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Expedient Trimethylaluminium-Promoted One-Pot Synthesis of Functional Heteroaromatic and Carbocyclic Trifluoroethylamines

Nadine Allendörfer,[a] Alexander Sudau,[b] and Stefan Bräse[a,*]

[a] Karlsruhe Institute of Technology (KIT), Institute of Organic Chemistry, Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany
Fax: (+49)-721-608-8581; phone: (+49)-721-608-2902; e-mail: braese@kit.edu
[b] Bayer CropScience AG, Alfred-Nobel-Str. 50, 40789 Monheim am Rhein, Germany

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Abstract: The synthesis of trifluoroethylamines as amide bond mimics is an interesting topic in current research. They are well known tools in pharmaceutical and agrochemical industry. Other methods described in literature are often restricted to few substrates. We herein report a new synthetic approach towards this class of substances. First, the trimethylaluminium-promoted generation of a trifluoromethyl-ketimine from the corresponding trifluoromethyl ketone and an aniline derivative was investigated. Next, the ketimine was converted into the trifluoroethylamines in a one-pot reaction by simple addition of borane-methyl sulfide complex.

Keywords: amide bond mimics; fluorine; one-pot synthesis; trifluoroethylamines

Introduction

Organofluorine compounds are frequently used as pharmaceuticals and agrochemicals.[1–4] Among the large number of marketed pharmaceuticals and agrochemicals 20% to 30% are fluorinated products.[3,5] These facts underline the great interest in novel fluorinated compounds and new methodologies towards these molecules.

The unique role of fluorine can be justified by its strong electronegativity, small size and the low polarisability of the C–F bond. Especially amide bond mimics are an interesting topic in current research due to the rapid *in vivo* degradation and low bioavailability of the parent peptides. In particular, α-trifluoromethylated amines are of ongoing significance[6–9] as amide bond mimics.[10] Since the investigation of the cathepsin K inhibitor *Odanacatib* (Figure 1), which is now in phase III clinical trial, there is an increased demand for trifluoroethylamines themselves as well as new synthetic accesses to this substance class.[11]

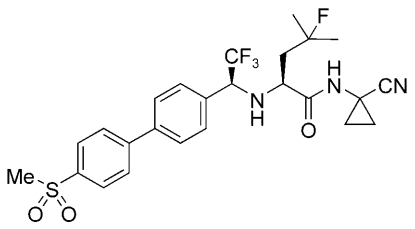
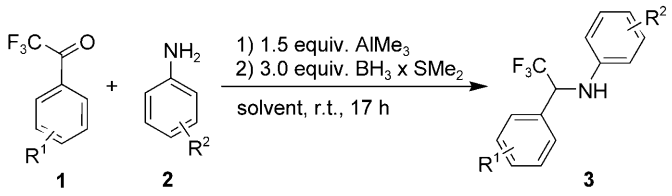


Figure 1. *Odanacatib*: a cathepsin K inhibitor in phase III clinical trials.[12]

Results and Discussion

Although there exist several methods to generate trifluoroethylamines,[6–13] there is a significant requirement on new synthetic approaches. A frequently deployed methodology for the introduction of the trifluoromethyl group is the addition of Ruppert's reagent to imines.[6,13] This reaction is often restricted to *N*-activated substrates. Therefore, we started our route from CF_3 ketones, which can be prepared easily or which are even commercially available.[14] The mentioned ketones **1** and the corresponding anilines **2** were dissolved in various solvents in a sealed vial. Then, trimethylaluminium (1.5 equivalents) was added dropwise under spontaneous heating to start the desired condensation reaction. The *in situ* formed CF_3-ketimine was subsequently reduced by simple addition of 3.0 equivalents of borane·methyl sulfide complex (Scheme 1). After aqueous work-up with 20% NaOH, the amidomimetic trifluoroethylamines **3** could be isolated.

To optimise the reaction conditions, a solvent screening was carried out. Several solvents like THF, DMF or cyclohexane were tested. After further efforts dichloromethane was figured out to be the appropriate solvent for this type of reaction. The product **3ag** could be obtained in an excellent yield of



Scheme 1. One-pot synthesis of trifluoroethylamines **3**.

94%. The use of other solvents led to decreased yields of 4% to 49% (Table 1).

After optimising the reaction conditions, the scope and limitations of the developed reaction were explored. For this purpose, 2,2,2-trifluoroacetophenone (**1a**), as a cost-effective and commercially available keto compound was chosen as starting material for the substance screening. A variety of differently substituted anilines was utilized as reactant. First, *ortho*- and *para*-substituted derivatives with alkyl, halogen, ether and thioether substituents were transformed into the corresponding trifluoroethylamines **3** (Table 2).

Table 1. Solvent screening with trifluoroethylamine **3ag** as model system, details in Scheme 1.

Entry	Solvent	Yield [%][a]
1	THF	4[b]
2	MeCN	10[b]
3	DMF	14[b]
4	toluene	21[b]
5	1,2-dichloroethane	23[b]
6	cyclohexane	49[b]
7	dichloromethane	94[c]

[a] One-pot synthesis.
[b] Yields determined by GC analysis.
[c] Isolated yield after column chromatography.

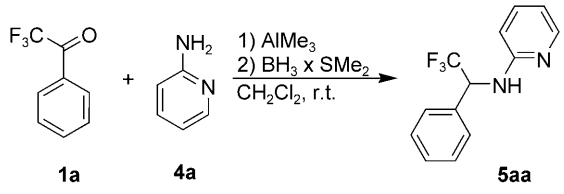
Both *ortho*- and *para*-monosubstituted anilines could be employed in the one-pot synthesis to give yields between moderate 37% and excellent 86%. The *tert*-butyl group in the 4-position led to the best result (Table 2, entries 1–6). If the substitution pattern was changed to the 3,5-positions, the trifluoroethylamine **3ag** was observed in an excellent yield of 94% (Table 2, entry 7). Despite its steric demand and trisubstitution, 2,4,6-trimethylaniline (**2h**) could be converted into the corresponding fluorinated amine **3ah** in good yield (Table 2, entry 8). Free hydroxy and amino groups in the *ortho*-position to the amino functionality were also tolerated during the reaction (Table 2, entries 9 and 10). The use of aminopyridines was not as successful as the reaction of anilines. In case of 2-chloro-3-aminopyridine no product was observed (data not shown). However, the use of 2-aminopyridine (**4a**) led to only a 10% yield of the desired amine **5aa** (Scheme 2).

Table 2. Trifluoroethylamines derived from 2,2,2-trifluoroacetophenones **1**. Details, see Scheme 1, solvent dichloromethane.

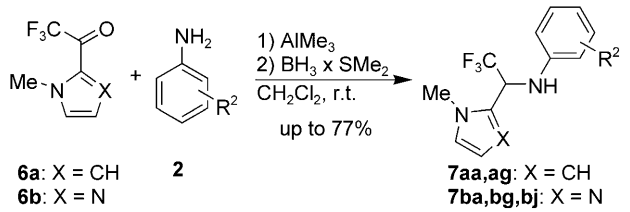
Entry	CF_3-ketone **1**: R^1	Aniline **2**: R^2	Amine **3**	Yield [%][a,b]
1	H	4-Cl	**3aa**[16]	52
2	H	2-I	**3ab**	44
3	H	2-OCH_3	**3ac**[16]	37
4	H	4-SCF_3	**3ad**	51
5	H	4-OCF_3	**3ae**	53
6	H	4-*t*-Bu	**3af**	86
7	H	3,5-CF_3	**3ag**[c]	94
8	H	2,4,6-CH_3	**3ah**	80
9	H	2-OH	**3ai**	18
10	H	2-NH_2	**3aj**	46
11	H	2-Py	**5aa**	10
12	3-CF_3	3,5-CF_3	**3bg**	13
13	4-Br	4-*t*-Bu	**3cf**	68
14	4-Br	3,5-CF_3	**3cg**	77
15	4-Me	4-*t*-Bu	**3df**	81
16	4-Me	3,5-CF_3	**3dg**	69
17	2-OMe	4-*t*-Bu	**3ef**	45
18	2-OMe	3,5-CF_3	**3eg**	26

[a] One-pot synthesis.
[b] Isolated yield after column chromatography.
[c] Intermediate imine of amine **3ag** has been isolated in quantitative yield.

Besides the variation of the aniline derivatives, a selection of differently substituted 2,2,2-trifluoroacetophenones **1** was examined to obtain a broad product range. In the case of 2,2,2-trifluoro-3′-(trifluoromethyl)acetophenone (**1b**) the formation of the corresponding trifluoroethylamines was not as effective as with unsubstituted acetophenone **1a**. Amine **3bg**, derived from 3,5-bis(trifluoromethyl)aniline (**2g**) could be isolated in 13% yield (Table 2). The reaction of trifluoro ketone **1b** and alkylated aniline **2f** yielded only traces of the corresponding amine (data not shown). Choosing 4-substiuted trifluoroacetophenones like **1c** and **1d** led to increased yields of the trifluoroethylamines (Table 2, entries 13–16). With a methoxy substituent in an *ortho*-position of the CF_3 ketone we were able to obtain the amines **3ef** and **3eg** in 26–45% yield (Table 2, entries 17 and 18).



Scheme 2. One-pot synthesis of pyridyl trifluoroethylamine **5aa**.



Scheme 3. One-pot synthesis of heterocyclic trifluoroethylamines **7**.

The screening of heterocyclic trifluoro ketones was performed with pyrrole **6a** and imidazole **6b**.[15,16] In most cases, the routine protocol was applicable without change to give the heterocycles **7** in moderate to very good yields (Scheme 3, Table 3).

