Synthesis and Molecular and Crystalline Structure of Polyfluoro-1,3-Diazafluorenes

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Abstract—Reactions of 2-amino-3-(1-imino-2,2,2-trifluoroethyl)hexafluoro-1*H*-indene with carboxylic acid anhydrides and chlorides afforded 2-alkyl(aryl)-4-trifluoromethyl-5,6,7,8,9,9-hexafluoro-1,3-diazafluorenes. The molecular and crystalline structure of the products was studied by NMR spectroscopy and X-ray diffraction. 5,6,7,8,9,9-Hexafluoro-2-phenyl-4-trifluoromethyl-1,3-diazafluorene in crystal gives rise to infinite ladder chains via π-stacking interaction between the benzene ring of one molecule and tetrafluorobenzene fragment of the other.

We recently synthesized first fluorine-containing derivatives of dihydro-2-selena-1,3-diazafluorene from 2-amino-3-(1-imino-2,2,2-trifluoroethyl)hexafluoro-indene (**I**) and SeCl$_4$. These compounds are representatives of a new polyfluoro-2-elementa-1,3-diazafluorene series [1]. Intramolecular cyclization of 2-dialkylamino-3-(1-imino-2,2,2-trifluoroethyl)hexa-fluoroindenes gave fluorinated 1,2,3,4-tetrahydro-1,3-diazafluorene derivatives [2]. With the goal of extending the synthetic potential of compound **I** and its analogs for the preparation of other polyfluoro-1,3-di-azafluorene derivatives we examined reactions of **I** with carboxylic acid anhydrides and chlorides.

By heating compound **I** [3] with benzoyl, penta-fluorobenzoyl and perfluoro(4-toluoyl) chlorides we obtained 5,6,7,8,9,9-hexafluoro-2-phenyl-4-trifluoro-methyl-1,3-diazafluorene (**II**), 5,6,7,8,9,9-hexafluoro-2-pentafluorophenyl-4-trifluoromethyl-1,3-diaza-

fluorene (**III**), and 5,6,7,8,9,9-hexafluoro-2-[perfluoro-(4-tolyl)]-4-trifluoromethyl-1,3-diazafluorene (**IV**), respectively (Scheme 1). In addition, 1-(2-aminohexa-fluoro-1*H*-inden-3-yl)-2,2,2-trifluoroethanone (**V**) was isolated.

Presumably, the reaction involves initial acylation of enaminoimine **I** at one nitrogen atom, and the subsequent dehydration leads to compounds **II**–**IV** (cf. [4]). Aminoketone **V** is likely to be formed via hydrolysis of initial compound **I** by the action of water and hydrogen chloride liberated during the condensa-tion. In fact, compound **I** was converted into **V** in the system H$_2$O–CH$_2$Cl$_2$/HCl even at ~20°C. Apart from products **II** and **V**, in the reaction of **I** with benzoyl chloride we isolated *N*-(3-trifluoroacetylhexafluoro-1*H*-inden-2-yl)benzamide (**VI**). By special experiment we showed that compound **VI** is formed by ben-zoylation of aminoketone **V**.

