Supporting Information

Iridium Complex-Catalyzed Highly Enantio- and Diastereoselective [2+2+2] Cycloaddition for the Synthesis of Axially Chiral Teraryl Compounds

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General. Optical rotation was measured using Jasco DIP-370 polarimeter. IR spectra were recorded with Horiba FT210 spectrophotometer. NMR spectra (300 MHz) were measured with Varian VXR-300 spectrometer using tetramethylsilane as an internal standard and CDCl₃ was used as solvent. Dehydrated xylene is commercially available and it was dried over molecular sieves 4A (MS 4A) and degassed by argon bubbling before use. All reactions were performed using an argon balloon.

General scheme for the preparation of diynes **1a-h**

Bis[3-(naphthalen-1-yl)prop-2-yl] ether (1a). IR (neat) 2225, 1074, 772cm⁻¹; ¹H NMR δ = 4.80 (s, 4H), 7.39-7.44 (m, 2H), 7.47-7.57 (m, 4H), 7.70-7.72 (m, 2H), 7.82-7.85 (m, 4H), 8.34-8.38 (m, 2H). ¹³C NMR δ = 57.6, 85.0, 89.2, 120.0, 125.1, 126.0, 126.3, 126.8, 128.2, 129.0, 130.7, 133.0, 133.2; HRMS for M found m/e 346.1332, calcd for C₂₆H₁₈O: 346.1358.

Bis[3-(2-methylphenyl)prop-2-yl] ether (1b). IR (neat) 2228, 1077, 758cm⁻¹; ¹H NMR δ = 2.45 (s, 6H), 4.61 (s, 4H), 7.11-7.43 (m, 8H). ¹³C NMR δ = 20.8, 57.3, 85.7, 88.1, 122.2, 125.4, 128.4, 129.3, 132.1, 140.2; HRMS for M+1 found m/e 275.1434, calcd for C₂₀H₁₉O: 275.1436.

Bis[3-(2-chlorophenyl)prop-2-yl] ether (1c). IR (neat) 2230, 1080, 754cm⁻¹; ¹H NMR δ = 4.64 (s, 4H), 7.17-7.28 (m, 4H), 7.37-7.50 (m, 4H). ¹³C NMR δ = 57.3, 83.6, 89.6, 122.3, 126.3, 129.1, 129.4, 133.4, 135.9; HRMS for M+1 found m/e 315.0317, calcd for C₁₈H₁₃Cl₂O: 315.0343.

Bis[3-(4-methoxynaphthalen-1-yl)prop-2-yl] ether (1d). IR (neat) 2217, 1098, 767cm⁻¹; ¹H NMR δ = 4.01 (s, 6H), 4.76 (s, 4H), 6.75 (d, J = 8.1Hz, 2H), 7.46-7.58 (m, 4H), 7.64 (d, J = 8.1Hz, 2H), 8.24-8.32 (m, 4H). ¹³C NMR δ = 56.6, 57.6, 85.2, 87.6, 103.4, 112.2, 122.1, 125.2, 125.6, 125.8, 127.3, 131.5, 134.2, 156.0; HRMS for M found m/e 406.1551, calcd for C₂₈H₂₂O₃: 406.1569.

N,N-Bis[3-(naphthalene-1-yl)prop-2-yl]tosylamine (1e). IR (CHCl₃) 2228, 1352, 1162,

1096, 953 cm^{-1} ; ^1H NMR δ = 2.12 (s, 3H), 4.69 (s, 4H), 7.15 (d, J = 8.3Hz, 2H), 7.32-7.49 (m, 8H), 7.78-7.85 (m, 6H), 8.06 (d, J = 8.3Hz, 2H). ^{13}C NMR δ =21.4, 37.9, 84.2, 86.4, 119.7, 124.9, 125.8, 126.3, 126.7, 127.8, 128.1, 128.9, 129.6, 130.7, 132.9, 133.0, 135.0, 143.8; HRMS for $M+1$ found m/e 500.1671, calcd for $\text{C}_{33}\text{H}_{26}\text{NO}_2\text{S}$: 500.1684.

1,7-Di(naphthalen-1-yl)-4,4-bis(ethoxycarbonyl)hepta-1,6-diyne (1f). IR (neat) 2230, 1735, 1052, 774 cm^{-1} ; ^1H NMR δ = 1.30 (t, J = 7.1Hz, 6H), 3.52 (s, 4H), 4.32 (q, J = 7.1Hz, 4H), 7.36-7.84 (m, 12H), 8.29-8.32 (m, 2H). ^{13}C NMR δ = 14.2, 24.4, 57.2, 62.2, 81.8, 89.0, 120.7, 125.0, 126.1, 126.2, 126.6, 128.1, 128.4, 130.4, 133.0, 133.3, 169.0; HRMS for $M+1$ found m/e 489.2048, calcd for $\text{C}_{33}\text{H}_{29}\text{O}_4$: 489.2066.

1,7-Di(naphthalen-1-yl)hepta-1,6-diyne (1g). IR (neat) 2224 cm^{-1} ; ^1H NMR δ = 2.07-2.17 (m, 2H), 2.85 (t, J = 7.1Hz, 4H), 7.37-7.42 (m, 2H), 7.46-7.57 (m, 4H), 7.63-7.65 (m, 2H), 7.77-7.84 (m, 4H), 8.35-8.37 (m, 2H). ^{13}C NMR δ = 19.2, 28.2, 79.4, 94.1, 121.4, 125.1, 126.1, 126.5, 128.0, 128.1, 130.0, 133.1, 133.4; HRMS for $M+1$ found m/e 345.1648, calcd for $\text{C}_{27}\text{H}_{21}$: 345.1643.

