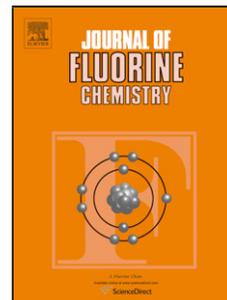


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# Improved synthesis of perfluoroalkyl substituted 1,3,4-oxadiazoles as precursors for corresponding 1,2,4-triazoles

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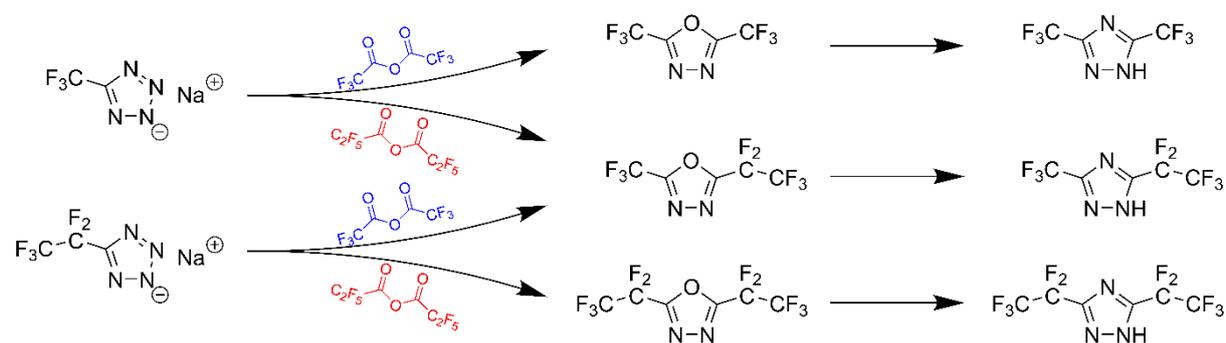
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## Graphical abstract



An improved, high yielding and easy extendable QIAO HUISGEN tetrazole rearrangement synthesis protocol was developed. The herein explained reaction conditions allow a facile access to perfluoroalkyl substituted 1,3,4-oxadiazoles via distillation at room temperature and under reduced pressure without further purification procedures. Moreover, the here desired 1,3,4-oxadiazoles are converted to 1,2,4-triazoles in the presence of ammonia and subsequent sublimation in mixture with phosphorous pentoxide.

## Highlights

- Simple and convenient access to perfluoroalkyl 1,3,4-oxadiazoles and 1,2,4-triazoles from low-cost starting materials.
- Improved reaction conditions that allow a direct access to pure materials without further purification.
- The described preparation protocol is easily scalable and can be transferred to higher substituted oxadiazoles & triazoles.
- Tailored or cross linked 1,2,4-triazoles are interesting candidates as ligands for transition metal chemistry.
- Additionally perfluorinated *N*-heterocycles are interesting precursors for conducting salts in lithium ion batteries.

## ABSTRACT

An improved and more efficient synthesis of 2,5-bis(trifluoromethyl)-1,3,4-oxadiazole (**2a**), 2,5-bis(perfluoroethyl)-1,3,4-oxadiazole (**2b**), 2-(perfluoroethyl)-5-(trifluoromethyl)-1,3,4-oxadiazole (**2d**) and 2-(perfluoroheptyl)-5-(trifluoromethyl)-1,3,4-oxadiazole (**2e**), via ring-opening reactions of the corresponding sodium 5-perfluoroalkyltetrazolates (**10a-b**) is described. Furthermore the named perfluoroalkyl-1,3,4-oxadiazoles (**2a-b** & **2d**) were converted into the corresponding 3,5-bis(trifluoromethyl)-1,2,4-triazole (**1a**), 3,5-bis(perfluoroethyl)-1,2,4-triazole (**1b**) and 5-(perfluoroethyl)-3-(trifluoromethyl)-1,2,4-triazole (**1d**), by *in situ* produced ammonia (urea and potassium hydroxide). All products were characterized using multinuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ) NMR spectroscopy and differential scanning calorimetry to determine the structure and thermodynamic characteristics. Additionally, the molecular structure of **1a** was determined by single crystal X-ray diffraction.

## KEYWORDS

Perfluoroalkyl-1,3,4-oxadiazole

Perfluoroalkyl-1,2,4-triazole

Ring-opening reaction

QIAO HUISGEN tetrazole rearrangement

Metal organic frameworks

Hydrogen storage

## 1. Introduction

1,2,4-triazoles are widely used as metal organic framework (MOF) precursors for applications in gas and energy storage devices [1]. Especially, perfluoroalkyl substituted 1,2,4-triazoles (**1**) in combination with e.g. zinc or coinage metals like silver are used as efficient and high temperature stable oxygen, nitrogen and hydrogen storage material [2-4]. In particular, molecular H<sub>2</sub> is one of the most promising energy carriers (120 kJ·g<sup>-1</sup>) [5] to replace gasoline-based fuels for automotive applications and therefore reducing greenhouse gases [6-8]. In that context, a cost reducing and facile preparation protocol of the named precursors from low-cost and easily accessible starting materials is desired. In 1962, a general preparation method for perfluoroalkyl-1,2,4-triazoles (**1a-c**) from bis(perfluoroalkyl)-1,3,4-oxadiazoles (**2a-c**) was published by Brown [9]. This two-step synthesis in liquid ammonia via dehydration with phosphorous pentoxide at elevated temperature leads to the corresponding perfluoroalkyl-1,2,4-triazoles (**1a-c**). The method was improved by Reitz in 1989 [10]. Additionally Reitz et al. described a three-step conversion method of bis(perfluoroalkyl)-1,3,4-oxadiazoles (**2a-c**) via reaction of hydrazine, acetic acid and subsequent deamination with nitrous acid to the corresponding perfluoroalkyl-1,2,4-triazoles (**1a-c**) [11]. Another approach to **1a** was also described by Brown in 1967 [12] by converting 5-perfluoropropyltetrazole (**3c**) with perfluorobutyronitrile (**4c**) in excess of hydrogen chloride under high pressure and elimination of nitrogen. In the early 1990s, **1a** was synthesized from 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahepta-2,5-diene (**5a**) and in 2003, a six-step synthesis route was published from commercially available starting materials with an overall yield of only 6% [13-15]. Considering these three introduced entrances as illustrated in Fig. 1, the conversion of 1,3,4-oxadiazoles in liquid ammonia has proven to be the most simple, efficient and highest yielding preparation method. Consequently, we focused on the development of a general, simple, time and cost reducing synthesis protocol of the

