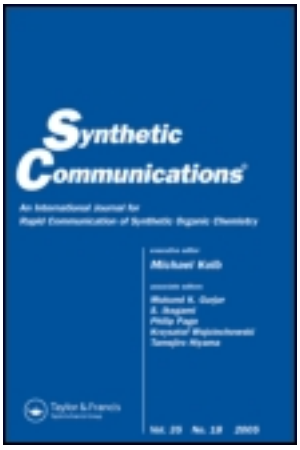

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Sulfur-Containing Chiral Bis(oxazolines) Tested in Copper-Catalyzed Asymmetric Cyclopropanation

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Sulfur-Containing Chiral Bis(oxazolines) Tested in Copper-Catalyzed Asymmetric Cyclopropanation

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Abstract: The novel C_2-symmetric sulfur-containing chiral bis(oxazoline) compound has been synthesized and characterized by X-ray crystallography. Highly enantioselective and diastereoselective cyclopropanation reactions have been performed using the copper-bis(oxazoline) catalyst.

Keywords: Asymmetric catalysis, bis(oxazolinyl)thiophene, bis(oxazolone), copper, cyclopropanation

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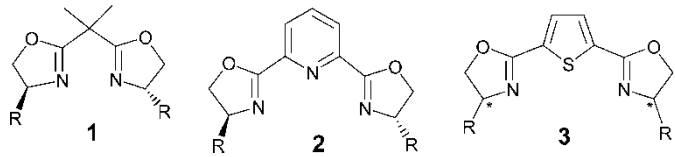
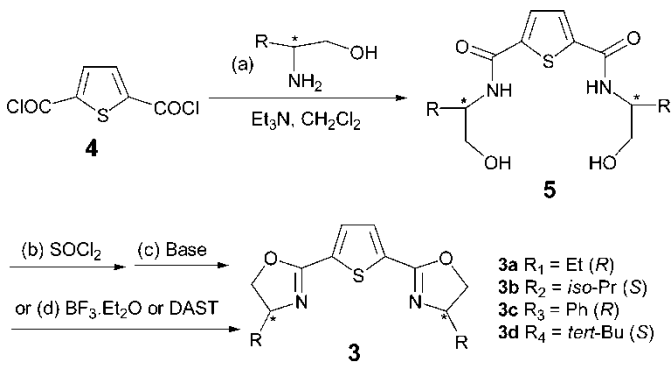
During the past decade, important advances in the field of asymmetric catalysis have been made.[1] The cyclopropanation of alkenes with diazoacetate has been one of the highlights of metal-catalyzed asymmetric synthesis since the report of Nozaki and coworkers.[2] Catalysts containing various metals and chiral ligands, such as Schiff Base–Cu,[3] salen–Co,[4] Rh_2(5S-MEPY),[5] porphyrin–Ru,[6] and especially the C_2-symmetric chiral bis(oxazolines) metal complexes, have proved to be efficient stereoselective catalysts for a wide range of asymmetric cyclopropanations.[7] Typical examples are the metal complexes of chiral bis(oxazolinyl)propane **1** and bis(oxazolinyl)pyridine **2**, which gave desirable enantioselectivity.[8]



Recently, we have reported some new sulfur-containing chiral bis(oxazolinyl)thiophenes **3**.[7b,9] Relatively little work has been reported on the sulfur-containing bis(oxazoline) for asymmetric catalysis.[10] This prompted us to report our preliminary results on the structure of the new ligand together with its application in catalytic asymmetric cyclopropanation reactions between alkenes and ethyl diazoacetate (EDA) using the copper complex.

The chiral bis(oxazolines) **3** (thiobox) have been prepared using two methods (Scheme 1). The reaction of the diacid chloride **4** with chiral β-amino alcohols forms dihydroxy diamide compounds **5** (a), which are subsequently treated with thionyl chloride to afford dichloride diamide compounds (b). These compounds are transformed into **3** by treatment with a base (c). The improved route includes one step (d, using $BF_3 \cdot Et_2O$ or DAST) instead of the two steps (b) and (c). This results not only in a simplification of procedures but also in an improved yield of the bis(oxazoline).



