Diastereoselective Synthesis of Arylglycine Derivatives by Cationic Palladium(II)-Catalyzed Addition of Arylboronic Acids to *N*-*tert*-Butanesulfinyl Imino Esters

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I. General.

Palladium acetate and Palladium trifluoroacetate was purchased from Aldrich. (*R*)-(+)-*N*-*tert*-butanesulfinamide was purchased from Cheng Du Li Kai Chiral Technology LTD. Ethyl glyoxylate (50% solution in toluene) was purchased from Lancaster. Phenylboronic acid was purchased from BeiJing Wisdom Chemicals Co., Ltd. All other arylboronic acids were purchased from HeBei DeLongTai Chemicals Co., Ltd. All solvents were dried and distilled before use according to the standard methods. Cat. **A**¹ and cat. **B**¹ were prepared according to the published procedures. NMR spectra were recorded on a Varian Mercury V_300 spectrometer. Infrared spectra were obtained on a Bio-Rad FTS-185 machine. Mass spectra were provided on Agilent 5973 or Agilent 1100 machines. All melting points were uncorrected. The optical rotation was measured on a Perkin-Elmer 341 polarimeter. The enantiomeric excess values were determined after separation of the enantiomers by HPLC on a Perkin-Elmer (785A, 200 IC Pump) or Waters (515 Pump, 2487. Dual Absorbance Detector) instruments.

II. Synthesis of Ethyl ((*R*_S)-*N*-*tert*-butanesulfinyl) imino acetate (**6**)²

To a 250 mL round-bottom flask were added ethyl glyoxylate (50% solution in toluene, 1.21 g, 5.95 mmol) under nitrogen atmosphere and the flask heated to about 50 °C for 1 min to depolymerize the reagent. The flask was allowed to cool to room

temperature and CH₂Cl₂ (150 mL) was introduced. To this rapidly stirred solution was added (*R*)-(+)-*N*-*tert*-butanesulfinamide (0.71 g, 5.95 mmol) and molecular sieve 4 Å (35 g, activated by drying overnight at > 500 °C). After 42 h the reaction mixture was filtered through celite and the residue was washed with CH₂Cl₂ (2 × 100 mL). The combined organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was subjected to silica gel chromatography (eluent: EtOAc/ petroleum ether) to afford ethyl ((*R*_S)-*N*-*tert*-butanesulfinyl) imino acetate (**6**) (1.20 g, 98%) as a colourless oil. $[\alpha]_{\text{D}}^{20} = -302.6$ (*c* 1.13, CHCl₃) [lit.² $[\alpha]_{\text{D}}^{20} = -313$ (*c* 1.01, CHCl₃)]. ¹H NMR (300 MHz, CDCl₃) δ 8.02 (s, 1H), 4.39 (q, *J* = 6.9 Hz, 2H), 1.39 (t, *J* = 6.9 Hz, 3H), 1.28 (s, 9H). IR (KBr): ν 2984, 1750, 1728, 1610, 1459, 1369, 1334, 1283, 1209, 1099, 1032 cm⁻¹; MS (70 eV, EI) *m/z*: 206 (*M*⁺ + 1), 150, 132 (100), 121, 57, 41.

III. Typical Procedure for the Addition of Arylboronic Acids to Ethyl ((*R*_S)-*N*-*tert*-Butanesulfinyl) Imino Acetate (**6**).

To a Schlenk tube were added cat.**B** (10.7 mg, 0.0125 mmol, 5 mol %) and molecular sieve 4 Å (120 mg, activated by drying overnight at > 500 °C) in nitrogen atmosphere. Dioxane (1 mL) was then added and the mixture was stirred at 60 °C for 10 mins. Ethyl ((*R*_S)-*N*-*tert*-butanesulfinyl) imino acetate (**6**) (0.25 mmol) and arylboronic acid (**2**) (0.50 mmol) were added sequentially and the mixture was stirred

at 60 °C for 24 h. The reaction mixture was allowed to cool to room temperature and diluted with EtOAc. The organic layer was washed with brine and the aqueous layer was extracted with EtOAc. The combined organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was subjected to silica gel chromatography (eluent: EtOAc/ petroleum ether) to isolate the product.

