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Highly asymmetric Pummerer-type reaction induced by ethoxy vinyl esters

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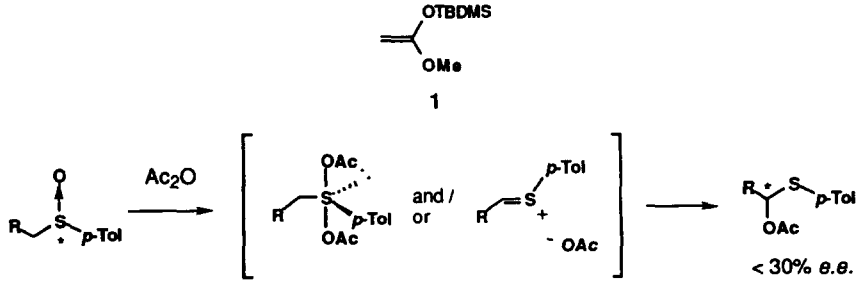
Abstract: Ethoxy vinyl esters (EVE:**2**) were efficient reagents for promoting the asymmetric Pummerer reaction with high enantioselectivity and high yield in contrast to the generally used acid anhydrides. Increasing the electron-donating ability on the R function in EVE **2** tended to increase enantioselectivity. Consequently, effective asymmetric rearrangements were achieved using EVEs **2b,c** bearing a methoxybenzoyloxy function.

Introduction

The Pummerer and Pummerer-type rearrangements of sulfoxides have received considerable attention both mechanistically and as a synthetically useful process for the preparation of α-substituted sulfides, including α-acetoxy-, α-alkyl-, α-aryl-, α-halo-, and α-siloxy-substituted species.[1] Although many useful applications have been reported for these reactions, there is no successful report on an asymmetric Pummerer rearrangement of optically active sulfoxides. This is probably due to the formation of a sulfurane intermediate and the dissociation of the intimate ion pair by reaction with the generated acetate anion (Scheme 1).[2] Although the addition of 1,3-dicyclohexylcarbodiimide (DCC) as an effective scavenger of acetic acid increased enantioselectivity, the chemical yield significantly decreased[3] and the Pummerer reaction of chiral benzyl tolylsulfoxide in the presence of DCC gave only the racemic adduct.[4] Recently, we reported the first highly asymmetric silicon-induced Pummerer-type reaction of chiral, non-racemic sulfoxides using *O*-methyl-*O*-*tert*-butyldimethylsilyl ketene acetal **1**, which gave chiral α-siloxysulfides under mild conditions in high yield.[5] Very recently we have also communicated[6] the highly asymmetric acyl-induced Pummerer-type reaction using ethoxy vinyl acetate **2a**, which is known as a powerful acylating reagent.[7] In this paper, we report the details of this work, especially the effect of the substituent of acyloxy groups on EVE **2** relative to asymmetric rearrangement and applications to other optically active sulfoxides.



Scheme 1. Pummerer reaction induced by acetic anhydride.

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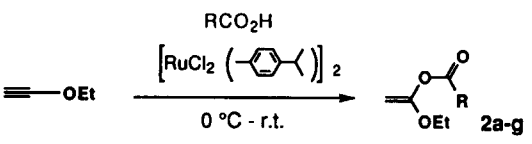
Table 1. Preparation of EVEs **2a–g**



R	Me	MeO, MeO, OMe	MeO	Ph	O2N	CH_2Cl	Me, Me
	2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**
solvent	THF	toluene	toluene	toluene	toluene	THF	toluene
yield (%)	75	72	96	80	40	82	100

Results and discussion

Recently we have reported an efficient method for the preparation of ethoxy vinyl esters bearing an acyloxy group by the reaction of ethoxyacetylene with the corresponding carboxylic acid in the presence of a catalytic amount of Bennett's ruthenium complex.[8] The method is superior to the other synthetic methods, because all classical synthetic routes to these types of reagents have their own particular synthetic problems: The mercury(II)-catalyzed addition of carboxylic acids to alkoxyacetylene restricts the use of these reagents due to the high toxicity.[9] The direct addition of carboxylic acids to alkoxyacetylene without a catalyst is limited to the use of strong acids such as trichloroacetic acid as the reactant.[10] When trifluoroacetic acid was used as the substrate, chloromethane must be used as the solvent.[10] On the other hand, our synthetic method which consists of the addition reaction of carboxylic acids to ethoxyacetylene in the presence of a catalytic amount of $[RuCl_2(p\text{-cymene})]_2$[11] generally gives various EVEs **2a–g** in excellent yields (Table 1). The advantage of this synthetic method is the ease of handling, and further the reactions gave EVEs which have proved difficult to prepare by the known non-catalytic method. Newly synthesized EVEs **2b,c,e–g** were identified by ^{1}H-NMR and IR spectra, and analytical data.

