SUPPORTING INFORMATION

A Novel Approach for the Asymmetric Synthesis of Fluorinated β -Amino Sulfones and Allylic Amines

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General Procedure for the Synthesis of β -iminosulfones **3**.

A solution of the arylmethylsulfone **2** (6.3 mmol) in THF (10 mL) was added dropwise to a stirred solution of LDA (14.0 mmol) at $-78\text{ }^{\circ}\text{C}$. After stirring for 1 hour at $-78\text{ }^{\circ}\text{C}$, a solution of the corresponding imidoyl chloride **1** (6.9 mmol) in THF (10 mL) was added slowly. TLC analysis was used to monitor the reaction mixture. After total disappearance of the starting material, the reaction mixture was quenched with saturated aqueous NH_4Cl . The phases were separated and the aqueous layer was extracted with methylene chloride (3x25 mL). The combined organic layers were dried over sodium sulfate. Filtration and evaporation furnished the crude products **3**, which were purified as indicated below.

(-)-N2-[(1S)-1-Phenylethyl]-1,1,1-trifluoro-3-phenylsulfonyl-2-propanimine (3a). Flash chromatography [*n*-hexane-EtOAc (5:1)] on silica gel ($R_f=0.45$) gave a yellow oil (84%): $[\alpha]_{\text{D}}^{25} -48.2$ (c 0.90, CHCl_3); ^1H NMR (400 MHz) (data taken from imino+enamino tautomer mixture) imino tautomer: 1.47 (d, $J = 6.3$ Hz, 3H), 4.15 (d, $J = 10.5$ Hz, 1H), 4.23 (d, $J = 10.5$ Hz, 1H), 4.92 (q, $J = 6.3$ Hz, 1H), 7.15-7.81 (m, 10 H); enamino tautomer: 1.44 (d, $J = 6.3$ Hz, 3H), 4.61 (m, 1H), 5.23 (s, 1H) [other minor tautomers 1.19 (d, $J = 6.3$ Hz, 3H) and 1.38 (d, $J = 6.3$ Hz, 3H)]; ^{13}C NMR (62.8 MHz) imino tautomer: 23.9 (q), 54.1 (t), 61.6 (d), 144.9 (q, $^2J_{\text{CF}} = 25.0$ Hz);

enamino tautomer: 24.2 (q), 52.9 (d), 94.5 (q, $^3J_{\text{CF}} = 5.0$ Hz), 116.2-143.0 (signals corresponding to aromatic carbons of the imino+enamino tautomeric mixture); ^{19}F NMR (235 MHz) -62.80 (s, 3F) (3.5 %), -66.06 (s, 3F) (enamino tautomer) (52 %), -71.23 (s, 3F) (imino tautomer) (42 %), -86.97 (s, 3F) (2.5 %); HRMS calc. for (M^+) $\text{C}_{17}\text{H}_{16}\text{F}_3\text{NO}_2\text{S}$, 355.0853, found 355.0841.

(-)-N2-[(1S)-1-Phenylethyl]-1,1,1-trifluoro-3-(4-methylphenylsulfonyl)-2-propanimine (3b). Flash chromatography [*n*-hexane-EtOAc (5:1)] on silica gel ($R_f = 0.50$) gave a yellowish oil (82%): $[\alpha]_{\text{D}}^{25} -56.2$ (*c* 0.90, CHCl_3); ^1H NMR (250 MHz) (data taken from imino+enamino tautomer mixture) imino tautomer: 1.44 (d, $J = 6.7$ Hz, 3H), 2.44 (s, 3H), 4.22 (d, $J = 11.8$ Hz, 1H), 4.31 (d, $J = 11.8$ Hz, 1H), 4.89 (q, $J = 6.7$ Hz, 1H), 7.26-7.79 (m, 9H); enamino tautomer: 1.60 (d, $J = 6.7$ Hz, 3H), 2.37 (s, 3H), 4.59 (m, 1H), 5.33 (s, 1H); ^{13}C NMR (62.8 MHz) imino tautomer: 21.4 (q), 24.3 (q), 54.1 (t), 61.5 (d); enamino tautomer: 21.3 (q), 24.0 (q), 53.1 (d), 95.1 (q, $^3J_{\text{CF}} = 5.0$ Hz), 116.3-145.8 (signals corresponding to aromatic carbons of the imino+enamino tautomeric mixture); ^{19}F NMR (235 MHz) -62.58 (s, 3F) (4.5 %), -65.92 (s, 3F) (35 %) (enamino tautomer), -71.05 (s, 3F) (60 %) (imino tautomer); HRMS calc. for (M^+) $\text{C}_{18}\text{H}_{18}\text{F}_3\text{NO}_2\text{S}$, 369.1010; found 369.0994.

(-)-N2-[(1S)-1-Phenylethyl]-1,1,1-trifluoro-3-(2-naphthylsulfonyl)-2-propanimine (3c). Flash chromatography [*n*-hexane-EtOAc (5:1)] on silica gel ($R_f = 0.45$) gave a brownish oil (90%): $[\alpha]_{\text{D}}^{25} -37.2$ (*c* 0.80, CHCl_3); ^1H NMR (250 MHz) (data taken from imino+enamino tautomer mixture) imino tautomer: 1.34 (d, $J = 6.7$ Hz, 3H), 4.15 (d, $J = 11.8$ Hz, 1H), 4.23 (d, $J = 11.8$ Hz, 1H), 4.85 (q, $J = 6.7$ Hz, 1H), 7.18-8.27 (m, 12H); enamino tautomer: 1.38 (d, $J = 6.7$ Hz, 3H), 4.49 (m, 1H), 5.23 (s, 1H); ^{13}C NMR (62.8 MHz) imino tautomer: 24.3 (q), 54.3 (t), 61.8 (d); enamino tautomer: 24.4 (q), 53.2 (d), 94.6 (q, $^3J_{\text{CF}} = 5.0$ Hz), 121.5-143.1 (signals corresponding to aromatic carbons of the imino+enamino tautomeric mixture); ^{19}F NMR (235 MHz) -62.62 (s, 3F) (2.6 %), -65.88 (s, 3F) (38.1 %) (enamino tautomer), -71.05 (s, 3F) (56.3

%) (imino tautomer), -76.05 (s, 3F) (3.0 %); HRMS calc. for (M^+) $C_{21}H_{18}F_3NO_3S$, 405.1010, found 405.1012.

(-)-N2-[(1S)-1-Phenylethyl]-1-chloro-1,1-difluoro-3-(2-naphthylsulfonyl)-2-propanimine (3d). Flash chromatography [*n*-hexane-EtOAc (5:1)] on silica gel (R_f = 0.45) gave a yellowish oil (93%): $[\alpha]^{25}_D$ -71.0 (*c* 1.0, $CHCl_3$); 1H NMR (300 MHz) (data taken from imino+enamino tautomer mixture) imino tautomer: 1.58 (d, J = 6.7 Hz, 3H), 4.39 (brs, 2H), 5.10 (q, J = 6.7 Hz, 1H), 7.25-8.46 (m, 12H); enamino tautomer: 1.61 (d, J = 6.7 Hz, 3H), 4.92 (m, 1H), 5.37 (s, 1H) [other minor tautomer 1.20 (d, J = 6.7 Hz, 3H)]; ^{13}C NMR (75 MHz) imino tautomer: 24.5 (q), 53.4 (t), 61.8 (d); enamino tautomer: 24.4 (q), 54.1 (d), 92.9 (q, $^3J_{CF}$ = 7.4 Hz), 121.6-143.2 (signals corresponding to aromatic carbons of the imino+enamino tautomeric mixture); ^{19}F NMR (282.4 MHz) -51.92 (s, 2F) (2.5 %), -54.6 (dd, 2J_1 = 170.6 Hz, 2J_2 = 575.7 Hz, 2F) (enamino tautomer) (53.0 %), -58.82 (s, 2F) (imino tautomer) (44.5 %); HRMS calc. for (M^+) $C_{21}H_{18}F_2NO_2SCl$, 421.0714, found 421.0712.

