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Synthesis of functionalized 2-arylpyridines from 2-halopyridines and various aryl halides via a nickel catalysis

Corinne Gosmini [a,*], Carine Bassene-Ernst [b], Muriel Durandetti [c]

[a] Département de Chimie, Laboratoire Hétéroéléments et Coordination, UMR CNRS 7653, Ecole Polytechnique, 91128 Palaiseau Cédex, France
[b] Equipe Electrochimie et Synthèse Organique, Institut de Chimie et des Materiaux Paris Est, ICMPE, C.N.R.S-Université Paris 12 val de Marne, UMR 7182, 2 rue Henri Dunant 94320 Thiais, France
[c] Laboratoire des Fonctions Azotées & Oxygénées Complexes de l'IRCOF—CNRS UMR 6014 & FR CNRS 3038, Université de Rouen and INSA de Rouen, 76821 Mont St Aignan Cedex, France

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ABSTRACT

An efficient nickel-catalyzed method devoted to the direct formation of functionalized 2-arylpyridines is described avoiding the prior preparation of organometallic species. Various functionalized 2-arylpyridines are obtained in moderate to excellent yields by a one-step chemical procedure from corresponding halides. The $NiBr_2$(2,2′-bipyridine) complex appears to be an extremely suitable catalyst for the activation in the presence of manganese dust of aromatic halides and pyridyl halides functionalized by reactive groups. The versatility of this original process represents a simple alternative to most known methods using organometallic reagents.

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1. Introduction

The broad use of biaryl compounds and especially 2-arylpyridines as key building blocks in materials[1] and in medicinal chemistry[2] has aroused considerable effort to facilitate their chemical accessibility. Among the diverse approaches developed for the construction of 2-aryl/heteroarylpyridines the use of a transition-metal catalyzed reaction has been the most successful. These reactions involve the preparation of an organometallic reagent and the presence of a transition metal for the cross-coupling reactions such as Pd, Ni, Fe or Co. A variety of aromatic organometallic reagents[3] could be implied in the coupling with 2-pyridylhalides. However, only a few examples using 2-pyridylmetals have been reported in the literature due to the instability of 2-pyridylmetal reagents.[4] More recently, a transition-metal free regiospecific sequential addition of Grignard reagents to pyridine *N*-oxides was reported.[5] To avoid the preparation of a stoichiometric organometallic reagent, different one-pot selective cross-coupling procedures have been reported. These include coupling of a 2-halopyridine with an aryl halide under phase-transfer conditions[6] or using a stoichiometric amount of hexamethylditin,[7] both in the presence of Pd-catalysis. Functionalized 2-arylpyridines could also be synthesized from 2-pyridylhalides and electron rich arenes in the presence of $AlCl_3$[8] or by Pd-catalyzed direct arylation of pyridine *N*-oxides with aryl bromide.[9] Alternatively, a method based on the intermolecular radical addition of aryl or heteroaryl radicals gives arylpyridines in low yields.[10] Few years ago, we have developed two electrochemical methods leading to 2-arylpyridines using $NiBr_2$(2,2′-bipyridine) as catalyst.[11] However, although theses methods lead to good yields in heterocoupling product, electrochemical reactions are generally considered as being more difficult to handle than conventional methods and electrochemical synthesis is rarely applied by organic chemists in a larger scale. Then, a conventional chemical is often preferred. Recently we have discovered an efficient cobalt catalyzed method devoted to the formation of unsymmetrical biaryls exhibiting high tolerance towards sensitive functional groups on the aromatic nucleus.[12] However, this protocol cannot be applied to 2-chloropyrimidine as coupling partners except in the case of 3-substituted pyridines. Therefore, we have decided to develop a cross-coupling chemical method using a nickel catalyst instead of electrochemical process. Moreover, we have reported recently a chemical method for activation of α-chloroesters leading to aryl propanoic esters using $NiBr_2$(Bipy) as catalyst in the presence of manganese as reducing metal.[13] The main advantages of the method are the use of an easily prepared Ni(II)bipy complex in catalytic amount, which is not air sensitive and the easy control of the overall reactions. Herein, we describe the details of a cross-coupling reaction using a nickel complex in combination with manganese dust as a reducing agent and establish its scope and synthetic utility for the efficient formation of a variety of functionalized 2-arylpyridines (Scheme 1).

* Corresponding author. Tel.: +33 1 69334412; fax: +33 1 69334440.
E-mail address: corinne.gosmini@polytechnique.edu (C. Gosmini).

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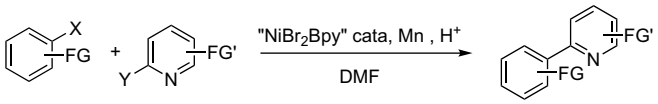


Scheme 1. Cross-coupling of 2-arylpyridines and functionalized aryl halides.

