*Organic Letters***Supporting Information to Accompany:****Unprecedented Catalytic Asymmetric Reduction of N-H Imines**

Francis Gosselin,^{†} Paul D. O'Shea,^{*‡} Stéphanie Roy,[†] Robert A. Reamer,[‡]
Cheng-yi Chen,[‡] and Ralph P. Volante[‡]*

*Department of Process Research, Merck Frosst Centre for Therapeutic Research,
16711 route transcanadienne, Kirkland, Québec, Canada H9H 3L1 and
Department of Process Research, Merck Research Laboratories, P.O. Box 2000,
Rahway, NJ 07065, USA.*

Experimental Section

General: Unless otherwise noted all reactions were run under a nitrogen atmosphere, solvents and reagents were transferred by syringe. Catecholborane was purchased from Aldrich (neat) or Digital Specialty Chemicals Inc. (2M in toluene). (*R*)- and (*S*)-Butyl-OAB solutions in toluene were prepared according to literature procedure [Mathre, D. J.; Jones, T. K.; Xavier, L. C.; Blacklock, T. J.; Reamer, R. A.; Mohan, J. J.; Turner Jones, E. T.; Hoogsteen, K.; Baum, M. W.; Grabowski, E. J. J. *J. Org. Chem.* **1991**, *56*, 751-762]. (*R*)-Methyl-OAB (1M in toluene) was purchased from Callery-BASF or Lancaster Synthesis. Anhydrous grade tetrahydrofuran (THF), toluene and *tert*-butyl methyl ether (MTBE) were purchased from Aldrich in Sure/SealTM bottles and used as received. Final reaction mixtures were dried over MgSO₄. Unless otherwise noted, ¹H NMR (500 MHz), ¹³C NMR (125 MHz) were recorded in CDCl₃ and ¹⁹F NMR (470 MHz) spectra were recorded in CDCl₃ on a Bruker AMX 500 or a Bruker Avance 500 instruments. Chemical shifts are reported in ppm (δ units) downfield of internal tetramethylsilane [(CH₃)₄Si], residual CHCl₃; or benzotrifluoride (C₆H₅CF₃, -61.5 ppm); coupling constants are reported in hertz (Hz). Multiplicities are as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. Chiral HPLC analysis was performed on Chiralcel OJ, Chiralcel OD-R or Chiralpak AD columns. HPLC method A: eluent: 10% EtOH (0.1% diethylamine) : 90% hexane (0.1% diethylamine), flow: 1 mL / min, 35 °C, UV detection: 220 nm, 10 uL injection. HPLC method B: eluent: 5% EtOH (0.1% diethylamine) : 95% hexane (0.1% diethylamine), flow: 1 mL / min, 35 °C, UV detection: 254 nm, 10 uL injection.

Representative Procedure for the One-Pot Synthesis of Racemic Trifluoromethyl Amines.

(*RS*)-1-Phenyl-2,2,2-trifluoroethylamine: 2,2,2-Trifluoromethyl acetophenone **1a** (491 mg, 2.82 mmol) was dissolved in toluene (10 mL) at rt. A solution of lithium bis(trimethylsilylamide) (3.15 mL, 3.15 mmol, 110 mol%, 1M in THF) was added over a 10 min period. The reaction was let stir at rt for 15 min and BH₃•Me₂S (2.82 mL, 5.73 mmol, 2M in toluene) was added. The reaction mixture was let stir at rt for 20 min. After cooling to 0 °C, aqueous 2N NaOH (4 mL) was carefully added dropwise over 5 min (*caution: gas evolution!*). The mixture was stirred at rt for 90 min. The layers were separated and the organic layer was washed with aqueous 2N NaOH (5mL) and water (5mL), dried with MgSO₄ and filtered. To the solution of crude free amine in toluene was added a solution of hydrogen chloride (1mL, 4M in 1,4-dioxane or 2 mL, 2M in diethyl ether). A white precipitate formed. After standing at rt for 1h, the slurry was filtered and the solids were washed with MTBE (10 mL) to afford (*RS*)-1-phenyl-2,2,2-trifluoroethylamine hydrochloride **3a** as a white powder (549 mg, 92% yield): ¹H NMR (CD₃OD) δ 7.52-7.58 (m, 5H), 5.37 (q, *J* = 7.5, 1H); ¹³C NMR (CD₃OD) δ 132.0, 130.6, 129.8, 129.5, 124.8 (q, *J* = 281), 56.7 (q, *J* = 33); ¹⁹F NMR (CD₃OD) δ – 72.0.

