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ORIGINAL PAPER

3,4,5,6-Tetrafluoro-1,2-dehydrobenzene in reactions with 1,2,4-triazines

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Abstract Tetrafluoro-substituted aryne, 3,4,5,6-tetrafluoro-1,2-dehydrobenzene, has been generated in situ from 2-amino-3,4,5,6-tetrafluorobenzoic acid, and its reactivity in reactions with 1,2,4-triazines as dienes has been studied. In these reactions, the corresponding azine ring transformation products, *i.e.*, 1,2,3,4-tetrafluoro-10-(1*H*-1,2,3-triazol-1-yl)pyrido[1,2-*a*]indoles, have been obtained, in the case of triazines activated by the presence of electron-withdrawing groups, such as 6-aryl-3-(2-pyridyl)-5-cyano-1,2,4-triazines. The crystal structure of the obtained products was confirmed by X-ray diffraction analysis.

Keywords 3,4,5,6-Tetrafluoro-1,2-dehydrobenzene · 1,2,4-Triazines · Ring transformations · X-ray data

Introduction

(Hetero)aromatic organofluorine compounds are of great interest due to the scope of their applications. Considerable attention is attracted by fluorinated quinolones or indoles because it is firmly established that the introduction of fluorine can influence the biological activity of organic molecules [1]. In particular, fluorinated isoquinolines are of great practical interest [2] due to their biological activity [3, 4] and photophysical properties [5, 6]. Pyrido[1,2-*a*]indole fragments are widely present in some naturally occurring alkaloids, and some important activities have been found in their synthetic derivatives, such as steroid hormone receptor binding and cytostatic activity [7, 8], antidepressant [9] and antitumor [10] activities. In addition, there are a number of biologically active functionalized indoles with fluorine atoms in the benzene ring. In particular, 4,5,6,7-tetrafluoroindoles exhibit cytotoxic activity [11], antibacterial [12], anti-HIV activity [13] and receptor binding properties [14].

Another important issue is that polyfluorination results in increasing fluorine nucleofugacity [15]. This opens new opportunities for the direct nucleophilic substitution of fluorine atom(s) in the benzene rings of heterocyclic systems. In view of the above, the development of a practical and efficient approach to the one-step construction of a isoquinoline or (benzo)indole skeleton with a polyfluorinated benzene moiety is an important problem in organic synthesis.

Previously, it has been demonstrated that the reactions of substituted 1,2,4-triazines with in situ generated aryne intermediates can afford 10-(1*H*-1,2,3-triazol-1-yl) pyrido[1,2-*a*]indoles or isoquinolines depending on the substituents in the starting triazine and aryne (Scheme 1) [16–18]. In addition to the simple aryne, 1,2-dehydrobenzene (benzyne), some substituted arynes have been used in these reactions, for instance 4,5-dimethoxy- [19], 4,5-difluoro- [20], and 3- or 4-methyl-substituted [18] arynes. In order to expand the use of "aryne" and "1,2,4-triazine" methodologies for the synthesis of pyridine-containing heterocycles such as 1,2,3,4-tetrafluoro-substituted pyrido[1,2-*a*]indoles and/or 5,6,7,8-tetrafluoroisoquinolines, we have studied the interactions of 1,2,4-triazines

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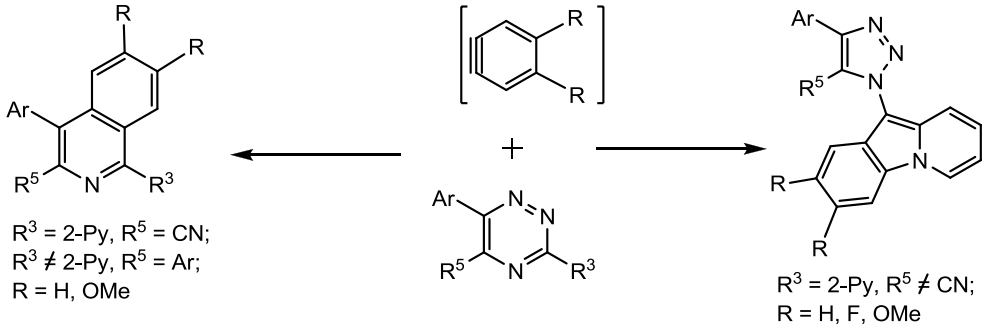
Scheme 1 Our previous work



with 3,4,5,6-tetrafluoro-1,2-dehydrobenzene. Fluorinated pyrido[1,2-*a*]indoles [20–23] as well as 5,6,7,8-tetrafluoroisoquinolines [24, 25] are reported only in a few publications from other research groups, while tetrafluoro-substituted pyrido[1,2-*a*]indoles are not reported at all.

