Supporting Information for
Fluorinated Chiral Secondary Amines as Catalysts for Epoxidation of Olefins with
Oxone

*Chun-Yu Ho, Ying-Chun Chen, Man-Kin Wong and Dan Yang**

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

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General Aspects: All reagents and solvents for reactions were used as received. Syntheses of amines were carried out under nitrogen atmosphere. Reactions were monitored by thin layer chromatography (TLC) using silica gel 60 precoated glass plates with 0.25 mm thickness. ^1H -NMR (300 or 400 MHz) and ^{13}C -NMR (75 or 100 MHz) spectra were recorded in CDCl_3 , with tetramethylsilane (TMS) as internal standard at ambient temperature. Enantiomeric excess of the epoxide were determined by either ^1H NMR using $\text{Eu}(\text{hfc})_3$ (Aldrich no. 16,474-7) as chiral shift reagent or HPLC using a Chiralcel OD column in hexane / isopropanol. Mass spectra were obtained using electron impact ionization (EI, 20 eV) for both high and low resolution. Melting points were uncorrected.

Procedure for the Preparation of Amines 9a–c

The experimental procedure for the preparation of amines **9a'** and **9a** is the same as reported in the literature with the exception that the cyclohexyl amine was used instead of 1-adamantanamine.¹

Scheme 1. General Synthetic Scheme for 2,4-Disubstituted Amines **9a–c**

Conditions: (a) Boc_2O , Et_3N , MeOH , 50–60 °C, 94%; (b) Ac_2O , pyridine, CH_2Cl_2 , rt, 73%; (c) Cyclohexyl amine, EDCI, HOBT, CH_2Cl_2 , rt, 78%; (d) K_2CO_3 , MeOH , H_2O , 89%; (e) MOMCl, diisopropylethylamine, CH_2Cl_2 , 0 °C to rt, 60%; (f) TFA, CH_2Cl_2 , 0 °C to rt, 80–100%.

Preparation of amine 9a

To compound **9a'** (0.23 g, 0.66 mmol) in CH_2Cl_2 (5 mL) at 0 °C was added trifluoroacetic acid (3 mL). The reaction mixture was stirred at 0 °C for 35 min and warmed up to room temperature for 1 h. The solvent was removed under reduced pressure, and the residue was azeotroped twice with toluene. The residue was basified with 2 M NaOH followed by extraction with CH_2Cl_2 (15 mL $\times$ 3). The combined organic layers were dried over anhydrous Na_2SO_4 , and the solvent was removed under reduced pressure to afford **9a** as a white solid (0.16 g, 0.64 mmol, 97% yield); M.p. 104–108 °C; $[\alpha]_D^{25}$ –11.61 (*c* 0.71 CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3) δ 7.49–7.46 (m, 1H), 5.31–5.22 (m, 1H), 3.91 (t, *J* = 8.2 Hz, 1H), 3.72–3.69 (m, 1H), 3.12 (d, *J* = 13.0 Hz, 1H), 2.91 (dd, *J* = 13.0, 3.5 Hz, 1H), 2.39–2.32 (m, 1H), 2.12–2.02 (m, 1H), 2.05 (s, 3H) 1.90–1.82 (m, 2H), 1.72–1.59 (m, 3H), 1.43–1.16 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 172.7, 170.4, 76.3, 59.9, 53.4, 52.9, 47.4, 36.8, 33.1, 32.9, 25.5, 24.7, 21.1; IR (CH_2Cl_2) 3347, 1735, 1662 cm^{-1} ; LRMS (EI) 128 ($\text{M}^+ - \text{CONHC}_6\text{H}_{11}$, 25); HRMS (EI) calcd for $\text{C}_6\text{H}_{10}\text{NO}_2$ ($\text{M}^+ - \text{CONHC}_6\text{H}_{11}$) 128.0712, found 128.0713.

Preparation of amine 9b

To a solution of **9a'** (1.13 g, 3.2 mmol) in methanol (30 mL) and water (10 mL) was added potassium carbonate (0.66 g, 4.8 mmol). After being stirred at room temperature for 3 h, the reaction mixture was washed with brine and extracted with EtOAc (3 × 25 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to afford **9b'** as a white solid (0.89 g, 2.85 mmol, 89% yield). M.p. 163–164 °C; $[\alpha]_D^{25}$ –81.70 (*c* 0.89 CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 6.92 (br s, 0.4H), 5.89 (br s, 0.6H), 4.47–4.35 (m, 2H), 3.75–3.72 (m, 1H), 3.51 (dd, *J* = 11.3, 4.7 Hz, 1H), 2.50–2.05 (m, 3H), 1.86–1.53 (m, 6H), 1.46 (s, 9H), 1.43–1.15 (m, 5H); ¹³C NMR (67.5 MHz, CDCl₃) δ 170.6, 155.3, 80.7, 69.8, 60.0, 58.6, 54.6, 47.9, 39.7, 36.4, 32.9, 28.3, 25.5, 24.6; IR (CH₂Cl₂) 3416, 3326, 1680 cm^{–1}; LRMS (EI) 312 (M⁺, 2), 186 (11); HRMS (EI) calcd for C₁₆H₂₈N₂O₄ (M⁺) 312.2049, found 312.2041.

