

# Reactions of 5-Methoxy-2-(4-methoxyphenyl)naphtho[1,8-*bc*]furylium Perchlorate with Nucleophiles

R. V. Tyurin, S. V. Ermolova, L. G. Minyaeva, and V. V. Mezheritskii

Research Institute of Physical and Organic Chemistry, Rostov State University,  
pr. Stachki 194/2, Rostov-on-Don, 344090, Russia  
e-mail: mezher@ipoc.rsu.ru

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**Abstract**—5-Methoxy-2-(4-methoxyphenyl)naphtho[1,8-*bc*]furylium perchlorate reacts with N-, O-, H-, and C-nucleophiles under conditions of kinetic or thermodynamic control to give products at both C<sup>2</sup> and C<sup>5</sup> centers of the heterocyclic system.

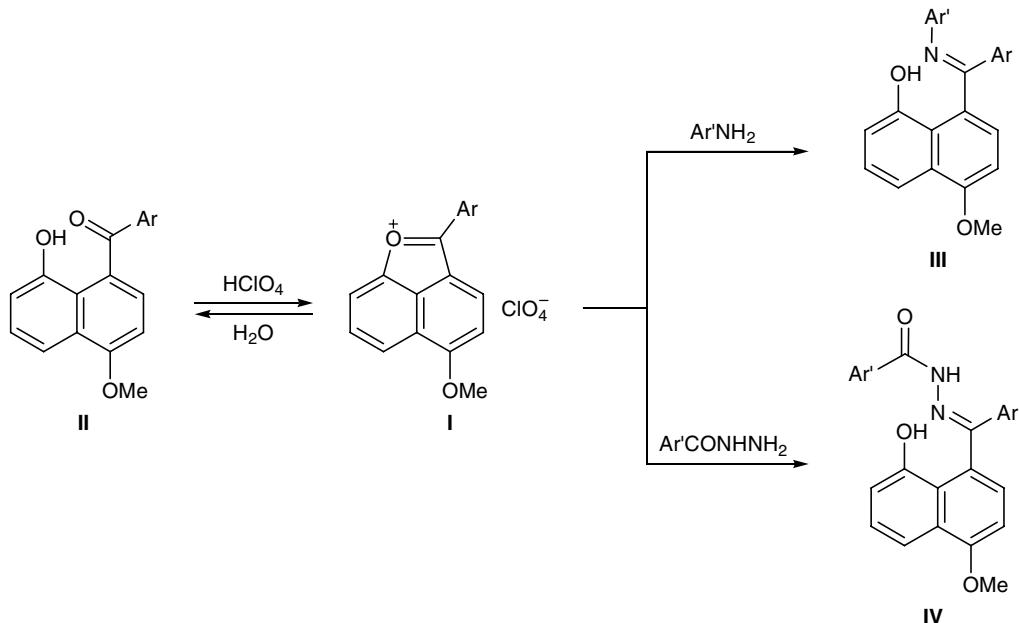
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Naphtho[1,8-*bc*]furan-1-yl cations are relatively new representatives [1] of heterocyclic oxonium ions with a closed π-system including a single heteroatom; prior to their synthesis, the only known compounds of this family were pyrylium ions. Unlike thoroughly studied pyrylium ions [2], only some condensations at alkyl group in the 2-position have been reported for naphtho[1,8-*bc*]furylium ions [1, 3]. The goal of the present work was to study the behavior of naphtho-

[1,8-*bc*]furylium salts in reactions with N-, O-, H-, and C-nucleophiles.

