Supporting Information for
Asymmetric phase-transfer catalyst catalyzed [4+1] cycloaddition of 
ortho-quinone methides and bromomalonate
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General Information: NMR spectra were recorded on a Brucker-400 MHz spectrometer. Mass spectra were recorded on a Thermo LTQ Orbitrap XL (ESI+) or a P-SIMS-Gly of Bruker Daltonics Inc (EI+). Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump, UV detection monitored at 254 nm). All chiral columns were purchased from Daicel Chemical Industries, LTD. Optical rotations were measured on Perkin Elmer Model 343 Polarimeter. Toluene, diethyl ether and tetrahydrofuran were dried over Na and distilled prior to use. Dichloromethane and dichloroethane were dried over CaH2 and distilled prior to use.

Materials: Analytical grade solvents for the column chromatography were used as received. Dimethyl bromomalonate 2 was purchased from TCI. All commercially available reagents were used directly unless indicated otherwise. Vinyl ortho-quinone methides 1 were prepared following the known procedures[1] and PTC 3 were synthesized according to the literatures[2].

General Procedure for Cycloaddition reaction:
The reaction of 1 (0.1 mmol) and 2 (0.12 mmol) was carried out in 2 mL toluene at -40 °C in the presence of catalyst 3a (10 mol%) and 1.5 eq Cs2CO3 (40mg) for 5-6 days. After completion of reaction the mixture is objected to flash column chromatography washed with PE:EtOAc = 4:1, by evaporation of solvent the product is collected.

Gram-Scale experiment:
A gram-scale experiment was performed at the standard reaction condition. A significant drop of enantioselectivity was observed.

Characterization of the Cycloaddition Products 4:
Dimethyl (S,E)-7-styryl-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4a)
Colorless oil. 37.5 mg, 98% yield. 1H NMR (400 MHz, CDCl3) δ 7.39 – 7.20 (m, 6H), 6.60 (dd, J = 23.2, 12.0 Hz, 3H), 6.06 (dd, J = 15.7, 9.0 Hz, 1H), 5.92 (d, J = 2.2 Hz, 2H), 4.93 (d, J = 9.0 Hz, 1H), 3.87 (s, 3H), 3.69 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 167.86, 166.49, 152.16, 148.31, 143.03, 136.25, 134.22, 128.65, 128.06, 126.52, 125.14, 117.94, 104.90, 101.57, 93.73, 93.31, 53.72, 53.02, 51.69. IR (KBr): γ 3437, 1745, 1630, 1552, 1474, 1265, 1089, 1036 cm⁻¹. HRMS (ESI): m/z [M + H]+ calcd for [C23H19O7]⁺ requires 383.11253, found 383.11368. [α]D²⁰ = +24.1 (c=0.64, CHCl3).

S1
Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 7.690 min (minor), tR = 10.797 min (major).

**Dimethyl (S,E)-7-(4-methylstyrlyl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4b)**

Colorless oil. 39.5 mg, 98% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.22 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.66 – 6.51 (m, 3H), 6.00 (dd, J = 15.7, 9.0 Hz, 1H), 5.91 (dd, J = 3.5, 1.2 Hz, 2H), 4.91 (d, J = 9.0 Hz, 1H), 3.86 (s, 3H), 3.68 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.90, 166.51, 152.14, 148.26, 143.00, 137.97, 134.09, 133.48, 129.34, 126.43, 124.05, 104.93, 101.55, 93.70, 93.36, 53.69, 52.99, 51.72, 21.23. IR (KBr): γ 3439, 1746, 1631, 1547, 1475, 1265, 1149, 1036 cm$^{-1}$. HRMS (ESI): m/z [M + H]$^+$ calcd for [C$_{22}$H$_{24}$O$_6$]+ requires 397.12818, found 397.12933. ($\alpha$)$_{D}^{20}$ = +108.2 (c=0.72, CHCl$_3$). Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 7.512 min (minor), tR = 11.549 min (major).

