Asymmetric Hydroformylation of 4-Vinyl-1,3-dioxolan-2-one

Péter Pongrácz[a] and László Kollár[a,b]*

[a]Department of Inorganic Chemistry, University of Pécs and Szentágothai Research Center, Ifjúság u. 6., H-7624 Pécs, Hungary
[b]MTA-PTE Research Group for Selective Chemical Syntheses, Ifjúság u. 6., H-7624 Pécs, Hungary
E-mail: kollar@gamma.ttk.pte.hu

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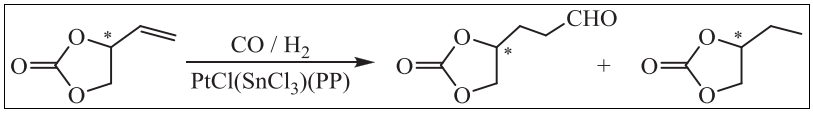

A chiral cyclic carbonate, 4-vinyl-1,3-dioxolan-2-one was used as racemic substrate in asymmetric hydroformylation. The catalysts were formed *in situ* from "pre-formed" $PtCl_2$(diphosphine) and tin(II) chloride. (*2S,4S*)-2,4-Bis(diphenylphosphinopentane ((*S,S*)-BDPP)), (*S,S*)-2,3-*O*-izopropylidine-2,3-dihydroxy-1,4-bis (diphenylphosphino)butane ((*S,S*)-DIOP)), and (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ((*R*)-BINAP)) were used as optically active diphosphine ligands. The platinum-containing catalytic systems provided surprisingly high activity. The hydroformylation selectivities of up to 97% were accompanied by perfect regioselectivity towards the dioxolane-based linear aldehyde. The enantiomeric composition of all components in the reaction mixture was determined and followed throughout the reaction. The unreacted 4-vinyl-1,3-dioxolan-2-one was recovered in optically active form. The kinetic resolution was rationalized using the enantiomeric composition of the substrate and the products.

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INTRODUCTION

The hydroformylation reaction has been considered as a powerful tool for the synthesis of chiral building blocks among them heterocyclic derivatives [1].

Since the early discovery of rhodium-catalyzed enantioselective hydroformylation [2,3], several classes of (functionalised) alkenes have been investigated as substrates [4–8]. Soon after, the hydroformylation of alkenes making use of platinum-phosphine-tin(II) halide systems [9,10] has also initiated some research activity. Although notable ee's were obtained in the asymmetric hydroformylation of alkenes (mainly of butene isomers as test substrates) using $PtCl_2$(chiral diphosphine) precursors [11], much higher enantioselectivities were observed in the enantioselective hydroformylation of vinylaromatics (mainly styrene and its derivatives) [12–16] and of unsaturated carboxylic acid derivatives (acrylates and itaconates) [17]. It is worth noting that the first approach includes a facile route towards the synthesis of optically active 2-arylpropanal derivatives, the direct precursors of 2-arylpropionic acid derivatives (such as the non-steroidal anti-inflammatory drug ibuprofen, naproxen, or suprofen [4,18,19]).

One of the milestones in enantioselective hydroformylation has been the application of Takaya's Rh-BINAPHOS catalyst, which resulted in both high regioselectivity towards branched aldehydes (2-arylpropanals) and high enantioselectivity [20,21]. Because of the enantioselectivities of higher than 90% in case of most vinylaromatics, this ligand is of potential for the manufacture of chiral fine chemicals. Further breakthroughs in chiral ligand design came with the disclosure of BISDIAZOPHOS [22,23], YANPHOS [24,25], CHIRAPHITE [26], and the biphen-based "BOBPHOS" [27]. The last ligand provided promising results in the asymmetric hydroformylation of both vinylaromatics and alkyl alkenes. All these chiral hydroformylation catalysts developed in the last decade have been reviewed recently [1].

The origin of the enantioselectivity, that is, the determination of the elementary catalytic step responsible for the stereochemical outcome of the hydroformylation reaction, has long been the main interest for both coordination and catalytic chemists. Catalytic evidences based on the rhodium-DIOP-catalyzed [28] and platinum-DIOP-catalyzed [11] enantioselective hydroformylation of butene isomers have proved that the determining step regarding formation of the corresponding enantiomers is the alkene coordination and alkene insertion into Rh-H and Pt-H bond, respectively.

