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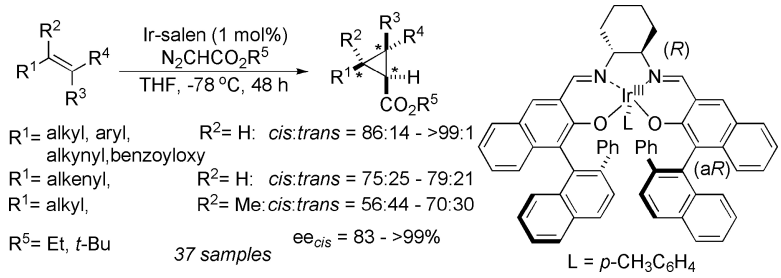

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Construction of Aryliridium−Salen Complexes: Enantio- and *Cis*-Selective Cyclopropanation of Conjugated and Nonconjugated Olefins

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Abstract: Two stable and optically active iridium−salen complexes were synthesized by introducing a tolyl or phenyl ligand at the apical position, respectively, via the S_EAr mechanism, and they were found to be efficient catalysts for *cis*-selective asymmetric cyclopropanation. The scope of the cyclopropanation was wide, and the reactions of not only conjugated mono-, di-, and trisubstituted olefins but also nonconjugated terminal olefins proceeded with high enantio- and *cis*-selectivity, even in the presence of a functional group such as an ether or ester. The utility of this cyclopropanation was demonstrated by a short step synthesis of 8-[(1*R*,2*S*)-2-hexylcyclopropyl]octanoate, isolated from *Escherichia coli* B-ATCC 11303, using the reaction as the key step.

1. Introduction

Chiral metal-catalyzed asymmetric carbene transfer from diazo compounds to olefins is a straightforward method for preparation of optically active cyclopropanes.[1] Since the seminal report by Nozaki et al.,[2] significant effort has been devoted to the development of transition metal-catalyzed enantioselective cyclopropanation, and many excellent catalysts have been introduced. As a matter of course, there are many reports of excellent methods for preparing thermodynamically stable *trans*-cyclopropanes,[3] while the methods for preparing *cis*-products are rather limited.[4–9] Recently, high *cis*- and enantioselectivity have been achieved with Ru(salen),[6] Co(salen),[7] and Ru(PNNP)[8] complexes as catalysts; however, the substrates are mostly limited to conjugated mono- or 1,1-disubstituted olefins, and *cis*-selective asymmetric cyclopropanation of conjugated olefins having other substitution patterns and nonactivated olefins remains a challenge. Recently, a modified Ru(PNNP) complex was found to show good *cis*-selectivity (85: 15) and excellent enantioselectivity (99% ee) in cyclopropanation of nonconjugated (nonactivated) olefins, though it was tested only toward 1-octene.[10]

Among group 9 metals, chiral cobalt and rhodium complexes are well-recognized as asymmetric carbene transfer catalysts.[3g3h3i3m11,12] To our knowledge, however, there are no reports on both asymmetric carbene transfer reactions using an iridium complex and the synthesis of a stable Ir−salen complex.[13] Thus, we were intrigued by construction of a new, chiral Ir−salen complex and its catalysis. Fortunately, we found that

(1) (a) Maas, G. *Chem. Soc. Rev.* **2004**, *33*, 183. (b) Müller, P. *Acc. Chem. Res.* **2004**, *37*, 243. (c) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977. (d) Davies, H. M. L.; Antoulinakis, E. *Org. React.* **2001**, *57*, 1. (e) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; John Wiley & Sons: New York, 1998. (f) Pfalz, A. *Comprehensive Asymmetric Catalysis*, Vol. 2; Jacobsen, E. N.,Pfaltz, A., Yamamoto, H. Eds.; Springer: Berlin, 1999; pp 513−603.

(2) (a) Nozaki, H.; Takaya, H.; Noyori, R. *Tetrahedron Lett.* **1965**, *6*, 2563–2567. (b) Nozaki, H.; Takaya, H.; Moriuti, S.; Noyori, R. *Tetrahedron* **1968**, *24*, 3655–3669.

(3) (a) Pfaltz, A. *Acc. Chem. Res.* **1993**, *26*, 339–345. (b) Nishiyama, H.; Itoh, Y.; Matsumoto, H.; Park, S.-B.; Itoh, K. *J. Am. Chem. Soc.* **1994**, *116*, 2223–2224. (c) Munslow, I. J.; Gillespie, K. M.; Deeth, R. J.; Scott, P. *Chem. Commun.* **2001**, 1638–1639. (d) Lowenthal, R. E.; Abiko, A.; Masamune, S. *Tetrahedron Lett.* **1990**, *31*, 6005–6008. (e) Evans, D. A.; Woerpel, K. A.; Scott, M. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 430–432. (f) Davies, H. M. L.; Bruzinski, P. R.; Lake, D. H.; Kong, N.; Fall, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 6897–6907. (g) Fukuda, T.; Katsuki, T. *Synlett* **1995**, 825–826. (h) Fukuda, T.; Katsuki, T. *Tetrahedron* **1997**, *38*, 3435–3438. (i) Bykowski, D.; Wu, K.-H.; Doyle, M. P. *J. Am. Chem. Soc.* **2006**, *128*, 16038–16039. (j) Denton, J. R.; Sukumaran, D.; Davies, H. M. L. *Org. Lett.* **2007**, *9*, 2625–2628. (k) Reddy, R. P.; Lee, G. H.; Davies, H. M. L. *Org. Lett.* **2006**, *8*, 3437–3440. (l) Davies, H. M. L.; Lee, G. H. *Org. Lett.* **2004**, *6*, 2117–2120. (m) Ikeno, T.; Sato, M.; Sekino, H.; Nishikazu, A.; Yamada, T. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2139–2150.

(4) (a) Aratani, T.; Yoneyoshi, Y.; Nagase, T. *Tetrahedron Lett.* **1982**, *23*, 685–688. (b) Ito, K.; Katsuki, T. *Synlett* **1993**, 638–640.

(5) (a) Doyle, M. P.; Zhou, Q.-L.; Simonsen, S. H.; Lynch, V. *Synlett* **1996**, 697–698. (b) Ishitani, H.; Achiwa, K. *Synlett* **1997**, 781–782. (c) Estevan, F.; Lloret, J.; Sanaú, M.; Úbeda, M. A. *Organometallics* **2006**, *25*, 4977–4984.

(6) (a) Uchida, T.; Irie, R.; Katsuki, T. *Synlett* **1999**, 1163–1165. (b) Uchida, T.; Irie, R.; Katsuki, T. *Synlett* **1999**, 1793–1795. (c) Uchida, T.; Irie, R.; Katsuki, T. *Tetrahedron* **2000**, *56*, 3501–3509.

(7) (a) Niimi, T.; Uchida, T.; Irie, R.; Katsuki, T. *Tetrahedron Lett.* **2000**, *41*, 3647–3651. (b) Niimi, T.; Uchida, T.; Irie, R.; Katsuki, T. *Adv. Synth. Catal.* **2001**, *343*, 79–88.

(8) Bachmann, S.; Furler, M.; Mezzetti, A. *Organometallics* **2001**, *20*, 2102–2108.

(9) Johansson, M. J.; Gorin, D. J.; Staben, S. T.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 18002–18003.

(10) Bonaccorsi, C.; Mezzetti, A. *Organometallics* **2005**, *24*, 4953–4960.

(11) (a) Nakamura, A.; Konishi, A.; Tsujitani, R.; Kudo, M-A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3449–3461. (b) Nakamura, A.; Konishi, A.; Tsujitani, R.; Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3443–3448.

(12) (a) Doyle, M. P.; Brandes, B. D.; Kazala, A. P.; Pieters, R. J.; Jarstfer, M. B.; Watkins, L. M.; Eagle, C. T. *Tetrahedron Lett.* **1990**, *31*, 6613–6616. (b) Doyle, M. P.; Winchester, W. R.; Hoom, J. A. A.; Lynch, V.; Simonsen, S. H.; Ghosh, R. *J. Am. Chem. Soc.* **1993**, *115*, 9968–9978.

Ir^{III}−salen complexes bearing an aryl ligand at the apical position were stable and could be handled even in air at room temperature. Moreover, some of the complexes showed potent *cis*- and enantioselective cyclopropanation catalysis. In this paper, we describe the synthesis of a new class of Ir^{III}−salen complexes and the full scope of asymmetric cyclopropanation using the complexes as catalysts.[14]

2. Results and Discussion

2.1. Preparation of Optically Active Aryliridium−Salen Complexes 2, 3, and 4. Most metal−salen complexes could be easily synthesized by mixing a suitable metal salt and salen ligand, followed, if required, by oxidation.[15] We expected that the Ir^{III}−salen complex could also be prepared by mixing $[Ir^{I}(cod)(toluene)]^{+}PF_6^{-}$ and the salen ligand in a conventional manner, but the resultant complex **1** was unstable. Fortunately, however, the stable Ir^{III}−salen complex **2** was obtained while attempting its crystallization from toluene. High-resolution fast atom bombardment mass spectrometric analysis of **2** indicated that a tolyl group was σ-coordinated to the iridium ion.[14] Finally, it was found that **2** could be synthesized in good yield by air treatment of complex **1**, followed by refluxing with toluene.[16] Other Ir−salen complexes **3**, **5**, and **6** could be synthesized in the same manner. When the air-treated complex **1** was refluxed in benzene, complex **4** was synthesized, and its crystallization from dichloromethane and methanol gave a single crystal suitable for X-ray analysis (Figure 1).

2.2. Asymmetric Cyclopropanation of Conjugated Olefins. With complexes **1** and **2** as catalysts, we examined asymmetric cyclopropanation of styrene using *tert*-butyl α-diazoacetate in tetrahydrofuran (THF). The reaction proceeded rapidly at room temperature; however, the yield of the desired product was unsatisfactory because of the competitive production of fumaric and maleic esters. Therefore, to suppress this undesired diazo coupling, we carried out the reaction in the presence of 10 equiv of styrene: both complexes showed modest *cis*-selectivity, but complex **2** showed superior enantioselectivity to complexes **1**. Hence, a further survey was conducted with complex **2**. Lowering the reaction temperature remarkably increased not only the enantioselectivity but also the *cis*-selectivity, and the best result was obtained when the reaction was carried out at −78 °C. In addition, the formation of the diesters was almost completely suppressed at that temperature (Table 1, entry 1).[14] High enantio- and excellent diastereoselectivity were also achieved, even with ethyl α-diazoacetate.[14] Complex **4** showed

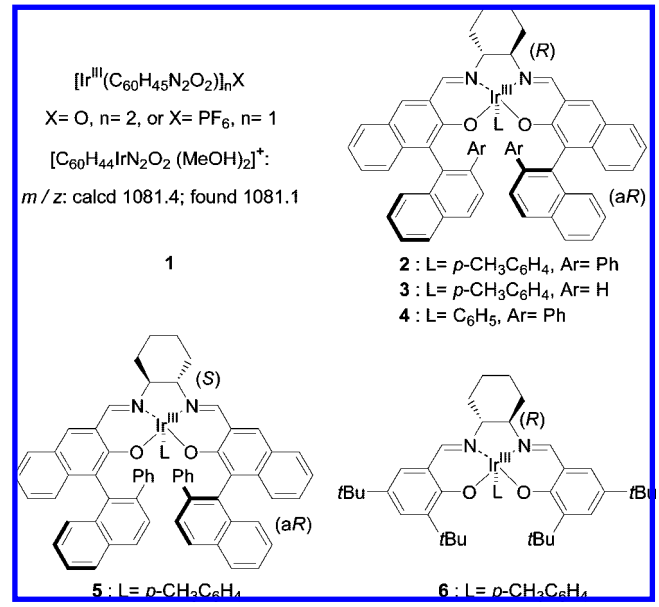
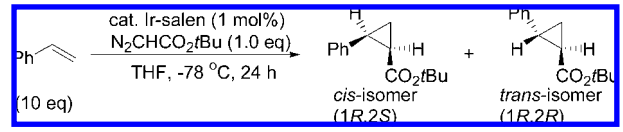


Figure 1. Molecular formula of **1** and structure of aryliridium−salen complexes **2**−**6**.

