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# Aminodefluorination of 2-X-pentafluoro-1,4-naphthoquinones (X = NH$^n$Bu, NEt$_2$, and OMe)

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ABSTRACT

Aminodefluorination of 2-*n*-butylamino- and 2-diethylaminopentafluoro-1,4-naphthoquinone by alkylamines HNR$^1$R$^2$ (NR$^1$R$^2$ = NHEt, NH$^n$Bu and NEt$_2$) occurs at the 6- or 8-position and further, accordingly, at the 8- or at one of the 5- and 6-sites. The isomer ratio changes significantly in favor of a β-replacement product with solvent variation in the sequence: toluene < 1,4-dioxane < DMSO. *n*-Butylaminodefluorination of 2-methoxypentafluoro-1,4-naphthoquinone gives mixtures of fluorine substitution products both on the benzene and quinone rings.



## 1. Introduction

Reactions of hexafluoro-1,4-naphthoquinone (**1**) with primary and secondary amines were recently reported to afford the respective 2-aminopentafluoro-1,4-naphthoquinone derivatives. The general electron-deficiency of the polyfluorinated naphthoquinone core anticipated their further nucleophilic modification to provide fluorinated di- and, probably, triamino derivatives of 1,4-naphthoquinone as potentially bioactive substances [1]. For these reasons, the present study deals with the reactions of **1**, 2-*n*-butylaminopentafluoro-1,4-naphthoquinone (**2**), 2-diethylaminopentafluoro-1,4-naphthoquinone (**2b**), and 2-methoxypentafluoro-1,4-naphthoquinone (**2c**) with *n*-butyl-, ethyl-, and diethylamine in dioxane, toluene, or DMSO.

## 2. Results and discussion

The reactions were monitored by the $^{19}$F NMR spectra. First obtained fluoronaphthoquinones were isolated by TLC, their structures were deduced from the $^1$H, $^{19}$F NMR, MS, HRMS data and, in some cases, the X-ray investigations.

### 2.1. Reactions of quinones 1, 2a, 2b, and 2c with n-butyl-, ethyl-, or 2-diethylamine

Quinone **1** was completely consumed with four equivalents of *n*-butylamine in dioxane at room temperature (17–19 °C) even for 3 h to give a mixture of **2a** and the products of further β- or α-fluorine replacement on the benzene moiety—2,6-bis-*n*-butylaminotetrafluoro-1,4-naphthoquinone (**3a**) and 2,8-bis-*n*-butylaminotetrafluoro-1,4-naphthoquinone (**4a**), accordingly. Some quantity of 2,6,8-tris-*n*-butylaminotrifluoro-1,4-naphthoquinone (**5a**) was also present in the product mixture (reaction **a** in Scheme 1; hereinafter, unless otherwise stated, a mol percentage is specified).

These results indicate that the *n*-butylamine group in the quinone part of **2a** retards replacing of the adjacent F-3 atom and directs a nucleophilic attack on the 6- and 8-positions. During 48 h the content of **3a** and **4a** in the product mixture initially increased and then decreased to yield **5a** and 2,5,8-tris-*n*-butylaminotrifluoro-1,4-naphthoquinone (**6a**). Thus, **4a** is consumed faster compared with its isomer **3a**, that was especially appreciable by results of separate *n*-butylaminodefluorinations of each of these quinones (the transformation degrees in reactions **b** and **c** for 6.5 h

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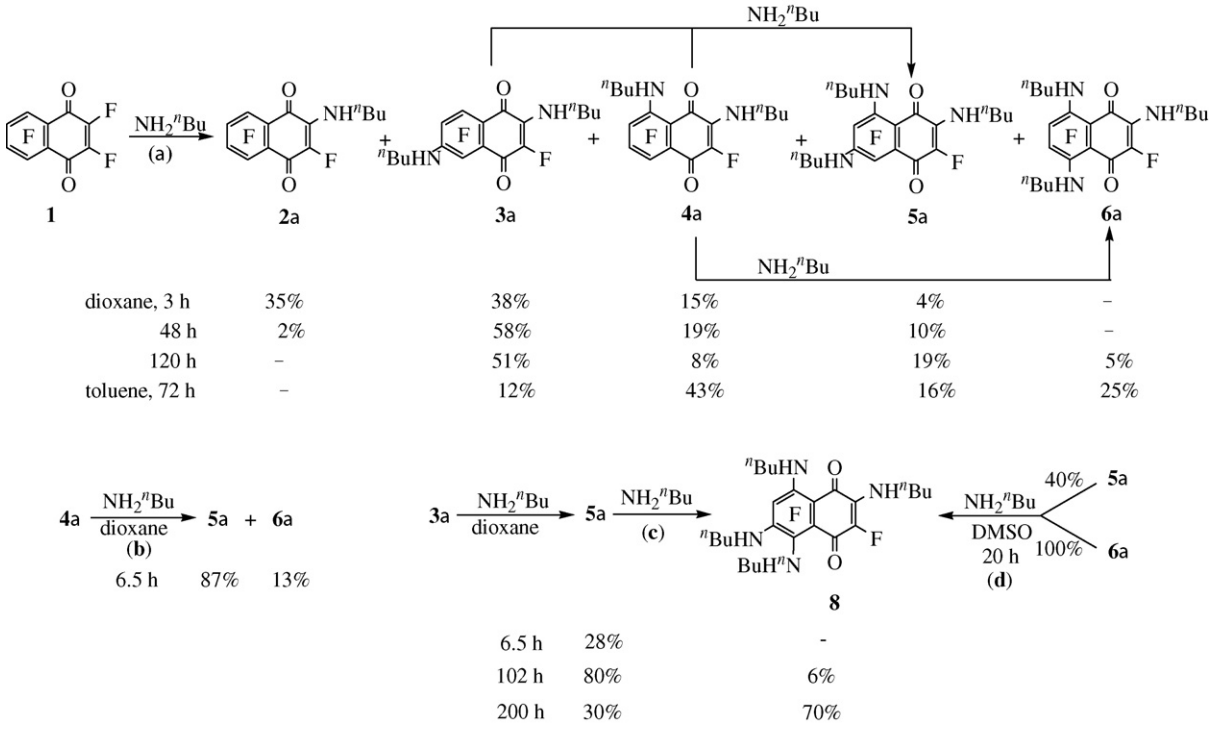



**Scheme 1.**

were 100% and 28%, accordingly). The larger activity of the 6-position in **4a** as compared with the 8-position in its isomer **3a** is obviously caused by the activating effect of two *ortho*-F in the former case unlike a blend of the single *ortho*-F activating and *para*-F deactivating influences in the latter one (cf. [2]).

