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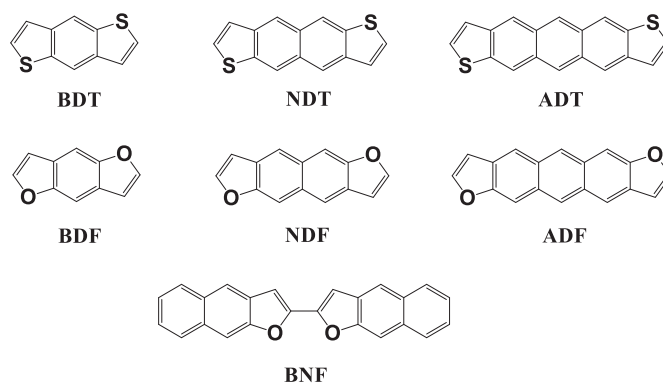
## CHIRAL 9,9'-BINAPHTHO[2,3-*b*]FURANS

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**Abstract** – A series of novel difuro-fused binaphthalenes are reported. Synthetic methods include methylation, halogenation, Sonogashira coupling as well as base-mediated cyclization are employed to furnish the title compounds from chiral BINOL (*R*-BINOL and *S*-BINOL). The final products are confirmed by NMR spectra and mass spectra.

Recent progress in organic electronics are stimulated by their potentials that can provide low-cost, large-area electronic devices.<sup>1</sup> Organic semiconductor as one of the key materials in this area has been significantly developed through tuning the molecular structures.<sup>2</sup> Numerous small organic molecules e.g. ladder-type  $\pi$ -conjugated molecules, often referred as acenes and heteroacenes, have been examined as promising organic semiconductors, which realized high-performance organic field-effect transistors (OFETs) and organic photo-voltaics (OPVs).<sup>3,4</sup> Among which benzothiophene- and benzofuran-based small molecules have been intensively investigated. For examples, Takimiya and coworkers have reported numerous acenedithiophenes (AcDTs), such as benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT), naphthodithiophenes (NDTs), and anthra[2,3-*b*:6,7-*b'*]dithiophenes (ADT), which have been widely utilized as important  $\pi$ -cores for molecular organic semiconductors and polymer semiconductors. Synthesis and properties of acenedifuran such as linear-shaped naphtho[2,3-*b*:6,7-*b'*]difurans (NDFs) and anthra[2,3-*b*:6,7-*b'*]difurans (ADFs) have also been reported by the same group for evaluation of optical properties in organic electronic area. Furthermore, [2,2']bi[naphtho[2,3-*b*]furanyl] (BNF) as a p-type semiconductor, a bis-benzofuran-based molecule was synthesized and examined as an organic semiconductor, which held moderately high mobility in thin-film OFETs, good photo conversion efficiency in bilayer OPVs as well as blue-green emission in OLETs (Scheme 1).<sup>5</sup>



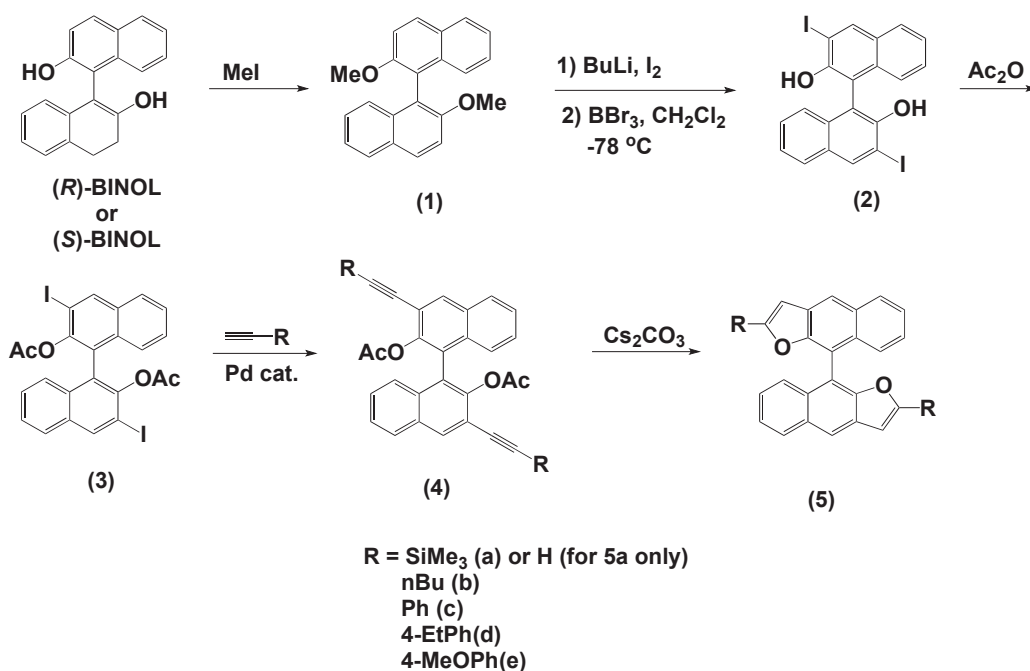
Scheme 1. Typical acenedithiophene and acenedifuran derivatives

