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Dedicated to Full Member of the Russian Academy of Sciences N.S. Zefirov on His 70th Anniversary

Fluoroalkyl-Containing Lithium 1,3-Diketonates in Reactions with Amines and Ammonium Salts

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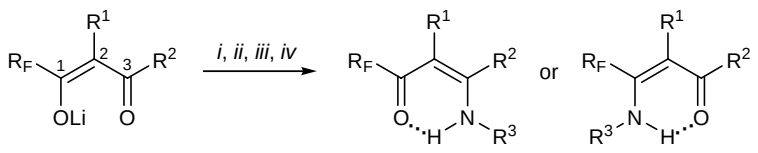
Abstract—Reactions of fluoroalkyl-containing lithium 1,3-diketonates with amines or ammonium salts in glacial acetic acid or methanol at 20°C provide an efficient synthetic route to fluoroalkyl-containing β-aminovinyl ketones. Depending on the conditions, reactions of lithium diketonates with 1-aminonaphthalene lead to formation of both β-aminovinyl ketones and cyclocondensation products, benzo[*h*]quinolines. The latter can be obtained in one step without isolation of β-aminovinyl ketones.

Fluorine-containing lithium 1,3-diketonates **I** are valuable and convenient synthons. They are readily accessible, stable on storage, and highly reactive. Effective methods for the synthesis of functionally substituted fluoroalkyl compounds and heterocycles have been developed using lithium diketonates **I** as starting compounds [1–5]. We previously demonstrated [1] some prospects in using lithium diketonates **I** for the preparation of fluoroalkyl-containing β-aminovinyl ketones as efficient complexing agents, catalysts, and synthons [6–10].

Fluorine-containing aminovinyl ketones are generally prepared by condensation of 1,3-diketones with ammonia and amines. However, this reaction is accompanied by formation of salts, retro-decomposition, and secondary condensations [11]. The use of lithium diketonates **I** instead of 1,3-diketones makes it possible to eliminate stages of isolation and purification of the latter and a number of concurrent reactions. Insofar as lithium diketonates like **I** possess two nonequivalent electrophilic centers, C^1 and C^3, the condensation could give rise to one or both regioisomeric products **II** and **III**. Furthermore, reactions of diketonates **I** with aromatic amines can be followed by intramolecular ring closure. Therefore, while developing an efficient procedure for the synthesis of fluoroalkyl-containing aminovinyl ketones and fused nitrogen-containing heterocycles, it was very important to elucidate the regioselectivity of reactions of lithium diketonates **I** with amines and ammonium salts.

In the present work we examined the formation of regioisomeric fluoroalkyl-containing aminovinyl

Scheme 1.



Ia–Ii **IIa–IIp** **IIIa–IIIn**

Ia–**Id**, **IIa**, **IIh**, **IIi**, **IIIa**, **IIIb**, **IIId**–**IIIg**, $R_F = F_2CH$; **Ie**–**Ih**, **IIc**–**IIe**, **IIk**–**IIn**, **IIIc**, **IIIh**–**IIIn**, $R_F = CF_3$; **Ii**, **IIb**, **IIj**, $R_F = F_2CHCF_2$; **Ij**, **IIf**, **IIo**, **IIp**, $R_F = C_4F_9$; **Ik**, **IIg**, $R_F = C_6F_{13}$; **Ia**–**Ic**, **Ie**, **If**, **Ii**–**Io**, **IIa**–**IIc**, **IIh**, **IIj**–**IIl**, **IIo**, **IIp**, **IIIa**–**IIIn**, R^1 = H; **Ia**, **Ie**, **Ii**, **Ij**, **IIa**–**IIc**, **IIf**, **IIh**, **IIj**–**IIl**, **IIo**, R^2 = Me; **Ib**, **IIIa**, R^2 = *t*-Bu; **Ic**, **If**, **Ik**, **Io**, **IIg**, **IIp**, **IIIb**–**IIIh**, R^2 = Ph; **Il**, **IIIi**, R^2 = 4-ClC_6H_4; **Im**, **IIIj**, R^2 = 4-MeC_6H_4; **In**, **IIIn**, $R^2 = CF_3$; **Id**, **Ig**, **IId**, **IIi**, **IIm**, $R^1R^2 = (CH_2)_3$; **Ih**, **IIe**, **IIn**, $R^1R^2 = (CH_2)_4$; **IIa**–**IIg**, **IIIa**–**IIIc**, R^3 = H; **IIk**, **IIId**, R^3 = Ph; **IIIe**, R^3 = 3,4-$Cl_2C_6H_3$; **IIh**–**IIj**, **IIl**–**IIp**, **IIIf**, **IIIh**–**IIIn**, R^3 = 1-naphthyl; **IIIg**, R^3 = 9-carbazolyl. Reagents and conditions: *i*: NH_4HCO_3, MeOH; *ii*: NH_4OAc, MeOH; *iii*: $PhNH_2 \cdot HCl$, MeOH; *iv*: R^3NH_2, AcOH.

