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Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 16 (2005) 665–673

Asymmetric synthesis of both enantiomers of esters and γ-lactones from optically active 1-chlorovinyl *p*-tolyl sulfoxides and lithium ester enolates with the formation of a tertiary or a quaternary carbon stereogenic center at the β-position

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Received 13 October 2004; accepted 4 November 2004
Available online 26 January 2005

Abstract—Treatment of optically active 1-chlorovinyl *p*-tolyl sulfoxides having two different substituents at the 2-position, which were synthesized from aldehydes or unsymmetrical ketones and (*R*)-(−)-chloromethyl *p*-tolyl sulfoxide in two or three steps, with the lithium enolate of *tert*-butyl acetate gave optically active adducts in 99% chiral induction from the sulfur stereogenic center. The adducts were converted to optically active esters, carboxylic acids, and γ-lactones, which have a tertiary or a quaternary carbon stereogenic center at the β-position. A synthesis of optically active spiro-lactones was realized starting from 2-cyclohexenone by this method.
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1. Introduction

Carboxylic acids, esters, amides, and their derivatives have long been recognized to be amongst the most important and fundamental compounds in organic chemistry,[1] bioorganic chemistry,[2,3] and synthetic organic chemistry. Innumerable studies on the preparation and chemistry of these compounds have already been reported. On the other hand, the synthesis of optically active esters and lactones is quite interesting and important in chemistry these days. Needless to say, the optically active compounds are most important in the science of drugs, bioactive compounds, and life.

Control of the stereochemistry of the stereogenic carbon of esters and lactones at the α-position is now relatively easy. For example, chiral aldol-type reactions[4] and chiral substitution of the α-position of esters[5] are widely used. However, control of the stereochemistry of the stereogenic carbon of esters and lactones at the β-position is still not an easy task.

Recently, we reported a novel method for the synthesis of esters **5** and lactones **6** having a tertiary or a quaternary carbon at the β-position from the adduct **4**.[6] The key reaction was the addition of the lithium ester enolate of *tert*-butyl acetate to 1-chlorovinyl *p*-tolyl sulfoxides **3**, which were derived from carbonyl compounds **1** and chloromethyl *p*-tolyl sulfoxide **2**, to afford the adducts **4** in almost quantitative yields (Scheme 1).

We thought that if unsymmetrical ketones or aldehydes **1** and homochiral chloromethyl *p*-tolyl sulfoxide were used in this reaction, optically active esters **5** and γ-lactones **6** could be synthesized. We recently investigated this idea and actually were able to obtain optically active esters, acids, and lactones with over 99% enantiomeric excess in good chemical yields.

2. Results and discussion

2.1. Synthesis of optically active 1-chlorovinyl *p*-tolyl sulfoxides from aldehydes and unsymmetrical ketones, and reaction with lithium enolate of *tert*-butyl acetate

For the substrates in this investigation, we synthesized optically active (*R*)-1-chloro-4-phenyl-1-(*p*-tolylsulfinyl)-1-butene **3a** and **3b** and (*R*)-1-chloro-2-methyl-4-phenyl-1-(*p*-tolylsulfinyl)-1-butene **3c** and **3d** from enantiomerically pure (*R*)-(−)-chloromethyl *p*-tolyl sulfoxide

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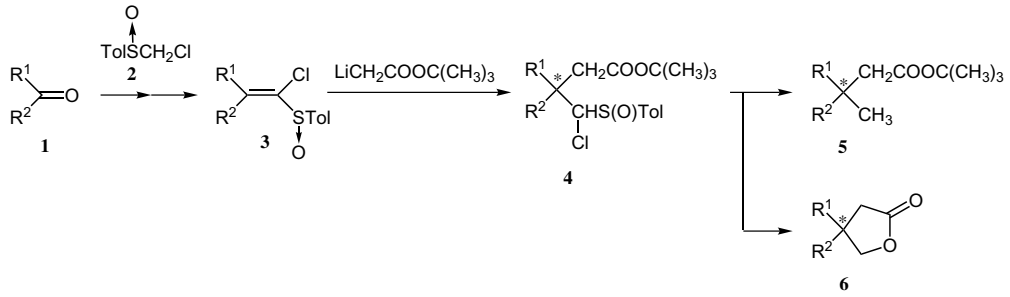
doi:10.1016/j.tetasy.2004.11.085



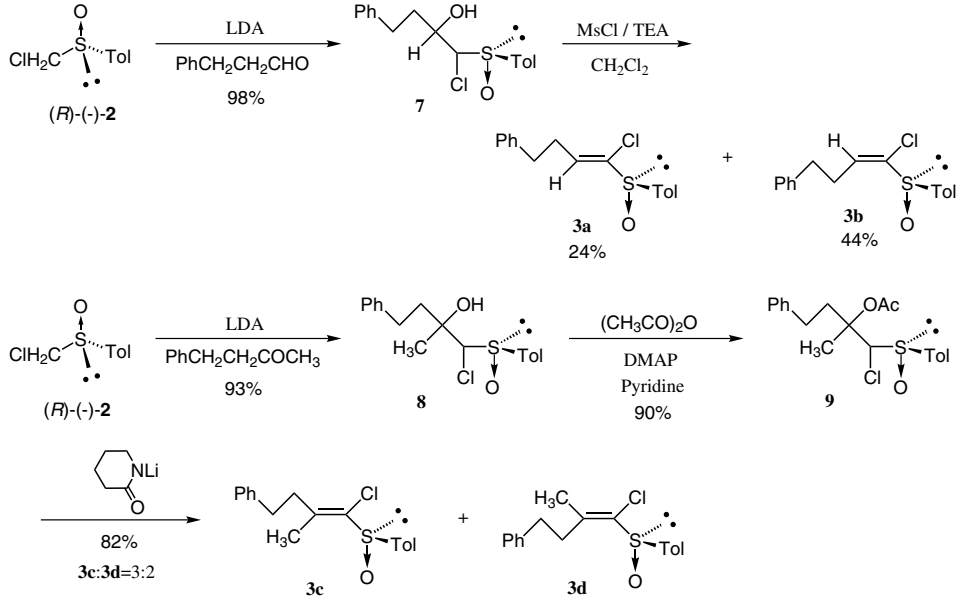
Scheme 1.

(*R*)-**2**[7] and 3-phenylpropanal and 4-phenyl-2-butanone, respectively. Thus, (*R*)-**2** was treated with LDA in THF at −65 °C followed by 3-phenylpropanal to give adduct **7** as a mixture of two diastereomers in a quantitative yield. The adduct was then treated with methanesulfonyl chloride with triethylamine (TEA) in CH_2Cl_2 at room temperature for 6 h to give a mixture of vinyl sulfoxides **3a** and **3b**, which were separated by silica gel column chromatography. The two-step overall yields of **3a** and **3b** were 24% and 44%, respectively, from 3-phenylpropanal (Scheme 2).

