Convenient synthesis of optically active 1,2-diol monosulfonates and terminal epoxides *via* oxazaborolidine-catalyzed asymmetric borane reduction of α-sulfonyloxy ketones

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A very convenient asymmetric synthesis of 1,2-diol monosulfonates and terminal epoxides with high optical purity *via* oxazaborolidine-catalyzed asymmetric borane reduction of α-sulfonyloxy ketones using *N*-ethyl-*N*-isopropylaniline–borane complex as borane carrier has been developed.

Introduction

Optically active 1,2-diol monosulfonates have been widely used as precursors for the synthesis of chiral epoxides,[1] chiral ligands[2] and chiral solvating agents.[3] For the synthesis of these compounds, biological methods such as enzymatic esterification[4a,b] or hydrolysis[1,4c] of the racemic mixtures and selective monosulfonylation[2,3,5] of optically active 1,2-diols have been reported. One of the most convenient methods for obtaining the compounds may be asymmetric reduction of α-sulfonyloxy ketones. However, to the best of our knowledge, no report on this reduction has been published.

Also, non-racemic aromatic and aliphatic terminal epoxides are extremely useful chiral building blocks for the synthesis of a variety of pharmaceutical products[6] and can be used as key intermediates[7] for the synthesis of more complex chiral organic compounds. In recent years, many chemical and biological methods for the synthesis of epoxides, such as asymmetric epoxidation of olefins, resolution of racemic epoxides, and indirect chemical transformation, have been reported. However, the direct asymmetric epoxidation of terminal olefins such as styrene analogues catalyzed by salen and porphyrin ligands,[8] or chiral dioxiranes[9] has been only moderately successful, to give products of 50–70% ee,[10] although they provide high enantioselectivity for the epoxidation of conjugated *Z*-substituted olefins and non-conjugated *E*-olefins with >90% ee.[11] The resolution of racemic epoxides with biocatalytic hydrolysis,[12] and chemically hydrolytic resolution methods,[13] both suffer from the fact that the theoretical yield is limited to 50%. Among the indirect methods such as chemical transformation of chiral sulfonium ylides,[6f] halohydrins[6c,g,14] and 1,2-diols[15] to epoxides, the conversion of chiral halohydrins to the epoxides may be one of the most simple and convenient procedures for the synthesis of chiral terminal epoxides, since halohydrins with high optical purity can be easily obtained from asymmetric reduction of α-halo ketones.[16] Indeed, Corey *et al.* reported the preparation of optically active styrene oxide with high ee using CBS oxazaborolidine-catalyzed asymmetric borane reduction of 2-chloroacetophenone.[14] However, this procedure has two major problems for large-scale applications. First, the use of borane–tetrahydrofuran THF, borane–dimethyl sulfide (BMS) and catechol–borane commonly employed as borane carriers for the reduction is not free from certain disadvantages, such as low concentration, thermal decomposition, high volatility, flammability, unpleasant odor and high sensitivity to air and moisture of these borane reagents. Secondly, α-halo ketones suffer from severe drawbacks to commercial applications, such as causing irritation to skin and eyes and their instability to light. In contrast, it is known that the amine–borane complexes offer the advantages of being soluble in most common solvents at high concentration and they have lower sensitivity to air and moisture.[17] In fact, we[18] and others[17b] have reported efficient oxazaborolidine-catalyzed reductions of prochiral ketones using *N*-phenylamine–borane complexes as a reductant. On the other hand, α-sulfonyloxy ketones can be used as starting materials for large-scale applications more readily than α-halo ketones, because they are not only stable and non-irritant, but also the sulfonyloxy groups appear to be much better leaving groups than do halogens.[1–3] Therefore, in order to develop a practical method useful for the large-scale synthesis of optically active aromatic, aliphatic and heterocyclic 1,2-diol monosulfonates and terminal epoxides, we studied oxazaborolidine-catalyzed asymmetric reduction of α-sulfonyloxy ketones using *N*-phenylamine–borane complexes as borane carriers. Very recently, we reported briefly on an efficient synthesis of enantiopure 3-chlorostyrene oxide using this methodology.[19] We report here, the details, scope, and limitations of such a reduction.

Results and discussion

The α-sulfonyloxy ketone derivatives **8a**–**p** used as substrates were prepared by sulfonyloxylation of aryl (or alkyl) methyl ketones or their trimethyl enol ethers with {hydroxy[aryl(or methyl)sulfonyloxy]iodo}benzenes in 46–87% yield according to the literature procedure.[20]

In order to examine effects of oxazaborolidines and hydride sources on asymmetric induction, we first compared the asymmetric borane reduction of 1-phenyl-2-(*p*-tolylsulfonyloxy)-ethanone **8b** catalyzed by four structurally different chiral oxazaborolidines, such as a proline-based oxazaborolidine (Corey's CBS reagents, **1**[21]), an aminodiphenylethanol-based oxazaborolidine (Pfizer's reagent, **2**[22]), an aminoindanol-based oxazaborolidine (Sepracor's reagent, **3**[23]) and a valine-based oxazaborolidine (Itsuno's reagent, **4**[24]) using *N*-ethyl-*N*-isopropylaniline–borane complex **5** as the borane source. Thus, slow addition of **8b** over a period of 1 h to a solution of 1.0 equiv. of the amine–borane reagent **5** in the presence of 10 mol% of each oxazaborolidine in THF at 25 °C afforded 1-phenyl-2-(*p*-tolylsulfonyloxy)ethanol **9b** within 10 min in almost quantitative yield (Scheme 1). This was easily converted

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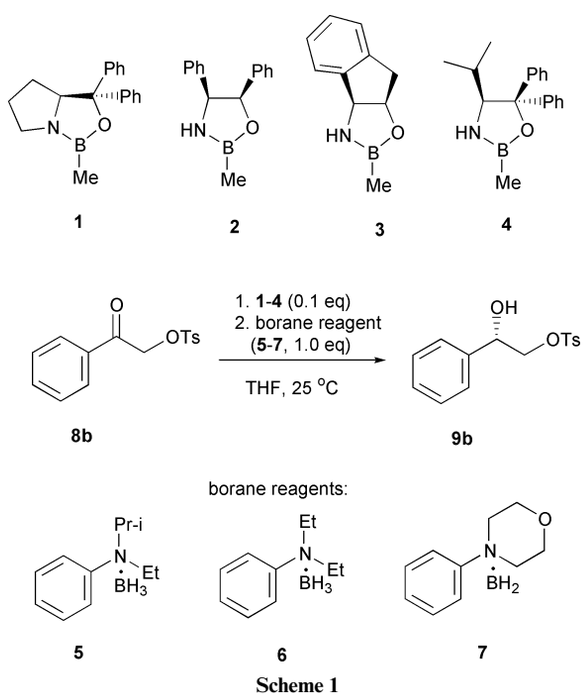
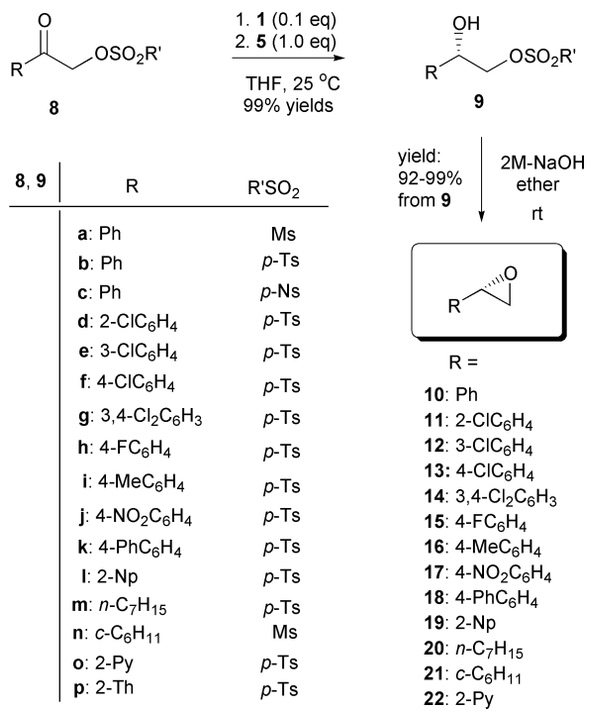
Table 1 Effect of oxazaborolidine and borane reagents on catalytic asymmetric borane reduction of 1-phenyl-2-(*p*-tolylsulfonyloxy)ethanone **8b**[a]

			9b			
Entry	Cat. (0.1 equiv.)	Borane reagent (1.0 equiv.)	Yield[b] (%)	$[a]_D^{22}$ (*c*, $CHCl_3$)	% ee	Config.
1	**1**	**5**	99	+50.4 (2.4)	99[c] (99)[d]	*S*[d]
2	**2**	**5**	98	[e]	77[c]	*S*[d]
3	**3**	**5**	96	[e]	78[c]	*S*[d]
4	**4**	**5**	96	[e]	94[c]	*S*[d]
5	**1**	**6**	94	[e]	95[c]	*S*[d]
6	**1**	**7**	93	[e]	90[c]	

[a] **[8b]** : [borane reagent] : [catalyst] = 1 : 1 : 0.1. **[7]** = 0.5 M. The reaction was carried out in THF at 25 °C. The reaction was complete within 10 min to give the product alcohol **9b**. [b] Isolated and purified yields. [c] Determined by HPLC analysis of phenyloxirane obtained from **9b** by treatment with 2 M NaOH using a Daicel Chiralcel OD; hexane–^{i}PrOH 99.8 : 0.2. [d] Based on literature value: ref. 14. [e] Not measured.



