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Asymmetric intramolecular cyclopropanation of diazo compounds with metallosalen complexes as catalyst: structural tuning of salen ligand

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Abstract—Intramolecular cyclopropanation of alkenyl α-diazoacetates and alkenyl diazomethyl ketones was examined by using optically active (ON^+)Ru(II)(salen) and Co(II)(salen) complexes as catalysts. For the cyclization of 2-alkenyl α-diazoacetates, Co(II)(salen) complexes **9** and **10** were found to be superior catalysts to the corresponding (ON^+)Ru(II)(salen) complexes **4** and **5**. On the other hand, (ON^+)Ru(II)(salen) complex **2** was found to be the catalyst of choice for the cyclization of 3-alkenyl diazomethyl ketones, and complex **4** was found to be a good catalyst for the cyclization of (*E*)-4-alkenyl diazomethyl ketones. The present study demonstrates that metallosalen complexes, especially optically active (ON^+)Ru(II)(salen) and Co(II)(salen) complexes, can serve as efficient catalysts for the cyclization of alkenyl diazocarbonyl compounds, if a suitable salen ligand is used as the chiral auxiliary.

1. Introduction

Molecules possessing a cyclopropane-ring substructure have received much attention because of their synthetic utility as building blocks and their occurrence as subunits of many natural products. Thus, a number of methodologies for the construction of cyclopropane units have already been reported. Among them, transition metal-catalyzed cyclopropanation of olefins with diazo compounds as carbenoid precursors is a highly useful method in terms of its simplicity and mild reaction conditions.[1] Furthermore, use of transition metal complexes bearing appropriate chiral ligand(s) enables control of the stereochemistry of the cyclopropanation.[1,2] Therefore, many transition metal complexes with chiral ligands have been prepared and employed as catalysts for asymmetric cyclopropanation.[1,2] Consequently, highly diastereo- (*trans*- or *cis*-) and enantioselective intermolecular cyclopropanations have been achieved in the last three decades.[1–3] In parallel with these studies, intramolecular cyclopropanation of diazocarbonyl compounds, which is an efficient method for construction of [*n*.1.0]bicyclic structures, has also been extensively studied using transition metal complexes as catalysts. Thus far, excellent catalysts such as Cu[bis(oxazoline)s],[4] Cu(semicorrin),[5] Cu(diamine),[6] Ru(Pybox),[7] Rh(MEPY) and its related complexes,[8] Rh_2(*S*-DOSP)$_2$,[9] (*R*)-β-*cis*-[Ru(II)(biaryldiamine)-$(CH_3CN)_2$][10] have been introduced and high enantioselectivity has been achieved in the intramolecular cyclopropanation of various kinds of α-diazocarbonyl compounds. Attempts have also been made using chiral Cu(I) complexes of biferrocene-based bis(oxazoline),[11] Ru(II)-diphenyl phosphino(oxazolinyl) quinoline,[12] Ru-based porphyrin,[13] though the enantioselectivity was moderate. However, the scope of each intramolecular cyclization reaction has been rather limited. For examples, chiral dirhodium(II)carboxamide complexes introduced by Doyle et al. are by far the best catalysts for cyclization of alkenyl diazoacetates and diazoacetamides,[8] although they are not very efficient for the cyclization of alkenyl α-diazoketones.[14] On the other hand, cyclization of alkenyl diazomethyl ketones with Cu(semicorrin) catalyst shows modest to high enantioselectivity (up to 95% ee), though it is less efficient for the cyclization of alkenyl α-diazoacetates.[5] Recently, Pérez-Píetro et al. reported that a rhodium complex, bearing a unique *o*-metallated aryl phosphine ligand, catalyzed cyclization of 4-alkenyl and 3-alkenyl diazomethyl ketones with good to

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high enantioselectivity (up to 95% and 80% ees, respectively).[15]

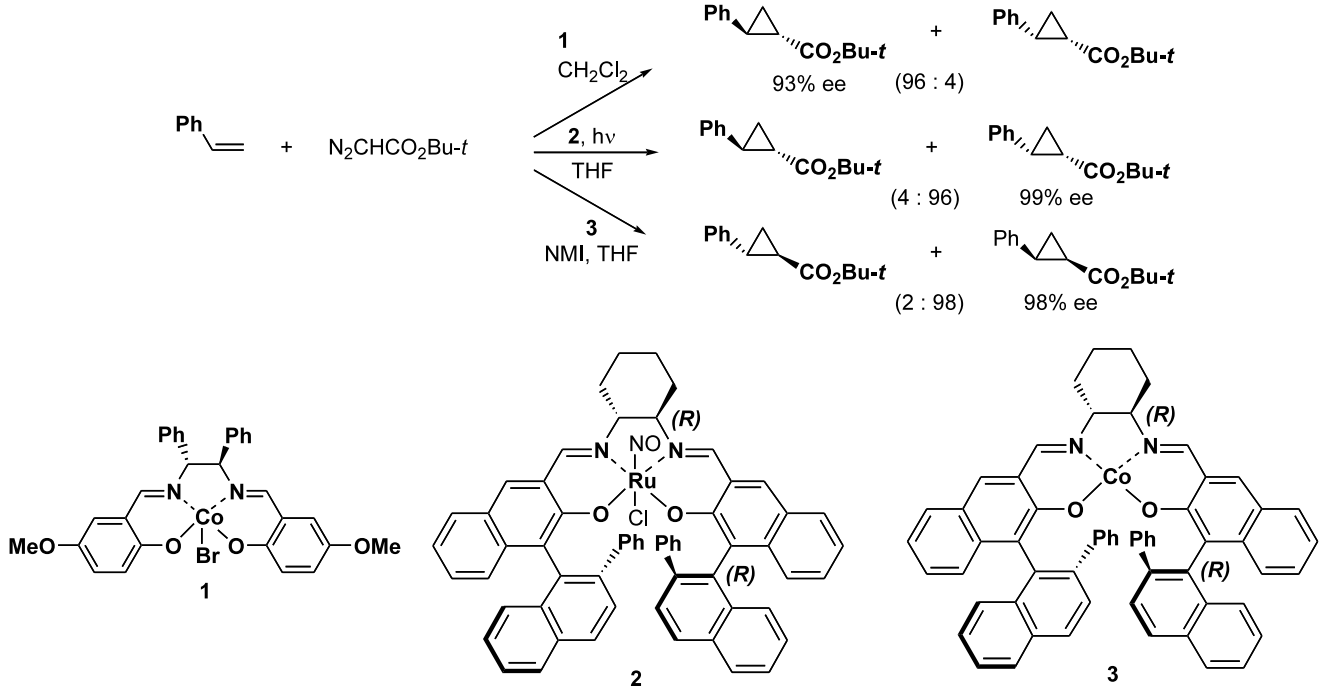
Despite the introduction of such excellent catalysts, no general catalyst for cyclization of alkenyl α-diazoesters and α-diazoketones is so far available. This might be mainly attributed to the fact that the transition state conformation of each cyclization varies with the substrate used.[14] It was considered to be difficult to control a wide variety of transition state conformations with only one catalyst. In contrast, use of a series of catalysts that can be readily derived from partial modification of a parent catalyst was considered to be a more attractive strategy for developing the general cyclization of alkenyl α-diazoesters and α-diazoketones.[1,2] We have recently demonstrated that some metallosalen complexes [hereafter denoted as M(salen)s] such as chiral Co(III)(salen), Co(II)(salen), and (ON$^+$)Ru(II)(salen) serve as efficient catalysts for intermolecular cyclopropanation.[3,16] As various types of salen ligands are easily derived from commercial or readily synthesized diamine and salicylaldehyde derivatives, the structure of M(salen)s was considered to be tunable in compliance with the substrate used and, therefore, M(salen)s were considered to be good candidates for the catalysts of various intramolecular cyclizations. Thus, we examined intramolecular cyclopropanation of alkenyl α-diazoesters[17] and of alkenyl diazomethyl ketones[18] using chiral M(salen)s as the catalysts.

2. Results and discussion

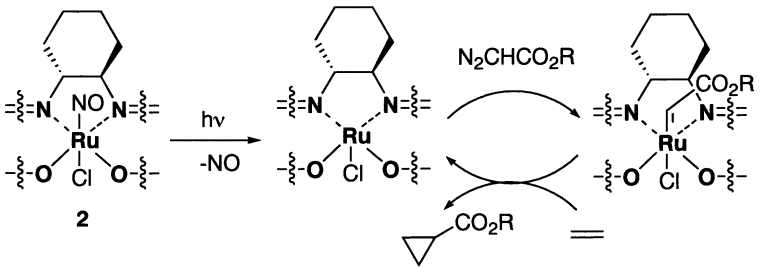
2.1. Intramolecular cyclopropanation of 2-alkenyl α-diazoacetates using metallosalen complexes

We have already reported that chiral Co(III)(salen) **1** catalyzes cyclopropanation of styrene with *t*-butyl α-diazoacetate in a highly *trans*- and enantioselective manner,[19] which chiral (ON$^+$)Ru(II)(salen) **2** and Co(II)(salen) **3** do in a highly *cis*- and enantioselective manner (Scheme 1).[3] It is also worth noting that complexes **2** and **3** show the opposite sense of enantioselection to each other, though they carry the same salen ligand. Based on this contrasting catalysis by Co- and Ru-(salen)s, we expected that the stereochemistry of cyclization of alkenyl α-diazoesters and of alkenyl diazomethyl ketones could be regulated by using appropriately designed Co- and Ru-(salen)s as the catalysts.

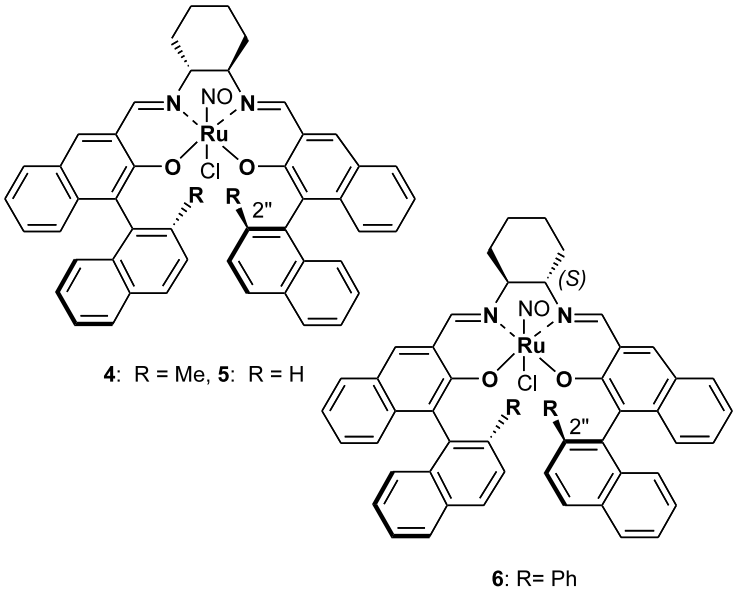
Accordingly, we first examined the cyclization of (*E*)-cinnamyl α-diazoacetate **7a** using complexes **1**–**3** as catalysts. The cyclization of Co(salen)s **1** and **3** was very slow when the reaction was carried out in 0.01 M substrate concentration. On the other hand, (ON$^+$)Ru(II)(salen) **2** catalyzed the desired reaction under the same reaction conditions, except that the reaction medium was irradiated with incandescent lamp.[3b] Complex **2** is coordinatively saturated and catalytically inactive. Therefore, photo-irradiation that promotes dissociation of the apical NO ligand and makes the catalyst active is indispensable for the present reaction (Scheme 2).[17,20] The enantioselectivity of the cyclization was moderate (70% ee), but the chemical yield was insufficient because dimerization of the diazoester forming the corresponding maleic and fumaric esters occurred competitively. Thus, the cyclization was performed under high dilution conditions to suppress the dimerization: a 0.074 M solution of the diazoester was added dropwise to the reaction medium including **3** over 24 h. Under the conditions, moderate enantioselectivity (70% ee) and acceptable chemical yield were obtained (Table 1, entry 1).