(-)-N2-[(1S)-1-Phenylethyl]-1-chloro-1,1-difluoro-3-(4-methylphenylsulfonyl)-2-propanimine (3e). Flash chromatography [*n*-hexane-EtOAc (5:1)] on silica gel (R_f = 0.45) gave a dark yellow oil (88%): $[\alpha]^{25}_D$ -69.8 (*c* 1.00, $CHCl_3$); 1H NMR (250 MHz) (data taken from imino+enamino tautomer mixture) imino tautomer: 1.55 (d, J = 6.7 Hz, 3H), 2.43 (s, 3H), 4.30 (d, J = 2.5 Hz, 2H), 5.05 (q, J = 6.7 Hz, 1H), 7.25-7.78 (m, 9H); enamino tautomer: 1.58 (d, J = 6.7 Hz, 3H), 2.42 (s, 3H), 4.91 (m, 1H), 5.30 (s, 1H); ^{13}C NMR (62.8 MHz) imino tautomer: 21.2 (q), 24.1 (q), 53.0 (t), 61.3 (d), 147.8 (t, $^2J_{CF}$ = 29.2 Hz); enamino tautomer: 20.8 (q), 23.9 (q), 53.7 (d), 93.1 (t, $^3J_{CF}$ = 7.4 Hz), 122.6-145.6 (signals corresponding to aromatic carbons of the imino+enamino tautomeric mixture); ^{19}F NMR (235 MHz) -51.86 (s, 2F) (2.7%), -54.54 (dd, 2J_1 = 170.6 Hz, 2J_2 = 575.7 Hz, 2F) (enamino tautomer) (23.0%), -58.82 (s, 2F) (imino tautomer) (74.3%); HRMS calc. for (M^+) $C_{18}H_{18}F_2NO_2SCl$, 385.0714, found 385.0705.

(±)-N2-[1-(1-Naphthyl)ethyl]-1,1,1-trifluoro-3-phenylsulfonyl-2-

propanimine (3f). Flash chromatography [*n*-hexane-EtOAc (6:1)] on silica gel (R_f =0.45) gave a yellow oil (72%): ^1H NMR (400 MHz) (data taken from imino+enamino tautomer mixture) imino tautomer: 1.60 (d, J = 6.7 Hz, 3H), 4.10 (dd, J_1 = 14.3 Hz, J_2 = 11.8 Hz, 2H), 5.64 (q, J = 6.7 Hz, 1H), 7.18-8.00 (m, 12H); enamino tautomer: 1.56 (d, J = 6.7 Hz, 3H), 5.31 (s, 1H), 5.42 (m, 1H); ^{13}C NMR (100 MHz) imino tautomer: 24.2 (q), 53.7 (t), 58.2 (d), 145.1 (q, $^2J_{\text{CF}}$ = 25 Hz); enamino tautomer: 24.5 (q), 50.4 (d), 95.2 (q, $^3J_{\text{CF}}$ = 5.5 Hz), 120.0-143.2 (signals corresponding to aromatic carbons of the imino+enamino tautomeric mixture); ^{19}F NMR (235 MHz) -62.90 (s, 3F) (3.0 %), -65.88 (s, 3F) (enamino tautomer) (30.0 %), -71.05 (s, 3F) (imino tautomer) (65.0 %), -76.08 (s, 3F) (2 %); HRMS calc. for (M^+) $\text{C}_{21}\text{H}_{18}\text{F}_3\text{NO}_2\text{S}$, 405.1010; found 405.1013.

(±)-N2-[1-(1-Naphthyl)ethyl]-1,1,1-trifluoro-3-(2-naphthylsulfonyl)-2-

propanimine (3g). Flash chromatography [*n*-hexane-EtOAc (6:1)] on silica gel (R_f =0.45) gave a yellow oil (68%): ^1H NMR (400 MHz) (data taken from imino+enamino tautomer mixture) imino tautomer: 1.55 (d, J = 6.7 Hz, 3H), 3.95 (dd, J_1 = 14.3 Hz, J_2 = 11.8 Hz, 2H), 5.57 (q, J = 6.7 Hz, 1H), 7.18-8.34 (m, 14H); enamino tautomer: 1.51 (d, J = 6.7 Hz, 3H), 5.37 (s, 1H), 5.40 (m, 1H); ^{13}C NMR (100 MHz) imino tautomer: 25.0 (q), 54.2 (t), 58.6 (d), 146.8 (q, $^2J_{\text{CF}}$ = 25.0 Hz); enamino tautomer: 24.7 (q), 51.0 (d), 95.8 (q, $^3J_{\text{CF}}$ = 5.5 Hz), 144.0 (q, $^2J_{\text{CF}}$ = 25.0 Hz), 118.1-143.1 (signals corresponding to aromatic carbons of the imino+enamino tautomeric mixture); ^{19}F NMR (235 MHz) -62.80 (s, 3F) (2.5%), -66.17 (s, 3F) (enamino tautomer) (47.5%), -70.75 (s, 3F) (imino tautomer) (50.0%); HRMS calc. for (M^+) $\text{C}_{25}\text{H}_{20}\text{F}_3\text{NO}_2\text{S}$, 455.1166, found 455.1169.

(±)-N2-[1-(1-Naphthyl)ethyl]-1,1,1-trifluoro-3-(1-naphthylsulfonyl)-2-

propanimine (3h). Flash chromatography [*n*-hexane-EtOAc (6:1)] on silica gel (R_f =0.45) gave a yellow oil (94%): ^1H NMR (300 MHz) (data taken from imino+enamino tautomer mixture) imino tautomer: 1.53 (d, J = 6.4 Hz, 3H), 4.27 (d, J = 14.1 Hz, 1H), 4.36 (d, J = 14.1 Hz, 1H), 5.52 (q, J = 6.4 Hz, 1H), 7.18-8.65 (m, 14 H);

enamino tautomer: 1.66 (d, $J = 6.4$ Hz, 3H), 5.47 (s, 1H), 5.49 (m, 1H); ^{13}C NMR (75 MHz) imino tautomer: 24.7 (q), 53.1 (t), 58.3 (d), 143.1 (q, $^2J_{\text{CF}} = 31.0$ Hz); enamino tautomer: 24.2 (q), 50.5 (d), 94.5 (q, $^3J_{\text{CF}} = 5.7$ Hz), 121.8-139.6 (signals corresponding to aromatic carbons of the imino+enamino tautomeric mixture); ^{19}F NMR (282.4 MHz) -62.96 (s, 3F) (2.0 %), -66.16 (s, 3F) (enamino tautomer) (30.0 %), -70.77 (s, 3F) (imino tautomer) (68.0 %); HRMS calc. for (M^+) $\text{C}_{25}\text{H}_{20}\text{F}_3\text{NO}_2\text{S}$, 455.1166, found 455.1160.

