Supporting Information for

4-Substituted- α , α -Diaryl-Prolinols Improve

the Enantioselective Catalytic Epoxidation of α , β -Enones

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General experimental

All the reagents were obtained from commercial source. THF and diethyl ether were freshly distilled over Na. Hexane and carbon tetrachloride were used without further treatment. α , β -Enones were prepared according to the reported procedures and further purified by silica gel column.¹ All NMR spectra were recorded in CDCl_3 as the solvent unless otherwise stated.

Synthesis of *trans*-4-substituted-L-prolinol **9** and **10a-b**.

The chiral catalysts **9** and **10a-b** were prepared from *trans*-4-hydroxyl-L-proline **4** according to the reported procedure (Scheme S1).² The amine group of 4-hydroxyproline **4** was protected using ethyl chloroformate and the acid was converted to a methyl ester to give the carbamate ester **11**. The prolinol **9** was isolated in good yield after a Grignard reaction and the hydrolysis of **12** with potassium hydroxide in a mixture of methanol and water. Treating the intermediate **12** with benzyl bromide using sodium hydride as a base in THF afforded compound **13** in moderate yields.^{2a} Hydrolysis of **13** gave the *trans*-4-benzyloxy- α , α -diaryl-L-prolinol **10** in good yield.

SCHEME S1 Synthesis of *trans*-4-Substituted-L-Prolinol Ligands.^a

^a Reagents and conditions: (a) ClCOOEt , MeOH , rt, 24 h, 50%; (b) ArMgBr , THF, rt, 5 h; (c) KOH , $\text{MeOH}/\text{H}_2\text{O}$, 100 °C, 24 h, 90%; (d) 1.2 equiv. NaH , 1.2 equiv. BnBr , THF, rt, 20 h.

Synthesis of *trans*-4-hydroxyl- α , α -bis-(3, 5-dimethylphenyl)-L-prolinol carbamate ester (12b**).**

To a solution of *trans*-4-hydroxyl-L-proline **4** in methanol was added ethyl chloroformate. The reaction mixture was stirred for 24 hours at room temperature and then filtered. The filtrate was extracted with ethyl acetate and concentrated to give product **11** in 50% yields. To a solution of **11** (500 mg, 2.30 mmol) in dry THF (10 mL) was added 3,5-dimethylphenyl magnesium bromide (1 M in THF, 23 mL, 23.02 mmol) at 0 °C under Ar. After being stirred for 5 h, the reaction solution was diluted with saturated aqueous NH₄Cl and washed with ether. The organic layer was dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated under reduced pressure to give a residue, which was chromatographed on silica gel (1:1 hexane/EtOAc as eluent) to give the product **12b** as a white foam (72% yield): mp 67-68 °C; $[\alpha]_D^{25.4} = -38.84$ (*c* 0.60, CHCl₃); IR (Film) 3419, 2918, 1670, 1603, 1432 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.57 (t, *J* = 6.9 Hz, 3H), 2.05 (m, 1H), 2.27 (s, 6H), 2.29 (s, 6H), 2.96 (m, 1H), 3.54 (d, *J* = 12.0 Hz, 1H), 3.91-3.98 (m, 2H), 4.10 (m, 2H), 5.03-5.08 (dd, *J* = 6.3, 8.4 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 4H); MS (ESI): *m/e* 380.4 (M-H₂O+H⁺, 100%); Anal. Calcd. for C₂₄H₃₁NO₄: C, 72.52; H, 7.86; N, 3.52. Found: C, 72.17; H, 7.75; N, 3.17.

Typical procedure for the synthesis of *trans*-4-substituted- α , α -diaryl-L-prolinol **10.**

To a solution of **12a** (200 mg, 0.58 mmol) and sodium hydride (16.9 mg, 0.70 mmol) in dry THF (5 mL) was added benzyl bromide dropwisely at rt under Ar. After being stirred for 20 h, the reaction was quenched with saturated aqueous NH₄Cl and the reaction mixture was extracted with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄ and concentrated under reduced pressure to give a residue, which was chromatographed on silica gel (10:1 hexane/EtOAc as eluent) to give the product **13a**. A suspension of the product **13a** (100 mg) and KOH (100 mg, 1.78 mmol) in methanol (5 mL) was heated at 80 °C for 24 h. After the reaction was completed, the mixture was extracted with CH₂Cl₂. The organic layer was concentrated and the residue was chromatographed on silica gel (first 5:1 hexane/EtOAc, then 3:1 acetone/dichloromethane as eluent) to get the product **10a**.