Scheme 1



8, 9	R	$R'SO_2$
	a: Ph	Ms
	b: Ph	*p*-Ts
	c: Ph	*p*-Ns
	d: 2-ClC_6H_4	*p*-Ts
	e: 3-ClC_6H_4	*p*-Ts
	f: 4-ClC_6H_4	*p*-Ts
	g: 3,4-$Cl_2C_6H_3$	*p*-Ts
	h: 4-FC_6H_4	*p*-Ts
	i: 4-MeC_6H_4	*p*-Ts
	j: 4-$NO_2C_6H_4$	*p*-Ts
	k: 4-PhC_6H_4	*p*-Ts
	l: 2-Np	*p*-Ts
	m: *n*-C_7H_{15}	*p*-Ts
	n: *c*-C_6H_{11}	Ms
	o: 2-Py	*p*-Ts
	p: 2-Th	*p*-Ts

Scheme 2

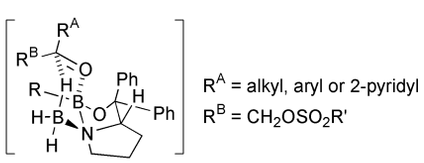
to phenyloxirane **10** by treatment with 2 M NaOH in diethyl ether at room temperature in almost quantitative yield. The ee of the epoxide **10** was determined by HPLC analysis using a Chiralcel OD (eluent: hexane–^{i}PrOH = 99.8 : 0.2). Among the catalysts examined, Corey's CBS reagent **1** provided the best enantioselectivity, approaching 100% ee (Table 1, entries 1–4). The same reduction of **8b** with other *N*-phenylamine–borane reagents such as *N*,*N*-diethylaniline–borane complex **6** and *N*-phenylmorpholine–borane complex **7** provided somewhat low enantioselectivity (entries 5,6).

Subsequently, the influence of different sulfonyl groups on the selectivity in the same reduction of 1-phenyl-2-sulfonyloxyethanones having mesyl and *p*-nitrobenzenesulfonyl (*p*-nosyl) groups was examined. As shown in Table 2, no differences in selectivity among mesyl, *p*-tosyl and *p*-nosyl groups were observed (entries 1–3). Next, we examined generality and limitations of such reactions by carrying out the same asymmetric reduction for other aromatic, aliphatic and heterocyclic α-sulfonyloxy ketone derivatives (Scheme 2). All the sulfonyloxy ketones **8** examined were reduced to the corresponding 1,2-diol monosulfonates **9** in almost quantitative yield. Also, all the product alcohols obtained except **9p** were easily converted into the corresponding terminal epoxides **10**–**22** by treatment with 2 M NaOH in high yield with no racemization. In the case of **9p**, it was observed that polymerization occurred during product isolation by silica gel column chromatography. With respect to enantioselectivity, the reduction of aromatic analogues **8g**–**l** bearing 3,4-dichlorophenyl, 4-fluorophenyl, 4-tolyl, 4-nitrophenyl, 4-biphenylyl and 2-naphthyl groups afforded the epoxides **14**–**19** with very high enantioselectivites (94–99% ee) (entries 7–12). Interestingly, the reduction of 1-(2-chlorophenyl)-2-(*p*-tosyloxy)ethanone **8d** provided 80% ee in contrast to 99% ee for 1-(3-chlorophenyl)-2-(*p*-tosyloxy)-ethanone **8e** and 1-(4-chlorophenyl)-2-(*p*-tosyloxy)ethanone **8f** (entries 4–6). These results indicate that the asymmetric induction was sensitive to steric effects of the substituent proximal to the carbonyl group. This is a common phenomenon in oxazaborolidine-catalyzed reductions.[18,25] For aliphatic analogues **8m**,**n**, the asymmetric reduction of the sulfonyloxy ketones **8n** having a branched alkyl group such as cyclohexyl provided high enantioselectivity, whereas **8m** containing an unbranched alkyl group afforded low enantioselectivity (entries 13,14). The reduction of heterocyclic analogues **9o**,**p** bearing 2-pyridyl and 2-thienyl groups afforded moderate to low enantioselectivities (entries 15,16). All the product epoxides **10**–**22** obtained are consistently enriched in the *S*-enantiomer. The stereochemical course of the asymmetric reduction showed that the α-sulfonyloxy ketones were attacked by hydride on their *Re* faces in the transition states **23**.[18,25]

Table 2 Asymmetric reduction of α-sulfonyloxy ketones **8** in the presence of 0.1 equiv. of **1** with 1.0 equiv. of **5** in THF at 25 °C[a]

	1,2-Diol monosulfonates **9**			Chiral epoxides **10**–**22**				
Entry	Cpd	Yield[b]	$[a]_D^{22}$ (*c*, solvent)	Cpd	Yield[c]	$[a]_D^{22}$ (*c*, solvent)	% ee	Config.
1	**9a**		+53.8 (1.12, $CHCl_3$)	**10**	96	−44.5 (1.15, C_6H_6)	99[d] (99)[e]	*S*[e]
2	**9b**		+50.4 (2.41, $CHCl_3$)	**10**	96	Not measured	99[d]	*S*[e]
3	**9c**		+40.0 (1.00, MeCOMe)	**10**	96	Not measured	99[d]	*S*[e]
4	**9d**		+43.8 (1.08, $CHCl_3$)	**11**	94	+43.7 (1.42, $CHCl_3$)	80[f] (100)[g]	*S*[g]
5	**9e**		+39.6 (1.32, $CHCl_3$)	**12**	95	+11.15 (1.56, $CHCl_3$)	99[h] (100)[i]	*S*[i]
6	**9f**		+45.5 (1.00, $CHCl_3$)	**13**	96	+25.5 (1.00, $CHCl_3$)	99[j] (100)[k]	*S*[k]
7	**9g**		+39.6 (1.04, $CHCl_3$)	**14**	94	+15.3 (1.18, $CHCl_3$)	94[j] (100)[l]	*S*[l]
8	**9h**		+47.0 (1.05, $CHCl_3$)	**15**	96	+19.2 (1.20, $CHCl_3$)	98[f] (100)[m]	*S*[m]
9	**9i**		+56.7 (1.01, $CHCl_3$)	**16**	95	−25.9 (1.02, C_6H_6)	97[d] (99)[n]	*S*[n]
10	**9j**		+30.3 (1.02, MeCOMe)	**17**	96	+37.8 (1.34, $CHCl_3$)	97[o] (100)[p]	*S*[p]
11	**9k**		+50.0 (1.01, $CHCl_3$)	**18**	96	+30.0 (1.06, $CHCl_3$)	98[q]	*S*[r]
12	**9l**		+57.2 (1.00, $CHCl_3$)	**19**	97	+11.4 (1.11, $CHCl_3$)	(100)[s]	*S*[s]
13	**9m**		+3.5 (1.20, $CHCl_3$)	**20**	99	−3.7 (1.14, $CHCl_3$)	(40)[t]	*S*[t]
14	**9n**		+12.10 (1.02, $CHCl_3$)	**21**	96	+2.1 (0.88, $CHCl_3$)	96[h]	*S*[u]
15	**9o**		+4.5 (1.01, $CHCl_3$)	**22**	92	+2.9 (0.41, $CHCl_3$)	21[h]	*S*[v]
16	**9p**		+34.2 (1.05, $CHCl_3$)[w]					

[a] [**8**] = 0.5 M. The reaction was complete within 10 min to give the α-sulfonyloxy alcohols **9**. [b] Isolated yields. [c] Isolated and purified yield of the corresponding epoxides obtained by treatment of **9** with 2 M NaOH. [d] Determined by HPLC analysis using a Daicel Chiralcel OD; hexane–^{i}PrOH 99.8 : 0.2. [e] Based on $[a]_D^{23}$ −44.9 (*c* 1.02, C_6H_6), *S*; ref. 14. [f] Determined by capillary GLC analysis using a β-DEX 120 chiral column (Supelco). [g] Based on $[a]_D^{25}$ +32.2 (*c* 1.19, $CHCl_3$), >99%, *S*; ref. 27. [h] Determined by capillary GLC analysis using a G-TA chiral column (Astec). [i] Based on $[a]_D^{20}$ −11.1 (*c* 1.23, $CHCl_3$), >99% ee, *R*, ref. 28. [j] HPLC analysis using a Daicel Chiralpak OT; hexane–^{i}PrOH 99 : 1. [k] Based on $[a]_D^{20}$ −24.0 (*c* 1.08, $CHCl_3$), >97% ee, *R*; ref. 12*b*. [l] Based on $[a]_D$ −11 (*c* 1.00, $CHCl_3$), 96% ee, *R*; ref. 6*f*. [m] Based on $[a]_D^{20}$ −17 (*c* 1.03, $CHCl_3$), 97% ee, *R*; ref. 12*b*. [n] Based on $[a]_D^{20}$ +25.5 (*c* 1.3, C_6H_6), 98% ee, *R*; ref. 29. [o] Determined by HPLC analysis using a Daicel Chiralpak OT; hexane–^{i}PrOH 40 : 1. [p] Based on $[a]_D^{25}$ +36.0 (*c* 1.25, $CHCl_3$), 95% ee, *S*; ref. 6*h*. [q] Determined by HPLC analysis using a Daicel Chiralcel OD; hexane–^{i}PrOH 99 : 1. [r] Based on the sign of optical-rotation value, (*R*)-(−); ref. 7*c*. [s] Based on $[a]_D$ −9 (*c* 1.2, $CHCl_3$), 92% ee, *R*; ref. 6*f*. [t] Based on $[a]_D^{24}$ −8.9 (*c* 1.14, $CHCl_3$), 97% ee, *S*; ref. 30; [u] Determined by optical-rotation value of **21** obtained from (*S*)-cyclohexylethane-1,2-diol, ref. 31. [v] Based on $[a]_D^{19}$ +14.0 (*c* 0.56, $CHCl_3$), 99% ee, *S*; ref. 32; [w] 80% ee by comparison with optical-rotation value of **9p** obtained from authentic (*R*)-(2-thienyl)ethane-1,2-diol.



