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Synthesis of 2-hydroxy-5,6-diarylnicotinonitriles and 2-chloro-5,6-diarylnicotinonitriles from β-chloroenones

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We dedicate this article to the memories of Dr. C. V. Asokan who was a great teacher and an eminent researcher

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ABSTRACT

Vilsmeier–Haack reaction of β-ketoaldehydes leads to the formation of β-chloroenones and these chloroenones on treatment with malononitrile afford 2-hydroxy-5,6-diarylnicotinonitriles. But a one-pot reaction of β-ketoaldehydes with Vilsmeier–Haack reagent and malononitrile or cyanoacetamide results in the formation of 2-chloro-5,6-diarylnicotinonitriles in good yields.

1. Introduction

Diarylnicotinonitriles form an important class of organic compounds and these kinds of molecules possess important biological properties.[1] Anti-inflammatory, analgesic, antimicrobial, and antipyretic properties of these compounds have already been reported.[2] A variety of chalcones were reported as important starting materials for the synthesis of 4,6-diarylnicotinonitriles.[3] There are reports on one-pot synthesis of diarylnicotinonitriles, but poor substrate selection, lower yield, and lack of selectivity of the product were the problems associated with the method.[4] Many 5,6-diarylnicotinonitriles were synthesized using deoxybenzoins as the staring materials, but the method required long hauling work and the yields of diarylnicotinonitriles derived from deoxybenzoins were very low.[5] Our investigations on the Vilsmeier–Haack reaction[6,7] of β-ketoaldehydes led to the development of an alternate facile method for the synthesis of β-chloroenones, which could be effectively transformed into 2-oxo/2-hydroxy-5,6-diarylnicotinonitriles and 2-chloro-5,6-diarylnicotinonitriles in good yields.

β-Ketoaldehydes, synthesized from chalcones, were treated with Vilsmeier–Haack reagent to form β-chloroenones.[8] These β-chloroenones on treatment with malononitrile in the presence of ammonium acetate and acetic acid afforded 2-hydroxy-5,6-diarylnicotinonitriles in good yields. Further β-ketoaldehydes, could be treated with malononitrile under Vilsmeier–Haack condition to synthesize 2-chloro-5,6-diarylnicotinonitriles. These series of reactions led to a novel facile method for the synthesis of β-chloroenones, 2-hydroxy-5,6-diarylnicotinonitriles, and 2-chloro-5,6-diarylnicotinonitriles in good yields. The results of the investigations are the topic of discussion of the paper.

2. Results and discussion

Ducker et al. have reported the reaction of β-ketoaldehydes with malononitrile/cyanoacetamide in the presence of sodium hydroxide to afford 2-pyridone derivatives.[9] However, the competing deformylation reactions of β-ketoaldehydes under basic conditions deteriorate the potential of the reaction as a valuable synthetic method. As per earlier reports on the synthesis of chalcones and chalcone aldehydes, a series of 1,3-diarylpropenones and 3-oxo-2,3-diarylpropanals were synthesized.[10] We tried an alternate method in which β-ketoaldehydes could be easily transformed into β-chloroenones under Vilsmeier–Haack condition and from these

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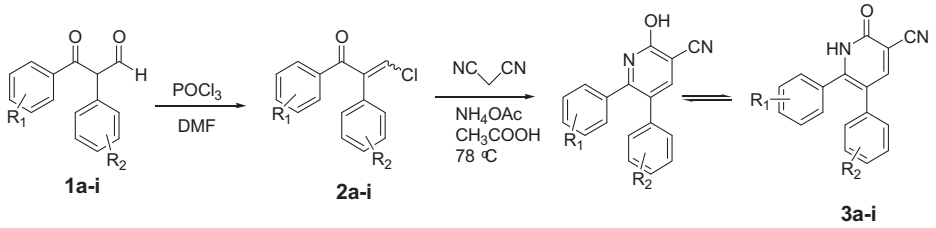
chloroenones 2-oxo/2-hydroxypyridines were synthesized in excellent yields. In a pilot experiment 3-oxo-2,3-diphenylpropanal **1a** was treated with 1.5 equiv of Vilsmeier–Haack reagent at room temperature(30 °C) forming 3-chloro-1,2-diphenyl-2-propen-1-one **2a**. The reaction was monitored by TLC and was found to be completed within 20 h with a yield of 94%. The product **2a** was then treated with malononitrile in the presence of ammonium acetate and acetic acid at 78 °C for 8 h to form 2-oxo/2-hydroxy-5,6-diphenylnicotinonitrile **3a**(Scheme 1).



Scheme 1. Synthesis of 2-hydroxy-5,6-diarylnicotinonitriles.

^{1}H NMR spectroscopic analyses showed that the product **3a** formed in this reaction is an equilibrium mixture of 2-hydroxypyridine/2-pyridone tautomers. The reaction is general and other 3-oxo-2,3-diarylpropanals **1b**–**i** were converted to 3-chloro-1,2-diaryl-2-propen-1-ones **2a**–**i** and 2-hydroxy/2-oxo-5,6-diarylnicotinonitriles **3b**–**i** (Table 1).

Table 1
Synthesis of 3-chloro-1,2-diaryl-2-propen-1-ones **2ai** and 5,6-diaryl-2-hydroxyni cotinonitriles **3a**–**i**

2, 3	R_1	R_2	Yield	
			2	**3**
a	H	H	94	85
b	Br	H	92	75
c	4-OCH_3	H	95	82
d	4-Cl	H	93	88
e	4-CH_3	H	92	78
f	4-Cl	2-Cl	91	82
g	H	2-Cl	91	77
h	4-CH_3	4-OCH_3	95	71
i	H	4-OCH_3	95	90

IR spectrum of **2a** exhibited absorption bands due to carbonyl group at 1670 cm^{-1} and C–Cl stretching at 694 cm^{-1}. The (M+2) peak at *m*/*z* 244 and molecular ion peak at *m*/*z* 242 in the GC–MS spectrum indicate the formation of **2a**. ^{1}H NMR and ^{13}C NMR spectra of **2a** revealed that a mixture of both *E* and *Z* isomers are formed in certain cases in the reaction, but for the derivatives **2f**, **2g**, and **2h** only one isomer is formed. The reason for favoring only one isomer in certain cases may be due to some stereoelectronic or steric factors and it is beyond the scope of the investigations. In the ^{1}H NMR spectrum of **2a** the vinylic hydrogen appeared twice at δ 6.76 and δ 7.01 and 16 aromatic protons were appeared as a multiplet between δ 7.33 and 7.59. The remaining four hydrogen atoms were observed at δ 7.79 and δ 8.01 as two doublets. In the ^{1}H decoupled ^{13}C NMR spectrum of **2a** the peaks corresponding to the vinylic carbon atoms were present at δ 137.1 and 143.0 and the carbonyl carbon atoms at δ 193.9 and 194.8.