Representative Procedure for the Synthesis of *N*-Trimethylsilyl Imines. 1-(4-Bromophenyl)-

2,2,2-trifluoroethyl-*N*-trimethylsilyl Imine (2c): 1-(4-bromophenyl)-2,2,2-trifluoroethanone **1c** (6.0 g, 23.73 mmol) was dissolved in toluene (23 mL) and the solution was cooled to 0 °C. A solution of lithium bis(trimethylsilylamide) (24 mL, 24 mmol, 110 mol%, 1M in THF) was added over 10 min. The solution was let stir at 0 °C for 1h. Water (20 mL) was added and the layers were separated. The organic layer was washed with water (2 × 10 mL), dried with MgSO₄, filtered, and concentrated to afford crude *N*-TMS imine **2c** as a yellow oil (7.54g, 98% yield): ¹H NMR (CDCl₃) δ 7.55 (d, 2H, *J* = 8.7), 7.48 (d, 2H, *J* = 8.0), 0.20 (s, 9H); ¹³C NMR (CDCl₃) δ 156.2 (q, *J* = 34) 134.0, 131.3, 129.2, 125.4, 117.4 (q, *J* = 288), 0.09; ¹⁹F NMR (CDCl₃) δ – 67.4.

Representative Procedure for the Synthesis of *N*-H imines. 1-(2,2,2-Trifluoro)-1-(4-

bromophenyl)ethyl imine (7): 1-(4-bromophenyl)-2,2,2-trifluoroethyl-*N*-trimethylsilyl ketimine **2c** (4.517 g, 13.93 mmol) was dissolved in MeOH (10.7 mL) and stirred at rt for 18h. The

volatiles were removed under vacuum and the residue was flushed with toluene (3×20 mL) to afford crude NH-imine **7** as a yellow-orange oil (3.33 g, 95% yield): A [65:19:16] mixture of (*Z*) / (*E*) imine isomers **7a/7b** along with a methanol adduct **7c**. Representative signals: ^1H NMR (CDCl_3) δ 10.82 (s, NH, minor), 10.75 (s, NH, major), 3.20 (s, methanol adduct); ^{13}C NMR (CDCl_3) minor imine isomer: δ 165.4 (q, $J = 34$), 120.0 (q, $J = 288$); major isomer: δ 162.0 (q, $J = 32$), 118.1 (q, $J = 282$); methanol adduct: δ 87.9 (q, $J = 30$), 48.0; ^{19}F NMR δ (CDCl_3) – 67.5 (minor isomer); – 68.5 (major isomer), – 81.6 (methanol adduct).

Representative Procedure for Oxazaborolidine-Catalyzed Enantioselective Reduction of NH-Imines.

(*S*)-2,2,2-Trifluoro-1-(4-bromophenyl)ethylamine hydrochloride [(*S*)-14c**]:** A solution of (*R*)-*B*-butyl-diphenylpyrrolidino-oxazaborolidine **4b** (3.14 mL, 0.94 mmol, 2.5 mol%, 0.3 M in toluene) was dissolved in toluene (10 mL), cooled to -15°C , and catecholborane (6.01 mL, 56.5 mmol, 150 mol%) was added to the solution. A solution of 1-(4-bromophenyl)-2,2,2-trifluoroethylimine **7** (10.0 g, 37.6 mmol) in toluene (40 mL) was added dropwise via syringe pump over a period of 2.5 h. After the addition was complete, the reaction mixture was let stir at -15°C for 18 h. The reaction was quenched with aqueous 1N HCl (50 mL), let warm to rt and the layers were separated. The aqueous layer was basified with 10N NaOH to pH 12. The aqueous layer was extracted with MTBE (1×50 mL). The layers were separated and the organic layer was washed with aqueous 2N NaOH ($2 \times 50\text{mL}$), and water (50 mL). The organic layer was treated with Amberlite IRC-50S ion exchange resin (5 g) for 40 min to remove (*R*)-diphenylprolinol and filtered. The organic layer was dried and filtered. A solution of hydrogen chloride (40 mL, 2M in diethyl ether) was added to the crude solution of amine. A white precipitate formed. After aging at rt for 1 h, the slurry was filtered and the solids were washed with MTBE (10 mL) to afford (*S*)-2,2,2-trifluoro-1-(4-bromophenyl)ethylamine hydrochloride (**S**)-**14c** as a white powder (10.9 g, 95 % yield): 91% ee HPLC: ^1H NMR (CD_3OD) δ 7.73 (d, 2H, $J = 8.5$), 7.51 (d, 2H, $J = 8.5$), 5.42 (q, 1H, $J = 7.4$); ^{13}C NMR (CD_3OD) δ 133.8, 131.6, 128.7, 126.3, 124.6 (q, $J = 280$), 55.9 (q, $J = 33$); ^{19}F NMR (CD_3OD) δ – 72.1. HRMS calcd for $\text{C}_8\text{H}_8\text{NF}_3\text{Br}$ [$\text{M}+\text{H}$]: 253.9792; found: 253.9790. Enantioselective reduction with (*S*)-butyl-OAB as catalyst gave amine (**R**)-**14c** in 95% yield and 91% ee HPLC (method A, AD column: $t_{\text{Rmajor}} =$