desired 1,3,4-oxadiazoles, particularly for our adoption as precursors for novel conducting salts in lithium ion batteries. 1,3,4-oxadiazoles (**2a-c**) were first prepared by Brown et al. via dehydrating reaction with phosphorous pentoxide of *N,N'*-bis(perfluoroalkyl)hydrazines (**6a-c**) in the early sixties [16] and in the following three decades, additional methods were published using oleum and phosphoryl chloride as dehydrating agents [17-19]. A further approach was made by Brown in 1967: 5-perfluoroalkyltetrazoles (**3a** & **3c**) or the corresponding silver salt **8c** were reacted in the presence of gaseous perfluoroacyl chlorides (**7a** & **7c**) under high pressure and high temperature (**3a** & **3c**) or at -78 °C in tetrahydrofuran under ring-opening reaction and evolution of nitrogen (Fig. 1) [12]. In this publication, an improved and high yielding preparation protocol for perfluorinated 1,3,4-oxadiazoles via modified QIAO HUISGEN tetrazole rearrangement [20] is described, using simple reflux conditions without high pressures, use of expensive silver salts and highly toxic phosphoryl chloride. Furthermore, the 1,3,4-oxadiazoles (**2a-b** & **2d**) are subsequently converted to the named fluorinated 1,2,4-triazoles (**1a-b** & **1d**) by *in situ* produced ammonia followed by dehydration with phosphorous pentoxide. Additionally, thermodynamic properties of the here investigated fluorinated heterocycles, as well as the crystal structure of 1,2,4-triazole **1a** are discussed.

## 2. Results and discussions

### 2.1. Preparation protocol

The simple combination of different perfluorinated carboxylic anhydrides (**9a-b**) and sodium 5-perfluoroalkyltetrazolates (**10a-b**) under otherwise equal reaction conditions lead to a series of perfluoroalkyl substituted 1,3,4-oxadiazoles (**2a-2b** & **2d**) with yields of 68-86% (Scheme 1). The first improvement is the application of thermal stable and solid sodium 5-perfluoroalkyltetrazolate salts (**10a-b**) instead of liquid and highly acidic 5-

perfluoroalkyltetrazoles (**3a** & **3c**) [21]. 5-perfluoroalkyltetrazolates (**10a-b**) are easily accessible by high yielding (90-97%) one-step preparation methods from low-cost starting materials (e.g. trifluoroacetic anhydride, trifluoroacetamide and sodium azide) as published by Crawford et al. [22]. The second approach is the convenient use of liquid perfluorinated carboxylic anhydrides instead of gaseous acid chlorides (**7a** & **7c**). Taking 1.5 equivalents in the case of trifluoroacetic anhydride increased the yield dramatically. One reason is probably the high volatility of the anhydride. Progress of the reaction could be controlled easily by monitoring the nitrogen evolution. For completion of the reaction, the mixture was heated under reflux until end of nitrogen evolution. To get rid of excess carboxylic anhydrides the solution is stirred with sodium carbonate for 1h to produce non-volatile sodium salts beside unreacted non-volatile 5-perfluoroalkyltetrazolates (**10a-b**) as by-product. Tetraglyme is used as a high boiling solvent (275 °C), so that only the 1,3,4-oxadiazoles (**2a-b** & **2d**) can easily be distilled off at room temperature and reduced pressure via a short path distillation bridge into a cooling trap at -78 °C. All investigated 1,3,4-oxadiazoles (**2a-b** & **2d**) are immiscible with water whereby they can be washed to separate them from small residues of tetraglyme and trifluoroacetic anhydride. Redistillation with small amounts of phosphorus pentoxide leads to analytical pure products (>99%, GC-MS). This improved synthesis protocol can easily be modified to receive higher substituted 1,3,4-oxadiazoles. To proof the transferability of the synthesis protocol for longer perfluorinated side chains, an additional experiment was made to obtain pentadecafluoroheptyl substituted 1,3,4-oxadiazole (**2e**) from sodium 5-trifluoromethyltetrazolate (**10a**) and pentadecafluorooctanoic anhydride (**9e**). Furthermore **2a-b** & **2d** are converted to the corresponding 1,2,4-triazoles (**1a-b** & **1d**) by *in situ* produced ammonia, formed by urea and potassium hydroxide under elevated temperature and condensed into a cooling trap at -78 °C. After evaporation of excessive ammonia by warming to room temperature, the resulting powders are mixed and heated with phosphorous pentoxide to form the desired 1,2,4-triazoles (Scheme 1). All reaction conditions and yields are listed in

Table 1. The corresponding NMR-spectra are available in the supplementary data.

