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Trifluoromethylation of non-activated aldimines with trimethyl(trifluoromethyl)silane in the presence of tetramethylammonium fluoride: A closer look into the reaction route

Nataliya V. Kirij [a], Lesya A. Babadzhanova [a], Valeria N. Movchun [a], Yurii L. Yagupolskii [a,*], Wieland Tyrra [b], Dieter Naumann [b], Hendrik T.M. Fischer [b], Harald Scherer [b]

[a] *Institute of Organic Chemistry, National Academy of Sciences of Ukraine, 5 Murmanskaya St., UA-02094 Kiev 94, Ukraine*
[b] *Institut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6, D-50939 Köln, Germany*

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Abstract

The reactions of non-activated aldimines with trimethyl(trifluoromethyl)silane and 1 equiv. of tetramethylammonium fluoride proceed via the formation of tetramethylammonium amides which were identified by low-temperature ^{19}F NMR experiments. Consecutive reactions of the salts formed *in situ* with electrophiles yielded trifluoromethylated amines. Fluoride elimination is observed in the absence of electrophilic substrates leading to the formation of difluoromethylated ketimines.

Keywords: Trifluoromethylation; Amines; Aldimines; Alkylation; Silylation

1. Introduction

The study and development of methods for the introduction of fluorinated moieties into organic molecules to change their properties by design is one of the challenges in synthetic chemistry. Fluorine-containing physiologically active substances and the methodologies making them easily accessible are of great interest. One of the general methods to obtain trifluoromethyl containing amines is based on the addition of the CF_3 group to imine double bonds. However, only the reactions of nucleophilic trifluoromethylation of activated aldimines such as azirines [1], nitrones [2], imines of hexafluoroacetone [3], *N*-(*t*-butylsulfinyl)imines [4] and sulfonylimines [5] using Me_3SiCF_3 are mentioned in the literature. In 1999 Blazejewski et al. showed that Me_3SiCF_3 also reacts with non-activated aldimines but only in the presence of trimethylsilylimidazole as an auxiliary reagent which is suggested to stabilize the intermediates [6]. An alternative approach has been presented in 2005 by Motherwell and Storey [7]. They achieved comparable results in conversion of imines into the corresponding aryl(2,2,2-trifluoro-1-aryl-ethyl)amines using the 1:1 adduct of trifluoroacetophenone and *N*,*N*-dimethylamino(trimethyl)silane as a trifluoromethylating reagent and 2-trimethylsiloxypyridine as an alternative to trimethylsilylimidazol in conjunction with caesium fluoride as initiator. Difluoromethyl containing ketimines are much more inaccessible. The only method to synthesize these compounds is based on the transformation of trifluoromethyl into difluoromethyl groups, i.e. trifluoromethylated pyridines can be converted into the difluoromethyl compounds by the reaction of DBU (1,8-diazabicyclo[4,5,0]undec-7-ene) [8]. Uneyama et al. reported a method to obtain difluoroenamines by C–F bond cleavage of trifluoromethylimines via the reaction of elemental magnesium in the presence of chlorotrimethylsilane; in a second reaction step these difluoroenamines were converted into difluoromethyl imines with tetrabutylammonium fluoride (TBAF) [9].

* Corresponding author. Tel.: +380 44 559 0349; fax: +380 44 573 2643.
E-mail address: Yagupolskii@bpci.kiev.ua (Y.L. Yagupolskii).

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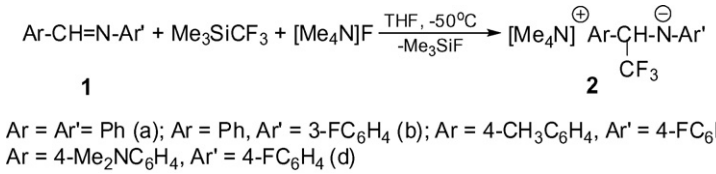


Scheme 1.

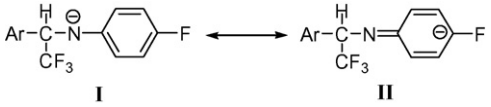
In 2006 Prakash et al. reported a route to obtain trifluoro- and difluoromethyl amines on a preparative scale [10] starting from non-activated aldimines and trimethyl(trifluoromethyl)silane in the presence of fluoride sources. Trifluoromethylated amines are formed in high yields using catalytic amounts (5–15%) of tetrabutylammonium triphenyldifluorosilicate (TBAT). The authors pointed out that the reaction proceeds via the formation of unstable silylated amines. The yields were determined exclusively by NMR spectroscopic experiments. Using 0.5 equiv. of tetramethylammonium fluoride (TMAF) gave product mixtures that contained difluoromethyl ketimines. One of the ketimines was isolated in 34% yield; the others were reduced to difluoromethyl amines.

We mentioned the smooth reaction of Schiff bases with Me_3SiCF_3 in a conference presentation in 2000 [11] and in parallel with Prakash et al. [10], we studied the reactions of non-activated aldimines with Me_3SiCF_3 in the presence of $[Me_4N]F$. We used 1 equiv. of fluoride and investigated the reaction, putting more emphasis on the intermediates involved.

2. Results and discussion

The reagent Me_3SiCF_3 reacts with aldimines **1** in the presence of 1 equiv. of $[Me_4N]F$ in THF at −50 °C to form the salts **2** (Scheme 1).

The salts **2c**,**d** were characterized by low-temperature NMR spectroscopic methods. In the ^{19}F NMR spectrum of **2c** at −30 °C the CF_3 group is detected at −72.0 ppm and the fluorine atom in four-position of the aromatic ring at −143.5 ppm. This signal is shifted by 25.7 ppm to higher field in comparison with the parent aldimine **1c**, indicating the presence of the free amide in solution. Due to the delocalization of the negative charge from the nitrogen atom into the aromatic ring, the following canonical forms (**I**, **II**) should be assumed with the right hand side being favoured (Scheme 2).



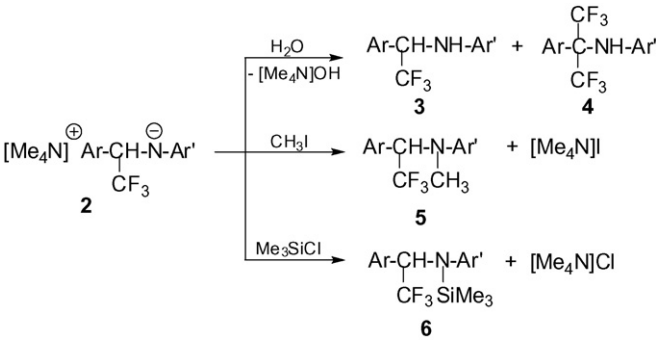
Scheme 2.

The strong nucleophilic salts **2** react with electrophiles under very mild conditions (−45 ± 5 °C). Aqueous work-up of salts **2** converts them into the secondary amines **3** in 70–90% yields.

