

Evaluation of the 2-Substituent Effect on the Reactivity of the 8-Haloimidazo[1,2-*a*]pyridine Series towards Suzuki-Type Cross-Coupling Reaction

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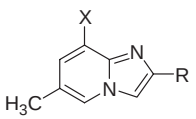
The purpose of this work was to complete a general study that we initiated on the influence of a 2-substitution on the reactivity of 8-haloimidazo[1,2-*a*]pyridines towards a Suzuki cross-coupling reaction, using conventional reactants in order to obtain easily performed (hetero)arylation methods with a high degree of flexibility with regard to functional groups.

Imidazo[1,2-*a*]pyridines are currently the object of a renewed interest in the pharmaceutical field. Lately, many publications have reported on their pharmacological properties in various biological areas [e.g., p38 MAP kinase inhibitors,[1] ligands for detecting β-amyloid plaques in the brain,[2] cyclin-dependent kinase inhibitors,[3] antiviral molecules[4]]. New approaches for the synthesis of functionalized imidazo[1,2-*a*]pyridines have also been described.[5–7] Nevertheless, methods for functionalization that allow the rapid preparation of a number of structural variants in these series, and notably on the pyridine moiety, are still needed.

During the course of our work to evaluate the applicability of metallo-catalyzed cross-coupling reactions in the imidazo[1,2-*a*]pyridine series,[8,9] we previously reported that the reactivity towards the Suzuki cross-coupling reaction[10–12] of 3-iodoimidazo[1,2-*a*]pyridine diversely substituted at C(2) is largely influenced by the nature of the 2-substituent.[13] More surprisingly, the reactivity of the 6-position in these series was also shown to be highly dependent on the 2-substitution.[14] With the aim to complete this study concerning the effect of the 2-substituent on the reactivity of the imidazo[1,2-*a*]pyridine core, we tried to evaluate the applicability of the Suzuki cross-coupling reaction to the 8-haloimidazo[1,2-*a*]pyridine. In this work, our purpose was to determine the best Suzuki reaction conditions applicable to the 8 position of the imidazo[1,2-*a*]pyridine, depending on the nature of the 2-substitution, using conventional reactants in order to obtain easily performed (hetero)arylation methods with a high degree of flexibility with regard to functional groups.

Results and Discussion

The reason for choosing 8-halo-6-methyl-2-substituted imidazo[1,2-*a*]pyridines **1**–**2** (Scheme 1) as the starting materials, instead of non-methyl substituted analogues, was that they are synthesized in better yield on a large scale. They were easily obtained by the condensation of 3-halo-5-methylpyridin-2-amine with a convenient α-halo ketone in refluxing ethanol, according to Tschitschibabin,[15] in moderate-to-good yields (45–84%). Three representative groupings were introduced at the 2-position: methyl, phenyl, and ester groups.



1a-c, 2a-c

X	R = CH_3	R = 4-FC_6H_4	R = $CO_2C_2H_5$
Br	1a	1b	1c
I	2a	2b	2c

Scheme 1.

In the first approach, the coupling reaction was applied to the 8-bromo-2,6-dimethylimidazo[1,2-*a*]pyridine **1a** under the traditional reaction conditions: 1.1 molar amount of (hetero)arylboronic acid, 5 mol% of $Pd(PPh_3)_4$, 2 molar amounts of NaOH in a refluxing mixture of 1,2-dimethoxyethane (8 mL/mmol) and water (4 mL/mmol) (Method A). As previously observed, the diversely substituted phenylboronic acids presented higher reactivities than the studied heteroarylboronic acids. The benzene coupling occurred within 3 h in more than 90% yields, with apparently no influence of the electronic effects of the benzene substituent (e.g., 4-F, 4-OCH_3, 2,4,6-tri-CH_3 and 3-CF_3). Only the 3-nitrophenylboronic acid was coupled in poor yield (40%). An attempt to use the 8-iodinated starting material **2a** even decreased the yield from 40 to 20%. The lowest efficiency of the nitrophenyl coupling was already noticed in the literature.[16]

Using the same conditions (Method A), the coupling of thien-2-ylboronic acid to **1a** proceeded very slowly, and only 34% of the desired compound **10a** was obtained after 3 h of heating. An attempt to switch to the iodinated derivative **2a** slightly improved the coupling efficacy (42% yield), but prolonging the reaction time to 8 h had no effect on the coupling yield. From these observations, we then decided to modify the

Published on the web January 13, 2005; DOI 10.1246/bcsj.78.154

reaction conditions in terms of the catalyst and the base, and to adopt the method that we previously determined in the 6-position of the imidazo[1,2-*a*]pyridine: 1.1 molar amount of (hetero)arylboronic acid, 5 mol% of $PdCl_2$dppf, 2 molar amounts of $Ba(OH)_2$ in a refluxing mixture of 1,2-dimethoxyethane (8 mL/mmol) and water (4 mL/mmol) (Method B). Under these modified conditions, the thien-2-yl coupling proceeded more efficiently from **2a**, leading to **10** in 67% yield after 8 h of heating. Traces of the starting material still remained at the end of the reaction, but no improvement of the yield was achieved from a prolonged reaction time. Furthermore, an attempt to associate $Ba(OH)_2$ to $Pd(PPh_3)_4$ as catalyst (Method C) was deleterious for the coupling efficacy (37% yield in 8 h). We noticed that the coupling yield of thien-2-ylboronic acid with **2a**, was inversely proportional to the strength of the base associated to $Pd(PPh_3)_4$, because the best result was obtained using Na_2CO_3 (68% yield). This correlation was not observed with $PdCl_2$dppf, which could be efficiently associated to $Ba(OH)_2$.

