Supporting Information

Rhodium-Catalyzed Asymmetric Cyclodimerization of Oxa- and Azabicyclic Alkenes

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General. All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^1H and 125 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal SiMe_4 standard for ^1H NMR, chloroform- d (δ 77.00), and DMSO- d_6 (δ 39.50) for ^{13}C NMR: the following abbreviations are used; s: singlet, d: doublet, t: triplet, m: multiplet. Optical rotations were measured on a JASCO DIP-370 polarimeter. Elemental analyses were performed at Center for Organic Elemental Microanalysis of Kyoto University.

Materials. 1,2-Dichloroethane was distilled over CaH_2 under nitrogen. Rhodium complexes, $[\text{RhCl}((R)\text{-binap})]_2$ ¹ and $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ ² were prepared according to the reported procedure. $\text{NaBAR}_4^{\text{F}}$ ³ and bicyclic alkenes⁴ were prepared by the reported procedures.

Compound **1a** [573-57-9]: white solid. ^1H NMR (CDCl_3) δ 5.70 (s, 2H), 6.96 (dd, $J = 4.9, 3.0$ Hz, 2H), 7.02 (s, 2H), 7.24 (dd, $J = 4.9, 3.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 82.3, 120.2, 125.0, 143.0, 149.0.

Compound **1b** [19061-36-0]: white solid. ^1H NMR (CDCl_3) δ 2.19 (s, 6H), 5.65 (s, 2H), 6.99 (s, 2H), 7.05 (s, 2H); ^{13}C NMR (CDCl_3) δ 19.7, 82.2, 122.1, 132.5, 143.1, 146.6.

Compound **1c** [173276-99-8]: colorless oil. ^1H NMR (CDCl_3) δ 5.68 (s, 2H), 7.02 (s, 2H), 7.07 (t, $J_{\text{F-H}} = 7.6$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 82.0, 110.5–110.9 (m), 143.0, 145.1 (t, $J_{\text{F-C}} = 4.1$ Hz), 147.2 (dd, $J_{\text{F-C}} = 248.0, 15.0$ Hz).

Compound **1d** [106750-88-3]: white solid. ^1H NMR (CDCl_3) δ 5.66 (s, 2H), 7.00 (s, 2H), 7.48 (s, 2H); ^{13}C NMR (CDCl_3) δ 81.8, 120.7, 125.5, 142.7, 150.2.

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Compound **1e** [115695-65-3]: white solid. ^1H NMR (CDCl_3) δ 2.41 (s, 6H), 5.77 (s, 2H), 7.03 (s, 2H); ^{13}C NMR (CDCl_3) δ 20.8, 82.0, 124.8, 130.1, 142.6, 147.5.

Compound **3** [5176-28-3]: white solid. ^1H NMR ($\text{DMSO}-d_6$, 80 $^\circ\text{C}$) δ 1.32 (s, 9H), 5.42 (s, 2H), 6.92 (dd, $J = 5.2, 3.0$ Hz, 2H), 7.00 (s, 2H), 7.28 (dd, $J = 5.2, 3.0$ Hz, 2H); ^{13}C NMR ($\text{DMSO}-d_6$, 80 $^\circ\text{C}$) δ 27.9, 66.1, 79.6, 120.7, 124.6, 143.0, 148.6, 154.2.

Compound **5** [1829-60-3]: colorless oil. ^1H NMR (CDCl_3) δ 3.82 (s, 6H), 5.68 (s, 2H), 7.22 (s, 2H); ^{13}C NMR (CDCl_3) δ 52.3, 85.0, 143.2, 153.0, 163.2.

Procedure for Rhodium-Catalyzed Asymmetric Cyclodimerization of Oxabicyclic Alkene 1a. To a mixture of $[\text{RhCl}((R)\text{-binap})]_2$ (3.0 mg, 0.004 mmol Rh) and **1a** (57.7 mg, 0.40 mmol) in 1,2-dichloroethane (0.40 mL) in a screw cap test tube was added $\text{NaBAr}^{\text{F}}_4$ ($\text{Ar} = 3,5\text{-bis(trifluoromethyl)phenyl}$) (7.1 mg, 0.008 mmol) under argon and the tube was capped tightly. Then, the mixture was stirred at 40 $^\circ\text{C}$ (bath temp.) for 1 h. The reaction mixture was cooled to room temperature and was concentrated under vacuum. The residue was subjected to column chromatography on silica gel with EtOAc-hexane (1/5) as an eluent to give **2a** (57.1 mg, 0.198 mmol; 99% yield). The absolute configuration of **2d** was determined by X-ray crystallographic analysis (Figure S1). For others, they were assigned by consideration of the stereochemical pathway (Scheme S1 for **6** and **7**). Racemic products **2**, **4**, **6**, and **7** were obtained by use of racemic binap and were used for the determination of their enantiomeric purity.