(Z)-1,8-Di(naphthalen-1-yl)oct-4-en-1,7-diyne (1h). IR (neat) 2400, 1215, 756 cm^{-1} ; ^1H NMR δ = 3.48 (d, J = 4.8Hz, 4H), 5.82-5.85 (m, 2H), 7.35-7.40 (m, 2H), 7.47-7.52 (m, 4H), 7.61-7.65 (m, 2H), 7.76-7.83 (m, 4H), 8.31-8.34 (m, 2H). ^{13}C NMR δ = 18.4, 22.8, 78.9, 92.3, 121.2, 125.1, 126.11, 126.14, 126.3, 126.5, 128.1, 130.1, 133.0, 133.3; HRMS for M found m/e 356.1577, calcd for $\text{C}_{28}\text{H}_{20}$: 356.1565.

Typical experimental procedures (Table 1, entry 3). (*S,S*)-MeDUPHOS (6.4 mg, 0.021 mmol) and $[\text{IrCl}(\text{cod})]_2$ (7.1 mg, 0.0105 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-2-butyne (36.0 mg, 0.315 mmol) and a xylene solution (1.5 ml) of diyne **1a** (36.5 mg, 0.105 mmol), the resulting mixture was further stirred under reflux for 1 h. The solvent was removed under reduced pressure, and purification of the crude products by thin layer chromatography (toluene/AcOEt = 15/1) gave pure **3aa** (40.3 mg, 0.086 mmol, 83% yield). The ratio of *dl/meso* isomers was determined by NMR spectrum and the ee was determined by HPLC analysis using a chiral column.

1,3-Dihydro-4,7-di(naphthalen-1-yl)-5,6-bis(methoxymethyl)isobenzofuran (3aa). White solid. mp 161-162 $^{\circ}\text{C}$ (Hexane); IR (CHCl_3) 2820, 1096, 756 cm^{-1} ; ^1H NMR δ = 3.06 (s, 6H), 4.02 (d, J = 9.9Hz, 2H), 4.46 (d, J = 9.9Hz, 2H), 4.63 (d, J = 11.3Hz, 2H), 4.77 (d, J = 11.3Hz, 2H), 7.40-7.39 (m, 14H); ^{13}C NMR δ = 58.4, 69.0, 74.1, 125.2, 125.8, 125.9, 126.3, 127.0, 128.0, 128.2, 131.3, 133.4, 134.9, 135.8, 136.2, 139.0; Anal. Calcd for $\text{C}_{32}\text{H}_{28}\text{O}_3$; C, 83.45; H, 6.13. Found: C, 83.29; H, 6.15. $[\alpha]_D^{26}$ = 43.37 (c 1.95, CHCl_3). Ee was determined by HPLC analysis using Daicel Chiralcel AD-H: (eluent: 2% 2-propanol in hexane, retention time: 9 min for major isomer and 12 min for minor isomer). The CD spectrum of **3aa** prepared by (*S,S*)-MeDUPHOS showed a negative first Cotton effect at 299 nm and a positive second Cotton effect at 278 nm, therefore, the product has negative chirality and its absolute configuration was determined to be the *S,S*-form. In contrast, the CD spectrum of **3aa** prepared by (*R,R*)-MeDUPHOS showed a positive first Cotton effect and a negative second Cotton effect, therefore, the product has positive chirality and its absolute configuration was determined to be the *R,R*-form.

5,6-Bis(*tert*-butyldimethylsiloxy)methyl)-1,3-dihydro-4,7-di(naphthalen-1-yl)isobenzofuran (3ac). White solid. mp 147-149 $^{\circ}\text{C}$; IR (CHCl_3) 1088, 756 cm^{-1} ; ^1H NMR δ = -0.50 (s, 6H), -0.37 (s, 6H), 0.69 (s, 18H), 4.45 (d, J = 10.5Hz, 2H), 4.61 (d, J = 11.0Hz, 2H), 4.65 (d, J = 10.5Hz, 2H), 4.78 (d, J = 11.0Hz, 2H), 7.39-7.58 (m, 10H), 7.89-7.92 (m, 4H). ^{13}C NMR δ = -5.9, -5.8, 18.2, 25.9, 59.4, 74.2, 125.2, 125.8, 126.1, 126.2, 126.9, 127.8, 128.1, 131.7, 133.5, 134.2, 136.3, 138.3, 138.4; HRMS for $M-1$ found

m/e 659.3409, calcd for $C_{42}H_{51}O_3Si_2$: 659.3377. $[\alpha]_D^{25} = 6.00$ (c 2.18, $CHCl_3$).

