Reactions of fluoroalkyl-containing lithium 1,3-diketonates with diaminoarenes and 2-aminobenzenethiol

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1,5-Benzo[*b*]- and 1,5-naphtho[2,3-*b*]diazepines were synthesized by the reaction of lithium 1,3-diketonates with 1,2-diaminobenzene and 2,3-diaminonaphthalene in an MeOH—AcOH—HCl mixture at 0 °C. The reactions of fluoroalkyl-containing lithium 1,3-diketonates with 1,2-diaminobenzene and 1,2-diamino-4,5-difluorobenzene under reflux in acetic acid afford 2-fluoroalkyl-containing benzimidazoles as the major products, whereas the reaction with 2-aminothiophenol gives 2-phenylbenzothiazole. The reactions of lithium diketonate containing the cyclohexane and cyclopentane moieties with 1,2-diaminoarenes and 2-aminobenzenethiol are accompanied by the opening of the carbocycle to form 2-(6-oxo-7,7,7-trifluoroheptyl)benzimidazole and 2-(5-oxo-6,6,6-trifluorohexyl)benzothiazole hydrates, respectively.

Key words: fluoroalkyl-containing lithium 1,3-diketonates, 1,2-diaminobenzene, 2,3-diaminonaphthalene, 1,2-diamino-4,5-difluorobenzene, 2-aminobenzenethiol, 1,5-benzo[*b*]diazepines, 1,5-naphtho[2,3-*b*]diazepines, 2-fluoroalkyl-containing benzimidazoles, 2-(6-oxo-7,7,7-trifluoroheptyl)benzimidazole hydrate, 2-(6,6,6-trifluoro-5-oxohexyl)benzothiazole hydrate, 11-hydroxy-4-trifluoroacetyl-11-trifluoromethyl-1,2,3,4,10,11-hexahydro-5*H*-dibenzo[*b*,*e*][1,4]diazepine, 1,3-dihydrospiro[benzimidazole-2,1′-cyclohexane].

The condensation of 1,3-diketones with 1,2-diaminoarenes is most commonly used for the synthesis of 1,5-benzodiazepine derivatives.[1—6] However, the reactions of fluoroalkyl-containing unsymmetrical 1,3-diketones with diaminoarenes generally afford complex mixtures, from which 3*H*-1,5-benzo[*b*]- and 3*H*-1,5-naphtho[2,3-*b*]-diazepines were isolated along with aminovinyl ketones, 2-substituted benzimidazoles, and other products.[7—9]

The use of lithium enolates instead of fluoroalkyl-containing unsymmetrical 1,3-diketones (the former compounds are more easily available, more stable during storage, and are more convenient for the use in chemical processes than the corresponding diketones) often results in an increase in the selectivity of the reactions.[10—20] Hence, we studied the reactions of diketonates **1a**—**i** with diaminoarenes and 2-aminobenzenethiol (Scheme 1).

The reaction of equimolar amounts of diketonate **1b** and 1,2-diamino-4,5-difluorobenzene under reflux in glacial acetic acid (the conventional conditions of heterocyclization of fluoroalkyl-containing lithium 1,3-diketonates with binucleophiles[10—20]) during 1 h gave 3*H*-1,5-benzo[*b*]diazepine **2b** in 67% yield. Under similar conditions, considerable amounts of the starting compounds remain intact in the reactions of diketonates **1a**—**i** with 1,2-diaminobenzene, 2,3-diaminonaphthalene, and 2-aminothiophenol (TLC monitoring of the reactions). Under reflux for a longer period of time, diketonates **1c** and **1d** react with 1,2-diamino-4,5-difluorobenzene to give 2-fluoroalkyl-containing benzimidazoles (2-R^F-benzimidazoles) **4a,b** (see Scheme 1, Table 1), whereas the reactions of diketonates **1a,e—i** with 1,2-diaminobenzene and 2-aminothiophenol afford complex mixtures of products.

The synthesis of 3*H*-1,5-benzo[*b*]- and 3*H*-1,5-naphtho[2,3-*b*]diazepines **2a—f** and **3a,b** from diketonates **1** was carried out under the conditions, which are generally used for the synthesis of benzodiazepines from fluoroalkyl-containing 1,3-diketones (glacial AcOH and concentrated HCl were successively added to a solution of equimolar amounts of the reagents in methanol at 0 °C)[7] (see Scheme 1, Table 1).

