# Abnormal Reactions of 2-Methoxy-4,9-dimethyl-1-nitroacridine with Selenous Acid and Selenium(IV) Oxide. Synthesis of 1*H*-Selenopheno[2,3,4-*k*,*l*]acridine-1-one: A New Seleno-Containing Ring System



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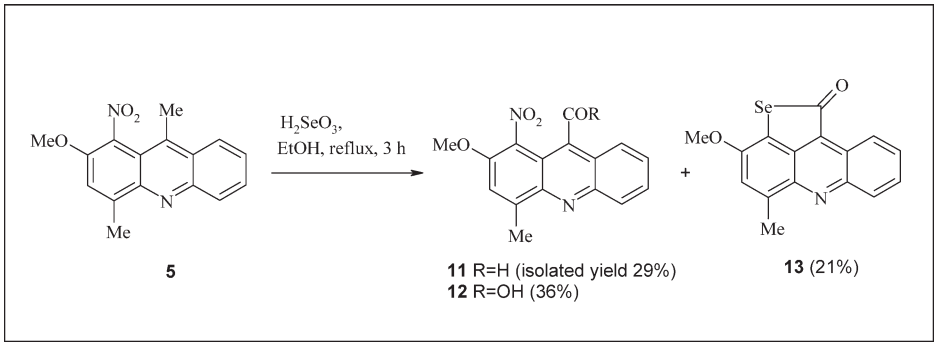


Unusual course of the reaction was revealed on the oxidation of functionally substituted acridine containing the activated methyl groups by well-known oxidants, such as selenous acid and selenium(IV) oxide. Treatment of 2-methoxy-4,9-dimethyl-1-nitroacridine (**5**) with an excess of $H_2SeO_3$ in boiling ethanol gave a mixture of the normal reaction products, 2-methoxy-4-methyl-1-nitro-9-formylacridine (**11**) (isolated yield 29%) and 2-methoxy-4-methyl-1-nitroacridine-9-carboxylic acid (**12**) (36%), together with an abnormal product, 3-methoxy-5-methyl-1*H*-selenopheno[2,3,4-*k*,*l*]acridine-1-one (**13**) (21%), which is the first example of a new seleno-containing ring system. With the use of $SeO_2$ the yield of selenolactone **13** was much lower.

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## INTRODUCTION

Recently, we reported a simple and effective approach to the synthesis of pyrido[4,3,2-*m*,*n*]pyrrolo[3,2,1-*d*,*e*]acridine skeleton of arnoamines A and B, cytotoxic marine alkaloids from the ascidian *Cystodytes* sp. [1]. In the course of developing our researches in this area we embarked on a study of a fresh approach to the total synthesis of arnoamines A (**1**) and B (**2**) based on the use of acridine **5** as the key intermediate (Scheme 1).

As part of an exploration program of this synthesis it was necessary to oxidize the activated methyl groups at the positions 4 and 9 of acridine **5** into the formyl groups.

One solution of this problem was proposed by applying the traditional oxidants, such as selenium(IV) oxide and selenous acid. These reagents have been successfully applied for various oxidations useful in practical organic syntheses [2], including the oxidation of the activated methyl groups of aromatic compounds to the formyl groups [3].

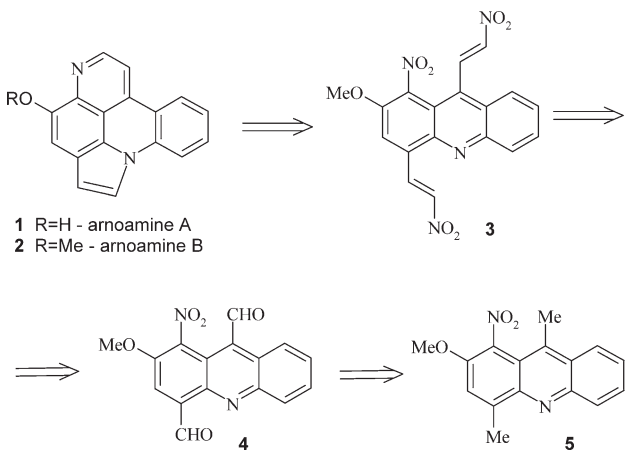
In this communication, we wish to report the results on using the selenium species for the oxidation of the activated methyl groups of 4,9-dimethyl-substituted acridine **5**.