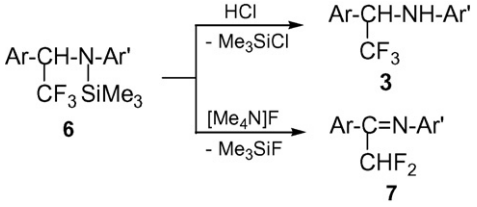
Amines **4** containing two CF_3 groups bonded to the former C=N carbon atom were detected in the ^{19}F NMR spectra as by-products; **4d** was obtained from aldimine **1d** in 25% yield and characterized. Salts **2** react with methyl iodide and chlorotrimethylsilane to form the tertiary amines **5** and the silylated amines **6**, respectively (Scheme 3). Compounds **3**, **5**, **6** were isolated and fully characterized.

On the basis of these investigations, it is concluded that silylated amines **6** are stable under neutral conditions but desilylate easily in the presence of acids to form amines **3** and in the presence of fluoride ions the difluoromethyl ketimines **7** (Scheme 4).

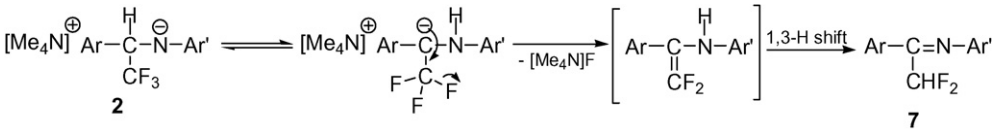
The elimination of a fluoride ion of the CF_3 group of **2** accompanied by hydrogen atom migration occurs on warming the salts **2** to room temperature yielding the ketimines **7** (Scheme 5).



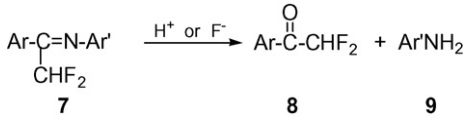
Scheme 3.



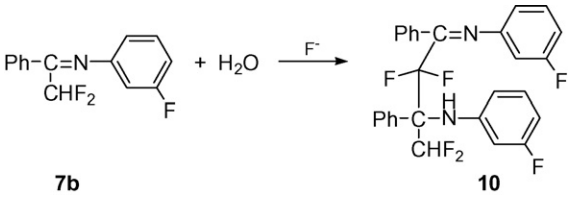
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

This reaction pathway is implied to be intramolecular due to the exclusive formation of CF_2H containing compounds even when the reactions were performed in carefully dried THF-d_8.

Ketimines **7** are formed in 65–75% yields as mixtures of *E*- and *Z*-isomers. The resulting 2D NOESY spectrum shows cross correlations between the two equilibrating structures, for example between the corresponding H-2,6 resonances (phenyl group bond to carbon/phenyl group bond to nitrogen) in the *E*-isomer (δ 7.29/6.79) and the *Z*-isomer (δ 8.15/6.94) of **7a**. The ratios vary significantly depending on the polarity of the solvent used. Imines **7** are stable under neutral conditions but hydrolyze easily under aqueous work-up in the presence of acids or $[Me_4N]F$ giving difluoromethyl ketones **8** and anilines **9** (Scheme 6).

The ketimine **7b** was an exception. Aqueous work-up yielded compound **10** in 42% yield together with the products of hydrolysis (Scheme 7).

Compound **7c** was taken as an example to show that ketimines also react with Me_3SiCF_3 in the presence of 1 equiv. of $[Me_4N]F$ to form amines with trifluoromethyl- and difluoromethyl groups bond to the same carbon atom (Scheme 8).

The reaction conditions and treatment of the reaction mixture were analogous to that of the conversion of aldimines **1** to amines **3**. Amine **11** was isolated in 78% yield and fully characterized.

2.1. The crystal structure of phenyl-(2,2,2-trifluoro-1-phenyl-ethyl)-trimethylsilanylamine (*6a*)

Compound **6a** crystallizes in the triclinic space group $P\bar{1}$ (no. 2) (Table 1). In the unit cell, two independent molecules are found (Table 2; Figs. 1 and 2). The two independent molecules exhibit identical structural motifs and differ only slightly in their interatomic distances and angles. Bond lengths and angles are found in the expected range and are comparable with those determined for related compounds (e.g. 12) although examples for comparison are rare. In the packing the molecules are well separated without significant intermolecular contacts.

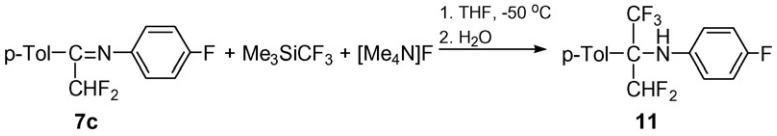
Within both molecules two chiral atoms (N1 and C1 as well as N2 and C2) with (*R*,*R*)-configuration are found. As expected the centre of inversion generates two molecules with

Table 1
Crystal data and structure refinement for **6a**

Formula	$C_{17}H_{20}F_3NSi$
Crystal system	Triclinic
Space group	*P*-1 (number 2)
Unit cell parameters	
a (pm)	862.7(2)
b (pm)	1331.1(4)
c (pm)	1563.8(4)
α (°)	84.02(3)
β (°)	82.00(3)
γ (°)	80.65(3)
V (10^6 pm^3)	1748.4(8)
Z	4
D (g cm^{-3})	1.229
μ (Mo Kα) (mm^{-1})	0.158
Crystal size (mm)	0.30 0.30 0.20
Number of data collected (θ range)	21,308(2.60–28.19)
F (0 0 0)	680
Maximum, minimum transmission	0.9857, 0.9073
R_1, wR_2 [$I > 2\sigma$(I)]	0.0464, 0.0686
Maximum, minimum residual electron density (e·10^{-6} pm)	0.142, −0.146
CCDC [24]	644,041

Table 2
Selected bond lengths (pm) and angles (°) for the two independent molecules of **6a** with estimated standard deviations in parantheses

Molecule 1		Molecule 2	
Si1–N1	175.2(4)	Si2–N2	174.4(4)
N1–C108	143.8(6)	N2–C208	147.4(8)
N1–C1	144.6(8)	N2–C2	145.8(6)
C1–C101	151.6(9)	C2–C201	148.8(7)
C1–C107	150.7(9)	C2–C207	151.7(9)
C107–F11	133.8(9)	C207–F21	132.5(9)
C107–F12	131.7(8)	C207–F22	132.7(9)
C107–F13	133.6(9)	C207–F23	132.0(7)
Si1–N1–C1	120.8(4)	Si2–N2–C2	121.7(3)
Si1–N1–C108	117.4(3)	Si2–N2–C208	118.3(3)
C108–N1–C1	118.4(4)	C208–N2–C2	117.5(4)
N1–C1–C101	117.0(5)	N2–C2–C201	115.7(4)
N1–C1–C107	112.0(5)	N2–C2–C207	112.1(5)
F11–C107–F12	105.4(6)	F21–C207–F22	105.4(6)
F12–C107–F13	107.15)	F22–C207–F23	107.5(5)
F13–C107–F11	105.0(5)	F23–C207–F21	105.8(6)



Scheme 8.