The reactions of lithium diketonates **1a—i** with 1,2-diaminoarenes can give two regioisomeric intermediates **A** and **B**, whose condensation can afford 3*H*-1,5-benzo[*b*]- and 3*H*-1,5-naphtho[2,3-*b*]diazepines **2a—f** and **3a,b**. 2-R^F-Benzimidazoles **4a,b** may be formed both as a result of the acid hydrolysis of diazepines **2** and through the

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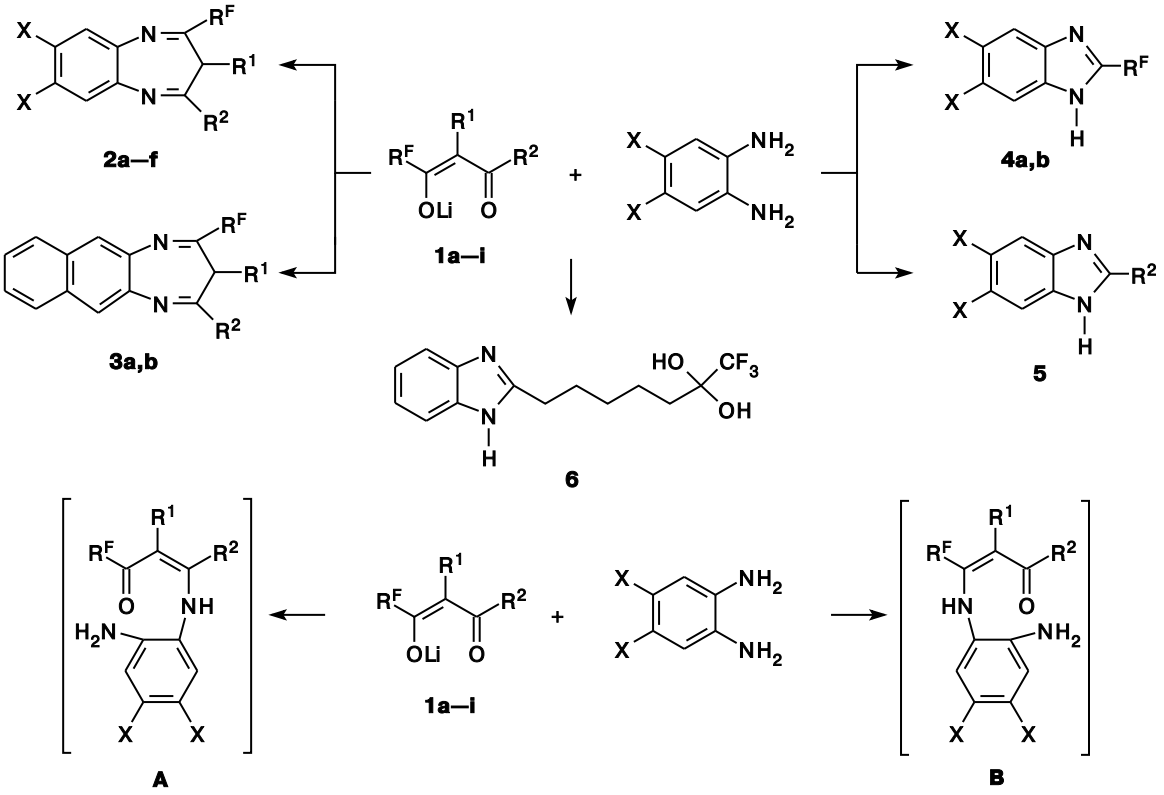
Scheme 1



condensation of the intermediate **B** accompanied by the elimination of ketone $R^1CH_2C(O)R^2$ (see Scheme 1). The former pathway seems to be more probable because it was shown[14,18] that the formation of the intermediate **A** is more favorable, and the transformation of benzo-1,5-diazepines into 2-substituted benzimidazoles upon heating

Table 1. Reaction products of lithium 1,3-diketonates **1** with 1,2-diaminoarenes

	Starting compounds				Reaction conditions[a]	Reaction product	Yield (%)
	Lithium diketonate			Arene, X			
1	R^F	R^1	R^2				
a	HCF_2	H	Me	H	*i*	**2a**	55
b	HCF_2	H	Ph	—(CH=CH)$_2$—[b]	*i*	**3a**	90
				F	*iii*	**2b**	67
c	HCF_2	—(CH$_2$)$_4$—[c]		F	*iii*	**4a**	58
d	CF_3	H	Ph	H	*i*	**2c**	72
				—(CH=CH)$_2$—[b]	*ii*	**3b**	79
				F	*iii*	**4b**	92
e	CF_3	—(CH$_2$)$_3$—[c]		H	*iii*	[d]	—
f	CF_3	—(CH$_2$)$_4$—[c]		H	*ii*	**6**	43[20]
g	$H(CF_2)_2$	H	Me	H	*i*	**2d**	67
h	$H(CF_2)_2$	H	Ph	H	*i*	**2e**	64
i	C_4F_9	H	Ph	H	*i*	**2f**	67

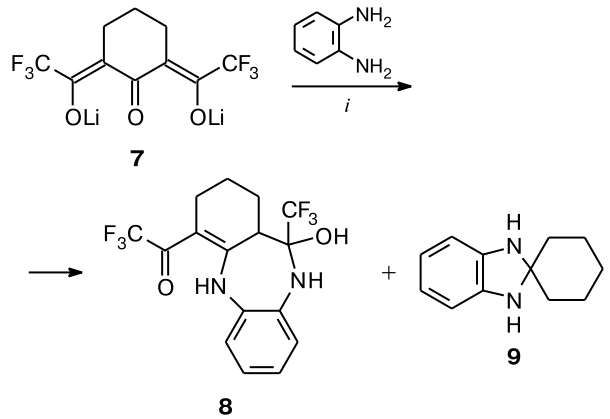
[a] *i.* MeOH, AcOH, HCl; *ii.* AcOH, HCl; *iii.* AcOH, reflux.
[b] X +X.
[c] $R^1 + R^2$.
[d] A mixture of adducts.

