Monatsh Chem (2011) 142:261–269
DOI 10.1007/s00706-011-0453-2

ORIGINAL PAPER

Synthesis of nicotinonitrile derivatives and study of their photophysical properties

Raghunath B. Toche · Muddassar A. Kazi · Prashant S. Nikam · Dinesh C. Bhavsar

Received: 12 April 2010 / Accepted: 31 January 2011 / Published online: 11 March 2011

Abstract A convenient route was developed for the synthesis of novel nicotinonitrile derivatives by a three-component Dimroth reaction of chalcones, malononitrile, and secondary heterocyclic amines or sodium alcoholate. Nicotinonitrile derivatives are obtained in fair to good yields. The structures of all new compounds were established by spectroscopic characteristics and their photophysical properties were studied.

Keywords Quinolone chalcone · Nicotinonitrile · Absorption and emission properties · Substituent effect

Introduction

Pyridine is a very common system in naturally occurring heterocyles [1–5]. Several methods were reported for synthesis of pyridine derivatives [6–9], including condensation of α,β-unsaturated ketones with malononitrile in the presence of ammonium acetate [10] and condensation of β-aminoenones with malononitrile [11]. Synthesis and photochemical properties of 2-aryl- and 2,6-diarylpyridines have also been reported [12]. 1,6-Naphthyridine [13] and terphenyl [14] systems derived from α,β-unsaturated ketones and malononitrile are also known. Pyridines have a wide range of biological activities, e.g., they have been used as herbicides [15], to enrich cereals [16], and to regulate blood cholesterol levels [17]. On the other hand, polysubstituted pyridines are also used as non-linear optical materials [18], electrical materials [19], in metal–ligand chemistry [20], as fluorescent liquid crystals [21], and for the preparation of fluorescent inks and security papers [22]. Therefore, the exploration of simple and convenient syntheses is essential to expand the scope and applications of pyridines which have photophysical properties. In our earlier communication, we reported the effects of aryl substituents in pyridine-3-carbonitriles on their photophysical properties [23]. Herein, we report the effect of C4-aryl substituents of pyridines and also prove that C2 substituents have no predominant effect on absorption and emission properties of nicotinonitriles.

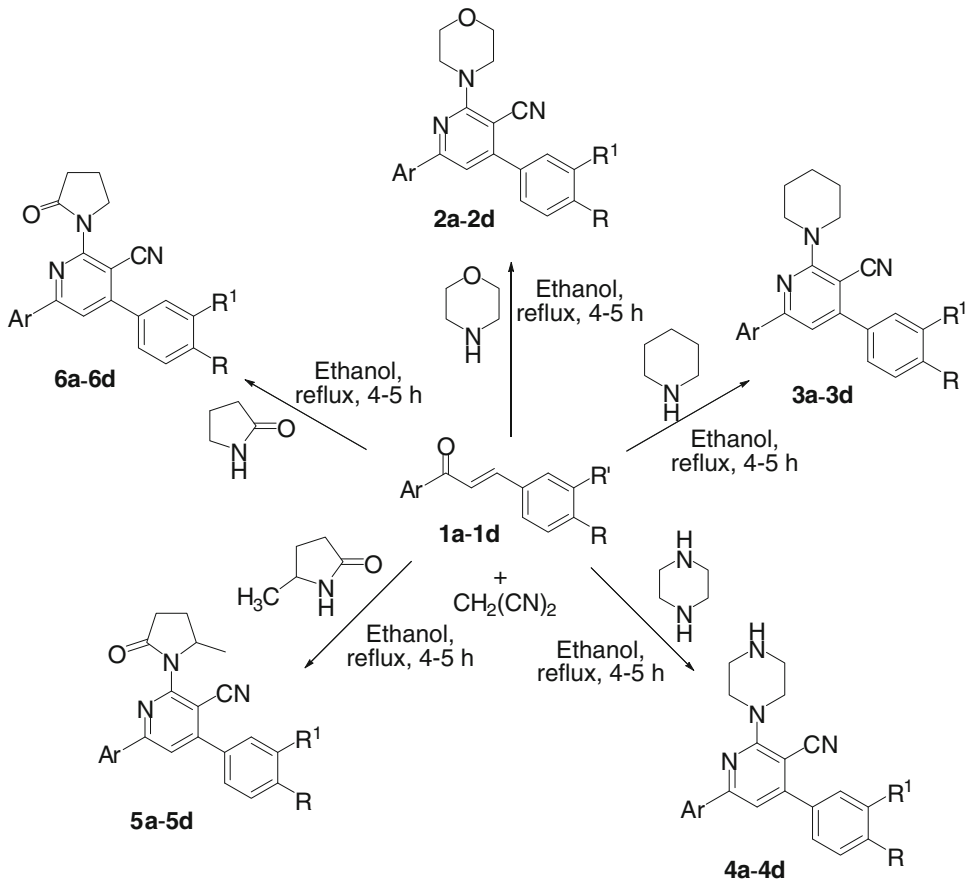
Results and discussion

The required chalcones **1a**–**1d** were prepared by condensation of 3-acetyl-4-hydroxyquinolone and the corresponding aromatic aldehydes [24]. Novel nicotinonitrile derivatives were synthesized by a Dimroth rearrangement of chalcones **1** with nucleophilic reagents such as secondary heterocyclic amines and sodium alcoholate. Thus, condensation of chalcones **1a**–**1d** with 1 equivalent of malononitrile and 2 equivalents of piperidine, piperazine, or morpholine in dry alcohol afforded nicotinonitrile derivatives **2a**–**4d** in 60–75% yield (Scheme 1). The obtained new compounds were well characterized by analytical and spectroscopic methods.

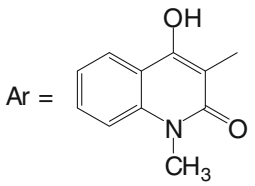
Analogously, reactions of chalcones **1** with malononitrile and pyrrolidone or 5-methylpyrrolidone afforded 2-pyrrolidone nicotinonitriles **5a**–**6d** in 66–70% yield. These compounds showed low carbonyl stretching

R. B. Toche (✉) · M. A. Kazi · P. S. Nikam · D. C. Bhavsar
Department of Chemistry, Organic Chemistry Research Center, K.T.H.M. College, University of Pune, Gangapur Road, Nashik 422002, Maharashtra, India
e-mail: raghunath_toche@rediffmail.com

Scheme 1



2-6	R	R^1
a	Cl	H
b	Br	H
c	OMe	H
d	OMe	OMe



frequency due to hydrogen bonding between the carbonyl (CO) of the pyrrolidone and the hydroxyl group of the quinolone ring. For instance, compound **5c** showed a broad IR stretching frequency at 3,119 cm^{-1} for the hydroxyl group, a strong stretching frequency at 2,216 cm^{-1} for the nitrile group, and two amide carbonyls at 1,667 and of 1,654 cm^{-1}. This showed that reaction of pyrrolidone occurred at the nitrogen atom instead of the oxygen.

Another series of reactions of chalcones **1a**–**1c** with 1 equivalent of malononitrile in the presence of sodium alcoholate furnished 2-alkoxynicotinonitriles **7a**–**11c** in 48–65% yield by a Dimroth reaction (Scheme 2). The alkoxy groups at the C2 position originate from the sodium alcoholate; the mechanism is discussed in Fig. 1.

All new compounds obtained were well characterized by analytical and spectroscopic methods.

