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cis- and Enantio-selective Cyclopropanation with Chiral (ON$^+$)Ru–Salen Complex as a Catalyst

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Abstract—Cyclopropanation of styrene with α-diazoacetate in the presence of (*R*,*R*)-(salen)ruthenium complex **4** in THF which dissolves the complex exhibits remarkable *cis*- and enantio-selectivity [*cis*:*trans*=97:3, >97% ee (1*S*,2*R*)], while the same reaction in hexane which does not dissolve it shows good but opposite sense of enantioselectivity [−83% ee (1*R*,2*S*)] together with moderate *cis*-selectivity (*cis*:*trans*=68:32). In homogeneous and heterogeneous conditions, (salen)ruthenium complexes are considered to have different ligand-conformation which, in turn, causes the opposite sense of enantioface selectivity in the cyclopropanation.

Introduction

Metallosalen complexes are well recognized to serve as catalysts for transfer reactions of oxene and its equivalents such as nitrene and carbene.[1] Among various metallosalen complexes (hereafter referred to as M–salen complexes), optically active second generation Mn(III)–salen complexes were found to be the most suitable catalysts for asymmetric oxene transfer reaction such as epoxidation, C–H hydroxylation, and oxidation of sulfides.[2] For these second generation Mn–salen catalysts, the presence of C3- and C3′-substituents is essential for achieving high enantioselectivity. On the other hand, optically active Co(III)–salen complexes bearing no substituent at C3 and C3′ are the excellent catalysts for carbene transfer reactions such as asymmetric cyclopropanation and *S*-ylide formation.[2,3]

Asymmetric cyclopropanation of olefins, typical carbene transfer reaction, is the most useful reaction for the synthesis of optically active cyclopropanes. The reaction of mono-substituted olefins and α-diazoacetates in the presence of metal complex gives a mixture of *cis*- and *trans*-isomers. Asymmetric version of this reaction started with the pioneering work by Nozaki et al.[4] Following this study, Aratani et al. for the first time achieved high enantioselectivity together with moderate *trans*-selectivity in metal-catalyzed cyclopropanation.[5] Subsequent to these studies, many highly enantioselective cyclopropanation reactions have been developed,[6] but most of them are *trans*-selective, except for a few examples.[7,8] Recently Doyle et al. reported that cyclopropanation using Rh_2(*S*-IBAZ)$_4$ complex showed modest *cis*-selectivity, though its enantioselectivity is dependent upon the α-diazoacetate used.[8a] For example, *cis*–*trans* ratio and enantioselectivity in the cyclopropanation of styrene with ethyl α-diazoacetate are 67:33 and 73% ee (*cis*-isomer) respectively, while those with bis-(cyclohexyl)methyl α-diazoacetate are 66:34 and 95% ee (*cis*-isomer). Still no satisfactory example of highly *cis*- and enantio-selective reaction is known.

As described above, we found that chiral Co(III)–salen complex was an excellent catalyst for highly enantio- and *trans*-selective cyclopropanation reaction.[3b] However, in contrast to Mn–salen complexes in which 2′-substituted naphthyl (or -phenyl) groups at C3 and C3′ play a very important role in enantioselection by the complexes,[2] the Co(III)–salen complexes bearing substituents such as methyl or *t*-butyl group at C3 and C3′ showed no catalysis for carbene transfer reactions like cyclopropanation and *S*-ylide formation.[3] These results strongly suggested that olefins and sulfides approach the intermediary Co-carbenoid complex from the side of C3 and C3′. This further suggested that stereochemistry of metallosalen-catalyzed asymmetric cyclopropanation would be controlled at need if olefins could approach between suitable chiral C3- and C3′-substituents to the carbenoid species. It was reasonable to expect that, if the distance between C3 and C3′ is appropriately expanded, olefins could approach the intermediary carbenoid from C3- and C3′ side even if bulky substituents reside at those carbons.

Recently we disclosed that chiral (*R*,*S*)-(ON$^+$)Ru(II)–salen complex (**1**) was an excellent catalyst for asymmetric epoxidation under photo-irradiation.[9] The structure of the complex **1** was unambiguously determined by X-ray analysis:[10] the length (2.04–2.05 Å) of the Ru–O$_{equatorial}$

Keywords: cyclopropanation; (salen)ruthenium; metallosalen; photo-activation.

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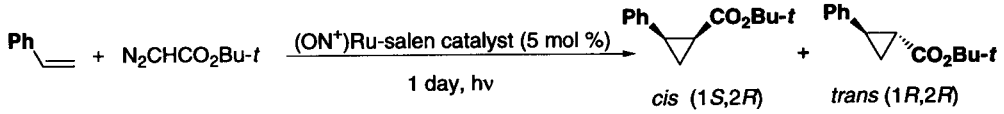
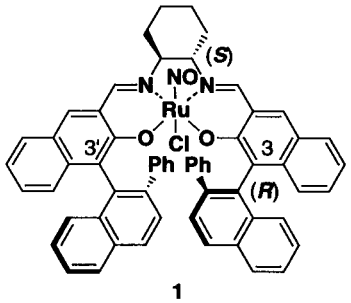
Table 1. Asymmetric cyclopropanation of styrene using (ON^+)Ru-salen complexes as catalysts (reaction was carried out in styrene at room temperature under irradiation of incandescent light, unless otherwise mentioned. Enantiomeric excess of the product was determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OD-H, hexane). Configuration was determined by the comparison of the elution order with the authentic samples)



Entry	Catalyst	Yield (%)[a]	*cis*:*trans*	*cis* (% ee)	*trans* (% ee)
1	**2**	10	18:82	31	35
2	**3**	45	11:89	58	−23[b]
3	**1**	12	37:63	12	51
4	**4**	53	80:20	81	51
5[c]	**4**	6	44:56	71	78
6	–	11	44:56	0	0

[a] Yield was calculated on the amount of α-diazoacetate used by ^{1}H NMR analysis (see the typical experimental procedure).
[b] The configuration of the product is 1*S*,2*S*.
[c] Reaction was carried out in the dark.