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Conclusions

We have established a simple and practical procedure for the synthesis of 1,2-diol monosulfonates and the corresponding terminal epoxides with very high optical purity in high yields *via* oxazaborolidine-catalyzed borane reduction of α-sulfonyloxy ketones using *N*-ethyl-*N*-isopropylaniline–borane complex as borane carrier. The reduction provided almost enantiopure epoxides in aromatic analogues. This procedure can be used as an excellent alternative to synthesis of such compounds. 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. 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 400 MHz for ^{1}H and 100 MHz for ^{13}C using Me_4Si as the internal standard in $CDCl_3$ or CD_3COCD_3. *J*-values are given in Hz. Optical rotations were measured with a high-resolution digital polarimeter. $[a]_D$-Values are given in units of 10^{-1} deg cm^2 g^{-1}. Mps were measured by the capillary method and are uncorrected. Enantiomeric excesses (% ee) of the product epoxides were determined with a GLC apparatus equipped with a 25 m β-Dex 120 (Supelco) or G-TA (Astec) chiral capillary column or with an HPLC apparatus fitted with a 25 cm Chiralcel OD or Chiralpak OT column (Daicel).

Materials

Most of 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 nitrogen atmosphere. The CBS reagent **1**, *N*,*N*-diethylaniline–borane complex, *N*-ethyl-*N*-isopropylaniline–borane complex, *N*-methylmorpholine–borane complex, (*1S*,*2R*)-*cis*-1-aminoindan-2-ol and (*1R*,*2S*)-2-amino-1,2-diphenylethanol were purchased from Aldrich Chemical Company. The chiral oxazaborolidines **2**–**4** were prepared by treatment of the corresponding amino alcohols with BH_3–THF according to the known procedure.[22–24]

Preparation of α-sulfonyloxyaryl ketone derivatives 8

According to the literature,[20] compounds **8** were prepared by refluxing aryl methyl ketones or their trimethylsilyl enol ethers with {hydroxy[aryl(or methyl)sulfonyloxy]iodo}benzenes in acetonitrile, 1,4-dioxane, toluene or diethylene glycol bis(methyl ether) (diglyme).

2-(Methylsulfonyloxy)-1-phenylethanone 8a. 84% Yield; mp 78–80 °C (lit.,[20b] 76–77 °C); ν_{max} (KBr/cm^{-1}) 1709, 1358, 1180; δ_H (400 MHz; $CDCl_3$) 3.29 (3 H, s, CH_3), 5.52 (2 H, s, CH_2O), 7.50–7.54 (2 H, m), 7.66 (1 H, m) and 7.89–7.91 (2 H, m) (ArH); δ_C (100 MHz; $CDCl_3$) 39.66 (CH_3SO_2), 70.62 (CH_2O), 128.19, 129.50, 133.84 and 134.89 (Ar-C), 191.51 (CO).

1-Phenyl-2-(*p*-tolylsulfonyloxy)ethanone 8b. 87% Yield; mp 91–92 °C (lit.,[20a] 91–92 °C); ν_{max} (KBr/cm^{-1}) 1715, 1377, 1194; δ_H (400 MHz; $CDCl_3$) 2.45 (3 H, s, C*H*$_3$), 5.28 (2 H, s, C*H*$_2$O), 7.35 (2 H, d, *J* 8.19), 7.46–7.49 (2 H, m), 7.59–7.63 (1 H, m) and 7.83–7.87 (4 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.70 (*C*H_3), 69.95 (*C*H_2O), 128.00, 128.16, 128.93, 129.92, 132.62, 133.76, 134.22 and 145.32 (Ar-*C*), 190.32 (*C*O).

2-(*p*-Nitrophenylsulfonyloxy)-1-phenylethanone 8c. 80% Yield; mp 128–130 °C (lit.,[20c] 129–131 °C); ν_{max} (KBr/cm^{-1}) 1711, 1527, 1377, 1349, 1207; δ_H (400 MHz; $CDCl_3$) 5.49 (2 H, s, CH_2O), 7.48–7.52 (2 H, m), 7.64 (1 H, m), 7.82–7.84 (2 H, m), 8.18–8.21 (2 H, m) and 8.39–8.42 (2 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 70.89 (*C*H$_2$O), 124.36, 127.85, 129.12, 129.47, 133.29, 134.60, 141.94 and 150.86 (Ar-*C*), 189.72 (*C*O).

1-(2-Chlorophenyl)-2-(*p*-tolylsulfonyloxy)ethanone 8d. 78% Yield; mp 65–67 °C (Found: C, 55.43; H, 4.02; S, 9.79. $C_{15}H_{13}ClO_4S$ requires C, 55.47; H, 4.03; S, 9.87%); ν_{max} (KBr/cm^{-1}) 1714, 1691, 1588, 1431, 1365, 1178, 1041; δ_H (400 MHz; $CDCl_3$) 2.45 (3 H, s, CH_3), 5.17 (2 H, s, CH_2O), 7.33–7.37 (3 H, m), 7.40–7.48 (2 H, m) and 7.52 (1 H, dd, *J* 1.63 and 7.71), 7.81 (1 H, d, *J* 8.34) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.70 (*C*H$_3$), 71.75 (*C*H$_2$O), 127.19, 128.13, 129.92, 130.26, 130.59, 131.64, 132.62, 133.15, 135.26 and 145.32 (Ar-*C*), 193.61 (*C*O).

1-(3-Chlorophenyl)-2-(*p*-tolylsulfonyloxy)ethanone 8e. 76% Yield; mp 54–56 °C (Found: C, 55.42; H, 4.01; S, 9.83. $C_{15}H_{13}ClO_4S$ requires C, 55.47; H, 4.03; S, 9.87%); ν_{max} (KBr/cm^{-1}) 1718, 1362, 1191, 987, 771; δ_H (400 MHz; $CDCl_3$) 2.46 (3 H, s, CH_3), 5.22 (2 H, s, CH_2O), 7.35 (2 H, d, *J* 8.19), 7.42 (1 H, m), 7.57–7.59 (1 H, m), 7.71–7.73 (1 H, m), 7.79 (1 H, m) and 7.83–7.85 (2 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.72 (*C*H$_3$), 69.85 (*C*H$_2$O), 126.15, 128.17, 129.98, 130.26, 132.48, 134.12, 135.25, 135.34 and 145.49 (Ar-*C*), 189.50 (*C*O).

1-(4-Chlorophenyl)-2-(*p*-tolylsulfonyloxy)ethanone 8f. 84% Yield; mp 123–124 °C (Found: C, 55.48; H, 4.06; S, 9.72. $C_{15}H_{13}ClO_4S$ requires C, 55.47; H, 4.03; S, 9.87%); ν_{max} (KBr/cm^{-1}) 1702, 1593, 1375, 1190, 1058; δ_H (400 MHz; $CDCl_3$) 2.45 (3 H, s, CH_3), 5.21 (2 H, s, CH_2O), 7.35 (2 H, d, *J* 8.19), 7.43–7.47 (2 H, m), 7.78–7.81 (2 H, m) and 7.84 (2 H, d, *J* 8.28) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.71 (*C*H$_3$), 69.82 (*C*H$_2$O), 128.16, 129.30, 129.51, 129.96, 132.10, 132.51, 140.79 and 145.44 (Ar-*C*), 189.48 (*C*O).

1-(3,4-Dichlorophenyl)-2-(*p*-tolylsulfonyloxy)ethanone 8g. 80% Yield; mp 130–132 °C (Found: C, 50.17; H, 3.27; S, 8.89. $C_{15}H_{12}Cl_2O_4S$ requires C, 50.15; H, 3.37; S, 8.93%); ν_{max} (KBr/cm^{-1}) 1709, 1399, 1348, 1189; δ_H (400 MHz; $CDCl_3$) 2.46 (3 H, s, CH_3), 5.18 (2 H, s, CH_2O), 7.36 (2 H, d, *J* 8.17), 7.56 (1 H, d, *J* 8.42), 7.68 (1 H, dd, *J* 2.06 and 8.33), 7.83 (2 H, d, *J* 8.35) and 7.90 (1 H, d, *J* 2.01) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.73 (*C*H$_3$), 69.77 (*C*H$_2$O), 127.12, 128.15, 130.00, 130.08, 131.05, 132.70, 133.26, 133.78, 138.92 and 145.60 (Ar-*C*), 188.85 (*C*O).

1-(4-Fluorophenyl)-2-(*p*-tolylsulfonyloxy)ethanone 8h. 82% Yield; mp 108–110 °C (Found: C, 58.28; H, 4.23; S, 10.25. $C_{15}H_{13}FO_4S$ requires C, 58.43; H, 4.25; S, 10.40%); ν_{max} (KBr/cm^{-1}) 1701, 1596, 1377, 1233, 1139; δ_H (400 MHz; $CDCl_3$) 2.45 (3 H, s, CH_3), 5.21 (2 H, s, CH_2O), 7.06–7.18 (2 H, m), 7.35 (2 H, d, *J* 8.13) and 7.84–7.92 (4 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.71 (*C*H$_3$), 69.81 (*C*H$_2$O), 116.31, 128.16, 129.95, 130.25, 130.94, 132.55, 145.42, 165.00 and 167.55 (Ar-*C*), 189.00 (*C*O).

