Highly Enantioselective Cyclopropanation with Co(II)-Salen Complexes: Control of *cis*- and *trans*-Selectivity by Rational Ligand-Design

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Abstract: Cyclopropanation of styrene derivatives with alkyl α-diazoacetate in the presence of the second-generation (salen)cobalt(II) complex **6** proceeded with excellent *cis*- and enantioselectivity. On the other hand, the cyclopropanation in the presence of complex **14** which was designed on the basis of the mechanism of asymmetric induction by complex **6** showed good *trans*- and excellent enantioselectivity.

Keywords: (salen)cobalt(II) complex; asymmetric cyclopropanation; cyclopropane; *cis*-selectivity; *trans*-selectivity

Introduction

Highly strained three-membered ring compounds such as oxirane, aziridine, and cyclopropane are important building blocks for organic synthesis and much effort has been directed towards exploitation of methodologies for their asymmetric synthesis.[1] Although various methodologies are available today, the cycloaddition of oxenoids, as well as their isoelectronic species, nitrenoids and carbenoids, to π-bonds is the practically most important one to construct this class of compounds. For these reactions, differentiation of the enantiotopic faces of the double bonds is the main stereochemical issue. However, another stereochemical issue, *cis-trans* selectivity, is imposed on the cyclopropanation reaction due to the presence of a substituent at the carbenoid carbon. Thus, simultaneous control of these two stereochemical issues is indispensable for achieving highly efficient cyclopropanation.

The first metal-catalyzed asymmetric cyclopropanation using a chiral copper complex as the catalyst was reported in 1965 by Nozaki, Noyori et al.[2] and this pioneering work was developed by Aratani et al.[3] into a practical, highly enantioselective process by modifying the chiral Schiff base ligand. Subsequent to these studies, many excellent metal-catalyzed methodologies[4] using copper-semicolines,[5] copper-bis(oxazolines),[6] copper-bipyridines,[7] copper-bis(azaferrocenes) of face-chirality,[8] ruthenium-PYBOX,[9] ruthenium-porphyrins,[10] rhodium-MEPY and its derivatives[11], dirhodium(II) tetrakis[3(*S*)-phthalimido-2-piperidinonate],[12] and (salen)cobalt(III) complexes[13] have been developed for asymmetric cyclopropanation. However, most of them are *trans*-selective while *cis*-selective reactions are limited to only a few examples:[14] Doyle et al. have recently reported that cyclopropanation using the Rh_2(*S*-IBAZ)$_4$ complex shows modest *cis*-selectivity, though its enantioselectivity is dependent upon the α-diazoacetate used.[14b–e] For example, the *cis-trans* ratio and the enantioselectivity in the cyclopropanation of styrene with ethyl α-diazoacetate are 69 : 31 and 76% ee (*cis*-isomer), respectively, while those with bis(cyclohexyl)methyl α-diazoacetate are 66 : 34 and 95% ee (*cis*-isomer). No satisfactory example of a highly *cis*- and enantioselective reaction is as yet known.

We have recently disclosed that chiral metallosalen complexes (hereafter referred to as M-salen complexes) are excellent catalysts for asymmetric transfer reactions of oxenoids and their isoelectronic species.[15] In connection with this study, we examined asymmetric cyclopropanation using Co-salen complexes as catalysts. A chiral Co(II)-salen complex was originally used as the catalyst for asymmetric cyclopropanation but the stereoselectivity was low.[16] Later, we found that chiral Co(III)-salen complexes catalyzed cyclopropanation reactions with high *trans*-selectivity and moderate enantioselectivity together with good chemical yield.[13a] Furthermore, high enantioselectivity was realized by using a modi-

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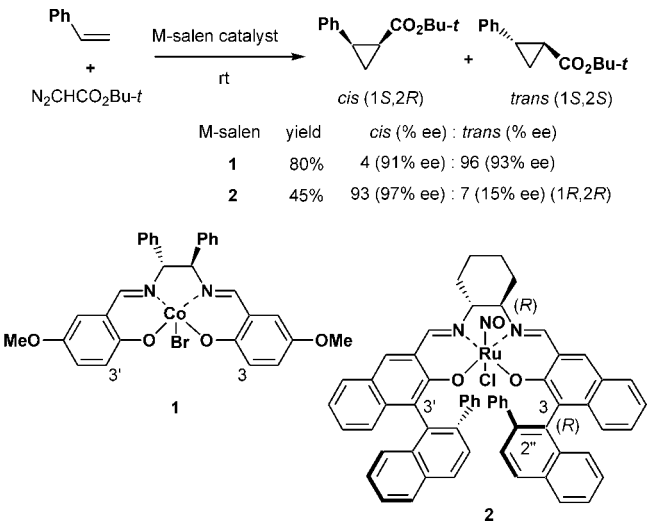
fied Co(III)-salen complex **1** bearing electron-donating methoxy groups at C5 and C5′ and an apical bromo ligand (Scheme 1).[13b] On the other hand, Co(III)-salen complexes bearing substituents like a methyl or *t*-butyl group at C3 and C3′ showed no catalytic activity. This suggested that olefins approached the intermediate Co(V)-carbenoid species from its C3 and C3′ side and that such an approach was strongly disfavored by the presence of 3- and 3′-substituents. However, it has been well recognized that, in many metallosalen-catalyzed reactions, 3- and 3′-substituents play important roles in determination of the stereochemistry.[15] These observations prompted us to use a chiral Ru-salen complex as the catalyst for asymmetric cyclopropanation for the following reasons: i) the Ru–O_{equat} bond in an Ru-salen complex is ca. 0.2 Å longer than the Co–O_{equat} bond in Co(III)-salen complexes, and ii) the longer Ru–O bond increases the distance between the C3- and C3′-carbons in the Ru-salen complex and thus makes the approach of the olefin from the C3 and C3′ side possible even if substituents are present at C3 and C3′. As expected, Ru-salen complexes bearing substituents at C3 and C3′ showed catalytic activity for cyclopropanation and high *cis*- as well as high enantioselectivity was achieved for the first time in the cyclopropanation with the (*R*,*R*)–(ON$^+$)Ru(II)-salen complex **2** as the catalyst.[17] However, the chemical yield was less than satisfactory due to the undesired reaction of the intermediate Ru-carbenoid with α-diazoacetate to give fumaric and maleic acid esters. The ligand of Ru-salen complex was expected to be highly pliable from X-ray structure analysis.[18] On the other hand, although the Co(II)–O_{equat} bond in a Co(II)-salen complex is roughly equal to that in a Co(III)-salen complex, the Co(II)-salen complexes have been reported to adopt various ligand conformations, depending on the ligand substituent or the apical ligand.[19] Furthermore, Co(III)-salen complexes catalyze high-yielding cyclopropanation reactions (*vide supra*).[15] Thus, we expected that a suitably substituted Co(II)-salen complex might serve as a catalyst for asymmetric and high-yielding cyclopropanation, even if the complex carries 3- and 3′-substituents. Accordingly, we examined Co(II)-salen catalyzed asymmetric cyclopropanation reactions.[20]



Scheme 1.