In one case, the α-methylated amine **8ba** was isolated (Scheme 4). This by-product **8ba** was only observed when the reaction was performed with trifluoro ketone **6b** and 4-chloroaniline (**2a**). In this case, 2.5 equivalents of $AlMe_3$ were added. With this large excess of the metal organic species one methyl group was transferred into the *in situ* formed CF_3-ketimine. In the literature the addition of $ZnMe_2$ to trifluoroketimines is described, even in a catalytic asymmetric manner.[7,17] However, the use of trimethylaluminium for the alkylation in this synthetic approach is completely unknown. So, we herein report the first example for the addition of trialkylaluminium reagents to CF_3-ketimines to generate α-trisubstituted amines. This structural feature is of high interest in medicinal chemistry.[18]

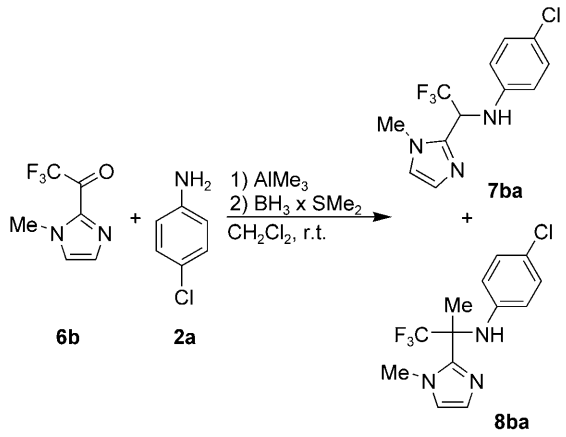
In our studies we first introduced aromatic amines, but also studied benzylic and aliphatic amines (**9a** and **10a**). Following the protocol described above, we were able to synthesise two further trifluoromethylated amines **11aa** and **12ea** (see Figure 2).

Both substrates were obtained in excellent yield and it was demonstrated that the $AlMe_3$-promoted one-pot synthesis is applicable to a wide range of amines and trifluoromethylated ketones.

Table 3. Trifluoroethylamines derived from heterocyclic CF_3 ketones **6**.

Entry	CF_3-ketone **6**	Aniline **2**: R^2	Amine **7**	Yield [%][a]
1	**6a**	4-Cl	**7aa**	77
2	**6a**	3,5-CF_3	**7ag**	54
3	**6b**	4-Cl	**7ba**	41
4	**6b**	3,5-CF_3	**7bg**	30
5	**6b**	3-NO_2	**7bj**	61

[a] Isolated yield after column chromatography.



Scheme 4. Formation of amine **7ba** and α-methylated amine **8ba**.

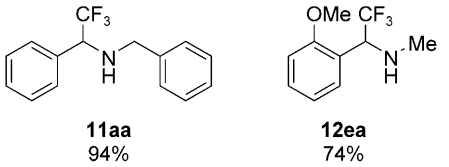


Figure 2. Benzylic and aliphatic CF_3-amines **11aa** and **12ea**.

Conclusions

In conclusion, we have developed a new protocol for the easy synthesis of aromatic, heterocyclic, benzylic and aliphatic trifluoroethylamines. With this method in hands, the design of novel amide bond mimics should be facilitated which could find an application as pharmaceuticals and agrochemicals.

Experimental Section

General Remarks

Compounds were purchased from ABCR, Apollo Scientific, Fluka, Merck, Sigma–Aldrich and Thermo Fisher Scientific and used without further purification. Solvents were dried and purified by standard methods. For TLC, aluminium foils layered with silica gel (silica gel 60 F_{254}) produced by Merck were used. Column chromatography was performed employing Merck silica gel Geduran Si 60 under flash conditions (EtOAc = ethyl acetate, *c*-Hex = cyclohexane). ^1H, ^{13}C and ^{19}F NMR spectra were measured with a Bruker Avance 400 spectrometer (400 MHz/100 MHz/376 MHz, respectively). $CDCl_3$ was used as solvent and residual $CHCl_3/CDCl_3$ as shift reference: δ ($CHCl_3$) = 7.26 ppm, δ ($CDCl_3$) = 77.0 ppm. The signals in ^{13}C spectra were characterised as follows: + = primary or tertiary C atom, C_{quart} = quaternary C atom. ^{19}F NMR spectra were recorded with internal software calibration. IR spectra were recorded with Bruker FT-IR device IFS 88. EI-MS, FAB-MS, FAB-HR-MS and EI-HR-MS: these spectra were measured with a Finnigan MAT 95 instrument; elemental analyses were performed using an Elementar Vario Micro device.

General Procedure for the Formation of Trifluoroethylamines

The CF_3 ketone (1.00 equiv.) and the corresponding aniline (1.00 equiv.) were dissolved under argon in dry CH_2Cl_2 (3.5 mL mmol^{-1}) in a vial. To the reaction mixture $AlMe_3$ (1.50–3.00 equiv., 1 M in heptane) was added dropwise *via* syringe. After a slight exothermal reaction (~40 °C), the vial was sealed and the solution was stirred at room temperature for 15 h. Then, $BH_3{\cdot}SMe_2$ in THF (2.00 equiv,, 2 M in THF) was added dropwise and the mixture was stirred for 2 h. The reaction was quenched by dropwise addition of 20% aqueos NaOH and the aqueous layer was extracted with CH_2Cl_2 (3×30 mL). The organic layer was dried over Na_2SO_4, the solvent removed under reduced pressure and the residue was purified by column chromatography (silica gel).

4-Chloro-*N*-(2,2,2-trifluoro-1-phenylethyl)aniline (3aa): According to the general procedure, 4-chloroaniline (**2a**, 73.0 mg, 0.575 mmol), 2,2,2-trifluoroacetophenone (**1a**, 100 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 24:1, v/v) afforded **3aa** as a yellow oil; yield: 85.0 mg (52%); R_f=0.63 (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ=4.35 (bs, 1H, N*H*), 4.87 (q, J=6.5 Hz, 1H, C*H*CF_3), 6.55–6.59 (m, 2H, Ar-H-3,5), 7.09–7.13 (m, 2H, Ar-H-2,6), 7.39–7.47 (m, 5H, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=60.7 (q, J=30.0 Hz, +, *C*HCF_3), 115.1 (+, C-Ar-3,5), 124.0 (C_{quart}, C-Ar-1), 124.9 (q, J=281.9 Hz, C_{quart}, *C*F_3), 127.8 (+, C-Ar-3′,5′), 129.0 (+, C-Ar-2′,6′), 129.2 (+, C-Ar-2,6), 129.3 (+, C-Ar-4′), 133.6 (C_{quart}, C-Ar-1′), 144.0 (C_{quart}, C-Ar-4); ^{19}F NMR (376 MHz, $CDCl_3$): δ=−74.0 (s, 3F, C*F*$_3$); IR (KBr): $\tilde{\nu}$=3421 (w), 3035 (vw), 2926 (vw), 1601 (m), 1499 (m), 1456 (w), 1404 (vw), 1345 (w), 1313 (m), 1293 (w), 1248 (m), 1178 (m), 1124 (s), 1096 (m), 1031 (vw), 1005 (vw), 891 (vw) cm^{-1}; MS (70 eV, EI): *m/z* (%)=287/286/285 (21/10/63) [M$^+$], 218/217/216 (32/15/100) [M-CF_3^+], 138 (11), 109 (13); EI-HR-MS: *m/z*=285.0530 ($C_{14}H_{11}NClF_3$), calcd.: 285.0532; anal. calcd. for $C_{14}H_{11}ClF_3N$: N 4.90, C 58.86, H 3.88; found: N 4.68, C 59.18, H 3.93.

2-Iodo-*N*-(2,2,2-trifluoro-1-phenylethyl)aniline (3ab): According to the general procedure, 2-iodoaniline (**2b**, 126 mg, 0.575 mmol), 2,2,2-trifluoroacetophenone (**1a**, 100 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 10:1, v/v) afforded **3ab** as a yellow oil; yield: 95.0 mg (44%); R_f=0.66 (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ=4.96 (m, 1H, C*H*CF_3), 5.02 (d, J=7.6 Hz, 1H, N*H*), 6.52 (m, 2H, Ar-H-3,5), 7.13 (dt, J=7.9 Hz, J=1.4 Hz, 1H, Ar-H-4), 7.39–7.44 (m, 3H, Ar-H-3‘,4‘,5‘), 7.48 (m, 2H, Ar-H-2‘,6‘), 7.69 (dd, J=8.3 Hz, J=1.5 Hz, 1H, Ar-H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ=60.8 (q, J=30.1 Hz, +, *C*HCF_3), 86.4 (C_{quart}, C-Ar-1), 111.9 (+, C-Ar-3), 120.5 (+, C-Ar-5), 124.8 (q, J=281.9 Hz, C_{quart}, *C*F_3), 127.9 (+, C-Ar-3′,5′), 129.0 (+, C-Ar-4′,6′), 129.3 (+, C-Ar-4), 129.4 (+, C-Ar-2′), 133.3 (C_{quart}, C-Ar-1′), 139.3 (+, C-Ar-6), 144.8 (C_{quart}, C-Ar-2); ^{19}F NMR (376 MHz, $CDCl_3$): δ=−74.1 (m, 3F, C*F*$_3$); IR (KBr): $\tilde{\nu}$=3389 (w), 3066 (w), 3034 (w), 2925 (w), 1677 (w), 1590 (m), 1512 (m), 1456 (m), 1433 (m), 1343 (m), 1317 (m), 1252 (s), 1180 (s), 1126 (s), 1073 (w), 1030 (w), 1008 (m), 923 (vw) cm^{-1}: MS (70 eV, EI): *m/z* (%)=379/378/377 (1/14/90) [M$^+$], 310/309/308 (0.5/13/100) [M−CF_3^+], 180 (42) [$C_{13}H_{10}N^+$], 109 (17), 91 (13); EI-HR-MS: *m/z*=376.9890 ($C_{14}H_{11}NIF_3$), calcd.: 376.9888.