Results and discussion

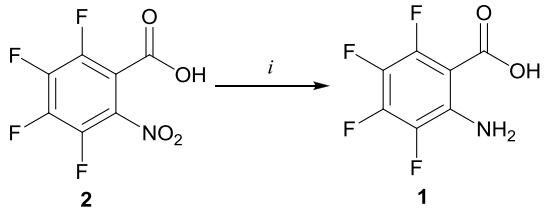
Tetrafluoroanthranilic acid **1** is the most readily available precursor for the generation of the corresponding aryne. However, according to the literature the direct generation of aryne from this acid is not very common [26–32]. In other cases, some rather inaccessible compounds are reported for the generation of this aryne, such as chloro- [33, 34] or bromo-pentafluorobenzene [35–37], and aryne generation takes place by the reaction of magnesium or *n*-butyllithium, or tetrafluorophthalic anhydride has been used [38]. On the other hand, 1-trimethylsilyl-2-trifluorosulfonyl-substituted benzenes [39] which are commonly used for the smooth generation of other arynes are not described at all for the preparation of perfluorinated benzyne derivatives.

To obtain tetrafluoroanthranilic acid **1**, we have employed the commercially available tetrafluoronitrobenzoic acid **2**. The reduction of the nitro-group with hydrogen over Pd/C quantitatively afforded the desired acid **1** (Scheme 2). Surprisingly, this approach has not been previously reported in the literature.

For in situ generation of aryne from 2-amino-3,4,5,6-tetrafluorobenzoic acid **1**, a standard procedure was used [16–20]. Earlier studies of the reactions of tetrafluorobenzyne with substituted 1,2,4-triazines showed that the first one has lower reactivity compared to previously reported arynes (Schemes 1, 3). In particular, for the dienes with low electron deficiency such as 3,6-diphenyl-1,2,4-triazine **3a** [40], no reaction was observed, either in boiling toluene or in *o*-xylene. Introduction of the strongly electron-withdrawing (EWD) cyano-group into C5 position of the 1,2,4-triazine core in case of compound **3b** [41], or the 2-pyridyl group in C3 position as in case of 3-(2-pyridyl)-6-phenyl-1,2,4-triazine **3c** [42], did not promote the reaction either. Only when two EWD moieties were introduced simultaneously, as in case of 6-aryl-3-(2-pyridyl)-5-cyano-1,2,4-triazines **3d, e** [43], the reaction with tetrafluorobenzyne in boiling *o*-xylene afforded the corresponding reaction products, namely 1,2,3,4-tetrafluoro-10-(1*H*-1,2,3-triazol-1-yl)pyrido[1,2-*a*]indoles **5** in fair yields of 40–44% (Scheme 3), while the rest of the reaction mixtures were unreacted 1,2,4-triazines **3**. It is worth to mention that in order to optimize the reaction conditions, compound **3d** was selected as model substrate and the results are summarized in Table 1. Thus, we did not observe the formation of the desired reaction products in toluene even during the prolonged reaction time at the temperature from 25 to 60 °C (Table 1, entries 1–2). After heating in toluene or *o*-xylene at 110 °C for 24 h, the reaction afforded only trace amount of compound **5a**, while the rest of the reaction mixtures was the unreacted 1,2,4-triazine **3d** (Table 1, entries 3–4). Only after refluxing in *o*-xylene for 0.5–4 h, the reaction afforded the 1,2,3,4-tetrafluoro-10-(1*H*-1,2,3-triazol-1-yl)pyrido[1,2-*a*]indole **5a** in 22% (Table 1, entry 5), 40% (Table 1, entry 6) or 41% (Table 1, entry 7) yields depending on the reaction time. It is noteworthy that in the last case the reaction proceeds with intense tarring of the reaction mixture, and the unreacted 1,2,4-triazine **3d** was recovered in lower yield. Therefore, the refluxing during 1 h in *o*-xylene (Table 1, entry 6) was selected as the best conditions for the reaction.

