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## Supporting Information

# Highly Stereoselective Cyclopropanation of Various Olefins with Diazosulfones Catalyzed by Ru(II)–Pheox Complexes

Manato, Kotozaki, Soda Chanthamath,\* Ikuhude Fujisawa, Kazutaka Shibatomi, and Seiji Iwasa\* Department of Environmental and Life Sciences, Toyohashi University of Technology, 1-1 Tempaku-cho, Toyohashi, Aichi 441-8580, JAPAN

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**General methods:** All non-aqueous reactions were carried out in glassware under argon atmosphere and stirred via magnetic stir-plates. Thin-layer chromatography analyses were performed using Merck pre-coated silica gel plates with 254 indicator. Visualization was accomplished by UV light (254 nm), potassium permanganate, phosphomolybdic acid, or anisaldehyde. Flash column chromatography was performed using silica gel 60 (mesh 40-100) supplied by Kanto Chemical Co., Inc. <sup>1</sup>H and <sup>13</sup>CNMR spectra were recorded on a JEOLJNM-ECS400 (400 MHz <sup>1</sup>H, 100 MHz <sup>13</sup>C) or a JEOL JNM-ECX500 (500 MHz <sup>1</sup>H, 126 MHz <sup>13</sup>C). Chemical shift values ( $\delta$ ) are reported in ppm (tetramethylsilane  $\delta$  0.00 ppm for <sup>1</sup>H; residual chloroform  $\delta$  77.0 ppm for <sup>13</sup>C). Optical rotations were measured on a JASCO P-1030 digital polarimeter. DART mass (positive mode) analyses were performed using a JEOL the Accu TOF TLC JMS-T100TD. Analytical HPLC was performed on a JASCO PU1586 with a UV-1575 UV/Vis detector using a chiral column.

#### 1. General procedure for catalytic asymmetric cyclopropanation of olefins with diazosulfones.

$$R + N_{2} Ts \qquad \frac{Ru(II)-Pheox}{(3 \text{ mol}\%)} CH_{2}CI_{2}, 5 \text{ min, } -10 ^{\circ}C$$

The solution of diazosulfones (0.2 mmol) in  $CH_2Cl_2$  (2.0 mL) was slowly added to a mixture of Ru(II)– Pheox catalyst (3.8 mg, 0.006 mmol) and olefins (1.0 mmol) in  $CH_2Cl_2$  (2.0 mL) under argon atmosphere at room temperature. After the addition completed, the reaction mixture was thenstirred for 5 min at –10 °C. The progress of the reaction was monitored by TLC. Upon completion, solvent was removed and the residue was purified by column chromatography to give desired product. The *trans/cis* ratio was determined from the crude <sup>1</sup>H NMR spectra, and the ee value was determined by chiral HPLC analysis.

## 2. Analytical data of asymmetric cyclopropanation reaction products.

#### 1-methyl-4-(((1R,2S)-2-phenylcyclopropyl)sulfonyl)benzene (3a)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between styrene (104.2 mg, 1.0 mmol) and  $TsCHN_2$  (39.2 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give 1-methyl-4-

(((1R,2S)-2-phenylcyclopropyl)sulfonyl)benzene **3a** (80% yield, 43.5 mg, 0.16 mmol), 96% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.81 (d, *J* = 8.41 Hz, 2H), 7.35 (d, *J* = 8.41 Hz, 2H), 7.30-7.15 (m, 3H), 7.02 (d, *J* = 7.26 Hz, 2H), 2.87 (ddd, *J* = 4.20, 6.12, 10.13 Hz, 1H), 2.65 (ddd, *J* = 4.78, 4.78, 8.22 Hz, 1H), 2.44 (s, 3H), 1.87 (ddd, *J* = 5.59, 5.59, 9.94 Hz, 1H), 1.45 (ddd, *J* = 6.12, 6.12, 8.41 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  144.4, 137.5, 137.5, 129.9, 128.6, 127.5, 127.0, 126.5, 41.9, 23.7, 21.6, 13.8;  $[\alpha]^{21}_{D}$  = -58.0 (c = 1.0, CHCl<sub>3</sub>); For C<sub>16</sub>H<sub>16</sub>O<sub>2</sub>S [M+NH<sub>4</sub>] + Calcd: 290.12147, Found: 290.12143; The enantiomeric ratio of **3a** was determined by HPLC (Hexane : IPA = 4 : 1, 1.0 mL/min) using a CHIRALCEL OJ-H column (0.46 cm x 25 cm): major isomer 42.9 min and minor isomer 40.5 min.

