Supporting Information for Organocatalytic Asymmetric Direct Alkylation of α -Diazoester via C-H Bond Cleavage

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Experimental Section

General Information: Infrared spectra were recorded on a Shimadzu FTIR-8600PC spectrometer. ^1H NMR spectra were recorded on a JEOL GSX-270 (270 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance as the internal standard (CDCl_3 : 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, br = broad, m = multiplet) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL GSX-270 (67.8 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard (CDCl_3 : 77.0 ppm). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm). Flash column chromatography was performed on silica gel 60N (spherical, neutral, 100-210 μm ; Kanto Chemical Co., Inc.). Mass spectra analysis was performed at the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University.

All reactions were carried out under a nitrogen (N_2) atmosphere in dried glassware. All substrate were purified by column chromatography or distillation prior to use. Dichloromethane and toluene were supplied from Kanto Chemical Co., Inc. as “Dehydrated solvent system”. Chloroform- d_1 was dried over activated molecular sieves 4A and used under nitrogen atmosphere. Other solvents and other simple chemicals were purchased and used as such.

1. Preparation of Imine

***N*-benzylidenebenzamide (2, $\text{R}' = \text{Ph}$, $\text{Ar} = \text{Ph}$):**¹ *N*-(methoxyphenylmethyl)benzamide (482 mg, 2.0 mmol) and dried K_2CO_3 were heated gradually to 120 $^\circ\text{C}$ under reduced pressure (0.5 mmHg). The solid residue melted partially during heating and then was distilled at 180 $^\circ\text{C}$ to give a yellow liquid of *N*-benzylidenebenzamide (245 mg, 60%). The imine was solidified in refrigerator prior to use. ^1H NMR (CDCl_3 , 270 MHz) δ 7.45-7.63 (6H, m), 7.97 (2H, d,

(1) Aggawal, V. K.; Vasse, J. *Org. Lett.* **2003**, 21, 3987.

$J = 7.8$ Hz), 8.16 (2H, d, $J = 8.4$ Hz), 8.78 (1H, s).

***N*-benzylidene-2-bromobenzamide (2, $R' = o\text{-Br-C}_6\text{H}_4$, $\text{Ar} = \text{Ph}$):** Reaction performed utilizing the same procedure for the preparation of *N*-benzylidenebenzamide. ^1H NMR (CDCl_3 , 270 MHz) δ 7.32-7.45 (2H, m), 7.48-7.63 (3H, m), 7.70 (1H, dd, $J = 8.7$, 1.6 Hz), 7.96 (2H, td, $J = 7.0$, 1.6 Hz), 8.07 (1H, dd, $J = 8.7$, 1.6 Hz), 8.80 (1H, s); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 121.5, 127.1, 128.8, 130.1, 132.4, 132.7, 133.3, 134.2, 134.5, 134.6, 164.5, 180.4; IR (KBr): 3063, 2966, 1678, 1628, 1599, 1213, 1080, 1018, 756, 694 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{10}\text{BrNaNO}$ ($[\text{M} + \text{Na}]^+$) 309.9838, 311.9818. Found 309.9839, 311.9819.

***N*-benzylidene-2-methylbenzamide (2, $R' = o\text{-Me-C}_6\text{H}_4$, $\text{Ar} = \text{Ph}$):** Reaction performed utilizing the same procedure for the preparation of *N*-benzylidenebenzamide. ^1H NMR (CDCl_3 , 270 MHz) δ 2.70 (3H, s), 7.24-7.31 (2H, m), 7.41-7.62 (4H, m), 7.96 (2H, dt, $J = 6.8$, 1.6 Hz), 8.10 (1H, dd, $J = 7.3$, 1.6 Hz), 8.71 (1H, s); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 22.3, 125.7, 128.9, 129.9, 132.0, 132.1, 132.3, 132.5, 133.1, 134.7, 140.8, 163.3, 182.5; IR (KBr): 3026, 2963, 1672, 1626, 1580, 1452, 1032, 731, 687 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{17}\text{NaNO}_2$ ($[\text{M} + \text{CH}_3\text{OH} + \text{Na}]^+$) 278.1151. Found 278.1151.

***N*-benzylidene-2-methoxybenzamide (2, $R' = o\text{-MeO-C}_6\text{H}_4$, $\text{Ar} = \text{Ph}$):** The imine was prepared from *N*-trimethylsilylimine and benzoyl chloride according to the literature procedure.² The imine was purified by recrystallization from CH_2Cl_2 /Hexane. ^1H NMR (CDCl_3 , 270 MHz) δ 3.86 (3H, s), 6.97-7.05 (2H, m), 7.48-7.55 (4H, m), 7.91 (2H, d, $J = 7.0$ Hz), 8.05 (1H, d, $J = 8.1$ Hz), 8.64 (1H, s); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 55.9, 112.0, 120.2, 122.8, 128.8, 129.6, 132.7₃, 132.7₈, 134.2, 134.8, 159.5, 162.1, 180.9; IR (KBr): 3065, 2910, 1638, 1599, 1524, 1483, 1238, 1024, 756, 704 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{17}\text{NaNO}_3$ ($[\text{M} + \text{CH}_3\text{OH} + \text{Na}]^+$) 294.1101. Found 294.1104.

(2) Kupfer, R.; Meier, S.; Wuerthwein, E. U, *Synthesis* **1984**, 8, 688.

***N*-benzylidene-3-methoxybenzamide (2, R' = *m*-MeO-C₆H₄, Ar = Ph):** Reaction performed utilizing the same procedure for the preparation of *N*-benzylidene-2-methoxybenzamide. ¹H NMR (CDCl₃, 270 MHz) δ 3.87 (3H, s), 7.14 (1H, ddd, *J* = 8.1, 2.7, 1.0 Hz), 7.38 (1H, t, *J* = 8.1 Hz), 7.48-7.63 (3H, m), 7.70 (1H, dd, *J* = 2.7, 1.4 Hz), 7.76 (1H, dt, *J* = 7.8, 1.4 Hz), 7.96-8.00 (2H, m), 8.77 (1H, s); ¹³C NMR (CDCl₃, 67.8 MHz) δ 55.5, 114.1, 120.1, 122.8, 128.9, 129.4, 129.9, 133.2, 134.5, 134.6, 159.6, 164.4, 180.6; IR (KBr): 3024, 2935, 1670, 1624, 1601, 1580, 1485, 1273, 1034, 764 cm⁻¹; HRMS (ESI) Calcd for C₁₆H₁₇NaNO₃ ([M + CH₃OH + Na]⁺) 294.1101. Found 294.1096.

***N*-benzylidene-1-naphthamide (2, R' = 1-Naphthyl, Ar = Ph):** Reaction performed utilizing the same procedure for the preparation of *N*-benzylidenebenzamide. ¹H NMR (CDCl₃, 270 MHz) δ 7.50-7.71 (6H, m), 7.91 (1H, d, *J* = 8.4 Hz), 7.99-8.02 (2H, m), 8.07 (1H, d, *J* = 8.4 Hz), 8.49 (1H, dd, *J* = 7.3, 1.4 Hz), 8.84 (1H, s), 9.23 (1H, d, *J* = 8.9 Hz); ¹³C NMR (CDCl₃, 67.8 MHz) δ 124.4, 126.2, 126.3, 128.1, 128.5, 128.9, 129.6, 129.9, 131.4, 132.5, 133.1, 133.9, 134.2, 134.6, 163.7, 182.4; IR (KBr): 3049, 2901, 1663, 1636, 1508, 1217, 1111, 968, 783, 687 cm⁻¹; HRMS (ESI) Calcd for C₁₉H₁₇NaNO₂ ([M + CH₃OH + Na]⁺) 314.1151. Found 314.1152.

