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Facile synthetic pathway to β-hydroxy-β-trifluoromethyl imines and their derivatives☆

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ABSTRACT

Synthetic approach based on mediated addition of different trifluoromethylated building blocks to selected acyclic imines giving access to a variety of β-hydroxy-β-trifluoromethyl imines are elaborated. A reaction between fluorinated adducts and imines proceed easily giving the condensation products in good to excellent yields. β-Hydroxy-β-trifluoromethyl imines possessing trifluoromethyl group and exhibiting strong intramolecular hydrogen bonding are great precursors to different β-hydroxy-β-trifluoromethyl ketones and alcohols.

1. Introduction

Design and synthesis of trifluoromethyl-containing compounds has received recently significant attention due to their application in various fields like pharmacy, medicine, agriculture, material science, etc. There are two commonly known methodologies applied for synthesizing of organofluorine molecules. First one, called "C–F bond formation", bases on the direct introduction of fluorine atoms into a certain position of the desired molecule through the use of fluorinating agents [1]. On the other hand, there is a methodology based on building block strategy [2–4]. This straightforward strategy allows for introducing to the desired molecule simple fluorinated agents which are relatively easily accessible and display appropriate reactivity [5]. Here the main place is occupied by derivatives of methyl trifluoropyruvic acid. Thus, molecules possessing trifluoromethyl group, which is of great value [6], can be in a facile way synthesize.

Furthermore, the preparation of different hydroxyl trifluorinated imines is well documented in the literature. Significantly, they are not only potential precursors to trifluoromethylated alcohols [7] but also to various bioactive compounds [8]. Furthermore, belonging to the class of fluorinated alkoxy-ligands (FAI) [9], they have found application in microelectronics as metal organic chemical vapor deposition (MOCVD) [10]. A common method for the synthesis of β-hydroxy-β-trifluoromethyl imines described some years ago was based on the reaction of trifluoroacetaldehyde ethyl hemiacetal with several imines [11] or enamines [12]. Marguet et al. [13] has reported recently acid-catalyzed condensation of primary amines onto carbonyl compounds giving access to variety of mono- and di-β-hydroxy-β-bis(trifluoromethyl)-(di)imines. Earlier, we have demonstrated simple route to the desired β-hydroxy-β-trifluoromethyl imines from various ketimines and aldimines or activated ketones like trifluoroacetone or trifluoroacetophenone [14] and hexafluoroacetone [15].

Herein, we present a convenient non-catalyzed synthetic pathway to novel β-hydroxy-β-trifluoromethyl imines in good to excellent yield starting from different methyltrifluoro ketones and selected imines.

2. Results and discussion

Our protocol design of novel β-hydroxy-β-trifluoromethyl imines was based on the condensation reaction between selected trifluorinated building blocks (**1a–c**) diketones (Fig. 1) and different substituted imines possessing in α position methyl group (**2a–d**) (Fig. 2) initiated through enamine tautomer. The mediated addition reaction proceeds easily in the absence of any catalyst.

Methyl trifluoropyruvate was prepared according to the procedure given by Paleta et al. [16] Having in hands, trifluoromethylated building block we found that the reaction between equimolar amount of methyl trifluoropyruvate (**1a**) and enamin tautomer of ketimines: propylidene amine (**2a**) and *N*-isopropylidene amine

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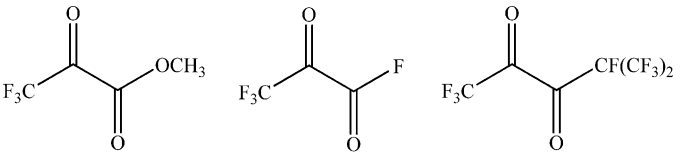
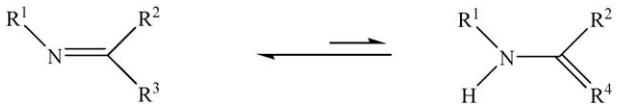


1a **1b** **1c**

Fig. 1. Selected fluorinated building blocks.

(**2b**) gives the addition products (**3a** and **3b**) as white solids (Scheme 1) in excellent yield.

Going into details, the reaction between enamine form of ketimines (**2a** and **2b**) reacts with first equivalent of methyl trifluoropyruvate (**1a**) yielding the addition products β-hydroxyimines (Scheme 1- intermediate **A,** see also ref. [14,15]). Continuously, the enamine tautomer of β-hydroxyimines (**B,** see also ref. [14,15]) reacts with second equivalent of MTFP leading to the desired β-dihydroxy-β-(bis)-trifluoromethyl imines (**3a** and **3b**). There is a presumption that the strong intramolecular hydrogen bonding present in molecule of intermediate **A** leads to insertion of second molecule of MTFP yielding only one



