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Aza-Henry Reaction with CF_3-Ketimines: An Efficient Approach to Trifluoromethylated β-Nitroamines, 1,2-Diamines, α-Aminooximes, and Imidazolidinones

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CF_3-Substituted ketimines synthesized from trifluoroacetone, hexafluoroacetone, and trifluoroacetophenones were studied in aza-Henry reactions with nitroalkanes. We found that nitromethane and nitropropane react with CF_3-substituted ketimines to form the target β-nitroamines in high yield. The aza-Henry reaction proceeded under mild conditions in the presence of an appropriate base. A new simple method for the synthesis of β-nitroamines bearing CF_3 group was developed. α-CF_3-β-nitroamines can easily be converted into trifluoromethylated 1,2-diamines, α-aminooximes, and imidazolidinones.

Introduction

The importance of fluorinated organic compounds for medicine and modern materials science is commonly known. Psychotropic and neuroleptic drugs, as well as many antiviral medications, often bear fluorine atoms (Figure 1). Nearly 25% of all pharmaceuticals contain a fluorine atom or a CF_3 group. Fluorinated compounds have increased metabolic stability compared to their nonfluorinated analogues, due to the fact that the carbon–fluorine bond is one of the strongest in organic chemistry.[1] The presence of a CF_3 group in a molecule also significantly increases the lipophilic properties, and can improve the binding affinity of the molecule, thereby enhancing the effectiveness of drugs. The steric effects of fluorination are also very important, and can bring about a change of preferred conformation (gauche effect for fluorinated fragments, and high conformation energy of CF_3 group).[2] As a result, research into convenient methods for the preparation of fluorine-containing molecules is very important.

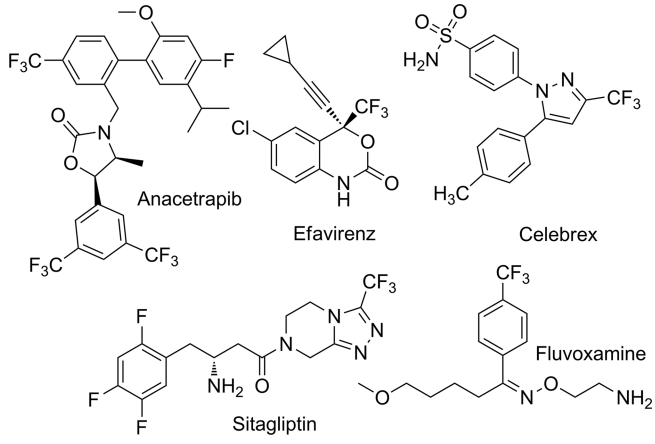

Figure 1. Examples of drugs containing a CF_3 group.

Fluoroorganic compounds occur only rarely in nature. The number of methods and reagents that allow the direct introduction of fluorine or fluorinated groups are limited.[3] Thus, methods that make use of fluorine-containing building blocks to incorporate a fluorinated fragment into a molecule are widely used for the preparation of target fluorinated compounds.[1,4]

Trifluoromethyl-substituted imines are interesting substrates for this purpose. Due to the electron-withdrawing effect of the CF_3 fragment, such imines are much more reactive than their nonfluorinated counterparts. Moreover, as a rule, ketimines are less reactive compounds, and a lot of the reactions that take place with aldimines do not proceed or have restricted use with ketimines. To date, only a few examples of the addition of aliphatic nitroalkanes to ketimines are known.[5] This is also true for fluorinated imines.

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The aza-Henry reaction allows the creation of new carbon–carbon bonds with fluorinated imines, and leads to attractive structures containing not only a CF_3 group, but also an amine moiety. The β-nitroamine products are very attractive from a synthetic point of view, because both of their nitrogen-containing groups can be easily converted into various other functional groups.[6] The most commonly used activators in aza-Henry reactions are organic[7] and inorganic[8] bases for the activation of the nitroalkane, and Lewis acids[9] for the activation of the imine.

First, we decided to study the interaction of fluorinated ketimines with nitroalkanes in detail. Imines derived from hexafluoroacetone, trifluoroacetone, and trifluoroacetophenones have not been studied before as substrates in the aza-Henry reaction with nitroalkanes. This is the first systematic investigation of this reaction.

The reduction of α-CF_3-β-nitroamines to vicinal diamines is of special interest, as this structural fragment often occurs in different medicines, catalysts, and natural products (Figure 2). Due to the presence of strongly electron-withdrawing CF_3 group, the basicity and nucleophilicity of the two amine groups in such diamines is dramatically different; this opens up the possibility of selective subsequent transformations of the trifluoromethylated diamines.

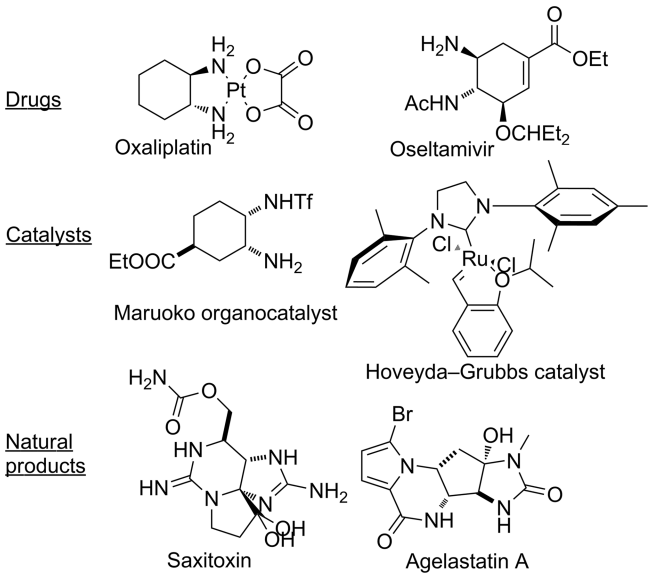


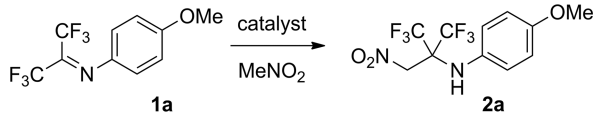
Figure 2. 1,2-Diamines.

Results and Discussion

Ketimines derived from hexafluoroacetone,[10] trifluoroacetone,[11] and trfluoroacetophenones[12] were synthesized according to published methods, and were used as starting materials for the reaction with nitromethane. We began our investigation by searching for an appropriate catalyst and solvent for the reaction of hexafluoroacetone imines with nitromethane. It should be noted that due to the presence of two electron-withdrawing groups, imines derived from hexafluoroacetone are much more reactive than imines derived from trifluoroacetone or trifluoroacetophenone.

4-Methoxy-*N*-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]aniline (**1a**) was chosen as a model compound. To find optimal reaction conditions, a wide range of catalysts [$ZnCl_2$ + *i*Pr_2NEt, $BF_3{\cdot}Et_2O$, $BF_3{\cdot}Et_2O$ + K_2CO_3, 1,8-diazabicycloundec-7-ene (DBU), 1,4-diazabicyclo[2.2.2]-octane (DABCO), K_2CO_3, KOH, CsF, *i*Pr_2NEt, $ZnCl_2$ + DBU, $ZnCl_2$, $ZnCl_2$ + DABCO, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), triazabicyclodecene (TBD)], solvents (toluene, acetonitrile, nitromethane), and amounts of the catalyst and of nitromethane were tested (Table 1).

Table 1. The aza-Henry reaction of **1a** with various catalysts.



1a **2a**

Catalyst	Amount of catalyst [equiv.]	Solvent	Reaction time [h]	Yield of **2a** [%]
$ZnCl_2$ + *i*Pr_2NEt	1	$MeNO_2$	44	46
$ZnCl_2$ + *i*Pr_2NEt	0.1	$MeNO_2$	6	71
$ZnCl_2$ + *i*Pr_2NEt	0.05	$MeNO_2$	20	68
$ZnCl_2$ + DBU	0.1	$MeNO_2$	2	74
DBU	0.1	$MeNO_2$	1.5	73
DBU	0.2	$MeNO_2$	1	88
DBU	1	$MeNO_2$	2.67	43
DBU	0.2	toluene[a]	0.1	45
DBU	0.2	toluene/$MeNO_2$	1	75
DBN	0.2	$MeNO_2$	0.5	66
TBD	0.2	$MeNO_2$	48	27
iPr_2NEt	0.1	$MeNO_2$	2	78
iPr_2NEt	0.2	$MeNO_2$	2	68
K_2CO_3	0.1	$MeNO_2$	48	23

[a] 10 equiv. of $MeNO_2$ was used.

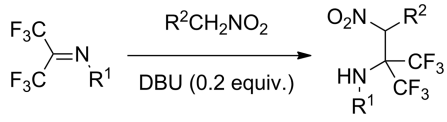
The use of $BF_3{\cdot}Et_2O$ + K_2CO_3, $ZnCl_2$, $BF_3{\cdot}Et_2O$, KOH, $ZnCl_2$ + DABCO, CsF, or DABCO as the catalyst in the reaction in nitromethane gave no reaction. When $ZnCl_2$ + *i*Pr_2NEt, DBU, *i*Pr_2NEt, DBN, TBD, or K_2CO_3 was ued, the target compound (i.e., **2a**) was isolated in good yield (Table 1). The best yield after a reasonable reaction time was achieved using DBU (0.2 equiv.) in nitromethane. Increasing the amount of DBU to 1 equiv. led to side-reactions, and the product (i.e., **2a**) could not be isolated in good yield. We also tried to use lower amounts of DBU, but when 0.1 equiv. of DBU was used, the transformation proceeded much more slowly.

We also tested different solvents. In toluene, the reaction finished within minutes, but there were a lot of by-products, and the target compound (i.e., **2a**) could not be isolated in good yield. In acetonitrile, no reaction between imine **1a** and nitromethane was observed at all.

Thus, the reaction of hexafluoroacetone imine **1a** with nitromethane was found to proceed in maximal yield when 0.2 equiv. of DBU was used as catalyst in nitromethane, with a reaction time of 1 h. Having identified these optimal conditions for substance **1a**, we carried out aza-Henry reactions of nitromethane with other imines **1b**–**1e** (Table 2; to

give compounds **2a**–**2e**). The reactions were monitored by TLC, and the reaction times were less than 2 h.

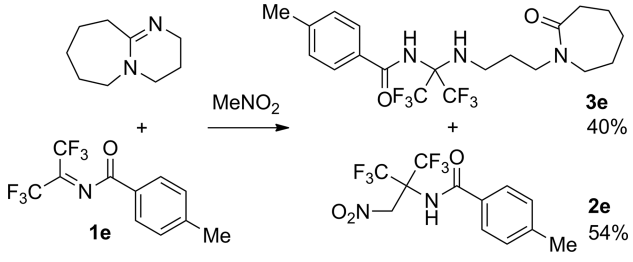
Table 2. The aza-Henry reaction of imines **1a**–**1e**.



1a–e **2a–e, 4a–e**

Nitroamine	R^1 (imine)	R^2 (nitroalkane)	Catalyst	Yield [%]
2a	4-$MeOC_6H_4$	H	DBU	88
2b	4-MeC_6H_4	H	DBU	84
2c	4-ClC_6H_4	H	DBU	96
2d	C_6H_5	H	DBU	89
2e	4-MeC_6H_4CO	H	DBU	54
2e	4-MeC_6H_4CO	H	iPr_2NEt	98
4a	4-$MeOC_6H_4$	Et	DBU	62
4b	4-MeC_6H_4	Et	DBU	60
4c	4-ClC_6H_4	Et	DBU	60
4d	C_6H_5	Et	DBU	80
4e	4-MeC_6H_4CO	Et	DBU	64

However, we found that these conditions were unsuitable for imine **1e**, which has an additional electron-withdrawing group at the nitrogen atom. In this case, we observed not only the formation of the target nitroamine, but also of product **3e**, resulting from the reaction of **1e** with DBU. The formation of **3e** can be explained by enhanced electrophilicity of **1e**. As a result, the 8-nitrogen of DBU can react as a nucleophile with the imine carbon of **1e** (Scheme 1). Subsequent ring opening and reaction with traces of water finally leads to the formation of **3e**. The use of iPr_2NEt with this substrate resulted in the formation of the required nitroamine (i.e., **2e**) in excellent yield.



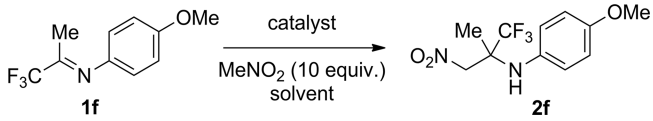
Scheme 1. Aza-Henry reaction of imine **1e** with nitromethane and DBU.

To determine the scope and limitations of aza-Henry reaction with fluorinated imines, we also studied the reaction of ketimines **1a**–**1e** with nitropropane. We also optimized the conditions for this reaction using **1a** as a model compound, and once again the best results were obtained with DBU. The reaction proceeded at room temperature for 1 d to give slightly lower yields (60–80%) than those obtained with nitromethane (**2a**–**2e**).

Next, we investigated the reaction between nitromethane and imines derived from trifluoroacetone. To screen the reaction conditions, 4-methoxy-*N*-[2,2,2-trifluoro-1-methylethylidene] aniline (**1f**) was chosen as a model imine. Various catalysts ($ZnCl_2$ + iPr_2NEt, $BF_3{\cdot}Et_2O$ + K_2CO_3, DBU, DABCO, K_2CO_3, KOH, CsF, iPr_2NEt, DBU + $ZnCl_2$, DBN, Py, Na_2CO_3, Cs_2CO_3, Et_3N, and TBD), solvents (toluene, DMSO, MeOH, Et_2O, acetonitrile, dichloromethane, and nitromethane) and different concentrations of nitromethane were tested to find optimal conditions.

The target product (i.e., **2f**) could only be detected in the reaction mixture when a rather strong base such as DBN (pK_a = 12.7), TBD (pK_a = 15.2), or DBU (pK_a = 12.5[13]) was used as the catalyst. The use of DBU, even in small quantities, resulted in the formation of the product (i.e., **2f**) in low yield (40%), although the process proceeded very quickly. Using a polar solvent or a large excess of nitromethane also led to a lot of side-reactions. The use of TBD as a catalyst gave satisfactory results (60% yield). The best results for this reaction were observed when DBN (1 equiv.) was used as an activator in an excess of nitromethane (Table 3).

Table 3. The aza-Henry reaction of **1f** with various catalysts.



1f **2f**

Catalyst	Amount of catalyst [equiv.]	Solvent	Reaction time [h]	Yield of **2f** [%]
DBU	0.2	toluene[a]	22	40
DBU	1	toluene[a]	2	21
DBU	0.2	$MeNO_2$	0.5	23
DBN	0.2	toluene[a]	12	48
DBN	1	toluene[a]	5	78
TBD	0.2	toluene[a]	20	35
TBD	1	toluene[a]	6	60

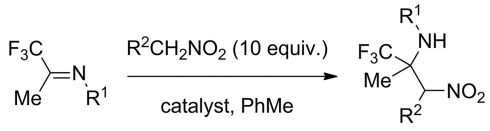
[a] 10 equiv. of $MeNO_2$ was used.

