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Catalytic asymmetric epoxidation of enones under phase-transfer catalyzed conditions

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Abstract—The development of the catalytic asymmetric epoxidation of enones promoted by aqueous H_2O_2 with chiral quaternary ammonium salts is described. The reaction smoothly proceeded to give α,β-epoxyketones with satisfactory enantioselectivities in both the *trans* and *cis* enone systems (up to 92% ee) by use of cinchonine or quinidine derivatives (5 mol%) as phase transfer catalysts.

Epoxides are well known as some of the most valuable building blocks which can be potential intermediates and precursors for further chemical transformations so that the development of the enantioselective synthesis of epoxides has been recognized as an important goal in modern organic synthesis. Particularly, electron deficient olefins such as α,β-unsaturated ketones are less reactive toward the usual oxidants which enable the highly enantioselective epoxidation. Thus, another methodology should be required for producing these types of substrates.[1] On the other hand, phase transfer catalysts (PTC)[2] have been known as quite effective reagents[3] to furnish this transformation because PTC, such as quaternary ammonium salts, can be easily converted to the corresponding active species (ammonium hydrogen peroxide) with a mild and inexpensive oxidant such as H_2O_2. As shown in Fig. 1, the epoxidation reactions of electron deficient olefins are smoothly accomplished in aqueous media to produce the desired product via a 1,4-addition and the following cyclization, producing water as a single side product in the presence of a catalytic amount of chiral quaternary salts. According to this methodology, Lygo and co-workers,[4a,b] Corey and Zhang,[4c] Tayor and co-workers,[4d] and our group[5] have already reported independently successful results for the catalytic asymmetric epoxidation of enones. Also, chiral metal reagents (Zn,[6a] Mg[6b]), a catalyst (La[6c,d]) or organic reagents[7,8] were recently reported to act as excellent chiral promoters. Herein we report the asymmetric epoxidation of both the *trans* and *cis* enones promoted by chiral PTC derived from cinchonine or quinidine under mild aqueous media.[5]

We initially tried to use the commercially available chiral quaternary salt derived from cinchonine (PTC **A1**) to examine the asymmetric epoxidation of chalcone (**1a**) (Table 1). At first, solvent screening was attempted and diethyl ether gave a better result than dichloromethane or

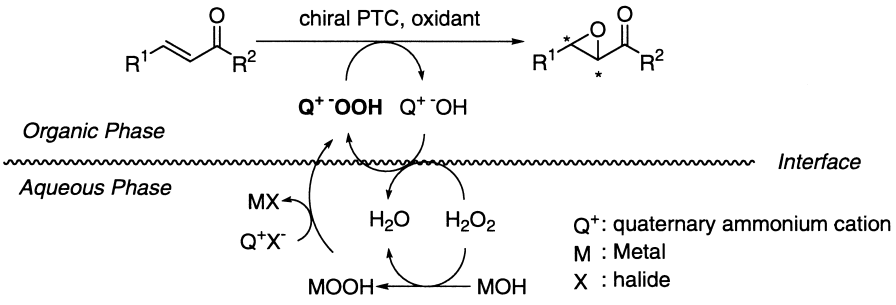

Figure 1. Mechanism of catalytic epoxidation of enones.

Keywords: asymmetric epoxidation; diastereoselection; epoxides; phase transfer.
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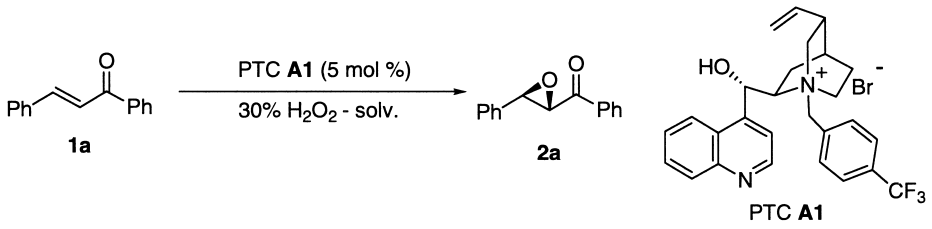
Table 1. Effect of solvent and base on asymmetric epoxidation of chalcone



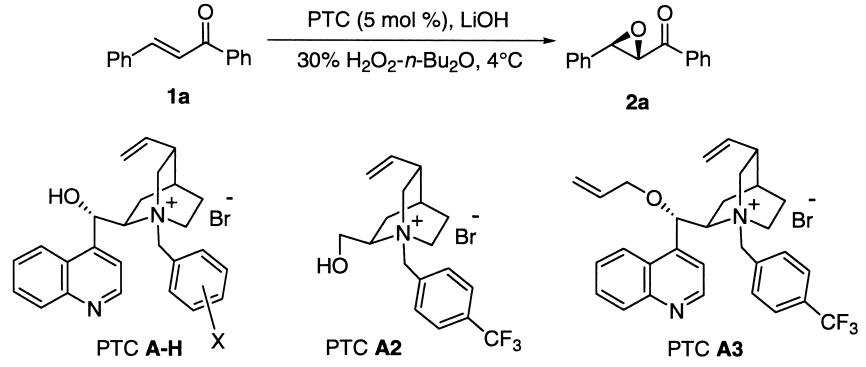
Entry	Base[a]	Solvent	Temperature (°C)	Time (h)	Yield (%)	ee (%)[b]
1	NaOH	CH_2Cl_2	Rt	15	94	14
2	NaOH	Toluene	Rt	18	93	14
3	NaOH	Et_2O	Rt	21	100	28
4	NaOH	Et_2O	4	19	100	35
5	LiOH	Et_2O	4	19	89	44
6	LiOH	*n*-Bu_2O	4	26	72	**73**
7	LiOH	THF	4	3	100	7

[a] NaOH (2.5 equiv.) and LiOH (3 equiv.) were used.
[b] Absolute configuration of **2a** was determined by comparison literature data, see Ref. 3d.

toluene in the presence of NaOH as the base (entries 1–3). A lower temperature also gave a slightly better enantioselectivity (35% ee), as shown in entry 4. Further optimization proved that a less polar solvent such as dibutyl ether was found to be the most effective to produce the epoxide **2a** with 73% ee using LiOH at 4°C, though a polar ether such as THF gave a quite lower ee (entries 6 and 7). Encouraged by these results, we next attempted the screening of chiral PTC under similar reaction conditions.