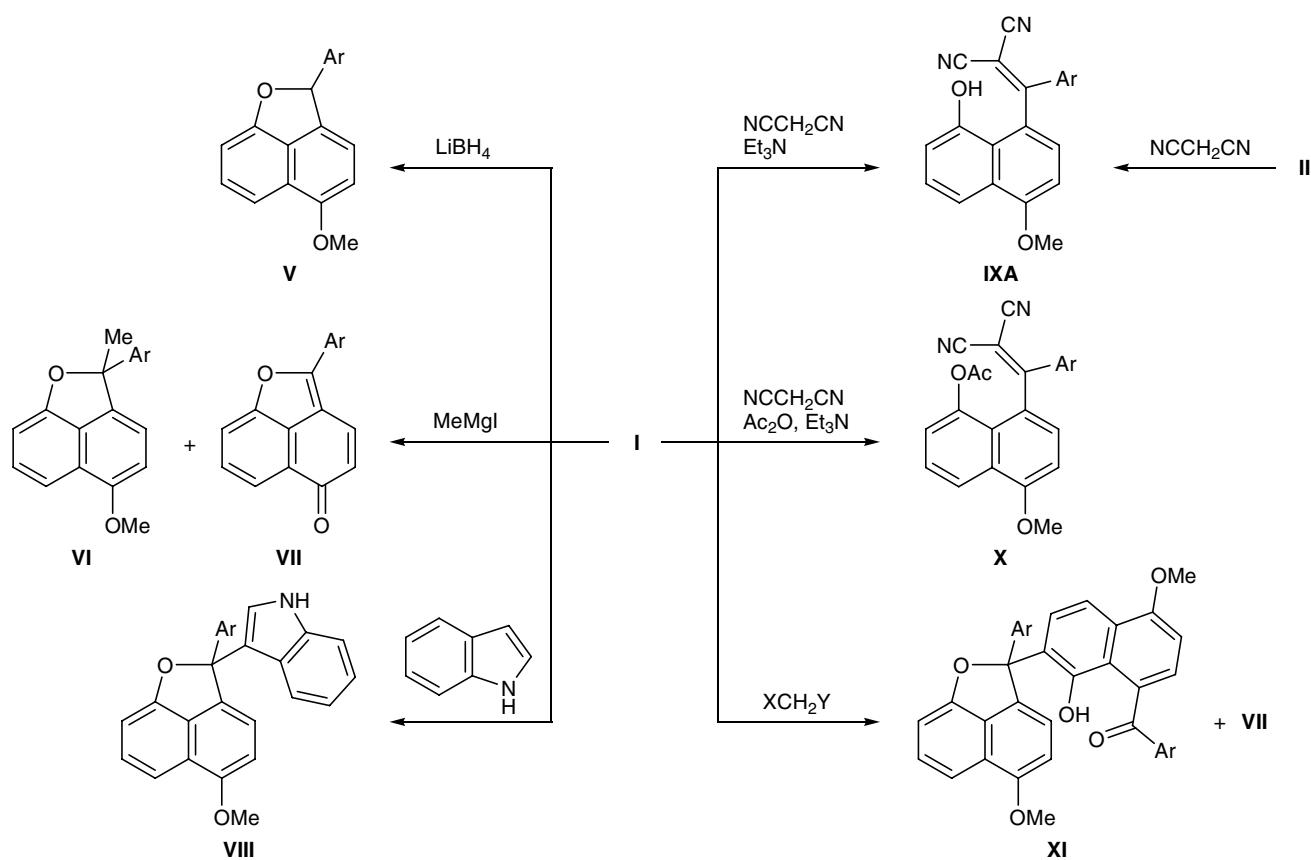
As model substrate we selected 5-methoxy-2-(4-methoxyphenyl)naphtho[1,8-*bc*]furylium perchlorate (**I**), taking into account its high electrophilicity and stability. This salt can be isolated, stored, and brought into various transformations without resorting to special techniques for protection from atmospheric moisture. Calculation of the charge densities in cation **I** in

Scheme 1.



$\text{Ar} = 4\text{-MeOC}_6\text{H}_4$ ,  $\text{Ar}' = 4\text{-MeC}_6\text{H}_4$ .

Scheme 2.



$\text{Ar} = 4\text{-MeOC}_6\text{H}_4$ ;  $\text{X} = \text{COMe}$ ;  $\text{X} = \text{CN}$ ,  $\text{Y} = \text{COOEt}$ .

terms of the MINDO-3 approximation showed that the largest positive charges are localized on the  $\text{C}^2$  and  $\text{C}^5$  atoms (+0.554 and +0.534, respectively) which are therefore the most probable centers for nucleophilic attack. Perchlorate **I** was synthesized by reaction of *peri*-hydroxy ketone **II** with perchloric acid [1]. The heterocyclization is reversible, and perchlorate **I** can be converted into initial hydroxy ketone **II** by treatment with water, i.e., water molecule as nucleophile attacks the 2-position in molecule **I**. Therefore, all reactions with nucleophiles were carried out in anhydrous acetonitrile.

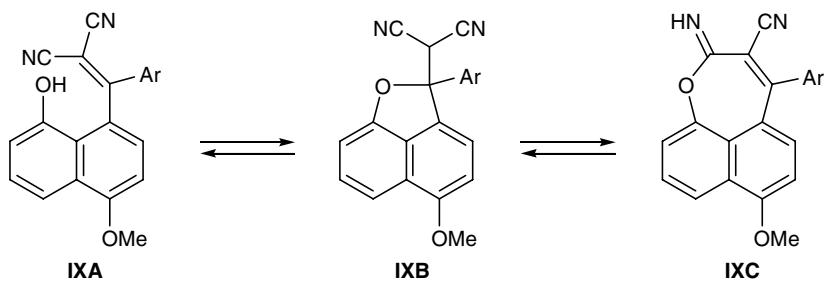
Compounds containing an amino group, namely *p*-toluidine and *p*-methylbenzohydrazide, reacted with salt **I** in a similar way: addition of the amino group at  $\text{C}^2$  was accompanied by opening of the five-membered heterocyclic ring with formation of Schiff base **III** or hydrazone **IV**, respectively (Scheme 1). Theoretically, imines **III** and **IV** may exist in a cyclic (semiacetal–hemiaminal) form; their open-chain structure was confirmed by spectral data. In the IR spectra of compounds **III** and **IV** we observed an absorption band at  $1630\text{ cm}^{-1}$ ,

