Catalytic enantioselective reactions. Part 16.[1] Oxazaborolidine-catalyzed asymmetric borane reduction of α-keto acetals

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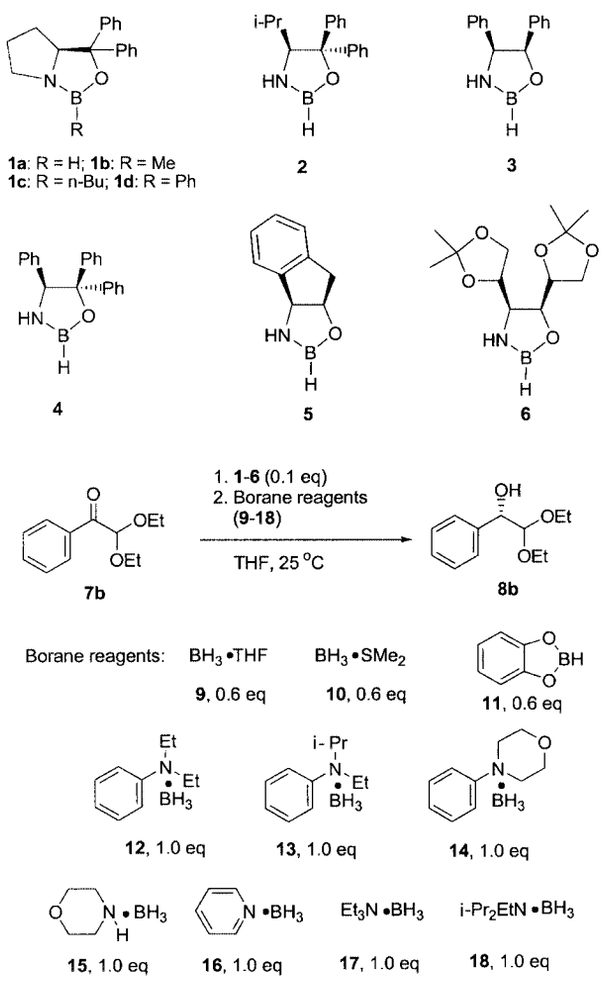
Received (in Cambridge) 27th April 1999, Accepted 7th June 1999

Asymmetric reductions of α-keto acetals using various oxazaborolidines and borane reagents as catalyst and the hydride source, respectively, were compared. The reduction catalyzed by Corey's CBS reagents with *N*-phenylamine–borane reagents provided α-hydroxy acetals with very high enantioselectivities for most aromatic analogues.

Introduction

Optically active α-hydroxy aldehydes are not only useful chiral building blocks for synthesis of natural products, such as rhodianose,[2] rocellaric acid,[3] lipoxine A,[4] *endo*-brevicomine,[5] grayanotoxins[6] and amino sugars,[7] but are also important substrates for diastereofacial selective reactions of the carbonyl groups, *e.g.* nucleophilic 1,2-addition or aldol reactions, and cycloadditions.[8] Accordingly, many synthetic methods, including transformation of chiral precursors such as α-hydroxy acids[9] and α-amino acids,[10] biocatalytic reduction[11] or catalytic asymmetric hydrogenation of α-keto (thio)acetals,[12] and asymmetric synthesis from achiral aldehydes[5b,13] have been developed. Asymmetric reduction of α-keto acetals offers a promising route to chiral α-hydroxy acetals. Recently we reported asymmetric reduction of α-keto acetals with a chiral borohydride, K xylide (potassium 9-*O*-(1,2-isopropylidene-5-deoxy-α-D-xylofuranosyl)-9-boratabicyclo[3.3.1]nonane), in a stoichiometric manner to afford α-hydroxy acetals with high enantioselectivities.[14] However, limitations to the use of this stoichiometric reagent include its availability, cost, ease of product purification and chiral auxiliary recovery on a large scale. On the other hand, the pioneering works of Itsuno[15] and Corey[16] have resulted in oxazaborolidines which catalytically provide alcohols of predictable absolute stereochemistry and high enantiomeric excess (ee). Accordingly, a number of oxazaborolidine-catalyzed asymmetric reductions of prochiral ketones have been reported.[17] In connection with our continuing efforts toward asymmetric reduction of functionalized ketones,[14,18] we undertook the study of oxazaborolidine-catalyzed asymmetric reduction of α-keto acetals using various borane reagents. During this study, we found a practically useful method for such a reduction using *N*,*N*-diethylaniline–borane complex (DEANB) as a borane source.[1] In this paper, we describe details of such an oxazaborolidine-catalyzed asymmetric reduction and the scope and limits of these reactions.



Scheme 1

Results and discussion

Effect of oxazaborolidines and boranes on asymmetric induction

Our first effort was to compare the asymmetric reduction of 2,2-diethoxy-1-phenylethanone **7b** catalyzed by structurally diverse oxazaborolidines such as proline-based oxazaborolidines (Corey's CBS reagents, **1**[16]), valine-based oxazaborolidine (Itsuno's reagent, **2**[15]), aminodiphenylethanol-based oxazaborolidine (Pfizer's reagent, **3**[19]), phenylglycine-based oxazaborolidine (**4**[20]), aminoindanol-based oxazaborolidine (Sepracor's reagent, **5**[21]) and aminoaltritol-based oxazaborolidine **6**[22] using borane–tetrahydrofuran (BH_3·THF, **9**) (Scheme 1). Thus, slow addition of **7b** over a period of 1 h to a solution of 0.6 mol equiv. of borane–THF in the presence of 10 mol% of one of the oxazaborolidines in THF at 25 °C afforded 2,2-diethoxy-1-phenylethanol **8b** within 10 min in 92–97% yield. The enantiomeric excess (ee) of the α-hydroxy acetal **8b** product was determined by HPLC analysis using a Chiralcel OD column (eluent: hexane–Pr^iOH = 40 : 1). As shown in Table 1, of the oxazaborolidines examined, Corey's CBS reagents **1a** and **1b** provided the best enantioselectivities such as 92% ee with **1a**, 91% ee with **1b**, 65% ee with **2**, 71% ee with **3**, 59% ee with **4**,

Table 1 Asymmetric borane reduction of 2,2-diethoxy-1-phenylethanone **7b** in the presence of 10 mol% of each of various oxazaborolidines in THF at 25 °C[a]

