# SYNTHESIS OF 6-METHOXY-5,8-QUINOLINEDIONES AND 8-METHOXY-5,6-QUINOLINEDIONES USING OXIDATIVE DEMETHYLATION WITH CERIUM (IV) AMMONIUM NITRATE

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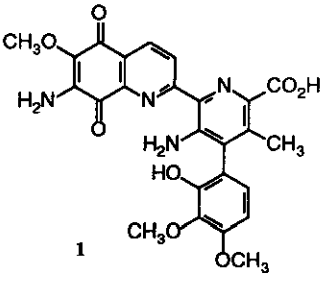
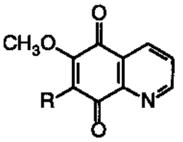
**Abstract** —— 6-Methoxy-5,8-quinolinediones (**14-19**) and 8-methoxy-5,6-quinolinediones (**20-25**) were synthesized by oxidative demethylation of the corresponding 5,6,8-trimethoxyquinolines (**5**, **7-9**, **12**, **13**) with cerium (IV) ammonium nitrate.

Streptonigrin (**1**), a highly substituted 5,8-quinolinedione, was first reported as an antitumor antibiotic produced by *Streptomyces flocculus*.[1] It was later found to be one of the most potent inhibitors of avian myeloblastosis virus reverse transcriptase (AMV-RT), but its remarkable cytotoxic activity seemed to be disadvantageous with respect to a specific inhibitor of retrovirus.[2] The 7-amino-6-methoxy-5,8-quinolinedione moiety in **1** was proved to be the minimum entity to show the inhibition of AMV-RT. We observed that 6-methoxy-5,8-quinolinedione (**16a**) and 6-methoxy-7-methyl-5,8-quinolinedione (**16b**) were much less toxic than **1**, while the activity of **16a, b** against AMV-RT was comparable to that of **1**.[2b] Furthermore, we examined the inhibitory activities agaist AMV-RT and cytotoxic activities against mouse lymphoblastoma L5178Y cells by a series of synthetic heterocyclic quinones, consisting of (6-methoxy-)5,8-quinolinediones, (8-methoxy-)5,6-quinolinediones, 5,8-isoquinolinediones, 5,6-isoquinolinediones, 7,8-isoquinolinediones, and 5,8-quinoxalinediones.[3] We wish to report here the synthetic details of 6-methoxy-5,8-quinolinediones and 8-methoxy-5,6-quinolinediones.



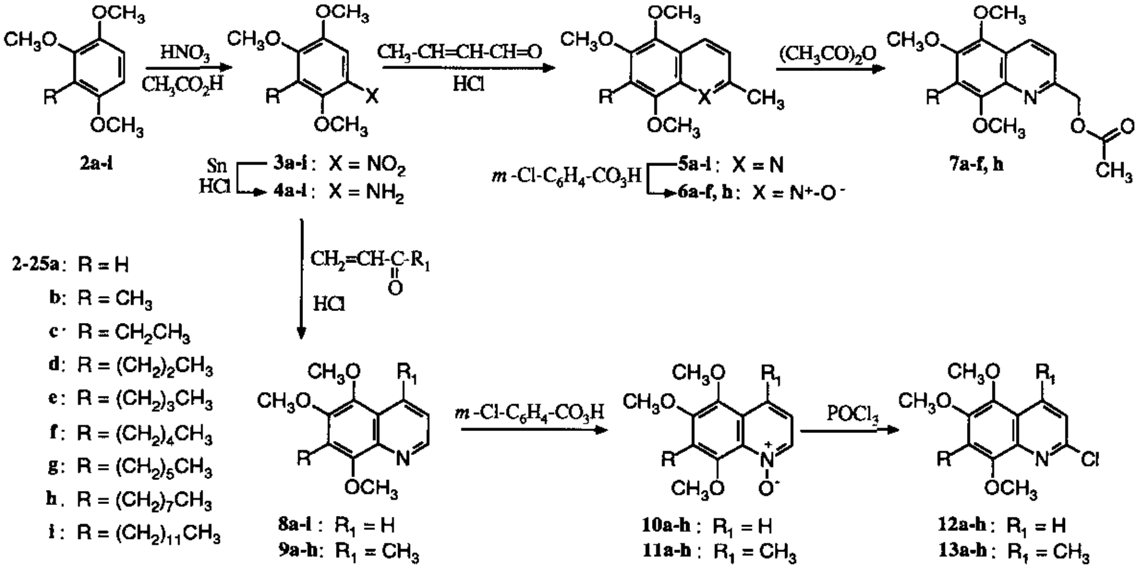
**1**

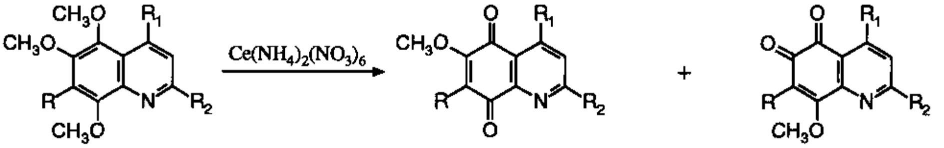


**16a**: R = H
**b**: R = $CH_3$

2,4,5-Trimethoxyanilines (**4a-i**) prepared from the corresponding 1,2,4-trimethoxybenzenes (**2a-i**), were heated with crotonaldehyde in 6 N hydrochloric acid to give 5,6,8-trimethoxy-2-methylquinolines (**5a-i**) in 51-88%

yields. 2-Methylquinoline *N*-oxides (**6a-f, h**) obtained by oxidation of the quinolines (**5a-f, h**) with *m*-chloroperoxybenzoic acid, were refluxed in acetic anhydride to afford the corresponding 2-acetoxymethylquinolines (**7a-f, h**) in 54-88% yields. Furthermore, the trimethoxyanilines (**4d-i**) were refluxed with acrolein in 6 N hydrochloric acid to give the corresponding 5,6,8-trimethoxyquinolines (**8d-i**) in 42-66% yields. Treatment of **4a-f** with methyl vinyl ketone in refluxing 6 N hydrochloric acid afforded the corresponding 4-methylquinolines (**9a-f**) in 22-68% yields. 5,6,8-Trimethoxy-4-methyl-7-hexyl- (or 7-octyl)quinoline (**9g, h**) was obtained by heating of **4g** (or **4h**) with methyl vinyl ketone in ethanol containing *m*-nitrobenzenesulfonic acid and hydrochloric acid in 69-75% yields. The *N*-oxides (**10a-h, 11a-h**) obtained by oxidation of the quinolines (**8a-h, 9a-h**) with *m*-chloroperoxybenzoic acid, were heated with phosphorous oxychloride to afford the corresponding 2-chloroquinolines (**12a-h, 13a-h**) in 63-89% yields.



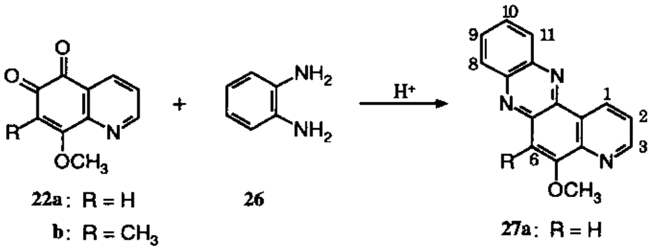


**5a-i** : $R_1$= H, $R_2$= $CH_3$
**7a-f, h** . $R_1$= H, $R_2$= $CH_2OCOCH_3$
**8a-i** : $R_1$= $R_2$= H
**9a-h** : $R_1$= $CH_3$, $R_2$= H
**12a-h** : $R_1$= H, $R_2$= Cl
**13a-h** : $R_1$= $CH_3$, $R_2$= Cl

**14a-i**: $R_1$= H, $R_2$= $CH_3$
**15a-f, h**: $R_1$= H, $R_2$= $CH_2OCOCH_3$
**16a-i** : $R_1$= $R_2$= H
**17a-h**: $R_1$= $CH_3$, $R_2$= H
**18a-h**: $R_1$= H, $R_2$= Cl
**19a-h**: $R_1$= $CH_3$, $R_2$= Cl

**20a-h**: $R_1$= H, $R_2$= $CH_3$
**21a** : $R_1$= H, $R_2$= $CH_2OCOCH_3$
**22a-c**: $R_1$= $R_2$= H
**23a-h** : $R_1$= $CH_3$, $R_2$= H
**24a**: $R_1$= H, $R_2$= Cl
**25b-d, g** : $R_1$= $CH_3$, $R_2$= Cl

Oxidative demethylation of 7-unsubstituted 5,6,8-trimethoxyquinolines (**5a**, **7a**, **8a**, **9a**) with cerium (IV) ammonium nitrate (CAN) in aqueous acetonitrile containing pyridine-2,6-dicarboxylic acid *N*-oxide[4] afforded the corresponding *p*-quinones (**14a**, **15a**, **16a**, **17a**; 32-54% yields) and *o*-quinones (**20a**, **21a**, **22a**, **23a**; 22-60% yields). 7-Alkyl-5,6,8-trimethoxy-2-methylquinolines (**5b-h**), 7-alkyl-5,6,8-trimethoxyquinolines (**8b**, **c**), 7-alkyl-5,6,8-trimethoxy-4-methylquinolines (**9b-h**) and 2-chloro-5,6,8-trimethoxy(-4-methyl)quinolines (**12a**, **13b-d**, **g**) were oxidized with CAN to give the corresponding *p*-quinones (**14b-h**, **16b**, **c**, **17b-h**, **18a**, **19b-d**, **g**; major products, 31-84% yields) and *o*-quinones (**20b-h**, **22b**, **c**, **23b-h**, **24a**, **25b-d**, **g**; minor products, 6-30% yields). In contrast, oxidative demethylation of other 5,6,8-trimethoxyquinolines (**5i**, **7b-f**, **h**, **8d-i**, **12b-h**, **13a**, **e**, **f**, **h**) afforded the corresponding *p*-quinones (**14i**, **15b-f**, **h**, **16d-i**, **18b-h**, **19a**, **e**, **f**, **h**) in 34-91% yields; but no *o*-quinones. The *o*-quinone structures for **22a**, **b** were further characterized by way of the *o*-phenylenediamine condensation products, *i.e.* pyridophenazines (**27a**, **b**). The spectral data of 6-methoxy-5,8-quinolinediones (**14-19**) and 8-methoxy-5,6-quinolinediones (**20-25**) are given in Table I.



**22a**: R = H
**b**: R = $CH_3$

**26**

**27a**: R = H
**b**: R = $CH_3$

## EXPERIMENTAL

All melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. $^1$H-Nmr spectra were measured at 270 (or 400) MHz in $CDCl_3$ (unless otherwise noted) with tetramethylsilane as an internal standard. All reactions were run with magnetic stirring. Anhydrous sodium sulfate was used for drying organic solvent extracts, and the solvent was removed with a rotary evaporator and finally under high vacuum. Column chromatography (flash chromatography) was performed with silica gel 60 (230-400 mesh). 1,2,4-Trimethoxybenzenes (**2a-c**, **e**, **g**, **h**), 1,2,4-trimethoxy-5-nitrobenzenes (**3a-c**), 2,4,5-trimethoxyanilines (**4a-c**), 5,6,8-trimethoxyquinolines (**8a-c**), and 5,6,8-trimethoxyquinoline *N*-oxides (**10a-c**) were prepared as described.[5]

**3-Alkyl-1,2,4-trimethoxybenzenes (2d, f, i)** *n*-Butyllithium (1.5 M hexane solution, 16 ml) was added dropwise to a solution of 1,2,4-trimethoxybenzene (**2a**) (3.36 g, 20 mmol) in dry THF (30 ml) at 0 – 5°C. The whole was kept at 0 – 5°C for 1 h, then 1-iodopropane (or 1-iodopentane, 1-iodododecane) (22 mmol) was added dropwise at 0 – 5°C. The mixture was allowed to warm to room temperature for 30 min, kept for 1.5 h, quenched with water (150 ml), and extracted with ether (3 x 80 ml). The extract was washed with brine, dried, and evaporated. The residue was chromatographed (eluting with ethyl acetate–hexane 1:9) to afford **2d**, **f**, **i** as an oil.

**2d**: Yield 77%. Ms *m/z* (%): 210 ($M^+$, 100), 195 (28), 181 (65), 166 (49). High-resolution ms Calcd for $C_{12}H_{18}O_3$: 210.1256. Found: 210.1237. $^1$H-Nmr (400 MHz) δ: 0.96 (3H, t, $J$ = 7.3 Hz, $CH_2CH_3$), 1.53 (2H, sextet, $J$ = 7.3 Hz, $CH_2CH_3$), 2.61 (2H, t, $J$ = 7.3 Hz, $CH_2CH_2CH_3$), 3.77 (3H, s, $OCH_3$), 3.82 (6H, s, 2$OCH_3$), 6.54 (1H, d, $J$ = 8.9 Hz, $C_5$-H), 6.70 (1H, d, $J$ = 8.9 Hz, $C_6$-H).