Scheme 1.
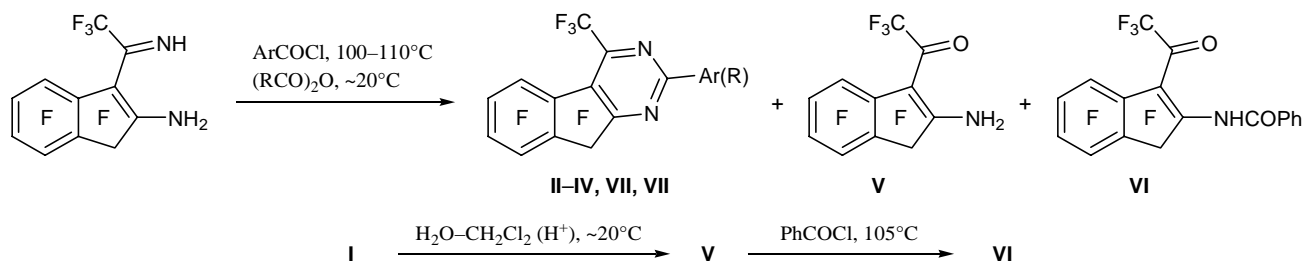
II, Ar = Ph; **III**, Ar = C$_6$F$_5$; **IV**, Ar = 4-CF$_3$C$_6$F$_4$; **VII**, R = Me; **VIII**, R = CF$_3$.
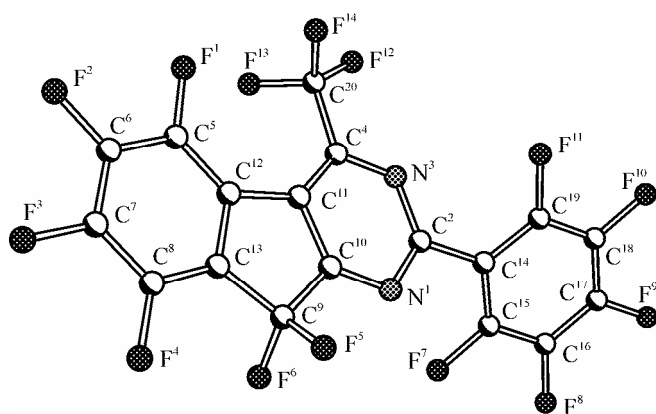
Fig. 1. Structure of the molecule of 5,6,7,8,9,9-hexafluoro-2-pentafluorophenyl-4-trifluoromethyl-1,3-diazafluorene (**III**) according to the X-ray diffraction data.

Compound **I** reacted with acetic and trifluoroacetic anhydrides at room temperature to give, respectively, 5,6,7,8,9,9-hexafluoro-2-methyl-4-trifluoromethyl-1,3-diazafluorene (**VII**) and 5,6,7,8,9,9-hexafluoro-2,4-bis(trifluoromethyl)-1,3-diazafluorene (**VIII**). Unlike the reactions with acetic anhydride and aroyl chlorides, only a small amount of **V** was formed in the reaction with trifluoroacetic anhydride. A probable reason is that the latter is the most electrophilic among the acylating agent used, and the acylation and subsequent cyclization of **I** are much faster than its hydrolysis.

The structure of compounds **II**, **III**, and **VI–VIII** was established by X-ray analysis and was confirmed (including compound **IV**) by the ^{19}F and ^{1}H NMR spectra (for compound **VII**, also by the ^{13}C and ^{15}N NMR spectra). A specific feature of the ^{19}F NMR spectra of diazafluorenes **II–IV**, **VII**, and **VIII** is a large coupling constant $J(CF_3,F^5)$ which is equal to
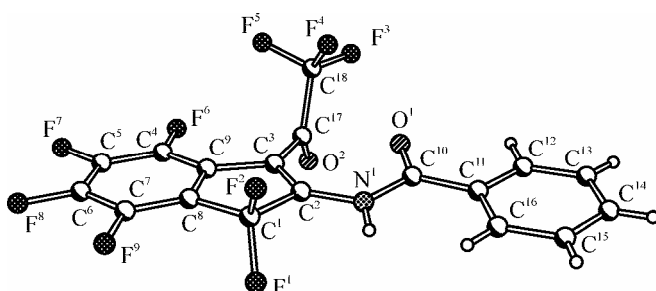

Fig. 2. Structure of the molecule of 2-benzoylamino-1,1,4,5,6,7-hexafluoro-3-trifluoroacetyl-1*H*-indene (**VI**) according to the X-ray diffraction data. Selected bond lengths (Å) and torsion angles (deg): C^1–C^8 1.490(3), C^1–C^2 1.519(3), C^2–C^3 1.340(3), C^2–N^1 1.377(3), C^3–C^9 1.485(3), C^3–C^{17} 1.500(3), C^8–C^9 1.394(3), C^{10}–N^1 1.367(3), C^{10}–O^1 1.212(2), C^{10}–C^{11} 1.480(3), $C^9C^3C^{17}C^{18}$ 88.2, $C^3C^2N^1C^{10}$ 8.2, $C^2N^1C^{10}C^{11}$ 179.0, $N^1C^{10}C^{11}C^{16}$ –5.0.

45 Hz. This is the result of close spatial arrangement of the F^3 and F^5 atoms. On the other hand, the coupling constant between CF_3 and F^4 in amide **VI** is 6 Hz, indicating that the interacting nuclei are fairly distant from each other and that there is no intramolecular hydrogen bonding between the amide proton and carbonyl oxygen atom of the trifluoroacetyl group. When such a hydrogen bond exists (as in compound **V**), the corresponding coupling constant is 42 Hz [3].

