Regular Article

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Planar Chiral [2.2]Paracyclophane-Based Bisoxazoline Ligands: Design, Synthesis, and Use in Cu-Catalyzed Inter- and Intramolecular Asymmetric O–H Insertion Reactions

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Centrally chiral bisoxazolines connected directly to a planar chiral [2.2]paracyclophane backbone were synthesized and evaluated as asymmetric ligands in Cu-catalyzed intermolecular ethanolic O–H insertion reactions of α-diazo esters. The reactivities and enantioselectivities of Cu complexes of the synthesized bisoxazoline ligands were lower than those of ligands without central chirality. However, planar chiral [2.2]paracyclophane-based bisoxazoline ligands with an inserted benzene spacer that had a sterically demanding isopropyl substituent showed good enantioselectivities in inter- and intramolecular aromatic O–H insertion reactions, without the aid of central chirality.

Key words cyclophane; planar chirality; bisoxazoline; O–H insertion; copper

Substituted [2.2]paracyclophanes (PCPs) have been used as planar chiral ligands or organocatalysts in a variety of asymmetric reactions because of PCP features such as configurational stability and a diversity of possible chiral structures.[1–5] However, most PCP-based ligands or catalysts with a high asymmetric induction ability have central chirality along with their intrinsic planar chirality, except in the cases of phanephos (4,12-bis(diphenylphosphino)[2.2]paracyclophane),[6] *N*-heterocyclic carbene (NHC) carbenes bearing two PCP units,[7] and others.[3,8–10] The potential ability of this planar chiral PCP backbone for asymmetric induction has therefore not yet been sufficiently investigated.

We were interested in the use of pseudo-*ortho*-substituted aryl-PCPs as catalyst scaffolds with no additional chiral sources, which are expected to provide efficient asymmetric environments different from those of known functionalized PCPs. Our design concept is as follows. One or two spacer aryl groups are connected to the pseudo-*ortho* position of the PCP backbone and two functional groups (R^1 and R^2) are located at the *meta* position of the spacer or directly on the backbone (Fig. 1). The spacer has the conformational flexibility to achieve a distance between the two functional groups that is suitable for a reaction to occur and also has a steric or electronic effect, which depends on the aryl group itself and/or its characteristic substituents (R^3 and R^4). We have already reported that the single spacer in PCP-based phosphine–phenol catalysts (S_p)-**A** (Fig. 1, left) is crucial for achieving higher reactivity and enantioselectivity in the aza-Morita–Baylis–Hillman reactions of *N*-tosylaldimines and vinyl ketones[11,12] (Chart 1a). The phosphine catalysts (S_p)-**A** can also be used in the highly enantioselective [3+2] annulations of allenoates and *N*-tosylaldimines[13] (Chart 1b). We envisaged that the planar chirality of the C_2-symmetric bisoxazoline (Box) ligand (S_p)-**1**, which has a PCP backbone, could strictly control the enantioselectivity of the metal-catalyzed asymmetric reaction without

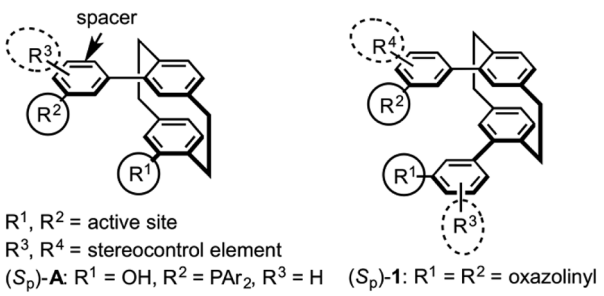

Fig. 1. Design Concept of Planar Chiral PCP Catalysts

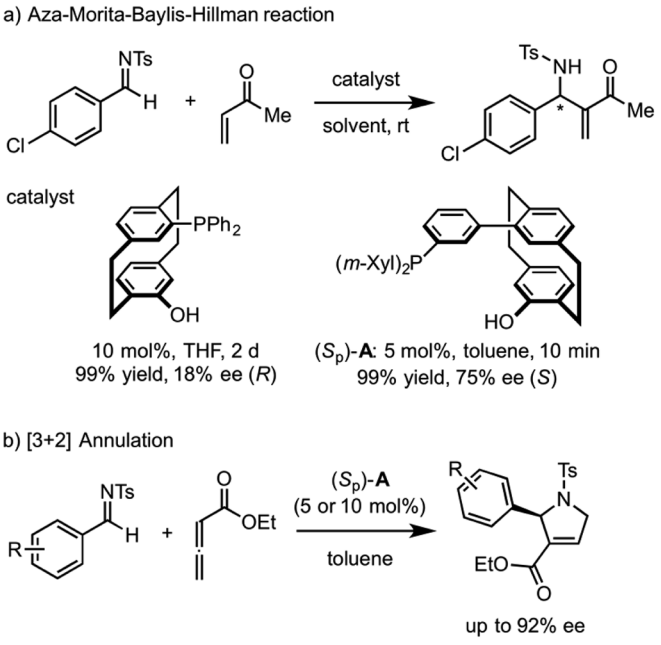

Chart 1. PCP-Based Phosphine–Phenol-Catalyzed Asymmetric Reactions

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the aid of central chirality (Fig. 1, right, R^1=R^2=oxazolinyl). The known chiral Box ligands are easily prepared from chiral amino alcohols and usually have two centrally chiral oxazoline rings.[14] There are therefore few examples of the use of chiral Box ligands bearing achiral oxazoline units in catalytic asymmetric reactions.[15–17]

The Cu-catalyzed O–H insertion of α-diazo esters is useful for the construction of α-alkoxycarbonyl structures, which are found in natural products and biologically active compounds.[18–20] A highly enantioselective version of this reaction has recently been accomplished with bisazaferrocene **I**,[21] Spirobox **II**,[17,22–26] or the imidazoindolephosphine ligand **III**[27–34] (Fig. 2). However, there is still a need to develop other ligands for this type of reaction because the more versatile Box ligands **IV** and **V** are unsuitable.[21–24,26] In this context, we recently used our designed PCP-based Box ligands (S_p)-**1**, in which two achiral oxazoline units are located at the *meta* positions of the spacer, in Cu-catalyzed O–H insertion reactions. We reported in a short communication that the ligands showed good enantioselectivities in intermolecular ethanolic and phenolic O–H insertions.[35] We now report the effects of the introduction of central chirality of the oxazoline ring in the PCP-based Box ligand on intermolecular ethanolic O–H insertion. Details of inter- and intramolecular aromatic O–H insertion reactions catalyzed by PCP-based Box (S_p)-**1**-Cu complexes are also given.

