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Synthesis of fluorinated *N*-arylpyrazoles with perfluoro-2-methyl-2-pentene and arylhydrazines

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Abstract

Reactions of arylhydrazines (phenyl, 2-nitrophenyl, 4-nitrophenyl, 2,4-dinitrophenyl, pentafluorophenyl, 4-trifluoromethyl-2,3,5,6-tetrafluorophenylhydrazine or 4,4′-dihydrazinooctafluorobiphenyl) with perfluoro-2-methyl-2-pentene in the presence of triethylamine have effectively produced 1-aryl-perfluoro-3-ethyl-4-methylpyrazole and 1-aryl-perfluoro-5-ethyl-4-methylpyrazole in various ratios depending on the reaction conditions and arylhydrazine used. *Syn*- and *anti*-aminoimines which might be the intermediates for pyrazoles have been isolated under appropriate conditions. The routes of formation for these products and the role of triethylamine have been discussed. The reaction of perfluoro-2-methyl-2-pentene with phenylhydrazine has been investigated in detail. The structure of 3-fluoro-5-pentafluoroethyl-1-phenyl-4-trifluoromethylpyrazole has been elucidated by X-ray crystallography.

Keywords: Perfluoro-2-methyl-2-pentene; Arylhydrazines; Pyrazoles; Fluorinated *N*-arylpyrazoles; Structure 3-fluoro-5-pentafluoroethyl-1-phenyl-4-trifluoromethylpyrazole

1. Introduction

The synthesis of heterocyclic compounds containing fluorine has become an important part of fluoroorganic chemistry [1]. Among nitrogen containing heterocyclic compounds, azoles take such a pivotal place due to their biological activities that various azole derivatives have been prepared for medicinal and agricultural applications. Moreover, an attachment of fluorine-containing substituents to an azole generally considerably increases its biological activity [2]. For example, the introduction of a polyfluorinated benzene ring to a pyrazole has resulted in a sharp increase in biological activity and these compounds have been applied for the synthesis of herbicides and plant growth regulators [3]. Fluoroalkyl derivatives of pyrazole have drawn much attention for use as biologically active substances: herbicides, fungicides, insecticides, analgesics, antipyretics and anti-inflammatores [4,5]. This, therefore, has led to the development of a few general, but somewhat limited, methods for their synthesis.

Among approaches to obtain heterocycles with both fluorine atoms and perfluoroalkyl groups, intermolecular nucleophilic cyclization between two molecules containing a potentially nucleophilic center at the double bond is important [6]. Internal perfluoroolefins appear to be interesting precursors in the above sense, because the creation of a heterocyclic system is possible by the treatment of an internal olefin with either mononucleophilic or binucleophilic reagents. The route of the intramolecular nucleophilic cyclization is determined by the electronic and steric factors of the nucleophile. The tautomeric process at a double bond, especially in the presence of a fragment containing a N–H bond, makes it possible to synthesize 7–9 membered heterocycles. Thus, Saloutin et al. [7,8] applied that concept for the reaction of perfluoro-2-pentene with ethylenediamine. Ikeda et al. [9,10] used a similar methodology for the reaction of perfluoro-2-methyl-2-pentene with amides or hydrazones. In these cases the authors suppose the formation of an intermediate with the conjugated system C=C–C=N followed by cyclization via a secondary nucleophilic addition to the

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terminal double bond. The synthesis of pyrazole derivatives has been conducted by using substituted hydrazines and perfluoroolefins [11–15].

In the process of our research on synthesizing azoles with polyfluorinated benzene rings, perfluoro-2-methyl-2-pentene(**1**) has been focused as a potential precursor for the synthesis of various fluorinated pyrazoles by reaction with arylhydrazines. The main purpose of this work consists in the investigation of an intramolecular cyclization during the reaction between an internal alkene and aryl hydrazines.

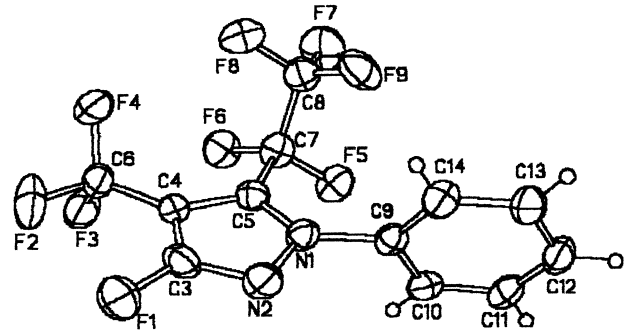
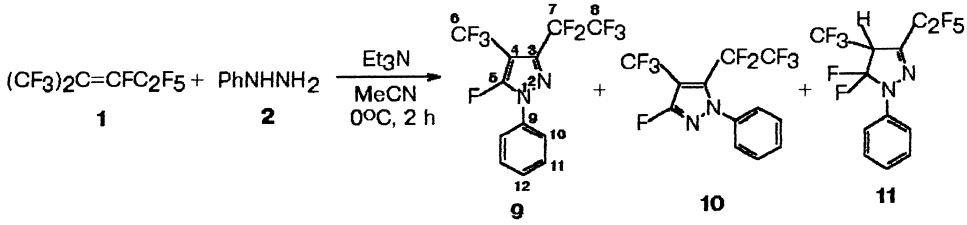


Fig. 1. The molecular geometry of the pyrazole **10** (ORTEP diagram).

2. Results and discussion

As hydrazine reactants, phenylhydrazine(2), pentafluorophenylhydrazine(**3**), 4-(trifluoromethyl)-2,3,5,6-tetrafluorophenylhydrazine(**4**), 4,4′-dihydrazinooctafluoro biphenyl(**5**) 2-nitrophenylhydrazine(**6**), 4-nitrophenylhydrazine(**7**) and 2,4-dinitrophenylhydrazine(**8**) were used since a substantial influence on the nuclophilicity of nitrogen atoms in the hydrazine moiety was expected from the introduction of nitro groups or fluorine atoms into the benzene ring. Triethylamine was used as a base and its function was carefully scrutinized.

Reaction of the internal alkene **1** with phenylhydrazine(**2**) in the presence of 2 equivalents of Et_3N gave a mixture of the pyrazole **9** and **10** in a 4:1 ratio and the pyrazoline **11**.



However, treatment of **1** and phenylhydrazine with more than 3 equivalents of Et_3N produce **9** and **11**, in yields 71% and 7% respectively.

IR spectra of the pyrazoles **9** and **10** differ from each other in the band intensities near 1300–1600 cm^{-1} and by the frequencies of the C=C vibration. The presence of the conjugated C=C and C=N bonds in a pyrazole ring leads to the appearance of two absorption bands at 1500–1600 cm^{-1}. The isomers **9** and **10** contain $FC{=}CCF_3$ and $CF_3C{=}CC_2F_5$ respectively. It is known that the replacement of perfluoroalkyl group at a C=C double bond by fluorine results in an increase of the frequency of the carbon–carbon vibration [16]. Indeed, the corresponding values of the C=C bond in isomer **9** are located at 1520 and 1595 cm^{-1} and for isomer **10**, they are observed at 1527 and 1579 cm^{-1}.

