# Synthesis and Characterisation of Novel Cationic Imidazolium Derivatives - on the Route to Possible Drugs

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# Synthese und Charakterisierung neuer kationischer Imidazol - Derivate auf dem Weg zu möglichen Wirkstoffen

**DISSERTATION**

der Fakultät für Chemie und Pharmazie
der Eberhard-Karls-Universität Tübingen

zur Erlangung des Grades eines Doktors
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# *Dedication*

To my

Parents, wife, brothers, sister and my lovely kid

This doctoral thesis was carried out from March 2007 to June 2009 at the Institut für Anorganische Chemie, Fakultät für Chemie und Pharmazie der Eberhard-Karls-Universität Tübingen, Germany, under the guidance of Prof. Dr. Norbert Kuhn.

I would like to express my deep and sincere gratitude to my supervisor

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**Publications:**

- Eyad Mallah, Markus Ströbele, Norbert Kuhn, Cäcilie Maichle-Mößmer, Klaus-Peter Zeller and Manfred Steimann, Nucleophilic Aromatic Substitution with 2,3-Dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, *Z. Naturforsch.* Teil B, in progress.

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- Ahmed Abu-Rayyan, Qutaiba Abu-Salem, Eyad Mallah, Cäcilia Maichle-Mößmer, Manfred Steimann, Norbert Kuhn, and Klaus-Peter Zeller, The Acetylacetonate Ion as its E/Z-Isomer in 1,3-Diisopropyl-4,5-dimethylimidazolium Acetylacetonate, *Z. Naturforsch.* **2008**, 63b, 1438-1440.

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## Glossary of Chemical Abbreviations and Units

### 1. List of Abbreviations

| | |
|---|---|
| Ad | adamantyl |
| Anal. | analysis |
| acac | acetylacetonate |
| Cat. | catalytic |
| Calc. | calculated |
| $CHCl_3$ | chloroform |
| $CH_2Cl_2$ | dichloromethane |
| DMSO | dimethylsulfoxide |
| d | doublet (NMR) |
| EI | electron impact (mass spectroscopy) |
| ESR | electron spin resonance |
| Et | ethyl |
| $Et_2O$ | diethyl ether |
| FAB | fast atom bombardment (mass spectroscopy) |
| Im | imidazole |
| i-Pr | *iso*-propyl |
| $J$ | coupling constant |
| MAS | magic angle spinning (solid-state NMR) |
| m | mutiplet (NMR) |
| Me | methyl |
| MeCN | acetonitrile |
| MeOH | methanol |
| Mes | mesityl |
| m.p. | melting point |
| m/z | mass/charge ratio |
| MS | mass spectroscopy |
| neg. | negative |
| NMR | nuclear magnetic resonance |
| Ph | phenyl |
| pos. | positive |

| | |
|---|---|
| Py | pyridine |
| q | quartet (NMR) |
| RT | room temperature |
| s | singlet (NMR) |
| $S_NAr$ | nucleophilic aromatic substitution reaction |
| sept | septet (NMR) |
| Sulfone | bis-methanesulfonyl-methane |
| $^t$Bu | *tert*-butyl |
| THF | tetrahydrofuran |
| TMS | tetramethylsilane |
| triaz. | triazine |
| t | triplet (NMR) |
| $\delta$ | chemical shift |
| $\theta$ | angle |
| $\lambda$ | wave length |

## 2. List of Units

| | |
|---|---|
| Å | angstrom (1Å = $10^{-10}$m) |
| ° | degree |
| eV | electron volt (1 eV = $1.602.10^{-19}$J) |
| g | grams |
| h | hour |
| Hz | hertz |
| L | liter |
| min | minute |
| mg | milligram |
| mL | milliliter |
| mmol | millimol |
| ppm | parts per million |

# Introduction 1

# 1. Introduction

## 1.1 Pharmaceutical applications of fluoroaromatic compounds and imidazolium salts

### 1.1.1 Fluoroaromatic compounds

Fluorinated compounds are the least abundant natural organohalides, until 1957, no F-containing drug had been developed. Since then, over 150 fluorinated drugs have come to market and now make up about 20% of all pharmaceuticals. Top-selling fluorinated pharmaceuticals include the antidepressant fluoxetine, the antibacterial ciprofloxacin,[1] and fluorine containing compounds have contributed to major developments in nonsteroidal anti-inflammatory drugs; the increased lipid solubility of fluorinated molecules has played a major role in development of new and important central nervous system agents. [2]

