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Microwave-Promoted Syntheses of Pyridine Carboxamides and *tert*-Carboximides from Novel 6-Acetylpyridine-2-carboxylic Acid

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Abstract: A novel 6-acetylpyridine-2-carboxylic acid (**4**) was obtained occasionally during the synthesis of asymmetric ethyl 6-acetylpyridine-2-carboxylate (**3**) from 2,6-dipiclinic acid (**1**). Compounds **3** and **4** could transform mutually under some specific conditions. Two reactions of distinctive types occurred when they reacted with the aromatic amines as precursors, due to different functional groups on the 2-position of pyridine in the molecules of **3** and **4**: one was Schiff base condensation and the other was an amidation reaction. From the latter reaction, two series of new compounds, pyridine carboxamides (**5a**–**d**) and pyridine *tert*-carboximides (**6a**–**h**), resulted. The relevant reaction mechanism is discussed in detail.

Keywords: 6-Acetylpyridine-2-carboxylic acid, amidation reaction, microwave irradiation, reaction mechanism

Twenty years after the pioneering work of Small et al.[1] and Britovsek et al.,[2] late-transition-metal catalysts incorporating bis(imino)pyridyl ligands have received much attention because they are robust and extremely active for polymerization of ethylene to linear, high-density polyethylene. Building on the work of Brookhart and others, chemists have developed a proprietary family of catalyst analogs.[3] We have previously

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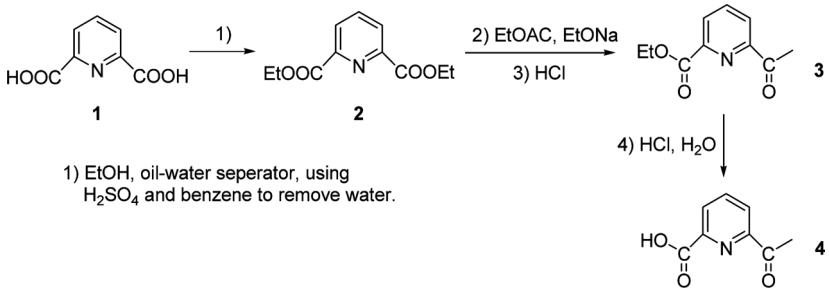
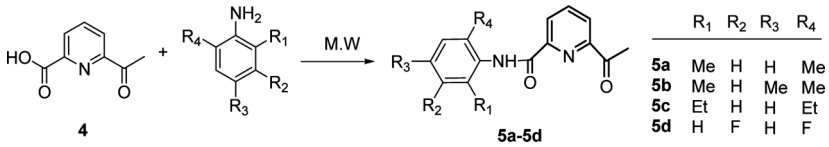


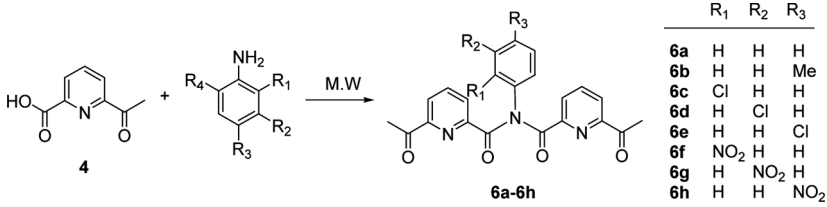
Scheme 1. Synthesis of the precursor 6-acetylpyridine-2-carboxylic acid (**4**).