We went on to test the reaction with other imines derived from trifluoroacetone (i.e., **1g**–**1i**) using this system (DBN/toluene/nitromethane). The target compounds (i.e., **2g**–**2i**) were obtained in 70–84% yield (Table 4). In a similar manner, the reaction of imines **1f**–**1i** with nitropropane was carried out. However, DBU was used as a catalyst, because DBN and TBD required longer reaction times in this case. The nitroamine products (i.e., **4f**–**4i**) contain two stereocentres, and according to NMR spectroscopy, each of these compounds was formed as a mixture of two diastereomers in a 1:1 ratio.

To obtain more general information about this reaction, imines derived from some trifluoroacetophenones were studied. Starting 1-alkyl-aryl-2,2,2-trifluoroethylidenecarbamates **1j**–**1r** are highly electrophilic due to the presence of two electron-withdrawing groups (trifluoromethyl and alkoxycarbonyl; Table 5). It was found that the reaction of compounds **1j**–**1r** with nitromethane proceeds cleanly in DMSO solution in the presence of catalytic amounts of triethylamine to give alkyl-*N*-(2-aryl-3-nitro-1,1,1-trifluoropropane-2-yl) carbamates **2j**–**2r** in excellent yields (82–90%).

Thus, we have found that trifluoromethyl-substituted imines of any type can be effectively transformed into the

Table 4. The aza-Henry reaction of imines **1f**–**1i**.

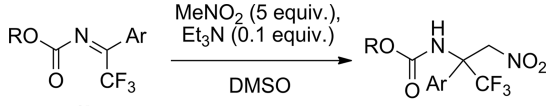


1f–i **2f–i, 4f–i**

Nitroamine	R^1 (imine)	R^2 (nitroalkane)	Catalyst	Yield [%]
2f	4-$MeOC_6H_4$	H	DBN, 1 equiv.	78
2g	4-MeC_6H_4	H	DBN, 1 equiv.	70
2h	4-ClC_6H_4	H	DBN, 1 equiv.	84
2i	C_6H_5	H	DBN, 1 equiv.	70
4f	4-$MeOC_6H_4$	Et	DBU, 0.2 equiv.	66[a]
4g	4-MeC_6H_4	Et	DBU, 0.2 equiv.	52[a]
4h	4-ClC_6H_4	Et	DBU, 0.2 equiv.	98
4i	C_6H_5	Et	DBU, 0.2 equiv.	37[a]

[a] The yield was calculated from the ^{19}F NMR spectra.

Table 5. The aza-Henry reaction of imines **1j**–**1r** with nitromethane.



1j–r **2j–r**

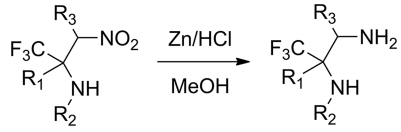
Nitroamine	Ar (imine)	R (nitroalkane)	Yield [%]
2j	4-FC_6H_4	Me	84
2k	4-MeC_6H_4	Me	84
2l	C_6H_5	Et	90
2m	4-FC_6H_4	Et	82
2n	4-$MeOC_6H_4$	Et	84
2o	C_6H_5	*t*Bu	85
2p	4-MeC_6H_4	*t*Bu	86
2q	4-FC_6H_4	*t*Bu	82

corresponding nitroamines using an aza-Henry reaction. However, it is necessary to use different bases as the catalyst, depending on the electrophilicity of the starting imines.

As compounds based on diamines are widely used in medicine and organic synthesis, we decided to study the reduction of nitroamine products **2a**–**2q** and **4a**–**4h** to give the corresponding 1,2-diamines. For this reduction, we added zinc powder portionwise to a solution of the nitroamine in methanol containing hydrochloric acid (8 M).[14]

In some cases, full conversion was not observed, and it was necessary to add additional zinc and hydrochloric acid. We found that this approach was general, and no limitations were observed. As a result, a number of diamines **5a**–**5h** and **6a**–**6h** were obtained in excellent yields (82–98%), irrespective of the substituents on the amine nitrogen and the carbon skeleton (Table 6). The 1,2-diamine products (i.e., **5a**–**5h** and **6a**–**6h**) containing a trifluoromethyl group are stable compounds. In contrast, nitroamines **2a**–**2q** and **4a**–**4h** should be stored in a refrigerator due to their limited stability. These trifluoromethylated diamines are attractive building blocks bearing a CF_3 group. It is quite important to point out that the two nitrogen atoms in these compounds have very different nucleophilicities (pK_{a1} = 3.89–4.61, pK_{a2} = –6.63–5.16 for diamines **5a**–**5d**, **6a**–**6d**; pK_{a1} ≈ 6.98–7.12, pK_{a2} = –0.54–0.47 for diamines **5h**, **6h**; pK_{a1} ≈ 5.79–6.85, pK_{a2} = –4.00–3.38 for diamines **5j**–**5p**, as calculated with ACDlabs[15]).[16]

Table 6. Reduction of nitroamines **2a**–**2h** and **4a**–**4h** to give 1,2-diamines.

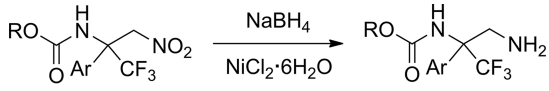


2a–h, 4a–h **5a–h, 6a–h**

Diamine	R^1	R^2	R_3	Yield [%]
5a	CF_3	4-$MeOC_6H_4$	H	97
5b	CF_3	4-MeC_6H_4	H	80
5c	CF_3	4-ClC_6H_4	H	98
5d	CF_3	C_6H_5	H	82
5g	CH_3	4-ClC_6H_4	H	88
6a	CF_3	4-$MeOC_6H_4$	Et	96
6b	CF_3	4-MeC_6H_4	Et	80
6c	CF_3	4-ClC_6H_4	Et	94
6d	CF_3	C_6H_5	Et	89
6g	CH_3	4-ClC_6H_4	Et	82

Reduction under acidic conditions is unsuitable for nitroamines **2j**–**2p**, due to the fact that carbamate groups (especially Boc) are not stable in acidic media. Therefore, in these cases we used reduction with $NaBH_4$ in the presence of an equimolar amount of $NiCl_2 \cdot 6H_2O$. This reductive system was also shown to be highly effective, and the corresponding monoprotected diamines (i.e., **5j**–**5r**) were obtained in high yields (Table 7).

Table 7. Reduction of nitroamines **2j**–**2p** to give 1,2-diamines.

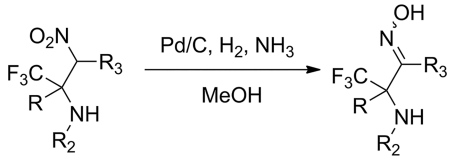


2j–p **5j–p**

Diamine	Ar	R	Yield [%]
5j	4-FC_6H_4	Me	81
5k	4-MeC_6H_4	Me	86
5l	C_6H_5	Et	86
5m	4-FC_6H_4	Et	81
5n	4-$MeOC_6H_4$	Et	88
5o	C_6H_5	*t*Bu	84
5p	4-MeC_6H_4	*t*Bu	82

We also found that trifluoromethylated nitroamine derivatives can be subjected to a partial reduction to obtain the corresponding aminooximes. This reaction was carried out in methanol solution with the addition of a small amount of saturated aqueous ammonia under an atmosphere of hydrogen (1 atm.) using palladium on charcoal (10%) as a catalyst for 1–2 d.[17] It is worth noting that in the absence of ammonia, or using 5% palladium on charcoal, the reaction proceeded very slowly. Compounds **7a**–**7h** and **8a**–**8h** were obtained in 72–94% yield (Table 8). Such aminooximes are very interesting in terms of their possible applications, because they are protected aminoaldehydes.

Table 8. Reduction of nitroamines **2a**–**2h** and **4a**–**4h** to give aminooximes.

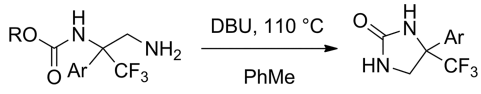


2a–h, 4a–h **7a–h, 8a–h**

Aminooxime	R^1	R^2	R_3	Yield [%]
7a	CF_3	4-$MeOC_6H_4$	H	82
7b	CF_3	4-MeC_6H_4	H	80
7c	CF_3	4-ClC_6H_4	H	94
7d	CF_3	C_6H_5	H	76
7h	CH_3	4-ClC_6H_4	H	90
8a	CF_3	4-$MeOC_6H_4$	Et	76
8c	CF_3	4-ClC_6H_4	Et	82
8d	CF_3	C_6H_5	Et	72
8h	CH_3	4-ClC_6H_4	Et	82

The presence in the structure of compounds **7** of two functional groups (amine and alkoxycarbonyl groups) creates favourable conditions for their intramolecular cyclization to the corresponding imidazolidin-2-ones (i.e., **9**; Table 9). This kind of cyclization is relatively easy to implement. Heating **7** in refluxing toluene in the presence of DBU resulted in clean heterocyclization. Previously, one compound of this type (Ar = C_6H_5) was synthesized by a three-step transformation from the corresponding α-aminonitrile.[18]

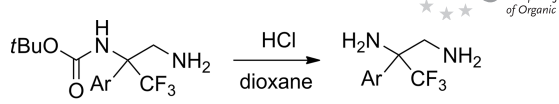
Table 9. Cyclization of diamines **5j**–**5l** and **5n** to give imidazoline-2-ones **9j**–**9l** and **9n**.



5j–l, 5n **9j–l, 9n**

Diamine	Imidazoline-2-one	Ar	R	Yield [%]
5j	**9j**	4-FC_6H_4	Me	90
5m	**9j**	4-FC_6H_4	Et	88
5k	**9k**	4-MeC_6H_4	Me	92
5p	**9k**	4-MeC_6H_4	*t*Bu	90
5l	**9l**	C_6H_5	Et	87
5o	**9l**	C_6H_5	*t*Bu	90
5n	**9n**	4-$MeOC_6H_4$	Et	82

Carbamates **4k** and **4l**, containing an *O*-*tert*-butyl substituent, may be considered as *N*-Boc-monosubstituted derivatives, and under the action of a saturated solution of hydrogen chloride in dioxane, they were smoothly converted into the dihydrochloride salts of 2-aryl-3,3,3-trifluoropropane-1,2-diamines **10k** and **10l** (Scheme 2). The method described here for the synthesis of these important compounds complements existing approaches described in the literature.[19]



4k, **4l** **10k**: Ar = C_6H_5, 90%
10l: Ar = 4-MeC_6H_4, 88%

Scheme 2. Preparation of diamines **10k** and **10l**.

Conclusions

In summary, the reaction of nitroalkanes and fluorinated ketimines derived from hexafluoroacetone, trifluoroacetophenone, and trifluoroacetone was systematically investigated. We found that the best catalysts for this reaction are strong organic bases such as DBU, DBN, Et_3N, and iPr_2NEt. Complete and partial reduction of the prepared nitroamines to give diamines and aminooximes was carried out. These reactions give access to attractive trifluoromethylated building blocks − diamines and aminooximes − in good and excellent yields, irrespective of the structure of the starting materials.

Experimental Section

General Remarks: 1D NMR (^1H, ^{19}F, and ^{13}C) spectra were obtained with Bruker VRX-400, Varian VXR-300, Bruker Avance DRX-500, and Agilent 400-MR spectrometers. Chemical shifts for ^1H NMR spectroscopic data were referenced to internal tetramethylsilane (δ = 0.0 ppm); chemical shifts for ^{13}C NMR spectroscopic data were referenced to $CDCl_3$ (δ = 77.0 ppm); chemical shifts for ^{19}F NMR spectroscopic data were referenced to $PhCF_3$ (δ = –63.90 ppm) or $CFCl_3$ (δ = 0.0 ppm). TLC was carried out on precoated silica plates (Silufol UV-254), which were visualized with UV light and/or staining with ninhydrin solution or aqueous $Ce(SO_4)_2$ solution with phosphomolybdic and sulfuric acids. Flash chromatography was carried out using MP Silica 60 (320–630 mesh) with the solvents indicated. All solvents and reagents for the reactions were of reagent grade, and were dried and distilled immediately before use as follows: dichloromethane from P_2O_5, triethylamine and pyridine from calcium hydride, diethyl ether and benzene from sodium.

General Procedure for the Preparation of Imines 1a–1e: In a 250 mL flask, a solution of aniline (0.1 mol) in dichloromethane (150 mL) was cooled to about –40 °C. Hexafluoroacetone gas, generated by the slow, dropwise addition of hexafluoroacetone trihydrate (26.5 g, 0.12 mol) to concentrated sulfuric acid (15 mL) at 90 °C, was then bubbled into the aniline solution over a period of 2 h. A moisture-sensitive precipitate, the adduct of hexafluoroacetone with aniline, was gradually formed. Then, triethylamine (41.5 mL, 0.3 mol) was added to the solution, and the precipitate dissolved. After that, the flask was equipped with a condenser, and phosphorus oxychloride (15.3 g, 0.1 mol) was added dropwise at such a rate that gentle reflux was maintained. The solution turned yellow, and a precipitate formed. The solvent and the tertiary amine were removed under vacuum, and the resulting residue was distilled under reduced pressure to give the crude product.[10]

4-Methoxy-*N*-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]aniline (1a): Yellow liquid (52%). b.p. 80–82 °C/ 28 Torr; ref.[10] b.p. 78–81 °C/ 28 Torr. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, CH_3-O), 6.93–6.95 (m, 2 H, Ar), 6.99–7.01 (m, 2 H, Ar) ppm. ^{19}F NMR

(376.5 MHz, $CDCl_3$): δ = –64.80 (CF_3), –72.09 (CF_3) ppm, in agreement with the literature data.[10]

4-Methyl-*N*-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]aniline (1b): Yellow liquid (49%). b.p. 96–97 °C /80 Torr; ref.[20] b.p. 85–86 °C/ 53 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3), 6.84–6.86 (m, 2 H, Ar), 7.22–7.24 (m, 2 H, Ar) ppm.

4-Chloro-*N*-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]aniline (1c): Yellow liquid (68%). b.p. 66–67 °C /20 Torr; ref.[20] b.p. 65–66 °C/ 21 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84–6.86 (m, 2 H, Ar), 7.38–7.40 (m, 2 H, Ar) ppm.

***N*-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]aniline (1d):** Yellow liquid (65%). b.p. 68–71 °C /60 Torr; ref.[20] b.p. 75–76 °C/ 91 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.93–6.95 (m, 2 H, Ar), 7.29–7.31 (m, 1 H, Ar), 7.41–7.45 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 117.0 (Ar), 126.4 (Ar), 128.5 (Ar), 141.9 (q, $^1J_{C,F}$ = 270.0 Hz, CF_3), 144.3 (C_q, Ar), 170.3 (sept, $^2J_{C,F}$ = 35.0 Hz, *C*-CF_3) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –71.89 (CF_3), –64.90 (CF_3) ppm.

