Synthesis of 2-Aminopentafluoro-1,4-naphthoquinone Derivatives

L. I. Goryunov[a], **N. M. Troshkova**[a], **G. A. Nevinskii**[b], **and V. D. Shteingarts**[a, c]

[a] *Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences,*
pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia
e-mail: shtein@nioch.nsc.ru

[b] *Institute of Chemical Biology and Fundamental Medicine, Siberian Division, Russian Academy of Sciences,*
*Novosibirsk, Russia*

[c] *Novosibirsk State University, Novosibirsk, Russia*

Abstract—Potential biologically active derivatives of 2-aminopentafluoro-1,4-naphthoquinone modified at the amino group were synthesized in 32–96% yield by reactions of hexafluoro-1,4-naphthoquinone with nitrogen-centered nucleophiles.

1,4-Naphthoquinone derivatives exhibit versatile physiological activity. For example, naturally occurring or synthetic compounds known as vitamins K_1–K_7 are efficient blood coagulants [1], while mono- and di-aminonaphthoquinone derivatives display antimalarial [2] and antitumor activity [3]. Such compounds as 2-(2-hydroxyethylsulfanyl)-3-methyl- and 2,3-bis(2-hydroxyethylsulfanyl)-1,4-naphthoquinones were also shown to inhibit growth of tumor cells, and the effect of their tetrafluoro-substituted analogs **Ia** and **Ib** was even stronger [4, 5].
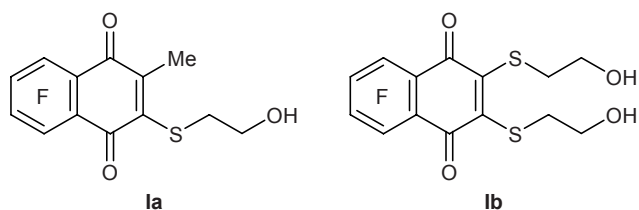

Compounds **Ia** and **Ib** were synthesized by replacement of fluorine atoms in 2-methylpentafluoro- and hexafluoro-1,4-naphthoquinones **II** and **III** by the action of 2-sulfanylethanol or its tetrahydropyran-2-yl ether, respectively, in methanol at room temperature [4, 5]. It was shown previously that fluorine atom in the quinone fragment is readily replaced by the action of methylene bases derived from nitrogen-containing heterocycles (compound **III**) [6] or sodium methoxide [2-(heptafluoronaphthalen-1-yloxy)pentafluoro-1,4-naphthoquinone (**IIa**)] [7]. Numerous examples of halogen replacement in chloro- and fluoroanil and 2-chloro- and 2,3-dichloro-1,4-naphthoquinone upon treatment with amines, alcohols, and other nucleophiles [8] have been reported. The above data illustrate prospects in using such reactions for the synthesis of potential biologically active polyfluorinated 1,4-naphthoquinone derivatives.

In the present communication we report on reactions of fluorinated 1,4-naphthoquinone **III** with aliphatic and aromatic amines with a view to obtain 2-aminopentafluoro-1,4-naphthoquinone derivatives as potential cell growth inhibitors and starting compounds for the preparation of polyfunctionalized fluorine-containing 1,4-naphthoquinones. The reactions of quinone **III** with primary and secondary amines were performed using 1.1–1.8 equiv of nucleophile, and their progress was monitored by ^{19}F NMR spectroscopy.

tert-Butylamine, 2-methylsulfanylethanamine, and 2-aminoethanol reacted with compound **III** at room temperature to give the corresponding 2-(alkylamino)-pentafluoro-1,4-naphthoquinones **IV–VIII** (Scheme 1). In the reaction with ethylamine, 2-ethylaminopentafluoro-1,4-naphthoquinone (**IV**) was obtained in 97% yield in 2 h. The reaction mixture obtained from quinone **III** and butylamine contained (after 3 h) ~70% of 2-(butylamino)pentafluoro-1,4-naphthoquinone (**V**), ~15% of di- and triamino-substituted quinones (assumingly), and ~15% of initial quinone **III**. The reaction of **III** with *tert*-butylamine gave in 2 h ~80% of