## RESULTS AND DISCUSSION

The synthesis of acridine **5** was carried out according to Scheme 2 starting with commercially available 4-bromo-3-methylanisole (**6**) to give the desired compound within three steps and an overall yield of 48%.

In the first stage of this sequence, there was a need to introduce the nitro group at the position 6 of anisole **6**. The nitration proceeded regioselectively and in good yield only under the action of 98% $HNO_3$ at the reduced temperature. Under these conditions the desired product **7** was obtained in 68% yield along with a slight amount (7%) of mononitro and trinitro derivatives **8** and **9,** respectively. The formation of the latter was

**Scheme 1**




accompanied by cleaving the O—$CH_3$ bond and replacing bromine by the nitro group. The mixture of these products was separated by flash column chromatography on $SiO_2$. A copper-catalyzed coupling reaction of bromide **7** with commercially available 2′-aminoacetophenone afforded secondary amine **10** in 87% yield. The electrophilic cyclization of amine **10** proceeded readily under the action of a mixture of HOAc/$H_2SO_4$ (3:1, v/v) at 85°C to give the target acridine **5** in 81% yield.

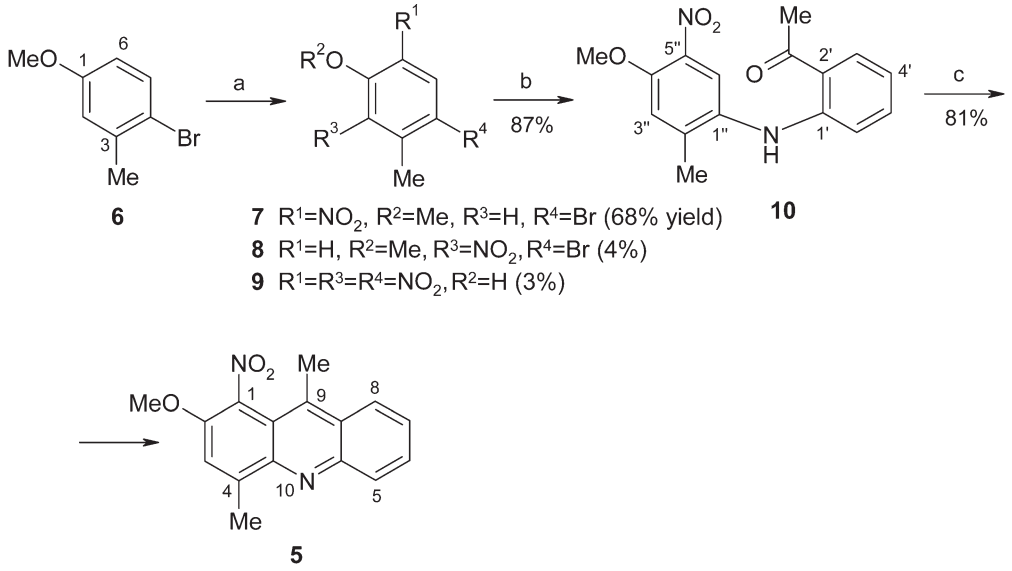
The oxidation of acridine **5** with an excess of $H_2SeO_3$ was investigated in various solvents such as THF, EtOH, methyl cellosolve, diglyme, and triglyme under reflux conditions (66–215°C). The reaction time varied between 1 and 8 h.

Unfortunately, we failed to oxidize both of the methyl groups of acridine **5** to the formyl groups on treatment of substrate with $H_2SeO_3$ under experimental conditions studied. In all cases, the formation of only a mixture of aldehyde **11** and acid **12** was observed (Scheme 3). On heating at high temperatures (180–215°C), substrate **5** was subjected to considerable decomposition but even under such rigid conditions the methyl group at the position 4 was not active toward oxidizing agent.

Contrary to the usual results of such reactions we found that the oxidation of acridine **5** with an excess of $H_2SeO_3$ in various solvents under reflux conditions leads also to a formation of selenolactone **13**, previously unknown seleno-containing heterocyclic system, in poor yield (Scheme 3). The most yields of this product were obtained by the use of EtOH or diglyme, probably, owing to the greatest solubility of $H_2SeO_3$ in these mediums. In diglyme, the oxidation occurred faster than in ethanol (30 min and 3 h, respectively). In this case, the yields of the products **11**–**13** were 12, 59, and 18%, respectively.