#### 1-methyl-4-((2-(p-tolyl)cyclopropyl)sulfonyl)benzene (3b)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between 4-methyl styrene (118.2 mg, 1.0 mmol) and TsCHN<sub>2</sub> (39.2 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an

eluent to give 1-methyl-4-((2-(*p*-tolyl)cyclopropyl)sulfonyl)benzene **3b** (91% yield, 52.2 mg, 0.18 mmol), 93% *ee.* <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.81(d, *J* = 8.41 Hz, 2H), 7.35 (d, *J* = 8.03 Hz, 2H), 7.05 (d, *J* = 7.26 Hz, 2H), 6.91 (d, *J* = 8.03 Hz, 2H), 2.83 (ddd, *J* = 4.30, 6.22, 10.22 Hz, 1H), 2.61 (ddd, *J* = 4.97, 4.97, 7.64 Hz, 1H), 2.44 (s, 3H), 2.28 (s, 3H), 1.85 (ddd, J = 5.30, 5.30, 9.94 Hz, 1H),

1.42 (ddd, 5.73, 6.50, 8.41 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  144.3, 137.6, 136.7, 134.4, 129.9, 129.2, 127.5, 126.4, 41.8, 23.4, 21.6, 21.9, 13.7;  $[\alpha]^{21}_{D} = -48.1$  (c = 1.0, CHCl<sub>3</sub>); For C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>S [M+H] <sup>+</sup> Calcd: 287.11057, Found: 287.11058; The enantiomeric ratio of **3b** was determined by HPLC (Hexane : IPA = 4 : 1, 1.0 mL/min) using a CHIRALCEL OJ-H column (0.46 cm x 25 cm): major isomer 18.1 min and minor isomer 20.2 min.

#### 1-(tert-butyl)-4-(2-tosylcyclopropyl)benzene (3c)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between 4-*t*butyl styrene (160.3 mg, 1.0 mmol) and TsCHN<sub>2</sub> (39.2 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an

eluent to give 1-(tert-butyl)-4-(2-tosylcyclopropyl)benzene **3c** (89% yield, 58.2 mg, 0.18 mmol), 92% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.81 (d, *J* = 6.50 Hz, 2H), 7.35 (d, *J* = 8.03 Hz, 2H), 7.27 (ddd, *J* = 2.1, 2.1, 8.41 Hz, 2H), 6.95 (ddd, *J* = 1.91, 1.91, 8.41 Hz, 2H), 2.84 (ddd, *J* = 4.21, 6.31, 10.13 Hz, 1H), 2.64 (ddd, *J* = 4.59, 5.35, 8.41 Hz 1H), 2.44 (s, 3H), 1.86 (ddd, *J* = 5.59, 5.59, 9.56 Hz, 1H), 1.44 (ddd, *J* = 5.64, 6.69, 8.22 Hz, 1H), 1.27 (s, 9H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  150.1, 144.3, 137.6, 134.4, 129.9, 127.6, 126. 2, 125.5, 41.7, 34.4, 31.2, 23.3, 21.6, 13.7; [ $\alpha$ ]<sup>24</sup><sub>D</sub> = -51.5 (c = 1.0, CHCl<sub>3</sub>); For C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>S [M+H]<sup>+</sup> Calcd: 329.15752, Found: 329.15750; The enantiomeric ratio of **3c** was determined by HPLC (Hexane : IPA = 4 : 1, 1.0 mL/min) using a CHIRALCEL OJ-H column (0.46 cm x 25 cm): major isomer 10.7 min and minor isomer 9.37 min.

#### 1-methoxy-4-(2-tosylcyclopropyl)benzene (3d)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between 4-methoxy styrene (134.2 mg, 1.0 mmol) and TsCHN<sub>2</sub> (39.2 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc

as an eluent to give 1-methoxy-4-(2-tosylcyclopropyl)benzene **3d** (96% yield, 58.1 mg, 0.19 mmol), 95% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.81 (d, *J* = 8.41 Hz, 2H), 7.36 (d, *J* = 8.03 Hz, 2H), 6.94 (ddd, *J* = 2.39, 2.39, 9.08 Hz, 2H), 6.78 (ddd, *J* = 2.48, 2.49, 8.79 Hz, 2H), 3.75 (s, 3H), 2.83 (ddd, *J* = 4.30, 6.22, 10.22 Hz, 1H), 4.97 (ddd, *J* = 4.97, 4.97, 7.84 Hz, 1H), 2.44 (s, 3H), 1.83 (ddd, *J* = 5.45, 5.45, 9.94 Hz, 1H), 1.40 (ddd, *J* = 5.73, 6.50, 8.41 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  158.6, 144.3, 137.6, 129.9, 129.4,127.7, 127.5, 114.0, 55.2, 41.7, 23.1, 21.6, 13.6;  $[\alpha]^{24}_{D} = -53.5$  (c = 1.0, CHCl<sub>3</sub>); For C<sub>17</sub>H<sub>18</sub>O<sub>3</sub>S [M+NH<sub>4</sub>]<sup>+</sup> Calcd: 320.13204, Found: 320.13203; The enantiomeric ratio of **3d** was determined by HPLC (Hexane : IPA = 4 : 1, 1.0 mL/min) using a CHIRALCEL OJ-H column (0.46 cm x 25 cm): major isomer 25.2 min and minor isomer 29.9 min.