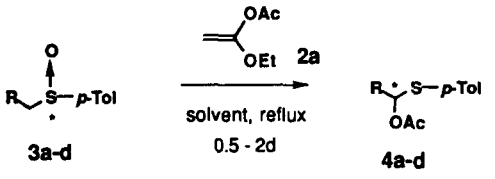
First, we examined the asymmetric Pummerer reaction of optically active sulfoxides **3a–d**[2–4] using ethoxy vinyl acetate **2a**. Treatment of (***R***)-**3a–d** with **2a** in refluxing $(CH_2Cl)_2$, benzene or toluene gave the corresponding optically active α-acetoxysulfides (***R***)-**4a–d** in high enantiomeric excess (Table 2).[6] Observed *e.e.* values and yields were higher than those of the reported asymmetric Pummerer rearrangements using acid anhydrides in all cases. Although the asymmetric induction of the present asymmetric Pummerer reaction is slightly lower than the silicon-induced Pummerer reaction,[5] it is quite interesting to increase the asymmetric induction probably by preventing the formation of the sulfurane intermediate[6] even if in refluxing in toluene.

Next, enantiomerically pure sulfoxide (***R***)-**3a** was reacted with EVEs **2a–g** bearing various acyloxy functions to examine the effect of the acyloxy substituent. Treatment of (***R***)-**3a** with EVEs **2a–g** in refluxing toluene gave the optically active α-acetoxysulfides (***R***)-**4a** and **5b–g** in high enantiomeric excess (Table 3). It is noteworthy that the enantiomeric excess of the products was influenced by the acyloxy function. That is to say, the electron-donating ability and steric bulkiness of the acyloxy function affect the enantiomeric excess of the products. Consequently, the highest enantioselectivity (81% *e.e.*) could be obtained by an EVE **2b** bearing a trimethoxyphenyl group as the R function (Table 3).

A similar trend in enantioselectivity was observed in the cyclization of an optically active sulfoxide **6**. A Pummerer-type ring closure reaction of enantiomerically pure sulfoxide **6** is shown in Table 4.[12] In this case, the enantiomeric excess on the sulfur atom was transferred in only 6–11% *e.e.* by use of acetic anhydride as a reagent, and in the case of using DCC as a reagent, up to 23–30% *e.e.* was obtained with the opposite configuration.[13]

We examined this cyclization of enantiomerically pure sulfoxide **6** using EVEs **2a–d** bearing various

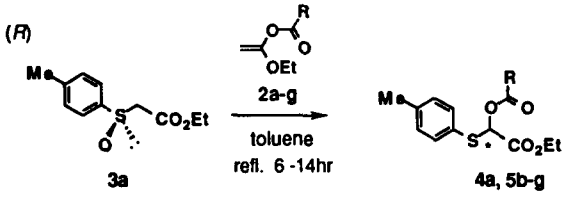
Table 2. Pummerer reaction induced by ethoxy vinyl acetate **2a**



substrate	3a-d config.	R	solvent	4a-d config.	product % *e.e.* (% yield)	product $[\alpha]_D$ (c, acetone)	reported method % *e.e.* (% yield)
3a	*R*	CO_2Et	EDC	*R*	77[b] (58)	-57.6 (0.91)	70 (10)
			benezene		76[b] (43)	-57.0 (1.0)	
			toluene		71[b] (42)	-53.4 (1.5)	
3b	*R*	$CONMe_2$	EDC	*R*	68[a] (72)	-35.4 (0.51)	65 (35)
			benezene		72[a] (52)	-38.2 (0.82)	
			toluene		84[a] (39)	-46.5 (0.50)	
3c	*R*	Ph	toluene	*R*	20[a] (64)	-5.29 (1.6)	0 (10)
3d	*S*	$P(O)(OMe)_2$	EDC	*S*	75[b] (44)	-12.5 (1.5)	24 (73)
			toluene		69[b] (38)	-11.5 (1.5)	

a) E.e. value was determined by ^{1}H-NMR ($CDCl_3$) with $Eu(hfc)_3$.
b) E.e. value was calculated by the reported $[\alpha]_D$ value. See Refs. 2-4.