## 2.2. Ring-opening mechanism

The rearrangement-type reaction of tetrazoles in the presence of perfluoroalkyl substituted acid chlorides was first described by Brown et al. [12]. An explanation of a ring-opening mechanism for non-fluorinated tetrazoles, known as QIAO HUISGEN tetrazole rearrangement is given by Li et al. [20] and Seldes et al. [23] and can be transferred to the herein discussed sodium 5-perfluoroalkyltetrazolate/carboxylic anhydride-system. The highly thermal stable tetrazolates are acylated in the first step (**I**), see proposed reaction mechanism in Fig. 2. The acyl tetrazole-intermediate is not stable, so that a ring-opening reaction takes place (**II**) followed by a nucleophilic attack of the enol oxygen on the ring-carbon atom to close to 1,3,4-oxadiazole (**2a-b**, **2d** & **2e**) under evolution of nitrogen.

## 2.3. Thermodynamic properties of (**2a-b** & **2d**) and (**1a-b** & **1d**).

All three investigated 1,3,4-oxadiazoles are colorless liquids with low boiling points (68 °C (**2a**), 97 °C (**2b**), 89 °C (**2d**)). Like most perfluoroalkyl substituted heterocycles, they are poorly soluble in water, but soluble in organic solvents like methanol, ethanol, acetonitrile, diethyl ether, tetrahydrofuran, dichloromethane, chloroform and *n*-pentane. One exception is given by very low solubility of **2b** in toluene. Furthermore, all three 1,3,4-oxadiazoles show low melting points (-22 °C (**2a**), -16 °C (**2b**) and -41 °C (**2d**)). Especially 1,3,4-oxadiazole (**2d**) has a very low melting point of -41 °C. This exception can be explained by the asymmetric substitution of the heterocyclic structure, resulting in lower melting enthalpy  $\Delta_m H$  (see Table 2) and therefore a phase transition at lower temperature given by  $\Delta_m G = \Delta_m H - T\Delta_m S$ . In contrast to the 1,3,4-oxadiazoles, the corresponding 1,2,4-triazoles (**1a-b** & **1d**) are

white, volatile and crystalline solids at room temperature ( $\vartheta_m = 85$  °C (**1a**), 109 °C (**1b**) and 81 °C (**1d**)) which is caused by strong N-H-N-hydrogen bond interactions. Furthermore, all three 1,2,4-triazoles are highly soluble in water under acidic reaction and in numerous polar solvents but poorly soluble in dichloromethane, chloroform and *n*-pentane. Additionally, all 1,2,4-triazoles show relatively high boiling points ( $\vartheta_{\text{vap}} = 181$  °C (**1a**), 177 °C (**1b**) and 182 °C (**1d**)). The investigated thermodynamic data (e.g. melting and boiling temperatures, enthalpies and entropies) are summarized in Table 2. Differential scanning calorimetry (DSC) spectra are available in the supplementary data.

#### 2.4. Crystal structure of **1a**

Single crystal X-ray diffraction spectroscopy was measured on a Nonius KappaCCD diffractometer to determine the molecular structure of perfluoroalkyl substituted 1,2,4-triazole **1a**. To evaluate the collected data from single crystal diffraction, the following programs were used: For data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands), for data reduction Denzo-SMN [24], for absorption correction, Denzo [25], for structure solution SHELXS-97 [26] and for structure refinement SHELXL-97 [27]. Thermal ellipsoids are shown with 15% probability, *R*-values are given for observed reflections and  $wR^2$  values for all reflections. *Exceptions and special features*: Two CF<sub>3</sub> groups were found disordered over two positions (not shown in Fig. 3). Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. The hydrogen atom at N1 was refined freely.

Suitable needle shaped crystals were obtained by slow sublimation at 100 °C and reduced pressure ( $5.0 \cdot 10^{-2}$  bar). The pure 1,2,4-triazole **1a** crystallized in the space group *Pbca* with 8 molecular units per unit cell and a calculated density of 1.809 g·cm<sup>-3</sup> at -50 °C. Additional calculated refinement and crystal data of substance **1a** can be found in the supplementary

data. The 1,2,4-triazole unit (see Fig. 3) exhibits bond lengths within the ring structure, ranging from 1.31 to 1.34 Å [1.342(5) Å N3-C4; 1.316(5) Å N3-C2; 1.317(5) Å N1-C2; 1.310(5) Å N5-C4; 1.344(5) Å N1-N5] which is evident for a delocalized aromatic  $\pi$ -system and not for alternating single and double bonds. Furthermore, these bond lengths are comparable to those for the unsubstituted 1,2,4-triazole according to the literature [28]. The molecule units form catemers (chains) along the *b*-axis (see Fig. 4a-b), wherein each unit is connected via hydrogen bridge bond (see Fig. 4a) with an observed distance N1-H...N3 of 1.93(5) Å and an angle of 169(4)°. An additional fluorine-fluorine distance between two neighboured molecule chains is shown in Fig. 4a with a length of 2.695 Å (F4...F4A). Furthermore, the molecule units show an alternating arrangement along the chains with a calculated angle of 77.5° between two triazole ring planes. For a better visualization, see projection along the *b*-axis in Fig. 4b.

### 3. Conclusions

High yields of symmetric and asymmetric substituted perfluorinated 1,3,4-oxadiazoles (**2a-b**, **2d** & **2e**) were obtained via rearrangement reactions of sodium 5-trifluoromethyltetrazolate (**10a**) and sodium 5-pentafluoroethyltetrazolate (**10b**) under simple reflux conditions. The corresponding perfluoroalkyl substituted 1,2,4-triazoles (**1a-b** & **1d**) were prepared by *in situ* produced ammonia (from urea and potassium hydroxide) and subsequent sublimation in the presence of phosphorous pentoxide. As a result, the herein presented preparation procedures allow a much more facile and convenient excess to perfluoroalkyl substituted 1,3,4-oxadiazoles and 1,2,4-triazoles by using low-cost starting materials. Additionally, thermodynamic properties were investigated and discussed as well as the crystal structure of substance **1a**.

