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Facile and selective synthesis of chloronicotinaldehydes by the Vilsmeier reaction

B. Gangadasu, P. Narender, S. Bharath Kumar, M. Ravinder, B. Ananda Rao, Ch. Ramesh, B. China Raju and V. Jayathirtha Rao*

Organic Chemistry Division II, Indian Institute of Chemical Technology, Uppal Road, Tarnaka, Hyderabad 500 007, Andhra Pradesh, India

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Abstract—Eleven enamides were prepared by adopting different procedures. The various enamides prepared were subjected to Vilsmeier reaction using (i) $POCl_3$/DMF; (ii) diphosgene/DMF; (iii) triphosgene/DMF leading to the formation of various multisubstituted chloronicotinaldehydes. Studies carried out indicate that Vilsmeier reagent concentration and the replacement of $POCl_3$ by diphosgene or triphosgene, provides excellent selectivity and higher yields. Under modified reaction conditions one can get only chloronicotinaldehydes and not the chloropyridines as products. The various advantages in using diphosgene and triphosgene are illustrated. The mechanism of formation of chloronicotinaldehyde was discussed.

1. Introduction

Among heterocyclic compounds, pyridine and its derivatives are important compounds and are present in many biological systems.[1,2] Among the various applications of these pyridine derivatives, the pharmaceutical and agrochemical[3] applications are more important. Extensive studies have been carried out on the synthesis of pyridine compounds owing to their wide importance as drugs, biologically active natural products, and for other various applications. Introducing a formyl group into the aromatic ring system of pyridine is particularly significant, considering the lack of reactivity of pyridines toward electrophilic substitution reactions compared to benzenoids. The formyl group present on the pyridine ring opens up the possibility of carrying out a diverse range of functional group transformations. Furthermore, chloronicotinaldehydes are very good precursors for annulation of a wide variety of heterocyclic ring systems.

Vilsmeier reaction was initially used for the formylation of activated aromatic substrates and carbonyl compounds;[4] it is now used as a powerful synthetic tool for the construction of many heterocyclic compounds[5–10] such as quinolines, indoles, quinozolines, and pyridines. The synthesis of various substituted chloronicotinaldehydes using Vilsmeier reaction have been much less reported in the literature.[11,12] Meth-Cohn and Westwood reported the synthesis of 2-chloropyridines, pyridones, and quinolines using enamides under Vilsmeier reaction conditions.[12] This led us to conduct a systematic investigation on the feasibility of cyclization of enamides under Vilsmeier conditions to synthesize chloronicotinaldehydes. These chloronicotinaldehydes are very good precursors for the synthesis of arachidonic acid metabolite heterocyclic analogues 8-HETE.[13,14] Our continuing interest in the synthesis of heterocycles for biological activity[15] led us to report a facile and an efficient method for the synthesis of various substituted chloronicotinaldehydes (pyridine-3-carboxaldehyde) from enamides. Studies carried out on the formation of chloronicotinaldehydes in Vilsmeier reactions dramatically improved the selectivity and yield by using diphosgene/triphosgene compared to classical method of using $POCl_3$ in the formation of Vilsmeier reagent.

2. Results and discussion

Various enamides (**1**–**11**; Scheme 1) were prepared for the purpose of synthesizing various chloronicotinaldehydes (**12**–**22**; Scheme 1). Enamides **1**–**5** were synthesized by condensing appropriate aldehyde with benzylamine[16] to form initially a Schiff base and followed by acetylation[17] using acetic anhydride and triethylamine. Aldol condensation of benzaldehyde/*p*-methoxybenzaldehyde with acetone provided an α,β-unsaturated ketones, which were converted into the corresponding oximes and subsequent treatment using PCl_5[11] afforded enamides **6** and **7**. Enamide **8** was prepared by treating propiophenone oxime with Fe powder in the presence of acetic anhydride and acetic acid.[18] β-Keto ester was first converted into an enamine derivative,

Keywords: Enamides; Vilsmeier reaction; Diphosgene/triphosgene; Chloronicotinaldehydes; Selectivity; Mechanism.
* Corresponding author. Tel.: +91 40 2716 0123x2541; fax: +91 40 2716 0757; e-mail: jrao@iict.res.in

