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Article

Catalyst- and Solvent-free Synthesis of Imidazo[1,2-*a*]pyridines

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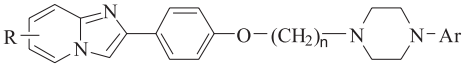
Um método altamente eficiente e simples foi descrito para a síntese de imidazo[1,2-*a*]piridinas pela condensação de α-halocetonas ($ArCOCHXR^2$, Ar = C_6H_5, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2,4-$Cl_2C_6H_3$; X = Br, Cl; R^2 = H, CH_3) com 2-aminopiridinas, apresentando rendimentos entre bons a excelentes sem a necessidade de adição de catalisador e solvente.

A highly efficient and facile method has been described for the synthesis of imidazo[1,2-*a*] pyridines in good to excellent yields by condensation of the α-haloketones ($ArCOCHXR^2$, Ar = C_6H_5, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2,4-$Cl_2C_6H_3$; X = Br, Cl; R^2 = H, CH_3) with 2-aminopyridines without the use of any additional catalyst and solvent.

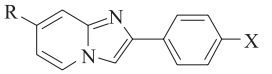
Keywords: imidazo[1,2-*a*]pyridines, α-haloketones, 2-aminopyridines, catalyst-free, solvent-free

Introduction

It has long been known that imidazo[1,2-*a*]pyridine derivatives exhibit diverse biological activities[1] and were used as antiviral,[2] antiulcer,[3] antibacterial,[4] antifungal,[5] antiprotozoal,[6] antiherpes,[7] anti-inflammatory.[8] Recently, Leopoldo *et al.*[9] reported synthetic approaches leading to 4-[ω-[4-arylpiperazin-1-yl]alkoxy]phenyl) imidazo[1,2-*a*] pyridine derivatives (Figure 1, **I**), which were described as fluorescent high-affinity dopamine D_3 receptor ligands as potential probes for receptor visualization, and the fluorescent moiety compound 2-(4-methoxyphenyl) imidazo[1,2-*a*]pyridine (Figure 1, **II**), which is characterized by the 2-phenylimidazo[1,2-*a*]pyridine moiety, presented an oxygen that can be easily functionalized to afford potential D_3 receptor ligands structurally related to the D_3 receptor ligands.[10] The majority of reported imidazo[1,2-*a*]pyridines syntheses proceeded from the condensation reaction of the α-bromocarbonyl compounds with 2-aminopyridine derivative under neutral[11] or weak basic conditions.[12] A mechanism for the reaction has been proposed,[13] which includes the nucleophilic substitution of the bromide by the pyridine-nitrogen in the 2-aminopyridine derivative. Imidazo[1,2-*a*]pyridine derivatives were also synthesized by solid support[14] and using catalyst such as Al_2O_3[15] and $TiCl_4$.[16] Other methodologies included treating 2-aminopyridines with α-tosyloxyketones,[17] a polymer supported [hydroxy(sulfonyloxy)iodo]benzene with ketones or alcohols,[18] alkynyl(phenyl)iodonium salts,[19] α-diazoketones,[20] and propargyl bromide.[21] Although these methods are suitable for certain synthetic conditions sometimes, however, some of these procedures are associated with one or more disadvantages such as hazardous organic solvents, high cost, long reaction time, low yield, use of stoichiometric and even excess amounts of reagents or catalysts, special apparatus and drastic reaction conditions, which leaves scope for further development of new environmentally clean syntheses.



I: n = 3, 4



II: R = H, X = OCH_3

III: R = X = H

Figure 1.

As the increase in environmental consciousness chemical research and industry,[22] the challenge for a sustainable environment calls for clean procedures that can avoid using harmful organic solvents, or even better, do not

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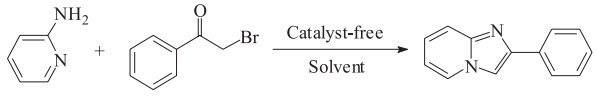
need solvent at all. In continuation of our interest in green chemistry,[23] we herein wish to report the neat reaction of 2-aminopyridine with α-haloketones under catalyst- and solvent-free conditions, affording imidazo[1,2-*a*]pyridine derivatives in good to excellent yields.

