catalysed formation of an ether from 1-phenylethanol.

We investigated the potential of the gold-catalysed method to form cyclic ethers **4** from diols **5**. Initially, diols **5a**–**h** were prepared, in each case from the reduction of a ketoacid or ester (Scheme 5).[10] The ester substrates were prepared by addition of a Grignard reagent to the precursor acid chloride in the presence of a copper salt,[11] whilst the ketoacid precursors were commercially available. Cyclisation of **5a**–**c** bearing phenyl groups was first conducted using 5 mol % of the three gold catalysts; chloroauric acid ($HAuCl_4$), gold(I) chloride (AuCl) and gold(III) chloride ($AuCl_3$), at 40 °C for 20 h. Of these, only the five-membered ring precursor **5a**, in the presence of $HAuCl_4$, was cyclised in any significant yield; 63%, whilst all other combinations gave only 0–4% conversion. At the higher temperature of 80 °C, further reagent/catalyst combinations were successfully cyclised (Table 1). In each case, $HAuCl_4$ was the most active catalyst, followed by $AuCl_3$, whilst as expected the rate of cyclisation was higher for the smallest ring product, and slowest for the largest of the series. The seven-membered product **4c** was formed in very low conversion and was accompanied by a second product, which could not be fully characterised but may be a dimer similar to that formed in the cyclisation of **5f** (see below).

Using the more electron-rich substrates **5d**–**f**, all the cyclisations, with each gold catalyst, were completed, at 40 °C within 1 h (5% catalyst initially used).[12] Further studies revealed that the catalyst loading could be reduced to 0.5 mol % and the temperature to 25 °C, for full cyclisations to be observed within reasonable reaction times (Table 1). Following these reactions using ^{1}H NMR spectroscopy revealed complete cyclisations in times as short as 6.5 min. The time-conversion graphs for the AuCl catalysts indicated the operation of an induction period (Fig. 1), which may be suggestive of the slow formation of an active catalytic species, or some form of autocatalysis.



Scheme 5. Preparation and intramolecular gold-catalysed cyclisation of 1,5-diols.

Table 1
Cyclisations of diols **5a**–**h** to cyclic ethers **4a**–**h** using Au(III) and Au(I) salts as catalysts

Substrate	Catalyst	Loading (%)	T/°C[a]	t/h[a]	Conv (%)[a]
5a	$HAuCl_4$	5	40 (80)	20 (20)	63 (100)
5a	AuCl	5	40 (80)	20 (20)	1 (13)
5a	$AuCl_3$	5	40 (80)	20 (20)	4 (28)
5b	$HAuCl_4$	5	40 (80)	20 (20)	0 (54)
5b	AuCl	5	40 (80)	20 (20)	0 (8)
5b	$AuCl_3$	5	40 (80)	20 (20)	0 (26)
5c	$HAuCl_4$	5	40 (80)	20 (20)	0 (11)[b]
5c	AuCl	5	40 (80)	20 (20)	0 (7)[b]
5c	$AuCl_3$	5	40 (80)	20 (20)	0 (15)[b]
5d	$HAuCl_4$	5 (0.5)	40 (25)	<1 (0.25)	100 (100)
5d	AuCl	5 (0.5)	40 (25)	<1 (0.25)	100 (100)
5d	$AuCl_3$	5 (0.5)	40 (25)	<1 (0.1)	100 (100)
5e	$HAuCl_4$	5 (0.5)	40 (25)	<1 (0.2)	100 (100)
5e	AuCl	5 (0.5)	40 (25)	<1 (1)	100 (100)
5e	$AuCl_3$	5 (0.5)	40	<1	100
5f	$HAuCl_4$	0.5	25	0.2	>95[c,d]
5f	AuCl	0.5	25	3.5	>95[c]
5f	$AuCl_3$	0.5	25	0.2	>95[c]
5g	$HAuCl_4$	5	80	20	100
5g	AuCl	5	80	20	19
5g	$AuCl_3$	5	80	20	47
5h	$HAuCl_4$	5	80	20	12[e]
5h	AuCl	5	80	20	3[e]
5h	$AuCl_3$	5	80	20	8[e]

Solvent=MeCN, [diol]=0.2 M. No cyclisation was observed in the absence of catalyst.
[a] Numbers in parenthesis represent a second data point.
[b] A second product was observed, which may be a cyclic dimer.
[c] A dimer, **4fD**, was also formed in this reaction in the following ratios of **4f**/**4fD**; $HAuCl_4$; 4:1, AuCl; 1:2, $AuCl_3$; 3:1.
[d] Cyclisation in $CDCl_3$ under the same conditions resulted in the formation of **4f** accompanied by <10% **4fD**.
[e] Product is tentatively assigned due to low conversions.

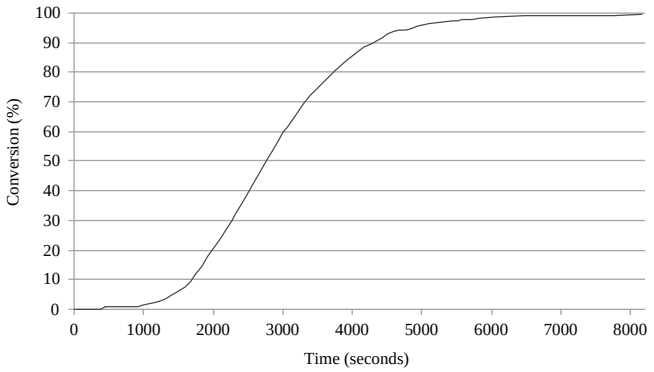


Fig. 1. Conversion versus time for the cyclisation of **5d** by AuCl (0.5 mol % AuCl, 25 °C).

