Pseudo-macrocyclic chelation control in remote asymmetric induction. Highly efficient 1,7-asymmetric inductive hydride reduction and Grignard reaction of γ-keto esters of 1,1′-binaphthalen-2-ols bearing an appropriate oligoether group as the 2′-substituent

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Highly efficient 1,7-asymmetric induction was achieved in DIBAL-H reduction and Grignard reaction of γ-keto esters of podand-type 1,1′-binaphthalen-2-ol derivatives bearing an appropriate oligoether group as the 2′-substituent. Thus, the DIBAL-H reduction of keto esters **4** in dichloromethane–toluene at −78 °C in the presence of an excess of $MgBr_2{\cdot}OEt_2$ afforded, after further reduction of the resulting diastereomeric hydroxy esters, 1,4-diol **8** with up to 92% optical yield. A similar treatment of keto esters **4**, **5** and **7** with Grignard reagents gave the corresponding 4,4-disubstituted butan-4-olides **10**–**13** with up to 99% optical yield. The complexation experiments of keto ester **4b** suggested that the highly efficient 1,7-asymmetric induction originated from the formation of a pseudo-macrocyclic magnesium complex composed of the podand keto ester and $MgBr_2$.

Introduction

Diastereoselective addition of nucleophiles to chirally modified keto acids is a potential method for the synthesis of optically active hydroxy acid derivatives, which are important intermediates in the synthesis of optically active functional molecules. However, the methodology requires remote asymmetric induction over at least a 1,4-relationship even in the reactions of α-keto acid derivatives. Although efficient 1,4- and 1,5-asymmetric induction in the addition of organometallic reagents to chirally modified α- and β-keto acid derivatives have been achieved,[1,2] only a few chiral auxiliaries have been reported in the reaction of γ-keto acid derivatives which requires 1,6-asymmetric induction.[3] Therefore, development of chiral auxiliaries for the remote asymmetric induction over a 1,6-relationship has been a challenging target in asymmetric synthesis.[4]

Previously, we reported that efficient 1,5-asymmetric induction was realised in alkylation of α-keto esters by using 2′-substituted 1,1′-binaphthalen-2-ols as the chiral auxiliary.[2,5] Thus, treatment of the phenylglyoxylate of 2′-*tert*-butyldimethylsiloxy-1,1′-binaphthalen-2-ol with organometallics gave the corresponding atrolactic acid esters with up to 84% de. In this article, we wish to describe that the methodology can effectively be extended to 1,7-asymmetric inductive hydride reduction and Grignard reaction of γ-keto esters by changing the 2′-substituent of the chiral auxiliary to a properly designed multidentate chelating group (**2**) to construct a stable chelated complex with the aid of an appropriate Lewis acid.[6]

Results and discussion

Synthesis of γ-keto esters 4–7

The prerequisite γ-keto esters **4**–**7** were readily prepared by DCC condensation of γ-keto acids **3a**–**c** with chiral auxiliaries **2a**–**j** which had been prepared from (*R*)-BINOL by its monoetherification with the corresponding alkylating reagents in the presence of an appropriate base (Scheme 1).

Diastereoselective hydride reduction of γ-keto esters 4 and 6

The hydride reduction of γ-keto ester **4g** was first examined to see the effect of reaction variables including the nature of the reducing reagent, Lewis acid and solvent as well as the concentration of the substrate, which might affect the complexation between the substrate and the Lewis acid.

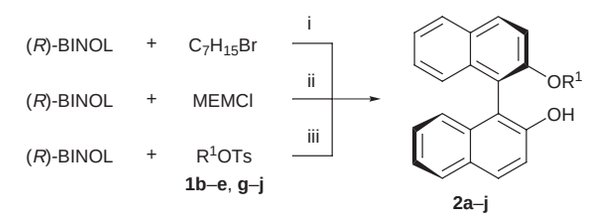
In a typical run, the keto ester **4g** was treated with an appropriate Lewis acid in dichloromethane ([**4g**] = 0.02 mol dm^{-3}) at ambient temperature for 1 h to preorganize the substrate–Lewis acid complex, which was then treated with a solution of an excess of DIBAL-H in toluene (1.0 mol dm^{-3}) at −78 °C until the substrate **4g** had disappeared by monitoring on TLC. The diastereomeric hydroxy esters thus obtained were further reduced to 1,4-diol **8** by treatment with LAH before workup to avoid enrichment of one diastereomer of the two during the purification procedure (Scheme 2). The ee value of the isolated product **8** was determined by a chiral HPLC analysis of the bis(3,5-dinitrophenylcarbamate)[7] and the absolute stereochemistry was deduced by chemical correlation to 1-phenylbutan-1-ol of known configuration (see Experimental section).[8,9]

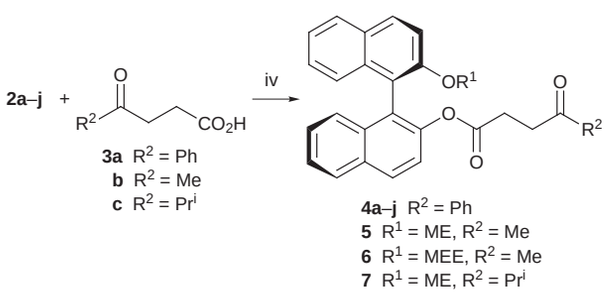
The DIBAL-H reduction of the keto ester **4g** in dichloromethane–toluene gave, after further reduction with LAH, diol **8** of low enantiomeric purity either in the presence or absence of a Lewis acid having only two empty coordination sites such as LiBr, $ZnCl_2$, $ZnBr_2$ and $TiCl_4$ (Table 1, runs 1–5). Magnesium halides have been claimed to have four empty coordination sites, but $MgCl_2$ did not improve the stereoselectivity (run 6). However, the stronger Lewis acid, $MgBr_2$ gave diol **8** in moder-

Table 1 Hydride reduction of γ-keto ester **4g**

Run	Reagent	Lewis acid (equiv.)	Solvent[a]	Yield (%)	Ee (%) (Abs. confign.)
1	DIBAL-H	none	A	90	10 (*R*)
2	DIBAL-H	LiBr (3.0)	A	97	8 (*S*)
3	DIBAL-H	$ZnCl_2$ (3.0)	A	84	39 (*R*)
4	DIBAL-H	$ZnBr_2$ (3.0)	A	93	32 (*R*)
5	DIBAL-H	$TiCl_4$ (1.0)	A	66	2 (*S*)
6	DIBAL-H	$MgCl_2$ (3.0)	A	93	8 (*R*)
7	DIBAL-H	$MgBr_2{\cdot}OEt_2$ (1.0)	A	94	60 (*S*)
8	DIBAL-H	$MgBr_2{\cdot}OEt_2$ (3.0)	A	82	82 (*S*)
9	DIBAL-H	$MgBr_2{\cdot}OEt_2$ (10)	A	86	78 (*S*)
10	DIBAL-H	$MgBr_2{\cdot}OEt_2$ (3.0)	A[b]	77	6 (*S*)
11	DIBAL-H	$MgBr_2{\cdot}OEt_2$ (3.0)	A[c]	89	74 (*S*)
12	DIBAL-H	$MgBr_2{\cdot}OEt_2$ (3.0)	B[d]	92	1 (*R*)
13	DIBAL-H	$MgBr_2{\cdot}OEt_2$ (3.0)	C[e]	93	5 (*S*)
14	$LiBu^s{}_3BH$	$MgBr_2{\cdot}OEt_2$ (3.0)	D	99	36 (*S*)
15	$KBu^s{}_3BH$	$MgBr_2{\cdot}OEt_2$ (3.0)	D	93	14 (*S*)
16	9-BBN	$MgBr_2{\cdot}OEt_2$ (3.0)	E	0	—
17	$Li(Bu^tO)_3AlH$	$MgBr_2{\cdot}OEt_2$ (3.0)	E	90	30 (*S*)

[a] Solvent: A, dichloromethane–toluene; B, diethyl ether–toluene; C, toluene; D, dichloromethane–THF; E, dichloromethane. Unless otherwise noted, the pretreatment was conducted in dichloromethane ([**4g**] = 0.02 mol dm^{-3}). [b] The pretreatment was conducted in dichloromethane ([**4g**] = 0.002 mol dm^{-3}). [c] The pretreatment was conducted in dichloromethane ([**4g**] = 0.1 mol dm^{-3}). [d] The pretreatment was conducted in diethyl ether ([**4g**] = 0.02 mol dm^{-3}). [e] The pretreatment was conducted in toluene ([**4g**] = 0.02 mol dm^{-3}).



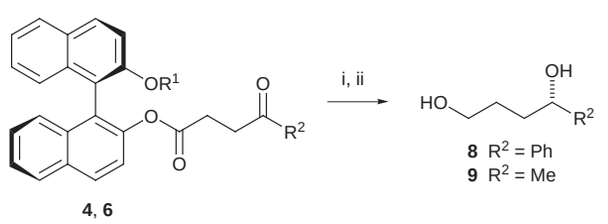


1, **2**, **4**	R^1
a	heptyl
b	ME = $[CH_2]_2OMe$
c	BE = $[CH_2]_2O[CH_2]_3Me$
d	MP = $[CH_2]_3OMe$
e	MPen = $[CH_2]_5OMe$
f	MEM = $CH_2O[CH_2]_2OMe$
g	MEE = $[CH_2]_2O[CH_2]_2OMe$
h	MEP = $[CH_2]_3O[CH_2]_2OMe$
i	IBEP = $[CH_2]_3O[CH_2]_2OCH_2CHMe_2$
j	MEEE = $[CH_2]_2O[CH_2]_2O[CH_2]_2OMe$

Scheme 1 *Reagents:* i, K_2CO_3, acetone; ii, NaH, THF; iii, NaH, DMF; iv, DCC, CH_2Cl_2.

ate to good optical yields,[10] which depended on the molar equivalence of the Lewis acid to the substrate **4g**, 3.0 equiv. of the Lewis acid being sufficient to obtain good results in the reduction (runs 7–9).