***N*-benzylidene-4-bromobenzamide (2, R' = *p*-Br-C₆H₄, Ar = Ph):** Reaction performed utilizing the same procedure for the preparation of *N*-benzylidenebenzamide. ¹H NMR (CDCl₃, 270 MHz) δ 7.50-7.65 (5H, m), 7.98-8.07 (4H, m), 8.82 (1H, s); ¹³C NMR (CDCl₃, 67.8 MHz) δ 128.8, 129.0, 130.2, 131.7, 131.8, 132.3, 133.6, 134.4, 165.5, 180.0; IR (KBr): 3026, 1674, 1626, 1585, 1215, 1045, 1011, 762, 685 cm⁻¹; HRMS (ESI) Calcd for C₁₅H₁₄BrNaNO₂ ([M + CH₃OH + Na]⁺) 342.0100, 344.0080. Found 342.0099, 344.0077.

***N*-benzylidene-4-methylbenzamide (2, R' = *p*-Me-C₆H₄, Ar = Ph):** Reaction performed utilizing the same procedure for the preparation of *N*-benzylidenebenzamide. ¹H NMR (CDCl₃, 270 MHz) δ 2.43 (3H, s), 7.28 (2H, d, *J* = 8.4 Hz), 7.48-7.62 (3H, m), 7.98 (2H, dt, *J* = 6.2, 1.6 Hz), 8.05 (2H, d, *J* = 8.4 Hz), 8.76 (1H, s); ¹³C NMR (CDCl₃, 67.8 MHz) δ 21.8, 128.9, 129.2, 130.0, 130.2, 130.7, 133.2, 134.7, 144.4, 164.3, 180.9; IR (KBr): 3063, 2918, 1676, 1611, 1578, 1454, 1047, 766, 691 cm⁻¹; HRMS (ESI) Calcd for C₁₆H₁₇NaNO₂ ([M + CH₃OH + Na]⁺) 278.1151. Found 278.1154.

***N*-benzylidene-4-methoxybenzamide (2, R' = *p*-MeO-C₆H₄, Ar = Ph):** Reaction performed utilizing the same procedure for the preparation of *N*-benzylidene-2-methoxybenzamide. ¹H NMR (CDCl₃, 270 MHz) δ 3.88 (3H, s), 6.96 (2H, d, *J* = 9.2 Hz), 7.49-7.59 (3H, m), 7.98 (2H, d, *J* = 7.2 Hz), 8.14 (2H, dt, *J* = 9.2, 2.2 Hz), 8.78 (1H, s); ¹³C NMR (CDCl₃, 67.8 MHz) δ 55.5, 113.8, 126.1, 128.9, 129.9, 132.4, 133.1, 134.7, 163.9, 164.4, 180.2; IR (KBr): 3057, 2910, 1661, 1611, 1508, 1259, 1165, 1053, 772 cm⁻¹; HRMS (ESI) Calcd for C₁₆H₁₇NaNO₃ ([M + CH₃OH + Na]⁺) 294.1101. Found 294.1099.

***N*-benzylidene-4-(dimethylamino)benzamide (2, R' = *p*-Me₂N-C₆H₄, Ar = Ph):** *N*-(methoxyphenylmethyl)-4-(dimethylamino)benzamide (569 mg, 2.0 mmol), dried K₂CO₃ (1.0 g, 7.2 mmol) and Na₂SO₄ (1.2 g, 8.4 mmol) in toluene were refluxed for 12 h with azeotropic removal of MeOH. The suspension was cooled to rt, and Ac₂O (0.3 ml) was subsequently added. After 30 min at room temperature, the suspension was filtered through a pad of celite and the filtrate was concentrated. The residue was purified by distillation (250 °C, 0.5 mmHg) to give a yellow solid of *N*-benzylidene-4-(dimethylamino)benzamide (404 mg, 80 %). ¹H NMR (CDCl₃, 270 MHz) δ 3.07 (6H, s), 6.68 (2H, d, *J* = 9.0 Hz), 7.46-7.56 (3H, m), 7.97 (2H, dd, *J* = 7.8, 1.4 Hz), 8.06 (2H, dt, *J* = 9.0, 2.4 Hz), 8.77 (1H, s); ¹³C NMR (CDCl₃, 67.8 MHz) δ 40.0, 110.7, 120.5, 128.8, 129.8, 132.3, 132.8, 135.0, 153.8, 163.7, 180.3; IR (KBr):

2910, 1647, 1591, 1528, 1369, 1169, 1040, 781 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{20}\text{NaN}_2\text{O}_2$ ($[\text{M} + \text{CH}_3\text{OH} + \text{Na}]^+$) 307.1417. Found 307.1417.

***N*-(4-fluorobenzylidene)-4-(dimethylamino)benzamide (2, $\text{R}' = p\text{-Me}_2\text{N-C}_6\text{H}_4$, $\text{Ar} = p\text{-F-C}_6\text{H}_4$):** Reaction performed utilizing the same procedure for the preparation of *N*-benzylidene-4-(dimethylamino)benzamide. ^1H NMR (CDCl_3 , 270 MHz) δ 3.07 (6H, s), 6.68 (2H, dt, $J = 9.0, 2.4$ Hz), 7.18 (2H, t, $J = 8.4$ Hz), 7.94-8.08 (4H, m), 8.76 (1H, s); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 40.0, 110.7, 116.1 (d, $J_{\text{C-F}} = 22.1$ Hz), 120.4, 131.4 (d, $J_{\text{C-F}} = 3.5$ Hz), 132.0 (d, $J_{\text{C-F}} = 8.9$ Hz), 132.3, 153.8, 162.5, 165.6 (d, $J_{\text{C-F}} = 254.0$ Hz), 180.0; IR (KBr): 2910, 2814, 1647, 1601, 1508, 1367, 1231, 1173, 1043, 822 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{15}\text{FNaN}_2\text{O}_2$ ($[\text{M} + \text{Na}]^+$) 325.1323. Found 325.1318.

***N*-(4-phenylbenzylidene)-4-(dimethylamino)benzamide (2, $\text{R}' = p\text{-Me}_2\text{N-C}_6\text{H}_4$, $\text{Ar} = p\text{-Ph-C}_6\text{H}_4$):** Reaction performed utilizing the same procedure for the preparation of *N*-benzylidene-4-(dimethylamino)benzamide. ^1H NMR (CDCl_3 , 270 MHz) δ 3.08 (6H, s), 6.69 (2H, dt, $J = 9.4, 2.2$ Hz), 7.41-7.52 (3H, m), 7.65-7.75 (4H, m), 8.03-8.10 (4H, m), 8.83 (1H, s); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 40.1, 110.7, 120.6, 127.2, 127.5, 128.1, 128.9, 130.3, 132.2, 133.9, 140.0, 145.4, 153.7, 163.3, 180.1; IR (KBr): 2895, 1655, 1601, 1551, 1371, 1169, 1045, 775, 694 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{20}\text{NaN}_2\text{O}$ ($[\text{M} + \text{Na}]^+$) 351.1468. Found 351.1468.

