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Lanthanide complexes combined with chiral salen ligands: application in the enantioselective epoxidation reaction of α,β-unsaturated ketones†

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Readily available lanthanide amides Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = Nd (**1**), Sm (**2**), Eu (**3**), Yb (**4**), La (**5**)), combined with chiral salen ligands H$_2$L^a ((*S*,*S*)-*N*,*N*′-di-(3,5-disubstituted-salicylidene)-1,2-cyclohexanediamine) and H$_2$L^b ((*S*,*S*)-*N*,*N*′-di-(3,5-disubstituted-salicylidene)-1,2-diphenyl-1,2-ethanediamine) were employed in the enantioselective epoxidation of α,β-unsaturated ketones. It was found that the salen–La complex shows the highest efficiency and enantioselectivity. A relatively broad scope of α,β-unsaturated ketones was investigated, and excellent yields (up to 99%) and moderate to good enantioselectivities (37–87%) of the target molecules were achieved.

Introduction

Salen ligands are a particular class of Schiff bases, which are produced by condensation of two salicylaldehydes with a diamine. The use of salen metal complexes for a large variety of catalytic transformations has emerged, mainly because the salen ligands are easily available and highly tunable, and are capable of coordinating to many different metals to form various catalysts.[1] In recent years, chiral salen ligands have become one of the most popular chiral ligands and a series of salen-transition metal catalysts have found application in enantioselective synthesis. In 2001, Kozlowski developed a set of modular bifunctional salen ligands, which showed enhanced reactivity in the asymmetric addition of diethylzinc to aldehydes and achieved excellent yield (up to 99%) with high enantioselectivity (up to 91%).[2] In 2003, Jiang used salen-Ti complexes to catalyze the enantioselective addition of TMSCN to ketones.[3] Rawal reported that the enantioselective carbonyl–ene reactions were catalyzed by a salen–Co complex, which generated chiral homoallylic alcohols in excellent yields, enantioselectivities and diastereoselectivities.[4] In 2014, the asymmetric conia-ene-type cyclization of α-functionalized ketones was catalyzed by a chiral salen–Fe complex.[5] Salen–Zr complexes catalyzed enantioselective α-hydroxylation of β-ketones esters using cumene hydroperoxide (CHP) as the oxidant in excellent yields and enantioselectivities.[6] Epoxidation of non-functionalised alkenes catalyzed by Mn–salen was investigated by Vyas.[7]

However, to the best of our knowledge, examples of highly active lanthanide complexes bearing chiral salen ligands are limited, and their applications are restricted to ring-opening reaction of epoxides,[8] aminoalkene hydroamination/cyclisation,[9] and nitro–mannich reaction.[10] Shibasaki developed asymmetric epoxidation of the electron-deficient C=C bonds in enones, α,β-unsaturated amides and esters, using the combination of lanthanide-BINOL-Ph$_3$As=O as catalyst.[11] Some lanthanide–BINOL and its derivatives have also been investigated in such a transformation, which gave rise to high enantioselectivities in many cases.[12] Feng employed Sc(OTf)$_3$/*N*,*N*′-dioxide as catalyst to realize the asymmetric epoxidation of α,β-unsaturated ketones with excellent enantioselectivities.[13] Recently, our group reported a series of rare-earth metal complexes together with phenoxy-functionalized chiral prolinols which are highly efficient catalysts in the epoxidation of α,β-unsaturated ketones. Both bisubstituted and trisubstituted chalcones produced the corresponding epoxides in excellent yields (up to 99%) and enantioselectivities (up to 99%) using *tert*-butylhydroperoxide (TBHP) as the oxidant.[14] As a continuation of our research on the lanthanide-mediated asymmetric transformation, we herein report rare-earth metal complexes bearing chiral salen ligands and their catalytic potential in the enantioselective epoxidation of α,β-unsaturated ketones.

Results and discussion

To test the reactivity and selectivity of lanthanide amides in combination with chiral salen ligands, five amides Ln[N(SiMe$_3$)$_2$]$_3$ (Ln = Nd (**1**), Sm (**2**), Eu (**3**), Yb (**4**), La (**5**)), two series of phenoxy-functionalized chiral salen ligands [(*S*,*S*)-*N*,*N*′-di-(3-R^1-5-R^2-salicylidene)-1,2-cyclohexanediamine, [R^1 = R^2 =

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† Electronic supplementary information (ESI) available. CCDC 1888891 (for **7e**) contains the supplementary crystallographic data for this paper. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9ra01529a

Me (H_2L^1); $R^1 = R^2 = {}^t$Bu (H_2L^2); R^1 = H, R^2 = Cl (H_2L^3); R^1 = H; $R^2 = {}^t$Bu (H_2L^4); $R^1 = {}^t$Bu, R^2 = H (H_2L^5); R^1 = Me, R^2 = H (H_2L^6); $R^1 = {}^t$Bu; R^2 = 1-adam (H_2L^7)] and (*S*,*S*)-*N*,*N*′-(3-R^1-5-R^2-salicylidene)-1,2-diphenyl-1,2-ethanediamine [$R^1 = R^2$ = Me (H_2L^8); $R^1 = R^2 = {}^t$Bu (H_2L^9)] were synthesized according to the previous study.[15] With the neodymium amide **1** and the salen ligand H_2L^1 in hand, the epoxidation reaction of chalcone was carried out in the presence of TBHP in THF. The results are listed in Table 1. The model reaction underwent quantitatively with unsatisfying enantioselectivity (99% yield and 31% ee). On the basis of this finding, the influence of the chiral salen ligands on enantioselectivity was carefully investigated *via* the modification of the phenol moiety. The yields of the corresponding epoxides remained excellent and the ee values varied from 11–31% (Table 1, entries 1–7). If the chiral linkage was changed to (*S*,*S*)-1,2-diphenyl-1,2-ethanediamine (H_2L^8 and H_2L^9), no significant improvement is observed (Table 1, entries 1–9).

Thus, the chiral salen ligand H_2L^1 was the optimal choice for the model reaction considering both yield and enantioselectivity. Lanthanide amides of different metal centers were studied, and the lanthanum amide **5** gave the best result. The ee value of **7a** reached 41% without sacrificing yield (Table 1, entries 1 and 10–13).

