Supporting Information

A highly diastereoselective formation of 1,2,3-trisubstituted cyclopropane derivatives

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Materials and Methods. Reactions were carried out in oven glassware under an argon atmosphere, unless otherwise noted. All solvents were reagent grade. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone under argon. *n*-Butyl lithium was prepared from *n*-Butyl bromide. Except as indicated otherwise, reactions were magnetically stirred and monitored by thin layer chromatography (TLC) with 0.25 mm prepared by ourselves. Flash chromatography was performed with silica gel 60 (particle size 0.040-0.062 mm) supplied by Qingdao Ocean Chemical Plant. Yields refer to chromatographically pure compounds, unless otherwise stated. Melting points were determined with a digital Koffler apparatus and were uncorrected. Microanalysis were performed with a Perkin-Elmer 240C instrument. Infrared spectra were reported on a Nicolet Nexus 670 FT/IR spectrometer. ¹H NMR spectra were recorded on a Bruker AM-400 spectrometer. ¹³C NMR spectra were recorded on a Bruker AM-400 spectrometer. Chemical shifts are reported relative to chloroform (7.26) for ¹H NMR and chloroform(77.0) for ¹³C NMR. Chiral analysis was performed on Varian Dynamax SD-300 using chiralcel column CDMPC (150×4.6 mm D). Mass spectra were measured on either a HP-5988A or Bruker Daltonics APEX spectrometer. Optical rotations were determined on a JASCO J-20C polarimeter with 0.2 dm tube.

Representative Procedures for preparation of racemic epoxides 1a-1g:

The racemic epoxides 1a-1g were prepared via *m*-CPBA epoxidation, Swern oxidation and Wittig olefination sequences.

A mixture of allyl alcohol **4a** (20 mmol), *m*-CPBA(22 mmol) and NaHCO₃ (30 mmol) in CH₂Cl₂ (50 mL) was stirred at room temperature for 2 h. Then it was purified by column chromatography on silica gel and the epoxide alcohol **5a** was obtained in 95% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.10-7.37 (m, 5H), 3.81(d, *J* = 3.6Hz, 1H), 3.73 (dd, *J* = 3.3, 1.7Hz, 1H), 3.54 (dd, *J* = 3.3, 1.7Hz, 1H), 3.12 (m, 1H), 1.91 (br, 1H).

To a solution of DMSO (22 mmol) in CH₂Cl₂ (50 mL) was added oxalyl chloride (11 mmol) at -78 °C. After 20 min, a solution of **5a** (10 mmol) in CH₂Cl₂ (15 mL) was added, and the resulting mixture was stirred for 90 min at -78 °C before addition of Et₃N (40 mmol). After an additional 30 min at -78 °C, the mixture was warmed to room temperature, poured into H₂O, and diluted with Et₂O (30 mL). The organic phase was washed with H₂O (20 mL) and brine (20 mL), dried (MgSO₄), and concentrated to give the crude epoxy aldehyde which was taken on directly to the next step.

To a slurry of (benzyl)triphenylphosphonium bromide (12 mmol) in toluene (30 mL) was added KHMDS (5.5 mL, 11 mmol, 2 M in THF) at -20 °C. The mixture was stirred at room temperature for 1 h and then cooled to -20 °C. A solution of the crude epoxy aldehyde in THF (10 mL) was added. After 20 min, the mixture was taken to room temperature and stirred for an additional 20 min. The mixture was poured into brine (20 mL) and the water phase extracted with Et₂O (3X15 mL). The combined organic phases were washed with H₂O (20 mL) and brine (20 mL), dried (MgSO₄), and concentrated. Then it was purified by column chromatography and the product **1a** was obtained in 70% yield (in 2 steps). ¹H NMR (300 MHz, CDCl₃) δ 7.41-7.20 (m, 10H), 6.81 (d, *J* = 15.9 Hz, 1H), 6.09 (dd, *J* = 15.9, 7.5 Hz, 1H), 3.89 (d, *J* = 2.1 Hz, 1H), 3.53 (dd, *J* = 7.5, 2.1 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 137.0, 136.0, 134.4, 128.7, 128.5, 128.2, 128.1, 126.5, 126.2, 125.5, 63.12, 60.70. Anal. Calcd for C₁₆H₁₄O: C, 86.45; H, 6.34. Found: C, 86.43; H, 6.55.

1b-1g were prepared via the same sequences starting from the corresponding allyl alcohols.

Preparation of epoxide **1a'**:

The epoxide **1a'** (optically pure **1a**) was prepared according to Shi's method starting from (*trans, trans*)-1, 4-diphenyl-1, 3-butadiene.