belonging to stretching vibrations of the  $\text{C}=\text{N}$  bond, while their  $^1\text{H}$  NMR spectra contained a downfield signal ( $\delta \sim 10\text{ ppm}$ ) from the *peri*-hydroxy group, indicating formation of a fairly strong intramolecular hydrogen bond between the hydroxy proton and nitrogen atom of the imino group.

It is known that the simplest nucleophile is hydride ion; metal hydrides or their complexes can serve as source of hydride ions. In the reaction of salt **I** with an equimolar amount of lithium tetrahydridoborate in anhydrous acetonitrile, the only identified product was substituted 2*H*-naphtho[1,8-*bc*]furan **V** (Scheme 2); it was isolated by chromatography on aluminum oxide. The 2-H proton in **V** showed a long-range coupling with a proton in the naphthalene fragment, and its signal appeared in the  $^1\text{H}$  NMR spectrum as a doublet at  $\delta 6.8\text{ ppm}$  ( $J = 1.5\text{ Hz}$ ), which is typical of structurally related compounds [4, 5].

Likewise, in the reaction with the Grignard compound  $\text{MeMgI}$ , methyl anion added at the 2-position of cation **I**, yielding 45% of 5-methoxy-2-(4-methoxyphenyl)-2-methyl-2*H*-naphtho[1,8-*bc*]furan (**VI**) and

Scheme 3.



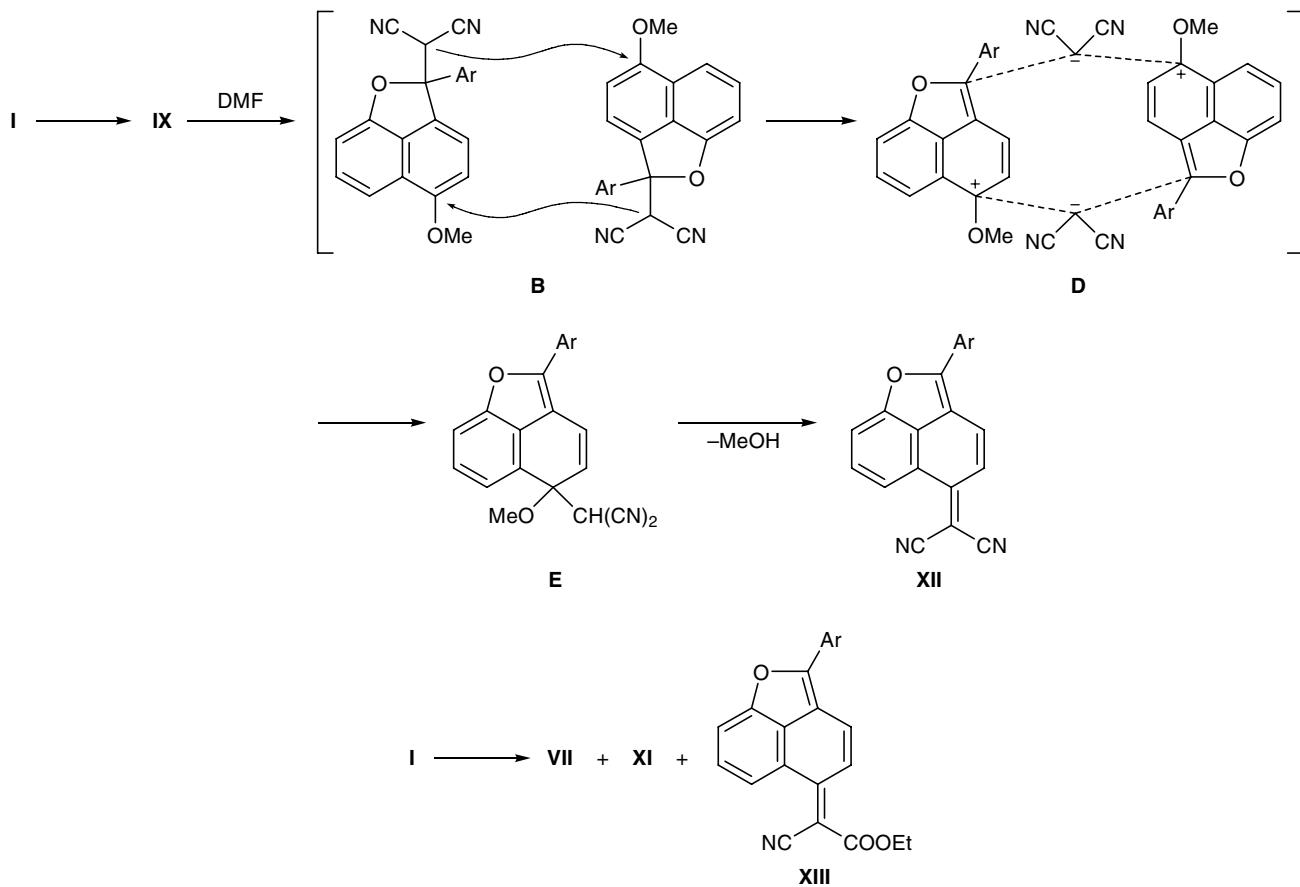
5–7% of naphtho[1,8-*bc*]furan-5-one (**VII**). The latter could result from attack by carbanion on the electron-deficient methyl group in the 5-methoxy substituent or by water molecule on C<sup>5</sup>, followed by elimination of methanol (Scheme 2). Compound **VI** showed in the <sup>1</sup>H NMR spectrum signals from protons in two methoxy and methyl groups, five protons in the naphthalene fragment, and four protons in the *para*-substituted benzene ring on C<sup>2</sup>. The <sup>1</sup>H NMR spectrum of 2-aryl-naphtho[1,8-*bc*]furan-5-one **VII** contained a three-proton singlet belonging to the aromatic methoxy group and a nine-proton multiplet in the aromatic region.