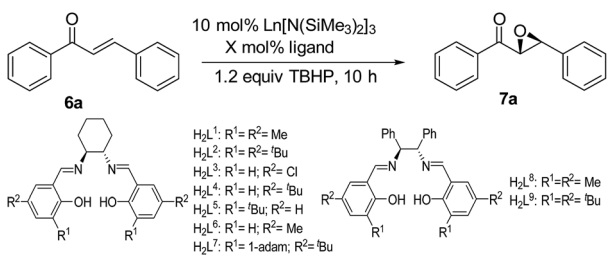
To further improve enantioselectivity, different solvents were screened. Fortunately, when acetonitrile was used as the solvent in the model reaction, the ee value increased to 57%, while the yield of 99% was maintained (Table 1, entries 13–17). Some successful cases in the asymmetric epoxidation reactions also achieved high ee values in acetonitrile.[14a,16] Perhaps the weak coordination of acetonitrile to the central lanthanide metal changes the coordination environment. And it leads to better match for the catalyst and substrate, which may plays an important role in the metal-based catalytic asymmetric reaction. A relatively low temperature is usually helpful to improve the enantioselectivity of the asymmetric reaction. To our delight, attempts to lower the reaction temperature have a positive effect on the enantioselectivity. The ee value significantly increased when the reaction temperature decreased, and the 80% ee of the epoxide **7a** was obtained at −20 °C (Table 1, entries 17–20). Finally, the ratio of the lanthanum amide **5** to the chiral salen ligand H_2L^1 was studied in CH_3CN and the results showed that the 1 : 1.2 molar ratio was optimal for the model reaction (Table 1, entries 19, 21–22). Thus, 10 mol% of La amide **5** in the combination of 12 mol% of chiral salen ligand H_2L^1 was an optimal catalytic system for the asymmetric epoxidation of chalcone with TBHP in CH_3CN at −20 °C.

Subsequently, various α,β-unsaturated ketones were synthesized and investigated, and the results are summarized in Chart 1. Most of the disubstituted α,β-unsaturated ketones underwent the transformation to give epoxides in excellent yields (92–99%) and good to high enantioselectivities (57–83%), with the exception of **7h** (37% ee) (Chart 1, **7a–7o**). Delightedly, much better enantioselectivities, ranging from 80–87%, were observed in reactions of trisubstituted α,β-unsaturated ketones, which are in general bulky and challenging substrates (Chart 1, **7p–7y**). It is noteworthy that these substrates are not only trisubstituted, but also cyclic with restricted mobility, hence more rigid transition states are supposed to generate, which may play a critical role in controlling the enantioselectivity. Relatively high results include the lanthanide–BINOL and its derivatives by Shibasaki,[11] Inanaga[12a] and Ding,[12b] and Sc(OTf)$_3$/*N*,*N*′-dioxide catalyst by Feng,[13] and rare-earth metal complexes together with phenoxy-functionalized chiral prolinols reported by us.[14]

The real active species in the current system was investigated. La amide **5** was treated with 1.2 equiv. chiral salen ligand H_2L^1 in THF. After workup, complex **8** was isolated as yellow crystals (Scheme 1). Its ^{1}H NMR spectrum shows absence of a peak at 0.1980 ppm, which is ascribed to the coordinated –N(SiMe$_3$)$_2$ group. Signals at 3.87–3.55, 1.60 and 1.02 ppm are assigned to cyclohexyl linkage. The peaks at 8.10, 7.91, 7.63, and 7.57 ppm are ascribed to the CH = N double bond. These observations prove the formation of complex **8** bearing the chiral salen ligand. Finally, the ratio of the lanthanum atom to chiral salen ligand is determined to be 2 : 3, based on results of elemental analysis and complex titration.

To find out whether complex **8** is the active species, it was tested in the model asymmetric epoxidation of chalcone under

Table 1 Optimization of the reaction conditions[a]



Entry	Cat	*n*	Ligand	*X*	Solvent	*T*/°C	Yield[b] (%)	ee[c] (%)
1	Nd-1	10	H_2L^1	12	THF	rt	99	31
2	Nd-1	10	H_2L^2	12	THF	rt	99	23
3	Nd-1	10	H_2L^3	12	THF	rt	86	31
4	Nd-1	10	H_2L^4	12	THF	rt	99	27
5	Nd-1	10	H_2L^5	12	THF	rt	99	30
6	Nd-1	10	H_2L^6	12	THF	rt	99	27
7	Nd-1	10	H_2L^7	12	THF	rt	86	11
8	Nd-1	10	H_2L^8	12	THF	rt	99	13
9	Nd-1	10	H_2L^9	12	THF	rt	99	23
10	Sm-2	10	H_2L^1	12	THF	rt	99	33
11	Eu-3	10	H_2L^1	12	THF	rt	89	35
12	Yb-4	10	H_2L^1	12	THF	rt	35	4
13	La-5	10	H_2L^1	12	THF	rt	99	41
14	La-5	10	H_2L^1	12	Tol	rt	99	5
15	La-5	10	H_2L^1	12	Hex	rt	87	37
16	La-5	10	H_2L^1	12	DME	rt	89	35
17	La-5	10	H_2L^1	12	CH_3CN	rt	99	57
18	La-5	10	H_2L^1	12	CH_3CN	0	99	70
19	La-5	10	H_2L^1	12	CH_3CN	-20	99	80
20	La-5	10	H_2L^1	12	CH_3CN	-40	82	56
21	La-5	10	H_2L^1	15	CH_3CN	-20	99	71
22	La-5	10	H_2L^1	20	CH_3CN	-20	99	75
23	La-5	5	H_2L^1	12	CH_3CN	-20	99	57

[a] The reaction was performed with chalcone (0.3 mmol), TBHP (0.36 mmol) in 1 mL of solvent. [b] HPLC yield. [c] Determined by chiral HPLC analysis.

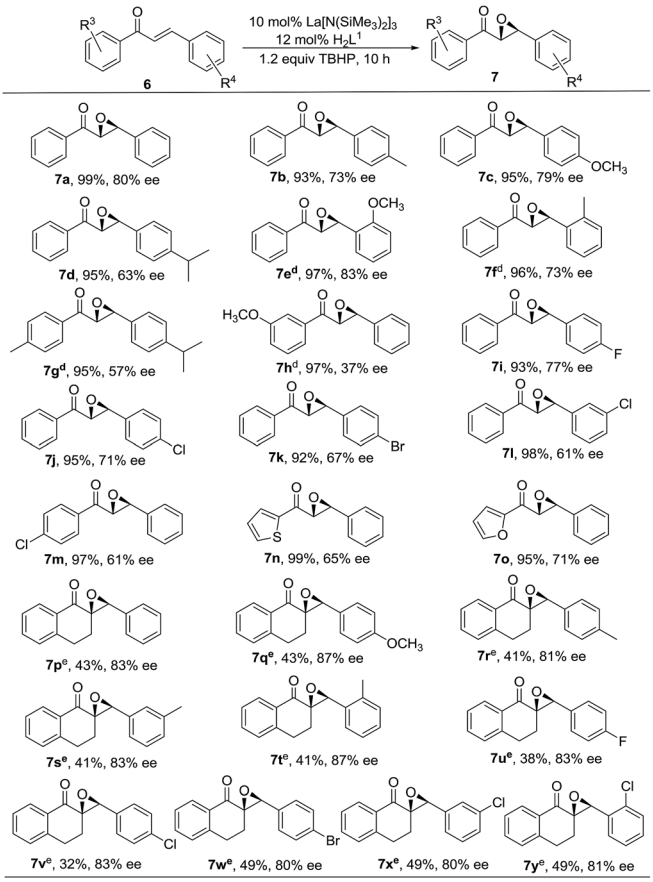
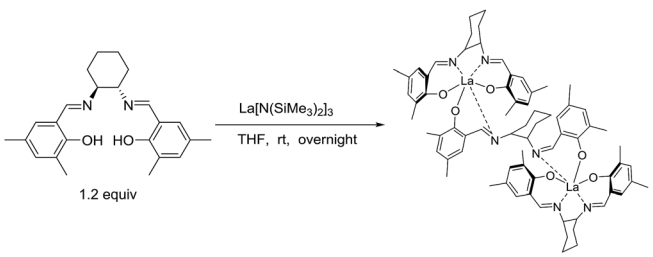