The 1-chlorovinyl *p*-tolyl sulfoxides **3c** and **3d** were prepared from 4-phenyl-2-butanone through the adduct **8** and its acetate **9**. Finally, acetate **9** was treated with *N*-lithio-2-piperidone[8] to afford a 3:2 mixture of **3c** and **3d** in 82% yield from **9**. These were separable by silica gel column chromatography.

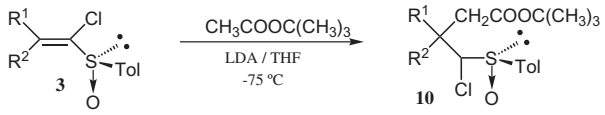
Initially, 5 equiv of the lithium ester enolate of *tert*-butyl acetate were generated from *tert*-butyl acetate and LDA in THF at −75 °C. To this solution were added 1-chlorovinyl *p*-tolyl sulfoxides **3a** and **3b**. The desired addition reaction took place within 5 min to afford adducts **10a** and **10b** in 91% and 89%, respectively (see Table 1, entries 1 and 2). Interestingly, although adducts **10a** and **10b** have three stereogenic centers, only a single product was obtained. No isomer was observed from detailed inspection of their ^1H NMR spectra. These results implied that the addition reaction took place with high 1,3-asymmetric induction from the sulfoxide stereogenic center. The enantiomeric excesses of **10a** and **10b** were also confirmed to be 99% by HPLC using Chiralcel OD as a chiral stationary column. The same reaction with **3c** and **3d** also proceeded within 5 min to give the single adducts **10c** and **10d** in high yields with about 99% diastereomeric excess (Table 1, entries 3 and 4). We had no doubt that successful asymmetric synthesis of carboxylic acids, which have a quaternary and a tertiary stereogenic carbon center at the β-position could be achieved at this stage.

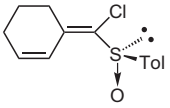
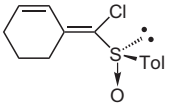
Next, the chlorine atom in adduct **10a** was reduced with tributyltin hydride in the presence of AIBN[9] in benzene to give **11a** in high yield. The sulfinyl group in **11a** was reduced with Raney-nickel in refluxing ethanol to afford ester **5a** in a quantitative yield (see Scheme 3). Adduct **10b** was also converted to the *tert*-butyl ester **5b** via **11b**, though the two-step overall yield was somewhat lower. The enantiomeric excesses of **5a** and **5b** were



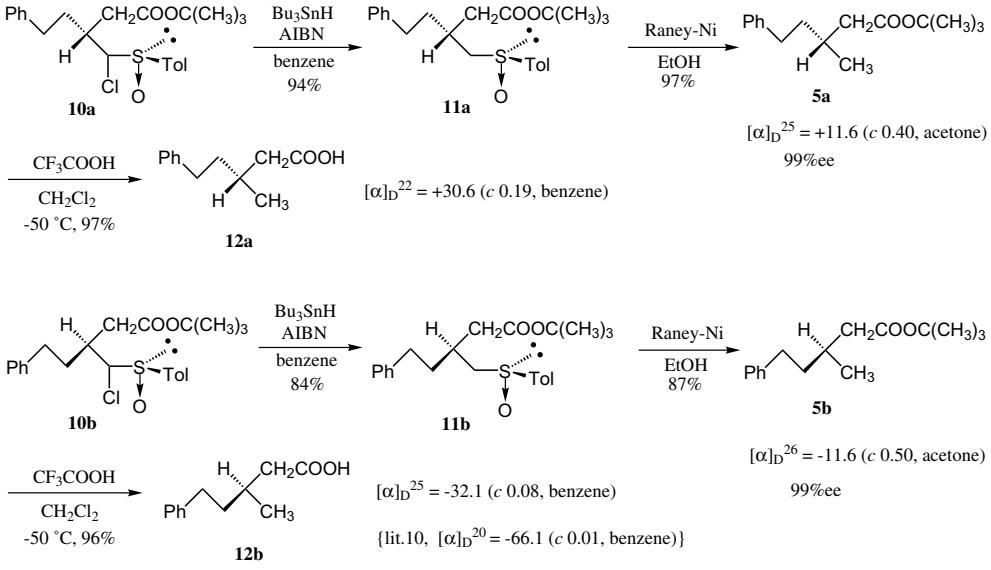
Scheme 2.

Table 1. Addition of lithium enolate of *tert*-butyl acetate to optically active 1-chlorovinyl *p*-tolyl sulfoxides



Entry	3			10		
		R^1	R^2		Yields (%)	De (%)[a]
1	**3a**	$PhCH_2CH_2$	H	**10a**	91	99
2	**3b**	H	$PhCH_2CH_2$	**10b**	89	99
3	**3c**	$PhCH_2CH_2$	CH_3	**10c**	86	99
4	**3d**	CH_3	$PhCH_2CH_2$	**10d**	91	99
5	**3e**			**10e**	97[b]	99
6	**3f**			**10f**	96[b]	99

[a] Diastereomeric excess (de) was determined from ^1H NMR and HPLC using chiral stationary column.
[b] The reaction temperature was −75 to −40 °C.



Scheme 3.

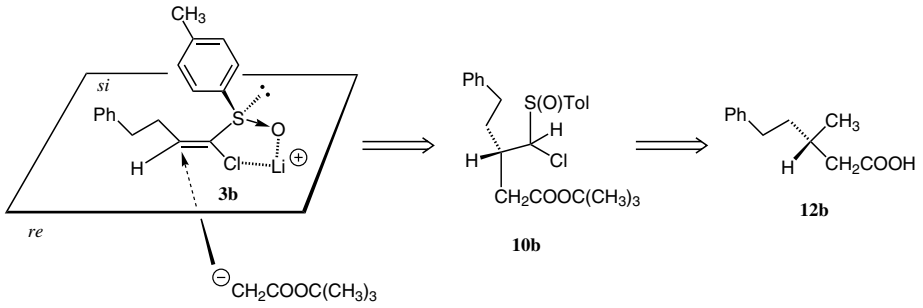
confirmed to be 99% by HPLC using Chiralpak AD as a chiral stationary column.

Finally, the *tert*-butyl esters **5a** and **5b** were treated with trifluoroacetic acid in CH_2Cl_2 at −50 °C to give both 3-methyl-5-phenylpentanoic acids **12a** and **12b** in quantitative yields. Pyne reported that (*S*)-3-methyl-5-phenylpentanoic acid had a negative specific rotation.[10] In our compound, carboxylic acid **12b**, which was derived from **3b**, had a negative specific rotation. Thus, the absolute configurations of all the compounds in Scheme 3 were unambiguously determined.

