JOC Note

Rational Tuning Chelate Size of Bis-Oxazoline Ligands to Improve Enantioselectivity in the Asymmetric Aziridination of Chalcones

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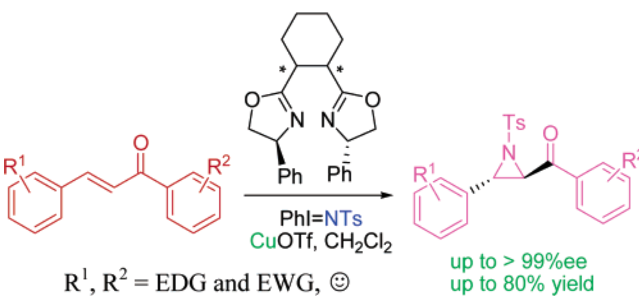

Chalcones were asymmetrically aziridinated with [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane (PhI=NTs) as a nitrene source under catalysis of CuOTf and a series of cyclohexane-linked bis-oxazolines (cHBOXes), which are chelate size rationally tuned bis-oxazolines. The results indicate that highly enantioselective aziridination of chalcones with up to >99% ee have been achieved under catalysis of (*S*,*S*)-1,2-bis[(*S*)-(4-phenyl)oxazolin-2-yl]cyclohexane, which is the most-matched stereoisomer among cyclohexane-linked bis-oxazolines. It was also found that the enantioselectivity is not substituent-dependent with respect to chalcones in the present case, unlike with 1,8-anthracene-linked bis-oxazolines (AnBOXes).

Chiral bis-oxazolines have emerged as one class of important and efficient C_2-symmetric ligands in numerous metal-catalyzed asymmetric transformations over the past decade.[1] They have been found to be excellent chiral ligands for a lot of asymmetric reactions, which include cyclopropanation of olefins, aziridination of olefins and imines, Dields–Alder reaction, Henry reaction, allylic substitution and oxidation, transhydrogenation, hydrosilylation and cyanosilylation of aldehydes and ketones, addition of dialkylzinc to aldehydes and ketones, addition of alkyllithiums to imines, addition of silylketene acetal to aldehyde, free radical-initiated addition of allyltributylstannane, and so on.[1]

During the past decade, numerous chiral bis-oxazolines with different backbones, such as aliphatic chains and cycles, including methylene,[2] dimethylmethylene,[3] ethylene,[2] 4,5-dioxolane, bicyclic compounds,[4] and dibenzo-[*a*,*c*]cycloheptadiene,[5] and aromatic rings, including 1,2- and 1,3-benzenes,[2,6] 2,6-pyridine,[7] 1,8-dibenzofuran,[8] 1,8-dibenzothiophen,[9] 1,8-dibenzopyrrole,[10] and 1,8-anthracene,[11] have been reported. The effects of the structure and chelate size of bidentate bis-oxazoline ligands in the asymmetric copper-catalyzed cyclopropanation and aziridination of olefins,[2,12] and in the asymmetric Diels–Alder reaction,[13] were investigated previously. The results indicated that the fine-tuning of the ligand backbone could improve enantioselectivity, and even reverse enantiofacial selectivity.[1,11,12] The chelate size in the reactive metal complex of bis-oxazolines is an important feature of the catalyst, because it can control both the orientation of the substituents on the two oxazolines around the metal ion and the distance of the substituents to the metal ions. This implies that the chelate size of bis-oxazolines can tune the chiral environment at the catalytic center and then affect the enantioselecivity of asymmetric catalytic reactions. To tune the substituents close to the catalytic center, we and Andersson et al. designed a series of rigid backbone-linked bis-oxazolines, and synthesized and evaluated them in certain asymmetric reactions.[2,11] The results indicate that bis-oxazoline ligands in which the substituents on the oxazoline rings are closer to the catalytic center show better enantioselectivity. To improve the enantioselectivity of chalcones with electron-withdrawing groups, we hope to use cyclohexane-linked bis-oxazolines (cHBOXes) to carry out our asymmetric aziridination of chalcones. cHBOXes have been synthesized previously, and have been applied in the asymmetric cyclization–carbonylation of 2-propargyl-1,3-dione[14] and in the asymmetric

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addition of methyllithium to an aromatic aldimine.[15] In cHBOXes, the two oxazoline rings, which are attached to the 1,2-positions of all isomeric cyclohexane rings, have two substituents that are closer together than those of Evans et al.'s BOXes.[3] They should have a better chiral environment near the reaction center.