The carbonyl group gave rise to IR absorption band at 1640 cm<sup>−1</sup>.

As neutral C-nucleophile we selected indole; it added at the 2-position of cation **I** to give 2-(1*H*-indol-3-yl)-5-methoxy-2-(4-methoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (**VIII**). According to the <sup>1</sup>H NMR data, the product contained two methoxy groups, one NH proton, and 14 aromatic protons in a molecule.

The most interesting transformations were observed in the reactions of perchlorate **I** with carbanions derived from compounds possessing an activated methylene group (malononitrile, ethyl cyanoacetate, and

Scheme 4.



acetylacetone). The reaction of **I** with malononitrile in the presence of triethylamine gave Michael adduct **IX**; the same compound was also formed in the reaction of malononitrile with Schiff base **III**. In the <sup>1</sup>H NMR spectrum of adduct **IX** we observed signals from two methoxy groups and 9 aromatic protons. One more expected signal was not detected, which may be due to fast proton exchange between three possible tautomers **A–C** (Scheme 3). The IR spectrum of the crystalline product dispersed in mineral oil displayed two broad bands in the region 3200–3500 cm<sup>-1</sup>. The electronic absorption spectra of orange compound **IX** and yellow acetate **X** (which is a fixed form of tautomer **A**) were not identical; therefore, we cannot assign only structure **A** to the adduct; presumably, it is a mixture of tautomers.

Compound **IX** underwent rearrangement on heating in dimethylformamide. As a result, bright red 2-[2-(4-methoxyphenyl)-5H-naphtho[1,8-*bc*]furan-5-ylidene]-malononitrile (**XII**) was obtained. Presumably, the transformation includes dissociation of tautomer **B** into naphthofuryl cation and malonodinitrile anion, migration of the latter from C<sup>2</sup> to C<sup>5</sup>, and subsequent elimination of methanol: **B**→**D**→**E**→**XII**. Insofar as such migration cannot occur intramolecularly, we believe that the process follows intermolecular mechanism, a possible version of which is shown in Scheme 4. We can conclude that the 2-adduct is a kinetically controlled product and that the formation of compound **XII** is controlled thermodynamically. The structure of dinitrile **XII** was confirmed by the IR, <sup>1</sup>H NMR, and mass spectra.

Our attempts to react perchlorate **I** with other active methylene compounds, namely ethyl cyanoacetate and acetylacetone, lead to the formation of mixtures of products which were difficult to separate. We succeeded in isolating two individual compounds. One of these was assigned the structure of dimer **XI** on the basis of the IR, <sup>1</sup>H NMR, and mass spectral data, while the other was identified as naphthofuran-5-one **VII**. Nevertheless, analysis of the <sup>1</sup>H NMR and mass spectra of the reaction mixtures suggests dimeric structure of most products formed in these reactions. Only in the reaction of **I** with ethyl cyanoacetate we isolated rearrangement product **XIII** analogous to **XII**. Presumably, resonance-stabilized carbanions generated from active methylene compounds are insufficiently reactive as nucleophiles but are capable of acting as single-electron donors. Electron addition to naphthofurylium cation **I** gives rise to radical species whose combination leads to dimeric products. In a blank experiment (no active

methylene compound was added) we isolated (after treatment of the reaction mixture with water) only the hydrolysis product of salt **I**, hydroxy ketone **II**.