Moreover, there is a substantial difference in the intensities of the stretching and in plane deformation C=C vibrations in the IR spectra of the compounds **9** and **10**. The absorption intensity of the isomer **10** between 1300 and 1600 cm^{-1} significantly exceeds the corresponding intensity of the isomer **9**: pyrazole **9** [wavenumber (intensity)] −1200(100), 1325(67), 1356(60), 1520(79), 1595(59); pyrazole **10** −1207(100), 1325(83), 1346(83), 1527(100), 1579(82). The frequency and intensity of C–F absorption are set as references. The explanation of this phenomenon lies in the effective conjugation of the electron pair of nitrogen with the π-system of C=C–C=N in pyrazole **10** because of the higher positive charge on the sp^2-hybridized carbon atom α to N–Ph. Alternatively, the less positive charge on this α-carbon reduces such conjugation in the isomer **9** due to the less electron-withdrawing effect of fluorine atom (σ_p 0.02) in respect to C_2F_5 group (σ_p 0.69) [17]. The structure of **10** is confirmed by X-ray diffraction. According to X-ray data (Fig. 1 and Tables 1 and 2), the pyrazole **10** is nonplanar and the dihedral angle between the two ring planes is 78.0°.

In the presence of Et_3N, reactions of **1** with hydrazine **3** or **4** at 0÷40°C in THF produced perfluoro-*N*-phenyl-3-ethyl-4-methyl-pyrazole(**12**)/perfluoro-*N*-phenyl-5-ethyl-4-methylpyrazole(**13**) and perfluoro-*N*-(4-methylphenyl)-3-ethyl-4-methylpyrazole(**14**)/ per-fluoro-*N*-(4-methylphenyl)-5-ethyl-4-methylpyrazole(**15**) in 4:1 or 3:1 ratios respectively. The compounds **12–15** were isolated and purified by preparative silica gel chromatography and all structures were confirmed by spectroscopy and mass data.

Reaction of **1** with 2-nitrophenylhydrazine(**6**) gave the pyrazole isomers **16** and **17** in an 1:1 ratio. However, treatment of the hydrazine **5** with olefin **1** gave a complex

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound **10** (U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor)

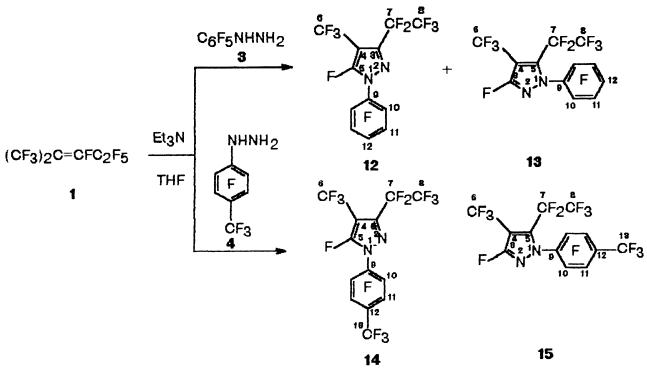
Atom	x	y	z	U(eq)
N(1)	35(3)	1936(4)	4656(10)	72(1)
N(2)	−649(4)	2001(5)	5720(11)	90(2)
C(3)	−1101(4)	2840(7)	4921(15)	90(2)
C(4)	−749(4)	3299(5)	3417(13)	72(2)
C(5)	−3(4)	2666(6)	3256	74(2)
C(6)	−1118(5)	4219(6)	2213(14)	95(3)
C(7)	646(5)	2748(7)	1806(12)	88(2)
C(8)	1357(6)	3553(8)	2227(13)	93(2)
C(9)	686(4)	1111(5)	5244(11)	67(2)
C(10)	749(5)	−22(5)	4442(12)	79(2)
C(11)	1345(5)	−805(6)	5082(13)	90(2)
C(12)	1863(6)	−522(6)	6398(14)	94(2)
C(13)	1792(5)	641(7)	7225(13)	96(2)
C(14)	1194(5)	1428(7)	6614(13)	84(2)
F(1)	−1825(3)	3130(5)	5625(14)	143(3)
F(2)	−1817(4)	4678(6)	2947(15)	157(3)
F(3)	−1390(4)	3822(5)	668(11)	119(2)
F(4)	−629(4)	5139(5)	1911(14)	135(3)
F(5)	967(3)	1603(4)	1420(9)	104(2)
F(6)	289(3)	3109(5)	258(8)	107(1)
F(7)	1904(4)	3491(7)	877(11)	149(3)
F(8)	1080(4)	4646(5)	2347(10)	117(2)
F(9)	1723(3)	3236(6)	3692(10)	129(2)
H(10)	396	−238	3511	80
H(11)	1391	−1563	4567	80
H(12)	2261	−1073	6788	80
H(13)	2149	850	8153	80
H(14)	1143	2185	7132	80

Table 2
Bond lengths [Å] and angles [deg] for compound **10**

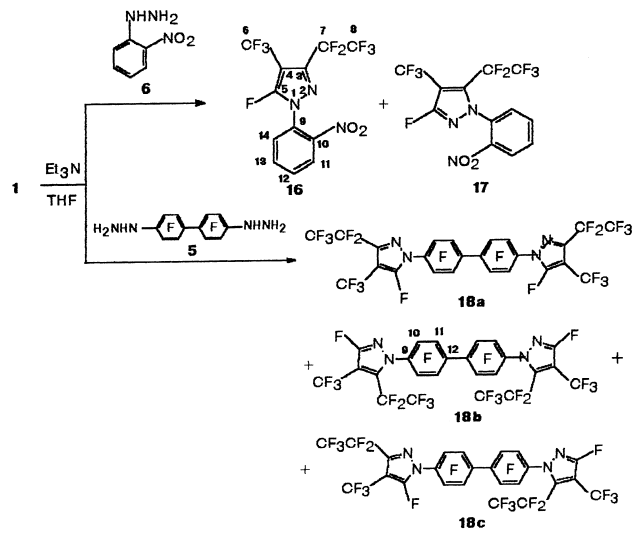
C(5)–N(1)	1.331(8)	C(5)–C(4)	1.388(9)
C(5)–C(7)	1.507(10)	C(4)–C(3)	1.362(12)
C(4)–C(6)	1.487(11)	C(3)–F(1)	1.311(9)
C(3)–N(2)	1.323(10)	C(9)–C(14)	1.357(11)
C(9)–C(10)	1.399(9)	C(9)–N(1)	1.454(8)
C(10)–C(11)	1.377(10)	C(11)–C(12)	1.327(12)
C(12)–C(13)	1.438(12)	C(13)–C(14)	1.374(11)
C(7)–F(6)	1.356(10)	C(7)–F(5)	1.401(9)
C(7)–C(8)	1.480(13)	C(8)–F(9)	1.296(11)
C(8)–F(8)	1.295(10)	C(8)–F(7)	1.341(10)
C(6)–F(4)	1.307(10)	C(6)–F(3)	1.316(10)
C(6)–F(2)	1.346(10)	N(2)–N(1)	1.356(8)
N(1)–C(5)–C(4)	106.2(5)	N(1)–C(5)–C(7)	125.3(6)
C(4)–C(5)–C(7)	128.5(6)	C(3)–C(4)–C(5)	103.8(6)
C(3)–C(4)–C(6)	126.8(7)	C(5)–C(4)–C(6)	129.4(7)
F(1)–C(3)–N(2)	118.1(9)	F(1)–C(3)–C(4)	127.4(8)
N(2)–C(3)–C(4)	114.6(6)	C(14)–C(9)–C(10)	121.2(6)
C(14)–C(9)–N(1)	119.6(6)	C(10)–C(9)–N(1)	119.1(6)
C(11)–C(10)–C(9)	117.8(7)	C(12)–C(11)–C(10)	122.8(7)
C(11)–C(12)–C(13)	119.1(7)	C(14)–C(13)–C(12)	118.8(8)
C(9)–C(14)–C(13)	120.3(7)	F(6)–C(7)–F(5)	104.1(7)
F(6)–C(7)–C(8)	109.1(7)	F(5)–C(7)–C(8)	108.2(7)
F(6)–C(7)–C(5)	110.5(6)	F(5)–C(7)–C(5)	110.3(6)
C(8)–C(7)–C(5)	114.1(7)	F(9)–C(8)–F(8)	110.5(9)
F(9)–C(8)–F(7)	109.6(7)	F(8)–C(8)–F(7)	108.9(7)
F(9)–C(8)–C(7)	111.4(7)	F(8)–C(8)–C(7)	108.6(7)
F(7)–C(8)–C(7)	107.8(8)	F(4)–C(6)–F(3)	107.8(8)
F(4)–C(6)–F(2)	105.7(7)	F(3)–C(6)–F(2)	102.4(7)
F(4)–C(6)–C(4)	114.0(6)	F(3)–C(6)–C(4)	116.0(6)
F(2)–C(6)–C(4)	109.9(8)	C(3)–N(2)–N(1)	102.1(6)
C(5)–N(1)–N(2)	113.4(5)	C(5)–N(1)–C(9)	131.1(6)
N(2)–N(1)–C(9)	115.5(6)		