Scheme 1.

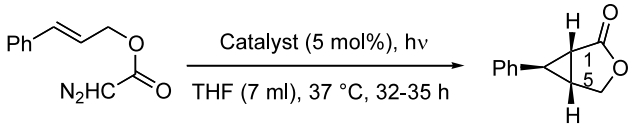


Scheme 2.



In the cyclopropanation using (ON$^+$)Ru(II)(salen) **2** as the catalyst, alkenes have been considered to approach the intermediary carbenoid species along Ru–O bond axis.[3b] In contrast to the intermolecular cyclopropanation, the intermediary carbenoid species in the cyclization of (*E*)-cinnamyl α-diazoacetate **7a** is linked to the alkenyl moiety. The linker necessarily causes steric repulsion with the 2″-phenyl group of the salen ligand upon the approach of the alkenyl moiety along the Ru–O bond (Fig. 1). Thus, we considered that the alkenyl moiety would approach the carbenoid species along the Ru–N_2 bond, reflecting the ligand conformation:[16,21] the alkenyl moiety would approach from the downwardly-bent naphthalene ring side of **2**. We also assumed that the C=O bond and the C=Ru bond in the

Table 1. Asymmetric intramolecular cyclopropanation of (*E*)-cinnamyl α-diazoacetate **7a** using (ON$^+$)Ru(II)(salen) complexes as catalysts under high dilution conditions



Entry	Catalyst	Yield (%)	% ee[a]	Config.[b]
1	**2**	66	70	1*S*,5*R*,6*R*
2	**4**	58	67	1*S*,5*R*,6*R*
3	**5**	54	82	1*S*,5*R*,6*R*
4	**6**	62	55	1*S*,5*R*,6*R*

[a] Enantiomeric excess was determined by GLC analysis using CHIRAL β-DEX column operated at 160°C.

[b] Determined by comparison with the reported specific rotation. $[\alpha]_D^{24.5}$ −90 (*c* 0.25, chloroform) (82% ee), [lit.[8a] $[\alpha]_D^{23}$ +130 (*c* 0.29, chloroform) for 1*R*,5*S*,6*S*-isomer].

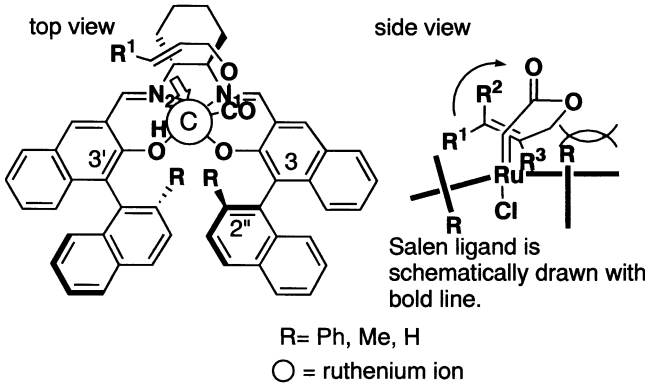
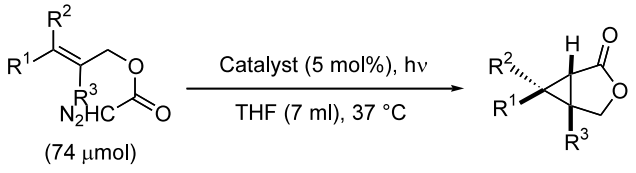


Figure 1.

carbenoid moiety would take antiperiplanar conformation, based on the proposal made by Doyle et al.[22] We further assumed that the alkenyl moiety would approach in a skewed-perpendicular manner to the C=Ru bond[3,8a,19,23] and that the moiety rotates clockwise as the reaction proceeds.[3a] These assumptions led us to the transition state model for the cyclization as described in Fig. 1. The model suggested that steric repulsion exists between the linker and the 2″-substituent (R) and the repulsion destabilizes the transition state, reducing enantioselectivity, especially when the 2″-substituent is bulky. Thus, we prepared complexes **4** and **5** bearing a small or no substituent at C2″ and examined the cyclization with them. Although the reaction with complex **4** showed moderate enantioselectivity, use of complex **5** improved enantioselectivities up to 82% ee (entries 2 and 3). We also examined the reaction with complex **6** as the catalyst but enantioselectivity was only moderate (entry 4). It is, however, noteworthy that the sense of asymmetric induction by complex **6** is opposite to that by complexes **2**, **4**, and **5**. These results suggest that the approach of the alkenyl moiety is dictated by the ligand conformation, which is primarily determined by the chirality of the diamine unit.[16] The configuration of the products was compatible with the proposed transition state model. The cyclization of several other 2-alkenyl α-diazoacetates with **4** or **5** as the catalyst was next examined (Table 2) but good substrates for the cyclization were found to be limited to (*E*)-2-alkenyl α-diazoactates. The cyclizations of *Z*- and 2-substituted alkenyl diazoacetates were less enantioselective. The *Z*-substituent was considered to cause steric repulsion with the C=O bond, especially upon the rotation of the alkenyl moiety and the C2 substituent (R^3) of the alkenyl moiety to cause with the salen ligand. These steric repulsions, especially the latter one, destabilized the desired transition state and reduced the enantioselectivity.

In the intermolecular cyclopropanation using Co(II)(salen) **3** as the catalyst, olefin has been considered to approach the intermediary carbenoid species along Co–N_2 bond axis.[3a] The above transition state model for the (ON^+)Ru(II)(salen)-catalyzed cyclization has also indicated that the alkenyl moiety approaches along the Co–N_2 bond axis. Therefore, Co(II)(salen) **3** or its derivatives was expected to be a better catalyst for the cyclization than (ON^+)Ru(II)(salen)s **2**, **4**, and **5**, though Co(II)(salen) **3** had shown very poor catalytic activity in the preliminary study (vide supra). Thus, we re-examined the cyclization of (*E*)-cinnamyl α-diazoacetate using complex **3** as the catalyst under much higher substrate concentration in the presence of *N*-methylimidazole.[24,25] The desired reaction proceeded slowly with moderate enantioselectivity, however, the undesired dimerization did not occur under the conditions (Table 3, entry 2). Based on the effect of the ligand structure on enantioselectivity observed in the (ON^+)Ru(II)(salen)-catalyzed reaction (vide supra), we next examined the cyclization with complex **10** and found that the reaction proceeded with excellent enantioselectivity of 96% ee, though the chemical yield was still

Table 2. Effect of olefinic substituent on enantioselectivity in the reactions using **4** or **5** as catalyst



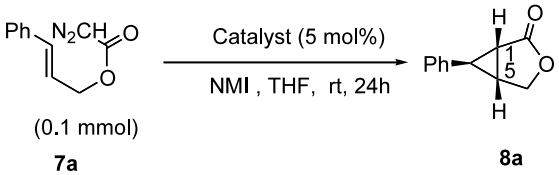
(74 μmol)

7b-h **8b-h**

Entry	Substrate	Catalyst	R^1	R^2	R^3	Temp. (°C)	Yield (%)	% ee[a]
1[b]	**7b**	**5**	*p*-ClC_6H_4	H	H	3	62	87[c]
2	**7c**	**4**	*p*-BrC_6H_4	H	H	37	56	87[d]
3	**7d**	**4**	*p*-$MeOC_6H_4$	H	H	37	63	87[e]
4	**7e**	**4**	PhC≡C	H	H	10	51	78[f]
5[g]	**7e**	**4**	PhC≡C	H	H	0	31	79[f]
6	**7f**	**5**	H	Ph	H	37	24	14[e]
7	**7g**	**5**	Ph	Me	H	37	44	40[h]
8	**7h**	**5**	Ph	H	Me	37	18	8[i]

[a] Absolute configuration has not been determined.
[b] Reaction was carried out with starting material (0.1 mmol) and THF (9 ml).
[c] Enantiomeric excess was determined by HPLC analysis using chiral column (DAICEL CHIRALPAK AD, hexane:isopropanol = 19:1, temperature = 40°C).
[d] Enantiomeric excess was determined by HPLC analysis using chiral column (DAICEL CHIRALPAK AD×2, hexane:isopropanol = 15:1, rt).
[e] Enantiomeric excess was determined by HPLC analysis using chiral column (DAICEL CHIRALPAK AD, hexanne:isopropanol = 15:1, rt).
[f] Enantiomeric excess was determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OD-H, hexane:isopropanol = 20:1, temperature = 40°C).
[g] Amount of THF was 1 ml.
[h] Enantiomeric excess was determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OB-H, hexane:isopropanol = 15:1, rt).
[i] Enantiomeric excess was determined by GLC analysis using CHIRAL β-DEX column operated at 200°C.

Table 3. Intramolecular cyclopropanation of (*E*)-cinnamyl α-diazoacetate using Co(II)-salen complexes as catalysts



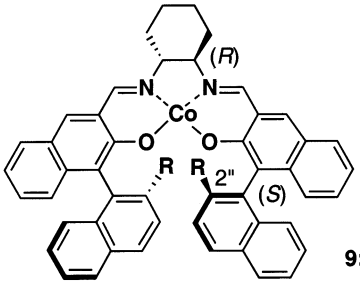
(0.1 mmol)

7a **8a**

Entry	Catalyst	THF (ml)	NMI (mmol)	Yield (%)	% ee[a]	Config.[b]
1	**3**	7	–	–	–	–
2	**3**	1	0.01	15	75	1*S*,5*R*,6*R*
3	**10**	1	0.01	24	96	1*S*,5*R*,6*R*
4	**10**	0.2	0.1	75	95	1*S*,5*R*,6*R*
5	**9**	0.2	0.1	67	97	1*S*,5*R*,6*R*

[a] Enantiomeric excess was determined by GLC analysis using CHIRAL β-DEX column operated at 160°C.
[b] Determined by comparison of specific optical rotation with the reported one. $[\alpha]_D^{24.5}$ −127 (*c* 0.25, chloroform) (97% ee) (entry 5), [lit.[8a] $[\alpha]_D^{23}$ +130 (*c* 0.29, chloroform) for 1*R*,5*S*,6*S*-isomer].

modest (entry 3). Further increase of substrate concentration improved the chemical yield to an acceptable level without decaying enantioselectivity (entry 4). Under the same conditions, the reaction with complex **9** also showed excellent enantioselectivity as well as acceptable chemical yield (entry 5). The configuration of the products obtained were compatible with the approach of alkenyl moieties along Co–N_2 bond axis.