Results and Discussion

To explore this possibility, we prepared five chiral Co(II)-salen complexes (**3–7**) and examined the reactions of styrene **8** and *t*-butyl α-diazoacetate with them as the catalysts (Table 1). Complex **3** which has the same ligand as **1** showed moderate *trans*- and enantioselectivity but it is noteworthy that the enantiomeric excess of the minor *cis*-isomer was good (86% ee). Furthermore, the direction of enantioselection by **3** was the opposite of that by **1**. This suggested that the conformation of the salen ligands of **3** and **1** or olefin's approaching paths to those catalysts differ from each other. To our delight, complexes **4** and **5** bearing substituents at C3 and C3′ were found to serve as catalysts for cyclopropanation and their stereochemistry was again moderately *trans*- and enantioselective (entries 2 and 3). The stereoselection realized by **4** and **5** were identical to that by **1** and the enantiomeric excesses of minor *cis*-isomers were also good. Since the presence or absence of C3- and C3′- groups did not affect the direction of enantioselection, it was considered that the olefins approached the carbenoid species derived from Co(II)-salen complexes from the ethylenediamine side. Although the formation of fumaric and maleic acid esters was detected in reactions using **4** and **5**, we were encouraged by these results and next examined the reaction with the (*R*,*R*)-Co(II)-salen complex **6** that has the same ligand as complex **2**. In contrast to the reactions with complexes **4** and **5**, the reaction with complex **6** proceeded smoothly with excellent *cis*- and enantioselectivity and only a trace amount of fumaric and maleic acid esters (< 1%) was detected (entry 4). It is noteworthy that the direction of enantioface selection of **8** by complex **6** was opposite to that by complex **2** bearing the same ligand as **6**, although the reaction conditions were the same except that the reaction with **2** was carried out under photo-irradiated conditions. This again suggested that substrates approach the carbenoid species derived from complexes **2** and **6** from different directions (*vide infra*). On the other hand, Yamada et al. recently reported that the rate and the enantioselectivity of the cyclopropanation using a chiral aldiminato-cobalt(II) complex as the catalyst, the ligand of

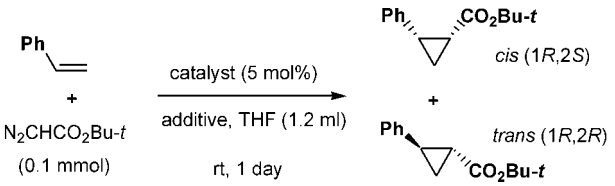


Table 1. Asymmetric cyclopropanation of styrene **8** using Co(II)-salen complexes as catalysts

entry	catalyst	yield[a]	*cis* (%)	:	*trans*[b]	*cis*[c] (% ee)	*trans*[c] (% ee)
1	**3**	9	19	:	81	86	58
2	**4**	39	17	:	83	84	64
3	**5**	23	33	:	67	74	20
4	**6**	88	92	:	8	96	72
5	**6**[d]	89	98	:	2	98	–[e]
6	**6**[d][f]	74	98	:	2	97	–[e]
7	**6**[g]	5	94	:	6	93	–[e]
8	**6**[h]	90	98	:	2	98	–[e]
9	**7**	18	97	:	3	–99[i]	–[e]

[a] 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.
[b] Determined by ^{1}H NMR analysis (400 MHz).
[c] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OD-H, hexane). Configuration was determined by comparison of the elution order with the authentic samples.
[d] NMI (10 μmol, 10 mol%) was added.
[e] Not determined.
[f] Reaction was carried out with the recovered complex: After completion of the first reaction, the mixture was concentrated in vacuo and washed with hexane to remove organic components. The resulting residue was used for the second reaction.
[g] Reaction was carried out with 1 mol% of catalyst in the presence of NMI (2 μmol, 2 mol%).
[h] Reaction in THF (0.1 mL) was carried out with 1 mol% of catalyst in the presence of NMI (10 μmol, 10 mol%).
[i] Absolute configuration was 1*S*,2*R*.

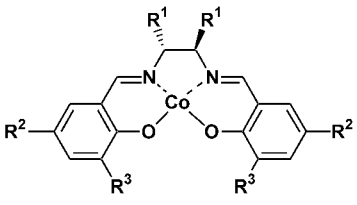
which is structurally similar to salen ligand, were improved by adding *N*-methylimidazole (NMI) to the reaction medium.[21] Based on this report, we also performed the present reaction in the presence of NMI and found that both *cis*- and enantioselectivity were further improved upto 98:2 and 98% ee (entry 5). It is noteworthy that **6** was reusable without any loss of *cis*- and enantioselectivity (entry 6). The turnover frequency of the catalyst in this reaction was estimated to be ca. 4.4 (mol product/mol catalyst/h) over the first hour. When catalyst-loading was reduced to 1 mol%, the reaction became slow and the stereoselectivity was slightly diminished (entry 7). However, it was found that, even if catalyst-loading was reduced to 1 mol%, the reaction proceeded smoothly with high stereoselectivity when it was carried out at a high substrate concentration in the presence of an excess amount of NMI (entry 8). Another advantage of **6** is its high stability: it is storable at least for 3 months at room temperature under dry air.

We also examined the reaction using the (*R*,*S*)-Co(II)-salen complex **7** in the presence of NMI. The reaction also exhibited excellent *cis*- and enantioselectivity, but the reaction was slow (entry 9). The diastereomeric complexes **6** and **7** differ in the chirality of their ethylenediamine units and show the opposite senses of enantioselectivity.

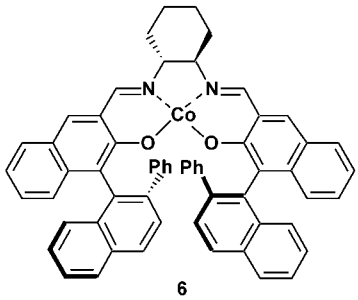
Table 2. Asymmetric cyclopropanation of various olefins using complex **6** as the catalyst at room temperature; reaction time = 24 h

entry	olefin[a]	THF[b] (ml)	yield[c] (%)	*cis*:*trans*[d]	*cis* (% ee)[e]	*trans* (% ee)[e]
1	**10**	1.2	85	97:3	96[f]	–[g]
2	**11**	0.5	84	97:3	96[f]	–[g]
3	**12**	1.2	94	98:2	97[h]	–[g]
4	**9**	0.5	39	83:17	99[i]	99[j]

[a] **9** = α-methylstyrene, **10** = *p*-chlorostyrene, **11** = *p*-methoxystyrene, **12** = 2-vinylnaphthalene.
[b] Olefins (0.5 mmol), *t*-butyl α-diazoacetate (0.1 mmol), catalyst **6** (5 mol%, based on α-diazoacetate used), and NMI (10 μmol).
[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 ^{1}H NMR analysis (400 MHz).
[e] Absolute configuration has not been determined.
[f] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OD-H, hexane).
[g] Not determined.
[h] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OD-H, hexane/*i*-PrOH = 200/1).
[i] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OJ, hexane).
[j] Determined by HPLC analysis using chiral column [DAICEL CHIRALCEL OD-H (×2), hexane].



