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Novel π-expanded chrysene-based axially chiral molecules: 1,1′-bichrysene-2,2′-diols and thiophene analogs

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Abstract

1,1′-Bichrysene-2,2′-diol and its thiophene analogs, 6,6′-biphenanthro-[1,2-*b*]thiophene-7,7′-diols, as a series of novel π-expanded chrysene-/phenanthro[1,2-*b*]thiophene-based axially chiral molecules are synthesized from 1,1′-bi-2-naphthols with key steps including a Suzuki coupling, a Wittig reaction, and acid-mediated cyclization.

Keywords

π-expanded, chrysene, oxidative coupling, synthesis, thiophene

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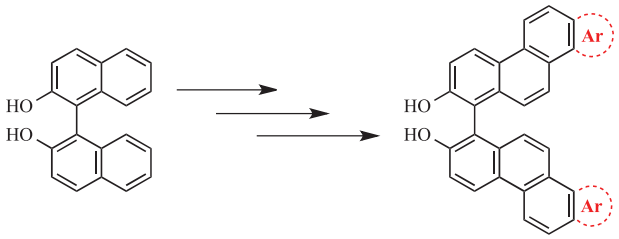

Ar = phenyl or thienyl

(ChemBioDraw version 13.0)

Introduction

Due to the superior electronic and optical properties, 1,1′-bi-2-naphthol (BINOL) and other axially binaphthol-related chiral molecules have recently been widely studied.[1–3] The functionalities of BINOL and their derivatives can be tuned through the expansion of their π-system and by chemical modifications at specific sites. Among them, the expansion of the π-system is the most common method to date.[4] Large π-extended polycyclic aromatic hydrocarbons (PAHs) such as anthracene,[5] phenanthrene,[6] pyrene,[7] and naphtho[2,3-*b*]furans,[8] as replacements of the naphthalene rings of BINOL, could increase the rotational isomeric space through larger dihedral angles (Figure 1). Other advantages of such replacements to be addressed are reduced molecular energy and stable molecular structure, higher luminescence efficiency and extended fluorescence lifetime, and so on.[9] These advantages lead to numerous applications of PAH-type BINOLs in the areas of circularly polarized luminescence (CPL) spectroscopy and as starting materials for the preparation of graphene nanoribbons[10] and complex polyarene architectures.[11]

Thiophene and its analogs are often regarded as electron-donating moieties in materials chemistry.[12] It was found that the electron transfer among molecules and the antioxidative capacity of compounds could both be improved by fusing thiophene onto PAHs.[13]

Results and discussion

As a part of our ongoing research on heterocycle-fused binaphthalenes and binaphthols (BINOLs), we have extended our interest on BINOL analogs using chrysene and phenanthro[1,2-*b*]thiophene as replacements for the naphthalene motifs. It was reported that pyrene-based BINOLs can lead to a broader application of π-expanded

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axially chiral molecules.[7] Generally, racemic BINOLs and their chiral analogs can be synthesized by the oxidation of β-naphthol with often-used catalysts such as $FeCl_3$ or Cu(OH)Cl·TMEDA.[14] In our case, 2-chrysenol and related analogs were very difficult to prepare through simple synthetic strategies, and therefore we thought that it would be possible to use commercial BINOLs as starting materials through well-defined and facile synthetic protocols in order to prepare the target molecules (Scheme 1). BINOL was functionalized as the dibromide in order to avoid any uncertainty in subsequent steps. 6,6′-Dibromo-2,2′-dimethoxy-1,1′-binaphthalenes [(*S*)-/(*R*)-/(±)-**2**] were thus obtained by bromination of (*S*)-/(*R*)-/(±)-BINOL, followed by protection of the hydroxy groups with MeI in the presence of K_2CO_3 in acetone. The palladium-catalyzed borylation of (*S*)-/(*R*)-/(±)-**2** with bis(pinacolato) diboron was employed to afford the key intermediates, 6,6′-diboro-2,2′-dimethoxy-1,1′-binaphthalenes [(*S*)-/(*R*)-/(±)-**3**].

