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Asymmetric epoxidation of substituted chalcones and chalcone analogues catalyzed by α-D-glucose- and α-D-mannose-based crown ethers

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ABSTRACT

The chiral monoaza-15-crown-5 lariat ethers annellated to methyl-4,6-*O*-benzylidene-α-D-glucopyranoside-**1** or mannopyranoside **2** have been applied as phase-transfer catalysts in the epoxidation of substituted chalcones and chalcone analogues with *tert*-butylhydroperoxide resulting in significant asymmetric induction. It was found that the position of the substituents in the aromatic ring of the chalcone had an influence both on the chemical yields and enantiomeric excesses. The lowest enantioselectivities (62–83% ee) were found in the case of *ortho*-substituted model compounds. The highest ee values (ee of 83–97%) were obtained in the case of *para*-substituted models. From among the chalcone analogues, the maximum ee (90–92%) was detected for the model compound having α-*tert*-butyl- and β-aryl groups. Using glucose-based crown ether **1**, formation of the (−)-enantiomer was preferred, while applying mannose-based **2** as the catalyst, the (+)-enantiomer was in excess.

1. Introduction

Chiral epoxides are well known as valuable building blocks which can be potential intermediates and precursors in the preparation of more complex enantiomerically pure bioactive compounds.[1] This explains the great interest in the enantioselective synthesis of chiral epoxides. A variety of methods have been developed particularly for the enantioselective epoxidation of electron-deficient olefins, such as α,β-unsaturated ketones. The epoxidation has been accomplished by homogeneous and heterogeneous catalysts.[2] One of the types of the heterogeneous methods is the chiral phase-transfer catalytic (chiral PTC) reaction, which has been increasingly useful for asymmetric synthesis, where there is no need to use special conditions, such as inert atmosphere or dry circumstances. The most common oxidants (NaOCl, NaOH/H_2O_2, or NaOH/*t*-BuOOH) are readily available and allow a convenient liquid–liquid phase realization of the reaction.[3]

The utility of chiral quaternary ammonium phase-transfer catalysts for the asymmetric epoxidation of α,β-unsaturated ketones was pioneered by Wynberg et al., who demonstrated that a quinine derivative was capable of promoting enantioselective Weitz–Scheffer epoxidation of chalcones under liquid–liquid phase-transfer conditions.[4] Later on, a variety of cinchonine or quinidine alkaloid derivatives were used as catalysts in the reaction under discussion.[5] Similarly, a well established and no less successful is the Julia–Colonna method applying a polyamino acid.[6] During the epoxidation of chalcone the oxidant is NaOH/H_2O_2 used in the presence of poly-L-leucine as the chiral inductor in a triphasic system.[7] It has been shown by us that beside chiral onium salts, monosaccharide-based chiral crown ethers are also suitable catalysts in the enantioselective epoxidation of α,β-enones by *tert*-butylhydroperoxide.[8] Recently, Hori et al. have applied quaternary ammonium salts of azacrown ethers as chiral phase-transfer catalysts in the asymmetric epoxidation of (*E*)-chalcone with alkaline hydrogen peroxide.[9]

During the oxidation of chalcones by *tert*-butylhydroperoxide, the glucopyranoside- and mannopyranoside-based monoaza-15-crown-5 type lariat ethers containing a γ-hydroxypropyl side arm on the nitrogen atom **1** and **2** were the most efficient phase-transfer catalysts among the chiral macrocycles synthesized by us (Fig. 1).[8]

Herein, the asymmetric epoxidation of chalcones and chalcone analogues is described. The epoxidation of a few substituted chalcones was investigated in the presence of the modified cinchona alkaloides,[5b,10a] dihydrocinchonidine derivatives,[5e,10b] polyethylene glycol-supported cinchona ammonium salts,[10c] quaternary ammonium salts containing a chiral binaphthyl unit,[10d] and poly-

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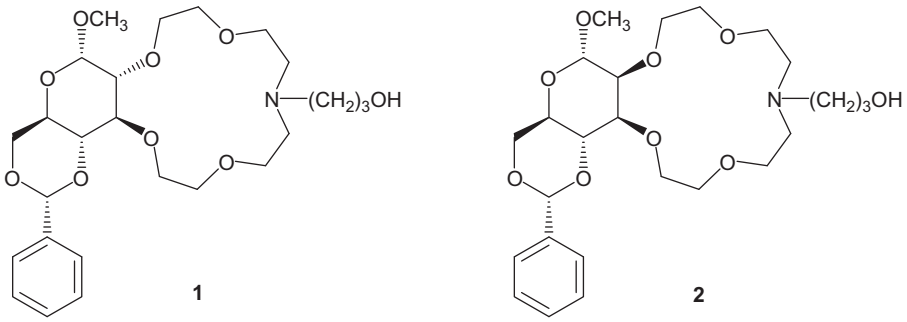
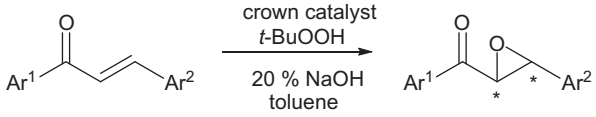


Figure 1.

L-leucine[10e] as the phase-transfer catalysts. The epoxidation of chalcone analogues (α,β-enones) was accomplished in the presence of quaternary ammonium salts derived from cinchonidine.[5b,10f] In the present study, the effect of substituents on the chalcone is studied in the presence of glucose-based crown ether **1**. Then the role of steric and electronic factors with regard to the enone substrate **3** is examined, in order to evaluate their role on the asymmetric epoxidation.