Conjugate addition of nucleophiles including organometallic reagents to chiral vinyl sulfoxides is already known; however, chiral induction from the sulfur stereogenic center proved in some cases unsatisfactory.[11] The results described above are one of the best examples in this category.

Previously, we reported a chiral addition reaction of cyanomethyllithium to 1-chlorovinyl *p*-tolyl sulfoxides[12] in which, we proposed a transition state model for the chiral induction from the sulfoxide chiral center. At this stage, in which the absolute configurations of all the compounds in Scheme 3 were confirmed, we applied the same transition state model in this investigation. The results are shown in Scheme 4.

As carboxylic acid **12b** has an (*S*)-configuration, the absolute configuration of the β-carbon of adduct **10b** must be also *S*. This means that the lithium ester enolate



Scheme 4.

should be introduced from the *re* face of the vinyl sulfoxide **3b**. This result is in good accordance with the proposed transition state model. Thus, the lithium cation forms a five-membered chelate between the oxygen of the sulfoxide and the chlorine atom. In this event, the bulky 4-methylphenyl group strongly hinders the *si* face. The lithium enolate of *tert*-butyl acetate was introduced from the *re* face to afford **10b** in very high chiral induction from the sulfoxide stereogenic center.

2.2. Synthesis of optically active lactones having a tertiary and a quaternary carbon stereogenic center at the β-position

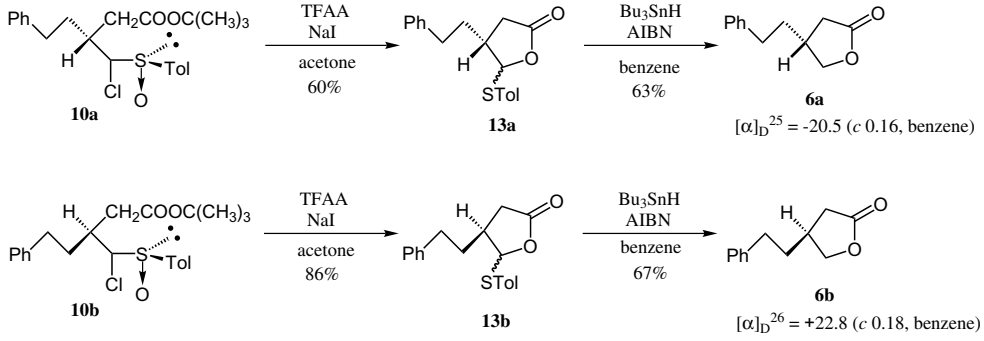
Previously, we found that treatment of adducts **10** with trifluoroacetic anhydride (TFAA) in the presence of NaI gave γ-lactones, which has a *p*-tolylsulfanyl group at the γ-position.[6] We applied this reaction to the optically active adducts **10a** and **10b** (Scheme 5). Thus, to a mixture of **10a** and NaI in acetone at −55 °C was added TFAA to afford the desired γ-lactone **13a** in 60% yield. The *p*-tolylsulfanyl group in **13a** was reduced with Bu_3SnH to give γ-lactone **6a** in 63% yield.

The same treatment of **10b** afforded the enantiomer **6b**, via **13b**, in somewhat higher yield. The enantiomeric excess of these two lactones was confirmed to be over 99% by HPLC using Chiralpak AD as a chiral stationary column.

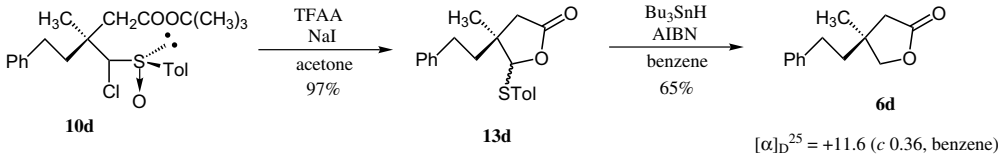
A γ-lactone having a quaternary stereogenic center at the β-position was also synthesized starting from the adduct **10d** (Scheme 6). Thus, adduct **10d** was treated with TFAA as described above to give a γ-lactone, which had *p*-tolylsulfanyl group **13d** in quantitative yield. The *p*-tolylsulfanyl group was reduced with Bu_3SnH to give **6d** in 65% yield. Again, the enantiomeric excess was found to be over 99% by using Chiralpak AD as a chiral stationary column.

2.3. Synthesis of optically active spiro-lactones by this procedure

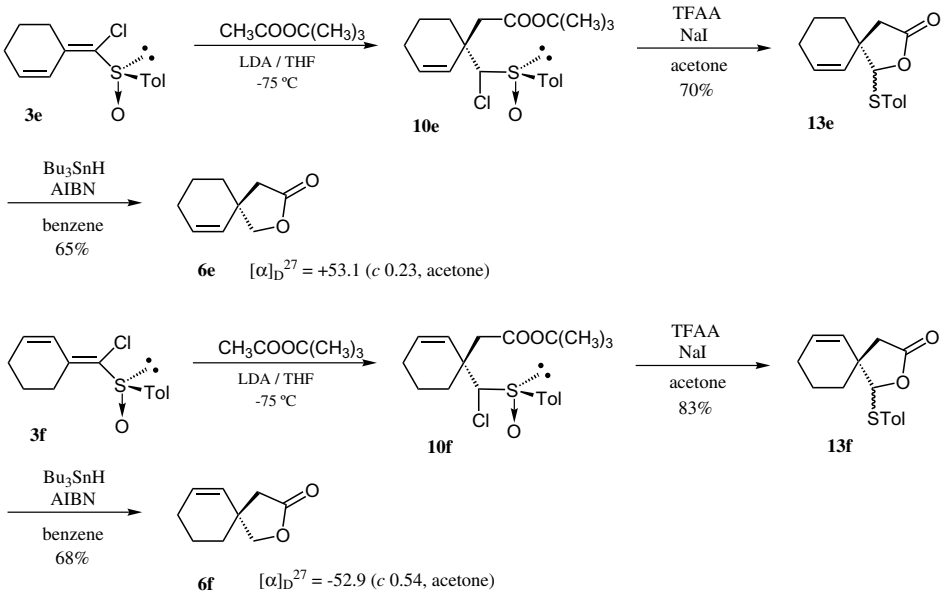
Spirocyclic compounds, which contain one carbon atom common to two rings, are interesting in organic and synthetic organic chemistry.[13] Spirocyclic compounds have a quaternary carbon, which is still difficult to



Scheme 5.



Scheme 6.



Scheme 7.

construct.[14] An even more difficult task is the enantiocontrolled synthesis of spirocycles. We extended our procedure described above to a novel method for the synthesis of optically active spiro-lactones (Scheme 7).

