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SUPPLEMENTARY MATERIAL

General. For standard laboratory praxis and techniques see related paper, ref. 1g. Unless indicated, ^1H , ^{19}F and ^{13}C NMR spectra, were taken in CDCl_3 solutions at 299.95, 282.24 and 75.42 MHz, respectively. Chemical shifts refer to tetramethylsilane (TMS) and CFCl_3 as the internal standards. Unless otherwise stated, R_f values were taken using *n*-hexane/ethyl acetate (4:1) as an eluting system.

Yields refer to isolated yields of products of greater than 95% purity as estimated by capillary GC and/or ^1H and ^{19}F NMR spectrometry. All new compounds were characterized by ^1H , ^{19}F , ^{13}C NMR, by mass spectrometry and/or elemental analysis.

Values ee determined by chiral HPLC analysis of the corresponding *N*-(3,5-dinitrobenzoyl) derivatives using SUMICHIRAL OA-4500 HPLC column, eluent hexane/dichloroethane/ethanol 60/30/10, $\lambda = 254$.

Starting Schiff bases were prepared by the direct condensation of (*S*)- α -phenylethylamine with the corresponding ketone, either by azeotropic method (**3a,b**) or in the presence of MS. Both procedures described in ref. 1g were followed except for (*S*)- α -phenylethylamine was used in the place of benzylamine.

(*S*)-*N*-(1-Phenyl-2,2,2-trifluoroethylidene)-1-phenylethylamine (3a): 82%, R_f 0.45. ^1H NMR δ 1.44 (d, 3H, $J = 6.6$ Hz), 4.54 (q, 1H, $J = 6.6$ Hz), 7.17-7.35 (m, 8H), 7.47-7.50 (m, 2H); ^{19}F NMR δ -71.63 (s). ^{13}C NMR δ 24.53 (s), 61.38 (s), 119.77 (q, J_{CF} (s), 127.60 (s), 128.61 (s), 128.77 (s), 130.02 (s), 130.56 (s), 143.76 (s), 156.58 (q, $J_{\text{CF}} = 33.2$ Hz). MS 277 (M, 7.6), 262 (M-Me, 2.1), 105 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{N}$: C, 69.31; H, 5.09; N, 5.05; F, 20.55. Found: C, 69.43; H, 5.19; N, 5.05; F, 20.33.

Literature (Pirkle, W.H.; Hauske, J.R. *J. Org. Chem.* **1977**, *42*, 2436.): NMR (CDCl_3) δ 1.40 (d, CCH_3), 4.59 (quartet, CH), 7.18-7.35 ppm (multiplet, $\text{C}_{12}\text{H}_{10}$); IR (neat) 3090, 3000, 1670 ($\text{C}=\text{N}$), 1500, 1460, 1380, 1340, 1220, 1150, 1020, 970 cm^{-1} ; mass spectrum (70 eV) m/e (rel intensity) 277 (5.4, M^+), 106 (8.7), 105 (100.0) 104 (4.6), 79 (9.6), 78 (4.3), 77 (14.2).

(S)-N-(1,1,1-Trifluoro-3-phenyl-*iso*-propylidene)-1-phenylethylamine

(3b): 98%, R_f 0.45. ^1H NMR δ 1.43 (d, 3H, $J = 6.6$ Hz), 3.83 (AB, 2H, $J = 15.6$ Hz), 4.83 (q, 1H, $J = 6.6$ Hz), 7.09-7.12 (m, 2H), 7.25-7.32 (m, 8H); ^{19}F NMR δ -72.70 (s); ^{13}C NMR δ 24.42 (s), 33.19 (s), 60.29 (s), 119.95 (q, $J_{\text{CF}} = 279.4$ Hz), 126.49 (s), 127.08 (s), 127.26 (s), 128.24 (s), 128.58 (s), 128.95 (s), 134.22 (s), 143.53 (s), 155.49 (q, $J_{\text{CF}} = 32.5$ Hz). MS 291 (M, 0.8), 276 (M-Me, 0.8), 105 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{F}_3\text{N}$: C, 70.09; H, 5.54; N, 4.81; F, 19.56. Found: C, 69.98; H, 5.55; N, 4.78; F, 19.61.

