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Synthesis of Metal–(Pentadentate-Salen) Complexes: Asymmetric Epoxidation with Aqueous Hydrogen Peroxide and Asymmetric Cyclopropanation (salenH_2: *N*,*N*′-bis(salicylidene)ethylene-1,2-diamine)

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Abstract: It is known that the rates and stereochemical outcomes of epoxidations and cyclopropanations using a metallosalen (salenH_2: *N*,*N*′-bis(salicylidene)ethylene-1,2-diamine) complex as catalyst are affected by a *trans* effect of the apical ligand of the complex. By taking into consideration this *trans* effect, we have synthesized optically active pentadentate salen ligands bearing an imidazole or pyridine derivative as the fifth coordinating group, and have prepared the corresponding manganese(III) and cobalt(II) complexes, in which the fifth ligand is expected to intramolecularly coordinate to the metal center and exert a *trans* effect. Indeed, high enantioselectivity has been achieved in epoxidations using aqueous hydrogen peroxide as the terminal oxidant and in cyclopropanations with these complexes as catalysts. In general, metallosalen-catalyzed reactions have been carried out in the presence of an excess of a donor ligand; however, the present reactions do not need the addition of any extra donor ligand.

Keywords: asymmetric catalysis · cyclopropanation · epoxidation · green chemistry · salen ligands

Introduction

Chiral metal-catalyzed reactions are potent tools for the synthesis of useful chiral compounds. Thus, various chiral metal complexes have been synthesized and used as asymmetric catalysts.[1] Some of them show high asymmetric induction and can be applied to a wide range of asymmetric reactions. Chiral metallosalen (salenH_2: *N*,*N*′-bis(salicylidene)ethylene-1,2-diamine) complexes constitute one such class of complexes: a wide variety of metallosalen complexes have been synthesized and these have been successfully used as catalysts for a range of asymmetric reactions, such as epoxidation, aziridination, cyclopropanation, and so on.[2] Although high enantioselectivity has been achieved in these transformations, some of the reactions are still unsatisfactory in terms of atom efficiency and ecological benignity, improvement of which is a key issue to realize a sustainable society from the synthetic viewpoint. Thus, for example, asymmetric epoxidation using aqueous hydrogen peroxide is a topic of current interest and much effort has been directed towards this field of chemistry.[3] Since Juliá and co-workers reported chiral-phase-transfer-mediated asymmetric epoxidation using aqueous hydrogen peroxide,[4] many such methodologies have been reported,[5] but only a few of them have yielded high enantioselectivity. Shi and co-workers reported that a fructose-derived ketone promoted epoxidation using aqueous hydrogen peroxide in acetonitrile with high enantioselectivity, albeit with moderate turnover number (TON).[6] Jørgensen and co-workers reported highly enantioselective epoxidation of α,β-unsaturated aldehydes using an organocatalyst in the presence of aqueous hydrogen peroxide.[7] We have recently disclosed that a di-μ-oxo-Ti(salalen) (salalen: half-reduced salen) complex serves as an efficient catalyst for enantioselective epoxidation using aqueous hydrogen peroxide. The epoxidation proceeds with high enantioselectivity and in good chemical yield in the presence of a stoichiometric amount of hydrogen peroxide and, moreover, the catalyst yields a good TON (up to 4500).[8] Quite recently, we have further found that a di-μ-oxo-Ti(salan) complex of around half the molecular size of the previous catalyst is almost as effective in catalyzing the epoxidation.[9] On the other hand, oxidizing enzymes, such as cytochrome P-450 and peroxidases, are known to efficiently catalyze various oxidations with complete stereoselectivity, and the catalysis by these enzymes that incorporate an iron–porphyrin complex as their active site has been well

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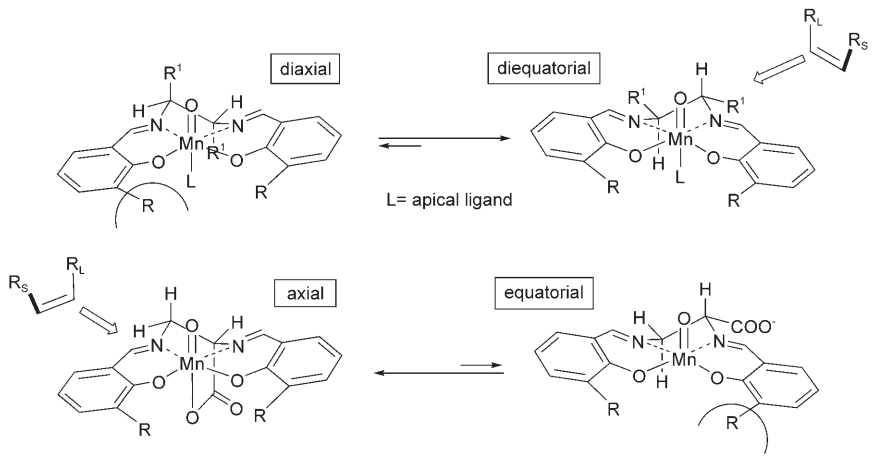
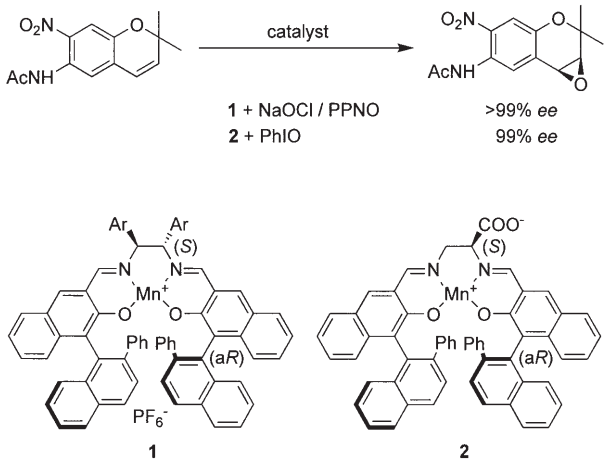
studied.[10] The iron–porphyrin complex is oxidized to the corresponding oxo–metal species via a hydroperoxo species, cleavage of the O–O bond in which is promoted through a synergistic push–pull mechanism, coordination of a donor ligand such as imidazole, and hydrogen bonding to the distal oxygen.[10c,d,11] The mechanisms of these biological oxidations inspired the study of biomimetic approaches using manganese–(salen) or related complexes as catalysts in the presence of a fifth donor ligand. In 1993, Berkessel et al. reported biomimetic asymmetric epoxidation using a manganese–(salalen) complex bearing an imidazole substituent at the C7 carbon in the presence of 1% aqueous hydrogen peroxide, albeit with moderate enantioselectivity,[12] wherein the imidazole group was considered to be coordinated at the apical position of the complex. Subsequently, Pietikäinen reported an intermolecular version of biomimetic asymmetric epoxidation using a system comprising a manganese–(salen) (hereafter referred to as [Mn(salen)]) complex, aqueous hydrogen peroxide, *N*-methylimidazole, and ammonium acetate.[13,14] We independently disclosed [Mn(salen)]-catalyzed asymmetric epoxidation using hydrogen peroxide under almost identical conditions.[15] During this study, we also found that if *N*-methylimidazole was used in excess, the epoxidation using hydrogen peroxide proceeded even in the absence of a protonic substance. However, these seminal studies achieved only moderate success, mainly because of a lack of understanding of the mechanism of asymmetric induction by [Mn(salen)] complexes. Several years later, after further study of asymmetric catalysis by [Mn(salen)] complexes, we could disclose that asymmetric induction by these complexes is related to their conformation.[16] Substituents on the ethylenediamine moiety of the [Mn(salen)] complex usually occupy equatorial positions, but certain coordinating substituents on this moiety, such as carboxylate groups, coordinate to the manganese ion, thereby forcing the [Mn(salen)] complex to adopt an axial conformation. This reverses the sense of asymmetric induction, at the same time improving the TON of the Mn catalyst without diminishing its enantioselectivity (Scheme 1).



Scheme 1. Plausible conformational equilibrium of an oxo(salen)manganese(V) complex bearing a noncoordinating or coordinating substituent and the proposed preferential substrate approach (R_S = smaller substituent; R_L = larger substituent).

For example, complexes **1** and **2** showed the same sense of asymmetric induction, though the chirality at their ethylenediamine moieties is mutually opposite (Scheme 2).[17] This finding prompted us to examine whether a donor substituent such as an (imidazolyl)methyl group could be coordinated to the manganese ion and exert a favorable *trans* effect for asymmetric epoxidation using hydrogen peroxide. On the other hand, Yamada et al. reported that the enantio-



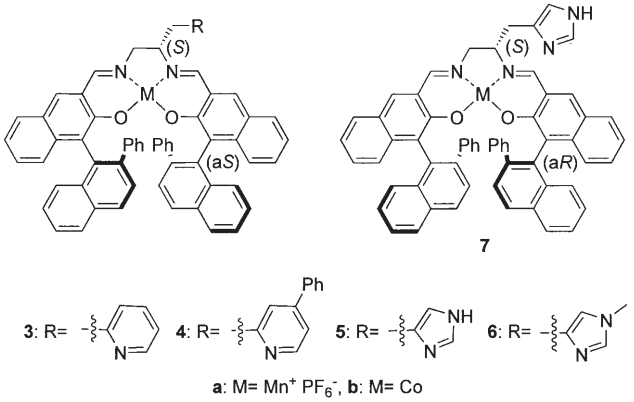
Scheme 2. Asymmetric epoxidation using chiral [Mn(salen)] complexes **1** (Ar = 3,5-$Me_2C_6H_3$) and **2**, which bear a noncoordinating and a coordinating substituent at the ethylenediamine moiety, respectively, as catalysts. PPNO: 4-phenylpyridine *N*-oxide.

