(Hetero)Arylation of 6-Halogenoimidazo[1,2-*a*]pyridines Differently Substituted at C(2): Influence of the 2-Substituent on the *Suzuki* Cross-Coupling Reaction

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We previously reported that reactivity towards the *Suzuki* cross-coupling reaction of 3-iodoimidazo[1,2-*a*]pyridines substituted at C(2) is largely influenced by the nature of this 2-substituent. Hence, with the aim to expand the scope of this coupling process to the 6-position of this series, it seemed important to similarly determine the influence of the nature of the 2-substituent (H, alkyl, or aryl) on the rate of coupling. From this work, the *Suzuki*-type cross-coupling was shown to proceed efficiently on 6-bromo-2-methyl- and 2-(4-fluorophenyl)imidazo[1,2-*a*]pyridines, whereas the 6-Br derivative unsubstituted at C(2) appeared to be poorly reactive. By modifying the reaction conditions in terms of catalyst and base, and the nature of the halogen, the reactivity of the unsubstituted series was largely enhanced. Finally, this work led us to establish efficient and convenient *Suzuki* reaction conditions for the 6-(hetero)arylation of 6-halogenoimidazo[1,2-*a*]pyridines depending on the nature of the 2-substituent and boronic acid.

Introduction. – As part of our continuing efforts to develop rapid pharmacomodulation methods of N-bridgehead heterocycles containing a fused imidazole ring, we turned our interest to the application of the *Suzuki*-type cross-coupling reaction [1][2]. We previously reported the good reactivity of the 2-substituted 3-iodoimidazo[1,2-*a*]pyridine series toward boronic acids, a reactivity largely influenced by the nature of the substituent present at C(2) [1]. Hence, we were interested in extending this coupling process to the pyridine part of the imidazo[1,2-*a*]pyridine ring system and, in a first approach, to the C(6) position. The poor reactivity towards traditional nucleophilic substitutions of 6-halogeno derivatives is now well-established. Only few examples of functionalization have been reported to date (see, *e.g.*, [3]). Thus, correct pharmacomodulation is generally required to be performed on the starting aminopyridines (see, *e.g.*, [4]) in contrast to a general and convenient synthetic approach. Generalization of the *Suzuki* coupling process could then provide an easy and convergent access to 6-(hetero)arylimidazo[1,2-*a*]pyridines with potential synthetic application as serotonin 5-HT_1 agonists [5]. To the best of our knowledge, application of this reaction has only been reported by *Tenbrink* [6] and *Momose* [7] on 6-bromo-2-(substituted-methyl)-imidazo[1,2-*a*]pyridines with $PhB(OH)_2$ acid under different reaction conditions, leading to 6-Ph derivatives in 78 and 30% yields, respectively. The lack of a general

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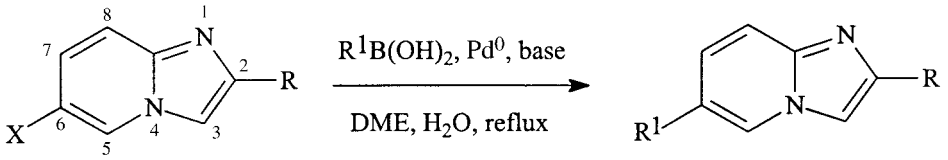
Suzuki-reaction study concerning this position emerges from the discrepancy between these results. Toward this goal, we decided to investigate the influence of various parameters: the nature of the 2-substituent and halogen atom in the starting material, the nature of boronic acid, and the conditions of the reaction in terms of catalyst and base.

Results. – The 6-halogenoimidazo[1,2-*a*]pyridines **1a**, **1b**, **2**, and **3** were easily obtained by reaction of 5-bromo- or 5-iodopyridin-2-amines with a convenient α-halogenocarbonyl compound in refluxing EtOH (*Scheme*).

Scheme



1a-b,2,3 **4-12**

1a R = H, X = Br
1b R = H, X = I
2 R = Me, X = Br
3 R = *p*-F–C_6H_4, X = Br

In a first approach, the coupling reaction was applied to 6-bromoimidazo[1,2-*a*]pyridine (**1a**) under the best reaction conditions previously determined in this series [1]: tetrakis(triphenylphosphine)palladium ([$Pd(PPh_3)_4$]), NaOH, with 1.1 equiv. of boronic acid in refluxing 1,2-dimethoxyethane to give 6-substituted derivatives (*Method A*). Three different boronic acids were evaluated: phenyl-, (thien-3-yl)- and (furan-2-yl)boronic acids.

