Investigation of the Diastereoselectivity in the Addition of Organometallics to the α-Keto Esters of Axially Chiral 1,1'-Binaphthalen-2-ol Derivatives

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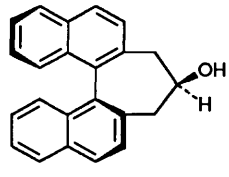
The inherent chiral induction abilities of axially chiral 2'-substituted 1,1'-binaphthalen-2-ols **2a–f** as the chiral auxiliary for the addition of organometallics to their α-keto acid esters were examined as a function of the following reaction variables: size of the 2'-substituent, nature of the organometallic reagent, solvent, and temperature. In the addition of MeMgI to the phenylglyoxylates **3a–f** of the alcohols **2a–f**, the corresponding atrolactic acid esters **5a–f** and **6a–f** were obtained with up to 52% diastereoisomeric excess (d.e.). The preferred diastereoisomer depended on the size of the 2'-substituent, and thus could not solely be determined by the helicity of the 1,1'-binaphthalene framework. By using MeZnI as the nucleophile, the selectivity increased up to 84% d.e. with the same diastereofacial selectivity as that of MeMgI. On the other hand, the diastereofacial selection was reversed when $MeTiCl_3$ was employed as the nucleophile, with low selectivity (14% d.e.).

It is concluded that MeMgI or MeZnI, as a nucleophile of low Lewis acidity, adds to the keto ester moiety in the s-*trans* conformation, while the strong Lewis acid $MeTiCl_3$ mainly adds to the s-*cis* conformer from the same direction as that of the Grignard addition, thus giving the opposite diastereoisomer.

Diastereoselective nucleophilic addition of an organometallic reagent to a chiral α-keto acid derivative is one of the most important methods to obtain optically active α,α-disubstituted α-hydroxy acid derivatives which are valuable synthetic intermediates in natural products syntheses.[1] A number of C-centro-chiral alcohols and amines have been employed as chiral auxiliaries,[2] and, recently, remarkably high stereoselectivity [>95% diastereoisomeric excess (d.e.)] has been achieved by using 8-phenylmenthol,[3] a C_2-chiral pyrrolidine derivative,[4] a chiral inositol derivative,[5] and *trans*-2-*tert*-butylcyclohexanol.[6] It is well known that the preferred diastereoisomer formed by the addition of a Grignard reagent to the α-keto acid esters of C-centro-chiral alcohols can correctly be predicted by Prelog's generalization.[2] On the other hand, in spite of the wide applicability of axially chiral 1,1'-binaphthalene derivatives as chiral inducers,[7] there have been only a handful of investigations using them as the chiral auxiliary for α-keto acids in the diastereoselective addition of organometallics.[8] Although Prelog's rule has been successfully extended to (−)-binaphthyl pentacycle **1** by Mislow *et al.* in an



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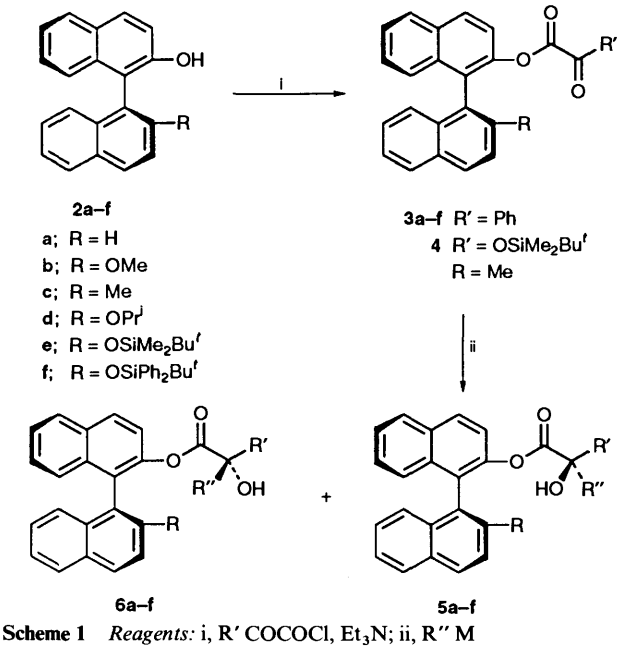
hydroxy acid asymmetric synthesis,[9] it has been claimed that Berson and Greenbaum's model proposed for 1,1'-binaphthalen-2-ol **2a** could not correctly predict the direction of asymmetric induction.[10,11] In this article, we wish to describe the results of a detailed study of the diastereoselectivity in the addition of several organometallics to the α-keto acid esters **3a–f** and **4** of 2'-substituted 1,1'-binaphthalen-2-ols **2a–f** (Scheme 1).[12]

Results and Discussion

Synthesis of Axially Chiral α-Keto Acid Esters.—Enantiomerically pure (*R*)-1,1'-binaphthalen-2-ol **2a**,[12] (*S*)-2'-alkoxy-1,1'-binaphthalen-2-ols **2b** and **2d**,[13] and (*S*)-2'-trialkylsiloxy-1,1'-binaphthalen-2-ols **2e** and **2f**[14] were synthesized according to literature methods. (*R*)-2'-Methyl-1,1'-binaphthalen-2-ol **2c** was synthesized from enantiomerically pure (*S*)-2'-methoxy-1,1'-binaphthalene-2-carboxylic acid **7**[15] as depicted in Scheme 2. Phenylglyoxylic acid esters **3a–f** and pyruvic acid ester **4** were prepared in high yields by the esterification of the hydroxy compounds **2a–f** with the corresponding acid chloride[16] in diethyl ether in the presence of triethylamine (Scheme 1).



