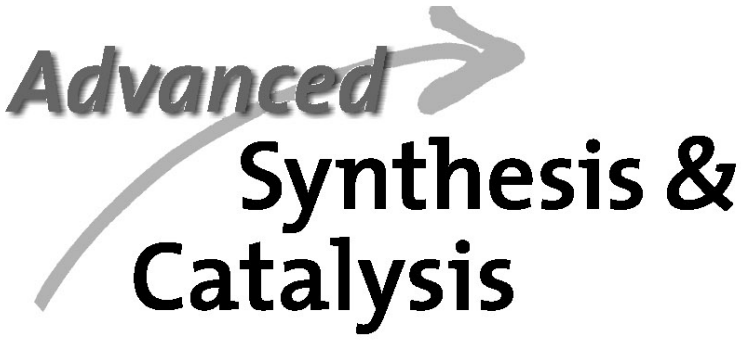

Supporting Information

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Supporting Information

Iridium-Catalyzed Enantioselective [2+2+2] Cycloaddition of Diynes and Monoalkynes for the Generation of Axial Chiralities

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General. IR spectra were recorded with Horiba FT730 spectrophotometer. NMR spectra were measured with JEOL AL-400 and Lambda500 spectrometers using tetramethylsilane as an internal standard and $CDCl_3$ was used as a solvent. Mass spectra were measured with JEOL JMS-SX102A and elemental analyses with Perkin Elmer PE2400II. Optical rotation was measured with Jasco DIP-1000 polarimeter.

Spectral data of diynes **1a-1d** and cycloadduct **3aa**, **3ab-3cb** were already reported in the supporting information of our preceding communication.[1] Monoalkynes **2a-2c** are commercially available.

Diethyl 1-(naphthalen-1-yl)octa-1,6-diyne-4,4-dicarboxylate (1e). Yellow oil. IR (neat) 1738, 1207, 802, 775 cm^{-1}, ^1H NMR δ = 1.28 (t, *J* = 7.2 Hz, 6H), 1.79 (t, *J* = 2.4 Hz, 3H), 3.07 (s, 2H), 3.35 (s, 2H), 4.27 (q, *J* = 7.2 Hz, 4H), 7.37-7.41 (m, 1H), 7.48-7.58 (m, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR δ = 3.5, 14.1, 23.3, 23.9, 57.1, 61.9, 73.2, 79.1, 81.5, 89.2, 120.9, 125.1, 126.2, 126.3, 126.6, 128.2, 128.4, 130.4, 133.1, 133.4, 169.2; HRMS (FAB) for M found m/z 376.1692, calcd for $C_{24}H_{24}O_4$: 376.1675.

Diethyl 1-(naphthalen-1-yl)-7-trimethylsilylhepta-1,6-diyne-4,4-dicarboxylate (1f). Yellow oil. IR (neat) 1739, 847 cm^{-1}, ^1H NMR δ = 0.16 (s, 9H), 1.28 (t, *J* = 7.0 Hz, 6H), 3.15 (s, 2H), 3.35 (s, 2H), 4.26 (q, *J* = 7.0 Hz, 4H), 7.26-7.40 (m, 1H), 7.48-7.50 (m, 2H), 7.61 (d, *J* = 1.2 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR δ = -0.0, 14.1, 23.9, 24.3, 57.0, 62.0, 81.6, 88.4, 89.1, 101.1, 120.9, 125.1, 126.2, 126.3, 126.6, 128.2, 128.4, 130.5, 133.1, 133.4, 168.9; HRMS (FAB) for M + 1 found m/z 435.1978, calcd for $C_{26}H_{31}O_4Si$: 435.1992.

Diethyl 1-(naphthalen-1-yl)-7-phenylhepta-1,6-diyne-4,4-dicarboxylate (1g). Yellow oil. IR

(neat) 1736, 802, 734 cm^{-1}, ^1H NMR δ = 1.29 (t, *J* = 7.0 Hz, 6H), 3.35 (s, 2H), 3.43 (s, 2H), 4.29 (q, *J* = 7.0 Hz, 4H), 7.27-7.30 (m, 3H), 7.37-7.41 (m, 3H), 7.48-7.61 (m, 2H), 7.63 (d, *J* = 1.2 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR δ = 14.1, 23.9, 24.1, 57.2, 62.0, 81.7, 83.8, 84.1, 89.1, 120.9, 123.2, 125.1, 126.2, 126.3, 126.7, 128.0, 128.2, 128.2, 128.4, 130.5, 131.7, 133.1, 133.4, 169.0; HRMS (FAB) for M + 1 found m/z 439.1932, calcd for $C_{29}H_{27}O_4$: 439.1909.

Diethyl 1-(2-methylphenyl)hepta-1,6-diyne-4,4-dicarboxylate (1h). Yellow oil. IR ($CHCl_3$) 2124, 1740, 1210, 1191, 760 cm^{-1}, ^1H NMR δ = 1.27 (t, *J* = 7.2 Hz, 6H), 2.04 (t, *J* = 2.7 Hz, 1H), 2.38 (s, 3H), 3.06 (d, *J* = 2.7 Hz, 2H), 3.25 (s, 2H), 4.24 (q, *J* = 7.2 Hz, 4H), 7.06-7.20 (m, 3H), 7.33 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR δ = 14.1, 20.7, 22.8, 23.7, 56.6, 62.0, 71.6, 78.6, 82.5, 87.6, 122.7, 125.3, 127.9, 129.2, 131.9, 139.9, 168.6; HRMS (FAB) for M + 1 found m/z 327.1595, calcd for $C_{20}H_{23}O_4$: 327.1596.

Diethyl 1-(2-methoxyphenyl)hepta-1,6-diyne-4,4-dicarboxylate (1i). Yellow oil. IR ($CHCl_3$) 2244, 2126, 1740, 1212, 1192, 754 cm^{-1}, ^1H NMR δ = 1.27 (t, *J* = 7.2 Hz, 6H), 2.03 (t, *J* = 2.4 Hz, 1H), 3.08 (d, *J* = 2.4 Hz, 2H), 3.25 (s, 2H), 3.84 (s, 3H), 4.47 (q, *J* = 7.2 Hz, 4H), 6.81-6.88 (m, 2H), 7.21-7.33 (m, 2H); ^{13}C NMR δ = 14.1, 22.7, 23.9, 55.7, 56.8, 62.0, 71.5, 78.8, 79.9, 88.0, 110.5, 112.2, 120.2, 129.2, 133.4, 159.9, 168.6; HRMS (FAB) for M + 1 found m/z 343.1560, calcd for $C_{20}H_{23}O_5$: 343.1545.

Diethyl 1-(2-chlorophenyl)hepta-1,6-diyne-4,4-dicarboxylate (1j). Yellow oil. IR ($CHCl_3$) 2240, 2126, 1740, 1210, 1193, 756 cm^{-1}, ^1H NMR δ = 1.27 (t, *J* = 7.2 Hz, 6H), 2.05 (t, *J* = 2.7 Hz, 1H), 3.09 (d, *J* = 2.7 Hz, 2H), 3.27 (s, 2H), 4.24 (q, *J* = 7.2 Hz, 4H), 7.13-7.23 (m, 2H), 7.33-7.41 (m, 2H); ^{13}C NMR δ = 14.1, 22.8, 23.7, 56.6, 62.1, 71.6, 78.6, 80.4, 89.5, 122.8, 126.2, 128.9, 129.0, 133.3, 135.7, 168.5; HRMS (FAB) for M + 1 found m/z 347.1048, calcd for $C_{19}H_{20}ClO_4$: 347.1050.