The formation of **4f** was accompanied by the formation of a second product, which precipitated from the reaction and when AuCl was used, was the major product. This was isolated and fully characterised, including by X-ray crystallography (Fig. 2; CCDC

796007), which revealed it to be **4fD**, a dimer of **4f**, with racemic stereochemistry. The ratio **4f**/**4fD** was determined by redissolution of the crude mixture in each case and proved to be dependent on the catalyst employed. Repeating the cyclisation of **5f** in $CDCl_3$, with one drop of CD_3CN to ensure catalyst solubility, resulted in selective formation of **4f** with <10% dimerisation and without precipitation being observed. An attempt to convert a purified sample of **4fD** into **4f** using using $HAuCl_4$ in $CDCl_3$ resulted in terminal alkenes being formed, whilst an attempt to cyclise **5f** using HCl in place of a gold catalyst also resulted in elimination products (see Supplementary data). These observations suggest that the formation of **4f** and **4fD** may be a solvent-dependent templating by the metal, rather than simply the result of an acid-promoted equilibrium process.

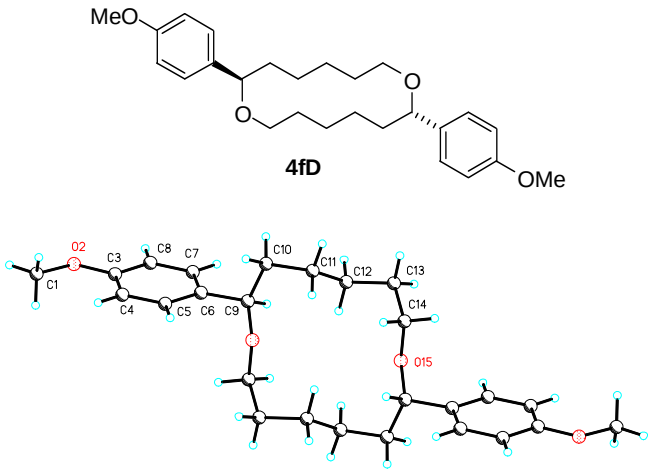
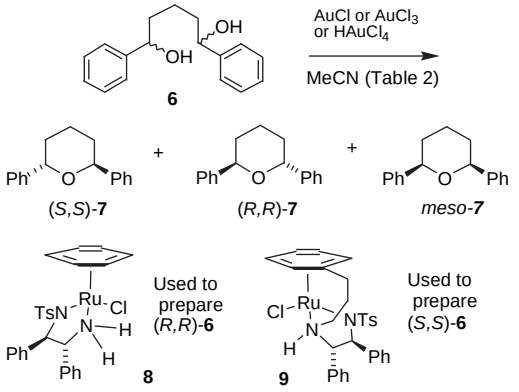


Fig. 2. X-ray crystallographic structure of **4fD**, formed in the cyclisation of diol **5f**.

Substrates **5g** and **5h** required 5 mol% of catalyst to promote cyclisation, and, with one exception, products were formed in incomplete conversions even after 20 h with 5 mol% catalyst, at 80 °C. Whilst the catalytic activity of the $HAuCl_4$ may be in part due to participation of the protic acid, the $AuCl_3$ and AuCl are presumably working primary as Lewis acids. The rapid rate of cyclisation of the 4-methoxyphenyl substrates suggests that the mechanism may involve an S_N1 mechanism in which a stabilised cation is formed adjacent to the arene ring.

In order to investigate the mechanism and to extend its synthetic utility, the study was extended to the intramolecular cyclisation reaction of 1,5-diphenyl-pentane-1,5-diol **6**[13,14] to the 2,6-diphenyltetrahydropyran **7** (Scheme 6).[9]



Scheme 6. Intramolecular gold-catalysed cyclisation of 1,5-diphenylpentane-1,5-diol.

Pt(II) catalysts, along with Ag salts, have previously been used in the dehydration; it was found that no product was formed with the use of $PtCl_2$ only or Ag salts only.[9a] Excellent yields were obtained using the combination of $PtCl_2$ and $AgSbF_6$ under an atmosphere of air.[9b] For our studies, a sample of 1,5-diol **6** was prepared from 1,5-diphenolpentanone by reduction of using sodium borohydride. Enantiomerically enriched (*R*,*R*)- and (*S*,*S*)-diols[13,14c,d] were also prepared by asymmetric transfer hydrogenation using Noyori catalyst [(*p*-cymene)RuCl(*R*,*R*-TsDPEN)] **8**[14a,b] and the tethered derivative **9**, respectively.[15] Chiral HPLC analysis of each product indicated that the samples of **6** prepared from the asymmetric reduction were each of >95% ee, and that the $NaBH_4$ reduction product contained a mixture of (*R*,*R*)/(*S*,*S*)/*meso* diols in a ca. 1:1:2 ratio (or a 1:1 *rac*/*meso* mixture), as would be predicted on the basis that there is no diastereocontrol in the second reduction. Incomplete isomer separation in the HPLC prevented a higher level of accuracy however (see Supplementary data).

Cyclisation of the *rac*/*meso* mixture and the (*R*,*R*)-diol was undertaken using the three gold catalysts previously employed (Table 2). In all cases, a mixture of the known *cis* and *trans* **7** was formed,[9,16] although the ratios of these varied slightly depending on the substrate and the catalyst. The ^1H NMR spectra of the products contained two chemical shifts around 4.58 and 4.86 ppm (Fig. 3), which are in agreement with the literature data and allowed the cis/trans ratio to be readily calculated.

