Supplementary Information

An Efficient Synthesis of Enantiomerically Pure Functionalized Imidazolidin-2-ones from Chiral Aziridines

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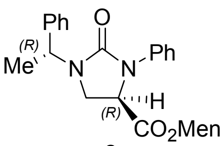
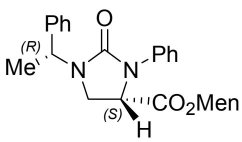
General ; All reactions were carried out using standard Schlenk technique in N_2 atmosphere. Solvents were dried by standard methods and distilled under N_2. Flash chromatography was performed with 230-400 mesh silica gel. Melting points were determined on a capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were obtained on 300 and 500 MHz spectrometers. NMR spectra were recorded in parts per million (δ) relative to the peak for tetramethylsilane (δ= 0.00) as an internal standard unless stated otherwise and are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, t = triplet, q =quartet, m = multiplet), coupling constant, and integration. Elemental analyses were performed by an elemental analyzer. Optical rotations were obtained on a digital polarimeter. Data are reported as follow: $[\alpha]^{24}_D$ (concentration (g/1000 mL), solvent). Solvents and liquid reagents were transferred using hypodermic syringes. All other reagents and solvents used were reagent grade. All glassware was dried in an oven at 150 °C prior to use. Small- and medium-scale purifications were performed using flash chromatography.

General procedure for the synthesis of imidazolidin-2-one-4-carboxylates via $MgBr_2$-catalyzed reaction. Preparation of N-[(R)-(+)-α-methylbenzyl]-N'-R-imidazolidin-2-one-4-carboxylates (**2a**). To a solution of **1** (100 mg, 0.30 mmol) in 1.80 mL of dioxane was added PhNCO (37□L, 0.30 mmol) and magnesium bromide (9 mg, 0.03 mmol) successively under nitrogen with stirring at room temperature. The mixture was stirred for 12 h at the same temperature. The mixture was filtered and concentrated in vacuo. Purification by silica gel flash chromatography (EtOAc/*n*-Hexane, 5:95) provided 89% of **2a** as a white solid.



2a

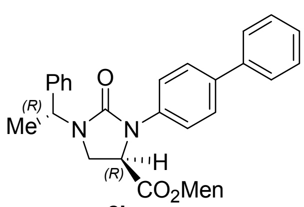
2a (R=Ph): Yield 89% (white solid); m.p. 92-94 °C; $[\alpha]^{24}_D$ = +307.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.44 (d, *J*= 7.5 Hz 2H), 7.39-7.36 (m, 2H), 7.33-7.29 (m, 1H), 7.28-7.24 (m, 2H), 7.18-7.16 (dd, *J*=8.5, 1.5 Hz, 2H), 7.00-6.96 (tt, *J*= 7.0, 1.5 Hz, 1H), 5.52 (q, *J*=7.0 Hz, 1H), 4.81 (dt, *J*= 9.0, 4.5 Hz, 1H) 4.77 (dd, *J* = 9.0, 5.0 Hz, 1H), 3.47 (dd, *J* = 9.0, 5.0 Hz, 1H)), 3.35 (t, *J* = 9.0 Hz, 1H), 2.04-2.00 (m, 1H), 1.91-1.85 (m, 1H), 1.74-1.72 (m, 1H), 1.71-1.69 (m, 1H), 1.58 (d, *J* = 7.5 Hz,3H), 1.59-1.45 (m, 2H), 1.12-1.01(m, 3H), 0.93 (dd, *J* = 5.0, 2.0 Hz, 6H), 0.76 (d, *J* = 7.0 Hz ,3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 169.2, 150.9, 147.4, 139.5, 128.6, 128.4, 127.7, 127.3, 123.5, 122.2, 76.7, 76.3, 72.7, 51.3, 46.9, 44.3, 44.3, 40.6, 34.0, 31.4, 26.1, 23.1, 21.9, 20.8, 16.2, 16.0; IR(CH_2Cl_2) υ(C=O) 1746 cm^{-1}, υ(C=O) 1684 cm^{-1}; Anal. Calcd for $C_{28}H_{36}N_2O_3$: C, 74.95; H, 7.98; N, 6.41. Found: C, 74.97; H, 8.09; N, 6.24; HRMS (EI) m/z exact mass calcd for $C_{28}H_{36}N_2O_3$: 448.2726, Found 448.2719.



$2a_d$

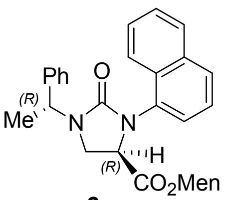
$2a_d$ (R=Ph): Yield 83% (colorless oil); $[\alpha]^{24}_D$ = +157.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.37-7.33(m, 4H), 7.27 (t, *J* = 8.0 Hz, 3H), 7.17 (d, *J* = 7.0 Hz, 2H), 6.98 (t, 7.0 Hz, 1H), 5.45 (q, *J* = 7.0 Hz, 1H), 4.83 (dd, *J* = 8.5, 3.0 Hz, 1H), 4.70 (dt, *J* = 11.0, 5.0 Hz, 1H), 3.67 (t, *J* = 9.0 Hz, 1H)), 3.21 (dd, *J* = 9.0, 3.0 Hz, 1H), 1.83-1.76 (m, 2H), 1.68-1.64 (m, 2H), 1.62 (d, *J* = 7.0 Hz, 3H), 1.47-

1.44 (m, 1H), 1.35 (tt, *J* = 12.0, 3.0 Hz, 1H), 1.04-1.01 (m, 1H), 0.90 (d, *J* = 6.5 Hz 3H), 0.85 (d, *J* = 7.5 Hz, 3H), 0.88-0.79 (m, 2H), 0.70 (d, *J* = 7.0 Hz, 3H.). ^{13}C NMR (125 MHz, $CDCl_3$) 69.1, 151.0, 147.7, 140.3, 128.7, 128.7, 127.7, 127.2, 76.4, 72.5, 51.4, 46.9, 40.5, 34.2, 31.5, 26.2, 23.4, 22.1, 20.9, 16.3, 15.1; HRMS (EI) m/z exact mass calcd for $C_{28}H_{36}N_2O_3$: 448.2726; Found 448.2729.



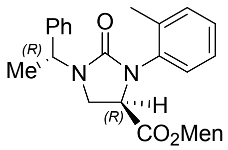
2b

2b (R=4-Biph): Yield 86% (white solid); m.p. 46-50□; $[\alpha]^{24}_D$ = +436.86 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.0, 1.5 Hz 2H), 7.50 (d, *J* = 8.5, 2H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.39 (dd, *J* = 9.0, 7.5 Hz, 4H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.27-7.25 (m, 3H), 5.54 (q, *J* = 7.0 Hz, 1H), 4.85- 4.77 (m, 2H), 3.48 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.35 (t, *J* = 9.0 Hz, 1H), 2.03 (t, *J* = 4.5 Hz, 1H), 1.91-1.88 (m, 1H), 1.73-1.69 (m, 2H), 1.59 (d, *J* = 7.0 Hz, 3H), 1.54-1.46 (m, 2H), 1.12-1.01 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 6H), 0.91-0.86(m, 1H), 0.77 (d, *J* = 7.0 Hz 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 151.4, 147.01, 146.99, 141.6, 139.6, 135.0, 128.74, 128.72 127.9, 127.4, 127.3, 126.9, 126.5, 123.99, 123.98, 76.4, 72.9, 51.5, 47.1, 44.5, 40.7, 34.2, 31.5, 26.3, 23.2, 22.1, 21.0, 16.3, 16.2, 16.1Anal. Calcd for $C_{34}H_{40}N_2O_3$: C, 77.83; H, 7.68; N, 5.34. Found: C, 77.87; H, 7.70; N, 5.36.