Amine **9b** was obtained in a similar way as **9a** from **9b'** using TFA (80% yield). $[\alpha]_D^{25}$ –45.35 (*c* 0.48 CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.62 (m, 1H), 4.40 (t, *J* = 3.4 Hz, 1H), 3.94 (t, *J* = 8.3 Hz, 1H), 3.75–3.62 (m, 1H), 3.01 (dd, *J* = 12.3, 3.3 Hz, 1H), 2.77 (dd, *J* = 12.3, 3.3 Hz, 1H), 2.45 (br s, 2 H), 2.30–2.23 (m, 1H), 1.94–1.80 (m, 3H), 1.74–1.57 (m, 3H), 1.44–1.30 (m, 2H), 1.25–1.09 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 173.9, 73.1, 59.7, 55.3, 47.4, 40.1, 33.1, 25.5, 24.7; IR (CH₂Cl₂) 3055, 1656 cm^{–1}; LRMS (EI) 194 (M⁺–H₂O, 3), 86 (100); HRMS (EI) calcd for C₁₁H₁₈N₂O (M⁺–H₂O) 194.1419, found 194.1417.

Preparation of amine **9c**

To a solution of **9b'** (0.28 g, 0.9 mmol) in CH₂Cl₂ (5 mL) were added *N,N'*-diisopropylethylamine (9 mL) and chloromethyl methyl ether (0.198 g, 1.8 mmol) under nitrogen atmosphere at 0 °C for 1 h. The reaction mixture was warmed to room temperature overnight. Water was added and the mixture was extracted with CH₂Cl₂ (25 mL × 3). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford **9c'** (0.138 g, 0.54 mmol, 60% yield) as a white solid; M.p. 107–109 °C; [α]_D²⁵ −75.14 (*c* 0.35 CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 6.95 (br s, 0.6H), 6.09 (br s, 0.4H), 4.64 (d, *J* = 1.6 Hz, 2H), 4.29 (br s, 2H), 3.73–3.60 (m, 3H), 3.35 (s, 3H), 2.60–2.30 (m, 1H), 2.21–2.04 (m, 1H), 1.88–1.53 (m, 5H), 1.46 (s, 9H), 1.43–1.17 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 171.1, 170.8, 170.1, 155.4, 154.5, 95.4, 95.1, 80.2, 75.2, 73.9, 60.1, 59.8, 58.3, 55.2, 52.1, 47.7, 37.2, 34.0, 32.9, 32.4, 28.0, 25.2, 24.6, 24.3; IR (CH₂Cl₂) 3416, 1680, 1518 cm^{−1}; LRMS (EI) 356 (M⁺, 3), 230 (27); HRMS (EI) calcd for C₁₈H₃₂N₂O₅ (M⁺) 356.2311, found 356.2313.

Amine **9c** was obtained in a similar way as **9a** from **9c'** using TFA (87% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.57–7.28 (m, 1H), 4.63 (m, 2H), 4.24 (s, 1H), 3.88 (t, *J* = 8.2, 3.9 Hz, 1H), 3.72–3.69 (m, 1H), 3.36 (s, 3H), 3.10 (d, *J* = 12.3 Hz, 1H), 2.76 (d, *J* = 12.3 Hz, 1H), 2.40–2.32 (m, 2H), 1.96–1.59 (m, 6H), 1.39–1.16 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 173.4, 94.9, 77.9, 59.8, 55.4, 53.0, 47.3, 36.9, 33.1, 33.0, 25.5, 24.8; IR (CH₂Cl₂) 3594, 3326, 1661 cm^{−1}; LRMS (EI) 256 (M⁺, 1), 130 (88); HRMS (EI) calcd for C₁₃H₂₄N₂O₃ (M⁺) 256.1787, found 256.1786.

Preparation of Amine 10

Amine **10** was prepared according to the literature procedure using L-proline as the starting material with the exception that ammonium formate and 10% Pd(OH)₂ were used in the final debenzylation step.²

Scheme 2. Procedure for Preparation of Amine **10**

Conditions: (a) Ammonium formate, 10% Pd(OH)₂, MeOH, reflux, 2 d, 80%.

To a mixture of amine **10'** (0.37 g, 1 mmol) and 10% Pd(OH)₂ (0.037g) in methanol (20 mL) was added ammonium formate (0.63 g, 10 mmol). After being refluxed for 2 d, the reaction mixture was cooled down to room temperature, filtered and concentrated under reduced pressure. Purification by flash column chromatography afforded amine **10** as an oil (0.21 g, 0.8 mmol, 80% yield).

Standard Procedure for the Preparation of Fluorinated Amines 12a–g

Amine **12a** was prepared according to the literature procedure using L-proline as the starting material.³ The amines **12b–g** were prepared in a similar way as amine **12a** (23–82%).

Scheme 3. Preparation of Fluorinated Amines 12a–g

Conditions: (a) K_2CO_3 , MeOH, ethyl chloroformate, 0 °C to rt, 84%; (b) RMgBr , THF, 0 °C to 65 °C, 18–72%; (c) 70% HF/pyridine, neat, 0 °C to rt, 23–82%.

Figure 1. Structures of Carbamates 12'a–g, 13'a–c and 13''b

Carbamate 12'a	Ar =	X = H	Y = H
Carbamate 12'b	Ar =	X = H	Y = H
Carbamate 12'c	Ar =	X = H	Y = H
Carbamate 12'd	Ar =	X = H	Y = H
Carbamate 12'e	Ar =	X = H	Y = H
Carbamate 12'f	Ar =	X = H	Y = H
Carbamate 12'g	Ar =	X = H	Y = H
Carbamate 13'a	Ar =	X = OTHP	Y = H
Carbamate 13''b	Ar =	X = OH	Y = H
Carbamate 13'b	Ar =	X = OMe	Y = H
Carbamate 13'c	Ar =	X = F	Y = F

Figure 2. Structures of Amines 12a–g and 13a–c

	Amine 12a	Ar =		X = H	Y = H
	Amine 12b	Ar =		X = H	Y = H
	Amine 12c	Ar =		X = H	Y = H
	Amine 12d	Ar =		X = H	Y = H
	Amine 12e	Ar =		X = H	Y = H
	Amine 12f	Ar =		X = H	Y = H
	Amine 12g	Ar =		X = H	Y = H
	Amine 13a	Ar =		X = OH	Y = H
	Amine 13b	Ar =		X = OMe	Y = H
	Amine 13c	Ar =		X = F	Y = F

Procedure for the preparation of carbamates **12'a–g**

12'a was selected as an example for the preparation of the carbamates.