Under the conditions described, the thienyl coupling proceeded very slowly. After refluxing for 24 h, thin-layer chromatography of the reaction mixture showed only traces of the desired 6-(thien-3-yl)imidazo[1,2-*a*]pyridine (**5**) that could not be isolated from the starting material. Under the same conditions, complete conversion of compound **1a** in the reaction with phenyl- and furylboronic acids was achieved in 3 h, leading to an unseparable mixture of 6-phenyl- or (furan-2-yl)imidazo[1,2-*a*]pyridine, traces of starting material, and a side-product that could not be isolated. A significant amount (30% estimated by ^{1}H-NMR spectrometry) of debrominated imidazo[1,2-*a*]pyridine was also formed during the coupling reaction with phenylboronic acid. In the two cases, ^{1}H-NMR spectra of the final mixtures presented, apart from signals of the 6-substituted product, intense *multiplets* between 7.45 and 7.70 ppm, which were attributed to a triphenylphosphine derivative. To confirm the origin of the contaminant and to overcome the purification problems encountered during preparation of the desired 6-substituted compounds **4**–**6**, we changed the catalyst to dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium ([$PdCl_2$(dppf)]) in the presence of

$Ba(OH)_2$, according to the literature [8] (*Method B*). In all cases, no aromatic side-product was detected at the end of the reaction, but purification still remained difficult, leading to poor yields of 6-(hetero)arylimidazo[1,2-*a*]pyridines **4**–**6** (27–35%; *Table*). Concerning the phenylboronic acid coupling, formation of the dehalogenated compound, which could hardly be separated from the attempted 6-phenyl derivative **4**, was again observed.

Table. *Synthesis of 2-Substituted 6-(Hetero)arylimidazo[1,2-*a*]pyridines* **4**–**12**

Compound	R	R^1	X	Catalyst	Base	Yield [%][a])
4	H	Ph	Br	$[Pd(PPh_3)_4]$	NaOH	0
			Br	$[PdCl_2(dppf)]$	$Ba(OH)_2$	27[b])
			I	$[PdCl_2(dppf)]$	$Ba(OH)_2$	58
5	H	Thien-3-yl	Br	$[Pd(PPh_3)_4]$	NaOH	0
			Br	$[PdCl_2(dppf)]$	$Ba(OH)_2$	34
			I	$[PdCl_2(dppf)]$	$Ba(OH)_2$	74
6	H	Furan-2-yl	Br	$[Pd(PPh_3)_4]$	NaOH	0
			Br	$[PdCl_2(dppf)]$	$Ba(OH)_2$	35
			I	$[PdCl_2(dppf)]$	$Ba(OH)_2$	60
7	Me	Ph	Br	$[Pd(PPh_3)_4]$	NaOH	68
			Br	$[PdCl_2(dppf)]$	$Ba(OH)_2$	41
8	Me	Thien-3-yl	Br	$[Pd(PPh_3)_4]$	NaOH	59
			Br	$[PdCl_2(dppf)]$	$Ba(OH)_2$	29
9	Me	Furan-2-yl	Br	$[Pd(PPh_3)_4]$	NaOH	88
			Br	$[PdCl_2(dppf)]$	$Ba(OH)_2$	32
10	4-F–C_6H_4	Ph	Br	$[Pd(PPh_3)_4]$	NaOH	93
			Br	$[PdCl_2(dppf)]$	$Ba(OH)_2$	71
11	4-F–C_6H_4	Thien-3-yl	Br	$[Pd(PPh_3)_4]$	NaOH	80
			Br	$[PdCl_2(dppf)]$	$Ba(OH)_2$	64
12	4-F–C_6H_4	Furan-2-yl	Br	$[Pd(PPh_3)_4]$	NaOH	68
			Br	$[PdCl_2(dppf)]$	$Ba(OH)_2$	66

[a]) Isolated yields. [b]) Yield estimated by ^{1}H-NMR spectrometry.