Photophysical properties

The UV absorption and emission of compounds **2a**–**6d** and **7a**–**11c** were studied in $CHCl_3$. Fluorescence quantum yields (Φ_F) were determined by standard literature procedures [25, 26] using quinine sulfate as the reference standard. The compounds **2a**–**6d** showed low λ_{max} of absorption and emission (blue shift), whereas compounds **7a**–**11c** showed higher absorption and emission maxima (red shift). The strong π-donor C_4–OCH_3 auxochrome on the phenyl ring (B-ring) remarkably increases absorption and emission maxima, whereas C2-alkoxy groups in nicotinonitrile do not affect the photophysical properties to a large extent (Table 2). For instance, compound **9c** having a C_2–$OCH_2CH_2CH_3$ group on the nicotinonitrile moiety and a C_4–OMe group on the phenyl ring (B-ring) showed an

Scheme 2

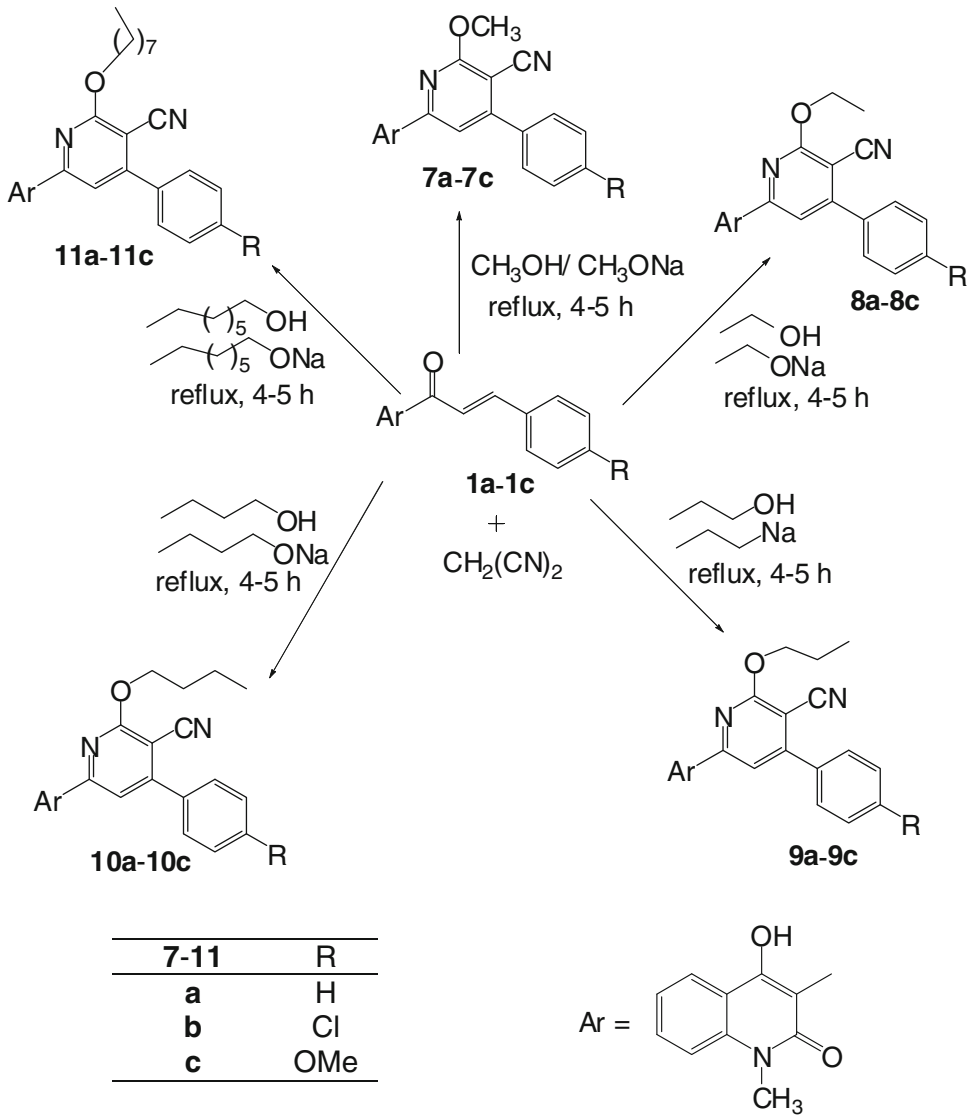


Fig. 1 Mechanism of nicotinonitrile formation

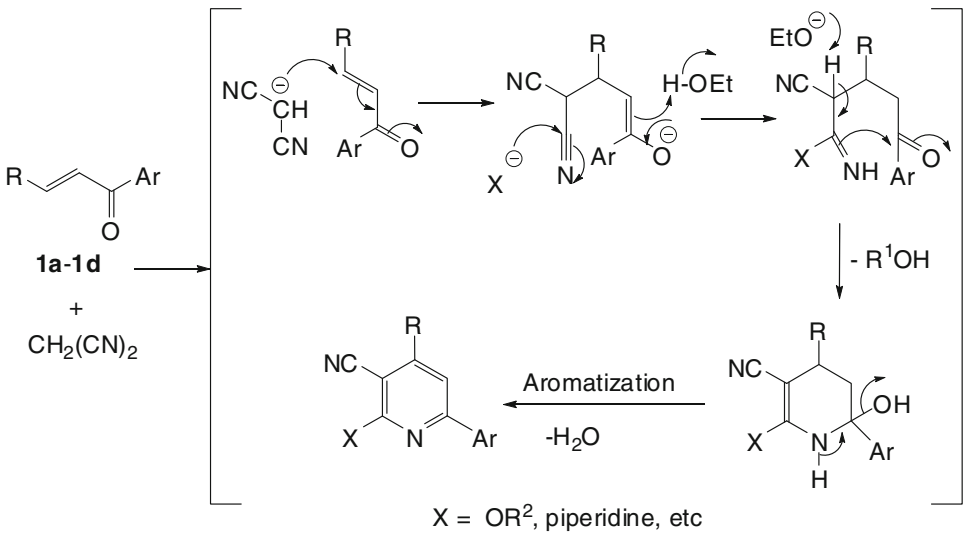


Table 1 Photophysical data for electronic absorption (λ_{abs}) and emission (λ_{em}) of nicotinonitriles **2–6**

2–6	R	R^1	λ_{abs} ($CHCl_3$) (nm)	λ_{em} ($CHCl_3$) (nm)	Φ_F
2a	H	H	315	378	0.156
2b	Cl	H	316	381	0.159
2c	OMe	H	324	386	0.162
2d	OMe	OMe	330	392	**0.164**
3a	H	H	287	366	0.155
3b	Cl	H	299	369	0.160
3c	OMe	H	302	382	0.164
3d	OMe	OMe	331	391	**0.168**
4a	H	H	322	388	0.160
4b	Cl	H	331	390	0.165
4c	OMe	H	338	393	0.168
4d	OMe	OMe	340	396	**0.170**
5a	H	H	314	371	0.157
5b	Cl	H	319	376	0.161
5c	OMe	H	327	381	0.165
5d	OMe	OMe	336	391	**0.171**
6a	H	H	314	371	0.158
6b	Cl	H	323	375	0.160
6c	OMe	H	331	382	0.166
6d	OMe	OMe	337	393	**0.172**