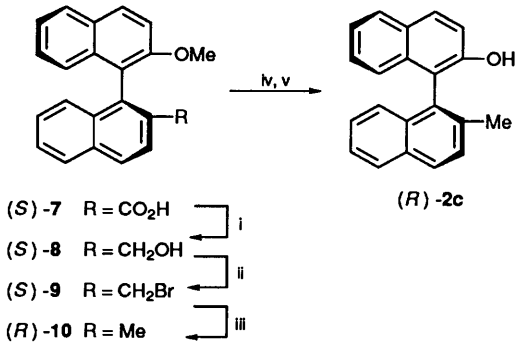
Scheme 1 *Reagents:* i, R' COCOCl, Et_3N; ii, R'' M

Addition of Organometallics to the Phenylglyoxylates **3a–f**.—In order to examine the role of the 2'-substituent of the chiral auxiliaries **2a–f** on the diastereoselectivity, MeMgI was added to the phenylglyoxylates **3a–f** in diethyl ether in the tempera-

Table 1 Nucleophilic addition of MeMgI to the α-keto esters **3a–f**[a]

Entry	Substrate	R	Temp. (T/°C)	Yield[b] (%)	5:6
1	**3a**	H	reflux	93 (99[c])	42:58 (41.5:58.5[c])
2	**3a**	H	−78	95	48:52
3	**3b**	OMe	reflux	88	37.5:62.5
4	**3b**	OMe	−78	76	47:53
5	**3c**	Me	reflux	63	38:62
6	**3c**	Me	0	67	41:59
7	**3c**	Me	−40	82	47.5:52.5
8	**3c**	Me	−78	74	58:42
9	**3d**	OPr^i	reflux	76	50:50
10	**3d**	OPr^i	−78	91	58:42
11	**3e**	$OSiMe_2Bu^t$	reflux	67	68:32
12	**3e**	$OSiMe_2Bu^t$	−78	97	75:25
13	**3f**	$OSiPh_2Bu^t$	reflux	76	68:32
14	**3f**	$OSiPh_2Bu^t$	−78	98	76:24

[a] The reactions were performed using MeMgI (1.0 mol dm^{-3}) in diethyl ether ([substrate] = 0.02 mol dm^{-3}). [b] Yields are based on the consumed starting materials. [c] Data from a duplicate experiment.



Scheme 2 *Reagents:* i, $LiAlH_4$, Et_2O; ii, HBr, AcOH; iii, $LiAlH_4$, THF; iv, BBr_3, CH_2Cl_2; v, H_3O^+

ture range −78 °C to reflux to afford the corresponding atrolactic acid esters **5a–f** and **6a–f** (Scheme 1 and Table 1). The ratio of diastereoisomeric products **5**:**6** was determined by ^1H NMR (250 MHz) spectroscopy by using the peak areas of the NMR singlets due to either the tertiary hydroxy protons or to the methyl protons of the atrolactic acid residue. The absolute configuration of the newly formed chiral centre of the preferred diastereoisomer was determined from the specific rotation of the corresponding atrolactic acid after complete hydrolysis of the diastereoisomeric mixture.

The reaction of compound **3a** at the reflux temperature preferentially afforded the diastereoisomer **6a** having (*S*)-centro-chirality on the atrolactic acid residue with 16% d.e. (entry 1, Table 1).* Similarly, the reactions of glyoxylates **3b** and **3c** at the same temperature preferentially gave the diastereoisomers **6b** and **6c**, respectively (entries 3 and 5). On the other hand, no diastereoselection was observed in the reaction of compound **3d**, which gave a 1 : 1 mixture of products **5d** and **6d** (entry 9). Eventually, (*R*)-centro-chirality was preferred in the reaction of the siloxy substrates **3e** and **3f** to yield the diastereoisomers **5e** and **5f**, respectively, with up to 36% d.e. (entries 10 and 13). The observed stereoselectivity seems to indicate that the formation of (*R*)-atrolactates **5** is favoured with an increase in the apparent bulk of the 2′-substituent (H < OMe < Me < OPr^i < $OSiMe_2Bu^t$ < $OSiPh_2Bu^t$), though the origin of the irregularity with compound **3a** is not clear at present. Thus, the sense of the diastereoselection could not solely be determined by the helicity of the 1,1′-binaphthalene framework.

Interestingly, contrary to the conventional Prelog atrolactic acid synthesis employing C-centro-chiral alcohols as chiral auxiliaries,[2] the diastereoselectivities were strongly influenced by the reaction temperature. In the reactions of compounds **3d–f**, the selectivities increased with a lowering of the temperature, while the reactions of compounds **3a** and **3b**, which have smaller 2′-substituents than do compounds **3d–f**, exhibited the opposite temperature dependence. Moreover, in the reaction of compound **3c**, lowering of the temperature from reflux to −78 °C even reversed the preferred diastereoisomer (entries 5–8). In other words, lowering of the temperature gave preferred formation of diastereoisomer **5** at the expense of diastereoisomer **6** in the reaction of compounds **3a–c**.

To gain more insight into the chiral induction mechanism and to improve the selectivity, the effect of the solvent and the nature of the organometallic reagent on the diastereoselectivity were examined for substrate **3e** at −78 °C and the results are presented in Table 2. By employing tetrahydrofuran (THF), toluene or dichloromethane as the solvent, the diastereoselectivity in the addition of MeMgI was depressed as compared with that obtained by using diethyl ether. On the other hand, the diastereoselectivity was greatly increased when MeMgX was added to a mixture of the substrate and ZnX_2; the addition of MeMgI to compound **3e** in the presence of ZnI_2 yielded the diastereoisomer **5e** in 84% d.e. (entry 6, Table 2). The reaction of an ethereal solution of MeZnI (0.5 mol dm^{-3}), prepared from MeMgI and ZnI_2 *in situ*, resulted in almost the same selectivity (80% d.e., entry 7), indicating that the active nucleophiles in entries 4–6 should be methylzinc species MeZnX. Furthermore, the halogen atom X of the nucleophiles apparently influenced the selectivity (entries 4–6 and 8–10); the selectivity increases in the order X = I > Br > Cl.†

Contrary to the reaction of MeMgX or MeZnX, the addition of $MeTiCl_3$ to compound **3e** in dichloromethane afforded the diastereoisomer **6e** in 14% d.e. (entry 11).[18] The preferred diastereoisomer also changed in the reaction of the pyruvate **4**; the addition of PhMgBr or PhZnBr yielded the diastereoisomer **5e** preferentially with up to 40% d.e. (entries 12–14), whereas $PhTiCl_3$ provided **6e** with 64% d.e. (entry 15).

