# A Novel Synthesis of Benzo[*h*]quinolines and Study of their Fluorescence Properties



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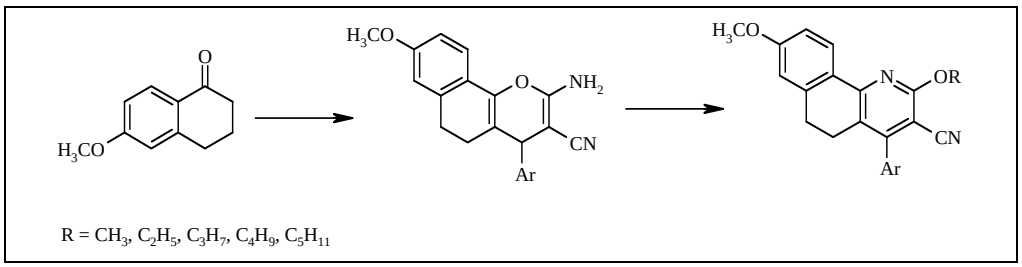


An elegant synthesis of highly fluorescent benzo[*h*]quinolines have been accomplished from readily available and highly economical 6-methoxy-1-tetralone in high purity and excellent yield.

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## INTRODUCTION

Benzo[*h*]quinolines have been described in bacteriology [1], chromosomal aberrations [2], fungal biotransformation [3], drug metabolizing enzyme induction [4] and are extensively used in hightechnology electronic applications such as light emitting device [5], electroluminescent device [6], electrolyte batteries [7] and fiber optics [8]. In contrast to the coumarins ubiquitously used as fluorescent dyes [9], less attention has been paid to the quinolines, particularly, benzo[*h*]quinolines probably because of their lower extinction coefficients, hypsochromic absorption maxima, and more cumbersome tuning of photophysical properties. However, benzo[*h*]-quinolines are more resistant against pH changes (ring opening) and bleaching caused by chemical or thermal tackles. Nonetheless quinolines, which absorb at 335 nm have found applications in fluorescence analysis as well as in 'antenna-sensitized' luminescence [10]. The benzo-[*h*]quinolines are highly fluorescent organic compounds and are used in the dying of specialty papers *e.g*. security papers [11]. The strong fluorescence of these compounds has attracted us to synthesize this particular family of compounds.

We have recently reported facile synthetic routes towards benzo[*h*]quinolines, fused quinolines, pyrazolopyridine, pyrazoloquinoline and pyrazolopyridopyrimidine derivatives, [12-15]. Here in we are reporting synthesis and study of photophysical properties of benzo-[*h*]quinolines. On the basis of spectral results of the synthesized benzo[*h*]quinoline analogues library, sixteen new benzo[*h*]quinolines were then designed, and all of them showed very good absorption and emission maxima.

## RESULTS AND DISCUSSION

The synthesis of benzo[*h*]quinolines **4** were achieved from a highly economical starting material, 6-methoxy-1-tetralone **1**. Compounds **3** were used as a precursor for the synthesis of compounds **4**. Thus the synthesis of benzo[*h*]quinolines **4** were achieved by the reaction of compounds **3** with primary alcohols such as methanol, ethanol, 1-propanol, 1-butanol or 1-pentanol containing catalytic amount of potassium hydroxide at 60-120 ºC furnished desired compounds **4**. Completion of reaction was monitored by thin layer chromatography (TLC). All products were collected by suction filtration, washed with methanol and purified by using suitable solvent, affording the titled compounds **4** in good yield.

It was interesting to note that the ether linkage at position 2 in benzo[*h*]quinolines **4** is dependent on the type of alcohol used at the time of reaction. The mechanism for the formation of benzo[*h*]quinolines **4** from compounds **3** is reported in the literature [16]. Isolated yields of benzo[*h*]quinolines **4** varied widely from 52 to 90 %. The highest yield 90 % was obtained when lower alkyl group such as methyl was used while the lowest yield was obtained when higher alkyl group such as pentyl was used this may be due to steric hindrance of the bulky group. Purity of benzo[*h*]-quinolines **4** were detected by using HPLC chromatogram and found to be more than 97 % pure and did not required any further purification.