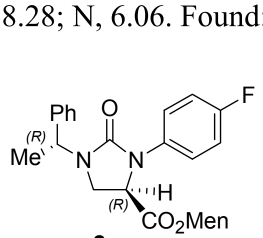
2c

2c (R=1-Naphthyl): Yield 89% (yellow oil); $[\alpha]^{24}_D$ = +240.0 (*c* 4.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32-8.30 (m, 1H), 7.85-7.83 (m, 1H), 7.56 (t, *J* = 8.0 Hz, 3H), 7.45-7.43 (m, 5H), 7.41 (td, *J* = 7.5, 1.0 Hz, 2H), 5.74 (q, *J* = 7.0 Hz, 1H), 4.88- 4.80 (m, 2H), 3.60 (dd, *J* = 9.5 4.0 Hz, 1H), 3.48 (t, *J* = 9.0 Hz, 1H), 2.07-2.05(m, 1H), 1.90-1.87 (m, 1H), 1.76-1.73 (m, 2H), 1.71 (d, *J* = 7.5 Hz, 3H), 1.57-1.53 (m, 1H), 1.49 (tt, *J* = 11.0, 3.0 Hz, 1H), 1.10(qt, *J* = 11.5 Hz, 3H), 0.99(d, J = 6.5 Hz, 3H), 0.94 (d, J = 7.5 Hz, 3H), 0.80 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 151.0, 144.0, 139.9, 134.5, 129.7128.8, 127.9, 127.8, 127.4, 126.0, 125.6, 124.9, 124.4, 122.2, 117.9, 76.4, 72.9, 51.8, 47.0, 44.7, 40.7, 34.2, 31.5, 26.3, 23.2, 22.1, 20.9, 16.7, 16.1; Anal. Calcd for $C_{32}H_{38}N_2O_3$: C, 77.08; H, 7.82; N, 5.59. Found: C, 77.08; H, 7.68; N, 5.62.



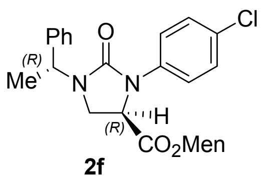
2d

2d (R=o-Tolyl): Yield 80% (colorless oil); $[\alpha]^{24}_D$ = 180.08 (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.14-7.07 (m, 3H), 6.92-6.88 (m, 1H), 5.52 (q, *J* = 7.0 Hz, 1H), 4.79 (td, *J* = 10.5, 4.5 Hz, 1H), 4.72 (dd, *J* = 8.5, 4.0 Hz, 1H), 3.48 (dd, *J* = 8.5, 4.0 Hz, 1H), 3.36 (t, *J* = 9.0 Hz, 1H), 2.27 (s, 3Hz), 2.01-1.99(m, 1H), 1.87-1.84 (m, 1H), 1.73-1.69 (m, 1H), 1.69(s, 1H), 1.69 (d, *J* = 7.0 Hz, 3H), 1.53-1.44 (m, 2H), 1.10-0.99 (m, 2H), 0.92(dd, *J* = 8.0, 1.5 Hz, 6H), 0.90-0.85 (m, 1H), 0.75 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 150.1, 146.3, 139.75, 139.73, 131.1, 130.0, 128.67, 128.66, 127.82, 127.41, 127.40, 126.0, 122.8, 122.8, 122.4, 76.9, 76.3, 72.6, 51.6, 51.5, 47.00, 46.99, 44.7, 40.7, 34.2, 31.5, 26.2, 23.2, 22.05, 22.03, 20.94, 20.93, 18.58, 18.56, 16.4, 16.1, 16.0; Anal. Calcd for $C_{29}H_{38}N_2O_3$: C, 75.29; H, 8.28; N, 6.06. Found: C, 75.27; H, 8.40; N, 6.00.



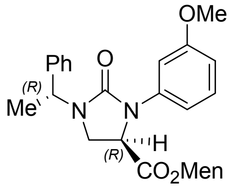
2e

2e (R=4-Fluorophenyl): Yield 91% (white solid); m.p. 81-83□; $[\alpha]^{24}_D$ = +288.7 (*c* 2.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.0 Hz, 1H), 7.14-7.10 (m, 2H), 6.95-6.91 (m, 1H), 5.48 (q, *J* = 7.0 Hz, 1H), 4.83-4.76 (m, 2H), 3.47 (dd, *J* = 9.0, 3.5 Hz, 1H), 3.35 (t, *J* = 8.5 Hz, 1H), 2.03-2.00 (m, 1H), 1.89-1.83 (m, 1H), 1.73-1.72 (m, 1H), 1.70 (bs, 1H), 1.57 (d, *J* = 7.0 Hz, 3H), 1.55-1.43 (m, 2H), 1.12-1.00 (m, 2H), 0.93 (d, *J* = 2.0 Hz, 3H), 0.92 (d, *J* = 1.5 Hz, 3H), 0.91-0.85 (m, 1H), 0.77 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 156.7 157.8, 151.2, 143.5, 139.6, 128.8, 127.9, 127.4, 124.67, 124.61, 115.2, 115.0, 76.5, 72.9, 51.4, 47.1, 44.5, 40.8, 34.2, 31.6, 26.4, 23.3, 22.1, 21.0, 16.3, 16.2; Anal. Calcd for $C_{28}H_{35}FN_2O_3$: C, 72.08; H, 7.56; N, 6.00. Found: C, 72.07; H, 7.72; N, 5.93..



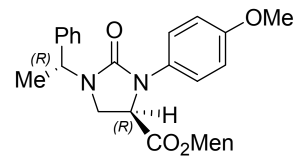
2f

2f (R=4-Chlorophenyl): Yield 89% (colorless oil); $[\alpha]^{24}_{D}$ = +266.8 (*c* 5.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 6.0 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.15 (dd, = 40, 7.0 Hz, 4H), 5.48 (q, *J* = 7.0 Hz, 1H), 4.83-4.75 (m, 2H), 3.47 (dd, *J* = 8.5, 3.5 Hz, 1H), 3.34 (t, *J* = 8.5 Hz, 1H), 2.02-2.00 (m, 1H), 1.88-1.84 (m, 1H), 1.72 (br, 1H), 1.70 (bs, 1H), 1.56 (d, *J* = 7.0 Hz, 3H), 1.54-1.43 (m, 2H), 1.11-0.99 (m, 2H), 0.93 (d, *J* = 3.5 Hz, 3H), 0.92 (d, *J* = 2.5 Hz, 3H), 0.90-0.85 (m, 1H), 0.77 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 151.3, 146.2, 139.4, 128.7, 128.5, 127.9, 127.4, 127.2, 125.0, 76.5, 72.9, 51.4, 47.1, 44.4, 40.7, 34.1, 31.5, 26.3, 23.2, 22.0, 20.9, 16.3, 16.1; Anal. Calcd for $C_{28}H_{35}ClN_2O_3$: C, 69.62; H, 7.30; N, 5.80. Found: C, 69.69; H, 7.31; N, 5.76.