Then, considering the contribution of *Method B* but also the remaining difficulties in the isolation of compound **4**–**6**, we turned our interest to studying 6-iodoimidazo[1,2-*a*]pyridine. Under the same reaction conditions ($[PdCl_2(dppf)]$, $Ba(OH)_2$)), coupling of the three boronic acids proceeded with significantly improved yields due to a greatly facilitated purification of the desired 6-(hetero)arylimidazo[1,2-*a*]pyridines **4**–**6** (58–74%). In all cases, these compounds appeared to be unstable to UV and air as is usually observed in this unsubstituted series.

Then, we investigated the coupling reactivity of the 6-bromo-2-methylimidazo[1,2-*a*]pyridine (**2**) according to both *Method A* and *B*. With the same three boronic acids, couplings were completed cleanly in 3 h in good yields, leading to compounds **7**–**9**. No aromatic side-product was observed at the end of the coupling reaction according to *Method A* as observed previously in the nonsubstituted series. Moreover, yields were significantly improved in the case of *Method A* (59–88%) compared to *Method B* (29–41%).

Finally, in the case of 6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine (**3**), *Method A* remained the best, as reaction led to yields higher than with *Method B*,

and purification of the 6-substituted derivative **10**–**12** was not perturbed by a catalyst derivative. The structure determinations of compounds **4**–**12** was achieved by ^{1}H- and ^{13}C-NMR spectroscopy.

Discussion. – As we anticipated, the *Suzuki* cross-coupling reaction on 6-bromoimidazo[1,2-*a*]pyridines was shown to be dependent upon the nature of the substituent at C(2). Starting from the 2-unsubstituted derivative, couplings of the three boronic acids studied were unsuccessful under classical conditions, namely [Pd(PPh_3)$_4$] in the presence of NaOH. (Thien-3-yl)boronic acid was shown to be unreactive. In contrast, couplings with (furan-2-yl)- and phenylboronic acids occurred rapidly, but led to inseparable mixtures of the desired derivatives, a by-product derived from Ph_3P, and, in the case of phenylboronic acid, a significant amount of the dehalogenated derivative. From this observation, it could be concluded that [$PdCl_2$(dppf)] as catalyst in the presence of $Ba(OH)_2$ avoided the by-product formation, establishing its origin. Unfortunately, purification remained problematic, leading to only poor yields. A solution for the problem was found in utilization of the 6-iodo derivative as the starting material, allowing the couplings to proceed very efficiently and cleanly by *Method B* and then facilitating the purification. Finally, the 6-substituted compounds **4**–**6** could be obtained in good yields, but were UV- and air-unstable.

In contrast, 2-alkyl- and 2-arylimidazo[1,2-*a*]pyridines appeared to be much more reactive towards *Suzuki*-coupling. Good yields were obtained from the 6-bromo derivatives with [Pd(PPh_3)$_4$] without formation of a side-product. In these cases, the use of [$PdCl_2$(dppf)] was not justified, as it led to lower or equivalent yields.

For the time being, the discrepancy in the reactivities of different imidazo[1,2-*a*]pyridine series remains unclear. Reactivity of the 2-unsubstituted 6-bromo series appeared to be surprisingly dependant upon the boronic acid used and the reaction conditions applied. Thus, under classical reaction conditions ([Pd(PPh_3)$_4$], NaOH), thienylboronic acid gave no coupling, whereas the reaction proceeded to completion with phenyl- and (furan-2-yl)boronic acids, although the following isolation failed. With [$PdCl_2$(dppf)] in the presence of $Ba(OH)_2$, conversion was complete in all cases.

In conclusion, the *Suzuki* cross-coupling procedure reported here presents a new general and convenient synthetic approach in good agreement with rapid pharmaco-modulation of 6-halogenoimidazo[1,2-*a*]pyridines.

Experimental Part

General. The compounds tetrakis(triphenylphosphine)palladium(0) [9], 6-bromoimidazo[1,2-*a*]pyridine [10], 6-bromo-2-methylimidazo[1,2-*a*]pyridine [11], and 5-iodopyridine-2-amine [12] were prepared according to literature procedures. M.p.: cap. apparatus; uncorrected. NMR Spectra: *Bruker DPX-200* or *AM-400-WB* instruments, and chemical shifts (δ) in ppm from residual $CHCl_3$ ($\delta = 7.3$ ppm (^{1}H)) and the central resonance of $CDCl_3$ ($\delta = 77.1$ ppm (^{13}C)); *: assignments may be interchanged. Elemental analyses were performed at the University of Rouen (Institut de Recherche en Chimie Organique Fine), France.