Compound **2a**: white solid; $[\alpha]_D^{20} +220$ (c 1.03, CHCl_3 , 99% ee). The enantiomeric excess was measured by HPLC (Chiralcel OD-H column, 0.5 mL/min, hexane/2-propanol = 4/1, 254 nm, $t_1 = 29.9$ min (minor), $t_2 = 35.4$ min (major)); ^1H NMR (CDCl_3) δ 2.92 (dd, $J = 9.6, 6.3$ Hz, 1H), 3.20–3.32 (m, 1H), 4.34 (d, $J = 6.3$ Hz, 1H), 5.00 (d, $J = 7.2$ Hz, 1H), 5.18 (s, 1H), 5.40 (s, 1H), 6.01 (dd, $J = 9.9, 3.0$ Hz, 1H), 6.60 (dd, $J = 9.9, 2.3$ Hz, 1H), 7.10–7.18 (m, 3H), 7.20–7.27 (m, 3H), 7.28 (dt, $J = 7.4, 1.5$ Hz, 1H), 7.35 (d, $J = 7.4$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 39.2, 52.5, 79.1, 81.6, 83.0, 83.1, 119.4, 120.5, 126.0, 126.6, 126.8, 127.1, 127.2, 127.4, 128.7, 128.7, 131.7, 132.4, 143.0, 146.1. Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{O}_2$: C, 83.31; H, 5.59. Found: C, 83.43; H, 5.60.

Compound **2b**: white solid; $[\alpha]_D^{20} +203$ (c 1.00, CHCl_3 , 98% ee). The enantiomeric excess was measured by HPLC (Chiralpak AS column $\times$ 2, 1.0 mL/min, hexane/2-propanol = 9/1, 254 nm, t_1 = 14.6 min (minor), t_2 = 17.7 min (major)); ^1H NMR (CDCl_3) δ 2.26 (s, 3H), 2.27 (s, 6H), 2.29 (s, 3H), 2.91 (dd, J = 9.6, 6.4 Hz, 1H), 3.20–3.26 (m, 1H), 4.32 (d, J = 6.4 Hz, 1H), 4.94 (d, J = 7.0 Hz, 1H), 5.16 (s, 1H), 5.38 (s, 1H), 5.96 (dd, J = 9.7, 3.0 Hz, 1H), 6.57 (dd, J = 9.7, 2.1 Hz, 1H), 6.96 (s, 1H), 7.05 (s, 1H), 7.06 (s, 1H), 7.16 (s, 1H); ^{13}C NMR (CDCl_3) δ 19.4, 19.4, 19.8, 19.9, 39.2, 52.9, 78.9, 81.5, 82.9, 83.1, 120.7, 121.7, 125.1, 126.0, 128.3, 128.8, 130.1, 130.1, 134.6, 135.0, 135.6, 136.9, 140.8, 143.9. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{O}_2$: C, 83.69; H, 7.02. Found: C, 83.95; H, 7.26.

