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The preparations of 4- and 5-nitro-1-vinylimidazole (**2** and **7**) are described. Selective reduction of the nitro group using Fe/dil.HCl is achieved for the 4-nitro derivative but this is not effective when ethoxymethylenemalononitrile is used to trap the amine. For 5-nitroimidazole studies the *N*-vinyl substituent is kept masked as a 2-chloroethyl group, which remains unchanged during catalytic reduction of the nitro function (Pd/C), and is revealed by HCl elimination at a later stage. In this way, the 1-deazapurine **13** and the tricyclic derivative **14** have been prepared.

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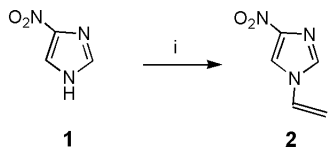
In previous studies we have shown that aminoimidazoles, prepared by catalytic reduction of nitroimidazoles, are useful synthetic intermediates for the preparation of purine analogues [1-9]. In order to extend the versatility of this approach we have investigated the preparation of new nitroimidazoles having synthetically useful functional groups at various ring positions. In this paper we describe the preparation of *N*-vinyl-nitroimidazoles and examples of related *N*-vinyl heterocycles.

Preparations of 4- and 5-nitro-1-vinylimidazole (**2** and **7**) have not previously been reported. Our initial approach to these compounds was based on direct vinylation of 4(5)-nitro-1*H*-imidazole **1**. Reaction of compound **1** with hot vinyl acetate in the presence of mercuric acetate and concentrated H_2SO_4 [10] gave a single product in 63% yield that was identified as the 4-nitro-1-vinylimidazole **2** (mp 136 °C) (Scheme 1). Structure **2** was fully supported by elemental analysis and spectroscopy. The 4-nitro constitution of compound **2** was confirmed by ^{13}C nmr spectroscopy: the shifts of the imidazole ring carbon atoms at 148 ppm (C-4) and 118 ppm (C-5) are entirely in accord with the expected values based on a study of a series of 4- and 5-nitroimidazole isomers by McKillop and co-workers [11].

Scheme 1

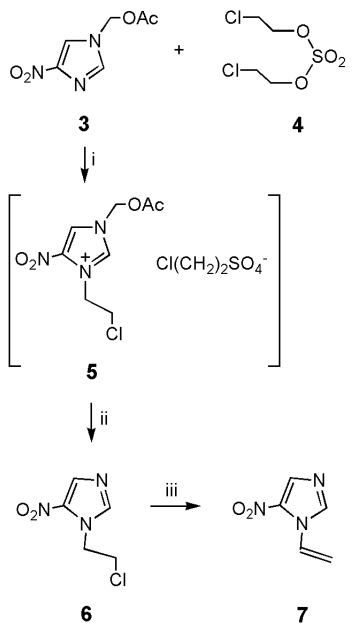


1 **2**

Reagents: i, CH_2=CHOAc / $Hg(OAc)_2$ / conc. H_2SO_4 / heat.

Preparation of the 5-nitro isomer **7** required a longer procedure involving *N*-protection. Heating the 1-acetoxymethyl derivative **3** [12] with bis-(2-chloroethyl)sulfate **4** and subsequent acidification gave 1-(2-chloroethyl)-5-nitroimidazole **6** in 74% yield, presumably *via* the imidazolium intermediate **5**. Treatment of the chloro derivative **6** with hot ethanolic NaOEt gave 5-nitro-1-vinylimidazole **7** (mp 24 °C) in 54% yield. Products **6** and **7** were both fully characterised and their 5-nitro constitutions were confirmed by ^{13}C nmr spectroscopy using the criteria of McKillop and co-workers [11]. Thus, compound **7** showed ^{13}C nmr shifts for the C-4 and C-5 imidazole ring carbons at 133 ppm and 138 ppm respectively, which are entirely consistent with the shifts expected for a 5-nitroimidazole, and in sharp contrast to those shown by the 4-nitro isomer **2** (148 and 118 ppm).

Scheme 2

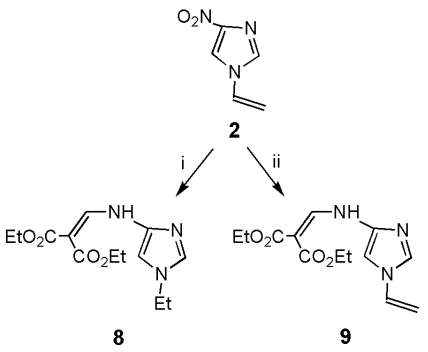


Reagents: i, 100 °C; ii, aq H_2SO_4 / reflux; iii, NaOEt/ EtOH / reflux.

