**Ir-catalyzed almost perfect enantioselective synthesis of helical polyaryls based on an axially-chiral sequence**

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## Supporting Information

**General.** Optical rotation was measured using Jasco DIP-1000 polarimeter. IR spectra were recorded with Horiba FT730 spectrophotometer. NMR spectra were measured JEOL AL-400, Lambda500 and BRUKER Avance600 spectrometers using tetramethylsilane as an internal standard and $CDCl_3$ was used as solvent. Mass spectra were measured with JEOL JMS-SX102A and elemental analyses with Perkin Elmer PE2400II. Dehydrated xylene and DME are commercially available and they were dried over molecular sieves 4A (MS 4A) and degassed by argon bubbling before use. All reactions were performed under argon.

**Typical experimental procedures (Table 1, Entry 1):** (*S,S*)-MeDUPHOS (6.1 mg, 0.02 mmol) and $[IrCl(cod)]_2$ (6.7 mg, 0.01 mmol) were stirred in degassed xylene (1.0 mL) at room temperature to give a reddish yellow solution. After the addition of a xylene solution (1.5 mL) of 1,4-dimethoxy-but-2-yne (34.2mg, 0.30 mmol) and a xylene solution (1.5 mL) of diyne **1a** (28.2 mg, 0.05 mmol), the resulting mixture was further stirred at 100 °C for 10 min. The solvent was removed under reduced pressure, and purification of the crude products by thin layer chromatography (hexane/AcOEt = 2/1) gave pure **2a** (35.4 mg, 89% yield). The ee was determined by HPLC analysis using a chiral column.

**1,4-Bis(1,3-Dihydro-5,6-bis(methoxymethyl)-4-(naphthalen-1-yl)isobenzofuran-7-yl)naphthalene (2a).** Colorless oil. IR ($CH_2Cl_2$), 1097, 777 $cm^{-1}$; $^1H$ NMR δ= 3.08 (s, 3H x 2), 3.10 (s, 3H x 2), 4.04 (d, *J* = 10.0Hz, 1H x 2), 4.08 (d, *J* = 10.0Hz, 1H x 2), 4.49 (d, *J* = 10.0Hz, 1H x 2), 4.55 (d, *J* = 10.0Hz, 1H x 2), 4.68 (d, *J* = 12.3Hz, 1H x 2), 4.74 (d, *J* = 12.3Hz, 1H x 2), 4.82 (d, *J* = 14.9Hz, 1H x 2), 4.86 (d, *J* = 14.9Hz, 1H x 2), 7.44-7.68 (m, 16H), 7.94-7.96 (m, 4H). $^{13}C$ NMR δ= 58.4, 58.5, 69.0, 69.2, 74.0, 74.2, 125.3, 125.8, 126.0, 126.2, 126.4, 126.5, 126.6, 127.1, 128.2, 128.3, 131.5, 131.5, 133.5, 135.0, 135.9, 136.1, 136.4, 136.5, 139.0, 139.2; HRMS for M+1 found m/e 793.3553, calcd for $C_{54}H_{49}O_6$: 793.3529. $[\alpha]^{26}_D$ = 41.28 (c 1.43, $CHCl_3$). Ee was determined by HPLC analysis using Daicel Chiralcel AD-H: (eluent: 10% 2-propanol in hexane, retention time: 6 min for major isomer and 5 min for minor isomer).

**1,4-Bis(1,3-Dihydro-5,6-bis(hydroxymethyl)-4-(naphthalen-1-yl)isobenzofuran-7-yl)naphthalene (2b).** White solid. mp >250 °C (decayed) (Hexane-$CH_2Cl_2$); IR (KBr disk) 3365, 1011, 775

$cm^{-1}$; $^1H$ NMR δ= 2.97 (s, 1H x 2), 3.25 (s, 1H x 2), 4.47-4.60 (m, 4H x 2), 4.65 (d, *J* = 13.2Hz, 1H x 2), 4.70 (d, *J* = 13.2Hz, 1H x 2), 4.83 (d, *J* = 14.9Hz, 1H x 2), 4.88 (d, *J* = 14.9Hz, 1H x 2), 7.36-7.63 (m, 16H), 7.94-7.96 (m, 4H). $^{13}C$ NMR δ= 60.3, 60.4, 74.1, 125.3, 125.5, 126.1, 126.2, 126.6, 126.7, 126.9, 126.9, 128.4, 128.6, 131.6, 131.8, 133.7, 133.9, 134.5, 135.7, 136.2, 138.8, 139.0, 139.1, 139.1; HRMS for M found m/e 736.2819, calcd for $C_{50}H_{40}O_6$: 736.2825. $[\alpha]^{24}_D$ = 14.08 (c 0.79, $CHCl_3$). Ee was determined by HPLC analysis using Daicel Chiralcel AD-H: (eluent: 50% 2-propanol in hexane, retention time: 5 min for major isomer and 4 min for minor isomer).