2. Results and discussion

In our experiments, the epoxidation of chalcones with *tert*-butylhydroperoxide (TBHP, 2 equiv) was carried out in a liquid–liquid two-phase system employing toluene and 20% aq NaOH (3.5 equiv) as the base and 7 mol % of chiral crown catalyst at a temperature of 0–2 °C (Scheme 1). In most cases, the reactions were complete after 1–10 h. After the usual work-up procedure, the product was isolated by preparative TLC. The asymmetric induction, expressed in terms of the enantiomeric excess (ee%), was determined by ^{1}H NMR spectroscopy using (+)-Eu(hfc)$_3$ as a chiral shift reagent. The *trans* epoxyketones were obtained in all experiments with a high diastereoselectivity (de >98%).

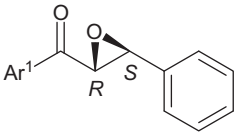


Scheme 1. Asymmetric epoxidation of α,β-enones (Ar^1 and Ar^2 listed in Tables 1–4).

At first, the effect of substituents in the aromatic ring (Ar^1) next to the carbonyl group was studied keeping Ar^2 as a phenyl substituent. The results of the epoxidation are shown in Table 1.

As a comparison, the earlier result for the epoxidation of unsubstituted chalcone has also been included. (Table 1, entry 1).[8b] The chlorophenyl epoxyketones **5**–**7** obtained in 65–71% yield were formed in increasing ee in the following order according to the position of the chloro-substituent: the 2-chlorophenyl-, 3-chlorophenyl-, and 4-chlorophenyl products were obtained in an ee of 69%, 79%, and 97%, respectively (Table 1, entries 2–4). In the electron-donating methyl-substituent cases, the products **8**–**10** were obtained in better yields (72–90%) and the ee values increased in the same order, as in the previous case (71%, 87%, and 92%, respectively) (Table 1, entries 5–7). A similar trend was experienced in the case of methoxy-substituents **11**–**13**. In the presence of catalyst **1**, the yields were 58–77%, while the ee values were in the range of 84–95% (Table 1, entries 8–10). The *para*-methoxy derivative (**13**) was formed in the highest ee (95%). In the electron-withdrawing nitro-substituted cases, the epoxyketones **14**–**16** were obtained in 55–66% yield with high (80–99%) ee values. In these instances, the 3-nitro derivative **15** was formed >99% ee value. (Table 1, entry 12). It can be concluded that the substituents in the aromatic ring influence the extent of asymmetric induction depending on their position. With the exception of the nitro series **14**–**16**, the tendency is that the further the substituent is located from the carbonyl group, the higher the ee value is. The maximum ee values were obtained for the *para*-substituted cases **7**, **10**, and **13**.

Table 1
Asymmetric epoxidation of chalcone with different Ar^1 substituent in the presence of chiral crown ether **1** at 0–2 °C

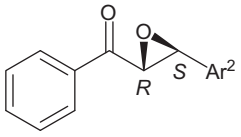


Entry	Product	Ar^1	Time (h)	Yield[a] (%)	$[\alpha]_D$[b]	ee[c] (%)
1	**4**	Ph	1	82	−196	94[8b]
2	**5**	2-Cl–C_6H_4	3	65	−121.2	69
3	**6**	3-Cl–C_6H_4	2	68	−168.1	79
4	**7**	4-Cl–C_6H_4	2	71	−182.4	97
5	**8**	2-CH_3–C_6H_4	4	72	−167	71
6	**9**	3-CH_3–C_6H_4	2	90	−188.1	87
7	**10**	4-CH_3–C_6H_4	2	81	−203.3	92
8	**11**	2-CH_3O–C_6H_4	8	69	−98.5	84
9	**12**	3-CH_3O–C_6H_4	2	77	−199.4	88
10	**13**	4-CH_3O–C_6H_4	3	58	−199.5	95
11	**14**	2-NO_2–C_6H_4	1	66	−285	80
12	**15**	3-NO_2–C_6H_4	1	55	−146.6	>99
13	**16**	4-NO_2–C_6H_4	2	63	−122.6	96

[a] Based on isolation by preparative TLC.
[b] In CH_2Cl_2 at 22 °C.
[c] Determined by ^{1}H NMR spectroscopy in the presence of Eu(hfc)$_3$ as the chiral shift reagent.

In the next experiments, the substituents of the β-phenyl group (Ar^2) of the chalcone were varied. Results of the enantioselectivity of the epoxidation carried out in the presence of catalyst **1** are listed in Table 2. The chlorophenyl epoxyketones **17**–**19** isolated in 74–88% yield were obtained in ee values of 75–83%. For the 2-chlorophenyl-, 3-chlorophenyl-, and 4-chlorophenyl cases, ee values of 75%, 82%, and 83%, respectively, were recorded, with good chemical yields (Table 2, entries 2–4). The trend was quite similar for the epoxidation of the methylphenyl chalcones: the 2-methylphenyl-, 3-methylphenyl-, and 4-methylphenyl products **20**–**22** were formed with 76%, 85%, and 86% ee values (Table 2, entries 5–7). A similar tendency can be seen for the methoxyphenyl derivatives: the 2-methoxyphenyl-, 3-methoxyphenyl-, and 4-methoxyphenyl products **23**–**25** were obtained in 62%, 82%, and 85% ee value, respectively (Table 2, entries 8–10). In the nitro-substituted cases, the presence of the electron-withdrawing substituents **26**–**28** caused a dramatic change: both the chemical yields and enantiomeric excesses were lower, as compared to the previous cases. For the 2-nitrophenyl-, 3-nitrophenyl-, and 4-nitrophenyl cases **26**–**28**, 14%, 21%, and 63% ee values, respectively, were obtained

Table 2
Asymmetric epoxidation of chalcone with different Ar^2 substituents in the presence of chiral crown ether **1** at 0–2 °C