Characterization Data of Compounds 7.

N-tert-butanesulfinyl phenylglycine ethyl ester (7a).^{2,3a}

7a

yellow oil, $[\alpha]_D^{20} = -167.9$ (*c* 1.35, CHCl₃); The absolute configuration was determined to be (*R*_S, 2*R*) according to literature [*lit*² $[\alpha]_D^{20} = -183$ (*c* 0.59, CHCl₃) for pure ethyl (*R*_S, 2*R*)-(-)-*N*-(*tert*-butanesulfinyl) iminoacetate]. ¹H NMR (300 MHz, CDCl₃): δ 7.34-7.38 (m, 5H), 5.06 (d, *J* = 4.5 Hz, 1H), 4.61 (d, *J* = 4.5 Hz, 1H), 4.14-4.23 (m, 2H), 1.24 (s, 9H), 1.21 (t, *J* = 7.2 Hz, 3H); IR (KBr): ν 3289, 2982, 1736, 1602, 1456, 1368, 1273, 1070, 733 cm⁻¹; MS (70 eV, EI) *m/z*: 210 (M⁺-CO₂Et, 100), 164, 163, 105, 149, 135, 41.

N-tert-butanesulfinyl-4-methoxyphenylglycine ethyl ester (7b).^{3a}

7b

yellow oil, $[\alpha]_D^{20} = -179.2$ (c 1.00, CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 7.29 (d, $J = 8.1$ Hz, 2H), 6.88 (d, $J = 8.7$ Hz, 2H), 5.01 (d, $J = 3.9$ Hz, 1H), 4.54 (d, $J = 4.2$ Hz, 1H), 4.13-4.22 (m, 2H), 3.81 (s, 3H), 1.23 (s, 9H), 1.20 (t, $J = 7.5$ Hz, 3H); IR (KBr): ν 3291, 2982, 1738, 1612, 1514, 1251, 1178, 1074, 755 cm^{-1} ; MS (70 eV, EI) m/z : 257 ($\text{M}^+ - \text{C}_4\text{H}_8$), 240 ($\text{M}^+ - \text{CO}_2\text{Et}$), 193 (100), 135, 121, 57, 41; HRMS Calcd for $\text{C}_{12}\text{H}_{18}\text{NO}_2\text{S}$ ($\text{M}^+ - \text{CO}_2\text{Et}$): 240.1058. Found: 240.1064.

***N-tert*-butanesulfinyl-4-tolylglycine ethyl ester (7c).** **7c**

yellow oil, $[\alpha]_D^{20} = -161.1$ (c 1.35, CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 7.26 (d, $J = 8.1$ Hz, 2H), 7.16 (d, $J = 7.8$ Hz, 2H), 5.03 (d, $J = 4.2$ Hz, 1H), 4.57 (d, $J = 4.5$ Hz, 1H), 4.12-4.23 (m, 2H), 2.35 (s, 3H), 1.24 (s, 9H), 1.20 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 171.5, 138.2, 134.2, 129.3, 127.6, 62.1, 60.1, 55.9, 22.5, 21.1, 13.9; IR (KBr): ν 3278, 2982, 1737, 1515, 1475, 1367, 1249, 1080 cm^{-1} ; MS (70 eV, EI) m/z : 298 ($\text{M}^+ + 1$), 241 ($\text{M}^+ - \text{C}_4\text{H}_8$), 177, 149, 105, 91, 57 (100), 47; HRMS Calcd for $\text{C}_{11}\text{H}_{15}\text{NO}_3\text{S}$ ($\text{M}^+ - \text{C}_4\text{H}_8$): 241.0773. Found: 241.0777.