reported a series of mono(imino)pyridyl compounds[4] coming from the precursor ethyl 6-acetylpyridine-2-carboxylate (**3**) and a series of aromatic amines. When incorporated with late transition metals, these mono(imino)pyridyl compounds have indicated considerable activity for ethylene polymerization and oligomerization.[5] In this article, we reported the synthesis of a new compound, 6-acetylpyridine-2-carboxylic acid (**4**), which was obtained occasionally during the synthesis of **3** from 2,6-dipiclinic acid (**1**) (Scheme 1). As is known, the microwave techniques for organic synthesis have been widely used in a variety of organic reactions since the first article on microwave-assisted synthesis was published by Gedye and Giguere in *Tetrahedron Letters* in 1986.[6,7] Use of microwave technology can enhance selectivity and reactivity, increase the chemical yields, and shorten the reaction time, so we attempted to employ this efficient method to synthesize carboxamides. When **4** reacted with aromatic amines as precursor under microwave irradiation without solvent, two exceptional series of new compounds, pyridine carboxamides (**5a**–**d**) (Scheme 2) and pyridine *tert*-carboximides (**6a**–**h**) (Scheme 3), resulted. Compared with the conventional solvent synthesis method,[8] microwave-assisted condensation[9–12] seemed to improve reaction rate, simplify workup procedure, and form cleaner products in preparing these pyridine carboxamides and pyridine *tert*-carboximides.



	R_1	R_2	R_3	R_4
5a	Me	H	H	Me
5b	Me	H	Me	Me
5c	Et	H	H	Et
5d	H	F	H	F

Scheme 2. Synthesis of pyridine carboxamides (**5a**–**d**).



	R_1	R_2	R_3
6a	H	H	H
6b	H	H	Me
6c	Cl	H	H
6d	H	Cl	H
6e	H	H	Cl
6f	NO_2	H	H
6g	H	NO_2	H
6h	H	H	NO_2

Scheme 3. Synthesis of pyridine *tert*-carboximides (**6a**–**h**).

RESULTS AND DISCUSSION

Mutual Transformation Between 3 and 4

The transformation from **3** to **4** involved acid hydrolysis of ester. The ester group in 2-position of the pyridine ring in **3** was not stable in acid aqueous solution; it could slowly hydrolyze into carboxyl group at a relatively higher temperature (more than 35°C). Compared with the ester group, other functional groups (the pyridine ring, and the acetyl group) were more stable at these conditions. The existence of the carboxyl group made **4** possess the general properties of carboxylic acid, such as relatively stronger polarity and less solubility in water, which made **4** and **3** separate more easily.

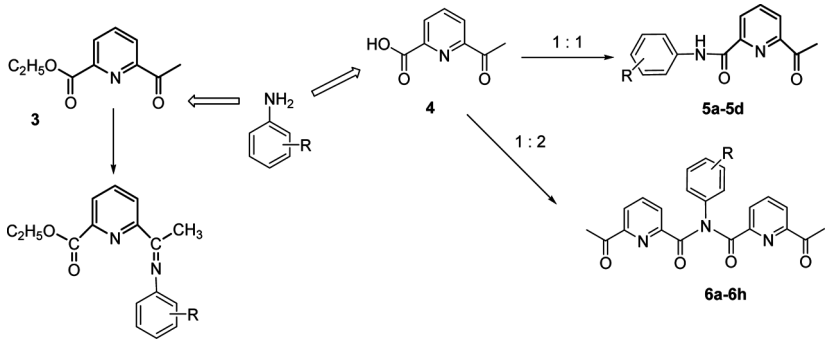
Not only **3** could change to **4** in a specific condition, **4** could also transform to **3** in another condition. The occurrence of latter transformation was very interesting: as highly pure **4** was dissolved in ethyl acetate and injected into gas chromatography–mass spectrometry (GC-MS), **3** and **4** were both detected at different peak times. This unexpected result implied part of **4** changed to **3** under the definite experimental condition of GC-MS. The possible reaction might be as follows: ethyl acetate reacted with part of **4** as a reactant to form **3** and acetic acid at high temperature in GC-MS, which involved the acid decomposition of ethyl acetate.