***N*-(4-methylbenzylidene)-4-(dimethylamino)benzamide (2, $\text{R}' = p\text{-Me}_2\text{N-C}_6\text{H}_4$, $\text{Ar} = p\text{-Me-C}_6\text{H}_4$):** Reaction performed utilizing the same procedure for the preparation of *N*-benzylidene-4-(dimethylamino)benzamide. ^1H NMR (CDCl_3 , 270 MHz) δ 2.44 (3H, s), 3.06 (6H, s), 6.67 (2H, dt, $J = 9.2, 2.4$ Hz), 7.30 (2H, d, $J = 8.0$ Hz), 7.81 (2H, d, $J = 8.0$ Hz), 8.06 (2H, dt, $J = 9.2, 2.4$ Hz), 8.75 (1H, s); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 21.8, 40.0, 110.6, 120.5, 129.4,

129.7, 132.1, 132.3, 143.4, 153.5, 163.5, 180.2; IR (KBr): 2903, 1651, 1603, 1369, 1167, 1043, 810, 723 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{22}\text{NaN}_2\text{O}_2$ ($[\text{M} + \text{CH}_3\text{OH} + \text{Na}]^+$) 321.1573. Found 321.1569.

***N*-(4-methoxybenzylidene)-4-(dimethylamino)benzamide (2, $\text{R}' = p\text{-Me}_2\text{N-C}_6\text{H}_4$, $\text{Ar} = p\text{-MeO-C}_6\text{H}_4$):** Reaction performed utilizing the same procedure for the preparation of *N*-benzylidene-4-(dimethylamino)benzamide. ^1H NMR (CDCl_3 , 270 MHz) δ 3.05 (6H, s), 3.87 (3H, s), 6.67 (2H, dt, $J = 9.2, 2.4$ Hz), 6.98 (2H, dt, $J = 8.9, 2.2$ Hz), 7.92 (2H, dt, $J = 8.9, 2.2$ Hz), 8.08 (2H, dt, $J = 9.2, 2.4$ Hz), 8.75 (1H, s); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 40.0, 55.4, 110.6, 114.2, 120.9, 127.9, 131.8, 132.2, 153.6, 164.4₀, 164.4₂, 180.2; IR (KBr): 3063, 2903, 1655, 1601, 1512, 1369, 1254, 1178, 1159, 1049, 750 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{19}\text{NaN}_2\text{O}_2$ ($[\text{M} + \text{Na}]^+$) 305.1260. Found 305.1260.

***N*-(2-fluorobenzylidene)-4-(dimethylamino)benzamide (2, $\text{R}' = p\text{-Me}_2\text{N-C}_6\text{H}_4$, $\text{Ar} = o\text{-F-C}_6\text{H}_4$):** Reaction performed utilizing the same procedure for the preparation of *N*-benzylidene-4-(dimethylamino)benzamide. ^1H NMR (CDCl_3 , 270 MHz) δ 3.06 (6H, s), 6.67 (2H, dt, $J = 9.2, 2.4$ Hz), 7.14 (1H, t, $J = 8.6$ Hz), 7.26 (1H, t, $J = 7.6$ Hz), 7.48-7.57 (1H, m), 8.02 (2H, dt, $J = 9.2, 2.4$ Hz), 8.21 (1H, td, $J = 7.6, 1.6$ Hz), 9.07 (1H, s); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 40.0, 110.6, 116.0 (d, $J_{\text{C-F}} = 20.6$ Hz), 120.1, 122.8 (d, $J_{\text{C-F}} = 10.8$ Hz), 124.4 (d, $J_{\text{C-F}} = 3.9$ Hz), 128.3 (d, $J_{\text{C-F}} = 2.0$ Hz), 132.2, 134.4 (d, $J_{\text{C-F}} = 8.8$ Hz), 153.7, 157.0 (d, $J_{\text{C-F}} = 4.9$ Hz), 163.5 (d, $J_{\text{C-F}} = 256.0$ Hz), 180.1; IR (KBr): 3080, 2910, 1655, 1607, 1529, 1377, 1271, 1175, 1030, 775 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{15}\text{FNaN}_2\text{O}_2$ ($[\text{M} + \text{Na}]^+$) 293.1061. Found 293.1060.

***N*-(2-methoxybenzylidene)-4-(dimethylamino)benzamide (2, $\text{R}' = p\text{-Me}_2\text{N-C}_6\text{H}_4$, $\text{Ar} = o\text{-MeO-C}_6\text{H}_4$):** Reaction performed utilizing the same procedure for the preparation of *N*-benzylidene-4-(dimethylamino)benzamide. ^1H NMR (CDCl_3 , 270 MHz) δ 3.03 (6H, s), 3.86 (3H, s), 6.65 (2H, dt, $J = 9.2, 2.4$ Hz), 6.94 (1H, d, $J = 8.4$ Hz), 7.04

(1H, t, $J = 7.8$ Hz), 7.46-7.52 (1H, m), 8.04 (2H, dt, $J = 9.2, 2.4$ Hz), 8.20 (1H, dd, $J = 7.8, 1.9$ Hz), 9.24 (1H, s); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 40.0, 55.5, 110.5, 111.2, 120.5, 120.6, 123.3, 127.9, 132.0, 134.2, 153.4, 159.5, 160.5, 180.7; IR (KBr): 2918, 1655, 1597, 1364, 1246, 1175, 1159, 1043, 758 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{18}\text{NaN}_2\text{O}_2$ ($[\text{M} + \text{Na}]^+$) 305.1260. Found 305.1261.

***N*-(3-fluorobenzylidene)-4-(dimethylamino)benzamide (2, $\text{R}' = p\text{-Me}_2\text{N-C}_6\text{H}_4$, $\text{Ar} = m\text{-F-C}_6\text{H}_4$):** Reaction performed utilizing the same procedure for the preparation of *N*-benzylidene-4-(dimethylamino)benzamide. ^1H NMR (CDCl_3 , 270 MHz) δ 3.07 (6H, s), 6.67 (2H, d, $J = 9.2$ Hz), 7.22-7.29 (1H, m), 7.47 (1H, td, $J = 8.2, 5.4$ Hz), 7.65-7.73 (2H, m), 8.04 (2H, dt, $J = 9.2, 2.4$ Hz), 8.74 (1H, s); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 40.0, 110.6, 115.1 (d, $J_{\text{C-F}} = 21.6$ Hz), 119.6 (d, $J_{\text{C-F}} = 21.6$ Hz), 120.0, 126.1 (d, $J_{\text{C-F}} = 3.0$ Hz), 130.3 (d, $J_{\text{C-F}} = 7.9$ Hz), 132.1, 137.1 (d, $J_{\text{C-F}} = 6.9$ Hz), 153.7, 162.2 (d, $J_{\text{C-F}} = 3.0$ Hz), 162.8 (d, $J_{\text{C-F}} = 247.2$ Hz), 179.6; IR (KBr): 3057, 2903, 1661, 1605, 1528, 1364, 1259, 1177, 1045, 795, 677 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{15}\text{FNaN}_2\text{O}$ ($[\text{M} + \text{Na}]^+$) 293.1061. Found 293.1060.

***N*-piperonyliden-4-(dimethylamino)benzamide (2, $\text{R}' = p\text{-Me}_2\text{N-C}_6\text{H}_4$, $\text{Ar} = \text{piperonyl}$):** Reaction performed utilizing the same procedure for the preparation of *N*-benzylidene-4-(dimethylamino)benzamide. ^1H NMR (CDCl_3 , 270 MHz) δ 3.05 (6H, s), 6.05 (2H, s), 6.65 (2H, dt, $J = 9.4, 2.4$ Hz), 6.88 (1H, d, $J = 8.0$ Hz), 7.35 (1H, dd, $J = 8.0, 1.6$ Hz), 7.59 (1H, d, $J = 1.6$ Hz), 8.05 (2H, dt, $J = 9.4, 2.4$ Hz), 8.69 (1H, s); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 40.0, 101.8, 107.2, 108.2, 110.6, 120.7, 127.8, 129.8, 132.2, 148.3, 151.7, 153.5, 163.2, 179.8; IR (KBr): 2895, 1655, 1597, 1369, 1256, 1173, 1036, 816 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{19}\text{FNaN}_2\text{O}_2$ ($[\text{M} + \text{Na}]^+$) 319.1053. Found 319.1054.