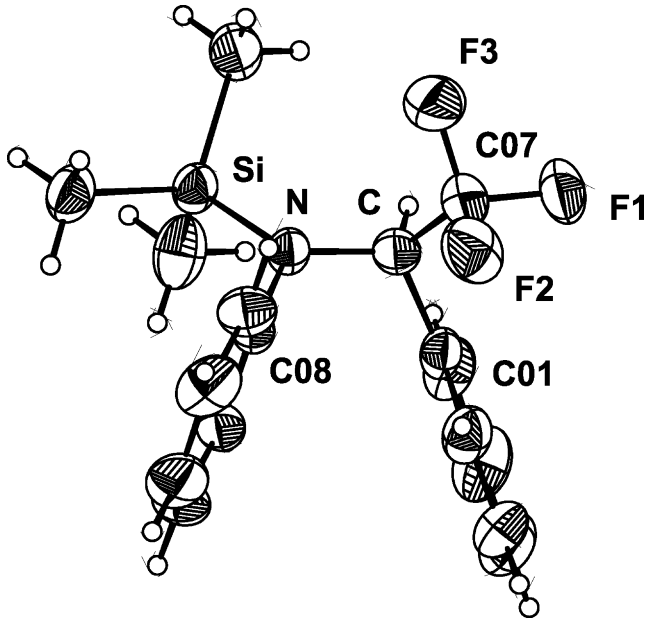


Fig. 1. ORTEP plot of one molecule of **6a** with the labeling scheme (thermal ellipsoids at the 50% probability level, cf. Table 2).

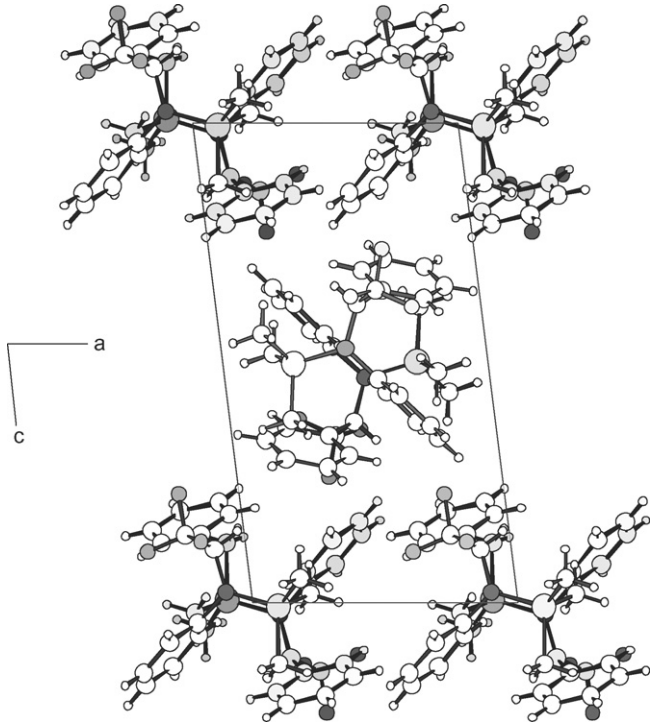


Fig. 2. View of the unit cell of **6a** along the *b*-axis.

(*S*,*S*)-configuration in the unit cell additionally giving two enantiomeric pairs of molecules.

3. Conclusion

The reaction of aldimines with Me_3SiCF_3 and 1 equiv. of $[Me_4N]F$ proceeds via the formation of the salts **2** which were identified by low-temperature ^{19}F NMR spectroscopic experiments. The reactions of the salts **2** formed *in situ* with water, methyl iodide and chlorotrimethylsilane led to secondary and tertiary amines. The conditions of selective conversion of the salts **2** into ketimines containing difluoromethyl group were elaborated.

4. Experimental

4.1. General

All reactions were carried out in a dry argon (or nitrogen) atmosphere using Schlenk techniques. Me_3SiCF_3 was purchased from ABCR, all aldehydes, anilines, Me_3SiCl from Aldrich. $[Me_4N]F$ [13] was synthesized according to a literature procedure. All solvents were purified according to literature procedures [14].

NMR spectra were recorded with the Bruker spectrometers AC 200 (^1H at 200 MHz, ^{19}F at 188.14 MHz, ^{13}C at 50.32 MHz), Avance II 300 (^{19}F at 282.4 MHz, ^{13}C at 75.5 MHz, ^{29}Si at 59.6 MHz), Avance 400 (^1H at 400 MHz, ^{13}C at 100.6 MHz), Avance DRX 500 (^1H at 500 MHz, ^{13}C at 125.77 MHz) and the Varian spectrometer VXR-300 (^1H at 300 MHz). Chemical shifts are given in ppm relative to Me_4Si (^1H, ^{13}C, ^{29}Si) and CCl_3F (^{19}F) as external standards. *J*-values are given in Hz. Assignments were made on the basis of different 2D NMR experiments. EI mass spectra were run on a Finnigan MAT 95 spectrometer (20 eV). Melting points were measured in one-end open glass capillaries and are uncorrected. CHNF-analyses were performed with the apparatus HEKAtech Euro EA 3000 and Analytikjena Spekol 1100.

Crystal structure determination. The compound forms single crystals which were sealed in glass capillaries and the suitability was checked with the help of an IP-diffractometer (STOE IPDS I). The same device was used to collect the reflection data of the respective best specimen using graphite-monochromated Mo K_α radiation (71.073 pm). The data were corrected for Lorentz and polarization effects. The programs used in this work are Stoe's X-area [15], including X-RED [16] and X-shape [17] for data reduction and numerical absorption correction, and SIR-97 [18] and SHELXL-97 [19] for structure solution and refinement. All hydrogen atoms were placed in idealized positions and constrained to ride on their parent atom. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all of the hydrogen atoms. Intensity data for details of crystal data and structure refinement parameters are summarised in Table 1; cf. [24].

4.2. Preparative procedures

4.2.1. Benzylidene-phenyl-amines (*1a–d*)

Benzylidene-phenyl-amines (**1a–d**) were synthesised according to literature procedures [20].

*4.2.1.1. Benzylidenephenylamine (**1a**).* Yield: 83%; colourless solid; mp 51–52 °C (lit. [20] mp 52 °C).

*4.2.1.2. Benzylidene(3-fluorophenyl)amine (**1b**).* Yield: 87%; yellow liquid; bp 106–108 °C/0.04 Torr. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.0–7.15 (3H, m, ArH), 7.4–7.6 (4H, m, ArH), 8.09 (2H, m, ArH), 8.62 (1H, s); ^{19}F NMR (188.14 MHz, acetone-d_6): δ −113.1 (s); ^{13}C NMR spectral data (lit. [21]). Anal. Calcd for $C_{13}H_{10}FN$: C, 78.4; H, 5.1; F, 9.5; N, 7.0. Found: C, 78.6; H, 5.3; F, 9.4; N, 6.8.

*4.2.1.3. (4-Fluorophenyl)(4-methylbenzylidene)amine (**1c**).* Yield: 89%; yellow solid; mp 67–69 °C (lit. [22] mp 68 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.41 (3H, s, CH_3), 7.00–7.35 (6H, m, ArH), 7.79 (2H, d, J = 8 Hz, ArH), 8.39 (1H, s); ^{19}F NMR spectral data (lit. [22]); ^{13}C {^{1}H} NMR (50.32 MHz, $CDCl_3$): δ 21.6 (CH_3), 115.8 (2C, d, $^2J_{CF}$ = 22 Hz), 122.3 (2C, d, $^3J_{CF}$ = 7.8 Hz), 128.7 (2C), 129.5 (2C), 133.5, 141.9, 148.1 (d, $^4J_{CF}$ = 2 Hz), 160.0 (C = N), 161.0 (d, $^1J_{CF}$ = 244 Hz). Anal. Calcd for $C_{14}H_{12}FN$: C, 78.8; H, 5.7; F, 8.9; N, 6.6. Found: C, 78.6; H, 5.4; F, 9.0; N, 6.7.