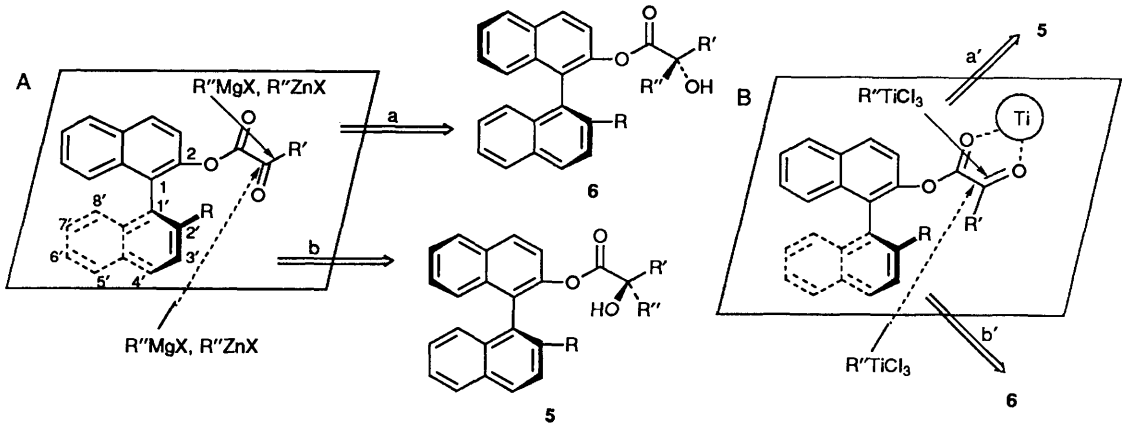
* The present experimental data are rather different from those reported by Berson and Greenbaum.[8] Several reinvestigations, and experiments varying the reaction conditions, could not reproduce their reported data.

† For the effect of ZnX_2 on the selectivity of the Grignard reaction of chiral α-keto esters, see ref. 17(*a*). Contrary to our results, they observed that the selectivity increased in the order X = Cl > Br for the reaction of RMgX (R ≠ Me); in the reaction of MeMgX, the addition of ZnX_2 showed almost no effect on the selectivity. See also refs 16 and 17(*b*).

Table 2 The addition of organometallics to α-keto esters **3e** and **4**[a]

Entry	Substrate	R′	R″M	Lewis acid[b]	Solvent	Yield[c] (%)	5:6
1	**3e**	Ph	MeMgI	none	THF	99	70:30
2	**3e**	Ph	MeMgI	none	CH_2Cl_2	99	70:30
3	**3e**	Ph	MeMgI	none	Toluene	99	64:36
4	**3e**	Ph	MeMgI	$ZnCl_2$	Et_2O	99 (99)[d]	82:18 (84:16)[d]
5	**3e**	Ph	MeMgI	$ZnBr_2$	Et_2O	99	87:13
6	**3e**	Ph	MeMgI	ZnI_2	Et_2O	98 (99)[d]	92:8 (92:8)[d]
7	**3e**	Ph	MeZnI[e]	none	Et_2O	98	90:10
8	**3e**	Ph	MeMgBr	none	Et_2O	89	66:34
9	**3e**	Ph	MeMgBr	$ZnBr_2$	Et_2O	99	66:34
10	**3e**	Ph	MeMgBr	ZnI_2	Et_2O	71	89:11
11	**3e**	Ph	$MeTiCl_3$[f]	none	CH_2Cl_2	62	43:57
12	**4**	Me	PhMgBr	none	Et_2O	74	67:33
13	**4**	Me	PhMgBr	$ZnBr_2$	Et_2O	86	70:30
14	**4**	Me	PhMgBr	ZnI_2	Et_2O	97	68:32
15	**4**	Me	$PhTiCl_3$[f]	none	CH_2Cl_2	71	18:82

[a] Unless otherwise noted, the reactions were performed by adding an ethereal solution of the Grignard reagent (1.0 mol dm^{-3}) to the substrate solution at −78 °C ([substrate] = 0.02 mol dm^{-3}). [b] ZnX_2 (ZnX_2/substrate = 1.1) was added to the substrate solution at ambient temperature prior to the addition of the Grignard reagent. [c] Yields are based on the consumed substrates. [d] Data from a duplicate experiment. [e] MeZnI (0.5 mol dm^{-3} in diethyl ether) was prepared from an ethereal solution of ZnI_2 (1.0 mol dm^{-3}) and MeMgI (1.0 mol dm^{-3}) at ambient temperature. [f] $RTiCl_3$ was prepared by adding an ethereal solution of RMgBr (1.0 mol dm^{-3}) to 1.1 mol equiv. of $TiCl_4$ in CH_2Cl_2 at −23 °C. The nucleophilic addition was carried out at −23 °C.



Scheme 3

Mechanistic Considerations with regard to the Asymmetric Induction.—The above mentioned diastereoselectivity, which depends on the size of the 2′-substituent, the solvent, and the nature of the nucleophile, gives some clues as to the chiral induction mechanism. The reversal of the preferred diastereoisomer by changing the organometallic reagent from RMgX or RZnX to $RTiCl_3$ may suggest that weakly Lewis acidic species RMgX and RZnX react with the keto esters *via* a non-chelation-controlled mechanism. The solvent effect also supports this mechanism; in chelation-controlled Grignard reactions of chiral carbonyl compounds,* higher diastereoselectivity has been usually observed when employing THF, toluene, or dichloromethane as the solvent compared with that obtained when using diethyl ether. From these results, the α-keto ester moiety of substrates **3a–f** seems to react as the s-*trans* conformer due to the dipole–dipole repulsion of the two carbonyl groups in the transition state for the addition of R^3MgX and R^3ZnX. A steric model depicted in Scheme 3 may explain the diastereoselectivity. In the reaction of substrates **3d–f** having a bulky 2′-substituent, the steric hindrance imposed by the C(2′)–R^1 grouping would be larger than that imposed by the C(5′)–C(8′) moiety; the dihedral angle of the two naphthalene planes of the 1,1′-binaphthalene skeleton seems to be ~90°.[19] Therefore, weakly Lewis acidic organometallics R^3MgX or R^3ZnX attack the s-*trans* keto carbonyl group from the lower side of the depicted plane to yield the diastereoisomer **5** (Scheme **3A**, path b), while strongly Lewis acidic reagents R^3TiCl_3 preferentially add to the carbonyl group in the s-*cis* conformation from the same direction to result in the opposite diastereoisomer **6** preferentially (Scheme **3B**, path b′). The rather low selectivity observed in the reaction of R^3TiCl_3 might be due to the unfavourable s-*cis* conformation imposed by the steric repulsion between the phenyl or methyl group and the naphthalene group bearing the 2′-substituent, as CPK-molecular models seem to indicate. When the 2′-substituent is H, OMe or Me, the steric hindrance caused by the C(2′)–R^1 grouping seems to be smaller than that by the C(5′)–C(8′) moiety; MeMgI attacks the keto carbonyl group preferentially from the less hindered upper, C(2′)–R^1 side to give the diastereoisomer **6** (Scheme 3A, path a). A plot of ln(**6c**/**5c**) against reciprocal temperature gives a straight line (Fig. 1), indicating that a single mechanism is operative in this diastereoselective reaction. Although it is difficult to explain clearly the temperature dependence of the selectivity in the reaction of compounds **3a–c**,[20] one possible explanation for

* In some reports, chelation-controlled Grignard additions to chiral ketones gave higher selectivities in THF than those in diethyl ether; see ref. 4 and references cited therein, and ref. 5.