On the other hand, 1,1'-bi-2-naphthol (BINOL) and its derivatives have been widely used in the area of molecular recognition and asymmetric synthesis. For example, chiroptical binaphthopyran could act as a possible modulation of the CD signal resulting from a significant chromophore change upon switching.<sup>6a</sup> Conformationally rigid BINOL-based diimidazolyl ligands bearing both hydrogen-bond-acceptors and -donors can form homochiral channel-like topologies through self-assembly *via* intermolecular O–H...N hydrogen bonds.<sup>6b</sup> The first highly enantioselective fluorescent sensor in the fluorous phase in solution was reported by Pu and co-workers through a novel 3,3'-perfluoroalkyl-BINOL-based chiral diketone, while the fluorescent responses of 3,3'-di(trifluoroacetyl)-1,1'-bi-2-naphthol toward a variety of amines have been studied by the same group. They demonstrated that the chiral trifluoromethyl BINOL ketone can act as an enantioselective fluorescent sensor for chiral 1,2-diamines, which could also be used to distinguish aliphatic 1,2- to 1,5-diamines from aromatic diamines, primary, secondary, and tertiary monoamines.<sup>6c-d</sup> 3,3'-Bis(2-pyridyl)-1,1'-binaphthyl derivatives are approached by a Pd-catalyzed Suzuki cross-coupling reaction, which could be good to excellent enantioselective catalysts for the alkynylzinc addition to aromatic and aliphatic aldehydes.<sup>6e</sup>

We are quite interested in synthesis of chiral furan-fused molecules, which might be used in organic electronics. Considering the availability of chiral source and accessibility of synthetic approach, we envisage that molecules with chiral furo-fused binaphthalene might be obtained by combining benzofuran and binaphthalene skeletons. Up to now, no difuro-fused binaphthalenes have been reported, and there is only one example of mono-furo-fused binaphthalene mentioned during the preparation of chiral binaphthalene-based cyclophanes as receptors for mono- and disaccharides by Diederich.<sup>7</sup> [2,2']Bi[naphtho[2,3-*b*]furanyl] (BNF) has been intensively investigated as a p-type semiconductor in organic electronics by Takimiya group.<sup>5f</sup> Hence it is worthy to explore chiral analogues for potential evaluation both in molecular recognition and organic electronics in due course.

The above described research encouraged us to explore chiral furan-fused binaphthalene due to their

potential application. In this paper, we report a series of chiral furan-fused molecules with binaphthalene skeleton from chiral BINOL. Initially 2,2'-dimethoxy-1,1'-binaphthalenes (*S*- or *R*-**1**) were obtained by the reaction of *S*- or *R*-BINOL with MeI in acetone in the presence of K<sub>2</sub>CO<sub>3</sub> (yields 96% and 98%).<sup>8, 6b</sup> Then lithiation reactions of *S*- or *R*-**1** were performed with BuLi and subsequently quenched by 1,1,2,2-tetrachloro-1,2-dibromoethane to afford 2,2'-dimethoxy-3,3'-dibromo-1,1'-binaphthalene, which were demethylated to 2,2'-dihydroxy-3,3'-dibromo-1,1'-binaphthalene and subsequent acylation with Ac<sub>2</sub>O was performed to afford 2,2'-di(acetoxy)-3,3'-dibromo-1,1'-binaphthalene. However, we were not successful to perform the palladium-catalyzed Sonogashira coupling of 2,2'-di(acetoxy)-3,3'-dibromo-1,1'-binaphthalene with various acetylenes.<sup>9a</sup> Then we had to select 3,3'-diiodo-2,2'-dimethoxy-1,1'-binaphthalene as our key intermediate, which was obtained by the lithiation reactions of *S*- or *R*-**1** and quenched with I<sub>2</sub> and followed by demethylation to afford 2,2'-dihydroxy-3,3'-diiodo-1,1'-binaphthalene (*S*- or *R*-**2**) with BBr<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at low temperature (isolated yields 47% and 51%).<sup>9b-d, 10</sup> Then the acylation of hydroxyl groups were furnished with Ac<sub>2</sub>O in the presence of pyridine to afford compounds **3** (*S*- or *R*-**3**) (yields 97% and 98%). The Sonogashira coupling reactions of **3** with five different alkynes by Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>/CuI/Et<sub>3</sub>N system in DMF were employed to afford 3,3'-dialkynyl-2,2'-diacetoxy-1,1'-binaphthalenes (**4a-e**) (yields range from 48% to 92%).<sup>10</sup> The final steps to 9,9'-binaphtho[2,3-*b*]furans were completed by Cs<sub>2</sub>CO<sub>3</sub>-assisted ring closure reactions of compounds **4a-e** to form target molecules **5a-5e** (yields from 24% to 82%) by adopting Takimiya's methods, it should be pointed out that the cyclization of **4a** in the presence of Cs<sub>2</sub>CO<sub>3</sub> gave nonsilylated product **5a**, the ring closure and desilylation occurred spontaneously in this case.<sup>6d-e</sup>



Scheme 2. Synthetic approach toward target molecules

In conclusion, we developed an easy and efficient access towards various optically active 9,9'-binaphtho[2,3-*b*]furan derivatives from chiral BINOL. This method might be applied to the construction of other heterocycle-fused chiral binaphthalene derivatives with intermediates described in this paper. This is the first example of chiral five-membered heterocycle-fused binaphthalene reported so far, which might be applied for further evaluation in opt-electrics and molecular recognition through structure modifications.