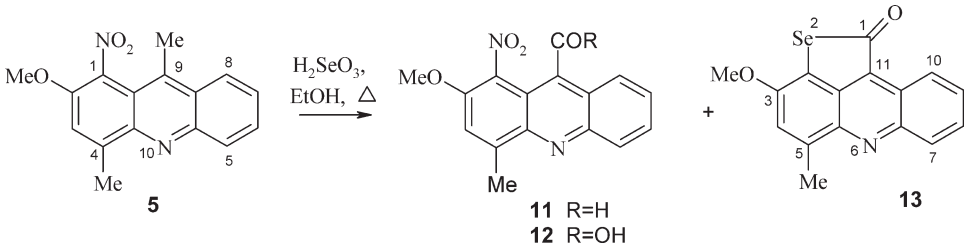
When using $SeO_2$ in place of $H_2SeO_3$, the formation of selenolactone **13** was also observed but in these cases acridine **5** was slow to react with oxidant and the yields of the products **11**–**13** were much less then are obtainable by the use of $H_2SeO_3$.

**Scheme 2**




Reagents and conditions: (a) $Ac_2O$, $HNO_3$ (98%), 10°C, 2 h; (b) 2-aminoacetophenone, $PhNO_2$, Cu, $K_2CO_3$, 165°C, 10 h; (c) HOAc/$H_2SO_4$ (3:1, v/v), 85°C, 30 min.

**Scheme 3**




The structure of **13** was confirmed by IR, mass- and $^{1}H$ and $^{13}C$ NMR measurements. The molecular formula of selenolactone **13** was deduced as $C_{16}H_{11}NO_2Se$ by HRMS.

Distribution of isotopes at the molecular ion peak of **13** calculated by ''Isoform'' program for formula $C_{16}H_{11}NO_2Se$ was coincident with the experimental molecular ion pattern, which demonstrates nine peaks with signs of *m*/*z* equal 332 (rel. int., 3%), 331 (19), 330 (18), 329 (100), 328 (9), 327 (49), 326 (18), 325 (18), and 323 (2).

Assigning resonances of $^{1}H$ and $^{13}C$ at the NMR spectra of **13** was made on the basis of the results of DEPT-135, DEPT-90, HSQC, and HMBC experiments (Fig. 1).

The formation of selenolactone **13** on the reaction of acridine **5** with $H_2SeO_3$ or with $SeO_2$ had come as a surprise to us. Although these reagents are widely used in organic chemistry as oxidants over more then 100 years, the data relative to obtaining the products of this type are lacking.

Based on the structure of selenolactone **13**, it may be concluded that the conversion of acridine **5** to this product involves several fundamental stages, such as the oxidation of C(9)—$CH_3$ group of substrate that must be accompanied by the formation of a low valent selenium, subsequent nucleophilic substitution of the nitro group by this selenium species and lactonization. An important key point might be whether there is an inter- or intramolecular nucleophilic substitution.

The proposed intermolecular mechanism can be represented by Scheme 4.

It is conceivable that the interaction of more active aminomethide form **A** of acridine **5** with the molecule of oxidant followed by the rearrangement of seleninic acid **B** to the intermediate **C** are the initial stages of this process. In a similar manner, $H_2SeO_3$ oxidizes alkenes to allylic alcohols [4,5]. If the intermediate **C** is turned to aldehyde **11** via a loss of HSeOH, the reduced selenium species generated by this pathway could further act as a nucleophile. Its attack on the most electrophilic center C(1) of aldehyde **11** could produce the σ-complex **D,** which by a loss of $HNO_2$ would do the intermediate **E**. A loss of $H_2O$ from the latter must complete the formation of the target compound **13**.

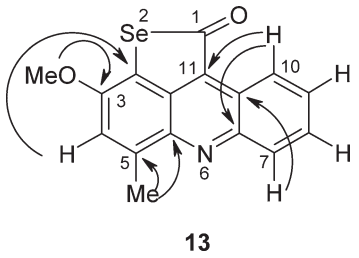
An intramolecular mechanism of nucleophilic substitution of the nitro group can be represented by Scheme 5. If seleninic acid **B** (see Scheme 4) underwent a Pummerer rearrangement to selenenic acid **J**, the selenium of this intermediate could act as an intramolecular nucleophile to displace the nitro group.

A similar *ipso*-replacement of $NO_2$ group by the amino group of hydrazone was noted in the syntheses of 1*H*-benzo[*d*,*e*]cinnolines (1*H*-1,2-diazaphenalenes) when 8-formyl-, 8-acetyl- and 8-benzoyl-1-nitronaphthalenes were heated with hydrazine in boiling ethylene glycol or ethanol [6].

