ELSEVIER

Journal of Fluorine Chemistry 104 (2000) 263–271

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

Reaction of perfluoro-2-methylpent-2-ene and perfluoro-5-azanon-4-ene with aniline and its derivatives

Ki-Whan Chi[a], Georgii G. Furin[b,*], Irina Yu. Bagryanskay[b], Yurii V. Gatilov[b]

[a]*Department of Chemistry, University of Ulsan, Ulsan 680-749, South Korea*

[b]*Institute of Organic Chemistry, Russian Academy of Sciences, 630090 Novosibirsk, Russia*

Received 14 December 1999; accepted 10 February 2000

Abstract

Reaction of perfluoro-2-methylpent-2-ene (**1**) and perfluoro-5-azanon-4-ene (**2**) with aniline, 4-fluoroaniline, 4-methoxyaniline and 2,6-dimethylaniline in the presence of Et_3N provides derivatives of quinoline and quinozaline, whereas reaction of **2** yields diazetine derivatives with 2- and 4-nitroanilines, 2,6-dichloroaniline and pentafluoroaniline. The structure of [2-(1,1,2,2,3,3,3-pentafluoroethyl)-3-trifluoromethyl-quinoline-4-yl]-phenylamine is confirmed by X-ray structural data. The routes of reactions and the ^{19}F and ^{13}C NMR spectral data of the products are discussed.

Keywords: Perfluoro-2-methylpent-2-ene; Perfluoro-5-azanon-4-ene; Nucleophilic addition; Intramolecular nucleophilic cyclization; 2-derivatives of azetine; Diazetine; Quinoline; Quinozaline; [2-(1,1,2,2,2-Pentafluoroethyl)-3-trifluoromethylqinouline-4-yl]-phenylamine

1. Introduction

Fluorine-containing aromatic compounds have drawn much attention because of their biological activities [1–3]. Many of them are used as new medicines or pesticides as themselves or as precursors for the synthesis of biologically active compounds. For example, azoles and pyrimidines with perfluoroalkyl substituents have shown interesting biological activities. This fact substantially triggers the development of effective methods for the synthesis of various heterocyclic systems with a fluorinated moiety, especially a perfluoroalkyl group. Among the known methods for the production of five- and six-membered heterocycles, heterocyclization by the reaction of binucleophilic reagents with available internal perfluoroolefins has been focused on as a useful methodology [4–7].

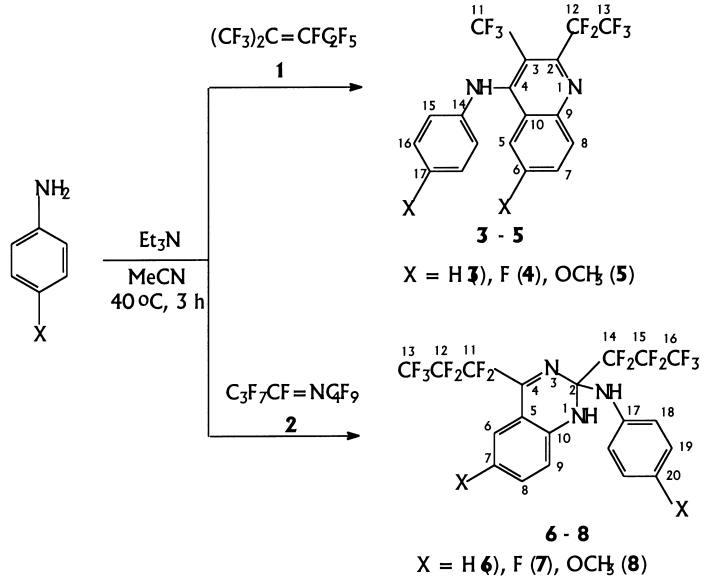
The azetine derivatives are also the prospective intermediates for new antibiotics [8,9]. Synthesis of four-membered heterocycles has been performed by the reaction of some internal perfluoroolefins with ammonia or primary amines [10–16]. Thus, reaction of tetrafluoroethylene trimer with cyclohexylamine led to 1-cyclohexyl-2-trifluoromethyl-3-(2,2,2-trifluoroethylidene)-cyclohexylamino-4-*N*-cyclohexyl-imino-2-azetine [10]. Treatment of perfluoro-3,4-dimethylhex-3-ene with butylamine or methylamine, respectively, gave *N*-butyl-aminoperfluoro-2,3,4-trimethyl-4-ethyl-2-azetine or 3-(1-methylamino-1-trifluoromethyl-perfluoropropyl)-4-methyl-imino-*N*-methyl-2-trifluoromethyl-2-azetine [13]. Moreover, perfluoro-2-methylpent-2-ene (**1**) is known to react with *tert*-butylamine, iso-propylamine and *n*-propylamine to yield azetine derivatives [12,14–16].

On the other hand, reaction of internal perfluoroolefins with aniline has been noted to provide quinoline derivatives [10,17,18]. Thus, treatment of aniline with 2*H*-heptafluorobut-2-ene produced phenyl-(2-trifluoromethyl-quinoline-4-yl)amine [13] and reaction of aniline with tetrafluoroethylene trimer provided 2-trifluoromethyl-3-(1-*N*-phenylimino-2,2,2-trifluoro-ethyl)-4-(*N*-phenylamino)quinoline [10]. The presence of electron-donating substituents in aromatic amines is supposed to facilitate the formation of quinoline derivatives. Reaction of **1** with 2,4-dimethoxyaniline gave 4-(2,4-dimethoxyanilino)-6,8-dimethoxy-2-pentafluoroethyl-3-trifluoromethylquinoline [17]. However, that kind of reaction remains unclear yet since reaction of aniline with octafluoro-3,4-bis(trifluoromethyl)hexa-2,4-diene yielded 1-phenyltetrakis(trifluoromethyl)-1*H*-pyrrole instead of 2,3,4,5-tetrakis(trifluoromethyl)-1*H*-benzo[b]-azetine [19].

To continue our research on the new methodology for the synthesis of heterocycles starting with internal perfluoroolefins, we have investigated in detail the reactions of **1** and perfluoro-5-azanon-4-ene (**2**) with aniline and its derivatives

* Corresponding author.

0022-1139/00/$ – see front matter
PII: S0022-1139(00)00247-5



Scheme 1.

4-fluoroaniline, 2,6-dimethylaniline, 2,6-dichloroaniline, 4-methoxyaniline, 2- and 4-nitroaniline and pentafluoroaniline. All reactions were carried out in the presence of triethylamine.

2. Results and discussion

The compounds **1** and **2** have been found to react smoothly with 2 equivalents of aniline, 4-fluoroaniline and 4-methoxyaniline in the presence of 3 equivalents of Et_3N in MeCN to give the compounds **3–8** (Scheme 1).

The structure of [2-(1,1,2,2,2-pentafluoroethyl)-3-trifluoromethylqinoline-4-yl]-phenyl amine (**3**) was confirmed by X-ray analysis, infrared (IR), ^1H, ^{13}C, ^{19}F NMR and mass spectroscopy. The X-ray structure of quinoline **3** is presented in Fig. 1, which shows two rotamers in a single crystal.

The trifluoromethyl group on C3 is disordered with the relative occupation of positions equal to 0.868(6):0.132(6). In the case of the second independent molecule, the disorder does not take place. The geometry of both molecules coincides with the limits of 3σ, excluding the CF_3 group. The quinoline framework has been found to be planar in the limits of ±0.055(3) and ±0.063(3) Å, respectively, for both molecules. The bond lengths in **3** are rather close to corresponding values in 4-anilino-2-diethoxyphosphonyl-3-chloroquinoline [20], the closest structural analogue from the Cambridge bank of structural data [21]. The different orientation of the aniline fragment is significant: the torsion angles C10–C4–N14–C15 and C4–N14–C15–C16 in molecule **3** are equal to 58.5(4), 58.6(4), 25.3(5) and 20.9(5)°, whereas in 4-anilino-2-diethoxyphosphonyl-3-chloroquinoline, they are equal to −132.2 and 15.2°. The crystal packing shows centro-symmetrical pairs of molecules, bonded by π-stacking interaction of the quinoline frameworks with interplane distance 3.586(5) and 3.546(5) Å.

