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ORIGINAL PAPER

Synthesis and study of the fluorescent behavior of 3-pyridinecarbonitriles

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Abstract A series of (2*E*)-3-(1-chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-1-(4-aryl)prop-2-en-1-ones (chalcones) have been synthesized by a new synthetic route. The 3-pyridinecarbonitrile derivatives were synthesized by the Michael reaction of malononitrile (in base) and aroylacetonitriles (in acid) with chalcones in one pot. The fluorescent properties and quantum yields of these compounds were studied.

Keywords Chalcone · 3-Pyridinecarbonitriles · Fluorescence · Wittig reaction · Grignard reaction

Introduction

Inspired by the pioneering work of Tang and vanSlyke [1] on electroluminescence (EL) devices that use organic molecular materials, research activity on organic light emitting diodes (OLEDs) has been expanding rapidly and has progressed substantially in recent years. The LEDs of this category are of great interest because of their potential applications for the production of low-cost display products. Continuing efforts include the development of new efficient materials and ingenious device fabrications [2]. There are many activities focused on blue-light emitting OLEDs and a wide variety of organic and organometallic compounds have been utilized for this purpose. Thus a suitable blue-light emitting material with high brightness and good thermal stability still remains to be developed.

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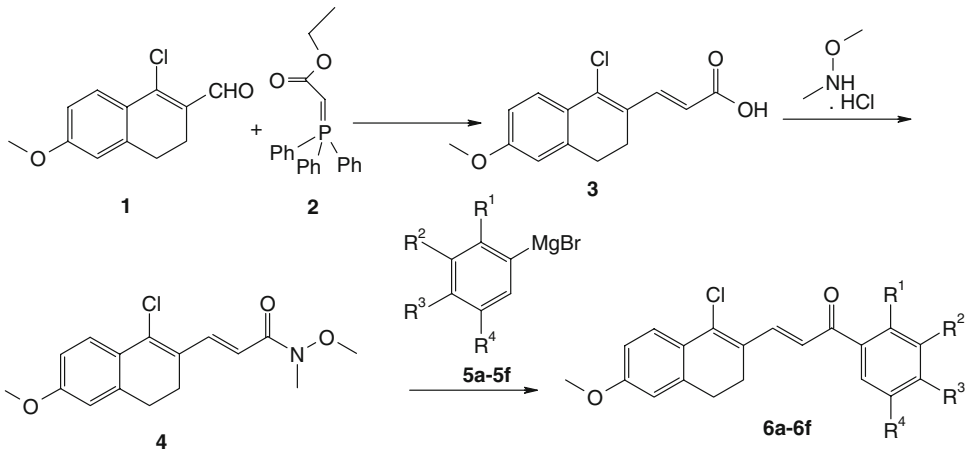
Derivatives of pyridines have application in light emitting [3] and electroluminescence devices [4]. Apart from this, 3-pyridinecarbonitriles have been used as dyes for synthetic fabrics [5–7] and paper [8, 9]. Pyridine derivatives have been synthesized by using chalcones as a starting material [10–12]. As a part of our ongoing interest in this area [13–15] we have reported the synthesis of pyrazolo[3,4-*b*]pyridines, pyrazolo[3,4-*b*]quinolines, pyrazolonaphthyridines, and pyrazolopyridopyrimidines by Friedländer condensation of reactive methylene compounds with 5-aminopyrazole. In our recent communications [16], the synthesis of highly fluorescent dipyrazolo[3,4-*b*:3,4-*d*]pyridines (DPP) has been reported. These literature reports and our ongoing research in this area prompted us to synthesize 3-pyridinecarbonitriles and to study their fluorescence behavior.

Results and discussion

The synthesis of acetophenones such as 1-(3,4,5-trimethoxyphenyl)ethanone requires lithiation of 3,4,5-trimethoxybenzoic acid and 3,5-dimethoxybenzoic acid, which involved multistep and tedious workup [17–19]. To avoid these multistep syntheses, we have developed a new route towards the synthesis of chalcones **6**. In our strategy the enone part of chalcone was synthesized at the beginning by starting with *ortho*-chloroaldehyde **1** [20]. The Wittig reaction on aldehyde **1** delivered enoic acid **3** in quantitative yield. The enoic acid **3** was converted to amide **4** by treatment **3** with *N*-methoxymethanamine hydrochloride. The amide **4** was successfully reacted with substituted aryl magnesium bromide **5** which is obtained from aryl bromide and magnesium in THF at 0 °C to yield the desired chalcones **6** in 79–84% yield (Scheme 1). On

Scheme 1



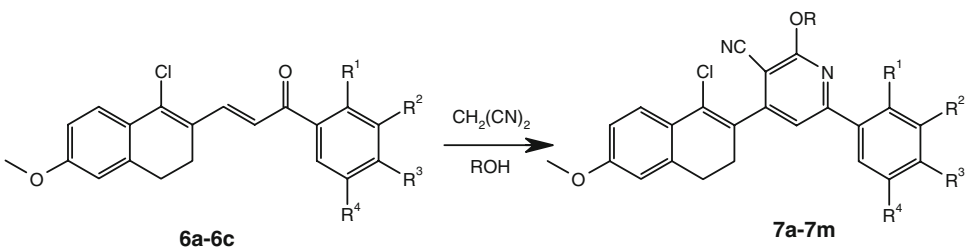
6	R^1	R^2	R^3	R^4
a	H	H	H	F
b	H	H	OMe	H
c	OMe	H	OMe	H
d	OMe	H	H	OMe
e	H	OMe	H	OMe
f	H	OMe	OMe	OMe

the basis of the coupling constant ($J = 15.3$ Hz) for olefinic protons in compounds **3**, **4**, and **6** an *E*-configuration was assigned to these compounds.