With (*S*)-/(*R*)-/(±)-**3** in hand, we initially attempted to prepare (*S*)-/(*R*)-/(±)-**4** via Suzuki coupling with 2-bromobenzaldehyde at 90 °C in a mixture of dioxane and H_2O (2:1). The reactions proceeded quite smoothly with isolated yields of (*S*)-/(*R*)-/(±)-**4** up to 73%. When 2-bromo-3-thiophenecarboxaldehyde was used, products (*S*)-/(*R*)-/(±)-**8** were obtained in yields ranging from 70% to 92%.

Next, the Wittig olefinations were applied to (*S*)-/(*R*)-/(±)-**4** or -**8** with (methoxymethyl)triphenylphosphonium chloride as the ylide precursor to construct (*S*)-/(*R*)-/(±)-**5** (E/Z ca. 3:1 according to ^{1}H NMR from crude mixture) and (S)-/(R)-/(±)-**9** (E/Z ca. 4:1 according to ^{1}H NMR from crude mixture), which were treated with TfOH to form (*S*)-/(*R*)-/(±)-**6** and -**10** via dehydrative cycloaromatization. Finally, deprotection with BBr_3 was accomplished in dichloromethane at low temperature to afford (*S*)-/(*R*)-/(±)-1,1′-bichrysene-2,2′-diol [(*S*)-/(*R*)-/(±)-**7**] and (*S*)-/(*R*)-/(±)-6,6′-biphenanthro[1,2-*b*]thiophene-7,7′-diol [(*S*)-/(*R*)-/(±)-**11**].

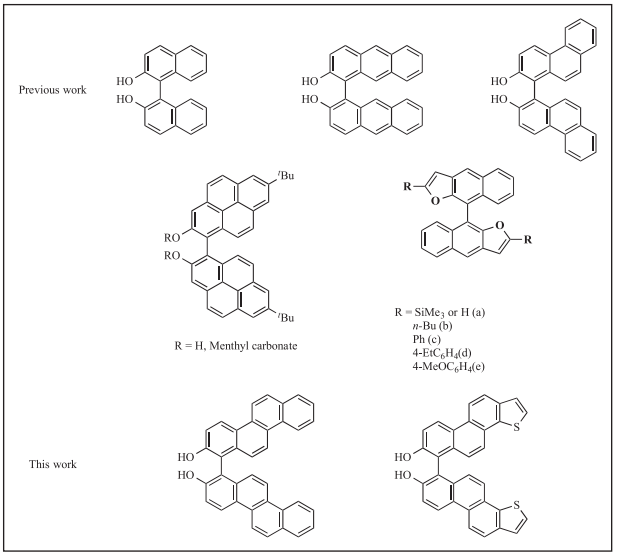
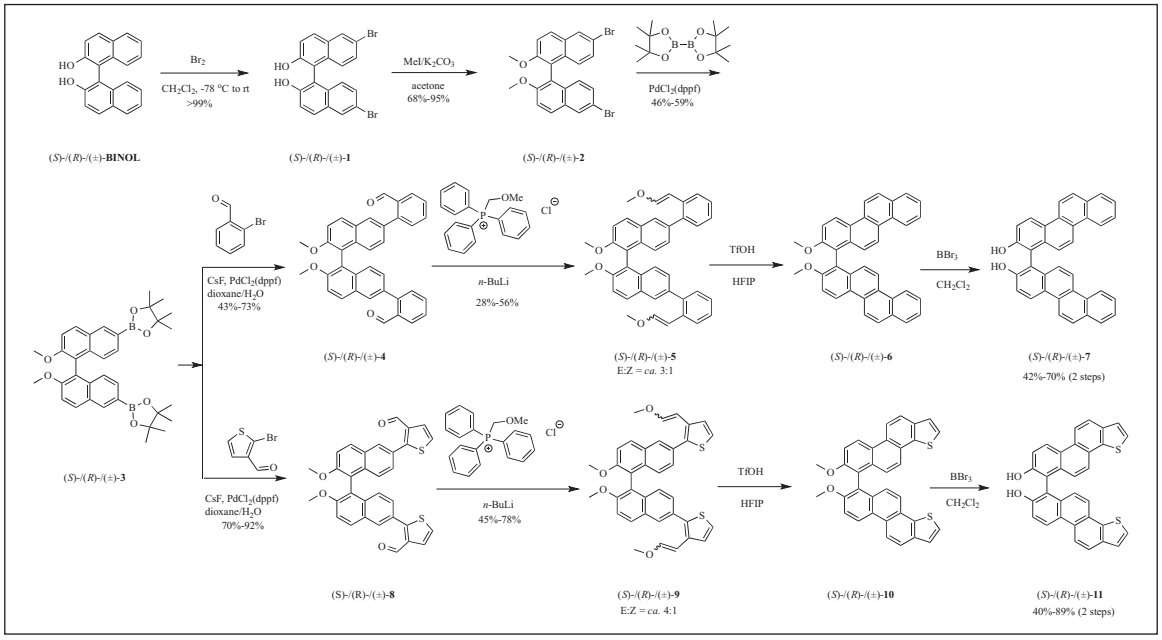


