

Fluorinated dihydroindeno[2,1-c][1,2,6]thiadiazines: The first synthesis, structural characterization and reactivity

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of his 80th birthday.

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ABSTRACT

3-(1-Amino-2,2,2-trifluoroethyliden)-1,1,4,5,6,7-hexafluoro-2-iminoindan (**1**) and 3-(1-amino-2,2,2-trifluoroethyliden)-1,1,4,5,6,7-hexafluoro-2-methyliminoindan (**7**) reacted with SOCl_2 to give previously unknown 4a-chloro-5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4a,9-dihydroindeno[2,1-c][1,2,6]thiadiazine (**2**) and 5,6,7,8,9,9-hexafluoro-1-methyl-4-(trifluoromethyl)-1,9-dihydroindeno[2,1-c][1,2,6]thiadiazine 2-oxide (**8**), respectively. When treated with methanol, compound **2** formed 5,6,7,8,9,9-hexafluoro-4a-methoxy-4-(trifluoromethyl)-4a,9-dihydroindeno[2,1-c][1,2,6]thiadiazine (**9**), whereas the reaction with water gave 5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-3,9-dihydroindeno[2,1-c][1,2,6]thiadiazine 2-oxide (**5**). The latter reacted with SOCl_2 , acetyl chloride and trifluoroacetic anhydride to give compound **2**, 5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4a,9-dihydroindeno[2,1-c][1,2,6]thiadiazin-4a-yl acetate (**13**) and trifluoroacetate **15**, respectively. Solution of compound **2** in trifluoromethanesulfonic acid generated 5,6,7,8,9,9-hexafluoro-4-trifluoromethyl-9H-indeno[2,1-c][1,2,6]thiadiazinylium (**11**), which was transformed, under the action of water, to sulfoxide **5**. The structures of compounds **8, 9, 13** were confirmed by single crystal X-ray diffraction. The reaction pathways were analyzed on the basis of DFT calculations

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1. Introduction

Fluorinated (hetero) aromatic compounds are essentially important to fundamental organic chemistry [1] and its applications, particularly to materials science, biomedicine and agriculture [1–3]. Of obvious interest are comparative studies of fluorocarbon derivatives and their hydrocarbon congeners.

Currently, polycyclic 1,2,6-thiadiazine 2,2-dioxides receive much attention in both fundamental and applied aspects whereas only a few polycyclic 1,2,6-thiadiazines are known [4]. Recently, the first indeno[2,1-c][1,2,6]thiadiazines and their [1,2-c] isomers were prepared by the reaction of indene enaminonitriles with sulfur dichloride to be of interest as building blocks in the design and synthesis of new functional materials [5]. Polyfluorinated indeno[2,1-c][1,2,6]thiadiazines are unknown. At the same time, fluorine-containing indeno[2,1-c][1,2,6]selenadiazines were obtained by the reaction between enaminoinime **1** and selenium tetrachloride (Scheme 1) [6]. Condensation of com-

ound **1** with alkanones gave derivatives of dihydroindeno[2,1-d]pyrimidine [7] and that with carboxylic acid anhydrides and chlorides afforded fluorine-containing indeno[2,1-d]pyrimidines (Scheme 1) [8].

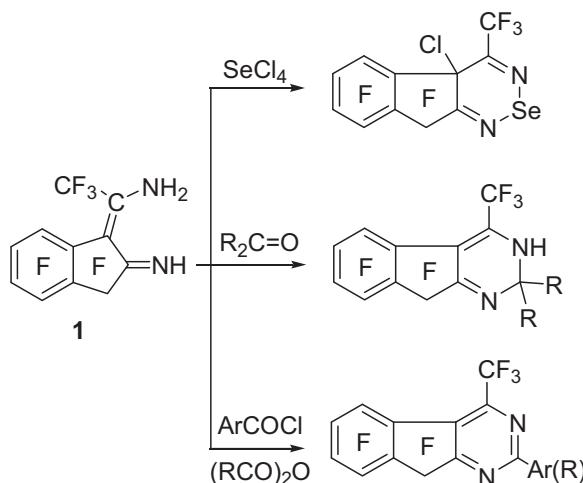
In this work, we report on the first synthesis of fluorine-containing dihydroindeno[2,1-c][1,2,6]thiadiazines by the reaction of fluorinated indene enaminoinimes with thionyl chloride, together with some chemical properties of the derivatives obtained. The structures of 3 new compounds were elucidated by single crystal X-ray diffraction (XRD). The reaction pathways were analyzed on the basis of DFT calculations.

2. Results and discussion

It has been shown that **1** (existing in solution in equilibrium with **1a**, Scheme 2) [9,10], heated with excess of thionyl chloride, formed 4a-chloro-5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4a,9-dihydroindeno[2,1-c][1,2,6]thiadiazine (**2**). The reaction between **1** and sulfur dichloride in the presence of pyridine or Et_3N also gave **2**, however **2** was contaminated and it was not isolated from the reaction mixture. The tentative mechanism for the reaction of **1** with thionyl chloride is shown in Scheme 2.

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Scheme 1.

At first, compound **1** reacts with SOCl_2 to give compound **3** (cf. transformation of **1** into **7** under the action of $(\text{CH}_3)_2\text{SO}_4$ [9], Scheme 2). Intramolecular cyclization of **3** (and/or product of its further transformation **4**) yields compounds **5a**, **5** (cf. cyclization of **7** into **8** by reaction with SOCl_2 , Scheme 2). Compound **5** (most likely existing in solution in the equilibrium with **5a**, **b**) reacts then with SOCl_2 to form compound **6** whose isomerization gives final product **2** (Scheme 2). DFT/B3LYP/6-311+G(d) calculations reveal that in the gas phase compound **2** is more stable than its isomer **6** by 8.3 kcal mol⁻¹.