## 4. Experimental

### 4.1. Chemicals

All used chemicals for the preparation of sodium 5-trifluoromethyltetrazolate (**10a**) and sodium 5-pentafluoroethyltetrazolate (**10b**) according to the literature and the here investigated 1,3,4-oxadiazoles (**2a-b** & **2d**) and 1,2,4-triazoles (**1a-b** & **1d**) are listed in Table 3.

### 4.2. Measurement techniques

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE(III) 400 UltraShield. The  $^1\text{H}$  and  $^{13}\text{C}$  shifts were given relative to the  $\text{CDCl}_3$  solvent (7.26 ppm for  $^1\text{H}$  and 77.16 ppm for  $^{13}\text{C}$ ), to  $\text{THF-d}_8$  (3.58 ppm for  $^1\text{H}$  and 67.57 ppm for  $^{13}\text{C}$ ) and to  $\text{C}_6\text{D}_6$  (7.27 ppm for  $^1\text{H}$  and 128.00 ppm for  $^{13}\text{C}$ ).  $^{19}\text{F}$  shifts were calculated from  $^1\text{H}$  log signals.

Differential scanning calorimetry (DSC) was measured using a NETSCH DSC 204F1 Phoenix® spectrometer in a temperature range of -150 °C up to 250 °C. Samples between 15 and 35 mg were loaded in aluminum crucibles. Thermodynamic properties were calculated from peak areas and the given phase transition temperature (peak maximum) by applying the formula  $\Delta G = \Delta H - T\Delta S$ .

### 4.3. General protocol for preparation of perfluoroalkyl substituted 1,3,4-oxadiazoles (**2a-b**, **2d** & **2e**)

1 equiv. (10 g for preparation of **2a-b** or 1.58 g for preparation of **2e**) of sodium 5-perfluoroalkyltetrazolate (**10a** or **10b**) were introduced into a 100 mL round bottom flask, equipped with a magnetic stirring bar and a reflux condenser. Then 20 mL of tetraglyme were

filled into the flask through the reflux condenser and the suspension was stirred for 10 minutes until most of the salt was dissolved. Afterwards 1.5 equiv. of trifluoroacetic anhydride **9a** (or 1.2 equiv. of pentafluoropropionic anhydride **9b** or rather 1.0 equiv. of pentadecafluorooctanoic anhydride **9e**) were introduced into the reaction mixture and the reflux condenser was closed with a gas bubbler. The mixture was stirred for 1 hour at room temperature and then subsequently heated to 70 °C (for 1 hour), 90 °C (for 1 hour) and 120 °C until evolution of nitrogen stopped (3 hours (**9a-b**) or 12 h in the case of pentadecafluorooctanoic anhydride **9e**). The yellowish/orange solution was cooled to room temperature and 0.5 g of sodium carbonate were introduced to neutralize an excess of perfluorinated acid anhydride (stirred for 12 h). To minimize losses of the corresponding 1,3,4-oxadiazoles, the round bottom flask was reequipped with the reflux condenser and the suspension was stirred overnight. After that time the condenser was exchanged by a short path distillation bridge, leading into a 100 mL round bottom flask which was cooled to -78 °C in a dry ice/acetone bath. The 1,3,4-oxadiazoles were slowly condensed under vacuum into the cooled flask to yield nearly pure products. To get rid of small amounts of tetraglyme and acid anhydrides, the 1,3,4-oxadiazoles were soaked into a syringe, washed two times with equal volumes of water and subsequently redistilled under vacuum in the presence of 0.5 g of phosphorous pentoxide.

#### 4.4. General protocol for preparation of perfluoroalkyl substituted 1,2,4-triazoles (**1a-b** & **1d**)

A large excess of ammonia was prepared by heating a mixture of 26.76 g of urea and 50 g of potassium hydroxide. The gas was led through a drying tube filled with anhydrous calcium chloride and condensed at -78 °C (dry ice/acetone) into a 100 mL Schlenk-flask with magnetic stirring bar. Afterwards 5 g of the previously synthesized 1,3,4-oxadiazoles (**2a-b** & **2d**) were slowly added to the liquid ammonia and the solution was stirred overnight until the

dry ice/acetone bath was thawed and the ammonia evaporated. The white residue was dried at room temperature and under vacuum for 6 hours. To receive pure crystalline perfluorinated 1,2,4-triazoles (**1a-b** & **1d**) the dried residue was mixed with an equal amount of phosphorous pentoxide and sublimated to a cold finger at 90 °C for 12 hours and at 150 °C for 3 hours.

#### 4.5. 2,5-bis(trifluoromethyl)-1,3,4-oxadiazole (**2a**)

Colorless and dense liquid, yield: 8.44 g (66%).  $^{13}\text{C}$  NMR{ $^1\text{H}$ } (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.6 (q,  $^2J_{\text{CF}} = 46.3$  Hz, 2C,  $C_{\text{ring}}$ ), 124.4 (q,  $^1J_{\text{CF}} = 272.8$  Hz, 2C,  $\text{CF}_3$ ).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -65.5 ppm (s, 6F,  $\text{CF}_3$ ).

#### 4.6. 2,5-bis(perfluoroethyl)-1,3,4-oxadiazole (**2b**)

Colorless and dense liquid, yield: 10.65 g (86%).  $^{13}\text{C}$  NMR{ $^1\text{H}$ } (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.3 (t,  $^2J_{\text{CF}} = 32.4$  Hz, 2C,  $C_{\text{ring}}$ ), 117.5 (tq,  $^1J_{\text{CF}} = 286.4$  Hz,  $^2J_{\text{CF}} = 34.1$  Hz, 2C,  $\text{CF}_2\text{-CF}_3$ ), 106.7 (qt,  $^1J_{\text{CF}} = 259.7$  Hz,  $^2J_{\text{CF}} = 42.5$  Hz, 2C,  $\text{CF}_2\text{-CF}_3$ ).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -83.79 (s, 6F,  $\text{CF}_2\text{-CF}_3$ ), -115.75 (s, 4F,  $\text{CF}_2\text{-CF}_3$ ).