			8b		
Entry	Borane reagent (equiv.)	Cat.	Yield[b]	% ee[c]	Config.[d]
1	**9** (0.6)	**1a**	96	92	*S*
2	**9** (0.6)	**1b**	97	91	*S*
3	**9** (0.6)	**1c**	95	83	*S*
4	**9** (0.6)	**1d**	92	84	*S*
5	**9** (0.6)	**2**	93	65	*S*
6	**9** (0.6)	**3**	95	71	*S*
7	**9** (0.6)	**4**	93	59	*S*
8	**9** (0.6)	**5**	95	71	*S*
9	**9** (0.6)	**6**	96	57	*S*
10	**10** (0.6)	**1b**	94	91	*S*
11	**11** (1.1)	**1b**	97	95	*S*
12	**12** (1.0)	**1a**	99	96	*S*
13	**12** (1.0)	**1b**	96	96	*S*
14	**13** (1.0)	**1b**	97	94	*S*
15	**14** (1.0)	**1b**	96	95	*S*
16	**15** (1.0)	**1b**	94	2	*S*
17	**17** (1.0)	**1b**	48[e]	16	*S*
18	**18** (1.0)	**1b**	47[e]	56	*S*

[a] **[7b]** = 0.3 M in the reaction with **9**; **[7b]** = 0.6 M in the reactions with **10**–**18**. [b] Isolated yield. [c] By HPLC analysis with a Chiralcel OD column using hexane–propan-2-ol (40:1) as eluent. [d] Based on (*S*)-(+)-2,2-dimethoxy-1-phenylethanol and (*S*)-(+)-1-phenylethane-1,2-diol: ref. 11*a* and 32. [e] In 24 h.

71% ee with **5**, and 57% ee with **6** (entries 1–9). *B*-Bu^n (**1c**, 83% ee) and *B*-Ph (**1d**, 84% ee) groups of the catalyst **1** afforded somewhat lower enantioselectivities than those obtained by *B*-H and *B*-Me groups. Such steric effects of *B*-substituents are a common phenomenon in oxazaborolidine-catalyzed reductions.[17a,23] Next, we examined the effect of the borane carriers for their enantioselectivity by comparing the reduction for **7b** in the presence of 10 mol% of the CBS reagent **1b** using various borane reagents, such as borane–dimethyl sulfide (BMS, **10**), catecholborane **11**, and amine–borane complexes, namely, *N*,*N*-diethylaniline–borane **12**, *N*-ethyl-*N*-isopropylaniline–borane **13**, *N*-phenylmorpholine–borane **14**, morpholine–borane **15**, pyridine–borane **16**, triethylamine–borane **17** and diisopropylethylamine–borane **18**. The reductions were carried out with 0.6 mol equiv. of **10**, 1.1 mol equiv. of **11** and 1.0 mol equiv. of each of the amine–borane reagents **12**–**18** in THF at 25 °C. With the exception of the reactions with **16**–**18**, all the reductions were complete within 10 min to produce **8b** in 92–99% yield. The reductions with **17** and **18** provided 48% and 47% yield after 24 h, respectively. No reaction with **16** was observed in 24 h. With respect to enantioselectivity, **10** and **11** afforded 91% ee and 95% ee, respectively (entries 10 and 11). Among the amine–borane reagents examined, *N*-phenylamine–borane complexes **12**–**14** emerge as the most valuable borane sources to give 94–96% ee (entries 12–15). The reduction with **15**, **17** and **18** provided low to moderate enantioselectivities (entries 16–18).

Effect of reaction temperature and solvent on asymmetric induction

It has been reported that reaction temperature[24] and solvents[25] in CBS reduction of prochiral ketones influence significantly the enantioselectivity. To examine the reaction temperature effect for the asymmetric reduction, **7b** was treated with the borane reagents **11** and **12** in the presence of 10 mol% of **1b** in THF at −25 and 0 °C. At these temperatures, we obtained **8b** in lower yields and enantioselectivities in comparison with those at 25 °C (entries 11 and 13 in Table 1; entries 1–4 in Table 2). Such phenomena appeared more significant in the case of **12**. We also examined solvent effects on such reactions by carrying out the same reduction in toluene and dichloromethane instead of THF at 25 °C. The reduction in these solvents provided **8b** in much lower enantioselectivity than those obtained at 25 °C in all the cases using the borane reagents **10**–**12** (entries 5–10 in Table 2).

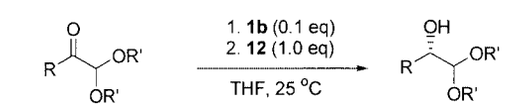
Table 2 Solvent and the reaction temperature effect on enantioselectivity for oxazaborolidine-catalyzed asymmetric reduction of **7b** using various borane reagents[a]

					8b		
Entry	Cat.	Solvent	Borane reagent	Temp (*T*/°)	Yield[b]	% ee[c]	Config.[d]
1	**1a**	THF	**11**	0	93	90	*S*
2	**1a**	THF	**11**	−25	86[e]	79	*S*
3	**1a**	THF	**12**	0	85	62	*S*
4	**1a**	THF	**12**	−25	65[e]	8	*S*
5	**1b**	toluene	**10**	25	96	90	*S*
6	**1b**	CH_2Cl_2	**10**	25	94	81	*S*
7	**1b**	toluene	**11**	25	91	51	*S*
8	**1b**	CH_2Cl_2	**11**	25	89	24	*S*
9	**1b**	toluene	**12**	25	90	77	*S*
10	**1b**	CH_2Cl_2	**10**	25	94	81	*S*
11	**1b**	CH_2Cl_2	**12**	25	90	58	*S*

[a–d] See the corresponding footnotes in Table 1. [e] In 6 h.

Asymmetric reduction of α-keto acetals 7 catalyzed by 1b with 12

The above results revealed that the reduction of compound **7b** in the presence of 10 mol% of **1b** with 1 mol equiv. of *N*-phenylamine–borane reagents **12**–**14** in THF at 25 °C was the optimum reaction with conditions giving high yields and enantioselectivities of product alcohol **8b**. It is noteworthy that amine–borane reagents as the borane carrier, are very effective for asymmetric reduction resulting in a practically useful synthesis of optically active α-hydroxy acetals on a large scale. This is because such borane reagents are not only less sensitive to air and moisture, but are also soluble in most solvents with high concentration compared with borane hydrides **9**–**11**. Thus we carried out the catalytic reduction of some other aromatic and aliphatic α-keto acetals using **12** as the hydride source under these optimum reaction conditions (Scheme 2). The results illustrated in Table 3 indicate that the



7 **8**

	R	R'	R''		R	R'	R''
a:	Ph	Me	Me	**h**:	2-Furyl	Me	Me
b:	Ph	Et	Et	**i**:	Me	Me	Me
c:	Ph	-$(CH_2)_3$-		**j**:	n-C_4H_9	Me	Me
d:	Ph	i-Pr	i-Pr	**k**:	n-C_6H_{13}	Et	Et
e:	*p*-ClC_6H_4	Me	Me	**l**:	n-C_6H_{13}	-$(CH_2)_3$-	
f:	*o*-ClC_6H_4	Me	Me	**m**:	c-C_6H_{11}	Et	Et
g:	2-Naphthyl	Me	Me				