in an acidic medium is well known.[2] The formation of 2-(fluoroalkyl)benzimidazoles **4a,b** in the reactions of diketonates **1c,d** with 1,2-diaminoarenes is not quite usual because it is known that unsymmetrical polyfluoroalkyl-containing 1,3-diketones react with 1,2-diaminobenzene to form benzimidazoles **5** containing the unfluorinated substituent in position 2. The formation of 2-R^F-benzimidazoles **4** was observed only when the starting diketone contained two R^F groups (R^2 is fluoroalkyl)[7] or the cyclohexanone moiety ($R^1 + R^2 = -(CH_2)_4-$).[9]

The reaction of diketonate **1f** containing the cyclohexanone moiety with 1,2-diaminobenzene is accompanied by the ring opening and the formation of 2-(6-oxo-7,7,7-trifluoroheptyl)benzimidazole hydrate **6** (see Scheme 1, Table 1).[20] The opening of the cyclohexanone ring was observed in the reactions of 2-(polyfluoroacyl)cyclohexanones with 1,2-diaminoarenes under the same conditions, as well as after the treatment of 1-[*N*-(2-aminophenyl)amino]-2-trifluoroacetylcyclohexene with a mixture of AcOH and HCl, which afforded 2-(6-oxo-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluorododecyl)-benzimidazole and 2-(6,6-dioxy-7,7,7-trifluoroheptyl)-benzimidazole, respectively.[8,9]

11-Hydroxy-4-trifluoroacetyl-11-trifluoromethyl-1,2,3,4,10,11-hexahydro-5*H*-dibenzo[*b*,*e*][1,4]diazepine (**8**) and 1,3-dihydrospiro[benzimidazole-2,1′-cyclohexane] (**9**) were isolated in 10% and 24% yields, respectively, as the reaction products of enolate of the trifluoroacyl derivative of diketonate **1f** (triketonate **7**) with 1,2-diaminobenzene (Scheme 2).

Scheme 2

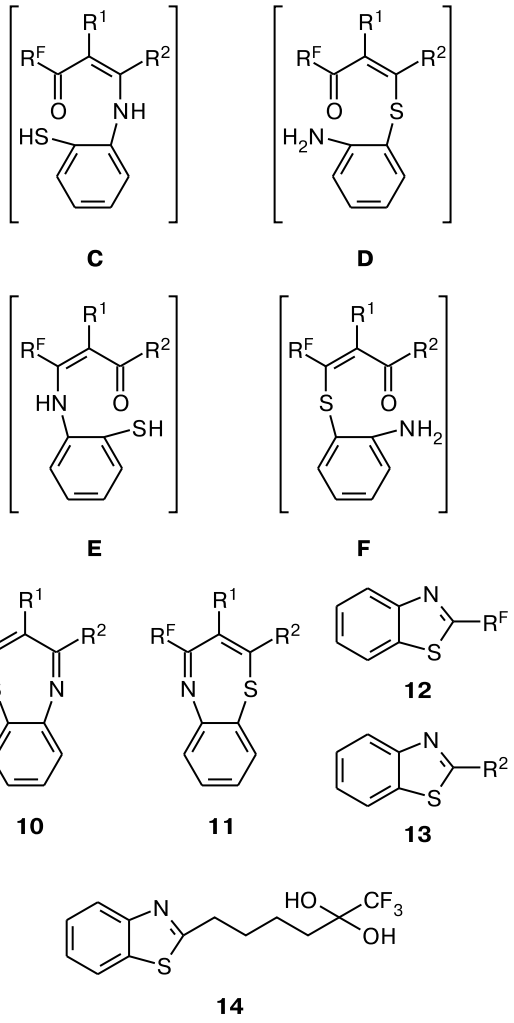


i. MeOH, 0→20 °C. 1) AcOH; 2)HCl_{conc}

The structure of compound **8** was confirmed by ^1H and ^{19}F NMR spectroscopy and mass spectrometry. The signals for the protons of the groups 11-OH and 10-NH (δ_H = 5.76 and 6.21, respectively, both are exchanged with CD_3COOD) and the chemical shifts of the fluorine nuclei of the trifluoromethyl group in position 11 of the heterocycle (δ_F = 83.09) correspond to the hemiaminal structure. The position of the NH signal of the enamino ketone moiety (δ_H = 13.3) in the ^1H NMR spectrum (acetone-d_6) indicates that it is involved in an intramolecular hydrogen bond and corresponds to the *U*-shaped structure of this moiety of the molecule. The mass spectrum has a peak of the molecular ion, whose fragmentation corresponds to structure **8**. Benzimidazole **9** is apparently formed as a result of the acid hydrolysis of diazepine **8** and the elimination of two trifluoroacetic acid molecules.