Scheme 1.

These new ligands were characterized by IR, NMR, MS and elemental analysis.

To better understand the structure of the new chiral bis(oxazoline) ligands **3**, the structure of the ligand 3a was determined by X-ray crystallography. Compound **3a** was obtained in the form of air-stable, colorless crystals by slow evaporation from a solution of **3a** in acetone–hexane (v/v 1 : 3). The perspective view of compound **3a** is shown in Figure 1.

Examination of the crystal structure of **3a** shows that the thiophene unit with two oxazoline moieties possesses a twist angle and that they do not lie in the same plane. The N-S-N angle is quite large; this differs from the structure of the previously reported pybox.[8c,11] In **3**, the thiophene functions as a backbone, and the sulfur atom is part of a strong π-donor system. The chiralty is introduced by the two-oxazoline moieties near the sulfur. These C_2-symmetric bis(oxazolines) present a new class of N-S-N chelating tridentate ligands.

These ligands were successfully utilized for the Cu(I)-catalyzed cyclopropanation of alkenes with ethyl diazoacetate. This is the commonly investigated model reaction with chiral ligands.[8,12] The asymmetric cyclopropanation was carried out in CH_2Cl_2 in the presence of 4% mol of Cu(I) catalyst by mixing $Cu(SO_2CF_3)_2$ and the bis(oxazoline) ligands **3** to give cyclopropanecarboxylate as a mixture of *trans* and *cis* isomers (Scheme 2).

The ratio of *trans* to *cis* isomers was determined by ^1H NMR, and the enantiomeric excess of these mixtures was determined by HPLC using a chiral column. The results are summarized in Table 1. Catalytic cyclopropanation experiments of 1,1-diphenylethene with ethyl diazoacetate afforded only low yields of cyclopropane products because of the presence of traces of water. Therefore, several desiccants such as $CaSO_4$ and $MgSO_4$ were tested and high yields were obtained using 4 Å molecular sieve.

Using ligand **3a** and substrate 1,1-diphenylethene, studies were carried out to determine the optimum reaction conditions. The choice of solvents has a great effect on both the enantioselectivity and the yield. Dichloromethane

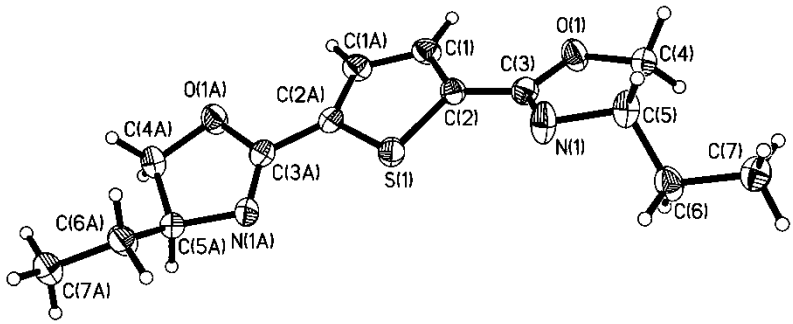
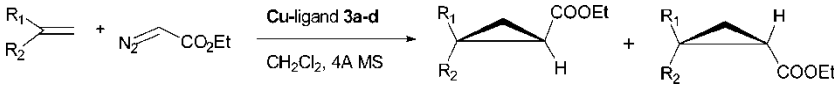


Figure 1. Molecular structure of **3a**.



Scheme 2.

was found to give the best results. Slightly lower enantioselectivities were obtained in chloroform and dichloroethane, and the enantioselectivity and yield decreased in THF (entry 1). Reduction of the reaction temperature from 40 °C to 0 °C did not noticeably affect the reaction, but increased enantioselectivity from 85% (entry 4) to 93% (entry 6) lowered the yield from 88% to 73%.