The NMR spectral data of products **3–8** show the same characteristic chemical shifts and coupling constants as those described earlier for similar compounds. The proton signals of compounds **3–8** are placed at 6.9–7.4 ppm, which is a typical range for aromatic protons. The ^{19}F NMR spectrum reveals three groups of signals with a 3:3:2 intensity ratio; the chemical shifts for compound **3** are equal

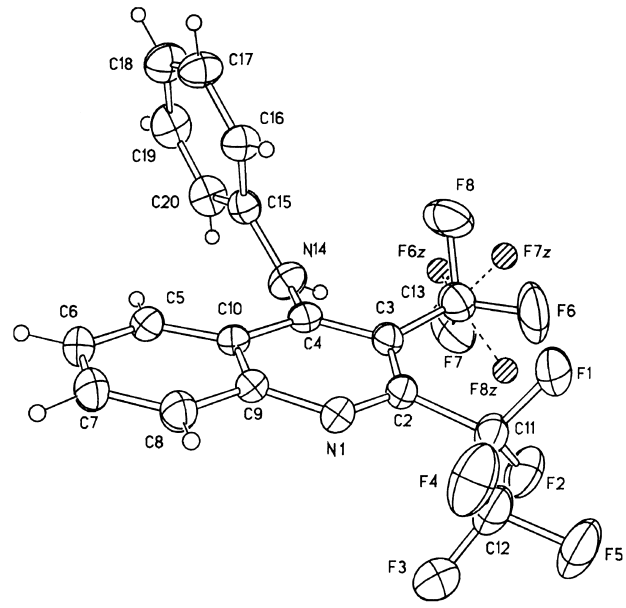
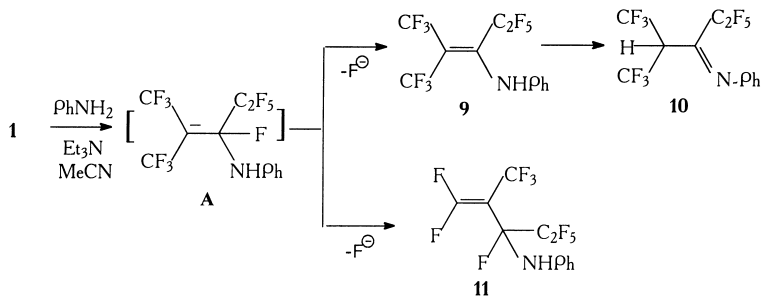


Fig. 1. The crystal structure of **3** as per X-ray analysis.



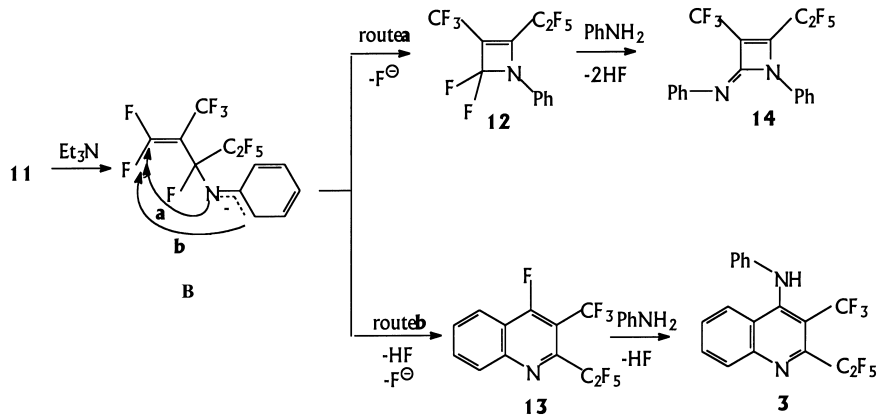
Scheme 2.

to 108.6 ppm (triplet J_{FF}=10 Hz), 82.3 ppm (singlet) and 49.6 ppm (quartet J_{FF}=10 Hz).

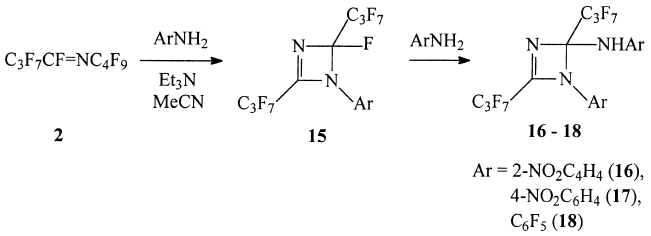
Reaction of **1** with aniline begins presumably with the attack of the N-nucleophile on the carbon atom of the double bond to form anion **A**. The following transformations of **A** might occur via two different routes (Scheme 2). Elimination of fluoride ion from **A** yields phenyl-[3,3,3-trifluoro-1-(pentafluoroethyl)-2-trifluoromethyl-propenyl]-amine (**9** or **11**). Enamine **9** undergoes enamine–imine isomerization by Et_3N to give the more stable imino isomer **10** [22]. The elimination of fluoride ion from the CF_3 fragment, however, leads to the formation of phenyl-[1,3,3-trifluoro-1-(pentafluoroethyl)-2-trifluoromethyl-allyl]-amine (**11**). Reaction of **11** with Et_3N provides anion **B**, and an intramolecular cyclization is followed between the terminal double bond and the N- or C-nucleophilic center of **B** (Scheme 3). Intramolecular cyclization could occur by two different ways to form 2,2-difluoro-4-(pentafluoroethyl)-1-phenyl-3-trifluoromethyl-1,2-dihydroazete (**12**) (route a) or 4-fluoro-2-(pentafluoroethyl)-3-trifluoromethyl-quinoline (**13**) (route b), respectively. Further reaction of **12** or **13** with another aniline produces [4-(pentafluoroethyl)-1-phenyl-3-trifluoromethyl-1*H*-azet-2-ylidene]-phenylamine **14** or **3**. It would be reasonable to think that the selectivity between routes a and b should be related to the nucleophilicity of the attacking atom and the stability of the product. MNDO (PM3, AM1) calculations show that the heat of formation (−326.707 kcal/mol) of the six-membered ring **3** is substantially less than that of the four-membered ring **14** (−276.06 kcal/mol). The greater stability of **3** compared to **14** should favor formation of the six-membered heterocycle **3** under thermodynamically controlled conditions. On the other hand, the calculation indicates that the negative charge on the nitrogen atom in **B** (q_N=−0.61*e*) is greater than that on the carbon atom (q_C=−0.23*e*) in the *ortho*-position. This should facilitate the formation of intermediate **12** instead of **13**.

In the actual system, the intramolecular nucleophilic cyclization of **B** occurs via route b to form the six-membered ring **3**. This indicates that the route of cyclic formation of **B** is determined only by thermodynamic factors. A similar reaction mechanism can be proposed for the reaction of compound **2** with aniline. In this case, the major step consists of the formation of the second C=N group to yield a six-membered ring. Therefore, formation of the six-membered rings **3**–**8** from the reaction of **1** and **2** with the substituted anilines might be rationalized if the route of intramolecular cyclization is determined thermodynamically.

On the other hand, reaction of **2** with 2-nitro-, 4-nitro- or pentafluoroaniline produces the diazetine derivative (2-nitrophenyl)-[1-(2-nitrophenyl)-2,4-bis(heptafluoropropyl)-1,2-dihydro-[1,3]-diazet-2-yl]-amine (**16**), (4-nitrophenyl)-[1-(4-nitrophenyl)-2,4-bis(heptafluoropropyl)-1,2-dihydro-



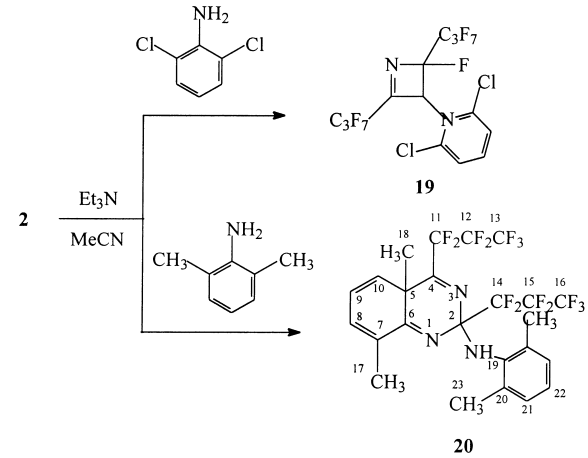
Scheme 3.



Scheme 4.

[1,3]-diazet-2-yl]-amine (**17**) or (pentafluorophenyl)-[1-(pentafluorophenyl)-2,4-bis(heptafluoropropyl)-1,2-dihydro-[1,3]-diazet-2-yl]-amine (**18**), respectively (Scheme 4). Formation of the four-membered rings **16–18** means that the fluorine atom in position 4 is substituted by the N-nucleophile instead of the C-nucleophile. Obviously, an introduction of an NO_2-group or five F atoms to the aniline ring lowers the nucleophilicity of the C-anionic center more than that of the N-anionic one. This fact in combination with the higher reactivity of fluoro-imine group derived from **2** makes the reaction proceed kinetically to give the diazetine intermediate **15**. Further substitution of the active fluorine atom in **15** by aniline gives **16–18** (Scheme 4).

