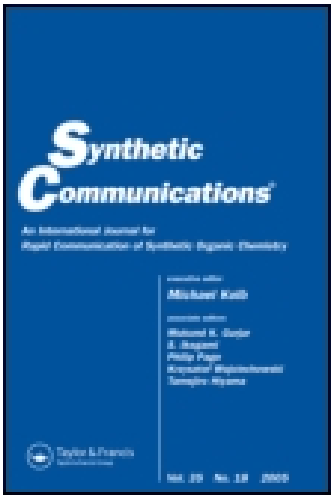

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Synthesis of Novel Chiral Semicrown Ether-Like Bis(oxazoline) Ligands and Application in Enantioselective Cyclopropanation of Styrene

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Synthesis of Novel Chiral Semicrown Ether-Like Bis(oxazoline) Ligands and Application in Enantioselective Cyclopropanation of Styrene

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Abstract: A series of chiral C_2-symmetric bis(oxazoline) ligands containing semicrown ether unit were synthesized. The copper complexes prepared in situ from copper(I)-triflate, and the new chiral oxazoline ligands were assessed as chiral catalysts in the enantioselective cyclopropanation of styrene with diazoacetates. Enantioselectivities up to 84% and up to 65%, respectively, for *trans*- and *cis*-2-phenylcyclopropanecarboxylate were observed.

Keywords: Bis(oxazoline), synthesis, enantioselective cyclopropanation, styrene, asymmetric catalysis

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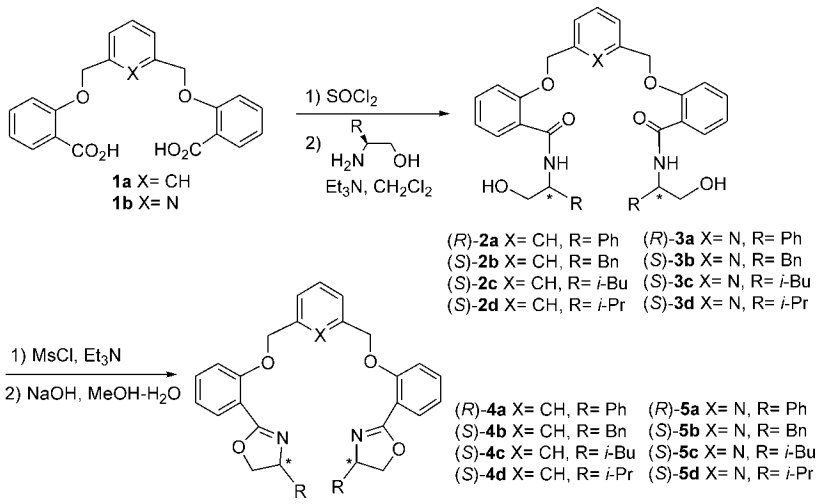
INTRODUCTION

Cyclopropane is found as a basic structural unit in a wide variety of synthetic and naturally occurring compounds[1–5] A number of catalyst systems have been developed for the asymmetric cyclopropanation of olefins.[6–10] Many of these are based on the decomposition of diazo compounds, and the corresponding reaction mechanism is believed to proceed through metal carbenoid intermediate. These systems include copper complexes of semicorrin, bis(oxazoline), chiral Schiff base and bipyridine as well as rhodium carboxamides and porphyrins, ruthenium pybox, and cobalt and ruthenium salen complexes. In recent years, C_2-symmetric bis(oxazoline) are versatile chiral ligands, and their metal complexes have been recognized as an effective class of chiral catalyst in a variety of transition metal catalyzed asymmetric reactions.[11–16] Thus, the design and synthesis of new chiral bis(oxazoline) ligands has inspired many chemists to work with great efforts. The search for chiral ligands with broad applicability is a particularly interesting aspect in the field of chemical research on enantioselective reactions promoted by chiral catalysts. Continuing on our ongoing project on the synthesis, structure and catalytic enantioselective reaction of novel chiral bis(oxazoline) ligands,[17–23] in this article, we report the synthesis and the primary catalytic enantioselective cyclopropanation of styrene by copper(I) complex of a series of new bis(oxazoline) ligands **4** and **5** containing semicrown ether unit. Crown ether has inclusion ability to a variety of ions and neutral molecules; we expect the combination of semicrown ether and chiral oxazoline unit in new ligands may result in unique characteristics for catalytic reaction.

RESULTS AND DISCUSSION

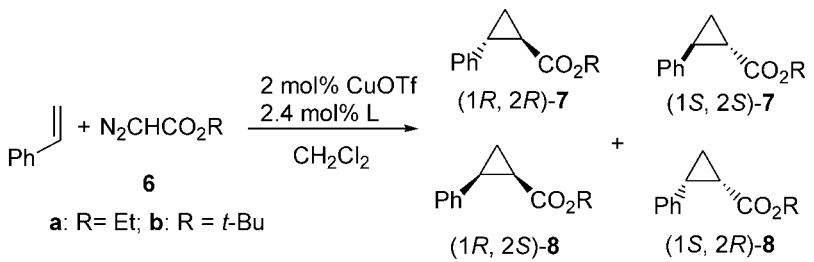
Many methods have been reported for the synthesis of oxazoline ligands.[24–27] The usual method for preparation of chiral bis(oxazoline) is the reaction of diacid derivatives with chiral β-amino alcohols. The enantiomerically pure β-amino alcohols are either commercially available or easily obtained by reduction of the corresponding α-amino acids.[28–31] The diacid **1** were synthesized according to literature procedure from corresponding dibromide and methyl salicylate.[32] The diacid **1** was refluxed with thionyl chloride to afford the diacyl chloride. The diacyl chloride was treated with β-amino alcohols and triethylamine to afford the corresponding chiral intermediate dihydroxy diamides **2** and **3** in 60–97% yields. The procedure for synthesis of bis(oxazoline) developed by Denmark et al.[33] was used to synthesize the desired chiral bis(oxazoline) ligands **4** and **5**. The dihydroxy diamides were treated with methanesulfonyl chloride (MsCl) (2.3 eq.) and Et_3N (5 eq.) in dichloromethane to afford the corresponding bismesylates,



Scheme 1. Synthesis of new bis(oxazoline) **4** and **5**.

which were treated with an aqueous methanolic solution of NaOH to furnish the bis(oxazoline) **4** and **5** in good yields (53–85%) (Scheme 1). The structures of these new chiral bis(oxazoline) ligands were characterized by ^{1}H NMR, MS, IR, and elemental analysis or HRMS.