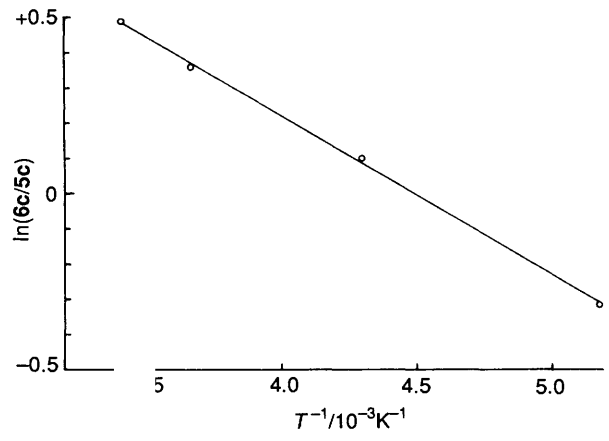


Fig. 1 Eyring diagram for the addition of MeMgI to compound **3c** in diethyl ether

the unusual temperature effect in the reaction of compounds **3a–c** is that raising the reaction temperature would enhance the flip-flop mobility of the two naphthalene rings around the 1,1′-axis. The 2′-substituents of compounds **3a–c** are considerably smaller than the C(5′)–C(8′) moiety, and thus the increased flip-flop motion seems to increase the exclusion volume of the C(5′)–C(8′) moiety more effectively than that of the 2′-substituent.

In conclusion, the preferred diastereoisomer of the Prelog atrolactic acid synthesis using axially chiral 1,1′-binaphthalen-2-ol derivatives as chiral auxiliaries depends on the size of the 2′-substituent, and thus could not solely be determined by the helicity of the 1,1′-binaphthalene framework. Furthermore, the degree of the diastereoselection is strongly influenced by the size of the 2′-substituent, reaction temperature, solvent, and the Lewis acidity of the organometallic reagent; the addition of the *in situ*-generated MeZnI to the phenylglyoxylate of 2′-(*tert*-butyldimethylsiloxy)-1,1′-binaphthalen-2-ol in diethyl ether at −78 °C gave the corresponding atrolactic acid ester with up to 84% d.e.

Experimental

General Methods.—M.p.s were measured on a Yamato MP-21 instrument and are uncorrected. Microanalyses were carried out in 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, and are given in units of 10^{-1} deg cm^2 g^{-1}. IR spectra were measured on a Shimadzu IR-460 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL JNM-FX60 instrument or a Bruker AC-250T instrument. Chemical shifts are reported relative to internal $SiMe_4$, and J values are given in Hz. Reactions were carried out under N_2 with the use of standard procedures for the exclusion of moisture unless otherwise noted. Column chromatography was performed by using silica gel (Nacalai Tesque, Inc., Silica Gel 60, 70–230 mesh). Na_2SO_4 was employed for the drying of extracts. Optically pure (*R*)-1,1′-binaphthalen-2-ol **2a**,[12] (*S*)-1,1′-binaphthalene-2,2′-diol,[21] (*S*)-2′-methoxy-1,1′-binaphthalen-2-ol **2b**,[13] and (*S*)-2′-(*tert*-butyldimethylsiloxy)-1,1′-binaphthalen-2-ol **2e**[14] were prepared according to the reported procedures. Other reagents were used as received. Solvents were freshly distilled prior to use: diethyl ether, THF and toluene were distilled from sodium diphenyl ketyl; dichloromethane was distilled from CaH_2. Other solvents were purified by distillation.

(S)-2′-*Isopropoxy*-1,1′-*binaphthalen*-2-*ol* **2d**.—To a solution of optically pure (*S*)-1,1′-binaphthalene-2,2′-diol (2.0 g, 6.98 mmol) in *N*,*N*-dimethylformamide (50 cm^3) was added sodium hydride (176 mg, 7.33 mmol) by portions at room temperature. After being stirred for 1 h, the yellow solution was treated with 2-bromopropane (900 mg, 7.33 mmol). The mixture was stirred at 50 °C for 4 h and was then poured into cold, dil. hydrochloric acid (50 cm^3; 2 mol dm^{-3}) and extracted with ethyl acetate. The extract was washed successively with water and brine, dried, and evaporated to dryness. Chromatography on silica gel with benzene as eluent yielded optically pure compound **2d** (1.32 g, 58%) as a glass (Found: C, 84.3; H, 6.2. $C_{23}H_{20}O$ requires C, 84.12; H, 6.14%); $[\alpha]_D$ +86.5 (*c* 0.52, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3400 (OH), 3055 (Ar C–H) and 1663 (Ar C=C); δ_H(250 MHz; $CDCl_3$) 0.98 (3 H, d, *J* 6, Me), 1.12 (3 H, d, *J* 6, Me), 4.43 (1 H, septet, *J* 6, C*H*Me$_2$), 5.07 (1 H, s, OH) and 7.04–8.01 (12 H, m, ArH).

(S)-2′-(tert-*Butyldiphenylsiloxy*)-1,1′-*binaphthalen*-2-*ol* **2f**.—To a stirred solution of optically pure (*S*)-1,1′-binaphthalene-2,2′-diol (2.0 g, 6.98 mmol) and triethylamine (918 mg, 9.1 mmol) in dichloromethane (200 cm^3) was added *tert*-butyl(chloro)(diphenyl)silane (2.49 g, 9.1 mmol) at room temperature. After being stirred for 12 h, the solution was washed successively with dil. hydrochloric acid and water, dried, and evaporated to dryness. Chromatography on silica gel with benzene–hexane (1:1) as eluent, followed by recrystallization from hexane, yielded optically pure title compound **2f** (2.99 g, 82%), m.p. 147.5–148.0 °C (Found: C, 82.6; H, 6.3. $C_{36}H_{32}O_2Si$ requires C, 82.40; H, 6.15%); $[\alpha]_D$ +38.7 (*c* 1.0, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3510 (OH), 3040 (Ar C–H) and 2925 (C–H); δ_H(250 MHz; $CDCl_3$) 0.49 (9 H, s, Bu^t), 5.03 (1 H, s, OH) and 6.87–7.95 (22 H, m, ArH).