4-Methyl-*N*-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]benzamide (1e): White solid (88%), m.p. 31–32 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 7.23–7.83 (m, 4 H, Ar) ppm, in agreement with the literature data.[21]

General Procedure for the Preparation of Imines 1f–1i: Trifluoroacetone (0.12 mol, 11 mL) and a solution of titanium tetrachloride (0.08 mol, 8.8 mL) in hexane (8 mL) were added to a vigorously stirred mixture of the appropriate aniline (0.2 mol) and anhydrous diethyl ether (100 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 h, then the precipitate of titanium dioxide was removed by filtration, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, dichloromethane/hexane, 1:1) to give the target imine.[22]

4-Methoxy-*N*-[2,2,2-trifluoro-1-methylethylidene]aniline (1f): Brown oil (98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.06 (s, 3 H, CH_3), 3.81 (s, 3 H, CH_3-O), 6.78–6.80 (m, 2 H, Ar), 6.91–6.93 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.6 (CH_3), 55.6 (CH_3), 114.5 (Ar), 120.5 (q, $^1J_{C,F}$ = 273.0 Hz, CF_3), 121.1 (C_q, Ar), 121.5 (Ar), 140.5 (C_q, Ar), 158.3 (q, $^2J_{C,F}$ = 33.0 Hz, *C*-CF_3) ppm, in agreement with the literature data.[23]

4-Methyl-*N*-[2,2,2-trifluoro-1-methylethylidene]aniline (1g): Brown oil (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.07 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 6.70–6.72 (m, 2 H, Ar), 6.83–6.85 (m, 2 H, Ar) ppm, in agreement with the literature data.[24]

4-Chloro-*N*-[2,2,2-trifluoro-1-methylethylidene]aniline (1h): Pale yellow oil (80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.02 (s, 3 H, CH_3), 6.72–6.74 (m, 2 H, Ar), 7.34–7.36 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4 (CH_3), 118.2 (Ar), 119.7 (q, $^1J_{C,F}$ = 278.5 Hz, CF_3), 129.3 (C_q, Ar), 130.7 (Ar), 146.1 (C_q, Ar), 158.1 (q, $^2J_{C,F}$ = 34.7 Hz, *C*-CF_3) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –74.60 (CF_3) ppm, in agreement with the literature data.[25]

***N*-[2,2,2-Trifluoro-1-methylethylidene]aniline(1i):** Yellow oil (70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.03 (q, $^4J_{H,F}$ = 0.4 Hz, 3 H, CH_3), 6.78–6.81 (m, 2 H, Ar), 7.17–7.20 (m, 1 H, Ar), 7.37–7.41 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4 (CH_3), 118.6 (Ar), 119.7 (q, $^1J_{C,F}$ = 278.3 Hz, CF_3), 125.2 (Ar), 129.2 (Ar), 147.2 (C_q, Ar), 157.4 (q, $^2J_{C,F}$ = 34.0 Hz, *C*-CF_3) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –75.00 (CF_3) ppm, in agreement with the literature data.[24]

General Procedure for the Aza-Henry Reaction of Hexafluoracetone Imines with Nitroalkanes: Nitroalkane [nitromethane (1 mL) for substances **2a**–**2e**; nitropropane (0.5 mL) for substances **4a**–**4e**] and base [DBU (0.05 mol, 8.5 μL) for substances **2a**–**2d**, **4a**–**4e**; Hünig's base (0.05 mol, 8.5 μL) for substance **2e**] were added to the imine (0.25 mmol). The reaction was monitored by TLC (ca. 1.5 h), then the mixture was concentrated under reduced pressure, and the product was isolated by column chromatography (eluent: hexane/dichloromethane, 3:1, for substances **2a**–**2e**; hexane/dichloromethane, 1:1, for substances **4a**–**4e**).

4-Methoxy-*N*-[2,2,2-trifluoro-1-(nitromethyl)-1-(trifluoromethyl)ethyl]aniline (2a): Yellow oil (88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, CH_3-O), 4.27 (br. s, 1 H, H-N), 4.86 (s, 2 H, CH_2), 6.84–6.86 (m, 2 H, Ar), 7.17–7.19 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4 (CH_3-O), 67.3 (sept, $^2J_{C,F}$ = 27.1 Hz, *C*-CF_3), 72.6 (CH_2), 114.4 (Ar), 122.3 (q, $^1J_{C,F}$ = 290.8 Hz, *C*F_3), 129.0 (Ar), 131.5 (C_q, Ar), 158.3 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –70.86 (CF_3) ppm. IR (neat): $\tilde{\nu}$ = 3373 (br., NH) , 1159 (CF), 1149 (CF) cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{13}F_6N_2O_3$ $[M + H]^+$ 333.0669; found 333.0666.

4-Methyl-*N*-[2,2,2-trifluoro-1-(nitromethyl)-1-(trifluoromethyl)ethyl]aniline (2b): Brown oil (84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 3 H, CH_3), 4.35 (br. s, 1 H, H-N), 4.89 (s, 2 H, CH_2), 7.09–7.15 (m, 4 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.4 (CH_3), 67.3 (sept, $^2J_{C,F}$ = 29.9 Hz, *C*-CF_3), 72.2 (CH_2), 114.4 (C_q, Ar), 121.9 (q, $^1J_{C,F}$ = 303.6 Hz, CF_3), 126.2 (Ar), 129.5 (Ar), 136.1 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –71.14 (CF_3) ppm. IR (neat): $\tilde{\nu}$ = 3300 (br., NH) cm^{-1}. $C_{11}H_{10}F_6N_2O_2$: C 41.78, H 3.19, N 8.86; found C 41.84, H 3.26, N 8.92.

4-Chloro-*N*-[2,2,2-trifluoro-1-(nitromethyl)-1-(trifluoromethyl)ethyl]aniline (2c): Yellow oil (94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.55 (br. s, 1 H, H-N), 4.91 (s, 2 H, CH_2), 7.14–7.17 (m, 2 H, Ar), 7.28–7.32 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.1 (sept, $^2J_{C,F}$ = 25.5 Hz, *C*-CF_3), 72.1 (CH_2), 121.8 (q, $^1J_{C,F}$ = 288.2 Hz, CF_3), 127.1 (Ar), 129.0 (Ar), 131.4 (C_q, Ar), 137.6 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –70.82 (CF_3) ppm. IR (neat): $\tilde{\nu}$ = 3420 (br., NH) cm^{-1}. $C_{10}H_7ClF_6N_2O_2$: C 35.68, H 2.10, N 8.32; found C 35.84, H 2.26, N 8.34.

***N*-[2,2,2-Trifluoro-1-(nitromethyl)-1-(trifluoromethyl)ethyl]aniline (2d):** Yellow oil (88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.49 (br. s, 1 H, H-N), 4.92 (s, 2 H, CH_2), 7.20–7.24 (m, 3 H, Ar), 7.32–7.36 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.3 (sept, $^2J_{C,F}$ = 28.5 Hz, *C*-CF_3), 72.2 (c, CH_2), 118.9 (q, $^1J_{C,F}$ = 292.3 Hz, *C*F_3), 123.3 (Ar), 125.7 (Ar), 128.9 (Ar), 139.0 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –71.04 (CF_3) ppm. IR (neat): $\tilde{\nu}$ = 3373 (br., NH) , 1159 (CF), 1149 (CF) cm^{-1}. $C_{10}H_8F_6N_2O_2$: C 39.75, H 2.67, N 9.27; found C 39.84, H 2.65, N 9.46.

4-Methyl-*N*-[2,2,2-trifluoro-1-(nitromethyl)-1-(trifluoromethyl)ethyl]benzamide (2e): Yellow solid (98%), m.p. 72–74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, CH_3), 5.66 (s, 2 H, CH_2), 6.47 (br. s, 1 H, H-N), 7.28–7.30 (m, 2 H, Ar), 7.66–7.68 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1 (CH_3), 67.2 (sept, $^2J_{C,F}$ = 29.3 Hz, *C*-CF_3), 67.3 (CH_2), 119.9 (Ar), 122.8 (q, $^1J_{C,F}$ = 289.3 Hz, CF_3), 126.8 (Ar), 129.3 (C_q, Ar), 143.5 (C_q, Ar), 167.2 (C=O) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –72.61 (CF_3) ppm. IR (neat): $\tilde{\nu}$ = 3350 (br., NH) , 1725 (C=O) cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{10}F_6N_2NaO_3$ $[M + Na]^+$ 367.0488; found 367.0482.

4-Methoxy-*N*-[2-nitro-1,1-bis(trifluoromethyl)butyl]aniline (4a): Yellow solid (62%), m.p. 69–73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, *CH*$_3$-*CH*$_2$), 2.16–2.24 (m, 1 H, CH_3-*CH*$_2$), 2.41–2.53 (m, 1 H, CH_3-*CH*$_2$), 3.79 (s, 3 H, CH_3-O), 4.76 (br. s, 1 H, H-N), 5.02 (dd, $^3J_{H,H}$ = 12.0, $^3J_{H,H}$ = 3.1 Hz, 1 H, CH),

6.80–6.84 (m, 2 H, Ar), 7.06–7.08 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.3 (CH_3-CH_2), 22.4 (CH_3-CH_2), 55.8 (CH_3-O), 67.3 (sept, $^2J_{C,F}$ = 26.0 Hz, C-CF_3), 88.5 (CH), 114.1 (Ar), 122.6 (q, $^1J_{C,F}$ = 290.4 Hz, CF_3), 127.7 (C_q, Ar), 132.8 (Ar), 157.6 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –64.53 (q, $^4J_{F,F}$ = 11.6 Hz, 3 F, CF_3), –67.59 (q, $^4J_{F,F}$ = 11.6 Hz, 3 F, CF_3) ppm. IR (neat): $\tilde{\nu}$ = 3353 (br., NH) cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{15}F_6N_2O_3$ $[M + H]^+$ 360.0909; found 360.0903.

4-Methyl-*N*-[2-nitro-1,1-bis(trifluoromethyl)butyl]aniline (4b): Yellow oil (60%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.03 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3-CH_2), 2.16–2.21 (m, 1 H, CH_3-CH_2), 2.32 (s, 3 H, CH_3), 2.42–2.51 (m, 1 H, CH_3-CH_2), 4.91 (br. s, 1 H, H-N), 5.03 (dd, $^3J_{H,H}$ = 12.0, $^3J_{H,H}$ = 3.0 Hz, 1 H, CH), 6.98–7.00 (m, 2 H, Ar), 7.08–7.10 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.3 (CH_3-CH_2), 20.8 (CH_3-CH_2), 29.7 (CH_3), 67.8 (sept, $^2J_{C,F}$ = 25.6 Hz, C-CF_3), 88.5 (CH), 122.4 (q, $^1J_{C,F}$ = 293.6 Hz, CF_3), 125.0 (Ar), 129.7 (Ar), 135.0 (C_q, Ar), 137.8 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –65.39 (q, $^4J_{F,F}$ = 11.1 Hz, 3 F, CF_3), –68.89 (q, $^4J_{F,F}$ = 11.1 Hz, 3 F, CF_3) ppm. IR (neat): $\tilde{\nu}$ = 3280 (br., NH) cm^{-1}. $C_{13}H_{14}F_6N_2O_2$: C 45.36, H 4.10, N 8.14; found C 45.25, H 4.04, N 8.17.

4-Chloro-*N*-[2-nitro-1,1-bis(trifluoromethyl)butyl]aniline (4c): Brownish-yellow solid (80%), m.p. 56–58 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.05 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3-CH_2), 2.15–2.17 (m, 1 H, CH_3-CH_2), 2.41–2.48 (m, 1 H, CH_3-CH_2), 5.03 (dd, $^3J_{H,H}$ = 12.0, $^3J_{H,H}$ = 3.3 Hz, 1 H, CH), 5.11 (br. s, 1 H, H-N), 7.01–7.03 (m, 2 H, Ar), 7.23–7.26 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.8 (CH_3-CH_2), 22.0 (CH_3-CH_2), 69.2 (sept, $^2J_{C,F}$ = 27.9 Hz, C-CF_3), 87.8 (CH), 122.9 (q, $^1J_{C,F}$ = 295.9 Hz, CF_3), 125.4 (Ar), 128.8 (Ar), 130.2 (C_q, Ar), 138.2 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –65.17 (q, $^4J_{F,F}$ = 11.6 Hz, 3 F, CF_3), –69.11 (q, $^4J_{F,F}$ = 11.6 Hz, 3 F, CF_3) ppm. IR (neat): $\tilde{\nu}$ = 3358 (br., NH) cm^{-1}. $C_{12}H_{11}ClF_6N_2O_2$: C 39.52, H 3.04, N 7.68; found C 39.62, H 3.09, N 7.55.

***N*-[2-Nitro-1,1-bis(trifluoromethyl)butyl]aniline (4d):** Brown oil (60%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.04 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3-CH_2), 2.18–2.21 (m, 1 H, CH_3-CH_2), 2.42–2.51 (m, 1 H, CH_3-CH_2), 5.06 (dd, $^3J_{H,H}$ = 11.7, $^3J_{H,H}$ = 3.4 Hz, 1 H, CH), 5.07 (br. s, 1 H, H-N), 7.08–7.15 (m, 2 H, Ar), 7.28–7.32 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.8 (CH_3-CH_2), 22.0 (CH_3-CH_2), 69.3 (sept, $^2J_{C,F}$ = 25.3 Hz, C-CF_3), 88.0 (CH), 122.2 (q, $^1J_{C,F}$ = 290.3 Hz, CF_3), 123.9 (Ar), 124.5 (Ar), 128.7 (Ar), 140.2 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –65.18 (q, $^4J_{F,F}$ = 11.6 Hz, 3 F, CF_3), –69.11 (q, $^4J_{F,F}$ = 11.6 Hz, 3 F, CF_3) ppm. IR (neat): $\tilde{\nu}$ = 3325 (br., NH) cm^{-1}. $C_{12}H_{12}F_6N_2O_2$: C 43.65, H 3.66, N 8.48; found C 43.84, H 3.67, N 8.64.

4-Methyl-*N*-[2-nitro-1,1-bis(trifluoromethyl)butyl]benzamide (4e): Yellow oil (64%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3-CH_2), 1.99–2.04 (m, 2 H, CH_3-CH_2), 2.43 (s, 3 H, CH_3), 4.76 (br. s, 1 H, H-N), 4.77–4.81 (m, 1 H, CH), 7.25–7.27 (m, 2 H, Ar), 7.91–7.94 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.8 (CH_3-CH_2), 21.4 (CH_3-CH_2), 23.6 (CH_3), 68.2 (sept, $^2J_{C,F}$ = 25.0 Hz, C-CF_3), 90.1 (CH), 115.3 (Ar), 123.6 (q, $^1J_{C,F}$ = 286.0 Hz, CF_3), 128.9 (C_q, Ar), 133.5 (Ar), 141.2 (C_q, Ar), 157.6 (C=O) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –64.53 (q, $^4J_{F,F}$ = 11.6 Hz, 3 F, CF_3), –64.59 (q, $^4J_{F,F}$ = 11.6 Hz, 3 F, CF_3) ppm. IR (nujol): $\tilde{\nu}$ = 3420 (br., NH) , 1670 (C=O), 1230 (CF) cm^{-1}. $C_{14}H_{14}F_6N_2O_3$: C 45.17, H 3.79, N 7.53; found C 45.04, H 3.67, N 7.64.

4-Methyl-*N*-(2,2,2-trifluoro-1-{[3-(2-oxoazepane-1-yl)propyl]amino}-1-(trifluoromethyl)ethyl)benzamide (3e): Pale yellow solid (47%), m.p. 90–93 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.61–1.76 (m, 2 H, CH_2), 1.94–2.02 (m, 2 H, CH_2), 2.35 (s, 3 H, CH_3), 2.74–2.80 (m, 6 H, 3 CH_2), 3.38–3.51 (m, 6 H, 3 CH_2), 6.23 (br. s, 1 H, H-N), 7.15–7.22 (m, 2 H, Ar), 7.84–7.91 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 21.0, 23.6, 26.4, 28.6, 31.9, 37.9, 48.2, 53.9, 64.2 (sept, $^2J_{C,F}$ = 29.3 Hz, C-CF_3), 122.6 (q, $^1J_{C,F}$ = 289.3 Hz, CF_3), 127.3 (Ar), 128.6 (C_q, Ar), 131.6 (Ar), 141.5 (C_q, Ar), 164.9 (c, C=O), 165.7 (c, C=O) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –70.55 (CF_3) ppm. IR (nujol): $\tilde{\nu}$ = 3110 (br., NH) , 1690 (C=O), 1670 (C=O) cm^{-1}. $C_{20}H_{25}F_6N_3O_2$: C 52.98, H 5.56, N 9.27; found C 52.84, H 5.71, N 9.18.