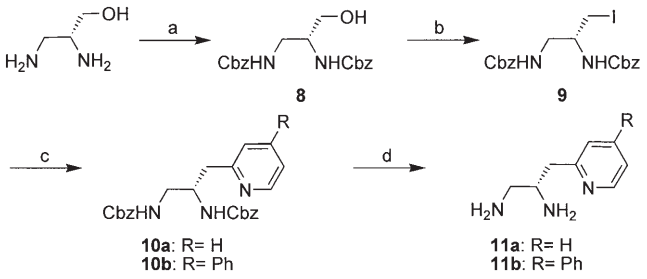
selectivity and the rate of asymmetric cyclopropanation using a cobalt(aldimine) complex as catalyst could be improved by the addition of *N*-methylimidazole.[18] We also found that the enantioselectivity of [Co(salen)]-catalyzed cyclopropanation was improved by the addition of *N*-methylimidazole.[19] Based on these results, we expected that a cobalt complex bearing the above-described pentadentate salen ligand could also be a good catalyst for asymmetric cyclopropanation. In this paper, we describe asymmetric epoxidation and cyclopropanation using manganese- and cobalt-(pentadentate-salen) complexes as catalysts, respectively.[20]

Results and Discussion

Syntheses of manganese- and cobalt(pentadentate-salen) complexes: Taking into consideration the above-described

previous studies, we synthesized manganese and cobalt complexes **3**–**7**, which bear a (2-pyridyl)methyl, (4-phenyl-2-pyridyl)methyl, (1*H*-imidazol-4-yl)methyl, or (*N*-methylimidazol-4-yl)methyl group as the donor substituent on the ethylenediamine moiety. For these syntheses, we first prepared the diamines bearing a pendant *N*-hetero ring, 1,2-diamino-3-(2-pyridyl)propane (**11a**), 1,2-diamino-3-[2-(4-phenylpyridyl)]propane (**11b**), 1,2-diamino-3-(4-imidazolyl)propane (**16**), and 1,2-diamino-3-[4-(1-methylimidazolyl)]propane (**20**). The preparations of diamines **11a**/**11b**, **16**, and **20** are shown in Schemes 3, 4, and 5, respectively.

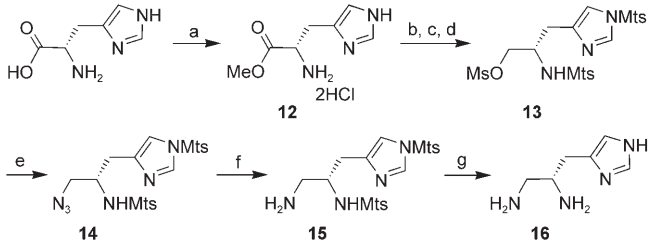




Scheme 3. Synthesis of diamines **11a** and **11b**: a) CbzCl, satd. $NaHCO_3$, RT, 24 h, 75%; b) Ph_3P, imidazole, I_2, CH_2Cl_2, 0°C to RT, 3 h, 54%; c) Zn, $[PdCl_2(PPh_3)_2]$, PPh_3, 2-iodopyridine (for **10a**) or 2-iodo-4-phenylpyridine (**10b**), DMF, 55°C, 20 h, **10a**: 84%, **10b**: 45%; d) H_2, 10% Pd/C, MeOH, RT, 12 h, **11a**: 100%, **11b**: 100%.

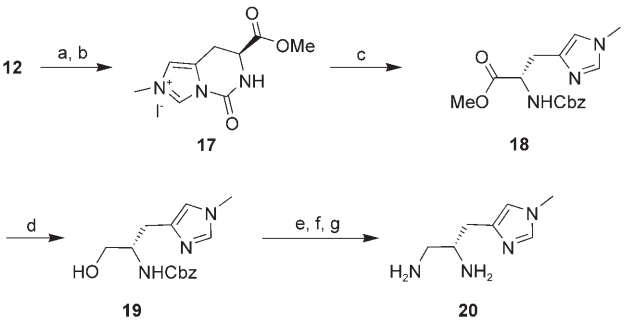
The synthesis of diamines **11a** and **11b** started from 2,3-diaminopropanol, which was prepared according to the reported procedure.[21] Its treatment with two equivalents of benzyl chloroformate (CbzCl) gave alcohol **8**. Treatment of **8** with triphenylphosphane and iodine gave the corresponding iodide **9**. Palladium-mediated coupling of 2-iodopyridine or 2-iodo-4-phenylpyridine with the organozinc reagent derived in situ from iodide **9** gave the protected 1,2-diamino-3-(2-pyridyl)propane **10a** and its phenyl derivative **10b**, respectively. Compounds **10a** and **10b** were subjected to hydrogenolysis by using Pd/C as catalyst to afford the desired **11a** and **11b**, respectively (Scheme 3).

The synthesis of diamine **16** started from bis-2,4,6-trimethylbenzenesulfonylated methanesulfonate **13**, which was prepared from L-histidine according to the known procedure[22] via compound **12**. Compound **13** was treated with NaN_3 in DMF at room temperature to give azide **14**. Azide **14** was then hydrogenated by using Pd/C as catalyst to afford amine **15**. Hydrolysis of compound **15** with HBr at 100°C, followed by ion-exchange chromatography, gave the desired diamine **16** (Scheme 4).



Scheme 4. Synthesis of diamine **16**: a) AcCl, MeOH, 0°C to reflux, 24 h, quant.; b) 2,4,6-trimethylbenzenesulfonyl chloride (MtsCl), Et_3N, $CHCl_3$, RT, 12 h, 90%; c) $NaBH_4$, MeOH, 0°C, 2 h, 63%; d) MsCl, Et_3N, AcOEt, 0°C to RT, 1.5 h, 94%; e) NaN_3, DMF, RT, 24 h, 93%; f) H_2, 10% Pd/C, EtOH, RT, 24 h, 71%; g) aq. HBr, PhOH, 100°C, 72 h then ion exchange, 70%.

The synthesis of diamine **20** started from methyl ester **18**, which was prepared from L-histidine methyl ester **12** via compound **17** according to the known procedure.[23] Reduction of compound **18** with $NaBH_4$ in MeOH gave the corresponding alcohol **19**. Compound **19** was then treated with methanesulfonyl chloride in the presence of triethylamine to give the methanesulfonate, which was treated with NaN_3 in DMF at 60°C to give the azide. The latter was hydrogenated by using Pd/C as catalyst to afford diamine **20** (Scheme 5).



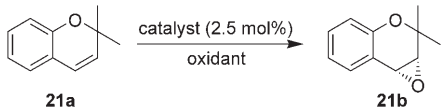
Scheme 5. Synthesis of diamine **20**: a) $(Im)_2CO$, DMF, 60°C, 12 h, 67%; b) MeI, CH_3CN, reflux, 24 h, 84%; c) $PhCH_2OH$, iPr_2NEt, CH_3CN, Ar, reflux, 2 d, 79%; d) $NaBH_4$, MeOH, 0°C, 3 h, 91%; e) MsCl, Et_3N, CH_2Cl_2, 0°C to RT, 3 h; f) NaN_3, DMF, 60°C, 12 h, 28% (two steps); g) H_2, 10% Pd/C, MeOH, RT, 24 h, 100%.

With diamines **11a**/**11b**, **16**, and **20** in hand, we synthesized (a*S*,*S*)-[Mn(pentadentate-salen)] complexes **3a**–**6a** from an (a*S*)-aldehyde ((a*S*)-3-formyl-2-hydroxy-2′-phenyl-1,1′-binaphthyl) and (a*R*,*S*)-[Mn(pentadentate-salen)] complex **7a** from the corresponding (a*R*)-aldehyde, respectively, in the conventional manner.[24] [Co(salen)] complexes were synthesized in a similar way (vide infra).

Asymmetric epoxidation using aqueous hydrogen peroxide: It is known that some 2,2-disubstituted 3,4-epoxychromane derivatives show unique physiological activity. An example

is the potent hypertensive activity shown by Cromakalim.[25] Thus, we first examined the epoxidation of 2,2-dimethylchromene (**21a**) with three equivalents of aqueous hydrogen peroxide as the terminal oxidant in the presence of the complexes **3a**–**7a** (Table 1).

Table 1. Asymmetric epoxidation of 2,2-dimethylchromene (**21a**) catalyzed by **3a**–**7a**.[a]



21a **21b**

Entry	Catalyst	Oxidant	T [°C]	Yield [%][b]	*ee* [%][c]
1	**3a**	30% aq. H_2O_2	RT	27	95
2	**3a**	UHP[d]	RT	22	92
3	**3a**	30% aq. H_2O_2	0	49–60	97
4[e]	**3a**	30% aq. H_2O_2	0	28	90
5	**4a**	30% aq. H_2O_2	0	67	96
6	**5a**	30% aq. H_2O_2	0	26	95
7	**6a**	30% aq. H_2O_2	0	63	97
8	**6a**[f]	30% aq. H_2O_2	0	85	98
9	**6a**[f]	30% aq. H_2O_2[g]	0	48	98
10	**6a**[f]	30% aq. H_2O_2[g,h]	0	56	98
11	**6a**[f]	30% aq. H_2O_2[i]	0	67	98
12	**6a**[f]	30% aq. H_2O_2[j]	0	80	98
13	**7a**	30% aq. H_2O_2	0	12	83

[a] All reactions were carried out for 24 h with 3 equiv of oxidant in the presence of 2.5 mol% of catalyst in CH_2Cl_2 unless otherwise stated. [b] Isolated yields. [c] Determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak OB-H; hexane/*i*PrOH, 9:1). The absolute configuration was determined to be 3*R*,4*R* by chiroptical comparison (ref. [26]). [d] 1 equiv of UHP was used as oxidant. [e] Acetonitrile was used as solvent. [f] 5 mol% of **6a** was used. [g] 1 equiv of H_2O_2 was used. [h] The reaction was carried out for 48 h. [i] 1 equiv of H_2O_2 was added over a period of 8 h and the mixture was stirred for a further 62 h. [j] After performing the reaction with 1 equiv of H_2O_2 for 24 h, 2 equiv of H_2O_2 were added and the reaction mixture was stirred for a further 24 h.