Preparation of (R)-2′-*Methyl*-1,1′-*binaphthalen*-2-*ol* **2c**.—Optically pure compound **2c** was prepared from enantiopure (*S*)-2′-methoxy-1,1′-binaphthalene-2-carboxylic acid **7**[15] by the sequence described below.

(S)-2′-*Methoxy*-1,1′-*binaphthalene*-2-*methanol* **8**.—To a stirred suspension of $LiAlH_4$ (330 mg, 8.80 mmol) in diethyl ether (10 cm^3) was added dropwise a solution of the acid **7** (262 mg, 0.80 mmol) in diethyl ether (10 cm^3) at 0 °C, and the reaction mixture was stirred at room temperature for 12 h. After being quenched with water (1 cm^3), the mixture was acidified with dil. hydrochloric acid (2 mol dm^{-3}) and then extracted with diethyl ether (20 cm^3 × 3). The combined extracts were washed successively with saturated aq. sodium hydrogen carbonate, water, and finally brine, and dried. The solvent was evaporated to yield the alcohol **8** (247 mg, 98%), which was recrystallized from hexane at −20 °C to yield an analytically pure sample, m.p. 130.5–131.0 °C; $[\alpha]_D$ +74.6 (*c* 0.19, $CHCl_3$) [lit.,[11] −71.4 (*c* 0.15, $CHCl_3$) for (*R*)-**8** of 96% e.e.]; ν_{max}(KBr)/cm^{-1} 3360 (OH), 1616, 1589 (Ar), 1503 (Ar) and 1263 (C–O–C); δ_H(250 MHz; $CDCl_3$) 2.5 (1 H, br s, OH), 3.66 (3 H, s, Me), 4.34 (2 H, s, CH_2) and 6.9–8.0 (12 H, m, ArH).

(S)-2-*Bromomethyl*-2′-*methoxy*-1,1′-*binaphthalene* **9**.—A large excess of hydrogen bromide gas (~60 mmol) was passed through a stirred acetic acid solution (10 cm^3) of the alcohol **8** (247 mg, 0.768 mmol) during 30 min at room temperature. After 1 h, water (10 cm^3) was added and the mixture was extracted with diethyl ether (30 cm^3 × 3). The combined extracts were washed successively with water, saturated aq. sodium hydrogen carbonate, and brine, and dried. The solvent was removed under reduced pressure to yield the bromide **9** (297 mg, 100%) as a pale brown syrup, δ_H(250 MHz; $CDCl_3$) 3.77 (3 H, s, OMe), 4.30 (2 H, ABq, $\Delta\nu$ 16, *J* 10, CH_2Br) and 6.95–8.04 (12

H, m, ArH). Owing to its instability, the crude product **9** was immediately used in the next step.

(R)-2-*Methoxy*-2'-*methyl*-1,1'-*binaphthalene* **10**.—To a stirred suspension of $LiAlH_4$ (300 mg, 7.90 mmol) in THF (10 cm^3) was added dropwise a solution of crude bromide (*S*)-**9** (297 mg, 0.787 mmol) in THF (10 cm^3) at 0 °C, and the mixture was stirred at room temperature for 12 h. After being quenched with water (1 cm^3), the mixture was acidified with dil. hydrochloric acid (2 mol dm^{-3}) and then extracted with diethyl ether (30 cm^3 × 3). The combined extracts were washed successively with saturated aq. sodium hydrogen carbonate, water, and finally brine, and dried. The solvent was removed under reduced pressure to give, after column chromatography (17% ethyl acetate in hexane), the product (*R*)-**10** (184 mg, 78%) as a glass (Found: C, 88.3; H, 6.2. $C_{22}H_{18}O$ requires C, 88.56; H, 6.08%); $[\alpha]_D$ +10.8 (*c* 1.39, $CHCl_3$); ν_{max}(neat)/cm^{-1} 2850 (C–H), 1590 and 1500 (Ar C=C) and 1240 (C–O); δ_H(250 MHz; $CDCl_3$) 2.08 (3 H, s, Me), 3.72 (3 H, s, OMe) and 6.97–7.98 (12 H, m, ArH).

(R)-2'-*Methyl*-1,1'-*binaphthalen*-2-*ol* **2c**.—A solution of BBr_3 (0.08 cm^3, 0.846 mmol) in dichloromethane (2 cm^3) was dropped into a stirred solution of compound **10** (184 mg, 0.617 mmol) in dichloromethane (5 cm^3) during 5 min at room temperature. After additional stirring of the mixture for 1 h, hydrochloric acid (2 mol dm^{-3}; 5 cm^3) was added and the mixture was extracted with dichloromethane (20 cm^3 × 3). The combined extracts were washed successively with water, saturated aq. sodium hydrogen carbonate, and brine, and dried. After the solvent was removed under reduced pressure, the residue was recrystallized from hexane at −20 °C to yield the enantiopure alcohol **2c** (158 mg, 90%), the e.e. of which was evidenced by HPLC on a Pirkle Type 1-A column eluted with 0.5% propan-2-ol in hexane, m.p. 129.0–129.5 °C (Found: C, 88.5; H, 5.85. $C_{21}H_{16}O$ requires C, 88.70; H, 5.67%); $[\alpha]_D$ +64.0 (*c* 0.6, THF); ν_{max}(KBr)/cm^{-1} 3450 (OH), 1590 and 1500 (Ar C=C), 1190 and 1170 (C–O); δ_H(60 MHz; $CDCl_3$) 2.06 (3 H, s, Me), 4.68 (1 H, s, OH) and 6.6–7.9 (12 H, m, ArH).

General Procedure for the Preparation of α-Keto Esters **3a–f** *and* **4**.—A 2'-substituted 1,1'-binaphthalen-2-ol (1 mmol) and triethylamine (1.5 mmol) were stirred in diethyl ether (10 cm^3) at room temperature. To the solution was added dropwise during 5 min a solution of α-keto acid chloride[16] (1.4 mmol) in diethyl ether (5 cm^3) and the mixture was stirred for 3 h. Then, after addition of aq. hydrochloric acid (2 mol dm^{-3}; 10 cm^3), the mixture was extracted with diethyl ether (30 cm^3 × 3). The combined extracts were washed with brine and dried. The solvent was removed under reduced pressure and the product was purified by column chromatography. The eluents for the chromatographic purification, the isolated yields, and the physical and spectral characteristics of the esters **3a–f** and **4** are given below.