3: R^1 = Ph, R^2 = OMe, R^3 = H
4: R^1 = Ph, R^2 = Cl, R^3 = Cl
5: R^1 = -$(CH_2)_4$-, R^2 = *t*-Bu, R^3 = *t*-Bu



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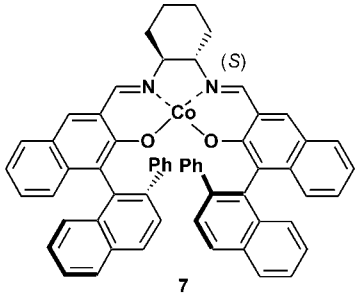

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Table 3. Asymmetric cyclopropanation with ethyl α-diazoacetate as the carbene source in the presence of **6** at room temperature; reaction time = 24 h

entry	olefin[a]	THF/olefin (v/v)	yield[b] (%)	*cis*: *trans*[c]	*cis* (% ee)	*trans* (% ee)
1	**8**	10/6	quant	99:1	96[d][e]	–[f]
2	**10**	10/6	quant	97:3	96[g]	–[f]
3	**11**	10/7	quant	95:5	93[g]	–[f]
4	**9**	10/7	quant	85:15	94[g]	94[g]

[a] Olefins (0.5 mmol), ethyl α-diazoacetate (0.1 mmol), catalyst **6** (5 mol%, based on α-diazoacetate used), and NMI (10 mol%, based on ethyl α-diazoacetate used).
[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] Absolute configuration of the product was 1*S*,2*R*.
[e] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OB-H, hexane).
[f] Not determined.
[g] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OD-H, hexane).

Under the optimized conditions, we examined the cyclopropanation of other substrates (Table 2). All the reactions examined also showed excellent *cis*- and enantioselectivity, except that the reaction of α-methylstyrene **9** showed a diminished *cis*-selectivity of 83%. Only trace amounts of fumaric and maleic acid esters were detected in all the reactions and the chemical yields of the desired cyclopropanes were good, except for the reaction of **9** which was much slower than other reactions. Although the absolute configurations of the products have not been determined, HPLC analyses revealed that the configurations of the major *cis*-isomers of these reactions were also opposite to the configurations of the corresponding *cis*-isomers obtained with complex **2** (*vide supra*). It is, however, noteworthy that the catalysts **2** and **6** showed the same sense of enantioface selection only in the cyclopropanation of **9**. The reason for this unusual behavior of **9** is unclear at present.

In general, the stereoselectivity of asymmetric cyclopropanation decreases as the steric requirement of the ester alkyl group of the α-diazoacetate becomes smaller. However, ethyl α-diazoacetate is more

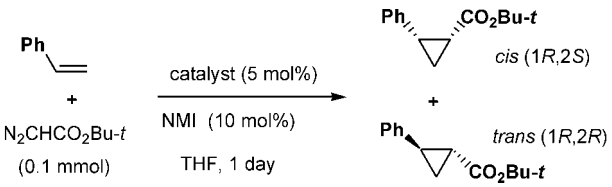


Table 4. Asymmetric cyclopropanation of styrene **8** using Co(II)-salen complexes as catalysts at room temperature; reaction time = 24 h

entry	catalyst	Yield[a]	*cis*	:	*trans*[b]	*cis* (% ee)	*trans* (% ee)
		(%)			(%)		
1	**13**	48	98	:	2	92	–[c]
2	**14**	19	25	:	75	91	98
3	**15**	29	18	:	82	78	86
4	**16**	25	97	:	3	–2[d]	–[c]
5	**5**	89	54	:	46	81	39
6	**17**	61	51	:	49	61	44

[a] 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.
[b] Determined by ^{1}H NMR analysis (400 MHz).
[c] Not determined.
[d] Absolute configuration is 1*S*,2*R*.

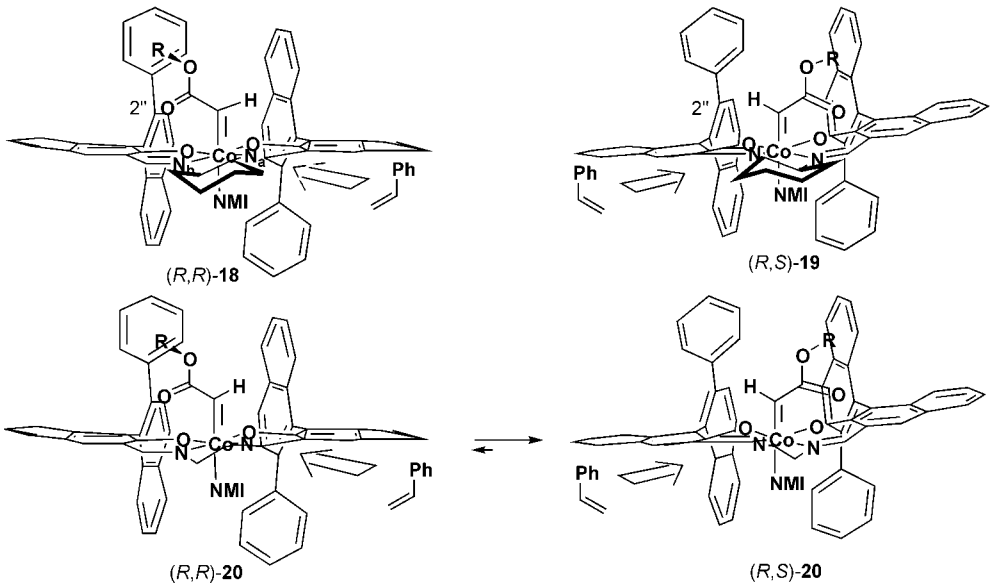
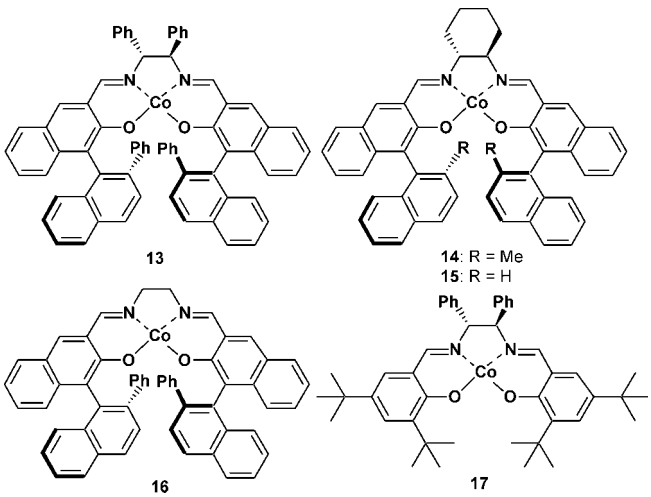


Figure 1. Proposed model for the conformation of Co(IV)-carbenoid species and substrate-approach.

readily available than *t*-butyl α-diazoacetate and we examined the cyclopropanation with ethyl α-diazoacetate (Table 3). Again, high *cis*- and enantioselectivities were observed, though slightly diminished as compared with the reactions with *t*-butyl α-diazoacetate. However, all the reactions examined proceeded smoothly to give the desired cyclopropanes in quantitative yields.