*4.2.1.4. (4-Dimethylaminophenyl)(4-fluorobenzylidene)amine (**1d**).* Yield: 79%; yellow solid; mp 136–137 °C (lit. [22] mp 137 °C). ^{19}F NMR spectral data (lit. [22]); ^{1}H, ^{13}C NMR spectral data (lit. [23]).

*4.2.2. Synthesis of the salts (**2a–d**)*

To a solution of the corresponding imine (**1a–d**) (5.1 mmol) and trimethyl(trifluoromethyl)silane (Me_3SiCF_3) (1.1 g, 7.6 mmol) in THF (25 mL) at −60 °C tetramethylammonium fluoride ([Me_4N]F) (0.64 g, 6.9 mmol) was added in small portions over a period of 90 min. The mixture was stirred for 2 h at −50 ± 5 °C.

*4.2.2.1. Tetramethylammonium (4-fluorophenyl)(2,2,2-trifluoro-1-p-tolyl-ethyl)amide (**2c**).* ^{19}F NMR (188.14 MHz, THF, −30 °C): δ −72.0 (3F, d, $^3J_{FH}$ = 7.4 Hz, CF_3), −143.5 (1F, br s).

*4.2.2.2. Tetramethylammonium (4-fluorophenyl)-[2,2,2-trifluoro-1-(4-dimethylaminophenyl)-ethyl]amide (**2d**).* ^{19}F NMR (188.14 MHz, THF, −30 °C): δ −72.0 (3F, d, $^3J_{FH}$ = 7.4 Hz, CF_3), −145.2 (1F, br s).

*4.2.3. Hydrolysis of salts (**2a–d**)*

To a solution of corresponding salt (**2a–d**) at −45 ± 5 °C H_2O (5 mL) was added and the amines obtained were extracted with Et_2O (2× 10 mL). The extracts were washed with H_2O (5 mL), dried ($MgSO_4$) and purified by vacuum distillation.

*4.2.3.1. Phenyl-(2,2,2-trifluoro-1-phenyl-ethyl)amine (**3a**).* Yield: 89%; yellow liquid; bp 65–67 °C/0.04 Torr (lit. [6] bp 272 °C, ^{1}H, ^{19}F, ^{13}C, mass spectral data agreed with literature data).

*4.2.3.2. (3-Fluorophenyl)-(2,2,2-trifluoro-1-phenyl-ethyl)amine (**3b**).* Yield: 83%; yellow liquid; bp 81–82 °C/0.03 Torr. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 4.57 (1H, br d, J = 7.2 Hz, NH), 4.93 (1H, qd, J = 7.4, 7.2 Hz, CH), 6.34 (1H, dt, J = 11.5, 2.2 Hz , ArH), 6.45 (2H, m, ArH), 7.09 (1H, dm, J = 6.5 Hz, ArH), 7.42 (5H, m, ArH); ^{19}F NMR (188.14 MHz, CD_2Cl_2): δ −73.9 (3F, d, $^3J_{FH}$ = 7.4 Hz, CF_3), −113.5 (1F, br s); ^{13}C {^{1}H} NMR (125.77 MHz, CD_2Cl_2): δ 60.2 (1C, q, $^2J_{CF}$ = 30.4 Hz, **C**CF_3), 100.7 (1C, d, $^2J_{CF}$ = 25.5 Hz), 105.5 (1C, d, $^2J_{CF}$ = 23 Hz), 109.7 (1C, d, $^4J_{CF}$ = 2.4 Hz), 125.0 (1C, q, $^1J_{CF}$ = 285.4 Hz, CF_3), 127.9, 129.0 (2C), 129.4 (2C), 130.5 (1C, d, $^3J_{CF}$ = 10 Hz), 133.5, 147.3 (1C, d, $^3J_{CF}$ = 10.5 Hz), 163.8 (1C, d, $^1J_{CF}$ = 236.3 Hz); EIMS: m/z (%) = 269 [M]$^+$ (80), 200 [M-CF_3]$^+$ (100). Anal. Calcd for $C_{14}H_{11}F_4N$: C, 62.4; H, 4.1; F, 28.2; N, 5.2. Found: C, 61.8; H, 4.4; F, 28.6; N, 4.9.

*4.2.3.3. (4-Fluorophenyl)-(2,2,2-trifluoro-1-p-tolyl-ethyl)amine (**3c**).* Yield: 72%; yellow liquid; bp 155–156 °C/0.03 Torr. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 2.38 (3H, s, CH_3), 4.38 (1H, br d, J = 6.4 Hz, NH), 4.90 (1H, qd, J = 7.4, 6.4 Hz, CH), 6.65 (2H, m, ArH), 6.92 (2H, t, J = 8.8 Hz, ArH), 7.46 (4H, dd J = 24.6, 8 Hz, ArH); ^{19}F NMR (188.14 MHz, CD_2Cl_2): δ −74.8 (3F, d, $^3J_{FH}$ = 7.4 Hz, CF_3), −126.8 (1F, m); ^{13}C {^{1}H} NMR (50.32 MHz, CD_2Cl_2): δ 21.5 (CH_3), 61.1 (1C, q, $^2J_{CF}$ = 29.8 Hz, **C**CF_3), 115.5 (2C, d, $^3J_{CF}$ = 7.5 Hz), 116.1 (2C, d, $^2J_{CF}$ = 22.6 Hz), 125.7 (1C, q, $^1J_{CF}$ = 281.9 Hz, CF_3), 128.2 (2C), 130.0 (2C), 131.2 (1C, d, $^4J_{CF}$ = 2 Hz), 139.8, 142.4, 157.0 (1C, d, $^1J_{CF}$ = 236.7 Hz); EIMS: m/z (%) = 283 [M]$^+$ (75), 214 [M-CF_3]$^+$ (100), 173 [M-NHC_6H_4F]$^+$ (16). Anal. Calcd for $C_{15}H_{13}F_4N$: C, 63.6; H, 4.6; F, 26.8; N, 4.9. Found: C, 64.1; H, 4.4; F, 27.1; N, 4.7.