General Procedure for the Aza-Henry Reaction of Trifluoracetone Imines with Nitroalkanes: Nitroalkane [nitromethane (2.5 mmol, 0.14 mL) for substances **2f**–**2i**; nitropropane (2.5 mmol, 0.26 mL) for substances **4f**–**4i**] and base [DBN (0.25 mmol, 31 μL) for substances **2f**–**2i**; DBU (0.05 mmol, 8.5 μL) for substances **4f**–**4i**] were added to a solution of the imine (0.25 mmol) in toluene (1 mL). The reaction was monitored by TLC (over about 20 h), then the reaction mixture was concentrated under reduced pressure. The product was isolated by column chromatography (hexane/dichloromethane, 1:1).

4-Methoxy-*N*-[2,2,2-trifluoro-1-methyl-1-(nitromethyl)ethyl]aniline (2f): Yellow oil (78%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.45 (s, 3 H, CH_3), 3.79 (s, 3 H, CH_3-O), 4.56 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, CH_2), 4.68 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, CH_2), 6.80–6.83 (m, 2 H, Ar), 7.01–7.04 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.4 (CH_3), 55.0 (CH_3-O), 61.0 (q, $^2J_{C,F}$ = 25.0 Hz, C-CF_3), 77.5 (CH_2), 113.8 (Ar), 122.6 (q, $^1J_{C,F}$ = 288.6 Hz, CF_3), 127.2 (C_q, Ar), 133.6 (Ar), 156.7 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –77.48 (CF_3) ppm. IR (neat): $\tilde{\nu}$ = 3120 (br., NH) cm^{-1}. $C_{11}H_{13}F_3N_2O_3$: C 47.49, H 4.71, N 10.07; found C 47.67, H 4.88, N 10.10.

4-Methyl-*N*-[2,2,2-trifluoro-1-methyl-1-(nitromethyl)ethyl]aniline (2g): Brownish-yellow oil (70%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.51 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 3.91 (br. s, 1 H, H-N), 4.55 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, CH_2), 4.67 (d, $^2J_{H,H}$ = 11.2 Hz, 1 H, CH_2), 6.94–6.96 (m, 2 H, Ar), 7.07–7.09 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.5 (CH_3), 20.3 (CH_3), 60.9 (q, $^2J_{C,F}$ = 27.3 Hz, C-CF_3), 77.6 (CH_2), 124.6 (Ar), 125.2 (q, $^1J_{C,F}$ = 286.0 Hz, CF_3), 129.2 (C_q, Ar), 133.7 (Ar), 138.5 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –78.67 (CF_3) ppm. IR (neat): $\tilde{\nu}$ = 3219 (br., NH) , 1120 (CF) cm^{-1}. $C_{11}H_{13}F_3N_2O_2$: C 50.38, H 5.00, N 10.68; found C 50.18, H 4.88, N 10.56.

4-Chloro-*N*-[2,2,2-trifluoro-1-methyl-1-(nitromethyl)ethyl]aniline (2h): Yellow oil (84%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.54 (s, 3 H, CH_3), 4.03 (br. s, 1 H, H-N), 4.58 (d, $^2J_{H,H}$ = 12.0 Hz, 1 H, CH_2), 4.74 (d, $^2J_{H,H}$ = 12.0 Hz, 1 H, CH_2), 6.95–6.97 (m, 2 H, Ar), 7.22–7.25 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.4 (CH_3), 61.0 (q, $^2J_{C,F}$ = 30.2 Hz, C-CF_3), 78.0 (CH_2), 125.0 (q, $^1J_{C,F}$ = 287.9 Hz, CF_3), 125.1 (Ar), 128.7 (Ar), 129.1 (C_q, Ar), 139.9 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –78.65 (CF_3) ppm. IR (neat): $\tilde{\nu}$ = 3380 (br., NH) cm^{-1}. $C_{10}H_{10}ClF_3N_2O_2$: C 42.49, H 3.57, N 9.91; found C 42.64, H 3.45, N 9.95.

***N*-[2,2,2-Trifluoro-1-methyl-1-(nitromethyl)ethyl]aniline (2i):** Brown oil (70%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.56 (s, 3 H, CH_3), 4.05 (br. s, 1 H, H-N), 4.60 (d, $^2J_{H,H}$ = 12.8 Hz, 1 H, CH_2), 4.75 (d, $^2J_{H,H}$ = 12.8 Hz, 1 H, CH_2), 7.01–7.11 (m, 3 H, Ar), 7.26–7.29 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.6 (CH_3), 61.0 (q, $^2J_{C,F}$ = 25.0 Hz, C-CF_3), 77.5 (CH_2), 123.7 (Ar), 124.8 (q, $^1J_{C,F}$ = 285.0 Hz, CF_3), 128.7 (Ar), 128.9 (Ar), 141.4 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –76.26 (CF_3) ppm. IR (neat): $\tilde{\nu}$ = 3349 (br., NH) cm^{-1}. $C_{10}H_{11}F_3N_2O_2$: C 48.39, H 4.47, N 11.29; found C 48.51, H 4.48, N 11.31.

4-Methoxy-*N*-[1-methyl-2-nitro-1-(trifluoromethyl)butyl]aniline (4f): Yellow oil (66%), diastereomeric mixture (1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, *CH*$_3$-CH$_2$), 1.10 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, *CH*$_3$-CH$_2$), 1.24–1.27 (m, 2 H, CH$_3$-*CH*$_2$), 1.28–1.31 (m, 2 H, CH$_3$-*CH*$_2$), 1.37 (s, 3 H, CH$_3$), 1.39 (s, 3 H, CH$_3$), 2.59–2.65 (m, 1 H, CH), 2.65–2.70 (m, 1 H, CH), 3.78 (s, 3 H, CH$_3$-O), 3.82 (s, 3 H, CH$_3$-O), 6.69–6.74 (m, 2 H, Ar), 6.77–6.80 (m, 2 H, Ar), 6.85–6.90 (m, 2 H, Ar), 6.91–6.93 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.8 (*CH*$_3$-*C*H$_2$), 11.9 (*CH*$_3$-*C*H$_2$), 14.6 (CH$_3$-*CH*$_2$), 14.8 (CH$_3$-*CH*$_2$), 18.2 (CH$_3$), 18.6 (CH$_3$), 54.9 (CH$_3$-O), 55.0 (CH$_3$-O), 62.7 (q, $^2J_{C,F}$ = 25.2 Hz, *C*-CF$_3$), 92.1 (CH), 92.8 (CH), 113.7 (Ar), 113.9 (Ar), 115.3 (q, $^1J_{C,F}$ = 270.0 Hz, CF$_3$), 120.1 (Ar), 120.4 (Ar), 134.1 (C$_q$, Ar), 134.3 (C$_q$, Ar), 140.0 (C$_q$, Ar), 140.3 (C$_q$, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –76.66 (CF$_3$), –77.65 (CF$_3$) ppm. IR (neat): $\tilde{\nu}$ = 3418 (br., NH) cm^{-1}. $C_{12}H_{16}F_3N_2O_3$: C 46.39, H 4.54, N 9.02; found C 46.53, H 4.74, N 9.12.

4-Methyl-*N*-[1-methyl-2-nitro-1-(trifluoromethyl)butyl]aniline (4g): Brownish-yellow oil (52%), diastereomeric mixture (1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, $^3J_{H,H}$ = 7.7 Hz, 3 H, *CH*$_3$-*C*H$_2$), 1.02 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, *CH*$_3$-*C*H$_2$), 1.27–1.35 (m, 2 H, CH$_3$-*CH*$_2$), 1.43–1.47 (m, 2 H, CH$_3$-*CH*$_2$), 1.99 (s, 3 H, CH$_3$), 2.04 (s, 3 H, CH$_3$), 2.30 (s, 3 H, CH$_3$), 2.36 (s, 3 H, CH$_3$), 4.47–4.61 (m, 1 H, CH), 4.72–4.77 (m, 1 H, CH), 6.70–6.72 (m, 2 H, Ar), 6.83–6.87 (m, 2 H, Ar), 7.03–7.07 (m, 2 H, Ar), 7.17–7.20 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.0 (*CH*$_3$-*C*H$_2$), 10.2 (*CH*$_3$-*C*H$_2$), 13.7 (CH$_3$), 13.9 (CH$_3$), 21.7 (CH$_3$-*CH*$_2$), 21.9 (CH$_3$-*CH*$_2$), 29.3 (CH$_3$), 29.7 (CH$_3$), 63.5 (q, $^2J_{C,F}$ = 22.2 Hz, *C*-CF$_3$), 91.8 (CH), 91.9 (CH), 118.5 (Ar), 118.6 (Ar), 123.0 (q, $^1J_{C,F}$ = 271.6 Hz, CF$_3$), 129.0 (Ar), 129.3 (Ar), 134.4 (C$_q$, Ar), 135.1 (C$_q$, Ar), 151.0 (C$_q$, Ar), 151.2 (C$_q$, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –74.80 (CF$_3$), –75.72 (CF$_3$) ppm. IR (neat): $\tilde{\nu}$ = 3420 (br., NH) cm^{-1}. $C_{13}H_{17}F_3N_2O_2$: C 53.79, H 5.90, N 9.65; found C 53.60, H 5.78, N 9.55.

4-Chloro-*N*-[1-methyl-2-nitro-1-(trifluoromethyl)butyl]aniline (4h): Yellow oil (98%), diastereomeric mixture (1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, *CH*$_3$-*C*H$_2$), 1.02 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, *CH*$_3$-*C*H$_2$), 1.44 (s, 3 H, CH$_3$), 1.49 (s, 3 H, CH$_3$), 1.80–1.87 (m, 1 H, CH$_3$-*CH*$_2$), 1.90–1.96 (m, 1 H, CH$_3$-*CH*$_2$), 2.12–2.18 (m, 1 H, CH$_3$-*CH*$_2$), 2.23–2.31 (m, 1 H, CH$_3$-*CH*$_2$), 3.72 (br. s, 1 H, H-N), 4.31 (br. s, 1 H, H-N), 4.72–4.74 (m, 1 H, CH), 4.75–4.77 (m, 1 H, CH), 6.73–6.76 (m, 2 H, Ar), 6.87–6.90 (m, 2 H, Ar), 7.09–7.11 (m, 2 H, Ar), 7.19–7.23 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.0 (*CH*$_3$-CH$_2$), 10.1 (*CH*$_3$-CH$_2$), 15.7 (CH$_3$), 15.9 (CH$_3$), 21.4 (CH$_3$-*CH*$_2$), 21.8 (CH$_3$-*CH*$_2$), 62.6 (q, $^2J_{C,F}$ = 26.7 Hz, *C*-CF$_3$), 91.9 (CH), 92.4 (CH), 119.8 (Ar), 120.0 (Ar), 124.7 (Ar), 124.8 (Ar), 125.5 (q, $^1J_{C,F}$ = 291.1 Hz, *C*F$_3$), 128.5 (Ar), 128.6 (Ar), 140.2 (C$_q$, Ar), 140.5 (C$_q$, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –75.03 (*CF*$_3$), –75.93 (*CF*$_3$) ppm. IR (neat): $\tilde{\nu}$ = 3283 (br., NH) cm^{-1}. $C_{12}H_{14}ClF_3N_2O_2$: C 46.39, H 4.54, N 9.09; found C 46.21, H 4.48, N 9.14.

***N*-[1-Methyl-2-nitro-1-(trifluoromethyl)butyl]aniline (4i):** Brown oil (37%), diastereomeric mixture (1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH$_3$-CH$_2$), 1.02 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, *CH*$_3$-CH$_2$), 1.48 (s, 3 H, CH$_3$), 1.52 (s, 3 H, CH$_3$), 1.91–1.98 (m, 2 H, CH$_3$-*CH*$_2$), 2.19–2.34 (m, 2 H, CH$_3$-*CH*$_2$), 4.74–4.79 (m, 1 H, CH), 4.81–4.82 (m, 1 H, CH), 6.85–6.90 (m, 2 H, Ar), 6.93–6.97 (m, 2 H, Ar), 7.03–7.09 (m, 1 H, Ar), 7.11–7.14 (m, 1 H, Ar), 7.22–7.28 (m, 2 H, Ar), 7.30–7.37 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.1 (*CH*$_3$-CH$_2$), 10.2 (*CH*$_3$-CH$_2$), 15.9 (CH$_3$), 16.0 (CH$_3$), 21.4 (CH$_3$-*CH*$_2$), 21.9 (CH$_3$-*CH*$_2$), 62.7 (q, $^2J_{C,F}$ = 26.8 Hz, *C*-CF$_3$), 91.9 (CH), 92.6 (CH), 123.0 (Ar), 123.2 (Ar), 123.3 (Ar), 123.4 (Ar), 125.7 (q, $^1J_{C,F}$ = 289.2 Hz, CF$_3$), 128.5 (Ar), 128.7 (Ar), 141.6 (C$_q$, Ar), 141.9 (C$_q$, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –76.11 (CF$_3$), –77.07 (CF$_3$) ppm. IR (neat): $\tilde{\nu}$ = 3305 (br., NH) , 1238 (CF) cm^{-1}. $2C_{12}H_{15}F_3N_2O_2{\cdot}H_2O$: C 46.70, H 4.70, N 10.89; found C 46.81, H 4.68, N 10.81.

General Procedure for the Aza-Henry Reaction of Trifluoroacetophenone Imines with Nitroalkanes: *N*-Alkylidencarbamate **1j**–**1q** (4 mmol) was added to a solution of nitromethane (1.1 mL, 0.02 mol) and triethylamine (0.055 mL, 0.4 mmol) in anhydrous DMSO (6 mL), and the mixture was kept at room temperature for 12 h. The mixture was then poured into water (30 mL), and extracted with CH_2Cl_2 (2 × 15 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was evaporated. The residue was purified by crystallization from hexane/2-propanol, 6:1 (compounds **2j**–**2n**), or hexane (compounds **2p** and **2q**).

Methyl [2,2,2-Trifluoro-1-(4-fluorophenyl)-1-(nitromethyl)ethyl]-carbamate (2j): Pale yellow solid (84%), m.p. 116–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.73 (s, 3 H, CH$_3$), 5.39 (d, $^2J_{H,H}$ = 12.2 Hz, 1 H, CH$_2$), 5.53 (d, $^2J_{H,H}$ = 12.2 Hz, 1 H, CH$_2$), 5.62 (br. s, 1 H, H-N), 7.12–7.14 (m, 2 H, Ar), 7.35–7.42 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.7 (CH$_3$), 63.3 (q, $^2J_{C,F}$ = 27.5 Hz, *C*-CF$_3$), 72.6 (CH$_2$), 115.9 (d, $^2J_{C,F}$ = 22.5 Hz, Ar), 123.5 (q, $^1J_{C,F}$ = 283.8 Hz, CF$_3$), 127.6 (d, $^4J_{C,F}$ = 2.5 Hz, Ar), 127.8 (d, $^3J_{C,F}$ = 8.7 Hz, Ar), 154.6 (C=O), 162.9 (d, $^1J_{C,F}$ = 250.0 Hz, Ar) ppm. ^{19}F NMR (280 MHz, $CDCl_3$): δ = –76.32 (CF$_3$), –112.25 (F) ppm. IR (KBr): $\tilde{\nu}$ = 3360–3450 (NH), 1750 (CO), 1575 (NO$_2$) cm^{-1}. $C_{11}H_{10}F_4N_2O_4$: C 42.59, H 3.25, N 9.03; found C 42.67, H 3.28, N 9.14.