As shown in Table 2, the enantioselectivities of **2a** were found to be strongly dependent on the substituents or PTC structure. For example, the PTCs, which include electron withdrawing groups on C-4 position such as NO_2, afforded **2a** with a good ee, though the electron donating group such as the MeO group or non-substituted one (PTC **B**) gave a significantly lower ee (entries 2–4). The most important functional groups to achieve a good to high ee were found to be not only the benzyl group but also the chiral secondary alcohol moiety. For example, PTC **A2**, which includes both a primary alcohol and the 4-CF_3 benzyl moieties, did not work as an enantioselective promoter to give the racemate of **2a** with a quite lower yield, due to the higher solubility in the water phase (entry 5). Moreover, the hydroxy group also had a significant influence on the enantioselectivity, as shown in entry 6. PTC **A3**, which includes the *O*-allyl moiety, readily available from PTC **A1** by using the reported method,[9] was found to be a less effective catalyst

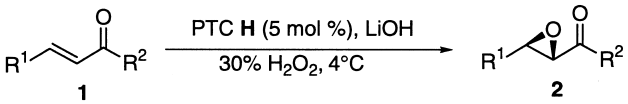
Table 2. Effect of PTC



Entry	PTC	X	Time (h)	Yield (%)	ee (%)
1	**A1**	4-CF_3	36	72	73
2	**B**	H	74	72	1
3	**C**	4-NO_2	37	61	72
4	**D**	4-OMe[a]	60	70	4
5	**A2**		41	20	0
6	**A3**		40	61	0
7	**E**	4-F	88	24	3
8	**F**	4-Cl	41	68	65
9	**G**	4-Br	36	56	77
10	**H**	4-I	37	97	*84*
11	**I**	4-I	38	94	7

[a] Ammonium chloride was used.

Table 3. Catalytic asymmetric epoxidation of various enones



Entry	Enone	Solvent	Time (h)	Yield of **2** (%)	ee of **2** (%)
1	**1b**: R^1=Ph, R^2=3-Me–C_6H_4	*n*-Bu_2O	36	**2b**: 99	87
2	**1c**: R^1=Ph, R^2=4-Me–C_6H_4	*n*-Bu_2O	36	**2c**: 95	89
3	**1d**: R^1=3-Me–C_6H_4, R^2=Ph	*n*-Bu_2O	64	**2d**: 100	*92*
4	**1e**: R^1=2-Me–C_6H_4, R^2=Ph	*n*-Bu_2O	64	**2e**: 96	67
5	**1f**: R^1=2-Cl–C_6H_4, R^2=Ph	*n*-Bu_2O	47	**2f**: 88	65
6	**1g**: R^1=*t*-$BuCH_2$, R^2=Ph	*n*-Bu_2O	68	**2g**: 41	57
7	**1h**: R^1=*t*-Bu, R^2=Ph	$CHCl_3$	43	**2h**: 41	55
8	**1i**:R^1=*c*-Hex, R^2=Ph	$CHCl_3$	37	**2i**: 70	53[a]
9	**1j**: R^1=*i*-Pr, R^2=Ph	$CHCl_3$	43	**2j**: 82	42

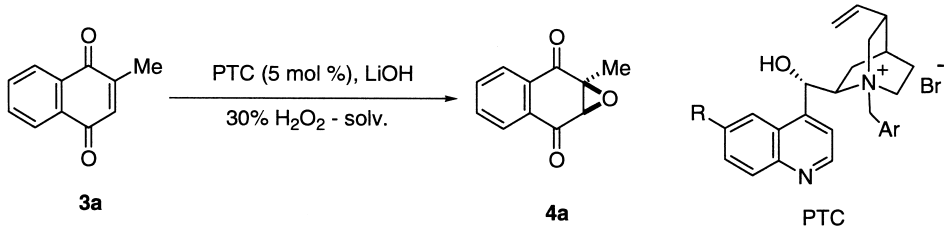
[a] PTC **B** was used.

with aqueous H_2O_2 in enantioselectivity. Next, screening of the 4-halogenated PTCs were examined (entries 7–9). Although the 4-fluoro derivative (PTC **E**) gave a quite lower ee, the chlorinated and brominated PTCs (PTC **F** and **G**) smoothly promoted the reaction to give **2a** with 65 and 77% ee, respectively. Moreover, the 4-iodo derivative (PTC **H**) gave the best result for the asymmetric epoxidation of **1a** with 84% ee, as shown in entry 10. The regioisomeric PTC (3-iodo derivative, PTC **I**) proved to be ineffective for asymmetric induction (entry 11). These results indicate that the substituent effect on PTC is quite important for achieving a higher enantioselectivity. Especially, the secondary alcohol and benzyl moieties are important.

According to these results, we next examined the generality in this asymmetric epoxidation through the substrate effect, as shown in Table 3. For the chalcone derivatives, PTC **H** acts as an effective catalyst, as expected, and the desired product was obtained with high enantioselectivities. For example, the methylated derivatives such as **1b** and **1c** were converted into **2b** and **2c** with 87 and 89% ee, respectively (entries 1 and 2). Especially, the enone **1d** was quantitatively transformed into the corresponding epoxide with 92% ee (entry 3), however, the *ortho*-substituted derivatives such as **2e** and **2f** resulted in moderate asymmetric induction (entries 4 and 5). On the other hand, we were pleased that the β-alkylated enones **1g–i** were also easily transformed into the corresponding epoxides in chloroform with moderate enantioselectivities (entries 6–9).

We next turned our attention to investigate the catalytic asymmetric epoxidation of the *cis* enones such as the naphthoquinones. The first example of the phase-transfer catalyzed asymmetric epoxidation of the naphthoquinone derivatives was attempted by Wynberg in 1976[10] but its enantioselectivities were very low. Although an excellent result for the catalytic asymmetric epoxidation of the *cis* enone using the metal reagent with an oxidant via a 1,4-addition was reported by Shibasaki and co-workers,[11] enantiocontrol by chiral PTCs for the epoxidation of the *cis* enone is still challenging. In the beginning, we chose the best PTC (PTC **H**) for the *trans* enone epoxidation as a chiral PTC to investigate the asymmetric reaction of 2-methylnaphthoquinone (**3a**) (entries 1–3 in Table 4). Although the desired epoxide **4a** was obtained in high yield in all solvents, their enantioselectivities were found to be lower and PTC **A1** was also not effective (entry 4).[5b] As a result of the catalyst screening, the PTCs, which include *ortho*-substituents on the benzene ring, gave the better results.[12] For example, PTCs **J**, **K** and **L** derived