With the new ligands in hand, we try to evaluate the efficiency of these bis(oxazoline) ligands in the copper (I)-catalyzed asymmetric cyclopropanation of olefins. We first carried out the model reaction of styrene with ethyl diazoacetate to give the *trans*- and *cis*-cyclopropanes **7** and **8** (Scheme 2). The asymmetric cyclopropanation was carried out in dichloromethane in the presence of 2% mol of copper(I) catalyst generated in situ by mixing $Cu(OTf).1/2C_6H_6$ and the bis(oxazoline). The reaction was first performed at room temperature by slow addition of ethyl diazoacetate to a solution of styrene in dichloromethane containing the copper (I)-bis(oxazoline) catalyst. The ratio of *trans*- and *cis*-isomers were determined by ^{1}H NMR analysis,



Scheme 2. Cyclopropanation reaction of styrene with diazoacetates.

Table 1. Asymmetric cyclopropanation of styrene with diazoacetate catalyzed by copper(I)-bis(oxazoline)

Entry	Ligand	Diazoacetate	Temp. (°C)	Yield[a] (%)	*Trans*/*cis*[b]	% ee[c] (*trans*)	Config.[d]	% ee[c] (*cis*)	Config.[d]
1	**4a**	**6a**	rt	74	70 : 30	24	1*S*, 2*S*	32	1*S*, 2*R*
2	**4b**	**6a**	rt	68	75 : 25	7	1*R*, 2*R*	10	1*R*, 2*S*
3	**4c**	**6a**	rt	71	77 : 23	32	1*R*, 2*R*	21	1*R*, 2*S*
4	**4d**	**6a**	rt	64	76 : 24	19	1*R*, 2*R*	14	1*R*, 2*S*
5	**5a**	**6a**	rt	83	75 : 25	45	1*S*, 2*S*	43	1*S*, 2*R*
6	**5b**	**6a**	rt	63	60 : 40	8	1*R*, 2*R*	5	1*R*, 2*S*
7	**5c**	**6a**	rt	85	74 : 26	35	1*R*, 2*R*	20	1*R*, 2*S*
8	**5d**	**6a**	rt	76	77 : 23	34	1*R*, 2*R*	22	1*R*, 2*S*
9	**5a**	**6a**	0	79	76 : 24	68	1*S*, 2*S*	61	1*S*, 2*R*
10	**5c**	**6a**	0	78	78 : 22	56	1*R*, 2*R*	41	1*R*, 2*S*
11	**5a**	**6b**	0	80	82 : 18	84	1*S*, 2*S*	65	1*S*, 2*R*

[a]Isolated yield, based on ethyl diazoacetate for the mixture of *trans* and *cis* products.
[b]Determined by ^{1}H NMR of the crude product.
[c]Determined by chiral HPLC using Chiralcel OJ column.
[d]Based on the sign of optical rotation.[34]

and the enantiomeric excesses were determined by HPLC analysis using a chiral column (Chiracel OJ). The results are summarized in Table 1.

Among the bis(oxazoline) ligands tested, **5a** containing phenyl substituent on its oxazolines gave the highest enantiomeric excess for *trans*-**7** in 45% ee and *cis*-**8** in 43% ee (entry 5), the ligands **4b** and **5b** containing benzyl group afforded comparably lower enantioselectivity (*trans*-7% ee and 8% ee, respectively, entries 2 and 6). In addition, the ligands **4c** and **5c** with *iso*-butyl substituent afford moderate enantioselectivity for cyclopropanation in 32% ee and 35% ee (entries 3 and 7). It is of interest that the phenyl substituent on the oxazoline **5a** provides the best enantiomeric excess of *trans*-**7** and *cis*-**8**. However, in the same reaction, the introduction of a phenyl substituent at the 4-position of the oxazoline has been previouly reported to have a pronounced effect on enantioselectivity.[17] This phenomenon may be ascribed to the flexibility of **5a**, resulting in little torsional strain between the two oxazoline units in corresponding copper(I) complex. Meanwhile, we examined the effect of temperature for cyclopropanation of the ligands **5a** and **5c** as shown in Table 1. The reactions were carried out under the same condition as above, except addition of diazoacetate for 4 hr and the reaction was proceeding for 18 hr at 0°C, the ee value of copper(I)-catalyzed cyclopropanation rise to 68% and 56% ee, respectively (entries 9 and 10). As expected, when the steric bulkier diazoacetate ester *t*-butyl diazoacetate was used instead of ethyl diazoacetate, the enantioselectivity was improved. The reaction of *t*-butyl diazoacetate with styrene in the presence of Cu(I)-ligand **5a** catalyst gave *trans*-*t*-butyl cyclopropanecarboxylates up to 84% ee and *cis* isomer in 65% ee (entry 8).

