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Supporting information

Stereoselective Barbier-Type Allylation Reaction of Trifluoromethyl Aldimines

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All the reactions were performed in an oven-dried apparatus under an inert atmosphere of argon. ¹⁹F NMR, ¹³C NMR, ¹H NMR spectra were recorded on a 200 MHz or 400MHz multinuclear spectrometer, ¹⁹F NMR spectra are referenced to external CFCl₃, ¹H NMR and ¹³C NMR spectra to TMS. In all NMR measurements CDCl₃ was used as a solvent. Elemental analyses were performed by the Service de Microanalyses of the Centre d'Etudes Pharmaceutiques, Châtenay-Malabry.

The diastereoselectivities were determined by ¹⁹F NMR and GC.

Allylation reaction with magnesium

N-Benzyl-1,1,1-trifluoro-4-penten-2-amine **3a**

To a solution of imine **1** (187 mg, 1.0 mmol) and allyl bromide **2a** (181 mg, 1.5 mmol) in ether was added successively magnesium turning (36 mg, 1.5 mmol) and 2 drops of TMSCl at room temperature. After 45 min of stirring, the reaction was quenched with a saturated aqueous NH₄Cl solution (15 mL). The mixture was extracted with ether (2 x 20 mL), dried

(MgSO₄), and the solvent was removed. The residue was purified by flash chromatography on silica gel (Petroleum ether/AcOEt: 9/1) to afford homoallyl amine **3a** (172 mg, 75%).

Allylation reaction with indium

N*-Benzyl-1,1,1-trifluoro-4-penten-2-amine **3a*

To a mixture of the imine **1** (374 mg, 2.0 mmol) and indium powder (252 mg, 2.2 mmol) in DMF (6 mL) was added allyl bromide (242 mg, 2.5 mmol). After 1 hour at room temperature, the reaction mixture was diluted with aqueous NaHCO₃ and extracted with ether. The combined organic extracts were dried, evaporated and the residue purified by flash chromatography on silica gel (petroleum ether/EtOAc : 9/1), to afford homoallyl amine **3a** (458 mg, 96%).

General procedure of allylation reaction with zinc

In DMF :

N*-Benzyl-1,1,1-trifluoro-4-penten-2-amine **3a*

The imine **1** (1.03 g, 5.5 mmol) and the allyl bromide **2a** (865 mg, 7.16 mmol, 1.3 eq) are dissolved in DMF (10 mL). The solution was cooled at 0°C, then zinc (467 mg, 7.16 mmol, 1.3 eq) was added, and 2 drops of TMSCl. After addition, the reaction was warmed slowly at room temperature (the reaction was followed by GC). After 45 min, the mixture was cooled at 0°C and hydrolyzed with a saturated aqueous solution of NH₄Cl (20 mL), then extracted with Et₂O (20 mL × 3). Organic layer was washed with a saturated solution of NaCl (30 mL), dried on MgSO₄, filtered, and solvents were evaporated. The residue was subjected to flash chromatography on silica gel (Petroleum ether/AcOEt, 9/1) affording a colorless corresponding homoallylic **3a** (1.19 g, 95%).

In THF :

To a solution of imine **1** (374 mg, 2.0 mmol) in 5 mL of THF was added allyl bromide **2a** (290 mg, 2.4 mmol), Zn (169 mg, 2.6 mmol) and 2 drops of TMSCl. The mixture was refluxed for 30 min, and then the solution was hydrolysed with a saturated aqueous solution of NH₄Cl (20 mL) and extracted with Et₂O (3 x 10 mL). The combined organic layers were dried over MgSO₄ and filtered. The solvents were removed and the residue was purified by flash chromatography on silica gel with petroleum ether/CH₂Cl₂ (3/2) as eluent to afford the homoallyl amine **3a** (390 mg, 85%).