*6-Bromoimidazo[1,2-*a*]pyridine* (**1a**). M.p. 74° ([10]: 76–78°). ^{13}C-NMR ($CDCl_3$, 50 MHz): 144.0 (C(8a)); 134.5 (C(2)); 128.0 (C(7)); 126.2 (C(5)); 118.5 (C(8)); 113.1 (C(3)); 107.2 (C(6)).

*6-Iodoimidazo[1,2-*a*]pyridine* (**1b**). A mixture of 4 g (18.2 mmol) of 5-iodopyridin-2-amine and 2.8 ml (20 mmol) of an aq. soln. of chloroacetaldehyde (45%) in 100 ml of EtOH was refluxed for 3 h and, after cooling, evaporated to dryness. The residue was suspended in H_2O, made alkaline with Na_2CO_3, and extracted with CH_2Cl_2. After drying ($CaCl_2$), the org. layers were evaporated to dryness. The residue (53%) was used

without further purification. M.p. 134°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.42 (*dd*, *J* = 1.6–0.8, H–C(5)); 7.61 (br. *s*, H–C(2)); 7.56 (br. *s*, H–C(3)); 7.44 (*dd*, *J* = 9.5–0.8, H–C(8)); 7.33 (*dd*, *J* = 9.5–1.6, H–C(7)). ^{13}C-NMR ($CDCl_3$, 50 MHz): 144.4 (C(8a)); 134.4 (C(2)); 132.6 (C(7)); 131.0 (C(5)); 119.4 (C(8)); 110.7 (C(3)); 75.7 (C(6)). Anal. calc. for C_7H_5IN: C 34.43, H 2.05, N 11.47; found: C 34.56, H 2.07, N 11.32.

6-Bromo-2-methylimidazo[1,2-a]pyridine (**2**). M.p. 102° ([11]: 101–105.5°). ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.18 (*dd*, *J* = 1.8–0.9, H–C(5)); 7.40 (br. *d*, *J* = 9.5, H–C(8)); 7.31 (*s*, H–C(3)); 7.16 (*dd*, *J* = 9.5–1.8, H–C(7)); 2.45 (*s*, Me). ^{13}C-NMR ($CDCl_3$, 50 MHz): 144.8 (C(8a)*); 143.9 (C(2)*); 127.7 (C(7)); 125.6 (C(5)); 117.8 (C(8)); 110.2 (C(3)); 106.7 (C(6)); 14.8 (Me).

6-Bromo-2-(4-fluorophenyl)imidazo[1,2-a]pyridine (**3**). A mixture of 5.6 g (32.4 mmol) of 5-bromopyridin-2-amine and 7.7 g (35.5 mmol) of ω-bromo-4-fluoroacetophenone in 100 ml of EtOH was refluxed for 5 h and, after cooling, evaporated to dryness. The residue was suspended in H_2O, made alkaline with Na_2CO_3, and extracted with CH_2Cl_2. After drying ($CaCl_2$), the org. layers were evaporated to dryness. The residue was chromatographed on neutral alumina eluting with CH_2Cl_2: 40%. M.p. 190°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.28 (*dd*, *J* = 1.9–0.9, H–C(5)); 7.93 (*dd*, *J* = 8.9–5.4, H–C(2), H–C(6) of C_6H_4); 7.78 (*s*, H–C(3)); 7.54 (br. *d*, *J* = 9.5 Hz, H–C(8)); 7.27 (*dd*, J = 9.5–1.9, H–C(7)); 7.16 (*t*, *J* = 8.9, H–C(3), H–C(5) of C_6H_4). ^{13}C-NMR ($CDCl_3$, 50 MHz): 163.3 (*J* = 246, C(4) of C_6H_4); 146.1 (C(8a)*); 144.5 (C(2)*); 129.8 (J = 3.5, C(1) of C_6H_4); 128.7 (C(7)); 128.2 (*J* = 8.5, C(2), C(6) of C_6H_4); 126.0 (C(5)); 118.4 (C(8)); 116.2 (*J* = 21.5, C(3), C(5) of C_6H_4); 108.4 (C(3)); 107.5 (C(6)). Anal. calc. for $C_{13}H_8BrFN_2$: C 53.61, H 2.75, N 9.62; found: C 53.56, H 2.78, N 9.42.