The following conclusion can also be made from the results gathered in Table 1. (1) The diastereoselectivity of the reaction is in favor of *trans*-selectivity. Preference for the *trans*-isomer has been previously observed for the same reaction using alternative bis(oxazoline) ligands.[35–41] (2) The enantioselectivity of *cis*-isomer is almost the same level as that of *trans*-isomer. (3) The enantioselectivity was improved when temperature was reduced with a slight lower chemical yield (entries 9 and 10 *vs* entries 5 and 7). (4) The enantioselectivity of **5a–d** was better than **4a–d**. (5) The predominant formation of (1*R*, 2*R*)-*trans*-cyclopropane **7** and (1*R*, 2*S*)-*cis*-cyclopropane **8** were observed irrespective of the reaction temperature (room temperature or 0°C) with *S*-bis(oxazoline). As expected, the preferred absolute configurations of *trans*-cyclopropane **7** and *cis*-cyclopropane **8** were antipodal when use *R*-bis(oxazoline) **4a** and **5a**.

Although the enantioselectivity is moderate for these new ligands, one advantage is that the moderate enantioselectivity can be obtained by using the very cheap ligand **5a** or **5c** synthesized from cheap β-amino alcohol (*R*-phenylglycinol or *S*-leucinol). In contrast, very expensive ligands derivated from *L*-*t*-leucinol were usually used in literature.[42–44] Furthermore, we obtained moderate enantioselectivity of the *cis*-isomer **8** and did

not need to use the bulky adamantyl substituted bis(oxazoline). There still exists potential to optimize the enantioselectivity; the enantioselectivity of the metal catalyzed cyclopropanation is usually higher when the steric bulky ester is used.[45–47] It seem that the combination of semicrown ether and chiral oxazoline unit in these new ligands may result in many coordination sites with copper for formation of suitable chiral complexes, which may explain the moderate enantioselectivity obtained.

In conclusion, an efficient synthetic procedure was developed for synthesis of new chiral semicrown ether-like bis(oxazoline) ligands. Preliminary results in asymmetric cyclopropanation of styrene with ethyl diazoacetate have been obtained. The C_2-symmetric bis(oxazoline) **4** and **5** derived from *m*-phenylenebis(methyleneoxy) and 2,6-pyridinediylbis(methyleneoxy) units present different reactivities in the asymmetric copper-catalyzed cyclopropanation. The highest enantioselectivity was obtained with phenyl substituted bis(oxazoline) **5a**. Although the *trans*-enantioselectivity is moderate, these primary results suggest that these novel semicrown ether-like bis(oxazolines) may have potential to become catalyst for other asymmetric reactions. The semicrown ether-like chiral bis(oxazolines) have many coordination sites may be suitable for chiral complexes formation with other metals such as zinc, cobalt, and rhodium. Further studies in other asymmetric reactions are in progress in our laboratory.

EXPERIMENTAL

Melting points were measured on an XT-4 melting point apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Mercury 300 MHz or 200 MHz spectrometer with tetramethylsilane (TMS) serving as internal standard. Infrared spectra were obtained on a Bruker Vector 22 spectrometer. Mass spectra were obtained on a VG-ZAB-HS mass spectrometer. Optical rotations were measured on a Perkin–Elmer 241 MC spectrometer. Elemental analyses were carried out on an Elementar Vario EL instrument. Solvents used were purified and dried by standard procedures. 2,2′-[1,3-phenylenebis(methyleneoxy)]-bisbenzoic acid **1a** and 2,2′-[2,6-pyridinediylbis(methyleneoxy)]-bisbenzoic acid **1b** were synthesized according to literature procedure (Elwahy and Abbas, 2000).

General Procedure A

1,3-Bis[2-[N-(2-hydroxy-(1R)-1-phenylethyl)carbamoyl] phenoxymethyl]benzene (**2a**)

A solution of diacid **1a** (3.0 g, 8 mmol), $SOCl_2$ (50 mL) and 3 drops of DMF was refluxed for 12 hr. The excess $SOCl_2$ was removed under reduced

pressure, and then anhydrous benzene (20 mL) was added and the solvent was removed again to dryness to remove the trace of $SOCl_2$ and afford the diacyl dichloride. The above diacyl dichloride in CH_2Cl_2 (150 mL) was added dropwise to a solution of R-phenylglycinol (2.19 g, 16 mmol) and Et_3N (10 mL) in CH_2Cl_2 (50 mL) at 0°C and stirred at room temperature for 24 hr. The reaction mixture was washed with 2 N HCl, 10% $NaHCO_3$, and H_2O. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to give crude product. Purification by silica gel column chromatography (petroleum ether-ethyl acetate-methanol 5 : 3 : 1) afforded the dihydroxy diamide **2a** as colorless solid (3.92 g, 79.5%). m.p. 78–80°C. $[\alpha]_D^{20} = +91.7^\circ$ (c = 0.38, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.07 (2H, s, OH), 3.54–3.68 (4H, m, CH_2), 5.09 (4H, s, OCH_2), 5.16–5.22 (2H, m, CH), 6.99–7.14 (14H, m, ArH), 7.37–7.45 (5H, m, ArH), 7.60 (1H, s, ArH), 8.14–8.17 (2H, s, ArH), 8.54 (2H, d, J = 7.8 Hz, NH). ^{13}C NMR ($CDCl_3$): δ 55.64, 66.29, 70.84, 112.37, 121.40, 121.59, 126.49, 127.27, 128.25, 128.46, 128.65, 129.27, 132.33, 132.93, 136.15, 139.19, 156.62, 165.29. IR(KBr): ν 3384, 3061, 3030, 2932, 1708,1638, 1599, 1530, 1482, 1450, 1384, 1300, 1223, 1162, 1105, 996, 755, 700 cm^{-1}. ESIMS: m/z 617 (M + H, 48), 639 (M + Na, 100), 360 (20), 223 (18). Anal. Calcd. for $C_{38}H_{36}N_2O_6 \cdot 0.5H_2O$: C, 72.94; H, 5.91; N, 4.47. Found: C, 72.89; H, 5.64; N, 4.35.