1-(*p*-Tolyl)-2-(*p*-tolylsulfonyloxy)ethanone 8i. 87% Yield; mp 92–94 °C (lit.,[26] 82–83 °C); ν_{max} (KBr/cm^{-1}) 1701, 1609, 1348, 1171, 1055; δ_H (400 MHz; $CDCl_3$) 2.41 (3 H, s, CH_3), 2.45 (3 H, s, Me), 5.24 (2 H, s, CH_2O), 7.25–7.28 (2 H, m), 7.35 (2 H, d, *J* 8.22), 7.74 (2 H, d, *J* 8.20) and 7.86 (2 H, d, *J* 8.26) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.67 (*C*H$_3$), 21.76 (*C*H$_3$), 69.86 (*C*H$_2$O), 128.07, 128.13, 129.57, 129.87, 131.25, 132.64, 145.23 and 145.28 (Ar-*C*), 189.81 (*C*O).

1-(4-Nitrophenyl)-2-(*p*-tolylsulfonyloxy)ethanone 8j. 86% Yield; mp 134–136 °C (lit.,[26] 130–131 °C); ν_{max} (KBr/cm^{-1}) 1712, 1527, 1378, 1348, 1191; δ_H (400 MHz; $CDCl_3$) 2.46 (3 H, s, CH_3), 5.25 (2 H, s, CH_2O), 7.37 (2 H, d, *J* 8.17), 7.83 (2 H, d, *J* 8.26), 8.01–8.05 (2 H, m) and 8.30–8.33 (2 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.73 (*C*H$_3$), 69.99 (*C*H$_2$O), 124.08, 128.16, 129.36, 130.06, 132.27, 138.23, 145.72 and 150.81 (Ar-*C*), 189.79 (*C*O).

1-(4-Phenylphenyl)-2-(*p*-tolylsulfonyloxy)ethanone 8k. 85% Yield; mp 137–138 °C (Found: C, 68.75; H, 4.92; S, 8.79. $C_{21}H_{18}O_4S$ requires C, 68.83; H, 4.95; S, 8.75%); ν_{max} (KBr/cm^{-1}) 1703, 1374, 1192; δ_H (400 MHz; $CDCl_3$) 2.45 (2 H, s, CH_3), 5.29 (2 H, s, CH_2O), 7.35 (2 H, d, *J* 8.18), 7.40–7.50 (3 H, m), 7.61 (2 H, d, *J* 7.35), 7.69 (2 H, d, *J* 8.34), 7.87 (2 H, d, *J* 8.21) and 7.92 (2 H, d, *J* 8.34) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.71 (*C*H$_3$), 69.98 (*C*H$_2$O), 127.28, 127.50, 128.18, 128.56, 128.65, 129.05, 129.93, 132.43, 132.66, 139.46, 145.32 and 146.91 (Ar-*C*), 189.94 (*C*O).

1-(2-Naphthyl)-2-(*p*-tolylsulfonyloxy)ethanone 8l. 83% Yield; mp 118–119 °C (Found: C, 67.15; H, 4.81; S, 9.45. $C_{19}H_{16}O_4S$ requires C, 67.04; H, 4.74; S, 9.42%); ν_{max} (KBr/cm^{-1}) 1698, 1343, 1186, 1046; δ_H (400 MHz; $CDCl_3$) 2.44 (3 H, s, CH_3), 5.40 (2 H, s, CH_2O), 7.34 (2 H, d, *J* 8.16), 7.56–7.66 (2 H, m), 7.87–7.90 (5 H, m), 7.95 (1 H, d, *J* 8.03) and 8.35 (1 H, s) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.70 (*C*H$_3$), 70.02 (*C*H$_2$O), 87.12, 123.28, 127.19, 127.89, 128.19, 128.92, 129.15, 129.64, 129.92, 130.00, 131.11, 132.29, 132.69, 135.97 and 145.31 (Ar-*C*), 190.28 (*C*O).

1-(Methylsulfonyloxy)nonan-2-one 8m. 46% Yield; mp 49–51 °C (Found: C, 50.92; H, 8.51; S, 13.47. $C_{10}H_{20}O_4S$ requires C, 50.82; H, 8.53; S, 13.57%); ν_{max} (KBr/cm^{-1}) 1730, 1301, 1167; δ_H (400 MHz; $CDCl_3$) 0.88 (3 H, t, *J* 7.06, CH_3CH$_2$), 1.28–1.32 (8 H, m, 4 × CH_2), 1.58–1.64 (2 H, m, CH_2CH$_2$CO), 2.46 (2 H, t, *J* 7.35, CH_2CO), 3.20 (3 H, s, CH_3SO$_2$), 4.79 (2 H, s, CH_2O); δ_C (100 MHz; $CDCl_3$) 14.05 (*C*H$_3$), 22.57, 23.13, 28.97, 29.01 and 31.59 (*C*H$_2$), 38.61 (*C*H$_2$CO), 38.84 (*C*H$_3$SO$_2$), 71.64 (*C*H$_2$O), 203.07 (*C*O).

1-Cyclohexyl-2-(*p*-tolylsulfonyloxy)ethanone 8n. 68% Yield; mp 53–55 °C (Found: C, 60.86; H, 6.92; S, 10.92. $C_{15}H_{20}O_4S$ requires C, 60.79; H, 6.80; S, 10.82%); ν_{max} (KBr/cm^{-1}) 1721, 1367, 1184; δ_H (400 MHz; $CDCl_3$) 1.20–1.32 (6 H, m, 3 × CH_2), 1.75–1.78 (5 H, m, 2 × CH_2 + CH), 2.46 (3 H, s, CH_3), 4.60 (2 H, s, CH_2O), 7.36 (2 H, d, *J* 8.20) and 7.82 (2 H, d, *J* 8.26) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.70 (*C*H$_3$), 25.38, 25.61 and 27.86 (*C*H$_2$), 46.80 (*C*H), 70.55 (*C*H$_2$O), 128.09, 128.92, 129.96, 132.53 and 145.36 (Ar-*C*), 205.30 (*C*O).

1-(2-Pyridyl)-2-(*p*-tolylsulfonyloxy)ethanone 8o. 72% Yield; mp 64–66 °C (lit.,[20e] 65–68 °C) (Found: C, 57.68; H, 4.43; N, 4.79; S, 10.96. $C_{14}H_{13}NO_4S$ requires C, 57.72; H, 4.50; N, 4.81; S, 11.01%); ν_{max} (KBr/cm^{-1}) 1722, 1365, 1190; δ_H (400 MHz; $CDCl_3$) 2.45 (3 H, s, CH_3), 5.63 (2 H, s, CH_2O), 7.36 (2 H, d, *J* 8.20), 7.50–7.53 (1 H, m), 7.84–7.91 (3 H, m), 8.02 (1 H, d, *J* 7.95) and 8.61 (1 H, d, *J* 4.44) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.69 (*C*H$_3$), 70.93 (*C*H$_2$O), 121.99, 128.15, 128.20, 129.86, 133.09, 137.21, 145.01, 149.11 and 151.13 (Ar-*C*), 191.11 (*C*O).

1-(2-Thienyl)-2-(*p*-tolylsulfonyloxy)ethanone 8p. 78% Yield; mp 93–95 °C (lit.,[20e] 94–96 °C) (Found: C, 52.78; H, 4.07; S, 21.81. $C_{13}H_{12}O_4S_2$ requires C, 52.68; H, 4.08; S, 21.64%); ν_{max} (KBr/cm^{-1}) 1683, 1416, 1384, 1187, 1043; δ_H (400 MHz; $CDCl_3$) 2.45 (3 H, s, CH_3), 5.09 (2 H, s, CH_2O), 7.16 (1 H, d, *J* 4.21), 7.35 (2 H, d, *J* 8.10), 7.73 (1 H, d, *J* 4.76), 7.80 (1 H, d, *J* 3.73) and 7.85 (2 H, d, *J* 8.21) (Ar-*H* and thienyl-*H*); δ_C (100 MHz; $CDCl_3$) 21.71 (*C*H$_3$), 69.90 (*C*H$_2$O), 128.20, 128.49, 129.97, 132.39, 133.16, 135.16, 140.03 and 145.46 (Ar-*C* and thienyl-*C*), 183.66 (*C*O).

General procedure for oxazaborolidine-catalyzed asymmetric borane reduction of α-sulfonyloxy ketones 8

To a solution of **1** (0.2 M; 1.0 cm³, 0.2 mmol) in THF was added a solution of *N*-ethyl-*N*-isopropylaniline–borane complex **5** (2.0 M; 1.0 cm³, 2.0 mmol) in THF. To this was added slowly 2 cm³ of a THF solution of **8** (2 mmol) over a period of 1 h using a syringe pump at 25 °C. After the addition, the reaction mixture was stirred for 10 min, quenched cautiously with methanol (0.5 cm³), and stirred for an additional 30 min. The solvent was evaporated off under reduced pressure. The crude products **9** obtained were further purified by flash column chromatography on silica gel (230–400 mesh), using hexane–ethyl acetate (1 : 1) as eluent, unless otherwise indicated.