## EXPERIMENTAL

All chemicals are commercially available as analytic grade and used without further purification. Solvents are purified according to standard methods prior to use. All  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured on a Bruker Avance III 500MHz spectrometer ( $^1\text{H}$  NMR 500 MHz,  $^{13}\text{C}$  NMR 125 MHz) in  $\text{CDCl}_3$ . Mass spectra were measured on Agilent 5973N or Bruker micrOTOF II spectrometer (HR-MS ESI). Melting point was measured on an X-4 micrographic melting point measuring instrument. The optical rotations were measured in  $\text{CH}_2\text{Cl}_2$  on a Perkin Elmer 343 automatic polarimeter.

**Starting materials.** *R*- and *S*-2,2'-Dimethoxy-1,1'-binaphthyl and 3,3'-diiodo-2,2'-binaphthol (see supplementary materials for details) were prepared by the appropriate reported procedure.<sup>8, 6b</sup> All other chemicals used were commercially available.

### Preparation of 2,2'-Diacetoxy-3,3'-diiodo-1,1'-binaphthalene[(*S*)-3/(*R*)-3]<sup>6b,10</sup>

To a solution of (*S*)- or (*R*)- 3,3'-diiodo-2,2'-binaphthol (5.2 g, 9.7 mmol) and pyridine (4.2 mL, 48 mmol) in  $\text{CH}_2\text{Cl}_2$  (100 mL) was added acetic anhydride (4.8 mL, 48 mmol) at room temperature. After stirring for 24 h, the product was extracted with  $\text{CH}_2\text{Cl}_2$  (100 mL  $\times$  3), washed with water (100 mL  $\times$  3), dried ( $\text{MgSO}_4$ ), and concentrated in vacuo. The white solid of (*S*)-**3** or (*R*)-**3** was obtained.

(*S*)-**3** White solid (5.8 g, 97%); mp 179-180 °C;  $R_f$  0.44 (5:1 PE-EtOAc);  $^1\text{H}$  NMR  $\delta$  8.53 (s, 2H), 7.80 (d,  $J = 8.2$  Hz, 2H), 7.46 (t,  $J = 7.9$  Hz, 2H), 7.31 - 7.26 (m, 2H), 7.07 (d,  $J = 8.2$  Hz, 2H), 1.91 (s, 6H).

(*R*)-**3** White solid (5.86 g, 98%); mp 176-178 °C;  $R_f$  0.44 (5:1 PE-EtOAc);  $^1\text{H}$  NMR  $\delta$  8.52 (s, 2H), 7.79 (d,  $J = 8.2$  Hz, 2H), 7.45 (t,  $J = 7.5$  Hz, 2H), 7.28 (t,  $J = 7.7$  Hz, 2H), 7.09 (d,  $J = 8.2$  Hz, 2H), 1.89 (s, 6H).

### Preparation of 2,2'-Diacetoxy-3,3'-di(trimethylsilylethynyl)-1,1'-binaphthalene[(*S*)-4/(*R*)-4]<sup>5f,10</sup>

To a deaerated solution of (*S*)-**3** (1.36 g, 2.2 mmol) or (*R*)-**3** (0.25 g, 0.4 mmol) in triethylamine (10 mL or 3 mL for (*R*)-**3**) and DMF (10 mL or 3 mL for (*R*)-**3**) was added trimethylsilylacetylene (1.3 mL, 8.5 mmol; or 0.23 mL, 1.6 mmol for (*R*)-**3**),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (93 mg, 0.13 mmol, or 17 mg, 0.024 mmol for (*R*)-**3**; 6% mol) and CuI (51 mg, 0.26 mmol or 9.2 mg, 0.048 mmol for (*R*)-**3**; 12 mol%). After stirring for 15 h at room temperature, the mixture was diluted with water (50 mL  $\times$  3) and extracted with  $\text{CH}_2\text{Cl}_2$  (50

mL  $\times$  3). The combined organic layer were washed with brine, dried ( $\text{MgSO}_4$ ), and concentrated in vacuo. Column chromatography on  $\text{SiO}_2$  (40:1 PE-EtOAc) gave (*S*)-4a/(*R*)-4a.

**(*S*)-4a** White solid (0.76 g, 62%); mp 185-187 °C;  $R_f$  0.79 (5:1 PE-EtOAc);  $^1\text{H NMR}$   $\delta$  8.19 (s, 2H), 7.86 (d,  $J = 8.2$  Hz, 2H), 7.45 (t,  $J = 7.5$  Hz, 2H), 7.28 (d,  $J = 8.3$  Hz, 2H), 7.07 (d,  $J = 7.0$  Hz, 2H), 1.95 (s, 6H), 0.26 (s, 18H);  $^{13}\text{C NMR}$   $\delta$  168.37, 146.98, 134.25, 133.01, 131.05, 127.83, 127.68, 126.41, 126.18, 124.14, 116.74, 100.31, 99.57, 20.48, 0.12.

