

**Supporting Information**  
**for Design of New Chiral Phase-Transfer Catalysts with Dual-Functions for**  
**Highly Enantioselective Epoxidation of  $\alpha,\beta$ -Unsaturated Ketones**

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**Characterization of Chiral Quaternary Ammonium Salts 1a, 1b, 1c and 2**

**Chiral Ammonium Salt 1a:**  $[\alpha]_D^{31} +179.7^\circ$  (*c* 0.15, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.04 (2H, d, *J* = 8.3 Hz, Ar-H), 7.89 (2H, d, *J* = 8.3 Hz, Ar-H), 7.62 (2H, t, *J* = 6.7 Hz, Ar-H), 7.47-7.34 (10H, m, Ar-H), 7.21 (2H, t, *J* = 7.5 Hz, Ar-H), 7.14 (2H, d, *J* = 7.5 Hz, Ar-H), 7.08 (6H, t, *J* = 7.5 Hz, Ar-H), 6.90-6.84 (4H, m, Ar-H), 6.77-6.71 (8H, m, Ar-H), 5.09 (2H, d, *J* = 13.7 Hz, ArCH<sub>2</sub>), 4.83 (2H, s, OH), 4.63 (2H, d, *J* = 12.5 Hz, ArCH<sub>2</sub>), 4.10 (2H, d, *J* = 13.7 Hz, ArCH<sub>2</sub>), 3.35 (2H, d, *J* = 12.5 Hz, ArCH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  147.4, 147.2, 144.9, 144.7, 136.3, 134.0, 131.2, 131.1, 130.0, 129.7, 128.9, 128.3, 128.1, 127.9, 127.7, 127.6, 127.3, 127.2, 127.0, 126.9, 126.7, 126.6, 82.3, 66.2, 60.2; IR (neat) 3198, 3053, 1595, 1491, 1447, 1356, 1306, 1165, 1047, 1026, 910, 835, 790, 764, 727 cm<sup>-1</sup>; HRMS (ESI) Calcd for C<sub>62</sub>H<sub>48</sub>NO<sub>2</sub> (M<sup>+</sup>): 838.3680, Found: 838.3672.

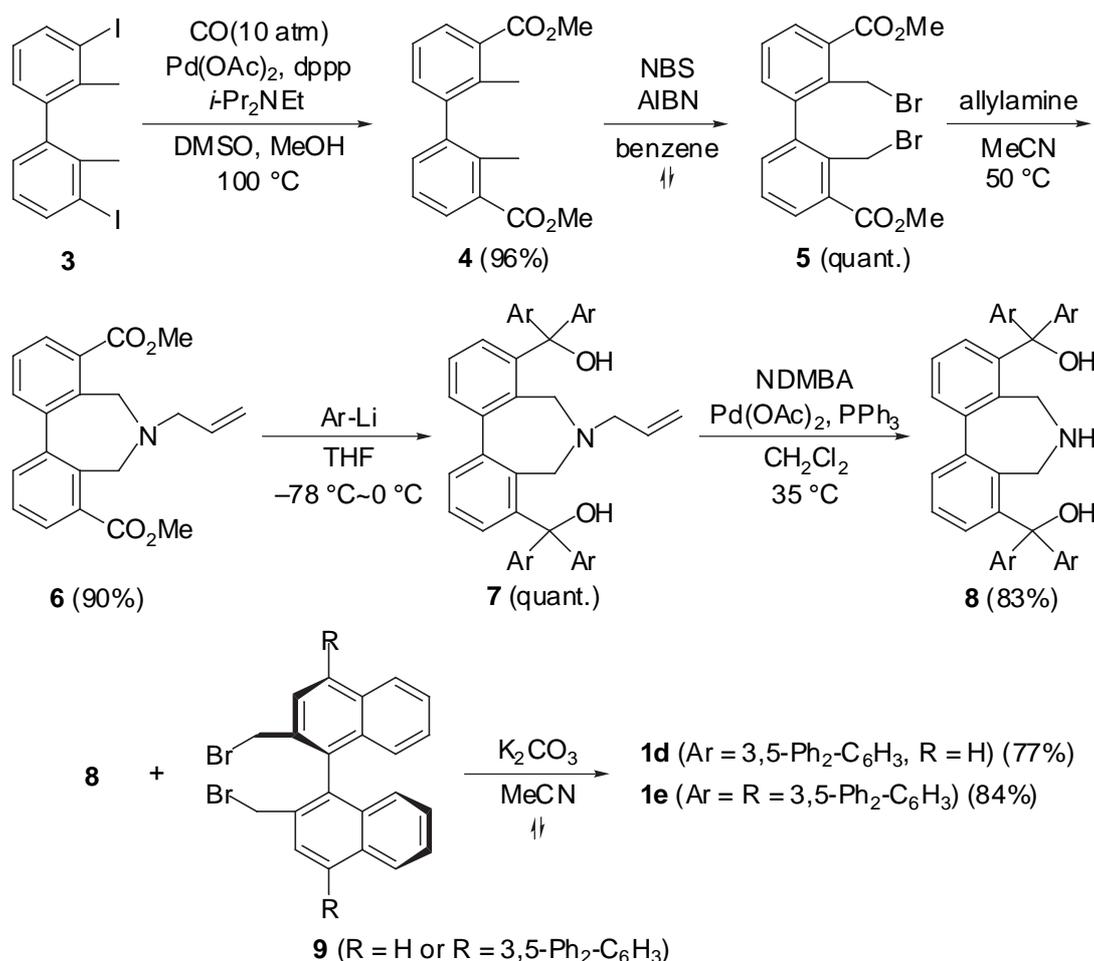
**Chiral Ammonium Salt 1b:**  $[\alpha]_D^{30} +135.9^\circ$  (*c* 0.45, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (2H, d, *J* = 7.9 Hz, Ar-H), 7.72 (2H, d, *J* = 8.7 Hz, Ar-H), 7.64 (2H, ddd, *J* = 7.9, 6.4, 1.6 Hz, Ar-H), 7.48-7.41 (8H, m, Ar-H), 7.33-7.31 (8H, m, Ar-H), 7.12 (2H, d, *J* = 7.9 Hz, Ar-H), 7.01-6.97 (8H, m, Ar-H), 6.91 (2H, dd, *J* = 7.9, 1.6 Hz, Ar-H), 6.73 (2H, br, OH), 5.02 (2H, br d, *J* = 11.9 Hz, ArCH<sub>2</sub>), 4.42 (2H, br, ArCH<sub>2</sub>), 4.06 (2H, d, *J* = 14.2 Hz, ArCH<sub>2</sub>), 3.26 (2H, br d, *J* = 11.9 Hz, ArCH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.9, 148.3, 145.9, 144.9, 136.2, 133.7, 131.1, 130.8, 130.4, 129.7, 129.5, 129.4, 129.2, 129.1, 128.3, 128.0, 127.6, 127.2, 127.1, 127.0, 126.9, 126.5, 125.1, 125.1, 124.7, 124.7, 122.3, 122.0, 81.8, 66.2, 59.9; <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>)  $\delta$  -60.4, -60.5; IR (neat) 3184, 3061, 1616, 1410, 1323, 1167, 1123, 1069, 1016, 908, 841, 816, 793, 770, 735, 654 cm<sup>-1</sup>; HRMS (ESI) Calcd for C<sub>66</sub>H<sub>44</sub>F<sub>12</sub>NO<sub>2</sub> (M<sup>+</sup>): 1110.3175, Found: 1110.3145.