Methyl [2,2,2-Trifluoro-1-(4-methylphenyl)-1-(nitromethyl)ethyl]-carbamate (2k): Pale yellow solid (86%), m.p. 114–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH$_3$), 3.73 (s, 3 H, CH$_3$), 5.38 (d, $^2J_{H,H}$ = 12.4 Hz, 1 H, CH$_2$), 5.50–5.70 (m, 2 H, CH, NH), 7.21–7.25 (m, 2 H, Ar), 7.22–7.38 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7 (CH$_3$), 52.6 (CH$_3$), 63.4 (q, $^2J_{C,F}$ = 27.5 Hz, *C*-CF$_3$), 72.6 (CH$_2$), 123.5 (q, $^1J_{C,F}$ = 285.0 Hz, CF$_3$), 125.5 (Ar), 128.7 (Ar), 129.5 (Ar), 139.7 (Ar), 154.6 (C=O) ppm. ^{19}F NMR (280 MHz, $CDCl_3$): δ = –76.27 (CF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3350–3450 (NH), 1735 (CO), 1575 (NO$_2$), 1370 (NO$_2$) cm^{-1}. $C_{12}H_{13}F_3N_2O_4$: C 47.06, H 4.28, N 9.15; found C 46.90, H 4.19, N 9.04.

Ethyl [2,2,2-Trifluoro-1-phenyl-1-(nitromethyl)ethyl]carbamate (2l): Pale yellow solid (90%), m.p. 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (t, $^3J_{H,H}$ = 6.8 Hz, 3 H, *CH*$_3$-CH$_2$), 4.11–4.17 (m, 2 H, CH$_3$-*CH*$_2$), 5.44 ($^2J_{H,H}$ = 12.0 Hz, 1 H, CH$_2$), 5.58 (br. s, 1 H, H-N), 5.60 (d, $^2J_{H,H}$ = 12.0 Hz, 1 H, CH$_2$), 7.36–7.48 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (*CH*$_3$-CH$_2$), 61.7 (CH$_3$-*CH*$_2$), 63.6 (q, $^2J_{C,F}$ = 28.8 Hz, *C*-CF$_3$), 72.6 (CH$_2$), 123.5 (q, $^1J_{C,F}$ = 285.0 Hz, CF$_3$), 125.7 (Ar), 128.8 (Ar), 129.5 (Ar), 131.9 (Ar), 154.2 (C=O) ppm. ^{19}F NMR (280 MHz, $CDCl_3$): δ = –76.25 (CF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3380–3450 (NH), 1750 (CO), 1580 (NO$_2$), 1320 (NO$_2$) cm^{-1}. $C_{12}H_{13}F_3N_2O_4$: C 47.06, H 4.28, N 9.15; found C 47.24, H 4.32, N 9.09.

Ethyl [2,2,2-Trifluoro-1-(4-fluorophenyl)-1-(nitromethyl)ethyl]carbamate (2m): Pale yellow solid (82%), m.p. 74–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, $^3J_{H,H}$ = 6.8 Hz, 3 H, *CH*$_3$-CH$_2$), 4.12–4.17 (m, 2 H, CH$_3$-*CH*$_2$), 5.41 (d, $^2J_{H,H}$ = 12.4 Hz, 1 H, CH$_2$), 5.51 (d, $^2J_{H,H}$ = 12.4 Hz, 1 H, CH$_2$), 5.56 (br. s, 1 H, H-N), 7.06–7.18 (m, 2 H, Ar), 7.38–7.43 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (*CH*$_3$-CH$_2$), 61.8 (CH$_3$-*CH*$_2$), 63.3 (q, $^2J_{C,F}$ = 28.8 Hz, *C*-CF$_3$), 72.6 (CH$_2$), 115.9 (d, $^2J_{C,F}$ = 22.5 Hz, Ar), 123.3 (q, $^1J_{C,F}$ = 283.8 Hz, CF$_3$), 127.7 (d, $^4J_{C,F}$ = 1.3 Hz, Ar), 127.8 (d, $^3J_{C,F}$ = 8.7 Hz, Ar), 154.1 (C=O), 162.9 (d, $^1J_{C,F}$ =

248.8 Hz, Ar) ppm. ^{19}F NMR (280 MHz, $CDCl_3$): δ = –76.16 (CF_3), –112.19 (F) ppm. IR (KBr): $\tilde{\nu}$ = 3350–3450 (NH), 1750 (CO), 1575 (NO_2), 1340 (NO_2) cm^{-1}. $C_{12}H_{12}F_4N_2O_4$: C 44.45, H 3.73, N 8.64; found C 44.61, H 3.64, N 8.46.

Ethyl [2,2,2-Trifluoro-1-(4-methylphenyl)-1-(nitromethyl)ethyl]carbamate (2n): Pale yellow solid (84%), m.p. 74–75 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.29 (t, $^3J_{H,H}$ = 6.6 Hz, 3 H, *CH*$_3$-CH_2), 3.82 (s, 3 H, CH_3), 4.13–4.18 (m, 2 H, CH_3-*CH*$_2$), 5.41 (d, $^2J_{H,H}$ = 12.3 Hz, 1 H, CH_2), 5.58 (br. s, 1 H, H-N), 5.59 (d, $^2J_{H,H}$ = 12.4 Hz, 1 H, CH_2), 6.91–6.99 (m, 2 H, Ar), 7.31–7.35 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (*CH*$_3$-CH_2), 55.0 (CH_3), 61.6 (CH_3-*CH*$_2$), 63.3 (q, $^2J_{C,F}$ = 28.8 Hz, *C*-CF_3), 72.6 (CH_2), 114.1 (Ar), 123.5 (q, $^1J_{C,F}$ = 285.0 Hz, CF_3), 123.6 (Ar), 127.1 (Ar), 154.2 (C=O), 160.1 (Ar) ppm. ^{19}F NMR (280 MHz, $CDCl_3$): δ = –76.33 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3380–3450 (NH), 1740 (CO), 1590 (NO_2), 1320 (NO_2) cm^{-1}. $C_{13}H_{15}F_3N_2O_5$: C 46.43, H 4.50, N 8.33; found C 46.27, H 4.61, N 8.21.

***tert*-Butyl [2,2,2-Trifluoro-1-phenyl-1-(nitromethyl)ethyl]carbamate (2o):** Pale yellow solid (85%), m.p. 87–88 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 9 H, 3 CH_3), 5.30–5.60 (3 H, m. NH, CH_2), 7.40–7.42 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.7 (*CH*$_3$-C), 63.6 (q, $^2J_{C,F}$ = 27.5 Hz, *C*-CF_3), 72.8 (CH_2), 81.4 (CH_3-*C*), 123.5 (q, $^1J_{C,F}$ = 286.3 Hz, CF_3), 125.8 (Ar), 128.6 (Ar), 129.3 (Ar), 132.2 (Ar), 153.2 (C=O) ppm. ^{19}F NMR (280 MHz, $CDCl_3$): δ = –76.18 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3350–3450 (NH), 1735 (CO), 1575 (NO_2), 1375 (NO_2) cm^{-1}. $C_{14}H_{17}F_3N_2O_4$: C 50.30, H 5.13, N 8.38; found C 50.45, H 5.27, N 8.51.

***tert*-Butyl [2,2,2-Trifluoro-1-(4-methylphenyl)-1-(nitromethyl)ethyl]-carbamate (2p):** Pale yellow solid (86%), m.p. 77–79 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 9 H, 3 CH_3), 2.34 (s, 3 H, CH_3), 5.38 (br. s, 1 H, NH), 5.43 ($^2J_{H,H}$ = 12.0 Hz, 1 H, CH_2), 5.52 ($^2J_{H,H}$ = 12.0 Hz, 1 H, CH_2), 7.16–7.28 (m, 2 H, Ar), 7.25–7.33 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.7 (*CH*$_3$-C), 63.6 (q, $^2J_{C,F}$ = 27.5 Hz, *C*-CF_3), 72.8 (CH_2), 81.4 (CH_3-*C*), 123.5 (q, $^1J_{C,F}$ = 286.3 Hz, CF_3), 125.8 (Ar), 128.6 (Ar), 129.3 (Ar), 132.2 (Ar), 153.2 (C=O) ppm. ^{19}F NMR (280 MHz, $CDCl_3$): δ = –76.22 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3350–3450 (NH), 1740 (CO), 1575 (NO_2), 1370 (NO_2) cm^{-1}. $C_{15}H_{19}F_3N_2O_4$: C 51.72, H 5.50, N 8.04; found C 51.55, H 5.37, N 8.21.

***tert*-Butyl [2,2,2-Trifluoro-1-(4-fluorophenyl)-1-(nitromethyl)ethyl]-carbamate (2q):** Pale yellow solid (82%), m.p. 71–72 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 9 H, 3 CH_3), 5.38 (br. s, 1 H, H-N), 5.56 (br. s, 2 H, CH_2), 7.09–7.15 (m, 2 H, Ar), 7.38–7.43 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.1 (3 CH_3), 63.6 (q, $^2J_{C,F}$ = 28.2 Hz, *C*-CF_3), 73.1 (CH_2), 82.1 (CH_3-*C*), 116.1 (d, $^2J_{C,F}$ = 22.1 Hz, Ar), 123.8 (q, $^1J_{C,F}$ = 285.7 Hz, CF_3), 128.3 (d, $^4J_{C,F}$ = 9.0 Hz, Ar), 128.4 (Ar), 153.6 (C=O), 163.3 (d, $^1J_{C,F}$ = 250.5 Hz, Ar) ppm. ^{19}F NMR (280 MHz, $CDCl_3$): δ = –76.40 (CF_3), –112.19 (F) ppm. IR (KBr): $\tilde{\nu}$ = 3350–3450 (NH), 1750 (CO), 1575 (NO_2), 1340 (NO_2) cm^{-1}. $C_{12}H_{12}F_4N_2O_4$: C 44.45, H 3.73, N 8.64; found C 44.61, H 3.64, N 8.46.

Reduction of Nitroamines 2a–2i to Diamines: Concentrated hydrochloric acid (3.65 mL) and water (4.2 mL) were added to a solution of the nitroamine (0.2 mmol) in methanol (15 mL). Then, zinc powder (3.2 mmol, 208 mg) was added in portions over 1 h with vigorous stirring under argon. The reaction mixture was stirred overnight at room temperature, then saturated aqueous sodium hydrogen carbonate solution was added (to pH 8). The aqueous phase was extracted with ethyl acetate (3× 50 mL), and then the combined organic layers were dried with sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography (dichloromethane/methanol, 100:3).

3,3,3-Trifluoro-N^2-(4-methoxyphenyl)-2-(trifluoromethyl)propane-1,2-diamine (5a): Brown oil (97%). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.47 (s, 2 H, CH_2), 3.78 (s, 3 H, CH_3-O), 4.14 (br. s, 1 H, H-N), 6.79–6.81 (m, 2 H, Ar), 6.95–6.97 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 40.7 (CH_2), 55.4 (CH_3-O), 67.2 (sept, $^2J_{C,F}$ = 29.3 Hz, *C*-CF_3), 114.2 (Ar), 122.7 (q, $^1J_{C,F}$ = 289.3 Hz, CF_3), 126.1 (Ar), 133.5 (C_q, Ar), 156.8 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –71.77 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3250 (br., NH) , 1360 (CF) cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{14}F_6N_2O$ $[M + H]^+$ 303.0927; found 303.0937.

3,3,3-Trifluoro-N^2-(4-methylphenyl)-2-(trifluoromethyl)propane-1,2-diamine (5b): Brown oil (80%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.34 (br. s, 2 H, NH_2), 2.30 (s, 3 H, CH_3), 3.32 (s, 2 H, CH_2), 4.79 (br. s, 1 H, H-N), 6.95–6.97 (m, 2 H, Ar), 7.06–7.08 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2 (CH_3), 29.3 (CH_2), 65.7 (sept, $^2J_{C,F}$ = 24.4 Hz, *C*-CF_3), 122.5 (Ar), 123.8 (q, $^1J_{C,F}$ = 291.1 Hz, CF_3), 129.2 (Ar), 132.5 (C_q, Ar), 139.1 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –71.49 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3295 (br., NH) cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{14}F_6N_2$ $[M + H]^+$ 287.0975; found 287.0977.

3,3,3-Trifluoro-N^2-(4-chlorophenyl)-2-(trifluoromethyl)propane-1,2-diamine (5c): Brown oil (98%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.29 (br. s, 2 H, NH_2), 3.31 (s, 2 H, CH_2), 5.19 (br. s, 1 H, H-N), 6.95–6.98 (m, 2 H, Ar), 7.20–7.22 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.3 (CH_2), 65.3 (sept, $^2J_{C,F}$ = 25.2 Hz, *C*-CF_3), 122.6 (Ar), 126.4 (q, $^1J_{C,F}$ = 248.3 Hz, CF_3), 128.6 (Ar), 128.7 (C_q, Ar), 140.7 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –71.31 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3340 (br., NH) cm^{-1}. $C_{10}H_9ClF_6N_2{\cdot}H_2O$: C 35.05, H 3.82, N 8.08; found C 35.18, H 3.93, N 8.02.

3,3,3-Trifluoro-N^2-(phenyl)-2-(trifluoromethyl)propane-1,2-diamine (5d): Brown oil (82%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.86 (br. s, 2 H, NH_2), 2.99 (s, 2 H, CH_2), 3.36 (br. s, 1 H, H-N), 6.92–6.94 (m, 1 H, Ar), 7.03–7.05 (m, 2 H, Ar), 7.23–7.28 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.8 (CH_2), 66.1 (sept, $^2J_{C,F}$ = 20.9 Hz, *C*-CF_3), 119.4 (q, $^1J_{C,F}$ = 296.2 Hz, CF_3), 120.9 (Ar), 121.4 (Ar), 122.7 (C_q, Ar), 128.7 (Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –71.56 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3273 (br., NH) , 1250 (CF) cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{11}F_6N_2$ $[M + H]^+$ 273.0813; found 273.0821.

N^2-(4-Chlorophenyl)-3,3,3-trifluoro-2-methylpropane-1,2-diamine (5h): Brown oil (88%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.37 (s, 3 H, CH_3), 1.56 (br. s, 2 H, NH_2), 2.70–2.73 (m, 1 H, CH_2), 3.21–3.24 (m, 1 H, CH_2), 4.66 (br. s, 1 H, H-N), 6.82–6.84 (m, 2 H, Ar), 7.14–7.17 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9 (CH_3), 29.3 (CH_2), 59.3 (q, $^2J_{C,F}$ = 25.6 Hz, *C*-CF_3), 119.7 (q, $^1J_{C,F}$ = 376.5.7 Hz, CF_3), 121.1 (Ar), 125.5 (C_q, Ar), 128.4 (Ar), 142.8 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –77.03 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3205 (br., NH) cm^{-1}. $C_{10}ClH_{12}F_3N_2$: C 47.54, H 4.79, N 11.09; found C 47.45, H 4.93, N 11.05.