Bis-(2-chloroethyl)sulfate **4** was prepared by addition of sulfuryl chloride to a chilled solution of 2-chloroethanol (2 equiv.) in CH_2Cl_2. Work-up gave a clear oil that was pure by ^1H nmr analysis but which turned yellow on standing.

Due to the potential toxicity of this reagent it was used immediately after preparation.

Scheme 3



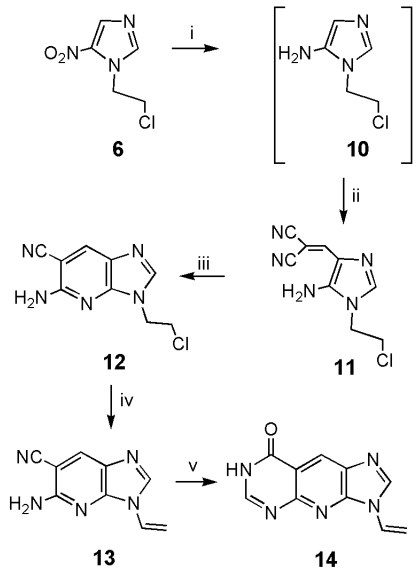
Reagents: i, H_2/ 5% Pd-C/ dioxane/ EMME; ii, Fe/ dil.HCl/ EtOH/ EMME.

A problem associated with conversion of *N*-vinylnitroimidazoles to the corresponding amines is the simultaneous reduction of the vinyl substituent. For example, catalytic reduction of compound **2** in the presence of ethoxymethylenemalonic acid diethyl ester (EMME) gave the *N*-ethyl derivative **8** (70%). Three ethyl substituents were clearly visible in the nmr spectra. Chemical reduction is more selective and reduction of compound **2** with iron powder and dilute HCl in ethanol in the presence of EMME gave the *N*-vinylimidazole **9** (65%). The unchanged *N*-vinyl substituent was observed in the ^{1}H nmr spectrum (J_{AX} 9.8, J_{BX} 15.7 and J_{AB} 2.0 Hz). Attempts to trap the 4-aminoimidazole using ethoxymethylenemalonitrile (EMMN), including the use of the milder reducing agent $FeCl_3$, were unsuccessful.

In view of the difficulties associated with (i) *in situ* trapping using EMMN and (ii) selective nitro group reduction, it was decided that for further studies using 5-nitroimidazoles the *N*-vinyl group would be kept masked as an *N*-(2-chloroethyl) function and generated at a later stage. At atmospheric pressure and room temperature alkyl C-Cl bonds are not usually reduced by catalytic hydrogenation.

Catalytic reduction of the 5-nitroimidazole **6** gave the amine **10** which was not isolated but was trapped by addition of EMMN giving the adduct **11** (77%). As with other 5-aminoimidazoles that we have studied [1-9], the EMMN gives exclusively the C-adduct in contrast to EMME which gives N-adducts. In particular, the product **11** shows a single imidazole proton (δ 7.79, C(2)H) and two amino protons (δ 7.61). In hot ethanol containing aqueous $NaHCO_3$ cyclisation of the adduct **11** readily occurred to give the 1-deazapurine **12** (65%) which was fully characterised. In this product the newly formed pyridine proton

Scheme 4



Reagents: i, H_2 / 5% Pd-C; ii, EMMN; iii, $NaHCO_3$ / EtOH; iv, NaOEt / EtOH; v, 95% HCO_2H.

and the imidazole 2-proton are observed at δ 8.26 and δ 8.27. The *N*-vinyl group was then introduced by elimination of HCl using NaOEt to give compound **13** in 87% yield. This product turns black at 250 °C and decomposes without melting. We believe that this crystal stability, and low solubility, is due to the high π stacking energy of the planar conjugated system. Finally, the tricyclic derivative **14** was prepared by heating compound **13** in 95% formic acid. This product, which was obtained in 57% yield after recrystallisation from DMSO, was also a high melting (> 280 °C) low solubility crystalline solid.