In the reaction with *n*-butylamine (a 1:4 mole ratio) in toluene at 20 °C after 72 h quinone **1** turned almost completely in compounds **3a**, **4a**, **5a**, and **6a**. The **3a** and **4a** structures were established by the X-ray investigations (Fig. 1). It is obvious that **6a** arises from the α-isomer **4a**, whereas both **3a** and **4a** can be precursors of **5a**. Noteworthily, methylamino- and dialkylamino-defluorination of 1,2,3,4-tetrafluoroanthraquinone **7** were earlier shown to give only the 1,4- or 1,3-disubstitution products similar to **5a** and **6a**, respectively [3,4]. *n*-Butylaminodefluorination of **5a** in dioxane and DMSO (reactions **c** and **d** in Scheme 1) occurred on the benzene ring yielding 2,5,6,7-tetra-*n*-butylaminodifluoro-1,4-naphthoquinone (**8**), which is also formed from **6a** (reaction **d**).

The conditions and results of the interaction of **2a** with ethylamine (reaction **a** in Scheme 2) were similar to that described above for *n*-butylamine.

Thus, 2-*n*-butylamino-6-ethylaminotetrafluoro-1,4-naphthoquinone (**3b**), 2-*n*-butylamino-8-ethylamino-tetrafluoro-1,4-naphthoquinone (**4b**), and some quantity of 2-*n*-butylamino-6,8-bis-ethylaminotrifluoro-1,4-naphthoquinone (**5b**) were basically formed in dioxane. Quinone **2a** with ethylamine (a 1:3 mole ratio) in toluene gave **3b**–**5b** and 2-*n*-butylamino-5,8-bis-(ethylamino)-trifluoro-1,4-naphthoquinone (**6b**) with an essential predominance of **4b**. On the contrary, the reaction in DMSO allowed to obtain mainly β-substituted quinone **3b**.

The influence of a solvent nature on a ratio of α- and β-replacement products in the benzene ring (Schemes 1 and 2) conform to that observed earlier in the reactions of anthraquinone **7** with ammonia and methylamine while the solvent varied from DMSO or DMFA to dioxane and, further to toluene or benzene. The predominant α-orientation in two last solvents was explained by a specific stabilization of the respective transition state (TS) by hydrogen bonding between N–H and carbonyl groups [5]. The easier β-fluorine replacement compared with the α-fluorine in the benzene ring of **2a** in DMSO can be owing to the TS stabilization by electron-withdrawing effects of two *ortho*- and one *meta*-F-substituents. Unlike this, the TS of α-fluorine replacement is stabilized by only one *ortho*- and one *meta*-F-atoms, the *para*-one exerting, obviously, a destabilizing effect (cf. [2]). Besides, the easier aminodefluorination of **2a** at the 6- and 8-positions

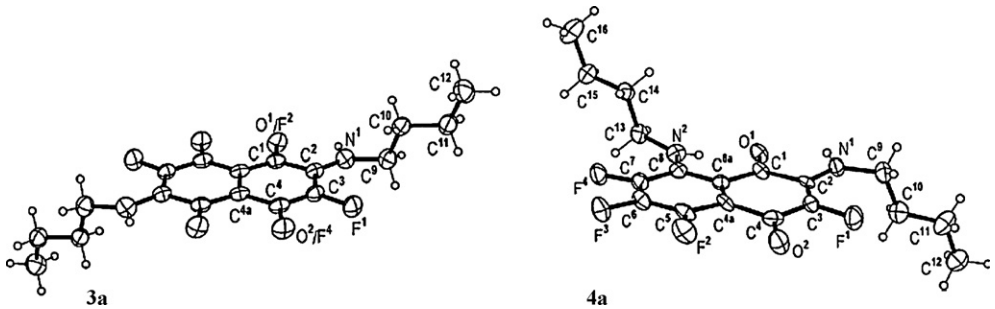
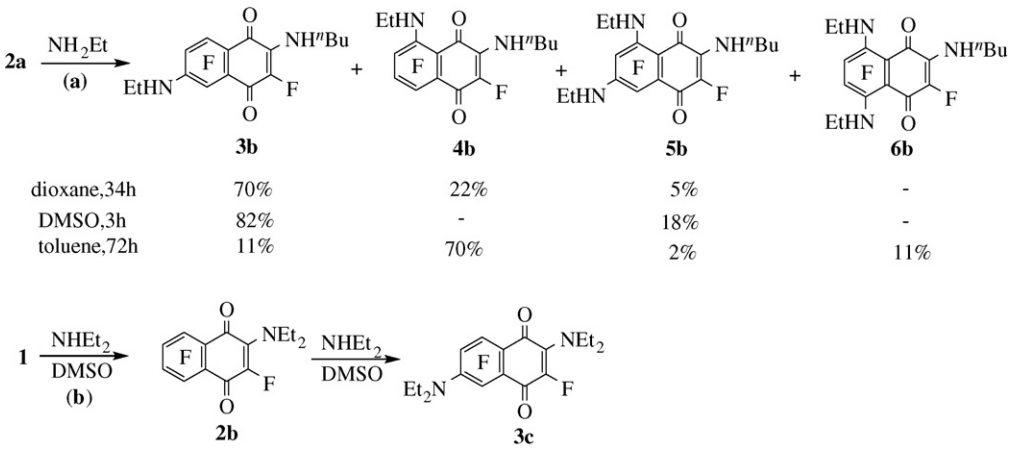
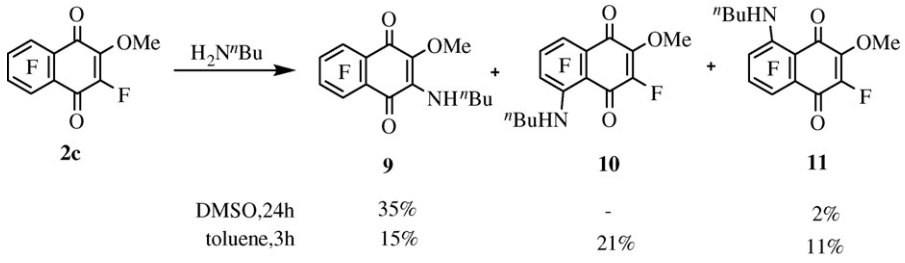



**Fig. 1.** X-ray molecular structures of **3a** and **4a**.

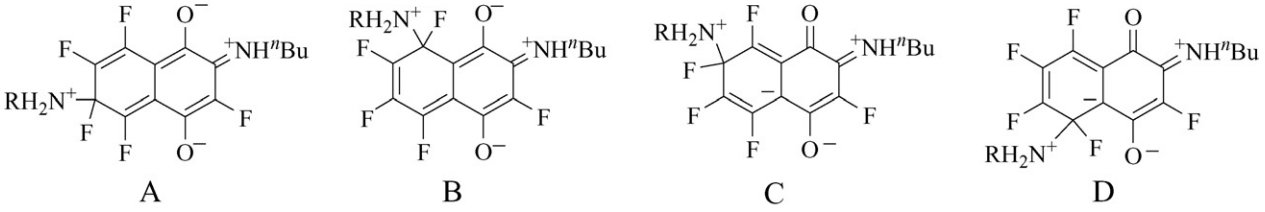



**Scheme 2.**




**Scheme 3.**

compared to the 7- and 5-ones (Schemes 1 and 2) is obviously caused by stronger stabilization of the TSs of F-6 and F-8 substitution, approximated by the σ-complex structures **A** and **B** (R = Et, $^n$Bu), by the *para*- and *ortho*-carbonyl[1] group (1-C=O), respectively, not conjugated with the 2-amino group. Unlike this, in the TSs of F-7 and F-5 substitution (the modelling structures **C** and **D**) a stabilizing influence of the similarly located 4-C=O group is substantially suppressed by its conjugation with the 2-amino group[2]:




Quinone **1** with diethylamine (a 1:1.5 mole ratio, dioxane, room temperature) gave the F-2 replacement product **2b** (reaction **b** in Scheme 2) [1], whereas with a threefold stoichiometric excess of the amine in DMSO at room temperature also the replacement of F-6 occurred to afford 2,6-bis-diethylaminotetrafluoro-1,4-naphthoquinone **3c** in 43% yield. The latter result is similar to that described above for ethylamine (Scheme 2, reaction **a**).