1,3-Dihydro-4,7-di(naphthalen-1-yl)-5,6-bis(methoxymethoxymethyl)isobenzofuran (3ad). White solid. mp 130 °C (Hexane); IR ($CHCl_3$) 1039, 738 cm^{-1} ; 1H NMR δ = 2.98 (s, 6H), 4.26 (d, J = 10.2Hz, 2H), 4.32 (s, 4H), 4.57 (d, J = 10.2Hz, 2H), 4.65 (d, J = 11.4Hz, 2H), 4.80 (d, J = 11.4Hz, 2H), 7.04-7.59 (m, 10H), 7.92 (m, 4H). ^{13}C NMR δ = 55.1, 64.6, 74.1, 96.6, 125.2, 125.7, 126.0, 126.3, 126.9, 128.1, 128.2, 131.4, 133.5, 135.1, 135.7, 135.9, 139.3; HRMS for M found m/e 520.2253, calcd for $C_{34}H_{32}O_5$: 520.2250. $[\alpha]_D^{27} = 17.07$ (c 1.92, $CHCl_3$). Ee was determined by HPLC analysis using Daicel Chiralcel AD-H: (eluent: 2% 2-propanol in hexane, retention time: 12 min for major isomer and 38 min for minor isomer).

1,3-Dihydro-5,6-bis(methoxymethyl)-4,7-bis(2-methylphenyl)isobenzofuran (3ba). White solid. mp 58-60 °C; IR ($CHCl_3$) 1094, 755 cm^{-1} ; 1H NMR δ = 2.10 (s, 6H), 3.14 (s, 6H), 4.15 (d, J = 10.1Hz, 2H), 4.36 (d, J = 10.1Hz, 2H), 4.71 (d, J = 11.4Hz, 2H), 4.80 (d, J = 11.4Hz, 2H), 7.14-7.29 (m, 8H). ^{13}C NMR δ = 20.0, 58.5, 68.8, 74.2, 125.5, 127.6, 129.0, 129.8, 135.0, 135.8, 135.8, 137.8, 138.0; Anal. Calcd for $C_{26}H_{28}O_3$; C, 80.38; H, 7.26. Found: C, 80.20; H, 6.92. $[\alpha]_D^{25} = 26.67$ (c 1.50, $CHCl_3$). Ee was determined by HPLC analysis using Daicel Chiralpak OJ-RH: (eluent: 50% acetonitrile in water, retention time: 14 min for major isomer and 27 min for minor isomer).

1,3-Dihydro-5,6-bis(methoxymethyl)-4,7-bis(2-chlorophenyl)isobenzofuran (3ca). White solid. mp 128-129 °C (Hexane); IR ($CHCl_3$) 1095, 754 cm^{-1} ; 1H NMR δ = 3.15 (s, 6H), 4.07 (d, J = 10.2Hz, 2H), 4.50 (d, J = 10.2Hz, 2H), 4.79 (d, J = 11.0Hz, 2H), 4.90 (d, J = 11.0Hz, 2H), 7.33-7.352 (m, 6H), 7.47-7.50 (m, 2H). ^{13}C NMR δ = 58.3, 68.7, 74.0, 126.5, 129.1, 129.3, 131.1, 133.0, 134.1, 135.2, 137.1, 138.3; Anal. Calcd for $C_{24}H_{22}Cl_2O_3$; C, 67.14; H, 5.16. Found: C, 66.83; H, 5.02. $[\alpha]_D^{26} = 44.92$ (c 1.80, $CHCl_3$). Ee was determined by HPLC analysis using Daicel Chiralcel AD-H: (eluent: 2% 2-propanol in hexane, retention time: 14 min for major isomer and 10 min for minor isomer).

1,3-Dihydro-5,6-bis(methoxymethyl)-4,7-bis(4-methoxynaphthalen-1-yl)isobenzofuran (3da). White solid. mp 230-233 °C (Hexane-benzene); IR ($CHCl_3$) 1091, 756 cm^{-1} ; 1H NMR δ = 3.10 (s, 6H), 4.05 (d, J = 9.9Hz, 2H), 4.08 (s, 6H), 4.46 (d, J = 9.9Hz, 2H), 4.64 (d, J = 11.3Hz, 2H), 4.78 (d, J = 11.3Hz, 2H), 6.91 (d, J = 8.0Hz, 2H), 7.40-7.52 (m, 8H), 8.35 (d, J = 8.0Hz, 2H). ^{13}C NMR δ = 55.6, 58.5, 69.1, 74.3, 103.2, 122.1, 125.2, 125.4, 125.6, 126.7, 127.0, 128.0, 132.3, 134.8, 136.5, 139.3, 155.0; Anal. Calcd for $C_{34}H_{32}O_5$; C, 78.44; H, 6.20. Found: C, 78.79; H, 6.27. $[\alpha]_D^{28} = 31.07$ (c 2.13, $CHCl_3$). Ee was determined by HPLC analysis using Daicel Chiralcel AD-H: (eluent: 2% 2-propanol in hexane, retention time: 10 min for major isomer and 8 min for minor isomer).

1,3-Dihydro-4,7-di(naphthalen-1-yl)-5,6-bis(methoxymethyl)-2-tosylisoindoline (3ea). White solid. mp 98-100 °C; IR ($CHCl_3$) 1348, 1163, 1095, 772 cm^{-1} ; 1H NMR δ = 2.42 (s, 3H), 3.02 (s, 6H), 3.93 (d, J = 9.9Hz, 2H), 4.13 (d, J = 12.9Hz, 2H), 4.26 (d, J = 12.9Hz, 2H), 4.40 (d, J = 9.9Hz, 2H), 7.18-7.95 (m, 18H). ^{13}C NMR δ = 21.6, 54.3, 58.5, 68.9, 125.2, 125.4, 126.0, 126.3, 127.0, 127.2, 128.3, 128.3, 129.6, 131.2, 133.4, 133.5, 135.1, 136.1, 136.2, 136.7, 143.4; HRMS for M+1 found m/e 614.2352, calcd for $C_{39}H_{36}NO_4S$: 614.2365. $[\alpha]_D^{26} = 92.47$ (c 2.03, $CHCl_3$). Ee was determined by HPLC analysis using Daicel Chiralcel AD-H: (eluent: 20% 2-propanol in hexane, retention time: 12 min for major isomer and 6 min for minor isomer).