2-Methoxy-*N*-(2,2,2-trifluoro-1-phenylethyl)aniline (3ac): According to the general procedure, *o*-anisidine (**2c**, 71.0 mg, 0.575 mmol), 2,2,2-trifluoroacetophenone (**1a**, 100 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 19:1, v/v) afforded **3ac** as a colourless oil; yield: 60.0 mg (37%); R_f=0.21 (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.84 (s, 3H, O*CH*$_3$), 4.97 (q, J=6.8 Hz, 1H, C*H*CF_3), 6.72–6.83 (m, 4H, Ar-H-3,4,5,6), 7.39–7.48 (m, 5H, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=55.4 (+, O*C*H$_3$), 72.6 (q, J=31.7 Hz, +, *C*HCF_3), 110.5 (+, C-Ar-6), 115.4 (+, C-Ar-3), 118.9 (+, C-Ar-5), 121.0 (+, C-Ar-4), 124.3 (q, J=282.0 Hz, C_{quart}, *C*F_3), 127.4 (+, C-Ar-3′,5′), 128.5 (+, C-Ar-2′,6′), 129.4 (+, C-Ar-4′), 134.2 (C_{quart}, C-Ar-2), 135.6 (C_{quart}, C-Ar-1′), 147.5 (C_{quart}, C-Ar-1); ^{19}F NMR (376 MHz, $CDCl_3$): δ=−74.0 (s, 3F, CHC*F*$_3$); IR (KBr): $\tilde{\nu}$=3394 (w), 2932 (w), 2841 (w), 1616(w), 1505 (m), 1458 (w), 1384 (w), 1353 (w), 1263 (m), 1225 (m), 1206 (w), 1168 (m), 1125 (m), 1066 (w), 1046 (w), 1028 (w) cm^{-1}. MS (70 eV, EI): *m/z* (%)=282/281 (8/49) [M$^+$], 212 (86) [M−CF_3^+], 210 (100), 195 (21), 43 (89); EI-HR-MS: *m/z*=281.1031, ($C_{15}H_{14}NOF_3$), calcd.: 281.1027.

***N*-(2,2,2-Trifluoro-1-phenylethyl)-4-(trifluoromethylthio)-aniline (3ad):** According to the general procedure, 4-(trifluoromethylthio)aniline (**2d**, 111 mg, 0.575 mmol), 2,2,2-trifluoroacetophenone (**1a**, 100 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 24:1, v/v) afforded **3ad** as a colourless oil; yield: 104 mg (51%); R_f=0.42 (*c*-Hex/EtOAc, 19:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ=4.65 (d, J=7.1 Hz, 1H, N*H*), 4.94 (dq, J=7.2 Hz , J=7.2 Hz, 1H, C*H*CF_3), 6.66 (m, 2H, Ar-H-3,5), 7.40–7.49 (m, 7H, Ar-H-2,2′,3′,4′,5′,6,6′); ^{13}C NMR (100 MHz, $CDCl_3$): δ=60.0 (q, J=30.2 Hz, +, *C*HCF_3), 112.4 (q, J=2.1 Hz, C_{quart}, C-Ar-1), 114.2 (+, C-Ar-3,5), 124.8 (q, J=282.0 Hz, C_{quart}, CH*C*F_3), 127.8 (+, C-Ar-3′,5′), 129.1 (+, C-Ar-2,6), 129.5 (+, C-Ar-4′), 129.6 (q, J=308.3 Hz, C_{quart}, S*C*F_3), 133.2 (C_{quart}, C-Ar-1′), 138.2 (+, C-Ar-2′,6′), 147.7 (C_{quart}, C-Ar-4); ^{19}F NMR (376 MHz, $CDCl_3$): δ=−73.9 (s, 3F, CHC*F*$_3$), −44.2 (s, 3F, SC*F*$_3$); IR (KBr): $\tilde{\nu}$=3437 (w), 3069 (vw), 3036 (vw), 2927 (vw), 2301 (vw), 1890 (vw), 1710 (vw), 1598 (m), 1509 (m), 1456 (w), 1409 (w), 1344 (w), 1322 (w), 1297 (w), 1252 (m), 1119 (m), 1089 (m), 1031 (vw), 1006 (vw), 922 (vw) cm^{-1}; MS (70 eV, EI): *m/z* (%)=353/352/351 (4/11/73) [M$^+$], 284/283/282 (5/15/100) [M−CF_3^+], 159 (18) [$C_8H_6F_3^+$], 109 (15), 58 (37), 43 (89); EI-HR-MS: *m/z*=351.0518 ($C_{15}H_{11}NSF_6$), calcd.: 351.0516.

***N*-(2,2,2-Trifluoro-1-phenylethyl)-4-(trifluoromethoxy)-aniline (3ae):** According to the general procedure, 4-(trifluoromethoxy)aniline (**2e**, 102 mg, 0.575 mmol), 2,2,2-trifluoroacetophenone (**1a**, 100 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 24:1, v/v) afforded **3ae** as a yellow oil; yield: 107 mg (55%); R_f=0.38 (*c*-Hex/EtOAc, 24:1, v/v). ^{1}H NMR (400 MHz,

$CDCl_3$): $\delta = 4.41$ (d, $J = 6.9$ Hz, 1H, N*H*), 4.86 (dq, $J = 7.2$ Hz, $J = 7.2$ Hz, 1H, C*H*CF_3), 6.59–6.63 (m, 2H, Ar-H-3,5), 7.01 (m, 2H, Ar-H-2,6), 7.40–7.46 (m, 5H, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 60.8$ (q, $J = 30.0$ Hz, *C*HCF$_3$), 120.6 (q, $J = 255.9$ Hz, C_{quart}, O*C*F$_3$), 124.9 (q, $J = 281.9$ Hz, C_{quart}, CH*C*F$_3$), 114.4 (+, C-Ar-2,6), 122.5 (+, C-Ar-3,5), 127.8 (+, C-Ar-3′,5′), 129.0 (+, C-Ar-2′,6′), 129.3 (+, C-Ar-4′), 133.6 (C_{quart}, C-Ar-1′), 141.7 (C_{quart}, C-Ar-1), 144.2 (C_{quart}, C-Ar-4); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -74.0$ (s, 3F, CHC*F*$_3$), -58.4 (s, 3F, OC*F*$_3$); IR (KBr): $\tilde{\nu} = 3433$ (w), 3039 (vw), 1615 (w), 1516 (m), 1456 (w), 1347 (w), 1248 (s), 1169 (m), 1125 (m), 1031 (vw), 919 (vw) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 337/336/335 (1/19/100) [M$^+$], 268/267/266 (0.4/10/80) [M−CF$_3^+$], 159 (2) [$C_8H_6F_3N^+$]; EI-HR-MS: *m/z* = 335.0746 ($C_{15}H_{11}F_6NO$), calcd.: 335.0744.

4-*tert*-Butyl-*N*-(2,2,2-trifluoro-1-phenylethyl)aniline (3af): According to the general procedure, 4-*tert*-butylaniline (**2f**, 120 mg, 0.575 mmol), 2,2,2-trifluoroacetophenone (**1a**, 100 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 24:1, v/v) afforded **3af** as a yellow oil; yield: 153 mg (86%); $R_f = 0.52$ (*c*-Hex/EtOAc, 19:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.28$ [s, 9H, C(C*H*$_3$)$_3$], 4.28 (bs, 1H, N*H*), 4.91 (q, $J = 7.3$ Hz, 1H, C*H*CF$_3$), 6.61–6.65 (m, 2H, Ar-H-2,6), 7.20–7.24 (m, 2H, Ar-H-3,5), 7.39–7.51 (m, 5H, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 31.4$ [+, C(*C*H$_3$)$_3$], 33.9 [C_{quart}, *C*(CH$_3$)$_3$], 60.8 (q, $J = 29.7$ Hz, +, C*H*CF$_3$), 113.8 (+, C-Ar-2,6), 125.1 (q, $J = 281.9$ Hz, C_{quart}, *C*F$_3$), 126.1 (+, C-Ar-3,5), 127.9 (+, C-Ar-3′,5′),128.9 (+, C-Ar-2′,6′), 129.0 (+, C-Ar-4′), 134.4 (C_{quart}, C-Ar-1′), 142.0 (C_{quart}, C-Ar-4), 143.2 (C_{quart}, C-Ar-1); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -74.0$ (s, 3F, C*F*$_3$); IR (KBr): $\tilde{\nu} = 3419$ (w), 3065 (w), 3033 (w), 2962 (s), 2867 (m), 1881 (vw), 1743 (vw), 1616 (m), 1520 (s), 1493 (m), 1456 (m), 1408 (w), 1394 (w), 1364 (m), 1345 (m), 1319 (m), 1300 (m), 1251 (s), 1173 (s), 1124 (s), 1074 (w), 1030 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 308/307 (2/35) [M$^+$], 293/292 (13/100) [M−CH$_3^+$], 239/238 (1/20) [M−CF$_3^+$], 159 (24) [$C_8H_6F_3^+$]; EI-HR-MS: *m/z* = 307.1546 ($C_{18}H_{20}F_3N$), calcd.: 307.1547.

***N*-(2,2,2-Trifluoro-1-phenylethyl)-3,5-bis(trifluoromethyl)-aniline (3ag):** According to the general procedure, 3,5-bis-(trifluoromethyl)aniline (**2g**, 132 mg, 0.575 mmol), 2,2,2-trifluoroacetophenone (**1a**, 100 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 14:1, v/v) afforded **3ag** as a colourless oil; yield: 209 mg (94%); $R_f = 0.59$ (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.79$ (d, $J = 7.3$ Hz, 1H, N*H*), 4.97 (dq, $J = 7.1$ Hz, $J = 7.1$ Hz, 1H, C*H*CF$_3$), 7.03 (s, 2H, Ar-H-2,6), 7.25 (s, 1H, Ar-H-4), 7.42–7.49 (m, 5H, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 60.1$ (q, $J = 30.1$ Hz, +, C*H*CF$_3$), 112.4 (sept, $J = 3.7$ Hz, +, C-Ar-4), 113.1 (q, $J = 3.3$ Hz, +, Ar-H-2,6), 123.2 (q, $J = 272.7$ Hz, C_{quart}, 2×*C*F$_3$), 124.6 (q, $J = 282.2$ Hz, C_{quart}, CH*C*F$_3$), 127.8 (+, C-Ar-3′,5′), 129.3 (+, C-Ar-2′,6′), 129.7 (+, C-Ar-4′), 132.5 (C_{quart}, C-Ar-1′), 132.7 (q, $J = 32.8$ Hz, C_{quart}, C-Ar-3,5), 146.3 (C_{quart}, C-Ar-1); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -73.9$ (s, 3F, C*F*$_3$), -63.3 (s, 6F, 2×C*F*$_3$); IR (KBr): $\tilde{\nu} = 3445$ (w), 3040 (vw), 1625 (s), 1527 (m), 1499 (w), 1475 (m), 1458 (w), 1440 (m), 1391 (s), 1352 (m), 1279 (s), 1176 (s), 1129 (s), 1076 (m), 1032 (vw), 997 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 388/387 (31/5) [M$^+$], 320/319/318 (1/16/100) [M−CF$_3^+$], 214/213 (1/17) [$C_8H_3F_6^+$], 109 (16), 77 (4) [$C_6H_5^+$]; EI-HR-MS: *m/z* = 387.0673 ($C_{16}H_{10}F_9N$), calcd.: 387.0669; anal. calcd. for $C_{16}H_{10}F_9N$: N 3.62, C 49.63, H 2.60; found: N 3.35, C 49.53, H 2.49.