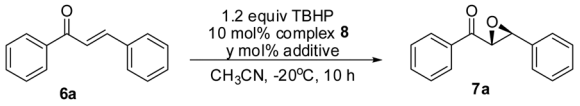
Chart 1 Epoxidation of α,β-unsaturated ketones catalyzed by complex **5**[a]. [a]Reactions were performed with the substrate (0.3 mmol), TBHP (0.36 mmol) in 1 mL CH_3CN at −20 °C for 10 h; isolated yield; ee value were determined by chiral HPLC analysis. [b]15 h. [c]48 h.



Scheme 1 The preparation of complex **8**.

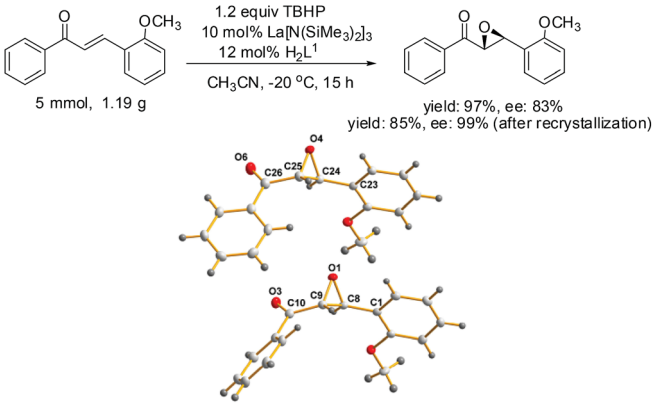
standard conditions. However, neither the yield nor ee value was comparable with results of *in situ* generated catalyst. The target epoxide was obtained in 91% yield and only 70% ee (Table 2, entry 1). Comparing described catalyst system with complex **8**, the difference is $HN(SiMe_3)_2$ generated *in situ* in the former, which may have the positive effects on the asymmetric transformation. To verify the hypothesis, complex **8** together with 20 mol% $HN(SiMe_3)_2$ were added to the model reaction. The outcome of 98% yield with 78% ee indicates that the addition of $HN(SiMe_3)_2$ indeed has a positive effect on the asymmetric catalytic process (Table 2, entry 2). Screening of

Table 2 The effect of additives on the asymmetric epoxidation of chalcone[a]



Entry	Additive	*Y*	Yeild[b] (%)	ee[c] (%)
1	—	20	91	70
2	$HN(SiMe_3)_2$	20	98	78
3	DBU	20	93	15
4	Pyridine	20	88	59
5	Et_3N	20	86	60
6	2,2-Bipyridine	20	85	56
7	$HN(SiMe_3)_2$	10	93	73
8	$HN(SiMe_3)_2$	30	95	75
9	$HN(SiMe_3)_2$	50	90	66

[a] Reactions were performed with chalcone (0.3 mmol), TBHP (0.36 mmol), 1 mL CH_3CN. [b] HPLC yield. [c] Determined by chiral HPLC analysis.



Scheme 2 The synthesis and the molecular structure of compound **7e**.

basic additives, including 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), Et_3N, pyridine, and 2,2′-bipyridine, proved that $HN(SiMe_3)_2$ (20 mol%) is the optimal choice (Table 2, entries 2–9).

Finally, the outcome of the model reaction on a gram scale was satisfactory with an appropriate prolonging of the reaction time and the absolute configuration of the epoxides was determined by single crystal diffraction analysis, chiral HPLC and optical rotation analysis of a representative crystal **7e** (Scheme 2).

The molecular structure of **7e** showing 20% probability ellipsoids. Selected bond lengths (Å) and bond angles (°): O(1)–C(8) 1.4235(3), O(1)–C(9) 1.430(4), C(8)–C(9) 1.494(4), O(4)–C(24) 1.435(4), O(4)–C(25) 1.415(4), C24–C25 1.482(4), O(1)–C(8)–C(1) 116.6(2), O(1)–C(9)–C(10) 115.1(3), O(1)–O(8)–C(9) 58.37(18), O(1)–C(9)–C(8) 58.74(18), C(9)–O(1)–C(8) 62.89(19), O(4)–C(24)–C(23) 116.1(2), O(4)–C(25)–C(26) 113.8(3), O(4)–C(24)–C(25) 58.02(19), O(4)–C(25)–C(24) 59.33(19), C(24)–O(4)–C(25) 62.6(2).

Conclusions

In summary, the asymmetric epoxidation of α,β-unsaturated ketones was catalyzed by a new series of lanthanide amides with chiral salen ligands. After careful screening, 10 mol% of the La amide $La[N(SiMe_3)_2]_3$ together with the chiral salen ligand (*S*,*S*)-*N*,*N*′-(3,5-dimethylsalicylidene)-1,2-cyclohexanediamine in a 1 : 1.2 molar ratio were found to be the optimal catalyst in CH_3CN at −20 °C. For the disubstituted chalcone derivatives, the target epoxides were obtained in excellent yields (92–99%) with moderate to good ee values (57–83%), while epoxides from the trisubstituted α,β-unsaturated ketones were generated in high enantioselectivities (80–87%) and relative low yields (32–57%). Complex **8** resulting from reaction of lanthanum amide and salen ligand was isolated and characterized, which, together with $HN(SiMe_3)_2$ additive, gave comparable catalytic result with that of *in situ* generated catalyst. The absolute configuration of the target chiral epoxides was determined by single crystal diffraction analysis.