bond is *ca*. 0.2 Å longer than that (1.85–1.86 Å) of the $Co-O_{equatorial}$ bond[11] and the substituent at C3 largely inclined toward the apical ligand, leaving a large open space between the C3- and C3′-substituents. Furthermore, there are several precedents of asymmetric cyclopropanation using chiral ruthenium complexes as catalysts, though they are highly *trans*- and enantio-selective.[12] Ruthenium ions in these complexes have a site available for coordination of α-diazoacetate. Although the ruthenium ion in **1** has no such site, photo-irradiation[9] has been considered to promote the dissociation of one of its apical ligands,[13] endowing the ion with an open apical site. Thus chiral Ru–salen complex, especially the complex bearing chiral C3- and C3′-substituents, was expected to serve as a catalyst for stereocontrolled cyclopropanation reaction. With this expectation, we examined Ru–salen catalyzed asymmetric cyclopropanation reaction.[14]



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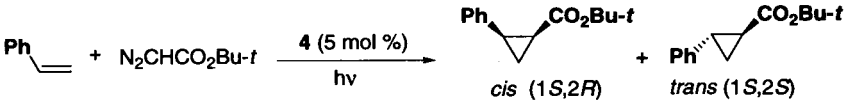
Results and Discussion

We synthesized three other chiral (ON^+)(salen)ruthenium(II) complexes **2**–**4** according to Bosnich's procedure[15] and examined the reaction of styrene and *t*-butyl α-diazoacetate in the presence of the complexes (without solvent). The results obtained are summarized in Table 1. In accord with other reactions such as epoxidation[9] and hetero Diels–Alder reaction[16] using (ON^+)(salen)ruthenium(II) complex (**1**) as a catalyst, the present reaction was also remarkably accelerated by photo-irradiation using incandescent lamp (National Panasonic LW100v57w) which illuminates light of wavelength of mostly >400 nm, as a light source. The reactions in the dark were very slow and gave poor and unreproducible results (cf. entries 4 and 5). Under incandescent light, the reaction with complex **2** showed *trans*-selectivity (entry 1) but enantioselectivity strongly suffered as compared with the reaction by using Co(III)-salen complex bearing the same ligand as the catalyst (93% ee, *trans*-isomer; *trans*:*cis*=96:4). Next, we examined the reactions using complexes (**1**, **3**, and **4**) bearing bulky substituents at C3 and C3′, as catalysts and found that these complexes also catalyzed the desired cyclopropanation. Complex **3** showed slightly better *trans*-selectivity but enantioselectivity was modest (entry 2). Reaction using (*R*,*S*)-complex **1** which has bulky 2-phenylnaphthyl groups as C3- and C3′-substituents proceeded with modest *trans*- and enantio-selectivity (entry 3). We were, however, gratified by the result obtained with (*R*,*R*)-complex **4** which also has bulky 2-phenylnaphthyl groups at 3- and 3′-carbons but is diastereomeric to (*R*,*S*)-complex **1** at the ethylenediamine moiety. The reaction catalyzed by **4** showed good level of *cis*- and enantio-selectivity (entry 4). Chemical yield was also acceptable, though there is still a room for improvement. Despite this, the obtained stereoselectivity was considered not to be an optimized one from the following observation: irradiation caused the decomposition of α-diazoacetate in the absence of a catalyst and promoted non-stereoselective cyclopropanation (entry 6). Therefore it was expected that stereoselectivity would be further improved if the uncatalyzed decomposition was suppressed by some means.

To suppress this undesired and uncatalyzed reaction, we first examined the effect of the wavelength of the light on stereoselectivity of the present reaction in THF (Table 2). The reaction irradiated by the light of about 390 nm suffered slightly lower enantioselectivity probably due to the photo-catalyzed decomposition of α-diazoacetate. Irradiation of the light of wave length longer than 500 nm promoted neither the decomposition of α-diazoacetate and

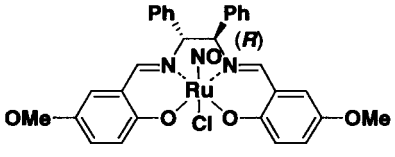
Table 2. Effect of wavelength of light on stereoselectivity (reaction was carried out in the presence of the catalyst **4** (5 mol %, based on α-diazoacetate used) at room temperature for 24 h in THF-styrene (10/1 v/v) under irradiation of light of the described wavelength, unless otherwise mentioned)



Entry	Wavelength (nm)	Yield (%)[a]	*cis*:*trans*[b]	*cis* (% ee)[c]	*trans* (% ee)[c]
1	~390	11	91:9	91	–[d]
2	~440	16	97:3	97	5
3	>500	3	71:29	79	−59[e]
4	IL[f]	18	96:4	99	9

[a] Yield was calculated on the basis of the amount of α-diazoacetate used. Total yield of *cis*- and *trans*-cyclopropanes was determined by ^{1}H NMR analysis (400 MHz) using 1-bromonaphthalene as an internal standard.
[b] Ratio of *cis*- and *trans*-isomers was determined by ^{1}H NMR analysis (400 MHz).
[c] Enantiomeric excess of the product was determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OD-H, hexane). Configuration was determined by the comparison of the elution order with the authentic samples.
[d] Not determined.
[e] Configuration of the product is 1*R*,2*R*.
[f] IL=incandescent light

nor the desired cyclopropanation. Finally, the light of *ca.* 440 nm was found to efficiently accelerate the desired dissociation of the apical ligand of (ON$^+$)Ru–salen complex, without promoting the undesired photo-decomposition of the α-diazoacetate. Thus, decomposition of the α-diazoacetate occurred on the Ru ion and resulted in the excellent stereoselectivity (entry 2). Fortunately, use of commercial incandescent lamp was also found to show enantioselectivity as high as the reaction irradiated by the light of *ca.* 440 nm (entry 4). In addition to this, it was found that the present reaction in THF was much better in terms of *cis*- and enantio-selectivity than the reaction carried out in styrene without adding extra solvent, though other reaction conditions were identical except for the solubility of the complex **4** to the reaction mediums used: the complex **4** was completely dissolved in THF, while **4** was partly solved in styrene (*cf.* Table 1, entry 4 and Table 2, entry 1). This suggested that the aggregation state of the complex **4** would affect the conformation of the salen ligand of the intermediary Ru–carbenoid complex and, in turn, influence the stereoselectivity of the present reaction.