Intermediate Imine of Amine 3ag

***N*-(2,2,2-Trifluoro-1-phenylethylidene)-3,5-bis(trifluoromethyl)aniline:** Under argon 3,5-bis(trifluoromethyl)aniline (**2g**, 0.132 g, 0.575 mmol), 2,2,2-trifluoroacetophenone (**1a**, 0.100 g, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). After aqueous work-up and column chromatography (*c*-Hex/EtOAc, 14/1) afforded the intermediate imine as a yellow oil; yield: 221 mg (>99%); $R_f = 0.61$ (*c*-Hex/EtOAc, 10/1). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.18$–7.20 (m, 4H, Ar-H-2,6,2′,6′), 7.35 (t, $J = 7.5$ Hz, 2H, Ar-3′,5′), 7.43 (t, $J = 7.4$ Hz, 1H, Ar-H-4′), 7.57 (s, 1H, Ar-H-4); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 118.9$ (m, +, C-Ar-4), 119.4 (q, $J = 279.4$ Hz, C_{quart}, CH*C*F$_3$), 120.9 (+, C-Ar-2,6), 122.8 (q, $J = 272.8$ Hz, C_{quart}, Ar*C*F$_3$), 128.4 (+, C-Ar-2′,6′), 128.7 (C_{quart}, C-Ar-1′), 129.0 (+, C-Ar-3′,5′), 131.2 (+, C-Ar-4′), 132.4 (q, $J = 33.8$ Hz, C_{quart}, C-Ar-3,5), 148.4 (C_{quart}, C-Ar-1), 160.4 (q, $J = 34.7$ Hz, C_{quart}, *C*CF$_3$); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -70.3$ (s, 3F, CHC*F*$_3$), -63.2 (s, 6F, ArC*F*$_3$); IR (KBr): $\tilde{\nu} = 3440$ (vw), 1667 (vw), 1460 (vw), 1374 (m), 1334 (w), 1280 (m), 1168 (m), 1134 (m), 976 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 386/385 (5/28) [M$^+$], 317/316 (16/100) [M−CF$_3^+$], 213 (5) [$C_8H_3F_6^+$], 77 (22) [$C_6H_5^+$]; HR-MS: *m/z* = 385.0510 ($C_{16}H_8F_9N$), calcd.: 385.0513.

2,4,6-Trimethyl-*N*-(2,2,2-trifluoro-1-phenylethyl)aniline (3ah): According to the general procedure, 2,4,6-trimethylaniline (**2h**, 71.0 mg, 0.575 mmol), 2,2,2-trifluoroacetophenone (**1a**, 100 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 24:1–10:1, v/v) afforded **3ah** as a colourless oil; yield: 135 mg (80%); $R_f = 0.20$ (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.16$ (s, 6H, 2×*o*-C*H*$_3$), 2.22 (s, 3H, *p*-C*H*$_3$), 5.01 (q, $J = 6.7$ Hz, 1H, C*H*CF$_3$), 6.78 (s, 2H, Ar-H-3,5), 7.40–7.49 (m, 5H, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 17.6$ (+, 2×*o*-C*H*$_3$), 20.3 (+, *p*-C*H*$_3$), 72.8 (q, $J = 31.9$ Hz, +, *C*HCF$_3$), 122.2 (C_{quart}, C-Ar-2,6), 124.2 (q, $J = 282.1$ Hz, C_{quart}, *C*F$_3$), 127.4 (+, C-Ar-3′,5′), 127.5 (C_{quart}, C-Ar-4), 128.6 (+, C-Ar-2′,6′), 128.8 (+, C-Ar-3,5), 129.5 (+, C-Ar-4′), 134.0 (C_{quart}, C-Ar-1′), 139.7 (C_{quart}, C-Ar-1); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -78.3$ (s, 3F, CHC*F*$_3$); IR (KBr): $\tilde{\nu} = 3406$ (vw), 2920 (w), 2861 (w), 1628 (vw), 1606 (vw), 1488 (m), 1455 (w), 1377 (w), 1336 (w), 1303 (w), 1259 (m), 1228 (m), 1168 (m), 1120 (m), 1072 (w), 1030 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 294/293 (17/100) [M$^+$], 224 (20) [M−CF$_3^+$], 134 (60) [$C_9H_{12}N^+$]; EI-HR-MS: *m/z* = 293.1393 ($C_{17}H_{18}F_3N$), calcd.: 293.1391.

2-(2,2,2-Trifluoro-1-phenylethylamino)phenol (3ai): According to the general procedure, 2-aminophenol (**2i**, 63.0 mg, 0.575 mmol), 2,2,2-trifluoroacetophenone (**1a**, 100 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of

$BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 14:1, v/v) afforded **3ai** as a brown oil; yield: 28.0 mg (18%); $R_f = 0.81$ (*c*-Hex/EtOAc, 1/1). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.62$ (bs, 1H), 4.84 (m, 1H, C*H*CF_3), 5.18 (bs, 1H), 6.56–6.59 (m, 1H, H_{arom}), 6.68–6.78 (m, 3H, H_{arom}), 7.35–7.50 (m, 5H, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 61.2$ (q, $J = 29.9$ Hz, +, *C*HCF_3), 114.7 (+, C-Ar-3), 114.7 (+, C-Ar-6), 120.1 (+, C-Ar-5), 121.4 (+, C-Ar-4), 125.1 (q, $J = 281.8$ Hz, C_{quart}, *C*F_3), 128.0 (+, C-Ar-2′,6′), 128.9 (+, C-Ar-3′,5′), 129.1 (+, C-Ar-4′), 134.0 (C_{quart}, C-Ar-1′), 134.1 (C_{quart}, C-Ar-2), 144.6 (C_{quart}, C-Ar-1); ^{19}FNMR (376 MHz, $CDCl_3$): $\delta = -74.1$ (s, 3F, C*F*$_3$); IR (ATR): $\tilde{\nu} = 3420$ (w), 2927 (vw), 1611 (w), 1512 (m), 1453 (m), 1341 (w), 1250 (m), 1169 (m), 1119(s), 1042 (w), 889 (w) cm^{-1}; MS (70 eV, EI): *m/z*(%) = 269/268/267 (1/15/100) [M$^+$], 199/198 (12/85) [M−CF_3^+], 108 (70) [$C_6H_6NO^+$]; HR-MS: *m/z* = 267.0875 ($C_{14}H_{12}F_3NO$), calcd.: 267.0870.

***N*^{1}-(2,2,2-Trifluoro-1-phenylethyl)benzol-1,2-diamine (3aj):** According to the general procedure, *o*-phenylenediamine (**2j**, 62.0 mg, 0.575 mmol), 2,2,2-trifluoroacetophenone (**1a**, 100 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 14:1, v/v) afforded **3aj** as a brown oil; yield 70.0 mg (46%); $R_f = 0.21$ (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.54$ (bs, 2H, N*H*$_2$), 4.10 (d, $J = 7.3$ Hz, 1H, N*H*), 4.87 (dq, $J = 7.5$ Hz, $J = 7.5$ Hz, 1H, C*H*CF_3), 6.51 (d, $J = 8.1$ Hz, 1H, Ar-H-3), 6.68 (ddd, $J = 8.9$ Hz, $J = 6.7$ Hz, $J = 3.8$ Hz, 1H, Ar-H-4), 6.73–6.79 (m, 2H, Ar-H-5,6), 7.35–7.50 (m, 5H, Ar-H-2′,3′,4′,5′,6′); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 60.7$ (q, $J = 29.4$ Hz, +, *C*HCF_3), 115.7 (+, C-Ar-6), 117.1 (+, C-Ar-3), 120.3 (+, C-Ar-4), 121.3 (+, C-Ar-5), 125.2 (q, $J = 281.5$ Hz, C_{quart}, *C*F_3), 128.0 (+, C-Ar-2′,6′), 128.8 (+, C-Ar-3′,5′), 129.0 (+, C-Ar-4′), 134.0 (C_{quart}, C-Ar-1′), 134.2 (C_{quart}, C-Ar-2), 136.2 (C_{quart}, C-Ar-1); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -74.0$ (s, 3F, C*F*$_3$); IR (KBr): $\tilde{\nu} = 3347$ (w), 3034 (w), 2926(w), 1619 (m), 1509 (m), 1456 (m), 1332 (m), 1255 (s), 1172 (s), 1123 (s), 1066 (w), 1031 (w), 1003 (vw), 922 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 267/266 (11/70) [M$^+$], 197 (27) [M−CF_3^+], 107 (100) [$C_6H_7N_2^+$]; EI-HR-MS: *m/z* = 266.1029 ($C_{14}H_{13}F_3N_2$), calcd.: 266.1030.

***N*-(2,2,2-Trifluoro-1-phenylethyl)pyridine-2-amine (5aa):** According to the general procedure, 2-aminopyridine (**4a**, 54.0 mg, 0.575 mmol), 2,2,2-trifluoroacetophenone (**1a**, 100 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 10:1–5:1, v/v) afforded **5aa** as a yellow solid; yield: 15.0 mg (10%); $R_f = 0.09$ (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.05$ (m, 1H, C*H*CF_3), 6.56 (d, $J = 8.7$ Hz, 1H, Ar-H-3), 6.72 (t, $J = 6.7$ Hz, 1H, Ar-H-5), 7.43–7.49 (m, 5H, Ph-H), 7.60 (t, $J = 7.3$ Hz, 1H, Ar-H-4), 8.29 (d, $J = 5.9$ Hz, 1H, Ar-H-6); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 59.2$ (q, $J = 31.2$ Hz, +, *C*HCF_3), 107.7 (+, C-Ar-3), 113.5 (+, C-Ar-5), 124.1 (q, $J = 282.2$ Hz, C_{quart}, *C*F_3), 127.8 (+, C-Ar-3′,5′), 129.2 (+, C-Ar-2′,6′), 129.9 (+, C-Ar-4′), 131.6 (C_{quart}, C-Ar-1′), 140.5 (+, C-Ar-4), 146.9 (+, C-Ar-6), 153.5 (C_{quart}, C-Ar-2); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -74.2$ (s, 3F, C*F*$_3$); IR (KBr): $\tilde{\nu} =$ 3350 (w), 2920 (w) , 2850 (w), 2417 (w), 2289 (w), 1630 (m), 1589 (m), 1533 (m), 1497 (w), 1475 (m), 1456 (m), 1361 (w), 1253 (m), 1188 (m), 1127 (m), 1076 (w), 1033 (w), 933 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 253/252 (2/13) [M$^+$], 183 (27) [M−CF_3^+], 78 (31), [$C_5H_4N^+$], 43 (100); EI-HR-MS: *m/z* = 252.0872 ($C_{13}H_{11}F_3N_2$), calcd.: 252.0874.

