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Preparation and characterization of some imidazoles and formimidoyl-1*h*-imidazoles from formamidines

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ABSTRACT

Imidazoles and formimidoyl-1H-imidazoles derivatives were prepared by reaction between formamidines and weak or strong base depending on reaction conditions in good yields. All these derivatives have been fully characterized by spectroscopic data.

Introduction

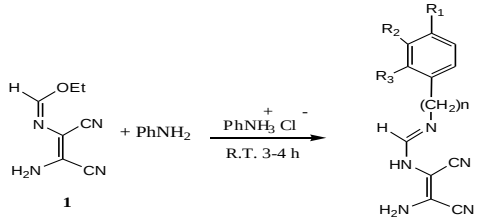
Starting from readily available ethyl (*Z*)-*N*-(2-amino-1,2-dicyanovinyl)formimidate, *N*-aryl-*N*'-[2-amino-1,2-dicyanovinyl]formamidines 2 can be prepared in good yields by reaction with aromatic amines at room temperature in the presence of an acid catalyst. Treatment of the amidines with a base (DBU) at room temperature gave the corresponding 5-amino-1-aryl-4-(cyanoformimidoyl)-1H-imidazoles 3 in high yield, whereas reaction with KOH solution afforded the respective 5-amino-4-cyano-1-arylimidazoles 4. These last compounds can also be prepared from compounds 3 by reaction with KOH solution.

5-amino-4-cyanoimidazoles have long been recognized as useful synthetic precursors to purines, but there is no simple, general synthesis available for 1-aryl derivatives of these compounds. In 1984, Sen and Mukhopadhyay reported the preparation of 5-amino-4-cyano-1-(*p*-aminosulfonylphenyl)imidazole via a multistep synthesis from the corresponding 1-methyl derivative [1]. Frank and Zeller have described the synthesis of a number of 1-aryl- and 1-heteroaryl-5-amino-4-cyanoimidazoles (aryl=2- and 4-ClC_6H_4, 2,4-$Cl_2C_6H_3$, 2,4-$Me_2C_6H_3$; heteroaryl=2- and 3-pyridyl, 5-Cl-2-Pyridyl, 3,5-diCl-2-pyridyl, 2-Cl-3-pyridyl, and 2- pyrimidine) in low to moderate yields by reaction of the corresponding ethyl *N*-substituted formimidate with 2-aminomalodinitrile tosylate in acetic acid [2].

We have been interested in the chemistry of diaminomaleonitrile (DAMN) and its derivatives, in particular, ethyl-2-(2-amino-1,2-dicyanovinyl)formimidate 1 which can be prepared in good yield from the reaction between DAMN and triethyl orthoformate in dioxane [3-6]. From our previous work in this area it appeared to us that 1 would be a useful starting material for the preparation of new N-aryl-N'–[2-amino-1,2-dicyanovinyl]formamidines 2. Using procedures developed in our laboratories it was envisaged that these could be readily converted into 5-amino-1-aryl-4-(cyanoformimidoyl)-1H-imidazoles 3 [7-13], which are expected to be useful precursors to new 6-carbamoyl-1, 2-dihydropurines and 6-substituted purines derivatives [14-20]. In addition, 2 could provide a simple route to the desired 5-amino-1-aryl-4-cyanoimidazoles 4. The results of this investigation are now reported.

Results and Discussion

Treatment of 1 with an equimolar amount of the appropriate aromatic amine at room temperature in ethanol in the presence of a catalytic amount of anilinium chloride afforded the corresponding formamidines 2a-c in 82-92% yields based on isolated product. In these cases, isolation is achieved by simple filtration of the product mixture and little or no further purification is required to give analytically pure products. The anilinium chloride is believed to act as a general acid catalyst and result in a significant acceleration of the rate of reaction. When it is absent, appreciable decomposition occurs and the amidine product becomes difficult to isolate from tarry by-products with consequent low yields. The amine hydrochloride salts of the arylamine reactions also catalyse these reactions, but it is often more convenient to use the anilinium salt.



a : R_1= H, R_2= R_3= H n=0
b : R_1=R_2=R_3= H n=1
c : R_1=CH_3, R_2=R_3=H n=0

The spectroscopy results obtained on these compounds 2a-c were satisfactory. The high resolution mass spectrum gave a molecular ion peak at 212, 226, 226 $(M+1)^+$ which fits with the