*4.2.3.4. (4-Fluorophenyl)-[2,2,2-trifluoro-1-(4-dimethylaminophenyl)-ethyl]-amine (**3d**).* Yield: 65%; yellow liquid; bp 148 °C/0.02 Torr. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 2.96 (6H, s, CH_3), 4.30 (1H, br d, J = 7.2 Hz, NH), 4.78 (1H, qd, J = 7.4, 7.2, Hz, CH), 6.67 (4H, m, ArH), 6.89 (2H, t, J = 8.8 Hz, ArH), 7.29 (2H, d, J = 8.4 Hz, ArH); ^{19}F NMR (188.14 MHz, CD_2Cl_2): δ −74.9 (3F, d, $^3J_{FH}$ = 7.4 Hz, CF_3), −126.9 (1F, m); ^{13}C {^{1}H} NMR (50.32 MHz, CD_2Cl_2): δ 40.4 (CH_3), 60.9 (1C, q, $^2J_{CF}$ = 29.6 Hz, **C**CF_3), 112.6 (2C), 115.5 (2C, d, $^3J_{CF}$ = 7.5 Hz), 116.1 (2C, d, $^2J_{CF}$ = 22.7 Hz), 121.0, 126.0 (1C, q, $^1J_{CF}$ = 281.7 Hz, CF_3), 128.9 (2C), 142.7 (1C, d, $^4J_{CF}$ = 2.1 Hz), 151.5, 157.0 (1C, d, $^1J_{CF}$ = 236.3 Hz); EIMS: m/z (%) = 312 [M]$^+$ (32), 297 [M-CH_3]$^+$ (15), 243 [M-CF_3]$^+$ (10), 217 [M-C_6H_4F]$^+$ (15), 202 [M-NHC_6H_4F]$^+$ (100). Anal. Calcd for $C_{16}H_{16}F_4N_2$: C, 61.5; H, 5.2; F, 24.3; N, 9.0. Found: C, 61.1; H, 5.4; F, 23.9; N, 8.7.

*4.2.3.5. (4-Fluorophenyl)-[1,1,1,3,3,3-hexafluoro-2-(4-dimethylaminophenyl)propyl]amine (**4d**).* Purified by silica gel column chromatography, Rf 0.8 (hexane: benzene = 4:1). Yield: 25%; yellow oil. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 3.0 (6H, s, CH_3), 4.47 (1H, br s, NH), 6.64 (2H, m, ArH), 6.84 (4H, m, ArH), 7.39 (2H, s, ArH), 7.54 (2H, d, J = 8.6, Hz, ArH); ^{19}F NMR (188.14 MHz, CD_2Cl_2): δ −70.6 (6F, s, CF_3), −125.2 (1F, m); ^{13}C {^{1}H} NMR (50.32 MHz, CD_2Cl_2): δ 40.2 (CH_3), 70.4 (1C, sept, $^2J_{CF}$ = 26.8 Hz, **C**$(CF_3)_2$), 112.0 (2C), 115.4 (2C, d, $^2J_{CF}$ = 22.5 Hz), 119.3 (2C, d, $^3J_{CF}$ = 7.5 Hz), 124.4 (2C, q, $^1J_{CF}$ = 289 Hz, CF_3), 128.7 (2C), 130.3, 139.2 (1C, d, $^4J_{CF}$ = 2.7 Hz), 151.7, 157.7 (1C, d, $^1J_{CF}$ = 238.4 Hz); EIMS:

m/z (%) = 380 $[M]^+$ (25), 311 $[M\text{-}CF_3]^+$ (7), 270 $[M\text{-}NHC_6H_4F]^+$ (100). Anal. Calcd for $C_{17}H_{15}F_7N_2$: C, 53.7; H, 4.0; F, 34.9. Found: C, 54.1; H, 4.2; F, 34.8.

*4.2.4. Alkylation of the salts (**2a**,**c**)*

To a solution of the corresponding salt (**2a**,**c**) (5.1 mmol) at −45 ± 5 °C, CH_3I (1.1 g, 5.7 mmol) was added and the reaction mixture was allowed to warm to room temperature. The solvent and all volatile compounds were evaporated. The products were extracted with pentane and purified by vacuum distillation.

*4.2.4.1. Methyl-phenyl-(2,2,2-trifluoro-1-phenylethyl)amine (**5a**).* Yield: 91%; yellow liquid; bp 89–90 °C/0.03 Torr. ^{1}H NMR (300 MHz, acetone-d_6): δ 2.75 (3H, s, CH_3), 5.86 (1H, q, *J* = 8.7 Hz, CH), 6.85 (1H, t, *J* = 7.2 Hz, ArH), 7.08 (2H, d, *J* = 7.2 Hz, ArH), 7.29 (2H, m, ArH), 7.45 (5H, m, ArH); ^{19}F NMR (188.14 MHz, acetone-d_6): δ −67.2 (d, $^3J_{FH}$ = 8.7 Hz). ^{13}C {^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 33.6 (CH_3), 64.8 (q, $^2J_{CF}$ = 29 Hz, **C**CF_3), 126.2 (q, $^1J_{CF}$ = 287 Hz, CF_3), (Ph bond to N) 150.2 (C-1), 114.2 (C-2,6), 129.6 (C-3,5), 119.1 (C-4), (Ph bond to C) 132.8 (C-1), 128.1 (C-2,6), 128.9 (C-3,5), 128.5 (C-4); EIMS: *m/z* (%) = 265 $[M]^+$ (78), 196 $[M\text{-}CF_3]^+$ (100), 181 $[M\text{-}CF_3\text{-}CH_3]^+$ (12). Anal. Calcd for $C_{15}H_{14}F_3N$: C, 67.9; H, 5.3; F, 21.5; N, 5.3. Found: C, 68.2; H, 5.6; F, 21.9; N, 5.6.

*4.2.4.2. Methyl-(4-fluorophenyl)-2,2,2-trifluoro-1-p-tolylethyl)amine (**5c**).* Yield: 79%; yellow liquid; bp 150–152 °C/0.02 Torr. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 2.42 (3H, s, CH_3), 2.74 (3H, s, CH_3), 5.42 (1H, q, *J* = 8.6, Hz, CH), 6.97 (4H, m, ArH), 7.28 (4H, m, ArH); ^{19}F NMR (188.14 MHz, CD_2Cl_2): δ −70.2 (3F, d, $^3J_{FH}$ = 8.6 Hz, CF_3), −128.6 (1F, s); ^{13}C {^{1}H} NMR (50.32 MHz, CD_2Cl_2): δ 21.2 (CH_3), 34.3 (CH_3), 66.2 (1C, q, $^2J_{CF}$ = 28.8 Hz, **C**CF_3), 116.1 (2C, d, $^2J_{CF}$ = 22.2 Hz), 116.5 (2C, d, $^3J_{CF}$ = 7.6 Hz), 126.8 (1C, q, $^1J_{CF}$ = 286 Hz, CF_3), 128.4 (2C), 129.7, 129.9 (2C), 139.1, 147.4 (d, $^4J_{CF}$ = 2.1 Hz), 157.1 (d, $^1J_{CF}$ = 237.3 Hz); EIMS: *m/z* (%) = 297 $[M]^+$ (67), 283 $[M\text{-}CH_3]^+$ (7), 228 $[M\text{-}CF_3]^+$ (100), 212 $[M\text{-}CF_3\text{-}CH_3]^+$ (10), 173 $[M\text{-}N(CH_3)C_6H_4F]^+$ (14). Anal. Calcd for $C_{16}H_{15}F_4N$: C, 64.6; H, 5.1; F, 25.6; N, 4.7. Found: C, 64.2; H, 5.4; F, 25.2; N, 4.5.