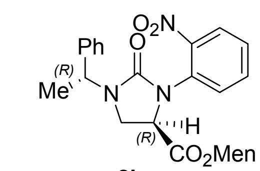
2g

2g (R=3-Methoxyphenyl): Yield 87 % (colorless solid); m.p. 84-86□; $[\alpha]^{24}_{D}$ = +233.0 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.0 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.31 (tt, *J* = 6.5, 1.5 Hz, 1H), 7.16 (t, *J* = 8.5 Hz, 1H), 6.79 (dd, *J* = 6.5, 4.5 Hz, 1H), 6.77 (t, *J* = 2.5 Hz, 1H), 6.57-6.55 (m, 1H), 5.51 (q, *J* = 7.0 Hz, 1H), 4.81 (dt, *J* = 11.5 5.0 Hz, 1H), 4.77 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.80 (s, 3H), 3.48 (dd, *J* = 8.5, 4.0 Hz, 1H), 3.37 (t, *J* = 9.0 Hz, 1H), 2.03-1.99 (m, 1H), 1.89-1.84 (m, 1H), 1.74-1.69 (m, 2H), 1.58 (d, *J* = 7.5 Hz, 3H), 1.55-1.44 (m, 2H), 1.11-1.01 (m, 2H), 0.93 (d, *J* = 1.5 Hz, 3H), 0.92 (d, *J* = 2.0 Hz, 3H), 0.90-0.85 (m, 1H), 0.76 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 160.2, 151.2, 148.9, 139.7, 129.2, 128.8, 127.9, 127.5, 116.2, 109.4, 108.3, 76.5, 72.9, 55.3, 51.5, 47.1, 44.5, 40.8, 34.2, 31.6, 26.4, 23.3, 22.1, 21.0, 16.3, 16.2; Anal. Calcd for $C_{29}H_{38}N_2O_4$: C, 72.77; H, 8.00; N, 5.85. Found: C, 72.74; H, 8.11; N, 5.88.



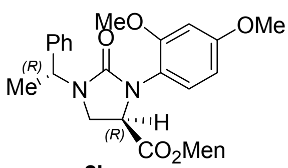
2h

2h (R=4-Methoxyphenyl): Yield 95 % (yellow oil); $[\alpha]^{24}_{D}$ = +300.0 (*c* 2.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 8.5 Hz, 1H), 7.13-7.10 (m, 2H), 6.83-6.80 (m, 2H), 5.50 (q, *J* = 7.0 Hz, 1H), 4.80 (dt, *J* = 11.5, 5.0 Hz, 1H), 4.76 (dd, *J* = 8.5, 4.0 Hz, 1H), 3.78 (s, 3H), 3.46 (dd, *J* = 9.5, 4.0 Hz, 1H), 3.33 (t, *J* = 9.0 Hz, 1H), 2.03-2.00 (m, 1H), 1.91-1.85 (m, 1H), 1.73-1.70 (m, 1H), 1.70 (bs, 1H), 1.57 (d, *J* = 7.5 Hz, 1H), 1.55-1.44 (m, 2H), 1.12-1.00 (m, 2H), 0.93 (dd, *J* = 7.0, 1.0 Hz, 6H), 0.91-0.85 (m, 1H), 0.77 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 155.1, 151.0, 140.76, 128.7, 127.8, 127.9, 127.5, 124.3, 114.00, 76.4, 72.8, 55.6, 51.4 ,47.1, 44.49, 40.8, 34.2, 31.6, 26.3, 23.3, 22.11, 21.04, 16.33, 16.14; Anal. Calcd for $C_{29}H_{38}N_2O_4$: C, 72.77; H, 8.00; N, 5.85. Found: C, 72.58; H, 8.25; N, 5.66.



2i

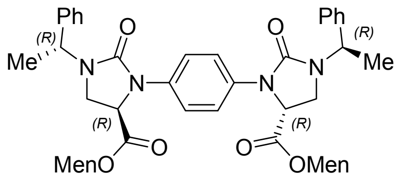
2i (R=2-Nitrophenyl): Yield 93% (pale green oil); $[\alpha]^{24}_{D}$ = +430.4 (*c* 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.47-7.31 (m, 5H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.03 (td, *J* = 8.0, 1.0 Hz, 1H), 5.48 (q, *J* = 7.5 Hz, 1H), 4.81-4.77 (m, 2H), 3.50 (dd, *J* = 9.5, 4.5 Hz, 1H), 3.37 (t, *J* = 9.5 Hz, 1H), 2.01-1.98 (m, 1H), 1.81-1.74 (m, 1H), 1.71 (br, 1H), 1.69 (bs, 1H), 1.61 (d, *J* = 7.0 Hz, 3H), 1.60 (s, 1H), 1.52-1.42 (m, 2H), 1.09-1.00 (m, 2H), 0.92 (d, *J* = 6.0 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H), 0.74 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 151.8, 143.9, 142.9, 139.1, 132.9, 128.9, 128.1, 127.5, 126.7, 124.7, 122.1, 76.7, 73.0, 51.7, 47.0, 44.6, 40.7, 34.2, 31.6, 26.4, 23.3, 22.1, 20.9, 16.2, 16.1; Anal. Calcd for $C_{28}H_{35}N_3O_5$: C, 70.85; H, 7.59; N, 8.55. Found: C, 70.58; H, 7.59; N, 8.55.



2j

2j (R=2,4-Dimethoxylphenyl): Yield 62% (pale yellow oil); $[\alpha]^{24}_{D}$ = +119.6 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.0 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.0 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.50 (d, *J* = 3.0 Hz, 1H), 6.43 (dd, *J* = 8.0, 3.0 Hz, 1H), 5.57 (q, *J* = 7.0 Hz, 1H), 4.78 (td, *J* = 11.0, 4.0 Hz, 1H), 4.72 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.45 (dd, *J* = 9.0, 3.5 Hz, 1H), 3.32 (t, *J* = 9.0 Hz, 1H), 2.01-1.98 (m, 1H), 1.88-

1.82 (m, 1H), 1.72(bs, 1H), 1.70 (bs, 1H), 1.61 (s, 1H), 1.59 (d, *J* = 7.0 Hz, 3H), 1.54-1.43 (m, 2H), 1.11-0.98 (m, 2H), 0.93-0.92 (m, 6H), 0.90-0.85 (m, 1H), 0.75 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 156.1, 153.2, 151.5, 139.8, 130.5, 128.6, 127.8, 127.7, 124.0, 104.1, 99.8, 76.3, 72.7, 56.1, 55.6, 51.5, 47.1, 44.7, 40.8, 34.2, 31.6, 26.3, 23.3, 22.1, 21.0, 16.2, 16.1; Anal. Calcd for $C_{28}H_{35}N_3O_5$: C, 70.84; H, 7.93; N, 5.51. Found: C, 70.76; H, 8.13; N, 5.34.