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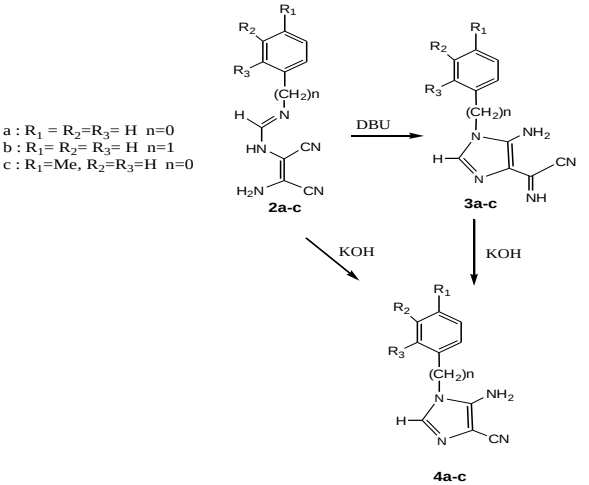
expected molecular weight of 211, 225, 225 for the formamidines 2a-c. The ^{1}H nmr spectra of compounds 2a-c in dimethyl sulfoxide had some interesting features. The HC=N proton appeared at δ7.30-7.74 ppm and NH proton appeared as a broad singlet at δ8.16-9.90 ppm and was confirmed by D_2O exchange. The ^{13}C nmr spectrum was fully consistent with the assigned structure. The infrared spectrum of amidine 2a-c showed two strong absorption in the region 2210-2225 cm^{-1} characteristic of CN stretching vibrations, together with an NH and a C=N stretching vibration at 3100-3460 and 1610-1650 cm^{-1} respectively.

When several drops of DBU are added to a suspension of the amidines 2a-c in ethyl acetate or ethanol, cyclization occurs in 1-3 hours to give the corresponding 5-amino-1-aryl-4-(cyanoformimidoyl)imidazoles 3a-c in good yields (85-91%). All the compounds were obtained in an analytically pure state and IR band show a strong band in the 2200-2230 cm^{-1} region for a C≡N bond and C=N stretching vibrations within the region of 1660-1635 cm^{-1}. In all cases the signals were sharp and in the ^{1}H nmr spectra the CH proton of the imidazole ring appears in the range δ7.42-7.72, the NH_2 protons at δ6.68-6.76 and the NH proton at δ10.88-11.20 ppm. The ^{13}C nmr spectrum was fully consistent with the assigned structure.

When a saturated solution of KOH in ethanol is added to a suspension of the amidines 2a-c in an alcohol at room temperature this affords the corresponding 5-amino-1-aryl-4-cyanoimidazoles 4a-c in good yields (75-90%). These compounds can also be made in comparable yield by the reaction of the compounds 3a-c with a saturated solution of KOH in ethanol under conditions similar to those described above.



Compounds 4a-c were recrystallised from mixture ofethanol/methanol (1:1) and gave pale yellow to off white crystals respectively. These were fully characterized by microanalysis, IR, ^{1}H, ^{13}C nmr and mass spectroscopy. The high resolution mass spectrum gave a molecular ion peak at 185, 199, 199 $(M+1)^+$ which fits with the expected molecular weight of 184, 198 and 198 for the imidazoles 4a-c. The infrared spectrum confirmed the presence of the NH and C=N stretching vibrations within the region of 3100-3380, and 1650-1680 cm^{-1} respectively. The infrared spectrum also showed a sharp absorption band within the range of 2210-2240 cm^{-1} for the C≡N stretching vibration. In the ^{1}H nmr spectra of the isolated 5-amino-1-aryl-4-cyanoimidazoles, the primary amine protons were observed in the region of δ6.12-6.42 ppm and in several cases the assignment were confirmed by D_2O exchange. The proton of the imidazole ring appeared as a sharp singlet in the range of δ7.34-7.42 ppm. The ^{13}C nmr spectra of the compounds 4a-c had the expected number of peaks. The C-2 carbon of the imidazole ring appeared in the region of 136.7-137.9 ppm.

Experimental

All solvents purified and dried using established procedures. The ^{1}H NMR spectra were recorded on Bruker XL 500 (500 MHz) instruments, ^{13}C NMR spectra on DRX-500 AVANCE spectrometer, and IR spectra on a Shimadzu IR-470 spectrophotometer. Mass spectra were recorded on a Kratos Concept instrument. The melting points were measured on an Electrothermal digital melting point apparatus and are uncorrected.