Figure 1. Comparison of axially chiral molecular structures based on anthracene,[5] phenanthrene,[6] pyrene,[7] and naphtho[2,3-*b*]furans[8] and those of our work.

Conclusion

In conclusion, a facile and atom-economic method for the synthesis of 1,1′-bichrysene-2,2′-diol and 6,6′-biphenanthro-[1,2-*b*]-thiophene-7,7′-diols has been presented. This method should also be applicable for the syntheses of different polycyclic aromatics such as polyarenes and nanographenes. Furthermore, the target molecules could contribute to molecular recognition and the further exploration of new π-expanded axially chiral molecules. Further



Scheme 1. Synthetic approach toward the target molecules.

studies on applications of the described molecules are now in progress in our laboratory.

Experimental

All chemicals were commercially available as analytical or chemical grade. Solvents were purified via standard methods before use. All reactions sensitive to air or water were conducted under an Ar or N_2 atmosphere. Reactions were monitored by thin-layer chromatography (TLC). Silica gel (Anhui Liangchen GF254) for column chromatography was 200–300 mesh. ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were measured on a Bruker DRx500 NMR spectrometer (^{1}H NMR: 500 MHz, ^{13}C NMR: 125 MHz). Low-resolution mass spectra were recorded on an Agilent 5973N or a Waters GCT Premier spectrometer (mass spectrometry electron ionization (MS EI)). High-resolution mass spectra were obtained using a Bruker MicroTof II mass spectrometer (high-resolution mass spectrometry electrospray ionization (HRMS ESI)). Melting points were measured on an X-4 micrographic melting point apparatus.

Starting materials

(*S*)-/(*R*)-/(±)-6,6′-dibromo-[1,1′-binaphthalene]-2,2′-diol [(*S*)-/(*R*)-/(±)-**1**], 6,6′-dibromo-2,2′-dimethoxy-1,1′-binaphthalene [(*S*)-/(*R*)-/(±)-**2**], and 2,2′-(2,2′-dimethoxy-[1,1′-binaphthalene]-6,6′-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) [(*S*)-/(*R*)-/(±)-**3**] were prepared according to previous work (see Supplemental Material for details).[15–17]

(*S*)-/(*R*)-/(±)-2,2′-(2,2′-dimethoxy-[1,1′-binaphthalene]-6,6′-diyl)dibenzaldehyde [(*S*)-**4**/(*R*)-**4**/(±)-**4**]

A 250-mL three-neck bottom flask was charged with (*S*)-**3**/(*R*)-**3**/(±)-**3** (4 g, 7.06 mmol, 1.0 equiv.), 2-bromobenzaldehyde (2.9 g, 15.52 mmol, 2.2 equiv.), CsF (6.45 g, 42.44 mmol, 6.0 equiv.), and dioxane/H_2O (180 mL, 2:1). The flask was filled with argon and evacuated. This procedure was repeated three times. Then Pd(dppf)Cl_2 (258.5 mg, 0.35 mmol, 0.05 equiv.) was added and the solution was heated under argon at 90 °C for 8–10 h. After cooling to room temperature (rt), the mixture was extracted with EtOAc (150 mL). The organic layer was washed with brine (3 × 50 mL) and dried over anhydrous $MgSO_4$. After removing the solvent, the crude residue was purified by silica gel chromatography (hexane/EtOAc, 15:1) to furnish the product as a white solid.