Scheme 2

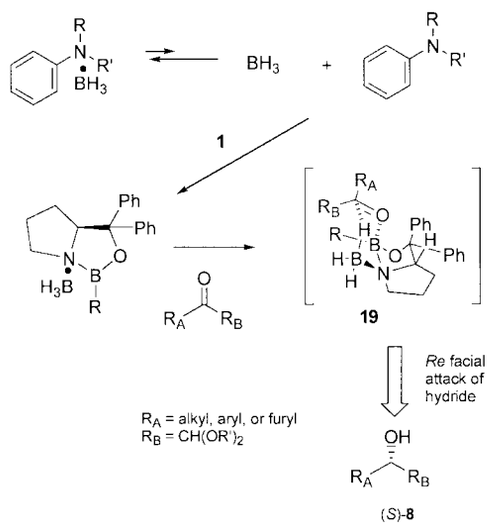
reduction of aromatic analogues such as **7e** and **7g** provided the corresponding α-hydroxy acetals (**8e** and **8g**) with very high optical purity in 99% ee. Interestingly, the reduction of 1-(2-chlorophenyl)-2,2-dimethoxyethanone **7f** provided **8f** in 30% ee in contrast to >99% ee for 1-(4-chlorophenyl)-2,2-dimethoxyethanone **7e** (entries 5 and 6). Similarly, we observed a remarkable decrease in enantioselectivity for reduction of **7d** possessing a diisopropyl group in $PhCOCH(OR)_2$, compared with those having the dimethoxy, diethoxy and propane-1,3-dioxy groups [95% ee for **7a**, 96% ee for **7b**, 93% ee for **7c** and 33% ee for **7d** (entries 1–4)]. These results indicate that the asymmetric induction is sensitive to steric effects of the sub-

Table 3 Asymmetric reduction of α-keto acetals **7** in the presence of 10 mol% of **1b** with 1 mol equiv. of **12** in THF at 25 °C[a]

		8			
Entry	**7**	Yield (%)[b]	$[\alpha]_D^{23}/10^{-1}$ deg cm^2 g^{-1}	% ee	Config.[i]
1	**7a**	93	+14.03 (*c* 5.02, $CHCl_3$)	95[c]	*S*
2	**7b**	96	+19.22 (*c* 5.11, $CHCl_3$)	96[c]	*S*
3	**7c**	94	+3.13 (*c* 5.10, $CHCl_3$)	93[c]	*S*
4	**7d**	97	4.11 (*c* 5.02, $CHCl_3$)	33[c]	*S*
5	**7e**	91	+11.14 (*c* 5.41, $CHCl_3$)	>99[d]	*S*
6	**7f**	97	+7.11 (*c* 5.41, $CHCl_3$)	30[d]	*S*
7	**7g**	97	+2.64 (*c* 5.11, $CHCl_3$)	99[e]	*S*
8	**7h**	85	+3.68 (*c* 4.80, $CHCl_3$)	71[f]	*S*
9	**7i**	65	−8.38 (*c* 3.11, MeOH)	60[g]	*S*
10	**7j**	73	−20.51 (*c* 1.15, CH_2Cl_2)	42[f]	*S*
11	**7k**	76	−18.71 (*c* 1.82, CH_2Cl_2)	47[f]	*S*
12	**7l**	98	−28.42 (*c* 1.83, CH_2Cl_2)	62[h]	*S*
13	**7m**	93	−10.98 (*c* 4.11, CH_2Cl_2)	66[h]	*S*[j]

[a] [**7**] = 0.6 M. [b] Isolated yield. [c] By HPLC analysis with a Chiralcel OD column using hexane–propan-2-ol (40 : 1) as eluent. [d] By HPLC analysis with a Chiralcel OD column using hexane–propan-2-ol (9 : 1) as eluent. [e] By HPLC analysis with a Chiralcel OT column using hexane–propan-2-ol (9 : 1) as eluent. [f] By GLC analysis of its trifluoroacetate using a 20 m Chiraldex GTA column. [g] By GLC analysis of its (−)-menthyl carbonate using a 25 m Supelcowax™ 10 capillary column. [h] By GLC analysis of its (*R*)-MPTA ester using a 25 m Supelcowax™ 10 capillary column. [i] By comparison of the absolute configurations of the known compounds, the corresponding diols and/or the elution orders of peaks in GLC or HPLC analyses. [j] Probably *S* based on comparison of the order of elution of GLC analysis and the sign of the optical rotation with those of aliphatic analogues.

stituent proximal to the carbonyl group. This is a common phenomenon in oxazaborolidine-catalyzed reductions.[18a,26] A heterocyclic α-keto acetal, 1-(2-furyl)-2,2-dimethoxyethanone **7h**, produced the α-hydroxy acetal **8h** with a moderate optical purity. In the case of aliphatic analogues, the asymmetric reduction afforded somewhat lower enantioselectivities than those obtained from aromatic analogues (entries 9–13). In all the cases examined, the product α-hydroxy acetals **8** obtained are consistently enriched in the *S*-enantiomer. The stereochemical course of the asymmetric reduction can be explained by the proposed mechanism involving a transition state **19**, where the α-keto acetals are attacked by hydride on their *re* faces to provide (*S*)-α-hydroxy acetals (Scheme 3).[18a,26,27] Although the



Scheme 3

reason why different reactivities and enantioselectivities of amine–borane reagents are observed for reduction of α-keto acetals is so far unclear, it might be attributable to differential dissociation of amine–borane adducts leading to liberation of free BH_3, which coordinates with oxazaborolidines to initiate catalytic asymmetric reduction. This asymmetric process is based on slow reduction of ketones with amine–borane adducts themselves and easier dissociation of *N*-phenylamine–borane complexes to the free BH_3 compared with other amine–borane adducts.[28]

Conclusion

We have developed a practical, useful method for the synthesis of chiral α-hydroxy acetals by oxazaborolidine-catalyzed asymmetric reduction of α-keto acetals using *N*-phenylamine–borane complexes as the hydride source. This is the first such example to obtain aromatic α-hydroxy acetals with high enantioselectivity approaching 100% ee. Further applications using this methodology are now under investigation.

Experimental

General

All operations with air-sensitive materials were carried out under a nitrogen atmosphere with oven-dried glassware. Liquid materials were transferred with a double-ended needle.[29] The reactions were monitored by TLC using silica gel plates and the products were purified by flash column chromatography on silica gel (Merck; 230–400 mesh). NMR spectra were recorded at 300 or 400 MHz for ^{1}H and 75 or 100 MHz for ^{13}C using Me_4Si as the internal standard in $CDCl_3$. *J*-Values are given in Hz. Optical rotations were measured with a high-resolution digital polarimeter, with $[\alpha]_D$-values given in units of 10^{-1} deg cm^2 g^{-1}. Mps were measured on a capillary tube apparatus and are uncorrected. Enantiomeric excesses (% ees) of the product α-hydroxy acetals were determined by capillary GLC analyses of their (*R*)-MTPA [methoxy(trifluoro)phenylacetate] esters or (−)-menthyl carbonates using a 25 m Spelcowax™ column or a 20 m Chiraldex G-TA chiral column or with an HPLC apparatus fitted with a 25 cm Chiralcel OB or OD column. Hex implies hexane.