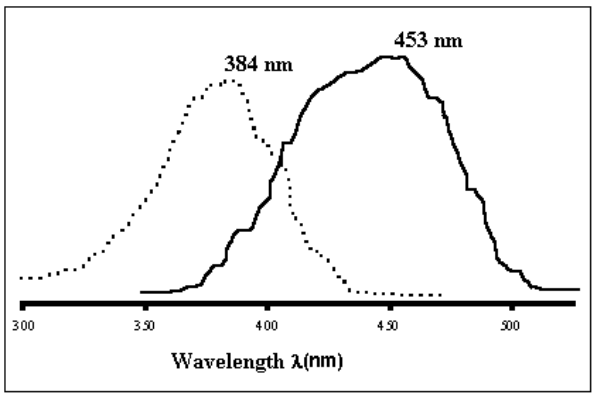



**Figure 1.** The Absorption (dotted line) and Emission spectra of compound (**4f**).

The structures of all the sixteen benzo[*h*]quinolines were confirmed by $^{1}H$ nmr, $^{13}C$ nmr, ir and elemental analysis and found to be in agreement with the structure proposed. From Table 1, it is evident that the incorporation of constituents on to the benzo[*h*]quinoline nucleus at 2-position has profound influence on the absorption and emission properties. It was observed that the substituent at 2-position has less effect on the absorption wavelength but there is considerable increase in the emission wavelength as the aliphatic chain of ether linkage increases. The compound **4f** showed good absorption and emission spectra as shown in the Figure 1.

The reactions reported here represents new synthetic methods towards synthesis of novel fluorescent benzo-[*h*]quinolines, with high yields, simple workup and clean products.

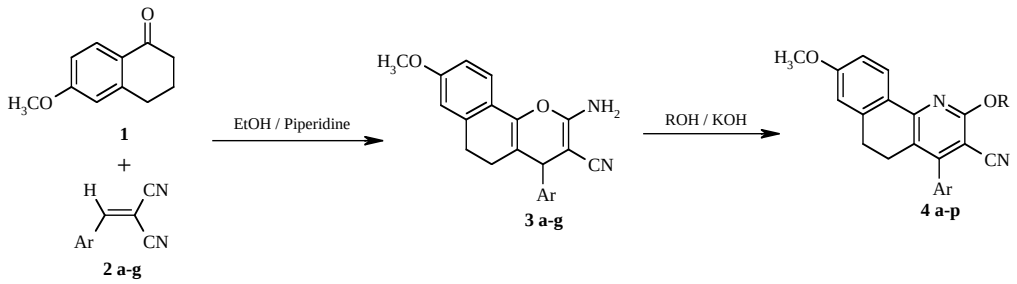
**Table 1.** The Absorbance and Emission $\lambda_{max}$ of benzo[*h*]quinolines (**4a-p**).

| Compd. | Absorbance $\lambda_{max}$ (nm) | Emission $\lambda_{max}$ (nm) | R |
|---|---|---|---|
| (**4a**) | 386 | 408 | $CH_3$ |
| (**4b**) | 390 | 405 | $CH_3$ |
| (**4c**) | 344 | 426 | $CH_3$ |
| (**4d**) | 386 | 430 | $C_2H_5$ |
| (**4e**) | 402 | 439 | $C_2H_5$ |
| (**4f**) | 384 | 453 | $C_3H_7$ |
| (**4g**) | 384.5 | 440 | $C_3H_7$ |
| (**4h**) | 385 | 420 | $C_3H_7$ |
| (**4i**) | 384 | 442 | $C_3H_7$ |
| (**4j**) | 385 | 446 | $C_4H_9$ |
| (**4k**) | 386 | 445 | $C_4H_9$ |
| (**4l**) | 386.5 | 440 | $C_4H_9$ |
| (**4m**) | 383.5 | 447 | $C_4H_9$ |
| (**4n**) | 384.5 | 450 | $C_5H_{11}$ |
| (**4o**) | 383 | 451 | $C_5H_{11}$ |
| (**4p**) | 384.5 | 412 | $C_5H_{11}$ |

## EXPERIMENTAL

Melting points were determined on a Gallenkamp Melting Point Apparatus, Mod. MFB-595 in open capillary tubes and are uncorrected. The $^{1}H$ and $^{13}C$ nmr spectra were recorded on a Varian XL-300 spectrometer (300 MHz). Chemical shifts are reported in ppm from internal tetramethylsilane standard and are given δ-units. The solvents for nmr spectra was duteriochloroform unless otherwise stated. Infrared spectra were taken on Shimadzu IR-408, a Shimadzu FTIR instrument in potassium bromide pellets unless otherwise stated. UV Spectra were recorded on a Shimadzu UV-1601 UV–visible Spectrophotometer. Compounds for UV scan were dissolved in methanol. Fluorescence spectra were recorded using RF-5301 PC Spectrofluorophotometer. Compounds for fluorescence