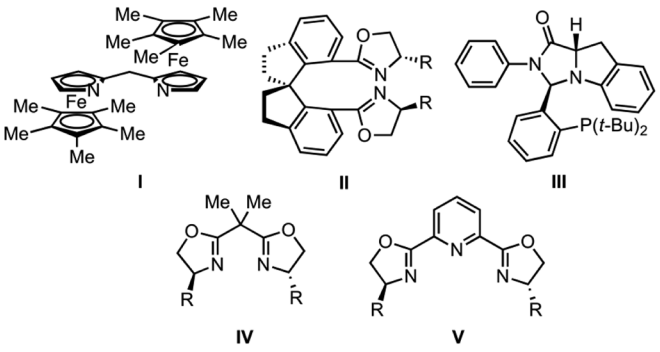


Fig. 2. Reported Bidentate Ligands Used in Cu-Catalyzed O–H Insertions

We previously investigated the use of five C_2-symmetric PCP-Box ligands (S_p)-**1**, which had spacers with different steric features, in the Cu-catalyzed insertion of methyl α-diazophenylacetate (**2**) into the O–H bond of ethanol under the conditions 5 mol% of $Cu(OTf)_2$, 6 mol% of the Box ligand, 6 mol% of $NaBAr_F$ (sodium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate) as an additive, and 5-Å molecular sieves in CH_2Cl_2 at 40°C[35] (Chart 2). The phenyl-substituted ligand (S_p)-**1b** showed the highest enantioselectivity, namely 76%. When the unsubstituted ligand (S_p)-**1a** was used, the enantioselectivity for product **3** decreased significantly, and ligands (S_p)-**1c** and (S_p)-**1d**, characterized by horizontal extension of the substituent on the spacer, also showed lower selectivities. However, the vertically extended ligand (S_p)-**1e** gave an enantiomeric excess (ee) similar to that for (S_p)-**1b**. Ligand (S_p)-**4a**, in which both oxazoline functionalities are directly connected to the PCP backbone, gave a moderate level of asymmetric induction (46% ee) in the opposite sense, despite having no bulky substituent that could provide stereocontrol. We therefore investigated installation of central chirality in the (S_p)-**4** ligand and use of the synthesized planar–central hybrid chiral ligands to achieve improved enantioselectivity.

The effects of central chirality of the oxazoline ring in PCP-based Box were investigated by using phenyl- and benzyl-substituted Box ligands **4b** and **4c**, in which substituted oxazolines were directly connected to the PCP backbone. Phenyl-substituted Box ligands (S_p,*S*,*S*)- and (R_p,*S*,*S*)-**4b** were prepared from the corresponding (*S*)-amino alcohol and ra-

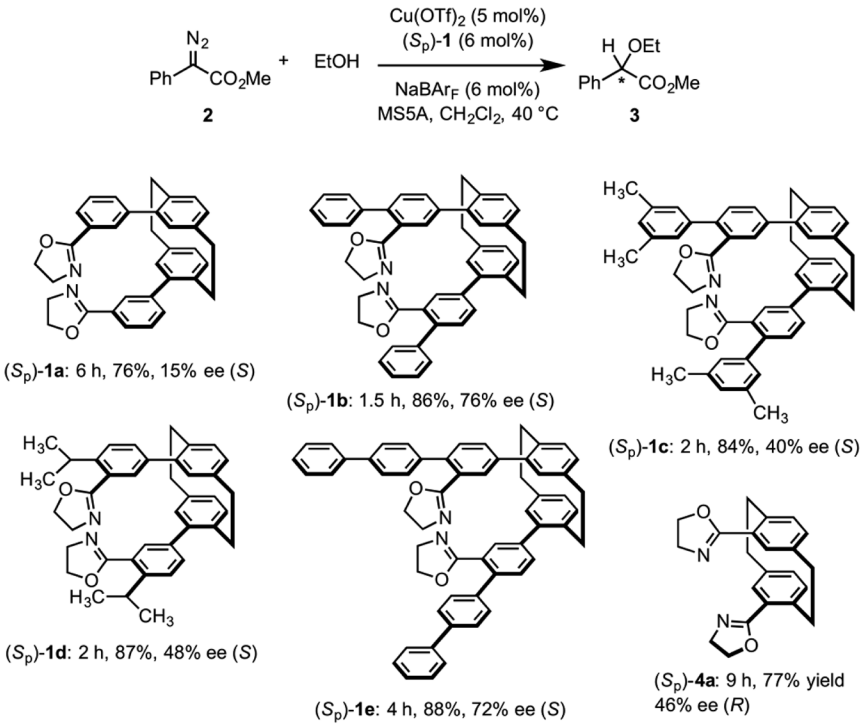


Chart 2. Box (S_p)-**1**-Cu-Catalyzed Intermolecular Ethanolic O–H Insertion of **2**

cemic pseudo-*ortho*-[2.2]cyclophanedicarboxylic acid (**6**), derived from bromocyclophanyl triflate (**5**),[36] as shown in Chart 3. The benzyl-substituted Box ligands (S_p,*S*,*S*)- and (R_p,*S*,*S*)-**4c** were prepared from (S_p)- and (R_p)-**6**, respectively.

With four Box ligands bearing both planar and central chiralities in hand, we explored their use in O–H insertion reactions. For all the ligands examined, the levels of asymmetric induction were lower than that of Box (S_p)-**4a** bearing achiral oxazoline rings, and the sense of the enantioselectivity depended on the planar chirality of the PCP backbone rather than the central chirality of the oxazoline ring (Table 1, entries 1–5). These results suggest that the alkyl groups on the oxazoline ring connected to the PCP do not contribute to provision of an efficient asymmetric environment for O–H insertion. When the benzyl-substituted PCP-Box ligands (S_p,*S*,*S*)- and (R_p,*S*,*S*)-**4c** were used, the reactions were sluggish and incomplete, even at 60°C. The benzyl group on the oxazoline ring can protrude toward the reaction site and prevent formation of a Cu–carbene complex.