2. Preparation of β -Amino- α -Diazoester.

Representative Procedure for the Direct Alkylation of α -Diazoester Catalyzed by Chiral Phosphoric Acid

((R)-5): To a dried test tube was weighted 1.40 mg of phosphoric acid ((R)-5) (2 mol%, 0.002 mmol) and 31.4 mg of *N*-benzylidenebenzamide (**2**, R', Ar = Ph, 1.5 equiv, 0.15 mmol). The atmosphere was replaced by nitrogen. After the catalyst and imine were dissolved into 1 mL of toluene, 11.4 mg of Ethyl diazoacetate (**1a**, 1.0 equiv, 0.10 mmol) were introduced as neat at rt. The resulting solution was stirred for 5 hours at the ambient temperature. The reaction mixture was directly purified by silica gel column chromatography (Hexane/EtOAc = 10/1-3/1 as eluent) to give β -amino- α -diazoester (**3a**, R = Ph) was obtained in 59% yield as yellow oil. Enantiomeric excess was determined by chiral stationary phase HPLC analysis. C-2 of β -amino- α -diazoester (**3a**, R = Ph) was not detected with ^{13}C NMR spectra, but vibration of diazo was observed at 2089-2104 cm^{-1} . **ethyl 3-(benzamido)-2-diazo-3-phenylpropanoate (**3a**, R', Ar = Ph):** R_f = 0.39 (Hexane/EtOAc = 2/1); HPLC analysis Chiralcel OD-H (Hexane/EtOH = 95/5, 1.0 mL/min, 254 nm, 10 °C) 17.5 (major), 19.9 min; ^1H NMR (CDCl_3 , 270 MHz) δ 1.27 (3H, t, J = 7.0 Hz), 4.24 (2H, q, J = 7.0 Hz), 6.20 (1H, d, J = 8.1 Hz), 7.29-7.56 (9H, m), 7.84 (2H, dt, J = 6.8, 1.6 Hz); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 14.5, 50.2, 61.2, 126.2, 127.0, 128.0, 128.6, 128.9, 131.8, 133.6, 138.8, 166.3, 166.5; IR (KBr): 3423, 2104, 1711, 1630, 1522, 1485, 1109, 719 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{18}\text{NaN}_3\text{O}_3$ ($[\text{M} + \text{Na}]^+$) 346.1162. Found 346.1160.

isopropyl 3-(benzamido)-2-diazo-3-phenylpropanoate (R', Ar = Ph): R_f = 0.40 (Hexane/EtOAc = 2/1); HPLC analysis Chiralcel OD-H (Hexane/EtOH = 98/2, 0.7 mL/min, 254 nm, 10 °C) 23.6 (major), 26.7 min; ^1H NMR (CDCl_3 , 270 MHz) δ 1.25 (6H, d, J = 6.4 Hz), 5.10 (1H, sept, J = 6.4 Hz), 6.20 (1H, d, J = 8.1 Hz), 7.28-7.56 (9H, m), 7.82-7.86 (2H, m); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 22.1, 50.2, 69.0, 126.2, 127.0, 128.0, 128.6, 128.8, 131.8, 133.7, 138.9, 165.9, 166.4; IR (KBr): 3337, 3080, 2984, 2104, 1697, 1632, 1524, 1489, 1101, 718, 702 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{19}\text{H}_{20}\text{NaN}_3\text{O}_3$ ($[\text{M} + \text{Na}]^+$) 360.1319. Found 360.1319.

tert-butyl 3-(benzamido)-2-diazo-3-phenylpropanoate (3b**, R' Ar = Ph):** R_f = 0.66 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/ i PrOH = 90/10, 1.0 mL/min, 254 nm, 10 °C) 13.0 (major), 19.9 min; ^1H NMR (CDCl_3 , 270 MHz) δ 1.46 (9H, s), 6.17 (1H, d, J = 8.4 Hz), 7.26-7.56 (9H, m), 7.83 (2H, dt, J = 6.4, 1.6 Hz); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 28.3, 50.1, 82.3, 126.3, 127.1, 128.0, 128.7, 128.9, 131.9, 133.8, 139.1, 165.8, 166.5; IR (KBr): 3298, 3032, 2976, 2093, 1692, 1638, 1541, 1105, 698 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{21}\text{NaN}_3\text{O}_3$ ($[\text{M} + \text{Na}]^+$) 374.1475. Found 374.1474. For a derivatization described below, the title compound was recrystallized from CH_2Cl_2 /hexane (99.6% ee).

tert-butyl 3-(2-bromobenzamido)-2-diazo-3-phenylpropanoate (3b, R' = *o*-Br-C₆H₄, Ar = Ph): R_f = 0.55 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/*i*PrOH = 90/10, 1.0 mL/min, 254 nm, 10 °C) 14.0 (major), 24.2 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.45 (9H, s), 6.16 (1H, d, J = 7.8 Hz), 7.11 (1H, brs), 7.29-7.46 (7H, m), 7.56-7.62 (2H, m); ¹³C NMR (CDCl₃, 67.8 MHz) δ 28.3, 50.4, 82.3, 119.3, 126.4, 127.6, 128.1, 128.9, 129.9, 131.6, 133.5, 137.0, 138.4, 165.4, 166.8; IR (KBr): 3423, 2984, 2935, 2095, 1686, 1647, 1522, 1462, 1169, 1132, 1024, 746, 694 cm⁻¹; HRMS (ESI) Calcd for C₂₀H₂₀BrNaN₃O₃ ([M + Na]⁺) 452.0580, 454.0560. Found 452.0578, 454.0558.

tert-butyl 3-(2-methylbenzamido)-2-diazo-3-phenylpropanoate (3b, R' = *o*-Me-C₆H₄, Ar = Ph): R_f = 0.62 (Hexane/EtOAc = 1/2); HPLC analysis Chiralpak AD-H (Hexane/*i*PrOH = 90/10, 1.0 mL/min, 254 nm, 10 °C) 12.2 (major), 17.5 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.46 (9H, s), 2.47 (3H, s), 6.13 (1H, d, J = 8.4 Hz), 6.91 (1H, brs), 7.19-7.43 (9H, m); ¹³C NMR (CDCl₃, 67.8 MHz) δ 19.9, 28.3, 50.0, 82.2, 125.8, 126.3, 126.9, 128.0, 128.9, 130.3, 131.2, 135.5, 136.4, 138.9, 165.5, 169.1; IR (KBr): 3267, 3072, 2978, 2095, 1686, 1638, 1508, 1103, 741 cm⁻¹; HRMS (ESI) Calcd for C₂₁H₂₃NaN₃O₃ ([M + Na]⁺) 388.1632. Found 388.1631.

tert-butyl 3-(2-methoxybenzamido)-2-diazo-3-phenylpropanoate (3b, R' = *o*-MeO-C₆H₄, Ar = Ph): R_f = 0.28 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/*i*PrOH = 80/20, 1.0 mL/min, 254 nm, 10 °C) 13.1 (major), 24.9 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.45 (9H, s), 3.97 (3H, s), 6.21 (1H, d, J = 8.1 Hz), 7.00 (1H, d, J = 8.4 Hz), 7.09 (1H, t, J = 7.8 Hz), 7.28-7.51 (6H, m), 8.23 (1H, dd, J = 7.8, 1.9 Hz), 9.00 (1H, brs); ¹³C NMR (CDCl₃, 67.8 MHz) δ 19.9, 28.3, 50.0, 82.2, 125.8, 126.3, 126.9, 128.0, 128.9, 130.3, 131.2, 135.5, 136.4, 138.9, 165.5, 169.1; IR (KBr): 3387, 2984, 2956, 2093, 1686, 1655, 1508, 1483, 1244, 1130, 754 cm⁻¹; HRMS (ESI) Calcd for C₂₁H₂₃NaN₃O₄ ([M + Na]⁺) 404.1581. Found 404.1578.