Results and Discussion

To optimize the reaction conditions, initial studies were concentrated on reactions of the α-bromoacetophenone with 2-aminopyridine as a model reaction. After careful screening, to our delight, the reaction occurred for 20 min affording 2-phenylimidazo[1,2-*a*]pyridine (**3a**) in 91% yield at 60 °C in the absence of catalyst and solvent (Table 1, entry 11). It was observed that the mixture was initially in a solid state, and then turned to liquid state during the process of stirring, finally solidified to a light yellow solid mass.

Table 1. The condensation of 2-aminopyridine with α-bromoacetophenone under different reaction conditions[a]



Entry	Solvent	T / (°C)	Yield / (%)[b]
1	*n*-Hexane	60	48
2	CCl_4	60	45
3	Toluene	60	50
4	CH_2Cl_2	60	53
5	THF	60	65
6	CH_3CN	60	59
7	C_2H_5OH	60	60
8	CH_3OH	60	63
9	PEG-400	60	60
10	H_2O	60	63
11	none	60	91
12	none	25	65[c]

[a]Reaction conditions: α-bromoacetophenone (1.0 mmol), 2-aminopyridine (1.0 mmol), solvent (1 mL) at 60 °C for 20 min. [b]Isolated yield. [c]The reaction was carried out at room temperature for 24 h.

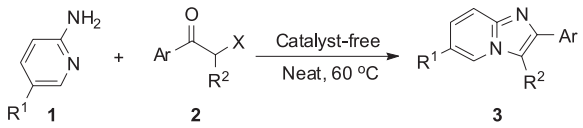
Encouraged by this result, we further carried out comparative reactions to optimize the reaction conditions. The results are summarized in Table 1. When the reaction was carried out at room temperature in the absence of catalyst and solvent, only 65% yield was obtained, even when the reaction time was prolonged to 24 h (Table 1, entry 12). The nonpolar solvents, such as *n*-hexane, toluene, CCl_4 gave lower yields under similar reaction conditions (Table 1, entries 1-3). The polar aprotic solvents (CH_2Cl_2, THF and CH_3CN) also afforded comparatively lower yields (Table 1, entries 4-6). The polar protic solvents (C_2H_5OH, CH_3OH, PEG-400 and H_2O) still gave comparatively lower conversions (Table 1, entries 7-10). It is remarkable that the reaction carried out at 60 °C in the absence of catalyst and solvent afforded **3a** in excellent yield (91%), which is significantly higher than those obtained for the nonpolar or polar solvents. The structure of **3a** was characterized by ^{1}H NMR, ^{13}C NMR, IR and by comparison with authentic samples prepared by literature procedure. The ^{1}H NMR spectra of **3a** shows a characteristic peak at δ 7.87 ppm corresponding to the hydrogen of imidazole ring, whereas in the ^{13}C NMR spectrum, the peak appearing of δ 108.1, 145.7 and 145.8 ppm corresponds to C-3, C-2 and C-9, respectively, of the imidazole ring. And in the IR spectrum, the structure of **3a** showed C=N stretching peak at 1625 cm^{-1}.

With the optimized conditions in hand, the reactions of different 2-aminopyridines with various α-haloketones were examined to explore the scope and generality of this present protocol for the synthesis of various imidazo[1,2-*a*] pyridines (Table 2). As expected, the reaction proceeded smoothly with yields ranging from good to excellent and tolerated various functional groups such as chloro, methyl and methoxy groups.

As shown in Table 2, the α-bromoacetophenone with electron-rich functionality as well as electron-poor functionality undergoes condensation reaction with 2-aminopyridine or substituted 2-aminopyridine equally well to afford the corresponding products in good to excellent yields. Even when employing the hindered α-methylphenacyl bromide and 2-aminopyridine or 2-amino-5-methylpyridine, good yields (Table 2, entries 10-11, 70% and 64%, respectively) were also obtained after slightly prolonging the reaction time to 60 min. Nevertheless, 2-aminopyridine with electron-withdrawing substituted group chloro is less nucleophilic and more slowly than electron-neutral or donating analogues.