Transition-metal chiral-ligand-catalyzed asymmetric aziridination is one of the most important methods developed during the past decade for the preparation of optically active aziridines.[16,17] The C_2-symmetric chiral bis-oxazolines have emerged as one class of the most efficient ligands in the reaction. We have recently reported the asymmetric aziridination of chalcones catalyzed by our 1,8-anthracene-linked bis-oxazoline ligand (AnBOX)−copper complex, and excellent enantioselectivities were achieved for electron-rich chalcones.[11] In the present paper, we report on our investigation on the preparation of cyclohexane-linked bis-oxazolines with a modified method, and on their application in the highly enantiomeric asymmetric catalytic aziridination of chalcones, especially electron-deficient chalcones.

Optically pure (*S*,*S*)-cyclohexane-1,2-dicarboxylic acid was obtained via chemical resolution of *trans*-cyclohexane-1,2-dicarboxylic acid, which was prepared from *cis*-cyclohexane-1,2-dicarboxylic anhydride according to the literature method,[18] with optically pure α-phenylethylamine.[19] (*S*,*S*)- and (*R*,*R*)-1,2-bis[(*S*)-(4-phenyl)-oxazolin-2-yl]cyclohexanes (*S*-cHBOX and *R*-cHBOX) have been synthesized previously via a stepwise method.[14] Herein, we prepared *S*-cHBOX, *R*-cHBOX, and *cis*-cHBOX via the classical method in one-pot reactions by using the corresponding diacids and L-phenylglycinol as starting materials. In all cases, the dihydroxy diamide intermediates were used directly without further purification because of their poor solubility. The final ligands were conveniently purified by silica gel chromatography (Scheme 1).

Because of a low yield of resolution, we attempted to synthesize *S*-cHBOX and *R*-cHBOX by using racemic *trans*-cyclohexane-1,2-dicarboxylic acid, and hoped that they could be separated on a silica gel column, as they are diastereomers. Actually, only *R*-cHBOX was obtained in the reaction.

First, the copper-catalyzed asymmetric aziridination of chalcone with [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane (PhI=NTs) as a nitrene source in the presence of the synthetic bis-oxazolines was investigated under our optimal conditions, CuOTf as copper salt in CH_2Cl_2 at 24 °C,[11] in order to determine the efficiency of the cHBOX ligand system. As a comparison, BOX of Evans et al. was also used as a model ligand. The results are summarized in Table 1 (entries 1−4). It was found that cHBOX ligands gave good enantioselectivities and moderate yields. *S*-cHBOX ligand is the best one among them in our asymmetric aziridination. Aziridination of other substituted chalcones with PhI=NTs as the nitrene precursor was conducted under optimal conditions with *S*-cHBOX−CuOTf as the catalyst. The results are summarized in Table 1 (entries 5−15). The results indicate that cHBOXes and BOX show the same enantiofacial selectivity. (2*R*,3*S*)-Aziridination products of chalcones were obtained in all cases. cHBOXes do not show substituent-dependent enantioselectivity, unlike AnBOXes, which show obviously substituent-dependent enantioselectivity.[11]

From entries 1−3 in Table 1, it can be seen that *S*-cHBOX is the most-matched one among the three

SCHEME 1. Synthesis of 1,2-Bisoxazolinylcyclohexanes

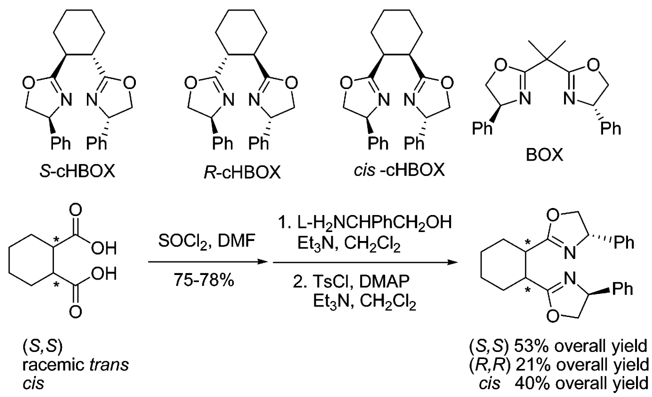
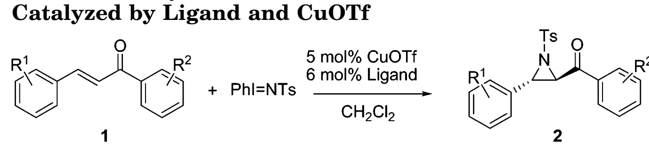


