Biomimetic Reductive Amination of Fluoro Aldehydes and Ketones *via* [1,3]-Proton Shift Reaction.[1] Scope and Limitations

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A systematic study of azomethine−azomethine isomerizations of the *N*-benzylimines **2**, derived from fluorinated aldehydes or ketones and benzylamine, has been made. The results reveal that, in sharp contrast to hydrocarbon analogs, fluorinated imines of **2** in triethylamine solution undergo isomerizations to give the corresponding *N*-benzylidene derivatives **5** (for **5**/**2** $K > 32$) in good isolated yields. The rates of the isomerizations depend on the starting imine structures and increase in the following order: aryl perfluoroalkyl ketimine **2m**, per(poly)fluoroalkyl aldimine **2a**,**d**−**g**, perfluoroaryl aldimine **2h**, alkyl perfluoroalkyl ketimine **2i**,**j**. The presence of chlorine or bromine atoms in the α-position to the C=N double bond of the starting imine favors a dehydrohalogenation reaction, giving rise to unsaturated products **6**−**9**. The azomethine−azomethine isomerization was studied and proven to proceed essentially (>98%) intramolecularly with isotope exchange experiments. High chemical yields, the simplicity of the experimental procedure, and the low cost of all reagents employed make this biomimetic transamination of fluorocarbonyl compounds a practical method for preparing fluorine-containing amines of biological interest.

Introduction

Since the amino functionality is often involved in the of biological activity of organic compounds, the development of new synthetic methodologies to create amino groups continues to be a topic of fundamental interest in organic chemistry. Reductive amination of a carbonyl group is the most direct approach to the synthesis of amino compounds, and accordingly, considerable effort has been expended to devise generalized approaches to this synthetic transformation.[2] The overwhelming majority of methods established for the reductive amination of carbonyl compounds employ external reducing reagents, among which sodium cyanoborohydride (Borch reduction)[3] and sodium triacetoxyborohydride (Gribble reduction)[4] are the most synthetically useful and powerful to perform the reduction of the C=N double bond.

We have been interested in a conceptually different approach to the reductive amination of carbonyl compounds, based on an intramolecular reduction−oxidation process *via* a base-catalyzed [1,3]-proton shift in the azaallylic system of appropriate imines (Figure 1). This transformation, an azomethine−azomethine isomerization, is a key step of the enzyme-catalyzed interconversion of α-amino and α-keto carboxylic acids, which proceeds through the corresponding imines derived from pyridoxal and pyridoxamine.[5] Chemical modeling of biological transamination has attracted a great deal of interest in the past.[6] It has been shown that the mechanism of the azomethine−azomethine isomerization involves azaallylic anions as intermediates and the equilibrium constants of the isomerization are adequately correlated by the Hammett equation.[6h,i] With respect to synthetic application of the azomethine−azomethine isomerization, some progress has been achieved with the development of synthetic pyridoxamine analogs for transamination of α-keto carboxylic acids to α-amino acids under reaction conditions which closely approximate those of biological transamination (*i.e.*, an aqueous medium and the presence of zinc ions).[7] In contrast, in organic solvents with the use of α-arylalkylamines as analogs of pyridoxamine, the azomethine−azomethine

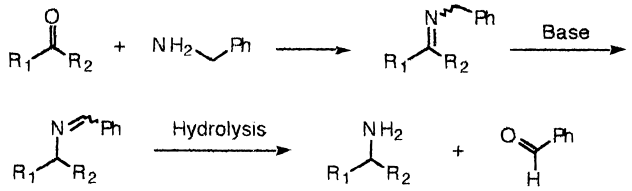

Figure 1.

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isomerization was shown to be rather immobile and strong base catalysts are necessary for isomerization to occur, with equilibrium usually not favoring the desired products.[6] Thus, no generalized synthetic applications of the biomimetic azomethine−azomethine isomerization have been reported to date.

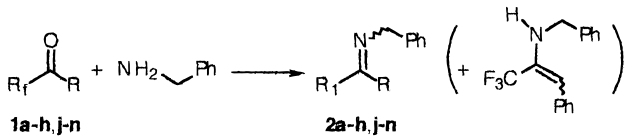
As a part of an ongoing study[8] on the viability of the biomimetic reductive amination approach for preparation of fluorinated amino compounds of high biomedicinal interest,[9] we present here a full account of our studies of this isomerization, a [1,3]-proton shift reaction, for the synthesis of α-fluoroalkyl-substituted amines starting with appropriate fluorinated aldehydes or ketones and benzylamine. In order to compare the effect of the structure of the reactant imine on the isomerization process, reactions with *N*-benzylimines derived from chlorofluoro and bromofluoro aldehydes and ketones also have been carried out under the standard conditions.

Our study indicates that, in sharp contrast to hydrocarbon carbonyl compounds, *N*-benzylimines derived from fluoroalkyl and fluoroaryl aldehydes and alkyl fluoroalkyl and aryl fluoroalkyl ketones in triethylamine solution under mild reaction conditions (room temperature reactions) easily undergo azomethine−azomethine isomerization ([1,3]-proton shift) to give *N*-benzylidene derivatives which, upon acidic hydrolysis, release the targeted fluorinated amines in high overall yield. In all cases studied, even in higher temperature reactions, no detectable dehydrofluorination of the *N*-benzylideneperfluoroalkylamines was observed. In contrast, when chloro- or bromofluoroalkyl derivatives are involved in the [1,3]-proton shift reaction, a sizable amount of products resulting from dehydrohalogenation are observed.

Results and Discussion

Initial *N*-benzylimines **2a**−**h**,**j**−**n** were prepared by the direct condensation of carbonyl compounds **1a**−**h**,**j**−**n** with benzylamine in the presence of a catalytic amount of *p*-toluenesulfonic acid in benzene or toluene solution (Scheme 1). Yields of the desired imines **2a**−**h**,**j**−**n** range from excellent for perfluoroaldehydes to poor for chlorine- and bromine-containing derivatives, since in these cases some side reactions, such as halogen substitution and haloform decomposition, take place. The reaction of benzyl trifluoromethyl ketone with benzylamine gave a mixture of desired ketimine **2l** and the corresponding enamine in a ratio of 1.3:1. Due to the low boiling point of trifluoroacetone, we have prepared *N*-benzylimine **2i**

Scheme 1

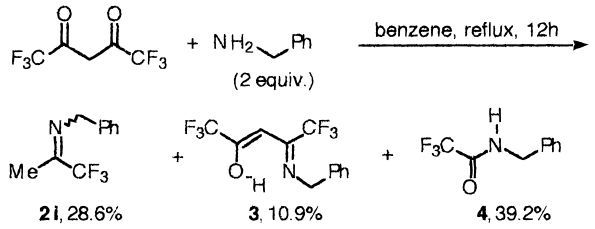


1a-h,j-n **2a-h,j-n**

	a	**b**	**c**	**d**	**e**	**f**	**g**
R_f	CF_3	$CClF_2$	CCl_3	C_3F_7	C_4F_9	$H(CF_2)_4$	$H(CF_2)_6$
R	H	H	H	H	H	H	H

	h	**j**	**k**	**l**	**m**	**n**
R_f	C_6F_5	C_3F_7	CF_3	CF_3	CF_3	$CClF_2$
R	H	Me	CH_2Br	CH_2Ph	Ph	Ph

Scheme 2



2i, 28.6% **3**, 10.9% **4**, 39.2%

starting with 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, which combined with benzylamine to give the targeted imine **2i** in 57% yield along with compounds **3** and **4** (Scheme 2).