Literature (Pirkle, W.H.; Hauske, J.R. *J. Org. Chem.* **1977**, *42*, 2436.): NMR (CDCl_3) δ 1.38 (d, CCH_3), 3.73 (AB multiplet, $=\text{CCH}_2$), 4.81 (quartet, CH), 7.00-7.46 ppm (multiplet, $\text{C}_{12}\text{H}_{10}$); IR (neat) 3095, 3000, 1670 ($\text{C}=\text{N}$), 1500, 1465, 1380, 1365, 1275, 1210, 1030, 925 cm^{-1} ; mass spectrum (70 eV) m/e (rel intensity) 291 (13.4, M^+), 107 (14.7), 106 (5.7), 105 (100.0) 104 (4.2), 79 (15.4), 78 (7.0), 77 (23.8).

(S)-N-(1,1,1-Trifluoro-*iso*-propylidene)-1-phenylethylamine (3c): 74%, R_f 0.46. ^1H NMR δ 1.49 (d, 3H, $J = 6.6$ Hz), 2.03 (s, 3H), 4.71 (q, 1H, $J = 6.6$ Hz), 7.25-7.38 (m, 5H); ^{19}F NMR δ -75.23 (s); ^{13}C NMR δ 12.65 (s), 24.31 (s), 59.93 (s), 119.87 (q, $J_{\text{CF}} = 278.5$ Hz), 126.46 (s), 127.20 (s), 128.62 (s), 143.75 (s), 154.60 (q, $J_{\text{CF}} = 33.4$ Hz). MS 215 (M, 1.8), 200 (M-Me, 2.1), 105 (100).

(S)-N-(1,1,1-Trifluoro-*iso*-butylidene)-1-phenylethylamine (3d): 69%, R_f 0.49. ^1H NMR δ 1.14 (tq, 3H, $J = 7.8$ Hz, $J = 0.6$ Hz), 1.52 (d, 3H, $J = 6.6$ Hz), 2.58 (q, 2H, $J = 7.8$ Hz), 4.82 (q, 1H, $J = 6.6$ Hz), 7.24-7.41 (m, 5H); ^{19}F NMR δ -73.20 (s); ^{13}C NMR δ 11.28 (s), 20.45 (s), 24.87 (s), 59.35 (s), 120.18 (q, $J_{\text{CF}} = 279.4$ Hz), 126.37 (s), 127.20 (s), 128.60 (s), 144.01 (s), 158.79 (q, $J_{\text{CF}} = 33.8$ Hz). MS 229 (M, 1.2), 214 (M-Me, 1.8), 105 (100).

(S)-N-(5,5,5,4,4,3,3-Heptafluoropent-2-ylidene)1-phenylethylamine (3e): 57%, R_f 0.46. ^1H NMR δ 1.48 (q, 3H, $J = 6.6$ Hz), 2.05 (t, 3H, $J = 0.9$ Hz), 4.76 (q, 1H, $J = 6.6$ Hz), 7.25-7.35 (m, 5H); ^{19}F NMR δ -80.63 (t, 3F, $J = 10.5$ Hz), 116.76 (q, 2F, $J = 10.5$ Hz), 126.22 (s, 2F); ^{13}C NMR δ 13.41 (s), 24.39 (s), 60.45 (s), 126.41 (s), 127.17 (s), 128.59 (s), 143.78 (s), four carbon resonances are obscured due to the numerous C-F coupling constants. MS 315 (M, 0.6), 300 (M- CH_3 , 2.3), 105 (100).

Isomerizations of 3a-e to 4a-e. The starting compound 3a-e was dissolved in the base (TEA, DBU as indicated in Tables 1,2), and the mixture was stirred at the temperature and for the time indicated in Tables 1,2. Progress of the reaction was monitored by NMR or GLC, and upon completion of the isomerization, the mixture was evaporated *in vacuo*, when TEA was used, or was passed through short column with silica gel, if DBU or DABCO was used as the base. Yields for isolated 4a-e are given in Tables 1,2.