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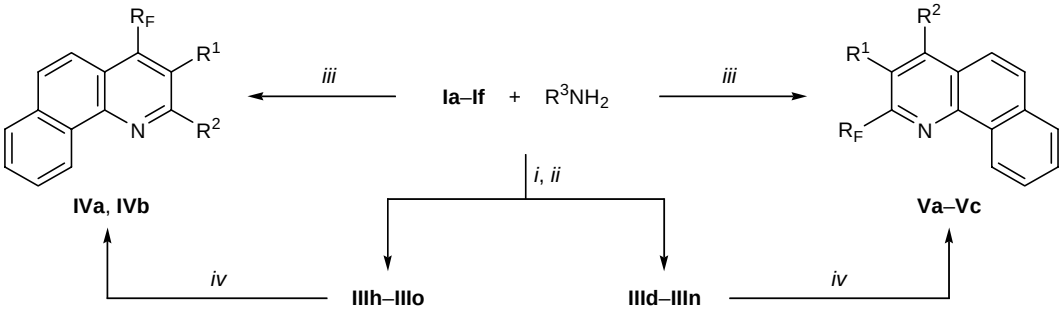
Scheme 2.



IVa, **Va**, $R_F = F_2CH$; **IVb**, **Vb**, **Vc**, $R_F = CF_3$; **IVa**, **IVb**, **Va**–**Vc**, R^1 = H; **IVa**, **IVb**, R^2 = Me; **Va**, **Vb**, R^2 = Ph; **Vc**, $R^2 = CF_3$; R^3 = 1-naphthyl, 9-carbazolyl. Reagents and conditions: *i*: $PhNH_2 \cdot HCl$, MeOH; *ii*: R^3NH_2, AcOH; *iii*: 1-aminonaphthalene, trifluoroacetic acid, reflux; *iv*: trifluoroacetic acid, reflux.

ketones and products of their cyclocondensation in reactions of lithium diketonates **I** with ammonium hydrogen carbonate or acetate, aromatic amines, and aromatic amine hydrochlorides. The reactions of lithium diketonates **Ia**–**Ii** with NH_4HCO_3 or NH_4OAc afforded regioisomeric aminovinyl ketones **IIa**–**IIg** or **IIIa**–**IIIc** in 44–93% yield (Scheme 1). Regardless of the length of the fluoroalkyl group in initial lithium diketonate **I** [R^1 = H, R^2 = Alk or $R^1R^2 = (CH_2)_3$, $(CH_2)_4$], the major condensation products were unsaturated ketones **IIa**–**IIf** in which the amino group was attached to the β-carbon atom with respect to the carbonyl group (lithium diketonate **Ib** was an exception). When $R^F = F_2CH$ or CF_3, R^1 = H, and R^2 = Ph, the major products were ketones **IIIa**–**IIIc** with the amino group and fluoroalkyl substituent located at contiguous carbon atoms. The ^{1}H NMR spectra of aminovinyl ketones with R^3 = H allowed us to reliably assign them structure **II** or **III**. The spectra of isomers **II** contain two broadened one-proton signals at δ 6.6–6.8 and 10 ppm from nonequivalent protons in the NH_2 group; one of these protons is involved in intramolecular hydrogen bond. Compounds **III** showed in the ^{1}H NMR spectra one broadened two-proton signal at δ 7.0–8.0 ppm [6]. Most products **II** and **III** were identified by comparing with authentic samples which were prepared by condensation of fluoroalkyl-containing 1,3-diketones with ammonia [11] or ammonium acetate [12] or of fluorinated nitriles with methyl ketones [13].