Reaction Mechanisms of Aromatic Amines with 4

Theoretically, there are two unique reactive sites in the asymmetric precursor 6-acetylpyridine-2-carboxylic acid (**4**), which are the carboxyl group in 2-position of the pyridine ring and the acetyl group in 6-position. When reacting with **4**, the aromatic amine would choose to attack the carboxyl group to engender amidation products but not react with acetyl group to give Schiff base products because of the

comparatively stronger activity of carboxyl group. Unlike the reaction of the aromatic amine with **4**, the aromatic amine would first attack the acetyl group of ethyl 6-acetylpyridine-2-carboxylate (**3**) to create Schiff base product mono(imino)pyridine but not react with the ester group to afford amidation product.[4] These results showed that the reactivity of different groups in the pyridine ring with aromatic amine complied with the sequence of carboxyl group, acetyl group, and ester group. The reactions of aromatic amine with **3** and **4** are illustrated in Scheme 4.

Our interest here is how aromatic amines with different structures influence the reaction and the product. According to the experiments, when aromatic amines with different substitute kinds and sites in the aryl ring reacted with a same precursor **4** under microwave irradiation without solvent, two kinds of new compounds, pyridine carboxamides and pyridine *tert*-carboximides, were produced (see Scheme 4). All of 2,6-dimethylaniline, 2,4,6-trimethylaniline, 2,6-diethylaniline and 2,5-difluoroaniline reacted with **4** according to a 1:1 molar ratio to afford pyridine carboxamides, whereas all of aniline, 4-methylaniline, 2-chloroaniline, 3-chloroaniline, 4-chloroaniline, 2-nitroaniline, 3-nitroaniline, and 4-nitroaniline reacted with **4** in a 2:1 molar ratio to engender pyridine *tert*-carboximides. These significant results suggest that the kind of product is only related to the number of substituents on the phenyl ring, not the kinds (electron-withdrawing or electron-donating group) or the sites (ortho, meta, or para position) of the substituent on the phenyl ring. Aromatic amines with a disubstituted or polysubstituted aryl ring are apt to afford pyridine carboxamides, whereas those with a nonsubstituted or monosubstituted aryl ring are inclined to give pyridine *tert*-carboximides. The possible reasons are demonstrated in detail as follows: for those aromatic amines with disubstituted or polysubstituted aryl ring, after



Scheme 4. Different reactions of aromatic amine with **3** and **4**.

the reaction stage (during which the lone pair electrons in the N atom of aromatic amine accessed the carboxyl group of **4** and attacked the carbon atom to afford carboxamide), the strong steric effect of amino in carboxamide prevented itself from approaching another molecule **4** to result in *tert*-carboximide. In case of those aromatic amines with nonsubstituted or monosubstituted aryl ring reacting with **4**, after the same reaction stage as aromatic amines with disubstituted or polysubstituted aryl ring, the smaller steric effect of amino in the obtained carboxamide allowed itself to approach another molecule **4** and attacked the C atom of carboxyl to give *tert*-carboximide.

In summary, a novel 6-acetylpyridine-2-carboxylic acid (**4**) was obtained occasionally during the synthesis of ethyl 6-acetylpyridine-2-carboxylate (**3**). Under microwave irradiation, the reactivity difference between the functional groups on the pyridine ring made the reactions of **3** and **4** with aromatic amines differ greatly, in which one was Schiff base condensation and the other was an amidation reaction. From the amidation reaction between **4** and aromatic amines, two kinds of new compounds, pyridine carboxamides and pyridine *tert*-carboximides, were prepared. The experiments indicated that the kind of product was related only to the number of substituents on the aryl ring, not the kinds (electron-withdrawing or electron-donating group) or the sites (ortho, meta, or para position) of substituent on the aryl ring. Aromatic amines with a disubstituted or polysubstituted aryl ring were apt to afford pyridine carboxamides (**5a**–**d**), whereas those with a nonsubstituted or monosubstituted aryl ring were inclined to give pyridine *tert*-carboximides (**6a**–**h**).