Ethyl chloroformate (10.85 g, 100 mmol) was added dropwise at 0 °C to a mixture of L-proline (5 g, 43.5 mmol) and K₂CO₃ (6 g, 43.5 mmol) in MeOH (40 mL), and the reaction mixture was warmed up to room temperature gradually. After completion of the reaction as shown by TLC, the reaction mixture was filtered and the filtrate was concentrated, diluted with Et₂O, washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. Purification by flash column chromatography afforded the precursor of the carbamate **12'a–g** as an oil (7.34 g, 36.5 mmol, 84% yield).

PhMgBr solution in THF (1 M, 80 mL, 80 mmol) was added dropwise at 0 °C to a solution of the above product (7.34 g, 36.5 mmol) in THF (200 mL), and the resulting reaction mixture was warmed up to room temperature gradually then heated up to 65 °C. After kept stirring for overnight, the reaction was quenched by aq NH₄Cl, extracted with Et₂O, washed with brine, dried over MgSO₄, and concentrated under reduced pressure. Purification by flash column chromatography afforded the corresponding carbamate **12'a** as a solid (7.13 g, 25.55 mmol, 70% yield).³

Carbamate 12'b: Yield 72%; [α]_D²⁵ -190.6 (*c* 0.90, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.19–7.11 (m, 4H), 4.49 (dd, *J* = 13.9, 7.4 Hz, 1H), 3.72–3.70 (m, 1H), 3.26–3.20 (m, 1H), 2.31 (s, 6H), 1.96–1.94 (m, 1H), 1.85–1.83 (m, 1H), 1.72–1.68 (m, 1H), 1.14–1.09 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 160.5, 138.0, 137.3, 129.1, 128.8, 125.8, 125.4, 85.9, 69.2, 46.0, 28.9, 24.9, 21.0; IR (CH₂Cl₂) 1752, 1422 cm⁻¹; LRMS (EI) 307 (M⁺) (87); HRMS (EI) calcd for C₂₀H₂₁NO₂ (M⁺) 307.1572, found 307.1570.

Carbamate 12'c: Yield 18%; [α]_D²⁵ -603.2 (*c* 0.5, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 8.31 (d, *J* = 7.3 Hz, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 8.11 (d, *J* = 7.4 Hz, 1H), 7.86–7.51 (m, 7H), 7.31–7.26 (m, 2H), 7.16–7.09 (m, 2H), 5.30–5.25 (dd, *J* = 9.9 Hz, 5.9 Hz, 1H), 3.84–3.75 (m, 1H), 3.44–3.36 (m, 1H), 1.96–1.81 (m, 2H), 1.34–1.06 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 160.4, 137.2, 136.3, 134.9, 134.2, 131.6, 130.6, 129.5, 129.1 (2 C), 128.7, 126.0, 125.9 (2 C), 125.5, 125.4, 124.9, 124.5, 124.4, 124.2, 124.1, 86.3, 67.1, 46.4, 28.0, 24.4; IR (CH₂Cl₂) 1755, 1422 cm⁻¹; LRMS (EI) 379 (M⁺) (32), 335 (100); HRMS (EI) calcd for C₂₆H₂₁NO₂ (M⁺) 379.1572, found 379.1565.

Carbamate 12'd: Yield 68%; $[\alpha]_D^{25} -351.6$ (*c* 0.5, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 8.09 (s, 1H), 8.02 (s, 1H), 7.80–7.74 (m, 6H), 7.63–7.60 (m, 1H), 7.49–7.44 (m, 4H), 7.31–7.28 (m, 1H), 4.75 (dd, *J* = 10.5, 5.5 Hz, 1H), 3.78–3.71 (m, 1H), 3.30–3.24 (m, 1H), 1.96–1.86 (m, 2H), 1.76–1.70 (m, 1H), 1.75–1.12 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 160.3, 140.0, 137.4, 132.9, 132.8, 132.7, 132.5, 128.6, 128.4, 128.3, 128.1, 127.6, 127.4, 126.6, 126.5, 126.4, 126.3, 124.8, 124.4, 124.1, 123.7, 86.1, 68.6, 46.0, 29.0, 24.9; IR (CH₂Cl₂) 1755, 1422 cm⁻¹; LRMS (EI) 379 (M⁺) (54), 282 (100); HRMS (EI) calcd for C₂₆H₂₁NO₂ (M⁺) 379.1572, found 379.1578.

Carbamate 12'e: Yield 70%; $[\alpha]_D^{25} -173.1$ (*c* 0.22, CH₂Cl₂); ¹H NMR (400 MHz, CD₃COCD₃ + DMSO) δ 7.78–7.60 (m, 12H), 7.46 (t, *J* = 7.6 Hz, 4H), 7.37 (t, *J* = 7.3 Hz, 2H), 4.82 (dd, *J* = 10.5, 5.2 Hz, 1H), 3.66–3.61 (m, 1H), 3.25–3.19 (m, 1H), 2.00–1.88 (m, 3H), 1.13–1.08 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 143.4, 140.7, 140.2, 140.1, 140.0, 129.0, 127.7, 127.3, 127.0, 126.8, 126.4, 126.3, 126.2, 126.1, 126.0, 125.9, 125.8, 85.1, 68.7, 46.1, 28.8, 24.4; IR (CH₂Cl₂) 1755, 1422 cm⁻¹; LRMS (EI) 431 (M⁺) (47), 204 (100); HRMS (EI) calcd for C₃₀H₂₅NO₂ (M⁺) 431.1885, found 431.1883.