**Chiral Ammonium Salt 1c:**  $[\alpha]_D^{31} +177.3^\circ$  (*c* 0.25, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (2H, d, *J* = 8.0 Hz, Ar-H), 7.92 (2H, d, *J* = 8.0 Hz, Ar-H), 7.57 (2H, t, *J* = 7.6 Hz, Ar-H), 7.46-7.33 (10H, m, Ar-H), 6.91 (2H, d, *J* = 8.0 Hz, Ar-H), 6.43 (4H, s, Ar-H), 6.35 (2H, t, *J* = 2.2 Hz, Ar-H), 6.22 (2H, t, *J* = 2.2 Hz, Ar-H), 5.87 (2H, d, *J* = 2.2 Hz, ArCH<sub>2</sub>), 4.98 (2H, d, *J* = 13.5 Hz, ArCH<sub>2</sub>), 4.85 (4H, br, ArCH<sub>2</sub> and OH), 4.37 (2H, d, *J* = 13.5 Hz, ArCH<sub>2</sub>), 3.96 (2H, d, *J* = 13.1 Hz, ArCH<sub>2</sub>), 3.60 (12H, s, OCH<sub>3</sub>), 3.50 (12H, s, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.2, 160.0, 149.0, 147.8, 146.2, 144.5, 136.3, 133.7, 131.2, 130.7, 130.0, 129.5, 129.0, 128.5, 128.1, 127.6, 127.3, 127.0, 126.7, 126.3, 106.6, 104.8, 98.9, 98.8, 82.3, 66.7, 60.3, 55.5, 55.2; IR (neat) 3248, 2938,

2840, 1595, 1458, 1423, 1339, 1290, 1204, 1153, 1053, 922, 839, 754, 733  $\text{cm}^{-1}$ ; HRMS (ESI) Calcd for  $\text{C}_{70}\text{H}_{64}\text{NO}_{10}$  ( $\text{M}^+$ ): 1078.4525, Found: 1078.4555.

**Chiral Ammonium Salt 2:**  $[\alpha]_{\text{D}}^{31} +57.4^\circ$  ( $c$  0.14,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (4H, t,  $J = 8.7$  Hz, Ar-H), 7.92 (2H, d,  $J = 8.3$  Hz, Ar-H), 7.65 (2H, t,  $J = 7.5$  Hz, Ar-H), 7.50-7.42 (8H, m, Ar-H), 7.18-7.10 (6H, m, Ar-H), 6.99 (2H, d,  $J = 7.1$  Hz, Ar-H), 6.90 (4H, d,  $J = 7.5$  Hz, Ar-H), 6.80 (2H, t,  $J = 7.3$  Hz, Ar-H), 6.67 (8H, t,  $J = 7.7$  Hz, Ar-H), 5.50 (2H, s,  $\text{Ph}_2\text{CH}$ ), 4.68 (2H, d,  $J = 12.1$  Hz,  $\text{ArCH}_2$ ), 4.59 (2H, d,  $J = 13.7$  Hz,  $\text{ArCH}_2$ ), 4.46 (2H, d,  $J = 13.7$  Hz,  $\text{ArCH}_2$ ), 2.95 (2H, d,  $J = 12.1$  Hz,  $\text{ArCH}_2$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.0, 143.4, 142.2, 141.2, 136.5, 134.2, 131.2, 131.0, 130.6, 130.1, 129.6, 129.1, 128.7, 128.6, 128.5, 127.5, 127.4, 127.3, 127.0, 126.9, 126.7, 126.6, 125.6, 63.7, 53.4; IR (neat) 3059, 3024, 2924, 2852, 1595, 1494, 1450, 1377, 1354, 1030, 921, 904, 823, 729, 702  $\text{cm}^{-1}$ ; HRMS (ESI) Calcd for  $\text{C}_{62}\text{H}_{48}\text{N}$  ( $\text{M}^+$ ): 806.3781, Found: 806.3811.

### Representative Procedure for the Synthesis of Chiral Ammonium Salts 1d and 1e



**Synthesis and Characterization of Secondary Amine 8:** A mixture of  $\text{3}^1$  (430 mg, 1.0 mmol),  $\text{Pd(OAc)}_2$  (11.6 mg, 5 mol%), bis(diphenylphosphino)propane (dppp) (20.6 mg, 5 mol%) and  $i\text{-Pr}_2\text{NEt}$  (790  $\mu\text{L}$ , 4.4 mmol) in degassed DMSO (4.0 mL) and MeOH (2.0 mL) was heated to 120  $^\circ\text{C}$

with stirring for 12 h under CO atmosphere (10 atm). After cooling to room temperature, the resulting mixture was poured into water and extracted with ether. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane = 1:10 as eluant) to give **4** (286 mg, 0.96 mmol, 96% yield): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 (2H, dd, *J* = 7.4, 1.6 Hz, Ar-H), 7.29 (2H, t, *J* = 7.4 Hz, Ar-H), 7.23 (2H, dd, *J* = 7.4, 1.6 Hz, Ar-H), 3.92 (6H, s, CO<sub>2</sub>CH<sub>3</sub>), 2.23 (6H, s, ArCH<sub>3</sub>).

Then, a mixture of **4** (186 mg, 0.62 mmol), *N*-bromosuccinimide (NBS) (222 mg, 1.24 mmol) and 2,2'-azobis(isobutyronitrile) (AIBN) (10.4 mg, 10 mol%) in benzene (4.0 mL) was heated and refluxed for 3 h. After being cooled to room temperature, this mixture was poured into water and extracted with ether. The organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane = 1:3 as eluant) to afford **5** (283 mg, 0.62 mmol, 99% yield): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (2H, dd, *J* = 6.8, 2.4 Hz, Ar-H), 7.49-7.43 (4H, m, Ar-H), 4.91 (2H, d, *J* = 10.0 Hz, CH<sub>2</sub>Br), 4.46 (2H, d, *J* = 10.0 Hz, CH<sub>2</sub>Br), 3.98 (6H, s, CO<sub>2</sub>CH<sub>3</sub>).