By reactions of lithium diketonates **Ia**–**If** with an equimolar amount of aniline hydrochloride in methanol and of aniline, 1-aminonaphthalene, or 9-aminocarbazole in glacial acetic acid at 20°C we obtained regioisomeric N-substituted ketones **IIh**–**IIp** or **IIId**–**IIIn** (Scheme 1). However, the product structure could not be determined unambiguously on the basis of their IR and ^{1}H NMR spectra. Therefore, condensation products of lithium diketonates **I** with aryl- and hetarylamines were subjected to transamination [14]. Treatment of N-substituted compounds **IIh**, **IIl**, **IIIf**, and **IIIg** with ammonia led to formation of the corresponding primary amines **IIa**, **IIc**, **IIIb**, and **IIIc** which were compared with authentic samples prepared as described above or by the procedures reported previously in [11–13].

Comparison of the ^{1}H NMR spectra of the *N*-aryl- and *N*-hetaryl-substituted aminovinyl ketones synthesized in the present work with those prepared previously [11] showed that the olefinic proton signal of isomers **II** (R^2 = Ph) is located at δ 5.40–5.90 ppm and that the corresponding signal of ketones **III** appears in a weaker field, at δ 6.40–6.60 ppm. Thus the position of the CH= proton signal can be used to distinguish isomeric aminovinyl ketones **II** and **III**.

Reactions of lithium diketonates **I** with aniline or 1-aminonaphthalene in boiling acetic acid resulted in formation of complex mixtures of products, among which only the corresponding ammonium acetates were isolated. Lithium diketonates **Ia**–**If** failed to react with aniline in boiling trifluoroacetic acid since the aromatic amine was deactivated due to formation of anilinium trifluoroacetate. Reactions of lithium diketonates **Ia**, **Ic**–**If**, and **In** with less basic 1-aminonaphthalene under analogous conditions afforded the corresponding cyclocondensation products: fluoroalkyl-containing benzo[*h*]quinolines **IVa** and **IVb** or **Va**–**Vc**. The absence of carbonyl absorption bands (1550–1630 cm^{-1}) in the IR spectra and signals from the olefinic (δ 5.5–6.7 ppm) and NH protons (δ 12.0–13.0 ppm) in the ^{1}H NMR spectra of the products, as well as the presence in their ^{1}H NMR spectra of a singlet at δ 8.00–8.50 ppm due to proton in heteroaromatic

ring, indicated that intramolecular ring closure occurred. The structure of isomeric benzo[*h*]quinolines **IV** and **V** was determined by comparing their spectral parameters with those of benzo[*h*]quinolines prepared from the corresponding *N*-naphthyl-substituted ketones **IIh** and **Ill** or **IIIf**, **IIIh**, and **IIIn** (Scheme 2).

Thus we have shown that fluoroalkyl-containing aminovinyl ketones can be synthesized by reaction of lithium 1,3-diketonates **I** with amines (or ammonium salts) in glacial acetic acid or methanol at 20°C. The use of lithium diketonates **I** instead of the corresponding 1,3-diketones increases the reaction selectivity and product yields due to elimination of side salt formation, retro-decomposition, and secondary condensation processes [11].

The formation of one or another or both regioisomeric aminovinyl ketones differing by mutual arrangement of the amino group and fluoroalkyl substituent is determined by the nature of R_F, R^1, and R^2 groups in initial lithium diketonate **I** and R^3 group in the amine; the regioselectivity of this reaction conforms to the general relations found previously for reactions of 1,3-diketones with ammonia and amines [11] and ammonium salts [12]. The reaction of lithium diketonates **I** with 1-aminonaphthalene, depending on the conditions, gives either the corresponding aminovinyl ketones or cyclocondensation products, benzo[*h*]quinolines **IV** and **V**. The latter can also be obtained in one step without isolation of intermediate aminovinyl ketone. The examined reactions may be regarded as effective methods for the synthesis of compounds **II**–**V**.

EXPERIMENTAL

The ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on Tesla BS-567A (80 MHz for ^{1}H and 75 MHz for ^{19}F) and Bruker DRX-400 spectrometers (400 MHz for ^{1}H, 376 MHz for ^{19}F, and 100 MHz for ^{13}C) using $CDCl_3$ as solvent and tetramethylsilane (^{1}H and ^{13}C) or C_6F_6 (^{19}F) as internal reference. The IR spectra were measured on a Perkin–Elmer Spectrum I Fourier spectrometer from samples dispersed in mineral oil. The progress of reactions was monitored by TLC on Silufol UV-254 plates using chloroform as eluent; spots were visualized by treatment with aqueous solutions of copper acetate and potassium permanganate. Silica gel L (100–250 μm) was used for column chromatography (eluent $CHCl_3$). Initial lithium diketonates **I** were prepared by the procedure described in [1].