Table 2
Cyclisations of diol **6** using Au(III) and Au(I) salts as catalysts

Substrate	Catalyst	*T*/°C	*t*/h	Conv (%)	trans/cis
rac/*meso*-**6**	$HAuCl_4$	80	2	100	1:0.90
rac/*meso*-**6**	$HAuCl_4$	rt	2	36	1:0.91
rac/*meso*-**6**	$AuCl_3$	80	22	85	1:0.88
(*R*,*R*)-**6**	$HAuCl_4$	80	2	100	1:1.19
(*R*,*R*)-**6**	AuCl	80	2	100	1:1.1
(*R*,*R*)-**6**	$AuCl_3$	80	2	100	1:1.23
(*R*,*R*)-**6**	$HAuCl_4$	rt	20	44	1:1.4
(*R*,*R*)-**6**	AuCl	rt	20	0	—
(*R*,*R*)-**6**	$AuCl_3$	rt	20	24	1:1.6

Reactions were carried out with 5 mol% of catalyst. [diol]=0.2 M.

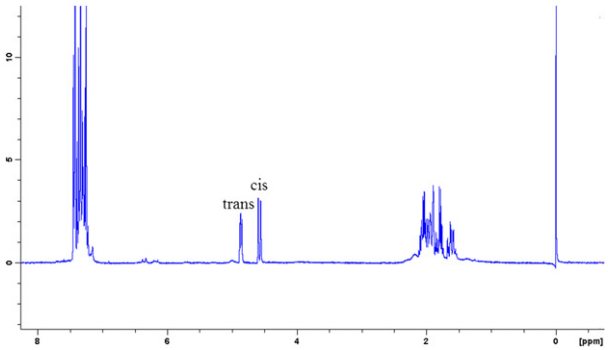


Fig. 3. NMR sample of *cis* and *trans* **7** formed in a gold-catalysed cyclisation.

The formation of a mixture of *cis*- and *trans*-cyclisation products **7** in the reaction of both the *rac*/*meso* substrate and the enantioenriched one suggests that the reaction proceeds via an S_N1 mechanism, i.e., in which a benzylic cation is trapped by the alternative hydroxyl group. The small excess of the *cis* product formed from the (*R*,*R*)-substrate indicates the contribution of a component of an S_N2 mechanism,[9d] however, since this would be the product resulting from inversion of configuration at one stereocentre.

An attempt was made to modify the catalyst in an asymmetric sense in order to establish whether it might be possible to achieve a kinetic resolution of a racemic diol using a chiral catalyst. Given the precedent[5] involving silver salts of phosphoric acids derived from BINOL, additives **10**, **11**, **12** and BINOL were selected for

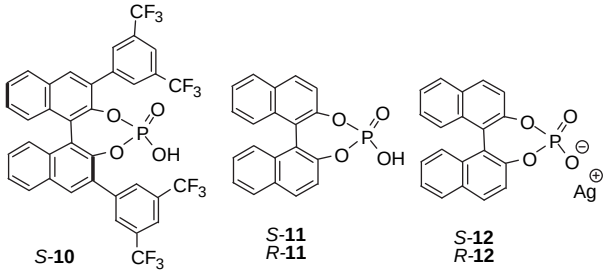
Table 3
Cyclisations of diols **7** using Au(III) and Au(I) salts, with BINOL-derived phosphoric acids additives **10**–**12**, as catalysts

Substrate	Catalyst (mol %)	Additive (mol %)	Conv (%)	trans/cis
(*R*,*R*)-**6**	$HAuCl_4$ (5)	*S*-**10** (5)	100	1:1.1
(*R*,*R*)-**6**	AuCl (5)	*S*-**10** (5)	63	1:1.5
(*R*,*R*)-**6**	$AuCl_3$ (5)	*S*-**10** (5)	100	1:1.1
(*R*,*R*)-**6**	$HAuCl_4$ (5)	*S*-BINOL (5)	92	1:1.14
(*R*,*R*)-**6**	AuCl (5)	*S*-BINOL (5)	9	1:0.7
(*R*,*R*)-**6**	$AuCl_3$ (5)	*S*-BINOL (5)	91	1:0.95
(*R*,*R*)-**6**	AuCl (5)	*R*-**11** (5)	0	—
(*R*,*R*)-**6**	AuCl (5)	*S*-**11** (5)	10	1:1.3
(*R*,*R*)-**6**	AuCl (5)	*R*-**12** (5)	0	—
(*R*,*R*)-**6**	AuCl (5)	*S*-**12** (5)	0	—
(*R*,*R*)-**6**	AuCl (20)	*R*-**11** (20)	100[a]	1:2.2
(*R*,*R*)-**6**	AuCl (20)	*S*-**11** (20)	100[a]	1:2.1
(*S*,*S*)-**6**	AuCl (5)	*R*-**11** (20)	49[a]	1:2.3
(*S*,*S*)-**6**	AuCl (5)	*S*-**11** (20)	82[a]	1:2.2

Reactions were carried out at 40 °C, for 48 h. [diol]=0.2 M. Other solvents tested (AuCl (5%), **10** (5%), 40 °C, 2d): EtOH; 0%, EtOAc; 100%, 1:1.8, hexane; 0%, DCM; 100%, 1:1.5.

[a] Reaction time (26 h).

investigation as additives (Table 3). The additive **10**, which has been used in a range of organocatalytic applications,[17] was compatible with the reaction and had a small influence on selectivity—the best de in favour of the cis isomer being obtained with AuCl. The use of the same enantiomer of BINOL, reduced the rate of catalysis and gave a preference for the *trans* product. Some solvents other than MeCN were tested, and the reaction was successful in both EtOAc and DCM, but failed in EtOH and hexane.



