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Highly Enantioselective Cyclopropanation of Styrene Derivatives Using Co(III)-Salen Complex as a Catalyst

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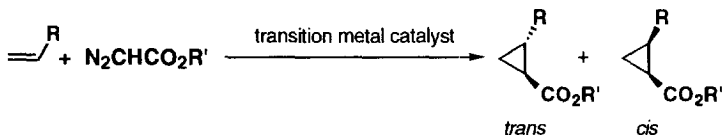
Abstract: Optically active (salen)cobalt(III) bromide complex **6-Br** was found to be an efficient catalyst for asymmetric cyclopropanation of styrene derivatives. For example, the reaction of 4-chlorostyrene and *tert*-butyl diazoacetate in the presence of **6-Br** proceeded with high enantioselectivity of 96% ee as well as high *trans-cis* selectivity (97:3) to give *tert*-butyl 2-(4-chlorophenyl)cyclopropane-1-carboxylate as a major product. © 1997 Elsevier Science Ltd.

Many transition metal complexes catalyze decomposition of α-diazo esters and the resulting metallocarbenoid species undergo methylene transfer reaction to olefins, giving the corresponding cyclopropane adducts (Scheme 1). Since cyclopropane derivatives have been widely seen as subunits of various natural products, control of the stereochemistry (enantioselectivity and *trans-cis* selectivity) of this reaction is an important objective in organic synthesis. Thus, various kinds of optically active transition metal complexes have been synthesized and used as catalysts for asymmetric cyclopropanation. As the results, high enantioselectivity has been realized by using Cu-Schiff base,[1] Co-bis(dioxime),[2] Cu-semicorrin,[3] Cu-bis(oxazoline),[4] Cu-bipyridine,[5] Rh_2(5*S*-MEPY)$_4$,[6] and Ru-Pybox[7] complexes as catalysts. However, most of these catalysts showed only moderate *trans-cis* selectivity, except for Ru-Pybox complex which shows high enantioselectivity as well as high *trans-cis* selectivity.

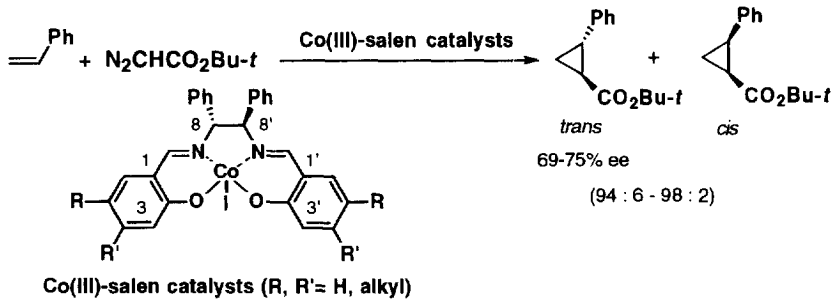


Scheme 1

On the other hand, optically active metallosalen complexes, especially (salen)manganese(III) complexes, have been found to be efficient catalysts for asymmetric oxo transfer reactions[8] including epoxidation and oxidation of sulfides[8b,9] and for asymmetric nitrene transfer reaction such as aziridination.[8b,10] Despite realization of high enantioselectivity in oxo and nitrene transfer reactions using chiral metallosalen complex as a catalyst, another similar class of reaction, asymmetric methylene transfer reaction, by using chiral metallosalen complex as a catalyst has been left unexplored. In 1978, Nakamura et al. reported asymmetric cyclopropanation using optically active (salen)cobalt(II) complex as a catalyst but its enantioselectivity was low.[2a]

This paper is dedicated to the memory of the late Professor Emeritus Masaru Yamaguchi.