1,1,1-Trifluoro-N^2-(4-methoxyphenyl)-2-(trifluoromethyl)pentane-2,3-diamine (6a): Yellow oil (96%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.06 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, *CH*$_3$-CH_2), 1.25–1.28 (m, 2 H, CH_3-*CH*$_2$), 3.20–3.23 (m, 1 H, CH), 3.78 (s, 3 H, CH_3), 4.66 (br. s, 1 H, H-N), 6.79–6.81 (m, 2 H, Ar), 7.01–7.04 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4 (*CH*$_3$-CH_2), 24.8 (CH_3-*CH*$_2$), 54.3 (CH), 54.9 (*C*H$_3$), 69.7 (sept, $^2J_{C,F}$ = 28.3 Hz, *C*-CF_3), 113.6 (Ar), 122.6 (q, $^1J_{C,F}$ = 294.5 Hz, *C*F$_3$), 125.8 (C_q, Ar), 134.5 (Ar), 156.1 (C_q, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –66.35 (q, $^4J_{F,F}$ = 9.2 Hz, CF_3), –68.28 (q, $^4J_{F,F}$ = 9.2 Hz, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3300 (br., NH) cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{17}F_6N_2O$ $[M + H]^+$ 331.1240; found 331.1244.

1,1,1-Trifluoro-N^2-(4-methylphenyl)-2-(trifluoromethyl)pentane-2,3-diamine (6b): Brown oil (80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.08 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, *CH*$_3$-CH$_2$), 1.27 (s, 3 H, CH$_3$), 1.42 (br. s, 2 H, NH$_2$), 2.02–2.08 (m, 2 H, CH$_3$-*CH*$_2$), 3.22–3.25 (m, 1 H, CH), 5.17 (br. s, 1 H, H-N), 7.00–7.03 (m, 2 H, Ar), 7.38–7.40 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4 (*CH*$_3$-CH$_2$), 20.2 (*C*H$_3$), 24.7 (CH$_3$-*CH*$_2$), 54.4 (*C*H), 69.5 (sept, $^2J_{C,F}$ = 27.8 Hz, *C*-CF$_3$), 122.7 (Ar), 126.2 (q, $^1J_{C,F}$ = 279.0 Hz, *C*F$_3$), 129.1 (C$_q$, Ar), 132.4 (Ar), 139.3 (C$_q$, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –66.38 (q, $^4J_{F,F}$ = 8.9 Hz, CF$_3$), –68.41 (q, $^4J_{F,F}$ = 8.9 Hz, CF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3373 (br., NH) , 1159 (CF), 1149 (CF) cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{17}F_6N_2$ [M + H]$^+$ 315.1292; found 315.1290.

1,1,1-Trifluoro-N^2-(4-chlorophenyl)-2-(trifluoromethyl)pentane-2,3-diamine (6c): Brown oil (94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.07 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, *CH*$_3$-CH$_2$), 1.45 (br. s, 2 H, NH$_2$), 1.65–1.68 (m, 2 H, CH$_3$-*CH*$_2$), 3.25–3.27 (m, 1 H, CH), 5.45 (br. s, 1 H, H-N), 6.93–6.96 (m, 2 H, Ar), 7.17–7.20 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4 (*CH*$_3$-CH$_2$), 24.8 (CH$_3$-*CH*$_2$), 54.7 (CH), 68.3 (sept, $^2J_{C,F}$ = 24.8 Hz, *C*-CF$_3$), 122.6 (Ar), 125.3 (Ar), 127.0 (q, $^1J_{C,F}$ = 206.4 Hz, CF$_3$), 128.4 (C$_q$, Ar), 141.2 (C$_q$, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –66.05 (q, $^4J_{F,F}$ = 9.1 Hz, CF$_3$), –68.58 (q, $^4J_{F,F}$ = 9.1 Hz, CF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3263 (br., NH) cm^{-1}. 4C$_{12}$ClH$_{13}$F$_6$N$_2$·5H$_2$O: C 40.35, H 4.37, N 7.84; found C 40.20, H 4.17, N 7.62.

1,1,1-Trifluoro-N^2-(phenyl)-2-(trifluoromethyl)pentane-2,3-diamine (6d): Yellow oil (89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (t, $^3J_{H,H}$ = 7.9 Hz, 3 H, *CH*$_3$-CH$_2$), 1.80–1.88 (m, 1 H, CH$_3$-*CH*$_2$), 1.97–2.07 (m, 1 H, CH$_3$-*CH*$_2$), 3.39–3.42 (m, 1 H, CH), 7.03–7.09 (m, 3 H, Ar), 7.23–7.29 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4 (*CH*$_3$-CH$_2$), 29.3 (CH$_3$-*CH*$_2$), 54.5 (CH), 69.3 (sept, $^2J_{C,F}$ = 25.8 Hz, *C*-CF$_3$), 116.5 (Ar), 122.3 (q, $^1J_{C,F}$ = 232.3 Hz, CF$_3$), 122.7 (Ar), 128.6 (Ar), 141.7 (C$_q$, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –66.48 (q, $^4J_{F,F}$ = 8.3 Hz, CF$_3$), –68.20 (q, $^4J_{F,F}$ = 8.3 Hz, CF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3220 (br., NH) cm^{-1}. $C_{12}H_{14}F_6N_2$: C 48.00, H 4.70, N 9.33; found C 48.20, H 4.63, N 9.22.

***N*^{2}-(4-Chlorophenyl)-3,3,3-trfluoromethyl-2-methylpentane-2,3-diamine (6h):** Brown oil (82%), diastereomeric mixture (1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, *CH*$_3$-CH$_2$), 1.05 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, *CH*$_3$-CH$_2$), 1.37 (s, 3 H, CH$_3$), 1.40 (s, 3 H, CH$_3$), 1.63–1.71 (m, 2 H, CH$_3$-*CH*$_2$), 1.87–1.95 (m, 2 H, CH$_3$-*CH*$_2$), 2.68 (dd, $^3J_{H,H}$ = 11.5, $^3J_{H,H}$ = 2.6 Hz, 1 H, CH), 3.15 (dd, $^3J_{H,H}$ = 10.1, $^3J_{H,H}$ = 2.7 Hz, 1 H, CH), 4.67 (br. s, 1 H, H-N), 4.99 (br. s, 1 H, H-N), 6.68–6.60 (m, 2 H, Ar), 6.78–6.83 (m, 2 H, Ar), 7.08–7.10 (m, 2 H, Ar), 7.11–7.16 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.6 (*CH*$_3$-CH$_2$), 11.8 (*CH*$_3$-CH$_2$), 16.3 (CH$_3$), 16.5 (CH$_3$), 22.7 (CH$_3$-*CH*$_2$), 24.8 (CH$_3$-*CH*$_2$), 55.6 (CH), 59.4 (CH), 61.6 (q, $^2J_{C,F}$ = 23.6 Hz, *C*-CF$_3$), 120.7 (Ar), 121.5 (Ar), 124.2 (q, $^1J_{C,F}$ = 230.0 Hz, CF$_3$), 124.7 (C$_q$, Ar), 125.3 (C$_q$, Ar), 128.3 (Ar), 128.9 (Ar), 142.9 (C$_q$, Ar), 143.3 (C$_q$, Ar) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –72.91 (CF$_3$), –75.27 (CF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3373 (br., NH) , 1159 (CF), 1149 (CF) cm^{-1}. $C_{12}ClH_{13}F_6N_2$: C 51.34, H 5.74, N 9.98; found C 51.17, H 5.94, N 9.76.

Reduction of Nitroamines 2j–2r to Diamines: $NiCl_2$·6H_2O (0.48 g, 2 mmol) and $NaBH_4$ (0.38 g, 10 mmol) were successively added to a cooled (0 °C) solution of carbamate **2j**–**2r** (2 mmol) in methanol (10 mL), and the resulting mixture was stirred for 30–40 min. The solvent was evaporated at room temperature. Ammonia (15% aqueous solution; 20 mL) was added to the residue, and the mixture was extracted with CH_2Cl_2 (3× 15 mL). The organic layer was washed with ammonia (15% aqueous solution; 10 mL), water (20 mL), dried with Na_2SO_4, and evaporated. The residue was recrystallized from hexane.

Methyl [1-(Aminomethyl)-2,2,2-trifluoro-1-(4-fluorophenyl)ethyl]-carbamate (5j): Pale yellow solid (81%), m.p. 87–89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42 (br. s, 2 H, NH$_2$), 3.19 (d, $^2J_{H,H}$ = 12.8 Hz, 1 H, CH$_2$), 3.55–3.70 (m, 4 H, CH$_3$, CH), 6.02 (br. s, 1 H, H-N), 7.06–7.08 (m, 2 H, Ar), 7.37–7.42 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.0 (CH$_3$), 46.5 (CH$_2$), 64.2 (*C*-CF$_3$), 115.2 (d, $^2J_{C,F}$ = 21.3 Hz, Ar), 125.5 (q, $^1J_{C,F}$ = 286.3 Hz, CF$_3$), 127.8 (d, $^4J_{C,F}$ = 7.5 Hz, Ar), 131.5 (Ar), 154.8 (C=O), 162.2 (d, $^1J_{C,F}$ = 247.5 Hz, Ar) ppm. ^{19}F NMR (280 MHz, $CDCl_3$): δ = –72.72 (CF$_3$), –114.88 (F) ppm. IR (KBr): $\tilde{\nu}$ = 3300–3420 (NH), 1735 (CO) cm^{-1}. $C_{11}H_{12}F_4N_2O_2$: C 47.15, H 4.32, N 10.00; found C 47.27, H 4.28, N 10.14.

Methyl [1-(Aminomethyl)-2,2,2-trifluoro-1-(4-methylphenyl)ethyl]-carbamate (5k): Pale yellow solid (86%), m.p. 121–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (br. s, 2 H, NH$_2$), 2.35 (s, 3 H, CH$_3$), 3.25–3.29 (m, 1 H, CH), 3.60–3.80 (m, 4 H, CH, CH$_3$), 5.91 (br. s, 1 H, NH), 7.13–7.27 (m, 2 H, Ar), 7.26–7.40 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6 (CH$_3$), 52.0 (CH$_3$), 46.0 (CH$_2$), 64.6 (*C*-CF$_3$), 125.6 (q, $^1J_{C,F}$ = 286.3 Hz, CF$_3$), 125.7 (Ar), 129.0 (Ar), 132.1 (Ar), 138.0 (Ar), 154.8 (C=O) ppm. ^{19}F NMR (280 MHz, $CDCl_3$): δ = –72.47 (CF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3300–3420 (NH), 1740 (CO) cm^{-1}. $C_{12}H_{15}F_3N_2O_2$: C 52.17, H 5.47, N 10.14; found C 52.37, H 5.38, N 10.19.

Ethyl [1-(Aminomethyl)-2,2,2-trifluoro-1-(phenyl)ethyl]carbamate (5l): Pale yellow solid (86%), m.p. 119–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, *CH*$_3$-CH$_2$), 1.42 (br. s, 2 H, NH$_2$), 3.27 (d, $^2J_{H,H}$ = 13.8 Hz, 1 H, CH$_2$), 3.68 (d, $^2J_{H,H}$ = 13.8 Hz, 1 H, CH$_2$), 4.10 (q, $^2J_{H,H}$ = 7.2 Hz, 2 H, CH$_3$-*CH*$_2$), 5.90 (br. s, 1 H, H-N), 7.30–7.55 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (*CH*$_3$-CH$_2$), 60.9 (CH$_3$-*CH*$_2$), 46.3 (CH$_2$), 64.8 (q, $^2J_{C,F}$ = 25.0 Hz, *C*-CF$_3$), 125.6 (q, $^1J_{C,F}$ = 286.3 Hz, CF$_3$), 125.9 (Ar), 128.1 (Ar), 128.3 (Ar), 135.3 (Ar), 154.5 (C=O) ppm. ^{19}F NMR (280 MHz, $CDCl_3$): δ = –72.30 (CF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3300–3420 (NH), 1740 (CO) cm^{-1}. $C_{12}H_{15}F_3N_2O_2$: C 52.17, H 5.47, N 10.14; found C 52.37, H 5.38, N 10.05.

Ethyl [1-(Aminomethyl)-2,2,2-trifluoro-1-(4-fluorophenyl)ethyl]carbamate (5m): Pale yellow solid (81%), m.p. 89–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (s, $^3J_{H,H}$ = 7.2 Hz, 3 H, *CH*$_3$-CH$_2$), 1.42 (br. s, 2 H, NH$_2$), 3.23 (d, $^2J_{H,H}$ = 13.0 Hz, 1 H, CH$_2$), 3.64 (d, $^2J_{H,H}$ = 13.0 Hz, 1 H, CH$_2$), 4.10 (q, $^2J_{H,H}$ = 7.2 Hz, 2 H, CH$_3$-*CH*$_2$), 6.01 (br. s, 1 H, H-N), 7.00–7.16 (m, 2 H, Ar), 7.28–7.36 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0 (*CH*$_3$-CH$_2$), 61.0 (CH$_3$-*CH*$_2$), 46.5 (CH$_2$), 64.4 (q, $^2J_{C,F}$ = 25.0 Hz, *C*-CF$_3$), 115.2 (d, $^2J_{C,F}$ = 21.3 Hz, Ar), 125.5 (q, $^1J_{C,F}$ = 286.3 Hz, CF$_3$), 127.8 (d, $^4J_{C,F}$ = 7.5 Hz, Ar), 131.1 (Ar), 154.4 (C=O), 162.2 (d, $^1J_{C,F}$ = 246.3 Hz, Ar) ppm. ^{19}F NMR (280 MHz, $CDCl_3$): δ = –72.70 (CF$_3$), –114.86 (F) ppm. IR (KBr): $\tilde{\nu}$ = 3300–3420 (NH), 1740 (CO) cm^{-1}. $C_{12}H_{14}F_4N_2O_2$: C 48.98, H 4.80, N 9.52; found C 48.78, H 4.64, N 9.66.

Ethyl [1-(Aminomethyl)-2,2,2-trifluoro-1-(4-methoxyphenyl)ethyl]-carbamate (5n): Pale yellow solid (88%), m.p. 78–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, *CH*$_3$-CH$_2$), 1.47 (br. s, 2 H, NH$_2$), 3.26 (d, $^2J_{H,H}$ = 14.0 Hz, 1 H, CH$_2$), 3.66 (d, $^2J_{H,H}$ = 14.0 Hz, 1 H, CH$_2$), 3.79 (s, 3 H, CH$_3$), 4.09 (q, $^2J_{H,H}$ = 7.2 Hz, 2 H, CH$_3$-*CH*$_2$), 5.77 (br. s, 1 H, H-N), 6.81–6.97 (m, 2 H, Ar), 7.26–7.42 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 (*CH*$_3$-CH$_2$), 54.9 (CH$_3$), 60.9 (CH$_3$-*CH*$_2$), 45.9 (CH$_2$), 64.5 (q, $^2J_{C,F}$ = 25.0 Hz, *C*-CF$_3$), 113.7 (Ar), 125.6 (q, $^1J_{C,F}$ = 286.3 Hz,

CF_3), 127.0 (Ar), 127.1 (Ar), 154.5 (C=O), 159.1 (Ar) ppm. ^{19}F NMR (280 MHz, $CDCl_3$): δ = –72.96 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3300–3420 (NH), 1735 (CO) cm^{-1}. $C_{13}H_{17}F_3N_2O_3$: C 50.98, H 5.59, N 9.15; found C 50.79, H 5.71, N 9.34.