Diethyl 1-(naphthalen-1-yl)hepta-1,6-diyne-4,4-dicarboxylate (1k). Yellow oil. IR ($CHCl_3$) 2236, 2126, 1738, 1206, 1193, 801, 775 cm^{-1}, ^1H NMR δ = 1.28 (t, *J* = 7.2 Hz, 6H), 2.08 (t, *J* = 2.7 Hz, 1H), 3.14 (d, *J* = 2.7 Hz, 2H), 3.38 (s, 2H), 4.27 (q, *J* = 7.2 Hz, 4H), 7.34-7.40 (m, 1H), 7.45-7.61 (m, 3H), 7.76-7.82 (m, 2H), 8.23-8.26 (m, 1H); ^{13}C NMR δ = 14.2, 23.0, 24.0, 56.7, 62.1, 71.7, 78.6, 81.7, 88.7, 120.6, 125.0, 126.0, 126.2, 126.6, 128.1, 128.4, 130.4, 133.0, 133.2, 168.7; HRMS (FAB) for M + 1 found m/z 363.1571, calcd for $C_{23}H_{23}O_4$: 363.1596.

Diethyl 1-(4-methylnaphthalen-1-yl)hepta-1,6-diyne-4,4-dicarboxylate (1l). Pale yellow solid. mp 41 °C; IR ($CHCl_3$) 2222, 2126, 1738, 1210, 1193, 835, 760 cm^{-1}, ^1H NMR δ = 1.27 (t, *J* = 7.2 Hz, 6H), 2.08 (t, *J* = 2.6 Hz, 1H), 2.96 (s, 3H), 3.13 (d, *J* = 2.6 Hz, 2H), 3.36 (s, 2H), 4.26 (q, *J* = 7.2 Hz, 4H), 7.20-7.23 (m, 1H), 7.48-7.58 (m, 3H), 7.93-7.99 (m, 1H), 8.25-8.31 (m, 1H); ^{13}C NMR δ = 14.2, 19.7, 23.0, 24.0, 56.8, 62.1, 71.7, 78.7, 81.9, 88.0, 118.9, 124.2, 125.9, 126.0, 126.2, 126.6,

130.2, 132.1, 133.2, 135.1, 168.7; HRMS (FAB) for M found m/z 376.1698, calcd for $C_{24}H_{24}O_4$: 376.1675.

Diethyl 1-(4-methoxynaphthalen-1-yl)hepta-1,6-diyne-4,4-dicarboxylate (1m). Yellow oil. IR ($CHCl_3$) 2224, 2128, 1738, 1210, 1193, 820, 766 cm^{-1}, ^1H NMR δ = 1.28 (t, *J* = 7.2 Hz, 6H), 2.07 (t, *J* = 2.6 Hz, 1H), 3.13 (d, *J* = 2.6 Hz, 2H), 3.35 (s, 2H), 3.99 (s, 3H), 4.26 (q, *J* = 7.2 Hz, 4H), 6.72 (d, *J* = 8.1 Hz, 1H), 7.53 (m, 3H), 8.21 (m, 2H); ^{13}C NMR δ = 14.2, 23.0, 24.0, 55.6, 56.8, 62.1, 71.7, 78.7, 81.8, 86.8, 103.3, 112.8, 122.0, 125.1, 125.5, 125.8, 127.0, 130.9, 134.1, 155.6, 168.8; HRMS (FAB) for M found m/z 392.1636, calcd for $C_{24}H_{24}O_5$: 392.1624.

1,4-Bis(*N*-acetyl-*N*-benzylamino)but-2-yne (2d). White solid. mp 88-89 °C. IR (neat) 1645 cm^{-1}, ^1H NMR δ = 2.14, 2.16, 2.18, 2.20 (4 x s, 6H), 3.89, 3.91 (2 x s, 2H), 4.20, 4.22 (2 x s, 2H), 4.58, 4.60, 4.61 (2 x s, bs + br, 4H), 7.16-7.39 (m, 10H); ^{13}C NMR δ = 21.7, 21.7, 21.8, 21.8, 34.5, 34.6, 37.5, 37.6, 48.3, 48.5, 51.0, 51.3, 77.9, 78.7, 78.8, 79.5, 126.3, 126.3, 127.3, 127.5, 127.5, 127.7, 128.1, 128.4, 128.4, 128.7, 128.8, 135.8, 136.0, 136.5, 136.7, 170.1, 170.2, 170.3, 170.3; HRMS (FAB) for M + 1 found m/z 349.1896, calcd for $C_{22}H_{25}N_2O_2$: 349.1916.

1-(*N*-Acetyl-*N*-benzylamino)but-2-yne (2e). Yellow oil. IR (neat) 1652 cm^{-1}, ^1H NMR δ= 1.79, 1.81 (2 x t, *J* = 2.5, 2.2 Hz, 3H), 2.15, 2.23 (2 x s, 3H), 3.85, 4.17 (2 x q, *J* = 2.2, 2.5 Hz, 2H), 4.66, 4.66 (2 x s, 2H), 7.20-7.38 (m, 5H); ^{13}C NMR δ = 3.4, 3.5, 21.6, 34.5, 37.5, 47.9, 50.8, 73.4, 73.9, 79.6, 80.3, 126.4, 127.2, 127.5, 128.2, 128.4, 128.7, 136.3, 137.0, 170.3, 170.4; HRMS (FAB) for M + 1 found m/z 202.1206, calcd for $C_{13}H_{16}NO$: 202.1232.

1-(*N*-Methyl-*N*-tosylamino)but-2-yne (2f). Pale yellow solid. mp 49-50 °C, IR (neat) 1344, 1164 cm^{-1}, ^1H NMR δ = 1.59 (t, *J* = 2.5 Hz, 3 H), 2.43 (s, 3H), 2.79 (s, 3 H), 3.94 (m, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR δ = 3.2, 21.4, 34.3, 40.3, 71.5, 81.8, 128.0, 129.3, 134.3, 143.3; HRMS (FAB) for M + 1 found m/z 238.0921, calcd for $C_{12}H_{16}NO_2S$: 238.0902.

4-(*N*-methyl-*N*-tosylamino)but-2-yn-4-ol (2g). Yellow oil. IR (neat) 3514, 1336, 1161 cm^{-1}, ^1H NMR δ = 1.26 (br, 1H), 2.44 (s, 3H), 2.82 (s, 3H), 4.03 (br, 2H), 4.04 (s, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR δ = 21.4, 34.5, 40.0, 50.6, 78.2, 84.1, 128.0, 128.0, 129.4, 134.1, 134.2, 143.7; HRMS (FAB) for M + 1 found m/z 254.0817, calcd for $C_{12}H_{16}NO_3S$: 254.0851.

(But-2-ynyl)diphenylphosphine oxide (2h). White solid. mp 112 °C, IR (neat) 1439, 1203 cm^{-1}, ^1H NMR δ = 1.26 (t, *J* = 7.6 Hz, 3H), 2.44-2.50 (m, 2H), 7.44-7.55 (m, 6H), 7.81-7.86 (m, 4H); ^{13}C NMR δ = 12.6, 13.5, 73.5, 74.8, 110.6, 110.9, 128.4, 128.5, 130.8, 130.9, 132.0, 132.0, 132.8, 133.8; Anal. Calcd for $C_{16}H_{15}OP$; C, 75.58; H, 5.95. Found: C, 75.56; H, 6.10.