The diastereoselectivity also depended on the concentration of the substrate and nature of the solvent. When the concentration of the keto ester **4g** was low, the DIBAL-H reduction proceeded in a non-diastereoselective fashion presumably due to the decreased proportion of the complexed **4g** in the complexation equilibrium (*vide infra*) (run 10), while too high a concentration of the keto ester **4g** seemed harmful to the



Scheme 2 *Reagents:* i, H^-, Lewis acid; ii, LAH.

diastereoselectivity (compare run 11 with run 8). Preorganization of the keto ester **4g** with $MgBr_2{\cdot}OEt_2$ in diethyl ether instead of dichloromethane caused the formation of a gummy precipitate and the reaction gave almost racemic diol **8** (run 12). Changing the solvent from diethyl ether to toluene did not improve the diastereoselectivity (run 13). The amount of the $MgBr_2$ dissolved in toluene was estimated to be 0.25 equiv. of the podand keto ester **4g** as revealed by the amount of Mg^{2+} remaining in the supernatant,[11] while the amount of the dissolved $MgBr_2$ was estimated to be 1.4 equiv. in the case of dichloromethane.[12] Therefore, in toluene, most of the keto ester **4g** should have been reduced in a non-complexed form to yield the product of low optical purity.

These observations indicate that complexation of the keto ester **4g** with a Lewis acid is critical to achieve high stereoselectivity in the DIBAL-H reduction and that $MgBr_2$ is the one to choose because of its strong Lewis acidity with four vacant coordination sites.

As for the reducing reagent, DIBAL-H showed the best performance among the typical hydride reagents employed (runs 14–17). Then, in the next step, keto esters **4a**–**f** and **4h**–**j** were subjected to the DIBAL-H reduction under the optimal reaction conditions disclosed above to examine how a change of the 2′-substituent of the chiral auxiliary affects the diastereoselectivity (Table 2). Comparison of the results of the reactions of the keto esters **4a**–**e**, which possess one or two oxygen atoms in the 2′-substituent, reveals that an ethylenedioxy or propylenedioxy component in the substituent is crucial to obtain good stereoselectivity (runs 1–5). This would be attributed to their ability to form a stable five- or six-membered chelate on treatment with $MgBr_2{\cdot}OEt_2$.

The keto ester **4h** bearing a 3-(2-methoxyethoxy)propoxy (MEP-O) group is supposed to coordinate to the magnesium cation of the Lewis acid in a bidentate manner through the terminal ethylenedioxy moiety rather than the internal propyl-

enedioxy moiety, considering the fact that the stereoselectivity was significantly increased compared to that of the keto ester **4d** bearing a 3-methoxypropoxy (MP-O) group (compare run 7 with run 4). The (2-methoxyethoxy)methoxy (MEM-O) group of keto ester **4f** would also coordinate through the terminal ethylenedioxy moiety (run 6). These observations, combined with the result of the reaction of the keto ester **4b** bearing a 2-methoxyethoxy (ME-O) group (run 2), may indicate that the stereoselectivity depends on not only the structure of the chelating group but also its spatial configuration. On the other hand, steric bulk of the terminal alkoxy moiety did not have much effect on the stereoselectivity (run 8).

In contrast to the reduction of the 3-benzoylpropionate **4g**, the reduction of the levulinate **6** gave poor diastereoselectivity (run 10). This may be attributable to the higher reactivity of the methyl ketone **6** than that of the phenyl ketone **4g** as was revealed in the related 1,2-addition reactions,[12] to permit the reduction of the non-chelated keto ester **6** present in the solution.

Diastereoselective Grignard reaction of γ-keto esters 4, 5 and 7

The Grignard reaction of γ-keto esters **4**, **5** and **7** was performed by a similar procedure to that used for the hydride reduction, using an ethereal solution of a Grignard reagent (1.0 mol dm^{-3}) instead of the hydride solution in toluene (Scheme 3). It was found that the resulting hydroxy esters were spontaneously cyclised to give butan-4-olides **10**–**13**. The ee values of the isolated products **10**–**13** were determined by chiral GLC analyses and the absolute configurations by comparison of their signs of specific rotations with those reported in the literature.[13–16]

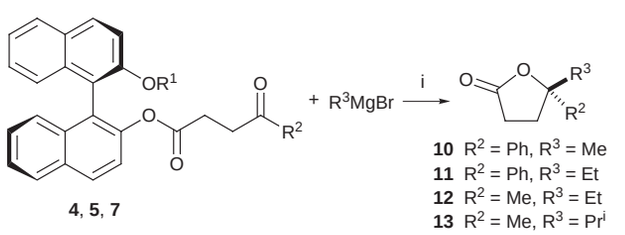
Table 3 lists the results of the Grignard reaction. Here again, the diastereoselectivity of the reaction was strongly affected by the 2′-substituent of the chiral auxiliary (runs 1, 3, 4, 6 and 7). However, contrary to the hydride reduction, keto esters bearing a mono(alkylene glycol)-type oligoether tether **4b**,**d** showed a better performance than those bearing a di- or tri-(alkylene glycol)-type substituent **4g**,**h**,**j**. This may indicate that in the Grignard reaction it is necessary to form a magnesium chelate close to the binaphthyl unit to achieve high diastereoselectivity.

It is of interest to note that the Grignard reaction proceeded with fairly good diastereoselectivity even if the precomplexation step had been omitted (runs 2, 5 and 8), which is crucial in the hydride reduction (Table 1, run 1). The keto ester **4b**, when pretreated with $MgBr_2{\cdot}OEt_2$ in THF instead of dichloromethane, afforded almost racemic lactone **10** in a low yield (run 9), indicating that the Grignard reaction proceeds rather slowly if the substrate does not form a magnesium complex in the Lewis basic solvent. In other words, the substrate should be activated by complex formation before the reaction proceeds. Therefore, in the case of the reaction without the precomplexation step, the substrate seems to have ligated to $MgBr_2$ present in the reaction mixture by the Schlenk equilibrium prior to the attack of the Grignard reagent. This explanation is entirely consistent with the fact that a high level of asymmetric induction was achieved even if the substrate was treated in toluene in which only a small amount of $MgBr_2$ dissolved (*vide supra*) (run 10).

The chelation-assisted mechanism opens a wide applicability of the Grignard reaction for the preparation of butan-4-olides having a quaternary carbon centre at the 4-position **10**–**13** (runs 11–15). In contrast to the low diastereoselectivity of the DIBAL-H reduction of levulinate **6** (Table 2, run 10), the reaction of levulinate **5** with phenyl- and ethyl-magnesium bromide proceeded with high stereoselectivity to give the corresponding lactones **10** and **12**[17] with up to 99% optical yield (run 12, 13). Isopropylmagnesium bromide also reacted with the levulinate **5** to give lactone **13** only in a low yield but with excellent stereoselectivity (**13** is an important precursor of a sex specific compound for a beetle[16]); as has been well known, the bulky and highly nucleophilic Grignard reagent seemed preferentially to

Table 2 DIBAL-H reduction of γ-keto ester **4a**–**f**, **4h**–**j** and **6**

Run	Substrate	R^1	R^2	Yield (%)	Ee (%) (Abs. confign.)
1	**4a**	heptyl	Ph	93	6 (*R*)
2	**4b**	ME	Ph	85	78 (*S*)
3	**4c**	BE	Ph	95	80 (*S*)
4	**4d**	MP	Ph	77	74 (*S*)
5	**4e**	MPen	Ph	80	26 (*S*)
6	**4f**	MEM	Ph	91	74 (*S*)
7	**4h**	MEP	Ph	85	92 (*S*)
8	**4i**	IBEP	Ph	51	88 (*S*)
9	**4j**	MEEE	Ph	86	76 (*S*)
10	**6**	MEE	Me	30	21 (*R*)



Scheme 3 *Reagents:* i, $MgBr_2{\cdot}OEt_2$ (3.0 equiv.).

Table 3 Grignard reaction of γ-keto ester **4**, **5** and **7**

Run	Substrate	R^1	R^2	R^3	Solvent[a]	Product	Yield (%)	Ee (%) (Abs. confign.)
1	**4b**	ME	Ph	Me	A	**10**	72	95 (*S*)
2[b]	**4b**	ME	Ph	Me	A	**10**	53	79 (*S*)
3	**4d**	MP	Ph	Me	A	**10**	93	94 (*S*)
4	**4g**	MEE	Ph	Me	A	**10**	75, 68[c]	14, 13[c] (*S*)
5[b]	**4g**	MEE	Ph	Me	A	**10**	50	26 (*S*)
6	**4h**	MEP	Ph	Me	A	**10**	64	69 (*S*)
7	**4j**	MEEE	Ph	Me	A	**10**	78	88 (*S*)
8[b]	**4j**	MEEE	Ph	Me	A	**10**	60	57 (*S*)
9	**4b**	ME	Ph	Me	B	**10**	25	4 (*R*)
10	**4b**	ME	Ph	Me	C	**10**	49	87 (*S*)
11	**4b**	ME	Ph	Et	A	**11**	85	92 (*S*)
12	**5**	ME	Me	Ph	A	**10**	72, 74[c]	99, 97[c] (*R*)
13	**5**	ME	Me	Et	A	**12**	85	87 (*S*)
14	**5**	ME	Me	Pr^i	A	**13**	<5	96 (*R*)
15	**7**	ME	Pr^i	Me	A	**13**	80	92 (*S*)

[a] Solvent A, dichloromethane–diethyl ether; B, THF–diethyl ether; C, toluene–diethyl ether. [b] The reaction was conducted in the absence of $MgBr_2{\cdot}OEt_2$. [c] Duplicate data.