General procedure for the preparation of the *N*-Aryl-*N'*-[2-amino-1,2-dicyanovinyl]formamidines 2a-c; the aromatic amines (5.64 mmol) were added to a suspension of imidate 1 (5.62 mmol) in dry ethanol or ethyl acetate, which contained anilinium chloride (0.01 g). The mixture was stirred at room temperature until TLC showed that all the formimidate had disappeared (usually 3 to 4 h) and the amidine was isolated by filtration. In a few cases precipitation had to be assisted by concentrating the solution and addition of a 1:1 mixture of light petroleum (b.r. 40-60 ^{o}C) and chloroform. In most cases the product was yellow to pale green. The precipitate was washed with diethyl ether or a light petroleum- chloroform mixture and was dried under vacuum to give the analytically pure product in the yields 82-92%.

***N*-Phenyl-(*Z*)-*N'*-[2-amino-1,2-dicyanovinyl]formamidine2a :**

Recristalization of the product from dry chloroform/petroleum ether (1:1) gave yellow crystals of 2a (1.05g, 4.97mmol, 82%). M.p. 132-134 ^{o}C (decomp.). [Found : C, 62.7; H, 4.2; N, 33.0. $C_{11}H_9N_5$ requires : C, 62.6; H, 4.3; N, 33.2 %] ; m/z (EI) 212 $(M+1)^+$ 100%, 211 $(M)^+$ 12.5 %, 185 $(M-CN)^+$ 18.4 %, 106 $[(M+1)-C_4H_2N_4]^+$ 2%, 94 $[(M+1)-C_5H_2N_4]^+$ 21%, 93 $[(M+1)-C_5H_3N_4]^+$ 7.5%; δ_H (500 MHz, d6-DMSO) 6.60 (br. s, NH_2), 7.10-7.15 (m, 1H, H9), 7.38-7.42 (m, 2H, H8 & H10), 7.55-7.70 (br. s, 2H, H7 & H11), 7.74 (s, 1H, H5), 8.16 (br. s, 1H, NH); δ_C (75 MHz, d6-DMSO) 151.7 (C5), 143.3 (C6), 133.1 (C8 & C10), 126.8 (C9), 122.9 (C7 & C11), 122.3 (C2), 119.7 and 118.8 (C3 & C4), 109.2 (C1) ppm ; ν_{max} (Nujol mull) 3450s, 3420 w, 3410w, 3345s, 3300m, 3240 w (N-H str.), 2210s, (CN str.), 2195 s (CN str.), 1655 s (C=N str.), 1600 s (N-H bend), 1590 s, 1500 w, 1320 m, 960s, 870s, 730 m cm^{-1}; λmax (EtOH) 202.1 (ε 16631), 205.2 (ε 13869), 262.5 (ε 10989), 262.8 (ε 10894) and 353.0 (ε 32456) nm.

N-Benzyl-(Z)-N'-[2-amino-1,2-dicyanovinyl]formamidine2b:

Recristalization of the product from dry chloroform/petroleum ether (1:1) gave white crystals of 2b (1.22 g, 5.4 mmol, 89%). M.p. 91-92 ^{o}C (decomp.). [Found : C, 64.2; H, 4.9; N, 31.1. $C_{12}H_{11}N_5$ requires : C, 64.0; H, 4.9; N, 31.1 %] ; m/z (EI) 226 $(M+1)^+$ 100%, 225 $(M)^+$ 62%, 199 $(M-CN)^+$ 11.4 %, 108 $[(M+1)-C_5H_2N_4]^+$ 66.0%; δ_H (500 MHz, d6-DMSO) 4.52 (d, 2H, $^3J_{6,\ NH}$ 6Hz, H6), 6.10 (s, 2H, NH_2), 7.20-7.38 (m, 5H, H8, H9, H10, H11 & H12), 7.74 (d, 1H, $^3J_{5,\ NH}$ 6Hz, H5), 8.18 (br. d, 1H, $^3J_{NH,\ 5}$ 6Hz, NH) ppm ; δ_C (75 MHz, d_6-DMSO) 154.4 (C5), 148.8 (C7), 132.4 (C10), 131.8 (C9 & C11), 131.0 (C8 & C12), 121.1 and 120.2 (C3 & C4), 119.2 (C2), 110.1 (C1), 47.9 (C6) ppm ; ν_{max} (Nujol mull) 3460s, 3355s (N-H str.), 2225s (CN str.), 2210s (CN str.), 1640 s (C=N str.), 1600s (N-H bend), 1580m, 1530m, 1350m, 1290m, 1200m, 1170s, 1070m, 960s, 790s, 700s cm^{-1}; λ_{max} (EtOH) 205.3 (ε 22688), 206.6 (ε 1907), 228.0 (ε 20813), 228.1 (ε 1931), 330.1 (ε 39938), and 330.2 (ε 3878) nm.

