Synthesis of Chiral 2,5-Bis(oxazolinyl)thiophenes and Their Application as Chiral Shift Reagents for 1,1′-Bi-2-naphthol

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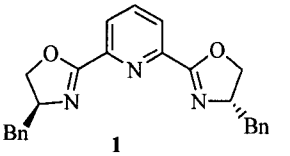
A series of C_2-symmetrical chiral 2,5-bis(4′-alkyloxazolin-2-yl) thiophenes (thiobox) have been synthesized from thiophene-2, 5-dicarboxylic acid by sequential amidation with a chiral ethanolamine, conversion of hydroxyl to chloro group, and base-promoted oxazoline ring formation. As demonstrated by (−)-2, 5-bis[4′-(*S*)-isopropyloxazolin-2′-yl] thiophene, these thiobox systems exhibited remarkable chirality recognition of 1,1′-bi-2-naphthol giving rise to pronounced shifts in the ^{1}H NMR signals of the latter axial chiral compound at the positions of C-3, C-4, C-5, and C-8.

Keywords C_2-symmetry, 2,5-bis(oxazolinyl)thiophene, chiral shift reagent

Introduction

In recent years, C_2-symmetrical chiral bisoxazolines have been used extensively in the field of catalytic asymmetric synthesis.[1,2] Since the early nineteen nineties, a variety of metal complexes containing these ligands have been found to be effective catalysts in many impressive enantioselective transformations including carbon-carbon bond formation, aziridation, hydrosilylation, oxidation, and reduction. Methods of preparation of these complexes as well as their synthetic applications have been reviewed.[3-7] While much of the attention of the bisoxazoline systems was placed on the catalytic efficacies of their metal complexes, very little work was directed toward the use of the ligands themselves as chiral shift reagents. To our knowledge, only one report,[8] *i.e.*, by Nishiyama's group, appeared in the literature describing the use of 2,6-bis[(*S*)-4′-benzyloxazolin-2′-yl]pyridine [pybox-(*S*, *S*)bn, **1**] as a chirality-recognizing agent for 1,1′-bi-2-naphthol. The main feature of Nishiyama's finding was that, through differentiative base-acid pairing, pybox-(*S*, *S*)bn was able to separate the phenolic -OH signals in (*R*)- and (*S*)-1,1′-bi-2-naphthol into two distinct peaks. Impressive as the discovery was, we felt that chemical shifts of the -OH signal might at times be interfered by the presence of moisture or acid contaminants in the sample. Far more desirable, therefore, would be a chiral host which is capable of differentiating (*R*)- from (*S*)-1,1′-bi-2-naphthol in such a manner that the resulting molecular complexes will display signals for the naphthalenic protons at different chemical shifts. Described herein is our finding that such an effect is achievable by replacing the pyridine ring in **1** by a thiophene ring and that a series of bis(oxazolinyl)thiophenes represented by **5** in Scheme 1 are useful chiral ^{1}H NMR shift reagents for assessing enantiomeric excess in samples of 1,1′-bi-2-naphthol.



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Results and discussion

The synthetic route to the series of 2,5-bis(4′-alkyloxazolin-2′-yl)thiophenes (**5**) is shown in Scheme 1. The conversion of thiophene-2, 5-dicarboxylic acid