EXPERIMENTAL

C, H, and N analyses were performed on a HP-MOD 1106 microanalyzer. Infrared (IR) spectra were carried out with a Perkin-Elemer Fourier transform (FT)–IR 2000 spectrometer. ^{1}H NMR spectra were recorded on an Inova-400 NMR spectrometer, using tetramethylsilane (TMS) as internal standard. Mass spectra were determined with a Kratos AEI MS-50 instrument using the electron impact (EI) method. The microwave-assisted condensations were performed in a domestic oven, Midea PJ 21B-A 800 w (21 L). Melting points were determined with a melting-point apparatus and were uncorrected. 2,6-Dipiclinic acid, 2,6-dimethylaniline, 2,4,6-trimethylaniline, 2,6-diethylaniline, 2,5-difluoroaniline, aniline, 4-methylaniline, 2-chloroaniline, 3-chloroaniline, 4-chloroaniline, 2-nitroaniline, 3-nitroaniline, and 4-nitroaniline were purchased from Albemarle Co. (USA).

Preparation of the Precursor 6-Acetylpyridine-2-carboxylic Acid (4)

Esterification of 2,6-dipiclinic acid (**1**) was done with modified procedure, generating a better yield (84%) than that reported[12] and resulting in 2,6-dicarbethoxypyridine (**2**), which was purified by a simplified method. The dry **2** was dissolved in freshly distilled EtOAc and refluxed with dry EtONa powder for 12 h. Excess concentrated HCl was added, and the mixture was refluxed for 7–8 h to produce ethyl 6-acetylpyridine-2-carboxylate (**3**). After water was added to dissolve the NaCl formed in the reaction, the aqueous phase was shaken with $CHCl_3$. After the organic solvent was evaporated under reduced pressure, the obtained mixture was allowed to stand for 3 days at 37°C. When a solvent (in which petroleum ether and EtOAc were mixed in a volume ratio of 8:1) was added into the mixture, the insoluble solid was filtered and recrystallized by mixed solvents of ethanol and water to afford pure 6-acetylpyridine-2-carboxylic acid (**4**) as white powder. Yield: 26.1%, mp 140–142°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, 1H, Py-Hm), 8.35 (d, 1H, Py-Hm), 8.17 (t, 1H, Py-Hp), 2.81 [s, 3H, O=C(CH_3)]. IR (KBr): $\nu_{C=O}$ 1758, $\nu_{C=O}$ 1694, ν_{O-H} 3087, 3023, 2934, 2700, $\nu_{OH\cdots O}$ 958 cm^{-1}. GC-MS Ins: m/z 165 (M^+), 193($M^+ + 2C_2H_2$). Anal. calcd. for $C_8H_7NO_3$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.62; H, 3.95; N, 8.40.

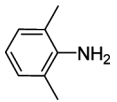
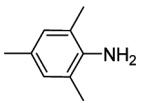
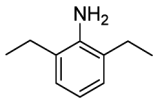
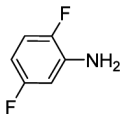
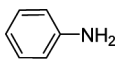
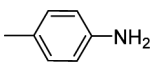
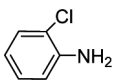
General Procedure for Syntheses of 5a–d and 6a–h

The microwave-assisted condensations of 6-acetylpyridine-2-carboxylic acid (**4**) and aromatic amines were performed in a domestic microwave oven. Compound **4** (2.0 mmol) and excess of aromatic amine (5.5 mmol) were put into an open vessel. The mixture was irradiated on a Low or M-High setting, using thin-layer chromatography (TLC) to monitor the progress of the reaction. After an optimized reaction time, the mixture gradually turned pink to red, and the obtained mixture was purified by recrystallization using the proper solvent under refrigeration to give desired product. The microwave power, reaction time, yield, melting point, and solvents used to purify products of **5a**–**d** and **6a**–**h** are reported in Table 1. Spectral data of these compounds are listed here.