2a : $R^1 = H$, R^2, $R^3 = CH_3$, $R^4 = CH_2$

2b : $R^1 = i\text{Pr}$, R^2, $R^3 = CH_3$, $R^4 = CH_2$

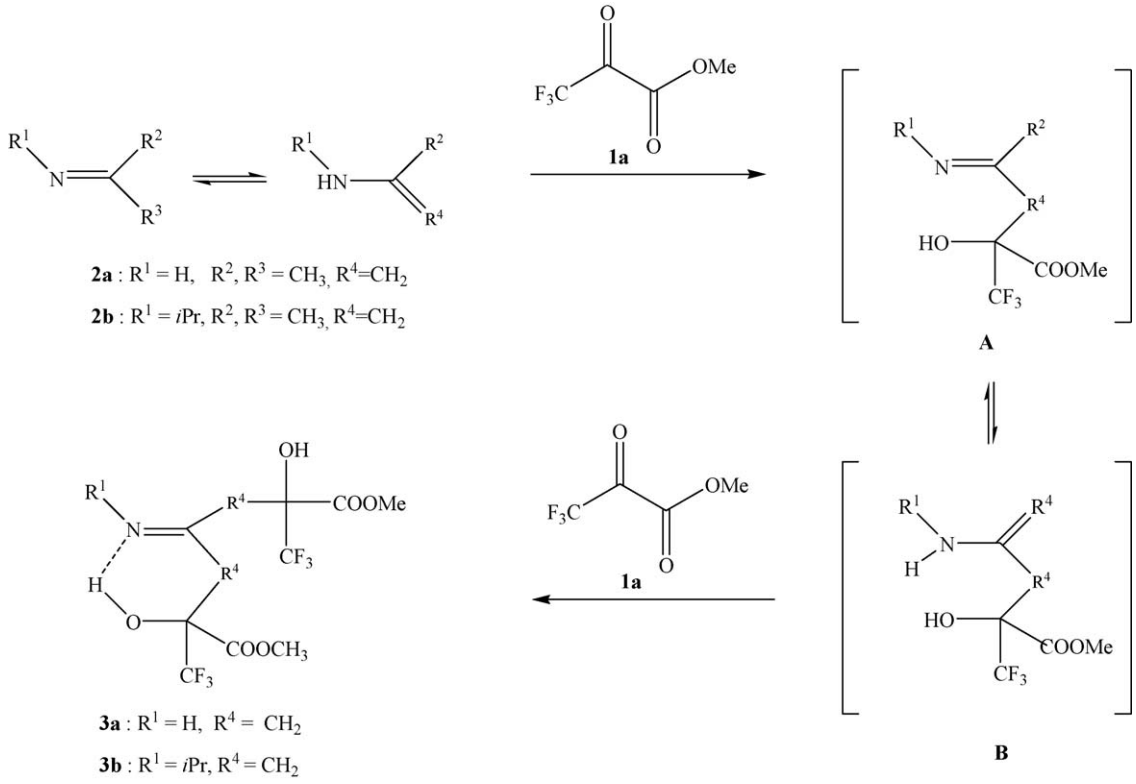
2c : $R^1 = i\text{Pr}$, $R^2 = CF_3$, $R^3 = CH_3$, $R^4 = CH_2$

2d: $R^1 = i\text{Pr}$, $R^2 = Ph$, $R^3 = CH_3$, $R^4 = CH_2$

Fig. 2. The imine–enamine equilibria of compounds (**2a–d**).

diastereoisomer. In the case of the compound (**3b**), the addition of the second equivalent of MTFP have shown that one of the hydroxyl group appears in the position *syn* and the other in the position *anti* to C=N double bond.

Furthermore, we investigated the acidic hydrolysis of the compound (**3b**) (Scheme 2). As a result the expected β-hydroxyketon (**4**) in a good yield was obtained. Interestingly, the



2a : $R^1 = H$, R^2, $R^3 = CH_3$, $R^4 = CH_2$

2b : $R^1 = i\text{Pr}$, R^2, $R^3 = CH_3$, $R^4 = CH_2$

1a

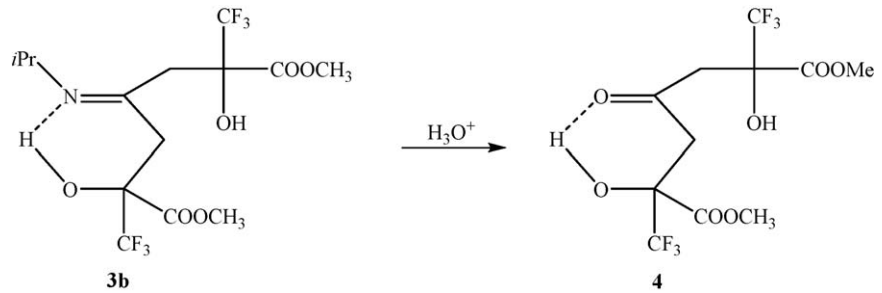
A

B

3a : $R^1 = H$, $R^4 = CH_2$

3b : $R^1 = i\text{Pr}$, $R^4 = CH_2$

Scheme 1.



3b **4**

Scheme 2.

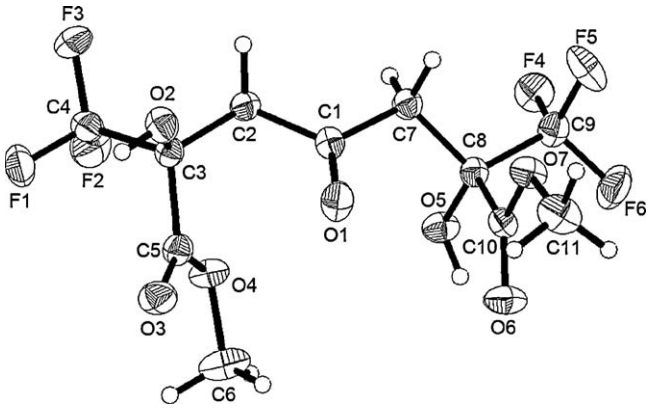


Fig. 3. View of molecular structure (**4**).

molecular structure of (**3b**) determines only one enantiomer. Moreover, due to the lack of isopropyl group, both trifluoromethyl- and methoxy-groups in NMR spectra were not distinguishable.

