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Asymmetric Darzens reaction utilizing chloromethyl phenyl sulfone under phase-transfer catalyzed conditions

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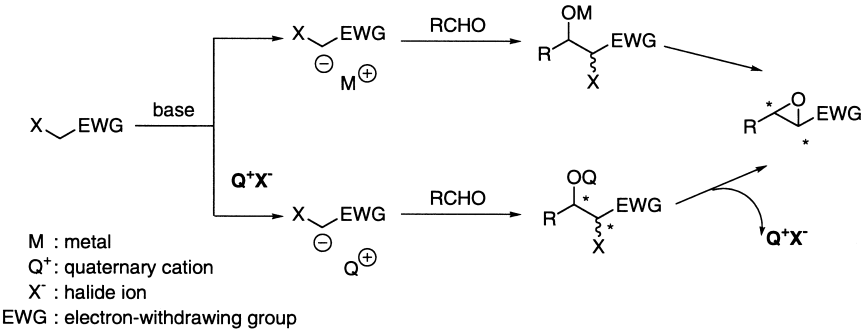
Abstract—The development of the catalytic asymmetric Darzens reaction utilizing chloromethyl phenyl sulfone is described. The reaction smoothly proceeded to give α,β-epoxysulfones with satisfactory enantioselectivity (up to 83% ee) using chiral quaternary ammonium salts as the phase transfer catalyst.

The Darzens reaction[1] has been recognized as one of the most important carbon–carbon bond forming reactions by controlling the two stereogenic centers to afford an epoxide so that its application to asymmetric synthesis is one of the major challenging goals in modern organic chemistry. Although one hundred years have passed since the discovery of this reaction, few successful examples of the catalytic asymmetric Darzens reaction are known.[2] Since the Darzens reaction includes an aldol (C–C bond formation) and the following intramolecular cyclization (C–O bond formation) steps, stoichiometric amounts of base should be required to achieve higher chemical yields (Scheme 1). For a strong base, proton abstraction quickly occurs to give the carbanion followed by C–C bond formation. Therefore, past examples of asymmetric synthesis are required to use a stoichiometric amount of a chiral source such as chiral auxiliaries[3a,b] or an external ligand.[3c] In order to obtain optically active epoxides via the Darzens reaction, many trials have been examined such as chiral reagents or substrates. On the other hand, phase transfer catalysts (PTC)[4] present one of the most efficient methodologies for this reaction because PTC, such as quaternary ammonium salts, can be converted into the corresponding base in situ in the presence of inorganic bases such as metal carbonates or hydroxides.[4] These species allow exchange of the counter ion to generate both a chiral nucleophile and metal halide as side products. Moreover, this methodology gives us practical, economic and operational advantages which lead to green chemistry. We have already reported[2a–d] the asymmetric Darzens reaction using chiral PTCs. In this paper, we report the asymmetric Darzens reaction utilizing phenyl sulfone with carbonyl compounds under PTC conditions.[2b]

The advantages of using sulfones are not only their capability for further chemical transformation[5] but also the stabilization effect of the α-anion. Thus, they act as good nucleophiles which are generated under quite mild basic conditions. Moreover, this type of anion does exist as a carbanion and not the enolate form so that chiral external molecules such as the chiral quaternary ammonium cation



Scheme 1. PTC-catalyzed Darzens reaction.

Keywords: asymmetric reaction; Darzens reaction; diastereoselection; epoxides; phase-transfer.
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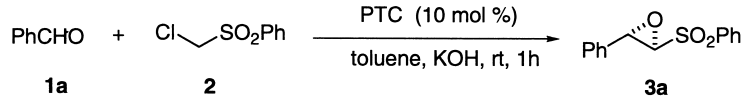
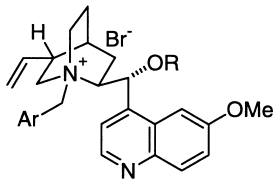
Table 1. PTC effect of Darzens reaction using chioromethyl phenyl sulfone **2**



1a **2** **3a**



PTC **A-F**

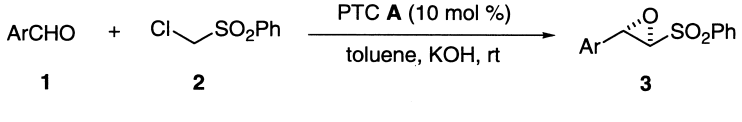
Entry	PTC	R	Yield of **3a** (%)	ee of **3a** (%)
1	None	–	60	–
2	**A**: Ar=4-CF_3–C_6H_4	H	85	**69**
3	**B**: Ar=Ph	H	68	54
4	**C**: Ar=4-OMe–C_6H_4	H	58	51
5	**D**: Ar=2,4-$(CF_3)_2$–C_6H_3	H	41	7
6	**E**: Ar=9-anthracenyl[a]	H	76	46
7	**F**: Ar=4-CF_3–C_6H_4	Allyl	44	15[b]

[a] Ammonium chloride was used.
[b] The reaction was carried out for 5 h.

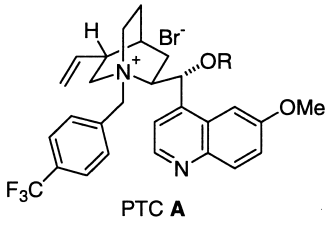
can affect the reaction carbon center more strongly during the enantioselective C–C bond formation step, shown in Scheme 1.