^{1}H NMR spectroscopic analyses showed that the product **3a** formed in this reaction is an equilibrium mixture of 2-hydroxypyridine/2-pyridone tautomers. The reaction is general to other 3-oxo-2,3-diarylpropanals **1b**–**i** to get 3-chloro-1,2-diaryl-2-propen-1-ones **2a**–**i** and 2-hydroxy/2-oxo-5,6-diarylnicotin onitriles **3b**–**i** (Table 1). In the FTIR spectrum of 2-hydroxy-5,6-diphenylnicotinonitrile **3a** showed the O–H stretching at 3463 cm^{-1} and the aromatic C–H stretching at 3284 cm^{-1}. The C=C stretching and C=N stretching were observed at 1627 and 1645 cm^{-1}, respectively. Elemental analysis results also support the formation of **3a**.

^{1}H NMR and ^{13}C NMR spectral analysis showed that in solution 5,6-diphenyl-2-hydroxynicotinonitrile **3a** exists in a pyridone–pyridol equilibrium, which is a general property of 2-pyridones.[11] In the ^{1}H NMR (DMSO-d_6) spectrum there was a broad singlet of two protons at δ 6.87, which disappeared in D_2O indicating the presence of NH and OH protons, which are D_2O exchangeable. The peaks at δ 7.82 and 7.92 correspond the CH of the heterocyclic ring. Other aromatic protons resonated in the δ 6.98–7.32 ppm region as multiplets with an integration of 20 protons. In the ^{13}C NMR spectrum signals at δ 160.4 (C=O), and 157.7 ppm (C–OH), 115.8 and 115.5 (CN) also indicate the existence of pyridone–pyridol equilibrium. However, the single crystal X-ray analysis of both compounds **3a** and **3i** showed that in solid state they exist as 2-hydroxy-5,6-diarylnicotinonitrile and two neighboring molecules are bound together with intermolecular hydrogen bonding between adjacent hydroxypyridine moieties (N–H–O) (Figs. 1 and 2). In 2-hydroxy-5-(4-methoxyphenyl)-6-phenylnicotinonitrile **3i** an interaction between nitrile nitrogen (N_1) and pyridine ring hydrogen (H9) was also observed, which may be due to weak polar interactions between methoxy group and aromatic stacking interaction (Fig. 2b). The O–H bond lengths in **3a** and **3i** are 0.821 Å and 0.820 Å respectively.

The mechanism for the formation of 2-hydroxy-5,6-diarylnicotinonitriles **3** from 3-oxo-2,3-diarylpropanal **1** via 3-chloro-1,2-diphenyl-2-propen-1-one **2** can be explained as follows.

Addition of Vilsmeier–Haack reagent to 3-oxo-2,3-diarylpropanal **1** forms an iminoalkylated intermediate **4** followed by elimination of one molecule of DMF resulting in the formation of β-chloroenone **2**. Michael reaction of **2** with malononitrile gives the adduct **5** and which undergoes subsequent cyclization and aromatization to afford nicotinonitrile **3** (Scheme 2).

β-Chloroenone **2** was treated with cyanoacetamide under similar conditions, but no 2-hydroxypyiridine derivative could be isolated.

In an earlier report we had shown that enones or enolizable ketones undergo condensation with malononitrile under Vilsmeier–Haack reaction condition, followed by in situ cyclization and aromatization to form 2-chloronicotinonitriles.[6] In light of the above reaction, 3-oxo-2,3-diphenylpropanal **1a** was treated with Vilsmeier–Haack reagent at room temperature for 20 h followed by addition of malononitrile/cyanoacetamide. The temperature was elevated to 70 °C and the reaction was continued for another 3 h to get 2-chloro-5,6-diphenylnicotinonitrile **7a** in 55% and 70% yield, respectively (Scheme 3, Table 2). The formation of product **7a** was via chloroenone intermediate **2**. The reaction was extended to other 3-oxo-2,3-diarylpropanals **1b**–**e** to get 2-chloro-5,6-diarylnicotin onitrile **7a**–**e** in good yields.

Apparently, under the Vilsmeier–Haack reaction condition, the 3-oxo-2,3-diphenylpropanal **1a** reacted with malononitrile or

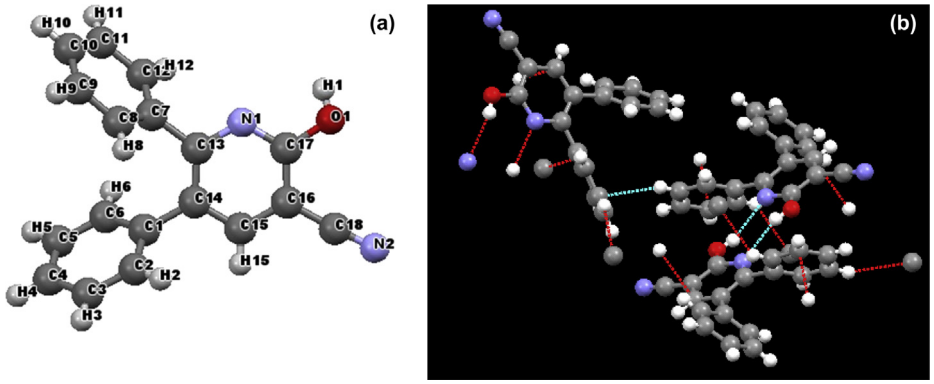


Fig. 1. . a. Ortep diagram of 2-hydroxy-5,6-diphenylnicotinonitrile **3a**. b. Three-dimensional arrays of 2-hydroxy-5,6-diphenylnicotinonitrile **3i** in its crystal lattice.