Fluoroaromatics have a diverse role in biomedical applications; for example, 1-fluoro-2,4-dinitrobenzene (Sanger's Reagent) is used as a reagent for labeling peptides and terminal amino acid groups in proteins. [3]

### 1.1.2 Imidazolium salts

Poor water solubility of drug candidates is a major problem in the pharmaceutical industry, and it has been estimated that 40% of all newly developed drugs are poorly soluble or insoluble in water.[4]

Room temperature ionic liquids are organic salts which are liquids at ambient temperature; they are composed of ions comprising a relatively large asymmetric organic cation (e.g. dialkyl imidazolium ions) and an inorganic or organic anion (e.g. halide, hexafluorophosphate, tetrafluoroborate and ions based on fluorinated amides). The solvency of some alky imidazolium salts ($PF_6$, Br and Cl) for poorly water-soluble model drugs, albendazole and danzol, indicating their potential application as pharmaceutical solvents. The solubility of albendazole, for example, was increased by more than 10,000 times by 1-butyl-3-methylimidazolium hexafluorophosphate.[4]

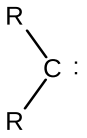
Imidazolium salts are also known as precursors for stable carbenes with many applications in organic synthesis.[5] This work will shed more light for N-heterocyclic carbenes reactions to obtain new imidazolium salts.

## 1.2 Carbenes

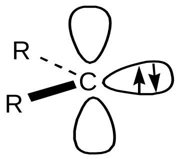
### 1.2.1 Definition

Carbenes are neutral compounds with a divalent carbon atom,[6,7] where the carbene carbon atom is linked to two adjacent groups by covalent bonds, and possesses two nonbonding electrons (A),[8] these electrons may have anitparallel spins, singlet state (B), or parallel spins, triplet state (C).[9,10]

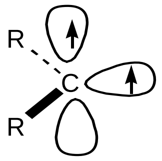
The spin multiplicity of a carbene can be assigned by spectroscopic techniques under extreme conditions. Molecular spectroscopy has been used to identify singlet or triplet carbenes generated by flash photolysis of dilute gaseous systems, and to determine the structures of these species.[11] Electron spin resonance (ESR) spectroscopy is a powerful tool for studying carbenes with triplet ground states at low temperatures in inert matrices.[12] Carbenes have played an important role in organic chemistry ever since the first firm evidence of their existence and have enjoyed a long history in the field of chemical sciences that started almost a 150 years ago.



**A**

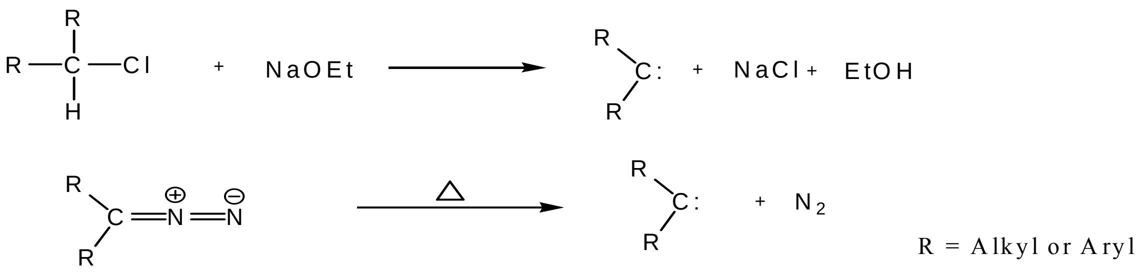


**B**



**C**

The existence of carbenes as reactive intermediates was established much later in the 1950s and the 1960s. They were usually synthesized by either the reaction of alkyl halides with a base or by the thermal decomposition of diazonium salts,[13] as shown in scheme 1. Since then, carbenes have become well-established reactive intermediates and their high reactivity make them versatile species for preparative, mechanistic and theoretical studies.[14]