Table 1. Asymmetric Cyclopropanation of Styrene Using Various Iridium−Salen Complexes as Catalyst[a]



entry	catalyst	yield/%[b]	*cis*:*trans*[c]	% ee_{cis}[d]	% ee_{trans}[d]
1	**2**	99	>99:1	>99[e]	
2	**3**	44	41:59	63[e]	60[f]
3	**4**	99	>99:1	98[e]	
4	**5**	43	58:42	−37[g]	70[f]
5	**6**	25	29:71	1	1

[a] Reactions were carried out in THF for 24 h on a 0.1 mmol scale with a molar ratio of iridium−salen/diazo ester/olefin = 0.01/1/10. [b] Total yield of the *cis*- and the *trans*-cyclopropanes. Yields were determined on the basis of the amount of diazoacetate by ^{1}H NMR analysis using 1-bromonaphtharene as the internal standard. [c] Determined by ^{1}H NMR analysis. [d] Determined by HPLC analysis using chiral column (DAICEL CHIRALCEL OD-H). [e] The absolute configuration was determined to be 1*R*,2*S* by comparison of the optical rotation with the literature value (ref 10). [f] The absolute configuration was determined to be 1*R*,2*R* by comparison of the optical rotation with the literature value (ref 10). [g] The absolute configurations was 1*S*,2*R*.

identical catalysis with **2**, while the catalysis of complexes **3**, **5**, and **6** was less efficient than that of complex **2** (entries 2, 4, and 5).

Cyclopropanation of substituted styrenes also proceeded with excellent enantio- (≥95% ee) and *cis*-selectivity (≥95%), irrespective of the electronic and steric natures and the location of the substituents, with the exception that the reaction of *p*-bromostyrene showed a slightly reduced enantioselectivity of 93% ee (Table 2).

Cyclopropanation of α- and *cis*-β-methylstyrenes proceeded with high stereoselectivity, although the yield of the latter reaction was modest even under slow addition conditions (Table 3, entries 1 and 2). In contrast, the reaction of *trans*-β-methylstyrene was sluggish (entry 3). On the other hand, cyclic olefins, such as indene, and heterocyclic compounds, such as benzofuran, also proceeded with high *cis*- and enantioselectivity

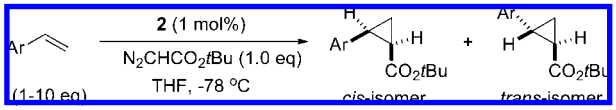
(13) For an example of a non-enantioselective carbene transfer reaction, aziridination of imines, catalyzed by an Ir complex, in which the complex served as a Lewis acid for activating imines, see: (a) Kubo, T.; Sakaguchi, S.; Ishii, Y. *Chem. Commun.* **2000**, 625–626. An Ir−salen complex that was prepared in situ and incorporated into a zeolite has been used as the catalyst for epoxidation: (b) Schuster, C.; Möllmann, E.; Tompos, A.; Hölderich, W. F. *Catal. Lett.* **2001**, *74*, 69–75. Periana et al. reported that the $Ir^{III}(acac)_2(OH)$ complex also underwent aryl C−H activation: (c) Tenn, W. J., III; Young, K. J. H.; Oxgaard, J.; Nielsen, R. J.; Goddard, W. A., III; Periana, R. A. *Organometallics* **2006**, *25*, 5173–5175.

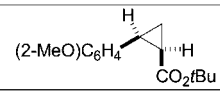
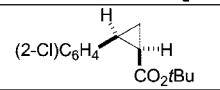
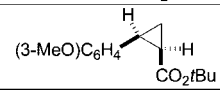
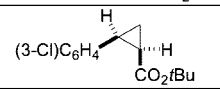
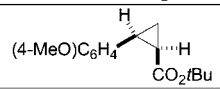
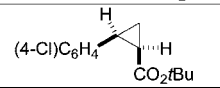
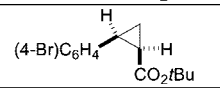
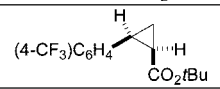
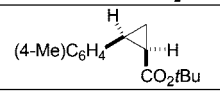
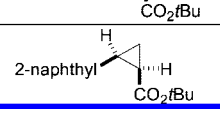
(14) A part of the study on asymmetric cyclopropanation has been communicated: Kanchiku, S.; Suematsu, H.; Uchida, T.; Katsuki, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 3889–3891.

(15) Katsuki, T. *Coord. Chem. Rev.* **1995**, *140*, 189–214.

(16) A similar substitution of the aromatic C−H bond of toluene by an S_EAr mechanism via a Rh^{III}(porphyrin) species to give the corresponding Rh^{III}(porphyrin)($C_6H_4CH_3$) complex has been reported: Collman, J. P.; Boulatov, R. *Inorg. Chem.* **2001**, *40*, 2461–2464.

Table 2. Asymmetric Cyclopropanation of Styrene Derivatives with **2** as the Catalyst[a]



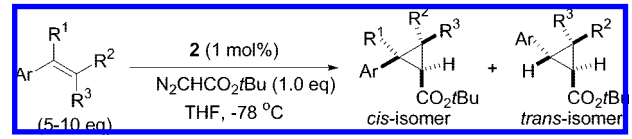
entry	product (*cis*-isomer)	yield/%[b]	*cis* : *trans*[c]	% ee$_{cis}$[d]
1		90	97 : 3	99
2		90	99 : 1	98
3		88	>99 : 1	97
4		91	>99 : 1	98
5[e]		>99	>99 : 1	97
6		>99	>99 : 1	98
7[f]		85	96 : 4	93
8		73	97 : 3	97
9		>99	95 : 5	95
10[f]		97	>99 : 1	97

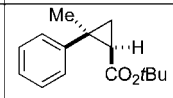
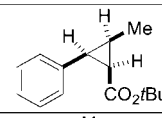
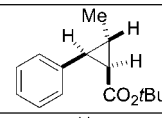
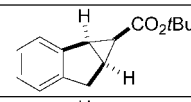
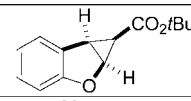
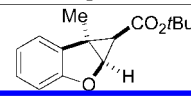
[a] Reactions were carried out in THF for 24 h on a 0.1 mmol scale with a molar ratio of iridium−salen **2**/diazo ester/olefin = 0.01/1/10, unless otherwise mentioned. [b] Yields are based on the amount of diazoacetate used. Total yields of the *cis*- and *trans*-cyclopropanes were determined by ^{1}H NMR analysis using 1-bromonaphtharene as the internal standard. [c] Determined by ^{1}H NMR analysis. [d] Determined as reported in the Experimental Section. [e] Reaction was carried out at −50 °C. [f] Five equivalents of olefin was used.

and acceptable yields via the slow addition technique (entries 4 and 5). It is noteworthy that the reaction of 3-methylbenzofuran, a trisubstituted olefin, showed excellent *cis*- and enantioselectivity, albeit with moderate yield even under the slow addition conditions (entry 6).

Under the same conditions, reactions of enyne and diene were also examined (Table 4). The reaction of 1-phenyl-3-buten-1-yne proceeded with high enantio- and *cis*-selectivity (entries 1 and 2). (*E*)-1-Phenyl-1,3-butadiene was insufficiently soluble at −78 °C, and its reaction was carried out at −45 °C. Although the reaction of (*E*)-1-phenyl-1,3-butadiene was moderately *cis*-selective, it was also highly enantioselective and occurred exclusively at the terminal olefin (entries 3 and 4). The stereoselectivity of these reactions was scarcely affected by the carbene source used: reactions with *tert*-butyl and ethyl α-diazoacetate showed similar levels of stereoselectivity (entries 1 vs 2 and 3 vs 4).

Table 3. Asymmetric Cyclopropanation of Multisubstituted Conjugated Olefins with **2** as the Catalyst[a]

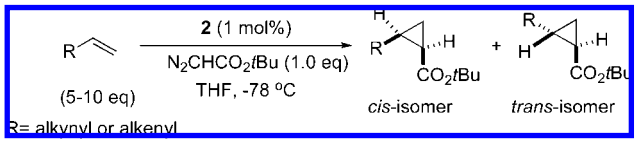


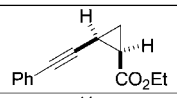
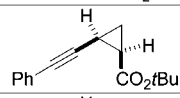
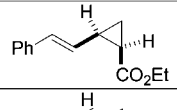
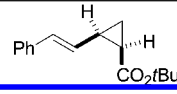
entry	product (*cis*-isomer)	yield/%[b]	*cis* : *trans*[c]	% ee$_{cis}$[d]
1		51	91 : 9	98
2		26	>99 : 1	89
3		trace	-	-
4[e]		80	>99 : 1	97
5		76	>99 : 1	99
6		42	>99 : 1	99

[a] Reactions were carried out in THF on a 0.2 mmol scale with a molar ratio of **2**/diazo ester/olefin = 0.01/1/10, unless otherwise mentioned. A THF solution of diazoacetate was added over the period of 24 h. [b] Yields are based on the amount of diazoacetate used. Total yields of the *cis*- and *trans*-cyclopropanes were determined by ^{1}H NMR analysis using 1-bromonaphtharene as an internal standard. [c] Determined by ^{1}H NMR analysis. [d] Determined as reported in the Experimental Section. [e] Carried out in dichloromethane.

2.3. Asymmetric Cyclopropanation of Nonactivated Alkenes. The above results prompted us to further examine the cyclopropanation of nonactivated terminal olefins (Table 5). The reaction of 4-phenyl-1-butene with *tert*-butyl α-diazoacetate was examined first. This reaction proceeded with high *cis*- and excellent enantioselectivity, albeit with moderate yield (52%, entry 1). Slow addition of the diazoacetate again significantly improved the yield without eroding *cis*- and enantioselectivity (entry 2). The reaction with ethyl α-diazoacetate also gave satisfactory results (entry 3). Excellent *cis*- and high enantioselectivity were also obtained for the reaction of 1-octene (entry 4). The stereoselectivity was only slightly affected by the presence of a functional group such as an ether or ester (entries 5−7). Although the reaction of vinyl benzoate, a nucleophilic olefin, with ethyl α-diazoacetate showed somewhat diminished stereoselectivity, high *cis*- and enantioselectivity were obtained by using *tert*-butyl α-diazoacetate instead (entries 8 and 9). On the other hand, the reaction of phenyl acrylate, which is poorly nucleophilic, was sluggish (entry 10). A terminal olefin branched at the allylic carbon also reacted with high *cis*- and enantioselectivity, albeit slowly (entry 11). Geminally disubstituted olefins reacted with good to excellent enantioselectivity, but the diastereoselectivity was modest (entries 12 and 13). Differentia-

Table 4. Asymmetric Cyclopropanation of Diene Derivatives and Eneyne with **2** as the Catalyst[a]



entry	product (*cis*-isomer)	yield/%[b]	*cis* : *trans*[c]	% ee$_{cis}$[d]
1		84	93 : 7	95
2		90	95 : 5	93
3[e]		99	79 : 21	94
4[e]		>99	75 : 25	97

[a] Reactions were carried out in THF on a 0.1 mmol scale with a molar ratio of **2**/diazo ester/olefin = 0.01/1/10, unless otherwise mentioned. [b] Yields are based on the amount of diazoacetate used. Total yields of the *cis*- and *trans*-cyclopropanes were determined by ^{1}H NMR analysis using 1-bromonaphtharene as the internal standard. [c] Determined by ^{1}H NMR analysis. [d] Determined as described in the Experimental Section. [e] Carried out at −45 °C.

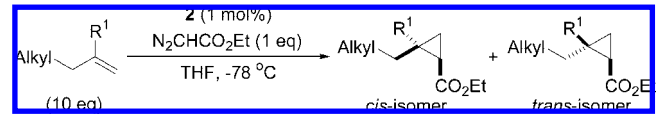
tion of methyl and simple alkyl groups was difficult, and the reaction of 2-methyloctene was poorly diastereoselective (entry 13).

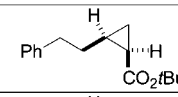
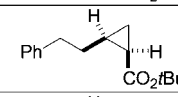
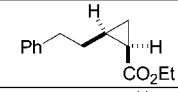
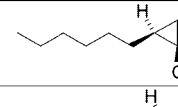
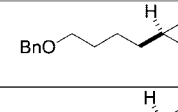
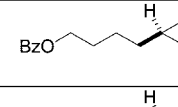
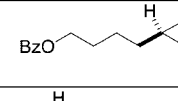
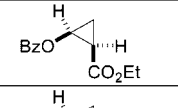
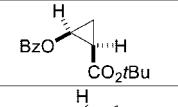
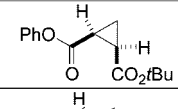
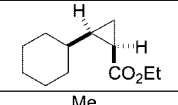
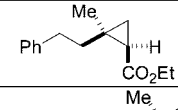
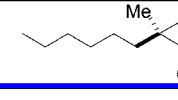
Electrophilic metal−carbenoid species have been postulated as possible intermediates for metal-mediated cyclopropanation using a diazo compound as the carbene precursor.[1] The above-described results (Table 5, entries 8−10) do not contradict the assumption of the participation of an electrophilic intermediate. We further investigated the reactions of nonconjugated 1,5- and 1,6-dienes. Although the internal olefin should be more nucleophilic than the terminal one, the reactions occurred only at the terminal olefin with high *cis*- and enantioselectivity (Scheme 1). This indicated that the regioselectivity is mainly dictated by a steric factor.