General procedure for the synthesis of aminovinyl ketones IIa–IIg and IIIa–IIIc (R^3 = H). A mixture of 0.01 mol of lithium diketonate **I** and 0.02 mol of ammonium hydrogen carbonate or ammonium acetate in 10 ml of methanol or glacial acetic acid was kept at 20°C until the initial compound disappeared (TLC). The mixture was poured into water, the precipitate was filtered off, and the filtrate was extracted with chloroform. The extract was evaporated, and the residue was combined with the precipitate and recrystallized from chloroform–hexane (1:10).

4-Amino-1,1-difluoro-3-penten-2-one (IIa). Yield 79%, colorless crystals, mp 44–45°C [12].

5-Amino-1,1,2,2-tetrafluoro-4-hexen-3-one (IIb). Yield 63%, colorless crystals, mp 61.5–62.5°C [15].

4-Amino-1,1,1-trifluoro-3-penten-2-one (IIc). Yield 76%, colorless crystals, mp 86°C [16].

1-Amino-2-trifluoroacetylcyclopentene (IId). Yield 62%, colorless crystals, mp 100 °C. IR spectrum, ν, cm^{-1}: 1600 (C=O); 3100, 3290 (NH). ^{1}H NMR spectrum, δ, ppm: 1.89–1.97, 2.58–2.6, 2.72–2.76 m (6H, CH_2); 5.94 br.s (1H, NH); 9.01 br.s (1H, NH). ^{19}F NMR spectrum: δ_F 86.11 ppm, s (CF_3). Found, %: C 47.13; H 4.52; F 31.65; N 7.89. $C_7H_8F_3NO$. Calculated, %: C 46.93; H 4.50; F 31.82; N 7.82.

1-Amino-2-trifluoroacetylcyclohexene (IIe). Yield 44%, colorless crystals, mp 140–141°C. IR spectrum, ν, cm^{-1}: 1590 (C=O); 3150, 3300 (NH). ^{1}H NMR spectrum, δ, ppm: 1.63–1.72, 2.39–2.49 m (8H, CH_2); 5.40 br.s (1H, NH); 10.32 br.s (1H, NH). ^{19}F NMR spectrum: δ_F 89.05 ppm, s (CF_3). ^{13}C NMR spectrum, δ_C, ppm: 21.11 s (C^5), 21.83 q (C^3, $^4J_{CF}$ = 3.7 Hz), 22.88 q (C^4, $^5J_{CF}$ = 0.9 Hz), 31.35 s (C^6), 97.89 s (C^2), 117.98 q (CF_3, $^1J_{CF}$ = 290.5 Hz), 166.92 s (C^1), 177.22 q (C=O, $^2J_{CF}$ = 31.6 Hz). Found, %: C 49.68; H 5.20; F 29.50; N 7.28. $C_8H_{10}F_3NO$. Calculated, %: C 49.74; H 5.22; F 29.50; N 7.25.

2-Amino-5,5,6,6,7,7,8,8,8-nonafluoro-2-octen-4-one (IIf). Yield 93%, colorless crystals, mp 97°C. IR spectrum, ν, cm^{-1}: 1600 (C=O); 3140, 3280 (NH). ^{1}H NMR spectrum, δ, ppm: 2.11 s (3H, Me), 5.43 s (1H, =CH), 6.14 br.s (1H, NH), 10.10 br.s (1H, NH). Found, %: C 31.72; H 2.00; F 56.12; N 4.63. $C_8H_6F_9NO$. Calculated, %: C 31.70; H 1.99; F 56.41; N 4.62.

1-Amino-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-1-phenyl-1-pentadecen-3-one (IIg). Yield 89%, colorless crystals, mp 76–77°C. IR spectrum, ν, cm^{-1}: 1607 (C=O); 3196, 3356 (NH). ^{1}H NMR spectrum, δ, ppm: 5.84 s (1H, =CH), 6.15 br.s (1H, NH), 10.29 br.s (1H, NH), 7.48–7.62 m (5H, Ph). ^{19}F NMR spectrum, δ_F, ppm: 35.72–36.06 m (2F, CF_2), 39.43–40.30 m (6F,

CF_2), 41.81–42.14 m (2F, CF_2), 81.07 t (3F, CF_3, J_{FF} = 9.8 Hz). Found, %: C 38.48; H 1.93; F 52.68; N 2.94. $C_{15}H_8F_{13}NO$. Calculated, %: C 38.73; H 1.73; F 53.09; N 3.01.

