Supporting Information for

Highly Efficient Synthesis of Chiral β -Amino Acid Derivatives via Asymmetric Hydrogenation

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1. Analytical data of new substrates

For general synthetic procedures of β -aryl β -acetamidoacrylate esters, see Zhou, Y.-G.; Tang, W.; Wang, W.-B.; Li, W.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 4952-4953. For general synthetic procedure of β -alkyl β -acetamidoacrylate esters, see Zhu, G.; Chen, Z.; Zhang, X. *J. Org. Chem.* **1999**, *64*, 6907-6910. For analytical data of known substrates and products, please also refer to the two aforementioned papers.

Methyl 3-Acetamido-3-(4-benzyloxyphenyl)-2-propenoate 4l: Z/E = 9:1; ^1H NMR (360 MHz, CDCl_3) δ (Z isomer) 2.06 (s, 3H), 3.65 (s, 3H), 4.98 (s, 2H), 5.18 (s, 1H), 6.86 (d, J = 6.8 Hz, 2H), 7.28 (m, 7H), 10.46 (s, 1H); (E isomer) 2.27 (s, 3H), 3.65 (s, 3H), 4.98 (s, 2H), 6.44 (s, 1H), 6.86 (d, J = 6.8 Hz, 2H), 7.28 (m, 7H).

2. General procedure for asymmetric hydrogenation of β -alkyl or β -aryl β -acetamidoacrylic esters

In a glovebox filled with nitrogen, to a solution of β -acetamidoacrylic ester (**2** or **4**, 0.5 mmol) in 4 mL of degassed THF was added $\text{Rh}[(\text{TangPhos})\text{nbd}]\text{SbF}_6$ (2.5 μmol). The whole solution was transferred into an autoclave. The autoclave was then purged three times with hydrogen and filled with hydrogen with 20 psi pressure. The resulting reactor was stirred at room temperature for 24 hr. After release of the hydrogen, the autoclave was opened and the reaction mixture was evaporated. The residue was passed through a short silica gel plug to give hydrogenation product β -amino acid derivatives. A small amount of sample was subjected to chiral GC or HPLC analysis.

Methyl 3-acetamido-3-(4-benzyloxyphenyl)-propanoate 5c: 98.5% ee, $[\alpha]_{\text{D}}^{25}$ = -79.5°; ^1H NMR (300 MHz, CDCl_3) δ 2.00 (s, 3H), 2.83 (dd, J = 15.7, 6.2 Hz, 1H), 2.93 (dd, J = 15.6, 6.0 Hz, 1H), 3.63 (s, 3H), 5.05 (s, 2H), 5.40 (m, 1H), 6.93 (d, 1H), 6.94 (dd, J = 6.7, 2.0 Hz, 2H), 7.23 (dd, J = 6.8, 1.8 Hz, 2H), 6.72 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 23.8, 40.2, 49.5, 52.2, 115.4, 127.9, 128.0, 128.4,

129.0, 133.3, 137.3, 158.6, 169.7, 172.1; MS (ESI) m/z 328 ($M^+ + 1$); HRMS calcd for $C_{19}H_{22}NO_4$ 328.1549, found 328.1553. Chiral HPLC conditions ((*s, s*)-whelk-01): solvent hexane:isopropanol(1:1); flow rate 1 mL/min; retention time 8.2 min (*R*), 13.1 min (*S*).

3. The X-ray structure of phosphine sulfide **1**

The crystallographic data for the X-ray structure of **1** have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC- 190907.

The X-ray structure of **1**