Table 2 Photophysical data for electronic absorption (λ_{abs}) and emission (λ_{em}) of C2-alkoxy nicotinonitriles **7–11**

7–11	R	C2	λ_{abs} ($CHCl_3$) (nm)	λ_{em} ($CHCl_3$) (nm)	Φ_F
7a	H	CH_3	370	455	0.184
7b	Cl	CH_3	362	467	0.188
7c	OMe	CH_3	391	477	**0.209**
8a	H	CH_2CH_3	375	460	0.186
8b	Cl	CH_2CH_3	370	468	0.191
8c	OMe	CH_2CH_3	390	482	**0.216**
9a	H	$(CH_2)_2CH_3$	376	461	0.185
9b	Cl	$(CH_2)_2CH_3$	372	469	0.189
9c	OMe	$(CH_2)_2CH_3$	391	486	**0.218**
10a	H	$(CH_2)_3CH_3$	376	462	0.186
10b	Cl	$(CH_2)_3CH_3$	373	471	0.190
10c	OMe	$(CH_2)_3CH_3$	390	484	**0.217**
11a	H	$(CH_2)_7CH_3$	377	462	0.185
11b	Cl	$(CH_2)_7CH_3$	372	472	0.190
11c	OMe	$(CH_2)_7CH_3$	391	481	**0.216**

absorption maximum of 391 nm, emission maximum of 486 nm, and a quantum yield of 0.218. Similarly, compound **10c** having a C_2–$OCH_2CH_2CH_2CH_3$ group on the nicotinonitrile moiety and a strong π-electron-donor C4–OMe group on the phenyl ring (B-ring) showed an absorption maxima of 390 nm, an emission maximum at 484 nm, and the quantum yield is nearly 0.217. These results indicate that C2-alkoxy substituents have no remarkable effect on photophysical properties, whereas compounds **5a–6d** having C2-amide and C2-tertiary amine groups showed comparatively lower absorption and emission properties as compared to compounds **9a–13c** (Tables 1, 2). These effects may be due to the higher charge transfer ability of oxygen versus nitrogen.

Conclusion

Differently substituted C2-alkoxy, amides, amines, and C4-aryl nicotinonitriles were obtained in fair to good yields by a one-pot Dimroth rearrangement on 4-hydroxyquinolone chalcones, malononitrile, and various nucleophiles. The photophysical properties of these new nicotinonitriles derivatives were dependent upon the C4-aryl substituents and independent of C2-alkoxy or C2-amide or C2-amine substituents on the pyridine ring. Efficient photophysical properties make nicotinonitrile derivatives promising materials and useful in organic light emitting diode (OLEDs) [27] and optoelectronic applications [28, 29].

Experimental

Common reagent-grade chemicals were either commercially available and used without further purification or prepared by standard literature procedures. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.2-mm silica gel 60 F_{254} (Merck) plates using UV light (254 and 366 nm) for detection. Melting points were determined on a Gallenkamp melting point apparatus (model MFB595) in open capillary tubes. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer (300 and 75 MHz). Chemical shifts are reported in ppm from internal tetramethylsilane standard. The solvents for NMR spectra were $CDCl_3$ and DMSO-d_6 and "s" in ^{13}C spectra indicates very *strong* signals. Infrared spectra were recorded on a Shimadzu FTIR-408 instrument in potassium bromide (KBr) pellets. Elemental analyses were performed on a Hosli CH-Analyzer and are within $\pm$0.3% of the theoretical values. High resolution mass spectra were obtained with a Mat 112 Varian Mat Bremen (70 eV) mass spectrometer. Solutions were concentrated on a rotary evaporator under reduced pressure. UV/Vis spectra were recorded using a Shimadzu UV/Vis scanning spectrophotometer UV-1601 PC in a concentration of

0.01 mg/cm^3 in chloroform. Excitation and emission spectra were recorded using a Shimadzu RF-5301 PC spectrofluorophotometer (150-W Xe lamp, 6 selectable slits: 1.5, 3, 5, 10, 15, 20 nm, R452-01 photomultiplier; monochromator: ion-blazed holographic concave grating *F*/2.5); concentration 0.001 mg/cm^3 in chloroform. Quantum yields were determined from relative area of emission signals of the unknown with standard quinine sulfate (reference standard) at pH 1.

General procedure for the synthesis of nicotinonitriles ***2a–6d***

A mixture of chalcone **1a**–**1d** (10 mmol), 0.66 g malononitrile (10 mmol), and secondary heterocyclic amine (10 mmol, piperidine, piperazine, morpholine, pyrrolidone, or 5-methylpyrrolidone) was refluxed in ethanol for 4–5 h (TLC check, *n*-hexane/ethyl acetate 8:2). After cooling to room temperature, the solvent was removed under reduced pressure. The residue was stirred in 100 cm^3 ice-cold water and the product was extracted with 10 cm^3 chloroform. The organic layer was dried over sodium sulfate and evaporated under reduced pressure. The obtained solid product was purified by column chromatography (silica gel 60–120 mesh) using *n*-hexane and ethyl acetate (8:2 v/v) as eluent to afford compounds **2a**–**6d** as pale yellow solids in 60–75% yield.

4-(4-Chlorophenyl)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-(morpholin-4-yl)pyridine-3-carbonitrile (**2a**, $C_{26}H_{21}ClN_4O_3$)
Yield 2.15 g (65%); m.p.: 188–190 °C; IR (KBr): $\bar{\nu}$ = 3,466 (OH), 2,235 (CN), 1,666 (CO), 1,548 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.40 (t, 4H, J = 6.7 Hz, 2 × CH_2), 3.82 (s, 3H, NCH_3), 4.65 (t, 4H, J = 6.7 Hz, 2 × CH_2), 6.85–7.25 (m, 4H, quinolone), 7.45 (d, 2H, J = 8.1 Hz, ArH), 7.72 (d, 2H, J = 8.1 Hz, ArH), 8.94 (s, 1H, pyridine), 14.65 (bs, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 23.2, 25.4, 44.6, 46.4, 56.5, 110.4, 112.4, 114.4 (s), 115.7, 116.4, 117.5, 118.7, 120.4 (s), 124.5, 130.4, 132.8, 134.9, 136.4 (s), 142.4 (s), 154.4, 164.5 ppm; MS: *m*/*z* (%) = 474 (M + 2, 36.9), 472 (M$^+$, 100).

4-(4-Bromophenyl)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-(morpholin-4-yl)pyridine-3-carbonitrile (**2b**, $C_{26}H_{21}BrN_4O_3$)
Yield 1.90 g (66%); m.p.: 214–216 °C; IR (KBr): $\bar{\nu}$ = 3,097 (OH), 2,941 (CH), 2,252 (CN), 1,677 (C=O), 1,612, 1,577, 1,276 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.88–1.90 (t, 4H, J = 6.7 Hz, 2 × CH_2), 3.56 (s, 3H, NCH_3), 3.94–4.00 (t, 4H, J = 6.7 Hz, 2 × CH_2), 6.95–7.30 (m, 4H, quinolone), 7.60 (d, 2H, J = 8.4 Hz, ArH), 7.80 (d, 2H, J = 8.4 Hz, ArH), 9.01 (s, 1H, pyridine), 13.50 (bs, 1H, OH) ppm.