Compound **2c**: white solid; $[\alpha]_D^{20} +181$ (c 1.00, CHCl_3 , 99% ee). The enantiomeric excess was measured by HPLC (Chiralcel OD-H column, 0.8 mL/min, hexane/2-propanol = 4/1, 254 nm, t_1 = 8.6 min (major), t_2 = 13.4 min (minor)); ^1H NMR (CDCl_3) δ 2.82 (dd, J = 9.7, 6.4 Hz, 1H), 3.20–3.28 (m, 1H), 4.36 (d, J = 6.4 Hz, 1H), 5.07 (s, 1H), 5.12 (d, J = 8.5 Hz, 1H), 5.24 (s, 1H), 5.99 (dd, J = 9.7, 3.9 Hz, 1H), 6.48 (dd, J = 9.7, 1.8 Hz, 1H), 6.89 (dd, $J_{\text{F-H}}$ = 10.6, 7.6 Hz, 1H), 7.03 (dd, $J_{\text{F-H}}$ = 8.8, 7.0 Hz, 1H), 7.07 (dd, $J_{\text{F-H}}$ = 8.8, 7.0 Hz, 1H), 7.18 (dd, $J_{\text{F-H}}$ = 10.4, 7.9 Hz, 1H); ^{13}C NMR (CDCl_3) δ 39.0, 52.3, 79.3 (d, $J_{\text{F-C}}$ = 1.6 Hz), 80.5 (d, $J_{\text{F-C}}$ = 1.0 Hz), 83.2 (d, $J_{\text{F-C}}$ = 2.1 Hz), 83.4 (d, $J_{\text{F-C}}$ = 1.6 Hz), 109.7 (d, $J_{\text{F-C}}$ = 19.6 Hz), 110.8 (d, $J_{\text{F-C}}$ = 20.2 Hz), 115.5 (d, $J_{\text{F-C}}$ = 18.1 Hz), 117.0 (d, $J_{\text{F-C}}$ = 18.1 Hz), 125.7 (d, $J_{\text{F-C}}$ = 2.6 Hz), 126.0 (t, $J_{\text{F-C}}$ = 2.1 Hz), 128.9 (dd, $J_{\text{F-C}}$ = 6.2, 3.6 Hz), 129.9 (t, $J_{\text{F-C}}$ = 4.1 Hz), 138.8 (dd, $J_{\text{F-C}}$ = 6.2, 3.1 Hz), 142.1 (dd, $J_{\text{F-C}}$ = 6.2, 3.1 Hz), 149.3 (dd, $J_{\text{F-C}}$ = 248.0, 13.4 Hz), 149.6 (dd, $J_{\text{F-C}}$ = 248.0, 13.2 Hz, 2C), 150.0 (dd, $J_{\text{F-C}}$ = 247.0, 12.9 Hz). Anal. Calcd for $\text{C}_{20}\text{H}_{12}\text{F}_4\text{O}_2$: C, 66.67; H, 3.36. Found: C, 66.41; H, 3.66.

Compound **2d**: white solid; $[\alpha]_D^{20} +169$ (c 0.51, CHCl_3 , 99% ee). The enantiomeric excess was measured by HPLC (Chiralcel OD-H column, 0.5 mL/min, hexane/2-propanol = 4/1, 254 nm, t_1 = 14.9 min (major), t_2 = 22.6 min (minor)); ^1H NMR (CDCl_3) δ 2.83 (dd, J = 9.8, 6.4 Hz, 1H), 3.24–3.32 (m, 1H), 4.41 (d, J = 6.4 Hz, 1H), 5.07 (s, 1H), 5.16 (d, J = 8.8 Hz, 1H), 5.21 (s, 1H), 6.04 (dd, J = 9.7, 3.9 Hz, 1H), 6.50 (dd, J = 9.7, 1.8 Hz, 1H), 7.35 (s, 1H), 7.46 (s, 1H), 7.50 (s, 1H), 7.62 (s, 1H); ^{13}C NMR (CDCl_3) δ 39.2, 51.9, 79.0, 80.0, 83.0, 83.4, 122.9, 123.2, 123.3, 124.1, 124.9, 126.0, 126.1, 126.6, 131.5, 132.4, 132.7, 133.8, 143.7, 146.9. Anal. Calcd for $\text{C}_{20}\text{H}_{12}\text{Br}_4\text{O}_2$: C, 39.78; H, 2.00. Found: C, 39.82; H, 2.09.