(S)-**4**: White solid (1.85 g, 50%); R_f = 0.47 (PE/EtOAc, 3:1); m.p. 134.6–136.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.10 (s, 2H), 8.09–8.06 (m, 4H), 7.89 (d, *J* = 1.7 Hz, 2H), 7.68 (td, *J* = 7.5, 1.4 Hz, 2H), 7.61–7.50 (m, 6H), 7.33 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.27 (d, *J* = 9.1 Hz, 2H), 3.87 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.77, 155.64, 146.07, 133.90, 133.54, 133.38, 132.76, 130.98, 129.96, 129.76, 128.71, 128.38, 127.61, 127.59, 125.47, 119.10, 114.87, 56.87; MS (EI): *m*/*z* $[M]^+$ calcd for $C_{36}H_{26}O_4$: 522.18; found: 522.

(R)-**4**: White solid (1.59 g, 43%); R_f = 0.47 (PE/EtOAc, 3:1); m.p. 138.1–142.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.10 (s, 2H), 8.09–8.05 (m, 4H), 7.89 (d, *J* = 1.7 Hz, 2H), 7.67 (td, *J* = 7.5, 1.5 Hz, 2H), 7.60–7.50 (m, 6H), 7.33 (dd, *J* = 8.7, 1.9 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.77, 155.64, 146.07, 133.89, 133.54, 133.37, 132.75, 130.98, 129.96, 129.76, 128.71, 128.38, 127.61, 127.59, 125.46, 119.09, 114.87, 56.86.

(±)-**4**: White solid (2.68 g, 73%); R_f = 0.47 (PE/EtOAc, 3:1); m.p. 233.3–236.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.10 (s, 2H), 8.10–8.05 (m, 4H), 7.89 (d, *J* = 1.9 Hz, 2H), 7.68 (td, *J* = 7.5, 1.5 Hz, 2H), 7.61–7.50 (m, 6H), 7.33 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.76, 155.65, 146.07, 133.90, 133.54, 133.38, 132.76, 130.98, 129.96, 129.76, 128.71, 128.38, 127.60, 127.60, 125.47, 119.10, 114.87, 56.87.

(*S*)-/(*R*)-/(±)-2,2′-dimethoxy-[6,6′-bis(2-methoxyethenyl)phenyl]-1,1′-binaphthalene [(*S*)-**5**/(*R*)-**5**/(±)-**5**]

A mixture of $Ph_3P(CH_2OMe)$·Cl (3.61 g, 10.52 mmol, 5.0 equiv.) and *n*-BuLi (674.14 mg, 10.52 mmol, 5.0 equiv.) was dissolved in anhydrous tetrahydrofuran (THF; 15 mL) at 0 °C. After stirring at 0 °C for 30 min, a THF (10 mL) solution of (*S*)-**4**/(*R*)-**4**/(±)-**4** (1.10 g, 2.10 mmol, 1.0 equiv.) was added. The mixture was stirred at rt for 2 h and then quenched with water. After removing spare THF, the water layer was extracted with EtOAc (3 × 20 mL). The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent, the crude residue was purified by silica gel column chromatography (hexane/EtOAc 15:1) to give a white solid.

(S)-**5**: White solid (340 mg, 28%); R_f = 0.49 (PE/EtOAc, 3:1); m.p. 89.3–92.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 9.0 Hz, 2H), 7.89 (s, 2H), 7.52 (dd, *J* = 9.0, 1.6 Hz, 2H), 7.44 (d, *J* = 7.4 Hz, 2H), 7.37 (dt, *J* = 7.4, 1.8 Hz, 2H), 7.34–7.30 (m, 4H), 7.27–7.20 (m, 4H), 6.95 (dd, *J* = 12.9, 1.6 Hz, 2H), 5.87 (d, *J* = 12.8 Hz, 2H), 3.85 (s, 6H), 3.52 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.13, 148.91, 139.87, 136.53, 134.29, 132.89, 130.47, 129.63, 129.10, 128.68, 128.37, 127.38, 125.98, 125.04, 124.90, 119.39, 114.43, 104.68, 56.94, 56.54; MS (EI): *m*/*z* $[M]^+$ calcd for $C_{40}H_{34}O_4$: 578.25; found: 578.