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-4-(4-methoxyphenyl)-2-(morpholin-4-yl)pyridine-3-carbonitrile (**2c**, $C_{27}H_{24}N_4O_4$)
Yield 2.60 g (71%); m.p.: 170–172 °C; IR (KBr): $\bar{\nu}$ = 3,510 (OH), 2,224 (CN), 1,667, 1,654 (C=O), 1,566 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.02–2.14 (t, 4H, J = 6.7 Hz, 2 × CH_2), 4.08 (s, 3H, NCH_3), 4.15 (s, 3H, OCH_3), 4.20–4.28 (t, 4H, J = 6.7 Hz, 2 × CH_2), 7.02–7.45 (m, 4H, quinolone), 7.75 (d, 2H, J = 8.4 Hz, ArH), 8.10 (d, 2H, J = 8.4 Hz, ArH), 9.15 (s, 1H, pyridine), 14.70 (bs, 1H, OH) ppm.

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-4-(3,4-dimethoxyphenyl)-2-(morpholin-4-yl)pyridine-3-carbonitrile (**2d**, $C_{28}H_{26}N_4O_5$)
Yield 2.44 g (68%); m.p.: 182–183 °C; IR (KBr): $\bar{\nu}$ = 3,482 (OH), 2,210 (CN), 1,690 (C=O), 1,570 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.90 (t, 4H, J = 6.7 Hz, 2 × CH_2), 3.87 (s, 3H, NCH_3), 4.00–4.15 (s, 6H, 2 × OCH_3), 4.18–4.22 (t, 4H, J = 6.7 Hz, 2 × CH_2), 7.29–7.36 (m, 4H, quinolone), 7.68–7.89 (m, 3H, ArH), 8.88 (s, 1H, pyridine), 10.10 (bs, 1H, OH) ppm.

4-(4-Chlorophenyl)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-(piperidin-1-yl)pyridine-3-carbonitrile (**3a**, $C_{27}H_{23}ClN_4O_2$)
Yield 2.12 g (68%); m.p.: 211–212 °C; IR (KBr): $\bar{\nu}$ = 3,510 (OH), 2,937 (CH), 2,211 (CN), 1630 (CO), 1,595, 1,566, 1,235 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.34–3.47 (t, 10H, J = 6.7 Hz, 5 × CH_2), 3.66 (s, 3H, NCH_3), 7.24–7.51 (m, 4H, quinolone), 7.74 (d, 2H, J = 8.1 Hz, ArH), 8.11 (d, 2H, J = 8.1 Hz, ArH), 8.90 (s, 1H, pyridine), 11.42 (bs, 1H, OH) ppm; MS: *m*/*z* (%) = 472 (M + 2, 36), 470 (M$^+$, 100), 395 (10).

4-(4-Bromophenyl)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-(piperidin-1-yl)pyridine-3-carbonitrile (**3b**, $C_{27}H_{23}BrN_4O_2$)
Yield 2.15 g (71%); m.p.: 177–179 °C; IR (KBr): $\bar{\nu}$ = 3,490 (OH), 2,220 (CN), 1,655 (CO), 1,535 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.02–2.25 (t, 6H, J = 7.1 Hz, 3 × CH_2), 3.65 (s, 3H, NCH_3), 4.02–4.16 (t, 4H, J = 6.8 Hz, 2 × CH_2), 6.89–7.25 (m, 4H, quinolone), 7.45 (d, 2H, J = 8.1 Hz, ArH), 7.89 (d, 2H, J = 8.1 Hz, ArH), 8.60 (s, 1H, pyridine), 14.16 (bs, 1H, OH) ppm.

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-4-(4-methoxyphenyl)-2-(piperidin-1-yl)pyridine-3-carbonitrile (**3c**, $C_{28}H_{26}N_4O_3$)
Yield 2.02 g (70%); m.p.: 208–209 °C; IR (KBr): $\bar{\nu}$ = 3,488 (OH), 2,236 (CN), 1,665 (CO), 1,535 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.66–1.78 (t, 6H,

$J = 6.6$ Hz, 3 × CH_2), 3.45 (s, 3H, NCH_3), 3.70 (s, 3H, OCH_3), 3.85–3.90 (t, 4H, $J = 6.4$ Hz, 2 × CH_2), 6.89–7.25 (m, 4H, quinolone), 7.50 (d, 2H, $J = 7.9$ Hz, ArH), 7.96 (d, 2H, $J = 7.9$ Hz, ArH), 8.80 (s, 1H, pyridine), 12.60 (bs, 1H, OH) ppm.

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-4-(3,4-dimethoxyphenyl)-2-(piperidin-1-yl)pyridine-3-carbonitrile (**3d**, $C_{29}H_{28}N_4O_4$)
Yield 1.90 g (66%); m.p.: 202–203 °C; IR (KBr): $\bar{\nu} = 3{,}404$ (OH), 2,924 (CH), 2,204 (CN), 1,660 (CO), 1,599, 1,575, 1,238 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 2.10$–2.15 (t, 6H, $J = 6.7$ Hz, 3 × CH_2), 3.25–3.64 (t, 2H, 2 × CH_2), 3.58 (s, 3H, NCH_3), 3.64–3.85 (s, 6H, 2 × OCH_3), 6.80–7.20 (m, 4H, quinolone), 7.53 (d, 1H, $J = 8.3$ Hz, ArH), 7.45 (dd, $J = 8.3$, 2.1 Hz, 1H, ArH), 7.80 (d, $J = 2.1$ Hz, 1H, ArH), 8.22 (s, 1H, pyridine) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 29.0$, 36.2, 40.1, 55.5, 55.5, 58.4, 109.0, 111.1, 111.7, 111.9, 112.1, 112.7, 114.9, 119.3, 119.8, 122.1, 122.1, 131.5, 136.8, 138.5, 147.7, 148.3, 149.9, 162.4 ppm; MS: *m/z* (%) = 497 (M + 1, 100), 456 (22), 395 (10).

4-(4-Chlorophenyl)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-(piperazin-1-yl)pyridine-3-carbonitrile (**4a**, $C_{26}H_{22}ClN_5O_2$)
Yield 1.66 g (60%); m.p.: 186–188 °C; IR (KBr): $\bar{\nu} = 3{,}480$ (OH), 2,240 (CN), 1,680 (CO), 1,540 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 2.04$–3.10 (t, 8H, $J = 6.6$ Hz, 4 × CH_2), 3.88 (s, 3H, NCH_3), 6.88–7.22 (m, 4H, quinolone), 7.35 (d, 2H, $J = 8.1$ Hz, ArH), 8.12 (d, 2H, $J = 8.1$ Hz, ArH), 8.44 (s, 1H, pyridine), 12.15 (bs, 1H, OH) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.2$, 21.4, 30.2, 30.7, 55.4, 99.8, 128.2 (s), 132.8 (s), 138.2, 141.4, 148.2, 149.4, 150.2, 157.4, 160.1, 1700.4 ppm; MS: *m/z* (%) = 473 (M + 2), 471 (M^+, 100).

4-(4-Bromophenyl)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-(piperazin-1-yl)pyridine-3-carbonitrile (**4b**, $C_{26}H_{22}BrN_5O_2$)
Yield 2.02 g (68%); m.p.: 212–213 °C; IR (KBr): $\bar{\nu} = 3{,}501$ (OH), 2,218 (CN), 1,674 (CO), 1,544 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 1.90$–2.90 (t, 8H, $J = 6.1$ Hz, 4 × CH_2), 3.66 (s, 3H, NCH_3), 6.90–7.35 (m, 4H, quinolone), 7.45 (d, 2H, $J = 8.1$ Hz, ArH), 8.20 (d, 2H, $J = 8.1$ Hz, ArH), 8.60 (s, 1H, pyridine), 12.60 (bs, 1H, OH) ppm.