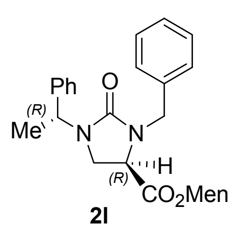


2k

2k (R=1,4-Diisocyanatophenyl): Yield 76% (yellow solid); m.p. 76-78℃; $[\alpha]^{24}_D$ = +425.6 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.0 Hz, 4H), 7.36 (t, *J* = 7.0 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.10 (s, 4H), 5.53 (q, *J* = 7.5 Hz, 1H), 4.80 (td, *J* = 11.5, 4.5 Hz, 1H), 4.75 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.45 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.30 (t, *J* = 8.5 Hz, 1H), 2.03-2.01 (m, 2H), 1.91-1.88 (m, 2H), 1.73-1.72(m, 2H), 1.70 (bs, 2H), 1.57(d, *J* = 7.0 Hz, 6H), 1.54-1.46 (m, 4H), 1.10-1.01 (m, 2H), 0.93 (t, *J* = 7.0 Hz, 6H), 0.89-0.86 (m, 2H), 0.77 (d, *J* = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 150.7, 141.8, 140.0, 128.7, 127.8, 127.6, 123.7, 76.3, 72.8, 51.3, 47.1, 44.4, 40.8, 34.2, 31.6, 26.3, 23.3, 22.1, 21.1, 16.3, 16.2; Anal. Calcd for $C_{50}H_{66}N_4O_6$: C, 73.32; H, 8.12; N, 6.84. Found: C, 73.33 H, 8.24; N, 6.82.

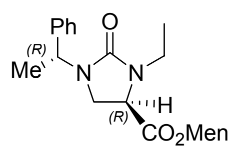
General procedure for the synthesis of imidazolidin-2-one-4-carboxylates via TMSCl-catalyzied reaction.

Preparation of N-[(*R*)-(+)-α-methylbenzyl]-N'-R-imidazolidin-2-one-4-carboxylates (**2l**). To a solution of **1** (110 mg, 0.33 mmol) in 2.10 mL of THF was added benzylisocyanate (42μL, 0.33 mmol) and TMSCl (85μL, 0.66mmol) successively under nitrogen with stirring at room temperature. The mixture was stirred for 1h at room temperature. The mixture was quenched by a saturated aqueous $NaHCO_3$ solution and extracted with EtOAc (1.5mL X 3). The organic layer was concentrated in vacuo. Purification by silica gel flash chromatography (EtOAc/*n*-Hexane, 15:85) provided 136 mg (88%) of **2l** as colorless oil.



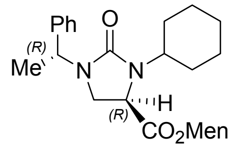
2l

2l (R=3-Nitrophenyl): Yield 88% (colorless oil); $[\alpha]^{24}_D$ =+ 125.8(*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.38 (m, 3H), 7.34-7.24 (m, 5H), 7.19 (t, *J* = 7.0 Hz 1H), 5.38 (q, *J* = 7.0 Hz, 1H), 4.80-4.73 (m, 2H), 4.56(s, 2H), 3.42 (dd, *J* = 9.0, 5.0 Hz, 1H), 3.30 (t, *J* = 8.5 Hz, 1H), 2.01-1.98 (m, 1H), 1.85-1.80 (m, 1H), 1.70-1.66 (m, 2H), 1.52 (d, *J* = 7.5 Hz, 3H), 1.53-1.46 (m, 1H), 1.41 (tt, *J* = 11.0, 3.0 Hz, 1H), 1.09-0.96(m, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.77 (d, *J*=7.0 Hz. 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 152.5, 142.6, 140.2, 128.6, 128.2, 127.7, 127.5, 127.50, 126.2, 76.3, 72.5, 51.4, 50.3, 47.0, 44.7, 40.7, 34.2, 31.5, 26.5, 23.5, 22.1, 20.9, 16.4, 16.0; HRMS (EI) m/z exact mass calcd for $C_{29}H_{36}N_2O_3$: 462.2828; Found 462.2814.



2m

2m (R=Ethyl): Yield 77% (white solid); m.p. 66-68℃; $[\alpha]^{24}_D$ = +46.1 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (m, 4H), 7.30-7.26 (m, 1H), 5.26 (q, *J* = 7.0 Hz, 1H), 4.77 (td, *J* = 11.0, 4.5 Hz, 1H), 4.70 (dd, *J* = 7.0, 3.0 Hz, 1H), 3.38-3.30 (m, 3H), 3.26-3.22 (m, 1H), 2.02-1.99 (m, 1H), 1.85-1.82 (m, 1H), 1.71 (bs, 1H), 1.68 (br, 1H), 1.49 (dd, *J* = 7.0, 2.5 Hz, 4H), 1.42 (tt, *J* = 11.0, 3.0 Hz, 1H), 1.18 (td, *J* = 8.5, 2.5 Hz, 2H), 1.10-0.97 (m, 2H), 0.91 (t, *J* = 7.0 Hz, 6H), 0.87-0.84 (m, 1H), 0.77 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 152.0, 140.2, 128.6, 127.6, 127.4, 76.2, 72.3, 51.2, 47.0, 44.5, 41.1, 40.7, 34.2, 31.5, .26.4, 23.4, 22.1, 20.9, 17.1, 16.3, 15.8; Anal. Calcd for $C_{24}H_{36}N_2O_3$: C, 71.96; H, 9.06; N, 6.99. Found: C, 71.95; H, 9.02; N, 6.78.



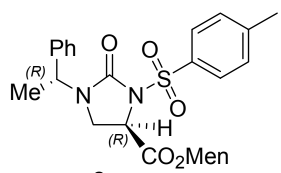
2n

2n (R=Cyclohexyl): Yield 66% (white solid); m.p. 76-80℃; $[\alpha]^{24}_D$ = +74.58 (*c* 2.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 1H), (m, 4H), 7.32 (t, *J* = 7.0 Hz ,1H), 7.27-7.24(m, 1H), 5.28 (q, *J* = 7.5 Hz, 1H), 4.75 (td, *J* =

11.0, 4.0 Hz, 1H), 4.68 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.32 (dd, *J* = 9.0, 5.0 Hz, 1H), 3.30 (t, *J* = 8.0 Hz, 1H), 2.01-1.99 (m, 1H), 1.89-1.81 (m, 2H), 1.75-1.68 (m, 5H), 1.60 (d, *J* = 7.0 Hz, 1H), 1.48 (d, *J* = 4.0 Hz, 4H), 1.42 (t, *J* = 11.5 Hz, 2H), 1.35-1.26 (m, 4H), 1.22-2.00 (m, 2H), 1.09-1.03 (m, 2H), 0.99 (q, *J* = 7.0 Hz, 1H), 0.93-0.87 (m, 7H), 0.76 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 150.7, 140.2, 128.5, 127.6, 127.5, 76.1, 72.3, 55.1, 51.2, 47.0, 44.6, 40.7, 35.6, 35.2, 34.2, 31.5, 26.2, 25.5, 23.3, 22.1, 20.9, 16.2, 15.97; Anal. Calcd for $C_{24}H_{36}N_2O_3$: C, 73.97; H, 9.27; N, 6.19. Found: C, 73.97; H, 9.31; N, 6.16.