***N*-{2,2,2-Trifluoro-1-[3-(trifluoromethyl)phenyl]ethyl}-3,5-bis(trifluoromethyl)aniline (3bg):** According to the general procedure, 3,5-bis(trifluoromethyl)aniline (**2g**, 132 mg, 0.575 mmol), 2,2,2-trifluoro-1-[3-(trifluoromethyl)phenyl]-ethanone (**1b**, 139 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 19:1, v/v) afforded **3bg** as a colourless oil; yield: 34.0 mg (13%); $R_f = 0.57$ (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 4.81 (d, $J = 7.3$ Hz, 1H, N*H*), 5.05 (dq, $J = 6.9$ Hz, $J = 6.9$ Hz, 1H, C*H*CF_3), 7.02 (s, 2H, Ar-H-2,6), 7.29 (s, 1H, Ar-H-4), 7.58–7.74 (m, 4H, Ar-H-2′,4′,5′,6′); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 59.8$ (q, $J = 30.8$ Hz, +, *C*HCF_3), 112.9 (m, +, C-Ar-4), 113.1 (q, $J = 3.5$ Hz, +, C-Ar-2,6), 123.1 (q, $J =$ 272.8 Hz, C_{quart}, 2×*C*F_3), 123.6 (q, $J = 272.4$ Hz, C_{quart}, *C*F_3), 124.4 (q, $J = 282.3$ Hz, C_{quart}, CH*C*F_3), 124.6 (q, $J = 3.3$ Hz, +, C-Ar-6′), 126.8 (q, $J = 3.6$ Hz, +, C-Ar-2′), 129.9 (+, C-Ar-5′), 131.2 (+, C-Ar-4′), 131.9 (q, $J = 32.9$ Hz, C_{quart}, C-Ar-1′), 132.9 (q, $J = 33.3$ Hz, C_{quart}, C-Ar-3,5), 133.7 (C_{quart}, C-Ar-3′), 145.8 (C_{quart}, C-Ar-1); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -73.8$ (s, 3F, CHC*F*$_3$), −63.3 (s, 6F, 2×C*F*$_3$), −62.8 (s, 3F, C*F*$_3$); IR (KBr): $\tilde{\nu} = 3845$ (vw), 3447 (w), 2928 (vw), 2286 (vw), 1710 (vw), 1625 (w), 1529 (w), 1475 (w), 1441 (w), 1390 (w), 1331 (w), 1280 (w), 1129 (w), 1076 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 457/456/455 (0.34/4/14) [M$^+$], 388/387/386 (1/14/100) [M−CF_3^+], 317 (0.36) [$C_{15}H_9F_6N^+$], 240 (8) [$C_6H_3F_6^+$], 213 (11); EI-HR-MS: *m/z* = 455.0540 ($C_{17}H_9NF_{12}$), calcd.: 455.0543.

***N*-[1-(4-Bromophenyl)-2,2,2-trifluoroethyl]-4-*tert*-butylaniline (3cf):** According to the general procedure, 4-*tert*-butylaniline (**2f**, 86.0 mg, 0.575 mmol), 4′-bromo-2,2,2-trifluoroacetophenone (**1c**, 145 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 49:1, v/v) afforded **3cf** as a colourless oil; yield: 151 mg (68%); $R_f = 0.63$ (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.27$ [s, 9H, C(C*H*$_3$)$_3$], 4.26 (d, $J =$ 6.5 Hz, 1H, N*H*), 4.87 (dq, $J = 7.1$ Hz, $J = 7.1$ Hz, 1H, C*H*CF_3), 6.55–6.59 (m, 2H, Ar-H-2′,6′), 7.19–7.23 (m, 2H, Ar-H-3′,5′), 7.37 (d, $J = 8.4$ Hz, 2H, Ar-H-3,5), 7.53–7.56 (m, 2H, Ar-H-2,6); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 31.4$ [+, C(*C*H$_3$)$_3$], 33.9 [C_{quart}, *C*(CH$_3$)$_3$], 60.3 (q, $J = 29.9$ Hz, +, *C*HCF_3), 113.6 (+, C-Ar-2′,6′), 123.2 (C_{quart}, C-Ar-1), 124.7 (q, $J = 281.8$ Hz, C_{quart}, *C*F_3), 126.2 (+, C-Ar-3′,5′), 129.6 (+, C-Ar-3,5), 132.1 (+, C-Ar-2,6), 133.3 (C_{quart}, C-Ar-4), 142.2 (C_{quart}, C-Ar-4′), 142.7 (C_{quart}, C-Ar-1′); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -74.1$ (s, 3F, CHC*F*$_3$); IR (KBr): $\tilde{\nu} = 3414$ (w), 3030 (w), 2963 (m), 2904 (w), 2868 (w), 2296 (vw), 1905 (vw), 1710 (m), 1616 (m), 1521 (m), 1489 (m), 1409 (m), 1363 (m), 1318 (m), 1302 (m), 1250 (m), 1174 (m), 1128 (m), 1095 (m), 1074 (m), 1012 (m) cm^{-1}; MS (70 eV, EI): *m/z* (%) = 387/386/385 (6/2/7) [M$^+$], 372/371/370 (14/3/16) [M−CH_3^+], 318/317/316 (2/1/3) [M−CF_3^+], 237 (2) [$C_{17}H_{19}N^+$], 58 (35), 43 (100); EI-HR-MS: *m/z* = 385.0650 ($C_{18}H_{19}BrF_3N$), calcd.: 385.0653; anal. calcd. for

$C_{18}H_{19}BrF_3N$: N 3.63, C 55.97, H 4.96; found: N 4.15, C 55.47, H 5.08.

***N*-[1-(4-Bromophenyl)-2,2,2-trifluoroethyl]-3,5-bis-(trifluoromethyl)aniline (3cg):** According to the general procedure, 3,5-bis(trifluoromethyl)aniline (**2g**, 132 mg, 0.575 mmol), 4′-bromo-2,2,2-trifluoroacetophenone (**1c**, 145 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 49:1, v/v) afforded **3cg** as a colourless oil; yield: 206 mg (77%); R_f = 0.53 (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.77 (d, J = 7.0 Hz, 1H, N*H*), 4.95 (dq, J = 6.9 Hz, J = 6.9 Hz, 1H, C*H*CF$_3$), 7.00 (s, 2H, Ar-H-2′,6′), 7.28 (s, 1H, Ar-H-4′), 7.35 (d, J = 8.1 Hz, Ar-H-3,5), 7.58 (d, J = 8.2 Hz, Ar-H-2,6); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 59.7 (q, J = 30.7 Hz, +, *C*HCF$_3$), 112.7 (m, +, C-Ar-4′), 113.1 (q, J = 3.2 Hz, +, C-Ar-2′,6′), 123.3 (q, J = 272.8 Hz, C_{quart}, 2 × *C*F$_3$), 124.1 (C_{quart}, C-Ar-1), 124.3 (q, J = 282.1 Hz, C_{quart}, CH*C*F$_3$), 129.4 (+, C-Ar-2,6), 131.5 (C_{quart}, C-Ar-4), 132.5 (+, C-Ar-3,5), 132.8 (q, J = 33.1 Hz, C_{quart}, C-Ar-3′,5′), 145.9 (C_{quart}, C-Ar-1′); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −73.9 (s, 3F, CHC*F*$_3$), −63.2 (6F, 2 × C*F*$_3$); IR (KBr): $\tilde{\nu}$ = 3443 (w), 3090 (vw), 2238 (vw), 1711 (w), 1625 (m), 1528 (m), 1492 (m), 1476 (m), 1441 (w), 1391 (m), 1352 (m), 1320 (w), 1292 (m), 1127 (m), 1092 (m), 1012 (m), 997 (w) cm^{-1}; MS (70 eV, EI): m/z (%) = 467/466/465 (34/7/37) [M$^+$], 398/397/396 (91/13/100) [M−CF$_3^+$], 317 (8) [$C_{15}H_9F_6N^+$], 240 (23) [$C_6H_3F_6^+$]; HR-MS: m/z = 464.9778 ($C_{16}H_9BrF_9N$), calcd.: 464.9774; anal. calcd. for $C_{16}H_9BrF_9N$: N 3.00, C 41.23, H 1.95; found: N 2.88, C 41.27, H 1.92.