Carbamate 12'f: Yield 72%; $[\alpha]_D^{25} -242.8$ (*c* 0.50, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.68–7.65 (m, 1H), 7.52–7.48 (m, 1H), 6.95–6.76 (m, 4H), 4.78–4.72 (m, 1H), 3.75–3.66 (m, 1H), 3.34–3.26 (m, 1H), 2.7–1.81 (m, 3H), 1.23–1.15 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 164.8, 164.7, 164.6, 164.5, 162.4, 162.2, 161.5, 161.3 (2 C), 161.1, 160.2, 160.0, 159.0, 158.9 (2 C), 156.9, 156.7, 128.8, 128.7 (2 C), 128.6, 128.4 (3 C), 128.3 (3 C), 128.2 (2 C), 124.4, 124.3, 123.2, 122.9, 111.4 (t, *J* = 17.6 Hz), 111.2 (t, *J* = 17.7 Hz), 105.1 (t, *J* = 26.0 Hz), 104.2 (t, *J* =

25.4 Hz), 81.6, 67.1, 45.7, 27.8, 24.8; IR (CH₂Cl₂) 1761, 1615, 1504, 1422 cm⁻¹; LRMS (EI) 351 (M⁺) (50), 182 (100); HRMS (EI) calcd for C₁₈H₁₃NF₄O₂ (M⁺) 351.0882, found 351.0876.

Carbamate 12'g : Yield 58%; [α]_D²⁵ -124.6 (*c* 0.46, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 8.00 (s, 2H), 7.92 (s, 2H), 7.89 (s, 2H), 4.59 (dd, *J* = 10.8, 5.3 Hz, 1H), 3.84–3.77 (m, 1H), 3.37–3.31 (m, 1H), 2.16–2.10 (m, 1H), 2.04–1.99 (m, 1H), 1.84–1.62 (m, 1H), 1.14–1.06 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 158.8, 144.6, 141.6, 132.8 (q, *J* = 33.6 Hz), 132.7 (q, *J* = 33.6 Hz), 125.8, 125.5, 124.2 (d, *J* = 4.4 Hz), 123.3 (d, *J* = 2.8 Hz), 122.8 (d, *J* = 2.8 Hz), 121.4 (d, *J* = 4.4 Hz), 83.5, 69.0, 46.3, 29.1, 24.6. IR (CH₂Cl₂) 1772, 1422, 1370, 1281, 1264 cm⁻¹; LRMS (EI) 551 (M⁺) (100); HRMS (EI) calcd for C₂₂H₁₃NO₂F₁₂ (M⁺) 551.0755, found 551.0753.

Procedure for the preparation of amines 12a–g

12a was selected as an example for the preparation of the amines.

Precooled 70% HF pyridine (8 mL) was added dropwise at 0 °C to carbamate **12'a** (0.56 g, 2 mmol) in a plastic reaction flask, and the reaction mixture was warmed up to room temperature gradually. After 24 h, the reaction was cooled down, diluted with Et₂O and quenched by 9 M aq KOH to pH 14, extracted with Et₂O (30 mL×3), dried over MgSO₄, and concentrated under reduced pressure. Purification by flash column chromatography afforded amine **12a** as an oil (0.42 g, 1.64 mmol, 82% yield).³ **Amine 12a**: Yield 82%; [α]_D²⁵ -8.1 (*c* 7.4, MeOH); ¹H NMR (300 MHz, CDCl₃) δ 7.54–7.20 (m, 10H), 4.16 (dt, *J* = 28.4, 7.4 Hz, 1H), 3.11–3.03 (m, 1H), 2.90–2.83 (m, 1H), 1.80–1.65 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 143.0 (d, *J* = 23.3 Hz), 142.6 (d, *J* = 23.3 Hz), 128.6 (d, *J* = 1.1 Hz), 128.5 (d, *J* = 1.1 Hz), 127.5 (d, *J* = 1.2 Hz), 127.3

(d, $J = 1.0$ Hz), 125.5 (d, $J = 9.0$ Hz), 124.9 (d, $J = 9.0$ Hz), 100.1 (d, $J = 181.4$ Hz), 64.4 (d, $J = 22.0$ Hz), 47.5, 26.5 (d, $J = 3.4$ Hz), 26.0; IR (CH₂Cl₂) 3414, 1634 cm⁻¹; LRMS (EI) 256 (M⁺+H) (1), 235 (100). HRMS (EI) calcd for C₁₇H₁₇N (M⁺-HF) 235.1361, found 235.1354.

Amine 12b: Yield 73%; [α]_D²⁵ -9.0 (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, $J = 8.2$ Hz, 2H), 7.28 (d, $J = 8.2$ Hz, 2H), 7.14–7.10 (m, 4H), 4.12 (dt, $J = 27.9, 7.3$ Hz, 1H), 3.08–3.03 (m, 1H), 2.85–2.82 (m, 1H), 2.29 (s, 6H), 1.76–1.63 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 140.4 (d, $J = 23.3$ Hz), 139.9 (d, $J = 24.4$ Hz), 136.9 (d, $J = 15.8$ Hz), 128.9 (d, $J = 12.3$ Hz), 125.4 (d, $J = 8.9$ Hz), 124.8 (d, $J = 9.0$ Hz), 100.2 (d, $J = 180.3$ Hz), 64.4 (d, $J = 22.2$ Hz), 47.4, 26.5 (d, $J = 3.5$ Hz), 26.0, 21.0; IR (CH₂Cl₂) 3411, 1643, 1511 cm⁻¹; LRMS (EI) 263 (M⁺-HF) (100); HRMS (EI) calcd for C₁₉H₂₂NF (M⁺) 283.1736, found 283.1747.