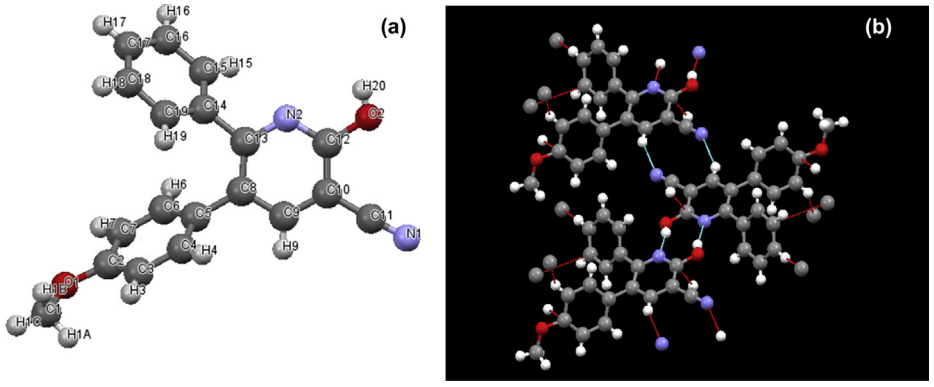
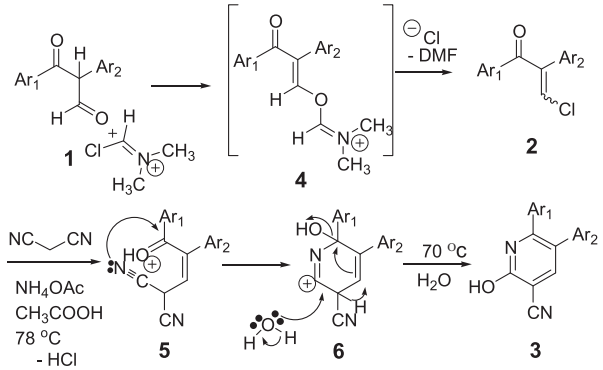
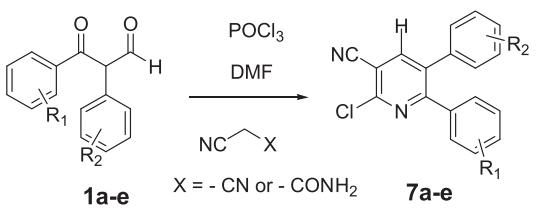


Fig. 2. . a. Ortep diagram of 2-hydroxy-5-(4-methoxyphenyl)-6-phenylnicotinonitrile **3i**. b. Three-dimensional arrays of 2-hydroxy-5-(4-methoxyphenyl)-6-phenylnicotinonitrile **3i** in its crystal lattice.



Scheme 2. Plausible mechanism for the formation of 2-hydroxy-5,6-diarylnicotinonitriles **3**.

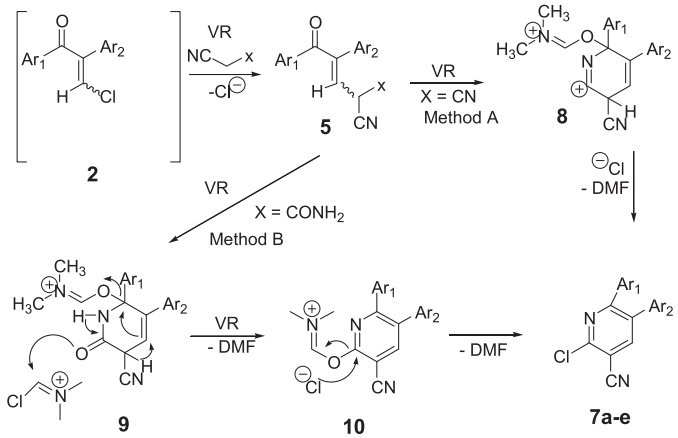
cyanoacetamide to get **5**, which was in situ cyclized and aromatized in the presence of chloromethyleneiminium salt (Vilsmeier–Haack reagent) present in the medium to afford 2-chloro-5,6-diarylnicotinonitriles **7a**–**e** (Scheme 4). The yields of **7** obtained from malononitrile were low when compared to cyanoacetamide. Malononitrile may react with excess Vilsmeier reagent (VR) present in the medium thereby lowering the yield. Reactivity of cyanoacetamide toward VR is less.



Scheme 3. Synthesis of 2-chloro-5,6-diarylnicotinonitrile **7a**–**e**.

Table 2
Synthesis of 2-chloro-5,6-diarylnicotinonitrile **7** from 3-oxo-2,3-diphenylpropanal **1** and malononitrile/cyanoacetamide

7	R1	R2	Yields (%)	
			Malononitrile	Cyanoacetamide
a	H	H	55	70
b	4-Cl	H	35	77
c	4-OMe	H	45	80
d	4-Br	H	36	90
e	4-CH3	4-OMe	12	67



Scheme 4. Plausible mechanism for the formation of 2-chloro-5,6-diarylnicotinonitriles **7a**–**e**.

In conclusion the Vilsmeier–Haack reaction of β-ketoaldehydes resulted in the formation of β-chloroenones, which could be easily transformed into 2-hydroxy-5,6-diarylnicotinonitriles, while reaction of β-ketoaldehydes with malononitrile or cyanoacetamide

under Vilsmeier–Haack reaction condition resulted in the formation of 2-chloro-5,6-diarylnicotinonitriles.

3. Experimental

Melting points were determined on a Buchi 530 melting point apparatus and were uncorrected. The IR spectra were recorded as KBr pellets on a Shimadzu IR-470 spectrometer and the frequencies are reported in cm^{-1}. The ^1H NMR spectra were recorded on a Brucker WM 400 (400 MHz) spectrometer using TMS as internal standard and $CDCl_3$ and DMSO-d_6 as solvents. The ^{13}C NMR spectra were recorded on a Brucker WM 400 (400 MHz) spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. The Electron Impact Mass spectra were obtained on a GC–MS-Shimadzu 5050 model instrument. The CHN analyses were done on an ElementarVario EL III Carlo Erba 1108 instrument. The X-ray single crystal analysis was done on Bruker AXS SMART APEX single crystal X-ray diffractometer. All reagents were commercially available and were purified before use. Anhydrous sodium sulfate was used as drying agent. All purified compounds gave a single spot upon TLC analyses on silica gel 7GF using ethyl acetate–hexane mixture as eluent. Iodine vapor or $KMnO_4$ solution in water was used as developing agent for TLC.

3.1. General procedure for the synthesis of 3-chloro-1,2-diaryl-2-propen-1-ones 2a–i

The Vilsmeier–Haack reagent was prepared by mixing DMF (8 mL, 100 mmol) and $POCl_3$ (1.4 mL, 15 mmol) at 0 °C followed by stirring at room temperature for 15 min. To the Vilsmeier–Haack reagent, appropriate 2-oxo-1,2-diarylpropanal **1** (10 mmol) was added and the solution was stirred at room temperature for 20 h. The reaction mixture was poured into ice-cold K_2CO_3 solution and extracted with ethyl acetate (3×20 mL). The organic layer was washed with water, dried on anhydrous sodium sulfate, and the solvent was removed by distillation. The crude reaction mixture was purified by column chromatography (60–120 mesh) using hexane/ethyl acetate (97:3) as the eluent.