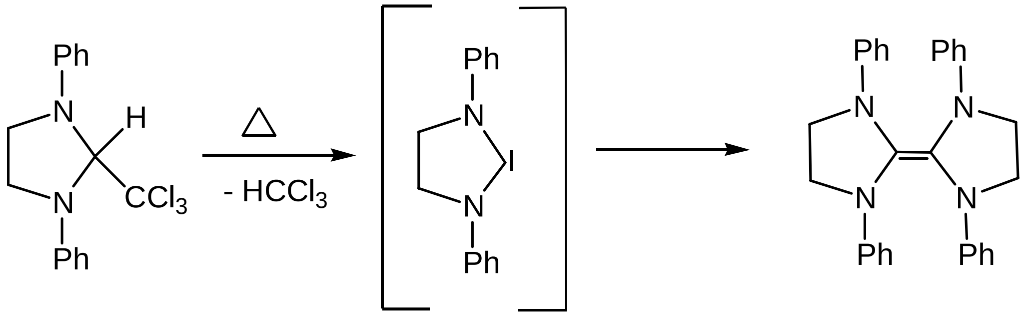
**Scheme 1. In-situ synthesis of carbenes**

The organometallic chemistry of carbenes was initiated with the synthesis of stable carbene complexes by Fischer in 1964,[15] and by Schrock in 1970,[16] it was not until 1968 that the first homonuclear carbene complex was reported, and isolation of a carbene containing the parent methylene group was not achieved until 1975.[17]

## 1.2.2 Diaminocarbenes

### 1.2.2.1 Synthesis of diaminocarbenes

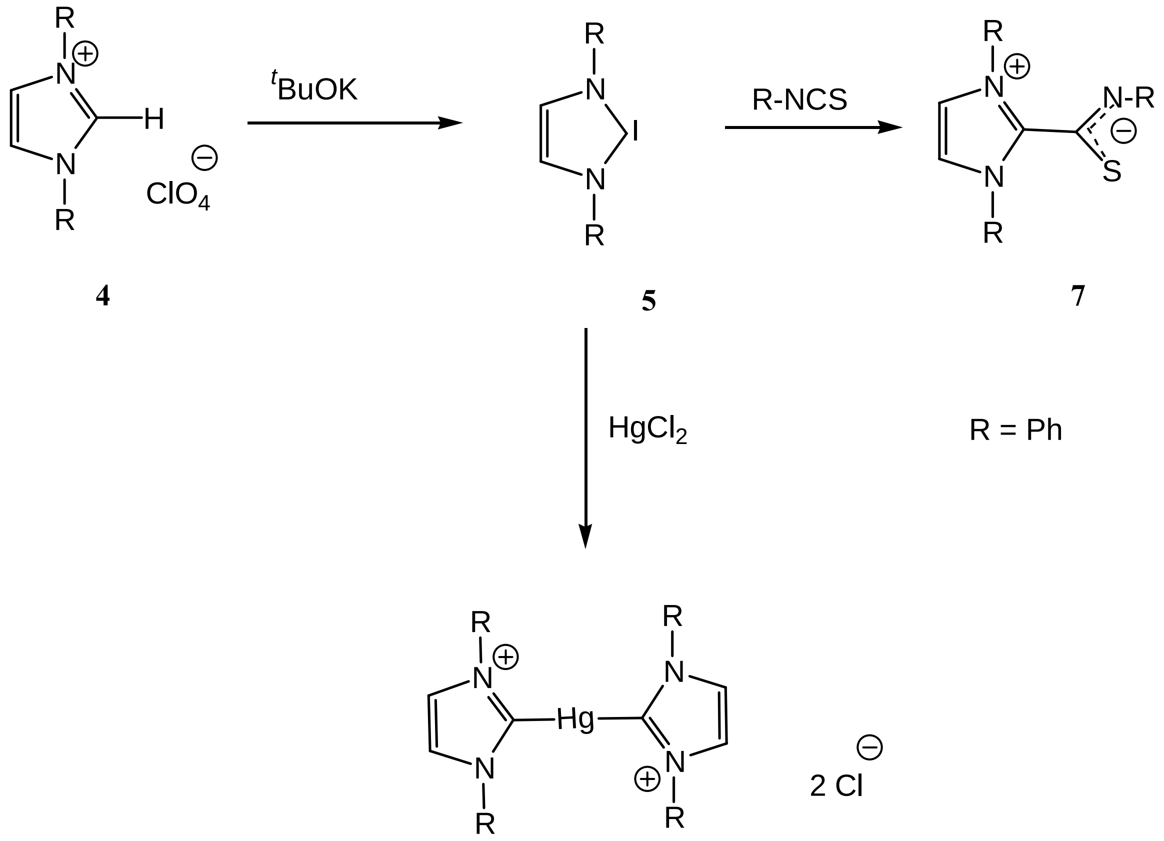
In the early 1960s, Wanzlick realized that the stability of carbenes could be dramatically enhanced by the presence of amino substituents and tried to prepare the 1,3-diphenylimidazolidin-2-ylidene **2** from **1** by thermal elimination of chloroform (scheme 2).[18] At that time, only the dimeric electron-rich olefin **3** was isolated and cross-coupling experiments did not support equilibrium between **3** and the two carbene units **2**.[19]