9: R = Me, **10:** R = H

Accordingly, we examined the cyclization of various 2-alkenyl α-diazoacetates **7b–k** using complexes **9** and **10** as catalysts. Good to excellent levels of enantioselectivities have been realized in the cyclization of (*E*)-2-alkenyl α-diazoacetates (Table 4, entries 1–13).

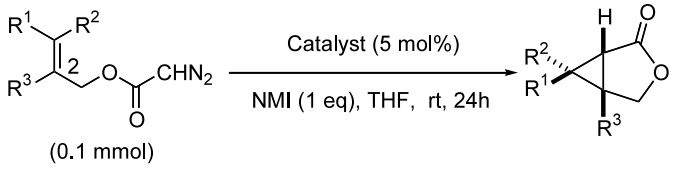
Amongst them, the cyclization of (*E*)-cinnamyl α-diazoacetate derivatives showed high enantioselectivity greater than 95% (entries 1–6). Cyclization of (*E*)-5-phenylpent-2-en-4-yn-1-yl α-diazoacetates with complex **9** also showed high enantioselectivity of 93% ee, though the chemical yield was moderate (entry 7). It is noteworthy that cyclization of non-conjugated (*E*)-2-alkenyl α-diazoacetates also proceeded with a good enantioselectivity of 79% ee, though slightly elevated reaction temperatures were needed to obtain an acceptable chemical yield (entry 11). Cyclization of 3,3-disubstituted substrates proceeded with good to high enantioselectivity, though higher reaction temperature was required in the cyclization of the substrate bearing *Z*-phenyl group (entries 14–18). Cyclization of (*Z*)-cinnamyl α-diazoacetates proceeded with moderate enantioselectivity but the reaction was slow (entry 19). The presence of a bulky *Z*-substituent like phenyl group is considered to destabilize the desired transition state and to decrease enantioselectivity (see Fig. 1). Introduction of a substituent at C2 also affected enantioselectivity adversely (entry 21), as observed in the (ON^+)Ru(II)(salen)-catalyzed reaction (vide supra).

Co(salen) and Ru(salen) possessing the same ligand showed similar catalytic performances: (*E*)-alkenyl diazoesters are the good substrates, 2-substituted alkenyl diazo compounds are poor substrate and both the Co- and Ru-(salen)s show the same sense of asymmetric induction, though the degrees of their asymmetric induction differ to considerable extent. As expected, these results suggested that the transition state conformation for Co(salen)-catalyzed cyclization is similar to that for (ON^+)Ru(II)(salen)-catalyzed cyclization (vide supra).

2.2. Intramolecular cyclopropanation of alkenyl diazomethyl ketones

With these results in hand, we next examined the cyclization of 3-alkenyl diazomethyl ketones. Only a few catalysts have been successfully applied to the stereocontrol of the cyclization of this class of compounds, as described earlier.[1,2,5,15] The cyclization of (*E*)-1-diazo-6-phenyl-5-hexen-2-one **11a** was first carried out with (ON^+)Ru(II)(salen) complex **5** as the catalyst under photo-irradiation conditions. The desired cyclization proceeded with a good yield but enantioselectivity of the cyclization was moderate (58% ee) (Table 5, entry 1). The cyclization with complex **4** also showed only moderate enantioselectivity (entry 2). In contrast to the cyclization of (*E*)-cinnamyl α-diazoacetate, however, the cyclization with **2** showed excellent enantioselectivity together with acceptable chemical yield (entry 3). The cyclization with complex **6** showed low enantioselectivity, though it proceeded smoothly (entry 4). It is noteworthy that the sense of enantioselection by complex **6** is opposite to that by complexes **2**, **4**, and **5**. This suggests that the approaching path of the alkenyl moiety is mainly dictated by the conformation

Table 4. Asymmetric intramolecular cyclopropanation using Co(II)-salen complexes **9** and **10** as catalyst

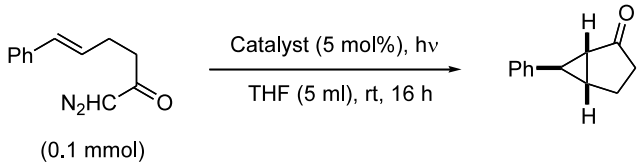


7b-k **8b-k**

Entry	Substrate	Catalyst	R^1	R^2	R^3	Yield (%)	% ee
1	**7b**	**9**	*p*-ClC_6H_4	H	H	72	98[a]
2	**7b**	**10**	*p*-ClC_6H_4	H	H	88	96[a]
3	**7c**	**9**	*p*-BrC_6H_4	H	H	70	97[b]
4	**7c**	**10**	*p*-BrC_6H_4	H	H	52	96[b]
5	**7d**	**9**	*p*-$MeOC_6H_4$	H	H	70	98[a]
6	**7d**	**10**	*p*-$MeOC_6H_4$	H	H	93	96[a]
7	**7e**	**9**	Ph-C≡C	H	H	32	93[c]
8	**7e**	**10**	Ph-C≡C	H	H	24	84[c]
9	**7i**	**10**	$PhCH_2CH_2$	H	H	10	91[d]
10[e]	**7i**	**10**	$PhCH_2CH_2$	H	H	48	82[d]
11[f]	**7i**	**10**	$PhCH_2CH_2$	H	H	81	79[d]
12[f]	**7i**	**9**	$PhCH_2CH_2$	H	H	18	73[d]
13[e]	**7k**	**10**	$(CH_3)_2CH$	H	H	34	75[g]
14	**7g**	**9**	Ph	Me	H	70	90[h]
15	**7g**	**10**	Ph	Me	H	47	91[h]
16	**7j**	**10**	Ph	Ph	H	23	79[i]
17[e]	**7j**	**10**	Ph	Ph	H	65	74[i]
18	**7j**	**9**	Ph	Ph	H	35	81[i]
19	**7f**	**9**	H	Ph	H	16	74[a]
20	**7f**	**10**	H	H	H	24	68[a]
21[f]	**7h**	**10**	Ph	H	Me	12	38[d]

[a] Enantiomeric excess was determined by HPLC analysis using chiral column (DAICEL CHIRALPAK AD, hexane:isopropanol = 15:1).
[b] Enantiomeric excess was determined by HPLC analysis using chiral column (DAICEL CHIRALPAK AD×2, hexane:isopropanol = 15:1).
[c] Enantiomeric excess was determined by HPLC analysis using chiral column (DAICEL CHIRALPAK AD, hexane:isopropanol = 20:1).
[d] Enantiomeric excess was determined by GLC analysis using CHIRAL β-DEX column operated at 160°C.
[e] Reaction was carried out at 35°C in the presence of 2 equiv. of *N*-methylimidazole.
[f] Reaction was carried out at 45°C in the presence of 2 equiv. of *N*-methylimidazole.
[g] Enantiomeric excess was determined by GLC analysis using CHIRAL β-DEX column operated at 120°C.
[h] Enantiomeric excess was determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OB-H hexane:isopropanol = 15:1).
[i] Enantiomeric excess was determined by HPLC analysis using chiral column (DAICEL CHIRALPAK AD, hexane:isopropanol = 9:1).

Table 5. Cyclization of (*E*)-1-diazo-6-phenyl-5-hexen-2-one **11a**



11a **12a**

Entry	Catalyst	Yield (%)	% ee[a]	Elution order[b]
1	**5**	62	58	+
2	**4**	60	44	+
3	**2**	78	94	+
4	**6**	81	12	–

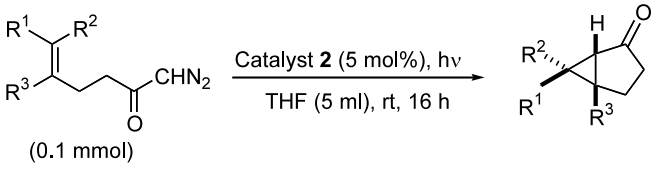
[a] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OD-H, hexane:isopropanol = 9:1).
[b] Plus sign means that the major enantiomer is eluted fast and minus sign means that the minor enantiomer is eluted fast.

of the salen ligand, as discussed in the cyclization of alkenyl α-diazoacetate (vide supra).[16] On the other hand, Co(salen)s **3**, **9**, and **10** showed no catalytic activity for this cyclization even under high substrate concentration.

Accordingly, we further examined the cyclization of several other 3-alkenyl diazomethyl ketones **11b–f** using complex **2** as the catalyst (Table 6). Good to excellent enantioselectivities as well as chemical yields were obtained in the reaction examined, except that the reaction of 3-substituted alkenyl diazomethyl ketone **11f** showed only modest enantioselectivity (entry 5). It is worth noting that the reactions of non-conjugated alkenyl diazomethyl ketones proceeded smoothly with high enantioselectivity (entries 1 and 2). The reaction of (*Z*)-3-alkenyl diazomethyl ketone, (*Z*)-1-diazo-6-phenyl-5-hexen-2-one, showed somewhat reduced enantioselectivity (79% ee, entry 4).

We also examined (ON^+)Ru(II)(salen)-catalyzed cyclization of 4-alkenyl diazomethyl ketones (Table 7).

Table 6. Cyclization of 3-alkenyl diazomethyl ketones **11b–f** with **2** as the catalyst

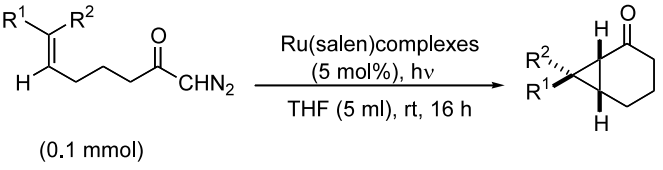


11b-f **12b-f**

Entry	Substrate	R^1	R^2	R^3	Yield (%)	% ee
1	**11b**	$(CH_3)_2$=CH$(CH_2)_2$	CH_3	H	72	93[a]
2	**11c**	CH_3	CH_3	H	65	87[b]
3	**11d**	PhC≡C	H	H	82	84[c]
4	**11e**	H	Ph	H	62	79[d]
5	**11f**	Ph	H	CH_3	31	12[e]

[a] Determined by GLC analysis using a 30 m×0.25 mm CHIRAL SUPELCO β-DEX column [column temperature: 130°C for 70 min, then programmed to 180°C at 5°C/min, and 180°C for 30 min]: 76.53 min (minor enantiomer), 77.31 min (major enantiomer)].
[b] Determined by GLC analysis using a 30 m×0.25 mm CHIRAL SUPELCO β-DEX column [column temperature: 90°C for 30 min, then programmed to 110°C at 2°C/min, and 110°C for 30 min]: 41.38 min (minor enantiomer), 41.94 min (major enantiomer)]. Absolute configuration was determined to be 2*R*,3*S* by comparing the reported specific optical rotation: $[\alpha]_D^{24}$ +45 (*c* 0.2, chloroform) (87% ee), [lit.[31] $[\alpha]_D^{23}$ −34.3 (*c* 1.0 chloroform) for 2*S*,3*R*-isomer (63% ee)].
[c] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OJ-H, hexane:isopropanol = 3:1).
[d] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OJ-H, hexane:isopropanol = 20:1).
[e] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OD-H hexane:isopropanol = 9:1).