From the heteroarylboronic acids studied, the thien-3-ylboronic acid appeared to be the most reactive substrate. Using method A, 72% of compound **11a** was obtained from **2a** after 8 h of heating. The less-reactive substrate was the fur-2-ylboronic acid with only 19% of compound **12a** obtained using method A after 24 h. Method B led to a significantly increased yield (55% after 8 h). Again, prolonging the reaction time was not beneficial for the Suzuki coupling. These results may have been due to competitive protodeboronation, which is a known issue for heteroarylboronic acids, specifically when the boron is on a carbon adjacent to a heteroatom. This could explain the order of reactivity of the different boronic acids tested (thien-3-yl > thien-2-yl > fur-2-yl) and the presence of the remaining starting material at the end of the reaction, even with a prolonged reaction time.[17,18]

The 8-halo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine derivatives **1b–2b** were then submitted to the same Suzuki reaction conditions as previously, to compare the reactivity of the 2-methyl and 2-phenyl series. Substituted phenylboronic acids were coupled in 82 to 95% yields from **1b** (Method A). Thien-2-yl coupling to **2b** using method B, led to 69% of compound **10b** after 8 h of heating (67% in the 2-methyl series), whereas 85% of thien-3-yl derivative **11b** were obtained using Method A (72% in the 2-methyl series). Thus, no dramatic differences were noticed concerning the reactivity of these two series of compounds towards the Suzuki coupling.

Concerning the 8-haloimidazo[1,2-*a*]pyridine-2-carboxylic ester derivatives **1c–2c**, the base sensitivity of the ester function prevented us from using bases stronger than Na_2CO_3 or K_3PO_4, or a too long reaction time. The reactions were carried out in the presence of $Pd(PPh_3)_4$ and Na_2CO_3 for 3 h. Phenyl, thien-2-yl, and thien-3-yl couplings were performed from **1c** in 69, 47, and 37% yields, respectively. Prolonged reaction times led to dramatically decreased yields. Only 19% of 8-furyl derivative **12c** were obtained after 8 h of heating. Using K_3PO_4 as a base improved the coupling efficacy, leading to 76% of 8-phenyl compound **3c** and 88% of 8-thienyl derivative **11c**.

In conclusion, the 2-methyl and 2-phenyl series exhibited very similar reactivity towards the Suzuki coupling reaction. Using $Pd(PPh_3)_4$ and NaOH, phenylboronic acids were coupled in more than 80% yields, while heteroarylboronic acids presented lower reactivities. For the couplings of these heteroarylboronic acids, two different catalytic systems could be used: $Pd(PPh_3)_4/Na_2CO_3$ or $PdCl_2$dppf/$Ba(OH)_2$. It appeared that the efficacy of $Pd(PPh_3)_4$ is inversely proportional to the strength of the base, while $PdCl_2$dppf doesn't seem to be sensitive to the nature of the base. As far as the 2-ester series is concerned, no effect of the 2-substitution was observed on the reactivity of the 8 position as it was noticed on the 3 position.[13] Indeed, the 3-position was highly activated by the presence of the ester group in the 2-position compared with the 2-phenyl series. We were then confronted with the base sensitivity of the ester function. The use of K_3PO_4 appeared to be a good alternative to utilising Na_2CO_3.

Experimental

General. The melting points were determined in a capillary apparatus, and are uncorrected. NMR experiments were performed at 200 MHz (^{1}H) and 50 MHz (^{13}C) in $CDCl_3$ on Bruker DPX 200 instruments. Possible inversion of two values in the NMR spectra is expressed by an asterisk.

Materials: Tetrakis(triphenylphosphine)palladium(0),[19] 3-bromo-5-methylpyridin-2-amine,[20] and 3-iodo-5-methylpyridin-2-amine[21] were prepared as described in the literature.

8-Bromo-2,6-dimethylimidazo[1,2-*a*]pyridine (1a). A mixture of 8 g (42.8 mmol) of 3-bromo-5-methylpyridin-2-amine and 5.26 mL (73 mmol) of 1,3-dichloroacetone in dry EtOH (50 mL) was refluxed for 24 h. After concentration to dryness of the reaction mixture, the residue was suspended in H_2O, made basic with Na_2CO_3, and the precipitate was filtered off. After dissolution of the solid in CH_2Cl_2 and drying with $CaCl_2$, the organic layer was evaporated under reduced pressure. Column chromatography on neutral alumina, eluting with CH_2Cl_2, led to **1a** (55%). mp 83–84 °C. ^{1}H NMR δ 7.77 (m, 1H, H-5), 7.31 (d, 1H, $J = 0.8$ Hz, H-3), 7.22 (d, 1H, $J = 1.4$ Hz, H-7), 2.46 (s, 3H, CH_3), 2.26 (s, 3H, CH_3). ^{13}C NMR δ 144.2 (C-2), 142.4 (C-8a), 129.7 (C-7), 122.8 (C-5), 122.0 (C-6), 111.5 (C-3), 110.4 (C-8), 18.2 (CH_3), 14.9 (CH_3). Anal. Calcd for $C_9H_9N_2Br$: C, 48.02; H, 4.03; N, 12.45%. Found: C, 47.86; H, 4.36; N, 12.57%.

8-Iodo-2,6-dimethylimidazo[1,2-*a*]pyridine (2a). The same conditions were applied starting from 8 g (34.2 mmol) of 3-iodo-5-methylpyridin-2-amine and 4.65 mL (58.2 mmol) of 1,3-dichloroacetone. Purification by column chromatography on neutral alumina, and eluting with CH_2Cl_2 gave **2a** (51%). mp 119–120 °C. ^{1}H NMR δ 7.82 (m, 1H, H-5), 7.49 (d, 1H, $J = 1.5$ Hz, H-7), 7.39 (d, 1H, $J = 0.7$ Hz, H-3), 2.49 (s, 3H, CH_3), 2.28 (s, 3H, CH_3). ^{13}C NMR δ 144.1 (C-2*), 143.9 (C-8a*), 136.7 (C-7), 123.7 (C-5), 122.7 (C-6), 111.8 (C-3), 83.0 (C-8), 18.0 (CH_3), 14.9 (CH_3). Anal. Calcd for $C_9H_9N_2I$: C, 39.73; H, 3.33; N, 10.30%. Found: C, 39.84; H, 3.27; N, 10.48%.