Isomerization of the imines **2a**−**n** was examined at various temperatures using triethylamine (TEA) as a base, since it could be easily removed *in vacuo* after completion of the reaction. The results are summarized in Table 1. Trifluoromethyl-containing aldimine **2a** was found to undergo a [1,3]-proton shift reaction to give *N*-benzylidene derivative **5a** in TEA solution at room temperature (14−18 °C), albeit with a slow reaction rate (entries 1−4). Thus, a 50% conversion of the starting aldimine **2a** to *N*-benzylidene derivative **5a** occurred after 9 h (entry 1), while final thermodynamic equilibration of the mixture, resulting in complete isomerization of **2a** to **5a** (over 99%, entry 4), was observed after 90 h. At higher temperatures, the rate of the isomerization markedly increased and nearly complete transformation of **2a** to **5a** was achieved within 24 h (entry 5). In both cases, at room temperature and at 50 °C, the isomerization was very clean. No byproducts were detected by NMR (^{1}H and ^{19}F) in the reaction mixture, and the desired *N*-benzylidenetrifluoroethylamine was isolated in preparatively valuable yields (87−91%). Substitution of one fluorine atom in the trifluoromethyl group of **2a** with a chlorine atom dramatically changed the reactivity and the outcome of the chlorodifluoroimine **2b** [1,3]-proton shift reaction. Thus, upon dissolving imine **2b** in TEA, a slightly exothermic reaction took place and precipitation of TEA hydrochloride was observed. GLC and ^{1}H and ^{19}F NMR analyses of the reaction mixture showed the presence of two main products, **5b** and **6**, in a ratio of 1:1. The structures of *N*-benzylideneamine **5b** and its dehydrochlorinated derivative **6** were assigned by their NMR spectra and GCMS analysis. It is interesting to note that the transformation of chlorodifluoro imine **2b** into a mixture of **5b** and **6** occurred with a higher reaction rate than the isomerization of **2a** to **5a** (entry 6 *vs* entry 5) and that a relative ratio of products **5b** and **6**, detected as a 1:1 mixture upon completion of the reaction (24 h,

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Table 1. Triethylamine-Catalyzed [1,3]-Proton Shift Reaction

	imine **2**		conditions[a]			
entry	R_f	R	temp, °C	time h	convrsn, %[c]	yield, %[b]
1	(**a**) CF_3	H	14−18	9	50	
2	(**a**) CF_3	H	14−18	35	90	
3	(**a**) CF_3	H	14−18	58	97.5	
4	(**a**) CF_3	H	14−18	90	>99	91
5	(**a**) CF_3	H	50	24	98	87
6	(**b**) $CClF_2$	H	14−18	24	98	74[d]
7	(**c**) CCl_3	H	14−18	60	>97	93[e]
8	(**d**) C_3F_7	H	14−18	90	>99	88
9	(**d**) C_3F_7	H	50	20	>99	86
10	(**e**) C_4F_9	H	14−18	86	99	91
11	(**e**) C_4F_9	H	50	21	98	89
12	(**f**) $H(CF_2)_4$	H	14−18	90	98	91
13	(**f**) $H(CF_2)_4$	H	50	15	97	89
14	(**g**) $H(CF_2)_6$	H	14−16	61	98	93
15	(**g**) $H(CF_2)_6$	H	50	18	98	90
16	(**h**) C_6F_5	H	14−16	36	78	
17	(**h**) C_6F_5	H	14−16	160	97	92
18	(**i**) CF_3	Me	50	47	50	
19	(**i**) CF_3	Me	50	119	85.5	
20	(**i**) CF_3	Me	50	190	98	95
21	(**j**) C_3F_7	Me	50	24	63	
22	(**j**) C_3F_7	Me	50	72	95	84
23	(**k**) CF_3	CH_2Br	14−16	24	>99	71[f]
24	(**l**) CF_3	CH_2Ph[g]	78	48	>99	92
25	(**m**) CF_3	Ph	12−14	24	>98	96
26	(**m**) CF_3	Ph	12−14[h]	36	>98	93
27	(**n**) $CClF_2$	Ph	14−16	15	>99	83[i]

[a] Reactions were run in NEt_3 solution. [b] Isolated (flash chromatography) yields of products. [c] Conversion of the starting materials to the products, monitored by GLC and ^1H and ^{19}F NMR. [d] Yield of a mixture of compounds **5b** and **6** in a ratio of 1:1. [e] Compound **7**. [f] Compound **8**. [g] A mixture of ketimine and enamine in a ratio of 1.3:1, respectively. [h] Reaction was run in a solution of methanol-d_4/NEt_3 (1:1). [i] Yield of a mixture of compounds **5n** and **9** in a ratio of 1:4, respectively.

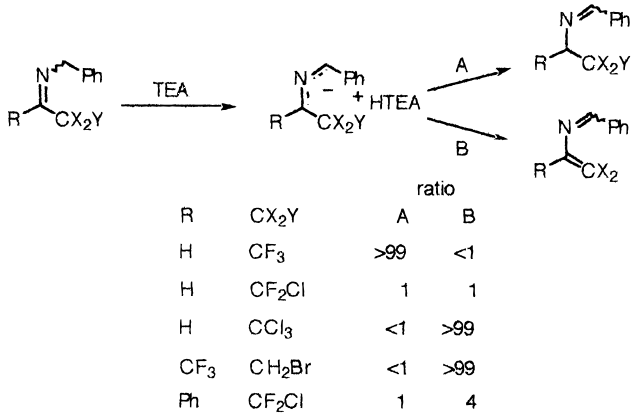
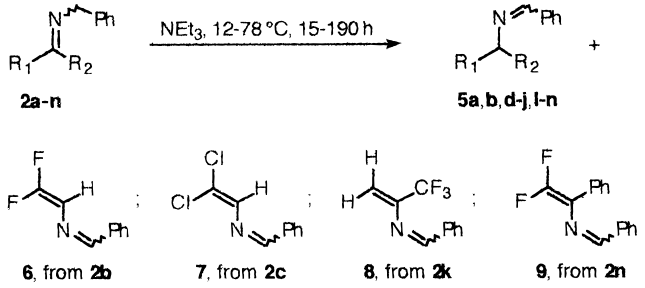