3.1.1. 3-Chloro-1,2-diphenyl-2-propen-1-one ***2a***. Yellow viscous liquid, yield=94% (2.28 g); IR (KBr, υ_{max})=3062, 3031, 1670, 1581, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=6.76 (1H, s, vinylic), 7.01 (1H, s, vinylic), 7.33–7.58 (16H, m, ArH), 7.81 (2H, d, J=7.2 Hz, ArH), 8.01 (2H, d, J=6.8 Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$) δ=117.3 (vinylic), 126.0, 128.4, 128.5, 128.6, 128.7, 128.8, 128.9, 129.0, 129.2, 129.7, 129.8, 129.98, 131.2, 132.9, 133.5, 134.0, 137.1 (vinylic), 143.0 (vinylic), 193.9 (CO), 194.8 (CO) ppm; GC–MS m/z (%) 244 (M+2, 19), 242 (M^+,56), 207 (56), 209 (10), 178 (100). Anal. Calcd for $C_{15}H_{11}ClO$: C, 74.23; H, 4.57. Found: C, 74.31; H, 4.59.

3.1.2. 1-(4-Bromophenyl)-3-chloro-2-phenyl-2-propen-1-one ***2b***. Yellow viscous liquid, yield=92% (2.96 g); (KBr, υ_{max})=3062, 3028, 1662, 1585, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=6.75 (1H, s, vinylic), 7.03 (1H, s, vinylic), 7.31–7.39 (5H, m, ArH), 7.51–7.65 (9H, m, ArH), 7.83 (4H, d, J=10 Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$) δ=96.0, 117.5 (vinylic), 125.9, 128.01, 128.4, 128.6, 128.9, 129.0, 129.1, 129.4, 129.8, 130.9, 131.2, 131.7, 132.2, 133.1, 134.1, 134.1, 135.7 (vinylic), 142.7 (vinylic), 192.3 (CO), 193.2 (CO) ppm; GC–MS m/z (%) 324 ((M+4), 2), 322 (M+2, 10), 320 (M^+, 8), 287 (15), 289 (10), 183 (98), 185 (97), 155 (40), 157 (35), 241 (10), 243 (8), 102 (100). Anal. Calcd for $C_{15}H_{10}BrClO$: C, 56.02; H, 3.13. Found: C, 55.9; H, 3.20.

3.1.3. 3-Chloro-1-(4-methoxyphenyl)-2-phenyl-2-propen-1-one ***2c***. Yellow viscous liquid, yield=95% (2.59 g); (KBr, υ_{max})=3066, 1670, 1604, 713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=3.78 (3H, s, OMe), 3.81 (3H, s, OMe), 6.66 (1H, s, vinylic), 6.91–6.93 (3H, m, vinylic and ArH), 6.85 (2H, d, J=8.8 Hz, ArH), 7.27 (2H, d, J=10.4 Hz, ArH), 7.37–7.58 (8H, m, ArH), 7.79 (2H, d, J=8.4 Hz, ArH), 7.99 (2H, d, J=7.2 Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$) δ=55.2 (OMe), 55.3 (OMe), 113.9, 114.5, 115.3 (vinylic), 125.7, 126.9, 127.3, 128.5, 128.9, 129.7, 129.8, 130.6, 132.9, 134.0, 135.4, 137.2, 142.5 (vinylic), 142.7 (vinylic), 159.6 (aromatic), 160.1 (aromatic), 194.3 (CO), 195.1 (CO) ppm; GC–MS m/z (%) 274 ((M+2), 3), 272 (M^+, 10), 237 (17), 209 (23), 132 (100). Anal. Calcd for $C_{16}H_{13}ClO_2$: C, 70.46; H, 4.80. Found: C, 70.50; H, 4.90.

3.1.4. 3-Chloro-1-(4-chlorophenyl)-2-phenyl-2-propen-1-one ***2d***. Yellow viscous liquid, yield=93% (2.58 g); (KBr, υ_{max})=3066, 3031, 1662, 1581, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=6.56 (1H, s, vinylic), 7.04 (1H, s, vinylic), 7.16–7.58 (14H, m, ArH), 7.79 (4H, d, J=7.2 Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$) δ=117.1 (vinylic), 128.6, 128.7, 129.3, 129.8, 130.7, 131.0, 131.8, 133.1, 134.6, 137.0, 142.0 (vinylic), 193.6 (CO) ppm; GC–MS m/z (%) 280 ((M+4), 2), 278 ((M+2), 20), 276 (M^+, 32), 241 (56), 212 (5), 139 (100), 141 (29), 139 (100). Anal. Calcd for $C_{15}H_{10}Cl_2O$: C, 65.01; H, 3.64. Found: C, 65.02; H, 3.70.

3.1.5. 3-Chloro-1-(4-methylphenyl)-2-phenyl-2-propen-1-one ***2e***. Yellow viscous liquid, yield=92% (2.36 g); (KBr, υ_{max})=3058, 3028, 1674, 1604, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=2.38 (3H, s, CH_3), 2.41 (3H, s, CH_3), 6.75 (1H, s, vinylic), 6.96 (1H, s, vinylic), 7.18–7.47 (14H, m, ArH), 7.72 (2H, d, J=8 Hz, ArH), 7.91 (2H, d, J=8 Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$) δ=21.2 (CH_3), 115.3 (vinylic), 116.7 (vinylic), 126.0, 128.1, 128.2, 128.9, 129.8, 133.4, 134.1, 143.7 (vinylic), 142.8 (vinylic), 193.0 (CO) 193.9 (CO) ppm; GC–MS m/z (%) 258 (M+2, 3), 256 (M^+, 7), 221 (58), 193 (7), 119 (100), 91 (65). Anal. Calcd for $C_{16}H_{13}ClO$: C, 74.85; H, 5.10. Found: C, 74.90; H, 5.17.

3.1.6. 3-Chloro-2-(2-chlorophenyl)-1-(4-chlorophenyl)-2-propen-1-one ***2f***. Yellow viscous liquid, yield=91% (2.84 g); IR (KBr, υ_{max})= 3085, 3060; 1660, 1587, 765 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=7.19 (1H, s, vinylic), 7.30–7.43 (6H, m, ArH), 7.78 (1H, d, J=6, ArH), 7.80 (1H, d, J=5, ArH); ^{13}C NMR (400 MHz, $CDCl_3$) δ=96.2, 126.8, 128.82, 129.7, 130.2, 131.1, 131.9, 132.9, 133.1, 135.1, 135.6, 139.3 (vinylic), 141.8 (vinylic), 191 (CO) ppm; GC–MS m/z (%) 312 ((M+2), 1), 310 (M^+, 1), 275 (65), 277 (43), 246 (6), 212 (8), 176 (4), 139 (100), 141 (30), 115 (15), 111 (50). Anal. Calcd for $C_{15}H_9Cl_3O$: C, 57.82; H, 2.91. Found: C, 57.91; H, 3.01.