2.4. Enantioenriched Synthesis of Methyl 8-[(1*R*,2*S*)-2-Hexylcyclopropyl]octanoate 14. The present reaction is a potent tool for the construction of a *cis*-disubstituted cyclopropane structure. In order to demonstrate its utility, we examined the synthesis of methyl 8-[(1*R*,2*S*)-2-hexylcyclopropyl]octanoate **14**, which was isolated from *Escherichia coli* B-ATCC 11303,[17,18]

(17) For the isolation of **15** and other cyclopropyl fatty acids, see: (a) Hofmann, K.; Lucas, R. A. *J. Am. Chem. Soc.* **1950**, *72*, 4328–4329. (b) O'Leary, W. M. *J. Bacteriol.* **1959**, *78*, 709–713. (c) Kaneshiro, T.; Marr, A. G. *J. Biol. Chem.* **1961**, *236*, 2615–2619. (d) Weinbaum, G.; Panos, C. *J. Bacteriol.* **1966**, *92*, 1576–1577. (e) Grogan, D. W.; Cronan, J. E., Jr *Microbiol. Mol. Biol. Rev.* **1997**, *61*, 429–441. (f) Murakami-Murofushi, K.; Shioda, M.; Kaji, K.; Yoshida, S.; Murofushi, H. *J. Biol. Chem.* **1992**, *267*, 21512–21517. (g) Stuart, L. J.; Buck, J. P.; Tremblay, A. E.; Buist, P. H. *Org. Lett.* **2006**, *8*, 79–81. (h) Stuart, L. J.; Buist, P. H. *Tetrahedron: Asymmetry* **2004**, *15*, 401–403. (i) Brian, B. L.; Gardner, E. W. *Appl. Microbiol.* **1968**, *16*, 549–522. (j) West, T. P. *Can. J. Microbiol.* **1998**, *44*, 1106–1109. (k) Doumenq, P.; Guiliano, M.; Bertrand, J. C.; Mille, G. *Appl. Spectrosc.* **1990**, *44*, 1355–1359. (l) Termonia, M.; Wybauw, M.; Bronckart, J.; Jacobs, H. *J. High Resolut. Chromatogr.* **1989**, *12*, 685–688.

Table 5. Asymmetric Cyclopropanation of Nonactivated Olefins with **2** as the Catalyst[a]

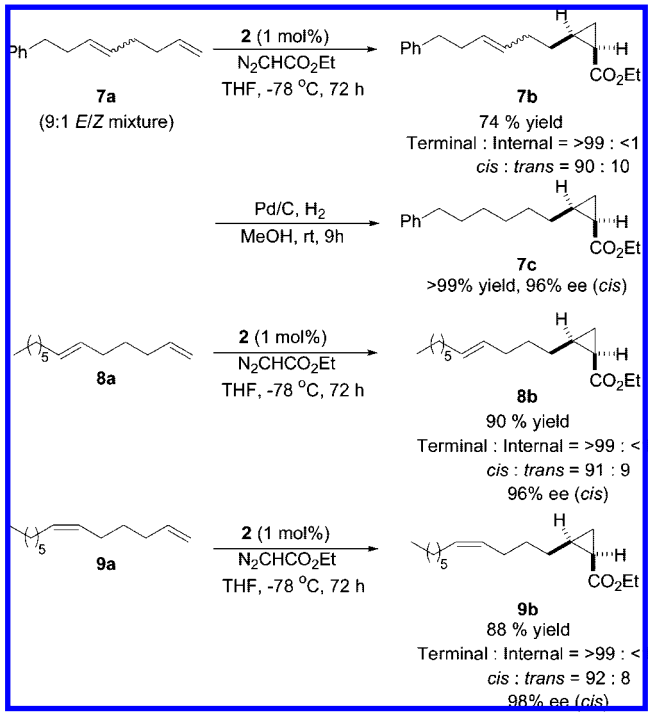


entry	product (*cis*-isomer)	yield/%[b]	*cis* : *trans*[c]	% ee$_{cis}$[d]
1[e,f]		52	95 : 5	98
2[e]		90	95 : 5	98
3		93	96 : 4	96
4[g]		62	98 : 2	98[h]
5		95	95 : 5	97
6		88	95 : 5	95
7[e]		90	97 : 3	99
8		83	86 : 14	92
9[e]		87	96 : 4	94
10		trace	-	-
11		46	96 : 4	98
12		87	70 : 30	83
13		65	56 : 44	99[i]

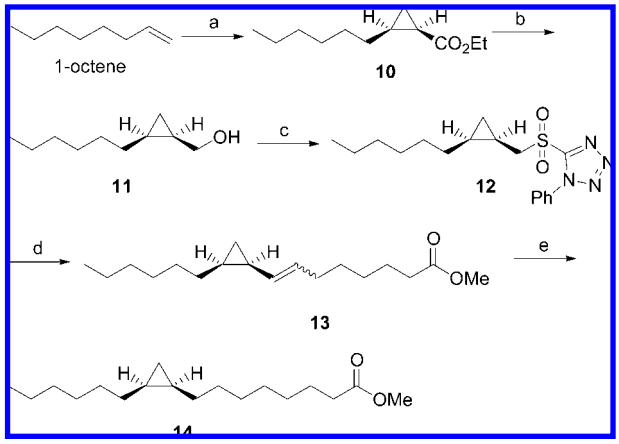
[a] Reactions were carried out in THF on a 0.2 mmol scale with a molar ratio of **2**/diazo ester/olefin = 0.01/1/10, unless otherwise mentioned. A THF solution of diazo ester was added over the period of 24 h. [b] Total isolated yield of *cis*- and *trans*-cyclopropanes. [c] Determined on the basis of the isolated yields of *cis*- and *trans*-products. [d] Determined as described in the Supporting Information. [e] *tert*-Butyl α-diazoacetate was used as the carbene source. [f] Diazoacetate was added without using a slow addition technique. [g] The reaction was carried out on a 9.5 mmol scale. [h] Absolute configuration was determined to be 1*R*,2*S* by comparison of the optical rotation with the literature value (ref 10). [i] The enantiomeric excess of the *trans*-isomer was determined to be 86%.

starting from 1-octene (Scheme 2). The cyclopropanation of 1-octene gave a 98:2 mixture of *cis*- and *trans*-cyclopropanecarboxylates, which was chromatographed on silica gel to give the *cis*-product **10** in 98% ee. Lithium aluminum hydride

Scheme 1. Cyclopropanation of 1,5- and 1,6-Dienes Using **2** as Catalyst



Scheme 2. Synthesis of Methyl 8-[(1*R*,2*S*)-2-Hexylcyclopropyl]-octanoate **14**[a]



[a] Reagents and conditions: (a) (a*R*,*R*)-Ir−salen **2** (1 mol %), N_2CHCO_2Et, THF, −78 °C, 48 h, 68% (after silica gel chromatography); (b) $LiAlH_4$, THF, 0 °C to rt, 2 h, 99%; (c) 1-phenyl-1*H*-tetrazole-5-thiol, DEAD, PPh_3, THF, 0 °C to rt, 3 h, then H_2O_2, EtOH, H_2O, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 24 h, 90%; (d) LiHMDS, THF, −78 °C, then $MeO_2C(CH_2)_5CHO$, −78 °C to rt, 73%; (e) $KO_2CN{=}NCO_2K$, AcOH, MeOH, reflux, 8 h, 88%. DEAD, diethyl azodicarboxylate; HMDS, 1,1,1,3,3,3-hexamethyldisilazane.

reduction of **10** gave alcohol **11**, which was further carbon-extended by using Kocieñski-Julia olefination[19] to yield ester **13** via **12**. Compound **13** was converted into **14** by using Kobayshi's procedure.[18a] Thus, **14** was obtained in a highly enantioenriched manner in only five steps.

2.5. X-ray Structure of 4 and Mechanistic Considerations. Although a single crystal of complex **2** could not be obtained, the phenyliridium−salen complex **4**, which showed an identical catalysis with complex **2**, produced a single crystal upon crystallization from dichloromethane and methanol. X-ray analysis of the crystal clearly showed that the phenyl group was σ-coordinated to the iridium ion at the apical position and

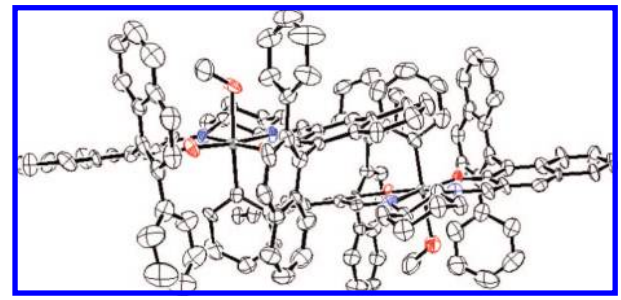


Figure 2. ORTEP drawing of **4**. Hydrogen atoms and solvent molecules were omitted for clarity (recrystallized from CH_2Cl_2:MeOH = 1:1; Ir, gray; C, black; N, blue; O, red).

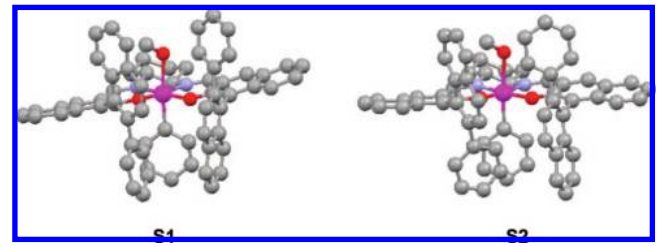


Figure 3. X-ray structures of the two stereoisomers of complex **4**. Horizontal view from the binaphthyl side. Ir, violet; C, black; N, blue; O, red.

perpendicular to the salen ligand, which is almost planar.[20] Methanol is weakly bound to the ion at another apical position: the lengths of the Ir−O_{eq} bonds range from 2.02 to 2.04 Å, while the lengths of the Ir−O_{ap} bond is ca. 2.5 Å (Figure 2). The analysis also revealed that two complexes with different conformations are present per unit cell, which are separately shown for clarity in Figure 3 (S1 and S2). The two complexes differ in the degree of distortion of the ONNO plane, the conformation of the apical phenyl substituent, and the conformation of the 2-phenyl substituent of the naphthyl ring on the top side (the side opposite the apical phenyl group). That is, these two complexes are conformational isomers to each other, and they should be in equilibrium in a solution.

Although the detailed mechanism of the stereochemical control in the present cyclopropanation is unclear, we propose a primitive model to explain its stereochemistry. Based on the X-ray structure of **4**, it is likely that a diazo compound replaces

(18) For the previous synthesis of **15** and its related compounds, see: (a) Kobayashi, S.; Tokunoh, R.; Shibasaki, M.; Shinagawa, R.; Murakami-Murofushi, K. *Tetrahedron Lett.* **1993**, *34*, 4047–4050. (b) Coxon, G. D.; Dulayymi, J. R. A.; Morehouse, C.; Brennan, P. J.; Besra, G. S.; Baird, M. S.; Minnikin, D. E. *Chem. Phys. Lipids* **2004**, *127*, 35–46. (c) Coxon, G. D.; Al-Dulayymi, J. R.; Baird, M. S.; Knobl, S.; Roberts, E.; Minnikin, D. E. *Tetrahedron: Asymmetry* **2003**, *14*, 1211–1222.

(19) (a) Charette, A. B.; Level, H. *J. Am. Chem. Soc.* **1996**, *118*, 10327–10328. (b) Liu, P.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2001**, *123*, 10772–10773. (c) Smith, A. B., III; Brandt, B. M. *Org. Lett.* **2001**, 1685–1688. (d) Blakemore, P. R.; Cole, W. J.; Kocieński, P. J.; Morley, A. *Synlett* **1998**, 26–28. (e) Julia, M.; Paris, J.-M. *Tetrahedron Lett.* **1973**, *14*, 4833–4836.

(20) CCDC 625076 contains the supplementary crystallographic data of **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(21) A methyl group was used as the alkyl group on the carbenoid ester for the calculation.

(22) (a) Maseras, F.; Morokuma, K. *J. Comput. Chem.* **1995**, *16*, 1170–1179. (b) Humbel, S.; Sieber, S.; Modrokuma, K. *J. Chem. Phys.* **1996**, *105*, 1959–1967. (c) Matsubara, T.; Sieber, S.; Morokuma, K. *Int. J. Quantum Chem.* **1996**, *60*, 1101–1109.