TABLE 1. Asymmetric Aziridination of Chalcones Catalyzed by Ligand and CuOTf



entry	ligand	product	R[1]	R[2]	yield[a] (%)	ee[b] (%)
1	(*R*)-cHBOX	**2a**	H	H	47	86
2	(*S*)-cHBOX	**2a**	H	H	56	91
3	*cis*-cHBOX	**2a**	H	H	45	80
4	BOX	**2a**	H	H	38	86
5	(*S*)-cHBOX	**2b**	*p*-Me	H	62	94
6	(*S*)-cHBOX	**2c**	*p*-F	H	62	90
7	(*S*)-cHBOX	**2d**	*p*-Cl	H	80	95
8	(*S*)-cHBOX	**2e**	*p*-Me	*p*-Me	50	>99
9	(*S*)-cHBOX	**2f**	H	*p*-Me	71	>99
10	(*S*)-cHBOX	**2g**	H	*p*-MeO	73	97
11	(*S*)-cHBOX	**2h**	*p*-Cl	*p*-Cl	80	95
12	(*S*)-cHBOX	**2i**	*p*-Cl	*p*-Me	72	85
13	(*S*)-cHBOX	**2j**	H	*p*-Br	63	86
14	(*S*)-cHBOX	**2k**	*m*-F	H	64	92
15	(*S*)-cHBOX	**2l**	*p*-CF_3	H	51	80

[a] Isolated yield after flash silica gel chromatographic separation. [b] The ee value was determined by HPLC analysis using chiralpak AS column, chiralcel OD, OD-H columns. The absolute configuration was determined by comparing the measured optical rotation with the reported one.[11,20]

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enantiomers of 1,2-cyclohexane-linked bis-oxazolines. The results are in good agreement with the observation in the asymmetric cyclization−carbonylation of 2-propargyl-1,3-dione,[14] and similar to the results of 4,5-dioxolane-1,2-linked bis-oxazoline-catalyzed asymmetric cyclopropanation and aziridination of olefins.[2]

After successful asymmetric aziridination of chalcones, we attempted to apply the CuOTf−cHBOX complexes to the aziridination of styrene under the optimized conditions. The aziridinated products were obtained in 78−88% yields, with only 6−15% ee values. *S*-cHBOX still gave the highest enantioselectivity in the aziridination of styrene.

In summary, three enantiomers of cHBOXes were synthesized in one-pot reactions by using the corresponding diacids and L-phenylglycinol as starting materials, and were applied in the asymmetric aziridination of chalcones with PhI=NTs as a nitrene precursor. The results indicate that highly enantioselective aziridination of chalcones with up to >99% ee has been achieved under catalysis of (*S*,*S*)-1,2-bis[(*S*)-(4-phenyl)oxazolin-2-yl]cyclohexane, which is the most matched stereoisomer among cyclohexane-linked bis-oxazolines. The results also indicate that the enantioselectivity is not substituent-dependent with respect to chalcones in the present case, unlike AnBOXes.

Experimental Section

Synthesis of Chiral Ligand 1,2-Bis[(*S*)-(4-phenyl)oxazolin-2-yl]cyclohexane (cHBOXes). *trans*-1,2-Cyclohexanedicarboxylic acid was prepared from *cis*-1,2-cyclohexanedicarboxylic anhydride as starting material according to the literature procedure.[18] (*S*,*S*)-Cyclohexane-1,2-dicarboxylic acid was obtained via chemical resolution of *trans*-cyclohexane-1,2-dicarboxylic acid with optically pure α-phenylethylamine.[19]

Preparation of (*S*,*S*)-1,2-Cyclohexanedicarboxylic Acid. (*S*,*S*)-1,2-Cyclohexanedicarboxylic acid was resolved by a modified reported method.[19] To a solution of (*S*)-1-phenylethylamine (6.80 g, 56.0 mmol) in EtOH (100 mL) was added racemic *trans*-1,2-cyclohexanedicarboxylic acid (9.60 g, 55.8 mmol) at room temperature. The mixture first became clear, and then a white solid formed. Toluene (100 mL) was added after the mixture was allowed to stir for another 3 h, and the reaction mixture was brought to reflux until the solid was dissolved completely. The solution was cooled, and colorless needle crystals were formed and filtered to give colorless crystals (6.10 g), which were recrystallized from hot EtOH/toluene (1:1) twice. The product obtained was dissolved in 1 mol/L aqueous HCl, and was extracted three times with Et_2O (80 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure, affording the enantiomerically pure (*S*,*S*)-1,2-cyclohexanedicarboxylic acid as colorless crystals (1.85 g, yield 19%): $[\alpha]^{20}_D = +18.3$ (*c* 1.03, acetone), lit.[19] $[\alpha]^{25}_D = +18.3$ (*c* 1.00, acetone).