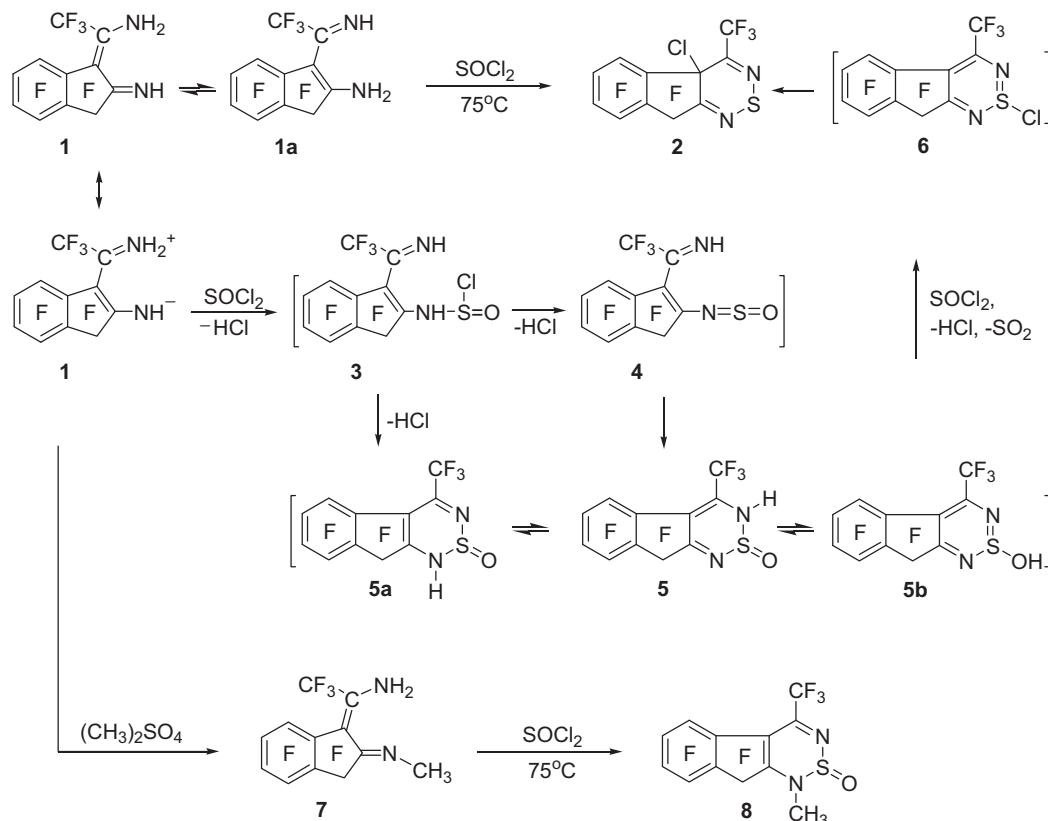
Compound **2** is chemically rather active. When treated with methanol, it formed derivative **9** (Scheme 3). Under the action of

water, compound **2** gave S-oxide **5** together with amine **10** (Scheme 3). It was shown by a separate experiment that **10** is a product of hydrolysis of **5**. Treating of oxide **5** with SOCl_2 regenerated compound **2** (Scheme 3).

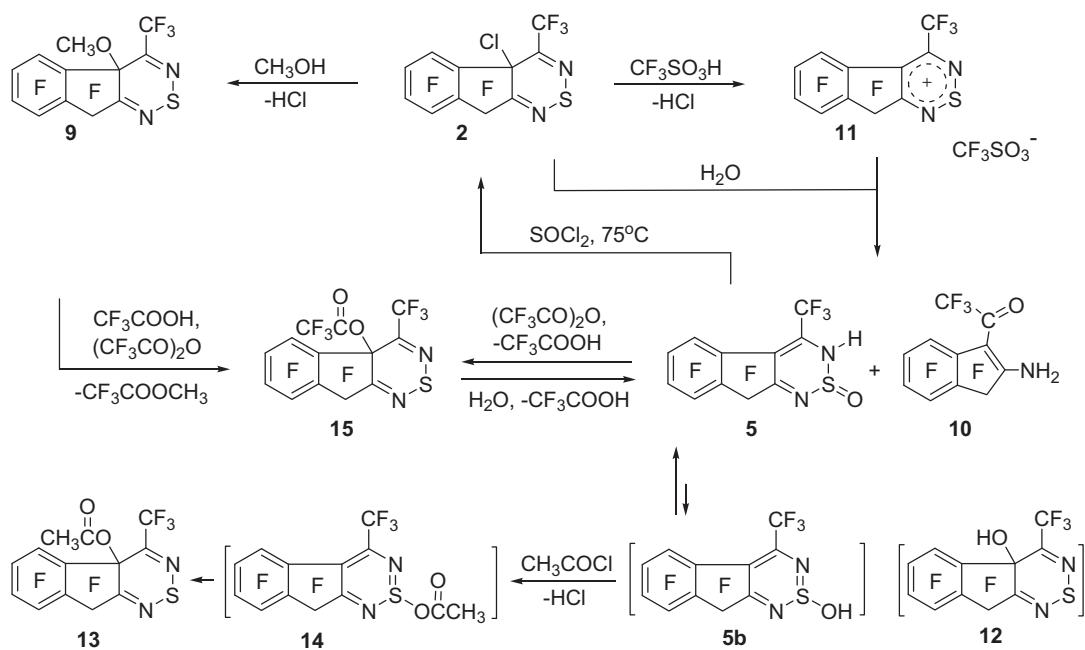
In trifluoromethanesulfonic acid, compound **2** generated thiadiazinium **11** which was characterized by ^{13}C , ^{19}F and ^{15}N NMR (the spectra of **11**, having 6π -electron heteroaromatic moiety, resemble those of its previously studied Se congener [6]). Hydrolysis of **11** gave oxide **5** together with amine **10** (Scheme 3). The formation of **5** agrees with charge distribution in the cation **11** (positive charge at the S atom (+0.717) is *ca.* 4-fold larger than at the C-4a atom (+0.183), PM3 calculations), and disagrees with relative stabilities of isomers **5** and **12** from the DFT/B3LYP/6-311+G(d) calculations. The latter revealed that in the gas phase (acetone solution) the isomer **5** is less stable than the isomer **12** by 8.9 (5.3) kcal mol⁻¹; and that **5** is more stable than **5a** and **5b** by 2.0 (2.1) and 8.0 (8.7) kcal mol⁻¹, respectively.