3.1.7. 3-Chloro-2-(2-chlorophenyl)-1-phenyl-2-propen-1-one ***2g***. Yellow viscous liquid, yield=91% (2.52 g); IR (KBr, υ_{max})=3066, 3037, 1658, 1596, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=6.82 (1H, s, vinylic), 7.26 (1H, br, ArH), 7.21 (2H, m, ArH), 7.35–7.49 (5H, m, ArH), 7.86 (1H, d, J=6.8, ArH); ^{13}C NMR (400 MHz, $CDCl_3$) δ=126.8, 128.5, 128.7, 129.6, 129.7, 130.1, 130.2, 131.2, 131.8, 132.7, 133.1, 135.5, 137.4 (vinylic), 188.5 (CO) ppm; GC–MS m/z (%) 278 ((M+2), 1), 276 (M^+, 2), 243 (35), 207 (7), 241 (100), 105 (77), 77 (79). Anal. Calcd for $C_{15}H_{10}Cl_2O$: C, 65.01; H, 3.64. Found: C, 65.2; H, 3.65.

3.1.8. 3-Chloro-2-(4-methoxyphenyl)-1-(4-methylphenyl)-2-propen-1-one ***2h***. Yellow viscous liquid, yield=95% (2.72 g); IR (KBr, υ_{max})= 3008, 3035, 1666, 1606, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=2.45 (3H, s, CH_3), 3.85 (3H, s, OMe), 6.97 (2H, d, J=8.7 Hz, ArH), 7.22–7.30 (4H, m, ArH), 7.46 (2H, d, J=8.1 Hz, ArH), 6.74 (1H, s, vinylic); ^{13}C NMR (400 MHz, $CDCl_3$) δ=21.4 (methyl), 55.0 (OMe), 96.1, 113.6 (vinylic), 126.0, 129.2, 130.2, 131.2, 133.1, 139.9, 141.2 (vinylic), 154.7, 159.4, 189.9 (carbonyl) ppm; GC–MS m/z (%) 288 ((M+2), 11), 286 (M^+, 31), 271 (17), 251 (13), 222 (17), 178 (16), 179 (12), 119 (37), 135 (100). Anal. Calcd for $C_{17}H_{15}ClO_2$: C, 71.20; H, 5.27. Found: C, 71.28; H, 5.31.

3.1.9. 3-Chloro-2-(4-methoxyphenyl)-1-phenyl-2-propen-1-one ***2i***. Yellow viscous liquid, yield=95% (2.59 g); IR (KBr, υ_{max})=3055, 1666, 1555, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=3.76 (3H, s,

OMe), 3.79 (3H, s, OMe), 6.76 (1H, s, vinylic), 6.85–6.99 (5H, m, vinylic and aromatic), 7.24–7.58 (8H, m, ArH), 7.82 (4H, d, J=8.4 Hz, ArH), 7.99 (2H, d, J=8 Hz, ArH); ^{13}C NMR (400 MHz, $CDCl_3$) δ=54.4 (OMe), 55.3 (OMe), 110.7, 114.4 (vinylic), 114.8 (vinylic), 115.1, 117.6, 118.6, 121.6, 128.5, 128.6, 128.9, 129.4, 129.7, 129.8, 130.2, 133.0, 134.1, 134.8, 137.1, 143.0 (vinylic), 143.2 (vinylic), 159.5, 160.0, 193.8 (CO), 194.7 (CO) ppm; GC–MS m/z (%) 274 ((M+2), 1), 272 (M^+, 4), 237 (18), 209 (23), 105 (100), 77 (56). Anal. Calcd for $C_{16}H_{13}ClO_2$: C, 70.46; H, 4.80. Found: C, 70.52; H, 4.91.

3.2. General procedure for the synthesis of 5,6-diaryl-2-hydroxynicotinonitriles3a–i

Appropriate 3-chloro-1,2-diaryl-2-propen-1-one **2a–i** (5 mmol) was treated with malononitrile (660 mg, 10 mmol) in the presence of ammonium acetate (5 mmol) and acetic acid (2 mL) at 78 °C. The reaction was monitored by TLC. After 8 h the reaction was completed and the reaction mixture was cooled and poured into ice-cold water. The product was extracted with chloroform (25×3), dried over anhydrous sodium sulfate, and the chloroform layer was distilled off to get the crude product, which was purified by column chromatography over 60–120 mesh silica gel using ethyl acetate/hexane (1:9) as eluent.

3.2.1. 2-Hydroxy-5,6-diphenylnicotinonitrile ***3a***. Pale yellow crystals; mp, 182–184 °C; yield, 85% (1.16 g); IR (KBr, υ_{max})=3463, 3452, 3155, 2216, 1645, 1627 cm^{-1}; ^{1}H NMR (400 MHz, DMSO) δ=6.87 (2H, br, NH and OH), 6.97–7.00 (4H, m, ArH), 7.07–7.11 (4H, m, ArH), 7.14–7.17 (6H, m, ArH), 7.21–7.32 (6H, m, ArH), 7.82 (1H, s, pyridine C(4)–H), 7.93 (1H, s, pyridine C(4)–H); ^{1}H NMR (400 MHz, DMSO-d_6, D_2O exchange) 6.98–7.01 (3H, m, ArH), 7.09–7.11 (2H, M, ArH), 7.16–7.17 (5H, m, ArH), 7.24–7.34 (9H, m, ArH), 7.81 (1H, s, pyridine C(4)–H), 7.92 (1H, s, pyridine C(4)–H); ^{13}C NMR (400 MHz, $CDCl_3$) δ=160.3 (CO), 157.7, 150.8, 149.4, 143.5, 138.9, 138.0, 136.4, 131.9, 129.6, 129.6, 129.4, 128.8, 128.8, 128.4, 128.3, 128.2, 128.0, 127.2, 126.8, 116.6, 115.8 (CN), 115.5 (CN), 99.1, 96.4, 89.9 ppm; GC–MS m/z (%) 272 (M^+,12), 271 (74), 270 (100), 253 (14), 226 (21), 135 (25), 140 (9), 121 (14), 94 (11), 77 (13). Anal. Calcd for $C_{18}H_{12}N_2O$: C, 79.39; H, 4.44; N, 10.29. Found: C, 79.45; H, 4.51; N, 10.36. Single crystal data: molecular formula=$C_{18}H_{12}N_2O$, space group=$P2_1/c$, cell lengths=a, 8.2637(4); b, 21.1060(10); c, 9.1661(6), cell angles=α, 90.00; β, 113.039(7); γ, 90.00; cell volume=1471.18, Z, Z'=Z: four Z': 0, R-factor [%]=6.82 and CCDC 996731.