#### N,N-dimethyl-4-(2-tosylcyclopropyl)aniline (3e)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between 4-N,N-dimethylamino styrene (147.2 mg, 1.0 mmol) and TsCHN<sub>2</sub> (39.2 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with

Hexane/EtOAc as an eluent to give N,N-dimethyl-4-(2-tosylcyclopropyl)aniline **3e** (88% yield, 55.7 mg, 0.18 mmol), 93% *ee*. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.81 (d, *J* = 8.03 Hz, 2H), 7.34 (d, *J* = 8.41 Hz, 2H), 6.88 (d, *J* = 8.79 Hz, 2H), 6.60 (d, *J* = 8.79 Hz, 2H), 2.88 (s, 6H), 2.79 (ddd, *J* = 4.21, 6.12, 9.94 Hz, 1H), 2.55 (ddd, *J* = 4.78, 4.78, 8.03 Hz, 1H), 2.44 (s, 3H), 1.81 (ddd, *J* = 5.07, 5.07, 9.56 Hz, 1H), 1.39 (ddd, *J* = 6.12, 6.12, 7.64 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  149.7, 144.2, 137.8, 129.8, 127.5, 127.4, 124. 9, 112.5, 41.5, 40.5, 23.3, 21.6, 13.3; [ $\alpha$ ]<sup>24</sup><sub>D</sub> = -66.9 (c = 1.0, CHCl<sub>3</sub>); For C<sub>18</sub>H<sub>21</sub>NO<sub>2</sub>S [M+H]<sup>+</sup> Calcd: 316.13712, Found: 316.13710; The enantiomeric ratio of **3e** was determined by HPLC (Hexane : IPA = 4 : 1, 2.0 mL/min) using a CHIRALCEL OJ-H column (0.46 cm x 25 cm): major isomer 19.7 min and minor isomer 28.3 min.

#### 1-methyl-2-(2-tosylcyclopropyl)benzene (3f)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between 2-methyl styrene (118.2 mg, 1.0 mmol) and TsCHN<sub>2</sub> (39.2 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give 1-

methyl-2-(2-tosylcyclopropyl)benzene **3f** (90% yield, 51.7 mg, 0.18 mmol), 76% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.82 (d, *J* = 8.41 Hz, 2H), 8.03 (d, *J* = 8.03 Hz, 2H), 7.13 (d, *J* = 4.20 Hz, 2H), 7.10-7.04 (m, 1H), 6.84 (d, *J* = 7.26 Hz, 1H), 2.90 (ddd, *J* = 4.44, 6.31, 10.13 Hz, 1H), 2.61 (ddd, *J* = 4.97, 4.97, 8.41 Hz, 1H), 2.45 (s, 3H), 2.34 (s, 3H), 1.81 (ddd, *J* = 5.07, 5.07, 9.75 Hz, 1H), 1.42 (ddd, *J* = 5.54, 6.79, 8.12 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  144.4, 138.0, 137.5, 135.3, 130.1, 129.9, 127.6, 127.2, 125.9, 125.8, 41.1, 21.9, 21.6, 12.8;  $[\alpha]^{21}{}_{D} = -26.4$  (c = 1.0, CHCl<sub>3</sub>); For C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>S [M+1]<sup>+</sup> Calcd: 287.11057, Found: 287.11055; The enantiomeric ratio of **3f** was determined by HPLC (Hexane : IPA = 4 : 1, 1.0 mL/min) using a CHIRALPAK AD-H column (0.46 cm x 25 cm): major isomer 14.1 min and minor isomer 15.6 min.

#### 1-chloro-4-(2-tosylcyclopropyl)benzene (3g)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between 4-chloro styrene (138.6 mg, 1.0 mmol) and TsCHN<sub>2</sub> (39.2 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an

eluent to give 1-chloro-4-(2-tosylcyclopropyl)benzene 3g (72% yield, 44.3 mg, 0.14 mmol), 94% ee.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.80 (d, *J* = 8.41 Hz, 2H), 7.36 (d, *J* = 8.41, 2H), 7.21 (ddd, *J* = 2.10, 2.10, 8.41 Hz, 2H), 6.95 (ddd, *J* = 2.29, 2.30, 8.60 Hz, 2H) 2.84 (ddd, *J* = 4.30, 6.22, 10.22 Hz, 1H), 2.61 (ddd, *J* = 4.78, 4.78, 8.03 Hz, 1H), 2.45 (s, 3H), 1.87 (ddd, *J* = 5.54, 5.54, 9.94 Hz, 1H), 1.42 (ddd, *J* = 6.17, 6.31, 8.41 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  144.6, 137.4, 136.0, 132.9, 129.9, 128.7, 127.9, 127.5, 41.9, 23.0, 21.6, 13.9;  $[\alpha]^{24}_{D} = -50.8$  (c = 1.0, CHCl<sub>3</sub>); For C<sub>16</sub>H<sub>15</sub>ClO<sub>2</sub>S [M+NH<sub>4</sub>]<sup>+</sup> Calcd: 324.08250, Found: 324.088251; The enantiomeric ratio of **3g** was determined by HPLC (Hexane : IPA = 4 : 1, 0.5 mL/min) using a CHIRALCEL OJ-H column (0.46 cm x 25 cm): major isomer 49.1 min and minor isomer 45.4 min.

