Tetrahedron Letters 50 (2009) 6264–6267

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Novel synthesis of 2,4-bis(2-pyridyl)-5-(pyridyl)imidazoles and formation of *N*-(3-(pyridyl)imidazo[1,5-*a*]pyridine)picolinamidines: nitrogen-rich ligands

Vijendra Kumar Fulwa, Rojalin Sahu, Himanshu Sekhar Jena, Vadivelu Manivannan *

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781 039, India

ARTICLE INFO

Article history:
Received 7 August 2009
Revised 27 August 2009
Accepted 1 September 2009
Available online 4 September 2009

Keywords:
Imidazole
Imidazo[1,5-*a*]pyridine
Ligand
Amidine

ABSTRACT

Heating a neat 1:2 mixture of 2-picolylamine and 2-cyanopyridine followed by treatment of the resultant red gummy substance with aqueous KOH resulted in the isolation of 2,4,5-tris(2-pyridyl)imidazole (**1a**) as the major product and *N*-(3-(2-pyridyl)imidazo[1,5-*a*]pyridine)picolinamidine (**2a**) in small amounts. Similarly, by using 3-picolylamine, 2,4,-bis(2-pyridyl)-5-(3-pyridyl)imidazole (**1b**) and *N*-(3-(3-pyridyl)imidazo[1,5-*a*]pyridine)picolinamidine (**2b**) were isolated, and by using 4-picolylamine, 2,4,-bis(2-pyridyl)-5-(4-pyridyl)imidazole (**1c**) and *N*-(3-(4-pyridyl)imidazo[1,5-*a*]pyridine)picolinamidine (**2c**) were isolated. The plausible mechanism of the formation of **1a–c** and **2a–c** is delineated.

The imidazole ring system is an important function in biology, chemistry as well as in pharmaceutical, veterinary, and agrochemical products.[1–4] They are useful ligands in coordination chemistry and the synthesis of the compounds containing the imidazole ring is an important area of scientific investigation.[1–3] Multicomponent reaction (MCR) methods involving the isocyanides as one of the components for the synthesis of imidazole derivatives have been reviewed.[5] The synthesis of the 1,2,4-trisubstituted imidazole by palladium-catalyzed cyclization of *O*-pentafluorobenzoylamidoximes is reported.[6] Addition reaction of imidazolium ylides to electron-deficient imines is a useful method for the synthesis of 2-(α-substituted-amidoalkyl)imidazoles.[7] An efficient, mild one-pot method for preparing polysubstituted imidazoles from aryl-substituted tosylmethyl isocyanide (TosMIC) reagents and in situ generated imines[8] as well as a new synthetic approach for the synthesis of chiral imidazoles using thio-Ugi reaction[9] have been reported. The synthesis of the annulated terpene-imidazole,[10] a microwave assisted organic synthesis (MAOS) method for the synthesis of 2,4,5-triaryl-imidazole[11a] as well as the synthesis, and p38 MAP kinase inhibitor property[11b] have been described.