**Dimethyl (S,E)-7-(2-methoxystyrlyl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4c)**

Colorless oil. 40.9 mg, 98% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 (dd, J = 7.6, 1.4 Hz, 1H), 7.25 – 7.19 (m, 1H), 6.95 (d, J = 15.8 Hz, 1H), 6.87 (dd, J = 13.2, 7.8 Hz, 2H), 6.57 (d, J = 17.9 Hz, 2H), 6.06 (dd, J = 15.8, 9.3 Hz, 1H), 5.91 (d, J = 1.8 Hz, 2H), 4.93 (d, J = 9.3 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.70 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.90, 166.56, 156.90, 152.05, 148.19, 142.98, 129.24, 129.06, 127.14, 125.72, 125.26, 120.61, 118.42, 110.84, 105.00, 101.51, 93.67, 93.36, 55.38, 53.66, 52.94, 52.35. IR (KBr): γ 3436, 1748, 1641, 1487, 1456, 1286, 1247, 1147 cm$^{-1}$. HRMS (ESI): m/z [M + H]$^+$ calcd for [C$_{22}$H$_{24}$O$_6$]+ requires 413.12309, found 413.12424. ($\alpha$)$_{D}^{20}$ = +126.2 (c=0.99, CHCl$_3$). Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 9.733 min (minor), tR = 16.673 min (major).

**Dimethyl (S,E)-7-(4-methoxystyrlyl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4d)**

Colorless oil. 40.5 mg, 98% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.28 (s, 1H), 7.25 (s, 1H), 6.83 (d, J = 8.7 Hz, 2H), 6.64 – 6.49 (m, 3H), 5.98 – 5.85 (m, 3H), 4.90 (d, J = 9.0 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 3.68 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.92, 166.54, 159.53, 152.12, 148.23, 142.99, 133.65, 129.03, 127.74, 122.83, 118.19, 114.03, 104.93, 101.54, 93.69, 93.39, 55.31, 53.68, 52.98, 51.75. IR (KBr): γ 3437, 1747, 1607, 1512, 1474, 1456, 1251, 1149, 1036 cm$^{-1}$. HRMS (ESI): m/z [M + H]$^+$ calcd for [C$_{22}$H$_{24}$O$_6$]+ requires 413.12309, found 413.12418. ($\alpha$)$_{D}^{20}$ = +91.3 (c=1.04, CHCl$_3$). Enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 11.505 min (minor), tR = 21.944 min (major).

**Dimethyl(S,E)-7-(4-bromostyrlyl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4e)**

Colorless oil. 45.6 mg, 98% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H), 6.56 (dd, J = 10.1, 5.6 Hz, 3H), 6.07 (dd, J = 15.8, 9.0 Hz, 1H), 5.92 (dd, J = 3.6, 1.2 Hz, 2H), 4.92 (d, J = 8.9 Hz, 1H), 3.87 (s, 3H), 3.68 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.79, 166.44, 152.20, 148.40, 143.08, 135.16, 132.98, 131.80, 128.00, 126.04, 122.88, 117.60, 104.83, 101.61, 93.78,
93.23, 53.76, 53.03, 51.58. IR (KBr): γ 3436, 1746, 1631, 1627, 1474, 1455, 1285, 1150, 1036 cm⁻¹. HRMS (ESI): m/z [M + H]^+ calcd for [C₂H₄O₂Br]^+ requires 461.02304, found 461.02448. [α]D²⁰ = +75.9 (c=0.90, CHCl₃). Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 8.211 min (minor), tR = 13.437 min (major).

**Dimethyl (S,E)-7-(4-chlorostyryl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4f)**

Colorless oil. 41.3 mg, 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.23 (m, 5H), 6.57 (dd, J = 10.2, 5.4 Hz, 3H), 6.05 (dd, J = 15.7, 9.0 Hz, 1H), 5.92 (d, J = 2.4 Hz, 2H), 4.92 (d, J = 8.9 Hz, 1H), 3.87 (s, 3H), 3.68 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.80, 166.45, 152.19, 148.39, 143.07, 134.72, 133.75, 132.93, 128.85, 127.69, 125.90, 117.65, 104.84, 101.60, 93.78, 93.26, 53.75, 53.03, 51.58. IR (KBr): γ 3433, 1747, 1630, 1474, 1456, 1287, 1150, 1094, 1036 cm⁻¹. HRMS (ESI): m/z [M + H]^+ calcd for [C₂H₄O₂Cl]^+ requires 417.07356, found 417.07471. [α]D²⁰ = +33.3 (c=0.91, CHCl₃). Enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 7.846 min (minor), tR = 12.724 min (major).