(*S*)-(+)-2-(Methylsulfonyloxy)-1-phenylethanol 9a. 99% Yield; R_f 0.51; oil (Found: C, 49.98; H, 5.61; S, 14.62. $C_9H_{12}O_4S$ requires C, 49.99; H, 5.59; S, 14.83%); $[a]_D^{22}$ +53.8 (*c* 1.12, $CHCl_3$); ν_{max} (neat/cm^{-1}) 3495, 3110, 1352, 1172, 979; δ_H (400 MHz; $CDCl_3$) 2.92 (3 H, s, CH_3), 4.17–4.26 (2 H, m, CH_2O), 4.94 (1 H, m, C*H*OH), 7.25–7.36 (5 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 37.33 (CH_3SO_2), 71.72 (CH_2O), 74.04 (*C*HOH), 126.24, 128.48, 128.65 and 138.62 (Ar-*C*).

(*S*)-(+)-1-Phenyl-2-(*p*-tolylsulfonyloxy)ethanol 9b. 99% Yield; R_f 0.74; mp 71–72 °C (lit.,[3] 65–66 °C; lit.,[2] 73 °C) (Found: C, 61.63; H, 5.63; S, 10.95. $C_{15}H_{16}O_4S$ requires C, 61.62; H, 5.52; S, 10.97%); $[a]_D^{22}$ +50.4 (*c* 2.41, $CHCl_3$) {lit.,[21] $[a]_D^{21}$ +51.1 (*c* 1.00, $CHCl_3$); lit.,[22] $[a]_D^{23}$ +55.0 (*c* 2.4, $CHCl_3$)}; ν_{max} (neat/cm^{-1}) 3539, 1376, 1177, 961, 867, 757, 704; δ_H (400 MHz; $CDCl_3$) 2.45 (3 H, s, CH_3), 4.04 (1 H, dd, *J* 8.57 and 10.45, OC*H*^{a}H^b), 4.14 (1 H, dd, *J* 3.20 and 10.39, OCH^a*H*^{b}), 4.98 (1 H, ddd, *J* 8.58, 3.20 and 3.24, C*H*OH), 7.26–7.36 (7 H, m) and 7.76–7.78 (2 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.68 (*C*H$_3$), 71.97 (*C*H$_2$O), 74.34 (*C*HOH), 126.19, 127.97, 128.56, 128.69, 129.96, 132.63, 138.17 and 145.10 (Ar-*C*).

(*S*)-(+)-2-(*p*-Nitrophenylsulfonyloxy)-1-phenylethanol 9c. 99% Yield; R_f 0.64; mp 106–107 °C (Found: C, 52.04; H, 4.24; N, 4.41; S, 9.80. $C_{14}H_{13}NO_6S$ requires C, 52.01; H, 4.05; N, 4.33; S, 9.92%); $[a]_D^{22}$ +40.0 (*c* 1.00, acetone); ν_{max} (neat/cm^{-1}) 3561, 3520, 1547, 1382, 1182; δ_H (400 MHz, acetone-d$_6$) 4.37–4.47 (2 H, m, CH_2O), 5.14 (1 H, m, C*H*OH), 7.44–7.54 (5 H, m), 8.30 (2 H, d, *J* 2.0) and 8.63 (2 H, d, *J* 2.0) (Ar*H*); δ_C (100 MHz, acetone-d$_6$) 72.06 (*C*H$_2$O), 76.83 (*C*HOH), 125.84, 127.58, 129.09, 129.51, 130.70, 141.43 and 142.83 (Ar-*C*).

(*S*)-(+)-1-(2-Chlorophenyl)-2-(*p*-tolylsulfonyloxy)ethanol 9d. 99% Yield; R_f 0.63; oil (Found: C, 53.34; H, 4.66; S, 9.66. $C_{15}H_{15}ClO_4S$ requires C, 53.13; H, 4.63; S, 9.81%); $[a]_D^{22}$ +43.8 (*c* 1.08, $CHCl_3$); ν_{max} (neat/cm^{-1}) 3471, 1355, 1176, 971; δ_H (400 MHz; $CDCl_3$) 2.44 (3 H, s, CH_3), 2.78 (1 H, br s, O*H*), 3.98 (1 H, dd, *J* 8.33 and 10.55, OC*H*^{a}H^b), 4.27 (1 H, dd, *J* 2.65 and 10.58, OCH^a*H*^{b}), 5.36 (1 H, m), 7.22–7.35 (5 H, m), 7.56–7.59 (1 H, m) and 7.77–7.79 (2 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.65 (*C*H$_3$), 68.82 (*C*H$_2$O), 72.74 (*C*HOH), 127.24, 127.81, 127.98, 129.41, 129.47, 129.92, 131.79, 132.52, 135.61 and 145.09 (Ar-*C*).

(*S*)-(+)-1-(3-Chlorophenyl)-2-(*p*-tolylsulfonyloxy)ethanol 9e. 99% Yield; R_f 0.65; oil (Found: C, 53.34; H, 4.59; S, 9.67. $C_{15}H_{15}ClO_4S$ requires C, 53.13; H, 4.63; S, 9.81%); $[a]_D^{22}$ +39.6 (*c* 1.32, $CHCl_3$); ν_{max} (neat/cm^{-1}) 3518, 1356, 1176, 974; δ_H (400 MHz; $CDCl_3$) 2.45 (3 H, s, CH_3), 2.86 (1 H, d, *J* 3.1, O*H*), 4.02 (1 H, dd, *J* 8.22 and 10.42, OC*H*^{a}H^b), 4.12 (1 H, dd, *J* 3.43 and 10.42, OCH^a*H*^{b}), 4.95 (1 H, m, C*H*OH), 7.17–7.34 (6 H, m) and 7.74 (2 H) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.68 (*C*H$_3$), 71.26 (*C*H$_2$O), 73.03 (*C*HOH), 124.41, 125.88, 126.36, 127.92, 128.15, 128.58, 129.92, 129.99, 132.39, 134.60, 140.40 and 145.24 (Ar-*C*).

(*S*)-(+)-1-(4-Chlorophenyl)-2-(*p*-tolylsulfonyloxy)ethanol 9f. 99% Yield; R_f 0.63; mp 89–90 °C (Found: C, 53.38; H, 4.67; S, 9.69. $C_{15}H_{15}ClO_4S$ requires C, 53.13; H, 4.63; S, 9.81%); $[a]_D^{22}$ +45.5 (*c* 1.00, $CHCl_3$); ν_{max} (neat/cm^{-1}) 3537, 1348, 1178; δ_H (400 MHz; $CDCl_3$) 2.45 (3 H, s, CH_3), 2.59 (1 H, br s, O*H*), 4.02 (1 H, dd, *J* 8.20 and 10.47, OC*H*^{a}H^b), 4.12 (1 H, dd, *J* 3.45 and 10.47, OCH^a*H*^{b}), 4.97 (1 H, m, C*H*OH), 7.24–7.35 (6 H, m) and 7.74–7.76 (2 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 22.08 (*C*H$_3$), 71.69 (*C*H$_2$O), 74.36 (*C*HOH), 127.95, 128.32, 129.22, 130.36, 132.86, 134.73, 137.11 and 145.62 (Ar-*C*).

(*S*)-(+)-1-(3,4-Dichlorophenyl)-2-(*p*-tolylsulfonyloxy)ethanol 9g. 99% Yield; R_f 0.57; mp 87–88 °C (Found: C, 49.83; H, 4.00; S, 8.93. $C_{15}H_{14}Cl_2O_4S$ requires C, 49.87; H, 3.91; S, 8.88%); $[a]_D^{22}$ +39.6 (*c* 1.04, $CHCl_3$); ν_{max} (neat/cm^{-1}) 3502, 1356, 1190; δ_H (400 MHz; $CDCl_3$) 2.46 (3 H, s, CH_3), 2.66 (1 H, br s, O*H*), 4.02 (1 H, dd, *J* 7.92 and 10.53, OC*H*^{a}H^b), 4.12 (1 H, dd, *J* 3.59 and 10.53, OCH^a*H*^{b}), 4.94 (1 H, m, C*H*OH), 7.14 (1 H, d, *J* 1.93 and 8.35), 7.33 (2 H, d, *J* 8.17), 7.38–7.40 (2 H, m) and 7.73 (2 H, d, *J* 8.35) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.71 (*C*H$_3$), 70.79 (*C*H$_2$O), 73.62 (*C*HOH), 125.53, 127.91, 128.21, 128.30, 129.99, 130.59, 132.33, 132.52, 132.89, 138.57 and 145.36 (Ar-*C*).

(*S*)-(+)-1-(4-Fluorophenyl)-2-(*p*-tolylsulfonyloxy)ethanol 9h. 99% Yield; R_f 0.58; mp 65–67 °C (Found: C, 58.09; H, 4.79; S, 10.46. $C_{15}H_{15}FO_4S$ requires C, 58.05; H, 4.87; S, 10.33%); $[a]_D^{22}$ +47.0 (*c* 1.05, $CHCl_3$); ν_{max} (neat/cm^{-1}) 3529, 1344, 1185; δ_H (400 MHz; $CDCl_3$) 2.45 (3 H, s, CH_3), 2.60 (1 H, d, *J* 3.19, O*H*), 4.02 (1 H, dd, *J* 8.39 and 10.44, OC*H*^{a}H^b), 4.12 (1 H, dd, *J* 3.44 and 10.47, OCH^a*H*^{b}), 4.97 (1 H, m, C*H*OH), 7.00–7.05 (2 H, m), 7.26–7.32 (2 H, m), 7.34 (2 H, d, *J* 8.18) and 7.75–7.78 (2 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.67 (*C*H$_3$), 71.33 (*C*H$_2$O), 74.12 (*C*HOH), 115.49, 115.71, 127.94, 128.01, 129.97, 132.59, 134.04, 134.07 and 145.19 (Ar-*C*).