(R)-1,1'-*Binaphthalen*-2-*yl phenylglyoxylate* **3a**. Eluent: 25% ethyl acetate in hexane; (89%) (Found: C, 83.5; H, 4.8. $C_{28}H_{18}O_3$ requires C, 83.56; H, 4.51%); $[\alpha]_D$ +2.1 (*c* 1.3, $CHCl_3$); ν_{max}(neat)/cm^{-1} 1758 (ester), 1687 (ketone), 1594 (Ar C=C), 1196 and 1163 (C–O); δ_H(60 MHz; $CDCl_3$) 7.0–8.1 (18 H, m, ArH); δ_C(62.9 MHz; $CDCl_3$) 185.78 (CO), 162.58 (CO_2Ar), 145.56 (C-2), 134.68 (Ar), 133.83 (Ar), 133.65 (Ar), 132.53 (Ar), 132.36 (Ar), 132.11 (Ar), 131.63 (Ar), 129.91 (Ar), 129.52 (Ar), 129.34 (Ar), 128.61 (Ar), 128.09 (Ar), 126.94 (Ar), 126.56 (Ar), 126.40 (Ar), 126.24 (Ar), 126.16 (Ar), 125.50 (Ar) and 120.88 (Ar).

(S)-2'-*Methoxy*-1,1'-*binaphthalen*-2-*yl phenylglyoxylate* **3b**. Eluent: benzene; (82%) (Found: C, 80.3; H, 4.7. $C_{29}H_{20}O_4$ requires C, 80.54; H, 4.66%); $[\alpha]_D$ +28.7 (*c* 2.18, $CHCl_3$); ν_{max}(neat)/cm^{-1} 1750 (ester), 1683 (ketone), 1590 (Ar C=C), 1260 and 1164 (C–O); δ_H(60 MHz; $CDCl_3$) 3.72 (3 H, s, OMe) and 7.0–8.1 (17 H, m, ArH); δ_C(62.9 MHz; $CDCl_3$) 185.90 (CO), 162.39 (CO_2Ar), 155.12 (C-2'), 146.02 (C-2), 134.61 (Ar), 133.63 (Ar), 132.17 (Ar), 131.75 (Ar), 130.32 (Ar), 129.51 (Ar), 128.98 (Ar), 128.60 (Ar), 128.22 (Ar), 127.81 (Ar), 126.95 (Ar), 126.80 (Ar), 126.16 (Ar), 125.98 (Ar), 125.63 (Ar), 125.31 (Ar), 123.87 (Ar), 121.05 (Ar), 116.90 (Ar), 113.62 (Ar) and 56.57 (OMe).

(R)-2'-*Methyl*-1,1'-*binaphthalen*-2-*yl phenylglyoxylate* **3c**. Eluent: 25% ethyl acetate in hexane; (88%) (Found: C, 83.6; H, 4.85. $C_{29}H_{20}O_3$ requires C, 83.63; H, 4.84%); $[\alpha]_D$ −9.4 (*c* 1.1, $CHCl_3$); ν_{max}(neat)/cm^{-1} 1758 (ester), 1685 (ketone), 1597 (Ar C=C), 1186 and 1165 (C–O); δ_H(60 MHz; $CDCl_3$) 2.12 (3 H, s, Me) and 6.9–8.1 (17 H, m, ArH); δ_C(62.9 MHz; $CDCl_3$) 185.93 (CO), 162.49 (CO_2Ar), 145.64 (C-2), 135.77 (Ar), 134.65 (Ar), 133.16 (Ar), 132.83 (Ar), 132.26 (Ar), 132.11 (Ar), 131.62 (Ar), 130.11 (Ar), 129.74 (Ar), 129.47 (Ar), 128.76 (Ar), 128.62 (Ar), 128.36 (Ar), 128.29 (Ar), 127.75 (Ar), 127.13 (Ar), 126.49 (Ar), 126.24 (Ar), 125.97 (Ar), 125.93 (Ar), 125.27 (Ar), 121.14 (Ar) and 20.28 (ArMe).

(S)-2'-*Isopropoxy*-1,1'-*binaphthalen*-2-*yl phenylglyoxylate* **3d**. Eluent: benzene; (79%) (Found: C, 80.8; H, 5.5. $C_{31}H_{24}O_4$ requires C, 80.85; H, 5.25%); $[\alpha]_D$ +12.6 (*c* 1.0, $CHCl_3$); ν_{max}(neat)/cm^{-1} 1746 (ester), 1684 (ketone), 1585 (Ar C=C), 1237, 1161 and 1104 (C–O); δ_H(250 MHz; $CDCl_3$) 0.96 (3 H, d, *J* 6, Me), 1.02 (3 H, d, *J* 6, Me), 4.45 (1 H, septet, *J* 6, C*H*Me_2) and 7.05–8.07 (17 H, m, ArH); δ_C(62.9 MHz; $CDCl_3$) 186.10 (CO), 162.48 (CO_2Ar), 153.79 (C-2'), 146.02 (C-2), 134.58 (Ar), 133.93 (Ar), 133.70 (Ar), 132.08 (Ar), 131.79 (Ar), 129.95 (Ar), 129.58 (Ar), 129.37 (Ar), 129.06 (Ar), 128.60 (Ar), 128.32 (Ar), 128.13 (Ar), 127.73 (Ar), 126.79 (Ar), 126.59 (Ar), 126.41 (Ar), 125.85 (Ar), 125.55 (Ar), 124.32 (Ar), 123.94 (Ar), 121.03 (Ar), 118.73 (Ar), 116.73 (Ar), 71.58 (*C*HMe_2) and 22.24 and 21.97 (2 × Me).

(S)-2'-(tert-*Butyldimethylsiloxy*)-1,1'-*binaphthalen*-2-*yl phenylglyoxylate* **3e**. Eluent: benzene; (87%), m.p. 144–144.5 °C (from benzene–cyclohexane) (Found: C, 76.5; H, 6.1. $C_{34}H_{32}O_4Si$ requires C, 76.66; H, 6.05%); $[\alpha]_D$ −9.2 (*c* 1.0, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 2925 (C–H), 1747 (ester), 1687 (ketone), 1249, 1186 and 1165 (C–O); δ_H(60 MHz; $CDCl_3$) −0.18 (3 H, s, SiMe), −0.03 (3 H, s, SiMe), 0.46 (9 H, s, SiBu^t) and 7.0–8.1 (17 H, m, ArH); δ_C(62.9 MHz; $CDCl_3$) 186.12 (CO), 162.49 (CO_2Ar), 151.51 (C-2'), 146.17 (C-2), 134.57 (Ar), 134.06 (Ar), 133.74 (Ar), 132.17 (Ar), 131.80 (Ar), 129.84 (Ar), 129.58 (Ar), 129.39 (Ar), 129.16 (Ar), 128.59 (Ar), 128.31 (Ar), 128.08 (Ar), 127.75 (Ar), 126.78 (Ar), 126.62 (Ar), 126.47 (Ar), 126.03 (Ar), 125.92 (Ar), 125.57 (Ar), 123.93 (Ar), 121.08 (Ar), 120.53 (Ar), 119.51 (Ar), 24.95 (CMe_3), 17.54 (*C*Me_3) and −4.36 and −4.50 (2 × SiMe).