***N*2-(4-Methoxyphenyl)-1,1,1-trifluoro-3-phenylsulfonyl-2-propanimine**

(3i). Flash chromatography [*n*-hexane-EtOAc (6:1)] on silica gel ($R_f=0.40$) gave a white solid (87%): m.p. 85-87 °C; ^1H NMR (250 MHz) imino tautomer: 3.81 (s, 3H), 4.37 (s, 2H), 6.70 - 7.88 (m, 9H); ^{13}C NMR (75 MHz) imino tautomer: 54.4 (t), 55.4 (q), 114.4 (d), 118.9 (q, $^1J_{\text{CF}} = 277.5$ Hz), 120.5 (d), 126.4 (s), 127.9 (d), 129.5 (d), 134.4 (d), 139.4 (s), 146.9 (q, $^2J_{\text{CF}} = 34.7$ Hz), 158.2 (s); ^{19}F NMR (235 MHz) (imino tautomer) -70.00 (s, 3F); HRMS calc. for (M^+) $\text{C}_{16}\text{H}_{15}\text{F}_3\text{NO}_3\text{S}$, 358.0742, found 358.0709.

***N*2-(4-Methoxyphenyl)-1,1-difluoro-1-phenyl-3-phenylsulfonyl-2-**

propanimine (3j). Flash chromatography [*n*-hexane-EtOAc (2:1)] on silica gel ($R_f=0.45$) gave an orange oil (77%): ^1H NMR (300 MHz) (data taken from imino+enamino tautomer mixture) imino tautomer: 3.72 (s, 3H), 4.36 (s, 2H), 6.67 (d, $J = 9.0$ Hz, 2H), 6.77 (d, $J = 9.0$ Hz, 2H), 7.39-7.90 (m, 10H); enamino tautomer: 3.67 (s, 3H), 5.60 (s, 1H), 8.51 (brs, 1H); ^{13}C NMR (75.5 MHz) imino tautomer: 54.8 (t), 55.4 (q), 154.8 (t, $^2J_{\text{CF}} = 34.5$ Hz), 157.5 (s); enamino tautomer: 55.3 (q), 113.3-140.5 (signals corresponding to aromatic carbons of the imino+enamino tautomeric mixture); ^{19}F NMR decoupling (282.4 MHz) -91.06 (s, 1F) (enamino tautomer) (80.0 %); -95.19 (s, 1F) (imino tautomer) (20.0 %); HRMS calc. for (M^+) $\text{C}_{22}\text{H}_{19}\text{F}_2\text{NO}_3\text{S}$, 415.1047, found 415.1053.

General procedure for the reduction of β -iminosulfones 3. Synthesis of β -aminosulfones 4a-j.

Sodium borohydride (10.0 equiv) was added in portions to a stirred solution of the β -iminosulfone **3** (2.0 mmol) in the corresponding solvent (20 mL) at the temperature indicated in the table 1. Stirring was continued until the starting material had totally disappeared, as detected with TLC monitoring. The reaction mixture was then quenched with saturated aqueous NH_4Cl . The phases were separated and the aqueous layer was extracted with methylene chloride (3x25 mL). The combined organic layers were then dried over sodium sulfate. Filtration and evaporation furnished the crude products **4**, which were purified as indicated below.

(-)-N2-[(1S)-1-Phenylethyl]-(2S)-1,1,1-trifluoro-3-phenylsulfonyl-2-propanamine (l-4a). Flash chromatography [*n*-hexane-EtOAc (9:1)] on silica gel ($R_f=0.40$) gave a yellow oil (99%): $[\alpha]_D^{25} -6.3$ (*c* 1.4, CHCl_3); ^1H NMR (250 MHz) 1.30 (d, $J = 6.5$ Hz, 3H), 1.60 (brd, $J = 6.5$ Hz, 1H), 3.18 (dd, $J_1 = 14.5$ Hz, $J_2 = 9.0$ Hz, 1H), 3.37 (dd, $J_1 = 14.5$ Hz, $J_2 = 3.0$ Hz, 1H), 3.70 (m, 1H), 4.08 (q, $J = 6.5$ Hz, 1H), 7.17-7.88 (m, 10H); ^{13}C NMR (62.8 MHz) 23.1 (q), 52.9 (q, $^2J_{\text{C-F}} = 30.0$ Hz), 55.9 (t), 56.2 (d), 124.9 (q, $^1J_{\text{C-F}} = 283.3$ Hz), 126.9 (d), 127.6 (d), 127.9 (d), 128.4 (d), 129.5 (d), 134.1 (d), 139.6 (s), 144.3 (s); ^{19}F NMR (235 MHz) -75.32 (d, $J_{\text{HF}} = 7.1$ Hz, 3F); HRMS calc. for (M^+) $\text{C}_{17}\text{H}_{18}\text{F}_3\text{NO}_2\text{S}$, 357.1010, found 357.1018.

(-)-N2-[(1S)-1-Phenylethyl]-(2S)-1,1,1-trifluoro-3-(4-methylphenylsulfonyl)-2-propanamine (l-4b). Flash chromatography [*n*-hexane-EtOAc (9:1)] on silica gel ($R_f=0.40$) gave a yellow oil (99%): $[\alpha]_D^{25} -3.2$ (*c* 1.1, CHCl_3); ^1H NMR (250 MHz) 1.28 (d, $J = 6.5$ Hz, 3H), 1.62 (brs, 1H), 2.37 (s, 3H), 3.16 (dd, $J_1 = 14.5$ Hz, $J_2 = 9.0$ Hz, 1H), 3.34 (dd, $J_1 = 14.5$ Hz, $J_2 = 3.0$ Hz, 1H), 3.69 (m, 1H), 4.08 (q, $J = 6.5$ Hz, 1H), 7.11-7.22 (m, 5H), 7.28 (d, $J = 6.9$ Hz, 2H), 7.70 (d, $J = 6.9$ Hz, 2H); ^{13}C NMR (62.8 MHz) 21.6 (q), 23.2 (q), 53.0 (q, $^2J_{\text{CF}} = 30.0$ Hz), 55.9 (t), 56.2 (d), 123.5 (q, $^1J_{\text{CF}} = 283.3$ Hz), 126.9 (d), 127.2 (d), 127.8 (d), 128.3 (d), 130.0 (d), 136.5 (s), 144.4 (s),

145.2 (s); ^{19}F NMR (235 MHz) -75.37 (d, $J_{\text{HF}} = 7.1$ Hz, 3F); HRMS calc. for (M^+) $\text{C}_{18}\text{H}_{20}\text{F}_3\text{NO}_2\text{S}$, 371.1166, found 371.1172.