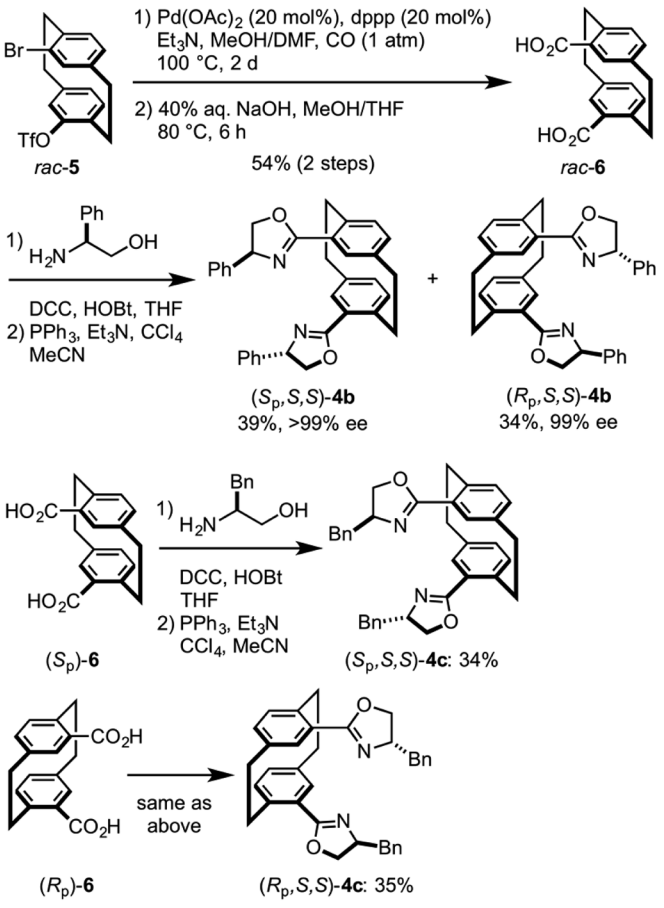


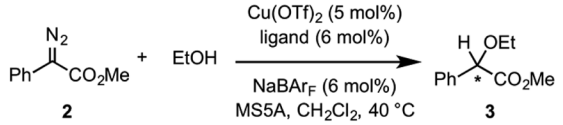
Chart 3. Preparation of PCP-Based Box Ligands with Central Chirality

The Box ligands **4** with both planar and central chiralities proved to be unsuitable for Cu-catalyzed intermolecular ethanolic O–H insertion, therefore we next investigated the use of the Box ligands (S_p)-**1**, with only planar chirality, in inter- and intramolecular aromatic O–H insertion reactions. For the intermolecular phenolic O–H insertion reaction of ethyl *α*-diazopropionate (**7**),[22,27] the enantioselectivity of the isopropyl-substituted ligand (S_p)-**1d** was better than that of phenyl-substituted (S_p)-**1b**, and 80% ee was achieved, with the *S* configuration being preferred[35] (Table 2, entries 1, 3). The insertion reaction proceeded smoothly at room temperature, and the use of CuCl as a Cu source gave the highest enantiocontrol, but the product yield was lower than that obtained with $Cu(OTf)_2$ (entry 6). Use of the sterically hindered *tert*-butyl ester, lowering the reaction temperature to 0°C, or the absence of 5-Å molecular sieves led to decreases in the product ee values (entries 4, 7, and 8).

A catalyst prepared *in situ* from $Cu(OTf)_2$ and (S_p)-**1d** was used to investigate the effects of the substituent on the benzene ring of the phenol. An electron-donating group at the *para* position led to a slight increase in the product enantioselectivity, whereas an electron-withdrawing group led to a decrease in both the reactivity and product ee (Table 3, entries 2 and 5). A substituent at the *ortho* position also led to a decrease in the reactivity (entries 3, 4, and 6). These trends are similar to those reported for a chiral imidazoindolephosphine–Cu complex.[27]

Finally, intramolecular aromatic O–H insertion reactions[17] with Box (S_p)-**1d**-Cu as the catalyst were examined. In the absence of a ligand, the $CuOTf(C_6H_6)_{1/2}$-catalyzed reaction of 2-diazo-*o*-hydroxyphenylpropanoate **10a** proceeded smoothly at room temperature to afford the desired dihydrobenzofuran product **11a** in only 12% yield, along with the *α*,*β*-unsaturated ester **12a** (60%) (Table 4, entry 1). In contrast, the reaction with the catalyst prepared *in situ* from $CuOTf(C_6H_6)_{1/2}$ and (S_p)-**1d** gave the cyclized product **11a** as the major product in 58% yield with 72% ee, although a prolonged reaction time (3 h) was required (entry 2). Use of the ligand (S_p)-**1d** not only induced an asymmetric reaction but also prevented production

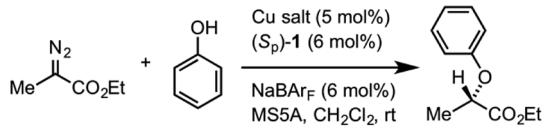
Table 1. Box **4**-Cu-Catalyzed Intermolecular Ethanolic O–H Insertion of **2**[a]



Entry	Ligand	Solvent	Temp (°C)	Time (h)	Yield (%)[b]	ee (%)[c]
1	(S_p)-**4a**	CH_2Cl_2	40	9	77	46 (*R*)
2	(S_p,*S*,*S*)-**4b**	CH_2Cl_2	40	4	83	15 (*R*)
3	(R_p,*S*,*S*)-**4b**	CH_2Cl_2	40	9	68	11 (*S*)
4	(S_p,*S*,*S*)-**4c**	$(CH_2Cl)_2$	60	20	13	25 (*R*)
5	(R_p,*S*,*S*)-**4c**	$(CH_2Cl)_2$	60	38	19	1 (*S*)

a) All reactions were performed with ligand (0.012 mmol), $Cu(OTf)_2$ (0.010 mmol), $NaBAr_F$ (0.012 mmol), 5-Å molecular sieves (300 mg), ethanol (1.0 mmol), and diazo ester **2** (0.20 mmol) in CH_2Cl_2 (total 2 mL). *b*) Isolated yield. *c*) Determined by HPLC analysis (Daicel CHIRALCEL OD-H).

Table 2. Box (S_p)-**1**-Cu-Catalyzed Intermolecular Phenolic O–H Insertion of **7**[a)]

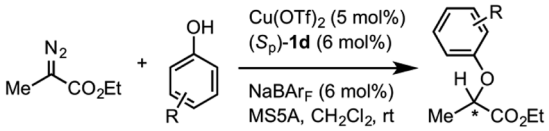


7 **8a** **9a**

Entry	Ligand	Cu salt	Time (h)	Yield (%)[b)]	ee (%)[c)]
1	(S_p)-**1b**	CuCl	2	73	61
2	(S_p)-**1c**	CuCl	2	65	39
3	(S_p)-**1d**	CuCl	1	66	80
4[d)]	(S_p)-**1d**	CuCl	2	68	36
5	(S_p)-**1d**	$CuOTf(C_6H_6)_{1/2}$	1	78	57
6	(S_p)-**1d**	$Cu(OTf)_2$	1	75	76
7[e)]	(S_p)-**1d**	$Cu(OTf)_2$	2	61	67
8[f)]	(S_p)-**1d**	$Cu(OTf)_2$	2	48	24

a) All reactions were performed with ligand (0.012 mmol), [Cu] (0.010 mmol), $NaBAr_F$ (0.012 mmol), 5-Å molecular sieves (300 mg), PhOH **8a** (1.0 mmol), and diazo ester **7** (0.20 mmol) in CH_2Cl_2 (total 2 mL) unless otherwise stated. *b*) Isolated yield. *c*) Determined by HPLC analysis (Daicel CHIRALCEL OD-H). *d*) *tert*-Butyl *α*-diazopropionate was used instead of ethyl *α*-diazopropionate (**7**). *e*) Reaction was performed at 0°C. *f*) Reaction was performed without 5-Å molecular sieves.