## EXPERIMENTAL

The IR spectra were recorded on a Specord 71IR spectrophotometer from samples dispersed in mineral oil. The <sup>1</sup>H NMR spectra were measured on Bruker Avance DPX-250 and Varian Unity-300 spectrometers relative to HMDS as internal reference; CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> were used as solvents. The mass spectra (electron impact, 70 eV) were obtained on a Varian MAT-44 instrument.

**5-Methoxy-8-[4-methoxyphenyl(4-methylphenylimino)methyl]naphthalen-1-ol (III).** *p*-Toluidine, 0.053 g (0.5 mmol), was added to a mixture of 0.2 g (0.5 mmol) of 5-methoxy-2-(4-methoxyphenyl)naphtho[1,8-*bc*]furan-1-ylum perchlorate (**I**) and 1 ml of acetonitrile, the mixture was heated, and 0.4 ml of triethylamine was added. When crystallization was complete, the precipitate was filtered off and recrystallized from DMF. Yield 0.189 g (75%), light gray substance, mp 256–257°C. IR spectrum: ν 1673 cm<sup>-1</sup> (C=N). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 2.1 s (3H, CH<sub>3</sub>), 3.8 s (6H, OCH<sub>3</sub>), 6.6–7.9 m (13H, H<sub>arom</sub>), 9.8 s (1H, OH). Found, %: C 78.97; H 5.84; N 3.05. C<sub>26</sub>H<sub>23</sub>NO<sub>3</sub>. Calculated, %: C 78.99; H 5.82; N 3.04.

**N'-[8-Hydroxy-4-methoxynaphthalen-1-yl-(4-methoxyphenyl)methylidene]-4-methylbenzohydrazide (IV).** 4-Methylbenzohydrazide, 0.057 g (0.38 mmol), was added to a mixture of 0.15 g (0.38 mmol) of 5-methoxy-2-(4-methoxyphenyl)naphtho[1,8-*bc*]furan-1-ylum perchlorate (**I**) and 1 ml of acetonitrile, the mixture was heated, and 0.3 ml of triethylamine was added. After 10 min, the mixture was poured into water, and the precipitate was filtered off and recrystallized from DMF. Yield 0.142 g (84%), dark green substance, mp 138–139°C. IR spectrum: ν 1660 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>), δ, ppm: 2.5 s (3H, CH<sub>3</sub>), 3.7 s (3H, 4-OCH<sub>3</sub>), 4.0 s (3H, C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>), 6.8–7.8 m (13H, H<sub>arom</sub>), 9.2 s (1H, NH), 10.0 s (1H, OH). Found, %: C 72.91; H 5.62; N 6.56. C<sub>26</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>. Calculated, %: C 72.90; H 5.61; N 6.54.

**5-Methoxy-2-(4-methoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan (V).** Lithium tetrahydridoborate, 0.05 g (0.002 mol), was added to a mixture of 0.2 g (0.5 mmol) of compound **I** and 1 ml of acetonitrile. The resulting solution was left to stand for 2 days until the reaction was complete, poured into water, and acidified with acetic acid. The precipitate was filtered off

and subjected to chromatography on aluminum oxide using chloroform as eluent. Yield 0.066 g (45%), colorless crystals, mp 118–120°C. <sup>1</sup>H NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 3.8 s (3H, 5-OCH<sub>3</sub>), 4.0 s (3H, 4'-OCH<sub>3</sub>), 6.7–7.5 m (10H, H<sub>arom</sub>). Found, %: C 78.06; H 5.49. C<sub>19</sub>H<sub>16</sub>O<sub>3</sub>. Calculated, %: C 78.08; H 5.48.

**Reaction of perchlorate I with methylmagnesium iodide.** 5-Methoxy-2-(4-ethoxyphenyl)naphtho[1,8-*bc*]furan-1-ylum perchlorate (**I**), 0.390 g (1 mmol), was added in small portions under vigorous stirring to 1.5 mmol of methylmagnesium iodide in diethyl ether, maintaining the temperature at 5–10°C. The resulting solution was kept for 30 min, poured into water, acidified with dilute (1:1) hydrochloric acid, and extracted with chloroform. The extract was subjected to chromatography on aluminum oxide using chloroform as eluent to isolate two fractions containing compounds **VI** and **VII**.