6-Acetyl-*N*-(2,6-dimethylphenyl)pyridine-2-carboxamide (**5a**)

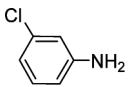
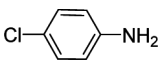
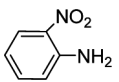
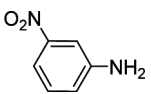
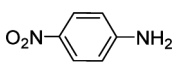
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, 1H, Py-Hm), 8.32 (d, 1H, Py-Hm), 8.14 (t, 1H, Py-Hp), 7.08 (d, 1H, Ph-Hm), 6.96 (d, 1H, Ph-Hm), 6.70 (t, 1H, Ph-Hp), 2.79 [s, 3H, O=C (CH_3)], 2.23 (d, 6 H, Ph-CH_3).

Table 1. Experimental data for the pyridine carboxamides **5a–d** and pyridine *tert*-carboximides **6a–h**

Product	Amine	Power	Time (min)	Yield (%)[a]	Mp[b]	Solvents (v/v)
5a		Low	5	31.0	70.5–71.8	Petroleum ether/$HCCl_3$/EtOH (1/1/1)
5b		Low	5	29.0	109.0–110.8	Petroleum ether/$HCCl_3$/EtOH (1/1/1)
5c		Low	5	25.5	267.0–270.0	Petroleum ether/$HCCl_3$/EtOH (1/1/1)
5d		M-High	5 + 5 + 5	64.9	179.0–181.0	Diethyl ether
6a		M-High	5 + 5	28.1	145.0–146.0	Diethyl ether
6b		Low	5	35.5	—	Diethyl ether
6c		M-High	5 + 5 + 5	25.6	151.6–152.3	Hexane

(*Continued*)

Table 1. Continued

Product	Amine	Power	Time (min)	Yield (%)[a]	Mp[b]	Solvents (v/v)
6d		Low	5	22.4	182.0–183.6	Diethyl ether
6e		Low	5 + 5	32.0	148.0–151.0	Diethyl ether
6f		Low	5 + 5	34.2	—	Hexane
6g		Low	5	25.1	—	Diethyl ether
6h		Low	6	28.6	—	Diethyl ether

[a]Yield refers to isolated yield.
[b]Melting points of compound **6b**, **6f**, **6g**, and **6h** are not available.

IR (KBr): ν_{N-H} 3404, $\nu_{C=O}$ 1697, 1654, δ_{N-H} 1578 cm^{-1}. MS (EI): m/z 269 ($M^+ + H$). Anal. calcd. for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 72.76; H, 6.62; N, 10.20.

6-Acetyl-*N*-(2,4,6-trimethylphenyl)pyridine-2-carboxamide (**5b**)

^1H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, 1H, Py-Hm), 8.34 (d, 1H, Py-Hm), 8.13 (t, 1H, Py-Hp), 6.91 (s, 1H, Ph-Hm), 6.82 (s, 1H, Ph-Hm), 2.78 [s, 3H, O=C(CH_3)], 2.36 [s, 3H, Ph-(CH_3)$_o$], 2.22 [s, 3H, Ph-(Me)$_o$], 1.99 [s, 3H, Ph-(Me)$_p$]. IR (KBr): ν_{N-H} 3284, $\nu_{C=O}$ 1643, 1603, δ_{N-H} 1579 cm^{-1}. MS (EI): m/z 282 (M^+). Anal. calcd. for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 71.82; H, 7.26; N, 9.36.

6-Acetyl-*N*-(2,6-diethylphenyl)pyridine-2-carboxamide (**5c**)

^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, 1H, Py-Hm), 8.33 (d, 1H, Py-Hm), 8.13 (t, 1H, Py-Hp), 6.83 (d, 1H, Ph-Hm), 6.75 (d, 1H, Ph-Hm), 6.70 (d, 1H, Ph-Hp), 3.56 [m, 2H, (CH_2)CH_3], 3.46 [m, 2H, (CH_2)CH_3], 2.80 [s, 3H, O=C(CH_3)], 1.23 [t, 3H, CH_2(CH_3)], 1.19 [t, 3H, CH_2(CH_3)]. IR (KBr): ν_{N-H} 3284, $\nu_{C=O}$ 1633, 1590, δ_{N-H} 1556 cm^{-1}. MS (EI): m/z 296 (M^+). Anal. calcd. for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 72.51; H, 6.66; N, 9.54.