Phosphoric acid **11** and the Ag(I) salt **12** (both enantiomers) were also evaluated in the cyclisation and, at the 5 mol % level, gave no products or low yields of products. Increasing the additive to 20 mol %, and then the AuCl loading to 20% increased the rate under the conditions tested. At this point it was thought that there may be potential for a kinetic resolution in the cyclisation. However there was no strong evidence for this. In all the cyclisations using a combination of AuCl and a BINOL-derived phosphoric acid, an increased preference for the *cis* product was again consistently observed, suggesting a contribution from an element of S_N2 reactivity to the cyclisation.

In conclusion, we have demonstrated that the cyclisation of diols can be achieved under mild conditions using catalytic amounts of gold(I) and (III) catalysts. In the best cases, full conversions can be achieved within reasonable reaction times and with a modest level of diastereoselectivity. The results suggest that the cyclisation proceeds primarily via an S_N1 mechanism (i.e., a benzylic cation) but that a contribution from an S_N2 process operates under certain conditions.

3. Experimental section

3.1. Synthesis of 1-phenylbutane-1,4-diol 5a

4-Oxo-4-phenylbutanoic acid (3.00 g, 16.8 mmol, 1.0 equiv) in THF (27 mL) was added dropwise to a stirred solution of $LiAlH_4$ (2.0 M) in anhydrous THF (32.0 mL, 64.0 mmol, 3.7 equiv) at room temperature. The cloudy solution was stirred for 1 h and then cooled to 0 °C. The excess hydride was cautiously quenched with water (2.4 mL), a 15% aqueous NaOH solution (2.4 mL) and water (7.2 mL). Effervescence and the formation of a white suspension were observed. The reaction mixture was warmed to room temperature under stirring. Filtration through Celite and concentration in vacuo afforded a colourless oil, which underwent crystallisation. The crude crystals were ground and washed with hexane, and the resulting white crystals of **5a** (2.56 g, 91.3%) were dried under high vacuum. Mp 62 °C; MS: *m*/*z* (ESI^+): 189.0 ($[M+Na]^+$); HRMS: calcd for $C_{10}H_{14}NaO_2$: 189.0883 ($[M+Na]^+$). Found 189.0886 ($[M+Na]^+$); ν_{max} 3323 (br), 3035 (w), 2927 (w), 1576 (m), 1041 (s) and 703 (s) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.35–7.22 (5H, m, Ph), 4.70 (1H, t, *J* 6.3, C*H*OH), 3.71–3.59 (2H, m, CH_2OH), 2.80 (2H, br s, 2×O*H*), 1.84 (2H, q, *J* 7.0, HCOHCH_2), 1.75–1.55 (2H, m, CH_2CH_2OH); δ_C (75 MHz, $CDCl_3$) 144.3, 127.8, 126.8, 125.2, 73.7, 62.1, 35.7, 28.7. The NMR data were consistent with those reported.[10b]

3.2. Synthesis of 1-phenylpentane-1,5-diol 5b

The procedure described for **5a** was followed utilising 5-oxo-5-phenylpentanoic acid (2.00 g, 10.4 mmol, 1.0 equiv) and $LiAlH_4$ (2.0 M) in anhydrous THF (20.0 mL, 40.0 mmol, 3.7 equiv). White crystals of **5b** (1.55 g, 82.6%) were afforded from the reaction. Mp 49 °C; MS: *m*/*z* (ESI^+): 203.0 ($[M+Na]^+$); HRMS: calcd for $C_{11}H_{16}NaO_2$: 203.1038 ($[M+Na]^+$). Found 203.1043 ($[M+Na]^+$); ν_{max} 3227 (br), 2942 (w), 1567 (br), 1048 (s) and 700 (s) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.36–7.24 (5H, m, Ph), 4.68 (1H, dd, *J* 7.4, 5.7, ArC*H*OH), 3.63 (2H, t, *J* 6.3, CH_2OH), 2.00 (2H, br s, 2×O*H*), 1.90–1.30 (6H, m, $(CH_2)_3CH_2OH$); δ_C (75 MHz, $CDCl_3$) 144.2, 127.9, 127.0, 125.2, 73.9, 62.2, 38.2, 32.0, 21.3. Data was consistent with that reported in the literature.[10a]

3.3. Synthesis of 1-phenylhexane-1,6-diol 5c

The procedure described for **5a** was followed utilising 6-oxo-6-phenylhexanoic acid (3.00 g, 14.5 mmol, 1.0 equiv) and $LiAlH_4$ (2.0 M) in anhydrous THF (27.0 mL, 54.0 mmol, 3.7 equiv). White crystals of **5c** (2.43 g, 86.0%) were afforded from the reaction. Mp 51 °C; MS: *m*/*z* (ESI^+): 217.0 ($[M+Na]^+$); HRMS: calcd for $C_{12}H_{18}NaO_2$: 217.1196 ($[M+Na]^+$). Found 217.1199 ($[M+Na]^+$); ν_{max} 3214 (br), 2943 (w), 1452 (w), 1042 (s) and 699 (s) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.28–7.15 (5H, m, Ph), 4.67 (1H, dd, *J* 7.5, 5.8, ArC*H*OH), 3.52 (2H, t, *J* 6.5, CH_2OH), 1.80–1.55 (3H, m, HCOHCH_2+O*H*), 1.50–1.40 (2H, m, CH_2CH_2OH), 1.40–1.15 (4H, m, CH_2CH_2); δ_C (75 MHz, $CDCl_3$) 144.2, 127.8, 126.9, 125.3, 73.9, 62.3, 38.4, 32.0, 25.0, 24.9. Data was consistent with that reported in the literature.[10a]