6-Benzyloxy-1, 1-diphenyl-tetrahydro-pyrrolo[1,2-c]oxazol-3-one 13a: white foam, mp 139-140 °C; $[\alpha]_D^{24.5} = 151.22$ (*c* 0.45, CHCl₃); IR (Film) 2921, 2852, 1760, 1495, 1450 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.21-1.28 (m, 1H), 1.90 (dd, *J* = 6.0, 14.1 Hz, 1H), 3.33 (d, *J* = 12.9 Hz, 1H), 4.03 (dd, *J* = 6.0, 13.5 Hz, 1H), 4.18 (m, 1H), 4.47(s, 2H), 4.87 (dd, *J* = 5.1, 12.3 Hz, 1H), 7.32-7.36 (m, 13H), 7.53 (d, *J* = 6.6 Hz, 2H); MS (ESI): *m/e* 386.2 (M⁺+1, 100%); Anal. Calcd. for C₂₅H₂₃NO₃ : C, 77.90; H, 6.01; N, 3.63. Found: C, 77.88; H, 6.22; N, 3.39.

6-Benzyloxy-1, 1-bis-(3,5-dimethyl-phenyl)-tetrahydro-pyrrolo[1, 2-c]oxazol-3-one 13b: white foam, mp 142-143 °C; $[\alpha]_D^{24.5} = 25.14$ (*c* 0.60, CHCl₃); IR (Film) 2917, 1754, 1606, 1455 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.14-1.20 (m, 1H), 1.87 (dd, *J* = 5.1, 13.5 Hz, 1H), 2.28 (s, 6H), 2.30 (s, 6H), 3.31 (d, *J* = 12.9 Hz, 1H), 4.03 (dd, *J* = 5.7, 12.6 Hz, 1H), 4.17 (t, *J* = 5.4 Hz, 1H), 4.47 (s, 2H), 4.82 (dd, *J* = 5.1, 11.1 Hz, 1H), 6.87 (s, 1H), 6.94 (s, 3H), 7.12 (s, 2H), 7.27-7.36 (m, 5H); MS (ESI): *m/e* 442.2 (M⁺+1, 100%); Anal. Calcd. for C₂₉H₃₁NO₃ : C, 78.88; H, 7.08; N, 3.17. Found: C, 78.87; H, 7.29; N, 2.93.

trans-4-benzyloxy- α , α -diphenyl-L-prolinol 10a: colorless oil; $[\alpha]_D^{25.5} = -57.40$ (*c* 1.10, CHCl₃); IR (Film) 3363, 3060, 2925, 1597, 1449, 1261 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.57-1.76 (m, 2H), 3.05-3.07 (m, 2H), 4.36 (s, 2H), 4.50 (t, *J* = 6.9 Hz, 1H), 7.06-7.29 (m, 11H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 7.5 Hz, 2H); MS (ESI): *m/e* 360.2 (M⁺+1, 100%); Anal. Calcd. For C₂₄H₂₅NO₂ : C, 80.19; H, 7.01; N, 3.90. Found: C, 80.43; H, 7.04; N, 3.80.

trans-4-benzyloxy- α , α -bis-(3, 5-dimethylphenyl)-L-prolinol 10b: white foam, mp 37-38 °C; $[\alpha]_D^{22.3} = -50.45$ (*c* 0.35, CHCl₃); IR (Film) 3441, 2921, 1604, 1495, 1454 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.70-1.77 (m, 2H), 2.28 (s, 12H), 3.13 (m, 2H), 4.05 (m, 1H), 4.45 (s, 2H), 4.50-4.56 (m, 1H), 6.81 (s, 2H), 7.09, (s, 2H), 7.18 (s, 2H), 7.27-7.33 (m, 5H); MS (ESI): *m/e* 416.4 (M⁺+1, 100%); Anal. Calcd. for C₂₈H₃₃NO₂ : C, 80.93; H, 8.00; N, 3.37. Found: C, 80.88; H, 8.20; N, 3.29.

trans-4-hydroxyl- α , α -diphenyl-L-prolinol 9^{2b}: ¹H NMR (300 MHz, CDCl₃) δ 1.49 (dd, *J* = 6.6, 13.8 Hz, 1H), 1.81-1.92 (m, 1H), 2.99 (d, *J* = 11.4 Hz, 1H), 3.16 (dd, *J* = 4.2, 11.4 Hz, 1H), 4.38 (m, 1H), 4.67 (dd, *J* = 6.3, 10.2 Hz, 1H), 7.14-7.33 (m, 6H), 7.46 (d, *J*

= 7.2 Hz, 2H), 7.58 (d, J = 6.9 Hz, 2H).