**(*R*)-4a** White solid (0.11 g, 48%); mp 185-187 °C;  $R_f$  0.79 (5:1 PE-EtOAc);  $^1\text{H NMR}$   $\delta$  8.18 (s, 2H), 7.84 (d,  $J = 8.2$  Hz, 2H), 7.44 (t,  $J = 7.5$  Hz, 2H), 7.27 (s, 2H), 7.07 (d,  $J = 8.3$  Hz, 2H), 1.95 (s, 6H), 0.16 (s, 18H);  $^{13}\text{C NMR}$   $\delta$  147.20, 134.35, 133.21, 131.24, 127.93, 127.77, 126.51, 126.40, 124.37, 117.02, 100.56, 99.68, 20.53, 1.13.

#### Preparation of 2,2'-Diacetoxy-3,3'-di(hexynyl)-1,1'-binaphthalene[(*S*)-4b/(*R*)-4b]<sup>5f</sup>

To a deaerated solution of (*S*)-3/ (*R*)-3 (0.248 g, 0.40 mmol) in triethylamine (4.5 mL) and DMF (4.5 mL) was added 1-hexyne (0.2 mL, 1.60 mmol),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (17 mg, 0.024 mmol, 6%) and  $\text{CuI}$  (9.2 mg, 0.048 mmol, 12%). After stirring for 15 h at room temperature, the mixture was diluted with water (20 mL  $\times$  3) and extracted with  $\text{CH}_2\text{Cl}_2$  (20 mL  $\times$  3). The combined organic layer were washed with brine, dried ( $\text{MgSO}_4$ ), and concentrated in vacuo. Column chromatography on  $\text{SiO}_2$  (PE) to give (*S*)-4b/(*R*)-4b.

**(*S*)-4b** Yellow oil (137 mg, 65%);  $R_f$  0.28 (10:1 PE-EtOAc);  $^1\text{H NMR}$   $\delta$  8.09 (s, 2H), 7.81 (d,  $J = 8.2$  Hz, 2H), 7.40 (t,  $J = 7.4$  Hz, 2H), 7.25 - 7.20 (m, 2H), 7.08 (d,  $J = 7.9$  Hz, 2H), 2.45 (t,  $J = 6.9$  Hz, 4H), 1.89 (s, 6H), 1.63 - 1.56 (m, 4H), 1.51 - 1.47 (m, 7.3Hz, 4H), 0.94 (t,  $J = 7.2$  Hz, 6H);  $^{13}\text{C NMR}$   $\delta$  167.28, 146.10, 132.65, 132.41, 131.60, 130.27, 126.52, 126.08, 125.28, 125.17, 123.25, 116.70, 94.30, 29.79, 20.96, 19.36, 18.30, 12.56.

**(*R*)-4b** Yellow oil (122 mg, 58%);  $R_f$  0.28 (10:1 PE-EtOAc);  $^1\text{H NMR}$   $\delta$  8.10 (s, 2H), 7.83 (d,  $J = 8.2$  Hz, 2H), 7.47 - 7.39 (m, 2H), 7.22 - 7.25 (m, 2H), 7.08 (s, 2H), 2.46 (t,  $J = 7.0$  Hz, 4H), 1.93 (s, 6H), 1.62 - 1.57 (m, 4H), 1.51 - 1.46 (m, 4H), 0.94 (t,  $J = 7.3$  Hz, 6H);  $^{13}\text{C NMR}$   $\delta$  168.56, 147.01, 133.46, 132.54, 131.23, 127.56, 127.14, 126.22, 124.17, 117.57, 95.36, 76.26, 30.76, 21.98, 20.45, 19.32, 13.64.

#### Preparation of 2, 2'-Diacetoxy-3, 3'-di(phenylethynyl)-1, 1'-binaphthalene[(*S*)-4c/(*R*)-4c]<sup>5f</sup>

To a deaerated solution of (*S*)-3/ (*R*)-3 (0.25 g, 0.40 mmol) in triethylamine (4 mL) and DMF (4 mL) was added phenylacetylene (0.2 mL, 1.6 mmol),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (17 mg, 0.024 mmol, 6%) and  $\text{CuI}$  (9.2 mg, 0.048 mmol, 12%). After stirring for 15 h at room temperature, the mixture was diluted with water (20 mL  $\times$  3) and extracted with  $\text{CH}_2\text{Cl}_2$  (20 mL  $\times$  3). The combined organic layer were washed with brine, dried ( $\text{MgSO}_4$ ), and concentrated in vacuo. Column chromatography on  $\text{SiO}_2$  (40:1 PE-EtOAc) gave (*S*)-4c or (*R*)-4c.

**(S)-4c** Light yellow solid (154 mg, 67%); mp 206-208 °C;  $R_f$  0.78 (5:1 PE-EtOAc);  $^1\text{H NMR}$   $\delta$  8.25 (s, 2H), 7.89 (d,  $J = 7.7$  Hz, 2H), 7.52 – 7.46 (m, 6H), 7.34 - 7.28 (m, 8H), 7.15 (d,  $J = 7.8$  Hz, 2H), 1.98 (s, 6H);  $^{13}\text{C NMR}$   $\delta$  168.38, 146.89, 133.68, 133.00, 131.60, 131.26, 128.60, 128.42, 127.81, 127.56, 126.41, 126.32, 124.36, 122.99, 117.03, 94.03, 85.17, 20.38.

