Supporting Information (General methods, Preparation of intermediates and final products in the synthesis of **6** and **7**.

General methods: Where mixtures of tautomers were obtained, the chemical shifts reported for the proton NMR belong to the major tautomer whereas the chemical shifts of all peaks were reported for the ^{13}C spectrum. Attached proton tests (APT) were performed to distinguish between different carbons in the ^{13}C NMR spectra. In some of the ^{13}C spectra, there were fewer peaks than expected. This was attributed to scalar relaxation of the second kind due to the high number of nitrogen atoms present in these molecules. Ethyl triethoxyacetate was prepared from diethyloxalate.[21] Dimethyl *trans*-2-ketoglutaconate was prepared from dimethyl 2-ketoglutarate.[11]

4-Methoxy-2-methyl-6-nitrobenzimidazole (9)

A solution of compound **8** (500 mg, 2.73 mmol) in glacial acetic acid (2 mL) was stirred at 100 °C. The solution quickly solidified, and was kept at 100 °C for 21 hours. The paste was cooled to room temperature and glacial acetic acid (2 mL) was added. The solution was neutralized by addition of 4 M NaOH in water and the resulting precipitate filtered and rinsed with cold water to yield 4-methoxy-2-methyl-6-nitrobenzimidazole (0.484 mg, 2.33 mmol, 86%). An analytical sample was recrystalized from methylene chloride–acetone to produce a light brown solid: mp 268–270 °C; ^{1}H NMR (CD_3OD δ) 2.59 (s, 3H), 4.05 (s, 3H), 7.60 (d, 1H, J = 2 Hz), 8.03 (d, 1H, J = 2 Hz). ^{13}C NMR (CD_3OD δ) 14.59, 56.80, 99.67, 145.50, 156.65; TLC Rf = 0.22 (5% CH_3OH in CH_2Cl_2). Anal. Calcd. for $C_{11}H_{11}N_3O_5$: C, 52.17; H, 4.38; N, 20.28. Found: C, 52.08; H, 4.43; N, 20.27.

6-Amino-4-methoxy-2-methylbenzimidazole (10)

Compound **9** (300 mg, 1.45 mmol) was suspended in absolute ethanol (50 mL). 10% Pd/C (54 mg) was added to the suspension. The mixture was stirred at room temperature under hydrogen (80 psi) for 4 hours. The catalyst was removed by filtration, and rinsed with ethanol. The solvent was removed *in vacuo* to yield ethyl 6-amino-4-methoxy-2-methylbenzimidazole (255 mg, 1.45 mmol, 100%). An analytical sample was recrystalized from ethyl acetate to yield brownish crystals: mp 111–115 °C; ^{1}H NMR (CD_3OD δ) 2.45 (s, 3H), 3.89 (s, 3H), 6.26 (d, 1H, *J* = 1.6 Hz), 6.43 (d, 1H, *J* = 1.6 Hz); ^{13}C NMR (CD_3OD δ) 14.01, 55.89, 93.05, 95.83, 124.22, 140.74, 144.96, 150.17, 150.26; TLC Rf = 0.10 (10% CH_3OH in CH_2Cl_2). Anal. Calcd. for $C_9H_{13}N_3O_2$: C, 55.37; H, 6.71; N, 21.52. Found: C, 55.80; H, 6.65; N, 21.00.

4-Methoxy-7,9-dimethoxycarbonyl-2-methyl-1H-imidazolo[5,4-f]quinoline (11)

Compound **10** (2.78 g, 15.7 mmol) and dimethyl *trans*-2-ketoglutaconate (3.36 g, 19.5 mmol) in dry methylene chloride (300 mL) was stirred under nitrogen at room temperature for 15 hours. Methylene chloride (100 mL) was added and dry HCl was bubbled through the solution for 3 hours, followed by both oxygen and dry HCl for an additional 6 hours. The solvent was then removed *in vacuo* and the resulting solid partially dissolved in methylene chloride (150 mL). The methylene chloride solution was washed with 0.2 M $NaHCO_3$ (200 mL). The aqueous phase was extracted with methylene chloride (4 x 150 mL). The combined organic extracts were washed with 0.2 M phosphate buffer at pH 3.5 (200 mL), and subsequently washed with brine (150 mL),

dried over anhydrous sodium sulfate and evaporated *in vacuo* to yield a yellow powder (4.05 g, 12.3 mmol, 78%). An analytical sample was recrystalized from methylene chloride–hexane to give a yellow powder: mp 198–201 ºC; ^{1}H NMR (DMSO-d_6 δ) 2.56 (s, 3H), 3.95 (s, 3H), 3.99 (s, 3H), 4.13 (s, 3H), 7.42 (s, 1H), 8.02 (s, 1H), 13.25 (br, 1H); ^{13}C NMR ($CDCl_3$ δ) 15.47, 53.48, 53.84, 56.37, 112.21, 121.39, 127.27, 128.54, 130.12, 138.00, 144.62, 149.62, 150.79, 154.64, 165.82, 168.99; TLC Rf = 0.34 (5% CH_3OH in CH_2Cl_2). Anal. Calcd. for $C_{16}H_{15}N_3O_5 \cdot 0.2H_2O$: C, 57.73; H, 4.66; N, 12.62. Found: C, 57.73; H, 4.56; N, 12.59.