Similarly, the elementary steps of platinum-catalyzed hydroformylation have been investigated both by analytical [29–31] and computational [32,33] means. The importance of cationic intermediates, that is, the formation of trichlorostannate counterion, was also shown by high-pressure NMR studies [34]. The importance of insertion/extrusion of alkene has been investigated by Casey *et al.* regarding the high temperature dependence of enantioselectivity [35].

This article describes the hydroformylation of a racemic *O*-heterocyclic substrate, 4-vinyl-1,3-dioxolane-2-one in the

presence of chiral platinum-containing catalysts. Two major purposes are aimed at these investigations: (i) to study the kinetic resolution of the racemic substrate in the presence of optically active catalysts and (ii) to synthesize novel building blocks possessing formyl functionality. It has to be added that the aforementioned model substrate meets both requirements. Although no novel stereogenic centers are created either in hydrogenation towards alkane or in hydroformylation towards linear aldehyde, because of catalytic kinetic resolution, chiral hydrogenated and linear formyl derivative applicable as chiral building blocks can be synthesized.

RESULTS AND DISCUSSION

Hydroformylation reactions. "Pre-formed" $PtCl(SnCl_3)$(diphosphine) complexes containing six-membered chelate ring (where diphosphine stands for (*2S,4S*)-2,4-bis(diphenylphosphinopentane) ((*S,S*)-BDPP) and 1,3-bis(diphenylphosphino)-propane (DPPP), respectively) were used as catalyst for the hydroformylation of racemic 4-vinyl-1,3-dioxolane-2-one (**1**) (Scheme 1) in the presence of a further equivalent of tin(II) chloride under "oxo-conditions" ($p(CO) = p(H_2) = 40$ bar, as described in Table 1).

Although the preferential formation of the linear regioisomer, which can be obtained with platinum catalysts containing bidentate *P*-ligands, is known for a long time [4–7], the regiospecific reaction resulting in the exclusive formation of the linear formyl regioisomer (**2**) is unexpected. The branched aldehyde (4-(1′-formylethyl)-1,3-dioxolan-2-one) could not be detected even in traces by gas chromatography/mass spectrometry. In addition to the linear aldehyde, some hydrogenation product (**3**) was also formed (Scheme 1). Although the formation of the linear aldehyde **2** was favored under all conditions, **3** was also present in the catalytic mixtures even under optimal conditions (*vide infra*). Gas chromatography (GC) and ^1H

Scheme 1. Hydroformylation of **1** in the presence of Pt-(chiral)diphosphine-tin(II) chloride catalytic system.

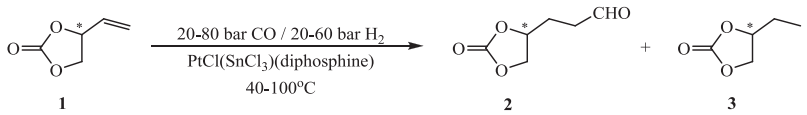


Table 1

Hydroformylation of 4-vinyl-1,3-dioxolan-2-one (**1**) with platinum complexes containing (*2S,4S*)-BDPP, DPPP, (*R*)-BINAP, and (*S,S*)-DIOP ligands[a].