Materials

Most of the organic compounds utilized in this study were commercial products of the highest purity. They were further purified by distillation when necessary. THF was distilled over sodium benzophenone ketyl and stored in ampoules under a nitrogen atmosphere. The chiral oxazaborolidines **1**–**6** except for **1b** were prepared from treatment of the corresponding amino alcohols with BH_3–THF according to the known procedure.[15,16,19–22] (*S*)-α,α-Diphenylpyrrolidine-2-methanol, (*1S,2R*)-*cis*-1-aminoindan-2-ol, (*1R,2S*)-2-amino-1,2-diphenylethanol, a CBS oxazaborolidine **1b**, 2,2-diethoxy-1-phenylethanone **7b**, pyruvic aldehyde dimethyl acetal **7i**, borane–tetrahydrofuran **9**, borane–dimethyl sulfide **10**, *N*,*N*-diethylaniline–borane **12**, *N*-ethyl-*N*-isopropylaniline–borane **13**, *N*-phenylmorpholine–borane **14**, morpholine–borane **15**, pyridine–borane **16**, triethylamine–borane **17** and diisopropylethylamine–borane **18** were purchased from the Aldrich Chemical Company. Catecholborane **11** was prepared from reaction of catechol with **10** according to the literature.[29]

Preparation of α-keto acetals

The α-keto acetals **7** used as substrates were prepared by addition of Grignard reagents to dialkoxyacetopiperidides[30] or the reaction of methyl ketones with catalytic amounts of diphenyl diselenide and an excess of ammonium peroxydisulfate in methanol.[31] 2-Acyl-1,3-dioxanes **7c** and **7l** were prepared by transacetalization of **7b** and **7k**, respectively, with 1 mol equiv. of propane-1,3-diol in the presence of a catalytic amount of toluene-*p*-sulfonic acid, (PTSA). The products **7** were isolated by distillation or further purified by flash column chromatography on silica gel when necessary.

2,2-Dimethoxy-1-phenylethanone 7a.[31] 86% yield; bp 130–132 °C/40 mmHg (Found: C, 66.62; H, 6.87. $C_{10}H_{12}O_3$ requires C, 66.65; H, 6.71%); ν_{max}(film)/cm^{-1} 2998, 2837, 1705, 1508, 1463, 1285, 1127, 868; δ_H(400 MHz) 3.48 (6 H, s, 2 × OCH_3), 5.25 [1 H, s, CH(OMe)$_2$], 7.25–7.61 (3 H, m, ArH), 8.00–8.15 (2 H, m, ArH); δ_C(100 MHz) 193.43 (*C*O), 133.73, 129.51, 128.49 and 127.51 (arom. *C*) 103.08 [*C*H(OMe)$_2$], 54.51 (O*C*H$_3$).

2-Benzoyl-1,3-dioxane 7c. 68% yield; 128–131 °C/0.25 mmHg; R_f 0.58 (AcOEt–Hex = 1 : 1), *oil* (Found: C, 68.80; H, 6.18. $C_{11}H_{12}O_3$ requires C, 68.74; H, 6.29%); ν_{max}(film)/cm^{-1} 3056, 2924, 1703, 1596, 1457, 1288, 1114, 1015, 928, 695; δ_H(300 MHz) 1.45–1.53 (1 H, m, OCH$_2$CH_aH$_b$CH$_2$O), 2.27–2.32 (1 H, m, OCH$_2$CH$_a$$H_bCH_2$O), 3.94–4.03 (2 H, m, O*CH*$_2$), 4.28–4.33 (2 H, m, O*CH*$_2$), 5.50 [1 H, s, CHO$_2$(CH$_2$)$_3$], 7.43–7.48 (2 H, m, ArH), 7.54–7.59 (1 H, m, ArH), 8.10–8.13 (2 H, m, ArH); δ_C(75 MHz) 192.02 (*C*O), 134.23, 134.17, 130.30 and 128.83 (arom. *C*), 100.63 [*C*HO$_2$(CH$_2$)$_3$], 67.59 (O*C*H$_2$), 25.73 (*C*H$_2$).

2,2-Diisopropoxy-1-phenylethanone 7d. R_f 0.72 (AcOEt–Hex = 1 : 4); 72% yield, *oil* (Found: C, 71.23: H, 8.45. $C_{14}H_{20}O_3$ requires C, 71.16; H, 8.53%); ν_{max}(film)/cm^{-1} 3031, 2887, 1706, 1599, 1466, 1284, 1120, 947, 787; δ_H(400 MHz) 1.14 (6 H, d, *J* 6.12, 2 × CH_3), 1.27 (6 H, d, *J* 6.2, 2 × CH_3), 3.90–3.99 (2 H, m, 2 × OC*H*Me$_2$), 5.19 [1 H, s, CH(OPr^i)$_2$], 7.42–7.57 (3 H, m, ArH), 8.20–8.22 (2 H, m, ArH); δ_C(100 MHz) 195.09 (CO), 133.50, 133.21, 130.28 and 128.13 (arom. *C*), 101.96 [*C*H(OPr^i)$_2$], 70.40 (O*C*HMe$_2$), 22.97 (*C*H$_3$), 22.32 (*C*H$_3$).

1-(4-Chlorophenyl)-2,2-dimethoxyethanone 7e. 88% yield; bp 140–143 °C/10 mmHg; R_f 0.65 (AcOEt–Hex = 1 : 2), *oil* (Found: C, 55.98; H, 5.17; Cl, 16.62. $C_{10}H_{11}ClO_3$ requires C, 55.96; H, 5.17; Cl, 16.52%); ν_{max}(film)/cm^{-1} 3000, 2837, 1702, 1589, 1489, 1286, 1092, 870; δ_H(400 MHz) 3.48 (6 H, s, 2 × OCH_3), 5.12 [1 H, s, CH(OMe)$_2$], 7.43 (2 H, d, *J* 8.7, ArH), 8.08 (2 H, d, *J* 8.6, ArH); δ_C(100 MHz) 192.43 (*C*O), 140.15, 131.11 and 128.80 (arom. *C*), 104.04 [*C*H(OMe)$_2$], 54.88 (O*C*H$_3$).