Oxide **5** reacted with acetyl chloride to give acetate **13**. This suggests that oxide **5** is transformed first to intermediate **14**, which isomerizes into product **13** (Scheme 3). The DFT calculations for the gas phase (acetone solution) show that compound **13** is more stable than its isomer **14** (Scheme 3) by 15.5 (14.5) kcal mol⁻¹. Analogously, compound **5** by reaction with trifluoroacetic anhydride gave trifluoroacetate **15**. The derivative **9** was also transformed into compound **15** by reaction with trifluoroacetic acid in the presence of trifluoroacetic anhydride. It should be noted that **15** is sensitive to traces of water, particularly it forms oxide **5** being exposed to moist air (Scheme 3).

The structures of compounds **8**, **9**, **13** were confirmed by single crystal X-ray diffraction (Tables 1 and 2 and Figs. 1–3). According to the Cambridge Structural Database (CSD) the compounds belong to a poorly studied species.



Scheme 2.



Scheme 3.

In compound **8** (Fig. 1), the five-membered ring C1C2C3C9C8 of the molecule adopts the C2-envelope conformation with a puckering angle equal 9.5(3)°. The conformation of the six-membered cycle N1C2C3C10N2S12 is a distorted envelope, atom S12 deviates for 0.728(2) Å from the N1N2C2C3C10 plane. According to the CSD, the closest structural analog of the heterocycle of **8** is 3,5-bis(diethylamino)-2*H*-1,2,4,6-thiatriazine

1-oxide [**11**] featuring envelope conformation of the heterocycle, deviation of the S atom is 0.475 Å.

In compound **9** (Fig. 2), the indan fragment of the molecule is planar within $\pm 0.047(3)$ Å. The conformation of the heterocycle with sp^3 hybridized C3 atom is distorted boat, deviations of the C3 and S12 atoms from the N1N2C2C3C10 plane equal to 0.627(5) and 0.327(5) Å, respectively. The intramolecular contact S12···O1 of 3.119(3) Å is

Table 1
Crystal data and structure refinement for **8**, **9**, **13**.

	8	9	13
Empirical formula	$C_{12}H_3F_9N_2OS$	$C_{12}H_3F_9N_2OS$	$C_{13}H_3F_9N_2O_2S$
Formula weight	394.22	394.22	422.23
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	<i>Pbca</i>	<i>P2</i> ₁	<i>P</i> –1
Unit cell dimensions:			
<i>a</i> (Å)	11.5540(6)	8.6585(7)	7.862(2)
<i>b</i> (Å)	8.5056(4)	8.5691(7)	9.356(2)
<i>c</i> (Å)	28.256(2)	9.435(1)	10.381(2)
α (°)	90	90	101.01(2)
β (°)	90	93.358(8)	97.16(2)
γ (°)	90	90	91.09(2)
Volume (Å ³)	2776.8(3)	698.8(1)	743.0
<i>Z</i>	8	2	2
Calculated density (g cm ^{–3})	1.886	1.874	1.887
Absorption coefficient (mm ^{–1})	0.348	0.345	3.116
<i>F</i> (000)	1552	388	416
Crystal size (mm)	0.70 × 0.60 × 0.40	0.80 × 0.60 × 0.40	0.80 × 0.35 × 0.11
Data collection range (°)	2.28–25.00	2.16–26.99	4.38–70.03
Reflections	2428	1720	3134
Unique reflections	2428 [<i>R</i> _{int} = 0.0000]	1617 [<i>R</i> _{int} = 0.0392]	2810 [<i>R</i> _{int} = 0.0162]
Absorption correction	Integration	Empirical	Integration
Max/min transmission factors	0.82/0.87	0.72/0.83	0.28/0.72
Data/restraints/parameters	2428/0/239	1617/1/226	2810/0/257
Goodness of fit on <i>F</i> ²	1.071	0.953	1.077
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]			
<i>R</i> ₁	0.0345	0.0381	0.0414
<i>wR</i> ₂	0.0980	0.1177	0.1141
Reflexions number [<i>I</i> > 2σ(<i>I</i>)]	2165	1527	2503
<i>R</i> indices all data			
<i>R</i> ₁	0.0385	0.0403	0.0456
<i>wR</i> ₂	0.1019	0.1219	0.1178
Extinction coefficient	0.0065(7)	–	0.0059(10)
Largest diff. peak and hole (e Å ^{–3})	0.225/–0.275	0.331/–0.229	0.249/–0.246

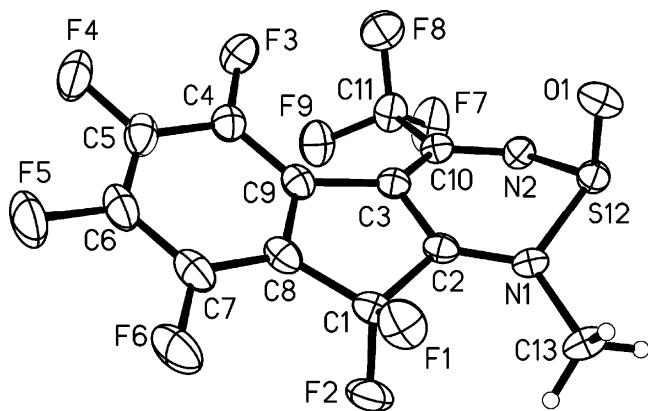


Fig. 1. Molecular structure of compound **8** (for selected bond lengths and angles, see Table 2). Thermal ellipsoids are drawn at the 50% probability level.

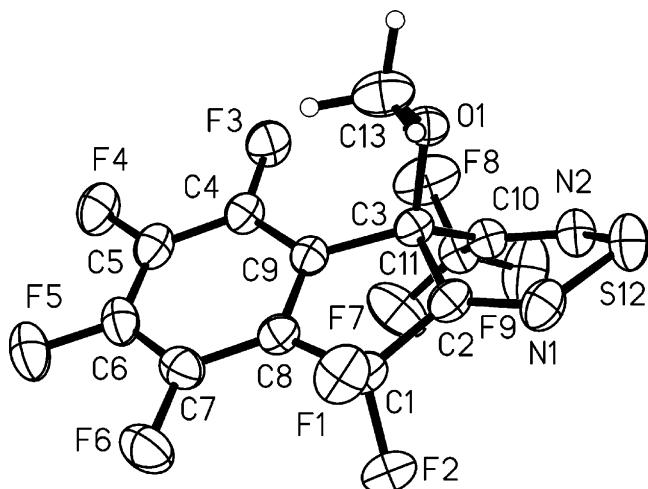


Fig. 2. Molecular structure of compound **9** (for selected bond lengths and angles, see Table 2). Thermal ellipsoids are drawn at the 50% probability level.

