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Trifluoromethyl-substituted heteroolefins (Schiff's bases): syntheses and chemical properties [1]

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Abstract

5,5,5-trifluoro-4-trifluoromethyl-pent-3-en-2-one (**1**) and 5,5,5-trifluoro-4-methyl-pent-3-en-2-one (**2**) are reacted with a number of ring-substituted anilines to give the corresponding imines **3–16** and **17**. The preparation of **2** is accompanied by three unsaturated ketones (**2a–c**). The bistrifluoromethylated imines **3–16** exist as a mixture of their non-separable *syn* and *anti* isomers, which were identified by ^{13}C, ^{19}F and ^{1}H NMR spectroscopy. Some of these imines react with 2,2-bis(trifluoromethyl)-ethylene-1,1-carbodinitrile (BTF) at room temperature to 4,4-bistrifluoro-1,4-dihydropyridinium derivatives (**18–22**). Two side-products, 1-amino-cyclo-pent-1-ene (**23–27**) and 1-imino-cyclopent-2-ene derivatives (**28–32**) are also obtained in these additions. Treatment of **1** with primary alkylamines yielded the anti-Michael products **33–38**. With 2-amino-benzylamine **1** formed the benzodiazepine derivative **39**. © Elsevier Science S.A.

Keywords: Anti-Michael addition; Trifluoromethyldienes; α,β-Unsaturated imines; Homonuclear FF long-range couplings; Cycloadditions involving 2,2-bis(trifluoromethyl)-ethylene-1,1-carbodinitrile (BTF); Benzodiazepine

1. Introduction

Ever since Laurent and Gerhard [1] synthesised the first organic imine by condensation of benzylaldehyde with aniline, numerous investigations deal with [3,4] this class of compounds, also known as Schiff's bases [2]. Knoevenagel [5] has described acetonanil, although there is confusion about its existence and structure [6,7]. Reddelien and Thurm [8] have proposed the structure of the material to be 2,2,4-trimethyl-1,2-dihydroquinoline. Later Craig [9] and Tung [10] have shown this structure to be correct. These authors showed, that acetonanil reacted with another mole of acetone to give mesityloxidanil which underwent an electrocyclisation process to the already mentioned 2,2,4-trimethyl-1,2-dihydroquinoline. Burger et al. [11] have shown, that a series of 2-substituted 4,4-bis(trifluoromethyl)-1-phenyl-1,3-diazabuta-1,3-dienes cyclised spontaneously to the corresponding 4,4-bis(trifluoromethyl)-3,4-dihydro-quinazoline derivatives. In numerous other reports [12–14] analogous reactions were presented. A simple route to these imines is the condensation of an enone with an aromatic amine. Such reactions were not yet known with electron-deficient compounds such as the enones 5,5,5-trifluoro-4-trifluoromethyl-pent-3-en-2-one (**1**) and 5,5,5-trifluoro-4-methyl-pent-3-en-2-one (**2**). During the study of the behaviour of **1** and **2** with ring-substituted anilines it was found that many of the resulting α,β-unsaturated imines were stable over several months. It was thus possible to investigate the reactions of these conjugated heterodienes with ring-building agents, such as isonitriles, olefins and especially 2,2-bis(trifluoromethyl)-ethylene-1,1-carbodinitrile (BTF).

2. Results and discussion

The starting material **1** $(CF_3)_2C{=}CH{-}C(O)CH_3$, was synthesised according to an optimised literature method [15] in 95% yield from $(CF_3)_2CO$ and $(C_6H_5)_3P{=}CHC(O)CH_3$ in the presence of hydroquinone without solvent [16]. Similarly **2** was obtained from $CF_3C(O)CH_3$ and $(C_6H_5)_3P{=}CHC(O)CH_3$ [17] in a yield of about 85%, and was fully characterised for the first time. This procedure provides besides the main compound E-5,5,5-trifluoro-4-methyl-pent-3-en-2-one (**2**) additionally three side-products as shown in Scheme 1, namely Z-5,5,5-trifluoro-4-methyl-pent-3-en-2-one (Z-$(CF_3)(CH_3)C{=}CHC(O)CH_3$, $C_6H_7F_3O$, **2a**), 4-trifluoromethyl-pent-4-en-2-one ($H_2C{=}C(CF_3)CH_2C(O)CH_3$, $C_6H_7F_3O$, **2b**) and 1,1,1,7,7,7-hexafluoro-2,6-dimethyl-6-hydroxy-hept-2-en-4-one ($CF_3C(CH_3){=}CH{-}$

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[1] Dedicated to Prof. Dr. W. Siebert on the occasion of his 60th birthday.

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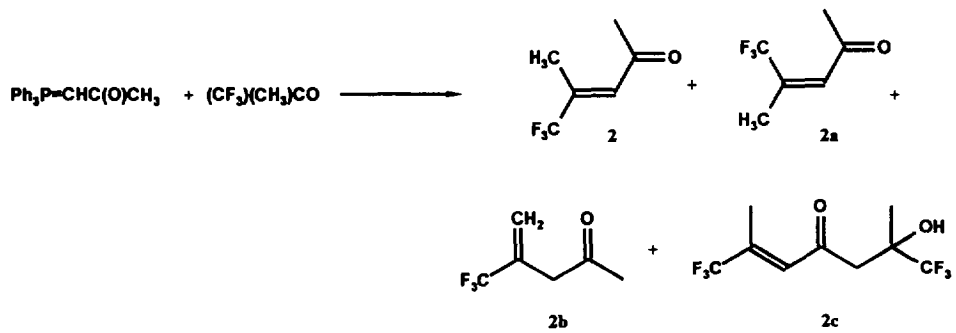
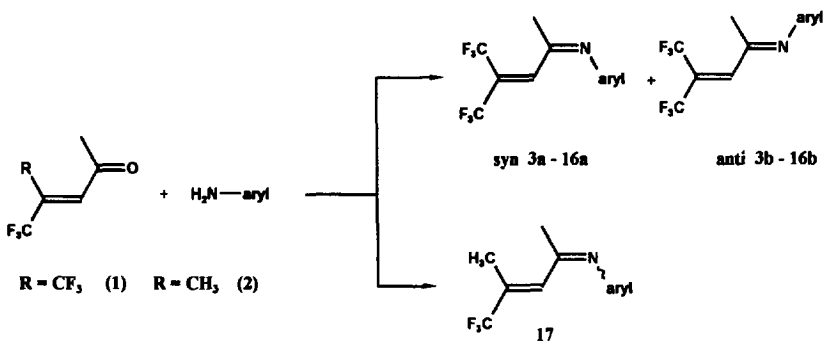


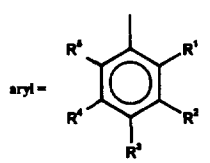
Scheme 1.

$C(O)CH_2C(CH_3)(OH)$–CF_3, $C_9H_{10}F_6O_2$, **2c**) which were also isolated and characterised.

During the preparation of **1** the side-product 5,5-bis(trifluoromethyl)-2-[(2,2,2-trifluoro-1-trifluoromethyl)-ethyl]-tetrahydrofurane-3-one is formed by cyclisation of **1** with additional $(CF_3)_2CO$. No such reaction takes place between **2** and $CF_3C(O)CH_3$; instead linear **2c** is obtained. This observation provides evidence for the lower electrophilicity of the trifluoroisopropylidene group compared with the hexafluoro moiety.