#### 1-methyl-4-((2-(4-(trifluoromethyl)phenyl)cyclopropyl)sulfonyl)benzene (3h)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between 4-trifluoromethyl styrene (172.2 mg, 1.0 mmol) and TsCHN<sub>2</sub> (39.2 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc

as an eluent to give 1-methyl-4-((2-(4-(trifluoromethyl)phenyl)cyclopropyl)sulfonyl)benzene **3h** (62% yield, 44.3 mg, 0.14 mmol), 93% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.81 (d, *J* = 6.5 Hz, 2H), 7.51 (d, *J* = 8.03 Hz, 2H), 7.37 (d, *J* = 8.03 Hz, 2H), 7.14 (d, *J* = 8.41 Hz, 2H), 2.92 (ddd, *J* = 4.40, 6.12, 10.13 Hz, 1H), 2.69 (ddd, *J* = 4.49, 5.45, 8.50 Hz, 1H), 2.46 (s, 3H), 1.93 (ddd, *J* = 5.64, 5.64, 9.56 Hz, 1H), 1.49 (ddd, *J* = 6.12, 6.12, 8.60 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  144.7, 141.7, 137.2, 130.0, 129.7 129.5, 129.2, 129.0 127.6, 127.2, 126.9, 125.6, 125.6, 125.0, 122.9, 120.7, 42.2, 23.3, 21.6, 14.2; [ $\alpha$ ]<sup>23</sup><sub>D</sub> = -41.2 (c = 1.0, CHCl<sub>3</sub>); For C<sub>17</sub>H<sub>15</sub>F<sub>3</sub>O<sub>2</sub>S [M+H]<sup>+</sup> Calcd: 341.08231, Found: 341.08233; The enantiomeric ratio of **3h** was determined by HPLC (Hexane : IPA = 4 : 1, 0.5 mL/min) using a CHIRALCEL OJ-H column (0.46 cm x 25 cm): major isomer 27.5 min and minor isomer 25.9 min.

#### 1-methyl-4-((2-(4-nitrophenyl)cyclopropyl)sulfonyl)benzene (3i)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between 4-nitro styrene (149.2 mg, 1.0 mmol) and TsCHN<sub>2</sub> (39.2 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with  $CH_2Cl_2$  as an eluent

to give 1-methyl-4-((2-(4-nitrophenyl)cyclopropyl)sulfonyl)benzene **3i** (43% yield, 34.8 mg, 0.13 mmol), 91% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.12 (d, *J* = 8.79 Hz, 2H), 7.81 (d, *J* = 8.41 Hz, 2H), 7.38 (d, *J* = 8.41 Hz, 2H), 7.18 (d, *J* = 8.79 Hz, 2H), 2.96 (ddd, *J* = 4.16, 6.12, 9.94 Hz, 1H), 2.74 (ddd, *J* = 4.59, 5.35, 8.41 Hz, 1H), 2.46 (s, 3H), 1.97 (ddd, *J* = 5.64, 5.64, 9.56 Hz, 1H), 1.52 (ddd, *J* = 6.12, 6.12, 8.41 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  147.0, 145.3, 144.9, 137.1, 130.1, 127.7, 127.3, 123.9, 42.6, 29.7, 21.6, 14.8;  $[\alpha]^{20}_{D} = -41.7$  (c = 1.0, CHCl<sub>3</sub>); For C<sub>16</sub>H<sub>15</sub>NO<sub>2</sub>S [M+NH4]<sup>+</sup>

Calcd:335.10655, Found: 335.10655; The enantiomeric ratio of 3i was determined by HPLC (Hexane : IPA = 1 : 1, 0.5 mL/min) using a CHIRALPAK IC column (0.46 cm x 25 cm): major isomer 37.6 min and minor isomer 46.8 min.

#### 1-methyl-4-((2-phenoxycyclopropyl)sulfonyl)benzene (3j)



cyclopropanation between phenyl vinyl ether (96.1 mg, 1.0 mmol) and TsCHN<sub>2</sub> (39.2 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc eluent give 1-methyl-4-((2as an to phenoxycyclopropyl)sulfonyl)benzene **3j** (89% yield, 51.4 mg, 0.18 mmol), 98% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.81 (d, J = 8.03 Hz, 2H), 7.38 (d, J = 7.64 Hz, 2H), 7.21 (dddd, J = 2.1, 2.1, 7.45, 8.60 Hz, 2H), 6.98 (ddt, J = 1.15, 1.15, 7.45 Hz, 1H), 6.91 (dd, J = 1.15, 8.79 Hz, 2H), 4.32 (ddd, J = 2.29, 4.20, 7.26 Hz, 1H), 2.72 (ddd, J = 2.20, 6.22, 9.65 Hz, 1H), 2.47 (s, 3H), 1.81 (ddd, J = 6.69, 6.80, 6.88, 1H), 1.58 (ddd, *J* = 4.11, 6.79, 9.65 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 157.2, 144.8, 137.1, 130.0, 129.5, 127.7, 122.0, 114.8, 54.5, 39.5, 21.6, 14.0;  $[\alpha]^{23}_{D} = +94.9$  (c = 1.0, CHCl<sub>3</sub>); For  $C_{16}H_{16}O_3S$  [M+H]<sup>+</sup> Calcd: 289.08984, Found: 289.08987; The enantiomeric ratio of **3** was determined by HPLC (Hexane : IPA = 4 : 1, 1.0 mL/min) using a CHIRALCEL OJ-H column (0.46 cm x 25 cm): major isomer 17.2 min and minor isomer 20.0 min.