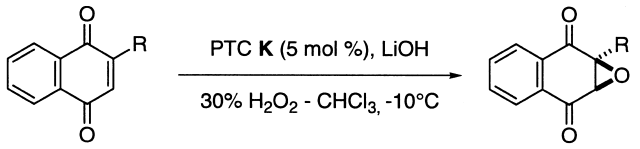
Table 4. Effect of solvent and PTC



Entry	PTC	R	Solvent	Temperature (°C)	Time (h)	Yield (%)	ee (%)
1	**H**: 1Ar=4-I-C_6H_4	H	*n*-Bu_2O	Rt	1	72	1
2	**H**: Ar=4-I-C_6H_4	H	Toluene	Rt	4	72	4
3	**H**: Ar=4-I-C_6H_4	H	$CHCl_3$	Rt	1	94	10
4	**A1**: Ar=4-CF_3–C_6H_4	H	$CHCl_3$	Rt	4	76	11
5	**J**: Ar=2,4-Me_2–C_6H_3	OMe	$CHCl_3$	Rt	1	93	26
6	**K**: Ar=α-naphthyl[a]	OMe	$CHCl_3$	Rt	1	82	31
7	**L**: Ar=9-anthracenyl[a]	OMe	$CHCl_3$	Rt	1	91	28
8	**K**: Ar=α-naphthyl[a]	OMe	$CHCl_3$	−10	1	86	34

[a] Ammonium chloride was used.

Table 5. Substituent effect on naphthoquinone epoxidation



3 **4**

Entry	Naphthoquinone	Time (h)	Yield of **4** (%)	ee of **4** (%)
1	**3b**: R=Et	16	**4b**: 99	41
2	**3c**: R=*n*-Pr	7	**4c**: 93	43
3	**3d**: R=*n*-Bu	21	**4d**: 87	44
4	**3e**: R=*i*-Pr	5	**4e**: 93	*70*
5	**3f**: R=*c*-Hex	23	**4f**: 60	*64*
6	**3g**: R=Ph	23	**4g**: 47	*76*
7	**3h**: R=C≡CPh	21	**4h**: 84	40

from quinidine were found to be better promoters for the naphthoquinone epoxidation that produced **4a** with around a 30% ee (entries 5–7). The reaction carried out at −10°C using PTC **K** gave the best result (entry 8).

Next, we investigated the substrate effect using the easily prepared naphthoquinones[13] under similar reaction conditions (Table 5). As expected, a longer carbon chain at the 2 position affected the enantioselectivity to give slightly better ees, as shown in entries 1–3. Moreover, we were pleased that the bulkier substituents such as the isopropyl or cyclohexyl functions dramatically raised the ees to give the desired products with 70 and 64% ee, respectively (entries 4 and 5). The aromatic moiety was also revealed to be effective and the corresponding product **4g** was obtained with 76% ee, though the linear substituent to produce in **3h** was unsuccessful, similar to the aliphatic system (entries 6 and 7).

In conclusion, we have demonstrated that chiral quaternary salts derived from cinchonine and quinidine are efficient PTCs for the asymmetric epoxidation of enones. The potential advantage of this methodology is that aqueous hydrogen peroxide, a mild, inexpensive, and environmentally benign oxidant, can be used under mild reaction conditions. This synthesis can be recognized as one of the most powerful methods for practical organic chemistry. Further studies of these novel PTCs are now under investigation.

1. Experimental

The ^{1}H and ^{13}C NMR spectra 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 the synthesis of chiral quaternary salts

A mixture of a cinchona alkaloid (5.00 mmol) and benzyl halide derivative (5.00 mmol) in THF (20 mL) was refluxed. The precipitated solid was filtered, washed with benzene, and recrystallized from MeOH to give pure compounds.

1.1.1. *N*-(4-Nitrobenzyl)cinchoninium bromide (PTC C). Prepared from cinchonine and 4-nitrobenzyl bromide under refluxed condition for 48 h. A white solid (1.51 g, 59%); mp: 240°C (decomp.); $[\alpha]_D^{23}=+107$ (*c* 1.0, $CHCl_3$); IR (nujol) ν: 3206, 1609, 1165, 1115 cm^{-1}; ^{1}H NMR (CD_3OD, 270 MHz) δ: 0.86–1.17 (m, 1H), 1.79–1.96 (m, 3H), 2.36–2.56 (m, 1H), 2.59–2.68 (m, 1H), 3.06–3.18 (m, 1H), 3.53–3.61 (m, 1H), 3.79–4.11 (m, 2H), 4.38–4.42 (m, 1H), 5.05–5.15 (m, 2H), 5.21–5.29 (m, 2H), 5.92–6.08 (m, 1H), 6.57 (s, 1H), 7.76–7.95 (m, 6H), 8.08–8.11 (m, 1H), 8.16–8.19 (m, 1H), 8.38–8.41 (m, 1H), 8.90 (d, *J*=4.6 Hz, 1H); MS (EI) *m*/*z* 429 (M^+-Br), 136 (base peak); Anal. calcd for $C_{26}H_{28}BrN_3O_3$: C, 61.18; H, 5.53; N, 8.23; Found: C, 60.70; H, 5.64; N, 8.06.

1.1.2. *N*-(4-Methoxybenzyl)cinchoninium chloride (PTC D). Prepared from cinchonine and 4-methoxybenzyl chloride under refluxed condition for 88 h. A white solid (1.32 g, 59%); mp: 226°C (decomp.); $[\alpha]_D^{23}=+130$ (*c* 1.0, MeOH); IR (nujol) ν: 3246, 1611, 1183, 1119 cm^{-1}; ^{1}H NMR (CD_3OD, 270 MHz) δ: 0.93–1.06 (m, 1H), 1.81–1.93 (m, 3H), 2.42–2.47 (m, 1H), 2.51–2.63 (m, 1H), 3.06–3.10 (m, 1H), 3.56–3.64 (m, 1H), 3.78–3.87 (m, 1H), 3.94 (s, 3H), 3.97–4.01 (m, 1H), 4.30–4.41 (m, 1H), 4.92–5.03 (m, 2H), 5.24–5.30 (m, 2H), 5.99–6.12 (m, 1H), 6.62 (s, 1H), 7.11 (d, *J*=8.6 Hz, 2H), 7.63 (d, *J*=8.6 Hz, 2H), 7.77–7.89 (m, 2H), 7.96 (d, *J*=4.6 Hz, 1H), 8.12 (d, *J*=8.9 Hz, 1H), 8.29 (d, *J*=7.9 Hz, 1H), 8.95 (d, *J*=4.6 Hz, 1H); MS (EI) *m*/*z* 415 (M^+-Cl), 121 (base peak); Anal. calcd for $C_{27}H_{31}ClN_2O_2$: C, 71.97; H, 6.94; N, 6.22; Found: C, 74.30; H, 7.05; N, 5.52.