							Composition of the reaction mixture		
Entry	Ligand	Temperature [°C]	$p(CO)/p(H_2)$	Reaction time [hours]	Conversion [%]	**1** (ee)[b] [%]	**2** (ee)[b] [%]	**3** (ee)[b] [%]	R_c[c] [%]
1	BDPP	100	40/40	1.5	41	59(13(*R*))	27(20(*S*))	14(11(*S*))	66
2	BDPP	100	40/40	2	63	37(16(*R*))	37(12(*S*))	26(6(*S*))	59
3	BDPP	100	40/40	2.75	>99.5	0	55(3(*S*))	45(1(*R*))	55
4	BDPP	100	40/60	1.5	41	59(14(*R*))	26(18(*S*))	15(11(*S*))	63
5	BDPP	100	40/60	19	65	35(23(*R*))	36(14(*S*))	29(5(*S*))	55
6	BDPP	100	60/40	2	38	62(12(*R*))	30(18(*S*))	8(10(*S*))	80
7	BDPP	100	60/40	7.5	61	39(22(*R*))	51(13(*S*))	10(14(*S*))	84
8	BDPP	60	40/40	10	73	27(0)	49(12(*S*))	24(4(*S*))	67
9	BDPP	60	40/40	19	>99.5	0	69(5(*S*))	31(4(*R*))	69
10	BDPP	40	40/40	24	21	79(11(*R*))	16(31(*S*))	5(18(*S*))	76
11	BDPP	40	40/40	72	>99.5	0	75(5(*S*))	25(8(*R*))	75
12	BDPP	40	60/40	21	32	68(14(*R*))	28(28(*S*))	4(11(*S*))	88
13	BDPP	40	60/40	41	49	51(33(*R*))	46(21(*S*))	3(3(*S*))	94
14	BDPP	40	80/20	24	13	87.6(5(*R*))	12(32(*S*))	0.4(14(*S*))	97
15	BDPP	100	0/40	0.6	12	88(1.7(*R*))	—	12(11(*S*))	–
16	BDPP	100	0/40	1	51	49(9.3(*R*))	—	51(8.8(*S*))	–
17	DPPP	100	40/40	2	58	42(0)	27(0)	31(0)	46
18	DPPP	100	40/40	24	>99.5	0	33(0)	67(0)	33
19[d]	BINAP	100	40/40	22	5	95(1(*S*)	4.2(7(*R*))	0.8(2(*R*))	84
20[d]	DIOP	100	40/40	24	>99.5	0	45(15(*S*))	55(12 (*R*))	45

[a]Reaction conditions (unless otherwise stated): Pt/**1** = 1:200; 0.05 mmol Pt-complex precursor, 0.05 mmol $SnCl_2$; solvent: toluene.
[b]Determined by chiral gas chromatography.
[c]R_c = chemoselectivity towards aldehyde [(moles of **2**)/(moles of **2** + moles of **3**) × 100].
[d]One millimole of $PtCl_2(PhCN)_2$, 1 mmol of phosphine ligand, and 2 mmol of $SnCl_2$ were used as *in situ* catalysts.

NMR analyses of the reaction products showed that no cleavage of the cyclic carbonate took place under hydroformylation conditions.

The hydroformylation activity of the aforementioned *in situ*-generated platinum-tin(II) chloride catalysts is moderate to high. In order to achieve practically complete conversion, 3, 19, and 72 h was necessary at 100, 60, and 40°C, respectively (entries 3, 9, and 11). The platinum-catalyst containing DPPP, the achiral analogue of BDPP equally forming six-membered chelate ring with the central metal, has shown comparable catalytic activity (entries 17 and 18).

Because the branched aldehyde regioisomer is completely missing from the reaction mixtures, the hydroformylation can be considered as regiospecific. The chemoselectivity towards aldehyde formation is slightly increasing by the decreasing of the reaction temperature. That is, chemoselectivity is varied between 66–76% while temperature is decreasing from 100 to 40°C (entries 1, 3, and 8–11).

A significant increase in chemoselectivity towards linear aldehyde was observed when the partial pressure of carbon monoxide was increased. A dramatic change was observed both at 100 and 40°C resulting in 80–84% and 88–97% chemoselectivities, respectively (entries 6, 7, and 12–14, respectively). Accordingly, higher hydrogen partial pressure resulted in lower chemoselectivity towards aldehyde, that is, the ratio of the hydrogenated product (**3**), was increased (entry 5).

Further *in situ* reactions with $PtCl_2(PhCN)_2$ and chiral ligands ((*S,S*)-2,3-*O*-izopropylidine-2,3-dihydroxy-1,4-bis (diphenylphosphino)butane ((*S,S*)-DIOP)), (*R*)-2,2′-bis (diphenylphosphino)-1.1′-binaphthyl ((*R*)-BINAP)) were carried out in the hydroformylation of **1** (entries 19 and 20). Much lower conversions and low chemoselectivities and enantioselectivities can be obtained compared with BDPP-containing catalyst.

Asymmetric induction during the hydroformylation of 1; determination of the absolute configuration of cyclic carbonates. Because the substrate (**1**), as well as the hydroformylation and hydrogenation products (**2** and **3**, respectively), is chiral, possessing a single central element of chirality, this system provides an excellent model to study the stereochemical outcome of the reaction. The kinetic resolution of the substrate and the formation of enantiomerically enriched chiral building blocks can be investigated.