8-Bromo-6-methyl-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine (1b). The same conditions were applied starting from 10 g (53 mmol) of 3-bromo-5-methylpyridin-2-amine and 12.76 g (58.9 mmol) of 2′-bromo-4-fluoroacetophenone in dry EtOH (150 mL) for 16 h. Purification by column chromatography on neutral alumina, and eluting with CH_2Cl_2, gave **1b** (45%). mp 192–193 °C. ^{1}H NMR δ 7.95 (dd, 2H, $J = 8.8$, 5.4 Hz, F–Ph-2,6), 7.85 (m, 1H, H-5), 7.78 (s, 1H, H-3), 7.31 (d, 1H, $J = 1.4$ Hz, H-7), 7.13 (t, 2H, $J = 8.8$ Hz, F–Ph-3,5), 2.29 (s, 3H, CH_3). ^{13}C NMR δ 163.2 ($J = 245.5$ Hz, F–Ph-4), 145.6 (C-2*), 143.1 (C-8a*), 130.6 (C-7), 130.1 ($J = 3.5$ Hz, F–Ph-1), 128.3 ($J = 8$ Hz,

F–Ph-2,6), 123.2 (C-5), 122.8 (C-6), 115.9 ($J = 21.5$ Hz, F–Ph-3,5), 111.2 (C-8), 109.6 (C-3), 18.3 (CH_3). Anal. Calcd for $C_{14}H_{10}N_2BrF$: C, 55.10; H, 3.30; N, 9.18%. Found: C, 55.24; H, 3.49; N, 8.99%.

8-Iodo-6-methyl-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine (2b). The same conditions were applied starting from 8 g (34.2 mmol) of 3-iodo-5-methylpyridin-2-amine and 8.16 g (37.6 mmol) of 2′-bromo-4-fluoroacetophenone in dry EtOH (150 mL) for 24 h. Purification by column chromatography on neutral alumina, and eluting with CH_2Cl_2, gave **2b** (61%). mp 173–174 °C. ^{1}H NMR δ 7.98 (dd, 2H, $J = 8.7$, 5.4 Hz, F–Ph-2,6), 7.90 (m, 1H, H-5), 7.86 (s, 1H, H-3), 7.51 (d, 1H, $J = 1.5$ Hz, H-7), 7.15 (t, 2H, $J = 8.7$ Hz, F–Ph-3,5), 2.35 (s, 3H, CH_3). ^{13}C NMR δ 163.2 ($J = 245.5$ Hz, F–Ph-4), 145.6 (C-2*), 144.5 (C-8a*), 137.5 (C-7), 130.2 ($J = 3$ Hz, F–Ph-1), 128.3 ($J = 7$ Hz, F–Ph-2,6), 124.0 (C-5), 123.4 (C-6), 115.9 ($J = 21.5$ Hz, F–Ph-3,5), 109.8 (C-3), 83.8 (C-8), 18.1 (CH_3). Anal. Calcd for $C_{14}H_{10}N_2FI$: C, 47.75; H, 2.86; N, 7.96%. Found: C, 47.85; H, 2.77; N, 8.03%.

Ethyl 8-Bromo-6-methylimidazo[1,2-*a*]pyridine-2-carboxylate (1c). A mixture of 8 g (47.8 mmol) of 3-bromo-5-methylpyridin-2-amine and 9.12 mL (73 mmol) of aq. sol. of ethyl bromopyruvate (90%) in DME (50 mL) was stirred at room temperature for 24 h. The resulting solid was filtered off, suspended in dry EtOH (150 mL), and the reaction mixture was refluxed for 24 h. After concentration to dryness, the residue was suspended in H_2O, made alkaline with Na_2CO_3 and the precipitate was filtered off. After dissolution of the solid in CH_2Cl_2 and drying with $CaCl_2$, the organic layer was evaporated under reduced pressure. Column chromatography on neutral alumina, and eluting with CH_2Cl_2, led to **1c** (84%). mp 149–150 °C. ^{1}H NMR δ 8.17 (s, 1H, H-3), 7.92 (m, 1H, H-5), 7.38 (d, 1H, $J = 1.4$ Hz, H-7), 4.44 (q, 2H, $J = 7.1$ Hz, CH_2), 2.36 (s, 3H, CH_3), 1.42 (t, 3H, $J = 7.1$ Hz, CH_3). ^{13}C NMR δ 163.4 (CO), 142.9 (C-8a*), 137.4 (C-2*), 132.2 (C-7), 124.4 (C-6), 123.5 (C-5), 118.7 (C-3), 112.5 (C-8), 61.6 (CH_2), 18.3 (CH_3), 14.8 (CH_3). Anal. Calcd for $C_{11}H_{11}N_2O_2Br$: C, 46.66; H, 3.92; N, 9.89%. Found: C, 46.52; H, 3.81; N, 10.02%.

Ethyl 8-Iodo-6-methylimidazo[1,2-*a*]pyridine-2-carboxylate (2c). The same conditions were applied using 8 g (34.2 mmol) of 3-iodo-5-methylpyridin-2-amine and 6.44 mL (51.3 mmol) of aq. sol. of ethyl bromopyruvate. Purification by column chromatography on neutral alumina gel using CH_2Cl_2 as an eluant gave **2c** (49%). mp 128–129 °C. ^{1}H NMR δ 8.23 (s, 1H, H-3), 7.94 (m, 1H, H-5), 7.65 (m, 1H, H-7), 4.45 (q, 2H, $J = 7.1$ Hz, CH_2), 2.32 (s, 3H, CH_3), 1.44 (t, 3H, $J = 7.1$ Hz, CH_3). ^{13}C NMR δ 163.4 (CO), 144.3 (C-8a), 139.3 (C-7), 137.2 (C-2), 124.9 (C-6), 124.4 (C-5), 119.0 (C-3), 84.8 (C-8), 61.5 (CH_2), 18.1 (CH_3), 14.8 (CH_3). Anal. Calcd for $C_{11}H_{11}N_2O_2I$: C, 40.02; H, 3.36; N, 8.49%. Found: C, 40.31; H, 3.61; N, 8.46%.

Suzuki Cross-Coupling Reaction: General Procedure. Into a three-necked round bottom flask was introduced the 8-halo-6-methyl-2-substituted imidazo[1,2-*a*]pyridine derivative **1–2** (1 mmol) in 1,2-dimethoxyethane (8 mL) under N_2. The catalyst (5 mol%), the boronic acid (1.1 molar amount) and the base (2 molar amounts) in H_2O (4 mL) were then added under vigorous stirring. The reaction mixture was warmed at 75 °C (Table 1). After cooling, the resulting mixture was diluted in H_2O and the aqueous layer extracted with CH_2Cl_2. The organic layers were dried on $CaCl_2$, filtered, and evaporated to dryness. Column chromatography afforded the pure product.