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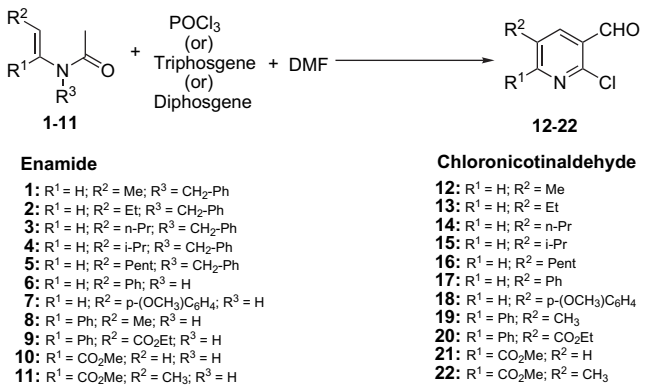
which was acetylated to give enamide[19] **9**. Serine and threonine methyl ester hydrochlorides[20] were prepared and then converted into the corresponding enamides[21,22] **10** and **11**.



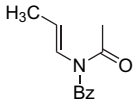
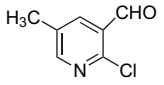
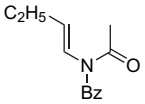
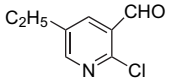
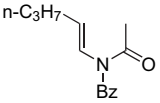
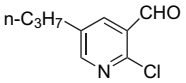
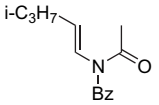
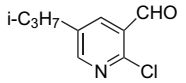
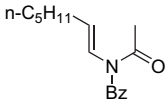
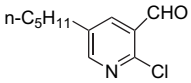
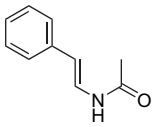
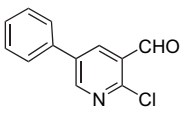
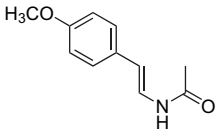
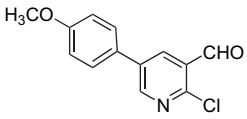
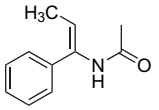
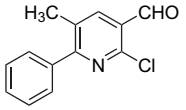
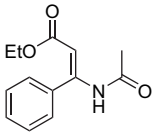
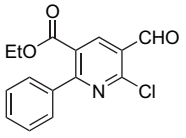
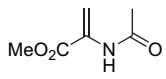
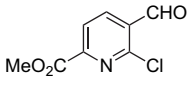
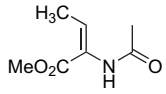
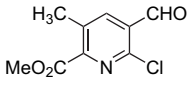
Scheme 1.

Scheme 1 illustrates the synthesis of various chloronicotinaldehydes (Table 1). A DMF solution of enamide was added to the excess Vilsmeier reagent (7 equiv) initially prepared from DMF and $POCl_3$/diphosgene/triphosgene. The reaction mixture was held at room temperature and then refluxed at ~75 °C. The crude product was extracted and purified by column chromatography (Table 1). Various chloronicotinaldehydes **12**–**22** were synthesized with very good yields by using enamides **1**–**11** that are listed in Table 1.

The results arranged in Table 2 show that the selectivity toward the formation of chloronicotinaldehyde improved upon increasing Vilsmeier reagent concentration. Enamide **1** was used for the studies as a representative example to understand selectivity and yield improvements. Upon using 2.5 equiv of Vilsmeier reagent (entry 1; Table 2) the yield of chloronicotinaldehyde **12** was less and 2-chloro-5-methylpyridine **23** was the major product (Scheme 2). Using excess of Vilsmeier reagent (7 equiv entry 5; Table 2), chloronicotinaldehyde **12** was obtained as the major product with a trace amount of 2-chloro-5-methylpyridine **23** (Scheme 2). Replacing $POCl_3$ by triphosgene (entries 9 and 10; Table 2) provided the same selectivity in the formation of chloronicotinaldehyde but with higher yields (Scheme 2). The diphosgene (liquid) or triphosgene (solid) are employed because they are safe substitutes for the toxic phosgene gas, offer mild reaction conditions, provide excellent yields, and avoid the formation of inorganic phosphorus salts. The same procedure was extended to other enamides **2**–**11** and the corresponding chloronicotinaldehydes **13**–**22** were synthesized in higher yields (Table 1).