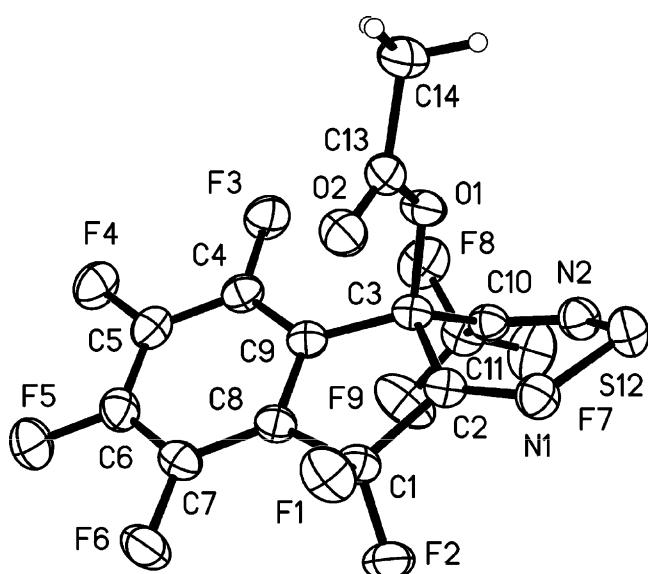


Fig. 3. Molecular structure of compound **13** (for selected bond lengths and angles, see Table 2). Thermal ellipsoids are drawn at the 50% probability level.

Table 2

Selected bond lengths (Å) and angles (°) of compounds **8**, **9**, **13**; experimental/from DFT/B3LYP/6-31+G(d) calculations (for atom numbering, see Figs. 1–3).

Bond/angle	8	9	13
N1–S12	1.759(2)/1.835	1.662(4)/1.678	1.660(2)/1.681
N1–C2	1.320(3)/1.327	1.276(5)/1.274	1.271(3)/1.272
S12–N2	1.651(2)/1.680	1.644(3)/1.659	1.644(2)/1.659
N2–C10	1.311(3)/1.304	1.274(5)/1.280	1.280(3)/1.281
C10–C3	1.411(3)/1.425	1.521(4)/1.531	1.516(3)/1.529
C3–C2	1.389(3)/1.393	1.520(4)/1.530	1.512(3)/1.526
C3–C9	1.489(3)/1.484	1.513(4)/1.536	1.509(3)/1.518
S12–O1	1.444(2)/1.477	–	–
N2–S12–N1	97.07(8)/95.9	105.5(2)/105.7	105.2(1)/105.3
N1–S12–O1	106.36(9)/106.7	–	–
N2–S12–O1	107.7(1)/109.4	–	–
C2–N1–S12–O1	68.9(2)/69.6	–	–

shortened as compared with the sum of corresponding van der Waals radii of 3.39 Å [12a], 3.32 Å [12b]. In the CSD, there is no any structure containing 4H-1,2,6-thiadiazine fragment.

In the crystal, the conformation and bond lengths of the tricyclic fragment of compound **13** (Fig. 3) are very similar to those of **9** (Fig. 2). The indan fragment is planar within $\pm 0.031(2)$ Å, deviations of the atoms C3 and S12 from the N1N2C2C10 plane equal to 0.604(3) and 0.344(4) Å, respectively. The shortened intramolecular contact S12...O1 is 3.163(2) Å.

Selected bond lengths and angles for **8**, **9** and **13** are given in Table 2.

Attempts to obtain single crystals of compound **5** suitable to XRD failed. Analysis of ^{13}C , ^{14}N and ^{19}F NMR spectra of compound **5** (with special emphasis on chemical shifts of the C-4, C-8a, C-9, C-9a and ^{14}N nuclei) and their comparison with those of compound **8**, **9**, **13**, 5,6,7,8,9,9-hexafluoro-2-R-4-(trifluoromethyl)-9H-indeno[2,1-d]pyrimidines [8], 5,6,7,8,9,9-hexafluoro-2,2-dimethyl-4-(trifluoromethyl)-3,9-dihydro-2H-indeno[2,1-d]pyrimidine (**16**) and 5,6,7,8,9,9-hexafluoro-1,2,2-trimethyl-4-(trifluoromethyl)-2,9-dihydro-1H-indeno[2,1-d]pyrimidine (**17**) [7], unambiguously confirm the structure **5** and reject structures **5a**, **5b**, **12** and **4**. For example, ^{14}N signals of compound **5** at 274.5 and 142 ppm belonging to sp^2 and sp^3 hybridized nitrogen atoms allow exclusion of structures **4**, **5b** and **12**, which do not contain sp^3 hybridized nitrogen atoms. Chemical shifts of the C-9a signals of compounds **5** (162.9 ppm) and **8** (150.5 ppm) are similar to those of compounds **16** (161.2) and **17** (154.1 ppm) and confirm the structure **5** and exclude structure **5a**.

3. Conclusions

The reaction of fluorinated indene enaminooimines with thionyl chloride readily proceeds in the absence of a base to give the first fluorine-containing dihydroindeno[2,1-c][1,2,6]thiadiazines. The heterocycles synthesized revealed non-common reactivity allowing their use as promising new sources of non-trivial polycyclic compounds hardly accessible by other approaches. Especially, they can be exploited as precursors of fluorinated indeno[2,1-c][1,2,6]thiadiazines that are of interest to fundamental organic chemistry and its applications to materials science.

4. Experimental

NMR spectra were recorded with Bruker WP-200 SY, Bruker AM-400, Bruker DRX-500 and Bruker AV-600 instruments. Chemical shifts (δ) are given relative to CCl_3F (^{19}F), TMS (^1H and ^{13}C) and NH_3 (^{15}N and ^{14}N) standards. During measurements, C_6F_6 ($\delta_{\text{F}} = -162.9$ ppm from CCl_3F), $(\text{Me}_3\text{Si})_2\text{O}$, CHCl_3 ($\delta_{\text{H}} = 0.04$ and

7.24 ppm from TMS), CDCl_3 , $(\text{CD}_3)_2\text{CO}$ ($\delta_{\text{C}} = 76.9$ and 29.8 ppm from TMS) were used as internal standards, and CH_3NO_2 ($\delta_{\text{N}} = 382.0$ ppm from NH_3) as external standard. The molecular masses of the compounds were determined by high-resolution mass spectrometry on a Finnigan Mat 8200 instrument (EI 70 eV).