First, optically active 1-chlorovinyl *p*-tolyl sulfoxides **3e** and **3f** were prepared from 2-cyclohexenone by the same procedure as for the synthesis of **3c** and **3d**.[8] The conjugate addition of **3e** and **3f** with the lithium ester enolate of *tert*-butyl acetate gave again a single product in almost quantitative yield (see Table 1 and Scheme 7). The enantiomeric excess of these adducts was found to be over 99% by using Chiralcel OD as a chiral stationary column.

The adducts were treated with TFAA in the presence of NaI to give spirocyclic lactones having a *p*-tolylsulfanyl group at the β-position (**13e** and **13f**) in good yields. Finally, the thioether was reduced with Bu_3SnH to afford the enantiomerically pure spiro-lactones **6e** and **6f** in about 65% yield.

3. Conclusion

In conclusion, we have developed a new and efficient method for the synthesis of optically active esters and lactones having a tertiary or a quaternary stereogenic center at the γ-position. The asymmetric induction from the sulfur stereogenic center was found to be almost complete and we believe that the method presented here is useful for the synthesis of homochiral esters and lactones.

4. Experimental

All melting points are uncorrected. ^1H NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 500 and Burker XWIN-600 spectrometer. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel 60 (Merck) containing 0.5% fluorescence reagent 254 and a quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry reagent and solvent, benzene, dichloromethane, *N*,*N*-diisopropylamine, and pyridine were distilled from CaH_2 while THF was distilled from diphenylketyl. Acetone was dried over $CaSO_4$ and distilled before use.

4.1. (*R*)-(*Z*)-1-Chloro-4-phenyl-1-(*p*-tolylsulfinyl)-1-butene 3a and the (*E*)-isomer 3b

A solution of (*R*)-(−)-**2** (973 mg; 5.2 mmol) in 4 mL of dry THF was added dropwise to a solution of LDA (6.24 mmol) in 15 mL of THF at −65 °C. The solution was stirred at −65 °C for 10 min, then 3-phenylpropanal (0.82 mL; 6.24 mmol) was added. The reaction mixture was stirred for 10 min and the reaction quenched by satd aq NH_4Cl after which it was extracted with CH_2Cl_2. The organic layer was washed with satd aq NH_4Cl and dried over $MgSO_4$. The solvent was evaporated to give chloro alcohol **7** as a light yellow viscous oil (1.64 g; 98%, a mixture of two diastereomers). IR (neat) 3351 (OH), 2925, 1086, 1047 (SO) cm^{-1}. To a solution of chloro alcohol **7** (1.64 g; 5.1 mmol) in dry CH_2Cl_2 (10 mL) was added triethylamine (5.1 mL; 38.2 mmol) followed by methanesulfonyl chloride (1.15 mL; 15.3 mmol) with stirring at 0 °C. The reaction mixture was stirred at 0 °C for 10 min, then at room temperature for 6 h. The reaction was quenched with water, and the whole was extracted with CH_2Cl_2. The organic layer was washed successively with 10% HCl and satd $NaHCO_3$. The usual work-up followed by silica gel column chromatography afforded **3a** (379 mg; 24%) and **3b** (680 mg; 44%).[15] Compound **3a**: light yellow viscous oil; IR (neat) 3027, 2924, 1596, 1495, 1455, 1089, 1063 (SO), 877,

809 cm^{-1}; ^1H NMR δ 2.41 (3H, s), 2.66–2.70 (2H, m), 2.81–2.84 (2H, m), 6.78 (1H, t, $J = 7.2$ Hz), 7.18–7.46 (9H, m). MS *m/z* (%) 304 (M^+, 1), 287 (100), 91(90). $[\alpha]_D^{29} = -47.5$ (*c* 0.65, acetone; 99% ee). (*E*)-isomer **3b**: light yellow viscous oil; IR (neat) 3026, 2924, 1602, 1494, 1455, 1091, 1062 (SO), 877 cm^{-1}; ^1H NMR δ 2.40 (3H, s), 2.78–2.84 (1H, m), 2.91–3.04 (3H, m), 6.32 (1H, t, $J = 7.8$ Hz), 7.21–7.36 (9H, m). MS *m/z* (%) 304 (M^+, 20), 197 (59), 91 (100). $[\alpha]_D^{27} = +215.1$ (*c* 0.47, acetone; 99% ee).

4.2. (*R*)-(*Z*)-1-Chloro-2-methyl-4-phenyl-1-(*p*-tolylsulfinyl)-1-butene 3c and the (*E*)-isomer 3d

A solution of (*R*)-(−)-**2** (515 mg; 2.75 mmol) in 3 mL of dry THF was added dropwise to a solution of LDA (3.3 mmol) in 15 mL of THF at −65 °C. The solution was stirred at −65 °C for 10 min, and then benzylactone (0.5 mL; 3.3 mmol) added. The reaction mixture was stirred for 10 min and the reaction quenched with satd aq NH_4Cl. The whole was then extracted with CH_2Cl_2. The organic layer was washed with satd aq NH_4Cl and dried over $MgSO_4$. The solvent was evaporated to give chloro alcohol **8** as crystals (861 mg; 93%; about 3:2 diastereomeric mixture). IR (KBr) 3384 (OH), 2924, 1494, 1084, 1037 (SO), 807 cm^{-1}; ^1H NMR δ 1.59 (1.8H, s), 1.65 (1.2H, s), 2.09–2.20 (2H, m), 2.42 (3H, s), 2.75–2.83 (2H, m), 4.30 (0.6H, s), 4.35 (0.4H, s), 7.18–7.49 (9H, m). MS *m/z* (%) 336 (M^+, 0.3), 179 (8), 140 (68), 139 (34), 105 (24), 91 (100). Calcd for $C_{18}H_{21}ClO_2S$: M, 336.0951. Found: *m/z* 336.0954.

4-(Dimethylamino)pyridine (51 mg, 0.41 mmol) was added to a solution of **8** (860 mg, 2.5 mmol) in a mixture of acetic anhydride (3.1 mL; 31.5 mmol) and pyridine (9.3 mL; 110 mmol). The mixture was stirred at room temperature for 11 h. The acetic anhydride and pyridine were evaporated under vacuum and the residue was purified by silica gel column chromatography to give **9** (853 mg; 90%) as a colorless oil (about 3:2 diastereomeric mixture). IR (neat) 3026, 2929, 1732 (CO), 1495, 1455, 1369, 1243, 1092, 1065 (SO), 1017, 810 cm^{-1}; ^1H NMR δ 1.70 (1.2H, s), 1.80 (1.8H, s), 2.09 (3H, s), 2.23–2.28 (0.6H, m), 2.31–2.37 (0.4H, m), 2.41 (1.2H, s), 2.42 (1.8H, s), 2.49–2.57 (0.6H, m), 2.61–2.66 (0.4H, m), 2.71–2.79 (2H, m), 5.27 (0.6H, s), 5.40 (0.4H, s), 7.16–7.48 (9H, m). MS *m/z* (%) 378 (M^+, 0.6), 239 (18), 179 (23), 140 (60), 139 (32), 91 (100). Calcd for $C_{20}H_{23}ClO_3S$: M, 378.1057. Found: *m/z* 378.1062.