2-Amino-1,1-difluoro-5,5-dimethyl-2-hexen-4-one (IIIa). Yield 91%, colorless crystals, mp 58–59°C. IR spectrum, ν, cm^{-1}: 1640 (C=O); 3185–3370 (NH). ^1H NMR spectrum, δ, ppm: 1.15 s (9H, *t*-Bu), 5.47 s (1H, =CH), 6.00 t (1H, HCF_2, $^2J_{HF}$ = 55.1 Hz), 7.26 br.s (2H, NH). ^{19}F NMR spectrum: δ_F 39.66 ppm, d (HCF_2, $^2J_{HF}$ = 55.1 Hz). Found, %: C 54.12; H 7.39; F 21.52; N 7.84. $C_8H_{13}F_2NO$. Calculated, %: C 54.23; H 7.39; F 21.44; N 7.90.

3-Amino-4,4-difluoro-1-phenyl-2-buten-1-one (IIIb). Yield 83%, colorless crystals, mp 60 °C [1].

3-Amino-4,4,4-trifluoro-1-phenyl-2-buten-1-one (IIIc). Yield 50%, colorless crystals, mp 80–81°C [1].

General procedure for the synthesis of *N*-phenyl-substituted aminovinyl ketones IIk and IIId. A solution of 0.01 mol of lithium diketonate **I** and 0.01 mol of aniline hydrochloride in 10 ml of methanol was kept at 20°C until the initial compounds disappeared (TLC). The mixture was poured into water, and the precipitate was filtered off and recrystallized from hexane.

1,1,1-Trifluoro-4-phenylamino-3-penten-2-one (IIk). Yield 91%, colorless crystals, mp 60–61°C [1].

4,4-Difluoro-1-phenyl-3-phenylamino-2-buten-1-one (IIId). Yield 81%, colorless crystals, mp 54–55°C. IR spectrum, ν, cm^{-1}: 1610 (C=O), 3350 (NH). ^1H NMR spectrum, δ, ppm: 6.32 t (1H, HCF_2, $^2J_{HF}$ = 53.1 Hz), 6.40 s (1H, =CH), 12.46 br.s (1H, NH), 7.25–7.99 m (10H, H_{arom}). ^{19}F NMR spectrum: δ_F 44.62 ppm, d (HCF_2, $^2J_{HF}$ = 53.1 Hz). Found, %: C 70.35; H 4.68; F 13.80; N 5.06. $C_{16}H_{13}F_2NO$. Calculated, %: C 70.32; H 4.80; F 13.90; N 5.13.

General procedure for the synthesis of *N*-aryl- and *N*-hetaryl-substituted aminovinyl ketones IIh–IIp and IIId–IIIn. A solution of 0.01 mol of lithium diketonate **I** and 0.01 mol of the corresponding amine in 10 ml of glacial acetic acid was kept at 20°C until the initial compounds disappeared (TLC). The mixture was poured into water, and the precipitate was filtered off and recrystallized from hexane.

1,1-Difluoro-4-(1-naphthylamino)-3-penten-2-one (IIh). Yield 89%, colorless crystals, mp 102–103°C. IR spectrum, ν, cm^{-1}: 1610 (C=O), 3350 (NH). ^1H NMR spectrum, δ, ppm: 2.00 s (3H, Me), 5.65 s (1H, =CH), 5.88 t (1H, HCF_2, $^2J_{HF}$ = 55.6 Hz), 7.32–7.96 m (7H, H_{arom}), 12.87 br.s (1H, NH). ^{19}F NMR spectrum: δ_F 36.84 ppm, d (HCF_2, $^2J_{HF}$ = 55.6 Hz). Found, %: C 69.16; H 5.02; F 14.30; N 5.49. $C_{15}H_{13}F_2NO$. Calculated, %: C 68.96; H 5.02; F 14.54; N 5.36.

2-Difluoroacetyl-1-(1-naphthylamino)cyclopentene (IIi). Yield 70%, colorless crystals, mp 67–68 °C. IR spectrum, ν, cm^{-1}: 1600 (C=O), 3270 (NH). ^1H NMR spectrum, δ, ppm: 1.88–1.96 m, 2.67–2.70 m, and 2.82–2.86 m (6H, CH_2); 6.00 t (1H, HCF_2, $^2J_{HF}$ = 54.6 Hz); 7.30–8.09 m (7H, H_{arom}); 12.15 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 22.85 s (C^4); 27.39 t (C^3, $^4J_{CF}$ = 2.8 Hz); 32.89 s (C^5); 104.79 s (C^2); 111.51 t (HCF_2, $^1J_{CF}$ = 250.1 Hz); 171.81 s (C^1); 181.81 t (C=O, $^2J_{CF}$ = 23.9 Hz); 120.80, 121.99, 125.20, 126.74, 126.88, 127.15, 128.21, 128.38, 134.19, 134.76 (naphthyl). ^{19}F NMR spectrum: δ_F 36.09 ppm, d (HCF_2, $^2J_{HF}$ = 54.6 Hz). Found, %: C 71.22; H 5.33; F 13.20; N 4.83. $C_{17}H_{15}F_2NO$. Calculated, %: C 71.07; H 5.26; F 13.22; N 4.87.