Cross-Coupling Reaction: General Procedures. Method A: Into a three-necked round-bottom flask was introduced the 6-bromoimidazo[1,2-*a*]pyridine derivative (2 mmol) in 1,2-dimethoxyethane (DME, 16 ml) under N_2. [$Pd(PPh_3)_4$] (0.1 mmol, 116 mg), the boronic acid (2.2 mmol), and NaOH (4 mmol, 160 mg) in H_2O (8 ml) were then added under stirring. The resulting mixture was refluxed for 3 h. After cooling, the mixture was diluted with H_2O, and the aq. layer was extracted with CH_2Cl_2. The org. layers were dried ($CaCl_2$), filtered, and evaporated under reduced pressure. Column chromatography on neutral alumina eluting with CH_2Cl_2 afforded the pure products.

Method B: The same conditions as described in *Method A* were applied starting from 6-bromoimidazo[1,2-*a*]pyridine (2 mmol) or 6-iodoimidazo[1,2-*a*]pyridine (1 mmol) derivative, but [$PdCl_2$(dppf)] (5%) was used as the catalyst, and the base was changed to $Ba(OH)_2$ (2 equiv.).

6-Phenylimidazo[1,2-a]pyridine (**4**). Oil. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.31 (*dd*, *J* = 1.8–1.0, H–C(5)); 7.70 (*d*, *J* = 9.4, H–C(8)); 7.68 (br. *s*, H–C(2)); 7.65 (br. *s*, 1 H–C(3)); 7.60–7.40 (*m*, H–C(7), 5 arom. H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 145.2 (C(8a)); 137.7 (C(1) of Ph); 134.4 (C(2)); 129.5 (C(3), C(5) of Ph); 128.3 (C(4) of Ph); 127.3 (C(2), C(6) of Ph); 127.3 (C(6)); 125.7 (C(7)); 123.5 (C(5)); 118.1 (C(8)); 113.3 (C(3)). Anal. calc. for $C_{13}H_{10}N_2$: C 80.41, H 5.15, N 14.43; found: C 80.34, H 5.18, N 14.23.

6-(Thien-3-yl)imidazo[1,2-a]pyridine (**5**). M.p. 96°. ^{1}H-NMR ($CDCl_3$, 400 MHz): 8.37 (br. *s*, H–C(5)); 7.74 (br. *d*, *J* = 9.4, H–C(8)); 7.71 (br. *s*, H–C(2)); 7.69 (br. *s*, H–C(3)); 7.51 (*dd*, *J* = 9.4–1.6, H–C(7)); 7.49–7.47 (*m*, H–C(2), H–C(4) of Th); 7.37 (*dd*, *J* = 4.2–2.2, H–C(5) of Th). ^{13}C-NMR ($CDCl_3$, 100 MHz): 145.0 (C(8a)); 138.4 (C(3) of Th); 134.2 (C(2)); 127.5 (C(2) of Th); 126.1 (C(5) of Th); 125.3 (C(7)); 122.8 (C(5)); 122.4 (C(6)); 121.2 (C(4) of Th); 118.1 (C(8)); 113.2 (C(3)). Anal. calc. for $C_{11}H_8N_2S$: C 66.00, H 4.00, N 14.00; found: C 65.92, H 4.11, N 14.13.

6-(Furan-2-yl)imidazo[1,2-a]pyridine (**6**). Oil. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.52 (br. *s*, H–C(5)); 7.67 (*d*, *J* = 9.6, H–C(8)); 7.68 (*d*, *J* = 1.2, H–C(2)); 7.65 (*d*, *J* = 1.2, H–C(3)); 7.51 (*dd*, *J* = 1.8–0.6, H–C(5) of Fur); 7.46 (*dd*, *J* = 9.6–1.8, H–C(7)); 6.67 (*dd*, *J* = 3.5–0.6, H–C(3) of Fur); 6.54 (*dd*, *J* = 3.5–1.8, H–C(4) of Fur). ^{13}C-NMR ($CDCl_3$, 50 MHz): 150.9 (C(2) of Fur); 144.9 (C(8a)); 142.7 (C(5) of Fur); 134.4 (C(2)); 122.3 (C(7)); 121.0 (C(5)); 118.2 (C(8)); 117.7 (C(6)); 113.5 (C(3)); 112.2 (C(4) of Fur); 106.3 (C(3) of Fur). Anal. calc. for $C_{11}H_8N_2O$: C 71.74, H 4.35, N 15.22; found: C 71.62, H 4.41, N 15.27.