Initially, we focused on using chloromethyl phenyl sulfone **2** as a nucleophile for the Darzens reaction. This substrate was found to possess acidic protons that allowed the reaction to proceed smoothly with aromatic aldehydes in toluene under PTC conditions. Although the reaction between benzaldehyde (**1a**) and the sulfone **2** quickly proceeded even in the absence of PTC at room temperature, a catalytic amount of the chiral quaternary ammonium salt (PTC **A**) derived from the quinine did act as a good catalyst to afford the desired product **3a** in 85% yield with 69% ee (Table 1, entry 1 vs 2). The diastereoselectivity of **3a** was determined by the coupling constant between H_α and H_β observed in the NMR analysis to be the *trans* form only and the absolute configuration was determined by an X-ray crystallographical analysis to be (1*R*,2*R*)-**4a**.[2b] The other type of PTC, which has electron donating or withdrawing groups on the benzene ring such as **B**, **C** or **D**, resulted in moderate to lower enantioselectivities so that the trifluoromethyl group on the C-4 position was found to be superior (Table 1, entries 3–5). Recently, the 9-anthracenylmethyl function was found to be quite useful for asymmetric phase transfer reactions.[6] However, it was not effective in this Darzens

Table 2. Catalytic asymmetric Darzens reaction using aromatic aldehydes



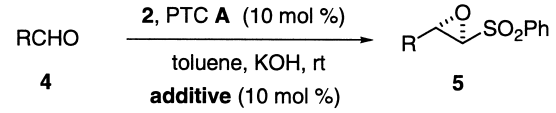
1 **2** **3**



PTC **A**

Entry	Ar	Time (h)	Yield of **3** (%)	ee of **3** (%)
1	**1b**: α-Np	1	**3b**: 42	65
2	**1c**: β-Np	1	**3c**: 82	65
3	**1d**: 4-Me–C_6H_4	2	**3d**: 84	78
4	**1e**: 3-Me–C_6H_4	1	**3e**: 82	74
5	**1f**: 4-Ph–C_6H_4	1.5	**3f**: 71	72
6	**1g**: 4-*t*-Bu–C_6H_4	2	**3g**: 70	**81**
7	**1h**: 3-PhO–C_6H_4	1.5	**3h**: 83	65
8	**1i**: 4-Cl–C_6H_4	1	**3i**: 72	64
9	**1j**: 4-Br–C_6H_4	1	**3j**: 80	64
10	**1k**: 3-Br–C_6H_4	1.5	**3k**: 69	71
11	**1m**: 4-CF_3–C_6H_4	1.5	**3m**: 78	65
12	**1n**: 3-CF_3–C_6H_4	1.5	**3n**: 83	64
13	**1p**: 2-Br–C_6H_4	1	**3p**: 27	47
14	**1q**: 2-CF_3–C_6H_4	2	**3q**: 90	33

Table 3. Phase-transfer catalyzed Darzens reaction using aliphatic aldehyde



Entry	R	Additive	Time (h)	Yield (%)	ee (%)
1	**4a**: *i*-Pr	None	3	**5a**: 100	–
2	**4a**: *i*-Pr	$Sn(OTf)_2$	20	**5a**: 81	32
3	**4b**: Et	$Sn(OTf)_2$	1	**5b**: 71	12
4	**4c**: *t*-Bu	$Sn(OTf)_2$	26	**5c**: 77	17
5	**4d**: Et_2CH	$Sn(OTf)_2$	24	**5d**: 75	31
6	**1a**: Ph	$Sn(OTf)_2$	20	**3a**: 66	83

reaction (see entry 6 in Table 1). Furthermore, the presence of the free hydroxy group at the C-9 position in the catalyst will be essential. These results are summarized in Table 1.

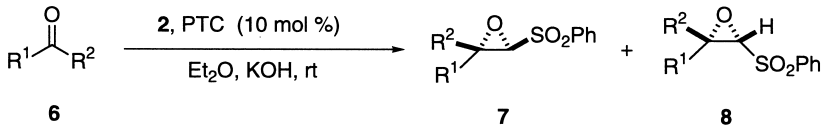
Encouraged by these results, we next examined other aromatic aldehydes. As shown in Table 2, this reaction system is quite general for aromatic aldehydes. For example, both the α and β-naphthaldehydes **1b** and **1c** gave the corresponding α,β-epoxysulfones **3b** and **3c** in moderate to good yields with 65% ee, respectively (entries 1 and 2 in Table 2). Other derivatives which possess alkyl or aryl-substituents on the para position such as **1d**–**1f** also gave moderate to good ee in higher chemical yields (entries 3–5). Especially, **1g** afforded **3g** with 81% ee in 70% yield (entry 6). An electron donating group was also effective to afford the desired product **3h** from **1h** with good yield and ee (entry 7). This reaction has also been found to be effective for the halogenated derivatives such as **1i**, **1j**, and **1k** or the trifluoromethyl derivatives **1m** and **1n**, as shown in entries 8–13 in Table 2. On the other hand, 2-substituted aldehydes gave a lower ee relative to the 3 or 4-substituted derivatives (entries 13 and 14). The reason is still unclear but we assume that it would depend on the steric repulsion between the catalyst and the functional group on the 2 position.

We next focused on the use of aliphatic aldehydes **4**. Despite the good enantioefficiency of aromatic aldehydes, isobutyraldehyde **4a** gave the Darzens product **5a** in quantitative yield as the racemate under similar reaction conditions (Table 3, entry 1). On the other hand, the addition of a catalytic amount of metal salts such as $Sn(OTf)_2$ was found to act as an effective additive in the aliphatic system to give the desired product **5a** with 32% ee (entry 2). The interaction between heteroatoms such as N or O in PTC and the metal center would be expected to form some kind of complex though the active species are still unclear. Although other aldehydes such as **4b**–**d** also gave unsatisfactory enantiomeric excesses, the addition of $Sn(OTf)_2$ was more effective, achieving up to a 31% ee than in the absence of $Sn(OTf)_2$ (entries 3–5, Table 3). This system also affected the aromatic system as shown in entry 6. We were pleased that the reaction of **1a** also proceeded to give **3a** in 66% yield with 83% ee in the presence of 10 mol% of $Sn(OTf)_2$, even though the reaction rate dramatically decreased.