To a solution of **5** thus obtained (283 mg, 0.62 mmol) in acetonitrile (2.0 mL) was added allylamine (140 μL, 1.86 mmol) at room temperature. The mixture was then heated to 50 °C and stirring was continued for 5 h. The resulting mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of solvents and purification of the residue by flash column chromatography on silica gel (ethyl acetate/hexane = 1:3 as eluant) gave **6** (196 mg, 0.58 mmol, 90% yield): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (2H, dd, *J* = 7.8, 1.6 Hz, Ar-H), 7.58 (2H, dd, *J* = 7.8, 1.6 Hz, Ar-H), 7.48 (2H, t, *J* = 7.8 Hz, Ar-H), 6.00 (1H, dddd, *J* = 16.8, 10.4, 6.4, 6.4 Hz, CH=CH<sub>2</sub>), 5.21-5.15 (2H, m, CH=CH<sub>2</sub>), 4.80-4.45 (2H, br, ArCH<sub>2</sub>), 3.94 (6H, s, CO<sub>2</sub>CH<sub>3</sub>), 3.70-2.60 (4H, br, ArCH<sub>2</sub> and NCH<sub>2</sub>C=C).

To a solution of 3,5-diphenyl-1-bromobenzene<sup>2</sup> (1.86 g, 6.0 mmol) in THF (10 mL) was added a 1.6 M hexane solution of *n*-BuLi (3.75 mL, 6.0 mmol) dropwise at -78 °C under argon atmosphere. The reaction mixture was allowed to warm to 0 °C and stirred for 1 h, then cooled back to -78 °C. A solution of **6** (351 mg, 1.0 mmol) in THF (5.0 mL) was added dropwise with stirring. After the addition was completed, the mixture was again allowed to warm to 0 °C and stirred there for 2 h. The resulting mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography on silica gel (ethyl acetate/hexane = 1:3 as eluant) to afford **7** (1.20 g, 1.0 mmol, 99% yield): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74 (2H, s, Ar-H), 7.70 (2H, s, Ar-H), 7.66 (2H, s, Ar-H), 7.60-7.53 (20H, m, Ar-H), 7.46 (2H, d, *J* = 7.5 Hz, Ar-H), 7.41-7.36 (18H, m, Ar-H), 7.33-7.21 (10H, m, Ar-H), 6.92 (2H, d, *J* = 7.5 Hz, Ar-H), 5.79 (1H, m, CH=CH<sub>2</sub>), 4.71 (1H, d, *J* = 17.0 Hz, *cis*-CH=CH<sub>2</sub>), 4.60 (1H, d, *J* = 10.3 Hz, *trans*-CH=CH<sub>2</sub>), 4.14 (2H, d, *J* = 13.5 Hz, ArCH<sub>2</sub>), 3.37

(1H, dd,  $J = 13.5, 3.6$  Hz,  $\text{NCH}_2\text{C}=\text{}$ ), 2.89 (2H, d,  $J = 13.5$  Hz,  $\text{ArCH}_2$ ), 2.71 (1H, dd,  $J = 13.5, 9.1$  Hz,  $\text{NCH}_2\text{C}=\text{}$ ).

A mixture of **7** (1.09 g, 0.9 mmol) prepared above, *N,N*-dimethylbarbituc acid (NDMBA) (453 mg, 2.9 mmol),  $\text{Pd}(\text{OAc})_2$  (10.4 mg, 5 mol%), triphenylphosphine (35.4 mg, 15 mol%) in dry, degassed  $\text{CH}_2\text{Cl}_2$  (5.0 mL) was heated to 35 °C and stirred overnight under argon atmosphere. After cooling,  $\text{CH}_2\text{Cl}_2$  was removed under vacuum and replaced by ethyl acetate. This mixture was washed twice with saturated  $\text{NaHCO}_3$ , dried over  $\text{Na}_2\text{SO}_4$  and concentrated. Purification of the residue by flash column chromatography on silica gel ( $\text{MeOH}/\text{CH}_2\text{Cl}_2 = 1:10$  as eluant) furnished **8** (876 mg, 0.75 mmol, 83% yield):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (4H, dt,  $J = 5.9, 1.4$  Hz, Ar-H), 7.62 (8H, d,  $J = 9.9$  Hz, Ar-H), 7.55 (16H, t,  $J = 7.9$  Hz, Ar-H), 7.48 (2H, d,  $J = 7.9$  Hz, Ar-H), 7.41-7.21 (26H, m, Ar-H), 6.91 (2H, d,  $J = 7.9$  Hz, Ar-H), 4.08 (2H, d,  $J = 12.7$  Hz,  $\text{ArCH}_2$ ), 2.95 (2H, d,  $J = 12.7$  Hz,  $\text{ArCH}_2$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.5, 148.1, 145.7, 143.3, 141.2, 141.1, 140.8, 140.7, 134.9, 129.2, 128.5, 127.6, 127.2, 127.1, 127.1, 127.0, 126.3, 126.0, 125.0, 124.9, 124.8, 83.5, 45.3; IR (neat) 3312, 3059, 3034, 1593, 1576, 1497, 1452, 1427, 1412, 1157, 1074, 1032, 907, 881, 758, 729, 696  $\text{cm}^{-1}$ ; HRMS (ESI) Calcd for  $\text{C}_{88}\text{H}_{66}\text{NO}_2$  ( $[\text{M}+\text{H}]^+$ ): 1168.5088, Found: 1168.5068.

Chiral bis(bromide) **9** ( $\text{R} = 3,5\text{-Ph}_2\text{-C}_6\text{H}_3$ ) was synthesized according to the reported procedure.<sup>3</sup> **9** ( $\text{R} = 3,5\text{-Ph}_2\text{-C}_6\text{H}_3$ ):  $[\alpha]_{\text{D}}^{28} -50.4^\circ$  ( $c$  0.85,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (2H, d,  $J = 7.9$  Hz, Ar-H), 7.97 (2H, s, Ar-H), 7.89 (4H, s, Ar-H), 7.84 (2H, s, Ar-H), 7.79 (8H, d,  $J = 7.9$  Hz, Ar-H), 7.51 (10H, t,  $J = 7.9$  Hz, Ar-H), 7.41 (4H, t,  $J = 7.9$  Hz, Ar-H), 7.37-7.28 (4H, m, Ar-H), 4.39 (4H, s,  $\text{ArCH}_2\text{Br}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.8, 141.2, 140.8, 140.6, 133.7, 133.5, 132.8, 131.5, 128.7, 128.6, 127.7, 127.4, 127.2, 127.1, 126.8, 126.6, 126.1, 125.2, 32.6; IR (KBr) 3059, 3036, 2924, 2851, 1728, 1593, 1497, 1454, 1423, 1373, 1261, 1211, 1076, 1030, 883, 799, 760, 698  $\text{cm}^{-1}$ ; HRMS (FAB) Calcd for  $\text{C}_{88}\text{H}_{66}\text{NO}_2$  ( $\text{M}^+$ ): 894.1497, Found: 894.1498.