To a 100 mL three-necked flask were added buffer (0.05 M Na₂B₂O₄·10 H₂O in 4X10⁻⁴ M EDTA, 10 mL), dimethoxymethane/acetonitrile (2:1, 15 mL), *trans, trans*-1,4-diphenyl- 1,3-butadiene (0.206 g, 1 mmol), tetrabutylammonium hydrogen sulfate (0.015 g, 0.04 mmol), and ketone **7** (0.065 g, 0.25 mmol). The reaction mixture was cooled to 0 °C with an ice bath. A solution of Oxone (0.69 g, 1.13 mmol) in aqueous EDTA (4X10⁻⁴ M, 6.0 mL) and a solution of K₂CO₃ (0.69 g, 4.99 mmol) in water (6.0 mL) were added separately via syringe pump over 1.5 h. The reaction was immediately quenched by the addition of hexanes (15 mL). The aqueous layer was extracted with hexanes (3X25 mL), washed with brine (50 mL), dried (Na₂SO₄), filtered, concentrated, and purified by flash chromatography (the silica gel was buffered with 1% Et₃N in hexane; 1% Et₃N in 3:1 CH₂Cl₂/hexane was used as the eluent) to afford (*R,R*)-2-phenyl-3-(*trans*-2-phenylvinyl) oxirane as a white solid (0.171 g, 77% yield). [α]_D²⁷, +252.2° (*c* 0.24, CHCl₃), 97% ee). The ee value was determined by HPLC analysis

(chiralcel OD column, IPA:hexane = 10:90, rate: 0.8 mL/min, 254 nm). ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.20 (m, 10H), 6.81 (d, J = 15.9 Hz, 1H), 6.09 (dd, J = 15.9, 7.5 Hz, 1H), 3.89 (d, J = 2.1 Hz, 1H), 3.53 (dd, J = 7.5, 2.1 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.0, 136.0, 134.4, 128.7, 128.5, 128.2, 128.1, 126.5, 126.2, 125.5, 63.12, 60.70. Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}$: C, 86.45; H, 6.34. Found: C, 86.43; H, 6.55.

Representative Procedure for Reaction of (-)-(2R, 3R)-2-phenyl-3-(trans-phenylvinyl oxirane(1a') with nucleophilic reagents (2):

A solution of the dithiane (1 mmol) and HMPA (0.30 mL, 1.65 mmol) in anhydrous THF (3 mL) was cooled to $-50\text{ }^\circ\text{C}$. *n*-BuLi (2.5 M in petroleum ether, 0.8 mmol) was added dropwise via syringe, and the reaction mixture allowed to warm to $-20\text{ }^\circ\text{C}$ while stirring for 0.5 h. The mixture was re-cooled to $-50\text{ }^\circ\text{C}$ and a solution of the (-)-(2R, 3R)-2-phenyl-3-(trans-phenylvinyl oxirane(0.50 mmol) in anhydrous THF (3 mL) was added dropwise via syringe. The mixture was warmed to $-20\text{ }^\circ\text{C}$ over 1 h. After stirring an additional 19 h the reaction was quenched with saturated aqueous NH_4Cl (6 mL) and then diluted with Et_2O (20 mL). The organic layers were separated, the aqueous phase extracted with Et_2O (3X5 mL), and the combined organic layers dried over anhydrous Na_2SO_4 , filtered and concentrated. Flash chromatography (petroleum ether /ethyl acetate as eluent) provided cyclopropane derivatives as either colorless oil or white solid (see Tables 2 for yields).

White crystal, mp = $120\text{-}121\text{ }^\circ\text{C}$. 98:2 dr determined by HPLC analysis (chiralcel OD column, IPA:hexane = 5:95, rate: 1mL/min, 254 nm). Retention time: $t_{\text{R}}(\text{major})$ = 13.48 and $t_{\text{R}}(\text{minor})$ = 15.87 min. $[\alpha]_{\text{D}}^{27}$, $+63^\circ$, (c, 0.9, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, J = 7.2 Hz, 2H), 7.30-7.11(m, 6H), 6.96(d, J = 7.2 Hz, 2H), 5.48 (d, J = 9.6 Hz, 1H), 4.17(s, 1H), 3.13 (ddd, J = 15.2, 11.6, 2.8 Hz, 1H), 3.01(ddd, J = 15.2, 11.6, 2.8 Hz, 1H), 2.78-2.70(m, 2H), 2.55 (dq, J = 14.4, 7.2 Hz, 1H), 2.49(t, J = 6.4 Hz, 1H), 2.21-2.15(m, 1H), 2.07(dq, J = 14.4, 7.2 Hz, 1H), 1.99-1.92(m, 1H), 1.74(ddd, J = 9.6, 8.8, 6.4 Hz, 1H), 1.54(dd, J = 8.8, 6.4 Hz, 1H), 1.01(t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.8, 140.6, 128.4, 128.2, 126.9, 126.1, 126.0, 125.7, 72.3, 53.7, 36.9, 35.7, 34.6, 27.3, 26.1, 25.8, 25.5, 10.4. IR (vcm^{-1}): 3412, 2924, 2854, 1495, 1457, 1119, 1034, 751, 696. MS (%); 370 (M^+ , 0.16), 295 (0.14), 279 (0.85), 263 (13.31), 189 (19.96), 173 (8.01), 160 (100.00), 147 (11.62), 129 (20.81), 121 (16.82), 115 (21.00), 107 (23.86), 105 (22.17), 91(24.48), 77 (33.55). HRMS(ESI) Calc. for $\text{C}_{22}\text{H}_{25}\text{S}_2$ ($\text{M}^+ - \text{H}_2\text{O} + \text{H}$): 353.1392. Found: 353.1394. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{OS}_2$: C, 71.30; H, 7.07; Found: C, 71.30; H, 6.95.