1.1.3. (2*R*,5*R*)-*N*-(4-Trifluoromethylbenzyl)-2-hydroxymethyl-5-ethynyl-quinuclidinium bromide (PTC A2). Prepared from (2*R*,5*R*)-2-hydroxymethyl-5-vinyl-quinuclidine and 4-trifluoromethyl benzyl bromide under refluxed condition for 40 h. A white solid (2.03 g, 100%); mp: 189°C (decomp.); $[\alpha]_D^{24}=+44.9$ (*c* 1.0, $CHCl_3$); IR (nujol) ν: 3274, 1623, 1325, 1169 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ: 1.78–2.17 (m, 4H), 2.28–2.46 (m, 2H), 2.69–2.80 (m, 1H), 3.24–3.33 (m, 1H), 3.87–3.92 (m, 1H), 4.01–4.19 (m, 1H), 4.20–4.31 (m, 2H), 4.53–4.58 (m, 1H), 5.10–5.22 (m, 4H), 5.40–5.45 (m, 1H), 5.79–5.92 (m, 1H), 7.53 (d, *J*=8.2 Hz, 2H), 7.77 (d, *J*=8.3 Hz, 2H); MS (EI) *m*/*z* 326 (M^+-Br), 159 (base peak); Anal. calcd for $C_{18}H_{23}BrF_3NO$: C, 53.21; H, 5.71; N, 3.45; Found: C, 53.18; H, 5.71; N, 3.14.

1.1.4. *O*(9)-Allyl-*N*-(4-trifluoromethylbenzyl)cinchoninium bromide (PTC A3). According to Corey's procedure,[9] prepared from PTC **A** and allyl bromide. To a suspension of PTC **A** (2.64 g, 5.0 mmol) in CH_2Cl_2 (20 mL) was added allyl bromide (2.2 mL, 15 mmol) and 50% KOH (3.5 g). The resulting mixture was stirred vigorously at room temperature for 6 h and then water was added. The mixture was diluted with water (30 mL) and extracted with CH_2Cl_2 (20 mL×2). The combined organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The resulting orange solid was

recrystallized from hexane–AcOEt. (2.85 g, 99%); A pale orange solid; mp: 150°C (decomp.); $[\alpha]_D^{26}$=+122 (*c* 2.0, $CHCl_3$); IR (nujol) ν: 3071, 1509, 1327, 1115 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 1.05–1.25 (m, 1H), 1.99 (br s, 2H), 2.20–2.57 (m, 2H), 2.70–2.85 (m, 1H), 3.40–3.58 (m, 1H), 3.97 (d, *J*=12.2, 6.5 Hz, 1H), 4.20–4.38 (m, 2H), 4.49 (d, *J*= 11.6 Hz, 1H), 4.84 (br s, 1H), 5.20–5.60 (m, 5H), 4.96–5.08 (m, 2H), 5.25–5.31 (m, 2H), 6.00–6.12 (m, 1H), 6.60 (s, 1H), 7.29–7.36 (m, 5H), 5.76–6.00 (m, 1H), 6.00–6.23 (m, 1H), 6.24 (s, 1H), 6.83 (d, *J*=11.6 Hz, 1H), 7.50–7.67 (m, 1H), 7.70–7.87 (m, 3H), 7.90–8.03 (m, 1H), 8.05–8.20 (m, 3H), 8.98 (d, *J*=4.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 21.9, 23.1, 26.7, 37.3, 54.5, 55.6, 60.3, 65.4, 65.9, 70.0, 117.9, 119.6, 121.1, 124.5, 125.5, 125.6, 128.4, 129.4, 129.7, 130.8, 131.7, 131.9, 134.2, 134.6, 138.9, 148.0, 149.0; MS (FAB) *m/z* 493 (M^+−Br), 159 (base peak); HRMS (FAB) calcd for $C_{30}H_{32}F_3N_2O$ 493.2467. Found 493.2488.

1.1.5. *N*-(4-Fluorobenzyl)cinchoninium bromide (PTC E). Prepared from cinchonine and 4-fluorobenzyl bromide under refluxed condition for 102 h. A white solid (1.27 g, 53%); mp: 233°C (decomp.); $[\alpha]_D^{23}$=+153 (*c* 1.0, MeOH); IR (nujol) ν: 3162, 1588, 1165, 1115 cm^{-1}; ^1H NMR (CD_3OD, 270 MHz) δ: 1.03–1.13 (m, 1H), 1.82–1.95 (m, 3H), 2.44–2.53 (m, 1H), 2.61–2.65 (m, 1H), 3.04–3.15 (m, 1H), 3.56–3.65 (m, 1H), 3.79–3.87 (m, 1H), 3.95–4.02 (m, 1H), 4.36–4.57 (m, 1H), 4.96–5.08 (m, 2H), 5.25–5.31 (m, 2H), 6.00–6.12 (m, 1H), 6.60 (s, 1H), 7.29–7.36 (m, 2H), 7.72–7.79 (m, 2H), 7.80–7.90 (m, 2H), 7.95 (d, *J*=4.6 Hz, 1H), 8.11–8.15 (m, 1H), 8.28–8.31 (m, 1H), 8.95 (d, *J*= 4.6 Hz, 1H); MS (EI) *m/z* 402 (M^+−Br), 109 (base peak); Anal. calcd for $C_{26}H_{28}BrFN_2O$: C, 64.60; H, 5.84; N, 5.79; Found: C, 64.62; H, 5.90; N, 5.90.

1.1.6. *N*-(4-Chlorobenzyl)cinchoninium bromide (PTC F). Prepared from cinchonine and 4-chlorobenzyl bromide under refluxed condition for 84 h. A white solid (1.29 g, 52%); mp: 249°C (decomp.); $[\alpha]_D^{23}$=+123 (*c* 1.0, MeOH); IR (nujol) ν: 3171, 1587, 1113, 1019 cm^{-1}; ^1H NMR (CD_3OD, 270 MHz) δ: 0.95–1.15 (m, 1H), 1.84–1.93 (m, 3H), 2.41–2.50 (m, 1H), 2.62–2.65 (m, 1H), 3.02–3.14 (m, 1H), 3.54–3.62 (m, 1H), 3.85–4.21 (m, 2H), 4.37–4.55 (m, 1H), 5.00–5.24 (m, 2H), 5.28–5.31 (m, 2H), 5.99–6.11 (m, 1H), 6.60 (s, 1H), 7.55–7.58 (m, 2H), 7.76–7.85 (m, 4H), 7.95 (d, *J*=4.6 Hz, 1H), 8.07–8.10 (m, 1H), 8.35–8.39 (m, 1H), 8.95 (d, *J*=4.6 Hz, 1H); MS (EI) *m/z* 418 (M^+−Br), 125 (base peak); Anal. calcd for $C_{26}H_{28}BrClN_2O$: C, 62.47; H, 5.65; N, 5.60; Found: C, 62.29; H, 5.65; N, 5.64.