**Preparation and Characterization of Chiral Quaternary Ammonium Salt 1d:** A mixture of **8** (117 mg, 0.1mmol), **9** (59.2 mg, 0.1 mmol) and  $\text{K}_2\text{CO}_3$  (34.6 mg, 0.25 mmol) in acetonitrile (4.0 mL) was heated to reflux and stirring was maintained for 10 h. The resulting mixture was poured into water and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic phase was dried over  $\text{Na}_2\text{SO}_4$  and evaporated. The residue was purified by flash column chromatography on silica gel ( $\text{MeOH}/\text{CH}_2\text{Cl}_2 = 1:10$  as eluant) to give **1d** (111 mg, 0.077 mmol, 77 %yield):  $[\alpha]_{\text{D}}^{30} +430.5^\circ$  ( $c$  0.55,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (2H, t,  $J = 1.6$  Hz, Ar-H), 7.67 (2H, t,  $J = 1.6$  Hz, Ar-H), 7.55 (2H, s, Ar-H), 7.53 (2H, dd,  $J = 7.6, 1.6$  Hz, Ar-H), 7.51-7.41 (30H, m, Ar-H), 7.39 (4H, m, Ar-H), 7.36 (2H, m, Ar-H), 7.32 (8H, m, Ar-H), 7.22-7.27 (10H, m, Ar-H), 7.19 (2H, d,  $J = 8.7$  Hz, Ar-H), 7.09 (2H, d,  $J = 8.7$  Hz, Ar-H), 6.99 (4H, d,  $J = 1.6$  Hz, Ar-H), 5.16 (2H, d,  $J = 13.5$  Hz,  $\text{ArCH}_2$ ), 4.90 (2H, d,  $J = 13.5$  Hz,  $\text{ArCH}_2$ ), 4.77 (2H, d,  $J = 13.5$  Hz,  $\text{ArCH}_2$ ), 3.96 (2H, d,  $J = 13.5$  Hz,  $\text{ArCH}_2$ );  $^{13}\text{C}$  NMR

(100 MHz, CDCl<sub>3</sub>)  $\delta$  149.2, 146.7, 146.2, 145.6, 144.7, 141.8, 141.5, 141.2, 140.7, 140.6, 140.2, 140.1, 140.0, 139.9, 135.7, 134.6, 132.1, 131.8, 131.2, 130.4, 129.0, 128.6, 128.4, 128.4, 127.9, 127.7, 127.4, 127.3, 127.1, 127.0, 126.9, 126.8, 126.4, 126.1, 125.6, 125.5, 125.0, 124.3, 124.1, 124.1, 67.4, 65.7, 60.7; IR (KBr) 3057, 1593, 1499, 1427, 1304, 1160, 1030, 880, 816, 760, 696 cm<sup>-1</sup>; HRMS (ESI) Calcd for C<sub>110</sub>H<sub>80</sub>NO<sub>2</sub> (M<sup>+</sup>): 1446.6184, Found: 1446.6189.

**Chiral Ammonium Salt 1e:** **1e** was prepared in a similar manner as described above. (84% yield):  $[\alpha]_D^{27} +43.2^\circ$  (*c* 0.4, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.11 (2H, d, *J* = 8.3 Hz, Ar-H), 7.83 (2H, s, Ar-H), 7.63-7.58 (12H, m, Ar-H), 7.50 (10H, m, Ar-H), 7.40-7.34 (24H, m, Ar-H), 7.24-7.17 (30H, m, Ar-H), 7.11-7.08 (14H, m, Ar-H), 5.73 (2H, d, *J* = 13.5 Hz, ArCH<sub>2</sub>), 4.51 (2H, d, *J* = 13.5 Hz, ArCH<sub>2</sub>), 4.39 (2H, d, *J* = 13.5 Hz, ArCH<sub>2</sub>), 4.33 (2H, d, *J* = 13.5 Hz, ArCH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  149.5, 146.5, 145.9, 144.9, 142.1, 141.8, 141.4, 140.9, 140.8, 140.4, 140.3, 140.2, 135.9, 135.7, 132.3, 132.0, 131.5, 130.6, 128.8, 128.6, 127.9, 127.6, 127.4, 127.2, 127.0, 125.8, 125.2, 124.3, 65.9; IR (KBr) 3061, 3036, 2926, 1593, 1578, 1496, 1427, 1217, 1030, 840, 758, 698 cm<sup>-1</sup>; HRMS (ESI) Calcd for C<sub>146</sub>H<sub>104</sub>NO<sub>2</sub> (M<sup>+</sup>): 1902.8062, Found: 1902.8079.

#### X-ray Structure Determination

**Chiral Ammonium Salt 1e-PF<sub>6</sub>:** Usual anion exchange of **1e-Br** using Amberlyst-A26 (OH<sup>-</sup> form) gave **1e-OH**. A methanolic solution of **1e-OH** was then treated with 60% HPF<sub>6</sub> aqueous solution at 0 °C. The resulting precipitate was collected by filtration and washed with water to afford **1e-PF<sub>6</sub>** which was recrystallized from acetone/ether/hexane solvents system at 0 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 (2H, d, *J* = 8.3 Hz, Ar-H), 7.72 (2H, s, Ar-H), 7.49-7.48 (12H, m, Ar-H), 7.43-7.35 (10H, m, Ar-H), 7.29-7.23 (20H, m, Ar-H), 7.12-7.09 (30H, m, Ar-H), 7.01-5.97 (10H, m, Ar-H), 5.63 (2H, d, *J* = 12.7 Hz, ArCH<sub>2</sub>), 4.40 (2H, d, *J* = 13.5 Hz, ArCH<sub>2</sub>), 4.28 (2H, d, *J* = 12.7 Hz, ArCH<sub>2</sub>), 4.23 (2H, d, *J* = 13.5 Hz, ArCH<sub>2</sub>).