The chalcones **6** were used as intermediates for the synthesis of 3-pyridinecarbonitriles. Thus the cyclocondensation of chalcones **6** with malononitrile in alcohol at 30–35 °C yielded the corresponding 3-pyridinecarbonitriles **7** in good yield (Scheme 2).

In compound **7** the alkoxy group at the C-2 position of the pyridine ring depends upon the alcohol used in the reaction. Similar cyclocondensation reactions of chalcones **6** with aroylacetonitriles by heating under reflux in acetic

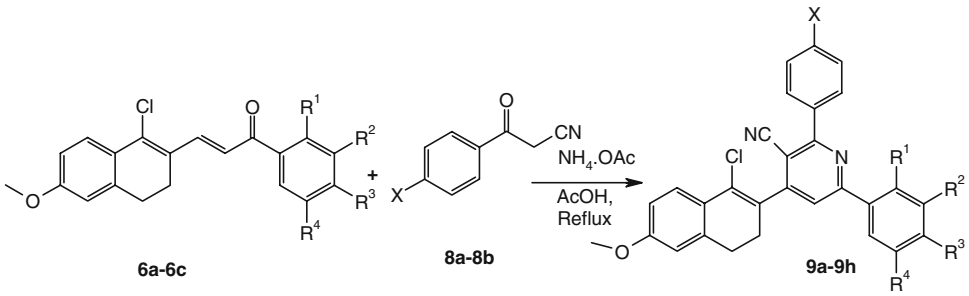
Scheme 2



7	R	R^1	R^2	R^3	R^4
a	Me	H	H	H	F
b	Et	H	H	H	F
c	*n*-Pr	H	H	H	F
d	Me	H	H	OMe	H

7	R	R^1	R^2	R^3	R^4
e	Et	H	H	OMe	H
f	*n*-Pr	H	H	OMe	H
g	Me	OMe	H	H	OMe
h	Et	OMe	H	H	OMe

Scheme 3



8	X
a	Cl
b	Br

9	R^1	R^2	R^3	R^4	X
a	H	H	F	H	Cl
b	H	H	F	H	Br
c	H	H	OMe	H	Cl
d	H	H	OMe	H	Br
e	OMe	H	H	OMe	Cl
f	OMe	H	H	OMe	Br

acid furnished corresponding 3-pyridinecarbonitriles **9** in 70–75% yield (Scheme 3).

The structures of all these compounds were confirmed by ^{1}H NMR, IR, and elemental analysis.

Photophysical properties

Compounds **7** and **9** showed absorption and fluorescence in the near visible region (380–400 nm). It was noted that incorporation of a substituent in 3-pyridinecarbonitriles **7** and **9** in the aryl ring at the C-6 position of the pyridine nucleus has profound influence on the absorption and emission properties. These findings reveal that 3-pyridinecarbonitriles **7d–7h** and **9c–9f** substituted with electron-donating substituents such as a methoxy group (strong donor) in the aryl ring at C-6 of pyridine enhanced the UV absorption in the range 378–400 nm, the fluorescence maxima in the range of 430–451 nm, and quantum yields in the range 0.198–0.219. When the substituent is fluoro (weak donor) in the 3-pyridinecarbonitriles **7a–7c** and **9a** and **9b** the UV absorption is in the range 376–385 nm and fluorescence maxima are in the range 432–442 nm along with quantum yields in the range 0.179–0.189. The absorption and fluorescence data are listed in Table 1. The absorption and emission spectra of compound **7d** are also shown in Fig. 1.

Table 1 Photophysical data for the electronic excitation (UV λ_{max}), fluorescence (Em λ_{max}), and quantum yield (Φ) of **7a–7h** and **9a–9f** in DMSO as the solvent at 25 °C

Cpd. No.	UV λ_{max}/nm	Em λ_{max}/nm	Φ
7a	385	452	0.189
7b	386	444	0.185
7c	386	441	0.179
7d	397	449	0.219
7e	398	439	0.210
7f	397	430	0.198
7g	399	446	0.221
7h	400	441	0.213
9a	381	437	0.189
9b	376	439	0.186
9c	383	441	0.215
9d	378	445	0.210
9e	386	449	0.217
9f	387	451	0.211

Conclusion

The reactions reported here represent a novel synthetic route towards chalcones. Highly fluorescent compounds **7**

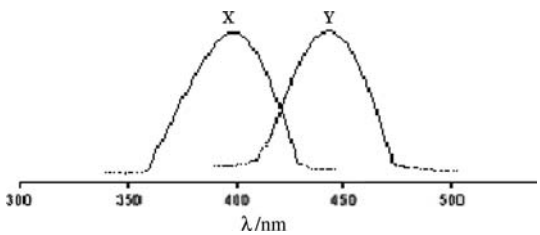


Fig. 1 The absorption (*X*) and emission (*Y*) spectra of compound **7d**

and **9** were synthesized. Thermal analysis of **7** and **9** by differential scanning calorimetry (DSC) revealed that they are thermally stable compounds up to 350 °C. Most important, fluorescence quantum yields are almost independent of solvents and pH and values of around 0.22 are obtained. The fluorescence properties of these compounds depend upon the nature of substituents present at the phenyl moiety at the 6-position of the pyridine ring.

Experimental

Melting points: Gallenkamp melting point apparatus; IR Spectra (KBr-compression mold): Shimadzu IR-408; ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz) Spectra: Varian XL-300 in DMSO-d_6 or $CDCl_3$ using TMS as internal standard; Mass spectra: hp 1100 LC–MSD mass spectrometer (positive and negative APCI ion source, 50–200 V, nitrogen); Elemental analyses (C, H, N, S) were conducted using the HOSLI CH-Analyzer; the results were in agreement with calculated values.