(+)-*N*2-[(1*S*)-1-Phenylethyl]-(2*S*)-1,1,1-trifluoro-3-(2-naphthylsulfonyl)-2-propanamine (*l*-4c). Flash chromatography [*n*-hexane-EtOAc (9:1)] on silica gel ($R_f=0.40$) gave a yellow oil (99%): $[\alpha]_{\text{D}}^{25} +5.3$ (c 0.8, CHCl_3); ^1H NMR (250 MHz) 1.28 (d, $J = 6.5$ Hz, 3H), 1.55 (brd, $J = 13.0$ Hz, 1H), 3.27 (dd, $J_1 = 14.5$ Hz, $J_2 = 9.0$ Hz, 1H), 3.45 (dd, $J_1 = 14.5$ Hz, $J_2 = 3.0$ Hz, 1H), 3.77 (m, 1H), 4.09 (q, $J = 6.5$ Hz, 1H), 7.06-8.43 (m, 12H); ^{13}C NMR (62.8 MHz) 23.1 (q), 52.9 (q, $^2J_{\text{CF}} = 30.0$ Hz), 55.8 (t), 56.2 (d), 122.2 (d), 125.1 (q, $^1J_{\text{CF}} = 283.3$ Hz), 126.8 (d), 127.3 (d), 127.4 (d), 127.9 (d), 128.0 (d), 128.3 (d), 129.4 (d), 129.6 (d), 129.9 (d), 132.1 (s), 135.4 (s), 136.4 (s), 144.3 (s); ^{19}F NMR (235 MHz) -75.17 (d, $J_{\text{HF}} = 7.1$ Hz, 3F); HRMS calc. for (M^+) $\text{C}_{21}\text{H}_{20}\text{F}_3\text{NO}_2\text{S}$, 407.1166, found 407.1173.

(+)-*N*2-[(1*S*)-1-Phenylethyl]-(2*S*)-1-chloro-1,1-difluoro-3-(2-naphthylsulfonyl)-2-propanamine (*l*-4d). Flash chromatography [*n*-hexane-EtOAc (9:1)] on silica gel ($R_f=0.40$) gave a white solid (99%): m.p. 46-48 °C; $[\alpha]_{\text{D}}^{25} +21.4$ (c 0.9, CHCl_3); ^1H NMR (400 MHz) 1.28 (d, $J = 6.5$ Hz, 3H), 1.55 (brd, $J = 13.0$ Hz, 1H), 3.27 (dd, $J_1 = 14.5$ Hz, $J_2 = 9.0$ Hz, 1H), 3.52 (dd, $J_1 = 14.5$ Hz, $J_2 = 3.0$ Hz, 1H), 3.89 (m, 1H), 4.11 (q, $J = 6.5$ Hz, 1H), 7.06-7.10 (m, 5H), 7.58-7.97 (m, 6H), 8.44 (s, 1H); ^{13}C NMR (100 MHz) 22.8 (q), 55.6 (d), 57.6 (t), 58.6 (t, $^2J_{\text{CF}} = 30.0$ Hz), 122.3 (d), 126.8 (d), 127.2 (d), 127.9 (d), 128.0 (d), 128.2 (d), 129.4 (d), 129.5 (d), 129.9 (d), 130.4 (d), 132.1 (s), 135.4 (s), 136.4 (s), 144.5 (s) (signals of the CClF_2 group are obscured due to their low intensity); ^{19}F NMR (235 MHz) -57.85 (dd, $J_1 = 162.3$ Hz, $J_2 = 5.1$ Hz, 1F), -58.68 (dd, $J_1 = 162.3$ Hz, $J_2 = 7.7$ Hz, 1F); HRMS calc. for (M^+) $\text{C}_{21}\text{H}_{20}\text{F}_2\text{NO}_2\text{SCl}$, 423.0871, found 423.0868.

(+)-*N*2-[(1*S*)-1-Phenylethyl]-(2*R*)-1-chloro-1,1-difluoro-3-(4-methylphenylsulfonyl)-2-propanamine (*l*-4e). Flash chromatography [*n*-hexane-EtOAc (9:1)] on silica gel ($R_f=0.40$) gave a white solid (99%): m.p. 55-57 °C; $[\alpha]_{\text{D}}^{25} +7.7$ (c 0.8, CHCl_3);

^1H NMR (400 MHz) 1.30 (d, $J = 6.5$ Hz, 3H), 1.60 (brs, 1H), 2.39 (s, 3H), 3.15 (dd, $J_1 = 14.5$ Hz, $J_2 = 9.0$ Hz, 1H), 3.41 (dd, $J_1 = 14.5$ Hz, $J_2 = 3.0$ Hz, 1H), 3.81 (m, 1H), 4.12 (q, $J = 6.5$ Hz, 1H), 7.13-7.24 (m, 5H), 7.30 (d, $J = 7.5$ Hz, 2H), 7.73 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (100 MHz) 22.0 (q), 23.4 (q), 56.3 (d), 58.1 (t), 58.6 (t, $^2J_{\text{CF}} = 25.1$ Hz), 127.4 (d), 127.7 (d), 128.4 (d), 128.7 (d), 130.5 (d), 130.8 (t, $^1J_{\text{CF}} = 298.5$ Hz), 137.2 (s), 145.0 (s), 145.6 (s); ^{19}F NMR (376.5 MHz) -58.50 (dd, $J_1 = 161.7$ Hz, $J_2 = 4.6$ Hz, 1F), -59.01 (dd, $J_1 = 161.7$ Hz, $J_2 = 8.0$ Hz, 1F); HRMS calc. for (M^+) $\text{C}_{18}\text{H}_{20}\text{F}_2\text{NO}_2\text{SCl}$, 387.0871, found 387.0852.

(±)-N2-[1(1-Naphthyl)ethyl]-1,1,1-trifluoro-3-phenylsulfonyl-2-

propanamine (l-4f). Flash chromatography [*n*-hexane-EtOAc (9:1)] on silica gel ($R_f=0.40$) gave a yellow oil (99%): ^1H NMR (400 MHz) 1.47, (d, $J = 6.5$ Hz, 3H), 1.75 (brs, 1H), 3.23 (dd, $J_1 = 14.5$ Hz, $J_2 = 9.0$ Hz, 1H), 3.38 (dd, $J_1 = 14.5$ Hz, $J_2 = 3.0$ Hz, 1H), 3.88 (m, 1H), 4.94 (q, $J = 6.5$ Hz, 1H), 7.17-8.08 (m, 12H); ^{13}C NMR (100 MHz) 22.1 (q), 51.4 (d), 53.6 (q, $^2J_{\text{CF}} = 30.0$ Hz), 56.1 (t), 122.9 (d), 123.6 (d), 125.1 (q, $^1J_{\text{CF}} = 283.3$ Hz), 125.4 (d), 125.5 (d), 125.9 (d), 127.7 (s), 127.9 (d), 128.8 (d), 129.4 (d), 130.8 (d), 133.8 (d), 134.0 (d), 139.6 (s), 140.1 (s); ^{19}F NMR (376.5 MHz) -74.9 (d, $J = 6.8$ Hz, 3F); HRMS calc. for (M^+) $\text{C}_{21}\text{H}_{20}\text{F}_3\text{NO}_2\text{S}$, 407.1166, found 407.1269.