TABLE I. 5,8-Quinolinediones and 5,6-Quinolinediones

| | Yield (%) | Appearance (Recrystn. solv.) | mp (°C) | Formula | Analysis or Hrms[a] Calcd (Found) C | H | N | Ms $m/z$ (%) | Ir (KBr) $\nu_{C=O}$ (cm$^{-1}$) | $^1$H-Nmr (400 MHz)[b] δ (CDCl$_3$, $J$ = Hz) |
|---|---|---|---|---|---|---|---|---|---|---|
| 5,8-Quinolinediones | | | | | | | | | | |
| **14a** | 42 | Yellow needles<br>($CH_2Cl_2$-hexane) | 204-206[c] | $C_{11}H_9NO_3$ | 65.02<br>(64.91 | 4.46<br>4.40 | 6.89<br>6.69) | 203 (M$^+$, 100) | 1680<br>1664 | 2.79 (3H, s, $C_2$-$CH_3$), 3.93 (3H, s, $OCH_3$), 6.33 (1H, s, $C_7$-H), 7.52 (1H, d, $J$ = 7.9, $C_3$-H), 8.35 (1H, d, $J$ = 7.9, $C_4$-H) |
| **14b** | 45 | Yellow needles<br>($CH_2Cl_2$-hexane) | 146-148 | $C_{12}H_{11}NO_3$ | 66.35<br>(66.41 | 5.10<br>5.00 | 6.45<br>6.44) | 217 (M$^+$, 100)<br>202 (98) | 1666 | 2.15 (3H, s, $C_7$-$CH_3$), 2.76 (3H, s, $C_2$-$CH_3$), 4.15 (3H, s, $OCH_3$), 7.48 (1H, d, $J$ = 8.2, $C_3$-H), 8.26 (1H, d, $J$ = 8.2, $C_4$-H) |
| **14c** | 57 | Yellow needles<br>(hexane) | 111-114 | $C_{13}H_{13}NO_3$ | 67.52<br>(67.29 | 5.67<br>5.72 | 6.06<br>5.95) | 231 (M$^+$, 81)<br>216 (100)<br>188 (34) | 1668 | 1.13 (3H, t, $J$ = 7.6, $\mathrm{CH_2C}\mathit{H}_3$), 2.67 (2H, q, $J$ = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.77 (3H, s, $C_2$-$CH_3$), 4.15 (3H, s, $OCH_3$), 7.49 (1H, d, $J$ = 7.9, $C_3$-H), 8.27 (1H, d, $J$ = 7.9, $C_4$-H) |
| **14d** | 49 | Yellow needles<br>(hexane) | 57-60 | $C_{14}H_{15}NO_3$ | 68.56<br>(68.37 | 6.16<br>6.17 | 5.71<br>5.65) | 245 (M$^+$, 65)<br>230 (100) | 1668 | 0.98 (3H, t, $J$ = 7.6, $\mathrm{CH_2C}\mathit{H}_3$), 1.54 (2H, sextet, $J$ = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.63 (2H, t, $J$ = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_3}$), 2.77 (3H, s, $C_2$-$CH_3$), 4.14 (3H, s, $OCH_3$), 7.48 (1H, d, $J$ = 7.9, $C_3$-H), 8.26 (1H, d, $J$ = 7.9, $C_4$-H) |
| **14e** | 51 | Yellow needles<br>(ether-hexane) | 40-41 | $C_{15}H_{17}NO_3$ | 69.48<br>(69.73 | 6.61<br>6.59 | 5.40<br>5.39) | 259 (M$^+$, 100)<br>244 (79)<br>230 (61)<br>202 (88) | 1666 | 0.93 (3H, t, $J$ = 7.3, $\mathrm{CH_2C}\mathit{H}_3$), 1.39 (2H, sextet, $J$ = 7.3, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.44-1.54 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_3}$), 2.65 (2H, t, $J$ = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{(CH_2)_2}$-$CH_3$), 2.76 (3H, s, $C_2$-$CH_3$), 4.14 (3H, s, $OCH_3$), 7.47 (1H, d, $J$ = 7.9, $C_3$-H), 8.25 (1H, d, $J$ = 7.9, $C_4$-H) |
| **14f** | 57 | Yellow needles<br>(hexane) | 38-41 | $C_{16}H_{19}NO_3$ | 273.1365<br>(273.1354) | | | 273 (M$^+$, 100)<br>258 (58)<br>230 (51)<br>202 (73) | 1670 | 0.89 (3H, t, $J$ = 7.0, $\mathrm{CH_2C}\mathit{H}_3$), 1.2-1.6 (6H, m, $\mathrm{CH_2(C}\mathit{H}_2\mathrm{)_3CH_3}$), 2.64 (2H, t, $J$ = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{(CH_2)_3CH_3}$), 2.76 (3H, s, $C_2$-$CH_3$), 4.14 (3H, s, $OCH_3$), 7.48 (1H, d, $J$ = 7.9, $C_3$-H), 8.25 (1H, d, $J$ = 7.9, $C_4$-H) |
| **14g** | 55 | Yellow oil | | $C_{17}H_{21}NO_3$ | 287.1521<br>(287.1510) | | | 287 (M$^+$, 98)<br>272 (59)<br>230 (68)<br>202 (100) | 1668 | 0.88 (3H, t, $J$ = 7.0, $\mathrm{CH_2C}\mathit{H}_3$), 1.2-1.55 (8H, m, $\mathrm{CH_2(C}\mathit{H}_2\mathrm{)_4CH_3}$), 2.64 (2H, t, $J$ = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{(CH_2)_4CH_3}$), 2.76 (3H, s, $C_2$-$CH_3$), 4.14 (3H, s, $OCH_3$), 7.47 (1H, d, $J$ = 7.9, $C_3$-H), 8.26 (1H, d, $J$ = 7.9, $C_4$-H) |
| **14h** | 34 | Yellow needles<br>(hexane) | 46-49 | $C_{19}H_{25}NO_3$ | 72.35<br>(72.16 | 7.99<br>8.00 | 4.44<br>4.32) | 315 (M$^+$, 100)<br>300 (40)<br>230 (55)<br>202 (70) | 1666 | 0.87 (3H, t, $J$ = 7.0, $\mathrm{CH_2C}\mathit{H}_3$), 1.2-1.55 (12H, m, $\mathrm{CH_2(C}\mathit{H}_2\mathrm{)_6CH_3}$), 2.63 (2H, t, $J$ = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{(CH_2)_6CH_3}$), 2.76 (3H, s, $C_2$-$CH_3$), 4.14 (3H, s, $OCH_3$), 7.47 (1H, d, $J$ = 7.9, $C_3$-H), 8.25 (1H, d, $J$ = 7.9, $C_4$-H) |
| **14i** | 34 | Yellow needles<br>(hexane) | 65-66 | $C_{23}H_{33}NO_3\cdot$<br>1/10 $H_2O$ | 74.00<br>(73.90 | 8.96<br>8.88 | 3.75<br>3.70) | 371 (M$^+$, 100)<br>356 (22)<br>230 (31)<br>202 (28) | 1666 | 0.88 (3H, t, $J$ = 7.0, $\mathrm{CH_2C}\mathit{H}_3$), 1.15-1.6 (20H, m, $\mathrm{CH_2(C}\mathit{H}_2\mathrm{)_{10}CH_3}$), 2.63 (2H, t, $J$ = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{(CH_2)_{10}CH_3}$), 2.76 (3H, s, $C_2$-$CH_3$), 4.14 (3H, s, $OCH_3$), 7.47 (1H, d, $J$ = 7.9, $C_3$-H), 8.26 (1H, d, $J$ = 7.9, $C_4$-H) |
| **15a** | 54 | Yellow needles<br>($CH_2Cl_2$-hexane) | 181-182 | $C_{13}H_{11}NO_5\cdot$<br>1/10 $H_2O$ | 59.36<br>(59.09 | 4.29<br>4.06 | 5.33<br>5.24) | 261 (M$^+$, 2)<br>219 (100)<br>218 (43) | 1734<br>1686<br>1666 | 2.22 (3H, s, $COCH_3$), 3.95 (3H, s, $OCH_3$), 5.44 (2H, s, $CH_2O$), 6.37 (1H, s, $C_7$-H), 7.71 (1H, d, $J$ = 8.3, $C_3$-H), 8.48 (1H, d, $J$ = 8.3, $C_4$-H) |
| **15b** | 53 | Yellow needles<br>(ether-hexane) | 119-122 | $C_{14}H_{13}NO_5$ | 61.09<br>(60.88 | 4.76<br>4.78 | 5.09<br>4.98) | 275 (M$^+$, 70)<br>233 (100)<br>218 (69) | 1738<br>1672 | 2.16 (3H, s, $C_7$-$CH_3$), 2.21 (3H, s, $COCH_3$), 4.17 (3H, s, $OCH_3$), 5.42 (2H, s, $CH_2O$), 7.68 (1H, d, $J$ = 8.2, $C_3$-H), 8.40 (1H, d, $J$ = 8.2, $C_4$-H) |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **15c** | 47 | Yellow needles<br>(ether-hexane) | 106-107 | $C_{15}H_{15}NO_5$ | 62.28<br>(62.19 | 5.23<br>5.27 | 4.84<br>4.79) | 289 (M$^+$, 60)<br>232 (61)<br>229 (100) | 1744<br>1676<br>1664 | 1.13 (3H, t, $J$ = 7.6, $\mathrm{CH_2C}H_3$), 2.21 (3H, s, $COCH_3$), 2.68 (2H, q, $J$ = 7.6, $\mathrm{C}H_2\mathrm{CH_3}$), 4.17 (3H, s, $OCH_3$), 5.42 (2H, s, $CH_2O$), 7.68 (1H, d, $J$ = 7.9, $C_3$-H), 8.40 (1H, d, $J$ = 7.9, $C_4$-H) |
| **15d** | 62 | Yellow needles<br>($CH_2Cl_2$-hexane) | 67-68 | $C_{16}H_{17}NO_5$ | 63.36<br>(63.19 | 5.65<br>5.75 | 4.62<br>4.47) | 303 (M$^+$, 46)<br>246 (44)<br>243 (100)<br>228 (52) | 1752<br>1672 | 0.98 (3H, t, $J$ = 7.6, $\mathrm{CH_2C}H_3$), 1.55 (2H, sextet, $J$ = 7.6, $\mathrm{C}H_2\mathrm{CH_3}$), 2.21 (3H, s, $COCH_3$), 2.64 (2H, t, $J$ = 7.6, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 4.16 (3H, s, $OCH_3$), 5.42 (2H, s, $CH_2O$), 7.67 (1H, d, $J$ = 7.9, $C_3$-H), 8.39 (1H, d, $J$ = 7.9, $C_4$-H) |
| **15e** | 52 | Yellow needles<br>(ether-hexane) | 56-57 | $C_{17}H_{19}NO_5$ | 64.34<br>(64.04 | 6.04<br>5.99 | 4.41<br>4.38) | 317 (M$^+$, 70)<br>260 (44)<br>257 (100)<br>228 (40) | 1746<br>1676 | 0.93 (3H, t, $J$ = 7.3, $\mathrm{CH_2C}H_3$), 1.39 (2H, sextet, $J$ = 7.3, $\mathrm{C}H_2\mathrm{CH_3}$), 1.45-1.55 (2H, m, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 2.21 (3H, s, $COCH_3$), 2.66 (2H, t, $J$ = 7.6, $\mathrm{C}H_2\mathrm{(CH_2)_2CH_3}$), 4.16 (3H, s, $OCH_3$), 5.41 (2H, s, $CH_2O$), 7.67 (1H, d, $J$ = 7.9, $C_3$-H), 8.39 (1H, d, $J$ = 7.9, $C_4$-H) |
| **15f** | 50 | Yellow needles<br>(hexane) | 64-65 | $C_{18}H_{21}NO_5$ | 65.24<br>(65.12 | 6.39<br>6.40 | 4.23<br>4.19) | 331 (M$^+$, 100)<br>274 (34)<br>271 (74) | 1744<br>1670 | 0.89 (3H, t, $J$ = 7.0, $\mathrm{CH_2C}H_3$), 1.2-1.6 (6H, m, $\mathrm{CH_2(C}H_2)_3\mathrm{CH_3}$), 2.21 (3H, s, $COCH_3$), 2.65 (2H, t, $J$ = 7.6, $\mathrm{C}H_2\mathrm{(CH_2)_3CH_3}$), 4.15 (3H, s, $OCH_3$), 5.42 (2H, s, $CH_2O$), 7.67 (1H, d, $J$ = 7.9, $C_3$-H), 8.39 (1H, d, $J$ = 7.9, $C_4$-H) |
| **15h** | 41 | Yellow needles<br>(hexane) | 84-85 | $C_{21}H_{27}NO_5\cdot$<br>1/10 $H_2O$ | 67.22<br>(67.13 | 7.31<br>7.27 | 3.73<br>3.59) | 373 (M$^+$, 100)<br>316 (29)<br>313 (55) | 1732<br>1674 | 0.87 (3H, t, $J$ = 7.0, $\mathrm{CH_2C}H_3$), 1.2-1.6 (12H, m, $\mathrm{CH_2(C}H_2)_6\mathrm{CH_3}$), 2.21 (3H, s, $COCH_3$), 2.64 (2H, t, $J$ = 7.6, $\mathrm{C}H_2\mathrm{(CH_2)_6CH_3}$), 4.15 (3H, s, $OCH_3$), 5.42 (2H, s, $CH_2O$), 7.67 (1H, d, $J$ = 7.9, $C_3$-H), 8.39 (1H, d, $J$ = 7.9, $C_4$-H) |
| **16a** | 32 | Yellow needles<br>($CH_2Cl_2$-ether) | 245-248[d)]<br>(decomp.) | $C_{10}H_7NO_3$ | 63.49<br>(63.22 | 3.73<br>3.63 | 7.40<br>7.26) | 189 (M$^+$, 100)<br>174 (19) | 1685<br>1670 | 3.96 (3H, s, $OCH_3$), 6.38 (1H, s, $C_7$-H), 7.68 (1H, dd, $J$ = 7.9, 4.6, $C_3$-H), 8.48 (1H, dd, $J$ = 7.9, 1.6, $C_4$-H), 9.06 (1H, dd, $J$ = 4.6, 1.6, $C_2$-H) |
| **16b** | 39 | Yellow needles<br>(ether-hexane) | 173-174 | $C_{11}H_9NO_3$ | 65.02<br>(64.92 | 4.46<br>4.26 | 6.89<br>6.76) | 203 (M$^+$, 100)<br>188 (73)<br>160 (38) | 1665 | 2.18 (3H, s, $C_7$-$CH_3$), 4.17 (3H, s, $OCH_3$), 7.64 (1H, dd, $J$ = 7.9, 4.6, $C_3$-H), 8.40 (1H, dd, $J$ = 7.9, 1.7, $C_4$-H), 9.01 (1H, dd, $J$ = 4.6, 1.7, $C_2$-H) |
| **16c** | 46 | Yellow needles<br>(ether-hexane) | 98-100 | $C_{12}H_{11}NO_3$ | 66.35<br>(66.13 | 5.10<br>5.12 | 6.45<br>6.29) | 217 (M$^+$, 79)<br>202 (100)<br>174 (36) | 1672 | 1.14 (3H, t, $J$ = 7.6, $\mathrm{CH_2C}H_3$), 2.69 (2H, q, $J$ = 7.6, $\mathrm{C}H_2\mathrm{CH_3}$), 4.17 (3H, s, $OCH_3$), 7.64 (1H, dd, $J$ = 7.9, 4.6, $C_3$-H), 8.39 (1H, dd, $J$ = 7.9, 1.7, $C_4$-H), 9.01 (1H, dd, $J$ = 4.6, 1.7, $C_2$-H) |
| **16d** | 38 | Yellow needles<br>(hexane) | 73-76 | $C_{13}H_{13}NO_3$ | 67.52<br>(67.28 | 5.67<br>5.67 | 6.06<br>5.96) | 231 (M$^+$, 49)<br>216 (100)<br>188 (29) | 1670<br>1660 | 0.99 (3H, t, $J$ = 7.6, $\mathrm{CH_2C}H_3$), 1.56 (2H, sextet, $J$ = 7.6, $\mathrm{C}H_2\mathrm{CH_3}$), 2.65 (2H, t, $J$ = 7.6, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 4.16 (3H, s, $OCH_3$), 7.63 (1H, dd, $J$ = 7.9, 4.6, $C_3$-H), 8.39 (1H, dd, $J$ = 7.9, 1.8, $C_4$-H), 9.00 (1H, dd, $J$ = 4.6, 1.8, $C_2$-H) |
| **16e** | 47 | Yellow needles<br>(ether-hexane) | 63-64 | $C_{14}H_{15}NO_3$ | 68.56<br>(68.33 | 6.16<br>6.16 | 5.71<br>5.63) | 245 (M$^+$, 69)<br>230 (67)<br>216 (77)<br>188 (100) | 1668 | 0.94 (3H, t, $J$ = 7.3, $\mathrm{CH_2C}H_3$), 1.40 (2H, sextet, $J$ = 7.3, $\mathrm{C}H_2\mathrm{CH_3}$), 1.45-1.55 (2H, m, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 2.67 (2H, t, $J$ = 7.6, $\mathrm{C}H_2\mathrm{(CH_2)_2CH_3}$), 4.16 (3H, s, $OCH_3$), 7.63 (1H, dd, $J$ = 7.9, 4.6, $C_3$-H), 8.39 (1H, dd, $J$ = 7.9, 1.8, $C_4$-H), 9.00 (1H, dd, $J$ = 4.6, 1.8, $C_2$-H) |
| **16f** | 53 | Yellow plates<br>(hexane) | 77-78 | $C_{15}H_{17}NO_3$ | 69.48<br>(69.34 | 6.61<br>6.73 | 5.40<br>5.32) | 259 (M$^+$, 100)<br>244 (61)<br>216 (65)<br>188 (98) | 1668 | 0.90 (3H, t, $J$ = 7.0, $\mathrm{CH_2C}H_3$), 1.3-1.6 (6H, m, $\mathrm{CH_2(C}H_2)_3\mathrm{CH_3}$), 2.66 (2H, t, $J$ = 7.6, $\mathrm{C}H_2\mathrm{(CH_2)_3CH_3}$), 4.15 (3H, s, $OCH_3$), 7.64 (1H, dd, $J$ = 7.9, 4.6, $C_3$-H), 8.39 (1H, dd, $J$ = 7.9, 1.8, $C_4$-H), 9.00 (1H, dd, $J$ = 4.6, 1.8, $C_2$-H) |

TABLE I. (Continued)