Encouraged by our success, we screened a few reactions of the commercially available and deactivated α-chloroketone with 2-aminopyridine or 2-amino-5-methylpyridine. To our delight, when employing α-chloroacetophenone and 2-aminopyridine or 2-amino-5-methylpyridine, excellent yields (Table 2, entries 12-13, 83% and 88%, respectively) were obtained after slightly prolonging the reaction time to 80 min and 40 min, respectively. Furthermore, the *para*- and *ortho*-substituted 2,2',4'-trichloroacetophenone with 2-aminopyridine or 2-amino-5-methylpyridine also can afford the corresponding products **3l** and **3m** in 75% and 65% yields, respectively (Table 2, entries 14-15).

Table 2. Synthesis of imidazo[1,2-*a*]pyridinepyrazoles under catalyst- and solvent-free conditions[a]



Entry	α-Haloketone			R^1	time / min	Product	Yield / (%)[b]	mp / °C
	Ar	X	R^2					
1	C_6H_5	Br	H	H	20	**3a**	91	136-137
2	C_6H_5	Br	H	CH_3	5	**3b**	92	171-173
3	C_6H_5	Br	H	Cl	15	**3c**	90	204-206
4	*p*-$MeOC_6H_4$	Br	H	H	10	**3d**	95	135-136
5	*p*-$MeOC_6H_4$	Br	H	CH_3	5	**3e**	93	179-181
6	*p*-$MeOC_6H_4$	Br	H	Cl	25	**3f**	80	234-236
7	*p*-ClC_6H_4	Br	H	H	15	**3g**	95	207-209
8	*p*-ClC_6H_4	Br	H	CH_3	5	**3h**	91	239-240
9	*p*-ClC_6H_4	Br	H	Cl	130	**3i**	75	205-207
10	C_6H_5	Br	CH_3	H	60	**3j**	70	159-161
11	C_6H_5	Br	CH_3	CH_3	60	**3k**	64	114-116
12	C_6H_5	Cl	H	H	80	**3a**	83	136-137
13	C_6H_5	Cl	H	CH_3	40	**3b**	88	171-173
14	2,4-$Cl_2C_6H_3$	Cl	H	H	50	**3l**	75	181-182
15	2,4-$Cl_2C_6H_3$	Cl	H	CH_3	50	**3m**	65	135-136

[a]Reaction conditions: α-haloketones (1.0 mmol), 2-aminopyridines (1.0 mmol) at 60 °C. [b]Isolated yield.

In summary, we have described a simple, highly efficient, and facile procedure for the synthesis of imidazo[1,2-*a*] pyridine derivatives from the readily available starting materials. To the best of our knowledge, this is the first report catalyst-free synthesis of imidazo[1,2-*a*]pyridines in the absence of solvent under mild conditions. The procedure offers simple experimental procedure, short reaction time, catalyst-free, solvent free, low cost, efficient yield and mild reaction conditions, which makes this method a useful and attractive strategy in view of economic and environmental advantages. Currently, studies on the extension of this protocol are ongoing in our laboratory.

Experimental

All reagents were commercial available and used without any purification. Melting points were recorded on Digital Melting Point Apparatus WRS-1B and are uncorrected. IR spectra were recorded on a Bruker-EQUINOX55 spectrometer. Mass spectra (EI, 70 ev) were measured with SHIMADZU GCMS-QP2010 Plus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker AC 300 instrument using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts were given in δ relative to TMS, the coupling constants *J* are given in Hz. Elemental analysis was determined on a Carlo-Erba 1108 instrument. All reactions were conducted using standard Schlenk techniques. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

General procedure for the preparation of pyrazoles

A mixture of α-haloketone **2** (1.0 mmol), 2-aminopyridine or substituted 2-aminopyridine **1** (1.0 mmol) was stirred at 60 °C under vigorous magnetic stirring for the specified time as mentioned in Table 2. The progress of the reaction was monitored by TLC. After completion of the reaction, the product was washed with dehydrated alcohol or ethyl acetate (3 × 10 mL). The combined organic solvent was removed under vacuum to obtain the crude solid product. The crude product was further purified by silica gel column chromatography using ethyl acetate-petroleum ether (1:3) as eluent to afford the pure product **3**.