(±)-N2-[1(1-Naphthyl)ethyl]-1,1,1-trifluoro-3-(2-naphthylsulfonyl)-2-

propanamine (l-4g). Flash chromatography [*n*-hexane-EtOAc (9:1)] on silica gel ($R_f=0.40$) gave a yellow oil (99%): ^1H NMR (400 MHz) 1.43 (d, $J = 6.5$ Hz, 3H), 1.70 (brs, 1H), 3.29 (dd, $J_1 = 14.5$ Hz, $J_2 = 9.0$ Hz, 1H), 3.38 (dd, $J_1 = 14.5$ Hz, $J_2 = 3.0$ Hz, 1H), 3.92 (m, 1H), 4.94 (q, $J = 6.5$ Hz, 1H), 7.09 - 7.86 (m, 14H); ^{13}C NMR (100 MHz) 22.0 (q), 51.3 (d), 53.5 (q, $^2J_{\text{CF}} = 30.0$ Hz), 56.2 (t), 122.2 (d), 122.8 (d), 123.5 (d), 125.3 (d), 125.4 (d), 125.9 (d), 127.6 (d), 127.9 (d), 128.0 (d), 128.8 (d), 129.4 (d), 129.5 (d), 129.7 (d), 129.8 (d), 130.7 (d), 133.8 (s), 135.3 (s) (signals of the CF_3 group are obscured due to their low intensity); ^{19}F NMR (376.5 MHz) -74.89 (d, $J = 6.8$ Hz, 3F); HRMS calc. for (M^+) $\text{C}_{25}\text{H}_{22}\text{F}_3\text{NO}_3\text{S}$, 457.1323, found 457.1325.

(±)-N2-[1(1-Naphthyl)ethyl]-1,1,1-trifluoro-3-(1-naphthylsulfonyl)-2-

propanamine (l-4h). Flash chromatography [*n*-hexane-EtOAc (20:1)] on silica gel ($R_f=0.40$) gave a white solid (99%): m.p. 50-51 °C; ^1H NMR (300 MHz) 1.40 (d, $J = 6.4$ Hz, 3H), 1.67 (brs, 1H), 3.43 (dd, $J_1 = 14.6$ Hz, $J_2 = 9.1$ Hz, 1H), 3.61 (dd, $J_1 = 14.6$ Hz, $J_2 = 2.6$ Hz, 1H), 3.97 (m, 1H), 4.91 (q, $J = 6.4$ Hz, 1H), 7.16 - 8.59 (m, 14 H); ^{13}C NMR (75 MHz) 22.6, (q), 51.7 (d), 53.8 (q, $^2J_{\text{CF}} = 29.1$ Hz), 56.4 (t), 123.3 (d), 123.9 (d), 124.0 (d), 124.8 (d), 125.8 (d), 125.9 (d), 126.3 (d), 127.6 (d), 128.0 (d), 129.0 (s), 129.3 (d), 129.5 (d), 129.9 (d), 131.1 (d), 131.2 (s), 134.2 (s), 134.6 (s), 134.8 (s), 136.0 (d), 140.0 (s) (signals of the CF_3 group are obscured due to their low intensity); ^{19}F NMR (282.4 MHz) -74.73 (d, $J = 7.2$ Hz, 3F); HRMS calc. for (M^+) $\text{C}_{25}\text{H}_{22}\text{F}_3\text{NO}_2\text{S}$, 457.1323, found 457.1326.

(±)-N2-(4-Methoxyphenyl)-1,1,1-trifluoro-3-phenylsulfonyl-2-

propanamine (4i). Flash chromatography [*n*-hexane-EtOAc (9:1)] on silica gel ($R_f=0.40$) gave a white solid (99%): m.p. 151-153 °C; ^1H NMR (400 MHz) 3.33 (dd, $J_1 = 14.5$ Hz, $J_2 = 7.5$ Hz, 1H), 3.47 (dd, $J_1 = 14.5$ Hz, $J_2 = 3.0$ Hz, 1H), 3.5 (brs, 1H), 3.69 (s, 3H), 4.27 (m, 1H), 6.5 (d, $J = 8.8$ Hz, 2H), 6.70 (d, $J = 8.8$ Hz, 2H), 7.4-7.7 (m, 5H); ^{13}C NMR (100 MHz) 54.8 (q, $^2J_{\text{CF}} = 26.4$ Hz), 55.9 (t), 56.2 (q), 115.3 (d), 116.2 (d), 128.7 (d), 129.9 (d), 134.7 (d), 139.5 (s), 139.6 (s), 154.2 (s); ^{19}F NMR (235 MHz) -76.10 (d, $J_{\text{HF}} = 6.5$ Hz, 3F); HRMS calc. for (M^+) $\text{C}_{16}\text{H}_{16}\text{F}_3\text{NO}_3\text{S}$, 359.0803, found 359.0795.

(±)-N2-(4-Methoxyphenyl)-1,1-difluoro-1-phenyl-3-phenylsulfonyl-2-

propanamine (4j). Flash chromatography [*n*-hexane-EtOAc (5:1)] on silica gel ($R_f=0.55$) gave a white solid (99%): m.p. 144-145 °C; ^1H NMR (300 MHz) 1.49 (brs, 1H), 3.19 (dd, $J_1 = 14.7$ Hz, $J_2 = 10.7$ Hz, 1H), 3.51 (dd, $J_1 = 14.7$ Hz, $J_2 = 2.6$ Hz, 1H), 3.66 (s, 3H), 4.29 (m, 1H), 6.31 (d, $J = 9.0$ Hz, 2H), 6.59 (d, $J = 9.0$ Hz, 2H), 7.32-7.64 (m, 10H); ^{13}C NMR (75.5 MHz) 55.6 (q), 56.5 (t), 57.3 (t, $^2J_{\text{CF}} = 25.1$ Hz), 114.5 (d), 115.0 (d), 125.7 (d), 125.8 (d), 128.1 (d), 128.5 (d), 129.0 (d), 130.5 (s), 133.7 (d), 139.3 (s), 139.9 (s), 152.9 (s) (signals of the CF_2 group are obscured due to their low

intensity); ^{19}F NMR (282.4 MHz) -102.72 (dd, $J_{\text{FF}} = 245.4$ Hz, $J_{\text{FH}} = 8.2$ Hz, 1F), -106.32 (dd, $J_{\text{FF}} = 245.4$ Hz, $J_{\text{FH}} = 11.4$ Hz, 1F); HRMS calc. for (M^+) $\text{C}_{22}\text{H}_{21}\text{F}_2\text{NO}_3\text{S}$, 417.1210, found, 417.1204.

General procedure for the oxidation of β -aminosulfoxides 6. Synthesis of β -aminosulfones 4k-m.

Metachloroperbenzoic acid was added slowly to a stirred solution of the β -aminosulfoxide **6** (2.0 mmol, 1.0 equiv) in dichloromethane (20 mL) at 0 °C. Stirring was continued until the starting material had totally disappeared, as detected with TLC monitoring. The reaction mixture was then quenched with NaOH 3N. The phases were separated and the aqueous layer was extracted with methylene chloride (3x25 mL). The combined organic layers were then dried over sodium sulfate. Filtration and evaporation furnished the crude products **4**, which were purified as indicated below.