1,3-Bis[2-[N-((1S)-1-benzyl-2-hydroxyethyl)carbamoyl] phenoxymethyl]benzene (**2b**)

Following general procedure A, from diacid **1a** (2.64 g, 7 mmol), $SOCl_2$ (45 mL), *S*-Phenylalanol (2.12 g, 14 mmol) and Et_3N (10 mL) to give a colorless solid **2b** in 71.8% yield (3.24 g). m.p. 59–60°C. $[\alpha]_D^{20} = -63.5^\circ$ (c = 0.38, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.72 (4H, d, $J = 7.2$ Hz, CH_2), 3.35–3.59 (6H, m, CH_2 + OH), 4.27–4.31 (2H, m, CH), 5.11 (4H, s, OCH_2), 6.94–7.54 (20H, m, ArH), 8.12–8.18 (4H, m, ArH + NH). ^{13}C NMR ($CDCl_3$): δ 36.89, 52.97, 63.40, 70.78, 112.58, 112.56, 121.61, 126.31, 127.31, 128.11, 128.31, 129.10, 132.13, 132.79, 136.39, 137.82, 156.53, 165.41. IR(KBr): ν 3389, 3072, 2960, 1735, 1637, 1599, 1537, 1479, 1449, 1385, 1298, 1221, 1161, 1101, 993, 754 cm^{-1}. ESIMS: m/z 645 (M + H, 76), 667 (M + Na, 100), 525 (80), 374 (20). Anal. Calcd. for $C_{40}H_{40}N_2O_6 \cdot 2H_2O$: C, 70.56; H, 6.51; N, 4.11. Found: C, 70.67; H, 6.39; N, 3.91.

1,3-Bis[2-[N-(2-hydroxy-(1S)-1-isobutylethyl)carbamoyl] phenoxymethyl]benzene (**2c**)

Following general procedure A, from diacid **1a** (2.64 g, 7 mmol), $SOCl_2$ (40 mL), *S*-leucinol (1.65 g, 14 mmol) and Et_3N (10 mL) to give a colorless

solid **2c** in 91.6% yield (3.7 g). m.p. 60–61°C. $[\alpha]_D^{20} = -65.8°$ (c = 0.39, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.74 (6H, d, $J = 6.8$ Hz, CH_3), 0.80 (6H, d, $J = 6.4$ Hz, CH_3), 0.95–1.28 (4H, m, CH_2), 1.28–1.48 (2H, m, CH), 3.25 (2H, s, OH), 3.37–3.66 (4H, m, CH_2), 4.05–4.16 (2H, m, CH), 5.19 (4H, s, OCH_2), 7.02–7.13 (4H, m, ArH), 7.40–7.62 (6H, m, ArH), 7.95 (2H, d, $J = 7.4$ Hz, ArH), 8.18 (2H, d, $J = 7.8$ Hz, NH). ^{13}C NMR ($CDCl_3$): δ 22.07, 22.92, 24.76, 40.08, 50.17, 66.18, 70.91, 112.43, 115.95, 121.58, 121.73, 128.52, 129.50, 132.32, 132.86, 136.38, 156.56, 165.80. IR(KBr): ν 3384, 3073, 2955, 2869, 1739, 1637, 1600, 1537, 1483, 1449, 1384, 1299, 1222, 1160, 1101, 754 cm^{-1}. ESIMS: m/z 577 (M + H, 100), 599 (M + Na, 86), 559 (15), 340 (40), 197 (70). Anal. Calcd. for $C_{34}H_{44}N_2O_6 \cdot 0.5H_2O$: C, 69.71; H, 7.74; N, 4.78. Found: C, 69.58; H, 7.65; N, 4.63.

1,3-Bis[2-[N-(2-hydroxy-(1S)-1-isopropylethyl)carbamoyl] phenoxymethyl]benzene (**2d**)

Following general procedure A, from diacid **1a** (2.64 g, 7 mmol), $SOCl_2$ (40 mL), *S*- leucinol (1.44 g, 14 mmol) and Et_3N (10 mL) to give a colorless oil **2c** in 97.4% yield (3.74 g). $[\alpha]_D^{20} = -47.5°$ (c = 0.48, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.67 (6H, d, $J = 7.0$ Hz, CH_3), 0.76 (6H, d, $J = 6.4$ Hz, CH_3), 1.65–1.76 (2H, m, CH), 3.31 (2H, s, OH), 3.45–3.60 (4H, m, CH_2), 3.82–3.90 (2H, m, CH), 5.20 (4H, s, OCH_2), 7.01–7.14 (4H, m, ArH), 7.41–7.49 (5H, m, ArH), 7.64 (1H, s, ArH), 8.02 (2H, d, $J = 8.2$ Hz, NH), 8.20 (2H, d, $J = 7.6$ Hz, ArH). ^{13}C NMR ($CDCl_3$): δ 18.33, 19.32, 28.95, 57.35, 64.06, 70.85, 112.30, 121.62, 121.67, 128.16, 128.73, 129.44, 132.42, 132.85, 136.28, 156.55, 166.10. IR(KBr): ν 3391, 3073, 2960, 2873, 1735, 1636, 1599, 1537, 1483, 1449, 1385, 1298, 1223, 1163, 1102, 996, 755 cm^{-1}. ESIMS: m/z 549 (M + H, 8), 571 (M + Na, 100), 197 (5). Anal. Calcd. for $C_{32}H_{40}N_2O_6 \cdot 0.5H_2O$: C, 68.92; H, 7.41; N, 5.02. Found: C, 68.70; H, 7.26; N, 4.83.