2,6-Dimethyl-8-phenylimidazo[1,2-*a*]pyridine (3a). Neutral alumina, eluting with CH_2Cl_2. mp 93–94 °C. ^{1}H NMR δ 8.02 (m, 2H, Ph-2,6), 7.84 (m, 1H, H-5), 7.50 (m, 3H, Ph-3,4,5), 7.35 (s, 1H, H-3), 7.11 (d, 1H, $J = 1.6$ Hz, H-7), 2.50 (s, 3H, CH_3), 2.37 (s, 3H, CH_3). ^{13}C NMR δ 143.6 (C-2*), 143.4 (C-8a*), 137.2 (Ph-1), 129.3 (C-8), 129.2 (Ph-2,6), 128.9 (Ph-3,5), 128.5 (Ph-4), 126.1 (C-7), 122.5 (C-5), 121.6 (C-6), 110.2 (C-3), 18.5 (CH_3), 15.1 (CH_3). Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60%. Found: C, 81.15; H, 6.33; N, 12.57%.

2,6-Dimethyl-8-(4-fluorophenyl)imidazo[1,2-*a*]pyridine (4a). Neutral alumina, eluting with CH_2Cl_2. mp 107–108 °C. ^{1}H NMR δ 8.02 (dd, 2H, $J = 8.6$, 5.6 Hz, F–Ph-2,6), 7.82 (s, 1H, H-5), 7.33 (s, 1H, H-3), 7.19 (t, 2H, $J = 8.6$ Hz, F–Ph-3,5), 7.05 (s, 1H, H-7), 2.49 (s, 3H, CH_3), 2.35 (s, 3H, CH_3). ^{13}C NMR δ 163.1 ($J = 245.5$ Hz, F–Ph-4), 143.6 (C-2*), 143.1 (C-8a*), 133.2 ($J = 3.5$ Hz, F–Ph-1), 130.5 ($J = 8$ Hz, F–Ph-2,6), 128.2 (C-8), 125.8 (C-7), 122.6 (C-5), 121.6 (C-6), 115.8 ($J = 21.5$ Hz, F–Ph-3,5), 110.3 (C-3), 18.4 (CH_3), 14.9 (CH_3). Anal. Calcd for $C_{15}H_{13}N_2F$: C, 74.98; H, 5.45; N, 11.66%. Found: C, 75.12; H, 5.54; N, 11.52%.

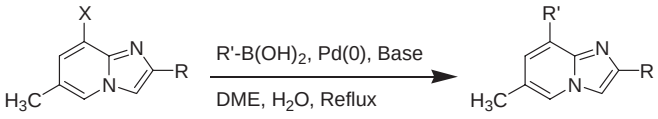
2,6-Dimethyl-8-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine (5a). Neutral alumina, eluting with CH_2Cl_2. mp 72–73 °C. ^{1}H NMR δ 7.99 (d, 2H, $J = 8.8$ Hz, CH_3O–Ph-2,6), 7.81 (m, 1H, H-5), 7.34 (s, 1H, H-3), 7.07 (m, 1H, H-7), 7.05 (d, 2H, $J = 8.8$ Hz, CH_3O–Ph-3,5), 2.50 (s, 3H, CH_3), 2.36 (s, 3H, CH_3). ^{13}C NMR δ 160.0 (CH_3O–Ph-4), 143.4 (C-2, C-8a), 130.4 (CH_3O–Ph-2,6), 129.7 (CH_3O–Ph-1), 128.9 (C-8), 125.3 (C-7), 122.0 (C-5), 121.6 (C-6), 114.4 (CH_3O–Ph-3,5), 110.1 (C-3), 55.8 (CH_3O), 18.6 (CH_3), 15.1 (CH_3). Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10%. Found: C, 76.28; H, 6.41; N, 11.25%.

2,6-Dimethyl-8-(2,4,6-trimethylphenyl)imidazo[1,2-*a*]pyridine (7a). Neutral alumina, eluting with CH_2Cl_2. mp 219–220 °C. ^{1}H NMR δ 7.87 (m, 1H, H-5), 7.33 (s, 1H, H-3), 6.99 (s, 2H, Ph-3,5), 6.77 (m, 1H, H-7), 2.44 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.01 (s, 6H, 2CH_3). ^{13}C NMR δ 143.7 (C-2*), 143.6 (C-8a*), 137.6 (Ph-1), 136.8 (Ph-2,6), 133.9 (Ph-4), 129.4 (C-8), 128.7 (Ph-3,5), 127.7 (C-7), 122.4 (C-5), 121.3 (C-6), 109.9 (C-3), 21.6 (CH_3), 20.8 (CH_3), 18.5 (CH_3), 15.2 (CH_3). Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.78; H, 7.63; N, 10.60%. Found: C, 81.83; H, 7.74; N, 10.59%.

2,6-Dimethyl-8-(3-trifluoromethylphenyl)imidazo[1,2-*a*]pyridine (8a). Neutral alumina, eluting with CH_2Cl_2. mp 105–106 °C. ^{1}H NMR δ 8.33 (m, 1H, Ph-6), 8.20 (m, 1H, Ph-2), 7.90 (m, 1H, H-5), 7.64 (m, 2H, Ph-4,5), 7.38 (d, 1H, $J = 0.8$ Hz, H-3), 7.13 (d, 1H, $J = 1.6$ Hz, H-7), 2.51 (s, 3H, CH_3), 2.40 (s, 3H, CH_3). ^{13}C NMR δ 143.91 (C-2*), 142.94 (C-8a*), 137.95 (Ph-1), 132.83 (Ph-6), 131.23 ($J = 31.5$ Hz, Ph-3), 129.33 (Ph-5), 127.75 (C-8), 126.30 (C-7), 125.87 ($J = 4$ Hz, Ph-2), 125.00 ($J = 3.5$ Hz, Ph-4), 124.70 ($J = 270.5$ Hz, CF_3), 123.20 (C-5), 121.60 (C-6), 110.37 (C-3), 18.47 (CH_3), 14.96 (CH_3). Anal. Calcd for $C_{16}H_{13}N_2F_3$: C, 66.20; H, 4.51; N, 9.65%. Found: C, 66.37; H, 4.44; N, 9.78%.