(R)-N-(1-Phenylethylidene)-1-phenyl-2,2,2-trifluoroethylamine (4a): R_f 0.34; as a 12:1 mixture of geometric isomers. ^1H NMR δ , major isomer: 2.18 (s, 3H), 5.08 (q, 1H, $J = 7.5$ Hz), 7.27-7.53 (m, 8H), 7.92-7.95 (m, 2H); ^{19}F NMR δ -74.90 (d, $J = 7.5$ Hz); minor isomer: 2.44 (s, 3H), 4.68 (q, 1H, $J = 7.7$ Hz); aromatic resonances are obscured by those of the major isomer. ^{19}F NMR δ -74.34 (d, $J_{\text{HF}} = 7.7$ Hz). MS 277 (M, 53.2), 109 (100). Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{N}$: C, 69.31; H, 5.09; N, 5.05; F, 20.55. Found: C, 69.52; H, 5.12; N, 4.93; F, 20.39.

(R)-N-(1-Phenylethylidene)-1,1,1-trifluoro-3-phenyl-iso-propylamine (4b): R_f 0.36; as a 10:1 mixture of geometric isomers. ^1H NMR δ , major isomer: 1.55 (s, 3H), 3.03, 3.28 (ABX, 2H, $J_{\text{AB}} = 13.2$ Hz, $J_{\text{AX}} = 2.4$ Hz, $J_{\text{BX}} = 10.5$ Hz), 4.25 (dq, 1H, $J_{\text{HH}} = 10.5$ Hz, $J_{\text{HF}} = 6.8$ Hz, $J_{\text{HH}} = 2.4$ Hz), 7.11-7.41 (m, 8H), 7.69-7.73 (m, 2H). ^{19}F NMR δ -75.30 (d, $J_{\text{HF}} = 6.8$ Hz); minor isomer: 2.24 (s, 3H), 3.01 (m, 2H), 3.81 (m, 1H); aromatic resonances are obscured by those of the major isomer. ^{19}F NMR δ -74.89 (d, $J_{\text{HF}} = 7.1$ Hz). MS 291 (M, 3.4), 276 (M-Me, 26.5), 159 (100). Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{F}_3\text{N}$: C, 70.09; H, 5.54; N, 4.81; F, 19.56. Found: C, 70.21; H, 5.59; N, 4.75; F, 19.39.

(R)-N-(1-Phenylethylidene)-1,1,1-trifluoro-iso-propylamine (4c): R_f 0.26; as a 12:1 mixture of geometric isomers. ^1H NMR δ , major isomer: 1.35 (d, 3H, $J = 6.9$ Hz), 2.28 (s, 3H), 4.17 (sep, 1H, $J_{\text{HH}} = J_{\text{HF}} = 6.9$ Hz), 7.38-7.40 (m, 3H), 7.82-7.85 (m, 2H). ^{19}F NMR δ -77.66 (d, $J_{\text{HF}} = 6.8$ Hz); minor isomer: 1.20 (d, 3H, $J = 6.6$ Hz), 2.35 (s, 3H), 3.79 (sep, 1H, $J_{\text{HH}} = J_{\text{HF}} = 6.6$ Hz); aromatic resonances are obscured by those of the major

isomer. ^{19}F NMR δ -76.65 (d, $J_{\text{HF}} = 6.6$ Hz). MS 215 (M, 24.8), 200 (M-Me, 43.1), 104 (100) .