Table 7. Intramolecular cyclopropanation of 4-alkenyl diazoketones **13a–e** with (ON$^+$)Ru(II)(salen) complexes as catalysts



13a-e **14a-e**

Entry	Substrate	Catalyst	R^1	R^2	Yield (%)	% ee
1	**13a**	**2**	Ph	H	42	54[a]
2	**13a**	**4**	Ph	H	63	88[a]
3	**13a**	**5**	Ph	H	56	71[a]
4	**13a**	**6**	Ph	H	45	13[a]
5	**13b**	**4**	*p*-ClC_6H_4	H	44	89[a]
6	**13c**	**4**	*p*-$MeOC_6H_4$	H	72	77[b]
7	**13d**	**4**	H	H	46	33[c]
8	**13e**	**4**	Ph	Me	36	5[d]

[a] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OD-H, hexane:isopropanol = 9:1).
[b] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OJ-H, hexane:isopropanol = 4:1).
[c] Determined by GLC analysis using a 30 m×0.25 mm CHIRAL SUPELCO β-DEX column.
[d] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OJ-H, hexane:isopropanol = 50:1).

We first examined the cyclization of (*E*)-1-diazo-7-phenyl-6-hexen-2-one **13a** with (ON$^+$)Ru(II)(salen) **2** as the catalyst (entry 1). Although the desired cyclization proceeded, enantioselectivity was moderate. The cyclization using complex **4** as the catalyst, however, showed high enantioselectivity of 88% (entry 2). Complex **5** was a less efficient catalyst (entry 3). Based on these results, we examined the cyclization of other 4-alkenyl diazomethyl ketones with complex **4** as the catalyst and found that the reactions of other (*E*)-substrates also showed moderate to good enantioselectivity (entries 5 and 6). Cyclization of non- and di-substituted alkenyl diazoketones (**13d** and **13e**), however, showed only modest enantioselectivity (entries 7 an 8).

3. Conclusion

It is well known that the catalyst of choice for asymmetric intramolecular cyclopropanation of alkenyl diazo compounds varies with the substrate used, probably because the transition state conformation for each

cyclization is strongly affected by several factors: the substitution pattern of the alkenyl moiety of the substrate, the length and the nature of the linker connecting the alkenyl and diazomethyl moieties, and metal ion.[1,2,14] This requires introduction of a structurally tunable catalyst in compliance with the substrate used. In this study, we were able to demonstrate that ruthenium and cobalt complexes carrying a salen ligand which can be readily modified are promising catalysts for asymmetric intramolecular cyclopropanation of various types of alkenyl diazo compounds.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded at 400 or 270 MHz on BRUKER DPX-400, JEOL GX-400, or JEOL EX-270 instruments. All signals were expressed as ppm down field from tetramethylsilane used as 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. High resolution EI mass spectra were obtained from JEOL JMX-SX/SX 102A spectrometer. Column chromatography was conducted on silica gel BW-820MH, 70–200 mesh ASTM, available from FUJI SILYSIA CHEMICAL LTD. Enantiomeric excesses were determined by HPLC analysis using SHIMADZU LC-10AT-VP and SHIMADZU GC–17A equipped with an appropriate optically active column, as described in the footnotes of the corresponding tables. Solvents were dried and distilled shortly before use. Reactions were performed under nitrogen if necessary.

Co(III)salen complex **1**,[19b] Co(II)salen complexes **3**, **9**, and **10**,[3a] and (ON$^+$)Ru(II)(salen) complexes **2**, **4**, and **6**[3b] were prepared according to the reported procedures. (*E*)-3-(4-Chlorophenyl)-2-propen-1-ol, (*E*)-3-(4-bromophenyl)-2-propen-1-ol, and (*E*)-3-(4-methoxyphenyl)-2-propen-1-ol were prepared from the corresponding acid by the sequence: (i) esterification with methanol in the presence of a catalytic amount of conc. H_2SO_4 and (ii) reduction with DIBAL-H.[26] (*E*)-5-Phenylpent-2-en-4-yn-1-ol, (*E*)-3-phenyl-2-methyl-2-propen-1-ol, (*E*)-5-phenyl-2-penten-1-ol, 3,3-diphenyl-2-propen-1-ol were prepared from the corresponding α,β-unsaturated ester by the reduction with DIBAL-H.[26] (*E*)-Cinnamyl α-diazoacetate **7a** and (*Z*)-cinnamyl α-diazoacetate **7f** were prepared according to the literature procedures.[8a] 5-Bromo-1-phenylpent-3-en-1-yne, (*Z*)-cinnamyl bromide, and (*E*)-4-bromo-1-methyl-1-phenyl-1-propene were prepared from the corresponding alcohols by treatment with PBr_3.[27] 4-Bromo-1-phenyl-1-butene was prepared according to the literature procedure.[28] 4-Bromo-1-(4-chlorophenyl)-1-butene, 4-bromo-1-(4-methoxyphenyl)-1-butene, and (*E*)-5-bromo-2-phenyl-2-pentene were prepared according to the procedure reported for the preparation of 4-bromo-1-phenylbutene.[28] All these compounds gave satisfactory ^{1}H NMR and MS data.

4.2. Synthesis of (ON$^+$)Ru(II)(salen) complex 5

Complex **5** was prepared according to an earlier reported procedure,[3b] except for the purification. The reaction mixture was concentrated under vacuum and the residue was purified quickly through SiO_2 chromatography using CH_2Cl_2/acetone (50:1) as eluent and the eluate was concentrated. Crystallization of the residue from CH_2Cl_2 and acetone afforded the desired complex as brown solid in 16% yield.

^{1}H NMR (400 MHz): δ 8.57 (s, 1H), 8.38 (s, 1H), 8.09 (d, $J=8.0$ Hz, 1H), 8.01–7.82 (m, 5H), 7.70–7.60 (m, 2H), 7.56–7.48 (m, 2H), 7.39–7.27 (m, 2H), 7.19 (t, $J=7.7$ Hz, 1H), 7.15–7.0 (m, 8H), 6.79–6.76 (m, 2H), 6.60 (t, $J=7.7$ Hz, 1H), 4.06 (br-t, $J=10.5$ Hz, 1H), 3.24 (br-q, $J=8.5$ Hz, 1H), 2.81 (br-s, 1H), 2.62 (br-s, 1H), 2.04–2.0 (br-m, 2H), 1.67–1.37 (br-m, 4H). IR (KBr): 3043, 2931, 2858, 2364, 2339, 1830, 1641, 1577, 1614, 1544, 1444, 1423, 1348, 1315, 1226, 1188, 1147, 1122, 1028, 952, 873, 777, 750, 688, 572, 538, 424 cm^{-1}. Anal. calcd for $C_{48}H_{36}ClN_3O_3Ru\cdot H_2O$: C, 67.24; H, 4.47; N, 4.90. Found: C, 67.35; H, 4.52; N, 4.90%.

4.3. Synthesis of 2-alkenyl α-diazoacetates

4.3.1. (*E*)-3-(4-Chlorophenyl)-2-propen-1-yl α-diazoacetate 7b. Diketene (0.47 mL, 6.1 mmol) in THF (2.5 mL) was added dropwise to a stirred solution of (*E*)-3-(4-chlorophenyl)-2-propen-1-ol (1.22 g, 4.81 mmol) and anhydrous NaOAc (26.3 mg, 0.33 mmol) in THF (10 mL) under refluxing conditions. The resulting solution was heated at reflux for 2 h. After cooling to room temperature, Et_2O (10 mL) and brine (5 mL) were added and the layers were separated. The aqueous layer was washed with Et_2O (2×15 mL). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the brown residue was chromatographed on silica gel (hexane/EtOAc=9:1) to afford (*E*)-3-(4-chlorophenyl)-2-propen-1-yl acetoacetate as a colorless liquid in 84% yield.

A solution of methanesulfonyl azide (0.56 g, 4.65 mmol) in acetonitrile (4 mL) was added dropwise over 10 min to a stirred solution of (*E*)-3-(4-chlorophenyl)-2-propen-1-yl acetoacetate (1.07 g, 4.23 mmol) and Et_3N (0.46 g, 0.64 mL, 4.6 mmol) in anhydrous acetonitrile (5 mL). The resulting yellow solution was monitored by TLC and stirred at room temperature until the acetoacetate was consumed (ca. 4 h). A 10% aqueous NaOH solution (5 mL) was added to the reaction mixture, stirred for 2 h, and diluted with water. The organic layer was separated and the water layer was washed twice with Et_2O/EtOAc (3:1, 15 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting orange residue was chromatographed on silica gel (hexane/EtOAc=19:1) to give **7b** in 68% yield. **7b**: a yellow solid, mp 34°C. ^{1}H NMR (270 MHz): δ 7.33 (d, $J=8.3$ Hz, 2H), 6.85 (d, $J=8.3$ Hz, 2H), 6.60 (d, $J=15.9$ Hz, 1H), 6.25 (dt, $J=15.9$, 6.5 Hz, 1H), 4.81 (dd, $J=6.5$, 1.2 Hz, 2H),

4.79 (br-s, 1H). IR (KBr): 3112, 2119, 1685, 1591, 1490, 1394, 1338, 1197, 1153, 1087, 974, 943, 846, 798, 736, 476 cm^{-1}. HREIMS m/z, calcd for $C_{11}H_9ClN_2O_2$ (M^+): 236.0353. Found: 236.0357.

4.3.2. (*E*)-3-(4-Bromophenyl)-2-propen-1-yl α-diazoacetate 7c. (*E*)-3-(4-Bromophenyl)-2-propen-1-ol (2.26 g, 10.6 mmol) was converted to **7c** in 47% yield, following the same procedure as that described for **7b**. **7c**: a yellow solid, mp 37°C. ^1H NMR (270 MHz): δ 7.44 (d, $J=8.3$ Hz, 2H), 7.25 (d, $J=8.3$ Hz, 2H), 6.58 (d, $J=15.8$ Hz, 1H), 6.27 (dt, $J=15.8$, 6.3 Hz, 1H), 4.80 (dd, $J=6.3$, 1.3 Hz, 2H), 4.78 (br-s, 1H). IR (KBr): 3112, 2927, 2113, 1676, 1585, 1487, 1452, 1390, 1350, 1240, 1180, 1070, 1010, 970, 800, 740 cm^{-1}. Anal. calcd for $C_{11}H_9BrN_2O_2$: C, 47.00; H, 3.23; N, 9.97. Found: C, 46.99; H, 3.37; N, 9.81.