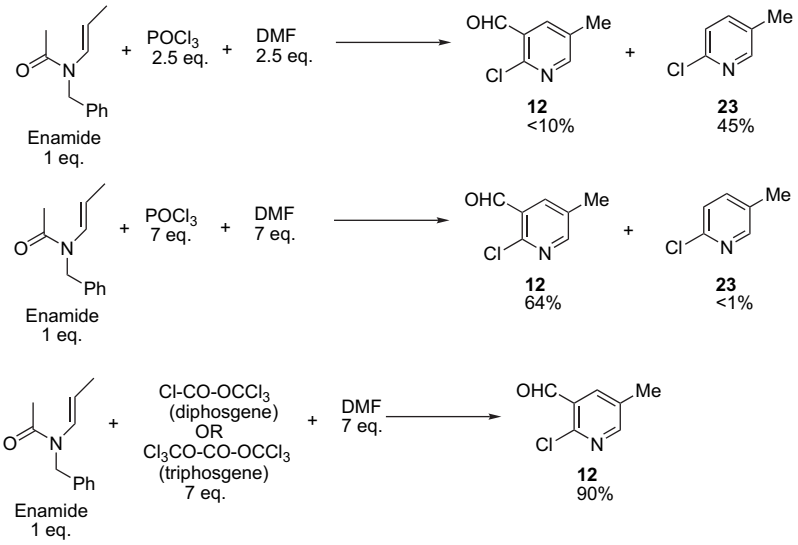
A mechanism is proposed to explain the formation of chloronicotinaldehydes with selectivity (Scheme 3). The enamide initially reacts with Vilsmeier reagent to form bis-enamine having a chloro group (Scheme 3). The net result is the formation of a more nucleophilic bis-enamine. The bis-enamine undergoes formylation to produce two possible mono-formylated bis-enamines. The mono-formylated bis-enamine can undergo cyclization to give 2-chloro-5-methyl pyridine[23] (**23**) or the mono-formylated bis-enamine can undergo second formylation before undergoing cyclization. The second formylation process is quite possible at higher concentrations

Table 1. Synthesis of substituted chloronicotinaldehydes

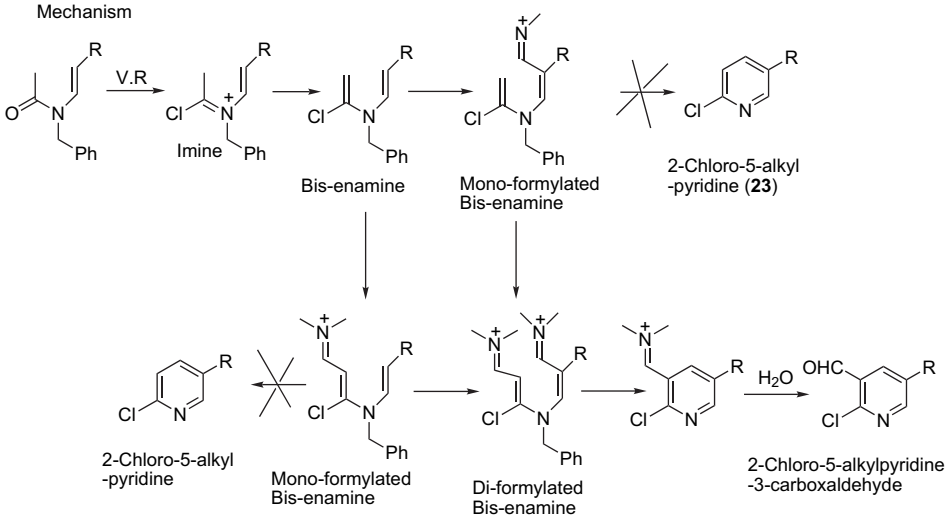
S.No.	Enamides (**1**–**11**)	Chloronicotinaldehydes (**12**–**22**)	Yields[a] (%)
1			94
2			92
3			92
4			91
5			90
6			92
7			92
8			90
9			88
10			90
11			90

[a] Isolated yields using diphosgene/triphosgene.

of Vilsmeier reagent and the same was observed (Table 2; Scheme 2). The di-formylated bis-enamine undergoes cyclization to give the substituted chloronicotinaldehyde (pyridine-3-carboxaldehyde), which is the main product. The products isolated were substituted chloronicotinaldehyde and benzyl chloride (in the case of enamides **1**–**5**). The dimethylamine remains in aqueous phase as amine hydrochloride after work up. These observations clearly indicate that under modified Vilsmeier reaction conditions (i.e., at higher Vilsmeier reagent concentrations) the enamide undergoes



Scheme 2.