#### 4.7. 2-(perfluoroethyl)-5-(trifluoromethyl)-1,3,4-oxadiazole (**2d**)

Colorless and dense liquid, yield: 11.09 g (69%) (received from sodium 5-trifluoroethyltetrazolate (**9a**) and pentafluoropropionic anhydride), yield: 8.00 g (67%) (received from sodium 5-pentafluoroethyltetrazolate (**9b**) and trifluoroacetic anhydride).  $^{13}\text{C}$  NMR{ $^1\text{H}$ } (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.4 (q,  $^2J_{\text{CF}} = 46.1$  Hz, 1C,  $C_{\text{ring}}\text{-CF}_3$ ), 157.3 (t,  $^2J_{\text{CF}} = 32.4$  Hz, 1C,  $C_{\text{ring}}\text{-CF}_2\text{-CF}_3$ ), 117.5 (tq,  $^1J_{\text{CF}} = 286.5$  Hz,  $^2J_{\text{CF}} = 34.1$  Hz, 1C,  $\text{CF}_2\text{-CF}_3$ ), 115.3 (q,  $^1J_{\text{CF}} = 272.7$  Hz, 1C,  $\text{CF}_3$ ), 106.8 (qt,  $^1J_{\text{CF}} = 259.8$  Hz,  $^2J_{\text{CF}} = 42.5$  Hz, 1C,  $\text{CF}_2\text{-CF}_3$ ).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -65.2 (s, 3F,  $\text{CF}_3$ ), -83.7 (s, 3F,  $\text{CF}_2\text{-CF}_3$ ), -115.7 (s, 2F,  $\text{CF}_2\text{-CF}_3$ ).

#### 4.8. 2-(perfluoroheptyl)-5-(trifluoromethyl)-1,3,4-oxadiazole (**2e**)

Colorless and dense liquid, yield: 2.25 g (45%).  $^{13}\text{C}$  NMR{ $^1\text{H}$ } (101 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  157.1 (q,  $^2J_{\text{CF}} = 46.1$  Hz, 1C,  $\text{C}_{\text{ring}}\text{-CF}_3$ ), 156.7 (t,  $^2J_{\text{CF}} = 32.4$  Hz, 1C,  $\text{C}_{\text{ring}}\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_3$ ), 117.5 (tq,  $^1J_{\text{CF}} = 286.3$  Hz,  $^2J_{\text{CF}} = 32.8$  Hz, 1C,  $\text{CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_3$ ), 115.6 (q,  $^1J_{\text{CF}} = 271.6$  Hz, 1C,  $\text{C}_{\text{ring}}\text{-CF}_3$ ), 114.0-105.0 (m, 6C).  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -62.6 (s, 3F,  $\text{CF}_3$ ), -83.0 (s, 3F,  $\text{CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_3$ ), -114.4 (s, 2F,  $-\text{CF}_2-$ ), -122.7 (s, 2F,  $-\text{CF}_2-$ ), -123.1 (s, 2F,  $-\text{CF}_2-$ ), -123.3 (s, 2F,  $-\text{CF}_2-$ ), -124.0 (s, 2F,  $-\text{CF}_2-$ ), -127.8 (s, 2F,  $-\text{CF}_2-$ ).

#### 4.9. 3,5-bis(trifluoromethyl)-1,2,4-triazole (**1a**)

White crystalline solid, yield: 3.62 g (73%).  $^1\text{H}$  NMR (400 MHz,  $\text{THF-d}_8$ ):  $\delta$  11.8 (broad s, 1H, N-H).  $^{13}\text{C}$  NMR{ $^1\text{H}$ } (101 MHz,  $\text{THF-d}_8$ ):  $\delta$  151.9 (q,  $^2J_{\text{CF}} = 38.3$  Hz, 2C,  $\text{C}_{\text{ring}}$ ), 119.6 (q,  $^1J_{\text{CF}} = 269.9$  Hz, 2C,  $\text{CF}_3$ ).  $^{19}\text{F}$  NMR (376 MHz,  $\text{THF-d}_8$ ):  $\delta$  -65.8 (s, 6F,  $\text{CF}_3$ ).

#### 4.10. 3,5-bis(perfluoroethyl)-1,2,4-triazole (**1b**)

White crystalline solid, yield: 3.95 g (79%).  $^1\text{H}$  NMR (400 MHz,  $\text{THF-d}_8$ )  $\delta$  = 14.1 (broad s, 1H, N-H).  $^{13}\text{C}$  NMR{ $^1\text{H}$ } (101 MHz,  $\text{THF-d}_8$ ):  $\delta$  151.3 (m, 2C,  $\text{C}_{\text{ring}}$ ), 119.4 (tq,  $^1J_{\text{CF}} = 286.1$  Hz,  $^2J_{\text{CF}} = 35.9$  Hz, 2C,  $-\text{CF}_2\text{-CF}_3$ ), 109.7 (qt,  $^1J_{\text{CF}} = 253.5$  Hz,  $^2J_{\text{CF}} = 40.4$  Hz, 2C,  $\text{CF}_2\text{-CF}_3$ ).  $^{19}\text{F}$  NMR (376 MHz,  $\text{THF-d}_8$ ):  $\delta$  -85.1 (s, 6F,  $-\text{CF}_2\text{-CF}_3$ ), -115.9 (s, 4F,  $-\text{CF}_2\text{-CF}_3$ ).