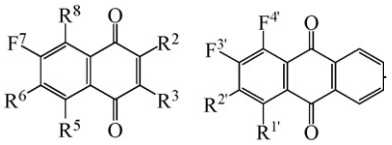
Thus, by contrast to the alkylaminodefluorination of **1** on the quinone fragment, the electron-donating 2-alkylamine group in **2a**,**b** inactivates an adjacent quinone position to a nucleophilic attack so substitution in the benzene ring is realized. A question seemed important, how the competition of these two reaction pathways depends on the nature of the electron-donating 2-substituent. In this connection, *n*-butylaminodefluorination of 2-methoxypentafluoro-1,4-naphthoquinone **2c** was found to proceed as depicted by Scheme 3 (isolated yields are specified).

The complete transformation of **2c** yielded a complex product mixture, some of them having not been identified. In DMSO 2-*n*-butylamino-3-methoxytetrafluoro-1,4-naphthoquinone (**9**) was the main monosubstitution product. Compared with quinones **2a,b** in the same solvent (see above), this result reveals decreasing an electron-donating effect of the 2-substituent in 2-X-pentafluoro-1,4-naphthoquinone in going from X = NH$^n$Bu and $NEt_2$ to X = OMe to reduce an inactivation of the 3-position. By contrast, comparable quantities of **9** and the products of 5- and 8-fluorine replacement – 5-*n*-butylamino-2-methoxytetrafluoro-1,4-naphthoquinone (**10**) and 8-*n*-butylamino-2-methoxytetrafluoro-1,4-naphthoquinone (**11**) – formed in toluene. For this reason, the above mentioned hydrogen bonding in the α-aminodefluorination TSs on the benzene ring is believed to

[1] Hereinafter carbonyl groups are named as *ortho*, *meta* or *para* according to their positions relative the site of nucleophilic attack on the benzene moiety of a naphthoquinone core.

[2] At the same time, if the TSs in the reactions under study are "early" (substrate-like) and, accordingly, the regioselectivity is analyzed in terms of the electronic density distribution in a substrate, one comes to the same qualitative conclusions.

**Table 1**
$^{1}H$ and $^{19}F$ NMR spectroscopic data of polyfluorinated 1,4-naphthoquinone and 9,10-anthraquinones derivatives