Scheme 1.
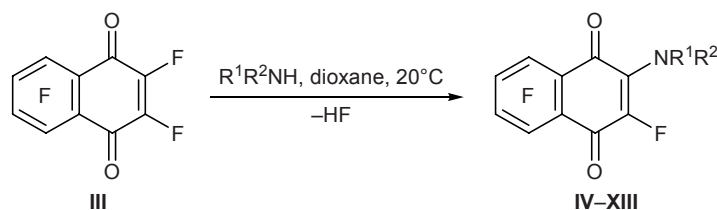
IV–IX, R^1 = H; **IV**, R^2 = Et; **V**, R^2 = Bu; **VI**, R^2 = t-Bu; **VII**, R^2 = MeSCH$_2$CH$_2$; **VIII**, R^2 = HOCH$_2$CH$_2$; **IX**, R^2 = Ph; **X**, R^1 = R^2 = Et; **XI**, R^{1}R^{2}N = morpholino; **XII**, R^1 = Me, R^2 = HOCH$_2$CH$_2$; **XIII**, R^1 = R^2 = HOCH$_2$CH$_2$.

2-(*tert*-butylamino)pentafluoro-1,4-naphthoquinone (**VI**) and ~20% of quinone **III**. The fraction of compound **VI** did not increase when the reaction time was extended to 24 h, but in this case the reaction mixture contained (in addition to initial quinone **III**) ~10% of products resulting from subsequent transformations of quinone **VI**. Compounds **V** and **VI** were isolated by preparative thin-layer chromatography in 63 and 62% yield, respectively.

The reaction of quinone **III** with 2-methylsulfanyl-ethanamine (2 h) gave 94% of 2-[2-(methylsulfanyl)-ethylamino]pentafluoro-1,4-naphthoquinone (**VII**). In the reaction with 2-aminoethanol, 2-(2-hydroxyethyl-amino)pentafluoro-1,4-naphthoquinone (**VIII**) was smoothly formed in 89% yield in 3 h. Quinone **III** reacted with aniline at 20°C to give in 15 h 2-(phenyl-amino)pentafluoro-1,4-naphthoquinone (**IX**, ~90%) and products of its further transformations (~10%). Compound **IX** was isolated in 62% yield by thin-layer chromatography.

Likewise, quinone **III** readily reacted with secondary amines. 2-Diethylaminopentafluoro-1,4-naphthoquinone (**X**) was obtained in 96% yield by reaction of **III** with 1.5 equiv of diethylamine (reaction time 2 h). Analogous reaction with morpholine at a ratio of 1:1.5 (2 h) led to the formation of 2-morpholinopentafluoro-1,4-naphthoquinone (**XI**) whose concentration in the reaction mixture was ~70% (preparative yield 59%); the reaction mixture also contained ~30% of products resulting from its further transformations. 2-[2-Hy-droxyethyl(methyl)amino]pentafluoro-1,4-naphtho-quinone (**XII**) was isolated in 87% yield from the product mixture obtained by reaction of quinone **III** with 1.8 equiv of 2-methylaminoethanol (2.5 h). In the reaction of **III** with 2,2′-iminodiethanol (reactant ratio 1:1.5), 2-[bis(2-hydroxyethyl)amino]pentafluoro-1,4-naphthoquinone (**XIII**) was formed; after 3.5 h, its concentration was ~70% (yield 32%); also, ~15% of the initial quinone and some other products were present in the reaction mixture.

Obviously, reactions of **III** with difunctional nucle-ophiles, such as 2-aminoethanol, 2-methylaminoetha-nol, and 2,2′-iminodiethanol, could follow two concur-rent pathways leading to the formation of both amino- and hydroxydefluorination products. To confirm the structure of the isolated compounds, quinone **III** was subjected to methanolysis which afforded 65% of 2-methoxypentafluoro-1,4-naphthoquinone (**XIV**) (Scheme 2).