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-4-(4-methoxyphenyl)-2-(piperazin-1-yl)pyridine-3-carbonitrile (**4c**, $C_{27}H_{25}N_5O_3$)
Yield 2.12 g (71%); m.p.: 222–223 °C; IR (KBr): $\bar{\nu} = 3{,}404$ (OH), 2,924 (CH), 2,204 (CN), 1,660 (CO), 1,599, 1,575, 1,238 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 1.80$–2.40 (t, 8H, $J = 6.7$ Hz, 4 × CH_2), 3.45 (s, 3H, NCH_3), 4.10 (s, 3H, OCH_3), 7.02–7.44 (m, 4H, quinolone), 7.64 (d, 2H, $J = 8.2$ Hz, ArH), 8.22 (d, 2H, $J = 8.2$ Hz, ArH), 9.02 (s, 1H, pyridine), 13.50 (bs, 1H, OH) ppm.

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-4-(3,4-dimethoxyphenyl)-2-(piperazin-1-yl)pyridine-3-carbonitrile (**4d**, $C_{28}H_{27}N_5O_4$)
Yield 2.44 g (75%); m.p.: 176–178 °C; IR (KBr): $\bar{\nu} = 3{,}540$ (OH), 2,245 (CN), 1,672 (CO), 1,556 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 1.90$–2.20 (t, 4H, $J = 6.9$ Hz, 2 × CH_2), 2.30–2.45 (t, 4H, $J = 6.9$ Hz, 2 × CH_2), 3.60 (s, 3H, NCH_3), 4.10–4.30 (s, 6H, 2 × OCH_3), 6.99–7.40 (m, 4H, quinolone), 7.60–7.88 (m, 3H, ArH), 8.90 (s, 1H, pyridine), 14.57 (bs, 1H, OH) ppm.

4-(4-Chlorophenyl)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-(2-methyl-5-oxopyrrolidin-1-yl)pyridine-3-carbonitrile (**5a**, $C_{27}H_{21}ClN_4O_3$)
Yield 2.66 g (66%); m.p.: 202–204 °C; IR (KBr): $\bar{\nu} = 3{,}447$ (OH), 2,218 (CN), 1,645 (CO), 1,630 (CO), 1,545 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 1.30$ (s, 3H, CH_3), 3.12 (t, 2H, CH_2), 3.40–3.81 (t, 3H, $J = 6.4$ Hz, CH_2, CH), 4.02 (s, 3H, NCH_3), 7.28-7.83 (m, 4H, quinolone), 7.94 (d, 2H, $J = 8.2$ Hz, ArH), 8.16 (d, 2H, $J = 8.2$ Hz, ArH), 8.68 (s, 1H, pyridine), 15.97 (bs, 1H, OH) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.5$, 22.4, 28.7, 30.2, 32.4, 64.4, 101.4, 114.4, 122.5, 124.5, 126.7, 128.7 (s), 129.5 (s), 134.5, 139.7, 140.5, 159.8, 165.4, 170.4 ppm.

4-(4-Bromophenyl)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-(2-methyl-5-oxopyrrolidin-1-yl)pyridine-3-carbonitrile (**5b**, $C_{27}H_{21}BrN_4O_3$)
Yield 2.88 g (68%); m.p.: 205–206 °C; IR (KBr): $\bar{\nu} = 3{,}087$ (OH), 2,942 (CH), 2,227 (CN), 1,656 (CO), 1,644 (CO), 1,595, 1,570, 1,540 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 1.45$ (s, 3H, CH_3), 2.87 (t, 2H, CH_2), 3.20–3.60 (t, 3H, $J = 6.4$ Hz, CH_2, CH), 3.90 (s, 3H, NCH_3), 7.12–7.54 (m, 4H, quinolone), 7.60 (d, 2H, $J = 8.6$ Hz, ArH), 8.10 (d, 2H, $J = 8.6$ Hz, ArH), 8.74 (s, 1H, pyridine), 15.44 (bs, 1H, OH) ppm.

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-4-(4-methoxyphenyl)-2-(2-methyl-5-oxopyrrolidin-1-yl)pyridine-3-carbonitrile (**5c**, $C_{28}H_{24}N_4O_4$)
Yield 2.90 g (70%); m.p.: 188–190 °C; IR (KBr): $\bar{\nu} = 3{,}119$ (OH), 2,970 (CH), 2,216 (CN), 1,667 (CO), 1,654 (CO), 1,602, 1,585 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 1.40$ (s, 3H, CH_3), 2.56 (t, 2H, CH_2), 2.90–3.23 (t, 3H, $J = 7.2$ Hz, CH_2, CH), 3.65 (s, 3H, NCH_3), 3.80 (s, 3H, OCH_3), 6.98–7.22 (m, 4H, quinolone), 7.46 (d, 2H, $J = 7.8$ Hz, ArH), 7.92 (d, 2H, $J = 7.8$ Hz, ArH), 8.55 (s, 1H, pyridine), 14.45 (bs, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): $\delta = 39.2$, 45.7, 47.3, 65.5,

68.4, 73.4, 106.2, 106.7, 107.6, 107.3, 115.1 (s), 121.4, 122.5, 127.8, 128.9, 130.4, 134.7, 134.8, 137.1, 158.7, 160.9 ppm.

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-4-(3,4-dimethoxyphenyl)-2-(2-methyl-5-oxopyrrolidin-1-yl)pyridine-3-carbonitrile (**5d**, $C_{29}H_{26}N_4O_5$)
Yield 3.02 g (68%); m.p.: 214–215 °C; IR (KBr): $\bar{\nu}$ = 3,410 (OH), 2,210 (CN), 1,670 (CO), 1,633 (CO), 1,550 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.44 (d, 3H, CH_3), 2.40 (t, 2H, CH_2), 2.44 (q, 1H, CH), 3.02 (t, 2H, CH_2), 3.52 (s, 3H, NCH_3), 3.72–3.90 (s, 6H, 2 × OCH_3), 6.90–7.28 (m, 4H, quinolone), 7.55–7.88 (m, 3H, ArH), 8.46 (s, 1H, pyridine), 14.52 (bs, 1H, OH) ppm.

4-(4-Chlorophenyl)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-(2-oxopyrrolidin-1-yl)pyridine-3-carbonitrile (**6a**, $C_{26}H_{19}ClN_4O_3$)
Yield 2.95 g (68%); m.p.: 176–177 °C; IR (KBr): $\bar{\nu}$ = 3,482 (OH), 2,213 (CN), 1,655 (CO), 1,645 (CO), 1,545 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.01 (t, 2H, CH_2), 3.40–3.95 (t, 4H, J = 6.4 Hz, 2 × CH_2), 4.14 (s, 3H, NCH_3), 7.31–7.86 (m, 4H, quinolone), 7.94 (d, 2H, J = 8.4 Hz, ArH), 7.94 (d, 2H, J = 8.4 Hz, ArH), 8.61 (s, 1H, pyridine), 15.85 (bs, 1H, OH) ppm; MS: m/z (%) = 472 (M + 2, 60), 471 (M + 1, 70), 470 (M^+, 100).