Experimental

General information

All manipulations and reactions involving air and water sensitive components were performed with the standard Schlenk techniques. Solvents, such as THF, toluene and hexane, were degassed and distilled from sodium benzophenone ketyl under argon before use. Analytical thin layer chromatography (TLC) was performed using F254 pre-coated silica gel plate (0.2 mm thickness). After elution, plates were detected using UV radiation (254 nm) on a UV lamp. Flash chromatography was performed using 200–300 mesh silica gel with freshly distilled solvents. Nuclear magnetic resonance spectra were obtained on a Bruker AV-400 apparatus ($CDCl_3$ as solvent). High Resolution Mass (HRMS) spectra were obtained using Bruker ESI-TOF. Rare-earth metal analysis was performed by EDTA titration with a xylenol orange indicator and a hexamine buffer. Carbon, hydrogen and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The ee values determination was carried out using HPLC (Agilent Technologies 1200 Series) with Daicel chiralcel columns at room temperature. Optical rotation was measured using an Autopol IV polarimeter equipped with a sodium vapor lamp at 589 nm. The absolute configuration of **7e** was determined by the detection of single crystal diffraction. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Cu–Kα radiation (λ = 1.54178 Å). Hence, the absolute configurations of **7a–7y** were assigned by analogy, assuming the same reaction pathway and the same analysis.

Synthesis of lanthanum complex 8

Under a standard Schlenk vacuum line, to a THF solution of 4 mmol $La[N(SiMe_3)_2]_3$, 6 mmol H_2L^1 in 4 mL THF was added dropwise at room temperature. The mixture was continued to stir overnight. Then, removing the THF solvent *in vacuo*, the crude product was washed with hexane for three times and a faint yellow solid was obtained by centrifugal separation. Finally, complex **8** was purified by recrystallization in the mixed solvent of toluene and hexane.

General procedure for the synthesis of the substituted epoxides 7a–7y

Under argon atmosphere, lanthanum amide $La[N(SiMe_3)_2]_3$ (0.03 mmol, 18.65 mg) was added to a solution of H_2L^1 (0.036 mmol, 13.62 mg) in CH_3CN (1 mL). After stirring for 30 min, unsaturated ketones (0.3 mmol) was added and stirred for further 30 min. After that, oxidant TBHP (0.36 mmol) was added to the mixture. The system was stirred for 10 h at −20 °C. Quenched by the saturated solution of Na_2SO_3, the crude product was extracted by ethyl acetate, then purified by column chromatography (ethyl acetate–petroleum ether, 1 : 10) to obtain the target epoxide. The enantiomeric excess of epoxide was determined by chiral HPLC analysis.

Spectroscopic data for ligands

(*S*,*S*)-*N*,*N*′-Di(3,5-dimethylsalicylidene)-1,2-cyclohexanediamine (H_2L^1). A yellow solid; yield: 70%; $[\alpha]_D^{25}$ −255° (*c*1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 13.39 (s, 2H, OH), 8.20 (s, 2H, CH), 6.94 (s, 2H, Ar–H), 6.80 (d, J = 1.5 Hz, 2H, Ar–H), 3.29 (m, 2H, CH), 2.20 (d, J = 6.7 Hz, 12H, CH_3), 1.88 (m, 4H, CH_2CH_2), 1.70 (m, 2H, CH_2), 1.46 (t, J = 9.6 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 156.5, 133.7, 128.6, 126.5, 124.8, 117.1, 72.2, 32.7, 23.7, 19.8, 14.9. ppm. HRMS (ESI-MS) calcd for $C_{24}H_{31}N_2O_2$ $[M + H]^+$: 379.2386, found: 379.2391.

(*S*,*S*)-*N*,*N*′-Di(3,5-di-butylsalicylidene)-1,2-cyclohexanediamine (H_2L^2). A yellow solid; yield: 80%. $[\alpha]_D^{25}$ −265° (*c*1.0 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 13.73 (s, 2H, OH), 8.32 (s, 2H, CH), 7.33 (d, J = 2.4 Hz, 2H, Ar–H), 7.01 (d, J = 2.4 Hz, 2H, Ar–H), 3.34 (m, 2H, CHCH), 1.93 (dd, J = 29.2, 11.5 Hz, 4H, CH_2CH_2), 1.76 (d, J = 10.0 Hz, 2H, CH_2), 1.49 (d, J = 9.7 Hz, 2H, CH_2), 1.44 (s, 18H, $C(CH_3)_3$), 1.26 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 158.0, 139.90, 136.4, 126.8, 126.1, 117.9, 72.4, 35.0, 34.1, 33.3, 31.4, 29.5, 24.4 ppm. HRMS (ESI-MS) calcd for $C_{36}H_{55}N_2O_2$ $[M + H]^+$: 547.4264, found: 547.4261.

(*S*,*S*)-*N*,*N*′-Di(5-chlorosalicylidene)-1,2-cyclohexanediamine (H_2L^3). A yellow solid; yield: 80%. $[\alpha]_D^{25}$ −195° (*c*1.0 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 13.20 (s, 2H, OH), 8.18 (s, 2H, CH), 7.19 (dd, J = 8.8, 2.6 Hz, 2H, Ar–H), 7.12 (d, J = 2.6 Hz, 2H, Ar–H), 6.84 (d, J = 8.8 Hz, 2H, Ar–H), 3.32 (m, 2H, CHCH), 1.91 (dd, J = 18.6, 9.3 Hz, 4H, CH_2CH_2), 1.72 (m, 2H, CH_2), 1.48 (t, J = 10.0 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 159.5, 132.2, 130.6, 123.3, 119.3, 118.4, 72.7, 32.9, 24.1 ppm. HRMS (ESI-MS) calcd for $C_{20}H_{21}ClN_2O_2$ $[M + H]^+$: 391.0980, found: 391.0987.

(*S*,*S*)-*N*,*N*′-Di(5-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (H_2L^4). A yellow solid; yield: 72%. $[\alpha]_D^{25}$ −175° (*c*1.0 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 13.13 (s, 2H), 8.25 (s, 2H, OH), 7.29 (m, 2H, Ar–H), 7.12 (d, J = 2.5 Hz, 2H, Ar–H), 6.83 (d, J = 8.6 Hz, 2H, Ar–H), 3.31 (m, 2H, CHCH), 1.89 (dd, J = 18.0, 9.9 Hz, 4H, CH_2CH_2), 1.72 (dd, J = 20.6, 9.8 Hz, 2H, CH_2), 1.47 (t, J = 10.1 Hz, 2H, CH_2), 1.24 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 158.6, 141.2, 129.5, 127.9, 118.0, 116.3, 72.8, 33.9, 33.2,

31.4, 24.2 ppm. HRMS (ESI-MS) calcd for $C_{28}H_{39}N_2O_2$ [M + H]$^+$: 435.3021, found: 435.3028.