2,6-Dimethyl-8-(3-nitrophenyl)imidazo[1,2-*a*]pyridine (9a). Neutral alumina, eluting with CH_2Cl_2. mp 114–115 °C. ^{1}H NMR δ 8.87 (m, 1H, Ph-2), 8.51 (dt, 1H, $J = 7.8$, 1.1 Hz, Ph-6), 8.27 (ddd, 1H, $J = 8.2$, 2.3, 1.1 Hz, Ph-4), 7.93 (m, 1H, H-5), 7.69 (dd, 1H, $J = 8.2$, 7.8 Hz, Ph-5), 7.39 (d, 1H, $J = 0.7$ Hz, H-3), 7.20 (d, 1H, $J = 1.6$ Hz, H-7), 2.51 (s, 3H, CH_3), 2.43 (s, 3H, CH_3). ^{13}C NMR δ 148.9 (Ph-3), 144.1 (C-2*), 142.7 (C-8a*), 138.8 (Ph-1), 135.5 (Ph-4), 129.9 (Ph-5), 126.6 (C-8), 126.5 (C-7), 124.0 (Ph-2), 123.6 (C-5), 123.2 (Ph-6), 121.6 (C-6), 110.5 (C-3), 18.5 (CH_3), 15.0 (CH_3). Anal. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.72%. Found: C, 67.55; H, 4.87; N, 15.63%.

Table 1. Synthesis of 8-(Hetero)arylimidazo[1,2-*a*]pyridines **3**–**12**[a)]



1a-c, 2a-c **3-12**

a: R = CH_3
b: R = 4-FC_6H_4
c: R = $CO_2C_2H_5$

Compd	R′	X	Catalyst	Base	R = CH_3 Yield/%[b)] (Time/h)	R = 4-FC_6H_4 Yield/%[b)] (Time/h)	R = $CO_2C_2H_5$ Yield/%[b)] (Time/h)
3	C_6H_5	Br	$Pd(PPh_3)_4$	NaOH	94 (3)	95 (3)	
		Br	$Pd(PPh_3)_4$	Na_2CO_3			69 (3), 25 (8)
		I	$Pd(PPh_3)_4$	Na_2CO_3			46 (3)
		Br	$Pd(PPh_3)_4$	K_3PO_4			49 (3), 76 (8)
4	4-FC_6H_4	Br	$Pd(PPh_3)_4$	NaOH	95 (3)	96 (3)	
		I	$Pd(PPh_3)_4$	Na_2CO_3			50 (3)
5	4-$CH_3OC_6H_4$	Br	$Pd(PPh_3)_4$	NaOH	94 (3)		
6	3-$CH_3OC_6H_4$	Br	$Pd(PPh_3)_4$	NaOH		82 (3)	
7	2,4,6-$(CH_3)_3C_6H_2$	Br	$Pd(PPh_3)_4$	NaOH	94 (3)		
8	3-$CF_3C_6H_4$	Br	$Pd(PPh_3)_4$	NaOH	91 (3)	88 (3)	
9	3-$NO_2C_6H_4$	Br	$Pd(PPh_3)_4$	NaOH	40 (3)		
		I	$Pd(PPh_3)_4$	NaOH	20 (3)		
10	Thien-2-yl	Br	$Pd(PPh_3)_4$	NaOH	34 (3)	55 (3)	
		Br	$Pd(PPh_3)_4$	Na_2CO_3		62 (8)	47 (3), 28 (8)
		I	$Pd(PPh_3)_4$	NaOH	42 (3), 42 (8)	54 (24)	
		I	$Pd(PPh_3)_4$	Na_2CO_3	68 (8)		
		I	$Pd(PPh_3)_4$	$Ba(OH)_2$	37 (8)		
		I	$PdCl_2$dppf	$Ba(OH)_2$	67 (8), 62 (24)	69 (8)	
11	Thien-3-yl	Br	$Pd(PPh_3)_4$	NaOH	55 (8)	58 (8)	
		I	$Pd(PPh_3)_4$	NaOH	72 (8)	85 (8)	
		Br	$Pd(PPh_3)_4$	Na_2CO_3		70 (8)	37 (3), 42 (8)
		Br	$Pd(PPh_3)_4$	K_3PO_4			88 (8)
12	Fur-2-yl	Br	$Pd(PPh_3)_4$	NaOH	19 (24)		
		I	$PdCl_2$dppf	$Ba(OH)_2$	55 (8), 50 (24)		
		Br	$Pd(PPh_3)_4$	Na_2CO_3			19 (8)
		Br	$Pd(PPh_3)_4$	K_3PO_4			traces (8)

a) Couplings were carried out in a mixture of DME (8 mL) and water (4 mL) at 75 °C. b) Isolated yields.

2,6-Dimethyl-8-(thien-2-yl)imidazo[1,2-*a*]pyridine (10a). Neutral alumina, eluting with CH_2Cl_2. mp 73–74 °C. ^{1}H NMR δ 8.19 (dd, 1H, $J = 3.7$, 1.2 Hz, Th-3), 7.79 (m, 1H, H-5), 7.41 (dd, 1H, $J = 5.1$, 1.2 Hz, Th-5), 7.32 (s, 1H, H-3), 7.30 (m, 1H, H-7), 7.19 (dd, 1H, $J = 5.1$, 3.7 Hz, Th-4), 2.53 (s, 3H, CH_3), 2.36 (s, 3H, CH_3). ^{13}C NMR δ 143.5 (C-2*), 142.0 (C-8a*), 138.9 (Th-2), 128.2 (Th-3), 127.8 (Th-4), 126.3 (Th-5), 123.7 (C-7), 122.6 (C-8), 122.2 (C-5), 121.4 (C-6), 110.4 (C-3), 18.5 (CH_3), 15.1 (CH_3). Anal. Calcd for $C_{13}H_{12}N_2S$: C, 68.39; H, 5.30; N, 12.27%. Found: C, 68.27; H, 5.41; N, 12.59%.

2,6-Dimethyl-8-(thien-3-yl)imidazo[1,2-*a*]pyridine (11a). Silica gel, eluting with ether. mp 108–109 °C. ^{1}H NMR δ 8.63 (dd, 1H, $J = 3.1$, 1.3 Hz, Th-2), 7.81 (m, 1H, H-5), 7.76 (dd, 1H, $J = 5.1$, 1.3 Hz, Th-4), 7.44 (dd, 1H, $J = 5.1$, 3.1 Hz, Th-5), 7.33 (s, 1H, H-3), 7.27 (d, 1H, $J = 1.5$ Hz, H-7), 2.52 (s, 3H, CH_3), 2.37 (s, 3H, CH_3). ^{13}C NMR δ 143.4 (C-2*), 142.8 (C-8a*), 137.1 (Th-3), 127.1 (Th-4), 125.8 (Th-2), 125.7 (Th-5), 124.4 (C-7), 123.7 (C-8), 122.0 (C-5), 121.4 (C-6), 110.1 (C-3), 18.6 (CH_3), 15.0 (CH_3). Anal. Calcd for $C_{13}H_{12}N_2S$: C, 68.39; H, 5.30; N, 12.27%. Found: C, 68.37; H, 5.31; N, 12.22%.