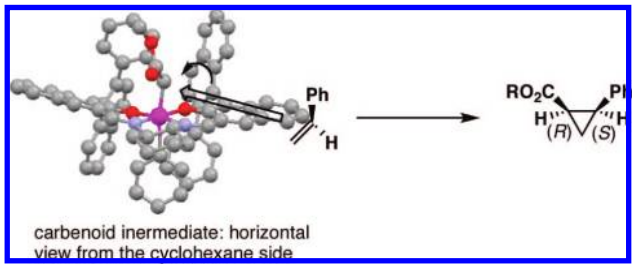


Figure 4. Explanation of the stereochemistry of the aryliridium−salen-catalyzed asymmetric cyclopropanation, based on the optimized structure of the phenyliridium−salen carbenoid intermediate.

the weakly bound methanol and gives the corresponding carbenoid species at the apical position. Thus, we optimized the structure of the phenyliridium−salen carbenoid intermediate[21] with the two-layered ONIOM approach[22] in the *Gaussian03W* package.[23] We assigned the phenyliridium−salen carbenoid complex, except for the C3- and C3′-substituents, to the high layer and the 2-phenylnaphthyl substituents at C3 and C3′ to the low layer. The high layer was optimized at the B3LYP density functional theory level.[24] Core electrons of the Ir atom were described with the effective-core pseudopotentials of Hay and Wadt,[25] and valence electrons were described with the standard LANL2DZ basis set associated with the effective core potential. H, C, N, and O atoms were described with the 6-31G basis set.[26] The low layer was treated by the universal force fields method.[27] This calculation suggested that the basal salen ligand of the intermediate has a stepped conformation and that the bond $C_{carbene}-C_{ester}$ is directed, bisecting the two Ir−N vectors (Figure 4). Olefin is considered to approach the carbenoid carbon from its sterically less hindered side, and the space over the downward naphthalene ring should be less crowded than that over the upward one. Thus, it is likely that olefin approaches the carbenoid carbon from the side of the downward ring. On the other hand, two proposals for access of the olefin, perpendicular[3f,h,7,28] and parallel approaches,[3a,b,10,29] have been made for the metal-mediated cyclopropanation. Although we cannot draw a conclusion on the substrate approach, the fact that *cis*-β-methylstyrene was a much better substrate for the present reaction than *trans*-β-methylstyrene agrees with the perpendicular approach.[30] The oncoming olefin should direct its substituent away from the carbenoid ester group, and this perpendicular approach, along with the subsequent counter-clockwise rotation, leads to the major product.[7b] The clockwise rotation causes steric repulsion between the phenyl substituent and the basal salen ligand, and it should be less favorable than the counter-clockwise one.

(23) Frisch, M. J.; et al. *Gaussian 03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
(24) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789. (b) Backe, D. J. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (c) Parr, R. G.; Yang, W.; *Density-functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
(25) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270–283. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299–310.
(26) Hehre, W.; Ditchfield, J. R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261.
(27) Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A.; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024–10035.
(28) (a) Davies, H. M. L.; Stafford, D. G.; Doan, B. D.; Houser, J. H. *J. Am. Chem. Soc.* **1988**, *120*, 3326–3331. (b) Brown, K. C.; Kodadek, T. *J. Am. Chem. Soc.* **1992**, *114*, 8336–8338. (c) Maxwell, J. L.; Brown, K. C.; Bartley, D.; Kodadek, T. *Science* **1992**, *256*, 1544–1547.

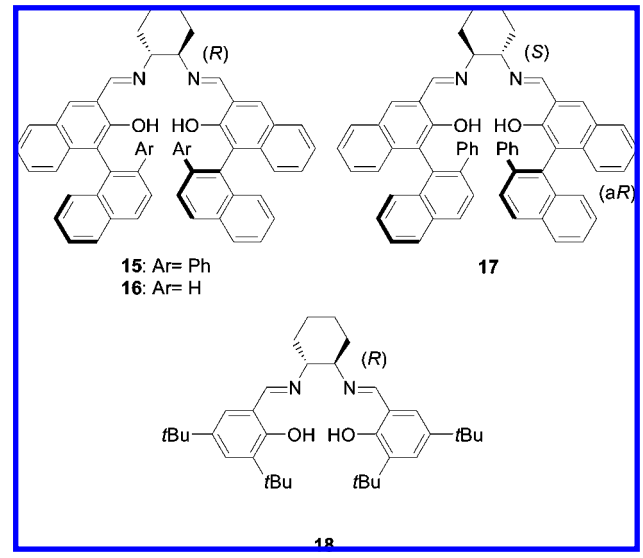
3. Conclusion

We were able to, for the first time, synthesize stable chiral Ir^{III}−salen complexes that carry a σ-coordinated aryl ligand like the tolyl (**2** and **3**) or phenyl (**4**) group. The present study also revealed that complexes **2** and **4** were unique and potent catalysts for *cis*-selective asymmetric cyclopropanation. This cyclopropanation can be applied to not only conjugated but also nonactivated olefins and provides a useful tool for enantioselective synthesis of *cis*-disubstituted cyclopropanes. To our knowledge, this is the first cyclopropanation method that can be applied to conjugated, polysubstituted olefins and nonactivated olefins with both high *cis*- and enantioselectivity.

4. Experimental Section

4.1. General. ^{1}H NMR spectra were recorded at 400 MHz on a JEOL JNM-AL-400 instrument. All signals were expressed as ppm downfield 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. High-resolution fast atom bombardment mass spectra (HRMS-FAB) were measured with a JEOL JMS-SX102A instrument. High-resolution electrospray ionization mass spectra (HRESI-MS) were measured with a Bruker Daltonics Micro TOF-KS1 focus. Electrospray ionization mass spectra (ESI-MS) were measured with a Perkin-Elmer SCIEX API 300 instrument. 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 silica gel 60 F_{254}-coated glass plates (Merck). Enantiomeric excesses were determined by high-performance liquid chromatographic (HPLC) analysis using a Shimadzu LC-10AT-VP instrument, equipped with an appropriate optically active column, as described in the footnotes to the tables. Solvents were dried and distilled shortly before use. Olefins and *tert*-butyl and ethyl α-diazoacetates were also distilled before use. The use of a non-freshly distilled olefin or α-diazoacetate may be detrimental to the stereoselectivity of the reaction. Reactions were carried out under a nitrogen atmosphere.

4.2. Preparation of Salen Ligands. The salen ligands (**15**,[31] **16**,[32] **17**,[33] and **18**[34]) used for this study were prepared according to the reported procedures.



4.3. Preparation of Iridium−Salen Complexes (2−6). 4.3.1. Preparation of Iridium−Salen Complex 2. $[Ir(cod)(toluene)]^+PF_6^-$ [14,35] (595 mg, 1.11 mmol) was added to a solution of (a*R*,*R*)-salen ligand **15** (965 mg, 1.11 mmol) in toluene (50 mL) under N_2. The mixture

was stirred for 10 min at room temperature, then for 10 h at reflux, and cooled to room temperature. The resultant solution was used for the next reaction without further purification. An aliquot of the solution was submitted to ESI-MS analysis, which showed the formation of a new complex, **19**.

19: ESI-MS (*m*/*z*) [M^+], calcd for $[C_{60}H_{46}IrN_2O_2(C_8H_{12})]^+$ 1127.4, found 1127.1.

The solution of **19** was exposed to air for 30 min and filtered through a pad of Celite. The filtrate was evaporated to give complex **1** (699 mg, 0.60 mmol). **1** was used for the next reaction or as the catalyst for asymmetric cyclopropanation without further purification. The ESI-MS of **1** was measured by using methanol as the matrix.

1: ESI-MS (*m*/*z*) [$M^+ + (MeOH)_2$], calcd for $[C_{60}H_{44}IrN_2O_2$-$(2MeOH)]^+$ 1081.4, found 1081.1.

Complex **1** (699 mg, 0.60 mmol) was dissolved in toluene (50 mL) under N_2 and stirred for 10 min at room temperature. The resultant solution was heated to reflux, stirred for 1 day at that temperature, and then cooled to room temperature and evaporated on a rotary evaporator. The residue was chromatographed on silica gel (CH_2Cl_2:THF = 100:1) to give Ir−salen complex **2** as a red-brown solid (405 mg, 33%).

2: IR (KBr) 3427.3, 3051.2, 2927.7, 2858.3, 1722.3, 1606.6, 1577.7, 1444.6, 1425.3, 1325.0, 817.8, 744.5, 700.1 cm^{-1}; HRMS-FAB (*m*/*z*) [M^+], calcd for $[C_{60}H_{44}IrN_2O_2(CH_3C_6H_4)]^+$ 1108.3580, found 1108.3577. Anal. Calcd for $C_{60}H_{44}IrN_2O_2(CH_3C_6H_4)(2H_2O)$: C, 70.32; H, 4.84; N, 2.45. Found: C, 70.11; H, 4.85; N, 2.54.

4.3.2. Preparation of Iridium−Salen Complex 3. Ir−salen complex **3** was synthesized with (a*S*,*R*)-ligand **16** by the same procedure as described for the preparation of complex **2**.

3: IR (KBr) 3423.4, 3055.0, 2933.5, 2860.2, 1610.5, 1579.6, 1446.5, 1427.2, 1353.9, 1323.1, 1186.1, 1145.6, 1122.5, 844.8, 798.5, 777.3, 750.3 cm^{-1}; HRESI-MS (*m*/*z*) [$M + H^+$], calcd for $[C_{48}H_{37}IrN_2O_2(CH_3C_6H_4)]^+$ 957.3030, found 957.3029.

4.3.3. Preparation of Iridium−Salen Complex 4. Complex **1** (699 mg, 0.60 mmol) was dissolved in benzene (50 mL) under N_2 and stirred for 10 min at room temperature. The resultant solution was heated to reflux, stirred for 1 day at that temperature, and then cooled to room temperature and evaporated on a rotary evaporator. The residue was chromatographed on silica gel (CH_2Cl_2:THF = 100:1) to give Ir−salen complex **4** as a red-brown solid (405 mg, 33%). A single crystal suitable for X-ray diffraction analysis was obtained by recrystallization from dichloromethane and methanol.[20]

4: IR (KBr) 3425.3, 3051.2, 2929.7, 2858.3, 1608.5, 1606, 1577.7, 1444.6, 1427.2, 1325.0, 819.7, 742.5, 700.1 cm^{-1}; HRESI-MS (*m*/*z*) [M^+], calcd for $[C_{60}H_{44}IrN_2O_2(C_6H_5)]^+$ 1094.3423, found 1094.3422.

4.3.4. Preparation of Iridium−Salen Complex 5. Ir−salen complex **5** was synthesized with (a*R*,*S*)-ligand **17** by the same procedure as described for the preparation of complex **2**.

5: IR (KBr) 3427.3, 3049.2, 2935.5, 2860.2, 1606.6, 1577.7, 1427.2, 1326.9, 759.9, 700.1 cm^{-1}; HRESI-MS (*m*/*z*) [M^+], calcd for $[C_{60}H_{44}IrN_2O_2(CH_3C_6H_4)]^+$ 1108.3580, found 1108.3511.

4.3.5. Preparation of Iridium−Salen Complex 6. Ir−salen complex **6** was synthesized with (*R*)-ligand **18** by the same procedure as described for the preparation of complex **2**.

6: IR (KBr) 3080.0, 2952.8, 2906.5, 2866.0, 1581.5, 1517.9, 1461.9, 1419.5, 1385.7, 1357.8, 1325.0, 1255.6, 1168.8, 1149.5, 1124.4, 1068.5, 835.1, 781.1 cm^{-1}. Anal. Calcd for $C_{43}H_{59}IrN_2O_2$(THF): C, 62.70; H, 7.50; N, 3.11. Found: C, 62.89; H, 7.36; N, 3.22.

4.4. Asymmetric Cyclopropanation of Conjugated Olefins. 4.4.1. General Procedure for Asymmetric Cyclopropanation of Conjugated Olefins. The reaction was carried out in a Schlenk tube (5 mL) under N_2. *tert*-Butyl α-diazoacetate (0.1 mmol) and 1-bromonaphthalene (4.0 μL, 28 μmol) were dissolved in absolute THF (0.24 mL). The molar ratio of *tert*-butyl α-diazoacetate and 1-bromonaphthalene was determined by ^1H NMR analysis. After conjugated olefin (1.0 mmol) was added to the solution, the mixture was cooled to −78 °C and stirred for 10 min. Subsequently, complex **2** (1.1 mg, 1.0 μmol) was added, and the whole mixture was stirred for 1 day at −78 °C. The mixture was allowed to warm to room temperature, passed through a pad of silica gel, and concentrated on a rotary evaporator. The residue was submitted to ^1H NMR analysis to determine the yield and the *cis*/*trans* ratio. The $CDCl_3$ solution was chromatographed on silica gel (hexane: *i*-Pr_2O 1:0 to 4:1) to yield a mixture of *cis*- and *trans*-products, which were further submitted to preparative thin-layer chromatography (TLC) to isolate the *cis*-product. The enantiomeric excess of the product was determined by HPLC analysis.