NMR (200 MHz) ^1H δ 1.38 (s, br, 1H), 2.28 (m, 1H), 2.47 (m, 1H), 3.10 (m, 1H), 3.75 (d, J = 13 Hz, 1H), 3.90 (d, J = 13 Hz, 1H), 5.06 (m, 1H), 5.19 (m, 1H), 5.70 (m, 1H), 7.19-7.41 (m, 5H). NMR (200 MHz) ^{13}C δ 33.3 (q, $J_{\text{C-F}}$ = 2.2 Hz), 52.1, 57.8 (q, $J_{\text{C-F}}$ = 28 Hz), 118.8, 126.9 (q, $J_{\text{C-F}}$ = 284 Hz), 127.2, 128.2, 128.4, 133.1, 139.6. NMR (200 MHz) ^{19}F δ -74.9 (d, $J_{\text{H-F}}$ = 7.3 Hz). Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{F}_3\text{N}$: C, 62.87; H, 6.16; N, 6.11. Found : C, 62.65; H, 6.31; N, 5.99.

***N*-Benzyl-1,1,1-trifluoro-3,3-dimethyl-4-penten-2-amine 3b**

From the imine **1** (1.03 g, 5.5 mmol), dimethallyl bromide **2b** (1.07 g, 7.15 mmol) and Zn (467 mg, 7.15 mmol), product **3b** was obtained as a yellow liquid (1.36 g, 97% in DMF/ 1.16 g, 82% in THF).

NMR (200 MHz) ^1H δ 1.00-1.11 (m, 6H), 1.38 (s, br, 1H), 2.70 (q, $J_{\text{H-F}}$ = 8.4 Hz, 1H), 3.68 (d, J = 13 Hz, 1H), 3.98 (d, J = 13 Hz, 1H), 4.90 (dd, J = 12 Hz, J = 5 Hz, 2H), 5.77 (dd, J = 16 Hz, J = 9 Hz, 1H), 7.10-7.31 (m, 5H). NMR (200 MHz) ^{13}C δ 24.4, 40.1, 54.4, 66.3 (q, $J_{\text{C-F}}$ = 25 Hz), 112.8, 127.2, 127.7 (q, $J_{\text{C-F}}$ = 286 Hz), 128.3, 128.4, 139.9, 144.3. NMR (200 MHz) ^{19}F δ -67.1 (d, $J_{\text{H-F}}$ = 8.4 Hz). Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{F}_3\text{N}$: C, 65.35; H, 7.05; N, 5.44. Found : C, 65.20; H, 7.00; N, 5.43.

***N*-Benzyl-1,1,1-trifluoro-4-methyl-4-penten-2-amine 3c**

From the imine **1** (1.03 g, 5.5 mmol), methallyl bromide **2c** (965 mg, 7.15 mmol) and Zn (467 mg, 7.15 mmol), product **3c** was obtained as a yellow liquid (1.0 g, 75% in DMF).

NMR (200 MHz) ^1H δ 1.40 (s, 3H), 1.98 (dd, $J = 14$ Hz, $J = 11$ Hz, 1H), 2.30 (m, 1H), 2.97 (m, 1H), 3.60 (d, $J = 13$ Hz, 1H), 3.89 (d, $J = 13$ Hz, 1H), 4.57 (s, 1H), 4.70 (s, 1H), 7.10-7.31 (m, 5H). NMR (200 MHz) ^{13}C δ 21.2, 37.3 (q, $J_{\text{C-F}} = 2.7$ Hz), 52.6, 55.8 (q, $J_{\text{C-F}} = 28$ Hz), 114.8, 127.0 (q, $J_{\text{C-F}} = 283$ Hz), 127.2, 128.3, 128.4, 139.4, 140.3. NMR (200 MHz) ^{19}F δ -75.7 (d, $J_{\text{H-F}} = 7.0$ Hz, CF_3). Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{F}_3\text{N}$: C, 64.18; H, 6.63; N, 5.76. Found : C, 64.08; H, 6.76; N, 6.05.

ethyl 2-[2-(Benzylamino)-3,3,3-trifluoropropyl]acrylate **3d**

From the imine **1** (374 mg, 2.0 mmol), allyl bromide **2d** (500 mg, 2.6 mmol) and Zn (170 mg, 2.6 mmol), product **3c** was obtained as a yellow liquid (452 mg, 75% in DMF).