*4.2.5. Silylation of salts (**2a**,**c**)*

To a solution of the corresponding salt (**2a**,**c**) (5.1 mmol) at −45 ± 5 °C, Me_3SiCl (0.62 g, 5.7 mmol) was added and the reaction mixture was allowed to warm to room temperature. The precipitate formed was filtered off, the solvent and all volatile compounds were evaporated. The products were extracted with pentane and purified by vacuum distillation or crystallization from pentane.

*4.2.5.1. Phenyl-(2,2,2-trifluoro-1-phenyl-ethyl)-trimethylsilanylamine (**6a**).* Yield: 76%; yellow solid; bp 75 °C/0.03 Torr, mp 37–38 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.21 (9H, s, $Si(CH_3)_3$), 4.95 (1H, q, *J* = 9 Hz, CH), 6.75 (2H, m, ArH), 7.17 (5H, m, ArH), 7.31 (3H, m, ArH); ^{19}F NMR (188.14 MHz, $CDCl_3$): δ −67.9 (d, $^3J_{FH}$ = 9 Hz). ^{13}C {^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 0.6 ($Si(CH_3)_3$), 64.0 (q, $^2J_{CF}$ = 29 Hz, **C**CF_3), 125.6 (q, $^1J_{CF}$ = 285 Hz, CF_3), (Ph bond to N) 143.1 (C-1), 127.9 (C-2,6), 129.7 (C-3,5), 124.9 (C-4), (Ph bond to C) 134.8 (C-1), 128.1 (q, $^4J_{CF}$ = 2Hz, C-2,6), 133.2 (C-3,5), 128.2 (C-4); ^{29}Si {^{1}H} NMR (59.6 MHz, $CDCl_3$): δ 9.6 ($Si(CH_3)_3$). EIMS: *m/z* (%) = 323 $[M]^+$ (92), 254 $[M\text{-}CF_3]^+$ (100). Anal. Calcd for $C_{17}H_{20}F_3NSi$: C, 63.1; H, 6.2; F, 17.6; N, 4.3. Found: C, 63.5; H, 6.4; F, 17.9; N, 4.1.

*4.2.5.2. (4-Fluorophenyl)-(2,2,2-trifluoro-1-p-tolylethyl)-trimethylsilylamine (**6c**).* Yield: 84%; yellow solid; bp 95 °C/0.03 Torr, mp 58–59 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.15 (9H, s, $Si(CH_3)_3$), 2.36 (3H, s, CH_3), 4.81 (1H, q, *J* = 8.8, Hz, CH), 6.63 (2H, m, H-2,6 (4-FC_6H_4)), 6.82 (2H, m, H-2,6 (4-FC_6H_4)), 6.94 (2H, m, H-2,6 (4-$CH_3C_6H_4$)), 7.08 (2H, m, H-3,5 (4-$CH_3C_6H_4$)); ^{19}F NMR (282.3 MHz, $CDCl_3$): δ −68.2 (d, $^3J_{FH}$ = 9 Hz, CF_3), −117.0 (1F, m); ^{13}C {^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 0.4 ($Si(CH_3)_3$), 21.1 (CH_3), 63.4 (q, $^2J_{CF}$ = 29 Hz, **C**CF_3), 126.2 (q, $^1J_{CF}$ = 286 Hz, CF_3), (4-FC_6H_4) 138.6 (1C, d, $^4J_{CF}$ = 3 Hz, C-1), 134.7 (2C, d, $^3J_{CF}$ = 9 Hz, C-2,6), 114.6 (2C, d, $^2J_{CF}$ = 22 Hz, C-3,5), 160.8 (2C, d, $^1J_{CF}$ = 245 Hz, C-4), (4-$CH_3C_6H_4$) 131.4 (C-1), 129.5 (2C, q, $^4J_{CF}$ = 2 Hz, C-2,6), 128.8 (C-3,5), 138.1 (C-4); ^{29}Si{^{1}H} NMR (59.6 MHz, $CDCl_3$): δ 9.8 ($Si(CH_3)_3$). EIMS: *m/z* (%) = 355 $[M]^+$ (48), 286 $[M\text{-}CF_3]^+$ (100). Anal. Calcd for $C_{18}H_{21}F_4NSi$: C, 60.8; H, 5.9; F, 21.4; N, 3.9. Found: C, 60.5; H, 6.1; F, 20.9; N, 3.7.

*4.2.6. Formation of difluoromethylated imines (**7a–c**)*

A solution of the salts (**2a–c**) was allowed to warm to room temperature. The solvent and volatile compounds were evaporated. The products were extracted with pentane. The products (**7a**,**b**) were purified by vacuum distillation, product (**7c**) by crystallization from EtOH.

*4.2.6.1. (2,2-Difluoro-1-phenyl-ethylidene)-phenyl-amine (E/Z-mixture) (**7a**).* Yield: 79%; yellow liquid; bp 72–73 °C/0.03 Torr. (2,2-Difluoro-1-phenyl-eth-(*E*)-ylidene)-phenyl-amine: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.42 (1H, t, $^2J_{HF}$ = 55.3 Hz, CHF_2), (Ph bond to N) 6.79 (2H, m, H-2,6), 7.06 (1H, m, H-4), 7.22 (2H, m, H-3,5), (Ph bond to C) 7.29 (4H, m, H-2,6; H-3,5), 7.30 (1H, m, H-4); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −117.0 (2F, d, $^2J_{FH}$ = 55.3 Hz), ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 115.5 (1C, t, $^1J_{CF}$ = 245 Hz, CHF_2), 162.1 (1C, t, $^2J_{CF}$ = 28 Hz, **C**CHF_2), (Ph bond to N) 148.1 (1C, C-1), 120.5 (2C, C-2,6), 124.9 (1C, C-4), 128.9 (2C, C-3,5); (Ph bond to C) 130.4 (1C, C-1), 128.5 (2C, t, $^4J_{CF}$ = 2 Hz, C-2,6), 129.9 (1C, C-4), 128.7 (2C, C-3,5). (2,2-Difluoro-1-phenyl-eth-(*Z*)-ylidene)-phenyl-amine: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.44 (1H, t, $^2J_{HF}$ = 52.4 Hz, CHF_2), (Ph bond to N) 6.94 (2H, m, H-2,6), 7.21 (1H, m, H-4), 7.42 (2H, m, H-3,5), (Ph bond to C) 7.51 (2H, m, H-3,5), 7.54 (1H, m, H-4), 8.15 (2H, m, H-2,6); ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −115.6 (2F, d, $^2J_{FH}$ = 52.3 Hz), ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 107.9 (1C, t, $^1J_{CF}$ = 247 Hz, CHF_2), 158.7 (1C, t, $^2J_{CF}$ = 23 Hz, **C**CHF_2), (Ph bond to N) 147.9 (1C, C-1), 119.2 (2C, C-2,6), 124.9 (1C, C-4), 129.4 (2C, C-3,5); (Ph bond to C) 133.1 (1C, C-1), 128.8 (2C, t, $^4J_{CF}$ = 2 Hz, C-2,6),

131.3 (1C, C-4), 128.6 (2C, C-3,5); EIMS: *m/z* (%) = 231 $[M]^+$ (38), 180 $[M\text{-}CF_2H]^+$ (100). Anal. Calcd for $C_{14}H_{11}F_2N$: C, 72.7; H, 4.8; F, 16.4; N, 6.1. Found: C, 72.9; H, 4.6; F, 16.1; N, 5.7.