Finally, we tried to use methyl ketone derivatives as the electrophilic agents. Still now, the enantiocontrol of the chiral quaternary carbons via direct C–C bond forming process is a challenging goal in organic synthesis. In the beginning, we investigated the use of acetophenone **6a** as a substrate. Although the reaction smoothly proceeded using tetrahexylammonium bromide (THAB, 10 mol%) as the PTC, the desired epoxides **7a** and **8b** were obtained as a diastereomixture (*cis*/*trans*=1.4: 1) in 94% yield (Table 4, entry 1). On the other hand, the reaction utilizing PTC A was found to be quite slow to give **7a** and **8b** with moderate yields under similar conditions. Their enantioselectivities were revealed to be 60% ee for **7a** and 22% ee for **8a** (entry 2). The diastereoselectivity is strongly dependent on the substituents in **6** and the catalyst structure. For example, an α-naphthyl group increased the ratio of *trans* in the THAB system though PTC A exclusively gave **7b** with a much lower ee and yield (entry 3 vs 4). Moreover, other sterically hindered substrates such as the *tert*-butyl ketone **6c** afforded the trans isomer **7c** only using THAB. Aliphatic ketones such as **6d** exhibited a higher reactivity in the presence of PTC **A** (10 mol%) and the reaction smoothly occurred even at 0°C though its diastereoselectivity was revealed to be 2.4:1 and the enantiomeric efficiency was around 30% ee (entry 7). The reaction of other types of sterically hindered ketones **6e** were quite ineffective, producing **8e** as a racemate in lower yield (entry 8).

In conclusion, we have found that chiral quaternary ammonium salts derived from cinchona alkaloids act as an efficient phase transfer catalyst in the asymmetric Darzens reaction. Especially, aromatic aldehydes **1** and the sulfone **2** with PTC **A** gave the desired product with moderate to high

Table 4. Reaction with ketone **6**



Entry	Ketone	PTC	Time (h)	Yield of **7** (ee)	Yield of **8** (ee)
1	**6a**: R^1=Ph, R^2=Me	THAB	13	**7a**: 54 (−)	**8a**: 40 (−)
2	**6a**: R^1=Ph, R^2=Me	**A**	18	**7a**: 29 (**60**)	**8a**: 14 (22)
3	**6b**: R^1=α-Np, R^2=Me	THAB	23	**7b**: 61 (−)	**8b**: 34 (−)
4	**6b**: R^1=α-Np, R^2=Me	**A**	60	**7b**: 30 (6)	**8b**: 0 (−)
5	**6c**: R^1=*t*-Bu, R^2=Me	THAB	45	**7c**: 47 (−)	**8c**: 0 (−)
6	**6c**: R^1=*t*-Bu, R^2=Me	**A**	60	**7c**: 11 (0)	**8c**: 0 (−)
7	**6d**: R^1=Ph$(CH_2)_2$, R^2=Me	**A**	27	**7d**: 69 (29)	**8d**: 29 (28)
8	**6e**: R^1=Ph, R^2=*i*-Pr	**A**	48	**7e**: 0	**8e**: 19 (0)

enantioselectivities (up to 83% ee). To the best of our knowledge, this is the highest value for the catalytic asymmetric Darzens reaction in the sulfone system. Furthermore, the addition of $Sn(OTf)_2$ was found to be more effective in these PTC catalyzed reactions. The development of more general system for a variety of substrates and the creation of novel catalysts are now under investigation.

1. Experimental

^1H and ^{13}C NMR were measured at 270 and 67.8 MHz, respectively, with Me_4Si as the internal reference and $CDCl_3$ as the solvent. Flash column chromatography was performed on Cica-MERCK Silica Gel 60 (230–400 mesh ASTM). Analytical thin layer chromatography (TLC) was carried out on precoated (0.25 mm) Merck silica gel F-254 plates. All the solvents were dried prior to use.

1.1. General procedure for asymmetric Darzens reaction of sulfone with aromatic aldehydes under phase-transfer catalyzed conditions

1.1.1. (1*R*,2*S*)-1,2-Epoxy-2-phenylethyl phenyl sulfone (3a). To a solution of chloromethyl phenyl sulfone **2** (95 mg, 0.5 mmol), benzaldehyde **1a** (61 μL, 0.6 mmol) and *N*-(4-trifluoromethylbenzyl)quininium bromide (PTC **A**) (28 mg, 0.05 mmol) in toluene (3.0 mL) was added a portion of KOH (113 mg, 2.0 mmol) at room temperature. After the reaction mixture was stirred for 1 h at room temperature, the reaction was quenched with 1N HCl (3.0 mL), and the mixture was extracted with ethyl acetate (15 mL×3), washed with brine, and dried over Na_2SO_4. Removal of the solvent followed by flash column chromatography (silica gel, hexane/diethyl ether=15:1) gave the desired product **3a** (110.8 mg, 85%, 69% ee). A colorless solid; mp 134–135°C; $[\alpha]_D^{20}=-36.0$ (*c* 1.0, CH_2Cl_2) (69% ee); IR (nujol): 1315, 1153 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 4.18 (d, *J*=1.3 Hz, 1H), 4.59 (d, *J*=1.3 Hz, 1H), 7.19–7.28 (m, 2H), 7.34–7.41 (m, 3H), 7.65 (d, *J*=7.6 Hz, 2H), 7.71–7.80 (m, 1H), 8.00 (d, *J*=7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 57.2, 70.8, 128.6, 129.3, 129.4, 132.5, 134.4, 136.5; MS *m*/*z* 260 (M^+), 103 (M^+-SO_2Ph), 77 (base peak); HPLC: DAICEL CHIRALPAK AD, flow rate 1.0 mL/min, hexane/*i*-PrOH=9:1, retention time 22.4, 25.0 min.

1.1.2. (1*R*,2*S*)-1,2-Epoxy-2-(1-naphthyl)ethyl phenyl sulfone (3b). A colorless solid; mp 97°C; $[\alpha]_D^{20}=+69.0$ (*c* 1.0, CH_2Cl_2). (65% ee); IR (nujol): 2932, 1321, 1151 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 4.19 (d, *J*=1.6 Hz, 1H), 5.18 (d, *J*=1.6 Hz, 1H), 7.36–7.46 (m, 2H), 7.52–7.70 (m, 4H), 7.72–7.79 (m, 1H), 7.82–7.93 (m, 2H), 8.05 (dd, *J*=7.3, 1.7 Hz, 2H), 8.11 (d, *J*=8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 55.8, 70.4, 122.5, 122.7, 125.0, 126.3, 127.0, 128.6, 128.7, 129.38, 129.43, 130.7, 133.1, 134.5, 136.8; MS *m*/*z* 310 (M^+), 169 (base peak), 141; HRMS calcd for $C_{18}H_{14}O_3S$ 310.0664, found 310.0628; HPLC: DAICEL CHIRALCEL OD, flow rate 1.0 mL/min, hexane/*i*-PrOH=9:1, retention time 17.8, 23.1 min.