2,6-Bis[2-[N-(2-hydroxy-(1R)-1-phenylethyl)carbamoyl] phenoxymethyl]pyridine (**3a**)

Following general procedure A, from diacid **1b** (2.28 g, 6 mmol), $SOCl_2$ (40 mL), *R*-phenylglycinol (1.65 g, 12 mmol) and Et_3N (8 mL) to give a colorless solid **3a** in 76.8% yield (2.85 g). m.p. 118–119°C. $[\alpha]_D^{20} = +81.4°$ (c = 0.35, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.41 (2H, t, $J = 6.0$ Hz, OH), 3.65–3.80 (4H, m, CH_2), 5.21(4H, s, OCH_2), 5.20–5.32 (2H, m, CH), 6.97–7.19 (14H, m, ArH), 7.27–7.44 (4H, m, ArH), 7.64 (1H, t, $J = 7.8$ Hz, ArH), 8.12–8.18 (2H, dd, $J = 1.6$, 7.6 Hz, ArH), 8.60 (2H, d, $J = 7.6$ Hz, NH). ^{13}C NMR ($CDCl_3$): δ 55.78, 66.25, 71.47, 112.72, 121.97, 122.27, 126.61, 127.40, 128.54, 132.39, 132.95, 138.25, 139.33, 155.31,

156.21, 165.42. IR(KBr): ν 3381, 3287, 3059, 2921, 1737, 1636, 1599, 1529, 1489, 1439, 1384, 1287, 1244, 1163, 1060, 1026, 752, 702 cm^{-1}. ESIMS: m/z 618 (M + H, 80), 640 (M + Na, 100), 600 (10), 498 (15), 481 (25), 343 (25), 225 (10). Anal. Calcd. for $C_{37}H_{35}N_3O_6 \cdot 0.5H_2O$: C, 70.91; H, 5.79; N, 6.70. Found: C, 71.13; H, 5.85; N, 6.48.

2,6-Bis[2-[N-((1S)-1-benzyl-2-hydroxyethyl)carbamoyl] phenoxymethyl]pyridine (**3b**)

Following general procedure A, from diacid **1b** (2.28 g, 6 mmol), $SOCl_2$ (40 mL), *S*-phenylalaninol (1.82 g, 12 mmol) and Et_3N (8 mL) to give a colorless solid **3b** in 68.2% yield (2.64 g). m.p. 173–175°C. $[\alpha]_D^{20} = -56.7°$ (c = 0.12, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.85 (4H, d, J = 7.2 Hz, CH_2), 3.34 (2H, J = 6.0 Hz, OH), 3.51–3.73 (4H, m, CH_2), 4.34–4.42 (2H, m, CH), 5.28 (4H, s, OCH_2), 6.96–7.29 (14H, m, ArH), 7.35–7.44 (4H, m, ArH), 7.69 (1H, t, J = 7.8 Hz, ArH), 8.13–8.18 (4H, dd, J = 1.6, 7.8 Hz, ArH + NH). ^{13}C NMR ($CDCl_3$): δ 37.07, 53.30, 63.93, 71.35, 112.99, 122.06, 122.34, 126.49, 128.47, 129.19, 132.27, 132.82, 137.86, 155.60, 156.00, 165.61. IR(KBr): ν 3300, 3027, 2931, 2873, 1637, 1599, 1534, 1489, 1439, 1375, 1239, 1113, 1045, 1027, 752, 700 cm^{-1}. ESIMS: m/z 646(M + H, 100), 668 (M + Na, 95), 628 (30), 495 (46), 362 (15), 344 (12), 225 (5). Anal. Calcd. for $C_{39}H_{39}N_3O_6 \cdot 0.5H_2O$: C, 71.50; H, 6.16; N, 6.41. Found: C, 71.67; H, 6.11; N, 6.24.

2,6-Bis[2-[N-(2-hydroxy-(1S)-1-isobutylethyl)carbamoyl] phenoxymethyl]pyridine (**3c**)

Following general procedure A, from diacid **1b** (2.28 g, 6 mmol), $SOCl_2$ (40 mL), *S*-leucinol (1.41 g, 12 mmol) and Et_3N (8 mL) to give a colorless solid **3c** in 87.3% yield (3.03 g). m.p. 116–118°C. $[\alpha]_D^{20} = -62.2°$ (c = 0.37, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.80 (6H, d, J = 6.4 Hz, CH_3), 0.86 (6H, d, J = 6.4 Hz, CH_3), 1.20–1.39 (4H, m, CH_2), 1.47–1.64 (2H, m, CH), 3.45–3.76 (6H, m, OH + CH_2), 4.10–4.25 (2H, m, CH), 5.32 (4H, s, OCH_2), 7.02–7.13 (4H, m, ArH), 7.38–7.49 (4H, m, ArH), 7.82 (1H, t, J = 7.8 Hz, ArH), 7.96 (2H, d, J = 7.8 Hz, NH), 8.12–8.17 (2H, dd, J = 1.8, 7.6Hz, ArH). ^{13}C NMR ($CDCl_3$): δ 22.16, 23.00, 24.86, 40.27, 50.19, 65.84, 71.44, 112.83, 122.02, 122.19, 122.41, 132.25, 132.73, 138.30, 155.62, 156.00, 165.75. IR(KBr): ν 3383, 3286, 3074, 2953, 2869, 1743, 1637, 1598, 1538, 1490, 1440, 1369, 1288, 1239, 1162, 1111, 1061, 750 cm^{-1}. ESIMS: m/z 578 (M + H, 100), 600 (M + Na, 35), 461 (30), 362 (12), 343(8). Anal. Calcd. for $C_{33}H_{43}N_3O_6 \cdot 0.5H_2O$: C, 67.55; H, 7.55; N, 7.16. Found: C, 67.90; H, 7.36; N, 6.85.