To study the mechanism of asymmetric induction in the present reaction, we synthesized several other Co(II)-salen complexes (**13–17**) according to the following hypotheses (Table 4). From the X-ray structures of Co(II)-salen complexes,[19d,f,g] we assumed that the five-membered chelate rings including cobalt ion and ethylenediamine unit in the Co(IV)-carbenoid species (*R*,*R*)-**18** derived from **6** would adopt a half-chair conformation and their salen ligands would take a moderately folded stepped-conformation (Figure 1).[22,23] We also assumed that a carbenoid ester group would protrude towards the N(b) atom because this carbenoid-ester conformation allows the olefin's approach along the Co–N(a) bond beyond a downward equatorial substituent [see Figure 1, (*R*,*R*)-**18**]. This is the sterically most favored approach and the approach from the opposite face of the carbenoid is intercepted by the C3-substituent.[24] The results described above supported this assumption (*vide supra*). In connection with this consideration, the slow reaction with the (*R*,*S*)-complex **7** as the catalyst was attributed to the following reason: 2′′-phenyl group is located near to the approaching path. Furthermore, since substrates approach along the Co–N bond, the presence of bulky substituents at the diamine part was considered to retard the reaction. This consideration was supported by the fact



that exchange of the cyclohexanediamine unit with a diphenylethylenediamine unit did not have much affect on the stereoselectivity of the reaction whereas the reaction rate was retarded (*cf.* Table 1, entry 5 and Table 4, entry 1). The same phenomena were observed in the reactions with complexes **5** and **17** (entries 5 and 6).

A carbenoid derived from complex **16** should adopt two equilibrium conformations, (*R*,*S*)-**20** and (*R*,*R*)-**20**, but the equilibrium was considered to lean towards (*R*,*S*)-**20** because of the steric repulsion between the carbenoid ester group and the 2′′-phenyl group which is located very close to the carbenoid group. However, because (*R*,*S*)-**20** has a structure similar to (*R*,*S*)-**19**, the catalytic activity of (*R*,*S*)-**20** was considered to be inferior to that of (*R*,*R*)-**20**. Since these two factors cancel each other out, complex **16** was not expected to show good enantioselectivity.

Table 5. Asymmetric cyclopropanation using complex **14** as the catalyst at room temperature; reaction time = 24 h

entry	olefin[a]	THF/olefin (v/v)	R	yield[b] (%)	*cis* : *trans*[c]	*cis* (% ee)	*trans* (% ee)
1	**8**	10/6	*t*-butyl	91	27 : 73	93[d]	98[d]
2	"	10/6	ethyl	quant	31 : 69	79[e]	95[e]
3	"[f]	10/6	ethyl	quant	99 : 1	96[e]	–[g]
4	**10**	10/6	*t*-butyl	88	15 : 85	87[d]	99[h]
5	"	10/6	ethyl	quant	22 : 78	73[d]	96[i]
6	**11**	10/7	*t* -butyl	51	25 : 75	82[d]	95[d]
7	"	10/7	ethyl	quant	33 : 67	82[d]	94[d]
8	**9**	10/7	*t*-butyl	quant	58 : 42	93[d]	99[j]
9	"	10/7	ethyl	quant	57 : 43	93[d]	97[d]

[a] Olefins (0.5 mmol), *t*-butyl or ethyl α-diazoacetate (0.1 mmol), catalyst **6** (5 mol%, based on α-diazoacetate used), and NMI (10 mol%, based on ethyl α-diazoacetate used).
[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 chiral column (DAICEL CHIRALCEL OD-H, hexane).
[e] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OB-H, hexane).
[f] This reaction was catalyzed by catalyst **6**.
[g] Not determined.
[h] Determined by HPLC analysis using optically active column (DAICEL CHIRALCEL OD, hexane:*i*-PrOH=100 : 1), after the ester was converted into the acetate by the sequence: i) LiAlH4 reduction and ii) acetylation.
[i] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OJ, hexane).
[j] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OD-H (×2), hexane).

Nevertheless, the two conformers (*R*,*S*)-**20** and (*R*,*R*)-**20** were expected to show high *cis*-selectivity on account of their conformational similarity with (*R*,*R*)-**18** and (*R*,*S*)-**19**, respectively. These expectations agreed with the results obtained with complex **16** (Table 4, entry 4). These results and the above hypothesis on enantioface selection by the carbenoid species (*R*,*R*)-**18** derived from **6** suggest that the presence of the 2″-phenyl group strengthens *cis*-selectivity by pushing the ester alkyl group towards the incoming olefin. Therefore, we were intrigued by the catalytic activity of the complexes **14** and **15** which carry a methyl group and a hydrogen atom at C2″ in place of the phenyl group, respectively (entries 2 and 3). The introduction of these small groups at the 2″-position should allow the ester alkyl group directing away from the incoming olefin and, in turn, induce *trans*-*cis* selectivity in cyclopropanation. In fact, both complexes **14** and **15** did show moderate *trans*-selectivity. Among them, complex **14** showed excellent enantioselectivity while complex **15** exhibited only moderate selectivity. This was attributed to the fact that the C3-naphthyl substituent lacking its 2″-substituent could not completely intercept the olefin's approach from the C3-side. Although the yields of cyclopropanes were less than satisfactory, they were improved by reducing the amount of THF without any decay of the stereoselectivity (Table 5, entry 1). With these results in hand, we examined the cyclopropanation of other olefins with complex **14** as the catalyst. The reactions of other olefins also showed moderate *trans*-selectivity, except for the reaction of α-methylstyrene **9**, and excellent enantioselectivity (>94% ee). The use of *t*-butyl α-diazoacetate (R = *t*-butyl) resulted in a slightly better selectivity than that of ethyl α-diazoacetate (R= ethyl) (Table 5).

Conclusion

In conclusion, we have demonstrated that the reasonable ligand-design of a Co(II)-salen complex based on its asymmetry-inducing mechanism enables both *cis*- and *trans*-selective asymmetric cyclopropanation. A study of the application of Co(II)-salen complex to other carbene transfer reactions is now in progress in our laboratory.

Experimental Section

General Methods

^{1}H NMR spectra were recorded at 400 MHz on a Bruker DPX–400 or a JEOL GX–400 instrument. All signals were expressed as ppm down field from tetramethylsilane used as an internal standard (δ value in $CDCl_3$). IR spectra were obtained with a Shimadzu FTIR–8600 instrument. Optical rotations were measured with a JASCO P–1020 polarimeter. Column chromatography was conducted on silica gel BW–820MH, 70–200 mesh ASTM, available from Fuji Silysia Chemical Ltd. Preparative thin layer chromatography was performed on 0.5 mm×20 cm×20 cm E. Merck silica gel plates (60 F–254). Enantiomeric excesses were determined by HPLC analysis using a Shimadzu LC–10AT–VP equipped

with an appropriate optically active column, as described in the footnotes of the corresponding Tables. Solvents were dried and distilled shortly before use. Olefins, *t*-butyl α-diazoacetate, and ethyl α-diazoacetate were also distilled before use. The use of non-freshly distilled olefins and α-diazoacetates may be detrimental to the stereoselectivity of the reaction. Reactions were carried out under an atmosphere of nitrogen.