1.1.3. (1*R*,2*S*)-1,2-Epoxy-2-(2-naphthyl)ethyl phenyl sulfone (3c). A colorless solid; mp 125°C; $[\alpha]_D^{20}=-13.1$ (*c* 1.0, CH_2Cl_2). (65% ee); IR (nujol): 2924, 1321, 1152 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 4.29 (d, *J*=1.3 Hz, 1H), 4.77 (d, *J*=1.3 Hz, 1H), 7.23–7.29 (m, 1H), 7.48–7.55 (m, 3H), 7.56–7.61 (m, 2H), 7.78–7.87 (m, 4H), 8.03 (dd, *J*=6.9, 1.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 57.7, 71.0, 122.3, 126.5, 126.8, 126.9, 127.8, 127.9, 128.8 (X2), 129.5, 130.0, 132.8, 133.7, 134.6, 136.9; MS *m*/*z* 310 (M^+), 169 (base peak), 141; Anal. calcd for $C_{18}H_{14}O_3S$: C, 69.66; H, 4.55. Found: C, 69.65; H, 4.53; HPLC: DAICEL CHIRALPAK AD, flow rate 1.0 mL/min, hexane/*i*-PrOH=4:1, retention time 18.1, 25.2 min.

1.1.4. (1*R*,2*S*)-1,2-Epoxy-2-(4-methylphenyl)ethyl phenyl sulfone (3d). A colorless solid; mp 109°C; $[\alpha]_D^{20}=-29.6$ (*c* 1.0, CH_2Cl_2). (77% ee); IR (nujol): 1458, 1377, 1154 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 2.35 (s, 3H), 4.18 (d, *J*=1.3 Hz, 1H), 4.55 (d, *J*=1.3 Hz, 1H), 7.10–7.23 (m, 5H), 7.59–7.82 (m, 3H), 7.99 (d, *J*=6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 21.1, 57.4, 70.9, 126.0, 128.7, 129.4, 129.5, 134.4, 136.8, 139.6; MS *m*/*z* 274 (M^+), 250, 141 (SO_2Ph), 133 (M^+-SO_2Ph), 77 (Ph, base peak); HRMS calcd for $C_{15}H_{14}O_3S$ 274.0664, found 274.0675; Anal. calcd for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 65.36; H, 5.16; HPLC: DAICEL CHIRALCEL OD, flow rate 1.0 mL/min, hexane/*i*-PrOH=4:1, retention time 14.3, 19.4 min.

1.1.5. (1*R*,2*S*)-1,2-Epoxy-2-(3-methylphenyl)ethyl phenyl sulfone (3e). A colorless solid; mp 121–123°C; $[\alpha]_D^{20}=-43.1$ (*c* 1.0, CH_2Cl_2). (74% ee); IR (nujol): 1458, 1377, 1154 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 2.33 (s, 3H), 4.18 (d, *J*=1.3 Hz, 1H), 4.55 (d, *J*=1.3 Hz, 1H), 7.06 (br s, 2H), 7.15–7.27 (m, 2H), 7.56–7.67 (m, 2H), 7.68–7.78 (m, 1H), 7.99 (dd, *J*=6.9, 1.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 21.1, 57.3, 70.8, 123.1, 126.5, 128.5, 128.6, 129.3, 130.2, 132.4, 134.4, 136.7, 138.5; MS *m*/*z* 274 (M^+), 133 (M^+-SO_2Ph), 105 (base peak), 141; HRMS calcd for $C_{15}H_{14}O_3S$ 274.0664, found 274.0664; HPLC: DAICEL CHIRALCEL OD, flow rate 1.0 mL/min, hexane/*i*-PrOH=4:1, retention time 7.7, 10.5 min.

1.1.6. (1*R*,2*S*)-1,2-Epoxy-2-(4-phenylphenyl)ethyl phenyl sulfone (3f). A colorless solid; mp 105–107°C; $[\alpha]_D^{23}=-8.5$ (*c* 1.0, CH_2Cl_2). (72% ee); IR (nujol): 1323, 1146 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 4.23 (d, *J*=1.3 Hz, 1H), 4.64 (d, *J*=1.3 Hz, 1H), 7.20–7.48 (m, 5H), 7.54–7.68 (m, 6H), 7.71–7.79 (m, 1H), 8.01 (dd, *J*=8.9, 1.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 57.2, 70.9, 126.5, 127.0, 127.4, 127.7, 128.8, 129.3, 129.4, 131.5, 134.5, 136.7, 140.0, 142.4; MS *m*/*z* 336 (M^+), 195 (base peak); HRMS calcd for $C_{20}H_{16}O_3S$ 336.0820, found 336.0823; HPLC: DAICEL CHIRALPAK AD, flow rate 1.0 mL/min, hexane/*i*-PrOH=4:1, retention time 19.7, 39.2 min.

1.1.7. (1*R*,2*S*)-1,2-Epoxy-2-(4-*tert*-butylphenyl)ethyl phenyl sulfone (3g). A colorless solid; mp 93–94°C; $[\alpha]_D^{24}=-32.4$ (*c* 1.0, CH_2Cl_2). (81% ee); IR (nujol): 1325, 1154 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 1.30 (s, 9H), 4.18 (d, *J*=1.7 Hz, 1H), 4.57 (d, *J*=1.7 Hz, 1H), 7.20 (d, *J*=8.6 Hz, 2H), 7.34 (d, *J*=8.6 Hz, 2H), 7.56–7.68 (m, 2H), 7.70–7.77 (m, 1H), 7.99 (dd, *J*=7.3, 1.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 31.1, 34.6, 57.3, 70.8, 125.6, 125.8, 128.7, 129.3, 129.5, 134.4, 136.8, 152.7; MS *m*/*z* 316

(M^+), 301 (M^+-Me), 287 (M^+-Me_2), 177 (base peak); HRMS calcd for $C_{14}H_{11}{}^{35}ClO_3S$ 294.0117, found 294.0117; Anal. calcd for $C_{18}H_{20}O_3S$: C, 68.33; H, 6.37. Found: C, 68.18; H, 6.34; HPLC: DAICEL CHIRALPAK AD, flow rate 1.0 mL/min, hexane/*i*-PrOH=4:1, retention time 10.2, 25.4 min.