1-(2-Chlorophenyl)-2,2-dimethoxyethanone 7f. 79% yield; bp 130–132 °C/10 mmHg; R_f 0.62 (AcOEt–Hex = 1 : 2), *oil* (Found: C, 56.02; H, 5.13; Cl, 16.45%. ν_{max}(film)/cm^{-1} 2944, 2838, 1713, 1591, 1436, 1288, 1069, 764; δ_H(400 MHz) 3.46 (6 H, s, 2 × OCH_3), 5.25 [1 H, s, CH(OMe)$_2$], 7.31–7.41 (3 H, m, ArH), 7.60–7.63 (1 H, m, ArH); δ_C(100 MHz) 190.60 (*C*O), 136.39, 132.19, 131.75, 130.41, 129.91 and 126.67 (arom. *C*), 103.05 [*C*H(OMe)$_2$], 56.66 (O*C*H$_3$).

2,2-Dimethoxy-1-(2-naphthyl)ethanone 7g.[31] 89% yield; R_f 0.65 (AcOEt–Hex = 1 : 2), *oil* (Found: C, 73.09; H, 6.04. $C_{14}H_{14}O_3$ requires C, 73.03; H, 6.13%); ν_{max}(film)/cm^{-1} 2999, 2836, 1695, 1466, 1294, 1069, 980, 817, 772; δ_H(400 MHz) 3.50 (6 H, s, 2 × OCH_3), 5.35 [1 H, s, CH(OMe)$_2$], 7.45–7.65 (2 H, m, ArH), 7.80–8.15 (4 H, m, ArH), 8.6–8.8 (1 H, m, ArH); δ_C(100 MHz) 193.46 (*C*O), 135.87, 132.45, 131.84, 131.05, 129.92, 128.77, 128.29, 127.44, 126.71 and 124.65 (arom. *C*), 103.34 [*C*H(OMe)$_2$], 54.55 (O*C*H$_3$).

1-(2-Furyl)-2,2-dimethoxyethanone 7h.[31] 69% yield; bp 120–122/12 mmHg; R_f 0.5 (AcOEt–Hex = 1 : 2), oil (Found: C, 56.43; H, 5.96. $C_8H_{10}O_4$ requires C, 56.47; H, 5.92%); ν_{max}(film)/cm^{-1} 3137, 2998, 2839, 1739, 1692, 1467, 1395, 1271, 1197, 1081, 1015, 769; δ_H(400 MHz) 3.48 (6 H, s, 2 × OCH_3), 5.10 [1 H, s, CH(OMe)$_2$], 6.57 (1 H, dd, *J* 1.5 and 3.5, furan *H*), 7.46 (1 H, d, *J* 3.41, furan *H*), 7.67 (1 H, d, *J* 1.09, furan *H*); δ_C(100 MHz) 182.31 (*C*O), 150.05, 147.60, 121.08 and 112.30 (furan *C*), 102.25 [*C*H(OMe)$_2$], 54.46 (O*C*H$_3$).

1,1-Dimethoxy-2-hexanone 7j.[31] 72% yield; bp 70–73 °C/10 mmHg); (Found: C, 59.87; H, 9.95. $C_8H_{16}O_3$ requires C, 59.97; H, 10.07%); ν_{max}(film)/cm^{-1} 2961, 1730, 1466, 1193, 1079, 998, 735; δ_H(400 MHz) 0.91 (3 H, t, *J* 7.5, CH_3), 1.11–1.85 (4 H, m, 2 × CH_2), 2.55 (2 H, t, *J* 7.5, CH_2CO), 3.45 (6 H, s, 2 × OCH_3), 4.45 [1 H, s, CH(OMe)$_2$]; δ_C(100 MHz) 205.82 (*C*O), 104.04 [*C*H(OMe)$_2$], 54.63 (O*C*H$_3$), 37.01 (*C*H$_2$CO), 24.98 and 22.25 (*C*H$_2$), 13.78 (*C*H$_3$).

1,1-Diethoxyoctan-2-one 7k. 78% yield; R_f 0.54 (AcOEt–Hex = 1 : 4), *oil* (Found: C, 66.53; H, 11.15. $C_{12}H_{24}O_3$ requires C, 66.63; H, 11.18%); ν_{max}(film)/cm^{-1} 2862, 1730, 1445, 1163, 1063; δ_H(400 MHz) 0.88 (3 H, t, *J* 7.02, CH_3), 1.25 (6 H, t, *J* 7.02, 2 × OCH$_2$CH_3), 1.28–1.37 (6 H, m, 3 × CH_2), 1.54–1.61 (2 H, m, CH_2), 2.58 (2 H, t, *J* 7.43, CH_2CO), 3.60 (2 H, m, O*CH*$_2$), 3.71 (2 H, m, O*CH*$_2$), 4.55 [1 H, s, CH(OMe)$_2$]; δ_C(100 MHz) 205.92 (*C*O), 102.14 [*C*H(OMe)$_2$], 62.71 (O*C*H$_2$), 36.24 (*C*H$_2$CO), 30.99, 28.28, 22.40 and 21.93 (*C*H$_2$), 14.58 and 13.45 (*C*H$_3$).

2-Octanoyl-1,3-dioxane 7l. 81% yield; R_f 0.58 (AcOEt–Hex = 1 : 2), *oil* (Found: C, 66.01; H, 10.15. $C_{11}H_{20}O_3$ requires C, 65.97; H, 10.07%); ν_{max}(film)/cm^{-1} 2959, 1737, 1467, 1377, 1150, 1115, 1021, 934; δ_H(400 MHz) 0.88 (3 H, t, *J* 7.0, CH_3), 1.28–1.33 (6 H, m, 3 × CH_2), 1.40–1.44 (1 H, m, OCH$_2$CH_a-H$_b$CH$_2$O), 1.54–1.61 (2 H, m, CH_2), 2.10–2.22 (1 H, m, OCH$_2$CH$_a$$H_bCH_2$O), 2.59 (2 H, t, *J* 7.42, CH_2CO), 3.14–3.88 (2 H, m, O*CH*$_2$), 4.19–4.13 (2 H, m, O*CH*$_2$), 4.77 [1 H, s, CHO$_2$-(CH$_2$)$_3$]; δ_C(100 MHz) 204.38 (*C*O), 100.88 [*C*HO$_2$(CH$_2$)$_3$], 67.45 (O*C*H$_2$), 37.65 (*C*H$_2$CO), 31.92, 29.16, 26.01, 23.10 and 22.86 (*C*H$_2$), 14.39 (*C*H$_3$).

1-Cyclohexyl-2,2-diethoxyethanone 7m. 84% yield; R_f 0.67 (AcOEt–Hex = 1 : 4), *oil* (Found: C, 67.28; H, 10.40. $C_{12}H_{22}O_3$ requires C, 67.26; H, 10.35%); ν_{max}(film)/cm^{-1} 2934, 1724, 1449, 1133, 1099, 1064; δ_H(400 MHz) 1.24 (6 H, t, *J* 7.12, 2 × CH_3), 1.31–1.37 (4 H, m, 2 × CH_2), 1.75–1.83 (6 H, m, 3 × CH_2), 2.82 (1 H, m, C*H*CO), 3.59 (2 H, m, O*CH*$_2$), 3.68 (2 H, m, O*CH*$_2$), 4.66 [1 H, s, CH(OMe)$_2$]; δ_C(100 MHz) 208.72 (*C*O), 102.10 [*C*HO(CH$_2$)$_3$], 63.10 (O*C*H$_2$), 45.33 (*C*HCO), 28.57, 25.84 and 25.62 (*C*H$_2$), 15.18 (*C*H$_3$).