#### 1-((2-isopropoxycyclopropyl)sulfonyl)-4-methylbenzene (3k)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between ipropyl vinyl ether (96.1 mg, 1.0 mmol) and TsCHN<sub>2</sub> (39.2 mg, 0.2 mmol). The resulting mixture was purified by silica gel column

This compound was prepared according to the general procedure for asymmetric

chromatography with Hexane/EtOAc as an eluent to give 1-((2-isopropoxycyclopropyl)sulfonyl)-4methylbenzene **3k** (98% yield, 49.7 mg, 0.18 mmol), 98% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.77 (d, J = 8.41 Hz, 2H), 7.36 (d, J = 8.03 Hz, 2H), 3.89 (ddd, J = 2.49, 4.59, 7.26 Hz, 1H), 3.63 (sept, J = 2.49, 7.26 Hz, 1H), 3.64 (sept, J = 2.49, 7.26 Hz, 1H), 3.65 (s 6.12 Hz, 1H), 2.50 (ddd, J = 2.29, 6.12, 9.56 Hz, 1H), 2.45 (s, 3H), 1.56 (ddd, J = 6.75, 6.88, 7.26 Hz, 1H), 1.37 (ddd, J = 4.30, 6.60, 9.65 Hz, 1H), 1.14 (d, J = 6.12 Hz, 3H), 1.08 (d, J = 6.12 Hz, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ 144.4, 137.5, 129.8, 127.5, 73.3, 55.7, 39.5, 21.9, 21.7, 21.6, 13.9; [α]<sup>22</sup><sub>D</sub> = +14.0 (c = 1.0, CHCl<sub>3</sub>); For C<sub>13</sub>H<sub>18</sub>O<sub>3</sub>S [M+NH<sub>4</sub>]<sup>+</sup> Calcd: 272.13204, Found: 272.13205.; The enantiomeric ratio of 3k was determined by HPLC (Hexane : IPA = 4 : 1, 1.0 mL/min) using a CHIRALPAK IF-3 column (0.46 cm x 25 cm): major isomer 26.4 min and minor isomer 23.8 min.

#### 1-(((1R,2R)-2-(tert-butoxy)cyclopropyl)sulfonyl)-4-methylbenzene (3l)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between *t*butyl vinyl ether (100.2 mg, 1.0 mmol) and TsCHN<sub>2</sub> (39.2 mg, 0.2 mmol). The resulting mixture was purified by silica

gel column chromatography with Hexane/EtOAc as an eluent to give 1-(((1R,2R)-2-(tertbutoxy)cyclopropyl)sulfonyl)-4-methylbenzene **3l** (98% yield, 53.2 mg, 0.20 mmol), 99% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.77 (d, *J* = 8.41 Hz, 2H), 7.35 (d, *J* = 8.03 Hz, 2H), 3.88 (ddd, *J* = 2.39, 4.30, 7.55 Hz, 1H), 2.47 (ddd, *J* = 2.29, 6.12, 9.56 Hz, 1H), 2.45 (s, 3H), 1.50 (ddd, *J* = 6.41, 6.41, 7.64 Hz, 1H), 1.28 (ddd, *J* = 4.40, 6.50, 9.36 Hz, 1H), 1.19 (s, 9H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  144.3, 137.6, 129.8, 127.5, 76.0, 51.1, 39.9, 27.6, 21.5, 13.2;  $[\alpha]^{23}_{D} = -6.75$  (c = 1.0, CHCl<sub>3</sub>); For C<sub>14</sub>H<sub>20</sub>O<sub>3</sub>S [M+H]<sup>+</sup> Calcd: 269.12114, Found: 269.12113; The enantiomeric ratio of **3l** was determined by HPLC (Hexane : IPA = 4 : 1, 1.0 mL/min) using a CHIRALCEL OJ-H column (0.46 cm x 25 cm): major isomer 8.1 min and minor isomer 7.2 min.

#### 9-(2-tosylcyclopropyl)-9H-carbazole (3m)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between 9-vinylcarbazole (193.2 mg, 1.0 mmol) and TsCHN<sub>2</sub> (39.2 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give 9-(2-tosylcyclopropyl)-9H-carbazolee **3m** (86% yield, 62.7

