Reactions of 3,3,3-trichloro(trifluoro)-1-nitropropenes with 2-morpholinoalk-1-enes

*V. Yu. Korotaev,[a] A. Yu. Barkov,[a] P. A. Slepukhin,[b] and V. Ya. Sosnovskikh[a]**

[a]A. M. Gorky Ural State University,
51 prosp. Lenina, 620083 Ekaterinburg, Russian Federation.
Fax: +7 (343) 261 5978. E-mail: Vyacheslav.Sosnovskikh@usu.ru
[b]I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences,
20 ul. S. Kovalevskoi, 620041 Ekaterinburg, Russian Federation

The reaction of 3,3,3-trichloro(trifluoro)-1-nitropropenes with 2-morpholinoalk-1-enes affords the nitroalkylated *Z*-enamines whose subsequent hydrolysis results in 2-trihalomethyl-1-nitroalkan-4-ones.

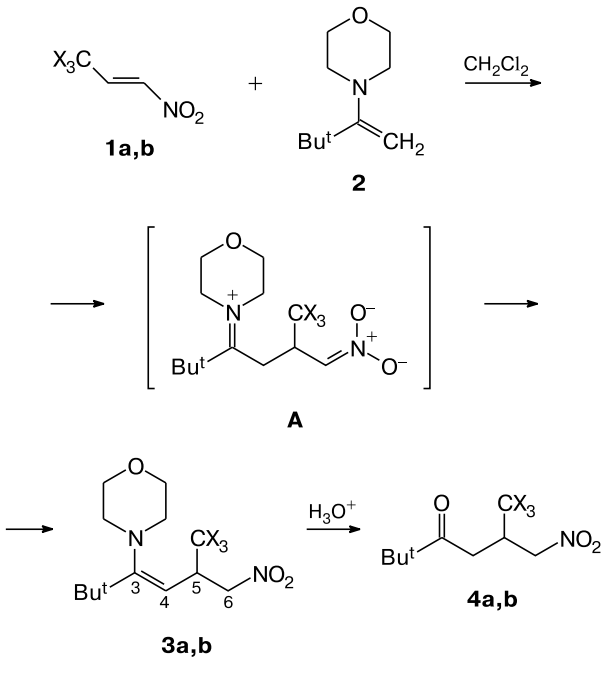
Key words: 3,3,3-trihalo-1-nitropropenes, enamines, Michael reaction, nitro compounds, fluorine organic compounds, X-ray diffraction study.

Due to high electrophilicity of the double bond, 3,3,3-trichloro(trifluoro)-1-nitropropenes find ever increasing application as CCl_3- and CF_3-containing synthons for the preparation of polyfunctional compounds in both the reactions with nucleophilic reagents[1—5] and the cycloaddition reactions.[6—11] Recently,[12] we have described an example of a tandem [4+2]/[3+2] cycloaddition where these nitroalkenes acted as the heterodiene and dipolarophile in the reaction with 2,3-dihydrofuran. The data on the reactions of polyhaloalkylated nitroolefins with enamines are very limited. It is only known that the reaction of 3,3,3-trifluoro-1-nitropropene with ethyl 3-morpholinocrotonate affords the cyclobutane derivative as a result of [2+2] carbocyclization[13] and the reactions of polyfluoroalkylated nitroalkenes with enamines of cycloalkanones and acetophenone afford β-polyfluoroalkyl γ-nitro ketones.[14] In the present work, we studied the features of the reactions of 3,3,3-trichloro and 3,3,3-trifluoro-1-nitropropenes (**1a**,**b**) with 2-morpholinoalk-1-enes (morpholine enamines of pinacoline and acetophenone) in polar (dichloromethane) and non-polar (benzene) solvents under the conditions of the kinetic control.