1,1,2,2-Tetrafluoro-5-(1-naphthylamino)-4-hexen-3-one (IIj). Yield 78%, colorless crystals, mp 80°C [11].

1,1,1-Trifluoro-4-(1-naphthylamino)-3-penten-2-one (IIl). Yield 86%, colorless crystals, mp 39°C [11].

1-(1-Naphthylamino)-2-trifluoroacetylcyclopentene (IIm). Yield 75%, colorless crystals, mp 65°C. IR spectrum, ν, cm^{-1}: 1610 (C=O), 3440 (NH). ^1H NMR spectrum, δ, ppm: 1.88–1.95 m, 2.67–2.70 m, and 2.83–2.87 m (6H, CH_2); 7.30–8.05 m (7H, H_{arom}); 12.16 br.s (1H, NH). ^{19}F NMR spectrum: δ_F 86.53 ppm, s (CF_3). Found, %: C 66.83; H 4.52; F 18.50; N 4.46. $C_{17}H_{14}F_3NO$. Calculated, %: C 66.88; H 4.62; F 18.67; N 4.59.

1-(1-Naphthylamino)-2-trifluoroacetylcyclohexene (IIn). Yield 75%, colorless crystals, mp 92–93°C. IR spectrum, ν, cm^{-1}: 1610 (C=O), 3070 (NH). ^1H NMR spectrum, δ, ppm: 1.53–1.69 m, 2.28–2.31 m, and 2.61–2.64 m (8H, CH_2); 7.29–7.92 m (7H, H_{arom}); 13.43 br.s (1H, NH). ^{19}F NMR spectrum: δ_F 89.91 ppm, s (CF_3). Found, %: C 67.73; N 4.90; F 17.94; N 4.33. $C_{18}N_{16}F_3NO$. Calculated, %: C 67.70; N 5.05; F 17.85; N 4.39.

5,5,6,6,7,7,8,8,8-Nonafluoro-2-(1-naphthylamino)-2-octen-4-one (IIo). Yield 82%, brown oily substance. IR spectrum, ν, cm^{-1}: 1600 (C=O), 3060 (NH). ^1H NMR spectrum, δ, ppm: 2.01 s (3H, Me), 5.79 s (1H, =CH), 7.39–7.97 m (7H, H_{arom}), 12.87 br.s (1H, NH). ^{19}F NMR spectrum, δ_F, ppm: 35.89–36.25 m (2F, CF_2), 38.47–38.89 m (2F, CF_2), 41.65–41.98 m (2F, CF_2), 80.94 t (3F, CF_3, J_{FF} = 9.8 Hz). Found, %: C 50.43; H 2.85;

F 39.75; N 3.30. $C_{18}H_{14}F_9NO$. Calculated, %: C 50.36; H 2.81; F 39.83; N 3.26.

4,4,5,5,6,6,7,7,7-Nonafluoro-1-(1-naphthylamino)-1-phenyl-1-hepten-3-one (IIp). Yield 53%, colorless crystals, mp 84–85°C. IR spectrum, ν, cm^{-1}: 1600 (C=O), 3420 (NH). ^1H NMR spectrum, δ, ppm: 5.90 s (1H, =CH), 6.76–8.25 m (12H, H_{arom}), 13.02 br.s (1H, NH). Found, %: C 56.49; H 2.83; F 34.43; N 2.92. $C_{23}H_{14}F_9NO$. Calculated, %: C 56.22; H 2.87; F 34.79; N 2.85.