Scheme 2.
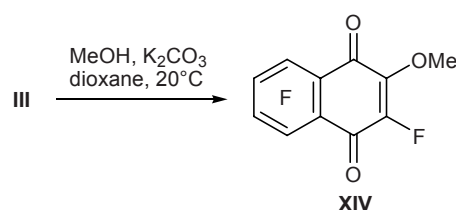
The chemical shift of 3-F (δ_F 17.5 ppm) in the ^{19}F NMR spectrum of **XIV** considerably differed from those observed in the spectra of 2-amino derivatives **VIII**, **XII**, and **XIII** (δ_F –0.01 to 6.8 ppm; see table). Moreover, the latter values approach the chemical shifts of 3-F for quinones **IV**, **V**, **VII**, and **XV** obtained from primary amines. An exception is compound **VI** having a relatively large *tert*-butylamino group (δ_F 16.5 ppm). The structure of **VIII** was confirmed by the ^{1}H NMR spectrum which contained signals from both NH and OH protons. In the ^{1}H NMR spectrum of **XII**, the NCH$_3$ signal was split due to coupling with the fluorine atom in position *3* (J_{HF} = 4.8 Hz); anal-ogous coupling was also observed for the methoxy protons in the spectrum of **XIV** (J_{HF} = 5.0 Hz). Like-wise, quinone **XIII** was assigned the structure corre-sponding to replacement of fluorine by the nucleophil-ic nitrogen center. We can conclude that aminoetha-nols act as just N-centered nucleophiles in reactions with quinone **III**. This conclusion is consistent with the results of the reaction of hexafluorobenzene with 2-aminoethanol, reported in [9].

^{1}H and ^{19}NMR spectra of polyfluoro-1,4-naphthoquinone derivatives in CDCl$_3$