General Procedure for Co(II)-salen Complex: Preparation of Complex 6

To a solution of (1*R*,2*R*)-1,2-cyclohexanediamine (34.2 mg, 0.3 mmol) in EtOH (10 mL) was added (*R*)-3-formyl-2-hydroxy-2′-phenyl-1,1′-binaphthyl[26] (220 mg, 0.6 mmol) and the mixture was stirred for 6 h at room temperature. The resulting light yellow precipitate was separated from the solution by filtration, and dried under vacuum. This precipitate was added to the solution of $Co(OAc)_2$ (74.9 mg, 0.3 mmol) which was prepared from $Co(OAc)_2 \cdot 4H_2O$ by heating at 70–80 °C under vacuum till its color turned from pink to purple in deaerated ethanol (8 mL) under nitrogen atmosphere. The resulting purple brown precipitate was separated from the solution by filtration, washed with degassed ethanol under N_2, and dried in vacuo to give the brown solid **6;** yield: 769.1 mg (87%); IR (KBr): 3443, 3051, 2934, 2860, 2363, 1603, 1547, 1491, 1450, 1331, 1298, 1225, 1186, 1148, 1028, 952, 870, 822, 758, 700, 581, 544 cm^{-1}; calcd. for $C_{60}H_{44}O_2N_2Co \cdot 0.5H_2O$: C, 80.7; H, 5.08; N, 3.14%; found: C, 80.86; H, 5.08; N, 3.09%.

Complexes **4, 7, 13–16** were prepared in the same manner as described for the synthesis of **6**.

Co(II)-salen complex 4

Vermilion solid; yield: 98%; IR (KBr): 3445, 3065, 3032, 1597, 1510, 1435, 1377, 1319, 1271, 1211, 1178, 1101, 1070, 1003, 951, 866, 791, 760, 698, 571, 548, 519 cm^{-1}; calcd. for $C_{28}H_{18}O_2N_2Cl_4Co$: C, 54.67; H, 2.95; N, 4.55%; found: C, 54.49; H, 2.92; N, 4.61%.

Co(II)-salen complex 7

Brown solid; yield: 76%; IR (KBr): 3445, 3051, 2936, 2860, 2363, 2336, 1593, 1547, 1491, 1447, 1427, 1327, 1296, 1225, 1186, 1148, 953, 868, 818, 787, 756, 700, 583, 544 cm^{-1}; calcd. for $C_{60}H_{44}O_2N_2Co \cdot 0.5H_2O$: C, 80.7; H, 5.08; N, 3.14%; found: C, 80.73; H, 4.90; N, 3.22%.

Co(II)-salen complex 13

Red brown solid; yield: 84%; IR (KBr): 3447, 3053, 2909, 2363, 2336, 1587, 1545, 1491, 1448, 1425, 1389, 1323, 1225, 1186, 1148, 1069, 1024, 953, 868, 816, 758, 700, 635, 611, 581, 542, 503, 436 cm^{-1}; calcd. for $C_{68}H_{46}O_2N_2Co$: C, 83.17; H, 4.72; N, 2.85%; found: C, 82.81; H, 4.70; N, 2.84%.

Co(II)-salen complex 14

Yellowish brown solid; yield: 86%; IR (KBr): 3439, 3049, 3007, 2932, 2858, 1591, 1553, 1445, 1421, 1337, 1227, 1190, 1148, 1123, 955, 887, 860, 806, 781, 746, 567, 430 cm^{-1}; calcd. for $C_{50}H_{40}O_2N_2Co$: C, 79.04; H, 5.31; N, 3.69%; found: C, 79.03; H, 5.35; N, 3.79%.

Co(II)-salen complex 15

Yellowish brown solid; yield: 80%; IR (KBr): 3443, 3049, 2932, 2856, 1595, 1551, 1423, 1352, 1329, 1227, 1188, 1150, 1123, 1043, 1018, 955, 891, 858, 797, 777, 748, 567, 503, 426 cm^{-1}; calcd. for $C_{48}H_{36}O_2N_2Co \cdot 0.5H_2O$: C, 77.83; H, 5.03; N, 3.78%; found: C, 78.03; H, 5.08; N, 3.79%.

Co(II)-salen complex 16

Brown solid; yield: 65%; IR (KBr): 3441, 3051, 2941, 2363, 2336, 1593, 1547, 1491, 1429, 1389, 1337, 1292, 1225, 1186, 1148, 951, 868, 820, 752, 700, 673, 577, 546 cm^{-1}; calcd. for $C_{56}H_{38}O_2N_2Co \cdot H_2O$: C, 79.33; H, 4.76; N, 3.30%; found: C, 79.51; H, 4.59; N, 3.39%.

General Procedure for *cis*-Selective Asymmetric Cyclopropanation of Styrene with Complex 6

To a THF solution (5 mL) of Co(II)-salen complex **6** (44 mg, 50 μmol) was added a THF solution of *N*-methylimidazole (0.2 mL, 0.5 M, 0.1 mmol) and the mixture was stirred for 2 min. Styrene (550 μL, 4.8 mmol) was added to this solution and the mixture was stirred for another 3 min before being treated with *t*-butyl α-diazoacetate (140 μL, 1.0 mmol). The whole mixture was stirred for 24 h at room temperature and then concentrated *in vacuo*. The residue was chromatographed on silica gel (hexane-AcOEt = 1 : 0 to 9 : 1) to give a 98 : 2 mixture of *cis*- and *trans*-products in 89% yield. An aliquot of the mixture was submitted to preparative TLC (silica gel, hexane-*i*-Pr_2O = 4 : 1) to yield the *cis*-product which was used for the determination of its enantiomeric excess by HPLC analysis (98% ee).