The spectral and analytical data of all compounds are given below.

*2-Phenylimidazo[1,2-a]pyridine (**3a**)*

White solid, mp 136-137 °C (lit. 131-133 °C);[20] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.12 (dd, *J* 1.04, 1.03, 1H), 7.98-7.96 (m, 2H), 7.88 (s, 1H), 7.64 (d, *J* 9.14, 1H), 7.45

(t, *J* 7.22, 2H), 7.35 (d, *J* 7.33, 1H), 7.20-7.17 (m, 1H), 6.79 (d, *J* 6.78, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 145.8, 145.7, 133.8, 128.7, 127.9, 126.0, 125.6, 124.6, 117.5, 112.4, 108.1. IR (KBr) ν_{max}/cm^{-1}: 2925, 2857, 1738, 1625, 1511, 1460, 1383, 1269, 1201, 1122, 1081, 1040, 744, 688, 458. MS (ESI): *m/z* (%) 195 ([M+H]$^+$, 100).

*6-Methyl-2-phenylimidazo[1,2-a]pyridine (**3b**)*

White solid, mp 171-173 °C (lit. 172-174 °C);[24] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.95 (d, *J* 7.05, 2H), 7.83 (s, 1H), 7.73 (s, 1H), 7.53 (d, *J* 9.09, 1H), 7.44 (t, *J* 6.63, 2H), 7.33 (d, *J* 6.44, 1H), 7.00 (d, *J* 8.82, 1H), 2.29 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 145.4, 144.7, 133.9, 128.7, 127.84, 127.78, 125.9, 123.3, 122.0, 116.7, 107.9, 18.0; IR (KBr) ν_{max}/cm^{-1}: 2921, 1628, 1525, 1471, 1418, 1342, 1259, 1206, 1159, 1079, 846, 805, 768, 715, 685, 571, 506.

*6-Chloro-2-phenylimidazo[1,2-a]pyridine (**3c**)*

White solid, mp 204-206 °C (lit. 204-207 °C);[25] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.15 (s, 1H), 7.94 (d, *J* 7.25, 2H), 7.82 (s, 1H), 7.57 (d, *J* 9.12, 1H), 7.51-7.38 (m, 2H), 7.34 (d, *J* 7.19, 1H), 7.14 (d, *J* 9.41, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 146.9, 144.1, 133.3, 128.8, 128.3, 126.1, 126.0, 123.4, 120.5, 117.9, 108.5; IR (KBr) ν_{max}/cm^{-1}: 2976, 2925, 1635, 1512, 1473, 1425, 1387, 1332, 1241, 1206, 1133, 1074, 938, 809, 772, 719, 506.

*2-(4-Methoxyphenyl)imidazo[1,2-a]pyridine (**3d**)*

White solid, mp 135-136 °C (lit. 133-134 °C);[17] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.09 (d, *J* 6.77, 1H), 7.89 (dd, *J* 1.95, 1.94, 2H), 7.77 (s, 1H), 7.61 (d, *J* 9.08, 1H), 7.17-7.15 (m, 1H), 6.97 (dd, *J* 1.97, 1.94, 2H), 6.76 (dd, *J* 0.82, 0.81, 1H), 3.85 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 159.6, 145.64, 145.57, 127.3, 126.4, 125.4, 124.5, 117.2, 114.1, 112.3, 107.2, 55.3; IR (KBr) ν_{max}/cm^{-1}: 2961, 2838, 1612, 1548, 1482, 1371, 1285, 1244, 1175, 1110, 1077, 1030, 924, 838, 743, 631, 536, 446.

*2-(4-Methoxyphenyl)-6-methylimidazo[1,2-a]pyridine (**3e**)*

White solid, mp 179-181 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.88 (d, *J* 2.26, 2H), 7.86 (d, *J* 2.11, 1H), 7.68 (s, 1H), 7.51 (d, *J* 9.48, 1H), 7.01 (d, *J* 1.57, 2H), 6.96 (dd, *J* 2.10, 2.06, 1H), 3.85 (s, 3H, OCH_3), 2.31 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 159.5, 145.3, 144.6, 127.7, 127.2, 126.6, 123.3, 121.9, 116.5, 114.1, 107.0, 55.3, 18.1; IR (KBr) ν_{max}/cm^{-1}: 2926, 1612, 1546, 1483, 1413, 1341, 1301, 1246, 1174, 1103, 1023, 839, 794, 744, 710, 591, 528; MS (ESI): *m/z* (%), 239 ([M+H]$^+$, 100); Anal. calc. for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92; N, 11.76. Found: C, 75.63; H, 5.90; N, 11.78.

