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Modification of the amino group in polyfluorinated arylenediamines by reactions with aldehydes and quinones

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Abstract: *Reaction of low-reactive polyfluoroaromatic diamines with benzaldehyde and hexafluoronaphthoquinone provide selective preparation of functionalized arylamines. Mono-N-benzylidene-arylenediamines were prepared in 30-35 % yield, polyfluoroarylaminonaphthoquinones in 50-55 % yield. The products were characterized by IR, ^{1}H and ^{19}F NMR spectroscopy, mass-spectrometry. Spectral characteristics of the compounds in the UV-visible range were studied and prospects of their usage as signal components of supramolecular sensors were evaluated*.

Keywords: *Polufluorinated arylenediamines, mono-N-benzylidene-polyfluoroarylenediamines, polyfluoroarylaminonaphthoquinones, chromophores.*

Polyhalogenaromatic mono- and diamines are widely used as structural blocks in the synthesis of high-tech materials, pharmaceuticals and agrochemicals [1]. Organic co-crystals seems to be promising objects for high technologies, materials possessing NLO, photochromic, magnetic and other useful properties are developed on their basis [2]. For example, the effect of reversible rearrangement of the supramolecular structure (solid-state transition) under the action of an external force can be used in thermo- and photochromic molecular sensors and switches [3]. We proposed and studied in detail a group of new objects for crystal engineering – associates of polyhalogenaromatic mono- and diamines with 18-crown-6, which are supramolecular hydrogen-bonded assembles [4,5]. For a number of substituted polyfluoroarylamines, significant changes in the fluorescence characteristics, both in intensity and wavelength, were observed in going from the free amine to the associate with 18-crown-6 [5]. These effects open the possibility to use the supramolecular assembles in developing solid-phase chemo-specific supramolecular indicators and sensors, where two simple organic compounds connected by the hydrogen bond performe their receptor and signal functions. Destruction of the intermolecular bond due to the capture of an analyte by the macrocycle receptor is accompanied by a change in the detectable characteristics of the signal group. To increase the sensitivity of the sensor, it is important to search for signal amine components that have effective chromo- or fluorophore properties.

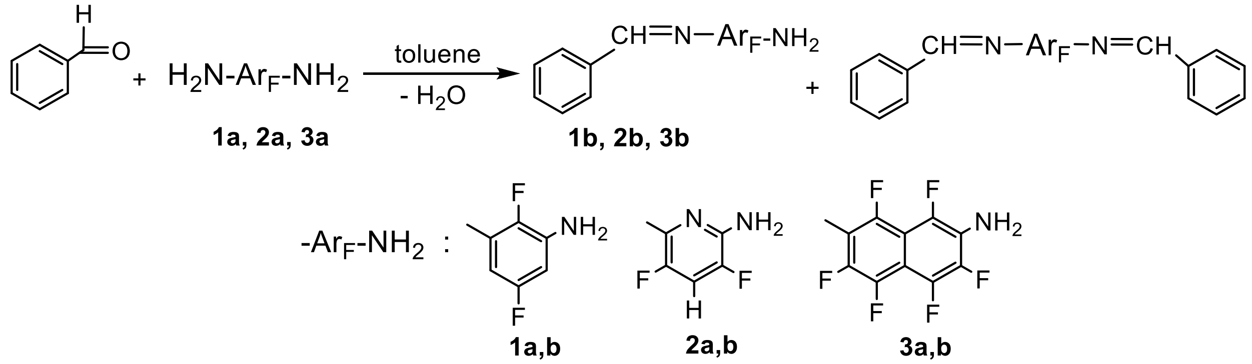
A rational approach to the synthesis of functionalized polyhalogenarylamines is the modification of one of the two amino groups in arylenediamines. Polyhalogenated arylenediamines are available compounds as there is a convenient and efficient method for their synthesis – mono- and bis-aminodefluorination of polyhalogenarenes of the benzene, naphthalene and pyridine series with anhydrous ammonia used as a reagent and a solvent in the same time [6-8]. The most obvious ways of functionalizing of the arylenediamines at the amino group to form chromo- and fluorophore systems, including conjugated ones, are their reactions with aldehydes and quinones. Condensation of amines with aldehydes to form aldimines (N-arylideneanilines) has a large potential due to the possibility of a wide variation in the structure of aromatic substituents at the polar double bond C=N, which gives a tool to control their properties. Aromatic aldimines, including those containing polyfluorinated fragments, are known as objects for supramolecular systems, liquid crystal media, molecular devices, etc. [9]. Effective quinonoid type chromo- and fluorophores can be attached to the amino group by nucleophilic substitution of a hydrogen or a halogen atom [10-14]. In addition to the stated objective, the combination of the amino group, polyfluoroarene and quinone fragments in the molecule is of interest for the study of its bioactivity [10-12]. The goal of this work is to study a possibility of the synthesis of functionalized polyfluoroarylamines by reactions of arylenediamines with aldehydes and quinones.