**Scheme I**




| **2** | **Ar** | **3** | **Ar** | **4** | **Ar** | **R** | **4** | **Ar** | **R** |
|---|---|---|---|---|---|---|---|---|---|
| **a** | $C_6H_5$ | **a** | $C_6H_5$ | **a** | *p*-F-$C_6H_5$ | $CH_3$ | **i** | *p*-Cl-$C_6H_5$ | $C_3H_7$ |
| **b** | *m*-Cl-$C_6H_5$ | **b** | *p*-CN-$C_6H_5$ | **b** | *p*-CN-$C_6H_5$ | $CH_3$ | **j** | $C_6H_5$ | $C_4H_9$ |
| **c** | *m*-Br-$C_6H_5$ | **c** | $C_4H_9O$ (Furyl) | **c** | $C_4H_9O$ (Furyl) | $CH_3$ | **k** | *m*-Cl-$C_6H_5$ | $C_4H_9$ |
| **d** | *p*-Cl-$C_6H_5$ | **d** | *p*-F-$C_6H_5$ | **d** | *p*-F-$C_6H_5$ | $C_2H_5$ | **l** | *p*-F-$C_6H_5$ | $C_4H_9$ |
| **e** | *p*-F-$C_6H_5$ | **e** | *m*-Cl-$C_6H_5$ | **e** | *p*-CN-$C_6H_5$ | $C_2H_5$ | **m** | *p*-Cl-$C_6H_5$ | $C_4H_9$ |
| **f** | *p*-CN-$C_6H_5$ | **f** | *m*-Br-$C_6H_5$ | **f** | $C_6H_5$ | $C_3H_7$ | **n** | $C_6H_5$ | $C_5H_{11}$ |
| **g** | $C_4H_9O$ (Furyl) | **g** | *p*-Cl-$C_6H_5$ | **g** | *m*-Cl-$C_6H_5$ | $C_3H_7$ | **o** | *m*-Br-$C_6H_5$ | $C_5H_{11}$ |
| | | | | **h** | *m*-Br-$C_6H_5$ | $C_3H_7$ | **p** | *p*-Cl-$C_6H_5$ | $C_5H_{11}$ |

measurements were dissolved in acetonitrile. UV and fluorescence scans were recorded from 200 to 500 nm. Elemental analyses were performed on a Hosli CH-Analyzer and are within ± 0.4 of the theoretical percentage. All reactions were monitored by thin layer chromatography, carried out on 0.2 mm silica gel 60 F-254 (Merk) plates using UV light (254 and 366 nm) for detection. Common reagents-grade chemicals are either commercially available and were used without further purification or prepared by standard literature procedures

**2-Arylidenemalononitrile (2) and 2-amino-5,6-dihy-dro-8-methoxy-4-aryl-4*H*-benzo[*h*]chromene-3-carbonitrile (3)**. These compounds were synthesized by the literature methods [17] and [13] respectively

**General Procedure for Synthesis of 8-methoxy-4-aryl-2-alcoxy-5,6-dihydrobenzo[*h*]quinoline-3-carbonitrile (4)**. A mixture of **(3)** (10 mmol) in primary alcohols such as methanol, ethanol, 1-propanol, 1-butanol, or 1-pentanol (15 ml) containing catalytic amount of potassium hydroxide (0.5 g) was heated at 60-120 °C for 1-3 h. Completion of reaction was monitored by thin layer chromatography (TLC). The solid obtained on cooling was filtered, washed with methanol, dried and recrystallizd from suitable solvent, furnished the compounds **4** in good yield.