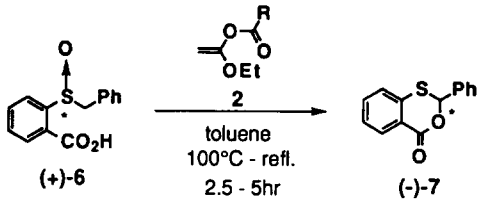
Table 3. Effect of R group in EVE **2** on stereoselectivity of (*R*)-**3a**

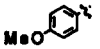


R	Me	MeO, MeO, OMe	MeO	Ph	O_2N	CH_2Cl	Me, Me
	2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**
e.e. (%)	71	81	76	69	66	54	53
yield (%)	42	19	37	35	20	63	39

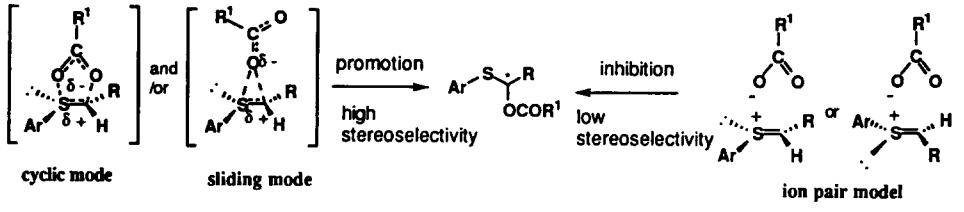
Enantiomeric excess was determined by HPLC (Chiral cel OD®).
Unreacted substrate was recovered in all cases.

Table 4. Effect of R group in EVE **2** on stereoselectivity of cyclization



R	 **2c**	Ph **2d**	 **2e**	Me **2a**	CH_2Cl **2f**
e.e. (%)	44	40	33	12	3
yield (%)	91	95	82	86	92

Enantiomeric excess was determined by HPLC (Chiral cel OD®).



Scheme 2. Speculation of reaction mechanism.

acyloxy functions. Treatment of (+)-**6** with EVEs **2a,c–f** at 100°C or in refluxing toluene gave the optically active cyclic sulfide (−)-**7** in moderate enantiomeric excess (Table 4).

Similar to the result obtained by the reaction of **3a–d** with **2** bearing various types of acyloxy function, increase in the electron-donating ability of **2** has a tendency to increase the enantiomeric excess of the products **7**. The using EVE **2c** bearing a methoxyphenyl group as the R function gave **7** in relatively high enantioselectivity (44% *e.e.*). In addition, it was proved by comparison of the sign of the products specific rotation that the configuration of the product was opposite to that in the case of EVE **2a,c–f** compared with the case of acetic anhydride.[14] Although how the products configuration becomes opposite in this case remains to be elucidated, a convenient explanation[3,4] of this effect of acyloxy function on enantioselectivity is depicted in Scheme 2.

It could be assumed that the major part of this reaction proceeded via a five-membered ring transition state (cyclic mode) and/or a three-membered ring transition state (sliding mode).[3,4] The cleavage of the *S–O* bond was inhibited in the case of using EVE bearing a powerful electron-donating R group, and hence high enantioselectivity was achieved owing to the acceleration of the rearrangement via an intramolecular process. (The powerful electron-donating R group inhibited the route via a dissociation ion pair model with disappearance of stereoselectivity.)