| Compound | Substituents | $\delta^{a}$, ppm ($J$, Hz) | | | | | |
|---|---|---|---|---|---|---|---|
| | | $F^{3}$ | $F^{5(1')}$ | $F^{6(2')}$ | $F^{7(3')}$ | $F^{8(4')}$ | H |
| **2a** | $R^{2}$ = NHBu$^{n}$ | −157.2 br.s | −138.8 d.d.d, | −143.2 d.d.t, | −148.0 d.t, | −137.2 d.t, | 0.93 (3H, t, 7.2, $CH_3$), 1.38 (2H, m, $CH_2$), 1.60 (2H, m, $CH_2$), 3.51 (2H, d.d.t, 7.0, 6.6, 3.3, $CH_2$), 5.44 (1H, br.s, NH) |
| | | | $J_{5,6}$ ~20, $J_{5,7}$ ~10, $J_{5,8}$ ~12 | $J_{5,6}$, $J_{6,7}$ ~20, $J_{6,8}$ ~12, $J_{3,6}$ 4.5 | $J_{5,7}$ ~10, $J_{6,7}$ $J_{7,8}$ ~20 | $J_{5,8}$, $J_{6,8}$ ~12, $J_{7,8}$ ~20 | |
| **3a** | $R^{2}$, $R^{6}$ = NHBu$^{n}$ | −160.6 s | −136.5 d.m, | | −153.9 t, | −139.4 d.d, | 0.94 (3H, t, 7.4, $CH_3$), 0.96 (3H, t, 7.2, $CH_3$), 1.40 (4H, m, $2CH_2$), 1.54–1.69 (4H, $2CH_2$), 3.46–3.60 (4H, $2CH_2$), |
| | | | $J_{5,7}$ 18.3 | | $J_{5,7}$, $J_{7,8}$ ~18 | $J_{5,8}$ 8.3, $J_{7,8}$ 17.6 | 4.62 (1H, br.s, NH), 5.54 (1H, br.s, NH) |
| **4a** | $R^{2}$, $R^{8}$ = NHBu$^{n}$ | −160.7 s | −148.4 d.d, $J_{5,6}$ 19.6, $J_{5,7}$ 4.6 | −147.2 d.t $J_{5,6}$, $J_{6,7}$ 16–20, $J_{3,6}$ 4.2 | −145.0 d.m, $J_{6,7}$ 15.6 | | 0.93–0.98 (6H, $2CH_3$), 1.35–1.55 (4H, $2CH_2$), 1.56–1.74 (4H, $2CH_2$), 3.49–3.67 (4H, $2CH_2$), 5.60 (1H, br.s, NH), 9.61 (1H, br.s, NH) |
| **5a** | $R^{2}$, $R^{6}$, $R^{8}$ = NHBu$^{n}$ | −163.6 s | −140.5 d [−146.1], $J_{5,7}$ 13.1 | | −148.7 br.d [−150.9], $J_{5,7}$ ~13 | | 0.89–0.98 (9H, $3CH_3$), 1.31–1.49 (6H, $3CH_2$), 1.52–1.68 (6H, $3CH_2$), 3.43–3.57 (6H, $3CH_2$), 4.39 (1H, br.s, NH), 5.69 (1H, br.s, NH), 9.60 (1H, br.s, NH) |
| **6a** | $R^{2}$, $R^{5}$, $R^{8}$ = NHBu$^{n}$ | −160.1 s | | −139.1 m [−144.2] | −145.1 m [−149.0] | | 0.90–1.00 (9H, $3CH_3$), 1.32–1.53 (6H, $3CH_2$), 1.54–1.72 (6H, $3CH_2$), 3.45–3.65 (6H, $3CH_2$), 5.45 (1H, br.s, NH), 10.52 (1H, br.s, NH), 10.60 (1H, br.s, NH) |
| **8** | $R^{2}$, $R^{5}$, $R^{6}$, $R^{8}$ = NHBu$^{n}$ | −164.4 s | | | −151.3 s [−151.0] | | 0.86–0.99 (12H, $4CH_3$), 1.29–1.49 (8H, $4CH_2$), 1.49–1.70 (8H, $4CH_2$), 2.81–2.92 (2H, $CH_2$), 3.40–3.61 (6H, $3CH_2$), 5.03 (1H, br.s, NH), 5.80 (1H, br.s, NH), 8.20 (1H, br.s, NH), 10.25 (1H, br.s, NH) |
| **3b** | $R^{2}$ = NHBu$^{n}$ | −160.5 s | −136.5 d.m [−136.5] | | −154.2 t [−153.9] | −139.5 d.d [−139.4] $J_{5,8}$ 8.5, $J_{7,8}$ 17.8 | 0.96 (3H, t, 7.3, $CH_3$), 1.33 (3H, d.t, 0.6, 7.2, $CH_3$), |
| | $R^{6}$ = NHEt | | $J_{5,7}$ 18.3 | | $J_{5,7}$, $J_{7,8}$ ~18 | | 1.37–1.49 (2H, $CH_2$), 1.58–1.70 (2H, $CH_2$), 3.53 (2H, m, $CH_2$), 3.64 (2H, m, $CH_2$), 4.62 (1H, br.s, NH), 5.55 (1H, br.s, NH) |
| **4b** | $R^{2}$ = NHBu$^{n}$ | −160.6 s | −148.4 d.d [−148.4] $J_{5,6}$ 19.4, $J_{5,7}$ 4.3 | −147.2 d.t [−147.2] $J_{5,6}$, $J_{6,7}$ 16–19, $J_{3,6}$ 4.3 | −145.4 d.m [−145.0] $J_{6,7}$ 16.4 | | 0.93 (3H, t, 7.3, $CH_3$), 1.31 (3H, d.t, 0.7, 7.2, $CH_3$), |
| | $R^{8}$ = NHEt | | | | | | 1.34–1.47 (2H, $CH_2$), 1.54–1.68 (2H, $CH_2$), 3.50 (2H, m, $CH_2$), 3.55–3.68 (2H, $CH_2$), 5.55 (1H, br.s, NH), 9.49 (1H, br.s, NH) |
| **5b** | $R^{2}$ = NHBu$^{n}$ $R^{6}$, $R^{8}$ = NHEt | −163.5 s | −140.6 d [−140.5] $J_{5,7}$ 13.7 | | −149.3 br.d [−148.3] $J_{5,7}$ ~14 | | 0.93 (3H, t, 7.3, $CH_3$), 1.21–1.31 (6H, $2CH_3$), 1.39 (2H, m, $CH_2$), 1.50–1.66 (2H, $CH_2$), 3.46–3.63 (6H, $3CH_2$), 4.35 (1H, br.s, NH), 5.69 (1H, br.s, NH), 9.54 (1H, br.s, NH) |
| **6b** | $R^{2}$ = NHBu$^{n}$ $R^{5}$, $R^{8}$ = NHEt | −160.1 s | | −139.5 m [−139.1] | −145.5 m [−145.1] | | 0.93 (3H, t, 7.3, $CH_3$), 1.23–1.35 (6H, $2CH_3$), 1.35–1.46 (2H, $CH_2$), 1.49–1.56 (2H, $CH_2$), 3.46–3.69 (6H, $3CH_2$), 5.45 (1H, br.s, NH), 10.42 (1H, br.s, NH), 10.52 (1H, br.s, NH) |
| **2b** | $R^{2}$ = $NEt_2$ | −144.3 br.s | −140.3 d.d.d, | −145.6 d.d.t, | −147.9 d.t, | −140.1 d.d.d, $J_{5,8}$ 13.2, | 1.26 (6H, d.t, 0.6, 7.0, $2CH_3$), 3.45 (4H, d.q, 1.9, 7.0, $2CH_2$,) |
| | | | $J_{5,6}$ 19.7, $J_{5,7}$ 9.5, $J_{5,8}$ 13.2 | $J_{5,6}$, $J_{6,7}$ 19–20, $J_{6,8}$ 10.2, $J_{3,6}$ 3.8 | $J_{5,7}$ 9.5, $J_{6,7}$ $J_{7,8}$ 19–20 | $J_{6,8}$ 10.2, $J_{7,8}$ 19 | |

**Table 1** (*Continued*)

| Compound | Substituents | $\delta^a$, ppm ($J$, Hz) | | | | | H |
|---|---|---|---|---|---|---|---|
| | | $F^3$ | $F^{5(1')}$ | $F^{6(2')}$ | $F^{7(3')}$ | $F^{8(4')}$ | |
| **3c** | $R^2$, $R^6 = NEt_2$ | −144.5 s | −125.7 t [−125.2] $J_{5,7}$, $J_{5,8}$ 11–13 | | −139.5 t [−139.2] $J_{5,7}$, $J_{7,8}$ 13–18 | −143.1 d.d [−143] $J_{5,8}$ 10.8, $J_{7,8}$ 17.7 | 1.14 (6H, t, 7.1, $2CH_3$), 1.24 (6H, t, 7.0, $2CH_3$), 3.34 (4H, t.q, 2.0, 7.0, $2CH_2$), 3.43 (4H, d.q, 1.9, 7.0, $2CH_2$) 4.30 (3H, d, 4.9, $CH_3$) |
| **2c** | $R^2$ = OMe | −145.5 m | −137.7 d.t, $J_{5,6}$ 19.8, $J_{5,7}J_{5,8}$ 11–12 | −143.8 d.d.t, $J_{5,6}$, $J_{6,7}$ 19–20, $J_{6,8}$ 12.1, $J_{3,6}$ 3.9 | −144.6 d.t, $J_{5,7}$ 11.3, $J_{6,7}$ $J_{7,8}$ 19–20 | −137.1 d.t, $J_{5,8}$, $J_{6,8}$ ~12, $J_{7,8}$ 19.7 | |
| **9** | $R^2$ = OMe $R^5$ = $NHBu^n$ | −149.2 m | | −141.6 d.m [−140.8] $J_{6,7}$ 16.0 | −148.0 d.t [−148.6] $J_{6,7}$, $J_{7,8}$ 16–20, $J_{3,7}$ 3.5 | −147.1 d.d [−146.7] $J_{6,8}$ 6.0, $J_{7,8}$ 19.8 | 0.94 (3H, t, 7.3, $CH_3$), 1.43 (2H, m, $CH_2$), 1.57–1.70 (2H, $CH_2$), 3.58 (2H, m, $NCH_2$), 4.22 (3H, d, 5.5, $OCH_3$), 9.75 (1H, br.s, NH) |
| **10** | $R^2$ = OMe | −145.0 m | −146.8 d.d [−147.3] $J_{5,6}$ 19.9, $J_{5,7}$ 6.5 | −148.7 d.t [−147.8] $J_{5,6}$, $J_{6,7}$ 16–20, $J_{3,6}$ 2.4 | −140.9 d.m [−141.6] $J_{6,7}$ 16.0 | | 0.96 (3H, t, 7.3, $CH_3$), 1.46 (2H, m, $CH_2$), 1.65 (2H, m, $CH_2$), 3.58 (2H, m, $NCH_2$), 4.19 (3H, d, 4.5, $OCH_3$), 9.65 (1H, br.s, NH) |
| **11** | $R^8$ = $NHBu^n$ $R^2$ = $NHBu^n$ $R^3$ = OMe | −140.3 d.d.d [−139.0] $J_{5,6}$ 19.4, $J_{5,7}$ 9.5, $J_{5,8}$ 12.5 | −144.7 d.t [−142.6] $J_{5,6}$, $J_{6,7}$ 19–20, $J_{6,8}$ 11.6 | −149.4 d.t [−148.2] $J_{5,7}$ 9.5, $J_{6,7}$ $J_{7,8}$ 19–20 | −138.8 d.t [−136.8] $J_{5,8}$, $J_{6,8}$ ~12, $J_{7,8}$ 19.8 | 0.95 (3H, t, 7.3, $CH_3$), 1.40 (2H, m, $CH_2$), 1.52–1.66 (2H, $CH_2$), 3.57 (2H, d.t, 6.4, 6.7, $NCH_2$,), 3.87 (3H, s, $OCH_3$), 5.45 (1H, br.s, NH) | |
| **12** | $R^{1'}$ = NHMe | | | −143.8 m | −148.8 d.d, $J_{3,4}$ 20.0, $J_{2,3}$16.6 | −149.2 d.d, $J_{3,4}$ 20.0, $J_{2,4}$ 5.0 | 10.0 (1H, br.s, NH), 8.21 (2H, m, 2CH), 7.74 (2H, m, 2CH), 3.26 (3H, d.d, 7.5, 4.0, $CH_3$) |
| **13** | $R^{2'}$ = NHMe | | −136.2 br.d.d, $J_{1,3}$ 20.9, $J_{1,4}$ 9.6 | | −150.0 t.m, $J_{3,4}$, $J_{1,3}$ ~21 | −140.9 d.d, $J_{1,4}$ 9.6, $J_{3,4}$ 17.2 | 4.58 (1H, br.s, NH), 3.26 (3H, m, $CH_3$) |