EXPERIMENTAL

The ^{1}H and ^{13}C nmr spectra were recorded on a Bruker Advance DPX300 NMR spectrometer; ir spectra on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer, mass spectra on an AEI MS1Z spectrometer and microanalyses on a Perkin-Elmer 240 elemental analyzer. Infrared spectra were measured as thin films (liquids) or potassium bromide discs (solids) and nmr spectra in deuteriochloroform (tetramethylsilane as internal standard) unless otherwise stated. Only significant bands for the ir spectra are quoted. Melting points were determined on a Reichert-Kofler block apparatus and are uncorrected.

4-Nitro-1-vinyl-1*H*-imidazole (**2**).

4-Nitroimidazole **1** (20.0 g, 177 mmol), mercuric acetate (2.8 g, 9 mmol) and concentrated sulphuric acid (0.86 g, 9 mmol) were added to vinyl acetate (15.2 g, 177 mmol). The mixture was stirred and heated under reflux (12 h) and then filtered while hot. The resulting cloudy solution was evaporated to give a beige solid that was recrystallised from ethanol and identified as the 4-

nitroimidazole **2** (15.4 g, 63%), small cream needles, mp 136 °C; ir (KBr): 826, 913, 982, 1142, 1292, 1323, 1348, 1492, 1514, 1543, 1648, 3120 and 3160 cm^{-1}; ^1H nmr (DMSO-d_6): δ 5.21 (1H, dd, *J* 1.0 and 8.9 Hz, CH=CH_2(cis)), 5.91 (1H, dd, *J* 1.0 and 15.8 Hz, CH=CH_2(trans)), 7.23 (1H, dd, *J* 8.9 and 15.8 Hz, N-C*H*=CH_2), 8.10 (1H, s, imidazole C(2)*H*), 8.30 (1H, s, imidazole C(5)*H*); ^{13}C nmr (DMSO-d_6): δ 106.0 (C=*C*H_2), 118.1 (*C*(5)H), 129.3 (C=*C*H), 136.0 (*C*(2)H), 147.9 (*C*(4)); ms: *m/z* 140(26%)($M+1^+$), 139(100%)(M^+), 54, 52, 39, 30, 27.

Anal. Calcd for $C_5H_5N_3O_2$: C, 43.17; H, 3.62; N, 30.21. Found: C, 43.10; H, 3.50; N, 30.24.

1-Acetoxymethyl-4-nitro-1*H*-imidazole (**3**).

A mixture of toluene (40 ml), acetic anhydride (9 ml, 95 mmol), glacial acetic acid (1.6 ml, 28 mmol), 4(5)-nitroimidazole (8.96 g, 79 mmol), paraformaldehyde (2.86 g, 95 mmol) and sodium acetate (0.26 g, 3.2 mmol) was stirred at 100 °C (90 h). The solution was evaporated and the solid residue partitioned between water (150 ml) and $CHCl_3$ (150 ml). The organic layer was dried ($MgSO_4$), evaporated and the product recrystallised from ethyl acetate and identified as compound **3** (12.2 g, 83%), colourless crystals, mp 80 °C (Lit.[12] mp 83.5-84.5 °C) ; ir (KBr): 757, 823, 982, 1143, 1222, 1491, 1543, 1753 and 3095 cm^{-1}; ^1H nmr: δ 2.09 (3H, s, CH_3), 5.83 (2H, s, CH_2), 7.61 (1H, d, *J* 1.5 Hz, imidazole C(5)*H*), 7.93 (1H, d, *J* 1.5 Hz, imidazole C(2)*H*); ^{13}C nmr: δ 20.5 (CO*C*H_3), 68.8 (*C*H_2), 121.9 (*C*(5)H), 138.4 (*C*(2)H), 147.4 (*C*(4)), 170.0 (*C*=O); ms: *m/z* 185(59%)(M^+), 155, 127, 126, 97, 73(100%), 68.

Anal. Calcd for $C_6H_7N_3O_4$: C, 38.92; H, 3.81; N, 22.70. Found: C, 38.76; H, 3.67; N, 22.69.

Sulfuric Acid Bis-(2-chloroethyl) Ester (**4**).