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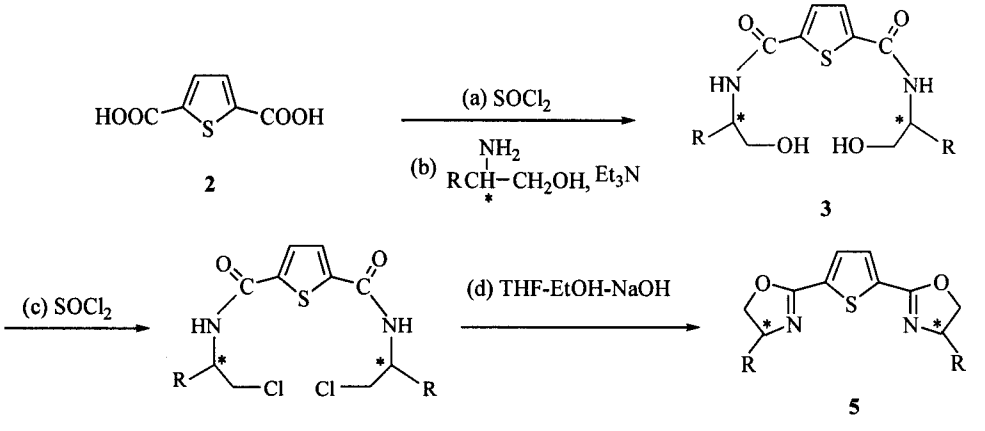
(**2**) into *N*,*N*′-bis[1′-alkyl-2′-hydroxyethyl]-2,5-thiophenediamide **3** was uneventful, and the overall yields ranged reproducibly from 70% to 80%. Dichlorides **4** were obtained from **3** in a routine manner and the crude products were used in the subsequent cyclization step without further purification. A number of cyclization procedures leading to bisoxazoline formation from precursors similar to **4** have been reported in the literature.[5(a),9,10] In our hands, reliable results were the most conveniently obtained by carrying out the cyclization [step (d)] in a suspension of NaOH in THF-EtOH, and the combined yields of steps (c) and (d) were consistently in the range of 37%—50%.

Scheme 1



a, R=Et (*R*); **b**, R=*i*-Pr (*S*); **c**, R=Ph (*R*); **d**, R=Bn (*S*); **e**, R=*t*-Bu (*S*).

Our motivation to install a thiophene ring as the central unit in the bisoxazoline system was driven by the notion that, if compounds such as **5** were to be used as chiral shift reagents for 1,1′-bi-2-naphthol, they would have the advantage that the aromatic proton NMR signal on the symmetrical 2,5-disubstituted thiophene ring appearing at ~7.6 is about 0.2 away from the nearest proton signals of the binaphthol ring, so that any spectral shifts on the part of the latter would be clearly discernible. Indeed, addition of slightly more than one equivalent each of **5a**, **5b** or **5d** into (±)-1,1′-bi-2-naphthol in $CDCl_3$ followed by heating at 60℃ for 10 min and re-cooling to rt resulted in a slight but noticeable upfield shift of the aromatic proton signals of the naphthalene ring with the most pronounced effect taking place at C-3, C-4, C-5 and C-8 protons. The change is best illustrated in the ^1H NMR spectrum of (±)-1,1′-bi-2-naphthol and **5b** (1:1.2) as shown in Fig. 1. In comparison with the corresponding spectrum of binaphthol itself (Fig. 2), the added **5b** caused a clear proton signal separation at C-3, C-4, C-5, and C-8, indicating complex formation between **5b** and the individual enantiomer of 1, 1′-bi-2-naphthol. Through differentiative base-acid pairings, the single doublet at 7.97 for the C-4 proton of racemic 1,1′-bi-2-naphthol was split into two doublets with each centering at 7.93 and 7.92 after **5b** had been added. Similarly, in the presence of **5b**, the doublet for the C-5 proton at 7.89 was split into two partially overlapped doublets at 7.88 and 7.84, the doublet for the C-3 proton at 7.38 into two clearly separate doublets at 7.37 and 7.33, and the doublet for the C-8 proton at 7.15 into two partially overlapped doublets at 7.13 and 7.12. Fig. 3 shows the ^1H NMR spectrum of (*R*)-1, 1′-bi-2-naphthol/(*S*)-1, 1′-bi-2-naphthol/**5b** (3:1:excess) in $CDCl_3$. From this spectrum, peak assignment for pairs (*R*)-binaphthol/**5b** and (*S*)-binaphthol/**5b** can easily be made (see Fig. 3). In addition, estimation of *ee*% of the binaphthol sample could be readily made within 5% error.