Amine 12c: Yield 64%; [α]_D²⁵ -44.8 (c 0.80, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 8.28–8.25 (m, 3H), 7.83–7.73 (m, 4H), 7.60–7.36 (m, 2H), 7.32–7.18 (m, 5H), 4.58–4.48 (m, 1H), 3.16–3.08 (m, 1H), 2.96–2.91 (m, 1H) 2.03–1.93 (m, 2H), 1.86–1.62 (m, 2H), 1.56 (brs, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 138.1 (d, $J = 20.4$ Hz), 137.1 (d, $J = 21.9$ Hz), 134.7, 134.5, 131.3, 130.6, 129.8, 129.2, 128.8 (d, $J = 7.9$ Hz), 126.8 (d, $J = 8.0$ Hz), 126.1 (d, $J = 6.5$ Hz), 125.8 (d, $J = 6.0$ Hz), 125.2, 125.0, 124.3, 65.1 (brs), 47.4, 28.2 (d, $J = 2.6$ Hz), 25.8; IR (CH₂Cl₂) 3434, 1651, 1509 cm⁻¹; LRMS (EI) 335 (M⁺-HF) (100); HRMS (EI) calcd for C₂₅H₂₂NF 355.1736 (M⁺), found 355.1745.

Amine 12d: Yield 23%; [α]_D²⁵ -23.5 (c 1.0, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 8.14 (s, 1H), 8.00 (s, 1H), 7.86–7.75 (m, 6H), 7.49–7.45 (m, 6H), 4.50–4.39 (dt, $J = 27.9$ Hz, 7 Hz, 1H),

3.12–3.09 (m, 1H), 2.92–2.90 (m, 1H), 1.90–1.74 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.1 (d, $J = 23.7$ Hz), 139.6 (d, $J = 23.9$ Hz), 133.0, 132.7, 132.5, 128.4, 128.3, 128.2, 128.1, 127.5, 127.0, 126.3, 126.2, 124.5 (d, $J = 9.8$ Hz), 124.0 (d $J = 7.7$ Hz), 123.7 (d, $J = 9.9$ Hz), 123.4 (d, $J = 7.9$ Hz), 100.6 (d, $J = 182.4$ Hz), 64.0 (d, $J = 21.9$ Hz), 47.5, 26.7 (d, $J = 3.3$ Hz), 26.0; IR (CH_2Cl_2) 3421, 3061, 2970, 1601, 1472, 1258, 1236, 759 cm^{-1} ; LRMS (EI) 335 ($\text{M}^+ - \text{HF}$) (100); HRMS (EI) calcd for $\text{C}_{25}\text{H}_{21}\text{N}$ ($\text{M}^+ - \text{HF}$) 335.1674, found 335.1658.

Amine 12e: Yield 66%; $[\alpha]_{\text{D}}^{25} -9.0$ (c 1.0, CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3) δ 7.61–7.52 (m, 12H), 7.42–7.30 (m, 6H), 4.22 (dt, $J = 27.8, 6.8$ Hz, 1H), 3.11–3.05 (m, 1H), 2.91–2.86 (m, 1H), 1.84–1.71 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.9 (d, $J = 23.6$ Hz), 141.5 (d, $J = 24.3$ Hz), 140.5 (d, $J = 9.5$ Hz), 140.3 (d, $J = 11.5$ Hz), 128.7, 128.6, 127.3, 127.2, 127.1, 127.0, 126.9, 125.9 (d, $J = 8.9$ Hz), 125.2 (d, $J = 9.0$ Hz), 100.0 ($J = 181.3$ Hz), 64.5 (d, $J = 22.0$ Hz), 47.5, 26.6 (d, $J = 3.2$ Hz), 26.0; IR (CH_2Cl_2) 3426, 1652, 1483 cm^{-1} ; LRMS (EI) 387 ($\text{M}^+ - \text{HF}$) (100); HRMS (EI) calcd for $\text{C}_{29}\text{H}_{25}\text{N}$ ($\text{M}^+ - \text{HF}$) 387.1987, found 387.1960.

Amine 12f: Yield 72%; $[\alpha]_{\text{D}}^{25} -19.1$ (c 1.5, CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3) δ 7.71–7.61 (m, 2H), 6.93–6.87 (m, 2H), 6.73–6.66 (m, 2H), 4.43 (dt, $J = 30.1, 7.7$ Hz, 1H), 3.06–3.01 (m, 1H), 2.96–2.92 (m, 1H), 2.55 (brs, 1H), 1.85–1.71 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.5, 164.4, 164.2, 161.3, 161.2, 161.1, 160.9, 160.2, 158.1, 158.0, 157.9, 157.1, 157.0, 129.9–129.6 (m), 128.4–128.1 (m), 125.2–124.0 (m), 111.0 (t, $J = 3.2$ Hz), 110.7 (t, $J = 3.2$ Hz), 104.5 (t, $J = 25.4$ Hz), 104.4 (t, $J = 25.4$ Hz), 96.8 (dt, $J = 183.4, 3.3$ Hz), 61.4 (d, $J = 20.9$ Hz), 47.8, 26.9 (d, $J = 3.9$ Hz), 26.4; IR (CH_2Cl_2) 3441, 1610, 1502 cm^{-1} ; LRMS (EI) 307 ($\text{M}^+ - \text{HF}$) (96), 287 (100); HRMS (EI). calcd for $\text{C}_{17}\text{H}_{13}\text{NF}_4$ ($\text{M}^+ - \text{HF}$) 307.0984, found 307.0984.