1.1.7. *N*-(4-Bromobenzyl)cinchoninium bromide (PTC G). Prepared from cinchonine and 4-bromobenzyl bromide under refluxed condition for 44 h. A white solid (1.11 g, 41%); mp: 237°C (decomp.); $[\alpha]_D^{24}$=+129 (*c* 1.0, MeOH); IR (nujol) ν: 3173, 1590, 1161, 1115 cm^{-1}; ^1H NMR (CD_3OD, 270 MHz) δ: 1.03–1.13 (m, 1H), 1.85–1.94 (m, 3H), 2.42–2.51 (m, 1H), 2.62–2.65 (m, 1H), 3.07–3.11 (m, 1H), 3.54–3.63 (m, 1H), 3.92–4.08 (m, 2H), 4.37–4.45 (m, 1H), 4.97–5.17 (m, 2H), 5.25–5.31 (m, 2H), 5.99–6.11 (m, 1H), 6.61 (s, 1H), 7.55–7.58 (m, 2H), 7.76–7.85 (m, 4H), 7.95 (d, *J*=4.6 Hz, 1H), 8.07–8.10 (m, 1H), 8.35–8.39 (m, 1H), 8.95 (d, *J*=4.6 Hz, 1H); MS (EI) *m/z* 462 (M^+−Br), 169 (base peak); Anal. calcd for $C_{26}H_{28}Br_2N_2O$: C, 57.37; H, 5.18; N, 5.15; Found: C, 57.13; H, 5.29; N, 5.05.

1.1.8. *N*-(4-Iodobenzyl)cinchoninium bromide (PTC H). Prepared from cinchonine and 4-iodobenzyl bromide under refluxed condition for 133 h. A white solid (1.03 g, 35%); mp: 218°C (decomp.); $[\alpha]_D^{24}$=+102 (*c* 1.0, $CHCl_3$); IR (nujol) ν: 3200, 1590, 1119, 1009 cm^{-1}; ^1H NMR (CD_3OD, 270 MHz) δ: 1.03–1.13 (m, 1H), 1.81–1.94 (m, 3H), 2.43–2.52 (m, 1H), 2.58–2.68 (m, 1H), 3.04–3.20 (m, 1H), 3.45–3.63 (m, 1H), 3.82–3.89 (m, 1H), 3.96–4.03 (m, 1H), 4.36–4.44 (m, 1H), 4.93–5.06 (m, 2H), 5.25–5.31 (m, 2H), 5.99–6.12 (m, 1H), 6.59 (s, 1H), 7.48–7.51 (m, 2H), 7.70–7.90 (m, 4H), 7.94–7.97 (m, 1H), 8.10–8.14 (m, 1H), 8.29–8.31 (m, 1H), 8.95 (d, *J*=4.6 Hz, 1H); MS (EI) *m/z* 510 (M^+−Br), 217 (base peak); Anal. calcd for $C_{26}H_{28}BrIN_2O{\cdot}1/2H_2O$: C, 52.02; H, 4.87; N, 4.67; Found: C, 51.96; H, 5.16; N, 4.61.

1.1.9. *N*-(3-Iodobenzyl)cinchoninium bromide (PTC I). Prepared from cinchonine and 3-iodobenzyl bromide under refluxed condition for 156 h. A white solid (1.00 g, 34%); mp: 209°C (decomp.); $[\alpha]_D^{24}$=+121 (*c* 1.0, MeOH); IR (nujol) ν: 3445, 1568, 1163, 1117 cm^{-1}; ^1H NMR (CD_3OD, 270 MHz) δ: 0.94–1.08 (m, 1H), 1.82–2.14 (m, 3H), 2.44–2.53 (m, 1H), 2.63–2.67 (m, 1H), 3.09–3.17 (m, 1H), 3.55–3.64 (m, 1H), 3.84–3.98 (m, 2H), 4.38–4.45 (m, 1H), 4.96–5.04 (m, 2H), 5.25–5.31 (m, 2H), 6.02–6.06 (m, 1H), 6.60 (s, 1H), 7.32–7.39 (m, 2H), 7.72–7.97 (m, 5H), 8.11–8.14 (m, 1H), 8.28 (d, *J*=7.9 Hz, 1H), 8.95 (d, *J*=4.6 Hz, 1H); MS (EI) *m/z* 510 (M^+−Br), 136 (base peak); Anal. calcd for $C_{26}H_{28}BrIN_2O$: C, 52.81; H, 4.77; N, 4.74; Found: C, 52.60; H, 4.87; N, 4.75.

1.1.10. *N*-(2,4-Dimethylbenzyl)quinidinium bromide (PTC J). Prepared from quinidine and 2,4-dimethylbenzyl bromide under refluxed condition for 64 h. A brown solid; mp: 229°C; $[\alpha]_D^{23}$=+257.4 (*c* 1.0, MeOH); IR (nujol) ν: 2924, 1620, 1582, 1123 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 0.88–0.92 (m, 1H), 1.77–1.81 (m, 3H), 2.30–2.33 (m, 4H), 2.41 (s, 3H), 2.89–2.93 (m, 1H), 3.12 (t, *J*=10.8 Hz, 1H), 3.70 (s, 3H), 4.10–4.21 (m, 2H), 5.20 (t, *J*=10.8 Hz, 1H), 5.17 (d, *J*=17.0 Hz, 1H), 5.22 (d, *J*=10.5 Hz, 1H), 5.62 (ABq, *J*=31.0, 12.2 Hz, 2H), 5.81–5.94 (m, 1H), 6.63 (s, 1H), 6.76 (d, *J*=5.6 Hz, 1H), 6.80 (s, 1H), 6.96 (d, *J*= 7.9 Hz, 1H), 7.13 (dd, *J*=8.1, 2.3 Hz, 1H), 7.70 (d, *J*= 7.9 Hz, 2H), 7.84 (d, *J*=4.6 Hz, 1H), 7.91 (d, *J*=9.2 Hz, 1H), 8.41 (d, *J*=9.6 Hz, 1H); MS (EI) *m/z* 543 (M^+−Br); Anal. calcd for $C_{29}H_{35}BrN_2O_2$: C, 66.54; H, 6.74; N, 5.35; Found: C, 66.34; H, 6.78; N, 5.18.