We were able to grow single crystals of the β-hydroxyketon (**4**) (Fig. 3). The unit cell of compounds (**4**) revealed four molecules, which are connected one to each other through short hydrogen bonds giving the "zig-zag" pattern (Fig. 4). In the studied crystal only one enantiomer was present. Both protons from hydroxyl groups form one intramolecular hydrogen bridge O(5)–H(5a)...O(6) and C(2)–H(2a)...F(2). A special feature of molecule (**4**) is the absence of hydrogen bridges to the central carbonyl oxygen. Two trifluoromethyl groups are in the *cis* position to the carbonyl group.

Our next attempt was investigation concerning reaction between propanoyl fluoride, 3,3,3-trifluoro-2-oxo and selected imines. After passing-in hexafluoropropenoxide into liquid benzophenon followed by "trap to trap" distillation, propanoyl

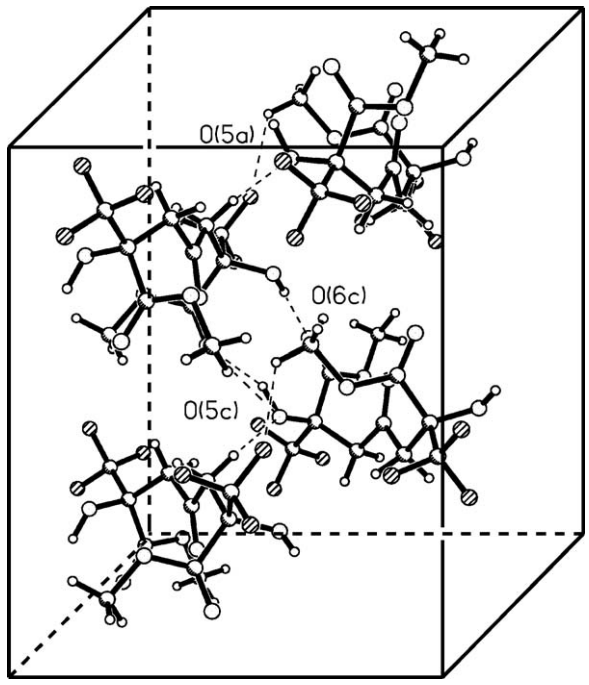
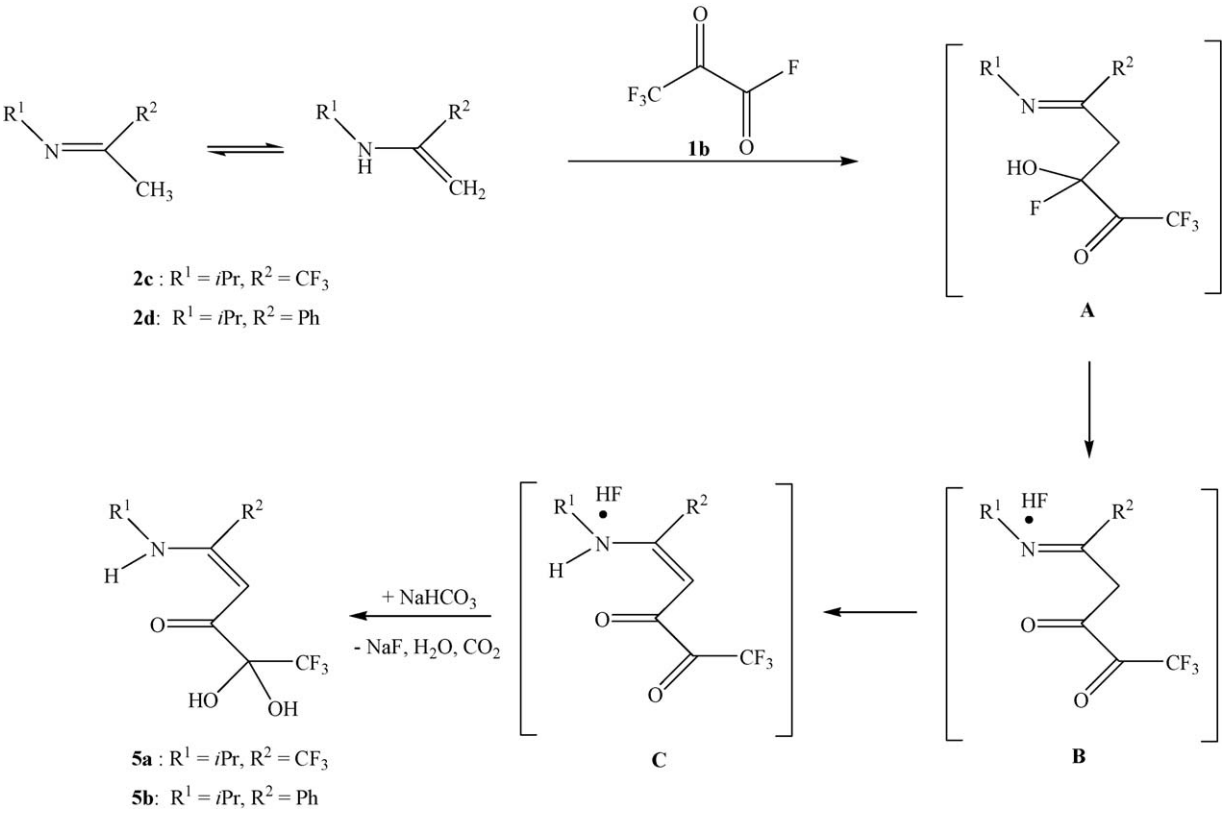


Fig. 4. Unit cell of compound β-hydroxyketon (**4**).

fluoride, 3,3,3-trifluoro-2-oxo was obtained in a very good yield and used directly for further transformations. We found that propanoyl fluoride, 3,3,3-trifluoro-2-oxo reacts easily with enamino form of imines 2-isopropylimino-2-phenylethane (**2c**) and 2-isopropylimino-2-trifluoroethane (**2d**) giving unstable adducts β-hydroxy-β-trifluoromethyl imines **A** (Scheme 3).