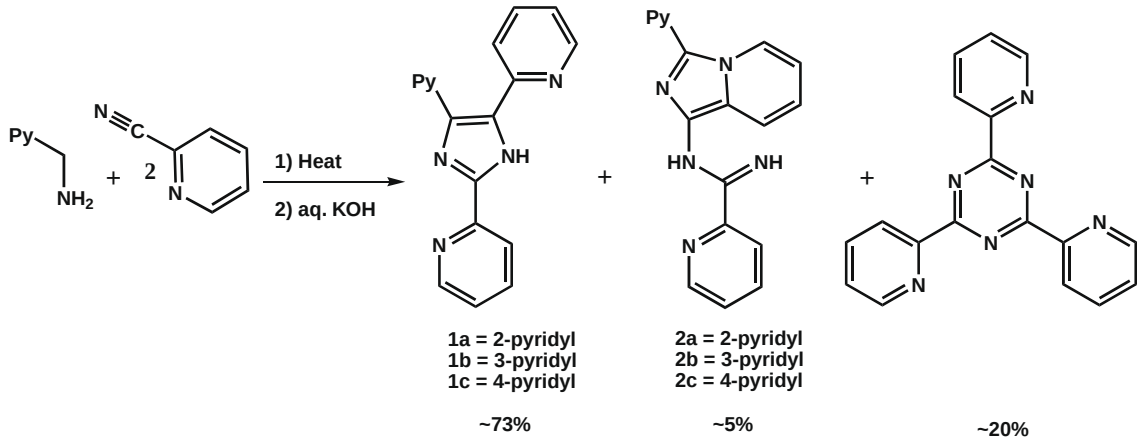
We recently described the $Cu(NO_3)_2{\cdot}3H_2O$-mediated conversion of the Schiff base *N*-(2-pyridylmethyl)pyridine-2-methylketimine to 4′-(2-pyridyl)-2,2′:6′,2″-terpyridine and have continuing interest in the synthesis of nitrogen-rich ligands.[12] In this Letter we report a facile formation of 2,4-bis(2-pyridyl)-5-(pyridyl)imidazoles (**1a–c**) using a simple two-component method. In addition the details of the other minor product, *N*-(3-(pyridyl)imidazo[1,5-*a*]pyridine)picolinamidines (**2a–c**) formed in this reaction are described. The synthesis of compounds containing the imidazo[1,5-*a*]pyridine ring is another general area of research.[13,14] Formation of the varying amounts of 2,4,5-trisubstituted imidazole and imidazo[1,5-*a*]pyridine ring systems from 2,2′-pyridil, aromatic aldehyde, ammonium acetate, and acetic acid is relevant to mention.[13]

Heating a neat 1:2 mixture of 2-picolylamine and 2-cyanopyridine at 100 °C, followed by the treatment of the resultant red gummy substance with alkali resulted in the formation of 2,4,5-tris(2-pyridyl)imidazole (**1a**) and *N*-(3-(2-pyridyl)imidazo[1,5-*a*]pyridine) picolinamidine (**2a**) (Scheme 1).[15] From the alkaline solution, **2a** and 2,4,6-tris(2-pyridyl)1,3,5-triazine (**3**), which precipitated were separated by filtration, while **1a** remained dissolved in the solution. On adjusting the pH of the aqueous solution to 7–8, **1a** separated as a yellow gel-like substance, which afforded yellow crystals from the ether medium. Since the formation of the triazine ring from cyanopyridines is already well established,[16] we limit our discussion only to **1a** and **2a**. Formation of these two compounds is believed to involve the presence of intermediate adducts **IA** and **IIA** (in Schemes 2 and 3), which may be present in major and minor quantities. In addition **3** could have formed at this stage. In the aqueous solution of KOH, **IA** and **IIA**, respectively, lead to the generation of the imidazole nucleus and to the imidazo[1,5-*a*]pyridine ring systems.

The plausible intermediates involved in the formation of **1a** are depicted in Scheme 2. One molecule of 2-cyanopyridine forms an adduct with 2-picolylamine leading to an amidine, which in turn forms an adduct with another molecule of 2-cyanopyridine through the $-NH_2$ nitrogen atom of the amidine function. One of the methylene hydrogen atoms in **IA** is removed by the base to generate **IB**; then the negative charge attacks the carbon atom of

* Corresponding author. Tel.: +91 361 258 2306; fax: +91 361 258 2349.
E-mail address: mani@iitg.ernet.in (V. Manivannan).