General Procedure for the Synthesis of 1,2-Cyclohexanedicarboxylic Dichloride. 1,2-Cyclohexanedicarboxylic acid (0.432 g, 2.51 mmol) was treated with $SOCl_2$ (1.49 g, 12.6 mmol) in the presence of a catalytic amount of dry DMF, and the mixture was allowed to stir for 41 h to give a colorless solution. The solution was evaporated in vacuo to remove the excess $SOCl_2$ to afford the clear liquid.

Racemic *trans*-1,2-cyclohexanedicarboxylic dichloride (126 °C, 10 mmHg) and *cis*-1,2-cyclohexanedicarboxylic dichloride (112−114 °C, 4 mmHg) were obtained in vacuo in yields of 77 and 78%, respectively.

(*S*,*S*)-1,2-Cyclohexanedicarboxylic dichloride was obtained after removal of solvent and excessive $SOCl_2$, and was used in the next step without further purification to avoid the racemization: $[\alpha]^{20}_D = -19.9$ (*c* 0.96, CCl_4), lit.[21] $[\alpha]^{24}_D = -19.5$ (*c* 2.6, CCl_4).

General Procedure for the Synthesis of 1,2-Bis[(*S*)-(4-phenyl)oxazolin-2-yl]cyclohexane. A 50 mL flask fitted with a magnetic stirring bar was charged with a solution of L-phenylglycinol (0.517 g, 3.77 mmol) and Et_3N (1.40 mL, 9.42 mmol) in 5 mL of dry CH_2Cl_2. The solution was cooled in an ice bath, and a solution of (*S*,*S*)-1,2-cyclohexanedicarboxylic dichloride (0.394 g, 1.89 mmol) in 19 mL of dry CH_2Cl_2 was added dropwise. The resulting mixture was allowed to warm to room temperature, and was stirred for 22 h. After addition of TsCl (0.718 g, 3.77 mmol), DMAP (0.023 g, 0.189 mmol), and additional Et_3N (1.20 mL, 8.29 mmol), the resulting mixture was stirred for 27 h at room temperature. The reaction was then quenched with 16 mL of saturated aqueous NH_4Cl, and a white solid formed. Water (6 mL) was added to dilute the solution, and the layers were separated after filtration to remove the white solid. The aqueous layer was back-extracted with CH_2Cl_2 (2 × 8 mL). The combined organic layer was washed successively with 30 mL of saturated aqueous $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to give crude product, which was purified by column chromatography (silica gel, acetone:petroleum ether, 1:7, v/v) to afford colorless crystals of product. Although (*R*,*R*)- and (*S*,*S*)-1,2-bis[(*S*)-(4-phenyl)-oxazolin-2-yl]cyclohexanes were prepared previously,[14] no characteristic data were reported. Their analytical data are given here.

(*S*,*S*)-1,2-Bis[(*S*)-(4-phenyl)oxazolin-2-yl]cyclohexane (*S*-cHBOX): colorless crystals, yield 53%, mp 122−122.5 °C; R_f = 0.09 (acetone:petroleum ether 1:4, v/v, silica gel plate); $[\alpha]^{20}_D = +11.4$ (*c* 0.58, CH_2Cl_2); IR (KBr, cm^{-1}) *υ* 1663 (C=N); ^1H NMR (400 MHz, $CDCl_3$) δ 1.37−1.42 (m, 2H), 1.57−1.66 (m, 2H), 1.83−1.84 (m, 2H), 2.13−2.17 (m, 2H), 2.84−2.86 (m, 2H), 4.02 (dd, *J* = 8.4, 8.4 Hz, 2H), 4.55 (dd, *J* = 8.4, 10.0 Hz, 2H), 5.15 (dd, *J* = 8.4, 10.0 Hz, 2H), 7.21−7.30 (m, 10H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 25.1, 30.2, 39.8, 69.4, 74.5, 126.6, 127.3, 128.5, 142.7, 170.5; MS (EI) *m/z* (relative intensity, %) 374 (M^+, 94), 297 (M^+ − Ph, 2), 256 (87), 228 (100, M^+ − Ph − oxazolinyl), 120 (51), 104 (85), 91 (60). Anal. Cacld for $C_{24}H_{26}N_2O_2$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.85; H, 6.96; N, 7.55.