Synthesis of *cis*-4-hydroxyl- α , α -bis-(3,5-dimethylphenyl)-D-prolinol carbamate ester **6.**

A stirred mixture of **4** (6.55 g, 50 mmol) and acetic anhydride (40 mL) was heated at 90 °C for 16 h under argon. The solution was evaporated under reduced pressure to give a thick oil that was dissolved in 2 N aqueous HCl (30 mL). The solution was heated under reflux for 2 h, then decolorized with charcoal while hot, filtered and neutralized to pH 6 with 5 N NaOH (10 mL) and then concentrated to give a crude product. To a solution of this crude product in methanol was added ethyl chloroformate. The reaction mixture was stirred for 24 hours at room temperature and then filtered. The filtrate was extracted with ethyl acetate and concentrated to give product **5** in 25% total yields. To a solution of **5** (500 mg, 2.30 mmol) in dry THF (10 mL) was added 3,5-dimethylphenyl magnesium bromide (1 M in THF, 23 mL, 23.02 mmol) at 0 °C under Ar. After being stirred for 5 h, the reaction solution was diluted with saturated aqueous NH₄Cl and washed with ether. The organic layer was dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated under reduced pressure to give a residue, which was chromatographed on silica gel (1:1 hexane/EtOAc as eluent) to give the product **6** as a white foam (70% yield): mp 77-78 °C; $[\alpha]_D^{23.7}$ = -118.46 (c 0.65, CHCl₃); IR (Film) 3337, 2918, 1668, 1604, 1431 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.92 (m, 3H), 1.88 (d, J = 14.7 Hz, 1H), 2.25 (s, 6H), 2.33 (s, 6H), 3.43 (m, 1H), 3.83 (m, 2H), 4.07 (m, 2H), 4.37 (m, 1H), 4.90 (d, J = 9.0 Hz, 1H), 6.83 (s, 1H), 6.93 (s, 1H), 6.98 (s, 2H), 7.08 (s, 2H); MS (ESI): m/e 380.3 (M-H₂O+H⁺, 100%); Anal. Calcd. for C₂₄H₃₁NO₄: C, 72.52; H, 7.86; N, 3.52. Found: C, 72.18; H, 7.85; N, 3.19.

Typical procedure for the synthesis of *cis*-4-substituted- α , α -bis-(3,5-dimethylphenyl)-D-prolinol **8.**

To a solution of **6** (200 mg, 0.50 mmol) and sodium hydride (14.4 mg, 0.60 mmol) in dry THF (5 mL) was added benzyl bromide (101.4 mg, 0.6 mmol) dropwisely at rt under Ar. After being stirred for 20 h, the reaction was quenched with saturated aqueous NH₄Cl and the reaction mixture was extracted with CH₂Cl₂. The organic layer was dried over

anhydrous MgSO₄ and concentrated under reduced pressure to give a residue, which was chromatographed on silica gel (10:1 hexane/EtOAc as eluent) to give the product **7a**. A suspension of the product **7a** (100 mg) and KOH (100 mg, 1.78 mmol) in methanol (5 mL) was heated at 80 °C for 24 h. After the reaction was completed, the mixture was extracted with CH₂Cl₂. The organic layer was concentrated and the residue was chromatographed on silica gel (first 5:1 hexane/EtOAc, then 3:1 acetone/dichloromethane as eluent) to get the product **8a**.

6-Benzoyloxy-1,1-bis-(3,5-dimethyl-phenyl)-7a-methyl-tetrahydro-pyrrolo[1,2-c]oxazol-3-one 7a: white foam, mp 46-47 °C; $[\alpha]_D^{24.4} = -89.37$ (*c* 0.45, CHCl₃); IR (Film) 2918, 1755, 1606, 1455 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.39-1.49 (m, 1H), 1.99-2.08 (m, 1H), 2.24 (s, 6H), 2.30 (s, 6H), 3.27 (dd, *J* = 6.0, 13.8 Hz, 1H), 3.92 (dd, *J* = 3.3, 12.3 Hz, 1H), 4.17-4.24 (m, 1H), 4.40 (q, *J* = 11.2 Hz, 2H), 4.59 (t, *J* = 6.6 Hz, 1H), 6.87 (s, 1H), 6.94 (s, 3H), 7.12 (s, 2H), 7.27-7.36 (m, 5H); MS (ESI): *m/e* 442.2 (M⁺+1, 100%); Anal. Calcd. for C₂₉H₃₁NO₃: C, 78.88; H, 7.08; N, 3.17. Found: C, 78.69; H, 7.16; N, 2.93.