Figure 2. Possible pathways for intermediate azaallylic carbanion stabilization: collapse of an anion to covalent state (A), β-elimination of a halogen atom (B).

entry 6), did not change while standing at room temperature in the TEA solution for about 1 week. These observations could be rationalized by assuming that the formation of the dehydrochlorinated product **6** was an irreversible process and that **6** was the result of intermediate azaallylic carbanion stabilization rather than the dehydrochlorination of the resultant *N*-benzylideneamine **5b** under the action of TEA, as shown in Figure 2. When trichloromethyl derivative **2c** was subjected to the action of TEA, only dehydrochlorination was realized to give azadiene **7** in high yield (entry 7). It is worth noting that this irreversible reaction was slower than the isomerizations of **2a**,**b**. This difference might be accounted for by a lower electron-withdrawing effect of the trichloromethyl group as compared with the trifluoro- and chlorodifluoromethyl analogs.[10] Thus, in the series of trifluoro-, chlorodifluoro-, and trichloromethyl imines **2a**−**c**, the chemical outcome of their TEA-catalyzed transformations greatly depended on the nature of the starting imines (Figure 2). Regioselective formation of *N*-benzylideneamine **5a** occurred in the case of the trifluoroderivative **2a**, and in contrast, the dehydrochlorinated compound **7** formed as the only observed product in the reaction of trichloroderivative **2c**. While such a sharp contrast in the reactivity of **2a**−**c** is rather surprising, it may be rationalized in the terms of the bond energies of C−F, C−Cl (in $CClF_2$), and C−Cl (in CCl_3), which decrease in the same order.[11]

Scheme 3



Due to the high chemical yield and mild reaction conditions, the transformation of *N*-benzyltrifluoroacetaldimine (**2a**) into the *N*-benzylidene derivative **5a** is of preparative value. Therefore, we decided to check the generality of this transamination reaction for a series of per(poly)fluoroalkyl aldehydes (see Scheme 3). The results (entries 8−15) reveal that the pattern of reactivity of the *N*-benzylimines containing perfluoropropyl (**2d**) and -butyl groups (**2e**) and ω-hydroperfluorobutyl (**2f**) and -hexyl (**2g**) groups is quite similar to that of the trifluoromethyl derivative **2a**. Thus, isomerization of imines **2d**−**g** to the *N*-benzylidene derivatives **5d**−**g** in TEA solution was essentially complete in 61−90 h at room temperature or in 15−21 h at 50 °C. In all **2d**−**g** to **5d**−**g** isomerizations, no detectable amounts of side products were observed and the targeted *N*-benzylidene derivatives **5d**−**g** were isolated in synthetically valuable (86−93%) yields.

Isomerization of pentafluorophenyl derivative **2h** is the most exciting example, since thermodynamic equilibration of hydrocarbon and fluorocarbon benzyl carbanions can be observed in this case. While standing in TEA solution at room temperature (entries 16 and 17), *N*-benzylimine **2h** gradually underwent azomethine−azomethine isomerization to give *N*-benzylidene derivative **5h**, following the general reactivity pattern observed for the per(poly)fluoroalkyl aldehydes. Thus, a 78% conversion of *N*-benzylimine **2h** to *N*-benzylidene derivative **5h** was detected in 36 h, whereas completion (97% of **5h**) of this transformation required about 1 week under the same reaction conditions. Nevertheless, the high isolated yield (92%) of the desired *N*-benzylidenepentafluorobenzylamine (**5h**) make this method preparatively appealing.

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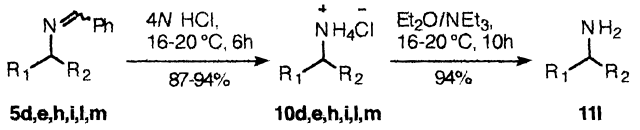
With these results in hand, we next explored transamination of fluoroalkyl alkyl and fluoroalkyl aryl ketones. We have found that in contrast to aldimines **2a**−**h**, the TEA-catalyzed isomerization of ketimine **2i** to the corresponding *N*-benzylidene derivative **5i** does not take place at room temperature. Thus, after 2 days *N*-benzyl ketimine **2i** was kept in TEA solution for 2 days, only a small amount (<5%) of **5i** was detected by NMR. Increasing the reaction temperature greatly accelerated the isomerization rate, allowing the reaction to reach at least a 98% conversion of **2i** to **5i** in 190 h (entries 18−20). Similar to that of the the per(poly)fluoro aldimines, this isomerization occurred very cleanly, giving rise to the desired product **5i** in preparatively valuable yield. It is very interesting to note that, as it is revealed by NMR analyses of the reaction mixtures, theoretically possible base-catalyzed ketimine−enamine isomerization of ketimine **2i** did not take place and the only process observed was transformation of ketimine **2i** to aldimine **5i**. Perfluoropropyl methyl ketimine **2j** showed reactivity similar to that of **2i**. Its conversion to *N*-benzylidene derivative **5j** in TEA solution was detectable at room temperature, but it occurred at a preparatively meaningful rate only at elevated temperatures (entries 21 and 22). Preliminary results showed that this pattern of reactivity might be common for *N*-benzylimines derived from *n*-alkyl *n*-perfluoroalkyl ketones and thus constitutes a general approach to α-(perfluoroalkyl)alkylamines.

As discussed above, chlorine substitution on a fluoroalkyl site (chlorodifluoromethyl imine **2b** reaction, entry 6) leads to the dehydrochlorinated product **6** (Figure 2). A ketone structure offers an opportunity to explore another type of substitution. To this end we investigated the behavior of bromomethyl trifluoromethyl ketimine **2k**. In contrast to ketimines **2i**,**j**, compound **2k** in TEA solution undergoes an irreversible reaction at room temperature to give an unsaturated derivative **8** as the main reaction product in 71% yield (entry 23). Accordingly, we can conclude that the presence of chlorine or bromine atoms at the α-position of a developing [1,3]-azaallylic carbanion favors dehydrohalogenation. However, it should be noted that this type of halogen-containing carbonyl compound is also a challenging target for conventional methods that use reducing agents.

Isomerization of trifluoromethyl benzyl *N*-benzylimine **2l** was expected to be most difficult, since the desirable ketimine **2l**−aldimine **5l** isomerization and undesirable ketimine−enamine transformation might compete with each other due to the relatively high C−H acidity of benzylmethylene at the ketimine bond. As was mentioned before, imine **2l** was prepared as a 1.3/1 mixture with the corresponding enamine. While standing in TEA solution at room temperature the imine:enamine ratio gradually changes to a 1:4 ratio favoring the enamine structure, as confirmed by NMR. Under these conditions not even a trace of the targeted aldimine **5l** was detected in the reaction mixture by NMR or GLC. However, at elevated temperatures (78 °C, entry 24) the desired ketimine **2l**−aldimine **5l** isomerization occurred smoothly, resulting in an essentially complete transformation of **2l** to **5l**. Despite the high reaction temperature required, the targeted product **5l** was isolated in high yield (92%).