*4.2.6.2. (2,2-Difluoro-1-phenyl-ethylidene)-(3-fluoro-phenyl)-amine (E/Z-mixture) (**7b**).* Yield: 47%; yellow liquid; bp 73–74 °C/0.03 Torr. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 6.35 (t, $^2J_{FH}$ = 52.8 Hz, CHF_2), 6.36 (t, $^2J_{FH}$ = 56.2 Hz, CHF_2), 6.47 (m, ArH), 6.64 (m, ArH), 6.71 (m, ArH), 6.87 (m, ArH), 7.11 (m, ArH), 7.23 (m, ArH), 7.28 (m, ArH), 7.34 (m, ArH), 7.46 (m, ArH), 7.52 (m, ArH), 8.02 (d, *J* = 7.5 Hz, ArH); ^{19}F NMR (188.14 MHz, $CDCl_3$): δ −111.5 (1F, br s), −112.3 (1F, br s), −115.7 (2F, d, $^2J_{FH}$ = 52.8 Hz, CHF_2), −117.4 (2F, d, $^2J_{FH}$ = 56.2 Hz, CHF_2); ^{13}C {^{1}H} NMR (125.77 MHz, CD_2Cl_2): δ 106.6 (d, $^2J_{CF}$ = 23.5 Hz), 107.6 (d, $^2J_{CF}$ = 25.5 Hz), 108.2 (t, $^1J_{CF}$ = 247.2 Hz, CHF_2), 111.4 (d, $^2J_{CF}$ = 20.2 Hz), 111.5 (d, $^2J_{CF}$ = 21.9 Hz), 114.8 (br s), 115.1 (t, $^1J_{CF}$ = 245.5 Hz, CHF_2), 116.0 (d, $^4J_{CF}$ = 2.8 Hz), 128.4, 128.5, 128.7, 130.1, 130.2 (d, $^3J_{CF}$ = 9.4 Hz), 130.7 (d, $^3J_{CF}$ = 9.4 Hz), 131.6, 132.9, 133.7, 146.9 (d, $^3J_{CF}$ = 9.2 Hz), 149.9 (d, $^3J_{CF}$ = 9.2 Hz), 162.9 (d, $^1J_{CF}$ = 246 Hz), 163.1 (t, $^2J_{CF}$ = 27.8 Hz, **C**CHF_2), 163.3 (1C, d, $^1J_{CF}$ = 248 Hz); EIMS: *m/z* (%) = 249 $[M]^+$ (34), 198 $[M\text{-}CF_2H]^+$ (100). Anal. Calcd for $C_{14}H_{10}F_3N$: C, 67.5; H, 4.04; F, 22.9; N, 5.6. Found: C, 67.3; H, 4.2; F, 23.4; N, 5.9.

*4.2.6.3. (2,2-Difluoro-1-p-tolyl-ethylidene)-(4-fluoro-phenyl)-amine (E/Z-mixture) (**7c**).* Yield: 66%; yellow solid; mp 58–59 °C. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 2.36 (s, CH_3), 2.48 (s, CH_3), 6.44 (t, $^2J_{FH}$ = 55.4 Hz, CHF_2), 6.48 (t, $^2J_{FH}$ = 53 Hz, CHF_2), 6.70–7.45 (m, ArH), 8.06 (d, *J* = 8 Hz, ArH); ^{19}F NMR (188.14 MHz, CD_2Cl_2): δ −116.0 (2F, d, $^2J_{FH}$ = 53 Hz, CHF_2), −117.8 (2F, d, $^2J_{FH}$ = 55.4 Hz, CHF_2), −119.1 (1F, m), −119.6 (1F, m); ^{13}C {^{1}H} NMR (50.32 MHz, CD_2Cl_2): δ 21.5 (CH_3), 26.6 (CH_3), 108.6 (t, $^1J_{CF}$ = 247.6 Hz, CF_2H), 116.0 (d, $^2J_{CF}$ = 22.5 Hz), 116.1 (t, $^1J_{CF}$ = 244.7 Hz, CF_2H), 116.4 (d, $^2J_{CF}$ = 22.2 Hz), 121.3 (d, $^3J_{CF}$ = 7.5 Hz), 122.8 (d, $^3J_{CF}$ = 7.9 Hz), 127.9, 129.2, 129.6, 130.8, 140.9, 141.5, 142.6, 144.6 (d, $^4J_{CF}$ = 2.8 Hz), 144.9 (m, $^4J_{CF}$ = 2.1 Hz), 154.9 (t, $^2J_{CF}$ = 22 Hz, **C**CHF_2), 160.6 (d, $^1J_{CF}$ = 243.4 Hz), 163.2 (d, $^1J_{CF}$ = 251.1 Hz); EIMS: *m/z* (%) = 263 $[M]^+$ (32), 212 $[M\text{-}CF_2H]^+$ (100). Anal. Calcd for $C_{15}H_{12}F_3N$: C, 68.4; H, 4.6; F, 21.6; N, 5.3. Found: C, 68.1; H, 4.7; F, 21.8; N, 4.9.

*4.2.7. Hydrolysis of difluoromethylated imines (**7a–c**)*

To a reaction mixture containing the corresponding imine (c.f. 4.2.6.), H_2O (2 mL) was added and the reaction mixture was stirred for 24 h. The formation of the difluoromethyl ketone **8** was confirmed by ^{19}F NMR experiments (relative to C_6H_5F): **8a** yield: 85%; **8c** yield: 83%. The imine **7b** formed the ''dimer'' **10**.