Conclusions

It has become apparent that various ethoxy vinyl esters (EVE:**2**) were effective reagents for promoting the asymmetric Pummerer reaction and that the enantioselectivity was influenced by the electron-donating ability of the R group in EVE **2**. Consequently, effective chirality transfer from an optically active sulfoxide to the prochiral α-carbon of the sulfur atom was achieved using EVEs

2b,c. This methodology may be applied to the synthesis of a biologically active substance through the optically active *S,O*-acetal.[5]

Experimental

Melting points were determined on a Yanaco Melting Point Apparatus and were uncorrected. ^{1}H NMR spectra were recorded on a Varian VXR-200 (200MHz), JEOL JNM-EX-270 (270MHz) and JEOL JNM-GX500 (500MHz) using $CDCl_3$ as the solvent with TMS as the internal standard. Mass spectra (MS) and high-resolution MS were obtained using ESCO EMD-05A and JEOL JMS-D300 mass spectrometers. IR spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. The *e.e.* values were determined by HPLC on a CHIRALCEL OD®(DAICEL) column (eluent: ^{i}PrOH/hexane=9:1). Optical rotations were measured on a Perkin–Elmer 241 polarimeter. E. Merck silica gel 60 (70–230 mesh ASTM) for column chromatography and E. Merck precoated TLC plates with silica gel F254 for preparative TLC (PLC) were used. The known sulfoxide **3a, 3b, 3c, 3d** and **6** were prepared by the reported methods.[2–4,13]

1-Ethoxy vinyl esters ***2a–g***

General procedure[7]

To a stirred solution of ethoxyacetylene (856 mg, 12.22 mmol) and Bennett's ruthenium complex[11] (25.0 mg, 0.0408 mmol) in dry toluene (50 ml) was added dropwise a solution of *p*-methoxybenzoic acid (1.24 g, 8.15 mmol) in toluene (60 ml) by cannulation at 0°C. The resulting solution was stirred for 5h. After concentration of the reaction mixture under reduced pressure, the brown residue was purified by flash column chromatography on silica gel (hexane/AcOEt/Et_3N, 100:10:1) to give the title ester **2b** (1.74 g, 95.9%) as a colorless oil. Exceptionally, **2a** and **2f** were prepared in dry THF and purified by direct distillation from the reaction mixture. Compounds **2b–e** and **2g** were purified by flash column chromatography on silica gel [**2b** (hexane/AcOEt/Et_3N, 80:20:1), **2d** (hexane/AcOEt, 10:1), **2e** (hexane/AcOEt, 20:1), **2g** (hexane/AcOEt, 10:1)]. The physical data for **2b,c** and **2e–f** are summarized below.

1-Ethoxy vinyl ester ***2b***

(71.6% yield, as pale yellow crystals) M.p. 87–89 °C. ^{1}H NMR ($CDCl_3$) δ: 1.38 (t, 3 H, *J*=7.0 Hz), 3.88 (d, 1 H, *J*=3.5 Hz), 3.92 (s, 9 H), 3.96 (d, 1 H, *J*=3.5 Hz), 3.97 (q, 2 H, *J*=7.0 Hz), 7.35 (s, 2 H). IR (KBr) cm^{-1}: 1744, 1676. MS *m/z* (%): 282 (M^+, 2), 195 (100). HRMS calcd. for $C_{14}H_{18}O_6$ 282.1104; found 282.1110. Anal. calcd. for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. found: C, 59.54; H, 6.28.

1-Ethoxy vinyl ester ***2c***

(95.9% yield, as a yellow oil) ^{1}H NMR ($CDCl_3$) δ: 1.36 (t, 3 H, *J*=6.0 Hz), 3.86 (d, 1 H, *J*=3.7 Hz), 3.87 (s, 3 H), 3.94 (q, 2 H, *J*=6.0 Hz), 3.94 (d, 1 H, *J*=3.7 Hz), 6.93 (d, 2 H, *J*=9.1 Hz), 8.05 (d, 2 H, *J*=9.1 Hz). IR (KBr) cm^{-1}: 1744, 1674. MS *m/z* (%): 222 (M^+, 8), 135 (100). HRMS calcd. for $C_{12}H_{14}O_4$ 222.0892; found 222.0892. Anal. calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. found: C, 64.88; H, 6.40.