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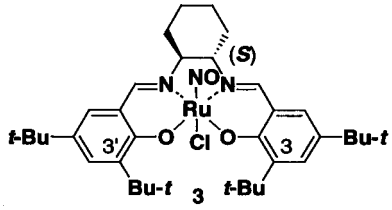

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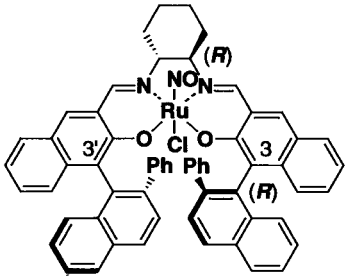

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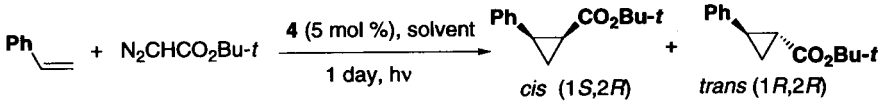
Based on the analysis of the second generation Mn(III)–salen complexes, we were able to propose that the salen ligand of oxo Mn(V)–salen complex was highly pliable and its conformation was regulated by weak interactions such as OH–π[17] and edge-to-face aromatic interactions.[18] We could also determine the structure of (*R*,*S*)-(ON$^+$)Ru(II)–salen complex **1**, in which neither the OH–π (between 2″-phenyl group and the apical ligand) nor the edge-to-face aromatic interaction (between C3- and C3′-substituents) exists and the five-membered chelate ring including ruthenium ion and ethylenediamine unit takes a twisted envelope conformation.[10] These results suggested that the ligand of complex **1** would be conformationally more flexible than the corresponding Mn–salen complex. The ligand of (*R*,*R*)-(ON$^+$)Ru(II)–salen complex **4** is also expected to be conformationally flexible because neither the OH–π nor the edge-to-face aromatic interaction also exists in the complex **4** and it is reasonable to consider that the five-membered chelate ring of the complex **4** also takes a twisted envelope conformation. These considerations suggested us that the ligand conformation of (ON$^+$)Ru(II)–salen complexes might be dependent on their association state which should be strongly related to the solvent used: the dissolved (homogeneous) and precipitated (heterogeneous) complexes might have different conformations, as discussed above. Thus, the effect of solvent on stereoselectivity was next examined by using incandescent lamp

Table 3. Solvent effect on enantioselectivity in cyclopropanation of styrene using **4** as a catalyst (reaction was carried out in the presence of *t*-butyl α-diazoacetate (0.1 mmol), styrene (0.3 mmol) and solvent [0.35 ml (solvent/styrene=10/1 v/v)] at room temperature under irradiation of incandescent light, unless otherwise mentioned. Enantiomeric excess of the product was determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OD-H, hexane). Configuration was determined by the comparison of the elution order with the authentic samples)



Entry	Solvent (ml)	Yield (%)[a]	*cis*:*trans*	*cis* (% ee)	*trans* (% ee)
1	THF	18	96: 4	99	−9[b]
2	DME	19	96: 4	98	10
3	AcOEt	17	92: 8	96	51
4	CH_2Cl_2	21	84:16	92	79
5	CH_3CN	0	–	–	–
6	Pyridine	0	–	–	–
7	Diethyl ether	10	63:37	−15[c]	64
8	Hexane	10	68:32	−83[c]	50
9	Heptane	14	74:26	−71[c]	72
10	Diisopropyl ether	5	67:33	−81[c]	48

[a] Yield was calculated on the amount of α-diazoacetate used by ^{1}H NMR analysis (see the experimental section).
[b] The configuration of the product is 1*S*,2*S*.
[c] The configuration of the product is 1*R*,2*S*.

as a light source with three different kinds of solvents: (i) solvents of high dissolving power such as THF, dimethoxyethane (DME), ethyl acetate, and dichloromethane; (ii) solvents of high dissolving power and high coordinating ability such as acetonitrile and pyridine; and (iii) solvents of poor dissolving power such as hexane, heptane, and diisopropyl ether (Table 3). Catalyst **4** was dissolved in the first class of solvents and the reactions in these solvents all showed high enantio- and *cis*-selectivity to give the (1*S*,2*R*)-isomer preferentially, though ethereal solvents gave slightly better results (entries 1–4). On the other hand, no reaction was observed in the second class of solvents, despite that **4** was dissolved in these solvents (entries 5 and 6). These results agreed with the proposed mechanism for metal-catalyzed diazo decomposition, in which diazo compound is coordinated to the metal ion and generates a metal–carbene complex.[19] Coordinating solvent should interrupt the coordination of α-diazoacetate to the ruthenium ion and the desired cyclopropanation did not occur in this kind of solvents. Complex **4** was insoluble to the third class of solvents and the reactions in these solvents were carried out under heterogeneous conditions, showing moderate *cis*- and good enantio-selectivity (entries 8–10). However, the sense of enantioselection in the formation of the major *cis*-isomer is opposite to that observed in the reactions in the first class of solvents (*cf.* entries 1–4 and 8–10). The reaction with the supernatant liquid of the hexane-suspension of complex **4** did not proceed at all even under the photo-irradiated conditions. Although the reaction mechanism is unclear at present, the obtained results indicated that the reversal of enantioselection has no relation to the functionality of solvents or to their polarity

Table 4. Asymmetric cyclopropanation of various olefins (reaction was carried out in the presence of the catalyst **4** (5 mol %, based on α-diazoacetate used) at room temperature in a mixture of THF and substrate under irradiation of incandescent light)