3.4. Synthesis of 1-(4-methoxyphenyl)butane-1,4-diol 5d

The procedure described for **5a** was followed utilising methyl-4-methoxyphenyl-4-oxobutanoate (1.20 g, 5.41 mmol, 1.0 equiv) and $LiAlH_4$ (2.0 M) in anhydrous THF (10.0 mL, 20.0 mmol, 3.7 equiv). The reaction mixture was stirred for 3 h and the crude yellow oil was purified by flash chromatography (graduated to 7:3 EtOAc/hexane). White crystals of **5d** (0.917 g, 86.5%) were afforded from the reaction. Mp 63–64 °C; MS: *m*/*z* (ESI^+): 219.0 ($[M+Na]^+$); HRMS: calcd for $C_{11}H_{16}NaO_3$: 219.0992 ($[M+Na]^+$). Found 219.0992 ($[M+Na]^+$); ν_{max} 3272 (br), 2942 (s), 1610 (m), 1511 (s), 1239 (s) and 835 (s) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.24 (2H, d, *J* 8.6, Ar*H*), 6.87 (2H, d, *J* 8.6, Ar*H*), 4.65 (1H, t, *J* 6.5, ArC*H*OH), 3.80 (3H, s, OCH_3), 3.70–3.60 (2H, m, CH_2OH), 2.80 (1H, br s, O*H*), 2.50 (1H, br s, O*H*), 1.90–1.75 (2H, m, HCOHCH_2), 1.70–1.60 (2H, m, CH_2CH_2OH); δ_C (75 MHz, $CDCl_3$) 158.4, 136.3, 126.4, 113.2, 73.4, 62.2, 54.7, 35.6, 28.7.

Data for ^{1}H NMR and melting point was consistent with that reported in the literature.[10c]

3.5. Synthesis of 1-(4-methoxyphenyl)pentane-1,5-diol 5e

The procedure described for **5a** was followed utilising methyl-5-methoxyphenyl-5-oxopentanoate (1.00 g, 4.24 mmol, 1.0 equiv) and $LiAlH_4$ (2.0 M) in anhydrous THF (8.00 mL, 16.0 mmol, 3.7 equiv). Product **5e** (0.843 g, 94.7%) was isolated as a colourless oil. MS: *m*/*z* (ESI$^+$): 233.0 ([M+Na]$^+$); HRMS: calcd for $C_{12}H_{18}NaO_3$: 233.1147 ([M+Na]$^+$). Found 233.1148 ([M+Na]$^+$); ν_{max} 3328 (br), 2936 (s), 1611 (m), 1511 (s), 1239 (s) and 830 (s) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.27 (2H, d, *J* 8.6, Ar*H*), 6.89 (2H, d, *J* 8.6, Ar*H*), 4.64 (1H, t, *J* 6.0, ArC*H*OH), 3.80 (3H, s, OCH_3), 3.63 (2H, dt, *J* 6.0, 3.9, CH_2OH), 1.90–1.75 (2H, m, HCOHCH_2), 1.63–1.53 (2H, m, CH_2CH$_2$OH), 1.41–1.25 (2H, m, CH$_2$CH_2CH$_2$); δ_C (75 MHz, $CDCl_3$) 158.4, 136.3, 126.5, 113.2, 73.5, 62.0, 54.7, 37.9, 31.8, 21.4.

3.6. Synthesis of 1-(4-methoxyphenyl)hexane-1,6-diol 5f

The procedure described for **5a** was followed utilising methyl-6-methoxyphenyl-6-oxohexanoate (1.00 g, 4.00 mmol, 1.0 equiv) and $LiAlH_4$ (2.0 M) in anhydrous THF (8.00 mL, 16.0 mmol, 3.7 equiv). The product **5f** (0.887 g, 98.9%) was formed as white crystals. Mp 45 °C; MS: *m*/*z* (ESI$^+$): 247.1 ([M+Na]$^+$); HRMS: calcd for $C_{13}H_{20}O_3Na$: 247.1297 ([M+Na]$^+$). Found 247.1305 ([M+Na]$^+$); ν_{max} 3405 (br), 2942 (s), 1612 (w), 1515 (m), 1026 (s) and 831 (s) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.23 (2H, d, *J* 8.7, Ar*H*), 6.84 (2H, d, *J* 8.7, Ar*H*), 4.60 (1H, t, *J* 7.0, ArC*H*OH), 3.80 (3H, s, OCH_3), 3.60 (2H, t, *J* 6.5, CH_2OH), 2.05 (1H, br s, O*H*) 1.85–1.60 (2H, m, HCOHCH_2), 1.60–1.50 (2H, m, CH_2CH$_2$OH), 1.45–1.28 (4H, m, CH$_2$(CH_2)$_2$CH$_2$); δ_C (75 MHz, $CDCl_3$) 158.4, 136.4, 126.5, 113.2, 73.5, 62.2, 54.7, 38.3, 32.0, 25.0, 25.0.

3.7. Synthesis of 1-cyclohexylbutane-1,4-diol 5g

The procedure described for **5a** was followed utilising methyl-4-cyclohexyl-4-oxobutanoate (0.501 g, 2.53 mmol, 1.0 equiv) and $LiAlH_4$ (2.0 M) in anhydrous THF (4.80 mL, 9.60 mmol, 3.7 equiv). The reaction mixture was stirred for 2 h. The product **5g** (0.380 g, 87.3%) was formed as white crystals. Mp 50–52 °C; MS: *m*/*z* (ESI$^+$): 195.1 ([M+Na]$^+$); HRMS: calcd for $C_{10}H_{20}O_2Na$: 195.1351 ([M+Na]$^+$). Found 195.1356 ([M+Na]$^+$); ν_{max} 3275 (br), 2933 (s), 1438 (m) and 1044 (s) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.70–3.60 (2H, m, CH_2OH), 3.41–3.34 (1H, m, C*H*OH), 2.05 (1H, br s, O*H*), 1.90–0.90 (16H, m, alkyl-C*H*+O*H*); δ_C (75 MHz, $CDCl_3$) 76.3, 63.2, 43.8, 31.1, 29.5, 29.2, 28.0, 26.5, 26.3, 26.2.