A solution of **9** (928 mg, 2.45 mmol) in dry THF (4 mL) was added dropwise to *N*-lithio-2-piperidone (7.2 mmol) prepared from *n*-BuLi (4.5 mL; 7.2 mmol) and 2-piperidone (730 mg, 7.2 mmol) in THF (12 mL) at 0 °C in THF at room temperature. The reaction mixture was stirred at room temperature for 1 h. The reaction was quenched by satd aq NH_4Cl and the whole extracted with $CHCl_3$ and washed with water. The organic layer was dried over $MgSO_4$. The solvent was evaporated and the residue purified by silica gel column chromatography to give 625 mg (82%) of **3c** and **3d** as an about 3:2 mixture. Compound **3c**: colorless crystals; mp 56–57 °C (hexane); IR (KBr) 3029, 2924, 1601, 1494, 1454, 1087, 1055 (SO), 889, 808 cm^{-1}; ^1H NMR δ 2.25 (3H, s), 2.42 (3H, s), 2.56–2.61 (1H, m), 2.70–2.86 (3H, m), 7.31–7.40 (9H, m). Anal. Calcd for $C_{18}H_{19}ClOS$: C, 67.80; H, 6.01. Found: C, 67.62; H, 5.75. $[\alpha]_D^{27} = +127.3$ (*c* 1.0, acetone; 99% ee). Compound **3d**: colorless crystals; mp 64–65 °C (hexane); IR (KBr) 3031, 2934, 1594, 1492, 1455, 1080, 1054 (SO), 814, 702 cm^{-1}; ^1H NMR δ 2.07 (3H, s), 2.39 (3H, s), 2.85–2.91 (1H, m), 2.94–3.01 (2H, m), 3.15–3.21 (1H, m), 7.08–7.38 (9H, m). Anal. Calcd for $C_{18}H_{19}ClOS$: C, 67.80; H, 6.01. Found: C, 67.73; H, 5.89. $[\alpha]_D^{28} = +244.4$ (*c* 1.0, acetone; 99% ee).

4.3. (*R*)-(*E*)-1-(Chlorocyclohex-2-enylidene-methanesulfinyl)-4-methylbenzene 3e and the (*Z*)-isomer 3f

These 1-chlorovinyl *p*-tolyl sulfoxides were synthesized from 2-cyclohexenone and (*R*)-(−)-**2** according to the procedure described above in similar yields. Compound **3e**: colorless crystals; mp 80–82 °C (AcOEt–hexane); IR (KBr) 2931, 2909, 1615, 1493, 1397, 1085, 1053 (SO), 875, 810 cm^{-1}; ^1H NMR δ 1.70–1.76 (1H, m), 1.80–1.85 (1H, m), 2.23–2.27 (2H, m), 2.41 (3H, s), 2.54–2.64 (2H, m), 6.26 (1H, dt, $J = 12.0$, 4.2 Hz), 7.13 (1H, dt, $J = 12.0$, 1.8 Hz), 7.31, 7.48 (each 2H, d, $J = 7.8$ Hz). MS *m/z* (%) 266 (M^+, 10), 250 (10), 218 (100), 183 (33), 139 (12), 124 (37), 123 (22), 91 (65), 79 (25), 65 (25). Calcd for $C_{14}H_{15}ClOS$: M, 266.0530. Found: *m/z* 266.0529. Anal. Calcd for $C_{14}H_{15}ClOS$: C, 63.03; H, 5.67; Cl, 13.29; S, 12.02. Found: C, 62.60; H, 5.54; Cl, 13.30, S, 12.16. $[\alpha]_D^{30} = +319.5$ (*c* 1.0, acetone; 99% ee). Compound **3f**: colorless crystals; mp 92–93 °C (AcOEt–hexane); IR (KBr) 2957, 2924, 1614, 1083, 1050 (SO), 952, 818 cm^{-1}; ^1H NMR δ 1.85–1.90 (2H, m), 2.27–2.31 (2H, m), 2.41 (3H, s), 2.73 (1H, ddd, $J = 15.3$, 10.5, 4.2 Hz), 3.21 (1H, ddd, $J = 15.3$, 6.6, 4.2 Hz), 6.34 (1H, dt, $J = 12.0$, 4.2 Hz). 6.56 (1H, dt, $J = 12.0$, 2.4 Hz), 7.31, 7.48 (each 2H, d, $J = 8.4$ Hz). MS *m/z* (%) 266 (M^+, 73), 249 (81), 218 (42), 183 (25), 169 (13), 139 (20), 124 (40), 123 (32), 91 (100), 65 (62). Calcd for $C_{14}H_{15}ClOS$: M, 266.0530. Found: *m/z* 266.0523. Anal. Calcd for $C_{14}H_{15}ClOS$: C, 63.03; H, 5.67; Cl, 13.29; S, 12.02. Found: C, 62.89; H, 5.53; Cl, 13.05; S, 12.30. $[\alpha]_D^{29} = +550.4$ (*c* 1.0, acetone; 99% ee).

4.4. (−)-*tert*-Butyl 3-[chloro(*p*-tolylsulfinyl)methyl]-5-phenylpentanoate 10a

tert-Butyl acetate (0.064 mL; 0.48 mmol) was added to a solution of LDA (0.48 mmol) in 4 mL of dry THF at −78 °C with stirring. The solution was stirred for 10 min and then a solution of **3a** (73 mg; 0.24 mmol) in THF (1 mL) was added. The solution was stirred for 5 min, then the reaction quenched by adding satd aq NH_4Cl. The whole was extracted with hexane–AcOEt. The product was purified by silica gel column chromatography to afford **10a** (92.4 mg; 91%). Colorless oil; IR (neat) 3027, 2929, 1732 (CO), 1598, 1367, 1154, 1055 (SO), 812 cm^{-1}; ^1H NMR δ 1.45 (9H, s), 1.71–1.77 (1H, m), 2.17–2.23 (1H, m), 2.43 (3H, s), 2.44 (1H, dd, $J = 15.6$, 7.8 Hz), 2.59 (1H, dd, $J = 16.2$,

4.8 Hz), 2.75–2.81 (2H, m), 3.08–3.12 (1H, m), 4.66 (1H, d, $J = 1.8$ Hz), 7.20–7.27 (3H, m), 7.26–7.33 (4H, m), 7.67 (2H, d, $J = 8.4$ Hz). MS *m/z* (%) 420 (M^+, trace), 347 (14), 188 (18), 140 (95), 129 (38), 91 (96). Calcd for $C_{23}H_{29}ClO_3S$: M, 420.1526. Found: *m/z* 420.1521. $[\alpha]_D^{32} = -84.0$ (*c* 0.15, acetone; 99% de).