(R)-N-(1-Phenylethylidene)-1,1,1-trifluoro-iso-butylamine (4d): R_f 0.27; as a 16:1 mixture of geometric isomers. ^1H NMR δ , major isomer: 1.91 (tq, 3H, $J = 7.5$ Hz, $J = 0.6$ Hz), 1.86, 1.97 (ABXY, 2H, $J_{\text{AB}} = 13.5$ Hz, $J_{\text{AX}} = 3.9$ Hz, $J_{\text{BX}} = 8.9$ Hz, $J_{\text{AY}} = J_{\text{BY}} = 7.5$ Hz), 2.29 (s, 3H), 4.02 (dq, 1H, $J_{\text{HH}} = 8.9$ Hz, $J_{\text{HF}} = 7.0$ Hz, $J_{\text{HH}} = 3.9$ Hz), 7.39-7.42 (m, 3H), 7.82-7.85 (m, 2H). ^{19}F NMR δ -74.84 (d, $J_{\text{HF}} = 7.0$ Hz); minor isomer: 0.76 (td, 3H, $J = 7.5$ Hz, $J = 0.6$ Hz), 2.38 (s, 3H), 3.63 (m, 1H); aromatic and methylene (ABXY) resonances are obscured by those of the major isomer. ^{19}F NMR δ -74.60 (d, $J_{\text{HF}} = 7.1$ Hz). MS 229 (M, 6.8), 214 (M-Me, 58.9), 104 (100) .

(R)-N-(1-Phenylethylidene)(5,5,5,4,4,3,3-heptafluoropent-2-yl)amine (4e): R_f 0.31; ^1H NMR δ : 1.36 (dd, 3H, $J = 6.6$ Hz, $J = 0.6$ Hz), 2.28 (s, 3H), 4.35 (m, 1H), 7.38-7.42 (m, 3H), 7.81-7.84 (m, 2H). ^{19}F NMR δ : -81.44 (dd, $J = 11.9$ Hz, $J = 8.5$ Hz), 118.74, 125.62 (ABm, 2F, $J_{\text{AB}} = 275.5$ Hz), 125.03, 126.79 (ABXY, 2F, $J_{\text{AB}} = 291.0$ Hz, $J_{\text{AX}} = J_{\text{BX}} = 12.2$ Hz, $J_{\text{AY}} = 7.1$ Hz); ^{13}C NMR δ 13.39 (m), 15.03 (s), 57.13 (dd, $J_{\text{CF}} = 20.1$ Hz, $J_{\text{CF}} = 26.8$ Hz), 125.31 (m), 126.95 (s), 126.32 (s), 128.90 (m), 130.25 (s), 140.17 (s), 167.01 (s). MS 315 (M, 12.6), 300 (M-CH₃, 12.6), 146 (M-C₃F₇, 100).

Preparation of N-3,5-Dinitrobenzoyl Derivatives. Typical procedure described for *N*-(3,5-Dinitrobenzoyl)-1-phenyl-2,2,2-trifluoroethylamine (from **4a**). Imine **4a** (262 mg, 0.95 mmol) was dissolved in 3 mL of ether, and 2 mL of 4 N HCl was added under stirring at ambient temperature. Progress of the hydrolysis was monitored by TLC, and upon completion (usually 2 h), the aqueous layer was separated, washed with ether, and evaporated *in vacuo* to give crystalline product (hydrochloride). The crystalline residue obtained was dissolved in 3 mL of CH₂Cl₂ and treated under stirring at ambient temperature first with TEA (288 mg, 2.84 mmol) and then (in 5 min) with the solution of 3,5-dinitrobenzoyl chloride (240 mg, 1.04 mmol) in 1 mL of CH₂Cl₂. The mixture was stirred at ambient temperature for 20 min and then evaporated and dried *in vacuo*. The crystalline residue

thus obtained (without any purification) was subjected to NMR and chiral HPLC analyses. Yield (of analytically pure after purification): 97%, R_f 0.68 (*n*-hexane/AcOEt 3/1); ^1H NMR (acetone- d_6) δ 6.03 (quin, 1H, $J_{\text{HH}} = 8.7$ Hz), 7.45-7.50 (m, 3H), 7.61-7.64 (m, 2H), 8.38 (d, 1H, $J_{\text{HH}} = 8.7$ Hz), 8.99 (d, 2H, $J_{\text{HH}} = 2.4$ Hz), 9.06 (t, 1H, $J_{\text{HH}} = 2.4$ Hz). ^{19}F NMR (acetone- d_6) δ -72.30 (d, $J_{\text{HF}} = 8.7$ Hz). MS 369 (M, 2.6), 349 (M-HF, 100).