2. Results and discussion

2.1. Cross-coupling of various aryl halides with 2-halopyridine

Some years ago, we have adapted some electrochemical reactions in 'pure chemical process' employing an appropriate reducing metal. After a brief survey of reducing metal, we have found that manganese powder was the best one for the reduction of cobalt,[12,14,15] iron[16] or nickel salt.[13] On the basis of these improvements, we investigated the chemical coupling between various 2-halopyridines and substituted aryl halides, using $NiBr_2$bipy as catalyst. Our work started with the synthesis of 2-arylpyridines functionalized on the arene moiety. According to our previous electrochemical studies, we assume that FG–C_6H_4NiX is the first formed intermediate, being further reduced to FG–C_6H_4Ni to react preferably with 2-halopyridine.[11b] Then, we would have the best halogen on the aryl halide according to the nature of the substituent for the coupling reaction to be efficient. Typical procedure: A 1:1.3 mixture of the aryl halide and the halopyridine is stirred at room temperature in the presence of the catalytic amount of $NiBr_2$bpy (10 mol %), excess of manganese powder (2.3 equiv) activated by trifluoroacetic acid in DMF. The manganese has proven to be the adequate metal in order to achieve the two successive oxidative additions followed by the reductive elimination that constitute the mechanism involved in this reaction. Reactions are conducted at room temperature except in the case of *ortho*-substituted aryl halides (60 °C).

2.1.1. Cross-coupling of various aryl halide with 2-bromopyridine

This coupling-process has been successfully applied to 2-bromopyridine and various aryl halides. However, the choice of both the substituent and the halogen on the aromatic nucleus was important. The reactions were performed only with an aryl bromide substituted by an electron-withdrawing group or with an aryl iodide substituted by an electron-donating group. Results are shown in Table 1.

Results show that the cross-coupling is efficient whatever the *meta* or *para* position of the substituent. On the other hand, the *ortho* position decreases the yield considerably (Table 1, entry 3). Generally, yields of coupling product are increased in some cases up to 30% compared to results obtained by the electrochemical coupling. An aryl bromide substituted by an halogen such as a fluorine (Table 1, entry 8), less electron-withdrawing, was not enough reactive to react with Ni(0) before the 2-bromopyridine. In this case the use of 2-chloropyridine was preferable as reported in the next section. To extend the scope of this process, we intend to show that this method can be suitable for coupling with less reactive 2-chloropyridine.

Table 1
Cross-coupling between 2-bromopyridine and substituted aryl halides

X=I FG= electron-donating
X=Br FG= electron-withdrawing goup

Entry	ArX		Product	Reaction time	Yield[a] (GC)%
	FG	X			
1	*p*-CO_2Et	Br	**1**	50 min	91 (93)
2	*m*-CO_2Et	Br	**2**	6 h	83 (84)
3	*o*-CO_2Et	Br	**3**	18 h	20 (48)
4	*p*-COMe	Br	**4**	22 h	86 (97)
5	*p*-CF_3	Br	**5**	1 h	76 (84)
6	*m*-CF_3	Br	**6**	30 min	63 (85)
7	*p*-CN	Br	**7**	4 h	83 (92)
8	*p*-F	Br	**8**	1 h	34 (43)
9	*p*-OMe	I	**9**	5 min	75 (85)

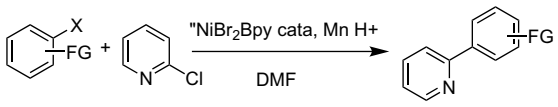
[a] Isolated yield.

2.1.2. Cross-coupling of various aryl halides with 2-chloropyridine

The use of 2-chloropyridine is of great interest due to their wide availability. As a consequence, the discovery of efficient procedures for the coupling of this compound with various aryl halides is highly desirable.

In this case, both an electro-withdrawing group and chlorine on the aromatic nucleus or both an electron-donating group and a bromide were necessary to react with 2-chloropyridine to avoid the formation of Ar–Ar. Results are reported in Table 2.

Table 2
Cross-coupling between 2-chloropyridine and substituted aryl halides



X=Br FG= electron-donating
X=Cl FG= electron-withdrawing goup

Entry	ArX		Product	Reaction time	Yield (GC)%
	FG	X			
1	*p*-CO_2Me	Cl	**10**	2 h	86 (94)
2	*m*-CO_2Me	Cl	**11**	18 h	74 (78)
3	*o*-CO_2Me[a]	Cl	**12**	48 h	45 (46)
4	*p*-CN	Cl	**7**	6 h	63 (76)
5	*m*-CN[a]	Cl	**13**	6 h	63 (77)
6	*p*-CF_3	Cl	**5**	3 h	83 (89)
7	*o*-CF_3[a]	Cl	**14**	18 h	63 (70)
8	*p*-OMe	Br	**9**	3 h	81 (92)
9	*o*-OMe[a]	Br	**15**	20 min	71 (90)
10	*p*-NH_2	Br	**16**	3 h 30 min	62 (76)
11	*o*-NH_2[a]	Br	**17**	16 h	56 (72)
12	*p*-N(Me)$_2$	Br	**18**	2 h 30 min	68 (80)
13	*o*-Me[a]	Br	**19**	1 h	61 (71)
14	*p*-F	Br	**8**	1 h 30 min	73 (86)
15	*p*-Cl	Br	**20**	1 h	54 (60)

[a] Reaction conducted at 60 °C.

One more time, yields are slightly superior than those obtained by our electrochemical method. An *ortho* substituent decrease the yield in spite of a good yield (Table 2, entries 3, 7, 9, 11 and 13) if the reaction is conducted at 60 °C. Interestingly, the reaction conditions allowed an efficient cross-coupling between 2-chloropyridine and aryl halides bearing relatively acidic NH_2 groups without protection (Table 2, entries 10 and 11).