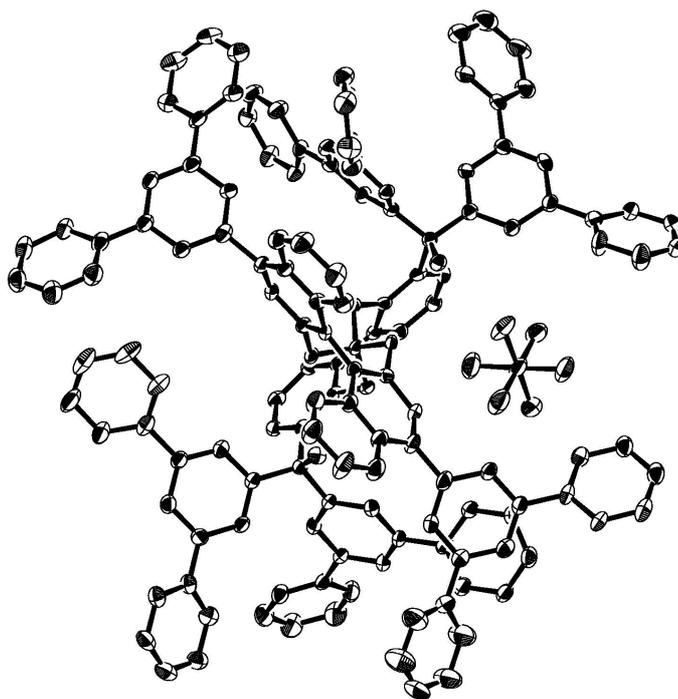
The single crystal thus obtained was mounted on a CryoLoop (Hampton Research Co. Ltd.). Data of X-ray diffraction were collected by Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated MoK $\alpha$  radiation ( $\lambda$  = 0.71070 Å) to a maximum 2 $\theta$  value of 63.0 °. All of the crystallographic calculation were performed using CrystalStructure software package of the Rigaku Corporation and Molecular Structure Corporation. The crystal structure was solved by the direct methods and refined by the full-matrix least squared using SIR-2002. All non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. The crystallographic data were summarized in the following table.

Chiral Ammonium Salt <b>1e-PF<sub>6</sub></b>	
empirical formula	C <sub>152</sub> H <sub>112.5</sub> F <sub>6</sub> NO <sub>4.25</sub> P
formula weight	2166.03
crystal system	Orthorhombic

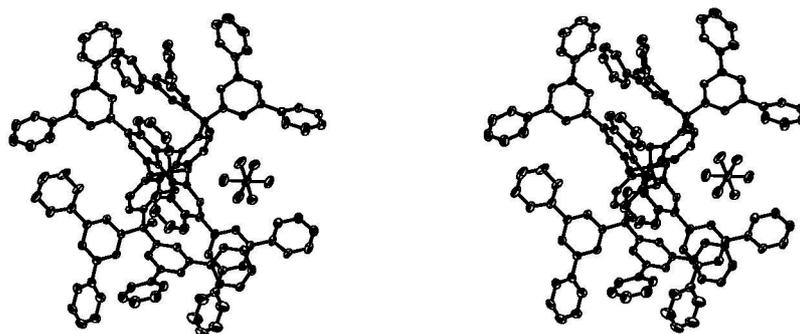
space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)
<i>a</i> , Å	17.311
<i>b</i> , Å	18.198
<i>c</i> , Å	40.790
<i>V</i> , Å <sup>3</sup>	12849.9
<i>Z</i>	4.0
<i>D</i> <sub>calc</sub> , g/cm <sup>3</sup>	1.120
<i>T</i> , °C	-150
$\mu$ (MoK $\alpha$ ), cm <sup>-1</sup>	0.084
no. of reflns meased	161437
no. of reflns obsd	18992
no. of reflns variable	1528
<i>R</i>	0.0810
<i>R</i> <sub>w</sub>	0.1200
goodness of fit	1.00

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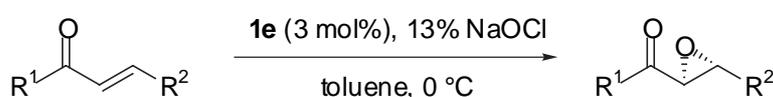
**ORTEP Diagram of Chiral Quaternary Ammonium Salt 1e-PF<sub>6</sub>** (from binaphthyl side; The solvent molecules (acetone and H<sub>2</sub>O) and all hydrogen atoms are omitted for clarity.)



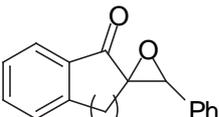
**Stereo View of 1e-PF<sub>6</sub>**



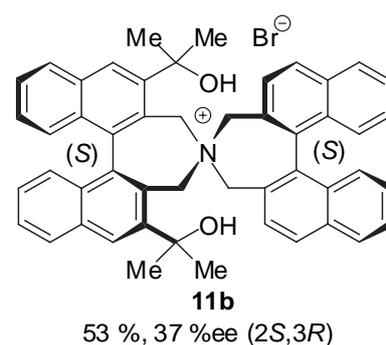
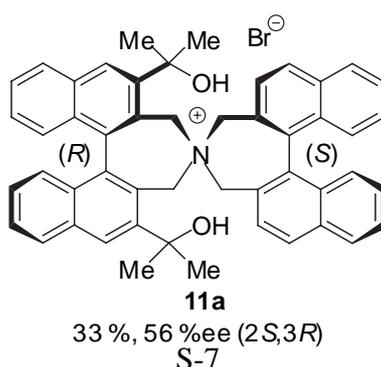
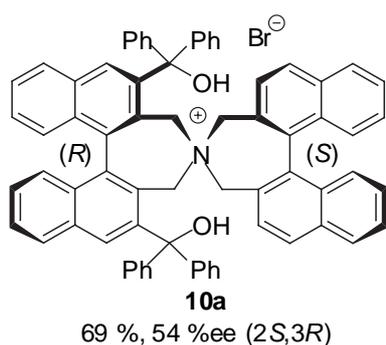
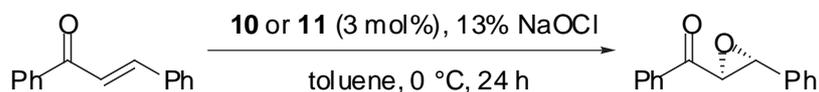
**General Procedure for Enantioselective Epoxidation of  $\alpha,\beta$ -Unsaturated Ketones.** To a mixture of enone (0.10 mmol) and chiral quaternary ammonium salt **1e** (6 mg, 0.003 mmol, 3 mol%) in toluene (0.3 mL) was added 13% aqueous sodium hypochlorite (NaOCl, 0.15 mL) and the mixture was stirred for several hours at 0 °C under argon atmosphere. The resulting mixture was diluted with water and organic phase was separated. The aqueous phase was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 times). The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>. The solvents were evaporated and the residual oil was purified by flash column chromatography on silica gel (ethyl acetate/hexane as eluant) to afford the corresponding epoxy ketone. An optical purity of the epoxy ketone was determined by chiral stationary-phase HPLC analysis. Table 1 shows the HPLC conditions and retention time for each epoxy ketone.