4-*tert*-Butyl-*N*-(2,2,2-trifluoro-1-*p*-tolylethyl)aniline (3df): According to the general procedure, 4-*tert*-butylaniline (**2f**, 86.0 mg, 0.575 mmol), 2,2,2-trifluoro-1-*p*-tolylethanone (**1d**, 108 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 49:1, v/v) afforded **3df** as a colourless oil; yield: 150 mg (81%); R_f = 0.69 (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 9H, C(C*H*$_3$)$_3$), 2.36 (s, 3H, C*H*$_3$), 4.85 (q, J = 7.3 Hz, 1H, C*H*CF$_3$), 6.61 (d, J = 8.6 Hz, 2H, Ar-H-2,6), 7.18–7.23 (m, 4H, Ar-H-3,5,3′,5′), 7.36 (d, J = 7.8 Hz, 2H, Ar-H-2′,6′); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2 (+, *C*H$_3$), 31.4 [+, C(*C*H$_3$)$_3$], 33.9 [C_{quart}, *C*(CH$_3$)$_3$], 60.5 (q, J = 29.8 Hz, 1H, *C*HCF$_3$), 113.6 (+, C-Ar-2,6), 125.2 (q, J = 281.8 Hz, C_{quart}, *C*F$_3$), 126.1 (+, C-Ar-3,5), 127.8 (+, C-Ar-3′,5′), 129.6 (+, C-Ar-2′,6′), 131.3 (C_{quart}, C-Ar-1′), 138.9 (C_{quart}, C-Ar-4′), 141.9 (C_{quart}, C-Ar-4), 143.2 (C_{quart}, C-Ar-1); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −74.1 (s, 3F, CHC*F*$_3$); IR (KBr): $\tilde{\nu}$ = 3420 (w), 3029 (w), 2963 (w), 2868 (w), 1907 (vw), 1729 (vw), 1617 (w), 1521 (w), 1483 (w), 1410 (w), 1363 (w), 1251 (w), 1122 (w), 1022 (vw), 898 (vw) cm^{-1}; MS (70 eV, EI): m/z (%) = 323/322/321 (1/10/54) [M$^+$], 308/307/306 (1/16/100) [M−CH$_3^+$], 252 (21) [M−CF$_3^+$], 173 (7) [$C_9H_8F_3^+$]; EI-HR-MS: m/z = 321.1701 ($C_{19}H_{22}F_3N$), calcd.: 321.1704; anal. calcd. for $C_{19}H_{22}F_3N$: N 4.36, C 71.01, H 6.90; found: N 4.12, C 71.09, H 6.96.

***N*-(2,2,2-Trifluoro-1-*p*-tolylethyl)-3,5-bis(trifluoromethyl)-aniline (3dg):** According to the general procedure, 3,5-bis-(trifluoromethyl)aniline (**2g**, 86.0 mg, 0.575 mmol), 2,2,2-trifluoro-1-*p*-tolylethanone (**1d**, 108 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 29:1, v/v) afforded **3dg** as a colourless solid; yield: 159 mg (69%); R_f = 0.66 (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3H, C*H*$_3$), 4.75 (d, J = 7.4 Hz, 1H, N*H*), 4.93 (dq, J = 7.1 Hz, J = 7.1 Hz, 1H, C*H*CF$_3$), 7.03 (s, 2H, Ar-H-2,6), 7.23–7.27 (m, 3H, Ar-H-4,3′,5′), 7.35 (d, J = 8.0 Hz, 2H, Ar-H-2′,6′); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1 (+, *C*H$_3$), 59.9 (q, J = 30.5 Hz, +, *C*HCF$_3$), 112.3 (+, C-Ar-4), 113.1 (+, C-Ar-2,6), 123.6 (q, J = 272.7 Hz, C_{quart}, 2 × *C*F$_3$), 124.7 (q, J = 282.1 Hz, C_{quart}, CH*C*F$_3$), 127.6 (+, C-Ar-3′,5′), 129.5 (C_{quart}, C-Ar-1′), 130.0 (+, C-Ar-2′,6′), 132.7 (q, J = 33.0 Hz, C_{quart}, C-Ar-3,5), 139.8 (C_{quart}, C-Ar-4′), 146.4 (C_{quart}, C-Ar-1); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −74.0 (s, 3F, CHC*F*$_3$), −63.2 (s, 6F, 2 × C*F*$_3$); IR (KBr): $\tilde{\nu}$ = 3437 (s), 3094 (m), 3034 (m), 2933 (m), 2233 (w), 1913 (w), 1807 (w), 1727 (w), 1625 (s), 1537 (s), 1517 (s), 1477 (s), 1443 (s), 1395 (s), 1347 (s), 1278 (s), 1179 (s), 1114 (s), 1043 (m), 1022 (m), 997 (m) cm^{-1}; MS (70 eV, EI): m/z (%) = 403/402/401 (0.4/6/35) [M$^+$], 334/333/332 (1/16/100) [M−CF$_3^+$], 213 (13) [$C_8H_3F_6^+$], 174/173 (3/34) [$C_9H_8F_3^+$]; EI-HR-MS: m/z = 401.0824 ($C_{17}H_{12}F_9N$), calcd.: 401.0826; anal. calcd. for $C_{17}H_{12}F_9N$: N 3.49, C 50.88, H 3.01; found: N 3.33, C 50.87, H 3.08.

4-*tert*-Butyl-*N*-[2,2,2-trifluoro-1-(2-methoxyphenyl)ethyl]-aniline (3ef): According to the general procedure, 4-*tert*-butylaniline (**2f**, 86.0 mg, 0.575 mmol), 2,2,2-trifluoro-1-(2-methoxyphenyl)ethanone (**1e**, 118 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 14:1, v/v) afforded **3ef** as a colourless solid; yield: 88.0 mg (45%); R_f = 0.54 (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 [s, 9H, C(C*H*$_3$)$_3$], 3.91 (s, 3H, OC*H*$_3$), 4.41 (d, J = 8.5 Hz, 1H, NH), 5.52 (dq, J = 7.7 Hz, J = 7.7 Hz, 1H, C*H*CF$_3$), 6.62 (m, 2H, Ar-H-2,6), 6.97 (m, 2H, Ar-H-3′,4′), 7.19 (m, 2H, Ar-H-3,5), 7.33 (ddd, J = 8.3 Hz, J = 7.5 Hz, J = 1.7 Hz, 1H, Ar-H-5′), 7.41 (d, J = 7.6 Hz, 1H, Ar-H-6′); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.4 [+, C(*C*H$_3$)$_3$], 33.9 [C_{quart}, *C*(CH$_3$)$_3$], 53.5 (q, J = 30.5 Hz, +, *C*HCF$_3$), 55.8 (+, O*C*H$_3$), 111.1 (+, C-Ar-3‘), 113.3 (+, C-Ar-2,6), 121.0 (+, C-Ar-5‘), 122.9 (C_{quart}, C-Ar-1‘), 125.5 (q, J = 282.3 Hz, C_{quart}, *C*F$_3$), 126.1 (+, C-Ar-3,5), 128.2 (+, C-Ar-4′), 130.0 (+, C-Ar-6′), 141.6 (C_{quart}, C-Ar-4), 143.4 (C_{quart}, C-Ar-1), 157.5 (C_{quart}, C-Ar-2′); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −74.1 (s, 3F, C*F*$_3$); IR (KBr): $\tilde{\nu}$ = 3419 (m), 2963 (s), 2905 (m), 2868 (m), 2842 (m), 1615 (s), 1521 (vs), 1493 (s), 1465 (s), 1440 (s), 1394 (m), 1364 (s), 1320 (s), 1300 (s), 1248 (vs), 1171 (vs), 1125 (vs), 1086 (m), 1051 (m), 1028 (s), 897 (m) cm^{-1}; MS (70 eV, EI): m/z (%) = 337 (64) [M$^+$], 322 (100) [M−CH$_3^+$], 268 (92) [M−CF$_3^+$], 189 (14) [$C_9H_8F_3O^+$], 109 (19) [$C_6H_5N^+$], 77 (8) [$C_6H_5^+$]; HR-MS: m/z = 337.1656 ($C_{19}H_{22}NOF_3$), calcd.: 337.1653.

***N*-[2,2,2-Trifluoro-1-(2-methoxyphenyl)ethyl]-3,5-bis(trifluoromethyl)aniline (3eg):** According to the general procedure, 3,5-bis(trifluoromethyl)aniline (**2f**, 132 mg, 0.575 mmol), 2,2,2-trifluoro-1-(2-methoxyphenyl)ethanone (**1e**, 118 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of $BH_3{\cdot}SMe_2$ in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 14:1, v/v) afforded **3eg** as a colourless solid; yield: 62.0 mg (26%); R_f = 0.52 (*c*-Hex/EtOAc,

10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.94 (s, 3H, CH_3), 4.99 (d, J = 8.9 Hz, 1H, NH), 5.59 (m, 1H, CHCF$_3$), 7.01 (dd, J = 14.7 Hz, J = 7.8 Hz, 2H, Ar-H-3′,4′), 7.08 (s, 2H, Ar-H-3,5), 7.23 (s, 1H, Ar-H-4), 7.35–7.42 (m, 2H, Ar-H-5′,6′); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.1 (q, J = 31.4 Hz, +, CHCF$_3$), 55.7 (+, CH$_3$), 111.2 (+, C-Ar-3′), 112.0 (m, +, C-Ar-4), 113.0 (q, J = 3.3 Hz, +, C-Ar-2,6), 121.1 (C$_{quart}$, C-Ar-1′), 121.3 (+, C-Ar-5′), 123.4 (q, J = 272.6 Hz, C$_{quart}$, 2 × CF$_3$), 125.0 (q, J = 282.1 Hz, C$_{quart}$, CHCF$_3$), 128.0 (+, C-Ar-4′), 130.8 (+, C-Ar-6′), 132.6 (q, J = 32.9 Hz, C-Ar-3,5), 146.6 (C$_{quart}$, C-Ar-1), 157.5 (C$_{quart}$, C-Ar-2′); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −63.3 (s, 6F, 2 × ArCF_3), −73.6 (s, 3F, CHCF_3); IR (ATR): $\tilde{\nu}$ = 3457 (vw), 2850 (vw), 1625 (w), 1604 (w), 1531 (vw), 1492 (w), 1467 (w), 1443 (w), 1396 (m), 1359 (w), 1274 (m), 1245 (m), 1166 (m), 1117 (m), 1084 (m), 1050 (w), 1025 (m), 995 (w) cm^{-1}; MS (70 eV, EI): m/z (%) = 419/418/417 (0.3/5/18) [M$^+$], 350/349/348 (1/12/100) [M−CF$_3^+$], 190/189 (1/7) [C$_9$H$_8$F$_3$O$^+$]; HR-MS: m/z = 417.0777 (C$_{17}$H$_{12}$F$_9$NO), calcd.: 417.0775.