***N*-(4-methylphenyl)-(*Z*)-*N*'-[2-amino-1,2-dicyanovinyl]formamidine 2c :**

Recristalization of the product from dry chloroform/petroleum ether (1:1) gave pale green crystals of 2c (1.35 g, 5.6 mmol, 92%). M.p. 123-124 ^{o}C (decomp.). [Found : C, 63.9; H, 4.8; N, 31.6. $C_{12}H_{11}N_5$ requires : C, 64.0; H, 4.9; N, 31.1 %] ; m/z (EI) 226 $(M+1)^+$ 100%, 225 $(M)^+$ 3.0 %, 195 $(M-CN)^+$ 40.9, 120 $[(M+1)-C_4H_2N_4]^+$ 6.0%, 91 $[(M+1)-C_5H_4N_5]^+$ 6.0 %; δ_H (500 MHz, d6-DMSO) 2.50 (s, 3H, CH_3), 6.40 (br. s, NH_2), 6.90 (d, 2H, $^3J_{8,7}$ 8Hz, H8 & H10), 7.30-7.42 (d, 1H, 6Hz, H5), 7.50-7.90 (br. complex m, 2H, H7& H11), 9.90 (br. s, NH) ppm ; δ_C (75 MHz, d_6-DMSO) 159.1 (C9), 150.9 (C5), 136.6 (C6), 124.5 (C7 & C11), 122.3 (C2), 119.9 and 118.8 (C3 & C4), 118.1 (C8 & C10), 109.6 (C1), 39.1 (C12) ppm ; ν_{max} (Nujol mull) 3460 w, 3450 s, 3340s, 3300m, 3250s, 3120m (N-H str.), 2210s (CN str.), 1650s (C=N str.), 1590s (N-H bend), 1575w, 1515m, 1310s, 1295m, 1245s, 1220s, 1175m, 1040s, 960m, 820s, 780m cm^{-1}; λ_{max} (EtOH) 201.1 (ε 14971), 202.2 (ε 15641), 269.0 (ε 12659) and 356.6 (ε 29334) nm.

General procedure for the preparation of the 5-amino-1-aryl-4-(cyanoformimidoyl)-1*H*-imidazoles 3a-c; to a stirred suspension of the formamidine (1.0 g) in either dry ethyl acetate, ethanol or a 1:1 mixture of ethyl acetate and isopropanol, was added DBU (10 drops) and the reaction was monitored by TLC . the solid went into solution and after 1-3 h the product precipitated as an off-white to pale yellow solid. This was filtered, washed with diethyl ether or light petroleum and dried under vacuum to give the title compounds in the yields 85-91%.

5-amino-1-phenyl-4-(cyanoformimidoyl)-1*H*-imidazole 3a : Recristalization of the product from dry chloroform/petroleum ether (1:1) gave pale yellow crystals of 3a (0.9 g, 4.2 mmol, 90%). M.p. 114-116 ^{o}C (decomp.). [Found : C, 64.8; H, 4.2; N, 31.0. $C_{11}H_9N_5$ requires : C, 64.9; H, 4.3; N, 30.4] ; m/z (EI) 212 $(M+1)^+$ 3.9%, 211 $(M)^+$ 14.6%, 159 $[(M+1)-CN]^+$ 14.8%; δ_H (500 MHz, d6-DMSO) 6.68 (br.s, 2H, NH_2), 7.42-7.60 (m, 5H, H9, H10, H11, H12& H13), 7.72 (s, 1H, H2), 11.20 (br. s, 1H, NH) ppm; δ_C (75 MHz, d_6-DMSO) 147.9 (C6), 147.1 (C5), 137.9 (C8), 136.1 (C2), 134.0 (C11), 132.6 (C9 & C13), 128.8 (C10 & C12), 120.5 (C7), 117.6 (C4) ppm; ν_{max} (Nujol mull) 3340s, 3300m, 3250 s, 3180m, 3120m (N-H str.), 2200s (CN str.), 1650s (C=N str.), 1600s (N-H bend), 1580s, 1290m, 1230s, 1170m, 960m, 820s, 780m cm^{-1}; λ_{max} (EtOH) 202.0 (ε 20057), 205.4 (ε 13194), 206.2 (ε 13218), 219.9 (ε 13531), 220.2 (ε 14046), 347.2 (ε 9207) and 347.3 (ε 9017) nm.