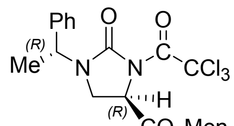
General procedure for the synthesis of imidazolidin-2-one-4-carboxylates via $MgBr_2{\cdot}Et_2O$-catalyzied reaction.

Preparation of N-[(*R*)-(+)-α-methylbenzyl]-N'-R-imidazolidin-2-one-4-carboxylates (**2o**). To a solution of **1** (110 mg, 0.33 mmol) in 1.7 mL of THF was added tosylisocyanate (52□L, 0.33 mmol) and $MgBr_2{\cdot}Et_2O$ (7 mg, 0.03 mmol) successively under nitrogen with stirring at room temperature. The mixture was stirred for 1h at room temperature. The mixture was quenched by a saturated aqueous $NaHCO_3$ solution and extracted with EtOAc (1.5 mL X 3). The organic layer was concentrated in vacuo. Purification by silica gel flash chromatography (EtOAc/*n*-Hexane, 15:85) provided 163 mg (93%) of **2o** as a white solid.



2o

2o (R=Tosyl): Yield 93% (white solid); m.p. 119-120□; $[\alpha]^{24}_D$ = +47.14 (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz 3H), 7.35-7.26 (m, 5H), 7.22 (d, 2H), 5.20 (q, *J* = 7.0 Hz, 1H), 4.78 (td, *J* = 11.0, 4.0 Hz, 1H), 4.74 (dd, *J* = 10.0, 5.0 Hz, 1H) 3.31 (t, *J* = 9.0 Hz, 1H), 3.25 (dd, *J* = 10.0, 5.0 Hz, 1H), 2.25 (s, 3H) 2.05-2.03 (m, 1H), 1.85-1.81 (m, 1H), 1.71 (bs, 1H), 1.69 (m, 1H), 1.54-1.46 (m, 1H), 1.45 (d, *J* = 7.5 Hz, 3H), 1.45-1.41 (m, 1H), 1.07-1.00 (m, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.91-0.87 (m, 1H), 0.74 (d, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 152.9, 144.9, 138.7, 135.9, 129.4, 129.1, 128.9, 128.2, 127.2, 76.7, 54.7, 50.6, 46.9, 41.8, 40.7, 34.2, 31.6, 26.3, 23.2, 22.1, 21.9, 21.0, 16.8, 16.0 Anal. Calcd for $C_{29}H_{38}N_2O_5S$: C, 66.13; H, 7.27; N, 5.32; S, 6.09. Found: C, 66.19; H, 7.00; N, 5.21; S, 6.26.

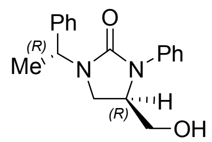


2p

2p (R=Trichloroacetyl): Yield 75% (white solid); m.p. 90-91□; $[\alpha]^{24}_D$ = +613.87 (*c* 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.31-7.29 (m, 3H), 6.84 (bs, 1H), 5.26 (q, *J* = 7.0 Hz, 1H), 4.77 (td, *J* = 11.5, 4.5 Hz, 1H), 4.15 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.60 (dd, *J* = 9.0, 3.5 Hz, 1H), 3.33 (t, *J* = 9.5 Hz, 1H), 1.99-1.97 (m, 1H), 1.82-1.79 (m, 1H), 1.71 (bs, 1H), 1.69 (bs, 1H), 1.54 (d, *J* = 7.5 Hz, 3H), 1.51-1.42 (m, 2H), 1.08-0.99 (m, 2H), 0.91 (d, *J* = 6.5 Hz, 6H), 0.89-0.85 (m, 1H), 0.76 (d, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 165.1, 162.3, 139.1, 128.9, 128.1, 127.2, 76.6, 52.4, 50.3, 47.0, 43.3, 40.7, 34.1, 31.5, 26.5, 23.3, 22.1, 20.9, 16.5, 16.2; Anal. Calcd for $C_{24}H_{31}Cl_3N_2O_4$: C, 55.66; H, 6.03; N, 5.41. Found: C, 55.61; H, 5.99; N, 5.36.

Representative example of the formation of 4-hydroxymethyl imidazolidin-2-one.

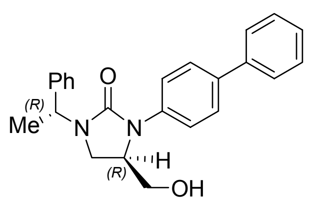
Preparation of 4-hydroxymethyl-N-[(*R*)-(+)-α-methylbenzyl]-N'-R-imidazolidin-2-ones (**6a**). To a solution of **1a** (115 mg, 0.26 mmol) in 1.30 mL of THF was added LAH (5 mg, 0.13 mmol) at 0 ^{o}C. The mixture was stirred for 0.5h at room temperature. The mixture was quenched by saturated aqueous potassium bisulfate solution, and was extracted by EtOAc (2 mL X 3). The organic layer was washed by brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. Purification by silica gel flash chromatography (EtOAc/*n*-Hexane, 3:7) provided 74 mg (98%) of **6a** as a white solid.



6a

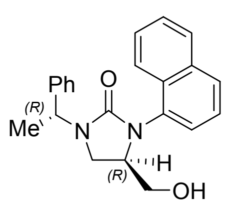
6a (R=Ph): Yield 98% (white solid); m.p. 107-109□; $[\alpha]^{24}_D$ = +145.7 (*c* 1.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.39 (m, 2H), 7.37-7.34 (m, 2H), 7.29 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.24-7.20 (m, 2H), 7.20-7.10 (m, 2H), 6.96 (tt, *J* = 7.0, 1.5

Hz, 1H), 5.54 (q, J = 7.0 Hz, 1H), 4.47-4.42 (m, 1H), 3.63 (ddd, J = 65, 12.0, 3.5 Hz, 2H), 3.35 (dd, J = 8.5, 7.0 Hz, 1H)), 3.09 (t, J = 3.5 Hz, 1H), 2.22 (bs, 1H), 1.57 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.7, 146.2, 139.7, 128.5, 127.6, 127.2, 123.6, 122.4, 76.8, 62.5, 51.5, 42.2, 15.4; Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 72.95; H, 6.83; N, 9.48. HRMS (EI) m/z exact mass calcd for $C_{18}H_{20}N_2O_2$: 296.1525; Found 296.1523