6.9 min; $t_{\text{Rminor}} = 7.9$ min) with identical spectral characteristics; $[\alpha]_{\text{D}}^{23} = -13.7$ ($c = 0.75$, MeOH). lit. (ref. 3g) $[\alpha]_{\text{D}}^{25} = +11.2$ ($c = 1.5$, MeOH).

Representative Procedure for Oxazaborolidine-Catalyzed Enantioselective Reduction of NH-Imines. **(*S*)-2,2,2-Trifluoro-1-(4-bromophenyl)ethylamine hydrochloride [(*S*)-14c]:** A solution of (*R*)-*B*-methyl-diphenylpyrrolidino-oxazaborolidine (1.88 mL, 1.88 mmol, 5 mol%, 1 M in toluene) was dissolved in toluene (12 mL), cooled to -15°C , and catecholborane (28.23 mL, 56.46 mmol, 150 mol%, 2 M in toluene) was added to the solution. A solution of 1-(4-bromophenyl)-2,2,2-trifluoroethylimine **7** (10 g, 37.6 mmol) in toluene (40 mL) was added dropwise via syringe pump over a period of 2.5 h. The same workup as in the previous example afforded (*S*)-2,2,2-trifluoro-1-(4-bromophenyl)ethylamine hydrochloride (**(*S*)-14c**) as a white powder in 95 % yield, 91% ee HPLC.

***N*-(Trimethylsilyl)-1-phenyl-1-(2,2,2-trifluoromethyl)ketimine (2a):** ^1H NMR (CDCl_3) δ 7.54 (d, 2H, $J = 7.7$), 7.44-7.48 (m, 1H), 7.39-7.43 (m, 2H), 0.16 (s, 9H); ^{13}C NMR (CDCl_3) δ 158.8 (q, $J = 34$), 135.7, 130.6, 127.7, 117.9 (q, $J = 287$), 0.25; ^{19}F NMR (CDCl_3) δ -68.2.

***N*-(Trimethylsilyl)-1-(3-bromophenyl)-1-(2,2,2-trifluoromethyl)ketimine (2b):** ^1H NMR (CDCl_3) δ 7.72 (s, 1H), 7.60 (d, 1H, $J = 8.0$), 7.51 (d, 1H, $J = 8.0$), 7.26-7.31 (m, 1H), 0.20 (s, 9H); ^{13}C NMR (CDCl_3) δ 156.2 (q, $J = 34$), 137.3, 133.7, 130.8, 129.8, 126.3, 122.5, 117.5 (q, $J = 288$), 0.25; ^{19}F NMR (CDCl_3) δ -67.6.

***N*-(Trimethylsilyl)-1-(2-methanesulfanyphenyl)-1-(2,2,2-trifluoromethyl)ketimine (2d):** ^1H NMR (CDCl_3) δ 7.37-7.41 (m, 1H), 7.30-7.31 (m, 1H), 7.17-7.20 (m, 1H), 7.10-7.12 (m, 1H), 2.48 (s, 3H), 0.03 (s, 9H); ^{13}C NMR (CDCl_3) δ 160.9 (q, $J = 35$), 136.9, 136.0, 130.0, 127.3, 126.7, 124.9, 117.9 (q, $J = 285$), 16.1, -0.70; ^{19}F NMR (CDCl_3) δ -71.4.