| | Yield (%) | Appearance (Recrystn. solv.) | mp (°C) | Formula | Analysis or Hrms[a] Calcd (Found) C | H | N | Ms m/z (%) | Ir (KBr) $\nu_{C=O}$ (cm$^{-1}$) | $^1$H-Nmr (400 MHz)[b] δ (CDCl$_3$, J = Hz) |
|---|---|---|---|---|---|---|---|---|---|---|
| **16g** | 55 | Yellow needles<br>(hexane) | 47-50 | $C_{16}H_{19}NO_3$ | 70.31<br>(70.13 | 7.01<br>7.01 | 5.12<br>5.01) | 273 (M$^+$, 89)<br>258 (46)<br>216 (76)<br>188 (100) | 1672 | 0.89 (3H, t, J = 7.0, $\mathrm{CH_2C}\mathit{H}_3$), 1.2-1.6 (8H, m, $\mathrm{CH_2(C}\mathit{H}_2\mathrm{)_4CH_3}$), 2.66 (2H, t, J = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{(CH_2)_4CH_3}$), 4.15 (3H, s, $OCH_3$), 7.63 (1H, dd, J = 7.9, 4.6, $C_3$-H), 8.38 (1H, dd, J = 7.9, 1.8, $C_4$-H), 9.00 (1H, dd, J = 4.6, 1.8, $C_2$-H) |
| **16h** | 51 | Yellow needles<br>(hexane) | 52-54 | $C_{18}H_{23}NO_3$ | 71.73<br>(71.61 | 7.69<br>7.72 | 4.65<br>4.55) | 301 (M$^+$, 100)<br>286 (33)<br>216 (66)<br>188 (68) | 1672 | 0.88 (3H, t, J = 7.0, $\mathrm{CH_2C}\mathit{H}_3$), 1.2-1.55 (12H, m, $\mathrm{CH_2(C}\mathit{H}_2\mathrm{)_6CH_3}$), 2.65 (2H, t, J = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{(CH_2)_6CH_3}$), 4.15 (3H, s, $OCH_3$), 7.63 (1H, dd, J = 7.9, 4.6, $C_3$-H), 8.38 (1H, dd, J = 7.9, 1.8, $C_4$-H), 9.00 (1H, dd, J = 4.6, 1.8, $C_2$-H) |
| **16i** | 36 | Yellow needles<br>(hexane) | 69-71 | $C_{22}H_{31}NO_3\cdot$<br>1/10 $H_2O$ | 73.54<br>(73.52 | 8.75<br>8.65 | 3.90<br>3.82) | 357 (M$^+$, 100)<br>342 (35)<br>216 (59)<br>188 (68) | 1664 | 0.88 (3H, t, J = 7.0, $\mathrm{CH_2C}\mathit{H}_3$), 1.15-1.6 (20H, m, $\mathrm{CH_2(C}\mathit{H}_2\mathrm{)_{10}CH_3}$), 2.66 (2H, t, J = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{(CH_2)_{10}CH_3}$), 4.15 (3H, s, $OCH_3$), 7.63 (1H, dd, J = 7.9, 4.6, $C_3$-H), 8.39 (1H, dd, J = 7.9, 1.8, $C_4$-H), 9.00 (1H, dd, J = 4.6, 1.8, $C_2$-H) |
| **17a** | 41 | Yellow needles<br>($CH_2Cl_2$-hexane) | 198-200 | $C_{11}H_9NO_3$ | 65.02<br>(64.95 | 4.46<br>4.23 | 6.89<br>6.69) | 203 (M$^+$, 100)<br>188 (37) | 1677 | 2.82 (3H, s, $C_4$-$CH_3$), 3.93 (3H, s, $OCH_3$), 6.32 (1H, s, $C_7$-H), 7.43 (1H, d, J = 4.9, $C_3$-H), 8.83 (1H, d, J = 4.9, $C_2$-H) |
| **17b** | 31 | Yellow needles<br>($CH_2Cl_2$-hexane) | 176-179 | $C_{12}H_{11}NO_3$ | 66.35<br>(66.09 | 5.10<br>5.12 | 6.45<br>6.28) | 217 (M$^+$, 100)<br>202 (81), 174 (44) | 1666 | 2.14 (3H, s, $C_7$-$CH_3$), 2.80 (3H, s, $C_4$-$CH_3$), 4.11 (3H, s, $OCH_3$), 7.40 (1H, d, J = 5.2, $C_3$-H), 8.79 (1H, d, J = 5.2, $C_2$-H) |
| **17c** | 53 | Yellow needles<br>($CH_2Cl_2$-hexane) | 107-108 | $C_{13}H_{13}NO_3$ | 67.52<br>(67.27 | 5.67<br>5.63 | 6.06<br>5.97) | 231 (M$^+$, 74)<br>216 (100)<br>188 (39) | 1668 | 1.13 (3H, t, J = 7.6, $\mathrm{CH_2C}\mathit{H}_3$), 2.65 (2H, q, J = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.80 (3H, s, $C_4$-$CH_3$), 4.12 (3H, s, $OCH_3$), 7.41 (1H, d, J = 5.0, $C_3$-H), 8.80 (1H, d, J = 5.0, $C_2$-H) |
| **17d** | 56 | Yellow needles<br>($CH_2Cl_2$-hexane) | 115-117 | $C_{14}H_{15}NO_3$ | 68.56<br>(68.30 | 6.16<br>6.19 | 5.71<br>5.56) | 245 (M$^+$, 52)<br>230 (100)<br>202 (25) | 1668 | 0.98 (3H, t, J = 7.6, $\mathrm{CH_2C}\mathit{H}_3$), 1.55 (2H, sextet, J = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.61 (2H, t, J = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_3}$), 2.79 (3H, s, $C_4$-$CH_3$), 4.10 (3H, s, $OCH_3$), 7.39 (1H, d, J = 4.9, $C_3$-H), 8.79 (1H, d, J = 4.9, $C_2$-H) |
| **17e** | 52 | Yellow needles<br>(ether-hexane) | 100-101 | $C_{15}H_{17}NO_3$ | 69.48<br>(69.41 | 6.61<br>6.57 | 5.40<br>5.38) | 259 (M$^+$, 90)<br>244 (91)<br>230 (52)<br>202 (100) | 1666 | 0.94 (3H, t, J = 7.3, $\mathrm{CH_2C}\mathit{H}_3$), 1.39 (2H, sextet, J = 7.3, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.45-1.55 (2H, m, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_3}$), 2.63 (2H, t, J = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{(CH_2)_2CH_3}$), 2.80 (3H, s, $C_4$-$CH_3$), 4.10 (3H, s, $OCH_3$), 7.40 (1H, d, J = 4.9, $C_3$-H), 8.79 (1H, d, J = 4.9, $C_2$-H) |
| **17f** | 43 | Yellow needles<br>(hexane) | 82-83 | $C_{16}H_{19}NO_3$ | 70.31<br>(70.09 | 7.01<br>7.01 | 5.12<br>4.97) | 273 (M$^+$, 100)<br>258 (76)<br>230 (42)<br>202 (87) | 1670 | 0.89 (3H, t, J = 7.0, $\mathrm{CH_2C}\mathit{H}_3$), 1.3-1.6 (6H, m, $\mathrm{CH_2(C}\mathit{H}_2\mathrm{)_3CH_3}$), 2.62 (2H, t, J = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{(CH_2)_3CH_3}$), 2.80 (3H, s, $C_4$-$CH_3$), 4.10 (3H, s, $OCH_3$), 7.40 (1H, d, J = 4.9, $C_3$-H), 8.79 (1H, d, J = 4.9, $C_2$-H) |
| **17g** | 37 | Yellow needles<br>(hexane) | 66-69 | $C_{17}H_{21}NO_3$ | 71.06<br>(71.20 | 7.37<br>7.42 | 4.87<br>4.82) | 287 (M$^+$, 100)<br>272 (58)<br>230 (38)<br>202 (79) | 1670 | 0.88 (3H, t, J = 7.0, $\mathrm{CH_2C}\mathit{H}_3$), 1.2-1.55 (8H, m, $\mathrm{CH_2(C}\mathit{H}_2\mathrm{)_4CH_3}$), 2.62 (2H, t, J = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{(CH_2)_4CH_3}$), 2.80 (3H, s, $C_4$-$CH_3$), 4.10 (3H, s, $OCH_3$), 7.40 (1H, d, J = 4.9, $C_3$-H), 8.79 (1H, d, J = 4.9, $C_2$-H) |
| **17h** | 53 | Yellow needles<br>(hexane) | 63-64 | $C_{19}H_{25}NO_3$ | 72.35<br>(72.11 | 7.99<br>8.18 | 4.44<br>4.37) | 315 (M$^+$, 100)<br>300 (59)<br>230 (48) | 1666 | 0.87 (3H, t, J = 7.0, $\mathrm{CH_2C}\mathit{H}_3$), 1.2-1.55 (12H, m, $\mathrm{CH_2(C}\mathit{H}_2\mathrm{)_6CH_3}$), 2.62 (2H, t, J = 7.6, $\mathrm{C}\mathit{H}_2\mathrm{(CH_2)_6CH_3}$), 2.79 (3H, s, $C_4$-$CH_3$), 4.10 (3H, s, $OCH_3$), 7.39 (1H, d, J = 4.9, $C_3$-H), 8.79 (1H, d, |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | 202 (88) | | $J$ = 4.9, $C_2$-H) |
| **18a** | 55 | Pale yellow needles<br>($CH_2Cl_2$-hexane) | 230-231 | $C_{10}H_6NO_3Cl$ | 53.71<br>(53.82 | 2.70<br>2.51 | 6.26<br>6.28) | 225 ($M^+$+2, 35)<br>223 ($M^+$, 100)<br>195 (45), 193 (38) | 1688<br>1668 | 3.95 (3H, s, $OCH_3$), 6.37 (1H, s, $C_7$-H), 7.68 (1H, d, $J$ = 8.2, $C_3$-H), 8.41 (1H, d, $J$ = 8.2, $C_4$-H) |
| **18b** | 91 | Yellow needles<br>(ether-hexane) | 152-154 | $C_{11}H_8NO_3Cl$ | 55.60<br>(55.52 | 3.39<br>3.42 | 5.89<br>5.87) | 239 ($M^+$+2, 39)<br>237 ($M^+$, 100)<br>224 (32), 222 (76) | 1668 | 2.16 (3H, s, $C_7$-$CH_3$), 4.17 (3H, s, $OCH_3$), 7.64 (1H, d, $J$ = 8.3, $C_3$-H), 8.33 (1H, d, $J$ = 8.3, $C_4$-H) |
| **18c** | 88 | Yellow needles<br>($CH_2Cl_2$-hexane) | 106-107 | $C_{12}H_{10}NO_3Cl$ | 57.27<br>(57.24 | 4.01<br>4.00 | 5.57<br>5.55) | 253 ($M^+$+2, 35)<br>251 ($M^+$, 82)<br>238 (40), 236 (100) | 1672 | 1.12 (3H, t, $J$ = 7.6, $CH_2C\mathit{H}_3$), 2.67 (2H, q, $J$ = 7.6, $C\mathit{H}_2CH_3$), 4.17 (3H, s, $OCH_3$), 7.64 (1H, d, $J$ = 8.3, $C_3$-H), 8.33 (1H, d, $J$ = 8.3, $C_4$-H) |
| **18d** | 79 | Yellow needles<br>(hexane) | 69-71 | $C_{13}H_{12}NO_3Cl$ | 58.77<br>(58.62 | 4.55<br>4.62 | 5.27<br>5.21) | 267 ($M^+$+2, 21)<br>265 ($M^+$, 43)<br>252 (35), 250 (100) | 1670 | 0.98 (3H, t, $J$ = 7.3, $CH_2C\mathit{H}_3$), 1.54 (2H, sextet, $J$ = 7.3, $C\mathit{H}_2CH_3$), 2.63 (2H, t, $J$ = 7.3, $C\mathit{H}_2CH_2CH_3$), 4.16 (3H, s, $OCH_3$), 7.64 (1H, d, $J$ = 8.2, $C_3$-H), 8.32 (1H, d, $J$ = 8.2, $C_4$-H) |
| **18e** | 59 | Yellow needles<br>(ether-hexane) | 65-66 | $C_{14}H_{14}NO_3Cl$ | 60.11<br>(60.00 | 5.04<br>4.94 | 5.01<br>4.97) | 281 ($M^+$+2, 31)<br>279 ($M^+$, 80)<br>252 (36), 250 (90)<br>224 (45), 222 (100) | 1668 | 0.93 (3H, t, $J$ = 7.3, $CH_2C\mathit{H}_3$), 1.38 (2H, sextet, $J$ = 7.3, $C\mathit{H}_2CH_3$), 1.45-1.55 (2H, m, $C\mathit{H}_2CH_2CH_3$), 2.65 (2H, t, $J$ = 7.6, $C\mathit{H}_2(CH_2)_2CH_3$), 4.16 (3H, s, $OCH_3$), 7.64 (1H, d, $J$ = 8.2, $C_3$-H), 8.32 (1H, d, $J$ = 8.2, $C_4$-H) |
| **18f** | 63 | Yellow needles<br>(hexane) | 57-59 | $C_{15}H_{16}NO_3Cl$ | 61.33<br>(61.43 | 5.49<br>5.60 | 4.77<br>4.65) | 295 ($M^+$+2, 40)<br>293 ($M^+$, 100)<br>252 (26), 250 (67)<br>224 (41), 222 (82) | 1670 | 0.89 (3H, t, $J$ = 7.0, $CH_2C\mathit{H}_3$), 1.2-1.6 (6H, m, $CH_2(C\mathit{H}_2)_3CH_3$), 2.64 (2H, t, $J$ = 7.6, $C\mathit{H}_2(CH_2)_3CH_3$), 4.16 (3H, s, $OCH_3$), 7.64 (1H, d, $J$ = 8.2, $C_3$-H), 8.32 (1H, d, $J$ = 8.2, $C_4$-H) |
| **18g** | 57 | Yellow needles<br>(hexane) | 70-73 | $C_{16}H_{18}NO_3Cl$ | 62.44<br>(62.51 | 5.90<br>6.00 | 4.55<br>4.46) | 309 ($M^+$+2, 42)<br>307 ($M^+$, 100)<br>252 (33), 250 (74)<br>224 (53), 222 (91) | 1670 | 0.88 (3H, t, $J$ = 6.9, $CH_2C\mathit{H}_3$), 1.2-1.6 (8H, m, $CH_2(C\mathit{H}_2)_4CH_3$), 2.64 (2H, t, $J$ = 7.6, $C\mathit{H}_2(CH_2)_4CH_3$), 4.16 (3H, s, $OCH_3$), 7.64 (1H, d, $J$ = 8.3, $C_3$-H), 8.32 (1H, d, $J$ = 8.3, $C_4$-H) |
| **18h** | 59 | Yellow needles<br>($CH_2Cl_2$-hexane) | 71-73 | $C_{18}H_{22}NO_3Cl$ | 64.38<br>(64.38 | 6.60<br>6.72 | 4.17<br>4.09) | 337 ($M^+$+2, 46)<br>335 ($M^+$, 100)<br>252 (29), 250 (61)<br>224 (42), 222 (63) | 1672 | 0.88 (3H, t, $J$ = 7.0, $CH_2C\mathit{H}_3$), 1.2-1.6 (12H, m, $CH_2(C\mathit{H}_2)_6CH_3$), 2.63 (2H, t, $J$ = 7.6, $C\mathit{H}_2(CH_2)_6CH_3$), 4.16 (3H, s, $OCH_3$), 7.64 (1H, d, $J$ = 8.2, $C_3$-H), 8.32 (1H, d, $J$ = 8.2, $C_4$-H) |
| **19a** | 77 | Yellow needles<br>($CH_2Cl_2$-hexane) | 260-262 | $C_{11}H_8NO_3Cl$ | 55.60<br>(55.46 | 3.39<br>3.18 | 5.89<br>5.86) | 239 ($M^+$+2, 40)<br>237 ($M^+$, 100)<br>224 (17), 222 (41) | 1686<br>1658 | 2.80 (3H, s, $C_4$-$CH_3$), 3.93 (3H, s, $OCH_3$), 6.31 (1H, s, $C_7$-H), 7.47 (1H, s, $C_3$-H) |
| **19b** | 84 | Yellow needles<br>(ether-hexane) | 175-179 | $C_{12}H_{10}NO_3Cl$ | 57.27<br>(57.08 | 4.01<br>4.01 | 5.57<br>5.52) | 253 ($M^+$,+2, 40)<br>251 ($M^+$, 100)<br>238 (27), 236 (66) | 1666 | 2.12 (3H, s, $C_7$-$CH_3$), 2.77 (3H, d, $J$ = 0.7, $C_4$-$CH_3$), 4.11 (3H, s, $OCH_3$), 7.43 (1H, q, $J$ = 0.7, $C_3$-H) |
| **19c** | 69 | Yellow needles<br>(hexane) | 125-127 | $C_{13}H_{12}NO_3Cl$ | 58.77<br>(58.59 | 4.55<br>4.53 | 5.27<br>5.19) | 267 ($M^+$+2, 26)<br>265 ($M^+$, 71)<br>252 (35), 250 (100) | 1668 | 1.11 (3H, t, $J$ = 7.6, $CH_2C\mathit{H}_3$), 2.63 (2H, q, $J$ = 7.6, $C\mathit{H}_2CH_3$), 2.77 (3H, d, $J$ = 0.7, $C_4$-$CH_3$), 4.11 (3H, s, $OCH_3$), 7.43 (1H, q, $J$ = 0.7, $C_3$-H) |
| **19d** | 65 | Yellow needles<br>($CH_2Cl_2$-hexane) | 135-136 | $C_{14}H_{14}NO_3Cl$ | 60.11<br>(59.97 | 5.04<br>5.05 | 5.01<br>4.94) | 281 ($M^+$+2, 23)<br>279 ($M^+$, 64)<br>266 (35), 264 (100) | 1666 | 0.97 (3H, t, $J$ = 7.6, $CH_2C\mathit{H}_3$), 1.53 (2H, sextet, $J$ = 7.6, $C\mathit{H}_2CH_3$), 2.59 (2H, t, $J$ = 7.6, $C\mathit{H}_2CH_2CH_3$), 2.77 (3H, s, $C_4$-$CH_3$), 4.10 (3H, s, $OCH_3$), 7.43 (1H, s, $C_3$-H) |

TABLE I. (Continued)