(2E)-3-(1-Chloro-(6-methoxy-3,4-dihydronaphthalen-2-yl)acrylic acid (**3**, $C_{14}H_{13}ClO_3$)

A mixture of 2.225 g 1-chloro-6-methoxy-3,4-dihydronaphthalene-2-carbaldehyde (**1**) [20] (10 mmol) and 4.537 g **2** (13 mmol) was heated under reflux in 10 cm^3 dichloromethane for 5 h. The solvent was removed under reduced pressure and the residue was dissolved in 10 cm^3 methanol and 52 cm^3 aqueous sodium hydroxide (10% solution), which was heated under reflux for 4 h. The solvent was removed under reduced pressure, 15 cm^3 water were added to the residue. The aqueous layer was extracted with 2 × 15 cm^3 dichloromethane to remove triphenylphosphine oxide. The aqueous layer was acidified with 2 M HCl upon which a solid precipitated which was isolated by suction filtration to afford 2.30 g (87%) **3**. M.p.: 260–261 °C; ^{1}H NMR (DMSO-d_6): $\delta = 2.52$ (t, $J = 7.0$ Hz, 2H, CH_2), 2.76 (t, $J = 7.2$ Hz, 2H, CH_2), 3.72 (s, 3H, OCH_3), 6.04 (d, $J = 15.3$ Hz, 1H, =CH), 6.81 (d, $J = 8.6$ Hz, 1H, Ar–H), 6.82 (dd, $J = 2.1$, 8.2 Hz, 1H, Ar–H), 7.49 (d, $J = 8.1$ Hz, 1H, Ar–H), 7.80 (d, $J = 15.3$ Hz, 1H, =CH) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 26.89$, 31.70, 55.47, 112.04, 112.14, 116.98, 127.08, 127.11, 133.14, 134.47, 138.85, 151.79, 159.43, 170.18 ppm; IR: $\bar{\nu} = 3{,}432$, 2,937, 2,832, 1,701, 1,636, 1,590 cm^{-1}.

(2E)-3-(1-Chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-N-methoxy-N-methylacrylamide (**4**, $C_{16}H_{18}ClNO_3$)

To a solution of 2.645 g **3** (10 mmol) in 26 cm^3 dry tetrahydrofuran (THF), 1.944 g 1,1′-carbonyldiimidazole (12 mmol) was added at room temperature, in portions, in the course of 5 min under nitrogen atmosphere. The reaction mixture was stirred for 1 h, then 1.67 g triethylamine (12 mmol) and 1.17 g *N*-methoxymethanamine hydrochloride (12 mmol) were added. After stirring at room temperature for another 3 h, 50 cm^3 water was added to the resulting reaction mass. The solid obtained was collected by filtration, washed with 50 cm^3 water, and dried to afford 2.74 g (89%) **4**. M.p.: 107–108 °C; ^{1}H NMR (DMSO-d_6): $\delta = 2.6$ 7 (t, $J = 6.9$ Hz, 2H, CH_2), 2.91 (t, $J = 7.0$ Hz, 2H, CH_2), 3.33 (s, 3H, –N CH_3), 3.78 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 6.65 (d, $J = 15.3$ Hz, 1H, =CH), 6.74 (d, $J = 7.2$ Hz, 1H, Ar–H), 6.81 (dd, $J = 2.4$, 6.2 Hz, 1H, Ar–H), 7.69 (d, $J = 8.1$ Hz, 1H, Ar–H), 8.19 (d, $J = 15.3$ Hz, 1H, =CH) ppm; ^{13}C NMR (DMSO-d_6); $\delta = 26.41$, 31.79, 32.68, 55.57, 62.16, 111.08, 111.21, 121.31, 127.05, 127.17, 132.99, 134.37, 139.01, 147.79, 159.59, 159.89 ppm; IR: $\bar{\nu} = 2{,}937$, 1,636, 1,590, 1,410, 1,337 cm^{-1}.

General procedure for the synthesis of compounds ***6***

To a suspension of 15 mmol magnesium foils in 3 cm^3 dry tetrahydrofuran (THF) containing a catalytic amount (0.02 g) of iodine crystals was added 15 mmol aryl bromide **5** at room temperature. The reaction mixture was stirred for 1 h at room temperature. The Grignard reagent thus formed was added slowly to a solution of 5 mmol **4** in 5 cm^3 dry THF under nitrogen atmosphere at 0–5 °C and stirred at room temperature for 1 h. The reaction mixture was cooled at 10 °C and 5 cm^3 0.5 M HCl was added at 10–15 °C. The solvent was evaporated under reduced pressure and the residue was dissolved in 10 cm^3 dichloromethane. The organic layer was washed with 10 cm^3 saturated sodium bicarbonate followed by saturated sodium chloride. The organic layer was collected and dried over sodium sulfate, and concentrated under reduced pressure. The remaining solid was recrystallized from ethanol.