#### 4.11. 5-(perfluoroethyl)-3-(trifluoromethyl)-1,2,4-triazole (**1d**)

White crystalline solid, yield: 3.39 g (68%).  $^1\text{H}$  NMR (400 MHz, THF- $d_8$ ):  $\delta$  13.4 (broad s, 1H, N-H).  $^{13}\text{C}$  NMR{ $^1\text{H}$ } (101 MHz, THF- $d_8$ ):  $\delta$  151.5 (m, 2C,  $C_{\text{ring}}$ ), 119.5 (tq,  $^1J_{\text{CF}} = 285.7$  Hz,  $^2J_{\text{CF}} = 35.9$  Hz, 1C,  $-\text{CF}_2\text{-CF}_3$ ), 119.4 (q,  $^1J_{\text{CF}} = 269.1$  Hz, 1C,  $\text{CF}_3$ ), 109.8 (qt,  $^1J_{\text{CF}} = 254.2$  Hz,  $^2J_{\text{CF}} = 40.3$  Hz, 1C,  $-\text{CF}_2\text{-CF}_3$ ).  $^{19}\text{F}$  NMR (376 MHz, THF- $d_8$ ):  $\delta$  -65.8 (s, 3F,  $\text{CF}_3$ ), -85.1 (s, 3F,  $-\text{CF}_2\text{-CF}_3$ ), -115.9 (s, 2F,  $-\text{CF}_2\text{-CF}_3$ ).

#### Acknowledgements

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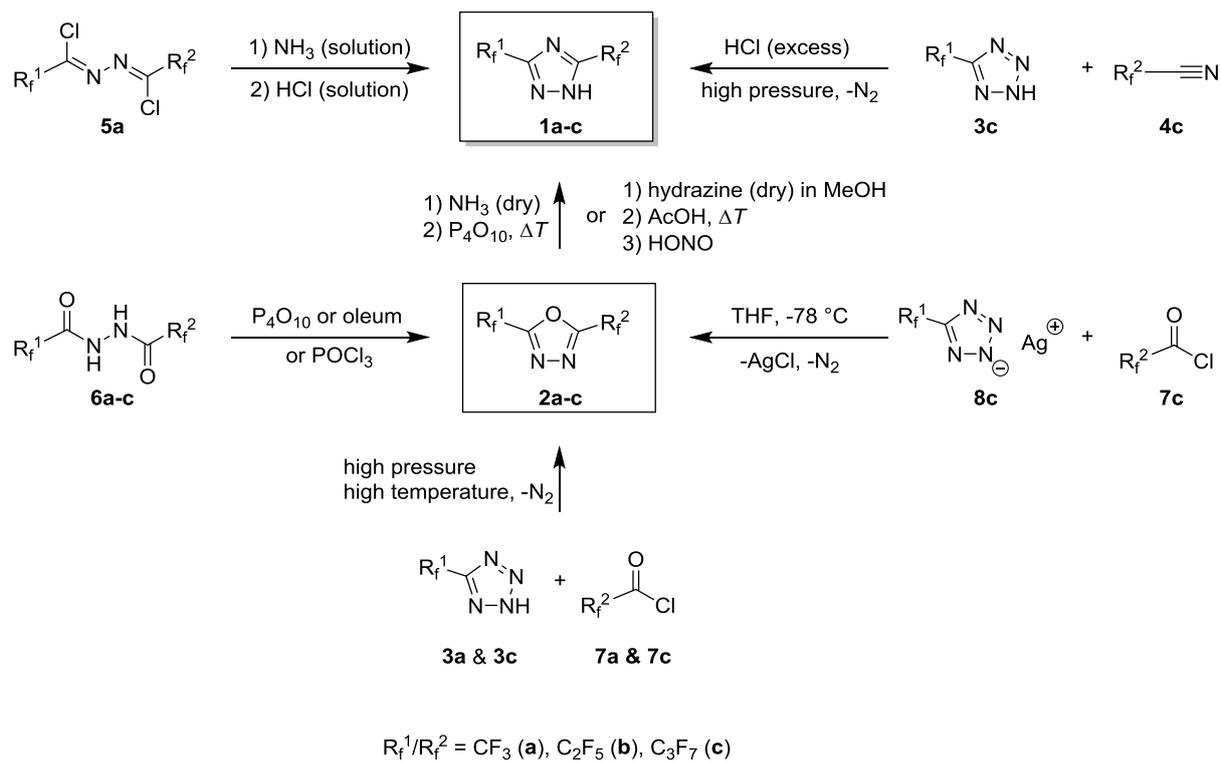
#### Supplementary data

Detailed descriptions of  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra, differential scanning calorimetry (DSC) spectra and Crystallographic Information (CIF-File and **CCDC ID: 1429636**) associated with this article can be found as supplementary data in the online version, at:

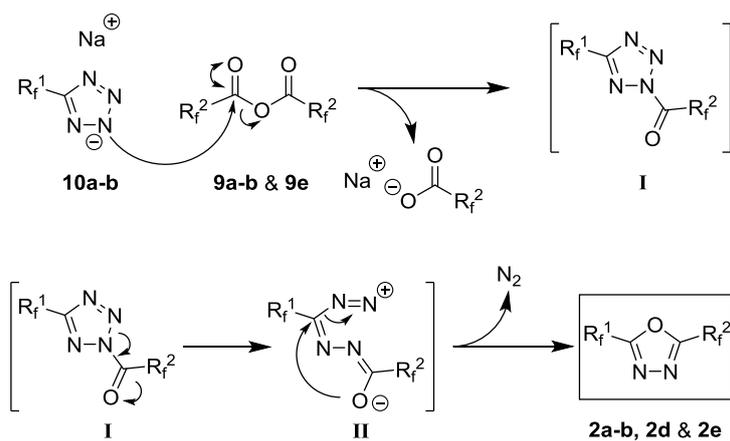
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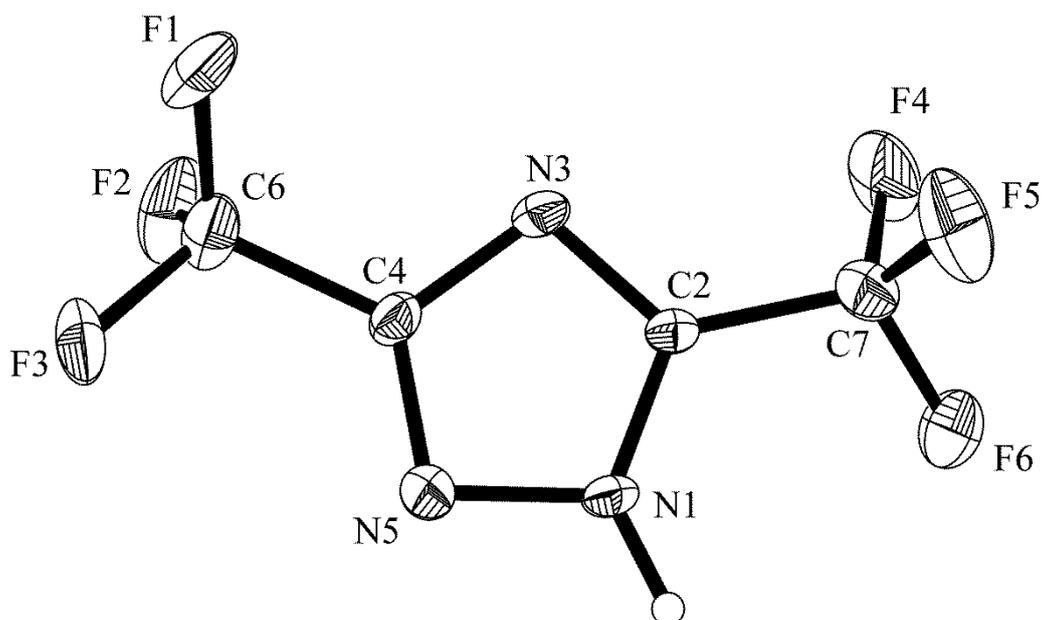


**Fig. 1.** Preparation methods of perfluoroalkyl substituted 1,3,4-oxadiazoles and 1,2,4-triazoles according to the literature [3, 9-18].

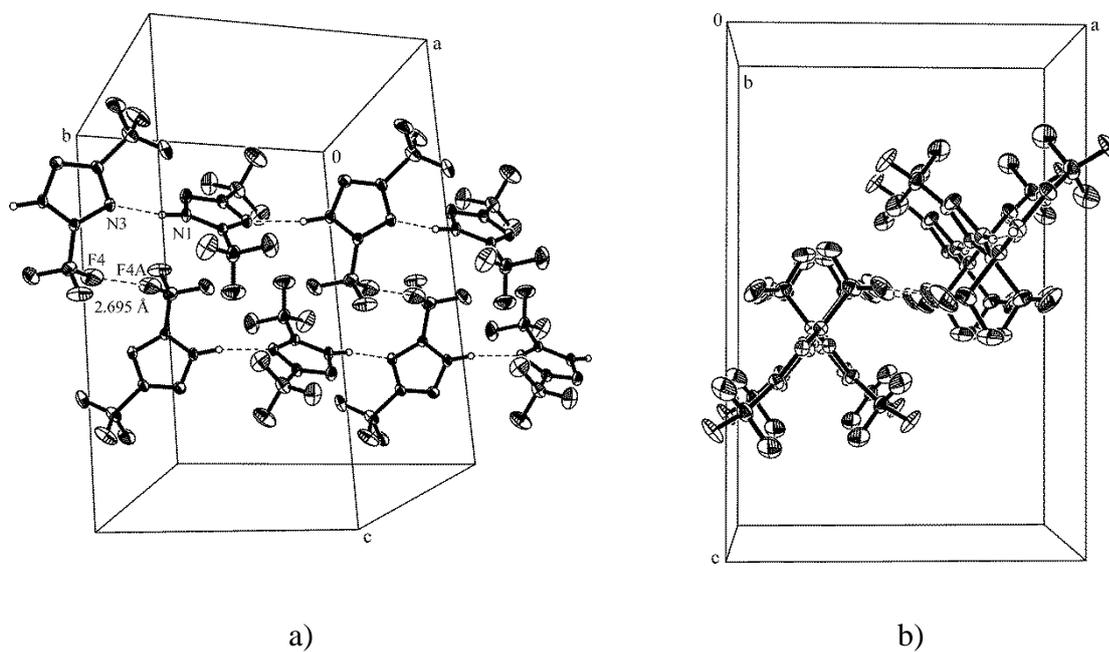


$R_f^1/R_f^2 = \text{CF}_3$  (a),  $\text{C}_2\text{F}_5$  (b),  $R_f^1 = \text{CF}_3$  &  $R_f^2 = \text{C}_2\text{F}_5$  (d) (and vice versa),  $R_f^1 = \text{CF}_3$  &  $R_f^2 = \text{C}_7\text{F}_{15}$  (e)

**Fig. 2.** Anticipated QIAO HUISGEN rearrangement mechanism [20] of fluorinated tetrazoles (**10a-b**) to 1,3,4-oxdiazoles (**2a-b**, **2d** & **2e**).