**5-Methoxy-2-(4-methoxyphenyl)-2-methyl-2*H*-naphtho[1,8-*bc*]furan (**VI**).**  $R_f$  0.8. Yield 0.137 g (45%), colorless crystals, mp 95–97°C. <sup>1</sup>H NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 2.1 s (3H, Me), 3.8 s (3H, 5-OCH<sub>3</sub>), 4.0 s (3H, 4'-OCH<sub>3</sub>), 6.73 d (1H, 4-H,  $J_{3,4}$  = 6.8 Hz), 6.83 s (1H, 6-H,  $J_{6,7}$  = 6.55 Hz), 6.85 d (2H, C<sub>6</sub>H<sub>4</sub>,  $J$  = 8.2 Hz), 7.07 d (1H, 3-H,  $J_{3,4}$  = 6.9 Hz), 7.25–7.5 m (4H, H<sub>arom</sub>). Found, %: C 78.5; H 5.85. C<sub>20</sub>H<sub>18</sub>O<sub>3</sub>. Calculated, %: C 78.43; H 5.88.

**2-(4-Methoxyphenyl)naphtho[1,8-*bc*]furan-5-one (**VII**).**  $R_f$  0.3. Yield 0.01 g (3.7%), light yellow substance, mp 158–160°C. IR spectrum:  $\nu$  1633 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 3.9 s (3H, OCH<sub>3</sub>), 6.7 d (1H, 3-H,  $J_{3,4}$  = 9.63 Hz), 7.1 d (2H, C<sub>6</sub>H<sub>4</sub>,  $J$  = 9.01 Hz), 7.55 t (1H, 7-H,  $J_{6,7}$  = 7.85 Hz), 7.7 d (1H, 6-H,  $J_{6,7}$  = 7.85 Hz), 7.98 d (1H, 4-H,  $J_{3,4}$  = 9.63 Hz), 8.03 d (2H, C<sub>6</sub>H<sub>4</sub>,  $J$  = 9.01 Hz), 8.05 d (1H, 8-H,  $J_{7,8}$  = 6.74 Hz). Found, %: C 78.25; H 4.34. C<sub>18</sub>H<sub>12</sub>O<sub>3</sub>. Calculated, %: C 78.26; H 4.35.

**3-[5-Methoxy-2-(4-methoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan-2-yl]-1*H*-indole (**VIII**).** Indole, 0.075 g (0.6 mmol), was added to a mixture of 0.25 g (0.6 mmol) of perchlorate **I** and 1 ml of acetonitrile. Diethyl ether was then added to the resulting solution, the mixture was left to stand overnight in a freezing chamber and poured into water, and diethyl ether was evaporated. The precipitate was filtered off and purified by chromatography on aluminum oxide using chloroform as eluent. Yield 0.190 g (73%), colorless crystals, mp 102–103°C. IR spectrum:  $\nu$  3420 cm<sup>-1</sup> (N–H). <sup>1</sup>H NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 3.8 s (3H,

5-OCH<sub>3</sub>), 4.0 s (3H, 4'-OCH<sub>3</sub>), 6.83 d (1H, 3-H,  $J_{3,4}$  = 7.4 Hz), 6.84 d (1H, 6-H,  $J_{6,7}$  = 7.15,  $J_{6,8}$  = 0.9 Hz), 6.85 d (2H, C<sub>6</sub>H<sub>4</sub>,  $J$  = 8.8 Hz), 6.89 d (1H, 2-H, indole,  $J_{1,2}$  = 2.6 Hz), 6.95 t (1H, 6-H, indole,  $J_{6,7}$  = 7.6,  $J_{4,6}$  = 1.1 Hz), 7.08 d (1H, 7-H, indole,  $J_{6,7}$  = 7.6 Hz), 7.14 t (1H, 5-H, indole,  $J_{5,6}$  = 7.6,  $J_{5,7}$  = 1.2 Hz), 7.16 d (1H, 4-H,  $J_{3,4}$  = 7.4 Hz), 7.28 d (1H, 4-H, indole,  $J_{4,5}$  = 7.6,  $J_{4,6}$  = 1.2 Hz), 7.44 t (1H, 7-H,  $J_{7,8}$  = 7.4 Hz), 7.48 d (2H, C<sub>6</sub>H<sub>4</sub>,  $J$  = 8.8 Hz), 7.51 d (1H, 8-H,  $J_{7,8}$  = 7.4,  $J_{6,8}$  = 0.9 Hz), 8.0 (1H, NH). Found, %: C 79.63; H 5.17; N 3.42. C<sub>27</sub>H<sub>21</sub>NO<sub>3</sub>. Calculated, %: C 79.61; H 5.16; N 3.44.

