

Supporting Information. NMR spectra were obtained in  $CDCl_3$ , with the exception of those for inhibitors, which were measured in acetone- $d_6$ . None of the yields have been optimized.

**2,3-difluorobenzylamine.** 2,3-difluorobenzonitrile (300 mg, 2.16 mmol) was added to a pink solution of  $CoCl_2 \cdot 6H_2O$  (53 mg, 0.22 mmol) in THF (6 mL) and water (3 mL) and stirred vigorously. The mixture was cooled intermittently as  $NaBH_4$  (163 mg, 4.32 mmol) was added over 8 min. The exothermic reaction evolved a large amount of hydrogen gas. After 1 h, TLC revealed a trace amount of starting material, so additional  $NaBH_4$  (40 mg) was added. After stirring for 2 h, concentrated  $NH_4OH$  (0.28 mL) was added and the solution was centrifuged. Both phases of the supernatant were decanted and the pellet was washed again with the same solvent mixture. The supernatants were combined and the bulk of the THF was removed *in vacuo*. The aqueous residue was extracted with  $CH_2Cl_2$  (4 x 15 mL), dried over  $MgSO_4$ , and the combined organic phases were removed *in vacuo* to afford a yellow oil (150 mg, 49%). The crude product mixture contained only one amine and was taken directly to the next step.  $^1H$  NMR  $\delta$  3.91 (s, 2H), 7.09 (m, 1H), 7.25 (s, 1H), 7.45 (s, 1H)

**3,5-difluorobenzylamine.** (310 mg, 100%), pale yellow oil,  $^1H$  NMR  $\delta$  3.88 (s, 2H), 6.69 (m, 1H), 6.87 (m, 2H)

**2,3,4-trifluorobenzylamine.** (113 mg, 37%), yellowish green oil,  $^1H$  NMR  $\delta$  3.91 (s, 2H), 6.95 (m, 1H), 7.06 (m, 1H)

**2,3,6-trifluorobenzylamine.** (134 mg, 43%), yellowish brown oil,  $^1H$  NMR  $\delta$  3.96 (s, 2H), 6.84 (m, 1H), 7.04 (m, 1H)

**2,4,5-trifluorobenzylamine.** (40 mg, 34%), yellowish brown oil,  $^1H$  NMR  $\delta$  3.84 (s, 2H), 6.89 (m, 1H), 7.18 (m, 1H)

**3,4,5-trifluorobenzylamine.** (180 mg, 58%), yellow oil,  $^1H$  NMR  $\delta$  3.84 (s, 2H), 6.97 (m, 2H)

**2,3,4,5-tetrafluorobenzylamine.** (214 mg, 52%), yellow oil,  $^1H$  NMR  $\delta$  3.83 (s, 1H), 7.06 (m, 1H)

**2,3,5,6-tetrafluorobenzylamine.** (228 mg, 56%), yellow oil,  $^1H$  NMR  $\delta$  3.98 (s, 2H), 7.01 (m, 1H)

**2,3,4,5,6-pentafluorobenzylphthalimide.** a-Bromopentafluorotoluene (230 mg, 0.88 mmol) was added to potassium phthalimide (160 mg, 0.88 mmol) in 8.0 mL of DMF. The solution was stirred o/n at 130 °C, affording an orange-brown solution that was chilled, and then diluted with  $dH_2O$  ( $\approx$ 50 mL). The light tan precipitate (253 mg) was recrystallized from ethanol (12 mL), to afford tan needles (219 mg, 76%).  $^1H$  NMR  $\delta$  4.96 (br s, 2H), 7.75 (m, 2H), 7.87 (m, 2H)

**2,3,4,5,6-pentafluorobenzylamine.** Hydrazine (33  $\mu$ L, 0.67 mmol) was added to 2,3,4,5,6-pentafluorobenzylphthalimide (220 mg, 0.67 mmol) in 4 mL absolute EtOH. The solution was refluxed 2 h, affording a white precipitate. 5 N HCl (1.2 mL) was added, and reflux was continued for 30 min. The white solid was removed by filtration. 3.75 N NaOH (2.0 mL) was added, and the resulting solution was extracted 3 x 20 mL with  $Et_2O$ . The combined organic phases were

dried with  $Na_2SO_4$ , and evaporated *in vacuo* to an oil (60.3 mg, 46%).  $^1H$  NMR  $\delta$  4.94 (m)