**1** **2** **3**

**Scheme 2. preparation of the 1,3-diphenylimidazolidin-2-ylidene by Wanzlick**

In 1970, Wanzlick and co-workers demonstrated that imidazolium salts **4** could be deprotonated by potassium *tert*butoxide to afford the corresponding imidazol-2-ylidenes **5**,[20] which were not isolated but trapped with reagents such as mercury to give **6** and isothiocyanate to give **7** (scheme 3) .[21]

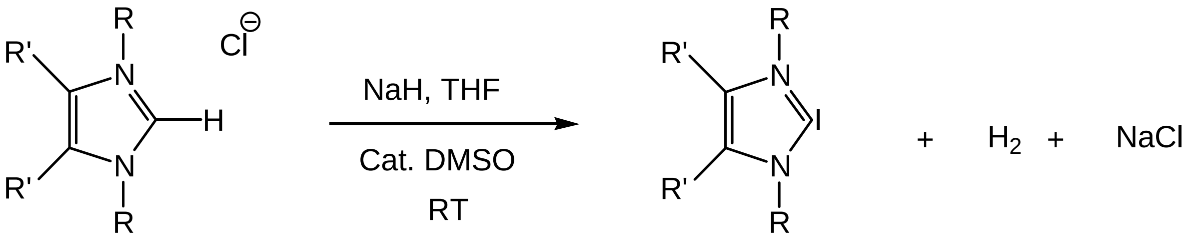


**4** **5** **7**

**6**

**Scheme 3. Preparation and trapping of an imidazole-2-Ylidene by Wanzlick**

Following this principle, after nearly 30 years Arduengo *et al.* revisited this area, and remarkably managed not only to isolate a stable carbene but also to acquire an X-ray structure of it, this carbene was found to be indefinitely stable at room temperature (in the absence of oxygen and moisture), and melted at 240-241 °C without decomposition.[22] Arduengo *et al.* found that simple deprotonation of an imidazolium chloride **8** with a strong base gave the carbene **9** (scheme 4).[23,24,25]