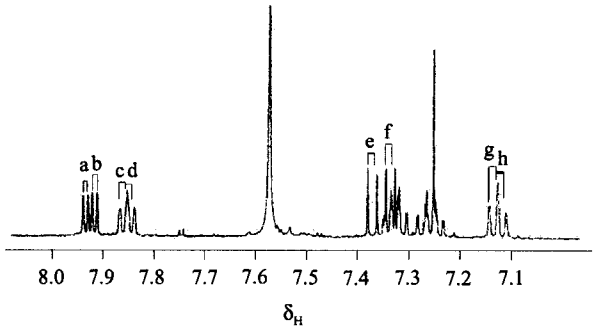


Fig. 1 ^{1}H NMR spectrum of (±)-1,1′-bi-2-naphthol and **5b** [a, $H_{C\text{-}4(R)}$; b, $H_{C\text{-}4(S)}$; c, $H_{C\text{-}5(S)}$; d, $H_{C\text{-}5(R)}$; e, $H_{C\text{-}3(R)}$; f, $H_{C\text{-}3(S)}$; g, $H_{C\text{-}8(S)}$; h, $H_{C\text{-}8(R)}$].

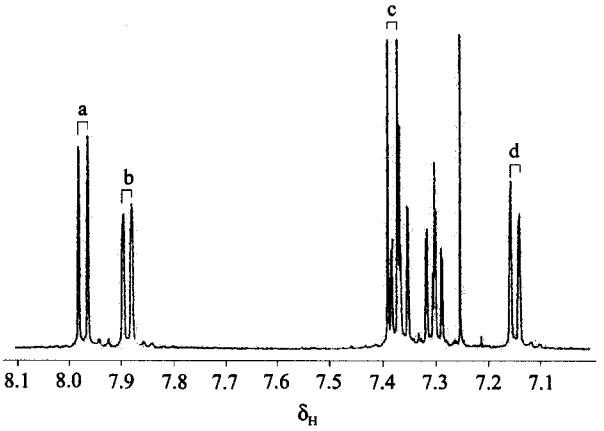


Fig. 2 ^{1}H NMR spectrum of (±)-1,1′-bi-2-naphthol (a, $H_{C\text{-}4}$; b, $H_{C\text{-}5}$; c, $H_{C\text{-}3}$; d, $H_{C\text{-}8}$).

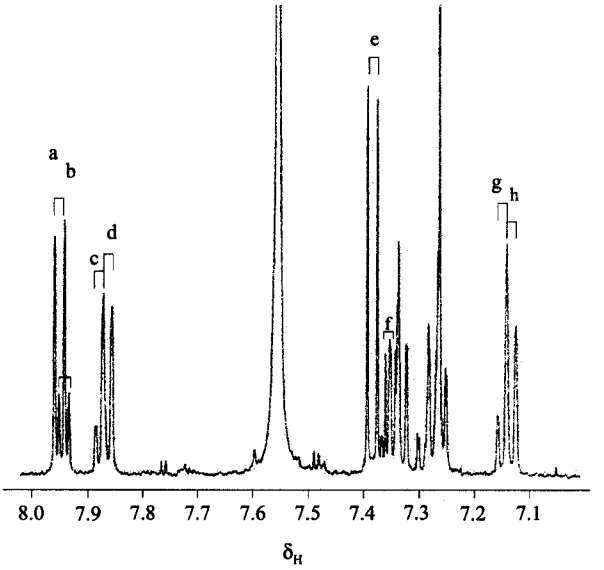


Fig. 3 ^{1}H NMR spectrum of (±)-1,1′-bi-2-naphthol (R:S = 3:1) and **5b** [a, $H_{C\text{-}4(R)}$; b, $H_{C\text{-}4(S)}$; c, $H_{C\text{-}5(S)}$; d, $H_{C\text{-}5(R)}$; e, $H_{C\text{-}3(R)}$; f, $H_{C\text{-}3(S)}$; g, $H_{C\text{-}8(S)}$; h, $H_{C\text{-}8(R)}$].