It should be noted that the reactions of "linear" (*i.e.*, those containing no cycloalkyl substituents) fluorinated 1,3,5-triketones with 1,2-diaminobenzene give exclusively 1,5-benzodiazepines.[21]

The reactions of lithium diketonates **1b,d,e** with 2-aminothiophenol can afford four isomeric products (**C**, **D**, **E**, and **F**), whose transformations can give 1,5-benzo[*b*]thiazepines **10** and **11** or benzothiazoles **12** and **13**. However, the reactions of diketonates **1b,d** with 2-aminothiophenol gave the only product, *viz.*, 2-phenyl-



benzothiazole **13** (R^2 = Ph), whereas the reaction of diketonate **1e** containing the cyclopentanone moiety with 2-aminothiophenol was accompanied by the ring opening to form 2-(5-oxo-6,6,6-trifluorohexyl)benzothiazole hydrate (**14**).

The possible pathway of the formation of compounds **6** and **14** is presented in Scheme 3.

The results of the condensation of fluoroalkyl-containing lithium diketonates **1** with 1,2-diaminoarenes and 2-aminothiophenol are determined not only by the structures of the reagents and the reaction conditions but also by the tendency of the reaction products to undergo further transformations. It should be noted that 3*H*-1,5-benzo[*b*]- and 3*H*-1,5-naphtho[2,3-*b*]diazepines **2** were synthesized only by the reactions of diketonates **1a,b,d,g—i** containing R^1 = H with 1,2-diaminoarenes. In other cases, the fragmentation of the carbon skeleton of the dicarbonyl or cycloalkanone moiety occurs to form 2-substituted benzimidazoles **4** and **6** and benzothiazoles **13** and **14**, respectively. The formation of the condensation products at one of the carbonyl groups (aminovinyl ketones), which were isolated in the reaction of 2-polyfluoroacylcyclohexanones with 1,2-diaminobenzene,[9] was not observed. Nevertheless, diketonates **1** act as synthetic equivalents of fluoroalkyl-containing diketones in the reactions under consideration.

Therefore, in spite of the fact that the condensation of lithium diketonates **1** with 1,2-diaminoarenes can follow different pathways, this reaction can be considered as a convenient method for the formation of fluoroalkyl-containing 3*H*-1,5-benzo[*b*]- and 3*H*-1,5-naphtho[2,3-*b*]-diazepines unsubstituted in position 3. The reactions of fluoroalkyl-containing lithium diketonates containing cycloalkanone moieties ($R^1 + R^2 = —(CH_2)_n—$) with 1,2-diaminobenzene and 2-aminothiophenol result in the opening of the carbocycle to form benzimidazole and benzothiazole derivatives **6** and **14**.

Experimental

Fluoroalkyl-containing lithium 1,3-diketonates **1** were synthesized according to a procedure described previously.[10] The names and characteristics of diketonates **1** were reported in the study.[19] Triketonate **7** was described in the study.[22]

The course of the reactions was monitored by TLC (Silufol UV-254, $CHCl_3$ as the eluent). The visualization of the spots was performed with the use of aqueous $KMnO_4$ solutions.

The ^1H, ^{19}F, and ^{13}C NMR spectra were recorded on Tesla BS-567A (80 MHz for ^1H and 75 MHz for ^{19}F), Bruker AC 200 (200 MHz for ^1H and 188 MHz for ^{19}F), and Bruker DRX-400 (400 MHz for ^1H, 376 MHz for ^{19}F, and 100 MHz for ^{13}C) spectrometers with the use of Me_4Si (^1H and ^{13}C) and C_6F_6 (^{19}F) as the internal standards. The IR spectra were recorded on a Spectrum I Fourier-transform infrared spectrometer (Perkin Elmer) in Nujol mulls. The mass spectrum (EI, 70 eV) was obtained on a Finnigan MAT-95 spectrometer.

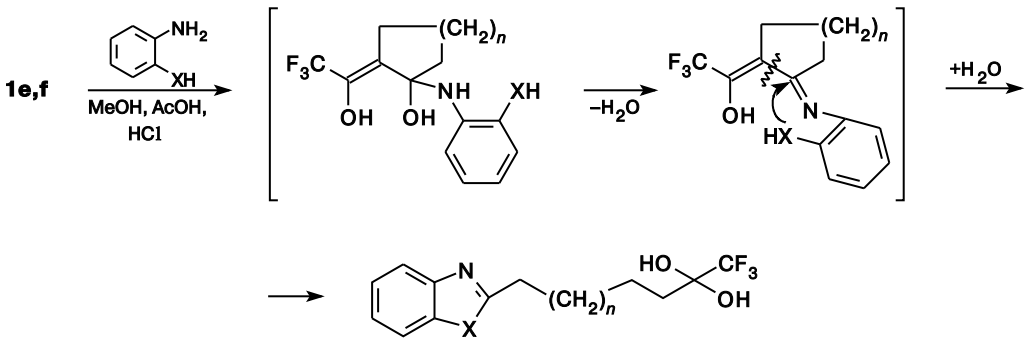
Reaction of diketonates 1 with diaminoarenes in glacial acetic acid. A mixture of equimolar amounts of diketonate **1** and diaminoarene in glacial AcOH (10 mL) was refluxed until the starting compounds were consumed (TLC monitoring). The reaction mixture was poured into water, and the precipitate that formed was filtered off, treated with sodium hydrocarbonate, dried, and recrystallized from MeOH or a mixture of chloroform and hexane (1 : 10).