Scheme 3.

Table 2. Studies to improve the formation of chloronicotinaldehydes

No.	DMF (mol equiv)	$POCl_3$/DP/TP (mol equiv)	Temperature (°C)	Time (h)	Yield (%)	
					12	**23**
1	2.5	2.5	75	5	<10	45
2	4.0	4.0	75	5	24	25
3	5.0	5.0	75	5	36	12
4	6.0	6.0	75	5	54	6
5	7.0	7.0	75	5	64	<1
6	8.0	8.0	75	5	64	<1
7	8.0	8.0	90	5	64	<1
8	8.0	8.0	90	8	64	<1
9	2.5	2.5	75	5	10	45
10	7.0	7.0	75	5	90	<1

DP = diphosgene; TP = triphosgene. Enamide used is **1**; isolated yields; addition of enamide to Vilsmeier reagent (DMF–$POCl_3$/DP/TP) was carried out at ~0 °C; mol equiv with respect to enamide.
For entries 1–8 $POCl_3$ was used and for 9 and 10 diphosgene/triphosgene was used.

di-formylation before undergoing cyclization to give selectively chloronicotinaldehyde.

3. Conclusions

Various enamides were prepared to synthesize substituted chloronicotinaldehydes. The selectivity toward the formation of chloronicotinaldehydes was achieved at higher Vilsmeier reagent concentration. The replacement of $POCl_3$ by diphosgene/triphosgene provides higher yields and avoids formation of inorganic phosphorus salts. A mechanism is proposed to explain the selectivity.

4. Experimental

4.1. General procedure for the preparation of aldimines

In the synthesis of enamides **1–5**, the aldimines were prepared by condensation of appropriate aldehyde and benzylamine.[16]

Benzylamine (5 g, 46 mmol) was added to a 50 mL round bottom flask fitted with magnetic stirrer and dropping funnel. Propionaldehyde (2.71 g, 46 mmol) was added gradually over a period of 1 h at 0 °C, with constant stirring. Potassium hydroxide flakes (1.3 g, 23 mmol) were added to the reaction mixture at 0 °C and the mixture was allowed to stand until separation into two layers appeared complete at 0 °C. The organic layer was then removed and allowed to stand over potassium hydroxide pellets in the refrigerator for over night. The same procedure was adopted for making other aldimines (Schiff bases).

4.2. Preparation of various enamides

4.2.1. General procedure for the preparation of *N*-alkenyl-*N*-benzyl acetamides (1–5).[17] Acetic anhydride (4.163 g, 40 mmol) was added to a stirred solution of *N*-benzyl propionaldimine (6 g, 40 mmol) and triethylamine (4.12 g, 40 mmol) at 0–5 °C for about 30 min. The reaction mixture was allowed to reach room temperature. Distillation under reduced pressure yields *N*-benzyl-*N*-[(1*E*)-prop-1-en-1-yl]-acetamide (**1**) in 88% yield. The same procedure was adopted in making other enamides (**2–5**).

4.2.2. Preparation of *N*1-[(*E*)-2-phenyl-1-ethenyl]acetamide (6) and *N*1-[(*E*)-2-(4-methoxyphenyl)-1-ethenyl]-acetamide (7).[11] Phosphorus pentachloride (3.1 g, 15 mmol) was added to 4-phenyl-3-butene-2-one-oxime (5.0 g, 30 mmol) in dry THF (50 mL) at 0 °C, and the mixture was shaken for 30 min. The mixture was then poured slowly into a vigorously stirred mixture of crushed ice (50 g) and 40% aqueous potassium carbonate (50 mL), the pH being maintained at 7 (pH paper) by the addition of solid potassium carbonate. The THF layer was then removed and the resultant solid was collected by filtration, and washed twice with light petroleum. TLC (7:3 light petroleum–ethyl acetate) showed the presence of *E* (R_f 0.40) and *Z* (R_f 0.52) isomers of *N*1-[2-phenyl-1-ethenyl]acetamide (**6**) and these two compounds were characterized by ^{1}H NMR.

The same is carried out for the synthesis of *N*1-[2-(4-methoxyphenyl)-1-ethenyl]acetamide (**7**) by using 4-[(*p*-methoxy)-phenyl]-3-butene-2-one-oxime.