4-(4-Bromophenyl)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-(2-oxopyrrolidin-1-yl)pyridine-3-carbonitrile (**6b**, $C_{26}H_{19}BrN_4O_3$)
Yield 2.95 g (68%); m.p.: 176–177 °C; IR (KBr): $\bar{\nu}$ = 3,501 (OH), 2,233 (CN), 1,658 (CO), 1,647 (CO), 1,549 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.98 (t, 2H, CH_2), 2.80–3.70 (t, 4H, J = 6.4 Hz, 2 × CH_2), 3.95 (s, 3H, NCH_3), 7.12–7.65 (m, 4H, quinolone), 7.90 (d, 2H, J = 8.4 Hz, ArH), 8.22 (d, 2H, J = 8.4 Hz, ArH), 8.66 (s, 1H, pyridine), 14.90 (bs, 1H, OH) ppm.

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-4-(4-methoxyphenyl)-2-(2-oxopyrrolidin-1-yl)pyridine-3-carbonitrile (**6c**, $C_{27}H_{22}N_4O_4$)
Yield 2.90 g (66%); m.p.: 201–202 °C; IR (KBr): $\bar{\nu}$ = 3,394 (OH), 2,929 (CH), 2,210 (CN), 1,676 (CO), 1,647 (CO), 1,606, 1,585, 1,496, 1,221 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.94 (t, 2H, CH_2), 3.02–3.92 (t, 4H, J = 6.4 Hz, 2 × CH_2), 3.98 (s, 3H, NCH_3), 4.12 (s, 3H, OCH_3), 7.08–7.90 (m, 4H, quinolone), 7.96 (d, 2H, J = 8.4 Hz, ArH), 8.14 (d, 2H, J = 8.4 Hz, ArH), 8.17 (s, 1H, pyridine), 14.87 (bs, 1H, OH) ppm.

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-4-(3,4-dimethoxyphenyl)-2-(2-oxopyrrolidin-1-yl)pyridine-3-carbonitrile (**6d**, $C_{28}H_{24}N_4O_5$)
Yield 3.10 g (70%); m.p.: 215–216 °C; IR (KBr): $\bar{\nu}$ = 3,508 (OH), 2,241 (CN), 1,666 (CO), 1,651 (CO), 1,564 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.02 (t, J = 6.45 Hz, 2H, CH_2), 2.66–3.45 (t, 4H, J = 6.4 Hz, 2 × CH_2), 3.80 (s, 3H, NCH_3), 4.02–4.20 (s, 6H, 2 × OCH_3), 6.90–7.30 (m, 4H, quinolone), 7.84–8.22 (m, 3H, ArH), 8.84 (s, 1H, pyridine), 14.66 (bs, 1H, OH) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.4 (s), 23.8 (s), 55.6, 64.8, 90.2, 109.7, 125.2, 126.4, 128.7, 128.9 (s), 130.4, 136.4, 137.8, 139.0, 141.7, 152.3, 165.4, 173.4 ppm; MS: m/z (%) = 498 (M + 2, 22), 497 (M + 1, 30), 496 (M^+, 95).

General procedure for the synthesis of 2-alkoxypyridine-3-carbonitriles ***7a–11c***

A mixture of chalcone **1a–1c** (10 mmol), 0.66 g malononitrile (10 mmol), and sodium alcoholate (prepared by dissolving 35 mg (15 mmol) of freshly cut sodium metal in 5 cm^3 dry methanol, ethanol, propanol, butanol, or octanol) was refluxed in the corresponding alcohol for 4–5 h (TLC check, *n*-hexane/ethyl acetate 8:2). After cooling, the solvent was removed under reduced pressure. The obtained residue was poured into 100 cm^3 ice-cold water, stirred further 30 min, and extracted with 10 cm^3 chloroform. The organic layer was dried over sodium sulfate and evaporated under reduced pressure. The obtained solid product was purified by column chromatography (silica gel 60–120 mesh) using *n*-hexane and ethyl acetate (8:2 v/v) as eluent to afford compounds **7a–11c** as yellow prisms in 48–65% yield.

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-methoxy-4-phenylpyridine-3-carbonitrile
(**7a**, $C_{23}H_{17}N_3O_3$)
Yield 1.88 g (65%); m.p.: 188–189 °C; IR (KBr): $\bar{\nu}$ = 3,360 (OH), 2,241 (CN), 1,670 (CO), 1,599, 1,485, 1,296 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.44 (s, 3H, NCH_3), 4.17 (s, 3H, OCH_3), 7.03–7.42 (m, 4H, quinolone), 7.60–8.12 (m, 5H, ArH), 8.97 (s, 1H, pyridine) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.4, 64.2, 114.1, 116.2 (s), 118.5 (s), 119.1, 121.2, 123.5, 126.4 (s), 128.8, 133.4, 138.7, 140.4, 143.5, 148.1, 165.4 ppm; MS: m/z (%) = 385 (M + 2, 26), 384 (M + 1, 45), 383 (M^+, 100).

4-(4-Chlorophenyl)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-methoxypyridine-3-carbonitrile
(**7b**, $C_{23}H_{16}ClN_3O_3$)
Yield 2.10 g (50%); m.p.: 211–212 °C; IR (KBr): $\bar{\nu}$ = 3,450 (OH), 2,232 (CN), 1,680 (CO), 1,560, 1,310 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.70 (s, 3H, NCH_3), 4.20 (s, 3H, OCH_3), 7.06–7.26 (m, 4H, quinolone), 7.55 (m, J = 7.8 Hz, 2H, ArH), 7.90 (d, J = 7.8 Hz, ArH), 9.22 (s, 1H, pyridine) ppm; MS: m/z (%) = 420 (M + 1, 25), 418 (M^+, 100).

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-methoxy-4-(4-methoxyphenyl)pyridine-3-carbonitrile
(**7c**, $C_{24}H_{19}N_3O_4$)
Yield 2.0 g (55%); m.p.: 224–225 °C; IR (KBr): $\bar{\nu}$ = 3,488 (OH), 2,241 (CN), 1,670 (CO), 1,601, 1,450, 1,300 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 3H, NCH_3), 4.05 (s, 3H, OCH_3), 4.20 (s, 3H, OCH_3), 7.02–7.22 (m, 4H, quinolone), 7.45 (d, J = 8.2 Hz, 2H, ArH), 7.88 (d, J = 8.2 Hz, 2H, ArH), 9.20 (s, 1H, ArH) ppm; MS: *m/z* (%) = 414.0 (M + 1, 20), 413 (M^+, 100).

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-ethoxy-4-phenylpyridine-3-carbonitrile
(**8a**, $C_{24}H_{19}N_3O_3$)
Yield 1.60 g (50%); m.p.: 196–197 °C; IR (KBr): $\bar{\nu}$ = 3,440 (OH), 2,232 (CN), 1,675 (CO), 1,602, 1,514, 1,302 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.10 (t, 3H, J = 6.7 Hz, CH_3), 3.46 (s, 3H, NCH_3), 4.52 (q, 2H, J = 6.7 Hz, CH_2), 6.88–7.20 (m, 4H, quinolone), 7.40–7.90 (m, 5H, ArH), 9.10 (s, 1H, pyridine) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 30.4, 66.2, 95.4, 100.5, 117.0, 118.5(s), 121.5(s), 124.3, 125.4(s), 126.6, 127.4, 135.3, 138.1, 140.4, 145.5, 149.2, 156.1, 158.1, 165.4 ppm.