The reactions of diketonates **1a,e—i** with 1,2-diaminobenzene, 2,3-diaminonaphthalene, and 2-aminothiophenol gave complex mixtures of products.

2-Difluoromethyl-5,6-difluorobenzimidazole (4a). Benzimidazole **4a** was synthesized from diketonate **1c** (0.77 g, 4.2 mmol) and 1,2-diamino-4,5-difluorobenzene (0.61 g, 4.2 mmol) in a yield of 0.5 g (58%). Colorless crystals, t.decomp. 161—162 °C. IR, ν/cm^{-1}: 1580, 1560 (C=N); 3019—3114 (NH). ^1H NMR ($CDCl_3$), δ: 7.12 (t, 1 H, HCF_2, $^2J_{H,F}$ = 53.5 Hz); 7.58 and 7.68 (both br.s, 1 H each, Ar); 12.50 (br.s, 1 H, NH). Found (%): C, 47.32; H, 1.81; F, 37.33; N, 13.79. $C_8H_4N_2F_4$. Calculated (%): C, 47.07; H, 1.98; F, 37.23; N, 13.72.

5,6-Difluoro-2-trifluoromethylbenzimidazole (4b). Benzimidazole **4b** was synthesized from diketonate **1d** (1.6 g, 6.9 mmol) and 1,2-diamino-4,5-difluorobenzene (1.0 g, 6.9 mmol) in a yield

Scheme 3



6,14

X = NH, *n* = 2 (**6**); X = S, *n* = 1 (**14**)

of 1.4 g (92%). Colorless crystals, m.p. 145—146 °C. IR, ν/cm^{-1}: 1580, 1560 (C=N); 3000—3300 (NH). ^{1}H NMR ($CDCl_3$), δ: 7.64 and 7.75 (both br.s, 1 H each, Ar); 12.96 (br.s, 1 H, NH). ^{19}F NMR ($CDCl_3$), δ: 99.60 (s, CF_3). Found (%): C, 43.32; H, 1.41; F, 42.33; N, 12.79. $C_8H_3N_2F_5$. Calculated (%): C, 43.26; H, 1.36; F, 42.77; N, 12.61.

2-Difluoromethyl-7,8-difluoro-4-phenyl-3*H*-1,5-benzodiazepine (2b). Benzodiazepine **2b** was synthesized from diketonate **1b** (0.6 g, 2.9 mmol) and 1,2-diamino-4,5-difluorobenzene (0.42 g, 2.9 mmol) in a yield of 0.6 g (67%). Colorless crystals, m.p. 123—124 °C. IR, ν/cm^{-1}: 1580, 1560 (C=N). ^{1}H NMR ($CDCl_3$), δ: 3.47 (br.s, 2 H, CH_2); 6.15 (t, 1 H, HCF_2, $^2J_{H,F}$ = = 55.0 Hz); 7.29—7.51 (m, 7 H, Ar). Found (%): C, 62.89; H, 3.39; F, 24.78; N, 9.17. $C_{16}H_{10}N_2F_4$. Calculated (%): C, 62.75; H, 3.29; F, 24.81; N, 9.14.

Reaction of diketonates 1 with 1,2-diaminobenzene and 2,3-diaminonaphthalene in a mixture of glacial acetic acid and hydrochloric acid. 1,2-Diaminoarene (0.01 mol) was added to a solution of diketonate **1** (0.01 mol) in methanol (10 mL). The reaction mixture was cooled to 0 °C. Then glacial AcOH (0.02 mol) and concentrated HCl (0.02 mol) were added. The reaction mixture was kept for 16 h. The precipitate that formed was filtered off, washed with sodium hydrocarbonate, dried, and recrystallized from hexane or methanol.

2-Difluoromethyl-4-methyl-3*H*-1,5-benzodiazepine (2a). Benzodiazepine **2a** was synthesized from diketonate **1a** (1.0 g, 7 mmol) and 1,2-diaminobenzene (0.76 g, 7 mmol) in a yield of 0.8 g (55%). Colorless crystals, m.p. 76—78 °C. IR, ν/cm^{-1}: 1630, 1585 (C=N). ^{1}H NMR ($CDCl_3$), δ: 2.38 (s, 3 H, Me); 2.97 (br.s, 2 H, CH_2); 6.18 (t, 1 H, HCF_2, $^2J_{H,F}$ = 55.2 Hz); 7.23—7.43 (m, 4 H, Ar). Found (%): C, 63.73; H, 4.85; F, 18.78; N, 13.48. $C_{11}H_{10}N_2F_2$. Calculated (%): C, 63.45; H, 4.84; F, 18.25; N, 13.45.