It should be also mentioned that in case of other arynes, such as 4,5-dimethoxy-, 4,5-difluoro-, or methyl-substituted benzynes [16–20] toluene or 1,4-dioxane was the most common solvent for the reaction.

A plausible mechanism for the rearrangement of 1,2,4-triazines **3d, e** into 1,2,3,4-tetrafluoro-10-(1*H*-1,2,3-triazol-1-yl)pyrido[1,2-*a*]indoles **5** has been outlined in Scheme 4 on the basis of previously reported cases for other arynes [16, 20]. Thus, after the concerted addition of aryne the intermediate **I** is formed. The further isomerization of **I** affords intermediate **II**,



Scheme 2 Synthesis of 2-amino-3,4,5,6-tetrafluorobenzoic acid. Reagents and conditions: (*i*) 10% Pd/C, hydrogen (P = 3.5 atm), methanol, 20 °C, 6 h

which further rearranges via the open-chained intermediate **III** into the desired product **5**.

The structure of the products **5** was confirmed based on the ^{1}H NMR data, ^{13}C and ^{19}F spectroscopy, mass spectrometry and elemental analysis. In particular, in the ^{1}H NMR spectra the signals of aromatic substituent protons along with the signals of protons of newly formed fused pyridine moiety were observed. The ^{19}F NMR spectrum of **5a–b** shows characteristic peaks of a tetrafluoro-substituted ABCD system, and in the case of **5b** an additional singlet for the fluorine atom of the aromatic substituent is seen. ^{13}C NMR spectra of products **5** are significantly complicated as a result of ^{13}C–^{19}F spin–spin interactions. For more conclusive evidence, a single-crystal X-ray crystallographic analysis of the compound **5a** was performed to provide the most direct description of the molecular packing features.

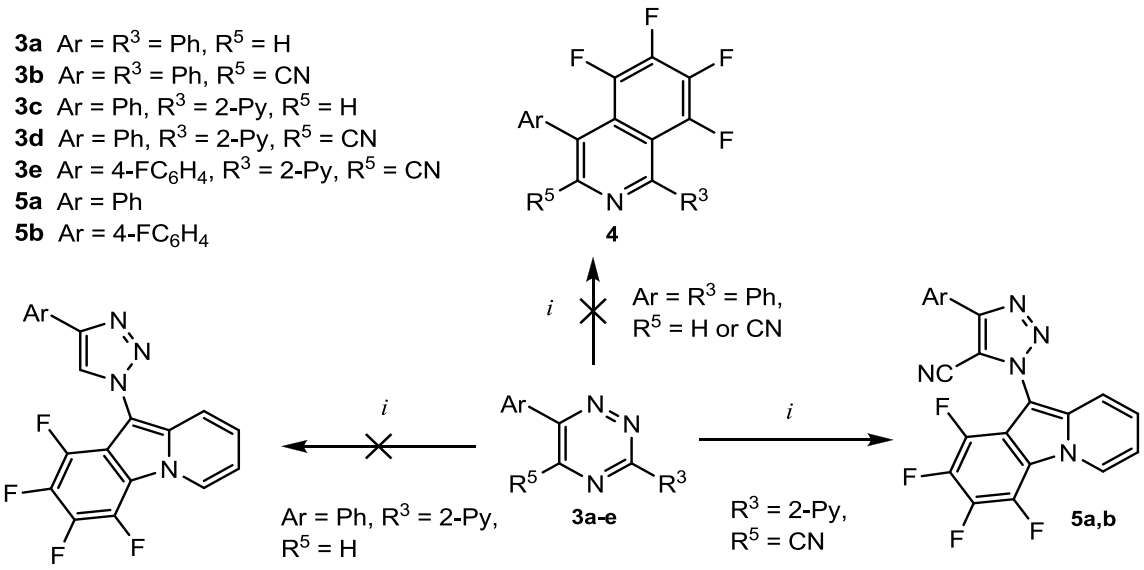
According to the XRD analysis, two independent molecules of **5a** are crystallized in the centrosymmetric space groups, one of which is shown in Fig. 1. The interatomic bond distances and angles in the molecules are near to standard. In the molecules, the azacarbazole rings are turned toward the triazole rings at angles of 51° and 62.5°; the aryl substituents are turned toward the triazole ring at angles of 18° and 13°. In addition, strong π–π interactions are observed between C(12) and C(11) [1-x,-y,1-z] atoms of the tetrafluorophenylene moieties with a minimum distance of 3.262 Å (see Fig. S1, ESI). A second interesting type of shortened contact is the coaxial F…F contacts F(3A)…F(2) and F(2A)…F(3) contacts with distances 2.766 and 2.848 Å (0.17 and 0.09 Å less than the sum of the V-d-W radii) (see Fig. S2, ESI).