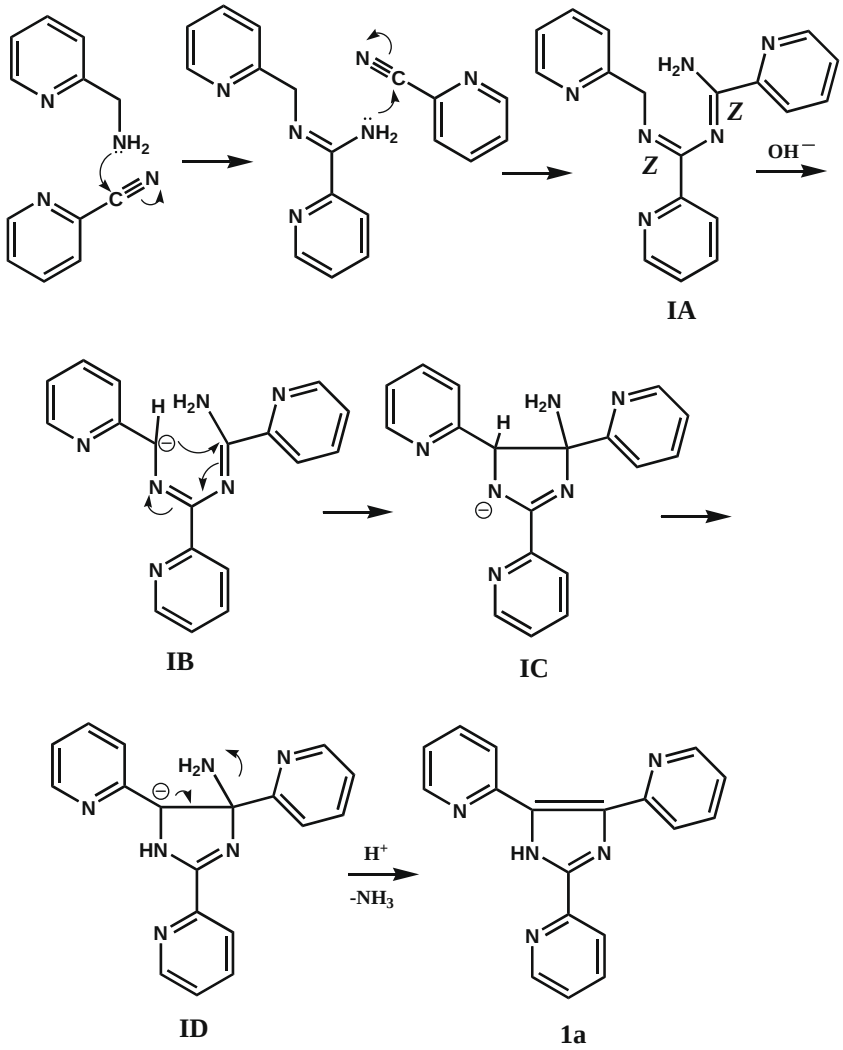
0040-4039/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2009.09.002



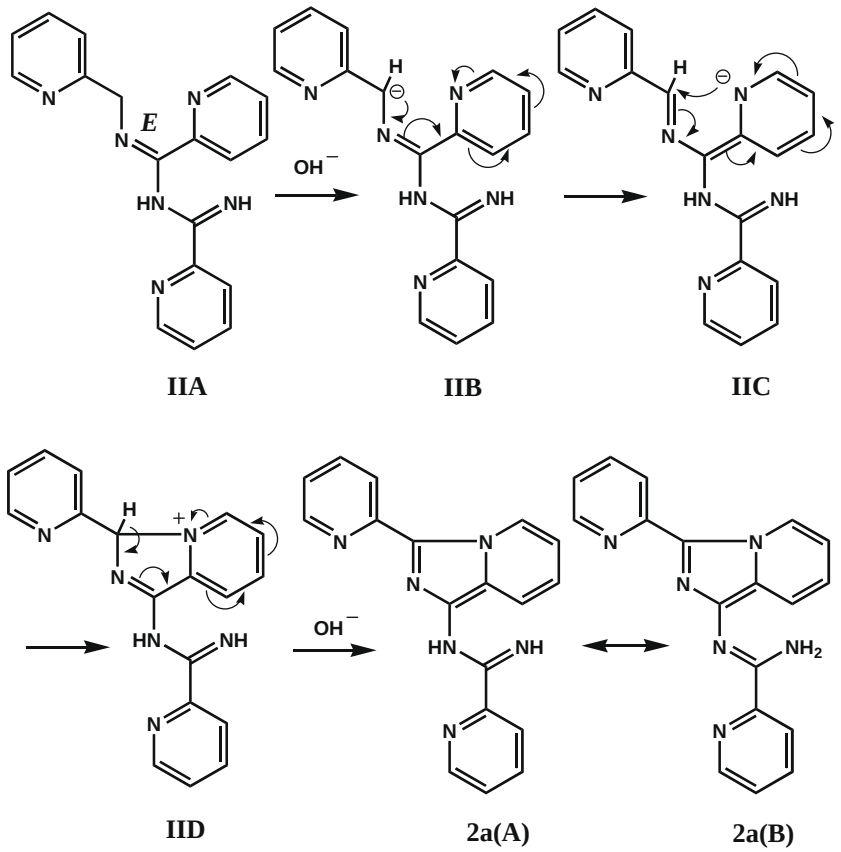
Scheme 1. Synthesis of **1a–c** and **2a–c**. Legend inside the scheme is for the substituent Py.