Results and Discussion

It was established that the reaction of nitroalkenes **1a,b** with 3,3-dimethyl-2-morpholinobut-1-ene (**2**), which is prepared from pinacoline and morpholine, in dichloromethane for 3 days (**1a**) or 2 h (**1b**) at room tempearature affords nitroalkylated enamines **3a,b** in yields of 68 and 72%, respectively, which are hydrolyzed almost quantitatively into γ-nitro ketones **4a,b** upon treatment with dilute HCl in ethanol (Scheme 1). In the case of more reactive CF_3-nitroalkene **1b**, the yield of compound **3b** increases to 87% if the reaction is performed without solvent for 0.5 h. The formation of compounds **3** proceeds as the Michael addition through the betaine intermediate **A**, which, under these conditions, does not undergo intramolecular cyclization into cyclobutane or cyclic nitronate (1,2-oxazine *N*-oxide). Such reaction pathway would be expected

Scheme 1



X = Cl (**a**), F (**b**)

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based on the known data[15—20] on the reactions of enamines with the non-halogenated analogs of nitroalkenes **1**. Compounds **3b** and **4b** have been prepared earlier[21] from enamine **2** and 2-diazo-3,3,3-trifluoro-1-nitropropane; however, the configuration of the double bond in **3b** was not established.

X-ray diffraction study of the sample of **3a** showed that its double bond has the *Z*-configuration (Fig. 1). This conclusion can be expanded to the fluorinated analog **3b**, since the ^{1}H NMR spectra of compounds **3a,b** in $CDCl_3$ are very similar and characterized by the close chemical shifts of the protons of the aliphatic chain (taking into account the large deshielding effect of the trichloromethyl group compared to the trifluoromethyl one) and the presence of the AMX spin system with the spin-spin coupling constants $J_{A,M}$ = 11.4—11.8 Hz, $J_{A,X}$ = 9.0 Hz, and $J_{M,X}$ = 3.8—5.1 Hz.

The replacement of dichloromethane for non-polar benzene or hexane in the case of compound **1b** does not result in new products, while, in the case of compound **1a**, the reaction proceeds mainly as [4+2] cycloaddition to afford a mixture of 1,2-oxazine *N*-oxide **5** (84%), cyclobutane **6** (8%), and enamine **3a** (8%) (^{1}H NMR spectral data) (Scheme 2). When the resulting mixture was treated with an aqueous solution of acetic acid for 6 h, enamine **3a** formed in a yield of 68%. We failed to isolate oxazine **5** in the pure form due to easy ring opening to form compound **3a**. The bulky trichloromethyl group occupies the equatorial *cis*-position in oxazine **5** in relation to the equatorial *tert*-butyl group, which is indicated by the large spin-spin coupling constans for the protons of the CH_2 group with the axial H(4) atom (^3J = 10.5 Hz and ^3J = 7.5 Hz).

It is known that the reactions of enamine **7** derived from morpholine and acetophenone with 2-diazo-3,3,3-trifluoro-1-nitropropane (C_6H_6, ~20 °C, 1 h)[21] and nitroalkene **1b** (CH_2Cl_2, ~20 °C, 2 h)[14] afford γ-nitro ketone **8b**. We performed the reaction of nitro alkenes **1a,b** with enamine **7** in benzene and, after acid hydrolysis of the

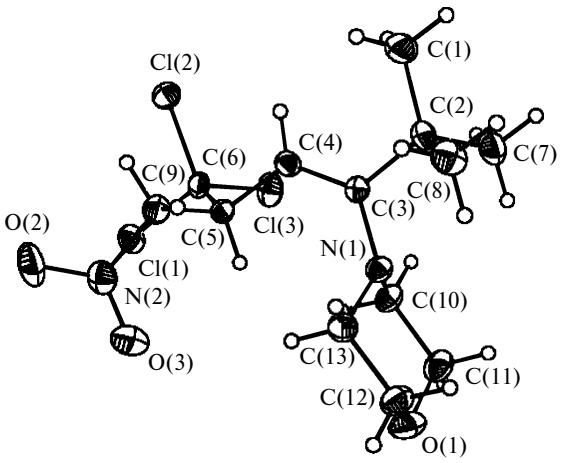
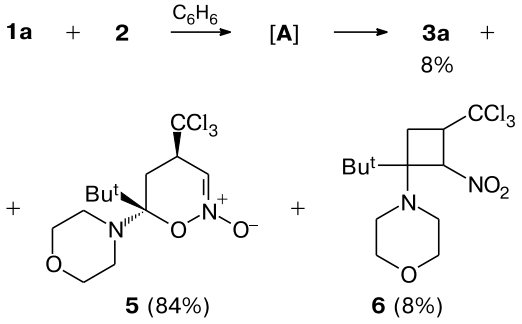


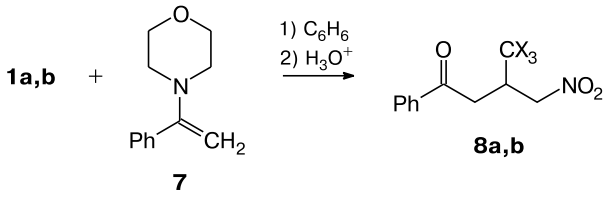
Fig. 1. Molecular structure of compound **3a**.