Conclusion

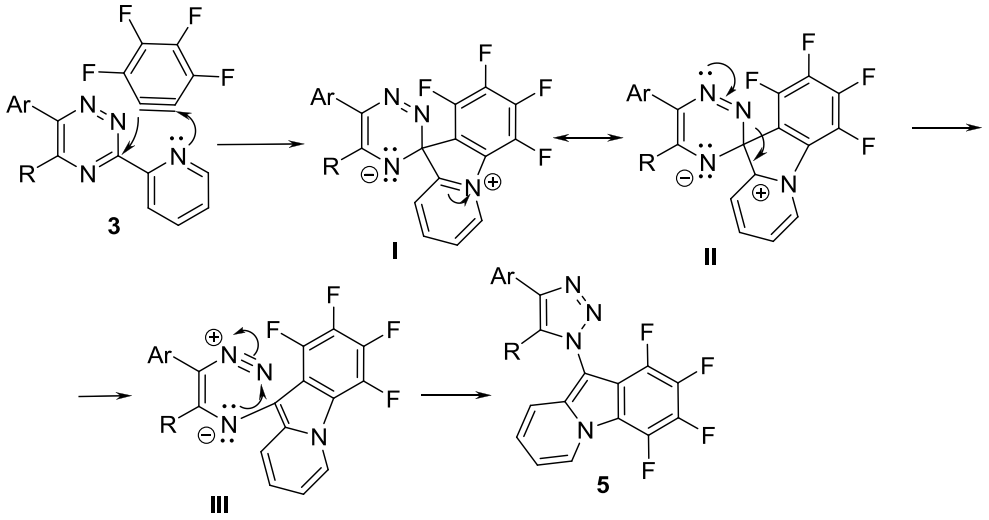
In conclusion, in this article we have described a convenient method for the preparation of a tetrafluorobenzyne precursor, 2-amino-3,4,5,6-tetrafluorobenzoic acid, from its commercially available nitro-derivative. We

Table 1 Results of interaction of triazine **3d** with tetrafluoroaryne under different conditions

No	Solvent	Temperature (°C)	Time (h)	Yield of product **5a**
1	Toluene	25	24	No reaction
2	Toluene	60	24	No reaction
3	Toluene	110	24	Traces
4	*o*-Xylene	110	24	Traces
5	*o*-Xylene	143	0.5	22
6	*o*-Xylene	143	1	40
7	*o*-Xylene	143	6	41



Scheme 3 Synthesis of 1,2,3,4-tetrafluoro-10-(1*H*-1,2,3-triazol-1-yl)pyrido[1,2-*a*]indoles. Reagents and conditions: (*i*) 2-amino-3,4,5,6-tetrafluorobenzoic acid, isoamyl nitrite, *o*-xylene, reflux, 1.5 h



Scheme 4 A plausible mechanism for the rearrangement of 1,2,4-triazines **3d, e** into 1,2,3,4-tetrafluoro-10-(1*H*-1,2,3-triazol-1-yl)pyrido[1,2-*a*] indoles **5**