the amidine function that leads to the formation of the five-membered central ring in **IC**. The proton shift occurs in **IC** that leads to **ID**, from which elimination of one molecule of NH_3 occurs, resulting in the formation of **1a** as the final product. The presence of strong ammonia stench in the reaction mixture is consistent with its evolution noted in the final step. It is pertinent to note that a low-yielding method of preparation of **1a** by the reduction of 2-cyanopyridine with sodium borohydride was described earlier.[17]

^{1}H and ^{13}C NMR spectra of **1a** are consistent with the structure. The ESI mass spectrum shows the presence of a characteristic



Scheme 2.



Scheme 3.

M^++H peak at $m/z = 300$. The single crystal X-ray structure was established[18] and a perspective view of **1a** is shown in Figure 1.

Formation of the small quantities of **2a** is interesting, which has separated as a solid from the basic reaction mixture. Pure fibrous solids of **2a** were obtained after chromatographic separation on basic alumina using 3:7 ethyl acetate–hexane mixtures. Probable intermediates involved are represented in Scheme 3.

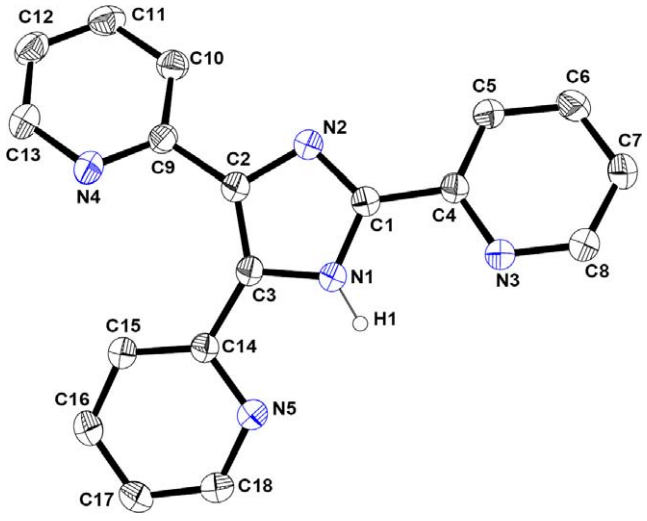


Figure 1. ORTEP (30% probability) diagram of **1a**. All the hydrogen atoms except H1 were omitted for clarity. Selected distances, Å: N1–C1 1.3462(16), N1–C3 1.3702(16), N2–C1 1.3256(15), N2–C2 1.3832 (15), C1–C2 1.3434(15).

The intermediate **IIA** (*E*) is a geometrical isomer of **IA** (*Z*) with respect to –N=C< group attached to the methylene group and hence the 2-pyridyl ring instead of the amidine group is in the vicinity of the methylene group. Abstraction of a proton from the methylene group generates a negative charge which is delocalized into the 2-pyridyl ring as shown in **IIB**. This leads to the concentration of electron density on the nitrogen atom of 2-pyridyl ring, **IIC**. The resultant negative charge on the nitrogen atom attacks the sp^2 carbon and generates the fused five-membered ring in **IID**. The proton abstraction by a base in **IID** leads to the formation of **2a** that contains the imidazo[1,5-*a*]pyridine nucleus, which could exist in two tautomeric forms **2a**(**A**) and **2a**(**B**). The ^{1}H NMR spectrum shows two broad signals for the NH protons and therefore is consistent with the **2a**(**A**) form.[19] A double triplet at $\delta = 6.81$, 6.85 ppm in the ^{1}H NMR, and the presence of M^++H peak at $m/z = 315$ in the ESI mass spectra of **2a** are characteristic.