tert-butyl 3-(3-methoxybenzamido)-2-diazo-3-phenylpropanoate (3b, R' = *m*-MeO-C₆H₄, Ar = Ph): R_f = 0.52 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/*i*PrOH = 90/10, 1.0 mL/min, 254 nm, 10 °C) 15.4 (major), 27.4 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.46 (9H, s), 3.85 (3H, s), 6.15 (1H, d, J = 8.4 Hz), 7.04-7.08 (1H, m), 7.28-7.43 (9H, m); ¹³C NMR (CDCl₃, 67.8 MHz) δ 28.4, 50.2, 55.5, 82.3, 112.4, 118.1, 118.7, 126.2, 127.9, 128.8, 129.6, 135.2, 139.0, 159.8, 165.6, 166.3; IR (KBr): 3418, 2984, 2935, 2095, 1686, 1638, 1528, 1483, 1248, 1117, 746, 706 cm⁻¹; HRMS (ESI) Calcd for C₂₁H₂₃NaN₃O₄ ([M + Na]⁺) 404.1581. Found 404.1579.

tert-butyl 3-(1-naphthamido)-2-diazo-3-phenylpropanoate (3b, R' = 1-Naphthyl, Ar = Ph): R_f = 0.62 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/*i*PrOH = 90/10, 1.0 mL/min, 254 nm, 10 °C) 18.9 (major), 28.3 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.47 (9H, s), 6.27 (1H, d, J = 8.1 Hz), 7.11 (1H, brs), 7.30-7.59 (8H, m), 7.67 (1H, dd, J = 7.3, 1.1 Hz), 7.86-7.90 (1H, m) 7.94 (1H, d, J = 8.4 Hz), 8.36 (1H, dd, J = 7.3, 3.0 Hz); ¹³C NMR (CDCl₃, 67.8 MHz) δ 28.3, 50.1, 82.3, 124.7, 125.2, 125.4, 126.3, 126.5, 127.3, 128.1, 128.3, 129.0, 130.2, 131.1, 133.6, 133.7, 138.8, 165.5, 168.7; IR (KBr): 3423, 3265, 2966, 2926, 2097, 1682, 1639, 1522, 1161, 710 cm⁻¹; HRMS (ESI) Calcd for C₂₄H₂₃NaN₃O₃ ([M + Na]⁺) 424.1632. Found 424.1635.

tert-butyl 3-(4-bromobenzamido)-2-diazo-3-phenylpropanoate (3b, R' = *p*-Br-C₆H₄, Ar = Ph): R_f = 0.72 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/*i*PrOH = 85/15, 1.0 mL/min, 254 nm, 10 °C) 15.9 (major), 29.4 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.46 (9H, s), 6.14 (1H, d, J = 8.4 Hz), 7.31-7.39 (6H, m), 7.58 (2H, d, J = 8.6 Hz), 7.69 (2H, d, J = 8.6 Hz); ¹³C NMR (CDCl₃, 67.8 MHz) δ 28.3, 50.2, 82.4, 126.2, 126.6, 128.1, 128.7, 128.9, 131.9, 132.6, 139.0, 165.6, 165.9; IR (KBr): 3321, 2991, 2918, 2093, 1686, 1638, 1528, 1481, 1163, 1113, 1011, 746, 698 cm⁻¹; HRMS (ESI) Calcd for C₂₀H₂₀BrNaN₃O₃ ([M + Na]⁺) 452.0580, 454.0560. Found 452.0579, 454.3560.

tert-butyl 3-(4-methylbenzamido)-2-diazo-3-phenylpropanoate (3b, R' = *p*-Me-C₆H₄, Ar = Ph): R_f = 0.62 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/*i*PrOH = 90/10, 1.0 mL/min, 254 nm, 10 °C) 17.1 (major), 38.9 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.45 (9H, s), 2.40 (3H, s), 6.16 (1H, d, J = 8.4 Hz), 7.24-7.43 (8H, m), 7.73 (2H, d, J = 8.1 Hz); ¹³C NMR (CDCl₃, 67.8 MHz) δ 21.4, 28.3, 50.0, 82.3, 126.3, 127.1, 128.0, 128.9, 129.3, 130.9, 139.3, 142.4, 165.8, 166.5; IR (KBr): 3385, 2991, 2926, 2095, 1686, 1638, 1528, 1499, 1117, 743, 698 cm⁻¹; HRMS (ESI) Calcd for C₂₁H₂₃NaN₃O₃ ([M + Na]⁺) 388.1632. Found 388.1631.

tert-butyl 3-(4-methoxybenzamido)-2-diazo-3-phenylpropanoate (3b, R' = *p*-MeO-C₆H₄, Ar = Ph): R_f = 0.24 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/*i*PrOH = 80/20, 1.0 mL/min, 254 nm, 10 °C) 11.9 (major), 22.1 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.46 (9H, s), 3.85 (3H, s), 6.15 (1H, d, J = 8.1 Hz), 6.94 (2H, dt, J = 8.6, 3.0 Hz), 7.29-7.43 (6H, m), 7.79 (2H, dt, J = 8.6, 3.0 Hz); ¹³C NMR (CDCl₃, 67.8 MHz) δ 28.3, 50.0, 55.4, 82.2, 113.8, 126.0, 126.3, 127.9, 128.8, 128.9, 139.3, 162.5, 165.9, 166.1; IR (KBr): 3304, 2991, 2926, 2095, 1686, 1638, 1501, 1254, 1109, 706 cm⁻¹; HRMS (ESI) Calcd for C₂₁H₂₃NaN₃O₄ ([M + Na]⁺) 404.1581. Found 404.1579.

tert-butyl 3-(4-dimethylaminobenzamido)-2-diazo-3-phenylpropanoate (3b, R' = *p*-Me₂N-C₆H₄, Ar = Ph): R_f = 0.45 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/*i*PrOH = 85/15, 1.0 mL/min, 254 nm, 10 °C) 26.4 (major), 43.7 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.45 (9H, s), 3.02 (6H, s), 6.17 (1H, d, J = 8.4 Hz), 6.68 (2H, dt, J = 9.2, 2.7 Hz), 7.20 (1H, brs), 7.28-7.43 (5H, m), 7.73 (2H, dt, J = 9.2, 2.7 Hz); ¹³C NMR (CDCl₃, 67.8 MHz) δ 28.3, 40.1, 49.8, 82.1, 111.0, 120.4, 126.3, 127.8, 128.6, 128.7, 139.6, 152.7, 165.9, 166.5; IR (KBr): 3416, 2974, 2926, 2093, 1686, 1609, 1508, 1369, 1171, 1124, 702 cm⁻¹; HRMS (ESI) Calcd for C₂₂H₂₆NaN₄O₃ ([M + Na]⁺) 417.1897. Found 417.1893.