Despite numerous crystallographic data for various compounds containing a fluorene fragment (more than 500 structures deposited to the Cambridge Structural Database [5]), we were the first to determine the molecular and crystalline structure of 1,3-diazafluorene derivatives (compounds **II**, **III**, **VII**, and **VIII**). The 1,3-diazafluorene fragment therein is planar within ±0.041(3), ±0.054(4), ±0.068(3), and ±0.065(5) Å, respectively (Fig. 1), and the bond lengths mostly coincide within the experimental error (Table 1). It should be noted that replacement of the methyl group in **VII** by trifluoromethyl (compound **VIII**) leads to shortening of the C^2–N^3 bond from 1.336(5) to 1.310(6) Å and elongation of the C^2–C^{14} bond from 1.506(6) to 1.532(8) Å. Quantum-chemical simulation of such replacement by the PM3 semiempirical method with pyrimidine as an example gives shortening of the N^1–C^2 and C^2–N^3 bonds by 0.009 Å and elongation of the C^2–C^{14} bond by 0.057 Å.

Molecule **II** is almost planar: the angle between the planes of the phenyl ring and 1,3-diazafluorenone fragment is 2.4(1)°, while the angle between the pentafluorophenyl ring plane and 1,3-diazafluorene moiety in molecule **III** is 40.5(2)°. Molecules of **II** in crystal give rise to infinite ladder chains via arene–polyfluoroarene π-stacking interaction between the phenyl ring of one molecule and tetrafluorophenylene fragment of the other. The distance between the centers of the interacting rings is 3.630 Å, the average interplanar distance is 3.52 Å, and the dihedral angle is 3.1°. The chains are arranged in layers, and the interchain interaction is weaker than the interaction between molecules in the chain: the distance between the centers of the benzene ring and tetrafluorophenylene fragment is 4.070 Å.

Slightly shortened [6] intramolecular F···F contacts (2.721 Å) between the CF_3 groups of compound **VIII** in crystal give rise to formation of infinite zigzag chains along the *b* axis. Except for C^{18} and O^2, all atoms in molecule **VI** lie almost in one plane (the mean-square deviation is 0.051 Å; fluorine

and hydrogen atoms were not taken into consideration; Fig. 2). Molecules **VI** in crystal are linked in pairs to form centrosymmetric dimers due to arene–polyfluoro-arene π-stacking interaction; the distance between the ring centroids is 3.622 Å, the average interplanar distance is 3.54 Å, and the angle is 5.1°.

EXPERIMENTAL

The ^{19}F and ^1H NMR spectra were recorded on a Bruker WP-200SY spectrometer at 188.3 and 200 MHz, respectively, and the ^{13}C and ^{15}N NMR spectra of compound **VII** were obtained on a Bruker DRX-500 instrument at 125.8 and 50.7 MHz, respectively. The chemical shifts are given downfield to C_6F_6 (^{19}F), TMS (^1H, ^{13}C), or liquid NH_3 (^{15}N); C_6F_6 and HMDS (δ 0.04 ppm) or $CDCl_3$ (δ_C 76.9 ppm) were used as internal references, and CH_3NO_2 (δ_N 382.0 ppm) was external reference. The elemental compositions were determined from the high-resolution mass spectra which were obtained on a Finnigan MAT-8200 spectrometer.

X-Ray analysis was performed on a Bruker P-4 diffractometer (MoK_α radiation, graphite mono-chromator, θ/2θ-scaning to 2θ < 50°). Single crystals were obtained at 30–70°C in an evacuated (2 mm) sealed ampule. The principal crystallographic data are given in Table 2. The structures were solved by the direct method using SHELXS-97 program (the structure of **VIII** was solved using SIR-97 software) and were refined by the least-squares procedure in anisotropic–isotropic approximation using SHELXL-97 program. The positions of hydrogen atoms were determined by the difference synthesis of electron density. The coordinates of non-hydrogen atoms are available from the authors; selected bond lengths and bond angles are given in Table 1. Figure 1 shows the molecular structure of compound **III** as an example for **II**, **III**, **VII**, and **VIII**, and the structure of **VI** is shown in Fig. 2.