**(R)-4c** Light yellow solid (190 mg, 83%); mp 206-208 °C;  $R_f$  0.78 (5:1 PE-EtOAc);  $^1\text{H NMR}$   $\delta$  8.25 (s, 2H), 7.89 (d,  $J = 8.2$  Hz, 2H), 7.51 (d,  $J = 5.0$  Hz, 4H), 7.47 (t,  $J = 7.5$  Hz, 2H), 7.39 - 7.32 (m, 6H), 7.29 (t,  $J = 7.6$  Hz, 2H), 7.15 (d,  $J = 8.4$  Hz, 2H), 1.98 (s, 6H);  $^{13}\text{C NMR}$   $\delta$  168.39, 146.91, 133.70, 133.01, 131.61, 131.27, 128.62, 128.43, 127.82, 127.58, 126.42, 126.34, 124.38, 124.35, 123.01, 117.05, 94.04, 85.18, 20.40.

#### Preparation of 2, 2'-Diacetoxy-3, 3'-di (4-ethylphenylethynyl)-1, 1'-binaphthalene [(S)-4d/(R)-4d]

To a deaerated solution of **(S)-3/ (R)-3** (0.500 g, 0.80 mmol) in triethylamine (9 mL) and DMF (9 mL) was added 4-ethylphenylacetylene (0.28 mL, 2.40 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (38 mg, 0.048 mmol, 6%) and CuI (19 mg, 0.096 mmol, 12%). After stirring for 15 h at room temperature, the mixture was diluted with water (20 mL  $\times$  3) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL  $\times$  3). The combined organic layer were washed with brine, dried (MgSO<sub>4</sub>), and concentrated in vacuo. Column chromatography on SiO<sub>2</sub> (PE) gave **(S)-4d/ (R)-4d**.

**(S)-4d** Yellow solid (0.455 g, 92%); mp 95-97 °C;  $R_f$  0.45 (5:1 PE-EA);  $^1\text{H NMR}$   $\delta$  8.25 (s, 2H), 7.89 (d,  $J = 8.2$  Hz, 2H), 7.46 (m, 6H), 7.29 (t,  $J = 7.7$  Hz, 2H), 7.16 (m, 6H), 2.66 (q,  $J = 7.6$  Hz, 4H), 2.00 (s, 6H), 1.24 (t,  $J = 7.6$  Hz, 6H);  $^{13}\text{C NMR}$  (125 MHz, CDCl<sub>3</sub>)  $\delta$  168.57, 146.85, 145.17, 133.57, 132.88, 131.61, 131.25, 128.03, 127.81, 127.51, 126.41, 124.28, 120.07, 117.13, 94.33, 84.45, 28.87, 20.51, 15.32.

**(R)-4d** Light yellow solid (0.440 g, 87%); mp 97-99 °C;  $R_f$  0.45 (5:1 PE-EtOAc);  $^1\text{H NMR}$   $\delta$  8.25 (s, 1H), 7.89 (d,  $J = 8.2$  Hz, 1H), 7.46 (m, 3H), 7.29 (t,  $J = 7.6$  Hz, 1H), 7.16 (m, 3H), 2.66 (q,  $J = 7.6$  Hz, 2H), 2.00 (s, 3H), 1.24 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C NMR}$  (CDCl<sub>3</sub>)  $\delta$  168.55, 146.85, 145.17, 133.57, 132.88, 131.61, 131.25, 128.03, 127.81, 127.51, 126.41, 124.28, 120.07, 117.13, 94.33, 84.45, 28.87, 20.51, 15.32.

#### Preparation of 2,2'-Diacetoxy-3,3'-di(4-methoxyphenylethynyl)-1,1'-binaphthalene [(S)-4e/(R)-4e]

To a deaerated solution of **(S)-3/(R)-3** (0.500 g, 0.80 mmol) in triethylamine (9 mL) and DMF (9 mL) was added 4-methoxyphenylacetylene (0.32 mL, 2.40 mmol), Pd (PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (38 mg, 0.048 mmol, 6%) and CuI (19 mg, 0.096 mmol, 12%). After stirring for 15 h at room temperature, the mixture was diluted with water (20 mL  $\times$  3) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL  $\times$  3). The combined organic layer were washed with brine, dried (MgSO<sub>4</sub>), and concentrated in vacuo. Column chromatography on SiO<sub>2</sub> (PE) gave **(S)-4e/(R)-4e**.



**(S)-4e** Orange solid (0.374, 74 %); mp 111-113 °C;  $R_f$  0.14 (5:1 PE-EtOAc);  $^1\text{H NMR}$   $\delta$  8.23 (s, 2H), 7.89 (d,  $J = 8.2$  Hz, 2H), 7.46 (t,  $J = 8.0$  Hz, 6H), 7.34 - 7.26 (m, 2H), 7.14 (d,  $J = 8.2$  Hz, 2H), 6.88 (d,  $J = 8.7$  Hz, 4H), 3.83 (s, 6H), 2.00 (s, 6H);  $^{13}\text{C NMR}$   $\delta$  159.93, 146.82, 133.38, 133.10, 132.80, 131.27, 127.77, 127.44, 126.39, 117.23, 115.01, 114.12, 94.17, 83.85, 55.34, 20.51.