***tert*-Butyl (1*R*,2*S*)-2-phenylcyclopropane-1-carboxylate (Table 1**, entry 1): colorless oil, 99% ee, >99% yield, $[\alpha]_D^{27} = -19.5$ (*c* 0.95, $CHCl_3$) [Lit.[6c] 98% ee, (1*S*,2*R*)-isomer, $[\alpha]_D^{26} = +18.0$ (*c* 0.73, $CHCl_3$)]; ^1H NMR ($CDCl_3$) $\delta = 7.34-7.15$ (m, 5H), 2.53 (pseudo-q, $J = 9.0$ Hz, 1H), 1.98 (ddd, $J = 9.5$, 7.8, 5.6 Hz, 1H), 1.64 (ddd, $J = 7.3$, 5.6, 5.0 Hz, 1H), 1.24 (ddd, $J = 8.5$, 7.8, 5.0 Hz, 1H), 1.13 (s, 9H); ^{13}C NMR ($CDCl_3$) $\delta = 169.9$, 136.7, 129.3, 127.6, 126.3, 80.0, 27.9, 25.2, 22.9, 10.7; IR (neat) 3100, 3090, 2976, 2932, 1724, 1603, 1499, 1452, 1389, 1367, 1292, 1254, 1211, 1169, 1148, 1080, 1032, 968, 849, 795, 721, 696, 569, 527 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.04; H, 8.38.

***tert*-Butyl (1*R**,2*S**)-2-(2-methoxyphenyl)cyclopropane-1-carboxylate (Table 2**, entry 1): colorless oil, 99% ee, 90% yield, $[\alpha]_D^{23} = -121.1$ (*c* 0.30, $CHCl_3$); ^1H NMR ($CDCl_3$): $\delta = 7.23-7.14$ (m, 2H), 6.89 (t, $J = 7.5$ Hz, 1H), 6.80 (d, $J = 8.5$ Hz, 1H), 3.78 (s, 3H), 2.43 (pseudo-q, $J = 8.5$ Hz, 1H), 2.05−1.93 (ddd, $J = 9.3$, 7.8, 5.6 Hz, 1H), 1.58−1.50 (m, 1H), 1.30−1.19 (m, 1H), 1.12 (s, 9H); ^{13}C NMR ($CDCl_3$) $\delta = 170.4$, 158.7, 130.2, 127.5, 125.5, 119.8, 109.4, 79.5, 55.3, 27.9, 22.1, 21.2, 10.9; IR (neat) 3070, 2976, 2934, 1722, 1600, 1585, 1497, 1462, 1440, 1391, 1366, 1288, 1248, 1213, 1146, 1115, 1084, 1030, 752 cm^{-1}. Anal. Calcd for: C, 72.55; H, 8.12. Found: C, 72.61; H, 8.07.

***tert*-Butyl (1*R**,2*S**)-2-(2-chlorophenyl)cyclopropane-1-carboxylate (Table 2**, entry 2): colorless oil, 98% ee, 90% yield, $[\alpha]_D^{24} = -115.4$ (*c* 0.29, $CHCl_3$) [Lit.[36] 96% ee, $[\alpha]_D^{26} = -122.5$ (*c* 0.63, $CHCl_3$)]; ^1H NMR ($CDCl_3$) $\delta = 7.35-7.24$ (m, 2H), 7.23−7.12 (m, 2H), 2.49 (pseudo-q, $J = 8.5$ Hz, 1H), 2.13 (ddd, $J = 9.3$, 8.1, 5.6 Hz, 1H), 1.62 (m, 1H), 1.33 (ddd, $J = 8.5$, 8.1, 5.1 Hz, 1H), 1.16 (s, 9H); ^{13}C NMR ($CDCl_3$) $\delta = 169.9$, 135.9, 135.1, 130.9,

(29) (a) Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Angew. Chem.* **1986**, *98*, 1028–1029. (b) Fritschi, H.; Leutenegger, U.; Pfaltz, A. *Helv. Chim. Acta* **1988**, *71*, 1553–1565. (c) Leutenegger, U.; Umbricht, G.; Fahrni, C.; von Matt, P.; Pfaltz, A. *Tetrahedron* **1992**, *48*, 2143–2156. (d) Nishiyama, H.; Itoh, Y.; Sugawara, Y.; Matsumoto, H.; Aoki, K.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1247–1262. (e) Ikeno, T.; Iwakura, I.; Yabushita, S.; Yamada, T. *Org. Lett.* **2002**, *4*, 517–520. (f) Cornejo, A.; Fraile, J. M.; García, J. I.; Gil, M. J.; Martínez-Merino, V.; Mayoral, J. A.; Salvatella, L. *Organometallics* **2005**, *24*, 3448.

(30) Based on the fact that *cis*-olefins are much better substrates for the epoxidation using planar metalloporphyrin or metallosalen complexes as catalyst than *trans*-olefins, a perpendicular approach (side-on approach) has been proposed for these epoxidations that proceed via a metal−oxo species isoelectronic to a metal−carbenoid species: McGarrigle, E. M.; Gilheany, D. G. *Chem. Rev.* **2005**, *105*, 1563–1602.

(31) (a) Kokubo, C.; Katsuki, T. *Tetrahedron* **1996**, *52*, 13895–13900. (b) Miyafuji, A.; Katsuki, T. *Tetrahedron* **1998**, *54*, 10339–10348.

(32) Saha, B.; Uchida, T.; Katsuki, T. *Tetrahedron: Asymmetry* **2003**, *14*, 823–836.

(33) Sasaki, H.; Irie, R.; Hamada, T.; Suzuki, K.; Katsuki, T. *Tetrahedron* **1994**, *50*, 11827–11838.

(34) Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063–7064.

(35) This iridium complex was prepared according to the reported procedure: Sievert, A. C.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 489–501.

(36) Shitama, H.; Katsuki, T. *Chem. Eur. J.* **2007**, *13*, 4849–4858.

128.6, 127.7, 126.0, 80.0, 27.8, 24.2, 22.6, 11.5; IR (neat) 3075, 2976, 2930, 1722, 1479, 1443, 1391, 1366, 1148, 1036, 791, 536 cm^{-1}. Anal. Calcd for: C, 66.53; H, 6.78. Found: C, 66.72; H, 6.67.

***tert*-Butyl (1*R**,2*S**)-2-(3-methoxyphenyl)cyclopropane-1-carboxylate (Table 2, entry 3)**: colorless oil, 97% ee, 88% yield, $[\alpha]_D^{24} = -20.9$ (*c* 0.35, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta = 7.16$ (t, $J = 8.1$ Hz, 1H), 6.91−6.79 (m, 2H), 6.74 (dd, $J = 8.1$, 2.5 Hz, 1H), 3.78 (s, 3H), 2.51 (pseudo-q, $J = 7.8$ Hz, 1H), 1.97 (ddd, $J = 9.3$, 7.8, 5.6 Hz, 1H), 1.68−1.58 (m, 1H), 1.23 (ddd, $J = 8.5$, 7.8, 5.1 Hz, 1H), 1.16 (s, 9H); ^{13}C NMR ($CDCl_3$) $\delta = 169.9$, 158.9, 138.4, 128.6, 121.8, 114.9, 112.1, 80.0, 55.2, 27.9, 25.2, 22.9, 10.9; IR (neat) 3080, 2974, 2934, 2833, 1722, 1600, 1583, 1437, 1389, 1366, 1288, 1255, 1209, 1144, 1045, 980, 853, 691, 581, 517 cm^{-1}. Anal. Calcd for: C, 72.55; H, 8.12. Found: C, 72.74; H, 8.12.

***tert*-Butyl (1*R**,2*S**)-2-(3-chlorophenyl)cyclopropane-1-carboxylate (Table 2, entry 4)**: colorless oil, 98% ee, 91% yield, $[\alpha]_D^{24} = -9.8$ (*c* 0.37, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta = 7.29-7.23$ (m, 1H), 7.22−7.13 (m, 3H), 2.49 (pseudo-q, $J = 8.5$ Hz, 1H), 1.99 (ddd, $J = 9.3$, 7.8, 5.7 Hz, 1H), 1.61 (m, 1H), 1.26 (ddd, $J = 8.5$, 7.5, 5.1 Hz, 1H), 1.18 (s, 9H); ^{13}C NMR ($CDCl_3$) $\delta = 169.6$, 138.9, 133.4, 129.5, 128.9, 127.6, 126.5, 80.4, 27.9, 24.7, 22.9, 10.9; IR (neat) 3070, 3001, 2978, 2932, 2872, 1724, 1599, 1568, 1479, 1448, 1391, 1367, 1292, 1213, 1148, 1082, 1036, 999, 866, 849, 833, 745, 532 cm^{-1}. Anal. Calcd for: C, 66.53; H, 6.78. Found: C, 66.38; H, 6.71.

***tert*-Butyl (1*R**,2*S**)-2-(4-methoxyphenyl)cyclopropane-1-carboxylate (Table 2, entry 5)**: colorless oil, 97% ee, >99% yield, $[\alpha]_D^{24} = +2.9$ (*c* 0.33, $CHCl_3$) [Lit.[6c] 96% ee, $[\alpha]_D^{26} = +3.2$ (*c* 0.85, $CHCl_3$)]; ^1H NMR ($CDCl_3$) $\delta = 7.19$ (d, $J = 9.6$ Hz, 2H), 6.80 (d, $J = 9.6$ Hz, 2H), 3.78 (s, 3H), 2.46 (pseudo-q, $J = 8.6$ Hz, 1H), 1.94 (ddd, $J = 9.3$, 7.8, 5.6 Hz, 1H), 1.58 (m, 1H), 1.21 (ddd, $J = 8.6$, 7.8, 4.9 Hz, 1H) 1.17 (s, 9H); ^{13}C NMR ($CDCl_3$) $\delta = 170.0$, 158.0, 130.3, 128.8, 113.1, 79.9, 55.3, 27.9, 24.5, 22.8, 10.9; IR (neat) 3080, 3000, 2976, 2934, 2835, 1711, 1612, 1582, 1516, 1447, 1389, 1367, 1294, 1250, 1211, 1148, 1082, 1036, 970, 833, 557 cm^{-1}. Anal. Calcd for: C, 72.55; H, 8.12. Found: C, 72.51; H, 8.16.

***tert*-Butyl (1*R**,2*S**)-2-(4-chlorophenyl)cyclopropane-1-carboxylate (Table 2, entry 6)**: colorless oil, 98% ee, >99% yield, $[\alpha]_D^{24} = +2.8$ (*c* 0.29, $CHCl_3$) [Lit.[36] 96% ee, $[\alpha]_D^{26} = +4.4$ (*c* 0.18, $CHCl_3$)]; ^1H NMR ($CDCl_3$) $\delta = 7.29-7.19$ (m, 4H), 2.47 (pseudo-q, $J = 8.5$ Hz, 1H), 1.99 (ddd, $J = 9.3$, 7.8, 5.6 Hz, 1H), 1.59 (ddd, $J = 7.3$, 5.6, 5.1 Hz, 1H), 1.25 (ddd, $J = 8.5$, 7.8, 5.1 Hz, 1H), 1.18 (s, 9H); ^{13}C NMR ($CDCl_3$) 169.7, 135.3, 132.1, 130.7, 127.8, 80.3, 27.9, 24.6, 22.9, 10.9; IR (neat) 3080, 3001, 2978, 2932, 2872, 1726, 1599, 1495, 1448, 1391, 1367, 1292, 1254, 1213, 1160, 1148, 1094, 1034, 1015, 970, 833, 756, 619, 515 cm^{-1}; Anal. Calcd for: C, 66.53; H, 6.78. Found: C, 66.83; H, 6.82.