Scheme 3.

After elimination of HF from intermediate **A** stable iminoketones **B** (see also ref. [14,15]) are obtained, which are in equilibrium with their tautomer enamine form **C**. These intermediates possess in their molecules two acidic centers and one basic center what leads to a reversible interconversion of structural isomers that involves the transfer of a proton, namely 1,5-prototrophy. Diketone **C** was not isolated. After neutralization of intermediate **C** with diluted solution of $NaHCO_3$, the geminal diols (**5a**) and (**5b**) were obtained.

The solid state structure of (**5a**) was determined by single-crystal X-ray diffraction analysis. The molecular structure of compound (**5a**) is depicted in Fig. 5, where the most important bond lengths and angles are listed. We found that the unit cell of the compound (**5a**) consists of eight molecules. It was found in X-ray structure that H(1) coordinates with N(1). Nevertheless, N(1)–C(4) bond with length 132 pm lies between single and double bond. The bonds C(4)–C(6)

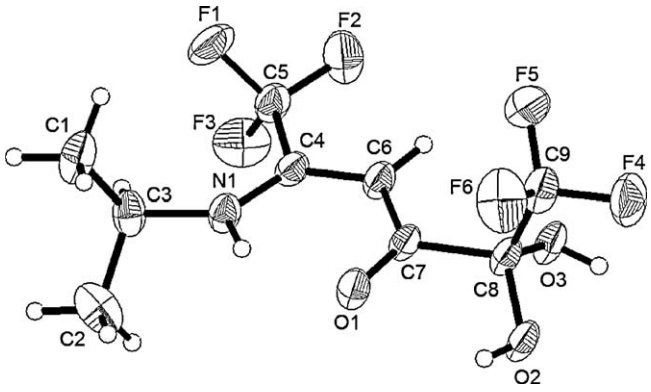
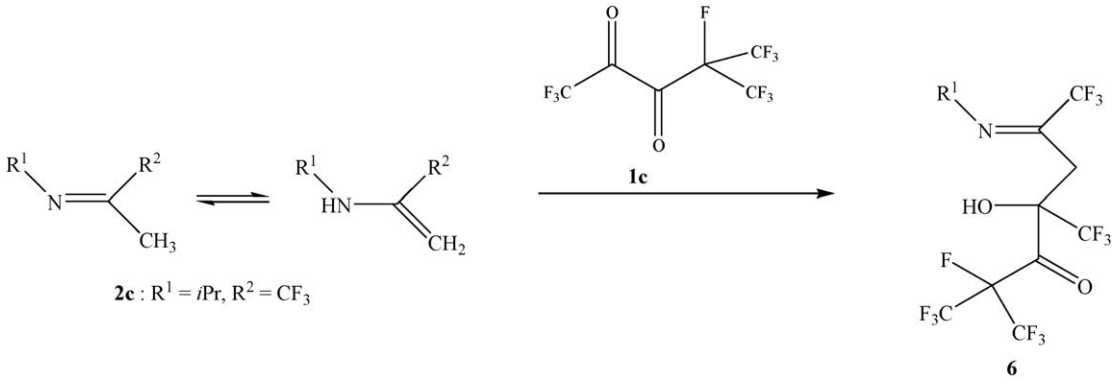
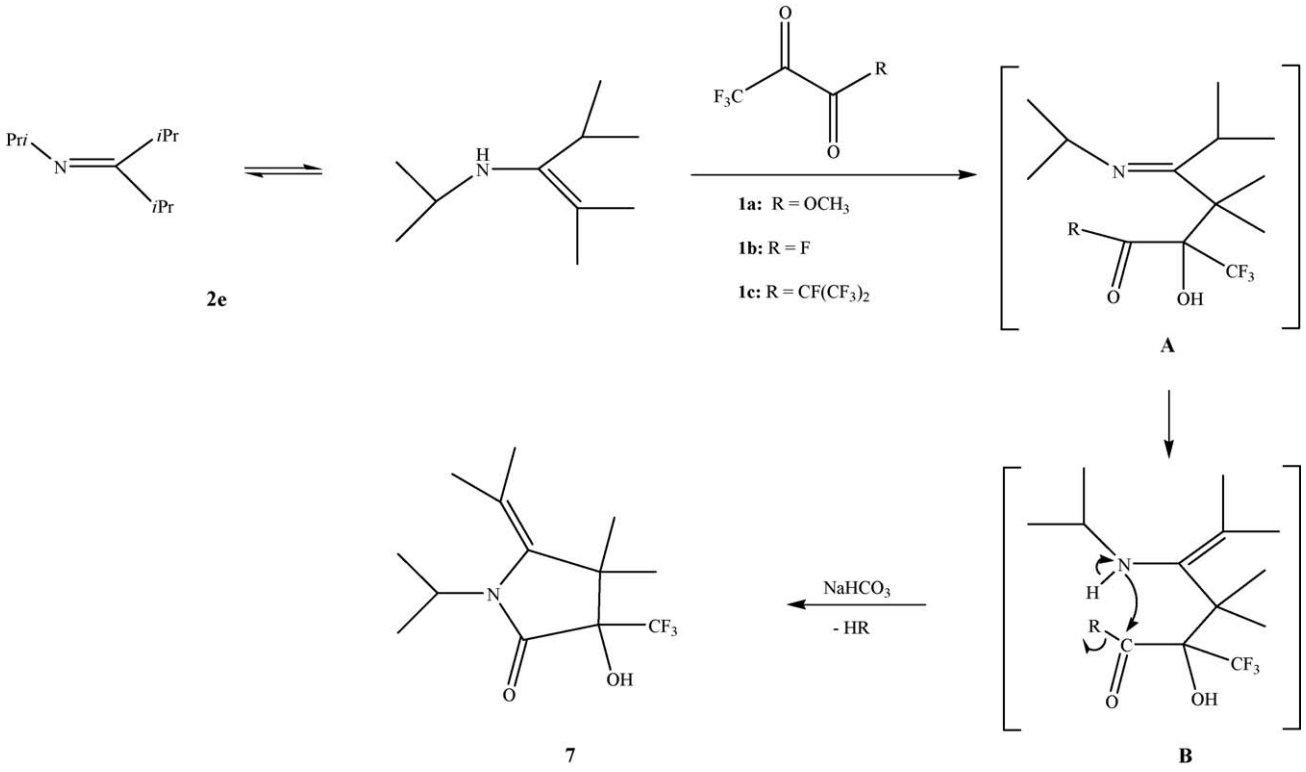