2,6-Dimethyl-8-(fur-2-yl)imidazo[1,2-*a*]pyridine (12a). Neutral alumina, eluting with CH_2Cl_2. mp 107–108 °C. ^{1}H NMR δ 7.78 (m, 1H, H-5), 7.77 (d, 1H, $J = 3.4$ Hz, Fu-3), 7.57 (d, 1H, $J = 1.8$ Hz, Fu-5), 7.48 (d, 1H, $J = 1.5$ Hz, H-7), 7.31 (d, 1H, $J = 1.5$ Hz, H-3), 6.62 (dd, 1H, $J = 3.4$, 1.8 Hz, Fu-4), 2.53 (s, 3H, CH_3), 2.37 (s, 3H, CH_3). ^{13}C NMR δ 149.8 (Fur-2), 143.4 (C-2*), 142.8 (Fur-5), 140.8 (C-8a*), 122.0 (C-5), 121.5 (C-7), 121.4 (C-6), 118.8 (C-8), 112.6 (Fur-3), 112.3 (Fur-4), 110.2 (C-3), 18.6 (CH_3), 15.0 (CH_3). Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20%. Found: C, 73.94; H, 5.57; N, 13.24%.

6-Methyl-2-(4-fluorophenyl)-8-phenylimidazo[1,2-*a*]pyridine (3b). Neutral alumina, eluting with CH_2Cl_2. mp 116–117 °C. ^{1}H NMR δ 8.23 (m, 2H, Ph-2,6), 7.98 (dd, 2H, $J = 8.7$, 5.5 Hz, F–Ph-2,6), 7.75 (m, 1H, H-5), 7.68 (s, 1H, H-3), 7.56 (m, 3H, Ph-3,4,5), 7.19 (d, 1H, $J = 1.6$ Hz, H-7), 7.15 (t, 2H, $J = 8.7$ Hz, F–Ph-3,5), 2.34 (s, 3H, CH_3). ^{13}C NMR δ 163.0 ($J = 244.5$ Hz, F–Ph-4), 144.9 (C-2*), 143.8 (C-8a*), 136.8 (Ph-1), 130.9 ($J = 3$ Hz, F–Ph-1), 129.5 (Ph-4), 129.4 (Ph-2,6),

128.9 (Ph-3,5), 128.8 (C-8), 128.1 ($J = 8$ Hz, F–Ph-2,6), 126.5 (C-7), 122.9 (C-5), 122.4 (C-6), 116.1 ($J = 21$ Hz, F–Ph-3,5), 108.4 (C-3), 18.6 (CH_3). Anal. Calcd for $C_{20}H_{16}N_2F$: C, 79.45; H, 5.00; N, 9.27%. Found: C, 79.51; H, 5.03; N, 9.38%.

6-Methyl-2,8-bis(4-fluorophenyl)imidazo[1,2-*a*]pyridine (4b). Silica gel, eluting with ether. mp 110–111 °C. ^{1}H NMR δ 8.19 (dd, 2H, $J = 9$, 5.5 Hz, F–Ph′-2,6), 7.99 (dd, 2H, $J = 9$, 5.5 Hz, F–Ph-2,6), 7.95 (m, 1H, H-5), 7.83 (s, 1H, H-3), 7.24 (t, 3H, $J = 9$ Hz, F–Ph′-3,5), 7.18 (d, 1H, $J = 1.4$ Hz, H-7), 7.15 (t, 2H, $J = 9$ Hz, F–Ph-3,5), 2.41 (s, 3H, CH_3). ^{13}C NMR δ 163.3 ($J = 246.5$ Hz, F–Ph′-4), 163.0 ($J = 244.6$ Hz, F–Ph-4), 145.0 (C-2*), 143.7 (C-8a*), 132.8 ($J = 3$ Hz, F–Ph′-1), 131.1 ($J = 8$ Hz, F–Ph′-2,6), 130.7 ($J = 3$ Hz, F–Ph-1), 128.5 (C-8), 128.1 ($J = 7.5$ Hz, F–Ph-2,6), 126.3 (C-7), 122.9 (C-5), 122.4 (C-6), 115.9 ($J = 21.5$ Hz, F–Ph′-3,5), 115.7 ($J = 21.5$ Hz, F–Ph-3,5*), 108.4 (C-3), 18.6 (CH_3). Anal. Calcd for $C_{16}H_{16}N_2O$: C, 74.99; H, 4.41; N, 8.75%. Found: C, 75.05; H, 4.38; N, 8.75%.

6-Methyl-2-(4-fluorophenyl)-8-(3-methoxyphenyl)imidazo-[1,2-*a*]pyridine (6b). Neutral alumina, eluting with a mixture ether/petroleum ether (2/1). mp 114–115 °C. ^{1}H NMR δ 7.99 (dd, 2H, $J = 8.6$, 5.5 Hz, F–Ph-2,6), 7.93 (m, 1H, H-5), 7.89 (m, 1H, CH_3O–Ph-2), 7.83 (s, 1H, H-3), 7.71 (bd, 1H, $J = 7.9$ Hz, CH_3O–Ph-6), 7.45 (t, 1H, $J = 7.9$ Hz, CH_3O–Ph-5), 7.24 (d, 1H, $J = 1.5$ Hz, H-7), 7.14 (t, 2H, $J = 8.6$ Hz, F–Ph-3,5), 7.02 (dd, 1H, $J = 7.9$, 2.3 Hz, CH_3O–Ph-4), 3.95 (s, 3H, CH_3O), 2.41 (s, 3H, CH_3). ^{13}C NMR δ 163.0 ($J = 245$ Hz, F–Ph-4), 160.0 (Ph-3), 145.0 (C-2*), 143.8 (C-8a*), 138.1 (Ph-1), 130.8 ($J = 3$ Hz, F–Ph-1), 129.8 (Ph-5), 129.4 (C-8), 128.1 ($J = 8$ Hz, F–Ph-2,6), 126.5 (C-7), 122.9 (C-5), 122.4 (C-6), 121.7 (Ph-6), 115.9 ($J = 21.5$ Hz, F–Ph-3,5), 115.0 (Ph-2), 114.6 (Ph-4), 108.3 (C-3), 55.8 (CH_3O), 18.6 (CH_3). Anal. Calcd for $C_{21}H_{17}N_2OF$: C, 75.89; H, 5.16; N, 8.43%. Found: C, 75.84; H, 5.12; N, 8.57%.