***N*-(4'-sulfamoylbenzoyl)-2-fluorobenzylamine.** A solution of *N*-hydroxysuccinimidyl-4-sulfamoylbenzenecarboxylate (133 mg, 0.5 mmol), 2-fluorobenzylamine (62 mg, 0.5 mmol), and acetone (6 mL) was added to 0.1 M  $K_2HPO_4$  (12 mL, pH 8) and stirred for 10 min to yield a white precipitate. The acetone was removed *in vacuo* and the product was extracted into ethyl acetate (4 x 15 mL). The organic phases were combined, dried over  $MgSO_4$ , and concentrated *in vacuo* to afford a white solid (52 mg, 34%).  $^1H$  NMR  $\delta$  4.67 (d, 2H,  $J$  = 5 Hz), 6.72 (s, 1H), 7.13 (m, 2H), 7.31 (m, 1H), 7.47 (m, 1H), 7.96 (d, 2H,  $J$  = 8 Hz), 8.08 (d, 2H,  $J$  = 8 Hz), 8.41 (br s, 1H),  $^{19}F$  NMR  $\delta$  -119.3 (m)

***N*-(4'-sulfamoylbenzoyl)-3-fluorobenzylamine.** white solid (71 mg, 46%),  $^1H$  NMR  $\delta$  4.63 (d, 2H,  $J$  = 6 Hz), 6.71 (s, 1H), 7.01 (m, 1H), 7.15 (d, 1H,  $J$  = 10 Hz), 7.21 (d, 1H,  $J$  = 8 Hz), 7.36 (m, 1H), 7.97 (d, 2H,  $J$  = 8 Hz), 8.08 (d, 2H,  $J$  = 8 Hz), 8.48 (br s, 1H),  $^{19}F$  NMR  $\delta$  -113.9 (m)

***N*-(4'-sulfamoylbenzoyl)-4-fluorobenzylamine.** white solid (82 mg, 53%),  $^1H$  NMR  $\delta$  4.61 (d, 2H,  $J$  = 6 Hz), 6.72 (s, 2H), 7.10 (m, 2H), 7.44 (m, 2H), 7.96 (d, 2H,  $J$  = 8 Hz), 8.06 (d, 2H,  $J$  = 8 Hz), 8.45 (br s, 1H),  $^{19}F$  NMR  $\delta$  -116.4 (m)

***N*-(4'-sulfamoylbenzoyl)-2,3-difluorobenzylamine.** pale yellow solid (35 mg, 10%),  $^1H$  NMR  $\delta$  4.71 (d, 2H,  $J$  = 6 Hz), 6.73 (s, 2H), 7.30 (m, 3H), 7.98 (d, 2H,  $J$  = 8 Hz), 8.08 (d, 2H,  $J$  = 8 Hz), 8.50 (br s, 1H),  $^{19}F$  NMR  $\delta$  -144.9 (m, 1F), -140.1 (m, 1F)

***N*-(4'-sulfamoylbenzoyl)-2,4-difluorobenzylamine.** white solid (95 mg, 58%),  $^1H$  NMR  $\delta$  4.63 (d, 2H,  $J$  = 5 Hz), 6.73 (s, 1H), 7.00 (m, 2H), 7.54 (m, 1H), 7.97 (d, 2H,  $J$  = 8 Hz), 8.08 (d, 2H,  $J$  = 8 Hz), 8.44 (br s, 1H),  $^{19}F$  NMR  $\delta$  -114.8 (m, 1F), -112.3 (m, 1F)

***N*-(4'-sulfamoylbenzoyl)-2,5-difluorobenzylamine.** white solid (81 mg, 50%),  $^1H$  NMR  $\delta$  4.66 (d, 2H,  $J$  = 5.9 Hz), 6.73 (s, 2H), 7.08 (m, 1H), 7.18 (m, 1H), 7.25 (m, 1H), 7.98 (d, 2H,  $J$  = 8.4 Hz), 8.10 (d, 2H,  $J$  = 8.4 Hz), 8.49 (br s, 1H),  $^{19}F$  NMR  $\delta$  -125.0 (m, 1F), 119.3 (m, 1F)

***N*-(4'-sulfamoylbenzoyl)-2,6-difluorobenzylamine.** white solid (98 mg, 60%),  $^1H$  NMR  $\delta$  4.70 (d, 2H,  $J$  = 5 Hz), 6.70 (s, 2H), 7.02 (m, 2H), 7.39 (m, 1H), 7.94 (d, 2H,  $J$  = 8 Hz), 8.04 (d, 2H,  $J$  = 8 Hz), 8.28 (br s, 1H),  $^{19}F$  NMR  $\delta$  -114.9 (m, 2F)