mixture of products, from which the pyrazole derivatives **18a** and **18b** were separated and identified.

When electron-withdrawing groups are attached to the phenyl ring in a arylhydrazine, its nucleophilicity is expected to decrease so that it would be reasonable to increase the reactivity of the counter-electrophile for a better reaction.

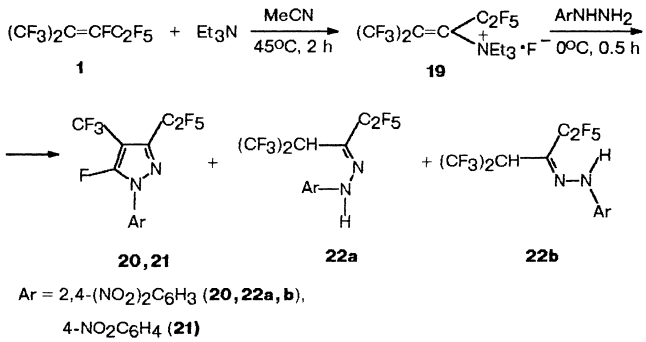


To increase the reaction rate of nucleophilic addition to the double bond, an activation of the internal double bond has been conducted by the preliminary substitution of the fluorine atom at the C=C bond with a quaternary ammonium group.



The salt **19** was prepared for this purpose from **1** and Et_3N [15]. The effectiveness of such approach was demonstrated by Shi et al. [16] for the synthesis of *N*-substituted 4-fluoropyrazolines. However, the yield of *N*-phenyl-substituted-4-fluoropyrazoline was only 10%. Reaction of the salt **19** with 4-nitrophenylhydrazine (**7**) smoothly produced pyrazole **21** in 65% yield. However, reaction of **19** with

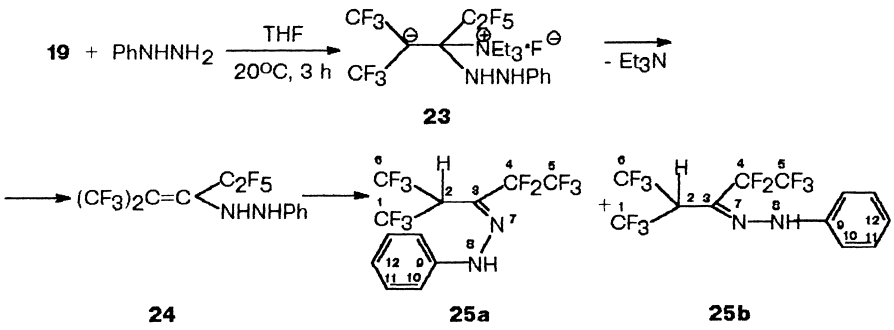
2,4-dinitrophenylhydrazine(**8**) in the presence of Et_3N gave the pyrazole **20** and the unexpected aminoimines **22a,b**. Compounds **22a** and **22b** were found to be the main products of the reaction between **1** and **8**, which is attributed to the decreased basicity of the nitrogen atom of the arylamino group.



These results clearly indicate that Et_3N is crucial for the formation of a terminal double bond from **25** which leads to the isomer **9**.

$$\mathbf{1} + 2\mathrm{PhNHNH_2} \xrightarrow[\substack{0^\circ\mathrm{C},\ 1\,\mathrm{h}\\ 20^\circ\mathrm{C},\ 2\,\mathrm{h}}]{\mathrm{MeCN}} \mathbf{9} + \mathbf{25a} + \mathbf{25b}$$

Since the catalytic effect of a dialkylamine for the isomerization of an internal olefin into a terminal one is known [6], production of the pyrazole **10** from **1** could be rationalized by the isomerization of **1** before the nucleophilic addition. In other words, addition of hydrazine **2** occurs on perfluoro-2-methyl-1-pentene, not on **1** for the formation of **10**. On the other hand, the presence of triethylamine evidently facilitates the nucleophilic attack of arylhydrazines by the formation of the salt **19** from **1**. Also, triethylamine acts as an acid scavenger to accelerate the irreversible formation of a pyrazole ring and

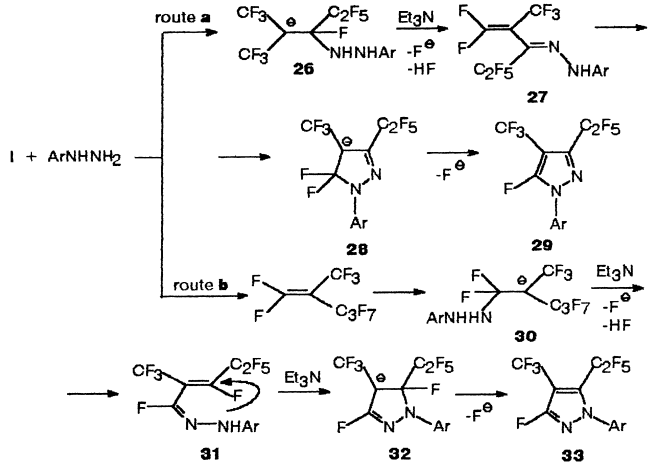


accordingly reduces the chances of isomerization of **1** to perfluoro-2-methyl-1-pentene. This explains the fact that more of isomer **10** is produced from **1** and phenylhydrazine if less of Et_3N is used.

Thus, it is possible to assume plausible reaction routes from **1** and arylhydrazine to the two pyrazole isomers.

Route **a**: An initial attack of arylhydrazine on the double bond of **1** gives intermediate **26** followed by elimination of hydrogen fluoride in the presence of Et_3N to form the terminal olefin **27**. Intramolecular nucleophilic cyclization of **27** produces pyrazole **29**.