Compound **2e**: white solid; $[\alpha]_D^{20} +108$ (*c* 0.98, CHCl_3 , 96% ee). The enantiomeric excess was measured by HPLC (Chiralcel OD-H column, 0.8 mL/min, hexane/2-propanol = 4/1, 254 nm, $t_1 = 8.5$ min (major), $t_2 = 22.3$ min (minor)); ^1H NMR (CDCl_3) δ 2.41 (s, 3H), 2.46 (s, 3H), 2.57 (s, 3H), 2.58 (s, 3H), 2.94 (dd, $J = 9.1, 6.4$ Hz, 1H), 3.18–3.25 (m, 1H),

4.24 (d, $J = 6.4$ Hz, 1H), 5.00 (d, $J = 6.7$ Hz, 1H), 5.27 (s, 1H), 5.53 (s, 1H), 6.07 (d, $J = 10.0$ Hz, 1H), 6.83 (d, $J = 10.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 20.6, 21.0, 21.1, 21.1, 38.5, 51.4, 78.7, 78.9, 81.4, 82.8, 123.2, 126.6, 127.0, 127.2, 127.7, 128.8, 129.5, 129.8, 130.7, 131.0, 133.9, 137.3, 141.5, 144.1. Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{Br}_4\text{O}_2$: C, 43.67; H, 3.05. Found: C, 43.45; H, 3.35.

Compound **4**: white solid; $[\alpha]_D^{20} +43$ (*c* 1.01, CHCl_3 , 99% ee). The enantiomeric excess was measured by HPLC (Chiralcel OD-H column, 0.5 mL/min, hexane/2-propanol = 2/1, 254 nm, $t_1 = 7.0$ min (minor), $t_2 = 10.6$ min (major)); ^1H NMR ($\text{DMSO}-d_6$, 80 °C) δ 0.95 (s,

9H), 1.55 (s, 9H), 2.54 (dd, $J = 9.5, 7.0$ Hz, 1H), 3.26 (ddd, $J = 11.2, 9.5, 5.5$ Hz, 1H), 4.07 (d, $J = 7.0$ Hz, 1H), 4.63 (s, 1H), 4.73 (s, 1H), 5.44 (d, $J = 11.2$ Hz, 1H), 5.98 (dd, $J = 9.7, 5.5$ Hz, 1H), 6.57 (d, $J = 9.7$ Hz, 1H), 6.95–7.30 (m, 8H); ^{13}C NMR ($\text{DMSO}-d_6$, 80 °C) δ 27.2, 27.8, 37.9, 51.4, 58.5, 61.7, 63.5, 66.0, 77.8, 79.1, 119.5, 120.4, 123.9, 124.9, 125.6, 125.9, 126.0, 126.4, 127.2, 128.0, 130.8, 135.5, 142.8, 146.4, 153.9, 154.1. Anal. Calcd for $\text{C}_{30}\text{H}_{34}\text{N}_2\text{O}_4$: C, 74.05; H, 7.04. Found: C, 73.82; H, 6.99.

Compound **6**: white solid; $[\alpha]_D^{20} -144$ (*c* 0.82, CHCl_3 , 99% ee). The enantiomeric excess was measured by HPLC (Chiralpak AD-H column, 0.55 mL/min, hexane/2-propanol = 1/1, 254 nm, $t_1 = 23.1$ min (minor), $t_2 = 42.0$ min (major));

^1H NMR (CDCl_3) δ 2.18 (dd, $J = 6.7, 4.8$ Hz, 1H, H^f), 2.56 (ddd, $J = 8.4, 5.2, 3.6$ Hz, 1H, H^b), 2.67 (dd, $J = 6.7, 3.6$ Hz, 1H, H^e), 2.80 (ddd, $J = 8.4, 4.9, 4.8$ Hz, 1H, H^g), 3.66 (d, $J = 5.2$ Hz, 1H, H^a), 3.78 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 5.14 (s, 1H, H^c), 5.21 (s, 1H, H^d), 7.18 (d, $J = 4.9$ Hz, 1H, H^h); ^{13}C NMR (CDCl_3) δ 28.3 (d), 32.2 (d), 38.6 (d), 42.9 (d), 52.1 (q), 52.3 (q), 52.6 (q), 52.7 (q), 57.0 (d), 82.3 (d), 82.5 (d), 126.9 (s), 141.3 (s), 141.9 (s), 142.9 (s), 142.9 (d), 162.2 (s), 162.3 (s), 165.5 (s), 169.3 (s). Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_{10}$: C, 57.14; H, 4.80. Found: C, 57.02; H, 4.69.

