Preparation of novel 5-alkoxy-1,1,1,2,2-pentafluoroalk-4-en-3-ones and their application to a one-pot synthesis of azoles

Marcos A. P. Martins,* Claudio M. P. Pereira, Sidnei Moura, Gabriela F. Fiss, Clarissa P. Frizzo, Daniel J. Emmerich, Nilo Zanatta, and Helio G. Bonacorso

Núcleo de Química de Heterociclos, Departamento de Quimica, Universidade Federal de Santa Maria, 97.105-900 Santa Maria, RS, Brazil
E-mail: mmartins@base.ufsm.br

Abstract

An improved procedure to prepare a series of five 5-alkoxy-1,1,1,2,2-pentafluoro-4-alken-3-ones [$CF_3CF_2C(O)C(R^2)=C(R^1)OR$, where R^2/R = H/Et, H/Me, Me/Et, $–(CH_2)_2–$, $–(CH_2)_3–$, and R^1 = H, Me] in good yields (71 – 82%) and in an up to molar scale from the acylation reaction of enol ethers with pentafluoropropionic anhydride is described. These compounds were cyclocondensed with different dinucleophiles, such as hydroxylamine, 1,2-dimethylhydrazine and phenylhydrazine, to obtain a series of pentafluoroethyl substituted 4,5-dihydroisoxazoles, pyrazolium chlorides and pyrazoles, respectively, in one-pot procedures with moderate to very good yields (60 – 95%).

Keywords: Fluorinated heterocycles, enones, isoxazoles, pyrazoles, pyrazolium chlorides

Introduction

Heterocycles containing perfluoroalkyl groups are very attractive compounds due to their biological properties.[1] In particular, pyrazoles containing polyfluoroalkyl groups are of considerable interest due to their herbicidal, fungicidal, insecticidal, analgesic, antipyretic and anti-inflammatory properties.[2] In addition, isoxazoles are reported to posses various types of biological activities.[3] Moreover, pyrazolium salt derivatives possess very interesting applications, particularly as herbicides, such as the patented herbicide difenzoquat.[4] Pyrazolium salts have also been used as coloring pigments[5a-c] and as reagents in organic synthesis.[5d]

The presence of a trifluoromethyl group into cyclic compounds especially at a strategic position of drug molecules has become an important aspect of pharmaceutical research owing to the unique physical and biological properties of fluorine.[6] The high electronegativity of fluorine enables a polyfluoromethyl groups to decrease the electron density and the basicity or enhance the electrophilicity of the neighboring functional groups within a molecule. In many systems, the

substitution by a trifluoromethyl group of the methyl group results in added lipophilicity, which may lead to easier absorption and transportation of the molecules within biological systems and thereby improve the overall pharmacokinetic properties of drug candidates.

Although the usefulness of 4-alkoxy-3-alken-2-ones [$R^3C(O)C(R^2)=C(R^1)OR$, where R^3 = CF_3, CCl_3 and $CHCl_2$],[7,8] which are important halogen-containing building blocks, in heterocyclic preparations,[9] *e.g.*, isoxazoles, pyrazoles, pyrazolium chlorides, pyrrolidinones, pyrimidines and pyridinones, pyridines, thiazines, diazepines and thiazolo pyrimidinones, has been extensively described by our research group, there is a lack of literature on the use of 4-alkoxy-3-alken-2-ones containing polyfluoroalkyl groups in heterocyclic synthesis. In general, the synthesis of isoxazoles or pyrazoles from α-per(poly)fluoroalkyl acetates or acetylenes has shown some disadvantages, because the synthesis is carried out in more than one step.[10] In addition, the most important route for the synthesis of 1,2-dialkylpyrazolium salts is the *N*-alkylation of pyrazoles.[11] There are a few reports of the synthesis of these compounds using cyclocondensation methods such as the reaction of a β-diketone derivative with 1,2-dialkylhydrazines.[12,13]