NMR (200 MHz) ^1H δ 1.19 (t, $J = 7.2$ Hz, 3H), 2.36 (dd, $J = 15$ Hz, $J = 10$ Hz, 1H), 2.77 (dd, $J = 13$ Hz, $J = 3.0$ Hz, 1H), 3.29 (m, 1H), 3.70 (d, $J = 3.6$ Hz, 1H), 4.01 (d, $J = 3.6$ Hz, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 5.62 (m, 1H), 6.28 (m, 1H), 7.20-7.42 (m, 5H). NMR (200 MHz) ^{13}C δ 13.9, 32.0 (q, $J_{\text{C-F}} = 2.7$ Hz), 52.0, 57.3 (q, $J_{\text{C-F}} = 27$ Hz), 60.7, 127.0 (q, $J_{\text{C-F}} = 284$ Hz), 127.1, 128.1, 128.2, 136.2, 139.5, 166.3. NMR (200 MHz) ^{19}F δ -75.3 (d, $J_{\text{H-F}} = 7.4$ Hz). Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{NO}_2$: C, 59.79; H, 6.02; N, 4.65. Found : C, 60.80; H, 6.28; N, 5.06.

N-(4-Methoxyphenyl)-*N*-[1-(trifluoromethyl)-3-butenyl]amine **5a**

From the imine **4** (1.12 g, 5.5 mmol), allyl bromide **2a** (865 mg, 7.15 mmol) and Zn (467 mg, 7.15 mmol), product **5a** was obtained as a brown liquid (1.06 g, 79% in DMF / 1.24 g, 92% in THF).

NMR (200 MHz) ^1H δ 2.40 (m, 1H), 2.60 (m, 1H), 3.40 (s, br, 1H), 3.80 (s, 3H), 3.85 (m, 1H), 5.10 (m, 1H), 5.20 (m, 1H), 5.80 (m, 1H), 6.60 (d, $J = 9.1$ Hz, 2H), 6.80 (d, $J = 9.1$ Hz, 2H). NMR (200 MHz) ^{13}C δ 33.7 (q, $J_{\text{C-F}} = 2.0$ Hz), 55.4, 56.6 (q, $J_{\text{C-F}} = 29$ Hz), 114.9, 115.3, 119.1, 126.2 (q, $J_{\text{C-F}} = 284$ Hz), 134.7, 140.6, 153.1. NMR (200 MHz) ^{19}F δ -75.8 (d, $J_{\text{H-F}} = 7.0$ Hz). Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{F}_3\text{NO}$: C, 58.77; H, 5.75; N, 5.71. Found : C, 58.08; H, 6.02; N, 5.95.

N*-[2,2-dimethyl-1-(trifluoromethyl)-3-butenyl]-N-(4-methoxyphenyl) amine **5b*

From the imine **4** (1.12 g, 5.5 mmol), dimethallyl bromide **2b** (1.07 g, 7.15 mmol) and Zn (467 mg, 7.15 mmol), product **5b** was obtained as a brown liquid (1.23 g, 82% in DMF).

NMR (200 MHz) ^1H δ 1.10 (s, 3H), 3.70 (q, $J_{\text{H-F}} = 7.0$ Hz, 1H), 4.90 (s, 3H), 5.30 (d, $J = 16$ Hz, 1H), 5.40 (d, $J = 8.0$ Hz, 1H), 6.09 (dd, $J = 16$ Hz, 7.8 Hz, 1H), 6.82 (d, $J = 9.1$ Hz, 2H), 7.02 (d, $J = 9.1$ Hz, 2H). NMR (200 MHz) ^{13}C δ 24.2, 25.2, 40.6, 55.5, 64.0 (q, $J_{\text{C-F}} = 26$ Hz), 114.4, 114.7, 114.9, 126.5 (q, $J_{\text{C-F}} = 282$ Hz), 141.6, 142.8, 152.7. NMR (200 MHz) ^{19}F δ -68.2 (d, $J_{\text{H-F}} = 7.0$ Hz). Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{F}_3\text{NO}$: C, 61.53; H, 6.64; N, 5.13. Found : C, 61.68; H, 6.75; N, 5.17.

N*-(4-Methoxyphenyl)-N-[-3-methyl-1-(trifluoromethyl)-3-butenyl]amine **5c*

From the imine **1** (1.12 g, 5.5 mmol), methallyl bromide **2c** (965 mg, 7.15 mmol) and Zn (467 mg, 7.15 mmol), product **5c** was obtained as a brown liquid (1.18 g, 83% in DMF).