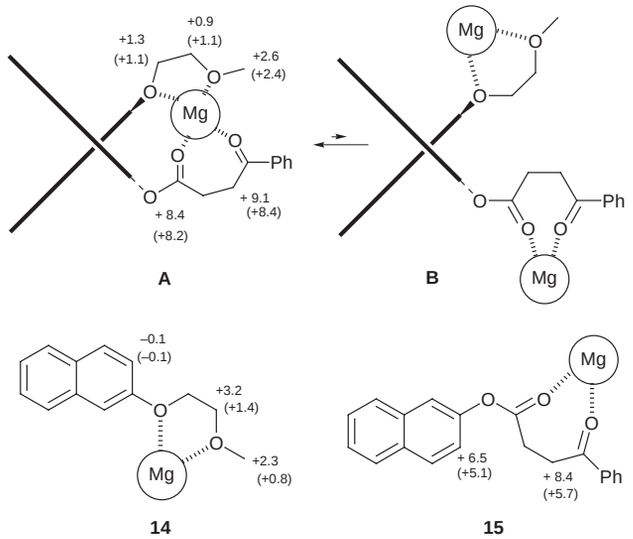


Fig. 1 Downfield shifts in ppm of the ^{13}C NMR signals for **4b**, **14** and **15** upon complexation with $MgBr_2 \cdot OEt_2$ in CD_2Cl_2. The downfield shifts of the complexes after addition of 7 vol% of diethyl ether are shown in parentheses.

abstract an α-proton of the keto moiety (run 14). We were pleased, however, to find that the relevant lactone **13** was obtained in a good yield with excellent stereoselectivity in the reaction of γ-isopropylcarbonyl ester **7** with methylmagnesium bromide (run 15).

It should be noted that the direction of the attack of the nucleophile to the keto carbonyl carbon is identical in all the Grignard reactions and hydride reductions, as long as the substrates may have coordinated to $MgBr_2$ in a bidentate manner through the 2′-substituent under the reaction conditions (*vide infra*). This suggests that the disposition of the keto carbonyl group in the chelated complex is identical in these complexes.

Mechanistic consideration of the 1,7-asymmetric induction

In order to gain insight into the mechanism of the highly efficient 1,7-asymmetric induction, complexation experiments were carried out (Fig. 1).[18] The keto ester **4b**, which showed good performance in both the hydride reduction and the Grignard reaction, was treated with an excess of $MgBr_2$ in [$^2H_2$]dichloromethane and the resulting complex was subjected to ^{13}C NMR analysis. The spectrum of the $MgBr_2$ complex of the keto ester **4b** showed considerable downfield shifts of both the carbonyl carbons and all the three carbons of the 2′-substituent, which obviously suggests that both the keto acid and oligoether moiety coordinate to $MgBr_2$. The question now arises: In which of the two possible ways (complexes A and B) do they coordinate to the Lewis acid? To determine the structure of the chelated complex, the same experiments were carried out for glycol ether **14** and keto ester **15** which are the model compounds of the two naphthyl halves of the keto ester **4b**. Similar downfield shifts were also observed upon complexation of the naphthalenes **14** and **15** with $MgBr_2$ but the chemical-shift differences between the complex and the free ligand were somewhat smaller than those of the keto ester **4b**. Furthermore, the shift differences of the model compounds were considerably reduced by addition of 7 vol% of diethyl ether, the amount of which is same as that in the reaction mixture, while those of the keto ester **4b** were only slightly changed by the same treatment. The different complexation behaviors between the keto ester **4b** and the model compounds **14** and **15** indicate that the complex of the keto ester **4b** is more stable than that of each of the naphthalene halves. Therefore, it may be concluded that the keto acid and oligoether moiety of the substrate **4b** cooperatively coordinate to $MgBr_2$ to construct the firm pseudo-macrocyclic complex A.

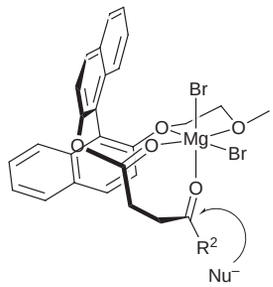


Fig. 2 Schematic view of pseudo-macrocyclic complex A derived from keto ester **4b** and $MgBr_2 \cdot OEt_2$.

Detailed CPK and Dreiding molecular model inspections suggested that formation of the pseudo-macrocyclic complex A will fix the orientation of the keto carbonyl group as schematically visualized in Fig. 2. Therefore, the attack of the nucleophile will occur preferentially from outside of the pseudo-macrocycle to give the high diastereoselectivity. The Grignard reaction might occur intramolecularly *via* an intermediate formed from the $MgBr_2$-complexed substrate and the Grignard reagent, which seems to explain why the optimal oligoether tether in the Grignard reaction is somewhat different from that in the hydride reduction.

Conclusion

In conclusion, we have achieved the efficient 1,7-asymmetric induction in the DIBAL-H reduction and the Grignard reaction of the γ-keto esters of 1,1′-binaphthalen-2-ols by introducing an appropriate oligoether group as the 2′-substituent. The latter reaction is of particular interest since chiral 4,4-disubstituted butan-4-olides[19] are not only the substances present in natural products,[20] but are also important intermediates for the synthesis of chiral functional molecules.[21]

Experimental

Melting points were measured on a Yamato MP-21 apparatus and are uncorrected. Microanalyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Reaction Science, Tohoku University. Optical rotations were obtained at ambient temperature (20–25 °C) using a Union Giken PM-101 polarimeter at 589 nm and are given in units of 10^{-1} deg cm^2 g^{-1}. IR spectra were measured on a Shimadzu IR-460 infrared spectrophotometer. ^1H (250 MHz) and ^{13}C (62.9 MHz) NMR spectra were recorded on a Bruker AC-250T instrument in $CDCl_3$ unless otherwise specified. ^1H (60 MHz) NMR spectra were recorded on a JEOL JNM-FX60 instrument in $CDCl_3$. Chemical shifts are reported relative to internal $SiMe_4$, and J values are given in Hz. The ees of the bis(3,5-dinitrophenyl carbamate)s of the diols were determined by chiral HPLC on a column developed in our laboratory;[7] the mobile phase was 30% EtOH in hexane at a flow rate of 1.0 cm^3 min^{-1}. The ees of the lactones **10**–**13** were determined by chiral GLC analysis using ASTEC Chiraldex G-TA column (20 m × 0.25 mm I.D.) at 140 °C (**10** and **11**) or 110 °C (**12** and **13**); the carrier gas was He. All reactions were carried out under a nitrogen atmosphere with the use of standard procedures for the exclusion of moisture. Column chromatography was performed by using silica gel (Nacalai Tesque, Inc., Silica Gel 60, 70–230 mesh) or alumina (Nacalai Tesque, Inc., Alumina Activated 300, 300 mesh). Analytical and preparative thin layer chromatography (TLC) was performed using precoated aluminum-backed plates (Merck, Silica gel 60 F_{254}). Na_2SO_4 was employed for the drying of extracts. The known tosylates **1b**–**d**,**g**,**j** were prepared according to the method described by Gokel *et al.*[22] from known 3-methoxypropanol[23] or commercially available alcohols. 5-Methyl-4-oxohexanoic acid was

prepared according to the method described by Ford.[24] Other reagents were the best grade commercially available and were used as received. Anhydrous solvents were freshly prepared prior to use in an atmosphere of N_2: Et_2O, THF and toluene were distilled from sodium benzophenone ketyl; CH_2Cl_2, DMF, and pyridine were distilled from CaH_2; ethyl acetate was distilled from P_2O_5. Other solvents were purified by distillation.

Preparation of the tosylates 1e,h,i

5-Methoxypentyl toluene-*p*-sulfonate 1e. To a stirred solution of 5-methoxypentanol[25] (2.5 g, 21 mmol) and pyridine (10 cm^3) was added toluene-*p*-sulfonyl chloride (6.5 g, 34 mmol) at 0 °C. The mixture was stirred overnight, after which it was cooled and poured into ice-cold hydrochloric acid (6 mol dm^{-3}; 50 cm^3). The mixture was extracted with CH_2Cl_2 (3 × 100 cm^3), and the combined extracts were dried and evaporated *in vacuo.* The residue was purified by column chromatography on silica using 10% ethyl acetate in benzene as eluent to give the *tosylate* **1e** as a colourless oil (3.7 g, 64%); ν_{max}(film)/cm^{-1} 2955, 1598, 1360 and 1190; δ_H 1.3–1.45 (2 H, m, $MeOCH_2CH_2CH_2$), 1.45–1.6 (2 H, m, $MeOCH_2CH_2$), 1.6–1.75 (2 H, m, $TsOCH_2CH_2$), 2.44 (3 H, s, *Me*Ar), 3.30 (3 H, s, MeO), 3.31 (2 H, t, *J* 6.2, $MeOCH_2$), 4.02 (2 H, t, *J* 6.4, $TsOCH_2$), 7.34 (2 H, d, *J* 8.0, Ar) and 7.78 (2 H, d, *J* 8.0, Ar).

3-(2-Methoxyethoxy)propyl toluene-*p*-sulfonate 1h. The starting alcohol, 3-(2-methoxyethoxy)propanol, was prepared according to the method described by Okano *et al.*[26] Thus, 1-chloro-2-methoxyethane (25.0 g, 0.26 mol) was added dropwise during 30 min to a refluxed solution of propane-1,3-diol (30.2 g, 0.40 mol) and NaOH (15.9 g, 0.40 mol) in distilled water (10 cm^3) with stirring. After 25 h, the cooled mixture was neutralised by concentrated hydrochloric acid and the resulting salt was filtered off. The filtrate was evaporated *in vacuo* to leave a pale yellow oil, which was distilled through a Widmer fractionating column. In contrast to the original report, the fractionated distillate (22.7 g; bp 114 °C/19 Torr, 1 Torr = 133.3 N m^{-2}) was the mixture of the desired 3-(2-methoxyethoxy)-propanol and propane-1,3-diol. Therefore, the mixture was used in the tosylation process without further purification.

To a stirred solution of the mixture (5.03 g) and pyridine (40 cm^3) was added toluene-*p*-sulfonyl chloride (14.3 g, 75.0 mmol) at 0 °C. The mixture was stirred overnight, after which it was cooled and poured into ice-cold hydrochloric acid (6 mol dm^{-3}; 100 cm^3). The mixture was extracted with CH_2Cl_2 (3 × 200 cm^3), and the combined extracts were dried and evaporated *in vacuo.* The residue was dissolved in the minimum amount of Et_2O and cooled in a refrigerator to crystallise most of the propane-1,3-diyl ditosylate, after which it was filtered. The mother liquid was evaporated *in vacuo* to give, after column chromatography on silica using 30% ethyl acetate in hexane as eluent, the *tosylate* **1h** (4.98 g, 30% from 1-chloro-2-methoxyethane) as a colourless oil; ν_{max}(film)/cm^{-1} 2930, 1598, 1360 and 1177; δ_H 1.90 (2 H, quintet, *J* 6.2, $CH_2CH_2CH_2$), 2.42 (3 H, s, Ar*Me*), 3.32 (3 H, s, OMe), 3.40–3.48 (6 H, m, $CH_2OCH_2CH_2OMe$), 4.11 (2 H, t, *J* 6.2, $TsOCH_2$), 7.32 (2 H, d, *J* 8.2, Ar) and 7.76 (2 H, d, *J* 8.2, Ar).