Entry	Product	Ar^2	Time (h)	Yield[a] (%)	$[\alpha]_D$[b]	ee[c] (%)
1	**4**	Ph	1	82	−196	94[8b]
2	**17**	2-Cl–C_6H_4	2	74	−7.4	75
3	**18**	3-Cl–C_6H_4	2	88	−196.4	82
4	**19**	4-Cl–C_6H_4	2	78	−209.5	83
5	**20**	2-CH_3–C_6H_4	4	75	−75.7	76
6	**21**	3-CH_3–C_6H_4	2	79	−201.1	85
7	**22**	4-CH_3–C_6H_4	2	88	−183.9	86
8	**23**	2-CH_3O–C_6H_4	4	49	−63.4	62
9	**24**	3-CH_3O–C_6H_4	3	78	−203.8	82
10	**25**	4-CH_3O–C_6H_4	2	79	−175.1	85
11	**26**	2-NO_2–C_6H_4	2	55	−30.8	14
12	**27**	3-NO_2–C_6H_4	1	59	−68	21
13	**28**	4-NO_2–C_6H_4	1	52	−152.6	63
14	**29**	2,4-DiCl–C_6H_3	2	50	−47.1	99
15	**30**	2,6-DiCl–C_6H_3	2	60	+48.3	70
16	**31**	2-Cl-6-F–C_6H_3	2	54	−20	24

[a] Based on isolation by preparative TLC.
[b] In CH_2Cl_2 at 22 °C.
[c] Determined by ^1H NMR spectroscopy in the presence of $Eu(hfc)_3$ as the chiral shift reagent.

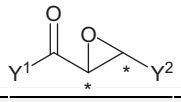
(Table 2, entry 11–13). It can be seen from the data of Table 2 that the substituents of the β-phenyl ring prevent the asymmetric induction to a greater extent than those of the other phenyl ring: products **17**–**28** were obtained in lower enantioselectivities than epoxyketones **5**–**16** (for these latter data see Table 1). It is also clear that independent of the electronic effect, position of the substituent in the β-aryl ring plays also a significant role in the asymmetric induction presumably due to steric effects. The enantioselectivity is the lowest for *ortho*-substituted models **17**, **20**, **23**, and **26** and the highest (83%, 86%, 85%, and 63%) for the *para*-substituted cases **19**, **22**, **25**, and **28**. The *meta*-substituted epoxyketones **18**, **21**, **24**, **27** were obtained in intermediate ee values. The reason for this experience is clear if the first step of the oxidation that is the attack of the hydroperoxy anion (the nucleophilic addition of the peroxy anion) on the β-carbon atom of the chalcone is considered as the configuration determining step.[8c] It is probable that the *ortho*-substituents close to this reaction center may prevent the asymmetric induction as compared to the epoxidation of unsubstituted chalcone **4**. As the substituents get further from the reaction centrum (as in the *meta*- and *para*-substituted models) the extent of the steric effect becomes less significant. In the *para*-substituted models **19**, **22**, **25**, and **26** there is practically no steric effect, although in these cases the ee values are somewhat below the ee of 94% detected for the unsubstituted chalcone. This can be seen well for the nitro-substituted models: as the nitro-group gets further from the reaction center, the enantiomeric excess increases from 14% to 63%.

The disubstituted halogen derivatives **29**–**31** were formed in a wide range of enantioselectivity: in the case of 2,4-dichlorophenyl-**29**, 2,6-dichlorophenyl-**30**, and 2-chloro-6-fluorophenyl epoxyketones ee values of 99%, 70%, and 24%, respectively, were obtained. Besides the steric effects of the substituents, the electronic properties are also prevailing as is shown by the comparison of compounds **30** and **31**: the ee value of 70% obtained for 2,6-dichloro derivative **30** decreased to an ee of 24% in case one of the chloro atoms was replaced by a fluoro atom as in **31**.

In all cases, the (2*R*,3*S*)-enantiomer with a negative specific rotation was formed in excess.[10e] There was only one exception, the 2,6-dichloro derivative **30** was formed with the predominance of the enantiomer with positive specific rotation.

Table 3 includes the results of the epoxidation of a few α,β-enones (chalcone analogues). In the first cases the effect of the Y^1 moiety (with Y^2 = Ph) was studied. In the instance of benzylideneacetone (Y^1 = Me) there was no reaction (Table 3, entry 2). Replacing the Me group by Bu^t, epoxyketone **33** was, however, obtained in good yield and with an ee of 90% (Table 3, entry 3). It is interesting to compare the results obtained for the 1 and 2-naphthyl-substituted models: product **34** was obtained in 64% yield and in an ee of 67%, while epoxyketone **35** was formed in low yield and in an ee of 87% (Table 3, entries 4 and 5). Then the Y^2 moiety was changed as shown by entries 6–9 of Table 3 (Y^1 = Ph). Product **36** (Y^2 = Me) was obtained with an ee value of 55%. The replacement of the Me group by Bu^t resulted in a decreased ee value of 34% and the enantiomer with positive specific rotation was formed in excess (Table 3, entry 7). In this case, the sterically demanding substituent in the proximity of the reaction center may prevent an efficient asymmetric induction. The 1- and 2-naphthyl-epoxyketones **38** and **39** were formed in an ee value of 83% and 66%, respectively (Table 3, entries 8 and 9). In the latter cases again the relevance of steric effects may be deduced. Finally, in the case of Y^2 = 1- and 2-naphthyl with $Y^1 = Bu^t$, the corresponding products **40** and **41** were formed in 85% and 92% ee, respectively

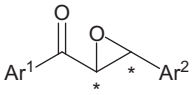
Table 3
Asymmetric epoxidation of chalcone analogues catalyzed by chiral crown ether **1** at 0–2 °C



Entry	Product	Y^1	Y^2	Time (h)	Yield[a] (%)	$[\alpha]_D$[b]	ee[c] (%)
1	**4**	Ph	Ph	1	82	−196	94
2	**32**	CH_3	Ph	20	—	—	—
3	**33**	Bu^t	Ph	16	86	−239.3	90
4	**34**	1-Naphthyl	Ph	10	64	−188.4	67
5	**35**	2-Naphthyl	Ph	3	30	−137.7	87
6	**36**	Ph	CH_3	6	60	−3.4	55
7	**37**	Ph	Bu^t	18	53	+9.2	34
8	**38**	Ph	1-Naphthyl	9	68	−167	83
9	**39**	Ph	2-Naphthyl	6	33	−61.6	66
10	**40**	Bu^t	1-Naphthyl	12	60	−47.8	85
11	**41**	Bu^t	2-Naphthyl	12	52	−253.2	92

[a] Based on isolation by preparative TLC.
[b] In CH_2Cl_2 at 22 °C.
[c] Determined by ^1H NMR spectroscopy in the presence of $Eu(hfc)_3$ as the chiral shift reagent.