**4-(4-Fluorophenyl)-2,8-dimethoxy-5,6-dihydrobenzo[*h*]-quinoline-3-carbonitrile (4a)**. This compound was obtained as colorless prism (methanol), 3.25 g (90%), mp 198-199 °C; ir: (potassium bromide): 2925, 2860, 2723, 2221, 1556, 1103, 844, 843, 731 $cm^{-1}$. $^1H$ nmr: ($CDCl_3$) δ 2.65 (m, 2H, $CH_2$), 2.82 (m, 2H, $CH_2$), 3.91 (s, 3H, $OCH_3$), 4.19 (s, 3H, $OCH_3$), 6.76 (d, J = 2.4 Hz, $C_{10}H$), 6.91(dd, J = 8.4, 2.4 Hz, $C_9H$), 7.25 (m, 4H, Ar-H), 8.30 (d, J = 8.3 Hz, $C_7H$); $^{13}C$ nmr: ($CDCl_3$) δ 24, 28, 54, 55, 93, 112, 113, 115, 121, 126, 127, 128, 128.5, 129, 135, 140, 153, 154, 161, 162. *Anal*. Calcd. for $C_{22}H_{17}FN_2O_2$: C, 73.34; H, 4.75; N, 7.77. Found: C, 73.22; H, 4.60; N, 7.61.

**4-(4-Cyanophenyl)-2,8-dimethoxy-5,6-dihydrobenzo[*h*]-quinoline-3-carbonitrile (4b)**. This compound was obtained as colorless prism (methanol), 3.11 g (85 %), mp 219-220 °C; ir: (potassium bromide): 2955, 2840, 2721, 2199, 2221, 1536, 1133, 834, 731 $cm^{-1}$; $^1H$ nmr: ($CDCl_3$) δ 2.02 (m, 2H, $CH_2$), 2.68 (m, 2H, $CH_2$), 3.81 (s, 3H, $OCH_3$), 4.17 (s, 3H, $OCH_3$), 6.75 (d, J = 2.4 Hz, $C_{10}H$), 6.90 (dd, J = 8.4, 2.4 Hz, $C_9H$), 7.27 (m, 4H, Ar-H), 8.31 (d, J = 8.4 Hz, $C_7H$); $^{13}C$ nmr: ($CDCl_3$) δ 24, 27, 53, 54, 93, 112, 113, 116, 117, 121, 125, 127, 128, 129, 130, 134, 141, 153, 154, 162, 163. *Anal*. Calcd. for $C_{23}H_{17}N_3O_2$: C, 75.19; H, 4.65; N, 11.43. Found: C, 75.22; H, 4.60; N, 11.51.

**4-(2-Furyl)-2,8-dimethoxy-5,6-dihydrobenzo[*h*]quinoline-3-carbonitrile (4c)**. This compound was obtained as colorless prism (methanol), 2.62 g (79 %), mp 168-169 °C; ir: (potassium bromide): 2931, 2906, 2840, 2723, 2212, 1534, 1425, 1133, 844, 715 $cm^{-1}$. $^1H$ nmr: ($CDCl_3$) δ 2.86 (m, 2H, $CH_2$), 3.01 (m, 2H, $CH_2$), 3.91 (s, 3H, $OCH_3$), 4.18 (s, 3H, $OCH_3$), 6.63 (d, J = 2.4 Hz, $C_{10}H$), 6.80 (dd, J = 8.4, 2.4 Hz, $C_9H$), 7.10 (m, 3H, Ar-H), 8.26 (d, J = 8.4 Hz, $C_7H$). *Anal*. Calcd. for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.43. Found: C, 72.15; H, 4.88; N, 8.59.

**2-Ethoxy-4-(4-fluorophenyl)-8-methoxy-5,6-dihydrobenzo-[*h*]quinoline-3-carbonitrile (4d)**. This compound was obtained as colorless prism (methanol), 3.21 g (86%), mp 185-186 °C; ir: (potassium bromide): 2228, 1606, 1437, 1151, 1028, 866 $cm^{-1}$. $^1H$ nmr: ($CDCl_3$) δ 1.52 (t, 3H, $CH_3$), 2.61 (m, 2H, $CH_2$), 2.81 (m, 2H, $CH_2$), 3.91 (s, 3H, $OCH_3$), 4.62 (q, 2H, $OCH_2$), 6.67 (d, J = 2.4 Hz, $C_{10}H$), 6.91(dd, J = 8.4, 2.4 Hz, $C_9H$), 7.27 (m, 4H,Ar-H), 8.25(d, J = 8.4 Hz, $C_7H$); $^{13}C$ nmr: ($CDCl_3$) δ 14, 24, 28, 55, 62, 93, 112, 113, 115, 121, 122, 126, 127, 128, 130, 137, 140, 152, 153, 161, 162. *Anal*. Calcd. for $C_{23}H_{19}FN_2O_2$: C, 73.80; H, 5.11; N, 7.48. Found: C, 73.70; H, 5.00; N, 7.25.