6-Methyl-2-(4-fluorophenyl)-8-(3-trifluoromethylphenyl)imidazo[1,2-*a*]pyridine (8b). Silica gel, eluting with ether. mp 104–105 °C. ^{1}H NMR δ 8.50 (s, 1H, Ph-2), 8.43 (d, 1H, $J = 7.1$ Hz, Ph-6), 7.97 (dd, 2H, $J = 8.9$, 5.4 Hz, F–Ph-2,6), 7.91 (s, 1H, H-5), 7.79 (s, 1H, H-3), 7.68 (m, 2H, Ph-4,5), 7.23 (s, 1H, H-7), 7.15 (t, 2H, $J = 8.9$ Hz, F–Ph-3,5), 2.40 (s, 3H, CH_3). ^{13}C NMR δ 163.9 ($J = 244.5$ Hz, F–Ph-4), 145.2 (C-2*), 143.5 (C-8a*), 132.6 (Ph-6), 131.2 ($J = 39$ Hz, Ph-3), 130.6 ($J = 3$ Hz, F–Ph-1), 129.2 (Ph-5), 128.0 ($J = 8$ Hz, F–Ph-2,6), 127.9 (C-8), 126.6 (C-7), 126.2 ($J = 4$ Hz, Ph-2), 125.2 ($J = 3.5$ Hz, Ph-4), 124.7 ($J = 270.5$ Hz, CF_3), 123.5 (C-5), 122.4 (C-6), 115.9 ($J = 21.5$ Hz, F–Ph-3,5), 108.4 (C-3), 18.5 (CH_3). Anal. Calcd for $C_{21}H_{14}N_2F_4$: C, 68.11; H, 3.81; N, 7.57%. Found: C, 68.54; H, 3.78; N, 7.75%.

6-Methyl-2-(4-fluorophenyl)-8-(thien-2-yl)imidazo[1,2-*a*]pyridine (10b). Neutral alumina, eluting with CH_2Cl_2. mp 149–150 °C. ^{1}H NMR δ 8.38 (dd, 1H, $J = 3.7$, 1.2 Hz, Th-3), 8.04 (dd, 2H, $J = 8.9$, 5.5 Hz, F–Ph-2,6), 7.82 (m, 1H, H-5), 7.75 (s, 1H, H-3), 7.47 (dd, 1H, $J = 5.1$, 1.2 Hz, Th-5), 7.36 (d, 1H, $J = 1.4$ Hz, H-7), 7.24 (dd, 1H, $J = 5.1$, 3.7 Hz, Th-4), 7.17 (t, 2H, $J = 8.9$ Hz, F–Ph-3,5), 2.37 (s, 3H, CH_3). ^{13}C NMR δ 163.0 ($J = 244.5$ Hz, F–Ph-4), 144.8 (C-2*), 142.4 (C-8a*), 138.7 (Th-2), 130.7 ($J = 3$ Hz, F–Ph-1), 128.1 (Th-3,4), 128.0 ($J = 8$ Hz, F–Ph-2,6), 126.8 (Th-5), 123.9 (C-7), 123.1 (C-8), 122.3 (C-5), 122.2 (C-6), 115.9 ($J = 21.5$ Hz, F–Ph-3,5), 108.3 (C-3), 18.6 (CH_3). Anal. Calcd for $C_{18}H_{13}N_2SF$: C, 70.11; H, 4.25; N, 9.08%. Found: C, 70.26; H, 4.22; N, 9.09%.

6-Methyl-2-(4-fluorophenyl)-8-(thien-3-yl)imidazo[1,2-*a*]pyridine (11b). Silica gel, eluting with ether. mp 149–150 °C. ^{1}H NMR δ 8.92 (dd, 1H, $J = 3$, 1.2 Hz, Th-2), 8.01 (dd, 2H, $J =$ 8.8, 5.5 Hz, F–Ph-2,6), 7.84 (dd, 1H, $J = 5.1$, 1.2 Hz, Th-4), 7.77 (s, 1H, H-5), 7.70 (s, 1H, H-3), 7.46 (dd, 1H, $J = 5.1$, 3 Hz, Th-5), 7.31 (d, 1H, $J = 1.3$ Hz, H-7), 7.16 (t, 2H, $J = 8.8$ Hz, F–Ph-3,5), 2.35 (s, 3H, CH_3). ^{13}C NMR δ 162.9 ($J = 244.5$ Hz, F–Ph-4), 144.6 (C-2*), 143.3 (C-8a*), 136.8 (Th-3), 130.8 ($J = 3$ Hz, F–Ph-1), 128.0 ($J = 8$ Hz, F–Ph-2,6), 126.9 (Th-4), 126.3 (Th-2), 125.6 (Th-5), 124.7 (C-7), 123.8 (C-8), 122.3 (C-5, C-6), 115.9 ($J = 21.5$ Hz, F–Ph-3,5), 108.2 (C-3), 18.6 (CH_3). Anal. Calcd for $C_{18}H_{13}N_2SF$: C, 70.11; H, 4.25; N, 9.08%. Found: C, 70.35; H, 4.36; N, 9.14%.