6-Acetyl-*N*-(2,5-difluorophenyl)pyridine-2-carboxamide (**5d**)

^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, 1H, Py-Hm), 8.37 (d, 1H, Py-Hm), 8.16 (t, 1H, Py-Hp), 6.90 (d, 1H, Ph-Ho), 6.46 (d, 1H, Ph-Hm), 6.37 (d, 1H, Ph-Hp), 2.78 [s, 3H, O=C(CH_3)]. IR (KBr): ν_{N-H} 3425, $\nu_{C=O}$ 1703, 1643, δ_{N-H} 1600 cm^{-1}. MS (EI): m/z 276 (M^+). Anal. calcd. for $C_{14}H_{10}F_2N_2O_2$: C, 60.87; H, 3.65; N, 10.14. Found: C, 60.65; H, 3.25; N, 10.06.

N-Phenyl-bis(6-acetylpyridine-2-carboximide) (**6a**)

^1H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, 2H, Py-Hm), 8.36 (d, 2H, Py-Hm), 8.10 (t, 2H, Py-Hp), 7.26 (d, 2H, Ph-Ho), 7.07 (t, 1H, Ph-Hm), 6.95 (t, 1H, Ph-Hm), 6.84 (t, 1H, Ph-Hp), 2.75 (s, 6H, Me). IR (KBr): $\nu_{C=O}$ 1708, $\nu_{C=O}$ 1600 cm^{-1}. MS (EI): m/z 387 (M^+). Anal. calcd. for $C_{22}H_{18}N_3O_{4.5}$: C, 66.66; H, 4.58; N, 10.60. Found: C, 66.80; H, 4.45; N, 10.23.

N-(4-Methylphenyl)-bis(6-acetylpyridine-2-carboximide) (**6b**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, 2H, Py-Hm), 8.34 (d, 2H, Py-Hm), 8.10 (t, 2H, Py-Hp), 7.15 (d, 2H, Ph-Ho), 7.11 (d, 1H, Ph-Hm), 7.05 (d, 1H, Ph-Hm), 2.76 (s, 6H, CH_3), 2.23 [s, 3H, Ph-$(Me)_p$]. IR (KBr): $\nu_{C=O}$ 1712, $\nu_{C=O}$ 1580 cm^{-1}. MS (EI): m/z 400 (M^+-H). Anal. calcd. for $C_{23}H_{19}N_3O_4$: C, 68.82; H, 4.77; N, 10.47. Found: C, 69.26; H, 5.13; N, 10.73.

N-(2-Chlorophenyl)-bis(6-acetylpyridine-2-carboximide) (**6c**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, 2H, Py-Hm), 8.34 (d, 2H, Py-Hm), 8.16 (t, 2H, Py-Hp), 7.23 (d, 1H, Ph-Ho), 7.07 (t, 1H, Ph-Hm), 6.77 (t, 1H, Ph-Hm), 6.69 (t, 1H, Ph-Hp), 2.80 (s, 6H, CH_3). IR (KBr): $\nu_{C=O}$ 1758, $\nu_{C=O}$ 1707 cm^{-1}. MS (EI): m/z 421 (M^+). Anal. calcd. for $C_{22}H_{18}ClN_3O_5$: C, 60.07; H, 4.12; N, 9.55. Found: C, 59.97; H, 3.80; N, 9.47.