Changing ligand (**3b**, **3c**, **3d**) on the cyclopropanation of alkenes has a great effect on the *trans*/*cis* diastereoselectivity and enantioselectivity. As can be seen from entries 10–15 in Table 1, when the R groups of the ligand are changed from ethyl to bulkier groups (iso-Pr; Ph; tert-butyl), higher *trans*:*cis* ratios and ee values for the cyclopropanation products of styrene, *p*-chlorostyrene, and 4-vinylanisole were observed in all cases. The best results were obtained with the tert-butyl group, where the enantioselectivity of 97% ee (entry 9) and a *trans*:*cis* ratio of 91 : 9 and 90% ee (entry 15) of *trans* product were obtained. This is consistent with the results previously reported.[13]

Compared with the results reported for catalyst Cu–pybox,[8d] the results of enantioselectivity and diastereoselectivity of cyclopropanation product are improved by the use of Cu–thiobox. Compared with result reported for the catalyst Ru–pybox,[8b,8c] with respect to ee values and yield of cycloprpanation of 1,1-diphenylethene, better results are reported herein. In the case of styrene and substituent styrenes, the ee values and *trans*/*cis* stereoselectivity of the cyclopropanation product are similar, but a little lower. These differences may result from the differences in catalyst structure. With respect to the structure of the catalyst, it is expected that the N-S-N bonds coordinated to Cu have a larger angle than that of N-N-N bonds coordinated to Cu. This may result in easier access to the reactive substrate and is favorable for a large sterically bulky substrate. In addition, Cu-S coordination is much stronger than Cu-N coordination, because sulfur and copper are both soft centers. The Cu-N coordination represents a soft–hard interaction, and a soft–soft interaction is expected to be much stronger.

In conclusion, a series of new chiral sulfur-containing bis(oxazolines) with thiophene as a backbone has been synthesized. Preliminary results in the asymmetric cyclopropanation of alkenes with diazoacetate have been obtained. A high enantioselectivity has been obtained in the cyclopropanation of diphenylethene using the Cu(I)-bis(oxazoline) catalyst. The *trans*/*cis* stereoselectivity and enantioselectivity are moderate to good. The preliminary results suggest that these novel bis(oxazolines) may function as new catalysts for asymmetric reactions. Further studies on the asymmetric reactions are currently being investigated.

Table 1. Enantioselective cyclopropanation catalyzed by the Cu-bis(oxazolines)

Entry	Ligand	R_1	R_2	T (°C)	Solvent	*Trans*:*cis*[a]	%ee (*trans*)[b]	%ee (*cis*)	Yield %[c]
1	**3a**	Ph	Ph	rt	THF	—	77	77	61
2	**3a**	Ph	Ph	rt	$ClCH_2CH_2Cl$	—	88	88	79
3	**3a**	Ph	Ph	rt	$CHCl_3$	—	86	86	80
4	**3a**	Ph	Ph	40	CH_2Cl_2	—	85	85	88
5	**3a**	Ph	Ph	rt	CH_2Cl_2	—	91	91	84
6	**3a**	Ph	Ph	0	CH_2Cl_2	—	93	93	73
7	**3b**	Ph	Ph	rt	CH_2Cl_2	—	89	89	76
8	**3c**	Ph	Ph	rt	CH_2Cl_2	—	86	86	56
9	**3d**	Ph	Ph	rt	CH_2Cl_2	—	97	97	71
10	**3a**	H	Ph	rt	CH_2Cl_2	63:37	60	64	89
11	**3b**	H	Ph	rt	CH_2Cl_2	84:16	81	83	80
12	**3c**	H	Ph	rt	CH_2Cl_2	76:24	73	75	72
13	**3d**	H	Ph	rt	CH_2Cl_2	89:11	88	84	78
14	**3d**	H	4-Cl-Ph	rt	CH_2Cl_2	88:12	85	82	80
15	**3d**	H	4-MeO-Ph	rt	CH_2Cl_2	91:9	90	87	76

[a]The ratio of *trans* and *cis* was determined by ^1H NMR.
[b]Ee values were determined by chiral HPLC analysis (Chiralcel OD-H or OJ column).
[c]Isolated yield of a mixture of *trans* and *cis* based on EDA.