4-Hydroxy-7,9-dimethoxycarbonyl-2-methyl-1H-imidazolo[5,4-f]quinoline (12)

Compound **11** (180 mg, 0.547 mmol) and 33% HBr in glacial acetic acid (18 mL) were placed in a round bottom flask equipped with a condenser. A balloon was placed on the condenser and the mixture was refluxed for 12 hours. The solvent was removed *in vacuo* and replaced with fresh solvent. A new balloon was placed on the condenser, and the mixture refluxed for an additional 14 hours. The solvent was then removed on the rotavapor. Dry methanol (35 mL) and 33% HBr in glacial acetic acid (1 drop) were added to the flask. The resulting solution was refluxed under nitrogen overnight. The solvent was removed *in vacuo* to yield a brown solid (170 mg, 0.537 mmol, 98%). An analytical sample was recrystalized from methanol to produce yellow crystals: mp 271–273 °C; ^{1}H NMR (DMSO-d_6 δ) 2.53 (s, 3H), 3.92 (s, 3H), 3.96 (s, 3H), 7.21 (s, 1H), 7.88 (s, 1H), 11.29 (s, 1H), 13.08 (br, 1H); ^{13}C NMR (DMSO-d_6 δ) 14.68 , 52.48, 52.68, 104.13, 112.93, 114.67, 125.82, 136.31, 137.14, 144.13, 146.88, 148.52, 150.65, 165.16, 168.35;

TLC Rf = 0.41 (7% CH_3OH in CH_2Cl_2). Anal. Calcd. for $C_{15}H_{15}N_3O_5 \cdot 0.5H_2O$: C, 55.56; H, 4.35; N, 12.96 . Found: C, 55.67; H, 4.30; N, 12.85.

7,9-Dimethoxycarbonyl-2-methyl-1H-imidazolo[5,4-f]quinoline-4,5-dione (6)

7,9-Dimethoxycarbonyl-4-hydroxy-2-methyl-1H-imidazole[5,4-f]quinoline **12** (122 mg, 0.387 mmol) and KH_2PO_4 (116 mg) were stirred in 5:1 acetonitrile–water (75 mL). The solution was adjusted to pH 7.3 with dilute NaOH. The mixture was cooled to 0 ºC in an ice–water bath. A solution of Fremy's salt (311 mg, 1.16 mmol), K_2HPO_4 (67.4 mg, 0.387 mmol) and KH_2PO_4 (61 mg, 0.445 mmol) in water (10 mL) was added in fractions. After stirring at room temperature for 18 hours, the pH of the solution was adjusted to 7.3 by addition of dilute NaOH. A solution of Fremy's salt (210 mg, 0.783 mmol) and K_2HPO_4 (80 mg, 0.459 mmol) in water (10 mL) was added in fractions. The mixture was then stirred at room temperature for an additional 24 hours. The mixture was extracted with methylene chloride (2 x 50 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* to yield an orange powder (76 mg, 0.231 mmol, 61%). An analytical sample was obtained by recrystallization from chloroform–hexane, as bright orange crystals: mp 245–247 ºC; ^{1}H NMR (DMSO-d_6, δ) 2.40 (s, 3H), 3.89 (s, 3H), 3.92 (s, 3H), 8.19 (s, 1H); ^{13}C NMR (DMSO-d_6, δ) 15.00, 53.48, 53.59, 125.85, 127.97, 129.94, 138.34, 145.12, 146.52, 148.15, 154.17, 164.73, 167.19, 167.89, 178.23; TLC Rf = 0.23 (5% CH_3OH in CH_2Cl_2). HRMS–FAB (m/z): $[M + Na]^+$ calcd. for $C_{15}H_{13}N_3O_5Na$ 352.0546. Found 352.0542.

4-Methoxy-7,9-dimethoxycarbonyl-1H-imidazolo[5,4-f]quinoline (14)

A solution of 6-amino-4-methoxybenzimidazole **13** (642 mg, 3.94 mmol) and dimethyl *trans*-2-ketoglutaconate (842 mg, 4.90 mmol) in dry methylene chloride (74 mL) was stirred under argon at room temperature for 12 hours. Dry methylene chloride (38 mL) was added and the mixture was stirred for an additional 24 hours. Dry HCl was then bubbled through the solution for 3 hours, followed by both oxygen and dry HCl for an additional 6 hours. The solvent was then removed in vacuo and the residue partially dissolved in 0.2 M KH_2PO_4 (40 mL). The aqueous phase was extracted with methylene chloride (3 x 20 mL). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate and evaporated to dryness. The residue was purified on a silica gel column (2% methanol in methylene chloride) to yield a yellow solid (450 mg, 1.43 mmol, 36%). An analytical sample was obtained by recrystalization from methylene chloride–hexane: mp 229–231 ºC; ^{1}H NMR ($CDCl_3$ δ) 4.13 (s, 3H), 4.15 (s, 3H), 4.18 (s, 3H), 7.56 (s, 1H), 8.25 (s, 1H), 8.83 (s, 1H); ^{13}C NMR ($CDCl_3$ δ) 53.31, 53.70, 56.24, 112.43, 121.12, 126.71, 128.29, 130.61, 136.56, 139.78, 145.01, 149.93, 154.74, 165.45, 168.60; TLC Rf = 0.32 (5% CH_3OH in CH_2Cl_2). Anal. Calcd. for $C_{15}H_{13}N_3O_5$: C, 57.14,; H, 4.16; N, 13.33. Found: C, 56.96Z; H, 4.25; N, 12.84.

