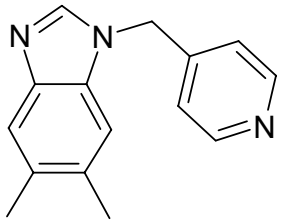
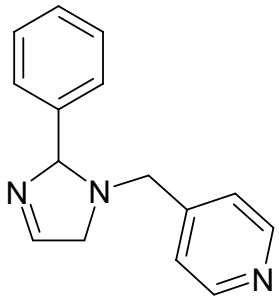
Supplementary Material (ESI) for Chemical Communications

Synthesis of 4-(5,6-dimethylbenzmidazol-1-yl)methyl pyridine (**1)**



5,6-dimethylbenzimidazole (2.175 g, 14.7 mmol) was dissolved in 30 mL dry THF with heat and stirring in a 250 mL round-bottomed flask under a N_2 atmosphere. NaOH (5.87 g, 147 mmol) was added and the mixture was stirred for 2 h, upon which, a suspension of 4-picolyl chloride hydrochloride (2.411 g, 14.7 mmol) in 30 mL dry THF, and subsequent washings with THF to ensure that all of the 4-picolyl chloride hydrochloride was transferred. The mixture was stirred at 75 °C for 16 h under a N_2 atmosphere, after which 15 mL distilled water was added to dissolve the NaOH and NaCl. The two layers were separated using a separatory funnel, and the THF was dried over anhydrous $MgSO_4$. The $MgSO_4$ was filtered by vacuum filtration, and the filtrate was concentrated *via* rotorary evaporation to produce a pale brown solid. The product was recrystallized from THF and ethanol to produce colourless cubes. Yield 2.387 g (69 %); m.p. 182-190 °C, ^{1}H NMR (DMSO-d_6, 200 MHz) δ 2.26 (s, 3H), 2.28 (s, 3H) 5.51 (s, 2H), 7.14 (d, 2H, J = 4.4 Hz), 7.23 (s, 1H), 7.45 (s, 1H), 8.25 (s, 1H), 8.51 (d, 2H, J = 4.6 Hz).

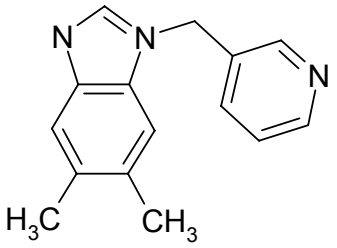
Synthesis of 4-(2-phenylimidazol-1-yl)methyl pyridine (**2**)



2-phenylimidazole (1.262 g, 8.75 mmol) was dissolved in 30 mL dry THF with stirring in a 250 mL round-bottomed flask under a N_2 atmosphere. NaOH (3.5 g, 87.5 mmol) was added and the mixture was stirred for 2 h, upon which, a suspension of 4-picolyl chloride hydrochloride (1.44 g, 8.75 mmol) in 30 mL dry THF, and subsequent washings with THF to ensure that all of the 4-picolyl chloride hydrochloride was transferred. The mixture was stirred at 75 °C for 2 days under a N_2 atmosphere, after which 10 mL distilled water was added to dissolve the NaOH and NaCl. The two layers were separated using a separatory funnel, and the THF was dried over anhydrous $MgSO_4$. The $MgSO_4$ was filtered by vacuum filtration, and the filtrate was concentrated *via* rotorary evaporation to produce a brown oil. Subsequent purification via column chromatography

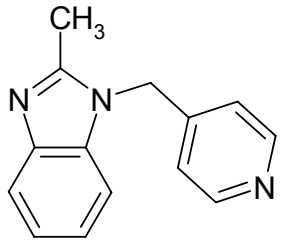
(3:1 hexanes/ethyl acetate) yielded a pale brown solid. Yield: 0.994 g (48%) m.p. 33-38 °C, ^{1}H NMR ($CDCl_3$-*d*, 400 MHz) δ 5.03 (s, 2H), 6.77 (d, 2H, *J* = 6 Hz), 6.81 (s, 1H), 7.03 (s, 1H), 7.18 (m, 3H), 7.29 (m, 2H), 8.36 (d, 2H, *J* = 6 Hz).