(*S*,*S*)-*N*,*N*′-Di(3-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (H_2L^5). A yellow solid; yield: 72%. $[\alpha]_D^{25}$ −398° (*c*1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.82 (s, 2H, OH), 8.22 (s, 2H, CH), 7.17 (dd, J = 7.9, 1.5 Hz, 2H, Ar–H), 6.92 (dd, J = 7.6, 1.4 Hz, 2H, Ar–H), 6.64 (t, J = 7.6 Hz, 2H, Ar–H), 3.25 (m, 2H, CHCH), 1.91 (d, J = 13.9 Hz, 2H, CH_2), 1.81 (m, 2H, CH_2), 1.68 (dd, J = 22.0, 11.4 Hz, 2H, CH_2), 1.40 (m, 2H, CH_2), 1.33 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 159.3, 133.2, 129.2, 125.7, 118.0, 72.6, 33.2, 24.2, 15.5 ppm. HRMS (ESI-MS) calcd for $C_{28}H_{39}N_2O_2$ [M + H]$^+$: 435.3021, found: 435.30323.

(*S*,*S*)-*N*,*N*′-Di(5-methylsalicylidene)-1,2-cyclohexanediamine (H_2L^6). A yellow solid; yield: 71%. $[\alpha]_D^{25}$ −495° (*c*1.0 in CHCl3). 1H NMR (400 MHz, CDCl3): δ 13.63 (s, 2H, OH), 8.27 (s, 2H, CH), 7.12 (d, J = 7.3 Hz, 2H, Ar–H), 7.01 (d, J = 7.6 Hz, 2H, Ar–H), 6.72 (t, J = 7.5 Hz, 2H, Ar–H), 3.31 (m, 2H, CH), 2.24 (s, 6H, H_3), 1.91 (m, 4H, CH_2CH_2), 1.71 (d, J = 10.1 Hz, 2H, CH_2), 1.48 (dd, J = 12.7, 6.1 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 158.8, 132.7, 128.7, 125.2, 117.5, 72.1, 32.7, 23.7, 15.0 ppm. HRMS (ESI-MS) calcd for $C_{22}H_{27}N_2O_2$ [M + H]$^+$: 351.2073, found: 351.2077.

(*S*,*S*)-*N*,*N*′-Di(5-methyl-3-adamantylsalicylidene)-1,2-cyclohexanediamine (H_2L^7). A yellow solid; yield: 45%. $[\alpha]_D^{25}$ −235° (*c*1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.66 (s, 2H, OH), 8.30 (s, 2H, CH), 7.24 (d, J = 2.4 Hz, 2H, Ar–H), 6.97 (d, J = 2.4 Hz, 2H, Ar–H), 3.31 (m, 2H, CH), 2.15 (s, 12H, CH_2), 2.07 (s, 6H, CH), 1.90 (m, 4H, CH_2CH_2), 1.79 (s, 12H, CH_2), 1.45 (m, 2H, CH_2), 1.30 (m, 2H, CH_2), 1.24 (s, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 158.6, 141.2, 129.5, 127.9, 118.0, 116.2, 72.8, 33.9, 33.2, 31.40, 24.2 ppm. HRMS (ESI-MS) calcd for $C_{48}H_{67}N_2O_2$ [M + H]$^+$: 703.5203, found: 703.5204.

(*S*,*S*)-*N*,*N*′-Di(3,5-dimethylsalicylidene)-1,2-diphenyl-1,2-ethanediamine (H_2L^8). A yellow solid; yield: 72%. $[\alpha]_D^{25}$ 189° (*c*1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.25 (s, 2H, OH), 8.27 (s, 2H, CH), 7.16 (m, 10H, Ar–H), 6.94 (s, 2H, Ar–H), 6.77 (s, 2H, Ar–H), 4.68 (s, 2H, CHCH), 2.24 (s, 6H, CH_3), 2.17 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 156.9, 139.7, 134.6, 129.5, 128.3, 128.0, 127.5, 127.2, 125.4, 117.6, 80.5, 20.3, 15.5 ppm. HRMS (ESI-MS) calcd for $C_{32}H_{33}N_2O_2$ [M + H]$^+$: 477.2542, found: 477.2549.

(*S*,*S*)-*N*,*N*′-Di(3,5-di-*tert*-butylsalicylidene)-1,2-diphenyl-1,2-ethanediamine (H_2L^9). A yellow solid; yield: 81%. $[\alpha]_D^{25}$ 203° (*c*1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.60 (s, 2H, OH), 8.40 (s, 2H, CH), 7.31 (s, 2H, Ar–H), 7.16 (m, 10H, Ar–H), 6.98 (s, 2H, Ar–H), 4.72 (s, 2H, CHCH), 1.42 (s, 18H, CH_3), 1.22 (s, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 158.0, 140.1, 139.9, 136.4, 128.3, 128.1, 127.5, 127.2, 126.4, 117.9, 80.2, 35.1, 34.1, 31.5, 29.5 ppm. HRMS (ESI-MS) calcd for $C_{44}H_{57}N_2O_2$ [M + H]$^+$: 645.4420, found: 645.4426.

Spectroscopic data for saymmetric epoxidation products

((2*R*,3*S*)-3-Phenyloxiran-2-yl)-phenylmethanone 7a.[14a] A white powder; yield 99%, ee 80%; $[\alpha]_D^{25}$ −112° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.3 Hz, 2H, Ar–H), 7.61 (t, J = 7.4 Hz, 1H, Ar–H), 7.47 (t, J = 7.7 Hz, 2H, Ar–H), 7.38 (m, 5H, Ar–H), 4.29 (d, J = 1.7 Hz, 1H, CH), 4.07 (d, J = 1.6 Hz, 1H, CH). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 7.6 min, t_r (major) = 8.4 min. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{14}O_2Na$ [M + Na]$^+$: 247.0735, found: 247.0738. Mp: 74–76 °C.

((2*R*,3*S*)-3-(4-Methphenyl)oxiran-2-yl)-(phenyl)methanone 7b.[14a] A white powder; yield 93%, ee 73%; $[\alpha]_D^{25}$ −110° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (m, 2H, Ar–H), 7.55 (m, 1H, Ar–H), 7.42 (m, 2H, Ar–H), 7.17 (q, J = 7.8 Hz, 5H, Ar–H), 4.22 (d, J = 1.9 Hz, 1H, CH), 3.97 (d, J = 1.8 Hz, 1H, CH), 2.31 (s, 3H, CH_3). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 6.5 min, t_r (major) = 7.3 min. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{14}O_2Na$ [M + Na]$^+$: 261.2758, found: 261.2753. Mp: 76 °C.