**(R)-4e** Orange solid (0.360 g, 71%); mp 116-118 °C;  $R_f$  0.14 (5:1 PE-EtOAc);  $^1\text{H NMR}$   $\delta$  8.23 (s, 2H), 7.89 (d,  $J = 8.2$  Hz, 2H), 7.47 (t,  $J = 8.7$  Hz, 6H), 7.34 - 7.26 (m, 4H), 6.88 (d,  $J = 8.8$  Hz, 4H), 3.83 (s, 6H), 2.00 (s, 6H);  $^{13}\text{C NMR}$   $\delta$  159.93, 146.82, 133.38, 133.10, 132.80, 131.27, 127.77, 127.44, 126.39, 117.23, 115.01, 114.12, 94.17, 83.85, 55.34, 20.51.

#### Preparation of 9,9'-Binaphtho[2,3-*b*]furan<sup>5d-f</sup>

To a suspension of cesium carbonate (1.43 g, 4.4 mmol) in DMF (10 mL) and H<sub>2</sub>O (2 mL) was added **(S)-4a/ (R)-4a** (0.308 g, 0.55 mmol), then stirred at 80 °C for 5 h. Poured into 100 mL of saturated aqueous ammonium chloride solution, then filtered with CH<sub>2</sub>Cl<sub>2</sub> (30 mL  $\times$  3), washed with water, dried (MgSO<sub>4</sub>), and concentrated in vacuo. Column chromatography on SiO<sub>2</sub> (PE) gave **(S)-5a/ (R)-5a**.

**(S)-5a** Yellow solid (107 mg, 46%); mp 289-291 °C;  $R_f$  0.70 (5:1 PE-EtOAc);  $^1\text{H NMR}$   $\delta$  8.27 (s, 2H), 8.08 (d,  $J = 8.4$  Hz, 2H), 7.59 (d,  $J = 2.3$  Hz, 2H), 7.44 (t,  $J = 8.0$  Hz, 2H), 7.39 (d,  $J = 8.6$  Hz, 2H), 7.30 - 7.25 (m, 2H), 6.97 (d,  $J = 2.3$  Hz, 2H);  $^{13}\text{C NMR}$   $\delta$  152.58, 147.58, 130.92, 130.65, 128.50, 128.20, 125.79, 125.22, 124.03, 119.88, 112.59, 106.31; Required for C<sub>24</sub>H<sub>14</sub>NaO<sub>2</sub> 337.0886, found: 357.0888, (M+Na<sup>+</sup>);  $[\alpha]$  20 (T 25 °C; c 0.1 g/ 100 mL in CH<sub>2</sub>Cl<sub>2</sub>).

**(R)-5a** White Solid (56 mg, 24%); mp 289-291 °C;  $R_f$  0.70 (5:1 PE-EtOAc);  $^1\text{H NMR}$   $\delta$  8.25 (s, 2H), 8.07 (d,  $J = 8.3$  Hz, 2H), 7.57 (s, 2H), 7.43 (t,  $J = 7.5$  Hz, 2H), 7.38 (d,  $J = 8.6$  Hz, 2H), 7.26 (s, 2H), 6.95 (s, 2H);  $^{13}\text{C NMR}$   $\delta$  152.57, 147.57, 130.91, 130.64, 128.49, 128.19, 125.78, 125.21, 124.02, 119.87, 112.58, 106.30; Required for C<sub>24</sub>H<sub>14</sub>NaO<sub>2</sub> 337.0886, found: 357.0878 (M+Na<sup>+</sup>);  $[\alpha]$  -24 (T 25 °C; c 0.1 g/ 100 mL in CH<sub>2</sub>Cl<sub>2</sub>).

#### Preparation of 2,2'-Dibutyl-9,9'-binaphtho[2,3-*b*]furan[(S)-5b/(R)-5b]

To a suspension of cesium carbonate (0.45 g, 1.4 mmol) in DMF (10 mL) and H<sub>2</sub>O (2 mL) was added **(S)-4/ (R)-4** (0.09 g, 0.17 mmol), then stirred at 80 °C for 5 h. After poured into 100 mL of saturated aqueous ammonium chloride solution, then filtered with CH<sub>2</sub>Cl<sub>2</sub> (20 mL  $\times$  3), washed with water, dried (MgSO<sub>4</sub>), and concentrated in vacuo. Column chromatography on SiO<sub>2</sub> (PE) gave **(S)-5b/ (R)-5b**.

**(S)-5b** White solid (38 mg, 50%); mp 108-109 °C;  $R_f$  0.85 (10:1 PE-EtOAc);  $^1\text{H NMR}$   $\delta$  8.07 (s, 2H), 8.01 (d,  $J = 8.3$  Hz, 2H), 7.40 - 7.35 (m, 4H), 7.19 (t,  $J = 7.6$  Hz, 2H), 6.55 (s, 2H), 2.61 (t,  $J = 7.5$  Hz, 4H), 1.65-1.53 (m, 4H), 1.37 - 1.28 (m, 4H), 0.85 (t,  $J = 7.4$  Hz, 6H);  $^{13}\text{C NMR}$   $\delta$  162.87, 152.65, 130.83, 130.12, 130.04, 128.11, 126.08, 124.34, 123.60, 118.00, 112.03, 101.26, 29.41, 28.23, 22.15, 13.62;

Required for  $C_{32}H_{30}NaO_2$ , 469.2138, found: 469.2142 ( $M+Na^+$ );  $[\alpha]$  26 (T 25 °C; c 0.1 g/ 100 mL;  $CH_2Cl_2$ ).