By treatment of **1** and **2** with substituted anilines in boiling benzene the generation of the stable α,β-unsaturated imines is possible. Starting with **1** the products **3–16** are obtained as mixtures of *syn* and *anti* isomers. The ratio of *syn* (**a**) to *anti*



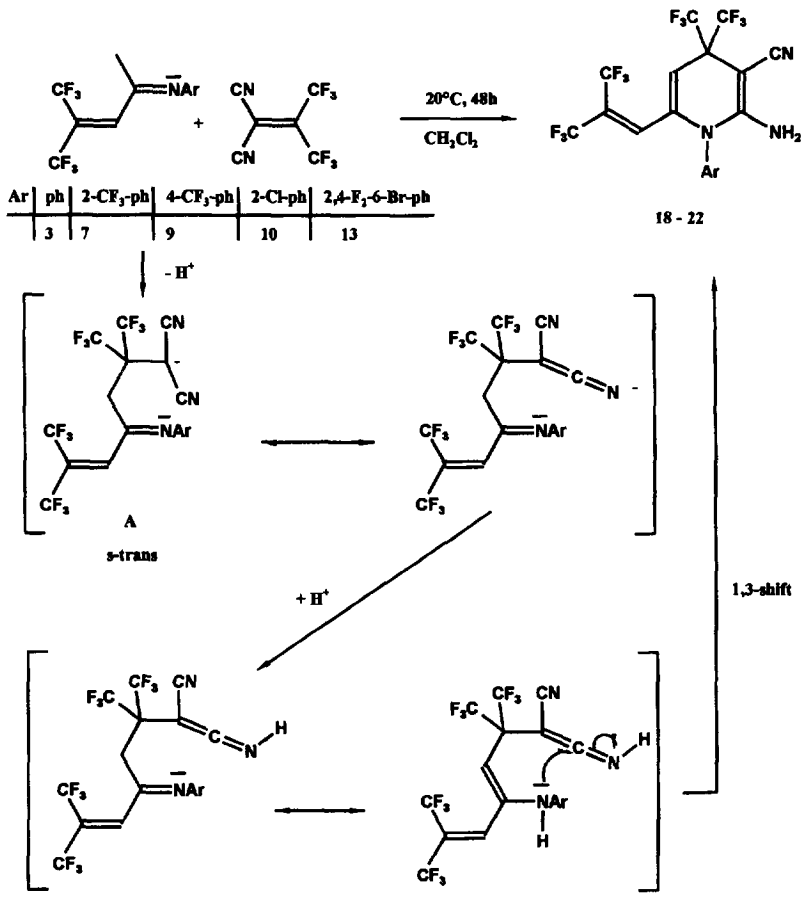


R	R^1	R^2	R^3	R^4	R^5	No.	*syn/anti* ratio
CF_3	H	H	H	H	H	3a/b	1:2.4
CF_3	F	H	H	H	H	4a/b	1:1.9
CF_3	H	F	H	H	H	5a/b	1:1.9
CF_3	H	H	F	H	H	6a/b	1:2.4
CF_3	CF_3	H	H	H	H	7a/b	1:3.4
CF_3	H	CF_3	H	H	H	8a/b	1:3.2
CF_3	H	H	CF_3	H	H	9a/b	1:1.7
CF_3	Cl	H	H	H	H	10a/b	1:2.9
CF_3	H	Cl	H	H	H	11a/b	1:2.8
CF_3	Cl	H	Cl	H	H	12a/b	1:2.9
CF_3	F	H	F	H	Br	13a/b	1:2.5
CF_3	CH_3	H	H	H	CH_3	14b	anti only
CF_3	F	F	F	F	F	15a/b	1:2.1
CF_3	SCF_3	H	H	H	H	16a/b	1:0.4
CH_3	CF_3	H	H	H	H	17	-

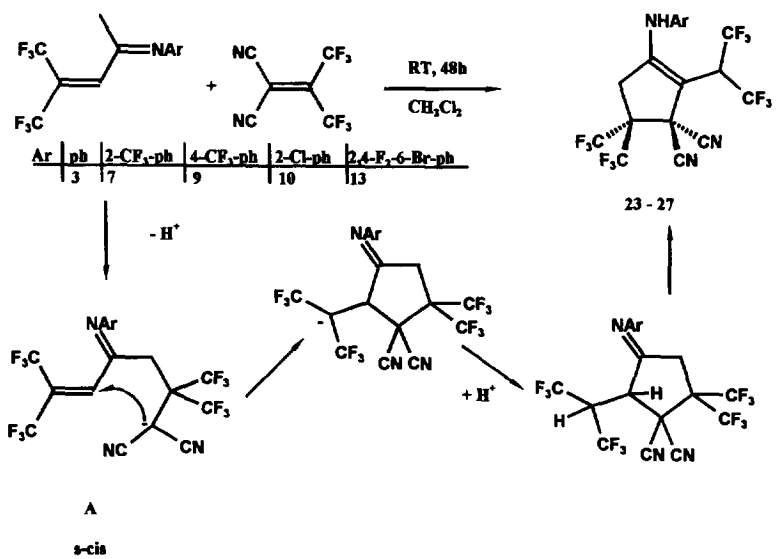
Scheme 2.

(**b**) isomers is determined by ^1H NMR spectroscopy and is given in Scheme 2. The materials **3–16** show no coalescence of the ^{19}F NMR signals up to 90 °C. Also H migration and formation of the eneamine cannot be observed, neither by spectroscopic methods nor by metalation reactions. It can hence be stated, that for $R = CF_3$ fixed isomers are produced and a dynamic isomer exchange can be excluded.

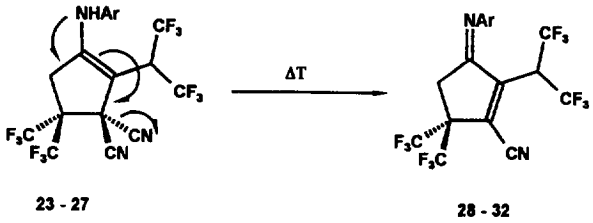
Except for o-SCF_3-anil (**16**) the *anti* moiety prevails. The described compounds **3–17** are obtained as yellow oils in good yields (ca. 60–95%). Neither variation of concentrations nor the presence of catalysts, such as PPh_3, $TiCl_4$ and trifluoroacetic anhydride (TFAA), initiate a cyclisation. Following the synthetic routes of Huisgen et al. [18,19], with the use of BTF as a building block for [4+2]-, [2+2]-



Scheme 3.



Scheme 4.

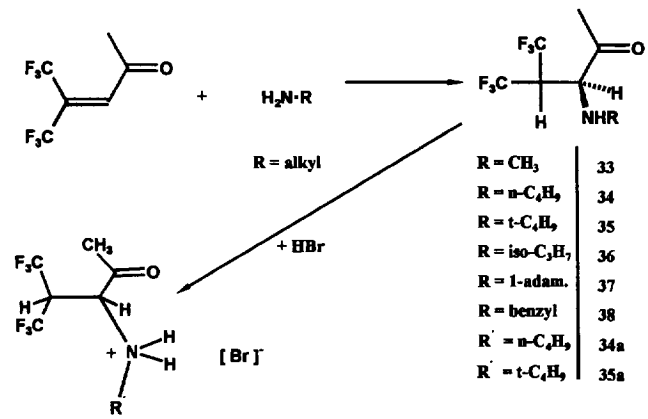


Scheme 5.

cycloadditions and vinylic proton substitution, the substances **3**, **7**, **9** and **13**, all containing a hexafluoroisopropylidene unit, are found to react with BTF. The reactions yield the 1-aryl-2-amino-4,4-bis(trifluoromethyl)-6-[(3,3,3-trifluoro-2-trifluoromethyl)-1-propanyl]-1,4-dihydropyridin-3-carbonitrile derivatives **18–22**, which are comparable with products in analogous reactions published by Fokin et al. [20,21] (see Scheme 3), 1-(*N*-aryl)-amino-2-[2,2,2-trifluoro-1-trifluoromethyl(ethyl)]-4,4-bis(trifluorome-thyl)-cyclopent-1-en-3,3-dicarbonitrile derivatives **23–27** (see Scheme 4) and the 1-(*N*-aryl)-imino-2-[2,2,2-trifluoro-1-trifluoromethyl(ethylene)]-4,4-bis(trifluoromethyl)-cyclopent-2-en-3-carbonitrile derivatives **28–32** (see Scheme 5). In contrast to Huisgen's results, compounds **3–16** do not undergo [4+2]-cycloaddition reactions with BTF or any other olefin and [4+1]-cycloaddition reactions with isonitriles by standard organic pathways. Formation of the dihydropyridinium derivatives **18–22** is explained by the mechanism given in Scheme 3.

Owing to the electrophilic properties of the hexafluoroisopropylidene group the initially generated bis-CN-substituted anion (**A'**) from the s-cis conformation (Scheme 4) attacks the double bond of this group. Conformation A, the s-trans form of the bis-CN-substituted anion, is involved in an ionic resonance and a six-membered ring system is formed, according to the mechanism suggested in Scheme 3. Ortho-substituted imines afforded the best yields.