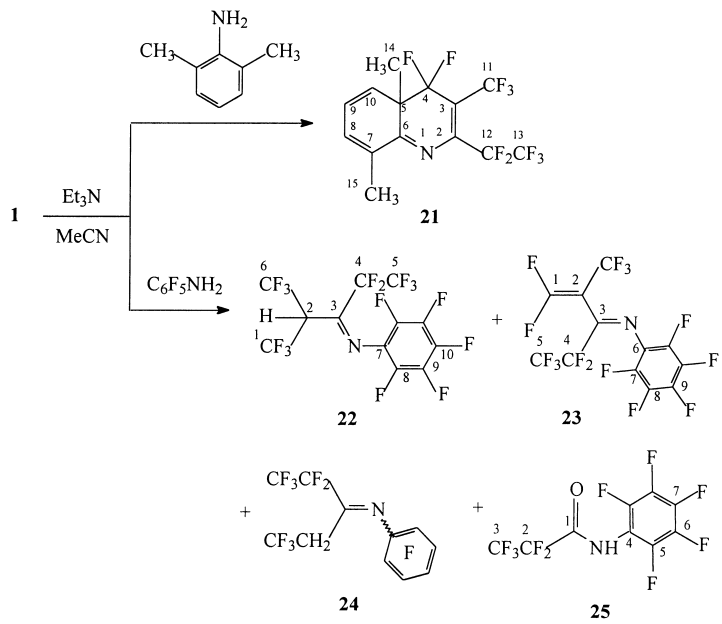
It is also interesting to note that reaction of **2** with 2,6-dichloroaniline provides the diazete derivative 1-(2,6-dichlorophenyl)-2-fluoro-2,4-bis-(heptafluoropropyl)-1,2-dihydro-[1,3]-diazete (**19**). However, treatment of **2** with 2,6-dimethylaniline produces a six-membered heterocycle — the dihydroquinazoline derivative [2,4-bis-(heptafluoropropyl)-4a,8-dimethyl-2,4a-dihydroquinazolin-2-yl]-(2,6-dimethylphenyl)-amine (**20**) (Scheme 5). Similarly,



Scheme 5.

reaction between **1** and 2,6-dimethylaniline yields the dihydroquinoline 4,4-difluoro-4a,8-dimethyl-2-(pentafluoroethyl)-3-trifluoromethyl-4,4a-dihydroquinoline (**21**) (Scheme 6).

Reaction of **1** with pentafluoroaniline produces a mixture of products **22–25**. The major product is **25**, formed by the addition of (pentafluorophenyl)-[3,3,3-trifluoro-1-(pentafluoroethyl)-2-trifluoromethylpropylidene]-amine (**22**) to a double bond, probably because of the low reactivity of the N-nucleophile. Also, the formation of compounds [3,3-difluoro-1-(pentafluoroethyl)-2-trifluoromethyl-allylidene]-(pentafluorophenyl)-amine (**23**) and (pentafluorophenyl)-[2,2,3,3,3-pentafluoro-1-(2′,2′,2′-trifluoroethyl)-propylidene]-amine (**24**) is observed by GC-MS data (Scheme 6).



Scheme 6.

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound **3**[a]

Atom	*x/a*	*Y/b*	*z/c*	*U* (eq)[b]	Atom	*x/a*	*y/b*	*z/c*	*U* (eq)
N(1)	3756(2)	−2131(2)	5071(2)	62(1)	N(1A)	2769(2)	74(2)	9580(2)	55(1)
C(2)	2680(3)	−2583(3)	5145(2)	59(1)	C(2A)	2821(3)	7(2)	8664(2)	54(1)
C(3)	2444(3)	−3614(3)	5659(2)	59(1)	C(3A)	1894(3)	653(2)	8170(2)	56(1)
C(4)	3460(3)	−4239(2)	6025(2)	56(1)	C(4A)	804(3)	1297(2)	8719(2)	55(1)
C(5)	5779(3)	−4338(3)	6245(2)	65(1)	C(5A)	−390(3)	1914(2)	10367(2)	61(1)
C(6)	6872(3)	−3819(3)	6155(2)	75(1)	C(6A)	−396(3)	1949(3)	11320(2)	69(1)
C(7)	6916(3)	−2721(3)	5743(3)	80(1)	C(7A)	670(3)	1410(3)	11697(2)	72(1)
C(8)	5878(3)	−2172(3)	5403(2)	72(1)	C(8A)	1708(3)	820(3)	11114(2)	65(1)
C(9)	4734(3)	−2691(3)	5485(2)	56(1)	C(9A)	1751(3)	764(2)	10123(2)	53(1)
C(10)	4665(3)	−3773(2)	5936(2)	55(1)	C(10A)	706(2)	1345(2)	9732(2)	51(1)
C(11)	1733(3)	−1891(3)	4589(2)	73(1)	C(11A)	3968(3)	−857(3)	8188(2)	66(1)
C(12)	2264(4)	−972(4)	3927(3)	92(1)	C(12A)	4590(3)	−1721(3)	8866(3)	76(1)
C(13)	1124(3)	−4009(4)	5909(3)	81(1)	C(13A)	2068(4)	671(3)	7103(2)	77(1)
N(14)	3388(3)	−5330(2)	6423(2)	71(1)	N(14A)	−230(3)	1844(2)	8332(2)	68(1)
C(15)	3612(3)	−5637(2)	7350(2)	59(1)	C(15A)	−715(3)	3053(2)	8450(2)	60(1)
C(16)	3436(3)	−4816(3)	8068(2)	66(1)	C(16A)	−1967(3)	3436(4)	8311(2)	76(1)
C(17)	3618(4)	−5139(3)	8964(2)	81(1)	C(17A)	−2448(4)	4612(4)	8390(3)	92(1)
C(18)	3982(4)	−6293(3)	9161(3)	90(1)	C(18A)	−1692(5)	5391(4)	8633(3)	94(1)
C(19)	4160(4)	−7107(3)	8448(3)	92(1)	C(19A)	−471(4)	5005(3)	8787(3)	84(1)
C(20)	3988(3)	−6795(3)	7543(3)	78(1)	C(20A)	33(3)	3837(3)	8692(2)	68(1)
F(1)	673(2)	−1331(2)	5167(2)	107(1)	F(1A)	4963(2)	−321(2)	7717(2)	92(1)
F(2)	1289(2)	−2610(2)	4033(2)	102(1)	F(2A)	3608(2)	−1539(2)	7549(1)	83(1)
F(3)	3283(2)	−1425(3)	3288(2)	121(1)	F(3A)	5189(2)	−1217(2)	9439(2)	93(1)
F(4)	2555(3)	−107(2)	4383(2)	133(1)	F(4A)	5486(2)	−2492(2)	8330(2)	110(1)
F(5)	1351(3)	−526(2)	3435(2)	129(1)	F(5A)	3718(2)	−2304(2)	9367(2)	90(1)
F(6)	168(2)	−3320(4)	5678(4)	145(2)	F(6A)	3287(2)	417(2)	6663(1)	102(1)
F(7)	1090(3)	−5061(3)	5569(3)	124(2)	F(7A)	1688(3)	1727(2)	6784(2)	118(1)
F(8)	791(3)	−4125(4)	6857(2)	124(2)	F(8A)	1391(3)	−54(3)	6771(2)	130(1)
F(6Z)	1040(2)	−4910(2)	6260(2)	121(8)					
F(7Z)	320(2)	−3320(2)	6362(19)	111(8)					
F(8Z)	730(2)	−4024(18)	5035(14)	98(7)					

[a]Secure positions for the atoms F(6), F(7), F(8) make up 0.868(6), and the atoms F(6Z), F(7Z), F(8Z), −0.132(6).
[b]*U* (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

In short, reaction of **1** or **2** with aniline or its derivatives containing an electron-donating substituent proceeds to form a six-membered heterocycle, whereas the presence of a strongly electron-withdrawing substituent in aniline facilitates the formation of four-membered heterocycles. We consider that these experiments illustrate the potential of using internal perfluoroolefins for the synthesis of heterocyclic compounds containing perfluoroalkyl groups (Table 1).

3. Experimental

3.1. Instrumentation

^{19}F NMR spectra were recorded in ppm downfield from internal standard C_6F_6 in $CDCl_3$ using a Bruker WP 200SY spectrometer operating at 188.324 MHz. ^{13}C NMR spectra were recorded in ppm downfield from internal standard (Me_4Si, δ 0.00) using a Bruker AM 400 spectrometer operating at 100.614 MHz in $CDCl_3$ (J_{CH} not recorded). Coupling constants are given in Hz. IR spectra were recorded on a Bruker Vector spectrometer (5% in CCl_4). UV spectra were taken with a Carl/Zeiss Jena Specord M-40. GC-MS spectra were obtained with the electron impact mode at 70 eV and reported as *m/z* (relative intensity) using a Finnigan MAT model 8200 spectrometer. Mass spectra (Table 2) were obtained with a gas chromatograph electron ionization detector (Hewlett–Packard G 1800A GCD system), 30 m capillary column 0.25 mm in diameter with a 0.25 μk film for co-polymer 5% diphenyl–95% dimethylsilicon (HP-5), gas: helium, 1 ml/min, column temperature: 280°C. All reactions were monitored routinely by ^{19}F NMR spectroscopy. Column chromatography was performed using silica gel 60 (0.063–0.2 mm). Merck TLC plates with silica gel 60 were used for TLC analysis with the indicated solvents. Melting points were recorded at atmospheric pressure and are uncorrected. All the commercially available reagents were of analytical grade and used without further purification. Compound **10** was also prepared by the known procedure [22].