As a final object of this study we have explored reactions of the non-enaminolizable phenyl fluoroalkyl ketimines **2m**,**n**. It is important to note that small amounts (5−10%) of the isomerized products **5m**,**n** were isolated from the reaction mixtures at the stage of ketimines **2m**,**n** preparation, suggesting that isomerization of **2m**,**n** to **5m**,**n** occurs in toluene solution under reflux. However, a control experiment demonstrated that pure **2m**,**n** does not undergo thermal isomerization to **5m**,**n** when refluxed in toluene. Accordingly, the catalytic influence of benzylamine as a base might account for partial isomerization of **2m**,**n** during their preparation. We have found that at room temperature in TEA solution phenyl trifluoromethyl ketimine **2m** easily undergoes isomerization to give the *N*-benzylidene derivative **5m** in good yield (entry 25). This transformation is very clean and essentially complete in 24 h. Thus, evaporation of TEA gave pure aldimine **5m**, which can be hydrolyzed to the targeted amine without any additional purification. In contrast to this result, isomerization of phenyl chlorodifluoromethyl ketimine **2n** gave a mixture of the desired *N*-benzylideneamine **5n** and the dehydrochlorinated product **9** in a ratio of 1:4, respectively (entry 27). From the results discussed above, two pathways were anticipated for the isomerization of **2n**. However, the domination of **5n** over **9** was rather surprising.

Scheme 4



Hydrolysis of the Schiff bases **5d**,**e**,**h**,**i**,**l**,**m** to the amine hydrochlorides **10d**,**e**,**h**,**i**,**l**,**m** (Scheme 4) can be easily performed in high yield by the action of 4 N HCl at room temperature on solutions of **5d**,**e**,**h**,**i**,**l**,**m** in diethyl ether. Upon completion of the reaction, the resultant hydrochlorides **10d**,**e**,**h**,**i**,**l**,**m** and benzaldehyde are completely separated in organic (benzaldehyde) and aqueous (hydrochlorides **10d**,**e**,**h**,**i**,**l**,**m**) layers. This also makes the synthesis of the target compounds **10** very simple and efficient. The preparation of free amines is demonstrated with the isolation of **11l** by the action of TEA on corresponding hydrochloride **10l**.

Finally, to gain insight into the mechanism of the [1,3]-proton shift reaction, we have investigated the isomerization of ketimine **2m** in a solution of TEA/MeOH-d_4 (1:1) (entry 26). Under these reaction conditions, the isomerization of ketimine **2m** to its *N*-benzylidene derivative proceeded with a reaction rate and chemical outcome similar to that of the reaction in neat TEA. Investigation of the resultant product **5m** (entry 26) by ^{1}H and ^{19}F NMR showed no differences in the patterns of its NMR spectra to those of **5m** prepared in neat TEA, except for a small singlet. This signal may be attributed to a deuterated product at $\delta = -74.57$ in the ^{19}F NMR spectrum with an intensity less than 2% of the major doublet of the trifluoromethyl group at $\delta = -74.39$. These results suggest that the [1,3]-proton shift occurs through the formation of a contact ion pair.[12] Thus, an intramolecular transfer of the abstracted proton occurs within an intermediate azaallylic anion to give a new covalent state. If this interpretation is correct, it is reasonable to expect the reaction to proceed in a stereo-

(12) (a) Vanthey, E.; Parker, A. W.; Nohova, B.; Phillips, D. *J. Am. Chem. Soc.* **1994**, *116*, 9182. (b) *Advances in Physical Organic Chemistry*; Gold, V., Bethel, D., Eds.; Academic Press: London, New York, San Francisco, 1977; pp 154−260.

controlled manner when an internal (chiral imine) or an external (chiral base) chiral auxiliary is employed.

In conclusion, a systematic study of azomethine−azomethine isomerizations of the *N*-benzylimines **2** derived from appropriate fluorinated aldehydes or ketones and benzylamine reveals that, in sharp contrast to hydrocarbon analogs, fluorinated imines **2** in TEA solution undergo [1,3]-proton shift reaction under very mild reaction conditions to give the corresponding *N*-benzylidene derivatives in good yields. The rates of isomerization depend on the starting imine structure and increase in the following order: aryl perfluoroalkyl ketimine **2m**, per(poly)fluoroalkyl aldimines **2a**,**d**−**g**, perfluoroaryl aldimine **2h**, alkyl perfluoroalkyl ketimines **2i**,**j**. The presence of halogen atoms, except fluorine, at the β-position of the developing carbanion, encourage β-elimination, giving rise to the unsaturated products **6**−**9**. The azomethine−azomethine isomerization studied was shown to proceed essentially (>98%) intramolecularly by isotope exchange experiment.

High chemical yields, the simplicity of the experimental procedure, and the low cost of all reagents employed make this biomimetic transamination approach a practical method for preparing the fluorine-containing amines of biological interest.

Experimental Section

General. All reagents, unless otherwise stated, are commercially available and were used as received. Benzyl trifluoromethyl ketone was prepared according to the literature procedure.[13] For column chromatography, silica gel 60 (230−400 mesh) was used. Melting points are uncorrected. Monitoring of the reactions by GLC was performed using a fused silica capillary column. Mass spectra (electron impact, 70 eV) were obtained on a quadrupolar mass spectrometer, and relative intensities are given in parentheses. ^{1}H, ^{19}F, and ^{13}C NMR spectra were measured at 299.95, 282.24, and 75.42 MHz, respectively. Unless indicated, NMR spectra were taken in $CDCl_3$ solutions using tetramethylsilane (TMS) and $CFCl_3$ as the internal standards. Eluting system for flash chromatography *n*-hexane/ethyl acetate (50:3); R_f values for all compounds described were taken on TLC plates silica gel 60 F_{254} precoated (Merck), using *n*-hexane/ethyl acetate (4:1) as the eluting system.

Unless otherwise stated, yields refer to isolated yields of products of greater than 95% purity as estimated by capillary GC and/or ^{1}H and ^{19}F NMR spectroscopies. All new compounds were characterized by ^{1}H, ^{19}F, and ^{13}C NMR and by mass spectrometry or elemental analysis.