*6-Chloro-2-(4-methoxyphenyl)imidazo[1,2-a]pyridine (**3f**)*

White solid, mp 234-236 °C (lit. 227-228 °C);[26] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.16-8.15 (m, 1H), 7.88 (dd, *J* 2.05, 2.04, 2H), 7.75 (s, 1H), 7.56 (d, *J* 9.54, 1H), 7.13 (dd, *J* 1.99, 1.96, 1H), 6.99 (dd, *J* 2.00, 2.01, 2H), 3.87 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 160.1, 147.1, 144.2, 127.6, 126.3, 126.0, 123.4, 120.5, 117.8, 114.4, 107.8, 55.5. IR (KBr) ν_{max}/cm^{-1}: 2995, 1610, 1551, 1487, 1371, 1305, 1250, 1176, 1108, 1070, 1030, 933, 841, 803, 742, 705, 575, 524; MS (ESI): *m/z* (%), 259 ([M+H]$^+$, 100).

*2-(4-Chlorophenyl)imidazo[1,2-a]pyridine (**3g**)*

White solid, mp 207-209 °C (lit. 201 °C);[18] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.09 (d, *J* 6.78, 1H), 7.87 (d, *J* 8.52, 2H), 7.82 (s, 1H), 7.61 (d, *J* 9.15, 1H), 7.39 (d, *J* 8.52, 2H), 7.17 (t, *J* 7.17, 1H), 6.77 (t, *J* 6.60, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 145.7, 144.6, 133.6, 132.3, 128.9, 127.2, 125.6, 124.9, 117.5, 112.6, 108.2; IR (KBr) ν_{max}/cm^{-1}: 2917, 1632, 1471, 1369, 1250, 1202, 1089, 1009, 933, 830, 742, 598, 510.

*2-(4-Chlorophenyl)-6-methylimidazo[1,2-a]pyridine (**3h**)*

White solid, mp 239-240 °C (lit. 240-242 °C);[15] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.89 (d, *J* 2.83, 2H), 7.88 (s, 1H), 7.75 (s, 1H), 7.54 (t, *J* 6.05, 1H), 7.39 (d, *J* 8.53, 2H), 7.05 (d, *J* 9.34, 1H), 2.33 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 144.8, 144.4, 133.5, 132.5, 128.9, 128.1, 127.1, 123.3, 122.3, 116.8, 107.9, 18.1; IR (KBr) ν_{max}/cm^{-1}: 2921, 1635, 1540, 1465, 1409, 1257, 1206, 1090, 1010, 944, 835, 803, 734, 511.

*6-Chloro-2-(4-chlorophenyl)imidazo[1,2-a]pyridine (**3i**)*

White solid, mp 205-207 °C (lit. 209 °C);[27] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.14-8.13 (m, 1H), 7.85 (dd, *J* 1.99, 1.97, 2H), 7.77 (s, 1H), 7.55 (d, *J* 9.57, 1H), 7.42-7.39 (m, 2H), 7.14 (dd, *J* 1.98, 1.97, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 145.9, 144.3, 134.3, 132.0, 129.2, 127.5, 126.6, 123.6, 121.0, 118.1, 108.7; IR (KBr) ν_{max}/cm^{-1}: 3130, 1653, 1525, 1470, 1419, 1336, 1260, 1202, 1071, 1009, 935, 833, 799, 734, 511; MS (ESI): *m/z* (%), 263 ([M+H]$^+$, 100), 265 ([M+2+H]$^+$, 70), 267 ([M+4+H]$^+$, 15).