4-(4-Chlorophenyl)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-ethoxypyridine-3-carbonitrile
(**8b**, $C_{24}H_{18}ClN_3O_3$)
Yield 2.20 g (50%); m.p.: 211–212 °C; IR (KBr): $\bar{\nu}$ = 3,450 (OH), 2,245 (CN), 1,680 (CO), 1,589, 1,560, 1,280 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 (t, 3H, J = 6.9 Hz, CH_3), 3.70 (s, 3H, NCH_3), 4.40 (q, 2H, J = 6.9 Hz, OCH_2), 6.90-7.22 (m, 4H, quinolone), 7.90 (d, J = 8.1 Hz, 2H, ArH), 8.20 (d, J = 8.1 Hz, 2H, ArH), 9.22 (s, 1H, pyridine) ppm; MS: *m/z* (%) = 434.0 (M + 1, 35), 433 (M+, 100).

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-ethoxy-4-(4-methoxyphenyl)pyridine-3-carbonitrile
(**8c**, $C_{25}H_{21}N_3O_4$)
Yield 2.45 g (60%); m.p.: 224–225 °C; IR (KBr): $\bar{\nu}$ = 3,477 (OH), 2,230 (CN), 1,670 (CO), 1,612, 1,450, 1,330 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.60 (t, 3H, J = 6.8 Hz, CH_3), 3.80 (s, 3H, NCH_3), 3.90 (s, 3H, OCH_3), 4.20 (q, 2H, J = 6.8 Hz, OCH_2), 6.88–7.15 (m, 4H, quinolone), 8.15 (d, J = 7.9 Hz, 2H, ArH), 8.40 (d, J = 7.9 Hz, ArH), 9.20 (s, 1H, ArH) ppm; MS: *m/z* = 428.0 (M + 1).

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-4-phenyl-2-(propyloxy)pyridine-3-carbonitrile
(**9a**, $C_{25}H_{21}N_3O_3$)
Yield 1.44 g (52%); m.p.: 188–189 °C; IR (KBr): $\bar{\nu}$ = 3,450 (OH), 2,232 (CN), 1,680 (CO), 1,604, 1,520 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.01 (t, J = 6.8 Hz, 3H, CH_3), 2.20 (sext, J = 6.8 Hz, 2H, CH_2), 3.85 (s, 3H, NCH_3), 4.50 (t, J = 6.8 Hz, 2H, CH_2), 7.20–7.61 (m, 4H, quinolone), 7.77–8.32 (m, 5H, ArH), 9.10 (s, 1H, pyridine), 13.40 (bs, 1H, OH) ppm; ^{13}C NMR (DMSO-d_6): δ = 16.2, 28.4, 46.4, 64.5, 111.4, 114.4, 118.2 (s), 120.5, 122.4, 124.6, 128.7 (s), 130.7, 132.5, 134.5, 135.4, 140.7, 142.6, 150.4, 156.7, 164.5 ppm.

4-(4-Chlorophenyl)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-(propyloxy)pyridine-3-carbonitrile
(**9b**, $C_{25}H_{20}ClN_3O_3$)
Yield 2.38 g (55%); m.p.: 211–212 °C; IR (KBr): $\bar{\nu}$ = 3,435 (OH), 2,241 (CN), 1,678 (CO), 1,608, 1,560, 1,415 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.01 (t, 3H, J = 6.8 Hz, CH_3), 2.10 (sext, 2H, J = 7.1 Hz, CH_2), 3.80 (s, 3H, NCH_3), 4.50 (t, 2H, J = 7.1 Hz, CH_2), 7.20–7.40 (m, 4H, ArH), 8.01 (d, 2H, J = 8.2 Hz, ArH), 8.20 (d, 2H, J = 8.2 Hz, ArH), 9.10 (s, 1H, pyridine), 13.60 (bs, 1H, OH) ppm.

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-4-(4-methoxyphenyl)-2-(propyloxy)pyridine-3-carbonitrile
(**9c**, $C_{26}H_{23}N_3O_4$)
Yield 1.90 g (48%); m.p.: 193–194 °C; IR (KBr): $\bar{\nu}$ = 3,502 (OH), 2,243 (CN), 1,676 (CO), 1,601, 1,450, 1,312 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 0.90 (t, 3H, J = 6.91 Hz, CH_3), 1.90 (sext, 2H, J = 6.9 Hz, CH_2), 3.50 (s, 3H, NCH_3), 3.90 (s, 3H, OCH_3), 4.45 (t, 2H, J = 6.8 Hz, CH_2), 7.10–7.25 (m, 4H, ArH), 7.90 (d, 2H, J = 8.2 Hz, ArH), 8.20 (d, 2H, J = 8.2 Hz, ArH), 9.10 (s, 1H, pyridine), 13.40 (bs, 1H, OH) ppm.

2-(Butyloxy)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxo-quinolin-3-yl)-4-phenylpyridine-3-carbonitrile
(**10a**, $C_{26}H_{23}N_3O_3$)
Yield 1.68 g (54%); m.p.: 192–193 °C; IR (KBr): $\bar{\nu}$ = 3,444 (OH), 2,238 (CN), 1,677 (CN), 1,599, 1,515 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.10 (s, 3H, CH_3), 1.20 (sext, J = 6.8 Hz, 2H, CH_2), 2.10 (quint, 2H, J = 6.9 Hz, CH_2), 3.85 (s, 3H, NCH_3), 4.60 (t, 2H, J = 6.9 Hz, CH_2), 7.28-7.65 (m, 4H, quinolone), 7.88-8.50 (m, 5H, ArH), 9.14 (s, 1H, pyridine), 16.02 (bs, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 13.2, 15.6, 22.8, 28.6, 29.6, 38.6, 68.4, 95.4, 100.4, 100.7, 115.7, 121.5, 127.4(s), 126.4, 126.6, 128.6, 129.3(s), 129.8, 135.5, 138.2, 138.8, 150.5, 162.4, 166.5 ppm.

2-(Butyloxy)-4-(4-chlorophenyl)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)pyridine-3-carbonitrile (**10b**, $C_{26}H_{22}ClN_3O_3$)
Yield 2.06 g (52%); m.p.: 198–200 °C; IR (KBr): $\bar{\nu}$ = 3,490 (OH), 2,237 (CN), 1,681 (CO), 1,588, 1,560, 1,410 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.07 (s, 3H, CH_3), 1.10 (sext, 2H, J = 6.7 Hz, CH_2), 1.88 (quint, 2H, J = 6.7 Hz, CH_2), 3.75 (s, 3H, NCH_3), 4.40 (t, 2H, J = 6.8 Hz, CH_2), 7.28–7.45 (m, 4H, quinolone), 7.70 (d,

2H, $J = 7.9$ Hz, ArH), 8.30 (d, 2H, $J = 7.94$ Hz, ArH), 9.14 (s, 1H, pyridine), 16.72 (bs, 1H, OH) ppm; MS: *m/z* (%) = 459 (M − 1, 60).