***N-tert*-butanesulfinyl-2-tolylglycine ethyl ester (7d).**

7d

yellow oil, $[\alpha]_D^{20} = -228.0$ (*c* 0.25, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 7.17-7.27 (m, 4H), 5.26 (d, *J* = 3.9 Hz, 1H), 4.57 (d, *J* = 3.3 Hz, 1H), 4.13-4.23 (m, 2H), 2.43 (s, 3H), 1.21 (s, 9H), 1.19 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 171.7, 136.8, 135.4, 130.8, 128.3, 128.0, 126.2, 62.1, 57.4, 55.8, 22.4, 19.4, 13.9; IR (KBr): ν 3291, 2982, 1735, 1474, 1367, 1215, 1074, 757 cm⁻¹; MS (70 eV, EI) *m/z*: 298 (*M*⁺ + 1), 241 (*M*⁺ - C₄H₈), 224, 177 (100), 149, 105, 91, 57; HRMS Calcd for C₁₁H₁₅NO₃S (*M*⁺ - C₄H₈): 241.0773. Found: 241.0769.

***N*-tert-butanesulfinyl-3-tolylglycine ethyl ester (7e).**

7e

yellow oil, $[\alpha]_D^{20} = -131.9$ (*c* 0.85, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 7.12-7.27 (m, 4H), 5.01 (d, *J* = 4.5 Hz, 1H), 4.58 (d, *J* = 4.2 Hz, 1H), 4.09-4.27 (m, 2H), 2.35 (s, 3H), 1.18-1.28 (m, 12H); ¹³C NMR (75 MHz, CDCl₃): δ 171.5, 138.3, 137.1, 129.1, 128.5, 128.4, 124.7, 62.1, 60.4, 55.9, 22.5, 21.4, 13.9; IR (KBr): ν 3292, 2982, 1738, 1367, 1187, 1076, 734 cm⁻¹; MS (70 eV, EI) *m/z*: 298 (*M*⁺ + 1), 241 (*M*⁺ - C₄H₈), 224,

177 (100), 149, 105, 91, 57; HRMS Calcd for $C_{11}H_{15}NO_3S$ ($M^+ - C_4H_8$): 241.0773.

Found: 241.0768.

***N*-tert-butanesulfinyl- α -naphthylglycine ethyl ester (7f).**

7f

yellow oil, $[\alpha]_D^{20} = -115.3$ (c 0.75, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$): δ 8.08-8.11 (m, 1H), 7.83-7.88 (m, 2H), 7.45-7.54 (m, 4H), 5.63 (d, $J = 3.6$ Hz, 1H), 4.73 (d, $J = 3.6$ Hz, 1H), 4.11-4.21 (m, 2H), 1.15 (s, 9H), 1.10 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.9, 134.1, 132.5, 130.9, 129.4, 128.8, 127.6, 126.3, 125.8, 125.1, 123.9, 62.2, 58.9, 55.7, 22.4, 13.8; IR (KBr): ν 3293, 2983, 1734, 1368, 1220, 1065, 755 cm^{-1} ; MS (70 eV, EI) m/z : 334 ($M^+ + 1$), 277 ($M^+ - C_4H_8$), 260, 228, 213 (100), 185, 154, 127, 57; HRMS Calcd for $C_{14}H_{15}NO_3S$ ($M^+ - C_4H_8$): 277.0773. Found: 277.0771.

***N*-tert-butanesulfinyl- β -naphthylglycine ethyl ester (7g).**

7g

yellow oil, $[\alpha]_D^{20} = -120.9$ (c 0.70, CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 7.84 (d, $J = 8.1$ Hz, 4H), 7.44-7.51 (m, 3H), 5.24 (d, $J = 3.6$ Hz, 1H), 4.70 (d, $J = 3.6$ Hz, 1H), 4.13-4.23 (m, 2H), 1.24 (s, 9H), 1.18 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 171.2, 134.4, 133.3, 133.0, 128.5, 127.9, 127.6, 127.4, 126.4, 126.3, 124.9, 62.2, 60.4, 55.9, 22.5, 13.9; IR (KBr): ν 3283, 2961, 1737, 1474, 1367, 1079, 753 cm^{-1} ; MS (70 eV, EI) m/z : 277 ($\text{M}^+ - \text{C}_4\text{H}_8$), 213, 156, 127, 105, 91, 57 (100), 41; HRMS Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_3\text{S}$ ($\text{M}^+ - \text{C}_4\text{H}_8$): 277.0773. Found: 277.0770.