Scheme 2



reaction mixture, obtained γ-nitro ketones **8a,b** in yields of 77—87% (Scheme 3). The intermediate nitroalkylated enamines have not been isolated in this case due to their easy hydrolysis by the atmospheric moisture. The distinctive feature of the ^{1}H NMR spectra of γ-nitro ketones **4a,b** and **8a,b**, among which **4a** and **8a** were prepared for the first time, is a significant difference in the values of constans for the geminal methylene protons at the C=O group (^2J = 18.2—18.6 Hz) and nitro group (^2J = 13.6—14.2 Hz).

Scheme 3

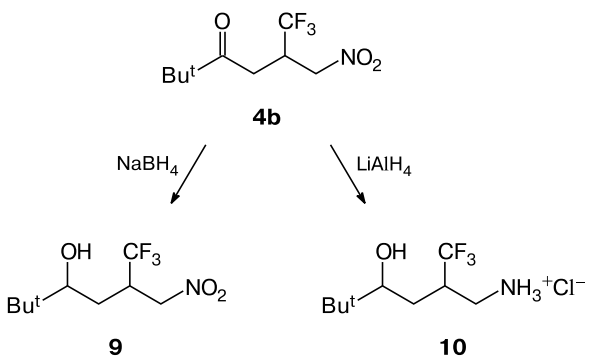


X = Cl (**a**), F (**b**)

The synthetic value of the carbonyl and nitro groups is well-known; therefore, the γ-nitro ketones desribed in the present work are of definite interest as substrates for subsequent syntheses based on them, in particular, for the preparation of γ-nitro and γ-amino β-trihalomethylalkanols. Our preliminary results on reduction of nitro ketone **4b** with sodium borohydride and lithium aluminum hydride showed that the former reaction is chemoselective (only the carbonyl group is reduced, the ratio of diastereomers **9** is 1 : 1, and the yield is 83%), and the latter is diastereoselective (both functional groups are reduced, the ratio of diastereomers **10** isolated in the form of hydrochlorides is 1 : 10, and the yield is 47%) (Scheme 4).

Thus, the reactions of 3,3,3-trichloro(trifluoro)-1-nitropropenes with 2-morpholinoalk-1-enes afford nitroalkylated *Z*-enamines and β-trihalomethyl-γ-nitroketones, which are of interest for the synthesis of polyfunctional CCl_3- and CF_3-containing compounds.

Scheme 4



Experimental

IR spectra were recorded on a Perkin—Elmer Spectrum BX-II instrument in KBr pellets. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on Bruker DRX-400 (400, 376, and 100 MHz, respectively) and Bruker Avance II (500 MHz) spectrometers in $CDCl_3$ and C_6D_6 using Me_4Si and C_6F_6 as internal standards. Nitro alkenes **1a,b** (see Refs 1 and 22), as well as enamines **2** and **7** (see Refs 23 and 24) were prepared according to known procedures.