| | Yield (%) | Appearance (Recrystn. solv.) | mp (°C) | Formula | Analysis or Hrms[a)] Calcd (Found) C | H | N | Ms $m/z$ (%) | Ir (KBr) $\nu_{C=O}$ (cm$^{-1}$) | $^1$H-Nmr (400 MHz)[b)] $\delta$ (CDCl$_3$, $J$ = Hz) |
|---|---|---|---|---|---|---|---|---|---|---|
| **19e** | 61 | Yellow needles (ether-hexane) | 104-105 | $C_{15}H_{16}NO_3Cl$ | 61.33<br>(61.08 | 5.49<br>5.43 | 4.77<br>4.72) | 295 (M$^+$+2, 33)<br>293 (M$^+$, 86)<br>280 (24), 278 (69)<br>266 (20), 264 (61)<br>238 (42), 236 (100) | 1666 | 0.92 (3H, t, $J$ = 7.3, $\mathrm{CH_2C}H_3$), 1.37 (2H, sextet, $J$ = 7.3, $\mathrm{C}H_2\mathrm{CH_3}$), 1.45-1.55 (2H, m, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 2.61 (2H, t, $J$ = 7.6, $\mathrm{C}H_2\mathrm{(CH_2)_2CH_3}$), 2.77 (3H, d, $J$ = 0.6, $C_4$-$CH_3$), 4.10 (3H, s, $OCH_3$), 7.43 (1H, q, $J$ = 0.6, $C_3$-H) |
| **19f** | 61 | Yellow needles (hexane) | 85-86 | $C_{16}H_{18}NO_3Cl$ | 62.44<br>(62.15 | 5.90<br>5.88 | 4.55<br>4.48) | 309 (M$^+$+2, 40)<br>307 (M$^+$, 100)<br>294 (21), 292 (59)<br>266 (19), 264 (49)<br>238 (42), 236 (89) | 1672 | 0.89 (3H, t, $J$ = 7.0, $\mathrm{CH_2C}H_3$), 1.25-1.55 (6H, m, $\mathrm{CH_2(C}H_2\mathrm{)_3CH_3}$), 2.60 (2H, t, $J$ = 7.6, $\mathrm{C}H_2\mathrm{(CH_2)_3CH_3}$), 2.77 (3H, d, $J$ = 0.6, $C_4$-$CH_3$), 4.10 (3H, s, $OCH_3$), 7.43 (1H, q, $J$ = 0.6, $C_3$-H) |
| **19g** | 62 | Yellow needles (hexane) | 84-85 | $C_{17}H_{20}NO_3Cl$ | 63.45<br>(63.17 | 6.26<br>6.16 | 4.35<br>4.38) | 323 (M$^+$+2, 37)<br>321 (M$^+$, 100)<br>308 (15), 306 (45)<br>266 (20), 264 (46)<br>238 (40), 236 (74) | 1668 | 0.88 (3H, t, $J$ = 6.9, $\mathrm{CH_2C}H_3$), 1.2-1.5 (8H, m, $\mathrm{CH_2(C}H_2\mathrm{)_4CH_3}$), 2.60 (2H, t, $J$ = 7.6, $\mathrm{C}H_2\mathrm{(CH_2)_4CH_3}$), 2.77 (3H, d, $J$ = 0.7, $C_4$-$CH_3$), 4.10 (3H, s, $OCH_3$), 7.42 (1H, q, $J$ = 0.7, $C_3$-H) |
| **19h** | 57 | Yellow needles (hexane) | 58-59 | $C_{19}H_{24}NO_3Cl$ | 65.23<br>(65.11 | 6.91<br>6.88 | 4.00<br>3.94) | 351 (M$^+$+2, 50)<br>349 (M$^+$, 100)<br>336 (14), 334 (38)<br>266 (28), 264 (54)<br>238 (48), 236 (71) | 1670 | 0.87 (3H, t, $J$ = 7.0, $\mathrm{CH_2C}H_3$), 1.2-1.6 (12H, m, $\mathrm{CH_2(C}H_2\mathrm{)_6CH_3}$), 2.60 (2H, t, $J$ = 7.3, $\mathrm{C}H_2\mathrm{(CH_2)_6CH_3}$), 2.77 (3H, s, $C_4$-$CH_3$), 4.10 (3H, s, $OCH_3$), 7.43 (1H, s, $C_3$-H) |
| 5,6-Quinolinediones | | | | | | | | | | |
| **20a** | 41 | Yellow needles ($CH_2Cl_2$-hexane) | 221-224 | $C_{11}H_9NO_3$ | 65.02<br>(64.93 | 4.46<br>4.27 | 6.89<br>6.89) | 203 (M$^+$, 19)<br>175 (M$^+$-CO, 65)<br>174 (68), 146 (100) | 1700<br>1648 | 2.75 (3H, s, $C_2$-$CH_3$), 4.09 (3H, s, $OCH_3$), 6.15 (1H, s, $C_7$-H), 7.41 (1H, d, $J$ = 7.9, $C_3$-H), 8.29 (1H, d, $J$ = 7.9, $C_4$-H) |
| **20b** | 20 | Orange needles ($CH_2Cl_2$-hexane) | 134-137 | $C_{12}H_{11}NO_3$ | 66.35<br>(66.34 | 5.10<br>5.14 | 6.45<br>6.41) | 217 (M$^+$, 5)<br>189 (M$^+$-CO, 72)<br>188 (59), 160 (100) | 1702<br>1654 | 2.07 (3H, s, $C_7$-$CH_3$), 2.69 (3H, s, $C_2$-$CH_3$), 4.23 (3H, s, $OCH_3$), 7.26 (1H, d, $J$ = 7.9, $C_3$-H), 8.18 (1H, d, $J$ = 7.9, $C_4$-H) |
| **20c** | 17 | Orange needles (hexane) | 66-68 | $C_{13}H_{13}NO_3$ | 231.0895<br>(231.0923) | | | 231 (M$^+$, 19)<br>203 (M$^+$-CO, 54)<br>188 (100), 174 (36) | 1696<br>1648 | 1.11 (3H, t, $J$ = 7.6, $\mathrm{CH_2C}H_3$), 2.58 (2H, q, $J$ = 7.6, $\mathrm{C}H_2\mathrm{CH_3}$), 2.69 (3H, s, $C_2$-$CH_3$), 4.25 (3H, s, $OCH_3$), 7.26 (1H, d, $J$ = 7.9, $C_3$-H), 8.18 (1H, d, $J$ = 7.9, $C_4$-H) |
| **20d** | 27 | Orange needles (hexane) | 44-47 | $C_{14}H_{15}NO_3$ | 68.56<br>(68.44 | 6.16<br>6.34 | 5.71<br>5.59) | 245 (M$^+$, 21)<br>217 (M$^+$-CO, 44)<br>202 (66), 188 (100) | 1700<br>1656 | 0.97 (3H, t, $J$ = 7.6, $\mathrm{CH_2C}H_3$), 1.53 (2H, sextet, $J$ = 7.6, $\mathrm{C}H_2\mathrm{CH_3}$), 2.53 (2H, t, $J$ = 7.6, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 2.69 (3H, s, $C_2$-$CH_3$), 4.24 (3H, s, $OCH_3$), 7.26 (1H, d, $J$ = 7.9, $C_3$-H), 8.18 (1H, d, $J$ = 7.9, $C_4$-H) |
| **20e** | 29 | Orange needles (hexane) | 45-47 | $C_{15}H_{17}NO_3$ | 259.1208<br>(259.1207) | | | 259 (M$^+$, 24)<br>231 (M$^+$-CO, 39)<br>216 (59), 202 (43)<br>188 (100), 174 (50) | 1698<br>1652 | 0.93 (3H, t, $J$ = 6.9, $\mathrm{CH_2C}H_3$), 1.3-1.55 (4H, m, $\mathrm{CH_2(C}H_2\mathrm{)_2CH_3}$), 2.55 (2H, t, $J$ = 7.9, $\mathrm{C}H_2\mathrm{(CH_2)_2CH_3}$), 2.69 (3H, s, $C_2$-$CH_3$), 4.24 (3H, s, $OCH_3$), 7.26 (1H, d, $J$ = 7.9, $C_3$-H), 8.18 (1H, d, $J$ = 7.9, $C_4$-H) |
| **20f** | 24 | Orange needles (hexane) | 54-56 | $C_{16}H_{19}NO_3$ | 70.31<br>(70.15 | 7.01<br>7.01 | 5.12<br>5.35) | 273 (M$^+$, 23)<br>245 (M$^+$-CO, 30) | 1698<br>1656 | 0.89 (3H, t, $J$ = 6.9, $\mathrm{CH_2C}H_3$), 1.25-1.55 (6H, m, $\mathrm{CH_2(C}H_2\mathrm{)_3CH_3}$), 2.54 (2H, t, $J$ = 7.6, $\mathrm{C}H_2\mathrm{(CH_2)_3CH_3}$), 2.69 (3H, s, $C_2$-$CH_3$), |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | 230 (59), 202 (31)<br>188 (100), 174 (58) | | 4.23 (3H, s, $\mathrm{OCH_3}$), 7.26 (1H, d, *J* = 7.9, $\mathrm{C_3}$-H), 8.18 (1H, d, *J* = 7.9, $\mathrm{C_4}$-H) |
| **20g** | 15 | Orange needles (hexane) | 58-61 | $C_{17}H_{21}NO_3$ | 71.06<br>(70.84 | 7.37<br>7.45 | 4.87<br>4.75) | 287 ($M^+$, 17)<br>259 ($M^+$-CO, 27)<br>244 (60), 189 (92)<br>188 (100), 174 (72) | 1700<br>1656 | 0.88 (3H, t, *J* = 6.9, $\mathrm{CH_2C}H_3$), 1.2-1.55 (8H, m, $\mathrm{CH_2(C}H_2)_4\mathrm{CH_3}$), 2.54 (2H, t, *J* = 7.6, $\mathrm{C}H_2\mathrm{(CH_2)_4CH_3}$), 2.68 (3H, s, $\mathrm{C_2}$-$\mathrm{CH_3}$), 4.23 (3H, s, $\mathrm{OCH_3}$), 7.26 (1H, d, *J* = 7.9, $\mathrm{C_3}$-H), 8.17 (1H, d, *J* = 7.9, $\mathrm{C_4}$-H) |
| **20h** | 11 | Red oil | | $C_{19}H_{25}NO_3$ | 315.1834<br>(315.1809) | | | 315 ($M^+$, 11)<br>287 ($M^+$-CO, 22)<br>272 (46), 189 (100)<br>188 (83) | 1700<br>1656 | 0.87 (3H, t, *J* = 7.0, $\mathrm{CH_2C}H_3$), 1.2-1.55 (12H, m, $\mathrm{CH_2(C}H_2)_6\mathrm{CH_3}$), 2.54 (2H, t, *J* = 7.6, $\mathrm{C}H_2\mathrm{(CH_2)_6CH_3}$), 2.68 (3H, s, $\mathrm{C_2}$-$\mathrm{CH_3}$), 4.23 (3H, s, $\mathrm{OCH_3}$), 7.25 (1H, d, *J* = 7.9, $\mathrm{C_3}$-H), 8.17 (1H, d, *J* = 7.9, $\mathrm{C_4}$-H) |
| **21a** | 22 | Yellow needles ($CH_2Cl_2$-hexane) | 182-183 | $C_{13}H_{11}NO_5$ | 261.0637<br>(261.0623) | | | 261 ($M^+$, 12)<br>233 ($M^+$-CO, 56)<br>204 (42), 190 (100) | 1750<br>1700<br>1644 | 2.22 (3H, s, $\mathrm{COCH_3}$), 4.10 (3H, s, $\mathrm{OCH_3}$), 5.38 (2H, s, $\mathrm{CH_2O}$), 6.18 (1H, s, $\mathrm{C_7}$-H), 7.60 (1H, d, *J* = 8.3, $\mathrm{C_3}$-H), 8.41 (1H, d, *J* = 8.3, $\mathrm{C_4}$-H) |
| **22a** | 60 | Yellow needles ($CH_2Cl_2$-ether) | 218-220 (decomp.) | $C_{10}H_7NO_3$ | 63.49<br>(63.53 | 3.73<br>3.62 | 7.40<br>7.32) | 189 ($M^+$, 9)<br>161 ($M^+$-CO, 66)<br>160 (54), 132 (100) | 1700<br>1642 | 4.11 (3H, s, $\mathrm{OCH_3}$), 6.19 (1H, s, $\mathrm{C_7}$-H), 7.58 (1H, dd, *J* = 7.9, 5.0, $\mathrm{C_3}$-H), 8.41 (1H, dd, *J* = 7.9, 1.7, $\mathrm{C_4}$-H), 8.95 (1H, dd, *J* = 5.0, 1.7, $\mathrm{C_2}$-H) |
| **22b** | 22 | Orange needles (ether-hexane) | 165-166 | $C_{11}H_9NO_3$ | 65.02<br>(64.96 | 4.46<br>4.24 | 6.89<br>6.78) | 203 ($M^+$, 9)<br>175 ($M^+$-CO, 68)<br>160 (57), 146 (100) | 1697<br>1647 | 2.10 (3H, s, $\mathrm{C_7}$-$\mathrm{CH_3}$), 4.22 (3H, s, $\mathrm{OCH_3}$), 7.44 (1H, dd, *J* = 7.9, 5.0, $\mathrm{C_3}$-H), 8.31 (1H, dd, *J* = 7.9, 1.7, $\mathrm{C_4}$-H), 8.87 (1H, dd, *J* = 5.0, 1.7, $\mathrm{C_2}$-H) |
| **22c** | 13 | Orange needles ($CH_2Cl_2$-hexane) | 98-100 | $C_{12}H_{11}NO_3$ | 217.0739<br>(217.0761) | | | 217 ($M^+$, 12)<br>189 ($M^+$-CO, 42)<br>174 (100) | 1698<br>1642 | 1.12 (3H, t, *J* = 7.6, $\mathrm{CH_2C}H_3$), 2.60 (2H, q, *J* = 7.6, $\mathrm{C}H_2\mathrm{CH_3}$), 4.24 (3H, s, $\mathrm{OCH_3}$), 7.43 (1H, dd, *J* = 7.9, 5.0, $\mathrm{C_3}$-H), 8.30 (1H, dd, *J* = 7.9, 1.7, $\mathrm{C_4}$-H), 8.86 (1H, dd, *J* = 5.0, 1.7, $\mathrm{C_2}$-H) |
| **23a** | 35 | Yellow needles ($CH_2Cl_2$-hexane) | 193-195 | $C_{11}H_9NO_3$ | 65.02<br>(64.80 | 4.46<br>4.37 | 6.89<br>6.79) | 203 ($M^+$, 15)<br>175 ($M^+$-CO, 48)<br>174 (62), 146 (100) | 1695<br>1655 | 2.78 (3H, s, $\mathrm{C_4}$-$\mathrm{CH_3}$), 4.09 (3H, s, $\mathrm{OCH_3}$), 6.16 (1H, s, $\mathrm{C_7}$-H), 7.34 (1H, d, *J* = 5.2, $\mathrm{C_3}$-H), 8.73 (1H, d, *J* = 5.2, $\mathrm{C_2}$-H) |
| **23b** | 30 | Orange needles ($CH_2Cl_2$-hexane) | 162-165 | $C_{12}H_{11}NO_3\cdot$<br>$1/10\,H_2O$ | 65.81<br>(65.79 | 5.15<br>5.34 | 6.40<br>6.01) | 217 ($M^+$, 5)<br>189 ($M^+$-CO, 68)<br>174 (52), 160 (100) | 1694<br>1650 | 2.09 (3H, s, $\mathrm{C_7}$-$\mathrm{CH_3}$), 2.72 (3H, s, $\mathrm{C_4}$-$\mathrm{CH_3}$), 4.16 (3H, s, $\mathrm{OCH_3}$), 7.21 (1H, d, *J* = 5.2, $\mathrm{C_3}$-H), 8.66 (1H, d, *J* = 5.2, $\mathrm{C_2}$-H) |
| **23c** | 29 | Orange needles ($CH_2Cl_2$-hexane) | 107-109 | $C_{13}H_{13}NO_3$ | 67.52<br>(67.36 | 5.67<br>5.68 | 6.06<br>5.80) | 231 ($M^+$, 8)<br>203 ($M^+$-CO, 50)<br>188 (100), 174 (34) | 1694<br>1648 | 1.12 (3H, t, *J* = 7.6, $\mathrm{CH_2C}H_3$), 2.58 (2H, q, *J* = 7.6, $\mathrm{C}H_2\mathrm{CH_3}$), 2.72 (3H, s, $\mathrm{C_4}$-$\mathrm{CH_3}$), 4.17 (3H, s, $\mathrm{OCH_3}$), 7.20 (1H, d, *J* = 5.0, $\mathrm{C_3}$-H), 8.66 (1H, d, *J* = 5.0, $\mathrm{C_2}$-H) |
| **23d** | 29 | Orange needles ($CH_2Cl_2$-hexane) | 80-82 | $C_{14}H_{15}NO_3$ | 68.56<br>(68.47 | 6.16<br>6.18 | 5.71<br>5.56) | 245 ($M^+$, 23)<br>217 ($M^+$-CO, 45)<br>202 (78), 188 (100) | 1696<br>1648 | 0.98 (3H, t, *J* = 7.6, $\mathrm{CH_2C}H_3$), 1.55 (2H, sextet, *J* = 7.6, $\mathrm{C}H_2\mathrm{CH_3}$), 2.54 (2H, t, *J* = 7.6, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 2.72 (3H, s, $\mathrm{C_4}$-$\mathrm{CH_3}$), 4.16 (3H, s, $\mathrm{OCH_3}$), 7.20 (1H, d, *J* = 5.2, $\mathrm{C_3}$-H), 8.65 (1H, d, *J* = 5.2, $\mathrm{C_2}$-H) |
| **23e** | 27 | Orange needles (ether-hexane) | 71-73 | $C_{15}H_{17}NO_3$ | 69.48<br>(69.21 | 6.61<br>6.64 | 5.40<br>5.09) | 259 ($M^+$, 20)<br>231 ($M^+$-CO, 58)<br>216 (64), 202 (52)<br>188 (100), 174 (51) | 1700<br>1650 | 0.93 (3H, t, *J* = 7.3, $\mathrm{CH_2C}H_3$), 1.39 (2H, sextet, *J* = 7.3, $\mathrm{C}H_2\mathrm{CH_3}$), 1.45-1.55 (2H, m, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 2.56 (2H, t, *J* = 7.6, $\mathrm{C}H_2\mathrm{(CH_2)_2CH_3}$), 2.71 (3H, s, $\mathrm{C_4}$-$\mathrm{CH_3}$), 4.16 (3H, s, $\mathrm{OCH_3}$), 7.20 (1H, d, *J* = 5.2, $\mathrm{C_3}$-H), 8.65 (1H, d, *J* = 5.2, $\mathrm{C_2}$-H) |
| **23f** | 28 | Orange needles (hexane) | 63-64 | $C_{16}H_{19}NO_3$ | 70.31<br>(70.17 | 7.01<br>7.06 | 5.12<br>4.86) | 273 ($M^+$, 24)<br>245 ($M^+$-CO, 38)<br>230 (64), 202 (38)<br>188 (100), 174 (63) | 1694<br>1648 | 0.89 (3H, t, *J* = 7.0, $\mathrm{CH_2C}H_3$), 1.25-1.55 (6H, m, $\mathrm{CH_2(C}H_2)_3\mathrm{CH_3}$), 2.55 (2H, t, *J* = 7.6, $\mathrm{C}H_2\mathrm{(CH_2)_3CH_3}$), 2.72 (3H, s, $\mathrm{C_4}$-$\mathrm{CH_3}$), 4.16 (3H, s, $\mathrm{OCH_3}$), 7.20 (1H, d, *J* = 5.2, $\mathrm{C_3}$-H), 8.66 (1H, d, *J* = 5.2, $\mathrm{C_2}$-H) |

TABLE I. (Continued)

| | Yield (%) | Appearance (Recrystn. solv.) | mp (°C) | Formula | Analysis or Hrms[a)] Calcd (Found) | | | Ms m/z (%) | Ir (KBr) $\nu_{C=O}$ (cm$^{-1}$) | $^1$H-Nmr (400 MHz)[b)] δ ($CDCl_3$, J = Hz) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | | | |
| **23g** | 19 | Orange needles<br>(hexane) | 57-59 | $C_{17}H_{21}NO_3$ | 71.06<br>(70.81 | 7.37<br>7.39 | 4.87<br>4.76) | 287 ($M^+$, 28)<br>259 ($M^+$-CO, 36)<br>244 (57), 189 (100)<br>188 (82), 174 (61) | 1702<br>1656 | 0.88 (3H, t, J = 7.0, $CH_2C\mathit{H}_3$), 1.25-1.55 (8H, m, $CH_2(C\mathit{H}_2)_4CH_3$), 2.55 (2H, t, J = 7.6, $C\mathit{H}_2(CH_2)_4CH_3$), 2.72 (3H, s, $C_4$-$CH_3$), 4.16 (3H, s, $OCH_3$), 7.21 (1H, d, J = 5.2, $C_3$-H), 8.66 (1H, d, J = 5.2, $C_2$-H) |
| **23h** | 19 | Orange needles<br>(hexane) | 66-68 | $C_{19}H_{25}NO_3$ | 72.35<br>(72.27 | 7.99<br>8.06 | 4.44<br>4.29) | 315 ($M^+$, 4)<br>287 ($M^+$-CO, 21)<br>272 (45), 189 (100)<br>188 (87), 174 (69) | 1702<br>1656 | 0.87 (3H, t, J = 7.0, $CH_2C\mathit{H}_3$), 1.2-1.55 (12H, m, $CH_2(C\mathit{H}_2)_6CH_3$), 2.54 (2H, t, J = 7.6, $C\mathit{H}_2(CH_2)_6CH_3$), 2.72 (3H, s, $C_4$-$CH_3$), 4.16 (3H, s, $OCH_3$), 7.20 (1H, d, J = 5.2, $C_3$-H), 8.65 (1H, d, J = 5.2, $C_2$-H) |
| **24a** | 6 | Yellow prisms<br>($CH_2Cl_2$-hexane) | 234-236 | $C_{10}H_6NO_3Cl$ | 223.0036<br>(223.0055) | | | 225 ($M^+$+2, 20)<br>223 ($M^+$, 33)<br>197 ($M^+$+2-CO, 32)<br>195 ($M^+$-CO, 91)<br>168 (37), 166 (100)<br>139 (62), 137 (84) | 1706<br>1646 | 4.09 (3H, s, $OCH_3$), 6.18 (1H, s, $C_7$-H), 7.59 (1H, d, J = 8.2, $C_3$-H), 8.34 (1H, d, J = 8.2, $C_4$-H) |
| **25b** | 10 | Orange needles<br>(ether-hexane) | 158-162 | $C_{12}H_{10}NO_3Cl$ | 251.0349<br>(251.0342) | | | 253 ($M^+$+2, 5)<br>251 ($M^+$, 15)<br>225 ($M^+$+2-CO, 23)<br>223 ($M^+$-CO, 68)<br>210 (14), 208 (41)<br>196 (34), 194 (100) | 1696<br>1662 | 2.07 (3H, s, $C_7$-$CH_3$), 2.70 (3H, s, $C_4$-$CH_3$), 4.17 (3H, s, $OCH_3$), 7.25 (1H, s, $C_3$-H) |
| **25c** | 9 | Orange needles<br>(ether-hexane) | 141-144 | $C_{13}H_{12}NO_3Cl$ | 265.0506<br>(265.0500) | | | 267 ($M^+$+2, 3)<br>265 ($M^+$, 7)<br>239 ($M^+$+2-CO, 16)<br>237 ($M^+$-CO, 47)<br>224 (34), 222 (100)<br>210 (14), 208 (40) | 1694<br>1656 | 1.11 (3H, t, J = 7.6, $CH_2C\mathit{H}_3$), 2.57 (2H, q, J = 7.6, $C\mathit{H}_2CH_3$), 2.70 (3H, s, $C_4$-$CH_3$), 4.18 (3H, s, $OCH_3$), 7.25 (1H, s, $C_3$-H) |
| **25d** | 8 | Orange needles<br>(hexane) | 144-146 | $C_{14}H_{14}NO_3Cl$ | 60.11<br>(59.96 | 5.04<br>4.99 | 5.01<br>4.85) | 281 ($M^+$+2, 3)<br>279 ($M^+$, 10)<br>253 ($M^+$+2-CO, 11)<br>251 ($M^+$-CO, 35)<br>224 (34), 222 (100) | 1694<br>1652 | 0.97 (3H, t, J = 7.6, $CH_2C\mathit{H}_3$), 1.51 (2H, sextet, J = 7.6, $C\mathit{H}_2CH_3$), 2.53 (2H, t, J = 7.6, $C\mathit{H}_2CH_2CH_3$), 2.70 (3H, s, $C_4$-$CH_3$), 4.17 (3H, s, $OCH_3$), 7.25 (1H, s, $C_3$-H) |
| **25g** | 14 | Orange needles<br>(hexane) | 88-89 | $C_{17}H_{20}NO_3Cl$ | 63.45<br>(63.26 | 6.26<br>6.24 | 4.35<br>4.62) | 323 ($M^+$+2, 9)<br>321 ($M^+$, 22)<br>295 ($M^+$+2-CO, 13)<br>293 ($M^+$-CO, 37)<br>224 (47), 222 (100) | 1696<br>1652 | 0.88 (3H, t, J = 6.9, $CH_2C\mathit{H}_3$), 1.2-1.55 (8H, m, $CH_2(C\mathit{H}_2)_4CH_3$), 2.53 (2H, t, J = 7.6, $C\mathit{H}_2(CH_2)_4CH_3$), 2.70 (3H, s, $C_4$-$CH_3$), 4.17 (3H, s, $OCH_3$), 7.24 (1H, s, $C_3$-H) |

*a*) High-resolution ms. *b*) Measured at 270 MHz (**15a, c, 16a-c, 17c, 18b, c, g, 19a-d, g, 20c-g, 21a, 22a-c, 23c, 25b-d, g**). *c*) Lit.,[6] mp 204-205°C. *d*) Lit.,[7] mp 250-251°C.

