Supporting Information

1-Acetoxy-3,5-dimethoxy-benzene (19a). 3,5-Dimethoxyphenol (3.08 g, 20 mmol) was refluxed with acetic anhydride (4.08 g, 40 mmol) at 110 °C for 3 h. After cooling and addition of ether (40 mL), the solution was washed with 2 N HCl (3×10 mL) and water (3×10 mL) and dried with MgSO₄. After evaporation of the solvent the acetate 19a was obtained (3.85 g, 97 %). ¹H NMR: δ 2.27 (s, 3H), 3.76 (s, 6H), 6.26 (d, J = 2.2 Hz, 2H), 6.33 (t, J = 2.1 Hz, 1H); ¹³C NMR: δ 21.0 (q), 55.4 (2q), 98.2 (d), 100.2 (2d), 152.2 (s), 161.3 (2s), 169.1 (s); MS m/z: 198 (8), 196 (33), 154 (100), 137 (3), 125 (100), 111 (12), 94 (30), 69 (20). Anal. Calcd for C₁₀H₁₂O₄ (196.2): C, 61.22; H, 6.17. Found: C, 61.08; H, 6.15. ¹H NMR data agree with published ones.¹⁵

1-Acetoxy-2-bromo-3,5-dimethoxybenzene (20). Compound 19a (3.85 g, 19.4 mmol) was added to a suspension of NBS (3.56 g, 20 mmol) in CH₂Cl₂ (25 mL) at 0 °C. After stirring at this temperature for 1 h the solution was poured into 7 % aqueous K₂CO₃ solution (100 mL) and extracted with CH₂Cl₂ (2×25 mL). The combined organic layer was dried with Na₂SO₄ and the solvent was removed to give 20 (4.80 g, 90 %) after drying on a vacuum line: Mp 90 °C (Lit.:¹⁶ Mp 92-93 °C).

2-Bromo-3,5-dimethoxyphenol (21). The acetate 20 (4.84 g, 17.5 mmol) was mixed with KOH (1.97 g, 36 mmol) in methanol (170 mL) and stirred at room temperature for 2.5 h. The solvent was evaporated, the residue was diluted with H₂O (250 mL) and adjusted to pH 8 with conc. H₂SO₄. After extraction with ethyl acetate, the combined organic layer was dried with MgSO₄ and the solvent was removed to yield 2.73 g (67 %) of 21 as colorless crystals: Mp 77 °C (Lit.:¹⁷ 79-81 °C); ¹H NMR: δ 3.77, 3.85 (2s, 6H, 7-H₃, 8-H₃); 5.65 (br s, 1H, OH); 6.10 (d, J₉,₉ = 2.9 Hz, 1H, 4-H); 6.25 (d, J₉,₉ = 2.6 Hz, 1H, 6-H); ¹³C NMR: δ 55.4, 56.2 (2q, C-7, C-8); 91.1 (s, C-1); 92.5 (d, C-4); 93.3 (d, C-6); 153.8 (s, C-1); 156.8, 160.6 (2s, C-
3, C-4); MS m/z: 234/232 (98/100), 205/203 (9/10), 174/172 (3), 159 (2), 124 (29), 95 (13), 81/79 (3/6), 69 (18), 53 (17), 39 (11).

2-Hydroxy-4,6-dimethoxybenzoic acid (17). To a solution, under argon, of 21 (2.68 g, 11.5 mmol) in THF (35 mL), a 1.6 M n-butyllithium solution in hexane (15.2 mL, 24.0 mmol) was added and the reaction mixture was stirred for 2 h at −25 °C. Two pieces of Dry Ice™ (carbon dioxide, 2×60 g) were washed with THF, and THF (25 mL) along with the reaction mixture were added immediately to these pieces. After 1-2 h at room temperature the mixture was hydrolyzed with HCl (120 mL of a 3 % aqueous solution). The organic solvent was removed and the aqueous phase was extracted with ethyl acetate. After extracting the combined layers of ethyl acetate with a 5 % aqueous solution of K₂CO₃ (2×25 mL), the combined aqueous extract was acidified with 2 N HCl and extracted again with ethyl acetate (3×10 mL). The combined organic phase was dried with MgSO₄, the solvent was removed in vacuo and the benzoic acid 17 was isolated as yellowish crystals (1.48 g, 65 %): Mp 150 °C (Lit. 18 Mp 152-154 °C); ¹H NMR: δ 3.83, 4.01 (2s, 6H), 6.03 (d, J = 2.4 Hz, 1H), 6.19 (d, J = 2.1 Hz, 1H), 8.02 (br s, 1H), 11.00 (br s, 1H); ¹³C NMR: δ 55.7 (q), 56.9 (q), 91.4 (d), 95.0 (d), 159.7 (s), 165.6 (s), 166.4 (s), 170.7 (s); MS (silylated 17) m/z: 342 (1), 327 (100), 297 (5), 253 (7), 73 (17). Anal. Calcd for C₉H₁₀O₅ (198.2): C, 54.55; H, 5.09. Found: C, 54.84; H; 5.13.
$^{19}$F NMR (282 MHz)