Comp. no.	^{1}H NMR spectrum, δ, ppm (J, Hz)	^{19}F NMR spectrum, δ$_F$, ppm (J, Hz)		
		2-F, 3-F	5-F, 8-F	6-F, 7-F
II	2.50 d (3H, CH$_3$, J = 3.6)	48.7	25.0, 25.8	19.3, 18.1
IIa		27.6	25.0	17.7
IIb	6.70 d (1H, J = 9.7)	51.0	24.0, 25.0	18.0, 16.5
IIc	4.2		25.9	18.5
IId		36.9	25.8	18.8
III		22.1	25.5	18.6
IV	5.39 br.s (1H, NH), 3.58 m (2H, CH$_2$), 1.29 d.t (3H, CH$_3$, J = 7.2, 0.9)	5.3 br.s	24.2 d.d.d, 25.8 d.t $J_{5,6}, J_{6,7}, J_{7,8}$ = 19.7–19.8;	19.8 d.d.t (J = 4.1), 15.1 d.t $J_{5,7}, J_{5,8}, J_{6,8}$ = 10.1–12.1
V	5.44 br.s (1H, NH), 3.51 d.d.t (2H, CH$_2$, J = 3.3, 7.0, 6.6), 1.60 m (2H, CH$_2$), 1.38 m (2H, CH$_2$), 0.93 t (3H, CH$_3$, J = 7.2)	5.8 br.s	24.2 d.d.d, 25.8 d.t $J_{5,6}, J_{6,7}, J_{7,8}$ = 19.4–20.1;	19.8 d.d.t (J = 4.5), 15.0 d.t $J_{5,7}, J_{5,8}, J_{6,8}$ = 10.8–12.7
VI	5.74 br.s (1H, NH), 1.43 s (9H, t-Bu)	16.5 br.c	24.2 d.d.d (J = 2.0), 26.0 d.t $J_{5,6}, J_{6,7}, J_{7,8}$ = 19.4–19.8;	19.8 d.d.t (J = 4.5), 15.1 d.t $J_{5,7}, J_{5,8}, J_{6,8}$ = 10.1–12.3
VII	5.80 br.s (1H, NH), 3.73 d.d.t (2H, CH$_2$, J = 2.6, 6.4, 6.6), 2.76 t (2H, SCH$_2$, J = 6.6), 2.13 s (3H, CH$_3$)	6.7 br.s	24.4 d.t, 26.1 d.t $J_{5,6}, J_{6,7}, J_{7,8}$ = 19.6;	19.9 d.d.t (J 4.4), 15.4 d.t $J_{5,7}, J_{5,8}, J_{6,8}$ = 9.8–12.0
VIII	5.80 br.s (1H, NH), 3.87 t (2H, CH$_2$, J = 4.9), 3.70 m (2H, CH$_2$), 3.68 s (1H, OH)	6.8 br.s	24.3 d.t, 26.0 d.t $J_{5,6}, J_{6,7}, J_{7,8}$ = 19.3–19.7;	19.8 d.d.t (J = 4.2), 15.4 d.t $J_{5,7}, J_{5,8}, J_{6,8}$ = 10.4–12.1
IX	7.34–7.42 m (2H, CH), 7.20–7.27 m (1H, CH), 7.09–7.17 m (2H, CH)	28.1 br.s	24.9 d.t, 26.6 d.t $J_{5,6}, J_{6,7}, J_{7,8}$ = 19.2–20.1;	20.2 d.d.t (J = 4.5), 16.3 d.t $J_{5,7}, J_{5,8}, J_{6,8}$ = 10.8–12.7
X	3.45 d.q (4H, CH$_2$, J = 1.9, 7.0), 1.26 d.t (6H, CH$_3$, J = 0.6, 7.0)	18.7 br.s	22.7 d.d.d, 22.9 d.d.d $J_{5,6}, J_{6,7}, J_{7,8}$ = 18.7–19.7;	17.4 d.d.t (J 3.8), 15.1 d.t $J_{5,7}, J_{6,8}$ = 9.3–10.7
XI	3.85 t (4H, CH$_2$, J = 4.7), 3.56 m (4H, CH$_2$)	23.5 br.s	23.9 m (2F)	18.3 m, 16.4 m
XII	4.34 d.t (1H, CH$_2$, J = 3.7, 9.7), 4.22 br.s (1H, OH), 3.97–4.17 m (2H, CH$_2$), 3.32 d (3H, CH$_3$, J = 4.8), 3.16 d.t (1H, CH$_2$, J = 3.7, 11.9)	−1.38 q (J = 4.8)	20.8 d.d.d, 23.1 d.d.d $J_{5,6}, J_{6,7}, J_{7,8}$ = 19.2–20.1;	13.4 d.t, 8.6 d.t $J_{5,7}, J_{5,8}, J_{6,8}$ = 4.8–13.3
XIII[a]	3.40–4.35 m	−0.01 s	19.9 d.d.d, 26.6 d.d.d $J_{5,6}, J_{6,7}, J_{7,8}$ = 19.9–20.1;	11.9 d.t, 7.3 d.t $J_{5,7}, J_{5,8}, J_{6,8}$ = 4.5–13.3
XIV	4.30 d (3H, CH$_3$, J = 4.9)	17.5 m	25.3 d.t, 25.9 d.t $J_{5,6}, J_{6,7}, J_{7,8}$ = 19.4–19.8;	19.2 d.d.t (J = 3.9), 18.4 d.t $J_{5,7}, J_{5,8}, J_{6,8}$ = 11.3–12.2
XV[b]	7.30 br.s (1H, NH), 3.70 m (2H, CH$_2$N), 2.90 t (2H, CH$_2$S, J = 6.7)	4.22 s	21.2 d.d.d, 23.4 d.t $J_{5,6}, J_{6,7}, J_{7,8}$ = 20.7;	17.4 d.d.t (J = 4.4), 13.6 d.t $J_{5,7}, J_{5,8}, J_{6,8}$ = 8.9–11.7
XVI[b]	8.80 d.m, 8.60 t.t (J = 10.3, 55.2), 8.20 m		20.4 d.d.d, 21.9 d.t $J_{5,6}, J_{6,7}, J_{7,8}$ = 18.7–19.3;	16.5 d.t, 11.4 d.t $J_{5,7}, J_{5,8}, J_{6,8}$ = 8.3–12.8

[a] In acetone-d_6.
[b] In DMSO-d_6.

In the ^{1}H NMR spectra of quinones **XII** and **XIII**, signals from the methylene protons (obviously, this applies to only one CH_2CH_2 fragment in **XIII**) give rise to a more complex pattern, as compared to quinone **VIII**, indicating nonequivalence of protons in each methylene group. By analogy with the data for 2-[bis(2-hydroxyethyl)amino]- and 2-[2-hydroxyethyl-(methyl)amino]-1,4-benzoquinones [10−12], the observed pattern may be interpreted in terms of ring–chain tautomerism, i.e., formation of closed structures **XIIa** and **XIIIa**.
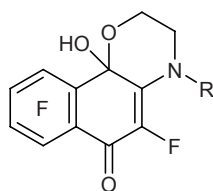
XIIa, **XIIIa**

XII, R = Me; **XIII**, R = HOCH₂CH₂.