4.5. (−)-*tert*-Butyl 3-[chloro(*p*-tolylsulfinyl)methyl]-5-phenylpentanoate 10b

Colorless oil; IR (neat) 2930, 1731 (CO), 1597, 1455, 1368, 1258, 1152, 1055 (SO), 812 cm^{-1}; ^1H NMR δ 1.46 (9H, s), 1.85–1.89 (1H, m), 1.95–1.97 (1H, m), 2.38 (1H, dd, $J = 16.2$, 9.6 Hz), 2.44 (3H, s), 2.65 (2H, t, $J = 8.4$ Hz), 2.86 (1H, dd, $J = 16.2$, 3.6 Hz), 3.07–3.09 (1H, m), 7.15–7.20 (3H, m), 7.25–7.29 (2H, m), 7.33, 7.63 (each 2H, d, $J = 8.4$ Hz). MS *m/z* (%) 420 (M^+, trace), 347 (8), 188 (28), 140 (62), 129 (29), 91 (94). Calcd for $C_{23}H_{29}ClO_3S$: M, 420.1526. Found: *m/z* 420.1526. $[\alpha]_D^{28} = -113.6$ (*c* 0.29, acetone; 99% de).

4.6. (−)-*tert*-Butyl 3-[chloro(*p*-tolylsulfinyl)methyl]-3-methyl-5-phenylpentanoate 10c

Colorless oil; IR (neat) 2978, 2931, 1731 (CO), 1597, 1455, 1367, 1219, 1155, 1054 (SO), 812 cm^{-1}; ^1H NMR δ 1.48 (9H, s), 1.51 (3H, s), 1.99–2.02 (2H, m), 2.43 (3H, s), 2.58–2.63 (1H, m), 2.66–2.71 (1H, m), 2.83, 3.07 (each 1H, d, $J = 15.6$ Hz), 5.12 (1H, s), 7.16–7.30 (5H, m), 7.32, 7.74 (each 2H, d, $J = 7.8$ Hz). MS *m/z* (%) 434 (M^+, trace), 361 (12), 203 (15), 140 (99), 91 (72). Calcd for $C_{24}H_{31}ClO_3S$: M, 434.1682. Found: *m/z* 434.1695. $[\alpha]_D^{28} = -44.5$ (*c* 0.85, acetone; 99% de).

4.7. (−)-*tert*-Butyl 3-[chloro(*p*-tolylsulfinyl)methyl]-3-methyl-5-phenylpentanoate 10d

Colorless oil; IR (neat) 2976, 2926, 1718 (CO), 1597, 1491, 1458, 1364, 1160, 1055 (SO), 812 cm^{-1}; ^1H NMR δ 1.42 (3H, s), 1.47 (9H, s), 2.19, 2.29 (each 1H, dt, $J = 9.6$, 5.4 Hz), 2.42 (3H, s), 2.67, 3.07 (each 1H, d, $J = 15.6$ Hz), 2.68, 2.75 (each 1H, dt, $J = 12.6$, 5.4 Hz), 5.21 (1H, s), 7.18 (1H, m), 7.23–7.26 (2H, m), 7.28–7.31 (4H, m), 7.72 (2H, d, $J = 8.4$ Hz). MS *m/z* (%) 434 (M^+, 0.5), 361 (13), 203 (20), 140 (100), 91 (69). Calcd for $C_{24}H_{31}ClO_3S$: M, 434.1682. Found: *m/z* 434.1689. $[\alpha]_D^{28} = -117.0$ (*c* 0.06, acetone; 99% de).

4.8. (−)-*tert*-Butyl {1-[chloro(*p*-tolylsulfinyl)methyl]-cyclohex-2-enyl}acetate 10e

Colorless oil; IR (neat) 2978, 2933, 1723 (CO), 1367, 1151, 1056 (SO), 812, 756 cm^{-1}; ^1H NMR δ 1.45 (9H, s), 1.68–1.78 (3H, m), 2.05–2.08 (2H, m), 2.11–2.16 (1H, m), 2.42 (3H, s), 2.68, 2.83 (each 1H, d, $J = 15.3$ Hz), 5.20 (1H, s), 5.88–5.95 (2H, m), 7.31, 7.69 (each 2H, d, $J = 8.0$ Hz). MS *m/z* (%) 382 (M^+, 90), 309 (10), 187 (15), 151 (45), 140 (100), 105 (35), 91 (58). Calcd for $C_{20}H_{27}ClO_3S$: M, 382.1369. Found: *m/z* 382.1371. $[\alpha]_D^{26} = -29.2$ (*c* 0.40, acetone; 99% de).

4.9. (−)-*tert*-Butyl {1-[chloro(*p*-tolylsulfinyl)methyl]-cyclohex-2-enyl}acetate 10f

Colorless oil; IR (neat) 2979, 2934, 1722 (CO), 1367, 1152, 1053 (SO), 812, 756 cm^{-1}; ^1H NMR δ 1.45 (9H, s), 1.63–1.72 (1H, m), 1.75–1.81 (1H, m), 2.04–2.11 (3H, m), 2.29–2.38 (1H, m), 2.42 (3H, s), 2.65, 3.19 (each 1H, d, $J = 15.9$ Hz), 5.33 (1H, s), 5.71 (1H, d, $J = 10.7$ Hz), 5.87–5.90 (1H, m), 7.23, 7.70 (each 2H, d, $J = 8.3$ Hz). MS *m/z* (%) 382 (M^+, 90), 309 (13), 187 (15), 140 (100), 91(30). Calcd for $C_{20}H_{27}ClO_3S$: M, 382.1369. Found: *m/z* 382.1383. $[\alpha]_D^{26} = -30.0$ (*c* 0.35, acetone; 99% de).

4.10. (−)-*tert*-Butyl 3-(*p*-tolylsulfinyl)methyl-5-phenylpentanoate 11a

AIBN (10 mg; 0.06 mmol) was added to a solution of **10a** (91 mg; 0.22 mmol) and Bu_3SnH (0.086 mL; 0.33 mmol) in 4 mL of dry benzene. The atmosphere in the flask was replaced with Ar, and the reaction mixture stirred and refluxed for 20 min. The benzene was evaporated, and the residue was purified by silica gel column chromatography to afford **11a** (79.6 mg; 94%) as a colorless oil; IR (neat) 2928, 1728 (CO), 1495, 1455, 1367, 1150, 1045 (SO), 810 cm^{-1}; ^1H NMR δ 1.44 (9H, s), 1.76–1.83 (1H, m), 1.91–1.98 (1H, m), 2.39–2.42 (1H, m), 2.42 (3H, s), 2.39, 2.52 (each 1H, dd, $J = 12$, 6 Hz), 2.63–2.66 (2H, m), 2.77, 2.95 (each 1H, dd, $J = 12$, 5.4 Hz), 7.13–7.28 (5H, m), 7.31, 7.51 (each, 2H, d, $J = 7.8$ Hz). MS *m/z* (%) 386 (M^+, 4), 370 (15), 369 (9), 313 (68), 191 (23), 173 (12), 140 (76), 129 (100), 91 (96). Calcd for $C_{23}H_{30}O_3S$: M, 386.1916. Found: *m/z* 386.1923. $[\alpha]_D^{29} = -94.3$ (*c* 0.22, acetone).