Entry	Substrate	THF-substrate (v/v)	Time (h)	Yield (%)[a]	*cis*:*trans*[b]	*cis* (%ee, confign)	*trans* (%ee, confign)
1	Styrene	2:1	48	36	93:7	98[c] (1*S*,2*R*)[d]	2[c] (1*R*,2*R*)[d]
2	Styrene	1:1	48	45	93:7	97[c] (1*S*,2*R*)[d]	15[c] (1*R*,2*R*)[d]
3	Styrene	1:2	48	43	76:24	88[c] (1*S*,2*R*)[d]	41[c] (1*R*,2*R*)[d]
4	*p*-Chlorostyrene	2:1	48	44	93:7	95[c,f]	–[e]
5	*p*-Methoxystyrene	2:1	48	62	94:6	96[c,f]	5[c,f]
6	*p*-Methoxystyrene	1:1	48	80	94:6	97[c,f]	17[c,f]
7	α-Methylstyrene	10:1	24	38	83:17	97[f,g]	23[f,h]
8	α-Methylstyrene	2:1	48	74	81:19	97[f,g]	53[f,h]
9	α-Methylstyrene	1:1	48	77	80:20	96[f,g]	–[e]

[a] Yield was calculated on the basis of the amount of α-diazoacetate used. Total yield of *cis*- and *trans*-cyclopropanes was determined by ^{1}H NMR analysis (400 MHz) using 1-bromonaphthalene as an internal standard.
[b] Ratio of *cis*- and *trans*- isomers was determined by ^{1}H NMR analysis (400 MHz).
[c] Enantiomeric excess of the product was determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OD-H, hexane).
[d] Configuration was determined by the comparison of the elution order with the authentic samples.
[f] Absolute configuration has not been determined.
[e] Enantiomeric excess has not been determined.
[g] Enantiomeric excess of the product was determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OJ, hexane).
[h] Enantiomeric excess of the product was determined by HPLC analysis using chiral column [DAICEL CHIRALCEL OD-H (x2), hexane].

Table 5. Asymmetric cyclopropanation using ethyl α-diazoacetate as the carbene source (reaction was carried out in the presence of the catalyst **4** (5 mol %, based on α-diazoacetate used) at room temperature in a mixture of THF and substrate under irradiation of incandescent light)

Entry	Substrate	THF-substrate (v/v)	Time (h)	Yield (%)[a]	*cis:trans*[b]	*cis*(% ee, confign)	*trans* (% ee, confign)
1	Styrene	2:1	48	33	93:7	88[c](1*S*,2*R*)[d]	35[c](1*R*,2*R*)[d]
2	*p*-Chlorostyrene	2:1	48	53	84:16	88[e,f]	50[f,g]
3	*p*-Chlorostyrene	1:1	48	53	79:21	86[e,f]	62[e,f]
4	*p*-Methoxystyrene	2:1	48	51	94:6	93[e,f]	24[e,f]
5	*p*-Methoxystyrene	1:1	48	56	92:8	92[e,f]	32[e,f]
6	α-Methylstyrene	2:1	48	61	73:27	90[e,f]	–[e]
7	α-Methylstyrene	1:1	48	57	72:28	91[e,f]	–[e]

[a] Yield was calculated on the basis of the amount of α-diazoacetate used. Total yield of *cis*- and *trans*-cyclopropanes was determined by ^{1}H NMR analysis (400 MHz) using 1-bromonaphthalene as an internal standard.
[b] Ratio of *cis*- and *trans*- isomers was determined by ^{1}H NMR analysis (400 MHz).
[c] Enantiomeric excess of the product was determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OB-H, hexane).
[d] Configuration was determined by the measurement of specific rotation.[21]
[e] Enantiomeric excess of the product was determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OJ, hexane).
[f] Absolute configuration has not been determined.
[g] Enantiomeric excess has not been determined.

(*cf.* entries 1–4 and 8–10). The following explanation seems to be the most rational at this moment. Complex **4** is dissolved completely in the first class of solvents and behaves as a monomeric catalyst which decomposes α-diazoacetate upon irradiation, while **4** is not dissolved in the third class of solvents and the activation (dissociation of apical ligand) should occur on the surface of the insoluble solid **4**. Therefore, the reversal of enantioselection is attributed to that these homo- and hetero-geneous catalysts have different ligand-conformation which is correlated with the sense of asymmetric induction.[14b] In connection with this problem, the substandard selectivity observed in the cyclopropanation of styrene without solvent (Table 1, entry 4) which had been attributed to the intervention of non-catalyzed reaction,[14a] should be explained as follow: the solubility of complex **4** to styrene is not very high and the reaction was performed under partly suspended conditions. Therefore, both homo- and hetero-geneous processes that show opposite sense of enantioselection to each other competed and diminished the stereoselectivity of the reaction to substandard level. In accord with these phenomena, the reaction in diethyl ether which has dissolving power inbetween THF and diisopropyl ether showed the mediate enantioselectivity [−15% ee (1*R*,2*S*)] between the stereochemistry of the reactions in these two ethereal solvents (entry 7).

As described in Table 2, the reaction irradiated by a suitable light in THF showed excellent *cis*- and enantioface-selectivity but the chemical yields of cyclopropanecarboxylates were unsatisfactory (entries 2 and 4). These low yields were attributed to slow reaction between the intermediary Ru–carbenoid and styrene, since the formation of a considerable amount of the mixture of fumaric and maleic acid esters was observed during the reactions. For example, the yield of a mixture of maleic and fumaric acid esters was 32%, when the reaction was performed in THF-styrene (10/1). We expected that the formation of fumaric and maleic acid esters would be suppressed by slowly adding α-diazoacetate to the reaction medium and the yield of cyclopropanecarboxylate would be improved. However, the slow addition of *t*-butyl α-diazoacetate did not improve the chemical yield. Then, we tried to reduce the amount of THF in the reaction medium to enhance the substrate concentration, because the present reaction is bimolecular reaction. As expected, the chemical yield of the cyclopropanecarboxylate was improved to some extent as the ratio of THF and styrene was reduced to 1:1 (v/v) without causing severe decay of stereoselectivity (Table 4, entries 1 and 2) but further reduction of THF decreased the stereoselectivity of the reaction to a considerable extent, as the reaction became suspended (entry 3). We also examined the cyclopropanation of other olefins with high substrate-concentration and could achieve excellent enantioselectivity (>95% ee) as well as high *cis*-selectivity (entries 4–8). Again, reduction of THF content improved the chemical yields of the desired products (entries 5–6 and 7–9).