***tert*-Butyl [1-(Aminomethyl)-2,2,2-trifluoro-1-(phenyl)ethyl]carbamate (5o):** Pale yellow solid (84%), m.p. 77–78 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.20–1.60 (m, 11 H, 3 CH_3, NH_2), 3.27 (d, $^2J_{H,H}$ = 14.1 Hz, 1 H, CH_2), 3.65 (d, $^2J_{H,H}$ = 14.1 Hz, 1 H, CH_2), 5.69 (br. s, 1 H, H-N), 7.32–7.58 (m, 5 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.7 (*C*H_3-C), 46.4 (CH_2), 64.9 (*C*-CF_3), 80.1 (CH_3-*C*), 125.7 (q, $^1J_{C,F}$ = 285.0 Hz, CF_3), 125.9 (Ar), 127.9 (Ar), 128.1 (Ar), 135.6 (Ar), 153.7 (C=O) ppm. ^{19}F NMR (280 MHz, $CDCl_3$): δ = –72.51 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3300–3420 (NH), 1740 (CO) cm^{-1}. $C_{14}H_{19}F_3N_2O_2$: C 55.26, H 6.29, N 9.21; found C 55.38, H 6.11, N 9.37.

***tert*-Butyl [1-(Aminomethyl)-2,2,2-trifluoro-1-(4-methylphenyl)ethyl]carbamate (5p):** Pale yellow solid (82%), m.p. 93–94 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.38 (s, 9 H, 3 CH_3), 1.45 (br. s, 2 H, NH_2), 2.32 (s, 3 H, CH_3), 3.24–3.28 (m, 1 H, CH_2), 3.61–3.65 (m, 1 H, CH_2), 5.59 (br. s, 1 H, NH), 7.09–7.25 (m, 2 H, Ar), 7.22–7.38 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6 (*C*H_3-C), 27.8 (CH_3), 46.0 (CH_2), 64.6 (q, $^2J_{C,F}$ = 25.0 Hz, *C*-CF_3), 80.0 (CH_3-*C*), 125.7 (q, $^1J_{C,F}$ = 286.3 Hz, CF_3), 125.9 (Ar), 128.9 (Ar), 132.5 (Ar), 137.8 (Ar), 153.7 (C=O) ppm. ^{19}F NMR (280 MHz, $CDCl_3$): δ = –72.59 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3300–3420 (NH), 1740 (CO) cm^{-1}. $C_{15}H_{21}F_3N_2O_2$: C 56.59, H 6.65, N 8.80; found C 56.80, H 6.70, N 8.64.

Reduction of Nitroamines 2a–2h, 3a–3h to Oximes: Nitroamine **2a**–**2h**, **3a**–**3h** (0.2 mmol) was dissolved in methanol (15 mL), and saturated aqueous ammonia (2 mL) and palladium on carbon (10%; 50 mg) as catalyst were added. The suspension was stirred under a hydrogen atmosphere for 28 h, then it was filtered through a Celite plug. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (dichloromethane/methanol, 100:1).

3,3,3-Trifluoro-2-[(4-methoxyphenyl)amino]-2-(trfluoromethyl)propanal Oxime (7a): Brown oil (82%). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.78 (s, 3 H, CH_3-O), 4.14 (br. s, 1 H, H-N), 6.79–6.81 (m, 2 H, Ar), 6.95–6.97 (m, 2 H, Ar), 7.47 (s, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4 (CH_3-O), 67.2 (sept, $^2J_{C,F}$ = 29.3 Hz, *C*-CF_3), 114.2 (Ar), 122.7 (q, $^1J_{C,F}$ = 289.3 Hz, CF_3), 126.1 (C_q, Ar), 133.5 (Ar), 141.3 (C_q, Ar), 156.8 (C=N) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –71.77 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3400 (br., OH, NH) cm^{-1}. $C_{10}H_{10}F_6N_2O_2$: C 41.78, H 3.19, N 8.86; found C 41.88, H 2.99, N 8.72.

3,3,3-Trifluoro-2-[(4-methylphenyl)amino]-2-(trfluoromethyl)propanal Oxime (7b): Reddish-brown oil (80%). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3 H, CH_3), 4.20 (br. s, 1 H, H-N), 6.85–6.87 (m, 2 H, Ar), 7.05–7.07 (m, 2 H, Ar), 7.51 (s, 1 H, CH), 8.05 (br. s, 1 H, H-O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.3 (CH_3), 67.4 (sept, $^2J_{C,F}$ = 21.2 Hz, *C*-CF_3), 120.7 (q, $^1J_{C,F}$ = 282.7 Hz, *C*F_3), 121.2 (Ar), 129.3 (C_q, Ar), 141.5 (Ar), 155.0 (C_q, Ar), 164.7 (C=N) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –72.21 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3400 (br., OH, NH) cm^{-1}. $C_{10}H_{10}F_6N_2O$: C 40.00, H 5.19, N 8.48; found C 40.28, H 5.23, N 8.52.

3,3,3-Trifluoro-2-[(4-chlorophenyl)amino]-2-(trfluoromethyl)propanal Oxime (7c): Yellowish-brown oil (94%). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.37 (br. s, 1 H, H-N), 6.86–6.88 (m, 2 H, Ar), 7.21–7.23 (m, 2 H, Ar), 7.52 (s, 1 H, CH), 8.98 (br. s, 1 H, H-O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.2 (sept, $^2J_{C,F}$ = 27.6 Hz, *C*-CF_3), 122.0 (q, $^1J_{C,F}$ = 252.5 Hz, *C*F_3), 122.5 (q, $^1J_{C,F}$ = 235.9 Hz, *C*F_3), 122.6 (Ar), 128.8 (Ar), 139.1 (C_q, Ar), 140.8 (C_q, Ar), 184.6 (C=N) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –72.20 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3420 (br., OH, NH) cm^{-1}. $C_{10}H_7ClF_6N_2O$: C 37.46, H 2.20, N 8.74; found C 37.50, H 2.17, N 8.86.

3,3,3- Trifluoro-2-[(phenyl)amino]-2-(trfluoromethyl)propanal Oxime (7d): Brown oil (76%). ^1H NMR (400 MHz, $CDCl_3$): δ = 4.34 (br. s, 1 H, H-N), 6.93–6.95 (m, 2 H, Ar), 7.05–7.07 (m, 1 H, Ar), 7.24–7.28 (m, 2 H, Ar), 7.54 (s, 1 H, CH), 8.26 (br. s, 1 H, H-O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.2 (sept, $^2J_{C,F}$ = 31.0 Hz, *C*-CF_3), 121.0 (Ar), 122.7 (q, $^2J_{C,F}$ = 292.1 Hz, CF_3), 122.9 (Ar), 128.8 (Ar), 141.4 (C_q, Ar), 167.2 (C=N) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –72.23 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3415 (br., OH, NH) cm^{-1}. $2C_{10}H_8F_6N_2O{\cdot}3H_2O$: C 38.35, H 3.54, N 8.94; found C 38.55, H 3.52, N 9.03.

2-[(4-Chlorophenyl)amino]-3,3,3-trifluoro-2-methylpropanal Oxime (7h): Yellow oil (90%). ^1H NMR (400 MHz, [D_6]DMSO): δ = 1.50 (s, 3 H, CH_3), 4.54 (br. s, 1 H, H-N), 5.68 (s, 1 H, CH), 6.81–6.85 (m, 2 H, Ar), 7.13–7.17 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 17.7 (CH_3), 59.5 (q, $^2J_{C,F}$ = 25.8 Hz, *C*-CF_3), 127.2 (q, $^2J_{C,F}$ = 276.4 Hz, CF_3), 120.3 (Ar), 120.8 (C_q, Ar), 128.9 (Ar), 144.7 (C_q, Ar), 166.7 (C=N) ppm. ^{19}F NMR (376.5 MHz, [D_6]DMSO): δ = –72.20 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3408 (br., OH, NH) cm^{-1}. $3C_{10}ClH_{10}F_3N_2O{\cdot}H_2O$: C 40.68, H 3.32, N 8.03; found C 40.79, H 3.50, N 7.94.

2-[(4-Methoxyphenyl)amino]-1,1,1-trfluoro-2-(trifluoromethyl)pentane-3-one Oxime (8a): Yellow oil (76%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.03 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, *C*H_3-CH_2), 1.24 (m, 2 H, CH_3-*C*H_2), 1.86 (br. s, 1 H, H-O), 3.80 (s, 3 H, CH_3), 4.74 (br. s, 1 H, H-N), 6.77–6.84 (m, 2 H, Ar), 7.05–7.08 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.9 (*C*H_3-CH_2), 22.0 (CH_3-*C*H_2), 55.4 (*C*H_3-O), 69.5 (sept, $^2J_{C,F}$ = 22.4 Hz, *C*-CF_3), 113.7 (Ar), 124.0 (q, $^1J_{C,F}$ = 220.0 Hz, CF_3), 127.3 (Ar), 131.6 (C_q, Ar), 157.2 (C_q, Ar), 167.2 (C=N) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –69.42 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3380 (br., OH, NH) cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{14}F_6N_2NaO_2$-OH^- $[M + Na]^+$ 367.0852; found 367.0852.

2-[(4-Chlorophenyl)amino]-1,1,1-trfluoro-2-(trifluoromethyl)pentane-3-one Oxime (8c): Yellowish-brown oil (82%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, *C*H_3-CH_2), 2.48 (q, $^3J_{H,H}$ = 7.4 Hz, 2 H, CH_3-*C*H_2), 4.34 (br. s, 1 H, H-N), 6.75–6.77 (m, 2 H, *Ar*), 7.03–7.09 (m, 2 H, Ar), 9.26 (br. s, 1 H, H-O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.5 (*C*H_3-CH_2), 20.1 (CH_3-*C*H_2), 69.3 (sept, $^2J_{C,F}$ = 26.4 Hz, *C*-CF_3), 116.5 (Ar), 120.8 (Ar), 122.5 (q, $^1J_{C,F}$ = 221.9 Hz, CF_3), 128.7 (C_q, Ar), 141.6 (C_q, Ar), 153.6 (C=N) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –69.63 (CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3380 (br., OH, NH) cm^{-1}. $3C_{12}H_{11}ClF_6N_2O{\cdot}H_2O$: C 40.68, H 3.32, N 8.03; found C 40.79, H 3.50, N 7.94.

2-[Phenylamino]-1,1,1-trfluoro-2-(trifluoromethyl)pentane-3-one Oxime (8d): Yellowish-brown oil (82%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.17 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, *C*H_3-CH_2), 2.46 (m, 2 H, CH_3-*C*H_2), 4.34 (br. s, 1 H, H-N), 6.74–6.76 (m, 2 H, Ar), 6.90–6.93 (m, 1 H, Ar), 7.18–7.20 (m, 2 H, Ar), 8.29 (br. s, 1 H, H-O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.4 (*C*H_3-CH_2), 20.5 (CH_3-*C*H_2), 70.0 (sept, $^2J_{C,F}$ = 26.3 Hz, *C*-CF_3), 117.0 (Ar), 121.2 (Ar), 123.7 (q, $^1J_{C,F}$ = 247.6 Hz, *C*F_3), 129.1 (Ar), 141.9 (C_q, Ar), 154.4 (C=N) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –69.66 (*C*F_3) ppm. IR (KBr): $\tilde{\nu}$ = 3380 (br., OH, NH) cm^{-1}. $C_{12}H_{12}F_6N_2O$: C 37.46, H 2.20, N 8.74; found C 37.28, H 2.23, N 8.62.

2-[(4-Chlorophenyl)amino]-1,1,1-trifluoro-2-methylpentane-3-one Oxime (8h): Yellowish-brown oil (82%). ^1H NMR (400 MHz, [D_6]

DMSO): δ = 1.00 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, *CH*$_3$-CH$_2$), 1.40 (s, 3 H, CH$_3$), 1.55–1.59 (m, 2 H, CH$_3$-*CH*$_2$), 3.36 (br. s, 1 H, H-N), 6.94–6.96 (m, 2 H, Ar), 7.14–7.17 (m, 2 H, Ar), 7.38 (br. s, 1 H, H-O) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 11.3 (*CH*$_3$-CH$_2$), 15.2 (CH$_3$), 21.6 (CH$_3$-*CH*$_2$), 62.7 (q, $^2J_{C,F}$ = 24.7 Hz, *C*-CF$_3$), 117.0 (q, $^1J_{C,F}$ = 263.3 Hz, CF$_3$), 119.7 (Ar), 120.8 (Ar), 128.6 (C$_q$, Ar), 144.5 (C$_q$, Ar), 155.0 (C=N) ppm. ^{19}F NMR (376.5 MHz, [D$_6$]DMSO): δ = –73.25 (CF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3400 (br., OH, NH) cm^{-1}. $C_{12}H_{14}ClF_3N_2O$: C 48.91, H 4.79, N 9.51; found C 48.88, H 4.73, N 9.52.

General Procedure for the Preparation of Imidazoline-2-ones 9j–9n: DBU (0.031 g, 0.02 mmol) was added to a solution of carbamate **4j**–**4n** (0.7 mmol) in toluene (5 mL). The mixture was heated for 2 h, then it was cooled to room temperature. The resulting precipitate was collected by filtration and dried in air.

4-(4-Fluorophenyl)-4-(trifluoromethyl)imidazoline-2-one (9j): Pale yellow solid [90% (from **5j**), 88% (from **5m**)], m.p. >220 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.65 (d, $^2J_{H,H}$ = 10.4 Hz, 1 H, CH$_2$), 4.00 (d, $^2J_{H,H}$ = 10.4 Hz, 1 H, CH$_2$), 6.79 (br. s, 1 H, H-N), 7.20–7.36 (m, 2 H, Ar), 7.53–7.56 (m, 2 H, Ar), 8.30 (br. s, 1 H, H-N) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 47.7 (CH$_2$), 64.1 (q, $^2J_{C,F}$ = 27.5 Hz, *C*-CF$_3$), 115.4 (d, $^2J_{C,F}$ = 21.3 Hz, Ar), 125.8 (q, $^1J_{C,F}$ = 283.8 Hz, CF$_3$), 129.2 (d, $^4J_{C,F}$ = 8.8 Hz, Ar), 133.4 (d, $^4J_{C,F}$ = 2.5 Hz, Ar), 161.2 (C=O), 162.2 (d, $^1J_{C,F}$ = 245.0 Hz, Ar) ppm. ^{19}F NMR (280 MHz, [D$_6$]DMSO): δ = –79.71 (CF$_3$), –114.17 (F) ppm. IR (KBr): $\tilde{\nu}$ = 3240–3320 (NH), 1740 (CO) cm^{-1}. $C_{10}H_8F_3N_2O$: C 48.40, H 3.25, N 11.29; found C 48.26, H 3.40, N 11.18.