(1R, 2S)-tert-Butyl cis-2-phenylcyclopropane-1-carboxylate

Colorless oil; yield: 36% (98% ee); $[\alpha]_D^{20}$ –18.4° (*c* 0.34, $CHCl_3$). Lit.[17c] [98% ee, (1*S*,2*R*)-isomer]; $[\alpha]_D^{24}$ 18.0° (*c* 0.73, $CHCl_3$); ^1H NMR (400 Hz): δ = 7.29–7.16 (m, 5H), 2.53 (ddd, *J* = 7.5, 8.0, 8.5 Hz, 1H), 1.98 (ddd, *J* = 5.5, 7.5, 8.0 Hz, 1H), 1.64 (ddd, *J* = 5.0, 5.5, 7.5 Hz, 1H), 1.24 (ddd, *J* = 5.0, 7.5, 8.5 Hz, 1H), 1.13 (s, 9H); IR (neat): 3582, 3059, 2976, 2930, 1722, 1603, 1456, 1389, 1366, 1290, 1254, 1211, 1169, 1148, 1082, 1032, 968, 901, 853, 795, 746, 721, 696 cm^{-1}; calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%; found: C, 77.01; H, 8.32%.

tert-Butyl cis-2-(4-chlorophenyl)cyclopropane-1-carboxylate

Colorless oil; yield: 82% (95% ee); $[\alpha]_D^{20}$ +4.4° (*c* 0.17, $CHCl_3$); ^1H NMR (400 Hz): δ = 7.24–7.19 (m, 4H), 2.47 (ddd, *J* = 7.3, 8.6, 9.3 Hz, 1H), 1.99 (ddd, *J* = 5.7, 7.8, 9.3 Hz, 1H), 1.59 (ddd, *J* = 5.1, 5.7, 7.3 Hz, 1H), 1.25 (ddd, *J* = 5.1, 7.8, 8.6 Hz, 1H), 1.18 (s, 9H); IR (neat): 3005, 2978, 2932, 1726, 1599, 1495, 1454, 1391, 1367, 1292, 1254, 1213, 1169, 1147, 1093, 1034, 1014, 970, 899, 833, 777, 756, 710, 617 cm^{-1}; anal. calcd. for $C_{14}H_{17}ClO_2$: C, 66.53; H, 6.78%; found: C, 6.55; H, 6.78%.

tert-Butyl cis-2-(4-methoxyphenyl)cyclopropane-1-carboxylate

Colorless oil; yield: 81% (96% ee); $[\alpha]_D^{20}$ +3.8° (*c* 0.38, $CHCl_3$); ^1H NMR (400 Hz): δ = 7.18 (d, 2H), 6.80 (d, 2H), 3.77 (s, 3H),2.46 (ddd, *J* = 7.0, 8.5, 9.0 Hz, 1H), 1.93 (ddd, *J* = 5.5, 7.5, 9.0 Hz, 1H), 1.57 (ddd, *J* = 5.0, 5.5, 7.0 Hz, 1H), 1.21 (ddd, *J* = 5.0, 7.5, 8.5 Hz, 1H), 1.17 (s, 9H); IR (neat): 3585, 3003 2976, 2932, 2837, 1724, 1612, 1582, 1516, 1460, 1460, 1391, 1367, 1292, 1250, 1211, 1173, 1148, 1113, 1082, 1036, 970, 899, 833, 800, 779, 745 cm^{-1}; anal. calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12%; found: C, 72.40; H, 8.16%.

***tert*-Butyl *cis*-2-methyl-2-phenylcyclopropane-1-carboxylate**

Colorless oil; yield: 77% (96% ee); $[\alpha]_D^{20}$ –40.8° (*c* 0.50, $CHCl_3$); ^1H NMR (400 Hz): δ = 7.19–7.16 (m, 5H), 1.80 (dd, *J* = 7.5, 5.5 Hz, 1H), 1.70 (dd, *J* = 5.5, 4.5 Hz, 1H), 1.45 (s, 3H), 1.13 (s, 9H), 1.07 (dd, *J* = 7.5, 4.5 Hz, 1H); IR (KBr): 3061, 3007, 2974, 2930, 2868, 1722, 1605, 1499, 1446, 1389, 1370, 1337, 1290, 1248, 1150, 1090, 978, 847, 781, 754, 700, 552, 476 cm^{-1}; anal. calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%; found: C, 77.43; H, 8.75%.

***tert*-Butyl *cis*-2-(2–naphthyl)cyclopropane-1-carboxylate**

Colorless crystals; yield: 94% (97 %ee); mp 82–83 °C; $[\alpha]_D^{20}$ +86.4° (*c* 0.72, $CHCl_3$); ^1H NMR (400 Hz): δ = 7.79–7.71 (m, 4H), 7.46–7.39 (m, 3H), 2.67 (ddd, *J* = 7.3, 8.6, 9.4 Hz, 1H), 2.05 (ddd, *J* = 5.7, 7.8, 9.4 Hz, 1H), 1.77 (ddd, *J* = 5.0, 5.7, 7.3 Hz), 1.33 (ddd, *J* = 5.0, 7.8, 8.6 Hz, 1H), 1.05 (s, 3H); IR (KBr): 3461, 3053, 2974, 2930, 2870, 1717, 1630, 1597, 1510, 1456, 1391, 1367, 1215, 1153, 1096, 1053, 984, 887, 856, 829, 783, 748, 478 cm^{-1}; anal. calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51%; found: C, 80.47; H, 7.50%.

The *cis*-geometry of the major product obtained in the cyclopropanation of **12** with **6** as the catalyst was confirmed by X-ray crystallographic analysis.[27]

***(1R, 2S)*-Ethyl *cis*-2-phenylcyclopropane-1-carboxylate**

Colorless oil; yield: 99% (98% ee); $[\alpha]_D^{24}$ –19.3° (*c* 0.48, $CHCl_3$); Lit. [17c] [88% ee (1*S*,2*R*)-isomer]; $[\alpha]_D^{24}$ 22.8° (*c* 0.43, $CHCl_3$); ^1H NMR (400 MHz): δ = 7.26–7.19 (m, 5H), 3.87 (q, *J* = 7.3 Hz, 2H), 2.58 (ddd, *J* = 7.4, 8.7, 9.3 Hz, 1H), 2.07 (ddd, *J* = 5.7, 7.8, 9.3 Hz, 1H), 1.71 (ddd, *J* = 5.1, 5.7, 7.4 Hz, 1H), 1.32 (ddd, *J* = 5.1, 7.8, 8.7 Hz, 1H), 0.97 (t, *J* = 7.3 Hz, 3H); IR (neat): 3059, 3026, 2982, 2933, 1728, 1605, 1499, 1454, 1381, 1275, 1182, 1161, 1086, 1034, 961, 862, 827, 795, 752, 721, 694, 476 cm^{-1}, anal. calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%; HRFABMS *m/z* calcd. for $C_{12}H_{15}O_2$ (M^++H): 191.1057; found: 191.1058.

Ethyl cis–2–(4–chlorophenyl)cyclopropane–1–carboxylate

Colorless oil; yield: 97% (96% ee); $[\alpha]_D^{24}$ +6.2° (*c* 0.46 $CHCl_3$); ^1H NMR (400 MHz): δ = 7.24–7.18 (m, 4H), 3.90 (q, *J* = 7.3, 2H), 2.51 (ddd, *J* = 7.5, 8.6, 9.2 Hz, 1H), 2.08 (ddd, *J* = 5.6, 7.8, 9.2 Hz, 1H), 1.67 (ddd, *J* = 5.1, 5.6, 7.5 Hz, 1H), 1.33 (ddd, *J* = 5.1, 7.8, 8.6 Hz, 1H) 1.02 (t, *J* = 7.3 Hz, 3H); IR (neat): 2983, 1726, 1495, 1387, 1277, 1184, 1161, 1094, 1034, 1020, 962, 903, 833, 762, 706 cm^{-1}; anal. calcd. for $C_{12}H_{13}ClO_2$: C, 64.15; H, 5.83%; found: C, 64.01; H, 5.86%.