**4-(4-Cyanophenyl)-2-ethoxy-8-methoxy-5,6-dihydrobenzo-[*h*]quinoline-3-carbonitrile (4e)**. This compound was obtained as colorless prism (methanol), 2.70 g (71 %), mp 205-206 °C; ir: (potassium bromide): 2920, 2854, 2218, 2267, 1427, 1161, 1011, 877 $cm^{-1}$. $^1H$ nmr: ($CDCl_3$) δ 1.51 (t, 3H, $CH_3$), 2.64 (m, 2H, $CH_2$), 280 (m, 2H, $CH_2$), 3.90 (s, 3H, $OCH_3$), 4.63 (q, 2H, $OCH_2$), 6.67 (d, J = 2.4 Hz, $C_{10}H$), 6.92 (dd, J = 8.4, 2.3 Hz, $C_9H$), 7.28 (m, 4H,Ar-H), 8.26 (d, J = 8.3 Hz, $C_7H$); $^{13}C$ nmr: ($CDCl_3$) δ 14, 23, 27, 56, 61, 94, 113, 114, 117, 118, 121, 123, 125, 127, 128, 129, 135, 141, 151, 154, 162, 163. *Anal*. Calcd. for $C_{24}H_{19}N_3O_2$: C, 75.57; H, 5.01; N, 11.01. Found: C, 75.40; H, 4.80; N, 11.19.

**8-Methoxy-4-phenyl-2-propoxy-5,6-dihydrobenzo[*h*]quinoline-3-carbonitrile (4f)**. This compound was obtained as colorless prism (methanol), 3.25 g (88 %), mp 119-120 °C; ir: (potassium bromide): 2947, 2938, 2881, 2218, 1554, 1494, 1375, 1151, 849, 792 $cm^{-1}$; $^1H$ nmr: ($CDCl_3$) δ 1.06 (t, 3H, $CH_3$), 1.87 (m, 2H, $CH_2$), 2.64 (m, 2H, $CH_2$), 2.75 (m, 2H, $CH_2$), 3.85 (s, 3H, $OCH_3$), 4.48 (t, 2H, $OCH_2$), 6.71 (d, J = 2.7 Hz, $C_{10}H$), 6.87 (dd, J = 8.4, 2.7 Hz, $C_9H$), 7.23 (m, 5H, Ar-H), 8.20 (d, J = 8.4 Hz, $C_7H$); $^{13}C$ nmr: ($CDCl_3$) δ 11, 22, 25, 28, 55, 69, 94, 113, 114, 116, 121, 127, 128, 129, 129.2, 129.5, 136, 141, 154, 155, 162, 163. *Anal*. Calcd. for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.70; H, 5.75; N, 7.61.

**4-(3-Chlorophenyl)-8-methoxy-2-propoxy-5,6-dihydrobenzo[*h*]quinoline-3-carbonitrile (4g)**. This compound was obtained as colorless prism (methanol), 3.44 g (85%), mp 130-131 °C; ir: (potassium bromide): 2968, 2941, 2885, 2222, 1558, 1498, 1379, 1155, 852, 796 $cm^{-1}$; $^1H$ nmr: ($CDCl_3$) δ 1.04 (t, 3H, $CH_3$), 1.84 (m, 2H, $CH_2$), 2.61 (m, 2H, $CH_2$), 2.72 (m, 2H, $CH_2$), 3.81 (s, 3H, $OCH_3$), 4.47 (t, 2H, $OCH_2$), 6.71 (d, J = 2.8 Hz, $C_{10}H$), 6.85 (dd, J = 8.4, 2.7 Hz, $C_9H$), 7.25 (m, 4H, Ar-H), 8.17 (d, J = 8.4 Hz, $C_7H$); $^{13}C$ nmr: ($CDCl_3$) δ 14, 22, 28, 38, 55, 64, 93, 115, 116, 119, 122, 124, 129, 130, 131, 133, 134, 135, 141, 146, 154, 156, 162, 164. *Anal*. Calcd. for $C_{24}H_{21}ClN_2O_2$: C, 71.19; H, 5.23; N, 6.92. Found: C, 71.03; H, 5.15; N, 6.81.