Results and discussion

A priori there are two problems that get in the way of the preparative use of the above reactions: low reactivity of the amino group in polyfluorinated substrates and the necessity to limit a conversion to a modification of only one of the two amino groups. It is known that the exhaustive fluorination of the benzene ring reduces the reactivity of phenylenediamines to acylating agents by a factor of 10^5 as a result of the total acceptor effect of electronegative fluorine atoms [15]. For this reason pentafluoroaniline does not react with benzaldehyde under conditions typical for non-fluorinated arylamines. To synthesize imines, pentafluoroaniline is preliminary treated with thionyl chloride to form N-sulfinylpentafluoroaniline, which then gives the desired products in high yields by the reaction with aromatic aldehydes [16]. However, the applicability of this approach for the modification of one of the two amino groups in arylenediamines is not obvious. In principle, the reaction of pentafluoroaniline with aldehydes can be carried out by prolonged refluxing in anhydrous solvents with water-removing agents (in the presence of $MgSO_4$ in CH_2Cl_2 [17], molecular sieves in toluene [18]), or by heating at 160 °C without solvent as well. [19]. Preparation of N,N'-bis-benzylidene derivatives of tetrafluoro-*meta*-phenylenediamine was also reported [20]. Examples of the arylenediamine modification when only one of the amino groups remains unchanged have not been described in literature.

To study the reactions with benzaldehyde as a model reagent, polyfluoroarylenediamines with three basic types of the aromatic framework were selected (Scheme 1): 2,5-difluoro-1,3-phenylenediamine (**1a**), 2,6-diamino-3,5-difluoropyridine (**2a**), and 2,7-diaminohexafluoronaphthalene (**3a**). Anhydrous toluene was used as a solvent and three types of water-removing agents, i.e. P_2O_5, $MgSO_4$, and activated molecular sieves. The conversion was monitored by ^{19}F NMR spectroscopy.

Activity of polyfluorinated substrates against benzaldehyde, as expected, was low: after heating at 110 ° C for 24 hours in the presence of molecular sieves, from 50 % (**1a**) to 70 % (**2a** and **3a**) of the unreacted diamine remain in the reaction mass. P_2O_5 and $MgS0_4$ accelerate the condensation but cause appreciable resinification of the reaction mixture. The most effective and gentle way for removing water is azeotropic distillation with the solvent; these conditions allow the full conversion of benzaldehyde to be achieved in ~10 hours. In all the cases, as mono-N-benzylidene-arylenediamine (compounds **1b**, **2b**, **3b**) accumulates in the reaction mixture, the free amino group in the product undergoes a modification in parallel with the amino group in the starting diamine. With an increase of the reaction time, the ratio of bis- to mono-modified products grows, regardless of the way of the water removing. Varying the temperature in the range of 80-110 ° C also has no significant effect on the reaction selectivity.

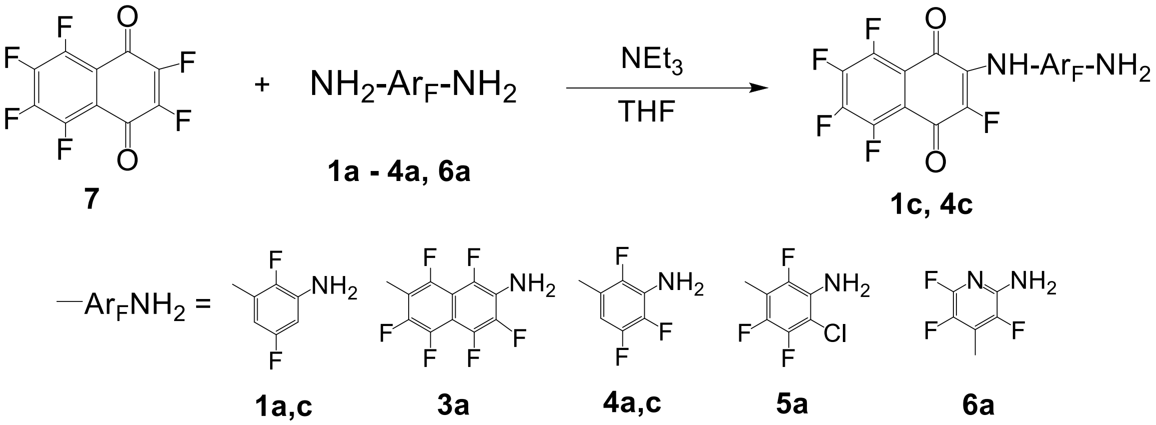


Scheme 1. Reaction of polyfluoroarylenediamines with benzaldehyde.