Table 3. Box (S_p)-**1d**-Cu-Catalyzed Intermolecular Aromatic O–H Insertion of **7**[a)]



7 **8** **9**

Entry	Phenol	Time (h)	Product	Yield (%)[b]	ee (%)[c]
1	**8a**	1	**9a**	75	76 (*S*)
2	**8b**	3	**9b**	73	79
3	**8c**	1	**9c**	61	71
4	**8d**	1	**9d**	61	71
5	**8e**	1	**9e**	58	48 (*S*)
6	**8f**	1	**9f**	44	75 (*S*)

a) All reactions were performed with ligand (0.006 mmol), $Cu(OTf)_2$ (0.005 mmol), $NaBAr_F$ (0.006 mmol), 5-Å molecular sieves (150 mg), phenol **8** (0.5 mmol), and diazo ester **7** (0.10 mmol) in CH_2Cl_2 (total 1 mL). *b*) Isolated yield. *c*) Determined by HPLC analysis.

of the undesired *β*-hydride elimination[37,38)] product **12**.[39)] In screening of the Cu source, copper(I) halides showed good enantioselectivities but low reactivities (entries 4 and 5). The reactivities and enantioselectivities of methoxy-substituted diazoarylpropanoates **10b** and **10c** were similar to those of **10a** in the presence of the Box (S_p)-**1d**-$CuOTf(C_6H_6)_{1/2}$ catalyst (entries 7 and 9). However, chloro-substituted **10d** gave a poor insertion product yield, as expected (entry 11). The dihydrobenzopyran product **11e** was obtained from diazobutanoate **10e** in moderate yield and with good enantioselectivity under the same conditions (entry 13).

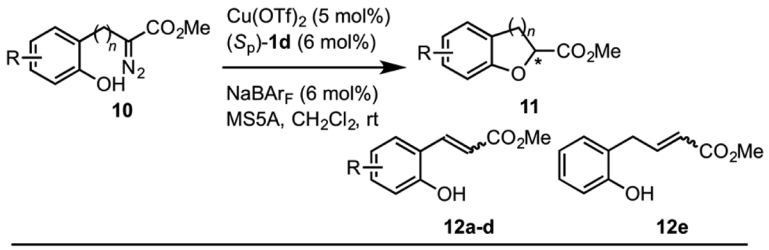
It is generally accepted that X–H insertion *via* metal-catalyzed decomposition proceeds by a stepwise mechanism, which involves generation of a metal-associated onium ylide and proton transfer from the metal-associated ylide or from the free ylide, if the X atom has lone-pair electrons.[19,20,40)] Zhou and colleagues reported that proton transfer is involved in the rate-limiting step in both Cu-catalyzed O–H insertion with water[23)] and N–H insertion with aniline.[41,42)] On the basis of the catalyst structure, Zhou proposed a chiral induction model for the N–H insertion process, in which the conformation of the copper carbenoid and the direction of attack of aniline followed by a configuration-retaining proton transfer are controlled by the C_2-symmetric chiral pocket[41,42)] (Fig. 3a). Considering the similarity between O–H insertion and N–H insertion, and the observation that the preferred absolute stereochemistries of all products (ethanolic O–H insertion product **3**, intramolecular aliphatic O–H insertion product,[35)] and inter- and intra-molecular aromatic O–H insertion products **9** and **11**) obtained with the Box (S_p)-**1**-Cu catalysts are opposite to those obtained with Zhou's Spirobox (S_a,*S*,*S*)-**5**-Cu,[22,24–26)] the C_2-symmetric catalyst conformation during the Cu-catalyzed O–H insertion reaction is proposed to be that shown in Fig. 3b. However, there is no experimental support for this active catalyst structure at this stage. In Box ligands **4**, the substituents at position 4 on the oxazoline ring come into close proximity to the Cu atom, because of their large bite angles. When the R groups at position 4 are bulky, copper carbenoid formation might be inhibited and/or catalyst dissociation before the stereochemistry-determining step might be accelerated because the R group is too close to the Cu atom, leading to lower reactivity and selectivity (Fig. 3c).

In summary, we found that Cu complexes with C_2-symmetric planar chiral PCP-Box ligands with no central chirality catalyzed inter- and intramolecular O–H insertion reactions. A bulky substituent on the benzene spacer of the PCP-based Box ligand was important for achieving a high level of planar-chirality-controlled asymmetric induction (up to 80% ee). The introduction of central chirality of the oxazoline ring connected directly to the PCP backbone led to unfavorable results. Further investigations of the catalyst structure and use of the planar chiral ligands in other catalytic asymmetric reactions are currently underway.

Experimental

General Information Melting point (mp) was measured by Yanaco melting point apparatus MP-500D and uncorrected. Optical rotations were measured on a JASCO P-2200. IR spectra were measured with a SHIMADZU FTIR-8700 spectrometer for samples in $CHCl_3$. ^{1}H- and ^{13}C-NMR spectra were recorded by a JNM-ECA500 or a JNM-ECA600 or a Bruker Avance III 600 spectrometer for samples in $CDCl_3$ with tetramethylsilane (δ=0.0 ppm) as an internal standard. The data are reported as follows: chemical shift in ppm (δ), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet,

Table 4. Box (S_p)-**1d**-Cu-Catalyzed Intramolecular Aromatic O–H Insertion of **10**[a)]



Entry	Substrate **10**	Cu source	Time (h)	Yield (%)[b,c]	ee (%)[d]
1[e]		$CuOTf(C_6H_6)_{1/2}$	10 min	12 (60)	–
2		$CuOTf(C_6H_6)_{1/2}$	3 h	58 (16)	72
3		$Cu(OTf)_2$	1 h	49 (33)	66
4		CuCl	19 h	54 (22)	74
5	**10a**	CuI	48 h	63 (21)	71
6[e]		$CuOTf(C_6H_6)_{1/2}$	10 min	25 (47)	–
7	**10b**	$CuOTf(C_6H_6)_{1/2}$	2.5 h	47 (27)	74
8[e]		$CuOTf(C_6H_6)_{1/2}$	10 min	17 (44)	–
9	**10c**	$CuOTf(C_6H_6)_{1/2}$	1 h	65 (19)	69
10[e]		$CuOTf(C_6H_6)_{1/2}$	10 min	11 (24)	–
11	**10d**	$CuOTf(C_6H_6)_{1/2}$	19.5 h	21 (31)	70 (*S*)
12[e]		$CuOTf(C_6H_6)_{1/2}$	24 h	7 (77)	–
13	**10e**	$CuOTf(C_6H_6)_{1/2}$	24 h	47 (24)	67

a) All reactions were performed with ligand (0.006 mmol), $CuOTf(C_6H_6)_{1/2}$ (0.005 mmol), $NaBAr_F$ (0.006 mmol), 5-Å molecular sieves (250 mg), and diazo ester **10** (0.10 mmol) in CH_2Cl_2 (total 1 mL), unless otherwise stated. *b*) Isolated yield of **11**. *c*) The values in parentheses are yields of *α,β*-unsaturated ester **12**. *d*) Determined by HPLC analysis. *e*) Reaction was performed without ligand (S_p)-**1d**.

