Supplementary Material (ESI) for Chemical Communications

Synthesis of 3-(benzimidazol-1-yl)methylpyridine; Benzimidazole (4.25 g, 36.0 mmol) was dissolved in 18 mL of anhydrous DMF with stirring under a N_2 atmosphere. To the clear, light-brown solution was added NaH (0.86 g, 36.0 mmol) inside a glove bag under a N_2 atmosphere. Effervescence was immediately observed, and once fizzing had subsided, the mixture was heated and stirred under reflux for 1 h under a N_2 atmosphere. After 1 h, the mixture was cooled to room temperature. To this solution was added dropwise a solution of 3-picolyl chloride hydrochloride (2.95 g, 18.0 mmol) in 36 mL of anhydrous DMF. The resulting mixture was heated and stirred under reflux under a N_2 atmosphere and monitored by TLC. After 48 h, the brown mixture was cooled to room temperature. NaCl that had formed during the reaction was filtered *via* vacuum filtration, and the clear, brown filtrate was concentrated by rotary evaporation to obtain a brown syrup. The syrup was purified by column chromatography using silica gel (200-425 mesh), and ethyl acetate:hexanes 1:1, ethyl acetate, followed by methanol as eluents. Concentration of the appropriate fractions *via* rotary evaporation afforded the pure product as a pale yellow crystalline solid. Yield 1.99 g (52.9%); m.p. 48-51˚C; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 5.56 (s, 2H), 7.21 (m, 2 H), 7.35 (dd, 1H, J_1 = 7.6 Hz, J_2 = 4.8 Hz), 7.57 (m, 1H), 7.68 (m, 2H), 8.45 (s, 1H), 8.49 (dd, 1H, J_1 = 5 Hz, J_2 = 1.6 Hz), 8.64 (s, 1H).

Synthesis of 3-(2-methylbenzimidazol-1-yl)methylpyridine; 2-Methylbenzimidazole (8.06 g, 61.0 mmol) was dissolved in 61 mL of anhydrous DMF with stirring under a N_2 atmosphere. To the clear, light-brown solution was added NaH (1.46 g, 61.0 mmol) inside a glove bag under a N_2 atmosphere. Effervescence was immediately observed, and once fizzing had subsided, the mixture was heated and stirred under reflux for 1 h under a N_2 atmosphere. After 1 h, the mixture was cooled to room temperature. To this solution was added dropwise a solution of 3-picolyl chloride hydrochloride (5.00 g, 30.5 mmol) in 61 mL of anhydrous DMF. The resulting mixture was heated and stirred under reflux under a N_2 atmosphere and monitored by TLC. After 96 h, the brown mixture was cooled to room temperature. NaCl that had formed during the reaction was filtered *via* vacuum filtration, and the clear, brown filtrate was concentrated by rotary evaporation to obtain a brown syrup. The syrup was purified by column chromatography using silica gel (200-425 mesh), and ethyl acetate:hexanes 1:2 followed by ethyl acetate as eluents. Concentration of the appropriate fractions *via* rotary evaporation afforded the pure product as a pale brown microcrystalline solid. Yield 1.43 g (21.0%); m.p. 91-93˚C; ^{1}H NMR (CD_3OD, 400 MHz) δ 2.60 (s, 3H), 5.55 (s, 2H), 7.25 (m, 2H), 7.39 (m, 2H), 7.52 (d, 1H, J = 8.8 Hz), 7.61 (m, 1H), 8.42 (s, 1H), 8.47 (dd, 1H, J_1 = 4.8 Hz, J_2 = 1.6 Hz).

Synthesis of 3,5-dinitrobenzoic acid 3-(benzimidazol-1-yl)methylpyridine 4-nitrobenzoic acid (1:1:1), **1**; 3,5-Dinitrobenzoic acid (0.020 g, 0.10 mmol) was dissolved in 1 mL of ethanol and added to a 2 mL ethanolic solution containing 4-nitrobenzoic acid (0.016 g, 0.10 mmol). To the resulting solution was added 3-(benzimidazol-1-yl)methylpyridine (0.020 g, 0.10 mmol) in 1 mL of ethanol. Slow evaporation of the solvent after two weeks yielded colorless plates. TLC of individual crystals showed spots corresponding to all three components. m.p. 133–136 °C.

*Synthesis of 3,5-dinitrobenzoic acid 3-(benzimidazol-1-yl)methylpyridine 3-*N,N-*dimethylaminobenzoic acid (1:1:1),* **2**; 3,5-Dinitrobenzoic acid (0.020 g, 0.10 mmol) was dissolved in 1 mL of ethanol and added to a 1 mL ethanolic solution containing 3-*N*,*N*-dimethylaminobenzoic acid (0.016 g, 0.10 mmol). To the resulting solution was added 3-(benzimidazol-1-yl)methylpyridine (0.020 g, 0.10 mmol) in 1 mL of ethanol. Slow evaporation of the solvent yielded a crop of yellow prisms after two weeks.[1] A few days later, a second crop consisting of red prisms formed. TLC of individual crystals showed spots corresponding to all three components. m.p. 110–113 °C.

Synthesis of 3,5-dinitrobenzoic acid 3-(2-methylbenzimidazol-1-yl)methylpyridine 4-nitrobenzoic acid (1:1:1), **3**; 3,5-Dinitrobenzoic acid (0.015 g, 0.070 mmol) was dissolved in 1 mL of ethanol and added to a 2 mL ethanolic solution containing 4-nitrobenzoic acid (0.012 g, 0.070 mmol). To the resulting solution was added 3-(2-methylbenzimidazol-1-yl)methylpyridine (0.016 g, 0.070 mmol) in 1 mL of ethanol. Slow evaporation of the solvent after two weeks yielded colorless plates. TLC of individual crystals showed spots corresponding to all three components. m.p. 158–161 °C.[2]

[1] A binary compound of the strong acid and the SR as determined by TLC and NMR.

[2] The overall yield of **2** was approximately 50% and significantly higher for **1** and **3**.