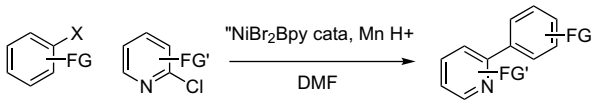
2.2. Cross-coupling of various aryl halides with functionalized 2-chloropyridines

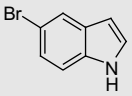
Encouraged by these previous works, we decided to go on with the coupling of some functionalized 2-chloropyridines and various functionalized aryl halides.

2.2.1. Cross-coupling of various aryl halides bearing an electro-donating group with functionalized 2-chloropyridines

The presence of an electron-donating substituent on 2-chloropyridines does not significantly change their reactivity. So, in this

Table 3
Cross-coupling between functionalized 2-chloropyridines and various aryl halides substituted by an electron-donating group



Entry	PyrCl FG′	ArX FG	X	Product	Time (min)	Yield[a] (GC)%
1	5-CF_3	*p*-NH_2	I	**21**	30	44 (65)
2	5-CF_3	*p*-OMe	I	**22**	50	35 (48)
3	6-Me	*p*-OMe	Br	**23**	240	82 (90)
4	6-OMe	*p*-OMe	Br	**24**	10	50 (76)
5	6-OMe	*p*-NMe_2	Br	**25**	20	54 (65)
6	6-OMe	*p*-NH_2	Br	**26**	20	47 (58)
7	6-Me			**27**	240	67 (70)

[a] Isolated yield.

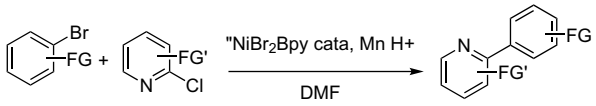
case, an aryl bromide should bear an electron-donating group (Table 3, entries 3–7). On the other hand, a chloropyridine activated by an electron-donating group should react with an aryl iodide bearing an electro-withdrawing group (Table 3, entries 1 and 2). Results are reported in Table 3.

Excellent to moderate yields are obtained depending on the nature of the substituent on 2-chloropyridine. A protected amine leads to similar yields than non-protected amine (Table 3, entries 5 and 6).

2.2.2. Cross-coupling of various aryl bromides bearing an electro-withdrawing group with functionalized 2-chloropyridines

We have envisioned to couple various functionalized 2-chloropyridines with different aryl bromides bearing an electron-withdrawing group. In this case, 2-chloropyridine could bear either an electron-donating or electron-withdrawing group due to the highest reactivity of the aryl bromide in each case. This is in keeping with our postulated mechanism, where the aryl halide should react faster than the pyridine halide with the Ni(0). Results are reported in Table 4.

Table 4
Cross-coupling between functionalized 2-chloropyridines and various aryl bromides substituted by an electron-withdrawing group



Entry	PyrCl FG′	ArBr FG	Product	Time (h)	Yield (GC)%
1	6-CN	*p*-CO_2Me	**28**	5	51 (58)
2	6-CN	*p*-COMe	**29**	1.5	42 (58)
3	5-CF_3	*p*-CO_2Et	**30**	1.2	50 (68)
4	3-CO_2Et	*p*-CN	**31**	4	40 (72)
5	3-CO_2Et	*p*-COMe	**32**	1	68 (78)
6	3-CO_2Et	*p*-CO_2Et	**33**	2.5	78 (86)
7	3-CO_2Et		**34**	18	50 (56)
8	3-CN, 6-Me	*p*-CO_2Et	**35**	6.5	47[a] (55)
9	5-Me	*p*-COMe	**36**	3.5	78 (87)
10	6-OMe	*p*-CO_2Me	**37**	0.2	53 (61)

[a] Reaction conducted at 80 °C.

3. Conclusion

In summary, we have devised an expedient route to functionalized 2-arylpyridines on the basis of nickel catalysis. The use of manganese powder as reducing reagent in combination with $NiBr_2Bpy$ catalyst enables the synthesis from commercially available chemicals of a broad spectrum of valuable compounds in satisfactory to high yields under simple and mild conditions.

4. Experimental

4.1. General

The synthesis was monitored with a Gas Chromatograph (Varian3300, apolar column CPSiL5CB, 25 m), dodecan $C_{12}H_{26}$ used as an intern standard. Products were purified by flash silica gel chromatography. ^1H, ^{13}C and ^{19}F NMR spectra were measured on spectrometers at 400.13, 100.62 and 376.46 MHz, respectively. ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm). The mass spectra were obtained by EI by GC–MS analysis. All the solvents are used in the commercially form. The dimethylformamide (HPLC quality) was kept under inert atmosphere. The starting materials are commercially available (Aldrich, Acros) and are used without further purification.

The nickel bromide 2,2′-bipyridine complex was prepared from nickel bromide and 2,2′-bipyridine according to the reported procedures[17] and stored in a hermetic flask.