In summary, a new type of C_2-symmetrical chiral bisoxazoline receptors were discovered capable of chirality recognition of (R)/(S)-1,1′-bi-2-naphthol, which is manifested in the ^{1}H NMR spectral shifts of the signals for the aromatic protons on the individual enantiomeric binaphthol, allowing convenient assessment of the *ee*% in samples of the latter.

Experimental

All melting points were determined on Thiele apparatus and uncorrected. ^{1}H and ^{13}C NMR spectra were measured on an INOVA 500NB NMR spectrometer at 500 MHz, using $CDCl_3$, CD_3OD or CD_3COCD_3 as solvent and TMS as internal standard. Optical rotation values were measured with a Perkin-Elmer 241 polarimeter in a 10 cm cell at 20℃. Elemental analyses were carried out on an Elementar Vario EL elemental analyzer. IR spectra were recorded on an EQUINOX 55-A590/3F instrument.

Preparation of N,N′-bis(1′-alkyl-2′-hydroxyethyl)-2,5-thiophenediamides (**3**)

Thiophene-2,5-dicarboxylic acid (**2**, 17.2 g, 0.1 mol) was heated with $SOCl_2$ (50 mL) and 3 drops of DMF at reflux temperature for 6 h. Excess $SOCl_2$ was then removed under reduced pressure to give the corresponding crude acid chloride. To a solution of a chiral ethanolamine (24 mmol) and 5 mL of triethylamine in 25 mL of CH_2Cl_2 was slowly added a solution of the crude acid chloride (2.13 g, 10 mmol) in 10 mL of CH_2Cl_2 at 0℃, and the solution was stirred for 3 h at 0℃ and 3 h at rt. After solvent removal the residue was poured into 50 mL of water. Upon standing at rt for 2 h the precipitate was collected by filtration, dried, and recrystallized from acetone-petroleum ether(60—90℃) (8:2), or purified by silica gel column chromatography with acetone-petroleum ether(60—90℃) (7:3) as eluent. Pure products **3** were obtained as white solids.

(−)-*N,N′-Bis*[1′(*R*)-*ethyl-2′-hydroxyethyl*]-2,5-*thiophenediamide* (**3a**) Using the general procedure above **3a** (2.29 g, 73%) was obtained. mp: 200—202℃. $[\alpha]_D^{20}$ = −52.53°(*c* 1.00, MeOH). IR ν: 3395, 3303, 2966, 2931, 2875, 1679, 1644, 1539,

842 cm^{-1}. ^1H NMR δ_H(CD_3COCD_3): 0.85 (t, J = 7.4 Hz, 6H, 2 × CH_3), 1.40—1.70 (m, 4H, 2 × CH_2Me), 3.30—3.46 (m, 2H, 2 × NCH), 3.66—3.96 (m, 4H, 2 × OCH_2), 4.66 (s, 2H, 2 × OH), 7.76 (s, 2H, thiophene-H), 8.14 (d, J = 7.5 Hz, 2H, NH). MS m/z(%, FAB): 314 (M + 1, 100), 283, 226, 90. Anal. $C_{14}H_{22}O_2N_4S$. Calcd: C 53.48, H 7.06, N 8.92. Found: C 53.05, H 6.88, N 9.26.