General Method for Preparation of *N*-Benzylimines 2a−n.[14] The starting carbonyl compound (typically 30−50 mmol) was first dissolved in 30−50 mL of benzene or toluene in a 100−150 mL round-bottomed flask equipped with a reflux condenser, a Dean−Stark trap, and a magnetic stirring bar. A stoichiometric amount of benzylamine and 1 mol % of *p*-toluenesulfonic acid monohydrate were added to the reaction flask, and the mixture was stirred at reflux. After the reaction was complete (theoretical amount of water removed; monitored by GLC, TLC, and ^{1}H and ^{19}F NMR), the solvent was removed *in vacuo* and imine products were purified by column chromatography.

***N*-(2,2,2-Trifluoroethylidene)benzylamine (2a)**: 46%, R_f 0.40; ^{1}H NMR δ 4.82 (m, 2H), 7.25−7.37 (m, 5H), 7.63 (m, 1H); ^{19}F NMR δ −72.02 (s); GS-MS *m*/*z* 187 (M, 10), 91 (100). Anal. Calcd for $C_9H_8F_3N$: C, 57.76; H, 4.31; N, 7.49; F, 30,45. Found: C, 57.51; H, 4.29; N, 7.53; F, 30.51. Along with targeted imine **2a**, the corresponding heminal amino alcohol was isolated in 31% yield. Spectral data are as follows: ^{1}H NMR δ 1.72 (br s, 2H), 3.84 (q, 1H, J_{H-F} = 5.6 Hz), 3.93 (s, 2H), 7.23−7.36 (m, 5H); ^{19}F NMR δ −78.05 (d, J_{H-F} = 5.6 Hz).

***N*-(2-Chloro-2,2-difluoroethylidene)benzylamine (2b)**: 58.6%, R_f 0.38; ^{1}H NMR δ 4.82 (d, 2H, J_{H-H} = 1.6 Hz), 7.25−7.39 (m, 5H), 7.68 (tt, 1H, J_{H-F} = 4.2 Hz, J_{H-H} = 1.6 Hz); ^{19}F NMR δ −60.29 (d, J_{H-F} = 4.2 Hz); MS *m*/*z* 203, 205 (M, 6.9, 2.3), 91 (100). Anal. Calcd for $C_9H_8ClF_2N$: C, 53.09; H, 3.96; N, 6.88; F, 18.66. Found: C, 52.93; H, 4.01; N, 6.74; F, 18.69.

***N*-(2,2,2-Trichloroethylidene)benzylamine (2c)**: 5%, R_f 0.25; ^{1}H NMR δ 4.85 (s, 2H), 7.25−7.38 (m, 5H), 7.78 (s, 1H); MS *m*/*z* 200, 202 (M − Cl, 1.4, 0.8), 91 (100).

***N*-(4,4,4,3,3,2,2-Heptafluorobutylidene)benzylamine (2d)**: 77%, R_f 0.41; ^{1}H NMR δ 4.88 (m, 2H), 7.24−7.41 (m, 5H), 7.70 (t, 1H, J_{H-F} = 6.0 Hz); ^{19}F NMR δ −81.01 (t, 3F, J_{F-F} = 8.6 Hz), −118.88 (m, 2F), −128.02 (s, 2F); MS *m*/*z* 287 (M, 4), 91 (100). Anal. Calcd for $C_{11}H_8F_7N$: C, 46.01; H, 2.81; N, 4.88; F, 46.31. Found: C, 45.94; H, 2.85; N, 4.93; F, 46.47.

***N*-(5,5,5,4,4,3,3,2,2-Nonafluoropentylidene)benzylamine (2e)**:[8a] 69%, R_f 0.42; ^{1}H NMR δ 4.78 (m, 2H), 7.19−7.37 (m, 5H), 7.65 (t, 1H, J_{H-F} = 6.0 Hz).

***N*-(5,5,4,4,3,3,2,2-Octafluoropentylidene)benzylamine (2f)**: 93%, R_f 0.34; ^{1}H NMR δ 4.89 (m, 2H), 6.09 (tt, 1H, J_{H-F} = 52.0, 5.4 Hz), 7.18−7.31 (m, 5H), 7.74 (t, 1H, J_{H-F} = 6.3 Hz). Anal. Calcd for $C_{12}H_9F_8N$: C, 45.15; H, 2.84; N, 4.39; F, 47.62. Found: C, 45.02; H, 2.76; N, 4.31; F, 47.75.

***N*-(7,7,6,6,5,5,4,4,3,3,2,2-Dodecafluoroheptylidene)-benzylamine (2g)**: 95%, R_f 0.36; ^{1}H NMR δ 4.87 (m, 2H), 6.03 (tt, 1H, J_{H-F} = 52.2, 5.4 Hz), 7.24−7.38 (m, 5H), 7.71 (t, 1H, J_{H-F} = 6.3 Hz); ^{19}F NMR δ −117.95 (m, 2F), −122.16 (br s, 2F), −123.73 (m, 2F), −124.02 (br s, 2F), −130.02 (m, 2F), −137.50 (d, J_{H-F} = 52.2 Hz); MS *m*/*z* 419 (M, 1), 91 (100). Anal. Calcd for $C_{14}H_9F_{12}N$: C, 40.11; H, 2.16; N, 3.34; F, 54.38. Found: C, 39.98; H, 2.11; N, 3.29; F, 54.50.

***N*-(Pentafluorobenzylidene)benzylamine (2h)**: 97%, R_f 0.28, mp 83−84 °C; ^{1}H NMR δ 4.91 (br s, 2H), 7.28−7.37 (m, 5H), 8.49 (br s, 1H); ^{19}F NMR δ −143.09 (m, 2F), −151.40 (m, 1F), 162.34 (m, 2F); MS *m*/*z* 285 (M, 4), 91 (100). Anal. Calcd for $C_{14}H_8F_5N$: C, 58.96; H, 2.83; N, 4.91; F, 33.31. Found: C, 59.03; H, 2.91; N, 4.96; F, 33.33.

***N*-(1,1,1-Trifluoroisopropylidene)benzylamine (2i).**[8a] 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione (6 g, 28.84 mmol) was first dissolved in benzene (40 mL), and then 2 equiv of benzylamine (6.18 g, 57.67 mmol) and 100 mg of *p*-toluenesulfonic acid were added under stirring. The mixture was stirred at reflux until water ceased to condense in a Dean−Stark trap (12 h). The solvent was removed *in vacuo* (30 mmHg, 30 °C), and the residue was purified by flash chromatography on SiO_2 (200 mL of eluent) to give products **2i**, **3**, and **4**. For **3**: 1.86 g (10.9%), R_f 0.30; ^{1}H NMR δ 4.65 (m, 2H), 5.89 (s, 1H), 7.25−7.41 (m, 5H), 10.73 (br s, 1H); ^{19}F NMR δ −67.28 (s, 3F), −77.86 (s, 3F); MS *m*/*z* 201 (M, 9), 132 (M − CF_3, 7), 91 (100). For imine **2i**: 3.33 g (28.6%), R_f 0.36; ^{1}H NMR δ 2.12 (br s, 3H), 4.68 (s, 2H), 7.28−7.37 (m, 5H); ^{19}F NMR δ −75.24 (s); MS *m*/*z* 201 (M, 9), 132 (M − CF_3, 7), 91 (100). For amide **4**:[8b] 4.96 g (39.2%), R_f 0.14, mp 70−71 °C; ^{1}H NMR δ 4.53 (d, 2H, J_{H-H} = 6.0 Hz), 6.58 (br s, 1H), 7.26−7.38 (m, 5H); MS *m*/*z* 203 (M, 74), 202 (M − H, 25), 134 (M − CF_3, 37), 91 (100).