Heating 1-amino-cyclopent-1-enes **23–27** either neat or in acetone solution results in the loss of HCN. It is not clear, however, whether HCN is released as a gas or in another form. After this rearrangement the 1-imino-cyclopent-2-ene derivatives **28–32** are obtained (see Scheme 5).



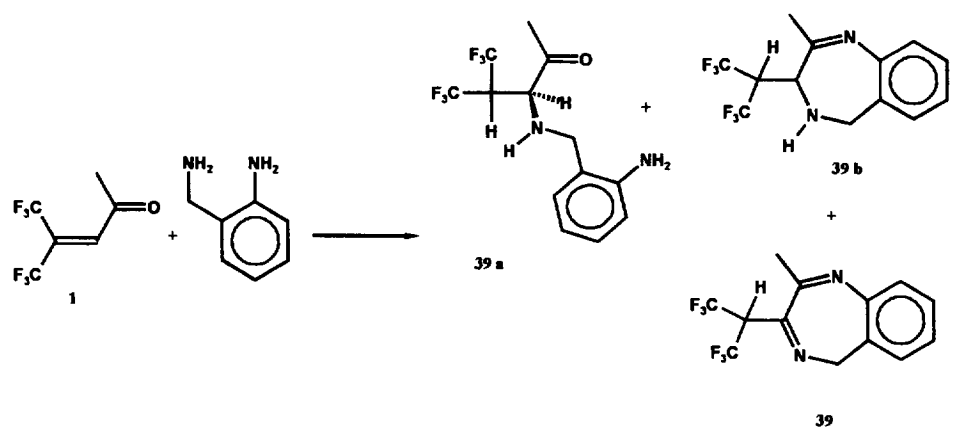
Scheme 6.

Treatment of **17** with BTF leads only to a dihydropyridine derivative. The formation of the corresponding cyclopentene derivatives is not observed owing to the lower electrophilicity of the trifluoroisopropylidene group.

With alkylamines, **1** reacts quantitatively as expected to give in a vigorous reaction the anti-Michael products **33–38** as shown in Scheme 6. The colourless liquids or white solids are unstable and decompose after about four weeks. The reaction with methylamine proceeds explosively and **33** is characterised only by GC–MS. Treatment of **34** and **35**, dissolved in benzene, with gaseous HBr provides the very stable white salts **34a** and **35a**. Both were characterised by elemental analysis and NMR spectroscopy. Their chemical shifts (^{1}H, ^{19}F and ^{13}C NMR) are less different from **34** and **35**.

The different behaviour of **1** in comparison with **2** toward primary aryl- and primary alkylamines leads to the idea to combine both types of reactions. Thus treatment of **1** with 2-amino-benzylamine leads to the benzodiazepine derivative **39** as the isolated main product. Additionally the side-products **39a**, which is formed by an anti-Michael addition, and **39b**, generated by intramolecular condensation of **39a** we observed (see Scheme 7). Both are only identified by GC–MS analysis and could not be separated as pure compounds.

Another interesting observation is a homonuclear FF long-range coupling in compounds **4a/b**, **7a/b**, **13a/b** and **15a/b**, proved by decoupling experiments. All these substances



Scheme 7.

are substituted in ortho positions. The ^{19}F NMR spectra of each of the E-CF_3 groups display splitting patterns according to the number of fluorine atoms at the ortho position of the aromatic ring. In case of compounds **4a/b** and **13a/b** we obtain ^{8}J couplings which result in doublets of quartets, in the case of **15a/b** in a triplet of quartets. In **7a/b** there are even ^{9}J couplings which result in a quartet of quartet. The following values are measured: **4a** 2.8 Hz, **4b** 4.3 Hz, **7a** 1.0 Hz, **7b** 1.9 Hz, **13a** 5.3 Hz, **13b** 5.3 Hz, **15a** 3.5 Hz, **15b** 4.1 Hz.

The signal patterns of the ortho fluorine atoms of compounds **13a/b** are more complex than those of **4a/b**, **7a/b** and **15a/b**. Apparently, there is a through-space coupling between the fluorine atoms and, in the case of **13a** (*syn*) the vinyl proton, and in the case of **13b** (*anti*) the methyl protons; both coupling constants are about 1 Hz.

3. Experimental

Volatile compounds were handled in a vacuum line and air-sensitive solids in a glove box (Co. M. Braun GmbH, München). Solvents were distilled before use and dried according to published procedures [22]. Deuterated solvents were dried and transferred from activated molecular sieves (4 Å). Microanalyses: Carlo-Erba Elemental analyser model 1106. NMR: $CDCl_3$ solutions, Bruker WM 250 PFT, standards used: $Si(CH_3)_4$ (^1H, ^{13}C) and $CFCl_3$ (^{19}F). IR: Bruker FT-IR IFS 85 (4000–400 cm^{-1}), solids as KBr pellets and liquids as capillary films. Very weak bands and shoulders are not recorded. MS: Varian MAT CH7 (70 eV). GC–MS: Hewlett Packard 5989 A, combined with a Hewlett Packard 5890 (12.5 m capillary column covered with OV1), 70 eV; CI, methane. Analytical gas chromatography: Hewlett Packard 5890 Serie III and Varian Aerograph 920, stationary phase: OV 1, OV 17, OV 101 and Carbowax 20M. Preparative gas chromatography: Perkin-Elmer F 21; stationary phase, OV 17 and OV 1.

Starting materials such as anilines and alkylamines are commercially available and were used without further purification. Compound **1** [16] and BTF [23] are prepared by published methods.

3.1. E-5,5,5-trifluoro-4-methyl-pent-3-en-2-one (2)

50.0 g (0.16 mol) of triphenylphosphoranyliden-2-propanone and 5.0 g (45.4 mmol) of 1,4-hydroquinone were mixed and filled into a 750 ml Carius tube with a Teflon-stemmed glass Young valve, into which 17.6 g (0.16 mol) of 1,1,1-trifluoroacetone were condensed in vacuo. The closed tube was shaken for about 15 minutes. While the reaction took place the mixture warmed up. After cooling to room temperature all liquids, including the three byproducts **2a–c**, were distilled. All four products were further purified by preparative gas chromatography (OV 17, 110 °C). Yield 14.4 g (59.2%). b.p. 102.5 °C. IR (Film) (cm^{-1}): 1706 (C=O), 1649 (C=C), 1104–1300 (C–F). ^1H NMR: $\delta = 1.9$ (d, CH_3, $^4J(HH) = 1.5$ Hz), 2.1 (d, CH_3, $^4J(HH) = 1.5$ Hz), 6.4 (m, C=C–H). ^{13}C NMR: $\delta = 11.8$ (dq, $^1J(CH) = 130.3$ Hz, $^3J(CH) = 6.7$ Hz, 4-CH_3), 31.4 (q, $^1J(CH) = 127.8$ Hz, C1), 123.2 (q, $^1J(CF) = 274$ Hz, C5), 126.7 (d, $^1J(CH) = 158.3$ Hz, C3), 138.7 (q, $^2J(CF) = 29.9$ Hz, C4), 197.7 (s, C2). ^{19}F NMR: $\delta = -71.6$ (s, E-CF_3). MS (EI), *m/z* (%): 152 (40) [M^+] 137 (100) [$M^+ - CH_3$], 132 (17) [$M^+ - HF$], 109 (10) [$M^+ - CH_3$–CO], 69 (8) [CF_3]. $C_6H_7F_3O$ (152.1): calc. C 47.4, H 4.6; found C 47.3, H 4.5%.