NMR (200 MHz) ^1H δ 1.71 (m, 3H), 2.30 (dd, $J = 15$ Hz, $J = 11$ Hz, 1H), 2.62 (m, 1H), 3.20 (s, br, 1H), 3.71 (s, 3H), 3.90 (m, 1H), 4.80 (m, 1H), 4.91 (m, 1H), 6.59 (d, $J = 9.1$ Hz, 2H), 6.80 (d, $J = 9.1$ Hz, 2H). NMR (200 MHz) ^{13}C δ 21.5, 37.5 (q, $J_{\text{C-F}} = 1.9$ Hz), 55.3 (q, $J_{\text{C-F}} = 29$ Hz), 55.4, 114.6, 114.8, 114.9, 132.0 (q, $J_{\text{C-F}} = 283$ Hz), 139.9, 141.1, 153.0. NMR (200 MHz) ^{19}F δ -76.4 (d, $J_{\text{H-F}} = 6.6$ Hz). Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{F}_3\text{NO}$: C, 60.22; H, 6.22; N, 5.40. Found : C, 60.09; H, 6.14; N, 5.30.

1,1,1-trifluoro-*N*-[(*R*)-1-phenylethyl]-4-penten-2-amine **7a**

From the imine **6** (201 mg, 1.0 mmol), allyl bromide **2a** (157 mg, 1.3 mmol) and Zn (85 mg, 1.3 mmol), product **7a** was obtained as a colorless liquid (211 mg, 87% in DMF; 190 mg, 78% in THF). These diastereomeric mixtures are not separable.

NMR (200 MHz) ^1H δ 1.25 (major) / 1.27 (d, $J = 6.5$ Hz, 3H), 1.40 (s, 1H), 1.90-2.50 (m, 2H), 2.78 (minor) / 2.96 (m, 1H), 3.93 (m, 1H), 5.10 (m, 2H), 5.50 (minor) / 5.80 (m, 1H), 7.10-7.30 (m, 5H). NMR (200 MHz) ^{13}C δ 24.0 (major) / 24.5, 33.2 (major) / 34.0 (q, $J_{\text{C-F}} = 2.0$ Hz), 55.6 (minor) / 56.1 (q, $J_{\text{C-F}} = 27$ Hz), 118.7 (minor) / 119.0, 126.4 (major) (q, $J_{\text{C-F}} = 284$ Hz) / 127.1 (q, $J_{\text{C-F}} = 282$ Hz), 126.8 / 127.0, 127.2 / 127.3, 128.4 / 128.45, 132.9 (major) / 133.3, 144.4 (minor) / 144.7. NMR (200 MHz) ^{19}F δ -74.6 (minor) (d, $J_{\text{H-F}} = 7.0$ Hz, CF_3), -75.0 (major) (d, $J_{\text{H-F}} = 7.4$ Hz, CF_3). Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{F}_3\text{N}$: C, 64.18; H, 6.62; N, 5.75. Found : C, 64.35; H, 6.58; N, 5.70.

3-methylene -[(*R*)-1-Phenylethyl-5-(trifluoromethyl)]-2-pyrrolidinone **8**

From the imine **6** (201 mg, 1.0 mmol), allyl bromide **2d** (251 mg, 1.3 mmol) and Zn (85 mg, 1.3 mmol), product **8** was obtained as a brown liquid (161 mg, 60 % in THF). These diastereomeric mixtures are not separable.

NMR (200 MHz) ^1H δ 1.66 (major)/1.85 (d, $J = 7.1$ Hz, 3H), 2.70-2.90 (m, 2H), 3.60 (minor) /4.10 (m, 1H), 5.00 (minor) / 5.50 (q, $J = 7.0$ Hz, 1H), 5.40 (m, 1H), 6.10 (m, 1H), 7.26-7.47 (m, 5H). NMR (200 MHz) ^{13}C δ 16.4 (minor)/16.7, 26.4 (minor)/26.9 (q, $J_{\text{C-F}} = 2.7$ Hz), 52.7 (major)/54.4, 54.4 (major)/56.1 (q, $J_{\text{C-F}} = 33$ Hz), 117.0 (major)/117.1, 124.7 (major)/124.9 (q, $J_{\text{C-F}} = 283$ Hz), 127.8 (major)/126.7, 128.2 (major)/127.3, 128.7 (major)/127.9, 136.3 (major)/136.6, 137.8 (major)/140.5, 168.8. NMR (200 MHz) ^{19}F δ -74.9 (d, $J_{\text{H-F}} = 7.0$ Hz) major, -75.6 (d, $J_{\text{H-F}} = 7.0$ Hz) minor. Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{F}_3\text{NO}$: C, 62.45; H, 5.24; N, 5.20. Found : C, 62.52; H, 5.11; N, 5.28.