With the composition of the reaction mixture and the ee's of the substrate (**1**) and products (**2** and **3**) in hand, the ratio of the enantiomers of each compound present in the reaction mixture could be determined (Table 2). The detailed analysis revealed that a slight kinetic resolution of **1** took place upon hydrogenation and hydroformylation. It turned out that both hydroformylation and hydrogenation is "enantiomer selective": the enantiomer of **1** eluted first (GC) reacts faster in both competing reactions yielding enantiomerically enriched **2** and **3** in the presence of chiral Pt-(*S,S*)-BDPP-tin(II) chloride catalytic system.

Table 2

Enantiomeric composition of the compounds **1**, **2**, and **3** formed in catalytic runs shown in Table 1[a].

Entry	Ratio of the enantiomers[b]			Sum of the enantiomers[c]
	1	**2**	**3**	
1	26/33	16/11	8/6	50/50
3	25.5/33.5	15.5/10.5	8.5/6.5	49.5/50.5
4	13.5/21.5	20.5/15.5	15/14	49/51
5	27/35	18/22	4.5/3.5	49.5/50.5
6	15/24	29/22	6/4	50/50
7	13.5/13.5	27.5/21.5	12.5/11.5	53.5/46.5
9	35/44	10.5/5.5	3/2	48.5/51.5
11	29/39	18/10	2.2/1.8	49.2/50.8
12	17/34	28/18	1.5/1.5	46.5/53.5
13	42/46	8/4	<0.2/0.2	50/50

[a]Representative examples where the starting material (**1**) is also present.
[b]Calculated from the ee's given in Table 1 (the amounts of enantiomers are rounded to 0.5%).
[c]The amount of the enantiomers of **1**, **2**, and **3** determined by chiral gas chromatography are summarized; [(*S*)-**1** + (*S*)-**2** + (*S*)-**3**]/[(*R*)-**1** + (*R*)-**2** + (*R*)-**3**].

Because the specific (−)-rotation of (*S*)-**3** and (+)-rotation of (*R*)-**3a** is known [36], and perfect retention of the configuration is supposed, the corresponding absolute configurations of the major/minor enantiomers of all products (**2**, **2a**, and **3a**) can also be given. On the basis of the integrals of the chiral-GC measurements, it can be stated that the first eluted enantiomers of **1**, **2**, and **3** are equally possessing *S* absolute configuration.

The formation of (*S*)-(**2**) was preferred in the temperature range of 40–100°C. Decreasing the temperature a slight increase of enantioselectivity towards the *S*-aldehyde observed (entries 3, 9, and 11). At the beginning of the reaction (at low conversions), the highest ee's of the products were obtained, (entries 1, 10, and 14) converting (*S*)-**1** to products. The ee of **2** is always higher than that of **3**, that is, higher enantioselection can be observed in hydroformylation than in hydrogenation. As the reaction goes to completion, the ee's are decreasing due to the lower amount of (*S*)-**1**. While the (*S*)-enantiomer is dominating in case of the products (**2** and **3**) throughout the reaction, the reversal of the dominating enantiomer can be observed for the hydrogenation product (**3**) when the reaction goes to completion, that is, in case of full conversion, the prevailing enantiomers are (*S*)-**2** and (*R*)-**3**.

Based on these observations, it can be stated that the (*S*)-enantiomer of **1** reacts faster in the catalytic reactions (both in hydroformylation and hydrogenation). In the presence of Pt-(*2S,4S*)-BDPP catalyst, the (*R*)-**1**

enantiomer is less reactive. However, when higher conversions are reached (i.e., when the substrate is enriched in (*R*)-**1** enantiomer), hydrogenation is favored over hydroformylation, which causes decreasing chemoselectivity towards aldehyde accompanied by decreasing ee of **2** (entries 1, 2, and 3) and even the reversal of the ee of **3** at all temperatures (entries 3, 9, and 11). Because the enantioselection is lower for hydrogenation than for hydroformylation at low conversions, the preferred hydrogenation of (*R*)-**1** at higher conversions resulted in the reversal of dominating enantiomer of the hydrogenated product, that is, (*R*)-**3** can be isolated from all reaction mixtures obtained at full conversion. In other words, an explanation for chemoselectivity decrease at higher conversions is the domination of hydrogenation of both enantiomers at the end of the reaction. Consequently, in case of **3**, reversal of the enantiomers can be seen ((*S*) to (*R*)), and the non-reversal of **2** may be due to excessive quantity of (S)-**2** formed.