***Ethyl cis*-2-(4-methoxyphenyl)cyclopropane-1-carboxylate**

Colorless oil; yield: 95% (93% ee); $[\alpha]_D^{24}$ +6.0° (*c* 0.39 $CHCl_3$); ^1H NMR (400 MHz): δ = 7.18 (pseudo-d, *J* = 8.6 Hz, 2H), 6.80 (pseudo-d, *J* = 8.6 Hz, 2H), 3.90 (q, *J* = 7.3 Hz, 2H), 3.77 (s, 3H), 2.52 (ddd, *J* = 7.5, 8.7, 9.2 Hz, 1H), 2.03 (ddd, *J* = 5.6, 7.8, 9.2 Hz, 1H), 1.66 (ddd, *J* = 5.0, 5.6, 7.5 Hz, 1H), 1.30 (ddd, *J* = 5.0, 7.8, 8.7 Hz, 1H), 1.02 (t, *J* = 7.3 Hz, 3H); IR (neat): 2984, 2837, 1726, 1612, 1581, 1516, 1462, 1381, 1296, 1250, 1182, 1090, 1034, 960, 899, 833, 773, 675, 471, 411 cm^{-1}; anal. calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%; found: C, 70.68; H, 7.35%.

***Ethyl cis*-2-methyl-2-phenylcyclopropane-1-carboxylate**

Colorless oil; yield: 85% (96% ee); $[\alpha]_D^{24}$ –43.8° (*c* 0.48, $CHCl_3$); ^1H NMR (400 MHz): δ = 7.29–7.17 (m, 5H), 3.85 and 3.81 (ABqq, *J* = 10.9, 7.1 Hz, 2H), 1.90 (dd, *J* = 7.8, 5.6 Hz, 1H), 1.78 (dd, *J* = 5.6, 4.9 Hz, 1H), 1.46 (s, 3H), 1.15 (dd, *J* = 7.8, 4.9 Hz, 1H), 0.94 (t, *J* = 7.1 Hz, 3H); IR (KBr): 3028, 2964, 2930, 2870, 1728, 1605, 1499, 1447, 1381, 1271, 1238, 1167, 1024, 970, 905, 845, 768, 698, 478 cm^{-1}; anal. calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%; HRFABMS *m/z* calcd. for $C_{13}H_{17}O_2$(M^++H): 205.1229; found: 205.1239.

General Procedure for *trans*-Selective Asymmetric Cyclopropanation of Styrene with Complex 9

To a THF solution (1 mL) of Co(II)-salen complex **9** (38 mg, 50 μmol) was added a THF solution of *N*-methylimidazole (0.2 mL, 0.5 M, 0.1 mmol) and the mixture was stirred for 2 min. Styrene (550 μL, 4.8 mmol) was added to this solution and the mixture was stirred for another 3 min before being treated with *t*-butyl α-diazoacetate (140 mL, 1.0 mmol). The whole mixture was stirred for 24 h at room temperature and then concentrated in vacuo. The residue was passed through a short silica gel column (hexane/*i*-Pr_2O = 1/0 to 4/1) to give a mixture of *tert*-butyl *trans*- and *cis*-2-phenylcyclopropane-1-carboxylates (218.0 mg) in quantitative yield. The ratio of *trans*- and *cis*-isomers was determined by ^1H NMR analysis to be 73 : 27. An aliquot of the mixture was submitted to preparative TLC (silica gel, hexane-*i*-Pr_2O = 4 : 1) to yield the *trans*- and *cis*-isomers, separately. Their enantiomeric excesses were determined as described in the footnotes of Table 5.

***(1R,2R)*-*tert*-Butyl *trans*-2-phenylcyclopropane-1-carboxylate**

Colorless oil; yield: 66% (98% ee); $[\alpha]_D^{20}$ –247.6° (*c* 0.20, $CHCl_3$). Lit. [15b] [93% ee (1*S*,2*S*)-isomer]; $[\alpha]_D^{24}$ 253.3° (*c* 0.73, $CHCl_3$); ^1H NMR (400 Hz): δ = 7.29–7.08 (m, 5H), 2.43 (ddd, *J* = 4.4, 6.4, 9.3 Hz, 1H), 1.83 (ddd, *J* = 4.4, 5.4, 9.3 Hz), 1.53 (ddd, *J* = 4.4, 5.4, 8.3 Hz, 1H), 1.47 (s, 3H),1.23 (ddd, *J* = 4.4, 6.3, 8.3 Hz, 1H); IR (neat): 3030, 2978, 2932, 1720, 1605, 1499, 1458, 1400, 1367, 1340, 1285, 1253, 1215, 1155, 1080, 1042, 1026, 935, 845, 783, 750, 696, 645, 409 cm^{-1}; anal. calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%; found: C, 76.80; H, 8.34%.

***tert*-Butyl *trans*-2-(4-chlorophenyl)cyclopropane-1-carboxylate**

Colorless crystals; yield: 75% (99% ee); mp 58–59 °C; $[\alpha]_D^{20}$ –222.3° (*c* 0.29, $CHCl_3$); ^1H NMR (400 Hz): δ = 7.23 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 2.40 (ddd, *J* = 4.4, 6.4, 9.3 Hz, 1H), 1.79 (ddd, *J* = 4.4, 5.4, 8.3 Hz), 1.53 (ddd, *J* = 4.4, 5.4, 9.3 Hz, 1H), 1.47 (s, 3H), 1.19 (ddd, *J* = 4..4, 6.4, 8.3 Hz, 1H); IR (KBr): 3003, 2982, 2937, 1904, 1717, 1651, 1493, 1450, 1394, 1366, 1335, 1302, 1254, 1217, 1151, 1094, 1043, 1011, 926, 849, 816, 743, 523, 471 cm^{-1}; anal. calcd. for $C_{14}H_{17}ClO_2$: C, 66.53; H, 6.78%; found: C, 66.57; H, 6.77%.