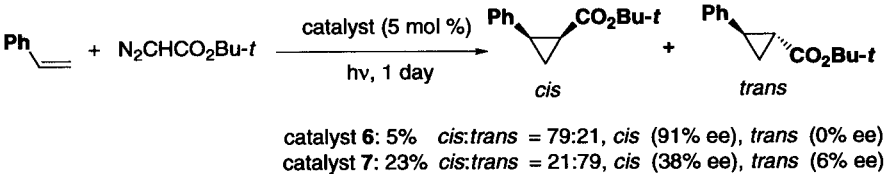
Up to here, *t*-butyl α-diazoacetate was used as a carbenoid source. However, it is well known that enantioselectivity of the metal-catalyzed cyclopropanation is dependent on the steric bulkiness of the ester alkyl group of the α-diazoacetate used and the selectivity generally improves as the bulkiness of the ester alkyl group increases. Ethyl α-diazoacetate has a small ethyl group as the ester alkyl group, but it is more readily available than *t*-butyl α-diazoacetate. Thus, we examined the cyclopropanation using ethyl α-diazoacetate as a carbene source (Table 5). Reactions also showed high *cis*- and good enantio-selectivity, though stereoselectivity is diminished to some extent.[20]

Complex **4** was purified by silica gel column chromatography and used for the present reaction. However, during the chromatographic purification, the formation of a new Ru–salen complex **5** was observed. The FABMS analysis of the new complex indicated that the apical chloro ligand of **4** was replaced with hydroxo ligand [measurement of FABMS (*m*-nitrobenzyl alcohol): *m/z* 973(M^+), 956(M^+-OH)]. We were interested in the catalysis of complex **5**. Thus, we examined the reaction of styrene and *t*-butyl α-diazoacetate in the presence of **5** (Table 6). It is noteworthy that the reaction proceeded even in the dark and showed high *cis*- (89:11) and enantio-selectivity [92% ee, *cis*-isomer (1*S*,2*R*)]. On the other hand, the reaction under incandescent light showed a similar level of *cis*- and enantioselectivity to that observed with the complex **4** under incandescent light (*cf.*, Table 1, entry 4 and Table 6, entry 2). This might suggest that the ligand dissociated upon irradiation is

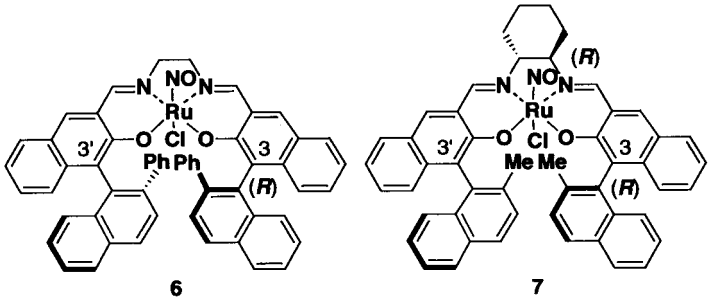
Table 6. Asymmetric cyclopropanation of styrene using (ON^+)Ru-salen complex **5** as the catalyst (reaction was carried out in styrene using **5** (5 mol %) at room temperature for 1 day. For the determination of enantiomeric excess of the product and the configuration of the products, see the footnote of Table 1)

Entry	Substrate	Yield (%)	*cis*:*trans*	*cis* (% ee, confign)	*trans* (% ee, confign)
1[a]	Styrene	62[b]	89:11	92 (1*S*,2*R*)	37 (1*R*,2*R*)
2[c]	Styrene	45[b]	78:22	81 (1*S*,2*R*)	54 (1*R*,2*R*)
3[a]	*p*-Chlorostyrene	32[d]	77:23	72[e]	34[e]

[a] The reaction was carried out in the dark.
[b] Isolated yield.
[c] The reaction was carried out under incandescent light.
[d] Yield was calculated by ^{1}H NMR analysis.
[e] Absolute configuration has not been determined.



Scheme 1.



not nitrosyl but chloro ligand.[9,13] However, further study is necessary to draw a conclusion on this issue. We also examined the cyclopropanation of *p*-chlorostyrene using **5** as the catalyst in the dark (entry 3). Although the reaction was *cis*-selective,[10] its *cis*- and enantio-selectivity decreased to a considerable extent.

Although the mechanism of asymmetric induction is unclear at present, we have assumed that olefins approach the carbenoid-carbon passing by the C3 (3′)-substituents as hypothesized. This assumption was supported from the following experiments. The complex **6** bearing the chirality only at the binaphthyl unit also showed good *cis*-selectivity (*cis*:*trans*=79:21) as well as good enantioselectivity [91% ee, *cis*-isomer (1*R*,2*R*); 0% ee, *trans*-isomer], though the chemical yield was poor. On the other hand, the modification of 3,3′-substituents of complex **4** by replacing 2″-phenyl group with methyl group decayed stereoselectivity: the reaction with complex **7** showed the moderate *trans*-selectivity and poor enantioselectivity (Scheme 1).

In general, cyclopropanations of styrene with α-diazoacetate in the presence of chiral Cu, Co, and Rh complexes give a mixture of *trans*- and *cis*-isomers, the configurations at C1 of which are the same.[6] In contrast to this, the present reaction under homogeneous conditions provided the *trans*- and *cis*-products isomeric at C1 (e.g., Table 3, entries 2–4), except for the reaction in THF (THF/styrene=10/1; Table 3, entry 1). The reason for this unusual selectivity is unclear at present.