Route **b**: The olefin **1** is isomerized to perfluoro-2-methyl-1-pentene which is considerably more reactive than the internal perfluoroolefin **1**. Presence of secondary amines and/or fluoride ions in the reaction accelerates the isomerization. It is interesting to note that 2H-perfluoro-2-methylpentane was detected in some reactions. This indicates that the formation of a corresponding carbanion which is responsible for the isomerization. Nucleophilic addition of arylhydrazine to perfluoro-2-methyl-1-pentene followed by elimination of HF and intramolecular cyclization provides the pyrazole **33**.



In conclusion, reaction of the internal perfluoroolefin **1** with arylhydrazine in the presence of triethylamine gives a mixture of two isomeric pyrazoles **29** and **33**. By using this method, various fluorinated *N*-arylhydrazines can be synthesized.

3. Experimental

3.1. Instrumentation

^{19}F NMR spectra were recorded at 282.2 MHz with a Varian UNITY plus-300 spectrometer and obtained in the presence of C_6F_6 as an internal standard; ^{13}C and ^{1}H NMR spectra were recorded at 75.4 MHz and 300.1 MHz with a

Bruker AM 400 spectrometer in ppm w.r.t. tetramethylsilane (J_{CH} not recorded). IR spectra were taken on a Mattson 5000 FTIR (NICAM) spectrometer (5% in CCl_4). Mass spectra were determined with a JEOL LMS-DX 303 spectrometer. All reactions were monitored routinely by ^{19}F NMR spectroscopy. Column chromatography was conducted with silica gel 60 (70-230 mest ASTM). GLC analysis was on an LKM-72 chromatograph (50–270°C), 4000×4 mm, SKTFW-803 on Chromosorb W. All the chemicals were of analytical grade and used without further purification. Tetrahydrofuran was distilled from potassium benzophenone ketyl.

X-ray structure analysis was carried out on a Syntex $P2_1$ diffractometer using Cu K_α radiation with a graphite monochromator. X-ray structure data for **10** $C_{12}H_5F_9N_2$, M=348.18, orthorhombic, space group $Pca2_1$, a=15.965(3), b=11.109(3), c=7.519(2) Å, V=1333.5(6) Å^3, D_c=1.734 g·cm^{-3}, Z=4, $F(000)$=688, m(Cu K_α)=1.77 mm^{-1}. 1293 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 0.63–0.97) 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 atoms refinements. The final R-factors are wR_2=0.2161, S=1.043 for all data (R=0.0721 for 898 Fo>4σ). Atomic coordinates, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Center.

3.2. Reaction compound **1** with arylhydrazines

3.2.1. Synthesis of 5-fluoro-3-pentafluoroethyl-4-trifluoromethyl-1-phenyl pyrazole (**9**) and 3-fluoro-5-pentafluoroethyl-4-trifluoromethyl-1-phenyl pyrazole (**10**)

A mixture of **1** (15.0 g, 0.050 mol) and Et_3N (10.1 g, 0.10 mol) in MeCN (45 ml) was stirred at 45°C for 2.5–3.0 h. To the resulting solution was added dropwise at 0°C phenylhydrazine (**2**) (5.4 g, 0.050 mol) over 15 min. After the addition, stirring was continued for 1 h at 0°C and then for an additional 2 h at room temperature. The reaction mixture was diluted with water, and extracted with CH_2Cl_2. The organic phase was concentrated and distilled under reduced pressure to give a yellow liquid (14.5 g, 60–62°C at 1.5 Torr). The distillate was further purified by column chromatography (hexane) to provide **9** and **10**. 5-Fluoro-3-pentafluoroethyl-4-trifluoromethyl-1-phenylpyrazole (**9**) (11.1 g, 64% yield); 60–62°C (1.5 Torr); ^1H NMR ($CDCl_3$) δ_H 7.61 (H^{10}, 2H, d, J_{HH}=5.1), 7.55 (H^{12}, 1H, t, J_{HH}=4.5), 7.50 (H^{11}, 2H, td, J_{HH}=5.1 and 4.5); ^{19}F NMR ($CDCl_3$) δ_F 41.7 (F^5, 1F, q, J_{FF}=15.3), 107.2 (F^6, 3F, dt, J_{FF}=15.3 and 9.2), 80.2 (F^8, 3F, s), 52.2 (F^7, 2F, q, J_{FF}=9.2); ^{13}C NMR ($CDCl_3$) δ_C 151.0, (C^5,$^1J_{CF}$ = 294;$^3J_{FF}$4.7), 137.5 (C^3,$^2J_{CF}$ = 32.2), 135.5 (C^9), 130.0 (C^{11}), 129.7 (C^{12}), 122.2 (C^{10}), 120.4 (C^6,$^1J_{CF}$ = 268;$^3J_{CF}$ = 4.7), 118.8 (C^8,$^1J_{CF}$ = 286;$^2J_{CF}$ = 36.4), 110.2 (C^7,$^1J_{CF}$ = 254;$^2J_{CF}$ = 40.2), 97.0 (C^4, $^2J_{CF}$ = 35; HRMS found 348.0313 $C_{12}H_5F_9N_2$ calcd. 348.0309. Mass spectrum, *m/e* 348 $[M]^+$, 329 $[M–F]^+$, 279 $[M–CF_3]^+$. 3-Fluoro-5-pentafluoroethyl-4-trifluoromethyl-1-phenylpyrazole (**10**) (2.8 g, 16% yield); m.p. 63–64°C (hexane); ^1H NMR ($CDCl_3$) δ_H 7.43 (H^{11}, 2H, m), 7.39 (H^{10}, 2H, m), 7.33 (H^{12}, 1H, m); ^{19}F NMR ($CDCl_3$) δ_F 102.2 (F^6, 3F, dt, J_{FF}=14 and 11.3), 83.0 (F^8, 3F, s), 55.8 (F^7, 2F, q, J_{FF}=11.3), 37.8 (F^3, 1F, q, J_{FF}=14); ^{13}C NMR ($CDCl_3$) δ_C 159.1 (C^3,$^1J_{CF}$ = 253;$^3J_{CF}$ = 4.7), 138.2 (C^9), 130.5 (C^{11}), 128.7 (C^{10}), 128.6 (C^{12}), 126.0 (C^5,$^2J_{CF}$ = 11.4), 120.2 (C^6,$^1J_{CF}$ = 268;$^3J_{CF}$ = 4.7), 117.9 (C^8,$^1J_{CF}$ = 286;$^2J_{CF}$ = 37.4), 109.0 (C^7,$^1J_{CF}$ = 259;$^2J_{CF}$ = 41.9), 99.2 (C^4,$^2J_{CF}$ = 41.5;$^3J_{CF}$ = 17.2). HRMS calcd. 348.0309 for $C_{12}H_5F_9N_2$ found 348.0306. Mass spectrum, *m/e* 348 $[M]^+$, 329 $[M–F]^+$, 279 $[M–CF_3]^+$, 259 $[M–CF_3–HF]^+$, 119 $[C_2F_5]^+$, 105 $[PhN_2]^+$, 92 $[PhNH]^+$, 69 $[CF_3]^+$.