(2E)-3-(1-Chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-1-(4-fluorophenyl)prop-2-en-1-one (**6a**, $C_{20}H_{16}ClFO_2$)

Yield 1.49 g (87%); m.p.: 130–131 °C (ethanol); ^{1}H NMR ($CDCl_3$): $\delta = 2.73$ (t, $J = 7.1$ Hz, 2H, CH_2), 2.94 (t, $J = 6.9$ Hz, 2H, CH_2), 3.87 (s, 3H, OCH_3), 6.76 (d, $J = 2.4$ Hz, 1H, Ar–H), 6.82 (dd, $J = 2.3$, 8.7 Hz, 1H, Ar–H), 7.07 (d, $J = 15.3$ Hz, 1H, =CH), 7.16 (t, $J = 8.2$ Hz, 2H, Ar–H), 7.72 (d, $J = 8.4$ Hz, 1H, Ar–H), 8.01 (t, $J = 6.0$ Hz, 2H, Ar–H), 8.28 (d, $J = 15.3$ Hz, 1H, =CH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 29.86$, 31.93, 55.44, 111.33, 111.52, 116.12 (2C), 127.14, 127.33, 129.62, 131.25 (2C), 133.38, 133.65, 133.91, 138.76, 148.82, 159.91, 168.90, 189.14 ppm; IR: $\bar{\nu} = 2{,}941$, 2,834, 1,647, 1,610, 1,579, 1,498, 1,306 cm^{-1}.

(2E)-3-(1-Chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-1-(4-methoxyphenyl)-prop-2-en-1-one (**6b**, $C_{21}H_{19}ClO_3$)
Yield 1.52 g (86%); m.p.: 127–128 °C (ethanol); ^{1}H NMR ($CDCl_3$): $\delta = 2.70$ (t, $J = 7.0$ Hz, 2H, CH_2), 2.89 (t, $J = 6.2$ Hz, 2H, CH_2), 3.84 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.75 (d, $J = 2.1$ Hz, 1H, Ar–H), 6.78 (dd, $J = 2.1$, 7.2 Hz, 1H, Ar–H), 6.95 (d, $J = 7.2$ Hz, 2H, Ar–H), 7.09 (d, $J = 15.0$ Hz, 1H, = CH), 7.67 (d, $J = 7.2$ Hz, 1H, Ar–H), 7.96 (d, $J = 6.9$ Hz, 2H, Ar–H), 8.23 (d, $J = 15.0$ Hz, 1H, =CH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 30.01$, 32.64, 55.77, 55.82, 111.17, 111.61, 114.53, 127.51, 127.72 (2C), 128.73, 129.51, 129.96 (2C), 133.84, 134.41, 139.12, 148.93, 159.72, 166.02, 189.51 ppm; IR: $\bar{\nu} = 2{,}939$, 2,842, 1,651, 1,596, 1,487, 1,315 cm^{-1}; MS: *m/z* (%) = 356.1 (25) [M + 2], 354.2 (100) [M], 318.1 (70).

(2E)-3-(1-Chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-1-(2,4-dimethoxyphenyl)prop-2-en-1-one
(**6c**, $C_{22}H_{21}ClO_4$)
Yield 1.59 g (83%); m.p.: 116–117 °C (ethanol); ^{1}H NMR ($CDCl_3$): $\delta = 2.67$ (t, $J = 6.4$ Hz, 2H, CH_2), 2.90 (t, $J = 7.0$ Hz, 2H, CH_2), 3.86 (s, 3H, OCH_3); 3.88 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.50 (d, $J = 1.8$ Hz, 1H, Ar–H), 6.58 (dd, $J = 2.1$, 8.7 Hz, 1H, Ar–H), 6.75 (d, $J = 2.1$ Hz, 1H, Ar–H), 6.80 (dd, $J = 2.1$, 8.7 Hz, 1H, Ar–H), 7.11 (d, $J = 15.6$ Hz, 1H, =CH), 7.70 (d, $J = 8.4$ Hz, 1H, Ar–H), 7.75 (d, $J = 8.6$ Hz, 1H, Ar–H), 8.13 (d, $J = 15.6$ Hz, 1H, =CH) ppm; IR: $\bar{\nu} = 2{,}937$, 2,834, 1,644, 1,609, 1,585, 1,491, 1,321 cm^{-1}; MS: *m/z* (%) = 386.1 (28) [M + 2], 384.1 (100) [M], 348.1 (22), 208.0 (21).

(2E)-3-(1-Chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-1-(2,5-dimethoxyphenyl)prop-2-en-1-one
(**6d**, $C_{22}H_{21}ClO_4$)
Yield 1.60 g (83%); m.p.: 119–120 °C (ethanol); ^{1}H NMR ($CDCl_3$): $\delta = 2.67$ (t, $J = 7.0$ Hz, 2H, CH_2), 2.90 (t, $J = 7.4$ Hz, 2H, CH_2), 3.85 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.50 (d, $J = 1.8$ Hz, 1H, Ar–H), 6.58 (dd, $J = 2.1$, 8.7 Hz, 1H, Ar–H), 6.75 (d, $J = 2.1$ Hz, 1H, Ar–H); 6.80 (dd, $J = 2.1$, 8.7 Hz, 1H, Ar–H); 7.11 (d, $J = 15.6$ Hz, 1H, =CH); 7.70 (d, $J = 8.4$ Hz, 1H, Ar–H), 7.75 (d, $J = 8.6$ Hz, 1H, Ar–H), 8.13 (d, $J = 15.6$ Hz, 1H, =CH) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 30.31$, 32.06, 55.40, 55.42, 55.44, 110.91, 111.21, 115.32, 116.11, 120.99, 121.81, 127.33, 127.62, 128.81, 133.57, 134.51, 139.03, 149.21, 153.75, 153.81, 159.97, 189.52 ppm; IR: $\bar{\nu} = 2{,}937$, 2,835, 1,646, 1,610, 1,589, 1,495, 1,328 cm^{-1}; MS: *m/z* (%) = 416.1 (31) [M + 2], 414.1 (100) [M], 379.2 (23).