m=multiplet), integration, and coupling constant (Hz). High resolution MS were measured with a JEOL JMS-T100TD. Analytical TLC was performed on MERCK silica gel, grade $60F_{254}$. The spots and bands were detected by UV light of irradiation (254 nm) and/or by staining with 5% phosphomolybdic acid followed by heating. Column chromatography for isolation of the products was carried out on KANTO Sillica Gel 60 (230–400 mesh). HPLC analyses were performed using Interigent UV/VIS Detector JASCO UV-7500. The chiral columns included CHIRALCEL OD-H, OJ-H and CHIRALPAK AS-H (Daicel Chemical Industries, Ltd., ϕ0.46×25 cm). All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Organic extracts were dried over anhydrous Na_2SO_4. Ligands (S_p)-**1b**, **1c**, **1d** and **4a**,[35] compounds *rac*-**5**[36] and **6**,[35] and diazo esters **2**,[21] **7**[43] and **10a–e**[17] were prepared according to the literature procedure.

Procedure for the Preparation of PCP-Based Box Ligands with the Central Chirality

(S_p,*S*,*S*)-(−)-4,12-Bis(4-phenyl-2-oxazolinyl)[2.2]paracyclophane ((S_p,*S*,*S*)-**4b**) and (R_p,*S*,*S*)-(+)-4,12-Bis(4-phenyl-2-oxazolinyl)[2.2]paracyclophane ((R_p,*S*,*S*)-**4b**)

To a mixture of *rac*-**6** (56.0 mg, 0.189 mmol), (*S*)-phenylglycinol (57.0 mg, 0.416 mmol), 1-hydroxybenzotriazole (HOBt) (56.2 mg, 0.416 mmol) and dicyclohexylcarbodiimide (DCC) (164 mg, 0.795 mmol) was added tetrahydrofuran (THF) (2 mL) at −5°C. After stirring for 1 h at the same temperature, the reaction mixture was warmed to room temperature, and further stirred for 16 h. The mixture was concentrated and chromatographed with AcOEt to afford a mixture of (R_p,*S*,*S*)- and (S_p,*S*,*S*)-4,12-bis[*N*-(2-hydroxy-1-phenylethyl)carbamoyl][2.2]-paracyclophane (78.6 mg, 78%) as a white solid.

To a solution of the above mixture of amides (78.6 mg, 0.148 mmol) and PPh_3 (253 mg, 0.964 mmol) in MeCN (2 mL) were added Et_3N (0.13 mL, 1.0 mmol) and CCl_4 (0.1 mL, 1 mmol) at room temperature. After stirring for 10 h at the same temperature, the reaction mixture was diluted with

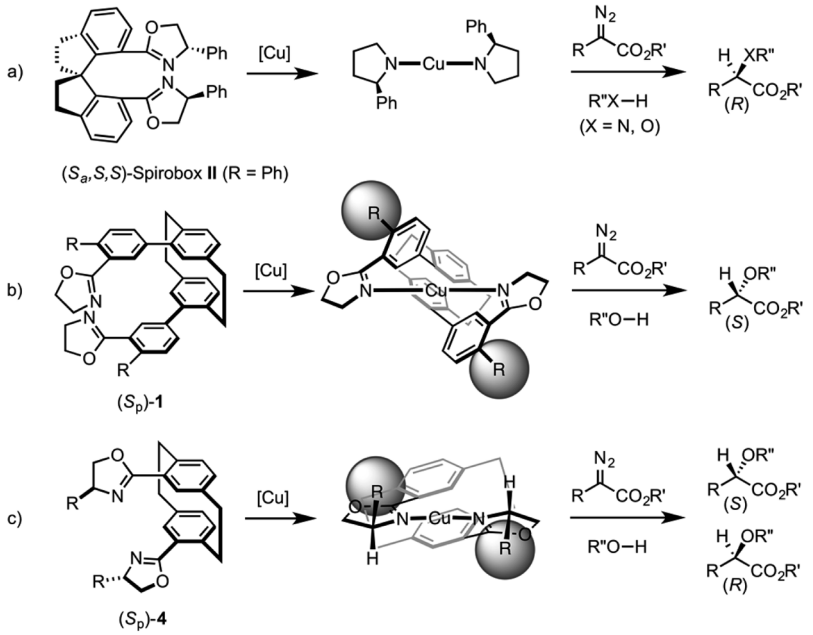


Fig. 3. Proposed Catalyst Structure Deduced from Product Stereochemistry

AcOEt, washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane–CH_2Cl_2–AcOEt (13 : 6 : 1) to afford (S_p,*S*,*S*)-**4b** (28.5 mg, 39%) as a white solid and (R_p,*S*,*S*)-**4b** (25 mg, 34%) as a white solid; (S_p,*S*,*S*)-**4b**: mp 193–195°C; $[\alpha]_D^{22}$ −178.6 (*c*=1.00, $CHCl_3$); IR ($CHCl_3$) cm^{-1}: 3009, 2932, 2899, 1632; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.50 (d, 4H, *J*=7.2 Hz), 7.39 (t, 4H, *J*=7.2 Hz), 7.33–7.30 (m, 4H), 6.67 (dd, 2H, *J*=7.2, 1.8 Hz), 6.59 (d, 2H, *J*=7.2 Hz), 5.38 (t, 2H, *J*=9.6 Hz), 4.69 (dd, 2H, *J*=9.6, 7.8 Hz), 4.37–4.33 (m, 2H), 4.17 (t, 2H, *J*=9.0 Hz), 3.17–3.09 (m, 4H), 2.87–2.80 (m, 2H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 164.1 (2C), 142.8 (2C), 141.2 (2C), 140.2 (2C), 135.8 (2C), 135.1 (2C), 132.6 (2C), 128.7 (4C), 127.7 (2C), 127.5 (2C), 127.0 (4C), 73.5 (2C), 71.1 (2C), 35.7 (2C), 33.9 (2C); MS (DART) *m/z* 499 (100.0, M^++1); high resolution (HR)-MS Calcd for $C_{34}H_{31}N_2O_2$: 499.2386. Found 499.2400; HPLC: OD-H column; λ=254 nm; eluent: hexane–isopropanol=85 : 15; flow rate: 1.0 mL/min; t_R=15.1 min for major; de%=>99.9%. (R_p,*S*,*S*)-**4b**: mp 43–45°C; $[\alpha]_D^{23}$ +55.4 (*c*=1.30, $CHCl_3$); IR ($CHCl_3$) cm^{-1}: 3032, 3009, 2932, 2897, 2856, 1634; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.37–7.35 (m, 8H), 7.30 (d, 2H, *J*=1.8 Hz), 7.29–7.24 (m, 2H), 6.69 (dd, 2H, *J*=7.8, 1.8 Hz), 6.60 (d, 2H, *J*=7.8 Hz), 5.46 (dd, 2H, *J*=10.2, 8.4 Hz), 4.63 (dd, 2H, *J*=10.2, 7.8 Hz), 4.37–4.33 (m, 2H), 4.12 (t, 2H, *J*=8.4 Hz), 3.20–3.14 (m, 4H), 2.84 (dt, 2H, *J*=13.2, 9.0 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 164.4 (2C), 142.9 (2C), 141.3 (2C), 140.1 (2C), 135.8 (2C), 135.0 (2C), 132.7 (2C), 128.6 (4C), 127.6 (2C), 127.4 (2C), 126.8 (4C), 73.8 (2C), 70.6 (2C), 36.3 (2C), 34.1 (2C); MS (DART) *m/z* 499 (100.0, M^++1); HR-MS Calcd for $C_{34}H_{31}N_2O_2$: 499.2386. Found 499.2394; HPLC: OD-H column; λ=254 nm; eluent: hexane–isopropanol=85 : 15; flow rate: 1.0 mL/min; t_R=15.6 min for minor, t_R=11.3 min for major; de%=98.7%.