4.2. Representative procedure for the direct cross-coupling reactions catalyzed by nickel bromide 2,2′-bipyridine

To a solution of nickel bromide 2,2′-bipyridine (0.5 mmol, 10%) and manganese powder (11.5 mmol) in dimethylformamide (8 mL) were successively added at room temperature the halogen–aryl or halogen–heteroaryl (5 mmol), the 2-halogenopyridine (6.5 mmol) and trifluoroacetic acid (100 μL), causing an immediate rise in temperature and colour change to dark grey. The medium was then stirred at room temperature until complete conversion of aryl halide. In all cases, the amounts of the coupling product were measured by GC using an internal reference (dodecane, 200 μL). The reaction mixture was poured into a saturated aqueous solution of NH_4Cl and extracted with diethyl ether (3×70 mL). The organic layer was washed with a saturated aqueous solution of NaCl and dried over $MgSO_4$. Evaporation of solvent and purification by column chromatography on silica gel (pentane/diethyl ether) afforded the coupling product.

*4.2.1. Ethyl 4-(pyridin-2-yl)benzoate (**1**)*

CAS 4385-61-9.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 14.3, 61.1, 121.6, 122.9, 126.8, 130.0, 130.8, 137.0, 143.2, 149.7, 156.1, 166.4. ^1H NMR ($CDCl_3$, 400 MHz) δ ppm 1.43 (t, 3H, J=7.1 Hz), 4.41 (q, 2H, J=7.1 Hz), 7.25–7.30 (m, 1H), 7.79 (t, 2H, J=3.3 Hz), 8.13 (d, 2H, J=8.2 Hz), 8.2 (d, 2H, J=8.2 Hz), 8.74 (d, 1H, J=3.3 Hz), EIMS m/z 227 (M), 199, 182 (base), 154, 127.

*4.2.2. Ethyl 3-(Pyridin-2-yl)benzoate (**2**)*

CAS 4550-32-7.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 14.2, 60.9, 120.3, 122.4, 127.7, 128.7, 129.8, 130.9, 131.0, 136.7, 139.4, 149.6, 155.9, 166.1. ^1H NMR ($CDCl_3$, 400 MHz) δ ppm 1.27 (t, 3H, J=7 Hz), 4.27(q, 2H, J=7 Hz), 7.07 (m, 1H), 7.39 (t, 1H, J=7 Hz), 7.58 (m, 2H), 7.97 (t, 1H, J=8 Hz), 8.08 (t, 1H, J=8 Hz), 8.56 (m, 2H). EIMS m/z 227 (M), 182, 155 (base), 154, 127.

*4.2.3. Ethyl 2-(pyridin-2-yl)benzoate (**3**)*

CAS 28901-52-2.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 13.8, 60.9, 120.3, 122.0, 123.0, 128.4, 129.8, 131.1, 131.7, 136.5, 140.6, 148.6, 158.7, 168.6. ^1H NMR ($CDCl_3$, 400 MHz) δ ppm 1.08 (t, 3H, J=7.1 Hz), 4.12(q, 2H, J=7.1 Hz),

7.28–7.30 (m, 1H), 7.52 (d, 2H, *J*=7.6 Hz), 7.59–7.60 (m, 2H), 7.78 (t, 1H, *J*=7.6 Hz), 7.85 (d, 1H, *J*=7.5 Hz), 8.64 (d, 1H, *J*=4.1 Hz). EIMS *m*/*z* 227 (M), 198, 182 (base), 154, 127.

*4.2.4. 2-(4-Acetoxyphenyl)pyridine (**4**)*

CAS 173681-56-6.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 26.6, 120.9, 122.3, 126.9, 128.7, 136.8, 137.0, 143.5, 149.8, 157.0, 197.0. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 2.6 (s, 3H), 7.2 (dd, 1H, *J*=4.4 and 8.1 Hz), 7.7 (d, 2H, *J*=8.1 Hz), 8.0–8.1 (m, 4H), 8.6 (dd, 1H, *J*=4.4 and 1.2 Hz). EIMS *m*/*z* 197 (M), 182 (base), 154, 127.

*4.2.5. 2-(4-Trifluoromethyl-phenyl)pyridine (**5**)*

CAS 203065-88-7.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 121.7, 124.4 (q, *J*=272 Hz), 127.1, 128.6, 128.9, 131.5 (q, *J*=32 Hz), 136.1, 144.1, 151.4, 157.2. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 7.1 (ddd, 1H, *J*=8.6, 4.7, 2.1 Hz), 7.55 (d, 4H, *J*=7.5 Hz), 7.93 (d, 2H, *J*=8 Hz), 8.56 (d, 1H, *J*=4.4 Hz). ^{19}F NMR ($CDCl_3$, 377 MHz) δ ppm −62.6. EIMS *m*/*z* 223 (M, base), 203, 184, 175, 154, 127.

*4.2.6. 2-(3-Trifluoromethyl-phenyl)pyridine (**6**)*

CAS 5957-84-6.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 122.3, 122.4, 128.7, 128.8, 129.7, 131.0, 136.4, 136.6, 139.7, 149.2, 149.5, 155.1. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 7.1 (m, 1H), 7.44 (t, 1H, *J*=7.8 Hz), 7.59–7.71 (m, 3H), 8.06 (d, 1H, *J*=7.8 Hz), 8.3 (s, 1H), 8.62 (dd, 1H, *J*=4.7 and 0.9 Hz). EIMS *m*/*z* 223 (M, base), 203, 184, 175, 154, 127.

*4.2.7. 4-Pyridin-2-yl-benzonitrile (**7**)*

CAS 32111-34-5.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 112.3, 118.6, 121.1, 123.3, 127.7, 132.2, 136.9, 143.4, 149.7, 155.0. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.2 (m, 1H), 7.68–7.81 (m, 4H), 8.0 (d, 2H, *J*=8.4 Hz), 8.62 (d, 1H, *J*=4.8 Hz). EIMS *m*/*z* 180 (M, base), 179, 153, 140, 125, 75.