As expected, the reaction with **3a** in dichloromethane proceeded at room temperature with a high enantioselectivity of 95%, albeit with only a modest chemical yield (Table 1, entry 1). The use of urea·hydrogen peroxide adduct instead of aqueous hydrogen peroxide led to slightly reduced enantioselectivity (Table 1, entry 2). Lowering the reaction temperature to 0°C somewhat improved both the enantioselectivity (up to 97% *ee*) and the chemical yield (Table 1, entry 3). The reaction in polar acetonitrile was slow and led to diminished enantioselectivity (Table 1, entry 4).[27] To our surprise, however, the reaction in methanol proceeded smoothly in a highly enantioselective manner (98% *ee*), but the resultant epoxide underwent ring-opening with methanol to give a mixture of (3*R*,4*S*)-4-methoxy-3-hydroxy-2,2-dimethylindane (the major *trans*-product) and the minor *cis*-product (*trans*/*cis* = 97:3) in 97% yield. It is also noteworthy that the observed sense of asymmetric induction by complex **3a** was opposite to that observed in the epoxidation with complex **1**, which bears no donating substituent on its ethylenediamine moiety. This result supports the assumption that the donating pyridyl substituent is apically coordinated to the manganese ion, forcing the salen ligand to adopt the reverse conformation, thereby promoting the generation of the desired oxo species (cf. Scheme 1). Under the optimized conditions, we next examined the epoxidation with complexes **4a**–**7a** as catalysts (Table 1, entries 5–7 and 13). It is noteworthy that each of the (a*S*,*S*)-complexes (**4a**–**6a**) showed high enantioselectivity in excess of 95% *ee* (Table 1, entries 5, 6, and 7), whereas the (a*R*,*S*)-complex **7a** showed considerably inferior enantioselectivity (Table 1, entry 13). As (a*R*,*S*)-[Mn(salen)] complex **1** is generally a superior catalyst for asymmetric epoxidation relative to the corresponding diastereomeric (a*S*,*S*)-[Mn(salen)] complex, this result is also consistent with our assumption. Of the (a*S*,*S*)-complexes (**3a**–**6a**), complex **6a** was found to be the catalyst of choice in terms of yield and enantioselectivity. The reaction using 5 mol% of complex **6a** and three equivalents of aqueous hydrogen peroxide at 0°C gave the desired epoxide with 98% *ee* in 85% yield (Table 1, entry 8). The reaction with one equivalent of aqueous hydrogen peroxide was much slower and the yield of the epoxide was reduced (Table 1, entry 9). An extended reaction time slightly increased the chemical yield (Table 1, entry 10). Slow addition of one equivalent of aqueous hydrogen peroxide to the mixture improved the yield to 67%, giving the same enantioselectivity of 98% *ee* (Table 1, entry 11). Furthermore, when two further equivalents of aqueous hydrogen peroxide were added to the reaction mixture after 24 h, the yield amounted to 80% (Table 1, entry 12). These results suggest that hydrogen peroxide is slowly decomposed during the reaction, but that the catalyst tolerates the conditions.

Next, we examined the asymmetric epoxidation of various 2,2-disubstituted chromene derivatives **22a**–**28a** with **6a** as the catalyst in the presence of three equivalents of aqueous hydrogen peroxide. The results are shown in Table 2. All of these reactions of 2,2-disubstituted chromene derivatives showed high enantioselectivity greater than or equal to 97% *ee*, irrespective of the electronic nature of the C6 substituent (Table 2, entries 1–6). The epoxidation of the trisubstituted alkene **28a** also proceeded with good chemical yield and high enantioselectivity (Table 2, entry 7). The scope of the present reaction is not limited to the epoxidation of chromene derivatives. Epoxidations of 1,2-benzo-1,3-cycloheptadiene **29a** and (*Z*)-1-phenyl-3-penten-1-yne **30a** also proceeded with high enantioselectivity. Complex **3a** showed better enantioselectivity in these reactions than complex **6a**, though the reason for this is unclear (cf. Table 2, entries 8 and 9). Epoxidations of 1,2-benzo-1,3-cycloheptadiene **29a** and (*Z*)-1-phenyl-3-penten-1-yne **30a** with **3a** showed *ee* values of 90% and 88% (face selectivity), respectively (Table 2, entries 9 and 10). As in the epoxidation of acyclic *cis*-enynes using a standard [Mn(salen)] complex as catalyst, epoxidation of **30a** in the presence of **3a** or **6a** gave a mixture of *cis*- and *trans*-epoxides (Table 2, entry 10).[14] Moreover, in agreement with the epoxidation with standard [Mn(salen)] complexes, epoxidation of *trans*-β-methylstyrene **31a** proceeded with low enantioselectivity (entry 11).

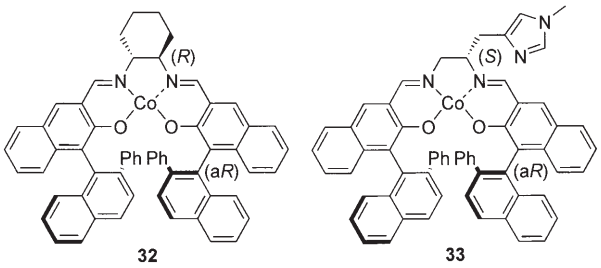
Asymmetric cyclopropanation: Most metal-mediated epoxidations have been considered to proceed via a metal oxe-

Table 2. Asymmetric epoxidations using aqueous hydrogen peroxide.[a]

Entry	Substrate	Product	Yield [%]	*ee* [%]
1	**22a**: R = CN	**22b**: R = CN	95[b]	99[c,d]
2	**23a**: R = Br	**23b**: R = Br	98[b]	98[e]
3	**24a**: R = NO_2	**24b**: R = NO_2	85[b]	99[c,d]
4	**25a**: R = Me	**25b**: R = Me	80[b]	97[e]
5	**26a**: R = OMe	**26b**: R = OMe	78[b]	98[f]
6	**27a**	**27b**	84[b]	98[e]
7	**28a**	**28b**	84[b]	97[g]
8	**29a**	**29b**	95[h]	88[i,j]
9[k]			92[h]	90[i,j]
10[k]	**30a**	**30b**	94 (4:1)[h,l,m]	83[n]
		30c		96[n]
11	**31a**	**31b**	58[h]	31[o,j]

[a] All reactions were carried out for 24 h with 5 mol% of **6a** and 3 equiv of 30% aqueous H_2O_2 in CH_2Cl_2 at 0°C unless otherwise stated. [b] Yield of isolated product. [c] Determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak OJ-H; hexane/*i*PrOH, 7:3). [d] Determined by chiroptical comparison (ref. [26]). [e] Determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak OJ-H; hexane/*i*PrOH, 9:1). [f] Determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak OB-H; hexane/*i*PrOH, 7:3). [g] Determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak OB-H; hexane/*i*PrOH, 99:1). [h] Determined by ^{1}H NMR (400 MHz) spectroscopic analysis. [i] Determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak OB-H; hexane/*i*PrOH, 99.9:0.1). [j] Determined by chiroptical comparison (ref. [28]). [k] Complex **3a** was used as catalyst. [l] The product was obtained as a mixture of *cis*- and *trans*-epoxides; numbers in parentheses indicate the ratio of *cis*- and *trans*-epoxides. [m] Face selectivity = 88% *ee*; the face selectivity was calculated by means of the equation: face selectivity = [% *ee*(*cis*) × %(*cis*) + % *ee*(*trans*) × %(*trans*)]/100; *ee* values were determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak OJ-H; hexane/*i*PrOH, 99.9:0.1). [n] Determined by chiroptical comparison (refs. [8] and [14b]). [o] Determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak IA; hexane/*i*PrOH, 99.9:0.1).

noid species, whereas metal-mediated cyclopropanation proceeds via a metal carbenoid species.[29] Metal oxenoid and metal carbenoid species are isoelectronic, and optically active metallosalen and related complexes have been used as catalysts not only for asymmetric epoxidations but also for asymmetric cyclopropanations, though the most suitable metal center varies with the asymmetric reaction examined.[30] For example, optically active [Mn(salen)] complexes catalyze asymmetric epoxidation as described above, whereas optically active [Co(salen)] and [Co(aldiminate)] complexes catalyze asymmetric cyclopropanation. The stereochemical induction and the rates of these cobalt-mediated cyclopropanations are improved by the addition of *N*-methylimidazole.[18,19,31] Therefore, we were also intrigued by the catalytic potential of [Co(pentadentate-salen)] complexes **6b** and **33**. Complexes **6b** and **33** were prepared by mixing

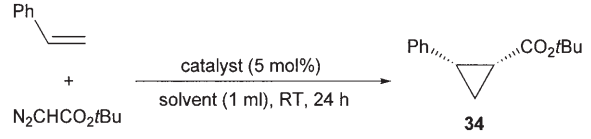


the salen ligands derived from diamines **11a** and **20** and the (a*S*)- or (a*R*)-aldehyde, respectively (vide supra), with $Co(OAc)_2$ at 80°C in deaerated ethanol. They were used as catalysts for cyclopropanation without further purification owing to their air-sensitivity. We recently found the (a*R*,*R*)-[Co^{II}(salen)] complex **32** to be an efficient catalyst for cyclopropanation, showing high *cis*- and enantioselectivity as well as high TON. On the other hand, the corresponding diastereomeric (a*R*,*S*)-[Co^{II}(salen)] complex proved to be much less catalytically active, though its *cis*- and enantioselectivity were slightly superior to those of **32**.[19,32] Thus, we expected that (a*R*,*S*)-**33** would be a good catalyst for cyclopropanation, whereas (a*S*,*S*)-**6b** would be an inferior one in terms of chemical yield. To verify this presumption, we examined the cyclopropanation of styrene with *tert*-butyl α-diazoacetate in the presence of **6b** and **33** (Table 3).