Amine 12g: Yield 66%; $[\alpha]_D^{25} -23.8$ (c 2.0, CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3) δ 8.11 (s, 2H), 7.94 (s, 2H), 7.86 (s, 2H), 4.19 (dt, $J = 21.4, 6.9$ Hz, 1H), 2.99–2.93 (m, 2H), 1.89–1.60 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 144.2 (d, $J = 23.8$ Hz), 143.1 (d, $J = 24.5$ Hz), 132.4 (q, $J = 32.7$ Hz), 132.0 (q, $J = 34.7$ Hz), 126.1, 125.4, 124.8 (d, $J = 7.0$ Hz), 122.4, 122.3, 121.2 (d, $J = 7.1$ Hz), 98.5 (d, $J = 183.4$ Hz), 64.8 (d, $J = 24.6$ Hz), 47.6, 27.2 (d, $J = 2.2$ Hz), 26.2; IR (CH_2Cl_2) 3434, 1637, 1426 cm^{-1} ; LRMS (EI) 527 (M^+) (2), 508 ($\text{M}^+ - \text{F}$) (100); HRMS (EI) calcd for $\text{C}_{21}\text{H}_{14}\text{NF}_{13}$ (M^+) 527.0919, found 527.0902.

Preparation of Amine 13a

Amines **13a–c** were as prepared in a similar way to that of amine **12a** using *trans*-4-hydroxyl L-proline as the starting material.^{3,4}

Scheme 4. Preparation of Amine 13a

Conditions: (a) K₂CO₃, MeOH, ethyl chloroformate, 0 °C to rt, 84%; (b) THP, PPTS, CH₂Cl₂, rt, 95%; (c) PhMgBr, THF, 0 °C to 65 °C, 90%; (d) 70% HF/pyridine, neat, 0 °C to rt, 69%

Compound **13** was prepared according to the literature procedure as follow.⁴ Ethyl chloroformate (12.7 mL, 133 mmol) was added dropwise at 0 °C to a mixture of *trans*-4-hydroxyl L-proline (5.69 g, 43 mmol) and K₂CO₃ (9.5 g, 69 mmol) in MeOH (80 mL), and the resulting mixture was warmed up to room temperature gradually. After the starting materials were consumed, the solid was filtered off and the filtrate was concentrated, diluted with Et₂O (200 mL), washed with brine (50 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by flash column chromatography afforded **13** as an oil (7.8 g, 36 mmol, 84% yield).

Compound **13** (1.57 g, 7.2 mmol) and 3,4-dihydro-2H-pyran (1 mL, 11 mmol) were dissolved in dichloromethane (15 mL), followed by the addition of PPTS (0.36 g, 1.5 mmol). After kept stirring stir at room temperature overnight, the reaction mixture was washed with water (10 mL), dried over MgSO₄, and concentrated under reduced pressure. Purification by flash column chromatography afforded the corresponding THP protected product as an oil (2.05 g, 6.8 mmol, 95% yield).

Carbamate **13'a** was then prepared according to the standard procedure using PhMgBr as described in the preparation of carbamate **12'a**. Yield 90%; $[\alpha]_D^{25} -234.1$ (*c* 0.33, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.55–7.25 (m, 10H), 4.90–4.80 (m, 1H), 4.57–4.55 (m, 1H), 4.43–4.39 (m, 1H), 4.10–3.97 (m, 1H), 3.82–3.77 (m, 1H), 3.50–3.45 (m, 1H), 3.35–3.20 (m, 1H), 1.82–1.18 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 160.3, 143.0, 140.1, 128.5, 128.4, 128.3, 127.7, 126.1, 125.4, 98.4, 97.9, 76.1, 75.3, 67.7, 67.3, 63.2, 62.9, 54.4, 53.9, 36.1, 37.6, 31.5, 30.8, 22.6, 20.9, 19.6, 19.8; IR (CH₂Cl₂) 1758, 1606, 1450, 1423 cm⁻¹; LRMS (EI) 379 (M⁺) (12); HRMS (EI) calcd for C₂₃H₂₅N₁O₄ 379.1784 (M⁺), found 379.1776.

Amine **13a** was prepared from **13'a** according to the standard procedure using 70% HF pyridine as described in the preparation of amine **12a**. Yield 69%; $[\alpha]_D^{25} -19.5$ (*c* 1.05, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.51–7.20 (m, 10H), 4.42 (dt, *J* = 28.2, 8.0 Hz, 1H), 4.33 (m, 1H), 3.12 (dd, *J* = 11.2, 4.2 Hz, 1H), 2.83 (d, *J* = 11.2 Hz, 1H), 2.43 (brs, 2H), 1.98–1.91 (m, 1H), 1.63 (dd, *J* = 13.7, 7.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 142.5 (d, *J* = 23.4 Hz), 142.2 (d, *J* = 24.2 Hz), 128.3 (d, *J* = 13.2 Hz), 127.4 (d, *J* = 19.1 Hz), 125.5 (d, *J* = 8.9 Hz), 124.7 (d, *J* = 9.3 Hz), 100.2 (d, *J* = 181.9 Hz), 72.4, 62.7 (d, *J* = 21.7 Hz), 55.5, 36.2 (d, *J* = 3.2 Hz); IR

(CH₂Cl₂) 3685, 3607, 3367, 1599, 1494 cm⁻¹; LRMS (EI) 233 (M⁺-HF, -H₂O) (100); HRMS (EI) calcd for C₁₇H₁₈NOF 271.1372 (M⁺), found 271.1327.