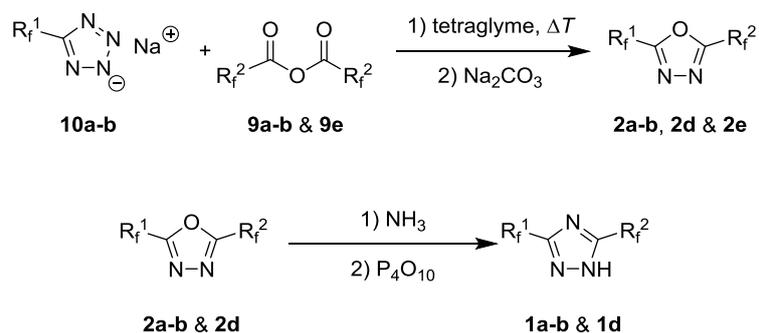


**Fig. 3.** Crystal structure of compound **1a** (thermal ellipsoids are shown with 15% probability).



**Fig. 4.** a) Packing diagram presenting the N-H...N and F...F interactions along the *b*-axis in compound **1a**.

b) View of the linear chains parallel to the *b*-axis.



$\text{R}_f^1/\text{R}_f^2 = \text{CF}_3$  (**a**),  $\text{C}_2\text{F}_5$  (**b**),  $\text{R}_f^1 = \text{CF}_3$  &  $\text{R}_f^2 = \text{C}_2\text{F}_5$  (**d**) (and vice versa),  $\text{R}_f^1 = \text{CF}_3$  &  $\text{R}_f^2 = \text{C}_7\text{F}_{15}$  (**e**)

**Scheme 1.** Synthetic routes to 1,3,4-oxdiazoles (**2a-b**, **2d** & **2e**) and 1,2,4-triazoles (**1a-b** & **1d**).

**Table 1**

Yields and reaction conditions of 1,3,4-oxadiazoles (**2a-b**, **2d** & **2e**) and 1,2,4-triazoles (**1a-b** & **1d**).

Starting material	Conditions	Ratio ( <b>10</b> : <b>9</b> )	Product	Yield %
<b>10a</b>	1) <b>9a</b> in Tetraglyme, rt 1h, 70 °C 1h, 90 °C 1h, 120 °C 3h, 2) Na <sub>2</sub> CO <sub>3</sub> , rt 12h	1 : 1.5	<b>2a</b>	66
<b>10b</b>	1) <b>9b</b> in Tetraglyme, rt 1h, 70 °C 1h, 90 °C 1h, 120 °C 3h, 2) Na <sub>2</sub> CO <sub>3</sub> , rt 12h	1 : 1.2	<b>2b</b>	86
<b>10a</b>	1) <b>9b</b> in tetraglyme, rt 1h, 70 °C 1h, 90 °C 1h, 120 °C 3h, 2) Na <sub>2</sub> CO <sub>3</sub> , rt 12h	1 : 1.2	<b>2d</b>	67
<b>10b</b>	1) <b>9a</b> in tetraglyme, rt 1h, 70 °C 1h, 90 °C 1h, 120 °C 3h, 2) Na <sub>2</sub> CO <sub>3</sub> , rt 12h	1 : 1.5	<b>2d</b>	69
<b>10a</b>	1) <b>9e</b> in tetraglyme, rt 1h, 100 °C 1h, 120 °C 12h, 2) Na <sub>2</sub> CO <sub>3</sub> , rt 12h		<b>2e</b>	45
<b>2a</b>	1) dry NH <sub>3</sub> at -78 °C 6 h, 2) P <sub>4</sub> O <sub>10</sub> , 90 °C 12 h, 150 °C 3h	-	<b>1a</b>	73
<b>2b</b>	1) dry NH <sub>3</sub> at -78 °C 6 h, 2) P <sub>4</sub> O <sub>10</sub> , 90 °C 12 h, 150 °C 3h	-	<b>1b</b>	79
<b>2d</b>	1) dry NH <sub>3</sub> at -78 °C 6 h, 2) P <sub>4</sub> O <sub>10</sub> , 90 °C 12 h, 150 °C 3h	-	<b>1d</b>	68

**Table 2**

Thermodynamic data from investigated 1,2,4-triazoles (**1a-b** & **1d**) and 1,3,4-oxadiazoles (**2a-b** & **2d**).

Compound	$\vartheta_m$ (°C)	$\vartheta_{vap}$ (°C)	$\Delta_m H$ (J·g <sup>-1</sup> )	$\Delta_m S$ (J·(K·g) <sup>-1</sup> )	$\Delta_{vap} H$ (J·g <sup>-1</sup> )	$\Delta_{vap} S$ (J·(K·g) <sup>-1</sup> )
<b>2a</b>	-22	68	46.3	0.18	137.2	0.40
<b>2b</b>	-16	97	43.5	0.15	91.6	0.25
<b>2d</b>	-41	89	36.0	0.16	116.9	0.39
<b>1a</b>	85	181	52.8	0.15	178.9	0.39
<b>1b</b>	109	177	75.6	0.20	119.0	0.26
<b>1d</b>	81	182	47.9	0.14	144.0	0.32

**Table 3**

Used chemicals and solvents.

chemical	Supplier	purity
trifluoroacetamide	abcr chemicals	99%
pentafluoropropionamide	abcr chemicals	97%
sodium azide	Acros	99.5%
pyridine	Alfa Aesar	>99%
acetonitrile	VWR chemicals	>99%
trifluoroacetic anhydride	Alfa Aesar	>99%
pentafluoroacetic anhydride	abcr chemicals	99%
pentadecafluorooctanoic anhydride	abcr chemicals	97%
phosphorous pentoxide	Sigma-Aldrich	>98%
tetraglyme	Sigma-Aldrich	99%
urea	Roth	>99.5%
potassium hydroxide	Grüssing	99%
anhydrous calcium chloride	Grüssing	99%
anhydrous sodium carbonate	Fisher Scientific	>99%