(-)-N2-(4-Methoxyphenyl)-(2S)-1,1,1-trifluoro-3-(1-naphthylsulfonyl)-2-propanamine (4k). Flash chromatography [*n*-hexane-EtOAc (7:1)] on silica gel ($R_f=0.40$) gave a white solid (83%): m.p. 125-127 °C; $[\alpha]_{\text{D}}^{25} -85.9$ (*c* 1.05, CHCl_3); ^1H NMR (300 MHz) 3.15 (brd, $J = 9.0$ Hz, 1H), 3.56 (dd, $J_1 = 14.7$ Hz, $J_2 = 10.2$ Hz, 1H), 3.68 (dd, $J_1 = 14.7$ Hz, $J_2 = 2.8$ Hz, 1H), 3.69 (s, 3H), 4.27 (m, 1H), 6.32 (d, $J = 9.0$ Hz, 2H), 6.65 (d, $J = 9.0$ Hz, 2H), 7.23-8.13 (m, 7H); ^{13}C NMR (75 MHz) 53.6 (q, $^2J_{\text{CF}} = 31.0$ Hz), 54.9 (t), 55.4 (q), 114.4 (d), 115.0 (d), 123.2 (d), 124.2 (d), 124.6 (q, $^1J_{\text{CF}} = 285.0$ Hz), 126.9 (d), 128.1 (s), 128.9 (d), 129.3 (d), 130.8 (d), 133.2 (s), 133.9 (s), 135.4 (d), 138.7 (s), 153.2 (s); ^{19}F NMR (282.4 MHz) -76.32 (d, $J = 7.2$ Hz, 3F); HRMS calc. for (M^+) $\text{C}_{20}\text{H}_{18}\text{F}_3\text{NO}_3\text{S}$, 409.0959, found 409.0962.

(-)-N2-(4-Methoxyphenyl)-(2S)-1-chloro-1,1-difluoro-3-(4-methylphenyl)-2-propanamine (4l). Flash chromatography [*n*-hexane-EtOAc (7:1)] on silica gel ($R_f=0.40$) gave a yellowish solid (75%): m.p. 114-116 °C; $[\alpha]_{\text{D}}^{25} -1.0$ (*c* 1.00, CHCl_3); ^1H NMR (300 MHz) 2.32 (s, 3H), 3.31 (dd, $J_1 = 14.7$ Hz, $J_2 = 10.5$ Hz, 1H), 3.37 (brs, 1H), 3.56 (dd, $J_1 = 14.7$ Hz, $J_2 = 2.5$ Hz, 1H), 3.69 (s, 3H), 4.34 (m, 1H), 6.51 (d, $J =$

9.0 Hz, 2H), 6.69 (d, $J = 9.0$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (75 MHz) 21.6 (q), 55.6 (q), 56.6 (t), 59.1 (t, $^2J_{\text{CF}} = 26.3$ Hz), 114.6 (d), 115.4 (d), 128.1 (d), 129.4 (t, $^1J_{\text{CF}} = 298.7$ Hz), 129.8 (d), 136.0 (s), 139.0 (s), 145.2 (s), 153.5 (s); ^{19}F NMR (282.4 MHz) -60.45 (dd, $J_1 = 125.1$ Hz, $J_2 = 6.0$ Hz, 1F), -60.60 (dd, $J_1 = 125.1$ Hz, $J_2 = 7.0$ Hz, 1F); HRMS calc. for (M^+) $\text{C}_{17}\text{H}_{18}\text{F}_2\text{NO}_3\text{SCl}$, 391.0634, found 391.0633.

(-)-N2-(4-Methoxyphenyl)-(2S)-1,1,1,2,2-pentafluoro-4-(1-naphthyl sulfonyl)-3-butanamine (4m). Flash chromatography [*n*-hexane-EtOAc (7:1)] on silica gel ($R_f=0.40$) gave a yellowish solid (45%): m.p.: 125-127 °C; $[\alpha]_{\text{D}}^{25} -125.3$ (c 1.00, CHCl_3); ^1H NMR (300 MHz) 3.05 (brd, $J = 10.0$ Hz, 1H), 3.65 (m, 2H), 3.69 (s, 3H), 4.58 (m, 1H), 6.30 (d, $J = 8.9$ Hz, 2H), 6.64 (d, $J = 8.9$ Hz, 2H), 7.18 - 8.52 (m, 7H); ^{13}C NMR (75 MHz) 52.4 (dd, $^2J_{\text{CF1}} = 25.7$ Hz, $^2J_{\text{CF2}} = 22.8$ Hz), 55.4 (t), 56.0 (q), 113.6 (t, $^1J_{\text{CF}} = 257.0$), 115.0 (d), 115.3 (d), 115.9 (q, $^1J_{\text{CF}} = 257.0$ Hz), 123.8 (d), 124.7 (d), 127.5 (d), 128.6 (s), 129.4 (d), 129.9 (d), 131.2 (d), 134.1 (s), 134.4 (s), 135.8 (d), 138.6 (s), 153.7 (s); ^{19}F NMR (282.4 MHz) -81.36 (s, 3F), -118.82 (dd, $J_{\text{FF}} = 271.1$ Hz, $J_{\text{FH}} = 7.3$ Hz, 1F), -125.34 (dd, $J_{\text{FF}} = 271.1$ Hz, $J_{\text{FH}} = 7.3$ Hz, 1F); HRMS calc. for (M^+) $\text{C}_{21}\text{H}_{18}\text{F}_5\text{NO}_3\text{S}$, 459.0927, found 459.0929.

General Procedure for the cleavage of the amino moiety on *N*-alkylsubstituted β -aminosulfones 4. Synthesis of β -aminosulfones 5.

Palladium on active carbon (10%) was added to a stirred solution of the corresponding β -aminosulfone **4** (6.3 mmol) in MeOH (20 mL) at room temperature (For **5c** see, scheme 1 and reference 15 in text). The flask was then put under vacuum and afterwards filled with hydrogen. The reaction mixture was stirred until the starting material totally disappeared. Finally, the reaction mixture was filtered through Celite® and the solvents were removed to yield the crude products **5**, which were purified as indicated below.

(+)-(1*S*)-2,2,2-Trifluoro-1-phenylsulfonyl ethylamine [(*S*)-5a]. Flash chromatography [*n*-hexane-EtOAc (4:1)] on silica gel ($R_f=0.40$) gave a white solid (90%): m.p. 55-57 °C; $[\alpha]_D^{25} +24.2$ (c 0.66, CHCl₃); ¹H NMR (300 MHz) 1.73 (brs, 2H), 3.15 (dd, $J_1 = 14.1$ Hz, $J_2 = 10.5$ Hz, 1H), 3.32 (dd, $J_1 = 14.1$ Hz, $J_2 = 2.0$ Hz, 1H), 3.89 (m, 1H), 7.54- 7.91 (m, 5H); ¹³C NMR (75 MHz) 50.0 (q, $^2J_{CF} = 31.2$ Hz), 56.3 (t), 125.0 (q, $^1J_{CF} = 279.0$ Hz), 128.0 (d), 129.5 (d), 134.3 (d), 139.0 (s); ¹⁹F NMR (282.4 MHz) -78.93 (s, 3F); HRMS calc. for (M^+) C₉H₁₀F₃NO₂S, 254.0462, found 254.0462.