***N*-tert-butanesulfinyl-4-trifluoromethylphenylglycine ethyl ester (7h).**

7h

yellow oil, $[\alpha]_D^{20} = -130.4$ (c 1.38, CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 7.63 (d, $J = 8.4$ Hz, 2H), 7.51 (d, $J = 8.1$ Hz, 2H), 5.13 (d, $J = 3.6$ Hz, 1H), 4.66 (d, $J = 3.6$ Hz, 1H), 4.14-4.24 (m, 2H), 1.25 (s, 9H), 1.21 (t, $J = 7.5$ Hz, 3H); ^{19}F NMR (282 MHz, CDCl_3): δ -63.1; ^{13}C NMR (75 MHz, CDCl_3): δ 170.5, 141.0, 134.4, 130.8, 128.1, 125.6 (q, $J = 4.0$ Hz), 114.1, 62.6, 59.8, 56.2, 22.5, 13.9; IR (KBr): ν 3289, 2984, 1741, 1620, 1327, 1128, 1068, 1019, 845 cm^{-1} ; MS (70 eV, EI) m/z : 352 ($\text{M}^+ + 1$), 295 ($\text{M}^+ - \text{C}_4\text{H}_8$), 278, 232, 221, 204, 172, 57 (100); HRMS Calcd for $\text{C}_{11}\text{H}_{12}\text{NO}_3\text{F}_3\text{S}$ ($\text{M}^+ - \text{C}_4\text{H}_8$): 295.0490. Found: 295.0500.

***N*-tert-butanesulfinyl-3-nitrophenylglycine ethyl ester (7i).**

7i

yellow oil, $[\alpha]_D^{20} = -136.5$ (c 1.25, CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 8.29 (s, 1H), 8.21 (d, $J = 8.1$ Hz, 1H), 7.75 (d, $J = 7.8$ Hz, 1H), 7.56 (d, $J = 7.8$ Hz, 1H), 5.20 (d, $J = 3.6$ Hz, 1H), 4.70 (d, $J = 3.6$ Hz, 1H), 4.14-4.26 (m, 2H), 1.28 (s, 9H), 1.22 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 170.0, 148.4, 139.3, 133.9, 129.6, 123.4, 122.7, 62.8, 59.4, 56.2, 22.4, 13.9; IR (KBr): ν 3285, 2982, 1739, 1533, 1351, 1073, 733 cm^{-1} ; MS (70 eV, EI) m/z : 272 ($\text{M}^+ - \text{C}_4\text{H}_8$), 254, 209, 198, 181, 57 (100); HRMS Calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_5\text{S}$ ($\text{M}^+ - \text{C}_4\text{H}_8$): 272.0467. Found: 272.0472.

IV. Methods for de Determination^{3,4}

To a solution of the the *N*-sulfinyl arylglycine esters (**7**) in 2 mL of dry ethanol was added a solution of dry HCl in 1,4-dioxane (7.5 M, 5.0 equiv based on **7**). The mixture was stirred at room temperature for 3 h and concentrated. The resulting amine hydrochloride was precipitated with diethyl ether. The amine hydrochloride (1.0 equiv) was dissolved in CH_2Cl_2 (0.1 M) and Hunig's base (6.0 equiv) was added dropwise. Then, Ac_2O (3.0 equiv) was added and the resulting mixture was stirred for 1 h at room temperature. The reaction mixture was quenched with a saturated solution of

ammonium chloride and diluted with CH₂Cl₂. The resulting mixture was separated, and the aqueous layer was extracted with CH₂Cl₂ three times. The combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was subjected to silica gel chromatography (eluent: EtOAc/petroleum ether) to isolate the product. The ee value of compounds **8** were determined by chiral HPLC as shown in the individual compounds. The de value of compounds **7** can be represented by the ee value of **8**.