(−)-*N,N'-Bis*[1'(*S*)-*isopropyl-2'-hydroxyethyl*]-2,5-*thiophenediamide* (**3b**) Using the general procedure above **3b** (2.43 g, 71%) was obtained. mp: 195—197 ℃. $[\alpha]_D^{20}$ = −24.94°(*c* 0.28, MeOH). IR ν: 3296, 3254, 3075, 2959, 2931, 1987, 1616, 1553, 1518, 1461, 1321, 1025, 744 cm^{-1}. ^1H NMR δ_H(CD_3OD): 0.89—1.01 (m, 12H, 4 × CH_3), 1.91—2.00 (m, 2H, 2 × $CHMe_2$), 3.67—3.75 (m, 4H, 2 × OCH_2), 3.83—3.89 (m, 2H, 2 × NCH), 4.89 (s, 2H, OH), 7.72 (s, 2H, thiophene-H). MS m/z (%, FAB): 343 (M + 1, 100), 325, 279, 240, 213, 165, 111. Anal. $C_{16}H_{26}O_4N_2S$. Calcd: C 56.12, H 7.65, N 8.18; Found: C 55.78, H 7.72, N 8.06.

(+)-*N,N'-Bis*[1'(*R*)-*phenyl-2'-hydroxyethyl*]-2,5-*thiophenediamide* (**3c**) Using the general procedure above **3c** (2.87 g, 70%) was obtained. mp: 201—204 ℃. $[\alpha]_D^{20}$ = +42.25°(*c* 0.14, MeOH). IR ν: 3332, 3083, 3029, 2952, 2875, 1630, 1539, 1518, 1454, 1285, 1039, 744 cm^{-1}. ^1H NMR δ_H (CD_3COCD_3): 3.71 (s, 2H, 2 × OH), 3.86 (d, J = 6.5 Hz, 4H, 2 × OCH_2), 5.19—5.21 (dd, J = 6.5, 7.5 Hz, 2H, 2 × CH), 7.22—7.45 (m, 10H, PhH), 7.76 (s, 2H, thiophene-H), 7.98 (d, J = 7.0 Hz, 2H, 2 × NH). MS m/z (%, FAB): 411 (M + 1, 3), 341, 274, 219. Anal. $C_{22}H_{22}O_4N_2S$. Calcd: C 64.37, H 5.40, N 6.82; Found: C 64.16, H 5.28, N 6.95.

(−)-*N,N'-Bis*[1'(*S*)-*benzyl-2'-hydroxyethyl*]-2,5-*thiophenediamide* (**3d**) Using the general procedure above **3d** (3.06 g, 74%) was obtained. mp: 188—191 ℃. $[\alpha]_D^{20}$ = −144.73°(*c* 0.14, acetone). IR ν: 3332, 3083, 3664, 3029, 2938, 2889, 1630, 1545, 1510, 1454, 1293, 1138, 1032, 751 cm^{-1}. ^1H NMR δ_H(CD_3COCD_3): 2.89—3.03 (m, 4H, 2 × CH_2Ph), 3.63 (d, J = 5.0 Hz, 4H, 2 × OCH_2), 3.72 (s, 2H, 2 × OH), 4.27—4.30 (m, 2H, 2 × CH), 7.15—7.30 (m, 10H, PhH), 7.49 (d, J = 8.0 Hz, 2H, 2 × NH), 7.59 (s, 2H, thiophene-H). MS m/z(%, FAB): 439 (M + 1, 70), 347, 288, 219, 194, 91. Anal. $C_{24}H_{26}O_4N_2S$. Calcd: C 65.73, H 7.98, N 6.39; Found: C 65.44, H 7.82, N 6.55.

(+)-*N,N'-Bis*[1'(*S*)-*tert-butyl-2'-hydroxyethyl*]-2,5-*thiophenediamide* (**3e**) Using the general procedure above **3e** (2.33 g, 63%) was obtained. mp: 169—171 ℃. $[\alpha]_D^{20}$ = +53.66° (*c* 0.17, acetone). IR ν: 3393, 3089, 2962, 2875, 1637, 1542, 1512, 1474, 1348, 1282, 1250, 1092, 1049, 823, 745 cm^{-1}. ^1H NMR δ_H(CD_3COCD_3): 0.86—1.00 [m, 18H, 2 × C(CH_3)$_3$], 3.63—3.67 (m, 2H, 2 × OCH**H**), 3.75—3.83 (m, 2H, 2 × OCH**H**), 4.00 (br, 2H, 2 × OH), 4.32—4.39 (m, 2H, NCH), 7.22 (d, J = 7.5 Hz, 2H, NH), 7.69 (s, 2H, thiophene-H). MS m/z(%, FAB): 371 (M + 1, 24), 254, 236, 111. Anal. $C_{18}H_{30}O_4N_2S$. Calcd: C 58.53, H 8.16, N 7.65; Found: C 58.72, H 8.31, N 7.37.