Sulphuryl chloride (122.8 g, 0.91 mol) was added dropwise (2 h) to a solution of 2-chloroethanol (146 g, 1.82 mol) in CH_2Cl_2 (250 ml) in an ice bath. The solution was stirred (2 h), washed with water (250 ml) and then the solvent was removed. The resulting crude oil was placed in a separating funnel with water (250 ml) and petroleum ether (bp 40-60 °C) (250 ml). Dichloromethane was then added to the triphasic mixture in 10 ml aliquots, until, with shaking, the mixture became biphasic. The organic fraction was removed and washed with sat. $NaHCO_3$ solution (200 ml), water (200 ml) and then dried (Na_2SO_4). Removal of solvent under reduced pressure yielded a clear oil, which discoloured on standing, that was identified as the ester **4** (138 g, 68%); ^1H nmr: 3.84 (4H, t, *J* 5.6, Cl-CH_2), 4.71 (4H, t, *J* 5.6, O-CH_2). This material was used without further purification.

1-(2-Chloroethyl)-5-nitro-1*H*-imidazole (**6**).

1-Acetoxymethyl-4-nitroimidazole **3** (18.5 g, 100 mmol) and sulfuric acid bis-(2-chloroethyl) ester **4** (2.05 g, 112 mmol) were heated at 100 °C (2 h). The biphasic mixture was then transferred to a flask containing 10% aqueous H_2SO_4 (70 ml) and heated under reflux (2 h). The reaction mixture was cooled and diluted with water (100 ml). Aqueous NaOH (10%) was added cautiously, with stirring in an ice bath, to pH 11. Extraction with CH_2Cl_2 (3 x 100 ml), followed by drying (Na_2SO_4) and removal of solvent yielded a pale yellow oil which crystallised slowly at room temperature. This product was recrystallised from H_2O and identified as the 5-nitroimidazole **6** (13.0 g, 74%), pale yellow rectangular crystals, mp 49 °C; ir (KBr): 656, 744, 1121, 1268, 1372, 1435, 1466, 1528, 3098 and 3122 cm^{-1}; ^1H nmr: δ 3.94 (2H, t, *J* 5.5 Hz, ClCH_2), 4.76 (2H, t, *J* 5.5 Hz, NCH_2), 7.83 (1H, d, *J* 0.9 Hz, imidazole C(4)*H*), 8.01 (1H, d, *J* 0.9 Hz, imidazole C(2)*H*); ^{13}C nmr: δ 43.0 (Cl*C*H_2), 49.5 (N*C*H_2), 134.0 (*C*(4)H), 138.3 (*C*(5)), 143.1 (*C*(2)H); ms: *m/z* 175(78%)(M^+), 140, 113, 98, 67, 63(100%), 53, 40, 27.

Anal. Calcd for $C_5H_6Cl\ N_3O_2$: C, 34.20; H, 3.44; N, 23.93. Found: C, 34.36; H, 3.48; N, 24.23.

5-Nitro-1-vinyl-1*H*-imidazole (**7**).

Sodium ethoxide (1.02 g, 15.0 mmol) was added to 1-(2-chloroethyl)-5-nitroimidazole **6** (1.76 g, 10.0 mmol) in refluxing EtOH (100 ml, anhydrous). The resulting orange solution was heated under reflux (30 minutes) before cooling to room temperature and stirring overnight. The precipitate was removed and the solution reduced in volume (10 ml) and partitioned between water (200 ml) and Et_2O (200 ml). The organic phase was separated, dried and reduced to a yellow oil. Column chromatography (silica gel; Et_2O as eluent) gave the nitroimidazole **7** (0.75 g, 54%), yellow crystalline solid, mp 24 °C; ir (film): 643, 826, 1119, 1526, 1376, 1473, 1530, 1641 and 3127 cm^{-1}; ^1H nmr: 5.36 (1H, dd, *J* 1.8 and 8.4 Hz, CH=CH_2(cis)), 5.57 (1H, dd, *J* 1.8 and 15.5 Hz, CH=CH_2(trans)), 7.44 (1H, dd, *J* 8.4 and 15.5 Hz, NC*H*=CH_2), 7.85 (1H, d, *J* 0.8 Hz, imidazole(4)-*H*), 8.00 (1H, d, *J* 0.8 Hz, imidazole(2)-*H*); ^{13}C nmr (DMSO-d_6): 110.1 (=*C*H_2), 128.8 (=*C*H), 133.2 (*C*(4)H), 138.0 (*C*(5)), 140.2 (*C*(2)H); ms: *m/z* 139(48%)(M^+), 94(37), 82(17), 67(30), 66(56), 55(24), 54(46), 40(44), 39(100), 28(91), 27(49).