3b

White crystal, Mp = 130-132 °C. ^1H NMR (300 MHz, CDCl_3) δ 7.40(d, J = 9.0Hz, 2H), 7.30-7.21(m, 5H), 6.96(d, J = 9.0Hz, 2H), 5.47(d, J = 9.9Hz, 1H), 3.17(ddd, J = 15.0, 11.6, 2.4Hz, 1H), 3.01(ddd, J = 15.0, 11.6, 2.4Hz), 2.76-2.58(m, 2H), 2.55(dq, J = 14.7, 7.5Hz, 1H), 2.46(t, J = 6.3Hz, 1H), 2.15-2.08(m, 1H), 2.08(dq, J = 14.7, 7.5Hz, 1H), 1.94-1.89(m, 1H), 1.70(ddd, J = 9.6, 8.7, 6.3Hz, 1H), 1.55(dd, J = 8.7, 6.3Hz, 1H), 0.96(t, J = 7.5Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 142.3, 140.2, 128.5, 128.3, 127.1, 126.1, 125.9, 71.7, 53.5, 36.9, 35.4, 34.6, 27.2, 26.9, 25.7, 25.4, 10.4. HRMS(ESI) Calc. for $\text{C}_{22}\text{H}_{24}\text{S}_2\text{Cl}$ ($\text{M}^+ - \text{H}_2\text{O} + \text{H}$): 387.5843. Found: 387.5841.

3c

White crystal, Mp = 130-131 °C. ^1H NMR (300 MHz, CDCl_3) δ 7.38(d, J = 9.0Hz, 2H), 7.30-7.21(m, 5H), 6.90(d, J = 9.0Hz, 2H), 5.39(d, J = 9.9Hz, 1H), 3.17(ddd, J = 15.3, 11.6, 2.4Hz, 1H), 3.01(ddd, J = 15.3, 11.6, 2.4Hz), 2.76-2.56(m, 2H), 2.55(dq, J = 14.7, 7.5Hz, 1H), 2.48(t, J = 6.3Hz, 1H), 2.15-2.08(m, 1H), 2.08(dq, J = 14.7, 7.5Hz, 1H), 1.92-1.89(m, 1H), 1.70(ddd, J = 9.6, 8.7, 6.3Hz, 1H), 1.55(dd, J = 8.7, 6.3Hz, 1H), 0.95(t, J = 7.5Hz, 3H). ^{13}C -NMR (75 MHz, CDCl_3) δ 142.1, 140.2, 128.5, 128.5, 127.1, 126.1, 126.0, 71.7, 53.5, 36.8, 35.4, 34.6, 27.2, 27.0, 25.7, 25.4, 10.3. HRMS(ESI) Calc. for $\text{C}_{22}\text{H}_{24}\text{S}_2\text{Cl}$ ($\text{M}^+ - \text{H}_2\text{O} + \text{H}$): 387.5843. Found: 387.5846.

3d

White crystal, Mp = 143-144 °C. ^1H NMR (300 MHz, CDCl_3) δ 7.38(d, J = 8.1Hz, 2H), 7.25(d, J = 8.4Hz, 2H), 7.18(d, J = 8.4Hz, 2H), 6.78(d, J = 8.1Hz, 2H), 5.54(d, J = 9.9Hz, 1H), 4.19(s, 1H), 3.08(ddd, J = 15.2, 11.6, 2.8Hz, 1H), 2.96(ddd, J = 15.2, 11.6, 2.8Hz, 1H), 2.76-2.68(m, 2H), 2.52(dq, J = 14.4, 7.2Hz, 1H), 1.93-1.89(m, 1H), 1.63(ddd, J = 9.6, 8.8, 6.3Hz, 1H), 1.50(dd, J = 8.8, 6.3Hz), 0.96(t, J = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 142.2, 138.8, 128.6, 128.3, 127.2, 127.0, 71.5, 53.4, 37.2, 35.7, 34.6, 27.2, 26.0, 25.4, 25.1, 10.4. HRMS(ESI) Calc. for $\text{C}_{22}\text{H}_{23}\text{S}_2\text{Cl}_2$ ($\text{M}^+ - \text{H}_2\text{O} + \text{H}$): 422.0294. Found: 422.0291.