***N*-(4'-sulfamoylbenzoyl)-3,4-difluorobenzylamine.** white solid (82 mg, 50%),  $^1H$  NMR  $\delta$  4.61 (d, 2H,  $J$  = 6 Hz), 6.73 (s, 2H), 7.26 (m, 3H), 7.97 (d, 2H,  $J$  = 8 Hz), 8.08 (d, 2H,  $J$  = 8 Hz), 8.52 (br s, 1H),  $^{19}F$  NMR  $\delta$  -141.7 (m, 1F), -139.2 (m, 1F)

***N*-(4'-sulfamoylbenzoyl)-3,5-difluorobenzylamine.** white solid (47 mg, 7%),  $^1H$  NMR  $\delta$  4.66 (d, 2H,  $J$  = 6 Hz), 6.73 (s, 2H), 6.90 (m, 1H), 7.05 (d, 2H,  $J$  = 7 Hz), 7.99 (d, 2H,  $J$  = 8 Hz), 8.10 (d, 2H,  $J$  = 8 Hz), 8.56 (br s, 1H),  $^{19}F$  NMR  $\delta$  -110.5 (m)

***N*-(4'-sulfamoylbenzoyl)-2,3,4-trifluorobenzylamine.** pale yellow solid (22 mg, 9%),  $^1H$  NMR  $\delta$  4.07 (d, 2H,  $J$

= 5 Hz), 6.81 (m, 2H), 7.45 (d, 2H, J = 8 Hz), 7.56 (d, 2H, J = 8 Hz), 8.81 (br s, 1H), <sup>19</sup>F NMR δ -161.5 (m, 1F), -138.9 (m, 1F), -136.4 (m, 1F)

*N*-(4'-sulfamoylbenzoyl)-2,3,6-trifluorobenzylamine. white solid (27 mg, 9%), <sup>1</sup>H NMR δ 4.73 (d, 2H, J = 5 Hz), (s, 2H), (m, 1H), (m, 1H), 7.95 (d, 2H, J = 8 Hz), 8.04 (d, 2H, J = 8 Hz), (s, 2H)

*N*-(4'-sulfamoylbenzoyl)-2,4,5-trifluorobenzylamine. yellow solid (11 mg, 11%), <sup>1</sup>H NMR δ 4.60 (d, 2H, J = 6 Hz), 6.91 (s, 2H), 7.26 (m, 1H), 7.46 (m, 1H), 7.96 (d, 2H, J = 8 Hz), 8.07 (d, 2H, J = 8 Hz), 8.81 (s, 1H), <sup>19</sup>F NMR δ -143.9 (m, 1F), -136.6 (m, 1F), -120.1 (m, 1F)

*N*-(4'-sulfamoylbenzoyl)-3,4,5-trifluorobenzylamine. white solid (138 mg, 36%), <sup>1</sup>H NMR δ 4.62 (d, 2H, J = 6 Hz), 6.73 (s, 2H), 7.24 (m, 2H), 7.99 (d, 2H, J = 8 Hz), 8.09 (d, 2H, J = 8 Hz), 8.57 (s, 1H), <sup>19</sup>F NMR δ -164.5 (m, 1F), -135.8 (m, 2F)

*N*-(4'-sulfamoylbenzoyl)-2,3,4,5-tetrafluorobenzylamine. white solid (111 mg, 24%), <sup>1</sup>H NMR δ 4.69 (d, 2H, J = 5 Hz), 6.75 (s, 2H), 7.35 (m, 1H), 7.98 (d, 2H, J = 8 Hz), 8.09 (d, 2H, J = 8 Hz), 8.58 (br s, 1H), <sup>19</sup>F NMR δ -157.2 (m, 1F), -155.8 (m, 1F), -142.6 (m, 1F), 139.0 (m, 1F)

*N*-(4'-sulfamoylbenzoyl)-2,3,5,6-tetrafluorobenzylamine. white solid (52 mg, 11%), <sup>1</sup>H NMR δ 4.79 (d, 2H, J = 5 Hz), 6.72 (s, 2H), 7.50 (m, 1H), 7.96 (d, 2H, J = 8 Hz), 8.04 (d, 2H, J = 8 Hz), 8.49 (s, 1H), <sup>19</sup>F NMR δ -142.1 (m, 2F), -139.0 (m, 2F)

*N*-(4'-sulfamoylbenzoyl)-2,3,4,5,6-pentafluorobenzylamine. pale yellow solid (96.8 mg, 95%), <sup>1</sup>H NMR δ 4.75 (d, 2H, J = 5 Hz), 6.72 (s, 2H), 7.96 (d, 2H, J = 8 Hz), 8.03 (d, 2H, J = 8 Hz), 8.53 (s, 1H), <sup>19</sup>F NMR δ -164.2 (m, 2F), -157.2 (m, 1F), -143.0 (m, 2F)