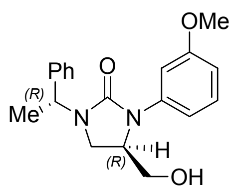
9b

6b (R=4-Biph): Yield 99% (white solid); m.p. 168-169□; $[\alpha]^{24}_D$ = +143.9 (c 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, J = 8.0, 1.5 Hz 2H), 7.51-7.49 (m, 2H), 7.44-7.36 (m, 6H), 7.32-7.25 (m, 2H), 7.17 (dt, J = 9.0, 2.0 Hz, 2H), 5.51 (q, J = 7.0 Hz, 1H), 4.56- 4.51 (m, 1H), 3.75 (ddd, J = 83.0, 12.0, 4.0 Hz, 1H), 3.35 (t, J = 8.5 Hz, 1H), 3.16 (t, J = 8.5 Hz, 1H), 2.01 (bs, 1H), 1.61 (d, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 147.4, 141.5, 140.4, 134.8, 128.8, 128.7, 127.44, 127.42, 126.9, 126.6, 76.4, 63.2, 51.6, 42.0, 15.6; Anal. Calcd for $C_{24}H_{24}N_2O_2$: C, 77.39; H, 6.49; N, 7.52. Found: C, 77.37; H, 6.63; N, 7.51.



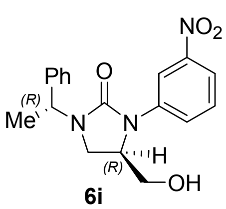
6c

6c (R=1-Naphthyl): Yield 99% (yellow solid); m.p. 58-57□ ; $[\alpha]^{24}_D$ = +107.7 (c 2.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17-8.15 (m, 1H), 7.78-7.76 (m, 1H), 7.48 (d, J = 7.5 Hz, 3H), 7.43-7.31 (m, 6H), 7.15 (d, J = 7.0 Hz, 1H), 5.63 (q, J = 7.0 Hz, 1H), 4.40-4.37 (m, 1H), 3.67-3.63 (m, 1H), 3.52-3.51 (m, 1H), 3.34-3.31 (m, 1H), 3.15-3.11 (m, 1H), 1.99 (bs, 1H), 1.68 (d, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 144.5, 140.5, 134.5, 129.6, 128.8, 128.0, 127.8, 127.4, 126.1, 125.7, 125.0, 124.2, 122.1, 118.0, 76.3, 62.9, 51.9, 42.3, 15.8; Anal. Calcd for $C_{22}H_{22}N_2O_2$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.20; H, 6.39; N, 8.13.



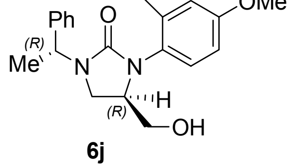
6g

6g (R=3-Methoxyphenyl): Yield 98% (white solid); $[\alpha]^{24}_D$ = +108.7 (c 1.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 7.0 Hz, 2H), 7.36 (t, J = 7.0 Hz, 2H), 7.29 (t, J = 7.0 Hz, 1H), 7.14 (t, J = 7.0 Hz 1H), 6.69 (d, J = 8.0 Hz, 1Hz), 6.66 (s, 1H), 6.53 (dd, J = 8.5, 2.5 Hz, 1H), 4.46 (d, J = 7.0 Hz 1H), 4.50-4.45 (m, 1H), 3.77 (s, 1H), 3.69 (ddd, J = 76.5, 12.0, 5.0 Hz, 2H), 3.31 (t, J = 8.0 Hz, 1H), 3.12 (t, J = 8.5 Hz, 1H), 2.18 (bs, 1H), 1.59 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 152.3, 149.3, 140.4, 129.2, 128.7, 127.7, 127.4, 116.4, 109.6, 107.8, 76.9, 76.4, 63.1, 55.3, 51.5, 42.0, 15.5; Anal. Calcd for $C_{19}H_{22}N_2O_3$: C, 69.92; H, 6.79; N, 8.58. Found: C, 69.88; H, 6.84; N, 8.57.



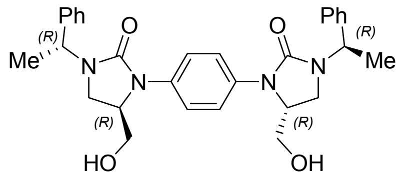
6i

6i (R=3-Nitrophenyl): Yield 98% (green solid); $[\alpha]^{24}_D$ = +82.3 (c 1.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (t, J = 2.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.42-7.30 (m, 7H), 5.48 (q, J = 7.5 Hz, 1H), 4.61-4.56 (m, 1H), 3.77 (ddd, J = 84.5, 15.5, 2.0 Hz, 2H), 3.41 (t, J = 7.0 Hz, 1H), 3.20 (t, J = 8.5 Hz, 1H), 2.26 (bs, 1H), 1.61 (d, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 149.4, 148.8, 140.0, 130.4, 129.1, 128.0, 127.9, 127.3, 118.6, 116.6, 76.8, 62.9, 51.7, 42.0, 15.7; HRMS (EI) m/z exact mass Calcd for $C_{18}H_{20}N_2O_2$: 341.1376; Found 341.1399



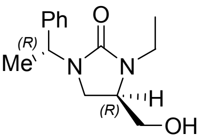
6j

6j (R=2,4-Dimethoxylphenyl): Yield 98% (pale yellow solid); m.p. 144-146□; $[\alpha]^{24}_D$ = +277.2 (c 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 7.0 Hz, 2H), 7.38(t, J = 7.5 Hz, 2H), 7.30 (t, J = 7.0 Hz, 1H), 6.92 (d, J = 7.5 Hz, 1H), 6.55 (d, J = 2.5 Hz, 1H), 6.48(dd, J = 9.0, 3.0 Hz, 1H), 5.48 (q, J = 7.0 Hz, 1H), 4.47-4.43 (m, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.662 (ddd, J = 147, 13.0, 3.0 Hz, 1H), 3.42-3.39 (m, 1H), 3.08 (t, J = 8.5 Hz, 1H), 2.90 (br, 1H), 1.63 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 153.0, 152.1, 140.4, 131.7, 128.7, 127.7, 127.5, 124.4, 105.4, 101.2, 75.6, 63.7, 56.9, 55.7, 51.7, 42.6, 15.4; HRMS (EI) m/z exact mass calcd for $C_{18}H_{20}N_2O_2$: 356.1736; Found 356.1743.



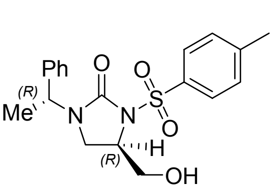
6k

6k (R=1,4-Diisocyanatophenyl): Yield 98% (yellow solid); m.p. 189-192□; $[\alpha]^{24}_D$ = +252.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.5 Hz, 4H), 7.35 (t, *J* = 7.0 Hz, 4H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.00 (s, 4H), 5.46 (q, *J* = 7.0 Hz, 2H), 4.43 (m, 2H), 3.65 (ddd, *J* = 59.0, 7.0, 3.0 Hz, 4H), 3.27 (t, *J* = 8.0 Hz, 2H), 3.09 (t, *J* = 8.0 Hz, 2H), 2.25 (br, 2H), 1.58 (d, *J* = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.7, 153.6, 146.4, 131.6, 130.0, 129.4, 126.6, 125.4, 119.6; Anal. Calcd for $C_{50}H_{66}N_4O_6$: C, 70.02; H, 6.66; N, 10.89. Found: C, 70.11; H, 6.66; N, 10.78.