***N*-(5,5,5,4,4,3,3-Heptafluoropent-2-ylidene)benzylamine (2j)**. 5,5,5,4,4,3,3-Heptafluoro-2-pentanone (2.45 g, 11.55 mmol) was first dissolved in benzene (30 mL), and then 1.24 g (11.57 mmol) of benzylamine, 50 mg of *p*-toluenesulfonic acid, and 3 g of 4A molecular sieves were added with stirring. The mixture was stirred at rt (14−18 °C) for 2 d. Benzene was removed under vacuum (30 mmHg, 30 °C), and the residue was purified by flash chromatography on SiO_2 (100 mL of eluent) to give product **2** (R_f 0.46) in 61.5% yield (2.14 g). While serving as an example for the synthesis of other compounds, this procedure is for a specific compound (**2j**). Spectral data are as follows: ^{1}H NMR δ 2.12 (s, 3H), 4.70 (s, 2H), 7.25−7.35 (m, 5H); ^{19}F NMR δ −80.78 (t, 3F, J_{F-F} = 8.7 Hz), −116.79 (q, 2F, J_{F-F} = 8.7 Hz), −126.26 (s, 2F); MS *m*/*z* 301 (M, 1), 132 (M − C_3F_7, 14.7), 91 (100).

(13) Nes, W. R.; Burger, A. *J. Am. Chem. Soc.* **1950**, *72*, 5409.

(14) Harada, K. In *Chemistry of the Carbon-Nitrogen Double Bond*; Patai, S., Ed.; Interscience: London, 1970; pp 69−147.

***N*-(1,1,1-Trifluoro-3-bromoisopropylidene)benzylamine (2k)**: 28.9%, R_f 0.23. ^{1}H NMR δ 4.00 (s, 2H), 4.83 (m, 2H), 7.38−7.39 (m, 5H); ^{19}F NMR δ −72.56 (s); MS *m*/*z* 279, 281 (M, 2.3, 2.1), 91 (100).

***N*-(1,1,1-Trifluoro-3-phenylisopropylidene)benzylamine (2l)** (in a 1.3/1 mixture with corresponding enamine): 89.5%, R_f 0.31; ^{1}H NMR δ 3.92 (s, 1.12H), 4.69 (s, 1.12H, ketimine), 3.65 (br s, 0.44H), 4.06 (d, 0.88H, J_{H-H} = 4.5 Hz), 6.10 (s, 0.44H, enamine), 7.16−7.35 (m, 10H); ^{19}F NMR δ −68.61 (s, enamine), −72.94 (s, ketimine); MS *m*/*z* 277 (M, 16), 91 (100). Anal. Calcd for $C_{16}H_{14}F_3N$: C, 69.30; H, 5.09; N, 5.05; F, 20.56. Found: C, 69.44; H, 5.17; N, 5.07; F, 20.34.

***N*-(1-Phenyl-2,2,2-trifluoroethylidene)benzylamine (2m)**:[8a] 67%, R_f 0.35; ^{1}H NMR δ 4.61 (s, 2H), 7.26−7.31 (m, 10H); ^{19}F NMR δ −71.41 (s); MS *m*/*z* 263 (M, 19), 91 (100).

***N*-(1-Phenyl-2-chloro-2,2-difluoroethylidene)benzylamine (2n)**: 27%, R_f 0.38; ^{1}H NMR δ 4.56 (s, 2H), 7.25−7.37 (m, 10H); ^{19}F NMR δ −61.35 (s, 1F), −58.54 (s, 1F); MS *m*/*z* 279 (M, 1), 244 (M − Cl, 3), 91 (100).

General Method of Isomerization of 2a−n to *N*-Benzylidene Derivatives 5a,b,d−j,l−n and 6−9. The starting compound **2a**−**n** (typically 25−30 mmol) was dissolved in 3−5 mL of TEA, and the mixture was stirred at the temperature and for the time indicated in Table 1. Progress of the isomerization was monitored by NMR or GLC, and upon completion, any undissolved solid was removed by filtration and TEA was evaporated *in vacuo*. The residual material was dried *via* an oil pump to completely remove the TEA or purified by column chromatography to give products listed below. Yields are given in Table 1.

***N*-Benzylidene-2,2,2-trifluoroethylamine (5a)**: R_f 0.35; ^{1}H NMR δ 4.12 (q, 2H, J_{H-F} = 9.3 Hz), 7.41−7.48 (m, 3H), 7.77−7.81 (m, 2H), 8.35 (s, 1H); ^{19}F NMR δ −71.42 (t, J_{H-F} = 9.3 Hz); MS *m*/*z* 187 (M, 61), 186 (M − H, 26), 118 (M − CF_3, 66), 91 (100). Anal. Calcd for $C_9H_8F_3N$: C, 57.76; H, 4.31; N, 7.49; F, 30,45. Found: C, 57.64; H, 4.33; N, 7.51; F, 30.40.

***N*-Benzylidene-2-chloro-2,2-difluoroethylamine (5b) and *N*-Benzylidene-2,2-difluorovinylamine (6) (1:1 Mixture).** For compound **5b**: ^{1}H NMR δ 4.25 (t, 2H, J_{H-F} = 11.1 Hz), 7.35−7.43 (m, 3H), 7.77−7.81 (m, 2H), 8.35 (s, 1H); ^{19}F NMR δ −57.78 (t, J_{H-F} = 11.1 Hz); GS-MS *m*/*z* 203, 205 (M, 4.8, 1.5), 91 (100). For compound **6**: ^{1}H NMR δ 6.13 (d, 1H, J_{H-F} = 17.0 Hz), 7.35−7.43 (m, 3H), 7.77−7.81 (m, 2H), 8.17 (s, 1H); ^{19}F NMR δ −85.77 (dd, 1F, J_{F-F} = 24.0 Hz, J_{H-F} = 17.0 Hz), −98.73 (d, 1F, J_{F-F} = 24.0 Hz); MS *m*/*z* 167 (M, 84), 166 (M − H, 29), 140 (100), 117 (22), 90 (98), 89 (72), 77 (55), 63 (39).