Crystallography. Single crystals of **8** were obtained by slow evaporation of its solution in CH_2Cl_2 –hexane, those of **9** and **13** by their solutions in hexane, at ambient temperature. The XRD data for **8** and **9** were collected on a Bruker P4 diffractometer with graphite monochromated Mo $\text{K}\alpha$ radiation, and for **13** on a Syntex P2₁ diffractometer with a graphite monochromated Cu $\text{K}\alpha$ (radiation at ambient temperature (Table 1). The structures were solved by direct methods using the SHELXS-97 program [13] and refined by the least-squares method in the full-matrix anisotropic (isotropic for H atoms) approximation using the SHELXL-97 program [13]. For compound **8**, positions of the hydrogen atoms were taken from difference Fourier map, for compounds **9** and **13** those were calculated geometrically and refined in riding model. Crystallographic data for the structures in this paper have been deposited by the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 800081–800083. 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).

Quantum chemical calculations. The DFT calculations of relative energies of the compounds in the gas phase and in solution (Polarizable Continuum Model) [14] were performed using GAMESS program [15] applying standard gradient techniques at the B3LYP level of theory using the 6-311+G(d) basis set on all atoms; the basis set was used as it is implemented in the program.

All chemicals were reagent grade. Compounds **1** and **7** were prepared as previously reported [9].

4.1. Synthesis of 4a-chloro-5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4a,9-dihydroindeno[2,1-c][1,2,6]thiadiazine (2)

SOCl_2 (1.36 g, 11.1 mmol) was added to 3-(1-amino-2,2,2-trifluoroethylidene)-1,1,4,5,6,7-hexafluoro-2-iminoindan (**1**) (0.4 g, 1.2 mmol) and a mixture was stirred at 70–75 °C for 10 h. Excess of SOCl_2 was distilled off under reduced pressure. Compound **2** was obtained as colorless liquid, 0.42 g (90%). An analytical sample of compound **2** was prepared by short-path distillation (70–80 °C, 2 Torr). ^{19}F NMR (188.3 MHz, CDCl_3): $\delta = -67.1$ (3F, CF_3), -89.4 (1F, F-9), -92.4 (1F, $J_{\text{A},\text{B}} = 288$ Hz, F-9), -130.6 (1F, F-5), -139.7 (1F, F-8), -144.1 (1F, F-6), -146.3 (1F, F-7) ppm; $J_{\text{CF}_3-\text{F}(5)} = 25$, $J_{5,6} = 20$, $J_{5,7} = 9$, $J_{5,8} = 16$, $J_{6,7} = 20$, $J_{6,8} = 7$, $J_{7,8} = 21$, $J_{8,9} = 5$ Hz. ^{13}C NMR (125.8 MHz, CDCl_3): $\delta = 145.1$ (dd, $^1\text{J}_{\text{CF}} = 263$, $^2\text{J}_{\text{CF}} = 13$ Hz) and 144.4 (dd, $^1\text{J}_{\text{CF}} = 263$, $^2\text{J}_{\text{CF}} = 12$ Hz, C-5,8), 144.9 (dt, $^1\text{J}_{\text{CF}} = 264$, $^2\text{J}_{\text{CF}} = 14$ Hz) and 143.3 (dt, $^1\text{J}_{\text{CF}} = 264$, $^2\text{J}_{\text{CF}} = 14$ Hz, C-6,7), 142.7 (dd, $^2\text{J}_{\text{CF}} = 27$ Hz, $^2\text{J}_{\text{CF}} = 23$ Hz, C-9a), 135.4 (q, $^2\text{J}_{\text{CF}} = 39$ Hz, C-4), 121.6 (d, $^2\text{J}_{\text{CF}} = 13$ Hz, C-4b), 118.5 (q, $^1\text{J}_{\text{CF}} = 278$ Hz, CF_3), 117.2 (td, $^2\text{J}_{\text{CF}} = 26$, $^2\text{J}_{\text{CF}} = 15$ Hz, C-8a), 115.3 (t, $^1\text{J}_{\text{CF}} = 251$ Hz, C-9), 47.7 (s, C-4a) ppm. ^{15}N NMR (50.7 MHz, CDCl_3): $\delta = 322.4$ (q, $^3\text{J}_{\text{NF}} = 4.4$ Hz, N-3), 317.8 (d, $^3\text{J}_{\text{NF}} = 1.8$ Hz, N-1) ppm. HRMS m/z , 362.9641 ($\text{M}^+ - \text{Cl}$). Calcd. for $\text{C}_{11}\text{F}_9\text{N}_2\text{S}$ = 362.9638. Anal. calcd. for $\text{C}_{11}\text{ClF}_9\text{N}_2\text{S}$: C 33.14, Cl 8.89, N 7.03, S 8.04; found: C 33.24, Cl 8.90, N 7.14, S, 8.10.

4.2. Preparation of 5,6,7,8,9,9-hexafluoro-1-methyl-4-(trifluoromethyl)-1,9-dihydroindeno[2,1-c][1,2,6]thiadiazine 2-oxide (8)