2,3-Dihydro-4,7-di(naphthalen-1-yl)-2,2-bis(ethoxycarbonyl)-5,6-bis(methoxymethyl)-1H-indene (3fa). White solid. mp 53-56 °C; IR ($CHCl_3$) 1731, 1095, 738 cm^{-1} ; 1H NMR δ = 1.05 (t, J = 7.1Hz, 6H), 2.99 (d, J = 16.8Hz, 2H), 3.03 (s, 6H), 3.24 (d, J = 16.8Hz, 2H), 3.91-4.08 (m, 4H), 3.95 (d, J = 9.8Hz, 2H), 4.41 (d, J = 9.8Hz, 2H), 7.37-7.61 (m, 10H), 7.90-

7.93 (m, 4H). ^{13}C NMR δ = 14.0, 40.3, 58.4, 59.8, 61.5, 69.3, 125.3, 125.7, 126.0, 126.0, 127.2, 127.6, 128.0, 131.7, 133.4, 135.5, 136.5, 137.4, 139.9, 171.1; HRMS for M+1 found m/e 603.2712, calcd for $\text{C}_{39}\text{H}_{39}\text{O}_6$: 603.2747. $[\alpha]_{\text{D}}^{27}$ = 129.46 (c 2.16, CHCl_3). Ee was determined by HPLC analysis using Daicel Chiralcel AD-H: (eluent: 2% 2-propanol in hexane, retention time: 8 min for major isomer and 9 min for minor isomer).

2,3-Dihydro-4,7-di(naphthalen-1-yl)-5,6-bis(methoxymethyl)-1H-indene (3ga). White solid. mp 160 °C (Hexane); IR (CHCl_3) 1215, 756 cm^{-1} ; ^1H NMR δ = 1.78 (dd, J = 15.0, 7.5Hz, 1H), 1.80 (dd, J = 15.0, 7.5Hz, 1H), 2.34-2.44 (m, 2H), 2.47-2.57 (m, 2H), 3.04 (s, 6H), 4.00 (d, J = 9.6Hz, 2H), 4.44 (d, J = 9.6Hz, 2H), 7.36-7.60 (m, 10H), 7.88-7.93 (m, 4H). ^{13}C NMR δ = 24.7, 32.9, 58.3, 69.5, 125.2, 125.6, 125.8, 126.3, 127.1, 127.3, 128.0, 131.8, 133.3, 134.5, 137.3, 137.5, 143.8. Anal. Calcd for $\text{C}_{33}\text{H}_{30}\text{O}_2$; C, 86.43; H, 6.59. Found: C, 86.13; H, 6.63. $[\alpha]_{\text{D}}^{27}$ = 67.52 (c 1.75, CHCl_3). Ee was determined by HPLC analysis using Daicel Chiralcel AD-H: (eluent: 2% 2-propanol in hexane, retention time: 10 min for major isomer and 9 min for minor isomer).

5,6-Bis(tert-butyldimethylsiloxymethyl)-2,3-dihydro-4,7-di(naphthalen-1-yl)-1H-indene (3gc). White solid. mp 75-77 °C; IR (CHCl_3) 1255, 775 cm^{-1} ; ^1H NMR δ = -0.52 (s, 6H), -0.39 (s, 6H), 0.69 (s, 18H), 1.76 (dd, J = 15.0, 7.5Hz, 1H), 1.79 (dd, J = 15.0, 7.5Hz, 1H), 2.34-2.42 (m, 2H), 2.46-2.56 (m, 2H), 4.43 (d, J = 10.5Hz, 2H), 4.54 (d, J = 10.5Hz, 2H), 7.36-7.59 (m, 10H), 7.85-7.91 (m, 4H). ^{13}C NMR δ = -6.0, -5.8, 18.3, 24.7, 25.9, 32.8, 59.9, 125.2, 125.5, 125.7, 126.6, 127.1, 127.2, 127.9, 132.2, 133.5, 136.6, 136.7, 138.0, 143.0; HRMS for M-1 found m/e 657.3607, calcd for $\text{C}_{43}\text{H}_{53}\text{O}_2\text{Si}_2$: 657.3584. $[\alpha]_{\text{D}}^{27}$ = 16.9 (c 2.75, CHCl_3).

2',3'-Dimethoxymethyl-1,1':4',1''-ter-5',8'-dihydronaphthalene (3ha). IR (CHCl_3) 1094, 756 cm^{-1} ; ^1H NMR δ = 2.68-2.77 (m, 2H), 2.95-3.04 (m, 2H), 2.96 (s, 6H), 3.83 (d, J = 9.8Hz, 2H), 4.34 (d, J = 9.8Hz, 2H), 5.52 (s, 2H), 7.36-7.61 (m, 10H), 7.89-7.93 (m, 4H). ^{13}C NMR δ = 29.1, 58.4, 69.6, 123.8, 125.3, 125.7, 126.0, 126.1, 127.4, 127.4, 128.0, 132.1, 133.3, 133.3, 134.2, 137.4, 140.2; HRMS for M found m/e 471.2306, calcd for $\text{C}_{34}\text{H}_{31}\text{O}_2$: 471.2324. $[\alpha]_{\text{D}}^{28}$ = -41.02 (c 1.49, CHCl_3).