Ethyl 6-Methyl-8-phenylimidazo[1,2-*a*]pyridine-2-carboxylate (3c). Neutral alumina, eluting with CH_2Cl_2. mp 107–108 °C. ^{1}H NMR δ 8.17 (s, 1H, H-3), 8.06 (m, 2H, Ph-2,6), 7.93 (m, 1H, H-5), 7.49 (m, 3H, Ph-3,4,5), 7.25 (d, 1H, $J = 1.6$ Hz, H-7), 4.46 (q, 2H, $J = 7.1$ Hz, CH_2), 2.40 (s, 3H, CH_3), 1.45 (t, 3H, $J = 7.1$ Hz, CH_3). ^{13}C NMR δ 163.9 (CO), 143.8 (C-2*), 137.0 (Ph-1), 136.2 (C-8a*), 131.3 (C-8), 129.3 (Ph-2,6), 128.9 (Ph-3,4,5), 128.0 (C-7), 124.1 (C-6), 123.0 (C-5), 117.6 (C-3), 61.4 (CH_2), 18.7 (CH_3), 14.8 (CH_3). Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99%. Found: C, 73.08; H, 5.61; N, 10.03%.

Ethyl 6-Methyl-8-(4-fluorophenyl)imidazo[1,2-*a*]pyridine-2-carboxylate (4c). Neutral alumina, eluting with CH_2Cl_2. mp 121–122 °C. ^{1}H NMR δ 8.16 (s, 1H, H-3), 8.07 (dd, 2H, $J =$ 8.7, 5.5 Hz, F–Ph-2,6), 7.94 (m, 1H, H-5), 7.23 (m, 1H, H-7), 7.21 (t, 2H, $J = 8.7$ Hz, F–Ph-3,5), 4.57 (q, 2H, $J = 7.1$ Hz, CH_2), 2.42 (s, 3H, CH_3), 1.46 (t, 3H, $J = 7.1$ Hz, CH_3). ^{13}C NMR δ 163.5 ($J = 246$ Hz, F–Ph-4), 163.8 (CO), 143.7 (C-2*), 137.1 (C-8a*), 132.2 ($J = 3$ Hz, F–Ph-1), 131.1 ($J = 8$ Hz, F–Ph-2,6), 130.2 (C-8), 127.8 (C-7), 124.1 (C-6), 123.0 (C-5), 117.7 (C-3), 115.9 ($J = 21.5$ Hz, F–Ph-3,5), 61.47 (CH_2), 18.70 (CH_3), 14.83 (CH_3). Anal. Calcd for $C_{17}H_{15}N_2O_2F$: C, 68.45; H, 5.07; N, 9.39%. Found: C, 68.54; H, 5.11; N, 9.48%.

Ethyl 6-Methyl-8-(thien-2-yl)imidazo[1,2-*a*]pyridine-2-carboxylate (10c). Neutral alumina, eluting with CH_2Cl_2. mp 149–150 °C. ^{1}H NMR δ 8.35 (dd, 1H, $J = 3.7$, 1.2 Hz, Th-3), 8.11 (s, 1H, H-3), 7.82 (m, 1H, H-5), 7.42 (dd, 1H, $J = 5.1$, 1.2 Hz, Th-5), 7.36 (d, 1H, $J = 1.4$ Hz, H-7), 7.18 (dd, 1H, $J =$ 5.1, 3.7 Hz, Th-4), 4.47 (q, 2H, $J = 7.1$ Hz, CH_2), 2.35 (s, 3H, CH_3), 1.46 (t, 3H, $J = 7.1$ Hz, CH_3). ^{13}C NMR δ 163.8 (CO), 142.4 (C-2*), 137.8 (C-8a*), 136.8 (Th-2), 129.1 (Th-3), 128.5 (Th-4), 126.9 (Th-5), 125.4 (C-7), 124.5 (C-8*), 123.9 (C-6*), 122.5 (C-5), 117.7 (C-3), 61.4 (CH_2), 18.6 (CH_3), 14.8 (CH_3). Anal. Calcd for $C_{15}H_{14}N_2O_2S$: C, 62.92; H, 4.93; N, 9.78%. Found: C, 63.05; H, 4.89; N, 9.75%.

Ethyl 6-Methyl-8-(thien-3-yl)imidazo[1,2-*a*]pyridine-2-carboxylate (11c). Silica gel, eluting with ether. mp 150–151 °C. ^{1}H NMR δ 8.79 (dd, 1H, $J = 3.1$, 1.3 Hz, Th-2), 8.15 (s, 1H, H-3), 7.87 (m, 1H, H-5), 7.76 (dd, 1H, $J = 5.1$, 1.3 Hz, Th-4), 7.44 (dd, 1H, $J = 5.1$, 3.1 Hz, Th-5), 7.39 (d, 1H, $J = 1.5$ Hz, H-7), 4.48 (q, 2H, $J = 7.1$ Hz, CH_2), 2.39 (s, 3H, CH_3), 1.48 (t, 3H, $J = 7.1$ Hz, CH_3). ^{13}C NMR δ 163.9 (CO), 143.3 (C-2*), 136.8 (C-8a*), 135.95 (Th-3), 127.0 (Th-2), 126.7 (Th-4), 126.0 (C-7), 125.9 (Th-5), 125.5 (C-8), 124.0 (C-6), 122.4 (C-5), 117.6 (C-3), 61.4 (CH_2), 18.7 (CH_3), 14.8 (CH_3). Anal. Calcd for $C_{15}H_{14}N_2O_2S$: C, 62.92; H, 4.93; N, 9.78%. Found: C, 62.97; H, 4.96; N, 9.84%.

Ethyl 6-Methyl-8-(fur-2-yl)imidazo[1,2-*a*]pyridine-2-carboxylate (12c). Silica gel, eluting with ether. mp 126–127 °C. ^{1}H NMR δ 8.14 (s, 1H, H-3), 7.91 (d, 1H, $J = 3.2$ Hz, Fu-3), 7.85 (s, 1H, H-5), 7.58 (m, 2H, H-7, Fu-5), 6.64 (m, 1H, Fu-4), 4.48 (q, 2H, $J = 7.1$ Hz, CH_2), 2.40 (s, 3H, CH_3), 1.48 (t, 3H, $J =$ 7.1 Hz, CH_3). ^{13}C NMR δ 163.8 (CO), 148.7 (Fu-2), 143.3 (Fu-5),

141.3 (C-2), 136.8 (C-8a*), 124.0 (C-8), 123.1 (C-7), 122.2 (C-5), 120.7 (C-6), 117.6 (C-3), 113.8 (Fu-3), 112.8 (Fu-4), 61.4 (CH_2), 18.8 (CH_3), 14.8 (CH_3). Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36%. Found: C, 66.58; H, 5.43; N, 10.32%.

We express our grateful acknowledgement to Frederic Montigny (SAVIT) for NMR data.

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