SOCl_2 (1.24 g, 10 mmol) was added to 3-(1-amino-2,2,2-trifluoroethylidene)-1,1,4,5,6,7-hexafluoro-2-methylimino-indan (**7**) (0.36 g, 1 mmol) and a mixture was stirred at 70–75 °C for 10 h. Excess of SOCl_2 was distilled off under reduced pressure, the

residue was dissolved in CH_2Cl_2 , the solution was washed with water and the solvent was distilled off. Compound **8** was obtained as orange crystals, 0.39 g (96%), mp 108–109 °C (CH_2Cl_2 –hexane). ^1H NMR (200 MHz, CDCl_3): $\delta = 3.91$ (s, CH_3) ppm. ^{19}F NMR (188.3 MHz, CDCl_3): $\delta = -70.1$ (3F, CF_3), -109.8 (1F, F-9), -118.1 (1F, $J_{\text{A},\text{B}} = 296$ Hz, F-9), -135.9 (1F, F-5), -140.7 (1F, F-8), -145.5 (1F, F-6), -154.8 (1F, F-7) ppm; $J_{\text{CF}_3-\text{F}(5)} = 37$, $J_{5,6} = 20$, $J_{5,7} = 5$, $J_{5,8} = 15$, $J_{6,7} = 18$, $J_{6,8} = 8$, $J_{7,8} = 21$, $J_{8,9} = 5$ Hz. ^{13}C NMR (125.8 MHz, $(\text{CD}_3)_2\text{CO}$, ^1H decoupled): $\delta = 150.5$ (t, $^2\text{J}_{\text{CF}} = 24$ Hz, C-9a), 149.6 (q, $^2\text{J}_{\text{CF}} = 38$ Hz, C-4), 146.2 (dt, $^1\text{J}_{\text{CF}} = 258$, $^2\text{J}_{\text{CF}} = 15$ Hz) and 141.1 (dt, $^1\text{J}_{\text{CF}} = 255$, $^2\text{J}_{\text{CF}} = 15$ Hz, C-6,7), 145.8 (dd, $^1\text{J}_{\text{CF}} = 257$, $^2\text{J}_{\text{CF}} = 13$ Hz) and 143.0 (dd, $^1\text{J}_{\text{CF}} = 254$, $^2\text{J}_{\text{CF}} = 14$ Hz, C-5,8), 120.7 (q, $^1\text{J}_{\text{CF}} = 278$ Hz, CF_3), 120.7 (t, $^1\text{J}_{\text{CF}} = 253$ Hz, C-9), 120.5 (d, $^2\text{J}_{\text{CF}} = 14$ Hz, C-4b), 112.7 (td, $^2\text{J}_{\text{CF}} = 26$, $^2\text{J}_{\text{CF}} = 14$ Hz, C-8a), 106.0 (s, C-4a), 35.9 (t, $^4\text{J}_{\text{CF}} = 2.5$ Hz, CH_3). ^{15}N NMR (50.7 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 266.5$ (q, $^3\text{J}_{\text{NF}} = 4$ Hz, N-3), 151.2 (br.s, N-1) ppm. HRMS m/z , 393.9827 (M^+). Calcd. for $\text{C}_{12}\text{H}_3\text{F}_9\text{N}_2\text{OS}$ = 393.9822.

4.3. Reaction of compound **2** with water

1. Compound **2** prepared from **1** (0.13 g, 0.39 mmol) as described above was dissolved in CH_2Cl_2 (3 mL), and the solution was stirred for 15 h in an atmosphere saturated with water vapor at ambient temperature. The precipitate was filtered off and washed with CH_2Cl_2 (2×2 mL) to give 0.11 g (74%, for **1**) of compound **5**. A filtrate was evaporated to dryness in the air to give a mixture (0.04 g) of **2** and **10** in the ratio 40:60 (^{19}F NMR).
2. CH_2Cl_2 (10 mL) and water (5 mL) were added to compound **2** prepared from **1** (0.34 g, 1 mmol) as described above, and the mixture was stirred for 15 h at ambient temperature. The organic part was evaporated to dryness in the air to give compound **10**, 0.29 g (85%) whose ^{19}F NMR spectrum was identical to that reported previously [10].

4.3.1. 5,6,7,8,9,9-Hexafluoro-4-(trifluoromethyl)-3,9-dihydroindeno[2,1-c][1,2,6]thiadiazine-2-oxide (5)

mp 161–163 °C (dec.). ^{19}F NMR (188.3 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = -67.0$ (3F, CF_3), -103.1 (1F, F-9), -106.9 (1F, $J_{\text{A},\text{B}} = 291$ Hz, F-9), -134.6 (1F, F-5), -141.3 (1F, F-8), -146.5 (1F, F-6), -153.0 (1F, F-7) ppm; $J_{\text{CF}_3-\text{F}(5)} = 38$, $J_{5,6} = 19$, $J_{5,7} = 6$, $J_{5,8} = 15$, $J_{6,7} = 19$, $J_{6,8} = 8$, $J_{7,8} = 21$, $J_{8,9} = 5$ Hz. ^{13}C NMR (100.6 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 162.9$ (t, $^2\text{J}_{\text{CF}} = 25$ Hz, C-9a), 145.9 (dt, $^1\text{J}_{\text{CF}} = 257$, $^2\text{J}_{\text{CF}} = 14$ Hz) and 141.8 (dt, $^1\text{J}_{\text{CF}} = 257$, $^2\text{J}_{\text{CF}} = 14$ Hz, C-6,7), 145.8 (dd, $^1\text{J}_{\text{CF}} = 257$, $^2\text{J}_{\text{CF}} = 12$ Hz) and 143.3 (dd, $^1\text{J}_{\text{CF}} = 257$, $^2\text{J}_{\text{CF}} = 13$ Hz, C-5,8), 135.2 (q, $^2\text{J}_{\text{CF}} = 37$ Hz, C-4), 120.5 (q, $^1\text{J}_{\text{CF}} = 277$ Hz, CF_3), 120.0 (d, $^2\text{J}_{\text{CF}} = 14$ Hz, C-4b), 115.6 (td, $^2\text{J}_{\text{CF}} = 24$, $^2\text{J}_{\text{CF}} = 14$ Hz, C-8a), 118.0 (t, $^1\text{J}_{\text{CF}} = 251$ Hz, C-9), 105.7 (s, C-4a) ppm. ^{15}N NMR (36.1 MHz, $(\text{CD}_3)_2\text{CO}$): $\delta = 274.5$ (N-1), 142 (N-3) ppm. HRMS m/z , 379.9669 (M^+). Calcd. for $\text{C}_{11}\text{HF}_9\text{N}_2\text{OS}$ = 379.9666.