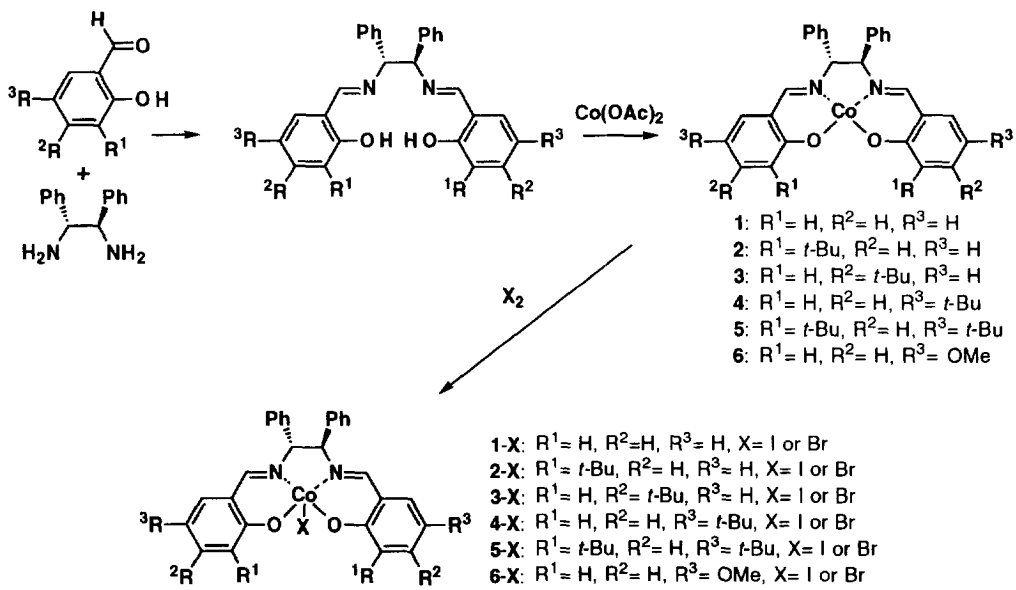
During the study on asymmetric epoxidation using optically active cationic (salen)manganese(III) complex, we found that addition of a donor ligand very often improved enantioselectivity of the reaction.[11] By analogy, we expected that chiral (salen)cobalt(III) complex bearing one axial ligand would be an efficient catalyst for asymmetric cyclopropanation. Indeed, optically active (salen)cobalt(III) complexes bearing no substituent at 3- and 3'-carbons showed high *trans-cis* selectivity, though enantioselectivity was insufficient (Scheme 2).[12] Thus, we further examined cyclopropanation using chiral (salen)cobalt(III) complex (hereafter referred to as Co(III)-salen complex). Herein we describe the detailed results of Co(III)-salen catalyzed asymmetric cyclopropanation.



Scheme 2

Preparation of Co(II)-Salen and Co(III)-Salen Complexes

Co(II)-salen complexes **1-6** were synthesized from $Co(OAc)_2$ and the corresponding salen ligands, which were in turn prepared from (1*R*,2*R*)-1,2-diphenylethylenediamine and the corresponding salicylaldehydes, in ethanol under nitrogen atmosphere.[13] Complexes **1-6** thus obtained were *in situ* oxidized by treatment with X_2 (iodine or bromine) in dichloromethane into the corresponding Co(III)-salen complexes which were used for asymmetric cyclopropanation without further purification (Scheme 3).[14]