3.2.2. 6-(4-Bromophenyl)-2-hydroxy-5-phenylnicotinonitrile ***3b***. Pale yellow crystals; mp, 204–206 °C; yield=75% (1.32 g); IR (KBr, υ_{max})=3402, 3150, 3050, 2221, 1656 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.74 (1H, s, pyridine C(4)–H), 7.64 (1H, s, pyridine C(4)–H), 7.43 (4H, d, J=10 Hz, ArH), 7.16–7.23 (5H, m, ArH), 7.03 (4H, d, J=10 Hz, ArH), 6.91–6.97 (5H, m, ArH), 5.83 (2H, br, NH and OH); ^{13}C NMR (400 MHz, $CDCl_3$) δ=207.0, 157.7, 150.9, 147.9, 143.7, 138.2, 137.9, 137.6, 135.3, 131.7, 131.6, 131.3, 131.2, 129.4, 129.3, 128.6, 128.3, 127.4, 126.7, 123.4, 116.4, 115.6 (CN), 115.4 (CN), 98.7, 96.7, 90.1 ppm; GC–MS m/z (%) 352 ((M+2), 10), 350 (M^+, 10), 288 (21), 286 (40), 270 (100), 255 (12), 242 (34), 227 (14), 214 (65), 184 (40), 156 (13), 140 (12), 75 (56). Anal. Calcd for $C_{18}H_{11}BrN_2O$: C, 61.56; H, 3.16; N, 7.98. Found: C, 61.63; H, 3.21; N, 8.21.

3.2.3. 2-Hydroxy-6-(4-methoxyphenyl)-5-phenylnicotinonitrile ***3c***. Pale yellow crystals; mp, 178–180 °C; yield=1.24 g (82%); IR (KBr, υ_{max})=3413, 3348, 3249, 3060, 3028, 3002, 2217, 1660, 1602, 1512, 1492, 1452, 1425 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.85 (1H, s, pyridine C(4)–H), 7.87 (1H, s, pyridine C(4)–H), 7.20–7.11 (4H, m, ArH), 7.39 (2H, d, J=8.8 Hz, ArH), 7.46 (2H, d, J=8.8 Hz, ArH), 6.95 (6H, m, ArH), 6.81 (2H, d, J=8.0 Hz, ArH), 6.74 (2H, d, J=8.0 Hz, ArH), 5.08, 5.10 (2H, NH and OH), 3.89 (3H, 3, OMe), 3.79 (3H, s, OMe); ^{13}C NMR (400 MHz, $CDCl_3$) δ=171.5, 164.0, 132.4, 131.1, 129.5, 128.2, 121.6, 113.8 (CN), 113.7 (CN), 55.5 ppm; GC–MS m/z (%) 325 ((M+Na)$^+$, 100), 309 (13), 294 (18), 281 (14), 265 (9), 227 (7), 155 (11), 141 (16), 127 (14), 114 (21), 100 (15). Anal. Calcd for $C_{19}H_{14}N_2O_2$: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.41; H, 4.77; N, 9.50.

3.2.4. 6-(4-Chlorophenyl)-2-hydroxy-5-phenylnicotinonitrile ***3d***. Pale yellow crystals; mp, 200–202 °C; yield=88% (1.35 g); IR (KBr, υ_{max})=3407, 3342, 3232, 2219, 1649, 1591 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.71 (1H, s, pyridine C(4)–H), 7.65 (1H, s, pyridine C(4)–H), 7.25–7.29 (5H, m, ArH), 7.17–7.22 (6H, m, ArH), 7.05–7.11 (4H, m, ArH), 6.91–6.96 (3H, m, ArH), 5.3 (2H, br, OH and NH); ^{13}C NMR (400 MHz, $CDCl_3$) δ=158.9, 157.7, 150.8, 147.9, 143.7, 138.2, 138.0, 137.6, 137.2, 135.1, 135.0, 134.8, 131.8, 131.1, 131.0, 129.4, 129.3, 128.9, 128.7, 128.6, 128.4, 128.2, 127.4, 126.8, 116.5, 115.6 (CN), 115.4 (CN), 98.8, 96.7, 90.1 ppm GC–MS m/z (%) 308 ((M+2)$^+$, 5), 307 (32), 306 (M^+, 47), 305 (100), 304 (98), 269 (53), 253 (8), 252 (16), 226 (7), 214 (7), 134 (47), 121 (17), 107 (29). Anal. Calcd for $C_{18}H_{11}ClN_2O$: C, 70.48. H, 3.61; N, 9.13. Found: C, 70.61; H, 3.71; N, 9.20.

3.2.5. 2-Hydroxy-6-(4-methylphenyl)-5-phenylnicotinonitrile ***3e***. Pale yellow crystals; mp, 178–180 °C; yield=78% (1.12 g); IR (KBr, υ_{max})=3456, 3402, 3350, 3340, 3249, 3056, 3029, 2223, 1656, 1649, 1589, 1546 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.09 (4H, d, J=10 Hz, ArH), 7.72 (1H, s, pyridine C(4)–H), 7.63 (1H, s, pyridine C(4)–H), 7.22–7.15 (6H, m, ArH), 7.02 (4H, d, J=10 Hz, ArH), 6.97–6.93 (4H, m, ArH), 5.24 (2H, br, OH and NH), 2.32 (6H, s, CH_3); ^{13}C NMR (400 MHz, $CDCl_3$) δ=160.0, 157.0, 150.8, 149.6, 143.5, 138.8, 138.1, 138.0, 133.4, 131.9, 129.6, 129.4, 129.0, 128.7, 128.4, 128.2, 127.1, 115.9 (CN), 115.7 (CN), 99.1, 96.1, 89.1, 21.3 ppm; GC–MS m/z (%) 286 (M^+, 14), 285 (80), 284 (100), 269 (13), 252 (12), 240 (6), 227 (4), 207 (46), 141 (15), 128 (8), 101 (3). Anal. Calcd for $C_{19}H_{14}N_2O$: C, 79.70; H, 4.93; N, 9.78. Found: C, 79.87; H, 4.97; N, 9.83.

3.2.6. 5-(2-Chlorophenyl)-6-(4-chlorophenyl)-2-hydroxynicotinonitrile ***3f***. Pale yellow crystals; mp, 178–180 °C; yield=82% (1.40 g); IR (KBr, υ_{max})=3417, 3342, 3245, 3184, 2221, 1649 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.57 (1H, s, pyridine ring hydrogen), 7.34–7.28 (3H, m, pyridine ring hydrogen, ArH), 7.25–7.21 (4H, m, ArH), 7.21–7.16 (2H, m, ArH), 7.14–7.07 (6H, m, ArH), 6.95–6.91 (2H, m, ArH), 5.35 (2H, br, OH and NH); ^{13}C NMR (400 MHz, $CDCl_3$) δ=162.1, 161.8, 152.1, 145.7, 140.7, 140.1, 139.5, 135.9, 134.8, 133.2, 132.6, 132.5, 132.0, 130.4, 130.0, 129.7, 129.0, 128.8, 128.5, 128.2, 125.4, 119.1, 116.1, 114.3 (CN), 114.8 (CN), 102.9, 96.8 ppm; GC–MS m/z (%) 344 ((M+4)$^+$, 14), 342 ((M+2)$^+$, 7), 340 (M^+, 45), 339 (100), 316 (20), 325 (21), 324 (5), 306 (18), 249 (41), 230 (6), 168 (7), 112 (21), 76 (24). Anal. Calcd for $C_{18}H_{12}Cl_2N_2O$: C, 63.36; H, 2.95; N, 8.21. Found: C, 63.39; H, 3.03; N, 8.23.