**2f**: Yield 80%. Ms *m/z* (%): 238 ($M^+$, 100), 223 (18), 181 (63), 166 (43). High-resolution ms Calcd for $C_{14}H_{22}O_3$: 238.1569. Found: 238.1574. $^1$H-Nmr (270 MHz) δ: 0.89 (3H, t, *J* = 6.9 Hz, $CH_2CH_3$), 1.3-1.6 (6H, m, $(CH_2)_3CH_3$), 2.62 (2H, t, *J* = 7.9 Hz, $CH_2(CH_2)_3CH_3$), 3.77 (3H, s, $OCH_3$), 3.81 (6H, s, $2OCH_3$), 6.54 (1H, d, *J* = 8.9 Hz, $C_5$-H), 6.70 (1H, d, *J* = 8.9 Hz, $C_6$-H).

**2i**: Yield 74%. Ms *m/z* (%): 336 ($M^+$, 100), 181 (35). High-resolution ms Calcd for $C_{21}H_{36}O_3$: 336.2664. Found: 336.2665. $^1$H-Nmr (400 MHz) δ: 0.88 (3H, t, *J* = 7.0 Hz, $CH_2CH_3$), 1.2-1.6 (20H, m, $(CH_2)_{10}CH_3$), 2.62 (2H, t, *J* = 7.9 Hz, $CH_2(CH_2)_{10}CH_3$), 3.76 (3H, s, $OCH_3$), 3.81 (6H, s, $2OCH_3$), 6.54 (1H, d, *J* = 8.9 Hz, $C_5$-H), 6.69 (1H, d, *J* = 8.9 Hz, $C_6$-H).

**3-Alkyl-1,2,4-trimethoxy-5-nitrobenzenes (3d-i)** Concentrated $HNO_3$ (20 ml) was added dropwise to a solution of 3-alkyl-1,2,4-trimethoxybenzene (**2d-i**) (50 mmol) in acetic acid (200 ml) for 5 min. The resulting solution was left for 1 h, poured into water (1000 ml), and extracted with $CH_2Cl_2$ (3 x 300 ml). The extract was washed with saturated aqueous $NaHCO_3$ solution and water, dried, and evaporated. The residue was chromatographed (eluting with $CH_2Cl_2$) to afford **3d-i**.

**3d**: Yield 96%. oil. Ms *m/z* (%): 255 ($M^+$, 100), 226 (31). $^1$H-Nmr (400 MHz) δ: 0.99 (3H, t, *J* = 7.3 Hz, $CH_2CH_3$), 1.56 (2H, sextet, *J* = 7.3 Hz, $CH_2CH_3$), 2.65 (2H, t, *J* = 7.3 Hz, $CH_2CH_2CH_3$), 3.85, 3.89, 3.92 (each 3H, s, $3OCH_3$), 7.36 (1H, s, $C_6$-H).

**3e**: Yield 92%. oil. Ms *m/z* (%): 269 ($M^+$, 100), 226 (26). $^1$H-Nmr (400 MHz) δ: 0.94 (3H, t, *J* = 7.3 Hz, $CH_2CH_3$), 1.40 (2H, sextet, *J* = 7.3 Hz, $CH_2CH_3$), 1.45-1.6 (2H, m, $CH_2CH_2CH_3$), 2.67 (2H, t, *J* = 7.6 Hz, $CH_2(CH_2)_2CH_3$), 3.86, 3.89, 3.92 (each 3H, s, $3OCH_3$), 7.36 (1H, s, $C_6$-H).

**3f**: Yield 96%. oil. Ms *m/z* (%): 283 ($M^+$, 100), 226 (37). $^1$H-Nmr (270 MHz) δ: 0.90 (3H, t, *J* = 7.0 Hz, $CH_2CH_3$), 1.3-1.6 (6H, m, $(CH_2)_3CH_3$), 2.66 (2H, t, *J* = 7.9 Hz, $CH_2(CH_2)_3CH_3$), 3.86, 3.89, 3.92 (each 3H, s, $3OCH_3$), 7.36 (1H, s, $C_6$-H).

**3g**: Yield 95%. oil. Ms *m/z* (%): 297 ($M^+$, 100), 226 (28). $^1$H-Nmr (400 MHz) δ: 0.89 (3H, t, *J* = 7.0 Hz, $CH_2CH_3$), 1.2-1.6 (8H, m, $(CH_2)_4CH_3$), 2.66 (2H, t, *J* = 7.6 Hz, $CH_2(CH_2)_4CH_3$), 3.85, 3.89, 3.91 (each 3H, s, $3OCH_3$), 7.36 (1H, s, $C_6$-H).

**3h**: Yield 98%. oil. Ms *m/z* (%): 325 ($M^+$, 100), 226 (24). $^1$H-Nmr (400 MHz) δ: 0.88 (3H, t, *J* = 7.0 Hz, $CH_2CH_3$), 1.2-1.6 (12H, m, $(CH_2)_6CH_3$), 2.65 (2H, t, *J* = 7.6 Hz, $CH_2(CH_2)_6CH_3$), 3.85, 3.89, 3.91 (each 3H, s, $3OCH_3$), 7.36 (1H, s, $C_6$-H).

**3i**: Yield 79%. mp 40–43°C (hexane). Ms *m/z* (%): 381 ($M^+$, 100), 226 (26). *Anal.* Calcd for $C_{21}H_{35}NO_5$: C, 66.11; H, 9.25; N, 3.67. Found: C, 66.03; H, 9.13; N, 3.63. $^1$H-Nmr (400 MHz) δ: 0.88 (3H, t, *J* = 7.0 Hz, $CH_2CH_3$), 1.2-1.6 (20H, m, $(CH_2)_{10}CH_3$), 2.65 (2H, t, *J* = 7.6 Hz, $CH_2(CH_2)_{10}CH_3$), 3.85, 3.88, 3.91 (each 3H, s, $3OCH_3$), 7.36 (1H, s, $C_6$-H).

**3-Alkyl-2,4,5-trimethoxyanilines (4d-i)** A mixture of **3d-i** (25 mmol), Sn (23.7 g, 0.2 mol) and concentrated HCl (60 ml) was heated at 60-70°C for 2 h. The reaction mixture was cooled, adjusted to pH 9–10 with 10% NaOH solution, and extracted with $CH_2Cl_2$ (3 x 100 ml). The extract was washed with water, dried, and evaporated. The residue was chromatographed (eluting with ethyl acetate–hexane 1:9–1:4) to afford **4d-i** as an oil.

**4d**: Yield 54%. Ms *m/z* (%): 225 ($M^+$, 55), 210 (100). High-resolution ms Calcd for $C_{12}H_{19}NO_3$: 225.1365. Found: 225.1374. $^1$H-Nmr (400 MHz) δ: 0.99 (3H, t, *J* = 7.3 Hz, $CH_2CH_3$), 1.59 (2H, sextet, *J* = 7.3 Hz, $CH_2CH_3$), 2.58 (2H, t, *J* = 7.3 Hz, $CH_2CH_2CH_3$), 3.71, 3.75, 3.79 (each 3H, s, $3OCH_3$), 6.23 (1H, s, $C_6$-H).

**4e**: Yield 64%. Ms *m/z* (%): 239 ($M^+$, 77), 224 (100). High-resolution ms Calcd for $C_{13}H_{21}NO_3$: 239.1521. Found: 239.1533. $^1$H-Nmr (400 MHz) δ: 0.94 (3H, t, *J* = 7.3 Hz, $CH_2CH_3$), 1.41 (2H, sextet, *J* = 7.3 Hz,

$CH_2CH_3$), 1.45-1.6 (2H, m, $CH_2CH_2CH_3$), 2.60 (2H, t, $J$ = 7.6 Hz, $CH_2(CH_2)_2CH_3$), 3.72, 3.75, 3.79 (each 3H, s, $3OCH_3$), 6.24 (1H, s, $C_6$-H).

**4f**: Yield 72%. Ms *m/z* (%): 253 ($M^+$, 78), 238 (100). High-resolution ms Calcd for $C_{14}H_{23}NO_3$: 253.1678. Found: 253.1681. $^1$H-Nmr (270 MHz) δ: 0.90 (3H, t, $J$ = 6.9 Hz, $CH_2CH_3$), 1.3-1.7 (6H, m, $(CH_2)_3CH_3$), 2.59 (2H, t, $J$ = 7.9 Hz, $CH_2(CH_2)_3CH_3$), 3.73, 3.75, 3.79 (each 3H, s, $3OCH_3$), 6.29 (1H, s, $C_6$-H).

**4g**: Yield 96%. Ms *m/z* (%): 267 ($M^+$, 89), 252 (100). High-resolution ms Calcd for $C_{15}H_{25}NO_3$: 267.1834. Found: 267.1812. $^1$H-Nmr (400 MHz) δ: 0.89 (3H, t, $J$ = 7.0 Hz, $CH_2CH_3$), 1.2-1.6 (8H, m, $(CH_2)_4CH_3$), 2.58 (2H, t, $J$ = 7.9 Hz, $CH_2(CH_2)_4CH_3$), 3.71, 3.75, 3.79 (each 3H, s, $3OCH_3$), 6.23 (1H, s, $C_6$-H).

**4h**: Yield 78%. Ms *m/z* (%): 295 ($M^+$, 100), 280 (82). High-resolution ms Calcd for $C_{17}H_{29}NO_3$: 295.2147. Found: 295.2119. $^1$H-Nmr (400 MHz) δ: 0.88 (3H, t, $J$ = 7.0 Hz, $CH_2CH_3$), 1.2-1.6 (12H, m, $(CH_2)_6CH_3$), 2.58 (2H, t, $J$ = 7.6 Hz, $CH_2(CH_2)_6CH_3$), 3.71, 3.75, 3.78 (each 3H, s, $3OCH_3$), 6.23 (1H, s, $C_6$-H).

**4i**: Yield 80%. Ms *m/z* (%): 351 ($M^+$, 100), 336 (72). High-resolution ms Calcd for $C_{21}H_{37}NO_3$: 351.2773. Found: 351.2789. $^1$H-Nmr (400 MHz) δ: 0.88 (3H, t, $J$ = 7.0 Hz, $CH_2CH_3$), 1.2-1.6 (20H, m, $(CH_2)_{10}$-$CH_3$), 2.58 (2H, t, $J$ = 7.6 Hz, $CH_2(CH_2)_{10}CH_3$), 3.71, 3.75, 3.78 (each 3H, s, $3OCH_3$), 6.22 (1H, s, $C_6$-H).

**(7-Alkyl-)5,6,8-trimethoxy-2-methylquinolines (5a-i)** Crotonaldehyde (2.80 g, 40 mmol) was added dropwise to a refluxing solution of trimethoxyaniline (**4a-i**) (10 mmol) in 6 N HCl (100 ml), and the resulting solution was refluxed for an additional 30 min. The reaction mixture was cooled, diluted with water (100 ml), washed with ether (2 x 100 ml), basified with 10% NaOH solution, and extracted with $CH_2Cl_2$ (3 x 100 ml). The extract was washed with water, dried, and evaporated. The residue was chromatographed (eluting with ethyl acetate-hexane 1:9-1:4) to afford **5a-i**.

**5a**: Yield 51%. mp 119–121°C (ethyl acetate-hexane). Ms *m/z* (%): 233 ($M^+$, 47), 218 (100). *Anal.* Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.95; H, 6.45; N, 5.93. $^1$H-Nmr (400 MHz) δ: 2.76 (3H, s, $C_2$-$CH_3$), 3.92, 4.02, 4.07 (each 3H, s, $3OCH_3$), 6.84 (1H, s, $C_7$-H), 7.30 (1H, d, $J$ = 8.5 Hz, $C_3$-H), 8.30 (1H, d, $J$ = 8.5 Hz, $C_4$-H).

**5b**: Yield 53%. oil. Ms *m/z* (%): 247 ($M^+$, 32), 232 (100). High-resolution ms Calcd for $C_{14}H_{17}NO_3$: 247.1208. Found: 247.1208. $^1$H-Nmr (270 MHz) δ: 2.39 (3H, s, $C_7$-$CH_3$), 2.75 (3H, s, $C_2$-$CH_3$), 3.94, 3.96, 4.05 (each 3H, s, $3OCH_3$), 7.22 (1H, d, $J$ = 8.6 Hz, $C_3$-H), 8.28 (1H, d, $J$ = 8.6 Hz, $C_4$-H).

**5c**: Yield 62%. oil. Ms *m/z* (%): 261 ($M^+$, 34), 246 (100). High-resolution ms Calcd for $C_{15}H_{19}NO_3$: 261.1365. Found: 261.1391. $^1$H-Nmr (400 MHz) δ: 1.24 (3H, t, $J$ = 7.3 Hz, $CH_2CH_3$), 2.75 (3H, s, $C_2$-$CH_3$), 2.87 (2H, q, $J$ = 7.3 Hz, $CH_2CH_3$), 3.95, 3.99, 4.11 (each 3H, s, $3OCH_3$), 7.22 (1H, d, $J$ = 8.6 Hz, $C_3$-H), 8.28 (1H, d, $J$ = 8.6 Hz, $C_4$-H).

**5d**: Yield 68%. mp 49–50°C (hexane). Ms *m/z* (%): 275 ($M^+$, 29), 260 (100). *Anal.* Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.66; H, 7.69; N, 5.08. $^1$H-Nmr (400 MHz) δ: 1.02 (3H, t, $J$ = 7.3 Hz, $CH_2CH_3$), 1.64 (2H, sextet, $J$ = 7.3 Hz, $CH_2CH_3$), 2.75 (3H, s, $C_2$-$CH_3$), 2.81 (2H, t, $J$ = 7.3 Hz, $CH_2CH_2CH_3$), 3.95, 3.98, 4.10 (each 3H, s, $3OCH_3$), 7.22 (1H, d, $J$ = 8.6 Hz, $C_3$-H), 8.28 (1H, d, $J$ = 8.6 Hz, $C_4$-H).

**5e**: Yield 78%. oil. Ms *m/z* (%): 289 ($M^+$, 57), 274 (100), 260 (37). High-resolution ms Calcd for $C_{17}H_{23}NO_3$: 289.1678. Found: 289.1696. $^1$H-Nmr (400 MHz) δ: 0.96 (3H, t, $J$ = 7.3 Hz, $CH_2CH_3$), 1.45 (2H, sextet, $J$ = 7.3 Hz, $CH_2CH_3$), 1.5-1.65 (2H, m, $CH_2CH_2CH_3$), 2.74 (3H, s, $C_2$-$CH_3$), 2.83 (2H, t, $J$ = 7.6 Hz, $CH_2(CH_2)_2CH_3$), 3.95, 3.98, 4.10 (each 3H, s, $3OCH_3$), 7.22 (1H, d, $J$ = 8.6 Hz, $C_3$-H), 8.27 (1H, d, $J$ = 8.6 Hz, $C_4$-H).

**5f**: Yield 64%. oil. Ms *m/z* (%): 303 ($M^+$, 80), 288 (100), 260 (38). High-resolution ms Calcd for $C_{18}H_{25}NO_3$: 303.1834. Found: 303.1862. $^1$H-Nmr (400 MHz) $\delta$: 0.90 (3H, t, $J$ = 7.0 Hz, $CH_2C\mathit{H}_3$), 1.3-1.7 (6H, m, $(C\mathit{H}_2)_3CH_3$), 2.74 (3H, s, $C_2$-$CH_3$), 2.82 (2H, t, $J$ = 7.6 Hz, $C\mathit{H}_2(CH_2)_3CH_3$), 3.95, 3.98, 4.10 (each 3H, s, $3OCH_3$), 7.22 (1H, d, $J$ = 8.6 Hz, $C_3$-H), 8.27 (1H, d, $J$ = 8.6 Hz, $C_4$-H).

**5g**: Yield 82%. oil. Ms *m/z* (%): 317 ($M^+$, 44), 302 (100), 260 (46). High-resolution ms Calcd for $C_{19}H_{27}NO_3$: 317.1991. Found: 317.2019. $^1$H-Nmr (400 MHz) $\delta$: 0.89 (3H, t, $J$ = 7.0 Hz, $CH_2C\mathit{H}_3$), 1.2-1.7 (8H, m, $(C\mathit{H}_2)_4CH_3$), 2.75 (3H, s, $C_2$-$CH_3$), 2.82 (2H, t, $J$ = 7.6 Hz, $C\mathit{H}_2(CH_2)_4CH_3$), 3.95, 3.97, 4.10 (each 3H, s, $3OCH_3$), 7.22 (1H, d, $J$ = 8.5 Hz, $C_3$-H), 8.28 (1H, d, $J$ = 8.5 Hz, $C_4$-H).

**5h**: Yield 88%. oil. Ms *m/z* (%): 345 ($M^+$, 47), 330 (100), 260 (51). High-resolution ms Calcd for $C_{21}H_{31}NO_3$: 345.2304. Found: 345.2302. $^1$H-Nmr (400 MHz) $\delta$: 0.88 (3H, t, $J$ = 7.0 Hz, $CH_2C\mathit{H}_3$), 1.2-1.7 (12H, m, $(C\mathit{H}_2)_6CH_3$), 2.74 (3H, s, $C_2$-$CH_3$), 2.82 (2H, t, $J$ = 7.9 Hz, $C\mathit{H}_2(CH_2)_6CH_3$), 3.95, 3.97, 4.10 (each 3H, s, $3OCH_3$), 7.21 (1H, d, $J$ = 8.6 Hz, $C_3$-H), 8.27 (1H, d, $J$ = 8.6 Hz, $C_4$-H).

**5i**: Yield 70%. oil. Ms *m/z* (%): 401 ($M^+$, 41), 386 (100), 260 (59). High-resolution ms Calcd for $C_{25}H_{39}NO_3$: 401.2930. Found: 401.2914. $^1$H-Nmr (400 MHz) $\delta$: 0.88 (3H, t, $J$ = 7.0 Hz, $CH_2C\mathit{H}_3$), 1.2-1.7 (20H, m, $(C\mathit{H}_2)_{10}CH_3$), 2.77 (3H, s, $C_2$-$CH_3$), 2.82 (2H, t, $J$ = 7.6 Hz, $C\mathit{H}_2(CH_2)_{10}CH_3$), 3.95, 3.98, 4.10 (each 3H, s, $3OCH_3$), 7.23 (1H, d, $J$ = 8.5 Hz, $C_3$-H), 8.29 (1H, d, $J$ = 8.5 Hz, $C_4$-H).