(+)-(1*R*)-2-Chloro-2,2-difluoro-1-(4-methylphenylsulfonyl)ethylamine [(*R*)-5b]. Flash chromatography [*n*-hexane-EtOAc (4:1)] on silica gel ($R_f=0.40$) gave a white solid (92%): m.p. 102-104 °C; $[\alpha]_D^{25} +24.3$ (c 1.02, CHCl₃); ¹H NMR (300 MHz) 1.76 (brs, 2H), 2.39 (s, 3H), 3.11 (dd, $J_1 = 14.1$ Hz, $J_2 = 10.3$ Hz, 1H), 3.36 (dd, $J_1 = 14.1$ Hz, $J_2 = 1.7$ Hz, 1H), 3.86 (m, 1H), 7.32 (d, $J = 8.3$ Hz, 2H), 7.76 (d, $J = 8.3$ Hz, 2H); ¹³C NMR (75 MHz) 22.1 (q), 55.7 (t, $^2J_{CF} = 26.8$ Hz), 57.5 (t), 128.5 (d), 130.1 (t, $^1J_{CF} = 300.0$ Hz), 130.5 (d), 136.5 (d), 145.9 (s); ¹⁹F NMR (282.4 MHz) -62.97 (dd, $J_{FF} = 163.3$ Hz, $J_{FH} = 7.3$ Hz, 1F), -64.30 (dd, $J_{FF} = 163.3$ Hz, $J_{FH} = 7.3$ Hz, 1F); HRMS calc. for (M^+) C₁₀H₁₂F₂NO₂SCl, 284.0323, found 284.0312.

(±)-2,2,2-Trifluoro-1-phenylsulfonyl ethylamine [(±)-5a]. Flash chromatography [*n*-hexane-EtOAc (4:1)] on silica gel ($R_f=0.40$) gave a white solid (80%): m.p. 55-57 °C; ¹H NMR (300 MHz) 1.73 (brs, 2H), 3.15 (dd, $J_1 = 14.1$ Hz, $J_2 = 10.5$ Hz, 1H), 3.32 (dd, $J_1 = 14.1$ Hz; $J_2 = 2.0$ Hz, 1H), 3.89 (m, 1H), 7.54- 7.91 (m, 5H); ¹³C NMR (75 MHz) 50.0 (q, $^2J_{CF} = 31.2$ Hz), 56.3 (t), 125.0 (q, $^1J_{CF} = 279.0$ Hz), 128.0 (d), 129.5 (d), 134.3 (d), 139.0 (s); ¹⁹F NMR (282.4 MHz) -78.93 (s, 3F); HRMS calc. for (M^+) C₉H₁₀F₃NO₂S, 254.0462, found 254.0462.

(±)-2,2,2-Trifluoro-1-(1-naphthylsulfonylmethyl)ethylamine [(±)-5c]. Flash chromatography [*n*-hexane-EtOAc (4:1)] on silica gel ($R_f=0.40$) gave a white solid (97%): m.p. 83-85 °C; ¹H NMR (300 MHz) 1.71 (brs, 2H), 3.33 (dd, $J_1 = 14.1$ Hz, $J_2 =$

10.3 Hz, 1H), 3.51 (dd, $J_1 = 14.1$ Hz, $J_2 = 1.9$ Hz, 1H), 3.97 (m, 1H), 7.54-8.62 (m, 7H); ^{13}C NMR (75 MHz) 49.0 (q, $^2J_{\text{CF}} = 30.8$ Hz), 54.9 (t), 122.4 (d), 123.4 (d), 123.8 (q, $^1J_{\text{CF}} = 279.3$ Hz), 126.3 (d), 127.5 (s), 128.2 (d), 128.5 (d), 129.8 (d), 132.8 (s), 133.2 (s), 134.9 (d); ^{19}F NMR (282.4 MHz) -78.82 (d, $J = 6.2$ Hz, 3F); HRMS calc. for (M^+) $\text{C}_{13}\text{H}_{12}\text{F}_3\text{NO}_2\text{S}$, 303.0540, found 303.0538.

General Procedure for the cleavage of the amino moiety on *N*-arylsubstituted β -aminosulfones 4. Synthesis of β -aminosulfones 5b-c.

A solution of ammonium cerium nitrate (2.5 mmol) in water (8 mL) was added slowly to a stirred solution of β -aminosulfone **4k-l** (0.5 mmol) in acetonitrile (11 mL) at room temperature. After 2 hours, a solution of NaHCO_3 5% was added until pH 6 was reached. Then sodium sulfite was added until the mixture became a brown suspension. The reaction mixture was extracted with ethyl acetate (4 x 25 mL) and the organic phases were mixed and dried over anhydrous sodium sulfate. The reaction mixture was then filtered and the solvents were removed *in vacuo* to yield the crude product **5b-c**, which were purified as indicated below.

(-)-(1*S*)-2-Chloro-2,2-difluoro-1-(4-methylphenylsulfonyl)ethylamine [(*S*)-5b]. Flash chromatography [*n*-hexane-EtOAc (4:1)] on silica gel ($R_f=0.40$) gave a white solid (60%); m.p. 102-104 °C; $[\alpha]_{\text{D}}^{25} -24.7$ (c 1.05, CHCl_3); ^1H NMR (300 MHz) 1.76 (brs, 2H), 2.39 (s, 3H), 3.11 (dd, $J_1 = 14.1$ Hz, $J_2 = 10.3$ Hz, 1H), 3.36 (dd, $J_1 = 14.1$ Hz, $J_2 = 1.7$ Hz, 1H), 3.86 (m, 1H), 7.32 (d, $J = 8.3$ Hz, 2H), 7.76 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (75 MHz) 22.1 (q), 55.7 (t, $^2J_{\text{CF}} = 26.8$ Hz), 57.5 (t), 128.5 (d), 130.1 (t, $^1J_{\text{CF}} = 300.0$ Hz), 130.5 (d), 136.5 (d), 145.9 (s); ^{19}F NMR (282.4 MHz) -62.97 (dd, $J_1 = 163.3$ Hz, $J_2 = 7.3$ Hz, 1F), -64.30 (dd, $J_1 = 163.3$ Hz, $J_2 = 7.3$ Hz, 1F); HRMS calc. for (M^+) $\text{C}_{10}\text{H}_{12}\text{F}_2\text{NO}_2\text{SCl}$, 284.0323, found 284.0312.

(+)-(1*S*)-2,2,2-Trifluoro-1-(1-naphthylsulfonylmethyl)ethylamine [(*S*)-5c]. Flash chromatography [*n*-hexane-EtOAc (4:1)] on silica gel ($R_f=0.40$) gave a white solid

(78%): m.p. 83-85 °C; $[\alpha]_D^{25} +11.5$ (*c* 0.62, CHCl₃). Spectroscopical data (¹H, ¹³C, ¹⁹F NMR) and HRMS are identical to (±)-**5c**.

General procedure for the methylation-desulfonation of β-aminosulfones

4. Synthesis of allylamines **7**.

A solution of *n*-butyl-lithium (2.9 mmol 2.5M in hexanes) was added to a stirred solution of the corresponding β-aminosulfone **4** (1.4 mmol) in THF (10 mL) at -78 °C. After 2 hours of stirring at this temperature, chloriodomethane (1.5 mmol) was added dropwise. After 10 more min. of stirring, methyl lithium (1.5 mmol) was added dropwise, after which the mixture was stirred for another 15 min. The mixture was then quenched with saturated aqueous NH₄Cl. The phases were separated and the aqueous layer was extracted with methylene chloride (3x25 mL). The combined organic layers were dried over sodium sulfate. Filtration and evaporation furnished the crude products **7**, which were purified as indicated below.