Retention times (ambient temperature; SUMICHIRAL OA-4500 HPLC column, eluent hexane/dichloroethane/ethanol 60/30/10, $\lambda = 254$): 18.475 (*S*)-enantiomer, 20.84 (*R*)-enantiomer (major).

This procedure was followed for preparing the rest of *N*-3,5-dinitrobenzoyl derivatives listed below.

***N*-(3,5-Dinitrobenzoyl)-1,1,1-trifluoro-3-phenyl-iso-propylamine (from 4b):** 94%, R_f 0.69 (*n*-hexane/AcOEt 3/1); ^1H NMR (acetone- d_6) δ 3.03, 3.32 (ABX, 2H, $J_{\text{AB}} = 14.4$ Hz, $J_{\text{AX}} = 3.6$ Hz, $J_{\text{BX}} = 11.7$ Hz), 5.12 (ddqd, 1H, $J_{\text{HH}} = 11.7$ Hz, $J_{\text{HH}} = 9.9$ Hz, $J_{\text{HF}} = 6.8$ Hz, $J_{\text{HH}} = 3.6$ Hz), 7.21-7.37 (m, 5H), 7.83 (d, 1H, $J_{\text{HH}} = 9.9$ Hz), 8.80 (d, 2H, $J_{\text{HH}} = 2.1$ Hz), 9.01 (t, 1H, $J_{\text{HH}} = 2.1$ Hz). ^{19}F NMR (acetone- d_6) δ -74.66 (d, $J_{\text{HF}} = 6.8$ Hz). MS 383 (M, 2.6), 172 (100).

Retention times (ambient temperature; SUMICHIRAL OA-4500 HPLC column, eluent hexane/dichloroethane/ethanol 60/30/10, $\lambda = 254$): 17.252 (*S*)-enantiomer, 21.682 (*R*)-enantiomer (major).

***N*-(3,5-Dinitrobenzoyl)-1,1,1-trifluoro-iso-propylamine (from 4c):** 91%, R_f 0.55 (*n*-hexane/AcOEt 3/1); ^1H NMR (MeCN- d_3) δ 1.48 (d, 3H, $J_{\text{HH}} = 7.2$ Hz), 4.95 (ddq, 1H, $J_{\text{HH}} = 7.2$ Hz, $J_{\text{HH}} = 9.8$ Hz, $J_{\text{HF}} = 7.1$ Hz), 7.80 (d, 1H, $J_{\text{HH}} = 9.8$ Hz), 9.01 (d, 2H, $J_{\text{HH}} = 2.1$ Hz), 9.05 (t, 1H, $J_{\text{HH}} = 2.1$ Hz). ^{19}F NMR (MeCN- d_3) δ -78.08 (d, $J_{\text{HF}} = 7.1$ Hz). ^{13}C NMR (MeCN- d_3) δ 12.98 (q, $J_{\text{CF}} = 2.0$ Hz), 47.45 (q, $J_{\text{CF}} = 31.4$ Hz), 121.50 (s), 125.85 (q, $J_{\text{CF}} = 280.8$ Hz), 127.97 (s), 127.20 (s), 136.73 (s), 148.81 (s), 163.10 (s). MS 307 (M, 3.2), 86 (M-HF, 100).

Retention times (ambient temperature; SUMICHIRAL OA-4500 HPLC column, eluent hexane/dichloroethane/ethanol 60/30/10, $\lambda = 254$): 9.997 (*S*)-enantiomer, 15.142 (*R*)-enantiomer (major).