4.11. (−)-*tert*-Butyl 3-(*p*-tolylsulfinyl)methyl-5-phenylpentanoate 11b

Colorless oil; IR (neat) 2978, 2923, 1724 (CO), 1495, 1455, 1367, 1150, 1045 (SO), 810, 751 cm^{-1}; ^1H NMR δ 1.43 (9H, s), 1.78–1.81(2H, m), 2.39–2.44 (1H, m), 2.41 (3H, s), 2.55 (2H, d, $J = 6$ Hz), 2.58–2.64 (1H, m), 2.66–2.71 (1H, m), 2.88 (2H, d, $J = 7.2$ Hz), 7.14–7.27 (5H, m), 7.31, 7.48 (each 2H, d, $J = 8.4$ Hz). MS *m/z* (%) 386 (M^+, 3), 370 (20), 369 (9), 313 (68), 191 (23), 173 (13), 140 (73), 129 (99), 91 (98). Calcd for $C_{23}H_{30}O_3S$: M, 386.1916. Found: *m/z* 386.1927. $[\alpha]_D^{27} = -110.9$ (*c* 0.30, acetone).

4.12. (*R*)-(+)-*tert*-Butyl 3-methyl-5-phenylpentanoate 5a

A solution of **11a** (82 mg; 0.21 mmol) and excess of Raney-Ni in 8 mL of EtOH was stirred and refluxed for 15 min. The Raney-Ni was filtered off, and the filtrate was evaporated to give a residue, which was purified by silica gel column chromatography to give **5a** (50.4 mg; 97%) as a colorless oil; IR (neat) 2975, 2931, 1731 (CO), 1455, 1367, 1147 cm^{-1}; ^1H NMR δ 1.00 (3H, d, $J = 7.0$ Hz), 1.44 (9H, s), 1.47–1.69 (2H, m), 1.94–2.03 (1H, m), 2.05–2.10 (1H, m), 2.23–2.28 (1H, m), 2.56–2.65 (2H, m), 7.13–7.28 (5H, m). MS *m/z* (%) 248 (M^+, 3), 192 (49), 174 (37), 131 (60), 91 (100). Calcd for $C_{16}H_{24}O_2$: M, 248.1775. Found: *m/z*

248.1773. $[\alpha]_D^{25} = +11.6$ (*c* 0.40, acetone). (*S*)-(−)-**5b**: $[\alpha]_D^{26} = -11.6$ (*c* 0.50, acetone).

4.13. (*R*)-(+)-3-Methyl-5-phenylpentanoic acid 12a

Trifluoroacetic acid (TFA) (0.12 mL; 0.6 mmol) was added to a solution of **5a** (50 mg; 0.20 mmol) in 5 mL of CH_2Cl_2 at −50 °C. The reaction mixture was stirred for 30 min and the reaction quenched by adding satd aq $NaHCO_3$. The whole was extracted with CH_2Cl_2 and the aqueous layer washed with CH_2Cl_2. The aqueous layer was acidified with 10% HCl and extracted with CH_2Cl_2. The organic solvent was evaporated to give **12a** (37 mg; 97%) as a colorless oil; IR (neat) 2929, 1706 (CO), 1455, 1304, 943 cm^{-1}; ^1H NMR δ 1.04 (3H, d, $J = 6.8$ Hz), 1.50–1.58 (1H, m), 1.66–1.73 (1H, m), 2.03 (1H, octet, $J = 7.0$ Hz), 2.17 (1H, dd, $J = 15.0$, 8.0 Hz), 2.41 (1H, dd, $J = 15.0$, 5.8 Hz), 2.57–2.71 (2H, m), 7.18–7.29 (5H, m). MS *m*/*z* (%) 192 (M^+, 25), 174 (23), 132 (14), 117 (15), 105 (25), 91 (100), 77 (11). Calcd for $C_{12}H_{16}O_2$: M, 192.1148. Found: *m*/*z* 192.1147. $[\alpha]_D^{22} = +30.6$ (*c* 0.19, benzene). (*S*)-(−)-**12b**: $[\alpha]_D^{25} = -32.1$ (*c* 0.08, benzene).

4.14. 4-(2-Phenylethyl)-5-(*p*-tolylsulfanyl)dihydrofuran-2-one 13a

TFAA (0.48 mL; 2.6 mmol) was added dropwise with stirring to a suspension of **10a** (217 mg; 0.52 mmol) and NaI (394 mg; 2.6 mmol) in 5 mL of dry acetone at −55 °C for 5 min and the reaction quenched by satd aq $NaHCO_3$ and satd aq Na_2SO_3. The whole was extracted with ether–benzene. The organic layer was washed with satd aq $NaHCO_3$ and dried over $MgSO_4$. The solvent was evaporated, and the residue purified by silica gel column chromatography to give **13a** (97 mg; 60%) as a colorless oil (about 3:2 diastereomeric mixture); IR (neat) 3026, 2922, 2859, 1783 (CO), 1495, 1456, 1144, 957, 812 cm^{-1}; ^1H NMR δ 1.72–1.77 (1H, m), 2.34 (3H, s), 2.54–2.81 (6H, m), 5.34 (0.6H, d, $J = 6.0$ Hz), 5.78 (0.4H, d, $J = 6.0$ Hz). 7.12–7.45 (9H, m). MS *m*/*z* (%) 312 (M^+, 25), 189 (19), 143 (17), 129 (100), 124 (35), 91 (68). Calcd for $C_{19}H_{20}O_2S$: M, 312.1182. Found: *m*/*z* 312.1160.

4.15. 4-(2-Phenylethyl)-5-(*p*-tolylsulfanyl)dihydrofuran-2-one 13b

Colorless oil (about 5:1 diastereomeric mixture); IR (neat) 3026, 2924, 1790 (CO), 1495, 1455, 1205, 1149, 958, 813 cm^{-1}; ^1H NMR δ 1.71–1.77 (1H, m), 2.34 (3H, s), 2.33–2.46 (2H, m), 2.54–2.79 (4H, m), 5.34 (0.83H, d, $J = 6.0$ Hz), 5.78 (0.17H, d, $J = 6.6$ Hz), 7.11–7.67 (9H, m). MS *m*/*z* (%) 312 (M^+, 9), 189 (18), 143 (20), 129 (100), 91 (91), 77 (11). Calcd for $C_{19}H_{20}O_2S$: M, 312.1183. Found: *m*/*z* 312.1188.