*4.2.8. 2-(4-Fluoro-phenyl)-pyridine (**8**)*

CAS 58861-53-3.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 115.5, 115.7, 120.1, 122.0, 128.6, 135.5, 136.8, 149.6, 156.4, 163.5 (d, J_{CF}=247 Hz). ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 7.03 (m, 3H), 7.55 (m, 2H), 7.84 (t, 2H, *J*=7.1 Hz), 8.57 (d, 1H, *J*=4.7 Hz).^{19}F NMR ($CDCl_3$, 377 MHz) δ ppm −112.95. EIMS *m*/*z* 173 (M, base), 172, 163, 153, 146, 133, 125.

*4.2.9. 2-(4-Methoxy-phenyl)-pyridine (**9**)*

CAS 5957-90-4.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 55.3, 114.1, 119.8, 121.4, 128.2, 132.0, 136.7, 149.6, 157.1, 160.5. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 3.7 (s, 3H), 6.9 (dd, 2H, *J*=9 and 1.2 Hz), 7.0 (m, 1H), 7.5–7.7 (m, 2H), 7.8 (d, 2H, *J*=9 Hz), 8.5 (dd, 1H, *J*=4.7 and 2.0 Hz). EIMS *m*/*z* 185 (M, base), 170, 154, 142, 115.

*4.2.10. 4-Pyridin-2-yl-benzoic acid methyl ester (**10**)*

CAS 98061-21-3.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 52.0, 120.5, 122.8, 127.0, 130.1, 130.6, 136.8, 143.4, 149.8, 155.9, 166.6. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 3.87 (s, 3H), 7.18 (m, 1H), 7.68 (m, 2H), 8.05 (2d, 4H, *J*=8.4 Hz), 8.66 (d, 1H, *J*=4.7 Hz). EIMS *m*/*z* 213 (M), 182 (base), 154, 127.

*4.2.11. 3-Pyridin-2-yl-benzoic acid methyl ester (**11**)*

CAS 98061-20-2.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 52.1, 120.2, 122.2, 127,5, 129.1, 130.1, 131.5, 136.5, 137.1, 139.6, 149.7, 156.0, 166.8. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 3.92 (s, 3H), 7.20 (m, 1H), 7.48 (t, 1H, *J*=7.8 Hz), 7.70 (m, 2H), 8.05 (d, 1H, *J*=7.7 Hz), 8.18 (d, 1H, *J*=7.8 Hz), 8.62 (s, 1H), 8.68 (s, 1H). EIMS *m*/*z* 213 (M), 182, 155 (base), 127, 101, 77.

*4.2.12. 2-Pyridin-2-yl-benzoic acid methyl ester (**12**)*

CAS 98061-19-9.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 51.9, 121.8, 122.9, 128.1, 129.6, 131.2, 132.7, 136.5, 140.5, 148.6, 158.4, 169.2. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 3.65 (s, 3H), 7.21 (m, 1H), 7.44–7.55 (m, 4H), 7.70 (t, 1H, *J*=7.2 Hz), 7.78 (d, 1H, *J*=8.0 Hz), 8.62 (d, 1H, *J*=4.5 Hz). EIMS *m*/*z* 213 (M), 182 (base), 169, 154, 127, 101, 77.

*4.2.13. 3-Pyridin-2-yl-benzonitrile (**13**)*

CAS 4350-51-0.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 112.9, 118.7, 120.4, 123.2, 129.5, 130.5, 130.9, 132.1, 137.1, 140.4, 149.9, 154.7. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 7.28 (m, 1H), 7.52 (m, 1H), 7.61 (d, 1H, *J*=7.7 Hz), 7.69 (d, 1H, *J*=7.9 Hz), 7.75 (dd, 1H, *J*=7.7 and 1.5 Hz), 8.17 (d, 1H, *J*=7.9 Hz), 8.27 (s, 1H), 8.65 (d, 1H, *J*=4.8 Hz). EIMS *m*/*z* 180 (M, base), 179, 170, 153, 140, 125, 100, 76.

*4.2.14. 2-(2-Trifluoromethyl-phenyl)-pyridine (**14**)*

CAS 441072-21-5.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 122.5, 123.9, 124.1 (q, *J*=272 Hz), 125.5, 126.3, 128.1, 128.2 (q, *J*=30 Hz), 131.5, 135.9, 140.0, 149.1, 157.8. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 7.2–7.6 (m, 4H), 7.49 (d, 1H, *J*=7.2 Hz), 7.55 (d, 1H, *J*=7.3 Hz), 7.65–7.8 (m, 1H), 8.60 (m, 1H). ^{19}F NMR ($CDCl_3$, 377 MHz) δ ppm −56.7. EIMS *m*/*z* 222 (M−1), 205 (base), 189, 177, 161, 145, 121.