EXPERIMENTAL

Melting points were on determined on a Thiele apparatus and are uncorrected. ^{1}H NMR spectra were recorded with a Varian 300 spectrometer. Optical rotations were measured using a Perkin-Elmer 241 polarimeter at 589 nm in a cell of path length 10 cm. Chiral HPLC analyses were performed on a Beckman 110B chromatographic system with a Beckman 168 UV detector (254 nm). The chiral columns were purchased from Daicel Chemical Industries, Ltd. The crystallographic measurements were carried out on a Siemens P4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and 12-kW rotating generator. The data were collected at 110 K. The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1997) and SHELXL (Sheldrick, 1997). The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs.

General Procedure for Cyclopropopanation Reaction

The ligand **3** (0.21 mmol) and $Cu(SO_2CF_3)_2$ (72 mg, 0.2 mmol) were taken under nitrogen in anhydrous CH_2Cl_2 (4 mL). The mixture was stirred at reflux temperature for 30 min. After cooling to rt, phenylhydrazine (three drops) and 4Å molecular sieves (MS, 0.6 g) were added. Then, the mixture was stirred for 5 min and the 1,1-diphenylethene or other alkene (10.0 mmol, excess) was added, followed by slow addition of diazoester (5.0 mmol) in CH_2Cl_2 (3 mL) for 4 h. The final reaction was stirred for another 16 h. The solvent was removed under reduced pressure and the crude product was separated by flash column chromatography to afford the cyclopropyl ester products in 56–89% isolated yield.

Ethyl 2,2-diphenylcyclopropane-1-carboxylate. Colorless oil. Analytical HPLC Chiralcel OD-H, isopropanol/hexane (0.4%, 0.5 mL/min^{-1}), $t_R = 20.1$ min [(−)-*R*], $t_R = 21.8$ min [(+)-*S*]. IR: 3061, 3039, 2998, 2935, 2908, 1746, 1601, 1506, 1449, 1421, 1372, 1344, 1264, 1182, 1086, 1026, 970, 918, 751 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H: 1.02 (t, $J = 7.2$ Hz, 3H, CH_2CH_3), 1.61 (dd, $J = 4.9$, 8.1 Hz, 1H, C*H*H), 2.18 (dd, $J = 5.9$, 4.9 Hz, 1H, CH*H*), 2.55 (dd, $J = 8.1$, 5.9 Hz, 1H, CH), 4.03–4.85 (m, 2H, CH_2Me), 7.16–7.40 (m, 10H, PhH). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C: 20.9, 28.8, 41.2, 126.9, 127.3, 127.9, 128.7, 128.8, 129.9, 144.8, 176.8. MS (FAB): 266 (M, 50%), 192 (100%), 164,120, 106, 91, 77, 59. Anal. calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.37; H, 6.69.

Ethyl *trans*-2-phenylcyclopropane-1-carboxylate. Colorless oil. GC-column CB1, helium 1.2 mL/min^{-1}. $t_R = 34.9$ min (1*S*, 2*R*), $t_R = 38.0$ min (1*R*, 2*S*), $t_R = 39.1$ min (1*R*, 2*R*), $t_R = 40.2$ min (1*S*, 2*S*). IR: 3031, 2984, 2935, 2910, 1899, 1726, 1498, 1452, 1407, 1395, 1328, 1270, 1220, 1188, 1095, 1046, 1015, 950, 857, 819, 789, 738, 468 cm^{-1}. ^{1}H NMR (300 MHz,