(R)-**5**: White solid (683 mg, 56%); R_f = 0.49 (PE/EtOAc, 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 9.0 Hz, 2H), 7.90 (s, 2H), 7.53 (d, *J* = 9.0 Hz, 2H), 7.44 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.37 (dd, *J* = 7.3, 1.8 Hz, 2H), 7.34–7.29 (m, 4H), 7.27–7.21 (m, 4H), 6.95 (d, *J* = 12.9 Hz, 2H), 5.87 (d, *J* = 12.9 Hz, 2H), 3.85 (s, 6H), 3.52 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.13, 148.91, 139.87, 136.53, 134.28, 132.89, 130.47, 129.63, 129.10, 128.68, 128.37, 127.38, 125.98, 125.03, 124.90, 119.39, 114.43, 104.68, 56.94, 56.54.

(±)-**5**: White solid (426 mg, 35%); R_f = 0.49 (PE/EtOAc, 3:1); m.p. 118.2–121.4 °C.

(*S*)-/(*R*)-/(±)-2,2′-dimethoxy-1,1′-bichrysene [(*S*)-**6**/(*R*)-**6**/(±)-**6**]

Trifluoromethane sulfonic acid (31 μL, 0.35 mmol, 0.6 equiv.) was added to a hexafluoroisopropanol (HFIP; 30 mL) solution of the crude mixture of (*S*)-**5**/(*R*)-**5**/(±)-**5** (340 mg, 0.59 mmol, 1.0 equiv.) at rt.[18] After stirring at rt for 2 h, the reaction was quenched with saturated $NaHCO_3$ aqueous solution (pH 9) and then filtered and dried to give the crude product of (*S*)-**6**/(*R*)-**6**/(±)-**6** as a pink solid.

(*S*)-/(*R*)-/(±)-[1,1′-bichrysene]-2,2′-diol [(*S*)-**7**/(*R*)-**7**/(±)-**7**]

The crude product of (*S*)-**6**/(*R*)-**6**/(±)-**6** (0.59 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2, and BBr_3 (2.3 mL, 23.6 mmol, 40.0 equiv.) was slowly added at 0 °C. The mixture was stirred at 0 °C for 1 h and then at rt for 4 h, poured into the water, and then filtered and dried to give a brown solid.

(*S*)-**7**: Brown solid (146 mg, 51%); R_f = 0.46 (PE/EtOAc, 1:1); m.p. > 300 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.56 (s, 2H), 8.93 (dd, *J* = 28.0, 9.3 Hz, 4H), 8.73 (d, *J* = 8.3 Hz, 2H), 8.57 (d, *J* = 9.6 Hz, 2H), 8.09 (dd, *J* = 18.8, 8.5 Hz, 4H), 7.62 (ddd, *J* = 35.6, 18.4, 8.3 Hz, 6H), 7.27 (d, *J* = 9.4 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 154.57, 133.49, 131.59, 130.58, 128.89, 128.84, 127.73, 127.24, 126.45, 125.91, 125.10, 124.91, 124.53, 123.37, 121.96, 118.63, 117.79, 99.98; MS (EI): *m*/*z* $[M]^+$ calcd for $C_{36}H_{22}O_2$: 486.16; found: 486.

(*R*)-**7**: Brown solid (200 mg, 70%); R_f = 0.46 (PE/EtOAc, 1:1); m.p. > 300 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.56 (s, 2H), 8.96 (d, *J* = 9.2 Hz, 2H), 8.90 (d, *J* = 9.2 Hz, 2H), 8.73 (d, *J* = 8.3 Hz, 2H), 8.57 (d, *J* = 9.4 Hz, 2H), 8.11 (d, *J* = 9.1 Hz, 2H), 8.07 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.70–7.59 (m, 4H), 7.57 (d, *J* = 9.1 Hz, 2H), 7.26 (d, *J* = 9.4 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 154.56, 133.49, 131.59, 130.58, 128.89, 128.85, 127.74, 127.24, 126.46, 125.90, 125.09, 124.92, 124.53, 123.37, 121.97, 121.93, 118.63, 117.79; MS (EI): *m*/*z* $[M]^+$ calcd for $C_{36}H_{22}O_2$: 486.16; found: 486.