4.3.3. (*E*)-3-(4-Methoxyphenyl)-2-propen-1-yl α-diazoacetate 7d. (*E*)-3-(4-Methoxyphenyl)-2-propen-1-ol (1.40 g, 7.8 mmol) was converted to **7d** in 53% yield, following the same procedure as that described for **7b**. **7d**: a yellow oil. ^1H NMR (270 MHz): δ 7.33 (d, $J=8.9$ Hz, 2H), 6.85 (d, $J=8.9$ Hz, 2H), 6.60 (d, $J=15.9$ Hz, 1H), 6.15 (dt, $J=15.8$, 6.5 Hz, 1H), 4.79 (dd, $J=6.5$, 1.0 Hz, 2H), 4.78 (br-s, 1H), 3.80 (s, 3H). IR (KBr): 3089, 2960, 2111, 1676, 1604, 1512, 1446, 1396, 1353, 1303, 1251, 1182, 1026, 966, 846, 812, 742, 719, 505 cm^{-1}. Anal. calcd for $C_{12}H_{12}N_2O_3$: C, 62.06; H, 5.21; N, 12.06. Found: C, 61.93; H, 5.25; N, 12.04%.

4.3.4. (*E*)-5-Phenylpent-2-en-4-yn-1-yl α-diazoacetate 7e. (*E*)-5-Phenylpent-2-en-3-yn-1-ol (0.77g, 4.86 mmol) was converted to **7e** in 52% overall yield, following the same procedure as that described for **7b**. **7e**: a yellow oil. ^1H NMR (400 MHz): δ 7.49–7.42 (m, 2H), 7.33–7.30 (m, 3H), 6.26 (dt, $J=15.6$, 6.0 Hz, 1H), 5.98 (d, $J=15.6$ Hz, 1H), 4.79 (br-s, 1H), 4.75 (dd, $J=6.0$, 1.4 Hz, 2H). IR (neat): 3114, 2943, 2111, 1697, 1595, 1488, 1442, 1388, 1350, 1240, 1174, 1074, 1045, 954, 912, 736, 682 cm^{-1}. HREIMS m/z, calcd for $C_{13}H_{10}N_2O_2$: 226.0742. Found: 226.0740.

4.3.5. (*E*)-3-Phenyl-2-buten-1-yl α-diazoacetate 7g. (*E*)-3-Phenyl-2-buten-1-ol (0.54 g, 3.67 mmol) was converted to **7g** in 48% overall yield, following the same procedure as that described for **7b**. **7g**: a yellow oil. ^1H NMR (400 MHz): δ 7.42–7.39 (m, 2H), 7.35–7.25 (m, 3H), 5.9 (td, $J=7.2$, 1.3 Hz, 1H), 4.88 (d, $J=7.2$ Hz, 2H), 4.77 (br-s, 1H), 2.12 (s, 3H). IR (neat): 3112, 2110, 1693, 1490, 1440, 1388, 1355, 1290, 1238, 1178, 1124, 985, 918, 740, 696, 669 cm^{-1}. Anal. calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.95. Found: C, 66.55; H, 5.60; N, 12.97%.

4.3.6. (*E*)-2-Methyl-3-phenyl-2-propen-1-yl α-diazoacetate 7h. (*E*)-2-Methyl-3-phenyl-2-propen-1-ol (1 g, 6.74 mmol) was converted to **7h** in 61% overall yield, following the same procedure as that described for **7b**. **7h**: a yellow oil. ^1H NMR (270 MHz): δ 7.37–7.2 (m, 5H), 6.52 (s, 1H), 4.81 (br-s, 1H), 4.73 (s, 2H), 1.89 (d, $J=1.3$ Hz, 3H). IR (neat): 3111, 2110, 1695, 1492, 1444, 1344, 1236, 1176, 1006, 964, 920, 854, 740, 700 cm^{-1}. Anal. calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.95. Found: C, 66.66; H, 5.63; N, 12.92%.

4.3.7. (*E*)-5-Phenyl-2-penten-1-yl α-diazoacetate 7i. (*E*)-5-Phenyl-2-penten-1-ol (0.32 g, 1.98 mmol) was converted to **7i** in 85% overall yield, following the same procedure as that described for **7b**. **7i**: a yellow oil. ^1H NMR (400 MHz): δ 7.30–7.16 (m, 5H), 5.81 (dt, $J=15.2$, 6.4 Hz, 1H), 5.62 (ddt, $J=15.2$, 6.4, 1.4 Hz, 1H), 4.74 (br-s, 1H), 4.59 (dd, $J=6.4$, 1.4 Hz, 2H), 2.71 (t, $J=7.8$ Hz, 2H), 2.38 (dt, $J=7.8$, 6.4 Hz, 2H). IR (neat): 3112, 3026, 2929, 2854, 2110, 1691, 1494, 1452, 1390, 1353, 1240, 1178, 970, 742, 700 cm^{-1}. Anal. calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.89; H, 6.17; N, 12.17%.

4.4. 3,3-Diphenyl-2-propen-1-yl α-diazoacetate 7j

3,3-Diphenyl-2-propen-1-ol (0.52 g, 2.5 mmol) was converted to **7j** in 63% overall yield, following the same procedure as that described for **7b**. **7j**: a yellow oil. ^1H NMR (400 MHz): δ 7.4–7.17 (m, 10H), 6.18 (t, $J=6.8$ Hz, 1H), 4.76 (br-s, 1H), 4.72 (d, $J=6.8$ Hz, 2H). IR (neat): 3057, 3026, 2110, 1693, 1629, 1598, 1577, 1492, 1444, 1388, 1357, 1334, 1128, 1240, 1178, 1109, 1076, 1026, 848, 763, 740, 700, 630 cm^{-1}. Anal. calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07. Found: C, 73.14; H, 5.13; N, 9.95%.

4.4.1. (*E*)-4-Methyl-2-penten-1-yl α-diazoacetate 7k[8a]. (*E*)-4-Methyl-2-penten-1-ol (0.37 g, 3.7 mmol) was converted to **7k** in 67% overall yield, following the same procedure as that described for **7b**. **7k**: a yellow oil. Spectroscopic data (^1H NMR and IR) were identical with the reported ones.[8a]

4.5. General procedure for intramolecular cyclopropanation of 2-alkenyl α-diazoacetates in the presence of (ON^+)Ru(II)(salen) complex (4 or 5) as catalyst

(ON^+)Ru(II)(salen) complex (3.7 μmol) was dissolved in THF (7 mL) under N_2. To the solution was added a solution of 2-alkenyl α-diazoacetate (74 μmol) in THF (1 mL) slowly over 24 h by using a syringe pump under the irradiation of incandescent light. The mixture was stirred for another 11 h and concentrated in vacuo. The residue was chromatographed on silica gel using an eluent suitable for each product to afford the corresponding bicyclic lactone. The enantiomeric excesses of products were determined by HPLC analysis using an optically active column, as described in the footnotes of Tables 1 and 2.

4.5.1. (1*S*,5*R*,6*R*)-6-Phenyl-3-oxabicyclo[3.1.0]hexan-2-one 8a[8a]. **8a** was obtained by SiO_2 chromatography with hexane/EtOAc (7:3) in 54% yield as a colorless solid; mp 104°C, $[\alpha]_D^{24}$ −106 (*c* 0.25, $CHCl_3$) (82% ee) (Table 1, entry 3). Lit.[8a] mp 106°C, $[\alpha]_D^{23}$ +130 (*c* 0.29, $CHCl_3$) for 1*R*,5*S*,6*S*-isomer. ^1H NMR spectrum of this sample was identical with the reported one.[8a]

4.5.2. 6-(4-Chlorophenyl)-3-oxabicyclo[3.1.0]hexan-2-one 8b. **8b** was obtained by SiO_2 chromatography with hexane/EtOAc (7:3) in 62% yield as a colorless solid; mp 130°C, $[\alpha]_D^{22}$ −103 (*c* 0.25, $CHCl_3$) (87% ee) (Table 2, entry 1). ^1H NMR (400 MHz): δ 7.28 (d, $J=8.6$ Hz, 2H), 7.0 (d $J=8.6$ Hz, 2H), 4.47 (dd, $J=9.6$, 4.8 Hz, 1H), 4.41 (d, $J=9.6$ Hz, 1H), 2.53–2.49 (m, 1H), 2.32 (dd, $J=3.2$, 2.8 Hz, 1H), 2.30 (dd, $J=4.0$, 2.8 Hz, 1H). IR (KBr): 1751, 1492, 1440, 1371, 1290, 1218, 1180, 1101, 1039, 1008, 962, 881, 856, 812, 754, 707, 626, 528, 495 cm^{-1}. Anal. calcd for $C_{11}H_9ClO_2$: C, 63.32; H, 4.35. Found: C, 63.11; H, 4.40%.

4.5.3. 6-(4-Bromophenyl)-3-oxabicyclo[3.1.0]hexan-2-one 8c. **8c** was obtained by SiO_2 chromatography with hexane/EtOAc (7:3) in 56% yield as a colorless solid; mp 124°C, $[\alpha]_D^{22}$ −91 (*c* 0.25, $CHCl_3$) (87% ee) (Table 2, entry 2). ^1H NMR (400 MHz): δ 7.43 (d, $J=8.5$ Hz, 2H), 6.94 (d, $J=8.5$ Hz, 2H), 4.47 (dd, $J=9.5$, 4.6 Hz, 1H), 4.41 (d, $J=9.5$ Hz, 1H), 2.53–2.49 (m, 1H), 2.30 (dd, $J=6.1$, 2.9 Hz, 1H), 2.28 (dd, $J=3.2$, 2.9 Hz, 1H). IR (KBr): 3033, 2964, 2900, 1747, 1490, 1369, 1290, 1217, 1180, 1101, 1037, 1004, 960, 875, 812, 746, 707, 626, 524, 484 cm^{-1}. Anal. calcd for $C_{11}H_9BrO_2$: C, 52.20; H, 3.58. Found: C, 52.25; H, 3.70%.

4.5.4. 6-(4-Methoxyphenyl)-3-oxabicyclo[3.1.0]hexan-2-one 8d. **8d** was obtained by SiO_2 chromatography with hexane/EtOAc (3:2) in 63% yield as a colorless solid; mp 79°C, $[\alpha]_D^{22}$ −101 (*c* 0.25, $CHCl_3$) (87% ee) (Table 2, entry 3). ^1H NMR (400 MHz): δ 7.01 (d, $J=9.5$ Hz, 2H), 6.84 (d, $J=8.7$ Hz, 2H), 4.45 (dd, $J=9.5$, 4.9 Hz, 1H), 4.40 (d, $J=9.5$ Hz, 1H), 3.79 (s, 3H), 2.50–2.46 (m, 1H), 2.30 (dd, $J=3.4$, 2.9 Hz, 1H), 2.27 (dd, $J=6.1$, 2.9 Hz, 1H). IR (KBr): 2918, 2841, 1745, 1610, 1579, 1515, 1446, 1369, 1296, 1184, 1153, 1099, 1037, 1004, 962, 873, 819, 786, 715, 621, 542, 493 cm^{-1}. Anal. calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.47; H, 5.99%.