Fig. 5. View of molecular structure (**5a**).



Scheme 4.



Scheme 5.

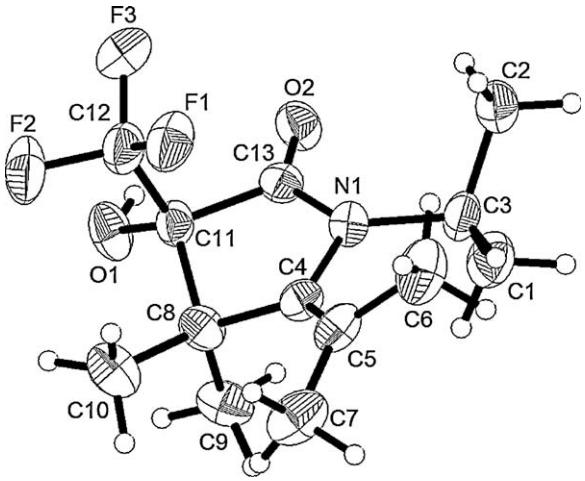


Fig. 6. View of molecular structure (**7**).

with length 138 pm and C(6)–C(7) with length 140 pm cause delocalization, however O(1) is not involved. The H(1)–N(1)–C(4)–C(6)–C(7)–O(1) unit is nearly planar with a maximum displacement of 4.41 pm for H(1). The unit O(1)–C(7)–C(8)–O(2)–H(4) with the torsion angle 170.6° is rotated. Besides, in the molecule two short intramolecular hydrogen bridges were observed: N(1)...O(1) 271.01 [N(1)–H(1)...O(1) 115.56], O(2)...O(1) 266.31 pm [O(2)–H(2)...O(1) 147.35°].

Continuously, we found that perfluoro-1-isopropyl-2-methylediketone (**1c**) reacts in ratio 1:1 with tautomer form of 2-isopropyimino-1,1,1-trifluoroaceton at −70 °C (Scheme 4) yielding 1,1,1,2,7,7,7-heptafluoro-4-hydroxy-6-(isopropylimino)-2,4-bis(-trifluoromethyl)-heptan-3-on **7** in an excellent yield (**6**). ^{31}P, ^{19}F and ^{1}H confirmed the proposed structure. The diastereotopic methylene groups reported in this study correspond to the simplest system AB.

Our further insight was gained by examination of the mediated addition of trifluorinated diketones (**1a–c)** to the same enamine form of ketimine (**2e**) in ratio 1:1. Surprisingly reaction leads in all cases to the same stable lactam (**7**) (Scheme 5). Going into details, there is a nucleophilic attack of the electron-rich of enamine **2e** on carbonyl center of (**1a–c**) yielding β-hydroxyimines **A**. The enamine tautomer **B** of intermediate **A** did not react with second equivalent of fluorinated building block in comparison to above presented examples. There is a presumption that the presence of bulky isopropyl group in α position prevents this mediated addition. Furthermore, the nucleophilic attack of nitrogen in the intermediate **B** on carbonyl group followed by elimination of HR yielded unexpected lactam (**7**).

The molecular structure of lactam (**7**) is depicted in (Fig. 6). We observed that each single molecule forms two intramolecular quite short hydrogen bridges O(1)...O(2a) with length 273.81 pm and O(1b)...O(2) with length 287.47 pm. The five member structure ring N(1)–C(4)–C(8)–C(11)–C(13) is slightly distorted, where C(11) and C(8) lie 15.98 pm and 70.99 pm under the plain of N(1)–(13)–C(11).

Besides, the unit cell lactam (**7**) revealed six molecules which are arranged in layers (Fig. 7). Hydrogen bonds between molecules are connecting them one to each other.

3. Conclusion

To summarize, we have demonstrated that easily accessible trifluorinated building blocks reacts readily with enamine tautomer of selected ketimines giving the desired condensation product in good or excellent yield. The mediated addition reaction did not require present of any catalyst and the reactions are easy to perform. Novel, β-hydroxy-β-trifluoromethyl imines derivatives are great precursors to variety of fluorinated ketones and alcohols. Further studies are under progress.