3.8. Synthesis of 1-cyclohexylpentane-1,5-diol 5h

The procedure described for **5a** was followed utilising methyl-5-cyclohexyl-5-oxopentanoate (0.600 g, 2.83 mmol, 1.0 equiv) and $LiAlH_4$ (2.0 M) in anhydrous THF (5.30 mL, 10.6 mmol, 3.7 equiv). Product **5h** (0.461 g, 87.6%) was isolated as white crystals. Mp 39–41 °C; MS: *m*/*z* (ESI$^+$): 209.1 ([M+Na]$^+$); HRMS: calcd for $C_{11}H_{22}NaO_2$: 209.1503 ([M+Na]$^+$). Found 209.1512 ([M+Na]$^+$); ν_{max} 3277 (br), 2914 (s), 1444 (m) and 1050 (s) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.65 (2H, dd, *J* 6.2, 6.2, CH_2OH), 3.38–3.28 (1H, m, C*H*OH), 1.83–0.91 (19H, m, alkyl-C*H*+O*H*); δ_C (75 MHz, $CDCl_3$) 75.5, 62.1, 43.1, 33.0, 32.0, 28.6, 27.2, 25.9, 25.7, 25.6, 21.5.

3.9. Cyclisation of diols 5a–h, to cyclic ethers 4a–h

A Radleys carousel was used to run up for twelve cyclisation reactions under the same conditions; each set of monosubstituted diols was run together. For each monosubstituted diol, four reactions were run; one blank reaction and one reaction for each of the three gold catalysts. To a solution of **5a** (100.1 mg, 0.6 mmol) in acetonitrile (3 mL), 5 mol % $HAuCl_4$ was added. The solution was stirred under argon at 40 °C for 20 h. A sample of the reaction mixture was taken and the solvent was evaporated in vacuo to give a crude yellow oil. The reaction was repeated for **5a** with AuCl and $AuCl_3$, and for the other diols with the three catalysts. The reactions were also tested at a higher temperature (80 °C).

*3.9.1. 2-Phenyltetrahydrofuran **4a**.* A crude yellow oil was isolated. δ_H (300 MHz, $CDCl_3$) 7.33–7.20 (5H, m, Ph), 4.90 (1H, t, *J* 7.1, C*H*OCH$_2$), 4.08 (1H, q, *J* 6.9, OC*H*H), 3.95 (1H, q, *J* 6.9, OCH*H*), 2.38–2.26 (1H, m, C*H*), 2.1 (2H, quin, *J* 7.0, CH_2), 1.87–1.74 (1H, m, C*H*). NMR data were consistent with those reported.[18]

*3.9.2. 2-Phenyltetrahydropyran **4b**.* A crude yellow oil was isolated. δ_H (300 MHz, $CDCl_3$) 7.36–7.20 (5H, m, Ph), 4.32 (1H, dd, *J* 10.6, 2.4, C*H*OCH$_2$), 4.14 (1H, dd, *J* 11.2, 3.8, OC*H*H), 3.60 (1H, dt, *J* 11.2, 2.5, OCH*H*), 2.02–1.90 (2H, m, CH_2), 1.86–1.79 (2H, m, CH_2), 1.70–1.55 (2H, m, CH_2). NMR data were consistent with those reported.[19]

*3.9.3. 2-Phenyltetrahydrooxepine **4c**.* Due to poor conversions, the crude yellow oil could not be fully characterised. Emerging peaks show the presence of two products. A five aryl hydrogen multiplet and an eight alkyl hydrogen multiplet for both products are assumed to be under the substrate multiplets at 7.40–7.10 ppm and 2.20–1.20 ppm, respectively (see Supplementary data). Product **4c**: δ_H (300 MHz, $CDCl_3$) 4.58 (1H, dd, *J* 6.9, 2.7, C*H*OCH$_2$), 4.00–3.90 (1H, m, OC*H*H), 3.68–3.75 (1H, m, OCH*H*). Unknown product: δ_H (300 MHz, $CDCl_3$) 4.15 (1H, dd, *J* 5.6, 4.2, C*H*OCH$_2$), 3.30–3.15 (2H, m, OCH_2). The unknown product may be a dimer similar to that formed from **5f** but insufficient quantities were obtained to characterise it.

*3.9.4. 2-(4-Methoxyphenyl)tetrahydrofuran **4d**.* Product **4d** was isolated as a colourless oil. MS: *m*/*z* (ESI$^+$): 201.0 ([M+Na]$^+$); HRMS: calcd for $C_{11}H_{14}NaO_2$: 201.0886 ([M+Na]$^+$). Found 201.0886 ([M+Na]$^+$); ν_{max} 2950 (b), 1613 (m), 1512 (s), 1244 (s) and 829 (s) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.25 (2H, d, *J* 8.6, Ar*H*), 6.86 (2H, d, *J* 8.8, Ar*H*), 4.82 (1H, t, *J* 7.1, OC*H*Ar), 4.07 (1H, dt, *J* 8.2, 6.9, OC*H*H), 3.90 (1H, dt, *J* 7.6, 6.4, OCH*H*), 3.80 (3H, s, OCH_3), 2.33–2.22 (1H, m, CH_2), 2.05–1.95 (2H, m, CH_2), 1.84–1.72 (1H, m, CH_2); δ_C (75 MHz, $CDCl_3$) 158.8, 135.3, 127.0, 113.7, 80.5, 68.5, 55.3, 34.5, 26.1. Data were consistent with those reported.[12a]