(S)-2'-(tert-*Butyldiphenylsiloxy*)-1,1'-*binaphthalen*-2-*yl phenylglyoxylate* **3f**. Eluent: benzene; (91%), m.p. 141.5–142.5 °C (from benzene–hexane) (Found: C, 80.2; H, 5.8. $C_{44}H_{36}O_4Si$ requires C, 80.45; H, 5.53%); $[\alpha]_D$ +20.4 (*c* 1.0, THF); ν_{max}(KBr)/cm^{-1} 1745 (ester), 1690 (ketone), 1620 and 1593 (Ar C=C), 1283 and 1166 (C–O); δ_H(60 MHz; $CDCl_3$) 0.42 (9 H, s, SiBu^t) and 6.64–8.14 (27 H, m, ArH); δ_C(62.9 MHz; $CDCl_3$) 186.16 (CO), 162.69 (CO_2Ar), 151.01 (C-2'), 146.27 (C-2), 135.21 (Ar), 134.58 (Ar), 133.92 (Ar), 133.83 (Ar), 132.37 (Ar), 132.30 (Ar), 132.15 (Ar), 131.69 (Ar), 129.83 (Ar), 129.70 (Ar), 129.50 (Ar), 129.36 (Ar), 128.90 (Ar), 128.70 (Ar), 128.29 (Ar), 128.16 (Ar), 127.68 (Ar), 127.57 (Ar), 126.81 (Ar), 126.29 (Ar), 126.02 (Ar), 125.52 (Ar), 123.95 (Ar), 121.09 (Ar), 120.35 (Ar), 116.80 (Ar), 25.37 (CMe_3) and 18.71 (*C*Me_3).

(S)-2'-(tert-*Butyldimethylsiloxy*)-1,1'-*binaphthalen*-2-*yl pyruvate* **4**. Eluent: benzene; (54%) (Found: C, 74.2; H, 6.4. $C_{29}H_{30}O_4Si$ requires C, 74.01; H, 6.43%); $[\alpha]_D$ −28.0 (*c* 0.19,

$CHCl_3$); ν_{max}(neat)/cm^{-1} 1770 (ester), 1737 (ketone), 1622 and 1594 (Ar C=C), 1277, 1249 and 1123 (C–O); δ_H(250 MHz; $CDCl_3$) −0.17 (3 H, s, SiMe), −0.02 (3 H, s, SiMe), 0.48 (9 H, s, SiBu^t), 1.83 (3 H, s, MeCO) and 7.17–8.02 (12 H, m, ArH); δ_C(62.9 MHz; $CDCl_3$) 191.17 (CO), 158.34 (*C*O_2Ar), 151.24 (C-2'), 146.03 (C-2), 133.74 (Ar), 133.58 (Ar), 132.02 (Ar), 129.88 (Ar), 129.17 (Ar), 129.07 (Ar), 128.30 (Ar), 128.04 (Ar), 127.86 (Ar), 126.67 (Ar), 126.60 (Ar), 125.89 (Ar), 125.21 (Ar), 123.83 (Ar), 120.64 (Ar), 120.52 (Ar), 119.37 (Ar), 26.48 (*Me*CO), 24.95 (C*Me*$_3$), 17.53 (*C*Me$_3$) and −4.46 and −4.54 (2 × SiMe).

Addition of MeMgI *to the Phenylglyoxylate* **3a**.—*A Reinvestigation of Berson's Experiment*. An ethereal solution of MeMgI (0.96 mol dm^{-3}; 0.65 cm^3, 0.62 mmol) was dropped into a solution of compound **3a** (200 mg, 0.497 mmol) in diethyl ether (3.0 cm^3) at room temperature during 30 min using a syringe pump, and the mixture was heated at reflux for 30 min. After cooling of the mixture to room temperature, saturated aq. ammonium chloride (5 cm^3) was added and the mixture was extracted with diethyl ether (20 cm^3 × 3). The combined extracts were washed successively with water, saturated aq. sodium hydrogen carbonate, and brine, and dried. The solvent was removed under reduced pressure to give the crude product; the ratio of products **5a**:**6a** was determined by ^{1}H NMR analysis. The crude product was purified by column chromatography (30% benzene in cyclohexane) to give a mixture of compounds **5a** and **6a** (177 mg, 85%) as a glass. Unchanged substrate **3a** was also recovered (35 mg, 9%). For mixed products **5a** + **6a**: (Found: C, 83.3; H, 5.45. $C_{29}H_{22}O_3$ requires C, 83.23; H, 5.30%); ν_{max}(neat)/cm^{-1} 3490 (OH), 1746 (ester), 1200 and 1139 (C–O); δ_H(250 MHz; C_6D_6) 1.09 (3 × 0.42 H, s, Me), 1.23 (3 × 0.58 H, s, Me), 3.28 (0.58 H, s, OH), 3.43 (0.42 H, s, OH) and 6.92–7.68 (18 H, m, ArH).

Representative Procedure for the Addition of Grignard Reagents or MeZnI *to the α-Keto Esters.—Addition of* MeMgI *to compound* **3d** *in diethyl ether at* −78 °C. An ethereal solution of MeMgI (0.1 mol dm^{-3}; 2.0 cm^3, 0.2 mmol) was dropped into a solution of compound **3d** (92 mg, 0.20 mmol) in diethyl ether (10 cm^3) at −78 °C during 5 min, and the mixture was stirred for 30 min. Then, hydrochloric acid (2 mol dm^{-3}; 10 cm^3) was added and the mixture was extracted with diethyl ether (30 cm^3 × 3). The combined extracts were washed with saturated aq. sodium thiosulfate until the pale brown colour of the organic layer disappeared, and then with water, and finally with brine, and were then dried. The solvent was removed under reduced pressure to give the crude product; the ratio **5d**:**6d** was determined by ^{1}H NMR analysis. The crude product was purified by column chromatography (eluted with benzene followed by ethyl acetate) to give a mixture of products **5d** and **6d** (83 mg, 87%). The starting ester **3d** was also recovered (4 mg, 4%).