In agreement with the presumption, the reaction with (a*S*,*S*)-complex **6b** gave only a modest chemical yield, though it showed excellent *cis*- and enantioselectivity (Table 3, entry 1). On the other hand, the reaction with (a*R*,*S*)-complex **33** gave a significantly improved chemical yield together with excellent *cis*- and good enantioselectivity (Table 3, entry 2). To further exploit the promise shown by **33**, we examined the reaction in other solvents (Table 3, entries 3–6) and found that the reaction in toluene proceeded in quantitative yield with the same stereoselectivity as the reaction using **6b** (Table 3, entry 6). The reaction employing **6b** in toluene also gave a considerably lower yield as compared with that employing **33**, though they resulted in identical stereochemistry (Table 3, entry 7). The relative rate of the reaction with **33** relative to that with **6b** was estimated to be roughly 4.1 based on the respective yields after 1 h (Figure 1, inset). It is noteworthy that complexes **6b**, **32**, and **33** showed the same sense of asymmetric induction, which supports the coordination of the appended *N*-methylimidazole group.

Under the optimized conditions, we also examined asymmetric cyclopropanation of various styrene derivatives

Table 3. Asymmetric cyclopropanation of styrene with *tert*-butyl α-diazoacetate.[a]



Entry	Catalyst	Solvent	Yield [%][b]	*cis*/*trans*[c]	*ee* of *cis* [%][d]
1	**6b**	THF	30	99:1	97
2	**33**	THF	82	99:1	94
3	**33**	CH_2Cl_2	59	99:1	93
4	**33**	AcOEt	95	99:1	95
5	**33**	MeOH	93	99:1	95
6	**33**	toluene	100	99:1	97
7	**6b**	toluene	72	99:1	98

[a] All reactions were carried out for 24 h at room temperature with a molar ratio of *tert*-butyl α-diazoacetate/styrene/catalyst of 1:10:0.05 unless otherwise stated. [b] Total yield of *trans*- and *cis*-cyclopropanes, calculated on the basis of the amount of α-diazoacetate used by ^{1}H NMR analysis (400 MHz) using 1-bromonaphthalene as an internal standard. [c] Determined by ^{1}H NMR analysis (400 MHz). [d] Determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak OD-H; hexane); the configuration was determined by comparison of the elution order with that of authentic samples.

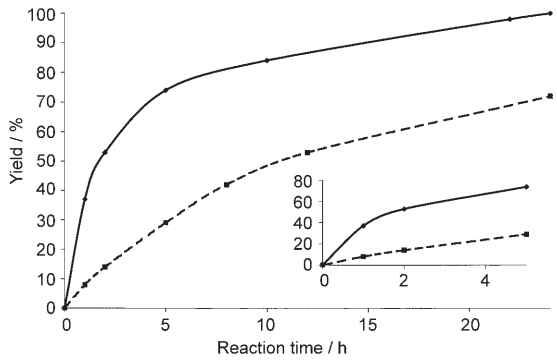
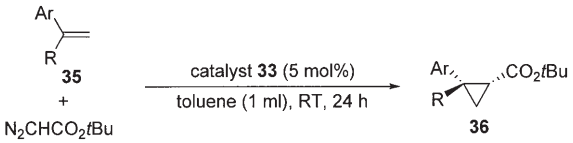
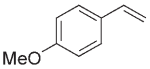
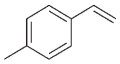
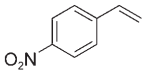
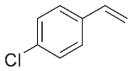
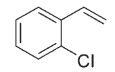


Figure 1. Cyclopropanation of styrene with **6b** (– – –) or **33** (——) as catalyst in toluene.

Table 4. Asymmetric cyclopropanation of styrene derivatives with *tert*-butyl α-diazoacetate.[a]



Entry	Substrate	Yield [%]	*cis*/*trans*[b]	*ee* of *cis* [%]	*ee* of *trans* [%]
1	**35a** 	95[c]	97:3	96[d]	–
2	**35b** 	99[c]	99:1	94[e]	–
3	**35c** 	93[f]	89:11	93[g]	–
4	**35d** 	100[c]	97:3	96[h]	–
5	**35e** 	100[c]	92:8	96[h]	–
6	**35f** 	45[c]	55:45	96[i]	97[e]

[a] All reactions were carried out in toluene (1 mL) for 24 h at room temperature with a molar ratio of *tert*-butyl α-diazoacetate/styrene derivative/catalyst **34** of 1:10:0.05 unless otherwise stated. [b] Determined by ^{1}H NMR analysis (400 MHz). [c] Total yield of *trans*- and *cis*-cyclopropanes, calculated on the basis of the amount of α-diazoacetate used by ^{1}H NMR analysis (400 MHz) using 1-bromonaphthalene as an internal standard. [d] Determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak OD-H; hexane/*i*PrOH, 99.5:0.5). [e] Determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak OB-H; hexane). [f] Total yield of *trans*- and *cis*-cyclopropanes, calculated on the basis of the amount of α-diazoacetate used by ^{1}H NMR analysis (400 MHz) using 2-bromonaphthalene as an internal standard. [g] Determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak OJ-H; hexane/*i*PrOH, 99.9:0.1). [h] Determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak OD-H; hexane). [i] Determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak OJ-H; hexane).

(Table 4). All of the reactions proceeded with high *cis*- and enantioselectivity, irrespective of the electronic nature and the location of the aryl substituent (Table 4, entries 1–5), except that the reaction of α-methylstyrene showed moderate *cis* selectivity albeit with high enantioselectivity (Table 4, entry 6).

Conclusion

We have demonstrated that a heteroaromatic substituent introduced at the ethylenediamine moiety of a salen ligand can coordinate to the metal center, thereby causing a reversal of the conformation of the ligand. The metallosalen complexes of the reverse conformation show a similar level of enantioselectivity to metallosalen complexes of the usual equatorial conformation, and the coordinating heteroaromatic substituent exerts a *trans* effect. This allows, for example, epoxidation with hydrogen peroxide as the oxidant. The present study has demonstrated the potential of five-coordinated metallosalen complexes as asymmetric catalysts.

Experimental Section

General: ^{1}H NMR spectra were recorded at 400 MHz on a Jeol JNM-AL-400 instrument. All signals are expressed in ppm downfield from tetramethylsilane used as an internal standard (δ value in $CDCl_3$). IR spectra were obtained with a Shimadzu FTIR-8400 instrument. Optical rotations were measured with a JASCO P-1020 polarimeter. Column chromatography was conducted on silica gel 60N (spherical, neutral), 63–210 μm, available from Kanto Chemical Co. Preparative thin-layer chromatography was performed on 0.5 mm × 20 cm × 20 cm silica gel plates (60F-254) from E. Merck. Enantiomeric excesses (*ee*) were determined by HPLC analysis using a Shimadzu LC-10AT-VP equipped with an appropriate optically active column, as described in the footnotes to the corresponding tables. For cyclopropanations, solvents were dried before

use. Alkenes and *t*-butyl α-diazoacetate were distilled before use. Reactions were carried out under an atmosphere of nitrogen.

(2*R*)-2,3-(*N*,*N*′-Dibenzyloxycarbonyl)diaminopropanol (8): Saturated aqueous $NaHCO_3$ solution (20 mL) was slowly added to (*R*)-2,3-diaminopropanol (0.27 g, 3.0 mmol) at room temperature, and after 15 min, benzyloxycarbonyl chloride (0.90 mL, 6.3 mmol) was added dropwise. After stirring for 24 h, the mixture was extracted with CH_2Cl_2, and the organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by means of column chromatography on silica gel (hexane/AcOEt, 1:1) to yield the product **8** as a white solid (0.81 g, 75%). $[\alpha]_D^{25} = -8.13$ ($c = 0.24$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.28$–3.67 (complex, 6H), 5.08 (s, 2H), 5.11 (s, 2H), 5.21 (br, 1H), 5.36 (br, 1H), 7.33 ppm (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 40.8$, 52.7, 61.5, 66.9, 67.4, 127.9, 128.02, 128.04, 128.2, 128.4, 128.5, 135.8, 136.1, 156.0, 157.8 ppm; FTIR (KBr disk): $\tilde{\nu} = 3312$(s), 3050(w), 3030(w), 2947(w), 2891(w), 1686(s), 1553(s), 1454(m), 1321(s), 1245(s), 1151(m), 1063(m), 1013(m), 972(w), 908(w), 845(w), 779(w), 737(m), 696 cm^{-1} (m); elemental analysis calcd (%) for $C_{19}H_{22}N_2O_5$ (358.39): C 63.67, H 6.19, N 7.82; found: C 63.80, H 6.16, N 7.88.

(2*R*)-(3-Iodo)-1,2-(*N*,*N*′-dibenzyloxycarbonyl)diaminopropane (9): I_2 (0.76 g, 6.0 mmol) was added in three portions to a solution of triphenylphosphane (1.6 g, 6.0 mmol) and imidazole (0.41 g, 6.0 mmol) in CH_2Cl_2 (20 mL) at 0°C. The solution was allowed to warm to room temperature, stirred for 10 min, and then cooled to 0°C once more. A solution of **8** (1.8 g, 5.0 mmol) in CH_2Cl_2 was added dropwise to the mixture and stirring was continued for 1 h at 0°C and for a further 2 h at room temperature. The mixture was then diluted with CH_2Cl_2, washed successively with saturated aqueous $Na_2S_2O_3$ solution and water, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by means of column chromatography on silica gel (CH_2Cl_2/AcOEt, 30:1) to yield the product **9** as a white solid (1.3 g, 54%). $[\alpha]_D^{25} = +1.50$ ($c = 0.25$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.23$–3.43 (complex, 4H), 3.71 (m, 1H), 5.09 (complex, 5H), 5.56 (br, 1H), 7.34 ppm (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 8.04$, 44.7, 52.0, 67.0, 67.2, 127.95, 128.02, 128.06, 128.14, 128.40, 128.43, 135.89, 136.00, 155.6, 157.0 ppm; FTIR (KBr disk): $\tilde{\nu} = 3321$(m), 3055(w), 3030(w), 2934(w), 1688(s), 1545(s), 1462(w), 1315(m), 1263(m), 1229(m), 1155(w), 1059(m), 1001(w), 972(w), 735(w), 696 cm^{-1} (w); elemental analysis calcd (%) for $C_{19}H_{21}IN_2O_4$ (468.29): C 48.73, H 4.52, N 5.98; found: C 49.08, H 4.57, N 5.98.