***tert*-Butyl *trans*-2-(4-methoxyphenyl)cyclopropane-1-carboxylate**

Colorless oil; yield: 38% (94% ee); $[\alpha]_D^{20}$ –238.0° (*c* 1.14, $CHCl_3$); ^1H NMR (400 Hz): δ = 7.02 (d, *J* = 8.5, 2H), 6.81 (d, *J* = 8.5, 2H), 2.40 (ddd, *J* = 3.9, 6.4, 9.3 Hz, 1H), 1.74 (ddd, *J* = 4.4, 5.4, 8.3 Hz, 1H), 1.47 (ddd, *J* = 3.9, 5.4, 8.3 Hz, 1H),

1.46 (s, 3H) 1.17 (ddd, J = 4.4, 6.4, 8.3 Hz, 1H); IR (neat): 3034, 3005, 2966, 2937, 2843, 1717, 1612, 1518, 1452, 1402, 1367, 1344, 1294, 1254, 1217, 1086, 1030, 934, 864, 818, 752, 472 cm^{-1}; anal. calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12%; found: C, 72.49; H, 8.13%.

tert–Butyl trans–2–methyl–2–phenylcyclopropane–1–carboxylate

Colorless oil; yield: 42% (99% ee); $[\alpha]_D^{20}$ –133.9° (c 0.10, $CHCl_3$); ^1H NMR (400 Hz): δ = 7.33–7.18 (m, 5H), 1.89 (dd, J = 5.9, 8.3 Hz, 1H), 1.51 (s, 3H), 1.49 (s, 9H), 1.36 (dd, J = 4.9, 5.9 Hz, 1H), 1.33 (dd, 4.9, 8.3, 1H); IR (neat): 3059, 2978, 2932, 2880, 1948, 1871, 1722, 1680, 1645, 1605, 1578, 1499, 1450, 1391, 1369, 1294, 1254, 1207, 1151, 1078, 972, 910, 847, 764, 739, 698, 434 cm^{-1}; anal. calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%; found: C, 77.37; H, 8.71%.

(1R, 2R)-Ethyl trans-2-phenylcyclopropane-1-carboxylate

Colorless oil; yield: 69% (98% ee); $[\alpha]_D^{24}$ –291.2° (c 0.23, $CHCl_3$); ^1H NMR (400 MHz): δ = 7.30–7.09 (m, 5H), 4.16 (q, J = 7.5 Hz, 2H), 2.52 (ddd, J = 4.2, 6.4, 9.2 Hz, 1H), 1.90 (ddd, J = 4.2, 5.3, 9.2 Hz, 1H), 1.59 (ddd, J = 4.6, 5.3, 9.2 Hz, 1H), 1.31 (ddd, J = 4.6, 6.4, 8.4 Hz, 1H), 1.28 (t, J = 7.5 Hz, 3H); IR (neat): 3030, 2984, 1724, 1661, 1605, 1499, 1458, 1408, 1369, 1331, 1269, 1219, 1184, 1082, 1043, 1020, 941, 853, 783, 756, 698, 459 cm^{-1}; HRFABMS m/z calcd. for $C_{12}H_{15}O_2$ (M^++H): 191.1072; found: 191.1073.

Ethyl trans-2-(4-chlorophenyl)cyclopropane-1-carboxylate

Colorless oil; yield: 78% (96% ee); $[\alpha]_D^{24}$ –258.0° (c 0.78 $CHCl_3$); ^1H NMR (400 MHz): δ = 7.24 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.5, 2H) 4.17 (q, J = 7.0 Hz, 2H), 2.48 (ddd, J = 4.1, 6.3, 9.2 Hz, 1H), 1.86 (ddd, J = 4.1, 5.3, 7.4 Hz, 1H), 1.60 (ddd, J = 4.6, 6.3, 7.4 Hz, 1H), 1.28 (t, J = 7.0 Hz, 3H), 1.28 (ddd, J = 4.6, 5.3, 9.2 Hz, 1H); IR (neat): 2984, 2934, 2909, 1898, 1726, 1497, 1450, 1406, 1394, 1327, 1269, 1219, 1186, 1094, 1045, 1014, 949, 856, 818, 789, 737, 467 cm^{-1}; anal. calcd. for $C_{12}H_{13}ClO_2$: C, 64.15; H, 5.83%; found: C, 64.14; H, 5.88%.

Ethyl trans-2-(4-methoxyphenyl)cyclopropane-1-carboxylate

Colorless oil; yield: 67% (96% ee); $[\alpha]_D^{24}$ –269.5° (c 0.28, $CHCl_3$); ^1H NMR (400 MHz): δ = 7.03 (d, J = 8.5, 2H), 6.82 (d, J = 8.5 Hz, 2H), 4.16 (q, J = 7.0 Hz, 2H), 3.78 (s, 3H), 2.48 (ddd, J = 4.1, 6.4, 9.3 Hz, 1H), 1.82 (ddd, J = 4.1, 5.2, 8.3 Hz, 1H), 1.28 (t, J = 7.0 Hz, 3H), 1.55 (ddd, J = 4.6, 5.2, 9.3 Hz, 1H), 1.25 (ddd, J = 4.6, 6.4, 8.3 Hz, 1H); IR (neat): 2984, 2837, 1724, 1614, 1582, 1518, 1450, 1408, 1331, 1294, 1252, 1182, 1113, 1040, 947, 856, 824, 758, 463 cm^{-1}; anal. calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%; found: C, 70.66; H, 7.35%.

Ethyl trans-2-methyl-2-phenylcyclopropane-1-carboxylate

Colorless oil; yield: 43% (93% ee); $[\alpha]_D^{24}$ –193.3° (c 0.05, $CHCl_3$); ^1H NMR (400 MHz): δ = 7.33–7.19 (m, 5H), 4.20 (ABqq, J = 8.5, 7.0 Hz, 2H), 1.96 (dd, J = 5.9, 8.3 Hz, 1H), 1.52 (s, 3H), 1.43 (dd, J = 4.9, 5.9 Hz, 1H), 1.41 (dd, J = 4.9, 8.3 Hz, 1H), 1.30 (t, J = 7.0 Hz, 3H); IR (neat): 3059, 2984, 2934, 1726, 1605, 1497, 1447, 1400, 1296, 1267, 1178, 1119, 1090, 1063, 1022, 968, 908, 853, 762, 700, 482 cm^{-1}; HRFABMS m/z calcd. for $C_{13}H_{17}O_2$ (M^++H): 205.1229; found: 205.1223.

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[22] X-ray structure analysis of second-generation Mn(III)-salen complexes bearing chiral units at ethylenediamine and binaphthyl parts disclosed that five-membered chelate rings including a manganese ion and an ethylenediamine unit adopt a half-chair conformation and that their salen ligands take stepped-conformation.[25] Although the degree of folding of the salen ligands depends upon the nature of the apical ligand and the relative configuration of the complexes, both (*R*,*R*)- and (*R*,*S*)-complexes bend in a similar moderate degree when they bear an aprotic donor ligand. Based on this study, we assumed that both (*R*,*R*)- and (*R*,*S*)-intermediate carbenoid species bearing NMI at their apical site would adopt a moderately folded stepped-conformation.

[23] The structures of the intermediate carbenoid species were schematically described on the assumption that the salen ligand of Co(IV) species adopts a stepped-conformation.[19d, 19f, 19g, 25]

[24] It is reasonable to consider that carbenoid species derived Co-salen complexes bearing a bulky substituent at C3 and C3′ do not allow substrate-approach from the C3 and C3′ side because of the short distance between the C3 and C3′ substituents.

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[27] Atomic coordinates, bond lengths and angles, and thermal parameters of *tert*-butyl *cis*-2-(2-naphthyl)cyclopropane-1-carboxylate will be available on request from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, U.K.