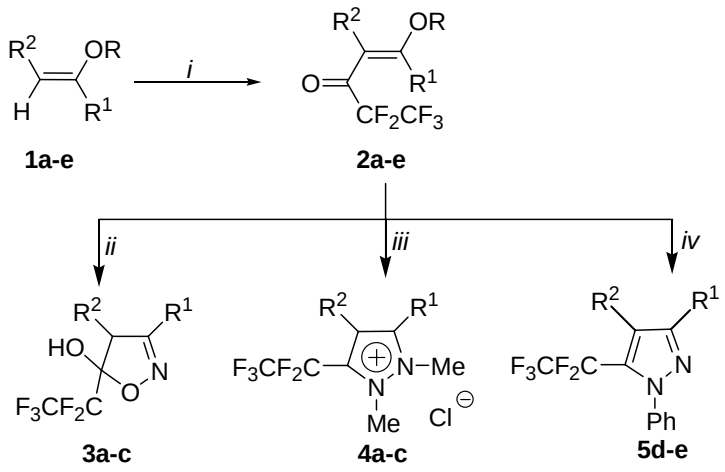
Thus, the aim of this work is to report a simple, efficient and general method towards novel intermediates heterocycles, β-acylated enol ethers (or 4-alkoxy-3-alken-2-ones), with a functionalized acyl group of the type CF_3CF_2-CO, and the azole derivatives, dihydroisoxazoles, pyrazoles and pyrazolium chlorides, in a one-pot procedure (Scheme 1).

Results and Discussion

The pentafluoroethylacylation of enol ethers occurred quite easily in carbon tetrachloride and a basic medium at room temperature to give the corresponding 5-alkoxy-1,1,1,2,2-pentafluoro-4-alken-3-ones (**2a-e**) in good yields (71-82%), according to methodology developed in our laboratory.[7] A typical experiment is carried out with the addition of pentafluoropropionic anhydride to a stirred mixture of enol ether (**1**) and pyridine (in a molar ratio of 1:1:1) in CCl_4 which is stirred for 24 hours at room temperature.

The coupling constant $J_{H4\text{-}H5}$ = 12Hz observed in the ^{1}H NMR spectrum (see Experimental Section) of compound **2a** suggests the *E*-configuration for compounds **2a-c**.

The 5-pentafluoroethyl-5-hydroxy-4,5-dihydroisoxazoles **3a-c** were prepared from the reaction of **2a-c** with hydroxylamine hydrochloride and pyridine (in a molar ratio of 1:1) in water as solvent, at 40 ^{o}C (70-75%, Scheme 1).



1, 2	R	R^2	R^1	**3, 4, 5**	R^1	R^2
a	Et	H	H	**a**	H	H
b	Me	H	Me	**b**	Me	H
c	Et	Me	H	**c**	H	Me
d	$–(CH_2)_2–$		H	**d**	H	$–(CH_2)_2OH$
e	$–(CH_2)_3–$		H	**e**	H	$–(CH_2)_3OH$

i: $(CF_3CF_2CO)_2O$, 0°C, pyridine, CCl_4, 24 h, Yields 71-82%
ii : $NH_2OH•HCl$/ pyridine, H_2O, 40 °C, 24 h, Yields 70-75%
iii: $CH_3NHNHCH_3•2HCl$, EtOH, 75 °C, 5 h, Yields 89-95%
iv: NH_2NHPh, EtOH, 75 °C, 16 h, Yields 60-62%

Scheme 1

The 5-pentafluoroethyl-1,2-dimethyl pyrazolium chlorides (**4a-c**) were obtained in 89–95% yield from the reaction of compounds **2a-c** with 1,2-dimethylhydrazine dihydrochloride in the presence of hydrochloric acid and with ethanol as solvent under reflux for 5 hours (Scheme 1).

Treatment of **2d**-**2e** with phenylhydrazine in ethanol under reflux furnished 4-(2-hydroxyethyl)-5-pentafluoroethyl-1-phenylpyrazole (**5d**) and 4-(3-hydroxypropyl)-5-pentafluoroethyl-1-phenylpyrazole (**5e**), respectively, with moderate yields (60-62%, Scheme 1). The products were identified by ^1H and ^{13}C NMR spectroscopy (see Experimental Section).