(S_p,*S*,*S*)-(−)-4,12-Bis(4-benzyl-2-oxazolinyl)[2.2]-paracyclophane ((S_p,*S*,*S*)-**4c**)

The amide precursor of title compound was prepared from (S_p)-**6** (14.2 mg, 0.0479 mmol), (*S*)-phenylalaninol (16.6 mg, 0.110 mmol), HOBt (14.9 mg, 0.110 mmol) and DCC (43.2 mg, 0.209 mmol), and the title compound (8.9 mg, 34%) was prepared using PPh_3 (52.4 mg, 0.200 mmol), Et_3N (30 μL, 0.22 mmol) and CCl_4 (19 μL, 0.20 mmol), according to the procedure for preparation of **4b**. A white solid; mp 109–111°C; $[\alpha]_D^{22}$ −68.5 (*c*=0.47, $CHCl_3$); IR ($CHCl_3$) cm^{-1}: 3009, 2934, 2856, 1636; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.39–7.35 (m, 8H), 7.29–7.25 (m, 2H), 7.17 (d, 2H, *J*=1.8 Hz), 6.65 (dd, 2H, *J*=7.8, 1.8 Hz), 6.55 (d, 2H, *J*=7.8 Hz), 4.64–4.59 (m, 2H), 4.32–4.28 (m, 4H), 4.07 (t, 2H, *J*=7.2 Hz), 3.37 (dd, 2H, *J*=13.8, 6.0 Hz), 3.25–3.18 (m, 2H), 3.13–3.09 (m, 2H), 2.88 (dd, 2H, *J*=13.8, 8.4 Hz), 2.85–2.79 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 163.4 (2C), 141.0 (2C), 140.1 (2C), 138.6 (2C), 135.8 (2C), 134.9 (2C), 132.0 (2C), 129.2 (4C), 128.6 (4C), 127.9 (2C), 126.4 (2C), 70.6 (2C), 68.7 (2C), 42.2 (2C), 35.6 (2C), 33.6 (2C); MS (DART) *m/z* 527 (100.0, M^++1); HR-MS Calcd for $C_{36}H_{35}N_2O_2$: 527.2699. Found 527.2697.

(R_p,*S*,*S*)-(+)-4,12-Bis(4-benzyl-2-oxazolinyl)[2.2]-paracyclophane ((R_p,*S*,*S*)-**4c**)

The amide precursor of title compound was prepared from (R_p)-**6** (9.6 mg, 0.032 mmol), (*S*)-phenylalaninol (10.8 mg, 0.0713 mmol), HOBt (9.6 mg, 0.071 mmol) and DCC (28.1 mg, 0.136 mmol), and the title compound (5.9 mg, 35%) was prepared using PPh_3 (24.6 mg, 0.0938 mmol), Et_3N (50 μL, 0.36 mmol) and CCl_4 (50 μL, 0.52 mmol), according to the procedure for preparation of **4b**. A white solid; mp 37–39°C; $[\alpha]_D^{24}$ +13.9 (*c*=0.72, $CHCl_3$); IR ($CHCl_3$) cm^{-1}: 3030, 3011, 2932, 2858, 1636; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.33–7.21 (m, 10H), 7.12 (d, 2H, *J*=1.8 Hz), 6.65 (dd, 2H, *J*=7.8, 1.8 Hz), 6.56 (d, 2H, *J*=7.8 Hz), 4.66–4.61 (m, 2H), 4.31–4.19 (m, 4H), 4.03 (t, 2H, *J*=7.2 Hz), 3.24 (dd, 2H, *J*=13.8, 4.8 Hz), 3.15–3.09 (m, 4H), 2.84–2.79 (m, 2H), 2.66 (dd, 2H, *J*=13.8, 9.6 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 163.6 (2C), 141.0 (2C), 140.1 (2C), 138.4 (2C), 135.7 (2C), 134.8 (2C), 132.5 (2C), 129.2 (4C), 128.5 (4C), 127.9 (2C), 126.4 (2C), 70.7 (2C), 68.4 (2C), 41.9 (2C), 36.0 (2C), 34.0 (2C); MS (DART) *m/z* 527 (100.0, M^++1); HR-MS Calcd for $C_{36}H_{35}N_2O_2$: 527.2699. Found

527.2687.

General Procedure for Asymmetric EtOH Insertion Reaction of 2

Methyl 2-Ethoxy-2-phenylacetate (**3**)[21]

To a suspension of ligand (0.012 mmol) and MS5A (300 mg) in CH_2Cl_2 (1 mL) were added $NaBAr_F$ (10.6 mg, 0.0120 mmol) and $Cu(OTf)_2$ (3.6 mg, 0.010 mmol) at room temperature under an argon atmosphere. After stirring for 4 h at the same temperature, EtOH (56 μL, 1.0 mmol) and then a solution of **2** (35 mg, 0.20 mmol) in CH_2Cl_2 (1 mL) were added to the reaction mixture at 40°C. The mixture was stirred at the same temperature for 4-38 h and filtered, and filtrate was concentrated to dryness. The residue was chromatographed with hexane–Et_2O (20 : 1) to afford **3** as a colorless oil; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.45 (d, 2H, J=7.6 Hz), 7.37–7.31 (m, 3H), 4.89 (s, 1H), 3.71 (s, 3H), 3.60 (m, 1H), 3.50 (m, 1H), 1.27 (t, 3H, J=7.0 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 171.4, 136.6, 128.6, 128.6, 127.1, 80.8, 65.3, 52.2, 15.1; HPLC: OD-H column; λ=254 nm; eluent: hexane–isopropanol=99.5 : 0.5; flow rate: 1.0 mL/min; t_R=11.6 min for (*R*)-enantiomer, t_R=9.9 min for (*S*)-enantiomer.