((2*R*,3*S*)-3-(4-Methoxyphenyl)oxiran-2-yl)-(phenyl)methanone 7c.[14a] A white powder; yield 95%, ee 79%; $[\alpha]_D^{25}$ −102° (*c*0.3in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (m, 2H, Ar–H), 7.62 (m, 1H, Ar–H), 7.49 (m, 2H, Ar–H), 7.30 (m, 2H, Ar–H), 6.93 (m, 2H, Ar–H), 4.29 (d, J = 1.9 Hz, 1H, CH), 4.03 (d, J = 1.8 Hz, 1H, CH), 3.83 (s, 3H, CH_3). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 9.4 min, t_r (major) = 10.4 min. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{14}O_2Na$ [M + Na]$^+$: 277.0841, found: 277.0846. Mp: 81–82 °C.

((2*R*,3*S*)-3-(4-Isopropylphenyl)oxiran-2-yl)-(phenyl)methanone 7d.[14a] A white powder; yield 95%, ee 63%; $[\alpha]_D^{25}$ −88° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (m, 2H, Ar–H), 7.60 (m, 1H, Ar–H), 7.47 (m, 2H, Ar–H), 7.28 (m, 4H, Ar–H), 4.31 (d, J = 1.9 Hz, 1H, CH), 4.05 (d, J = 1.8 Hz, 1H, CH), 2.93 (m, 1H, CH), 1.26 (d, J = 6.9 Hz, 6H, CH_3). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 5.7 min, t_r (major) = 6.4 min. HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{18}O_2Na$ [M + Na]$^+$: 289.1204, found: 289.1205. Mp: 74–76 °C.

((2*R*,3*S*)-3-(2-Methoxyphenyl)oxiran-2-yl)-(phenyl)methanone 7e.[14a] A white powder; yield 97%, ee 83%; $[\alpha]_D^{25}$ −94° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (m, 2H, Ar–H), 7.62 (t, J = 7.4 Hz, 1H, Ar–H), 7.49 (t, J = 7.7 Hz, 2H, Ar–H), 7.31 (m, 2H, Ar–H), 7.00 (t, J = 7.5 Hz, 1H, Ar–H), 6.92 (d, J = 8.2 Hz, 1H, Ar–H), 4.39 (d, J = 1.8 Hz, 1H, CH), 4.20 (d, J = 1.9 Hz, 1H, CH), 3.83 (s, 3H, CH_3). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, 8.3 min (minor), 10.1 (major). t_r (minor) = 8.3 min, t_r (major) = 10.1 min. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{14}O_3Na$ [M + Na]$^+$: 277.0841, found: 277.08443. Mp: 89–90 °C.

((2*R*,3*S*)-3-(2-Methphenyl)oxiran-2-yl)-(phenyl)methanone 7f.[14a] A white powder; yield 96%, ee 73%; $[\alpha]_D^{25}$ −77° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (m, 2H, Ar–H), 7.63 (m, 1H, Ar–H), 7.50 (t, J = 7.7 Hz, 2H, Ar–H), 7.34 (dd, J = 6.8, 2.3 Hz, 1H, Ar–H), 7.26 (m, 2H, Ar–H), 7.19 (m, 1H, Ar–H), 4.21 (t, J = 1.8 Hz, 2H, CH), 2.36 (s, 3H, CH_3). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 6.8 min, t_r (major) = 7.7 min. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{14}O_2Na$ [M + Na]$^+$: 261.2758, found: 261.2759. Mp: 70–72 °C.

(4-Methylphenyl)-[(2*R*,3*S*)-3-(4-isopropylphenyl)-2-oxiran]-methanone 7g.[14a] A white powder; yield 95%, ee 57%; $[\alpha]_D^{25}$ −97° (*c*0.3 in acetone).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 2H, Ar–H), 7.20 (m, 6H, Ar–H), 4.20 (d, J = 1.9 Hz, 1H, CH), 3.95 (d, J = 1.8 Hz, 1H, CH), 2.84 (m, 1H, CH), 2.33 (s, 3H, CH_3), 1.18 (d, J = 6.9 Hz, 6H, CH_3). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, 7.8 min (minor), 8.2 (major). t_r (minor) = 7.8 min, t_r (major) = 8.2 min. HRMS (ESI,

m/*z*) calcd for $C_{19}H_{20}O_2Na$ [M + Na]$^+$: 303.1361, found: 303.1367. Mp: 64–67 °C.

(3-Methoxyphenyl)-[(2*R*,3*S*)-3-phenyloxiran-2-yl]-methanone 7h.[14a] A white powder; yield 93%, ee 37%; $[\alpha]_D^{25}$ −49° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, J = 4.9, 3.6 Hz, 1H, Ar–H), 7.52 (m, 1H, Ar–H), 7.38 (m, 6H, Ar–H), 7.16 (m, 1H, Ar–H), 4.29 (d, J = 1.9 Hz, 1H, CH), 4.07 (d, J = 1.8 Hz, 1H, CH), 3.84 (s, 3H, CH_3). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 7.5 min, t_r (major) = 8.7 min. HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{14}O_3Na$ [M + Na]$^+$: 277.0841, found: 277.0849. Mp: 74–76 °C.

((2*R*,3*S*)-3-(4-Fluorophenyl)oxiran-2-yl)-(phenyl)methanone 7i.[14a] A white powder; yield 93%, ee 77%; $[\alpha]_D^{25}$ −98° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (m, 2H, Ar–H), 7.56 (m, 1H, Ar–H), 7.44 (m, 4H, Ar–H), 7.17 (dd, J = 6.2, 4.5 Hz, 2H, Ar–H), 4.17 (d, J = 1.8 Hz, 1H, CH), 3.98 (d, J = 1.7 Hz, 1H, CH). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 8.4 min, t_r (major) = 9.4 min. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{11}FO_2Na$ [M + Na]$^+$: 265.0641, found: 265.0647. Mp: 91.5–94.2 °C.

((2*R*,3*S*)-3-(4-Chlorophenyl)oxiran-2-yl)-(phenyl)methanone 7j.[14a] A white powder; yield 95%, ee 71%; $[\alpha]_D^{25}$ −80° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (m, 2H, Ar–H), 7.63 (m, 1H, Ar–H), 7.49 (m, 2H, Ar–H), 7.35 (m, 2H, Ar–H), 7.10 (m, 2H, Ar–H), 4.26 (s, 1H, CH), 4.07 (d, J = 1.8 Hz, 1H, CH). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 8.0 min, t_r (major) = 8.8 min. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{11}ClO_2Na$ [M + Na]$^+$: 281.0345, found: 281.0349. Mp: 114 °C.