4. Experimental

Solvents were freshly distilled from the appropriate drying agents directly before use. All other reagents were recrystallized or distilled when necessary. Melting points were determined with an Eletrothermal IA9100 Digital Melting Point Apparatus and are uncorrected. NMR spectra were obtained on Bruker DPX-200 (1H, 200.13, 19F, 188.31, and 13C, 50.32 MHz) spectrometer using the residual proton signals of the deuterated solvent as an internal standard (1H, 13C) relative to TMS, or $CFCl_3$ (19F) as external standards. High-resolution mass spectra were obtained on a Varian MAT CH7A instrument at 70 eV. All reactions and manipulations were conducted under an atmosphere of dry nitrogen. The X-ray structural study was carried out on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation (λ = 71.073 pm). The structure was solved by direct methods and anisotropically refined based on F^2 using the SHELX-97 program package (ref. G. M: Sheldrick, SHELX-97, University of Göttingen). The C–H hydrogen atoms were placed in calculated positions, assigned common isotropic thermal parameters and allowed to ride on their parent atoms. Crystallographic data for (**5a**), (**7**), (**4**) have been deposited with Cambridge Crystallographic Data Centre as supplementary publications CCDC 697161–697163. Copies of the data can be obtained free of charge via the Internet http://www.ccdc.cam.ac.uk, or on application to the director; CCDC; 12 Union Road, Cambridge CB2 1EZ, UK; Tel.: +44 1223 336 408; fax: +44 1223 336 033; deposit@ccdc.cam.ac.uk. The ketimines have been prepared according to the literature procedure. Propan 2-imine (**2a**) and *N*-(propan-2-ylidene)-propan-2amine (**2b**) [17], (N-(1,1,1-trifluorobutan-2-ylidene)propan-2-amine (**2c**), *N*-(1-phenylpropylidene)propan-2-amine (**2d**) [18], *N*-(2,4-dimethyl-

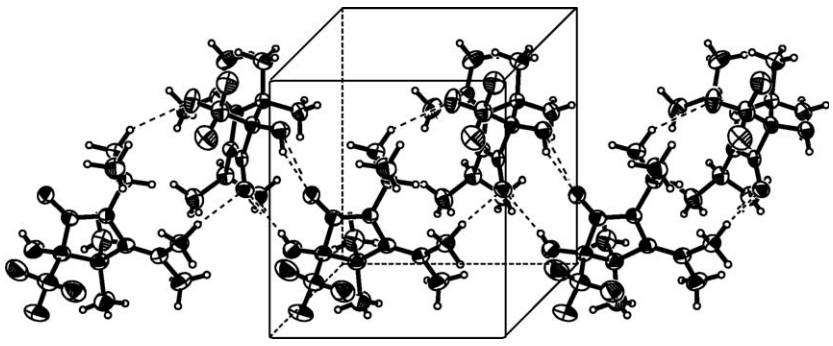


Fig. 7. The unit cell of compound (**7**).

pentane-3-ylidene)-propan-2-amine (**2e**) [19]. For synthesis of the compound (**1c**) please find references [17].

4.1. General procedure for the preparation of the compounds (3a, 3b, 7)

Methyl trifluoropyruvate **1** (3.12 g, 20.0 mmol) was added at 0 °C to a solution of (3.1 g, 20.0 mmol) corresponding imine (**2a**, **2b**, **2e**) in dry diethylether. The reaction mixture was stirred 10 h. All volatiles were removed under reduced pressure. The crude product was recrystallized from n-hexane.

4.2. Dimethyl 2,6-dihydroxy-4-imino-2,6-bis(trifluoromethyl)heptanedioate (3a)

Yield 91% (white crystals), mp 52–54 °C. ^{1}H NMR ($CDCl_3$) δ: 3.20 (m, 4H, CH_2), 3.87 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 4.20 (s, 2H, OH), ^{19}F NMR ($CDCl_3$) δ: −75.64 (q, CF_3). Calculated for $C_{11}H_{13}F_6NO_6$: (M–MeOH) 337.17562, found 337.17585.

4.3. Dimethyl 2,6-dihydroxy-4-(isopropylimino)-2,6-bis(trifluoromethyl)heptanedioate (3b)

Yield 94% (white crystals), mp 72–74 °C. ^{1}H NMR ($CDCl_3$) δ: 1.03 (d, 6H, CH_3, *i*Pr, $^3J_{HH}$ = 6.11 Hz), 2.84 (dd, 4H, CH_2, AB-system J_{HH} = 16.88 Hz), 3.78 (sep, 1H, *i*Pr), 3.78 (s, 3H, OCH_3), 7.82 (s, 2H, OH). ^{19}F NMR ($CDCl_3$): δ −80.17 (s, CF_3), −80.24 (s, CF_3). MS (EI), *m*/*e* (%): 411 (M+, 6), 396 ([M–CH_3]$^+$, 10), 352 ([M–$NiPr_3$]$^+$, 50), 334 ([M–H_2O–NiPr]$^+$, 10), 292 ([M–2CH_3]$^+$, 11), 260 ([M–2CH_3–2CO_2–2OH]$^+$, 8), 240 ([M–$CH_2C(OH)(CF_3)COOCH_3$]$^+$, 50), 198 ([M–NiPr–$CH_2C(OH)(CF_3)COOCH_3$]$^+$, 100), 180 ([M–NiPr–$CH_2C(OH)(CF_3)COOCH_3$–CH_3]$^+$, 40), 170 (–$CH_2C(OH)(CF_3)COOCH_3$, 7), 160 (–$C(OH)(CF_3)COOCH_3$, 4), 69 (–CF_3, 9), 43 (*i*Pr, 20) and other fragments. HRMS calculated for $C_{14}H_{19}F_6NO_6$: (M+) 411.11166, found 411.11146.