3-(2-Isobutoxyethoxy)propyl toluene-*p*-sulfonate 1i. The starting alcohol, 3-(2-isobutoxyethoxy)propanol, was prepared as for the synthesis of 3-(2-methoxyethoxy)propanol described above. The following reagents and quantities were used: 1-chloro-2-isobutoxyethane (5.46 g, 40.0 mmol),[27] propane-1,3-diol (4.53 g, 59.5 mmol), NaOH (2.35 g, 58.8 mmol), and distilled water (1.6 cm^3). After distillation (bp 72–76 °C/1.5 Torr), the desired *alcohol* was obtained as a colourless oil (3.19 g, 45%); ν_{max}(film)/cm^{-1} 3441, 2868 and 1110; δ_H 0.90 (6 H, d, *J* 6.6, $CHMe_2$), 1.79–1.93 (3 H, m, $CHMe_2$ and $HOCH_2CH_2$), 2.96 (1 H, br s, OH), 3.22 (2 H, d, *J* 6.6, OCH_2CHMe_2) and 3.57–3.80 (8 H, m, $HOCH_2CH_2CH_2OCH_2CH_2O$).

The tosylate **1i** was prepared as described for **1h** from 3-(2-isobutoxyethoxy)propanol. The following reagents and quantities were used: 3-(2-isobutoxyethoxy)propanol (1.93 g, 10.9 mmol), toluene-*p*-sulfonyl chloride (2.09 g, 11.0 mmol) and pyridine (15 cm^3). The *tosylate* **1i** was obtained as a colourless oil (2.55 g, 71%) after purification by column chromatography on silica using 30% ethyl acetate in hexane as eluent; ν_{max}(film)/cm^{-1} 2955, 1598, 1360, 1177 and 1097; δ_H 0.88 (6 H, d, *J* 6.8, $CHMe_2$), 1.80–1.96 (3 H, m, $CHMe_2$ and $TsOCH_2CH_2$), 2.45 (3 H, s, Ar*Me*), 3.19 (2 H, d, *J* 6.8, OCH_2CHMe_2), 3.46–3.57 (6 H, m, $TsOCH_2CH_2CH_2OCH_2CH_2O$), 4.14 (2 H, t, *J* 6.3, $TsOCH_2$), 7.35 (2 H, d, *J* 8.3, Ar) and 7.79 (2 H, d, *J* 8.3, Ar).

Preparation of the chiral auxiliaries 2a–j and the model compound 14

(*R*)-2′-Heptyloxy-1,1′-binaphthalen-2-ol 2a. The chiral auxiliary **2a** was prepared according to the method described by Pirkle and Schreiner.[28] To a suspension of (*R*)-BINOL (0.488 g, 1.70 mmol) and anhydrous K_2CO_3 (0.300 g, 2.17 mmol) in acetone (2.0 cm^3) was added 1-bromoheptane (0.34 g, 1.9 mmol) at room temperature. After being stirred for 12 h, the mixture was filtered and the filtrate was evaporated *in vacuo*. The residue was purified by column chromatography on silica using 30% ethyl acetate in hexane as eluent to give the *ether* **2a** [0.290 g, 45% (97% based on the consumed BINOL)] as a colourless glass (Found: C, 84.5; H, 7.4. $C_{27}H_{28}O_2$ requires C, 84.3; H, 7.3%); $[\alpha]_D^{23}$ −25 (*c* 0.62 in $CHCl_3$); ν_{max}(film)/cm^{-1} 3498, 2927, 1620, 1591, 1263 and 1205; δ_H 0.80 (3 H, t, *J* 7.0, Me), 0.8–1.2 [8 H, m, $(CH_2)_4Me$], 1.35–1.5 (2 H, m, $ArOCH_2CH_2$), 3.85–4.05 (2 H, m, $ArOCH_2$), 4.96 (1 H, s, OH) and 7.06–7.98 (12 H, m, Ar).

(*R*)-2′-(2-Methoxyethoxy)methoxy-1,1′-binaphthalen-2-ol 2f. The chiral auxiliary **2f** was prepared according to the method described by Corey *et al.*[29] To a solution of (*R*)-BINOL (2.00 g, 6.98 mmol) in THF (70 cm^3) was added NaH (276 mg, 6.90 mmol) portionwise at 0 °C. After 30 min, MEMCl (1.31 g, 10.5 mmol) was added dropwise during 15 min to the solution which was stirred for 4 h at room temperature. The reaction was quenched with saturated aqueous NH_4Cl (20 cm^3) and the mixture was extracted with ethyl acetate (3 × 50 cm^3). The combined extracts were washed successively with saturated aqueous Na_2CO_3 and brine, dried and evaporated *in vacuo*. The residue was purified by column chromatography on silica using 30% ethyl acetate in hexane as eluent to give the *monoether* **2f** [1.59 g, 61% (74% based on the consumed BINOL)] (Found: C, 77.0; H, 6.0. $C_{24}H_{22}O_4$ requires C, 77.0; H, 5.9%); $[\alpha]_D^{23}$ −26.0 (*c* 1.00 in $CHCl_3$); ν_{max}(film)/cm^{-1} 3225, 2925, 1621, 1595, 1504, 1229, 1144, 1033 and 1012; δ_H 3.17 (3 H, s, OMe), 3.2–3.63 (4 H, m, OCH_2CH_2OMe), 5.19 (2 H, ABq, $\Delta\nu$ 31.0, *J* 7.1, OCH_2O), 5.33 (1 H, s, OH) and 7.03–8.08 (12 H, m, Ar).

General procedure for synthesis of the chiral auxiliaries 2b–e, g–j and the model compound 14. To a solution of (*R*)-BINOL (10 mmol) in DMF (50 cm^3) was added NaH (10 mmol) portionwise at ambient temperature. The appropriate tosylate **1** (9.5 mmol) was added to the yellow solution thus obtained. The mixture was immediately heated at 100 °C for 30 min and then cooled in an ice bath. The mixture was poured into dilute hydrochloric acid (2 mol cm^{-3}; 20 cm^3) and evaporated *in vacuo*. Water (20 cm^3) was added to the residue, after which it was extracted with Et_2O (3 × 50 cm^3). The combined extracts were washed successively with water, brine, and dried. After evaporation of the solvent, the residue was purified by column chromatography on alumina (for **2b**, **c**, **e**) or silica (for **2g**–**j**) to give the chiral auxiliaries **2b**, **c**, **e**, **g**–**j**. The eluents for the chromatographic purification, the isolated yields, the yields based on the consumed BINOL, and the physical and spectral characteristics of the chiral auxiliaries are given below.

(R)-2′-(2-Methoxyethoxy)-1,1′-binaphthalen-2-ol ***2b***. Eluent: 30–100% ethyl acetate in $CHCl_3$ (gradient); yield 42% (90%); $[a]_D^{20}$ −37.8 (*c* 1.00 in $CHCl_3$) (Found: C, 80.4; H, 6.05. $C_{23}H_{20}O_3$ requires C, 80.2; H, 5.85%); ν_{max}(film)/cm^{-1} 3417, 2931, 1620, 1592, 1264 and 1146; δ_H 3.03 (3 H, s, OMe), 3.39 (2 H, t, *J* 4.8, CH_2OMe), 4.0–4.2 (2 H, m, ArOCH_2), 5.30 (1 H, br s, OH) and 7.02–7.99 (12 H, m, Ar).

(R)-2′-(2-Butoxyethoxy)-1,1′-binaphthalen-2-ol ***2c***. Eluent: ethyl acetate; yield 45% (92%); mp 86.5–87.5 °C (from benzene–hexane); $[a]_D^{22}$ −33 (*c* 0.24 in $CHCl_3$) (Found: C, 80.5; H, 6.6. $C_{26}H_{26}O_3$ requires C, 80.8; H, 6.8%); ν_{max}(KBr)/cm^{-1} 3425, 2935, 1619, 1594, 1273 and 1142; δ_H 0.76 (3 H, t, *J* 7.1, Me), 1.0–1.3 (4 H, m, CH_2CH_2Me), 2.95–3.15 (2 H, m, OCH_2CH_2-CH_2Me), 3.35–3.40 (2 H, m, ArOCH$_2CH_2$O), 3.95–4.15 (2 H, m, ArOCH_2), 5.40 (1 H, s, OH) and 7.05–7.90 (12 H, m, Ar).

(R)-2′-(3-Methoxypropoxy)-1,1′-binaphthalen-2-ol ***2d***. Eluent: 10–20% ethyl acetate in chloroform (gradient); yield 63% (71%); $[a]_D^{16}$ −16.0 (*c* 1.00 in $CHCl_3$) (Found: C, 80.5; H, 6.3. $C_{24}H_{22}O_3$ requires C, 80.4; H, 6.2%); ν_{max}(film)/cm^{-1} 3405, 2925, 1621, 1594, 1509, 1265, 1145 and 1080; δ_H 1.70 (2 H, quintet, *J* 4.6, OCH$_2CH_2CH_2$O), 2.90–3.07 (2 H, m, CH_2OMe), 3.04 (3 H, s, OMe), 3.99–4.16 (2 H, m, ArOCH_2), 5.03 (1 H, br s, OH) and 7.03–8.03 (12 H, m, Ar).

(R)-2′-(5-Methoxypentyloxy)-1,1′-binaphthalen-2-ol ***2e***. Eluent: 30–100% ethyl acetate in hexane (gradient); yield 42% (56%); $[a]_D^{23}$ −24 (*c* 0.56 in $CHCl_3$) (Found: C, 80.9; H, 6.9. $C_{26}H_{26}O_3$ requires C, 80.8; H, 6.8%); ν_{max}(film)/cm^{-1} 3300, 2936, 1619, 1591, 1263, 1146 and 1081; δ_H 0.90–1.05 (2 H, m, CH_2CH_2OMe), 1.15–1.30 (2 H, m, ArOCH$_2CH_2$), 1.39 (2 H, quintet, *J* 6.9, ArOCH$_2CH_2CH_2CH_2CH_2$OMe), 3.00 (2 H, t, *J* 6.5, CH_2OMe), 3.15 (3 H, s, OMe), 3.75–3.95 (2 H, m, ArOCH_2), 5.48 (1 H, s, OH) and 7.06–7.89 (12 H, m, Ar).