1-Benzyl-3-methylene-5-trifluoromethyl 2-pyrrolidinone **9**

A solution of the imine **1** (374 mg, 2 mmol), ethyle 2-(bromomethyl) acrylate (617 mg, 3.2 mmol) in DMF (4 mL), was cold at 0°C , and Zn was added (195 mg, 3.0 mmol). After 1 h at room temperature, the mixture was warmed at reflux of DMF. After 3h, the reaction was quenched at 0°C with a saturated solution aqueous of NH_4Cl (20 mL), extracted with Et_2O (3×10 mL). The combined organic layers were washed with a saturated solution aqueous of NaCl (10 mL), dried over MgSO_4 , filtered, and the solvents were removed. The crude product was purified by chromatography on silica gel (Petroleum ether/AcOEt, 70 : 30) to afford the butyrolactam **9** as white solid (188 mg, 37%). m.p. = 35°C .

NMR (200 MHz) ^1H δ 2.80 (m, 2H), 3.70 (m, 1H), 4.02 (d, $J = 15$ Hz, 1H), 5.30 (d, $J = 15$ Hz, 1H), 5.41 (t, $J = 2.4$ Hz, 1H), 6.10 (t, $J = 2.6$ Hz, 1H), 7.21 (m, 2H), 7.32 (m, 3H). NMR (200 MHz) ^{13}C δ 25.4 (q, $J_{\text{C-F}} = 2.4$ Hz), 45.6, 54.2 (q, $J_{\text{C-F}} = 32$ Hz), 117.4, 125.1 (q, $J_{\text{C-F}} = 284$ Hz), 127.8, 128.1, 128.6, 135.0, 135.7, 168.0. NMR (200 MHz) ^{19}F δ -75.2 (d, $J_{\text{H-F}} = 6.2$ Hz). Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{F}_3\text{NO}$: C, 61.17; H, 4.74; N, 5.49. Found : C, 61.11; H, 4.87; N, 5.18.

(2*R*)-2-Phenyl-2-[[[(1-trifluoromethyl)-3-butenyl]amino]-1-ethanol **11**

From the oxazolidine **10** (217 mg, 1.0 mmol), allyl bromide **2a** (302 mg, 2.5 mmol) and Zn (163 mg, 2.5 mmol), product **11** was obtained as a brown liquid (168 mg, 65 % in DMF). These diastereomeric mixtures are not separable.

NMR (400 MHz) ^1H δ 1.9 (s broad, OH, NH), 2.22 (minor)/ 2.36 (dt, $J = 8.7$ Hz, $J = 14.5$ Hz, 1H), 2.41 (minor)/ 2.53 (m, 1H), 3.02 (minor) (m, 1H)/ 3.1 (quint.d, $J = 5.0$ Hz, $J = 7.8$ Hz), 3.6 (major) (dd, $J = 8.0$ Hz, $J = 10.8$ Hz, 1H), 3.71 (minor)/ 3.73 (dd, $J = 4.4$ Hz, $J = 10.8$ Hz, 1H), 4.03 (dd, $J = 4.4$ Hz, $J = 8.0$ Hz, 1H), 5.13 (minor) (dd, $J = 1.5$ Hz, $J = 17.0$ Hz, 1H)/ 5.24 (dd, $J = 1.3$ Hz, $J = 17.0$ Hz, 1H), 5.14 (minor) (d, $J = 8.6$ Hz, 1H)/ 5.23 (d, $J = 10.2$ Hz), 5.55 (minor)/5.87 (m, 1H), 7.26-7.38 (m, 5H). NMR (200 MHz) ^{13}C δ 33.1 (q, $J = 2.0$ Hz)/34.0 (q, $J = 2.5$ Hz), 56.3 (q, $J = 27.6$ Hz), 62.1 (major)/ 63.2 (q, $J = 1.3$ Hz), 66.9 (minor)/ 67.0, 119.2, 126.2 (major)/ 126.9 (q, $J = 285$ Hz), 127.59 (minor)/ 127.62, 127.9 (major)/ 128.0, 128.58 (major)/ 128.6, 132.7 (major)/ 132.9, 139.54 (minor)/ 139.6. NMR (400 MHz) ^{19}F δ -74.76 (minor) (d, $J = 7.0$ Hz), -74.95 (major) (d, $J = 7.8$ Hz). Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{F}_3\text{NO}$: C, 60.22; H, 6.22; N, 5.40. Found : C, 60.60; H, 6.26; N, 5.45.