Typical Procedure for Asymmetric Intermolecular Aromatic O–H Insertion Reaction of 7 (Table 2, Entry 3)

(*S*)-(−)-Ethyl 2-Phenoxypropionate (**9a**)[22]

To a suspension of (S_p)-**1d** (7.3 mg, 0.013 mmol) and MS5A (315 mg) in CH_2Cl_2 (1 mL) were added $NaBAr_F$ (11.2 mg, 0.0126 mmol) and CuCl (1.0 mg, 0.010 mmol) at room temperature under an argon atmosphere. After stirring for 4 h at the same temperature, a solution of PhOH (**8a**) (98.8 mg, 1.05 mmol) in CH_2Cl_2 (0.5 mL) was added to the mixture. After 20 min, a solution of **7** (28.0 mg, 0.219 mmol) in CH_2Cl_2 (0.6 mL) was added to the mixture, which was stirred at room temperature for 1 h. The mixture was filtered and filtrate was concentrated to dryness. The residue was chromatographed with hexane–AcOEt (30 : 1) to afford **9a** (28.0 mg, 66%) as a colorless oil; $[\alpha]_D^{23}$ −37.5 (c=0.43, MeOH) [lit.: $[\alpha]_D^{18}$ +47.2 (c=0.5, MeOH) for (*R*)][22]; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.29–7.25 (m, 2H), 6.97 (t, 1H, J=7.8 Hz), 6.88 (d, 2H, J=7.8 Hz), 4.74 (q, 1H, J=6.6 Hz), 4.22 (q, 2H, J=6.6 Hz), 1.61 (d, 3H, J=6.6 Hz), 1.25 (t, 3H, J=6.6 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 172.3, 157.6, 129.5, 121.5, 115.1, 72.6, 61.2, 18.6, 14.1; HPLC: OD-H column; λ=254 nm; eluent: hexane–isopropanol=9 : 1; flow rate: 1.0 mL/min; t_R=8.8 min for (*R*)-enantiomer, t_R=4.9 min for (*S*)-enantiomer. Compound **9a** was determined to be 80% ee.

(−)-Ethyl 2-(4-Methoxyphenoxy)propionate (**9b**)[22]

A colorless oil; 73% yield; $[\alpha]_D^{26}$ −43.8 (c=0.51, EtOH); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 6.85–6.80 (m, 4H), 4.65 (q, 1H, J=7.0 Hz), 4.21 (q, 2H, J=7.0 Hz), 3.76 (s, 3H), 1.59 (d, 3H, J=7.0 Hz), 1.25 (t, 3H, J=7.0 Hz); HPLC: OJ-H column; λ=254 nm; eluent: hexane–isopropanol=9 : 1; flow rate: 1.5 mL/min; t_R=13.17 min for major isomer, t_R=11.02 min for minor isomer. Compound **9b** was determined to be 79% ee.

(−)-Ethyl 2-(2-Methoxyphenoxy)propionate (**9c**)[22]

A yellow oil; 61% yield; $[\alpha]_D^{25}$ −43.3 (c=0.43, EtOH); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 6.98–6.85 (m, 4H), 4.75 (q, 1H, J=7.0 Hz), 4.23–4.19 (m, 2H), 3.86 (s, 3H), 1.64 (d, 3H, J=7.0 Hz), 1.25 (t, 3H, J=7.0 Hz); HPLC: OD-H column; λ=254 nm; eluent: hexane–isopropanol=9 : 1; flow rate: 1.5 mL/min; t_R=10.80 min for minor isomer, t_R=5.45 min for major isomer. Compound **9c** was determined to be 71% ee.

(−)-Ethyl 2-(2,4-Dimethylphenoxy)propionate (**9d**)[22]

A colorless oil; 61% yield; $[\alpha]_D^{25}$ −21.0 (c=0.36, EtOH); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 6.95 (s, 1H), 6.88 (dd, 1H, J=8.5, 1.5 Hz), 6.59 (d, 1H, J=8.5 Hz), 4.67 (q, 1H, J=7.0 Hz), 4.20 (q, 2H, J=7.0 Hz), 2.24 (s, 3H), 2.24 (s, 3H), 1.60 (d, 3H, J=7.0 Hz), 1.25 (t, 3H, J=7.0 Hz); HPLC: OJ-H column; λ=230 nm; eluent: hexane–isopropanol=99 : 1; flow rate: 0.8 mL/min; t_R=28.96 min for major isomer, t_R=11.74 min for minor isomer. Compound **9d** was determined to be 71% ee.

(*S*)-(−)-Ethyl 2-(4-Chlorophenoxy)propionate (**9e**)[22]

A colorless oil; 58% yield; $[\alpha]_D^{26}$ −23.0 (c=0.41, CH_2Cl_2) [lit.: $[\alpha]_D^{18}$ +47.6 (c=1.0, CH_2Cl_2) for (*R*)][22]; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.22 (d, 2H, J=9.3 Hz), 6.81 (d, 2H, J=9.3 Hz), 4.69 (q, 1H, J=7.0 Hz), 4.21 (q, 2H, J=7.0 Hz), 1.61 (d, 3H, J=7.0 Hz), 1.25 (t, 3H, J=7.0 Hz); HPLC: OJ-H column; λ=254 nm; eluent: hexane–isopropanol=9 : 1; flow rate: 1.0 mL/min; t_R=8.92 min for major isomer, t_R=6.88 min for minor isomer. Compound **9e** was determined to be 48% ee.

(*S*)-(+)-Ethyl 2-(Naphtalen-1-yloxy)propionate (**9f**)[22]

A colorless oil; 44% yield; $[\alpha]_D^{26}$ +24.7 (c=0.34, $CHCl_3$) [lit.: $[\alpha]_D^{18}$ −35.0 (c=0.4, $CHCl_3$) for (*R*)][22]; ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.36 (m, 1H), 7.79 (m, 1H), 7.50–7.45 (m, 3H), 7.32 (t, 1H, J=8.0 Hz), 6.70 (d, 1H, J=7.5 Hz), 4.93 (q, 1H, J=6.5 Hz), 4.22 (q, 2H, J=7.0 Hz), 1.75 (d, 3H, J=6.5 Hz), 1.23 (t, 3H, J=7.0 Hz); HPLC: OD-H column; λ=210 nm; eluent: hexane–isopropanol=93 : 7, flow rate: 1.0 mL/min; t_R=9.81 min for minor isomer, t_R=6.27 min for major isomer. Compound **9f** was determined to be 75% ee.