1.1.11. *N*-(1-Naphthylmethyl)quinidinium chloride (PTC K). Prepared from quinidine and 1-chloromethylnaphthalene under refluxed condition for 27 h. White crystals; mp: 187–190°C (hexane–MeOH); $[\alpha]_D^{23}$=+271.7 (*c* 1.1, $CHCl_3$); IR (nujol) ν: 3100, 2855, 1622, 1510 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 0.81–0.88 (m, 1H), 1.57–1.83 (m, 3H), 2.01–2.21 (m, 2H), 2.56–2.67 (m, 1H), 2.91–2.99 (m, 1H), 3.75 (s, 3H), 4.20–4.29 (m, 1H), 4.44 (t, *J*=8.6 Hz, 1H), 4.56 (t, *J*=10.2 Hz, 1H), 5.05 (d, *J*= 17.5 Hz, 1H), 5.14 (d, *J*=10.6 Hz, 1H), 5.68–5.81 (m, 1H), 6.16 (d, *J*=12.2 Hz, 1H), 6.51 (d, *J*=11.5 Hz, 1H),

6.66 (br s, 2H), 7.02 (dd, J=2.3, 9.2 Hz, 1H), 7.31–7.43 (m, 2H), 7.54–7.62 (m, 2H), 7.75–8.00 (m, 5H), 8.30–8.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 22.2, 24.0, 26.8, 38.0, 54.7, 56.2, 56.3, 57.5, 67.4, 68.5, 103.5, 117.6, 119.9, 120.7, 122.8, 124.4, 124.5, 143.1, 143.9, 146.9, 157.8; MS (EI) m/z 465 (M^+-Cl), 325, 141 (base peak); Anal. calcd for $C_{31}H_{33}ClN_2O_2\cdot 1/2H_2O$: C, 73.00; H, 6.72; N, 5.49; Found: C, 72.67; H, 6.96; N, 5.50.

1.1.12. *N*-(9-Anthracenylmethyl)quinidinium chloride (PTC L). Prepared from cinchonine and 9-chloromethylanthracene under refluxed condition for 77 h. Yellow crystals; mp: 180°C; $[\alpha]_D^{23}$=+334.8 (c 1.0, MeOH); IR (nujol) ν: 2953, 1622, 1507, 1227, 1124 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ: 1.02–1.1 (m, 1H), 1.24–1.27 (br s, 1H), 1.40–1.56 (m, 1H), 1.66–1.79 (m, 2H), 1.91–1.98 (m, 1H), 2.22–2.26 (m, 1H), 2.48 (t, J=10.6 Hz, 1H), 2.96 (t, J=10.6 Hz), 3H), 3.97 (s, 3H), 3.98–4.07 (m, 1H), 4.56–4.67 (m, 2H), 5.03 (d, J=17.2 Hz, 1H), 5.15 (d, J=10.3 Hz, 1H), 5.75–5.89 (m, 1H), 6.34 (d, J=13.2 Hz, 1H), 6.75 (d, J=13.2 Hz, 1H), 7.16–7.43 (m, 4H), 7.65–7.79 (m, 3H), 8.04 (d, J=9.2 Hz, 1H), 8.12 (d, J=4.3 Hz, 1H), 8.13–8.20 (m, 1H), 8.33 (d, J=3.6 Hz, 1H), 8.66–8.70 (m, 1H), 8.82 (d, J=8.9 Hz, 1H); MS (EI) m/z 514 (M^+-HCl); HRMS (M^+-HCl) calcd for $C_{35}H_{34}N_2O_2$ 514.2620; Found: 514.2621.

1.2. A general procedure for asymmetric epoxidation of *trans* enones

To a solution of enone (1.00 mmol) and chiral quaternary ammonium salt (5 mol%) in a biphase-system, n-Bu_2O or $CHCl_3$ (3.0 mL) and 30% H_2O_2 (1.0 mL) at 4°C was added LiOH (3.00 mmol) and the reaction mixture was stirred for 36–68 h (see Table 3). The reaction mixture was quenched with 1N HCl (3.0 mL), extracted with Et_2O, washed with saturated brine and dried over Na_2SO_4. Removal of the solvent followed by chromatography on silica gel column (Silica Gel 60 particle size 40–63 mm: Cica-MERCK) gave compounds **2a–j**.

1.2.1. (α*S*,β*R*)-2,3-Epoxy-3-phenylpropiophenone (2a). A white solid (218 mg, 97% yield, 84% ee ($[\alpha]_D^{25}$=+184 (c 1.0, $CHCl_3$)). The spectral data was identical with the reported one; [3d] HPLC: DAICEL CHIRALCEL OD, hexane–i-PrOH=20:1, flow rate: 0.5 mL/min. The retention time was 25.4 min (αS,βR) and 27.5 min (αR,βS).

1.2.2. (α*S*,β*R*)-2,3-Epoxy-3′-methyl-3-phenylpropiophenone (2b). A pale yellow oil (236 mg, 99% yield, 87% ee ($[\alpha]_D^{18}$=+193 (c 1.0, $CHCl_3$)); IR (neat) ν: 2923, 1686, 1258, 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ: 2.41 (s, 3H), 4.08 (d, J=2.0 Hz, 1H), 4.29 (d, J=2.0 Hz, 1H), 7.34–7.82 (m, 9H); MS (EI) m/z 238 (M^+), 119 (base peak); HRMS calcd for $C_{16}H_{14}O_2$: 238.0994; Found: 238.0990; HPLC: DAICEL CHIRALCEL OD, hexane–i-PrOH=20:1, flow rate: 1.0 mL/min. The retention time was 12.0 min (αS,βR) and 12.8 min (αR,βS).

1.2.3. (α*S*,β*R*)-2,3-Epoxy-4′-methyl-3-phenylpropiophenone (2c). A white solid (226 mg, 95% yield, 89% ee ($[\alpha]_D^{18}$=+162 (c 1.0, $CHCl_3$)). Mp: 51–53°C; IR (neat) ν: 3006, 1682, 1237, 1181 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ: 2.43 (s, 3H), 4.07 (d, J=2.0 Hz, 1H), 4.28 (d, J=2.0 Hz, 1H), 7.27–7.96 (m, 9H); MS (EI) m/z 238 (M^+), 119 (base peak); HRMS calcd for $C_{16}H_{14}O_2$: 238.0994; Found: 238.0995; HPLC: DAICEL CHIRALPAK OP, hexane–i-PrOH=50:1, flow rate: 1.0 mL/min. The retention time was 11.6 min (αS,βR) and 13.1 min (αR,βS).