$CDCl_3$), δ_H: 1.30 (t, $J = 7.5$ Hz, 3H, CH_3), 1.33 (ddd, $J = 4.5$, 6.5, 8.5 Hz, 1H, C*H*H), 1.60 (ddd, $J = 4.5$, 5.4, 9.1 Hz, 1H, CH*H*), 1.91 (ddd, $J = 4.2$, 5.4, 9.1 Hz, 1H, CH), 2.53 (ddd, $J = 4.2$, 6.5, 9.1 Hz, 1H), 4.17 (q, $J = 7.5$ Hz, CH_2Me), 7.11–7.32 (m, 5H, PhH). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C: 11.5, 14.5, 22.2, 25.3, 60.5, 127.1, 128.3, 129.8, 136.9, 172.3. HRMS (EI), calcd. for $C_{12}H_{15}O_2$ (M + H): 191.1072; found: 191.1075.

Selected data for **3a**, (−)-2,5-bis[4′(*R*)-ethyloxazolin-2′-yl]thiophene. Mp = 89–90°C. $[\alpha]_D^{22} = -94.8°$ (c 1.00, CH_2Cl_2). IR: 2966, 2931, 2896, 1644, 1461, 1361, 1293, 1039, 1011, 934, 842 cm^{-1}. ^1H NMR ($CDCl_3$), δ_H: 0.98 (t, $J = 7.4$ Hz, 6H, 2 × CH_3), 1.61–1.71 (m, 4H, 2 × CH_2), 4.05 (dd, $J = 7.7$, 8.0 Hz, 2H, 2 × OC*H*H), 4.48 (dd, $J = 7.7$, 8.0 Hz, 2H, 2 × OCH*H*), 4.18–4.30 (m, 2H, 2 × NCH), 7.54 (s, 2H, thiophene-H). ^{13}C NMR ($CDCl_3$), δ_c: 9.83, 26.4, 66.3, 72.6, 130.1, 133.6, 158.6; MS (FAB): 279 (M + 1, 100%), 249, 208, 195, 111. Anal. calcd. for $C_{14}H_{18}N_2O_2S$: C, 59.68; H, 6.44; N, 9.94. Found: C, 59.80; H, 6.56; N, 10.02.

3b, (−)-2,5-bis[4′(*S*)-isopropylaxazolin-2′-yl]thiophene. Mp = 66–68°C. $[\alpha]_D^{20} = -29.5°$ (c 0.36, acetone). IR: 2958, 2902, 2871, 1645, 1524, 1362, 1310, 1250, 1043, 1010, 948, 828 cm^{-1}; ^1H NMR ($CDCl_3$),δ_H: 0.92 (d, $J = 7.0$ Hz, 6H, 2 × CH_3), 1.13 (d, $J = 7.0$ Hz, 6H, 2 × CH_3), 1.82–1.89 (m, 2H, $CHMe_2$), 4.10 (dd, $J = 9.0$, 15.0 Hz, 2H, 2 × OC*H*H), 4.14 (dd, $J = 8.0$, 15.5 Hz, 2H, 2 × OH*H*), 4.41 (dd, $J = 8.0$, 9.0 Hz, 2H, 2 × NCH), 7.56 (s, 2H, thiophene-H). ^{13}C NMR,δ_C: 18.09, 18.83, 32.76, 70.74, 72.80, 130.24, 133.79, 158.59; MS (FAB): 307 (M + 1, 100%), 263, 221, 151, 111. Anal. calcd. for $C_{16}H_{22}N_2O_2S$: C, 62.72, H, 7.26; N, 9.14; S, 10.47; Found: C, 62.85; H, 7.52; N, 8.99; S, 10.20.