(2E)-3-(1-Chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-1-(3,5-dimethoxyphenyl)prop-2-en-1-one
(**6e**, $C_{22}H_{21}ClO_4$)
Yield 1.57 g (82%); m.p.: 114–115 °C (ethanol); ^{1}H NMR ($CDCl_3$): $\delta = 2.69$ (t, $J = 7.2$ Hz, 2H, CH_2), 2.91 (t, $J = 7.1$ Hz, 2H, CH_2), 3.84 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.66 (d, $J = 2.1$ Hz, 1H, Ar–H), 6.74 (d, $J = 1.2$ Hz, 1H, Ar–H), 6.80 (dd, $J = 2.3$, 8.7 Hz, 1H, Ar–H), 7.02 (d, $J = 15.6$ Hz, 1H, =CH), 7.10 (d, $J = 2.1$ Hz, 2H, Ar–H), 7.70 (d, $J = 8.7$ Hz, 1H, Ar–H), 8.25 (d, $J = 15.3$ Hz, 1H, =CH) ppm; IR: $\bar{\nu} = 2{,}938$, 2,836, 1,652, 1,569, 1,495, 1,315 cm^{-1}.

(2E)-3-(1-Chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one
(**6f**, $C_{23}H_{23}ClO_5$)
Yield 1.64 g (79%); m.p.: 135–136 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.71$ (t, $J = 6.9$ Hz, 2H, CH_2), 2.92 (t, $J = 7.0$ Hz, 2H, CH_2), 3.84 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3), 6.74 (d, $J = 2.4$ Hz, 1H, Ar–H), 6.80 (dd, $J = 2.4$, 8.7 Hz, 1H, Ar–H), 6.99 (d, $J = 15.6$ Hz, 1H, =CH), 7.22 (d, $J = 2.1$ Hz, 2H, Ar–H), 7.70 (d, $J = 8.7$ Hz, 1H, Ar–H), 8.25 (d, $J = 15.3$ Hz, 1H, =CH) ppm; IR: $\bar{\nu} = 2{,}938$, 2,839, 1,653, 1,569, 1,495, 1,344 cm^{-1}.

General procedure for the synthesis of ***7***

A mixture of **6** (0.15 mmol) and malononitrile (0.15 mmol) in 10 cm^3 alcohol containing a catalytic amount (0.005 g) of potassium hydroxide was stirred at 30–35 °C for 14 h. The precipitated solid was isolated by filtration, washed with water, dried, and recrystallized from a suitable solvent to furnish compounds **7** in 68–74% yield.

4-(1-Chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-6-(4-fluorophenyl)-2-methoxynicotinonitrile
(**7a**, $C_{24}H_{18}ClFN_2O_2$)
Yield 0.046 g (73%); m.p.: 206–207 °C (methanol); ^{1}H NMR ($CDCl_3$): $\delta = 2.75$ (t, $J = 7.0$ Hz, 2H, CH_2), 2.99 (t, $J = 6.9$ Hz, 2H, CH_2), 3.84 (s, 3H, OCH_3), 4.17 (s, 3H, OCH_3), 6.76 (d, $J = 2.3$ Hz, 1H, Ar–H), 6.79 (dd, $J = 2.1$, 7.8 Hz, 1H, Ar–H), 7.16 (t, $J = 8.1$ Hz, 2H, Ar–H), 7.32 (s, 1H, Ar–H), 7.63 (d, $J = 8.4$ Hz, 1H, Ar–H), 8.06 (t, $J = 7.2$ Hz, 2H, Ar–H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 20.02$, 32.24, 55.23, 55.54, 94.29, 111.19, 111.42, 116.01 (2C), 116.29, 120.21, 123.09, 127.01, 129.13 (2C), 129.49, 132.21, 133.19, 139.14, 139.62, 141.12, 159.65, 160.70, 164.47 ppm; IR: $\bar{\nu} = 2{,}956$, 2,935, 2,230, 1,600, 1,580, 1,543, 1,449, 1,350, 1,263 cm^{-1}.

4-(1-Chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-2-ethoxy-6-(4-fluorophenyl)nicotinonitrile
(**7b**, $C_{25}H_{20}ClFN_2O_2$)
Yield 0.047 g (72%); m.p.: 163–164 °C (ethanol); ^{1}H NMR ($CDCl_3$): $\delta = 1.54$ (t, $J = 7.2$ Hz, 3H, CH_3), 2.75 (t, $J = 7.1$ Hz, 2H, CH_2), 3.02 (t, $J = 6.9$ Hz, 2H, CH_2), 3.84 (s, 3H, OCH_3), 4.63 (q, $J = 6.8$ Hz, 2H, CH_2), 6.74 (d, $J = 2.1$ Hz, 1H, Ar–H), 6.79 (dd, $J = 2.3$, 8.1 Hz, 1H,

Ar–H), 7.15 (t, $J = 8.1$ Hz, 2H, Ar–H), 7.29 (s, 1H, Ar–H), 7.62 (d, $J = 8.1$ Hz, 1H, Ar–H), 8.04 (t, $J = 7.4$ Hz, 2H, Ar–H) ppm; IR: $\bar{\nu} = 2{,}935$, 2,218, 1,607, 1,585, 1,431, 1,324, 1,257 cm^{-1}; MS: *m/z* (%) = 436.5 (38) [M + 2], 434.6 (100) [M], 390.6 (21), 278.2 (43).