[a] The values of $\delta_F$ calculated with using the additive scheme are specified in square brackets.

compete with the electronic effect of a carbonyl group thus favoring a nucleophilic attack on the 5- and 8-positions.

### 2.2. X-ray data

The molecular structures of **3a** and **4a** were determined using single crystal X-ray diffraction. The suitable crystals were obtained by slow evaporation of a solutions of **3a** and **4a** in acetone at room temperature. The molecular frameworks of **3a** and **4a** (Fig. 1) are plane within the limits of ±0.012 and ±0.065 Å, accordingly. *n*-Butylamino groups are out of the ring plane with the torsion angle values: for **3a** $C^3C^2N^1C^9$ −11.0(5)°, $C^2N^1C^9C^{10}$ −73.3(4)°; for **4a** $C^3C^2N^1C^9$ 4(2)°, $C^2N^1C^9C^{10}$ 91(1)°, $C^7C^8N^2C^{13}$ 17(1)°, and $C^8N^2C^{13}C^{14}$ 68(1)°.

Because of a disordered structure of the **3a** crystal and low accuracy of the data for **4a** the detailed discussion of geometry is complicated, only closeness of bond lengths in the **4a** molecule to those for 3-anilino-2-chloro-1,4-naphthoquinone [6] being noted. The similar molecular packing was found for both the **3a** and **4a** crystals with the layers formed by the N–H···O and N–H···F interactions, the *n*-butyl groups being located between the layers. The parameters of these interactions are: for **3a** $N^1$–H···$O^1$/$F^2$ (H···O/F 2.20(3) Å, N–H···O/F 145(3)°); for **4a** $N^1$–H···$O^2$ (H···O 2.34 Å, N–H···O 144°), $N^1$–H···$F^2$ (H···F 2.44 Å, N–H···F 122°), $N^2$–H···$F^2$ (H···F 2.49 Å, N–H···F 144°).

### 2.3. $^1H$ and $^{19}F$ NMR spectroscopic data

The NMR spectroscopic data of **2a**–**11** are presented in Table 1.

In the $^{19}F$ NMR spectra the F-3 signals were easily identified due to their shape and location. Quinones **3a**–**6a**, **3b**–**6b** and **8** display the F-3 singlet between $\delta_F$ −164.4 to −160.1 ppm which is up-field shifted compared with $\delta_F$ −157.2 ppm observed for **2a** [1]. This is a natural consequence of the 6- and 8-alkylamine group conjugation with the 1-C=O group. The F-3 singlets of **2b** and **3c** are at $\delta_F$ −145 to −144 ppm. Unlike this, the F-3 signals of **2c**, **9**, and **10** are multiplets at $\delta_F$ −150 to −145 ppm due to the F-3–$CH_3$ coupling of $J_{FH}$ ~4–5 Hz. The assignment of F-(5–8) resonances was more complicated and based on the additivity of $\delta_F$ values using the spectra of **3a** and **4a**, the structures of which were proved by X-ray method, as benchmarks. For the increments ($\Delta\delta_F$) corresponding to the substitution of $NHCH_3$ group for F-1 and F-2 accepted were the changes of the $\delta_F$ values in going from anthraquinone **7** ($\delta_F$ for F-1,4 −138.1, F-2,3 −145.6 ppm [7]) to 1-methylamino-2,3,4-trifluoro- and 2-methylamino-1,3,4-trifluoroanthraquinones **12** and **13** [8]. The previously not interpreted $^{19}F$ NMR characteristics of **12** and **13** are listed in Table 1. In the $^{19}F$ NMR spectrum of **12** there are three signals of equal intensity at $\delta_F$ −143.8, −148.8 and −149.2 ppm assigned to F-2–F-4, accordingly. The first one is a multiplet, and two others are doublets of doublets. The multiplicity of the F-2 signal is due to the neighbourhood of an alkylamine group [9]. A doublet of doublets at −149.2 ppm with $^{ortho}J_{F,F}$ 20.0 Hz and $^{meta}J_{F,F}$ 5.0 Hz was attributed to F-4 and the signal at −148.8 ppm with two $^{ortho}J_{F,F}$ 20.0 and 16.6 Hz – to F-3. Antraquinone **13** also displays three peaks of equal intensity at $\delta_F$ −136.2, −140.9 and −150 ppm. A doublet of doublets at $\delta_F$ −140.9 ppm with $^{ortho}J_{F,F}$ 17.2 Hz and $^{para}J_{F,F}$ 9.6 Hz indicates an absence of the *ortho*-$NHCH_3$ group and, on this basis, was attributed to F-4. Unlike this, two other signals display unresolved F–$NHCH_3$ couplings. A broad doublet of doublets at $\delta_F$ −136.2 ppm with $^{meta}J_{F,F}$ 20.9 Hz and $^{para}J_{F,F}$ 9.6 Hz, and a triplet of multiplets at $\delta_F$ −150 ppm with $^{ortho}J_{F,F}$, $^{meta}J_{F,F}$ 17–21 Hz were assigned, accordingly, to F-1 and F-3. In the $^{19}F$ NMR spectrum of **13** of particular emphasis is the seeming abnormally large $^{meta}J_{F,F}$, which is close to typical $^{ortho}J_{F,F}$ values and exceeds considerably the $^{meta}J_{F,F}$ value for **12**. It is obvious that this distinction is caused by a