1.1.8. (1*R*,2*S*)-1,2-Epoxy-2-(3-phenoxyphenyl)ethyl phenyl sulfone (3h). A colorless solid; mp 58°C; $[\alpha]_D{}^{22}=-27.7$ (*c* 1.0, CH_2Cl_2). (65% ee); IR (nujol): 1584, 1489, 1327 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 4.14 (d, *J*=1.3 Hz, 1H), 4.55 (d, *J*=1.3 Hz, 1H), 6.87 (d, *J*=2.0 Hz, 1H), 7.94–7.05 (m, 4H), 7.10–7.17 (m, 1H), 7.28–7.40 (m, 3H), 7.58–7.67 (m, 2H), 7.70–7.77 (m, 1H), 7.88 (dd, *J*=7.3, 1.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 56.9. 70.7, 115.8, 119.0, 119.5, 120.6, 123.6, 128.6, 129.3, 129.7, 130.1, 134.4, 134.6, 136.6, 156.3, 157.8; MS *m/z* 352 (M^+), 211 (M^+-SO_2Ph, base peak), 183, 118; HRMS calcd for $C_{20}H_{16}O_4S$ 352.0769, found 352.0764; HPLC: DAICEL CHIRALPAL AD, flow rate 1.0 mL/min, hexane/*i*-PrOH=4:1, retention time 12.2, 14.8 min.

1.1.9. (1*R*,2*S*)-1,2-Epoxy-2-(4-chlorophenyl)ethyl phenyl sulfone (3i). A colorless solid; mp 93°C; $[\alpha]_D{}^{25}=-12.9$ (*c* 1.0, CH_2Cl_2). (64% ee); IR (nujol): 1449, 1327, 1154 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 4.14 (d, *J*=1.7 Hz, 1H), 4.57 (d, *J*=1.7 Hz, 1H), 7.20 (d, *J*=8.6 Hz, 2H), 7.35 (d, *J*=8.6 Hz, 2H), 7.62–7.69 (m, 2H), 7.70–7.79 (m, 1H), 7.99 (dd, *J*=6.9, 2.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 56.7, 70.8, 127.4, 128.8, 129.0, 129.5, 131.2, 134.6, 135.5, 136.6; MS *m/z* 296, 294 (M^+), 155, 153 (M^+-SO_2Ph), 125 (base peak), 127; HRMS calcd for $C_{14}H_{11}{}^{35}ClO_3S$ 294.0117, found 294.0117; Anal. calcd for $C_{14}H_{11}ClO_3S$: C, 57.05; H, 3.76. Found: C, 57.03; H, 3.88; HPLC: DAICEL CHIRALCEL OD, flow rate 1.0 mL/min, hexane/*i*-PrOH=4:1, retention time 15.7, 20.0 min.

1.1.10. (1*R*,2*S*)-1,2-Epoxy-2-(4-bromophenyl)ethyl phenyl sulfone (3j). A colorless solid; mp 123°C; $[\alpha]_D{}^{20}=-16.9$ (*c* 1.0, CH_2Cl_2). (64% ee); IR (nujol): 1449, 1331, 1156 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 4.14 (d, *J*=1.3 Hz, 1H), 4.57 (d, *J*=1.3 Hz, 1H), 7.51 (d, *J*=7.9 Hz, 2H), 7.58 (d, *J*=7.9 Hz, 2H), 7.60–7.68 (m, 2H), 7.71–7.79 (m, 1H), 7.99 (dd, *J*=7.3, 1.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 56.8, 70.7, 123.6, 127.6, 128.7, 129.5, 131.7, 131.9, 134.6, 136.5; MS *m/z* 211, 209, 183 (M^+-SO_2Ph, base peak), 157, 155; Anal. calcd for $C_{14}H_{11}BrO_3S$: C, 49.57; H, 3.27. Found: C, 49.37; H, 3.35; HPLC: DAICEL CHIRALPAK AD, flow rate 1.0 mL/min, hexane/*i*-PrOH=4:1, retention time 17.1, 23.3 min.

1.1.11. (1*R*,2*S*)-1,2-Epoxy-2-(3-bromophenyl)ethyl phenyl sulfone (3k). A colorless solid; mp 102–103°C; $[\alpha]_D{}^{20}=-24.2$ (*c* 1.0, CH_2Cl_2). (71% ee); IR (nujol): 1464, 1377, 1152 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 4.15 (d, *J*=1.7 Hz, 1H), 4.56 (d, *J*=1.7 Hz, 1H), 7.39 (br s, 1H), 7.46–7.53 (m, 1H), 7.53–7.60 (m, 1H), 7.60–7.68 (m, 2H), 7.70–7.79 (m, 1H), 7.99 (dd, *J*=7.3, 1.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 56.4, 70.7, 122.8, 124.9, 128.7, 129.2, 129.4, 130.3, 132.5, 134.6, 134.9, 136.5; MS *m/z* 340, 338 (M^+), 199, 197 (M^+-SO_2Ph), 171, 169, 118 (base peak); Anal. calcd for $C_{14}H_{11}BrO_3S$: C, 49.57; H, 3.27. Found: C, 49.37; H, 3.39; HPLC: DAICEL CHIRALCEL OD-H, flow rate 0.8 mL/min, hexane/*i*-PrOH=4:1, retention time 10.0, 11.3 min.

1.1.12. (1*R*,2*S*)-1,2-Epoxy-2-(4-trifluoromethylphenyl)ethyl phenyl sulfone (3m). A colorless solid; mp 102–103°C; $[\alpha]_D{}^{22}=-23.1$ (*c* 1.0, CH_2Cl_2). (65% ee); IR (nujol): 1325, 1156, 1127 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 4.16 (d, *J*=1.7 Hz, 1H), 4.66 (d, *J*=1.7 Hz, 1H), 7.40 (d, *J*=8.3 Hz, 2H), 7.64 (d, *J*=8.3 Hz, 2H), 7.61–7.69 (m, 2H), 7.72–7.80 (m, 1H), 8.00 (d, *J*=7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 56.5, 70.8, 121.6, 125.7 (q, *J*=3.7 Hz), 126.4, 128.8, 129.5, 131.5 (q, *J*=33 Hz), 134.7, 136.5, 136.7; MS *m/z* 328 (M^+), 309 (M^+-F), 187, 159 (base peak); Anal. calcd for $C_{15}H_{11}F_3O_3S$: C, 54.88; H, 3.38. Found: C, 54.58; H, 3.39; HPLC: DAICEL CHIRALPAK AD, flow rate 1.0 mL/min, hexane/*i*-PrOH=4:1, retention time 12.5, 19.9 min.