6-Allyloxy-1,1-bis-(3,5-dimethyl-phenyl)-7a-methyl-tetrahydro-pyrrolo[1,2-c]oxazol-3-one 7b: white foam, mp 136-137 °C; $[\alpha]_D^{25.5} = 179.58$ (*c* 0.40, CHCl₃); IR (Film) 2922, 1758, 1607, 1459 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.35-1.43 (m, 1H), 1.98-2.07 (m, 1H), 2.28 (s, 6H), 2.30 (s, 6H), 3.30 (dd, *J* = 6.0, 12.0 Hz, 1H), 3.74-3.91 (m, 3H), 4.15-4.22 (m, 1H), 4.55-4.61 (m, 1H), 4.58 (t, *J* = 6.6 Hz, 1H), 5.13-5.26 (m, 2H), 5.75-5.86 (m, 1H), 6.88 (s, 1H), 6.93 (s, 1H), 6.96 (s, 2H), 7.12 (s, 2H); MS (ESI): *m/e* 392.2 (M⁺+1, 100%); Anal. Calcd. for C₂₅H₂₉NO₃: C, 76.70; H, 7.47; N, 3.58. Found: C, 76.59; H, 7.69; N, 3.26.

1,1-Bis-(3,5-dimethyl-phenyl)-7a-methyl-6-(naphthalen-2-ylmethoxy)-tetrahydro-pyrrolo[1,2-c]oxazol-3-one 7c: white foam, mp 52-53 °C; $[\alpha]_D^{21.0} = 159.53$ (*c* 0.35, CHCl₃); IR (Film) 2917, 1753, 1655, 1509, 1459 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.42-1.56 (m, 1H), 1.99-2.08 (m, 1H), 2.22 (s, 6H), 2.29 (s, 6H), 3.29 (dd, *J* = 6.3, 12.9 Hz, 1H), 3.94 (d, *J* = 11.4 Hz, 1H), 4.25 (m, 1H), 4.50 (d, *J* = 11.2 Hz, 1H), 4.58 (m, 2H), 6.86 (s, 1H), 6.94 (s, 2H), 7.12 (s, 2H), 7.26 (s, 1H), 7.38-7.82 (m, 7H); MS (ESI): *m/e* 514.2 (M⁺+Na, 100%); Anal. Calcd. for C₃₃H₃₃NO₃: C, 80.62; H, 6.77; N, 2.85. Found: C, 80.57; H, 7.08; N, 2.62.

1,1-Bis-(3,5-dimethyl-phenyl)-6-(4-methoxy-benzyloxy)-7a-methyl-tetrahydro-pyrrolo[1,2-c]oxazol-3-one 7d: white foam, mp 42-43 °C; $[\alpha]_D^{22.3} = 155.65$ (*c* 1.15, CHCl₃); IR (Film) 2920, 1756, 1609, 1514, 1455, 1247 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.30-1.35 (m, 1H), 1.89-1.96 (m, 1H), 2.17 (s, 6H), 2.22 (s, 6H), 3.19 (dd, *J* = 6.3, 12.0 Hz, 1H), 3.72 (s, 3H), 3.80 (d, *J* = 14.7 Hz, 1H), 4.11 (m, 1H), 4.25 (q, *J* = 11.1 Hz, 2H), 4.50 (t, *J* = 8.1 Hz, 1H), 6.77-7.18 (m, 10H); MS (ESI): *m/e* 472.4 (M⁺+1, 100%); Anal. Calcd. for C₃₀H₃₃NO₄: C, 76.41; H, 7.05; N, 2.97. Found: C, 76.40; H, 7.16; N, 2.77.

cis-4-Benzyloxy- α , α -bis-(3, 5-dimethylphenyl)-D-prolinol 8a: white foam, mp 127 °C; $[\alpha]_D^{21.7} = 44.69$ (*c* 0.45, CHCl₃); IR (Film) 3360, 2916, 2854, 1604, 1453 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.85-1.91 (m, 2H), 2.28 (s, 12H), 3.01 (dd, *J* = 5.4, 11.1 Hz, 1H), 3.16 (d, *J* = 10.8 Hz, 1H), 4.04 (m, 1H), 4.30 (t, *J* = 7.2 Hz, 1H), 4.46 (q, *J* = 12.0 Hz, 2H), 6.81 (s, 2H), 7.11 (s, 2H), 7.18 (s, 2H), 7.28-7.34 (m, 5H); MS (ESI): *m/e* 416.2 (M⁺+1, 100%); Anal. Calcd. for C₂₈H₃₃NO₂: C, 80.93; H, 8.00; N, 3.37. Found: C, 80.74; H, 8.02; N, 3.15.