different location of two fluorines *meta* to each other relatively the $NHCH_3$ group: in **12** this is an *ortho*, *para* location, whereas in **13**— an *ortho*, *ortho* one. $^{meta}J_{F,F}$ is known to significantly depend on a nature and location of other substituents in an aromatic nucleus. Thus, in the $C_6F_5X$ series in going from X = $NH_2$ to X = $SO_2Cl$ the change of the $J_{F\text{-}2,F\text{-}4}$ and $J_{F\text{-}2,F\text{-}6}$ values makes up 15–17 Hz [10]. Taking into account an additivity of substituent increments [11], the expected distinctions of these values between **12** and **13** can be estimated starting from $J_{F\text{-}2,F\text{-}4}$ 2.5 Hz, $J_{F\text{-}2,F\text{-}6}$ −5.0 Hz, $J_{F\text{-}3,F\text{-}5}$ ~0.2 Hz, $J_{F\text{-}2,F\text{-}5}$ 9.1 Hz found for 1,2,3,4,5-pentafluorobenzophenone ([10]) and by using the changes of $J_{F,F}$ in going from $C_6F_6$ [12] to $C_6F_5COC_6H_5$ [10] and $C_6F_5NHCH_3$ [10,13] for increments corresponding an introduction of the second C=O and $NHCH_3$ groups, accordingly. Such an estimation leads to $J_{F\text{-}2,F\text{-}4}$ 3.8 Hz for **12** and $J_{F\text{-}1,F\text{-}3}$ 14.6 Hz, $J_{F\text{-}1,F\text{-}4}$ 10.7 Hz for **13**, which allows one to conclude that $^{meta}J_{F,F}$ calculated for **12** and $^{para}J_{F,F}$ calculated for its isomer **13** are close to the observed values and that the computationally predicted tendency of $^{meta}J_{F,F}$ variation between **12** and **13** as well as the $^{meta}J_{F,F}$ to $^{para}J_{F,F}$ ratio for **13** are consistent with the experimental data. The similar correlations are valid for other 1- and 2-X-1,3,4-trifluoroantraquinones (X = $NH_2$, $NMe_2$, $NEt_2$, etc.) [7,9].

The above regularities allowed to reliably assign the $^{19}F$ signals of **3a** and **4a**. In the $^{19}F$ NMR spectrum of **3a** the up-field signal at $\delta_F$ −153.9 ppm which is triplet-like due to the expected vicinity of $^{ortho}J_{F,F}$ and $^{meta}J_{F,F}$ ~18 Hz (see above) was attributed to F-7 and a doublet of doublets at $\delta_F$ −139.4 ppm with $^{ortho}J_{F,F}$ ~18 and $^{para}J_{F,F}$ ~8 Hz – to F-8. A doublet of multiplets at $\delta_F$ −136.5 with $^{meta}J_{F,F}$ ~18 Hz and an additional poorly resolved structure due to a coupling with protons of the NH$^n$Bu group (see above) was attributed to F-5. By similar reasons, three signals of equal intensity observed for **4a** at $\delta_F$ −148.4, −147.2 and −150.0 ppm were assigned, accordingly, to F-5, F-6 and F-7 since in each of the first and third peaks there is an only one doublet splitting with $^{ortho}J_{F,F}$ ~18 Hz, whereas in the second peak two such splittings were observed. The assignment of the F-7 signal is affirmed by the multiplicity of its doublet components.

With the use of the $\delta_F$ and $J_{F,F}$ values for **3a** and **4a** and the above chemical shift increments, firstly, the signals observed in the spectrum of **2a** were assigned more strictly than earlier [1] and, secondly, the spectra of other compounds obtained were interpreted. The appropriate experimental $^{19}F$ NMR characteristics and the $\delta_F$ values calculated by means of the additive scheme are given in Table 1. As seen in these data, the calculated $\delta_F$ values agree reasonably the experimental ones and, for each compound, correctly reproduce the correlation of these values. Besides, in the spectrum of **2a** the up-field position of the F-7 signal ($\delta_F$ −148.0 ppm) compared with the F-6 signal ($\delta_F$ −143.2 ppm) corresponds to the F-7 location *para* to the C=O function which is less electron-accepting due to its conjugation with the NH$^n$Bu group.

Additionally, the structure of **5a** agrees also with the obvious formation of this compound via *n*-butylaminodefluorination of both **3a** and **4a** (Scheme 1).

The NH*n*–Bu signals in the $^1H$ NMR spectra of **3a**–**6a** are characteristic of a substituent location. Thus, when the NH*n*–Bu group is in the quinone ring, the N–H proton resonance was found at $\delta_H$ 5.5–5.7 ppm (for **2a** – at $\delta_H$ 5.5 ppm [1]), in the α-position of the benzene ring – at $\delta_H$ 9.6–10.6 ppm (the down-field shift is caused by intramolecular hydrogen bonding with the neighboring C=O group; cf. [14]), in the β-position – at $\delta_H$ 4.4–4.6 ppm. In two last cases the given location corresponds to that mentioned above for **12** and **13**.

These data were used to assign the alkylamine group signals in other cases (Table 1). In the $^1H$ NMR spectra of **9** and **10** there are doublets of the OMe groups ($J_{HF}$ 4.5 and 5.5 Hz), signals of the NH*n*–Bu group as well as those of NH protons at $\delta_H$ 9.65 and 9.75 ppm, both being close to the respective values mentioned above for quinones **4a**–**6a**. In the spectrum of **11** the OMe signal was observed as a singlet and the location of the NH signal ($\delta_H$ 5.5 ppm) was practically the same as in the **2a**–**6a** spectra.

## 3. Conclusions

In summary, in the present article the regiochemistry of the single and multiple alkylaminodefluorination of 2-alkylamino- and 2-alkoxypentafluoro-1,4-naphthoquinone has been revealed, including the product ratio variation with the change of solvent and reaction conditions. This affords a predictive basis for nucleophilic functionalization of polyfluorinated 1,4-naphthoquinones. A series of new fluorinated poly(alkylamino)-1,4-naphthoquinones have been synthesized which are of expediency to be assayed as potential antitumor agents.

## 4. Experimental

### 4.1. Materials

Hexafluoro-1,4-naphthoquinone [15], 2-*n*-butylamino- and 2-methoxypentafluoro-1,4-naphthoquinones [1] were prepared according to the literature protocols. Diethylamine, triethylamine and DMSO were distilled in vacuo (0.03 mmHg) to the molecular sieves 4 Å. *n*-Butylamine (Acros Organics, 99.5%) and ethylamine hydrobromide (pure) were used without further purification. 1,4-Dioxane and toluene were distilled and stored over potassium hydroxide. TLC plates (Sorbfil) were used for products purification.