entry	R ¹	product	yield(%) ^a
1	Ph	8a	89
2	4-MeOC ₆ H ₄	8b	90
3	4-CH ₃ C ₆ H ₄	8c	90
4	2-CH ₃ C ₆ H ₄	8d	79
5	3-CH ₃ C ₆ H ₄	8e	87
6	α-naphthyl	8f	93
7	β-naphthyl	8g	93
8	4-CF ₃ C ₆ H ₄	8h	92
9	3-NO ₂ C ₆ H ₄	8i	94

a. The total yield from **7** to **8**.

Characterization Data of Compounds **8**.

N-acetylphenylglycine ethyl ester (**8a**).^{4,5}

8a

White solid, mp: 57-59 °C. (lit⁶: 65-66°C); ¹H NMR (300 MHz, CDCl₃): δ 7.26-7.37 (m, 5H), 6.52 (d, *J* = 6.6 Hz, 1H), 5.57 (d, *J* = 7.2 Hz, 1H), 4.08-4.29 (m, 2H), 2.03 (s, 3H), 1.19-1.33 (m, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 171.0, 169.3, 136.6, 128.9, 128.4, 127.2, 61.9, 56.4, 23.1, 13.9; IR (KBr): ν 3292, 2984, 1744, 1653, 1540, 1374, 1211, 1131, 1023, 803 cm⁻¹; MS (70 eV, EI) *m/z*: 148(M⁺ - CO₂Et), 106(100), 104, 77, 43. The ee value was determined by chiral HPLC using a Chiralcel OJ-H column with hexane : isopropanol = 90 : 10, flow = 0.7 mL/min; ee: 95.5%; [α]_D²⁰ = -125.7 (*c* 0.90, ethanol). The absolute configuration was determined to be (*R*) according to literature. [lit⁶ [α]_D²⁰ = -138.7 (*c* 1.6, ethanol) for pure *R*-(-)-*N*-acetylphenylglycine ethyl ester]

***N*-acetyl-4-methoxyphenylglycine ethyl ester (8b).**⁷

8b

White solid, mp: 92-94°C; ¹H NMR (300 MHz, CDCl₃): δ 7.28 (d, *J* = 9.3 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.43 (d, *J* = 6.6 Hz, 1H), 5.51 (d, *J* = 7.5 Hz, 1H), 4.11-4.26 (m, 2H), 3.80 (s, 3H), 2.03 (s, 3H), 1.25-1.94 (m, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 171.2, 169.3, 159.6, 128.7, 128.4, 114.2, 61.8, 55.8, 55.2, 23.1, 13.9; IR (KBr): ν 3317, 2965, 1733, 1651, 1539, 1306, 1180, 1028, 795 cm⁻¹; MS (70 eV, EI) *m/z*: 251 (M⁺), 205, 178, 136(100), 109, 77, 43. The ee value was determined by chiral HPLC using a Chiralcel OJ-H column with hexane : isopropanol = 90 : 10, flow = 0.7 mL/min; ee 94.8%; [α]_D²⁰ = -182.7 (*c* 0.80, CHCl₃).

***N*-acetyl-4-tolylglycine ethyl ester (8c).⁸**

8c

White solid, mp: 72-73°C. (lit⁸: 77-79°C); ¹H NMR (300 MHz, CDCl₃): δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.47 (d, *J* = 6.3 Hz, 1H), 5.54 (d, *J* = 7.2 Hz, 1H), 4.10-4.27 (m, 2H), 2.34 (s, 3H), 2.03 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 171.2, 169.3, 138.3, 133.7, 129.6, 127.1, 61.8, 56.1, 23.1, 21.1, 13.9; IR (KBr): ν 3260, 2990, 1749, 1640, 1547, 1375, 1118, 1024, 761 cm⁻¹; MS (70 eV, EI) *m/z*: 235 (M⁺), 162, 120 (100), 91, 77, 43. The ee value was determined by chiral HPLC using a Chiralcel OJ-H column with hexane : isopropanol = 95 : 5, flow = 0.7 mL/min; ee: 96.9%; [α]_D²⁰ = -208.4 (*c* 1.90, CHCl₃).