(2*S*)-3-(2-Pyridyl)-1,2-(*N*,*N*′-dibenzyloxycarbonyl)diaminopropane (10a): Dibromoethane (16 μL, 0.19 mmol) was added to Zn dust (0.25 g, 3.8 mmol) suspended in DMF (1.0 mL) and the resulting slurry was briefly heated to 80°C for 5 min and then allowed to cool. While it was still moderately warm, chlorotrimethylsilane (4.5 μL, 0.038 mmol) was added and the resulting mixture was stirred vigorously for 30 min at 25°C. A solution of **9** (0.30 g, 0.63 mmol) in DMF (1.0 mL) was added dropwise to the suspension of activated zinc thus formed, and the mixture was stirred vigorously for 2 h at room temperature. In a separate flask, [$PdCl_2$-(PPh_3)$_2$] (22 mg, 0.032 mmol) and PPh_3 (34 mg, 0.13 mmol) were added to a solution of 2-iodopyridine (87 μL, 0.82 mmol) in DMF (1.0 mL), and the above suspension was added dropwise to this mixture. The resulting mixture was heated at 55°C for 12 h and then allowed to cool to room temperature. It was then diluted with AcOEt, washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by means of column chromatography on silica gel (CH_2Cl_2/AcOEt, 1:1) to yield the product **10a** as a white solid (0.22 g, 84%). $[\alpha]_D^{24} = +8.11$ ($c = 0.19$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.03$ (d, $J = 6.0$ Hz, 2H), 3.21 (m, 1H), 3.42 (m, 1H), 4.10 (m, 1H), 5.07–5.08 (complex, 4H), 5.56 (br, 1H), 6.11 (br, 1H), 7.11–7.70 (complex, 13H), 8.48 ppm (d, $J = 4.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 39.7$, 44.5, 52.0, 66.6, 66.8, 121.6, 123.9, 127.89, 127.92, 128.32, 128.34, 131.8, 131.9, 132.0, 136.3, 136.6, 148.9, 156.2, 156.8, 157.7 ppm; FTIR (KBr disk): $\tilde{\nu} = 3325$(s), 3065(w), 3036(w), 3009(w), 2924(w), 1684(s), 1589(w), 1547(s), 1439(w), 1313(m), 1259(s), 1231(m), 1151(m), 1067(m), 1043(w), 1007(w), 752(m), 725(w), 696 cm^{-1} (m); elemental analysis calcd (%) for $C_{24}H_{25}N_3O_4$ (419.47): C 68.72, H 6.01, N 10.02; found: C 68.86, H 6.11, N 9.84.

(2*S*)-3-[2-(4-Phenylpyridyl)]-1,2-(*N*,*N*′-dibenzyloxycarbonyl)diaminopropane (10b): Compound **10b** was prepared in the same manner as described for the synthesis of **10a**, except that 2-iodo-4-phenylpyridine (0.37 g, 1.3 mmol) was used instead of 2-iodopyridine and the chromatographic conditions were modified. After workup, the reaction mixture was purified by means of column chromatography on silica gel (CH_2Cl_2/AcOEt, 4:1 to 1:1) to yield the product **10b** as a white solid (0.29 g, 45%). $[\alpha]_D^{24} = +9.96$ ($c = 0.60$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.10$ (d, $J = 6.0$ Hz, 2H), 3.25 (m, 1H), 3.44 (m, 1H), 4.15 (m, 1H), 5.08 (complex, 4H), 5.61 (br, 1H), 6.16 (br, 1H), 7.29–7.69 (complex, 17H), 8.52 ppm (d, $J = 5.6$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 39.9$, 44.5, 52.3, 66.7, 66.8, 119.7, 121.8, 126.9, 127.89, 127.92, 128.3 (two peaks overlap), 128.9, 129.0, 131.8, 131.9, 132.0, 136.3, 137.7, 149.0, 149.4, 156.2, 156.9, 158.2 ppm; FTIR (KBr disk): $\tilde{\nu} = 3315$(s), 3063(w), 3032(w), 2928(w), 1688(s), 1601(m), 1547(s), 1472(w), 1454(w), 1437(w), 1402(w), 1319(m), 1261(s), 1151(m), 1057(m), 1007(m), 910(w), 843(w), 762(m), 735(m), 694 cm^{-1} (m); elemental analysis calcd (%) for $C_{30}H_{29}N_3O_4$ (495.57): C 72.71, H 5.90, N 8.48; found: C 72.35, H 5.97, N 8.19.

(2*S*)-1,2-Diamino-3-(2-pyridyl)propane (11a): A solution of **10a** (0.10 g, 0.25 mmol) in MeOH (10 mL) was stirred under a slight overpressure of hydrogen in the presence of 10% Pd/C (13 mg) for 12 h at room temperature. After removal of the catalyst by filtration through Celite, the solvent was removed in vacuo to yield pure **11a** (38 mg, 100%) as a colorless oil, which was used for the preparation of complex **3a** without further purification. ^{1}H NMR (400 MHz, CD_3OD): $\delta = 2.54$ (dd, $J = 7.6$, 13.1 Hz, 1H), 2.70 (dd, $J = 4.4$, 12.8 Hz, 1H), 2.78 (dd, $J = 7.6$, 13.6 Hz, 1H), 2.93 (dd, $J = 6.0$, 13.8 Hz, 1H), 3.13 (m, 1H), 7.27 (m, 1H), 7.73 (d, $J = 15.6$ Hz, 1H), 7.76 (t, $J = 7.2$ Hz, 1H), 8.48 ppm (d, $J = 4.0$ Hz, 1H).

(2*S*)-1,2-Diamino-3-[2-(4-phenylpyridyl)]propane (11b): Preparation similar to that for **11a** but using **10b** as the starting material to give **11b** as a colorless oil (57 mg, 100%), which was used for the preparation of complex **4a** without further purification. ^{1}H NMR (400 MHz, CD_3OD): $\delta = 2.56$ (dd, $J = 7.4$, 13.0 Hz, 1H), 2.72 (dd, $J = 4.4$, 13.2 Hz, 1H), 2.83 (dd, $J = 7.8$, 13.4 Hz, 1H), 2.99 (dd, $J = 6.0$, 13.6 Hz, 1H), 3.17 (m, 1H), 7.46–7.76 (complex, 7H), 8.52 ppm (d, $J = 5.2$ Hz, 1H).

Complex 3a: $Mn(OAc)_2 \cdot 4H_2O$ (0.12 g, 0.5 mmol) was added to a solution of diamine **11a** (76 mg, 0.5 mmol) in EtOH (20 mL) and the reaction mixture was stirred for 1 h at room temperature. Thereafter, (a*S*)-3-formyl-2-hydroxy-2′-phenyl-1,1′-binaphthyl[24] (0.37 g, 1.0 mmol) was added and the resulting mixture was stirred for 8 h at 60°C in air. Then, $NaPF_6$ (0.84 g, 5.0 mmol) was added and the reaction mixture was stirred for a further 24 h. It was then cooled to room temperature and concentrated in vacuo. The residue was purified by means of column chromatography on silica gel (CH_2Cl_2/MeOH, 1:0 to 19:1) to afford **3a** as a dark-brown solid (0.37 g, 69%). FTIR (KBr disk): $\tilde{\nu} = 3450$(br), 3053(w), 1653(m), 1609(s), 1583(m), 1558(m), 1495(w), 1441(w), 1423(w), 1394(w), 1344(w), 1323(m), 1294(m), 1273(m), 1223(m), 1190(w), 1171(w), 1150(w), 1126(w), 951(w), 843(s), 760(m), 702(m), 671(w), 559 cm^{-1} (m); elemental analysis calcd (%) for $C_{62}H_{43}F_6MnN_3O_2P \cdot H_2O$ (1079.94): C 68.95, H 4.20, N 3.89; found: C 68.83, H 4.31, N 4.20.

Complex 4a: Preparation from **11b** similar to that for complex **3a** to give **4a** as a dark-brown solid (68%). FTIR (KBr disk): $\tilde{\nu} = 3449$(br), 3053(w), 1653(w), 1607(s), 1583(m), 1564(w), 1547(w), 1495(w), 1441(w), 1423(w), 1394(w), 1344(w), 1323(m), 1294(m), 1273(w), 1223(w), 1190(w), 1150(w), 1126(w), 951(w), 843(s), 748(m), 700(m), 671(w), 559 cm^{-1} (m); elemental analysis calcd (%) for $C_{68}H_{47}F_6MnN_3O_2P \cdot 1.5H_2O$ (1165.05): C 70.10, H 4.33, N 3.61; found: C 70.10, H 4.27, N 3.74.