5,6,7,8,9,9-Hexafluoro-2-phenyl-4-trifluoro-methyl-1,3-diazafluorene (II). A mixture of 0.3 g (0.9 mmol) of compound **I** and 0.38 g (2.7 mmol) of benzoyl chloride was heated for 7 h at 100–110°C. According to the ^{19}F NMR data, a mixture of compounds **II**, **V**, and **VI** was obtained at a ratio of ~62:11:27. The mixture was treated with a solution of potassium hydroxide and extracted with methylene chloride, the extract was washed with water, dried over $MgSO_4$, and evaporated, and the residue (0.32 g) was subjected to column chromatography on silica gel

Table 1. Selected bond lengths (*d*) and bond and dihedral angles (ω, φ) in molecules **II**, **III**, **VII**, and **VIII**[a]

d, Å, or ω (φ), deg	II	III	VII	VIII
N^1–C^{10}	1.312(4)	1.315(5)	1.315(4)	1.316(6)
N^1–C^2	1.342(4)	1.340(6)	1.336(5)	1.333(7)
C^2–N^3	1.345(4)	1.335(5)	1.336(5)	1.310(6)
C^2–C^{14}	1.483(4)	1.479(6)	1.506(6)	1.532(8)
N^3–C^4	1.340(4)	1.335(5)	1.333(4)	1.339(6)
C^4–C^{11}	1.384(4)	1.402(5)	1.386(5)	1.392(7)
C^4–C^{20}	1.526(4)	1.504(6)	1.500(5)	1.494(8)
C^5–C^6	1.376(5)	1.392(6)	1.370(5)	1.374(8)
C^5–C^{12}	1.378(4)	1.376(5)	1.375(4)	1.389(7)
C^6–C^7	1.376(5)	1.366(6)	1.374(5)	1.355(9)
C^7–C^8	1.377(5)	1.367(6)	1.386(5)	1.374(9)
C^8–C^{13}	1.360(4)	1.376(6)	1.353(5)	1.366(8)
C^9–C^{13}	1.491(4)	1.492(6)	1.497(5)	1.504(8)
C^9–C^{10}	1.504(4)	1.500(6)	1.499(5)	1.504(7)
C^{10}–C^{11}	1.400(4)	1.394(5)	1.404(4)	1.388(6)
C^{11}–C^{12}	1.494(4)	1.492(5)	1.478(5)	1.490(6)
C^{12}–C^{13}	1.402(4)	1.398(5)	1.406(4)	1.384(7)
$C^{10}N^1C^2$	114.9(3)	114.0(3)	114.4(3)	113.4(4)
$N^1C^2N^3$	124.6(3)	125.6(4)	125.1(4)	127.4(5)
$C^4N^3C^2$	118.5(3)	118.8(3)	118.8(3)	117.9(5)
$N^3C^4C^{11}$	121.5(3)	120.9(3)	121.6(3)	120.6(4)
$N^3C^2C^{14}C^{19}$	0.8	42.9	1.8[b]	–5.8[c]
$N^3C^4C^{20}F^{12}$	1.9	6.8	9.0	7.2

[a] For atom numbering, see Fig. 1.
[b] $N^3C^2C^{14}H$.
[c] $N^3C^2C^{14}F$.

using $CHCl_3$ as eluent to isolate 0.19 g (0.45 mmol, 50%) of compound **II**, mp 168–169°C (from CH_2Cl_2–hexane). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 8.58 (2H, 2'-H, 6'-H), 7.55 (3H). ^{19}F ($CDCl_3$), δ_F, ppm: 94.4 (CF_3), 45.8 (9-F), 32.9 (5-F), 23.4 (8-F), 17.0 (6-F), 14.1 (7-F); J_{FF}, Hz: $J_{4-CF_3,5} = 45$, $J_{5,6} = 19$, $J_{5,7} = 8$, $J_{5,8} = 15$, $J_{6,7} = 18$, $J_{6,8} = 7$, $J_{7,8} = 21$, $J_{8,9} = 5$. Found: M^+ 420.03035. $C_{18}H_5N_2F_9$. Calculated: *M* 420.03089.