1,3-Dihydro-4,7-di(naphthalen-1-yl)-5,6-bis(hydroxymethyl)isobenzofuran (4a). White solid. mp 278-280 °C; IR (CHCl_3) 3391, 1070, 748 cm^{-1} ; ^1H NMR δ = 2.89 (s, 2H), 4.45 (d, J = 12.0Hz, 2H), 4.54 (d, J = 12.0Hz, 2H), 4.63 (d, J = 11.1Hz, 2H), 4.81 (d, J = 11.1Hz, 2H), 7.41-7.60 (m, 10H), 7.91-7.949 (m, 4H). ^{13}C NMR δ = 60.4, 74.1, 125.2, 125.4, 126.1, 126.6, 126.8, 128.2, 128.5, 131.5, 133.6, 134.1, 135.7, 138.7, 138.9; HRMS for M-1 found m/e 431.1609, calcd for $\text{C}_{30}\text{H}_{23}\text{O}_3$: 431.1647. $[\alpha]_{\text{D}}^{29}$ = 27.38 (c 0.44, CHCl_3). Ee was determined by HPLC analysis using Daicel Chiralcel AD-H: (eluent: 10% 2-propanol in hexane, retention time: 14 min for major isomer and 12 min for minor isomer).

1,3-Dihydro-4,7-di(naphthalen-1-yl)-5,6-bis(hydroxymethyl)-2-tosylisoindoline (4e). White solid. mp 178-179 °C; IR (neat) 3345, 1347, 1161, 800, 776, 768 cm^{-1} ; ^1H NMR δ = 2.39 (s, 3H), 2.80 (s, 2H), 4.11 (d, J = 12.9Hz, 2H), 4.30 (d, J = 12.9Hz, 2H), 4.36 (d, J = 12.3Hz, 2H), 4.46 (d, J = 12.0Hz, 2H), 7.18-7.21 (m, 2H), 7.32-7.46 (m, 8H), 7.50-7.59 (m, 4H), 7.93-7.96 (m, 4H); ^{13}C NMR δ = 21.6, 54.1, 60.3, 124.9, 125.5, 126.2, 126.6, 126.8, 127.2, 128.5, 128.6, 129.6, 131.3, 133.5, 133.6, 134.9, 135.5, 136.0, 139.1, 143.4; Anal. Calcd for $\text{C}_{37}\text{H}_{32}\text{N}_2\text{O}_4\text{S}$; C, 75.87; H, 5.33; N, 2.39. Found: C, 75.77; H, 5.56; N, 2.14. $[\alpha]_{\text{D}}^{26}$ = 98.71 (c 1.57, CHCl_3). Ee was determined by HPLC analysis using Daicel Chiralcel AD-H: (eluent: 20% 2-propanol in hexane, retention time: 17 min for major isomer and 12 min for minor isomer).

2,3-Dihydro-4,7-di(naphthalen-1-yl)-5,6-bis(hydroxymethyl)-1H-indene (4g). White solid. mp 148-151 °C; IR (neat) 3332, 1007, 780 cm^{-1} ; ^1H NMR δ = 1.81 (dd, J = 15.0, 7.5Hz,

1H), 1.84 (dd, $J = 15.0, 7.5\text{Hz}$, 1H), 2.36-2.46 (m, 2H), 2.53-2.64 (m, 2H), 2.74 (s, 2H), 4.41 (d, $J = 12.0\text{Hz}$, 2H), 4.51 (d, $J = 12.0\text{Hz}$, 2H), 7.39-7.61 (m, 10H), 7.89-7.94 (m, 4H). ^{13}C NMR $\delta = 24.5, 32.9, 60.9, 125.5, 125.6, 125.8, 126.2, 126.9, 127.6, 128.3, 132.0, 133.6, 136.6, 137.0, 137.3, 143.7$; HRMS for M found m/e 430.1900, calcd for $\text{C}_{31}\text{H}_{26}\text{O}_2$: 430.1933. $[\alpha]_{\text{D}}^{28} = 31.07$ (c 1.13, CHCl_3). Ee was determined by HPLC analysis using Daicel Chiralcel AD-H: (eluent: 2% 2-propanol in hexane, retention time: 51 min for major isomer and 47 min for minor isomer).

2',3'-Dimethoxymethyl-1,1':4',1''-ternaphthalene (5ha). White solid. mp 191-193 °C (Hexane); IR (CHCl_3) 1215, 756 cm^{-1} ; ^1H NMR $\delta = 3.09$ (s, 6H), 4.12 (d, $J = 9.9\text{Hz}$, 2H), 4.56 (d, $J = 9.9\text{Hz}$, 2H), 7.14-7.36 (m, 8H), 7.46-7.51 (m, 2H), 7.59-7.68 (m, 4H), 7.95-8.01 (m, 4H). ^{13}C NMR $\delta = 58.5, 70.1, 125.2, 125.8, 125.9, 126.0, 126.7, 127.2, 127.8, 127.9, 128.6, 132.9, 133.1, 133.3, 133.8, 136.4, 139.2$; HRMS for M found m/e 468.2095, calcd for $\text{C}_{34}\text{H}_{28}\text{O}_2$: 468.2089. $[\alpha]_{\text{D}}^{28} = 6.89$ (c 0.96, CHCl_3). Ee was determined by HPLC analysis using Daicel Chiralcel AD-H: (eluent: 2% 2-propanol in hexane, retention time: 5.5 min for major isomer and 6.3 min for minor isomer). The CD spectrum of **5ha** prepared by (*S,S*)-MeDUPHOS showed a negative first Cotton effect at 293 nm and a positive second Cotton effect at 265 nm, therefore, the product has negative chirality and its absolute configuration was determined to be the *S,S*-form.