Anal. Calcd. for $C_5H_5N_3O_2$: C, 43.17; H, 3.62; N, 30.21. Found C, 43.44; H, 3.50; N, 30.19.

2-[(1-Ethyl-1*H*-imidazol-4-ylamino)-methylene]-malonic Acid Diethyl Ether (**8**).

4-Nitro-1-vinylimidazole **2** (1.39 g, 10 mmol), ethoxymethylenemalonic acid diethyl ester (EMME) (2.16 g, 10 mmol) and 5% Pd/C (0.87 g, 50% w/w) were placed in dry 1,4-dioxane (35 ml). The mixture was hydrogenated at atmospheric pressure with vigourous shaking until the uptake of hydrogen had ceased (approx. 680 ml). The mixture was filtered through celite to yield a yellow solution which was concentrated and purified by column chromatography (silica gel; EtOAc:60-80 pet. ether; 1:1 as eluent). The largest fraction was collected, recrystallised from ethyl acetate:hexane and identified as the *N*-ethylimidazole **8** (1.97 g, 70%), yellow crystals, mp 63 °C; ir (KBr): 791, 996, 1095, 1256, 1311, 1424, 1620, 1648, 1694, 2978 and 3119 cm^{-1}; ^1H nmr: δ 1.30 (3H, t, *J* 7.1 Hz, OCH_2CH_3), 1.36 (3H, t, *J* 7.1 Hz, OCH_2CH_3), 1.45 (3H, t, *J* 7.3 Hz, NCH_2CH_3), 3.94 (2H, q, *J* 7.3 Hz, NCH_2CH_3), 4.21 (2H, q, *J* 7.1 Hz, $OCH_2\ CH_3$), 4.26 (2H, q, *J* 7.1 Hz, OCH_2CH_3), 6.60 (1H, d, *J* 1.2 Hz, imidazole C(5)*H*), 7.28 (1H, d, *J* 1.2 Hz, imidazole C(2)*H*), 8.70 (1H, d, *J* 13.6 Hz, NHC*H*), 10.94 (1H, d, *J* 13.6 Hz, CHN*H*); ^{13}C nmr: δ 14.4 (*C*H_3), 14.5 (*C*H_3), 16.2 (*C*H_3), 42.4 (*C*H_2), 59.7 (*C*H_2), 60.2 (*C*H_2), 92.0 (*C*), 103.7 (*C*H), 134.1 (*C*H), 140.3 (*C*), 152.5 (*C*H), 165.6 (*C*), 169.3 (*C*); ms: *m/z* 281(63%)(M^+), 235, 190(100%), 163, 141, 135, 122, 56, 56, 29.

Anal. Calcd. for $C_{13}H_{19}N_3O_4$: C, 55.50; H, 6.81; N, 14.94. Found: C, 55.59; H, 6.93; N, 14.93.

2-[(1-Vinyl-1*H*-imidazol-4-ylamino)-methylene]-malonic Acid Diethyl Ether (**9**).

4-Nitro-1-vinylimidazole **2** (1.39 g, 10 mmol), ethoxymethylenemalonic acid diethyl ester (EMME) (2.16 g, 10 mmol), hydro-

gen reduced iron powder (3.0 g), concentrated hydrochloric acid (0.1 ml) and water (10 ml) were placed in EtOH (40 ml) and the solution heated to reflux. The reaction was monitored by tlc until all the vinylimidazole had been consumed. The reaction mixture was then cooled, filtered through celite and concentrated. Column chromatography (silica gel: EtOAc:60-80 pet. ether; 1:1 as eluent) gave a solid that was identified as the vinylimidazole **9** (1.80 g, 65%), yellow solid, mp 56 °C; ir (KBr): 598, 675, 790, 1081, 1239, 1267, 1570, 1622, 1651, 1699, 2978, 3099 and 3124 cm^{-1}; ^1H nmr: δ 1.23 (3H, t, *J* 7.1 Hz, CH_2-CH_3), 1.29 (3H, t, *J* 7.1 Hz, CH_2-CH_3), 4.14 (2H, q, *J* 7.1 Hz, CH_3-CH_2), 4.21 (2H, q, *J* 7.1 Hz, CH_3-CH_2), 4.84 (1H, dd, *J* 2.0 and 9.8 Hz, CH=CH_2(*cis*)), 5.17 (1H, dd, *J* 2.0 and 15.7 Hz, CH=CH_2(*trans*)), 6.78 (1H, dd, *J* 9.8 and 15.7 Hz, NC*H*=CH_2), 6.83 (1H, d, *J* 1.4 Hz, imidazole C(5)*H*), 7.40 (1H, d, *J* 1.4 Hz, imidazole C(2)*H*), 8.64 (1H, d, *J* 13.4 Hz, NHC*H*), 10.91 (1H, d, *J* 13.4 Hz, CHN*H*); ^{13}C nmr: δ 14.3 (*C*H_3), 14.5 (*C*H_3), 59.9 (*C*H_2), 60.3 (*C*H_2), 92.8 (*C*), 100.1 (*C*H), 101.8 (*C*H_2), 129.0 (*C*H), 134.3 (*C*H), 141.0 (*C*), 152.1 (*C*H), 165.4 (*C*), 169.1 (*C*); ms: *m/z* 279(50%)(M^+), 233, 188, 161(100%), 133, 120, 54 , 29, 28, 27.