5,6,7,8,9,9-Hexafluoro-2-pentafluorophenyl-4-trifluoromethyl-1,3-diazafluorene (III). A mixture of 0.2 g (0.6 mmol) of compound **I** and 0.41 g (1.8 mmol) of pentafluorobenzoyl chloride was heated for 5 h at 100–105°C. According to the ^{19}F NMR data, the resulting mixture contained compounds **III** and **V** at a ratio of ~1.5:1). The mixture was treated with

Table 2. Crystallogaphic parameters of compounds **II**, **III**, and **VI**–**VIII**

Parameter	II	III	VI	VII	VIII
Formula	$C_{18}H_5F_9N_2$	$C_{18}F_{14}N_2$	$C_{18}H_6F_9NO_2$	$C_{13}H_3F_9N_2$	$C_{13}F_{12}N_2$
Molecular weight	420.24	510.20	439.24	358.17	412.15
Crystal system	Monoclinic	Rhombic	Rhombic	Monoclinic	Rhombic
Space group	$C2/c$	$Pca2_1$	$Pbca$	$C2/c$	$P2_12_12_1$
Unit cell parameters:					
a, Å	11.491(2)	12.5042(12)	9.5999(7)	39.914(15)	9.0756(4)
b, Å	9.5306(19)	14.257(2)	15.8623(11)	7.054(2)	9.7105(7)
c, Å	29.605(7)	10.1004(11)	22.0493(12)	9.529(3)	15.8801(11)
β, deg	99.721(9)			101.55(3)	
V, Å^3	3195.6(12)	1800.6(4)	3357.6(4)	2628.8(16)	1399.49(15)
Z (d_{calc}, g/cm^3)	8 (1.747)	4 (1.882)	8 (1.738)	8 (1.810)	4 (1.956)
μ, mm^{-1}	0.178	0.215	0.181	0.199	0.231
Crystal habit, mm	0.45×0.45×0.12	0.09×0.40×0.90	1.2×0.60×0.60	0.15×0.56×1.0	0.15×0.45×0.90
Number of reflections, total/independent	2902/2751	1678/1678	2933/2933	2349/2315	1436/1436
Number of reflections with $I > 2\sigma(I)$	1811	1319	2396	1317	1109
Number of refined parameters	283	308	296	218	245
R for $I > 2\sigma(I)$	$R_1 = 0.0509$	$R_1 = 0.0339$	$R_1 = 0.0373$	$R_1 = 0.0500$	$R_1 = 0.0459$
	$wR_2 = 0.1332$	$wR_2 = 0.0761$	$wR_2 = 0.0960$	$wR_2 = 0.1345$	$wR_2 = 0.1317$
R for all reflections	$R_1 = 0.0834$	$R_1 = 0.0495$	$R_1 = 0.0476$	$R_1 = 0.0885$	$R_1 = 0.0603$
	$wR_2 = 0.1543$	$wR_2 = 0.0836$	$wR_2 = 0.1032$	$wR_2 = 0.1632$	$wR_2 = 0.1436$
GOOF	1.012	1.065	1.044	1.024	1.065
Correction for absorption	By facet	By facet	By facet	Not taken into account	Semiempirical

a solution of potassium hydroxide and extracted with methylene chloride, the extract was washed with water, dried over $MgSO_4$, and evaporated, and the residue (0.16 g) was subjected to column chromatography on silica gel using chloroform as eluent to isolate 0.14 g (0.27 mmol, 46%) of compound **III**, mp 85–86°C (from hexane). ^{19}F NMR spectrum (CHCl$_3$), δ_F, ppm: 94.7 (CF$_3$), 45.3 (9-F), 34.8 (5-F), 24.6 (8-F), 18.3 (6-F), 16.9 (7-F), 21.1 (2'-F, 6'-F), 13.2 (4'-F), 1.4 (3'-F, 5'-F); J_{FF}, Hz: $J_{4\text{-}CF_3,5} = 45$, $J_{5,6} = 19$, $J_{5,7} = 9$, $J_{5,8} = 15$, $J_{6,7} = 18$, $J_{6,8} = 8$, $J_{7,8} = 21$, $J_{8,9} = 5$. Found: M^+ 509.98337. $C_{18}N_2F_{14}$. Calculated: M 509.98378.