We found that crystalline quinone **X** underwent deethylation to give compound **IV** upon prolonged storage (for several months) in a vessel made of colorless glass. Presumably, this transformation occurs with participation of atmospheric moisture. When quinone **X** was kept for 4 weeks in dioxane containing a few drops of water on exposure to daylight, it was completely converted into a mixture of solvolysis products, from which we isolated 39% of quinone **IV**. No transformation was observed in the dark. Analogous deethylation was reported previously for 3-chloro-2-[ethyl(phenyl)amino]-1,4-naphthoquinone which was

converted into 2-chloro-3-phenylamino-1,4-naphthoquinone upon irradiation of its alcoholic solution with sunlight [13].

All newly synthesized compounds were characterized by ^{1}H and ^{19}F NMR spectra (see table) and high-resolution mass spectra or elemental analyses. The ^{19}F NMR parameters of quinones **IV–XIII** were very consistent with published data for compounds **II** [14], **III**, **IIa** [7], 2,5,6,7,8-pentafluoro-1,4-naphthoquinone (**IIb**) [15], 2-(heptafluoronaphthalen-1-yloxy)-3-methoxytetrafluoro-1,4-naphthoquinone (**IIc**), and 2-(pentafluorobenzoyloxy)pentafluoro-1,4-naphthoquinone (**IId**) [7]. Fluorine nuclei in the quinone fragment (2-F or 3-F) resonated as slightly broadened singlets or multiplets, obviously due to weak spin–spin couplings with fluorine nuclei in the benzene ring. Signals from the latter appear in the ^{19}F NMR spectra as multiplets in the regions δ_F 24–27 ppm (5-F, 8-F) and 15–20 ppm (6-F, 7-F).

Quinone **III** reacted with 2,2′-dithiodiethanamine to give *N*,*N*′-bis(3,5,6,7,8-pentafluoro-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-2,2′-dithiodiethanamine (**XV**) in 75% yield (Scheme 3). The ^{1}H NMR spectrum of disulfide **XV** contained signals from protons in the NH and CH₂ groups.

The reaction of **III** with pyridine in moist methanol is likely to begin with replacement of fluorine in position *2* to produce pyridinium salt **A**. The presence of a positively charged group in position *2* activates the neighboring position of the quinoid ring to nucleophilic attack, and the 3-fluorine atom in **A** is rapidly replaced by methoxy or hydroxy group (due to the

Scheme 3.
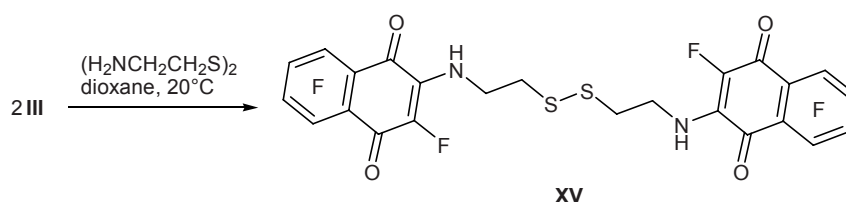
Scheme 4.
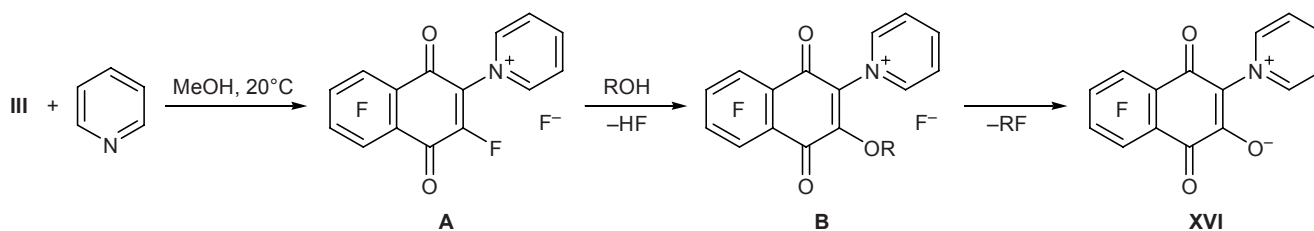
R = H, Me.

presence of water in the solvent) with formation of quinone **B**. The final product is zwitterionic 1,4-dioxo-3-pyridinio-1,4-dihydronaphthalen-2-olate (**XVI**, yield 90%; Scheme 4). The ^{19}F NMR spectrum of **XVI** contained signals from the fluorine atoms on C^5–C^8 with equal intensities, and signals from protons in the pyridinium fragment were observed in its ^{1}H NMR spectrum.