(±)-**7**: Brown solid (120 mg, 42%); R_f = 0.46 (PE/EtOAc, 1:1); m.p. > 300 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.56 (s, 2H), 8.96 (d, *J* = 9.2 Hz, 2H), 8.90 (d, *J* = 9.2 Hz, 2H), 8.72 (d, *J* = 8.2 Hz, 2H), 8.56 (d, *J* = 9.5 Hz, 2H), 8.11 (d, *J* = 9.2 Hz, 2H), 8.07 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.69–7.60 (m, 4H), 7.57 (d, *J* = 9.1 Hz, 2H), 7.26 (d, *J* = 9.3 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 154.57, 133.49, 131.58, 130.58, 128.89, 128.84, 127.72, 127.24, 126.45, 125.90, 125.10, 124.91, 124.53, 123.36, 121.95, 121.94, 118.63, 117.78; MS (EI): *m*/*z* $[M]^+$ calcd for $C_{36}H_{22}O_2$: 486.16; found: 486.

(*S*)-/(*R*)-/(±)-2,2′-(2,2′-dimethoxy-[1,1′-binaphthalene]-6,6′-diyl)bis(thiophene-3-carbaldehyde) [(*S*)-**8**/(*R*)-**8**/(±)-**8**]

A 250-mL three-neck round-bottom flask was charged with (*S*)-**3**/(*R*)-**3**/(±)-**3** (1.40 g, 2.47 mmol, 1.0 equiv.), 2-bromo-3-thiophenecarboxaldehyde (1.04 g, 5.44 mmol, 2.2 equiv.), CsF (2.25 g, 14.83 mmol, 6.0 equiv.), and dioxane/H_2O (120 mL, 2:1). The flask was filled with argon and evacuated. This procedure was repeated three times. Then Pd(dppf)Cl_2 (90.45 mg, 123.61 μmol, 0.05 equiv.) was added, and the solution was heated under argon at 90 °C for 8–10 h. After cooling to rt, the mixture was extracted with EtOAc. The organic layer was washed with brine (3 × 50 mL) and dried over anhydrous $MgSO_4$. After removing the solvent, the crude residue was purified by silica gel chromatography (hexane/EtOAc, 10:1) to furnish the product as a white solid.

(*S*)-**8**: White solid (1.22 g, 92%); R_f = 0.7 (PE/EtOAc, 1:1); m.p. 137.3–140.1 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.90 (s, 2H), 8.27 (d, *J* = 8.7 Hz, 4H), 7.74 (d, *J* = 9.1 Hz, 2H), 7.69 (dd, *J* = 5.4, 0.8 Hz, 2H), 7.54–7.48 (m, 4H), 7.07 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 185.99, 156.20, 155.74, 136.96, 133.74, 130.97, 130.19, 128.87, 128.34, 127.14, 126.94, 126.54, 125.70, 118.32, 115.55, 56.71; MS (EI): *m*/*z* $[M]^+$ calcd for $C_{32}H_{22}O_4S_2$: 534.10; found: 534.

(*R*)-**8**: White solid (1.20 g, 89%); R_f = 0.7 (PE/EtOAc, 1:1); m.p. 131.7–134.2 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.90 (s, 2H), 8.27 (d, *J* = 9.5 Hz, 4H), 7.74 (d, *J* = 9.1 Hz, 2H), 7.69 (d, *J* = 5.3 Hz, 2H), 7.56–7.48 (m, 4H), 7.07 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 185.99, 156.20, 155.74, 136.96, 133.74, 130.97, 130.19, 128.87, 128.34, 127.14, 126.94, 126.54, 125.70, 118.32, 115.55, 56.71.