cis-4-Allyloxy- α , α -bis-(3, 5-dimethylphenyl)-D-prolinol 8b: colorless oil; $[\alpha]_D^{25.5} = 40.80$ (*c* 2.25, CHCl₃); IR (Film) 3448, 2916, 1604, 1459 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.78-1.93 (m, 2H), 2.28 (s, 12H), 2.98 (dd, *J* = 5.4, 10.8 Hz, 1H), 3.13 (d, *J* = 10.8 Hz, 1H), 3.91-4.01 (m, 3H), 4.29 (t, *J* = 6.9 Hz, 1H), 5.20 (dd, *J* = 8.4, 12.9 Hz, 2H), 5.83-5.29 (m, 1H), 6.80 (s, 2H), 7.09 (s, 2H), 7.17 (s, 2H); MS (ESI): *m/e* 366.2 (M⁺+1, 100%); Anal. Calcd. for C₂₄H₃₁NO₂: C, 78.86; H, 8.55; N, 3.83. Found: C, 78.65; H, 8.81; N, 3.54.

cis-4-(naphthalen-2-ylmethoxy)- α , α -bis-(3, 5-dimethylphenyl)-D-prolinol 8c: white foam, mp 39-40 °C; $[\alpha]_D^{21.0} = 29.82$ (*c* 0.35, CHCl₃); IR (Film) 3368, 2921, 1603, 1495 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.89-1.94 (m, 2H), 3.01 (dd, *J* = 5.1, 10.8 Hz, 1H), 3.20 (d, *J* = 10.8 Hz, 1H), 4.08 (m, 1H), 4.30 (t, *J* = 7.5 Hz, 1H), 4.63 (q, *J* = 12.0 Hz, 2H), 6.81 (s, 2H), 7.12 (s, 2H), 7.18 (s, 2H), 7.49-7.83 (m, 7H); MS (ESI): *m/e* 466.4 (M⁺+1, 100%); Anal. Calcd. for C₃₂H₃₅NO₂: C, 82.54; H, 7.58; N, 3.01. Found: C, 82.43; H, 7.64; N, 2.80.

cis-4-(4-Methyloxy-benzyloxy)- α , α -bis-(3,5-dimethylphenyl)-D-prolinol 8d: colorless oil; $[\alpha]_D^{27.3} = 37.15$ (*c* 0.35, CHCl₃); IR (Film) 3425, 2914, 1606, 1513, 1463, 1248 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.76-1.82 (m, 2H), 2.21 (s, 12H), 2.91 (dd, *J* = 5.1, 10.8

Hz, 1H), 3.09 (m, 1H), 3.73 (s, 3H), 3.94 (m, 1H), 4.22 (t, $J = 7.5$ Hz, 1H), 4.32 (q, $J = 11.1$ Hz, 2H), 6.73-7.19 (m, 10H); MS (ESI): m/e 446.4 ($M^+ + 1$, 100%); Anal. Calcd. for $C_{29}H_{35}NO_3$: C, 78.17; H, 7.92; N, 3.14. Found: C, 78.31; H, 8.21; N, 2.91.

General procedure for the asymmetric epoxidation of α , β -Enones.

To a solution of the α , β -enones (0.2 mmol) and catalyst (30 mol%) in hexane (1 mL) was added TBHP (0.26 mmol, 36 μ L) at room temperature and stirring was maintained for the indicated time. The crude reaction mixture was concentrated on the rotary evaporator. And the residue was directly purified by flash chromatography on silica gel (petroleum ether/diethyl ether 40/1) to get the pure epoxides **2**.

***trans*-(2*S*, 3*R*)-Epoxy-1, 3-diphenyl-propan-1-one **2a**:^{3c}**

Yield: 75%; $[\alpha]_D^{24.3} = 152.1$ (c 0.20, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$) δ 4.01 (s, 1H), 4.23 (s, 1H), 7.32-7.45 (m, 7H), 7.54 (d, $J = 7.2$ Hz, 1H), 7.94 (d, $J = 7.8$ Hz, 2H). HPLC-separation conditions: Chiralcel OD, 20 $^{\circ}C$, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{major} = 15.8$ min, $t_{minor} = 16.9$ min.

***trans*-(2*S*, 3*R*)-Epoxy-3-phenyl-1-(4-methoxyphenyl)-propan-1-one **2b**:^{3c}**

Yield: 70%; $[\alpha]_D^{24.0} = 220.6$ (c 0.80, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$) δ 3.88 (s, 3H), 4.07 (s, 1H), 4.26 (s, 1H), 6.96 (d, $J = 7.8$ Hz, 2H); 7.39 (s, 5H), 8.02 (d, $J = 8.1$ Hz, 2H). HPLC-separation conditions: Chiralcel AD, 20 $^{\circ}C$, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{major} = 30.6$ min, $t_{minor} = 32.2$ min.