6m

6m (R=Ethyl): Yield 95% (white solid); m.p. 118-119□; $[\alpha]^{24}_D$ = +108.6 (*c* 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.32(m, 4H), 7.26 (q, *J* = 6.0 Hz, 1H), 5.26 (q, *J* = 7.5 Hz, 1H), 4.45-4.41 (m, 1H), 3.73 (ddd, *J* = 56.5, 7.5, 3.5 Hz, 1H), 3.33-3.23 (m, 3H), 3.21 (t, *J* = 8.0 Hz, 1H) , 3.03 (t, *J* = 8.0 Hz, 1H), 2.52 (br, 1H), 1.51 (d, *J* = 7.0 Hz, 3H), 1.15 (t, *J* = 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 140.8, 128.6, 127.5, 127.4, 75.8, 63.3, 51.3, 42.4, 401.0, 17.3, 15.3; Anal. Calcd for $C_{24}H_{36}N_2O_3$: C, 67.71; H, 8.12; N, 11.28 Found: C, 67.79; H, 8.16; N, 11.04.

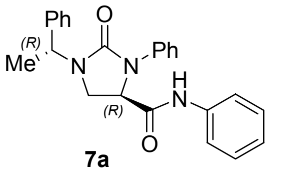


6o

6o (R=Tosyl): Yield 93% (white solid); m.p. 81-83□; $[\alpha]^{24}_D$ = +169.3 (*c* 1.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.0 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 3H), 7.09-7.07 (m, 2H), 5.19 (q, *J* = 8.0 Hz, 1H), 4.42-4.17 (m, 1H), 3.963.92 (m, 1H), 3.82-3.77 (m, 1H), 3.27 (dd, *J* = 9.0, 5.0 Hz, 1H), 3.01 (t, *J* = 9.5 Hz, 1H), 2.46 (s, 3H), 2.37 (bs, 1H), 1.49 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.7, 145.0, 139.0, 135.8, 129.8, 128.7, 128.2, 127.9, 127.1, 64.3, 55.4, 50.5, 40.4, 21.8, 16.1; Anal. Calcd for$C_{19}H_{22}N_2O_4S$: C, 60.94; H, 5.92; N, 7.48; S, 8.56. Found: C, 60.97; H, 6.01; N, 7.47; S, 8.48; HRMS (EI) m/z exact mass calcd for Calcd for $C_{19}H_{22}N_2O_4S$: 374.1300; Found 374.1303.

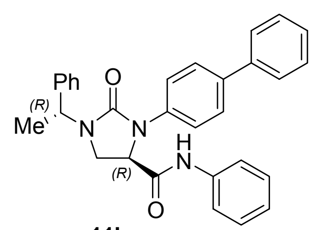
Representative example of the formation of imidazolidin-2-one-4-carboxamides.

Preparation of N-[(*R*)-(+)-α-methylbenzyl]-N'-R-imidazolidin-2-one-4-carboxylic acid benzamide (**7a**). To a solution of aniline hydrochloride (39 mg, 0.30 mmol) in 0.8 mL of THF was added isopropyl magnesium chloride (2.0 M, 0.30 mL, 0.60 mmol) under nitrogen with stirring in an ice bath. The mixture was treated with imidazolidin-2-one-4-carboxylate **1a** (120 mg, 0.25 mmol) in 0.5 mL of THF via cannula. The mixture was stirred for 10 min at room temperature. The mixture was quenched with aqueous saturated NH_4Cl solution, and extracted with EtOAc (1.5 mL X 3). The organic layer was washed by brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. Purification by silica gel flash chromatography (EtOAc/*n*-Hexane, 15:85) and (CH_2Cl_2/*n*-Hexane, 1:9) provided 83 mg (92%) of **7a** as a white solid.



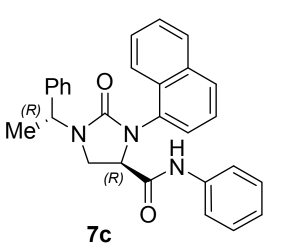
7a

7a (R=Ph): Yield 92% (white solid); m.p. 120-122□; $[\alpha]^{24}_D$ = + 312.6 (*c* 2.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.52-7.31 (m, 11H), 7.19-7.03 (m, 4H), 5.45 (q, *J* = 7.0 Hz, 1H), 4.81 (dd, *J* = 12.0, 3.5 Hz, 1H), 3.77 (dd, *J* = 12.0, 3.5 Hz, 1H), 3.46 (t, *J* = 3.5 Hz, 1H), 1.60 (d, *J* = 7.0 Hz,3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.7, 146.2, 139.7, 128.5, 127.6, 127.2, 123.6, 122.4, 76.8, 62.5, 51.5, 42.2, 15.4. Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 72.95; H, 6.83; N, 9.48.



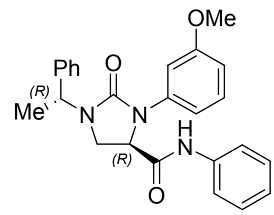
11b

7b (R=4-Biph): Yield 98% (white solid); m.p. 124-128℃; $[\alpha]^{24}_{D}$ = +412.7 (*c* 3.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.03 (s, 1H), 7.62 (d, *J* = 7.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.47-7.30 (m, 10H), 7.18-7.15 (m, 4H), 5.49 (q, *J* = 7.5 Hz, 1H), 4.86 (dd, *J* = 8.0, 4.5 Hz, 1H), 3.79 (dd, *J* = 9.0, 5.0 Hz, 1H), 3.50 (t, *J* = 9.5 Hz, 1H), 1.62 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 167.4, 150.0, 177.1, 141.2, 139.5, 136.6, 135.6, 129.4, 128.90, 128.88, 128.1, 127.8, 127.5, 127.0, 126.9, 125.4, 123.6, 120.0, 73.9, 52.0, 44.3, 16.4; Anal. Calcd for $C_{30}H_{27}N_3O_2$: C, 78.07; H, 5.90; N, 9.10. Found: C, 78.07; H, 6.03; N, 9.07.