X-ray structure analysis was carried out on a Syntex $P2_1$ diffractometer using Cu Kα radiation with a graphite monochromator. X-ray structure data for **3**: $C_{18}H_{10}F_8N_2$, M=

Table 2
Mass-spectral data for new compounds

Compound	*m/e* (I_{rel} (%))
3	406 $[M]^+$ (100), 387 $[M–F]^+$ (11.92), 337 $[M–CF_3]^+$ (32.11), 317 $[M–CF_3–HF]^+$ (8.64), 268 $[M–2CF_3]^+$ (4.83), 145 $[C_2F_5CN]^+$ (0.44), 119 $[C_2F_5]^+$ (2.40), 100 $[CF_2=CF_2]^+$ (0.49), 77 $[C_6H_5]^+$ (13.76), 76 $[C_6H_4]^+$ (1.21), 69 $[CF_3]^+$ (1.69)
4	442 $[M]^+$ (100), 423 $[M–F]^+$ (13.38), 422 $[M–HF]^+$ (27.21), 403 $[M–HF–F]^+$ (32.91), 373 $[M–CF_3]^+$ (10.80), 333 $[M–FC_6H_4N]^+$ (17.93), 239 $[FC_6H_3N=CC_2F_5]^+$ (0/83), 203 $[FC_6H_4NHC=CCF_3]$ (2.11), 169 $[C_3F_7]^+$ (3.84), 119 $[C_2F_5]^+$ (5.20), 110 $[FC_6H_4NH]^+$, 95 $[FC_6H_4]$ (10.87), 69 $[CF_3]^+$ (18.58)
5	466 $[M]^+$ (2.37), 335 (55.49), 324 $[M–OCH_3C_6H_4NH–HF]^+$ (3.40), 310 (2.70), 216 (100), 122 $[CH_3OC_6H_4NH]^+$ (5.42), 107 $[CH_3OC_6H_4]^+$ (19.29), 77 $[C_6H_4]^+$ (25.31), 69 $[CF_3]^+$ (3.27)
6	559 $[M]^+$ (42.65), 540 $[M–F]^+$ (4.82), 390 $[M–C_3F_7]^+$ (100), 169 $[C_3F_7]^+$ (0.71), 119 $[C_2F_5]^+$ (1.00), 69 $[CF_3]^+$ (18.58)
7	595 $[M]^+$ (40.42), 576 $[M–F]^+$ (6.37), 426 $[M–C_3F_7]^+$ (100), 365 $[M–FC_6H_3N=CNHC_6H_4F]^+$ (7.25), 307 $[C_3F_7C(NH_2)NHC_6H_4F]^+$ (7.84), 290 $[C_3F_7C=NC_6H_4F]^+$ (26.59), 169 $[C_3F_7]^+$ (5.92), 135 $[FC_6H_3N=C=NH]^+$ (14.35), 119 $[C_2F_5]^+$ (3.06), 95 $[C_6H_4F]^+$ (45.82), 69 $[CF_3]^+$ (10.82)
8	619 $[M]^+$ (10.01), 600 $[M–F]^+$ (0.98), 450 $[M–C_3F_7]^+$ (16.23), 328 $[M–C_3F_7–CH_3OC_6H_4NH]^+$ (0.72), 122 $[CH_3OC_6H4NH]^+$ (63.54), 169 $[C_3F_7]^+$ (9.50), 119 $[C_2F_5]^+$ (6.95), 107 $[CH_3OC_6H_4]^+$ (5.69), 100 $[CF_2=CF_2]^{+\cdot}$ (4.90), 69 $[CF_3]^+$ (17.17)
18	649 $[M]^+$ (5.36), 630 $[M–F]^+$ (0.78), 480 $[M–C_3F_7]^+$ (4.24), 446 $[M–C_3F_7]^+$ (19.71), 334 (69.42), 288 (100), 169 $[C_3F_7]^+$ (49.42), 148 $[C_6H_4(CN)NO_2]^+$ (6.62), 138 $[C_6H_4(NH_2)NO_2]^+$ (40.25), 119 $[C_2F_5]^+$ (20.07), 100 $[CF_2=CF_2]^+$ (7.48), 69 $[CF_3]^+$ (64.88)
19	649 $[M]^+$ (42.93), 630 $[M–F]^+$ (6.28), 480 $[M–C_3F_7]^+$ (100), 434 $[M–C_3F_7–NO_2]^+$ (12.60), 388 $[M–C_3F_7–2NO_2]^+$ (3.24), 317 (23.97), 169 $[C_3F_7]^+$ (1.27), 119 $[C_2F_5]^+$ (0.41), 76 $[C_6H_4]^+$ (16.29), 69 $[CF_3]^+$ (2.75)
22	615 $[M]^+$ (36.95), 596 $[M–F]^+$ (5.21), 496 $[M–C_2F_5]^+$ (3.80), 446 $[M–C_3F_7]^+$ (74.77), 343 (100), 316 (16.08), 300 (18.59), 169 $[C_3F_7]^+$ (16.07), 148 (23.10), 130 (39.00), 122 $[C_3H_3(CH_3)_2]^+$ (1.49), 121 (17.52), 119 $[C_2F_5]^+$ (9.64), 100 $[CF_2=CF_2]^+$ (3.74), 86 (39.13), 77 (16.53), 69 $[CF_3]^+$ (29.03), 44 (66.60)
24	463 $[M]^+$ (26.70), 444 $[M–F]^+$ (6.52), 344 $[M–C_2F_5]^+$ (100), 324 $[M–C_2F_5–HF]^+$ (13.68), 312 $[M–(CF_3)_2CH]^+$ (19.38), 275 $[M–C_2F_5–CF_3]^+$ (6.83), 212 $[M–(CF_3)_2CH–CF_2=CF_2]^+$ (32.35), 193 $[C_6F_5NC]^+$ (6.42), 167 $[C_6F_5]^+$ (12.80), 131 $[CF_3C=CF_2]^+$ (0.83), 119 $[C_2F_5]^+$ (11.85), 100 $[CF_2=CF_2]^+$ (1.04), 69 $[CF_3]^+$ (18.25)
25	329 $[M]^+$ (61.00), 310 $[M–F]^+$ (3.27), 210 $[M–C_2F_5]^+$ (53.01), 209 $[C_6F_5NCO]^+$ (2.90), 182 $[C_6F_5NH]^+$ (100), 167 $[C_6F_5]^+$ (1.95), 162 $[M–C_6F_5]^+$ (8/09), 155 $[C_5F_5]^+$ (42.55), 119 $[C_2F_5]^+$ (42.01), 100 $[CF_2=CF_2]^+$ (3.69), 69 $[CF_3]^+$ (40.58)

406.28, triclinic, space group P-1, a=10.569(2) Å, b=11.582(2) Å, c=14.267(4) Å, α=89.20(3)°, β=79.21(1)°, γ=81.82(1)°, V=1698.0(5) Å^3, Z=4, D_{cal}=1.592 g/cm^3, μ=1.406 mm^{-1}. 6475 intensities of independent reflections were measured ($\theta/2\theta$-scan, 2θ<140°) for a crystal sample sealed in a polyethylene capillary. Evaporation (10% drop) and empirical absorption (transmission 0.68–0.95) corrections were applied. The structure was solved by direct methods and refined in an anisotropic approximation using program SHELXL-97. Riding model was used for hydrogen atom refinements. The final R-factors are wR_2=0.1485, S=1.022 (R=0.0530 for 4024 $F>4\sigma$). Atomic coordinates, thermal parameters, bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre. Nonhydrogen atom coordinates are shown in Table 1.

*3.2. Reaction of the compounds **1** and **2** with aniline and its derivatives in the presence of Et_3N*

3.2.1. General procedure

To a solution of **1** (or **2**) and Et_3N in MeCN (15–20 ml) at 0°C was added dropwise a solution of aniline or its derivative in MeCN (10 ml). The resulting solution was stirred for 1–2 h at room temperature and then for 2–4 h at 45°C. The reaction mixture was washed with water (2 ml×50 ml), neutralized with 5% aqueous H_2SO_4 and extracted with CH_2Cl_2 (3 ml×50 ml). The concentrate was distilled under reduced pressure to give a liquid, which was further purified by column chromatography (hexane/CH_2Cl_2).

*3.2.2. Synthesis of phenyl-[3,3,3-trifluoro-1-(1,1,2,2,2-pentafluoroethyl)-2-trifluoromethylpropylidene] amine (**9**), [2-(1,1,2,2,2-pentafluoroethyl)-3-trifluoromethylqinoline-4-yl]-phenyl amine (**3**) and [2,4-bis(1,1,2,2,3,3,3-heptafluoropropyl)-1,2-dihydroquinozaline-2-yl]phenyl amine (**6**)*

1. The general procedure with **1** (15.0 g, 0.050 mol), Et_3N (15.2 g, 0.15 mol) and aniline (4.65 g, 0.05 mol) in CH_3CN (30 ml) provided **3** (13.2 g, 65% yield) and **10** (3.73 g, 20% yield).