***N*-(Trimethylsilyl)-1-(3-methanesulfanyphenyl)-1-(2,2,2-trifluoromethyl)ketimine (2e):** ^1H NMR (CDCl_3) δ 7.40 (s, 1H), 7.33-7.34 (m, 1H), 7.31-7.32 (m, 1H), 7.28-7.31 (m, 1H), 2.50 (s,

3H), 0.17 (s, 9H); ^{13}C NMR (CDCl_3) δ 158.0 (q, $J = 34$), 139.2, 136.1, 128.6, 128.3, 125.3, 124.1, 118.0 (q, $J = 287$), 15.5, 0.2; ^{19}F NMR (CDCl_3) δ – 68.2.

***N*-(Trimethylsilyl)-1-[2-phenyl(phenyl)]-1-(2,2,2-trifluoromethyl)ketimine (2f):** ^1H NMR (CDCl_3) δ 7.48-7.51 (m, 1H), 7.42-7.44 (m, 1H), 7.37-7.41 (m, 3H), 7.29-7.36 (m, 4H), -0.16 (s, 9H); ^{13}C NMR (CDCl_3) δ 162.1 (q, $J = 35$), 140.4, 139.8, 135.8, 130.4, 129.8, 129.1, 128.5, 127.69, 127.67, 127.0, 117.7 (q, $J = 286$), – 0.84; ^{19}F NMR (CDCl_3) δ – 69.5.

***N*-(Trimethylsilyl)-1-(2-naphthyl)-1-(2,2,2-trifluoromethyl)ketimine (2g):** ^1H NMR (CDCl_3) δ 8.07 (s, 1H), 7.90-7.94 (m, 1H), 7.86-7.87 (m, 2H), 7.69-7.70 (m, 1H), 7.53-7.58 (m, 2H), 0.21 (s, 9H); ^{13}C NMR (CDCl_3) δ 158.1 (q, $J = 34$), 134.2, 132.8, 132.5, 128.9, 128.2, 128.1, 127.7, 127.6, 126.7, 124.5, 118.0 (q, $J = 290$), 0.25; ^{19}F NMR (CDCl_3) δ – 67.1.

***N*-(Trimethylsilyl)-1-(9-phenanthryl)-1-(2,2,2-trifluoromethyl)ketimine (2h):** ^1H NMR (CDCl_3) δ 8.74-8.75 (m, 1H), 8.71 (d, 1H, $J = 8.25$), 7.91 (d, 1H, $J = 7.45$), 7.70-7.75 (m, 3H), 7.64-7.67 (m, 2H), 7.62 (s, 1H), -0.12 (s, 9H); ^{13}C NMR (CDCl_3) δ 162.5 (q, $J = 35$), 133.3, 130.5, 130.20, 130.18, 129.3, 129.0, 127.8, 127.2, 127.15, 127.12, 126.2, 125.9, 123.1, 122.6, 118.4 (q, $J = 285$), – 0.49; ^{19}F NMR (CDCl_3) δ – 71.9.

(*RS*)-2,2-Difluoro-1-(4-bromophenyl)ethylamine hydrochloride (3i): ^1H NMR (CD_3OD) δ 7.69 (d, 2H, $J = 8.5$), 7.44 (d, 2H, $J = 8.4$), 6.33 (tq, 1H, $J = 54$, 2.8), 4.84-4.80 (m, 1H) ^{13}C NMR (CD_3OD) δ 133.7, 131.4, 130.5, 125.6, 115.1 (t, $J = 245$), 56.5-56.8 (app t, $J = 22$); ^{19}F NMR (CD_3OD) δ – 122 (d, $J = 288$), – 128.4 (d, $J = 288$). HRMS calcd for $\text{C}_8\text{H}_9\text{F}_2\text{NBr}$ [$\text{M}+\text{H}$]: 235.9886; found: 235.9883.