Under the same experimental conditions and using the same quantities of the respective reagents, the reaction proceeded very well with 3- and 4-picolylamines.[20] The products isolated using 3-picolylamine are 2,4,-bis(2-pyridyl)-5-(3-pyridyl)imidazole (**1b**) and *N*-(3-(3-pyridyl)imidazo[1,5-*a*]pyridine)picolinamidine (**2b**). With 4-picolylamine, 2,4,-bis(2-pyridyl)-5-(4-pyridyl)imidazole (**1c**) and *N*-(3-(4-pyridyl)imidazo[1,5-*a*]pyridine)picolinamidine (**2c**) were isolated in similar yields. The ^{1}H, ^{13}C NMR, and ESI mass spectra of **1b**, **1c**, **2b,** and **2c** are in accordance with the structures.

In conclusion, we have described an efficient and simple two-component method for the synthesis of 2,4-bis(2-pyridyl)-5-(pyridyl)imidazoles (**1a**–**c**) and for the formation of *N*-(3-(pyridyl) imidazo[1,5-*a*]pyridine)picolinamidines (**2a**–**c**) in small amounts as the minor product. This method could provide insights into the synthesis of derivatives of the imidazole as well as the substituted

imidazo[1,5-*a*]pyridine nucleus. Our investigations in this regard and the coordination chemistry of these ligands are in progress.

Acknowledgments

We are grateful to the Council of Scientific and Industrial Research (CSIR), New Delhi, for financial grant and the Department of Science and Technology (DST), New Delhi, for establishing single crystal X-ray diffractometer facility under FIST scheme. The authors are thankful to Mr. Babulal Das for the X-ray data.

Supplementary data

CIF for **1a** and ^{1}H NMR, ^{13}C NMR, and ESI Mass spectra of **1a–c** and **2a–c**. Crystallographic data (excluding structure factors) for the structure **1a** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 742608. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.09.002.