The regiochemistry of the cyclocondensation reaction can be understood by the acid-base concept. In both cases, cyclization to dihydroisoxazoles (**3**) pyrazoles (**5**), we found the harder basic site of the dinucleophile, hydroxylamine or phenylhydrazine bound to the harder carbonylic carbon acidic site of the enone **2**. Aromatic pyrazoles similar to **5** were normally produced from the cyclocondensation reactions, however 4,5-dihydro-1-phenylpyrazole intermediates were detected only in some cases.[9,14] The reactions regiospecifically produced the

4,5-dihydroisoxazole derivatives **3**, which are derived from exclusive coupling (amino group to olefinic carbon and hydroxyl group to carbonylic carbon) between the enone **2** and hydroxylamine. The pair of doublets (H4) observed in the ^{1}H NMR spectra centered near 3.1 and 3.4 ppm, with J = 17-20 Hz are typical spectroscopic data for 4,5-dihydro-isoxazoles (**3a**, **3b**).[15]

The 4,5-dihydroisoxazole products **3** are stable compounds and they were not converted to the aromatic isoxazoles. However, the aromatization of **3** can be obtained easily by stirring these compounds in concentrated sulfuric acid for a few hours at room temperature.[15]

The dehydration reactions of 4,5-dihydropyrazoles and 4,5-dihydroisoxazoles are elimination reactions in which the stability of the activated complex depends on the participation of the electron-pair of the neighbor heteroatom atom present in the azole ring. Thus, based on the experimental data[15] we believe that the easier dehydration of 4,5-dihydropyrazoles compared to 4,5-dihydroisoxazole is caused by the larger electron-donating strength of the nitrogen atom (N-1) in the pyrazole ring than the oxygen atom (O-1) in the oxazole ring.

The assignments of *N*-methyl groups (compounds **4**) were based on HMBC two-dimensional correlation spectra (Heteronuclear Multiple Bond Correlation).[16,17] The coupling constant (*J*) was optimized for 7 Hz (three bond ^{13}C–^{1}H coupling constants). The experiment showed that the ring C–3 (R^1) presented a crosspeak with the N–methyl hydrogens (more shielded ^{1}H and ^{13}C NMR signals) attached on N–2 for all compounds. To **4**, the ^{35}Cl chemical shifts of the chloride anion for all compounds presented an average chemical shift of –2.2 ppm (S.D. 1.4) in a range of –3.0 to –1.5 ppm. The importance of the ^{35}Cl chemical shifts for this work is that it proves that the counter ion of the pyrazolium cations studied is the chloride anion. The heterocycles (**3-5**) showed satisfactory elemental analyses (see Experimental Section).

Experimental Section

General Procedures. All common reagents and solvents were used as obtained from commercial suppliers without further purification. The ^{1}H, ^{13}C, and ^{35}Cl spectra were recorded on a Bruker DPX 400 spectrometer (^{1}H at 400 MHz, ^{13}C at 100.6 MHz, and ^{35}Cl at 39.2 MHz), digital resolution of ± 0.01 ppm, with 0.5 M solutions in DMSO–d_6 and $CDCl_3$ as solvent. Elemental Analyses were performed on a Perkin Elmer CHN elemental analyzer.

Synthesis of (*E*)-5-alkoxy-1,1,1,2,2-pentafluoroalk-4-en-3-ones (2a-e). General procedure. A solution of pentafluoropropionic anhydride (10 mmol) was added dropwise to a stirred solution of enol ether **1** (10 mmol) and pyridine (10 mmol) in carbon tetrachloride (15 mL) at –5 °C. The mixture was stirred for 24 hours at room temperature (25–30 °C). The mixture was washed with a solution of hydrochloric acid 0.1 M (1 × 20 mL) and water (2 × 20 mL). The organic layer was dried with sodium sulfate, the solvent was evaporated under reduced pressure and the product **2** was isolated without purification, with satisfactory purity as oil.

Synthesis of 5-hydroxy-5-pentafluoroethyl-4,5-dihydroisoxazoles (3a-c). General procedure. solution of hydroxylamine hydrochloride (2.2 mmol) in water (10 mL) was added to a stirred solution of **2** (2 mmol) in pyridine (2.2 mmol) at room temperature. The mixture was stirred for 24 hours at 40 °C. The mixture with water was then extracted with ethyl ether (3 × 10 mL). The combined organic layers were washed with a 10% aqueous solution of HCl (2 × 10mL), dried (Na_2SO_4), and the solvent was evaporated under reduced pressure and the solid product **3** was recrystallized from chloroform.