Scheme 3

Asymmetric Cyclopropanation of Styrene Derivatives Using Co(III)-Salen Complexes

Cyclopropanation of styrene was examined by using these Co(III)-salen complexes as catalysts and *tert*-butyl diazoacetate as a carbene source in dichloromethane. Since Mn-salen complexes bearing bulky and/or chiral substituents at 3- and 3'-carbons have been known to be efficient catalysts for asymmetric epoxidation,[8] we first examined asymmetric cyclopropanation using Co(III)-salen complexes (**2-I**, **2-Br**, or **5-Br**) as catalysts. Contrary to our expectation, these complexes showed no or very poor catalytic activity (Table 1, entries 3, 4, and 9). Complexes **1-I**, **3-I**, and **4-I** which had no C3 and C3' substituent, however, catalyzed the desired reaction with moderate enantioselectivity (64-75% ee) and high *trans-cis* selectivity (Table 1, entries 1, 5, and 7). The presence of sterically bulky *tert*-butyl group at 4(4')- or 5(5')-carbons only slightly imploves the enantioselectivity (entries 5 and 7). Therefore, we tried to improve asymmetry-inducing ability of the catalyst by changing the electronic nature of the ligand. We first examined the replacement of axial iodine ligand with bromine ligand, since a bromide ligand was expected to lower the activity of carbenoid species due to its weaker *trans*-effect, as compared with an iodide ligand. Although, the complex **1-Br** showed slightly imploved enantioselectivity (66% ee) than **1-I** (entry 2), complexes **3-Br** and **4-Br** showed better enantioselectivity than the corresponding iodides **3-I** and **4-I** (entries 6 and 8). To further improve enantioselectivity, we next modified the substituent of the salen ligand. Fujita *et al.*, had reported that chiral (salen)vanadium complex bearing electron-donating methoxy group at 3- and 3'-carbons showed better asymmetric induction in the oxidation of sulfides than the (salen)vanadium complex bearing sterically bulky *tert*-butyl group at 3- and 3'-carbons.[15] A similar phenomenon was also observed in Mn-salen catalyzed asymmetric oxidation of sulfides.[9a,9c,16] Thus, we examined cyclopropanation using complex

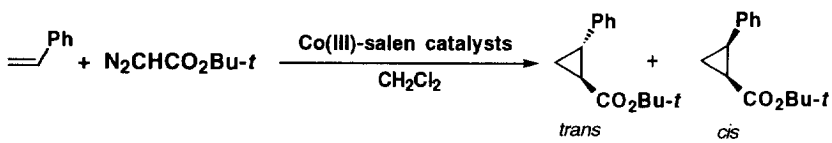


Table 1. Asymmetric cyclopropanation of styrene using Co(III)-salen complex as a catalyst.

entry	catalyst	yield (%)	*trans*:*cis*[a]	% ee[b] (*trans*)[c]	% ee[d] (*cis*)[e]
1	**1-I**	79	95:5	64(1*S*,2*S*)	51(1*S*,2*R*)
2	**1-Br**	83	95:5	66(1*S*,2*S*)	82(1*S*,2*R*)
3	**2-I**	0	-	-	-
4	**2-Br**	-[f]	-	-	-
5	**3-I**	76	98:2	73(1*S*,2*S*)	-
6	**3-Br**	85	96:4	89(1*S*,2*S*)	93(1*S*,2*R*)
7	**4-I**	76	95:5	75(1*S*,2*S*)	-
8	**4-Br**	55	94:6	83(1*S*,2*S*)	42(1*S*,2*R*)
9	**5-Br**	-[f]	-	-	-
10	**6-Br**	80	96:4	93(1*S*,2*S*)	91(1*S*,2*R*)

a) Determined by ^{1}H NMR analysis (270 MHz).
b) Determined by HPLC analysis using optically active column (Daicel Chiralcel OJ; hexane : *i*-PrOH=9 : 1), after the ester was reduced to the corresponding alcohol by $LiAlH_4$.
c) Determined by the comparison of HPLC elution order of the enantiomers of *trans*-2-(phenylcyclopropyl)methanol after $LiAlH_4$-reduction, with the authentic samples prepared according to the reported procedure (ref. 5).
d) Determined by GC analysis (SUPELCO ß-DEX 120 fused silica capillary column, 30 m x 0.25 mm ID, 0.25 µm film, col. temp.: 110 °C), after the *tert*-butyl ester was converted into the corresponding methyl ester by the sequence: i) TFA deprotection and ii) CH_2N_2 methylation.
e) Determined by the comparison of GC elution order of the enantiomers of methyl *cis*-2-(phenylcyclopropyl)carboxylate derived from the obtained *cis* isomer by hydrolysis and the subsequent CH_2N_2 treatment, with the authentic sample prepared according to the reported procedure (ref. 5).
f) The formation of only a trace amount of the product was detected by TLC analysis.