Compound **7**: white solid; $[\alpha]_D^{20} +16$ (*c* 1.00, CHCl_3 , 99% ee). The enantiomeric excess was measured by HPLC (Chiralcel OD-H column, 0.5 mL/min, hexane/2-propanol = 1/1, 254 nm, $t_1 = 14.9$ min (major), $t_2 = 16.8$ min (minor)); ^1H NMR

(CDCl₃) δ 1.88 (dt, J = 12.2, 4.2 Hz, 1H), 2.19 (dd, J = 12.2, 8.5 Hz, 1H), 3.50 (dd, J = 8.5, 4.2 Hz, 1H), 3.83 (s, 3H), 3.85 (s, 3H), 3.88 (s, 3H), 3.93 (s, 3H), 5.19 (d, J = 1.2 Hz, 1H), 5.37 (dd, J = 4.8, 0.9 Hz, 1H), 7.00 (d, J = 7.9 Hz, 1H), 7.52 (d, J = 7.9 Hz, 1H), 10.80 (s, 1H); ¹³C NMR (CDCl₃) δ 34.1, 35.7, 52.4, 52.4, 52.6, 52.9, 80.9, 85.2, 110.6, 119.1, 131.7, 133.1, 134.0, 143.7, 145.0, 158.5, 162.5, 162.8, 169.1, 169.7. Anal. Calcd for C₂₀H₂₀O₁₀: C, 57.14; H, 4.80. Found: C, 56.86; H, 4.68.

Scheme S1. Plausible pathway of the formation of **6** and **7**

Procedure for Rhodium-Catalyzed Asymmetric Cyclodimerization of Oxabicyclic Alkene **1a with DMAD (dimethyl 2-butyndioate).** To a mixture of [RhCl((*R*)-binap)]₂ (3.0 mg, 0.004 mmol Rh) and **1a** (28.8 mg, 0.20 mmol) in 1,2-dichloroethane (0.40 mL) in a screw cap test tube was added DMAD (85.3 mg, 0.60 mmol) and NaBAR₄^F (Ar = 3,5-bis(trifluoromethyl)phenyl) (7.1 mg, 0.008 mmol) under argon and the tube was capped tightly. Then, the mixture was stirred at 80 °C (bath temp.) for 3 h. The reaction mixture was cooled to room temperature and was concentrated under vacuum. The residue was subjected to column chromatography on silica gel with EtOAc-hexane (1/5) as an eluent to give **8a** (54.5 mg, 0.190 mmol; 95% yield). The absolute configuration of **8e** was determined by X-ray crystallographic analysis (Figure S2). For others, they were assigned by consideration of the stereochemical pathway (Scheme S3). Racemic products **8a–8e** were obtained by use of racemic binap and were used for the determination of their enantiomeric purity.

Compound **8a**: pale yellow oil; $[\alpha]_D^{20}$ +615 (c 1.19, CHCl₃, 99% ee). The enantiomeric excess was measured by HPLC Chiralcel OD-H column, 0.6 mL/min, hexane/2-propanol = 4/1, 254 nm, t_1 = 11.6 min

(minor), $t_2 = 12.7$ min (major)); ^1H NMR (CDCl_3) 3.78 (s, 3H), 3.83 (s, 3H), 4.14 (ddd, $J = 10.7, 2.7, 2.1$ Hz, 1H), 5.84 (d, $J = 10.3$ Hz, 1H), 6.00 (dd, $J = 9.7, 2.7$ Hz, 1H), 6.50 (dd, $J = 9.7, 2.1$ Hz, 1H), 7.14 (d, $J = 7.6$ Hz, 1H), 7.27 (td, $J = 7.6, 1.2$ Hz, 1H), 7.35 (td, $J = 7.6, 1.2$ Hz, 1H), 7.40 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 41.8, 51.6, 52.8, 83.7, 110.4, 124.7, 125.5, 126.9, 127.3, 127.9, 130.2, 130.4, 132.5, 156.4, 161.2, 163.6. Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_5$: C, 67.13; H, 4.93. Found: C, 67.39; H, 5.13.

Compound **8b**: white solid; $[\alpha]_{\text{D}}^{20} +205$ (c 1.05, CHCl_3 , 98% ee).