References and notes

1. Grimmett, M. R.. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Ress, C. W., Scriven, E. F. V., Eds.; Pergamon Press: Oxford, 1996; Vol. 3, pp 77–220.
2. (a) Grimmett, M. R. *Imidazole and Benzimidazole Synthesis*; Academic Press: New York, 1997, 1997. and references therein; (b) Grimmett, M. R. *Adv. Heterocycl. Chem.* **1970**, *12*, 103–183.
3. Novelli, A.; De Santis, A. *Tetrahedron Lett.* **1967**, *8*, 265–269.
4. Huang, N.; Xi, Q.; Liu, L.. In *Comprehensive Heterocyclic Chemistry III*; Katritzky, A., Ramsden, C., Scriven, E., Taylor, R., Eds.; Elsevier, 2008; Vol. 4, pp 143–364.
5. (a) Dömling, A. *Chem. Rev.* **2006**, *106*, 17–89; (b) Dömling, A.; Ugi, I. *Angew. Chem., Int. Ed.* **2000**, *39*, 3168–3210.
6. Zaman, S.; Mitsuru, K.; Abell, A. D. *Org. Lett.* **2005**, *7*, 609–611.
7. Zificsak, C. A.; Hlasta, D. J. *Tetrahedron Lett.* **2005**, *46*, 4789–4792.
8. (a) Sisko, J.; Mellinger, M. *Pure Appl. Chem.* **2002**, *74*, 1349–1357; (b) Sisko, J.; Kassick, A. J.; Mellinger, M.; Filan, J. J.; Allen, A.; Olsen, M. A. *J. Org. Chem.* **2000**, *65*, 1516–1524; (c) Sisko, J. *J. Org. Chem.* **1998**, *63*, 4529–4531.
9. Gulevich, A. V.; Balenkova, E. S.; Nenajdenko, V. G. *J. Org. Chem.* **2007**, *72*, 7878–7885.
10. Kulhánek, J.; Bureš, F.; Šimon, P.; Schweizer, W. B. *Tetrahedron: Asymmetry* **2008**, *19*, 2462–2469.
11. (a) Sparks, R. B.; Combs, A. P. *Org. Lett.* **2004**, *6*, 2473–2475; (b) Boehm, J. C.; Smietana, J. M.; Sorenson, M. E.; Garigipati, R. S.; Gallagher, T. F.; Sheldrake, P. L.; Bradbeer, J.; Badger, A. M.; Laydon, J. T.; Lee, J. C.; Hillegass, L. M.; Griswold, D. E.; Breton, J. J.; Chabot-Fletcher, M. C.; Adams, J. L. *J. Med. Chem.* **1996**, *39*, 3929–3937.
12. Padhi, S. K.; Manivannan, V. *Inorg. Chem.* **2006**, *45*, 7994–7996.
13. Wang, J.; Mason, R.; VanDerveer, D.; Feng, K.; Bu, X. R. *J. Org. Chem.* **2003**, *68*, 5415–5418.
14. (a) Shibahara, F.; Sugiura, R.; Yamaguchi, E.; Kitagawa, A.; Murai, T. *J. Org. Chem.* **2009**, *74*, 3566–3568; (b) Salassa, L.; Garino, C.; Albertino, A.; Volpi, G.; Nervi, C.; Gobetto, R.; Hardcastle, K. I. *Organometallics* **2008**, *27*, 1427–1435; (c) Shibahara, F.; Kitagawa, A.; Yamaguchi, E.; Murai, T. *Org. Lett.* **2006**, *8*, 5621–5624; (d) Wang, J.; Dyers, L.; Mason, R., Jr.; Amoyaw, P., Jr.; Bu, X. R. *J. Org. Chem.* **2005**, *70*, 2353–2356; (e) Katritzky, A. R.; Qiu, G. *J. Org. Chem.* **2001**, *66*, 2862–2864; (f) Sasaki, K.; Tsurumori, A.; Hirota, T. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3851–3856; (g) Krapcho, A. P.; Powell, J. R. *Tetrahedron Lett.* **1986**, *27*, 3713–3714.