Synthesis of 5-pentafluoroethyl-1,2-dimethylpyrazolium chlorides (4a-c). General procedure. A solution of 1,2-dimethylhydrazine dihydrochloride (0.29 g, 2.2 mmol) in 36 % HCl (1 mL) was added to a stirred solution of **2** (2 mmol) in dry ethanol (10 mL) at room temperature. The mixture was stirred for 5 hours at reflux. After evaporation of the solvent, the residue containing **4** was dissolved in methanol (5mL) and the solution was dried with magnesium sulfate. After filtration and evaporation of this solvent, the organic impurities were extracted with dry dichloromethane (1 × 5 mL). Finally, the products **4-c** were obtained in good purity by evaporation of the solvent excess in vacuum.

Synthesis of 5-pentafluoroethyl-4-hydroxyalkyl-1*H*-1-phenylpyrazoles (5d-e). General procedure. Compound **2** (2 mmol) was added to a stirred solution of phenylhydrazine (2.2 mmol) at room temperature in ethanol (15 mL). The mixture was stirred under reflux for 16h. The solvent was evaporated, H_2O (10mL) was added to the residue and the aqueous mixture was extracted with dichloromethane (15 mL). The organic phase was washed with water (1 × 10 mL). The organic extract was dried (Na_2SO_4) and the solvent was removed under reduced pressure. The products **5d-e** were purified by recrystallization in chloroform.

(*E*)-5-Ethoxy-1,1,1,2,2-pentafluoropent-4-en-3-one (2a). Yield: 71%; oil (n_D^{20} 1.3813). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (t, 3H, CH_3), 4.12 (q, 2H, CH_2), 5.97 (d, *J* = 12, 1H, H4), 7.92 (d, *J* = 12, 1H, H5). ^{13}C NMR (100 MHz, $CDCl_3$) δ (J_{CF} , Hz) 14.2 (CH_3), 69.2 (OCH_2), 98.4 (C4), 14.2 (CH_3), 69.2 (OCH_2), 98.4 (C4), 119.0 (q/t, ^1J = 287, ^2J = 35, C1, CF_3), 107.5 (t/q, ^1J = 261, ^2J = 36, C2, CF_2), 168.1 (C5), 182.1 (t, ^2J = 25, C3) Anal. Calcd for $C_7H_7F_5O_2$ (218.12): C, 38.55; H, 3.23. Found: C, 38.27; H, 3.21.

(*E*)-5-Methoxy-1,1,1,2,2-pentafluorohex-4-en-3-one (2b). Yield: 75%; oil (n_D^{20} 1.3883). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H, CH_3), 3.90 (s, 3H, OCH_3), 5.78 (s, 1H, H4). ^{13}C NMR (100 MHz, $CDCl_3$) δ (J_{CF} , Hz) 21.0 (C6), 56.4 (OCH_3), 92.2 (C4), 107.7 (t/q, ^1J = 266, ^2J = 37, C2, CF_2), 118.3 (q/t, ^1J = 286, ^2J = 35, C1, CF_3), 181.7 (C5), 182.7 (t, ^2J = 24, C3). Anal. Calcd for $C_7H_7F_5O_2$ (218.12): C, 38.55; H, 3.23. Found: C, 38.42; H, 3.22.

(*E*)-5-Ethoxy-4-methyl-1,1,1,2,2-pentafluoropent-4-en-3-one (2c). Yield: 71%; oil (n_D^{20} 1.3581). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (t, 3H, CH_3), 1.80 (s, 3H, CH_3-C4), 4.24 (q, 2H, OCH_2), 7.70 (s, 1H, H5). ^{13}C NMR (100 MHz, $CDCl_3$) δ (J_{CF} , Hz) 8.2 (CH_3-C4), 14.1 (CH_3), 71.9 (OCH_2), 107.5 (t/q, ^1J = 265, ^2J = 35, C2, CF_2), 111.7 (q/t, ^1J = 286, ^2J = 35, C1, CF_3), 113.8 (C4), 159.5 (t, ^2J = 29, C3), 165.4 (C5). Anal.Calcd for $C_8H_9F_5O_2$ (232.14): C, 41.39; H, 4.86. Found: C, 41.09; H, 4.78.