Based on the optimization results, the following mode was selected for the synthesis of mono-N-benzylidene-arylenediamines: use of 20% excess of the substrate relative to the aldehyde, removing the water formed during the condensation as an azeotrope with toluene (solvent), termination of the reaction at 60-70% conversion. After this, unreacted benzaldehyde was distilled off with toluene under reduced pressure, and a mixture of mono- and bis-imines with the starting diamine was obtained (the approximate molar ratio is 5: 1: 5 respectively, according to ^{19}F NMR and GC-MS). Due to the significant difference in polarity of these compounds, the target mono-N-benzylidene-arylenediamine can be isolated by chromatography using a mixture of anhydrous eluents hexane + diethyl ether with a polarity gradient 12÷5 : 1 respectively. The first fractions of eluate contain a trace amount of benzaldehyde and bis-imine, intermediate – a mixture of bis- and monoimines, then a practically pure monoimine is isolated, the most polar diamine is eluated with diethyl ether. In this manner, mono-N-benzylidene-arylenediamines **1b**, **2b**, **3b** (Scheme 1) were obtained in a yield of ~30% (see Experimental). The compounds were synthesized for the first time and characterized with a set of spectral methods. It should be noted that the imines obtained are sensitive to air moisture and residual moisture in solvents. When studying the optical characteristics of the substances in the UV-visible range (solutions in acetonitrile, $c = 10^{-4}$ M), low-intensity absorption bands of the corresponding diamines were recorded in the spectra, their intensity being increased upon solution standing. This is due, most likely, to hydrolysis of the imine function. For this reason, the spectral characteristics of mono-N-benzylidene-arylenediamines **1b**, **2b**, **3b** were obtained by subtracting the spectra of the starting diamines from the spectra of the experimental samples. The exact ratio of the compounds in solutions could not be determined in all cases, therefore the optical densities are given as an intensity indicator for the absorption bands in the UV spectra of imines **1b** and **3b**. It follows from the data obtained that mono-N-benzylidene-arylenediamines **1b**, **2b**, **3b** have absorption bands in the longer wavelength region than the starting diamines (the difference between λ_{max} is 40-80 nm, spectral characteristics are presented in Experimental), which is the consequence of increasing the length of the conjugated system. Thus, it was shown by the model reaction, that the proposed method of modification of polyfluorinated arylenediamines can be used to synthesize the amine-containing chromophores in the visible range.

Reaction of non-fluorinated arylamines with benzoquinone occurs in methanol at room temperature and result in the formation of 2,5-bis-amino derivatives in high yields [10]. Substitution of halogens in polyhalogenated (Hal = Cl, F) benzo- and naphthoquinones for various uncharged nucleophiles – amines, alcohols, thioalcohols – proceeds even faster [11, 13]. We used polyfluorinated arylenediamines with different framework and the number of fluorine atoms as nucleophiles: 2,5-difluoro-1,3-

phenylenediamine (**1a**), 2,7-diaminohexafluoronaphthalene (**3a**), 2,4,5-trifluoro-1,3-phenylenediamine (**4a**), 4-chloro-trifluoro-1,3-phenylenediamine (**5a**), and 2,4-diaminotrifluoropyridine (**6a**). It was found that *para*-benzoquinone does not react with these diamines even under refluxing in toluene for 72 hours; the starting compounds were returned. Hexafluoro-1,4-naphthoquinone (**7**) also gives no substitution products under the action of the exhaustively halogenated diamines **3a**, **5a**, **6a** in tetrahydrofuran under heating. The addition of triethylamine to bind HF does not affect the result. Within a day, naphthoquinone **7** is completely destroyed under these conditions while diamines are unchanged. In contrast, the more nucleophilic compounds **1a** and **4a** with one of the *ortho*-positions to the amino group not occupied by a fluorine atom, react with naphthoquinone **7** in the presence of NEt_3 in tetrahydrofuran at 45-50 °C in an argon atmosphere to form polyfluoroarylaminonaphthoquinones **1c** and **4c** (Scheme 2). The highest yield of the products is observed when a reaction time is 20 h. It should be noted that this conversion, in contrast to the reaction with benzaldehyde, occurs selectively at one amino group; polyfluorinated bis-quinone derivatives of arylenediamines are not detected. The isomer selectivity in the reaction of non-symmetric phenylenediamine **4a** is also high, only the amino group having a hydrogen atom at the *ortho*-position undergoes modification. Compounds **1c** and **4c**, synthesized for the first time, were isolated by chromatography in yields of 50-60% and were characterized by spectral methods.