In conclusion, we were able to achieve high *cis*- and enantioselective cyclopropanation with (*R*,*R*)-(ON^+)Ru–salen complex **4** for the first time. Although the mechanism of stereoselection of this reaction by the (ON^+)Ru–salen complex is still unclear, its ligand conformation was suggested to affect enantioselection by examining the solvent effect on enantioselectivity. The possible approaching path of olefins was also proposed on the basis of the stereochemistry of the reactions with various (ON^+)Ru–salen complexes as catalysts.

Experimental

^{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 plate (60 F-254). Enantiomeric excesses were determined by HPLC analysis using 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 and *t*-butyl α-diazoacetate were also distilled before

use. Use of non-freshly distilled olefins and *t*-butyl α-diazoacetate may decay stereoselectivity of the reaction. Reactions were carried out under an atmosphere of nitrogen if necessary.

(NO^+)Ru(II)–salen complex 1

To a solution of (1*S*,2*S*)-1,2-diaminocyclohexane (0.17 g, 1.5 mmol) in EtOH (20 ml) was added (a*R*)-3-formyl-2-hydroxy-2′-phenyl-1,1′-binaphthyl (1.1 g, 3.0 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 dissolved in *N*,*N*-dimethylformamide (DMF). NaH (60% dispersion in mineral oil, 0.13 g, 3.3 mmol) was weighed into a flask and washed with dry hexane (3×1.0 ml). To the flask were added the above yellow solution with stirring (hydrogen evolved and the mixture turned to a clear red solution). After 1 h, $Ru(NO)Cl_3{\cdot}H_2O$ (0.42 g, 1.6 mmol) was added to the suspension and the mixture was stirred at 110°C for 48 h. The resulting opaque red-brown mixture was concentrated under high vacuum. The residue was dissolved in CH_2Cl_2 and washed with water. The CH_2Cl_2 layer was dried over $MgSO_4$ and evaporated to dryness. The residue was recrystallized from CH_2Cl_2/CH_3CN to give Ru(II)-salen complex **1** as red-brown crystals (0.63 g, 42%). ^{1}H NMR (400 MHz): δ 8.34 (d, J=1.0 Hz, 1H), 8.27 (d, J=1.5 Hz, 1H), 8.09 (d, J=8.0 Hz, 1H), 7.99 (d, J=8.0 Hz, 1H), 7.95 (d, J=8.0 Hz, 1H), 7.82 (s, 1H), 7.78 (d, J=8.0 Hz, 1H), 7,74 (s, 1H), 7.63 (d, J=8.0 Hz, 1H), 7.53 (d, J=8.0 Hz, 1H), 7.46–7.40 (m, 2H), 7.31–7.22 (m, 5H), 7.17–6.96 (m, 6H), 6.91 (d, J=8.5 Hz, 1H), 6.70 (pseudo-q, J=7.0 Hz, 2H), 6.45–6.36 (m, 6H), 6.18 (pseudo-d, J=7.0 Hz, 2H), 4.04 (br t, J=10.5 Hz, 1H), 3.14 (br t, J=10.5 Hz, 1H), 2.77 (br d, J=10.5 Hz, 1H), 2.67 (br d, J=10.0 Hz, 1H), 2.07–2.00 (br m, 2H), 1.74–1.66 (br m, 1H), 1.58–1.36 (br m, 3H). IR (KBr): 3051, 2933, 2858, 1844, 1641, 1614, 1578, 1491, 1446, 1423, 1391, 1321, 1225, 1192, 1147, 1028, 955, 868, 818, 756, 700, 581, 544, 428 cm^{-1}. Anal. Calcd for $C_{60}H_{44}ClN_3O_3Ru{\cdot}1/2H_2O$: C, 72.03; H, 4.53; N, 4.20%. Found: C, 72.16; H, 4.73; N, 4.25%. HRFABMS *m*/*z*. Calcd for $C_{60}H_{44}O_3N_3ClRu(M^+)$: 991.2128. Found: 991.2104.

(NO^+)Ru(II)–salen complex 2

(NO^+)Ru(II)–salen complex **2** was prepared in the same procedure as described for the synthesis of **1**, except for the purification. The residue was quickly chromatographed on silica gel ($CHCl_3$/acetone=100/1) to give the Ru(II)–salen complex 2 as red-brown crystals (15%). ^{1}H NMR (400 MHz): δ 7.77 (d, J=1.5 Hz, 1H), 7.72 (d, J=1.5 Hz, 1H), 7.42–7.22 (m, 10H), 7.14–7.06 (m, 4H), 6.38 (d, J=7.3 Hz, 1H), 6.37 (d, J=7.3 Hz, 1H), 5.67 (dd, J=1.5 and 11.2 Hz, 1H), 4.93 (dd, J=1.5 and 11.2 Hz, 1H), 3.68 (s, 3H), 3.67 (s, 3H). IR (KBr): 3059, 3030, 3001, 2936, 2833, 1834, 1622, 1531, 1464, 1418, 1364, 1294, 1258, 1221, 1159, 1040, 1009, 970, 918, 826, 800, 760, 704, 667, 621, 552, 517, 469 cm^{-1}. HRFABMS *m*/*z*. Calcd for $C_{30}H_{26}O_3N_5ClRu(M^+)$: 645.0610. Found: 645.0593.