**2-[5-Methoxy-2-(4-methoxyphenyl)-2*H*-naphtho[1,8-*bc*]furan-2-yl]malononitrile (**IX**).** *a.* Malononitrile, 0.05 g (0.77 mmol), acetonitrile, 2 ml, and triethylamine, 0.6 ml, were added to 0.3 g (0.77 mmol) of perchlorate **I**. After 10 min, the solution was poured into water, and the precipitate was filtered off and purified by chromatography on aluminum oxide using benzene as eluent. Yield 0.014 g (5%), orange substance, mp 106–107°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 2200 (C≡N); 3500, 3400 (OH). <sup>1</sup>H NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 3.8 s (3H, 5-OCH<sub>3</sub>), 4.0 s (3H, 4'-OCH<sub>3</sub>), 6.72 d (1H, 5-H,  $J$  = 7.6 Hz), 6.81 d (2H, C<sub>6</sub>H<sub>4</sub>,  $J$  = 9.0 Hz), 6.86 d (1H, 3-H,  $J$  = 8.06 Hz), 7.26 d (1H, 2-H,  $J$  = 7.91 Hz), 7.31 t (1H, 6-H,  $J$  = 7.8 Hz), 7.44 d (2H, C<sub>6</sub>H<sub>4</sub>,  $J$  = 9.0 Hz), 7.9 d (1H, 7-H,  $J$  = 8.4 Hz). Found, %: C 72.4; H 4.75; N 8.45. C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>. Calculated, %: C 72.29; H 4.82; N 8.43.

*b.* Compound **IV**, 0.032 g (0.07 mmol), was mixed with 0.005 g (0.07 mmol) of malononitrile and 1 ml of DMF. The resulting solution was heated for 5 min at 60–70°C, cooled, and poured into water, and the precipitate was filtered off and recrystallized from dimethylformamide. Yield 0.012 g (52%), orange substance, mp 106–107°C.

**8-[2,2-Dicyano-1-(4-methoxyphenyl)vinyl]-5-methoxynaphthalen-1-yl acetate (**X**).** Acetic anhydride, 1 ml, malononitrile, 0.042 g (0.6 mmol), and triethylamine, 0.5 ml, were added to 0.25 g (0.6 mmol) of perchlorate **I**. The resulting solution was kept for 10 min and poured into water, and the precipitate was filtered off and purified by chromatography on aluminum oxide using chloroform as eluent. Yield 0.096 g (38%), light yellow substance, mp 126–127°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1767 (C=O), 2200 (C≡N). <sup>1</sup>H NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 2.0 s (3H, COCH<sub>3</sub>), 3.8 s (3H, 5-OCH<sub>3</sub>), 4.0 s (3H, 4'-OCH<sub>3</sub>), 6.75 d (1H, 6-H,  $J$  = 8.1 Hz), 7.44 d (2H, C<sub>6</sub>H<sub>4</sub>,  $J$  = 9.3 Hz), 7.17 d (1H, 7-H,  $J$  = 8.1 Hz), 7.25 d (1H, 4-H,  $J_{3,4}$  = 8.8,  $J_{2,4}$  =

0.8 Hz), 7.55 t (1H, 3-H,  $J_{3,4} = 8.5$  Hz), 7.6 d (2H, C<sub>6</sub>H<sub>4</sub>,  $J = 9.3$  Hz), 8.3 d (1H, 4-H,  $J_{2,3} = 8.5$ ,  $J_{2,4} = 0.8$  Hz). Found, %: C 71.53; H 4.64; N 7.25. C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>. Calculated, %: C 71.50; H 4.66; N 7.25.