(*Z*)-2,2-Dimethyl-3-morpholino-6-nitro-5-trichloromethylhex-3-ene (3a). To a solution of enamine **2** (1.69 g, 10.0 mmol) in dry dichloromethane (2 mL), a solution of nitro alkene **1a** (1.90 g, 10.0 mmol) in dry dichloromethane (5 mL) was added dropwise with stirring over 15 min. The mixture was stirred for three days at ~20 °C, the solvent was evaporated, and the residue was recrystallized from pentane to give enamine **3a** in a yield of 2.43 g (68%), m.p. 79—80 °C. Found (%): C, 43.38; H, 5.94; N, 7.76. $C_{13}H_{21}Cl_3N_2O_3$. Calculated (%): C, 43.41; H, 5.88; N, 7.79. IR, ν/cm^{-1}: 1645, 1561, 1377, 1353. ^{1}H NMR ($CDCl_3$), δ: 1.16 (s, 9 H, Bu^t); 2.84—2.93 (m, 2 H, N(C<u>H</u>H)$_2$); 3.00—3.08 (m, 2 H, N(CH<u>H</u>)$_2$); 3.70 (br.s, 4 H, O(CH$_2$)$_2$); 4.46 (dd, 1 H, H(6a), J = 11.4 Hz, J = 9.0 Hz); 4.86 (td, 1 H, H(5), J = 9.4 Hz, J = 3.8 Hz); 5.06 (dd, 1 H, H(6b), J = 11.4 Hz, J = 3.8 Hz); 5.40 (d, 1 H, H(4), J = 9.8 Hz). ^{1}H NMR (C_6D_6), δ: 0.97 (s, 9 H, Bu^t); 2.65—2.80 (m, 4 H, N(CH$_2$)$_2$); 3.52—3.64 (m, 4 H, O(CH$_2$)$_2$); 3.86 (dd, 1 H, H(6a), J = 11.4 Hz, J = 9.0 Hz); 4.44 (dd, 1 H, H(6b), J = 11.4 Hz, J = 3.9 Hz); 4.82 (td, 1 H, H(5), J = 9.3 Hz, J = 3.9 Hz); 5.22 (d, 1 H, H(4), J = 9.7 Hz). ^{13}C NMR (C_6D_6), δ: 30.4 (C(1)), 40.4 (C(2)), 52.5 (NCH$_2$), 56.6 (C(6)), 67.7 (OCH$_2$), 78.0 (C(5)), 99.9 (CCl_3), 116.3 (C(4)), 164.9 (C(3)).

(*Z*)-2,2-Dimethyl-3-morpholino-6-nitro-5-trifluoromethylhex-3-ene (3b) was prepared from enamine **2** and nitro alkene **1b** according to the procedure described for compound **3a** (the duration of stirring was 2 h and the yield was 72%); if the reaction is performed without solvent for 0.5 h, the yield was 87%, m.p. 98—99 °C (*cf.* Ref. 21: m.p. 98—99 °C). IR, ν/cm^{-1}: 1653, 1562, 1383, 1351. ^{1}H NMR ($CDCl_3$), δ: 1.12 (s, 9 H, Bu^t); 2.95 (t, 4 H, N(CH$_2$)$_2$, J = 4.4 Hz); 3.70 (t, 4 H, O(CH$_2$)$_2$, J = 4.4 Hz); 4.36 (dd, 1 H, H(6a), J = 11.8 Hz, J = 9.0 Hz); 4.45—4.57 (m, 1 H, H(5)); 4.71 (dd, 1 H, H(6b), J = 11.8 Hz, J = 5.1 Hz); 5.19 (d, 1 H, H(4), J = 10.1 Hz). ^{19}F NMR ($CDCl_3$), δ: 92.1 (d, CF_3, J = 8.2 Hz).

2,2-Dimethyl-6-nitro-5-trichloromethylhexan-3-one (4a). A mixture of enamine **3a** (0.36 g, 1.0 mmol), 0.1 *M* HCl (2 mL), and ethanol (2 mL) was stirred for 4 h at 50 °C, cooled to ~20 °C, extracted with dichloromethane (3×2 mL), and dried with Na_2SO_4. After removal of the solvent, a light-yellow oil of the title compound was obtained. The yield was 0.26 g (88%). Found (%): C, 37.04; H, 4.75; N, 4.97. $C_9H_{14}Cl_3NO_3$. Calculated (%): C, 37.20; H, 4.86; N, 4.82. IR, ν/cm^{-1}: 1711, 1563, 1377, 1355. ^{1}H NMR ($CDCl_3$), δ: 1.21 (s, 9 H, Bu^t); 2.96 (dd, 1 H, H(4a), J = 18.6 Hz, J = 8.1 Hz); 3.36 (dd, 1 H, H(4b), J = 18.6 Hz, J = 3.3 Hz); 4.16 (dddd, 1 H, H(5), J = 8.1 Hz, J = 5.9 Hz, J = 4.7 Hz, J = 3.3 Hz); 4.52 (dd, 1 H, H(6a), J = 13.8 Hz, J = 5.9 Hz); 4.92 (dd, 1 H, H(6b), J = 13.8 Hz, J = 4.7 Hz).