(R)-2′-[2-(2-Methoxyethoxy)ethoxy]-1,1′-binaphthalen-2-ol ***2g***. Eluent: 40% ethyl acetate in hexane; yield 42% (98%); $[a]_D^{21}$ −14.1 (*c* 1.05 in $CHCl_3$) (Found: C, 77.5; H, 6.5. $C_{25}H_{24}O_4$ requires C, 77.3; H, 6.2%); ν_{max}(film)/cm^{-1} 3325, 2925, 1621, 1594, 1507, 1264, 1144 and 1101; δ_H 3.05 (3 H, s, OMe), 3.1–3.3 (4 H, m, OCH_2CH_2OMe), 3.54 (2 H, t, *J* 4.5, ArOCH$_2CH_2$O), 4.08 (1 H, dt, *J* 11.2 and 4.5, ArOCH*H*CH$_2$), 4.26 (1 H, dt, *J* 11.2 and 4.5, ArOC*H*HCH$_2$), 5.54 (1 H, s, OH) and 7.03–8.01 (12 H, m, Ar).

(R)-2′-[3-(2-Methoxyethoxy)propoxy]-1,1′-binaphthalen-2-ol ***2h***. Eluent: 30–50% ethyl acetate in hexane (gradient); yield 68% (83%); $[a]_D^{16}$ −25.4 (*c* 1.06 in $CHCl_3$) (Found: C, 77.7; H, 6.6. $C_{26}H_{26}O_4$ requires C, 77.6; H, 6.5%); ν_{max}(film)/cm^{-1} 3310, 2920, 1620, 1594, 1506, 1264, 1143 and 1098; δ_H 1.70–1.81 (2 H, m, OCH$_2CH_2CH_2$O), 3.04–3.38 (6 H, m, $CH_2OCH_2CH_2$O), 3.25 (3 H, s, OMe), 4.06–4.17 (2 H, m, ArOCH_2), 5.27 (1 H, s, OH) and 7.02–8.03 (12 H, m, Ar).

(R)-2′-[3-(2-Isobutoxyethoxy)propoxy]-1,1′-binaphthalen-2-ol ***2i***. Eluent: 10–30% ethyl acetate in benzene (gradient); yield 65% (76%); $[a]_D^{18}$ −23.0 (*c* 1.00 in $CHCl_3$) (Found: C, 78.3; H, 7.3. $C_{29}H_{32}O_4$ requires C, 78.35; H, 7.3%); ν_{max}(film)/cm^{-1} 3335, 2960, 1622, 1594, 1507, 1264, 1125 and 1079; δ_H 0.84 and 0.85 (each 3 H, d, *J* 6.8, CHMe_2), 1.68–1.96 (3 H, m, OCH$_2CH_2$-CH_2O and C*H*Me$_2$), 3.02–3.41 (8 H, m, $CH_2OCH_2CH_2OCH_2$-CHMe$_2$), 4.06–4.17 (2 H, m, ArOCH_2), 5.21 (1 H, br s, OH) and 7.02–8.02 (12 H, m, Ar).

(R)-2′-{2-[2-(2-Methoxyethoxy)ethoxy]ethoxy}-1,1′-binaphthalen-2-ol ***2j***. Eluent: 50% ethyl acetate in $CHCl_3$; yield 48% (83%); $[a]_D^{20}$ −21.1 (*c* 0.97 in $CHCl_3$) (Found: C, 75.15; H, 6.8. $C_{27}H_{28}O_5$ requires C, 75.0; H, 6.5%); ν_{max}(film)/cm^{-1} 3345, 2930, 1621, 1593, 1506, 1266, 1144 and 1097; δ_H 3.27 (3 H, s, OMe), 3.2–3.6 [10 H, m, $CH_2O(CH_2CH_2O)_2$Me], 4.05–4.30 (2 H, m, ArOCH_2CH_2), 5.70 (1 H, br s, OH) and 7.0–8.0 (12 H, m, Ar).

2-(2-Methoxyethoxy)naphthalene ***14***. Eluent: CH_2Cl_2; yield 77% (Found: C, 77.5; H, 6.8. $C_{13}H_{14}O_2$ requires C, 77.2; H, 7.0%); ν_{max}(film)/cm^{-1} 2926, 1628, 1600, 1258, 1217, 1183 and 1118; δ_H 3.49 (3H, s, OMe), 3.82 (2 H, t, *J* 4.8, ArOCH_2), 4.25 (2 H, t, *J* 4.8, ArOCH$_2CH_2$), 7.14–7.77 (7 H, m, Ar); δ_C (CD_2Cl_2) 59.2, 67.7, 71.3, 106.9, 119.2, 124.0, 126.7, 127.0, 127.9, 129.4, 129.7, 134.9 and 157.2.

General procedure for preparation of the γ-keto esters 4a–j and 5–7, and the model compound 15

To a stirred solution of chiral auxiliary **2** (10 mmol) and DCC (15 mmol) in CH_2Cl_2 (200 cm^3) was added the appropriate γ-keto acid **3** (12 mmol) at ambient temperature. After a few minutes, 4-pyrrolidin-1-ylpyridine (2.5 mmol) was added to the solution and the reaction mixture was stirred for 1 h. After evaporation of the solvent, Et_2O (50 cm^3) was added to the residue. The insoluble *N,N′*-dicyclohexylurea (DCU) was filtered off and the filtrate was washed successively with saturated aqueous $NaHCO_3$, dilute hydrochloric acid (2 mol cm^{-3}), water, brine, and dried. The solvent was evaporated *in vacuo* and the residue was subjected to column chromatography on alumina (for **4e**, **f** and **7**) or silica [for **4a**, **e** (after alumina column), **4b**–**d**, **g**–**j**, **5**, **6** and **15**]. Because the product-containing fraction includes residual DCU, the fraction was evaporated and then dissolved in a minimum amount of Et_2O, after which it was cooled in a refrigerator at −20 °C overnight in order to precipitate the DCU. The precipitated DCU was filtered off and the filtrate was evaporated *in vacuo* to give the γ-keto ester. The eluents for the chromatographic purification, the isolated yields, and the physical and spectral characteristics of the esters are given below.

(*R*)-2′-Heptyloxy-1,1′-binaphthalen-2-yl 3-benzoylpropionate 4a. Eluent: 20% ethyl acetate in hexane; yield 90%; $[a]_D^{20}$ +23.1 (*c* 1.17 in $CHCl_3$) (Found: C, 81.9; H, 6.8. $C_{37}H_{36}O_4$ requires C, 81.6; H, 6.7%); ν_{max}(film)/cm^{-1} 2916, 1759, 1687, 1212 and 1139; δ_H 0.79 (3 H, t, *J* 7.1, Me), 0.8–1.2 [8 H, m, $(CH_2)_4$Me], 1.3–1.45 (2 H, m, ArOCH$_2CH_2$), 2.35–2.75 (4 H, m, ArO$_2$-CCH_2CH_2COPh), 3.8–4.0 (2 H, m, ArOCH_2) and 7.15–7.95 (17 H, m, Ar); δ_C 14.0, 22.4, 25.4, 28.4, 28.7, 29.1, 31.5, 33.2, 69.6, 115.3, 118.5, 121.8, 123.6, 125.1, 125.3, 125.4, 126.1, 126.2, 126.5, 127.7, 127.9, 128.4, 128.8, 128.9, 129.7, 131.7, 133.1, 133.7, 136.1, 146.6, 154.5, 170.9 (*C*O$_2$Ar) and 197.3 (Ph*C*O).

(*R*)-2′-(2-Methoxyethoxy)-1,1′-binaphthalen-2-yl 3-benzoylpropionate 4b. Eluent: 17% ethyl acetate in benzene; yield 72%; mp 91.9–92.3 °C (from Et_2O); $[a]_D^{23}$ +42.8 (*c* 1.01 in $CHCl_3$) (Found: C, 78.3; H, 5.8. $C_{33}H_{28}O_5$ requires C, 78.55; H, 5.6%); ν_{max}(KBr)/cm^{-1} 2900, 1752, 1679, 1261, 1208 and 1146; δ_H 2.35–2.85 (4 H, m, ArO$_2$CCH_2CH_2COPh), 2.96 (3 H, s, OMe), 3.25–3.40 (2 H, m, CH_2OMe), 4.04 (2 H, t, *J* 5.2, ArOCH_2) and 7.14–7.98 (17 H, m, Ar); δ_C (CD_2Cl_2) 28.7, 33.6, 59.0, 69.9, 71.3, 116.0, 118.8, 122.3, 124.2, 125.4, 125.6, 125.8, 126.4, 126.7, 126.8, 128.2, 128.4, 128.8, 129.2, 129.6, 130.3, 132.1, 133.5, 134.0, 136.6, 147.2, 154.9, 171.2 (*C*O$_2$Ar) and 197.5 (Ph*C*O).

(*R*)-2′-(2-Butoxyethoxy)-1,1′-binaphthalen-2-yl 3-benzoylpropionate 4c. Eluent: 10% ethyl acetate in benzene (for first chromatography) and 20% ethyl acetate in hexane (for second chromatography); yield 73%; $[a]_D^{17}$ +28 (*c* 0.69 in $CHCl_3$) (Found: C, 79.35; H, 6.0. $C_{36}H_{34}O_5$ requires C, 79.1; H, 6.3%); ν_{max}(film)/cm^{-1} 2930, 1757, 1686, 1247, 1209 and 1138; δ_H 0.76 (3 H, t, *J* 7.1, Me), 1.0–1.3 (4 H, m, OCH$_2CH_2CH_2$Me), 2.35–2.8 (4 H, m, ArO$_2$CCH_2CH_2COPh), 2.95–3.10 (2 H, m, OCH_2-CH_2CH_2Me), 3.30–3.45 (2 H, m, ArOCH$_2CH_2$O), 4.05 (2 H, t, *J* 5.1, ArOCH_2) and 7.15–7.96 (17 H, m, Ar); δ_C (CD_2Cl_2) 13.8, 18.4, 19.0, 31.6, 33.2, 69.0, 69.7, 71.1, 115.4, 118.5, 121.8, 123.8, 125.0, 125.4, 126.2, 126.3, 126.6, 127.8, 128.0, 128.3, 128.4, 128.9, 129.1, 129.8, 131.7, 133.1, 133.7, 136.2, 146.7, 154.4, 170.9 (*C*O$_2$Ar) and 197.3 (Ph*C*O).