15. *Synthesis:* 2-Picolylamine (1 g, 9.26 mmol) and 2-cyanopyridine (1.93 g, 18.6 mmol) were heated at 100 °C in an oil-bath for 12 h. The resultant red gummy oil was suspended in 30 mL of water, KOH (3.11 g, 55.6 mmol) was added and stirred for 12 h. The yellow solid obtained was filtered, washed with water and dried in vacuum over fused $CaCl_2$. The dry solid was subjected to chromatographic separation using basic alumina column. Firstly compound **2a** was eluted with ethyl acetate–hexane (3:7) mixture and the yellow fibrous solid of **2a** was obtained after removal of the solvents. Yield: 150 mg (5%). Then tris(2-pyridyl)triazine (**3**) was eluted using methanol. Yield: 390 mg (20%). The filtrate had a strong ammonia smell, the pH of which was adjusted to 7–8 using 5 M HCl. **1a** separated as yellow gel-like substance and was separated from the aqueous solution by decantation. The gel on crystallization from ether afforded single-crystals suitable for X-ray diffraction studies. Yield: 1.42 g. The decanted aqueous solution was extracted with ether affording another crop of **1a**. Yield: 600 mg, which was recrystallized from ether. Combined yield of **1a**: 73% *2,4,5-Tris(2-pyridyl)imidazole* (**1a**): mp 144 °C; ESI-MS: *m/z* calcd for $C_{18}H_{13}N_5^+$ 299.117 found (M^++H) 300.114. 400 MHz ^{1}H NMR (δ (*J*, Hz), $CDCl_3$): 11.4 (1NH, s), 8.69 (1H, d, 4.8), 8.61 (2H, d, 4.4), 8.54 (1H, d, 8.0), 8.29 (1H, d, 8.0), 8.09 (1H, d, 7.6), 7.80 (2H, dd, 7.5), 7.65 (1H, t, 7.6), 7.27 (2H, dd, 4.8), 7.17 (1H, t, 6.2). 100 MHz ^{13}C NMR (δ, $CDCl_3$): 148.9, 148.7, 148.4, 147.8, 145.3, 136.6, 136.4, 136.1, 123.2, 122.4, 122.0, 120.0. FTIR (KBr, cm^{-1}): 3439, 3053, 1586, 1566, 1530, 1478, 1452, 1435, 1422, 1387, 1291, 1274, 1250, 1212, 1151, 1119, 1075, 1042, 993, 980, 968, 897, 800, 789, 776, 737, 716, 696, 658, 626, 605, 552, 507, 486, 413, 400. *N-(3-(2-Pyridyl)imidazo[1,5-a]pyridine)picolinamidine* (**2a**): mp 186 °C. ESI-MS: *m/z* calcd for $C_{18}H_{14}N_6^+$ 314.128 found (M^++H) 315.135. R_f = 0.66. 400 MHz ^{1}H NMR (δ (*J*, Hz), $CDCl_3$): 9.94 (1H, d, 7.2), 9.32 (1NH, s), 8.63 (3H, m), 8.28 (1H, d, 8.0), 7.99 (1H, d, 8.8), 7.80 (2H, qu, 8.0), 7.51 (1NH, s), 7.35 (1H, t, 5.6), 7.15 (1H, t, 5.6), 6.85 (1H, t, 7.6), 6.81 (1H, t, 6.4). 100 MHz ^{13}C NMR (δ, $CDCl_3$): 152.9, 151.3, 151.2, 148.4, 148.2, 140.7, 136.6, 136.5, 130.0, 127.5, 125.4, 124.5, 121.7, 121.6, 121.0, 118.9, 118.7, 115.2. FTIR (KBr, cm^{-1}): 3366, 3250, 3058, 1689, 1621, 1587, 1563, 1542, 1495, 1469, 1454, 1429, 1397, 1252, 1190, 1137, 1090, 1048, 995, 879, 816, 785, 747, 730, 700, 685, 622, 594, 460, 421, 404. Anal. Calcd for $C_{18}H_{14}N_6$: C, 68.78; H, 4.49; N, 26.74. Found: C, 68.71; H, 4.44; N, 26.68.
16. Case, F. H.; Koft, E. *J. Am. Chem. Soc.* **1959**, *81*, 905–906.
17. Yamada, S.; Kuramoto, M.; Kikugawa, Y. *Tetrahedron Lett.* **1969**, *10*, 3101–3104.
18. X-ray diffraction data: **1a** (296(2) K, Mo Kα): $C_{18}H_{13}N_5$, 299.33, $P2_1/c$, a = 16.3582(6), b = 11.5830(4), c = 7.6079(3) Å, β = 92.996(2)°, V = 1439.55(9) Å^3, Z = 4, D_c = 1.381 g cm^{-3}, μ = 0.87 mm^{-1}, $F(0\,0\,0)$ = 624, R_{int} = 0.0336, R_1 ($I > 2\sigma$) = 0.0425, wR_2 ($I > 2\sigma$) = 0.1140 (260 param., 2832 obsd refl., 3958 unique).
19. We could obtain a very weakly diffracting crystals of Ni(II) complex of **2a** and from the data, only the structure of **2a** could be ascertained.