3.2.7. 5-(2-Chlorophenyl)-2-hydroxy-6-phenylnicotinonitrile ***3g***. Pale yellow crystals; mp, 132–134 °C; yield=77% (1.18 g); IR (KBr, υ_{max})=3417, 3340, 3244, 3056, 2219, 1650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.55 (2H, br s, pyridine C4–H), 7.31–7.27 (2H, m, ArH), 7.18–7.13 (2H, m, ArH), 7.09–7.02 (12H, m, ArH), 6.94–6.90 (2H, m, ArH), 5.35 (2H, br, OH and NH); ^{13}C NMR (400 MHz, $CDCl_3$) δ=151.3, 150.4, 138.8, 138.5, 136.8, 133.5, 133.0, 132.0, 129.4, 129.1, 129.0, 128.8, 126.4, 115.7 (CN), 115.6 (CN), 98.7, 95.7 ppm; GC–MS m/z (%) 308 ((M+2)$^+$, 3), 306 (M^+, 37), 305 (68), 304 (53), 281 (22), 270 (34), 253 (12), 242 (19), 226 (4), 207 (48), 191 (14), 174 (6), 147 (6), 134 (13), 121 (15), 107 (14), 94 (6), 83 (100). Anal. Calcd for $C_{18}H_{12}N_2O$: C, 70.48; H, 3.61; N, 9.13. Found: C, 70.56; H, 3.73; N, 9.22.

3.2.8. 2-Hydroxy-5-(4-methoxyphenyl)-6-(4-methylphenyl)nicotinonitrile ***3h***. Pale yellow crystals; mp, 188–190 °C; yield=71%

(1.12 g); IR (KBr, υ_{max})=3481, 3363, 3234, 3014, 2217, 1631 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=7.60 (2H, br s, pyridine ring hydrogen), 7.11 (4H, m, ArH), 7.03 (4H, d, J=10 Hz, ArH), 6.89–6.83 (4H, m, ArH), 6.70 (4H, d, J=10 Hz, ArH), 5.22 (2H, br, OH and NH), 3.75 (6H, s, OMe), 2.33 (6H, s, CH_3); ^{13}C NMR (400 MHz, $CDCl_3$) δ=170.5, 164, 155.7, 150.6, 149.4, 138.7, 137.9, 133.6, 132.3, 131.6, 130.5, 130.4, 130.2, 129.4, 129.2, 129.1, 127.9, 126.5, 122.8, 121.6, 117.5, 116.0, 115.8, 114.8 (CN), 113.7 (CN), 113.6, 99.1, 96.1, 30.9, 21.5, 21.3 ppm; GC–MS m/z (%) 316 (M^+, 20), 315 (100), 314 (63), 300 (17), 285 (4), 271 (12), 257 (9), 256 (12), 239 (3), 227 (3), 207 (3), 170 (4), 150 (16), 135 (16), 128 (13), 101 (6), 88 (5). Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.99; H, 5.13; N, 8.93.

3.2.9. 2-Hydroxy-5-(4-methoxyphenyl)-6-phenylnicotinonitrile ***3i***. Pale yellow crystals; mp, 204–206 °C; yield=90% (1.36 g); IR (KBr, υ_{max})=3479, 3296, 3186, 2212, 1620 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=3.74 (3H, s, OMe), 3.79 (3H, s, OMe), 5.2 (2H, br, NH and OH), 6.72–6.68 (2H, m, ArH), 6.80–6.75 (2H, m, ArH), 6.86–6.83 (2H, m, ArH), 7.01–6.97 (2H, m, ArH), 7.16–7.12 (2H, m, ArH), 7.34–7.21 (8H, m, ArH), 7.63 (1H, s, pyridine ring hydrogen), 7.72 (1H, s, pyridine hydrogen); ^{13}C NMR (400 MHz, $CDCl_3$) δ=160.2 (CO), 158.8, 157.5, 150.5, 149.2, 144.3, 143.4, 142.0, 139.0, 138.0, 136.6, 131.6, 130.5, 130.5, 130.2, 129.6, 129.5, 128.7, 128.7, 128.3, 128.0, 126.5, 116.7, 115.9, 115.5, 113.9 (CN), 113.6 (CN), 104.2, 99.1, 96.4, 89.8, 77.3, 77.0, 76.7, 67.6, 61.2, 55.2, 30.9 ppm; GC–MS m/z (%) 302 (M^+, 20), 301 (100), 300 (60), 287 (3), 286 (13), 285 (5), 270 (8), 214 (8), 143 (14), 128 (23), 89 (4), 76 (4). Anal. Calcd for $C_{19}H_{14}N_2O_2$: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.53; H, 4.73; N, 9.33; Single crystal data: molecular formula=$C_{19}H_{14}N_2O_2$, space group=$P2_1/c$, cell lengths=a, 12.0731(14); b, 14.1000(17); c, 9.8157(12), cell angles=α, 90.00; β, 108.797(7); γ, 90.00; cell volume=1581.82, Z, Z'=Z: 4, Z': 0, R-factor [%]=5.91 and CCDC 791271.

3.3. General procedure for the synthesis of 2-chloro-5,6-diarylnicotinonitriles 7a–e

The Vilsmeier–Haack reagent was prepared by mixing DMF (12 ml, 150 mmol) and $POCl_3$ (1.4 ml, 15 mmol) at 0 °C, followed by stirring at room temperature for 15 min. 3-Oxo-2,3-diarylpropanal (10 mmol) was added and the reaction mixture was stirred at room temperature for 20 h. Malononitrile (2 g, 30 mmol) or cyanoacetamide (2.5 g, 30 mmol) was added to this mixture, the temperature was raised to 70 °C, stirred for another 3 h, and poured into ice-cold saturated potassium carbonate solution (120 ml). The crude product was extracted with ethyl acetate (3×50 ml). The combined organic layer was distilled off to get the crude product, which was purified by column chromatography over silica gel (60–120 mesh) using ethyl acetate/hexane (2:98) as eluent.