*4.2.15. 2-(2-Methoxy-phenyl)-pyridine (**15**)*

CAS 5957-89-1.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 55.4, 111.4, 120.9, 121.5, 125.2, 129.0, 129.9, 131.2, 135.6, 149.4, 156.0, 156.9. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 3.7 (s, 3H), 6.9–7.2 (m, 3H), 7.3–7.4 (m, 1H), 7.6 (dt, 1H, *J*=7.7 and 2.0 Hz), 7.8 (d, 2H, *J*=7.8 Hz), 8.7 (d, 1H, *J*=5.1 Hz). EIMS *m*/*z*: 184 (M−1, base), 167, 154, 141, 127, 115.

*4.2.16. 4-Pyridin-2-yl-phenylamine (**16**)*

CAS 18471-73-3.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 115.1, 119.4, 121.0, 128.0, 129.5, 136.7, 147.6, 149.4, 157.4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 3.80 (s, 2H), 6.75 (d, 2H, *J*=8.3 Hz), 7.10–7.30 (m, 1H), 7.64 (m, 2H), 7.84 (d, 2H, *J*=8.3 Hz), 8.63 (d, 1H, *J*=4.7 Hz). EIMS *m*/*z* 170 (M, base), 154, 143, 117.

*4.2.17. 2-Pyridin-2-yl-phenylamine (**17**)*

CAS 19528-30-1.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 117.3, 117.7, 121.0, 122.3, 129.4, 129.5, 130.0, 137.0, 144.3, 147.9, 159.5. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 5.63 (s, 2H), 6.85 (m, 2H), 7.23 (m, 2H), 7.58 (d, 1H, *J*=7.8 Hz), 7.65–7.85 (m, 2H), 8.65 (d, 1H, *J*=3.7 Hz). EIMS *m*/*z* 169 (M−1, base), 142, 115.

*4.2.18. Dimethyl-(4-pyridin-2-yl-phenyl)-amine (**18**)*

CAS 100381-45-1.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 40.4, 112.3, 119.3, 120.6, 128.0, 136.9, 148.9, 151.0, 167.0. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 3.03 (s, 6H), 6.82 (d, 2H, *J*=8.0 Hz), 7.13 (m, 1H), 7.67 (m, 2H), 7.98 (d, 2H, *J*=8.0 Hz), 8.66 (m, 1H). EIMS *m*/*z* 198 (M, base), 182, 168, 154, 127.

*4.2.19. 2-o-Tolyl-pyridine (**19**)*

CAS 10273-89-9.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 20.3, 123.0, 123.6, 128.1, 129.8, 130.5, 135.5, 136.5, 137.5, 138.0, 149.8, 160.1. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 2.28 (s, 3H), 7.20–7.40 (m, 6H), 7.66 (m, 1H), 8.56–8.62 (m, 1H). EIMS *m*/*z* 169 (M, base), 141, 115, 84.

*4.2.20. 2-(4-Chloro-phenyl)-pyridine (**20**)*

CAS 5969-83-5.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 120.2, 122.3, 124.4, 128.4, 128.9, 134.7, 138, 149.4, 156.0. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 7.03 (m, 1H), 7.28 (d, 2H, J=8.3 Hz), 7.5 (m, 2H), 7.8 (d, 2H, J=8.3 Hz), 8.53 (d, 1H, J=3.8 Hz). EIMS m/z 189–191(M), 154 (base), 127.

*4.2.21. 4-(5-Trifluoromethyl-pyridine-2-yl)-phenylamine (**21**)*

CAS 910036-88-3.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 115.0, 118.4, 123.4 (q, J=32.0 Hz), 124.0 (q, J=270 Hz), 127.9, 128.6, 133.6, 146.3, 148.5, 160.6. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 3.92 (s, 2H), 6.77 (d, 2H, J=8.1 Hz), 7.72 (d, 1H, J=7.3 Hz), 7.89 (m, 3H), 8.88 (s, 1H). ^{19}F NMR ($CDCl_3$, 377 MHz) δ ppm −62.08. EIMS m/z 238 (M, base), 217, 197, 185, 169.

*4.2.22. 2-(4-Methoxy-phenyl)-5-trifluoromethyl-pyridine (**22**)*

CAS 296776-84-6.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 55.4, 114.4, 119.1, 123.8 (q, J=272 Hz), 124.1 (q, J=33.1 Hz), 128.9, 130.3, 133.9, 146.3, 160.2, 161.4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 3.90 (s, 3H), 7.04 (d, 2H, J=8.8 Hz), 7.78 (d, 1H, J=8.3 Hz), 7.93 (d, 1, H, J=8.3 Hz), 8.03 (d, 2H, J=8.8 Hz), 8.92 (s, 1H). ^{19}F NMR ($CDCl_3$, 377 MHz) δ ppm −62.39. EIMS m/z 253 (M, base), 238, 210, 190, 141.

*4.2.23. 2-(4-Methoxy-phenyl)-6-methyl-pyridine (**23**)*

CAS 4385-63-1.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 22.5, 53.1, 112.2, 114.9, 118.9, 126.4, 130.1, 134.8, 154.3, 155.9, 159.2. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 2.62 (s, 3H), 3.82 (s, 3H), 6.99 (d, 3H, J=8.8 Hz), 7.43 (d, 1H, J=7.8 Hz), 7.55 (d, 1H, J=7.8 Hz), 7.97 (d, 2H, J=7.8 Hz). EIMS m/z 199 (M, base), 184, 156, 141, 128.