Crystal data for CH_2Cl_2 adduct of ferrocenyl diester of 3bb. $C_{60}H_{49}NO_6SCl_2Fe$, M = 1094.71, monoclinic, Space Group $P2_1$ (#4), a = 8.456(3) Å, b = 18.197(5) Å, c = 16.296(7) Å, β = 93.165(15)°, V = 2503.6(14) Å^3, T = 123 K, Z = 2, μ(MoKα) = 7.823 cm^{-1} Number of Reflections Measured: Total 23095, Unique: 10802 (R_{int} = 0.027), $R1$ = 0.0435, $wR2$ = 0.1136, Flack Parameter (Friedel Pairs = 4929) 0.000(12). CCDC 610351.

1,3-Dihydro-5,6-bis(hydroxymethyl)-4,7-bis(2-methylphenyl)isobenzofuran (3db). Yellow oil. IR ($CHCl_3$) 3330, 1098, 752cm^{-1}, ^{1}H NMR δ = 2.09 (s, 6H), 3.10 (s, 2H), 4.44 (d, J = 11.6 Hz, 2H), 4.50 (d, J = 11.6 Hz, 2H), 4.69 (d, J = 11.0 Hz, 2H), 4.80 (d, J = 11.0 Hz, 2H), 7.11 (d, J = 7.2 Hz, 2H), 7.19-7.28 (m, 6H); ^{13}C NMR δ = 20.1, 60.0, 74.2, 125.8, 127.8, 128.7, 130.1, 135.1, 135.7, 137.4, 137.6, 137.7; HRMS (FAB) for M - 1 found m/z 359.1656, calcd for $C_{24}H_{23}O_3$: 359.1647. $[\alpha]^{22}_D$ = 14.4 (*c* 2.34, $CHCl_3$, >99% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 5% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 18 min for major isomer and 27 min for minor isomer).

1,3-Dihydro-4,7-di(naphthalen-1-yl)-5-hydroxymethyl-6-methylisobenzofuran (3ac). White solid. mp 257 °C, IR (neat) 3441, 1054, 776 cm^{-1}, ^{1}H NMR δ = 1.29 (bs, 1H), 2.19 (s, 3H), 4.39 (d, J = 8.8 Hz, 1H), 4.49 (d, J = 8.8 Hz, 1H), 4.60-4.63 (m, 2H), 4.80 (d, J = 14.2 Hz, 1H), 4.86 (d, J = 14.2 Hz, 1H), 7.42-7.60 (m, 10H), 7.91-7.96 (m, 4H); ^{13}C NMR δ = 16.3, 60.3, 74.0, 74.2, 125.3, 125.4, 125.5, 125.9, 126.1, 126.2, 126.3, 126.5, 126.5, 127.8, 128.1, 128.3, 128.4, 131.1, 131.6, 133,4, 133.6, 133.6, 134.0, 136.2, 136.3, 136.6, 136.8, 137.1, 138.6; HRMS (FAB) for M found m/z 416.1794, calcd for $C_{30}H_{24}O_2$: 416.1776. $[\alpha]^{27}_D$ = 17.0 (*c* 0.27, $CHCl_3$, >99% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 5% 2-propanol in hexane, flow rate: 0.5 mL/min, retention time: 42 min for minor isomer and 48 min for major isomer).

1,3-Dihydro-4,7-di(naphthalen-1-yl)-5-hydroxymethyl-6-methyl-2-tosylisoindoline (3bc). Dark yellow solid. mp 239 °C, IR (neat) 3592, 1346, 1168, 804, 780, 739 cm^{-1}, ^{1}H NMR δ = 1.21 (bs, 1H), 2.13 (s, 3H), 2.41 (s, 3H), 4.10 (d, J = 13.6 Hz, 2H), 4.27-4.42 (m, 4H), 7.21-7.61 (m, 14H), 7,94-7.99 (m, 4H); ^{13}C NMR δ = 16.4, 21.6, 54.0, 54.2, 60.2, 125.0, 125.1, 125.4, 125.6, 126.1, 126.2, 126.3, 126.4, 126.5, 126.6, 127.3, 128.1, 128.4, 128.5, 128.6, 129.6, 131.0, 131.6, 133.4, 133.7, 133.7, 134.8, 135.4, 135.6, 135.7, 136.4, 137.2, 137.3, 143.3; HRMS (FAB) for M + 1 found m/z 570.2106, calcd for $C_{37}H_{32}NO_3S$: 570.2103. $[\alpha]^{21}_D$ = 81.9 (*c* 1.59, $CHCl_3$, 97% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 50% 2-propanol in hexane, flow rate: 0.5 mL/min, retention time: 11 min for minor isomer and 17 min for major isomer).

Crystal data for 3bc. $C_{37}H_{31}NO_3S$, M = 569.71, orthorhombic, Space Group $P2_12_12_1$ (#19), a = 9.8479(8) Å, b = 13.6222(13) Å, c = 22.0593(5) Å, V = 2959.3(4) Å^3, T = 123 K, Z = 4, μ (MoKα)

= 1.575 cm^{-1} Number of Reflections Measured: Total 27683, Unique: 6761 (R_{int} = 0.098), *R1* = 0.0479, *wR2* = 0.1298, Flack Parameter (Friedel Pairs = 2965) 0.00(8). CCDC 619290.

2,3-Dihydro-4,7-di(naphthalen-1-yl)-5-hydroxymethyl-6-methyl-1*H*-indene (3cc). White solid. mp 179 °C, IR (neat) 3421, 1016, 777 cm^{-1}, ^{1}H NMR δ = 0.96 (bs, 1H), 1.72-1.77 (m, 2H), 2.38 (s, 3H), 2.49-2.55 (m, 2H), 2.63-2.74 (m, 2H), 4.41 (d, *J* = 10.5 Hz, 1H), 4.51 (d, *J* = 10.5 Hz, 1H), 7.27-7.58 (m, 8H), 7.81-7.87 (m, 6H); ^{13}C NMR δ = 16.4, 24.5, 32.5, 32.9, 60.8, 125.5, 125.6, 125.8, 125.8, 125.9, 125.9, 126.0, 126.3, 126.6, 126.7, 127.3, 127.6, 128.3, 128.4, 131.8, 132.3, 133.7, 133.8, 134.7, 135.4, 136.1, 136.7, 138.2, 139.0, 141.0, 143.5; Anal. Calcd for $C_{31}H_{26}O$; C, 89.82; H, 6.32. Found: C, 89.54; H, 6.32. $[\alpha]^{22}_D$ = 49.4 (*c* 0.63, $CHCl_3$, 99% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 5%, 2-propanol in hexane, flow rate: 4.0 mL/min, retention time: 9 min for minor isomer and 10 min for major isomer).