Scheme 2. Reaction of polyfluoroarylenediamines with hexafluoronaphthoquinone.

Compounds **1c** and **4c** comprising a pentafluoronaphthoquinone fragment have a burgundy color, the color of their concentrated tetrahydrofuran solutions turns into dark orange when diluted by ~3 orders of magnitude. The absorption spectra of these compounds in the UV-visible range differ from those of diamines **1a**, **4a**, and quinone **7**. In the spectra of polyfluoraminonaphthoquinones **1c** and **4c**, the new absorption maximum at 455-460 nm appears, which is located in the longer wavelength region in comparison to the characteristics of the starting compounds (the difference between λ_{max} is 110 nm). This indicates the interaction of a lone electron pair on the nitrogen atom with π-systems of the quinone and benzene fragments. Thus, the reaction of partially fluorinated arylenediamines with naphthoquinone **7** is an acceptable method for the synthesis of bipolar chromophores with a long conjugation chain.

The results obtained show that the reactions with aldehydes and polyfluoroquinones can be used to modify one of the amino groups in the low reactive polyfluoroarylenediamines to form chromo- and fluorophore systems. The yields of the target products in the reactions with benzaldehyde are 30-35%, and in the reactions of hexafluoronaphthoquinone with polyfluorophenylenediamines that contain no fluorine atom at the *ortho*-position to the amino group – 50-55%. Polyfluorinated arylaminonaphthoquinones such as **1c** and **4c** appear to be promising signal components for supramolecular sensors, since lone electron pairs on the nitrogen atoms of amino groups ensure the formation of a bipolar chromophore with an extended π-system and, accordingly, the transfer of electronic effects when forming/breaking the associates with a macrocyclic receptor. The possibility of using mono-N-benzylidene-arylenediamines **1b**, **2b**, and **3b** to make supramolecular objects is limited by their high sensitivity to moisture. Nevertheless, this method is in principle productive for the preparation of conjugated chromo- and fluorophore polyfluoroarylamines. Development of this synthetic approach requires searching for such pairs of reagents (diamines and aldehydes) which will ensure the formation of relatively stable aldimines.

Experimental

^{1}H and ^{19}F NMR spectra were recorded on a NMR spectrometer Bruker AV-300 (300.13 and 282.36 MHz, respectively) using residual proton signals of the deuterated solvent relative to TMS (δ = 0 ppm) and C_6F_6 (δ = 0 ppm) as internal standard. Fourier transform infrared (FTIR) spectra were measured on a Bruker Tensor 27 instrument for KBr pellets. UV-vis spectra were recorded on a Varian Cary 5000 spectrometer for solutions of samples in acetonitrile. The precise molecular weights of ions were determined by high resolution mass spectrometry on a Thermo Scientific DFS instrument, EI, 70 eV. GC-MS analysis was performed using a Hewlett Packard G1081A equipment comprising an HP 5890 Series II gas chromatograph and an HP5971 mass selective detector; electron ionization energy of 70 eV; HP5 column (5% of biphenyl and 95% of dimethylsiloxane), 30 m×0.25 mm×0.25 μm; with helium as carrier gas, flow rate 1 mL min^{-1}; column temperature programming from 50 ºC (2 min) at an increment of 10 ºC min^{-1} to 280 ºC (5 min); injector temperature 280 ºC; ion source temperature 173 ºC; data acquisition rate 1.2 scan s^{-1} in the mass range 30 to 650 amu.