5,6,7,8,9,9-Hexafluoro-2-(heptafluoro-4-tolyl)-4-trifluoromethyl-1,3-diazafluorene (IV) was synthesized as described above for compound **III** from 0.2 g (0.6 mmol) of enaminoimine **I** and 0.2 g

(0.71 mmol) of perfluoro(4-toluoyl) chloride. Yield 0.13 g (0.23 mmol, 39%), mp 117.5–119°C (after vacuum sublimation at 120°C/5 mm). ^{19}F NMR spectrum (CHCl$_3$), δ_F, ppm: 94.7 (CF$_3$), 45.2 (9-F), 35.1 (5-F), 24.8 (8-F), 18.5 (6-F), 17.4 (7-F), 105.2 (4'-CF$_3$), 22.9 and 22.7 (2'-F, 3'-F, 5'-F, 6'-F); J_{FF}, Hz: $J_{4\text{-}CF_3,5} = 45$, $J_{5,6} = 19$, $J_{5,7} = 9$, $J_{5,8} = 15$, $J_{6,7} = 18$, $J_{6,8} = 8$, $J_{7,8} = 21$, $J_{8,9} = 5$. Found: M^+ 559.98123. $C_{19}N_2F_{16}$. Calculated: M 559.98058.

1-(2-Aminohexafluoro-1*H*-inden-3-yl)-2,2,2-trifluoroethanone (V) (*by hydrolysis of compound I*). To a solution of 0.07 g (0.21 mmol) of compound **I** in 1 ml of methylene chloride we added 1 ml of water and 2 drops of concentrated hydrochloric acid, and the mixture was stirred for 20 h at ~20°C. The organic phase was separated, washed with water, dried over $MgSO_4$, and transferred onto a watch glass to isolate

0.065 g (0.19 mmol, 92%) of compound **V**. The IR and ^{19}F NMR spectra of the product coincided with those of an authentic sample [3].

N-(1,1,5,6,7,8-Hexafluoro-3-trifluoroacetyl-1H-inden-2-yl)benzamide (VI). A mixture of 0.06 g (0.18 mmol) of compound **V** and 0.03 g (0.21 mmol) of benzoyl chloride was heated for 7 h at 100–105°C. The product was extracted into methylene chloride, and the extract was washed with water, dried over MgSO$_4$, and transferred onto a watch glass. After evaporation of the solvent, the residue (0.075 g) was a mixture of compounds **V** and **VI** at a ratio of ~1:3 (according to the ^{19}F NMR data). The product mixture was subjected to column chromatography on silica gel using chloroform as eluent to isolate 0.04 g (0.09 mmol, 50%) of compound **VI**, mp 169–170°C (from CH$_2$Cl$_2$–hexane). ^{1}H NMR spectrum (acetone), δ, ppm: 11.09 (NH), 8.01 quasi-d (2H, 2'-H, 6'-H, J = 7.6 Hz), 7.69 quasi-t (1H, 4'-H, J = 7.6 Hz), 7.56 quasi-t (2H, 3'-H, 5'-H, J = 7.6 Hz). ^{19}F NMR spectrum (acetone), δ$_F$, ppm: 86.3 (CF$_3$), 48.3 (1-F), 21.7 (7-F), 20.7 (4-F), 15.2 (5-F), 7.3 (6-F); J_{FF}, Hz: $J_{1,7}$ = 4.5, $J_{3,4}$ = 6, $J_{4,5}$ = 19, $J_{4,6}$ = 3, $J_{4,7}$ = 15, $J_{5,6}$ = 17, $J_{5,7}$ = 7, $J_{6,7}$ = 20.5. Found: M^+ 439.02687. C$_{18}$H$_6$NF$_9$O$_2$. Calculated: M 439.02547.

5,6,7,8,9,9-Hexafluoro-2-methyl-4-trifluoromethyl-1,3-diazafluorene (VII). A solution of 0.5 g (1.5 mmol) of compound **I** in 0.94 g (9.2 mmol) of acetic anhydride was kept at ~20°C. According to the ^{19}F NMR data, after 45 h, the mixture contained compounds **V** and **VII** at a ratio of ~35:50 and ~15% of initial enaminoimine **I**; after 135 h, compound **I** disappeared. The mixture was transferred onto a watch glass, and the solid residue (0.48 g) was subjected to column chromatography on silica gel using chloroform as eluent to isolate 0.26 g (0.73 mmol, 48%) of diazafluorene **VII**, mp 112–113°C (from hexane), and 0.15 g (0.45 mmol, 30%) of ketone **V**.