1-Ethoxy vinyl ester ***2e***

(40.0% yield, as pale yellow crystals) M.p. 76.0–78.0 °C. ^{1}H NMR ($CDCl_3$) δ: 1.38 (t, 3 H, *J*=7.0 Hz), 3.92 (d, 1 H, *J*=3.6 Hz), 3.98 (q, 2 H, *J*=7.0 Hz), 4.01 (d, 1 H, *J*=3.6 Hz), 8.29 (s, 2 H), 8.30 (s, 2 H). IR (KBr) cm^{-1}: 1755, 1676. MS *m/z* (%): 237 (M^+, 2), 150 (100). HRMS calcd. for $C_{11}H_{11}NO_5$ 237.0635; found 237.0635. Anal. calcd. for $C_{11}H_{11}NO_5$: C, 55.70; H, 4.67; N 5.90. found: C, 55.67; H, 4.64; N, 5.89.

1-Ethoxy vinyl ester ***2f***

(81.6% yield, as a colorless oil) B.p. 84–85 °C/17 mmHg. ^{1}H NMR ($CDCl_3$) δ: 1.35 (t, 3 H, *J*=6.0 Hz), 3.82 (d, 1 H, *J*=4.0 Hz), 3.89 (q, 2 H, *J*=6.0 Hz), 3.91 (d, 1 H, *J*=4.0 Hz), 4.18 (s, 2 H). IR

($CHCl_3$) cm^{-1}: 1790, 1678. MS *m/z* (%): 166 (M^+, 10), 164 (M^+, 29), 115 (100). HRMS calcd. for $C_6H_9ClO_3$ 164.0237; found 164.0237.

1-Ethoxy vinyl ester ***2g***

(99.9% yield, as a colorless oil) ^1H NMR ($CDCl_3$) δ: 1.37 (t, 3 H, *J*=6.0 Hz), 2.40 (s, 6 H), 3.86 (d, 1 H, *J*=3.8 Hz), 3.94 (q, 2 H, *J*=6.0 Hz), 3.96 (d, 1 H, *J*=3.8 Hz), 7.03–7.22 (m, 3 H). IR (KBr) cm^{-1}: 1761, 1674. MS *m/z* (%): 220 (M^+, 5), 134 (100). HRMS calcd. for $C_{13}H_{16}O_3$ 220.1100; found 220.1105.

Ethyl 1-acetoxy-[(4-methylphenyl)sulfanyl]acetate ***(R*)-4a***

General procedure for the Pummerer-type reaction of ethoxy vinyl esters (EVE:2) with various sulfoxides

To a stirred solution of a sulfoxide ***(R)*-3a** (59.0 mg, 0.261 mmol) in dry 1,2-dichloroethane was added dropwise ethoxy vinyl acetate **2a** (304 mg, 2.61 mmol) at room temperature under nitrogen, and the mixture was stirred for 48h at reflux. After the solvent was evaporated, the residue was purified by PLC to give the α-acetyloxysulfide ***(R*)*-4a** (40.4 mg, 57.8%; 76.8% *e.e.*) as a colorless oil. $[\alpha]_D^{18}$ −57.6 (c=0.91, acetone). ^1H NMR ($CDCl_3$) δ: 1.21 (t, 3 H, *J*=6.0 Hz), 2.17 (s, 3 H), 2.35 (s, 3 H), 4.13 (q, 2 H, *J*=6.0 Hz), 6.13 (s, 1 H), 7.14 (d, 2 H, *J*=6.0 Hz), 7.43 (d, 2 H, *J*=6.0 Hz). IR (KBr) cm^{-1}: 1745, 1732. HRMS calcd. for $C_{13}H_{16}O_4S$ 268.0769; found 268.0797. Anal. calcd. for $C_{13}H_{16}O_4S$: C, 58.19; H, 6.01. found: C, 58.24; H, 6.18.

(1R)-Acetoxy-[(4-methylphenyl)sulfanyl] N,N-*dimethylcarboxamide* ***(R)-4b***

(38.8% yield, 83.7% *e.e.*, as white crystals) M.p. 78.0–79.0°C. $[\alpha]_D^{18}$ −46.5 (c=0.50, acetone). ^1H NMR ($CDCl_3$) δ: 2.09 (s, 3 H), 2.27 (s, 3 H), 2.87 (s, 3 H), 3.10 (s, 3 H), 6.29 (s, 1 H), 7.07 (d, 2 H, *J*=5.8 Hz), 7.33 (d, 2 H, *J*=5.8 Hz). IR (KBr) cm^{-1}:1750, 1674. HRMS calcd. for $C_{13}H_{17}NO_3S$ 267.0929; found 267.0947. Anal. calcd. for $C_{13}H_{17}NO_3S$: C, 58.41; H, 6.41; N, 5.24; S, 11.99. found: C, 58.29; H, 6.28; N, 5.18; S, 11.78.

