Supporting Information.

1'-Cyano-3,4-dimethoxybenzylamine (**2**). To a solution of sodium cyanide (2.5 g, 50 mmol) and ammonium chloride (3.0 g, 56 mmol) in concentrated NH_4OH (30%, 57 mL) was added a solution of 3,4-dimethoxybenzaldehyde (8.5 g, 50 mmol) in methanol (25 mL). After stirring overnight under argon, a pale yellow solid was removed by filtration; the filtrate was evaporated to a yellow suspension, which was diluted with water (100 mL) and extracted with ethyl acetate (5 x 100 mL). The organic phases (which contained a *uv* active spot with $R_f \approx 0.2$ in CH_2Cl_2; aldehyde at $R_f \approx 0.9$) were collected and dried, yielding an oil on removal of the solvent *in vacuo*. A portion of the crude product was purified by chromatography on silica (elution with 80:1 dichloromethane/methanol), to give **2**: ^{1}H NMR ($CDCl_3$) δ 7.03 (d, 1H), 7.01 (s, 1H), 6.85 (d, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 1.94 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 150.3, 150.2, 129.6, 121.9, 119.8, 112.0, 110.5, 56.8, 56.8, 47.8.

3,4-Dimethoxyphenylglycine hydrochloride (**3**). Crude **2** (0.49 g, 2.95 mmol) was extracted into 6 *M* hydrochloric acid as its hydrochloride salt (2 x 60 mL) and refluxed for 2.5 h. The solution was concentrated *in vacuo*. Filtration of the resulting yellow suspension gave **3** as a white solid (0.43 g, 69%). The filtrate was further concentrated *in vacuo* and gave a second crop of **3** on cooling (0.13 g, 20%): ^{1}H NMR (DMSO-d_6) δ 7.06 (s, 1H), 6.95 (apparent br s, 2H), 4.58 (s, 1H), 3.74 (s, 6H).

(*N*-4'-carboxybenzenesulfonyl)-3,4-dimethoxyphenylglycine (**4**). To a solution of **3** (110 mg, 0.52 mmol) in water (4 mL, pH 10) was added a few drops of a solution of 4-(chlorosulfonyl)benzoic acid (120 mg, 0.52 mmol) in THF (2 mL) with stirring. The pH of the reaction mixture was adjusted to 8 by the addition of 1 *N* NaOH. The sulfonyl chloride and base were added alternately, to maintain pH > 8 throughout the reaction. The reaction was diluted with water and extracted with ether (3 x 20 mL). The solvent was removed *in vacuo* to afford 126 mg of **4** (61%) as a white solid: ^{1}H NMR (acetone-d_6) δ 8.05 (d, 2H), 7.86 (d, 2H), 7.58 (d, 1H), 6.84 (m, 3H), 5.08 (d, 1H), 3.74 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (acetone-d_6) δ 171.3, 166.5, 150.3, 150.2, 145.1, 134.4, 130.6, 129.3, 127.9, 121.0, 112.4, 111.6, 60.3, 56.0, 55.9.

Pentafluorobenzylamide of **4** (**5**). To a CH_3CN suspension of **4** (126 mg, 0.32 mmol in 2.7 mL) was added TBTU (103 mg, 0.32 mmol) and triethylamine (89 μL, 0.64 mmol), affordinga pale yellow solution. After stirring o/n at room temperature, the solvent was removed *in vacuo* to give 250 mg of pale yellow solid. The amide was purified by column chromatography with a gradient of CH_2Cl_2/CH_3OH, affording 34 mg of **5** as a white solid (18%): ^{1}H NMR (acetone-d_6) δ 8.48 (t, 1H), 7.93 (d, 2H), 7.81 (d, 2H), 7.60 (d, 1H), 6.87 (s 1H), 6.79 (apparent br s, 2H), 5.02 (br s, 1H), 4.75 (d, 2H), 3.74 (s, 3H), 3.70 (s 3H).

Nitration of **5** (**1**). Dissolution of **5** (30 mg) in concentrated HOAc (1.0 mL) and addition of concentrated HNO_3 (0.5 mL) gave an orange solution, which was stirred at room temperature overnight. Dilution with water (30 mL) affordeda pale yellow solid, which was purified by column chromatography with a gradient of CH_2Cl_2/CH_3OH, affording**1** as a pale yellow solid (16.8 mg, 48%): ^{1}H NMR (acetone-d_6) δ 8.48 (br, 1H), 7.93 (d, 2H), 7.83 (d, 2H), 7.68 (d, 1H), 7.53 (s, 1H), 7.11 (s, 1H), 5.91 (d, 1H), 4.75 (br, 2H), 3.89 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (acetone-d_6) δ 168.9, 165.8, 154.3, 149.6, 144.5, 138.2, 128.5, 127.8, 127.7, 126.8, 113.4, 109.0, 62.5, 57.8, 56.7, 56.5 (note that carbons of pentafluorobenzyl ring are not resolved, due to α, β and γ coupling to fluorines).