mg, 0.17 mmol), 95% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.01 (d, *J* = 8.01 Hz, 2H), 7.96-7.91 (m, 2H), 7.46 (d, *J* = 8.41 Hz, 2H), 7.37-7.31 (m, 2H), 7.28 (d, *J* = 8.41 Hz, 2H), 7.25-7.19 (m, 2H), 4.04 (ddd, *J* = 3.06, 4.59, 7.64 Hz, 1H), 3.03 (ddd, *J* = 3.06, 6.12, 9.17 Hz, 1H), 2.52 (s, 3H), 2.62 (ddd, *J* = , 6.02, 6.02, 7.62 Hz, 1H), 1.85 (ddd, *J* = 4.88, 6.02, 9.27 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  145.3, 140.4, 136.7, 130.3, 128.2, 126.0, 123.2, 120.3, 119.9, 109.6, 40.4, 30.4, 21.7, 14.8; [ $\alpha$ ]<sup>21</sup><sub>D</sub> = -124.4 (c = 1.0); For C<sub>22</sub>H<sub>19</sub>NO<sub>2</sub>S [M+H]<sup>+</sup> Calcd: 362.12147, Found: 362.12148; The enantiomeric ratio of **3m** was determined by HPLC (Hexane : IPA = 5 : 1, 1.0 mL/min) using a CHIRALPAK IC column (0.46 cm x 25 cm): major isomer 26.7 min and minor isomer 22.4 min.

#### benzyl (2-tosylcyclopropyl)carbamate (3n)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between benzyl vinylcarbamate (177.2 mg, 1.0 mmol) and TsCHN<sub>2</sub> (39.2 mg, 0.2 mmol). The resulting mixture was purified

by silica gel column chromatography with Hexane/EtOAc as an eluent to give 9-(2-tosylcyclopropyl)-9H-carbazolee **3n** (86% yield, 62.7 mg, 0.17 mmol), trans/cis = 90:10, 95% trans ee, 89% *cis* ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) (*trans* isomer):  $\delta$  7.80 (brs, 2H), 7.53-7.10 (m, 7H), 5.15

(brs, 1H), 5.02 (s, 2H), 3.38 (brs, 1H), 2.58 (brs, 1H), 2.43 (s, 3H), 1.74 (ddd, J = 5.92, 6.02, 8.41 Hz, 1H), 1.33 (brs, 1H). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) (*cis* isomer):  $\delta$  7.72 (d, J = 8.03 Hz, 2H), 7.44-7.28 (m, 5H), 7.23 (d, J = 8.03 Hz, 2H), 5.73 (d, J = 8.41 Hz, 1H), 5.13 (d, J = 12.23 Hz, 1H), 5.09 (d, J = 12.23 Hz, 1H), 3.59 (ddd, J = 7.45, 7.45, 14.33 Hz, 1H), 2.57 (ddd, J = 6.69, 6.69, 9.17 Hz, 1H), 2.42 (s, 3H), 1.70 (ddd, J = 6.50, 6.50, 6.50 Hz, 1H), 1.51 (ddd, J = 7.26, 7.84, 8.03 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) (*trans* isomer):  $\delta$  156.0, 144.6, 136.9, 135.9, 129.8, 128.4, 128.2, 128.0, 127.8, 67.0, 40.0, 30.5, 21.6, 13.1. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) (*cis* isomer):  $\delta$  156.2, 144.7, 137.3, 136.2, 129.9, 128.6, 128.2, 128.2, 127.3, 67.0, 36.7, 31.8, 21.6, 10.8; (*trans* isomer) [ $\alpha$ ]<sup>23</sup><sub>D</sub> = -9.65 (c = 1.0), (*cis* isomer) [ $\alpha$ ]<sup>24</sup><sub>D</sub> = +34.9 (c = 0.35); For C<sub>18</sub>H<sub>19</sub>NO4S [M+NH4]<sup>+</sup> Calcd: 363.13785, (*trans* isomer)) Found: 363.13791, (*cis* isomer) Found: 363.13777; The enantiomeric ratio of **3n** (*trans* isomer)) was determined by HPLC (Hexane : IPA = 4 : 1, 2.0 mL/min) using a CHIRALPAK IC column (0.46 cm x 25 cm): major isomer 27.4 min and minor isomer 36.0 min. The enantiomeric ratio of **3n** (*cis* isomer)) was determined by HPLC (Hexane : IPA = 4 : 1, 1.0 mL/min) using a CHIRALPAK IA column (0.46 cm x 25 cm): major isomer 17.3 min and minor

#### benzyl methyl(2-tosylcyclopropyl)carbamate (30)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between benzyl methyl(vinyl)carbamate (191.2 mg, 1.0 mmol) and TsCHN<sub>2</sub> (39.2 mg, 0.2 mmol). The resulting mixture was

purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give benzyl methyl(2-tosylcyclopropyl)carbamate **30** (71% yield, 51.2 mg, 0.14 mmol), 98% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.79 (d, *J* = 8.03 Hz, 2H), 7.45-7.15 (m, 7H), 4.96 (s, 2H), 3.33 (ddd, *J* = 3.16, 5.07, 8.12 Hz, 1H), 2.74 (s, 3H), 2.65 (ddd, *J* = 3.06, 6.12, 9.17 Hz, 1H), 2.42 (s, 3H), 1.82 (ddd, *J* = 6.31, 6.31, 8.03 Hz, 1H), 1.49 (brs, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  156.3, 144.6, 136.9, 136.3, 129.8, 128.4, 128.0, 127.8, 127.7, 67.1, 40.7, 36.7, 34.5, 21.5, 14.9; [ $\alpha$ ]<sup>30</sup><sub>D</sub> = -33.2 (c = 0.35); For C<sub>19</sub>H<sub>21</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> Calcd: 360.12695, Found: 360.12692; The enantiomeric ratio of **30** was determined by HPLC (Hexane : IPA = 1 : 1, 2.0 mL/min) using a CHIRALPAK IC column (0.46 cm x 25 cm): major isomer 13.4 min and minor isomer 16.2 min.