3e

White crystal, Mp = 124-125 °C. ^1H NMR (300 MHz, CDCl_3) δ 7.35(d, J = 7.5Hz, 2H), 7.25-7.10(m, 5H), 6.97(d, J = 7.5Hz, 2H), 5.44(d, J = 10.2Hz, 1H), 4.12(s, 1H), 3.12(ddd, J = 15.6, 11.2, 2.1Hz, 1H), 3.00(ddd, J = 15.6, 11.2, 2.1Hz, 1H), 2.78-2.71(m, 2H), 2.52(dq, J = 14.2, 7.2Hz, 1H), 2.46(t, J = 6Hz, 1H), 2.29(s, 3H), 2.21-2.14(m, 1H), 2.06(dq, J = 14.2, 7.2Hz, 1H), 1.75(ddd, J = 9.9, 8.6, 6.6Hz, 1H), 1.53(dd, J = 8.6, 6.6Hz, 1H), 0.96(t, J = 7.2Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 140.6, 128.8, 128.4, 126.1, 125.6, 72.1, 53.6, 37.0, 35.6, 34.6, 27.2, 26.1, 25.8, 25.4, 21.0, 10.4. HRMS(ESI) Calc. for $\text{C}_{23}\text{H}_{26}\text{S}_2(\text{M}^+ - \text{H}_2\text{O} + \text{H})$: 367.1660. Found: 367.1663.

3f

White crystal, mp = 82-83 °C. 99:1 dr determined by HPLC analysis (chiralcel OD column, IPA:hexane = 5:95, rate: 1mL/min, 254 nm). Retention time: $t_{\text{R}}(\text{minor})$ = 14.75 and $t_{\text{R}}(\text{major})$ = 23.68 min. $[\alpha]_{\text{D}}^{19}$, +39°, (c, 1.0, CHCl_3), ^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, J = 8.0Hz, 2H), 7.35-7.12(m, 6H), 6.99 (d, J = 8.0Hz, 2H), 5.22 (d, J = 10.0 Hz, 1H), 3.81(s, 1H), 3.12-3.05 (m, 2H), 2.97-2.86 (m, 2H), 2.61(t, J = 6.4 Hz, 1H), 2.17-2.11(m, 1H), 2.02(s, 3H), 2.04-1.97(m, 1H), 1.91(dd, J = 8.8, 6.4Hz, 1H), 1.78(ddd, J = 10.0, 8.8, 6.4Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 140.7, 128.4, 128.3, 127.2, 127.2, 126.9, 125.7, 72.9, 48.8, 37.8, 37.0, 30.0, 27.4, 26.8, 26.1, 25.3. IR (vcm^{-1}) 3438, 2929, 1599, 1495, 1450, 1121, 1040. MS (%): 356 (M^+ , 0.19), 281(0.50), 265(1.39), 249(26.53), 175(32.04), 159(13.93), 146(100.00), 141(13.15), 133(11.21), 128(44.89), 121(2.40), 115(24.99), 107(29.70), 105(23.39), 91(32.61), 77(71.80). Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{OS}_2$: C, 70.74; H, 6.78; Found: C, 70.74; H, 6.65.

3g

Colorless oil. 96:4 dr determined by HPLC analysis (chiralcel OD column, IPA:hexane = 5:95, rate: 1mL/min, 254 nm). Retention time: $t_{\text{R}}(\text{minor})$ = 5.04 and $t_{\text{R}}(\text{major})$ = 7.56 min. $[\alpha]_{\text{D}}^{19}$, +31°, (c, 1.0, CHCl_3), ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.14(m, 10H), 6.00(d, J = 10.0 Hz, 1H), 4.63(d, J = 5.1 Hz, 1H), 3.39-3.32(m, 1H), 2.80(dd, J = 13.5, 5.4Hz, 1H), 2.72-2.67(m, 2H), 2.55(dd, J = 13.5, 9.3Hz, 1H), 2.48-2.42(m, 2H), 2.03-1.97(m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 140.5, 128.5, 128.2, 127.2, 127.1, 126.8, 125.7, 72.1, 49.1, 37.6, 37.1, 27.4, 26.7, 26.2, 25.4. IR (vcm^{-1}): 3420, 2966, 2927, 2903, 1598, 1492, 1451, 1388, 1273, 1189, 1125, 1038. MS (%): 342(M^+ , 0.78), 251(1.80),

235(100.00), 119((13.73), 115(19.61), 107(18.21), 106(19.61), 91(29.64), 77(23.80).
 Anal. Calcd for C₂₀H₂₂OS₂: C, 70.13; H, 6.47. Found: C, 70.05; H, 6.52.