5-Amino-1-phenyl-4-(cyanoformimidoyl)-1*H*-imidazole 3b : Recristalization of the product from dry chloroform/petroleum ether, gave white crystals of 3b (0.85 g, 3.7 mmol, 85%). M.p. 136-137 ^{o}C (decomp.). [Found : C, 64.2; H, 4.8; N, 31.0. . $C_{12}H_{11}N_5$ requires : C, 64.0; H, 4.9; N, 31.1 %]; m/z (EI) 226 $(M+1)^+$ 100%, 225 $(M)^+$ 12.6%, 199 $(M-CN)^+$ 22%, 91 $(M-C_5H_4N_5)^+$ 20.8%; δ_H (500 MHz, d6-DMSO) 5.10 (s, 2H, H8), 6.76 (br. s. 2H, NH_2), 7.20-7.38 (m, 6H, H10, H11, H12, H13& H14), 7.42 (s, 1H, H2), 10.88 (br. s, 1H, NH) ppm; δ_C (75 MHz, d_6-DMSO) 148.3 (C6), 147.1 (C5), 140.4 (C9), 136.4 (C2), 132.4 (C12), 131.7 (C11 & C13), 131.2 (C10 & C14), 120.2 (C7), 117.5 (C4), 49.7 (C8); ν_{max} (Nujol mull) 3350s, 4260s, 3180m, 3120m (N-H str.), 2225s (CN str.), 1659s (C=N str.), 1595s (N-H bend), 1550s, 1520n, 1350s, 1300s, 1220s, 1195s, 970s, 940s, 820 cm^{-1}; λ_{max} (EtOH) 207.5 (ε 15935), 208.5 (ε 16015), 225.0 (ε 12222) and 348.4 (ε 10945) nm.

5-Amino-1-(4-methylphenyl)-4-(cyanoformimidoyl)-1*H*-imidazole 3c:

Recristalization of the product from dry diethyl ether (1:1) gave pale green crystals of 3c (0.82 g, 3.8g, mmol, 91%). M.p. 124-125 ^{o}C (decomp.). [Found : C, 59.7; H, 4.9; N, 28.9. $C_{12}H_{11}N_5$ requires : C, 59.8; H, 4.6; N, 29.0%]; m/z (EI) 242 $(M+1)^+$ 22%, 241 $(M)^+$ 55.5%, 240 $(M-1)^+$ 27.3%, 106 $[(M+1)-C_5H_4N_5]^+$ 17%; δ_H (500 MHz, d6-DMSO) 2.54 (s, 3H, CH_3), 6.72 (br.s, 2H, NH_2), 7.22 (d, 2H, $^3J_{10,9}$ 8 Hz, H10 &H12), 7.46 (s, 1H, H2), 7.54 (d, 2H, $^3J_{13,12}$ 8Hz, H9 & H13), 11.12 (br. s, 1H, NH) ppm ; δ_C (75 MHz, d_6-DMSO) 163.5 (C6), 148.3 (C11), 147.2 (C5), 136.5 (C2), 130.6 (C9 & C13), 130.6 (C8), 120.3 (C7), 119.2 (C10 & C12), 117.5 (C4), 34.4 (C14) ppm; ν_{max} (Nujol mull) 3420m, 3260s, 3120m (N-H srr.), 2230s (CN str.), 1635m (C=N str.), 1600s (N-H bend), 1580s, 1550s, 1525s, 1250s, 1180m, 1170m, 1015s, 930s, 800m cm^{-1}; λ_{max} (EtOH) 201.8 (ε 22405), 205.0 (ε 13933), 205.5 (ε 14021), 206.2 (ε 13977), 211.9 (ε 11736), 227.3 (ε 16098), 228.1 (ε 15539), 348.1 (ε 9722) and 348.5 (ε 9571) nm.

General procedure for the preparation of the 5-Amino-1-aryl-4-cyanoimidazoles 4a-c;

An aqueous solution of 1M potassium hydroxide (1cm^3) was added to a suspension of the formamidine (0.5 g) in ethanol (1cm^3) and the mixture was stirred at room temperature for approximately 1h. the white solid which precipitated was washed with water, a few drops of ethanol and finally diethyl ether before drying under vacuum. The yields of these reactions were 75-90%.