4.2.3. Preparation of *N*1-[(*E*)-1-phenyl-1-propenyl]acetamide (8).[18] 1-Phenyl-1-propanone oxime (5 g, 33 mmol) was heated in acetic anhydride (3.3 g, 33 mmol) and acetic acid (10 mL, 3 mol equiv) in the presence of iron powder (1 g) for 4 h at 100 °C. The mixture was then filtered, extracted with dichloromethane, and the organic layer was washed with water and aqueous K_2CO_3, dried, and evaporated.

4.2.4. Preparation of ethyl (*E*)-3-(acetylamino)-3-phenyl-2-propenoate (9).[19] A solution of β-keto ester, ethyl benzoylacetate (2.3 g, 12 mmol), and NH_4OAc (4.6 g, 60 mmol) in MeOH (15 mL) was stirred at room temperature for 3 days. After the solvent was evaporated under reduced pressure, the residue was diluted with $CHCl_3$ (30 mL). The resulting solid was filtered off and washed with $CHCl_3$ (2×30 mL). The combined filtrate was washed with water and brine, and dried over sodium sulfate. Evaporation of the solvent gave 3-amino-2-alkenoate, which was used for the next step without purification.

To a solution of 3-amino-2-alkenoate in THF (12 mL) were added pyridine (2 mL) and acetic anhydride (6 mL). The reaction mixture was then heated under reflux for 24 h. Reaction mixture was rotary evaporated to remove solvent and triethylamine. The residue was dissolved in EtOAc (20 mL) and the solution was washed with water (10 mL), 1 N HCl (10 mL), 1 M KH_2PO_4 (10 mL), $NaHCO_3$ (saturated, 10 mL), and brine (15 mL). After the solution was dried over sodium sulfate, the solvent was evaporated under reduced pressure. Chromatography of the residue on silica gel with a solvent gradient of EtOAc in hexane (15–70%) as eluant gave compound **9**.

4.2.5. Preparation of methyl 2-(acetylamino)acrylate (10) and methyl (*E*)-2-(acetylamino)-2-butenoate (11).[20,21] Triethylamine (30 mL) was added to methyl ester of L-serine hydrochloride (5 g, 27.9 mmol) at 0 °C. After 10 min stirring acetic anhydride (7.0 g, 70 mmol) was added drop wise. The reaction mixture was allowed to stir at room temperature over night. The reaction mixture was washed with 10% sodium bicarbonate solution and extracted with dichloromethane solvent. The obtained methyl 2-(acetylamino)acrylate (**10**) was characterized with ^{1}H NMR and Mass spectroscopies. The same procedure using methyl ester of L-threonine afforded methyl (*E*)-2-(acetylamino)-2-butenoate (**11**).

4.3. Synthesis of substituted chloronicotinaldehydes

4.3.1. General procedure for the synthesis of substituted 2-chloronicotinaldehydes (substituted 2-chloro-pyridine-3-carboxaldehydes) using $POCl_3$ (12–22). *N*,*N*-Dimethylformamide (13.5 g, 185 mmol) was added to a well stirred and cooled solution of phosphorus oxychloride (28.3 g, 185 mmol) at 0 °C for 30 min and followed by *N*-benzyl-*N*-[(1*E*)-prop-1-en-1-yl]acetamide (**1**) (5 g, 26 mmol) at the same temperature. The ice bath was removed and the mixture was further stirred for 2 h at room temperature. The reaction mixture was heated to 75 °C for 5 h. The orange-yellow colored organic mass was poured into crushed ice (200 g) with stirring. The mass was extracted with methylene chloride (2×200 mL) and the layers were separated. The organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure. Thus obtained residue was subjected to column chromatography purification on silica gel to give 2-chloro-5-methylnicotinaldehyde (2-chloro-5-methylpyridine-3-carboxaldehyde) (**12**) in 64% yield. The same procedure was adopted in making other chloronicotinaldehydes (**13–22**).

4.3.2. General procedure for the synthesis of substituted 2-chloronicotinaldehydes (substituted 2-chloro-pyridine-3-carboxaldehydes) using triphosgene or diphosgene (12–22). *N*,*N*-Dimethylformamide (13.5 g, 185 mmol) was added to a cooled solution of triphosgene (28.3 g, 185 mmol), in the case of diphosgene (36.6 g, 185 mmol) at 0–10 °C for 30 min and followed by *N*-benzyl-*N*-[(1*E*)-prop-1-en-1-yl]acetamide (**1**) (5 g, 26 mmol) at the same temperature. The ice bath was removed and the mixture was further stirred for 2 h at room temperature. The reaction mixture was heated to 75 °C for 5 h. The orange-yellow colored organic mass was poured into ice cold water (200 g) with stirring. The mass was extracted with methylene chloride

(2×200 mL). The organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure. Thus obtained residue was subjected to column chromatography purification on silica gel to give 2-chloro-5-methylnicotinaldehyde (**12**) in 92% yield. The same procedure was adopted for the preparation of other chloronicotinaldehydes (**13**–**22**).