Table 4
Asymmetric epoxidation of substituted chalcones and chalcone analogues catalyzed by chiral crown ether **2** at 0–2 °C



Entry	Product	Ar^1	Ar^2	Time (h)	Yield[a] (%)	$[\alpha]_D$[b]	ee[c] (%)
1	**4a**	Ph	Ph	8	47	+171.4	82[8b]
2	**7a**	4-Cl–C_6H_4	Ph	3	70	+167.1	89
3	**13a**	4-CH_3O–C_6H_4	Ph	4	57	+176.8	86
4	**19a**	Ph	4-Cl–C_6H_4	3	72	+194.7	77
5	**25a**	Ph	4-CH_3O–C_6H_4	2	75	+160.5	78
6	**33a**	Bu^t	Ph	8	80	+221.1	83
7	**34a**	1-Naphthyl	Ph	10	61	+174.3	62

[a] Based on isolation by preparative TLC.
[b] In CH_2Cl_2 at 22 °C.
[c] Determined by ^1H NMR spectroscopy in the presence of Eu(hfc)$_3$ as the chiral shift reagent.

(Table 3, entries 10 and 11). It can be seen that the best enantiomeric excesses were obtained for the models with $Y^1 = Bu^t$ and Y^2 = Ph, as product **33** or Y^2 = 2-naphthyl as in product **41**.

A few experiments were also carried out using the related, but mannopyranozide-based, catalyst **2**. The results are listed in Table 4.

Comparing the data obtained for products **7a**, **13a**, **19a**, **25a**, **33a**, and **34a** with those measured in the presence of the glucose-based catalyst **1** (Table 1–3), the following tendencies can be seen. In the case of catalyst **2**, both the chemical yields and enantiomeric excesses are somewhat lower. The main difference is that while the glucose-based catalyst **1** results in most cases the formation of the enantiomer with negative specific rotation in excess that is the antipode with (2*R*,3*S*)-configuration, the mannose-based catalyst **2** promotes the predominant formation of the enantiomer with positive specific rotation. The reason for this may be that already in the first step of the epoxidation of the chalcone, transient complexes of different types are formed with crown ethers **1** and **2**.[8c]

3. Conclusion

The use of glucopyranoside-based crown ether **1** as a catalyst in the asymmetric epoxidation of substituted chalcones and α,β-enones led to comparable and, in a few cases, better results with respect to enantioselectivities, compared to those obtained in the presence of cinchona alkaloids. The significantly shorter reaction times (1–10 h vs 48–120 h) represent the major advantage for the use of crown catalyst **1**. Applying lariat ether **1**, the position of the substituents in the aromatic ring had a great impact on the chemical yield and enantiomeric excesses. The results suggest that the substituents close to the reaction center prevent the asymmetric induction, hence the further the substituents are placed from the reaction center, the higher the extent of enantioselectivity. The epoxyketones substituted on the α-aryl unit **5**–**16** were generally formed in a higher ee value than those substituted on the β-site **17**–**28**. The monosaccharide unit of the catalyst is decisive with respect to the configuration of the epoxiketone. The glucose-based catalyst **1** promoted mostly the formation of the (2*R*,3*S*)-enantiomer with negative specific rotation, while the mannose-based crown **2** enhanced the predominant formation of the enantiomer with positive specific rotation.

4. Experimental

4.1. General procedures

Melting points were taken using a Büchi 510 apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 polarimeter at 22 °C. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 and a Bruker DRX-500 or a Varian Inova 500 instrument in $CDC1_3$ with TMS as the internal standard. Analytical and preparative thin layer chromatography was performed on silica gel plates (60 GF-254, Merck), while column chromatography was carried out using 70–230 mesh silica gel (Merck). Chemicals and the shift reagent Eu(hfc)$_3$ were purchased from Aldrich Chem. Co.

4.2. General procedure for the epoxidation of chalcones

To a solution of α,β-enones (1.44 mmol) and the appropriate catalyst (0.1 mmol) in toluene (3 mL) was added 20% aq NaOH (1 mL) and the mixture was treated with 0.5 mL 5.5 M *tert*-butyl hydroperoxide in decane (2.88 mmol). The mixture was stirred at 0–2 °C for 1–10 h. A fresh portion of toluene (7 mL) and water (10 mL) was added and the mixture was stirred for several minutes. The organic phase was washed with 10% aqueous hydrochloric acid (2 × 10 mL) and then with water (10 mL). The organic phase was dried (Na_2CO_3). The crude product obtained after evaporating the solvent was purified by preparative TLC (silica gel, hexane–ethyl acetate, 10:1 as the eluant) to give the chiral epoxyketone in a pure form. The enantiomer excess was determined by ^1H NMR spectroscopy in the presence of Eu(hfc)$_3$ as the chiral shift reagent.

The configuration of the major enantiomer was in each case determined by comparison with the literature data. For products **5**–**13**, **16**–**28**, **33**–**39** the ^1H NMR data were practically identical with those reported in the literature earlier.