4-Pentafluoropropionyl-2,3-dihydrofuran (2d). Yield: 80%; oil (n_D^{20} 1.3993). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (t, 2H, CH_2), 4.70 (q, 2H, CH_2O), 7.71 (s, 1H, H5). ^{13}C NMR (100 MHz,

$CDCl_3$) δ (J_{CF} , Hz) 27.5 (CH_2), 73.3 (OCH_2), 107.0 (t/q, ^1J = 268, ^2J = 34, C2, CF_2), 115.9 (q/t, ^1J = 285, ^2J = 34, C1, CF_3), 115.4 (C4), 164.0 (C5), 181.1 (t, ^2J = 24, C3). Anal. Calcd for $C_7H_5F_5O_2$ (216.10): C, 38.91; H, 2.33. Found: C, 38.70, H, 2.31.

5-Pentafluoropropionyl-3,4-dihydro-2-*H*-pyrane (2e). Yield: 82%; oil (n_D^{20} 1.4044). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.87 (m, 2H, CH_2) 2.24 (t, 2H, CH_2) 4.12 (t, 2H, CH_2-O-) 7.82 (s, 1H, H4). ^{13}C NMR (100 MHz, $CDCl_3$) δ (J_{CF}, Hz) 20.3, 18.2 ($2CH_2$), 67.8 (OCH_2), 108.8 (t/q, ^1J = 267, ^2J = 35, C2, CF_2), 118.0 (q/t, ^1J = 300, ^2J = 34, C1, CF_3), 112.8 (C4), 162.7 (C5), 181.1 (t, ^2J = 24, C3). Anal. Calcd for $C_8H_7F_5O_2$ (230.13): C, 41.75; H, 3.07. Found: C, 41.66, H, 3.05.

5-Pentafluoroethyl-5-hydroxy-4,5-dihydroisoxazole (3a). Yield: 70%; m.p. 68-70°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.08 (d, J = 20.0, 1H, H4b), 3.44 (d, J = 20.0, 1H, H4a), 7.61 (s, 1H, H3), 8.48 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ (J_{CF}, Hz) 44.0 (C4), 102.7 (t, ^2J = 25, C5), 111.7 (t/q, ^1J = 258, ^2J = 36, CF_2), 118.7 (q/t, ^1J = 287, ^2J = 36, CF_3), 148.0 (C3). Anal. Calcd for $C_5H_4F_5NO_2$ (205.08): C, 29.28; H, 1.97; N, 6.83. Found: C, 29.22; H, 1.96; N, 6.80.

5-Pentafluoroethyl-5-hydroxy-3-methyl-4,5-dihydroisoxazole (3b). Yield: 72%; m.p. 90-92°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.15 (d, J = 19.0, 1H, 4b), 3.47 (d, J = 19.0, 1H, 4a), 1.94 (s, 3H, Me), 8.41 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ (J_{CF}, Hz) 12.4 (Me), 46.2 (C4), 103.7 (t, ^2J = 25, C5), 111.4 (t/q, ^1J = 261, ^2J = 35, CF_2), 118.5 (q/t, ^1J = 286, ^2J = 35, CF_3), 156.4 (C3). Anal. Calcd for $C_6H_6F_5NO_2$ (219.10): C, 32.89; H, 2.76; N, 6.39. Found: C, 32.75; H, 2.74; N, 6.32.

5-Pentafluoroethyl-5-hydroxy-4-methyl-4,5-dihydroisoxazole (3c). Yield: 75%; oil (n_D^{20} 1.3309). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (d, 3H, Me), 3.40 (q, 1H, H4), 7.27 (s, 1H, H3), 8.06 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ (J_{CF}, Hz) 9.2 (Me), 47.0 (C4), 103.4 (t, ^2J = 25, C5), 112.0 (t/q, ^1J = 262, ^2J = 36, CF_2), 118.7 (q/t, ^1J = 287, ^2J = 36, CF_3), 152.8 (C3). Anal. Calcd for $C_6H_6F_5NO_2$ (219.10): C, 32.89; H, 2.76; N, 6.39. Found: C, 32.68; H, 2.75; N, 6.34.

5-Pentafluoroethyl-1,2-dimethylpyrazolium chloride (4a). Yield: 89%; oil (n_D^{20} 1.43055). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 (s, 6H, 2NMe), 7.44 (s, 1H, H4), 8.89 (s, 1H, H3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (J_{CF}, Hz) 37.7 (N1Me, N2Me), 109.7 (C4), 110.0 (t/q, ^1J = 262, ^2J = 42, CF_2), 117.8 (q/t, ^1J = 287, ^2J = 36, CF_3), 134.7 (t, ^2J = 31, C5), 137.9 (C3). ^{35}Cl (Cl^-) NMR δ -3.0. Anal. Calcd for $C_7H_8ClF_5N_2$ (250.60): C, 33.55; H, 3.22; N, 11.18. Found: C, 33.34; H, 3.20, N, 11.11.