The aforesaid raises the question about the possibility of a Pummerer rearrangement under the reaction conditions. This question presents a difficult theoretical problem. As far as we know, there is no information on such rearrangements of α-$CH_2$-containing selenoxides to analogs of α-hydroxy sulfides as it is in the case of the classical Pummerer rearrangement of α-$CH_2$-containing sulfoxides.

To decide between an inter- or intramolecular mechanism of nucleophlic substitution of $NO_2$ group in acridine **5** there is a need to make many additional investigations.

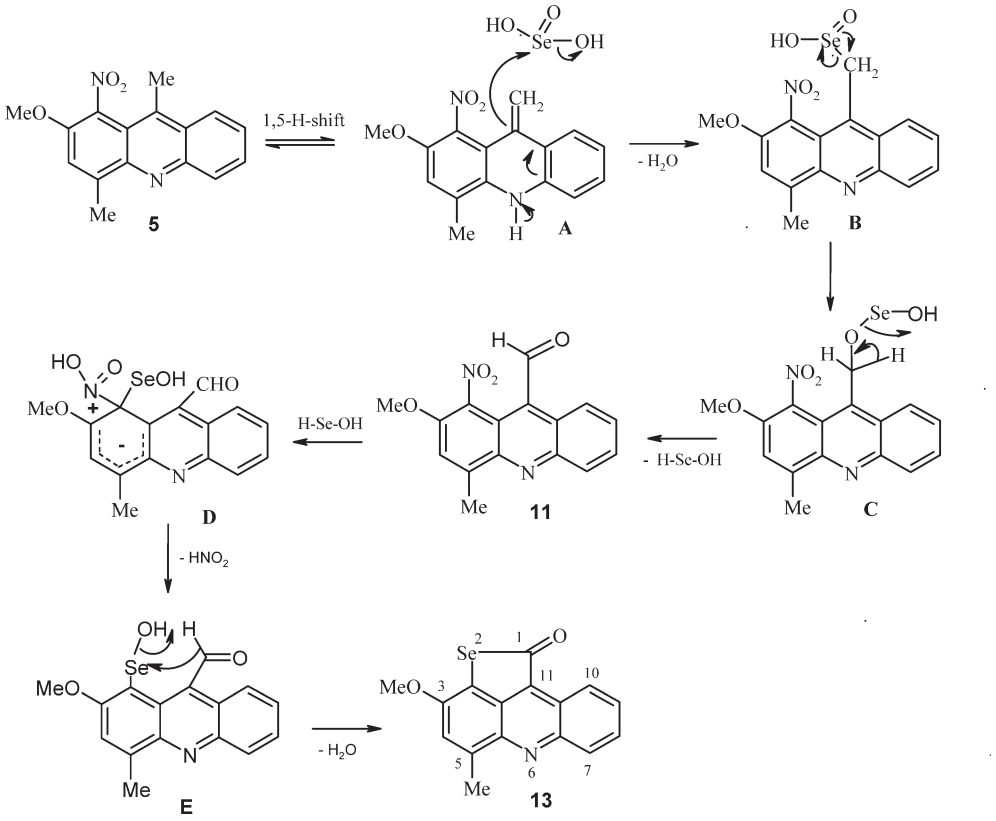
Selenolactone **13** showed considerable antimicrobial activity against Gram-positive bacteria *Staphylococcus aureus* and *Bacillus subtilis* and pathogenic fungus *Candida albicans* but it was inactive against Gram-negative bacteria *Escherichia coli* and *Pseudomonas aeruginosa*.