The enantiomeric excess was measured by HPLC Chiralcel OD–H column, 0.8 mL/min, hexane/2-propanol = 9/1, 254 nm, $t_1 = 9.3$ min (minor), $t_2 = 10.8$ min (major)); ^1H NMR (CDCl_3) 2.26 (s, 6H), 3.78 (s, 3H), 3.84 (s, 3H), 4.12 (d, $J = 10.5$ Hz, 1H), 5.83 (d, $J = 10.5$ Hz, 1H), 5.93 (d, $J = 7.8$ Hz, 1H), 6.45 (d, $J = 7.8$ Hz, 1H), 6.93 (s, 1H), 7.19 (s, 1H); ^{13}C NMR (CDCl_3) δ 19.5, 19.6, 42.0, 51.7, 52.9, 84.1, 110.7, 123.9, 124.3, 125.4, 128.6, 130.3, 131.6, 136.5, 138.9, 156.5, 161.4, 163.9. Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_5$: C, 68.78; H, 5.77. Found: C, 68.96; H, 5.78.

Compound **8c**: white solid; $[\alpha]_{\text{D}}^{20} +554$ (c 0.50, CHCl_3 , 99% ee).

The enantiomeric excess was measured by HPLC (Chiralcel OD–H column, 0.6 mL/min, hexane/2-propanol = 1/1, 254 nm, $t_1 = 8.0$ min (minor), $t_2 = 9.4$ min (major)); ^1H NMR (CDCl_3) δ 3.79 (s, 3H), 3.86 (s, 3H), 4.16 (ddd, $J = 10.6, 2.9, 2.3$ Hz, 1H), 5.80 (d, $J = 10.6$ Hz, 1H), 6.06 (dd, $J = 10.0, 2.9$ Hz, 1H), 6.41 (dd, $J = 10.0, 2.3$ Hz, 1H), 6.96 (dd, $J_{\text{F-H}} = 10.4, 7.6$ Hz, 1H), 7.25 (dd, $J_{\text{F-H}} = 10.0, 7.6$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 41.7, 51.8, 53.0, 82.2 (d, $J_{\text{F-C}} = 1.6$ Hz), 110.4, 115.9 (d, $J_{\text{F-C}} = 18.1$ Hz), 119.5 (dd, $J_{\text{F-C}} = 18.1, 1.0$ Hz), 123.6 (dd, $J_{\text{F-C}} = 5.7, 3.6$ Hz), 123.8 (t, $J_{\text{F-C}} = 2.1$ Hz), 125.5 (d, $J_{\text{F-C}} = 2.6$ Hz), 129.9 (dd, $J_{\text{F-C}} = 6.7, 3.6$ Hz), 149.4 (dd, $J_{\text{F-C}} = 250.1, 12.9$ Hz), 151.2 (dd, $J_{\text{F-C}} = 250.6, 12.9$ Hz), 156.0, 160.9, 163.5. Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{F}_2\text{O}_5$: C, 59.63; H, 3.75. Found: C, 59.55; H, 3.80.

Compound **8d**: white solid; $[\alpha]_{\text{D}}^{20} +495$ (c 0.52, CHCl_3 , 99% ee).

The enantiomeric excess was measured by HPLC (Chiralcel OD–H column, 0.6 mL/min, hexane/2-propanol = 1/1, 254 nm, $t_1 = 9.6$ min (minor), $t_2 = 11.5$ min (major)); ^1H NMR (CDCl_3) δ 3.79 (s, 3H), 3.86 (s, 3H), 4.16 (ddd, $J = 10.7, 2.7, 2.1$ Hz, 1H), 5.77 (d, $J = 10.7$ Hz, 1H), 6.11 (dd, $J = 9.7, 2.7$ Hz, 1H), 6.41 (dd, $J = 9.7, 2.1$ Hz, 1H), 7.41 (s, 1H), 7.66 (s, 1H); ^{13}C NMR (CDCl_3) δ 42.0, 51.9, 53.0, 81.8, 110.4, 123.3, 123.7, 126.6, 127.6, 131.9, 133.1, 135.2, 155.9, 160.8, 163.4. Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{Br}_2\text{O}_5$: C, 43.27; H, 2.72. Found: C, 43.43; H, 2.56.

Compound **8e**: white solid; $[\alpha]_D^{20} +530$ (*c* 0.50, CHCl_3 , 87% ee).