Thus the results of the present study demonstrate that reactions of quinone **III** with amines ensure fairly selective replacement of one fluorine atom in the quinoid ring by amino group (obviously, due to de-activating effect of the entering amino group). The resulting 2-aminopentafluoro-1,4-naphthoquinone derivatives attract interest from the viewpoint of their subsequent modifications at the amino group to obtain new potential biologically active compounds.

EXPERIMENTAL

The ^{1}H and ^{19}F NMR spectra were recorded on Bruker WP-200SY (200.13 MHz for ^{1}H and 188.28 MHz for ^{19}F) and Bruker AV-300 spectrometers (300.13 MHz for ^{1}H and 282 MHz for ^{19}F); the chemical shifts were measured relative to CD_3COCD_3 (δ 2.04 ppm), $CDCl_3$ (δ 7.24 ppm), and C_6F_6 ($δ_F$ 0.0 ppm) as internal references. The molecular weights were determined from the high-resolution mass spectra which were obtained on a Finnigan MAT-8200 instrument.

1,4-Dioxane was distilled under reduced pressure (0.1 mm) and stored over 3-Å molecular sieves. Methanol was distilled under reduced pressure (0.03 mm) and stored over 3-Å molecular sieves. Diethylamine, aniline, morpholine, *tert*-butylamine, and 2,2′-iminodi-ethanol of chemically pure grade were purified by vacuum distillation (0.03 mm). Butylamine (99.5%, Acros Organics), 2-methylaminoethanol (99%, Riedel-deHaen), and 2-(methylsulfanyl)ethanamine (95%, Maybridge) were used without additional purification. Pyridine of chemically pure grade was distilled under reduced pressure (0.03 mm) and stored over 3-Å molecular sieves. Hexafluoro-1,4-naphthoquinone **III** was synthesized according to the procedure reported in [16]; 2,2′-Dithiodiethanamine was prepared as described in [17] and was isolated as the corresponding dihydrochloride according to [18].

2-Ethylamino-3,5,6,7,8-pentafluoro-1,4-dihydro-naphthalene-1,4-dione (IV). A mixture of 0.070 g (0.556 mmol) of ethylamine hydrobromide, 0.094 g

(1.675 mmol) of potassium hydroxide, and 2 ml of dioxane was stirred for 30 min at room temperature. The precipitate was separated by centrifugation, 0.101 g (0.379 mmol) of quinone **III** was added to the solution, and the mixture was stirred for 2 h at 20°C, and diluted with 10 ml of water. The precipitate was separated by centrifugation and washed with water. Yield 0.106 g (97%); after vacuum sublimation (150°C, 0.03 mm), yield 0.095 g (88%), dark red crystals, mp 184–185°C. Found, %: C 49.23; H 1.85; N 4.86. $C_{12}H_6F_5NO_2$. Calculated, %: C 49.5; H 2.08; N 4.81.

2-Butylamino-3,5,6,7,8-pentafluoro-1,4-dihydro-naphthalene-1,4-dione (V). A mixture of 0.200 g (0.751 mmol) of quinone **III**, 0.099 g (1.354 mmol) of butylamine, and 2 ml of dioxane was stirred for 3 h at 20°C. The mixture was diluted with 10 ml of water, and the precipitate was separated by centrifugation, washed with water (2×3 ml), and purified by preparative thin-layer chromatography on silica gel using chloroform–hexane (3:1) as eluent. Yield 0.15 g (63%), bright red crystals, mp 135–137°C. Found: m/z 319.0618 $[M]^+$. $C_{14}H_{10}F_5NO_2$. Calculated: M 319.06316.