***tert*-Butyl (1*R**,2*S**)-2-(4-bromophenyl)cyclopropane-1-carboxylate (Table 2, entry 7)**: colorless oil, 93% ee, 85% yield, $[\alpha]_D^{24} = +9.9$ (*c* 0.52, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta = 7.34$ (m, 2H), 7.14 (d, $J = 8.3$ Hz, 2H), 2.44 (pseudo-q, $J = 8.7$ Hz, 1H), 1.99 (ddd, pseudo-q, $J = 9.3$, 7.8, 5.6 Hz, 1H), 1.59 (m, 1H), 1.25 (m, 1H), 1.18 (s, 9H); ^{13}C NMR ($CDCl_3$) $\delta = 169.6$, 135.8, 131.0, 130.7, 120.2, 80.3, 27.9, 24.6, 22.9, 10.9; IR (neat) 3003, 2979, 2968, 2933, 1709, 1491, 1447, 1393, 1367, 1252, 1217, 1148, 1167, 1105, 1074, 1009, 833, 773, 746, 522 cm^{-1}. Anal. Calcd for: C, 56.58; H, 5.77. Found: C, 56.74; H, 5.78.

***tert*-Butyl (1*R**,2*S**)-2-[4-(trifluoromethyl)phenyl]cyclopropane-1-carboxylate**[37] (Table 2, entry 8): colorless oil, 97% ee, 73% yield, $[\alpha]_D^{24} = -14.5$ (*c* 0.11, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta = 7.52$ (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 8.2$ Hz, 2H), 2.55 (pseudo-q, $J = 8.6$ Hz, 1H), 2.05 (ddd, $J = 9.3$, 7.8, 5.6 Hz, 1H) 1.67 (m, 1H), 1.31 (m, 1H), 1.15 (s, 9H); ^{13}C NMR ($CDCl_3$) $\delta = 169.3$, 140.7, 129.4, 124.4, 124.3, 80.2, 27.7, 24.6, 22.9, 10.8; IR (neat) 3050, 3003, 2986, 2937, 1711, 1618, 1479, 1452, 1396, 1369, 1327, 1252, 1223, 1159, 1119, 1070, 1016, 972, 847, 734, 611 cm^{-1}. Anal. Calcd for: C, 62.93; H, 5.99. Found: C, 62.89; H, 5.98.

***tert*-Butyl (1*R**,2*S**)-2-(4-methylphenyl)cyclopropane-1-carboxylate (Table 2, entry 9)**: colorless oil, 95% ee, >99% yield, $[\alpha]_D^{24} = -4.3$ (*c* 0.38, $CHCl_3$) [Lit.[36] 94% ee, $[\alpha]_D^{26} = -6.8$ (*c* 0.18, $CHCl_3$)]; ^1H NMR ($CDCl_3$) $\delta = 7.15$ (d, $J = 7.8$ Hz, 2H), 7.05 (d, $J = 7.8$ Hz, 2H), 2.48 (pseudo-q, $J = 8.4$ Hz, 1H), 1.95 (ddd, $J = 9.5$, 8.6, 7.8 Hz, 1H), 1.59 (m, 1H), 1.21 (ddd, $J = 8.7$, 7.8, 5.1 Hz, 1H), 1.16 (s, 9H); ^{13}C NMR ($CDCl_3$) $\delta = 169.9$, 135.8, 133.6, 129.2, 128.3, 79.9, 27.9, 24.9, 22.8, 21.2, 10.8; IR (neat) 3007, 2976, 2928, 2868, 1717, 1519, 1479, 1454, 1393, 1367, 1249, 1213, 1148, 1113, 1092, 1038, 972, 829, 769, 744, 547 cm^{-1}. Anal. Calcd for: C, 77.55; H, 8.68. Found: C, 77.48; H, 8.72.

***tert*-Butyl (1*R**,2*S**)-2-(2-naphthyl)cyclopropane-1-carboxylate (Table 2, entry 10)**: colorless crystal, 97% ee, 97% yield, $[\alpha]_D^{24} = +85.3$ (*c* 1.0, $CHCl_3$) [Lit.[7b] 97% ee, $[\alpha]_D^{25} = +86.4$ (*c* 0.72, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta = 7.85-7.63$ (m, 4H), 7.50−7.32 (m, 3H), 2.67 (pseudo-q, $J = 8.5$ Hz, 1H), 2.06 (ddd, $J = 9.3$, 7.6, 5.6 Hz, 1H), 1.77 (ddd, $J = 7.3$, 5.6, 5.1 Hz, 1H), 1.33 (ddd, $J = 8.5$, 7.6, 5.1 Hz, 1H), 1.06 (s, 9H); ^{13}C NMR ($CDCl_3$) $\delta = 169.9$, 134.3, 133.0, 132.2, 127.9, 127.8, 127.4, 127.3, 127.1, 125.7, 125.2, 80.1, 27.9, 25.4, 23.1, 11.0; IR (neat) 3051, 2976, 2932, 2868, 2372, 1715, 1629, 1597, 1510, 1437, 1390, 1367, 1250, 1215, 1155, 1092, 1053, 862, 829, 783, 748, 646 cm^{-1}. Anal. Calcd for: C, 80.56; H, 7.51. Found: C, 80.59; H, 7.60.

***tert*-Butyl (1*R**,2*S**)-2-methyl-2-phenylcyclopropane-1-carboxylate (Table 3, entry 1)**: colorless oil, 98% ee, 51% yield, $[\alpha]_D^{24} = -40.8$ (*c* 0.07, $CHCl_3$) [Lit.[6c] 96% ee, $[\alpha]_D^{25} = -42.1$ (*c* 0.43, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta = 7.19-7.16$ (m, 5H), 1.80 (dd, $J = 7.5$, 5.5 Hz, 1H), 1.70 (dd, $J = 5.5$, 4.5 Hz, 1H), 1.45 (s, 3H), 1.13 (s, 9H), 1.07 (dd, $J = 7.5$, 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) $\delta = 170.2$, 141.9, 128.8, 127.9, 126.4, 79.8, 31.8, 29.7, 28.8, 27.9, 19.3; IR (neat) 3059, 3004, 2974, 2927, 2868, 1726, 1497, 1477, 1446, 1389, 1367, 1290, 1244, 1148, 1085, 844, 700 cm^{-1}. Anal. Calcd for: C, 77.55; H, 8.68. Found: C, 77.42; H, 8.70.

***tert*-Butyl (1*R**,2*S**,3*R**)-3-methyl-2-phenylcyclopropane-1-carboxylate (Table 3, entry 2)**: colorless oil, 89% ee, 26% yield, $[\alpha]_D^{27} = +2.8$ (*c* 0.01, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta = 7.36-7.17$ (m, 5H), 2.58 (pseudo-t, $J = 9.0$ Hz, 1H), 1.97 (pseudo-t, $J = 8.9$ Hz, 1H), 1.76−1.62 (m, 1H), 1.33 (s, 9H), 1.30 (d, $J = 1.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$) $\delta = 170.2$, 135.2, 130.5, 127.6, 126.1, 81.6, 28.2, 28.1, 23.9, 19.4, 9.8; IR (neat) 3010, 3000, 2976, 2932, 2883, 1726, 1499, 1479, 1448, 1392, 1367, 1309, 1258, 1144, 979, 847, 698 cm^{-1}; Anal. Calcd for: C, 77.55; H, 8.68. Found: C, 77.43; H, 8.67.

***tert*-Butyl (1*S**,1a*R**,6a*S**)-6*H*-1a,6a-dihydrocyclopropa[*a*]indene-1-carboxylate (Table 3, entry 4)**: colorless oil, 97% ee, 80% yield, $[\alpha]_D^{27} = +150.3$ (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta = 7.35-7.28$ (m, 1H), 7.15−7.08 (m, 3H), 3.35 (dd, $J = 17.1$, 0.5 Hz, 1H), 3.18 (dd, $J = 17.1$, 6.8 Hz, 1H), 2.85 (ddd, $J = 8.5$, 6.1, 1.5 Hz, 1H), 2.2−2.12 (m, 1H), 1.97 (pseudo-t, $J = 8.5$ Hz, 1H), 1.07 (s, 9H); ^{13}C NMR ($CDCl_3$) $\delta = 168.7$, 143.9, 140.7, 126.1, 125.8, 124.7, 124.2, 80.2, 32.6, 30.8, 27.7, 26.6, 22.7; IR (neat) 3050, 2976, 2909, 2843, 1724, 1587, 1477, 1460, 1393, 1367, 1348, 1323, 1244, 1134, 1026, 1003, 941, 860, 806, 752, 528 cm^{-1}. Anal. Calcd for: C, 78.23; H, 7.88. Found: C, 78.14; H, 7.79.

***tert*-Butyl (1*R**,1a*R**,6a*S**)-1a,6a-dihydro-6-oxacyclopropa[*a*]indene-1-carboxylate (Table 3, entry 5)**: colorless oil, 99% ee, 76% yield, $[\alpha]_D^{27} = +139.6$ (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$) $\delta = 7.36$ (d, $J = 7.6$ Hz, 1H), 7.16 (t, $J = 8.1$ Hz, 1H), 6.92 (td, $J = 7.6$, 1.0 Hz, 1H), 6.85 (d, $J = 8.1$ Hz, 1H), 4.97 (t, $J = 5.3$ Hz, 1H), 3.18 (dd, $J = 9.4$, 5.3 Hz, 1H), 1.81 (dd, $J = 9.4$, 5.6 Hz, 1H), 1.14 (s, 9H); ^{13}C NMR ($CDCl_3$) $\delta = 166.0$, 161.1, 127.6, 125.3, 124.9, 120.8, 109.5, 80.9, 65.3, 27.8, 27.7, 19.8; IR (neat) 3057, 3003, 2972, 2932, 2870, 1726, 1690, 1614, 1597, 1477, 1460, 1406, 1369, 1346, 1327, 1252, 1227, 1202, 1140, 1074, 999, 976, 939, 862, 802, 787, 691, 599 cm^{-1}. Anal. Calcd for: C, 72.39; H, 6.94. Found: C, 72.38; H, 6.95.

(37) Hu, W.; Timmons, D. J.; Doyle, M. P. *Org. Lett.* **2002**, *4*, 901–904.

***tert*-Butyl (1*R**,1a*R**,6a*R**)-1a-methyl-6a-hydro-6-oxacyclopropa[*a*]indene-1-carboxylate (Table 3, entry 6)**: colorless oil, 98% ee, 42% yield, $[\alpha]_D^{24} = +84.1$ (*c* 0.21, $CHCl_3$); ^{1}H NMR ($CDCl_3$) 7.28 (dd, $J = 7.3$, 1.5 Hz, 1H), 7.16 (td, $J = 7.8$, 1.5 Hz, 1H), 6.95 (td, $J = 7.3$, 1.0 Hz, 1H), 6.84 (d, $J = 8.0$ Hz, 1H), 4.71 (d, $J = 5.7$ Hz, 1H), 1.74 (d, $J = 5.7$ Hz, 1H), 1.65 (s, 3H), 1.12 (s, 1H); ^{13}C NMR ($CDCl_3$) $\delta = 166.2$, 160.5, 128.8, 127.5, 123.7, 120.7, 109.5, 80.7, 70.5, 34.5, 27.8, 25.9, 18.2; IR (neat) 3060, 3040, 3004, 2972, 2932, 2870, 1720, 1614, 1595, 1479, 1448, 1414, 1392, 1366, 1339, 1277, 1248, 1190, 1146, 1092, 1061, 1016, 974, 908, 870, 853, 825, 790, 752, 692, 652 cm^{-1}. Anal. Calcd for: C, 73.15; H, 7.37. Found: C, 73.03; H, 7.38.

Ethyl (1*R,2*S**)-2-phenylethynylcyclopropane-1-carboxylate (Table 4, entry 1)**: colorless oil, 95% ee, 84% yield, $[\alpha]_D^{27} = +99.5$ (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta = 7.48-7.35$ (m, 2H), 7.32−7.22 (m, 3H), 4.27−4.16 (m, 2H), 2.07−1.97 (m, 2H), 1.61−1.51 (m, 1H), 1.35−1.23 (m, 1H), 1.27 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$) $\delta = 169.9$, 131.6, 128.0, 127.6, 123.4, 87.2, 79.5, 60.8, 21.9, 14.7, 14.6, 10.1; IR (neat) 3050, 3010, 2980, 2973, 1730, 1597, 1491, 1443, 1402, 1381, 1354, 1279, 1186, 1113, 1026, 758, 692 cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{14}H_{14}O_2Na]^+$ 237.0886, found 237.0873.