(±)-**8**: White solid (0.92 g, 70%); R_f = 0.7 (PE/EtOAc, 1:1); m.p. 138.2–141.3 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.90 (s, 2H), 8.27 (d, *J* = 9.3 Hz, 4H), 7.74 (d, *J* = 9.2 Hz, 2H), 7.69 (d, *J* = 5.3 Hz, 2H), 7.55–7.47 (m, 4H), 7.07 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 186.00, 156.19, 155.75, 136.94, 133.73, 130.97, 130.18, 128.86, 128.32, 127.15, 126.93, 126.53, 125.69, 118.30, 115.55, 56.72.

(*S*)-/(*R*)-/(±)-2,2′-dimethoxy-[6,6′-bis(2-methoxyethenyl)thiophene]-1,1′-binaphthalene [(*S*)-**9**/(*R*)-**9**/(±)-**9**]

A mixture of $Ph_3P(CH_2OMe)\cdot Cl$ (1.64 g, 4.78 mmol, 5.0 equiv.) and *n*-BuLi (306.43 mg, 4.78 mmol, 5.0 equiv.) was dissolved in anhydrous THF (10 mL) at 0 °C. After stirring at 0 °C for 30 min, a THF (5 mL) solution of (*S*)-**4**/(*R*)-**4**/(±)-**4** (500 mg, 0.96 mmol, 1.0 equiv.) was added. The mixture was stirred at rt for 2 h and then quenched with water. After removing THF, the water layer was extracted with EtOAc (3 × 10 mL). The combined extracts were washed with brine and dried over Na_2SO_4. After removing the solvent, the crude product was purified by silica gel column chromatography (hexane/EtOAc 15:1) to give a white solid.

(*S*)-**9**: White solid (246 mg, 45%); R_f = 0.46 (PE/EtOAc, 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 9.0 Hz, 2H), 7.99 (s, 2H), 7.52 (d, *J* = 9.0 Hz, 2H), 7.41 (dd, *J* = 8.8, 1.9 Hz, 2H), 7.25 (d, *J* = 5.4 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 5.3 Hz, 2H), 7.05 (d, *J* = 12.9 Hz, 2H), 6.02 (d, *J* = 13.0 Hz, 2H), 3.84 (s, 6H), 3.62 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.30, 149.76, 136.33, 133.03, 132.48, 129.76, 129.70, 129.16, 128.13, 127.96, 125.56, 125.41, 124.33, 119.28, 114.59, 99.96, 56.90, 56.63.

(*R*)-**9**: White solid (305 mg, 55%); R_f=0.46 (PE/EtOAc, 3:1); m.p. 138.9–144.3 °C.

(±)-**9**: White solid (430 mg, 78%); R_f=0.46 (PE/EtOAc, 3:1); m.p. 112.7–115.1 °C.

(*S*)-/(*R*)-/(±)-7,7′-dimethoxy-6,6′-biphenanthro[1,2-b]thiophene [(*S*)-**10**/(*R*)-**10**/(±)-**10**]

Trifluoromethane sulfonic acid (14.52 µL, 0.16 mmol, 0.6 equiv.) was added to an HFIP (20 mL) solution of the crude mixture of (S)-**9**/(R)-**9**/(±)-**9** (162 mg, 0.27 mmol, 1.0 equiv.) at rt. After stirring at rt for 2 h, the reaction was quenched with saturated $NaHCO_3$ aqueous solution (pH 9) and then filtered and dried to give the crude product of (*S*)-**10**/(*R*)-**10**/(±)-**10** as a gray solid.

(*S*)-/(*R*)-/(±)-[6,6′-biphenanthro[1,2-b]thiophene]-7,7′-diol [(*S*)-**11**/(*R*)-**11**/(±)-**11**]

The crude product (*S*)-**10**/(*R*)-**10**/(±)-**10** (0.27 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2, and BBr_3 (1.06 mL, 11.01 mmol, 40.0 equiv.) was slowly added at 0 °C. The mixture was stirred at 0 °C for 1 h and then at rt for an additional 4 h, poured into the water, and then filtered and dried to give a brown solid.