Further hydrogenation reactions were performed, in order to explain the changes of the enantioselectivity during the reaction. These reactions showed that the hydrogenation of **1** takes place much faster in the absence of carbon monoxide (entries 15 and 16). However, the ee's obtained for hydrogenation does not differ significantly in the presence or absence of carbon monoxide, which means that the optical yields of hydrogenated product **3** are not influenced by the hydroformylation reaction (compare entries 1, 15 and 2, 16).

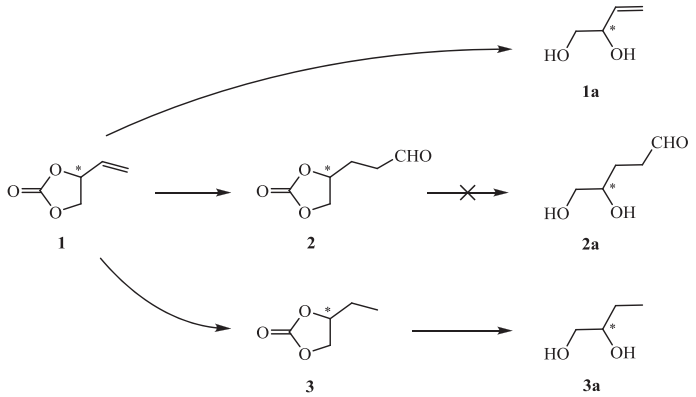
Because no new stereogenic center(s) are created (see succeeding text), the enantiomers of **1** are transformed to the corresponding enantiomers of **2** and **3**. In fact, the sum of the enantiomers of each compound eluted first matched perfectly with those eluted second. That is, a perfect balance regarding enantiomers could be made (Table 2).

Chiral building blocks formed in methanolysis. Compounds **1–3** were treated with methanol in the presence of potassium carbonate (Experimental; 2.4.). The corresponding vicinal 1,2-diols **1a** and **3a** were quantitatively formed in the reaction (Scheme 2). As the ring opening of cyclic carbonates proceed with retention of configuration, the enantiomeric composition of the products of methanolysis (**1a** and **3a**) cannot change, that is, (*S*)-**1** gives (*S*)-**1a**; (*S*)-**3** gives (*S*)-**3a**. The methanolysis of **2** resulted in a rather complex mixture of forming hemiacetals or acetals; therefore, **2a** could not be isolated in analytically pure form.

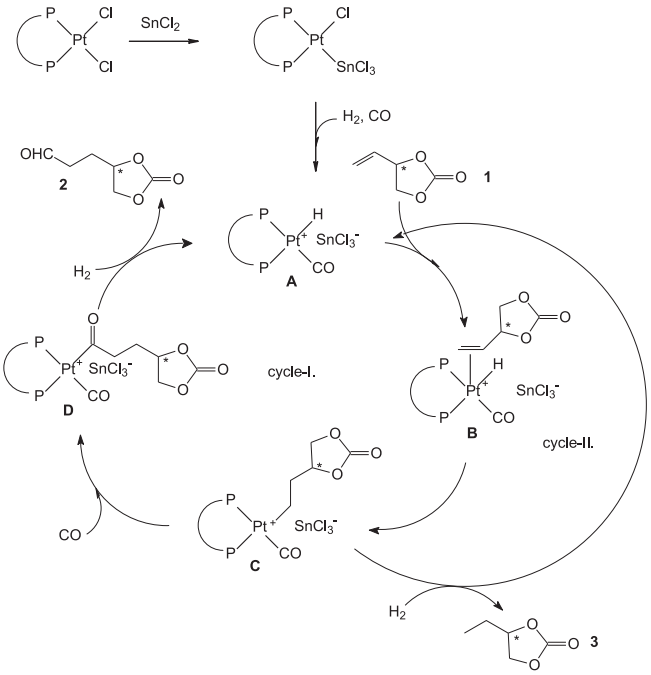
The fact that the sum of the corresponding enantiomers is close to 50% implies several points regarding mechanistic details. A simplified mechanism rationalizing the formation of **2** and **3** is depicted in Scheme 3.