2,2-Dimethyl-6-nitro-5-trifluoromethylhexan-2-one (4b) was prepared analogously. The yield was 91%, b.p. 90—91 °C (2 Torr) (*cf.* Ref. 21: b.p 90—91 °C (2 Torr)). IR, ν/cm^{-1}: 1712, 1566, 1380, 1339. ^{1}H NMR ($CDCl_3$), δ: 1.19 (s, 9 H, Bu^t); 2.85 (dd, 1 H, H(4a), J = 18.5 Hz, J = 8.6 Hz); 2.97 (dd, 1 H, H(4b), J = 18.5 Hz, J = 4.4 Hz); 3.64—3.76 (m, 1 H, H(5)); 4.52 (dd, 1 H, H(6a), J = 13.6 Hz, J = 5.1 Hz); 4.63 (dd, 1 H, H(6b), J = 13.6 Hz, J = 6.3 Hz). ^{19}F NMR ($CDCl_3$), δ: 91.9 (d, CF_3, J = 8.0 Hz).

Reaction of nitro alkene 1a with 3,3-dimethyl-2-morpholinobut-1-ene (2). To a solution of enamine **2** (1.69 g, 10.0 mmol) in dry benzene (5 mL), a solution of nitro alkene **1a** (1.90 g, 10.0 mmol) in dry benzene (5 mL) was added dropwise with stirring over 15 min. The resulting mixture was stirred for 30 min at ~20 °C and the precipitate that formed was filtered off and washed with pentane. A mixture (1.97 g, 55%) of products **3a**, **5**, and **6** in a ratio of 8 : 84 : 8 was obtained as a white powder, m.p. 119—120 °C. Found (%): C, 43.27; H, 5.94; N, 7.97. $C_{13}H_{21}Cl_3N_2O_3$. Calculated (%): C, 43.41; H, 5.88; N, 7.79. IR, ν/cm^{-1}: 1624, 1560, 1454, 1369, 1354, 1243, 1111. When this mixture was treated with aqueous acetic acid for 6 h, enamine **3a** was obtained in a yield of 68%.

6-*tert*-Butyl-6-morpholino-4-trichloromethyl-5,6-dihydro-4*H*-1,2-oxazine-2-oxide (5) was prepared as a mixture with compounds **3a** (8%) and **6** (8%) and was not isolated in the pure form due to its instability. ^{1}H NMR (500 MHz, C_6D_6), δ: 0.81 (s, 9 H, Bu^t); 2.12 (dd, 1 H, H(5a), J = 14.5 Hz, J = 10.5 Hz); 2.24 (dd, 1 H, H(5b), J = 14.5 Hz, J = 7.5 Hz); 2.46—2.54 (m, 2 H, N(C<u>H</u>H)$_2$); 2.83—2.90 (m, 2 H, N(CH<u>H</u>)$_2$); 3.27 (ddd, 1 H, H(4), J = 10.5 Hz, J = 7.5 Hz, J = 3.2 Hz); 3.26—3.33 (m, 4 H, O(CH$_2$)$_2$); 6.44 (d, 1 H, H(3), J = 3.2 Hz). ^{13}C NMR (126 MHz, C_6D_6), δ: 26.1, 26.8, 43.1, 48.4, 54.2, 67.4, 68.2, 100.9, 106.5.

1-*tert*-Butyl-1-morpholino-2-nitro-3-trichloromethylcyclobutane (6) was detected by ^{1}H NMR spectroscopy in a mixture with compounds **3a** (8%) and **5** (84%). ^{1}H NMR (500 MHz, C_6D_6), δ: 1.77 (ddd, 1 H, H(4a), J = 12.8 Hz, J = 10.2 Hz, J = 0.8 Hz); 1.84 (dd, 1 H, H(4b), J = 12.8 Hz, J = 9.0 Hz); 2.55—2.65 (m, 4 H, N(CH$_2$)$_2$); 3.42—3.46 (m, 4 H, O(CH$_2$)$_2$); 4.05 (dt, 1 H, H(3), J = 10.2 Hz, J = 9.0 Hz); 5.10 (dd, 1 H, H(2), J = 9.0 Hz, J = 0.6 Hz).