3.3.1. 2-Chloro-5,6-diphenylnicotinonitrile ***7a***. Pale yellow crystals; yield, 55% (1.60 g, Method A) and 70% (2.04 g, Method B); mp, 168–170 °C; IR (KBr, υ_{max})=3045, 3031, 2221, 1566, 1548, 765, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=7.60–7.45 (9H, m, ArH), 7.35–7.28 (2H, m, ArH); ^{13}C NMR (400 MHz, $CDCl_3$) δ=156.4, 152, 136.2, 136.0, 134.6, 131.7, 130.0, 129.9, 129.9, 129.3, 129.0, 114.4 (CN), 109.8, 84.9 ppm; GC–MS m/z (%) 292 (($M+2$)$^+$, 7), 290 (M^+, 22), 255 (100), 227 (35), 212 (12), 201 (10), 189 (8), 149 (15), 127 (7), 113 (28), 99 (32), 77 (18). Anal. Calcd for $C_{18}H_{11}ClN_2$: C,74.38; H, 3.84; N, 9.68. Found: C, 74.5; H, 4.1; N, 9.80.

3.3.2. 2-Chloro-6-(4-chlorophenyl)-5-phenylnicotinonitrile ***7b***. Pale yellow crystals; yield, 35% (1.14 g, Method A) and 77% (2.50 g, Method B); mp, 120–122 °C; IR (KBr, υ_{max})=3168, 3080, 2219, 1641, 1554, 1535, 700, 639 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=7.95–7.85 (3H, m, ArH), 7.44–7.2 (7H, m, ArH) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ=143.4, 139.5, 135.0, 129.5, 129.5, 128.9, 128.9, 128.7, 128.7, 128.1, 127.3, 126.8 ppm; GC–MS m/z (%) 326 (($M+2$), 16), 324 (M^+, 39), 323 (25), 299 (13), 297 (13), 281 (13), 278 (7), 253 (6), 245 (37), 218 (11), 207 (45), 190 (15), 178 (7), 164 (3), 139 (15), 113 (13), 103 (17), 77 (100). Anal. Calcd for $C_{18}H_{10}Cl_2N_2$: C, 66.48; H, 3.10; N, 8.61. Found: C, 66.53; H, 3.2; N, 8.68.

3.3.3. 2-Chloro-6-(4-methoxyphenyl)-5-phenylnicotinonitrile ***7c***. Pale yellow crystals; yield, 45% (1.44 g, Method A) and 80% (2.56 g, Method B); mp, 200–202 °C; IR (KBr, υ_{max})=2991, 2836, 2215, 1599, 1553, 709 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=7.67–7.50 (4H, m, ArH), 7.46 (2H, d, J=8.4 Hz, ArH), 7.4–7.2 (m, 2H, ArH), 7.01 (2H, d, J=8.4 Hz, ArH), 3.92 (3H, s, OMe); ^{13}C NMR (400 MHz, $CDCl_3$) δ=162.6, 157.1, 152.3, 135.1, 134.8, 132.2, 130.0, 129.7, 129.2, 128.5, 114.7, 114.4 (CN), 110.1, 83.8, 55.7 ppm; GC–MS m/z (%) 322 (($M+2$), 15), 320 (M^+, 45), 305 (2), 294 (11), 285 (100), 270 (20), 253 (5), 242 (48), 227 (7), 214 (26), 189 (7), 165 (12), 158 (9), 139 (7), 121 (6), 113 (5), 93 (6), 88 (6), 77 (15). Anal. Calcd data for $C_{19}H_{13}ClN_2O$: C, 71.14; H, 4.08; N, 8.73. Found: C, 71.19; H, 4.10; N, 8.78.

3.3.4. 2-Chloro-6-(4-bromophenyl)-5-phenylnicotinonitrile ***7d***. Pale yellow crystals; yield, 36% (1.33 g, Method A) and 90% (3.33 g, Method B); mp, 178–180 °C; IR (KBr, υ_{max})=3085, 3064, 3028, 2221, 1677, 1583, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=7.68 (2H, d, J=8.4 Hz, ArH), 7.54–7.52 (3H, m, ArH), 7.49 (1H, s, pyridine ring hydrogen), 7.37 (2H, d, J=8.4 Hz, ArH), 7.31–7.28 (2H, m, ArH); ^{13}C NMR (400 MHz, $CDCl_3$) δ=155.8, 150.2, 136.3, 135.0, 134.3, 132.4, 131.4, 130.1, 129.8, 129.3, 126.5, 114.2 (CN), 109.6, 85.6 ppm; GC–MS m/z (%) 372 (($M+4$), 15), 370 (($M+2$), 46), 368 (M^+, 38), 368 (12), 336 (16), 335 (30), 333 (17), 332 (21), 291 (13), 289 (39), 255 (27), 254 (100), 253 (54), 227 (57), 201 (11), 176 (14), 175 (7), 151 (13), 127 (77), 113 (77), 100 (89), 88 (20), 77 (35). Anal. Calcd data for $C_{18}H_{10}BrClN_2$: C, 58.49; H, 2.73; N, 7.58. Found: C, 58.50; H, 2.80; N, 7.60.

3.3.5. 2-Chloro-5-(4-methoxyphenyl)-6-(4-methylphenyl)nicotinonitrile ***7e***. Pale yellow crystals; yield, 12% (0.40 g, Method A) and 67% (2.24 g, Method B); mp, 172–174 °C; IR (KBr, υ_{max})=3033, 3003, 2218, 1608, 1546, 738, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=7.56 (1H, s, pyridine ring hydrogen), 7.37 (2H, d, J=8.4 Hz, ArH), 7.31 (2H, d, J=8.4 Hz, ArH), 7.21 (2H, d, J=8 Hz, ArH), 7.02 (2H, d, J=8 Hz, ArH), 3.87 (3H, s, OMe), 2.46 (3H, s, $-CH_3$); ^{13}C NMR (400 MHz, $CDCl_3$) δ=160.7, 157.6, 152.0, 142.6, 135.2, 133.6, 131.3, 130.1, 129.7, 127.1, 114.6 (CN), 110.2, 84.4, 55.3, 21.6 ppm; GC–MS m/z (%) 336 (($M+2$), 19), 334 (M^+,100), 319 (21), 299 (92), 284 (29), 278 (70), 269 (37), 256 (65), 241 (10), 226 (61), 207 (68), 191 (13), 189 (11), 163 (42), 152 (30), 128 (26), 119 (34), 99 (22), 91 (31). Anal. Calcd for $C_{20}H_{15}ClN_2O$: C, 71.75; H, 4.52; N, 8.37. Found: C, 71.78; H, 4.58; N, 8.41.

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Supplementary data

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References and notes

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