6-Br bearing methoxy group at C5- and C5'-carbons and could achieve high enantioselectivity 93% ee, as expected, without decaying high *trans-cis* selectivity (entry 10).[17]

Asymmetric cyclopropanation of other styrene derivatives also showed high enantioselectivity as well as high trans selectivity (Table 2). However, the reaction of disubstituted olefins such as inden was sluggish.

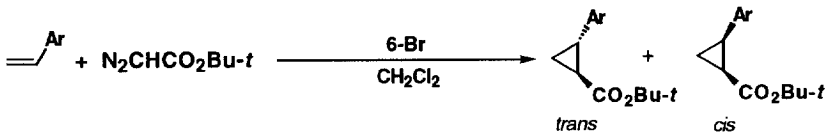


Table 2. Asymmetric cyclopropanation of styrene derivatives using complex **6-Br** as a catalyst.

entry	Ar	yield (%)	*trans:cis*[a]	% ee(trans)[b]
1	4-ClC_6H_4	86	97:3	96[c]
2	2-naphthyl	87	95:5	92[d]

a) Determined by ^1H NMR analysis (270 MHz).
b) Absolute configuration has not been determined.
c) Determined by HPLC analysis using optically active column (Daicel Chiralcel OD; hexane : *i*-PrOH=100 : 1), after the ester was converted into the acetate by the sequence: i) $LiAlH_4$ reduction and ii) acetylation.
d) Determined by HPLC analysis using optically active column (Daicel Chiralcel OB-H; hexane : *i*-PrOH=50 : 1)

In the course of our study on Mn-salen catalyzed epoxidation, we have obtained some data suggesting that the ligands of the intermediary oxo Mn(V)-salen complexes had non-planar structures and that non-planarity of the salen ligand played very important role in asymmetric induction by Mn-salen catalyst.[18] Although the mechanism of asymmetric induction by Co(III)-salen catalyst is unclear at present, we assumed that the ligand of the intermediary Co(V)-salen carbenoid species also had a non-planar structure, as shown in Fig. 2, which was drawn by using TRIPOS-SYBYL on an IRIS Indigo 2. Differing from the oxygen atom of oxo Mn(V)-salen species, however, the carbenoid carbon of Co(V)-salen species carries a bulky *tert*-butoxycarbonyl group on it, which is considered to protrude over the downward benzene ring (**A**). In Mn(III)-salen catalyzed epoxidation, olefins are considered to approach metal oxo bond passing over the downward benzene ring.[8a] In the present reaction, however, this pathway is blocked by the presence of the carbenoid ester group. Thus we assumed that styrene would approach the carbenoid carbon from the front side (Fig. 1), directing its phenyl group away from the ester group to give (1*S*,2*S*)-isomer in preferential. This assumption is

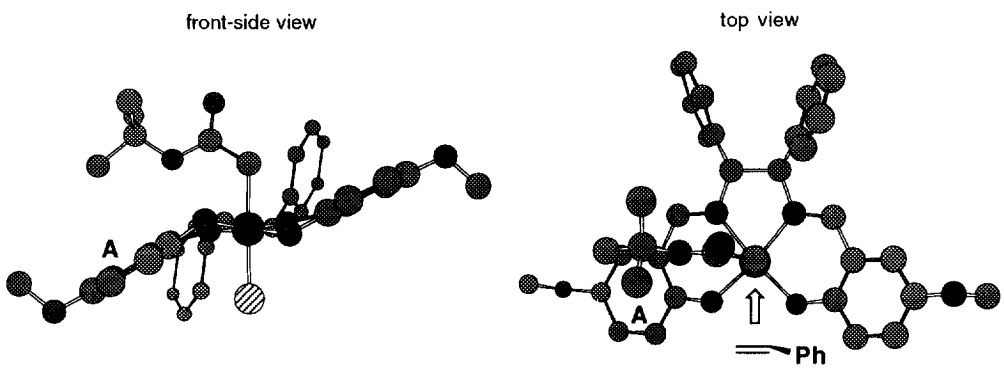


Fig. 1 The frontside and top views of carbene Co(V)-salen complex derived from the corresponding Co(III)-complex (**6-Br**)