*3.9.5. 2-(4-Methoxyphenyl)tetrahydropyran **4e**.* Product **4e** was isolated as white crystals. Mp 44–45 °C; MS: *m*/*z*<GK> (ESI$^+$): 215.3 ([M+Na]$^+$); HRMS: calcd for $C_{12}H_{16}NaO_2$: 215.1039 ([M+Na]$^+$). Found 215.1043 ([M+Na]$^+$); ν_{max} 2936 (m), 1611 (w), 1511 (m), 1248 (s) and 817 (s); δ_H (300 MHz, $CDCl_3$) 7.27 (2H, d, *J* 8.6, Ar*H*), 6.86 (2H, d, *J* 8.6, Ar*H*), 4.24 (1H, dd, *J* 10.5, 2.5, OC*H*Ar), 4.10 (1H, dd, *J* 10.6, 3.9, OC*H*H), 3.75 (3H, s, OCH_3), 3.57 (1H, dt, *J* 10.6, 2.7, OCH*H*), 1.95–1.90 (1H, m, CH_2), 1.80–1.73 (1H, m, CH_2), 1.70–1.50 (4H, m, CH_2); δ_C (75 MHz, $CDCl_3$) 158.9, 135.6, 127.6, 127.2, 113.7, 113.2, 79.8, 69.1, 55.3, 33.9, 25.9, 24.1. Data were consistent with those reported.[12b]

*3.9.6. 2-(4-Methoxyphenyl)tetrahydrooxepine **4f**.* A mixture of product **4f** and the dimer **4fD** were formed, in the ratios given in Table 1 and the Supplementary data. Product **4f** was a colourless oil. MS: *m*/*z* (ESI$^+$): 229.4 ([M+Na]$^+$); HRMS: calcd for $C_{13}H_{18}NaO_2$: 229.1199 ([M+Na]$^+$). Found 229.1199 ([M+Na]$^+$); ν_{max} 2936 (b), 1612 (m), 1511 (s), 1250 (s) and 816 (s) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.27 (2H, d, *J* 8.6, Ar*H*), 6.86 (2H, d, *J* 8.6, Ar*H*), 4.55 (1H, dd, *J* 9.2, 3.7, OC*H*Ar), 3.90 (1H, m, OC*H*H), 3.80 (3H, s, OCH_3), 3.70 (1H, m, OCH*H*), 2.10–1.20 (8H, m, alkyl-*H*). Data were consistent with those reported.[20] Dimer **4fD** was isolated as a white crystalline solid. MS: *m*/*z* (ESI$^+$): 435.2

([M+Na]$^+$); HRMS: calcd for $C_{26}H_{36}NaO_4$: 435.2506 ([M+Na]$^+$). Found 435.2514 ([M+Na]$^+$); ν_{max} 2934 (br), 2852 (br), 1611 (w), 1511 (s), 1252 (s) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.22 (4H, d, *J* 8.7, Ar*H*), 6.88 (4H, d, *J* 8.7, ArH), 4.28 (2H, dd, *J* 11.3, 2.5, ArC*H*O), 3.80 (6H, s, OCH_3), 3.45–3.40 (2H, br dt, *J* 11.5, 5.0, CH_2OCH), 3.21 (2H, br dt, *J* 2.1, 11.5, CH_2OCH), 2.06–1.76 (8H, m, CH_2), 1.61–1.24 (8H, m, CH_2); δ_C (75 MHz, $CDCl_3$) 158.75, 136.0, 127.4, 113.7, 79.2, 66.3, 55.2, 39.0, 29.5, 24.1, 23.8. The X-ray crystallographic structure of **4fD** is described in the Supplementary data, and full data are available as a.cif file from the Cambridge Crystallographic Data Centre (CCDC 796007).

*3.9.7. 2-Cyclohexyltetrahydrofuran **4g**.* A crude yellow oil was isolated. HRMS: calcd for $C_{10}H_{19}O$: 155.1431 ([M+H]$^+$). Found 155.1430 ([M+H]$^+$); ν_{max} 2922 (s), 2851 (s), 1449 (s), 1060 (s) cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.86–3.79 (1H, m, OC*H*H), 3.75–3.68 (1H, m, OCH*H*), 3.52–3.45 (1H, m, *H*COCH_2), 1.95–0.79 (15H, m, alkyl-CH); δ_C (75 MHz, $CDCl_3$) 84.0, 67.7, 43.0, 29.9, 29.2, 29.1, 26.5, 26.1, 25.9, 25.8. Data were consistent with those reported.[21]

*3.9.8. 2-Cyclohexyltetrahydropyran **4h**.* Due to poor conversions, the product was not fully characterised. Emerging peaks in the crude product mixture show the presence of the product **4h**. A seventeen alkyl hydrogen multiplet is assumed to be under the substrate multiplet at 2.00–0.80 ppm δ_H (300 MHz, $CDCl_3$) 3.95 (1H, m, OC*H*H), 3.90 (1H, m, OCH*H*), 2.94 (1H, ddd, *J* 10.8, 6.4, 2.0, *H*COCH_2).