**4-(3-Bromophenyl)-8-methoxy-2-propoxy-5,6-dihydrobenzo[*h*]quinoline-3-carbonitrile (4h)**. This compound was obtained as colorless prism (methanol), 3.86 g (86 %), mp 141-142 °C; ir: (potassium bromide): 2961, 2935, 2879, 2216, 1552, 1492, 1373, 1149, 846, 790 $cm^{-1}$; $^1H$ nmr: ($CDCl_3$) δ 1.05 (t, 3H, $CH_3$), 1.83 (m, 2H, $CH_2$), 2.64 (m, 2H, $CH_2$), 2.70 (m, 2H, $CH_2$), 3.83 (s, 3H, $OCH_3$), 4.49 (t, 2H, $OCH_2$), 6.70 (d, J = 2.8 Hz, $C_{10}H$), 6.81 (dd, J = 8.4, 2.7 Hz, $C_9H$), 7.27 (m, 4H, Ar-H), 8.19 (d, J = 8.4 Hz, $C_7H$); $^{13}C$ nmr: ($CDCl_3$) δ 11, 22, 25, 28, 55, 69, 94, 113, 114, 116, 124, 128, 129, 130, 132, 133, 134, 137, 141, 146, 154, 156, 162, 164. *Anal*. Calcd. for $C_{24}H_{21}BrN_2O_2$: C, 64.15; H, 4.71; N, 6.23. Found: C, 64.00; H, 4.53; N, 6.12.

**4-(4-Chlorophenyl)-8-methoxy-2-propoxy-5,6-dihydrobenzo[*h*]quinoline-3-carbonitrile (4i)** This compound was obtained as colorless prism (methanol), 3.19 g (71%), mp 135-136 °C; ir (potassium bromide): 2957, 2917, 2871, 2239, 1554, 1494, 1376, 1152, 849, 794 $cm^{-1}$; $^1H$ nmr: ($CDCl_3$) δ 1.03 (t, 3H, $CH_3$), 1.84 (m, 2H, $CH_2$), 2.60 (m, 2H, $CH_2$), 2.73 (m, 2H, $CH_2$), 3.83 (s, 3H, $OCH_3$), 4.46 (t, 2H, $OCH_2$), 6.69 (d, J = 2.8 Hz, $C_{10}H$), 6.85 (dd, J = 8.4, 2.7 Hz, $C_9H$), 7.21 (m, 4H, Ar-H), 8.17 (d, J = 8.4 Hz, $C_7H$); $^{13}C$ nmr: ($CDCl_3$) δ 11, 22, 25, 28, 55, 69, 94, 113, 114, 116, 121, 124, 126, 129, 130, 133, 135, 141, 144, 152, 153, 163. *Anal*. Calcd. for $C_{24}H_{21}ClN_2O_2$: C, 71.19; H, 5.23; N, 6.92. Found: C, 71.30; H, 5.35; N, 6.80.

**2-Butoxy-8-methoxy-4-phenyl-5,6-dihydrobenzo[*h*]quinoline-3-carbonitrile (4j)**. This compound was obtained as colorless prism (methanol), 2.42 g (63 %), mp 118-119 °C; ir: (potassium bromide): 2925, 2860, 2723, 2221, 1556, 1103, 844, 843, 731 $cm^{-1}$; $^1H$ nmr: ($CDCl_3$) δ 1.00 (t, 3H, $CH_3$), 1.50 (m, 2H, $CH_2$), 1.85 (m, 2H, $CH_2$), 2.62 (m, 2H, $CH_2$), 2.73 (m, 2H, $CH_2$), 3.84 (s, 3H, $OCH_3$), 4.52 (t, 2H, $OCH_2$), 6.71 (d, J = 2.8 Hz, $C_{10}H$), 6.86 (dd, J = 8.4, 2.7 Hz, $C_9H$), 7.21 (m, 5H, Ar-H), 8.21 (d, J = 8.4 Hz, $C_7H$); $^{13}C$ nmr: ($CDCl_3$) δ 14, 19, 25, 28, 31, 55, 67, 113, 114, 116, 121, 123, 126, 127, 128, 129, 130, 131, 134, 139, 141, 154, 162. *Anal*. Calcd. for $C_{25}H_{24}N_2O_2$: C, 78.10; H, 6.29; N, 7.29. Found: C, 78.00; H, 6.30; N, 7.15.