(*R*)-2′-(3-Methoxypropoxy)-1,1′-binaphthalen-2-yl 3-benzoylpropionate 4d. Eluent: 10% ethyl acetate in benzene; yield 93%;

mp 98.2–98.8 °C (from benzene–hexane); $[\alpha]_D^{23}$ +34.0 (*c* 1.00 in $CHCl_3$) (Found: C, 78.5; H, 5.8. $C_{34}H_{30}O_5$ requires C, 78.7; H, 5.8%); ν_{max}(KBr)/cm^{-1} 2920, 1744, 1678, 1203 and 1142; δ_H 1.66 (2 H, quintet, *J* 6.2, $OCH_2CH_2CH_2O$), 2.35–2.80 (4 H, m, $ArO_2CCH_2CH_2COPh$), 2.8–3.0 (2 H, m, CH_2OMe), 3.01 (3 H, s, OMe), 3.98–4.10 (2 H, m, $ArOCH_2$) and 7.19–8.0 (17 H, m, Ar); δ_C (CD_2Cl_2) 28.4, 29.5, 33.2, 58.3, 66.2, 66.7, 115.0, 121.9, 123.7, 125.1, 125.4, 126.2, 126.3, 126.6, 127.8, 128.0, 128.4, 128.8, 129.8, 131.7, 133.2, 133.7, 136.2, 146.3, 154.3, 170.9 (CO_2Ar) and 197.3 (Ph*C*O).

(*R*)-2′-(5-Methoxypentyloxy)-1,1′-binaphthalen-2-yl 3-benzoylpropionate 4e. Eluent: 10% ethyl acetate in benzene (for both alumina and silica); yield 90%; $[\alpha]_D^{20}$ +25 (*c* 0.39 in $CHCl_3$) (Found: C, 79.4; H, 6.3. $C_{36}H_{34}O_5$ requires C, 79.1; H, 6.3%); ν_{max}(film)/cm^{-1} 3056, 1759, 1686, 1246, 1210, 1139 and 1082; δ_H 0.9–1.0 (2 H, m, CH_2CH_2OMe), 1.2–1.3 (2 H, m, $ArOCH_2CH_2$), 1.35–1.45 (2 H, m, $ArOCH_2CH_2CH_2CH_2CH_2OMe$), 2.35–2.8 (4 H, m, $ArO_2CCH_2CH_2COPh$), 3.0–3.1 (2 H, m, CH_2OMe), 3.20 (3 H, s, OMe), 3.85–3.97 (2 H, m, $ArOCH_2$) and 7.15–8.0 (17 H, m, Ar); δ_C 22.0, 28.4, 28.9, 33.2, 58.4, 69.4, 72.5, 115.2, 118.5, 121.8, 123.7, 125.1, 125.4, 126.2, 126.3, 126.5, 127.7, 128.0, 128.4, 128.8, 128.9, 129.8, 131.7, 133.1, 133.7, 136.1, 146.6, 154.4, 170.9 (CO_2Ar) and 197.3 (Ph*C*O).

(*R*)-2′-(2-Methoxyethoxy)methoxy-1,1′-binaphthalen-2-yl 3-benzoylpropionate 4f. Eluent: 30% ethyl acetate in hexane; yield 69%; $[\alpha]_D^{23}$ +54.7 (*c* 1.05 in THF) (Found: C, 76.6; H, 6.0. $C_{34}H_{30}O_6$ requires C, 76.4; H, 5.7%); ν_{max}(film)/cm^{-1} 2920, 1759, 1687, 1209 and 1137; δ_H 2.4–2.75 (4 H, m, $ArO_2CCH_2CH_2COPh$), 3.25–3.55 (4 H, m, CH_2CH_2OMe), 3.25 (3 H, s, OMe), 5.06 and 5.12 (2 H, ABq, *J* 7.2, $\Delta\nu$ 5.4, OCH_2O) and 7.13–8.00 (17 H, m, Ar); δ_C 28.4, 33.2, 58.8, 67.4, 71.3, 93.9, 116.4, 119.1, 121.9, 124.2, 124.9, 125.5, 126.1, 126.4, 126.6, 127.7, 128.0, 128.1, 128.3, 128.4, 129.1, 129.5, 129.9, 131.7, 133.2, 133.6, 136.1, 146.7, 152.7, 171.0 (CO_2Ar) and 197.2 (Ph*C*O).

(*R*)-2′-[2-(2-Methoxyethoxy)ethoxy]-1,1′-binaphthalen-2-yl 3-benzoylpropionate 4g. Eluent: 20% ethyl acetate in benzene; yield 93%; $[\alpha]_D^{20}$ +31.8 (*c* 1.01 in MeOH) (Found: C, 76.9; H, 6.1. $C_{35}H_{32}O_6$ requires C, 76.6; H, 5.9%); ν_{max}(film)/cm^{-1} 2910, 1758, 1685, 1204 and 1138; δ_H 2.35–2.85 (4 H, m, $ArO_2CCH_2CH_2COPh$), 2.95–3.15 (4 H, m, OCH_2CH_2OMe), 3.20 (3 H, s, OMe), 3.4–3.55 (2 H, m, $ArOCH_2CH_2O$), 4.10 (2 H, t, *J* 6.2, $ArOCH_2$) and 7.15–7.95 (17 H, m, Ar); δ_C (CD_2Cl_2) 28.7, 33.6, 58.8, 70.1, 70.8, 72.0, 115.6, 118.8, 122.4, 124.2, 125.3, 125.6, 125.9, 126.4, 126.7, 126.8, 128.3, 128.5, 128.9, 129.2, 129.6, 130.4, 132.1, 133.6, 134.0, 147.2, 155.0, 171.3 (CO_2Ar) and 197.6 (Ph*C*O).

(*R*)-2′-[3-(2-Methoxyethoxy)propoxy]-1,1′-binaphthalen-2-yl 3-benzoylpropionate 4h. Eluent: 40–50% ethyl acetate in hexane (gradient); yield 74%; $[\alpha]_D^{20}$ +25.2 (*c* 0.99 in $CHCl_3$) (Found: C, 76.8; H, 6.2. $C_{36}H_{34}O_6$ requires C, 76.85; H, 6.1%); ν_{max}(film)/cm^{-1} 2920, 1759, 1687, 1211 and 1140; δ_H 1.6–1.8 (2 H, m, $OCH_2CH_2CH_2O$), 2.35–2.80 (4 H, m, $ArO_2CCH_2CH_2COPh$), 2.9–3.4 (6 H, m, $CH_2OCH_2CH_2O$), 3.29 (3 H, s, OMe), 3.95–4.15 (2 H, m, $ArOCH_2$) and 7.2–8.0 (17 H, m, Ar); δ_C 28.3, 29.4, 33.1, 58.9, 66.1, 67.3, 69.7, 71.6, 114.9, 118.2, 121.6, 123.7, 125.0, 125.3, 126.1, 126.2, 126.5, 127.7, 127.9, 128.2, 128.4, 128.7, 128.9, 129.8, 131.6, 133.1, 133.6, 136.1, 146.6, 154.2, 170.8 (CO_2Ar) and 197.2 (Ph*C*O).

(*R*)-2′-[3-(2-Isobutoxyethoxy)propoxy]-1,1′-binaphthalen-2-yl 3-benzoylpropionate 4i. Eluent: 10% ethyl acetate in benzene; yield 90%; $[\alpha]_D^{20}$ +20.6 (*c* 1.00 in $CHCl_3$) (Found: C, 77.2; H, 6.7. $C_{39}H_{40}O_6$ requires C, 77.5; H, 6.7%); ν_{max}(film)/cm^{-1} 2950, 1760, 1688, 1211 and 1140; δ_H 0.86 (6 H, d, *J* 6.5, $CHMe_2$), 1.68 (2 H, quintet, *J* 6.1, $OCH_2CH_2CH_2O$), 1.82 (1 H, septet, *J* 6.5, $CHMe_2$), 2.35–2.80 (4 H, m, $ArO_2CCH_2CH_2COPh$), 2.96–3.38 (8 H, m, $CH_2OCH_2CH_2OCH_2CHMe_2$), 3.99–4.08 (2 H, m, $ArOCH_2$) and 7.18–7.99 (17 H, m, Ar); δ_C 19.3, 28.2, 28.4, 29.6, 33.2, 66.3, 67.3, 70.0, 115.0, 121.9, 123.7, 125.1, 125.4, 126.2, 126.3, 126.6, 127.8, 128.0, 128.4, 128.8, 129.0, 129.8, 131.7, 133.1, 133.7, 136.3, 146.7, 154.3, 170.9 (CO_2Ar) and 197.3 (Ph*C*O).

(*R*)-2′-{2-[2-(2-Methoxyethoxy)ethoxy]ethoxy}-1,1′-binaphthalen-2-yl 3-benzoylpropionate 4j. Eluent: 50% ethyl acetate in benzene; yield 76%; $[\alpha]_D^{23}$ +26.4 (*c* 1.19 in $CHCl_3$) (Found: C, 74.95; H, 6.2. $C_{37}H_{36}O_7$ requires C, 75.0; H, 6.1%); ν_{max}(film)/cm^{-1} 2875, 1759, 1682, 1206 and 1147; δ_H 2.35–2.85 (4 H, m, $ArO_2CCH_2CH_2COPh$), 3.0–3.50 [10 H, m, $CH_2O(CH_2CH_2O)_2Me$], 3.32 (3 H, s, OMe), 4.08 (2 H, t, *J* 4.9, $ArOCH_2$) and 7.15–8.0 (17 H, m, Ar); δ_C (CD_2Cl_2) 28.7, 33.6, 58.9, 69.8, 70.1, 70.5, 70.6, 70.9, 72.2, 115.7, 118.6, 122.4, 124.2, 125.5, 125.9, 126.4, 126.9, 128.3, 128.4, 128.7, 128.8, 129.1, 129.5, 130.4, 132.1, 133.5, 134.0, 136.6, 147.2, 154.8, 171.2 (CO_2Ar) and 197.5 (Ph*C*O).