3-(3,4-Dichlorophenylamino)-4,4-difluoro-1-phenyl-2-buten-1-one (IIIe). Yield 58%, colorless crystals, mp 56–57°C. IR spectrum, ν, cm^{-1}: 1633 (C=O), 3360 (NH). ^1H NMR spectrum, δ, ppm: 6.29 t (1H, HCF_2, $^2J_{HF}$ = 53.1 Hz), 6.40 s (1H, =CH), 12.34 br.s (1H, NH), 7.34–7.99 m (8H, H_{arom}). ^{19}F NMR spectrum: δ_F 45.26 ppm, d (HCF_2, $^2J_{HF}$ = 53.1 Hz). Found, %: C 55.93; H 3.41; N 4.11. $C_{16}H_{11}Cl_2F_2NO$. Calculated, %: C 56.16; H 3.24; N 4.09.

4,4-Difluoro-3-(1-naphthylamino)-1-phenyl-2-buten-1-one (IIIf). Yield 95%, colorless crystals, mp 82°C. IR spectrum, ν, cm^{-1}: 1625 (C=O), 3460 (NH). ^1H NMR spectrum, δ, ppm: 6.19 t (1H, HCF_2, $^2J_{HF}$ = 53.4 Hz), 6.52 s (1H, =CH), 7.41–8.17 m (12H, H_{arom}), 12.76 br.s (1H, NH). ^{19}F NMR spectrum: δ_F 41.32 ppm, d (HCF_2, $^2J_{HF}$ = 53.4 Hz). Found, %: C 74.27; H 4.51; F 11.52; N 4.26. $C_{20}H_{15}F_2NO$. Calculated, %: C 74.29; H 4.68; F 11.75; N 4.33.

3-(9-Carbazolylamino)-4,4-difluoro-1-phenyl-2-buten-1-one (IIIg). Yield 95%, colorless crystals, mp 168–169°C. IR spectrum, ν, cm^{-1}: 1620 (C=O), 3190 (NH). ^1H NMR spectrum, δ, ppm: 6.05 t (1H, HCF_2, $^2J_{HF}$ = 53.6 Hz), 6.57 s (1H, =CH), 7.21–8.07 m (13H, H_{arom}), 11.76 br.s (1H, NH). ^{19}F NMR spectrum: δ_F 41.32 ppm, d (HCF_2, $^2J_{HF}$ = 53.6 Hz). Found, %: C 70.11; H 4.20; F 9.54; N 7.83. $C_{22}N_{16}F_2N_2O$. Calculated, %: C 70.00; H 4.27; F 9.82; N 7.42.

4,4,4-Trifluoro-3-(1-naphthylamino)-1-phenyl-2-buten-1-one (IIIh). Yield 91%, colorless crystals, mp 125°C [11].

1-(4-Chlorophenyl)-4,4,4-trifluoro-3-(1-naphthylamino)-2-buten-1-one (IIIi). Yield 85%, colorless crystals, mp 121–122°C [11]. ^{19}F NMR spectrum: δ_F 97.96 ppm, s (CF_3).

4,4,4-Trifluoro-3-(1-naphthylamino)-1-(4-tolyl)-2-buten-1-one (IIIj). Yield 79%, colorless crystals, mp 120°C. IR spectrum, ν, cm^{-1}: 1620 (C=O), 3050 (NH). ^1H NMR spectrum, δ, ppm: 2.45 s (3H, Me), 6.55 s (1H, =CH), 7.29–8.07 m (11H, H_{arom}), 12.53 br.s (1H, NH). ^{19}F NMR spectrum: δ_F: 98.03 ppm, s (CF_3). Found, %: C 70.36; H 4.65; F 15.94; N 4.02. $C_{21}H_{16}F_3NO$. Calculated, %: C 70.97; H 4.54; F 16.04; N 3.94.

1,1,1,5,5,5-Hexafluoro-4-(1-naphthylamino)-3-penten-2-one (IIIn). Yield 54%, colorless crystals, mp 85–86°C. IR spectrum, ν, cm^{-1}: 1640 (C=O), 3150 (NH). ^1H NMR spectrum, δ, ppm: 6.15 s (1H, =CH), 7.43–8.13 m (7H, H_{arom}), 12.09 br.s (1H, NH). ^{19}F NMR spectrum, δ_F, ppm: 84.59 s (CF_3), 97.53 s (CF_3). Found, %: C 54.17; H 2.88; F 34.24; N 4.10. $C_{15}H_9F_6NO$. Calculated, %: C 54.07; H 2.72; F 34.21; N 4.20.

Transamination of aminovinyl ketones. Gaseous ammonia was bubbled through a solution of 0.01 mol aminovinyl ketone **II** or **III** in 10 ml of methanol until the mixture turned cold. The mixture was left to stand overnight and was poured into water, and the precipitate was filtered off and recrystallized from diethyl ether–hexane (1:10).