4.2.1. *trans*-(2*R*,3*S*)-2,3-Epoxy-1-(2-chlorophenyl)-3-phenylpropan-1-one 5[10e]

Yield: 65%; oil; $[\alpha]_D^{22} = -121.2$ (*c* 1, CH_2Cl_2, 69% ee). ^1H NMR (500 MHz, $CDCl_3$) δ 4.09 (d, *J* = 1.7 Hz, 1H), 4.15 (d, *J* = 1.7 Hz, 1H), 7.33–7.36 (m, 5H, Ar-H), 7.37–7.62 (m, 4H, Ar-H).

4.2.2. *trans*-(2*R*,3*S*)-2,3-Epoxy-1-(3-chlorophenyl)-3-phenylpropan-1-one 6[10e]

Yield: 68%; mp 86–88 °C; $[\alpha]_D^{22} = -168.1$ (*c* 1, CH_2Cl_2, 79% ee). ^1H NMR (500 MHz, $CDCl_3$) δ 4.08 (d, *J* = 1.5 Hz, 1H), 4.23 (d, *J* = 1.5 Hz, 1H), 7.36–7.42 (m, 5H, Ar-H), 7.44–8.0 (m, 4H, Ar-H).

4.2.3. *trans*-(2*R*,3*S*)-2,3-Epoxy-1-(4-chlorophenyl)-3-phenylpropan-1-one 7[10e]

Yield: 71%; mp 92–94 °C; $[\alpha]_D^{22} = -182.4$ (*c* 1.0, CH_2Cl_2, 97% ee). Lit. $[\alpha]_{577}^{25} = -202$ (*c* 2, CH_2Cl_2, 98% ee).[6d] ^1H NMR (500 MHz, $CDCl_3$) δ 4.08 (d, *J* = 1.6 Hz, 1H), 4.23 (d, *J* = 1.8 Hz, 1H), 7.35–7.42 (m, 5H, Ar-H), 7.47–7.97 (m, 4H, Ar-H).

4.2.4. *trans*-(2*R*,3*S*)-2,3-Epoxy-1-(2-methylphenyl)-3-phenylpropan-1-one 8[10e]

Yield: 72%; oil; $[\alpha]_D^{22} = -167.0$ (*c* 1, CH_2Cl_2, 71% ee). ^1H NMR (500 MHz, $CDCl_3$) δ 2.55 (s, 3H, CH_3), 4.04 (d, *J* = 1.6 Hz, 1H), 4.10 (d, *J* = 1.8 Hz, 1H), 7.27–7.68 (m, 9H, Ar-H).

4.2.5. *trans*-(2*R*,3*S*)-2,3-Epoxy-1-(3-methylphenyl)-3-phenylpropan-1-one 9[10e]

Yield: 90%; oil; $[\alpha]_D^{22} = -188.1$ (*c* 1.0, CH_2Cl_2, 87% ee). ^1H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 3H, CH_3), 4.07 (d, *J* = 1.4 Hz, 1H), 4.29 (d, *J* = 1.5 Hz, 1H), 7.35–7.82 (m, 9H, Ar-H).

4.2.6. *trans*-(2*R*,3*S*)-2,3-Epoxy-1-(4-methylphenyl)-3-phenylpropan-1-one 10[10e]

Yield: 81%; mp 57–59 °C; $[\alpha]_D^{22} = -203.3$ (*c* 1, CH_2Cl_2, 92% ee). ^1H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H, CH_3), 4.07 (d, *J* = 1.6 Hz, 1H), 4.27 (d, *J* = 1.8 Hz, 1H), 7.28–7.93 (m, 9H, Ar-H).

4.2.7. *trans*-(2*R*,3*S*)-2,3-Epoxy-1-(2-methoxyphenyl)-3-phenylpropan-1-one 11[10e]

Yield: 69%; oil; $[\alpha]_D^{22} = -98.5$ (*c* 1, CH_2Cl_2, 84% ee). ^1H NMR (500 MHz, $CDCl_3$) δ 3.61 (s, 3H, OCH_3), 4.01 (d, *J* = 1.8 Hz, 1H), 4.31 (d, *J* = 1.8 Hz, 1H), 7.0–7.83 (m, 9H, Ar-H).

4.2.8. *trans*-(2*R*,3*S*)-2,3-Epoxy-1-(3-methoxyphenyl)-3-phenylpropan-1-one 12[10e]

Yield: 77%; oil; $[\alpha]_D^{22} = -199.4$ (*c* 1, CH_2Cl_2, 88% ee). ^1H NMR (500 MHz, $CDCl_3$) δ 3.85 (s, 3H, OCH_3), 4.07 (d, *J* = 1.8 Hz, 1H), 4.27 (d, *J* = 1.8 Hz, 1H), 7.15–7.85 (m, 9H, Ar-H).

4.2.9. *trans*-(2*R*,3*S*)-2,3-Epoxy-1-(4-methoxyphenyl)-3-phenylpropan-1-one 13[10e]

Yield: 58%; mp 60–62 °C; $[\alpha]_D^{22} = -199.5$ (*c* 1, CH_2Cl_2, 95% ee). Lit. $[\alpha]_D^{22} = -164$ (*c* 2, CH_2Cl_2, 87% ee).[6d] ^1H NMR (500 MHz, $CDCl_3$) δ 3.88 (s, 3H, OCH_3), 4.07 (d, *J* = 1.7 Hz, 1H), 4.25 (d, *J* = 1.8 Hz, 1H), 6.96–8.02 (m, 9H, Ar-H).

4.2.10. *trans*-(2*R*,3*S*)-2,3-Epoxy-1-(2-nitrophenyl)-3-phenylpropan-1-one 14

Yield: 66%; mp 74–75 °C; $[\alpha]_D^{22} = -285.0$ (*c* 1, CH_2Cl_2, 80% ee). ^1H NMR (300 MHz, $CDCl_3$) δ 3.72 (d, *J* = 1.7 Hz, 1H), 3.87 (d, *J* = 1.8 Hz, 1H), 7.22–7.35 (m, 5H, Ar-H), 7.53–8.18 (m, 4H, Ar-H). HRMS calcd for $C_{15}H_{11}NO_4$ 269.0690, found 269.0686.