α-Acetoxy-α-phenyl p-*tolyl sulfide* ***(R*)-4c***

(63.8% yield, 20.1% *e.e.*, as colorless crystals) M.p. 79.0–79.5°C. $[\alpha]_D^{18}$ −5.29 (c=1.6, acetone). ^1H NMR ($CDCl_3$) δ: 1.18 (s, 3 H), 1.55 (s, 3 H), 6.40 (s, 1 H), 6.55–6.67 (m, 2 H), 6.95–7.05 (m, 2 H). IR (KBr) cm^{-1}: 1734. Anal. calcd. for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92; S, 11.77. found: C, 70.58; H, 5.95; S, 11.79.

α-Acetoxy-α-dimethylphosphorylmethyl p-*tolyl sulfide* ***(S*)-4d***

(38.2% yield, 69.1% *e.e.*, as a colorless oil) $[\alpha]_D^{18}$ −11.5 (c=1.5, acetone). ^1H NMR ($CDCl_3$) δ: 2.13 (s, 3 H), 2.33 (s, 3 H), 3.75 (d, 3 H, *J*=8.9 Hz), 3.79 (d, 3 H, *J*=8.9 Hz), 6.34 (d, 1 H, *J*=10.6 Hz), 7.13 (d, 2 H, *J*=7.9 Hz), 7.43 (d, 2 H, *J*=8.0 Hz). IR (KBr) cm^{-1}: 1757. Anal. calcd. for $C_{12}H_{17}O_5PS$: C, 47.37; H, 5.63; S, 10.54. found: C, 47.57; H, 5.53; S, 10.30.

Ethyl 3,4,5-trimethoxybenzoyloxy-[(4-methylphenyl)sulfanyl]acetate ***(R*)-5b***

(18.5% yield, 80.9% *e.e.*, as a colorless oil) $[\alpha]_D^{18}$ −66.3 (c=0.14, acetone). ^1H NMR ($CDCl_3$) δ: 1.19 (t, 3 H, *J*=6.9 Hz), 2.24 (s, 3 H), 3.82 (bs, 9 H), 4.15 (q, 2 H, *J*=6.9 Hz), 6.25 (s, 1 H), 7.05 (d, 2 H, *J*=8.1 Hz), 7.42 (d, 2 H, *J*=8.1 Hz). IR (KBr) cm^{-1}: 1750, 1725. MS *m/z* (%): 420 (M^+, 41), 195 (100). HRMS calcd. for $C_{21}H_{24}O_7S$ 420.1240; found 420.1237.

Ethyl 4-methoxybenzoyloxy-[(4-methylphenyl)sulfanyl]acetate ***(R*)-5c***

(37.0% yield, 76.4% *e.e.*, as a colorless oil) $[\alpha]_D^{18}$ −88.9 (c=0.045, acetone). ^1H NMR ($CDCl_3$) δ: 1.20 (t, 3 H, *J*=6.9 Hz), 2.35 (3 H, s), 3.89 (3 H, bs), 4.16 (q, 2 H, *J*=6.9 Hz), 6.36 (s, 1 H), 6.95 (d, 2 H, *J*=8.1 Hz), 7.15 (d, 2 H, *J*=8.0 Hz), 7.50 (d, 2 H, *J*=8.0 Hz), 8.08 (d, 2 H, *J*=8.1 Hz). IR (KBr) cm^{-1}: 1751, 1721. MS *m/z* (%): 360 (M^+, 22), 135 (100). HRMS calcd. for $C_{19}H_{20}O_5S$ 360.1031; found 360.1032.