tert-butyl 3-(4-dimethylaminobenzamido)-2-diazo-3-(4-fluorophenyl)propanoate (3b, R' = *p*-Me₂N-C₆H₄, Ar = *p*-F-C₆H₄): R_f = 0.39 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/ⁱPrOH = 80/20, 1.0 mL/min, 254 nm, 10 °C) 18.6 (major), 33.7 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.45 (9H, s), 3.03 (6H, s), 6.13 (1H, d, *J* = 8.4 Hz), 6.67 (2H, dt, *J* = 8.9, 2.4 Hz), 7.03 (2H, tt, *J* = 7.7, 2.4 Hz), 7.26 (1H, brs), 7.36-7.41 (2H, m), 7.72 (2H, dt, *J* = 8.9, 2.4 Hz); ¹³C NMR (CDCl₃, 67.8 MHz) δ 28.4, 40.1, 49.4, 82.2, 111.0, 115.5 (d, *J*_{C-F} = 21.6 Hz), 120.1, 127.9 (d, *J*_{C-F} = 8.9 Hz), 128.5, 135.4 (d, *J*_{C-F} = 2.9 Hz), 152.6, 162.1 (d, *J*_{C-F} = 245.2 Hz), 165.7, 166.4; IR (KBr): 3435, 2991, 2926, 2095, 1686, 1609, 1508, 1369, 1225, 1159, 772 cm⁻¹; HRMS (ESI) Calcd for C₂₂H₂₅FN₄O₃ ([M + Na]⁺) 435.1803. Found 435.1805.

tert-butyl 3-(4-dimethylaminobenzamido)-2-diazo-3-(4-biphenyl)propanoate (3b, R' = *p*-Me₂N-C₆H₄, Ar = *p*-Ph-C₆H₄): R_f = 0.29 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/ⁱPrOH = 75/25, 1.0 mL/min, 254 nm, 10 °C) 19.9 (major), 34.5 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.47 (9H, s), 3.03 (6H, s), 6.22 (1H, d, *J* = 8.1 Hz), 6.69 (2H, d, *J* = 8.9, 2.4 Hz), 7.20 (1H, brs), 7.32-7.37 (1H, m), 7.41-7.50 (4H, m), 7.57-7.60 (4H, m), 7.76 (2H, dt, *J* = 8.9, 2.4 Hz); ¹³C NMR (CDCl₃, 67.8 MHz) δ 28.4, 40.1, 49.7, 82.1, 111.0, 120.2, 126.7, 127.0, 127.2, 127.4, 128.6, 128.7, 138.6, 140.5, 140.6, 152.6, 165.8, 166.4; IR (KBr): 3423, 2984, 2926, 2089, 1686, 1609, 1543, 1369, 1173, 1121, 762 cm⁻¹; HRMS (ESI) Calcd for C₂₈H₃₀NaN₄O₃ ([M + Na]⁺) 493.2210. Found 493.2211.

tert-butyl 3-(4-dimethylaminobenzamido)-2-diazo-3-(4-methylphenyl)propanoate (3b, R' = *p*-Me₂N-C₆H₄, Ar = *p*-Me-C₆H₄): R_f = 0.40 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/ⁱPrOH = 80/20, 1.0 mL/min, 254 nm, 10 °C) 23.2 (major), 35.1 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.45 (9H, s), 2.33 (3H, s), 3.02 (6H, s), 6.12 (1H, d, *J* = 8.4 Hz), 6.68 (2H, dt, *J* = 9.2, 2.4 Hz), 7.16 (2H, d, *J* = 8.0 Hz, and 1H, brs), 7.30 (2H, d, *J* = 8.0 Hz), 7.72 (2H, dt, *J* = 9.2, 2.4 Hz); ¹³C NMR (CDCl₃, 67.8 MHz) δ 21.0, 28.3, 40.1, 49.7, 82.0, 111.0, 120.5, 126.2, 128.6,

129.4, 136.6, 137.5, 152.7, 165.9, 166.5; IR (KBr): 3385, 2991, 2926, 2093, 1686, 1609, 1508, 1369, 1169, 1124, 775 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{28}\text{NaN}_4\text{O}_3$ ($[\text{M} + \text{Na}]^+$) 431.2054. Found 431.2056.

tert-butyl 3-(4-dimethylaminobenzamido)-2-diazo-3-(4-methoxyphenyl)propanoate (3b, $\text{R}' = p\text{-Me}_2\text{N-C}_6\text{H}_4$, $\text{Ar} = p\text{-MeO-C}_6\text{H}_4$): $\text{R}_f = 0.18$ (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/ i PrOH = 75/25, 1.0 mL/min, 254 nm, 10 $^\circ\text{C}$) 21.4 (major), 37.3 min; ^1H NMR (CDCl_3 , 270 MHz) δ 1.45 (9H, s), 3.02 (6H, s), 3.79 (3H, s), 6.10 (1H, d, $J = 8.4$ Hz), 6.67 (2H, dt, $J = 8.9, 2.4$ Hz), 6.88 (2H, dt, $J = 8.4, 3.0$ Hz), 7.13 (1H, brs), 7.33 (2H, d, $J = 8.4$ Hz), 7.72 (2H, dt, $J = 8.9, 2.4$ Hz); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 28.4, 40.1, 49.4, 55.3, 82.0, 111.0, 114.1, 120.4, 127.5, 128.6, 131.8, 152.7, 159.1, 165.9, 166.4; IR (KBr): 3422, 2926, 2854, 2089, 1691, 1610, 1508, 1369, 1247, 1177, 1028, 743 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{28}\text{NaN}_4\text{O}_4$ ($[\text{M} + \text{Na}]^+$) 447.2003. Found 447.2002.

tert-butyl 3-(4-dimethylaminobenzamido)-2-diazo-3-(2-fluorophenyl)propanoate (3b, $\text{R}' = p\text{-Me}_2\text{N-C}_6\text{H}_4$, $\text{Ar} = o\text{-F-C}_6\text{H}_4$): $\text{R}_f = 0.32$ (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/EtOH = 90/10, 1.0 mL/min, 254 nm, 10 $^\circ\text{C}$) 26.9, 30.0 (major) min; ^1H NMR (CDCl_3 , 270 MHz) δ 1.44 (9H, s), 3.03 (6H, s), 6.35 (1H, d, $J = 8.4$ Hz), 6.68 (2H, dt, $J = 8.9, 2.4$ Hz), 7.04-7.14 (2H, m), 7.35 (1H, brs), 7.23-7.31 (1H, m), 7.44 (1H, t, $J = 7.6$ Hz), 7.73 (2H, dt, $J = 8.9, 2.4$ Hz); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 28.4, 40.1, 45.0, 82.1, 111.0, 115.6 (d, $J_{\text{C-F}} = 21.6$ Hz), 120.2, 124.1 (d, $J_{\text{C-F}} = 2.9$ Hz), 126.8 (d, $J_{\text{C-F}} = 13.7$ Hz), 128.1 (d, $J_{\text{C-F}} = 3.9$ Hz), 128.5, 129.4 (d, $J_{\text{C-F}} = 7.9$ Hz), 152.6, 160.3 (d, $J_{\text{C-F}} = 244.3$ Hz), 165.5, 166.0; IR (KBr): 3337, 2984, 2918, 2093, 1690, 1609, 1508, 1369, 1300, 1173, 1113, 758 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{25}\text{FNaN}_4\text{O}_3$ ($[\text{M} + \text{Na}]^+$) 435.1803. Found 435.1800.