4.4. Preparation of 5,6,7,8,9,9-hexafluoro-4a-methoxy-4-(trifluoromethyl)-4a,9-dihydroindeno[2,1-c][1,2,6]thiadiazine-2-oxide (9)

A solution of compound **2** (0.16 g, 0.38 mmol) in 0.5 mL of CH_2Cl_2 was added dropwise to CH_3OH (1.5 mL), and the mixture was stirred for 1 h at ambient temperature. The solvents were distilled off under reduced pressure, and the residue was sublimed at 70 °C, 1 Torr. Compound **9** was obtained as colorless crystals, 0.11 g (70%), mp 58–60 °C (hexane). ^1H NMR (200 MHz, CDCl_3): $\delta = 2.81$ (s, CH_3) ppm. ^{19}F NMR (188.3 MHz, CDCl_3): $\delta = -67.2$ (3F, CF_3), -93.6 (1F, F-9), -94.5 (1F, $J_{\text{A},\text{B}} = 287$ Hz, F-9), -133.5 (1F, F-5), -139.8 (1F, F-8), -144.8 (1F, F-6), -146.9 (1F, F-7) ppm; $J_{\text{CF}_3-\text{F}(5)} = 22$, $J_{5,6} = 20$, $J_{5,7} = 8$, $J_{5,8} = 17$, $J_{6,7} = 19$, $J_{6,8} = 7$, $J_{7,8} = 21$, $J_{8,9} = 5$ Hz. ^{13}C NMR (125.8 MHz, CDCl_3): $\delta = 145.2$ (dd, $^1\text{J}_{\text{CF}} = 260$, $^2\text{J}_{\text{CF}} = 13$ Hz) and 144.6 (dd, $^1\text{J}_{\text{CF}} = 263$, $^2\text{J}_{\text{CF}} = 13$ Hz, C-5,8), 144.5 (dt, $^1\text{J}_{\text{CF}} = 263$, $^2\text{J}_{\text{CF}} = 13$ Hz) and 143.0 (dt, $^1\text{J}_{\text{CF}} = 262$, $^2\text{J}_{\text{CF}} = 14$ Hz, C-6,7), 143.4 (dd, $^1\text{J}_{\text{CF}} = 25$ Hz, $^2\text{J}_{\text{CF}} = 23$ Hz, C-9a), 136.4 (q,

$^2J_{CF} = 38$ Hz, C-4), 119.7 (d, $^2J_{CF} = 14$ Hz, C-4b), 119.4 (td, $^2J_{CF} = 26$, $^2J_{CF} = 14$ Hz, C-8a), 118.6 (q, $^1J_{CF} = 277$ Hz, CF₃), 115.3 (t, $^1J_{CF} = 250$ Hz, C-9), 67.7 (s, C-4a), 51.1 (q, $^1J_{CH} = 144$ Hz, CH₃) ppm. ¹⁵N NMR (50.7 MHz, CDCl₃): δ 315.6 (q, $^3J_{NF} = 4.3$ Hz, N-3), 314.1 (d, $^3J_{NF} = 1.7$ Hz, N-1) ppm. HRMS *m/z*, 393.9826 (M⁺). Calcd. for C₁₂H₃F₉N₂OS = 393.9822.

4.5. Synthesis of 5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4a,9-dihydroindeno[2,1-c][1,2,6]thiadiazin-4a-yl acetate (13)

At ambient temperature, CH₃COCl (0.066 g, 0.84 mmol) and NEt₃ (0.072 g, 0.71 mmol) were added to a stirred solution of compound **5** (0.16 g, 0.42 mmol) in acetone (0.5 mL). After 0.5 h, the reaction mixture was diluted with CH₂Cl₂ (5 mL) and washed with water. The organic part was evaporated to dryness in the air to give a dark residue (0.176 g). Column chromatography (silica, CHCl₃) of the residue gave compound **13** (0.064 g, 36%) as a light yellow crystals, mp 123–125 °C (hexane). ¹H NMR (200 MHz, CDCl₃): δ 2.86 (s, CH₃) ppm. ¹⁹F NMR (188.3 MHz, CDCl₃): δ –66.9 (3F, CF₃), –88.0 (1F_A, F-9), –99.8 (1F_B, $J_{A,B} = 285$ Hz, F-9), –136.1 (1F, F-5), –140.0 (1F, F-8), –145.8 (1F, F-6), –147.2 (1F, F-7) ppm; $J_{CF_3-F(5)} = 21$, $J_{5,6} = 20$, $J_{5,7} = 7$, $J_{5,8} = 16$, $J_{6,7} = 19$, $J_{6,8} = 7$, $J_{7,8} = 21$, $J_{8,9A} = 4$, $J_{8,9B} = 5$ Hz, ¹³C NMR (125.8 MHz, CDCl₃): δ 168.8 (q, $^2J_{CH} = 7$ Hz, CO), 144.6 (dd, $^1J_{CF} = 262$, $^2J_{CF} = 12$ Hz) and 144.5 (dd, $^1J_{CF} = 259$, $^2J_{CF} = 12$ Hz, C-5,8), 144.1 (dt, $^1J_{CF} = 262$, $^2J_{CF} = 14$ Hz) and 143.0 (dt, $^1J_{CF} = 261$, $^2J_{CF} = 13$ Hz, C-6,7), 144.0 (dd, $^2J_{CF} = 26$ Hz, $^2J_{CF} = 23$ Hz, C-9a), 131.2 (q, $^2J_{CF} = 39$ Hz, C-4), 119.5 (d, $^2J_{CF} = 12$ Hz, C-4b), 119.4 (td, $^2J_{CF} = 26$, $^2J_{CF} = 15$ Hz, C-8a), 118.3 (q, $^1J_{CF} = 277$ Hz, CF₃), 115.2 (dd, $^1J_{CF} = 259$ Hz, $^1J_{CF} = 244$ Hz, C-9), 64.5 (s, C-4a), 19.3 (q, $^1J_{CH} = 131$ Hz, CH₃) ppm. ¹⁵N NMR (50.7 MHz, CDCl₃): δ 321.6 (q, $^3J_{NF} = 4.1$ Hz, N-3), 312.0 (d, $^3J_{NF} = 2.0$ Hz, N-1) ppm. HRMS *m/z*, 421.9772 (M⁺). Calcd. for C₁₃H₃F₉N₂O₂S = 421.9771.