The ^{1}H NMR spectra of the diastereoisomeric mixtures **5b–f** and **6b–f** are given below (integrals have been normalized for each molecule).

Compounds **5b** + **6b**: δ_H(250 MHz; C_6D_6) 1.23 (3 H, s, Me), 3.13 (3 H, s, OMe of **6b**), 3.20 (3 H, s, OMe of **5b**), 3.42 (1 H, br s, OH of **6b**), 3.48 (1 H, br s, OH of **5b**) and 6.90–7.71 (17 H, m, ArH).

Compounds **5c** + **6c**: δ_H(250 MHz; C_6D_6) 1.10 (3 H, s, Me of **5c**), 1.14 (3 H, s, Me of **6c**), 1.98 (3 H, s, Ar*Me* of **6c**), 2.04 (3 H, s, Ar*Me* of **5c**), 3.34 (1 H, br s, OH of **6c**), 3.44 (1 H, br s, OH of **5c**) and 6.91–7.72 (17 H, m, ArH).

Compounds **5d** + **6d**: δ_H(250 MHz; C_6D_6) 0.73 and 0.82 (each 3 H, d, *J* 6.4, CH*Me*$_2$ of **6d**), 0.76 and 0.92 (each 3 H, d, *J* 6.4, CH*Me*$_2$ of **5d**), 1.22 (3 H, s, Me of **6d**), 1.33 (3 H, s, Me of **5d**), 3.48 (1 H, s, OH of **6d**), 3.59 (1 H, s, OH of **5d**), 4.12 (1 H, septet, *J* 6.4, C*H*Me$_2$) and 6.96–7.72 (17 H, m, ArH).

Compounds **5e** + **6e**: δ_H(250 MHz; C_6D_6) −0.22 and −0.09 (3 H, s, SiMe of **6e**), −0.18 and −0.01 (3 H, s, SiMe of **5e**), 0.54 (9 H, s, SiBu^t of **6e**), 0.58 (9 H, s, SiBu^t of **5e**), 1.19 (3 H, s, Me of **6e**), 1.35 (3 H, s, Me of **5e**), 3.41 (1 H, s, OH of **6e**), 3.52 (1 H, s, OH of **5e**) and 6.96–7.66 (17 H, m, ArH).

Compounds **5f** + **6f**: δ_H(250 MHz; C_6D_6) 0.59 (9 H, s, SiBu^t of **6f**), 0.61 (9 H, s, SiBu^t of **5f**), 1.21 (3 H, s, Me of **5f**), 1.28 (3 H, s, Me of **6f**), 3.41 (1 H, s, OH of **6f**), 3.58 (1 H, s, OH of **5f**) and 6.96–7.88 (17 H, m, ArH).

Representative Procedure for the Nucleophilic Addition of Grignard Reagents to α-Keto Esters **3e** *and* **4** *in the Presence of* ZnX_2.—*Addition of* MeMgI *to glyoxylate* **3e** *in the presence of* ZnI_2. A solution of compound **3e** (53 mg, 0.1 mmol) and anhydrous ZnI_2 (35 mg, 0.11 mmol) in diethyl ether (5 cm^3) was stirred at room temperature for 1 h and was then cooled to −78 °C. After the mixture had been stirred for 30 min at −78 °C, an ethereal solution of MeMgI (0.2 mol dm^{-3}; 0.55 cm^3, 0.11 mmol) was added dropwise during 5 min and the mixture was stirred for 2 h. Then the mixture was worked up according to the procedure for the reaction of Grignard reagent to give the crude product; the ratio **5e**:**6e** was determined by ^{1}H NMR analysis. The crude product was purified by preparative TLC (PLC) (benzene) to give a mixture of compounds **5e** and **6e** (46 mg, 85%) and recovered **3e** (7 mg, 13%).

Representative Procedure for the Addition of $RTiCl_3$ *to α-Keto Esters* **3e** *and* **4**.—*Addition of* $MeTiCl_3$ *to glyoxylate* **3e**. An ethereal solution of MeMgBr (0.2 mol dm^{-3}; 1.4 cm^3, 0.28 mmol) was dropped into a stirred solution of freshly distilled $TiCl_4$ (0.03 cm^3, 0.28 mmol) in dichloromethane (5.5 cm^3) at −23 °C during 5 min, and the resultant dark brown mixture was stirred for 30 min. Then a solution of glyoxylate **3e** (53 mg, 0.1 mmol) in dichloromethane (1.5 cm^3) was added dropwise and the mixture was stirred for 3 h at −23 °C. The reaction mixture was worked up according to the procedure used for the Grignard reaction to give the crude product; the ratio **5e**:**6e** was determined by ^{1}H NMR analysis. The crude product was purified by PLC (benzene) to give a mixture of compounds **5e** and **6e** (32 mg, 62%) and recovered **3e** (17 mg, 35%).

Representative Procedure for Hydrolysis of the Mixture of Atrolactic Acid Esters **5a–f** *and* **6a–f**.—*Hydrolysis of the mixture of compounds* **5a** *and* **6a**. To the aforementioned mixture of **5a** and **6a** (159 mg, 0.379 mmol) was added a 5% solution of KOH in ethanol (5 cm^3) and the mixture was stirred at room temperature for 2 h. After the solvent was removed under reduced pressure, water was added to the residue and the mixture was extracted with diethyl ether (20 cm^3 × 3). The combined extracts were washed successively with water and brine, and dried. Evaporation of the solvent gave the chiral auxiliary **2a** (102 mg, 99.5%). The aqueous layer from the extraction was acidified with dil. hydrochloric acid (2 mol dm^{-3}) and then extracted with diethyl ether (30 cm^3 × 3). The extract was washed with brine, dried, and evaporated under reduced pressure to yield (*S*)-(+)-atrolactic acid (α-hydroxy-α-phenylpropionic acid) (58 mg, 93%), $[\alpha]_D$ +5.2 (*c* 1.16, EtOH) [lit.,[22] +37.7 in EtOH, for the optically pure (*S*)-isomer]. The acid shows ^{1}H NMR and IR spectral data nearly identical with those of a commercial sample of racemic atrolactic acid monohydrate.

The mixtures of diastereoisomeric esters **5b–f** and **6b–f** obtained above by the reaction in diethyl ether at −78 °C were hydrolysed as mentioned above for compounds **5a** and **6a**, to

afford the alcohols **2b–f** and the corresponding atrolactic acids in high yields (> 90%).

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