3.2. Z-5,5,5-trifluoro-4-methyl-pent-3-en-2-one (2a)

Yield 0.6 g (2.5%). IR (film) (cm^{-1}): 1712 (C=O), 1133–1286 (C–F). ^1H NMR: $\delta = 1.9$ (s, CH_3), 2.2 (s, CH_3), 6.1 (s, C=C–H). ^{13}C NMR: $\delta = 17.3$ (dq, $^1J(CH) = 131.0$ Hz, $^3J(CH) = 6.4$ Hz, 4-CH_3), 30.3 (q, $^1J(CH) = 128.4$ Hz, C1), 122.6 (q, $^1J(CF) = 274.7$ Hz, C5), 130.3 (q, $^2J(CF) = 31.8$ Hz, C4), 134.0 (m, C3), 199.5 (m, C2). ^{19}F NMR: $\delta = -64.6$ (s, Z-CF_3). MS (EI), *m/z* (%):152 (13) [M^+] 137 (100) [$M^+ - CH_3$], 109 (7) [$M^+ - CH_3$–CO], 83 (2) [$M - CF_3$], 69 (7) [CF_3]. $C_6H_7F_3O$ (152.1): calc. C 47.4, H 4.6; found C 47.8, H 4.6%.

3.3. 4-Trifluoromethyl-pent-4-en-2-one (2b)

Yield 1.76 g (7.2%), b.p. 126.0 °C. IR (film) (cm^{-1}): 1730 (C=O), 1126–1240 (C–F). ^1H NMR: $\delta = 2.15$ (s,

Table 1
Educts, yields, boiling points, formulae and analyses

Educts [a] [amounts, g]	Product g (yield %)	Boiling point (°C/1 Torr)	Formula (mol weight)	Analysis							
				Found (%)				Calculated (%)			
				C	H	N	Cl	C	H	N	Cl
1, H_2N–C_6H_5 [2.3]	**3**, 3.1 (45.9)	56.5	$C_{12}H_9F_6N$ (281.2)	51.3	3.4	5.3	–	51.3	3.2	5.0	–
1, H_2N-2-F-C_6H_4 [2.7]	**4**, 5.8 (79.5)	58.5	$C_{12}H_8F_7N$ (299.2)	48.4	2.9	5.0	–	48.1	2.7	4.7	–
1, H_2N-2-CF_3-C_6H_4 [3.9]	**7**, 7.1 (83.0)	62.5	$C_{13}H_8F_9N$ (349.2)	44.5	2.7	4.2	–	44.7	2.3	4.0	–
1, H_2N-2,4-F_2-6-Br-C_6H_2 [4.7]	**13**, 8.4 (86.8)	83.5	$C_{12}H_6F_8BrN$ (395.9)	36.4	1.4	3.8	–	36.4	1.5	3.5	–
1, H_2N–C_6F_5 [4.4]	**15**, 5.0 (55.4)	76	$C_{12}H_4F_{11}N$ (371.2)	39.0	1.0	4.2	–	38.8	1.1	3.8	–

[a] Stirring and refluxing for 24 h in benzene solution.

CH_3), 3.22 (s, CH_2) 5.46 (q, ^3J(HF) = 1.1 Hz, 1-H), 5.85 (q, ^3J(HF) = 1.4 Hz, 1-H). ^{13}C NMR: δ = 30.4 (q, ^1J(CH) = 127.8 Hz, C1), 43.8 (tt, ^1J(CH) = 128.7 Hz, ^3J(CH) = 7.6 Hz, C3), 122.8 (qtt, ^1J(CH) = 162.1 Hz, ^3J(CH) = 5.7 Hz, ^3J(CF) = 5.7 Hz, C5), 131.5 (q, ^2J(CF) = 31.2 Hz, C4), 123.0 (q, ^1J(CF) = 273.4 Hz, CF_3), 203.1 (q, ^2J(CH) = 5.7 Hz, C2). ^{19}F NMR δ = −69.5 (s, CF_3). MS (EI), *m/z* (%):152 (17) [M^+] 137 (13) [$M^+ - CH_3$], 133 (20) [$M^+ - F$], 109 (100) [$M^+ - CH_3$–CO], 83 (14) [$M^+ - CF_3$], 69 (53) [CF_3]. $C_6H_7F_3O$ (152.1): calc. C 47.4, H 4.6; found C 47.3, H 4.7%.

3.4. 1,1,1,7,7,7-Hexafluoro-2,6-dimethyl-6-hydroxy-hept-2-en-4-one (2c)

Yield 0.4 g (0.95%), characterised only by NMR spectroscopy. ^{1}H NMR: δ = 1.4 (s, CH_3), 2.2 (s, C=C–CH_3), 2.7 and 3.1 (AB system, ^2J(HH) = 16.5 Hz, CH_2), 6.6 (m, C=C–H). ^{19}F NMR: δ = −71.9 (s, C=C–CF_3), −83.3 (s, CF_3). ^{13}C NMR: δ = 12.6 (dq, ^1J(CH) = 124.0 Hz, ^3J(CH) = 5.7 Hz, C=C–CH_3), 21.4 (q, ^1J(CH) = 127.8 Hz, CH_3), 46.6 (t, ^1J(CH) = 127.8 Hz, CH_2), 73.2 (qq, ^2J(CF) = 30.5 Hz, ^2J(CH) = 3.8 Hz, C-6), 126.3 (dqq, ^1J(CH) = 160.3 Hz, ^3J(CF) = 3.8 Hz, ^3J(CH) = 3.5 Hz, C3), 141.9 (q, ^2J(CF) = 30.6 Hz, C2), 199.5 (s, C4).

3.5. General procedure for synthesising compounds 3–17

In a 250 ml three-necked flask equipped with a water selector, magnetic stirring bar and reflux condenser 24.3 mmol of **1** (5.0 g) or **2** (3.7 g), 24.3 mmol of the substituted aniline and 0.2 g of TFAA were dissolved in 100 ml of benzene. This mixture was stirred and refluxed for about 30 h. If the ratio aniline/product remained constant for about 4 h (detected by GC–MS analysis), a little TFAA was added, or aniline is used completely, the solvent is removed by distillation and the compounds were isolated by fractionated distillation in vacuo. In the trap cooled to 0 °C unreacted aniline and benzene condensed and in the trap cooled to −196 °C there is pure **3–17**. Essential data from substances **3, 4, 7, 13** and **15** are provided in Tables 1–3. Spectroscopic data on the other imines are available at the authors' address.

Characteristic spectroscopic data (^{1}H, ^{13}C and ^{19}F NMR) can be attributed to the following groups: $C_6H_{5-x}R_x$ and CF_3. The ^{1}H, ^{13}C and ^{19}F NMR chemical shifts d and the ^1J(CH) and ^1J(CF) coupling constants of the aromatic rings linked to nitrogen are observed to be nearly the same as in the already known corresponding anilines. The ^{13}C chemical shifts of the trifluoromethyl groups and the trans ^4J(HF) and ^3J(HC) coupling constants are observed to be within very narrow limits and are given as mean values. The other chemical shifts are given in Table 3.

For CF_3 groups in all molecules: δ(C) = 122 ± 2.5 ppm; ^1J(FC) = 273.5 ± 1.5 Hz; ^3J(HC) = 7.4 ± 1.5 Hz; ^4J(HF) = 1.5 ± 0.5 Hz.

3.6. General procedure for synthesising compounds 18–32

Into a 100 ml two-necked flask equipped with magnetic stirring bar, 4.3 mmol of compounds **3, 7, 10** and **13**, respectively 0.5 mmol of **9**, dissolved in 20 ml CH_2Cl_2 were filled. An equimolar amount of 0.92 g (4.3 mmol) BTF was added. After 96 h stirring at 20 °C a white solid precipitated and was isolated by filtration. It consisted mainly of dihydropyridinium derivatives **18–22**. The crude products were purified by thin layer chromatography (2 mm, 20 cm × 20 cm, Macherey and Nagel, eluent:pentane/CH_2Cl_2 1:1). The area containing the two side-products was extracted with CH_2Cl_2 and isolated by evaporating the solvent to dryness. The residue