(1*R*)-2-methoxy-1-phenyl-*N*-[(*E*)-2,2,2-trifluoroethylidene]-1-ethanamine **12**

A solution of trifluoroacetaldehyde hydrate (4.1g, 35.2 mmol), methyl ether of the (*R*)-phenylglycinol (4g, 27 mmol), and *p*-toluenesulfonic acid (1%) in toluene (100 mL) was refluxed for 2h in a Dean-Stark apparatus. After the toluene was evaporated and the crude was directly distilled (65°C, 1.5 mmHg), leading to the imine **12** (4.9g, 79%).

$[\alpha]_{\text{D}}^{20} = -55.8$ ($c = 1.21$, CHCl_3)

NMR (200 MHz) ^1H δ 3.35 (s, 3H), 3.65 (d, $J = 6.9$ Hz, 2H), 4.55 (t, $J = 6.6$ Hz, 1H), 7.35 (m, 5H), 7.70 (q, $J = 3.5$ Hz, 1H). NMR (200 MHz) ^{13}C δ 59.0, 73.4, 76.1 (q, $J = 1$ Hz), 118.8 (q, $J = 275$ Hz), 127.2, 128.0, 128.7, 138.4, 150.1 (q, $J = 38.1$ Hz). NMR (200 MHz) ^{19}F δ -71.9

(d, $J = 3.5$ Hz). Anal. Calcd for $C_{11}H_{12}F_3NO$: C, 57.14; H, 5.23; N, 6.05. Found : C, 56.95; H, 5.26; N, 6.01.

1,1,1-trifluoro-*N*-[(*IR*)-2-methoxy-1-phenylethyl]-4-penten-2-amine 13a

From the imine **12** (231 mg, 1.0 mmol), allyl bromide **2a** (157 mg, 1.3 mmol) and Zn (85 mg, 1.3 mmol), product **13a** was obtained as a brown liquid (232 mg, 68% in DMF, d.e. = 84% and 185 mg, 85% in THF, d.e. = 96%). These diastereomeric mixtures are not separable.

$[\alpha]_D^{20} = -86.4$ ($c = 1.4$, $CHCl_3$)

NMR (200 MHz) 1H : δ 2.06 (bl, 1H), 2.2-2.6 (m, 3H), 3.34 (s, 3H), 3.40 (m, 2H), 4.16 (major)/ 4.3 (dd, $J = 5.6$ Hz, $J = 7.6$ Hz, 1H), 5.10 (minor) (dd, $J = 1.4$ Hz, $J = 16.0$ Hz, 1H)/ 5.22 (dq, $J = 1.5$ Hz, $J = 17.0$ Hz, 1H), 5.2 (major) (m, 1H), 5.60 (minor) / 5.84 (m, 1H), 7.20-7.50 (m, 5H). NMR (200 MHz) ^{13}C δ 32.8 (major)/ 34.3 (q, $J = 2.0$ Hz), 55.2 (minor)/ 56.0 (q, $J = 27.5$ Hz), 58.2 (minor)/58.3, 59.6 (minor)/ 60.2, 77.8, 118.7 (minor)/ 118.9, 126.2 (q, $J = 281.7$ Hz), 127.7 (major)/ 127.89, 127.8 (major)/ 127.92, 128.39 (minor)/ 128.32, 132.4, 139.57 (major)/ 139.6. NMR (200 MHz) ^{19}F : δ -73.5 (minor) (d, $J = 8.1$ Hz), -74.9 (major) (d, $J = 8.5$ Hz). Anal. Calcd for $C_{14}H_{18}F_3NO$: C, 61.52; H, 6.63; N, 5.12. Found : C, 61.66; H, 6.75; N, 5.01.