Toluene was dried by boiling over $CaCl_2$ followed by distillation. Tetrahydrofuran was purified by boiling over benzophenone ketyl sodium salt followed by distillation in argon atmosphere. Commercial benzaldehyde and triethylamine were purified using distillation. HPLC grade acetonitrile was dried over CaH_2 and distilled before UV spectra recording. 2,6-Diamino-3,5-difluoropyridine (**2a**), 2,4,5-trifluoro-1,3-phenylenediamine (**4a**), and 2,4-diamino-3,5,6-trifluoropyridine (**6a**) were prepared as described in [6], 2,7-diaminohexafluoronaphthalene (**3a**) – as described in [7], 2,5-difluoro-1,3-phenylenediamine (**1a**) and 2,4,5-trifluoro-6-chloro-1,3-phenylenediamine (**5a**) – as described in [8], hexafluoro-1,4-naphthoquinone (**7**) – as described in [21]; melting points and NMR spectra correspond to the literature data. UV-visible spectra, λ_{max}/nm (logε): **1a** 245 (4.0), 279 (3.0); **2a** 227 (3.8), 319 (3.9); **3a** 219 (4.2), 252 (4.9), 290 (3.6); **4a** 205 (4.3), 230 (3.7), 283 (2.8). UV-visible spectra of compound **7** in chloroform, λ_{max}/nm (logε): 246 (3.9), 260 (4.2), 268 (4.2), 343 (3.3) [22].

Reaction of polyfluorinated arylenediamines with benzaldehyde (a typical procedure).

Polyfluorinated arylenediamine (2.4 mmol) was dissolved in toluene (8-10 ml), and benzaldehyde (0.21 g, 2 mmol) was added with stirring. The mixture was stirred at 120 °C for 4-6 h, water being distilled off as azeotrope with solvent. The reaction was terminated after reaching the conversion of arylenediamine 55-60% (according to ^{19}F NMR). Toluene and unreacted benzaldehyde were distilled off under reduced pressure.

The product was isolated by column chromatography on SiO_2 using a mixture of anhydrous eluents of variable polarity (hexane–diethyl ether = 12÷5 : 1).

***N^1*-benzylidene-2,5-difluoro-1,3-phenylenediamine** (**1b**) was synthesized from diamine **1a** (0.35 g), yield 0.15 g (32%). The yellow oil. UV-vis, λ_{max}/nm (D): 261 (0.47), 315 (0.21). ^{1}H NMR, chloroform-d, δ/ppm, J/Hz: 5.06 (br.s, 2H, NH_2), 6.28 (ddd, 1H, H4, J_{FH} = 10, J_{FH} = 6, J_{HH} = 3), 6.52 (ddd, 1H, H6, J_{FH} = 9, J_{FH} = 6, J_{HH} = 3), 7.48-7.57 (m, 3H, H3', H5', H4'), 8.0 (m, 2H, H2', H6'), 8.57 (br.s, 1H, C=H). ^{19}F NMR, chloroform-d, δ/ppm, J/Hz: 8.5 (ddd, 1F, F2, J_{FF} = 13, J_{FH} = 6, J_{FH} = 6), 44.5 (ddd, 1F, F5, J_{FF} = 13, J_{FH} = 10, J_{FH} = 9). Found: *m/z* 232.0816 $[M]^+$. $C_{13}H_{10}N_2F_2$. Calculated: M = 232.0812.

***N^2*-benzylidene-3,5-difluoro-2,6-diaminipyridine** (**2b**) was synthesized from diamine **2a** (0.35 g), yield 0.17 g (37%). Viscous orange mass, vitrifies when standing. UV-vis, λ_{max}/nm (logε): 268 (4.1), 358 (3.9). ^{1}H NMR, chloroform-d, δ/ppm, J/Hz: 4.49 (br.s, 2H, NH_2), 7.21 (dd, 1H, H4, J_{FH} ~9), 7.45-7.51 (m, 3H, H3', H5', H4'), 7.97 (m, 2H, H2', H6'), 9.08 (br.s, 1H, C=H). ^{19}F NMR, chloroform-d, δ/ppm, J/Hz: 22.5, 24.9 (both d, in 1F, F3 and F5, J_{FH} ~9). Found: *m/z* 233.0771 $[M]^+$. $C_{12}H_9N_3F_2$. Calculated: M = 233.0764.