4-Nitro-1-phenyl-3-trichloromethylbutan-1-one (8a). To a solution of enamine **7** (1.89 g, 10.0 mmol) in dry benzene (5 mL), a solution of nitro alkene **1a** (1.90 g, 10.0 mmol) in dry benzene (5 mL) was added dropwise with stirring over 15 min. The resulting mixture was stirred for 30 min at ~20 °C, the solvent was removed under reduced pressure, and 0.1 *M* HCl (10 mL) was added to the residue. The resulting mixture was

stirred for 30 min at ~20 °C, extracted with dichloromethane (3×3 mL), and the extract was dried with Na_2SO_4. After removal of the solvent, the residue was recrystallized from hexane. The yield was 2.39 g (77%), m.p. 68—69 °C. Found (%): C, 42.53; H, 3.36; N, 4.49. $C_{11}H_{10}Cl_3NO_3$. Calculated (%): C, 42.54; H, 3.25; N, 4.51. IR, ν/cm^{-1}: 1685, 1597, 1581, 1552, 1375, 1354. ^{1}H NMR ($CDCl_3$), δ: 3.44 (dd, 1 H, H(2a), J = 18.2 Hz, J = 8.5 Hz); 3.87 (dd, 1 H, H(2b), J = 18.2 Hz, J = 3.4 Hz); 4.40 (dtd, 1 H, H(3), J = 8.5 Hz, J = 5.1 Hz, J = 3.4 Hz); 4.64 (dd, 1 H, H(4a), J = 14.2 Hz, J = 5.3 Hz); 4.98 (dd, 1 H, H(4b), J = 14.2 Hz, J = 4.9 Hz); 7.52 (t, 2 H, H(3′), H(5′), J = 7.6 Hz); 7.64 (tt, 1 H, H(4′), J = 7.4 Hz, J = 1.2 Hz); 8.00 (d, 2 H, H(2′), H(6′), J = 8.0 Hz).

4-Nitro-1-phenyl-3-trifluoromethylbutan-1-one (8b) was prepared according to the procedure described for compound **8a** in a yield of 87%, m.p. 59—60 °C (from pentane) (*cf.* Ref. 21: m.p. 60—61 °C). IR, ν/cm^{-1}: 1680, 1598, 1581, 1551, 1387, 1347. ^{1}H NMR ($CDCl_3$), δ: 3.35 (dd, 1 H, H(2a), J = 18.4 Hz, J = 9.2 Hz); 3.47 (dd, 1 H, H(2b), J = 18.4 Hz, J = 4.0 Hz); 3.87—4.00 (m, 1 H, H(3)); 4.64 (dd, 1 H, H(4a), J = 13.8 Hz, J = 4.7 Hz); 4.72 (dd, 1 H, H(4b), J = 13.8 Hz, J = 6.6 Hz); 7.52 (t, 2 H, H(3′), H(5′), J = 7.7 Hz); 7.64 (tt, 1 H, H(4′), J = 7.4 Hz, J = 1.2 Hz); 7.97 (d, 2 H, H(2′), H(6′), J = 8.0 Hz). ^{19}F NMR ($CDCl_3$), δ: 90.9 (d, CF_3, J = 8.7 Hz).

6,6,6-Trifluoro-2,2-dimethyl-5-nitromethylhexan-3-ol (9). To a solution of nitro ketone **4b** (2.41 g, 10.0 mmol) in ethanol (5 mL), $NaBH_4$ (0.19 g, 5.0 mmol) was added with stirring portionwise over 5 min. The resulting mixture was stirred for 3 h at ~20 °C, 0.1 *M* HCl (6 mL) was added, and the mixture was extracted with dichloromethane (3×4 mL). The extract was dried with Na_2SO_4. After removal of the solvent, the residue was distilled *in vacuo*. The yield was 2.02 g (83%), b.p. 117—119 °C (2 Torr). Found (%): C, 44.47; H, 6.81; N, 5.71. $C_9H_{16}F_3NO_3$. Calculated (%): C, 44.44; H, 6.63; N, 5.76. ^{1}H NMR ($CDCl_3$), δ: 0.91 (s, 9 H, Bu^t); 1.41 (ddd, 1 H, C<u>H</u>H, J = 14.6 Hz, J = 10.8 Hz, J = 7.6 Hz); 1.68—1.76 (m, 1 H, CH); 1.95 (ddt, 1 H, CH<u>H</u>, J = 14.6 Hz, J = 5.0 Hz, J = 1.8 Hz); 3.30—3.52 (m, 2 H, $CHCF_3$, OH); 4.56 (dd, 1 H, C<u>H</u>HNO_2, J = 14.2 Hz, J = 4.8 Hz); 4.81 (dd, 1 H, CH<u>H</u>NO_2, J = 14.2 Hz, J = 5.3 Hz) (52%); 0.92 (s, 9 H, Bu^t); 1.68—1.76 (m, 2 H, C<u>H</u>H, CH); 1.80 (ddd, 1 H, CH<u>H</u>, J = 14.6 Hz, J = 10.8 Hz, J = 3.5 Hz); 3.30—3.52 (m, 2 H, $CHCF_3$, OH); 4.60 (dd, 1 H, C<u>H</u>HNO_2, J = 14.0 Hz, J = 7.0 Hz); 4.66 (dd, 1 H, CH<u>H</u>NO_2, J = 14.0 Hz, J = 6.8 Hz) (48%). ^{19}F NMR ($CDCl_3$), δ: 91.0 (d, CF_3, J = 9.0 Hz) (52%); 90.6 (d, CF_3, J = 8.7 Hz) (48%).