3.2.2. Synthesis of the pyrazole **9** and 5,5-difluoro-3-pentafluoroethyl-4-trifluoromethyl-1-phenyl-4[H]-pyrazoline (**11**)

To a solution of compound **1** (10 g, 0.033 mol) in THF (40 ml) was added dropwise at 0°C a mixture of phenylhydrazine (**2**) (3.6 g, 0.033 mol) and Et_3N (10.1 g, 0.10 mol) with stirring for 15 min. After addition, stirring was continued for 1 h at 0°C and then for additional 1 h at room temperature. The resulting solution was neutralized with 5% aqueous H_2SO_4 and extracted with CH_2Cl_2 (3×50 ml). The concentrate was distilled under reduced pressure to give a liquid, which was further purified by column chromatography (hexane). 5-Fluoro-3-penta-fluoroethyl-; 4-trifluoromethyl-1-phenylpyrazole (**9**) (8.1 g, 71% yield). 5,5-Difluoro-3-pentafluoroethyl-; 4-trifluoromethyl-1-phenyl-4[H]-pyrazoline (**11**) (0.8 g, 7% yield); b.p. 66–67°C (1.5 Torr); ^1H NMR ($CDCl_3$) δ_H 3.94 (H^4, 1H, m), 7.07 (H^{11}, 2H, m), 6.78 ($H^{10,12}$, 3H, m); ^{19}F NMR δ_F 100.2 (F^6, 3F, m), 82.5 (F^8, 3F, s), 49.3 (F^5, 2F, m), 37.4 (F^7, 2F, m); HRMS calcd. 368.0371 for $C_{12}H_6F_{10}N_2$ found 368.0376.

3.2.3. Synthesis of perfluoro-3-ethyl-4-methyl-1-phenylpyrazole (**12**) and perfluoro-5-ethyl-4-methyl-1-phenylpyrazole (**13**)

To a solution of **1** (10.0 g, 0.033 mol) and Et_3N (10.1 g, 0.10 mol) in THF (35 ml) at 0°C was added dropwise a solution of pentafluorophenylhydrazine (**3**) (6.53 g, 0.033 mol) in THF (10 ml). The resulting solution was stirred for 3 h at room temperature and then for 2 h at 45°C. The reaction mixture was filtered and the filtrate was washed with water (2×50 ml) and dried ($MgSO_4$). Distillation of the crude product under reduced pressure gave a colorless oil (b.p. 58–80°C at 3 Torr) which was purified by column chromatography (hexane-CH_2Cl_2, 5:1). Perfluoro-3-ethyl-4-methyl-1-phenylpyrazole (**12**) (9.2 g, 63% yield); b.p. 58–59°C (3 Torr); ^{19}F NMR ($CDCl_3$) δ_F 107.8 (F^6, 3F, s), 79.7 (F^8, 3F, s), 52.2 (F^7, 2F, s), 42.2 (F^5,

1F, m), 19.5 (F^{10}, 2F, m), 15.3 (F^{12}, 1F, m), 2.4 (F^{11}, 2F, m); ^{13}C NMR ($CDCl_3$) δ_C 161.4 (C^5,^{1} $J_{CF} = 258$;^{3} $J_{CF} = 4.4$), 145.3 (C^{10},^{1} $J_{CF} = 256$;^{2} $J_{CF} = 30$), 144.6 (C^{12},^{1} $J_{CF} = 266$;^{2} $J_{CF} = 29.0$), 138.4 (C^3,^{2} $J_{CF} = 30.3$), 134.1 (C^9,^{2} $J_{CF} = 29.1$), 120.1 (C^6,^{1} $J_{CF} = 268$;^{3} $J_{CF} = 4.5$), 118.4 (C^8,^{1} $J_{CF} = 286$;^{2} $J_{CF} = 41.9$), 109.4 (C^7,^{1} $J_{CF} = 259$;^{2} $J_{CF} = 42.2$), 103.8 (C^4,^{2} $J_{CF} = 42.2$;^{2} $J_{CF} = 42.8$); IR 1596 (C=C), 1537 (C=N), 1523 (C=Car), 1350 (C–N), 1213–1116 (C–F) cm^{-1}; HRMS calcd. 437.9838 for $C_{12}F_{14}N_2$ found 437.9833; Mass spectrum, *m/e* 438 $[M]^+$, 419 $[M–F]^+$, 369 $[M–CF_3]^+$, 319 $[M–C_2F_5]^+$, 300 $[M–2CF_3]^+$. 281, 255, 69 $[CF_3]^+$. Perfluoro-5-ethyl-4-methyl-1-phenylpyrazole (**13**) (2.3 g, 16% yield); b.p. 89–90°C (3 Torr); ^{19}F NMR ($CDCl_3$) δ_F 107.0 (F^6, 3F, s), 80.2 (F^8, 3F, s), 51.9 (F^7, 2F, s), 43.2 (F^3, 1F, m), 18.3 (F^{10}, 2F, m), 15.3 (F^{12}, 1F, m), 3.2 (F^{11}, 2F, m); ^{13}C NMR ($CDCl_3$) δ_C 152.9 (C^3,^{1} $J_{CF} = 296$;^{3} $J_{CF} = 5.4$), 144.8 (C^{12},^{1} $J_{CF} = 265$;^{2} $J_{CF} = 31.2$), 145.4 (C^{10},^{1} $J_{CF} = 267$;^{2} $J_{CF} = 29.8$), 141.5 (C^9,^{2} $J_{CF} = 28.4$), 138.1 (C^{11},^{1} $J_{CF} = 268$;^{2} $J_{CF} = 29.7$), 121.5 (C^6,^{1} $J_{CF} = 268$;^{3} $J_{CF} = 5.4$), 118.5 (C^8,^{1} $J_{CF} = 286$;^{2} $J_{CF} = 41.9$), 109.7 (C^7,^{1} $J_{CF} = 260$;^{2} $J_{CF} = 41.2$), 113.7 (C^5,^{2} $J_{CF} = 29.0$), 94.0 (C^4,^{2} $J_{CF} = 42.8$); IR 1600 (C=C), 1540 (C=N), 1520 (C=Car), 1352 (C–N), 1200–1170 (C–F) cm^{-1}.

3.2.4. Synthesis of perfluoro-3-ethyl-4-methyl-1-(4-tolyl)pyrazole (**14**) and perfluoro-5-ethyl-4-methyl-1(4′-tolyl)pyrazole (**15**)