(±)-4-Methoxyphenyl[(1*RS*)-1-trifluoromethylallyl]amine [(±)-7a**].** Flash chromatography [*n*-hexane-EtOAc (10:1)] on silica gel (*R_f*=0.4) gave a yellow oil (73%): ¹H NMR (300 MHz) 3.49 (brs, 1H), 3.65 (s, 3H), 4.25 (m, 1H), 5.32 (d, *J* = 10.3 Hz, 1H), 5.4 (d, *J* = 17.1 Hz, 1H), 5.80 (m, 1H), 6.57 (d, *J* = 9.0 Hz, 2H), 6.71 (d, *J* = 9.0 Hz, 2H); ¹³C NMR (75 MHz) 55.6 (q), 59.5 (q, ²*J*_{CF} = 29.7 Hz), 114.8 (d), 115.5 (d), 120.6 (t), 125.1 (q, ¹*J*_{CF} = 281.0 Hz), 130.1 (d), 139.6 (s), 153.2 (s); ¹⁹F NMR (282.4 MHz) -75.8 (d, *J* = 7.2 Hz, 3F); HRMS calc. for (M⁺) C₁₁H₁₂NF₃O, 231.0870, found 231.0863.

(+)-4-Methoxyphenyl[(1*R*)-1-trifluoromethylallyl]amine [(*R*)-7a**].** Flash chromatography [*n*-hexane-EtOAc (10:1)] on silica gel (*R_f*=0.40) gave a yellow oil (70%): $[\alpha]_D^{25} +3.6$ (*c* 1.20, CHCl₃); ¹H NMR (300 MHz) 3.49 (brs, 1H), 3.65 (s, 3H), 4.25 (m, 1H), 5.32 (d, *J* = 10.3 Hz, 1H), 5.4 (d, *J* = 17.1 Hz, 1H), 5.80 (m, 1H), 6.57 (d, *J* = 9.0 Hz, 2H), 6.71 (d, *J* = 9.0 Hz, 2H); ¹³C NMR (75 MHz) 55.6 (q), 59.5 (q, ²*J*_{CF} = 29.7 Hz), 114.8 (d), 115.5 (d), 120.6 (t), 125.1 (q, ¹*J*_{CF} = 281.0 Hz), 130.1 (d), 139.6 (s),

153.2 (s); ^{19}F NMR (282.4 MHz) -75.8 (d, $J = 7.2$ Hz, 3F); HRMS calc. for (M^+) $\text{C}_{11}\text{H}_{12}\text{NF}_3\text{O}$, 231.0870, found 231.0863.

(-)-(1*S*)-1-Chloro-1,1-difluoromethyl-2-propenyl(4-methoxyphenyl)amine

[(*S*)-7b]. Flash chromatography [*n*-hexane-EtOAc (10:1)] on silica gel ($R_f=0.40$) gave a yellow oil (70%): $[\alpha]_D^{25} -38.2$ (c 0.9, CHCl_3); ^1H NMR (300 MHz) 3.55 (brs, 1H), 3.68 (s, 3H), 4.36 (m, 1H), 5.36 (d, $J = 10.3$ Hz, 1H), 5.43 (d, $J = 17.0$ Hz, 1H), 5.85 (m, 1H), 6.60 (d, $J = 9.0$ Hz, 2H), 6.73 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (75 MHz) 55.6 (q), 64.6 (t, $^2J_{\text{CF}} = 25.3$ Hz), 114.8 (d), 115.6 (d), 120.6 (t), 129.8 (t, $^1J_{\text{CF}} = 297.6$ Hz), 130.9 (d), 139.5 (s), 153.2 (s); ^{19}F NMR (282.4 MHz) -60.22 (ddd, $J_1 = 241.2$ Hz, $J_2 = 161.8$ Hz, $J_3 = 8.2$ Hz, 2F); HRMS calc. for (M^+) $\text{C}_{11}\text{H}_{12}\text{F}_2\text{NOCl}$, 247.0575, found 247.0574.

(-)-4-Methoxyphenyl[(1*R*)-1-(1,1,2,2,2-pentafluoroethyl)-3-butenyl]amine

[(*R*)-7c]. Flash chromatography [*n*-hexane-EtOAc (10:1)] on silica gel ($R_f=0.40$) gave a yellow oil (45%): $[\alpha]_D^{25} -7.1$ (c 0.9, CHCl_3); ^1H NMR (300 MHz) 3.43 (brs, 1H), 3.67 (s, 3H), 4.34 (m, 1H), 5.33 (d, $J = 3.2$ Hz, 1H), 5.37 (d, $J = 10.0$ Hz, 1H), 5.78 (m, 1H), 6.57 (d, $J = 9.0$ Hz, 2H), 6.72 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (75 MHz) 54.6 (q), 57.4 (dd, $^2J_{\text{CF}1} = 25.1$ Hz, $^2J_{\text{CF}2} = 21.7$ Hz), 113.8 (d), 114.5 (q, $^1J_{\text{CF}} = 248.4$ Hz), 114.8 (d), 115.0 (t, $^1J_{\text{CF}} = 248.4$ Hz), 120.0 (t), 128.4 (d), 138.2 (s), 152.3 (s); ^{19}F NMR (282.4 MHz) -81.41 (s, 3F), -120.62 (dd, $J_1 = 274.2$ Hz, $J_2 = 9.2$ Hz), -125.8 (dd, $J_1 = 274.2$ Hz, $J_2 = 9.2$ Hz); HRMS calc. for (M^+) $\text{C}_{12}\text{H}_{12}\text{F}_5\text{NO}$, 281.0839, found 281.0846.

(±)-4-Methoxyphenyl[(1*RS*)-1-difluoro(phenyl)methylallyl]amine [(±)-7d].

Flash chromatography [*n*-hexane-EtOAc (5:1)] on silica gel ($R_f=0.55$) gave a yellow oil (47%): ^1H NMR (300 MHz) 2.7 (brs, 1H), 3.65 (s, 3H), 4.29 (m, 1H), 5.19 (d, $J = 1.3$ Hz, 1H), 5.23 (d, $J = 6.0$ Hz, 1H), 5.73 (m, 1H), 6.48 (d, $J = 9.0$ Hz, 2H), 6.67 (d, $J = 9.0$ Hz, 2H), 7.35-7.42 (m, 5H); ^{13}C NMR (75.5 MHz) 55.7 (q), 63.1 (t, $^2J_{\text{CF}} = 29.3$ Hz), 114.7 (d), 115.3 (d), 119.4 (d), 121.6 (t, $^1J_{\text{CF}} = 249.0$ Hz), 125.9 (t, $^3J_{\text{CF}} = 6.3$ Hz), 128.2 (d), 130.0 (d), 132.3 (t, $^4J_{\text{CF}} = 3.4$ Hz), 134.7 (t, $^2J_{\text{CF}} = 25.9$ Hz), 140.5 (s), 152.7

(s); ^{19}F NMR (282.4 MHz) -103.18 (dd, $J_{\text{FF}} = 245.4$ Hz, $J_{\text{FH}} = 11.4$ Hz, 1F), -104.55 (dd, $J_{\text{FF}} = 245.4$ Hz, $J_{\text{FH}} = 10.3$ Hz, 1F); HRMS calc. for (M^+) $\text{C}_{17}\text{H}_{17}\text{NF}_2\text{O}$, 289.1278, found 289.1282.