4.3.2.1. 2-Chloro-5-ethylnicotinaldehyde (13). White solid. Mp 67–69 °C; δ_H (200 MHz, $CDCl_3$) 1.35 (t, 3H, *J* 7.56 Hz, *Me*), 2.75 (m, 2H, CH_2), 8.02 (s, 1H, hetero aromatic), 8.42 (s, 1H, hetero aromatic), 10.4 (s, 1H, C*H*O); δ_C (50 MHz, $CDCl_3$) 188.6, 153.2, 150.2, 138.8, 136.3, 127.6, 24.6, 14.2; EIMS (*m*/*z*) 169 (M^+) (100), 153 (55), 140 (27), 132 (56), 105 (31), 90 (22), 77 (50), 63 (30), 51 (43); IR (KBr) ν 2362, 1696, 1559, 1426, 1374, 1275, 1220, 1058, 746 cm^{-1}; HRMS (EI^+), exact mass calcd for C_8H_8NOCl: 169.0292. Found: 169.0292.

4.3.2.2. 2-Chloro-5-propylnicotinaldehyde (14). White solid. Mp 34–36 °C; δ_H (200 MHz, $CDCl_3$) 0.9 (t, 3H, *J* 7.56 Hz, *Me*), 1.7 (m, 2H, CH_2), 2.64 (t, 2H, *J* 7.52 Hz, CH_2), 8.0 (s, 1H, hetero aromatic), 8.38 (s, 1H, hetero aromatic), 10.4 (s, 1H, C*H*O); δ_C (50 MHz, $CDCl_3$) 189.2, 154.0, 150.7, 137.7, 137.2, 127.9, 33.7, 23.6, 13.2; EIMS (*m*/*z*) 183 (M^+) (57), 154 (100), 147 (15), 99 (15), 90 (20), 40 (36); IR (KBr) ν 3376, 2960, 2871, 2364, 1695, 1587, 1432, 1378, 768 cm^{-1}; HRMS (EI^+), exact mass calcd for $C_9H_{10}NOCl$: 183.0450. Found: 183.0467.

4.3.2.3. 2-Chloro-5-isopropylnicotinaldehyde (15). White solid. Mp 38–39 °C; δ_H (200 MHz, $CDCl_3$) 1.2–1.4 (m, 6H, 2*Me*), 3.0 (m, 1H, *CH*), 8.04 (s, 1H, hetero aromatic), 8.44 (s, 1H, hetero aromatic), 10.4 (s, 1H, C*H*O); δ_C (50 MHz, $CDCl_3$) 189.1, 152.7, 150.7, 143.7, 135.3, 128.1, 30.9, 23.1; EIMS (*m*/*z*) 183 (M^+) (44), 168 (100), 104 (40), 77 (40), 51 (24); IR (KBr) ν 2966, 2873, 2361, 1695, 1586, 1432, 1378, 1281, 1090, 959, 771, 607 cm^{-1}; HRMS (EI^+), exact mass calcd for $C_9H_{10}NOCl$: 183.0450. Found: 183.0448.

4.3.2.4. 2-Chloro-5-pentylnicotinaldehyde (16). White solid. Mp 44–46 °C; δ_H (200 MHz, $CDCl_3$) 0.9 (t, 3H, *J* 7.56 Hz, *Me*), 1.38 (m, 4H, 2CH_2), 1.70 (m, 2H, CH_2), 2.7 (t, 2H, *J* 7.52 Hz, CH_2), 8.0 (s, 1H, hetero aromatic), 8.44 (s, 1H, hetero aromatic), 10.4 (s, 1H, C*H*O); δ_C (50 MHz, $CDCl_3$) 189.2, 153.9, 150.7, 138.0, 137.2, 128.0, 31.8, 30.9, 30.2, 22.1, 13.7; EIMS (*m*/*z*) 211 (M^+) (40), 168 (75), 155 (100), 141 (27), 126 (8), 119 (15), 103 (21), 91 (47); IR (KBr) ν 2930, 2864, 1696, 1588, 1431, 1337, 1281, 1154, 1071 cm^{-1}; HRMS (EI^+), exact mass calcd for $C_{11}H_{14}NOCl$: 211.0763. Found: 211.0767.