*Ethyl benzoyloxy-[(4-methylphenyl)sulfanyl]acetate (**R***)-**5d***

(34.5% yield, 68.9% *e.e.*, as a colorless oil) $[\alpha]_D^{18}$ −32.5 (c=0.040, acetone). ^{1}H NMR ($CDCl_3$) δ: 1.21 (t, 3 H, *J*=6.9 Hz), 2.35 (3 H, s), 4.18 (q, 2 H, *J*=6.9 Hz), 6.38 (s, 1 H), 7.15 (d, 2 H, *J*=8.1 Hz), 7.40–7.55 (7 H, m). IR (KBr) cm^{-1}:1750, 1730. MS *m/z* (%): 330 (M^+, 40), 105 (100). HRMS calcd. for $C_{18}H_{18}O_4S$ 330.0926; found 330.0927.

*Ethyl 4-nitrobenzoyloxy-[(4-methylphenyl)sulfanyl]acetate (**R***)-**5e***

(19.5% yield, 65.6% *ee*, as a pale yellow oil) $[\alpha]_D^{18}$ −52.7 (c=0.055, acetone). ^{1}H NMR ($CDCl_3$) δ: 1.21 (t, 3 H, *J*=6.9 Hz), 2.27 (s, 3 H), 4.20 (q, 2 H, *J*=6.9 Hz), 6.39 (s, 1 H), 7.18 (d, 2 H, *J*=8.0 Hz), 7.45 (d, 2 H, *J*=8.0 Hz), 8.21 (d, 2 H, *J*=8.1 Hz), 8.35 (d, 2 H, *J*=8.1 Hz). IR (KBr) cm^{-1}:1750, 1730. MS *m/z* (%): 375 (M^+, 10), 150 (100). HRMS calcd. for $C_{18}H_{17}NO_6S$ 375.0777; found 375.0777.

*Ethyl chloroacetyloxy-[(4-methylphenyl)sulfanyl]acetate (**R***)-**5f***

(62.5% yield, 53.8% *ee*, as a colorless oil) $[\alpha]_D^{18}$ −36.1 (c=0.20, acetone). ^{1}H NMR ($CDCl_3$) δ: 1.21 (t, 3 H, *J*=7.1 Hz), 2.35 (3 H, s), 4.14 (q, 2 H, *J*=7.2 Hz), 4.18 (s, 2 H), 6.20 (s, 1 H), 7.15 (d, 2 H, *J*=7.8 Hz), 7.43 (d, 2 H, *J*=7.9 Hz). IR (KBr) cm^{-1}: 1770, 1750. MS *m/z* (%): 304 (M^+, 7), 302 (M^+, 17), 124 (100). HRMS calcd. for $C_{13}H_{15}ClO_4S$ 302.0377; found 302.0376.

*Ethyl 2,6-dimethylbenzoyloxy-[(4-methylphenyl)sulfanyl]acetate (**R***)-**5g***

(39.1% yield, 53.0% *ee*, as a colorless oil) $[\alpha]_D^{18}$ −40.0 (c=0.16, acetone). ^{1}H NMR ($CDCl_3$) δ: 1.22 (t, 3 H, *J*=7.0 Hz), 2.30 (s, 6 H), 2.35 (s, 3 H), 4.17 (q, 2 H, *J*=7.0 Hz), 6.40 (s, 1 H), 7.05–7.21 (m, 5 H), 7.43 (d, 2 H, *J*=8.0 Hz). IR (KBr) cm^{-1}: 1750, 1730. MS *m/z* (%): 358 (M^+, 27), 133 (100). HRMS calcd. for $C_{20}H_{22}O_4S$ 358.1237; found 358.1217.

2-Phenyl-3,1-benzoxathian-4-one 7

(81.5% yield by the use of **2e**, 33.0% *ee*, as white crystals) $[\alpha]_D^{22}$ −61.6 (c=0.10, EtOH). ^{1}H NMR ($CDCl_3$) δ: 6.59 (s, 1 H), 7.31–7.52 (m, 9 H), 8.21 (dd, 1 H, *J*=8.1, 2.0 Hz). HRMS calcd. for $C_{14}H_{16}O_2S$ 242.0401; found 242.0401.

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14. In the case of acetic anhydride, this reaction gave (−)-**7** as a product from (−)-**6**. On the other hand in the case of using EVE (**2**), the reaction gave (−)-**7** as a product from (+)-**6**.

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