**(7-Alkyl-)5,6,8-trimethoxy-2-methylquinoline *N*-Oxides (6a-f, h)** *m*-Chloroperoxybenzoic acid (80% purity, 270 mg, 1.25 mmol) was added to a solution of quinoline (**5a-f, h**) (1 mmol) in $CH_2Cl_2$ (10 ml). The resulting mixture was left for 16 h, and the precipitated crystals were filtered off. The filtrate was washed with saturated aqueous $NaHCO_3$ solution (3 x 10 ml) and water, dried, concentrated, and chromatographed. Elution with ethyl acetate was discarded, and further elution with ethyl acetate-$CH_3OH$ (100:1-7:3) afforded *N*-oxide (**6a-f, h**).

**6a**: Yield 44%. Ms *m/z* (%): 249 ($M^+$, 48), 233 (50), 232 (84), 218 (100). High-resolution ms Calcd for $C_{13}H_{15}NO_4$: 249.1001. Found: 249.1016. $^1$H-Nmr (270 MHz) $\delta$: 2.59 (3H, s, $C_2$-$CH_3$), 3.91, 4.01, 4.03 (each 3H, s, $3OCH_3$), 6.87 (1H, s, $C_7$-H), 7.23 (1H, d, $J$ = 8.9 Hz, $C_3$-H), 7.82 (1H, d, $J$ = 8.9 Hz, $C_4$-H).

**6b**: Yield 61%. Ms *m/z* (%): 263 ($M^+$, 68), 247 (49), 246 (100), 232 (77). High-resolution ms Calcd for $C_{14}H_{17}NO_4$: 263.1157. Found: 263.1145. $^1$H-Nmr (270 MHz) $\delta$: 2.40 (3H, s, $C_7$-$CH_3$), 2.63 (3H, s, $C_2$-$CH_3$), 3.94, 3.95, 3.98 (each 3H, s, $3OCH_3$), 7.21 (1H, d, $J$ = 8.6 Hz, $C_3$-H), 7.82 (1H, d, $J$ = 8.6 Hz, $C_4$-H).

**6c**: Yield 68%. Ms *m/z* (%): 277 ($M^+$, 49), 260 (100), 230 (50). High-resolution ms Calcd for $C_{15}H_{19}NO_4$: 277.1314. Found: 277.1315. $^1$H-Nmr (270 MHz) $\delta$: 1.23 (3H, t, $J$ = 7.6 Hz, $CH_2C\mathit{H}_3$), 2.63 (3H, s, $C_2$-$CH_3$), 2.87 (2H, q, $J$ = 7.6 Hz, $C\mathit{H}_2CH_3$), 3.94, 3.99, 4.00 (each 3H, s, $3OCH_3$), 7.21 (1H, d, $J$ = 8.6 Hz, $C_3$-H), 7.81 (1H, d, $J$ = 8.6 Hz, $C_4$-H).

**6d**: Yield 57%. Ms *m/z* (%): 291 ($M^+$, 18), 275 (53), 274 (48), 260 (100). High-resolution ms Calcd for $C_{16}H_{21}NO_4$: 291.1470. Found: 291.1477. $^1$H-Nmr (270 MHz) $\delta$: 1.02 (3H, t, $J$ = 7.6 Hz, $CH_2C\mathit{H}_3$), 1.63 (2H, sextet, $J$ = 7.6 Hz, $C\mathit{H}_2CH_3$), 2.63 (3H, s, $C_2$-$CH_3$), 2.81 (2H, t, $J$ = 7.6 Hz, $C\mathit{H}_2CH_2CH_3$), 3.93 (3H, s, $OCH_3$), 3.98 (6H, s, $2OCH_3$), 7.21 (1H, d, $J$ = 8.6 Hz, $C_3$-H), 7.82 (1H, d, $J$ = 8.6 Hz, $C_4$-H).

**6e**: Yield 70%. Ms *m/z* (%): 305 ($M^+$, 31), 289 (46), 288 (100), 274 (61), 260 (27). High-resolution ms Calcd for $C_{17}H_{23}NO_4$: 305.1627. Found: 305.1631. $^1$H-Nmr (270 MHz) $\delta$: 0.96 (3H, t, $J$ = 7.3 Hz, $CH_2C\mathit{H}_3$), 1.44 (2H, sextet, $J$ = 7.3 Hz, $C\mathit{H}_2CH_3$), 1.5-1.65 (2H, m, $C\mathit{H}_2CH_2CH_3$), 2.63 (3H, s, $C_2$-$CH_3$), 2.82 (2H, t, $J$ = 7.7 Hz, $C\mathit{H}_2(CH_2)_2CH_3$), 3.93 (3H, s, $OCH_3$), 3.98 (6H, s, $2OCH_3$), 7.21 (1H, d, $J$ = 8.6 Hz, $C_3$-H), 7.81 (1H, d, $J$ = 8.6 Hz, $C_4$-H).

**6f**: Yield 72%. Ms *m/z* (%): 319 ($M^+$, 35), 303 (38), 302 (100), 288 (35). High-resolution ms Calcd for $C_{18}H_{25}NO_4$: 319.1783. Found: 319.1786. $^1$H-Nmr (270 MHz) δ: 0.91 (3H, t, *J* = 6.9 Hz, $CH_2C\mathit{H}_3$), 1.3-1.7 (6H, m, $(C\mathit{H}_2)_3CH_3$), 2.71 (3H, s, $C_2$-$CH_3$), 2.82 (2H, t, *J* = 7.6 Hz, $C\mathit{H}_2(CH_2)_3CH_3$), 3.94, 3.99, 4.00 (each 3H, s, $3OCH_3$), 7.26 (1H, d, *J* = 8.3 Hz, $C_3$-H), 7.95 (1H, d, *J* = 8.3 Hz, $C_4$-H).

**6h**: Yield 45%. Ms *m/z* (%): 361 ($M^+$, 24), 345 (70), 344 (100), 330 (61), 260 (26). High-resolution ms Calcd for $C_{21}H_{31}NO_4$: 361.2253. Found: 361.2263. $^1$H-Nmr (400 MHz) δ: 0.88 (3H, t, *J* = 7.0 Hz, $CH_2C\mathit{H}_3$), 1.2-1.7 (12H, m, $(C\mathit{H}_2)_6CH_3$), 2.66 (3H, s, $C_2$-$CH_3$), 2.81 (2H, t, *J* = 7.9 Hz, $C\mathit{H}_2(CH_2)_6CH_3$), 3.94, 3.98, 3.99 (each 3H, s, $3OCH_3$), 7.23 (1H, d, *J* = 8.5 Hz, $C_3$-H), 7.87 (1H, d, *J* = 8.5 Hz, $C_4$-H).

**2-Acetoxymethyl-(7-alkyl-)5,6,8-trimethoxyquinolines (7a-f, h)** A mixture of *N*-oxide (**6a-f, h**) (1 mmol) and acetic anhydride (5 ml, 53 mmol) was refluxed for 1 h, and then evaporated. The residue was chromatographed (eluting with ethyl acetate-hexane 1:9-3:2) to afford **7a-f, h**.

**7a**: Yield 54%. mp 73-75°C (ether-hexane). Ms *m/z* (%): 291 ($M^+$, 96), 276 (96), 231 (100), 216 (52), 202 (57). *Anal.* Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81. Found: C, 61.83; H, 5.89; N, 4.85. $^1$H-Nmr (270 MHz) δ: 2.18 (3H, s, $COCH_3$), 3.93, 4.04, 4.09 (each 3H, s, $3OCH_3$), 5.43 (2H, s, $CH_2O$), 6.88 (1H, s, $C_7$-H), 7.50 (1H, d, *J* = 8.6 Hz, $C_3$-H), 8.43 (1H, d, *J* = 8.6 Hz, $C_4$-H).

**7b**: Yield 87%. mp 67-68°C (hexane). Ms *m/z* (%): 305 ($M^+$, 91), 290 (68), 245 (100), 230 (82), 216 (38). *Anal.* Calcd for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59. Found: 62.91; H, 6.29; N, 4.47. $^1$H-Nmr (270 MHz) δ: 2.20 (3H, s, $COCH_3$), 2.40 (3H, s, $C_7$-$CH_3$), 3.96, 3.97, 4.06 (each 3H, s, $3OCH_3$), 5.42 (2H, s, $CH_2O$), 7.40 (1H, d, *J* = 8.6 Hz, $C_3$-H), 8.41 (1H, d, *J* = 8.6 Hz, $C_4$-H).

**7c**: Yield 78%. oil. Ms *m/z* (%): 319 ($M^+$, 100), 304 (83), 259 (59), 244 (62). High-resolution ms Calcd for $C_{17}H_{21}NO_5$: 319.1419. Found: 319.1403. $^1$H-Nmr (270 MHz) δ: 1.24 (3H, t, *J* = 7.6 Hz, $CH_2C\mathit{H}_3$), 2.20 (3H, s, $COCH_3$), 2.88 (2H, q, *J* = 7.6 Hz, $C\mathit{H}_2CH_3$), 3.96, 4.00, 4.12 (each 3H, s, $3OCH_3$), 5.42 (2H, s, $CH_2O$), 7.40 (1H, d, *J* = 8.9 Hz, $C_3$-H), 8.41 (1H, d, *J* = 8.9 Hz, $C_4$-H).

**7d**: Yield 88%. oil. Ms *m/z* (%): 333 ($M^+$, 98), 318 (100), 273 (71). High-resolution ms Calcd for $C_{18}H_{23}NO_5$: 333.1576. Found: 333.1593. $^1$H-Nmr (400 MHz) δ: 1.02 (3H, t, *J* = 7.3 Hz, $CH_2C\mathit{H}_3$), 1.64 (2H, sextet, *J* = 7.3 Hz, $C\mathit{H}_2CH_3$), 2.20 (3H, s, $COCH_3$), 2.82 (2H, t, *J* = 7.3 Hz, $C\mathit{H}_2CH_2CH_3$), 3.95, 3.99, 4.11 (each 3H, s, $3OCH_3$), 5.42 (2H, s, $CH_2O$), 7.40 (1H, d, *J* = 8.9 Hz, $C_3$-H), 8.41 (1H, d, *J* = 8.9 Hz, $C_4$-H).

**7e**: Yield 81%. oil. Ms *m/z* (%): 347 ($M^+$, 100), 332 (91), 318 (44), 287 (65). High-resolution ms Calcd for $C_{19}H_{25}NO_5$: 347.1732. Found: 347.1750. $^1$H-Nmr (400 MHz) δ: 0.96 (3H, t, *J* = 7.3 Hz, $CH_2C\mathit{H}_3$), 1.45 (2H, sextet, *J* = 7.3 Hz, $C\mathit{H}_2CH_3$), 1.5-1.65 (2H, m, $C\mathit{H}_2CH_2CH_3$), 2.20 (3H, s, $COCH_3$), 2.84 (2H, t, *J* = 7.6 Hz, $C\mathit{H}_2(CH_2)_2CH_3$), 3.95, 4.00, 4.11 (each 3H, s, $3OCH_3$), 5.45 (2H, s, $CH_2O$), 7.41 (1H, d, *J* = 8.6 Hz, $C_3$-H), 8.43 (1H, d, *J* = 8.6 Hz, $C_4$-H).

**7f**: Yield 76%. oil. Ms *m/z* (%): 361 ($M^+$, 100), 346 (66), 318 (35), 301 (50). High-resolution ms Calcd for $C_{20}H_{27}NO_5$: 361.1889. Found: 361.1884. $^1$H-Nmr (400 MHz) δ: 0.91 (3H, t, *J* = 7.0 Hz, $CH_2C\mathit{H}_3$), 1.3-1.7 (6H, m, $(C\mathit{H}_2)_3CH_3$), 2.20 (3H, s, $COCH_3$), 2.83 (2H, t, *J* = 7.6 Hz, $C\mathit{H}_2(CH_2)_3CH_3$), 3.95, 3.99, 4.11 (each 3H, s, $3OCH_3$), 5.44 (2H, s, $CH_2O$), 7.40 (1H, d, *J* = 8.6 Hz, $C_3$-H), 8.42 (1H, d, *J* = 8.6 Hz, $C_4$-H).

**7h**: Yield 76%. oil. Ms *m/z* (%): 403 ($M^+$, 100), 388 (62), 343 (48), 318 (37). High-resolution ms Calcd for $C_{23}H_{33}NO_5$: 403.2358. Found: 403.2343. $^1$H-Nmr (400 MHz) δ: 0.88 (3H, t, *J* = 7.0 Hz, $CH_2C\mathit{H}_3$), 1.2-1.7 (12H, m, $(C\mathit{H}_2)_6CH_3$), 2.20 (3H, s, $COCH_3$), 2.82 (2H, t, *J* = 7.6 Hz, $C\mathit{H}_2(CH_2)_6CH_3$), 3.95, 3.99, 4.10 (each 3H, s, $3OCH_3$), 5.41 (2H, s, $CH_2O$), 7.39 (1H, d, *J* = 8.6 Hz, $C_3$-H), 8.40 (1H, d, *J* = 8.6 Hz, $C_4$-H).

**7-Alkyl-5,6,8-trimethoxyquinolines (8d-i)** Acrorein (3.36 g, 60 mmol) was added dropwise to a refluxing solution of 3-alkyl-2,4,5-trimethoxyaniline (**4d-i**) (10 mmol) in 6 N HCl (100 ml), and the resulting solution was refluxed for an additional 20 min. The reaction mixture was cooled, diluted with water (100 ml), washed with ether (2 x 100 ml), basified with 10% NaOH solution, and extracted with $CH_2Cl_2$ (3 x 100 ml). The extract was washed with water, dried, and evaporated. The residue was chromatographed (eluting with ethyl acetate-hexane 1:9-3:7) to afford **8d-i**.

**8d**: Yield 54%. oil. Ms *m/z* (%): 261 ($M^+$, 47), 246 (100). High-resolution ms Calcd for $C_{15}H_{19}NO_3$: 261.1365. Found: 261.1348. $^1$H-Nmr (400 MHz) δ: 1.04 (3H, t, $J$ = 7.3 Hz, $\mathrm{CH_2C}H_3$), 1.65 (2H, sextet, $J$ = 7.3 Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 2.83 (2H, t, $J$ = 7.3 Hz, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 3.96, 4.00, 4.10 (each 3H, s, $3OCH_3$), 7.36 (1H, dd, $J$ = 8.5, 4.3 Hz, $C_3$-H), 8.41 (1H, dd, $J$ = 8.5, 1.8 Hz, $C_4$-H), 8.85 (1H, dd, $J$ = 4.3, 1.8 Hz, $C_2$-H).

**8e**: Yield 60%. oil. Ms *m/z* (%): 275 ($M^+$, 60), 260 (100), 246 (38). High-resolution ms Calcd for $C_{16}H_{21}NO_3$: 275.1521. Found: 275.1533. $^1$H-Nmr (400 MHz) δ: 0.98 (3H, t, $J$ = 7.3 Hz, $\mathrm{CH_2C}H_3$), 1.47 (2H, sextet, $J$ = 7.3 Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 1.55-1.65 (2H, m, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 2.85 (2H, t, $J$ = 7.6 Hz, $\mathrm{C}H_2\mathrm{(CH_2)_2CH_3}$), 3.96, 4.00, 4.10 (each 3H, s, $3OCH_3$), 7.35 (1H, dd, $J$ = 8.6, 4.3 Hz, $C_3$-H), 8.40 (1H, dd, $J$ = 8.6, 1.8 Hz, $C_4$-H), 8.84 (1H, dd, $J$ = 4.3, 1.8 Hz, $C_2$-H).

**8f**: Yield 49%. oil. Ms *m/z* (%): 289 ($M^+$, 67), 274 (100), 246 (39). High-resolution ms Calcd for $C_{17}H_{23}NO_3$: 289.1678. Found: 289.1686. $^1$H-Nmr (400 MHz) δ: 0.92 (3H, t, $J$ = 7.0 Hz, $\mathrm{CH_2C}H_3$), 1.3-1.7 (6H, m, $\mathrm{(C}H_2\mathrm{)_3CH_3}$), 2.84 (2H, t, $J$ = 7.9 Hz, $\mathrm{C}H_2\mathrm{(CH_2)_3CH_3}$), 3.96, 4.00, 4.10 (each 3H, s, $3OCH_3$), 7.35 (1H, dd, $J$ = 8.6, 4.3 Hz, $C_3$-H), 8.41 (1H, dd, $J$ = 8.6, 1.8 Hz, $C_4$-H), 8.84 (1H, dd, $J$ = 4.3, 1.8 Hz, $C_2$-H).

**8g**: Yield 44%. oil. Ms *m/z* (%): 303 ($M^+$, 62), 288 (100), 246 (39). High-resolution ms Calcd for $C_{18}H_{25}NO_3$: 303.1834. Found: 303.1849. $^1$H-Nmr (400 MHz) δ: 0.90 (3H, t, $J$ = 7.0 Hz, $\mathrm{CH_2C}H_3$), 1.2-1.7 (8H, m, $\mathrm{(C}H_2\mathrm{)_4CH_3}$), 2.84 (2H, t, $J$ = 7.9 Hz, $\mathrm{C}H_2\mathrm{(CH_2)_4CH_3}$), 3.96, 4.00, 4.10 (each 3H, s, $3OCH_3$), 7.35 (1H, dd, $J$ = 8.5, 4.3 Hz, $C_3$-H), 8.40 (1H, dd, $J$ = 8.5, 1.8 Hz, $C_4$-H), 8.84 (1H, dd, $J$ = 4.3, 1.8 Hz, $C_2$-H).

**8h**: Yield 66%. oil. Ms *m/z* (%): 331 ($M^+$, 44), 316 (100), 246 (48). High-resolution ms Calcd for $C_{20}H_{29}NO_3$: 331.2147. Found: 331.2142. $^1$H-Nmr (400 MHz) δ: 0.88 (3H, t, $J$ = 7.0 Hz, $\mathrm{CH_2C}H_3$), 1.2-1.7 (12H, m, $\mathrm{(C}H_2\mathrm{)_6CH_3}$), 2.84 (2H, t, $J$ = 7.9 Hz, $\mathrm{C}H_2\mathrm{(CH_2)_6CH_3}$), 3.96, 4.00, 4.10 (each 3H, s, $3OCH_3$), 7.35 (1H, dd, $J$ = 8.5, 4.3 Hz, $C_3$-H), 8.40 (1H, dd, $J$ = 8.5, 1.8 Hz, $C_4$-H), 8.84 (1H, dd, $J$ = 4.3, 1.8 Hz, $C_2$-H).

**8i**: Yield 42%. oil. Ms *m/z* (%): 387 ($M^+$, 41), 372 (100), 246 (58). High-resolution ms Calcd for $C_{24}H_{37}NO_3$: 387.2773. Found: 387.2795. $^1$H-Nmr (400 MHz) δ: 0.88 (3H, t, $J$ = 7.0 Hz, $\mathrm{CH_2C}H_3$), 1.2-1.7 (20H, m, $\mathrm{(C}H_2\mathrm{)_{10}CH_3}$), 2.84 (2H, t, $J$ = 7.9 Hz, $\mathrm{C}H_2\mathrm{(CH_2)_{10}CH_3}$), 3.96, 4.00, 4.10 (each 3H, s, $3OCH_3$), 7.36 (1H, dd, $J$ = 8.6, 4.3 Hz, $C_3$-H), 8.42 (1H, dd, $J$ = 8.6, 1.8 Hz, $C_4$-H), 8.85 (1H, dd, $J$ = 4.3, 1.8 Hz, $C_2$-H).