**1,4-Bis(5,6-bis(methoxymethyl)-4-(naphthalen-1-yl)2-tosylisoindolin-7-yl)naphthalene (2c).** White solid. mp >300 °C; IR ($CH_2Cl_2$) 1350, 1163, 1095, 673 $cm^{-1}$; $^1H$ NMR δ= 1.94 (s, 3H x 2), 2.94 (s, 3H x 2), 3.08 (s, 3H x 2), 4.18 (d, *J* = 3.5Hz, 1H x 2), 4.20 (d, *J* = 3.5Hz, 1H x 2), 4.63 (d, *J* = 2.7Hz, 1H x 2), 4.64 (d, *J* = 2.7Hz, 1H x 2), 4.68-4.72 (m, 1H x 4), 4.78 (d, *J* = 12.6Hz, 1H x 2), 4.86 (d, *J* = 14.9Hz, 1H x 2), 6.68-6.69 (m, 4H), 7.19 (d, *J* = 3.3Hz, 1H), 7.20 (d, *J* = 3.3Hz, 1H), 7.24-7.27 (m, 2H), 7.35-7.41 (m, 4H), 7.46-7.47 (m, 4H), 7.56-7.57 (m, 4H) , 7.68-7.71 (m, 4H) , 7.78-7.80 (m, 4H). $^{13}C$ NMR δ= 21.5, 54.3, 54.3, 58.5, 58.7, 68.9, 69.2, 125.4, 125.4, 126.1, 126.5, 126.7, 126.7, 127.1, 127.3, 128.5, 128.5, 129.7, 131.3, 131.4, 133.7, 133.7, 135.2, 135.7, 136.1, 136.3, 136.3, 136.5, 137.0, 137.0, 143.7; HRMS for M+1 found m/e 1099.4006, calcd for $C_{68}H_{63}N_2O_8S_2$: 1099.4026. $[\alpha]^{30}_D$ = 78.07 (c 1.025, $CHCl_3$). Ee was determined by HPLC analysis using Daicel Chiralcel OD-H x 2: (eluent: 50% 2-propanol in hexane, retention time: 19 min for major isomer and 16 min for minor isomer).

**1,4-Bis(2,3-bis(methoxymethyl)-4-(naphthalen-1-yl)naphthalen-1-yl)naphthalene (3d).** White solid. mp 159-160 °C; IR ($CH_2Cl_2$) 1105, 768 $cm^{-1}$; $^1H$ NMR δ= 3.14 (s, 3H x 2), 3.23 (s, 3H x 2), 4.18 (d, *J* = 10.0Hz, 1H x 2), 4.33 (d, *J* = 10.1Hz, 1H x 2), 4.65 (d, *J* = 10.1Hz, 1H x 2), 4.77 (d, *J* = 10.0Hz, 1H x 2), 7.22-7.40 (m, 14H), 7.50-7.53 (m, 4H), 7.68-7.70 (m, 4H), 7.82 (s, 2H), 7.99-8.04 (m, 4H). $^{13}C$ NMR δ= 58.5, 58.7, 70.2, 70.5, 125.3, 125.9, 126.1, 126.2, 126.2, 126.2, 126.8, 127.0, 127.1, 127.5, 128.0, 128.1, 128.2, 128.7, 133.1, 133.1, 133.2, 133.3, 133.4, 134.0, 134.1, 136.5, 136.6, 139.4, 139.5; HRMS for M found m/e 808.3567, calcd for $C_{58}H_{48}O_4$: 808.3553. $[\alpha]^{32}_D$ = -58.36 (c 0.65, $CHCl_3$). Ee was determined by HPLC analysis using Daicel Chiralcel OD-H: (eluent: 10% 2-propanol in hexane, retention time: 8 min for major isomer and 6 min for minor isomer).

**1,4-Bis(2,3-bis(bromomethyl)-4-(naphthalen-1-yl)naphthalen-1-yl)naphthalene (4d).** White crystal. mp >250 °C (decayed); IR ($CH_2Cl_2$) 779, 764 $cm^{-1}$; $^1H$ NMR δ= 4.41 (d, *J* = 10.5Hz, 1H x 2), 4.58 (d, *J* = 10.5Hz, 1H x 2), 4.92 (d, *J* = 10.5Hz, 1H x 2), 5.03 (d, *J* = 10.5Hz, 1H x 2), 7.21-7.44 (m, 14H), 7.51-7.57 (m, 4H), 7.73-7.80 (m, 4H), 8.00-8.10 (m, 6H); Anal. Calcd for $C_{54}H_{36}Br_4$: C, 64.57; H, 3.61. Found: C, 64.57; H, 3.70.

**Noviaryl 2e.** White solid. mp >250 °C (decayed); IR (KBr disk) 1097, 768 $cm^{-1}$; $^1H$ NMR δ= 3.10 (s, 3H x 2), 3.10 (s, 3H x 2), 3.11 (s, 3H x 2), 3.12 (s, 3H x 2), 4.06 (d, *J* = 10.0Hz, 1H x 2), 4.09-4.13 (m, 6H), 4.50 (d, *J* = 10.0Hz, 1H x 2), 4.55-4.59 (m, 6H), 4.66-4.93 (m, 16H), 7.48-7.70 (m, 28H), 7.95-7.97 (m, 4H). $^{13}C$ NMR δ= 58.4, 58.6, 58.6, 58.6, 69.0, 69.2, 69.2, 74.0, 74.1, 74.2, 125.3, 125.8, 126.0, 126.2, 126.2, 126.3, 126.4, 126.6, 126.6, 126.6, 126.6, 127.1, 128.2, 128.3, 131.4, 131.5, 131.5, 133.5, 135.0, 135.0, 135.1, 135.1, 135.9, 136.0, 136.1, 136.1, 136.4, 136.4,

136.5, 136.5, 139.0, 139.1, 139.1, 139.2; HRMS for M found m/e 1456.6278, calcd for $C_{98}H_{88}O_{12}$: 1456.6276. $[\alpha]^{27}_{D}$ = 35.50 (c 1.45, $CHCl_3$). Ee was determined by HPLC analysis using Daicel Chiralcel AD-H: (eluent: 10% 2-propanol in hexane, retention time: 9 min for major isomer and 7 min for minor isomer).