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 N₂ atmosphere. To the clear, light-brown solution was added NaH (0.86 g, 36.0 mmol) inside a glove bag under a N₂ atmosphere. Effervescence was immediately observed, and once fizing had subsided, the mixture was heated and stirred under reflux for 1 h under a N₂ atmosphere. After 1 h, the mixture was cooled to room temperature. To this solution was added dropwise a solution of 3-picoly 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 N₂ 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; ¹H NMR (DMSO-d₆, 400 MHz) δ 5.56 (s, 2H), 7.21 (m, 2H), 7.35 (dd, 1H, J₁ = 7.6 Hz, J₂ = 4.8 Hz), 7.57 (m, 1H), 7.68 (m, 2H), 8.45 (s, 1H), 8.49 (dd, 1H, J₁ = 5 Hz, J₂ = 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 N₂ atmosphere. To the clear, light-brown solution was added NaH (1.46 g, 61.0 mmol) inside a glove bag under a N₂ atmosphere. Effervescence was immediately observed, and once fizing had subsided, the mixture was heated and stirred under reflux for 1 h under a N₂ atmosphere. After 1 h, the mixture was cooled to room temperature. To this solution was added dropwise a solution of 3-picoly 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 N₂ 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; ¹H NMR (CD₃OD, 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, J₁ = 4.8 Hz, J₂ = 1.6 Hz).

Synthesis of 3,5-dinitrobenzoic acid 3-(benzimidazol-1-yl)methylpyridine 4-nitrobenzoic acid (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); 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 (0.020 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. 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); 3,5-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 (0.016 g, 0.10 mmol). 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.

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.