   [2-(1,1,2,2,2-Pentafluoroethyl)-3-trifluoromethylqinouline-4-yl]-phenyl amine (**3**): bp 164–165°C (4 Torr); mp 88–89°C (from aq. alcohol). ^{1}H NMR ($CDCl_3$) δ_H 7.62 (d, H^8, 8), 7.46 (d, H^8, 8), 7.32 (t, H^7, 8), 6.98 (t, H^6, 8), 6.54 (d, H^{15}, 7.4), 6.56 (t, H^{17}, 7.4), 6.78 (t, 16, 7.4). ^{13}C NMR ($CDCl_3$) δ_C 149.6 (C^9), 146.4 (C^{10}), 143.8 (C^2, $^2J_{CF}$=28.1), 143.8 (C^4), 131.4 (C^8), 129.6 (C^5), 128.4 (C^7), 127.6 (C^6), 124.7 (C^{14}), 122.6 (C^{15}), 122.8 (C^{11}, $^1J_{CF}$=274.0), 122.1 (C^{17}), 118.5 (C^{16}), 118.7 (C^{13}, $^1J_{CF}$=286.3; $^2J_{CF}$=36.2), 112.1 (C^{12}, $^1J_{CF}$=259.6; $^2J_{CF}$=34.6), 111.1 (C^3, $^2J_{CF}$=33.1). ^{19}F NMR ($CDCl_3$) δ_F 108.2 (F^{11}, t, 23), 83.7 (F^{13}, s), 55.3 (F^{12}, q, 23). IR 3430 (N–H), 2900 (C–H); 1600 (C=N); 1565 (C=N); 1490 (C=C$_{Ar}$); 1415 (C=C$_{ar}$), 1370 and 1340 (N–C); 1310, 1110–1240 (C–F) [23]. HRMS calc. 406.0716 for $C_{18}H_{10}F_8N_2$, found 406.0724. UV spectra, λ_{max} (C_2H_5OH) 350 nm (ε=8400). Found (%): C, 53.22; 52.99; H, 2.33; 2.59; F, 37.58; 37.56; N, 6.74. Calc. (%): C, 53.20; H, 2.46; F, 37.44; N, 6.90.

Phenyl-[3,3,3-trifluoro-1-(1,1,2,2,2-pentafluoroethyl)-2-trifluoromethylpropylidene] amine (**10**): bp 36°C (3 Torr); ^{1}H NMR ($CDCl_3$), δ_H 4.63 (m, H^2), 6.58 (m, H^8, 7 Hz), 7.11 (H^{10}, 7 Hz), and 7.26 (H^9, 7 Hz). ^{13}C NMR ($CDCl_3$) δH: 151.7 (C^3, $^2J_{CF}$=32), 145.5 (C^7), 125.6 (C^{10}), 129.4 (C^8), 120.3 ($C^{1,6}$, $^1J_{CF}$=268.3; $^2J_{CF}$=32.2), 117.9 (C^9), 118.2 (C^5, $^1J_{CF}$=287.5; $^2J_{CF}$=34.0), 110.0 (C^4, $^1J_{CF}$=267.0; $^2J_{CF}$=37.4), 50.4 (C^2, $^2J_{CF}$=33.1). ^{19}F NMR ($CDCl_3$) δ_F 101.7 (6F, $F^{1,6}$), 83.3 and 82.4 (3F, F^5), 49.2 and 47.8 (2F, F^4). IR 3090 and 3020 (C–H); 1670 (C=C); 1595 (C=C_{Ar}); 1490 (C=C_{Ar}); 1360 (N–C); 1340, 1290, 1100–1250 (C–F) [23]. HRMS calc. 373.0325 for $C_{12}H_6F_{11}N$, found 373.0239.

2. The general procedure with **2** (14 g, 0.032 mol), Et_3N (14 g, 0.14 mol) and aniline (6.2 g, 0.066 mol) in MeCN (50 ml) gave **6** (12.1 g, 67% yield).

   [2,4-Bis(1,1,2,2,3,3,3-heptafluoropropyl)-1,2-dihydroquinozaline-2-yl]phenyl amine (**6**); mp 89–90°C (hexane). ^{13}C NMR ($CDCl_3$) δ_C 145.8 (C^4, $^2J_{CF}$=10.8), 145.2 (C^5), 140.5 (C^2, $^2J_{CF}$=16.5), 133.5 (C^6), 133.5 (C^{16}), 132.8 (C^{17}), 129.2 (C^{10}), 128.4 (C^6), 128.2 (C^8), 125.5 (C^{18}), 125.4 (C^{20}), 122.5 (C^{19}), 115.3 ($C^{13,16}$, $^1J_{CF}$=287.8; $^2J_{CF}$=33.7), 107.5 ($C^{11,14}$, $^1J_{CF}$=263.4; $^2J_{CF}$=40.4), 106.2 ($C^{12,15}$, $^1J_{CF}$=268.3; $^2J_{CF}$=35.5). ^{19}F NMR ($CDCl_3$) δ_F 82.8 (6F, $F^{13,16}$), 43.7 (4F, $F^{11,14}$), 36.9 (4F, $F^{12,15}$). IR 3416 (N–H), 3029 (C–H); 1696 (C=N); 1650 (N=C); 1563 (C=C_{Ar}); 1512 (C=C_{ar}), 1450 and 1350 (N–C), 1230–1210 (C–F) [23]. HRMS calc. 559.0729 for $C_{20}H_{11}F_{14}N_3$, found 559.0732. Found (%): C, 42.97; H, 2.27; F, 47.77; N, 7.52. Calc. (%): C, 42.93; H, 1.97; F, 47.58; N, 7.51.

*3.2.3. Synthesis of [4-fluoro-2-(1,1,2,2,2-pentafluoroethyl)-3-trifluoromethylquinolin-4-yl]-(4-fluorophenyl)-amine (**4**)*

The general procedure with **1** (6 g, 0.02 mol), Et_3N (6.06 g, 0.06 mol) and 4-fluoroaniline (4.4 g, 0.04 mol) in MeCN (15 ml) provided **4** (7.3 g, 82.5% yield); mp 92–93°C (hexane). ^{1}H NMR ($CDCl_3$) δ_H 7.95 (d, H^8, 8), 7.48 (d, H^5, 8), 6.90 (t, H^7, 8), 6.90 (m, H^{15}), 6.90 (m, H^{16}), 5.26 (N–H). ^{13}C NMR ($CDCl_3$) δ_C 159.6 (C^6, $^1J_{CF}$=243.9), 151.4 (C^{17}, $^1J_{CF}$=252.7), 149.9 (C^9), 139.6 (C^{10}), 144.5 (C^4), 143.9 (C^2, $^2J_{CF}$=29.9), 133.6 (C^{14}, $^3J_{CF}$=9.4), 123.8 (C^{15}, $^3J_{CF}$=10.1), 123.7 (C^{11}, $^1J_{CF}$=274.6), 122.4 (C^{16}, $^2J_{CF}$=25.9), 119.5 (C^{13}, $^1J_{CF}$=286.5; $^2J_{CF}$=36.0), 116.5 (C^7, $^2J_{CF}$=23.0), 112.9 (C^{12}, $^1J_{CF}$=260.2; $^2J_{CF}$=34.4), 112.3 (C^3, $^2J_{CF}$=31.8), 109.6 (C^5, $^2J_{CF}$=24.9). ^{19}F NMR (CDCl) δ_F 108.7 (F^{11}, t, 20), 84.4 (F^{13}, s), 55.7 (F^{12}, q, 23). IR 3438 (N–H), 3122 (C–H); 1629 (C=C); 1582 (C=N); 1500 (C=C_{Ar}); 1448 (C–N), 1408 and 1382 (N–C); 1339, 1313, 1230–1192 (C–F) [23]. UV spectrum λ_{max} (C_2H_5OH) 348 nm (ε=7460). HRMS calc. 442.0528 for $C_{18}H_{10}F_8N_2$, found 442.0523. Found (%): C, 49.49; H, 1.99; F, 44.44; N, 6.24. calc. (%): C, 48.87; H, 1.81; F, 42.99; N, 6.33.

*3.2.4. Synthesis of [4-methoxy-2-(pentafluoroethyl)-3-trifluoromethylquinolin-4-yl]-(4-methoxyphenyl)-amine (**5**)*

The general procedure with **1** (6 g, 0.02 mol), Et_3N (6.06 g, 0.06 mol) and 4-methoxyaniline (4.9 g, 0.04 mol) in MeCN (25 ml) gave **5**: (6 g, 65% yield); bp 165–168°C (Torr). ^{1}H NMR ($CDCl_3$) δ_H 6.92 (d, H^8, 8), 6.86 (d, H^5, 8), 6.77 (d, H^7, 8), 7.34 (m, H^{15}), 7.20 (m, H^{16}), 5.26 (N–H), 3.66 ($H^{18,19}$). ^{13}C NMR ($CDCl_3$) δ_C 158.1 (C^9), 155.5 (C^{10}), 148.8 (C^4), 142.1 (C^{17}), 141.1 (C^2, $^2J_{CF}$=29.4), 136.6 (C^6), 130.9 (C^{14}), 123.5 (C^5), 123.0 (C^7), 121.7 (C^{15}), 120.4 (C^{11}, $^1J_{CF}$=264.4), 118.7 (C^{13}, $^1J_{CF}$=286.2; $^2J_{CF}$=36.4), 113.4 (C^{16}), 112.3 (C^{12}, $^1J_{CF}$=258.7; $^2J_{CF}$=34.4), 109.1 (C^3, $^2J_{CF}$=32.0), 103.1 (C^8), 54.1 ($C^{18,19}$). ^{19}F NMR ($CDCl_3$) δ_F 105.4 (F^{11}, t, 20), 81.0 (F^{13}, s), 52.9 (F^{12}, q, 20). IR 3446 (N–H), 3018, 2968 (C–H); 1621 (C=C); 1574 (C=N); 1509 (C=C_{Ar}); 1455 (C–N), 1428 (N–C) 1240–1188 (C–F) [23]. UV spectrum λ_{max} 246 nm (ε=41 500), 358 nm (ε=6200). HRMS calc. 466.0927 for $C_{20}H_{14}F_8N_2O_2$, found 466.0928.