tert-butyl 3-(4-dimethylaminobenzamido)-2-diazo-3-(2-methoxyphenyl)propanoate (3b, $\text{R}' = p\text{-Me}_2\text{N-C}_6\text{H}_4$, $\text{Ar} = o\text{-MeO-C}_6\text{H}_4$): $\text{R}_f = 0.19$ (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/ i PrOH = 85/15, 1.0

mL/min, 254 nm, 10 °C) 26.2 (major), 37.0 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.44 (9H, s), 3.02 (6H, s), 3.90 (3H, s), 6.30 (1H, d, *J* = 9.2 Hz), 6.68 (2H, dt, *J* = 8.9, 2.4 Hz), 6.90-6.95 (2H, m), 7.26 (1H, td, *J* = 7.6, 1.8 Hz), 7.37 (1H, d, *J* = 7.3 Hz), 7.50 (1H, brs), 7.71 (2H, dt, *J* = 8.9, 2.4 Hz); ¹³C NMR (CDCl₃, 67.8 MHz) δ 28.5, 40.2, 46.0, 55.4, 81.7, 110.5, 111.0, 120.6, 120.8, 127.5, 128.0, 128.4, 128.8, 152.4, 156.7, 165.7, 165.9; IR (KBr): 3443, 2974, 2926, 2093, 1690, 1609, 1508, 1491, 1367, 1246, 1169, 1051, 750 cm⁻¹; HRMS (ESI) Calcd for C₂₃H₂₈NaN₄O₄ ([M + Na]⁺) 447.2003. Found 447.2003.

tert-butyl 3-(4-dimethylaminobenzamido)-2-diazo-3-(3-fluorophenyl)propanoate (3b, R' = *p*-Me₂N-C₆H₄, Ar = *m*-F-C₆H₄): R_f = 0.39 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/ⁱPrOH = 80/20, 1.0 mL/min, 254 nm, 10 °C) 17.2 (major), 23.6 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.45 (9H, s), 3.03 (6H, s), 6.16 (1H, d, *J* = 8.4 Hz), 6.68 (2H, dt, *J* = 8.9, 2.4 Hz), 6.97 (1H, td, *J* = 8.1, 2.2 Hz), 7.11-7.20 (3H, m), 7.32 (2H, td, *J* = 8.1, 5.9 Hz), 7.73 (2H, dt, *J* = 8.9, 2.4 Hz); ¹³C NMR (CDCl₃, 67.8 MHz) δ 28.4, 40.2, 49.6, 82.4, 110.0, 113.4 (d, *J*_{C-F} = 22.6 Hz), 114.6 (d, *J*_{C-F} = 20.6 Hz), 120.0, 121.9 (d, *J*_{C-F} = 2.9 Hz), 128.6, 130.2 (d, *J*_{C-F} = 8.8 Hz), 142.3 (d, *J*_{C-F} = 5.9 Hz), 152.7, 162.9 (d, *J*_{C-F} = 246.2 Hz), 165.6, 166.4; IR (KBr): 3435, 2984, 2935, 2095, 1686, 1609, 1508, 1369, 1292, 1168, 1132, 775 cm⁻¹; HRMS (ESI) Calcd for C₂₂H₂₅FN₄O₃ ([M + Na]⁺) 435.1803. Found 435.1803.

tert-butyl 3-(4-dimethylaminobenzamido)-2-diazo-3-(piperonyl)propanoate (3b, R' = *p*-Me₂N-C₆H₄, Ar = piperonyl): R_f = 0.25 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/EtOH = 80/20, 1.0 mL/min, 254 nm, 10 °C) 25.7 (major), 36.2 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.46 (9H, s), 3.02 (6H, s), 5.95 (2H, s), 6.06 (1H, d, *J* = 8.1 Hz), 6.67 (2H, dt, *J* = 9.2, 2.4 Hz), 6.77 (1H, d, *J* = 7.8 Hz), 6.89-6.91 (2H, m), 7.18 (1H, brs), 7.72 (2H, dt, *J* = 9.2, 2.4 Hz); ¹³C NMR (CDCl₃, 67.8 MHz) δ 28.4, 40.1, 49.7, 82.1, 101.1, 107.0, 108.3, 111.0, 119.6, 120.3, 128.5, 133.6, 147.1, 148.0, 152.6, 165.7, 166.3; IR (KBr): 3426, 2984, 2926, 2095, 1686, 1609, 1502, 1491, 1369, 1234, 1169, 1040, 743 cm⁻¹; HRMS (ESI) Calcd for C₂₃H₂₆NaN₄O₅ ([M + Na]⁺) 461.1795. Found 461.1794.

3. Synthesis of *tert*-butyl-(*R*)-3-amino-3-phenylpropanoate (6).

Reduction of diazo moiety of *tert*-butyl 3-(benzamido)-2-diazo-3-phenylpropanoate ($R' = p\text{-Me}_2\text{N-C}_6\text{H}_4$, $\text{Ar} = \text{Ph}$): To a solution of *tert*-butyl 3-(4-dimethylaminobenzamido)-2-diazo-3-phenylpropanoate (**3b**, $R' = p\text{-Me}_2\text{N-C}_6\text{H}_4$, $\text{Ar} = \text{Ph}$, 39.5 mg, 0.1 mmol) in EtOAc/AcOH (v/v = 10/1, 1.1 mL) was added 10 mol% PtO_2 (2.27 mg, 0.01 mmol). The reaction mixture was stirred for 6 h under 1 atm hydrogen atmosphere. After removing of PtO_2 by filtration, the filtrate was diluted with CH_2Cl_2 and washed with saturated aqueous NaHCO_3 . The organic extract was dried over Na_2SO_4 and filtered. After being concentrated, the resulting residue was purified by fractional HPLC (hexane/EtOAc = 2/1) to give the title compound in 79% yield (97% ee) as white solid. ***tert*-butyl 3-(4-dimethylaminobenzamido)-3-phenylpropanoate ($R' = p\text{-Me}_2\text{N-C}_6\text{H}_4$, $\text{Ar} = \text{Ph}$):** $R_f = 0.39$ (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/ i PrOH = 85/15, 0.8 mL/min, 254 nm, 10 °C) 18.5, 34.0 (major) min; ^1H NMR (CDCl_3 , 270 MHz) δ 1.34 (9H, s), 2.83 (1H, dd, $J = 15.4, 5.7$ Hz), 2.93 (1H, dd, $J = 15.4, 5.7$ Hz), 3.02 (6H, s), 5.59 (1H, td, $J = 8.6, 5.7$ Hz), 6.68 (2H, dt, $J = 9.2, 2.7$ Hz), 7.21-7.38 (6H, m), 7.74 (2H, dt, $J = 9.2, 2.7$ Hz); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 28.0, 40.2, 41.4, 49.8, 81.3, 111.0, 121.0, 126.2, 127.2, 128.3₉, 128.4₂, 141.0, 152.4, 166.2, 170.8; IR (KBr): 3435, 3285, 2978, 2926, 1726, 1624, 1508, 1367, 1148, 1057, 768 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{28}\text{N}_3\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$) 391.1992. Found 391.1992.