*3-Methyl-2-phenylimidazo[1,2-a]pyridine (**3j**)*

Pale yellow solid, mp 159-161 °C (lit. 153-154 °C);[17] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.88 (d, *J* 6.87, 1H), 7.82-7.78 (m, 2H), 7.64 (d, *J* 9.06, 1H), 7.49-7.44 (m, 2H), 7.36 (d, *J* 7.38, 1H), 7.17-7.16 (m, 1H), 6.84 (d, *J* 6.75, 1H), 2.63 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 144.3, 142.4, 134.9, 128.5, 128.3, 127.3, 123.5, 122.8, 117.4, 115.9, 112.0, 9.6; IR (KBr) ν_{max}/cm^{-1}: 3027, 1629, 1494, 1443, 1393, 1351, 1243, 1143, 1072, 909, 751, 697, 583, 505; MS (ESI): *m/z* (%), 209 ([M+H]$^+$, 100).

*3,6-Dimethyl-2-phenylimidazo[1,2-a]pyridine (**3k**)*

Pale yellow solid, mp 114-116 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.82-7.79 (m, 2H), 7.66 (s, 1H), 7.54 (d, *J* 9.16, 1H), 7.46 (t, *J* 7.36, 2H), 7.34 (t, *J* 7.49, 1H), 7.02 (d, *J* 9.17, 1H), 2.61 (s, 3H, CH_3), 2.36 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 143.5, 142.3, 135.1, 128.5, 128.2, 127.2, 126.6, 121.5, 120.6, 116.8, 115.6, 18.4, 9.7; IR (KBr) ν_{max}/cm^{-1}: 2920, 1634, 1496, 1447, 1388, 1332, 1261, 1188, 1127, 1043, 777, 699, 581, 507; MS (ESI): *m/z* (%), 223 ([M+H]$^+$, 100); Anal. calc. for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 81.08; H, 6.34; N, 12.58.

*2-(2,4-Dichlorophenyl)imidazo[1,2-a]pyridine (**3l**)*

Pale yellow solid, mp 181-182 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.28-8.26 (m, 2H), 8.14 (d, *J* 6.77, 1H), 7.62 (d, *J* 9.11, 1H), 7.49-7.48 (m, 1H), 7.36 (dd, *J* 2.01, 1.99, 1H), 7.23-7.18 (m, 1H), 6.81 (t, *J* 6.76, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 144.5, 140.8, 133.6, 132.1, 131.7, 130.9, 130.0, 127.4, 125.8, 125.1, 117.6, 112.6, 112.4; IR (KBr) ν_{max}/cm^{-1}: 3042, 1632, 1544, 1461, 1367, 1242, 1105, 1043, 931, 826, 749, 704, 623, 555; MS (ESI): *m/z* (%), 263 ([M+H]$^+$, 100), 265 ([M+2+H]$^+$, 70), 267 ([M+4+H]$^+$, 15); Anal. calc. for $C_{15}H_{12}Cl_2N_2$: C, 61.87; H, 4.15; N, 9.62. Found: C, 61.88; H, 4.17; N, 9.59.

*2-(2,4-Dichlorophenyl)-6-methylimidazo[1,2-a]pyridine (**3m**)*

Pale yellow solid, mp 134-135 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.25 (d, *J* 8.55, 1H), 8.17 (s, 1H), 7.91 (s, 1H), 7.51 (d, *J* 9.33, 1H), 7.46 (d, *J* 2.13, 1H), 7.34 (dd, *J* 2.16, 2.07, 1H), 7.04 (dd, *J* 1.47, 1.50, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 143.6, 140.5, 133.4, 132.0, 131.6, 131.1, 130.0, 128.3, 127.3, 123.4, 122.2, 116.8, 112.2, 18.1; IR (KBr) ν_{max}/cm^{-1}: 2960, 1641, 1540, 1458, 1419, 1380, 1342, 1256, 1201, 1142, 1096, 1039, 938, 853, 793, 743, 700, 563, 461; MS (ESI): *m/z* (%), 277 ([M+H]$^+$, 100), 279 ([M+2+H]$^+$, 70), 281 ([M+4+H]$^+$, 15); Anal. calc. for $C_{14}H_{10}Cl_2N_2$: C, 60.67; H, 3.64; N, 10.11. Found: C, 60.69; H, 3.65; N, 10.09.

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Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br, as PDF file.

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