White crystal, mp = 132-133 °C. 95:5 dr determined by HPLC analysis (chiralcel OD column, IPA:hexane = 5:95, rate: 1mL/min, 254 nm). Retention time: t_R (minor) = 7.31 and t_R (major) = 15.34 min. $[\alpha]_D^{19}$, +64°, (c, 1.0, CHCl₃), ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, J = 7.6Hz, 2H), 7.31-7.11(m, 6H), 6.95(d, J = 7.6Hz, 2H), 5.48 ((d, J = 9.6 Hz, 1H), 4.17(s, 1H), 3.13 (ddd, J = 14.4, 14.4, 2.4Hz, 1H), 3.06 (ddd, J = 14.4, 14.4, 2.4Hz, 1H), 2.78-2.72(m, 2H), 2.49(t, J = 6.4 Hz, 1H), 2.44(ddd, J = 16.4, 14.0, 4.4Hz, 1H), 2.17(m, 1H), 2.02(ddd, J = 16.4, 14.0, 4.4Hz, 1H), 2.05-1.93(m, 1H), 1.73(ddd, J = 9.6, 8.8, 6.4Hz, 1H), 1.61(dd, J = 8.8, 6.4Hz, 1H), 1.57-1.52(m, 1H), 1.43-1.36(m, 1H), 0.90(t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.8, 140.6, 128.4, 128.2, 127.0, 126.2, 126.0, 125.7, 72.3, 53.1, 44.1, 37.1, 35.9, 27.3, 26.2, 25.9, 25.5, 19.1, 14.2. IR (vcm⁻¹): 3414, 2951, 2911, 1600, 1495, 1451, 1197, 1113, 1031. MS (%): 384(M⁺, 0.45), 309(0.27), 301(1.49), 293(1.05), 277(17.35), 203(17.07), 187(6.51), 174(100.00), 161(57.10), 141(11.42), 133(7.75), 129(26.58), 117(32.02), 115(25.23), 107(41.23), 105(58.29), 91(88.59), 77 (48.01). Anal. Calcd for C₂₃H₂₈OS₂: C, 71.83; H, 7.34; Found: C, 71.92; H, 7.31.

White crystal, mp = 164-165 °C. 99:1 dr determined by HPLC analysis (chiralcel OD column, IPA:hexane = 5:95, rate: 1mL/min, 254 nm). Retention time: t_R (minor) = 13.54 and t_R (major) = 15.10 min. $[\alpha]_D^{19}$, +89°, (c, 1.0, CHCl₃), ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, J = 8.0Hz, 2H), 7.29-7.11(m, 6H), 6.96 (d, J = 8.0Hz, 2H), 5.57 (d, J = 10.0 Hz, 1H), 4.32(s, 1H), 3.14-3.01 (m, 2H), 2.77-2.66 (m, 3H), 2.47(t, J = 6.0 Hz, 1H), 2.18-2.14 (m, 1H), 1.99-1.90 (m, 1H), 1.72 (ddd, J = 10.0, 9.6, 6.4Hz, 1H), 1.57(dd, J = 9.6, 6.4Hz, 1H), 1.17 (d, J = 6.8Hz, 3H), 1.07(d, J = 6.8Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.8, 140.5, 128.4, 128.2, 126.9, 125.9, 125.8, 125.7, 72.2, 57.7, 35.3, 34.2, 32.1, 26.9, 26.2, 26.1, 25.3, 19.0, 18.4. IR (vcm⁻¹): 3422, 2955, 2915, 1601, 1497, 1455, 1420, 1391, 1197, 1115, 1033. MS (%): 384 (M⁺, 0.43), 309 (0.33), 277(16.25), 235(9.94), 221(3.13), 203(8.82), 187(4.54), 174(100.00), 161(23.84), 147(7.25), 141(7.75), 115(27.07), 107(42.64), 105(31.87), 91(41.47), 79(82.44), 77(72.36). Anal. Calcd for C₂₃H₂₈OS₂: C, 71.83; H, 7.34; Found: C, 71.78; H, 7.35.

3j

White crystal, mp = 65-66 °C. 94:6 dr determined by HPLC analysis (chiralcel OD column, IPA:hexane = 5:95, rate: 1mL/min, 254 nm). Retention time: t_R (msjor) = 10.20 and t_R (minor) = 18.44 min. $[\alpha]_D^{19}$, +48°, (c, 1.0, CHCl₃), ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 7.2Hz, 2H), 7.31-7.11(m, 6H), 6.96 (d, J = 7.2Hz, 2H), 5.47 (d, J = 9.6 Hz, 1H), 4.14(s, 1H), 3.17-3.10(m, 1H), 3.06-2.99(m, 1H), 2.78-2.72(m, 2H), 2.51(t, J = 6.0 Hz, 1H), 2.48-2.44(m, 1H), 2.19-2.15(m, 1H), 2.05-1.89(m, 2H), 1.75(ddd, J = 9.6, 8.8, 6.0Hz, 1H), 1.57(dd, J = 8.8, 6.0Hz, 1H), 1.55-1.48(m, 1H), 1.42-1.24(m, 3H), 0.83(t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.8, 140.5, 138.5, 128.4, 128.2, 127.0, 126.2, 125.7, 72.3, 53.1, 41.5, 37.3, 35.7, 27.9, 27.3, 26.3, 25.9, 25.5, 22.7, 13.9. IR (y_{cm}⁻¹): 3417, 2954, 2900, 2865, 1598, 1497, 1453, 1420, 1387, 1270, 1195, 1116, 1032. MS (%): 398(M⁺, 0.15), 323(0.22), 307(0.30), 291(12.24), 235(0.84), 221(0.55), 217(10.72), 209(0.23), 205(0.58), 203(2.17), 201(3.95), 188(66.46), 175(4.76), 173(3.63), 165(3.17), 161(7.41), 147(4.69), 143(8.22), 141(12.92), 129(27.74), 115(33.83), 107(48.98), 105(33.25), 91(58.89), 79(100.00), 77(85.46). Anal. Calcd for C₂₄H₃₀OS₂: C, 72.31; H, 7.59; Found: C, 72.35; H, 7.38.