1.2.4. (α*S*,β*R*)-2,3-Epoxy-3-(3-methylphenyl)propiophenone (2d). A white solid (238 mg, 100% yield, 92% ee ($[\alpha]_D^{27}$=+195 (c 1.0, CH_2Cl_2)). Mp: 36–37°C; IR (neat) ν: 3057, 1688, 1231, 1061 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ: 2.39 (s, 3H), 4.05 (d, J=2.0 Hz, 1H), 4.30 (d, J=2.0 Hz, 1H), 7.19–7.33 (m, 4H), 7.47–7.52 (m, 2H), 7.59–7.65 (m, 1H), 8.00–8.03 (m, 2H); MS (EI) m/z 238 (M^+), 105 (base peak); HRMS calcd for $C_{16}H_{14}O_2$: 238.0994; Found: 238.0995; HPLC: DAICEL CHIRALPAK AD, hexane–i-PrOH=50:1, flow rate: 1.0 mL/min. The retention time was 18.3 min (αS,βR) and 23.9 min (αR,βS).

1.2.5. (α*S*,β*R*)-2,3-Epoxy-3-(2-methylphenyl)propiophenone (2e). A pale yellow oil (229 mg, 96% yield, 67% ee ($[\alpha]_D^{27}$=+47 (c 1.0, CH_2Cl_2)); IR (neat) ν: 3065, 1690, 1231, 1007 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ: 2.39 (s, 3H), 4.05 (d, J=2.0 Hz, 1H), 4.30 (d, J=2.0 Hz, 1H), 7.19–7.33 (m, 4H), 7.47–7.52 (m, 2H), 7.59–7.65 (m, 1H), 8.00–8.03 (m, 2H); MS (EI) m/z 238 (M^+), 105 (base peak); HRMS calcd for $C_{16}H_{14}O_2$: 238.0994; Found: 238.0993; HPLC: DAICEL CHIRALCEL OD, hexane–i-PrOH=20:1, flow rate: 1.0 mL/min. The retention time was 9.5 min (αS,βR) and 10.5 min (αR,βS).

1.2.6. (α*S*,β*R*)-2,3-Epoxy-3-(2-chlorophenyl)propiophenone (2f). A colorless oil (228 mg, 88% yield, 65% ee ($[\alpha]_D^{17}$=−4.6 (c 2.0, $CHCl_3$)); IR (neat) ν: 3021, 1694, 1451 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ: 4.17 (d, J=2.0 Hz, 1H), 4.42 (d, J=2.0 Hz, 1H), 7.31–7.46 (m, 4H), 7.47–7.57 (m, 2H), 7.61–7.68 (m, 1H), 8.08 (d, J=7.9 Hz, 2H); MS (EI) m/z 258 (M^+), 105 (base peak); HRMS calcd for $C_{15}H_{11}ClO_2{}^{35}Cl$: 258.0448; Found: 258.0457; HPLC: DAICEL CHIRALPAK AD, hexane–i-PrOH=20:1, flow rate: 1.0 mL/min. The retention time was 10.1 min (αS,βR) and 11.2 min (αR,βS).

1.2.7. (α*S*,β*R*)-2,3-Epoxy-4,4-dimethylbutanophenone (2h). A colorless oil (184 mg, 90% yield, 55% ee ($[\alpha]_D^{25}$=−11 (c 1.0, $CHCl_3$)); IR (neat) ν: 2961, 1694, 1231, 1007 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ: 1.04 (s, 9H), 2.96 (d, J=2.0 Hz, 1H), 4.12 (d, J=2.0 Hz, 1H), 7.48–7.53 (m, 2H), 7.60–7.62 (m, 1H), 7.99–8.02 (m, 2H); MS (EI) m/z 147 (M^+-t-Bu), 105 (base peak); HPLC: DAICEL CHIRALPAK AD, hexane–i-PrOH=20:1, flow rate: 1.0 mL/min. The retention time was 5.9 min (αS,βR) and 7.3 min (αR,βS). The compounds **2g**, **2i** and **2j** were assigned by comparison with the reported results.[3d]

1.3. A typical procedure for catalytic asymmetric epoxidation of 2-substituted 1,4-naphthoquinones under phase-transfer-catalyzed conditions

To a mixture of naphthoquinone derivative (1.0 mmol) and PTC (0.05 mmol) in $CHCl_3$ (3.0 mL) and 30% aqueous H_2O_2 (1.0 mL) was added LiOH (47.9 mg, 2.0 mmol) at

−10°C. After being stirred, the reaction mixture was quenched with 1N HCl and extracted with Et_2O. The combined organic layer was dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash column chromatography (Silica Gel 60, hexane–Et_2O=3:1) to give the desired products.

1.3.1. (2*S*,3*S*)-2-Methyl-2,3-epoxy-1,4-naphthoquinone (4a). A white solid; mp: 94–96°C (Et_2O), lit.[10c] 96–97°C; $[\alpha]_D^{24}=-2.2$ (*c* 1.0, $CHCl_3$, 34% ee); ^1H NMR spectrum was identical with that reported;[13] CD ($CHCl_3$) λ_{ext} ($\Delta\varepsilon$): 361 (+0.75). ($c'=5.32\times10^{-2}$ M, 34% ee); HPLC: DAICEL CHIRALPAK AD, flow rate: 1.0 mL/min, hexane–*i*-PrOH=20:1. The retention time was 10.3 min (2*S*,3*S*) and 11.2 min (2*R*,3*R*).

1.3.2. (2*S*,3*S*)-2-Ethyl-2,3-epoxy-1,4-naphthoquinone (4b). A white solid; mp: 43–45°C (Et_2O), lit.[10c] 49–50°C; $[\alpha]_D^{24}=-2.8$ (*c* 1.0, $CHCl_3$, 41% ee); IR (neat) ν: 2924, 1699, 1163 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.08 (br m, 3H), 2.03 (br m, 1H), 2.29 (br m, 1H), 3.88 (s, 1H), 7.75 (br m, 2H), 7.95–8.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 8.9, 21.6, 64.9, 127.0, 127.7, 132.2, 132.8, 134.6, 134.8, 192.1, 192.3; MS (EI) *m*/*z* 202 (M^+), 187, 173 (base peak); Anal. calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98; Found: C, 71.17; H, 5.09; CD ($CHCl_3$) λ_{ext} ($\Delta\varepsilon$): 348 (+0.46). ($c'=4.95\times10^{-2}$ M, 41% ee); HPLC: DAICEL CHIRALPAK AD, flow rate: 1.0 mL/min, hexane–*i*-PrOH=20:1. The retention time was 7.9 min (2*S*,3*S*) and 8.7 min (2*R*,3*R*).