*4.2.7.1. (2,2,4,4-Tetrafluoro-3-(3-fluoro-anilino)-1,3-diphenyl-butylidene)-(3-fluoro-phenyl)-amine (**10**).* Yield: 42%; pink solid; mp 139–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.55 (1H, m, NH), 6.87 (1H, t, $^1J_{HF}$ = 54 Hz, CHF_2), (3-FC_6H_4 bond to N =) 6.45 (1H, dm, $^3J_{HF}$ = 8.8 Hz, H-2), 6.50 (1H, dm, $^5J_{HF}$ = 3 Hz, H-6), 6.77 (1H, dm, $^3J_{HF}$ = 9.4 Hz, H-4), 7.18 (1H, dm, $^4J_{HF}$ = 6.2 Hz, H-5) (Ph bond to C = N) 7.00 (2H, m, H-2,6), 7.33 (1H, m, H-4), 7.25 (2H, m, H-3,5), (3-FC_6H_4 bond to NH) 6.1 (1H, dm, $^3J_{HF}$ = 8.3 Hz, H-2), 6.27 (1H, dm, $^5J_{HF}$ = 3 Hz, H-6), 6.43 (1H, dm, $^3J_{HF}$ = 11.5 Hz, H-4), 7.0 (1H, dm, $^4J_{HF}$ = 6.9 Hz, H-5) (Ph bond to C-NH) 7.49 (3H, m, H-3,4,5), 7.73 (2H, m, H-2,6); ^{19}F NMR (282.4 MHz, $CDCl_3$): (CF_2-group) δ −97.6 (1F, d, $^2J_{Fa\text{-}Fb}$ = 269 Hz, $\mathbf{F_A}$), −100.5 (1F, ddd, $^2J_{Fb\text{-}Fa}$ = 269 Hz, $J_{Fb\text{-}H}$ = 19.1 Hz, $^4J_{Fb\text{-}CHF_2}$ = 6.7 Hz, $\mathbf{F_B}$), (3-FC_6H_4 bond to N =) −111.9 (1F, ddd, $^3J_{FH}$ = 9.4 Hz, $^3J_{FH}$ = 8.8 Hz, $^4J_{FH}$ = 6.2 Hz, 3-**F**C_6H_4), (3-FC_6H_4 bond to NH) −112.5 (1F, ddd, $^3J_{FH}$ = 11.5 Hz, $^3J_{FH}$ = 8.3 Hz, $^4J_{FH}$ = 6.9 Hz, 3-**F**C_6'H_4), (CHF_2-group) −119.5 (1F, ddt, $^2J_{Fa\text{-}Fb}$ = 288 Hz, $^2J_{Fa\text{-}H}$ = 54 Hz, $^4J_{Fa\text{-}CF2}$ = 5.6 Hz, $\mathbf{F_A}$), −124.1 (1F, dddd, $^2J_{Fb\text{-}Fa}$ = 288 Hz, $^2J_{Fb\text{-}H}$ = 54 Hz, $J_{Fb\text{-}H}$ = 19.1 Hz, $^4J_{Fb\text{-}CF_2}$ = 7.9 Hz, $\mathbf{F_B}$); ^{13}C {^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 70.4 (1C, m, **C**$(CF_2)CHF_2$), 114.7 (1C, t, $^1J_{CF}$ = 259 Hz, CF_2), 115.8 (1C, t, $^1J_{CF}$ = 251 Hz, CF_2H), 166.7 (C = N), (3-FC_6H_4 bond to N =) 148.8 (1C, d, $^3J_{CF}$ = 9.9 Hz, C-1), 107.9 (1C, d, $^2J_{CF}$ = 23.8 Hz, C-2), 116.2 (1C, d, $^4J_{CF}$ = 2 Hz, C-6), 112.0 (1C, d, $^2J_{CF}$ = 21.5 Hz, C-4), 162.8 (1C, d, $^1J_{CF}$ = 247 Hz, C-3), 130.2 (1C, d, $^3J_{CF}$ = 9.5 Hz, C-5), (Ph bond to C = N) 131.1 (1C, C-1), 128.6 (2C, C-2,6), 128.2 (2C, C3,5), 130.0 (1C, C-4), (3-FC_6H_4 bond to NH) 145.4 (1C, d, $^3J_{CF}$ = 11.5 Hz, C-1), 103.4 (1C, d, $^2J_{CF}$ = 26.6 Hz, C-2),112.2 (1C, d, $^4J_{CF}$ = 2 Hz, C-6), 105.4 (1C, d, $^2J_{CF}$ = 20.8 Hz, C-4), 163.2 (1C, d, $^1J_{CF}$ = 243 Hz, C-3), 129.8 (1C, d, $^3J_{CF}$ = 10.1 Hz, C-5), (Ph bond to C-NH) 131.0 (1C, C-1), 129.7 (2C, C-2,6), 129.4 (1C, C-4), 128.6 (2C, C-3,5); EIMS: *m/z* (%) = 498 $[M]^+$ (52), 388 $[M\text{-}NHC_6H_4F]^+$ (100), 250 $[C_6H_5C(CHF_2)NHC_6H_4F]^+$ (56), 198 $[C_6H_5C{=}NC_6H_4F]^+$ (37). Anal. Calcd for $C_{28}H_{20}F_6N_2$: C, 67.5; H, 4.0; F, 22.9. Found: C, 67.9; H, 4.2; F, 22.8.

*4.2.7.2. (1-Difluoromethyl-2,2,2-trifluoro-1-p-tolylethyl)-(4-fluorophenyl)amine (**11**).* To a solution of ketimine **(7c)** (0.62 g, 2.4 mmol) and Me_3SiCF_3 (0.44 g, 3.1 mmol) in THF (20 mL) at −55 ± 5 °C $[Me_4N]F$ (0.28 g, 3.1 mmol) was added in portions over 60 min. The mixture was stirred for 2 h at −50 ± 5 °C. H_2O (5 mL) was added and the product was extracted with Et_2O (2× 10 mL). The extract was washed with H_2O (5 mL), dried ($MgSO_4$) and purified by silica gel column chromotography (hexane). Yield: 78 % (0.5 g); yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.44 (3H, s, CH_3), 4.46 (1H, br s, $\Delta_{1/2}$ = 10 Hz, NH), 6.17 (1H, t, $^2J_{HF}$ = 54 Hz, CHF_2), 6.47 (2H, m, ArH), 6.78 (2H, m, ArH), 7.29 (2H, m, ArH), 7.57 (2H, m, ArH); ^{19}F NMR (188.14 MHz, $CDCl_3$): δ −67.5 (3F, dd, $^4J_{CF_3\text{-}FA}$ = 11 Hz, $^4J_{CF_3\text{-}FB}$ = 8 Hz, CF_3), −124.5 (1F, m), CHF_2-group–ABM_3X spin system: −127.8 (1F, ddq, $^2J_{Fa\text{-}Fb}$ = 280 Hz, $^2J_{Fa\text{-}H}$ = 54 Hz, $^4J_{Fa\text{-}CF_3}$ = 11 Hz, F_A), −129.1 (1F, ddq, $^2J_{Fb\text{-}Fa}$ = 280 Hz, $^2J_{Fb\text{-}H}$ = 54 Hz, $^4J_{Fb\text{-}CF_3}$ = 8 Hz, F_B); ^{13}C {^{1}H} NMR (50.32 MHz, $CDCl_3$): δ 21.1 (CH_3), 68.2 (1C, qt, $^2J_{C\text{-}CF_3}$ = 25 Hz, $^2J_{C\text{-}CF_2H}$ = 18 Hz, **C**$(CF_3)CHF_2$), 114.7 (1C, tq, $^1J_{CF}$ = 255 Hz, $^3J_{CF}$ = 2 Hz, CHF_2) 115.2 (2C, d, $^2J_{CF}$ = 22 Hz), 118.5 (2C, d, $^3J_{CF}$ = 8 Hz), 124.7 (1C, qt, $^1J_{CF}$ = 291 Hz, $^3J_{CF}$ = 2 Hz, CF_3), 126.8, 128.3 (2C), 129.7

(2C), 139.0 (1C, d, $^4J_{CF}$ = 2 Hz), 139.8, 157.3 (1C, d, $^1J_{CF}$ = 240 Hz); EIMS: *m/z* (%) = 333 $[M]^+$ (74), 282 $[M\text{-}CHF_2]^+$ (100), 264 $[M\text{-}CF_3]^+$ (20). Anal. Calcd for $C_{16}H_{13}F_6N$: C, 57.7; H, 3.9; F, 34.2. Found: C, 58.1; H, 4.2; F, 34.1.

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[24] Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-644041. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).