General procedure for the synthesis of benzo[*h*]-quinolines IVa, IVb, and Va–Vc. *a. From lithium diketonates **I** and 1-aminonaphthalene.* A solution of 0.01 mol of lithium diketonate **I** and 0.01 mol of 1-aminonaphthalene in 10 ml of trifluoroacetic acid was heated under reflux until the initial compound disappeared (TLC). The mixture was poured into water, and the precipitate was filtered off and recrystallized from hexane.

*b. From aminovinyl ketones **II** and **III**.* A solution of 0.01 mol of ketone **II** or **III** in 10 ml of trifluoroacetic acid was heated under reflux until the initial compound disappeared (TLC). The mixture was poured into water, and the precipitate was filtered off and recrystallized from hexane.

4-Difluoromethyl-2-methylbenzo[*h*]quinoline (IVa). Yield 82% (from **Ia**), 47% (from **IIh**); colorless crystals, mp 109–110°C. ^1H NMR spectrum, δ, ppm: 2.81 s (3H, Me), 6.87 t (1H, HCF_2, $^2J_{HF}$ = 56.0 Hz), 7.69–7.77 m (3H, H_{arom}), 7.88–7.93 m (2H, H_{arom}), 9.32–9.35 m (1H, H_{arom}). ^{19}F NMR spectrum: δ_F 48.12 ppm, d (HCF_2, $^2J_{HF}$ = 56.0 Hz). Found, %: C 74.30; H 4.56; F 15.46; N 5.59. $C_{15}H_{11}F_2N$. Calculated, %: C 74.05; H 4.56; F 15.62; N 5.76.

2-Methyl-4-trifluoromethylbenzo[*h*]quinoline (IVb). Yield 81% (from **Ie**), 45% (from **IIl**); colorless crystals, mp 137°C. ^1H NMR spectrum, δ, ppm: 2.79 s (3H, Me), 7.67 s (1H, H_{arom}), 7.72–7.76 m (2H, H_{arom}), 7.86–7.92 m (3H, H_{arom}), 9.35–9.37 m (1H, H_{arom}). ^{19}F NMR spectrum: δ_F 94.58 ppm, s (CF_3). Found, %: C 68.87; H 3.78; F 21.85; N 5.31. $C_{15}H_{10}F_3N$. Calculated, %: C 68.96; H 3.85; F 21.82; N 5.36.

2-Difluoromethyl-4-phenylbenzo[*h*]quinoline (Va). Yield 73% (from **Ic**), 60% (from **IIIf**); colorless crystals, mp 111–112°C. ^{1}H NMR spectrum, δ, ppm: 7.25 t (1H, HCF_2, $^2J_{HF}$ = 54.6 Hz), 7.50–8.18 m (10H, H_{arom}), 8.34–9.35 m (1H, H_{arom}). ^{19}F NMR spectrum: δ_F 48.12 ppm, d (HCF_2, $^2J_{HF}$ = 54.6 Hz). Found, %: C 74.30; H 4.56; F 15.46; N 5.59. $C_{15}H_{11}NF_2$. Calculated, %: C 74.05; H 4.56; F 15.62; N 5.76.

4-Phenyl-2-trifluoromethylbenzo[*h*]quinoline (Vb). Yield 82% (from **If**), 63% (from **IIIh**); colorless crystals, mp 79–80°C. ^{1}H NMR spectrum, δ, ppm: 7.53–8.34 m (10H, H_{arom}), 9.42–9.44 m (1H, H_{arom}). ^{19}F NMR spectrum: δ_F 100.33 ppm, s (CF_3). Found, %: C 74.16; H 3.76; F 17.74; N 4.33. $C_{20}H_{12}F_3N$. Calculated, %: C 74.29; H 3.74; F 17.63; N 4.33.

2,4-Bis(trifluoromethyl)benzo[*h*]quinoline (Vc). Yield 53% (from **In**), colorless crystals, mp 122°C. ^{1}H NMR spectrum, δ, ppm: 7.79–7.84 m (2H, H_{arom}), 7.93–7.96 m (1H, H_{arom}), 8.01–8.12 m (3H, H_{arom}), 9.33–9.36 m (1H, H_{arom}). ^{19}F NMR spectrum, δ_F, ppm: 94.47 s (CF_3), 100.83 s (CF_3). Found, %: C 55.15; H 2.21; F 37.40; N 4.60. $C_{14}H_7F_6N$. Calculated, %: C 55.46; H 2.33; F 37.59; N 4.62.

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