5,6-Bis(*N*-benzyl-*N*-ethylaminomethyl)-1,3-dihydro-4,7-di(naphthalen-1-yl)isobenzofuran (3ad). *dl* Isomer: Pale yellow solid. mp 68-69 °C. IR (neat) 777, 736 cm^{-1}, ^{1}H NMR δ= 0.56 (t, *J* = 7.1 Hz, 6H), 2.08-2.28 (m, 4H), 3.16 (d, *J* = 13.5 Hz, 2H), 3.30 (d, *J* = 12.7 Hz, 2H), 3.49 (d, *J* = 13.5 Hz, 2H), 4.29 (d, *J* = 12.7 Hz, 2H), 4.54 (d, *J* = 11.1 Hz, 2H), 4.92 (d, *J* = 11.1 Hz, 2H), 7.13-7.37 (m, 11H), 7.46-7.62 (m, 9H), 7.92-7.96 (m, 4H); ^{13}C NMR δ = 11.3, 47.3, 52.3, 57.1, 74.3, 125.3, 125.6, 125.8, 126.2, 126.3, 126.9, 127.7, 127.9, 128.3, 128.5, 131.9, 133.5, 135.0, 137.2, 137.9, 138.3, 140.6; HRMS (FAB) for M + 1 found m/z 667.3679, calcd for $C_{48}H_{47}N_2O$: 667.3688. $[\alpha]^{22}_D$ = -94.3 (*c* 1.35, $CHCl_3$, >99% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak Doubly-arrayed AS-H: 4 x 250mm, 254nm UV detector, rt, eluent: 20% 2-propanol in hexane, flow rate: 0.3 mL/min, retention time: 22 min for major isomer and 26 min for minor isomer). ***meso* Isomer**: Pale yellow solid. mp 143-144 °C. IR (neat) 777, 736 cm^{-1}, ^{1}H NMR δ = 0.53 (t, *J* = 7.1 Hz, 6H), 2.06-2.19 (m, 4H), 3.20 (s, 4H), 3.70 (d, *J* = 12.8 Hz, 2H), 3.91 (d, *J* = 12.8 Hz, 2H), 4.60 (d, *J* = 10.5 Hz, 2H), 4.75 (d, *J* = 10.5 Hz, 2H), 6.99-7.01 (m, 4H), 7.14-7.22 (m, 6H), 7.37-7.43 (m, 4H), 7.51-7.58 (m, 6H), 7.91-7.97 (m, 4H); ^{13}C NMR δ = 11.5, 47.0, 52.5, 57.5, 74.2, 125.2, 125.8, 125.9, 126.2, 126.3, 127.0, 127.7, 127.8, 128.3, 128.5, 131.6, 133.6, 135.0, 137.3, 137.8, 138.3, 140.3; HRMS (FAB) for M + 1 found m/z 667.3696, calcd for $C_{48}H_{47}N_2O$: 667.3688.

5,6-Bis(*N*-benzyl-*N*-ethylaminomethyl)-2,3-dihydro-4,7-di(naphthalen-1-yl)-1*H*-indene (3cd). *dl* Isomer: Pale yellow solid. mp 59-61 °C. IR (neat) 798, 777 cm^{-1}, ^{1}H NMR δ = 0.55 (t, *J* = 7.1 Hz, 6H), 1.74-1.81 (m, 2H), 2.08-2.33 (m, 6H), 2.61-2.69 (m, 2H), 3.16 (d, *J* = 13.5 Hz, 2H), 3.27 (d, *J* = 12.5 Hz, 2H), 3.52 (d, *J* = 13.5 Hz, 2H), 4.27 (d, *J* = 12.5 Hz, 2H), 7.14-7.25 (m, 10H), 7.30-7.34 (m, 2H), 7.46-7.51 (m, 6H), 7.59-7.62 (m, 2H), 7.89-7.95 (m, 4H); ^{13}C NMR δ = 11.4, 24.4, 33.0, 47.4, 52.7, 57.1, 125.2, 125.5, 125.8, 126.0, 126.2, 127.0, 127.4, 127.9, 128.1, 128.5, 132.4, 133.5, 136.4, 137.5, 138.8, 141.1, 142.4; HRMS (FAB) for M + 1 found m/z 665.3881, calcd for

$C_{49}H_{49}N_2$: 665.3896. $[\alpha]^{25}_D$ = -54.0 (*c* 0.76, $CHCl_3$, >99% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel OD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 3% 2-propanol in hexane, flow rate: 0.3 mL/min, retention time: 14 min for major isomer and 16 min for minor isomer). ***meso* Isomer**: Yellow oil. IR (neat) 798, 777, 737 cm^{-1}, ^1H NMR δ = 0.53 (t, *J* = 7.1 Hz, 6H), 1.69-1.83 (m, 2H), 2.07-2.16 (m, 4H), 2.32-2.40 (m, 2H), 2.47-2.54 (m, 2H), 3.21 (s, 4H), 3.67 (d, *J* = 12.7 Hz, 2H), 3.88 (d, *J* = 12.7 Hz, 2H), 7.00-7.02 (m, 4H), 7.15-7.20 (m, 5H), 7.35-7.39 (m, 4H), 7.49-7.58 (m, 7H), 7.88-7.95 (m, 4H); ^{13}C NMR δ = 11.4, 24.5, 32.9, 47.1, 52.8, 57.5, 125.3, 125.5, 125.8, 126.2, 126.4, 127.1, 127.3, 127.9, 128.2, 128.6, 132.2, 133.7, 136.6, 137.7, 139.1, 140.9, 142.4; HRMS (FAB) for M + 1 found m/z 665.3863, calcd for $C_{49}H_{49}N_2$: 665.3896.

5-(*N*-Benzyl-*N*-ethylaminomethyl)-1,3-dihydro-4,7-di(naphthalen-1-yl)-6-methylisobenzofuran (3ae). Major diastereomer: Pale yellow solid. mp 90-92 °C. IR (neat) 1059, 800, 779 cm^{-1}, ^1H NMR δ = 0.71 (t, *J* = 7.0 Hz, 3H), 2.04-2.13 (m, 1H), 2.22 (s, 3H), 2.25-2.34 (m, 1H), 3.06 (d, *J* = 13.4 Hz, 1H), 3.20 (d, *J* = 12.7 Hz, 1H), 3.49 (d, *J* = 13.4 Hz, 1H), 3.66 (d, *J* = 12.7 Hz, 1H), 4.55 (d, *J* = 8.4 Hz, 1H), 4.58 (d, *J* = 8.4 Hz, 1H), 4.81 (d, *J* = 12.7 Hz, 1H), 4.89 (d, *J* = 12.7 Hz, 1H), 7.11-7.25 (m, 5H), 7.38-7.61 (m, 10H), 7.90-7.96 (m, 4H); ^{13}C NMR δ = 11.7, 17.3, 47.2, 53.0, 57.7, 74.2, 125.2, 125.5, 125.6, 125.7, 125.8, 125.9, 126.2, 126.2, 126.2, 126.4, 126.9, 127.7, 127.8, 127.9, 128.3, 128.3, 128.6, 131.4, 132.1, 133.5, 133.7, 133.8, 134.2, 135.9, 136.0, 137.3, 137.5, 137.5, 137.7, 140.5; HRMS (FAB) for M + 1 found m/z 534.2829, calcd for $C_{39}H_{36}NO$: 534.2797. $[\alpha]^{20}_D$ = -42.1 (*c* 1.52, $CHCl_3$, >99% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel OD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 10% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 5 min for major isomer and 17 min for minor isomer). **Minor diastereomer**: Pale yellow oil. IR (neat) 1061, 795, 785 cm^{-1}, ^1H NMR δ = 0.70 (t, *J* = 7.1 Hz, 3H), 2.08-2.17 (m, 1H), 2.21 (s, 3H), 2.25-2.29 (m, 1H), 3.15 (d, *J* = 13.1 Hz, 1H), 3.29 (d, *J* = 9.9 Hz, 1H), 3.32 (d, *J* = 9.9 Hz, 1H), 3.60 (d, *J* = 13.1 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 12.5 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.84 (d, *J* = 12.5 Hz, 1H), 7.08-7.26 (m, 5H), 7.39-7.59 (m, 10H), 7.90-7.97 (m, 4H); ^{13}C NMR δ = 11.5, 17.2, 47.0, 53.0, 57.7, 74.2, 125.3, 125.5, 125.6, 125.8, 125.9, 126.0, 126.3, 126.3, 126.4, 126.4, 127.1, 127.7, 127.8, 127.9, 128.4, 128.4, 128.7, 131.4, 131.9, 133.6, 133.7, 133.8, 134.3, 136.0, 136.0, 137.2, 137.6, 137.6, 137.8, 140.5; HRMS (FAB) for M + 1 found m/z 534.2787, calcd for $C_{39}H_{36}NO$: 534.2797. $[\alpha]^{22}_D$ = 26.5 (*c* 0.10, $CHCl_3$, >99% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel OD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 10% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 10 min for minor isomer and 13 min for major isomer).