***N*-Benzylidene-2,2-dichlorovinylamine (7)**: R_f 0.35, mp 50−52 °C; ^{1}H NMR δ 7.20 (s, 1H), 7.42−7.47 (m, 3H), 7.83−7.86 (m, 2H), 8.26 (s, 1H); ^{13}C NMR δ 123.25 (s), 128.92 (s), 129.19 (s), 132.06 (s), 135.71 (s), 139.73 (s), 162.40 (s); MS *m*/*z* 199, 201, 203 (M, 94.5, 57.3, 8.4), 164 (100).

***N*-Benzylidene-4,4,4,3,3,2,2-heptafluorobutylamine (5d)**: R_f 0.38; ^{1}H NMR δ 4.20 (t, 2H, J_{H-F} = 15.6 Hz), 7.43−7.48 (m, 3H), 7.77−7.80 (m, 2H), 8.36 (s, 1H); ^{19}F NMR δ −81.22 (t, 3F, J_{F-F} = 8.5 Hz), −118.06 (m, 2F), −127.66 (br s, 2F). Anal. Calcd for $C_{11}H_8F_7N$: C, 46.01; H, 2.81; N, 4.88; F, 46.31. Found: C, 46.17; H, 2.87; N, 4.73; F, 46.26.

***N*-Benzylidene-5,5,5,4,4,3,3,2,2-nonafluoropentylamine (5e)**:[8a] R_f 0.39; ^{1}H NMR δ 4.20 (t, 2H, J_{H-F} = 15.8 Hz), 7.44−7.49 (m, 3H), 7.75−7.79 (m, 2H), 8.32 (s, 1H).

***N*-Benzylidene-5,5,4,4,3,3,2,2-octafluoropentylamine (5f)**: R_f 0.35; ^{1}H NMR δ 4.23 (t, 2H, J_{H-F} = 15.6 Hz), 6.10 (tt, 1H, J_{H-F} = 52.0, 5.4 Hz), 7.42−7.49 (m, 3H), 7.76−7.80 (m, 2H), 8.35 (s, 1H). Anal. Calcd for $C_{12}H_9F_8N$: C, 45.15; H, 2.84; N, 4.39; F, 47.62. Found: C, 45.21; H, 2.87; N, 4.27; F, 47.58.

***N*-Benzylidene-7,7,6,6,5,5,4,4,3,3,2,2-dodecafluoroheptylamine (5g)**: R_f 0.35; ^{1}H NMR δ 4.21 (t, 2H, J_{H-F} = 15.3 Hz), 6.05 (tt, 1H, J_{H-F} = 51.6, 5.4 Hz), 7.40−7.49 (m, 3H), 7.77−7.80 (m, 2H), 8.36 (s, 1H); ^{19}F NMR δ -117.11 (m, 2F), −122.49 (br s, 2F), −123.35 (br s, 2F), −124.02 (br s, 2F), −130.11 (m, 2F), −137.51 (d, J_{H-F} = 51.6 Hz). Anal. Calcd for $C_{14}H_9F_{12}N$: C, 40.11; H, 2.16; N, 3.34; F, 54.38. Found: C, 39.93; H, 2.19; N, 3.30; F, 54.43.

***N*-Benzylidenepentafluorobenzylamine (5h)**: R_f 0.30, mp 61−62 °C; ^{1}H NMR δ 4.84 (m, 2H), 7.40−7.43 (m, 3H), 7.71−7.74 (m, 2H), 8.40 (m, 1H); ^{19}F NMR δ −143.79 (m, 2F), −155.81 (m, 1F), −162.75 (m, 2F); MS *m*/*z* 285 (M, 72), 284 (M − H, 46), 181 (100). Anal. Calcd for $C_{14}H_8F_5N$: C, 58.96; H, 2.83; N, 4.91; F, 33.31. Found: C, 59.05; H, 2.74; N, 4.87; F, 33.25.

***N*-Benzylidene-1,1,1-trifluoroisopropylamine (5i)**:[8a] R_f 0.41; ^{1}H NMR δ 1.44 (d, 3H, J_{H-H} = 6.6 Hz), 3.84 (septet, 1H, J_{H-H} = J_{H-F} = 6.6 Hz), 7.42−7.46 (m, 3H), 7.77−7.80 (m, 2H), 8.33 (m, 1H); ^{19}F NMR δ −76.86 (d, J_{H-F} = 6.6 Hz); ^{13}C NMR δ 15.95 (q, J_{C-F} = 2.0 Hz), 66.80 (q, J_{C-F} = 28.4 Hz), 125.76 (q, J_{C-F} = 279.7 Hz), 128.74, 128.78, 131.62, 135.45, 164.60; MS *m*/*z* 201 (M, 38), 200 (M − H, 9), 186 (M − CH_3, 4), 132 (M − CF_3, 100).

***N*-Benzylidene-5,5,5,4,4,3,3-heptafluoropent-2-ylamine (5j)**: R_f 0.30; ^{1}H NMR δ 1.46 (d, 3H, J_{H-H} = 6.6 Hz), 4.03 (m, 1H), 7.43−7.47 (m, 3H), 7.76−7.79 (m, 2H), 8.32 (s, 1H); ^{19}F NMR δ −81.32 (t, 3F, J_{F-F} = 10.2 Hz), −119.19, −124.15 (ABX, 2F, J_{AB} = 278.9 Hz, J_{AX} = 10.2 Hz), −124.71, −126.52 (ABXY, 2F, J_{AB} = 291.0 Hz, J_{AX} = 14.4 Hz, J_{AY} = 7.1 Hz, J_{BX} = 12.1 Hz); MS *m*/*z* 301 (M, 5), 132 (M − C_3F_7, 100).

***N*-Benzylidene-3,3,3-trifluoropropen-2-ylamine (8)**: R_f 0.25; ^{1}H NMR δ 5.11 (m, 1H), 5.24 (br s, 1H), 7.48−7.52 (m, 3H), 7.87 (m, 2H), 8.42 (s, 1H); ^{19}F NMR δ −70.25 (s); MS *m*/*z* 199 (M, 65), 198 (M − H, 30), 130 (M − CF_3, 87), 103 (100).

***N*-Benzylidene-1,1,1-trifluoro-3-phenylisopropylamine (5l)**: R_f 0.39; ^{1}H NMR δ 3.06, 3.26 (ABX, 2H, J_{AB} = 13.2 Hz, J_{AX} = 2.1 Hz, J_{BX} = 10.8 Hz), 3.78 (dqd, 1H, J_{H-H} = 10.8 Hz, J_{H-F} = 7.1 Hz, J_{H-H} = 2.1 Hz), 7.09−7.65 (m, 10H), 7.66 (s, 1H); ^{19}F NMR δ −75.36 (d, J_{H-F} = 7.1 Hz); MS *m*/*z* 277 (M, 24), 186 (M − $PhCH_2$, 100). Anal. Calcd for $C_{16}H_{14}F_3N$: C, 69.30; H, 5.09; N, 5.05; F, 20.56. Found: C, 69.39; H, 5.03; N, 5.11; F, 20.47.