**8-Hydroxy-4-methoxy-7-[5-methoxy-2-(4-methoxyphe-nyl)-2H-naphtho[1,8-bc]furan-2-yl]naphthalen-1-yl(4-methoxyphenyl)methanone (XI).** Triethylamine, 0.1 ml, was added to a suspension of 0.8 g (0.002 mol) of perchlorate **I** and 0.14 ml (0.002 mol) of acetylacetone in 3.5 ml of acetonitrile. The resulting solution was kept for 10 min and poured into water, and the precipitate was filtered off and subjected to chromatography on aluminum oxide using chloroform as eluent. A fraction with  $R_f$  0.5 was collected. Yield 0.066 g (4.5%), light yellow substance, mp 145–146°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3327 (OH), 1660 (C=O). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 3.7 s and 3.8 s (3H each, 4-OCH<sub>3</sub>, 5'-OCH<sub>3</sub>), 3.98 s and 4.02 s (3H each, C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>), 6.72 (2H, C<sub>6</sub>H<sub>4</sub>,  $J = 8.9$  Hz), 6.76 d (1H,  $J = 7.25$  Hz), 6.8 d (1H,  $J = 8.1$  Hz), 6.86 d (2H, C<sub>6</sub>H<sub>4</sub>,  $J = 9.0$  Hz), 6.88 d (1H,  $J = 7.95$  Hz), 7.08 d (2H, C<sub>6</sub>H<sub>4</sub>,  $J = 8.9$  Hz), 7.38 t (1H,  $J = 7.3$  Hz), 7.4 d (1H,  $J = 8.02$  Hz), 7.44 d (1H,  $J = 7.6$  Hz), 7.5 d (2H,  $J = 8.25$  Hz), 7.72 d (2H, C<sub>6</sub>H<sub>4</sub>,  $J = 8.9$  Hz), 7.88 d (1H,  $J = 8.9$  Hz), 8.4 s (1H, OH). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 598 [M]<sup>+</sup> (10), 308 (30), 291 (45), 261 (10), 200 (100), 185 (20), 135 (20), 115 (10), 85 (10), 58 (5), 43 (30). Found, %: C 76.3; H 5.0. C<sub>38</sub>H<sub>30</sub>O<sub>7</sub>. Calculated, %: C 76.25; H 5.02.

**2-[2-(4-Methoxyphenyl)-5H-naphtho[1,8-bc]-furan-5-ylidene]malononitrile (XII).** *a.* A solution of 0.062 g (0.17 mmol) of compound **IX** in 1 ml of acetic acid was heated for 2.5 h under reflux, cooled, and poured into water. The precipitate was filtered off and purified by chromatography on aluminum oxide using chloroform as eluent. Yield 0.016 g (28%), violet substance, mp 246–247°C. IR spectrum:  $\nu$  2200 cm<sup>-1</sup> (C≡N). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 3.9 s (3H, OCH<sub>3</sub>), 7.1 d (2H, C<sub>6</sub>H<sub>4</sub>,  $J = 8.9$  Hz), 7.4 d (1H, 4-H,  $J = 9.25$  Hz), 7.55 t (1H, 7-H,  $J = 8.1$  Hz), 7.65 d (1H, 6-H,  $J = 7.7$  Hz), 7.8 d (1H, 3-H,  $J = 9.25$  Hz), 8.05 d (2H, C<sub>6</sub>H<sub>4</sub>,  $J = 8.9$  Hz), 8.8 d (1H, 8-H,  $J = 8.1$  Hz). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 324 [M]<sup>+</sup> (100), 309 (30), 281 (30), 254 (10), 225 (10), 199 (5). Found, %: C 77.8; H 3.7; N 8.55. C<sub>21</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>. Calculated, %: C 77.78; H 3.7; N 8.64.

*b.* A solution of 0.274 g (0.5 mmol) of compound **III** and 0.036 g (0.5 mmol) of malononitrile in 2.5 ml of DMF was heated for 20 min under reflux, cooled, and poured into water. An oily material separated and was subjected to chromatography on aluminum oxide using chloroform as eluent. Yield 0.054 g (30%), violet substance, mp 246–247°C.

**Reaction of perchlorate **I** with ethyl cyanoacetate.** Ethyl cyanoacetate, 0.225 ml (2 mmol), was added to a solution of 0.8 g (2 mmol) of perchlorate **I** in 3.5 ml of acetonitrile, the mixture was cooled, and 1.3 ml of triethylamine was added. The dark solution was diluted with water, and the precipitate was subjected to chromatography on aluminum oxide using chloroform as eluent. Three fractions were collected.

**Ethyl 2-cyano-2-[2-(4-methoxyphenyl)-5H-naphtho[1,8-bc]furan-5-ylidene]acetate (XIII)** was isolated from fraction 1. Yield 10 mg (1.5%),  $R_f$  0.8, pale pink substance, mp 115°C. Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 371 [M]<sup>+</sup> (70), 326 (25), 299 (95), 291 (40), 284 (25), 276 (100), 261 (45), 254 (25), 227 (30), 200 (35), 176 (20), 149 (20), 95 (15), 77 (15), 44 (15).

Fraction 2 contained 8-hydroxy-4-methoxy-7-[5-methoxy-2-(4-methoxyphe-nyl)-2H-naphtho[1,8-bc]furan-2-yl]naphthalen-1-yl(4-methoxyphenyl)methanone (**XI**). Yield 0.1 mg (9%),  $R_f$  0.5, light yellow substance, mp 144–145°C. Fraction 3 contained 2-(4-methoxyphenyl)naphtho[1,8-bc]furan-5-one (**VII**). Yield 0.028 g (5%),  $R_f$  0.3, light yellow substance, mp 158–160°C.

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