5-(*N*-Benzyl-*N*-ethylaminomethyl)-2,3-dihydro-4,7-di(naphthalen-1-yl)-6-methyl-1*H*-indene (3ce). Major diastereomer: Pale yellow solid. mp 131-132 °C. IR (neat) 798, 779 cm^{-1}, ^1H NMR δ = 0.69 (t, *J* = 7.1 Hz, 3H), 1.74-1.81 (m, 2H), 2.02-2.11 (m, 1H), 2.19 (s, 3H), 2.16-2.37 (m, 3H), 2.50-2.66 (m, 2H), 3.06 (d, *J* = 13.5 Hz, 1H), 3.17 (d, *J* = 12.7 Hz, 1H), 3.49 (d, *J* = 13.5 Hz, 1H),

3.63 (d, J = 12.7 Hz, 1H), 7.11-7.23 (m, 5H), 7.35-7.60 (m, 10H), 7.87-7.95 (m, 4H); ^{13}C NMR δ = 11.7, 17.5, 24.6, 32.9, 32.9, 47.2, 53.4, 57.6, 125.2, 125.5, 125.6, 125.7, 125.8, 126.0, 126.2, 126.2, 126.4, 127.0, 127.1, 127.2, 127.8, 128.1, 128.2, 128.6, 131.9, 132.6, 133.5, 133.7, 134.1, 135.5, 136.4, 136.8, 138.9, 139.4, 140.4, 140.9, 142.0; HRMS (FAB) for M + 1 found m/z 532.3010, calcd for $C_{40}H_{38}N$: 532.3004. $[\alpha]^{18}_D$ = -32.0 (*c* 1.31, $CHCl_3$, >99% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel Double-arrayed OD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 20% 2-propanol in hexane, flow rate: 0.5 mL/min, retention time: 16 min for major isomer and 17 min for minor isomer). **Minor diastereomer**: Pale yellow oil. IR (neat) 798, 777 cm^{-1}, ^{1}H NMR δ = 0.68 (t, J = 7.0 Hz, 3H), 1.70-1.84 (m, 2H), 2.07-2.15 (m, 1H), 2.17 (s, 3H), 2.20-2.25 (m, 1H), 2.28-2.38 (m, 2H), 2.48-2.64 (m, 2H), 3.16 (d, J = 13.3 Hz, 1H), 3.27 (d, J = 4.6 Hz, 1H), 3.30 (d, J = 4.6 Hz, 1H), 3.56 (d, J = 13.3 Hz, 1H), 7.08-7.23 (m, 5H), 7.29-7.45 (m, 4H), 7.49-7.60 (m, 6H), 7.88-7.96 (m, 4H); ^{13}C NMR δ = 11.6, 17.4, 24.5, 32.8, 32.8, 47.1, 53.5, 57.7, 125.3, 125.6, 125.7, 125.7, 125.9, 125.9, 126.0, 126.2, 126.3, 126.5, 127.1, 127.1, 127.4, 127.8, 128.3, 128.3, 128.7, 131.9, 132.4, 133.6, 133.7, 134.2, 135.8, 136.5, 137.0, 138.9, 139.5, 140.6, 140.9, 142.1; HRMS (FAB) for M + 1 found m/z 532.2973, calcd for $C_{40}H_{38}N$: 532.3004. $[\alpha]^{25}_D$ = 6.4 (*c* 0.17, $CHCl_3$, >99% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralcel Double-arrayed OD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 20% 2-propanol in hexane, flow rate: 0.5 mL/min, retention time: 16 min for major isomer and 17 min for minor isomer).

1,3-Dihydro-4,7-di(naphthalen-1-yl)-5-methyl-6-(*N*-methyl-*N*-tosylaminomethyl)isobenzofuran (3af). Colorless oil. IR (neat) 1342, 1162, 1060, 804, 779, 734 cm^{-1}, ^{1}H NMR δ = 2.20 (s, 3H), 2.25 (s, 3H), 2.32 (s, 3H), 3.68 (d, J = 12.8 Hz, 1H), 4.28 (d, J = 12.8 Hz, 1H), 4.57 (d, J = 9.2 Hz, 1H), 4.60 (d, J = 9.2 Hz, 1H), 4.78-4.87 (m, 2H), 6.95 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.2Hz, 2H), 7.37-7.60 (m, 10H), 7.77 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.91-7.95 (m, 2H); ^{13}C NMR δ = 16.6, 21.4, 33.4, 48.6, 74.2, 74.2, 125.0, 125.1, 125.2, 125.6, 126.1, 126.3, 126.5, 126.9, 127.3, 127.9, 128.1, 128.3, 128.5, 129.0, 130.9, 131.2, 131.5, 131.8, 133.6, 133.8, 134.4, 134.6, 135.9, 136.6, 136.8, 138.0, 139.2, 142.9; HRMS (FAB) for M + 1 found m/z 584.2263, calcd for $C_{38}H_{34}NO_3S$: 584.2259. $[\alpha]^{22}_D$ = -14.0 (*c* 1.14, $CHCl_3$, >95% ee). Ee was determined using ^{1}H NMR after tosyl amide was transformed into camphor sulfonyl amide.

2,3-Dihydro-4,7-di(naphthalen-1-yl)-5-methyl-6-(*N*-methyl-*N*-tosylaminomethyl)-1*H*-indene (3cf). White solid. mp 108-109 °C. IR (neat) 1342, 1163, 800, 777 cm^{-1}, ^{1}H NMR δ = 1.74-1.82 (m, 2H), 2.13 (s, 3H), 2.25 (s, 3H), 2.29-2.40 (m, 2H), 2.33 (s, 3H), 2.48-2.63 (m, 2H), 3.68 (d, J = 12.4 Hz, 1H), 4.22 (d, J = 12.4 Hz, 1H), 6.94 (d, J = 8.1 Hz, 2H), 7.19-7.23 (m, 3H), 7.35-7.51 (m, 8H), 7.56-7.59 (m, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.84-7.94 (m, 3H); ^{13}C NMR δ = 16.8, 21.4, 24.4, 32.7, 32.9, 33.1, 48.9, 125.0, 125.5, 125.6, 125.7, 125.7, 125.7, 125.8, 126.1, 126.5, 127.1, 127.2, 127.4, 128.1, 128.4, 129.0, 129.0, 131.6, 131.9, 131.9, 133.5, 133.7, 136.1, 136.9, 137.1, 137.5, 138.6, 141.1, 142.7, 143.8; HRMS (FAB) for M + 1 found m/z 582.2455, calcd for $C_{39}H_{36}NO_2S$: 582.2467.

$[\alpha]^{24}_D$ = 6.5 (*c* 0.98, $CHCl_3$, >99% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 5% 2-propanol in hexane, flow rate: 0.5 mL/min, retention time: 31 min for major isomer and 36 min for minor isomer).