4.16. (*R*)-(−)-4-(2-Phenylethyl)dihydrofuran-2-one 6a

AIBN (51 mg; 0.31 mmol) was added to a solution of **13a** (97 mg; 0.31 mmol) and Bu_3SnH (0.33 mL; 1.24 mmol) in 7 mL dry benzene. The atmosphere in the flask was replaced with Ar, and the reaction mixture stirred and refluxed for one day. The benzene was evaporated and the residue purified by silica gel column chromatography to give **6a** (37 mg; 63%) as a colorless oil; IR (neat) 2925, 1777 (CO), 1172, 1022, 751, 701 cm^{-1}; ^1H NMR δ 1.78–1.87 (2H, m), 2.21 (1H, dd, $J = 16.8$, 7.8 Hz), 2.55 (1H, sep, $J = 7.2$ Hz), 2.60–2.68 (3H, m), 3.94 (1H, dd, $J = 9.0$, 7.2 Hz), 4.40 (1H, dd, $J = 9.0$, 7.8 Hz), 7.15–7.31 (5H, m). MS *m*/*z* (%) 190 (M^+, 42), 159 (19), 130 (12), 104 (48), 91 (100), 65 (11). Calcd for $C_{12}H_{14}O_2$: M, 190.0992. Found: *m*/*z* 190.0990. $[\alpha]_D^{25} = -20.5$ (*c* 0.16, benzene; 99% ee). (*S*)-(+)-**6b**: $[\alpha]_D^{25} = +22.8$ (*c* 0.18, benzene; 99% ee).

4.17. 4-Methyl-4-(2-phenylethyl)-5-(*p*-tolylsulfanyl)-dihydrofuran-2-one 13d

Colorless oil (about 7:3 diastereomeric mixture); IR (neat) 2926, 1790 (CO), 1495, 1179, 957, 812 cm^{-1}; ^1H NMR δ 1.31 (3H, s), 1.77–1.82 (1H, m), 1.98–2.02 (1H, m), 2.40–2.49 (2H, m), 2.54–2.59 (1H, m), 2.72–2.79 (1H, m), 5.41 (0.7H, s), 5.45 (0.3H, s), 7.13–7.46 (9H, m). MS *m*/*z* (%) 326 (M^+, 3), 203 (25), 157 (12), 143 (79), 124 (22), 105 (11), 91 (100), 77 (9). Calcd for $C_{20}H_{22}O_2S$: M, 326.1338. Found: *m*/*z* 326.1330.

4.18. (*S*)-(+)-4-Methyl-4-(2-phenylethyl)dihydrofuran-2-one 6d

Colorless oil; IR (neat) 2919, 1774 (CO), 1495, 1176, 1078, 812 cm^{-1}; ^1H NMR δ 1.26 (3H, s), 1.79–1.82 (2H, m), 2.31, 2.43 (each 1H, d, $J = 17.4$ Hz), 2.61–2.64 (2H, m), 3.99, 4.07 (each 1H, d, $J = 9$ Hz), 7.17–7.31 (5H, m). MS *m*/*z* (%) 204 (M^+, 45), 173 (31), 144 (9), 129 (12), 104 (48), 91 (100), 77 (8). Calcd for $C_{13}H_{16}O_2$: M, 204.1148. Found: *m*/*z* 204.1144. $[\alpha]_D^{25} = +11.6$ (*c* 0.36, benzene; 99% ee).

4.19. 1-(*p*-Tolylsulfanyl)-2-oxaspiro[4.5]dec-6-en-3-one 13e

Colorless oil (about 1:1 diastereomeric mixture); IR (neat) 2929, 1790 (CO), 1493, 1197, 1156, 959, 812 cm^{-1}; ^1H NMR δ 1.57–2.12 (6H, m), 2.34 (3H, s), 2.43, 2.58 (each 0.5H, d, $J = 17$ Hz), 2.45, 2.69 (each 0.5H, d, $J = 17.5$ Hz), 5.45 (0.5H, s), 5.47 (0.5H, s), 5.56, 5.73 (each 0.5H, d, $J = 10$ Hz), 5.87–5.91 (0.5H, m), 5.97–6.00 (0.5H, m), 7.14 (2H, d, $J = 6.5$ Hz), 7.42–7.44 (2H, m). MS *m*/*z* (%) 274 (M^+, 21), 151 (100), 133 (20), 109 (18), 94 (24), 81 (20), 79 (41). Calcd for $C_{16}H_{18}O_2S$: M, 274.1026. Found: *m*/*z* 274.1026.

4.20. 1-(*p*-Tolylsulfanyl)-2-oxaspiro[4.5]dec-6-en-3-one 13f

Colorless oil (about 3:2 diastereomeric mixture); IR (neat) 2928, 1790 (CO), 1493, 1179, 1156, 958 cm^{-1}; ^1H NMR δ 1.56–2.15 (6H, m), 2.34 (3H, s), 2.43, 2.59 (each 0.4H, d, $J = 18$ Hz), 2.46, 2.69 (each 0.6H, d, $J = 18$ Hz), 5.46 (0.6H, s), 5.48 (0.4H, s), 5.56 (0.4H, d, $J = 9.6$ Hz), 5.73 (0.6H, d, $J = 10.2$ Hz), 5.87–5.92 (0.4H, m), 5.97–6.02 (0.6H, m), 7.14 (2H, d, $J = 7.8$ Hz), 7.43–7.46 (2H, m). MS *m*/*z* (%) 274 (M^+,

23), 151 (100), 123 (23), 109 (18), 94 (27), 81 (28), 79 (57). Calcd for $C_{16}H_{18}O_2S$: M, 274.1025. Found: *m/z* 274.1019.

4.21. (*R*)-(+)-2-Oxaspiro[4.5]dec-6-en-3-one 6e

Colorless oil; IR (neat) 2928, 1780 (CO), 1417, 1216, 1168, 1020, 840 cm^{-1}; ^1H NMR δ 1.61–1.67 (4H, m), 2.02–2.05 (2H, m), 2.36, 2.50 (each 1H, d, $J = 17.4$ Hz), 4.02, 4.08 (each 1H, d, $J = 9.0$ Hz), 5.51 (1H, d, $J = 9.6$ Hz), 5.86–5.88 (1H, m). MS *m/z* (%) 152 (M^+, 10), 124 (8), 94 (100), 79 (72). Calcd for $C_9H_{12}O_2$: M, 152.0835. Found: *m/z* 152.0832. $[\alpha]_D^{27} = +53.1$ (*c* 0.23, acetone). (*S*)-(−)-**6f**: $[\alpha]_D^{27} = -52.9$ (*c* 0.54, acetone).

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan, which is gratefully acknowledged.

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