2,6-Bis[2-[N-(2-hydroxy-(1S)-1-isopropylethyl)carbamoyl] phenoxymethyl]pyridine (**3d**)

Following general procedure A, from diacid **1b** (2.28 g, 6 mmol), $SOCl_2$ (40 mL), *S*-leucinol (1.24 g, 12 mmol) and Et_3N (8 mL) to give a colorless solid **3d** in 59.7% yield (1.97 g). m.p. 140–142°C. $[\alpha]_D^{20} = -43.5^\circ$ (c = 0.23, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.78 (6H, d, $J = 6.6$ Hz, CH_3), 0.85 (6H, d, $J = 6.8$ Hz, CH_3), 1.74–1.85 (2H, m, CH), 3.52–3.70 (6H, m, OH + CH_2), 3.89–3.96 (2H, m, CH), 5.32 (4H, s, OCH_2), 7.01–7.13 (4H, m, ArH), 7.37–7.48 (4H, m, ArH), 7.80 (1H, t, $J = 7.8$ Hz, ArH), 8.04 (2H, d, $J = 8.2$ Hz, NH), 8.13–8.18 (2H, dd, $J = 1.8$, 7.6 Hz, ArH). ^{13}C NMR ($CDCl_3$): δ 18.65, 19.48, 29.04, 57.41, 63.69, 71.41, 112.69, 121.95, 122.37, 122.45, 132.32, 132.71, 138.33, 155.51, 156.03, 165.97. IR(KBr): ν 3406, 3311, 3075, 2956, 2870, 1771, 1616, 1580, 1535, 1491, 1441, 1384, 1296, 1234, 1170, 1109, 1078, 754 cm^{-1}. ESIMS: m/z 550 (M + H, 100), 572 (M + Na, 38), 532 (32), 447 (35), 362 (18), 343 (15), 225 (10). Anal. Calcd. for $C_{31}H_{39}N_3O_6 \cdot 0.5H_2O$: C, 66.65; H, 7.21; N, 7.52. Found: C, 67.01; H, 6.86; N, 7.35.

General Procedure B

1,3-Bis[2-((4R)-4-phenyl-4,5-dihydro-1,3-oxazol-2-yl)phenoxymethyl] benzene (**4a**)

To an ice-cooled solution of the dihydroxy diamide **2a** (1.23 g, 2.0 mmol) and Et_3N (1.4 mL, 10 mmol) in CH_2Cl_2 (20 mL) was added, dropwise MsCl (0.36 mL, 4.6 mmol). The mixture was allowed to warm to room temperature and was stirred for 12 hr. The mixture was quenched with water and extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness *in vacuo* to give the crude bismesylate as a yellow oil. The crude bismesylate was dissolved in CH_3OH (30 mL) and NaOH solution (11 mL, 0.25 N), The mixture was refluxed for 3 hr. The methanol was removed *in vacuo* and the residue was extracted with CH_2Cl_2 (2 × 30 mL). The combined organic phase was washed with 1 N HCl, 5% $NaHCO_3$ and H_2O. The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to give a pale yellow oil. Purification by silica gel column chromatography (petroleum ether-ethyl acetate 1 : 1) to afford light yellow oil **4a** 0.85 g (73.3 yield). $[\alpha]_D^{20} = +28.5^\circ$ (c = 0.33, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.18 (2H, t, $J = 8.2$ Hz, CH_2), 4.71 (2H, dd, $J = 8.2$, 9.8 Hz, CH_2), 5.07 (4H, s, OCH_2), 5.40 (2H, dd, $J = 8.2$, 9.8 Hz, CH), 6.90–7.43 (19H, m, ArH), 7.71 (1H, s, ArH), 7.85 (2H, dd, $J = 1.8$, 7.8 Hz, ArH). ^{13}C NMR ($CDCl_3$): δ 70.15, 70.19, 74.19, 113.40, 117.63, 120.53, 125.16, 125.87, 126.62, 127.29, 128.39, 128.50, 131.22, 132.17,

136.98, 142.53, 157.39, 163.54. IR(KBr): ν3061, 3029, 2959, 2894, 1643, 1600, 1582, 1494, 1451, 1384, 1355, 1250, 1163, 1034, 949, 752, 699 cm^{-1}. EIMS: m/z 580 (M^+, 28), 355 (20), 341 (15), 239 (32), 121 (40), 104 (38). HREIMS Calcd. for $C_{38}H_{32}N_2O_4$: 580.23621. Found: 580.23656.

1,3-Bis[2-((4S)-4-benzyl-4,5-dihydro-1,3-oxazol-2-yl)phenoxymethyl] benzene (**4b**)

Following general procedure B, from dihydroxy diamide **2b** (0.95 g, 1.47 mmol) to afford light yellow oil 0.723 g (76.1% yield). $[\alpha]_D^{20} = -4.5^\circ$ (c = 0.27, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.74 (2H, dd, J = 8.8, 13.6 Hz, CH_2), 3.24 (2H, dd, J = 5.0, 13.6 Hz, CH_2), 4.08 (2H, t, J = 8.2 Hz, CH_2), 4.29 (2H, t, J = 8.2 Hz, CH_2), 4.55–4.67 (2H, m, CH), 5.17 (4H, s, OCH_2), 6.93–7.46 (19H, m, ArH), 7.68 (1H, s, ArH), 7.77 (2H, dd, J = 1.4, 7.6 Hz, ArH). ^{13}C NMR ($CDCl_3$): δ 41.62, 67.75, 70.36, 71.23, 74.19, 113.53, 117.85, 120.59, 124.94, 125.87, 126.24, 128.31, 128.41, 129.08, 131.13, 132.04, 137.05, 137.86, 157.25, 162.81. IR(KBr): ν3062, 3027, 2922, 1647, 1601, 1581, 1495, 1453, 1384, 1356, 1256, 1164, 1030, 965, 752, 700 cm^{-1}. EIMS: m/z 608 (M^+, 25), 517 (48), 489 (15), 355 (45), 264 (26), 213 (40), 105 (100). HREIMS Calcd. for $C_{40}H_{36}N_2O_4$: 608.26751. Found: 608.26829.