*3.2.5. Synthesis of [6-fluoro-2,4-bis(heptafluoropropyl)-1,2-dihydroquinazolin-2-yl]-(4-fluorophenyl)-amine (**7**)*

The general procedure with **2** (8.6 g, 0.02 mol), Et_3N (6.06 g, 0.06 mol) and 4-fluoroaniline (4.4 g, 0.04 mol) in MeCN (15 ml) produced **7** (9.1 g, 77% yield); mp 126–127°C (hexane). ^{1}H NMR ($CDCl_3$) δ_H 7.47 (N–H), 6.98 (Ph). ^{13}C NMR ($CDCl_3$) δ_C 159.6 ($C^{7,20}$, $^1J_{CF}$=244.9), 158.6 (C^4, $^2J_{CF}$=22.3), 154.9 (C^2, $^2J_{CF}$=26.2), 131.7 (C^{17}), 128.6 (C^{10}), 126.6 (C^{18}), 123.0 (C^5), 122.6 (C^{19}), 122.3 (C^9), 117.0 ($C^{13,16}$, $^1J_{CF}$=286.8; $^2J_{CF}$=33.7), 114.7 ($C^{6,8}$, $^3J_{CF}$=29.2), 110.4 ($C^{11,14}$, $^1J_{CF}$=263.4; $^2J_{CF}$=40.4), 107.8 ($C^{12,15}$, $^1J_{CF}$=268.4; $^2J_{CF}$=35.4). ^{19}F NMR ($CDCl_3$) δ_F 81.9 (3F, F^{13}), 81.8 (3F, F^{16}), 42.8 and 41.9 (2F, F^{11}), 44.1 and 42.8 (2F, F^{14}, AB-system J_{FF}=234 Hz), 35.8 (2F, F^{12}), 35.4 (2F, F^{15}). IR 3415 (N–H), 3140 (C–H); 1739 (C=N); 1696 (C=N); 1651 (C=C_{Ar}); 1540 and 1511 (C=C_{ar}), 1410 and 1350 (N–C), 1234–1200 (C–F) [23]. UV spectrum λ_{max} 334 nm (ε=1350). HRMS calc. 595.0541 for $C_{20}H_9F_{16}N_3$, found 595.0540. Found (%): C, 40.46; H, 1.51; F, 50.47; N, 6.06. Calc. (%): C, 40.34; H, 1.51; F, 51.09; N, 7.06.

*3.2.6. Synthesis of [2,4-bis(heptafluoropropyl)-6-methoxy-1,2-dihydroquinazolin-2-yl]-(4-methoxyphenyl)-amine (**8**)*

The general procedure with **2** (8.6 g, 0.02 mol), Et_3N (6.06 g, 0.06 mol) and 4-methoxyaniline (4.9 g, 0.04 mol) in MeCN (15 ml) gave **8** (8.9 g, 72% yield); mp 100–101°C (CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ_H 7.47 (N–H), 6.98–7.11 (Ph), 3.72 (CH_3O). ^{13}C NMR ($CDCl_3$) δ_C 158.4 (C^4, $^2J_{CF}$=28.6), 157.6 (C^{10}), 156.8 (C^5), 154.6 (C^2, $^2J_{CF}$=25.8), 144.6 ($C^{7,20}$), 129.3 (C^{17}), 128.4 (C^8), 127.7 (C^6), 124.2 (C^{19}), 121.9 (C^{18}), 117.0 ($C^{13,16}$, $^1J_{CF}$=287.4; $^2J_{CF}$=33.5), 113.7 (C^9), 109.2 ($C^{11,14}$, $^1J_{CF}$=261.3; $^2J_{CF}$=30.2), 107.7 ($C^{12,15}$, $^1J_{CF}$= 266.7; $^2J_{CF}$=38.4), 54.1 ($C^{21,22}$). ^{19}F NMR ($CDCl_3$) δ_F 82.08 (3F, F^{13}), 82.5 (3F, F^{16}), 43.6 (2F, F^{11}), 43.1 (2F, F^{14}), 36.7 (2F, F^{12}), 36.4 (2F, F^{15}). IR 3380 (N–H), 2902, 2941 (C–H); 1693 (C=N); 1465 (C=C_{Ar}); 1230–1196 (C–F) [23]. HRMS calc. 619.0941 for $C_{22}H_{15}F_{14}N_3O_2$, found 619.0938.

*3.2.7. Synthesis of (2-nitrophenyl)-[1-(2-nitrophenyl)-2,4-bis(heptafluoropropyl)-1,2-dihydro-[1,3]-diazet-2-yl]-amine (**16**)*

The general procedure with **2** (9.4 g, 0.02 mol), Et_3N (6.06 g, 0.06 mol) and 2-nitroaniline (3 g, 0.02 mol) in MeCN (35 ml) provided **16** (9.02 g, 64% yield); mp 73–74°C (hexane). ^1H NMR ($CDCl_3$) δ_H 6.20 (N–H), 6.57–7.92 (Ph). ^{13}C NMR ($CDCl_3$) δ_C 155.5 (C^2, $^1J_{CF}$=274.0), 139.8 (C^{21}), 144.8 (C^{15}), 135.9 (C^{13}), 135.3 (C^{19}), 133.7 (C^{16}), 131.3 (C^{14}), 116.2 (C^{12}), 118.6 (C^{11}), 125.9 (C^{20}), 125.6 (C^{22}), 121.9 (C^{18}), 121.7 (C^{17}), 115.3 ($C^{7,10}$, $^1J_{CF}$=287.8; $^2J_{CF}$=33.6), 107.5 ($C^{5,8}$, $^1J_{CF}$=263.4; $^2J_{CF}$=40.2), 106.2 ($C^{6,9}$, $^1J_{CF}$=268.3; $^2J_{CF}$=35.1). ^{19}F NMR ($CDCl_3$) δ_F 82.9 (F^7), 82.7 (F^{10}), 45.9 (F^5), 44.9 (F^8), 36.9 (F^6), 36.7 (F^9). IR 3400 (N–H), 3200 (C–H); 1703 (C=N); 1625 (N=C); 1435 and 1347 (NO_2), 1288 (N–C), 1223–1123 (C–F) [23]. UV spectrum (C_2H_5OH) λ_{max} 231 nm (ε=20 000), 273 nm (ε=6900), 404 nm (ε=4300). HRMS calc. 649.0431 for $C_{20}H_9F_{14}N_5O_4$, found 649.0476.

*3.2.8. Synthesis of (4-nitrophenyl)-[1-(4-nitrophenyl)-2,4-bis(heptafluoropropyl)-1,2-dihydro-[1,3]-diazet-2-yl]-amine (**17**)*

The general procedure with **2** (9.4 g, 0.02 mol), Et_3N (6.06 g, 0.06 mol) and 4-nitroaniline (3 g, 0.02 mol) in MeCN (35 ml) produced **17** (9.6 g, 68% yield); mp 157–158°C (CH_2Cl_2). ^1H NMR ($CDCl_3$) δ_H 7.10 (N–H), 6.98–8.19 (Ph). ^{13}C NMR ($CDCl_3$) δ_C 156.7 (C^4, $^2J_{CF}$=10.2), 153.9 (C^2, $^2J_{CF}$=16.2), 142.8 (C^{13}), 140.4 (C^{12}), 121.1 (C^{14}), 122.7 (C^{11}), 115.3 ($C^{7,10}$, $^1J_{CF}$=287.8; $^2J_{CF}$=33.7), 107.5 ($C^{5,8}$, $^1J_{CF}$=263.4; $^2J_{CF}$=40.4), 106.2 ($C^{6,9}$, $^1J_{CF}$=268.3, $^2J_{CF}$=35.5). ^{19}F NMR ($CDCl_3$) δ_F 82.1 (F^7), 81.7 (F^{10}), 46.8 (F^5), 46.0 (F^8), 37.7 (F^6), 35.9 (F^9). IR 3373 (N–H), 3078 (C–H); 1696 (C=N); 1634 (N=C); 1585 ($C=C_{Ar}$); 1520 ($C=C_{ar}$), 1414 and 1344 (NO_2), 1273–1190 (C–F) [23]. UV spectrum λ_{max} 205 nm (ε=30 700), 317 nm (ε=17 500), 401 nm (ε=4700). HRMS calc. 649.0431 for $C_{20}H_9F_{14}N_5O_4$, found 649.0418. Found (%): C, 36.73; 36.70; H, 1.68; 1.95; F, 39.69; 39.80; N, 10.51. Calc. (%): C, 36.98; H, 1.39; F, 40.99; N, 10.79.