1,1,1-trifluoro-*N*-[(*IR*)-2-methoxy-1-phenylethyl]-3,3-dimethyl-4-penten-2-amine 13b

From the imine **12** (231 mg, 1.0 mmol), allyl bromide **2b** (194 mg, 1.3 mmol) and Zn (85 mg, 1.3 mmol), product **13b** was obtained as a brown liquid (195 mg, 65% in THF, d.e. = 98%).

$[\alpha]_D^{20} = -45.9$ ($c = 1.02$, $CHCl_3$)

NMR (200 MHz) 1H : δ 1.13 (s, 6H), 1.99 (bl, 1H), 2.86 (q, $J = 8.8$ Hz, 3H), 3.27 (s, 3H), 3.37 (m, 2H), 4.06 (dd, $J = 4.3$ Hz, $J = 8.3$ Hz, 1H), 5.01 (dd, $J = 1.2$ Hz, $J = 10.8$ Hz, 1H), 5.02

(dd, $J = 1.2$ Hz, $J = 17.6$ Hz, 1H), 5.87 (ddd, $J = 1.6$ Hz, $J = 10.8$ Hz, $J = 17.6$ Hz, 1H), 7.32-7.12 (m, 5H). NMR (200 MHz) ^{13}C : δ 33.0 (q, $J = 2.0$ Hz), 64.3 (q, $J = 25.1$ Hz), 58.7, 62.7, 78.0, 113.0, 126.9 (q, $J = 285.6$ Hz), 127.7, 128.1, 128.3, 140.6, 144.4 (q, $J = 1.4$ Hz). NMR (200 MHz) ^{19}F : δ -65.0 (d, $J = 8.5$ Hz) minor, -67.4 (d, $J = 8.3$ Hz) major. Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{F}_3\text{NO}$: C, 63.77; H, 7.36; N, 4.64. Found : C, 63.66; H, 7.41; N, 4.58.

Ethyl 2-(3,3,3-trifluoro-2-[(*IR*)-2-methoxy-1-phenylethyl]amino}propyl)acrylate **13d**

From the imine **12** (231 mg, 1.0 mmol), allyl bromide **2d** (251 mg, 1.3 mmol) and Zn (85 mg, 1.3 mmol), product **13d** was obtained as a brown liquid (248 mg, 72% in DMF, d.e. = 85%). These diastereomeric mixtures are not separable.

$[\alpha]_{\text{D}}^{20} = -46.4$ ($c = 1.23$, CHCl_3)

NMR (200 MHz) ^1H : δ 1.25 (t, $J = 7.2$ Hz, 3H), 1.95 (br, 1H), 2.80 (dd, $J = 7.5$ Hz, $J = 14.0$ Hz, 1H), 2.76 (dd, $J = 5.5$ Hz, $J = 14.0$ Hz, 1H), 3.32 (s, 3H), 3.34 (m, 2H), 4.13 (m, 1H), 4.19 (q, $J = 7.2$ Hz, 2H), 5.71 (d, $J = 1.0$ Hz, 1H), 6.30 (d, $J = 1$ Hz, 1H), 7.12-7.36 (m, 5H). NMR (200 MHz) ^{13}C : δ 14.0, 32.8 (major)/ 32.85 (q, $J = 1.9$ Hz), 55.2 (minor)/ 55.7 (q, $J = 28$ Hz), 58.7, 60.5, 60.8 (major)/ 60.85, 77.7, 126.2 (q, $J = 282$ Hz), 127.7, 127.9, 128.3, 128.6, 136.08 (major)/ 136.1, 139.75 (major)/ 139.85, 166.4 (major)/ 166.9. NMR (200 MHz) ^{19}F : δ -74.2 (minor) (dd, $J = 1.3$ Hz, $J = 6.9$ Hz), -75.7 (major) (d, $J = 7.6$ Hz) major. Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{F}_3\text{NO}_3$: C, 59.12; H, 6.42; N, 4.05. Found : C, 59.50; H, 6.30; N, 4.16.