4-(4-Methylphenyl)-4-(trifluoromethyl)imidazoline-2-one (9k): Pale yellow solid [92% (from **5k**), 90% (from **5p**)], m.p. >230 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.30 (s, 3 H, CH$_3$), 3.62 (d, $^2J_{H,H}$ = 10.0 Hz, 1 H, CH$_2$), 3.97 (d, $^2J_{H,H}$ = 10.0 Hz, 1 H, CH$_2$), 6.72 (br. s, 1 H, H-N), 7.16–7.30 (m, 2 H, Ar), 7.29–7.43 (m, 2 H, Ar), 8.22 (br. s, 1 H, H-N) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 20.7 (CH$_3$), 47.7 (CH$_2$), 64.2 (q, $^2J_{C,F}$ = 27.5 Hz, *C*-CF$_3$), 125.9 (q, $^1J_{C,F}$ = 283.8 Hz, CF$_3$), 126.7 (Ar), 129.0 (Ar), 134.2 (Ar), 134.3 (Ar), 161.3 (C=O) ppm. ^{19}F NMR (280 MHz, [D$_6$]DMSO): δ = –79.47 (CF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3140–3320 (NH), 1740 (CO) cm^{-1}. $C_{11}H_{11}F_3N_2O$: C 54.10, H 4.54, N 11.47; found C 54.31, H 4.36, N 11.58.

4-Phenyl-4-(trifluoromethyl)imidazoline-2-one (9l): Pale yellow solid [87% (from **5l**), 90% (from **5o**)], m.p. >230 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.66 (d, $^2J_{H,H}$ = 10.4 Hz, 1 H, CH$_2$), 4.01 (d, $^2J_{H,H}$ = 10.4 Hz, 1 H, CH$_2$), 6.77 (br. s, 1 H, H-N), 7.00–7.16 (m, 2 H, Ar), 7.36–7.60 (m, 5 H, Ar), 8.29 (br. s, 1 H, H-N) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 47.6 (CH$_2$), 64.3 (q, $^2J_{C,F}$ = 27.5 Hz, *C*-CF$_3$), 125.8 (q, $^1J_{C,F}$ = 285.0 Hz, CF$_3$), 126.8 (Ar), 128.4 (Ar), 128.8 (Ar), 137.1 (Ar), 161.2 (C=O) ppm. ^{19}F NMR (280 MHz, [D$_6$]DMSO): δ = –79.15 (CF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3220–3320 (NH), 1750 (CO) cm^{-1}. $C_{12}H_{14}ClF_3N_2O$: C 52.18, H 3.94, N 12.17; found C 52.01, H 3.80, N 11.98.

4-Methoxyphenyl-4-(trifluoromethyl)imidazoline-2-one (9n): Pale yellow solid (82%), m.p. >230 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.62 (d, $^2J_{H,H}$ = 10.4 Hz, 1 H, CH$_2$), 3.76 (s, 3 H, CH$_3$), 3.97 (d, $^2J_{H,H}$ = 10.4 Hz, 1 H, CH$_2$), 6.73 (br. s, 1 H, H-N), 6.90–7.04 (m, 2 H, Ar), 7.34–7.48 (m, 2 H, Ar), 8.22 (br. s, 1 H, H-N) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 47.7 (CH$_3$), 55.2 (CH$_2$), 64.0 (q, $^2J_{C,F}$ = 28.8 Hz, *C*-CF$_3$), 113.8 (Ar), 125.9 (q, $^1J_{C,F}$ = 283.8 Hz, CF$_3$), 128.1 (Ar), 129.0 (Ar), 159.4 (Ar), 161.3 (C=O) ppm. ^{19}F NMR (280 MHz, [D$_6$]DMSO): δ = –79.23 (CF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3150–3320 (NH), 1740 (CO) cm^{-1}. $C_{11}H_{11}F_3N_2O_2$: C 50.77, H 4.26, N 10.77; found C 50.62, H 4.36, N 10.69.

General Procedure for the Preparation of 1,2-Diamines 10k and 10l: Carbamate **2k** or **2l** (0.5 mmol) was added to a saturated solution of hydrogen chloride in dioxane (2 mL). The mixture was stirred for 4 h. The resulting precipitate was collected by filtration and dried under reduced pressure.

3,3,3-Trifluoro-2-(phenyl)propane-1,2-diamine Dihydrochloride (10k): Pale yellow solid (90%), m.p. ca. 170 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.55 (d, $^2J_{H,H}$ = 13.4 Hz, 1 H, CH$_2$), 3.88 (d, $^2J_{H,H}$ = 13.4 Hz, 1 H, CH$_2$), 3.80–6.00 (m, 6 H, 2 NH$_3^+$), 7.45–7.51 (m, 3 H, Ar), 7.66–7.71 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 41.4 (CH$_2$), 61.2 (q, $^2J_{C,F}$ = 27.5 Hz, *C*-CF$_3$), 124.9 (q, $^1J_{C,F}$ = 285.0 Hz, CF$_3$), 127.5 (Ar), 128.5 (Ar), 129.5 (Ar), 131.4 (Ar) ppm. ^{19}F NMR (280 MHz, [D$_6$]DMSO): δ = –75.77 (CF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3320–3420 (NH) cm^{-1}. $C_9H_{13}Cl_2F_3N_2$: C 41.25, H 5.19, N 9.62; found C 41.46, H 5.35, N 9.41.

3,3,3-Trifluoro-2-(4-methylphenyl)propane-1,2-diamine Dihydrochloride (10l): Pale yellow solid (88%), m.p. ca. 180 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.33 (s, 3 H, CH$_3$), 3.61 (d, $^2J_{H,H}$ = 15.0 Hz, 1 H, CH$_2$), 3.95 (d, $^2J_{H,H}$ = 15.0 Hz, 1 H, CH$_2$), 4.05–7.10 (br. s, 6 H, 2 NH$_3^+$), 7.26 (m, 2 H, Ar), 7.49 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 20.7 (CH$_3$), 41.3 (CH$_2$), 61.3 (q, $^2J_{C,F}$ = 28.8 Hz, *C*-CF$_3$), 80.0 (CH$_3$-*C*), 126.0 (q, $^1J_{C,F}$ = 285.0 Hz, CF$_3$), 127.6 (Ar), 128.0 (Ar), 129.4 (Ar), 139.3 (Ar) ppm. ^{19}F NMR (280 MHz, [D$_6$]DMSO): δ = –70.04 (CF$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3310–3420 (NH) cm^{-1}. $C_{10}H_{15}Cl_2F_3N_2$: C 41.25, H 5.19, N 9.62; found C 41.36, H 5.35, N 9.48.

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[1] P. Kirsch, *Modern Fluoroorganic Chemistry: Synthesis Reactivity, Applications*, Wiley-VCH, Weinheim, Germany, **2004**.
[2] P. Maienfisch, R.-G. Hall, *Chimia* **2004**, *58*, 93–99.
[3] For selected publications, see: a) O. A. Tomashenko, V. V. Grushin, *Chem. Rev.* **2011**, 4475–4521; b) N. Shibata, A. Matsnev, D. Cahard, *Beilstein J. Org. Chem.* **2010**, *6*, 1–19; c) J.-A. Ma, D. Cahard, *Chem. Rev.* **2004**, *104*, 6119–6146; d) M. Oishi, H. Kondo, H. Amii, *Chem. Commun.* **2009**, 1909–911; e) G. K. S. Prakash, A. K. Yudin, *Chem. Rev.* **1997**, 757–86; f) V. M. Muzalevskiy, V. G. Nenajdenko, A. V. Shastin, E. S. Balenkova, G. Haufe, *Synthesis* **2009**, 3905–929.
[4] For selected publications, see: a) R. Filler, Y. Kobayashi, L. M. Yagulpolskii (Eds.), *Organofluorine Compounds in Medicinal Chemistry and Biomedical Applications*, Elsevier, Amsterdam, **1993**; b) V. P. Kukhar, V. A. Soloshonok (Eds.), *Fluorine-containing Amino Acids: Synthesis and Properties*, John Wiley & Sons, Chichester, UK, **1995**; c) T. Hiyama, in: *Organofluorine Compounds: Chemistry and Applications*, (Ed.: H. Yamamoto), Springer, Berlin, **2000**, chapter 5, p. 137–182; d) B. E. Smart, *J. Fluorine Chem.* **2001**, *109*, 3–11; e) O. I. Shmatova, V. G. Nenajdenko, *Eur. J. Org. Chem.* **2013**, 6397–6404; f) N. E. Shevchenko, O. I. Shmatova, E. S. Balenkova, G.-V. Röschenthaler, V. G. Nenajdenko, *Eur. J. Org. Chem.* **2013**, 2237–2245; g) O. I. Shmatova, N. E. Shevchenko, E. S. Balenkova, G.-V. Röschenthaler, V. G. Nenajdenko, *Eur. J. Org. Chem.* **2013**, 3049–3058; h) O. I. Shmatova, V. G. Nenajdenko, *J. Org. Chem.* **2013**, *78*, 9214–9222; i) O. I. Shmatova, N. E. Shevchenko, E. S. Balenkova, G.-V. Röschenthaler, V. G. Nenajdenko, *Mendeleev Commun.* **2013**, *23*, 92–93; j) R. D. Chambers, *Fluorine in Organic Chemistry*, Blackwell, Oxford, UK, **2004**.

[5] For selected publications, see: a) A. Kumar, J. Kaur, S. Chimni, A. Jassa, *RSC Adv.* **2014**, *4*, 24816–24819; b) B. Tan, X. Liu, L. Wang, J. Wang, X. Feng, *Org. Lett.* **2008**, *10*, 5305–5308; c) M. Nunez, A. J. M. Farley, D. J. Dixon, *J. Am. Chem. Soc.* **2013**, *135*, 16348–16351; d) V. P. Ananikov, L. L. Khemchyan, Y. V. Ivanova, V. I. Bukhtiyarov, A. M. Sorokin, I. P. Prosvirin, S. Z. Vatsadze, A. V. Medved'ko, V. N. Nuriev, A. D. Dilman, V. V. Levin, I. V. Koptyug, K. V. Kovtunov, V. V. Zhivonitko, V. A. Likholobov, A. V. Romanenko, P. A. Simonov, V. G. Nenajdenko, O. I. Shmatova, V. M. Muzalevskiy, M. S. Nechaev, A. F. Asachenko, O. S. Morozov, P. B. Dzhevakov, S. N. Osipov, D. V. Vorobyeva, M. A. Topchiy, M. A. Zotova, S. A. Ponomarenko, O. V. Borshchev, Y. N. Luponosov, A. A. Rempel, A. A. Valeeva, A. Y. Stakheev, O. V. Turova, I. S. Mashkovsky, S. V. Sysolyatin, V. V. Malykhin, G. A. Bukhtiyarova, A. O. Terent'ev, I. B. Krylov, *Russ. Chem. Rev.* **2014**, *83*, 885–985. For fluorinated imines, see: e) V. M. Tkachuk, V. A. Sukach, K. V. Kovalchuk, M. V. Vovka, V. G. Nenajdenko, *Org. Biomol. Chem.* **2014**, *13*, 1420–1428; f) H. Xie, X. Zhang, S. Zhang, X. Chen, W. Wang, *Angew. Chem. Int. Ed.* **2011**, *50*, 11773–11776; *Angew. Chem.* **2011**, *123*, 11977–11980; g) S. Fioravanti, L. Pellacani, M. C. Vergari, *Org. Biomol. Chem.* **2012**, *10*, 8207–8210; h) F. Zhang, Z.-J. Liu, J.-T. Liu, *Org. Biomol. Chem.* **2011**, *9*, 3625–3628.

[6] For selected publications, see: a) A. Noble, J. Anderson, *Chem. Rev.* **2013**, *113*, 2887–2939; b) T. Severin, M. Adam, *Chem. Ber.* **1964**, *97*, 186–189; c) Z. Pei, X. Li, T. W. von Geldern, K. Longenecker, D. Pireh, K. D. Stewart, B. J. Backes, C. Lai, T. H. Lubben, S. J. Ballaron, D. W. A. Beno, A. J. Kempf-Grote, H. L. Sham, J. M. Trevillyan, *J. Med. Chem.* **2007**, *50*, 1983–1987; d) T. A. Davis, M. W. Danneman, J. N. Johnston, *Chem. Commun.* **2012**, *48*, 5578–5580.

[7] a) N. Pahadi, H. Ube, M. Terada, *Tetrahedron Lett.* **2007**, *48*, 8700–8703; b) R. Kober, W. Hammes, W. Steglich, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 203–204; *Angew. Chem.* **1982**, *94*, 213–214; c) N. Amarasinghe, P. Turner, M. Todd, *Adv. Synth. Catal.* **2012**, *354*, 2954–2958.

[8] a) L. Wang, C. Tan, X. Liu, X. Feng, *Synlett* **2008**, *13*, 2075–2077; b) M. Petrini, M. Seri, *Tetrahedron* **2006**, *62*, 960–967; c) H. Rodríguez-Solla, C. Concellón, N. Alvaredo, R. G. Soengas, *Tetrahedron* **2012**, *68*, 1736–1744; d) J. S. Yadav, B. V. S. Reddy, N. N. Yadav, M. K. Gupta, *Synthesis* **2009**, 1131.

[9] a) L. Zhang, H. Wu, S. Su, S. Wang, *Chin. J. Chem.* **2009**, *27*, 2061–2065; b) J. Wang, Z.-J. Lu, L.-Y. Wang, J. Bai, Y. Pan, *Lett. Org. Chem.* **2008**, *5*, 286–289.

[10] Y. Guo, K. Fujiwara, K. Uneyama, *Org. Lett.* **2006**, *8*, 827–829.

[11] A. V. Gulevich, N. E. Shevchenko, E. S. Balenkova, G.-V. Röschenthaler, V. G. Nenajdenko, *Tetrahedron* **2008**, *64*, 11706–11712.

[12] a) V. N. Fetyukhin, A. S. Koretskii, V. I. Gorbatenko, L. I. Samarai, *Zh. Org. Khim.* **1977**, *13*, 271–274; b) N. V. Mel'nichenko, M. V. Vovk, *Russ. J. Org. Chem.* **2008**, *44*, 149–150.

[13] K. Kaupmees, A. Trummal, I. Leito, *Croat. Chem. Acta* **2014**, *87*, 385–395.

[14] B.-M. Xi, Z.-Z. Jiang, J.-W. Zou, P.-Z. Ni, W.-H. Chen, *Bioorg. Med. Chem.* **2011**, *19*, 783–788.

[15] www.acdlabs.com.

[16] a) A. S. Kende, J. S. Mendosa, *Tetrahedron Lett.* **1991**, *32*, 1699–1702; b) M. A. Sturges, D. J. Yarberry, *Tetrahedron Lett.* **1993**, *34*, 4743–4746.

[17] B. Han, Q.-P. Liu, R. Li, X. Tian, *Chem. Eur. J.* **2008**, *14*, 8094–8097.

[18] Y.-L. Liu, T.-D. Shi, F. Zhou, X. Zhao, X. Wanh, J. Zhou, *Org. Lett.* **2011**, *13*, 3826–3829.

[19] F. Huguenot, T. Brigaud, *J. Org. Chem.* **2006**, *71*, 7075–7078.

[20] N. Ishikawa, T. Kitazume, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3260–3263.

[21] W. Steglich, K. Burger, M. Durr, E. Burgis, *Chem. Ber.* **1974**, *107*, 1488–1498.

[22] J. A. Barten, E. Lork, G.-V. Roschenthaler, *J. Fluorine Chem.* **2004**, *125*, 1039–1049.

[23] S. Stauffer, J. Sun, B. S. Katzenellenbogen, J. A. Katzenellenbogen, *Bioorg. Med. Chem.* **2000**, *8*, 1293–1316.

[24] T. Kino, Y. Nagase, Y. Horino, T. Yamakawa, *J. Mol. Catal. A* **2008**, *282*, 34–51.

[25] S. Perrone, F. Rosato, A. Salomone, L. Troisi, *Tetrahedron* **2013**, *69*, 3878–3884.

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