**13**

**Figure 1.** The basic HMBC correlations of $^{1}H \rightarrow ^{13}C$ at the NMR spectrum of selenolactone **13**.

**Scheme 4**



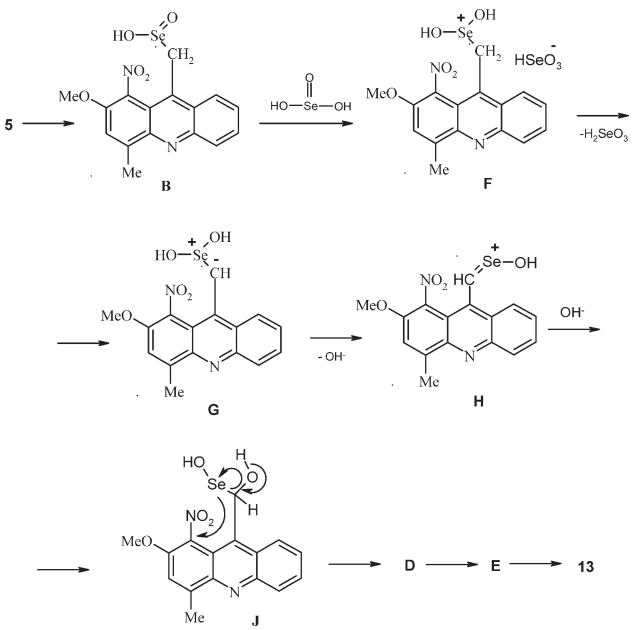
## EXPERIMENTAL

Melting points were determined on a Boetius hot-stage apparatus and are not corrected. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker AVANCE DPX 300 instrument (300 MHz for $^{1}H$, 75 MHz for $^{13}C$). The reported chemical shifts were against TMS. Mass spectra were determined using a AMD 604S spectrometer. IR spectra were obtained on a Bruker Vector 22 spectrophotometer. Microanalyses were performed on a Flash EA 1112 apparatus.

4-Bromo-3-methylanisole (**6**), 2′-aminoacetophenone and copper powder were purchased from Lancaster.

**Synthesis of 4-bromo-5-methyl-2-nitroanisole (7), 4-bromo-3-methyl-2-nitroanisole (8), and 3-methyl-2,4,6-trinitrophenol (9).** To a stirred and cooled (0°C) solution of 4-bromo-3-methylanisole (**6**) (10.05 g, 50 mmol) in freshly distilled acetic anhydride (15 mL), 98% nitric acid (3.38 g, 55 mmol) was added dropwise for 30 min, and the reaction mixture was stirred at that temperature for an additional 30 min. The yellow precipitate of the product **7** (7.9 g) was filtered and washed with cooled methanol (2 mL). Evaporation of filtrate *in vacuo* gave the yellow solid, which was purified by flash-chromatography on a silica gel column (2.5 × 80 cm), prepacked in hexane. Elution of the column with hexane:acetone (20:1, v/v) gave an additional amount of the product **7** (0.63 g). The combined product was recrystallized from benzene to give 8.36 g (68%) of pure 4-bromo-5-methyl-2-nitroanisole (**7**) as a slight yellow needles, m.p. 111–113°C; IR ($CHCl_3$): 1039, 1106, 1174, 1192, 1210, 1220, 1257, 1285, 1347, 1372, 1444, 1463, 1483, 1524, 1575, 1606, 2835, 2944, 2976, 3041, 3083 $cm^{-1}$; $^{1}H$ NMR ($CDCl_3$): δ 2.46 (s, 3H, $CH_3$), 3.94 (s, 3H, $OCH_3$), 6.96 (s, 1H, 3-H), 8.07 (s, 1H, 6-H); EIMS (15 eV): *m/z* (%) 248 ($M^+$ + 1, 10), 247 ($M^+$, 98), 246 ($M^+$ + 1, 10),

**Scheme 5**



245 ($M^+$, 98), 216 (32), 214 (32), 200 (100), 198 (100), 186 (45), 184 (45), 77 (72). Anal. Calcd. for $C_8H_8BrNO_3$: C, 39.05; H, 3.28; N, 5.69. Found: C, 39.13; H, 3.24; N, 5.82.

Elution of the column with hexane: acetone (8:1, v/v) gave 0.56 g (4%) of the product **8** as a slight yellow needles (benzene), m.p. 97–99°C (lit. [7] 98–100°C); IR ($CHCl_3$): 1037, 1111, 1169, 1196, 1213, 1231, 1249, 1291, 1349, 1370, 1446, 1465, 1481, 1520, 1575, 1608 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 2.37 (s, 3H, $CH_3$), 3.87 (s, 3H, $OCH_3$), 6.78 (d, 1H, 5-H, $J$ = 8.9 Hz), 7. 58 (d, 1H, 4-H, $J$ = 8.9 Hz); EIMS (15 eV): *m*/*z* (%) 248 ($M^+$ + 1, 12), 247 ($M^+$, 100), 246 ($M^+$ + 1, 12), 245 ($M^+$, 100).