### 4.2. General

$^1H$ and $^{19}F$ NMR spectra were recorded on NMR spectrometers Bruker AC-200 (200.13 MHz and 188.28 MHz for $^1H$ and $^{19}F$ correspondingly) and AV-300 (300.13 MHz and 282.36 MHz for $^1H$ and $^{19}F$ correspondingly) using $CDCl_3$ ($\delta_H$ 7.24 ppm) and $CCl_3F$ as internal standards. The melting-points were determined for the samples obtained by crystallization from $CHCl_3$.

The precise molecular weights were determined by high-resolution mass spectrometry on a DFS instrument. The crystallographic data were collected at 23 °C using a Bruker P4 diffractometer (Mo Kα radiation, $2\theta/\omega$-scan). The crystallographic data for compound **3a**: $C_{18}H_{20}F_4N_2O_2$, $M$ = 372.36, the monoclinic space group $C2/c$, $a$ = 24.822(14), $b$ = 4.699(3), $c$ = 15.171(8) Å, $\beta$ = 99.83(3)°, $V$ = 1743.6(17) Å$^3$, $Z$ = 4, $d_{calc}$ = 1.419 g cm$^{-3}$, $\mu$ = 0.122 mm$^{-1}$, 1629 independent reflections with $2\theta < 51°$, 880 observed reflections with $I > 2\sigma$. The absorption correction was applied by an integration method on crystal faces (the transmission 0.98–1.00). The crystallographic data for compound **4a**: $C_{18}H_{20}F_4N_2O_2$, $M$ = 372.36, the orthorhombic space group $Pna2_1$, $a$ = 15.446(4), $b$ = 4.6485(14), $c$ = 24.052(7) Å, $V$ = 1726.9(8) Å$^3$, $Z$ = 4, $d_{calc}$ = 1.432 g cm$^{-3}$, $\mu$ = 0.123 mm$^{-1}$, 1579 independent reflections with $2\theta < 50°$, 778 observed reflections with $I > 2\sigma$. The absorption correction was not applied. The structures were solved by a direct method using the programs SHELXS-97 (**3a**) and SIR2002 (**4a**) and refined at first in isotropical, and then in anisotropical approximation using the program SHELXL-97.

The hydrogens of **3a** were located from the difference density map and were refined isotropically, all other hydrogen atoms (and also in **4a**) were placed in the geometrically calculated positions and refined in riding model. Let us note, that in a crystal of **3a** the molecules are disordered (located at the centres of symmetry), therefore in the O-1 and O-2 positions the oxygen and fluorine atoms were placed with weight 0.5 and identical $x, y, x, U_{ij}$. The final

values of *R*-factors: for **3a** – $R = 0.0483$ (observed), $wR_2 = 0.1698$ (all), $S = 1.037$; for **4a** – $R = 0.0709$ (observed), $wR_2 = 0.1979$ (all), $S = 0.939$.

Crystallographic data (excluding structural factors) for **3a** and **4a** presented in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 733537 and 733536. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

### 4.3. Synthetic procedures

#### 4.3.1. 2,6-Bis-n-butylaminotetrafluoro-1,4-naphthoquinone (3a), 2,8-bis-n-butylaminotetrafluoro-1,4-naphthoquinone (4a) 2,6,8-tris-n-butylaminotrifluoro-1,4-naphthoquinone (5a) and 2,5,8-tris-n-butylaminotrifluoro-1,4-naphthoquinone (6a)

*Method A*: A mixture of **1** (0.200 g, 0.75 mmol), *n*-butylamine (0.197 g, 2.69 mmol) and dioxane (2 mL) were stirred at room temperature for 48 h. After the addition of water (~5 mL) the precipitate was centrifugated off, washed with water (2× 3 mL) and air-dried. Separation by TLC (chloroform–hexane, 3:1) gave **3a** (0.085 g, 30%), red crystals, m.p. 179–183 °C; HRMS Calc. for $C_{18}H_{20}F_4N_2O_2$: 372.1455. Found: 372.1433. EIMS (probe) 70 eV, *m/z* (rel. int.): 372 $[M]^+$ (50), 329 $[M-Pr]^+$ (100); **4a** (0.033 g, 12%), red crystals, m.p. 71–74 °C; HRMS Calc. for $C_{18}H_{20}F_4N_2O_2$: 372.1455. Found: 372.1457. EIMS (probe) 70 eV, *m/z* (rel. int.): 372 $[M]^+$ (29), 329 $[M-Pr]^+$ (20), 315 $[M-Bu]^+$ (100); **5a** (0.045 g, 14%), reddish-brown crystals, m.p. 110–114 °C; HRMS Calc. for $C_{22}H_{30}F_3N_3O_2$: 425.2285. Found: 425.2289. EIMS (probe) 70 eV, *m/z* (rel. int.): 425 $[M]^+$ (18), 368 $[M-Bu]^+$ (100).

*Method B*: A mixture of **1** (0.050 g, 0.19 mmol), *n*-butylamine (0.068 g, 0.93 mmol) and toluene (1.5 mL) were stirred at room temperature for 72 h. Reaction mixture was washed with water (2× 3 mL), toluene was evaporated *in vacuo* (0.03 mmHg). Separation by TLC (chloroform–hexane, 3:1) gave **3a** (0.008 g, 11%), **4a** (0.030 g, 43%), **5a** (0.007 Γ, 9%), and **6a** (0.011 g, 14%). Quinone **6a**: blue crystals, m.p. 71–73 °C; HRMS Calc. for $C_{22}H_{30}F_3N_3O_2$: 425.2285. Found: 425.2291. EIMS (probe) 70 eV, *m/z* (rel. int.): 425 $[M]^+$ (100), 382 $[M-Pr]^+$ (87), 368 $[M-Bu]^+$ (98).

#### 4.3.2. 2,5,6,8-Tetra-n-butylaminodifluoro-1,4-naphthoquinone (8)

A mixture of **3a** (0.012 g, 0.03 mmol), *n*-butylamine (0.008 g, 0.11 mmol) and dioxane (0.7 mL) were stirred at room temperature for 18 days. After the addition of water (~3 mL) the precipitate formed was centrifugated off, washed with water (2× 2 mL) and air-dried. Purification by TLC ($CHCl_3$) gave quinone **8** (0.0057 g, 38%), purple crystals m.p. 44–45 °C; HRMS Calc. for $C_{26}H_{40}F_2N_4O_2$: 478.3114. Found: 478.3117. EIMS (probe) 70 eV, *m/z* (rel. int.): 478 $[M]^+$ (18), 421 $[M-Bu]^+$ (100).