(i) The asymmetric induction (even if to a small or moderate extent) takes place when the alkene (**1**) is activated by the platinum complex (**B**) and inserted into the Pt-H bond leading to platinum-alkyl intermediate (**C**). It should be noted that these diastereomeric platinum-alkyl complexes serve as key intermediates both for hydrogenation and hydroformylation.
(ii) Both reactions proceed without changing the configuration, that is, the stereogenic center is not involved in elementary reactions (alkene insertion/extrusion, carbon monoxide insertion/extrusion, aldehyde formation via reductive elimination) involved in the catalytic cycle (cycle-I.).
(iii) No racemization of partially resolved **1** (and consequent dynamic resolution) takes place.
(iv) The decarbonylation of **2** towards **3** does not take place to high extent, that is, the chemoselective formation of **2** is maintained throughout the reaction.

Scheme 2. The products obtained in methanolysis of the cyclic carbonates (**1–3**).



Scheme 3. A simplified catalytic cycle (ionic mechanism is depicted only) for the hydroformylation/hydrogenation of **1**.



(v) The temperature dependence of the optical yields of **2** shows that the formation of the acyl complex (**D**), upon carbon monoxide insertion in to the platinum-alkyl bond, is reversible at higher temperatures [35]. That is, the extrusion of carbon monoxide takes place to higher extent at 100°C.

SUMMARY

In summary, moderate to high chemoselectivity towards aldehyde as well as regiospecific formation of the linear aldehyde was observed in the platinum-catalyzed hydroformylation of racemic 4-vinyl-1,3-dioxolan-2-one. Chemoselectivity is significantly influenced by temperature and partial pressures. The formation of chiral products and the resolution of the starting substrate were rationalized based on kinetic chiral resolution when optically active platinum-chiral diphosphine catalyst was used.

EXPERIMENTAL

General. The $PtCl_2(PhCN)_2$ precursors were synthesized from $PtCl_2$ (Aldrich) according to standard procedures, respectively [37]. BDPP was purchased from Strem. $PtCl(SnCl_3)$[(*2S,4S*)-BDPP], and the analogous complexes were synthesized as described before [38] Toluene was distilled and purified by standard methods and stored under argon. All reactions were carried out under argon using standard Schlenk techniques.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 500 spectrometer. Chemical shifts are reported in parts per million relative to TMS (downfield) for ^1H and ^{13}C NMR spectroscopy.

Hydroformylation experiment. In a typical experiment, a solution of 0.005 mmol of $PtCl(SnCl_3)$BDPP and 0.005 mmol (0.95 mg) of tin(II) chloride in toluene (5 mL) containing 1 mmol of substrate (**1**) was transferred under argon into a 100-mL stainless steel autoclave. The autoclave was pressurized to 80 bar total pressure ($CO/H_2 = 1:1$) and placed in an oil bath. The mixture was stirred with a magnetic stirrer for the time given in Table 1. The pressure was monitored throughout the reaction. After cooling and venting of the autoclave, the pale yellow solution was removed and immediately analyzed by GC and gas chromatography/mass spectrometry. The enantiomeric excess was determined by using a chiral capillary column (CycloSil-B (30 m × 0,25 mm)): (injection temperature: 250°C; starting oven temperature: 50°C; rate: 4°C/min; final temperature: 200°C; carrier gas: He 1.30 mL/min).

General procedure for the preparation of diols (1a, 3a) [39]. Cyclic carbonates **1**, **2,** or **3** (1.0 mmol) and potassium carbonate (2.0 mmol) in 10 mL of anhydrous methanol at 60°C for 2.5 h led to the quantitative transformation of the carbonate into the corresponding diol. After evaporation of the solvent

and dissolution of the salt in water, the diol was extracted with diethyl ether. The solution was dried on Na_2SO_4, filtered, and distilled under reduced pressure. The corresponding diols (**1a** or **3a**) were collected as colorless liquids.

Characterization of the products

(R)-(+)-4-Vinyl-1,3-dioxolan-2-one (1) [40]: colorless viscous liquid; δ_H (500 MHz, $CDCl_3$) 5.92 (1 H, ddd, 7.5 Hz, 10.1 Hz, 17.1 Hz, C*H*=CH_2), 5.54 (1 H, d, 17.1 Hz, CH=CH_aH_b) 5.47 (1 H, d, 10.1 Hz, CH=CH_aH_b), 5.15 (1 H, q, 7.5 Hz, OCH), 4,62 (1 H, t, 8.3 Hz, OCH_aH_b), 4.18 (1 H, t, 8.0 Hz, OCH_aH_b); δ_C (125.7 MHz, $CDCl_3$) 154.8, 132.2, 121.3, 77.4, 69.0. IR (KBr (cm^{-1})): 1810. MS *m/z* (rel int. %): 84 (27), 69 (67), 55 (100). $[\alpha]_D^{20}$ = +20.5° (c 2.80, $CHCl_3$).