1.1.13. (1*R*,2*S*)-1,2-Epoxy-2-(3-trifluoromethylphenyl)ethyl phenyl sulfone (3n). A colorless solid; mp 102–103°C; $[\alpha]_D{}^{22}=-22.5$ (*c* 1.0, CH_2Cl_2). (64% ee); IR (nujol): 1464, 1377, 1327 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 4.18 (d, *J*=1.7 Hz, 1H), 4.67 (d, *J*=1.7 Hz, 1H), 7.45–7.55 (m, 3H), 7.60–7.70 (m, 2H), 7.71–7.82 (m, 1H), 8.00 (dd, *J*=6.9, 1.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 56.6, 70.9, 122.6, 126.3, 128.8, 129.4, 129.5, 129.6, 1331.6, 134.0, 134.7, 136.6; MS *m/z* 328 (M^+), 309 (M^+-F), 187, 159 (base peak); Anal. calcd for $C_{15}H_{11}F_3O_3S$: C, 54.88; H, 3.38. Found: C, 54.78; H, 3.38; HPLC: DAICEL CHIRALCEL OD, flow rate 1.0 mL/min, hexane/*i*-PrOH=9:1, retention time 10.4, 12.6 min.

1.1.14. (1*R*,2*S*)-1,2-Epoxy-2-(2-bromophenyl)ethyl phenyl sulfone (3p). A colorless solid; mp 110°C; $[\alpha]_D{}^{20}=+12.5$ (*c* 1.0, CH_2Cl_2). (47% ee); IR (nujol): 1445, 1325, 1154 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 4.05 (d, *J*=1.7 Hz, 1H), 4.75 (d, *J*=1.7 Hz, 1H), 7.13 (dd, *J*=7.3, 2.0 Hz, 1H), 7.18–7.33 (m, 2H), 7.53–7.66 (m, 2H), 7.71–7.78 (m, 1H), 8.02 (dd, *J*=7.3, 1.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 57.3, 70.3, 122.4, 126.1, 127.6, 128.8, 129.3, 130.4, 132.4, 132.5, 134.6, 136.3; MS *m/z* 340, 338 (M^+), 199, 197 (M^+-SO_2Ph), 171, 169, 118 (base peak); Anal. calcd for $C_{14}H_{11}BrO_3S$: C, 49.57; H, 3.27. Found: C, 49.40; H, 3.30; HPLC: DAICEL CHIRALPAK AD, flow rate 1.0 mL/min, hexane/*i*-PrOH=4:1, retention time 10.6, 14.2 min.

1.1.15. (1*R*,2*S*)-1,2-Epoxy-2-(2-trifluoromethylphenyl)ethyl phenyl sulfone (3q). A colorless solid; mp 71°C; $[\alpha]_D{}^{20}=+3.4$ (*c* 1.0, CH_2Cl_2). (33% ee); IR (nujol): 1586, 1451, 1327, 1177 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 4.04 (d, *J*=1.7 Hz, 1H), 4.77 (d, *J*=1.7 Hz, 1H), 7.36 (d, *J*=7.6 Hz, 1H), 7.42–7.80 (m, 5H), 7.92–8.09 (m, 3H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 54.4, 70.4, 121.7, 125.5, 125.8, 128.8, 129.1, 129.3, 131.2, 132.4, 134.6, 135.5, 136.1; MS *m/z* 328 (M^+), 187, 159 (base peak); Anal. calcd for $C_{15}H_{11}F_3O_3S$: C, 54.88; H, 3.38. Found: C, 54.92; H, 3.44; HPLC: DAICEL CHIRALPAK AD, flow rate 1.0 mL/min, hexane/*i*-PrOH=4:1, retention time 7.7, 8.8 min.

1.2. A general procedure for asymmetric Darzens reaction of sulfone with aliphatic aldehydes under phase-transfer catalyzed conditions

1.2.1. (1*R*,2*S*)-1,2-Epoxy-3-methylbutyl phenyl sulfone (5a). To a suspension of chloromethyl phenyl sulfone **2**

(190 mg, 1.0 mmol), isobutyraldehyde **4a** (0.11 mL, 1.2 mmol), *N*-(4-trifluoromethylbenzyl)quininium bromide (PTC **A**) (56 mg, 0.10 mmol) and tin(II) triflate (42 mg, 0.10 mmol) in toluene (3.0 mL) was added a portion of KOH (113 mg, 2.0 mmol) at room temperature. After the reaction mixture was stirred for 20 h at room temperature, the reaction mixture was poured into silica gel, and following flash column chromatography (hexane/diethyl ether=5:1) gave the desired product **5a** (183.2 mg, 81%, 32% ee). A colorless oil; $[\alpha]_D^{20}=-29.1$ (*c* 2.0, CH_2Cl_2). (32% ee); IR (neat): 2968, 1470, 1327, 1156 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 1.01 (d, *J*=6.6 Hz, 3H), 1.03 (d, *J*=6.6 Hz, 3H), 1.68–1.82 (m, 1H), 3.51 (d, *J*=6.6, 1.7 Hz, 1H), 3.93 (d, *J*=1.7 Hz, 1H), 7.55–7.64 (m, 2H), 7.66–7.75 (m, 1H), 7.94 (dd, *J*=6.9, 1.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 17.7, 18.1, 28.7, 62.3, 67.2, 128.4, 129.1, 134.2, 136.9; MS *m*/*z* 211 (M^+-Me), 143, 78 (base peak); Anal. calcd for $C_{11}H_{14}O_3S$: C, 58.28; H, 6.24. Found: C, 58.38; H, 6.38; HPLC: DAICEL CHIRALCEL OD, flow rate 1.0 mL/min, hexane/*i*-PrOH=9:1, retention time 7.4, 8.2 min.