**(7-Alkyl-)5,6,8-trimethoxy-4-methylquinolines (9a-f)** Methyl vinyl ketone (1.40 g, 20 mmol) was added dropwise to a refluxing solution of (3-alkyl-)2,4,5-trimethoxyaniline (**4a-f**) (10 mmol) in 6 N HCl (100 ml), and the resulting solution was refluxed for an additional 90 min. The reaction mixture was cooled, diluted with water (100 ml), washed with ether (2 x 100 ml), basified with 10% NaOH solution, and extracted with $CH_2Cl_2$ (3 x 100 ml). The extract was washed with water, dried, and evaporated. The residue was chromatographed (eluting with ethyl acetate-hexane 1:1–4:1) to afford **9a-f**.

**9a**: Yield 22%. mp 47–49°C (ether-hexane). Ms *m/z* (%): 233 ($M^+$, 35), 218 (100). *Anal.* Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 67.11; H, 6.52; N, 5.97. $^1$H-Nmr (400 MHz) δ: 2.89 (3H, s, $C_4$-$CH_3$), 3.85, 4.03, 4.08 (each 3H, s, $3OCH_3$), 6.89 (1H, s, $C_7$-H), 7.16 (1H, d, $J$ = 4.3 Hz, $C_3$-H), 8.62 (1H, d, $J$ = 4.3 Hz, $C_2$-H).

**9b**: Yield 32%. oil. Ms *m/z* (%): 247 ($M^+$, 25), 232 (100). High-resolution ms Calcd for $C_{14}H_{17}NO_3$: 247.1208. Found: 247.1212. $^1$H-Nmr (270 MHz) δ: 2.42 (3H, s, $C_7$-$CH_3$), 2.89 (3H, s, $C_4$-$CH_3$), 3.91, 3.93, 4.02 (each 3H, s, 3$OCH_3$), 7.12 (1H, d, *J* = 4.3 Hz, $C_3$-H), 8.69 (1H, d, *J* = 4.3 Hz, $C_2$-H).

**9c**: Yield 50%. oil. Ms *m/z* (%): 261 ($M^+$, 43), 246 (100). High-resolution ms Calcd for $C_{15}H_{19}NO_3$: 261.1365. Found: 261.1374. $^1$H-Nmr (270 MHz) δ: 1.27 (3H, t, *J* = 7.6 Hz, $CH_2CH_3$), 2.89 (2H, q, *J* = 7.6 Hz, $CH_2CH_3$), 2.91 (3H, s, $C_4$-$CH_3$), 3.90, 3.98, 4.08 (each 3H, s, 3$OCH_3$), 7.15 (1H, d, *J* = 4.6 Hz, $C_3$-H), 8.71 (1H, d, *J* = 4.6 Hz, $C_2$-H).

**9d**: Yield 68%. oil. Ms *m/z* (%): 275 ($M^+$, 39), 260 (100). High-resolution ms Calcd for $C_{16}H_{21}NO_3$: 275.1521. Found: 275.1545. $^1$H-Nmr (400 MHz) δ: 1.04 (3H, t, *J* = 7.3 Hz, $CH_2CH_3$), 1.66 (2H, sextet, *J* = 7.3 Hz, $CH_2CH_3$), 2.82 (2H, t, *J* = 7.3 Hz, $CH_2CH_2CH_3$), 2.87 (3H, s, $C_4$-$CH_3$), 3.88, 3.96, 4.05 (each 3H, s, 3$OCH_3$), 7.09 (1H, d, *J* = 4.3 Hz, $C_3$-H), 8.65 (1H, d, *J* = 4.3 Hz, $C_2$-H).

**9e**: Yield 67%. oil. Ms *m/z* (%): 289 ($M^+$, 46), 274 (100), 260 (27). High-resolution ms Calcd for $C_{17}H_{23}NO_3$: 289.1678. Found: 289.1704. $^1$H-Nmr (270 MHz) δ: 0.97 (3H, t, *J* = 7.3 Hz, $CH_2CH_3$), 1.46 (2H, sextet, *J* = 7.3 Hz, $CH_2CH_3$), 1.55-1.7 (2H, m, $CH_2CH_2CH_3$), 2.84 (2H, t, *J* = 7.6 Hz, $CH_2(CH_2)_2$-$CH_3$), 2.88 (3H, s, $C_4$-$CH_3$), 3.89, 3.97, 4.06 (each 3H, s, 3$OCH_3$), 7.11 (1H, d, *J* = 4.3 Hz, $C_3$-H), 8.67 (1H, d, *J* = 4.3 Hz, $C_2$-H).

**9f**: Yield 59%. oil. Ms *m/z* (%): 303 ($M^+$, 63), 288 (100), 260 (27). High-resolution ms Calcd for $C_{18}H_{25}NO_3$: 303.1834. Found: 303.1839. $^1$H-Nmr (400 MHz) δ: 0.92 (3H, t, *J* = 7.0 Hz, $CH_2CH_3$), 1.3-1.7 (6H, m, $(CH_2)_3CH_3$), 2.83 (2H, t, *J* = 7.9 Hz, $CH_2(CH_2)_3CH_3$), 2.87 (3H, s, $C_4$-$CH_3$), 3.88, 3.96, 4.05 (each 3H, s, 3$OCH_3$), 7.08 (1H, d, *J* = 4.3 Hz, $C_3$-H), 8.63 (1H, d, *J* = 4.3 Hz, $C_2$-H).

**7-Hexyl- (or 7-Octyl-)5,6,8-trimethoxy-4-methylquinoline (9g, h)** Methyl vinyl ketone (2.50 g, 35 mmol), *m*-nitrobenzenesulfonic acid (1.88 g, 9 mmol), $ZnCl_2$ (0.18 g, 1.3 mmol), and concentrated HCl (1.5 ml) were added to a solution of 3-hexyl- (or 3-octyl-)2,4,5-trimethoxyaniline (**4g, h**) (10 mmol) in ethanol (200 ml). The resulting solution was refluxed for 3 h, and evaporated. The residue was diluted with water (100 ml), basified with 10% NaOH solution, and extracted with $CH_2Cl_2$ (3 x 100 ml). The extract was washed with water, dried, concentrated, and chromatographed (eluting with ethyl acetate-hexane 1:9–3:7) to afford **9g, h**.

**9g**: Yield 69%. oil. Ms *m/z* (%): 317 ($M^+$, 47), 302 (100), 260 (28). High-resolution ms Calcd for $C_{19}H_{27}NO_3$: 317.1991. Found: 317.1996. $^1$H-Nmr (400 MHz) δ: 0.90 (3H, t, *J* = 7.0 Hz, $CH_2CH_3$), 1.3-1.7 (8H, m, $(CH_2)_4CH_3$), 2.83 (2H, t, *J* = 7.9 Hz, $CH_2(CH_2)_4CH_3$), 2.87 (3H, s, $C_4$-$CH_3$), 3.88, 3.96, 4.05 (each 3H, s, 3$OCH_3$), 7.08 (1H, d, *J* = 4.6 Hz, $C_3$-H), 8.64 (1H, d, *J* = 4.6 Hz, $C_2$-H).

**9h**: Yield 75%. oil. Ms *m/z* (%): 345 ($M^+$, 61), 330 (100), 260 (28). High-resolution ms Calcd for $C_{21}H_{31}NO_3$: 345.2304. Found: 345.2320. $^1$H-Nmr (400 MHz) δ: 0.88 (3H, t, *J* = 7.0 Hz, $CH_2CH_3$), 1.2-1.7 (12H, m, $(CH_2)_6CH_3$), 2.83 (2H, t, *J* = 7.9 Hz, $CH_2(CH_2)_6CH_3$), 2.87 (3H, s, $C_4$-$CH_3$), 3.88, 3.96, 4.05 (each 3H, s, 3$OCH_3$), 7.08 (1H, d, *J* = 4.6 Hz, $C_3$-H), 8.64 (1H, d, *J* = 4.6 Hz, $C_2$-H).

**(7-Alkyl-)5,6,8-trimethoxy(-4-methyl)quinoline *N*-Oxides (10d-h, 11a-h)** *m*-Chloroperoxybenzoic acid (80% purity, 270 mg, 1.25 mmol) was added to a solution of quinoline (**8d-h, 9a-h**) (1 mmol) in $CH_2Cl_2$ (10 ml). The resulting mixture was left for 16 h, and the precipitated crystals were filtered off. The filtrate was washed with saturated aqueous $NaHCO_3$ solution (3 x 10 ml) and water, dried, concentrated, and chromatographed. Elution with ethyl acetate was discarded, and further elution with ethyl acetate-$CH_3OH$ (100:1-7:3) afforded *N*-oxide (**10d-h, 11a-h**).

**10d**: Yield 72%. Ms *m/z* (%): 277 ($M^+$, 15), 261 (53), 260 (38), 246 (100). High-resolution ms Calcd for $C_{15}H_{19}NO_4$: 277.1314. Found: 277.1314. $^1$H-Nmr (270 MHz) δ: 1.03 (3H, t, *J* = 7.6 Hz, $CH_2CH_3$), 1.64 (2H, sextet, *J* = 7.6 Hz, $CH_2CH_3$), 2.82 (2H, t, *J* = 7.6 Hz, $CH_2CH_2CH_3$), 3.94, 3.97, 4.00 (each 3H, s, $3OCH_3$), 7.17 (1H, dd, *J* = 8.6, 6.3 Hz, $C_3$-H), 7.98 (1H, dd, *J* = 8.6, 1.0 Hz, $C_4$-H), 8.44 (1H, dd, *J* = 6.3, 1.0 Hz, $C_2$-H).

**10e**: Yield 95%. Ms *m/z* (%): 291 ($M^+$, 31), 275 (41), 274 (100), 260 (45). High-resolution ms Calcd for $C_{16}H_{21}NO_4$: 291.1470. Found: 291.1463. $^1$H-Nmr (400 MHz) δ: 0.97 (3H, t, *J* = 7.3 Hz, $CH_2CH_3$), 1.46 (2H, sextet, *J* = 7.3 Hz, $CH_2CH_3$), 1.5-1.65 (2H, m, $CH_2CH_2CH_3$), 2.84 (2H, t, *J* = 7.6 Hz, $CH_2(CH_2)_2CH_3$), 3.95, 3.97, 4.01 (each 3H, s, $3OCH_3$), 7.23 (1H, dd, *J* = 8.6, 6.1 Hz, $C_3$-H), 8.06 (1H, d, *J* = 8.6 Hz, $C_4$-H), 8.52 (1H, d, *J* = 6.1 Hz, $C_2$-H).

**10f**: Yield 75%. Ms *m/z* (%): 305 ($M^+$, 31), 289 (45), 288 (100), 274 (45). High-resolution ms Calcd for $C_{17}H_{23}NO_4$: 305.1627. Found: 305.1623. $^1$H-Nmr (270 MHz) δ: 0.92 (3H, t, *J* = 6.9 Hz, $CH_2CH_3$), 1.3-1.7 (6H, m, $(CH_2)_3CH_3$), 2.82 (2H, t, *J* = 7.6 Hz, $CH_2(CH_2)_3CH_3$), 3.94, 3.97, 4.00 (each 3H, s, $3OCH_3$), 7.18 (1H, dd, *J* = 8.6, 6.3 Hz, $C_3$-H), 7.97 (1H, d, *J* = 8.6 Hz, $C_4$-H), 8.43 (1H, d, *J* = 6.3 Hz, $C_2$-H).

**10g**: Yield 71%. Ms *m/z* (%): 319 ($M^+$, 5), 303 (64), 288 (100), 246 (38). High-resolution ms Calcd for $C_{18}H_{25}NO_4$: 319.1783. Found: 319.1787. $^1$H-Nmr (270 MHz) δ: 0.90 (3H, t, *J* = 6.9 Hz, $CH_2CH_3$), 1.2-1.7 (8H, m, $(CH_2)_4CH_3$), 2.81 (2H, t, *J* = 7.6 Hz, $CH_2(CH_2)_4CH_3$), 3.94, 3.96, 4.00 (each 3H, s, $3OCH_3$), 7.15 (1H, dd, *J* = 8.6, 5.9 Hz, $C_3$-H), 7.91 (1H, dd, *J* = 8.6, 1.3 Hz, $C_4$-H), 8.36 (1H, dd, *J* = 5.9, 1.3 Hz, $C_2$-H).

**10h**: Yield 80%. Ms *m/z* (%): 347 ($M^+$, 25), 331 (77), 330 (100), 316 (56). High-resolution ms Calcd for $C_{20}H_{29}NO_4$: 347.2096. Found: 347.2098. $^1$H-Nmr (400 MHz) δ: 0.88 (3H, t, *J* = 7.0 Hz, $CH_2CH_3$), 1.2-1.7 (12H, m, $(CH_2)_6CH_3$), 2.81 (2H, t, *J* = 7.6 Hz, $CH_2(CH_2)_6CH_3$), 3.94, 3.96, 4.00 (each 3H, s, $3OCH_3$), 7.16 (1H, dd, *J* = 8.6, 6.1 Hz, $C_3$-H), 7.94 (1H, dd, *J* = 8.6, 1.2 Hz, $C_4$-H), 8.39 (1H, dd, *J* = 6.1, 1.2 Hz, $C_2$-H).

**11a**: Yield 31%. Ms *m/z* (%): 249 ($M^+$, 17), 233 (45), 218 (100). High-resolution ms Calcd for $C_{13}H_{15}NO_4$: 249.1001. Found: 249.0993. $^1$H-Nmr (270 MHz) δ: 2.79 (3H, s, $C_4$-$CH_3$), 3.83, 4.01, 4.02 (each 3H, s, $3OCH_3$), 6.89 (1H, d, *J* = 6.3 Hz, $C_3$-H), 6.92 (1H, s, $C_7$-H), 8.16 (1H, d, *J* = 6.3 Hz, $C_2$-H).

**11b**: Yield 67%. Ms *m/z* (%): 263 ($M^+$, 16), 247 (45), 246 (31), 232 (100). High-resolution ms Calcd for $C_{14}H_{17}NO_4$: 263.1157. Found: 263.1143. $^1$H-Nmr (270 MHz) δ: 2.39 (3H, s, $C_7$-$CH_3$), 2.79 (3H, s, $C_4$-$CH_3$), 3.87, 3.92, 3.93 (each 3H, s, $3OCH_3$), 6.88 (1H, d, *J* = 6.3 Hz, $C_3$-H), 8.24 (1H, d, *J* = 4.3 Hz, $C_2$-H).

**11c**: Yield 66%. Ms *m/z* (%): 277 ($M^+$, 16), 261 (35), 260 (27), 246 (100). High-resolution ms Calcd for $C_{15}H_{19}NO_4$: 277.1314. Found: 277.1323. $^1$H-Nmr (270 MHz) δ: 1.24 (3H, t, *J* = 7.6 Hz, $CH_2CH_3$), 2.79 (3H, s, $C_4$-$CH_3$), 2.87 (2H, q, *J* = 7.6 Hz, $CH_2CH_3$), 3.87, 3.94, 3.97 (each 3H, s, $3OCH_3$), 6.88 (1H, d, *J* = 6.3 Hz, $C_3$-H), 8.22 (1H, d, *J* = 6.3 Hz, $C_2$-H).

**11d**: Yield 60%. Ms *m/z* (%): 291 ($M^+$, 5), 275 (38), 274 (19), 260 (100). High-resolution ms Calcd for $C_{16}H_{21}NO_4$: 291.1470. Found: 291.1469. $^1$H-Nmr (270 MHz) δ: 1.03 (3H, t, *J* = 7.6 Hz, $CH_2CH_3$), 1.63 (2H, sextet, *J* = 7.6 Hz, $CH_2CH_3$), 2.79 (3H, s, $C_4$-$CH_3$), 2.80 (2H, t, *J* = 7.6 Hz, $CH_2CH_2CH_3$), 3.86, 3.93, 3.95 (each 3H, s, $3OCH_3$), 6.88 (1H, d, *J* = 6.3 Hz, $C_3$-H), 8.22 (1H, d, *J* = 6.3 Hz, $C_2$-H).

**11e**: Yield 63%. Ms *m/z* (%): 305 ($M^+$, 45), 289 (54), 288 (82), 274 (100), 260 (33). High-resolution ms Calcd for $C_{17}H_{23}NO_4$: 305.1627. Found: 305.1631. $^1$H-Nmr (270 MHz) δ: 0.96 (3H, t, *J* = 7.3 Hz, $CH_2CH_3$), 1.45 (2H, sextet, *J* = 7.3 Hz, $CH_2CH_3$), 1.5-1.7 (2H, m, $CH_2CH_2CH_3$), 2.79 (3H, s, $C_4$-$CH_3$), 2.82 (2H, t, *J* = 7.6 Hz, $CH_2(CH_2)_2CH_3$), 3.86, 3.93, 3.95 (each 3H, s, $3OCH_3$), 6.87 (1H, d, *J* = 6.3 Hz, $C_3$-H), 8.22 (1H, d, *J* = 6.3 Hz, $C_2$-H).

**11f**: Yield 60%. Ms *m/z* (%): 319 ($M^+$, 28), 303 (36), 302 (100), 288 (36). High-resolution ms Calcd for $C_{18}H_{25}NO_4$: 319.1783. Found: 319.1757. $^1$H-Nmr (400 MHz) δ: 0.92 (3H, t, $J$ = 7.0 Hz, $\mathrm{CH_2C}H_3$), 1.3-1.7 (6H, m, $(\mathrm{C}H_2)_3\mathrm{CH_3}$), 2.79 (3H, s, $C_4$-$CH_3$), 2.81 (2H, t, $J$ = 7.9 Hz, $\mathrm{C}H_2(\mathrm{CH_2})_3\mathrm{CH_3}$), 3.86, 3.93, 3.95 (each 3H, s, $3OCH_3$), 6.88 (1H, d, $J$ = 6.4 Hz, $C_3$-H), 8.24 (1H, d, $J$ = 6.4 Hz, $C_2$-H).

**11g**: Yield 59%. Ms *m/z* (%): 333 ($M^+$, 19), 317 (60), 316 (51), 302 (100), 260 (29). High-resolution ms Calcd for $C_{19}H_{27}NO_4$: 333.1940. Found: 333.1941. $^1$H-Nmr (270 MHz) δ: 0.90 (3H, t, $J$ = 6.9 Hz, $\mathrm{CH_2C}H_3$), 1.3-1.7 (8H, m, $(\mathrm{C}H_2)_4\mathrm{CH_3}$), 2.79 (3H, s, $C_4$-$CH_3$), 2.81 (2H, t, $J$ = 7.6 Hz, $\mathrm{C}H_2(\mathrm{CH_2})_4\mathrm{CH_3}$), 3.86, 3.93, 3.95 (each 3H, s, $3OCH_3$), 6.88 (1H, d, $J$ = 6.3 Hz, $C_3$-H), 8.22 (1H, d, $J$ = 6.3 Hz, $C_2$-H).