***tert*-butyl-(*R*)-3-amino-3-phenylpropanoate (**6**):**³ To a solution of *tert*-butyl 3-(4-dimethylaminobenzamido)-3-phenylpropanoate ($R' = p\text{-Me}_2\text{N-C}_6\text{H}_4$, $\text{Ar} = \text{Ph}$, 36.8 mg, 0.1 mmol) in CH_2Cl_2 (2.0 mL) was added 2,6-lutidine (30.0 mg, 0.28 mmol). The reaction mixture was cooled to -78 °C. TiF_2O (33.9 mg, 0.12 mmol) was added and the resulting yellowish solution was gradually warmed to 0 °C. After addition of MeOH (32.0 mg, 1.0 mmol) at 0 °C, the reaction mixture was gradually warmed to room temperature. The resulting solution was diluted with saturated aqueous NaHCO_3 and extracted with CH_2Cl_2 . The combined organic extracts were dried over Na_2SO_4 and filtered. After being concentrated, the residue was purified by column chromatography (Hexane/EtOAc = 10/1 as eluent) to give the corresponding imino ether in 70% yield as clear liquid. $R_f = 0.62$ (Hexane/EtOAc = 2/1); ^1H NMR (CDCl_3 , 270 MHz) δ 1.35 (9H, s), 2.59 (1H, dd, $J = 14.0, 8.9$ Hz), 2.93 (1H, dd, $J = 14.0, 4.0$ Hz), 2.96 (6H, s), 3.84 (3H, s), 4.96 (1H, dd, $J = 8.9, 4.9$ Hz), 6.63 (2H, dt, $J = 9.2, 2.4$ Hz), 7.15 (2H, dt, $J = 9.2, 2.4$ Hz), 7.20-7.42 (5H, m). To a solution of imino ether (39.5 mg, 0.05 mmol) in MeOH (1.0 mL) was added 10% Pd/C. The reaction mixture was stirred for 12 h under 1 atm hydrogen atmosphere. Pd/C was removed by filtration. After being concentrated, the resulting residue was purified by column chromatography (Hexane/EtOAc = 10/1-1/1 as eluent) to give the title compound in 60% yield as clear liquid. $R_f = 0.10$ (Hexane/EtOAc = 2/1); ^1H NMR (CDCl_3 , 270 MHz) δ 1.32 (9H, s), 1.69 (2H, brs), 2.49 (1H, d, $J = 6.8$ Hz), 4.28 (1H, t, $J = 6.8$ Hz), 7.16-7.28 (5H, m); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 28.0, 45.3, 52.8, 80.7, 126.3, 127.3, 128.5, 144.7, 171.3.

(3) Doi, H.; Sasai, T.; Iguchi, M.; Yamada, K.; Tomioka, K. *J. Am. Chem. Soc.* **2003**, *125*, 2887.

***tert*-butyl (*R*)-2-(*tert*-butoxycarbonyl)-1-phenylethylcarbamate:**⁴ To a solution of *tert*-butyl-(*R*)-3-amino-3-phenylpropanoate (**6**) (6.64 mg, 0.03 mmol) in CH₂Cl₂ (1.0 mL) was added Boc₂O (1.31 mg, 0.06 mmol). The reaction mixture was stirred for 2 h. After being concentrated, the resulting residue was purified by column chromatography (Hexane/EtOAc = 20/1-16/1 as eluent) to give the title compound in quant (97% ee) as white solid. *R*_f = 0.70 (Hexane/EtOAc = 2/1); HPLC analysis Chiralpak AD-H (Hexane/*i*PrOH = 97/3, 1.0 mL/min, 254 nm, 10 °C) 27.1, 31.2 (major) min; ¹H NMR (CDCl₃, 270 MHz) δ 1.33 (9H, s), 1.42 (9H, s), 2.70 (1H, dd, *J* = 14.9, 5.9 Hz), 2.77 (1H, dd, *J* = 14.9, 5.9 Hz), 5.05 (1H, brs), 5.47 (1H, brs), 7.21-7.35 (5H, m).

4. Synthesis of *tert*-butyl (2*S*, 3*S*) 3-benzoyloxy-2-hydroxy-3-phenylpropanoate (**7**).

Oxidation of the diazo moiety of *tert*-butyl 3-(benzamido)-2-diazo-3-phenylpropanoate (3b**, *R'*, *Ar* = *Ph*):** To a suspension of Oxone (153.7 mg, 0.25 mmol, 5 equiv) in water and acetone (2/1, 1.50 mL/0.75 mL) was added a solution of *tert*-butyl 3-(benzamido)-2-diazo-3-phenylpropanoate (**3b**, *R'*, *Ar* = *Ph*, 17.6 mg, 0.05 mmol, 99.6% ee) in CH₂Cl₂ (1.50 mL) over 5 min at 0 °C and stirring was continued for additional 30 min at room temperature. The resulting white suspension was diluted with water and extracted with CH₂Cl₂. The combined organic extracts were dried over Na₂SO₄ and filtered. After being concentrated, the resulting residue was used for the next reaction without further purification. (*S*)-*tert*-butyl-3-(benzamido)-2-oxo-3-phenylpropanoate (*R'*, *Ar* = *Ph*): *R*_f = 0.31 (Hexane/EtOAc = 2/1); ¹H NMR (CDCl₃, 270 MHz) δ 1.39 (9H, s), 6.40 (1H, d, *J* = 6.8 Hz), 7.26-7.51 (9H, m), 7.79-7.82 (2H, m); ¹³C NMR (CDCl₃, 67.8 MHz) δ 27.6, 60.6, 85.1, 127.0, 128.5, 128.7, 128.9, 129.1, 131.8, 133.3, 133.8, 158.6, 166.4, 189.9.

Synthesis of the α -hydroxy- β -amino acid ester: A solution of crude *tert*-butyl 3-(benzamido)-2-oxo-3-phenylpropanoate in MeOH (1 mL) was cooled to -78 °C. NaBH₄ (2.08 mg, 0.055 mmol) was added portionwise and the resulting colorless solution was stirred for 1.0 hour. The mixture was diluted with saturated aqueous NH₄Cl and extracted with CH₂Cl₂ twice. The combined organic extracts were dried over Na₂SO₄ and filtered. The resulting residue was purified by column chromatography (Hexane/EtOAc = 8/1-2/1 as eluent) to give *tert*-butyl (2*S*, 3*S*) 3-Benzoyloxy-2-hydroxy-3-phenylpropanoate (**7**) in 95% yield (2 steps) as white solid (99.6% ee). ***tert*-butyl (2*S*, 3*S*) 3-benzoyloxy-2-hydroxy-3-phenylpropanoate (**7**):** *R*_f = 0.21 (Hexane/EtOAc = 2/1); Chiralpak AD-H (Hexane/*i*PrOH = 80/20, 1.0 mL/min, 254 nm, 10 °C) 11.7 (major), 28.6 min; ¹H NMR (CDCl₃, 270 MHz) δ 1.37 (9H,

(4) Wenzel, A. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 12964.

s), 3.18 (1H, d, $J = 5.4$ Hz), 4.58 (1H, dd, $J = 5.4, 3.6$ Hz), 5.57 (1H, dd, $J = 8.6, 3.6$ Hz), 7.17 (1H, brd, $J = 8.6$ Hz), 7.27-7.35 (3H, m), 7.40-7.53 (5H, m), 7.81 (2H, dt, $J = 6.5, 1.6$ Hz); ^{13}C NMR (CDCl_3 , 67.8 MHz) δ 28.0, 55.2, 72.7, 83.8, 127.0, 128.0, 128.2, 128.3, 128.5, 131.6, 134.1, 136.8, 166.3, 170.7; IR (KBr): 3422, 2991, 2935, 1730, 1647, 1508, 1483, 1157, 700 cm^{-1} ; HRMS (ESI) Calcd for $\text{C}_{20}\text{H}_{23}\text{NaNO}_4$ ($[\text{M} + \text{Na}]^+$) 364.1519. Found 364.1519. Absolute configuration was assigned to be (2*S*, 3*S*) by optical rotation; $[\alpha]_{\text{D}} = -17.1$ (c 0.5, CHCl_3) {lit.⁵ (2*R*, 3*R*)-(7), $[\alpha]_{\text{D}} = +21.5$ (c 0.98, CHCl_3)}.

(5) Mark E. B.; Stephen G. D.; Christopher J. G. *J. Chem. Soc., Perkin Trans 1* **1994**, 2385.