4-Methyl-2-(1,1,2,2-tetrafluoroethyl)-3*H*-1,5-benzodiazepine (2d). Benzodiazepine **2d** was synthesized from diketonate **1g** (1.0 g, 5.2 mmol) and 1,2-diaminobenzene (0.56 g, 5.2 mmol) in a yield of 0.9 g (67%). Colorless crystals, m.p. 109—110 °C (*cf.* lit. data[7]).

4-Phenyl-2-(1,1,2,2-tetrafluoroethyl)-3*H*-1,5-benzodiazepine (2e). The reaction of diketonate **1h** (1.0 g, 3.9 mmol) with 1,2-diaminobenzene (0.43 g, 3.9 mmol) gave benzodiazepine **2e** in a yield of 0.8 g (64%). Colorless crystals, m.p. 87 °C (*cf.* lit. data[7]).

4-Phenyl-2-trifluoromethyl-3*H*-1,5-benzodiazepine (2c). The reaction of diketonate **1d** (1.0 g, 4.5 mmol) with 1,2-diaminobenzene (0.48 g, 4.5 mmol) gave benzodiazepine **2c** in a yield of 0.89 g (72%). Colorless crystals, m.p. 83—84 °C. The ^{1}H NMR spectroscopic data and m.p. are consistent with those published in the study.[23] IR, ν/cm^{-1}: 1611, 1590 (C=N).

2-Nonafluorobutyl-4-phenyl-3*H*-1,5-benzodiazepine (2f). The reaction of diketonate **1i** (0.9 g, 2.4 mmol) with 1,2-diaminobenzene (0.26 g, 2.4 mmol) gave benzodiazepine **2f** in a yield of 0.7 g (67%). Colorless crystals, m.p. 78—79 °C. IR, ν/cm^{-1}: 1620, 1590 (C=N). ^{1}H NMR ($CDCl_3$), δ: 3.49 (br.s, 2 H, CH_2); 7.35—8.11 (m, 9 H, Ar). Found (%): C, 52.27; H, 2.42; F, 38.96; N, 6.24. $C_{19}H_{11}N_2F_9$. Calculated (%): C, 52.07; H, 2.53; F, 39.01; N, 6.39.

11-Hydroxy-4-trifluoroacetyl-11-trifluoromethyl-1,2,3,4,10,11-hexahydro-5*H*-dibenzo[*b*,*e*][1,4]diazepine (8) and 1,3-dihydrospiro[benzimidazole-2,1′-cyclohexane] (9). Glacial AcOH (1 mL) was added with stirring to a cold (0 °C) solution of the dilithium salt of triketone **7** (1.70 g, 5.6 mmol) and 1,2-diaminobenzene (0.61 g, 5.6 mmol) in methanol (10 mL). The reaction mixture was stirred at this temperature for 5 min. Then concentrated HCl (5 mL) was added dropwise. The reaction mixture was stirred at room temperature for 16 h. The resulting system (a yellow precipitate in an orange solution) was poured into ice water (100 mL), and the reaction mixture was brought to pH = 10 with a 30% NaOH solution. The precipitate that formed was filtered off, washed on the filter with water (5 mL), dried, and recrystallized from a heptane—toluene system (3 : 2). Compound **8** was obtained in a yield of 200 mg (10 %). Yellow crystals, m.p. 210—212 °C. ^{1}H NMR (acetone-d_6), δ: 1.43 and 1.83 (both m, 1 H each, CH_2); 2.00—2.18 (m, 2 H, CH_2); 2.35—2.51 (m, 2 H, CH_2); 3.22 (t, 1 H, *CH, $^3J_{H,H}$ = 6.4 Hz); 5.76 and 6.21 (both s, 1 H each, OH, 10-NH); 7.23 (m, 4 H, Ar); 13.3 (br.s, 1 H, 5-NH). The signals at δ 5.76, 6.21, and 13.3 disappeared after the addition of CD_3COOD. ^{19}F NMR (acetone-d_6), δ: 83.09 (s, 3 F, 11-CF_3); 90.14 (s, 3 F, $COCF_3$). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 380 $[M]^+$ (100); 362 $[M - H_2O]^+$ (84); 311 $[M - CF_3]^+$ (80); 293 $[M - CF_3 - H_2O]^+$ (98); 283 $[M - COCF_3]^+$ (22); 265 $[M - COCF_3 - H_2O]^+$ (24). Found (%): C, 50.75; H, 3.84. $C_{16}H_{14}F_6N_2O_2$. Calculated (%): C, 50.53; H, 3.71.