4.2.11. *trans*-(2*R*,3*S*)-2,3-Epoxy-1-(3-nitrophenyl)-3-phenylpropan-1-one 15

Yield: 55%; mp 189–191 °C; $[\alpha]_D^{22} = -146.6$ (*c* 1, CH_2Cl_2, 99% ee). ^1H NMR (300 MHz, $CDCl_3$) δ 3.87 (d, *J* = 1.8 Hz, 1H), 3.72 (d, *J* = 1.7 Hz, 1H), 7.22–7.35 (m, 5H, Ar-H), 7.53–8.18 (m, 4H, Ar-H); HRMS calcd for $C_{15}H_{11}NO_4$ 269.0690, found 269.0688.

4.2.12. *trans*-(2*R*,3*S*)-2,3-Epoxy-1-(4-nitrophenyl)-3-phenylpropan-1-one 16[8b]

Yield: 63%; mp 120–122 °C; $[\alpha]_D^{22} = -122.6$ (*c* 1, CH_2Cl_2, 96% ee). Lit. $[\alpha]_D^{22} = -37.8$ (*c* 1, CH_2Cl_2, 16% ee).[8b] ^1H NMR (300 MHz, $CDCl_3$) δ 4.21 (d, *J* = 1.7 Hz, 1H), 4.25 (d, *J* = 1.8 Hz, 1H), 7.35–7.44 (m, 5H, Ar-H), 8.19–8.34 (m, 4H, Ar-H).

4.2.13. *trans*-(2*R*,3*S*)-2,3-Epoxy-3-(2-chlorophenyl)-1-phenylpropan-1-one 17[10e]

Yield: 74%; mp 48–50 °C; $[\alpha]_D^{22} = -7.4$ (*c* 1, CH_2Cl_2, 75% ee). ^1H NMR (300 MHz, $CDCl_3$) δ 4.17 (d, *J* = 1.9 Hz, 1H), 4.41 (d, *J* = 1.8 Hz, 1H), 7.31–7.42 (m, 4H, Ar-H), 7.51–8.06 (m, 5H, Ar-H).

4.2.14. *trans*-(2*R*,3*S*)-2,3-Epoxy-3-(3-chlorophenyl)-1-phenylpropan-1-one 18[10e]

Yield: 88%; mp 72–74 °C; $[\alpha]_D^{22} = -196.4$ (*c* 1, CH_2Cl_2, 82% ee). ^1H NMR (300 MHz, $CDCl_3$) δ 4.06 (d, *J* = 1.6 Hz, 1H), 4.26 (d, *J* = 1.8 Hz, 1H), 7.30–7.37 (m, 4H, Ar-H), 7.50–8.01 (m, 5H, Ar-H).

4.2.15. *trans*-(2*R*,3*S*)-2,3-Epoxy-3-(4-chlorophenyl)-1-phenylpropan-1-one 19[10e]

Yield: 78%; mp 112–114 °C; $[\alpha]_D^{22} = -209.5$ (*c* 1.0, CH_2Cl_2, 83% ee). Lit. $[\alpha]_{578}^{20} = -148$ (*c* 2, CH_2Cl_2, 66% ee).[6b] ^1H NMR (300 MHz, $CDCl_3$) δ 4.05 (d, *J* = 1.7 Hz, 1H), 4.24 (d, *J* = 1.8 Hz, 1H), 7.30–7.38 (m, 4H, Ar-H), 7.49–7.99 (m, 5H, Ar-H).

4.2.16. *trans*-(2*R*,3*S*)-2,3-Epoxy-3-(2-methylphenyl)-1-phenylpropan-1-one 20[10e]

Yield: 75%; oil; $[\alpha]_D^{22} = -75.7$ (*c* 1, CH_2Cl_2, 76% ee). ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H, CH_3), 4.21 (d, *J* = 1.8 Hz, 1H), 4.23 (d, *J* = 1.6, 1H), 7.19–7.30 (m, 4H, Ar-H), 7.51–8.05 (m, 5H, Ar-H).

4.2.17. *trans*-(2*R*,3*S*)-2,3-Epoxy-3-(3-methylphenyl)-1-phenylpropan-1-one 21[10e]

Yield: 79%; mp 41–42 °C; $[\alpha]_D^{22} = -201.1$ (*c* 1, CH_2Cl_2, 85% ee). ^1H NMR (300 MHz, $CDCl_3$) δ 2.38 (s, 3H, CH_3), 4.04 (d, *J* = 1.9 Hz, 1H), 4.30 (d, *J* = 2.0 Hz, 1H), 7.19–7.31 (m, 4H, Ar-H), 7.47–7.53 (m, 2H, Ar-H), 7.58–7.65 (m, 1H, Ar-H), 8.02–8.05(m, 2H, Ar-H).

4.2.18. *trans*-(2*R*,3*S*)-2,3-Epoxy-3-(4-methylphenyl)-1-phenylpropan-1-one 22[10e]

Yield: 88%; mp 71–72 °C; $[\alpha]_D^{22} = -183.9$ (*c* 1, CH_2Cl_2, 86% ee). ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H, CH_3), 4.03 (d, *J* = 1.6 Hz, 1H), 4.28 (d, *J* = 1.7 Hz, 1H), 7.21–7.26 (m, 4H, Ar-H), 7.47–8.0 (m, 5H, Ar-H).