***N*-(3,5-Dinitrobenzoyl)-1,1,1-trifluoro-*iso*-butylamine (from 4d):** 98%, R_f 0.63 (*n*-hexane/AcOEt 3/1); ^1H NMR (MeCN- d_3) δ 1.02 (td, 3H, $J_{\text{HH}} = 7.2$ Hz, $J_{\text{HH}} = 0.6$ Hz), 1.79 (m, 1H), 1.94 (m, 1H), 4.75 (m, 1H), 7.71 (d, 1H, $J_{\text{HH}} = 9.2$ Hz), 8.99 (d, 2H, $J_{\text{HH}} = 2.1$ Hz), 9.07 (t, 1H, $J_{\text{HH}} = 2.1$ Hz). ^{19}F NMR (MeCN- d_3) δ -74.73 (d, $J_{\text{HF}} = 7.1$ Hz). ^{13}C NMR (MeCN- d_3) δ 10.18 (s), 21.54 (q, $J_{\text{CF}} = 1.96$ Hz), 53.80 (q, $J_{\text{CF}} = 30.1$ Hz), 122.49 (s), 126.58 (q, $J_{\text{CF}} = 280.4$ Hz), 128.94 (s), 127.20 (s), 137.54 (s), 149.76 (s), 164.69 (s). MS 321 (M, 9.7), 306 (M-CH₃, 3.1), 75 (100).

Retention times (ambient temperature; SUMICHIRAL OA-4500 HPLC column, eluent hexane/dichloroethane/ethanol 60/30/10, $\lambda = 254$): 8.617 (*S*)-enantiomer, 14.8 (*R*)-enantiomer (major).

***N*-(3,5-Dinitrobenzoyl)-5,5,5,4,4,3,3-heptafluoropent-2-ylamine (from 4e):** 91%, R_f 0.26; ^1H NMR (MeCN- d_3) δ 1.02 (dm, 3H, $J_{\text{HH}} = 7.2$ Hz), 5.15 (m, 1H), 7.78 (d, 1H, $J_{\text{HH}} = 8.7$ Hz), 8.96 (d, 2H, $J_{\text{HH}} = 2.1$ Hz), 9.06 (t, 1H, $J_{\text{HH}} = 2.1$ Hz). ^{19}F NMR δ -80.34 (t, $J = 10.5$ Hz), 118.73, 120.97 (ABm, 2F, $J_{\text{AB}} = 278.9$ Hz), 125.06 (dd, 2F, $J = 15.5$ Hz, $J = 7.1$ Hz); ^{13}C NMR δ 13.92 (m), 46.88 (dd, $J_{\text{CF}} = 21.9$ Hz, $J_{\text{CF}} = 27.0$ Hz), 110.23 (m), 116.30 (m), 122.49 (s), 128.90 (m), 128.88 (s), 137.62 (s), 149.77 (s), 163.88 (s). MS 407 (M, 0.6), 195 (100).

Retention times (ambient temperature; SUMICHIRAL OA-4500 HPLC column, eluent hexane/dichloroethane/ethanol 60/30/10, $\lambda = 254$): 7.117 (*S*)-enantiomer, 8.247 (*R*)-enantiomer (major).

For hydrolysis of *Schiff* bases **4a-c** to the corresponding hydrochlorides, the general procedure described in ref. 1g for hydrolysis of the analogous *N*-benzylidene derivatives was followed.

(*R*)-2,2,2-Trifluoro-1-phenylethylamine hydrochloride (from 4a): 95% from the corresponding *N*-1-phenylethylidene derivative (Table 1, entry 6); $[\alpha]_{\text{D}}^{25} -16.45$ (c 0.75, EtOH) (81% ee by chiral HPLC of the corresponding *N*-3,5-dinitrobenzoyl derivative); ^1H NMR (CD₃CN/CD₃OD, 3/1) δ 5.17 (d, 1H, $J_{\text{H-F}} = 7.5$ Hz), 7.56 (s, 5H); ^{19}F NMR (CD₃CN/CD₃OD, 3/1) δ -72.69 (d, $J_{\text{H-F}} = 7.5$ Hz).