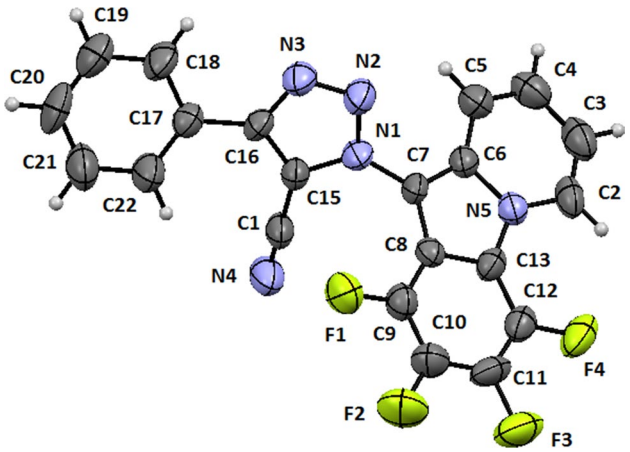


Fig. 1 Crystal structure of compound **5a**

have studied the possibilities of using 3,4,5,6-tetrafluoro-1,2-dehydrobenzene generated in situ from this acid as a dienophile in reactions with substituted 1,2,4-triazines, used as dienes for aza-Diels–Alder reactions. It was found that for these reactions the tetrafluoroaryne demonstrated much lower reactivity compared to the simplest aryne, benzyne, and its 4,5-difluoro-, 4,5-dimethoxy- or methyl-substituted derivatives. Thus, 3,4,5,6-tetrafluoro-1,2-dehydrobenzene reacts only with highly electron-deficient dienes such as 3-(2-pyridyl)-1,2,4-triazine-5-carbonitriles and only under harsh reaction conditions. These interactions afforded no classical aza-Diels–Alder reaction products, *i.e.*, 5,6,7,8-tetrafluoroquinolines, but 1,2,4-triazine ring rearrangement products, such as hardly synthetically available 1,2,3,4-tetrafluoro-substituted 10-(1*H*-1,2,3-triazol-1-yl)pyrido[1,2-*a*]indoles, which are prospective pharmacophores and building blocks in the synthesis of pharmaceuticals. Based on previously published results, a plausible mechanism of the transformation is reported. The structure of one of the reaction products (compound **5a**) was confirmed by X-ray data. Based on X-ray data, strong π–π interactions as well as F…F short contacts in a solid state were suggested.

Experimental section

Unless otherwise indicated, all common reagents and solvents were used from commercial suppliers without further purification. Melting points were measured on a Boetius instrument. ^{1}H, ^{13}C and ^{19}F NMR spectra were acquired on a Bruker Avance 400 spectrometer at 298 K, digital resolution ±0.01 ppm, using TMS as internal reference for ^{1}H and ^{13}C NMR or $CFCl_3$ for ^{19}F NMR. Mass spectra were recorded on MicrOTOF-Q II (Bruker Daltonics) with electrospray ionization. Microanalyses (C, H, N) were performed using a Perkin-Elmer 2400 elemental analyzer. The structure of compound **5a** was determined on a X-ray diffractometer "Xcalibur E."

Triazines **3a** [40], **3b** [41], **3c** [42], **3d, e** [43] were synthesized as described in the literature.

2-Amino-3,4,5,6-tetrafluorobenzoic acid (1). 2,3,4,5-Tetrafluoro-6-nitrobenzoic acid **2** (4 g, 16.74 mmol) was suspended in methanol (40 ml). Palladium on activated charcoal (10%, 400 mg) was added, and the resulting mixture was stirred under hydrogen atmosphere (P = 3 atm) for 6 h. The catalyst was then filtered off, and solvent from the filtrate was removed under reduced pressure. The

product was used in the next step without further purification. Yield 3.46 g (16.55 mmol, 99%). M.p. 140–142 °C (Lit. [44] 141.5–142.5 °C). NMR ^{19}F (DMSO-d_6): −177.65 (ddd, 1F, *J* 22.9, 22.9, 6.9 Hz), −162.39 (m, 1F), −153.90 (m, 1F), −136.59 (m, 1F). NMR ^{13}C (DMSO-d_6): 98.3 (m, C2), 130.3 (m), 135.3 (m), 137.0 (m, C1), 142.4 (m), 147.3 (m), 165.8 (m, carbonyl). ESI–MS, *m/z*: found 208.00, calculated 208.00 $(M-H)^-$.

General procedure for the synthesis of 4-aryl-1-(1,2,3,4-tetrafluoropyrido[1,2-*a*]indol-10-yl)-1*H*-1,2,3-triazole-5-carbonitriles 5. The corresponding 1,2,4-triazine **3d, e** (1 mmol) was dissolved in dry *o*-xylene (25 ml). Isoamyl nitrite (0.47 ml, 3.5 mmol) was added to this mixture. The resulting mixture was stirred under reflux in argon, while a solution of 2-amino-3,4,5,6-tetrafluorobenzoic acid (0.73 g, 3.5 mmol) in dry 1,4-dioxane (10 ml) was added by means of dropping funnel for 30 min. The reaction mixture was heated under reflux for 1 h and then cooled to room temperature. Then, the reaction mass was washed with potassium hydroxide solution (3 M, 3 × 50 ml) and dried with anhydrous sodium sulfate. Solvents were removed under reduced pressure. Products were separated by column chromatography (silica gel, ethylacetate as eluent, $Rf = 0.8$). Analytical samples of products were obtained by recrystallization (acetonitrile).