4.2.19. *trans*-(2*R*,3*S*)-2,3-Epoxy-3-(2-methoxyphenyl)-1-phenylpropan-1-one 23[10e]

Yield: 49%; oil; $[\alpha]_D^{22} = -63.4$ (*c* 1, CH_2Cl_2, 62% ee). Lit. $[\alpha]_{577}^{25} = -22$ (*c* 2, CH_2Cl_2, 76% ee).[6d] ^1H NMR (300 MHz, $CDCl_3$) δ 3.84 (s, 3H, CH_3O), 4.19 (d, *J* = 1.9 Hz, 1H), 4.39 (d, *J* = 1.8 Hz, 1H), 6.92–7.31 (m, 4H, Ar-H), 7.49–8.0 (m, 5H, Ar-H).

4.2.20. *trans*-(2*R*,3*S*)-2,3-Epoxy-3-(3-methoxyphenyl)-1-phenylpropan-1-one 24[10e]

Yield: 78%; oil; $[\alpha]_D^{22} = -203.8$ (*c* 1, CH_2Cl_2, 82% ee). ^1H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 3H, CH_3O), 4.06 (d, *J* = 1.7 Hz, 1H), 4.27 (d, *J* = 1.8 Hz, 1H), 6.90–7.32 (m, 4H, Ar-H), 7.62–8.01 (m, 5H, Ar-H).

4.2.21. *trans*-(2*R*,3*S*)-2,3-Epoxy-3-(4-methoxyphenyl)-1-phenylpropan-1-one 25[10e]

Yield: 79%; oil; $[\alpha]_D^{22} = -175.1$ (*c* 1, CH_2Cl_2, 85% ee). Lit. $[\alpha]_{577}^{25} = -305$ (*c* 2, CH_2Cl_2, 90% ee).[6d] ^1H NMR (300 MHz, $CDCl_3$) δ 3.8 (s, 3H, CH_3O), 4.0 (d, *J* = 1.9 Hz, 1H), 4.28 (d, *J* = 1.9 Hz, 1H), 6.91–7.27 (m, 4H, Ar-H), 7.49–7.99 (m, 5H, Ar-H).

4.2.22. *trans*-(2*R*,3*S*)-2,3-Epoxy-3-(2-nitrophenyl)-1-phenylpropan-1-one 26[11]

Yield: 55%; mp 105–107 °C; $[\alpha]_D^{22} = -30.8$ (*c* 1, CH_2Cl_2, 14% ee). Lit. $[\alpha]_D^{22} = -48.7$ (*c* 1, CH_2Cl_2, 29% ee).[11] ^1H NMR (300 MHz, $CDCl_3$) δ 4.22 (d, *J* = 2.0 Hz, 1H), 4.65 (d, *J* = 2.0 Hz, 1H), 7.50–8.23 (m, 9H, Ar-H).

4.2.23. *trans*-(2*R*,3*S*)-2,3-Epoxy-3-(3-nitrophenyl)-1-phenylpropan-1-one 27[12]

Yield: 59%; mp 118–119 °C; $[\alpha]_D^{22} = -68.0$ (*c* 1, CH_2Cl_2, 21% ee). ^1H NMR (300 MHz, $CDCl_3$) δ 4.22 (d, *J* = 1.6 Hz, 1H), 4.31 (d, *J* = 1.8 Hz, 1H), 7.52–8.25 (m, 9H, Ar-H).

4.2.24. *trans*-(2*R*,3*S*)-2,3-Epoxy-3-(4-nitrophenyl)-1-phenylpropan-1-one 28[11]

Yield: 52%; mp 124 °C; $[\alpha]_D^{22} = -169.6$ (*c* 1, CH_2Cl_2, 63% ee). Lit. $[\alpha]_D^{22} = -161$ (*c* 1, CH_2Cl_2, 61% ee)[11] ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.21 (d, *J* = 1.4 Hz, 1H), 4.27 (d, *J* = 1.8 Hz, 1H), 7.52–8.28 (m, 9H, Ar-H).

4.2.25. *trans*-(2*R*,3*S*)-2,3-Epoxy-3-(2,4-dichlorophenyl)-1-phenylpropan-1-one 29

Yield: 50%; mp 106 °C; $[\alpha]_D^{22} = -47.1$ (*c* 1, CH_2Cl_2, 99% ee). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.14 (d, *J* = 1.8 Hz, 1H), 4.37 (d, *J* = 1.4 Hz, 1H), 7.31–7.41 (m, 3H, Ar-H), 7.51–8.04 (m, 5H, Ar-H); HRMS calcd for $C_{15}H_{10}Cl_2O_2$ 292.0060 found 292.0057.

4.2.26. *trans*-(+)-2,3-Epoxy-3-(2,6-dichlorophenyl)-1-phenylpropan-1-one 30

Yield: 60%; mp 99–10 °C; $[\alpha]_D^{22} = +48.3$ (*c* 1, CH_2Cl_2, 70% ee). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.30 (d, *J* = 1.9 Hz, 1H), 4.53 (d, *J* = 2.0 Hz, 1H), 7.27–7.35 (m, 3H, Ar-H), 7.55–8.18 (m, 5H, Ar-H); HRMS calcd for $C_{15}H_{10}Cl_2O_2$ 292.0060 found 292.0056.

4.2.27. *trans*-(−)-2,3-Epoxy-3-(2-chloro-6-fluorophenyl)-1-phenylpropan-1-one 31

Yield: 54%; mp 121–123 °C; $[\alpha]_D^{22} = -20.0$ (*c* 1, CH_2Cl_2, 24% ee). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.27 (d, *J* = 1.7 Hz, 1H), 4.69 (d, *J* = 1.9 Hz, 1H), 7.05–7.34 (m, 3H, Ar-H), 7.53–8.14 (m, 5H, Ar-H); HRMS calcd for $C_{15}H_{10}ClFO_2$ 276.0353 found 276.0356.

4.2.28. (1*S*,2*R*)-4,4-Dimethyl-1,2-epoxy-1-phenylpentan-3-one 33[7a]

Yield: 86%; mp: 66–67 °C; $[\alpha]_D^{22} = -239.3$ (*c* 1, CH_2Cl_2, 90% ee). Lit. $[\alpha]_D^{22} = -261.2$ (*c* 1.05 CH_2Cl_2, 97% ee).[7a] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (s, 9H, ^{t}Bu), 3.85 (d, *J* = 1.6 Hz, 1H), 3.87 (d, *J* = 1.8), 7.31–7.38 (m, 5H, Ar-H).