Table 2
IR and mass spectra

	IR frequency (cm^{-1})	Mass spectra: *m/z* (%) [fragment]
3	1659 (s), 1486 (s), 1388 (s), 1291 (vvs), 1211 (vvs), 1166 (vvs), 961 (s), 754 (s), 721 (s), 698 (s)	281 (56) [M^+], 266 (62) [$M^+ - CH_3$], 262 (8) [$M^+ - F$], 212 (8), 118 (35), 77 (100), 69 (73)
4	1662 (s), 1490 (vs), 1455 (s), 1389 (vs), 1294 (vvs), 1221 (vvs), 1169 (vvs), 1104 (s), 962 (s), 752 (vs), 727 (s)	299 (70) [M^+], 284 (100) [$M^+ - CH_3$], 280 (14) [$M^+ - F$], 230 (2), 163 (14), 136 (57), 95 (42), 69 (14)
7	1665 (vs), 1605 (s), 1581 (s), 1489 (s), 1453 (s), 1389 (vs), 1320 (vvs), 1293 (vvs), 1264 (vvs), 1213 (vvs), 1168 (vvs), 1059 (vs), 1036 (vs), 962 (s), 905 (s), 806 (s), 780 (s), 762 (s), 720 (s), 661 (s), 649 (s)	349 (66) [M^+], 334 (100) [$M^+ - CH_3$], 330 (18) [$M^+ - F$], 280 (2), 186 (46), 145 (59), 95 (13), 69 (9)
13	1661 (s), 1609 (s), 1584 (s), 1469 (s), 1423 (s), 1387 (s), 1290 (vs), 1212 (vs), 1167 (vvs), 1111 (s), 995 (s), 961 (s), 842 (s)	(^{79}Br) 395 (100) [M^+], 380 (91) [$M^+ - CH_3$], 376 (14) [$M^+ - F$], 301 (15), 232 (69), 191 (11), 163 (41), 112 (59), 75 (33), 69 (30)
14	1293 (vs), 1208 (s), 1169 (vvs)	309 (32) [M^+], 294 (18) [$M^+ - CH_3$], 290 (5) [$M^+ - F$], 240 (12), 146 (52), 131 (12), 105 (100), 77 (79), 69 (36)
15	1662 (s), 1519 (vs), 1506 (vvs), 1387 (vs), 1290 (vs), 1221 (vs), 1173 (vvs), 996 (vs), 957 (vs)	–

Table 3
Spectroscopic data

	^{1}H NMR (ppm)	^{13}C NMR [ppm]	^{19}F NMR (ppm)
3a	2.3 (s, CH_3); 6.9 (s, C=C–H)	25.7 (q, ^1J(CH) = 129.1 Hz, C1), 122.9 (dqq, ^2J(CH) = 4.4 Hz, ^2J(CF) = ^2J(CF) = 30 Hz, C4), 140.7 (d, ^1J(CH) = 160.2 Hz, C3), 161.2 (q, ^2J(CF) = 5.7 Hz, C2)	−61.2 (q, ^4J(FF) = 6.7 Hz, E-CF_3), −64.9 (dq, ^4J(FF) = 6.8 Hz, ^4J(FH) = 1.5 Hz, Z-CF_3)
3b	1.9 (s, CH_3); 7.2 (s, C=C–H)	18.9 (q, ^1J(CH) = 129.7 Hz, C1), 123.4 (dqq, ^2J(CH) = 3.7 Hz, ^2J(CF) = ^2J(CF) = 29.4 Hz, C4), 142.5 (d, ^1J(CH) = 161.2 Hz, C3), 162.1 (q, ^2J(CF) = 5.7 Hz, C2)	−58.9 (q, ^4J(FF) = 6.8 Hz, E-CF_3), −65.0 (dq, ^4J(FF) = 6.8 Hz, ^4J(FH) = 1.6 Hz, Z-CF_3)
4a	2.3 (s, CH_3)	25.3 (q, ^1J(CH) = 129.5 Hz, C1), 123.8 (dqq, ^2J(CH) = 4.5 Hz, ^2J(CF) = ^2J(CF) = 32.8 Hz, C4), 140.3 (d, ^1J(CH) = 160.8 Hz, C3), 164.5 (q, ^2J(CH) = 6.9 Hz, C2)	−61.5 (dq, ^4J(FF) = 6.5 Hz, ^8J(FF) = 2.8 Hz, E-CF_3), −64.9 (m, Z-CF_3), −126.8 (m, F, ring)
4b	1.9 (s, CH_3)	19.2 (q, ^1J(CH) = 129.5 Hz, C1), 123.8 (dqq, ^2J(CH) = 4.5 Hz, ^2J(CF) = ^2J(CF) = 32.8 Hz, C4), 142.1 (dqq, ^1J(CH) = 162.3 Hz, ^3J(CF) = 2.6 Hz, ^3J(CH) = 3.0 Hz, C3), 164.9 (q, ^2J(CH) = 6.5 Hz, C2)	−58.9 (dq, ^4J(FF) = 6.8 Hz, ^8J(FF) = 4.3 Hz, E-CF_3), −64.9 (q, ^4J(FF) = 6.9 Hz, Z-CF_3), −126.8 (m, F, ring)
7a	2.4 (s, CH_3), 6.8 (s, C=C–H)	25.8 (q, ^1J(CH) = 129.7 Hz, C1), 139.6 (d, ^1J(CH) = 162.1 Hz, C3), 163.4 (q, ^2J(CH) = 7.3 Hz, C2)	−61.0 (qq, ^4J(FF) = 6.8 Hz, ^9J(FF) = 1.0 Hz, E-CF_3), −65.2 (dq, ^4J(FF) = 6.8 Hz, ^4J(FH) = 1.5 Hz, Z-CF_3), −62.48 (q, ^9J(FF) = 1.0 Hz, CF_3, ring)
7b	1.9 (s, CH_3), 7.2 (s, C=C–H)	19.8 (q, ^1J(CH) = 129.7 Hz, C1), 123.9 (dqq, ^2J(CH) = 3.7 Hz, ^2J(CF) = ^2J(CF) = 33.3 Hz, C4), 141.8 (d, ^1J(CH) = 164.0 Hz, C3), 164.3 (q, ^2J(CH) = 5.7 Hz, C2)	−59.3 (qq, ^4J(FF) = 6.8 Hz, ^9J(FF) = 1.9 Hz, E-CF_3), −65.3 (dq, ^4J(FF) = 6.8 Hz, ^4J(FH) = 1.5 Hz, Z-CF_3), −62.41 (q, ^9J(FF) = 2.0 Hz, CF_3, ring)
13a	2.5 (s, CH_3), 7.0 (s, C=C–H)	26.1 (q, ^1J(CH) = 129.7 Hz, C1), 124.7 (m, C4), 139.5 (d, ^1J(CH) = 164.0 Hz, C3), 167.3 (q, ^2J(CH) = 5.7 Hz, C2)	−61.2 (dq, ^4J(FF) = 5.3 Hz, ^8J(FF) = 5.3 Hz, E-CF_3), −64.8 (dq, ^4J(FF) = 5.3 Hz, ^4J(FH) = 1.5 Hz, Z-CF_3), −114.0 (m, p-F, ring), −117.9 (m, o-F, ring)
13b	2.0 (s, CH_3), 7.3 (s, C=C–H)	21.1 (q, ^1J(CH) = 129.7 Hz, C1), 124.6 (dqq, ^2J(CH) = 3.8 Hz, ^2J(CF) = ^2J(CF) = 34.3 Hz, C4), 141.2 (d, ^1J(CH) = 162.1 Hz, C3), 168.2 (q, ^2J(CH) = 5.7 Hz, C2)	−59.1 (dq, ^4J(FF) = 5.3 Hz, ^8J(FF) = 5.3 Hz, E-CF_3), −64.9 (dq, ^4J(FF) = 5.3 Hz, ^4J(FH) = 1.5 Hz, Z-CF_3), −114.7 (m, p-F, ring), −118.3 (m, o-F, ring)
15a	2.4 (s, CH_3), 6.9 (s, C=C–H)	26.3 (q, ^1J(CH) = 131.7 Hz, C1), 170.6 (m, C2)	−61.9 (tq, ^4J(FF) = 6.8 Hz, ^8J(FF) = 3.5 Hz, E-CF_3), −65.2 (dq, ^4J(FF) = 6.7 Hz, ^4J(FH) = 1.5 Hz, Z-CF_3), −151.5 (m, o-F, ring), −160.5 (m, p-F, ring)
15b	2.0 (s, CH_3), 7.1 (s, C=C–H)	21.2 (q, ^1J(CH) = 129.7 Hz, C1), 170.5 (m, C2)	−59.6 (tq, ^4J(FF) = 6.9 Hz, ^8J(FF) = 4.1 Hz, E-CF_3), −65.4 (dq, ^4J(FF) = 6.9 Hz, ^4J(FH) = 1.5 Hz, Z-CF_3), −151.7 (m, o-F, ring), −161.1 (m, p-F, ring), −163.3 (m, m-F)

was dissolved in 2.5 ml pentane and refluxed for 2 h. While cooling to room temperature the white solids **23–27** precipitated. This procedure was repeated several times. Finally the solvent was removed and compounds **28–32** were purified by sublimation in vacuo at 35 °C. Essential data are given in Tables 4–6.