Synthesis of 3-(5,6-dimethylbenzimidazol-1-yl)methyl pyridine (**3**)



5,6-dimethylbenzimidazole (1.040g, 7.1 mmol) was dissolved in 20 mL dry THF with heat and stirring in a 250 mL round-bottomed flask under a N_2 atmosphere. NaOH (2.84 g, 71.0 mmol) was added and the mixture was stirred for 2 h, upon which, a suspension of 3-picolyl chloride hydrochloride (1.17 g, 7.1 mmol) in 20 mL dry THF, and subsequent washings with THF to ensure that all of the 3-picolyl chloride hydrochloride was transferred. The mixture was stirred at 75 °C for 3 days under a N_2 atmosphere, after which 7 mL distilled water was added to dissolve the NaOH and NaCl. The two layers were separated using a separatory funnel, and the THF was dried over anhydrous $MgSO_4$. The $MgSO_4$ was filtered by vacuum filtration, and the filtrate was concentrated *via* rotorary evaporation to produce a brownish-orange solid. The product was recrystallized from hot toluene to produce brown rods. Yield 0.703 g (42 %); m.p. 150-153 °C, ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.72 (s, 6H), 5.50 (s, 2H), 7.35 (s, 1H), 7.35 (m, 1H), 7.42 (s, 1H), 7.64 (d, 1H, *J* = 8 Hz), 8.28 (s, 1H), 8.48 (d, 1H *J* = 4 Hz), 8.6 (s, 1H).

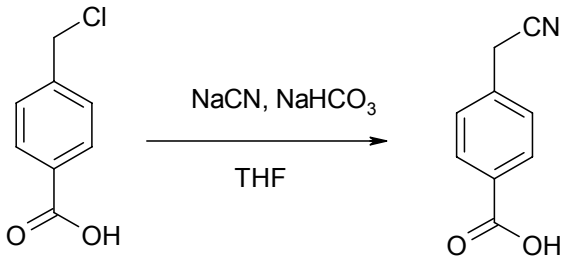
Synthesis of 4-(2-methylbenzmidazol-1-yl)methyl pyridine (**4)**



2-Methylbenzimidazole (2.0 g, 15.13 mmol), was dissolved in 40 ml dry tetrahydrofuran with stirring under N_2. NaOH (6.06 g, 150 mmol) was added and the mixture was left to stir for 2 h, upon which 4-picolyl chloride hydrochloride (2.46 g, mmol) was added in a suspension of dry THF. The mixture was left to stir under reflux for 2 days after which 10 ml water was added to dissolve the NaOH and NaCl that had formed, and the two layers were separated. The water layer was washed with ethyl acetate and the fractions

collected and combined with the THF layer. The organic layer was dried over magnesium sulfate and subsequently removed via rotary evaporation and the resulting brown solid was chromatographed on silica with a mixture of hexane/ethyl acetate as the eluent to produce a pale brown oil. Yield: 2.566 g/80%. ^{1}H NMR ($CDCl_3$-*d*, 400 MHz) δ 2.54 (s, 3H), 5.31 (s, 2H), 6.93 (d, 2H, *J* = 6 Hz), 7.15-7.28 (m, 3H), 7.74 (d, 1H, *J* = 12 Hz), 8.54 (d, 2H, *J* = 8 Hz).

Synthesis of 1,4-carboxyphenylacetonitrile



5.028g (29.5 mmol) 4-chloro(methyl)benzoic acid was dissolved in 40 mL THF. To this solution was added a 25 mL solution of saturated $NaHCO_3$, whereby fizzing occurred. 8.49g (173 mmol) NaCN was added, followed by the addition of 30 mL H_2O. The solution was left to stir for ~10 days after which it was cooled in an ice bath and acidified to pH=2. The THF was then removed under vacuum. A brown precipitate emerged which was filtered off, and dissolved in 1M NaOH. Two spatulas of decolorizing charcoal were added to the solution and the mixture was filtered. The basic solution was then acidified with 1M HCl, upon which a tan-colored precipitate appeared, which was subsequently filtered off. Yield: 4.695g (98%). ^{1}H NMR (DMSO-d_6, 200 MHz): δ 4.16 (s, 2H), 7.48 (d, 2H, J = 8 Hz), 7.96 (d, 2H, J = 8 Hz). IR: 3421 cm^{-1} (O-H), 2248 cm^{-1} (C≡N), 1680 cm^{-1} (C=O). MP: 195-200 ° C

Synthesis of 1,4-carboxyphenylcyanoxime (**5**)

The conversion of 1,4-carboxyphenylacetonitrile into the corresponding cyanoxime was carried out using a previously reported method for the synthesis of cyanoximes[1]. 2-Propanol (240 mL) was placed in a 500 mL Erlenmeyer flask. Nitrogen gas was bubbled through the solution for a few minutes after which sodium metal 0.049g (2.1 mmol) cut into small pieces and was added to the solution. After all the sodium had dissolved, 1,4-carboxyphenylacetronitrile (0.344g/2.14 mmol) was dissolved in ~50 mL 2-propanol with heat. This solution was then added to the iso-propoxide solution, upon which a small amount of precipitate was observed, and the solution turned yellow after a few minutes. 15 g of $NaNO_2$, 100 mL distilled water, and 50 mL methanol were placed in a separate 500 mL three necked flask. The solution was stirred until all the $NaNO_2$ had dissolved. A greased septum was placed in one of the necks, a greased one-hole rubber stopper was placed in the central neck, and a dropper funnel (125 mL) was also greased and attached to the third neck with a Keck clip. A solution of H_2O/H_2SO_4 (2:1, 50 mL) was measured out and placed in an ice bath (4 °C). A glass U-tube was then placed