***N*-acetyl-2-tolylglycine ethyl ester (8d).**

8d

White solid, mp: 84-86°C; ¹H NMR (300 MHz, CDCl₃): δ 7.19-7.21 (m, 4H), 6.36 (d, *J* = 6.0 Hz, 1H), 5.79 (d, *J* = 7.5 Hz, 1H), 4.09-4.26 (m, 2H), 2.49 (s, 3H), 2.03 (s, 3H), 1.20 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 171.5, 169.4, 136.9, 135.2, 130.9, 128.4, 126.4, 126.2, 61.8, 53.0, 22.9, 19.4, 13.9; IR (KBr): ν 3350, 2996, 1746, 1653, 1524, 1216, 1118, 1025, 757 cm⁻¹; MS (70 eV, EI) *m/z*: 235 (M⁺), 162,

120(100), 91, 77, 43; HRMS Calcd for C₁₃H₁₇NO₃: 235.1208. Found: 235.1214. The ee value was determined by chiral HPLC using a Chiralcel OD-H column with hexane : isopropanol = 90 : 10, flow = 0.7 mL/min; ee: 93.3%; $[\alpha]_D^{20} = -28$ (*c* 0.25, CHCl₃).

***N*-acetyl-3-tolylglycine ethyl ester (8e).**

8e

yellow oil, ¹H NMR (300 MHz, CDCl₃): δ 7.25 (t, *J* = 7.5 Hz, 1H), 7.12-7.17 (m, 3H), 6.50 (d, *J* = 6.6 Hz, 1H), 5.54 (d, *J* = 7.2 Hz, 1H), 4.10-4.28 (m, 2H), 2.35 (s, 3H), 2.04 (s, 3H), 1.22 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 171.1, 169.3, 138.7, 136.5, 129.2, 128.8, 127.9, 124.2, 61.9, 56.3, 23.1, 21.4, 13.9; IR (KBr): ν 3285, 2983, 1743, 1654, 1539, 1372, 1192, 1027 cm⁻¹; MS (70 eV, EI) *m/z*: 236 (*M*⁺ + 1), 177, 162, 120 (100), 91, 77, 65, 43; HRMS Calcd for C₁₃H₁₇NO₃: 235.1208. Found: 235.1209. The ee value was determined by chiral HPLC using a Chiralcel As-H column with hexane : isopropanol = 70 : 30, flow = 0.6 mL/min; ee: 89.4%; $[\alpha]_D^{20} = -72.9$ (*c* 0.60, CHCl₃).

***N*-acetyl-α-naphthylglycine ethyl ester (8f).**

8f

White solid, mp: 143-145°C; ^1H NMR (300 MHz, CDCl_3): δ 8.16 (d, J = 8.4 Hz, 1H), 7.84-7.90 (m, 2H), 7.41-7.61 (m, 4H), 6.37 (s, 2H), 4.14-4.29 (m, 2H), 2.03 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 171.6, 169.5, 134.0, 132.6, 130.9, 129.4, 128.9, 127.0, 126.2, 125.4, 125.2, 123.3, 61.9, 53.3, 23.0, 13.9; IR (KBr): ν 3314, 2987, 1754, 1647, 1540, 1372, 1212, 1121, 780 cm^{-1} ; MS (70 eV, EI) m/z : 271 (M^+), 225, 198, 156 (100), 129, 127, 43; HRMS Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_3$: 271.1208. Found: 271.1215. The ee value was determined by chiral HPLC using a Chiralcel AD-H column with hexane : isopropanol = 95 : 5, flow = 0.7 mL/min; ee: 87.3%; $[\alpha]_{\text{D}}^{20}$ = -192.3 (c 1.50, CHCl_3).