*3.2.9. Synthesis of (pentafluorophenyl)-[1-(pentafluorophenyl)-2,4-bis(heptafluoropropyl)-1,2-dihydro-[1,3]-diazet-2-yl]-amine (**18**)*

The general procedure with **2** (5.6 g, 0.013 mol), Et_3N (5.3 g, 0.052 mol) and pentafluoroaniline (4.8 g, 0.026 mol) in MeCN (15 ml) gave **18** (5.5 g, 57% yield); bp 110–115°C (0.2 Torr). mp 117–118°C (CH_2Cl_2). ^{13}C NMR ($CDCl_3$) δ_C 158.4 (C^2, $^2J_{CF}$=25.9), 155.8 (C^4), 140.5 ($C^{9,14}$, $^1J_{CF}$=250.4), 137.2 ($C^{10,14}$, $^1J_{CF}$=249.4), 135.7 (C^{15}, $^1J_{CF}$=240.4), 131.5 (C^{11}, $^1J_{CF}$=240.1), 130.3 (C^8, $^2J_{CF}$=33.7), 116.6 ($C^{7,7'}$, $^1J_{CF}$=287.5; $^2J_{CF}$=33.6), 109.2 ($C^{5,5'}$, $^1J_{CF}$=264.4, $^2J_{CF}$=32.5), 108.4 ($C^{6,6'}$, $^1J_{CF}$=275.4, $^2J_{CF}$=30.9). ^{19}F ($CDCl_3$) δ_F 82.8 (F^7), 82.1 ($F^{7'}$), 47.9 (F^5), 44.2 (F^5), 36.7 (F^6), 36.4 ($F^{6'}$), 13.8 (F^9), 12.3 (F^{13}), 12.1 (F^{11}), 12.1 (F^{15}), −2.9 (F^{10}), −3.6 (F^{14}). Found (%): C, 32.59; 32.68; H, 0.34; 0.39; F, 62.50; 62.32; N, 5.36; M (mass spectrometry), 739. $C_{20}HF_{24}N_3$: Calc. (%): C, 32.48; H, 0.14; F, 61.71; N, 5.68; M, 739.

*3.2.10. Synthesis of 1-(2,6-dichlorophenyl)-2-fluoro-2,4-bis-(heptafluoropropyl)-1,2-dihydro-[1,3]-diazete (**19**)*

The general procedure with **2** (4.33 g, 0.01 mol), Et_3N (3.03 g, 0.03 mol) and 2,6-dichloroaniline (1.62 g, 0.01 mol) in MeCN (15 ml) provided **19** (2.4 g, 47% yield); bp 112–113°C (0.5 Torr). ^1H NMR ($CDCl_3$) δ_H 1.08 (H^{18}), 1.12 (H^{17}), 1.52 (H^{10}), 2.09 (H^9), 2.79 (H^8), 6.93–7.02 (Ph). ^{13}C NMR ($CDCl_3$) δ_C 161.9 (C^6, $^2J_{CF}$=10.4), 159.4 (C^2, $^2J_{CF}$=15.9), 144.0 (C^6), 130.4 (C^8), 129.7 (C^9), 129.0 (C^{10}), 125.8 (C^5), 129.1 (C^{22}), 127.3 (C^{21}), 116.4 (C^{19}), 117.8 (C^{20}), 109.7 ($C^{11,14}$, $^1J_{CF}$=268.4; $^2J_{CF}$=35.4), 118.0 ($C^{13,16}$, $^1J_{CF}$=288.5; $^2J_{CF}$=33.2), 108.5 ($C^{12,15}$, $^1J_{CF}$=263.9; $^2J_{CF}$=40.2), 16.7 (C^{23}), 45.4 ($C^{17,18}$). ^{19}F ($CDCl_3$) δ_F 82.4 (F^{16}), 81.8 (F^{13}), 48.8 (F^{14}), 44.8 (F^{11}), 38.0 (F^{15}), 35.7 (F^{12}). 3435 (N–H), 2986 (C–H); 1745 (C=C); 1697 (C=C); 1662 (C=N); 1506 and 1470 ($C=C_{ar}$), 1399 and 1349 (N–C); 1310, 1230–1125 (C–F) [23]. UV spectrum λ_{max} 240 nm (ε=8600). HRMS calc. 615.1355 for $C_{24}H_{19}F_{14}N_3$, found 615.1340.

*3.2.11. Synthesis of [2,4-bis-(heptafluoropropyl)-4a,8-dimethyl-2,4a-dihydroquinazolin-2-yl]-(2,6-dimethyl-phenyl)-amine (**20**)*

The general procedure with **2** (12.5 g, 0.029 mol), Et_3N (8.08 g, 0.08 mol) and 2,6-dimethylaniline (3.5 g, 0.029 mol) in MeCN (55 ml) produced **20** (10.8 g, 60.8% yield); bp 150–155°C (0.4 Torr). ^1H NMR ($CDCl_3$) δ_H 1.08 (H^{18}), 1.12 (H^{17}), 1.52 (H^{10}), 2.09 (H^9), 2.79 (H^8), 6.93–7.02 (Ph). ^{13}C NMR ($CDCl_3$) δ_C 161.9 (C^6, $^2J_{CF}$=10.4), 159.4 (C^2, $^2J_{CF}$=15.9), 144.0 (C^6), 130.4 (C^8), 129.7 (C^9), 129.0 (C^{10}), 125.8 (C^5), 129.1 (C^{22}), 127.3 (C^{21}), 116.4 (C^{19}), 117.8 (C^{20}), 109.7 ($C^{11,14}$, $^1J_{CF}$=268.4; $^2J_{CF}$=35.4), 118.0 ($C^{13,16}$, $^1J_{CF}$=288.5; $^2J_{CF}$=33.2), 108.5 ($C^{12,15}$, $^1J_{CF}$=263.9; $^2J_{CF}$=40.2), 45.4 ($C^{17,18}$), 16.7 (C^{23}). ^{19}F NMR ($CDCl_3$) δ_F 82.4 (3F, F^{16}), 81.8 (3F, F^{13}), 48.8 (2F, F^{14}), 44.8 (2F, F^{11}), 38.0 (2F, F^{15}), 35.7 (2F, F^{12}). IR 3435 (N–H), 2986 (C–H), 1745 (C=C), 1697 (C=C), 1662 (C=N), 1506 and 1470 ($C=C_{ar}$), 1399 and 1349 (N–C), 1310, 1230–1125 (C–F) [23]. UV spectrum λ_{max} (C_2H_5OH) 240 nm (ε=8600). HRMS calc. 615.1355 for $C_{24}H_{19}F_{14}N_3$, found 615.1340.

*3.2.12. Synthesis of 4,4-difluoro-4a,8-dimethyl-2-(pentafluoroethyl)-3-trifluoromethyl-4,4a-dihydroquinoline (**21**)*

The general procedure with **1** (8.7 g, 0.029 mol), Et_3N (8.08 g, 0.08 mol) and 2,6-dimethylaniline (3.5 g, 0.029 mol) in MeCN (40 ml) gave **21** (3.0 g, 27% yield); bp 93–95°C (0.4 Torr), mp 178–179°C (aq. C_2H_5OH).

^1H NMR ($CDCl_3$) δ_H 1.22 (H^{14}, 7.3), 2.05 (H^8, 7.3), 2.30 (H^9, 7.3), 2.97 (H^{10}, 7.3). ^{13}C NMR ($CDCl_3$) δ_C 153.2 (C^6), 130.4 (C^8), 129.7 (C^9), 129.0 (C^{10}), 125.8 (C^5), 124.8 (C^{11},

$^1J_{CF}$=269.1), 118.1 (C^{13}, $^1J_{CF}$=287.2; $^2J_{CF}$=31.0), 115.4 (C^4, $^1J_{CF}$=256.8; $^2J_{CF}$=32.3), 109.4 (C^{12}, $^1J_{CF}$=270.0; $^2J_{CF}$=38.2), 46.0 (C^{14}), 17.9 (C^{15}). ^{19}F NMR ($CDCl_3$) δ_F 110.7 (3F, F^{11}, m), 82.7 (3F, F^{13}, s), 60.6 (2F, F^{12}, q, 10), 37.2 (2F, F^4, q, 10). IR 2935 (C–H); 1742 (C=C); 1652 (C=C); 1590 (C=N); 1476 (C–N), 1443 and 1410 (N–C); 1340, 1312, 1230–1190 (C–F) [23]. UV spectrum λ_{max} 244 nm (ε=14 300), 334 nm (ε=1100). HRMS calc. 381.0575 for $C_{14}H_9F_{10}N$, found 381.0561.