3.10. NMR kinetic study of the cyclisation of 1-methoxyphenylbutane-1,4-diol 5d, 1-methoxyphenylpentane-1,5-diol 5e and 1-methoxyphenylhexane-1,6-diol 5f

To a solution of 1-methoxyphenyl-1, 4-butadiol **5d** (70 mg, 0.36 mmol) in deuturated acetonitrile (2.1 mL), 0.5 mol% catalyst (0.002 mmol, 0.002 equiv) was added. The time of catalyst addition was recorded. The solution was stirred quickly and an aliquot of the reaction mixture was transferred to an NMR tube. The mixture was submitted for a ^{1}H NMR kinetic study on a 400 MHz NMR spectrometer. The study was run at 25 °C and the spectrometer was programmed to record 25 spectra, with a delay of fifteen seconds between each measurement. Further measurements were taken if full conversion was not achieved in that time period. For each spectra the FID file creation time was used as the reference time for calculated conversion.

3.11. Synthesis of *rac*/*meso* 1:1 1,5-diphenolpenta-1,5-diol 6

A solution of 1,5-diphenylpentanone (1 g, 3.98 mmol) in MeOH/H_2O (60 mL/1.5 mL) was cooled to 0 °C in an ice bath. To the solution was added $NaBH_4$ (456 mg, 12 mmol) in ten portions with one portion per minute and the resultant solution was stirred for 1 h. The completion of reaction was followed by TLC versus starting material. To the reaction mixture was then slowly added $NaHCO_3$ (20 mL) and it was stirred well to consume all the sodium borohydride. The MeOH was removed in vacuo. Product **6** was extracted with Et_2O (3×50 mL) and the organic layers were combined, dried and filtered. The solvent was evaporated to give a white solid (918.9 mg, 90.2%) and an ^{1}H NMR spectrum of the crude product was recorded. δ_H ($CDCl_3$, 300 MHz, TMS) 1.13–1.85 (6H, m, 3×CH_2), 4.55 (2H, m, 2×C*H*OH), 7.15–7.25 (10H, m, Ar*H*); δ_C (75 MHz, $CDCl_3$) 21.6, 38.2, 73.9, 125.2, 128.0, 128.9, 144.1. ^{1}H and ^{13}C NMR data matches reported literature data.[13] Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel IB, 0.46×25 cm column, IPA/hexane 5:95, 0.5 mL/min, *T*=18 °C, *R*,*R* enantiomer 53.12 min, *S*,*S* enantiomer 54.45 min, *meso* isomer 56.95). *m*/*z* (ESI) 239 (M−OH) and 221 (M−2OH).

3.12. Synthesis of 2,6-diphenyltetrahydropyran 7

A typical procedure is as follows: to a solution of 1,5-diphenylpentadiol **6** (98.5 mg, 0.39 mmol) in acetonitrile (3 mL) was added 5 mol% $HAuCl_4$ (7.84 mg, 0.02 mmol). The solution was stirred at 80 °C for 2 h. Reaction progress was monitored by TLC. The solvent was evaporated in vacuo to give **7** as a yellow solid (88 mg, 0.37 mmol, 95%). δ_H ($CDCl_3$, 300 MHz, TMS) 7.15–7.45 (10H, m, Ar*H*), 4.85 (1H, d, 2C*H*OH (*trans*)), 4.54 (1H, m, 2C*H*OH (*cis*)) 1.70–2.01 (6H, m, 3×CH_2); δ_C (75 MHz, $CDCl_3$) 127.9, 127.6, 125.9, 125.2, 76.4. ^{1}H NMR data matches reported literature data.[9a]

3.13. Synthesis of (*R*,*R*)-1,5-diphenylpenta-1,5-diol 6

A mixture of 1,5-diphenolpentanone (1 g, 3.97 mmol), *R*,*R*-**8** (100 mg, 0.156 mmol, 3.9 mol%) and HCO_2H/Et_3N 5:2 (5 mL) in DCM (10 mL) was stirred at 40 °C under reflux for 22 h. The solvent was removed in vacuo and the residue was poured into water, filtered and dried under reduced pressure. Purification by column chromatography on silica (EtOAc/hexane, 0–60%) gave a brown solid. Recrystallisation from IPA/hexane afforded white crystals (510 mg, 2 mmol, 51%). δ_H ($CDCl_3$, 300 MHz, TMS) 7.15–7.22 (10H, m, ArH), 4.55 (2H, m, 2C*H*OH), 1.60–1.80 (4H, m, 2CH_2CH_2CHOHPh), 1.40 (2H, m, CH_2CH$_2$CHOHPh); δ_C (75 MHz, $CDCl_3$) 21.7, 38.2, 73.8, 125.2, 127.0, 127.9, 144.1. ^{1}H and ^{13}C NMR data match reported literature data.[13,14] *m*/*z* (ESI) 239 (M−OH) and 221 (M−2OH). Enantiomeric excess and conversion determined by HPLC analysis (Chiralcel IB, 0.46×25 cm column, IPA/hexane 5:95, 0.5 mL/min, *T*=20 °C, (*R*,*R*) enantiomer 55.258 min. 100% ee).

3.14. Synthesis of 2,6-diphenyltetrahydropyran 7 with a co-catalyst

A solution of 5 mol% $AuCl_3$ (5.85×10^{-3} mmol) and 5 mol% catalyst *R*-**11** (5.85×10^{-3} mmol) in acetonitrile (2 mL) was stirred at 60 °C under argon for 1 h. After the solution was cooled to 40 °C, to the reaction solution (*R*,*R*)-1,5-diphenolpentadiol **6** (30 mg, 0.117 mmol) in acetonitrile (1 mL) was added. The resultant mixture was stirred at 40 °C under argon for two days. The solvent was evaporated in vacuo to give a yellow solid. NMR spectra of the crude product were taken in order to establish the cis/trans ratio.

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Supplementary data

Supplementary data includes general experimental procedures, synthesis of ketoester precursors to diols, selected NMR and kinetic data and graphs. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.10.068. These data include MOL files and InCHiKeys of the most important compounds described in this article.

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