(2*S*)-2-(2,4,6-Trimethylbenzenesulfonamido)-3-[1-(2,4,6-trimethylbenzenesulfonyl)imidazol-4-yl]propanoazide (14): NaN_3 (0.98 g, 15 mmol) was added to a solution of methanesulfonate **13** (3.5 g, 6.0 mmol) in DMF (60 mL) and the mixture was stirred for 5 h at room temperature. It was then diluted with AcOEt, and the whole mixture was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by means of column chromatography on silica gel (CH_2Cl_2/AcOEt, 25:1) to yield **14** as a white solid (3.0 g, 93%). $[\alpha]_D^{26} = +4.81$ ($c = 0.52$ in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.29$ (s, 3H), 2.32 (s, 3H), 2.50–2.70 (m, 2H), 2.59 (s, 6H), 2.62 (s, 6H), 3.16 (dd, $J = 7.2$, 12.4 Hz, 1H), 3.40 (dd, $J = 4.4$, 12.4 Hz, 1H), 3.55–3.60 (m, 1H), 6.01 (d, $J = 8.0$ Hz, 1H), 6.88 (s, 1H), 6.93 (s, 2H), 7.01 (s, 2H), 7.83 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 21.1$, 21.3, 22.9, 23.1, 29.5, 52.0, 53.8, 114.7,

131.1, 131.9, 132.6, 134.1, 136.1, 138.7, 138.8, 140.3, 142.0, 145.3 ppm; FTIR (KBr disk): $\tilde{\nu}$ = 3277(br), 3030(m), 2984(m), 2939(m), 2106(s), 1734(w), 1603(m), 1564(w), 1470(w), 1452(w), 1406(w), 1371(m), 1335(m), 1265(w), 1231(w), 1192(s), 1175(s), 1157(s), 1076(s), 1036(m), 953(w), 854(w), 775(w), 743(m), 660(m), 596(m), 534 cm^{-1} (m); elemental analysis calcd (%) for $C_{24}H_{30}N_6O_4S_2$ (530.67): C 54.32, H 5.70, N 15.84; found: C 54.30, H 5.71, N 15.70.

(2*S*)-2-(2,4,6-Trimethylbenzenesulfonamido)-3-[1-(2,4,6-trimethylbenzenesulfonyl)imidazol-4-yl]propylamine (15): A solution of azide **14** (2.6 g, 5.0 mmol) in MeOH (50 mL) was stirred under a slight overpressure of hydrogen in the presence of 10% Pd/C (0.27 g) for 24 h. After removal of the catalyst by filtration through Celite, the solvent was removed in vacuo and the residue was purified by means of column chromatography on silica gel (CH_2Cl_2/EtOH, 1:1) to yield amine **15** as a white solid (1.8 g, 71%). $[\alpha]_D^{26}$ = +9.37 (c = 0.43 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3H), 2.33 (s, 3H), 2.30–2.70 (m, 4H), 2.58 (s, 6H), 2.63 (s, 6H), 3.36–3.39 (m, 1H), 5.97 (br, 1H), 6.83 (s, 1H), 6.92 (s, 2H), 7.01 (s, 2H), 7.83 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 21.3, 22.9, 23.2, 30.2, 44.7, 54.7, 114.3, 131.2, 131.8, 132.6, 134.5, 135.8, 138.6, 139.7, 140.3, 141.7, 145.2 ppm; FTIR (KBr disk): $\tilde{\nu}$ = 3391(br, m), 3130(w), 2939(w), 2866(w), 1659(w), 1603(m), 1564(m), 1445(m), 1319(m), 1175(s), 1153(s), 1078(s), 950(w), 853(m), 667(s), 596(s), 534 cm^{-1} (s); elemental analysis calcd (%) for $C_{24}H_{32}N_4O_4S_2{\cdot}H_2O$ (522.68): C 55.15, H 6.56, N 10.72; found: C 55.16, H 6.31, N 10.32.

(2*S*)-1,2-Diamino-3-(4-imidazolyl)propane (16): A mixture of amine **15** (2.3 g, 4.5 mmol), 48% aqueous HBr (40 mL), and phenol (4.2 g, 45 mmol) was heated at 100°C for 72 h. It was then diluted with H_2O and washed with CH_2Cl_2 (six times). The aqueous phase was concentrated in vacuo and the residue was purified by means of chromatography on a column of Amberlite IRA-400 anion-exchange resin (OH^- form), which was eluted with H_2O. Collection of the ninhydrin-positive fractions yielded **16** as a colorless oil (0.44 g, 70%), which was used for the preparation of complexes **5a** and **7a** without further purification. ^{1}H NMR (400 MHz, D_2O): δ = 2.57 (dd, J = 8.0, 14.8 Hz, 1H), 2.66 (dd, J = 8.0, 13.6 Hz, 1H), 2.71 (dd, J = 5.8, 14.6 Hz, 1H), 2.84 (dd, J = 4.8, 13.2 Hz, 1H), 3.14 (m, 1H), 6.88 (s, 1H), 7.59 ppm (s, 1H).

Complex 5a: Preparation similar to that for complex **3a** to give **5a** as a dark-brown solid (91%). FTIR (KBr disk): $\tilde{\nu}$ = 3315(s), 3063(w), 3032(w), 2928(w), 1688(s), 1601(m), 1547(s), 1472(w), 1454(w), 1437(w), 1402(w), 1319(m), 1261(s), 1151(m), 1057(m), 1007(m), 910(w), 843(w), 762(m), 735(m), 694 cm^{-1} (m); elemental analysis calcd (%) for $C_{60}H_{42}F_6MnN_4O_2P{\cdot}1.5\,H_2O$ (1077.93): C 66.85, H 4.21, N 5.20; found: C 66.88, H 4.20, N 4.98.

Complex 7a: Preparation similar to that for complex **3a** to give **7a** as a dark-brown solid (99%). FTIR (KBr disk): $\tilde{\nu}$ = 3315(s), 3063(w), 3032(w), 2928(w), 1688(s), 1601(m), 1547(s), 1472(w), 1454(w), 1437(w), 1402(w), 1319(m), 1261(s), 1151(m), 1057(m), 1007(m), 910(w), 843(w), 762(m), 735(m), 694 cm^{-1} (m); elemental analysis calcd (%) for $C_{60}H_{42}F_6MnN_4O_2P{\cdot}1.5\,H_2O$ (1077.93): C 66.85, H 4.21, N 5.20; found: C 66.61, H 4.29, N 5.02.

3-[1-(Methyl)imidazol-4-yl]-(2*S*)-2-(benzyloxycarbonylamino)propanol (19): A solution of methyl ester **18** (3.2 g, 10 mmol) in MeOH (50 mL) was cooled to 0°C and $NaBH_4$ (3.8 g, 100 mmol) was added in small portions. After the mixture had been stirred for 3 h at 0°C, the MeOH was removed in vacuo. The residue was redissolved in a mixture of CH_2Cl_2 and water, and the aqueous phase was adjusted to pH 7 with 1N HCl. The organic layer was separated, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by means of column chromatography on silica gel (CH_2Cl_2/MeOH, 20:1) to yield alcohol **19** as a colorless oil (2.6 g, 91%). $[\alpha]_D^{26}$ = +51.1 (c = 0.30 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.87 (ddd, J = 5.6, 14.6, 30.6 Hz, 2H), 3.59–3.62 (complex, 4H), 3.76 (dd, J = 3.4, 11.4 Hz, 1H), 3.92 (m, 1H), 5.07 (s, 2H), 5.64 (d, J = 7.6 Hz, 1H), 6.64 (s, 1H), 7.31–7.34 ppm (complex, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.3, 33.4, 51.9, 64.2, 66.4, 118.2, 127.78, 127.81, 128.2, 136.5, 136.9, 137.9, 155.9 ppm; FTIR (KBr disk): $\tilde{\nu}$ = 3346(s), 3223(m), 3063(w), 3034(w), 2932(m), 1688(s), 1562(w), 1526(s), 1458(w), 1356(w), 1269(m), 1234(m), 1190(w), 1167(w), 1057(m), 1130(w), 733(m), 698(m), 633(m), 615 cm^{-1} (m); elemental analysis calcd (%) for $C_{15}H_{19}N_3O_3$ (289.33): C 62.27, H 6.62, N 14.52; found: C 62.22, H 6.65, N 14.29.

(2*S*)-1,2-Diamino-3-[1-(methyl)imidazol-4-yl]propane (20): A solution of alcohol **19** (2.6 g, 9.0 mmol) in CH_2Cl_2 (50 mL) was cooled to 0°C and treated first with Et_3N (2.9 mL, 21 mmol) and then with MsCl (1.4 mL, 18 mmol). The resulting mixture was stirred for 3 h at room temperature. It was then diluted with CH_2Cl_2, and the organic layer was washed with water, dried over Na_2SO_4, and concentrated in vacuo to yield the corresponding mesylate as an orange oil, which was used for the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.87 (m, 2H), 3.00 (s, 3H), 3.63 (s, 3H), 4.09 (m, 1H), 4.19 (m, 2H), 5.10 (s, 2H), 6.22 (m, 1H), 6.73 (s, 1H), 7.31–7.37 ppm (complex, 6H).

NaN_3 (3.6 g, 56 mmol) was added to a solution of the mesylate (2.6 g, 7.0 mmol) in DMF (30 mL) and the mixture was stirred at 60°C for 12 h. After removal of the DMF in vacuo, the reaction mixture was diluted with CH_2Cl_2, and the organic layer was washed with water, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by means of column chromatography on silica gel (CH_2Cl_2/MeOH, 30:1) to yield the corresponding azide as a colorless oil (0.66 g, 28%; two steps). $[\alpha]_D^{26}$ = +9.72 (c = 0.94 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.82 (d, J = 4.8 Hz, 2H), 3.24 (dd, J = 7.2, 12.0 Hz, 1H), 3.44 (dd, J = 4.6, 11.4 Hz, 1H), 3.63 (s, 3H), 4.06 (m, 1H), 5.10 (s, 2H), 6.10 (d, J = 7.2 Hz, 1H), 6.68 (s, 1H), 7.30–7.36 ppm (complex, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.4, 33.4, 50.6, 53.0, 66.6, 118.1, 127.87, 127.94, 128.3, 136.4, 137.4, 137.7, 155.7 ppm; FTIR (KBr disk): $\tilde{\nu}$ = 3223(s), 3134(m), 3034(s), 2995(m), 2953(m), 2920(m), 2208(w), 2098(s), 1711(s), 1560(s), 1508(m), 1439(s), 1410(w), 1373(m), 1348(w), 1304(m), 1265(s), 1227(s), 1161(m), 1140(m), 1059(s), 1034(m), 989(m), 955(m), 935(m), 843(m), 789(w), 766(w), 741(s), 694(m), 625 cm^{-1} (m); elemental analysis calcd (%) for $C_{15}H_{18}N_6O_2$ (314.34): C 57.31, H 5.77, N 26.74; found: C 57.44, H 5.71, N 26.68.