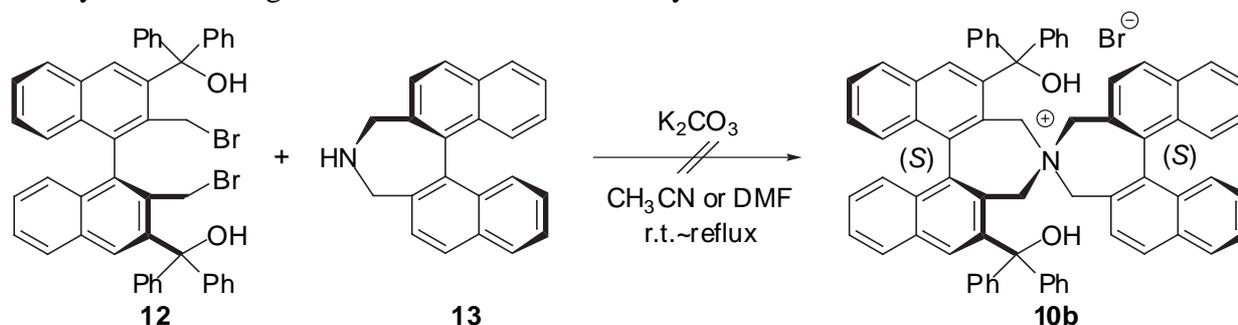
**Table 1.** HPLC Conditions for Epoxy Ketones.

epoxy ketone R <sup>1</sup> R <sup>2</sup>	chiral column	eluants (hexane/2-propanol)	flow rate (mL/min)	retention time (min)		ref.
				( $\alpha$ S, $\beta$ R)	( $\alpha$ R, $\beta$ S)	
Ph $\beta$ -Np	CHIRALCEL OD	50:1	0.5	50.9	62.8	4
Ph <i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>				44.0	48.1	
Ph <i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub>				49.8	57.4	
<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> Ph	CHIRALCEL OD-H	95:5	0.5	43.1	41.2	5
<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> <i>n</i> -Hex				(13.3	17.1)	
<i>t</i> Bu Ph	CHIRALCEL AD	20:1 (hexane/EtOH)	1.0	8.1	11.6	6
<i>t</i> Bu <i>c</i> -Hex	CHIRALPAK AS	100:1	0.5	(17.5	20.5)	
<i>t</i> Bu <i>n</i> -Hex				(11.7	16.6)	
 <i>n</i> = 1	CHIRALCEL AD	10:1	0.5	27.0	30.8	7
<i>n</i> = 2				27.9	23.3	

**Results of the Epoxidation of Chalcone with Structurally Rigid Hetero- and Homochiral Quaternary Ammonium Bromides **10** and **11** as Catalysts.**



Structurally rigid, heterochiral quaternary ammonium bromide **10a** was prepared and evaluated in the epoxidation of chalcone; this revealed that **10a** exerted adequate catalytic activity to give epoxy chalcone in good yield with promising enantioselectivity, though it was not as good as that with catalyst **1a**. It was of interest that our attempt to prepare homochiral **10b** by the quaternization of secondary amine **12** with bis(bromide) **13** turned out to be unsuccessful, resulting in the total recovery of the starting materials even under relatively harsh conditions.



This is probably due to the steric demand of the diphenylhydroxymethyl functionality. Since we were able to prepare hetero- and homochiral ammonium bromides **11a** and **11b** having dimethylhydroxymethyl group, comparison of their chiral efficiency was made in the epoxidation, demonstrating that heterochiral **11a** afforded higher enantioselectivity. This is in contrast to the tendency observed in the alkylation of glycinate Schiff base.<sup>8</sup>

#### Characterization of Chiral Quaternary Ammonium Salts **10a**, **11a** and **11b**

**Chiral Ammonium Salt 10a:**  $[\alpha]_D^{31} +99.3^\circ$  (*c* 0.31,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (2H, d,  $J = 8.3$  Hz, Ar-H), 7.89 (2H, d,  $J = 8.3$  Hz, Ar-H), 7.72 (2H, d,  $J = 8.3$  Hz, Ar-H), 7.62 (2H, t,  $J = 6.7$  Hz, Ar-H), 7.48-7.38 (8H, m, Ar-H), 7.29-7.22 (10H, m, Ar-H), 7.15 (4H, t,  $J = 7.5$  Hz, Ar-H), 6.97 (2H, d,  $J = 8.3$  Hz, Ar-H), 6.92 (4H, t,  $J = 7.5$  Hz, Ar-H), 6.85 (2H, t,  $J = 6.7$  Hz, Ar-H), 6.70 (4H, t,  $J = 7.5$  Hz, Ar-H), 5.31 (2H, br s, OH), 5.02 (2H, d,  $J = 13.5$  Hz,  $\text{ArCH}_2$ ), 4.26 (2H, br d,  $J = 12.7$  Hz,  $\text{ArCH}_2$ ), 4.10 (2H, d,  $J = 13.5$  Hz,  $\text{ArCH}_2$ ), 3.27 (2H, br d,  $J = 12.7$  Hz,  $\text{ArCH}_2$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.5, 144.2, 142.8, 139.9, 136.2, 133.8, 132.2, 131.1, 131.0, 129.5, 128.7, 128.2, 128.0, 127.7, 127.6, 127.5, 127.1, 127.0, 126.9, 126.9, 126.8, 126.4, 82.1, 65.5, 60.7; IR (neat) 3196, 3055, 2926, 1595, 1490, 1447, 1342, 1254, 1217, 1167, 1051, 1026, 893, 864, 818, 746, 702  $\text{cm}^{-1}$ ; HRMS (ESI) Calcd for  $\text{C}_{70}\text{H}_{52}\text{NO}_2$  ( $\text{M}^+$ ): 938.3993, Found: 938.4001.

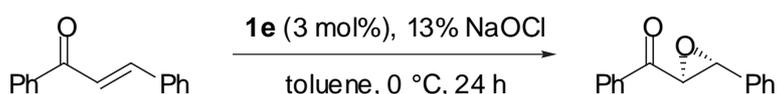
**Chiral Ammonium Salt 11a:**  $[\alpha]_D^{29} +83.0^\circ$  (*c* 0.35,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (2H, s, Ar-H), 7.99 (2H, d,  $J = 8.3$  Hz, Ar-H), 7.98 (2H, d,  $J = 8.3$  Hz, Ar-H), 7.96 (2H, d,  $J = 8.3$  Hz, Ar-H), 7.70 (2H, d,  $J = 8.3$  Hz, Ar-H), 7.58-7.52 (4H, m, Ar-H), 7.46 (2H, d,  $J = 8.3$  Hz, Ar-H), 7.33 (2H, t,  $J = 7.9$  Hz, Ar-H), 7.24 (2H, t,  $J = 7.9$  Hz, Ar-H), 6.96 (2H, d,  $J = 8.3$  Hz, Ar-H), 5.88 (2H, d,  $J = 12.7$  Hz,  $\text{ArCH}_2$ ), 4.77 (2H, d,  $J = 13.5$  Hz,  $\text{ArCH}_2$ ), 4.60 (2H, d,  $J = 13.5$  Hz,  $\text{ArCH}_2$ ), 4.36 (2H, d,  $J = 12.7$  Hz,  $\text{ArCH}_2$ ), 3.42 (2H, s, OH), 1.90 (6H, s,  $\text{CH}_3$ ), 1.37 (6H, s,  $\text{CH}_3$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.1, 140.0, 136.8, 134.1, 133.2, 131.2, 130.8, 129.6, 128.7, 128.5, 128.0,

127.8, 127.6, 127.4, 127.0, 127.0, 126.8, 126.6, 126.4, 125.5, 73.0, 66.1, 60.2, 34.3, 31.8; IR (neat) 3265, 3053, 2976, 2191, 1593, 1464, 1364, 1163, 920, 868, 816, 750, 729  $\text{cm}^{-1}$ ; HRMS (ESI) Calcd for  $\text{C}_{50}\text{H}_{44}\text{NO}_2$  ( $\text{M}^+$ ): 690.3367, Found: 690.3388.