(S)-(+)-4-(2-Formylethyl)-1,3-dioxolan-2-one (2): colorless liquid; δ_H (500 MHz, $CDCl_3$) 9.80 (1 H, s, CHO), 4.78 (1 H, qd, 4.0 Hz, 7.9 Hz, OCH), 4.58 (1 H, t, 8.3 Hz, OCH_aH_b), 4.11 (1 H, t, 7.9 Hz, OCH$_aH_b$), 2.73 (2 H, 2.67-2.78, CH_2CHO), 2.09 (1 H, tdd, 4.0 Hz, 7.4 Hz, 15.2 Hz, CHCH_aH_b), 1.99 (1 H, tdd, 6.5 Hz, 7.9 Hz, 15.2 Hz, CHCH$_aH_b$); δ_C (125.7 MHz, $CDCl_3$) 200.2, 154.8, 76.0, 69.4, 38.8, 26.3. IR (KBr (cm^{-1})): 1722 (CHO); 1795 (CO). MS *m/z* (rel int. %): 116 (45), 101 (100), 87 (13), 71 (16), 57 (84), 54 (86). $[\alpha]_D^{20}$ = +8.58° (c 20, $CHCl_3$) (measured for a sample possessing e.e. of 16%)

(S)-(-)-4-Ethyl-1,3-dioxolan-2-one (3) [41]: colorless liquid; δ_H (500 MHz, $CDCl_3$) 4.68 (1 H, quintet, 7.2 Hz, OCH), 4.55 (1 H, dd, 4.2 Hz, 8.2 Hz, OCH_aH_b), 4.11 (1 H, dd, 7.2 Hz, 8.2 Hz, OCH$_aH_b$), 1.83 (1 H, qd, 7.2 Hz, 15.0 Hz, C$H_aH_bCH_3$), 1.78 (1 H, qd, 7.2 Hz, 15.0 Hz, CH$_aH_bCH_3$), 1.05 (1 H, t, 7.4 Hz, CH_3); δ_C (125.7 MHz, $CDCl_3$) 155.2, 78.0, 69.0, 27.0, 8.5. IR (KBr (cm^{-1})): 1801. MS *m/z* (rel int. %): 116 (2), 87 (100), 71 (6), 57 (27). $[\alpha]_D^{20}$ = −8.61° (c 5.80, $CHCl_3$) (measured for a sample possessing e.e. of 5%).

(R)-(+)-3,4-Dihydroxy-1-butene (1a) [40]: colorless liquid; δ_H (500 MHz, D_2O) 5.77 (1 H, ddd, 6.0 Hz, 10.6 Hz, 17.0 Hz, C*H*=CH_2), 5.24 (1 H, d, 17.0 Hz, CH=CH_tH_c), 5.16 (1 H, d, 10.6 Hz, CH=CH$_tH_c$), 4.12 (1 H, q, 5.6 Hz, C*H*OH), 3.51 (1 H, dd, 4.5 Hz, 11.6 Hz, CH_2OH), 3.42 (1 H, dd, 7.0 Hz, 11.6 Hz, CH_2OH); δ_C (125.7 MHz, D_2O) 136.7, 116.8, 72.8, 64.9. IR (KBr (cm^{-1}) 3374. MS *m/z* (rel int. %): 70 (7), 57 (100), 39 (9), 29 (30). $[\alpha]_D^{20}$ = +35.3° (c 1.80, *i*-PrOH).

(R)-(+)-1,2-Dihydroxybutane (3a) [36]: colorless liquid; δ_H (500 MHz, D_2O) 3.49 (2 H, CH_aH_bOH and C*H*OH), 3.35 (1 H, dd, 6.6 Hz, 11.3 Hz CH_aH_bOH), 1.41 (1 H, m, CH_2CH_3), 0.80 (3 H, t, 7.5 Hz, CH_3); δ_C (125.7 MHz, D_2O) 73.7, 66.3, 26.0, 10.0; IR (KBr (cm^{-1})) 3375. MS *m/z* (rel int. %): 73 (2), 61 (21), 59 (100), 45 (31), 43 (21), 41 (23), 31 (56). $[\alpha]_D^{20}$ = +15.35° (c 2.6, EtOH).

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