***trans*-(2*S*, 3*R*)-Epoxy-3-phenyl-1-(4-chlorophenyl)-propan-1-one **2c**:^{3c}**

Yield: 80%; $[\alpha]_D^{27.6} = 150.4$ (c 0.40, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$) δ 4.08 (d, $J = 1.8$ Hz, 1H), 4.25 (d, $J = 1.5$ Hz, 1H), 7.37-7.49 (m, 7H), 7.96-7.99 (m, 2H). HPLC-separation conditions: Chiralcel OJ, 20 $^{\circ}C$, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{minor} = 17.4$ min, $t_{major} = 22.0$ min.

***trans*-(2*S*, 3*R*)-Epoxy-3-phenyl-1-(4-fluorophenyl)-propan-1-one **2d**:^{3c}**

Yield: 82%; $[\alpha]_D^{24.2} = 114.5$ (c 0.60, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$) δ 4.01 (s, 1H), 4.17 (s, 1H), 7.10 (t, $J = 8.4$ Hz, 2H), 7.33 (s, 5H), 7.80 (t, $J = 6.4$ Hz, 2H). HPLC-separation conditions: Chiralcel AD, 20 $^{\circ}C$, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{minor} = 29.9$ min, $t_{major} = 36.3$ min.

***trans*-(2*S*, 3*R*)-Epoxy-3-phenyl-1-(4-nitrophenyl)-propan-1-one **2e**:^{3a}**

Yield: 86%; $[\alpha]_D^{27.7} = 136.8$ (c 0.25, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$) δ 4.11 (d, $J =$

1.5 Hz, 1H), 4.28 (d, $J = 2.1$ Hz, 1H), 7.36-7.45 (m, 5H), 8.20 (dd, $J = 8.7, 2.1$ Hz, 2H), 8.36 (dd, $J = 8.7, 1.8$ Hz, 2H). HPLC-separation conditions: Chiralcel OD-H, 20 °C, 254 nm, 40/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{major}} = 51.8$ min, $t_{\text{minor}} = 67.2$ min.

***trans*-(2*S*, 3*R*)-Epoxy-3-(4-methylphenyl)-1-phenyl-propan-1-one 2f:^{3d}**

Yield: 72%; $[\alpha]_{\text{D}}^{25.2} = 209.4$ (c 0.80, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 4.04 (d, $J = 1.6$ Hz, 1H), 4.31 (d, $J = 1.7$ Hz, 1H), 7.21-7.29 (m, 4H), 7.49 (t, $J = 7.5$ Hz, 2H), 7.63 (t, $J = 7.8$ Hz, 1H), 8.00 (dd, $J = 8.1, 1.2$ Hz, 2H). HPLC-separation conditions: Chiralcel OD, 20 °C, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{major}} = 12.5$ min, $t_{\text{minor}} = 13.8$ min.

***trans*-(2*S*, 3*R*)-Epoxy-3-(4-chlorophenyl)-1-phenyl-propan-1-one 2g:^{3c}**

Yield: 76%; $[\alpha]_{\text{D}}^{24.6} = 184.1$ (c 0.30, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 4.07 (s, 1H), 4.27 (s, 1H), 7.26-7.38 (m, 4H), 7.51-7.53 (m, 2H), 7.65 (t, $J = 7.8$ Hz, 1H), 8.01 (dd, $J = 7.8, 1.2$ Hz, 2H). HPLC-separation conditions: Chiralcel OD, 20 °C, 254 nm, 55/1 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{major}} = 40.5$ min, $t_{\text{minor}} = 43.0$ min.

***trans*-(2*S*, 3*R*)-Epoxy-3-(4-nitrophenyl)-1-phenyl-propan-1-one 2h:^{3c}**

Yield: 90%; $[\alpha]_{\text{D}}^{27.6} = 104.1$ (c 0.15, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 4.21 (s, 1H), 4.29 (s, 1H), 7.50-7.66 (m, 5H), 8.02 (d, $J = 7.8$ Hz, 2H); 8.28 (d, $J = 8.1$ Hz, 1H). HPLC-separation conditions: Chiralcel AD, 20 °C, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{major}} = 44.5$ min, $t_{\text{minor}} = 56.7$ min.

***trans*-(2*S*, 3*R*)-Epoxy-3-(4-chlorophenyl)-1-(4-methoxyphenyl)-propan-1-one 2i:^{3c}**

Yield: 66%; $[\alpha]_{\text{D}}^{27.7} = 117.4$ (c 0.10, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 3.88 (s, 3H), 4.05 (s, 1H), 4.21 (s, 1H), 6.96 (d, $J = 8.7$ Hz, 2H); 7.29-7.39 (m, 4H), 8.00 (d, $J = 7.8$ Hz, 2H). HPLC-separation conditions: Chiralcel AD, 20 °C, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{major}} = 43.4$ min, $t_{\text{minor}} = 56.8$ min.