4.2.29. *trans*-(−)-2,3-Epoxy-1-(naphth-1-yl)-3-phenylpropan-1-one 34[5b]

Yield: 64%; mp: 127–129 °C; $[\alpha]_D^{22} = -188.4$ (*c* 1, CH_2Cl_2, 67% ee). Lit. $[\alpha]_D^{22} = -188$ (*c* 1, $CHCl_3$, 71% ee).[5b] ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.14 (d, *J* = 1.7 Hz, 1H), 4.25 (d, *J* = 1.8 Hz, 1H), 7.37–7.42 (m, 5H, Ar-H), 7.50–8.67 (m, 7H, Ar-H).

4.2.30. *trans*-(2*R*,3*S*)-Epoxy-1-(naphth-2-yl)-3-phenylpropan-1-one 35[10g]

Yield: 30%; mp: 101–103 °C; $[\alpha]_D^{22} = -137.7$ (*c* 1, CH_2Cl_2, 87% ee). Lit. $[\alpha]_D^{22} = -100$ (*c* 1, CH_2Cl_2, 73% ee).[10g] ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.16 (d, *J* = 1.7 Hz, 1H), 4.30 (d, *J* = 1.8 Hz, 1H), 7.39–7.44 (m, 5H, Ar-H), 7.56–8.56 (m, 7H, Ar-H).

4.2.31. *trans*-(2*R*,3*S*)-Epoxy-1-phenylbutan-1-one 36[10g]

Yield: 60%; oil; $[\alpha]_D^{22} = -3.4$ (*c* 1, CH_2Cl_2, 55% ee). Lit. $[\alpha]_D^{22} = -10$ (*c* 0.6, $CHCl_3$ 63% ee).[10g] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.52 (d, *J* = 5.1 Hz, 3H, CH_3), 3.22 (dq, *J* = 4.9, 1.8 Hz, 1H), 3.99 (d, *J* = 1.6 Hz, 1H), 7.5–8.01 (m, 5H, Ar-H).

4.2.32. *trans*-(+)-2,3-Epoxy-3-(*tert*-butyl)-1-phenylpropan-1-one 37[10h]

Yield: 53%; oil; $[\alpha]_D^{22} = +9.2$ (*c* 1, CH_2Cl_2, 34% ee). Lit. $[\alpha]_D^{22} = +10$ (*c* 0.53, $CHCl_3$, 76% ee).[10h] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (s, 9H, Bu^t), 2.96 (d, *J* = 2.2, 1H), 4.12 (d, *J* = 2.2 Hz, 1H), 7.5–8.01 (m, 5H, Ar-H).

4.2.33. *trans*-(−)-2,3-Epoxy-3-(naphth-1-yl)-1-phenylpropan-1-one 38[5b]

Yield: 68%; mp: 109–111 °C; $[\alpha]_D^{22} = -167.0$ (*c* 1, CH_2Cl_2, 83% ee). Lit. $[\alpha]_D^{25} = -67.0$ (*c* 2, $CHCl_3$, 78% ee)[10f] ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.30 (d, *J* = 1.5 Hz, 1H), 4.72 (d, *J* = 1.6, 1H), 7.40–7.68 (m, 7H, Ar-H), 7.82–7.92 (m, 2H, Ar-H), 7.93–8.0 (m, 1H, Ar-H), 8.01–8.11 (m, 2H, Ar-H).

4.2.34. *trans*-(−)-2,3-Epoxy-3-(naphth-2-yl)-1-phenylpropan-1-one 39[10f]

Yield: 33%; mp: 101–103 °C; $[\alpha]_D^{22} = -61.7$ (*c* 1, CH_2Cl_2, 66% ee). Lit. $[\alpha]_D^{22} = -84.0$ (*c* 1.6, CH_2Cl_2, 93% ee).[5e] ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.25 (d, *J* = 1.6 Hz, 1H), 4.40 (d, *J* = 1.8 Hz, 1H), 7.50–7.63 (m, 8H, Ar-H), 7.84–7.91 (m, 3H, Ar-H), 8.03 (d, *J* = 8.0, 1H, Ar-H).

4.2.35. (−)-4,4-Dimethyl-1,2-epoxy-1-(naphth-1-yl)pentan-3-one 40

Yield: 60%; oil; $[\alpha]_D^{22} = -47.8$ (*c* 1, CH_2Cl_2, 85% ee). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.29 (s, 9H, Bu^t), 3.86 (d, *J* = 1.9 Hz, 1H), 4.55 (d, *J* = 1.9 Hz, 1H), 7.48 (m, 1H, H-3, Ar-H), 7.52–7.56 (m, 3H, H-2,6,7, Ar-H), 7.85–8.0 (m, 3H, H-4,5,8, Ar-H); HRMS calcd for $C_{17}H_{18}O_2$ 254.1306, found 254.1305.

4.2.36. (−)-4,4-Dimethyl-1,2-epoxy-1-(naphth-2-yl)pentan-3-one 41

Yield: 52%; mp: 99–101 °C; $[\alpha]_D^{22} = -253.2$ (*c* 1, CH_2Cl_2, 92% ee). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (s, 9H, Bu^t), 3.96 (d, *J* = 1.8 Hz, 1H), 4.02 (d, *J* = 1.8 Hz, 1H), 7.35 (m, 1H, H-3, Ar-H), 7.50–7.52 (m, 2H, H-6,7, Ar-H), 7.82–7.87 (m, 4H, H-1,4,5,8, Ar-H); HRMS calcd for $C_{17}H_{18}O_2$ 254.1306, found 254.1307.

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