(R)-1,1,1-Trifluoro-3-phenyl-*iso*-propylamine hydrochloride (from 4b): 93% from the corresponding *N*-1-phenylethylidene derivative; $[\alpha]_{\text{D}}^{25} +22.19$ (*c* 1, EtOH) (87% ee by chiral HPLC of the corresponding *N*-3,5-dinitrobenzoyl derivative); ^1H NMR (CD_3CN) δ 3.25, 3.43 (ABX, 2H, $J_{\text{AB}} = 14.7$ Hz, $J_{\text{AX}} = 6.6$ Hz, $J_{\text{BX}} = 7.6$ Hz), 4.31 (dq, 1H, $J_{\text{H-H}} = 7.6$, $J_{\text{H-F}} = 7.1$, $J_{\text{H-H}} = 6.6$ Hz), 7.30-7.43 (m, 5H), 9.05 (br.s, 3H); ^{19}F NMR (CD_3CN) δ -71.39 (d, $J_{\text{H-F}} = 7.1$ Hz).

(R)-1,1,1-Trifluoro-*iso*-propylamine hydrochloride (from 4c): 94% from the corresponding *N*-1-phenylethylidene derivative; $[\alpha]_{\text{D}}^{25} -2.94$ (*c* 1, MeOH); $[\alpha]_{\text{D}}^{25} -4.24$ (*c* 1, EtOH), after crystallization from MeCN; >98% ee by chiral HPLC of the corresponding *N*-3,5-dinitrobenzoyl derivative; ^1H NMR ($\text{CD}_3\text{CN}/\text{CD}_3\text{OD}$, 3/1) δ 1.49 (dq, 3H, $J_{\text{H-H}} = 6.9$, $J_{\text{H-F}} = 0.6$ Hz), 4.08 (dd, 1H, $J_{\text{H-H}} = 6.9$, $J_{\text{H-F}} = 6.7$ Hz); ^{19}F NMR ($\text{CD}_3\text{CN}/\text{CD}_3\text{OD}$, 3/1) δ -75.67 (d, $J_{\text{H-F}} = 6.7$ Hz).

(R)-2,2,2-Trifluoro-1-phenylethylamine (5a). The starting hydrochloride (4.8 g, 21.3 mmol) was suspended in 20 mL of dry ether, and TEA (4.3 g, 42.6 mmol) was added under stirring at ambient temperature. In 10 h, TEA hydrochloride was removed by filtration and the solvent was evaporated *in vacuo* to give amine **5a** (3.85 g, 95.7%), purified by distillation, bp 66—68 °C (2 mmHg): $[\alpha]_{\text{D}}^{25} -17.72$ (*c* 3.44, EtOH) (81% ee by HPLC); ^1H NMR δ 1.76 (br.s, 2H), 4.39 (q, 1H, $J = 7.2$ Hz), 7.26-7.45 (m, 5H); ^{19}F NMR δ -77.22 (d, $J_{\text{HF}} = 7.2$ Hz); ^{13}C NMR δ 57.91 (q, $J_{\text{CF}} = 29.9$ Hz), 125.68 (q, $J_{\text{CF}} = 281.4$ Hz), 127.81 (s), 128.68 (s), 128.96 (s), 135.45 (q, $J_{\text{CF}} = 1.2$ Hz).

Literature for (*S*)-enantiomer (Pirkle, W.H.; Hauske, J.R. *J. Org. Chem.* **1977**, *42*, 2436.): bp 88 °C (20 mm); NMR (CDCl_3) δ 1.80 (broad s, NH), 4.34 (quartet, CH), 7.23-7.41 ppm (multiplet, C_6H_5); IR (neat) 3390 (NH), 3000, 1595, 1500, 1460, 1340, 1170, 1120, 860 cm^{-1} ; $[\alpha]_{\text{D}}^{25} +24.11$ (*c* 12.0, EtOH)

Literature for (*R*)-enantiomer (Wang, Y.; Mosher, H.S. *Tetrahedron Lett.* **1991**, *32*, 987.): $[\alpha]_{\text{D}}^{20} -21.6$ (*c* 3.1, EtOH).