3.7. General procedure for synthesising the compounds ***33–38***

Into a 250 ml three-necked flask equipped with magnetic stirring bar, dropping funnel and reflux condenser 2.0 g (9.7 mmol) of **1** were dissolved in 50 ml diethyl ether. After

Table 4
Educts, yields, melting points, formulae and analyses

Educts [a] [amounts, g]	Product (g) (yield %)	Melting point (°C)	Formula (mol weight)	Analysis							
				Found (%)				Calculated (%)			
				C	H	N	Cl	C	H	N	Cl
3 [1.2]	**18**, 51.7 mg (2.4)	256	$C_{18}H_9F_{12}N_3$ (495.2)	43.3	1.6	8.1	–	43.6	1.8	8.5	–
7 [1.5]	**19**, 2.18 (90.0)	278	$C_{19}H_8F_{15}N_3$ (563.0)	40.7	1.2	7.5	–	40.5	1.4	7.5	–
9 [0.2] [b]	**20**, traces	[c]	$C_{19}H_8F_{15}N_3$ (563.0)	563 (4) $[M^+]$, 494 (100) $[M^+ - CF_3]$, 145 (7.5)							
10 [1.4]	**21**, 1.4 (61.0)	268	$C_{18}H_8F_{12}ClN_3$ (529.5)	41.4	1.4	8.1	8.1	40.8	1.5	7.9	6.7
13 [1.7]	**22**, 18.6 mg (0.7)	211	$C_{18}H_6F_{14}BrN_3$ (609.9)	36.1	0.7	6.8	–	35.4	1.0	6.9	–
3 [1.2]	**23** traces	[c]	$C_{18}H_9F_{12}N_3$ (495.2)	495 (11) $[M^+]$, 468 (41) $[M^+ - HCN]$, 344 (88) $[M^+ - (CF_3)_2CH]$, 324 (100), 77 (28), 69 (22)							
7 [1.5]	**24**, 12.8 mg (0.5)	156	$C_{19}H_8F_{15}N_3$ (563.0)	40.6	1.7	7.3	–	40.5	1.4	7.5	–
9 [0.2] [b]	**25** traces	[c]	$C_{19}H_8F_{15}N_3$ (563.0)	563 (12) $[M^+]$, 536 (36), $[M^+ - HCN]$, 494 (3), 447 (25), 412 (86), 392 (100), 145 (34)							
10 [1.4]	**26**, 8.2 mg (0.4)	152	$C_{18}H_8F_{12}ClN_3$ (529.5)	41.0	1.5	7.9	7.1	40.8	1.5	7.9	6.7
13 [1.7]	**27**, 16.5 mg (0.6)	135	$C_{18}H_6F_{14}BrN_3$ (609.9)	36.0	0.5	6.9	–	35.4	1.0	6.9	–
3 [1.2]	**28** traces	[c]	$C_{17}H_8F_{12}N_2$ (468.2)	468 (100) $[M^+]$, 449 (24), 399 (22), 379 (83)							
7 [1.5]	**29**, 5.3 mg (0.2)	[d]	$C_{18}H_7F_{15}N_3$ (536.2)	41.2	2.0	5.0	–	40.3	1.3	5.2	–
9 [0.2] [b]	**30** traces	[d]	$C_{18}H_7F_{15}N_2$ (536.2)	536 (100) $[M^+]$, 517 (18) $[M^+ - F]$, 467 (18), 447 (83), 145 (41)							
10 [1.4]	**31** traces	[d]	$C_{17}H_7F_{12}ClN_2$ (502.7)	(^{35}Cl): 502 (100) $[M^+]$, 483 (9) $[M^+ - F]$, 433 (17), 413 (39), 111 (80)							
13 [1.7]	**32** traces	[d]	$C_{17}H_5F_{14}BrN_2$ (583.1)	(^{79}Br): 582 (59) $[M^+]$, 563 (5) $[M^+ - F]$, 513 (7), 493 (40), 69 (100)							

[a] Stirring for 96 h in CH_2Cl_2 solution at 20 °C.
[b] 0.5 mmol.
[c] Characterized only by GC–MS analysis.
[d] Decomposition at 80 °C.

Table 5
IR and mass spectra

	IR frequency [cm^{-1}]	Mass spectra: m/z (%) [fragment]
18	–	495 (5) $[M^+]$, 426 (100), 77 (29)
19	1545 (vs), 1320 (s), 1296 (s), 1249 (vs), 1203 (vs), 1187 (vs), 1131 (s), 1112 (s), 977 (s)	563 (5) $[M^+]$, 494 (100), 145 (8.5)
21	1545 (s), 1249 (vvs), 1202 (vvs), 1170 (s), 977 (s)	(^{35}Cl): 529 (3) $[M^+]$, 460 (100), 111 (9)
22	3372 (s), 2186 (s), 1675 (s), 1625 (s), 1589 (s), 1557 (vs), 1444 (s), 1398 (s), 1308 (s), 1248 (vs), 1216 (s), 1200 (s), 1174 (vvs), 1149 (s), 1120 (s), 979 (s), 956 (s), 851 (s)	(^{79}Br): 609 (3) $[M^+]$, 540 (100)
24	1659 (vs), 1417 (s), 1365 (s), 1355 (s), 1323 (s), 1282 (s), 1266 (vs), 1236 (vvs), 1219 (vvs), 1202 (s), 1174 (vvs), 1160 (s), 1133 (s), 1109 (s), 1093 (s), 1061 (s), 1036 (s), 769 (s), 706 (s)	563 (14) $[M^+]$, 536 (35), $[M^+ - HCN]$, 494 (4), 467 (8), 447 (23), 412 (90), 392 (100), 145 (27)
26		– (^{35}Cl): 529 (14) $[M^+]$, 502 (6) $[M^+ - HCN]$, 460 (2), 378 (100), 309 (33), 111 (24)
27	3458 (s), 1664 (vvs), 1609 (s), 1593 (s), 1491 (vvs), 1455 (s), 1430 (s), 1413 (s), 1368 (s), 1355 (vs), 1310 (vs), 1283 (vvs), 1263 (vvs), 1218 (vvs), 1188 (vvs), 1139 (s), 1114 (s), 1091 (s), 1072 (s), 1044 (s), 995 (s), 857 (vs), 814 (s), 710 (s), 705 (s), 698 (s)	(^{79}Br): 609 (10) $[M^+]$, 582 (14) $[M^+ - HCN]$, 540 (2), 458 (69), 379 (25), 69 (100)
29	1679 (s), 1371 (s), 1322 (vvs), 1272 (vvs), 1225 (vvs), 1174 (vvs), 1134 (vs), 1109 (vs), 1091 (s), 1005 (s), 765 (s), 704 (s)	536 (100) $[M^+]$, 517 (21) $[M^+ - F]$, 467 (19), 447 (79), 145 (36)