1,3-Bis[2-((4S)-4-isobutyl-4,5-dihydro-1,3-oxazol-2-yl) phenoxymethyl]benzene (**4c**)

Following general procedure B, from dihydroxy diamide **2c** (1.5 g, 2.6 mmol) to afford a colorless oil 1.16 g (82.3% yield). $[\alpha]_D^{20} = -76.5^\circ$ (c = 0.27, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.97 (12H, t, J = 5.8 Hz, CH_3), 1.33–1.46 (2H, m, CH), 1.68–1.89 (4H, m, CH_2), 3.95 (2H, t, J = 7.6 Hz, CH_2), 4.31–4.53 (4H, m, CH + CH_2), 5.20 (4H, s, OCH_2), 6.97–7.03 (4H, m, ArH), 7.33–7.53 (5H, m, ArH), 7.61 (1H, s, ArH), 7.77 (2H, dd, J = 1.8, 8.0 Hz, ArH). ^{13}C NMR ($CDCl_3$): δ 22.70, 22.78, 25.38, 45.58, 65.20, 70.45, 72.63, 113.57, 118.28, 120.70, 124.90, 126.01, 128.48, 131.25, 131.94, 137.15, 157.31, 162.20. IR(KBr): ν3045, 2956, 2867, 1651, 1637, 1579, 1498, 1443, 1385, 1356, 1256, 1166, 1057, 1029, 792, 750 cm^{-1}. EIMS: m/z 540 (M^+, 14), 483 (10), 429 (15), 321 (60), 219 (36), 121 (37), 105 (100). HREIMS Calcd. for $C_{34}H_{40}N_2O_4$: 540.29881. Found: 540.29790.

1,3-Bis[2-((4S)-4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl) phenoxymethyl]benzene (**4d**)

Following general procedure B, from dihydroxy diamide **2d** (1.1 g, 2.0 mmol) to afford a colorless oil 0.665 g (64.6% yield). $[\alpha]_D^{20} = -84.5^\circ$ (c = 0.20,

$CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.92 (6H, d, $J = 6.8$ Hz, CH_3), 1.02 (6H, d, $J = 6.6$ Hz, CH_3), 1.81–1.91 (2H, m, CH), 4.04–4.19 (4H, m, CH_2), 4.31–4.41 (2H, m, CH), 5.19 (4H, s, OCH_2), 6.97–7.03 (4H, m, ArH), 7.33–7.51 (5H, m, ArH), 7.61 (1H, s, ArH), 7.7 (2H, dd, $J = 1.8$, 7.8 Hz, ArH). ^{13}C NMR ($CDCl_3$): δ 18.16, 18.87, 32.77, 69.72, 70.44, 72.79, 113.43, 118.35, 120.68, 125.16, 126.19, 128.50, 131.24, 131.92, 137.10, 157.31, 162.32. IR(KBr): ν3069, 2958, 2898, 1647, 1601, 1581, 1496, 1449, 1384, 1354, 1256, 1165, 1042, 752 cm^{-1}. EIMS: m/z 512 (M^+, 8), 469 (8), 415 (5), 321 (6), 307 (48), 105 (54). HREIMS Calcd. for $C_{32}H_{36}N_2O_4$: 512.26751. Found: 512.26562.

2,6-Bis[2-((4R)-4-phenyl-4,5-dihydro-1,3-oxazol-2-yl) phenoxymethyl]pyridine (**5a**)

Following general procedure B, from dihydroxy diamide **3a** (1.22 g, 1.97 mmol) to afford a colorless oil 0.963 g (83.7% yield). $[\alpha]_D^{20} = +43.1^\circ$ (c = 0.13, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.30 (2H, t, $J = 8.2$ Hz, CH_2), 4.81 (2H, dd, $J = 8.2$, 10.0 Hz, CH_2), 5.29 (4H, s, OCH_2), 5.47 (2H, dd, $J = 8.2$, 10.0 Hz, CH), 7.01–7.09 (5H, m, ArH), 7.29–7.50 (12H, m, ArH), 7.66 (2H, d, $J = 7.8$ Hz, ArH), 7.90 (2H, dd, $J = 1.6$, 7.8 Hz, ArH). ^{13}C NMR ($CDCl_3$): δ 70.54, 70.84, 74.07, 112.97, 117.35, 120.02, 120.79, 126.86, 127.49, 128.66, 131.49, 132.55, 142.57, 156.24, 157.19, 163.29. IR(KBr): ν 3062, 3026, 2893, 1640, 1595, 1579, 1494, 1441, 1375, 1356, 1294, 1252, 1126, 1063, 1030, 952, 748, 699 cm^{-1}. EIMS: m/z 581 (M^+, 32), 550 (8), 431 (10), 342 (44), 238 (100), 121 (73), 104 (49). HREIMS Calcd. for $C_{37}H_{31}N_3O_4$: 581.23280. Found: 581.23214.