(*RS*)-2,2,3,3,3-Pentafluoro-1-phenylethylamine hydrochloride (3j): ^1H NMR (CD_3OD) δ 7.53-7.59 (m, 5H), 5.47 (dd, 1H, $J = 22$, 6.7); ^{13}C NMR (CD_3OD) δ 132.3, 130.7, 130.2, 129.3, 119.5 (dt, $J = 286$, 35), 114.7 (tq, $J = 262$, 38), 55.5 (t, $J = 21$); ^{19}F NMR (CD_3OD) δ – 79.9, – 114.7 (dd, $J = 270$, 6.3), – 124.4 (dd, $J = 270$, 21.7). HRMS calcd for $\text{C}_9\text{H}_9\text{F}_5\text{N}$ [$\text{M}+\text{H}$]: 226.0655; found: 226.0655.

1-(2,2,2-Trifluoro)-1-phenylethylimine + methanol adduct (5): Isolated as a [18:8:74] mixture of (*Z*) / (*E*) N-H imine geometric isomers **5a/5b** along with a methanol adduct **5c** as determined by ^1H NMR spectroscopy in CDCl_3 . Representative signals: ^1H NMR (CDCl_3) δ 10.78 (s, minor), 10.69 (s, major), 3.21 (s, methanol adduct); ^{19}F NMR (CDCl_3) δ – 68.4 (major), – 70.2 (minor), – 81.7 (methanol adduct).

1-(2,2,2-Trifluoro)-1-(3-bromophenyl)ethylimine + methanol adduct (6): Isolated as a [41:15:44] mixture of (*Z*) / (*E*) N-H imine geometric isomers **6a/6b** along with a methanol adduct **6c** as determined by ^1H NMR spectroscopy in CDCl_3 . Representative signals: ^1H NMR (CDCl_3) δ 10.84 (s, minor), 10.82 (s, major), 3.21 (s, methanol adduct); ^{19}F NMR (CDCl_3) δ – 67.7 (minor), – 68.6 (major), δ – 81.5 (methanol adduct).

1-(2,2,2-Trifluoro)-1-(2-methanesulfanyphenyl)ethylamine (8): Isolated as a [68:32:0] mixture of (*E*) / (*Z*) N-H imine geometric isomers **8a/8b** as determined by ^1H NMR spectroscopy in CDCl_3 . Representative signals: ^1H NMR (CDCl_3) δ 11.3 (s, minor), 10.8 (s, major), 2.48; ^{13}C NMR (CDCl_3) δ 166.6 (q, $J = 34$, major), 163.6 (q, $J = 32$, minor), 119.7 (q, $J = 287$, major), 117.7 (q, $J = 282$, minor); ^{19}F NMR (CDCl_3) δ – 69.4 (major), – 70.3 (minor).

1-(2,2,2-Trifluoro)-1-(3-methanesulfanyphenyl)ethylimine + methanol adduct (9): Isolated as a [57:23:20] mixture of (*Z*) / (*E*) N-H imine geometric isomers **9a/9b** along with a methanol adduct **9c** as determined by ^1H NMR spectroscopy in CDCl_3 . Representative signals: ^1H NMR (CDCl_3) δ 10.8 (s, minor), 10.7 (s, major), 3.21 (s, methanol adduct); ^{19}F NMR (CDCl_3) δ – 67.5 (minor), – 68.3 (major), – 81.6 (methanol adduct).

1-(2,2,2-Trifluoro)-1-(2-naphthyl)ethylimine + methanol adduct (11): Isolated as a [45:15:46] mixture of (*Z*) / (*E*) N-H imine isomer **11a/11b** along with a methanol adduct **11c** as determined by ^1H NMR spectroscopy in CDCl_3 . Representative signals: ^1H NMR (CDCl_3) δ 10.92 (s, minor) 10.78 (s, major), 3.25 (s, methanol adduct); ^{19}F NMR (CDCl_3) δ – 67.0 (minor), – 67.9 (major), – 81.3 (methanol adduct).

(R)-2,2,2-Trifluoro-1-phenylethylamine hydrochloride (14a): 86% ee HPLC (method B, Chiralcel OD-R column: $t_{R\text{major}} = 11.0$ min; $t_{R\text{minor}} = 9.8$ min); ^1H NMR (CD_3OD) δ 7.52-7.58 (m, 5H), 5.37 (q, 1H, $J = 7.5$); ^{13}C NMR (CD_3OD) δ 132.0, 130.6, 129.8, 129.5, 124.8 (q, $J = 281$), 56.7 (q, $J = 34$); ^{19}F NMR (CD_3OD) $\delta - 72.0$; $[\alpha]_{\text{D}}^{23} = -14.4$ ($c = 0.33$, MeOH), lit. (ref. 6a) $[\alpha]_{\text{D}}^{25} = +28.6$ ($c = 0.65$, MeOH); HRMS calcd for $\text{C}_8\text{H}_9\text{F}_3\text{N}$ $[\text{M}+\text{H}]$: 176.0687; found: 176.0689.