4.5.5. 6-(2-Phenylethynyl)-3-oxabicyclo[3.1.0]hexan-2-one 8e. **8e** was obtained by SiO_2 chromatography with hexane/EtOAc (4:1) in 51% yield as a colorless solid; mp 71°C, $[\alpha]_D^{24}$ −107 (*c* 0.18, $CHCl_3$) (78% ee) (Table 2, entry 4). ^1H NMR (400 MHz): δ 7.38 (d, $J=8.6$ Hz, 2H), 7.32–7.16 (comp, 3H), 4.40 (dd, $J=9.5$, 4.6 Hz, 10H), 4.34 (d, $J=9.5$ Hz, 1H), 2.60 (m, 1H), 2.47 (dd, $J=6.1$, 2.7 Hz, 1H), 1.95 (dd, $J=3.2$, 2.7 Hz, 1H). IR (KBr): 3084, 2966, 2906, 1755, 1490, 1446, 1371, 1278, 1176, 1055, 1031, 962, 904, 867, 763, 698, 626, 532 cm^{-1}. HREIMS *m*/*z*, calcd for $C_{13}H_{10}O_2$ (M^+): 198.0681. Found: 198.0689.

4.5.6. 6-Phenyl-3-oxabicyclo[3.1.0]hexan-2-one 8f[7b,8a]. **8f** was obtained by SiO_2 chromatography with hexane/EtOAc (7:3) in 24% yield as a colorless solid; mp 81°C, $[\alpha]_D^{22}$ −32 (*c* 0.16, CH_2Cl_2) (14% ee) (Table 2, entry 6). Lit.[7b] $[\alpha]_D^{25}$ −52 (*c* 1.01, CH_2Cl_2) (24% ee); mp 79–80°C. Spectroscopic data (^1H NMR and IR) of this sample were identical with the reported ones.[8a]

4.5.7. 6-Methyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one 8g. **8g** was obtained by SiO_2 chromatography with hexane/EtOAc (4:1) in 44% yield as a colorless solid; mp 59°C, $[\alpha]_D^{22}$ −38 (*c* 0.25, $CHCl_3$) (40% ee) (Table 2, entry 7). ^1H NMR (400 MHz): δ 7.35–7.23 (m, 5H), 4.54 (dd, $J=10.0$, 5.6 Hz, 1H), 4.36 (ddd, $J=10.0$, 1.2, 0.8 Hz, 1H), 2.54 (ddd, $J=6.6$, 5.6, 1.2 Hz, 1H), 2.46 (dd, $J=6.6$, 0.8 Hz, 1H), 1.49 (s, 3H). IR (KBr): 1762, 1440, 1357, 1188, 1070, 1045, 995, 968, 866, 833, 758, 698 cm^{-1}. HREIMS *m*/*z*, calcd for $C_{12}H_{12}O_2$ (M^+): 188.0837. Found: 188.0839.

4.5.8. 5-Methyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one 8h. **8h** was obtained by SiO_2 chromatography with hexane/EtOAc (4:1) in 18% yield as an oil. $[\alpha]_D^{23}$ −13 (*c* 0.14, $CHCl_3$) (8% ee) (Table 2, entry 8). ^1H NMR (400 MHz): δ 7.35–7.27 (m, 3H), 7.15 (d, $J=6.8$ Hz, 2H), 4.40 (d, $J=9.2$ Hz, 1H), 4.21 (d, $J=9.2$ Hz, 1H), 2.49 (d, $J=3.2$ Hz, 1H), 2.38 (d, $J=3.2$ Hz, 1H), 1.17 (s, 3H). IR (KBr): 1762, 1602, 1496, 1448, 1375, 1326, 1261, 1164, 1029, 889, 864, 742, 700 cm^{-1}. HREIMS *m*/*z*, calcd for $C_{12}H_{12}O_2$ (M^+): 188.0837. Found: 188.0838.

4.6. General procedure for intramolecular cyclopropanation of 2-alkenyl α-diazoacetates in the presence of Co(II)-salen complexes 9 or 10 as catalyst

2-Alkenyl α-diazoacetate (0.1 mmol) was placed in a S tube and the tube was purged with nitrogen. To the tube were added a 0.5 M solution of *N*-methylimidazole in THF (0.2 mL) and Co(II) salen complex (5 μmol), successively. The reaction mixture was stirred for 24 h at room temperature and the solvent was removed under vacuo. The residue was chromatographed on silica gel using an appropriate eluent to afford the corresponding bicyclic lactone. The enantiomeric excesses of products were determined by HPLC analysis using an optically active column, as described in the footnotes of Tables 3 and 4.

4.6.1. (1*S*,5*R*,6*R*)-6-Phenyl-3-oxabicyclo[3.1.0]hexan-2-one 8a. A colorless solid, 67% yield, $[\alpha]_D^{22}$ −127 (*c* 0.25, $CHCl_3$) (97% ee) (Table 3, entry 5).

4.6.2. 6-(4-Chlorophenyl)-3-oxabicyclo[3.1.0]hexan-2-one 8b. A colorless solid, 72% yield, $[\alpha]_D^{22}$ −118 (*c* 0.25, $CHCl_3$) (98% ee) (Table 4, entry 1).

4.6.3. 6-(4-Bromophenyl)-3-oxabicyclo[3.1.0]hexan-2-one 8c. A colorless solid, 70% yield, $[\alpha]_D^{25}$ −102 (*c* 0.16, $CHCl_3$) (97% ee) (Table 4, entry 3).

4.6.4. 6-(4-Methoxyphenyl)-3-oxabicyclo[3.1.0]hexan-2-one 8d. A colorless solid, 70% yield, $[\alpha]_D^{22}$ −113 (*c* 0.25, $CHCl_3$) (98% ee) (Table 4, entry 5).

4.6.5. 6-(2-Phenylethynyl)-3-oxabicyclo[3.1.0]hexan-2-one 8e. A colorless solid, 32% yield, $[\alpha]_D^{25}$ −130 (*c* 0.175, $CHCl_3$) (93% ee) (Table 4, entry 7).

4.6.6. 6-Phenyl-3-oxabicyclo[3.1.0]hexan-2-one 8f. A colorless solid, 16% yield, $[\alpha]_D^{25}$ −168 (*c* 0.16, CH_2Cl_2) (74% ee) (Table 4, entry 19).

4.6.7. 6-Methyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one 8g. A colorless solid, 70% yield, $[\alpha]_D^{22}$ −92 (*c* 0.25, $CHCl_3$) (90% ee) (Table 4, entry 14).

4.6.8. 5-Methyl-6-phenyl-3-oxabicyclo[3.1.0]hexan-2-one 8h. An oil, 12% yield, $[\alpha]_D^{23}$ −61 (*c* 0.14, $CHCl_3$) (38% ee) (Table 4, entry 21).

4.6.9. 6-(2-Phenylethyl)-3-oxabicyclo[3.1.0]hexan-2-one 8i. **8i** was obtained by SiO_2 chromatography with hexane/EtOAc (7:3) in 81% yield as an oil. $[\alpha]_D^{24}$ −10 (*c* 0.7, $CHCl_3$) (79% ee) (Table 4, entry 11). ^{1}H NMR (400 MHz): δ 7.31–7.16 (m, 5H), 4.26 (dd, J=9.3, 4.9 Hz, 1H), 4.16 (d, J=9.3 Hz, 1H), 2.83–2.69 (m, 2H), 1.94 (br-q, J=4.9 Hz, 1H), 1.86 (dd, J=5.8, 2.7 Hz, 1H), 1.76–1.59 (m, 2H), 1.24–1.17 (m, 1H). IR (KBr): 3033, 2964, 2922, 2856, 1770, 1452, 1373, 1174, 975, 754, 702, 626 cm^{-1}. Anal. calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.94; H, 7.05%.

4.6.10. 6,6-Diphenyl-3-oxabicyclo[3.1.0]hexan-2-one 8j. **8j** was obtained by SiO_2 chromatography with hexane/EtOAc (7:3) in 35% yield as a colorless solid; mp 117°C, $[\alpha]_D^{23}$ +34 (*c* 0.5, $CHCl_3$) (81% ee) (Table 4, entry 18). ^{1}H NMR (400 MHz): δ 7.44–7.14 (m, 10H), 4.48 (dd, J=10.0, 5.4 Hz, 1H), 4.23 (ddd, J=10.0, 1.0, 0.7 Hz, 1H), 2.95 (ddd, J=6.5, 5.4, 1.0 Hz, 1H), 2.81 (dd, J=6.5, 0.7 Hz, 1H). IR (KBr): 3060, 3028, 2962, 2906, 1766, 1664, 1598, 1492, 1446, 1361, 1286, 1172, 1082, 1043, 981, 925, 881, 846, 759, 705, 665, 609, 547, 470 cm^{-1}. Anal. calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.47; H, 5.63%.

4.6.11. 6-(1-Methylethyl)-3-oxabicyclo[3.1.0]hexan-2-one 8k[8a]. **8k** was obtained by SiO_2 chromatography with hexane/EtOAc (7:3) in 34% yield as a colorless oil. $[\alpha]_D^{23}$ −17 (*c* 0.175, $CHCl_3$) (75% ee) (Table 4, entry 13). Spectroscopic data (^{1}H NMR and IR) of this sample were identical with the reported ones.[8a]

4.7. Synthesis of alkenyl diazomethyl ketones

4.7.1. (*E*)-1-Diazo-6-phenyl-5-hexen-2-one 11a[29]. NaH (0.22 g, 5.5 mmol) was washed twice with hexane (2 mL) and dried under N_2. Freshly distilled THF (14 mL) was added to NaH under N_2. The suspension was cooled to 0°C and acetylacetone (0.5 mL, 5.5 mmol) was added dropwise and stirred for 10 min. To this solution was added a solution of *n*-BuLi (1.69 M, 3.25 mL, 5.25 mmol) in hexane and the resulting yellowish orange solution was stirred at 0°C for an additional 20 min. To this solution was added a solution of cinnamyl bromide (1.08 g, 5.5 mmol) in THF (2 mL) at 0°C and the reaction mixture was slowly warmed to room temperature with stirring. After 30 min, the reaction was quenched with aqueous NH_4Cl solution (5 mL). Diethyl ether (10 mL) was added to the mixture and the organic layer was separated. The aqueous layer was extracted twice with Et_2O (10 mL). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was chromatographed on silica gel with hexane/EtOAc (12:1) to afford 8-phenyl-7-octene-2,4-dione (0.77 g) in 72% yield.

A solution of methanesulfonyl azide (0.4 g, 3.38 mmol) in acetonitrile (1 mL) was added dropwise over 5 min to a stirred solution of 8-phenyl-7-octene-2,4-dione (0.61 g, 2.82 mmol) and Et_3N (0.47 mL, 3.38 mmol) in anhydrous acetonitrile (10 mL). The resulting yellow solution was stirred at room temperature for another 4 h for completion of diazo transfer. The reaction mixture was quenched with aqueous NH_4Cl (10 mL) and extracted twice with Et_2O (25 mL). The organic layer was concentrated in vacuo. Then, aqueous NaOH solution (10%, 3 mL) was added to the crude 3-diazo-8-phenyl-7-octene-2,4-dione, stirred for 30 min, diluted with water (10 mL) and extracted twice with Et_2O/EtOAc (3:1, 25 mL). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The orange residue was chromatographed on silica gel with hexane/EtOAc (10:1) to give **11a** in 64% yield. **11a**: a yellow oil. ^{1}H NMR (400 MHz): δ 7.34–7.18 (m, 5H), 6.42 (d, J=15.9 Hz, 1H), 6.19 (dt, J=15.9, 6.8 Hz, 1H), 2.55–2.51 (m, 4H). IR (neat): 3018, 2931, 2106, 1639, 1492, 1373, 1325, 1147, 966, 744, 694, 496 cm^{-1}.