through the hole in the rubber septum of the three-necked flask and into the Erlenmeyer flask. The acid/water solution was slowly added dropwise to the $NaNO_2/H_2O$/MeOH solution, and bubbles of evolving CH_3ONO gas are immediately seen flowing into the Erlenmeyer flask containing the *i*-PrONa/acetonitrile solution. The acid/water mixture was continuously added to the $NaNO_2$/H2O/MeOH solution in small aliquots until all was added. The U-tube apparatus was dismantled, and the Erlnemeyer flask containing the yellow *i*-PrONa/acetonitrile/CH3ONO solution was stoppered and left to stir in an ice bath overnight. The next morning a small amount of solid had precipitated from the solution, which was filtered off. The remaining solvent was removed from the reaction mixture via rotary evaporation, resulting in a light yellow solid. This solid was filtered off and determined to be the sodium salt of the compound via ^{1}H NMR. All of the salt was collected in a beaker and dissolved in distilled water. A magnetic stir bar was added, and the beaker was placed in an ice bath on a stir plate. HCl (1M) was added in small aliquots until a white precipitate began to form. The acid was continued to be added until the pH was around 5. The solid precipitated was filtered off and shown to be the free carboxyphenylcyanoxime. *Yield: 0.316g (79%). ^{1}H NMR (DMSO-d_6, 200 MHz): δ* 7.84 *(*d, 2H*, J = 8.8 Hz),* 8.06 *(*d, 2H, *J = 9 Hz),*14.1 (s, 1H) *IR: MP: 195-200 °C*

Synthesis of 4-(5,6-dimethylbenzimidazol-1-yl)methylpyridine 4-carboxyphenyl cyanoxime (1:1) (**15**)
5 (0.010 g, 0.0526 mmol) was dissolved in 2 mL methanol and to this solution was added a methanolic solution of **1** (0.006 g, 0.0236 mmol). Colorless prisms were obtained after three weeks. Found: C: 65.70; H: 4.78; N: 15.58. Calculated for $C_{24}H_{21}N_5O_3$: C: 67.44; H: 4.95; N: 16.38. MP: 195-200 °C.

Synthesis of 4-(2-phenylimidazol-1-yl)methylpyridine 4-hydroxybenzoic acid (1:1), **26**

2 (0.015g, 0.063 mmol) was dissolved in 2 mL ethanol. 4-hydroxybenzoic acid (0.009 g, 0.063 mmol) was dissolved in ethanol with heat and subsequently added to the ethanolic solution of **2.** Colourless plates were obtained after approximately 12 days. Found: C: 69.56; H: 5.74; N: 10.43. Calculated for $C_{22}H_{19}N_3O_3$: C: 70.76; H: 5.13; N: 11.25. MP: 165-168 °C.

Synthesis of 3-(5,6-dimethylbenzimidazol-1-yl)methylpyridine 4-bromocyanophenyloxime (1:1), **39**.

3 (0.015 g, 0.063 mmol) and 4-bromocyanophenyloxime (0.014 g, 0.063 mmol) were placed in a beaker. The mixture was dissolved in a 1:1 mixture of ethanol and ethyl acetate. Colourless plates were yielded after about 1 month. Found: C: 59.81; H: 4.99; N: 14.24. Calculated for $C_{23}H_{20}BrN_5O$: C: 59.75; H: 4.36; N: 15.15. MP: 110-115 °C.

Synthesis of pentamethylbenzoic acid 4-(2-methylbenzimidazol-1-yl)methylpyridine phenylcyanoxime (1:1:1) (**478***)*
To a 2 mL solution of 4-(2-methylbenzimidazole-1-yl)methyl pyridine (0.017g, 0.076 mmol) was added pentamethylbenzoic acid (0.015 g, 0.076 mmol) in 3 mL methanol and phenylcyanoxime (0.011g, 0.076 mmol) in 3 mL methanol. Slow evaporation of the

solvent yielded a white solid. This solid was subsequently redissolved in ethyl acetate to yield colorless plates after 2 weeks. Found: C: 72.26; H: 6.44; N: 12.42. Calculated for $C_{34}H_{35}N_5O_3$: C: 72.71; H: 6.28; N: 12.47. MP: 122-126 °C

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[1] (a) Robertson, D.; Barnes, C.; Gerasimchuk, N. *J. Coord. Chem.* **2004**, *57*, 1205 (b) Robertson, D.; Cannon, J. F.; Gerasimchuk, N. *Inorg. Chem.* **2005**, *44*, 8326.