4-Chloro-*N*-[2,2,2-trifluoro-1-(1-methyl-1*H*-pyrrole-2-yl)-ethyl]aniline (7aa): According to the general procedure, 4-chloroaniline (**2a**, 426 mg, 3.34 mmol), CF$_3$ ketone **6a** (581 mg, 3.34 mmol) and AlMe$_3$ in heptane (8.5 mL, 8.5 mmol) were reacted in dry CH_2Cl_2 (30 mL). Addition of BH_3·SMe$_2$ in THF (7.1 mL, 14.1 mmol) and column chromatography (*c*-Hex/EtOAc, 25:1, v/v) afforded **7aa** as a yellow solid; yield: 963 mg (77%); R_f = 0.42 (*c*-Hex/EtOAc, 40/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.54 (s, 3H, CH_3), 3.95 (d, J = 7.8 Hz, 1H, NH), 4.97 (m, 1H, CHCF$_3$), 6.14 (dd, J = 3.7 Hz, J = 2.8 Hz, 1H, pyrrole-H-4), 6.33 (m, 1H, pyrrole-H-5), 6.64 (t, J = 2.1 Hz, 1H, Ar-H-5), 6.66 (t, J = 1.9 Hz, 1H, Ar-H-3), 6.67 (m, 1H, pyrrole-H-3), 7.15 (t, J = 3.3 Hz, 1H, Ar-H-6), 7.18 (t, J = 3.3 Hz, Ar-H-2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.2 (+, CH$_3$), 53.5 (q, J = 32.1 Hz, +, CH-CF$_3$), 107.5 (+, pyrrole-C-3), 108.5 (+, pyrrole-C-4), 114.5 (+, C-Ar-3,5), 124.0 (C$_{quart}$, C-pyrrole-2), 124.0 (+, C-pyrrole-5), 124.7 (C$_{quart}$, CCl), 125.0 (q, J = 282.8 Hz, C$_{quart}$, CF$_3$), 129.3 (+, C-Ar-2,6), 144.3 (C$_{quart}$, CNH); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −73.5 (s, 3F, CF_3); IR (KBr): $\tilde{\nu}$ = 3410 (m), 3107 (w), 3034 (w), 2977 (w), 2748 (w), 2819 (w), 2726 (vw), 2549 (vw), 1859 (w), 1751 (w), 1673 (w), 1597 (m), 1508 (m), 1421 (m), 1404 (m), 1355 (m), 1312 (m), 1294 (m), 1266 (m), 1239 (m), 1169 (s), 1130 (m), 1105 (m), 1090 (m), 1064 (m), 1003 (w), 914 (w) cm^{-1}; MS (70 eV, EI): m/z (%) = 290/289/288 (5/2/15) [M$^+$], 219 (1) [M−CF$_3^+$], 162 (100) [C$_7$H$_7$F$_3$N$^+$]; EI-HR-MS: m/z = 288.0639 (C$_{13}$H$_{12}$ClN$_2$F$_3$), calcd.: 288.0641; anal. calcd. for C$_{13}$H$_{12}$ClF$_3$N$_2$: N 9.70, C 54.08, H 4.19; found: N 9.39, C 54.37, H 4.51.

***N*-[2,2,2-Trifluoro-1-(1-methyl-1*H*-pyrrole-2-yl)ethyl]-3,5-bis(trifluoromethyl)aniline (7ag):** According to the general procedure, 3,5-bis(trifluoromethyl)aniline (**2g**, 123 mg, 0.565 mmol), CF$_3$ ketone **6a** (100 mg, 0.565 mmol) and AlMe$_3$ in heptane (0.85 mL, 0.85 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of BH_3·SMe$_2$ in THF (0.56 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 10:1, v/v) afforded **7ag** as a yellow solid; yield: 118 mg (54%); R_f = 0.39 (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.60 (s, 3H, CH_3), 4.43 (d, J = 7.9 Hz, 1H, NH), 5.07 (m, 1H, CHCF$_3$), 6.17 (dd, J = 3.7 Hz, J = 2.8 Hz, 1H, pyrrole-H-4), 6.39 (m, 1H, pyrrole-H-3), 6.70 (m, 1H, pyrrole-H-5), 7.09 (s, 2H, Ar-H-2,6), 7.31 (s, 1H, Ar-H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.1 (+, CH$_3$), 52.7 (q, J = 32.5 Hz, +, CHCF$_3$), 107.6 (+, C-pyrrole-3), 109.0 (+, C-pyrrole-4), 112.4 (m, +, C-Ar-2,4,6), 123.3 (q, J = 272.7 Hz, C$_{quart}$, CHCF$_3$), 123.6 (C$_{quart}$, C-pyrrole-2), 124.5 (+, C-pyrrole-5), 124.8 (q, J = 282.8 Hz, C$_{quart}$, 2 × Ar-CF$_3$), 132.8 (q, J = 33.0 Hz, C$_{quart}$, C-Ar-3,5), 146.4 (C$_{quart}$, C-Ar-6); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −73.4 (s, 3F, CHCF_3), −63.2 (s, 6F, 2 × Ar-CF_3); IR (KBr): $\tilde{\nu}$ = 3446 (w), 3397 (m), 3061 (w), 2954 (w), 2924 (w), 2854 (w), 2824 (w), 2675 (vw), 2527 (vw), 2236 (vw), 2122 (vw), 2025 (vw), 1969 (vw), 1743 (w), 1620 (w), 1526 (w), 1475 (m), 1441 (w), 1389 (w), 1352 (w), 1267 (m), 1170 (m), 1090 (m), 1064 (w), 996 (w) cm^{-1}; MS (70 eV, EI): m/z (%) = 391/390 (2/14) [M$^+$], 322/321 (1/6) [M−CF$_3^+$], 163/162 (8/100) [C$_7$H$_7$F$_3$N$^+$]; EI-HR-MS: m/z = 390.0777 (C$_{15}$H$_{11}$N$_2$F$_9$), calcd.: 390.0778; anal. calcd. for C$_{15}$H$_{11}$F$_9$N$_2$: N 7.18, C 46.17, H 2.84; found: N 7.04, C 46.39, H 2.81.

4-Chloro-*N*-[2,2,2-trifluoro-1-(1-methyl-1*H*-imidazole-2-yl)ethyl]aniline (7ba): According to the general procedure, 4-chloroaniline (**2a**, 214 mg, 1.68 mmol), CF$_3$ ketone **6b** (300 mg, 1.68 mmol) and AlMe$_3$ in heptane (5.05 mL, 5.05 mmol) were reacted in dry CH_2Cl_2 (10 mL). Addition of BH_3·SMe$_2$ in THF (1.68 mL, 3.36 mmol) and column chromatography (*c*-Hex/EtOAc, 10:1, v/v) afforded **7ba** as a yellow solid; yield: 198 mg (41%); R_f = 0.11 (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.70 (s, 3H, CH_3), 4.93 (m, 1H, CHCF$_3$), 5.14 (d, J = 7.9 Hz, 1H, NH), 6.68–6.72 (m, 2H, Ar-H-3,5), 6.91 (d, J = 1.0 Hz, 1H, imidazole-H-4), 7.07 (d, J = 1.1 Hz, 1H, imidazole-H-5), 7.14–7.18 (m, 2H, Ar-H-2,6); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.1 (+, CH$_3$), 53.6 (q, J = 32.6 Hz, +, CHCF$_3$), 115.3 (+,C-Ar-3,5), 122.7 (+, C-imidazole-4), 128.4 (+, C-imidazole-5), 124.4 (C$_{quart}$, C-Ar-1), 124.4 (q, J = 283.8 Hz, C$_{quart}$, CF$_3$), 129.3 (+, C-Ar-2,6), 140.3 (C$_{quart}$, C-Ar-4), 144.3 (C$_{quart}$, C-imidazole-2); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −73.9 (s, 3F, CF_3); IR (KBr): $\tilde{\nu}$ = 3391 (w), 3254 (w), 3175 (w), 3108 (w), 3035 (w), 2926 (w), 1871 (vw), 1601 (m), 1494 (m), 1420 (w), 1402 (w), 1345 (m), 1315 (m), 1269 (m), 1135 (m), 1093 (m), 1006 (w), 935 (w) cm^{-1}; MS (70 eV, EI): m/z (%) = 291/290/289 (15/7/46) [M$^+$], 222/221/220 (32/13/100) [M−CF$_3^+$], 164/163 (3/14) [C$_6$H$_6$F$_3$N$_2^+$], 83 (37), 58 (25), 43 (81); EI-HR-MS: m/z = 289.0596 (C$_{12}$H$_{11}$ClF$_3$N$_3$), calcd.: 289.0593.

***N*-[2,2,2-Trifluoro-1-(1-methyl-1*H*-imidazole-2-yl)ethyl]-3,5-bis(trifluoromethyl)aniline (7bg):** According to the general procedure, 3,5-bis(trifluoromethyl)aniline (**2g**, 123 mg, 0.561 mmol), CF$_3$ ketone **6b** (100 mg, 0.561 mmol) and AlMe$_3$ in heptane (0.84 mL, 0.84 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of BH_3·SMe$_2$ in THF (0.56 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 10:1, v/v) afforded **7bg** as a yellow oil; yield: 66.0 mg (30%); R_f = 0.06 (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.76 (s, 3H, CH_3), 5.03 (dq, J = 7.6 Hz, J = 5.7 Hz, 1H, CHCF$_3$), 5.83 (d, J = 7.6 Hz, 1H, NH), 6.97 (d, J = 1.1 Hz, 1H, imidazole-H-5), 7.10 (d, J = 1.1 Hz, 1H, imidazole-H-4), 7.13 (s, 2H, Ar-H-2,6), 7.28 (s, 1H, Ar-H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.2 (+, CH_3), 52.5 (q, J = 33.2 Hz, +, CHCF$_3$), 112.5 (m, +, C-Ar-4), 113.1 (m, +, C-Ar-2,6), 123.1 (+, C-imidazole-5), 123.2 (q, J = 272.6 Hz, C$_{quart}$, CHCF$_3$), 124.1 (q, J = 283.1 Hz, C$_{quart}$, 2 × Ar-CF$_3$), 128.5 (+, C-imidazole-4), 132.7 (q, J = 33.1 Hz, C$_{quart}$, C-Ar-3,5), 139.2 (C$_{quart}$, C-Ar-1), 146.5 (C$_{quart}$, C-imidazole-2); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −73.8 (m, 3F,

CHCF_3), −63.3 (m, 6F, 2×CF_3); IR (KBr): $\tilde{\nu}$=3228 (w), 3076 (w), 2923 (w), 2852 (w), 2372 (vw), 2098 (vw), 1741 (vw), 1625 (w), 1570 (w), 1526 (w), 1475 (w), 1398 (w), 1353 (w), 1325 (vw), 1278 (w), 1171 (w), 1140 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%)=392/391 (5/29) [M$^+$], 324/323/322 (1/12/89) [M−CF_3^+], 164/163 (1/7) [$C_6H_6F_3N_2^+$], 83 (21), 58 (28), 43 (100); HR-MS: *m/z*=391.0729 ($C_{14}H_{10}F_9N_3$), calcd.: 391.0730.