Anal. Calcd for $C_{13}H_{17}N_3O_4$: C, 55.91; H, 6.14; N, 15.05. Found: C, 55.84; H, 6.38; N, 14.65.

2-[5-Amino-1-(2-chloroethyl)-1*H*-imidazol-4-ylmethylene]-malononitrile (**11**)

A mixture of 1-(2-chloroethyl)-5-nitroimidazole **6** (1.75 g, 10 mmol) and 5% Pd/C (0.87 g, 50% w/w) in dry 1,4-dioxane (35 ml) was hydrogenated at atmospheric pressure with vigourous shaking until uptake of hydrogen (approx. 680 ml) had ceased. The mixture was filtered through celite to yield a yellow solution that darkened to orange. A solution of ethoxymethylene malononitrile (1.22 g, 10 mmol) in 1,4-dioxane (20 ml) was added and the mixture was stirred overnight under a nitrogen atmosphere. The resulting yellow precipitate was collected, washed with dioxane and, after drying under vacuum, identified as the imidazole derivative **11** (1.71 g, 77%), bright yellow solid, mp 190-192 °C; ir (KBr): 846, 1121, 1338, 1462, 1560, 1604, 1656, 2204, 2220, 2927, 3336 and 3456 cm^{-1}; ^1H nmr (DMSO-d_6): δ 3.87 (2H, t, *J* 5.8 Hz, ClCH_2), 4.18 (2H, t, *J* 5.8 Hz, NCH_2), 7.54 (1H, s, C=C*H*), 7.61 (2H, s, NH_2), 7.79 (1H, s, imidazole C(2)*H*); ^{13}C nmr (DMSO-d_6): δ 42.1 (*C*H_2), 44.3 (*C*H_2), 57.6 (*C*), 116.4 (*C*), 118.0 (*C*N), 118.8 (*C*N), 138.1 (*C*(2)H), 143.2 (*C*), 150.3 (C=*C*H); ms: *m/z* 221(64%)(M^+), 172, 159(100%), 118, 104, 63, 28.

Anal. Calcd. for $C_9H_8ClN_5$: C, 48.77; H, 3.64; N, 31.60. Found: C, 48.49; H, 3.57; N, 31.65.

5-Amino-3-(2-chloroethyl)-3*H*-imidazo[4,5-*b*]pyridine-6-carbonitrile (**12**).

2-[5-Amino-1-(2-chloroethyl)-imidazol-4-ylmethylene]-malononitrile **11** (1.71 g, 77.3 mmol) and 5% aqueous sodium bicarbonate (1 ml) were placed in EtOH (30 ml) and heated under reflux with stirring (1 h). The mixture was allowed to cool slowly and the product was collected, washed with cold EtOH (2 x 40 ml), dried under vacuum and identified as the imidazo[4,5-*b*]pyridine **12** (1.12 g, 65%), golden crystals (EtOH), mp 231 °C; ir (KBr): 668, 763, 913, 1156, 1304, 1429, 1517, 1570, 1636, 2212, 2924, 3186, 3305 and 3475 cm^{-1}; ^1H nmr (DMSO-d_6): δ 4.07 (2H, t, *J* 6.0 Hz, ClCH_2), 4.45 (2H, t, *J* 6.0 Hz, NCH_2), 6.82 (2H, s, NH_2), 8.26 (1H, s, pyridine C(7)*H*), 8.27 (1H, s, imidazole C(2)*H*); ^{13}C nmr (DMSO-d_6): δ 42.5 (*C*H_2), 44.4 (*C*H_2), 85.8 (*C*), 117.8 (*C*), 126.6 (*C*), 134.0 (*C*H), 144.3 (*C*H), 149.0 (*C*), 157.6 (*C*); ms: *m/z* 221(84%)(M^+), 172, 159(100%), 104, 63, 28.