**2-Butoxy-4-(3-chlorophenyl)-8-methoxy-5,6-dihydrobenzo-[*h*]quinoline-3-carbonitrile (4k)**. This compound was obtained as colorless prism (methanol), 2.72 g (65 %), mp 127-128 °C; ir: (potassium bromide): 2994, 2957, 2874, 2225, 1554, 1494, 1369, 1159, 848, 792 $cm^{-1}$; $^1H$ nmr: ($CDCl_3$) δ 1.01 (t, 3H, $CH_3$), 1.53 (m, 2H, $CH_2$), 1.82 (m, 2H, $CH_2$), 2.65 (m, 2H, $CH_2$), 2.73 (m, 2H, $CH_2$), 3.84 (s, 3H, $OCH_3$), 4.54 (t, 2H, $OCH_2$), 6.70 (d, J = 2.8 Hz, $C_{10}H$), 6.84 (dd, J = 8.4, 2.7 Hz, $C_9H$), 7.24 (m, 4H, Ar-H), 8.17 (d, J = 8.4 Hz, $C_7H$); $^{13}C$ nmr: ($CDCl_3$) δ 14, 18, 27, 28, 33, 54, 66, 111, 114, 117, 121, 122, 123, 125, 126, 127, 128, 129, 130, 131, 132, 140, 143, 151, 165. *Anal*. Calcd. for $C_{25}H_{23}ClN_2O_2$: C, 71.68; H, 5.53; N, 6.69. Found: C, 71.70; H, 5.61; N, 6.55.

**2-Butoxy-4-(4-fluorophenyl)-8-methoxy-5,6-dihydrobenzo-[*h*]quinoline-3-carbonitrile (4l)**. This compound was obtained as colorless prism (methanol), 2.77 g (69%), mp 138-139 °C; ir: (potassium bromide): 2963, 2937, 2881, 2221, 1553, 1494, 1375, 1151, 849, 792 $cm^{-1}$; $^1H$ nmr: ($CDCl_3$) δ 1.00 (t, 3H, $CH_3$), 1.51 (m, 2H, $CH_2$), 1.83 (m, 2H, $CH_2$), 2.60 (m, 2H, $CH_2$), 2.76 (m, 2H, $CH_2$), 3.85 (s, 3H, $OCH_3$), 4.53 (t, 2H, $OCH_2$), 6.72 (d, J = 2.8 Hz, $C_{10}H$), 6.88 (dd, J = 8.4, 2.7 Hz, $C_9H$), 7.14 (m, 4H, Ar-H), 8.20 (d, J = 8.4 Hz, $C_7H$); $^{13}C$ nmr: ($CDCl_3$) δ 14, 19, 25, 28, 31, 55, 67, 113, 114, 116, 121, 123, 124, 127, 128, 129, 130, 131, 132, 137, 140, 151, 162.. *Anal*. Calcd. for $C_{25}H_{23}FN_2O_2$: C, 74.61; H, 5.76; N, 6.96. Found: C, 74.70; H, 5.60; N, 6.79.

**2-Butoxy-4-(4-chlorophenyl)-8-methoxy-5,6-dihydrobenzo-[*h*]quinoline-3-carbonitrile (4m)**. This compound was obtained as colorless prism (methanol), 2.55 g (61%), mp 113-114 °C; ir: (potassium bromide): 2984, 2917, 2855, 2244, 1544, 1435, 1375, 1154, 828, 764 $cm^{-1}$; $^1H$ nmr: ($CDCl_3$) δ 1.00 (t, 3H, $CH_3$), 1.50 (m, 2H, $CH_2$), 1.80 (m, 2H, $CH_2$), 2.61 (m, 2H, $CH_2$), 2.76 (m, 2H, $CH_2$), 3.81 (s, 3H, $OCH_3$), 4.56 (t, 2H, $OCH_2$), 6.76 (d, J = 2.8 Hz, $C_{10}H$), 6.84 (dd, J = 8.4, 2.7 Hz, $C_9H$), 7.23 (m, 4H, Ar-H), 8.17 (d, J = 8.4 Hz, $C_7H$); $^{13}C$ nmr: ($CDCl_3$) δ 14, 19, 25, 28, 31, 55, 67, 113, 114, 116, 121, 122, 125, 127, 128, 129, 130, 131, 133, 138, 142, 155, 162. *Anal*. Calcd. for $C_{25}H_{23}ClN_2O_2$: C, 71.68; H, 5.53; N, 6.69. Found: C, 71.58; H, 5.41; N, 6.45.