**(R)-5b** White solid (37 mg, 49%); mp 108-109 °C;  $R_f$  0.85 (10:1 PE-EtOAc);  $^1H$  NMR  $\delta$  8.15 - 7.94 (m, 4H), 7.40 - 7.35 (m, 4H), 7.19 (t,  $J = 7.6$  Hz, 2H), 6.55 (s, 2H), 2.61 (t,  $J = 7.5$  Hz, 4H), 1.72 - 1.53 (m, 4H), 1.35 - 1.30 (m, 4H), 0.85 (t,  $J = 7.3$  Hz, 6H);  $^{13}C$  NMR  $\delta$  162.93, 152.71, 130.89, 130.18, 130.10, 128.17, 126.14, 124.40, 123.66, 118.06, 112.09, 101.32, 29.47, 28.29, 22.21, 13.69; Required for  $C_{32}H_{30}NaO_2$ , 469.2138, found: 469.2138 ( $M+Na^+$ );  $[\alpha]$  -30 (T 25 °C; c 0.1 /100 mL in  $CH_2Cl_2$ ).

#### Preparation of 2,2'-Diphenyl-9,9'-binaphtho[2,3-*b*]furan [(S)-5c/(R)-5c]<sup>5d-f</sup>

To a suspension of cesium carbonate (0.69 g, 2.1 mmol) in DMF (10 mL) and  $H_2O$  (2 mL) was added **(S)-4c/(R)-4c** (0.15 g, 0.26 mmol), then stirred at 80 °C for 5 h. After poured into 100 mL of saturated aqueous ammonium chloride solution, then filtered with  $CH_2Cl_2$  (30 mL  $\times$  3), washed with water, dried ( $MgSO_4$ ), and concentrated in vacuo. Column chromatography on  $SiO_2$  (PE) gave **(S)-5c/(R)-5c**.

**(S)-5c** White solid (101 mg, 78%); mp 268-270 °C;  $R_f$  0.61 (5:1 PE-EtOAc);  $^1H$  NMR  $\delta$  8.26 (s, 2H), 8.09 (d,  $J = 8.3$  Hz, 2H), 7.61 (d,  $J = 7.5$  Hz, 4H), 7.47 - 7.43 (m, 4H), 7.30 - 7.20 (m, 10H);  $^{13}C$  NMR  $\delta$  158.41, 152.62, 131.15, 130.81, 130.00, 128.93, 128.59, 128.31, 126.15, 125.37, 124.97, 124.05, 119.24, 112.36, 100.92; Required for  $C_{36}H_{22}NaO_2$ , 509.1512, found: 509.1516 ( $M+Na^+$ );  $[\alpha]$  40 (T 25 °C; c 0.1 g/ 100 mL in  $CH_2Cl_2$ ).

**(R)-5c** White solid (106 mg, 82%); mp 268-270 °C;  $R_f$  0.61 (5:1 PE-EtOAc);  $^1H$  NMR  $\delta$  8.23 (s, 2H), 8.06 (d,  $J = 8.3$  Hz, 2H), 7.59 (d,  $J = 7.1$  Hz, 4H), 7.52 - 7.37 (m, 4H), 7.24 (s, 10H);  $^{13}C$  NMR  $\delta$  158.50, 152.70, 131.24, 130.91, 130.11, 130.07, 128.90, 128.60, 128.32, 126.20, 125.42, 124.97, 124.05, 119.23, 112.45, 100.93; Required for  $C_{36}H_{22}NaO_2$ , 509.1512, found: 509.1520 ( $M+Na^+$ );  $[\alpha]$  -40 (T 25 °C; c 0.1 g/ 100 mL in  $CH_2Cl_2$ ).

#### Preparation of 2, 2'-Di(4-ethylphenyl)-9, 9'-binaphtho[2, 3-*b*]furan [(S)-5d/(R)-5d]

To a suspension of cesium carbonate (1.85 g, 5.6 mmol) in DMF (10 mL) and  $H_2O$  (5 mL) was added **(S)-4d** (0.435 g, 0.70 mmol), then stirred at 80 °C for 5 h. After poured into 100 mL of saturated aqueous ammonium chloride solution, then filtered with  $CH_2Cl_2$  (30 mL  $\times$  3), washed with water, dried ( $MgSO_4$ ), and concentrated in vacuo. Column chromatography on  $SiO_2$  (PE) gave **(S)-5d**.

To a suspension of cesium carbonate (0.30 g, 0.8 mmol) in DMF (8 mL) and  $H_2O$  (4 mL) was added **(R)-4d** (0.065 g, 0.104 mmol), then stirred at 80 °C for 5 h. After poured into 100 mL of saturated aqueous ammonium chloride solution, then filtered with  $CH_2Cl_2$  (20 mL  $\times$  3), washed with water, dried ( $MgSO_4$ ), and concentrated in vacuo. Chromatography on  $SiO_2$  (PE) gave **(R)-5d**.