1,3-Dihydro-4,7-di(naphthalen-1-yl)-5-hydroxymethyl-6-(*N*-methyl-*N*-tosylaminomethyl)isobenzofuran (3ag). Colorless oil. IR (neat) 3523, 1340, 1161, 1068, 804, 781, 737 cm^{-1}, ^1H NMR δ = 2.25 (s, 3H), 2.33(s, 3H), 2.74 (bs, 1H), 3.89 (d, *J* = 13.2 Hz, 1H), 4.37 (d, *J* = 13.2 Hz, 1H), 4.49 (d, *J* = 12.4 Hz, 1H), 4.56-4.62 (m, 2H), 4.77-4.83 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.41-7.61 (m, 9H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* =, 8.0 Hz, 1H), 7.93-7.96 (m, 2H); ^{13}C NMR δ = 21.4, 34.3, 48.5, 59.0, 74.1, 74.2, 114.2, 125.1, 125.2, 125.3, 125.5, 126.2, 126.6, 126.7, 126.9, 127.0, 127.6, 128.2, 128.4, 128.4, 128.5, 129.3, 131.3, 131.4, 131.5, 132.2, 133.6, 133.7, 135.2, 135.2, 135.5, 135.6, 138.9, 139.6, 139.7, 143.5; HRMS (FAB) for M + 1 found m/z 600.2198, calcd for $C_{38}H_{34}NO_4S$: 600.2209. $[\alpha]^{28}_D$ = -13.7 (*c* 0.98, $CHCl_3$, >95% ee). Ee was determined using ^1H NMR after alcohol was transformed into camphor sulfonate ester. The absolute configuration was determined by X-ray measurements after transformation of the hydroxy group into ferrocenyl ester.

Crystal data for CH_2Cl_2 adduct of ferrocenyl ester of 3ag. $C_{49}H_{43}NO_5SCl_2Fe$, *M* = 884.70, orthorhombic, Space Group $P2_12_12_1$ (#19), *a* = 10.139(3) Å, *b* = 12.854(4) Å, *c* = 33.718(7) Å, *V* = 4394.1(21) $Å^3$, *T* = 123 K, *Z* = 4, μ(MoKα) = 5.593 cm^{-1} Number of Reflections Measured: Total 40885, Unique: 10029 (R_{int} = 0.098), *R1* = 0.0856, *wR2* = 0.2138, Flack Parameter (Friedel Pairs = 4433) 0.06(4). CCDC 610350.

1,3-Dihydro-4,7-di(naphthalen-1-yl)-5-(diphenylphosphinylmethyl)isobenzofuran (3ah). White solid. mp >300 °C, IR (neat) 1439, 1227, 1063, 731 cm^{-1}, ^1H NMR δ = 2.17 (s, 3H), 4.61-4.66 (m, 2H), 4.79 (d, J = 12.8 Hz, 2H), 4.86-4.95 (m, 2H), 7.13-7.16 (m, 4H), 7.29-7.36 (m, 2H), 7.41-7.63 (m, 14H), 7.91-8.00 (m, 4H); ^{31}P NMR δ = 30.9; LRMS (MALDI) for M + 1 found m/z 601.62, calcd for $C_{42}H_{34}O_2P$: 601.23. $[\alpha]^{24}_D$ = 15.0 (*c* 0.56, $CHCl_3$, >99% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak Doubly-arrayed AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 30% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 20 min for major isomer and 27 min for minor isomer).

Dimethyl 1,3-dihydro-4,7-di(naphthalen-1-yl)isobenzofuran-5,6-dicarboxylate (3ai). Colorless crystal. mp 216 °C, IR (neat) 1743, 1733, 1065, 737 cm^{-1}, ^1H NMR δ = 3.29 (s, 0.2 x 6H), 3.30 (s, 0.8 x 6H), 4.74-4.87 (m, 4H), 7.35-7.93 (m, 14H); ^{13}C NMR δ = 52.1, 73.9, 125.1, 125.4, 126.1, 126.6, 128.3, 128.6, 130.9, 133.0, 133.2, 133.4, 134.8, 141.8, 167.7; Anal. Calcd for $C_{32}H_{24}O_5$; C, 78.43; H, 4.99. Found: C, 78.67; H, 4.95. $[\alpha]^{29}_D$ = -21.8 (*c* 1.14, $CHCl_3$, 99% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak Doubly-arrayed AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 10% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 22 min for major isomer and 29 min for minor isomer).

Dimethyl 4,7-di(naphthalen-1-yl)-2-tosylisoindoline-5,6-dicarboxylate (3bi). Colorless crystal. mp 232 °C, IR (neat) 1737, 1352, 1165, 802, 781, 735 cm^{-1}, ^1H NMR δ = 2.43 (s, 3H), 3.26 (s, 6H), 4.24-4.33 (m, 4H), 7.23-7.95 (m, 18H); ^{13}C NMR δ = 21.6, 52.2, 54.0, 125.1, 125.1, 126.1, 126.2, 126.6, 127.3, 128.5, 128.9, 129.8, 130.8, 133.5, 134.1, 134.3, 138.9, 143.8, 167.3; HRMS (FAB) for M + 1 found m/z 642.1940, calcd for $C_{39}H_{32}NO_6S$: 642.1950. $[\alpha]^{29}_D$ = 30.7 (*c* 1.71, $CHCl_3$, 99% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak Doubly-arrayed AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 50% 2-propanol in hexane, flow rate: 0.5 mL/min, retention time: 31 min for minor isomer and 43 min for major isomer).

Crystal data for 3bi·hexane. $C_{45}H_{45}NO_6S$, *M* = 727.91, monoclinic, Space Group $P2_1$ (#4), *a* = 9.76(3) Å, *b* = 22.345(8) Å, *c* = 10.551(3) Å, *β* = 114.53(1)°, *V* = 1905(1) $Å^3$, *T* = 123 K, *Z* = 2, μ(MoKα) = 1.35 cm^{-1} Number of Reflections Measured: Total 18135, Unique: 8374 (R_{int} = 0.039), *R1* = 0.064, *wR2* = 0.145, Flack Parameter (Friedel Pairs = 3947) 0.0(1). CCDC 610352.

Methyl 1,3-dihydro-4,7-di(naphthalen-1-yl)-6-methylisobenzofuran-5-carboxylate (3aj). White solid. mp 110 °C, IR (neat) 1727, 1063, 737 cm^{-1}, ^1H NMR δ = 2.06 (s, 3H), 3.27 (s, 3H), 4.61-4.91 (m, 4H), 7.41-7.95 (m, 14H); ^{13}C NMR δ = 17.1, 51.6, 73.9, 125.1, 125.2, 125.5, 125.7, 125.9, 126.1, 126.3, 126.3, 126.5, 126.6, 128.2, 128.2, 128.3, 128.4, 131.0, 131.4, 133.4, 133.7, 133.8, 133.9, 134.8, 135.5, 136.0, 136.8, 140.3, 169.7; HRMS (FAB) for M found m/z 444.1723, calcd for $C_{31}H_{24}O_3$: 444.1725. $[\alpha]^{30}_D$ = -20.6 (*c* 1.57 , $CHCl_3$, 99% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak Doubly-arrayed AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 5% 2-propanol in hexane, flow rate: 0.5 mL/min, retention time: 26 min for major isomer and 31 min for minor isomer).

Methyl 4,7-di(naphthalen-1-yl)-6-methyl-2-tosylisoindoline-5-carboxylate (3bj). White solid. mp 210 °C, IR (neat) 1727, 1348, 1165, 802, 781, 737 cm^{-1}, ^1H NMR δ = 1.99 (s, 3H), 2.41 (s, 3H), 3.24 (s, 3H), 4.09-4.40 (m, 4H), 7.21-7.97 (m, 18H); ^{13}C NMR δ = 17.1, 21.6, 51.7, 54.0, 54.1, 124.9, 125.1, 125.4, 125.6, 126.1, 126.2, 126.3, 126.4, 126.5, 126.6, 127.3, 128.4, 128.5, 128.6, 129.7, 130.9, 130.9, 132.7, 133.5, 133.6, 133.8, 133.9, 134.3, 134.7, 135.2, 135.2, 135.3, 137.3, 143.5, 169.3; HRMS (FAB) for M + 1 found m/z 598.2066, calcd for $C_{38}H_{32}NO_4S$: 598.2052. $[\alpha]^{28}_D$ = 54.8 (*c* 0.51, $CHCl_3$, 99% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 50% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 6 min for minor isomer and 8 min for major isomer).