**Dimethyl (S,E)-7-(4-fluorostyryl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4g)**

Colorless oil. 39.7 mg, 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.27 (m, 2H), 6.99 (dd, J = 12.0, 5.3 Hz, 2H), 6.58 (dd, J = 11.2, 6.9 Hz, 3H), 5.98 (dd, J = 15.7, 9.0 Hz, 1H), 5.92 (dd, J = 3.5, 1.1 Hz, 2H), 4.91 (d, J = 9.0 Hz, 1H), 3.87 (s, 3H), 3.69 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.83, 166.48, 163.78, 161.32, 152.16, 148.35, 143.05, 132.42 (d, J = 3.3 Hz), 128.06 (d, J = 8.1 Hz), 124.93 (d, J = 2.3 Hz), 117.81, 115.61 (d, J = 21.7 Hz), 104.85, 101.59, 93.76, 93.29, 53.73, 53.01, 51.61. IR (KBr): γ 3434, 1747, 1631, 1508, 1474, 1226, 1149, 1036 cm⁻¹. HRMS (ESI): m/z [M + H]^+ calcd for [C₂H₄O₂F]^+ requires 401.10311, found 401.10408. [α]D²⁰ = +76.3 (c=0.88, CHCl₃). Enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 7.609 min (minor), tR = 12.803 min (major).

**Dimethyl (S,E)-7-(2-(naphthalen-1-yl)vinyl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4h)**

Colorless oil. 42.9 mg, 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.60 – 7.46 (m, 3H), 7.40 (dd, J = 15.4, 7.7 Hz, 2H), 6.67 (s, 1H), 6.59 (s, 1H), 6.11 (dd, J = 15.5, 8.9 Hz, 1H), 5.93 (d, J = 1.2 Hz, 2H), 5.07 (d, J = 8.9 Hz, 1H), 3.89 (s, 3H), 3.68 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.91, 166.59, 152.27, 148.37, 143.11, 134.09, 133.55, 131.84, 131.08, 128.57, 128.48, 128.40, 126.27, 125.93, 125.59, 124.10, 123.70, 117.99, 104.88, 101.61, 93.82, 93.42, 53.76, 53.10, 51.93. IR (KBr): γ 3435, 1746, 1632, 1474, 1455, 1286, 1149, 1036 cm⁻¹. HRMS (ESI): m/z [M + H]^+ calcd for [C₂H₄O₂]^+ requires 433.12818, found 433.12924. [α]D²⁰ = +73.3 (c=0.94, CHCl₃). Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 8.437 min (minor), tR = 13.695 min (major).
Dimethyl (S,E)-7-(2-(thiophen-2-yl)vinyl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4i)

Colorless oil. 38.5 mg, 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.18 – 7.11 (m, 1H), 6.94 (d, J = 3.3 Hz, 2H), 6.73 (d, J = 15.6 Hz, 1H), 6.58 (s, 1H), 6.55 (s, 1H), 5.97 – 5.83 (m, 3H), 4.90 (d, J = 8.8 Hz, 1H), 3.86 (s, 3H), 3.72 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.78, 166.46, 152.23, 148.37, 143.04, 141.25, 127.46, 127.40, 126.53, 124.80, 124.55, 117.59, 104.89, 101.59, 93.72, 93.26, 53.73, 53.07, 51.52. IR (KBr): γ 3435, 1746, 1632, 1474, 1455, 1447, 1425, 1303, 1248, 1242, 1177, 1147, 1036 cm⁻¹. HRMS (ESI): m/z [M + H]^+ calcd for [C₂₀H₂₃O₆S]^+ requires 389.06895, found 389.06895. [α]₀⁺ = +81.2 (c = 0.68, CHCl₃).

Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak OD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 10.710 min (minor), tR = 11.783 min (major).