2-*tert*-Butylamino-3,5,6,7,8-pentafluoro-1,4-dihy-dronaphthalene-1,4-dione (VI). An NMR ampule was charged with 0.175 g (0.657 mmol) of quinone **III** and cooled with liquid nitrogen, and 1.5 ml of dioxane and 0.086 g (1.17 mmol) of *tert*-butylamine were condensed thereto under reduced pressure (0.03 mm). The ampule was sealed, kept for 24 h at 20°C, and opened, the mixture was poured into ~6 ml of water, and the precipitate was separated by centrifugation, evacuated for 2 h at a residual pressure of 0.03 mm at 20°C, and purified by thin-layer chromatography on Silufol using chloroform–hexane (3:1) as eluent. Yield 0.128 g (62%), orange crystals, mp 186–190°C. Found: m/z 319.06247 $[M]^+$. $C_{14}H_{10}F_5NO_2$. Calculated: M 319.06316.

2,5,6,7,8-Pentafluoro-3-[2-(methylsulfanyl)-ethylamino]-1,4-dihydronaphthalene-1,4-dione (VII) was synthesized as described above for quinone **V** from 0.100 g (0.376 mmol) of quinone **III** and 0.051 g (0.559 mmol) of 2-(methylsulfanyl)ethan-amine in 1.5 ml of dioxane (20°C, 2 h). Yield 0.119 g (94%), dark red crystals, mp 136–139°C. Found, %: C 46.41; H 2.52; F 28.15; N 4.13. $C_{13}H_8F_5NO_2S$. Calculated, %: C 46.3; H 2.39; F 28.16; N 4.15.

2-(2-Hydroxyethylamino)-3,5,6,7,8-pentafluoro-1,4-dihydronaphthalene-1,4-dione (VIII). A mixture

of 0.200 g (0.751 mmol) of quinone **III** and 0.069 g (1.127 mmol) of 2-aminoethanol in 2 ml of dioxane was stirred for 3 h at 20°C. The red precipitate was separated by centrifugation and washed with water. Yield 0.204 g (89%), dark red crystals, mp 159–160°C. Found, %: C 47.24; H 2.08; N 4.59. $C_{12}H_6F_5NO_3$. Calculated, %: C 46.92; H 1.97; N 4.56.

2,5,6,7,8-Pentafluoro-3-phenylamino-1,4-dihydronaphthalene-1,4-dione (IX) was synthesized as described above for compound **V** from 0.174 g (0.653 mmol) of quinone **III** and 0.067 g (0.719 mmol) of aniline in 1.5 ml of dioxane (20°C, 15 h). The product was purified by TLC on Silufol using chloroform–carbon tetrachloride (1:1) as eluent. Yield 0.136 g (62%), red–brown crystals, mp 211–212°C. Found: m/z 339.03150 $[M]^+$. $C_{16}H_6F_5NO_2$. Calculated: M 339.03186.

2-Diethylamino-3,5,6,7,8-pentafluoro-1,4-dihydronaphthalene-1,4-dione (X) was synthesized as described above for compound **V** from 0.174 g (0.653 mmol) of quinone **III** and 0.071 g (0.971 mmol) of diethylamine in 1.5 ml of dioxane under argon (20°C, 2 h). The product was precipitated with water. Yield 0.2 g (96%), dark red crystals, mp 90–92°C. Found: m/z 319.06220 $[M]^+$. $C_{14}H_{10}F_5NO_2$. Calculated: M 319.06316.

2,5,6,7,8-Pentafluoro-3-morpholino-1,4-dihydronaphthalene-1,4-dione (XI) was synthesized as described above for compound **V** from 0.175 g (0.658 mmol) of quinone **III** and 0.085 g (0.975 mmol) of morpholine in 1.5 ml of dioxane (20°C, 2 h). The product was purified by TLC on a Sorbfil plate using chloroform as eluent. Yield 0.112 g (52%), dark red crystals, mp 158–161°C. Found: m/z 333.0422 $[M]^+$. $C_{14}H_8F_5NO_3$. Calculated: M 333.04242.

2,5,6,7,8-Pentafluoro-2-[2-hydroxyethyl(methyl)-amino]-1,4-dihydronaphthalene-1,4-dione (XII). 2-methylaminoethanol, 0.102 g (1.353 mmol), was added to a suspension of 0.200 g (0.751 mmol) of compound **III** in 2 ml of dioxane, and the mixture was stirred for 2.5 h at room temperature. The mixture was diluted with ~8 ml of water, and the precipitate was separated by centrifugation, washed with water (2× 2 ml), and evacuated for 2 h at a residual pressure of 0.03 mm (20°C). Yield 0.21 g (87%), yellow–brown crystals, mp 146–147°C. Found: m/z 321.04168 $[M]^+$. $C_{13}H_8F_5NO_3$. Calculated: M 321.04242.