A scheme for the preparation of diyne 6

4,4-Bis(ethoxycarbonyl)-1-(2-methylphenyl)octa-1,6-diyne (6). Diyne 6 was prepared by stepwise alkylation of diethyl malonate IR (CHCl_3) 1738 cm^{-1} ; ^1H NMR $\delta = 1.26$ (t, $J = 7.1\text{Hz}$, 6H), 1.76 (t, $J = 2.6\text{Hz}$, 3H), 2.38 (s, 3H), 2.98-2.99 (m, 2H), 3.23 (s, 2H), 4.23 (q, $J = 7.2\text{Hz}$, 4H), 7.04-7.33 (m, 4H). ^{13}C NMR $\delta = 3.6, 14.1, 20.8, 23.2, 23.8, 57.0, 61.8, 73.2, 79.0, 82.3, 88.1, 122.9, 125.3, 127.8, 129.2, 131.9, 140.0, 169.0$; HRMS for M+1 found m/e 341.1751, calcd for $\text{C}_{21}\text{H}_{24}\text{O}_4$: 341.1753.

2,3-Dihydro-2,2-bis(ethoxycarbonyl)-5,6-bis(methoxymethyl)-4-methyl-7-(2-methylphenyl)-1H-indene (7). White solid. mp 82-83 °C (Hexane); IR (CHCl_3) 1733 cm^{-1} ; ^1H NMR $\delta = 1.20$ (t, $J = 7.1\text{Hz}$, 6H), 2.01 (s, 3H), 2.34 (s, 3H), 3.11 (s, 2H), 3.12 (s, 3H), 3.45 (s, 3H), 3.59 (s, 2H), 4.01 (d, $J = 10.2\text{Hz}$, 1H), 4.10-4.18 (m, 4H), 4.21 (d, $J = 10.2\text{Hz}$, 1H), 4.53 (d, $J = 10.5\text{Hz}$, 1H), 4.59 (d, $J = 10.5\text{Hz}$, 1H), 7.01-7.26 (m, 4H). ^{13}C NMR $\delta = 14.1, 15.8, 19.9, 40.3, 40.4, 58.2, 58.6, 59.6, 61.6, 68.6, 69.2, 125.4, 127.2, 129.3, 129.6, 133.4, 133.7, 134.7, 136.1, 136.2, 138.5, 138.9, 138.4, 171.4, 171.5$; Anal. Calcd for $\text{C}_{27}\text{H}_{34}\text{O}_6$; C, 71.34; H, 7.54. Found: C, 71.27; H, 7.56. $[\alpha]_{\text{D}}^{26} = 2.51$ (c 1.54, CHCl_3). Ee was determined by HPLC analysis using Daicel Chiralcel AD-H: (eluent: 2% 2-propanol in hexane, retention time: 10 min for major isomer and 9 min for minor isomer).

¹H-NMR

1a

STANDARD 1H OBSERVE

Pulse Sequence: #2pul

Solvent: CDCl3

Ambient temperature

Mercury-300 #smat2

DATA PROCESSING

PT size 65536

Total time 1 minute

OBSERVE H1, 300.0706299

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 3.200 sec

Width 5402.5 Hz

8 repetitions

¹³C-NMR

1a

¹H-NMR

1b

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "schar2"

DATA PROCESSING
FT size 65516
Total time 1 minute

OBSERVE H1, 300.0706307

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degree
Acq. time 2.200 sec
Width 5402.5 Hz
8 repetitions

¹³C-NMR

1b

13C OBSERVE

Pulse Sequence: #2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 *acnhr2*

DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 12 minutes

OBSERVE C13, 75.4528235
DECOUPLE H1, 300.0720883
Power 40 dB
continuously on
WALTZ-16 modulated

PULSE SEQUENCE
Relax. delay 1.185 sec
Pulse 45.0 degrees
Acq. time 1.015 sec
Width 18761.7 Hz
256 repetitions

¹H-NMR

1c

2-Cl-Ph
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "acmar2"

DATA PROCESSING
FT size 6556
Total time 1 minute

OBSERVE H1, 300.076284

PULS2 SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5402.5 Hz
8 repetitions

¹³C-NMR

1c

13C OBSERVE
Pulse Sequence: zgpg30
Solvent: CDCl3
Ambient temperature
Mercury-300 -samar2-

DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 6 minutes

OBSERVE C13, 75.4328232
DECOUPLE H1, 300.0720883
Power 40 dB
Continuously on
WALTZ-16 modulated
128 repetitions

PULSE SEQUENCE
Relax. delay 1.185 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
128 repetitions