4.3.2.5. 2-Chloro-5-methyl-6-phenylnicotinaldehyde (19). Light yellow solid. Mp 67–69 °C; δ_H (200 MHz, $CDCl_3$) 2.42 (s, 3H, *Me*), 7.39–7.61 (m, 5H), 8.04 (s, 1H, hetero aromatic), 10.42 (s, 1H, C*H*O); δ_C (50 MHz, $CDCl_3$) 189.2, 163.1, 149.9, 140.1, 137.8, 130.8, 129.1, 128.8, 128.1, 126.6, 19.2; EIMS (*m*/*z*) 231 (M^+) (50), 230 (100), 166 (20), 139 (12), 115 (10), 77 (9); IR (KBr) ν 2442, 1690, 1540, 1420, 1370, 1265, 1224, 1048, 746 cm^{-1}. Anal. Calcd for $C_{13}H_{10}ClNO$: C, 67.39; H, 4.35; N, 6.05. Found: C, 67.46; H, 4.50; N, 6.11.

4.3.2.6. 2-Chloro-5-(ethoxyacetate)-6-phenylnicotinaldehyde (20). Light yellow solid. Mp 72–73 °C; δ_H (200 MHz, $CDCl_3$) 1.12 (t, 3H, *J* 7.26 Hz, *Me*), 4.20 (q, 2H, *J* 7.26 Hz, OCH_2), 7.25–7.35 (m, 5H, aromatic), 9.05 (s, 1H, hetero aromatic), 10.55 (s, 1H, C*H*O); δ_C (50 MHz, $CDCl_3$) 188, 165, 144, 143, 138, 131, 129, 128, 123, 122, 116, 57, 14; EIMS (*m*/*z*) 289 (M^+) (14), 260 (100), 244 (34), 216 (13), 153 (14), 126 (12), 77 (7); IR (KBr) ν 1736, 1560, 1450, 1369, 1310, 1261, 1189, 735 cm^{-1}. Anal. Calcd for $C_{15}H_{12}ClNO_3$: C, 62.18; H, 4.17; N, 4.83. Found: C, 62.21; H, 4.21; N, 4.88.

4.3.2.7. Methyl 6-chloro-5-formyl-2-pyridincarboxylate (21). White solid. Mp 70–72 °C; δ_H (200 MHz, $CDCl_3$) 4.0 (s, 3H, OCH_3), 8.2 (d, *J* 3.2 Hz, 1H, hetero aromatic), 8.4 (d, *J* 3.2 Hz, 1H, hetero aromatic), 10.5 (s, 1H, C*H*O); δ_C (50 MHz, $CDCl_3$) 188, 163, 153, 151, 139, 131, 124, 53; EIMS (*m*/*z*) 199 (M^+) (6), 169 (23), 141 (100), 112 (23), 76 (50), 59 (29); IR (KBr) ν 3433, 1730, 1554, 1445, 1359, 1314, 1251, 1199, 1137, 1063, 956, 874, 813, 735 cm^{-1}. Anal. Calcd for $C_8H_6ClNO_3$: C, 48.14; H, 3.02; N, 7.01. Found: C, 48.21; H, 3.21; N, 7.08.

4.3.2.8. Methyl 6-chloro-5-formyl-3-methyl-2-pyridincarboxylate (22). White solid. Mp 43–45 °C; δ_H (200 MHz, $CDCl_3$) 2.60 (s, 3H, *Me*), 4.0 (s, 3H, OCH_3), 8.1 (s, 1H, hetero aromatic), 10.45 (s, 1H, C*H*O); δ_C (50 MHz, $CDCl_3$) 188, 164, 152, 148, 142, 135, 129, 53, 18; EIMS (*m*/*z*) 213 (M^+) (44), 181 (54), 155 (52), 149 (75), 97 (29), 71 (56), 43 (100); IR (KBr) ν 1730, 1559, 1440, 1359, 1319, 1069, 966, 874, 755 cm^{-1}. Anal. Calcd for $C_9H_8ClNO_3$: C, 50.60; H, 3.77; N, 6.55. Found: C, 50.62; H, 3.81; N, 6.58.

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