(*R*)-2′-(2-Methoxyethoxy)-1,1′-binaphthalen-2-yl 4-oxopentanoate 5. Eluent: 17% ethyl acetate in benzene; yield 83%; $[\alpha]_D^{21}$ +44.8 (*c* 1.21 in $CHCl_3$) (Found: C, 75.8; H, 6.0. $C_{28}H_{26}O_5$ requires C, 76.0; H, 5.9%); ν_{max}(film)/cm^{-1} 2925, 1750, 1718, 1211 and 1137; δ_H 1.92 (3 H, s, COMe), 2.12–2.41 (4 H, m, $ArO_2CCH_2CH_2COMe$), 2.99 (3 H, s, OMe), 3.27–3.40 (2 H, m, CH_2OMe), 4.06 (2 H, t, *J* 5.0, $ArOCH_2$) and 7.16–7.99 (12 H, m, Ar); δ_C (CD_2Cl_2) 28.3, 29.5, 37.9, 59.0, 69.9, 71.3, 116.0, 118.7, 122.3, 124.2, 125.6, 125.8, 126.4, 126.7, 126.8, 128.2, 128.4, 129.1, 129.6, 130.3, 132.0, 134.0, 147.2, 154.9, 171.1 (CO_2Ar) and 206.0 (Me*C*O).

(*R*)-2′-[2-(2-Methoxyethoxy)ethoxy]-1,1′-binaphthalen-2-yl 4-oxopentanoate 6. Eluent: 10% ethyl acetate in benzene; yield 69%; $[\alpha]_D^{24}$ +32.6 (*c* 1.30 in $CHCl_3$) (Found: C, 73.8; H, 6.2. $C_{30}H_{30}O_6$ requires C, 74.05; H, 6.2%); ν_{max}(film)/cm^{-1} 2876, 1757, 1715, 1211 and 1139; δ_H 1.90 (3 H, s, COMe), 2.1–2.4 (4 H, m, $ArO_2CCH_2CH_2COMe$), 3.20 (3 H, s, OMe), 3.0–3.15 and 3.4–3.6 (6 H, m, $CH_2OCH_2CH_2OMe$), 4.10 (2 H, t, *J* 4.8, $ArOCH_2$) and 7.1–8.0 (12 H, m, Ar); δ_C 28.0, 29.5, 37.6, 58.8, 69.4, 69.8, 70.4, 71.6, 115.0, 118.3, 121.8, 123.8, 125.0, 125.4, 125.5, 126.2, 126.4, 126.6, 127.8, 128.0, 128.8, 129.1, 129.9, 131.6, 133.7, 146.7, 154.3, 170.8 (CO_2Ar) and 205.9 (Me*C*O).

(*R*)-2′-(2-Methoxyethoxy)-1,1′-binaphthalen-2-yl 5-methyl-4-oxohexanoate 7. Eluent: 10% ethyl acetate in benzene; yield 98%; $[\alpha]_D^{10}$ +36.9 (*c* 1.00 in $CHCl_3$) (Found: C, 76.9; H, 6.5. $C_{30}H_{30}O_5$ requires C, 76.6; H, 6.4%); ν_{max}(film)/cm^{-1} 2970, 1759, 1713, 1212 and 1144; δ_H 0.96 and 0.97 (each 3 H, d, *J* 6.9, $CHMe_2$), 2.12–2.41 (5 H, m, $ArO_2CCH_2CH_2COCHMe_2$), 2.98 (3 H, s, OMe), 3.25–3.40 (2 H, m, CH_2OMe), 4.06 (2 H, t, *J* 5.1, $ArOCH_2$) and 7.16–7.98 (12 H, m, Ar); δ_C 18.1, 28.0, 34.4, 40.5, 58.9, 69.9, 70.9, 115.8, 118.8, 121.8, 123.9, 124.9, 125.4, 125.5, 126.2, 126.3, 126.5, 127.7, 127.9, 128.3, 128.9, 129.2, 129.9, 131.6, 133.6, 133.7, 146.7, 154.4, 171.0 (CO_2Ar) and 212.0 (Pr^iCO).

2-Naphthyl 3-benzoylpropionate 15. Eluent: 10% ethyl acetate in benzene; yield 89%; mp 99.6–100.1 °C (from benzene–hexane) (Found: C, 79.15; H, 5.5. $C_{20}H_{16}O_3$ requires C, 78.9; H, 5.3%); ν_{max}(KBr)/cm^{-1} 1752, 1680, 1210 and 1149; δ_H 3.08 (2 H, t, *J* 6.5, ArO_2CCH_2), 3.47 (2 H, t, *J* 6.5, CH_2COPh) and 7.24–8.05 (12 H, m, Ar); δ_C (CD_2Cl_2) 28.8 (CH_2CO_2Ar), 33.9 ($PhCOCH_2$), 116.8, 121.6, 126.1, 126.9, 127.9, 128.1, 128.3, 129.0, 129.6, 131.8, 133.6, 134.1, 136.9, 148.9, 172.1 (CO_2Ar) and 198.2 (Ph*C*O).

Representative procedure for the DIBAL-H reductions (Table 2, run 7)

To a stirred solution of the keto ester **4h** (54 mg, 0.096 mmol) in

CH_2Cl_2 (4.8 cm^3) was added $MgBr_2 \cdot OEt_2$ (78 mg, 0.30 mmol) at ambient temperature. The resulting dispersion was stirred for 1 h and then cooled to −78 °C. After 1 h, an excess of DIBAL-H solution in toluene (1.0 mol dm^{-3}; 0.4 cm^3, 0.4 mmol) was added dropwise during 5 min to the dispersion. The mixture was stirred for 2 h at −78 °C to complete the reduction of the ketocarbonyl group. Then, LAH (20 mg, 0.53 mmol) was added to the mixture which was then stirred at room temperature until the hydroxy ester was completely converted into the chiral auxiliary and the diol. Ethyl acetate (1 cm^3) and dilute hydrochloric acid (2 mol dm^{-3}; 5 cm^3) were added successively to the reaction mixture, after which it was extracted with $CHCl_3$ (3 × 30 cm^3). The combined extracts were washed with brine, dried, and evaporated *in vacuo*. The crude product was purified by preparative TLC (20% ethyl acetate in benzene) to yield 1-phenylbutane-1,4-diol **8** (14 mg, 85%) and the recovered chiral auxiliary **2h** (37 mg, 95%). The diol thus obtained was converted to its bis(3,5-dinitrophenylcarbamate) by the procedure reported by Pirkle *et al.*[30] and then subjected to HPLC determination of the ee. The physical and spectral characteristics of the diols **8** and **9** are given below.

(*S*)-(−)-1-Phenylbutane-1,4-diol 8.[31] $[a]_D^{20}$ −39.3 (*c* 0.52 in benzene), 82% ee; ν_{max}(KBr)/cm^{-1} 3325, 2890, 1072, 1042 and 1013; δ_H (60 MHz) 1.5–2.0 (4 H, m, $CH_2CH_2CH_2OH$), 2.1 (2 H, br s, OH), 3.68 (2 H, t, *J* 6, CH_2OH), 4.72 (1 H, t, *J* 6, PhC*H*OH) and 7.32 (5 H, br s, Ph).

(*R*)-(−)-Pentane-1,4-diol 9. $[a]_D^{20}$ −1.9 (*c* 0.98 in EtOH), 21% ee {lit.,[32] $[a]_D^{16}$ −11.7 (*c* 1.0 in EtOH) for (*R*)-**9** of 90% ee}; ν_{max}(film)/cm^{-1} 3320, 2932, 1134, 1057 and 1011; δ_H 1.19 (3 H, d, *J* 6, Me), 1.4–1.7 (4 H, m, $CH_2CH_2CH_2OH$), 3.63 (2 H, m, CH_2OH), 3.80 (1 H, br s, MeC*H*OH), 4.15 (1 H, br s, OH) and 4.31 (1 H, br s, OH).

Representative procedure for the Grignard reactions (Table 3, run 12)

To a stirred solution of the keto ester **5** (52 mg, 0.12 mmol) in CH_2Cl_2 (5.9 cm^3) was added $MgBr_2 \cdot OEt_2$ (91 mg, 0.35 mmol) at ambient temperature. The resulting dispersion was stirred for 1 h and then cooled to −78 °C. After 1 h, an excess of PhMgBr solution in Et_2O (1.0 mol dm^{-3}; 0.4 cm^3, 0.4 mmol) was added dropwise during 5 min to the dispersion. The mixture was stirred for 5 h at −78 °C to complete the reaction. Then, distilled water (5 cm^3) was added to the mixture which was then extracted with Et_2O (5 × 30 cm^3). The combined extracts were washed with brine, dried, and evaporated *in vacuo*. The crude product was purified by preparative TLC (15% ethyl acetate in benzene) to yield 4-methyl-4-phenylbutan-4-olide **10** (15 mg, 74%) and the recovered chiral auxiliary **2b** (39 mg, 95%). The physical and spectral characteristics of the lactones **10**–**13** are given below.

(*S*)-(−)-4-Phenyl-4-methylbutan-4-olide 10. $[a]_D^{15}$ −59 (*c* 1.2 in $CHCl_3$), 95% ee [lit.,[13] +72.4 (*c* 1.3 in $CHCl_3$) for (*R*)-**10** of 100% ee]; ν_{max}(film)/cm^{-1} 2980, 1770, 1242 and 1134; δ_H 1.73 (3 H, s, Me), 2.35–2.70 (4 H, m, CH_2CH_2), 7.26–7.40 (5 H, m, Ph).