¹H-NMR

1d

MeO-Np SUB
Pulse Sequence: #2pul
Solvent: CDCl₃
Ambient temperature
Mercury-300 "acnar2"

DATA PROCESSING
F2 size 65536
Total time 1 minute

OBSERVE H1, 300.0706295

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5402.5 Hz
8 repetitions

¹³C-NMR

1d

MeO-Np SUB
Pulse Sequence: a2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "semar2"

DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 9 minutes

OBSERVE C13, 75.4528229
DECOUPLE H1, 300.0720803
power 40 dB
continuously on
WALTZ-16 modulated

PULSE SEQUENCE
Relax. delay 1.185 sec
Pulse 45.0 degrees
Acq. time 1.015 sec
Width 10761.7 Hz
132 repetitions

1e

T8N-Np
 Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 Mercury-300 "scmr2"

DATA PROCESSING
PT size 65536
Total time 1 minute

OBSERVE H1, 300.0706304

PULSE SEQUENCE

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 3.200 sec

Width 5402.5 Hz

8 repetitions

¹³C-NMR

1e

TM-NP
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 *schm2*

DATA PROCESSING
Time broadening 1.0 Hz
FT size 131072
Total time 9 minutes

OBSERVE C13, 75.4528241
DECOUPLE H1, 300.0720883
Power 40 dB
continuously on
WALTZ-16 modulated

PULS2 SEQUENCE
Relax. delay 1.185 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
192 repetitions

¹H-NMR

1f

E-1p, sub
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
Mercury-100 "schar2"

DATA PROCESSING
F1 size 65536
Total time 1 minute

OBSERVE H1, 300.0706279

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degree
Acq. time 3.200 sec
Width 5402.5 Hz
8 repetitions

¹³C-NMR

1f

S-Np. sub
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "acmr2"

DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 6 minutes

OBSERVE C13, 75.4528235
DECOUPLE H1, 300.0720881
Power 40 dB
continuously on
WALTZ-16 modulated

PULSE SEQUENCE
Relax. delay 1.185 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
128 repetitions

¹H-NMR

19

0.000

1.542

1.540

2.096

2.120

2.143

2.873

2.849

7.246

7.369

7.393

7.396

7.420

7.483

7.487

7.509

7.244

7.511

7.515

7.539

7.543

7.628

7.631

7.652

7.766

7.793

7.809

7.815

7.839

8.345

8.373

ppm

0

1

2

3

4

5

6

7

8

9

9.12

10.39

18.72

8.02

5.02

16.38

24.31

8.04

C-4p SUB
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
Mercury-300 "acnmr2"

DATA PROCESSING
Ft size 65516
Total time 1 minute

OBSERVE H1, 300.0706281

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5402.5 Hz
8 repetitions

¹³C-NMR

1g

13C OBSERVE

Pulse Sequence: a2pul
Solvent: CDCl3
Ambient temperature
Mercury-100 "wcnar2"

DATA PROCESSING

Line broadening 1.0 Hz
FT size 131072
Total time 6 minutes

OBSERVE CL3, 75.4528238

DECOUPLE H1, 300.0720883

Power 40 dB
continuously on
WALTZ-16 modulated

PULSE SEQUENCE

Relax. delay 1.185 sec
Pulse 45.0 degrees
Acq. time 1.915 sec
Width 18761.7 Hz
128 repetitions

¹H-NMR

1h

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5402.5 Hz
8 repetitions

DATA PROCESSING
FI size 65536
Total time 1 minute

OBSERVE H1, 300.0706276

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "acnmt2"

¹³C-NMR

1h

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
Mercury-300 "echm2"

DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 6 minutes

OBSERVE C13, 75.4520244
DECOUPLE H1, 300.0720883
Power 40 dB
continuously on
WALTZ-16 modulated

PULSE SEQUENCE
Relax delay 1.185 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
128 repetitions

¹H-NMR

3ac

Pulse Sequence: e2pul
Solvent: CDCl₃
Ambient temperature
Mercury-300 "acmar2"

DATA PROCESSING
File: 65536
Total time: 1 minute

OBSERVE H1, 300.0706322

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5402.5 Hz
8 repetitions

¹³C-NMR

3ac

TBS
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "acnmf2"

DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 3 minutes

OBSERVE C13, 75.4528238
DECOUPLE H1, 300.0720883
Power 40 dB
continuously on
WALTZ-16 modulated

PULSE SEQUENCE
Relax. delay 1.185 sec
Pulse 45.0 degree
Acq. time 1.935 sec
Width 19761.7 Hz
64 repetitions

¹H-NMR

3ad

NAME: 3ad
Pulse Sequence: zgpg30
Solvent: CDCl3
Ambient temperature
Mercury-300 "sonar2"

DATA PROCESSING
PT size 65536
Total time 1 minute

OBSERVE W1, 300.0706292

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5402.5 Hz
8 repetitions

¹³C-NMR

3ad

NAME: 3ad
Pulse Sequence: zgpg30
Solvent: CDCl3
Ambient temperature
Mercury-300 "acnmc2"

DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 3 minutes

OBSERVE: C13, 75.4528241
DECOUPLE: H1, 300.0720803
Power 40 dB
continuously on
WALTZ-16 modulated

PULSE SEQUENCE
Relax. delay 1.185 sec
Pulpro 45.0 degree
Acq. time 1.815 sec
Width 18761.7 Hz
64 repetitions