Scheme 5. Preparation of Amine 13b

Conditions: (a) AcOH, THF, H₂O, 45 °C, 100%; (b) NaH, MeI, THF, 0 °C to rt, 81%; (c) 70% HF/pyridine, neat, 0 °C to rt, 96%

Carbamate **13'a** (0.164 g, 0.54 mmol) was dissolved in the solvent (AcOH/THF/H₂O, 8/4/2, 14 mL), and heated to 45 °C overnight. After concentrated under reduced pressure, and followed by flash column chromatography, afforded the deprotected alcohol **13''b** as an oil (0.159 g, 0.54 mmol, quantitative yield). [α]_D²⁵ -213.6 (c 0.27, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.52–7.26 (m, 10H), 4.95 (dd, *J* = 11.3, 5.0 Hz, 1H), 4.47 (t, *J* = 5.3 Hz, 1H), 3.98 (dd, *J* = 12.7, 5.6 Hz, 1H), 3.17 (d, *J* = 12.7 Hz, 1H), 3.05–2.45 (br, s, 1H), 1.73 (dd, *J* = 13.3, 5.0 Hz, 1H), 1.38–1.15 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 160.5, 142.9, 140.0, 128.4, 128.2, 128.2, 127.6, 125.8, 125.1, 86.0, 71.0, 67.0, 56.0, 39.0; IR (CH₂Cl₂) 3600, 1758, 1494, 1450 cm⁻¹; LRMS (EI) 295 (M⁺) (12); HRMS (EI) calcd for C₁₈H₁₇NO₃ 295.1208 (M⁺), found 295.1209.

NaH (60% in mineral oil, 24 mg, 0.6 mmol) was added to carbamate **13''b** (0.122 g, 0.4 mmol) in THF (5 mL) at 0 °C under nitrogen atmosphere, and the reaction was stirred at that temperature for 30 min followed by dropwise addition of iodomethane (50 μ L, 0.8 mmol). After the completion of the reaction as shown by TLC, the reaction was quenched by aq NH₄Cl (20

mL), extracted with Et₂O (100 mL), washed with brine (20 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by flash column chromatography afforded **13'b** as an oil (0.099 g, 0.32 mmol, 81% yield). $[\alpha]^{25}_{\text{D}} -233.7$ (*c* 0.134, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.54–7.26 (m, 10H), 4.81 (dd, *J* = 11.2, 5.0 Hz, 1H), 4.02–3.95 (m, 2H), 3.28–3.23 (m, 4H), 1.85 (dd, *J* = 11.2, 5.0 Hz, 1H), 1.24–1.11 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 160.2, 142.9, 140.1, 128.6, 128.4, 128.4, 127.8, 126.0, 125.4, 85.7, 80.4, 67.2, 56.8, 53.3, 35.6; IR (CH₂Cl₂) 1758, 1606, 1450, 1423, 1420 cm⁻¹; LRMS (EI) 309 (M⁺) (48); HRMS (EI) calcd for C₁₉H₁₉NO₃ 309.1365 (M⁺), found 309.1355.

Amine **13b** was prepared in 96% yield from **13'b** according to the standard procedure using 70% HF pyridine as described in the preparation of amine **12a**. $[\alpha]^{25}_{\text{D}} -17.84$ (*c* 0.5, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.53–7.20 (m, 10H), 4.39 (dt, *J* = 27.7, 7.4 Hz, 1H), 3.92–3.87 (m, 1H), 3.26 (s, 3H), 3.13 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.02–2.96 (m, 1H), 1.94–1.72 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 142.7 (d, *J* = 23.3 Hz), 142.4 (d, *J* = 24.1 Hz), 128.3 (d, *J* = 1.3 Hz), 127.5 (d, *J* = 1.0 Hz), 127.4 (d, *J* = 1.0 Hz), 125.5 (d, *J* = 9.0 Hz), 124.8 (d, *J* = 9.4 Hz), 99.9 (d, *J* = 181.5 Hz), 81.7, 63.1 (d, *J* = 21.8 Hz), 56.4, 52.4, 33.0 (d, *J* = 3.5 Hz); IR (CH₂Cl₂) 3689, 3602, 3066, 2983, 2929, 2826, 1601, 1493, 1439, 1347, 1217, 1086, 979, 894 cm⁻¹; LRMS (EI) 233 (M⁺–HF, –MeOH) (100); HRMS (EI) calcd for C₁₈H₁₈NO 264.1388 (M⁺–H₂F), found 264.1389.