well compatible with the observation that the Co(III)-salen complexes bearing C3(3')-substituents show no or very poor catalytic activity. C3(3')-Substituents probably interfere with the incoming olefins. Introduction of axial bromide ligand and 5(5')-methoxy groups[19] decreases the reactivity of carbenoid species and the reaction of the less reactive carbenoid species with olefins proceeds via a more product-like transition state, resulting in more specific nonbonded interactions between the complex and the incoming olefin and, as a result, high stereoselectivity.

In conclusion, we could demonstrate that a well-designed Co(III)-salen complex such as **6-Br** was an efficient catalyst for asymmetric cyclopropanation of styrene derivatives and could control both enantioselectivity and *trans-cis* selectivity at the same time.

Experimental

NMR spectra were recorded at 270 MHz on a JEOL EX-270 instrument. All signals were expressed as ppm down field from tetramethylsilane used as an internal standard (δ-value in $CDCl_3$). IR spectra were obtained with a SHIMADZU FTIR-8600 instrument. Optical rotation was measured with a JASCO DIP-360 automatic digital polarimeter. High resolution mass spectra were recorded on a JEOL JMS-SX/SX 102A 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 0.5 mm x 20 cm x 20 cm E. Merck silica gel plate (60 F-254). Solvents were dried and distilled shortly before use. Reactions were carried out under an atmosphere of nitrogen if necessary. HPLC analysis of enantiomeric excess was carried out using Hitachi L-4000 equipped with an appropriate optically active column, as described in the footnote of Table 1 and Table 2. GC analysis of enantiomeric excess was carried out using GASUKURO KOGYO GC-380 with SUPELCO ß-DEX 120 fused silica capillary column, as described in the footnote of Table 1.

Co(II)-salen complex 6

(1*R*,2*R*)-1,2-Diphenylethylenediamine (102 mg, 0.48 mmol) was added to a solution of 2-hydroxy-5-methoxybenzaldehyde[20] (145 mg, 0.96 mmol) in ethanol (2 ml) and stirred overnight at room temperature. The mixture was concentrated *in vacuo* and to this residue were added deairated ethanol (8 ml) and a freshly prepared ethanol solution (960 µl) of $Co(OAc)_2$[21] (0.5 M, 0.48 mmol) under nitrogen atmosphere. The mixture was refluxed for 9 h, and then allowed to cool to room temperature. The resulting brown precipitate was separated from the solution by filtration, washed with deairated ethanol under nitrogen atmosphere, and dried under vacuum to give **6** (198 mg, 77%). **6**; IR (KBr): 3028, 3001, 2943, 2905, 2833, 1595, 1533, 1462, 1421, 1362, 1302, 1256, 1219, 1167, 1030, 824, 698 cm^{-1}. Calcd. for $C_{30}H_{26}N_2O_4Co$: C, 67.04; H, 4.88; N, 5.21%. Found: C, 66.98; H, 4.90; N, 5.20%.

Co(II)-salen complex 1

Co(II)-salen complex **1** was synthesized from salicylaldehyde and (1*R*,2*R*)-1,2-diphenylethylenediamine in the same procedure as described for the synthesis of **6**. **1** (82%); IR (KBr): 3057, 1603, 1533, 1497, 1437, 1348, 1317, 1205, 1148, 1126, 908, 849, 752, 702, 532, 467 cm^{-1}. Calcd. for $C_{28}H_{22}N_2O_2Co$: C, 70.44; H, 4.64; N, 5.87%. Found: C, 70.56; H, 4.63; N, 5.70%.