Elution of the column with hexane:acetone (3:1, v/v) gave 0.35 g (3%) of the product **9** as a slight yellow needles (benzene), m.p. 105–106°C (lit. [8] 106–108°C); IR ($CHCl_3$): 1066, 1172, 1228, 1277, 1341, 1382, 1459, 1548, 1594, 1636, 3109, 3207 (OH) $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 2.64 (s, 3H, $CH_3$), 8.99 (s, 1H, 5-H), 11.14 (br. s, 1H, OH); EIMS (15 eV): *m*/*z* (%) 243 ($M^+$, 5), 242 ($M^+$-1, 100), 225 (8), 224 (8), 212 (3), 196 (3), 195 (5).

**1-[2-(4-Methoxy-2-methyl-5-nitrophenylamino)phenyl]ethanone (10).** A mixture of bromide **7** (3.16 g, 12.4 mmol), 2′-aminoacetophenone (1.674 g, 12.4 mmol), copper powder (0.794 g, 12.4 g. atom), anhydrous potassium carbonate (2.422 g, 24.8 mmol), and nitrobenzene (25 mL) was stirred at 165°C for 10 h. A solid inorganic residue was separated by filtration, filtrate was diluted by water (150 mL) and nitrobenzene was removed by steam distillation. The product **10** was isolated from residue by extraction with ethyl acetate (3 × 15 mL). The organic layer was dried ($Na_2SO_4$), filtered and evaporated to dryness. Purification of the residue by column chromatography on a silica gel (2.5 × 80 cm) using hexane:acetone (30:1→7:1, v/v) as eluent gave 2.74 g (87%) diphenylamine **10** as an orange powder (ethanol), m.p. 146–147°C; IR ($CHCl_3$): 1070, 1165, 1197, 1210, 1221, 1247, 1284, 1346, 1399, 1419, 1454, 1524, 1572, 1603, 1639 (C=O), 3008, 3018, 3034, 3256 (NH) $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 2.34 (s, 3H, $CH_3$), 2.67 (s, 3H, $COCH_3$), 3.98 (s, 3H, $OCH_3$), 6.76 (dd,1H, 5′-H, $J_1$ = 7.3 Hz, $J_2$ = 8.4 Hz), 6.79 (d, 1H, 3′-H, $J$ = 8.4 Hz), 6.99 (s, 1H, 3′′-H), 7.32 (dd, 1H, 4′-H, $J_1$ = 7.3 Hz, $J_2$ = 8.0 Hz), 7.84 (d, 1H, 6′-H, $J$ = 8.0 Hz), 7.89 (s, 1H, 6′′-H), 10.32 (s, 1H, NH); $^{13}C$ NMR ($CDCl_3$): δ 18.7, 28.0, 56.7, 113.5, 115.8, 116.7, 118.7, 122.4, 131.4, 132.6, 135.0, 137.4, 141.8, 148.3, 150.3, 201.5; EIMS (15 eV): *m*/*z* (%) 300 ($M^+$, 100), 285 (5), 270 (5), 252 (7), 239 (8), 225 (20), 208 (28), 196 (16), 180 (22), 167 (20), 159 (13), 149 (8), 120 (37), 83 (25), 77 (14), 57 (6), 44 (39), 32 (53). Anal. Calcd. for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33. Found: C, 64.11; H, 5.40; N, 9.50.