Anal. Calcd for $C_9H_8ClN_5$: C, 48.77; H, 3.64; N, 31.60. Found: C, 48.89; H, 3.67; N, 31.89.

5-Amino-3-vinyl-3*H*-imidazo[4,5-*b*]pyridine-6-carbonitrile (**13**).

5-Amino-3-(2-chloroethyl)-imidazo[4,5-*b*]pyridine-6-carbonitrile **12** (1.11 g, 5.0 mmol) was dissolved in hot dry EtOH (50 ml) and sodium ethoxide (0.4 g, 5.9 mmol) was added with rapid stirring. The solution was then heated under reflux and the reaction monitored by tlc. Extra portions of sodium ethoxide (0.15 g, 1.5 mmol) were added until all the starting material was consumed. The mixture was cooled and the precipitate collected. The solid product was washed repeatedly with water (5 x 50 ml), dried under vacuum and identified as the vinyl-imidazo[4,5-*b*]pyridine **13** (805 mg, 87%), buff crystals (EtOH), mp 251 °C (dec.); ir (KBr): 880, 1243, 1303, 1416, 1437, 1509, 1570, 1634, 2211, 3104, 3158, 3296 and 3480 cm^{-1}; ^1H nmr (DMSO-d_6): δ 5.20 (1H, d, *J* 8.9 Hz, CH=CH_2(*cis*)), 6.13 (1H, d, *J* 15.9 Hz, CH=CH_2(*trans*)), 7.01 (2H, s, NH_2), 7.29 (1H, dd, *J* 8.9 and 15.9 Hz, NC*H*=CH_2), 8.40 (1H, s, pyridine C(7)*H*), 8.64 (1H, s, imidazole C(2)*H*); ^{13}C nmr (DMSO-d_6): δ 86.8 (*C*), 103.6 (*C*H_2), 118.1 (*C*), 127.2 (*C*H), 127.5 (*C*), 134.8 (*C*H), 142.2 (*C*H), 148.3 (*C*), 158.4 (*C*); ms: *mz* 185(100%)(M^+), 158, 131, 78, 28.

Anal. Calcd for $C_9H_7N_5$: C, 58.37; H, 3.81; N, 37.82. Found: C, 58.45; H, 3.81; N, 37.65.

3,7-Dihydro-3-vinylimidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidin-8-one (**14**).

5-Amino-3-vinylimidazo[4,5-*b*]pyridine-6-carbonitrile **13** (740 mg, 4.0 mmol) was dissolved in 95% formic acid (50 ml) and heated under reflux (24 h). The reaction mixture was then reduced to a volume of approximately 5 ml and diluted with water (50 ml). The solution was adjusted to pH 7 using 2 *M* aqueous NaOH and chilled overnight. The solid precipitate was collected and dried. Recrystallisation from DMSO gave a light brown solid that was identified as the imidazo[4',5':5,6]-pyrido[2,3-*d*]pyrimidin-8-one **14** (477 mg, 56%), m.p. > 280 °C; ir (KBr): 3453, 2628, 1688, 1602, 1401, 1264, 922 and 805 cm^{-1}; ^1H nmr (DMSO-d_6): δ 5.20 (1H, d, *J* 8.9 Hz, CH=CH_2(*cis*)), 6.13 (1H, d, *J* 15.9 Hz, CH=CH_2(*trans*)), 7.29 (1H, dd, *J* 8.9 and 15.9 Hz, NC*H*=CH_2), 8.40 (1H, s, pyridine-*H*), 8.64 (1H, s, imidazole-*H*); ms: *m/z* 213(100%)(M^+), 186(98), 160(21), 131(11), 104(9), 78(12), 63(13), 54(10), 52(8), 27(10); HRMS. $C_{10}H_7N_5O$: M^+ calc. 213.0651, found 213.0650

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