Scheme 6. Preparation of Amines **13c**

Conditions: (a) PDC, celite, CH₂Cl₂, rt, 45%; (b) DAST, CH₂Cl₂, -78 °C to rt, 80%; (c) PhMgBr, THF, 0 °C to 65 °C, 45%; (d) 70% HF/pyridine, neat, 0 °C to rt, 93%

Compound **13** (2.4 g, 11 mmol) was dissolved in CH₂Cl₂ (100 mL) and cooled down to 0 °C. Celite (6 g) and PDC (8.3 g, 22 mmol) were added together in one portion. After kept stirring overnight, the reaction mixture was filtered, and the filtrate was concentrated and purified by flash column chromatography to afford the ketone as an oil (1 g, 4.95 mmol, 45% yield).⁵

DAST (0.63 mL, 6.4 mmol) was added dropwise to the above ketone (0.7 g, 3.2 mmol) in CH₂Cl₂ (5 mL) at -78 °C under nitrogen atmosphere. After the addition, the reaction was allowed to stir at that temperature for 2 h and then warmed up gradually to room temperature. The reaction was diluted with CH₂Cl₂ (50 mL), added saturated aq NaHCO₃ (50 mL) and stirred for 15 min. The mixture was extracted with CH₂Cl₂ (50 mL × 2), and the organic layer was dried over MgSO₄, and concentrated under reduced pressure. Purification by flash column chromatography afforded **13''c** as an oil (0.61 g, 2.56 mmol, 80% yield). ¹H NMR (400 MHz, CDCl₃) δ 4.62–4.51 (m, 1H), 4.24–4.05 (m, 2H), 3.95–3.81 (m, 2H), 3.76 (s, 3H), 2.82–2.65 (m, 1H), 2.58–2.40 (m, 1H), 1.35–1.15 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.5 (d, *J* = 14.8 Hz), 154.0 (d, *J* = 62 Hz), 126.7 (dd, *J* = 151.4, 67.0 Hz), 61.8 (d, *J* = 14.8 Hz), 56.7, 53.0 (td, *J*

= 32.4, 8.9 Hz), 52.3, 38.2 (dt, J = 79.0, 25.0 Hz), 14.3; IR (CH₂Cl₂) 1778, 1603, 1500 cm⁻¹; LRMS (EI) 217 (M⁺-HF) (28); HRMS (EI) calcd for C₉H₁₂NO₄F 217.0750 (M⁺-HF), found 217.0755.

Carbamate **13'c** was prepared in 45% yield from **13''c** according to the standard procedure using PhMgBr as described in the preparation of carbamate **12'a**. [α]_D²⁵ -192.9 (c 0.40, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.51–7.15 (m, 10H), 4.92 (dd, J = 11.2, 5.7 Hz, 1H), 4.14 (td, J = 12.8, 11.7 Hz, 1H), 3.60–3.51 (m, 1H), 2.21 (td, J = 11.2, 5.7 Hz, 1H), 1.88–1.65 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 159.0, 141.8, 139.1, 133.3, 128.9, 128.8, 128.7, 128.7, 128.3, 125.8, 125.2, 85.9, 66.6 (d, J = 6.0 Hz), 55.0 (t, J = 66.4 Hz), 39.7 (t, J = 51.3 Hz); IR (CH₂Cl₂) 1773, 1603, 1491 cm⁻¹; LRMS (EI) 315 (M⁺) (48); HRMS (EI) calcd for C₁₈H₁₅NO₂F₂ 315.1071 (M⁺), found 315.1076.

Amine **13c** was prepared in 93% yield from **13'c** according to the standard procedure using 70% HF pyridine as described in the preparation of amine **12a**. [α]_D²⁵ -12.89 (c 0.9, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.52–7.48 (m, 2H), 7.41–7.22 (m, 8H), 4.40 (dt, J = 26.3, 7.6 Hz, 1H), 3.35 (dd, J = 24.7, 12.7 Hz, 1H), 3.15 (dd, J = 24.7, 12.7 Hz, 1H), 2.41–2.05 (m, 2H), 1.91 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 141.2 (d, J = 23.1 Hz), 141.0 (d, J = 24.0 Hz), 133.2, 130.7, 128.5 (d, J = 2.6 Hz), 127.9 (d, J = 7.0 Hz), 125.3 (d, J = 9.0 Hz), 124.6 (d, J = 10.0 Hz), 100.0 (d, J = 182.3 Hz), 63.0 (dq, J = 22.0, 2.2 Hz), 54.7 (t, J = 29.0 Hz), 36.7 (td, J = 25.0, 3.6 Hz); IR (CH₂Cl₂) 3691, 3598, 3378, 1605, 1495 cm⁻¹; LRMS (EI) 271 (M⁺-HF) (23), HRMS (EI) calcd for C₁₇H₁₅NF₂ 271.1173 (M⁺-HF), found 271.1162.

Preparation of Amine 14

Amine **14** was prepared from the corresponding carbamate **12'b** using hydrogen and 10% Pd/C in MeOH.

Scheme 7. Preparation of Amine 14

Conditions: (a) 10% Pd/C, MeOH, H₂, rt, 30%.

The mixture of **12'b** (0.307 g, 1 mmol) in MeOH (10 mL) and 10% Pd/C was subjected to the H₂ atmosphere and stir at room temperature for 2 d. The solid was filtered off and the filtrate was concentrated under reduced pressure. Purification by flash column chromatography afforded the **14** as oil (0.08 g, 0.3 mmol, 30% yield). **Amine 14**: Yield 30%; $[\alpha]_D^{25} +2.2$ (*c* 1.0, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.22 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.09–7.04 (m, 4H), 3.77–3.73 (m, 1H), 3.69–3.66 (m, 1H), 3.01–2.97 (m, 1H), 2.84–2.80 (m, 1H), 2.27 (s, 6H), 2.11(bris, 1H), 1.80–1.71 (m, 3H), 1.40–1.36 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 140.9, 140.8, 135.7, 135.6, 129.2, 129.0, 121.8, 62.3, 57.5, 46.0, 30.4, 24.6, 20.9; IR (CH₂Cl₂) 3434, 1610, 1502 cm⁻¹; LRMS (EI) 264 (M⁺–H) (6); HRMS (EI) calcd for C₁₉H₂₃N (M⁺) 265.1830, found 265.1803.

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