A solution of the azide (0.63 g, 2.0 mmol) in MeOH (10 mL) was stirred under a slight overpressure of hydrogen in the presence of 10% Pd/C (0.10 g) for 24 h. After removal of the catalyst by filtration through Celite, the solvent was removed in vacuo to yield diamine **20** (0.31 g, 100%) as a colorless oil, which was used for the preparation of complex **6a** without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47 (dd, J = 8.4, 14.4 Hz, 1H), 2.56 (dd, J = 7.6, 12.8 Hz, 1H), 2.69 (dd, J = 4.4, 14.4 Hz, 1H), 2.79 (dd, J = 4.4, 12.4 Hz, 1H), 3.02 (m, 1H), 3.64 (s, 3H), 6.67 (s, 1H), 7.35 ppm (s, 1H).

Complex 6a: Preparation similar to that for complex **3a** to give **6a** as a dark-brown solid (85%). FTIR (KBr disk): $\tilde{\nu}$ = 3450(br), 3053(w), 2924(w), 1606(s), 1583(m), 1494(w), 1479(w), 1462(w), 1445(m), 1425(m), 1394(m), 1344(m), 1325(m), 1294(m), 1273(w), 1225(w), 1191(w), 1141(w), 1126(w), 1067(w), 1001(w), 951(w), 845(s), 746(m), 700(w), 673(w), 559 cm^{-1} (m); elemental analysis calcd (%) for $C_{61}H_{44}F_6MnN_4O_2P{\cdot}H_2O$ (1082.95): C 67.65, H 4.28, N 5.17; found: C 67.62, H 4.52, N 5.10.

Complex 33: (a*R*)-3-Formyl-2-hydroxy-2′-phenyl-1,1′-binaphthyl (220 mg, 0.6 mmol) was added to a solution of diamine **20** (46 mg, 0.3 mmol) in EtOH (10 mL) and the mixture was stirred for 6 h at room temperature. The light-yellow precipitate produced was collected by filtration and dried under vacuum. This precipitate was added to a solution of $Co(OAc)_2$ (75 mg, 0.3 mmol) [which was prepared from $Co(OAc)_2{\cdot}4H_2O$ by heating at 80°C under vacuum until it turned from pink to purple] in deaerated ethanol (8 mL) under nitrogen atmosphere. The resulting purple-brown precipitate was collected by filtration, washed with degassed ethanol under N_2, and dried in vacuo to afford **33** (0.22 g, 79%) as a brown solid. FTIR (KBr disk): $\tilde{\nu}$ = 3425(br), 3053(w), 2922(w), 1611(s), 1583(m), 1423(m), 1402(m), 1333(m), 1294(w), 1215(w), 1190(w), 1148(w), 1124(w), 1024(w), 953(w), 820(w), 750(m), 702(m), 671 cm^{-1} (w); elemental analysis calcd (%) for $C_{61}H_{44}CoN_4O_2{\cdot}2.5\,H_2O$ (969.00): C 75.61, H 5.10, N 5.78; found: C 75.86, H 4.75, N 5.49.

General procedure for asymmetric epoxidation: [Mn(salen)] complex **6a** (5.3 mg, 5.0 μmol) and 2,2-dimethylchromene (0.1 mmol) were dissolved in CH_2Cl_2 (1 mL). After the addition of 30% aqueous hydrogen peroxide (0.3 mmol) at 0°C, the resulting mixture was stirred for 24 h. The solvent was then removed in vacuo and the residue was purified by means of

column chromatography on silica gel (pentane/Et_2O, 20:1) to afford the corresponding epoxide. The *ee* of the epoxide was determined by HPLC analysis under the conditions described in the footnotes to Table 1.

3,4-Epoxy-2,2-dimethylchromene (21b): 98% *ee*, $[\alpha]_D^{27}=+0.62$ ($c=0.57$ in $CHCl_3$) ($[\alpha]_D^{25}=-0.60$ ($c=0.93$ in $CHCl_3$) for the material of 99% *ee*[24]); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.25$ (s, 3H), 1.58 (s, 3H), 3.49 (d, $J=4.4$ Hz, 1H), 3.90 (d, $J=4.4$ Hz, 1H), 6.81 (d, $J=8.4$ Hz, 1H), 6.93 (dt, $J=1.2$, 7.6 Hz, 1H), 7.24 (dt, $J=1.7$, 8.1 Hz, 1H), 7.33 ppm (dd, $J=1.7$, 7.3 Hz, 1H); elemental analysis calcd (%) for $C_{11}H_{12}O_2$ (176.21): C 74.98, H 6.86; found: C 75.02, H 7.09.

6-Cyano-3,4-epoxy-2,2-dimethylchromene (22b): 99% *ee*, $[\alpha]_D^{26}=+71.3$ ($c=0.34$ in $CHCl_3$) ($[\alpha]_D^{20}=+53.8$ ($c=0.16$ in $CHCl_3$) for the material of 64% *ee*[16b]); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.30$ (s, 3H), 1.60 (s, 3H), 3.54 (d, $J=4.4$ Hz, 1H), 3.91 (d, $J=4.4$ Hz, 1H), 6.87 (d, $J=8.4$ Hz, 1H), 7.53 (dd, $J=2.2$, 8.6 Hz, 1H), 7.66 ppm (d, $J=2.0$ Hz, 1H); elemental analysis calcd (%) for $C_{12}H_{11}NO_2$ (201.22): C 71.63, H 5.51, N 6.96; found: C 71.68, H 5.59, N 6.88.

6-Bromo-3,4-epoxy-2,2-dimethylchromene (23b): 98% *ee*, $[\alpha]_D^{25}=+38.0$ ($c=0.96$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.17$ (s, 3H), 1.49 (s, 3H), 3.41 (d, $J=4.4$ Hz, 1H), 3.77 (d, $J=4.4$ Hz, 1H), 6.62 (d, $J=8.8$ Hz, 1H), 7.25 (dd, $J=2.6$, 8.6 Hz, 1H), 7.38 ppm (d, $J=2.4$ Hz, 1H); elemental analysis calcd (%) for $C_{11}H_{11}BrO_2$ (255.11): C 51.79, H 4.35; found: C 52.02, H 4.47.

3,4-Epoxy-2,2-dimethyl-6-nitrochromene (24b): 99% *ee*, $[\alpha]_D^{26}=+160.0$ ($c=0.55$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.33$ (s, 3H), 1.62 (s, 3H), 3.57 (d, $J=4.4$ Hz, 1H), 3.99 (d, $J=4.4$ Hz, 1H), 6.89 (d, $J=8.8$ Hz, 1H), 8.15 (dd, $J=3.0$, 9.0 Hz, 1H), 8.30 ppm (d, $J=2.8$ Hz, 1H); elemental analysis calcd (%) for $C_{11}H_{11}NO_4$ (221.21): C 59.73, H 5.01, N 6.33; found: C 60.09, H 5.16, N 6.28.

3,4-Epoxy-2,2,6-trimethylchromene (25b): 97% *ee*, $[\alpha]_D^{26}=+13.2$ ($c=0.28$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.23$ (s, 3H), 1.57 (s, 3H), 2.28 (s, 3H), 3.47 (d, $J=4.4$ Hz, 1H), 3.85 (d, $J=4.4$ Hz, 1H), 6.70 (d, $J=8.0$ Hz, 1H), 7.03 (d, $J=8.4$ Hz, 1H), 7.13 ppm (d, $J=2.0$ Hz, 1H); elemental analysis calcd (%) for $C_{12}H_{14}O_2$ (190.24): C 75.76, H 7.42; found: C 76.16, H 7.81.

3,4-Epoxy-6-methoxy-2,2-dimethylchromene (26b): 98% *ee*, $[\alpha]_D^{26}=+16.4$ ($c=0.48$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.22$ (s, 3H), 1.56 (s, 3H), 3.46 (d, $J=4.4$ Hz, 1H), 3.78 (s, 3H), 3.86 (d, $J=4.4$ Hz, 1H), 6.74 (d, $J=9.0$ Hz, 1H), 6.80 (dd, $J=2.9$, 8.8 Hz, 1H), 6.89 ppm (d, $J=2.7$ Hz, 1H); elemental analysis calcd (%) for $C_{12}H_{14}O_3$ (206.24): C 69.88, H 6.84; found: C 70.10, H 7.22.

3,4-Epoxyspiro(chroman-2,1′-cyclohexane) (27b): 98% *ee*, $[\alpha]_D^{26}=-11.0$ ($c=0.68$ in $CHCl_3$) ($[\alpha]_D^{24}=+11.2$ ($c=1.03$ in $CHCl_3$) for the material of 90% *ee*[13b]); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.33$–2.07 (m, 10H), 3.49 (d, $J=4.4$ Hz, 1H), 3.87 (d, $J=4.4$ Hz, 1H), 6.85 (d, $J=8.0$ Hz, 1H), 6.92 (dt, $J=1.2$, 7.4 Hz, 1H), 7.24 (dt, $J=1.6$, 7.7 Hz, 1H), 7.32 ppm (dd, $J=1.4$, 7.4 Hz, 1H); elemental analysis calcd (%) for $C_{14}H_{16}O_2$ (216.28): C 77.75, H 7.46; found: C 77.86, H 7.72.