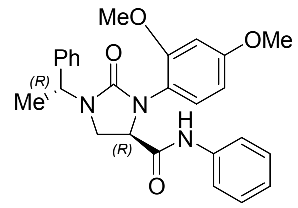
7c

7c (R=1-Naphthyl): Yield 99% (pale red solid); m.p. 143-145 ℃; $[\alpha]^{24}_{D}$ = +201.4 (*c* 1.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.03 (d, *J* = 9.5 Hz 1H), 7.88 (d, *J* = 8.0 Hz 1H), 7.77 (s, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.50-7.43 (m, 4H), 7.40 -7.36 (m, 2H), 7.32-7.26 (m, 4H), 7.15-7.12 (m, 2H), 5.62 (q, *J* = 7.0 Hz, 1H), 4.78 (dd, *J* = 9.0, 4.5 Hz, 1H), 3.87 (dd, *J* = 8.5, 4.5 Hz, 1H), 3.58 (t, *J* = 9.5 Hz, 1H), 1.72 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 167.4, 150.0, 144.7, 139.6, 136.5, 134.7, 129.2m 129.03, 128.96, 128.5, 128.2, 127.7, 126.3, 126.0, 125.7, 125.3, 123.6, 123.0, 120.0, 117.6, 73.6, 52.4, 44.7, 27.2, 16.7; Anal. Calcd for $C_{28}H_{25}N_3O_2$: C, 77.22; H, 5.79; N, 9.65. Found: C, 77.25; H, 5.83; N, 9.65.



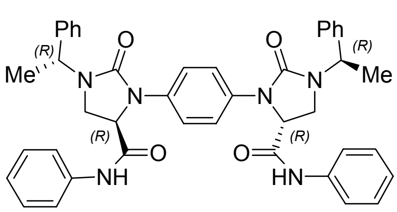
7g

7g (R=3-Methoxyphenyl): Yield 92% (white solid); m.p. 66-68℃; $[\alpha]^{24}_{D}$ = +313.1 (*c* 2.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.03 (s, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.40-7.31 (m, 5H), 7.26-7.23 (m, 1H), 7.16 (t, *J* = 7.5 Hz, 1Hz), 6.69-0.67 (m, 1H), 6.64-6.62 (m, 2H), 5.43 (q, *J* = 7.5 Hz, 1H), 4.82 (dd, *J* = 9.0, 5.0 Hz 1H), 3.80 (s, 1H), 3.76 (d, *J* = 9.5, 5.0 Hz, 1H), 3.45 (t, *J* = 9.0 Hz, 1H), 1.59 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 167.5, 160.6, 150.1, 149.4, 139.7, 136.8, 129.8, 129.5, 129.0, 128.2, 127.6, 125.5, 120.1, 115.8, 109.3, 108.473.9, 55.5, 52.1, 44.4, 16.5; Anal. Calcd for $C_{25}H_{25}N_3O_3$: C, 72.27; H, 6.06; N, 10.11. Found: C, 72.18; H, 6.27; N, 10.16.



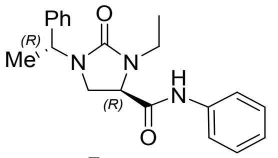
7j

7j (R=2,4-Dimethoxylphenyl): Yield 97% (white solid); m.p. 78-80℃; $[\alpha]^{24}_{D}$ = +342.7 (*c* 2.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 9.01 (2, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.42-7.37 (m, 3H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.0 Hz, 1H), 6.94 (d, *J* = 7.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.58 (dd, *J* = 9.0, 3.0 Hz, 1H), 5.50 (q, *J* = 7.5 Hz, 1H), 4.76 (dd, *J* = 9.5, 4.5 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 3.74 (dd, *J* = 8.5, 4.0 Hz, 1H), 3.46 (t, *J* = 9.5 Hz, 1H), 1.62 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 168.6, 156.4, 152.2, 151.4, 139.4, 137.2, 132.1, 129.4, 128.8, 128.2, 127.8, 125.5, 124.8, 121.1, 107.4, 103.8, 73.7, 58.6, 55.8, 52.1, 45.5, 16.9; Anal. Calcd for $C_{28}H_{35}N_3O_5$: C, 70.09; H, 6.11; N, 9.43 Found: C, 70.04; H, 6.12; N, 9.56.



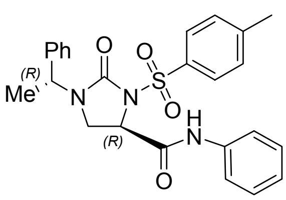
7k

7k (R=1,4-Diisocyanatophenyl): Yield 73% (yellow solid); m.p. 93-95℃; $[\alpha]^{24}_{D}$ = +522.9 (*c* 1.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.09 (s, 2H), 7.55 (d, *J* = 8.0 Hz, 4H), 7.50 (d, *J* = 7.5 Hz, 4H), 7.43 (t, *J* = 7.0 Hz, 4H), 7.36 (t, *J* = 8.0 Hz, 6H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.12 (s, 4H), 5.51 (q, *J* = 7.0 Hz, 2H), 4.88 (dd, *J* = 9.0, 5.0 Hz, 2H), 3.80 (dd, *J* = 8.5, 4.5 Hz, 2H), 3.52 (t, *J* = 9.0 Hz, 2H), 1.64(d, *J* = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 167.6, 149.9, 142.6, 139.8, 139.8, 136.7, 129.5, 128.9, 128.1, 127.6, 125.4, 123.7., 120.1, 73.8, 52.0, 44.4, 16.4; Anal. Calcd for $C_{50}H_{66}N_4O_6$: C, 72.81; H, 5.82; N, 12.13. Found: C, 72.83; H, 85.82; N, 12.13.



7m

7m (R=Ethyl): Yield 94% (white solid); m.p. 123-125□; $[\alpha]^{24}_D$ = +124.4 (*c* 2.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.39-7.33 (m, 6H), 7.31-7.27 (m, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 5.28 (q, *J* = 7.0 Hz, 1H), 4.84 (t, *J* = 5.5 Hz, 1H), 3.59 (dd, *J* = 9.0, 5.5 Hz, 1H), 3.48-3.35 (m, 3H), 1.51 (d, *J* = 6.5 Hz, 3H), 1.25 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7, 139.8, 136.7, 129.4, 128.7, 127.9, 127.5, 125.3, 120.1, 73.6, 51.8, 44.7, 41.1, 17.5, 16.0; Anal. Calcd for $C_{24}H_{36}N_2O_3$: C, 71.96; H, 9.06; N, 6.99. Found: C, 71.95; H, 9.02; N, 6.78.



7o

7o (R=Tosyl): Yield 93% (white solid); m.p. 194-196□; $[\alpha]^{24}_D$ = +585.4 (*c* 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 8.5 Hz, 2H), 7.36-7.31 (m, 4H), 7.27-7.21 (m, 3H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.0 Hz, 1H), 5.19 (q, *J* = 7.0 Hz, 1H), 3.65 (dd, *J* = 10.5, 4.0 Hz, 1H), 3.64 (dd, *J* = 10.0, 4.5 Hz, 1H), 3.14 (t, *J* = 10.0 Hz, 1H), 2.46 (s, 3H), 1.49 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 153.0, 145.8, 138.7, 137.1, 134.7, 130.1, 129.4, 128.9, 128.6, 128.2, 127.1, 125.4, 120.4, 56.2, 51.0, 41.4, 22.0, 16.4; Anal. Calcd for $C_{19}H_{22}N_2O_4S$: C, 64.78; H, 5.44; N, 9.06; S, 6.92. Found: C, 64.77; H, 5.58; N, 9.14; S, 7.10.