¹H-NMR

3ea

TsN-Hp-Product
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 -acmr2-

DATA PROCESSING
F1 size 65516
Total time 1 minute

101 OBSERVE H1, 300.0706304

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.200 sec
Width 5402.5 Hz
8 repetitions

¹³C-NMR

3ea

13C OBSERVE

Pulse Sequence: a2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 *acnmt2-

DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 9 minutes

OBSERVE C13, 75.4528250
DECOUPLE H1, 300.0720803
Power 40 dB
continuously on
WALTZ-16 modulated

PULSE SEQUENCE
Relax. delay 1.185 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
192 repetitions

COCC1=C(C2=CC=CC=C3C=CC=CC=C32)C(=C(C4=CC=CC=C5C=CC=CC=C54)C6=CC=CC=C7C=CC=CC=C76)C1(C(=O)OCC)C(=O)OCC

3fa

PULSE SEQUENCE

PULSE SEQUENCE

Pulse 45.0 degrees

Acq. time 3.200 sec

Width 5402.5 H

8 repetitions

OBSERVE 11, 300.0706302

DATA PROCESSING

DATA PROCESSING
FT size 65536

Total time 1 minute

E-Np product

Pulse Sequence: s2pul

Solvent: CDCl₃

Ambient temperature

МФРСУ-100 "Ясний 2"™

Chemical structure of compound 1: A central cyclopentane ring substituted with two naphthalen-1-yl groups and two (2-methoxyethyl)carbamoyl groups.

13.955

399

CS-TBS
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "scmr2"

DATA PROCESSING
FT size 65536
Total time 1 minute

OBSERVE W1, 100.0706J35

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5402.5 Hz
8 repetitions

CS-TBS
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "scmr2"

DATA PROCESSING
Line broadening 1.0 Hz
FFT size 131072
Total time 3 minutes

OBSERVE C10, 75.4528235
DECOUPLE H1, 300.0720883
Power 40 dB
continuously on
WALTZ-16 modulated

PULSE SEQUENCE

Relax. delay 1.185 sec

Pulse 45.0 degrees

Acq. time 1.815 sec

Width 18761.7 Hz

64 repetitions

3ha

STANDARD III OBSERVE

Pulse Sequence: zgpg30
Solvent: CDCl₃
Ambient temperature
Mercury-300 "acnmr2"

DATA PROCESSING
FT size 65536
Total time 1 minute

OBSERVE H1, 300.0706309

PULSE SEQUENCE

Relax. delay 1.00 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5402.5 Hz
8 repetitions

¹³C-NMR

3ha

13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
Mercury-300 *acnhr2*

DATA PROCESSING

Line broadening 1.0 Hz
FT size 131072
Total time 3 minutes

OBSERVE C13, 75.4528238
DECOUPLE H1, 300.0720883
Power 40 dB
continuously on
WALTZ-16 modulated

PULSE SEQUENCE

Relax. delay 1.185 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
64 repetitions

¹H-NMR

4a

¹³C-NMR

4a

THP-OH, MeDPHOS
Pulse Sequence: a2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "acnmr2"

DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 6 minutes

OBSERVE C13, 75.4520212
DECOUPLE H1, 300.0720803
Power 40 dB
continuously on
WALTZ-16 modulated

PULSE SEQUENCE
Relax. delay 1.185 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
128 repetitions

¹H-NMR

4g

C5-OH.chiral
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 *acnmr2

DATA PROCESSING
F1 size 65536
Total time 1 minute

OBSERVE H1. 300.0706297

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degree
Acq. time 3.200 sec
Width 5402.5 Hz
8 repetitions

¹³C-NMR

4g

¹³C OBSERVE

DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 6 minutes

OBSERVE C13, 75.4526232
DECOUPLE H1, 300.0720883
Power 40 dB
continuously on
WALTZ-16 modulated

PULSE SEQUENCE
Relax. delay 1.185 sec
Pulse 45.0 degree
Acq. time 1.815 sec
Width 18761.7 Hz
128 repetitions

Pulse Sequence: #2pul
Solvent: CDCl3
Ambient temperature
Mercury.300 "acnmar2"

¹H-NMR

5ha

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "gcnmr2"

DATA PROCESSING
FT size 65516
Total time 1 minute

OBSERVE H1, 300.0706304

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5402.5 Hz
8 repetitions

¹³C-NMR

5ha

PULSE SEQUENCE
Relax. delay 1.185 sec
Pulse 45.0 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
64 repetitions

DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 3 minutes

OBSERVE C13, 75.4528235
DECOUPLE U1, 100.0720803
Power 40 dB
continuously on
WALTZ-16 modulated

¹³C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "ecnmr2"

¹H-NMR

6

STANDARD 1H OBSERVE

DATA PROCESSING
PT size 65536
Total time 1 minute

OBSERVE M1, 300.0771417

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.200 sec
Width 5402.5 Hz
8 repetitions

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury.300 "acnmc2"

¹³C-NMR

6

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300 "ecnmz2"

DATA PROCESSING
Line broadening 1.0 Hz
PT size 131072
Total time 9 minutes

OBSERVE c13, 75.4528229
DECOUPLE H1, 100.0720803
Power 40 dB
continuously on
WALTZ-16 modulated

PULSE SEQUENCE
Relax. delay 1.185 sec
Pulse 45.0 degree
Acq. time 1.815 sec
Width 18761.7 Hz
192 repetitions