**11h**: Yield 62%. Ms *m/z* (%): 361 ($M^+$, 20), 345 (73), 344 (57), 330 (100), 260 (31). High-resolution ms Calcd for $C_{21}H_{31}NO_4$: 361.2253. Found: 361.2246. $^1$H-Nmr (400 MHz) δ: 0.88 (3H, t, $J$ = 7.0 Hz, $\mathrm{CH_2C}H_3$), 1.2-1.7 (12H, m, $(\mathrm{C}H_2)_6\mathrm{CH_3}$), 2.80 (2H, t, $J$ = 7.9 Hz, $\mathrm{C}H_2(\mathrm{CH_2})_6\mathrm{CH_3}$), 2.80 (3H, s, $C_4$-$CH_3$), 3.86, 3.93, 3.95 (each 3H, s, $3OCH_3$), 6.90 (1H, d, $J$ = 6.4 Hz, $C_3$-H), 8.27 (1H, d, $J$ = 6.4 Hz, $C_2$-H).

**(7-Alkyl-)2-chloro-5,6,8-trimethoxy(-4-methyl)quinolines (12a-h, 13a-h)** A mixture of *N*-oxide **(10a-h, 11a-h)** (1 mmol) and phosphorous oxychloride (4 ml, 43 mmol) was heated at 90–100°C for 10 min. The reaction mixture was cooled, poured into ice-water (40 ml), and extracted with $CH_2Cl_2$ (3 x 40 ml). The extract was washed with water, dried, and evaporated. The residue was chromatographed (eluting with ethyl acetate-hexane 3:7) to afford 2-chloroquinoline **(12a-h, 13a-h)**.

**12a**: Yield 77%. mp 146–147°C (ether-hexane). Ms *m/z* (%): 255 ($M^+$+2, 20), 253 ($M^+$, 61), 240 (34), 238 (100). *Anal.* Calcd for $C_{12}H_{12}NO_3Cl$: C, 56.82; H, 4.77; N, 5.52. Found: C, 56.96; H, 4.70; N, 5.46. $^1$H-Nmr (270 MHz) δ: 3.92, 4.03, 4.06 (each 3H, s, $3OCH_3$), 6.88 (1H, s, $C_7$-H), 7.38 (1H, d, $J$ = 8.9 Hz, $C_3$-H), 8.34 (1H, d, $J$ = 8.9 Hz, $C_4$-H).

**12b**: Yield 83%. mp 47–51°C ($CH_2Cl_2$-hexane). Ms *m/z* (%): 269 ($M^+$+2, 20), 267 ($M^+$, 59), 254 (36), 252 (100). *Anal.* Calcd for $C_{13}H_{14}NO_3Cl$: C, 58.32; H, 5.27; N, 5.23. Found: C, 58.14; H, 5.30; N, 5.18. $^1$H-Nmr (270 MHz) δ: 2.39 (3H, s, $C_7$-$CH_3$), 3.95, 3.97, 4.06 (each 3H, s, $3OCH_3$), 7.31 (1H, d, $J$ = 8.9 Hz, $C_3$-H), 8.33 (1H, d, $J$ = 8.5 Hz, $C_4$-H).

**12c**: Yield 86%. mp 53–55°C (hexane). Ms *m/z* (%): 283 ($M^+$+2, 14), 281 ($M^+$, 41), 268 (35), 266 (100). *Anal.* Calcd for $C_{14}H_{16}NO_3Cl$: C, 59.68; H, 5.72; N, 4.97. Found: C,59.62; H, 5.73; N, 4.92. $^1$H-Nmr (270 MHz) δ: 1.23 (3H, t, $J$ = 7.6 Hz, $\mathrm{CH_2C}H_3$), 2.87 (2H, q, $J$ = 7.6 Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 3.95, 3.99, 4.11 (each 3H, s, $3OCH_3$), 7.31 (1H, d, $J$ = 8.9 Hz, $C_3$-H), 8.33 (1H, d, $J$ = 8.9 Hz, $C_4$-H).

**12d**: Yield 74%. mp 65–66°C (hexane). Ms *m/z* (%): 297 ($M^+$+2, 23), 295 ($M^+$, 58), 284 (34), 280 (100). *Anal.* Calcd for $C_{15}H_{18}NO_3Cl$: C, 60.91; H, 6.13; N, 4.74. Found: C, 60.75; H, 6.11; N, 4.69. $^1$H-Nmr (400 MHz) δ: 1.02 (3H, t, $J$ = 7.3 Hz, $\mathrm{CH_2C}H_3$), 1.63 (2H, sextet, $J$ = 7.3 Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 2.81 (2H, t, $J$ = 7.3 Hz, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 3.95, 3.98, 4.10 (each 3H, s, $3OCH_3$), 7.30 (1H, d, $J$ = 8.6 Hz, $C_3$-H), 8.33 (1H, d, $J$ = 8.6 Hz, $C_4$-H).

**12e**: Yield 84%. oil. Ms *m/z* (%): 311 ($M^+$+2, 25), 309 ($M^+$, 68), 296 (35), 294 (100), 282 (11), 280 (35). High-resolution ms Calcd for $C_{16}H_{20}NO_3Cl$: 309.1131. Found: 309.1129. $^1$H-Nmr (400 MHz) δ: 0.96 (3H, t, $J$ = 7.3 Hz, $\mathrm{CH_2C}H_3$), 1.45 (2H, sextet, $J$ = 7.3 Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 1.5-1.65 (2H, m, $\mathrm{C}H_2\mathrm{CH_2CH_3}$), 2.83 (2H, t, $J$ = 7.6 Hz, $\mathrm{C}H_2(\mathrm{CH_2})_2\mathrm{CH_3}$), 3.95, 3.98, 4.10 (each 3H, s, $3OCH_3$), 7.30 (1H, d, $J$ = 8.6 Hz, $C_3$-H), 8.32 (1H, d, $J$ = 8.6 Hz, $C_4$-H).

**12f**: Yield 87%. oil. Ms *m/z* (%): 325 ($M^+$+2, 31), 323 ($M^+$, 89), 310 (35), 308 (100), 282 (12), 280 (36). High-resolution ms Calcd for $C_{17}H_{22}NO_3Cl$: 323.1288. Found: 323.1312. $^1$H-Nmr (270 MHz) δ: 0.91 (3H, t,

$J$ = 7.0 Hz, $CH_2CH_3$), 1.3-1.7 (6H, m, $(CH_2)_3CH_3$), 2.82 (2H, t, $J$ = 7.6 Hz, $CH_2(CH_2)_3CH_3$), 3.95, 3.98, 4.10 (each 3H, s, $3OCH_3$), 7.30 (1H, d, $J$ = 8.6 Hz, $C_3$-H), 8.32 (1H, d, $J$ = 8.6 Hz, $C_4$-H).

**12g**: Yield 84%. oil. Ms *m/z* (%): 339 ($M^+$+2, 29), 337 ($M^+$, 78), 324 (36), 322 (100), 282 (12), 280 (35). High-resolution ms Calcd for $C_{18}H_{24}NO_3Cl$: 337.1444. Found: 337.1449. $^1$H-Nmr (400 MHz) δ: 0.90 (3H, t, $J$ = 7.0 Hz, $CH_2CH_3$), 1.2-1.7 (8H, m, $(CH_2)_4CH_3$), 2.82 (2H, t, $J$ = 7.9 Hz, $CH_2(CH_2)_4CH_3$), 3.95, 3.98, 4.10 (each 3H, s, $3OCH_3$), 7.30 (1H, d, $J$ = 8.6 Hz, $C_3$-H), 8.32 (1H, d, $J$ = 8.6 Hz, $C_4$-H).

**12h**: Yield 75%. oil. Ms *m/z* (%): 367 ($M^+$+2, 36), 365 ($M^+$, 100), 352 (30), 350 (80), 282 (12), 280 (35). High-resolution ms Calcd for $C_{20}H_{28}NO_3Cl$: 365.1757. Found: 365.1734. $^1$H-Nmr (400 MHz) δ: 0.88 (3H, t, $J$ = 7.0 Hz, $CH_2CH_3$), 1.2-1.7 (12H, m, $(CH_2)_6CH_3$), 2.81 (2H, t, $J$ = 7.6 Hz, $CH_2(CH_2)_6CH_3$), 3.95, 3.98, 4.10 (each 3H, s, $3OCH_3$), 7.30 (1H, d, $J$ = 8.9 Hz, $C_3$-H), 8.32 (1H, d, $J$ = 8.9 Hz, $C_4$-H).

**13a**: Yield 63%. mp 148–149°C ($CH_2Cl_2$-ether). Ms *m/z* (%): 269 ($M^+$+2, 20), 267 ($M^+$, 57), 254 (35), 252 (100). *Anal.* Calcd for $C_{13}H_{14}NO_3Cl$: C, 58.32; H, 5.27; N, 5.23. Found: C, 58.32; H, 5.28; N, 5.19. $^1$H-Nmr (270 MHz) δ: 2.85 (3H, d, $J$ = 0.7 Hz, $C_4$-$CH_3$), 3.85, 4.02, 4.05 (each 3H, s, $3OCH_3$), 6.89 (1H, s, $C_7$-H), 7.14 (1H, q, $J$ = 0.7 Hz, $C_3$-H).

**13b**: Yield 86%. mp 68–72°C ($CH_2Cl_2$-hexane). Ms *m/z* (%): 283 ($M^+$+2, 17), 281 ($M^+$, 50), 268 (33), 266 (100). *Anal.* Calcd for $C_{14}H_{16}NO_3Cl$: C, 59.68; H, 5.72; N, 4.97. Found: 59.45; H, 5.71; N,4.89. $^1$H-Nmr (270 MHz) δ: 2.39 (3H, s, $C_7$-$CH_3$), 2.83 (3H, d, $J$ = 0.7 Hz, $C_4$-$CH_3$), 3.89, 3.91, 4.01 (each 3H, s, $3OCH_3$), 7.08 (1H, q, $J$ = 0.7 Hz, $C_3$-H).

**13c**: Yield 71%. mp 82–84°C (hexane). Ms *m/z* (%): 297 ($M^+$+2, 17), 295 ($M^+$, 48), 282 (34), 280 (100). *Anal.* Calcd for $C_{15}H_{18}NO_3Cl$: C, 60.91; H, 6.13; N, 4.74. Found: C, 60.90; H, 6.23; N, 4.67. $^1$H-Nmr (270 MHz) δ: 1.23 (3H, t, $J$ = 7.6 Hz, $CH_2CH_3$), 2.83 (3H, s, $C_4$-$CH_3$), 2.86 (2H, q, $J$ = 7.6 Hz, $CH_2CH_3$), 3.88, 3.96, 4.06 (each 3H, s, $3OCH_3$), 7.07 (1H, s, $C_3$-H).

**13d**: Yield 84%. mp 41–43°C (hexane). Ms *m/z* (%): 311 ($M^+$+2, 16), 309 ($M^+$, 46), 296 (35), 294 (100). *Anal.* Calcd for $C_{16}H_{20}NO_3Cl$: C, 62.03; H, 6.51; N, 4.52. Found: 61.93; H, 6.56; N, 4.49. $^1$H-Nmr (270 MHz) δ: 1.02 (3H, t, $J$ = 7.6 Hz, $CH_2CH_3$), 1.63 (2H, sextet, $J$ = 7.6 Hz, $CH_2CH_3$), 2.79 (2H, t, $J$ = 7.6 Hz, $CH_2CH_2CH_3$), 2.83 (3H, d, $J$ = 1.0 Hz, $C_4$-$CH_3$), 3.87, 3.94, 4.05 (each 3H, s, $3OCH_3$), 7.07 (1H, q, $J$ = 1.0 Hz, $C_3$-H).

**13e**: Yield 84%. oil. Ms *m/z* (%): 325 ($M^+$+2, 17), 323 ($M^+$, 50), 310 (35), 308 (100). High-resolution ms Calcd for $C_{17}H_{22}NO_3Cl$: 323.1288. Found: 323.1288. $^1$H-Nmr (270 MHz) δ: 0.96 (3H, t, $J$ = 7.3 Hz, $CH_2CH_3$), 1.44 (2H, sextet, $J$ = 7.3 Hz, $CH_2CH_3$), 1.5-1.65 (2H, m, $CH_2CH_2CH_3$), 2.81 (2H, t, $J$ = 7.9 Hz, $CH_2(CH_2)_2CH_3$), 2.83 (3H, d, $J$ = 1.0 Hz, $C_4$-$CH_3$), 3.87, 3.95, 4.05 (each 3H, s, $3OCH_3$), 7.07 (1H, q, $J$ = 1.0 Hz, $C_3$-H).

**13f**: Yield 85%. oil. Ms *m/z* (%): 339 ($M^+$+2, 24), 337 ($M^+$, 68), 324 (36), 322 (100), 296 (9), 294 (27). High-resolution ms Calcd for $C_{18}H_{24}NO_3Cl$: 337.1444. Found: 337.1437. $^1$H-Nmr (400 MHz) δ: 0.91 (3H, t, $J$ = 7.0 Hz, $CH_2CH_3$), 1.3-1.7 (6H, m, $(CH_2)_3CH_3$), 2.80 (2H, t, $J$ = 7.9 Hz, $CH_2(CH_2)_3CH_3$), 2.83 (3H, d, $J$ = 0.6 Hz, $C_4$-$CH_3$), 3.87, 3.94, 4.05 (each 3H, s, $3OCH_3$), 7.07 (1H, q, $J$ = 0.6 Hz, $C_3$-H).

**13g**: Yield 89%. oil. Ms *m/z* (%): 353 ($M^+$+2, 20), 351 ($M^+$, 55), 338 (36), 336 (100), 296 (9), 294 (26). High-resolution ms Calcd for $C_{19}H_{26}NO_3Cl$: 351.1601. Found: 351.1608. $^1$H-Nmr (400 MHz) δ: 0.89 (3H, t, $J$ = 7.0 Hz, $CH_2CH_3$), 1.3-1.7 (8H, m, $(CH_2)_4CH_3$), 2.80 (2H, t, $J$ = 7.9 Hz, $CH_2(CH_2)_4CH_3$), 2.83 (3H, d, $J$ = 0.9 Hz, $C_4$-$CH_3$), 3.87, 3.94, 4.05 (each 3H, s, $3OCH_3$), 7.07 (1H, q, $J$ = 0.9 Hz, $C_3$-H).

**13h**: Yield 86%. oil. Ms *m/z* (%): 381 ($M^+$+2, 37), 379 ($M^+$, 100), 366 (34), 364 (96), 296 (9), 294 (28). High-resolution ms Calcd for $C_{21}H_{30}NO_3Cl$: 379.1914. Found: 379.1909. $^1$H-Nmr (400 MHz) δ: 0.88 (3H, t, *J* = 7.0 Hz, $CH_2CH_3$), 1.3-1.7 (12H, m, $(CH_2)_6CH_3$), 2.80 (2H, t, *J* = 7.9 Hz, $CH_2(CH_2)_6CH_3$), 2.83 (3H, d, *J* = 0.9 Hz, $C_4$-$CH_3$), 3.87, 3.94, 4.05 (each 3H, s, 3$OCH_3$), 7.07 (1H, q, *J* = 0.9 Hz, $C_3$-H).

**Oxidative Demethylation of 5,6,8-Trimethoxyquinolinones (5, 7-9, 12, 13)** A solution of CAN (1370 mg, 2.5 mmol) in acetonitrile-water (1:1, 5 ml) was added dropwise to 5,6,8-trimethoxyquinoline (**5, 7-9, 12, 13**) (0.5 mmol) dissolved in acetonitrile-water (3:1, 10 ml) (or acetonitrile, 10 ml) containing (suspended) pyridine-2,6-dicarboxylic acid *N*-oxide (458 mg, 2.5 mmol) at 0-5°C. The mixture was kept at 0-5°C for 30 min, diluted with water (50 ml), and extracted with $CH_2Cl_2$ (3 x 25 ml). The extract was washed with brine, dried and evaporated. The residue was chromatographed (eluting with ethyl acetate-hexane, ethyl acetate-methanol, or ethyl acetate-$CH_2Cl_2$) to afford the corresponding *p*-quinone (**14-19**) and/or *o*-quinone (**20-25**).

**Condensation of *o*-Quinones (22a, b) with *o*-Phenylenediamine (26)** A mixture of *o*-quinone (**22a, b**) (0.2 mmol) and *o*-phenylenediamine (**26**) (22 mg, 0.2 mmol) in ethanol (8 ml) containing acetic acid (0.2 ml) was refluxed for 30 min, and then evaporated. The residue was dissolved in $CH_2Cl_2$ (20 ml). The solution was washed with 10% $NaHCO_3$ solution (20 ml) and water, dried, concentrated, and chromatographed (eluting with $CH_2Cl_2$-ethanol (19:1) or ethyl acetate-benzene (3:17)) to afford the corresponding pyridophenazine (**27a, b**).

**27a**: Yield 86%. mp 184-186°C ($CH_2Cl_2$-hexane). Ms *m/z* (%): 261 ($M^+$, 100), 260 (83), 232 (95), 231 (45), 230 (33). *Anal.* Calcd for $C_{16}H_{11}N_3O\cdot 1/4\ H_2O$: C, 72.30; H, 4.36; N, 15.81. Found: C, 72.25; H, 4.63; N, 15.90. $^1$H-Nmr (400 MHz) δ: 4.25 (3H, s, $OCH_3$), 7.39 (1H, s, $C_6$-H), 7.74 (1H, dd, *J* = 8.1, 4.4 Hz, $C_2$-H), 7.77-7.90 (2H, m, $C_9$-H, $C_{10}$-H), 8.18 (1H, dd, *J* = 8.4, 1.1 Hz, $C_8$-H), 8.27 (1H, dd, *J* = 8.4, 1.1 Hz, $C_{11}$-H), 9.13 (1H, dd, *J* = 4.4, 1.8 Hz, $C_3$-H), 9.58 (1H, dd, *J* = 8.1, 1.8 Hz, $C_1$-H).

**27b**: Yield 82%. mp 187-189°C (ether-hexane). Ms *m/z* (%): 275 ($M^+$, 100), 260 (69), 246 (64). *Anal.* Calcd for $C_{17}H_{13}N_3O$: C, 74.17; H, 4.76; N, 15.26. Found: C, 74.12; H, 4.55; N, 15.24. $^1$H-Nmr (270 MHz) δ: 2.91 (3H, s, $C_6$-$CH_3$), 4.23 (3H, s, $OCH_3$), 7.69 (1H, dd, *J* = 7.9, 4.3 Hz, $C_2$-H), 7.82-7.94 (2H, m, $C_9$-H, $C_{10}$-H), 8.28-8.39 (2H, m, $C_8$-H, $C_{11}$-H), 9.12 (1H, dd, *J* = 4.3, 1.7 Hz, $C_3$-H), 9.64 (1H, dd, *J* = 7.9, 1.7 Hz, $C_1$-H).

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