4-Phenyl-1-(1,2,3,4-tetrafluoropyrido[1,2-*a*]indol-10-yl)-1*H*-1,2,3-triazole-5-carbonitrile (5a): yield 159 mg (0.4 mmol, 40%). M.p. 169–171 °C. NMR ^{1}H ($CDCl_3$): 6.89 (m, 1H), 7.31 (m, 1H), 7.43 (m, 1H), 7.50–7.60 (m, 3H, Ph), 8.19 (m, 2H, Ph), 8.72 (m, 1H). NMR ^{19}F ($CDCl_3$): −164.14 (m, 1F), −159.42 (dd, 1F, *J* 19.5, 19.5 Hz), −157.23 (dd, 1F, *J* 19.5, 16.1 Hz), −152.02 (m, 1F). NMR ^{13}C ($CDCl_3$): 98.2 (m), 109.7, 110.6, 110.8 (m), 112.1, 112.9 (m), 115.6, 118.9, 123.2, 126.8, 127.0 (d, *J* 10.4 Hz), 127.5 (d, *J* 6.3 Hz), 129.3, 129.7, 130.6, 134.8 (m), 136.6 (m), 137.9 (m), 151.8. ESI–MS, *m/z*: found 408.09, calculated 408.09 $(M + H)^+$. Calcd for $C_{21}H_9F_4N_5$: C 61.92; H 2.23; N 17.19. Found: C 61.80; H 2.03; N 16.97%.

Crystals suitable for XRD analysis were obtained by slow evaporation of a $CDCl_3$ solution. CCDC number 1473730. XRD analysis of the compound (colorless block 0.25 × 0.20 × 0.15 mm) was performed on Xcalibur 3 diffractometer on standard procedure (MoKα irradiation, graphite monochromator, $T = 295(2)$ K, ω-scans with the step 1°). Empirical absorption correction was applied. The crystal is monoclinic, space group P21/c, a = 7.8250(11) Å, b = 31.146(3) Å, c = 14.5401(16) Å, α = 90 °, β = 102.583(10)°, γ = 90°−-, V = 3458.6(7) Å^3, Z = 8, μ = 0.127 mm^{-1}. On the angles from 2.82° to 26.37°, 13225 reflections were collected, independent reflections 6798 ($R_{int} = 0.0209$), 3095 reflections with $I > 2\sigma(I)$. Completeness to $\Theta = 26.00°$ 96.4%. The structure was solved by direct method and refined by full-matrix least-squares on F^2 with using SHELXTL program package [45]. The results of the structure refinement: $R_1 = 0.0508$, $wR_2 = 0.0705$ for $I > 2\sigma(I)$, $R_1 = 0.1629$, $wR_2 = 0.0768$ for all data, goodness of fit on F^2 1.003, largest diff. peak and hole 0.165 and −0.156 ēÅ^{-3}.

4-(4-Fluorophenyl)-1-(1,2,3,4-tetrafluoropyrido[1,2-*a*]indol-10-yl)-1*H*-1,2,3-triazole-5-carbonitrile (5b). Yield 188 mg (0.44 mmol, 44%). M.p. 174–176 °C. NMR ^{1}H ($CDCl_3$): 6.90 (m, 1H), 7.60 (m, 2H, 4-FPh), 7.31 (m, 1H), 7.42 (m, 1H), 8.19 (m, 2H, 4-FPh), 8.72 (m, 1H). NMR ^{19}F ($CDCl_3$): −164.03 (m, 1F), −159.32 (dd, 1F, *J* 19.7, 19.7 Hz), −157.15 (dd, 1F, *J* 20.5, 17.2 Hz), −152.05 (m, 1F), −108.98 (s, 1F, 4-FPh). ESI–MS, *m/z*: found 426.08, calculated 426.08 $(M + H)^+$. Calcd for $C_{21}H_8F_5N_5$: C 59.30; H 1.90; N 16.47. Found: C 59.14; H 1.77; N 16.21%.

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