Supporting information：

1. Chem. 3D for catalyst (1-4):



**1**: [64.5943 kcal/mol] & **2**: [67.3417kcal/mol]



**3**: [62.4002 kcal/mol] & **4**: [62.0021kcal/mol]

 (**1** corresponds to Quinine, **2** corresponds to Quindine, **3** corresponds to Cinchonidine, **4** corresponds to Cinchonine)

1. Typical synthesis of catalyst **3**: To a solution of cinchonidine (0.735 g, 2.5mmol) in THF (15 ml) was added **5** (0.668 g, 2.5 mmol), and the mixture was stirred at room temperature for 8 hours. Then filtered and washed the solids with THF to afford 1.384 g desired product with light yellow color (98.72% yield). 1H-NMR(500MHz, CD3COCD3) δ: 9.02(d, *J*=4.3Hz, 1H), 8.61(d, *J*=8.35Hz, 1H), 8.22(d, *J*=8.15Hz, 2H), 8.13-8.11(m, 1H), 8.09(d, *J*=4.3Hz, 1H), 7.96(d, *J*=8.35Hz, 1H), 7.82(d, *J*=8.15Hz, 2H), 7.68-7.65(m, 1H), 6.14-6.07(m, 1H), 5.69-5.67(m, 1H), 5.30-5.26(m, 1H), 5.18-5.16(m, 1H), 5.03-5.01(m, 1H), 4.48-4.42(m, 2H), 4.24-4.20(m, 1H), 4.15-4.10(m, 1H), 3.24-3.19(m, 1H), 3.13-2.87(m, 1H), 2.16-2.13(m, 1H), 2.11-2.10(m, 1H), 2.01-1.99(m, 1H), 1.88-1.85(m, 1H), 1.46-1.39(m, 1H), 1.22-1.19(m,1H). ESI-MS: [M-Br] +:481.3, [M] -:561.3. [*α*]D20 = -310.5°(c = 0.20 in CH2Cl2).

Data for **1** and **2**: **1**, 99%(yield),1H-NMR (500MHz, CD3COCD3) δ: 8.83(d, *J*=4.4Hz, 1H), 8.18(d, *J*=8.0Hz, 2H), 8.00(d, *J*=4.4Hz, 1H), 7.98-7.92(m, 1H), 7.82(d, *J*=8.0Hz, 2H), 7.40-7.35(m, 2H), 6.03-6.10(m, 1H), 5.94-5.89(m, 1H), 5.55-5.52(m, 1H), 5.28-5.25(m, 1H), 5.07-5.22(m, 1H), 4.44- 4.51(m, 1H), 4.27-4.24(m, 2H), 4.16(s, 3H), 4.07-4.0 (m, 2H), 3.20-3.16(m, 1H), 2.98-2.96(m, 1H), 2.16-2.33(m, 2H), 1.90-1.84(m, 1H), 1.43-1.37(m, 1H), 1.29-1.27(m, 1H). [*α*]D21 = -324.9°(c = 0.20 in CH2Cl2). ESI-MS: [M] -:591.3.

**2**, 97.22%(yield), 1H-NMR (500MHz, CD3COCD3) δ: 8.86(d, *J*=4.4Hz, 1H), 8.22(d, *J*=8.0Hz, 2H), 8.05(d, *J*=4.4Hz, 1H), 7.99(d, *J*=9.2Hz, 1H), 7.85(d, *J*=8.0Hz, 2H), 7.40(d, *J*=9.2Hz, 1H), 7.39-7.36(m, 1H), 5.80- 5.70(m, 2H), 5.32-5.30(m, 1H), 5.11-5.09(m, 1H), 5.05-5.01(m, 1H), 4.36-4.28(m, 2H), 4.16(s, 3H), 4.11-4.07(m, 1H), 3.84-3.80(m, 1H), 3.32-3.37(m, 1H), 2.74-2.72(m, 1H), 2.30-2.20(m, 1H), 2.12-2.08 (m, 1H), 1.98-1.96(m, 1H), 1.80-1.78(m, 1H), 1.54-1.49(m, 1H), 1.18-1.12 (m, 1H). [*α*]D22 = +314.6°(c = 0.20 in CH2Cl2). ESI-MS: [M] -:591.3

2. Typical asymmetric sulfenylation of glycine derivatives for entry 3: To a mixture of **6** (0.148 g, 5 mmol), catalyst **3** (10% mol, 28 mg) in 5 ml toluene was added 1.1eq sulfenylation reagent and 20eq 50% KOH aqueous at 10 °C. The reaction mixture was stirred vigorously at the same temperature for 18 hours. Then added 5 ml water, and separated two phases. Aqueous layer was extracted with CH2Cl2 twice. The organic extracts were washed with brine and dried over Na2SO4. Evaporation of solvents and purification of the residual oil by column chromatography on silica gel (PE/EA = 30:1) gave the sulfenylation product (131 mg, 65% yield) as a colorless oil. 7a:1H-NMR (500MHz, CDCl3) 1HNMR: 7.83-7.80 (m, 2H), 7.52-7.33 (m, 8H), 7.26-7.21 (m, 5H), 5.71 (m, 1H), 1.38 (s, 9H). HPLC analysis retention time: 10.72 min (major), 15.31 min (Daicel Chiralcel OD-H, hexane/*i*-PrOH = 99.5/0.5, flow rate = 0.5 mL/min).