Compound **VII**. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm: 2.95 (CH$_3$). ^{19}F NMR spectrum (CDCl$_3$), δ$_F$, ppm: 94.7 (CF$_3$), 45.5 (9-F), 33.1 (5-F), 23.6 (8-F), 17.2 (6-F), 14.7 (7-F); J_{FF}, Hz: $J_{4\text{-CF}_3,5}$ = 45, $J_{5,6}$ = 19, $J_{5,7}$ = 8, $J_{5,8}$ = 15, $J_{6,7}$ = 18, $J_{6,8}$ = 7, $J_{7,8}$ = 21, $J_{8,9}$ = 5. ^{13}C NMR spectrum (CDCl$_3$), δ$_C$, ppm: 169.9 q (C^2, $^2J_{CH}$ = 7 Hz), 166.5 t (C^{9a}, $^2J_{CF}$ = 24 Hz), 149.7 q (C^4, $^2J_{CF}$ = 39 Hz), 145.2 d.d.t (C^8, $^1J_{CF}$ = 260, $^2J_{CF}$ = 12, $^3J_{CF}$ = 93 Hz), 144.8 d.d.d.d (C^6, $^1J_{CF}$ = 260, $^2J_{CF}$ = 17, $^2J_{CF}$ = 13, $^3J_{CF}$ = 4 Hz), 144.1 d.d.d (C^5, $^1J_{CF}$ = 263,

$^2J_{CF}$ = 13, $^3J_{CF}$ = 3 Hz), 142.4 d.t (C^7, $^1J_{CF}$ = 263, $^2J_{CF}$ = 14 Hz), 120.5 s (C^{4a}), 119.8 q (CF$_3$, $^1J_{CF}$ = 275 Hz), 117.3 t.d (C^{8a}, $^2J_{CF}$ = 24, $^2J_{CF}$ = 14 Hz), 117.2 t (C^9, $^1J_{CF}$ = 250 Hz), 116.8 d (C^{4b}, $^2J_{CF}$ = 14 Hz), 25.5 q (CH$_3$, $^1J_{CH}$ = 129 Hz). ^{15}N NMR spectrum (CDCl$_3$), δ$_N$, ppm: 293.2 (N^1), 290.8 q (N^3, $^3J_{NF}$ = 4.7 Hz). Found: M^+ 358.01395. C$_{13}$H$_3$N$_2$F$_9$. Calculated: M 358.01524.

5,6,7,8,9,9-Hexafluoro-2,4-bis(trifluoromethyl)-1,3-diazafluorene (VIII). A solution of 0.337 g (1 mmol) of compound **I** in 1.27 g (6 mmol) of trifluoroacetic anhydride (mixing of the reactants was accompanied by spontaneous heating to ~40°C) was kept for 18 h at ~20°C. The resulting solution contained compounds **V** and **VIII** at a ratio of ~1:10 (according to the ^{19}F NMR data). The solution was transferred onto a watch glass, and the solid residue (0.385 g) was subjected to chromatography on silica gel using chloroform as eluent to isolate 0.296 g (0.71 mmol, 71%) of compound **VIII**, mp 92–93°C (vacuum sublimation at 95°C/20 mm), and 0.026 g (0.08 mmol, 8%) of enaminoketone **V**, mp 158–159°C (in a sealed capillary). The IR and ^{19}F NMR spectra of product **V** were identical to those reported in [3].

Compound **VIII**. ^{19}F NMR spectrum (CHCl$_3$), δ$_F$, ppm: 95.0 (4-CF$_3$), 91.9 (2-CF$_3$), 45.3 (9-F), 36.0 (5-F), 25.2 (8-F), 18.9 (6-F), 18.3 (7-F); J_{FF}, Hz: $J_{4\text{-CF}_3,5}$ = 45, $J_{5,6}$ = 19, $J_{5,7}$ = 10, $J_{5,8}$ = 15, $J_{6,7}$ = 18, $J_{6,8}$ = 8, $J_{7,8}$ = 21, $J_{8,9}$ = 5. Found: M^+ 411.98698. C$_{13}$N$_2$F$_{12}$. Calculated: M 411.98697.

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