((2*R*,3*S*)-3-(4-Bromophenyl)oxiran-2-yl)-(phenyl)methanone 7k.[14a] A white powder; yield 92%, ee 67%; $[\alpha]_D^{25}$ −78° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (m, 2H, Ar–H), 7.63 (m, 1H, Ar–H), 7.49 (dd, J = 10.7, 4.8 Hz, 2H, Ar–H), 7.38 (m, 2H, Ar–H), 7.31 (m, 2H, Ar–H), 4.25 (d, J = 1.8 Hz, 1H, CH), 4.06 (d, J = 1.8 Hz, 1H, CH). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 7.7 min, t_r (major) = 8.2 min. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{11}BrO_2Na$ [M + Na]$^+$: 324.9840, found: 324.9843. Mp: 89–90 °C.

((2*R*,3*S*)-3-(3-Chlorophenyl)oxiran-2-yl)-(phenyl)methanone 7l.[14a] A white powder; yield 98%, ee 61%; $[\alpha]_D^{25}$ −78° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (m, 2H, Ar–H), 7.63 (m, 1H, Ar–H), 7.49 (m, 2H, Ar–H), 7.38 (m, 2H, Ar–H), 7.30 (m, 2H, Ar–H), 4.25 (d, J = 1.9 Hz, 1H, CH), 4.06 (d, J = 1.8 Hz, 1H, CH). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 8.0 min, t_r (major) = 8.8 min. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{11}ClO_2Na$ [M + Na]$^+$: 281.0345, found: 281.0346. Mp: 74–75 °C.

(3-Chlorophenyl)-[(2*R*,3*S*)-3-phenyloxiran-2-yl]-methanone 7m.[14a] A white powder; yield 97%, ee 61%; $[\alpha]_D^{25}$ −89° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (m, 2H, Ar–H), 7.48 (m, 2H, Ar–H), 7.38 (m, 5H, Ar–H), 4.23 (d, J = 1.9 Hz, 1H, CH), 4.08 (d, J = 1.8 Hz, 1H, CH). HPLC: OD-H column, 97% hexanes, 3% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 21.1 min, t_r (major) = 22.0 min. HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{11}ClO_2Na$ [M + Na]$^+$: 281.0345, found: 281.0354. Mp: 67–68 °C.

[(2*R*,3*S*)-3-Phenyloxiran-2-yl](thien-2-yl)-methanone 7n.[14a] A white powder; yield 99%, ee 65%; $[\alpha]_D^{25}$ −43° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 3.9, 1.0 Hz, 1H, CH), 7.72 (dd, J = 4.9, 1.0 Hz, 1H, CH), 7.34 (m, 5H, Ar–H), 7.15 (dd, J = 4.9, 3.9 Hz, 1H, CH), 4.15 (d, J = 1.7 Hz, 1H, CH), 4.08 (d, J = 1.8 Hz, 1H, CH). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 10.8 min, t_r (major) = 10.1 min. HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{10}O_2SNa$ [M + Na]$^+$: 253.0229, found: 253.0233. Mp: 54–56 °C.

[(2*R*,3*S*)-3-Phenyloxiran-2-yl](furan-2-yl)-methanone 7o.[15a] A white powder; yield 95%, ee 71%; $[\alpha]_D^{25}$ −57° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 1.0 Hz, 1H, CH), 7.45 (d, J = 3.6 Hz, 1H, CH), 7.35 (m, 5H, Ar–H), 6.59 (dd, J = 3.6, 1.7 Hz, 1H, CH), 4.14 (s, 2H, CH). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 10.8 min, t_r (major) = 11.3 min. HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{10}O_3Na$ [M + Na]$^+$: 237.0528, found: 237.0533. Mp: 44–47 °C.

(2*R*,3′*S*)-3′-Phenyl-3,4-dihydro-1*H*-spiro[naphthalene-2,2′-oxiran]-1-one 7p.[14b] A white powder; yield 43%, ee 83%; $[\alpha]_D^{25}$ −96° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 7.8, 0.9 Hz, 1H, Ar–H), 7.51 (m, 1H, Ar–H), 7.37 (m, 6H, Ar–H), 7.22 (d, J = 7.6 Hz, 1H, Ar–H), 4.35 (s, 1H, CH), 2.82 (dd, J = 8.5, 4.1 Hz, 2H, CH_2), 2.43 (m, 1H, CH_2), 1.85 (m, 1H, CH_2). HPLC: OD-H column, 97% hexanes, 3% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 19.5 min, t_r (major) = 21.1 min. HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{14}O_2Na$ [M + Na]$^+$: 273.0891, found: 273.0897. Mp: 73.5–75.5 °C.

(2*R*,3′*S*)-3′-(4-Methoxyphenyl)-3,4-dihydro-1*H*-spiro[naphthalene-2,2′-oxiran]-1-one 7q.[14b] A white powder; yield 43%, ee 87%; $[\alpha]_D^{25}$ −111° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.8 Hz, 1H, Ar–H), 7.51 (m, 1H, Ar–H), 7.35 (t, J = 7.5 Hz, 1H, Ar–H), 7.29 (d, J = 8.6 Hz, 2H, Ar–H), 7.22 (d, J = 7.6 Hz, 1H, Ar–H), 6.93 (dd, J = 6.6, 4.8 Hz, 2H, Ar–H), 4.30 (s, 1H, CH), 3.83 (s, 3H, CH_3), 2.83 (dd, J = 8.5, 4.0 Hz, 2H, CH_2), 2.44 (m, 1H, CH_2), 1.86 (m, 1H, CH_2). HPLC: OD-H column, 97% hexanes, 3% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 30.0 min, t_r (major) = 28.7 min. HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{16}O_3Na$ [M + Na]$^+$: 303.0997, found: 303.0999. Mp: 76–79 °C.

(2*R*,3′*S*)-3′-(4-Methphenyl)-3,4-dihydro-1*H*-spiro[naphthalene-2,2′-oxiran]-1-one 7r.[14b] A white powder; yield 41%, ee 81%; $[\alpha]_D^{25}$ −41° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, J = 7.9, 1.0 Hz, 1H, Ar–H), 7.51 (m, 1H, Ar–H), 7.36 (t, J = 7.5 Hz, 1H, Ar–H), 7.25 (m, 6H, Ar–H), 4.32 (s, 1H, CH), 2.83 (dd, J = 8.5, 4.1 Hz, 2H, CH_2), 2.44 (m, 1H, CH_2), 2.38 (s, 3H, CH_3), 1.86 (m, 1H, CH_2). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 14.9 min, t_r (major) = 20.9 min. HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{16}O_2Na$ [M + Na]$^+$: 287.1048, found: 287.1051. Mp: 165–169 °C.