Reaction of **1** (10.0 g, 0.033 mol) with 4-(trifluoromethyl)-2,3,5,6-tetrafluorophenylhydrazine (**4**) (8.18 g, 0.033 mol) and Et_3N (10.1 g, 0.10 mol) was conducted by the same procedure as for **12**. Fractional distillation of the crude product afforded a colorless liquid (b.p. 73–82°C at 3 Torr), which was further purified by column chromatography (hexane-CH_2Cl_2, 5:1). Perfluoro-3-ethyl-4-methyl-1-(4-tolyl)pyrazole (**14**) (9.0 g, 55% yield); b.p. 73–74°C (3 Torr); ^{19}F NMR ($CDCl_3$) δ_F 107.8 (F^{13}, 3F, s), 106.7 (F^6, 3F, s), 79.7 (F^8, 3F, s), 52.0 (F^7, 2F, m), 42.8 (F^5, 1F, m), 25.3 (F^{10}, 2F, m), 21.6 (F^{11}, 2F, m); ^{13}C NMR ($CDCl_3$) δ_C 161.4 (C^5,^{1} $J_{CF} = 259$;^{3} $J_{CF} = 5.4$), 144.7 (C^{10},^{1} $J_{CF} = 262$), 144.8 (C^{11},^{1} $J_{CF} = 256$), 133.4 (C^9,^{2} $J_{CF} = 31.9$), 120.5 (C^{13},^{1} $J_{CF} = 278$), 119.6 (C^6,^{1} $J_{CF} = 265$;^{3} $J_{CF} = 5.4$), 118.1 (C^8,^{1} $J_{CF} = 287$;^{2} $J_{CF} = 37.0$), 114.4 (C^3,^{2} $J_{CF} = 30.0$), 113.8 (C^{12},^{2} $J_{CF} = 35.8$), 109.1 (C^7,^{1} $J_{CF} = 259$;^{2} $J_{CF} = 42.2$), 103.8 (C^4,^{2} $J_{CF} = 42.3$); IR 1593 (C=C), 1539 (C=N), 1510 (C=C_{ar}), 1352 (C–N), 1200–1164 (C–F) cm^{-1}; HRMS calcd. 487.9805 for $C_{13}F_{16}N_2$ found 487.9805; Mass spectrum, *m/e* 488 $[M]^+$, 469 $[M–F]^+$, 419 $[M–CF_3]^+$, 369 $[M–C_2F_5]^+$, 319 $[M–C_3F_7]^+$, 281, 274, 254, 217 $[C_6F_4CF_3]^+$, 69 $[CF_3]^+$. Perfluoro-5-ethyl-4-methyl-1(4′-tolyl)pyrazole (**15**) (2.9 g, 18% yield); b.p. 80–82°C (3 Torr); ^{19}F NMR ($CDCl_3$) δ_F 107.7 (F^{13}, 3F, s), 106.7 (F^6, 3F, s), 80.3 (F^8, 3F, s), 51.9 (F^7, 2F, m), 43.8 (F^3, 1F, m), 26.0 (F^{10}, 2F, m), 20.1 (F^{11}, 2F, m); ^{13}C NMR ($CDCl_3$) δ_C 152.5 (C^3,^{1} $J_{CF} = 298$;^{3} $J_{CF} = 5.4$), 145.2 (C^{10},^{1} $J_{CF} = 265$), 143.5 (C^{11},^{1} $J_{CF} = 257$), 141.9 (C^9,^{2} $J_{CF} = 32.3$), 120.5 (C^{13},^{1} $J_{CF} = 278$), 119.7 (C^6,^{1} $J_{CF} = 264$;^{3} $J_{CF} = 5.4$), 118.1 (C^8,^{1} $J_{CF} = 264$;^{2} $J_{CF} = 38.0$), 117.4 (C^5,^{2} $J_{CF} = 30.0$), 109.8 (C^7,^{1} $J_{CF} = 254$;^{2} $J_{CF} = 40.5$), 96.4 (C^4,^{2} $J_{CF} = 42.4$); IR 1658 (C=C), 1539 (C=N), 1510 (C=C_{ar}), 1352 (C–N), 1200–1170 (C–F) cm^{-1}.

3.2.5. Synthesis of 5-fluoro-1-(2-nitrophenyl)-3-pentafluoroethyl-4-trifluoromethylpyrazole (**16**) and 3-fluoro-1-(2-nitrophenyl)-5-pentafluoroethyl-4-trifluoromethylpyrazole (**17**)

Reaction of **1** (15.0 g, 0.05 mol) with 2-nitrophenylhydrazine (**6**) (7.65 g, 0.05 mol) and Et_3N (12.6 g, 0.12 mol) in THF (40 ml) was conducted at 0°C for 30 min and then for 6 h at 20°C. Fractional distillation of the crude product afforded **16** and **17** with an 1:1 ratio (by ^{19}F NMR data) as a colorless liquid (5.8 g, 30% yield); b.p. 127–128°C (0.5 Torr); HRMS calcd. 393.0159 for $C_{12}H_4F_9N_3O_2$ found 393.0153; Mass spectrum, *m/e* $[M]^+$ (100), 374 $[M–F]^+$, 346, 327, 324 $[M–CF_3]^+$, 277, 169 $[C_3F_7]^+$, 150, 119 $[C_2F_5]^+$, 100 $[CF_2{=}CF_2]^+$, 69 $[CF_3]^+$. The distillate was further purified by column chromatography (hexane-CH_2Cl_2, 5:2). 5-Fluoro-1-(2-nitrophenyl)-3-pentafluoroethyl-4-trifluoromethylpyrazole (**16**), 3.4 g; b.p. 127–128°C (0.5 Torr); ^1H NMR ($CDCl_3$) δ_H 8.15, 7.74, 7.75; ^{19}F NMR ($CDCl_3$) δ_F 107.2 (F^6, 3F, s), 80.0 (F^8, 3F, t, J_{FF}=9), 57.8 (F^7, 2F, q, J_{FF}=9), 42.5 (F^5, 1F, m); ^{13}C NMR ($CDCl_3$) δ_C 159.4 (C^5,^{1} $J_{CF} = 255$), 144.0 (C^9), 138.1 (C^3,^{2} $J_{CF} = 32.5$), 133.5 (C^{10}), 131.3 (C^{11}), 130.4 (C^{13}), 127.8 (C^{12}), 124.9 (C^{14}), 119.3 (C^6,^{1} $J_{CF} = 268$), 117.6 (C^8,^{1} $J_{CF} = 286$;^{2} $J_{CF} = 36.2$), 109.0 (C^7,^{1} $J_{CF} = 254$;^{2} $J_{CF} = 39.9$), 94.3 (C^4,^{2} $J_{CF} = 42.3$;^{2} $J_{CF} = 9.1$); IR (5% CCl_4) 1610, 1590, 1545 (C=C–C=N), 1520, 1350 (NO_2), 1270 (C–N), 1220–1150 (C–F) cm^{-1}. 3-Fluoro-1-(2-nitrophenyl)-5-pentafluoroethyl-4-trifluoromethylpyrazole (**17**), 1.5 g; b.p. 127–128°C (0.5 Torr); ^1H NMR ($CDCl_3$) δ_H 8.05, 7.74, 7.60; ^{19}F NMR ($CDCl_3$) δ_F 107.9 (F^6, 3F, s), 80.0 (F^8, 3F, t, J_{FF}=9), 56.2 and 51.7 (F^7, 2F, AB-system, J_{FF}=307), 39.6 (F^5, 1F, m); ^{13}C NMR ($CDCl_3$) δ_C 151.1 (C^5,^{1} $J_{CF} = 293$), 143.4 (C^9), 138.1 (C^3,^{2} $J_{CF} = 32.5$), 133.3 (C^{10}), 131.1 (C^{11}), 129.3 (C^{13}), 126.4 (C^{12}), 124.8 (C^{14}), 119.2 (C^6,^{1} $J_{CF} = 268$), 117.0 (C^8,^{1} $J_{CF} = 287$;^{2} $J_{CF} = 37.2$), 108.2 (C^7,^{1} $J_{CF} = 253$;^{2} $J_{CF} = 44.4$), 100.8 (C^4,^{2} $J_{CF} = 41.4$;^{2} $J_{CF} = 17.7$); IR (5% CCl_4): 1615, 1545, 1590, 1520, 1320 (NO_2), 1270 (C–N), 1220–1150 (C–F) cm^{-1}.