3,4-Epoxy-2,2,3-trimethylchromene (28b): 97% *ee*, $[\alpha]_D^{26}=+56.4$ ($c=0.80$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.27$ (s, 3H), 1.52 (s, 3H), 1.55 (s, 3H), 3.69 (s, 1H), 6.81 (d, $J=8.1$ Hz, 1H), 6.92 (dt, $J=1.2$, 7.5 Hz, 1H), 7.23 (dt, $J=1.7$, 7.6 Hz, 1H), 7.30 ppm (dd, $J=1.7$, 7.3 Hz, 1H); elemental analysis calcd (%) for $C_{12}H_{14}O_2$ (190.24): C 75.76, H 7.42; found: C 75.81, H 7.54.

5,6-Epoxy-6,7,8,9-tetrahydro-5*H*-benzocycloheptene (29b): 90% *ee*, $[\alpha]_D^{23}=-21.1$ ($c=0.18$ in $CHCl_3$) ($[\alpha]_D^{20}=-23.4$ ($c=0.82$ in $CHCl_3$) for the material of 91% *ee*[28]); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.52$–2.27 (m, 4H), 2.84 (m, 2H), 3.41 (m, 1H), 4.02 (d, $J=4.4$ Hz, 1H), 7.23–7.59 ppm (m, 4H); elemental analysis calcd (%) for $C_{11}H_{12}O$ (160.21): C 82.46, H 7.55; found: C 82.26, H 7.78.

***cis*-3,4-Epoxy-1-phenyl-1-pentyne (30b)**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.51$ (d, $J=5.0$ Hz, 3H), 3.25 (dq, $J=3.9$, 5.0 Hz, 1H), 3.64 (d, $J=3.9$ Hz, 1H), 7.28–7.48 ppm (m, 5H); elemental analysis calcd (%) for $C_{11}H_{10}O$ (158.20): C 83.51, H 6.37; found: C 83.43, H 6.61 (mixture of *cis* and *trans* isomers).

***trans*-3,4-Epoxy-1-phenyl-1-pentyne (30c)**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.39$ (d, $J=5.3$ Hz, 3H), 3.23–3.30 (m, 2H), 7.27–7.34 (m, 3H), 7.42–7.45 ppm (m, 2H).

***trans*-1,2-Epoxy-1-phenylpropane (31b)**: 31% *ee*, $[\alpha]_D^{27}=-16.6$ ($c=0.63$ in $CHCl_3$) ($[\alpha]_D^{25}=-50.4$ ($c=0.42$ in $CHCl_3$) for the material of 86% *ee*[33]); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.46$ (d, $J=5.1$ Hz, 3H), 3.04 (dq, $J=2.2$, 5.1 Hz, 1H), 3.58 (d, $J=2.2$ Hz, 1H), 7.25–7.36 ppm (m, 5H).

General procedure for asymmetric cyclopropanation: Styrene (115 μL, 1.0 mmol) was added to a solution of [Co(salen)] complex **33** (4.6 mg, 5.0 μmol) in toluene (1 mL). *tert*-Butyl α-diazoacetate (14 μL, 0.1 mmol) was then added, and the mixture was stirred for 24 h at room temperature. The mixture was then concentrated in vacuo and the residue was purified by means of column chromatography on silica gel (hexane/iPr_2O, 1:0 to 4:1) to give a 99:1 mixture of the *cis*- and *trans*-products in 100% yield. An aliquot of the mixture was submitted to preparative TLC (silica gel, hexane/iPr_2O, 4:1) to yield the *cis*-product, the enantiomeric excess of which was determined by HPLC analysis (97% *ee*).

(1*R*,2*S*)-*tert*-Butyl *cis*-2-phenylcyclopropane-1-carboxylate (34): 97% *ee*, $[\alpha]_D^{26}=-17.0$ ($c=0.19$ in $CHCl_3$) ($[\alpha]_D^{24}=+18.0$ ($c=0.73$ in $CHCl_3$) for the material of 98% *ee*[34]); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.13$ (s, 9H), 1.24 (ddd, $J=5.0$, 7.5, 8.5 Hz, 1H), 1.64 (ddd, $J=5.0$, 5.5, 7.5 Hz, 1H), 1.98 (ddd, $J=5.5$, 7.5, 8.0 Hz, 1H), 2.53 (ddd, $J=7.5$, 8.0, 8.5 Hz, 1H), 7.16–7.29 ppm (m, 5H).

***tert*-Butyl *cis*-2-(4-methoxyphenyl)cyclopropane-1-carboxylate (36a)**: 96% *ee*, $[\alpha]_D^{26}=+3.44$ ($c=0.18$ in $CHCl_3$) ($[\alpha]_D^{26}=-3.2$ ($c=0.85$ in $CHCl_3$) for the material of 96% *ee*[34]); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.17$ (s, 9H), 1.21 (ddd, $J=5.0$, 7.5, 8.5 Hz, 1H), 1.57 (ddd, $J=5.0$, 5.5, 7.0 Hz, 1H), 1.93 (ddd, $J=5.5$, 7.5, 9.0 Hz, 1H), 2.46 (ddd, $J=7.0$, 8.5, 9.0 Hz, 1H), 3.77 (s, 3H), 6.80 (d, $J=8.5$ Hz, 2H), 7.18 ppm (d, $J=8.5$ Hz, 2H).

***tert*-Butyl *cis*-2-(4-methylphenyl)cyclopropane-1-carboxylate (36b)**: 94% *ee*, $[\alpha]_D^{26}=-6.84$ ($c=0.18$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.16$ (s, 9H), 1.20 (m, 1H), 1.59 (m, 1H), 1.94 (ddd, $J=5.7$, 7.6, 9.3 Hz, 1H), 2.27 (s, 3H), 2.47 (q, $J=8.5$ Hz, 1H), 7.05 (d, $J=8.0$ Hz, 2H), 7.15 ppm (d, $J=8.0$ Hz, 2H); elemental analysis calcd (%) for $C_{15}H_{20}O_2$ (232.32): C 77.55, H 8.68; found: C 77.27, H 8.69.

***tert*-Butyl *cis*-2-(4-nitrophenyl)cyclopropane-1-carboxylate (36c)**: 93% *ee*, $[\alpha]_D^{26}=-35.5$ ($c=0.10$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.18$ (s, 9H), 1.37 (ddd, $J=5.3$, 8.1, 8.2 Hz, 1H), 1.69 (ddd, $J=5.5$, 5.6, 7.3 Hz, 1H), 2.11 (ddd, $J=6.0$, 7.6, 9.3 Hz, 1H), 2.56 (q, $J=8.5$ Hz, 1H), 7.43 (d, $J=8.8$ Hz, 2H), 8.13 ppm (d, $J=8.8$ Hz, 2H); elemental analysis calcd (%) for $C_{14}H_{17}NO_4$ (263.29): C 63.87, H 6.51, N 5.32; found: C 64.16, H 6.54, N 5.20.

***tert*-Butyl *cis*-2-(4-chlorophenyl)cyclopropane-1-carboxylate (36d)**: 96% *ee*, $[\alpha]_D^{26}=+4.43$ ($c=0.18$ in $CHCl_3$) ($[\alpha]_D^{20}=+4.4$ ($c=0.17$ in $CHCl_3$) for the material of 95% *ee*[19b]); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.18$ (s, 9H), 1.25 (ddd, $J=5.1$, 7.8, 8.6 Hz, 1H), 1.59 (ddd, $J=5.1$, 5.7, 7.3 Hz, 1H), 1.99 (ddd, $J=5.7$, 7.8, 9.3 Hz, 1H), 2.47 (ddd, $J=7.3$, 8.6, 9.3 Hz, 1H), 7.19–7.24 ppm (m, 4H).

***tert*-Butyl *cis*-2-(2-chlorophenyl)cyclopropane-1-carboxylate (36e)**: 96% *ee*, $[\alpha]_D^{26}=-122.5$ ($c=0.63$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.17$ (s, 9H), 1.33 (ddd, $J=4.9$, 7.6, 8.2 Hz, 1H), 1.62 (ddd, $J=5.2$, 5.4, 7.6 Hz, 1H), 2.13 (ddd, $J=5.6$, 7.6, 9.1 Hz, 1H), 2.49 (q, $J=8.4$ Hz, 1H), 7.13–7.20 (m, 2H), 7.26–7.33 ppm (m, 2H); elemental analysis calcd (%) for $C_{14}H_{17}ClO_2$ (252.74): C 66.53, H 6.78; found: C 66.53, H 6.80.

***tert*-Butyl *cis*-2-methyl-2-phenylcyclopropane-1-carboxylate (36f)**: 96% *ee*, $[\alpha]_D^{26}=-48.6$ ($c=0.10$ in $CHCl_3$) ($[\alpha]_D^{24}=-42.1$ ($c=0.43$ in $CHCl_3$) for the material of 96% *ee*[34]); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.07$ (dd, $J=4.5$, 7.5 Hz, 1H), 1.13 (s, 9H), 1.45 (s, 3H), 1.70 (dd, $J=4.5$, 5.5 Hz, 1H), 1.80 (dd, $J=5.5$, 7.5 Hz, 1H), 7.16–7.19 ppm (m, 5H).

***tert*-Butyl *trans*-2-methyl-2-phenylcyclopropane-1-carboxylate (36f)**: 97% *ee*, $[\alpha]_D^{26}=-130.5$ ($c=0.14$ in $CHCl_3$) ($[\alpha]_D^{20}=-133.9$ (c=0.10 in $CHCl_3$) for the material of 99% *ee*[19b]); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.33$ (dd, $J=4.9$, 8.3 Hz, 1H), 1.36 (dd, $J=4.9$, 5.9 Hz, 1H), 1.49 (s, 9H), 1.51 (s, 3H), 1.89 (dd, $J=5.9$, 8.3 Hz, 1H), 7.18–7.33 ppm (m, 5H).

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