(NO^+)Ru(II)–salen complex 4

(NO^+)Ru(II)–salen complex **4** was prepared in the same procedure as described for the synthesis of **1**, except for the purification. The reaction mixture was concentrated under vacuum and the residue was quickly chromatographed on silica gel (CH_2Cl_2/acetone=50/1) to give (NO^+)Ru(II)–salen complex **4** as red–brown crystals (60%). ^{1}H NMR (400 MHz): δ 8.25 (d, J=2.0 Hz, 1H), 8.22 (d, J=1.5 Hz, 1H), 8.16 (d, J=8.0 Hz, 1H), 8.03 (d, J=8.5 Hz, 1H), 7.99 (d, J=8.5, 1H) 7.87–7.82 (m, 3H), 7.67 (d, J=8.0 Hz, 1H), 7.63–7.58 (m, 3H), 7.45–7.34 (m, 3H), 7.29–6.95 (m, 9H), 6.59–6.55 (m 2H), 6.30 (pseudo-d, J=7.5 Hz, 2H), 6.20–6.10 (m, 6H), 3.99 (br t, J=10.4 Hz, 1H), 3.03 (br t, J=10.4 Hz, 1H), 2.677 (br d, J=12.0 Hz, 1H), 2.60 (br d, J=11.0 Hz, 1H), 2.05–1.98 (br m, 2H), 1.71–1.63 (br m, 1H), 1.53–1.33 (br m, 3H). IR (KBr): 3051, 2937, 2860, 1824, 1707, 1639, 1614, 1577, 1546, 1490, 1446, 1423, 1384, 1346, 1319, 1296, 1274, 1246, 1226, 1190, 1169, 1145, 1124, 1091, 1072, 1028, 951, 864, 818, 793, 775, 760, 696, 667, 640, 582, 548, 499, 470, 428 cm^{-1}. Anal. Calcd for $C_{60}H_{44}ClN_3O_3{\cdot}H_2O$: C, 71.38; H, 4.59; N, 4.16%. Found: C, 71.24; H, 4.59; N, 4.13%. HRFABMS *m*/*z*. Calcd for $C_{60}H_{44}O_3N_3ClRu(M^+)$: 991.2128. Found: 991.2114.

(NO^+)Ru(II)–salen complex 5

(NO^+)Ru–salen complex **4** (115.2 mg, 0.12 mmol) was dissolved in $CHCl_3$. To the solution was added silica gel (3 g) and the mixture were stirred for 1 day. The suspension was filtered and the filtrate was concentrated in vacuo. The residue was chromatographed on silica gel (CH_2Cl_2/acetone/MeOH=50/1/1) to give (NO^+)Ru–salen complex **5** as red crystals (53.6 mg, 47%). ^{1}H NMR (400 MHz): δ 8.20–8.18 (m, 4H), 7.99 (d, J=7.5 Hz, 1H), 7.97 (d, J=6.5 Hz, 1H), 7.86 (s, 1H), 7.83 (s, 1H), 7.69 (d, J=8.0 Hz, 1H), 7.67 (d, J=8.5 Hz, 1H), 7.55 (d, J=7.5 Hz, 1H), 7.53 (d, J=8.0 Hz, 1H), 7.46–7.40 (m, 2H), 7.30–7.15 (m, 6H), 7.11–7.00 (m, 4H), 6.64 (t, J=7.0 Hz, 1H), 6.55 (t, J=7.0 Hz, 1H), 6.15–6.08 (m, 8H), 3.79 (br t, J=10.5 Hz, 1H), 3.06 (br t, J=10.5 Hz, 1H), 2.65 (br d, J=14.0 Hz, 1H), 2.55 (br d, J=10.5 Hz, 1H), 2.06–2.01 (br m, 2H), 1.85–1.75 (br m, 1H), 1.62–1.50 (br m, 1H), 1.38–1.33 (br m, 2H). IR (KBr): 3545, 3051, 2931, 2860, 1815, 1699, 1643, 1614, 1579, 1549, 1491, 1446, 1423, 1387, 1348, 1321, 1296, 1246, 1229, 1190, 1170, 1145, 1124, 1091, 1030, 951, 864, 820, 794, 762, 746, 696, 611, 582, 546, 499, 467, 430 cm^{-1}. HRFABMS *m*/*z*. Calcd for $C_{60}H_{45}O_4N_3(M^+)$: 973.2471. Found: 973.2463.

(NO^+)Ru(II)–salen complex 6

(NO^+)Ru(II)–salen complex **6** was prepared in the same procedure as described for the synthesis of **1**, except for the purification. The resulting opaque red–brown mixture was concentrated under high vacuum. The residue was dissolved in CH_2Cl_2, washed with water and dried under vacuum to give complex **6** as orange crystals (53%). IR (KBr): 3053, 1838, 1645, 1614, 1578, 1551, 1495, 1425, 1389, 1312, 1227, 1190, 1148, 1124, 1082, 1049, 953, 820, 746, 702, 665, 578, 517, 430 cm^{-1}. HRFABMS *m*/*z*.

Calcd for $C_{56}H_{38}O_3N_3ClRu(M^+)$: 937.1658. Found 937.1646.

(NO^+)Ru(II)–salen complex 7

(NO^+)Ru(II)–salen complex **7** was prepared in the same procedure as described for the synthesis of **1**, except for the purification. The reaction mixture was concentrated under vacuum and the residue was quickly chromatographed on silica gel (CH_2Cl_2/acetone=50/1) followed by recrystallization from CH_2Cl_2 and acetone to give complex **7** as red–brown crystals (10%). ^{1}H NMR (400 MHz): δ 8.58 (s, 1H), 8.44 (s, 1H), 8.02–7.89 (m, 5H), 7.75 (d, J=8.5 Hz, 1H), 7.70–7.65 (m, 2H) 7.39 (t, J=7.5 Hz, 1H), 7.30 (t, J=7.2 Hz, 1H), 7.23 (d, J=9.0 Hz, 1H), 7.18–7.13 (m, 2H), 7.09–6.99 (m, 6H), 6.94 (d, J=8.5 Hz, 1H), 6.68–6.62 (m, 2H), 4.22 (br t, J=10.8 Hz, 1H), 3.36 (br t, J=10.5 Hz, 1H), 2.92 (br d, J=13.0 Hz, 1H), 2.78 (br d, J=12.0 Hz, 1H), 2.18–2.13 (br m, 2H), 1.97–1.88 (br m, 1H), 1.77–1.67 (br m, 1H), 1.77 (s, 3H), 1.55–1.43 (br m, 2H), 1.48 (s, 3H). IR (KBr): 3051, 2941, 2860, 1840, 1643, 1614, 1577, 1550, 1508, 1485, 1446, 1421, 1386, 1342, 1319, 1226, 1190, 1147, 1124, 1068, 1028, 954, 873, 812, 779, 746, 688, 650, 572, 499, 430 cm^{-1}. Anal. Calcd for $C_{50}H_{40}ClN_3O_3Ru\cdot H_2O$: C, 67.83; H, 4.78; N, 4.75%. Found: C, 67.53; H, 4.78; N, 4.89%.