5-Amino-1-phenyl-4-cyanoimidazole 4a :

Recristalization of the product from mixture of dry diethyl ether/ethanol (10:1) gave off-white solid of 4a (0.38 g, 2.07 mmol, 90%). M.p. 194-196 ^{o}C (decomp.). [Found : C, 65.1; H, 4.6; N, 30.4 . $C_{10}H_8N_4$ requires : C, 65.2; H, 4.3; N, 30.4%] : m/z (EI) 185 $(M+1)^+$ 5.8%, 184 $(M)^+$ 24%, 77 $(M-C_4H_3N_4)^+$ 12%; δ_H (500 MHz, d6-DMSO) 6.20 (s, 2H, NH_2), 7.42 (s, 1H, H2), 7.48-7.68 (m, 5H, H8, H9, H10, H11 & H12) ppm; δ_C (75 MHz, d_6-DMSO) 151.2 (C5), 137.9 (C2), 136.6 (C7), 133.8 (C10), 132.6 (C9& C11), 129.3 (C8 & C12), 121.1 (C6), 95.0 (C4) ppm; ν_{max} (Nujol mull) 3370m, 3300s, 3180s, 3110m, (N-H str.), 2210s (CN str.), 1680s (C=N str.), 1600s (N-H bend), 1530s, 1265s, 1230s, 1100s, 915s, 780s, 755s cm^{-1}; λ_{max} (EtOH) 202.7 (ε 16643), 223.8 (ε 16407), 248.0 (ε 11075) and 346.2 (ε 177) nm.

5-Amino-1-benzyl-4-cyanoimidazole 4b :

Recristalization of the product from mixture of dry diethyl ether/ethanol (10:1) gave off-white solid of 4b (0.36 g, 1.8 mmol, 82%). M.p. 197-198 ^{o}C (decomp.). [Found : C, 66.7; H, 5.3; N, 28.3 . Calc. for $C_{11}H_{10}N_4$: C, 66.7; H, 5.1; N, 28.3%] ; m/z (EI) 199 $(M+1)^+$ 100%, 198 $(M)^+$ 4.5%, 108 $[(M+1)-C_7H_7]^+$ 9.6%; δ_H (500 MHz, d6-DMSO) 5.12 (s, 2H, CH_2), 6.42 (s, 2H, NH_2), 7.22-7.28 (m, 2H, H10 & H12), 7.32 (s, 1H, H2), 7.34-7.48 (m, 3H, H9, H11 & H13) ppm ; δ_C (75 MHz, d_6-DMSO) 152.6 (C5), 140.3 (C8), 136.7 (C2), 132.4 (C11), 131.6 (C10 & C12), 131.5 (C13 & C9), 121.4 (C6), 94.2 (C4), 49.9 (C7) ppm ; ν_{max} (Nujol mull) 3380 s, 3340w, 3200s, 3100w (N-H str.), 2200s (CN str.), 1650s (C=N str.), 1590s (N-H bend), 1530 s, 1180s, 1000s, 850m, 800s cm^{-1}; λ_{max} (EtOH) 202.2 (ε 13538), 245.7 (ε 12771) and 340.0 (ε 250) nm.

5-Amino-1-(4-methylphenyl)-4-cyanoimidazole 4c : Recristalization of the product from mixture of dry diethyl ether/ethanol (10 : 1) gave white solid of 4c (0.33 g, 1.68 mmol, 75%). M.p. 167-169 ^{o}C (decomp.). [Found : C, 66.3; H, 5.2; N, 28.8 . $C_{11}H_{10}N_4$ requires : C, 66.7; H, 5.1; N, 28.3%] ; m/z (EI) 198 $(M)^+$ 100%, 91 $(M-C_4H_3N_4)^+$ 4.0%; δ_H (500 MHz, d6-DMSO) 2.42 (s, 3H, CH_3), 6.12 (s, 2H, NH_2), 7.14 (d, 2H, $^3J_{8,9}$ 9Hz, H9 & H11), 7.39 (d, 2H, $^3J_{12,11}$ 9Hz, H8 & H12), 7.41 (s, 1H, H2) ppm ; δ_C (75 MHz, d_6-DMSO) 163.4 (C10), 151.5 (C5), 136.8 (C2), 131.1 (C8& C12), 130.5 (C7), 121.4 (C6), 119.4

(C9& C11), 94.2 (C4), 35.6 (C13) ppm ; ν_{max} (Nujol mull) 3360 w, 3340s, 3200s, 3170m (N-H str.), 2240s (CN str.), 1650s (C=N str.), 1580s (N-H bend), 1530s, 1260s, 960s, 810s cm^{-1} ; λ_{max} (EtOH) 202.5 (ε 12808) and 232.8 (ε 13632) nm.

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