Oxazaborolidine-catalyzed reduction of α-keto acetals 7

The asymmetric reduction of **7e** is representative. To a stirred solution of **1b** (0.2 M; 0.1 mmol, 0.5 cm^3) in dry THF was added neat DEANB **12** (1 mmol, 163 mg, 0.18 cm^3) in an atmosphere of nitrogen. To this was added slowly 1.1 cm^3 of a THF solution of **7d** (1 mmol, 0.215 g) over a period of 1 h using a syringe pump at 25 °C. The reaction mixture was stirred for 10 min at the same temperature and then quenched cautiously with methanol (0.5 cm^3). Solvent was evaporated off under reduced pressure to leave an oil, which was purified by flash-column chromatography on silica gel (230–400 mesh) using ethyl acetate–hexane (1 : 2) as eluent to give (*S*)-*chlorophenyl*-2,2-dimethoxyethanol **8e** (197 mg, 91%); R_f 0.43 (AcOEt–Hex = 1 : 2), *oil* (Found: C, 55.41; H, 6.10; Cl, 16.37. $C_{10}H_{13}ClO_3$ requires C, 55.44; H, 6.05; Cl, 16.36%); $[a]_D^{23}$ +11.14 (*c* 5.41, $CHCl_3$); ν_{max}(film)/cm^{-1} 3436, 2930, 1597, 1490, 1187, 1120, 1076, 1012, 972, 823; δ_H(400 MHz) 2.72 (1 H, br s, O*H*), 3.29 (3 H, s, OCH_3), 3.42 (3 H, s, OCH_3), 4.23 [1 H, d, *J* 6.46, CH(OMe)$_2$], 4.59 (1 H, d, *J* 6.44, C*H*OH), 7.31–7.37 (4 H, m, ArH); δ_C(100 MHz) 137.87, 133.63, 128.47 and 128.37 (arom. *C*), 107.54 [*C*H(OMe)$_2$], 73.32 (*C*HOH), 56.23 and 55.00 (O*C*H$_3$). HPLC analysis of the product **8e** with a Chiralcel OD column using hexane–propan-2-ol (9 : 1) as eluent showed a composition 99.9% *S*-isomer and 0.1% *R*-isomer (*i.e.*, 99.8% ee).

(*S*)-2,2-Dimethoxy-1-phenylethanol 8a.[11a] 93% yield; bp 132–134 °C/40 mmHg; R_f 0.37 (AcOEt–Hex = 1 : 2), oil (Found: C, 65.91; H, 7.75. $C_{10}H_{14}O_3$ requires C, 65.87; H, 7.83%); $[a]_D^{23}$

+14.03 (*c* 5.02, $CHCl_3$), which shows 95% ee by HPLC analysis with a Chiralcel OD using hexane–propan-2-ol (40:1) as eluent; ν_{max}(film)/cm^{-1} 3435, 2929, 1493, 1451, 1187, 1121, 1080, 971; δ_H(300 MHz) 2.64–2.65 (1 H, br s, O*H*), 3.28 (3 H, s, OCH_3), 3.48 (3 H, s, OCH_3), 4.30 [1 H, d, *J* 6.44, C*H*(OMe)$_2$], 4.62 (1 H, d, *J* 6.32, C*H*OH), 7.27–7.44 (5 H, m, ArH); δ_C(75 MHz) 140.01, 128.42, 127.81 and 127.62 (arom. *C*), 108.01 [*C*H(OMe)$_2$], 74.28 (*C*HOH), 58.16 and 57.60 (O*C*H$_3$).

(*S*)-2,2-Diethoxy-1-phenylethanol 8b.[14] 96% yield; bp 146–149 °C/40 mmHg; R_f 0.37 (AcOEt–Hex = 1:4), oil (Found: C, 73.02; H, 6.13. $C_{12}H_{18}O_3$ requires C, 73.01; H, 6.04%); $[\alpha]_D^{23}$ +19.22 (*c* 5.11, $CHCl_3$), which corresponds to an optical purity of 96% ee by HPLC analysis with a Chiralcel OD using hexane–propan-2-ol (40:1) as eluent; ν_{max}(film)/cm^{-1} 3447, 3056, 2921, 1452, 1116, 758, 697; δ_H(300 MHz) 1.02 (3 H, t, *J* 7.02, CH_2CH_3), 1.24 (3 H, t, *J* 7.02, CH_2CH_3), 2.90 (1 H, br s, O*H*), 3.22 (1 H, dq, *J* 7.01 and 4.68, $OCH_aH_bCH_3$), 3.55 (2 H, m, OCH_2CH_3), 3.79 (1 H, dq, *J* 7.02 and 4.82, $OCH_aH_bCH_3$), 4.37 [1 H, d, *J* 6.44, C*H*(OEt)$_2$], 4.58 (d, 1 H, d, *J* 6.43, C*H*OH), 7.24–7.44 (m, 5 H, m, ArH); δ_C(75 MHz) 139.96, 128.34, 128.03 and 127.48 (arom. *C*), 106.26 [*C*H(OMe)$_2$], 74.84 (*C*HOH), 64.67 and 63.70 (O*C*H$_2$), 15.35 and 15.11 (*C*H$_3$).

(*S*)-1-(1,3-Dioxan-2-yl)-1-phenylmethanol 8c.[14] 94% yield; mp 80–82 °C; R_f 0.42 (AcOEt–Hex = 1:1), white solid (Found: C, 68.02; H, 7.35. $C_{11}H_{14}O_3$ requires C, 68.02; H, 7.26%); $[\alpha]_D^{23}$ +3.13 (*c* 5.10, $CHCl_3$), which shows 93% ee by HPLC analysis with a Chiralcel OD using hexane–propan-2-ol (40:1) as eluent; ν_{max}(KBr)/cm^{-1} 3490, 2855, 1493, 1460, 1236, 1137, 1085, 971, 766; δ_H(300 MHz) 1.26–1.40 (1 H, m, $OCH_2CH_aH_b$-CH_2O), 2.01–2.25 (1 H, m, $OCH_2CH_aH_bCH_2O$), 2.80 (1 H, br s, O*H*), 3.66–3.87 (2 H, m, O*C*H$_2$), 4.07–4.24 (2 H, m, O*C*H$_2$) 4.61 [2 H, s, C*H*OH and C*H*O$_2$(CH$_2$)$_3$], 7.26–7.44 (5 H, m, ArH); δ_C(75 MHz) 140.00, 128.45, 128.21 and 127.40 (arom. *C*), 103.36 [*C*HO$_2$(CH$_2$)$_3$], 75.20 (*C*HOH), 67.13 (O*C*H$_2$), 25.79 ($OCH_2CH_2CH_2O$).