4.7.2. (5*E*)-1-Diazo-6,7,10-dimethylundec-5,9-dien-2-one 11b. Compound **11b** was prepared in 45% yield from geranyl bromide (2 g, 9.20 mmol) in the same procedure as described for **11a**. **11b**: a yellow oil. ^{1}H NMR (400 MHz): δ 5.24 (br-s, 1H), 5.08 (m, 2H), 2.33 (br-m, 4H), 2.06 (dt, J=7.6, 7.2 Hz, 2H), 1.98 (t, J=7.2 Hz, 2H), 1.67 (s, 3H), 1.61 (s, 3H), 1.59 (s, 3H). IR (KBr): 2966, 2922, 2854, 2104, 1641, 1444, 1375, 1321, 1259, 1141, 1109, 806 cm^{-1}. HREIMS m/z, calcd for $C_{13}H_{20}N_2O$: 220.1576. Found: 220.1572.

4.7.3. 1-Diazo-6-methyl-5-hepten-2-one 11c30a. Compound **11c** was prepared in 47% yield from prenyl bromide (1.22 g, 4.81 mmol) in the same procedure as described for **11a**. **11c**: a yellow oil. ^{1}H NMR (400 MHz) δ 5.23 (br-s, 1H), 5.09 (t, J=6.2 Hz, 1H), 2.32 (pseud-s, 4H), 1.68 (s, 3H), 1.62 (s, 3H). IR (KBr): 3084, 2918, 2858, 2102, 1639, 1452, 1317, 1089, 1029, 983, 891, 859, 773, 638, 495 cm^{-1}.

4.7.4. (*E*)-1-Diazo-8-phenyloct-5-en-7-yn-2-one 11d. Compound **11d** was prepared in 47% yield from 5-bromo-1-phenylbut-3-en-1-yne (0.35 g, 1.52 mmol) in the same procedure as described for **11a**. **11d**: a yellow oil. ^{1}H NMR (400 MHz): δ 7.34–7.31 (m, 2H), 7.30–7.28 (m, 3H), 6.21 (dt, J=15.6, 7.7 Hz, 1H), 5.76 (d, J=15.6, Hz, 1H), 5.26 (br-s, 1H), 2.51–2.44 (m, 4H). IR (neat): 3018, 2925, 2106, 1638, 1488, 1373, 1325, 1166, 954, 758, 690, 528 cm^{-1}. HREIMS m/z, calcd for $C_{14}H_{12}N_2O$ (M^+): 224.0950. Found: 224.0946.

4.7.5. (*Z*)-1-Diazo-6-phenyl-5-hexen-2-one 11e. Compound **11e** was prepared in 53% yield from (*Z*)-cinnamyl bromide (1.08 g, 5.5 mmol) in the same

procedure as described for **11a**. **11e**: a yellow oil. ^{1}H NMR (400 MHz): δ 7.35–7.20 (m, 5H), 6.47 (d, $J=11.1$ Hz, 1H), 5.62 (dt, $J=11.1$, 6.6 Hz, 1H), 5.21 (br-s, 1H), 2.67 (ddd, $J=15.1$, 7.5, 1.7 Hz, 2H), 2.44 (br-s, 2H). IR (neat): 3018, 2925, 2106, 1730, 1639, 1492, 1373, 1325, 1147, 966, 918, 769, 700 cm^{-1}. HREIMS m/z, calcd for $C_{12}H_{12}N_2O$ (M^+-N_2): 172.0888. Found: 172.0894.

4.7.6. (*E*)-1-Diazo-5-methyl-6-phenyl-5-hexen-2-one 11f. Compound **11f** was prepared in 53% yield from (*E*)-3-bromo-2-methyl-1-phenyl-1-propene (1.56 g, 7.39 mmol) in the same procedure as described for **11a**. **11f**: a yellow oil. ^{1}H NMR (400 MHz): δ 7.33–7.29 (m, 2H), 7.22–7.17 (m, 3H), 6.29 (s, 1H), 5.28 (br-s, 1H), 2.51 (br-m, 4H), 1.87 (d, $J=1.2$ Hz, 3H). IR (neat): 2920, 2104, 1641, 1492, 1444, 1369, 1329, 1142, 1024, 918, 744, 700, 511 cm^{-1}. HREIMS m/z, calcd for $C_{13}H_{14}N_2O$ (M^+-N_2): 186.1045. Found: 186.1055.

4.7.7. (*E*)-1-Diazo-7-phenyl-6-hepten-2-one 13a[31]. Freshly distilled THF (13 mL), diisopropylamine (1.84 mL, 13.26 mmol), and *n*-BuLi (1.69 M of hexane solution, 8.2 mL, 13.26 mmol) were successively placed in a 100 mL flask, cooled at −78°C, and stirred for 1 h at the temperature. To this mixture was added acetylacetone (0.67 mL, 6.63 mmol) dropwise and stirred for another 1 h at −78°C. To the solution, were successively and slowly added a solution of (*E*)-4-bromo-1-phenyl-1-butene (1.4 g, 6.63 mmol) in THF (2 mL) and *N*,*N*′-dimethylpropyleneurea (13 mL) over 20 min, and the mixture was further stirred for 6 h and quenched with aqueous NH_4Cl. Then, 20 mL of Et_2O was added and the organic layer was separated. The aqueous layer was extracted twice with Et_2O (10 mL). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel with hexane/EtOAc (19:1–12:1) to afford (*E*)-9-phenyl-8-octene-2,4-dione in 56% yield.

(*E*)-9-Phenyl-8-octene-2,4-dione (0.61 g, 2.82 mmol) was dissolved in acetonitrile (10 mL) and, to this solution, triethylamine (0.47 mL, 3.38 mmol) was added. Then, a solution of methanesulfonyl azide (0.4 g, 3.38 mmol) in acetonitrile (1 mL) was added dropwise over 5 min with stirring. The resulting yellow solution was further stirred for 4 h at room temperature to complete diazo transfer. The reaction mixture was quenched with aqueous NH_4Cl (10 mL) and extracted twice with Et_2O (25 mL). The organic layer was concentrated in vacuo. Aqueous NaOH solution (10%, 2 mL) was added to the crude (*E*)-3-diazo-9-phenyl-8-octene-2,4-dione, stirred for 30 min, diluted with water and extracted twice with Et_2O/EtOAc (3:1, 25 mL). The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the orange residue was chromatographed on silica gel with hexane/EtOAc (10:1) to give **13a** in 54% yield. **13a**: a yellow oil. ^{1}H NMR spectrum of this sample was identical with the reported ones.[31]

4.7.8. (*E*)-1-Diazo-7-(4-chlorophenyl)-6-hepten-2-one 13b. Compound **13b** was prepared in 29% yield from (*E*)-4-bromo-1-(4-chlorophenyl)-1-butene (2 g, 8.14 mmol) in the same procedure as described for **13a**. **13b**: a yellow oil. ^{1}H NMR (400 MHz): δ 7.38–7.25 (m, 4H), 6.34 (d, $J=15.6$ Hz, 1H), 6.14 (dt, $J=15.6$, 7.2 Hz, 1H), 5.23 (br-s, 1H), 2.40 (br-s, 2H), 2.25 (dt, $J=7.4$, 7.2 Hz, 2H), 1.80 (tt, $J=7.4$, 7.2 Hz, 2H). IR (neat): 3105, 3026, 2933, 2102, 1639, 1490, 1373, 1321, 1091, 1010, 966, 846, 802, 678 cm^{-1}. HREIMS m/z, calcd for $C_{13}H_{13}N_2ClO$ (M^+-N_2): 220.0655. Found: 220.0659.

4.7.9. (*E*)-1-Diazo-7-(4-methoxyphenyl)-6-hepten-2-one 13c. Compound **13c** was prepared in 71% yield from (*E*)-4-bromo-1-(4-methoxyphenyl)-1-butene (1.5 g, 6.21 mmol) in the same procedure as described for **13a**. **13c**: a yellow solid, mp 53°C. ^{1}H NMR (400 MHz): δ 7.26 (d, $J=8.8$ Hz, 2H), 6.83 (d, $J=8.8$ Hz, 2H), 6.33 (d, $J=15.8$ Hz, 1H), 6.01 (dt, $J=15.8$, 7.1 Hz, 1H), 5.23 (br-s, 1H), 3.79 (s, 3H), 2.36 (br-s, 2H), 2.24 (dt, $J=7.3$, 7.1 Hz, 2H), 1.80 (tt, $J=7.5$, 7.3 Hz, 2H). IR (KBr): 3091, 3003, 2933, 2904, 2835, 2100, 1637, 1604, 1510, 1458, 1384, 1303, 1176, 1149, 1107, 1028, 975, 806, 731, 553, 497 cm^{-1}. Anal. calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.85; H, 6.57; N, 11.44%.

4.7.10. (*E*)-1-Diazo-6-hepten-2-one 13d[31]. Compound **13d** was prepared in 63% yield from 4-bromo-1-butene (2 g, 14.81 mmol) in the same procedure as described for **13a**. **13d**: a yellow oil. Spectroscopic data (^{1}H NMR and IR) of this sample were in agreement with the reported ones.[31]

4.7.11. (*E*)-1-Diazo-7-phenyl-6-octen-2-one 13e. Compound **13e** was prepared in 43% yield from (*E*)-5-bromo-2-phenyl-2-pentene (1.5 g, 6.63 mmol) in the same procedure as described for **13a**. **13e**: a yellow oil. ^{1}H NMR (400 MHz): δ 7.38–7.20 (m, 5H), 5.73 (t, $J=7.1$ Hz, 1H), 5.23 (br-s, 1H), 2.37 (br-s, 2H), 2.25 (dt, $J=7.3$, 7.1 Hz, 2H), 2.02 (s, 3H), 1.80 (tt, $J=7.6$, 7.3 Hz, 2H). IR (neat): 3026, 2931, 2100, 1641, 1492, 1444, 1373, 1143, 1107, 1080, 1024, 758, 698, 578, 462 cm^{-1}. HREIMS m/z, calcd for $C_{14}H_{16}N_2O$ (M^+-N_2): 200.1201. Found: 200.1201.

4.8. General procedure for intramolecular cyclopropanation of 3-alkenyl diazomethyl ketones using (ON^+)Ru(II)(salen) complex 2 as the catalyst

(ON^+)Ru(II)(salen) complex **2** 4.9 mg, 5 μmol) was dissolved in 4 mL of THF under N_2. To this mixture was added a THF solution (1 mL) of 3-alkenyl diazomethyl ketone (0.1 mmol) dropwise over a period of 12 h using a syringe pump under irradiation of incandescent light. The reaction mixture was stirred for another 4 h and concentrated in vacuo. The residue was chromatographed on silica gel using hexane and ethyl acetate (11:1) as eluent to yield the corresponding [3.1.0]bicyclic ketone. The enantiomeric excess of the product was determined as described in the footnotes of Tables 5 and 6.