1.3.3. (2*S*,3*S*)-2-Propyl-2,3-epoxy-1,4-naphthoquinone (4c). A colorless oil; $[\alpha]_D^{24}=-5.2$ (*c* 1.0, $CHCl_3$, 40% ee); IR (neat) ν: 2915, 1698, 1597, 1300 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 1.01 (app. t, *J*=7 Hz, 3H), 1.46–1.60 (m, 2H), 1.81–1.92 (m, 1H), 2.22–2.33 (m, 1H), 3.87 (s, 1H), 7.70–7.77 (m, 2H), 7.91–8.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 14.1, 17.9, 30.2, 60.1, 63.9, 126.7, 127.5, 131.8, 132.5, 134.3, 134.5, 191.7, 192.0; MS (EI) *m*/*z* 216 (M^+), 173 (base peak); Anal. calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 59; Found: C, 72.16; H, 5.73; CD ($CHCl_3$) λ_{ext} ($\Delta\varepsilon$): 346 (+0.55). ($c'=4.62\times10^{-2}$ M, 40% ee); HPLC: DAICEL CHIRALCEL OJ, flow rate: 1.0 mL/min, hexane–*i*-PrOH=20:1. The retention time was 9.1 min (2*S*,3*S*) and 10.8 min (2*R*,3*R*).

1.3.4. (2*S*,3*S*)-2-Butyl-2,3-epoxy-1,4-naphthoquinone (4d). A colorless oil; $[\alpha]_D^{24}=-6.2$ (*c* 1.0, $CHCl_3$, 44% ee);[10d] IR (neat) ν: 2959, 1698, 1597, 1300 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 0.94 (app. t, *J*=7 Hz, 3H), 1.33–1.54 (m, 4H), 1.83–1.94 (m, 1H), 2.24–2.35 (m, 1H), 3.87 (s, 1H), 7.71–7.78 (m, 2H), 7.91–8.05 (m, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 13.8, 22.7, 26.5, 27.9, 60.1, 64.0, 126.7, 127.4, 131.8, 132.4, 134.3, 134.5, 191.7, 192.0; CD ($CHCl_3$) λ_{ext} ($\Delta\varepsilon$): 346 (+0.59). ($c'=4.34\times10^{-2}$ M, 44% ee); HPLC: DAICEL CHIRALCEL OJ, flow rate: 1.0 mL/min, hexane–*i*-PrOH=50:1. The retention time was 18.5 min (2*S*,3*S*) and 24.8 min (2*R*,3*R*). This compound is reported in Ref. 10(c).

1.3.5. (2*S*,3*S*)-2-Isopropyl-2,3-epoxy-1,4-naphthoquinone (4e). A colorless oil; ^1H NMR spectrum was identical with that reported.[13] $[\alpha]_D^{24}=-19.6$ (*c* 1.0, $CHCl_3$, 70% ee); CD ($CHCl_3$) λ_{ext} ($\Delta\varepsilon$): 341 (+1.37). ($c'=4.26\times10^{-2}$ M, 70% ee); HPLC: DAICEL CHIRALCEL OD, flow rate: 0.5 mL/min, hexane–*i*-PrOH=50:1, The retention time 12.5 min was (2*R*,3*R*) and 13.0 min (2*S*,3*S*).

1.3.6. (2*S*,3*S*)-2-Cyclohexyl-2,3-epoxy-1,4-naphthoquinone (4f). A white solid (Et_2O); mp 77–78°C, lit.[10d] 78–79°C; $[\alpha]_D^{24}=-29.1$ (*c* 1.0, $CHCl_3$, 64% ee); IR (nujol) ν: 2930, 2855, 1696, 1593, 1291 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 0.82–1.82 (m, 10H), 2.47–2.58 (m, 1H), 3.90 (s, 1H), 7.71–7.79 (m, 2H), 7.91–8.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 25.8, 25.9, 26.5, 29.1, 34.7, 58.1, 66.6, 126.6, 127.5, 131.6, 132.9, 134.2, 134.5, 191.6, 192.3; MS (EI) *m*/*z* 256 (M^+, base peak), 227, 173, 159; Anal. calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29; Found: C, 75.10; H, 6.43; CD ($CHCl_3$) λ_{ext} ($\Delta\varepsilon$): 340 (+1.39), 384 (−0.22). ($c'=3.90\times10^{-2}$ M, 64% ee); HPLC: DAICEL CHIRALCEL OJ, flow rate: 1.0 mL/min, hexane–*i*-PrOH=99:1, retention time 9.8 min (2*S*,3*S*), 12.3 min (2*R*,3*R*).

1.3.7. (2*S*,3*S*)-2-Phenyl-2,3-epoxy-1,4-naphthoquinone (4g). A white solid; mp: 62°C (Et_2O), lit.[10c] 62–63°C; $[\alpha]_D^{24}=+97.3$ (*c* 1.0, $CHCl_3$, 76% ee); IR (nujol) ν: 3069, 1699, 1597, 1122 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 3.97 (s, 1H), 7.46 (br m, 5H), 7.80 (br m, 2H), 8.06 (br m, 2H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 63.0, 64.3, 126.9, 127.6, 127.9, 128.5, 129.3, 130.7, 131.8, 132.5, 134.6, 134.7, 190.4, 191.0; CD ($CHCl_3$) λ_{ext} ($\Delta\varepsilon$): 322 (+0.31), 381 (−1.29). ($c'=4.00\times10^{-2}$ M, 76% ee); HPLC: DAICEL CHIRALPAK AD, flow rate: 1.0 mL/min, hexane–*i*-PrOH=20:1. The retention time 11.2 min (2*S*,3*S*) was 17.8 min (2*R*,3*R*). This compound is reported in Ref. 10(c).

1.3.8. (2*S*,3*S*)-2-(1-Phenylethynyl)-2,3-epoxy-1,4-naphthoquinone (4h). A pale yellow solid; mp: 133°C (Et_2O); $[\alpha]_D^{24}=+35.0$ (*c* 1.1, $CHCl_3$, 40% ee); IR (nujol) ν: 2200, 1699, 1597, 1122 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ: 4.32 (s, 1H), 7.33–7.44 (m, 3H), 7.56–7.60 (m, 2H), 7.76–7.82 (m, 2H), 7.96–8.01 (m, 1H), 8.07–8.11 (m, 1H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ: 55.9, 62.6, 78.8, 88.9, 120.8, 127.1, 128.0, 128.4, 129.7, 131.5, 131.6, 132.3, 134.8, 134.9, 186.7, 189.7; MS (EI) *m*/*z* 274 (M^+), 273, 189 (base peak); HRMS calcd for $C_{18}H_{10}O_3$ 274.0630; Found: 274.0635; CD ($CHCl_3$) λ_{ext} ($\Delta\varepsilon$): 328 (+0.67), 364 (−1.00). ($c'=4.01\times10^{-2}$ M, 40% ee); HPLC: DAICEL CHIRALPAK AD, flow rate: 1.0 mL/min, hexane–*i*-PrOH=20:1. The retention time was 13.8 min (2*S*,3*S*) and 21.3 min (2*R*,3*R*).

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