(*S*)-(+)-1-(4-Tolyl)-2-(*p*-tolylsulfonyloxy)ethanol 9i. 99% Yield; R_f 0.60; mp 84–85 °C (Found: C, 62.76; H, 5.99; S, 10.31. $C_{16}H_{18}O_4S$ requires C, 62.72; H, 5.92; S, 10.47%); $[a]_D^{22}$ +56.7 (*c* 1.01, $CHCl_3$); ν_{max} (neat/cm^{-1}) 3502, 1350, 1185; δ_H (400 MHz; $CDCl_3$) 2.33 (3 H, s, CH_3), 2.46 (3 H, s, CH_3), 2.47 (1 H, br s, O*H*), 4.03 (1 H, dd, *J* 8.63 and 10.37, OC*H*^{a}H^b), 4.13 (1 H, dd, *J* 3.28 and 10.29, OCH^a*H*^{b}), 4.95 (1 H, m, C*H*OH), 7.13–7.34 (6 H, m) and 7.76–7.78 (2 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.14 and 21.66 (*C*H$_3$), 71.78 (*C*H$_2$O), 74.37 (*C*HOH), 126.09, 127.95, 129.32, 129.91, 132.65, 135.17, 138.38 and 145.03 (Ar-*C*).

(*S*)-(+)-1-(4-Nitrophenyl)-2-(*p*-tolylsulfonyloxy)ethanol 9j. 99% Yield; R_f 0.42; mp 168–169 °C (Found: C, 53.32; H, 4.54; N, 4.19; S, 9.49. $C_{15}H_{15}NO_6S$ requires C, 53.40; H, 4.48; N, 4.15; S, 9.51%); $[a]_D^{22}$ +30.3 (*c* 1.02, acetone); ν_{max} (neat/cm^{-1}) 3507, 1516, 1346, 1172; δ_H (400 MHz, acetone-d$_6$) 2.31 (3 H, s, CH_3), 4.02–4.11 (2 H, m, CH_2O), 4.99 (1 H, m, C*H*OH), 7.27 (d, 2 H, *J* 8.16), 7.49–7.52 (2 H, m), 7.54–7.57 (2 H, m) and 8.01–8.05 (2 H, m) (Ar*H*); δ_C (100 MHz, acetone-d$_6$) 71.41 (*C*H$_2$O), 75.01 (*C*HOH), 124.46, 128.79, 129.07, 131.16, 134.25, 146.30 and 149.31 (Ar-*C*).

(*S*)-(+)-1-(4-Phenylphenyl)-2-(*p*-tolylsulfonyloxy)ethanol 9k. 99% Yield; R_f 0.61; mp 101–102 °C (Found: C, 68.34; H, 5.62; S, 8.57. $C_{21}H_{20}O_4S$ requires C, 68.46; H, 5.47; S, 8.70%); $[a]_D^{22}$ +50.0 (*c* 1.01, $CHCl_3$); ν_{max} (neat/cm^{-1}) 3530, 1330, 1187; δ_H (400 MHz; $CDCl_3$) 2.43 (3 H, s, CH_3), 2.61 (1 H, d, *J* 3.24, O*H*), 4.09 (1 H, dd, *J* 8.41 and 10.39, OC*H*^{a}H^b), 4.19 (1 H, dd, *J* 3.34 and 10.39, OCH^a*H*^{b}), 5.03 (1 H, m, C*H*OH), 7.31–7.39 (5 H, m), 7.42–7.46 (2 H, m), 7.55–7.57 (4 H, m) and 7.77–7.79 (2 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.66 (*C*H$_3$), 71.74 (*C*H$_2$O), 74.27 (*C*HOH), 126.65, 127.08, 127.38, 127.53, 127.97, 128.83, 129.95, 132.63, 137.19, 140.48, 141.49 and 145.10 (Ar-*C*).

(*S*)-(+)-1-(2-Naphthyl)-2-(*p*-tolylsulfonyloxy)ethanol 9l. 99% Yield; R_f 0.62; mp 113–115 °C (Found: C, 66.69; H, 5.41; S, 9.27. $C_{19}H_{18}O_4S$ requires C, 66.65; H, 5.30; S, 9.37%); $[a]_D^{22}$ +57.2 (*c* 1.00, $CHCl_3$); ν_{max} (neat/cm^{-1}) 3553, 1350, 1173; δ_H (400 MHz; $CDCl_3$) 2.41 (3 H, s, CH_3), 2.68 (1 H, br s, O*H*), 4.14 (1 H, dd, *J* 8.30 and 10.35, OC*H*^{a}H^b), 4.24 (1 H, dd, *J* 3.38 and 10.38, OCH^a*H*^{b}), 5.15 (1 H, m, C*H*OH), 7.25–7.27 (2 H, m), 7.38 (1 H, m), 7.47–7.51 (2 H, m), 7.72–7.74 (2 H, m) and 7.79–7.84 (4 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 21.63 (*C*H_3), 72.04 (*C*H_2O), 74.23 (*C*HOH), 123.69, 125.41, 126.33, 126.40, 126.63, 127.89, 127.98, 128.48, 129.87, 132.51, 133.11, 133.26, 135.61 and 145.04 (Ar-*C*).

(*S*)-(+)-1-(Methylsulfonyloxy)nonan-2-ol 9m. 99% Yield; R_f 0.42; mp 39–41 °C (Found: C, 50.43; H, 9.51; S, 13.42. $C_{10}H_{22}O_4S$ requires C, 50.39; H, 9.30; S, 13.45%); $[a]_D^{22}$ +3.5 (*c* 1.20, $CHCl_3$); ν_{max} (KBr/cm^{-1}) 3426, 1346, 1173; δ_H (400 MHz; $CDCl_3$) 0.88 (3 H, t, *J* 7.02, CH_3), 1.28–1.30 (9 H, m) and 1.48–1.52 (3 H, m) (6 × CH_2), 2.10–2.11 (1 H, m, O*H*), 3.07 (3 H, s, CH_3SO$_2$), 3.91–3.94 (1 H, m, C*H*OH), 4.10 (1 H, dd, *J* 7.51 and 10.54, OC*H*^{a}H^b), 4.26 (1 H, dd, *J* 2.80 and 10.55, OCH^a*H*^{b}); δ_C (100 MHz; $CDCl_3$) 13.47, 23.01, 25.67, 29.52, 29.80, 32.12, 33.13 and 37.93 (*C*H_3 and *C*H_2), 70.12 (*C*H_2O), 74.07 (*C*HOH).

(*S*)-(+)-1-Cyclohexyl-2-(*p*-tolylsulfonyloxy)ethanol 9n. 99% Yield; R_f 0.55 (Et_2O–$CHCl_3$ 1 : 2); oil (Found: C, 60.34; H, 7.65; S, 10.47. $C_{15}H_{22}O_4S$ requires C, 60.38; H, 7.43; S, 10.75%); $[a]_D^{22}$ +12.1 (*c* 1.02, $CHCl_3$); ν_{max} (neat) 3535, 1598, 1450, 1358, 1175; δ_H (400 MHz; $CDCl_3$) 0.96–1.22 (6 H, m, 3 × CH_2), 1.53–1.61 (5 H, m, 2 × CH_2 + CH), 2.00 (1 H, d, *J* 4.95, O*H*), 2.45 (3 H, s, CH_3), 3.55–3.60 (1 H, m, C*H*OH), 3.97 (1 H, dd, *J* 7.31 and 10.11, OC*H*^{a}H^b), 4.12 (1 H, dd, *J* 2.90 and 10.11, OCH^a*H*^{b}), 7.36 (2 H, d, *J* 8.21) and 7.80 (2 H, d, *J* 8.23) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 15.28, 21.67, 25.82, 25.95, 26.19, 28.09, 28.86, 40.22 and 65.86 (*C*H_2 and *C*H), 72.70 (*C*H_2O), 73.56 (*C*HOH), 127.97, 129.95, 132.73 and 145.03 (Ar-*C*).

(*S*)-(+)-1-(2-Pyridyl)-2-(*p*-tolylsulfonyloxy)ethanol 9o. 99% Yield; mp 66–68 °C (Found: C, 57.37; H, 5.35; N, 4.77; S, 10.92. $C_{14}H_{15}NO_4S$ requires C, 57.32; H, 5.15; N, 4.77; S, 10.93%); $[a]_D^{22}$ +4.5 (*c* 1.01, $CHCl_3$); ν_{max} (KBr/cm^{-1}) 3132, 1597, 1374, 1187; δ_H (400 MHz; $CDCl_3$) 2.44 (3 H, s, CH_3), 4.22–4.27 (2 H, m, CH_2), 4.94 (1 H, m, C*H*OH), 7.23–7.37 (4 H, m), 7.68–7.75 (3 H, m) and 8.51 (1 H, d, *J* 4.72) (Ar-*H* + pyridyl-*H*); δ_C (100 MHz; $CDCl_3$) 21.66 (*C*H_3), 70.55 (*C*H_2O), 73.18 (*C*HOH), 121.31, 123.24, 127.98, 129.86, 132.66, 136.96, 144.92, 148.53 and 156.87 (Ar-*C* + pyridyl-*C*).