4.8.1. 6-Phenylbicyclo[3.1.0]hexan-2-one 12a. Colorless solid, mp 101°C. Yield: 78%, 94% ee, $[\alpha]_D^{22}$ −95 (*c* 0.275, $CHCl_3$) (Table 5, entry 3). ^1H NMR (400 MHz): δ 7.28 (dd, $J=8.4$, 7.1 Hz, 2H), 7.21 (d, $J=8.4$ Hz, 1H), 2.41 (comp, 2H), 2.32–2.11 (m, 4H). IR (KBr): 2935, 2873, 1712, 1658, 1599, 1494, 1458, 1404, 1296, 1267, 1219, 1191, 1072, 1036, 875, 798, 752, 700, 601, 522, 462 cm^{-1}. Anal. calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02; Found: C, 83.42; H, 7.04%.

4.8.2. 6-Methyl-6-(4-methyl-3-penten-1-yl)bicyclo-[3.1.0]hexan-2-one 12b. Colorless oil. Yield: 72%, 93% ee, $[\alpha]_D^{24}$ +27 (*c* 0.46, $CHCl_3$) (Table 6, entry 1). ^1H NMR (400 MHz) δ 5.05 (tt, $J=7.1$, 1.5 Hz, 1H), 2.34–2.18 (m, 2H), 2.09–2.00 (m, 3H), 1.95–1.86 (m, 2H), 1.68 (comp, 4H), 1.60 (s, 3H), 1.33–1.20 (m, 2H), 1.14 (s, 3H). IR (KBr): 2935, 2858, 1720, 1652, 1600, 1494, 1296, 1267, 1190, 1078, 1026, 968, 875, 802 cm^{-1}. HREIMS *m*/*z*, calcd for $C_{13}H_{20}O$ (M^+): 192.1514. Found: 192.1529.

4.8.3. (1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.0]hexan-2-one 12c[32,33]. Colorless oil. Yield: 65%, 87% ee, $[\alpha]_D^{24}$ +45 (*c* 0.2 $CHCl_3$) (87% ee). Lit.[32] $[\alpha]_D^{23}$ −34.3 (*c* 1.0 $CHCl_3$) for 1*S*,5*R*-isomer (63% ee) (Table 6, entry 2). ^1H NMR spectrum of this sample was in agreement with the reported one.[33b]

4.8.4. 6-(2-Phenylethynyl)bicyclo[3.1.0]hexan-2-one 12d. Colorless oil. Yield: 82%, 84% ee, $[\alpha]_D^{22}$ −121 (*c* 0.27, $CHCl_3$) (Table 6, entry 3). ^1H NMR (400 MHz): δ 7.37 (d, $J=7.3$ Hz, 2H), 7.30–7.26 (m, 3H), 2.42 (br-q, $J=4.5$ Hz, 1H), 2.27–2.16 (m, 3H), 2.09 (dd, $J=9.3$, 1.0 Hz, 1H), 2.05 (dd, $J=9.2$, 8.3 Hz, 1H), 1.96 (dd, $J=3.7$, 2.9 Hz, 1H). IR (neat): 2949, 1722, 1596, 1488, 1321, 1272, 1182, 1151, 1020, 869, 798, 760, 694, 530 cm^{-1}. HREIMS *m*/*z*, calcd for $C_{14}H_{12}O$ (M^+): 196.0888. Found: 196.0885.

4.8.5. 6-Phenylbicyclo[3.1.0]hexan-2-one 12e. Colorless oil. Yield: 62%, 79% ee, $[\alpha]_D^{22}$ +36 (*c* 0.28, $CHCl_3$) (Table 6, entry 4). ^1H NMR (400 MHz): δ 7.33–7.23 (m, 5H), 2.79 (dd, $J=8.7$, 8.0 Hz, 1H), 2.42 (ddd, $J=10.7$, 8.0, 5.4 Hz, 1H), 2.29 (dd, $J=9.3$, 6.5 Hz, 1H), 2.26–2.17 (m, 1H), 1.96 (dd, $J=13.4$, 9.3 Hz, 1H), 1.86 (dd, $J=19.0$, 10.7 Hz, 1H), 0.926 (dd, $J=19.0$, 8.7 Hz, 1H); IR (neat): 2941, 2858, 1720, 1602, 1494, 1406, 1305, 1186, 933, 867, 779, 758, 702, 461 cm^{-1}. HREIMS *m*/*z*, calcd for $C_{12}H_{12}O$ (M^+): 172.0888. Found: 172.0888.

4.8.6. 5-Methy-6-phenylbicyclo[3.1.0]hexan-2-one 12f. Colorless oil. Yield: 31%, 12% ee, $[\alpha]_D^{24}$ +3 (*c* 0.22, $CHCl_3$) (Table 6, entry 5). ^1H NMR (400 MHz): δ 7.32–7.23 (m, 3H), 7.14 (d, $J=7.6$ Hz, 2H), 2.59 (d, $J=3.2$ Hz, 1H), 2.36–2.16 (m, 3H), 2.14 (d, $J=3.2$ Hz, 1H), 2.08–2.05 (m, 1H), 1.15 (s, 3H). IR (neat): 2927, 2872, 2384, 1714, 1485, 1452, 1414, 1252, 1175, 1068, 870, 843, 756, 704, 482 cm^{-1}. HREIMS *m*/*z*, calcd for $C_{13}H_{14}O$ (M^+): 186.1045. Found: 186.1046.

4.9. General procedure for intramolecular cyclopropanation of 4-alkenyl diazomethyl ketones using (ON^+)-Ru(II)(salen) complex 4 as the catalyst

(ON^+)Ru(II)(salen) complex **4** (4.4 mg, 5 μmol) was dissolved in 4 mL of THF under N_2. To this mixture was added a THF solution (1 mL) of 4-alkenyl diazomethyl ketone (0.1 mmol) dropwise over a period of 12 h using a syringe pump under irradiation of incandescent light. The reaction mixture was stirred for another 4 h and concentrated in vacuo. The residue was chromatographed on silica gel using hexane and ethyl acetate (11:1) as eluent to yield the corresponding [4.1.0]bicyclic ketone. The enantiomeric excess of the product was determined as described in the footnotes of Table 7.

4.9.1. 7-Phenylbicyclo[4.1.0]heptan-2-one 14a. Colorless oil. Yield: 63%, 88% ee, $[\alpha]_D^{25}$ −87 (*c* 0.19, $CHCl_3$) (Table 7, entry 2). ^1H NMR (400 MHz): δ 7.27 (dd, $J=7.3$, 7.1 Hz, 2H), 7.19 (d, $J=7.3$ Hz, 1H), 7.06 (d, $J=7.1$ Hz, 2H), 2.66 (br-t, $J=4.6$ Hz, 1H), 2.39 (br-dt, $J=18.1$, 4.8 Hz, 1H), 2.16 (ddd, $J=17.6$, 9.7, 7.5 Hz, 1H), 2.13–2.07 (m, 4H), 1.83–1.77 (m, 2H). IR (neat): 3030, 2931, 2858, 1685, 1602, 1494, 1452, 1338, 1244, 1166, 1068, 1028, 966, 900, 875, 744, 698, 520, 472, 430 cm^{-1}. HREIMS *m*/*z*, calcd for $C_{13}H_{14}O$ (M^+): 186.1045. Found: 186.1045.

4.9.2. 7-(4-Chlorophenyl)bicyclo[4.1.0]heptan-2-one 14b. Colorless oil. Yield: 44%, 89% ee, $[\alpha]_D^{25}$ −83 (*c* 0.1, $CHCl_3$) (Table 7, entry 5). ^1H NMR (400 MHz): δ 7.24 (d, $J=8.5$ Hz, 2H), 7.00 (d, $J=8.5$ Hz, 2H), 2.62 (br-t, $J=4.4$ Hz, 1H), 2.38 (br-dt, $J=18.1$, 4.7 Hz, 1H), 2.15 (ddd, $J=17.6$, 11.0, 6.5 Hz, 1H), 2.13–2.08 (m, 1H), 2.03–1.95 (m, 3H), 1.85–1.74 (m, 2H). IR (neat): 2923, 2895, 1681, 1492, 1342, 1245, 1164, 1089, 1066, 1012, 968, 875, 839, 787, 520, 414 cm^{-1}. HREIMS *m*/*z*, calcd for $C_{13}H_{13}ClO$ (M^+): 220.0654. Found: 220.0656.

4.9.3. 7-(4-Methoxyphenyl)bicyclo[4.1.0]heptan-2-one 14c. Colorless solid, mp 93°C. Yield: 72%, 77% ee, $[\alpha]_D^{25}$ −93 (*c* 0.28, $CHCl_3$) (Table 7, entry 6). ^1H NMR (400 MHz): δ 7.00 (d, $J=8.5$ Hz, 2H), 6.81 (d, $J=8.5$ Hz, 2H), 3.78 (s, 3H), 2.63 (br-t, $J=3.6$ Hz, 1H), 2.37 (br-dt, $J=18.1$, 4.7 Hz, 1H), 2.15 (ddd, $J=18.3$, 10.4, 7.3 Hz, 1H), 2.13–2.09 (m, 1H), 2.05–1.95 (m, 3H), 1.82–1.72 (m, 2H). IR (KBr): 2833, 1676, 1612, 1514, 1458, 1404, 1344, 1278, 1245, 1170, 1031, 964, 900, 877, 833, 785, 619, 532, 478 cm^{-1}. Anal. calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.47; H, 7.39%.

4.9.4. (1*R*,6*S*)-Bicyclo[4.1.0]heptan-2-one 14d[34,35]. Colorless oil. Yield: 46%, 33% ee, $[\alpha]_D^{25}$ +5 (*c* 0.2, $CHCl_3$) (Table 7, entry 7). Lit.[35] $[\alpha]_D^{25}$ +15.6 (*c* 3.7, $CHCl_3$) (for >99% ee, 1*R*,6*S* isomer). Spectroscopic data (^1H NMR and IR) of this sample were in agreement with the reported ones.[34]

4.9.5. 7-Methyl-7-phenylbicyclo[4.1.0]heptan-2-one 14e. Colorless oil. Yield: 36%, 5% ee. $[\alpha]_D^{24}$ +10 (*c* 0.1, $CHCl_3$) (Table 7, entry 8). ^1H NMR (400 MHz): δ 7.32–7.19 (m, 5H), 2.39 (br-d, $J=17.3$ Hz, 1H), 2.28–

2.20 (m, 1H), 2.18–1.92 (m, 4H), 1.88–1.76 (m, 1H), 1.74–1.65 (m, 1H), 1.45 (s, 3H). IR (neat): 2925, 2854, 1689, 1494, 1446, 1327, 1240, 1147, 1026, 875, 765, 702 cm^{-1}. HREIMS m/z, calcd for $C_{14}H_{16}O$ (M^+): 200.1201. Found: 200.1201.

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