The filtrate was extracted with $CHCl_3$ (2×10 mL). The combined extracts were dried with $MgSO_4$ and concentrated. The oily residue rapidly crystallized. The residue was purified by recrystallization from heptane. (1,3-Dihydrospiro[benzimidazole-2,1′-cyclohexane]) (**9**) was obtained in a yield of 250 mg (24%). Yellowish crystals, m.p. 139—140 °C. The ^{1}H NMR spectroscopic data and m.p. are consistent with the data published in the literature.[24]

2-Difluoromethyl-4-phenyl-3*H*-1,5-naphtho[2,3-*b*]diazepine (3a). The reaction of diketonate **1b** (0.5 g, 2.5 mmol) with 2,3-diaminonaphthalene (0.4 g, 2.5 mmol) gave compound **3a** in a yield of 0.7 g (90%). Colorless crystals, m.p. 122—123 °C. IR, ν/cm^{-1}: 1640, 1625 (C=N). ^{1}H NMR ($CDCl_3$), δ: 4.79 (br.s, 2 H, CH_2); 6.60 (t, 1 H, HCF_2, $^2J_{H,F}$ = 53.5 Hz); 7.31—7.73 (m, 11 H, Ar). Found (%): C, 75.15; H, 4.38; F, 11.80; N, 8.69. $C_{20}H_{14}N_2F_2$. Calculated (%): C, 75.01; H, 4.40; F, 11.86; N, 8.74.

4-Phenyl-3-trifluoromethyl-3*H*-1,5-naphtho[2,3-*b*]diazepine (3b). The reaction of diketonate **1d** (1.0 g, 4.5 mmol) with 2,3-diaminonaphthalene (0.71 g, 4.5 mmol) gave compound **3b** in a yield of 1.02 g (79%). Colorless crystals, m.p. 154 °C. IR, ν/cm^{-1}: 1666, 1599 (C=N). ^{1}H NMR ($CDCl_3$), δ: 3.56 (br.s, 2 H, CH_2); 7.53—8.13 (m, 11 H, Ar). Found (%): C, 70.84; H, 3.80; F, 17.03; N, 8.28. $C_{20}H_{13}N_2F_3$. Calculated (%): C, 71.01; H, 3.87; F, 16.85; N, 8.28.

Reaction of lithium 4,4-difluoro-1-phenylbutane-1,3-dionate (1b) with 2-aminothiophenol. 2-Aminothiophenol (0.61 g, 4.9 mmol) was added to a solution of diketonate **1b** (1 g, 4.9 mmol) in methanol. The reaction mixture was cooled to 0 °C. Then glacial AcOH (0.42 g, 7 mmol) and concentrated HCl (0.26 g, 7 mmol) were added. The reaction mixture was kept for 16 h. The precipitate that formed was filtered off, treated with sodium hydrocarbonate, dried, and recrystallized from hexane. 2-Phenylbenzothiazole (**13**) was obtained in a yield of 0.9 g (87%), m.p. 113 °C (*cf.* lit. data[25]). IR, ν/cm^{-1}: 1589 (C=N). ^{1}H NMR, δ: 7.37—8.10 (m, Ar).

Reaction of lithium 4,4,4-trifluoro-1-phenylbutane-1,3-dionate (1d) with 2-aminothiophenol. The similar reaction of diketonate **1d** (1 g, 4.5 mmol) with 2-aminothiophenol (0.56 g, 4.5 mmol)

afforded 2-phenylbenzothiazole (**13**) in a yield of 0.9 g (95%), m.p. 111 °C. The IR spectrum is identical to the IR spectrum of the compound prepared in the previous experiment.

Reaction of lithium 2-trifluoroacetylcyclopentanoate (1e) with 2-aminothiophenol. The similar reaction of diketonate **1e** (0.9 g, 5 mmol) with 2-aminothiophenol (0.63 g, 5 mmol) afforded 2-(5,5-dihydroxy-6,6,6-trifluorohexyl)benzothiazole in a yield of 1.46 g (96%) (**14**). M.p. 104—105 °C. Found (%): C, 51.98; H, 4.64; N, 4.20; F, 18.63; S, 10.03. $C_{13}H_{14}N F_3O_2S$. Calculated (%):C, 51.14; H, 4.62; N, 4.58; F, 18.67; S, 10.50. IR, ν/cm^{-1}: 3363.60 (OH). ^{1}H NMR (DMSO-d_6), δ: 1.52—1.59, 1.67—1.71, and 1.80—1.86 (all m, 2 H each, three CH_2 groups); 3.12 (t, 2 H, CH_2, J = 7.5 Hz); 6.64 (s, 2 H, OH); 7.36—7.38, 7.46—7.49, 7.82—7.86, and 7.96—7.98 (all m, 1 H each, Ar). ^{19}F NMR, δ: 82.48 (s, CF_3).