2-(Butyloxy)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxo-quinolin-3-yl)-4-(4-methoxyphenyl)pyridine-3-carbonitrile (**10c**, $C_{27}H_{25}N_3O_4$)
Yield 2.18 g (58%); m.p.: 209–210 °C; IR (KBr): $\bar{\nu} = 3{,}354$ (OH), 2,225 (CN), 1,675 (CO), 1,603, 1,560, 1,310 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): $\delta = 1.09$ (s, 3H, CH_3), 1.27 (sext, 2H, $J = 6.7$ Hz, CH_2), 1.91 (quint, 2H, $J = 6.7$ Hz, CH_2), 3.75 (s, 3H, OCH_3), 3.80 (s, 3H, NCH_3), 4.50 (t, 2H, $J = 6.4$ Hz, CH_2), 7.32–7.48 (m, 4H, quinolone), 7.73 (d, 2H, $J = 7.9$ Hz, ArH), 8.27 (d, 2H, $J = 7.9$ Hz, ArH), 9.21 (s, 1H, pyridine), 16.40 (bs, 1H, OH) ppm.

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-(octyloxy)-4-phenylpyridine-3-carbonitrile
(**11a**, $C_{30}H_{31}N_3O_3$)
Yield 1.68 g (54%); m.p.: 200–202 °C; IR (KBr): $\bar{\nu} = 3{,}460$ (OH), 2,241 (CN), 1,665 (CO), 1,586, 1,520 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): $\delta = 0.90$ (t, 3H, $J = 6.7$ Hz, CH_3), 1.42–1.50 (m, 12H, $(CH_2)_6$), 3.80 (s, 3H, NCH_3), 4.60 (t, 2H, $J = 6.7$ Hz, OCH_2), 7.10–7.60 (m, 4H, quinolone), 7.60–8.15 (m, 5H, ArH), 9.10 (s, 1H, pyridine), 12.30 (bs, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): $\delta = 15.6$, 23.6, 26.4, 29.3, 29.7(s), 31.3, 33.7, 58.4, 95.2, 101.5, 102.7, 117.6, 121.4, 124.3, 126.6, 127.6(s), 128.2, 129.8(s), 130.5, 132.3, 135.8, 145.5, 148.1, 150.5, 156.1, 165.4 ppm.

4-(4-Chlorophenyl)-6-(1,2-dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-2-(octyloxy)pyridine-3-carbonitrile
(**11b**, $C_{30}H_{30}ClN_3O_3$)
Yield 1.80 g (48%); m.p.: 189–190 °C (ethanol); IR (KBr): $\bar{\nu} = 3{,}454$ (OH), 2,247 (CN), 1,692 (CO), 1,596, 1,544, 1,461 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): $\delta = 0.75$ (t, 3H, $J = 6.8$ Hz, CH_3), 1.45–2.66 (m, 12H, $(CH_2)_6$), 3.60 (s, 3H, OCH_3), 3.70 (s, 3H, NCH_3), 4.45 (t, 2H, $J = 6.8$ Hz, OCH_2), 7.10–7.25 (m, 4H, quinolone), 7.45 (d, 2H, $J = 8.1$ Hz, ArH), 7.65 (d, 2H, $J = 8.1$ Hz, ArH), 9.10 (s, 1H, pyridine), 12.30 (bs, 1H, OH) ppm.

6-(1,2-Dihydro-4-hydroxy-1-methyl-2-oxoquinolin-3-yl)-4-(4-methoxyphenyl)-2-(octyloxy)pyridine-3-carbonitrile
(**11c**, $C_{31}H_{33}N_3O_4$)
Yield 1.88 g (56%); m.p.: 214–215 °C (ethanol); IR (KBr): $\bar{\nu} = 3{,}490$ (OH), 2,235 (CN), 1,682 (CO), 1,585, 1,322 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): $\delta = 0.80$ (t, 3H, $J = 6.8$ Hz, CH_3), 1.50–2.45 (m, 12H, $(CH_2)_6$), 3.75 (s, 3H, NCH_3), 4.10 (s, 3H, OCH_3), 4.65 (t, 2H, $J = 6.8$ Hz, CH_2), 7.15–7.35 (m, 4H, quinolone), 7.50 (d, 2H, $J = 8.1$ Hz, ArH), 7.80 (d, 2H, $J = 8.1$ Hz, ArH), 9.20 (s, 1H, pyridine), 11.40 (bs, 1H, OH) ppm.

Acknowledgments The authors thank CSIR, New Delhi, for financial support. The authors thank the Department of Chemistry, University of Pune, Pune, for spectral and analytical data and Principal, K.T.H.M. College, Nashik-422 002, India, for facilities.

References

1. Courts RT, Casy AF (1975) In: Abramovitch RA (ed) Pyridine and its derivatives, supplement IV. Wiley, New York
2. Yates FS (1984) In: Katritzky AR, Rees CW (eds) Comprehensive heterocyclic chemistry, vol 2. Pergamon, Oxford
3. Forlano EA, Deferrari JO, Cadenas RA (1972) Carbohydr Res 21:484
4. Glennon RA, Dukat M (1996) Med Chem Res 6:465
5. McDonald IA, Cosford N, Vemier JM (1995) Ann Rep Med Chem 30:41
6. Boodman NS, Hawthome JO, Masciantonia PX, Simon AW (1972) In: Abramovitch RA (ed) Pyridine and its derivatives, vol 14, supplement I. Wiley, New York
7. Balasubramaniam M, Keay JG (1995) In: Abramovitch RA (ed) Pyridine and its derivatives, supplement V. Wiley, New York
8. Newkome GR, Paudler WW (1982) Contemporary heterocyclic chemistry. Wiley, New York
9. Brody F, Rudy PR (1960) In: Klingsberg E (ed) Pyridine and its derivatives, vol 14, Part 1, Chapter 2. Interscience, New York
10. Salem MAI, Madkour HMF, Soliman ESA, Mahmoud NFH (2000) Heterocycles 53:1129
11. Alberola A, Calvo LA, Ortega AG, Sanudo RMC, Yustos PJ (1999) Org Chem 64:9493
12. Oda K, Nakagami R, Nishizono N, Machida M (1999) Chem Commun 2371
13. Murugan P, Raghukumar V, Ramakrishnan VT (1999) Synth Commun 29:3881
14. Raghukumar V, Murugan P, Ramakrishnan VT (2001) Synth Commun 31:97
15. Temple C, Rener GA, Waud WR, Noker PE (1992) J Med Chem 35:3686
16. Badgett CO, Woodward CF (1947) J Am Chem Soc 69:2907
17. Dorner G, Fischer WR (1961) Arzneim Forsch 11:110
18. Wang H, Helgeson R, Ma B, Wudl F (2000) J Org Chem 65:5862
19. Kanbara T, Koshida T, Sato N, Kuwajima I, Kubota K, Yamamoto T (1992) Chem Lett 21:583
20. Meyer TJ (1989) Acc Chem Res 22:163
21. Pavluchenko AI, Petrov VF, Smirnova NI (1995) Liq Cryst 19:811
22. Basta AH, Girgis AS, Saied EH (2002) Dyes Pigm 54:1
23. Jachak MN, Bagul SM, Ghotekar BK, Toche RB (2009) Monatsh Chem 140:655
24. Abbas M (2000) Synth Commun 30:2735
25. Lakowicz JR (1999) Principals of fluorescence spectroscopy, 2nd edn. Springer, New York
26. Fletcher AN (2008) Photochem Photobiol 9:439
27. Tang CW, Vanslyke SA (1987) Appl Phys Lett 51:913
28. He Z, Milburn GHW, Baldwin KJ, Smith DA, Danel A, Tomasik P (2000) J Lumin 86:1
29. Indirapriyadharshini VK, Ramamurthy P, Raghukumar V, Ramakrishna VT (2002) Spectrochim Acta A 58:1535