5-Aminomethyl-6,6,6-trifluoro-2,2-dimethylhexan-3-ol hydrochloride (10). To a suspension of $LiAlH_4$ (1.52 g, 40 mmol) in dry THF (50 mL), a solution of nitro ketone **4b** (2.41 g, 10.0 mmol) in dry THF (15 mL) was added dropwise over 20 min. The resulting mixture was refluxed with stirring for 2 h, cooled to 0 °C, and H_2O (1.52 g), a 10% solution of KOH (2.11 g), and H_2O (4.56 g) were added successively dropwise. The mixture was stirred for 15 min and filtered and the solvent was removed *in vacuo*. The residue was dissolved in dry benzene (20 mL), cooled to 15 °C, and dry HCl was bubbled until saturation, and the mixture was kept for 30 min. Benzene was removed *in vacuo*, the residue was dissolved in ethyl acetate (10 mL), filtered, and hexane (5 mL) was added. The precipitate that formed was filtered off and dried *in vacuo*. The yield of the title compound was 1.17 g (47%), m.p. 158—162 °C. Found (%): C, 43.43; H, 7.80; N, 5.56. $C_9H_{19}ClF_3NO$. Calculated (%): C, 43.29; H, 7.67; N, 5.61. ^{1}H NMR (DMSO-d_6), δ: 1.53 (ddd, 1 H, C<u>H</u>H, J = 14.8 Hz, J = 10.8 Hz, J = 4.4 Hz); 1.75 (ddd, 1 H, CH<u>H</u>, J = 14.8 Hz, J = 7.1 Hz, J = 1.8 Hz); 2.88—2.98 (m, 1 H, $CHCF_3$); 3.03 (dd, 1 H, C<u>H</u>HN, J = 13.3 Hz, J = 6.5 Hz); 3.08 (dd, 1 H, CH<u>H</u>N, J = 13.3 Hz, J = 6.0 Hz); 3.17 (d, 1 H, CH, J = 10.2 Hz); 7.50—9.00 (br.s, 4 H, OH, NH_3^+). ^{19}F NMR (DMSO-d_6), δ: 93.9 (d, CF_3, J = 9.4 Hz) (91%); 93.8 (d, CF_3, J = 9.5 Hz) (9%).

X-ray diffraction study of compound 3a was performed on a Xcalibur 3 automatic single-crystal diffractometer (T = 150(2) K, Mo-Kα radiation, graphite monochromator, ω/2θ scanning in the region of 2θ < 56.5°). Crystallographic data: a = 26.518(3) Å, b = 7.9003(5) Å, c = 18.2210(12) Å, α = γ = 90°, β = 114.574(8)°, V = 3471.6(5) Å^3, space group $C2/c$, monoclinic crystal system, Z = 8, $C_{13}H_{21}Cl_3N_2O_3$, d_{calc} = 1.376 g cm^{-3}. The intensities of 5798 reflections were measured, among which 4178 were independent (R_{int} = 0.0264). The structure was solved by the direct method using the SHELXS-97 program.[25] The refinement of structural parameters was performed by the least-squares method in the anisotropic isotropic (for the H atoms) approximation using the SHELXL-97 software system.[25] The positions of the H atoms were calculated geometrically (the riding model). The final values of the divergence factors were wR_2 = 0.2535, R_1 = 0.0580 for 3170 reflections with $I > 2\sigma$ (S = 1.013). The peaks of maximum and minimum residual densities were 0.798 and −0.362 e Å^{-3}, respectively. The details for X-ray diffraction study are deposited in the Cambridge Crystallographic Data Centre (CCDC 785766).

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