Dimethyl (S)-7-(4-methoxyphenyl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4j)

Colorless oil. 38.3 mg, 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.07 (d, J = 8.6 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 6.60 (s, 1H), 6.45 (s, 1H), 5.92 (dd, J = 7.1, 1.1 Hz, 2H), 5.39 (s, 1H), 3.86 (s, 3H), 3.77 (s, 3H), 3.27 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.09, 166.24, 159.23, 152.50, 148.22, 143.13, 130.39, 129.80, 119.12, 113.63, 104.93, 101.55, 94.31, 93.50, 55.24, 53.71, 53.56, 52.50. IR (KBr): γ 3435, 1746, 1612, 1512, 1249, 1177, 1147, 1036 cm⁻¹. HRMS (ESI): m/z [M + H]^+ calcd for [C₂₆H₂₅O₆]^+ requires 387.10744, found 387.10837. [α]₀⁺ = +58.7 (c = 0.72, CHCl₃). Enantiomeric excess: 73%, determined by HPLC (Daicel Chirapak IC-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 9.877 min (minor), tR = 14.521 min (major).

Dimethyl (S,E)-7-(2-methylprop-1-en-1-yl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4k)

Colorless oil. 33.1 mg, 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 6.50 (d, J = 4.9 Hz, 2H), 5.90 (s, 2H), 5.05 (d, J = 10.2 Hz, 1H), 4.96 (d, J = 10.2 Hz, 1H), 3.84 (s, 3H), 3.74 (s, 3H), 1.83 (s, 3H), 1.73 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.12, 166.79, 151.75, 147.84, 142.88, 137.69, 120.91, 119.64, 104.51, 101.43, 93.53, 93.41, 53.57, 52.63, 47.41, 25.89, 18.24. IR (KBr): γ 3435, 1747, 1632, 1474, 1284, 1182, 1150, 1036 cm⁻¹. HRMS (ESI): m/z [M + H]^+ calcd for [C₁₁H₁₀O₄]^+ requires 335.11253, found 335.11365. [α]₀⁺ = +61.5 (c = 0.75, CHCl₃). Enantiomeric excess: 44%, determined by HPLC (Daicel Chirapak IC-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 7.029 min (minor), tR = 10.489 min (major).

**Synthesis of 5b for X-ray analysis:**

A solution of lithium aluminium tetrahydride in ether (2 mL, 0.4 mmol) was added dropwise to a solution of 4b (23mg, 0.06 mmol) in ether (1 mL) at 0 °C under nitrogen. The reaction was allowed to warm to ambient temperature and was stirred for 16 h. The reaction mixture was quenched with water
(5 mL), and extracted with DCM (3 x 5 mL). The organic phases were combined and evaporated to dryness. The residue was purified by flash silica gel chromatography to afford 5b as a colourless oil (95%, 19 mg).^1H NMR (400 MHz, CDCl$_3$) δ 7.27 (d, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 7.7$ Hz, 2H), 6.57 (d, $J = 14.0$ Hz, 2H), 6.41 (s, 1H), 6.21 (dd, $J = 15.7$, 9.3 Hz, 1H), 5.90 (d, $J = 3.2$ Hz, 2H), 4.12 (d, $J = 9.2$ Hz, 1H), 3.90 (t, $J = 11.4$ Hz, 2H), 3.79 (s, 2H), 2.34 (s, 3H), 2.23 (s, 1H), 2.06 (s, 1H).^13C NMR (101 MHz, CDCl$_3$) δ 152.48, 147.88, 142.07, 133.78, 133.62, 129.38, 126.38, 124.74, 120.55, 105.41, 101.32, 93.34, 93.11, 64.95, 63.10, 50.09, 21.24. HRMS (ESI): m/z [M + H]$^+$ calcd for [C$_{20}$H$_{21}$O$_5$]$^+$ requires 341.1384, found 341.1387.

**X-ray Single Crystal Data for 5b**

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**References**


**$^1$H- and $^{13}$C-NMR Spectra**
(4b)
(4i)
(5b)
(4b)
(4c)
(4e)

![Chemical structure of 4e](image)

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![Graph of chromatography](image)

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**Graph 1**

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**Graph 2**

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