Typical Procedure for Asymmetric Intramolecular Aromatic O–H Insertion Reaction of 10 (Table 4, Entry 4)

(−)-Methyl 2,3-Dihydrobenzofuran-2-carboxylate (**11a**)[17] and (*E*)-Methyl 3-(2′-Hydroxyphenyl)-2-propenoate (**12a**)[44]

To a suspension of (S_p)-**1d** (7.0 mg, 0.012 mmol, 6 mol%) and MS5A (250 mg) in CH_2Cl_2 (1 mL) were added CuCl (1.1 mg, 0.011 mmol, 5 mol%) and $NaBAr_F$ (10.6 mg, 0.012 mmol, 6 mol%) at room temperature under an argon atmosphere. After stirring for 4 h at the same temperature, a solution of **10a** (42.4 mg, 0.206 mmol) in CH_2Cl_2 (0.5 mL) was added to the mixture, which was stirred for 19 h. The mixture was filtered and filtrate was concentrated to dryness. The residue was chromatographed with hexane–AcOEt (8 : 1) to affored **11a** (20.1 mg, 54%) as a colorless oil and **12a** (8.1 mg, 22%) as a white solid. **11a**: $[\alpha]_D^{26}$ −11.7 (c 0.9, $CHCl_3$); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.16–7.13 (m, 2H), 6.90–6.87 (m, 2H), 5.20 (dd, 1H, J=10.8, 6.6 Hz), 3.80 (s, 3H), 3.55 (dd, 1H, J=15.6, 10.8 Hz), 3.38 (dd, 1H, J=15.6, 6.6 Hz); HPLC: OD-H column; λ=280 nm; eluent: hexane–isopropanol=75 : 25; flow rate: 1.0 mL/min; t_R=7.18 min for minor isomer, t_R=6.33 min for major isomer. Compound **11a** was determined to be 74% ee. **12a**: ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 8.02 (d, 1H, J=16.2 Hz), 7.46 (dd, 1H, J=7.8, 1.8 Hz), 7.23 (td, 1H, J=7.8, 1.8 Hz), 6.93 (td, 1H, J=7.8, 0.6 Hz), 6.82 (dd, 1H, J=7.8, 0.6 Hz), 6.60 (d, 1H, J=16.2 Hz), 6.04 (s, 1H), 3.81 (s, 3H).

(−)-Methyl 5-Methoxy-2,3-dihydrobenzofuran-2-carboxylate (**11b**)[17]

A colorless oil (entry 7); 47% yield; $[\alpha]_D^{26}$ −3.7 (c=0.43, $CHCl_3$); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 6.79 (d, 1H, J=9.0 Hz), 6.75 (d, 1H, J=2.4 Hz), 6.68 (dd, 1H, J=9.0, 2.4 Hz), 5.19 (dd, 1H, J=10.2, 6.6 Hz), 3.80 (s, 3H), 3.75 (s, 3H), 3.53 (dd, 1H, J=15.9, 10.2 Hz), 3.36 (dd, 1H, J=15.9, 6.6 Hz). HPLC: OD-H column; λ=230 nm; eluent: hexane–isopropanol=70 : 30; flow

rate: 1.0 mL/min; t_R=8.57 min for minor isomer, t_R=6.53 min for major isomer. Compound **11b** was determined to be 74% ee.

(−)-Methyl 7-Methoxy-2,3-dihydrobenzofuran-2-carboxylate (**11c**)[17]

A colorless oil (entry 9); 65% yield; $[\alpha]_D^{26}$ −29.3 (c=0.54, $CHCl_3$); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 6.84 (t, 1H, J=7.8 Hz), 6.78 (dd, 1H, J=7.8, 1.2 Hz), 6.76 (d, 1H, J=7.8 Hz), 5.24 (dd, 1H, J=10.2, 6.6 Hz), 3.88 (s, 3H), 3.79 (s, 3H), 3.57 (dd, 1H, J=15.6, 10.2 Hz), 3.40 (dd, 1H, J=15.6, 6.6 Hz); HPLC: OD-H column; λ=220 nm; eluent: hexane–isopropanol=70 : 30; flow rate: 1.0 mL/min; t_R=31.96 min for minor isomer, t_R=11.01 min for major isomer. Compound **11c** was determined to be 69% ee.

(*S*)-(+)-Methyl 5-Chloro-2,3-dihydrobenzofuran-2-carboxylate (**11d**)[17]

A white solid; 21% yield (entry 11); $[\alpha]_D^{26}$ +5.2 (c=0.11, $CHCl_3$) [lit.: $[\alpha]_D^{17}$ −12.8 (c=2.1, $CHCl_3$) for (*R*)][17]; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.15–7.08 (m, 2H), 6.79 (d, 1H, J=9.0 Hz), 5.21 (dd, 1H, J=10.8, 6.6 Hz), 3.79 (s, 3H), 3.53 (dd, 1H, J=16.2, 10.8 Hz), 3.35 (dd, 1H, J=16.2, 6.6 Hz); HPLC: OD-H column; λ=230 nm; eluent: hexane–isopropanol=95 : 5; flow rate: 1.0 mL/min; t_R=10.23 min for minor isomer, t_R=9.57 min for major isomer. Compound **11d** was determined to be 70% ee.

(+)-Methyl Chroman-2-carboxylate (**11e**)[17]

A colorless oil (entry 13); 47% yield; $[\alpha]_D^{26}$ +0.83 (c=0.43, $CHCl_3$); ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.12 (td, 1H, J=7.8, 1.2 Hz), 7.03 (dd, 1H, J=7.8, 1.2 Hz), 6.93 (dd, 1H, J=7.8, 1.2 Hz), 6.87 (td, 1H, J=7.8, 1.2 Hz), 4.73 (dd, 1H, J=7.8, 3.6 Hz), 3.80 (s, 3H), 2.93–2.74 (m, 2H), 2.30–2.17 (m, 2H); HPLC: AS-H column; λ=220 nm; eluent: hexane–isopropanol=95 : 5; flow rate: 1.0 mL/min; t_R=8.00 min for minor isomer, t_R=7.45 min for major isomer. Compound **11e** was determined to be 67% ee.

(*E*)-Methyl 4-(2′-Hydroxyphenyl)-2-butenoate (**12e**)[45]

A white solid; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.17–7.08 (m, 3H), 6.89 (td, 1H, J=7.8, 1.2 Hz), 6.77 (dd, 1H, J=7.8, 1.2 Hz), 5.82 (dt, 1H, J=15.6, 1.8 Hz), 4.90 (s, 1H), 3.69 (s, 3H), 3.53 (dd, 2H, J=6.6, 1.2 Hz).

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Conflict of Interest The authors declare no conflict of interest.

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