(*R*)-(+)-1-(2-Thienyl)-2-(*p*-tolylsulfonyloxy)ethanol 9p. 99% Yield; R_f 0.55 (Et_2O–$CHCl_3$ 1 : 2); mp 75–76 °C (Found: C, 52.38; H, 4.71; S, 21.51. $C_{13}H_{14}O_4S_2$ requires C, 52.33; H, 4.73; S, 21.49%); $[a]_D^{22}$ +34.2 (*c* 1.05, $CHCl_3$); ν_{max} (KBr/cm^{-1}) 3541, 1357, 1188; δ_H (400 MHz; $CDCl_3$) 2.46 (3 H, s, CH_3), 2.64 (1 H, d, *J* 3.81, O*H*), 4.12–4.24 (2 H, m, CH_2O), 5.21–5.25 (1 H, m, C*H*OH), 6.96–6.98 (2 H, m), 7.27–7.29 (1 H, m), 7.35 (2 H, d, *J* 8.20) and 7.79 (2 H, d, *J* 8.24) (Ar-*H* and thienyl-*H*); δ_C (100 MHz; $CDCl_3$) 21.69 (*C*H_3), 68.31 (*C*H_2O), 73.67 (*C*HOH), 125.00, 125.67, 126.96, 128.01, 129.99, 132.65, 141.39 and 145.21 (Ar-*C* and thienyl-*C*).

General procedure for preparation of optically active terminal oxiranes 10–22 from 1,2-diol monosulfonates 9

A solution of the crude product **9** (2 mmol), obtained from the above experiments, in diethyl ether (15 cm^3) was directly treated with 2 M NaOH (5 cm^3) for 3 h at room temperature. The ether layer was separated and the aqueous layer was extracted with diethyl ether (3 × 15 cm^3). The combined ether layer was dried over anhydrous $MgSO_4$. The solvent was evaporated off under reduced pressure, and the residue was further purified by flash column chromatography on silica gel (230–400 mesh), using ethyl acetate–hexane (1 : 2) as eluent, unless otherwise indicated.

(*S*)-(−)-Phenyloxirane 10. 96% Yield; R_f 0.82; oil (Found: C, 79.91; H, 6.65. C_8H_8O requires C, 79.97; H, 6.71%); $[a]_D^{22}$ −44.5 (*c* 1.15, PhH); {lit.,[14] $[a]_D^{23}$ −44.9 (*c* 1.02, PhH), *S*}; HPLC analysis using a Chiralcel OD column showed it to be 99% ee [^{i}PrOH–hexane 0.2 : 99.8, flow rate 0.2 cm^3 min^{-1}, t_R(*S*) 56.79 min and t_R(*R*) 60.99 min]; ν_{max} (neat/cm^{-1}) 1496, 1476, 1452, 1390; δ_H (400 MHz; $CDCl_3$) 2.81 (1 H, dd, *J* 2.62 and 5.46, C*H*^{a}CH^{b}O), 3.15 (1 H, dd, *J* 4.13 and 5.45, CH^{a}C*H*^{b}O), 3.87 (1 H, dd, *J* 2.65 and 3.92, C*H*O), 7.26–7.36 (5 H, m, Ar-*H*) ; δ_C (100 MHz; $CDCl_3$) 51.22 (*C*H_2O), 52.36 (*C*HOH), 125.47, 128.18, 128.39 and 137.57 (Ar-*C*).

(*S*)-(+)-(2-Chlorophenyl)oxirane 11. 94% Yield; R_f 0.76; oil (Found: C, 62.18; H, 4.61. C_8H_7ClO requires C, 62.15; H, 4.56%); $[a]_D^{22}$ +43.7 (*c* 1.42, $CHCl_3$); {lit.,[27] $[a]_D^{25}$ +32.2 (*c* 1.19, $CHCl_3$), >99% ee, *S*}; GLC analysis using a β-Dex 120 chiral column (Supelco) showed it to be 80% ee [100 °C (isothermal), t_R(*R*) 54.00 min and t_R(*S*) 55.68 min]; ν_{max} (neat/cm^{-1}) 1498, 1441, 1381, 1250; δ_H (400 MHz; $CDCl_3$) 2.67 (1 H, dd, *J* 2.64 and 5.72, C*H*^{a}CH^{b}O), 3.20 (1 H, dd, *J* 4.09 and 5.68, CH^a-C*H*^{b}O), 4.22 (1 H, dd, *J* 2.59 and 4.03, C*H*O), 7.21–7.26 (3 H, m) and 7.35–7.38 (1 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 50.05 (*C*H_2O), 50.73 (*C*HOH), 125.68, 127.07, 128.93, 129.15, 133.28 and 135.60 (Ar-*C*).

(*S*)-(+)-(3-Chlorophenyl)oxirane 12. 95% Yield; R_f 0.72; oil (Found: C, 62.16; H, 4.59. C_8H_7ClO requires C, 62.15; H, 4.56%); $[a]_D^{22}$ +11.15 (*c* 1.56, $CHCl_3$) {lit.,[28] $[a]_D^{20}$ +11.1 (*c* 1.23, $CHCl_3$), >99% ee, *R*}. GLC analysis using a G-TA column (Astec) showed it to be 99.3% ee [120 °C (isothermal); t_R (*R*) 9.34 min and t_R(*S*) 6.97 min]; ν_{max} (neat/cm^{-1}) 1481, 1434; δ_H (400 MHz; $CDCl_3$) 2.76 (1 H, dd, *J* 2.52 and 5.45, C*H*^{a}-CH^{b}O), 3.15 (1 H, dd, *J* 4.08 and 5.45, CH^{a}C*H*^{b}O), 3.84 (1 H, dd, *J* 2.57 and 3.96, C*H*O), 7.16–7.29 (4 H, m, Ar-*H*); δ_C (100 MHz; $CDCl_3$) 51.24 (*C*H_2O), 51.70 (*C*HOH), 123.72, 125.50, 129.78, 134.59 and 139.82 (Ar-*C*).

(*S*)-(+)-(4-Chlorophenyl)oxirane 13. 96% Yield; R_f 0.76; oil (Found: C, 62.12; H, 4.51. C_8H_7ClO requires C, 62.15; H, 4.56%); $[a]_D^{22}$ +25.5 (*c* 1.00, $CHCl_3$); {lit.,[12b] $[a]_D^{20}$ −24.0 (*c* 1.08, $CHCl_3$), >97% ee, *R*}; HPLC analysis using a Chiralpak OT column showed it to be 99% ee [^{i}PrOH–hexane 1 : 99, flow rate 0.2 cm^3 min^{-1}, t_R(*S*) 30.90 min and t_R(*R*) 33.47 min]; ν_{max} (neat/cm^{-1}) 1496, 1089; δ_H (400 MHz; $CDCl_3$) 2.76 (1 H, dd, *J* 2.51 and 5.47, C*H*^{a}CH^{b}O), 3.15 (1 H, dd, *J* 4.24 and 5.13, CH^a-C*H*^{b}O), 3.84 (1 H, dd, *J* 2.87 and 3.62, C*H*O), 7.20–7.26 (2 H, m) and 7.31–7.34 (2 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 51.28 (*C*H_2O), 51.81 (*C*HOH), 126.85, 128.73, 133.95 and 136.19 (Ar-*C*).

(*S*)-(+)-(3,4-Dichlorophenyl)oxirane 14. 94% Yield; R_f 0.75 (ethyl acetate–hexane 1 : 1); oil (Found: C, 50.79; H, 3.21. $C_8H_6Cl_2O$ requires C, 50.83; H, 3.20%); $[a]_D^{22}$ +15.3 (*c* 1.18, $CHCl_3$); {lit.,[6f] $[a]_D$ −11 (*c* 1.00, $CHCl_3$), 96% ee, *R*}; HPLC analysis using a Chiralpak OT column showed it to be 94% ee [^{i}PrOH–hexane 1 : 99, flow rate 0.2 cm^3 min^{-1}, t_R(*S*) 32.84 min and t_R(*R*) 34.91 min]; ν_{max} (neat/cm^{-1}) 1469, 1410, 1370, 1132, 1029; δ_H (400 MHz; $CDCl_3$) 2.73 (1 H, dd, *J* 2.49 and 5.47, C*H*^{a}CH^{b}O), 3.15 (1 H, dd, *J* 4.08 and 5.43, CH^{a}C*H*^{b}O), 3.82 (1 H, dd, *J* 2.55 and 3.90, C*H*O), 7.12 (1 H, dd, *J* 1.99 and 8.31), 7.37 (1 H, d, *J* 1.97) and 7.42 (1 H, d, *J* 8.22) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 51.23 (*C*H_2O), 51.27 (*C*HOH), 124.84, 127.42, 130.55, 132.13, 132.86 and 138.08 (Ar-*C*).

(*S*)-(+)-(4-Fluorophenyl)oxirane 15. 96% Yield; R_f 0.77 (ethyl acetate–hexane 1 : 1); oil (Found: C, 69.71; H, 5.27. C_8H_7FO

requires C, 69.56; H, 5.11%); $[\alpha]_D^{22}$ +19.2 (*c* 1.20, $CHCl_3$); {lit.,[12b] $[\alpha]_D$ −17 (*c* 1.03, $CHCl_3$), 97% ee, *R*}; GLC analysis using a β-Dex 120 chiral column (Supelco) showed it to be 98% ee [110 °C (isothermal), t_R(*R*) 18.21 min and t_R(*S*) 18.93 min]; ν_{max} (neat/cm^{-1}) 1607, 1514, 1223; δ_H (400 MHz; $CDCl_3$) 2.77 (1 H, dd, *J* 2.55 and 5.41, C*H*^{a}CH^{b}O), 3.14 (1 H, dd, *J* 4.08 and 5.35, CH^{a}C*H*^{b}O), 3.85 (1 H, dd, *J* 2.69 and 3.83, C*H*O), 7.02–7.06 (2 H, m), 7.23–7.27 (2 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 51.18 (*C*H_2O), 51.58 (*C*HOH), 115.39, 115.61, 127.14, 127.22, 133.33, 161.48 (Ar-*C*).