1.2.2. (1*R*,2*S*)-1,2-Epoxybutyl phenyl sulfone (5b). A colorless oil; $[\alpha]_D^{20}=-10.7$ (*c* 1.0, CH_2Cl_2). (10% ee); IR (neat): 2972, 1325, 1156 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 1.02 (t, *J*=7.3 Hz, 3H), 1.64–1.84 (m, 2H), 3.66 (dt, *J*=5.0, 2.0 Hz, 1H), 3.92 (d, *J*=2.0 Hz, 1H), 7.55–7.64 (m, 2H), 7.66–7.75 (m, 1H), 7.94 (dd, *J*=6.9, 1.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 9.1, 23.2, 58.6, 67.8, 128.5, 129.2, 134.2, 136.9; MS *m*/*z* 183 (M^+-Et), 125, 78 (base peak); HRMS calcd for $C_8H_7O_3S$ 183.0116, found 183.0116; Anal. calcd for $C_{10}H_{12}O_3S$: C, 56.87; H, 5.70. Found: C, 56.89; H, 5.79; HPLC: DAICEL CHIRALCEL OD, flow rate 1.0 mL/min, hexane/*i*-PrOH=9:1, retention time 9.0, 10.8 min.

1.2.3. (1*R*,2*S*)-3,3-Dimethyl-1,2-epoxybutyl phenyl sulfone (5c). A colorless oil; $[\alpha]_D^{23}=-17.7$ (*c* 1.0, CH_2Cl_2). (17% ee); IR (neat): 2963, 1325, 1156 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 0.97 (s, 9H), 3.51 (d, *J*=1.7 Hz, 1H), 3.96 (d, *J*=1.7 Hz, 1H), 7.48–7.59 (m, 2H), 7.60–7.68 (m, 1H), 7.93 (dd, *J*=8.6, 1.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 25.4, 30.5, 64.9, 66.1, 128.5, 129.2, 134.3, 137.0; MS *m*/*z* 225 (M^+-Me), 143, 125, 77 (base peak); HRMS calcd for $C_{12}H_{16}O_3S$ 240.0820, found 240.08; Anal. calcd for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71. Found: C, 59.74; H, 6.79; HPLC: DAICEL CHIRALPAK AS, flow rate 0.5 mL/min, hexane/*i*-PrOH=9:1, retention time 13.7, 15.0 min.

1.2.4. (1*R*,2*S*)-1,2-Epoxy-3-ethylpentyl phenyl sulfone (5d). A colorless oil; $[\alpha]_D^{26}=-25.6$ (*c* 2.0, CH_2Cl_2). (31% ee); IR (neat): 2967, 1325, 1156 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 0.95 (t, *J*=7.3 Hz, 3H), 0.97 (t, *J*=7.3 Hz, 3H), 1.08–1.20 (m, 1H), 1.33–1.53 (m, 2H), 3.47 (dd, *J*=8.3, 1.7 Hz, 1H), 3.91 (d, *J*=1.7 Hz, 1H), 7.54–7.64 (m, 2H), 7.66–7.74 (m, 1H), 7.89 (dd, *J*=7.3, 1.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 10.8, 11.4, 23.3, 24.8, 42.6, 61.0, 67.8, 128.5, 129.2, 134.2, 137.1; MS *m*/*z* 225 (M^+-Me_2), 143, 77 (base peak); Anal. calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13. Found: C, 61.30; H, 7.24; HPLC: DAICEL CHIRALPAK AD, flow rate 1.0 mL/min, hexane/*i*-PrOH=9:1, retention time 8.3, 10.0 min.

1.3. A general procedure for asymmetric Darzens reaction of sulfone with ketones under phase-transfer catalyzed conditions

1.3.1. (1*R*,2*S*)-1,2-Epoxy-2-phenylpropyl phenyl sulfone (7a) and (1*S*,2*S*)-1,2-epoxy-2-phenylpropyl phenyl sulfone (8a). To a suspension of chloromethyl phenyl sulfone **2** (190 mg, 1.0 mmol), acetophenone **6a** (0.14 mL, 1.2 mmol) and *N*-(4-trifluoromethylbenzyl)quininium bromide (PTC **A**) (56 mg, 0.1 mmol) in diethyl ether (3.0 mL) was added a portion of KOH (220 mg, 3.9 mmol) at room temperature. After the reaction mixture was stirred for 18 h at room temperature, the mixture was poured into silicagel, and following flash column chromatography (hexane/AcOEt=6:1) gave the desired products **7a** (79.8 mg, 29, 60% ee) and **8a** (14 and 22% ee, respectively; chemical yield of **8a** was determined by ^1H NMR due to purification difficulty).

Compound **7a**. A colorless oil; $[\alpha]_D^{25}=-2.0$ (*c* 2.0, $CHCl_3$). (37% ee); IR (neat): 1447, 1327, 1156 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 2.12 (s, 3H), 3.80 (s, 1H), 7.20–7.30 (m, 8H), 7.91 (d, *J*=7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 17.1, 65.5, 75.5, 124.9, 128.1, 128.4, 128.5, 134.2, 138.6, 139.1; MS *m*/*z* 274 (M^+), 133 (M^+-SO_2Ph, base peak), 105, 77; HRMS calcd for $C_{15}H_{14}O_3S$ 274.0664, found 274.0666; HPLC: DAICEL CHIRALPAK AD, flow rate 1.0 mL/min, hexane/*i*-PrOH=9:1, retention time 12.4, 16.1 min.

Compound **8a**. A colorless oil; IR (neat): 1147, 1333, 1306, 1156 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 1.68 (s, 3H), 4.23 (s, 1H), 7.21–7.47 (m, 7H), 7.50–7.80 (m, 3H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 25.7, 66.3, 75.3, 126.3, 128.0, 128.4, 128.6, 128.8, 133.8, 135.0, 137.4; MS *m*/*z* 274 (M^+), 133 (M^+-SO_2Ph, base peak), 105, 77; HRMS calcd for $C_{17}H_{18}O_3S$ 274.0664, found 274.0683; HPLC: DAICEL CHIRALPAK AD, flow rate 1.0 mL/min, hexane/*i*-PrOH=9:1, retention time 10.5, 13.1 min.