(*S*)-(−)-4-Phenyl-4-ethylbutan-4-olide 11. $[a]_D^{23}$ −70 (*c* 0.56 in CCl_4), 92% ee [lit.,[14] $[a]_D^{25}$ +84.7 (*c* 4.4 in CCl_4) for (*R*)-**11** of 100% ee]; ν_{max}(film)/cm^{-1} 2972, 1770, 1195, 1148 and 1108; δ_H 0.82 (3 H, t, *J* 6.1, CH_2CH_3), 2.00 (2 H, q, *J* 6.1, CH_2CH_3), 2.35–2.70 (4 H, m, CH_2CH_2) and 7.16–7.40 (5 H, m, Ph).

(*S*)-(−)-4-Ethyl-4-methylbutan-4-olide 12. $[a]_D^{25}$ −7.46 (*c* 1.12 in $CHCl_3$), 87% ee {lit.,[13,15] $[a]_D^{15}$ +10.4 (*c* 1.2 in $CHCl_3$) for (*R*)-**12** of 100% ee,[13] and −10.3 for (*S*)-**12**[15]}; ν_{max}(film)/cm^{-1} 2975, 1765, 1240, 1166 and 1134; δ_H 0.97 (3 H, t, *J* 7.5, CH_2CH_3), 1.38 (3 H, s, Me), 1.57–1.83 (2 H, m, CH_2CH_3), 1.88–2.20 (2 H, m, CH_2CH_2C=O) and 2.48–2.75 (2 H, m, CH_2CH_2C=O).

(*S*)-(+)-4-Isopropyl-4-methylbutan-4-olide 13. $[a]_D^{23}$ +10.4 (*c* 1.05 in $CHCl_3$), 92% ee {lit.,[16] $[a]_D^{21}$ −10.2 (*c* 1.07 in $CHCl_3$) for (*R*)-**13** of 92.4% ee}; ν_{max}(film)/cm^{-1} 2960, 1764, 1258, 1171 and 1085; δ_H 0.86 and 0.91 (each 3 H, d, *J* 6.8, $CHMe_2$), 1.23 (3 H, s, Me), 1.78–1.90 (2 H, m, CH_2CH_2C=O), 1.97–2.10 (1 H, m, $CHMe_2$) and 2.42–2.68 (2 H, m, CH_2CH_2C=O).

Conversion of the optically active diol (*S*)-(−)-8 into (*S*)-(−)-1-phenylbutan-1-ol

To a solution of the optically active 1-phenylbutane-1,4-diol **8** {124 mg, 0.746 mmol, $[a]_D^{20}$ −39.3 (*c* 0.52 in benzene), 82% ee} in anhydrous ethyl acetate (15 cm^3) was added alumina for column chromatography (10 g) at ambient temperature. The mixture was heated to reflux for 24 h and then cooled and the aluminia was filtered off. The filtrate was evaporated *in vacuo* and the residue was purified by column chromatography on silica using 30% ethyl acetate in benzene as eluent to give *4-acetoxy-1-phenylbutan-1-ol* (87 mg, 56%) as a colourless oil, ν_{max}(film)/cm^{-1} 3440, 2995 and 1738; δ_H 1.58–1.84 (5 H, m, $AcOCH_2CH_2CH_2$ and OH), 2.04 (3 H, s, Me), 4.08 (2 H, m, CH_2OAc), 4.69 (1 H, m, PhC*H*OH) and 7.30 (5 H, s, Ph).

To a stirred solution of the monoacetate thus obtained (50 mg, 0.24 mmol) in DMF (2 cm^3) was added successively *tert*-butyl(chloro)dimethylsilane (73 mg, 0.48 mmol) and imidazole (66 mg, 0.96 mmol) at ambient temperature. After being stirred for 3 h, dilute hydrochloric acid (2 mol dm^{-3}; 1 cm^3) was added dropwise to the mixture which was then extracted with $CHCl_3$ (3 × 30 cm^3). The combined extracts were washed successively with saturated aqueous $NaHCO_3$ and brine, dried, and evaporated to dryness. The residue was purified by preparative TLC (20% ethyl acetate in hexane) to yield *1-acetoxy-4-(tert-butyldimethylsiloxy)-4-phenylbutane* (69 mg, 89%) as a colourless oil, ν_{max}(film)/cm^{-1} 2955, 2850, 1743, 1245, 1093 and 1045; δ_H(60 MHz) −1.60 (3 H, s, SiMe), 0.00 (3 H, s, SiMe), 0.87 (9 H, s, Bu^t), 1.52–1.72 (4 H, m, $AcOCH_2CH_2CH_2$), 1.99 (3 H, s, OAc), 4.00 (2 H, m, CH_2OAc), 4.64 (1 H, m, PhC*H*OSi) and 7.23 (5 H, s, Ph).

To a stirred solution of the silyl ether thus obtained (69 mg, 0.21 mmol) in Et_2O (5 cm^3) was added LAH (16 mg, 0.42 mmol) portionwise at ambient temperature. After being stirred for 1 h, ethyl acetate (1 cm^3) and then dilute hydrochloric acid (2 mol dm^{-3}; 1 cm^3) were added dropwise to the mixture which was then extracted with $CHCl_3$ (3 × 30 cm^3). The combined extracts were dried and evaporated to dryness. The residue was purified by preparative TLC (30% ethyl acetate in benzene) to yield *4-(tert-butyldimethylsiloxy)-4-phenylbutan-1-ol* (51 mg, 86%) as a colourless oil, ν_{max}(film)/cm^{-1} 3330, 2930, 2855, 1467, 1251, 1092 and 1056; δ_H(60 MHz) −1.60 (3 H, s, SiMe), 0.00 (3 H, s, SiMe), 0.87 (9 H, s, Bu^t), 1.53–1.80 (5 H, m, $AcOCH_2CH_2CH_2$ and OH), 3.57 (2 H, t, *J* 5, CH_2OAc), 4.68 (1 H, t, *J* 6, PhC*H*OSi) and 7.23 (5 H, s, Ph).

To a stirred solution of the siloxyalcohol thus obtained (37 mg, 0.13 mmol) in pyridine (2 cm^3) was added successively toluene-*p*-sulfonyl chloride (75 mg, 0.39 mmol) and DMAP (32 mg, 0.26 mmol) at ambient temperature. After being stirred for 2 h, dilute hydrochloric acid (2 mol dm^{-3}; 10 cm^3) was added dropwise to the mixture which was then extracted with $CHCl_3$ (3 × 30 cm^3). The combined extracts were dried and evaporated to dryness. The residue was purified by preparative TLC (30% ethyl acetate in hexane) to yield *1-(tert-butyldimethylsiloxy)-4-(p-tolylsulfonyloxy)-1-phenylbutane* (30 mg, 52%) as a colourless oil, ν_{max}(film)/cm^{-1} 2955, 2855, 1596, 1468, 1363, 1255, 1176 and 1096; δ_H(60 MHz) −1.60 (3 H, s, SiMe), 0.00 (3 H, s, SiMe), 0.87 (9 H, s, Bu^t), 1.53–1.76 (4 H, m, $TsOCH_2CH_2CH_2$), 2.45 (3 H, s, Ar*Me*), 4.00 (2 H, m, CH_2OAc), 4.61 (1 H, m,

PhC*H*OSi), 7.3 (5 H, s, Ph), 7.36 (2 H, d, *J* 8, Ar-H of Ts) and 7.81 (2 H, d, *J* 8, Ar-H of Ts).

To a stirred solution of the tosylate thus obtained (25 mg, 0.057 mmol) in Et_2O (2 cm^3) was added LAH (22 mg, 0.56 mmol) portionwise at ambient temperature. After being stirred for 1 h, ethyl acetate (1 cm^3) and then dilute hydrochloric acid (2 mol dm^{-3}; 1 cm^3) were added dropwise to the mixture which was then extracted with $CHCl_3$ (3 × 30 cm^3). The combined extracts were dried and evaporated to dryness. The residue was purified by preparative TLC (30% ethyl acetate in hexane) to yield *1-(tert-butyldimethylsiloxy)-1-phenylbutane* (14 mg, 92%) as a colourless oil, ν_{max}(film)/cm^{-1} 2955, 2855, 1459, 1254, 1106, 1082, 1063 and 1037; δ_H(60 MHz) −1.60 (3 H, s, SiMe), 0.00 (3 H, s, SiMe), 0.87 (9 H, s, Bu^t), 0.76–0.96 (3 H, m, $CH_3CH_2CH_2$), 1.18–1.76 (4 H, m, $CH_3CH_2CH_2$), 4.62 (1 H, t, *J* 6, PhC*H*OSi) and 7.23 (5 H, s, Ph).

To a stirred solution of the silylether (14 mg, 0.050 mmol) in THF (0.5 cm^3) was added 66% aqueous acetic acid (1 cm^3) at ambient temperature. The mixture was heated at 40 °C for 24 h and then cooled to room temperature. To the solution was added saturated aqueous $NaHCO_3$ and the mixture was extracted with $CHCl_3$ (3 × 30 cm^3). The combined extracts were washed with saturated aqueous $NaHCO_3$ (2 × 10 cm^3), dried and evaporated to dryness. The residue was purified by preparative TLC (50% ethyl acetate in benzene) to yield *1-phenylbutan-1-ol* (7.0 mg, 93%) as a colourless solid, $[\alpha]_D^{22}$ −43 (*c* 0.64 in benzene) [lit.,[33] −45.2 (*c* 4.81 in benzene), for the (*S*)-isomer of 100% ee]; ν_{max}(KBr)/cm^{-1} 3250, 2929, 2855, 1444, 1301 and 1030; δ_H(60 MHz) 0.48–1.88 (8 H, m, *Me*CH_2CH_2 and OH), 4.58 (1 H, t, *J* 6, PhC*H*OH) and 7.22 (5 H, s, Ph).

Complexation studies

In a typical experiment, CD_2Cl_2 (2.0 cm^3) was added to a mixture of the keto ester **5e** (0.04 mmol) and $MgBr_2{\cdot}OEt_2$ (0.12 mmol) at ambient temperature. The mixture was stirred for 1 h and then transferred to an NMR tube under an nitrogen atmosphere *via* syringe after filtration through a polytetrafluoroethylene membrane filter (mean pore size: 0.1 μm). The ^{13}C NMR spectrum was recorded, and then 7 vol% of Et_2O was added to the NMR tube and the spectrum was recorded again.

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