4-(1-Chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-6-(4-fluorophenyl)-2-propoxynicotinonitrile
(**7c**, $C_{26}H_{22}ClFN_2O_2$)
Yield 0.048 g (71%); m.p.: 139–140 °C (methanol); ^1H NMR ($CDCl_3$): $\delta = 1.6$ (t, $J = 6.8$ Hz, 3H, CH_3), 1.92 (sext, $J = 6.4$ Hz, 2H, CH_2), 2.75 (t, $J = 7.4$ Hz, 2H, CH_2), 3.12 (t, $J = 7.0$ Hz, 2H, CH_2), 3.84 (s, 3H, OCH_3), 4.53 (t, $J = 6.9$ Hz, 2H, CH_2), 6.73 (d, $J = 2.3$ Hz, 1H, Ar–H), 6.81 (dd, $J = 2.1$, 7.4 Hz, 1H, Ar–H), 7.15 (t, $J = 8.1$ Hz, 2H, Ar-H), 7.28 (s, 1H, Ar–H), 7.29 (d, $J = 8.1$ Hz, 1H, Ar–H), 8.05 (t, $J = 8.4$ Hz, 2H, Ar–H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 10.22$, 20.29, 22.12, 32.80, 55.62, 69.92, 94.69, 111.41, 111.60, 116.03 (2C), 116.70, 120.62, 123.59, 127.19, 129.23 (2C), 130.31, 131.92, 132.83, 139.24, 139.69, 141.72, 159.85, 161.20, 163.49 ppm; IR: $\bar{\nu} = 2{,}951$, 2,939, 2,231, 1,601, 1,576, 1,469, 1,359, 1,241 cm^{-1}.

4-(1-Chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-6-(4-methoxyphenyl)-2-methoxynicotinonitrile
(**7d**, $C_{25}H_{21}ClN_2O_3$)
Yield 0.047 g (72%); m.p.: 182–183 °C (methanol); ^1H NMR ($CDCl_3$): $\delta = 2.75$ (t, $J = 6.9$ Hz, 2H, CH_2), 3.00 (t, $J = 7.8$ Hz, 2H, CH_2), 3.84 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 6.76 (d, $J = 2.3$ Hz, 1H, Ar–H), 6.79 (dd, $J = 2.1$, 9.3 Hz, 1H, Ar–H), 7.16 (d, $J = 8.1$ Hz, 2H, Ar–H), 7.32 (s, 1H, Ar–H), 7.63 (d, $J = 8.4$ Hz, 1H, Ar–H), 8.06 (d, $J = 8.2$ Hz, 2H, Ar–H) ppm; IR: $\bar{\nu} = 2{,}917$, 2,848, 2,219, 1,608, 1,583, 1,423, 1,338 cm^{-1}.

4-(1-Chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-2-ethoxy-6-(4-ethoxyphenyl) nicotinonitrile
(**7e**, $C_{26}H_{23}ClN_2O_3$)
Yield 0.048 g (72%); m.p.: 137–138 °C (ethanol); ^1H NMR ($CDCl_3$): $\delta = 1.50$ (t, $J = 7.0$ Hz, 3H, CH_3), 2.74 (t, $J = 7.4$ Hz, 2H, CH_2), 3.01 (t, $J = 7.0$ Hz, 2H, CH_2), 3.84 (s, 3H, OCH_3),; 3.87 (s, 3H, OCH_3), 4.64 (t, $J = 6.9$ Hz, 2H, CH_2), 6.73 (d, $J = 2.1$ Hz, 1H, Ar–H), 6.80 (dd, $J = 2.3$, 8.1 Hz, 1H, Ar–H), 6.98 (d, $J = 8.4$ Hz, 2H, Ar–H), 7.26 (s, 1H, Ar–H), 7.63 (d, $J = 8.1$ Hz, 1H, Ar–H), 8.02 (d, $J = 8.1$ Hz, 2H, Ar–H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 14.09$, 19.71, 33.17, 55.66, 55.91, 64.74, 94.52, 111.21, 111.37, 114.31 (2C), 116.90, 120.52, 122.88, 127.41, 128.42, 128.87 (2C), 130.62, 132.50, 139.01, 139.51, 141.91, 159.03, 159.92, 163.77 ppm; IR: $\bar{\nu} = 2{,}928$, 2,848, 2,220, 1,605, 1,583, 1,515, 1,474, 1,257 cm^{-1}.

4-(1-Chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-6-(4-methoxyphenyl)-2-propoxynicotinonitrile
(**7f**, $C_{27}H_{25}ClN_2O_3$)
Yield 0.048 g (69%); m.p.: 131–132 °C (methanol); ^1H NMR ($CDCl_3$): $\delta = 1.12$ (t, $J = 7.0$ Hz, 3H, CH_3), 1.92 (sext, $J = 6.9$ Hz, 2H, CH_2), 2.76 (t, $J = 6.9$ Hz, 2H, CH_2), 3.04 (t, $J = 7.2$ Hz, 2H, CH_2), 3.87 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 4.55 (t, $J = 6.8$ Hz, 2H, CH_2), 6.77 (d, $J = 2.4$ Hz, 1H, Ar–H), 6.83 (dd, $J = 2.7$, 8.7 Hz, 1H, Ar–H), 7.02 (d, $J = 9.0$ Hz, 2H, Ar–H), 7.31 (s, 1H, Ar–H), 7.66 (d, $J = 8.4$ Hz, 1H, Ar–H), 8.05 (t, $J = 8.7$ Hz, 2H, Ar–H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 10.59$, 20.09, 22.24, 28.45, 55.39, 55.44, 68.82, 102.71, 111.45, 112.13, 114.22 (2C), 115.28, 120.90, 123.14, 126.88, 128.83, 128.97 (2C), 130.03, 132.31, 138.87, 139.35, 141.56, 159.26, 159.92, 164.39 ppm; IR: $\bar{\nu} = 2{,}956$, 2,871, 2,220, 1,600, 1,540, 1,422, 1,345 cm^{-1}.