*3.2.13. Reaction of **1** with pentafluoroaniline*

A mixture of **1** (10 g, 0.033 mol), pentafluoroaniline (6.1 g, 0.033 mol) and Et_3N (6.7 g, 0.066 mol) in MeCN (65 ml) was stirred at 45°C for 3.5 h. The resulting solution was neutralized with 5% aqueous H_2SO_4 and extracted with CH_2Cl_2 (3 ml×50 ml). The concentrate was distilled under reduced pressure to give a liquid fraction 1 (bp 45–55°C (4 Torr), 9.0 g) and fraction 2 (bp 118–125°C (9 Torr), 6.5 g). Fraction 1 was analyzed by ^{19}F NMR and GC-MS and consisted of **24** (21%), **23** (6%) and **22** (73%); fraction 2 was further purified by column chromatography (hexane/CH_2Cl_2) to provide **25**.

(Pentafluorophenyl)-[3,3,3-trifluoro-1-(pentafluoroethyl)-2-trifluoromethylpropylidene]-amine (**22**): 3.5 g, bp 118–119°C (9 Torr). ^{1}H NMR ($CDCl_3$) δ_H 4.33 (C–H). ^{13}C NMR ($CDCl_3$) δ_C 153.3 (C^3, $^2J_{CF}$=10.0), 139.2 (C^{10}, $^1J_{CF}$=253.9), 138.5 (C^8, $^1J_{CF}$=252.8), 135.4 (C^7), 135.4 (C^9, $^1J_{CF}$=249.9), 121.3 ($C^{1,6}$, $^1J_{CF}$=282.3), 118.1 (C^5, $^1J_{CF}$=286.3; $^2J_{CF}$=34.0), 109.4 (C^4, $^1J_{CF}$=268.1; $^2J_{CF}$=40.4), 51.8 (C^2, $^2J_{CF}$=31.9). ^{19}F NMR ($CDCl_3$) δ_F 90.9 (6F, $F^{1,6}$), 81.7 (3F, F^5), 46.6 (F^4), 12.2 (2F, F^8), 2.7 (F, F^{10}), 0.1 (2F, F^9). IR 1740 (C=C); 1710 (C=C); 1660 (C=N); 1615 (C=N), 1500 (C=C_{ar}), 1360 and 1340 (N–C); 1320, 1230–1160 (C–F) [23]. HRMS calc. 462.9853 for $C_{12}HF_{16}N$, found 462.9847.

[3,3-Difluoro-1-(pentafluoroethyl)-2-trifluoromethyl-allylidene]-(pentafluorophenyl)-amine (**23**): bp 26–27°C (6 Torr). ^{19}F NMR ($CDCl_3$) δ_F 103.2 (1F, F^1), 101.8 (3F, F^6), 91.4 (1F, F^1), 83.5 (3F, F^5), 50.5 (2F, F^4), 14.8 (2F, F^8), 4.8 (F, F^{10}), 0.1 (2F, F^9). GC-MS 443 $[M]^+$, 424 $[M–F]^+$, 324 $[M–C_2F_5]^+$, 312, 167 $[C_6F_5]^+$, 148 $[C_6F_4]^+$, 117 $[C_5F_3]^+$, 93 $[C_3F_3]^+$, 69 $[CF_3]^+$.

(Pentafluorophenyl)-[2,2,3,3,3-pentafluoro-1-(2′,2′,2′-trifluoroethyl)-propylidene]-amine (**24**): bp 50–51°C (6 Torr). ^{19}F NMR ($CDCl_3$) δ_F 102.4 (3F, F^1), 82.8 (3F, F^5), 51.8 (2F, F^4), 13.3 (2F, F^7), 6.8 (2F, F^9), 0.1 (2F, F^8). GC-MS 395 $[M]^+$, 376 $[M–F]^+$, 344 $[M–CHF_2]^+$, 276 $[M–C_2F_5]^+$, 167 $[C_6F_5]^+$, 148 $[C_6F_4]^+$, 117 $[C_5F_3]^+$, 93 $[C_3F_3]^+$, 69 $[CF_3]^+$.

2,2,3,3,3-Pentafluoro-*N*-(pentafluorophenyl)-propionamide (**25**): 6.5 g, mp 110–112°C (CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ_H 5.46 (N–H). ^{13}C NMR ($CDCl_3$) δ_C 156.1 (C^1, $^2J_{CF}$=27.2), 142.9 (C^5, $^1J_{CF}$=256.4; $^2J_{CF}$=11.6), 140.4 (C^7, $^1J_{CF}$=254; $^2J_{CF}$=13.7), 137.1 (C^7, $^1J_{CF}$=255.4; $^2J_{CF}$=10.6), 117.1 (C^3, $^1J_{CF}$=286.2; $^2J_{CF}$=34.4), 109.5 (C^4, $^2J_{CF}$=10.1), 106.2 (C^6, $^1J_{CF}$=266.4; $^2J_{CF}$=39.0). ^{19}F NMR ($CDCl_3$) δ_F 80.6 (3F, F^3), 41.4 (2F, F^2), 18.5 (2F, F^5), 7.6 (1F, F^7), 0.2 (2F, F^6). HRMS calc. 328.9898 for $C_9HF_{10}NO$, found 328.9895.

Acknowledgements

The authors are grateful to the Korea Research Foundation and KISTEP in Korea for their financial support for this work.

References

[1] R. Filler, Y. Kobayashi, L.M. Yagupolskii (Eds.), Organofluorine Compounds in Medicinal Chemistry and Biomedical Applications, Elsevier, Amsterdam, 1993, p. 386.
[2] R.E. Banks, D.E. Smart, J.C. Tatlow (Eds.), Organofluorine Chemistry, Principles and Commercial Applications, Plenum Press, New York, 1994, p. 287.
[3] J.F. Liebman, A. Greenberg, W.R. Dolbier (Eds.), Fluorine-Containing Molecules. Structure, Reactivity, Synthesis and Applications, VCH Publishers, New York, 1988, pp. 259–308.
[4] K. Burger, U. Wucherpfennig, E. Brunner, in: A.R. Katritzky, A.J. Boulton (Eds.), Adv. Heterocyc. Chem., Vol. 60, Academic Press, New York, 1994, p. 1064.
[5] G.G. Furin, Chemistry Rev. 20 (1996) 1.
[6] G.G. Furin, Zh. Org. Khim. 30 (1994) 1708 [Russ. J. Org. Chem. 30 (1994) (Engl. Transl.)].
[7] R.D. Chambers, C.R. Sargent, in: A.R. Katritzky, A.J. Boulton (Eds.), Adv. Heterocyc. Chem., Vol. 28, Academic Press, New York, 1981, p. 1.
[8] J.-P. Genet, J.-O. Durand, S. Roland, M. Savignac, F. Jung, Tetrahedron Lett. 38 (1997) 69.
[9] S. Roland, J.-O. Durand, M. Savignac, J.-P. Genet, F. Jung, Tetrahedon Lett. 36 (1995) 3007.
[10] P.L. Coe, N.C. Ray, J. Fluorine Chem. 88 (1998) 169.
[11] W.-Y. Huang, Q.-G. Chen, Adv. Sci. China Chem. 2 (1987) 31.
[12] D.P. Del'tsova, L.L. Gervits, A.A. Kadyrov, J. Fluorine Chem. 79 (1996) 97.
[13] S. Bartlett, R.D. Chambers, A.A. Lindley, H.C. Fielding, J. Chem. Soc., Perkin Trans. I (1980) 1551.
[14] G.G. Furin, V.G. Kiriyanko, V.A. Lopirev, E.L. Zhuzhgov, N.I. Prozuk, Zh. Org. Khim. 36 (2000) 19.
[15] G.G. Furin, V.A. Lopirev, E.L. Zhuzhgov, N.I. Prozuk, Zh. Org. Khim. 36 (2000) 120.
[16] G.G. Furin, V.G. Kiriyanko, E.L. Zhuzhgov, Zh. Org. Khim. 36 (2000) 33.
[17] W.T. Flowers, R.N. Haszeldine, C. Owen, A. Thomas, J. Chem. Soc., Chem. Commun. (1994) 134.
[18] R.D. Chambers, A.R. Edwards, Tetrahedron 54 (1998) 4949.
[19] M.W. Briscoe, R.D. Chambers, S.J. Mullins, T. Nakamura, J.F.S. Vaughan, J. Chem. Soc., Perkin Trans. I (1994) 3119.
[20] Yu.A. Sokolova, O.A. D'yachenko, L.O. Atovmyan, M.O. Lozunsky, A.F. Shibanyak, Izv. Akad. Nauk SSSR, Ser. Khim. (1983) 815.
[21] F.H. Allen, O. Kennard, Chem. Design Automation News 8 (1993) 31.
[22] Yu.V. Zeifman, L.S. German, Izv. Akad. Nauk, Ser. Khim. (1994) 1678.
[23] L.L. Bellamy, The Infrared Spectra of Complex Molecules, Methuen and Co., London; Wiley, New York, 1954, pp. 295–315.