Diethyl 2,3-dihydro-5,6-bis(methoxymethyl)-4-methyl-7-(naphthalen-1-yl)-1H-indene-2,2-dicarboxylate (3ea). Colorless oil. IR (neat) 1730, 1250, 1097, 804, 783, 733 cm^{-1}, ^1H NMR δ = 1.12 (t, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.0 Hz, 3H), 2.40 (s, 3H), 2.95 (d, *J* = 7.0 Hz, 1H), 2.99 (s, 3H), 3.14 (d, *J* = 17.0 Hz, 1H), 3.48 (s, 3H), 3.58 (d, *J* = 16.7 Hz, 1H), 3.67 (d, *J* = 16.7 Hz, 1H), 3.90 (d, *J* = 10.2 Hz, 1H), 4.03-4.14 (m, 4H), 4.21 (d, *J* = 10.2 Hz, 1H), 4.55 (d, *J* = 10.5 Hz, 1H), 4.64 (d, *J* =

10.5 Hz, 1H), 7.31-7.39 (m, 3H), 7.44-7.54 (m, 2H), 7.87-7.91 (m, 2H); ^{13}C NMR δ = 13.9, 14.2, 15.7, 40.2, 40.2, 58.0, 58.6, 59.5, 60.3, 61.6, 68.6, 69.3, 125.3, 125.8, 126.0, 126.1, 127.1, 127.6, 128.0, 132.0, 133.5, 134.1, 134.9, 135.0, 137.0, 139.6, 139.6, 171.5; HRMS (FAB) for M found m/z 490.2358, calcd for $C_{30}H_{34}O_6$: 490.2355. $[\alpha]^{25}_D$ = 23.7 (*c* 0.40, $CHCl_3$, 41% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 2% 2-propanol in hexane, flow rate: 0.5 mL/min, retention time: 27 min for minor isomer and 28 min for major isomer).

Diethyl 2,3-dihydro-5,6-bis(methoxymethyl)-4-(naphthalen-1-yl)-7-trimethylsilyl-1*H*-indene-2,2-dicarboxylate (3fa). Yellow oil. IR (neat) 1732, 1271, 1095, 783, 737 cm^{-1}, ^{1}H NMR δ = 0.47 (s, 9H), 1.11 (t, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H), 2.86 (d, *J* = 16.8 Hz, 1H), 2.97 (s, 3H), 3.06 (d, *J* = 16.8 Hz, 1H), 3.42 (s, 3H), 3.67 (d, *J* = 16.1 Hz, 1H), 3.76 (d, *J* = 16.1 Hz, 1H), 3.91 (d, *J* = 10.0 Hz, 1H), 4.03-4.12 (m, 4H), 4.20 (d, *J* = 10.0 Hz, 1H), 4.60 (s, 2H), 7.31-7.36 (m, 3H), 7.45-7.54 (m, 2H), 7.87-7.90 (m, 2H); ^{13}C NMR δ = 2.4, 13.9, 13.9, 39.2, 43.1, 58.1, 58.1, 60.3, 61.5, 61.5, 69.4, 70.8, 125.3, 125.8, 126.0, 126.2, 126.8, 127.6, 128.0, 131.8, 133.5, 135.0, 136.5, 136.9, 138.5, 139.6, 142.3, 146.1, 171.4 ; HRMS (FAB) for M + 1 found m/z 549.2699, calcd for $C_{32}H_{41}O_6Si$: 549.2672. $[\alpha]^{25}_D$ = 34.4 (*c* 0.76, $CHCl_3$, 89% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 5% 2-propanol in hexane, flow rate: 0.5 mL/min, retention time: 9 min for minor isomer and 11 min for major isomer).

Diethyl 2,3-dihydro-5,6-bis(methoxymethyl)-4-(naphthalen-1-yl)-7-phenyl-1*H*-indene-2,2-dicarboxylate (3ga). Yellow oil. IR (neat) 1730, 1267, 1095, 739, 704 cm^{-1}, ^{1}H NMR δ = 1.08 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H), 3.00 (s, 3H), 3.00 (d, *J* = 16.4 Hz, 1H), 3.17 (d, *J* = 16.4 Hz, 1H), 3.24 (s, 3H), 3.36 (s, 2H), 3.98 (d, *J* = 10.2 Hz, 1H), 4.02-4.09 (m, 4H), 4.23 (d, *J* = 9.6 Hz, 1H), 4.30 (d, *J* = 10.2 Hz, 1H), 4.60 (d, *J* = 9.6 Hz, 1H), 7.36-7.57 (m, 10H), 7.89-7.93 (m, 2H); ^{13}C NMR δ = 13.9, 13.9, 40.3, 40.7, 58.3, 58.3, 59.9, 61.5, 61.5, 69.1, 69.3, 125.3, 125.8, 126.0, 126.2, 127.1, 127.7, 128.1, 128.1, 129.2, 129.4, 131.9, 133.5, 134.5, 135.6, 136.7, 137.1, 139.1, 139.3, 139.8, 140.1, 171.3, 171.3; HRMS (FAB) for M + 1 found m/z 553.2596, calcd for $C_{35}H_{37}O_6$: 553.2590. $[\alpha]^{25}_D$ = 116.3 (*c* 0.70, $CHCl_3$, 94% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 5% 2-propanol in hexane, flow rate: 0.5 mL/min, retention time: 20 min for major isomer and 22 min for minor isomer).

Diethyl 2,3-dihydro-5,6-bis(hydroxymethyl)-4-(2-methylphenyl)-1*H*-indene-2,2-dicarboxylate (3hb). Yellow oil. IR ($CHCl_3$) 3314, 1731, 1189, 756 cm^{-1}, ^{1}H NMR δ = 1.21 (t, *J* = 7.2 Hz, 6H), 2.01 (s, 3H), 2.81 (s, 1H), 3.07 (d, *J* = 16.8 Hz, 1H), 3.14 (d, *J* = 16.8 Hz, 1H), 3.28 (s, 1H), 3.60 (d, *J* = 16.8 Hz, 1H), 3.66 (d, *J* = 16.8 Hz, 1H), 4.10-4.20 (m, 4H), 4.33 (d, *J* = 11.7 Hz, 1H), 4.45 (d, *J* = 11.7 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 7.03-7.05 (m, 1H), 7.19-7.28

(m, 4H); ^{13}C NMR δ = 14.1, 19.9, 40.1, 40.7, 59.9, 60.2, 61.7, 64.8, 125.0, 125.8, 127.6, 128.8, 130.0, 135.7, 135.8, 138.2, 138.5, 139.3, 139.4, 139.8, 171.2, 171.4; HRMS (FAB) for M + 1 found m/z 413.1939, calcd for $C_{24}H_{29}O_6$: 413.1964. $[\alpha]^{28}_D$ = -3.00 (*c* 2.25, $CHCl_3$, 83% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 5% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 34 min for minor isomer and 38 min for major isomer).