***trans*-(2*S*, 3*R*)-Epoxy-3-(4-methylphenyl)-1-(4-chlorophenyl)-propan-1-one 2j:⁴**

Yield: 70%; $[\alpha]_{\text{D}}^{25.6} = 180.5$ (c 0.50, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 2.37 (s, 3H), 4.04 (d, $J = 1.8$ Hz, 1H), 4.24 (d, $J = 2.1$ Hz, 1H), 7.21-7.27 (m, 4H), 7.46 (dd, $J = 7.0, 1.8$ Hz, 2H), 7.96 (dd, $J = 6.6, 2.1$ Hz, 2H). HPLC-separation conditions: Chiralcel OD, 20 °C, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{minor}} = 14.4$ min, $t_{\text{major}} = 15.7$ min.

***trans*-(3*S*, 4*R*)-Epoxy-4-phenyl-butan-2-one 2k:^{3c}**

Yield: 49%; $[\alpha]_{\text{D}}^{27.7} = 105.2$ (c 0.60, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 2.18 (s, 3H),

3.44 (s, 1H), 3.93 (s, 1H), 7.22-7.41 (m, 5H). HPLC-separation conditions: Chiralcel AD, 20 °C, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{major}} = 13.5$ min, $t_{\text{minor}} = 14.9$ min.

***trans*-(2*S*, 3*R*)-Epoxy-3-phenyl-1-furan-2-yl-propan-1-one 2m:**^{3b}

Yield: 78%; $[\alpha]_{\text{D}}^{27.7} = 112.4$ (*c* 0.25, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 4.15 (d, *J* = 1.8 Hz, 2H), 6.6 (dd, *J* = 3.6 Hz, 1H), 7.35-7.41 (m, 5H), 7.46 (d, 1H), 7.68 (dd, *J* = 1.8 Hz, 1H). HPLC-separation conditions: Chiralcel AD, 20 °C, 254nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{major}} = 16.5$ min, $t_{\text{minor}} = 18.2$ min.

***trans*-(3*S*, 4*R*)-Epoxy-nonan-2-one 2n:**^{3e}

Yield: 61%; $[\alpha]_{\text{D}}^{20.5} = 56.2$ (*c* 0.50, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 0.83 (m, 3H), 1.21-1.46 (m, 8H), 1.99 (s, 3H), 3.00 (t, *J* = 5.7 Hz, 1H), 3.11 (s, 1H). HPLC-separation conditions: Chiralcel AD, 20 °C, 280nm, 100/1 hexane/*i*-PrOH, 0.4 mL/min; $t_{\text{major}} = 18.6$ min, $t_{\text{minor}} = 22.6$ min.

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HPLC-separation conditions of **2a**: Chiralcel OD, 20 °C, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; t_{major} = 15.8 min, t_{minor} = 16.9 min.

Peak Results

	Name	RT	Area	% Area	Amount	Height	% Height	Units
1		15.794	321812	97.10		13372	96.93	
2		16.876	9614	2.90		424	3.07

Peak Results

	Name	RT	Area	% Area	Amount	Height	% Height	Units
1		14.191	4989262	50.21		216176	51.98	
2		15.167	4948258	49.79		199719	48.02	

HPLC-separation conditions of **2b**: Chiralcel AD, 20 °C, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{major}} = 30.6$ min, $t_{\text{minor}} = 32.2$ min

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	30.587	4754075	98.34		105306	97.71	
2	32.150	80112	1.66		2472	2.29

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	38.781	7203627	49.96		137691	51.57	
2	41.147	7214473	50.04		129321	48.43	

HPLC-separation conditions of **2c**: Chiralcel OJ, 20 °C, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{minor}} = 17.4$ min, $t_{\text{major}} = 22.0$ min.

HPLC-separation conditions of **2d**: Chiralcel AD, 20 °C, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{minor}} = 29.9$ min, $t_{\text{major}} = 36.3$ min.

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	29.924	94787	5.54		1669	7.11	
2	36.305	1616946	94.46		21790	92.89

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	25.428	159518130	47.65		3310297	50.90	
2	31.522	175280224	52.35		3192626	49.10	

HPLC-separation conditions of **2e**: Chiralcel OD-H, 20 °C, 254 nm, 40/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{major}} = 51.8$ min, $t_{\text{minor}} = 67.2$ min.

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	56.423	20325450	50.68		196533	57.64	
2	70.281	19778806	49.32		144426	42.36	

HPLC-separation conditions of **2f**: Chiralcel OD, 20 °C, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{major}} = 12.5$ min, $t_{\text{minor}} = 13.8$ min.