**2-Methoxy-4,9-dimethyl-1-nitroacridine (5).** A solution of diphenylamine **10** (1.931g, 6.44 mmol) in a mixture of acetic and sulfuric acids (20 mL, 3:1, v/v) was heated at 80–85°C for 30 min. After cooling to room temperature, to a vigorously stirred mixture a saturated solution of sodium bicarbonate (300 mL) was added dropwise. The product **5** was isolated by extraction with ethyl acetate (3 × 10 mL). The organic layer was washed with a saturated solution of NaCl (8 mL), dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure to give the residue, which was purified by column chromatography on a silica gel (2 × 60 cm) treated with a small amount of $NH_4OH$. Elution of the column with hexane:acetone (7:1, v/v) gave 1.452 g (81%) of 2-methoxy-4,9-dimethyl-1-nitroacridine **5** as a light yellow needless (ethanol), m.p. 179–180°C; IR ($CHCl_3$): 1009, 1026, 1078, 1131, 1166, 1180, 1204, 1236, 1258, 1288, 1338, 1372, 1400, 1419, 1466, 1528, 1615, 1629, 2857, 2946, 2983, 3027, 3094, 3116 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 2.79 (s, 3H, C(9)—$CH_3$), 2.89 (d, 3H, C(4)—$CH_3$, $J$ = 1.2 Hz), 4.07 (s, 3H, $OCH_3$), 7.68 (dd, 1H, 6-H, $J_1$ = 7.5 Hz, $J_2$ = 8.0 Hz), 7.83 (dd, 1H, 7-H, $J_1$ = 7.5 Hz, $J_2$ = 7.8 Hz), 7.93 (q, 1H, 3-H, $J$ = 1.2 Hz), 8.12 (d, 1H, 5-H, $J$ = 7.8 Hz), 8.34 (d, 1H, 8-H, $J$ = 8.0 Hz); $^{13}C$ NMR ($CDCl_3$): δ 13.4 (q, C(9)—$CH_3$), 19.0 (q, C(4)—$CH_3$), 57.5 (q, $OCH_3$), 117.3 (d, 3-C), 117.8 (s, 9a-C), 124.1 (d, 8-C), 126.3 (s, 8a-C), 127.2 (d, 7-C), 129.9 (d, 6-C), 130.0 (d, 5-C), 131.8 (s, 4a-C), 137.6 (s, 9-C), 141.9 (s, 2-C), 143.3 (s, 4-C), 145.7 (s, 10a-C), 149.1 (s, 1-C); EIMS (15 eV): *m*/*z* (%) 284 ($M^+$+2, 4), 283 ($M^+$ + 1, 17), 282 ($M^+$, 100), 267 [($M^+$ + 2) - 17, 6], 266 [($M^+$ + 1) – 17, 18], 265 ($M^+$ - 17, 96), 252 ($M^+$ - 30, 11), 250 ($M^+$ - 32, 11), 237 ($M^+$ - 45, 21), 236 ($M^+$ - 46, 22), 235 [($M^+$ - 17) - 30, 25], 209 (37), 208 (25), 207 (28), 206 (35), 205 (18), 204 (33), 195 (13), 192 (42), 191 (28), 180 (29), 178 (16), 167 (18), 165 (17), 152 (10), 120 (10), 83 (9), 77 (10), 61 (11), 44 (35), 32 (16). Anal. Calcd. for $C_{16}H_{14}N_2O_3$: C, 68.06; H, 5.00; N, 9.93. Found: C, 68.19; H, 5.04; N, 10.06.

**Synthesis of 3-methoxy-5-methyl-1*H*-selenopheno[2,3,4-*k*,*l*]acridine-1-one (13), 2-methoxy-4-methyl-1-nitro-9-formylacridine (11) and 2-methoxy-4-methyl-1-nitroacridine-9-carboxylic acid (12).** A solution of acridine **5** (80 mg, 0.28 mmol) and selenous acid (400 mg, 3.12 mmol) in 8 mL of ethanol was stirred at reflux for 3 h. The solvent was evaporated *in vacuo* and the resulting residue was purified on a silica sheet (Merck, 20 cm × 20 cm × 0.2 mm), using hexane:acetone (3:1, v/v).

Isolation of the upper orange-red zone ($R_f$ 0.77) gave 19 mg (21%) of selenolactone **13**. This compound was obtained as red prisms (ethanol), m.p. 215–216°C; IR ($CHCl_3$): 1030, 1070, 1123, 1157, 1176, 1214, 1239, 1262, 1298, 1334, 1350, 1379, 1391, 1470, 1520, 1552, 1608 (C=C), 1622 (C=C), 1681 (C=O), 2852, 2929 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 2.99 (d, 3H, C(5)—$CH_3$, $J$ = 1.1 Hz), 4.13 (s, 3H, $OCH_3$), 7.50 (d, 1H, 4-H, $J$ = 1.1 Hz), 7.82 (m, 2H, 8-H, 9-H), 8.42 (d, 1H, 7-H, $J$ = 8.1 Hz), 9.18 (d, 1H, 10-H, $J$ = 8.1 Hz); $^{13}C$ NMR ($CDCl_3$): δ 17.7 (q, C(5)—$CH_3$), 56.8 (q, $OCH_3$), 110.6 (s, 2a-C), 120.4 (d, 4-C), 123.6 (s, 10a-C), 123.8 (d, 10-C), 129.1 (d, 8-C), 130.5 (d, 7-C), 130.6 (d, 9-C), 131.3 (s, 5-C), 133.5 (s, 11-C), 139.7 (s, 11a-C), 145.6 (s, 5a-C), 148.5 (s, 6a-C), 155.1 (s, 3-C), 197.8 (s, 1-C); EIMS (15 eV): *m*/*z* (%) 332 ($M^+$, 4), 331 ($M^+$, 20), 330 ($M^+$, 18), 329 ($M^+$, 100), 328 ($M^+$, 9), 327 ($M^+$, 50), 326 ($M^+$, 19), 325 ($M^+$, 19), 323 ($M^+$, 3), 314 (23), 312 (13), 288 (9), 286 (48), 284 (21), 270 (6), 258 (39), 256 (20), 190 (6), 178 (30), 177 (19), 166 (7), 151 (23), 139 (19); HREIMS. Calcd for $C_{16}H_{11}NO_2Se$: 328.99547. Observed: 328.99572. Anal. Calcd. for $C_{16}H_{11}NO_2Se$: C, 58.55; H, 3.38; N, 4.27. Found: C, 58.69; H, 3.41; N, 4.38.