***tert*-Butyl (1*R**,2*S**)-2-phenylethynylcyclopropane-1-carboxylate (Table 4, entry 2)**: colorless oil, 93% ee, 90% yield, $[\alpha]_D^{24} = +105.8$ (*c* 0.63, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta = 7.40-7.34$ (m, 2H), 7.31−7.22 (m, 3H), 1.98−1.90 (m, 2H), 1.53−1.27 (m, 1H), 1.39 (s, 9H), 1.27−1.17 (m, 1H); ^{13}C NMR ($CDCl_3$) $\delta = 169.0$, 131.5, 127.9, 127.5, 123.4, 87.5, 80.8, 79.2, 28.3, 22.8, 14.2, 9.8; IR (neat) 3092, 3002, 2976, 2929, 1726, 1661, 1491, 1445, 1389, 1367, 1292, 1256, 1213, 1151, 1115, 756, 692 cm^{-1}. Anal. Calcd for: C, 79.31; H, 7.49. Found: C, 79.28; H, 7.50.

Ethyl (1*R,2*R**)-2-styrylcyclopropane-1-carboxylate**[38] (Table 4, entry 3): colorless oil, 94% ee, 99% yield, $[\alpha]_D^{26} = +17.9$ (*c* 0.16, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta = 7.38-7.25$ (m, 4H), 7.22−7.16 (m, 1H), 6.58 (d, $J = 15.9$ Hz, 1H), 6.23 (dd, $J = 15.9$, 9.2 Hz, 1H), 4.24−4.07 (m, 2H), 2.15−1.95 (m, 2H), 1.45−1.22 (m, 2H), 1.26 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR ($CDCl_3$) $\delta = 171.7$, 137.2, 131.2, 128.3, 127.4, 126.9, 125.8, 60.6, 24.7, 21.6, 14.9, 14.5; IR (neat) 3024, 2980, 2959, 2928, 1724, 1599, 1583, 1446, 1404, 1381, 1354, 1184, 1150, 966, 766, 741, 694 cm^{-1}; HRESI-MS (*m*/*z*) [M + K^+], calcd for $[C_{14}H_{16}O_2K]^+$ 255.0782, found 255.0944.

***tert*-Butyl (1*R**,2*R**)-2-styrylcyclopropane-1-carboxylate (Table 4, entry 4)**: colorless oil, 97% ee, >99% yield, $[\alpha]_D^{26} = +48.9$ (*c* 0.08, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta = 7.42-7.24$ (m, 4H), 7.21−7.14 (m, 1H), 6.57 (d, $J = 15.7$ Hz, 1H), 6.21 (dd, $J = 15.7$, 9.2 Hz, 1H), 2.08−1.98 (m, 1H), 1.96−1.89 (m, 1H), 1.44 (s, 9H), 1.35−1.18 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 170.9$, 137.4, 130.9, 128.3, 127.6, 126.8, 125.7, 80.6, 28.4, 24.3, 22.8, 14.3; IR (neat) 3100, 2978, 2890, 1722, 1661, 1585, 1481, 1389, 1367, 1211, 1170, 1142, 966, 818, 748, 692 cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{16}H_{20}O_2Na]^+$ 267.1311, found 267.1356.

4.4.2. General Procedure for Asymmetric Cyclopropanation of Nonconjugated Olefins. Reaction was carried out in a Schlenk tube (5 mL) under N_2. Nonconjugated olefin (2.0 mmol) was dissolved in absolute THF (0.48 mL). The mixture was cooled to −78 °C and stirred for 10 min. Subsequently, complex **2** (2.2 mg, 2.0 μmol) was added. After an 8.6 M THF solution of α-diazoacetate (0.2 mmol) was added over 24 h, the reaction mixture was stirred for 2 days at −78 °C. The mixture was directly chromatographed on a short silica gel (hexane/*i*-Pr_2O = 1/0 to 30/1). The fractions including the *cis*- and *trans*-products were collected and concentrated on a rotary evaporator to yield a mixture of the products. Unreacted alkene was also recovered upon chromatography. The *cis*- and *trans*-product mixture was chromatographed again on silica gel (hexane/*i*-Pr_2O = 1/0 to 30/1) to obtain the *cis*-product. The *cis*/*trans* ratio was calculated on the basis of the respective isolated yields of the *cis* and *trans* isomers. The enantiomeric excess of the *cis*-product was determined by HPLC analysis.

***tert*-Butyl (1*R**,2*S**)-2-(2-phenylethyl)cyclopropane-1-carboxylate (Table 5, entry 2)**: colorless oil, 98% ee, 90% yield, $[\alpha]_D^{26} = -14.6$ (*c* 0.57, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta = 7.33-7.12$ (m, 5H), 2.64 (dd, $J = 7.8$, 7.8 Hz, 2H), 1.96−1.74 (m, 2H), 1.69−1.38 (m, 1H), 1.47 (s, 9H), 1.35−1.11 (m, 1H), 0.99−0.81 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 171.9$, 141.9, 128.3, 128.1, 125.6, 80.1, 36.1, 29.1, 28.4, 21.3, 19.4, 13.2; IR (neat) 3061, 3026, 3003, 2976, 2928, 2860, 1720, 1603, 1497, 1481, 1391, 1367, 1252, 1209, 1151, 872, 851, 831, 746, 698 cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{16}H_{22}O_2Na]^+$ 269.1512, found 269.1500.

Ethyl (1*R,2*S**)-2-(2-phenylethyl)cyclopropane-1-carboxylate (Table 5, entry 3)**: colorless oil, 96% ee, 93% yield, $[\alpha]_D^{25} = -47.5$ (*c* 0.49, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta = 7.30-7.23$ (m, 2H), 7.22−7.14 (m, 3H), 4.13 (q, $J = 7.1$ Hz, 2H), 2.68−2.57 (m, 2H), 1.96−1.76 (m, 2H), 1.72−1.65 (m, 1H), 1.30−1.18 (m, 1H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.05−0.89 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 172.7$, 141.8, 128.4, 128.1, 125.6, 60.3, 35.9, 29.0, 21.5, 18.4, 14.5, 13.6; IR (neat) 3061, 3024, 2979, 2926, 2858, 1724, 1603, 1585, 1549, 1495, 1450, 1402, 1381, 1354, 1273, 1173, 1130, 1092, 1034, 1007, 962, 827, 748, 700, 577, 511 cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{14}H_{18}O_2Na]^+$ 241.1199, found 241.1165.

Ethyl (1*R*,2*S*)-*cis*-2-hexylcyclopropane-1-carboxylate (Table 5, entry 4): colorless oil, 98% ee, 62% yield, $[\alpha]_D^{26} = -41.0$ (*c* 1.00, $CHCl_3$) [Lit.[10] 94% ee, (1*S*,2*R*)-isomer, $[\alpha]_D^{20} = +41.0$ (*c* 0.75, $CHCl_3$)]; ^{1}H NMR ($CDCl_3$) $\delta = 4.13$ (q, $J = 7.1$ Hz, 2H), 1.66 (ddd, $J = 8.9$, 7.9, 5.5 Hz, 1H), 1.60−1.41 (m, 1H), 1.40−1.07 (m, 10H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.50−0.88 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ =172.8, 60.2, 31.9, 29.7, 29.1, 27.2, 22.8, 22.0, 18.4, 14.5, 14.2, 13.5; IR (neat) 2957, 2924, 2856, 1728, 1464, 1448, 1402, 1381, 1354, 1269, 1177, 1097, 1043, 829 cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{12}H_{22}O_2Na]^+$ 221.1512, found 221.1506.

Ethyl (1*R,2*S**)-2-[4-(benzyloxy)butyl]cyclopropane-1-carboxylate (Table 5, entry 5)**: colorless oil, 97% ee, 95% yield, $[\alpha]_D^{26} = -28.1$ (*c* 1.06, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta = 7.37-7.23$ (m, 5H), 4.49 (s, 2H), 4.12 (q, $J = 7.0$ Hz, 2H), 3.46 (t, $J = 6.6$ Hz, 2H), 1.70−1.38 (m, 7H), 1.32−1.16 (m, 1H), 1.24 (t, $J = 7.0$ Hz, 3H), 1.05−0.86 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 172.7$, 138.5, 128.2, 127.4, 127.3, 72.9, 70.4, 60.2, 29.6, 26.9, 26.4, 21.9, 18.3, 14.5, 13.5; IR (neat) 3020, 2980, 2932, 2858, 1722, 1448, 1402, 1381, 1356, 1177, 1099, 1047, 1028, 831, 737, 698 cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{17}H_{24}O_3Na]^+$ 299.1618, found 299.1676.

4-[(1*S,2*R**)-2-(Ethoxycarbonyl)cyclopropyl]butyl benzoate (Table 5, entry 6)**: colorless oil, 95% ee, 88% yield, $[\alpha]_D^{27} = -29.6$ (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta = 8.10-7.99$ (m, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.43 (dd, $J = 7.4$, 7.3 Hz, 2H), 4.31 (t, $J = 6.7$ Hz, 2H), 4.11 (q, $J = 7.2$ Hz, 2H), 1.83−1.73 (m, 2H), 1.73−1.35 (m, 5H), 1.30−1.17 (m, 1H), 1.24 (t, $J = 7.2$ Hz, 3H), 1.06−0.90 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 172.7$, 166.4, 132.6, 130.4, 129.4, 128.1, 65.0, 60.3, 28.6, 26.8, 26.3, 21.8, 18.3, 14.5, 13.5; IR (neat) 3050, 2979, 2953, 2934, 1722, 1600, 1583, 1448, 1404, 1381, 1313, 1275, 1177, 1115, 1026, 714 cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{17}H_{22}O_4Na]^+$ 313.1410, found 313.1454.

4-[(1*S,2*R**)-2-(*tert*-Butoxycarbonyl)cyclopropyl]butyl benzoate (Table 5, entry 7)**: colorless oil, 99% ee, 90% yield, $[\alpha]_D^{24} = -30.7$ (*c* 0.25, $CHCl_3$); ^{1}H NMR ($CDCl_3$) $\delta = 8.04$ (d, $J = 8.3$ Hz, 2H), 7.55 (t, $J = 7.7$ Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 2H), 4.31 (t, $J = 6.7$ Hz, 2H), 1.85−1.73 (m, 2H), 1.69−1.38 (m, 5H), 1.44 (s, 9H), 1.29−1.13 (m, 1H), 0.98−0.91 (m, 1H), 0.90−0.81 (m, 1H); ^{13}C NMR ($CDCl_3$) $\delta = 171.9$, 166.4, 132.6, 130.4, 129.4, 128.2, 80.0, 65.1, 28.7, 28.3, 26.9, 26.4, 21.5, 19.4, 13.1; IR (neat) 3080, 2976, 2929, 2860, 1720, 1601, 1585, 1450, 1391, 1367, 1275, 1211, 1148, 1115, 1070, 1028, 851, 833, 714 cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{19}H_{26}O_4Na]^+$ 341.1723, found 341.1733.

(38) Doyle, M. P.; Dorow, R. L.; Buhro, W. E.; Griffin, J. H.; Tamblyn, W. H.; Trudell, M. L. *Organometallics* **1984**, *3*, 44–52.

(1*S,2*R**)-2-(Ethoxycarbonyl)cyclopropyl benzoate (Table 5, entry 8)**: colorless oil, 92% ee, 83% yield, $[\alpha]_D^{25} = -4.2$ (*c* 0.46, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 8.00 (ddd, *J* = 8.0, 0.7, 0.7 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.42 (dd, *J* = 8.0, 7.6 Hz, 2H), 4.52 (m, 1H), 4.12 (q, *J* = 7.3 Hz, 2H), 2.11−2.09 (m, 1H), 1.78−1.69 (m, 1H), 1.41−1.27 (m, 1H), 1.19 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ = 169.0, 166.7, 133.0, 129.5, 129.4, 128.2, 60.9, 52.9, 20.2, 14.3, 12.4; IR (neat) 3063, 2982, 2937, 2905, 1730, 1601, 1583, 1450, 1400, 1381, 1273, 1209, 1178, 1146, 1097, 1069, 1026, 964, 712 cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{13}H_{14}O_4Na]^+$ 257.0784, found 257.0790.

(1*S,2*R**)-2-(*tert*-Butoxycarbonyl)cyclopropyl benzoate (Table 5, entry 9)**: colorless oil, 94% ee, 87% yield, $[\alpha]_D^{25} = -7.6$ (*c* 0.88, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 8.0 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.55 (tt, *J* = 7.3, 1.5 Hz, 1H), 7.42 (tt, *J* = 8.1, 1.5 Hz, 2H), 4.45 (ddd, *J* = 7.1, 6.6, 4.6 Hz, 1H), 2.0 (ddd, *J* = 8.8, 7.1, 7.0 Hz, 1H), 1.68 (ddd, *J* = 7.1, 7.0, 4.6 Hz, 1H), 1.38 (s, 9H), 1.29 (*J* = 8.8, 7.1, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 167.9, 166.8, 132.9, 129.5, 129.4, 128.2, 80.9, 52.9, 28.1, 21.4, 11.8; IR (neat) 3050, 2978, 2934, 2872, 1730, 1601, 1583, 1452, 1435, 1273, 1217, 1151, 1099, 1069, 1028, 1007, 964, 839, 712, 574 cm^{-1}. Anal. Calcd for: C, 68.68; H, 6.92. Found: C, 68.60; H, 6.90.