(2*R*,3′*S*)-3′-(3-Methphenyl)-3,4-dihydro-1*H*-spiro[naphthalene-2,2′-oxiran]-1-one 7s.[17] A white powder; yield 99%, ee 80%; $[\alpha]_D^{25}$ −78° (*c*0.3 in acetone). 1H NMR (400 MHz, $CDCl_3$) δ 8.11 (m, 1H, Ar–H), 7.51 (m, 1H, Ar–H), 7.36 (t, J = 7.6 Hz, 1H, Ar–H), 7.25 (m, 2H, Ar–H), 7.17 (m, 3H, Ar–H), 4.32 (s, 1H, CH), 2.83 (dd, J = 8.4, 4.1 Hz, 2H, CH_2), 2.44 (m, 1H, CH_2), 2.37 (s, 3H, CH_3), 1.87 m, 1H, CH_2). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 7.8 min, t_r (major) = 6.9 min. HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{16}O_2Na$ [M + Na]$^+$: 287.1048, found: 287.1052. Mp: 96–98 °C.

(2*R*,3′*S*)-3′-(2-Methphenyl)-3,4-dihydro-1*H*-spiro[naphthalene-2,2′-oxiran]-1-one 7t.[17] A white powder; yield 99%, ee 87%; $[\alpha]_D^{25}$ −88° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, J = 7.9, 1.0 Hz, 1H, Ar–H), 7.53 (m, 1H, Ar–H), 7.36 (dd, J = 12.4, 5.4 Hz, 2H, Ar–H), 7.25 (m, 3H, Ar–H), 7.18 (dd, J = 6.4, 2.2 Hz, 1H, Ar–H), 4.36 (s, 1H, CH), 2.83 (m, 2H, CH_2), 2.37 (m, 1H, CH_2), 2.25 (s, 3H, CH_3), 1.74 (m, 1H, CH_2). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 6.6 min, t_r (major) = 6.9 min. HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{16}O_2Na$ $[M + Na]^+$: 287.1048, found: 287.1051. Mp: 114–116 °C.

(2*R*,3′*S*)-3′-(4-Fluorophenyl)-3,4-dihydro-1*H*-spiro[naphthalene-2,2′-oxiran]-1-one 7u.[17] A yellow powder; yield 38%, ee 81%; $[\alpha]_D^{25}$ −54° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.9 Hz, 1H, Ar–H), 7.53 (t, J = 7.5 Hz, 1H, Ar–H), 7.36 (m, 3H, Ar–H), 7.23 (d, J = 7.7 Hz, 1H, Ar–H), 7.09 (t, J = 8.4 Hz, 2H, Ar–H), 4.34 (s, 1H, CH), 2.85 (m, 2H, CH_2), 2.43 (m, 1H, CH_2), 1.82 (m, 1H, CH_2). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 8.6 min, t_r (major) = 8.1 min. HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{13}FO_2Na$ $[M + Na]^+$: 291.0907, found: 291.0913. Mp: 99.5–101.5 °C.

(2*S*,3′*R*)-3′-(4-Chlorophenyl)-3,4-dihydro-1*H*-spiro[naphthalene-2,2′-oxiran]-1-one 7v.[14b] A white powder; yield 32%, ee 83%; $[\alpha]_D^{25}$ −102° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 7.9, 1.0 Hz, 1H, Ar–H), 7.53 (m, 1H, Ar–H), 7.34 (m, 5H, Ar–H), 7.24 (d, J = 7.6 Hz, 1H, Ar–H), 4.33 (s, 1H, CH), 2.83 (m, 2H, CH_2), 2.44 (m, 1H, CH_2), 1.81 (m, 1H, CH_2).HPLC: OD-H column, 90% hexanes, 10% iPrOH, 1.0 mL min^{-1}, t_r (minor) = 9.1 min, t_r (major) = 8.5 min. HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{13}ClO_2Na$ $[M + Na]^+$: 307.0502, found: 307.0509. Mp: 138–142 °C.

(2*R*,3′*S*)-3′-(4-Bromophenyl)-3,4-dihydro-1*H*-spiro[naphthalene-2,2′-oxiran]-1-one 7w.[14b] A white powder; yield 49%, ee 80%; $[\alpha]_D^{25}$ −113° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.8 Hz, 1H, Ar–H), 7.53 (dd, J = 6.6, 4.4 Hz, 3H, Ar–H), 7.37 (t, J = 7.5 Hz, 1H, Ar–H), 7.25 (m, 3H, Ar–H), 4.31 (s, 1H, CH), 2.83 (m, 2H, CH_2), 2.44 (m, 1H, CH_2), 1.81 (m, 1H, CH_2). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 9.5 min, t_r (major) = 8.9 min. HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{13}BrO_2Na$ $[M + Na]^+$: 350.9997, found: 351.0002. Mp: 122–125 °C.

(2*R*,3′*S*)-3′-(3-Chlorophenyl)-3,4-dihydro-1*H*-spiro[naphthalene-2,2′-oxiran]-1-one 7x.[17] A white powder; yield 99%, ee 80%; $[\alpha]_D^{25}$ −99° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 7.9, 1.1 Hz, 1H, Ar–H), 7.53 (m, 1H, Ar–H), 7.35 (m, 4H, Ar–H), 7.26 (m, 2H, Ar–H), 4.34 (s, 1H, CH), 2.35 (m, 2H, CH_2), 2.44 (m, 1H, CH_2), 1.84 (m, 1H, CH_2). HPLC: OD-H column, 90% hexanes, 10% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 8.1 min, t_r (major) = 7.6 min. HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{13}ClO_2Na$ $[M + Na]^+$: 307.0502, found: 307.0506. Mp: 94–97 °C.

(2*R*,3′*S*)-3′-(2-Chlorophenyl)-3,4-dihydro-1*H*-spiro[naphthalene-2,2′-oxiran]-1-one 7y.[17] A white powder; yield 99%, ee 80%; $[\alpha]_D^{25}$ −110° (*c*0.3 in acetone). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J = 7.9, 1.2 Hz, 1H, Ar–H), 7.53 (m, 1H, Ar–H), 7.44 (m, 1H, Ar–H), 7.39 (m, 2Hm, Ar–H), 7.34 (m, 2H, Ar–H), 7.25 (d, J = 7.7 Hz, 1H, Ar═H), 4.44 (s, 1H, CH), 3.02 (m, 1H, CH_2), 2.85 (m, 1H, CH_2), 2.39 (m, 1H, CH_2), 1.64 (m, 1H, CH_2). HPLC: OD-H column, 97% hexanes, 3% ^{i}PrOH, 1.0 mL min^{-1}, t_r (minor) = 21.1 min, t_r (major) = 19.5 min. HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{13}ClO_2Na$ $[M + Na]^+$: 307.0502, found: 307.0506. Mp: 132–134 °C.

Conflicts of interest

The authors declare no competing financial interest.

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