4-(1-Chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-6-(2,5-dimethoxyphenyl)-2-methoxynicotinonitrile
(**7g**, $C_{26}H_{23}ClN_2O_4$)
Yield 0.050 g (72%); m.p.: 173–174 °C (methanol); ^1H NMR ($CDCl_3$): $\delta = 2.78$ (t, $J = 7.1$ Hz, 2H, CH_2), 3.03 (t, $J = 6.4$ Hz, 2H, CH_2), 3.83 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 6.78 (d, $J = 2.3$ Hz, 1H, Ar–H), 6.83 (dd, $J = 2.4$, 8.4 Hz, 1H, Ar–H), 6.98 (dd, $J = 2.1$, 8.2 Hz, 2H, Ar–H), 7.62 (d, $J = 2.4$ Hz, 1H, Ar–H), 7.66 (s, 1H, Ar–H), 7.67 (d, $J = 8.7$ Hz, 1H, Ar–H) ppm; IR: $\bar{\nu} = 2{,}956$, 2,931, 2,231, 1,600, 1,580, 1,538, 1,443, 1,350 cm^{-1}.

4-(1-Chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-2-ethoxy-6-(2,5-dimethoxyphenyl)nicotinonitrile
(**7h**, $C_{27}H_{25}ClN_2O_4$)
Yield 0.050 g (70%); m.p.: 150–151 °C (ethanol); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.52$ (t, $J = 6.9$ Hz, 3H, CH_3); 2.78 (t, $J = 7.2$ Hz, 2H, CH_2); 3.04 (t, $J = 6.8$ Hz, 2H, CH_2); 3.84 (s, 3H, OCH_3); 3.85 (s, 3H, OCH_3); 3.86 (s, 3H, OCH_3); 4.63 (t, $J = 7.8$ Hz, 2H, CH_2); 6.77 (d, $J = 2.3$ Hz, 1H, Ar–H), 6.83 (dd, $J = 2.4$, 8.4 Hz, 1H, Ar–H); 6.98 (dd, $J = 2.1$, 8.2 Hz, 2H, Ar–H), 7.62 (d, $J = 2.4$ Hz, 1H, Ar–H), 7.66 (s, 1H, Ar–H), 7.67 (d, $J = 8.7$ Hz, 1H, Ar–H) ppm; IR: $\bar{\nu} = 2{,}974$, 2,928, 2,218, 1,603, 1,574, 1,543, 1,449, 1,347, 1,268 cm^{-1}.

General procedure for the synthesis of ***9***

A mixture of **6** (0.15 mmol), aroylacetonitriles **8a** or **8b** (0.15 mmol), and 0.035 g ammonium acetate (0.45 mmol) in 10 cm^3 acetic acid was heated under reflux for 12 h. The reaction mixture was cooled to room temperature, the solid precipitated was isolated by filtration, washed with 5 cm^3 water, and dried.

2-(4-Chlorophenyl)-4-(1-chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-6-(4-fluorophenyl)nicotinonitrile (**9a**, $C_{29}H_{19}Cl_2FN_2O$)

Yield 0.055 g (73%); m.p.: 188–189 °C; ^{1}H NMR ($CDCl_3$): $\delta = 2.79$ (t, $J = 7.1$ Hz, 2H, CH_2), 3.01 (t, $J = 7.8$ Hz, 2H, CH_2), 3.80 (s, 3H, OCH_3), 6.90 (d, $J = 2.3$ Hz, 1H, Ar–H), 6.94 (dd, J = 2.4, 8.3 Hz, 1H, Ar–H), 7.39 (t, $J = 8.7$ Hz, 2H, Ar–H), 7.57 (s 1H, Ar–H), 7.67 (d, J = 8.4 Hz, 2H, Ar–H), 8.01 (d, $J = 8.1$ Hz, 2H, Ar–H), 8.25 (d, $J = 8.4$ Hz, 1H, Ar–H), 8.35 (t, $J = 6.6$ Hz, 2H, Ar–H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 27.99$, 30.06, 54.83, 105.04, 112.36, 114.03, 116.41, 116.58, 117.31, 118.83, 124.58, 126.65, 129.16 (2C), 130.27, 130.43, 130.64, 131.11, 131.37 (2C), 133.63, 135.71, 136.67, 138.59, 155.82, 158.11, 159.99, 160.59, 163.67 ppm; IR: $\bar{\nu} = 2{,}959$, 2,837, 2,363, 2,344, 1,670, 1,599, 1,410, 1,390, 1,284 cm^{-1}; MS: *m/z* (%) = 505.2 (32) [M + 4], 503.2 (26) [M + 2], 501.3 (100) [M], 430.1 (58), 326.3 (24).

2-(4-Bromophenyl)-4-(1-chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-6-(4-flurophenyl)nicotinonitrile (**9b**, $C_{29}H_{19}BrC1FN_2O$)

Yield 0.059 g (72%); m.p.: 201–202 °C; ^{1}H NMR ($CDCl_3$): $\delta = 2.82$ (t, $J = 6.9$ Hz, 2H, CH_2), 3.03 (t, $J = 7.2$ Hz, 2H, CH_2), 3.87 (s, 3H, OCH_3), 6.90 (d, $J = 2.1$ Hz, 1H, Ar–H), 6.95 (dd, $J = 2.3$, 8.7 Hz, 1H, Ar–H), 7.40 (t, $J = 8.6$ Hz, 2H, Ar–H), 7.82 (d, $J = 8.2$ Hz, 2H, Ar–H), 7.95 (d, $J = 8.7$ Hz, 2H, Ar–H), 8.25 (d, $J = 8.3$ Hz, 1H, Ar–H), 8.27 (s 1H, Ar–H), 8.36 (t, $J = 8.7$ Hz, 2H, Ar–H) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 27.89$, 31.14, 55.61, 104.84, 112.55, 113.93, 116.43 (2C), 117.63, 118.91, 121.79, 126.82, 129.28 (2C), 129.97 (2C), 130.88, 132.21, 132.39 (2C), 132.59, 134.78, 136.34, 138.85, 154.98, 158.35, 160.04, 161.01, 163.89 ppm; IR: $\bar{\nu} = 2{,}979$, 2,828, 2,347, 2,326, 1,661, 1,615, 1,423, 1,401, 1,274 cm^{-1}.