20. *2,4,-Bis(2-pyridyl)-5-(3-pyridyl)imidazole* (**1b**): Yield: 2.05 g, 75% mp 193 °C; ESI-MS: *m/z* calcd for $C_{18}H_{13}N_5^+$ 299.117 found (M^++H) 300.124. 400 MHz ^{1}H NMR (δ (*J*, Hz), $CDCl_3$): 11.3 (1NH, s), 8.95 (1H, s), 8.63 (3H, m), 8.25 (1H, d, 8.0), 8.07 (1H, d, 8.0), 7.80 (1H, t, 7.8), 7.55 (1H, t, 7.8), 7.41 (2H, m), 7.30 (1H, t, 6.2), 7.16 (1H, t, 6.2). 100 MHz ^{13}C NMR (δ, $CDCl_3$): 149.9, 149.2, 148.9, 148.1, 146.7, 137.2, 136.7, 136.5, 123.7, 122.4, 120.6. FTIR (KBr, cm^{-1}): 3458, 1641, 1625, 1590, 1562, 1530, 1502, 1472, 1438, 1389, 1321, 1302, 1254, 1181, 1140, 1097, 1029, 955, 797, 727, 702, 624. Anal. Calcd for $C_{18}H_{13}N_5$: C, 72.23; H, 4.38; N, 23.40. Found: C, 72.15; H, 4.36; N, 23.36. *N-(3-(3-Pyridyl)imidazo[1,5-a]pyridine)picolinamidine* (**2b**): Yield: 150 mg, 5% mp 195 °C; ESI-MS: *m/z* calcd for $C_{18}H_{14}N_6^+$ 314.128 found (M^++H) 315.135. R_f = 0.64. 400 MHz ^{1}H NMR (δ (*J*, Hz), $CDCl_3$): 9.21 (1NH, s), 9.14 (1H, s), 8.63 (2H, m), 8.22 (1H, d, 8.0), 8.17 (1H, d, 12.0), 7.95 (1H, d, 11.2), 7.82 (1H, t, 8.8), 7.46 (2H, dd, 7.0), 7.35 (1H, t, 6.6), 6.74 (1H, t, 8.0), 6.67 (1H, t, 7.6). 100 MHz ^{13}C NMR (δ, $CDCl_3$): 152.8, 151.3, 149.0, 148.6, 148.2, 141.4, 136.6, 134.8, 129.8, 127.1, 126.2, 124.6, 123.9, 121.7, 120.1, 120.0, 117.4, 115.5. FTIR (KBr, cm^{-1}): 3414, 3052, 2853, 1651, 1589, 1562, 1489, 1469, 1447, 1427, 1393, 1289, 1263, 1185, 1137, 1090, 1084, 1046, 1025, 995, 967, 847, 790, 743, 719, 700, 621, 500. Anal. Calcd for $C_{18}H_{14}N_6$: C, 68.78; H, 4.49; N, 26.74. Found: C, 68.68; H, 4.42; N, 26.70. *2,4,-Bis(2-pyridyl)-5-(4-pyridyl)imidazole* (**1c**): Yield: 2.02 g, 73% mp 196 °C; ESI-MS: *m/z* calcd for $C_{18}H_{13}N_5^+$ 299.117 found (M^++H) 300.123. 400 MHz ^{1}H NMR (δ (*J*, Hz), $CDCl_3$): 11.41 (1NH, s), 8.66 (2H, m), 8.59 (2H, d, 4.0), 8.25 (1H, d, 8.0), 7.81 (1H, t, 7.2), 7.68 (2H, d, 5.2), 7.60 (1H, t, 7.4), 7.53 (1H, d, 7.6), 7.30 (1H, t, 7.6), 7.20 (1H, t, 6.0). 100 MHz ^{13}C NMR (δ, $CDCl_3$): 149.8, 149.7, 149.0, 147.9, 146.8, 137.1, 136.6, 124.0, 123.0, 122.5, 121.5, 120.5. FTIR (KBr, cm^{-1}): 3498, 3218, 1644, 1608, 1574, 1567, 1496, 1471, 1447, 1418, 1398, 1332, 1320, 1293, 1272, 1246, 1218, 1143, 1105, 1090, 1049, 1001, 994, 917, 822, 807, 790, 764, 754, 738, 720, 705, 683, 666, 632, 612, 547, 520, 498, 459. Anal. Calcd for $C_{18}H_{13}N_5$: C, 72.23; H, 4.38; N, 23.40. Found: C, 72.17; H, 4.33; N, 23.34. *N-(3-(4-Pyridyl)imidazo[1,5-a]pyridine)picolinamidine* (**2c**): Yield: 135 mg, 4.5% mp 183 °C; ESI-MS: *m/z* calcd for $C_{18}H_{14}N_6^+$ 314.13 found (M^++H) 315.14. R_f = 0.60. 400 MHz ^{1}H NMR (δ (*J*, Hz), $CDCl_3$): 9.19 (1NH, s), 8.70 (2H, d, 6.0), 8.57 (2H, d, 8.8), 8.34 (1H, d, 7.2), 7.95 (1H, d, 10.0), 7.77 (3H, m), 7.48 (1NH, s), 7.34 (1H, t, 6.8), 6.79 (1H, t, 8.0), 6.74 (1H, t, 6.8). 100 MHz ^{13}C NMR (δ, $CDCl_3$): 152.7, 151.6, 150.6, 148.2, 141.9, 137.7, 136.6, 129.7, 127.2, 124.7, 121.7, 120.8, 120.7, 120.1, 118.0, 116.0. FTIR (KBr, cm^{-1}): 3438, 3305, 1643, 1624, 1598, 1564, 1527, 1497, 1472, 1454, 1325, 1289, 1247, 1218, 1182, 1112, 998, 961, 815, 800, 724, 703, 658, 507, 484. Anal. Calcd for $C_{18}H_{14}N_6$: C, 68.78; H, 4.49; N, 26.74. Found: C, 68.70; H, 4.40; N, 26.65.