3c, (−)-2,5-bis[4′-(*R*)-phenyloxozolin-2′-yl]thiophene. Mp: 128–131°C; $[\alpha]_D^{26} = -57.3°$(c 0.20, CH_2Cl_2); IR: 3089, 3058, 3032, 2965, 2926, 2900, 1642, 1553, 1476, 1452, 1359, 1303, 1274, 1240, 1048, 1028, 934, 817, 698, 538 cm^{-1}. ^1H NMR ($CDCl_3$), δ_H: 4.32 (dd, $J = 8.0$, 8.5 Hz, 2H, 2 × NCH), 4.81 (dd, $J = 8.5$, 10.0 Hz, 2H, OC*H*H), 5.40 (dd, $J = 8.0$, 9.5 Hz, 2H, OCH*H*), 7.28–7.38 (m, 10H, PhH), 7.67 (s, 2H, thiophene-H). ^{13}C NMR, δ_C: 70.33, 75.36, 126.72, 127.77, 128.80, 130.83, 133.80, 141.75, 159.87; MS (FAB): 375 (M + 1, 58%), 256, 229, 165, 149, 52 (100%). Anal. calcd. for $C_{22}H_{18}N_2O_2S$: C, 70.57; H, 4.84; N, 7.48. Found: C, 70.21; H, 5.03; N, 7.24.

3d, (+)-2,5-bis[4′-(*S*)-terebutyloxazolin-2′-yl]thiophene. Mp: 119–122°C, $[\alpha]_D^{20} = +5.44°$(c 0.55, acetone); IR: 3053, 3026, 2970, 2901, 2853, 1650, 1602, 1477, 1451, 1032, 1008, 949, 819, 696 cm^{-1}. ^1H NMR ($CDCl_3$), δ_H: 0.97 (s, 18H, 2 × $C(CH_3)_3$), 4.03 (dd, $J = 8.0$, 10.0 Hz, 2H, 2 × O*H*H), 4.23 (dd, $J = 8.0$, 8.5 Hz, 2H, 2 × NCH), 4.34 (dd, $J = 8.5$, 10.0 Hz, 2H, 2 × OCH*H*), 7.52 (2H, s, thiophene-H). ^{13}C NMR, δ_C: 25.79, 34.05, 53.79, 69.25, 129.91, 133.80, 158.39; MS (FAB): 335 (M + 1, 100%), 277, 223, 221, 179, 165, 95, 69. Anal. calcd. for $C_{18}H_{24}N_2O_2S$: C, 64.64; H, 7.83; N, 8.37; S, 9.58. Found: C, 64.97; H, 8.08; N, 8.14; S, 9.13.

X-Ray Crystallography

X-ray crystallographic data for **3a** was deposited with Cambridge Crystallographic Data Center, No. CCDC-232494. These data can be obtained free of charge via web, www.ccdc.cam.ac.uk/conts/retrieving.html; e-mail, deposit@ccdc.cam.ac.uk; or mail, the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK. Empirical formula: $C_7H_9NOS_{0.50}$. Formula weight: 139.18. Temperature: 110(2) K. Wavelength: 0.71073 Å. Crystal system: Monoclinic. Space group: C2. Unit cell dimensions: a = 15.010 (2) Å, $\alpha = 90^\circ$; b = 6.3193 (9) Å, $\beta = 107.126\ (2)^\circ$; c = 7.6881 (11) Å, $\gamma = 90^\circ$. Volume: 696.93 (17) $Å^3$. Z: 4. Density (calculated): 1.326 mg/m^3. Absorption coefficient: 0.232 mm^{-1}. F(000): 296 Crystal size: 0.93 × 0.60 × 0.14 mm^3. Theta range for data collection: 2.84 to 28.23°. Index ranges: $-18 \le h \le 19$, $-7 \le k \le 8$, $-9 \le l \le 10$. Reflections collected: 2165. Independent reflections: 1367 [R(int) = 0.0120]. Completeness to theta = 28.23°: 92.1%. Absorption correction: SADABS. Refinement method: Full-matrix least-squares on F^2. Data/restraints/parameters: 1367/1/89. Goodness of fit on F^2: 1.049. Final R indices [I > 2sigma(I)]: R1 = 0.0290, wR2 = 0.0734. R indices (all data): R1 = 0.0292, wR2 = 0.0737. Absolute structure parameter: 0.00 (8). Extinction coefficient: 0.0029 (16). Largest diff. peak and hole: 0.226 and −0.196 e.Å.

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