**Chiral Ammonium Salt 11b:**  $[\alpha]_{\text{D}}^{31} -8.52^\circ$  ( $c$  0.90,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.33 (2H, d,  $J = 8.3$  Hz, Ar-H), 8.17 (2H, s, Ar-H), 8.16 (2H, d,  $J = 8.3$  Hz, Ar-H), 8.01 (2H, d,  $J = 8.3$  Hz, Ar-H), 7.98 (2H, d,  $J = 8.3$  Hz, Ar-H), 7.52 (4H, dd,  $J = 15.8, 8.3$  Hz, Ar-H), 7.25-7.12 (6H, m, Ar-H), 6.75 (2H, d,  $J = 8.3$  Hz, Ar-H), 6.36 (2H, d,  $J = 13.8$  Hz,  $\text{ArCH}_2$ ), 4.83 (2H, d,  $J = 13.3$  Hz,  $\text{ArCH}_2$ ), 4.37 (2H, s, OH), 4.28 (2H, d,  $J = 13.8$  Hz,  $\text{ArCH}_2$ ), 3.77 (2H, d,  $J = 13.3$  Hz,  $\text{ArCH}_2$ ), 2.28 (6H, s,  $\text{CH}_3$ ), 1.44 (6H, s,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.8, 139.3, 136.8, 134.0, 132.9, 131.1, 129.6, 128.9, 128.3, 128.1, 127.5, 127.3, 127.2, 126.7, 126.5, 126.3, 126.3, 125.8, 125.7, 73.8, 63.5, 60.1, 35.2, 31.5; IR (neat) 3260, 3051, 2972, 2926, 2853, 2193, 1724, 1595, 1454, 1362, 1163, 1150, 1032, 953, 920, 837, 750, 729, 652  $\text{cm}^{-1}$ ; HRMS (ESI) Calcd for  $\text{C}_{50}\text{H}_{44}\text{NO}_2$  ( $\text{M}^+$ ): 690.3367, Found: 690.3366.

### Catalyst Recycles in the Epoxidation of Chalcone

To a mixture of chalcone (20.8 mg, 0.10 mmol) and chiral quaternary ammonium salt **1e** (6.0 mg, 0.003 mmol, 3 mol%) in toluene (0.3 mL) was added 13% aqueous sodium hypochlorite (0.3 mL) and the mixture was stirred for 24 hours at  $0^\circ\text{C}$  under argon atmosphere. The resulting mixture was directly purified by flash column chromatography on silica gel (ethyl acetate/hexane = 1:3 as eluant) to afford epoxy chalcone, and subsequent elution with methanol/dichloromethane (1:5) gave chiral quaternary ammonium salt **1e** quantitatively.



**Table 2.** Epoxidation of Chalcone with Catalyst **1e**.

number of cycle	catalyst recovery yield (%) <sup>a</sup>	yield (%) <sup>a</sup>	ee (%) <sup>b</sup> (config) <sup>c</sup>
1	99	99	96 ( $\alpha S, \beta R$ )
2	99	99	96 ( $\alpha S, \beta R$ )
3	99	99	95 ( $\alpha S, \beta R$ )
4	99	99	96 ( $\alpha S, \beta R$ )
5	99	99	94 ( $\alpha S, \beta R$ )

<sup>a</sup> Isolated yield. <sup>b</sup> Enantiomeric excess was determined by HPLC analysis using a chiral column (DAICEL Chiralcel OD-H, *i*-PrOH/hexane = 5:95,  $\lambda = 254$  nm, flow rate = 0.5 mL/min,  $t_{\text{R}} = 24.3$  min ( $\alpha S, \beta R$ ) and 26.3 min ( $\alpha R, \beta S$ ). <sup>c</sup> Absolute configuration was determined by comparison of the retention time with that reported.<sup>9</sup>

## Characterization of Substrates and Epoxy Ketones.

**1-(4-Chlorophenyl)-3-decen-2-one:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (1H, d,  $J = 8.5$  Hz, Ar-H), 7.44 (1H, d,  $J = 8.5$  Hz, Ar-H), 7.07 (1H, dt,  $J = 15.4, 6.9$  Hz, C=CH), 6.83 (1H, d,  $J = 15.4$  Hz, COCH=C), 2.32 (2H, dt,  $J = 7.2, 6.9$  Hz,  $\text{CH}_2$ ), 1.55-1.48 (2H, m,  $\text{CH}_2$ ), 1.39-1.26 (6H, m,  $\text{CH}_2$ ), 0.90 (3H, t,  $J = 7.2$  Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  189.3, 150.6, 138.8, 136.2, 129.8, 128.7, 125.3, 33.0, 31.7, 29.0, 28.2, 22.6, 14.1; IR (neat) 2930, 2856, 2120, 1672, 1620, 1589, 1400, 1300, 1225, 1092, 1013, 972, 818, 729  $\text{cm}^{-1}$ ; HRMS (ESI) Calcd for  $\text{C}_{15}\text{H}_{20}\text{ClO}$  ( $[\text{M}+\text{H}]^+$ ): 251.1197, Found: 251.1206.

**5-Cyclohexyl-2,2-dimethyl-4-penten-3-one:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.88 (1H, dd,  $J = 7.5, 6.7$  Hz, COC=CH), 6.44 (1H, d,  $J = 7.5$  Hz, COCH=C), 2.17-2.10 (1H, m, CH), 1.77-1.75 (4H, m,  $\text{CH}_2$ ), 1.35-1.16 (6H, m,  $\text{CH}_2$ ), 1.15 (9H, s, *t*-Bu);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  204.4, 152.3, 121.4, 43.0, 40.8, 32.0, 26.3, 26.0, 25.8; IR (neat) 3013, 2932, 2855, 2118, 1684, 1620, 1477, 1450, 1367, 1072, 1009, 983, 964  $\text{cm}^{-1}$ ; HRMS (ESI) Calcd for  $\text{C}_{13}\text{H}_{22}\text{NaO}$  ( $[\text{M}+\text{Na}]^+$ ): 217.1563, Found: 217.1573.