(*S*)-2,2-Diisopropoxy-1-phenylethanol 8d. 97% yield; R_f 0.53 (AcOEt–Hex = 1:4), *oil* (Found: C, 70.63; H, 9.18. $C_{14}H_{22}O_3$ requires C, 70.56; H, 9.30%); $[\alpha]_D^{23}$ +4.11 (*c* 5.02, $CHCl_3$), which corresponds to an optical purity of 33% ee by HPLC analysis with a Chiralcel OD using hexane–propan-2-ol (40:1) as eluent and the (*S*)-isomer on the basis of (*S*)-(+)-1-phenylethane-1,2-diol;[32] ν_{max}(film)/cm^{-1} 3558, 2932, 1466, 1432, 1320, 1381, 1125, 1044, 760, 699; δ_H(400 MHz) 0.74 (3 H, d, *J* 6.14, CH_3), 1.13 (3 H, d, *J* 6.15, CH_3), 1.16 (3 H, d, *J* 6.07, CH_3), 1.26 (3 H, d, *J* 6.16, CH_3), 2.81 (1 H, s, O*H*), 3.51 (1 H, heptet, *J* 6.1, C*H*Me$_2$), 3.92 (1 H, heptet, *J* 6.11, C*H*Me$_2$), 4.50 [2 H, m, C*H*OH and C*H*(OPr^i)$_2$], 7.25–7.35 (3 H, m, ArH), 7.41–7.44 (2 H, m, ArH); δ_C(100 MHz) 139.58, 127.97, 127.77 and 127.46 (arom. *C*), 102.82 [*C*H(OPr^i)$_2$], 75.59 (*C*HOH), 70.69 and 69.54 (O*C*HMe$_2$), 23.51, 22.96, 22.32 and 21.93 (*C*H$_3$).

(*S*)-1-(2-Chlorophenyl)-2,2-dimethoxyethanol 8f. 97% yield; R_f 0.35 (AcOEt–Hex = 1:2), *oil* (Found: C, 55.51; H, 5.98, Cl, 16.56. $C_{10}H_{13}ClO_3$ requires C, 55.44; H, 6.05, Cl, 16.36%); $[\alpha]_D^{23}$ +7.11 (*c* 5.41, $CHCl_3$), which corresponds to an optical purity of 30% ee by HPLC analysis with a Chiralcel OD using hexane–propan-2-ol (9:1) as eluent and the (*S*)-isomer on the basis of (*S*)-(+)-1-(2-chlorophenyl)ethane-1,2-diol;[33] ν_{max}(film)/cm^{-1} 3444, 2941, 1597, 1477, 1442, 1194, 1122, 1080, 979, 757; δ_H(400 MHz) 2.84 (1 H, d, *J* 3.95, O*H*), 3.39 (3 H, s, OCH_3), 3.40 (3 H, s, OCH_3), 4.47 [1 H, d, *J* 4.36, C*H*(OMe)$_2$], 5.20 (1 H, d, *J* 4.01, C*H*OH), 7.23–7.36 (3 H, m, ArH), 7.56–7.59 (1 H, m, ArH); δ_C(100 MHz) 137.03, 132.82, 129.31, 128.92, 128.58 and 126.92 (arom. *C*), 106.04 [*C*H(OMe)$_2$], 70.54 (*C*HOH), 55.87 and 55.59 (O*C*H$_3$).

(*S*)-2,2-Dimethoxy-1-(2-naphthyl)ethanol 8g.[14] 97% yield; R_f 0.32 (AcOEt–Hex = 1:2), thick oil (Found: C, 72.30; H, 6.98. $C_{14}H_{16}O_3$ requires C, 72.34; H, 6.94%); $[\alpha]_D^{23}$ +2.64 (*c* 5.11, $CHCl_3$), 99% ee by HPLC analysis with a Chiralcel OT using hexane–propan-2-ol (9:1) as eluent; ν_{max}(film)/cm^{-1} 3433, 2920, 1600, 1507, 1463, 1361, 1189, 1119, 1073, 972, 746; δ_H(300 MHz) 2.86 (1 H, br s, O*H*), 3.26 (3 H, s, OCH_3), 3.48 (3 H, s, OCH_3), 4.37 [1 H, d, *J* 6.4, C*H*(OMe)$_2$], 4.78 (1 H, d, *J* 6.3, CHOH), 7.46–7.55 (3 H, m, ArH), 7.81–7.89 (4 H, m, ArH); δ_C(75 MHz) 137.48, 133.71, 128.56, 128.34, 128.13, 126.63, 126.46, 126.37 and 125.49 (arom. C), 108.12 [*C*H(OMe)$_2$], 74.41 (*C*HOH), 56.31 and 55.16 (O*C*H$_3$).

(*S*)-1-(2-Furyl)-2,2-dimethoxyethanol 8h. 85% yield; R_f 0.27 (AcOEt–Hex = 1:2), *oil* (Found: C, 55.65; H, 6.92. $C_8H_{12}O_4$ requires C, 55.81; H, 7.02%); $[\alpha]_D^{23}$ +3.68 (*c* 4.80, $CHCl_3$), which corresponds to an optical purity of 71% ee by GLC analysis using a 20 m Chiraldex GTA column and the (*S*)-isomer on the basis of (*S*)-(+)-1-(2-furyl)ethane-1,2-diol;[34] ν_{max}(film)/cm^{-1} 3445, 2943, 1504, 1466, 1369, 1193, 1149, 1120, 1081, 976, 787, 761; δ_H(300 MHz) 2.72 (1 H, br s, O*H*), 3.34 (3 H, s, OCH_3), 3.48 (3 H, s, OCH_3), 4.57 [1 H, d, *J* 6.42, C*H*(OMe)$_2$], 4.66 [1 H, d, *J* 6.44, C*H*OH], 6.35–6.37 (2 H, m, furan *H*), 7.40–7.41 (1 H, m, furan *H*); δ_C(75 MHz) 153.23, 142.89, 110.77 and 108.58 (furan *C*), 105.64 [*C*H(OMe)$_2$], 68.27 (*C*HOH), 55.68 and 57.36 (O*C*H$_3$).