(R)-2,2,2-Trifluoro-1-(3-bromophenyl)ethylamine hydrochloride (14b): 86% ee HPLC (method A, Chiralcel OJ column: $t_{R\text{major}} = 7.1$ min; $t_{R\text{minor}} = 6.6$ min); ^1H NMR (CD_3OD) δ 7.80 (s, 1H), 7.75 (d, 1H, $J = 8.0$), 7.58 (d, 1H, $J = 8.0$), 7.48 (t, 1H, $J = 8.0$), 5.44 (q, 1H, $J = 7.0$); ^{13}C NMR (CD_3OD) δ 135.2, 132.7, 132.4, 131.8, 128.6, 124.6 (q, $J = 282$), 124.2, 56.0 (q, $J = 34$); ^{19}F NMR (CD_3OD) $\delta - 71.9$; HRMS calcd for $\text{C}_8\text{H}_9\text{F}_3\text{NBr}$ $[\text{M}+\text{H}]$: 253.9792; found: 253.9794.

(R)-2,2,2-Trifluoro-1-(4-bromophenyl)ethylamine hydrochloride (14c): 91% ee HPLC (method A, Chiralpak AD column: $t_{R\text{major}} = 6.9$ min; $t_{R\text{minor}} = 7.9$ min); ^1H NMR (CD_3OD) δ 7.73 (d, 2H, $J = 8.5$), 7.51 (d, 2H, $J = 8.5$), 5.42 (q, 1H, $J = 7.4$); ^{13}C NMR (CD_3OD) δ 133.8, 131.6, 128.7, 126.3, 124.6 (q, $J = 282$), 55.9 (q, $J = 34$); ^{19}F NMR (CD_3OD) $\delta - 72.1$; $[\alpha]_{\text{D}}^{23} = -13.7$ ($c = 0.75$, MeOH), lit. (ref. 6a) $[\alpha]_{\text{D}}^{25} = +11.2$ ($c = 1.5$, MeOH); HRMS calcd for $\text{C}_8\text{H}_9\text{F}_3\text{NBr}$ $[\text{M}+\text{H}]$: 253.9792; found: 253.9790.

(R)-2,2,2-Trifluoro-1-[(2-methanesulfanyl)phenyl]ethylamine hydrochloride (14d): 88% ee HPLC (method A, Chiralcel OJ column: $t_{R\text{major}} = 8.2$ min; $t_{R\text{minor}} = 7.6$ min); ^1H NMR (CD_3OD) δ 7.63-7.67 (m, 2H), 7.54-7.57 (m, 1H), 7.41-7.45 (m, 1H), 5.86 (q, 1H, $J = 7.3$), 2.55 (s, 3H); ^{13}C NMR (CD_3OD) δ 141.2, 132.7, 131.8, 128.9, 128.7, 128.3, 124.8 (q, $J = 281$), 53.1 (q, $J = 33$), 18.3; ^{19}F NMR (CD_3OD) $\delta - 71.5$; $[\alpha]_{\text{D}}^{23} = -4.3$ ($c = 0.76$, MeOH); HRMS calcd for $\text{C}_9\text{H}_{11}\text{F}_3\text{NS}$ $[\text{M}+\text{H}]$: 222.0564; found: 222.0564.

(R)-2,2,2-Trifluoro-1-[(3-methanesulfanyl)phenyl]ethylamine hydrochloride (14e): 85% ee HPLC (method A, Chiralpak AD column: $t_{R\text{major}} = 10.9$ min; $t_{R\text{minor}} = 9.3$ min); ^1H NMR (CD_3OD) δ 7.43-7.47 (m, 3H), 7.32 (d, 1H, $J = 6.85$), 5.37 (q, 1H, $J = 7.45$), 2.52 (s, 3H); ^{13}C NMR (CD_3OD) δ 142.5, 130.9, 130.3, 129.4, 126.9, 125.8, 124.7 (q, $J = 282$), 56.5 (q, $J = 34$ Hz); ^{19}F NMR (CD_3OD) $\delta - 71.9$; $[\alpha]_{\text{D}}^{23} = -16.8$ ($c = 0.75$, MeOH); HRMS calcd for $\text{C}_9\text{H}_{11}\text{F}_3\text{NS}$ $[\text{M}+\text{H}]$: 222.0564; found: 222.0562.