4-Hydroxy-7,9-dimethoxycarbonyl-1H-imidazolo[5,4-f]quinoline (15)

A solution of **14** (1.28 g, 4.06 mmol) and 33% HBr in glacial acetic acid (50 mL) was placed in a round bottom flask equipped with a condenser. A balloon was placed on top of the condenser. The mixture was heated under vigorous reflux for 10 days. Every 24 hours, the acid mixture was removed *in vacuo* and replaced with fresh acid mixture, and a new balloon was placed on top of the condenser. The solvent was evaporated to dryness.

Dry methanol (100 mL) and 33% HBr in AcOH (2 drops) were added to the flask. The resulting solution was refluxed under nitrogen overnight. The solvent was removed under vacuum to yield a brown solid (1.22 g, 4.06 mmol, 100%). An analytical sample was recrystalized from methanol as a yellow powder: mp >300 °C; ^{1}H NMR (DMSO-d_6 δ) 3.95 (s, 3H), 4.02 (s, 3H), 7.39 (s, 1H), 8.15 (s, 1H), 8.85 (s, 1H); ^{13}C NMR (DMSO-d_6 δ) 52.68, 53.23, 105.96, 111.91, 116.94, 126.24, 135.27, 145.10, 147.79, 148.68, 149.26, 164.66, 167.49; TLC Rf = 0.09 (5% CH_3OH in CH_2Cl_2). HRMS–FAB (m/z): $[M + Na]^+$ calcd for $C_{14}H_{11}N_3O_5Na$ 324.0596. Found 324.0592.

7,9-Dimethoxycarbonyl-1H-imidazolo[5,4-f]quinoline-4,5-dione (7)

A mixture of **15** (100 mg, 0.279 mmol), KH_2PO_4 (50 mg) and K_2HPO_4 (100 mg) was dissolved in 5:1 acetonitrile–water (150 mL). The solution was adjusted to pH 7.2 by addition of dilute NaOH and cooled to 0 ºC in an ice–water bath. A solution of Fremy's salt (200 mg, 0.746 mmol) and K_2HPO_4 (80 mg) in water (8 mL) was added in fractions and the mixture was warmed to room temperature and stirred for 12 hours. The solution was brought to pH 7 by addition of dilute NaOH. A solution of Fremy's salt (200 mg, 0.746 mmol) and K_2HPO_4 (80 mg) in water (8 mL) was added in fractions. The mixture was then stirred at room temperature for an additional 24 hours. The mixture was extracted with methylene chloride (1 x 100 mL and 2 x 50 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and the residue recrystalized from methylene chloride–hexane to yield an orange powder (50 mg, 0.159 mmol, 48%): mp 226–230 ºC; ^{1}H NMR (DMSO-d_6 δ) 3.90 (s, 3H), 3.93 (s, 3H), 8.21 (s, 1H), 8.22 (s, 1H); ^{13}C NMR (DMSO-d_6 δ) 52.78 , 52.89 , 125.19, 127.16, 128.92,

137.73, 143.74, 145.84, 147.45, 164.01, 166.43, 168.07, 177.02; TLC Rf = 0.17 (5% CH_3OH in CH_2Cl_2). HRMS–FAB (m/z): $[M + Na]^+$ calcd for $C_{14}H_9N_3O_6Na$ 338.0389. Found 338.0390.

Supporting Information (Analytical data on Compounds **8** and **13**)

Compound **8**: ^1H NMR (CD_3OD, δ) 3.89 (s, 3H), 4.89 (s, 3H), 7.29 (d, 1H, *J* = 2.4 Hz), 7.38 (d, 1H, *J* = 2.4 Hz); ^{13}C NMR (CD_3OD, δ) 56.52 , 99.25 , 106.81, 133.59, 134.31, 139.15, 146.90. Anal. Calcd. for $C_7H_9N_3O_3$: C, 45.89; H, 4.96; N, 22.94. Found: C, 45.95; H, 4.89; N, 22.82.

Compound **13**: mp 214-216 ^oC. 1H NMR (CD3OD, δ) 3.92 (s, 3H), 6.31 (d, 1H, *J* = 1.2 Hz), 6.51 (d, 1H, *J* = 1.2 Hz), 7.82 (s, 1H); ^{13}C NMR (CD_3OD, δ) 55.91, 96.15, 145.72.