Table 6
Spectroscopic data

	^{1}H NMR (ppm)	^{13}C NMR (ppm)	^{19}F NMR (ppm)
18	5.5 (s, C^5-H) 7.1 (m, $(CF_3)_2C{=}C{-}H$) 7.4–7.9 (m, 5H)	47.9 (s, C3), 52.6 (qq, $^2J(CF) = 28.6$ Hz, $^2J(CF) = 28.6$ Hz, C4), 95.2 (d, $^1J(CH) = 175.5$ Hz, C5), 126.1 (qq, $^2J(CF) = {}^2J(CF) = 32.5$ Hz, $(CF_3)_2C{=}C$), 118.5 (s, CN), 126.8 (s, C6), 137.1 (d, $^1J(CH) = 161.1$ Hz, $(CF_3)_2C{=}C$), 155.6 (s, C2)	−58.0 (q, $^4J(FF) = 7.0$ Hz, E-CF_3) −65.4 (dq, $^4J(FF) = 7.0$ Hz, $^4J(FH) = 1.6$ Hz, Z-CF_3) −70.5 (dq, $^4J(FF) = 9.9$ Hz, $^4J(FH) = 1.8$ Hz, CF_3) −72.3 (dq, $^4J(FF) = 9.9$ Hz, $^4J(FH) = 1.4$ Hz, CF_3)
19	5.3 (s, C^5-H) 6.9 (m, $(CF_3)_2C{=}C{-}H$) 7.6–8.0 (m, 4H)	47.9 (s, C3), 52.4 (qq, $^2J(CF) = 28.6$ Hz, $^2J(CF) = 28.6$ Hz, C4), 95.2 (d, $^1J(CH) = 175.5$ Hz, C5), 126.0 (qq, $^2J(CF) = {}^2J(CF) = 31.9$ Hz, $(CF_3)_2C{=}C$), 118.5 (s, CN), 126.7 (s, C6), 137.1 (d, $^1J(CH) = 161.1$ Hz, $(CF_3)_2C{=}C$), 156.6 (s, C2)	−57.9 (q, $^4J(FF) = 7.0$ Hz, E-CF_3) −64.4 (dq, $^4J(FF) = 7.0$ Hz, $^4J(FH) = 1.2$ Hz, Z-CF_3) −70.7 (dq, $^4J(FF) = 10.4$ Hz, $^4J(FH) = 1.8$ Hz, CF_3) −72.5 (dq, $^4J(FF) = 9.1$ Hz, $^4J(FH) = 1.8$ Hz, CF_3) −60.7 (s, CF_3, ring)
21	5.3 (s, C^5-H) 7.2 (m, $(CF_3)_2C{=}C{-}H$) 7.6–8.0 (m, 4H)	47.4 (s, C3), 52.7 (qq, $^2J(CF) = 28.6$ Hz, $^2J(CF) = 28.6$ Hz, C4), 94.6 (d, $^1J(CH) = 175.5$ Hz, C5), 125.6 (qq, $^2J(CF) = {}^2J(CF) = 32.4$ Hz, $(CF_3)_2C{=}C$), 118.3 (s, CN), 126.6 (s, C6), 137.2 (d, $^1J(CH) = 161.1$ Hz, $(CF_3)_2C{=}C$), 155.8 (s, C2)	−57.7 (q, $^4J(FF) = 6.7$ Hz, E-CF_3) −64.4 (dq, $^4J(FF) = 6.7$ Hz, $^4J(FH) = 1.8$ Hz, Z-CF_3) −71.5 (dq, $^4J(FF) = 9.2$ Hz, $^4J(FH) = 1.8$ Hz, CF_3) −71.6 (dq, $^4J(FF) = 9.8$ Hz, $^4J(FH) = 1.8$ Hz, CF_3)
24	3.1 (s, CH_2) 3.9 (sep, $^3J(HF) = 8.3$ Hz), 7.1–7.7 (m, 4H)	33.4 (t, $^1J(CH) = 139.2$ Hz, C5), 47.2 (dsep, $^1J(CH) = 127.8$ Hz, $^2J(CF) = 31.5$ Hz, $(CF_3)_2CH$), 61.5 (m, C4), 85.1 (s, C2), 110.2 (s, CN), 135.5 (m, C1)	−63.5 (d, $^3J(HF) = 7.8$ Hz, 6F, $(CF_3)_2CH$) −67.7 (s, 6F, $C^4(CF_3)_2$) −62.3 (s, 3F, CF_3, ring)
26	3.1 (s, CH_2) 3.9 (sep, $^3J(HF) = 8.5$ Hz), 7.1–7.5 (m, 4H)	33.5 (t, $^1J(CH) = 141.1$ Hz, C5), 47.2 (dsep, $^1J(CH) = 127.8$ Hz, $^2J(CF) = 30.5$ Hz, $(CF_3)_2CH$), 62.0 (m, C4), 84.5 (s, C2), 110.4 (s, CN), 135.9 (m, C1)	−63.1 (d, $^3J(HF) = 7.5$ Hz, 6F, $(CF_3)_2CH$) −67.6 (s, 6F, $C^4(CF_3)_2$)
29	2.9 (s, CH_2) 5.2 (sep, $^3J(HF) = 8.3$ Hz, $(CF_3)_2CH$) 6.8–7.8 (m 4H)	30.8 (t, $^1J(CH) = 139.4$ Hz), 45.0 (dsep, $^1J(CH) = 128.3$ Hz, $(CF_3)_2CCH$), 61.5 (m, C4), 109.9 (s, CN), 167.5 (s, C1)	−63.5 (d, $^3J(FH) = 8.2$ Hz, 6F, $(CF_3)_2CCH$) −70.4 (s, 6F, $C^4(CF_3)_2$) −62.8 (s, 3F, CF_3, ring)

Table 7
Educts, yields, boiling points, formulae and analyses

Educts [a] [amounts, g]	Product (g) (yield %)	Melting point (°C)	Formula (mol weight)	Analysis					
				Found (%)			Calculated (%)		
				C	H	N	C	H	N
H_2N–CH_3 [0.3]	**33**, traces	[b]	$C_7H_9F_6NO$ (237.1)	194 (100) $[M^+ - C(O)CH_3]$, 86 (52) $[M^+ - (CF_3)_2CH]$ [4]					
H_2N–n-C_4H_9 [0.7]	**34**, 2.3 (84)	[c]	$C_{10}H_{15}F_6ON$ (279.2)	43.1	5.6	5.2	43.0	5.4	5.0
H_2N–t-C_4H_9 [0.7]	**35**, 2.0 (77.8)	[c]	$C_{10}H_{15}F_6ON$ (279.2)	43.8	5.4	5.2	43.0	5.4	5.0
H_2N–iso-C_3H_7 [0.57]	**36**, 1.83 (71.1)	[c]	$C_9H_{13}F_6ON$ (265.2)	41.3	4.7	4.9	40.8	4.9	5.3
H_2N–1-adamantyl [1.5]	**37**, 2.7 (77.3)	[c]	$C_{16}H_{21}F_6ON$ (357.1)	54.1	6.1	3.7	53.8	5.9	3.9
H_2N–CH_2–C_6H_5 [1.0]	**38**, 2.1 (73.2)	[c]	$C_{13}H_{13}F_6ON$ (313.0)	49.4	4.2	4.7	50.2	3.5	4.5

[a] Stirring for 2 h in diethylether solution at 0 °C.
[b] Characterized only by GC–MS analysis.
[c] Decomposition at 50 °C.
[d] EI-mode.

cooling to 0 °C by means of an ice bath an equimolar amount of the primary alkylamine, dissolved in 50 ml diethyl ether, was added dropwise while stirring. After 2 h the reaction was complete and the compounds **34–38** were isolated as described for **3–17**. Except **37** which was purified by column chromatography (Stationary phase: Silica gel, particle size: 60 mm, eluent:hexane/chloroform 1:1). For synthesising compound **33** 2.0 g of **1** dissolved in 65 ml diethyl ether was

placed into a 250 ml Carius tube with a Teflon-stemmed glass Young valve. An equimolar amount of methylamine was condensed into this solution in vacuo. After warming the mixture to the temperature of solid CO_2 **33** was identified in traces by GC–MS analysis. Essential data are given in Tables 7–9.