2-[Bis(2-hydroxyethyl)amino]-3,5,6,7,8-pentafluoro-1,4-dihydronaphthalene-1,4-dione (XIII). A mixture of 0.100 g (0.376 mmol) of quinone **III**,

0.059 g (0.56 mmol) of 2,2′-iminodiethanol, and 1.5 ml of dioxane was stirred for 3.5 h at room temperature. The solvent was distilled off under reduced pressure (0.03 mm), the residue was dissolved in acetone, and the product was precipitated with hexane–diethyl ether (4:1), separated by centrifugation, and purified by TLC using acetone–hexane (1:1) as eluent. Yield 0.042 g (32%), yellow–brown crystals, mp 147–150°C. Found: m/z 351.05165 $[M]^+$. $C_{14}H_{10}F_5NO_4$. Calculated: M 351.05299.

2-Methoxy-3,5,6,7,8-pentafluoro-1,4-dihydronaphthalene-1,4-dione (XIV). A reactor was charged with 0.026 g (0.188 mmol) of potassium carbonate and 0.050 g (0.188 mmol) of quinone **III**, the reactor was cooled with liquid nitrogen, 1.5 ml of dioxane was condensed thereto under reduced pressure (0.03 mm), and 0.018 g (0.53 mmol) of methanol was then added under argon. The progress of the reaction was monitored by ^{19}F NMR spectroscopy. After 9 days, the mixture was diluted with ~5 ml of water. The precipitate was separated by centrifugation, washed with water (3×3 ml), and dissolved in 1 ml of methanol on heating. After cooling, the yellow crystalline solid was separated by centrifugation. Yield 0.034 g (65%), mp 189–191°C. Found, %: C 47.64; H 0.76. $C_{11}H_3F_5O_3$. Calculated, %: C 47.5; H 1.09.

N,N′-Bis(3,5,6,7,8-pentafluoro-1,4-dihydro-1,4-dioxonaphthalen-2-yl)-2,2′-dithiodiethanamine (XV). A mixture of 0.050 g (0.188 mmol) of quinone **III**, 0.021 g (0.093 mmol) of 2,2′-dithiodiethanamine dihydrochloride, 0.019 g (0.188 mmol) of triethylamine, and 1.5 ml of dioxane was stirred for 2 h at 20°C and was then left overnight. The red precipitate was separated by centrifugation, washed with 2 ml of dioxane and 5 ml of water, and evacuated for 2 h at a residual pressure of 0.03 mm at 20°C. Yield 0.045 g (75%), mp 230–235°C. Found; m/z 643.9919 $[M]^+$. $C_{24}H_{10}F_{10}N_2O_4S_2$. Calculated: M 643.9922.

1,4-Dioxo-3-pyridinio-1,4-dihydronaphthalen-2-olate (XVI). Pyridine, 0.590 g (7.459 mmol), was added under argon to a solution of 0.200 g (0.751 mmol) of quinone **III** in 3 ml of methanol, and the mixture was stirred for 1 h at room temperature. The precipitate was separated by centrifugation and washed with methanol (3×2 ml). Yield 0.22 g (90%), orange crystals, mp 317–319°C. Found, %: C 55.59; H 1.55; F 23.51; N 4.29. $C_{15}H_5F_4NO_3$. Calculated, %: C 55.74; H 1.56; F 23.51; N 4.33.

Deethylation of quinone (X). An NMR ampule was charged with a solution of 0.014 g (0.043 mmol)

of naphthoquinone **X** in 0.5 ml of dioxane, one drop of water was added, and the mixture was kept for 23 days, the progress of the reaction being monitored by ^{19}F NMR spectroscopy. The mixture was then diluted with ~3 ml of water, and the precipitate was separated by centrifugation and purified by TLC on a Sorbfil plate using chloroform–hexane (1:1) as eluent. Yield of quinone **IV** 0.005 g (39%).

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