Diethyl 2,3-dihydro-5,6-bis(hydroxymethyl)-4-(2-methoxyphenyl)-1*H*-indene-2,2-dicarboxylate (3ib). Yellow oil. IR ($CHCl_3$) 3346, 1734, 1189, 756 cm^{-1}, ^{1}H NMR δ = 1.21 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 2.98 (s, 1H), 3.14 (d, *J* = 16.6 Hz, 1H), 3.34 (d, *J* = 16.6 Hz, 1H), 3.49 (s, 1H), 3.65 (s, 2H), 3.72 (s, 3H), 4.11-4.20 (m, 4H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.83 (d, *J* = 12.0 Hz, 1H), 7.01-7.08 (m, 2H), 7.12-7.15 (m, 1H), 7.25 (s, 1H), 7.34-7.40 (m, 1H); ^{13}C NMR δ = 14.1, 40.2, 40.7, 56.2, 60.1, 60.7, 61.7, 61.7, 64.9, 120.0, 121.4, 125.1, 127.6, 129.1, 130.9, 135.0, 136.1, 139.6, 139.7, 140.0, 156.1, 171.1, 171.4; HRMS (FAB) for M found m/z 428.1849, calcd for $C_{24}H_{28}O_7$: 428.1835. $[\alpha]^{28}_D$ = -4.65 (*c* 1.22, $CHCl_3$, 65% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AS-H: 4 x 250mm, 254nm UV detector, rt, eluent: 5% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 70 min for minor isomer and 92 min for major isomer).

Diethyl 4-(2-chlorophenyl)-2,3-dihydro-5,6-bis(hydroxymethyl)-1*H*-indene-2,2-dicarboxylate (3jb). Yellow oil. IR ($CHCl_3$) 3292, 1734, 1189, 758 cm^{-1}, ^{1}H NMR δ = 1.21 (t, *J* = 7.2 Hz, 6H), 2.79 (s, 1H), 3.16 (d, *J* = 16.8 Hz, 1H), 3.23 (d, *J* = 16.8 Hz, 1H), 3.25 (s, 1H), 3.57 (d, *J* = 16.8 Hz, 1H), 3.70 (d, *J* = 16.8 Hz, 1H), 4.08-4.21 (m, 4H), 4.31 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 7.19-7.36 (m, 4H), 7.45-7.51 (m, 1H); ^{13}C NMR δ = 14.1, 39.9, 40.6, 60.1, 60.2, 61.8, 64.7, 125.6, 127.0, 129.1, 129.4, 130.9, 133.0, 135.8, 136.1, 137.4, 139.5, 139.5, 140.1, 171.0, 171.3; HRMS (FAB) for M + 1 found m/z 433.1462, calcd for $C_{23}H_{26}ClO_6$: 433.1418. $[\alpha]^{26}_D$ = 25.5 (*c* 1.25, $CHCl_3$, 92% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AS-H: 4 x 250mm, 254nm UV detector, rt, eluent: 5% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 58 min for minor isomer and 74 min for major isomer).

Diethyl 2,3-dihydro-5,6-bis(hydroxymethyl)-4-(naphthalen-1-yl)-1*H*-indene-2,2-dicarboxylate (3kb). Yellow oil. IR ($CHCl_3$) 3364, 1734, 1187, 803, 781, 758 cm^{-1}, ^{1}H NMR δ = 1.12 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 2.56 (s, 1H), 2.93 (d, *J* = 17.0 Hz, 1H), 3.17 (d, *J* = 17.0 Hz, 1H), 3.36 (s, 1H), 3.62 (d, *J* = 16.5 Hz, 1H), 3.70 (d, *J* = 16.5 Hz, 1H), 4.01-4.16 (m, 4H), 4.24 (d, *J* = 11.7 Hz, 1H), 4.39 (d, *J* = 11.7 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 7.28-7.38 (m, 4H), 7.44-7.55 (m, 2H), 7.89 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR δ = 14.0, 14.0, 39.9, 40.7, 60.1, 61.6, 61.7, 64.8, 125.3, 125.4, 125.4, 125.9, 126.3, 126.6, 127.8, 128.3, 131.7, 133.5, 136.2, 136.6, 137.0, 139.7, 140.0, 140.2, 171.2; HRMS (FAB) for M found m/z 448.1901, calcd for

$C_{27}H_{28}O_6$: 448.1886. $[\alpha]^{29}_D$ = 54.8 (*c* 1.01, $CHCl_3$, 90% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 5% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 41 min for major isomer and 50 min for minor isomer).

Diethyl 2,3-dihydro-5,6-bis(hydroxymethyl)-4-(4-methylnaphthalen-1-yl)-1*H*-indene-2,2-dicarboxylate (3lb). Yellow oil. IR ($CHCl_3$) 3326, 1729, 1187, 835, 756 cm^{-1}, ^1H NMR δ = 1.12 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H), 2.45 (s, 1H), 2.75 (s, 3H), 2.93 (d, *J* = 17.0 Hz, 1H), 3.18 (d, *J* = 17.0 Hz, 1H), 3.32 (s, 1H), 3.61 (d, *J* = 16.6 Hz, 1H), 3.70 (d, *J* = 16.6 Hz, 1H), 4.02-4.15 (m, 4H), 4.25 (d, *J* = 11.6 Hz, 1H), 4.40 (d, *J* = 11.6 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.29-7.38 (m, 4H), 7.48-7.54 (m, 1H), 8.06 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR δ = 14.0, 14.0, 19.6, 40.0, 40.7, 60.1, 60.2, 61.6, 61.7, 64.8, 124.4, 125.2, 125.8, 125.9, 125.9, 126.2, 126.3, 131.8, 132.6, 134.1, 134.4, 136.7, 137.3, 139.7, 139.9, 140.3, 171.2, 171.2; HRMS (FAB) for M found m/z 462.2044, calcd for $C_{28}H_{30}O_6$: 462.2042. $[\alpha]^{25}_D$ = 54.0 (*c* 1.45, $CHCl_3$, 92% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 3% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 69 min for major isomer and 84 min for minor isomer).

Diethyl 2,3-dihydro-5,6-bis(hydroxymethyl)-4-(4-methoxynaphthalen-1-yl)-1*H*-indene-2,2-dicarboxylate (3mb). Pale yellow solid. mp 137 °C (ether); IR ($CHCl_3$) 3310, 1189, 824, 758 cm^{-1}, ^1H NMR δ = 1.12 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 2.40 (s, 1H), 2.94 (d, *J* = 16.8 Hz, 1H), 3.20 (s, 1H), 3.20 (d, *J* = 16.8 Hz, 1H), 3.61 (d, *J* = 16.8 Hz, 1H), 3.70 (d, *J* = 16.8 Hz, 1H), 4.05 (s, 3H), 3.99-4.16 (m, 4H), 4.27 (d, *J* = 11.7 Hz, 1H), 4.43 (d, *J* = 11.7 Hz, 1H), 4.73 (d, *J* = 11.9 Hz, 1H), 4.81 (d, *J* = 11.9 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.31 (s, 1H), 7.34-7.40 (m, 1H), 7.44-7.49 (m, 1H), 8.32-8.35 (m, 1H); ^{13}C NMR δ = 14.0, 14.1, 40.0, 40.7, 55.6, 60.1, 60.2, 61.6, 61.7, 64.9, 103.4, 122.3, 125.0, 125.2, 125.2, 125.5, 126.6, 126.8, 128.2, 132.6, 137.0, 137.1, 139.6, 139.8, 140.7, 155.0, 171.2, 171.3; HRMS (FAB) for M found m/z 478.2008, calcd for $C_{28}H_{30}O_7$: 478.1992. $[\alpha]^{26}_D$ = 39.2 (*c* 1.11, $CHCl_3$, 87% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak AD-H: 4 x 250mm, 254nm UV detector, rt, eluent: 5% 2-propanol in hexane, flow rate: 1.0 mL/min, retention time: 39 min for major isomer and 53 min for minor isomer).

[1] T. Shibata, T. Fujimoto, K. Yokota, K. Takagi, *J. Am. Chem. Soc*. **2004**, *126*, 8382-8383.