General procedure for asymmetric cyclopropanation using (NO^+)Ru(II)–salen complex 4 as a catalyst

To a THF solution (0.24 ml) of (NO^+)Ru(II)–salen complex **4** (4.9 mg, 5 μmol) was added styrene (0.12 ml) under N_2. To the mixture, was added *tert*-butyl α-diazoacetate (14 μl, 0.1 mmol), stirred for 48 h under incandescent light (100 V, 57 W), 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 7:93 mixture of *tert*-butyl *trans*- and *cis*-2-phenylcyclopropane-1-carboxylates. Their enantiomeric excesses and configuration were determined as described in the footnote d of Table 4. Further purification by preparative TLC (silica gel, hexane/*i*-Pr_2O=4/1) gave *tert*-butyl *cis*-2-phenylcyclopropane-1-carboxylates as a single isomer.

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

Colorless oil. Yield 36% (98% ee); $[\alpha]_D^{24}$=+18.0° (*c* 0.73, $CHCl_3$). ^{1}H NMR (400 MHz): δ 7.29–7.16 (m, 5H), 2.53 (ddd, J=7.5, 8.5 and 9.5 Hz, 1H), 1.98 (ddd, J=5.5, 7.5 and 9.5 Hz, 1H), 1.64 (ddd, J=5.0, 5.5 and 7.5 Hz, 1H), 1.24 (ddd, J=5.0, 7.5 and 8.5 Hz, 1H), 1.13 (s, 9H). IR (neat): 3059, 2976, 2930, 1722, 1603, 1456, 1389, 1366, 1290, 1254, 1211, 1169, 1148, 1082, 1032, 968, 901, 853, 795, 746, 721, 696 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%. Found: C, 77.00; H, 8.37%.

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

Colorless oil. Yield 18% (97% ee); $[\alpha]_D^{26}$=−4.9° (*c* 0.76, $CHCl_3$). ^{1}H NMR (400 MHz): δ 7.23 and 7.20 (pseudo-ABq, J=8.5 Hz, 4H), 2.47 (ddd, J=7.3, 8.6 and 9.3 Hz, 1H), 1.99 (ddd, J=5.7, 7.8 and 9.3 Hz, 1H), 1.59 (ddd, J=5.1, 5.7 and 7.3 Hz, 1H), 1.25 (ddd, J=5.1, 7.8 and 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, 66.82; H, 6.97%.

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

Colorless oil. Yield 62% (96% ee); $[\alpha]_D^{26}$=−3.2° (*c* 0.85, $CHCl_3$). ^{1}H NMR (400 MHz): δ 7.18 (d, J=8.5 Hz, 2H), 6.80 (d, J=8.5 Hz, 2H), 3.77 (s, 3H), 2.46 (ddd, J=7.0, 8.5 and 9.0 Hz, 1H), 1.93 (ddd, J=5.5, 7.5 and 9.0 Hz, 1H), 1.57 (ddd, J=5.0, 5.5 and 7.0 Hz, 1H), 1.21 (ddd, J=5.0, 7.5 and 8.5 Hz, 1H), 1.17 (s, 9H). IR (neat): 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, 72.83; H, 8.34%.

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

Colorless oil. Yield 77% (96% ee); $[\alpha]_D^{24}$=−42.1° (*c* 0.43, $CHCl_3$). ^{1}H NMR (400 MHz): δ 7.19–7.16 (m, 5H), 1.80 (dd, J=7.6 and 5.5 Hz, 1H), 1.70 (dd, J=5.5 and 4.5 Hz, 1H), 1.45 (s, 3H), 1.13 (s, 9H), 1.07 (dd, J=7.6 and 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, 77.67; H, 8.68%.

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

Colorless oil. Yield 30% (88% ee); $[\alpha]_D^{24}$=+22.8° (*c*0.25, $CHCl_3$). ^{1}H 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 and 9.3 Hz, 1H), 2.07 (ddd, J=5.7, 7.8 and 9.3), 1.71 (ddd, J=5.1, 5.7 and 7.4 Hz, 1H), 1.32 (ddd, J=5.1, 7.8 and 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%. Found: C, 75.62; H, 7.57%.

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

Colorless oil. Yield 42% (86% ee); $[\alpha]_D^{24}$=−6.5° (*c* 0.74 $CHCl_3$). ^{1}H 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 and 9.2 Hz, 1H), 2.08 (ddd, J=5.6, 7.8 and 9.2 Hz, 1H), 1.67 (ddd, J=5.1, 5.6, and 7.5 Hz, 1H), 1.33 (ddd, J=5.1, 7.8 and 8.6) 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, 64.06; H, 5.94%.

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

Colorless oil. Yield 48% (91% ee); $[\alpha]_D^{24}$=−6.6° (*c* 0.27, $CHCl_3$). ^{1}H 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 and 9.2 Hz, 1H), 2.03 (ddd, J=5.6, 7.8 and 9.2 Hz, 1H), 1.66 (ddd, J=5.0, 5.6 and 7.5 Hz, 1H), 1.30 (ddd, J=5.0, 7.8 and 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, 70.72; H, 7.33%.

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

Colorless oil. Yield 44% (91% ee); $[\alpha]_D^{24}=-47.6°$ (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 and 7.1 Hz, 2H), 1.90 (dd, J=7.8 and 5.6 Hz, 1H), 1.78 (dd, J=5.6 and 4.9 Hz, 1H), 1.46 (s, 3H), 1.15 (dd, J=7.8 and 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%. Found: C, 76.21; H, 7.92%.

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