The enantiomeric excess was measured by HPLC (Chiralcel OD-H column, 0.6 mL/min, hexane/2-propanol = 1/1, 254 nm, t_1 = 8.7 min (minor), t_2 = 10.0 min (major)); ^1H NMR (CDCl_3) δ 2.56 (s, 3H), 2.60 (s, 3H), 3.80 (s, 3H), 3.86 (s, 3H), 4.11 (ddd, J = 10.7, 2.6, 2.4 Hz, 1H), 6.02 (d, J = 10.7 Hz, 1H), 6.07 (dd, J = 10.4, 2.6 Hz, 1H), 6.76 (dd, J = 10.4, 2.4 Hz, 1H); ^{13}C NMR (CDCl_3) δ 21.0, 21.0, 41.6, 51.8, 53.0, 81.0, 110.2, 122.5, 125.5, 125.9, 128.3, 130.9, 131.1, 134.1, 138.3, 156.5, 161.1, 163.5. Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{Br}_2\text{O}_5$: C, 45.79; H, 3.42. Found: C, 45.73; H, 3.62.

Scheme S3. Plausible pathway of the formation of **8a**

Isomerization of **2a** to **9**

To a solution of **2a** (57.7 mg, 0.20 mmol) in dichloromethane (2.0 mL) was added conc. HCl (ca. 300 mg) and the mixture was stirred at room temperature for 12 h. After concentration of the mixture under vacuum, the residue was subjected to short column chromatography on silica gel with EtOAc-hexane (1/1) as an eluent to give **9** (57.0 mg, 0.198 mmol; 99% yield). Compound **9**: white solid; $[\alpha]_D^{20} +116$ (*c* 1.00, CHCl_3 , 99% ee). The enantiomeric excess was measured by HPLC (Chiralcel OD-H column, 1.0 mL/min, hexane/2-propanol = 4/1, 254 nm, t_1 = 8.3 min (minor), t_2 = 14.9 min (major)); ^1H NMR (CDCl_3) δ 1.58 (br s, 1H), 3.40 (d, J = 6.7 Hz, 1H), 4.26 (br s, 1H), 5.31 (s, 1H), 5.56 (s, 1H), 7.20–7.28 (m, 3H), 7.35–7.40 (m, 1H), 7.44–7.51 (m, 3H), 7.80–7.86 (m, 3H), 7.89 (s, 1H); ^{13}C NMR (CDCl_3) δ 51.8, 74.2, 84.5, 86.0, 119.1, 120.9, 125.9, 126.3, 127.0, 127.5, 127.5, 127.5, 127.6, 127.8, 128.5, 132.6, 133.5, 135.0, 142.6, 146.6. Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{O}_2$: C, 83.31; H, 5.59. Found: C, 83.21; H, 5.47.

Hydrogenation of **8a**

A mixture of **8a** (860 mg, 3.0 mmol) and $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{py})]\text{PF}_6^5$ (121 mg, 0.15 mmol) in dichloromethane (30 mL) was stirred at room temperature under H_2 (1 atm). After 1 h the reaction mixture was concentrated under vacuum. The residue was subjected to column chromatography on silica gel with EtOAc-hexane (1/5) as an eluent to give **10** (807 mg, 2.8 mmol; 93% yield). Compound **10**: pale yellow oil; $[\alpha]_D^{20} +277$ (c 1.03, CHCl_3 , 99% ee). The enantiomeric excess was measured by HPLC (Chiralcel OD-H column, 0.5 mL/min, hexane/2-propanol = 1/1, 254 nm, t_1 = 9.7 min (minor), t_2 = 11.3 min (major)); ^1H NMR (CDCl_3) δ 1.75–1.84 (m, 1H), 2.05–2.13 (m, 1H), 2.61 (ddd, J = 15.8, 9.4, 3.9 Hz, 1H), 2.80 (ddd, J = 15.8, 7.3, 3.6 Hz, 1H), 3.53 (ddd, J = 9.4, 8.5, 5.5 Hz, 1H), 3.77 (s, 3H), 3.86 (s, 3H), 5.71 (d, J = 9.4 Hz, 1H), 7.15–7.19 (m, 1H), 7.24–7.32 (m, 2H), 7.43–7.46 (m, 1H); ^{13}C NMR (CDCl_3) δ 25.9, 27.3, 41.6, 51.6, 52.8, 83.9, 112.2, 126.7, 128.4, 128.8, 130.1, 131.2, 139.4, 155.4, 161.3, 164.1. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_5$: C, 66.66; H, 5.59. Found: C, 66.87; H, 5.74.