Co(II)-salen complex 2

Co(II)-salen complex **2** was synthesized from 2-hydroxy-3-*tert*-butylbenzaldehyde[22] and (1*R*,2*R*)-1,2-diphenylethylenediamine in the same procedure as described for the synthesis of **6**. **2** (73%); IR (KBr): 2947, 2905, 2866, 1591, 1531, 1491, 1484, 1416, 1400, 1387, 1337, 1312, 1234, 1200, 1146, 1084, 1065, 868, 760, 698 513 cm^{-1}. Calcd. for $C_{36}H_{38}N_2O_2Co$: C, 73.33; H, 6.50; N, 4.75%. Found: C, 73.22 H, 6.47; N, 4.71%.

Co(II)-salen complex 3

Co(II)-salen complex **3** was synthesized from 2-hydroxy-4-*tert*-butylbenzaldehyde[22] and (1*R*,2*R*)-1,2-diphenylethylenediamine in the same procedure as described for the synthesis of **6**. **3** (82%); IR (KBr): 2955, 2901, 2866, 1609, 1520, 1456, 1412, 1379, 1302, 1225, 1200, 1090, 1020, 962, 868, 789, 766, 700, 669 cm^{-1}. Calcd. for $C_{36}H_{38}N_2O_2Co$: C, 73.33; H, 6.50; N, 4.75%. Found: C, 73.42; H, 6.59; N, 4.77%.

Co(II)-salen complex 4

Co(II)-salen complex **4** was synthesized from 2-hydroxy-5-*tert*-butylbenzaldehyde[22] and (1*R*,2*R*)-1,2-diphenylethylenediamine in the same procedure as described for the synthesis of **6**. **4** (78%); IR (KBr): 3061, 2953, 2901, 2866, 1614, 1591, 1526, 1474, 1454, 1417, 1377, 1362, 1317, 1256, 1219, 1188, 1146, 831, 698 561 cm^{-1}. Calcd. for $C_{36}H_{38}N_2O_2Co$: C, 73.33; H, 6.50; N, 4.75%. Found: C, 73.17; H, 6.57; N, 4.50%.

Co(II)-salen complex 5

Co(II)-salen complex **5** was synthesized from 2-hydroxy-3,5-di-*tert*-butylbenzaldehyde[22] and (1*R*,2*R*)-1,2-diphenylethylenediamine in the same procedure as described for the synthesis of **6**. **5** (80%); IR (KBr): 2957, 2903, 2866, 1612, 1589, 1526, 1454, 1429, 1387, 1358, 1319, 1252, 1202, 1178, 787, 698 cm^{-1}. Calcd. for $C_{44}H_{54}N_2O_2Co$: C, 75.30; H, 7.76 N, 3.99%. Found: C, 75.32; H, 7.75; N, 4.00%.

General procedure for asymmetric cyclopropanation using Co(III)-salen complex 6-Br as a catalyst

To a dichloromethane solution (0.5 ml) of Co(II)-salen catalyst **6** (2.3 mg, 4.2 μmol) was added a dichloromethane solution of Br_2 (17 μl, 0.12 M, 2.1 μmol) and the mixture was stirred for 1 h at room temperature to give Co(III)-salen complex **6-Br**.[14] To this solution was added styrene (49 μl, 0.42 mmol) and the whole mixture was stirred for another 10 min. *tert*-Butyl diazoacetate (11.9 μl, 85 μmol) was added to this mixture at room temperature, stirred for 24 h, and then concentrated *in vacuo*. The residue was passed through a short silica gel column (hexane-AcOEt=1:0 to 9:1) to give a 96:4 mixture of *tert*-butyl *trans*- and *cis*-2-phenylcyclopropane-1-carboxylates (14.9 mg, 80%). The % ee and configuration of *trans*- and *cis*- isomers were determined as described in the footnote of Table 1. Further purification by preparative TLC (silica gel, hexane-(i-Pr)$_2$O=4:1) gave *tert*-butyl *trans*-2-phenylcyclopropane-1-carboxylate as a single isomer.