Preparation of 2,5-*bis*(4'-*alkyloxazolin-2'-yl*)*thiophene* (**5**)

A mixture of 2,5-thiophene diamides **3** (6 mmol) and $SOCl_2$ (15 mL) was refluxed for 5 h. After removal of $SOCl_2$, ice-water was added to the residue, and the resulting mixture was extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over Na_2SO_4, and evaporated to give the crude dichlorides **4**. Without further purification, a solution of **4** (3 mmol) in 20 mL of THF was added to a suspension of 6 g of NaOH in 20 mL of EtOH, and the mixture was stirred at 70℃ for 2 h under a N_2 atmosphere. After filtration, the residue was washed with THF and the filtrate concentrated. The residue was purified by silica gel column chromatography with acetone-petroleum ether (60—90 ℃) (1:50) as eluent to give bis(oxazolinyl)thiophene **5** as white or pale-yellow solid.

(−)-2,5-*Bis*[4'(*R*)-*ethyloxazolin-2'-yl*]*thiophene* (**5a**) Using the general procedure above **5a** (0.42 g, 50%) was obtained. mp: 89—90 ℃. $[\alpha]_D^{20}$ = −94.80°(*c* 1.00, CH_2Cl_2). IR ν: 2966, 2931, 2896, 1644, 1461, 1361, 1293, 1039, 1011, 934, 842 cm^{-1}. ^1H NMR δ_H($CDCl_3$): 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 × OCH**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, ArH). ^{13}C NMR δ_C ($CDCl_3$): 9.83, 26.4, 66.3, 72.6, 130.1, 133.6, 158.6. MS m/z (%, FAB): 279 (M + 1, 100),

249, 208, 195, 111. Anal. $C_{14}H_{18}N_2O_2S$. Calcd: C 59.68, H 6.44, N 9.94; Found: C 59.80, H 6.56, N 10.02.

(−)-2,5-*Bis*[4′(*S*)-*isopropyloxazolin*-2′-*yl*]*thiophene* (**5b**) Using the general procedure above **5b** (0.40 g, 43%) was obtained. mp: 66—68 ℃. $[\alpha]_D^{20} = -29.05°$ (*c* 0.36, acetone). IR ν: 2958, 2902, 2871, 1645, 1524, 1362, 1310, 1250, 1043, 1010, 948, 828 cm^{-1}. ^1H NMR δ_H($CDCl_3$): 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, 2 × $CHMe_2$), 4.10 (dd, *J* = 9.0, 15.0 Hz, 2H, 2 × OCH**H**), 4.14 (dd, *J* = 8.0, 15.5 Hz, 2H, 2 × OC**H**H), 4.41 (dd, *J* = 8.0, 9.0 Hz, 2H, 2 × NCH), 7.56 (s, 2H, ArH); ^{13}C NMR δ_C ($CDCl_3$): 18.09, 18.83, 32.76, 70.74, 72.80, 130.24, 133.79, 158.59. MS *m*/*z* (%, FAB): 307 (M + 1, 100), 263, 221, 151, 111. Anal. $C_{16}H_{22}N_2O_2S$. Calcd: 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.