2-(4-Chlorophenyl)-4-(1-chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-6-(4-methoxyphenyl)nicotinonitrile (**9c**, $C_{30}H_{22}Cl_2N_2O_2$)

Yield 0.055 g (71%); m.p.: 176–177 °C; ^{1}H NMR ($CDCl_3$): $\delta = 2.79$ (t, J = 6.6 Hz, 2H, CH_2), 3.02 (t, $J = 6.8$ Hz, 2H, CH_2), 3.83 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.75 (d, $J = 2.4$ Hz, 1H, Ar–H), 6.79 (dd, $J = 2.7$, 6.9 Hz, 1H, Ar–H), 7.00 (d, $J = 9.0$ Hz, 2H, Ar–H), 7.49 (d, $J = 8.7$ Hz, 2H, Ar–H), 7.65 (s, 1H, Ar–H), 7.78 (d, $J = 8.7$ Hz, 2H, Ar–H), 7.98 (d, $J = 8.4$ Hz, 1H, Ar–H), 8.10 (d, J = 9.0 Hz, 2H, Ar–H) ppm; IR: $\bar{\nu} = 2{,}933$, 2,839, 2,331, 2,336, 1,578, 1,497, 1,278 cm^{-1}.

2-(4-Bromophenyl)-4-(1-chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-6-(4-methoxyphenyl)nicotinonitrile (**9d**, $C_{30}H_{22}BrClN_2O_2$)

Yield 0.06 g (72%); m.p.: 188–189 °C; ^{1}H NMR ($CDCl_3$): $\delta = 2.81$ (t, $J = 7.6$ Hz, 2H, CH_2), 3.05 (t, $J = 6.8$ Hz, 2H, CH_2), 3.83 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.77 (d, $J = 2.4$ Hz, 1H, Ar–H), 6.82 (dd, $J = 2.7$, 6.9 Hz, 1H, Ar–H), 7.00 (d, $J = 8.4$ Hz, 2H, Ar–H), 7.58 (d, $J = 8.7$ Hz, 2H, Ar–H), 7.68 (s, 1H, Ar–H), 7.74 (d, $J = 8.7$ Hz, 2H, Ar–H), 7.95 (d, $J = 8.4$ Hz, 1H, Ar–H), 8.06 (d, $J = 9.0$ Hz, 2H, Ar–H) ppm; IR: $\bar{\nu} = 2{,}940$, 2,828, 2,336, 2,234, 1,571, 1,487, 1,270 cm^{-1}.

2-(4-Chlorophenyl)-4-(1-chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-6-(2,5-dimethoxyphenyl)nicotinonitrile (**9e**, $C_{31}H_{24}Cl_2N_2O_3$)

Yield 0.057 g (70%); m.p.: 182–183 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.78$ (t, $J = 7.2$ Hz, 2H, CH_2), 3.02 (t, $J = 7.8$ Hz, 2H, CH_2), 3.86 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.79 (d, $J = 2.4$ Hz, 1H, Ar–H), 6.82 (d, $J = 2.3$, 8.2 Hz, 1H, Ar–H), 6.80 (dd, $J = 2.1$, 6.7 Hz, 1H, Ar–H), 6.89 (d, $J = 2.3$ Hz, 1H, Ar–H), 7.01 (dd, $J = 8.7$ Hz, 1H, Ar–H), 7.53 (d, $J = 8.7$ Hz, 2H, Ar–H), 7.61 (d, $J = 2.4$ Hz, 1H, Ar–H), 7.67 (d, $J = 8.7$ Hz, 1H, Ar–H), 7.81 (s, 1H, Ar–H), 8.21 (d, $J = 8.7$ Hz, 2H, Ar–H) ppm; IR (KBr): $\bar{\nu} = 2{,}923$, 2,869, 2,309, 2,266, 1,578, 1,458, 1,271 cm^{-1}.

2-(4-Bromophenyl)-4-(1-chloro-6-methoxy-3,4-dihydronaphthalen-2-yl)-6-(2,5-dimethoxyphenyl)nicotinonitrile (**9f**, $C_{31}H_{24}BrClN_2O_3$)

Yield 0.062 g (70%); m.p.: 198–199 °C; ^{1}H NMR ($CDCl_3$): $\delta = 2.80$ (t, $J = 7.0$ Hz, 2H, CH_2), 3.04 (t, $J = 7.2$ Hz, 2H, CH_2), 3.85 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 6.79 (d, $J = 2.1$ Hz, 1H, Ar–H), 6.84 (dd, $J = 2.4$, 8.7 Hz, 1H, Ar–H), 6.99 (d, $J = 2.4$ Hz, 1H, Ar–H), 7.01 (dd, $J = 8.7$ Hz, 1H, Ar–H), 7.58 (d, $J = 8.7$ Hz, 2H, Ar–H), 7.64 (d, $J = 2.4$ Hz, 1H, Ar–H), 7.70 (d, $J = 8.7$ Hz, 1H, Ar–H), 7.99 (d, $J = 8.7$ Hz, 2H, Ar–H), 8.02 (s, 1H, Ar–H) ppm; IR: $\bar{\nu} = 3{,}012$, 2,815, 2,342, 2,236, 1,558, 1,507, 1,318 cm^{-1}.

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