3k

White crystal, mp = 121-122 °C. 98:2 dr determined by HPLC analysis (chiralcel OD column, IPA:hexane = 5:95, rate: 1mL/min, 254 nm). Retention time: t_R (minor) = 6.27 and t_R (major) = 13.26 min. $[\alpha]_D^{19}$, +69°, (c, 1.0, CHCl₃), ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, J = 7.2Hz, 2H), 7.30-7.10(m, 6H), 6.96 (d, J = 7.2Hz, 2H), 5.51 (d, J = 9.6 Hz, 1H), 4.20(s, 1H), 3.12(ddd, J = 14.8, 12.8, 2.8Hz, 1H), 3.06(ddd, J = 4.8, 12.8, 2.8Hz, 1H), 2.80-2.75(m, 2H), 2.38(t, J = 6.4 Hz, 1H), 2.42(dd, J = 14.8, 4.4Hz, 1H), 2.20-2.14(m, 1H), 2.01(dd, J = 14.8, 4.4Hz, 1H), 1.97-1.89(m, 2H), 1.77(ddd, J = 9.6, 8.8, 6.4Hz, 1H), 1.66(dd, J = 8.8, 6.4Hz, 1H), 0.97(d, J = 6.8Hz, 3H), 0.78 (d, J = 6.8Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.8, 140.6, 128.4, 128.2, 126.9, 126.0, 125.9, 125.7, 72.3, 53.3, 50.2, 37.5, 36.0, 27.5, 26.6, 26.1, 25.8, 25.4, 24.8, 24.7. IR (y_{cm}⁻¹): 3410, 2967, 2930, 2901, 1600, 1493, 1452, 1424, 1391, 1322, 1274, 1195, 1115, 1033. MS (%): 398(M⁺, 0.33), 323(0.32), 307(0.86), 291(18.46), 249(0.98), 235(2.38), 221(1.45), 217(17.47), 209(1.38), 203(2.92), 201(5.46), 188(100.00), 175(3.97), 173(3.03), 165(2.58), 161(6.20), 147(4.44), 145(8.77), 143(7.42), 141(12.44), 129(22.02), 115(21.85), 107(31.73), 105(25.23), 79(59.14), 77(50.09). Anal. Calcd for C₂₄H₃₀OS₂: C, 72.31; H, 7.59; Found: C, 72.45; H, 7.50.

3l

Colorless oil. 93:7 dr determined by HPLC analysis (chiralcel OD column, IPA:hexane = 5:95, rate: 1mL/min, 254 nm). Retention time: $t_R(\text{minor}) = 10.45$ and $t_R(\text{major}) = 15.33$ min. $[\alpha]_D^{19}$, +27°, (c, 1.0, CHCl₃), ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, $J = 8.4$ Hz, 2H), 7.36-7.07(m, 6H), 6.89(d, $J = 8.4$ Hz, 2H), 6.04(d, $J = 9.6$ Hz, 1H), 4.61(d, $J = 10.0$ Hz, 1H), 2.96-2.84(m, 5H), 2.22-2.16(m, 2H), 2.00(m, 1H), 1.85(t, $J = 5.6$ Hz, 1H), 1.72(ddd, $J = 9.6, 8.8, 4.2$ Hz, 1H), 1.31(d, $J = 6.8$ Hz, 3H), 1.24(m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 144.3, 141.8, 139.8, 128.5, 128.2, 127.6, 126.5, 125.9, 125.6, 124.4, 74.3, 34.6, 34.4, 33.7, 30.5, 30.1, 27.0, 25.3, 20.8. IR (ycm⁻¹): 3347, 3024, 2924, 2854, 1708, 1682, 1601, 1457, 1375, 1278, 1154, 1068, 1018. MS (%): 382(M⁺, 2.45), 307(2.42), 291(0.25), 281(0.70), 275(24.25), 262(6.04), 250(1.68), 235(0.65), 221(11.94), 185(6.47), 159(100.00), 132(18.27), 119(23.62), 107(19.42), 105(71.73), 91(38.69), 85(40.81), 77(44.25). Anal. Calcd for C₂₃H₂₆OS₂: C, 72.21; H, 6.85; Found: C, 72.36; H, 6.97.