#### 1-methoxy-4-((2-phenylcyclopropyl)sulfonyl)benzene (3p)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between styrene (104.2 mg, 1.0 mmol) and 1-((diazomethyl)sulfonyl)-4-methoxybenzene (42.4 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with

Hexane/EtOAc as an eluent to give 1-methoxy-4-((2-phenylcyclopropyl)sulfonyl)benzene 3p (87%

yield, 50.2 mg, 0.17 mmol), 95% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.86 (d, *J* = 8.79 Hz, 2H), 7.24 (dd, *J* = 7.07, 7.07 Hz, 2H), 7.22-7.17 (m, 1H), 7.05-6.99 (m, 4H), 3.87 (s, 3H), 2.85 (ddd, *J* = 4.30, 6.02, 10.03 Hz, 1H), 2.64 (ddd, *J* = 4.49, 4.49, 8.50, 1H), 1.86 (ddd, *J* = 5.26, 5.26, 10.03 Hz, 1H), 1.45 (ddd, *J* = 6.12, 6.12, 8.41 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  163.5, 137.5, 132.1, 129.7, 128.6, 127.0, 126.5, 114.5, 55.6, 42.1, 23.7, 13.8; [ $\alpha$ ]<sup>30</sup><sub>D</sub> = -46.9 (c = 1.0); For C<sub>16</sub>H<sub>16</sub>O<sub>3</sub>S [M+H]<sup>+</sup> Calcd: 289.08984, Found: 289.08981; The enantiomeric ratio of **3p** was determined by HPLC (Hexane : IPA = 4 : 1, 1.0 mL/min) using a CHIRALPAK IC column (0.46 cm x 25 cm): major isomer 35.4 min and minor isomer 39.5 min.

#### ((2-phenylcyclopropyl)sulfonyl)benzene (3q)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between styrene (104.2 mg, 1.0 mmol) and ((diazomethyl)sulfonyl)benzene (36.4 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give ((2-

phenylcyclopropyl)sulfonyl)benzene **3q** (72% yield, 37.7 mg, 0.15 mmol), 95% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.97-7.91 (m, 2H), 7.68-7.62 (m, 1H), 7.60-7.53 (m, 2H), 7.27-7.16 (m, 3H), 7.05-6.97 (m, 2H), 2.89 (ddd, *J* = 4.21, 6.12, 9.94 Hz, 1H), 2.66 (ddd, *J* = 4.97, 4.97, 8.41 Hz, 1H), 1.89 (ddd, *J* = 5.54, 5.54, 9.94 Hz, 1H), 1.48 (ddd, *J* = 5.73, 6.50, 8.41 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  140.5, 137.3, 133.5, 129.3, 128.6, 127.5, 127.1, 126.6, 41.7, 23.7, 12.8; [ $\alpha$ ]<sup>30</sup><sub>D</sub> = -63.0 (c = 1.0); For C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>S [M+H]<sup>+</sup> Calcd: 259.07927, Found: 259.07929; The enantiomeric ratio of **3q** was determined by HPLC (Hexane : IPA = 4 : 1, 1.0 mL/min) using a CHIRALCEL OJ-H column (0.46 cm x 25 cm): major isomer 23.8 min and minor isomer 28.0 min.

#### 1-chloro-4-((2-phenylcyclopropyl)sulfonyl)benzene (3r)



This compound was prepared according to the general procedure for asymmetric cyclopropanation between styrene (104.2 mg, 1.0 mmol) and 1-chloro-4-((diazomethyl)sulfonyl)benzene (43.3 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give 1-chloro-

4-((2-phenylcyclopropyl)sulfonyl)benzene **3r** (67% yield, 39.0 mg, 0.13 mmol), 90% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.93-7.83 (m, 2H), 7.59-7.49 (m, 2H), 7.31-7.16 (m, 3H), 7.02 (d, *J* = 6.88 Hz, 2H), 2.89 (ddd, *J* = 4.21, 6.12, 10.13 Hz, 1H), 2.65 (ddd, *J* = 4.97, 4.97, 8.22 Hz, 1H), 1.88 (ddd, *J* = 5.54, 5.54, 9.56 Hz, 1H), <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  140.2, 138.9, 137.1, 129.6, 129.0, 128.7, 127.2, 126.5, 41.7, 23.8, 13.9;  $[\alpha]^{25}_{D} = -48.0$  (c = 1.0); For C<sub>15</sub>H<sub>13</sub>ClO<sub>2</sub>S [M+NH<sub>4</sub>]<sup>+</sup> Calcd: 310.06688; The enantiomeric ratio of **3r** was determined by HPLC (Hexane : IPA

= 4 : 1, 1.0 mL/min) using a CHIRALPAK IB column (0.46 cm x 25 cm): major isomer 16.0 min and minor isomer 17.2 min.