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	12.545	660071	97.06		43952	96.95	
2	13.777	26145	2.92		1384	3.05

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	12.529	722509	56.94		36662	59.23	
2	13.658	546341	43.06		25238	40.77	

HPLC-separation conditions of **2g**: Chiralcel OD, 20 °C, 254 nm, 55/1 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{major}} = 40.5$ min, $t_{\text{minor}} = 43.0$ min.

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	40.485	21928671	98.02		332296	97.12	
2	42.967	442744	1.98		9843	2.88

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	31.560	14402915	50.77		194595	54.87	
2	34.073	13963449	49.23		160022	45.13	

HPLC-separation conditions of **2h**: Chiralcel AD, 20 °C, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{major}} = 44.5$ min, $t_{\text{minor}} = 56.7$ min.

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	44.478	4736338	96.98		65739	97.14	
2	56.745	147596	3.02		1938	2.86

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	43.820	31820603	51.24		417886	55.04	
2	55.798	30275374	48.76		341316	44.96	

HPLC-separation conditions of **2i**: Chiralcel AD, 20 °C, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{major}} = 43.4$ min, $t_{\text{minor}} = 56.8$ min.

Peak Results

	Name	RT	Area	% Area	Amount	Height	% Height	Units
1		43.409	24256186	97.06		381065	97.43	
2		56.780	734736	2.94		10043	2.57

Peak Results

	Name	RT	Area	% Area	Amount	Height	% Height	Units
1		35.741	2692442	49.12		51792	58.15	
2		46.884	2789434	50.88		40441	43.85	

HPLC-separation conditions of **2j**: Chiralcel OD, 20 °C, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{minor}} = 14.4$ min, $t_{\text{major}} = 15.7$ min.

Peak Results							
Name	RT	Area	% Area	Amount	Height	% Height	Units
1	14.373	621227	3.95		27400	4.65	
2	15.738	15122637	96.05		561718	95.35

Peak Results							
Name	RT	Area	% Area	Amount	Height	% Height	Units
1	14.313	27067114	51.48		1051007	53.64	
2	15.767	25499057	48.51		908503	46.36	

HPLC-separation conditions of **2k**: Chiralcel AD, 20 °C, 254 nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; $t_{\text{major}} = 13.5$ min, $t_{\text{minor}} = 14.9$ min.

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	13.492	69816316	97.02		2722364	96.68	
2	14.925	2145702	2.98		93394	3.32

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	13.760	97521909	46.30		3223537	50.37	
2	15.038	113110273	53.70		3175720	49.63	

HPLC-separation conditions of **2m**: Chiralcel AD, 20 °C, 254nm, 90/10 hexane/*i*-PrOH, 1.00 mL/min; t_{major} =16.5 min, t_{minor} =18.2 min.

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	16.540	14887917	97.66		531201	97.18	
2	18.184	351188	2.34		15406	2.82

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	12.565	1136112	49.19		61252	50.82	
2	13.480	1173529	50.81		59270	49.18	

HPLC-separation conditions of **2n**: Chiralcel AD, 20 °C, 280nm, 100/1 hexane/*i*-PrOH, 0.40 mL/min; t_{major} =18.6 min, t_{minor} =22.6 min.

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	18.811	10741329	85.78		304790	87.13	
2	22.640	1780079	14.22		45031	12.87

Peak Results

Name	RT	Area	% Area	Amount	Height	% Height	Units
1	17.536	65824141	49.12		1575081	52.02	
2	21.070	68171950	50.88		1452580	47.98	

^1H NMR of **9** in CDCl_3

^1H NMR of **10a** in CDCl_3

^1H NMR of **10b** in CDCl_3

^1H NMR of **8a** in CDCl_3

^1H NMR of **8b** in CDCl_3

^1H NMR of **8c** in CDCl_3

[illegible]

¹H NMR spectrum (400 MHz, CDCl₃) of (S)-1-((S)-1-phenyl-2-oxiranyl)-2-phenylethan-1-one. The spectrum shows peaks at 8.01 (d, 2H), 7.00 (m, 2H), 6.94 (m, 2H), 6.83 (m, 2H), 6.74 (m, 2H), 6.64 (m, 2H), 6.54 (m, 2H), 4.23 (d, 2H), and 4.01 (d, 2H). The chemical structure of the compound is shown above the spectrum.

^1H NMR of **2b** in CDCl_3

^1H NMR of **2c** in CDCl_3

^1H NMR of **2d** in CDCl_3

^1H NMR of **2e** in CDCl_3

^1H NMR of **2f** in CDCl_3

^1H NMR of **2g** in CDCl_3

^1H NMR of **2h** in CDCl_3

^1H NMR of **2i** in CDCl_3

^1H NMR of **2j** in CDCl_3

^1H NMR of **2k** in CDCl_3

^1H NMR of **2m** in CDCl_3

^1H NMR of **2n** in CDCl_3