(*R*,*R*)-1,2-Bis[(*S*)-(4-phenyl)oxazolin-2-yl]cyclohexane (*R*-cHBOX): yellow viscous oil, yield 21%; R_f = 0.16 (acetone:petroleum ether 1:4, v/v, silica gel plate); $[\alpha]^{20}_D = -107$ (*c* 0.94, CH_2Cl_2); IR (KBr, cm^{-1}) *υ* 1663 (C=N); ^1H NMR (300 MHz, $CDCl_3$) δ 1.35−1.43 (m, 2H), 1.62−1.66 (m, 2H), 1.83−1.86 (m, 2H), 2.09−2.14 (m, 2H), 2.82−2.85 (m, 2H), 4.02 (dd, *J* = 8.1, 8.4 Hz, 2H), 4.58 (dd, *J* = 8.1, 10.2 Hz, 2H), 5.14 (dd, *J* = 8.4, 10.2 Hz, 2H), 7.19−7.32 (m, 10H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 25.1, 30.1, 40.3, 69.4, 74.5, 126.6, 127.3, 128.5, 142.5, 170.5; MS (EI) *m/z* (relative intensity, %) 374 (M^+, 82), 297 (M^+ − Ph, 2), 256 (57), 228 (60, M^+ − Ph − oxalyl), 120 (51), 104 (89), 91 (100). Anal. Cacld for $C_{24}H_{26}N_2O_2$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.81; H, 6.83; N, 7.64.

***cis*-1,2-Bis[(*S*)-(4-phenyl)oxazolin-2-yl]cyclohexane (*cis*-cHBOX):** yellow viscous oil, yield 40%; R_f = 0.26 (acetone:petroleum ether 1:4, v/v, silica gel plate); $[\alpha]^{20}_D = -13.0$ (*c* 1.02, CH_2Cl_2); IR (KBr, cm^{-1}) *υ* 1663 (C=N); ^1H NMR (200 MHz, $CDCl_3$) δ 1.39−1.43 (m, 2H), 1.59−1.65 (m, 2H), 1.83−1.86 (m, 2H), 2.11−2.17 (m, 2H), 2.83−2.87 (m, 2H), 4.02 (dd, *J* = 8.2, 8.2 Hz, 2H), 4.55 (dd, *J* = 8.2, 10.2 Hz, 2H), 5.15 (dd, *J* = 8.4, 10.2 Hz, 2H), 7.20−7.33 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.1, 20.3, 39.8, 69.4, 74.5, 126.6, 127.3, 128.6, 142.7, 170.5; MS (EI) *m/z* (relative intensity, %) 374 (M^+, 100), 297 (M^+ − Ph, 3), 256 (86), 228 (69), 120 (65), 104 (96), 91 (84); HRMS Calcd for $C_{24}H_{26}N_2O_2$ (M^+) 374.1994, found 374.2007.

General Procedure for the Asymmetric Aziridination of Chalcones. A three-necked flask (25 mL) was charged with chalcone **6** or olefin (1.50 mmol), cHBOX or BOX (0.06 mmol),

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and $CuOTf\cdot{}^1/_2C_6H_6$ (13 mg, 0.05 mmol) under a nitrogen atmosphere. Dichloromethane (8 mL) was added by syringe, and the resulting mixture was stirred for 1 h at 24 °C. PhI=NTs (373 mg, 1.00 mmol) was added portionwise to the mixture over 2 h. After the addition, the reaction mixture was stirred for another 3 h. The aziridine product was obtained after flash silica gel chromatography with a mixture of petroleum ether (60−90 °C) and ethyl acetate (6:1, v/v) as an eluent.

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Supporting Information Available: Analytic data of unknown aziridination products **2b**−**l** of chalcones; ^{1}H NMR and ^{13}C NMR spectra of bis-oxazolines; *R*-cHBOX, *S*-cHBOX, *cis*-cHBOX, and unknown aziridination products **2b**−**l** of chalcones; and the chromatograms for the determination of the enantiomeric excess values of the aziridination products **2** of chalcones. This material is available free of charge via the Internet at http://pubs.acs.org.

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