3.2.6. Synthesis of 4,4′-bis(perfluoro-3-ethyl-4′-methylpyrazolyl-1)-octafluorobiphenyl (**18a**) and 4,4′-bis(perfluoro-5-ethyl-4-methylpyrazolyl-1)-octafluorobiphenyl (**18b**)

A reaction mixture of **1** (12.0 g, 0.040 mol), 4,4′-dihydrazinooctafluorobiphenyl (**5**) (7.16 g, 0.020 mol) and Et_3N (12.1 g, 0.12 mol) in THF (45 ml) was stirred at room temperature for 3 h and then for 2 h at 50°C. Fractional distillation of the crude product gave compounds **18a**,**b** (10.2 g, 61% yield) as a colorless liquid; b.p. 177–179°C

(0.2 Torr); elemental analysis calcd. C 34.37, F 58.95, N 6.68 for $C_{12}F_{13}N_2$ found C 34.21, F 59.07, N 7.21%. The distillate was further purified by column chromatography (hexane-CH_2Cl_2, 3:1). 4,4′-Bis-(perfluoro-3-ethyl-4-methylpyrazolyl-1)-octafluorobiphenyl (**18a**) (6.4 g, 38% yield); ^{19}F NMR ($CDCl_3$-acetone) δ_F 107.2 (F^6, 3F, s), 80.5 (F^8, 3F, t, J_{FF}=9), 52.3 (F^7, 2F, q, J_{FF}=9), 45.1 (F^5, 1F, m), 28.1 (F^{10}, 2F, m), 19.1 (F^{11}, 2F, m); ^{13}C NMR ($CDCl_3$) δ_C 151.9 ($C^{5,1}$ J_{CF} = 297), 143.8 ($C^{10,1}$ J_{CF} = 251), 142.4 ($C^{11,1}$ J_{CF} = 268), 141.3 ($C^{9,2}$ J_{CF} = 28.0), 132.3 ($C^{3,2}$ J_{CF} = 32.0), 119.0 ($C^{6,1}$ J_{CF} = 268), 117.6 ($C^{8,1}$ J_{CF} = 286;^{2} J_{CF} = 39.7), 108.6 ($C^{7,1}$ J_{CF} = 260;^{2} J_{CF} = 30.8), 108.5 ($C^{12,2}$ J_{CF} = 39.5), 94.7 ($C^{4,2}$ J_{CF} = 34.2). 4,4′-Bis-(perfluoro-5-ethyl-4-methylpyrazolyl-1)-octafluorobiphenyl (**18b**) 93.2 g, 19% yield); ^{19}F NMR ($CDCl_3$-acetone) δ_F 107.9 (F^6, 3F, s), 79.7 (F^8, 3F, t, J_{FF}=9), 52.0 (F^7, 2F, q, J_{FF}=9), 42.4 (F^3, 1F, m), 25.3 (F^{10}, 2F, m), 20.2 (F^{11}, 2F, m); ^{13}C NMR ($CDCl_3$) δ_C 160.3 ($C^{3,1}$ J_{CF} = 260), 143.8 ($C^{10,1}$ J_{CF} = 251), 142.4 ($C^{11,1}$ J_{CF} = 268), 141.3 ($C^{9,2}$ J_{CF} = 28.0), 132.3 ($C^{5,2}$ J_{CF} = 32.0), 119.1 ($C^{6,1}$ J_{CF} = 268), 117.5 ($C^{8,1}$ J_{CF} = 286;^{2} J_{CF} = 39.7), 108.4 ($C^{7,1}$ J_{CF} = 260;^{2} J_{CF} = 30.8), 108.4 ($C^{12,2}$ J_{CF} = 39.5), 94.6 ($C^{4,2}$ J_{CF} = 34.2).

3.2.7. Synthesis of 1-(2,4-dinitrophenyl)-5- fluoro-3-pentafluoroethyl-4-trifluoromethylpyrazole (**20**) and N-2,4-dinitrophenyl-N-[3,3,3-trifluoro-1 pentafluoroethyl-2-trifluoromethyl-propylidene]hydrazines (**22a**,**b**)

A solution of **1** (15.1 g, 0.050 mol) and Et_3N (10.1 g, 0.10 mol) in MeCN (40 ml) was stirred at 45°C for 2–3 h. To the resulting solution was added dropwise at 0°C a mixture of 2,4-dinitrophenylhydrazine (**8**) (6.6 g, 0.033 mol) and Et_3N (5.05 g, 0.050 mol) over 15 min. After the addition, stirring was continued for 1 h at 0°C and then for 2 h at room temperature. The reaction mixture was diluted with water and extracted with CH_2Cl_2. The organic phase was concentrated and distilled to give liquid products, which were further separated by column chromatography with hexane-CH_2Cl_2 (10:1). *Syn-* and *anti-N*-2,4-Dinitrophenyl-*N*-[3,3,3-trifluoro-1(pentafluoroethyl-2-trifluoromethylpropylidene]hydrazine (**22a**,**b**) (2:1 ratio, 11.5 g, 48% yield); b.p. 102–103°C (1 Torr); ^{1}H NMR ($CDCl_3$) δ_H 4.33 (H^2, 1H, m), 8.40 (H^{11}, 1H, m), 8.04 ($H^{13,14}$, 2H, m), 12.36 (H^8, 1H, s); ^{19}F NMR ($CDCl_3$) δ_F 98.1 ($F^{1,6}$, 6F, s), 79.9 (F^5, 3F, s), 45.9 (F^4, 2F, s); HRMS calcd. 478.0135 for $C_{12}H_5F_{11}N_4J_4$ found 478.0131; Mass spectrum, *m/e* 478 $[M]^+$, 393, 324, 259, 168, 69 $[CF_3]^+$. 1-(2,4-Dinitrophenyl)-5-fluoro-3-pentafluoroethyl-4-trifluoromethylpyrazole (**20**) – a yellow solid (5.22 g, 36% yield), m.p. 80–81°C (hexane); ^{1}H NMR ($CDCl_3$) δ_H 9.05 (H^{11}, 1H, s), 8.75 (H^{13}, 1H, d, J_{HH}=8.7), 8.03 (H^{14}, 1H, d, J_{HH}=8.7); ^{19}F NMR ($CDCl_3$) δ_F 43.7 (F^5, q, J_{FF}=14.6), 106.6 (F^6, 3F, qt, J_{FF}=16.6 and 9.8), 79.9 (F^8, 3F, s), 51.4 (F^7, 2F, q, J_{FF}=9.8); ^{13}C NMR ($CDCl_3$) δ_C 151.9 ($C^{5,1}$ J_{CF} = 299;^{3} J_{CF} = 5.4), 148.9 (C^9), 144.3 (C^{12}), 140.7 ($C^{3,2}$ J_{CF} = 32.0), 132.1 (C^{10}), 132.2 (C^{13}), 130.6 (C^{11}), 129.0 (C^{14}), 119.7 ($C^{6,1}$ J_{CF} = 269;^{3} J_{CF} = 5.4), 118.3 ($C^{8,1}$ J_{CF} = 286;^{2} J_{CF} = 35.9), 109.6 ($C^{7,1}$ J_{CF} = 254;^{2} J_{CF} = 40.2), 96.6 ($C^{4,2}$ J_{CF} = 51.8); IR 3117, 1626 (C=C), 1547 (C=N), 1352 (C–N), 1200–1170 (C–F) cm^{-1}; HRMS calcd. 438.0008 for $C_{13}H_3F_9N_4O_4$ found 437.9292; Mass spectrum, *m/e* 438 $[M]^+$, 419 $[M–HF]^+$, 391 $[M–NO_2]^+$.