**(S)-5d** Yellow solid (210 mg, 56%); mp 288-291 °C;  $R_f$  0.60 (5:1 PE-EtOAc);  $^1H$  NMR  $\delta$  8.23 (s, 2H), 8.07 (d,  $J = 8.3$  Hz, 2H), 7.52 (d,  $J = 8.2$  Hz, 4H), 7.48 - 7.43 (m, 4H), 7.25 - 7.21 (m, 2H), 7.18 (s, 2H),



7.09 (d,  $J = 8.2$  Hz, 4H), 2.58 (q,  $J = 7.6$  Hz, 4H), 1.16 (t,  $J = 7.6$  Hz, 6H);  $^{13}\text{C}$  NMR  $\delta$  158.70, 152.59, 145.40, 131.13, 130.68, 130.19, 128.12, 128.21, 127.51, 126.18, 125.44, 124.78, 123.95, 118.89, 112.30, 100.13, 28.71, 15.37; Required for  $\text{C}_{40}\text{H}_{30}\text{NaO}_2$ , 565.2138, found: 565.2139 (M+Na<sup>+</sup>);  $[\alpha]$  +79 (T 25 °C, c 0.2).

**(R)-5d** Light yellow solid (35 mg, 63%); mp 288-290 °C;  $R_f$  0.60 (5:1 PE-EtOAc);  $^1\text{H}$  NMR  $\delta$  8.23 (s, 2H), 8.07 (d,  $J = 8.3$  Hz, 2H), 7.52 (d,  $J = 8.2$  Hz, 4H), 7.48 - 7.34 (m, 4H), 7.25 - 7.20 (m, 2H), 7.18 (s, 2H), 7.09 (d,  $J = 8.2$  Hz, 4H), 2.57 (q,  $J = 7.6$  Hz, 4H), 1.16 (t,  $J = 7.6$  Hz, 6H);  $^{13}\text{C}$  NMR  $\delta$  158.70, 152.59, 145.40, 131.12, 130.68, 130.19, 128.11, 128.20, 127.52, 126.18, 125.43 (, 124.78, 123.94, 118.89, 112.30, 100.13, 28.71, 15.37; Required for  $\text{C}_{40}\text{H}_{30}\text{NaO}_2$ , 565.2138, found: 565.2153 (M+Na<sup>+</sup>);  $[\alpha]$  -74 (T 25 °C, c 0.2).

#### Preparation of 2, 2'-Di(4-methoxyphenyl)-9, 9'-binaphtho[2, 3-*b*]furan [(S)-5e/(R)-5e]

To a suspension of cesium carbonate (1.30 g, 3.9 mmol) in DMF (10 mL) and H<sub>2</sub>O (5 mL) was added **(S)-4e** (0.304 g, 0.48 mmol), then stirred at 80 °C for 5 h. After poured into 100 mL of saturated aqueous ammonium chloride solution, then filtered with CH<sub>2</sub>Cl<sub>2</sub> (30 mL  $\times$  3), washed with water, dried (MgSO<sub>4</sub>), and concentrated in vacuo. Column chromatography on SiO<sub>2</sub> (PE) gave **(S)-5e**.

To a suspension of cesium carbonate (0.40 g, 1.2 mmol) in DMF (8 mL) and H<sub>2</sub>O (4 mL) was added **(R)-4e** (0.096 g, 0.150 mmol), then stirred at 80 °C for 5 h. After poured into 100 mL of saturated aqueous ammonium chloride solution, then filtered with CH<sub>2</sub>Cl<sub>2</sub> (20 mL  $\times$  3), washed with water, dried (MgSO<sub>4</sub>), and concentrated in vacuo. Column chromatography on SiO<sub>2</sub> (PE) gave **(R)-5e**.

**(S)-5e** Yellow solid (214 mg, 81%); mp 295-297 °C;  $R_f$  0.30 (5:1 PE-EtOAc);  $^1\text{H}$  NMR  $\delta$  8.18 (s, 2H), 8.05 (d,  $J = 8.3$  Hz, 2H), 7.52 (d,  $J = 8.8$  Hz, 4H), 7.48 - 7.28 (m, 4H), 7.24 - 7.13 (m, 2H), 7.08 (s, 2H), 6.77 (d,  $J = 8.9$  Hz, 4H), 3.73 (s, 6H);  $^{13}\text{C}$  NMR  $\delta$  160.24, 158.52, 152.55, 131.16, 130.56, 130.36, 128.17, 126.90, 126.18, 124.69, 123.94, 122.84, 118.63, 114.06, 112.22, 99.17, 55.26; Required for  $\text{C}_{38}\text{H}_{26}\text{NaO}_4$ , 569.1723, found: 569.1733 (M+Na<sup>+</sup>);  $[\alpha]$  +120 (T 25 °C, c 0.2).

**(R)-5e** Yellow solid (61 mg, 72%); mp 294-296 °C;  $R_f$  0.30 (5:1 PE-EtOAc); No good resolved  $^1\text{H}$ -NMR could be obtained after several attempts due to the scanning problems;  $^{13}\text{C}$  NMR (100 MHz)  $\delta$  160.19, 158.47, 152.50, 131.10, 130.51, 130.30, 128.11, 126.85, 126.13, 124.63, 123.88, 122.80, 118.57, 114.02, 112.17, 99.12, 55.23. Required for  $\text{C}_{38}\text{H}_{26}\text{NaO}_4$ , 569.1723, found: 569.1739 (M+Na<sup>+</sup>). No optical rotation was obtained in this case.

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