(R)-2,2,2-Trifluoro-1-[(2-phenyl)phenyl]ethylamine hydrochloride (14f): 98% ee HPLC (method A, Chiralcel OJ column: $t_{R\text{major}} = 6.5$ min; $t_{R\text{minor}} = 5.8$ min); ^1H NMR (CD_3OD) δ 7.79-7.82 (m, 1H), 7.60-7.64 (m, 2H), 7.45-7.54 (m, 2H), 7.41-7.43 (m, 1H), 7.33-7.35 (m, 2H), 5.07 (q, 1H, $J = 7.25$); ^{13}C NMR (CD_3OD) δ 145.4, 140.3, 132.3, 131.8, 130.3, 130.0, 129.9, 129.3, 128.4, 126.9, 124.7 (q, $J = 281$ Hz), 53.2 (q, $J = 33$); ^{19}F NMR (CD_3OD) $\delta - 71.1$; $[\alpha]_{\text{D}}^{23} = +12.5$ ($c = 0.75$, MeOH); HRMS calcd for $\text{C}_{14}\text{H}_{12}\text{F}_3\text{N}$ $[\text{M}+\text{H}]$: 252.1000; found: 252.0998.

(R)-2,2,2-Trifluoro-1-(2-naphthyl)ethylamine hydrochloride (14g): 75% ee HPLC (method A, Chiralpak AD column: $t_{R\text{major}} = 18.2$ min; $t_{R\text{minor}} = 11.7$ min); ^1H NMR (CD_3OD) δ 8.12 (s, 1H), 8.05 (d, 1H, $J = 8.6$), 7.95-7.98 (m, 2H), 7.59-7.63 (m, 3H), 5.55 (q, 1H, $J = 7.5$); ^{13}C NMR (CD_3OD) δ 135.4, 134.3, 130.6, 130.4, 129.4, 129.0, 128.9, 128.4, 126.7, 125.4, 125.0 (q, $J = 282$), 56.9 (q, $J = 33$); ^{19}F NMR (CD_3OD) $\delta - 71.8$; $[\alpha]_{\text{D}}^{23} = -14.2$ ($c = 0.75$, MeOH), lit. (ref. 6a) $[\alpha]_{\text{D}}^{25} = +26.0$ ($c = 0.75$, MeOH); HRMS calcd for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{N}$ $[\text{M}+\text{H}]$: 226.0844; found: 226.0848.

(R)-2,2,2-Trifluoro-1-(9-phenanthryl)ethylamine hydrochloride (14h): 97% ee HPLC (method A, Chiralpak AD column: $t_{R\text{major}} = 8.1$ min; $t_{R\text{minor}} = 10.9$ min); ^1H NMR (CD_3OD) δ 8.94 (d, 1H, $J = 7.55$), 8.85 (d, 1H, $J = 8.45$), 8.29 (d, 1H, $J = 7.45$), 8.15 (s, 1H), 8.03 (d, 1H, $J = 7.9$), 7.77-7.83 (m, 3H), 7.71-7.74 (m, 1H), 6.36 (q, 1H, $J = 6.6$); ^{13}C NMR (CD_3OD) δ 132.3, 132.1, 131.5, 130.4, 130.3, 129.9, 129.2, 128.8, 128.7, 128.6, 125.2 (q, $J = 282$), 124.8, 124.6, 124.4, 123.8, 51.9 (q, $J = 34$); ^{19}F NMR (CD_3OD) $\delta - 71.4$. $[\alpha]_{\text{D}}^{23} = -26.8$ ($c = 0.74$, MeOH), lit. (ref. 6a) $[\alpha]_{\text{D}}^{25} = +28.8$ ($c = 0.65$, MeOH); HRMS calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{N}$ $[\text{M}+\text{H}]$: 276.1000; found: 276.0999.