2-Methyl-6-phenylimidazo[1,2-a]pyridine (**7**). Filtered through *Florisil*®. M.p. 120°. ^{1}H-NMR ($CDCl_3$, 400 MHz): 8.25 (br. *s*, H–C(5)); 7.65 (*d*, *J* = 9.3, H–C(8)); 7.57 (*d*, *J* = 7.5, H–C(2), H–C(6) of Ph); 7.49 (*t*, *J* = 7.5, H–C(3), H–C(5) of Ph); 7.45 (*dd*, *J* = 9.3–1.7, H–C(7)); 7.43–7.39 (*m*, H–C(3) and H–C(4) of Ph); 2.51 (*s*, Me). ^{13}C-NMR ($CDCl_3$, 100 MHz): 144.6 (C(8a)*); 144.0 (C(2)*); 137.8 (C(1) of Ph); 129.5 (C(3), C(5) of Ph); 128.2 (C(4) of Ph); 127.3 (C(2), C(6) of Ph); 126.9 (C(6)); 125.4 (C(7)); 122.9 (C(5)); 116.9 (C(8)); 110.3 (C(3)); 14.7 (Me). Anal. calc. for $C_{14}H_{12}N_2$: C 80.77, H 5.77, N 13.46; found: C 80.81, H 5.86, N 13.33.

2-Methyl-6-(thien-3-yl)imidazo[1,2-a]pyridine (**8**). Filtered through *Florisil*®. M.p. 127°. ^{1}H-NMR ($CDCl_3$, 400 MHz): 8.28 (br. *s*, H–C(5)); 7.63 (*d*, *J* = 9.4, H–C(8)); 7.48–7.45 (*m*, H–C(7) and H–C(2), H–C(4) of Th); 7.39 (br. *s*, H–C(2)); 7.35 (*dd*, *J* = 4.5–1.7, H–C(5) of Th); 2.51 (*s*, Me). ^{13}C-NMR ($CDCl_3$, 50 MHz): 144.6 (C(8a)*); 144.2 (C(2)*); 138.6 (C(3) of Th); 127.3 (C(2) of Th); 126.0 (C(5) of Th); 124.4 (C(7)); 122.2 (C(5));

121.6 (C(6)); 120.7 (C(4) of Th); 116.9 (C(8)); 110.3 (C(3)); 14.8 (Me). Anal. calc. for $C_{12}H_{10}N_2S$: C 67.29, H 4.67, N 13.08; found: C 69.31, H 4.67, N 13.14.

*6-(Furan-2-yl)-2-methylimidazo[1,2-*a*]pyridine* (**9**). M.p. 96°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.35 (*s*, H–C(5)); 7.50 (*d*, *J* = 9.4, H–C(8)); 7.45 (*d*, *J* = 1.8, C(5) of Fur); 7.35 (*dd*, *J* = 9.4–1.6, H–C(7)); 7.33 (*s*, H–C(3)); 6.58 (*d*, *J* = 3.4, H–C(3) of Fur); 6.48 (*dd*, *J* = 3.4–1.8, H–C(4) of Fur); 2.46 (*s*, Me). ^{13}C-NMR ($CDCl_3$, 50 MHz): 151.2 (C(2) of Fur); 144.5 (C(8a)*); 144.4 (C(2)*); 142.5 (C(5) of Fur); 121.8 (C(7)); 120.5 (C(5)); 117.1 (C(8), C(6)); 112.1 (C(4) of Fur); 110.6 (C(3)); 105.8 (C(3) of Fur); 14.8 (Me). Anal. calc. for $C_{12}H_{10}N_2O$: C 72.73, H 5.05, N 14.14; found: C 72.67, H 5.16, N 14.33.