3m

Colorless oil. 85:15 dr determined by HPLC analysis (chiralcel OD column, IPA:hexane = 5:95, rate: 1mL/min, 254 nm). Retention time: $t_R(\text{major}) = 14.87$ and $t_R(\text{minor}) = 18.30$ min. $[\alpha]_D^{19}$, +32°, (c, 1.0, CHCl₃), ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, $J = 7.2$ Hz, 2H), 7.33-7.14(m, 6H), 6.93(d, $J = 7.2$ Hz, 2H), 6.15(d, $J = 9.6$ Hz, 1H), 4.68(m, 1H), 2.97-2.87(m, 4H), 2.45(m, 1H), 2.15(m, 3H), 1.61(m, 1H), 1.48(s, 3H), 1.42(s, 3H), 0.88(m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 144.5, 142.2, 140.0, 128.4, 128.1, 127.5, 127.3, 126.6, 125.8, 125.6, 73.8, 39.3, 37.5, 35.6, 30.8, 30.1, 29.8, 29.3, 25.7, 24.1. IR (ycm⁻¹): 3345, 3064, 3033, 2925, 2856, 1680, 1602, 1493, 1455, 1372, 1276, 1155, 1068, 1020. MS (%): 396(M⁺, 3.20), 381(0.38), 337(4.95), 321(1.41), 305(0.71), 296(4.65), 291(4.65), 289(9.18), 277(1.51), 269(4.67), 264(9.16), 247(15.07), 221(85.69), 186(48.65), 173(68.86), 158(57.40), 145(66.04), 132(21.99), 119(54.85), 115(42.72), 107(40.77), 106(100.00), 105(83.53), 91(87.22), 85(11.37), 77(67.48). Anal. Calcd for C₂₄H₂₈OS₂: C, 72.68; H, 7.12; Found: C, 72.56; H, 6.99.

3n

Colorless oil. 68:32 dr determined by ¹H NMR. $[\alpha]_D^{19}$, -25°, (c, 1.0, CHCl₃), ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.18(m, 6H), 7.09 (d, $J = 8.0$ Hz, 2H), 6.94(d, $J = 8.0$ Hz, 2H),

4.00(d, $J = 9.6\text{Hz}$, 1H), 1.99(dd, $J = 8.8, 5.6\text{Hz}$, 1H), 1.58 (br s, 1 H), 1.72-1.32(m, 2H), 1.31(d, $J = 6.0\text{Hz}$, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 138.3, 128.9, 128.1, 128.0, 127.3, 126.0, 125.9, 74.4, 33.39, 22.5, 22.1, 14.1. IR (vcm^{-1}): 3374, 2952, 2926, 2850, 1601, 1493, 1450, 1312, 1280, 1245, 1196, 1083, 1028. MS (%): 238(M^+ , 2.45), 223(0.55), 219(0.71), 209(1.11), 205(1.63), 191(1.55), 165(2.66), 150(3.49), 141(2.69), 132(20.34), 120(100.00), 117(30.55), 115(20.06), 107(50.23), 105(19.94), 91(48.25), 79(45.99), 77(45.85). Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{O}$: C, 85.67; H, 7.61; Found: C, 85.56; H, 7.68.

Colorless oil. 95:5 dr determined by HPLC analysis (chiralcel OD column, IPA:hexane = 5:95, rate: 1mL/min, 254 nm). Retention time: $t_R(\text{major}) = 10.20$ and $t_R(\text{minor}) = 18.44$ min. $[\alpha]_D^{19}$, -28° , (c, 1.0, CHCl_3), ^1H NMR (400 MHz, CDCl_3) δ 7.27-7.17(m, 6H), 7.10 (d, $J = 8.4\text{Hz}$, 2H), 6.95(d, $J = 8.4\text{Hz}$, 2H), 3.97(d, $J = 9.6\text{Hz}$, 1H), 2.02(dd, $J = 9.6, 5.6\text{Hz}$, 1H), 1.71 (br s, 1 H), 1.67-1.32(m 8H), 0.94(t, $J = 7.2\text{Hz}$, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 138.3, 128.9, 127.9, 127.3, 126.0, 125.9, 73.7, 34.6, 33.4, 31.7, 29.0, 22.5, 22.2, 14.1. IR (vcm^{-1}): 3376, 2956, 2924, 2854, 1602, 1496, 1453, 1274, 1194, 1080, 1023, MS (%): 280(M^+ , 0.03), 228(18.7), 223(0.25), 219(0.45), 209(1.77), 205(1.95), 193(1.26), 189(0.97), 174(8.49), 160(18.93), 120(100.00), 117(44.11), 115(16.73), 107(41.75), 105(25.99), 104(27.83), 91(42.70), 77(29.34). Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}$: C, 85.67; H, 8.63; Found: C, 85.52.