*(*S*)*-**11**: Brown solid (121 mg, 89%); R_f=0.4 (PE/EtOAc, 1:1); m.p. 165.6–168.2 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ=8.79 (d, *J*=9.1 Hz, 2H), 8.75 (d, *J*=8.9 Hz, 2H), 8.33 (s, 2H), 8.07 (d, *J*=8.9 Hz, 2H), 7.77 (d, *J*=5.3 Hz, 2H), 7.69 (d, *J*=9.2 Hz, 2H), 7.62 (d, *J*=5.3 Hz, 2H), 7.42 (d, *J*=9.0 Hz, 2H), 7.16 (d, *J*=9.2 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ=154.49, 138.09, 137.46, 132.99, 127.61, 126.57, 125.73, 125.56, 125.07, 124.79, 124.54, 123.13, 122.92, 120.29, 118.61, 118.51; HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{32}H_{18}NaO_2S_2$: 521.0648; found: 521.0640.

*(*R*)*-**11**: Brown solid (54 mg, 40%); R_f=0.4 (PE/EtOAc, 1:1); m.p. 164.2–166.8 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ=9.54 (s, 2H), 8.89 (d, *J*=9.5 Hz, 2H), 8.80 (d, *J*=9.4 Hz, 2H), 8.12 (d, *J*=8.9 Hz, 2H), 7.85–7.80 (m, 4H), 7.64 (d, *J*=5.3 Hz, 2H), 7.53 (d, *J*=9.1 Hz, 2H), 7.18 (d, *J*=9.2 Hz, 2H); ^{13}C NMR (125 MHz, DMSO): δ=154.48, 138.09, 137.46, 132.99, 127.60, 126.58, 125.73, 125.57, 125.07, 124.80, 124.54, 123.13, 122.93, 120.29, 118.60, 118.50; MS (EI): *m/z* $[M]^+$ calcd for $C_{32}H_{18}O_2S_2$: 498.07; found: 498.

(±)-**11**: Brown solid (92 mg, 68%); R_f=0.4 (PE/EtOAc, 1:1); m.p. 164.6–167.2 °C; MS (EI): *m/z* $[M]^+$ calcd for $C_{32}H_{18}O_2S_2$: 498.07; found: 498.

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Supplemental material

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References

1. Chen Y, Yekta S and Yudin AK. *Chem Rev* 2003; 103: 3155.
2. Pu L. *Chem Rev* 2004; 104: 1687.
3. Parmar D, Sugiono E, Raja S, et al. *Chem Rev* 2014; 114: 9047.
4. Hassan K, Yamashita KI, Hirabayashi K, et al. *Chem Lett* 2015; 44: 1607.
5. Bell F and Waring DH. *J Chem Soc* 1949; 337: 1579.
6. Snyder SA, Tang ZY and Gupta R. *J Am Chem Soc* 2009; 131: 5744.
7. Rajbangshi S and Sugiura KI. *Synthesis* 2017; 49: 3145.
8. Ye P, Li Q, Bai Z, et al. *Heterocycles* 2015; 91: 1986.
9. Zheng L, Urian RC, Liu Y, et al. *Chem Mater* 2000; 12: 13.
10. Yang W, Bam R, Catalano VJ, et al. *Angew Chem Int Ed* 2018; 57: 14773.
11. Danz M, Tonner R and Hilt G. *Chem Commun* 2012; 48: 377.
12. de Bettencourt-Dias A, Viswanathan S and Rollett A. *J Am Chem Soc* 2007; 129: 15436.
13. Ebata H, Miyazaki E, Yamamoto T, et al. *Org Lett* 2007; 9: 4499.
14. Ogunlaja AS, Hosten E, Betz R, et al. *RSC Adv* 2016; 6: 39024.
15. Lv N, Xie M, Gu W, et al. *Org Lett* 2013; 15: 2382.
16. Ou-Yang JK, Zhang YY, He ML, et al. *Org Lett* 2014; 16: 664.
17. Benmansour H, Shioya T, Sato Y, et al. *Adv Funct Mater* 2003; 13: 883.
18. Fujita T, Takahashi I, Hayashi M, et al. *Eur J Org Chem* 2017; (2): 262.