5-Pentafluoroethyl-1,2,3-trimethylpyrazolium chloride (4b). Yield: 95%; oil (n_D^{20} 1.4395). ^{1}H NMR (400 MHz, $CDCl_3$) δ1.95 (s, 3H, Me), 3.51 (s, 3H, N2Me), 3.56 (s, 3H, N1Me), 6.57 (s, 1H, H4). ^{13}C NMR (100 MHz, $CDCl_3$) δ (J_{CF}, Hz) 13.2 (Me-C3), 36.5 (N1Me), 35.7 (N2Me), 111.3 (C4), 109.7 (t/q, ^1J = 221, ^2J = 41, CF_2), 118.7 (q/t, ^1J = 259, ^2J = 36, CF_3), 135.2 (t, ^2J = 31, C5), 149.5 (C3). ^{35}Cl (Cl^-) NMR δ -1,5. Anal. Calcd for $C_8H_{10}ClF_5N_2$ (264.63): C, 36.31; H, 3.81; N, 10.59. Found: C, 36.05; H, 3.78; N, 10.50.

5-Pentafluoroethyl-1,2,4-trimethylpyrazolium chloride (4c). Yield: 90%; oil (n_D^{20} 1.4436). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83 (s, 3H, Me), 3.73 (s, 3H, N2Me), 3.76 (s, 3H, N1Me), 7.88 (s, 1H, H3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (J_{CF}, Hz) 9.2 (Me-C4), 38.9 (N1Me), 38.7 (N2Me), 110.5 (t/q, ^1J = 251, ^2J = 42, CF_2), 119.1 (q/t, ^1J = 287, ^2J = 37, CF_3), 123.2 (C4), 133.0 (t, ^2J =

31, C5), 139.1 (C3). ^{35}Cl (Cl^-) NMR δ -2,0. Anal. Calcd for $C_8H_{10}ClF_5N_2$ (264.63): C, 36.31; H, 3.81; N, 10.59. Found: C, 36.11; H, 3.79; N, 10.53.

5-Pentafluoroethyl-4-(2-hydroxyethyl)-1*H*-1-phenylpyrazole (5d). Yield: 60%; m.p. 63-65°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (t, 2H, CH_2), 3.78 (t, 2H, CH_2), 7.93 (s, 1H, H3), 7.30 – 7.93 (m, 5H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$) δ (J_{CF}, Hz) 19.9 (CH_2), 62.0 (CH_2), 120.0 (C3), 117.0 (t, ^2J = 25, C5), 110.1 (t/q, CF_2, $^1J_{CF}$ = 245, $^2J_{CF}$ = 40), 119.0 (q/t, CF_3, $^1J_{CF}$ = 280, $^2J_{CF}$ = 30), 122.7, 127.4, 128.5, 129.4 (Ph), 139.0 (C4). Anal. Calcd for $C_{13}H_{11}F_5N_2O_2$ (306.23): C, 50.99; H, 3.62; N, 9.15. Found: C, 50.75; H, 3.59; N, 9.10.

5-Pentafluoroethyl-4-(3-hydroxypropyl)-1*H*-1-phenylpyrazole (5e). Yield: 62%; m.p. 65-67°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1,83 (t, 2H, CH_2), 2,83 (m, 2H, CH_2), 3,85 (t, 2H, CH_2), 7,94 (s, 1H, H3), 7,30 – 7,93 (m, 5H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$) δ (J_{CF}, Hz) 19.9 (CH_2), 33.0 (CH_2), 61.4 (CH_2), 120.3 (t, ^2J = 24, C5), 124.4 (C3), 113.4 (t/q, CF_2, $^1J_{CF}$ = 250, $^2J_{CF}$ = 40), 119.9 (q/t, CF_3, $^1J_{CF}$ = 285, $^2J_{CF}$ = 30), 124.4, 127.1, 128.9, 129.3 (Ph), 139.2 (C4). Anal. Calcd for $C_{14}H_{13}F_5N_2O$ (320.26): C, 52.51; H, 4.09; N 8.75. Found: C, 52.20; H, 4.04; N, 8.71.

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