3-Nitro-*N*-[2,2,2-trifluoro-1-(1-methyl-1-imidazole-2-yl)-ethyl]aniline (7bj): According to the general procedure, 3-nitroaniline (**2j**, 77.0 mg, 0.561 mmol), CF_3 ketone **6b** (100 mg, 0.561 mmol) and $AlMe_3$ in heptane (0.84 mL, 0.84 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of BH_3·SMe_2 in THF (0.56 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 5:1, v/v) afforded **7bj** as a yellow oil; yield: 168 mg (61%); R_f=0.48 (*c*-Hex/EtOAc, 1:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.76 (s, 3H, CH_3), 5.07 (qd, *J*=5.9 Hz, *J*=7.9 Hz, 1H, C*H*CF_3), 5.68 (d, *J*=8.0 Hz, 1H, NH), 6.95 (d, *J*=1.1 Hz, 1H, imidazole-H-5), 7.07 (dd, *J*=8.2 Hz, *J*=2.4 Hz, 1H, Ar-H-4‘), 7.09 (d, *J*=1.2 Hz, 1H, imidazole-H-4), 7.33 (t, *J*=8.1 Hz, 1H, Ar-H-5′), 7.58 (t, *J*=2.2 Hz, 1H, Ar-H-2′), 7.64 (ddd, *J*=8.1 Hz, *J*=2.0 Hz, *J*=0.7 Hz, 1H, Ar-H-6′); ^{13}C NMR (100 MHz, $CDCl_3$): δ=29.7 (+, *C*H$_3$), 52.6 (q, *J*=32.9, +, *C*HCF$_3$), 107.1 (+, C-Ar-2), 114.1 (+, C-imidazole-5), 120.4 (+, C-Ar-4′), 122.9 (+, C-Ar-6′), 124.2 (q, *J*=283.6 Hz, C_{quart}, *C*F$_3$), 128.5 (C-Ar-5′), 130.1 (+, C-imidazole-4), 139.7 (C_{quart}, C-Ar-1′), 146.6 (C_{quart}, C-Ar-3′), 149.3 (C_{quart}, C-imidazole-2); ^{19}F NMR (376 MHz, $CDCl_3$): δ=−73.8 (s, 3F, C*F*$_3$); IR (KBr): $\tilde{\nu}$=3260 (m), 3148 (w), 3091 (w), 2924 (w), 2853 (w), 1950 (vw), 1620 (m), 1525 (m), 1495 (m), 1480 (m), 1438 (w), 1340 (m), 1264 (m), 1191 (m), 1162 (m), 1137 (m), 1114 (m), 995 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%)=301/300 (3/21) [M$^+$], 233/232/231 (0.6/6/46) [M−CF_3^+], 163 (4) [$C_6H_6F_3N_2^+$], 58 (36), 43 (100); EI-HR-MS: *m/z*=300.0836 ($C_{12}H_{11}O_2F_3N_4$), calcd.: 300.0834.

4-Chloro-*N*-[1,1,1-trifluoro-2-(1-methyl-1*H*-imidazole-2-yl)propan-2-yl]aniline (8ba): For preparation see general procedure and details for **7ba**. R_f=0.20 (*c*-Hex/EtOAc, 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.95 (s, 3H, CH_3), 3.69 (s, 3H, NCH_3), 4.21 (bs, 1H, N*H*), 6.14 (m, 2H, Ar-H-3,5), 6.87 (m, 1H, imidazole-H-5), 7.02 (m, 2H, Ar-H-2,6), 7.09 (m, 1H, imidazole-H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ=19.6 (+, *C*H$_3$), 34.8 (+, N*C*H$_3$), 61.5 (q, *J*=27.8 Hz, C_{quart}, *C*CF$_3$), 116.4 (+, C-Ar-3,5), 124.7 (C_{quart}, C-Ar-1), 124.8 (+, C-imidazole-5), 125.7 (q, *J*=286.0 Hz, C_{quart}, *C*F$_3$), 127.8 (+, C-imidazole-4), 129.3 (+, C-Ar-2,6), 141.1 (C_{quart}, C-Ar-4), 142.1 (C_{quart}, C-imidazole-2); ^{19}F NMR (376 MHz, $CDCl_3$): δ=−77.5 (s, 3F, C*F*$_3$); IR (KBr): $\tilde{\nu}$=3256 (s), 3178 (m), 3099 (m), 3033 (m), 2957 (w), 1876 (w), 1754 (w), 1706 (w), 1601 (s), 1522 (m), 1495 (s), 1400 (m), 1383 (m), 1347 (m), 1318 (m), 1277 (s), 1186 (s), 1169 (s), 1140 (s), 1093 (s), 1006 (m), 958 (m) cm^{-1}; MS (70 eV, EI): *m/z* (%)=305/304/303 (28/13/80) [M$^+$], 290/289/288 (3/3/9) [M−CH_3^+], 236/235/234 (32/13/100) [M−CF_3^+], 178/177 (7/40) [$C_7H_8F_3N_2^+$]; EI-HR-MS: *m/z*=303.0752 ($C_{13}H_{13}ClF_3N_3$), calcd.: 303.0750; anal. calcd. for $C_{13}H_{13}ClF_3N_3$: N 13.84, C 51.41, H 4.31; found: N 13.78, C 51.59, H 4.35.

***N*-Benzyl-2,2,2-trifluoro-1-phenylethanamine (11aa):** According to the general procedure, benzylamine (**9a**, 62.0 mg, 0.575 mmol), 2,2,2-trifluoroacetophenone (**1a**, 100 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of BH_3·SMe_2 in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 19:1, v/v) afforded **11aa** as a colourless oil; yield: 144 mg (94%); R_f=0.72 (*c*-Hex/EtOAc, 10/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.67 (d, *J*=13.4 Hz, 1H, CH_2), 3.83 (d, *J*=13.4 Hz, 1H, CH_2), 4.14 (q, *J*=7.5 Hz, 1H, C*H*CF$_3$), 7.28–7.36 (m, 5H, H_{arom}), 7.39–7.44 (m, 5H, H_{arom}); ^{13}C NMR (100 MHz, $CDCl_3$): δ=51.0 (-, *C*H$_2$), 63.4 (q, *J*=28.6 Hz, +, *C*HCF$_3$), 125.4 (q, *J*=281.3 Hz, C_{quart}, *C*F$_3$), 127.4 (+, C-Ar-4), 128.2 (+, C_{arom}), 128.5 (+, C_{arom}), 128.6 (+, C_{arom}), 128.7 (+, C_{arom}), 129.0 (+, C-Ar-4′), 134.2 (C_{quart}, C-Ar-1), 139.0 (C_{quart}, C-Ar-1′); ^{19}F NMR (376 MHz, $CDCl_3$): δ=−73.9 (s, 3F, C*F*$_3$); IR (KBr): $\tilde{\nu}$=3346 (w), 3065 (m), 3032 (m), 2853 (w), 1955 (vw), 1605 (w), 1495 (m), 1455 (m), 1375 (m), 1263 (s), 1169 (s), 1124 (s), 1078 (m), 1029 (m), 973 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%)=265 (45) [M$^+$], 196 (100) [M−CF_3^+], 159 (58) [$C_8H_6F_3^+$], 109 (53), 91 (83) [$C_7H_7^+$], 77 (15) [$C_6H_5^+$]; HR-MS: *m/z*=265.1078 ($C_{15}H_{14}NF_3$), calcd.: 265.1078.

2,2,2-Trifluoro-1-(2-methoxyphenyl)-*N*-methylethanamine (12ea): According to the general procedure, methylamine (**10a**, 0.58 mL, 1.15 mmol, 2 M in THF), 2,2,2-trifluoro-1-(2-methoxyphenyl)ethanone (**1e**, 118 mg, 0.575 mmol) and $AlMe_3$ in heptane (0.86 mL, 0.86 mmol) were reacted in dry CH_2Cl_2 (2 mL). Addition of BH_3·SMe_2 in THF (0.58 mL, 1.15 mmol) and column chromatography (*c*-Hex/EtOAc, 14:1, v/v) afforded **12ea** as a colourless oil; yield: 94.0 mg (74%); R_f=0.32 (*c*-Hex/EtOAc, 10/1). ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.41 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 4.64 (q, *J*=7.8 Hz, 1H, C*H*CF$_3$), 6.93 (d, *J*=8.3 Hz, 1H, Ar-H-3), 7.01 (td, *J*=7.6 Hz, *J*=0.9 Hz, 1H, Ar-H-4), 7.33 (ddd, *J*=8.3 Hz, *J*=7.6 Hz, *J*=1.7 Hz, 1H, Ar-H-5), 7.38 (d, *J*=8.3 Hz, 1H, Ar-H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ=34.6 (+, *C*H$_3$), 55.7 (+, O*C*H$_3$), 58.6 (q, *J*=29.2 Hz, +, *C*HCF$_3$), 111.0 (+, C-Ar-3), 120.9 (+, C-Ar-5), 122.8 (C_{quart}, C-Ar-1), 125.7 (q, *J*=281.8 Hz, C_{quart}, *C*F$_3$), 128.2 (+, C-Ar-6), 129.8 (+, C-Ar-4), 158.0 (C_{quart}, C-Ar-2); ^{19}F NMR (376 MHz, $CDCl_3$): δ=−73.5 (s, 3F, C*F*$_3$); IR (KBr) $\tilde{\nu}$=3347 (w), 2945 (m), 2843 (w), 2807 (w), 1604 (m), 1590 (m), 1494 (m), 1466 (m), 1441 (m), 1363 (m), 1247 (s), 1162 (s), 1131 (s), 1052 (m), 1029 (m), 989 (w) cm^{-1}; MS (70 eV, EI): *m/z* (%)=219 (2) [M$^+$], 189 (2) [M−NHCH_3^+], 150 (100) [M−CF_3^+], 107 (14) [$C_7H_7NO^+$], 77 (11) [$C_6H_5^+$]; HR-MS: *m/z*=219.0869 ($C_{10}H_{12}NOF_3$), calcd.: 219.0870.

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