Isolation of the middle zone ($R_f$ 0.36) gave 24 mg (29%) of aldehyde **11**. This compound was obtained as yellow needless (ethanol), m.p. 193–195°C; IR ($CHCl_3$): 1079, 1131, 1297, 1337, 1359, 1374, 1401, 1471, 1529, 1537, 1557, 1602 (C=C), 1614 (C=C), 1630 (C=C), 1679, 1703(C=O), 2857, 2929, 2935, 2958 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 3.02 (d, 3H, C(4)—$CH_3$, $J$ = 1.3 Hz), 4.13 (s, 3H, $OCH_3$), 7.59 (q, 1H, 3-

H, $J$ = 1.3 Hz), 7.69 (ddd, 1H, 6-H, $J_1$ = 7.0 Hz, $J_2$ = 6.8 Hz, $J_3$ = 1.2 Hz), 7.82 (ddd, 1H, 7-H, $J_1$ = 7.2 Hz, $J_2$ = 6.8 Hz, $J_3$ = 1.2 Hz), 8.29 (dd, 1H, 5-H, $J_1$ = 7.0 Hz, $J_2$ = 1.2 Hz), 8.31 (dd, 1H, 8-H, $J_1$ = 7.2 Hz, $J_2$ = 1.2 Hz), 10.99 (s, 1H, CHO); EIMS (15 eV): *m*/*z* (%) 296 ($M^+$, 82), 279 (30), 267 (26), 252 (22), 251 (97), 250 (95), 238 (50), 236 (53), 235 (48), 222 (35), 207 (63), 195 (60), 179 (100), 167 (31), 152 (41), 140 (17). Anal. Calcd. for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08; N, 9.45. Found: C, 64.91; H, 4.03; N, 9.31.

Isolation of the under zone ($R_f$ 0.32) gave 32 mg (36%) of acid **12**. This compound was obtained as light yellow powder (ethanol), m.p. 219–222°C; IR ($CHCl_3$): 1059, 1109, 1137, 1289, 1334, 1356, 1379, 1442, 1464, 1523, 1554, 1603 (C=C), 1612 (C=C), 1622 (C=C), 1682, 1714 (C=O), 1729 (C=O), 2250–3400 (OH), 2857, 2902, 2930, 3013 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 3.03 (d, 3H, C(4)-$CH_3$, $J$ = 1.2 Hz), 4.15 (s, 3H, $OCH_3$), 7.64 (q, 1H, 3-H, $J$ = 1.2 Hz), 7.85 (ddd, 1H, 6-H, $J_1$ = 8.0 Hz, $J_2$ = 7.5 Hz, $J_3$ = 1.2 Hz), 7.88 (ddd, 1H, 7-H, $J_1$ = 8.3 Hz, $J_2$ = 7.5 Hz, $J_3$ = 1.2 Hz), 8.32 (dd, 1H, 5-H, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz), 8.41 (dd, 1H, 8-H, $J_1$ = 8.3 Hz, $J_2$ = 1.2 Hz); EIMS (15 eV): *m*/*z* (%) 312 ($M^+$, 31), 295 (100), 294 (18), 268 (30), 267 (69), 266 (51), 251 (56), 238 (57), 208 (32), 206 (34), 205 (29), 194 (62), 167 (58). Anal. Calcd. for $C_{16}H_{12}N_2O_5$: C, 61.54; H, 3.87; N, 8.97. Found: C, 61.87; H, 3.95; N, 9.11.

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