2,6-Bis[2-((4S)-4-benzyl-4,5-dihydro-1,3-oxazol-2-yl) phenoxymethyl]pyridine (**5b**)

Following general procedure B, from dihydroxy diamide **3b** (0.969 g, 1.5 mmol) to afford a colorless oil 0.784 g (85.7% yield). m.p. 117–118 °C. $[\alpha]_D^{20} = -16.4^\circ$ (c = 0.14, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.82 (2H, dd, $J = 8.8$, 13.8 Hz, CH_2), 3.31 (2H, dd, $J = 5.2$, 13.6 Hz, CH_2), 4.14 (2H, t, $J = 8.0$ Hz, CH_2), 4.38 (2H, t, $J = 8.8$ Hz, CH_2), 4.64–4.72 (2H, m, CH), 5.30 (4H, s, OCH_2), 6.99–7.06 (5H, m, ArH), 7.20–7.46 (11H, m, ArH), 7.58–7.84 (5H, m, ArH). ^{13}C NMR ($CDCl_3$): δ 41.84, 68.13, 70.85, 71.24, 113.04, 117.54, 119.91, 120.80, 126.45, 128.53, 129.24, 131.41, 132.38, 137.71, 138.08, 156.43, 157.03, 162.69. IR(KBr): ν 3084, 3025, 2923, 1642, 1625, 1593, 1492, 1441, 1384, 1355, 1294, 1253, 1128, 1064, 1026, 962, 798, 751, 701 cm^{-1}. EIMS: m/z 609 (M^+, 20), 518 (100), 490 (15), 356 (56), 266 (24), 213 (33), 162 (48). Anal. Calcd. for $C_{39}H_{35}N_3O_4 \cdot 0.5H_2O$: C, 75.71; H, 5.86; N, 6.79. Found: C, 75.84; H, 5.80; N, 6.56.

2,6-Bis[2-((4S)-4-isobutyl-4,5-dihydro-1,3-oxazol-2-yl) phenoxymethyl]pyridine (**5c**)

Following general procedure B, from dihydroxy diamide **3c** (0.967 g, 1.67 mmol) to afford a colorless solid 0.756 g (83.5% yield). m.p. 97–98°C. $[\alpha]_D^{20} = -86.9^\circ$ (c = 0.236, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.02 (12H, t, $J = 6.8$ Hz, CH_3), 1.37–1.51 (2H, m, CH), 1.71–2.00 (4H, m, CH_2), 3.97 (2H, t, $J = 7.0$ Hz, CH_2), 4.38–4.57 (4H, m, CH + CH_2), 5.30 (4H, s, OCH_2), 6.98–7.06 (4H, m, ArH), 7.37–7.46 (2H, m, ArH), 7.74–7.90 (5H, m, ArH). ^{13}C NMR ($CDCl_3$): δ 22.57, 23.01, 25.47, 45.70, 65.48, 70.76, 72.43, 112.88, 117.68, 119.96, 120.77, 131.38, 132.25, 137.52, 156.51, 157.00, 161.85. IR(KBr): ν 3073, 2950, 2868, 1635, 1595, 1580, 1495, 1446, 1384, 1368, 1292, 1256, 1167, 1063, 1028, 799, 749 cm^{-1}. EIMS: m/z 541 (M^+, 18), 498 (15), 484 (34), 430 (28), 322 (100), 268 (55), 224 (65), 121 (72), 106 (53). Anal. Calcd. for $C_{33}H_{39}N_3O_4$: C, 73.17; H, 7.26; N, 7.76. Found: C, 72.84; H, 7.26; N, 7.60.

2,6-Bis[2-((4S)-4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl) phenoxymethyl]pyridine (**5d**)

Following general procedure B, from dihydroxy diamide **3d** (1.26 g, 2.29 mmol) to afford a colorless solid 0.625 g (53% yield). m.p. 91–93°C. $[\alpha]_D^{20} = -74.1^\circ$ (c = 0.116, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.99 (6H, d, $J = 6.8$ Hz, CH_3), 1.09 (6H, d, $J = 6.8$ Hz, CH_3), 1.87–1.97 (2H, m, CH), 4.07–4.25 (4H, m, CH_2), 4.36–4.47 (2H, m, CH), 5.29 (4H, s, OCH_2), 6.98–7.05 (5H, m, ArH), 7.37–7.46 (2H, m, ArH), 7.71 (4H, m, ArH). ^{13}C NMR ($CDCl_3$): δ 18.27, 18.99, 32.83, 69.59, 70.73, 73.07, 112.84, 117.73, 120.03, 120.75, 131.37, 132.21, 137.57, 156.45, 156.97, 162.08. IR(KBr): ν 3078, 2958, 2869, 1644, 1595, 1579, 1497, 1443, 1384, 1369, 1291, 1253, 1171, 1064, 748 cm^{-1}. EIMS: m/z 513 (M^+, 25), 470 (42), 416 (13), 385 (11), 308 (100), 266 (15), 224 (33), 106 (32). HREIMS Calcd. for $C_{31}H_{35}N_3O_4$: 513.26410. Found: 513.26441.

Typical Procedure

Asymmetric Cyclopropanation

A solution of the ligand (2.4 mol%) in CH_2Cl_2 (2 mL) was added $[Cu(OTf)(C_6H_6)_{0.5}]$ (2 mol%). After being stirred at room temperature for 1.5 hr, styrene (8 mmol) was added, followed by dropwise addition of ethyl diazoacetate (2 mmol) in CH_2Cl_2 (1 mL) solution during 4 hr. The mixture was stirred for another 18 hr and then quenched with 10% NH_4Cl (5 mL). The mixture was extracted with ether (25 mL), and then the organic phase

was separated. The organic phase was washed with water and brine, dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 15 : 1) to afford the mixture of *trans*- and *cis*-2-phenylcyclopropane-1-carboxylates as colorless oil. The *trans*/*cis* ratio of this mixture was analyzed by ^{1}H NMR (300 MHz) in $CDCl_3$ using TMS as internal standard. The diastereomeric and enantiomeric excess were determined by HPLC with a chiral column (Daicel Chiralcel OJ; eluent, hexane-isopropyl alcohol 90 : 10; flow rate, 0.5 mL/min; UV detector, 220 nm).

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