(−)-2,5-*Bis*[4′(*R*)-*phenyloxozolin*-2′-*yl*]*thiophene* (**5c**) Using the general procedure above **5c** (0.42 g, 37%) was obtained. mp: 128—131 ℃; $[\alpha]_D^{26} = -57.30°$ (*c* 0.20, CH_2Cl_2). IR ν: 3089, 3058, 3032, 2965, 2926, 2900, 1642, 1553, 1476, 1452, 1359, 1303, 1274, 1240, 1048, 1028, 934, 817, 698, 538 cm^{-1}. ^1H NMR δ_H($CDCl_3$): 4.32 (dd, *J* = 8.0, 8.5 Hz, 2H, 2 × NCH), 4.81 (dd, *J* = 8.5, 10.0 Hz, 2H, 2 × OCH**H**), 5.40 (dd, *J* = 8.0, 9.5 Hz, 2H, 2 × OC**H**H), 7.28—7.38 (m, 10H, PhH), 7.67 (s, 2H, thiophene-H); ^{13}C NMR δ_C ($CDCl_3$): 70.33, 75.36, 126.72, 127.77, 128.80, 130.83, 133.80, 141.75, 159.87. MS *m*/*z* (%, FAB): 375 (M + 1, 58), 256, 229, 165, 149, 52 (100). Anal. $C_{22}H_{18}N_2O_2S$. Calcd: C 70.57, H 4.84, N 7.48; Found: C 70.21, H 5.03, N 7.24.

(+)-2,5-*Bis*[4′(*S*)-*benzyloxazolin*-2′-*yl*]*thiophene* (**5d**) Using the general procedure above **5d** (0.49 g, 41%) was obtained. mp: 107—109 ℃. $[\alpha]_D^{20} = +90.60°$ (*c* 0.24, acetone). IR ν: 3053, 3026, 2970, 2901, 2853, 1650, 1602, 1477, 1451, 1032, 1008, 949, 819, 696 cm^{-1}. ^1H NMR δ_H($CDCl_3$): 2.76 (dd, *J* = 8.5, 14.0 Hz, 2H, 2 × C**H**HPh), 3.21 (dd, *J* = 5.0, 14.0 Hz, 2H, 2 × CH**H**Ph), 4.15 (dd, *J* = 7.0, 8.5 Hz, 2H, 2 × OCH**H**), 4.35 (dd, *J* = 8.5, 9.0 Hz, 2H, 2 × OC**H**H), 4.57—4.60 (m, 2H, NCH), 7.21—7.32 (m, 10H, PhH), 7.51 (s, 2H, ArH); ^{13}C NMR δ_C ($CDCl_3$): 41.54, 68.13, 72.35, 126.59, 128.56, 129.30, 130.30, 133.89, 137.61, 159.12. MS *m*/*z* (%, FAB): 403 (M + 1, 100), 311, 270, 257, 220, 176, 154, 107, 91. Anal. $C_{24}H_{22}N_2O_2S$. Calcd: C 71.62, H 5.51, N 6.96, S 7.97; Found: C 71.81, H 5.84, N 6.74, S 7.55.

(+)-2,5-*Bis*[4′(*S*)-*tert*-*butyloxazolin*-2′-*yl*]-*thiophene* (**5e**) Using the general procedure above **5e** (0.31 g, 31%) was obtained. mp: 119—122 ℃. $[\alpha]_D^{20} = +5.44°$ (*c* 0.55, acetone). IR ν: 2958, 2903, 2875, 1645, 1534, 1479, 1362, 1305, 1252, 1212, 1066, 1014, 949, 831, 748, 675 cm^{-1}. ^1H NMR δ_H($CDCl_3$): 0.97 [s, 18H, 2 × C(CH_3)$_3$], 4.03 (dd, *J* = 7.5, 10 Hz, 2H, 2 × OCH**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 (s, 2H, ArH); ^{13}C NMR δ_C($CDCl_3$): 25.79, 34.05, 53.79, 69.25, 129.91, 133.80, 158.39. MS *m*/*z* (%, FAB): 335 (M + 1, 100), 277, 223, 221, 179, 165, 95, 69. Anal. $C_{18}H_{24}N_2O_2S$. Calcd: 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.

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