**(2S,3R)-Epoxy-1-chlorophenyldecan-1-one:**  $[\alpha]_{\text{D}}^{30} +6.6^\circ$  [*c* 0.58,  $\text{CHCl}_3$  (96% ee)];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (2H, d,  $J = 7.3$  Hz, Ar-H), 7.47 (2H, d,  $J = 7.3$  Hz, Ar-H), 3.94 (1H, d,  $J = 2.0$  Hz, COCH-O), 3.14 (1H, dt,  $J = 5.5, 2.0$  Hz, CH-O), 1.79-1.26 (10H, m,  $\text{CH}_2$ ), 0.89 (3H, t,  $J = 7.1$  Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  193.5, 140.2, 133.7, 129.6, 129.0, 60.0, 57.6, 32.0, 31.7, 29.1, 25.9, 22.6, 14.1; IR (neat) 2924, 2855, 1686, 1622, 1591, 1543, 1467, 1437, 1286, 1232, 1092, 1012, 1002, 897, 839, 745  $\text{cm}^{-1}$ ; HRMS (ESI) Calcd for  $\text{C}_{15}\text{H}_{20}\text{ClO}_2$  ( $[\text{M}+\text{H}]^+$ ): 267.1146, Found: 267.1156. Absolute configuration was determined by Mosher's Method after derivatization to 1-phenylnonan-3-ol<sup>10</sup> with  $\text{H}_2/\text{Pd-C}$  in methanol;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.26 (2H, m, Ar-H), 7.23-7.16 (3H, m, Ar-H), 3.66-3.60 (1H, m,  $\text{HCOH}$ ), 2.83-2.76 (1H, m,  $\text{ArCH}_2$ ), 2.71-2.63 (1H, m,  $\text{ArCH}_2$ ), 1.84-1.68 (2H, m,  $\text{CH}_2$ ), 1.56 (1H, s, OH), 1.49-1.43 (2H, m,  $\text{CH}_2$ ), 1.28-1.25 (8H, br,  $\text{CH}_2$ ), 0.88 (3H, t,  $J = 5.5$  Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.8, 128.3, 125.7, 71.4, 39.2, 37.7, 32.2, 31.9, 29.4, 25.7, 22.7, 14.2; IR (neat) 3350, 2927, 2856, 1603, 1497, 1454, 1377, 1126, 1088, 1040, 1028, 1014, 914, 745, 698  $\text{cm}^{-1}$ ; HRMS (ESI) Calcd for  $\text{C}_{15}\text{H}_{24}\text{NaO}$  ( $[\text{M}+\text{Na}]^+$ ): 243.1717, Found: 243.1719.

**(R)-MTPA Ester of 1-Phenylnonan-3-ol:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (2H, t,  $J = 3.6$  Hz, Ar-H), 7.41-7.39 (3H, m, Ar-H), 7.30-7.26 (2H, m, Ar-H), 7.20 (1H, t,  $J = 7.5$  Hz, Ar-H), 7.14 (2H, d,  $J = 7.5$  Hz, Ar-H), 5.16-5.13 (1H, m, CH-O), 3.58 (3H, s,  $\text{OCH}_3$ ), 2.66-2.59 (2H, m,  $\text{CH}_2$ ), 2.02-1.90 (2H, m,  $\text{CH}_2$ ), 1.59 (2H, br,  $\text{CH}_2$ ), 1.26-1.19 (8H, m,  $\text{CH}_2$ ), 0.86 (3H, t,  $J = 6.9$  Hz,  $\text{CH}_3$ ).

**(S)-MTPA Ester of 1-Phenylnonan-3-ol:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58-7.56 (2H, m, Ar-H), 7.42-7.40 (3H, m, Ar-H), 7.28-7.14 (3H, m, Ar-H), 7.06 (2H, d,  $J = 7.1$  Hz, Ar-H), 5.15-5.11 (1H, m, CH-O), 3.58 (3H, s,  $\text{OCH}_3$ ), 2.57-2.42 (2H, m,  $\text{CH}_2$ ), 1.92-1.86 (2H, m,  $\text{CH}_2$ ), 1.70-1.58 (2H, m,

CH<sub>2</sub>), 1.30-1.20 (8H, br, CH<sub>2</sub>), 0.88 (3H, t, *J* = 6.5 Hz, CH<sub>3</sub>).

**trans-Epoxy-5-cyclohexyl-2,2-dimethylpentan-3-one:** [ $\alpha$ ]<sub>D</sub><sup>29</sup> +36.6 ° [*c* 0.50, CHCl<sub>3</sub> (96% ee)]; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.69 (1H, d, *J* = 2.0 Hz, COCH-O), 3.73 (1H, dd, *J* = 6.7, 2.0 Hz, CH-O), 1.89-1.86 (1H, m, CH), 1.78-1.67 (4H, m, CH<sub>2</sub>), 1.23 (9H, s, *t*-Bu), 1.36-1.07 (6H, m, CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.1, 64.4, 54.4, 43.7, 40.2, 29.7, 28.8, 26.2, 26.0, 25.6, 25.5; IR (KBr) 2928, 2853, 1713, 1477, 1450, 1396, 1367, 1227, 1072, 1005, 964, 926, 905, 880, 789 cm<sup>-1</sup>; HRMS (ESI) Calcd for C<sub>13</sub>H<sub>22</sub>NaO<sub>2</sub> ([M+Na]<sup>+</sup>): 233.1512, Found: 233.1513.

**trans-Epoxy-2,2-dimethylundecan-3-one:** [ $\alpha$ ]<sub>D</sub><sup>26</sup> +20.4 ° [*c* 0.94, CHCl<sub>3</sub> (91% ee)]; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.61 (1H, d, *J* = 2.0 Hz, COCH-O), 2.93 (1H, dt, *J* = 5.5, 2.0 Hz, CH-O), 1.64 (2H, dt, *J* = 7.5, 5.5 Hz, CH<sub>2</sub>), 1.50-1.41 (2H, m, CH<sub>2</sub>), 1.39-1.26 (6H, m, CH<sub>2</sub>), 1.23 (9H, s, *t*-Bu), 0.89 (3H, t, *J* = 7.1 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  209.2, 60.1, 55.4, 43.6, 32.0, 31.7, 29.1, 25.9, 25.8, 22.6, 14.1; IR (liquid film) 2991, 2960, 2858, 1716, 1477, 1429, 1367, 1261, 1084, 1016, 901 cm<sup>-1</sup>; HRMS (ESI) Calcd for C<sub>13</sub>H<sub>24</sub>NaO<sub>2</sub> ([M+Na]<sup>+</sup>): 235.1669, Found: 235.1668.

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