Ethyl (1*R,2*R**)-2-cyclohexylcyclopropane-1-carboxylate (Table 5, entry 11)**: colorless oil, 98% ee, 46% yield, $[\alpha]_D^{27} = -41.5$ (*c* 0.29, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 4.13 (q, *J* = 7.1 Hz, 2H), 1.84−1.47 (m, 6H), 1.33−0.88 (m, 9H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ = 172.9, 60.2, 35.9, 33.5, 33.3, 28.7, 26.6, 26.3, 26.1, 18.1, 14.5, 12.6; IR (neat) 2982, 2924, 2849, 1726, 1583, 1447, 1404, 1381, 1180, 1157, 831 cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{12}H_{20}O_2Na]^+$ 219.1356, found 219.1351.

Ethyl (1*R,2*S**)-2-methyl-2-(2-phenylethyl)cyclopropane-1-carboxylate (Table 5, entry 12)**: colorless oil, 83% ee, 87% yield, $[\alpha]_D^{27} = -26.0$ (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 7.30−7.21 (m, 2H), 7.20−7.12 (m, 3H), 4.12 (dq, *J* = 7.2, 0.7 Hz, 2H), 2.76−2.64 (m, 1H), 2.57−2.47 (m, 1H), 1.94−1.78 (m, 2H), 1.59−1.49 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.22 (s, 3H), 1.12 (pseudo-t, *J* = 4.9 Hz, 1H), 0.91−0.81 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 172.4, 142.1, 128.2, 128.1, 125.5, 60.3, 34.7, 33.6, 27.1, 26.9, 24.2, 22.1, 14.5; IR (neat) 3080, 3060, 3026, 2959, 2930, 2862, 1722, 1495, 1454, 1406, 1381, 1315, 1267, 1248, 1175, 1099, 1061, 1028, 829, 746, 700 cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{15}H_{20}O_2Na]^+$ 255.1356, found 255.1321.

Ethyl (1*R,2*S**)-2-hexyl-2-methylcyclopropane-1-carboxylate (Table 5, entry 13)**: colorless oil, 99% ee, 65% yield, $[\alpha]_D^{27} = -66.1$ (*c* 0.08, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 4.12 (q, *J* = 6.9 Hz, 2H), 1.61−1.34 (m, 4H), 1.33−1.16 (m, 10H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.15−1.04 (m, 1H), 0.93−0.78 (m, 1H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ = 172.6, 60.2, 32.4, 32.0, 29.5, 27.3, 27.1, 26.9, 24.2, 22.8, 21.9, 14.5, 14.2; IR (neat) 2957, 2926, 2856, 1726, 1464, 1447, 1406, 1381, 1306, 1167, 1097, 833 cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{13}H_{24}O_2Na]^+$ 235.1669, found 235.1662.

Ethyl (1*R,2*S**)-2-(6-phenylhex-3-enyl)cyclopropane-1-carboxylate (*E*/*Z* = 9/1) 7b (Scheme 1)**: colorless oil, 96% ee, 74% yield, $[\alpha]_D^{27} = -48.2$ (*c* 0.73, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 7.31−7.09 (m, 5H), 5.47−5.33 (m, 2H), 4.17−4.02 (m, 2H), 2.66 (pseudo-t, *J* = 7.3 Hz, 2H), 2.40−2.25 (m, 2H), 2.10−1.94 (m, 2H), 1.70−1.43 (m, 3H), 1.29−1.11(m, 1H), 1.23 (t, *J* = 7.3 Hz, 3H), 1.02−0.85 (m, 2H); ^{13}C NMR ($CDCl_3$) (for *E*-isomer) δ = 172.7, 141.9, 129.6, 129.1, 128.3, 128.1, 125.6, 60.2, 36.1, 29.2, 27.3, 27.1, 21.6, 18.4, 14.5, 13.5; IR (neat) 3024, 3003, 2979, 2926, 2856, 1724, 1628, 1603, 1583, 1448, 1404, 1381, 1354, 1177, 1132, 1096, 831, 746, 719, 700 cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{18}H_{24}O_2Na]^+$ 295.1669, found 295.1662.

Ethyl (1*R,2*S**)-2-[(*E*)-undec-4-enyl]cyclopropane-1-carboxylate 8b (Scheme 1)**: colorless oil, 96% ee, 90% yield, $[\alpha]_D^{26} = -27.49$ (*c* 0.38, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 5.44−5.32 (m, 2H), 4.12 (q, *J* = 7.3 Hz, 2H), 2.03−1.89 (m, 4H), 1.66 (ddd, *J* = 8.8, 7.8, 5.3 Hz, 1H), 1.59−1.15 (m, 13H), 1.26 (t, *J* = 7.3 Hz, 3H), 1.02−0.95 (m, 1H), 0.94−0.80 (m, 1H), 0.88 (t, *J* = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ = 172.0, 130.5, 129.8, 60.2, 32.7, 32.3, 31.9, 29.8, 29.7, 28.9, 26.7, 22.8, 21.9, 18.4, 14.5, 14.2, 13.5; IR (neat) 2955, 2925, 2855, 1728, 1462, 1447, 1402, 1381, 1354, 1269, 1165, 1096, 1043, 966, 860, 829 cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{17}H_{30}O_2Na]^+$ 289.2138, found 289.2135.

Ethyl (1*R,2*S**)-2-[(*Z*)-undec-4-enyl]cyclopropane-1-carboxylate 9b (Scheme 1)**: colorless oil, 98% ee, 88% yield, $[\alpha]_D^{26} = -27.2$ (*c* 0.73, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 5.42−5.25 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.09−1.91 (m, 4H), 1.75−1.10 (m, 14H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.08−0.75 (m, 2H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ = 172.7, 130.0, 129.4, 60.2, 31.9, 29.9, 29.8, 29.1, 27.4, 27.1, 26.9, 22.8, 21.9, 18.4, 14.5, 14.2, 13.5; IR (neat) 3001, 2955, 2926, 2855, 1728, 1463, 1448, 1402, 1381, 1354, 1165, 1096, 1043, 829 cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{17}H_{30}O_2Na]^+$ 289.2138, found 289.2151.

4.4.3. Synthesis of Methyl 8-[(1*R*,2*S*)-2-hexylcyclopropyl]-octanoate 14. [(1*R*,2*S*)-2-Hexylcyclopropyl]methanol 11 (Scheme 2): colorless oil, 99% yield, $[\alpha]_D^{26} = +22.73$ (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 3.68−3.52 (m, 2H), 1.76−1.63 (m, 1H), 1.50−1.18 (m, 9H), 1.15−1.01 (m, 1H), 0.93−0.82 (m, 1H), 0.89 (t, *J* = 6.7 Hz, 3H), 0.76−0.68 (m, 1H), −0.04 (pseudo-q, *J* = 4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 63.4, 31.9, 30.2, 29.3, 28.7, 22.8, 18.3, 16.3, 14.2, 9.6; IR (neat) 3352, 2991, 2955, 2924, 2855, 1464, 1448, 1425, 1409, 1379, 1032 cm^{-1}; HRESI-MS (*m*/*z*) [M + K^+ + H_2O], calcd for $[C_{10}H_{20}OK(H_2O)]^+$ 213.1251, found 213.1441.

5-[{(1*R*,2*S*)-(2-Hexylcyclopropyl)}methanesulfonyl]-1-phenyl -1*H*-tetrazole 12 (Scheme 2): colorless oil, 90% yield, $[\alpha]_D^{26} = -36.90$ (*c* 0.53, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 7.72−7.57 (m, 5H), 3.96 (dd, *J* = 5.6, 14.6 Hz, 1H), 3.56 (dd, *J* = 9.2, 14.6 Hz, 1H), 1.51−1.09 (m, 11H), 1.06−0.95 (m, 1H), 0.94−0.76 (m, 1H), 0.89 (t, *J* = 6.5 Hz, 3H), 0.24 (pseudo-q, *J* = 5.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 153.6, 132.9, 131.3, 129.5, 125.1, 57.2, 31.9, 29.7, 29.2, 22.8, 16.0, 14.2, 11.5, 8.2; IR (neat) 3508, 3072, 2999, 2955, 2926, 2855, 1661, 1641, 1628, 1597, 1497, 1464, 1342, 1151, 764, 691, 627cm^{-1}; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{17}H_{24}N_4O_2SNa]^+$ 375.1512, found 375.1505.

Methyl 8-[(1*R*,2*S*)-2-hexylcyclopropyl]oct-7-enoate 13 (*E*/*Z* = 2.3:1) (Scheme 2): colorless oil, 73% yield, $[\alpha]_D^{26} = +31.6$ (*c* 0.18, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 5.54−5.44 (m, 0.7H), 5.42−5.33 (m, 0.3H), 5.22−5.13 (dd, *J* = 15.1, 8.3 Hz, 0.7H), 5.08−4.98 (m, 0.3H), 3.68 (s, 3H), 2.34−2.25 (m, 2H), 2.14 (q, *J* = 6.8 Hz, 0.6H), 2.00 (q, *J* = 6.6 Hz, 1.4H), 1.71−1.49 (m, 2H), 1.46−1.14 (m, 15H), 0.93−0.74 (m, 2.3H), 0.88 (t, *J* = 7.5 Hz, 3H), 0.14−0.04 (m, 0.7H); IR (neat) 3090, 2991, 2953, 2924, 2855, 1742, 1661, 1641, 1627, 1607, 1583, 1481, 1464, 1443, 1381, 1169; HRESI-MS (*m*/*z*) [M + Na^+], calcd for $[C_{18}H_{32}O_2Na]^+$ 303.2295, found 303.2280.

Methyl 8-[(1*R*,2*S*)-2-hexylcyclopropyl]octanoate[17g,18a] 14 (Scheme 2): colorless oil, 88% yield, $[\alpha]_D^{26} = -0.09$ (*c* 1.00, $CHCl_3$) [Lit.[11] 100% ee, (1*R*,2*S*)-isomer, $[\alpha]_D^{20} = -0.10$ (*c* 5.4, $CHCl_3$)]; ^1H NMR ($CDCl_3$) δ = 3.67 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.62−1.09 (m, 22H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.72−0.57 (m, 2H), 0.56 (m, 1H), −0.28 to −0.34 (m, 1H); ^{13}C NMR ($CDCl_3$) δ = 174.4, 51.5, 34.1, 32.0, 30.2, 30.1, 29.5, 29.4, 29.3, 29.2, 28.7, 28.6, 25.0, 22.7, 15.8, 15.7, 14.2, 10.9. Anal. Calcd for $C_{18}H_{34}O_2$: C, 76.54; H, 12.13. Found: C, 76.44; H, 12.21.

4.5. Conversion of Some Cyclopropanation Products [Products in Table 5 (entries 4, 11, and 13) and Scheme 1] into the Corresponding Dinitrobenzoates To Be Used for HPLC Analysis. Cyclopropanecarboxylate (0.1 mmol) was dissolved in THF (0.40 mL). The solution was cooled to 0 °C and stirred for 10 min. $LiAlH_4$ (0.2 mmol) was added to the solution and stirred for 10 min at 0 °C. The mixture was allowed to warm to room temperature, stirred for another 2 h, and cooled to 0 °C again. A saturated aqueous KF solution (0.40 mL) and $MgSO_4$ (40 mg) were added, and the resultant suspension was filtered through a pad of Celite and concentrated on a rotary evaporator. The residue

was submitted to preparative TLC (hexane/AcOEt = 4/1) to yield the corresponding alcohol.

The resulting alcohol (0.05 mmol) was dissolved in CH_2Cl_2 (0.20 mL). Triethylamine (0.15 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (0.5 μmol) were added to this solution. The mixture was stirred for 10 min at room temperature, and 3,5-dinitrobenzoyl chloride (0.10 mmol) was added. The whole mixture was stirred for 2 h and concentrated on a rotary evaporator. The residue was submitted to preparative TLC (hexane/AcOEt = 4/1) to yield the corresponding 3,5-dinitrobenzoate.

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Supporting Information Available: X-ray crystallographic data in CIF format for complex **4**; description of the analyses and analytical data; complete ref 23. This material is available free of charge via the Internet at http://pubs.acs.org.

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