***N*-acetyl- β -naphthylglycine ethyl ester (8g).**

8g

White solid, mp: 121-123°C; ^1H NMR (300 MHz, CDCl_3): δ 7.80-7.84 (m, 4H), 7.44-7.50 (m, 3H), 6.71 (d, J = 6.9 Hz, 1H), 5.75 (d, J = 7.2 Hz, 1H), 4.11-4.28 (m, 2H), 2.05 (s, 3H), 1.20 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 171.0, 169.4, 133.9, 133.2, 133.1, 128.8, 128.0, 127.6, 126.5, 126.4, 124.7, 61.9, 56.5, 23.1, 13.9; IR (KBr): ν 3303, 2975, 1733, 1651, 1548, 1323, 1280, 1130, 1002, 808 cm^{-1} ; MS (70 eV, EI) m/z : 271 (M^+), 225, 198, 156 (100), 129, 127, 43; HRMS Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_3$: 271.1208. Found: 271.1220. The ee value was determined by chiral HPLC using a Chiralcel OJ-H column with hexane : isopropanol = 80 : 20, flow = 0.7

mL/min; er: 88 : 12; $[\alpha]_{\text{D}}^{20} = -201.5$ (c 0.75, CHCl_3).

***N*-acetyl-4-trifluoromethylphenylglycine ethyl ester (8h).**

8h

White solid, mp: 81-82°C; ^1H NMR (300 MHz, CDCl_3): δ 7.61 (d, $J = 8.1$ Hz, 2H), 7.50 (d, $J = 8.1$ Hz, 2H), 6.79 (d, $J = 6.3$ Hz, 1H), 5.64 (d, $J = 7.2$ Hz, 1H), 4.15-4.26 (m, 2H), 2.05 (s, 3H), 1.22 (t, $J = 6.9$ Hz, 3H); ^{19}F NMR (282 MHz, CDCl_3): δ -63.1; ^{13}C NMR (75 MHz, CDCl_3): δ 170.3, 169.4, 140.7, 130.3, 127.5, 125 (q, $J = 3.9$ Hz), 122.0, 62.3, 56.0, 45.2, 22.9, 13.9; IR (KBr): ν 3332, 2984, 1734, 1652, 1532, 1334, 1122, 1071, 1019, 834 cm^{-1} ; MS (70 eV, EI) m/z : 289 (M^+), 216, 174 (100), 172, 149, 127, 43; HRMS Calcd for $\text{C}_{13}\text{H}_{14}\text{NO}_3\text{F}_3$: 289.0926. Found: 289.0928. The ee value was determined by chiral HPLC using a Chiralcel OD-H column with hexane : isopropanol = 97 : 3, flow = 0.7 mL/min; ee: 90.8%; $[\alpha]_{\text{D}}^{20} = -116.6$ (c 1.50, CHCl_3).

***N*-acetyl-3-nitrophenylglycine ethyl ester (8i).**

8i

White solid, mp: 147-149°C; ^1H NMR (300 MHz, CDCl_3): δ 8.23 (s, 1H), 8.18 (d, $J = 8.1$ Hz, 1H), 7.76 (d, $J = 7.8$ Hz, 1H), 7.55 (t, $J = 7.8$ Hz, 1H), 6.92 (d, $J = 6.0$ Hz,

1H), 5.69 (d, $J = 6.6$ Hz, 1H), 4.15-4.30 (m, 2H), 2.09 (s, 3H), 1.23 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 169.8, 169.5, 148.4, 139.1, 133.6, 129.7, 123.3, 121.8, 62.6, 55.7, 23.0, 13.9. IR (KBr): ν 3323, 2982, 1735, 1646, 1534, 1351, 1201, 1007, 734 cm^{-1} ; MS (70 eV, EI) m/z : 267 ($\text{M}^+ + 1$), 193, 151 (100), 105, 77, 43; HRMS Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_5$: 266.0903. Found: 266.0912. The ee value was determined by chiral HPLC using a Chiralcel OJ-H column with hexane : isopropanol = 80 : 20, flow = 0.7 mL/min; ee: 88%; $[\alpha]_{\text{D}}^{20} = -91.3$ (c 0.65, CHCl_3).

V. References

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