***tert*-Butyl *trans*-2-phenylcyclopropane-1-carboxylate**. (93% ee); $[\alpha]_D^{20}$ +253.3° (c 0.73, $CHCl_3$). IR (KBr): 2980, 2934, 1720, 1607, 1458, 1402, 1367, 1342, 1288, 1258, 1209, 1153, 1078, 1045, 1024, 937, 843, 781, 758, 743, 725, 696, 525 cm^{-1}. ^1H NMR: δ 7.31-7.07 (m, 5H), 2.43 (ddd, J= 4.2, 6.4 and 9.2 Hz, 1H), 1.83 (ddd, J= 4.2, 5.2 and 8.4 Hz, 1H), 1.53 (ddd, J= 4.4, 5.2 and 9.2 Hz, 1H), 1.47 (s, 9H), 1.23 (ddd, J= 4.4, 6.4 and 8.4 Hz, 1H). HRFABMS m/z. Calcd. for $C_{14}H_{19}O_2$ (M^++H): 219.1385. Found 219.1385.

***tert*-Butyl *trans*-2-(4-chlorophenyl)cyclopropane-1-carboxylate**.[23] (96% ee); $[\alpha]_D^{21}$ +232.8° (c 1.08 $CHCl_3$). IR (KBr): 3003, 2984, 2939, 1717, 1497, 1447, 1396, 1367, 1335, 1302, 1277, 1250, 1219, 1151, 1099, 1047, 1011, 943, 930, 847, 818, 748, 525, 473 cm^{-1}. ^1H NMR: δ 7.23 (d, J= 8.4 Hz, 2H), 7.01 (d, J= 8.4 Hz, 2H), 2.41 (ddd, J= 4.2, 6.3 and 9.2 Hz, 1H), 1.79 (ddd, J= 4.2, 5.3 and 8.4 Hz, 1H), 1.53 (ddd, J= 4.5, 5.3 and 9.2 Hz, 1H), 1.47 (s, 9H), 1.19 (ddd, J= 4.5, 6.3 and 8.4 Hz, 1H). HRFABMS m/z. Calcd. for $C_{14}H_{18}O_2Cl$ (M^++H): 253.0995. Found 253.0995.

***tert*-Butyl *trans*-2-(2-naphthyl)cyclopropane-1-carboxylate**.[23] (92% ee); $[\alpha]_D^{21}$ +211.8° (c 0.56 $CHCl_3$). IR (KBr): 2980, 2932, 1717, 1508, 1450, 1404, 1389, 1367, 1310, 1252, 1207, 1146, 1045, 964, 935, 901, 868, 845, 820, 748, 484 cm^{-1}. ^1H NMR: δ 7.80-7.74 (br t, 3H), 7.56 (br s, 1H), 7.49-7.38 (m, 2H), 7.19 (dd, J= 1.7 and 8.5 Hz, 1H), 2.61 (ddd, J= 4.2, 6.4 and 9.2 Hz, 1H), 1.94 (ddd, J= 4.2, 5.3 and 8.4 Hz, 1H), 1.60 (ddd, J= 4.5, 5.3 and 9.2 Hz, 1H), 1.48 (s, 9H), 1.35 (ddd, J= 4.5, 6.4 and 8.4 Hz, 1H). HRFABMS m/z. Calcd. for $C_{18}H_{20}O_2$ (M^+): 268.1463. Found 268.1463.

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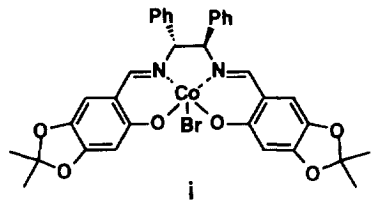

i

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