4.6. Preparation of 5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-4a,9-dihydroindeno[2,1-c][1,2,6]thiadiazin-4a-yl trifluoroacetate (15)

1. A mixture of compound **5** (0.1 g, 0.26 mmol) and (CF₃CO)₂O (0.6 g, 2.83 mmol) was stirred for 7 h at ambient temperature. ¹⁹F NMR spectrum of a solution revealed that it contains compound **15**, CF₃COOH and (CF₃CO)₂O in the molar ratio 8:9:83. The solution was evaporated to dryness in the air. compound **5** (0.09 g) was recovered.
2. CF₃COOH (0.15 g, 1.32 mmol) was added to a solution of compound **9** (0.13 g, 0.33 mmol) in (CF₃CO)₂O (0.64 g, 3.05 mmol). The resulting solution was kept at ambient temperature for 7 days. Then CDCl₃ was added and ¹H, ¹³C, ¹⁵N and ¹⁹F NMR spectra of the solution were measured to identify compound **15**. According to the spectra, the solution contained compound **15**, CF₃COOCH₃, CF₃COOH and (CF₃CO)₂O in the molar ratio 7:7:29:57. The solution was evaporated to dryness in the air. Compound **5** (0.1 g) was obtained.

4.6.1. Compound 15

NMR (CDCl₃ + (CF₃CO)₂O + CF₃COOH + CF₃COOCH₃): ¹⁹F NMR (564.8 MHz): δ –65.6 (3F, CF₃-4), –74.1 (bs, 3F, CF₃COO-4a, exchange between CF₃COO-4a and CF₃COOH), –88.2 (1F_A, F-9), –97.3 (1F_B, $J_{A,B} = 285$ Hz, F-9), –133.3 (1F, F-5), –138.2 (1F, F-8), –144.1 (1F, F-6), –144.6 (1F, F-7) ppm; $J_{CF_3-F(5)} = 21$, $J_{5,6} = 18$, $J_{5,7} = 8$, $J_{5,8} = 16$, $J_{6,7} = 17$, $J_{6,8} = 8$, $J_{7,8} = 19$ Hz, ¹³C NMR (150.9 MHz): δ 162 (bs, CO, exchange between CF₃COO-4a and CF₃COOH), 145.3 (dd, $^1J_{CF} = 261$, $^2J_{CF} = 12$ Hz) and 145.5 (dd, $^1J_{CF} = 262$, $^2J_{CF} = 12$ Hz, C-5,8), 145.1 (dt, $^1J_{CF} = 263$, $^2J_{CF} = 14$ Hz) and 144.5 (dt, $^1J_{CF} = 264$, $^2J_{CF} = 14$ Hz, C-6,7), 141.8 (t, $^2J_{CF} = 26$ Hz, C-9a), 131.0 (q, $^2J_{CF} = 40$ Hz, C-4), 120.1 (td, $^2J_{CF} = 26$, $^2J_{CF} = 15$ Hz, C-8a), 118.7 (q, $^1J_{CF} = 277$ Hz, CF₃-4), 117.7 (d, $^2J_{CF} = 13$ Hz, C-4b), 115.6 (t, $^1J_{CF} = 253$ Hz, C-9),

114.5 (bq, $^1J_{CF} = 284$ Hz, CF₃COO-4a, exchange between CF₃COO-4a and CF₃COOH), 67 (s, C-4a) ppm. ¹⁵N NMR (60.8 MHz): δ 321.9 (q, $^3J_{NF} = 3.9$ Hz, N-3), 315.7 (bs, N-1) ppm.

Since compound **15** is very sensitive to traces of moisture, direct inlet of its solution in mixture of (CF₃CO)₂O with CF₃COOH was used in MS measurements. HRMS *m/z*, 475.9553 (M⁺). Calcd. for C₁₃F₁₂N₂O₂S = 475.9489.

4.7. Generation of 5,6,7,8,9,9-hexafluoro-4-(trifluoromethyl)-9H-indeno[2,1-c][1,2,6]thiadiazinylum (11)

At 10 °C, CF₃SO₃H (0.43 g, 2.87 mmol) was added to a mixture of compound **2** (0.14 g, 0.35 mmol) and CD₂Cl₂ (0.1 mL). The mixture was warmed-up with stirring to 20 °C, and ¹³C, ¹⁵N and ¹⁹F NMR spectra of cation **11** were measured.

4.7.1. Cation 11

¹⁹F NMR (188.3 MHz): δ –67.5 (3F, CF₃), –108.5 (1F, F-5), –116.9 (2F, F-9), –121.3 (1F, F-7), –131.1 (1F, F-8), –137.8 (1F, F-6) ppm; $J_{CF_3-F(5)} = 50$, $J_{5,6} = 17$, $J_{5,7} = 23$, $J_{5,8} = 13$, $J_{6,7} = 17$, $J_{6,8} = 11$, $J_{7,8} = 20$, $J_{8,9} = 5$ Hz. ¹³C NMR (125.8 MHz): δ 173.9 (t, $^2J_{CF} = 28$ Hz, C-9a), 157.1 (q, $^2J_{CF} = 45$ Hz, C-4), 151.5 (dt, $^1J_{CF} = 284$, $^2J_{CF} = 13$ Hz, C-7), 150.3 (dd, $^1J_{CF} = 280$, $^2J_{CF} = 13$ Hz, C-5), 147.3 (dt, $^1J_{CF} = 270$, $^2J_{CF} = 13$ Hz, C-6), 147.3 (dd, $^1J_{CF} = 270$, $^2J_{CF} = 13$ Hz, C-8), 135.8 (s, C-4a), 119.9 (td, $^2J_{CF} = 24$, $^2J_{CF} = 15$ Hz, C-8a), 118.5 (q, $^1J_{CF} = 280$ Hz, CF₃), 117.0 (d, $^2J_{CF} = 12$ Hz, C-4b), 116.0 (t, $^1J_{CF} = 258$ Hz, C-9) ppm. ¹⁵N NMR (50.7 MHz): δ 375.0 (q, $^3J_{NF} = 3.0$ Hz, N-3), 359.3 (t, $^3J_{NF} = 1.5$ Hz, N-1) ppm.

The ¹⁹F NMR spectrum of the solution was repeatedly measured after one week to be unchanged. The solution was poured into water and extracted with CH₂Cl₂ (3 × 10 mL). The extract was washed with water and dried over MgSO₄. The solvent was distilled off to give 0.11 g of a mixture of **5** and **10** in the ratio 60:40 (¹⁹F NMR).

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