Preparation of **11**⁶

To a mixture of **10** (57.6 mg, 0.20 mmol) and urea (12.0 mg, 0.20 mmol) was added NaOEt in EtOH (1.0M, 0.40 mL, 0.40 mmol) and the mixture was stirred at 60 °C (bath temp.) for 20 h. The reaction mixture was cooled to room temperature and was acidified with diluted hydrochloric acid. The mixture was extracted with ethyl acetate three times and the combined organic layer was dried over Na_2SO_4 , filtered, and concentrated on a rotary evaporator. The residue was subjected to column chromatography on silica gel with EtOAc-hexane (2/3) as an eluent to give **11** (38.4 mg, 0.14 mmol, 69% yield). Compound **11**: white solid; $[\alpha]_D^{20} +313$ (c 0.80, THF, 99% ee). The enantiomeric excess was measured by HPLC (Chiralcel OD-H column, 1.0 mL/min, hexane/2-propanol = 1/1, 254 nm, t_1 = 18.9 min (minor), t_2 = 26.2 min (major)); ^1H NMR ($\text{DMSO}-d_6$) δ 1.35–1.47 (m, 1H), 2.05–2.15 (m, 1H), 2.65–2.75 (m, 2H),

⁵ Crabtree, R. H.; Morris, G. E. *J. Organomet. Chem.* **1977**, 135, 395.

⁶ Lehmann, J. *Arch. Pharm.* **1984**, 317, 459.

3.85–3.95 (m, 1H), 5.54 (d, $J = 6.4$ Hz, 1H), 7.22 (d, $J = 7.0$ Hz, 1H), 7.24–7.35 (m, 2H), 7.44 (d, $J = 6.7$ Hz, 1H), 10.7 (s, 1H), 11.6 (br s, 1H); ^{13}C NMR (DMSO- d_6) δ 25.5, 27.4, 37.3, 76.6, 110.8, 126.4, 128.4, 128.6, 130.4, 131.2, 133.4, 138.4, 154.5, 164.4, 169.4. Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_4$: C, 63.38; H, 4.25. Found: C, 63.18; H, 4.26.

X-ray Crystal Structure of Compound 2d. Colorless crystals of compound **2d** suitable for X-ray crystallographic analysis were obtained by recrystallization from CH₂Cl₂–hexane. The ORTEP drawing of **2d** is shown in Figure S1. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 627866). The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Figure S1. ORTEP illustration of **2d** with thermal ellipsoids drawn at 50% probability level. Crystal data for **2d**: C₂₀H₁₂Br₄O₂, $M_w = 603.93$, space group $P2_1$ (No. 4), $a = 10.419(5)$ Å, $b = 7.186(3)$ Å, $c = 12.309(6)$ Å, $V = 921.4(7)$ Å³, $Z = 2$, $D_{\text{calcd}} = 2.177$ g/cm³, $T = 123$ K, 1345 measured reflections, 427 unique reflections, $R = 0.0559$, $R_w = 0.0611$ (all data), GOF = 1.341, Flack parameter⁷ = 0.035(13).

⁷ Flack, H. D. *Acta Cryst.* **1983**, A39, 876.

X-ray Crystal Structure of Compound 8e. Colorless crystals of compound **8e** suitable for X-ray crystallographic analysis were obtained by recrystallization from ethyl acetate–hexane. The ORTEP drawing of **8e** is shown in Figure S2 (deposition number: CCDC 627867).

Figure S2. ORTEP illustration of **8e** with thermal ellipsoids drawn at 50% probability level. Crystal data for **8e**: $C_{18}H_{16}Br_2O_5$, $M_w = 472.13$, space group $P2_1$ (No. 4), $a = 12.210(10)$ Å, $b = 4.332(3)$ Å, $c = 16.228(12)$ Å, $V = 844.0(11)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.858$ g/cm³, $T = 123$ K, 1165 measured reflections, 320 unique reflections, $R = 0.0664$ ($I > 2.00\sigma(I)$), $R_w = 0.0877$ ($I > 2.00\sigma(I)$), GOF = 1.060, Flack parameter = 0.02(2).