*4.2.24. 2-Methoxy-6-(4-methoxy-phenyl)-pyridine (**24**)*

CAS 296776-83-5.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 53.2, 108.3, 110.9, 111.9, 113.6, 114.0, 128.3, 131.7, 139.2, 153.4, 154.4, 160.4, 163.4. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 3.95 (s, 6H), 6.70 (d, 1H, J=8.2 Hz), 6.89 (d, 2H, J=8.4 Hz), 7.20 (d, 1H, J=7.6 Hz), 7.60 (t, 1H, J=7.5 Hz), 7.93 (m, 2H). EIMS m/z 215 (M), 214 (base), 199, 186, 170, 157, 142.

4.2.25. [4-(6-methoxy-pyridin-2-yl)-phenyl]-dimethyl-amine (25)

CAS 31640-81-0.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 40.6, 53.0, 107.4, 111.3, 112.5, 124.1, 127.6, 139.0, 150.7, 154,9, 163.6. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 2.83 (s, 6H), 3.95 (s, 3H), 6.47 (d, 1H, J=8.1 Hz), 6.71 (d, 2H, J=8.4 Hz), 7.15 (d, 1H, J=7.4 Hz), 7.46 (m, 1H), 7.88 (d, 2H, J=8.4 Hz). EIMS m/z 228 (M, base), 211, 199, 183, 169, 154.

*4.2.26. 4-(6-Methoxy-pyridin-2-yl)-phenylamine (**26**)*

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 53.1, 107.7, 111.4, 114.9, 127.9, 129.5, 139.1, 147.3, 154.9, 163.6. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 3.79 (s, 2H), 4.07 (s, 3H), 6.60 (d, 1H, J=6.9 Hz), 6.70 (d, 2H, J=6 Hz), 7.23 (d, 1H, J=6 Hz), 7.6 (m, 1H), 7.95 (d, 2H, J=6 Hz). EIMS m/z 200 (M, base); 171, 169, 155, 144, 130, 115, 103. Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99; O, 7.99. Found: C, 71.82; H, 5.95; N, 13.93.

*4.2.27. 5-(6-Methyl-pyridin-2-yl)-1H-indole (**27**)*

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 24.5, 103.3, 111.3, 117.9, 119.8, 120.8, 121.6, 125.0, 128.3, 131.2, 136.5, 137.3, 157.8, 158.1. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 2.69 (s, 3H), 6.62 (s, 1H), 7.06 (d, 1H, J=7.4 Hz), 7.21 (s, 1H), 7.42 (d, 1H, J=8.4 Hz), 7.58 (d, 1H, J=7.7 Hz), 7.65 (m, 1H), 7.86 (d, 1H, J=8.4 Hz), 8.27 (s, 1H), 8.59 (s, 1H). EIMS m/z 208 (M, base), 192, 180, 166, 152, 142. HRMS for $C_{14}H_{12}N_2$: calcd 208.2586; found: 208.2582.

*4.2.28. 4-(6-Cyano-pyridin-2-yl)-benzoic acid methyl ester (**28**)*

CAS 296776-88-0.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 52.3, 116.4, 121.5, 122.4, 123.9, 126.9, 130.3, 131.6, 141.2, 150.6, 157.6, 166.5. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 3.99 (s, 3H), 7.50 (d, 1H, J=4.4 Hz), 8.00 (t, 1H, J=4.4 Hz), 8.10 (d, 2H, J=4.4 Hz), 8.20 (d, 2H, J=8.1 Hz), 8.92 (d, 1H, J=8.1 Hz). EIMS m/z 238 (M), 207 (base), 194, 179, 170, 152.

*4.2.29. 6-(4-Acetyl-phenyl)-pyridine-2-carbonitrile (**29**)*

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 26.8, 116.3, 121.8, 123.1, 125.8, 127.1, 129.0, 138.1, 144.3, 150.3, 155.5, 197.5. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 2.80 (s, 3H), 7.60 (d, 1H, J=4.6 Hz), 7.70 (d, 2H, J=8.2 Hz), 8.10 (m, 3H), 8.87 (d, 1H, J=4.7 Hz). EIMS m/z 222 (M), 207 (base), 179, 170, 152, 125. Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.6; O, 7.20. Found: C, 75.40; H, 4.33; N, 12.81.

*4.2.30. 4-(5-Trifluoromethyl-pyridin-2-yl)-benzoic acid ethyl ester (**30**)*

CAS 1089330-74-4.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 14.3, 61.2, 120.4, 123.6 (q, J=271 Hz), 125.5 (q, J=33 Hz), 127.2, 130.0, 131.8, 134.2, 141.6, 146.6, 159.4, 166.1. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 1.33 (t, 3H, J=7.5 Hz), 4.33 (q, 2H, J=7.5 Hz), 7.53 (d, 1H, J=8.3 Hz), 7.74 (d, 1H, J=8.3 Hz), 7.95–8.05 (m, 4H), 8.85 (s, 1H). ^{19}F NMR ($CDCl_3$, 377 MHz) δ ppm −62.48. EIMS m/z 295 (M), 267, 250 (base), 222, 202, 182, 153. HRMS for $C_{14}H_{12}N_2$: calcd 208.2586; found: 208.2582.