(*S*)-(−)-(4-Tolyl)oxirane 16. 95% Yield; R_f 0.76; oil (Found: C, 80.58; H, 7.63. $C_9H_{10}O$ requires C, 80.56; H, 7.51%); $[\alpha]_D^{22}$ −25.9 (*c* 1.02, PhH); {lit.,[29] $[\alpha]_D^{20}$ +25.5 (*c* 1.3, PhH), 98% ee, *R*}; HPLC analysis using a Chiralcel OD column showed it to be 97% ee [^{i}PrOH–hexane 0.2 : 99.8, flow rate 0.5 cm^3 min^{-1}, t_R(*S*) 18.63 min and t_R(*R*) 20.57 min]; ν_{max} (neat/cm^{-1}) 1518, 1383; δ_H (400 MHz; $CDCl_3$) 2.35 (3 H, s, C*H*$_3$), 2.80 (1 H, dd, *J* 2.55 and 5.47, C*H*^{a}CH^{b}O), 3.13 (1 H, dd, *J* 4.08 and 5.41, CH^a-C*H*^{b}O), 3.93 (1 H, dd, *J* 2.67 and 3.94, C*H*O), 7.14–7.19 (4 H, m, Ar-*H*); δ_C (100 MHz; $CDCl_3$) 21.58, 51.52 (*C*H_2O), 52.74 (*C*HOH), 125.86, 129.59, 134.89 and 138.39 (Ar-*C*).

(*S*)-(+)-(4-Nitrophenyl)oxirane 17. 96% Yield; R_f 0.53; mp 84–85 °C (lit.,[6h] mp 84 °C) (Found: C, 58.21; H, 4.28; N, 8.51. $C_8H_7NO_3$ requires C, 58.18; H, 4.27; N, 8.48%); $[\alpha]_D^{22}$ +37.8 (*c* 1.34, $CHCl_3$); {lit.,[6h] $[\alpha]_D^{25}$ +36.0 (*c* 1.25, $CHCl_3$), 95% ee, *S*}; HPLC analysis using a Chiralpak OT column showed it to be 97% ee [^{i}PrOH–hexane 1 : 40, flow rate 0.2 cm^3 min^{-1}, t_R(*S*) 52.40 min and t_R(*R*) 56.47 min]; ν_{max} (KBr/cm^{-1}) 1606, 1522, 1345; δ_H (400 MHz; $CDCl_3$) 2.78 (1 H, dd, *J* 2.46 and 5.51, C*H*^{a}CH^{b}O), 3.24 (1 H, dd, *J* 4.16 and 5.45, CH^{a}C*H*^{b}O), 3.97 (1 H, dd, *J* 2.54 and 3.91, C*H*O), 7.45–7.47 (2 H, m) and 8.21–8.24 (2 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 51.66 (*C*H_2O), 51.89 (*C*HOH), 126.04, 126.42, 145.44 and 148.60 (Ar-*C*).

(*S*)-(+)-(4-Phenylphenyl)oxirane 18. 96% Yield; R_f 0.80 (ethyl acetate–hexane 1 : 1); mp 102–104 °C (lit.,[7c] 115–117 °C) (Found: C, 85.69; H, 6.14. $C_{14}H_{12}O$ requires C, 85.68; H, 6.16%); $[\alpha]_D^{22}$ +30.0 (*c* 1.06, $CHCl_3$); HPLC analysis using a Chiralcel OD column showed it to be 98% ee [^{i}PrOH–hexane 1 : 99, flow rate 0.6 cm^3 min^{-1}, t_R(*S*) 18.07 min and t_R(*R*) 22.22 min]; ν_{max} (KBr/cm^{-1}) 1488, 1415, 1381; δ_H (400 MHz; $CDCl_3$) 2.85 (1 H, dd, *J* 2.53 and 5.49, C*H*^{a}CH^{b}O), 3.19 (1 H, dd, *J* 4.09 and 5.45, CH^{a}C*H*^{b}O), 3.91 (1 H, dd, *J* 2.67 and 3.90, C*H*O), 7.35–7.37 (3 H, m), 7.42–7.46 (2 H, m) and 7.57–7.60 (4 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 51.26 (*C*H_2O), 52.22 (*C*HOH), 121.12, 125.97, 127.08, 127.28, 127.41, 128.80, 136.63, 140.68 and 141.20 (Ar-*C*).

(*S*)-(+)-(2-Naphthyl)oxirane 19. 97% Yield; R_f 0.70; mp 68–69 °C (lit.,[6f] mp 61–63 °C) (Found: C, 84.64; H, 5.96. $C_{12}H_{10}O$ requires C, 84.68; H, 5.92%); $[\alpha]_D^{22}$ +11.4 (*c* 1.11, $CHCl_3$), 100% ee {lit.,[6f] $[\alpha]_D$ −9 (*c* 1.2, $CHCl_3$), 92% ee, *R*}; ν_{max} (KBr/cm^{-1}) 1508, 1334; δ_H (400 MHz; $CDCl_3$) 2.91 (1 H, dd, *J* 2.54 and 5.45, C*H*^{a}CH^{b}O), 3.23 (1 H, dd, *J* 4.10 and 5.37, CH^{a}C*H*^{b}O), 4.04 (1 H, dd, *J* 2.66 and 3.92, C*H*O), 7.33 (1 H, m), 7.47–7.50 (2 H, m) and 7.81–7.84 (4 H, m) (Ar*H*); δ_C (100 MHz; $CDCl_3$) 51.29 (*C*H_2O), 52.61 (*C*HOH), 122.62, 125.15, 126.06, 126.34, 127.74, 128.38, 133.15, 133.29 and 135.02 (Ar-*C*).

(*S*)-(−)-Heptyloxirane 20. 99% Yield; R_f 0.83; oil (Found: C, 75.90; H, 12.67. $C_9H_{18}O$ requires C, 76.00; H, 12.76%); $[\alpha]_D^{22}$ −3.7 (*c* 1.14, $CHCl_3$), 40% ee {lit.,[30] $[\alpha]_D$ −8.9 (*c* 1.14, $CHCl_3$), 97% ee, *S*}; ν_{max} (neat/cm^{-1}) 2924, 1480; δ_H (400 MHz; $CDCl_3$) 0.83–0.93 (4 H, m), 1.18–1.41 (8 H, m) and 1.42–1.57 (3 H, m) (*n*-heptyl-*H*), 2.46 (1 H, dd, *J* 2.73 and 5.02, C*H*^{a}CH^{b}O), 2.74 (1 H, t, *J* 4.68, CH^{a}C*H*^{b}O), 2.90 (1 H, m, C*H*O); δ_C (100 MHz; $CDCl_3$) 14.09 (*C*H_3), 22.65, 25.99, 29.23, 29.42, 31.78 and 32.52 (*C*H_2), 47.14 (*C*H_2O), 52.42 (*C*HOH).

(*S*)-(+)-Cyclohexyloxirane 21. 96% Yield; R_f 0.31 (Et_2O–$CHCl_3$ 1 : 2); oil (Found: C, 76.09; H, 11.26. $C_8H_{14}O$ requires C, 76.14; H, 11.18%); $[\alpha]_D^{22}$ +2.1 (*c* 0.88, $CHCl_3$); GLC analysis using a G-TA chiral column (Astec) showed it to be 96% ee [65 °C (isothermal), t_R(*R*) 12.13 min and t_R(*S*) 13.12 min]. Absolute configuration of product **21** was determined by comparison with the optical rotation value of the same compound obtained from (*S*)-(+)-cyclohexylethane-1,2-diol;[31] ν_{max} (neat) 2927, 1449; δ_H (400 MHz; $CDCl_3$) 1.08–1.30 (6 H, m, 3 × C*H*$_2$), 1.66–1.76 (4 H, m, 2 × C*H*$_2$), 1.86–1.89 (1 H, m, C*H*), 2.52 (1 H, t, *J* 4.24, C*H*^{a}CH^{b}O), 2.69–2.72 (2 H, m, CH^a-C*H*^{b}O + C*H*O); δ_C (100 MHz; $CDCl_3$) 25.94, 26.10, 26.72, 29.22, 30.12 and 40.78 (cyclohexyl-*C*), 46.42 (*C*H_2O), 57.07 (*C*HOH).

(*S*)-(+)-(2-Pyridyl)oxirane 22. 92% Yield; R_f 0.63 (ethyl acetate–hexane 1 : 4); oil (Found: C, 69.45; H, 5.79; N, 11.58. C_7H_7NO requires C, 69.41; H, 5.81; N, 11.56%); $[\alpha]_D^{22}$ +2.9 (*c* 0.41, $CHCl_3$) {lit.,[32] $[\alpha]_D^{19}$ +14.0 (*c* 0.56, $CHCl_3$), >99% ee, *S*}; GLC analysis using a G-TA chiral column (Astec) showed it to be 21% ee [95 °C (isothermal), t_R(*R*) 12.66 min and t_R(*S*) 13.41 min]; ν_{max} (neat) 3014, 1594, 1476, 1438; δ_H (400 MHz; $CDCl_3$) 2.94 (1 H, dd, *J* 2.46 and 5.82, C*H*^{a}CH^{b}O), 3.18 (1 H, dd, *J* 3.22 and 5.69, CH^{a}C*H*^{b}O), 4.02 (1 H, dd, *J* 2.58 and 3.98, C*H*O), 7.25 (2 H, m), 7.68 (1 H, m) and 8.57 (1 H, d, *J* 4.55) (pyridyl-*H*); δ_C (100 MHz; $CDCl_3$) 50.76 (*C*H_2O), 53.22 (*C*HOH), 120.06, 123.48, 137.18, 149.80 and 157.59 (pyridyl-*C*).

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