#### 1-methyl-4-((-1-methyl-2-phenylcyclopropyl)sulfonyl)benzene (7)



To solution of **3a** (108.9 mg, 0.4 mmol) in dry THF (2 mL) was added dropwise butylliphium (1.6 mo/L in hexane, 0.5 mL, ) at -78 °C under Ar, and stirring was continued for 30 min at -78 °C after which MeI (123.6 mg, 0.8 mmol) was added dropwise to the solution. The resultant solution was stirred at -78 °C for

30 min and then allowed to warm to room temperature over a period of 1 h before being treated with saturated aqueous NH<sub>4</sub>Cl. The aqueous layer was extracted with ethyl acetate, and the combined organic layer was washed with brine, dried over with Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by column chromatography to give desired product. The *trans/cis* ratio was determined from the crude <sup>1</sup>H NMR spectra, and the ee value was determined by chiral HPLC analysis. **7** (80% yield, 101.9 mg, 0.36 mmol), 94% ee. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.82 (d, *J* = 8.41 Hz, 2H), 7.39 (d, *J* = 8.41 Hz, 2H), 7.30-7.19 (m, 3H), 7.05 (d, *J* = 7.26 Hz, 2H), 3.21 (dd, *J* = 7.07, 9.75 Hz, 1H), 2.48 (s, 3H), 2.02 (dd, *J* = 5.54, 9.75 Hz, 1H), 1.27 (dd, *J* = 5.73, 6.88 Hz, 1H), 1.01 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  144.4, 135.2, 135.0, 129.7, 128.8, 128.3, 127.1, 42.8, 27.5, 21.6, 16.2, 13.6; [ $\alpha$ ]<sup>27</sup><sub>D</sub> = -39.8 (c = 1.0, CHCl<sub>3</sub>); For C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>S [M+H] + Calcd: 287.11057, Found: 287.11055; The enantiomeric ratio of **7** was determined by HPLC (Hexane : IPA = 3 : 1, 1.0 mL/min) using a CHIRALPAK ID column (0.46 cm x 25 cm): major isomer 11.3 min and minor isomer12.2 min.

3. X-ray Crystal structure.

 $1\label{eq:linear} 1\label{eq:linear} 1\label{eq:$ 



Empirical formula	$C_{14} H_{20} O_3 S$		
Formula weight	268.36		
Temperature	296(2) K		
Wavelength	0.71069 Å		
Crystal system	Monoclinic		
Space group	<i>C</i> 2		
Unit cell dimensions	a = 16.720(7)  Å	$\alpha = 90^{\circ}$	
	b = 9.987(4) Å	$\beta=90.306(9)^\circ$	
	c = 8.832(4)  Å	$\gamma=90^\circ$	
Volume	1474.7(10) Å <sup>3</sup>		
Ζ	4		
Density (calculated)	1.209 Mg/m <sup>3</sup>		
Absorption coefficient	$0.218 \text{ mm}^{-1}$		
<i>F</i> (000)	576		
Crystal size	0.60 x 0.20 x 0.10 mm <sup>3</sup>		
Theta range for data collection	2.31 to 28.46°		
Index ranges	-21<=h<=22, -13<=k<=12, -11<=l<=11		
Reflections collected	13131		
Independent reflections	3152 [ $R(int) = 0.0326$ ]		
Completeness to theta = $28.46^{\circ}$	= 28.46° 94.7 %		
Max. and min. transmission	0.9732 and 0.9154		
Refinement method	Full-matrix least-squares on $F^2$		
Data / restraints / parameters	3152 / 1 / 167		
Goodness-of-fit on $F^2$	1.031		
Final <i>R</i> indices $[I > 2 \operatorname{sigma}(I)]$	R1 = 0.0467, wR2 = 0.1275		
<i>R</i> indices (all data)	R1 = 0.0581, wR2 = 0.1375		
Absolute structure parameter	0.02(10)		
Largest diff. peak and hole	0.307 and -0.222 e Å-3		

4. NMR and HPLC spectral data.









2

42.945

HPLC racemic



1592806



No.	tR [min]	Area	Area%
1	39.425	4924223	49.497
2	42.018	5024278	50.503

98.181















001 - CH6

14.0 15.0

Area%

49.574

50.426

12.0 13.0















13C NMR





17

















HPLC racemic



















No.	tR [min]	Area	Area%	No.	tR [min]	Area	Area%
1	37.570	16903968	95.644	1	37.835	16552033	49.949
2	46.740	816988	4.610	2	45.340	16586150	50.051

































HPLC racemic

















HPLC racemic



No.	tR [min]	Area	Area%	No.	tR [min]	Area	Area%
1	13.815	1585052	5.349	1	13.592	2794879	49.802
2	17.252	28049940	94.651	2	16.978	2817131	50.198
				-			





2

16.212

125463





28

1.155

2

15.992

15985933

50.064















<sup>13</sup>C NMR



HPLC optically active

HPLC racemic



No.	tR [min]	Area	Area%	No.	tR [min]	Area	Area%
1	16.080	993879	8.055	1	16.180	44503087	49.210
2	17.305	11344869	91.945	2	17.483	45931580	50.790