*4.2.31. 2-(4-Cyano-phenyl)-nicotinic acid ethyl ester (**31**)*

CAS 296776-85-7.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 13.7, 61.8, 112.3, 118.7, 122.6, 127.1, 129.4, 131.8, 138.4, 144.7, 151.5, 157.2, 166.8. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 1.05 (t, 3H, J=7.3 Hz), 4.11 (q, 2H, J=7.3 Hz), 7.36 (dd, 1H, J=4.8 and 7.7 Hz), 7.56 (d, 2H, J=8.1 Hz), 7.65 (d, 2H, J=8.1 Hz), 8.14 (d, 1H, J=7.7 Hz), 8.72 (d, 1H, J=4.8 Hz). EIMS m/z 252 (M), 223 (base), 207, 179, 152, 140, 125.

*4.2.32. 2-(4-Acetyl-phenyl)-nicotinic acid ethyl ester (**32**)*

CAS 296776-86-8.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 13.7, 26.8, 61.7, 122.3, 127.3, 128.1, 128.9, 136.8, 138.2, 144.7, 151.4, 157.9, 167.4, 197.8. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 1.10 (t, 3H, J=7 Hz), 2.67 (s, 3H), 4.20 (q, 2H, J=7 Hz), 7.40 (dd, 1H, J=5 and 8 Hz), 7.66 (d, 2H, J=8 Hz), 8.05 (d, 2H, J=8 Hz), 8.11 (dd, 1H, J=8.and 2 Hz), 8.81 (dd, 1H, J=5 and 1.5 Hz). EIMS m/z 269 (M), 254 (base), 240, 226, 198, 182, 170, 154.

4.2.33. 2-(4-ethoxycarbonyl-phenyl)-nicotinic acid ethyl ester (33)

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 13.6, 14.2, 60.9, 61.5; 122.1, 127.3, 128.3, 129.4, 130.6, 137.7, 144.4, 151.2, 157.8, 166.1, 167.3. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 0.97 (t, 3H, J=7.1 Hz), 1.3 (t, 3H, J=7.1 Hz), 4.07 (q, 2H, J=7.1 Hz), 4.31 (q, 2H, J=7.1 Hz), 7.26 (dd, 1H, 4.8 and 7.8 Hz), 7.53 (d, 2H, J=8.1 Hz), 8.04 (m, 3H), 8.67 (d, 1H, J=4.8 Hz). EIMS m/z 299 (M), 270 (base), 254, 242, 226, 198, 170, 154. Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.72; N, 4.68; O, 21.38. Found: C, 68.11; H, 5.65; N, 4.70.

*4.2.34. 2-Thiophen-3-yl-nicotinic acid ethyl ester (**34**)*

CAS 296776-91-5.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 14.1, 61.6, 121.4, 125.2, 125.3, 127.2, 128.0, 137.4, 140.9, 151.1, 153.1, 168.1. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 1.15 (t, 3H, J=7.1 Hz), 4.23 (q, 2H, J=7.1 Hz), 7.23 (dd, 1H, J=4.8 and 7.8 Hz), 7.32 (m, 2H), 7.61 (d, 1H, J=4.1 Hz), 7.8 (dd, 1H, J=1.6 and 7.8 Hz), 8.69 (dd, 1H, J=4.8 and 1.6 Hz). EIMS m/z 233(M), 204 (base), 188, 176, 161, 148, 133, 116, 89.

*4.2.35. 4-(3-Cyano-6-methyl-pyridin-2-yl)-benzoic acid ethyl ester (**35**)*

CAS 296776-90-4.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 14.3, 25.2, 61.2, 104.8, 117.7, 121.9, 129.8, 130.3, 131.7, 141.3, 141.7, 159.5, 162.9, 166.1. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 1.43 (t, 3H, J=7.1 Hz), 2.7 (s, 3H), 4.42 (q, 2H, J=7.1 Hz), 7.27 (d, 1H, J=7.8 Hz), 7.98 (dd, 3H, J=8.2 and 7.8 Hz), 8.19 (d, 2H, J=8.2 Hz). EIMS m/z 266 (M, base), 237, 221, 193, 166, 140.

*4.2.36. 1-[4-(5-Methyl-pyridin-2-yl)-phenyl]-ethanone (**36**)*

CAS 953420-67-2.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 18.2, 26.7, 120.6, 126.8, 128.8, 132.8, 137.0, 137.7, 143.3, 150.1, 153.2, 197.7. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 2.40 (s, 3H), 2.65 (s, 3H), 7.62 (dd, 1H, J=8 and 1.4 Hz), 7.71 (d, 1H, J=8 Hz), 8.07 (2d, 4H, J=8.4 Hz), 8.57 (s, 1H). EIMS m/z 211 (M), 196 (base), 168, 115.

*4.2.37. 4-(6-Methoxy-pyridin-2-yl)-benzoic acid methyl ester (**37**)*

CAS 223127-56-8.

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 52.1, 53.3, 110.3, 113.4, 128.6, 129.9, 130.2, 139.3, 143.1, 153.3, 163.8, 166.9. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 3.96 (s, 3H), 4.06 (s, 3H), 6.77 (d, 1H, J=8.2 Hz), 7.42 (d, 1H, J=7.4 Hz), 7.74 (t, 1H, J=7.8 Hz), 8.13 (s, 4H). EIMS m/z 243 (M), 242 (base), 212, 198, 184, 169, 154, 141, 127, 114. HRMS for $C_{14}H_{13}NO_3$: calcd 243.0894; found: 243.0891.

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