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References

1. K. I. Pashkevich, V. I. Saloutin, I. Ya. Postovskii, *Usp. Khim.*, 1981, **50**, 325 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1981, **50**].
2. *Comprehensive Organic Chemistry: the Synthesis and Reactions of Organic Compounds*, Eds D. Barton, W. D. Ollis, Vol. **4**, *Heterocyclic Compounds*, Ed. P. G. Sammes, Pergamon Press, Oxford—New York, 1979.
3. *Fluorine Compounds. Synthesis and Application*, Ed. N. Ishikawa, Kodansha, Tokyo, 1986.
4. *Modern Application Technology of Fluorine Compounds*, Ed. N. Ishikawa, CCMC, Tokyo, 1981.
5. G. G. Furin, *Ftorsoderzhashchie geterotsiklicheskie soedineniya* [*Fluorine-Containing Heterocyclic Compounds*], Ed. G. A. Tolstikov, Nauka, Novosibirsk, 2001, pp. 304 (in Russian).
6. G. A. Archer, L. H. Sternbach, *Chem. Rev.*, 1968, **68**, 747.
7. K. I. Pashkevich, V. I. Saloutin, I. Ya. Postovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1172 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1980, **29**].
8. K. I. Pashkevich, D. V. Sevenard, O. G. Khomutov, *Zh. Org. Khim.*, 1998, **34**, 1878 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 1998, **34**, 1804].
9. K. I. Pashkevich, D. V. Sevenard, O. G. Khomutov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 562 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1999, **48**, 557].
10. V. I. Filyakova, N. S. Karpenko, O. A. Kuznetsova, K. I. Pashkevich, *Zh. Org. Khim.*, 1998, **34**, 411 [*Russ. J. Org. Chem.* (*Engl.Transl.*), 1998, **34**, 381].
11. V. I. Filyakova, O. A. Kuznetsova, E. N. Ulomskii, T. V. Rybalova, Yu. V. Gatilov, M. I. Kodess, V. L. Rusinov, K. I. Pashkevich, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 313 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 332].
12. O. A. Kuznetsova, V. I. Filyakova, K. I. Pashkevich, E. N. Ulomskii, P. V. Plekhanov, G. L. Rusinov, M. I. Kodess, V. L. Rusinov, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 1127 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 1190].
13. N. S. Karpenko, V. I. Filyakova, E. G. Matochkina, M. I. Kodes, K. I. Pashkevich, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 1149 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 1215].
14. N. S. Boltacheva, V. I. Filyakova, V. N. Charushin, *Zh. Org. Khim.*, 2005, **41**, 1483 [*Russ. J. Org. Chem.* (*Engl. Transl.*), 2005, **41**, 1452].
15. N. S. Boltachova, O. V. Fedorova, I. G. Ovchinnikova, O. N. Kazheva, A. N. Chekhlov, O. A. Dyachenko, G. L. Rusinov, V. I. Filyakova, V. N. Charushin, *J. Fluor. Chem.*, 2007, **128**, 762.
16. V. I. Filyakova, O. A. Kuznetsova, N. S. Karpenko, P. A. Slepukhin, V. N. Charushin, in *Karbonil´nye soedineniya v sinteze geterotsiklov* [*Carbonyl Compounds in Heterocyclic Synthesis*], Nauchnaya kniga, Saratov, 2004, p. 288 (in Russian).
17. O. A. Kuznetsova, Ph. D. (Chem.) Thesis, I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, Ekaterinburg, 2002 (in Russian).
18. N. S. Karpenko, Ph. D. (Chem.) Thesis, I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, Ekaterinburg, 2004 (in Russian).
19. N. S. Boltacheva, V. I. Filyakova, E. F. Khmara, O. V. Koryakova, V. N. Charushin, *Ros. Khim. Zh.* (*Zh. Vsesoyuz. Khim. Obshch. im. D. I. Mendeleeva*), 2009, **53**, No. 1, 54 [*Mendeleev Chem. J.*, 2009, **53**, No. 1].
20. D. V. Sevenard, O. G. Khomutov, N. S. Boltachova, V. I. Filyakova, V. Vogel, E. Lork, V. Ya. Sosnovskikh, V. O. Iaroshenko, G.-V. Röschenthaler, *Z. Naturforsch.*, 2009, **64b**, 541.
21. D. S. Yachevskii, D. L. Chizhov, M. I. Kodess, K. I. Pashkevich, *Monatsh. Chem.*, 2004, **135**, 23.
22. D. V. Sevenard, O. Kazakova, D. L. Chizhov, D. S. Yachevskii, E. Lork, J. Poveleit, V. N. Charushin, G.-V. Röschenthaler, *Helv. Chim. Acta*, 2007, **90**, 369.
23. H. G. Bonacorso, L. M. L. Marques, N. Zanatta, M. A. Pinto Martins, *Synth. Commun.*, 2002, **32**, 3225.
24. J. T. Kuethe, J. Varon, K. G. Childers, *Tetrahedron*, 2007, **63**, 11489.
25. *Beilstein's Handbuch der organischen Chemie*, 1937, **27**, 74.

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