4.4. Dimethyl 2,6-dihydroxy-4-oxo-2,6-bis(trifluoromethyl)heptanedioate (4)

3.6 mmol (1.5 g) of (**3b**) was dissolved in 10 ml of acetone and some drops of diluted solution of HCl was added dropwise. The reaction mixture was refluxed for 2 h. All volatiles were removed under reduced pressure. The crude product was recrystallized from the mixture of petroleum ether and acetone (1:5). Yield 74% (white crystals), mp 127–130 °C. ^{1}H NMR ($CDCl_3$) δ: 3.20 (d, 4H, CH_2, AB-system J_{HH} = 16.68), 3.81 (s, 6H, OCH_3), 4.64 (s, 2H, OH).^{19}F NMR ($CDCl_3$): δ −80.50 (s, CF_3), −80.24 (s, CF_3). MS (EI), *m*/*e* (%): 370 (M^+, 6), 355 ([M–CH_3]$^+$, 10), 213 ([M–$C(OH)(COOCH_3)CF_3$]$^+$, 100), and other fragments. Calculated for $C_{11}H_{12}F_6O_7$: C, 35.69; H, 3.27; F, 30.79. Found: C, 37.70; H, 3.75; F, 30.00.

4.5. General procedure for (5a) and (5b)

To a solution of 50 mmol of corresponding imine (**2c**, **2d**) in dry diethyl ether 50 mmol of 3,3,3-trifluoro-2-oxo-pyruvoyl fluoride was condensed. The reaction mixture was allowed to warm up slowly till room temperature. All volatiles were removed under reduced pressure. The crude product was dissolved in solution of $NaHCO_3$ and mixed. Then, organic layer was separated from water layer and dried over $MgSO_4$. After removing of solvent, the crude product was recrystallized form the mixture of diethylether and n-hexan (1:5).

4.6. 1,1,1,6,6,6-Hexafluoro-2,2-dihydroxy-5-(isopropylamino)hex-4-en-3-one (5a)

Yield 57% (colorless crystals), mp 62–64 °C. ^{1}H NMR ($CDCl_3$) δ: 1.25 (d, 6H, CH_3, *i*Pr, $^3J_{HH}$ = 6.71), 3.92 (sep, 1H, CH, *i*Pr, $^3J_{HH}$ = 6.70 Hz), 5.83 (s, 1H, CH), 7.19 (s, 1H, NH), 10.2 (s, 2H, OH). ^{19}F NMR ($CDCl_3$): δ −70.47 (s, CF_3), −86.94 (s, CF_3). MS (EI), *m*/*e* (%): 295 (M+, 9), 278 ([M–OH]$^+$, 5), 180 ([M–$C(OH)_2CF_3$]$^+$, 92), 138 ([M–$C(OH)_2CF_3$–*i*Pr]$^+$, 100), 96 ([$C(OH)CF_3$ + 2H]$^+$, 10), 69 (CF_3, 18), 43 (*i*Pr, 40) and other fragments. Calculated for $C_9H_{11}F_6NO_3$: C, 36.62; H, 3.76; F, 38.68. Found: C, 36.47; H, 3.43; F, 38.50.

4.7. 5,5,5-Trifluoro-4,4-dihydroxy-1-(isopropylamino)-1-phenylpent-1-en-3-one (5b)

Yield 63% (white crystals), mp 73–77 °C. ^{1}H NMR ($CDCl_3$) δ: 1.11 (d, 6H, CH_3, *i*Pr, $^3J_{HH}$ = 7.00 Hz), 3.84 (sep, 1H, CH, *i*Pr, $^3J_{HH}$ = 6.90 Hz), 5.62 (s, 1H, CH), 6.91 (s, 1H, NH), 7.64 (m, 5H, Ph), 10.00 (s, 2H, OH). ^{19}F NMR ($CDCl_3$): δ −79.47 (s, CF_3). MS (EI), *m*/*e* (%): 303 (M+, 6), 285 ([M–OH_2]$^+$, 5), 145 ([M–$C(OH)_2CF_3$–*i*Pr]$^+$, 100), 69 (CF_3, 18), 43 (*i*Pr, 40) and other fragments. HRMS calculated for $C_{14}H_{16}F_3NO_3$: (M+) 303.27814, found 303.27851.

4.8. 1,1,1,2,7,7,7-Heptafluoro-4-hydroxy-6-(isopropylimino)-2,4-bis(trifluoromethyl)-heptan-3-on (6)