**8-Methoxy-2-pentyloxy-4-phenyl-5,6-dihydrobenzo[*h*]-quinoline-3-carbonitrile (4n)**. This compound was obtained as colorless prism (methanol), 2.39 g (60 %), mp 140-141°C; ir: (potassium bromide): 2969, 2872, 2219, 1544, 1494, 1376, 1141, 848, 792 $cm^{-1}$; $^1H$ nmr: ($CDCl_3$) δ 0.92 (t, 3H, $CH_3$), 1.37 (m, 4H, $2CH_2$), 1.85 (m, 2H, $CH_2$), 2.62 (m, 2H, $CH_2$), 2.75 (m, 2H, $CH_2$), 3.85 (s, 3H, $OCH_3$), 4.52 (t, 2H, $OCH_2$), 6.71 (d, J = 2.8 Hz, $C_{10}H$), 6.87 (dd, J = 8.4, 2.7 Hz, $C_9H$), 7.23 (m, 5H, Ar-H), 8.20 (d, J = 8.4 Hz, $C_7H$); $^{13}C$ nmr: ($CDCl_3$) δ 14, 23, 25, 28, 29, 41, 55, 67, 113, 114, 116, 121, 127, 128, 129, 130, 134, 135, 138, 141, 154, 155, 162, 163. *Anal*. Calcd. for $C_{26}H_{26}N_2O_2$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.20; H, 6.40; N, 7.14.

**4-(3-Bromophenyl)-8-methoxy-2-pentyloxy-5,6-dihydrobenzo[*h*]quinoline-3-carbonitrile (4o)**. This compound was obtained as colorless prism (methanol), 2.76 g (58 %), mp 155-126 °C; ir: (potassium bromide): 2967, 2941, 2871, 2228, 1559, 1478, 1379, 1159, 846, 782 $cm^{-1}$; $^1H$ nmr: ($CDCl_3$) δ 0.93 (t, 3H, $CH_3$), 1.37 (m, 4H, $2CH_2$), 1.82 (m, 2H, $CH_2$), 2.60 (m, 2H, $CH_2$), 2.76 (m, 2H, $CH_2$), 3.83 (s, 3H, $OCH_3$), 4.51 (t, 2H, $OCH_2$), 6.68 (d, J = 2.8 Hz, $C_{10}H$), 6.84 (dd, J = 8.4, 2.7 Hz, $C_9H$), 7.28 (m, 4H, Ar-H), 8.19 (d, J = 8.4 Hz, $C_7H$); $^{13}C$ nmr: ($CDCl_3$) δ 14, 23, 25, 28, 29, 42, 55, 67, 113, 115, 116, 122, 123, 126, 127, 128, 129, 130, 134, 135, 138, 141, 154, 155, 162, 163. *Anal*. Calcd. for $C_{26}H_{25}BrN_2O_2$: C, 65.41; H, 5.28; N, 5.87. Found: C, 65.50; H, 5.40; N, 5.84.

**4-(4-Chlorophenyl)-8-methoxy-2-pentyloxy-5,6-dihydrobenzo[*h*]quinoline-3-carbonitrile (4p)**. This compound was obtained as colorless prism (methanol), 2.25 g (52 %), mp 170-171 °C; ir: (potassium bromide): 2964, 2937, 2881, 2218, 1554, 1494, 1375, 1151, 848, 792 $cm^{-1}$; $^1H$ nmr: ($CDCl_3$) δ 0.92 (t, 3H, $CH_3$), 1.38 (m, 4H, $2CH_2$), 1.83 (m, 2H, $CH_2$), 2.60 (m, 2H, $CH_2$), 2.76 (m, 2H, $CH_2$), 3.85 (s, 3H, $OCH_3$), 4.52 (t, 2H, $OCH_2$), 6.71 (d, J = 2.8 Hz, $C_{10}H$), 6.87 (dd, J = 8.4, 2.7 Hz, $C_9H$), 7.23 (m, 4H, Ar-H), 8.20 (d, J = 8.4 Hz, $C_7H$); $^{13}C$ nmr: ($CDCl_3$) δ 14, 23, 25, 28, 29, 40, 55,

67, 113, 114, 116, 121, 123, 124, 125, 127, 128, 129, 133, 135, 138, 151, 159, 163. *Anal*. Calcd. for $C_{26}H_{25}ClN_2O_2$: C, 72.13; H, 5.82; N, 6.47. Found: C, 72.00; H, 5.80; N, 6.30.

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