tang
 Archive directory: /export/home/panxf/vnmr/sy5/data
 Sample directory:
 File: PROTON
 Pulse Sequence: szpu1

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138.848

128.667
128.392
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77.000
76.573
71.566

53.403

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35.743
34.629

27.210
26.081
25.409
25.165

10.421

tang050303-H
 Archive directory: /export/home/sheueug/vnmr/sys/data
 Sample directory:
 File: PROTON
 Pulse Sequence: szpul1

3e

HPLC Conditions

Column: Chiralcel OD (Column No. OD00CE-IG151)
 Eluent: Hexane / IPA (95 / 5)
 Flow rate: 1.0ml / min
 Detection: UV 254 nm

Peak No.	Peak Name	Result	Ret. Time (min)	Area (counts)
1		0	4.3378	383660
2	3a	95.6622	5.044	8460851
Totals		100.0000	7.569	8844511

HPLC Conditions

Column: Chiralcel OD (Column No. OD00CE-JG151)

Eluent: Hexane / IPA (95 / 5)

Flow rate: 1.0ml / min

Detection: UV 254 nm

Peak No.	Peak Name	Result	Ret. Time (min)	Area (counts)
1		0.8377	14.754	57243
2	3b	99.1623	23.685	6776185
Totals		100.0000		6833428

HPLC Conditions

Column: Chiralcel OD (Column No. OD00CE-IG151)
 Eluent: Hexane / IPA (95 / 5)
 Flow rate: 1.0ml / min
 Detection: UV 254 nm

Peak No.	Peak Name	Result	Ret. Time (min)	Area (counts)
1	3c	98.0405	13.486	6180879
2		1.9595	15.876	123532
Totals		100.0000		6304411

HPLC Conditions

Column: Chiralcel OD (Column No. OD00CE-JG131)

DAICEL CHEMICAL INDUSTRIES, LTD.

Eluent: Hexane / IPA (95 / 5)

Flow rate: 1.0ml / min

Detection: UV 254 nm

Peak No.	Peak Name	Result	Ret. Time (min)	Area (counts)
1		5.2996	7.312	269542
2	3d	94.7004	15.344	4816536
Totals		100.0000		5086078

HPLC Conditions

Column: Chiralcel OD (Column No. OD00CE-JG151)

DAICEL CHEMICAL INDUSTRIES, LTD.

Eluent: Hexane / IPA (95 / 5)

Flow rate: 1.0ml / min

Detection: UV 254 nm

Peak No.	Peak Name	Result	Ret. Time (min)	Area (counts)
1	3e	0	15.104	18966666
Totals		100.0000		18966666

HPLC Conditions

Column: Chiralcel OD (Column No. OD00CE-JG151)

DAICEL CHEMICAL INDUSTRIES, LTD.

Eluent: Hexane / IPA (95 / 5)

Flow rate: 1.0ml / min

Detection: UV 254 nm

Peak No.	Peak Name	Result	Ret. Time (min)	Area (counts)
1		0.9354	7.315	172166
2	3f	99.0446	13.638	17848518
Totals		100.0000		18020684

HPLC Conditions

Column: Chiralcel OD (Column No. OD00CE-JG151)
 DAICEL CHEMICAL INDUSTRIES, LTD.
 Eluent: Hexane / IPA (95 / 5)
 Flow rate: 1.0ml / min
 Detection: UV 254 nm

Peak No.	Peak Name	Result (%)	Ret. Time (min)	Area (counts)
1	3i	94.9808	10.207	4523970
2		5.0192	18.441	239065
Totals		100.0000		4763035

HPLC Conditions

Column: Chiralcel OD (Column No. OD00CE-JG151)
 Eluent: Hexane / IPA (95 / 5)
 Flow rate: 1.0ml / min
 Detection: UV 254 nm

Peak No.	Peak Name	Result	Ret. Time (min)	Area (counts)
1		0	6.5180	1708448
2	4a	93.4820	10.457	24502696
Totals		100.0000	15.336	26211144

HPLC Conditions
 Column: Chiralcel OD (Column No. OD00CE-1015)
 Eluent: Hexane / IPA (95 / 5)
 Flow rate: 1.0ml / min
 Detection: UV 254 nm

Peak No.	Peak Name	Result	Ret. Time (min)	Area (counts)
1	4b	0	14.871	17803574
2		0	18.300	3165019
Totals		100.0000		20968593

HPLC Conditions
 Column: Chiral OD (Column No. OD00CE-G1031)
 Eluent: Hexane / IPA (95 / 5)
 Flow rate: 1.0ml / min
 Detection: UV 254 nm

Peak No.	Peak Name	Result	Ret. Time (min)	Area (counts)
1		1.7576	6.271	9134
2	3g	98.2424	13.262	510089
Totals		100.0000		519223