(*S*)-1,1-Dimethoxypropan-2-ol 8i.[12] 65% yield; bp 62–64 °C/40 mmHg; $[\alpha]_D^{23}$ −8.38 (*c* 3.11, MeOH), which shows 60% ee by GLC analysis of its (−)-menthyl carbonate using a 25 m Supelcowax™ 10 capillary column; ν_{max}(film)/cm^{-1} 3440, 2930, 1459, 1379, 1112, 975; δ_H(300 MHz) 1.19 (3 H, d, *J* 6.4, CH_3), 2.05 (1 H, br s, O*H*), 3.43 and 3.46 (each 3 H, s, OCH_3), 3.77 (1 H, quintet, *J* 6.3, C*H*OH), 4.08 [1 H, d, *J* 6.3, C*H*(OMe)$_2$]; δ_C(75 MHz) 107.93 [*C*H(OMe)$_2$], 67.25 (*C*HOH), 54.84 (O*C*H$_3$), 17.11 (*C*H$_3$).

(*S*)-1,1-Dimethoxyhexan-2-ol 8j.[11a] 73% yield; bp 73–75°/10 mmHg; $[\alpha]_D^{23}$ –20.51 (*c* 1.15, CH_2Cl_2), which corresponds to an optical purity of 42% ee by GLC analysis of the trifluoroacetate using a 20 m Chiraldex GTA column; ν_{max}(film)/cm^{-1} 3468, 2956, 1467, 1372, 1195, 1118, 1079, 975; δ_H(300 MHz) 0.91 (3 H, t, *J* 7.3, CH_3), 1.11–1.87 (4 H, m, 2 × CH_2), 2.04 (1 H, br s, O*H*), 2.54 (2 H, m, CH_2CH_2CHOH), 3.41 (6 H, s, OCH_3), 3.81 (1 H, m), 4.23 [1 H, d, *J* 6.3, C*H*(OMe)$_2$]; δ_C(75 MHz) 108.93 [*C*H(OMe)$_2$], 66.35 (*C*HOH), 53.45 (O*C*H$_3$), 29.15, 25.48 and 22.59 (*C*H$_2$), 15.38 (*C*H$_3$).

(*S*)-1,1-Diethoxyoctan-2-ol 8k. 76% yield; R_f 0.30 (AcOEt–Hex = 1:4), *oil* (Found: C, 66.05; H, 12.08. $C_{12}H_{26}O_3$ requires C, 66.01; H, 12.00%); $[\alpha]_D^{23}$ +18.71 (*c* 1.82, CH_2Cl_2), which shows 47% ee by GLC analysis of its trifluoroacetate using a 20 m Chiraldex GTA column and the (*S*)-isomer on the basis of (*S*)-(+)-octane-1,2-diol;[35] ν_{max}(film)/cm^{-1} 3455, 2916, 1467, 1368, 1190, 1109, 1074, 977; δ_H(400 MHz) 0.87 (3 H, t, *J* 6.5, CH_3), 1.23 (6 H, t, *J* 6.72, 2 × OCH_2CH_3), 1.25–1.42 (8 H, m, 4 × CH_2), 1.51–1.61 (2 H, m, CH_2), 2.07 (1 H, br s, OH), 3.52–3.59 (2 H, m, OCH_2CH_3), 3.63–3.73 (2 H, m, OCH_2CH_3), 3.77 (1 H, m, C*H*OH), 4.24 [1 H, d, *J* 5.8, C*H*(OEt)$_2$]; δ_C(100 MHz) 105.14 [*C*H(OMe)$_2$], 71.77 (*C*HOH), 63.36 and 63.27 (O*C*H$_2$), 29.35, 28.83, 25.48, 22.97 and 22.59 (*C*H$_2$), 15.38, 15.12 and 14.04 (*C*H$_3$).

(*S*)-(1,3-Dioxan-2-yl)heptan-1-ol 8l. 98% yield; R_f 0.38 (AcOEt–Hex = 1:2), *oil* (Found: C, 65.23; H, 10.89. $C_{11}H_{22}O_3$ requires C, 65.31; H, 10.96%); $[\alpha]_D^{23}$ −28.42 (*c* 1.83, CH_2Cl_2), which corresponds to an optical purity of 62% ee by GLC analysis of its (*R*)-MTPA ester using a 25 m Supelcowax™ 10 capillary column and to the (*S*)-isomer on the basis of (*R*)-(+)-octane-1,2-diol;[35] ν_{max}(film)/cm^{-1} 3400, 2957, 2951, 1467, 1378,

1242, 1148, 1018; δ_H(400 MHz) 0.86 (3 H, t, *J* 6.84, CH_3), 1.27–1.58 (11 H, m, 5 × $CH_2CH_2CH_2$ and $OCH_2CH_aH_bCH_2O$), 2.04–2.14 (1 H, m, $OCH_2CH_aH_bCH_2O$), 2.23 (1 H, br s, OH), 3.51 (1 H, m, CHOH), 3.77 (2 H, dt, *J* 11.47 and 2.44, OCH_2CH_2), 4.11–4.16 (2 H, m, OCH_2CH_2), 4.37 [1 H, d, *J* 4.50, $CHO_2(CH_2)_3$]; δ_C(100 MHz) 102.74 [$CHO_2(CH_2)_3$], 72.54 (*C*HOH), 66.81 and 66.77 (O*C*H_2), 31.72, 31.36, 29.27, 25.79, 25.31 and 22.55 (CH_2), 14.00 (*C*H_3).

(*S*)-1-Cyclohexyl-2,2-diethoxyethanol 8m. 93% yield; R_f 0.43 (AcOEt–Hex = 1 : 2.4), *oil* (Found: C, 66.54; H, 11.23. $C_{12}H_{24}O_3$ requires C, 66.63; H, 11.18%); $[\alpha]_D^{23}$ −10.98 (*c* 4.11, CH_2Cl_2), which shows 66% ee by GLC analysis of its (*R*)-MTPA ester using a 25 m Supelcowax™ 10 capillary column and probably the (*S*)-isomer on the basis of comparison of the order of elution of GLC analysis and the sign of the optical rotation with those of aliphatic analogues; ν_{max}(film)/cm^{-1} 3491, 2913, 2857, 1450, 1346, 1161, 1068, 995; δ_H(400 MHz) 1.16–1.28 (10 H, m, 2 × CH_3 and 2 × CH_2), 1.53–1.74 (7 H, m, 3 × CH_2 and CH_2CHCH_2), 2.16 (1 H, br s, O*H*), 3.35 (1 H, m, C*H*OH), 3.53–3.60 (2 H, m, OCH_2), 3.70 (1 H, dq, *J* 7.60 and 6.84, OCH_aH_b), 3.78 (1 H, dq, *J* 7.80 and 6.84, OCH_aH_b), 4.41 [1 H, d, *J* 6.35, C*H*$(OEt)_2$]; δ_C(100 MHz) 102.85 [*C*H$(OEt)_2$], 75.32 (*C*HOH), 63.19 and 62.95 (O*C*H_2), 39.15, 29.87, 26.92, 26.49, 26.47 and 26.19 (*C*H_2), 15.39 (*C*H_3).

Acknowledgements

This research was financially supported by the Hallym Academy of Sciences, Hallym University.

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