*2-(4-Fluorophenyl)-6-phenylimidazo[1,2-*a*]pyridine* (**10**). M.p. 191°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.32 (*dd*, *J* = 1.8–0.8, H–C(5)); 7.98 (*dd*, *J* = 8.9–5.4, H–C(2), H–C(6) of C_6H_4); 7.89 (*s*, H–C(3)); 7.72 (*dd*, *J* = 9.4, 0.8, H–C(8)); 7.41–7.63 (*m*, H–C(7), 5 H of Ph); 7.17 (*t*, *J* = 8.9, H–C(3), H–C(5) of C_6H_4). ^{13}C-NMR ($CDCl_3$, 50 MHz): 163.1 (*J* = 245.5, C(4) of C_6H_4); 145.8 (C(8a)*); 145.4 (C(2)*); 137.6 (C(1) of Ph); 130.4 (*J* = 3.5, C(1) of C_6H_4); 129.5 (C(3), C(5) of Ph); 128.5 (*J* = 7.5, C(2), C(6) of C_6H_4); 128.0 (C(4) of Ph); 127.3 (C(6)); 127.2 (C(2), C(6) of Ph); 125.9 (C(7)); 123.2 (C(5)); 117.6 (C(8)); 116.1 (*J* = 21.5, C(3), C(5) of C_6H_4); 108.6 (C(3)). Anal. calc. for $C_{19}H_{13}FN_2$: C 79.17, H 4.51, N 9.72; found: C 79.29, H 4.54, N 9.66.

*2-(4-Fluorophenyl)-6-(thien-3-yl)imidazo[1,2-*a*]pyridine* (**11**). M.p. 206°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.36 (*dd*, *J* = 1.8, 1.0, H–C(5)); 7.97 (*dd*, *J* = 8.9, 5.4, H–C(2), H–C(6) of C_6H_4); 7.87 (*s*, H–C(3)); 7.68 (*d*, *J* = 9.4, H–C(8)); 7.52–7.45 (*m*, H–C(7) and H–C(2), H–C(4) of Th); 7.38 (*dd*, *J* = 3.5, 2.9, H–C(5) of Th); 7.17 (*t*, *J* = 8.9, H–C(3), H–C(5) of C_6H_4). ^{13}C-NMR ($CDCl_3$, 50 MHz): 163.2 (*J* = 245.5, C(4) of C_6H_4); 145.8 (C(8a)*); 145.4 (C(2)*); 138.4 (C(3) of Th); 130.3 (*J* = 3.5, C(1) of C_6H_4); 128.8 (*J* = 8, C(2), C(6) of C_6H_4); 127.5 (C(2) of Th); 126.1 (C(5) of Th); 125.5 (C(7)); 122.5 (C(6)); 122.4 (C(5)); 121.2 (C(4) of Th); 117.8 (C(8)); 116.1 (*J* = 21.5, C(3), C(5) of C_6H_4); 108.6 (C(3)). Anal. calc. for $C_{17}H_{11}FN_2S$: C 69.39, H 3.74, N 9.52; found: C 69.46, H 3.78, N 6.48.

*2-(4-Fluorophenyl)-6-(furan-2-yl)imidazo[1,2-*a*]pyridine* (**12**). M.p. 193°. ^{1}H-NMR ($CDCl_3$, 200 MHz): 8.46 (br. *s*, H–C(5)); 7.95 (*dd*, *J* = 8.9, 5.6, H–C(2), H–C(6) of C_6H_4); 7.84 (*s*, H–C(3)); 7.65 (*d*, *J* = 9.4, H–C(8)); 7.51 (*d*, *J* = 1.8, H–C(5) of Fur); 7.46 (*dd*, *J* = 9.4, 1.7, H–C(7)); 7.16 (*t*, *J* = 8.9, H–C(3), H–C(5) of C_6H_4); 6.67 (*d*, *J* = 3.4, H–C(3) of Fur); 6.54 (*dd*, *J* = 3.4, 1.8, H–C(4) of Fur). ^{13}C-NMR ($CDCl_3$, 50 MHz): 163.1 (*J* = 245.5, C(4) of C_6H_4); 150.9 (C(2) of Fur); 145.8 (C(8a)*); 145.2 (C(2)*); 142.8 (C(5) of Fur); 130.2 (*J* = 3.5, C(1) of C_6H_4); 128.0 (*J* = 8, C(2), C(6) of C_6H_4); 122.8 (C(7)); 120.7 (C(5)); 117.8 (C(6)); 117.8 (C(8)); 116.1 (*J* = 21.5, C(3), C(5) of C_6H_4); 112.2 (C(4) of Fur); 108.8 (C(3)); 106.3 (C(3) of Fur). Anal. calc. for $C_{17}H_{11}FN_2O$: C 73.38, H 3.96, N 10.07; found: C 73.51, H 4.15, N 10.11.

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