#### 4.3.3. 2-n-Butylamino-6-ethylaminotetrafluoro-1,4-naphthoquinone (3b), 2-n-butylamino-8-ethylaminotetrafluoro-1,4-naphthoquinone (4b) 2-n-butylamino-6,8-bis-ethylaminotrifluoro-1,4-naphthoquinone (5b) and 2-n-butylamino-5,8-bis-ethylaminotrifluoro-1,4-naphthoquinone (6b)

*Method A*: A mixture of **2a** (0.127 g, 0.40 mmol), ethylamine hydrobromide (0.055 g, 0.44 mmol), potassium carbonate (0.219 g, 1.59 mmol) and DMSO (2.5 mL) were stirred at room temperature for 3 h. After the addition of water (~8 mL) the precipitate formed was centrifugated off, washed with water (2× 3 mL) and air-dried. Separation by TLC (chloroform–hexane, 3:1) gave **3b** (0.137 g, 63%), red crystals, m.p. 187–191 °C; HRMS Calc. for $C_{16}H_{16}F_4N_2O_2$: 344.1148. Found: 344.1142; EIMS (probe) 70 eV, *m/z* (rel. int.): 344 $[M]^+$ (32), 301 $[M-Pr]^+$ (100); **5b** (0.025 g, 17%), red crystals, m.p. 117–120 °C; HRMS Calc. for $C_{18}H_{22}F_3N_3O_2$: 369.1664. Found: 369.1671; EIMS (probe) 70 eV, *m/z* (rel. int.): 369 $[M]^+$ (43), 340 $[M-Et]^+$ (100), 312 $[M-Bu]^+$ (63).

*Method B*: A mixture of **2a** (0.101 g, 0.31 mmol), ethylamine hydrobromide (0.043 g, 0.34 mmol), potassium carbonate (0.173 g, 1.25 mmol) and toluene (2 mL) were stirred at room temperature for 72 h. The reaction mixture was worked up as described for quinones **3a**–**6a** (*Method B*) to afford **4b** (0.065 g, 60%), red crystals, m.p. 99–103 °C; HRMS Calc. for $C_{16}H_{16}F_4N_2O_2$: 344.1142. Found: 344.1142; EIMS (probe) 70 eV, *m/z* (rel. int.): 344 $[M]^+$ (45), 315 $[M-Et]^+$ (100), 301 $[M-Pr]^+$ (28), 287 $[M-Bu]^+$ (38); **6b**, (0.008 g, 7%), blue crystals, m.p. 91–95 °C; HRMS Calc. for $C_{18}H_{22}F_3N_3O_2$: 369.1664. Found: 369.1656; EIMS (probe) 70 eV, *m/z* (rel. int.): 369 $[M]^+$ (100), 340 $[M-Et]^+$ (86), 312 $[M-Bu]^+$ (37).

*Method C*: A mixture of ethylamine hydrobromide (0.029 g, 0.24 mmol), potassium hydroxide (0.026 g, 0.47 mmol) and dioxane (1.5 mL) were stirred at room temperature for 30 min. Mother liquor separated from the solid by centrifugation was added to quinone **2a** (0.050 g, 0.19 mmol) and the mixture was stirred at room temperature for 24 h. Then ethylamine hydrobromide (0.009 g, 0.07 mmol) and potassium carbonate (0.022 g, 0.16 mmol) were added. After 10 h reaction the mixture was worked up as described for quinones **3b, 5b** (*Method A*) to afford **3b** (0.032 g, 59%), **4b** (0.011 g, 21%), and **5b** (0.003 g, 5%).

#### 4.3.4. 2,6-Bis-diethylaminotetrafluoro-1,4-naphthoquinone (3c)

A mixture of **1** (0.051 g, 0.19 mmol), diethylamine (0.041 g, 0.56 mmol) and DMSO (1 mL) was stirred at room temperature for 5 h. After the addition of water (~5 mL) the precipitate formed was centrifugated off, crystallized from chloroform and dried *in vacuo* (0.03 mmHg) to give **3c** (0.030 g, 43%), red crystals, m.p. 80–83 °C; HRMS Calc. for $C_{18}H_{20}F_4N_2O_2$: 372.1455. Found: 372.1453. EIMS (probe) 70 eV, *m/z* (rel. int.): 372 $[M]^+$ (98), 357 $[M-Me]^+$ (35), 343 $[M-Et]^+$ (100).

#### 4.3.5. 5-n-Butylamino-3-methoxytetrafluoro-1,4-naphthoquinone (9), 8-n-butylamino-3-methoxy-tetra-fluoro-1,4-naphthoquinone (10) and 2-n-butylamino-3-methoxy-5,6,7,8-tetrafluoro-1,4-naphtho-quinone (11)

*Method A*: A mixture of **2c** (0.020 g, 0.07 mmol), *n*-butylamine (0.006 g, 0.08 mmol) and DMSO (1 mL) was stirred at room temperature for 24 h. After the addition of water (~5 mL) the precipitate formed was centrifugated off, washed with water (3× 3 mL) and dried *in vacuo* (0.04 mmHg). Separation by TLC (chloroform–hexane, 1:1) afforded **10** (0.0005 g, 2%) and **11** (0.0084 g, 35%). Quinone **11**: purple crystals, m.p. 90–95 °C; HRMS Calc. for $C_{15}H_{13}F_4NO_3$: 331.0826. Found: 331.0835. EIMS (probe) 70 eV, *m/z* (rel. int.): 331 $[M]^+$ (61), 316 $[M-Me]^+$ (40), 288 $[M-Pr]^+$ (100).

*Method B*: A mixture of **2c** (0.020 g, 0.07 mmol), *n*-butylamine (0.006 g, 0.08 mmol) and toluene (1 mL) were stirred at room temperature for 2 h. After the addition of water (~5 mL) the toluene layer was separated and the solvent was distilled off *in vacuo* (0.04 mmHg). The residue was warked up as described for **10** and **11** to give **9** (0.005 g, 21%), crimson crystals, m.p. 83–86 °C; HRMS Calc. for $C_{15}H_{13}F_4NO_3$: 331.0826. Found: 331.0822; **10** (0.003 g, 11%), dark-red crystals, m.p. 104–107 °C; HRMS Calc. for $C_{15}H_{13}F_4NO_3$: 331.0826. Found: 331.0822; EIMS (probe) 70 eV, *m/z* (rel. int.): 331 $[M]^+$ (74), 316 $[M-Me]^+$ (28), 288 $[M-Pr]^+$ (100); **11** (0.004 g, 15%).

#### 4.3.6. Reactions of quinones (3a)–(6a) with n-butylamine

The reagent amounts and solvents were as follows: **3a** or **4a** (0.012 g, 0.03 mmol), *n*-butylamine (0.005 g, 0.07 mmol), dioxane (0.7 mL); **5a** (0.017 g, 0.04 mmol), *n*-butylamine (0.004 g, 0.06 mmol), DMSO (0.7 mL); **6a** (0.015 g, 0.03 mmol), *n*-butylamine (0.003 g, 0.05 mmol), DMSO (0.7 mL). A reaction mixture was kept at room temperature, the reaction progress was monitored by

$^{19}F$ NMR spectroscopy. The results are presented in Scheme 1 (reactions **b**, **c** and **d**). Additionally *n*-butylamine (0.008 g, 0.1 mmol) was added to the reaction **c** after 54 h.

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