3.2.8. Synthesis of 5-fluoro-3-pentafluoroethyl-4-trifluoromethyl-1-(4-nitrophenyl)pyrazole (**21**)

Treatment of 4-nitrophenylhydrazine (**7**) (5.1 g, 0.033 mol) with **1** (10.0 g, 0.033 mol) and Et_3N (10.1 g, 0.10 mol) in MeCN (65 ml) by the same procedure for **20** produced 5-fluoro-3-pentafluoroethyl-4-trifluoromethyl-1-(4-nitrophenyl)pyrazole (**21**) as a yellow liquid (8.4 g, 65% yield); b.p. 66–67°C (2.5 Torr); ^{1}N NMR ($CDCl_3$) δ_H 8.46 (H^{11}, 2H, d, J_{HH}=9.1), 8.08 (H^{10}, 2H, d, J_{HH}=9.1); ^{19}F NMR ($CDCl_3$) δ_F 43.8 (F^5, 1F, q, J_{FF}=14.6), 106.7 (F^6, 3F, qt, J_{FF}=14.6 and 9.7), 79.3 (F^8, 3F, s), 51.6 (F^7, 2F, q, J_{FF} =9.7); ^{13}C NMR ($CDCl_3$) δ_C 152.3 ($C^{5,1}$ J_{CF} = 296;^{3} J_{CF} = 4.7), 148.6 (C^9), 141 (C^{12}), 140 ($C^{3,2}$ J_{CF} = 32.3), 126.2 (C^{11}), 123.4 (C^{10}), 120.8 ($C^{6,1}$ J_{CF} = 268;^{3} J_{CF} = 4.7), 119.4 ($C^{8,1}$ J_{CF} = 286;^{2} J_{CF} = 36.2), 110.5 ($C^{7,1}$ J_{CF} = 254;^{2} J_{CF} = 32.5), 97.5 ($C^{4,2}$ J_{CF} = 32.3); IR 3115 (C–H_{ar}), 1622 (C=C), 1522 (C=N), 1350 (C–N), 1200–1150 (C–F) cm^{-1}; HRMS calcd. 393.0159 for $C_{12}H_4F_9N_3O_2$ found 393.0158; Mass spectrum, *m/e* 393 $[M]^+$, 374 $[M–F]^+$, 363 $[M–NO]^+$, 347 $[M–NO_2]^+$, 324 $[M–CF_3]^+$.

3.2.9. Synthesis of N-phenyl-N-[3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethylpropylidene]-hydrazines (**25a**,**b**)

To a solution of **1** (30 g, 0.10 mol) in THF (30 ml) at 0°C was added dropwise phenylhydrazine (21.6 g, 0.20 mol) in THF (20 ml) with stirring. After the addition, stirring was continued for 1 h at 0°C and then for 2 h at 20°C. The reaction mixture was filtered and the filtrate was distilled under reduced pressure to give a yellow liquid (32 g), b.p. 64–65°C at 0.3 Torr, which was a mixture of *syn-* and *anti-*isomers *N*-phenyl-*N*′-[3,3,3-trifluoro-1-pentafluoroethyl-2-trifluoromethylpropylidene]hydrazine (**25a** and **25b**) (3:2 ratio) and **9**. The mixture **25a** and **25b** – HRMS calcd. 388.0433 for $C_{12}H_7F_{11}N_2$ found 388.0432; Mass spectrum, *m/e* 388 $[M]^+$, 369 $[M–F]^+$, 319 $[M–CF_3]^+$, 119 $[C_2F_5]^+$, 105 $[PhN_2]^+$, 92, 77 $[Ph]^+$. **25a** – ^{1}H NMR ($CDCl_3$) δ_H 3.83 (C–H, m), 8.73 (H–N, s), 7.08 (H^{11}) and 6.90 ($H^{10,12}$); ^{19}F NMR ($CDCl_3$) δ_F 97.9 ($F^{1,6}$, 6F, s), 79.3 (F^5, 3F, s), 47.2 (F^4, 2F, s); ^{13}C NMR ($CDCl_3$) δ_C 141.1 (C^9), 128.4 (C^{11}), 122.9 (C^{12}), 113.1 (C^{10}), 118.0 ($C^{1,6,1}$ J_{CF} = 283), 48.0 ($C^{2,2}$ J_{CF} = 30.5), 118.4 ($C^{5,1}$ J_{CF} = 282;^{2} J_{CF} = 35.0), 110.0 ($C^{4,1}$ J_{CF} = 264;^{2} J_{CF} = 35.0). **25b** – ^{1}H NMR ($CDCl_3$) δ_H 4.07 (C–H, m), 8.57 (H–N, s), 7.24 ($H^{10,12}$) and 7.36 (H^{11}, m); ^{19}F NMR ($CDCl_3$) δ_F 101.7 ($F^{1,6}$, 6F, s), 82.5 (F^5, 3F, s), 51.9 (F^4, 2F, s); ^{13}C NMR ($CDCl_3$) δ_C 141.4 (C^9), 128.1 (C^{11}), 122.7 (C^{12}), 121.0 ($C^{1,6,1}$ J_{CF} = 321),

113.1 (C^{10}), 118.3 (C^{5},^{1} $J_{CF} = 285$;^{2} $J_{CF} = 34.5$), 48.6 (C^{2},^{2} $J_{CF} = 30.2$), 111.9 (C^{4},^{1} $J_{CF} = 264$;^{2} $J_{CF} = 37.1$), 134.6 (C^{3},^{2} $J_{CF} = 35.0$).

3.2.10. Reaction of **25a** *and* **25b** *with triethylamine*

A mixture of Et_3N (3.1 g, 0.030 mol) and the compounds **25a** and **25b** (3.88 g, 0.010 mol) in MeCN (20 ml) was stirred at 20°C for 3 h. The reaction mixture was diluted with water (60 ml) and extracted with diethyl ether (3×50 ml). The combined extracts were dried ($MgSO_4$) and concentrated. The residual was distilled under reduced pressure to give **9** as a yellow liquid (3.3 g, 95% yield), b.p. 60–62°C at 1.5 Torr.

3.2.11. Reaction of **25a** *and* **25b** *with* K_2CO_3

A mixture of K_2CO_3 (5.5 g, 0.040 mol) and the compounds **25a** and **25b** (5.87 g, 0.015 mol) in MeCN (80 ml) was stirred at 20°C for 3 h. The resulting solution was diluted with water (100 ml) and extracted with diethyl ether (3×70 ml). The extracts were dried ($MgSO_4$) and concentrated. The residual was distilled under reduced pressure to give a yellow liquid (4.2 g), b.p. 60–65°C at 1.5 Torr, which consisted of **9** and **25b** in a 9:1 ratio (by ^{19}F NMR and GLC analysis).

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