***N*-Benzylidene-1-phenyl-2,2,2-trifluoroethylamine (5m)**:[8a] R_f 0.32; ^{1}H NMR δ 4.80 (q, 1H, J_{H-F} = 7.5 Hz), 7.37−7.47 (m, 6H), 7.54−7.58 (m, 2H), 7.82−7.85 (m, 2H), 8.38 (s, 1H); ^{19}F NMR δ −74.39 (d, J_{H-F} = 7.5 Hz); ^{13}C NMR [H,F decouple] δ 75.23, 124.64, 128.69, 128.78, 128.92 (2 C), 129.02, 131.77, 135.13, 135.49, 165.89; MS *m*/*z* 263 (M, 20), 194 (M − CF_3, 100).

***N*-Benzylidene-1-phenyl-2-chloro-2,2-difluoroethylamine (5n)**: R_f 0.35; ^{1}H NMR δ 4.88 (dd, 1H, J_{H-F} = 8.5, 10.5 Hz), 7.39−7.51 (m, 6H), 7.59−7.61 (m, 2H), 7.86−7.90 (m, 2H), 8.42 (s, 1H); ^{19}F NMR δ −59.47, −61.00 (ABX, J_{AB} = 162.0 Hz, J_{AX} = 8.5 Hz, J_{BX} = 10.5 Hz); MS *m*/*z* 279 (M, 1), 244 (M − Cl, 2), 194 (100).

***N*-Benzylidene-1-phenyl-2,2-difluorovinylamine (9)**: R_f 0.31; ^{1}H NMR δ 7.37−7.50 (m, 10H), 8.01 (s, 1H); ^{19}F NMR δ −91.27 (d, 1F, J_{F-F} = 22.3 Hz), −95.27 (d, 1F, J_{F-F} = 22.3 Hz); MS *m*/*z* 243 (M, 27), 140 (100).

General Method of Hydrolysis of *N*-Benzylidene Derivatives 5d,e,h,i,l,m to Hydrochlorides 10d,e,h,i,l,m. The starting Schiff base **5d**,**e**,**h**,**i**,**l**,**m** (typically 20 mmol) was dissolved in 5 mL of ether, and 5 mL of 4 N HCl was added under stirring at ambient temperature. Progress of the hydrolysis was monitored by TLC, and upon completion, the aqueous layer was separated, washed with ether, and evaporated *in vacuo* to give crystalline hydrochloride **10d**,**e**,**h**,**i**,**l**,**m**, purified by recrystallization from acetone or acetonitrile. Hydrochlorides **10d**,**e**,**h**,**i**,**l**,**m** give no definite melting points but easily sublimate over 180 °C.

1,1-Dihydroperfluorobutylamine hydrochloride (10d): 96% from *N*-benzylidene derivative **5d**; ^{1}H NMR (CD_3CN/CD_3OD, 3:1) δ 4.83 (tt, J_{H-F} = 16.7, J_{H-F} = 1.2 Hz); ^{19}F NMR (CD_3CN/CD_3OD, 3:1) δ −80.24 (t, 3F, J_{F-F} = 8.5 Hz), −117.49 (m, 2F), −127.138 (d, 2F, J_{H-F} = 1.2 Hz).

1,1-Dihydroperfluoropentylamine hydrochloride (10e):[8a] 91% from *N*-benzylidene derivative **5e**; ^{1}H NMR (CD_3CN/CD_3OD, 3:1) δ 4.87 (tt, J_{H-F} = 16.9, J_{H-F} = 1.2 Hz).

Pentafluorobenzylamine hydrochloride (10h): 94% from *N*-benzylidene derivative **5h**; ^{1}H NMR (CD_3CN/CD_3OD, 3:1) δ 4.24 (t, J_{H-F} = 1.2 Hz); ^{19}F NMR (CD_3CN/CD_3OD, 3:1) δ −142.90 (m, 2F), −154.49 (m, 1F), −164.23 (m, 2F).

1,1,1-Trifluoroisopropylamine hydrochloride (10i): 92% from *N*-benzylidene derivative **5i**; ^{1}H NMR (CD_3CN/CD_3OD, 3:1) δ 1.49 (dq, 3H, J_{H-H} = 6.9, J_{H-F} = 0.6 Hz), 4.08 (dd, 1H,

J_{H-H} = 6.9, J_{H-F} = 6.7 Hz); ^{19}F NMR (CD_3CN/CD_3OD, 3:1) δ −75.67 (d, J_{H-F} = 6.7 Hz).

1,1,1-Trifluoro-3-phenylisopropylamine hydrochloride (10l): 93% from *N*-benzylidene derivative **5l**; ^{1}H NMR (CD_3CN) δ 3.25, 3.43 (ABX, 2H, J_{AB} = 14.7 Hz, J_{AX} = 6.6 Hz, J_{BX} = 7.6 Hz), 4.31 (dqd, 1H, J_{H-H} = 7.6, J_{H-F} = 7.1, J_{H-H} = 6.6 Hz), 7.30−7.43 (m, 5H), 9.05 (br s, 3H); ^{19}F NMR (CD_3CN) δ −71.39 (d, J_{H-F} = 7.1 Hz).

2,2,2-Trifluoro-1-phenylethylamine hydrochloride (10m):[8a] 97% from *N*-benzylidene derivative **5m**; ^{1}H NMR (CD_3CN/CD_3OD, 3:1) δ 5.17 (d, 1H, J_{H-F} = 7.5 Hz), 7.56 (s, 5H); ^{19}F NMR (CD_3CN/CD_3OD, 3:1) δ −72.69 (d, J_{H-F} = 7.5 Hz).

1,1,1-Trifluoro-3-phenylisopropylamine (11l).[13] The starting hydrochloride **10l** (20 g, 88.7 mmol) was suspended in 70 mL of dry ether, and TEA (17.9 g, 177.4 mmol) was added under stirring at ambient temperature. In 10 h, TEA hydrochloride was removed by filtration and the solvent was evaporated *in vacuo* to give amine **11l** (15.8 g, 94.3%), purified by distillation, bp 66−69 °C (2 mmHg): ^{1}H NMR δ 1.28 (br s, 2H), 2.61, 3.13 (ABX, 2H, J_{AB} = 14.0 Hz, J_{AX} = 3.3 Hz, J_{BX} = 10.5 Hz), 3.45 (br m, 1H), 7.23−7.37 (m, 5H); ^{19}F NMR δ −78.94 (d, J_{H-F} = 6.8 Hz); MS *m*/*z* 189 (M, 10), 98 (M − $PhCH_2$, 69), 91 (100).

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