***N^2*-benzylidene-hexafluoro-2,7-diaminonaphthalene** (**3b**) was synthesized from diamine **3a** (0.64 g), yield 0.2 g (29%). Fusible yellow-orange powder. UV-vis, λ_{max}/nm (D): 266 (0.43), 328 (0.13). ^{1}H NMR, chloroform-d, δ/ppm, J/Hz: 4.14 (br.s, 2H, NH_2), 7.47-7.55 (m, 3H, H3', H5', H4'), 7.95 (m, 2H, H2', H6'), 8.65 (br.s, 1H, C=H). ^{19}F NMR, chloroform-d, δ/ppm, J/Hz: 8.9 (m, 1F, F6), 10.4 (m, 1F, F3), 11.4 (m, 2F, F4, F5), 16.5 (dm, 1F, F8, J_{FF} = 66), 23.4 (dm, 1F, F1, J_{FF} = 66). Found: *m/z* 354.0589 $[M]^+$. $C_{17}H_8N_2F_6$. Calculated: M = 354.0592.

Reaction of polyfluorinated arylenediamines with hexafluoronaphthoquinone 7 (a typical procedure). Arylenediamine (1 mmol) was dissolved in THF (5-7 ml) and quinone 7 (0.27 g, 1 mmol) was added with stirring, after dissolving of which triethylamine (0.10 g, 1 mmol) was added dropwise. The mixture obtained was stirred at 45-50 °C in an argon atmosphere for 20 h. On completion, water (20 ml) was added and products were extracted with diethyl ether (3x20 ml); the combined ether extract was washed with water and dried over $MgSO_4$. Solvent was evaporated under reduced pressure. The product was isolated by column chromatography on SiO_2, eluent hexane–diethyl ether (5:1).

2-(3'-amino-2',5'-difluorophenylamino)-pentafluoro-1,4-dihydronaphthalene-1,4-dione (**1c**) was synthesized from diamine **1a** (0.14 g), yield 0.22 g (57%). Mp 198-201 °C. UV-vis, λ_{max}/nm (logε): 228 (4.4), 270 (4.3), 333 (3.6), 453 (3.5). FTIR, ν/cm^{-1}: 3462, 3371, 3232 (N-H), 3086 (C_{ar}-H), 1682 (C=O). ^{1}H NMR, acetone-d$_6$, δ/ppm, J/Hz: 5.12 (br.s, 2H, NH_2), 6.32 (ddd, 1H, H4', J_{FH} = 9, J_{FH} = 6, J_{HH} = 3), 6.48 (ddd, 1H, H6', J_{FH} = 10, J_{FH} = 7, J_{HH} = 3), 7.93 (br.s, 1H, NH). ^{19}F NMR, acetone-d$_6$, δ/ppm, J/Hz: 11.6 (ddd, 1F, F2', J_{FF} = 12, J_{FH} = 7, J_{FH} = 6), 15.0, 17.8 (both m, in 1F, F6, F7), 21.7 (br.s, 1F, F2), 23.4, 25.0 (both m, in 1F, F5, F8), 44.4 (ddd, 1F, F5', J_{FF} = 12, J_{FH} = 10, J_{FH} = 9). Found: *m/z* 390.0232 $[M]^+$. $C_{16}H_5O_2N_2F_7$. Calculated: M = 390.0234.

2-(3'-amino-2',4',5'-trifluorophenylamino)-pentafluoro-1,4-dihydronaphthalene-1,4-dione (**4c**) was synthesized from diamine **4a** (0.16 g), yield 0.21 g (52%). Mp 179-180 °C. UV-vis, λ_{max}/nm (logε): 228 (4.4), 269 (4.4), 335 (3.6), 457 (3.6). FTIR, ν/cm^{-1}: 3417, 3367, 3259 (NH_2), 3081 (C_{ar}-H), 1691 (C=O). ^{1}H NMR, acetone-d$_6$, δ/ppm, J/Hz: 5.22 (br.s, 2H, NH_2), 6.58 (ddd, 1H, H6', J_{FH} = 11, J_{FH} ~8, J_{FH} ~8), 7.97 (br.s, 1H, NH). ^{19}F NMR, acetone-d$_6$, δ/ppm, J/Hz: 4.1 (ddd, 1F, F4', J_{FF} = 21, J_{FF} =11, J_{FH} = 8), 15.0, 17.9

(both m, in 1F, F6, F7), 17.6 (ddd, 1F, F2', J_{FF} ~11, J_{FF} ~11, J_{FH} = 8), 18.9 (ddd, 1F, F5', J_{FF} = 21, J_{FF} ~11, J_{FH} ~11), 19.8 (br.s, 1F, F2), 23.4, 25.0 (both m, in 1F, F5, F8). Found: *m/z* 408.0145 $[M]^+$. $C_{16}H_4O_2N_2F_8$. Calculated: M = 408.0140.

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