1.3.2. (1*R*,2*S*)-1,2-Epoxy-2-(1-naphthyl)propyl phenyl sulfone (7b). A white amorphous solid; $[\alpha]_D^{25}=+5.4$ (*c* 1.0, CH_2Cl_2). (6% ee); IR ($CHCl_3$): 1449, 1327, 1312, 1156 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 2.25 (s, 3H), 4.09 (s, 1H), 7.27–7.78 (m, 9H), 8.00–8.25 (m, 3H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 19.4, 66.4, 74.0, 123.3, 125.0, 126.0, 126.9, 128.1, 128.6, 128.9, 129.2, 134.2, 136.2, 138.6; MS *m*/*z* 324 (M^+), 183 (M^+-SO_2Ph, base peak), 155, 77; HRMS calcd for $C_{19}H_{16}O_3S$ 324.0819, found 324.0816; HPLC: DAICEL CHIRALCEL OD, flow rate 1.0 mL/min, hexane/*i*-PrOH=9:1, retention time 9.5, 11.6 min.

1.3.3. *cis*-1,2-Epoxy-2-(1-naphthyl)propyl phenyl sulfone (8b). A colorless oil; IR (neat): 1449, 1327, 1312, 1157 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 1.81, 1.82 (s, 3H), 4.33 (s, 0.22×1H), 4.48 (s, 0.68×1H), 7.10–8.18 (m, 12H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 25.7, 26.5, 66.1, 67.0, 73.9, 75.9, 124.1, 124.2, 124.5, 124.6, 125.3, 125.7, 125.9, 126.2, 126.3, 128.3, 128.4, 128.50, 128.53, 128.6, 128.8, 129.0, 129.7, 130.0, 132.0, 133.1, 133.8, 136.3; MS *m*/*z* 324 (M^+), 183 (M^+-SO_2Ph, base peak), 155, 77; HRMS calcd for $C_{19}H_{16}O_3S$ 324.0820, found 324.0816.

1.3.4. *trans*-1,2-Epoxy-2,3,3-trimethylbutyl phenyl sulfone (7c). A colorless oil; IR (neat): 1449, 1325, 1156 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 0.95 (s, 9H), 1.78 (s, 3H), 3.97 (s, 1H), 7.55–7.75 (m, 3H), 7.96 (d, J=7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 13.0, 25.4, 35.2, 71.1, 72.1, 128.0, 129.3, 134.1, 139.1; MS m/z 239 (M^+-Me), 197 (M^+-tert-Bu), 77 (base peak); HRMS calcd for $C_{12}H_{15}O_3S$ 239.0742, found 239.0741; Anal. calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13. Found: C, 61.16; H, 7.08; HPLC: DAICEL CHIRALPAK AD, flow rate 1.0 mL/min, hexane/*i*-PrOH=9:1, retention time 6.5, 7.0 min.

1.3.5. (1*R*,2*S*)-1,2-Epoxy-2-methyl-4-phenylbutyl phenyl sulfone (7d). A colorless oil; $[\alpha]_D^{25}=-16.6$ (c 4.0, $CHCl_3$). (27% ee); IR (neat): 1455, 1327, 1156 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 1.72–2.05 (m, 2H), 1.85 (s, 3H), 2.69 (d, J=8.2 Hz, 2H), 3.74 (s, 1H), 7.05–7.32 (m, 5H), 7.53–7.74 (m, 3H), 7.91 (d, J=7.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 16.2, 30.7, 40.0, 66.1, 73.5, 126.1, 128.0, 128.3, 128.4, 129.3, 134.1, 138.6, 140.0; MS m/z 302 (M^+), 161 (M^+-SO_2Ph), 91 (base peak), 77; Anal. calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00. Found: C, 67.24; H, 6.20; HPLC: DAICEL CHIRALCEL OD, flow rate 1.0 mL/min, hexane/*i*-PrOH=9:1, retention time 13.4, 15.8 min.

1.3.6. (1*S*,2*S*)-1,2-Epoxy-2-methyl-4-phenylbutyl phenyl sulfone (8d). A colorless oil; $[\alpha]_D^{25}=-24.4$ (c 2.0, $CHCl_3$). (28% ee); IR ($CHCl_3$): 1449, 1327, 1156 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 1.34 (s, 3H), 2.30–2.55 (m, 2H), 2.72–3.04 (m, 2H), 3.78 (s, 1H), 7.20–7.40 (m, 5H), 7.50–7.72 (m, 3H), 7.93 (d, J=7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 22.6, 32.2, 34.0. 67.4, 74.5, 126.1, 128.1, 128.2, 128.4, 129.4, 134.2, 138.8, 140.9; MS m/z 301 (M^+-H), 189, 161 (M^+-SO_2Ph), 91 (base peak); Anal. calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00. Found: C, 67.27; H, 6.21; HPLC: DAICEL CHIRALPAK AS, flow rate 1.0 mL/min, hexane/*i*-PrOH=9:1, retention time 8.6, 9.8 min.

1.3.7. *cis*-1,2-Epoxy-3-methyl-2-phenylbutyl phenyl sulfone (8e). A colorless oil; IR (neat): 2971, 1449, 1331, 1156 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 0.88 (d, J= 6.8 Hz, 3H), 0.98 (d, J=7.1 Hz, 3H), 1.80–1.92 (m, 1H), 4.22 (s, 1H), 7.20–7.30 (m, 5H), 7.35–7.45 (m, 3H), 7.50–7.67 (m, 3H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 16.9, 18.1, 35.7, 71.9, 74.1, 127.3, 127.7, 127.9, 128.3, 128.4, 130.0, 133.5, 137.3; MS m/z 302 (M^+), 161 (M^+-SO_2Ph), 91 (base peak); Anal. calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00. Found: C, 67.29; H, 6.12; HPLC: DAICEL CHIRALPAK AD, flow rate 1.0 mL/min, hexane/*i*-PrOH=9:1, retention time 8.7, 10.3 min.

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