3.8. 1,2-Dehydro-2-methyl-3-[2,2,2-trifluoro-1-trifluoromethyl(ethyl)]-5H-1,4-diazepin (39)

In a 250 ml three-necked flask equipped with a magnetic stirring bar, a dropping funnel, a water selector and a reflux condenser 2.9 g (24.3 mmol) of 2-aminobenzylamine and

Table 8
IR and mass spectra

	IR frequency (cm^{-1})	Mass spectra: m/z (%) [fragment] PCI-mode
34	2962 (s), 2936 (s), 1726 (vs), 1380 (s), 1286 (vvs), 1211 (vs), 1091 (vs), 901 (s), 712 (s)	280 (3) [$M^+ + 1$], 236 (100) [$M^+ - C(O)CH_3$], 194 (57) [$236 - C_3H_6$, McLafferty], 180 (62) [$236 - C_4H_8$, Onium], 128 (8) [$M^+ - (CF_3)_2CH$], 57 (50) [n-C_4H_9]
35	2970 (s), 1732 (s), 1385 (s), 1369 (s), 1345 (s), 1286 (vs), 1214 (vs), 1175 (vvs), 1092 (vs), 713 (s), 660 (s)	280 (<0.5) [$M^+ + 1$], 236 (34) [$M^+ - C(O)CH_3$], 180 (100) [$236 - C_4H_8$, Onium], 128 (2) [$M^+ - (CF_3)_2CH$], 57 (83) [t-C_4H_9]
36	1284 (vvs), 1232 (s), 1213 (vs), 1163 (vs), 1090 (s)	266 (1) [$M^+ + 1$], 222 (50) [$M^+ - C(O)CH_3$], 180 (100) [$222 - C_3H_6$, Onium]
37	1281 (s), 1223 (s), 1176 (s), 1095 (s)	358 (11) [$M^+ + 1$], 314 (5) [$M^+ - C(O)CH_3$], 206 (14) [$M^+ - (CF_3)_2CH$], 135 (100) [$C_{10}H_{15}$]
38	1725 (s), 1284 (vvs), 1213 (vs), 1168 (vvs), 1092 (vs)	314 (3) [$M^+ + 1$], 270 (33) [$M^+ - C(O)CH_3$], 162 (6) [$M^+ - (CF_3)_2CH$], 91 (100) [C_6H_5–CH_2]

Table 9
Spectroscopic data

	^{1}H NMR (ppm)	^{13}C NMR (ppm)	^{19}F NMR (ppm)
34	2.3 (s, $C(O)CH_3$)	26.6 (q, ^1J(CH) = 128.4 Hz, C5), 49.0 (ddqq, ^1J(CH) = 129.7 Hz, ^2J(CH) = 5.7 Hz, ^2J(CF) = ^2J(CF) = 26.7 Hz, C2), 63.9 (d, ^1J(CH) = 133.5 Hz, C3), 205.8 (s, C=O)	−62.4 (dq, ^3J(HF) = 8.7 Hz, ^4J(FF) = 8.7 Hz, CF_3) −65.6 (dq, ^3J(HF) = 8.7 Hz, ^4J(FF) = 8.7 Hz, CF_3)
35	0.9 (s, 9H, $C(CH_3)_3$), 1.9 (d, ^3J(HH) = 10.1 Hz, NH), 2.2 (s, $C(O)CH_3$), 3.4 (qq, ^3J(HF) = ^3J(FH) = 8.2 Hz, $(CF_3)_2CH$), 3.8 (d, ^3J(HH) = 9.8 Hz, C^3-H)	26.7 (q, ^1J(CH) = 128.4 Hz, C5), 51.2 (ddqq, ^1J(CH) = 128.7 Hz, ^2J(CH) = 5.7 Hz, ^2J(CF) = ^2J(CF) = 26.7 Hz, C2), 58.4 (d, ^1J(CH) = 135.4 Hz, C3), 206.4 (s, C=O)	−61.3 (dq, ^3J(HF) = 8.9 Hz, ^4J(FF) = 8.9 Hz, CF_3) −63.9 (dq, ^3J(HF) = 8.4 Hz, ^4J(FF) = 8.4 Hz, CF_3)
36	0.95 (d, ^3J(HH) = 6.4 Hz, 3H, CH_3), 0.99 (d, ^3J(HH) = 6.4 Hz, 3H, CH_3), 1.6 (breit, NH), 2.2 (s, $C(O)CH_3$), 2.7 (qq, ^3J(HH) = 6.2 Hz, ^3J(HH) = 6.2 Hz, $(CH_3)_2CH$), 3.6 (d, ^3J(HH) = 3.1 Hz, C^3-H), 3.7 (dqq, ^3J(HH) = 3.1 Hz, ^3J(HF) = 8.4 Hz, ^3J(FH) = 8.4 Hz, $(CF_3)_2CH$)	26.8 (q, ^1J(CH) = 128.4 Hz, C5), 49.3 (ddqq, ^1J(CH) = 133.6 Hz, ^2J(CH) = 5.7 Hz, ^2J(CF) = ^2J(CF) = 26.8 Hz, C2), 61.3 (d, ^1J(CH) = 133.5 Hz, C3), 206.7 (m, C=O)	−61.5 (dq, ^3J(HF) = 8.4 Hz, ^4J(FF) = 8.4 Hz, CF_3) −64.6 (dq, ^3J(HF) = 8.2 Hz, ^4J(FF) = 8.2 Hz, CF_3)
37	2.3 (s, $C(O)CH_3$), 3.4 (dqq, ^3J(HH) = 2.4 Hz, ^3J(FH) = 8.2 Hz, ^3J(FH) = 8.2 Hz, $(CF_3)_2CH$), 4.0 (m, C^3-H)	26.9 (q, ^1J(CH) = 127.8 Hz, C5), 51.3 (ddqq, ^1J(CH) = 128.7 Hz, ^2J(CH) = 6.7 Hz, ^2J(CF) = ^2J(CF) = 26.7 Hz, C2), 56.4 (d, ^1J(CH) = 135.4 Hz, C3), 206.5 (m, C=O)	−61.4 (dq, ^3J(HF) = 8.5 Hz, ^4J(FF) = 8.5 Hz, CF_3) −63.9 (dq, ^3J(HF) = 8.6 Hz, ^4J(FF) = 8.6 Hz, CF_3)
38	2.2 (s, $C(O)CH_3$), 3.7 (m, C^3-H)	27.0 (q, ^1J(CH) = 127.8 Hz, C5), 49.0 (ddqq, ^1J(CH) = 129.7 Hz, ^2J(CH) = 5.7 Hz, ^2J(CF) = ^2J(CF) = 26.7 Hz, C2), 62.8 (d, ^1J(CH) = 136.4 Hz, C3), 205.4 (m, C=O)	−61.8 (dq, ^3J(HF) = 8.6 Hz, ^4J(FF) = 8.6 Hz, CF_3) −64.7 (dq, ^3J(HF) = 8.6 Hz, ^4J(FF) = 8.6 Hz, CF_3)

0.2 g of TFAA were dissolved in 75 ml benzene. Into the boiling mixture an equimolar amount of **1**, dissolved in 50 ml benzene, was added dropwise. After 48 h of boiling, no **1** can be obtained. The solvent is removed by distillation. From the remaining brown oil **39** can be isolated by sublimation in vacuo at 50 °C as a colourless liquid. Yield 32.8 mg (0.4%), decomposition at 60 °C. IR (film) (cm^{-1}): 1639 (C=N), 1095–1364 (CF). ^1H NMR: $\delta = 2.5$ (s, CH_3), 3.8 (breit, 1H, CH_2), 4.1 (qq, $^3J(HF) = 7.6$ Hz, $^3J(HF) = 7.6$ Hz, $(CF_3)_2CH$), 4.8 (breit, 1H, CH_2), 7.2–7.4 (m, 4H). ^{13}C NMR: $\delta = 24.5$ (q, $^1J(CH) = 129.7$ Hz, CH_3), 51.3 (dqq, $^1J(CH) = 129.7$ Hz, $^2J(CF) = 28.6$ Hz, $^2J(CF) = 28.6$ Hz, $(CF_3)_2CH$), 54.5 (dd, $^1J(CH) = 135.4$ Hz, $^1J(CH) = 135.4$ Hz, CH_2), 150.7 (m, C3), 161.8 (q, $^2J(CH) = 5.7$ Hz, C2). ^{19}F NMR: $\delta = -63.9$ (m, CF_3), -64.7 (m, CF_3). MS (EI), m/z (%): 314 (3) $[M^+ + 1]$, 270 (33) $[M^+ - C(O)CH_3]$, 162 (6) $[M^+ - (CF_3)_2CH]$, 91 (100) $[C_6H_5\text{–}CH_2]$. $C_{13}H_{13}F_6ON$ (313.0): calc. C 50.2, H 3.5, N 4.5; found C 49.4, H 4.2, N 4.7%.

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