To a cooled (−70 °C) solution of 10 mmol (1.5 g) imine of (**2c**) in dry diethylether 10 mmol (3.0 g) of perfluoromethylpentandion (**1c**) was added dropwise. The reaction mixture was stirred overnight and allowed to warm up till room temperature. All volatiles were removed under reduced pressure. The crude product was recrystallized from hexan. Yield 99% (white crystals), mp 117–120 °C. ^{1}H NMR ($CDCl_3$) δ: 1.11 (d, 3H, CH_3, *i*Pr, $^3J_{HH}$ = 5.87 Hz), 1.20 (d, 3H, CH_3, *i*Pr, $^3J_{HH}$ = 5.87 Hz), 3.20 (AB-System, 2H, CH_2, $^{AB}J_{HH}$ = 17.61 Hz), 4.21 (m, 1H, CH, *i*Pr), 7.22 (s, 1H, OH). ^{19}F NMR ($CDCl_3$): δ −68.50 (s, 3F, CF_3), −71.23 (s, 3F, CF_3), −71.27 (s, 3F, CF_3), −71.80 (s, 3F, CF_3), 176.00 (s, 1F, CF). ^{13}C NMR ($CDCl_3$) δ: 22.50 (s, 1C, CH_3), 23.00 (s, 1C, CH_3), 33.00 (s, 1C, CH_2), 54.50 (s, 1C, CH), 84.50 (q, 1C, N=**C**–CF_3, $^3J_{CF}$ = 29.39 Hz), 93.00 (dgg, 1C, CF_3–**C**(F)–CF_3, $^1J_{CF}$ = 230.58 Hz, $^3J_{CF}$ = 32.4 Hz), 116.23 (q, 1C, N=C–**C**F_3, $^1J_{HH}$ = 289.35 Hz), 118.25 (dq, 1C, CF_3–C(F)–**C**F_3, $^1J_{CF}$ = 291.61 Hz, $^3J_{CF}$ = 12.09 Hz), 118.50 (dq, 1C, **C**F_3–C(F)–**C**F_3, $^1J_{CF}$ = 285.58 Hz, $^3J_{CF}$ = 12.06 Hz), 154.0 (q, 1C, HO–**C**–CF_3, $^3J_{CF}$ = 30.89 Hz), 191.50 (d, 1C, $FC(CF_3)_2$–C(O)–, $^2J_{CF}$ = 24.87 Hz). Calculated for $C_{12}H_{10}F_{13}NO_2$: C, 32.23; H, 2.25; F, 55.23. Found: C, 32.15; H, 2.35; F, 55.0.

4.9. 3-Hydroxy-1-isopropyl-4,4-dimethyl-5-(propanyl-2-ylidene)-3-(trifluoromethyl)pyrrolidin-2-one (7)

Yield 70% (white crystals), mp 77–79 °C. ^{1}H NMR ($CDCl_3$) δ: 1.12 (s, 3H, CH_3), 1.36 (d, 3H, *i*Pr, $^3J_{HH}$ = 6.73 Hz), 1.47 (q, 3H, CH_3, $^5J_{FH}$ = 1.96 Hz), 1.57 (d, 3H, CH_3, *i*Pr, $^3J_{HH}$ = 6.96 Hz), 1.74 (s, 3H, CH_3, $C(CH_3)_2$), 1.76 (s, 3H, CH_3, $C(CH_3)_2$), 3.5 (s, 1H, OH), 3.84 (sep, 1H, CH, –Pr, $^3J_{HH}$ = 6.88 Hz). ^{19}F NMR ($CDCl_3$) δ: −75.64 (q, CF_3). Calculated for $C_{13}H_{20}F_3NO_2$: C, 55.91; H, 7.17; F, 20.43. Found: C, 55.19; H, 6.71; F, 20.22.

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References

[1] S. Rozen, Methods of Organic Chemistry, Houben-Weyl, Ed, Thieme, Stuttgart, 2000.
[2] X. Ren, W. Wan, H. Jiang, J. Hao, Mini-Rev. Org. Chem. 4 (2007) 330.
[3] M. Shimizu, T. Hiyama, Angew. Chem. Int. Ed. 44 (2005) 214.
[4] J.M. Percy, Top. Curr. Chem. 193 (1977) 131.
[5] B. Dolenský, J. Kvičala, O. Paleta, J. Fluorine Chem. 126 (2005) 745.
[6] K. Burger, K. Mütze, W. Hollweck, B. Koksch, Tetrahedron 54 (1998) 5915.
[7] P. Bravo, L. Bruche, G. Fronza, G. Zecchi, Tetrahedron 48 (1992) 9775.

[8] G.K.S. Prakash, M. Mandal, S. Schweizer, N.A. Petasis, G.A. Olah, Org. Lett. 2 (2000) 3171.
[9] E. Konefal, S.J. Loeb, D.W. Stephan, Ch.J. Wills, Inorg. Chem. 23 (1984) 538.
[10] (a) Y.L. Chen, C.C. Hsu, Y.H. Song, Y. Chi, A.J. Carty, S.M. Peng, G.H. Lee, Chem. Vap. Deposit. 12 (2006) 442;
(b) Y.H. Liu, Y.C. Tung, Y.L. Tung, Y. Chi, Y.L. Chen, C.S. Lui, S.M. Peng, G.H. Lee, J. Mater. Chem. 13 (2003) 135;
(c) E. Lay, Y.H. Song, Y.C. Chiu, Y.M. Lin, Y. Chi, A.J. Carty, S.M. Peng, G.H. Lee, Inorg. Chem. 44 (2005) 7226.
[11] K. Funabiki, K. Matsanaga, M. Matsui, K. Shibata, Synlett (1999) 1477.
[12] K. Funabiki, M. Nojiri, M. Matsui, K. Shibata, J. Chem. Soc., Chem. Commun. (1998) 2051.
[13] N. Marguet, E. Grunova, E. Kirillov, M. Bouyanyi, Ch.M. Thomas, J.-F. Carpentier, Tetrahedron 64 (2008) 75.
[14] J.A. Barten, K. Funabiki, G.-V. Röschenthaler, J. Fluorine Chem. 113 (2002) 105.
[15] J.A. Barten, E. Lork, G.-V. Röschenthaler, J. Fluorine Chem. 125 (2004) 1039.
[16] B. Dolenský, J. Kvičala, O.J. Paleček, Paleta, J. Fluorine Chem. 115 (2002) 67.
[17] A.A. Kadyrov, I. Neda, T. Kaukorat, A. Fischer, P.G. Jones, J. Fluorine Chem. 72 (1995) 29.
[18] K. Findeisen, H. Heitzer, K. Dehnicke, Synthesis (1981) 702.
[19] H. Weingarten, J.P. Chupp, W.A. White, J. Org. Chem. 32 (1967) 3246.