N-(3-Chlorophenyl)-bis(6-acetylpyridine-2-carboximide) (**6d**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, 2H, Py-Hm), 8.32 (d, 2H, Py-Hm), 8.14 (t, 2H, Py-Hp), 7.24 (s, 1H, Ph-Ho), 7.18 (t, 1H, Ph-Ho), 6.91 (t, 1H, Ph-Hm), 6.67 (d, 1H, Ph-Hp), 2.76 (s, 6H, CH_3). IR (KBr): $\nu_{C=O}$ 1730, $\nu_{C=O}$ 1588 cm^{-1}. MS (EI): m/z 420 (M^+-H). Anal. calcd. for $C_{22}H_{16}ClN_3O_4$: C, 62.64; H, 3.82; N, 9.96. Found: C, 63.02; H, 3.47; N, 10.03.

N-(4-Chlorophenyl)-bis(6-acetylpyridine-2-carboximide) (**6e**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, 2H, Py-Hm), 8.33 (d, 2H, Py-Hm), 8.15 (t, 2H, Py-Hp), 7.26 (s, 1H, Ph-Ho), 7.21 (t, 1H, Ph-Ho), 7.08 (t, 1H, Ph-Hm), 6.72 (t, 1H, Ph-Hm), 2.70 (s, 6H, CH_3). IR (KBr): $\nu_{C=O}$ 1720, $\nu_{C=O}$ 1631 cm^{-1}. MS (EI): m/z 420 (M^+-H). Anal. calcd. for $C_{22}H_{16}ClN_3O_4$: C, 62.64; H, 3.82; N, 9.96. Found: C, 63.10; H, 3.87; N, 9.91.

N-(2-Nitrophenyl)-bis(6-acetylpyridine-2-carboximide) (**6f**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, 2H, Py-Hm), 8.10 (d, 2H, Py-Hm), 7.89 (t, 2H, Py-Hp), 7.32 (d, 1H, Ph-Ho), 7.14 (t, 1H, Ph-Hm),

7.13 (t, 1H, Ph-Hm), 7.09 (t, 1H, Ph-Hp), 2.35 (s, 6H, CH_3). IR (KBr): $\nu_{C=O}$ 1700, $\nu_{C=O}$ 1642 cm^{-1}. MS (EI): m/z 432 (M^+). Anal. calcd. for $C_{22}H_{16}N_4O_6$: C, 61.11; H, 3.73; N, 12.96. Found: C, 61.26; H, 4.12; N, 13.30.

N-(3-Nitrophenyl)-bis(6-acetylpyridine-2-carboximide) (**6g**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, 2H, Py-Hm), 8.11 (d, 2H, Py-Hm), 7.89 (t, 2H, Py-Hp), 7.34 (s, 1H, Ph-Ho), 7.20 (t, 1H, Ph-Ho), 7.18 (t, 1H, Ph-Hm), 7.08 (d, 1H, Ph-Hp), 2.38 (s, 6H, CH_3). IR (KBr): $\nu_{C=O}$ 1696, $\nu_{C=O}$ 1579 cm^{-1}. MS (EI): m/z 432 (M^+). Anal. calcd. for $C_{22}H_{16}N_4O_6$: C, 61.11; H, 3.73; N, 12.96. Found: C, 61.45; H, 3.96; N, 13.43.

N-(4-Nitrophenyl)-bis(6-acetylpyridine-2-carboximide) (**6h**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, 2H, Py-Hm), 8.02 (d, 2H, Py-Hm), 7.91 (t, 2H, Py-Hp), 7.35 (s, 1H, Ph-Ho), 7.34 (t, 1H, Ph-Ho), 7.32 (t, 1H, Ph-Hm), 7.10 (d, 1H, Ph-Hm), 2.33 (s, 6H, CH_3). IR (KBr): $\nu_{C=O}$ 1712, $\nu_{C=O}$ 1653 cm^{-1}. MS (EI): m/z 431 (M^+-H). Anal. calcd. for $C_{22}H_{16}N_4O_6$: C, 61.11; H, 3.73; N, 12.96. Found: C, 61.05; H, 4.06; N, 13.27.

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