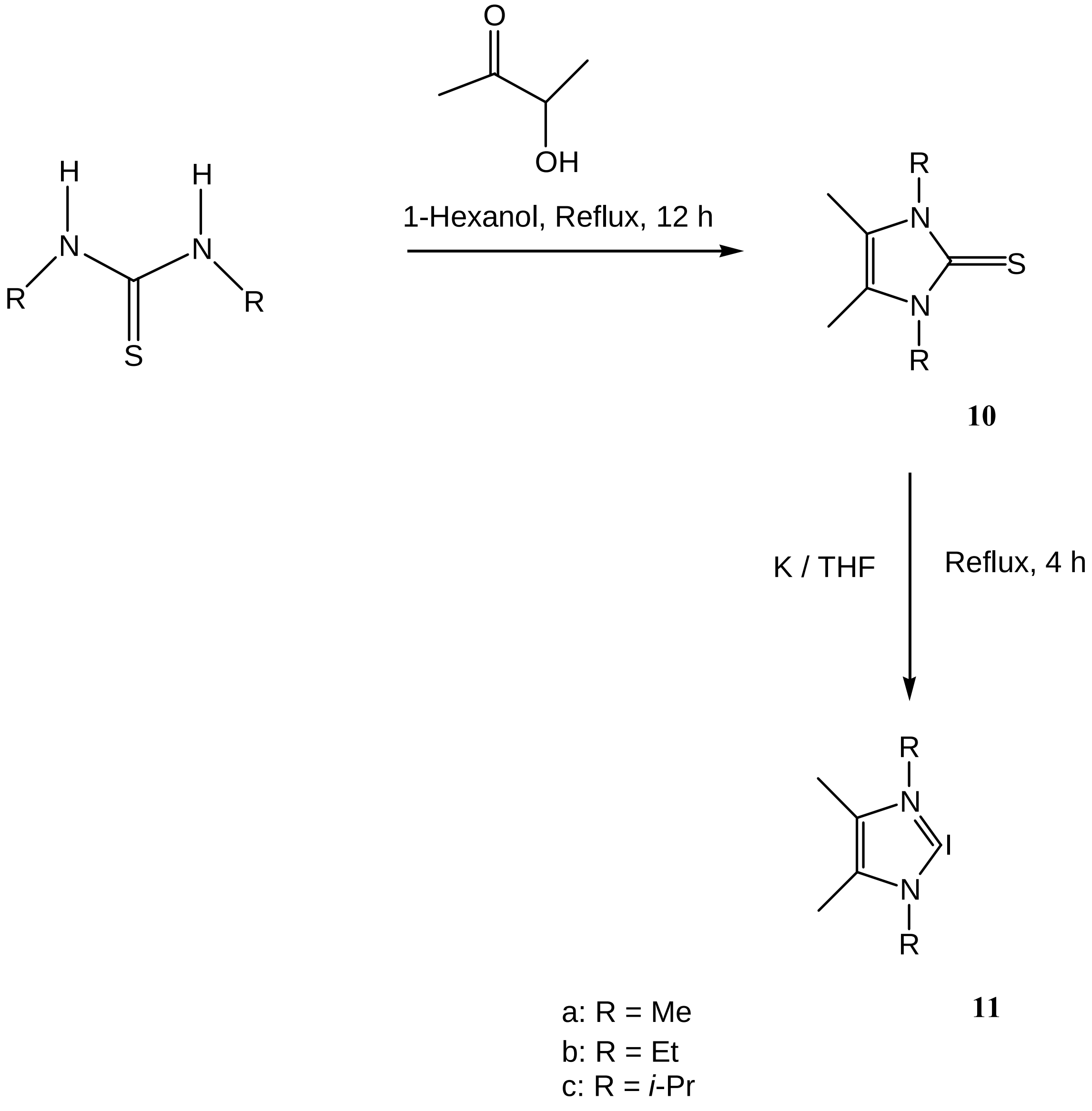


**8** **9**

R = Ad, R' = H

**Scheme 4. preparation of a stable crystalline carbene by Arduengo**.

In 1993, Kuhn *et al.* reported a versatile two-step approach to thermally stable, alkyl-substituted N-heterocyclic carbenes.[26] The imidazol-2-ylidenes **11** are obtained in almost quantitative yield from the reaction of **10** with stoichiometric amounts of potassium in boiling THF. The compounds may be isolated in an analytically pure state after evaporation of the solvent from the filtered solution and no further purification is necessary (scheme 5).[26]



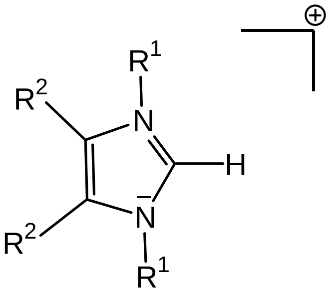
**Scheme 5. Desulfurisation of an imidazole-2-thione by Kuhn.**

### 1.2.2.2 Reactions of diaminocarbenes

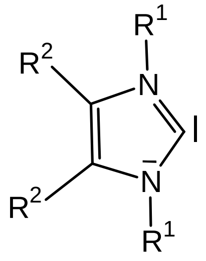
#### 1.2.2.2.1 Reactions with hydrogen compounds

As result of the strongly basic character of heterocyclic carbenes **13**,[27,28,29] they react with *Broenstedt* acids and have consequently been used as selective deprotonation reagents. The 2H-imidazolium salts **12**[30] formed by this method are accessible by other routes, alkylation of 2H-imidazoles,[31] cyclization reactions or from the thiones and nitric acid, [32] and may be used as precursors in the synthesis of **13** through deprotonation. The reaction of **13** with deuterated solvents starting with the deuteration at $C_2$ has been discussed.[33] In the solid state, a couple of salts containing ion pairs linked by hydrogen bonds **14** have been characterized by structural analysis (e.g. X = $HF_2$,[34] Cl,[35,36,37] Br,[38,39] I,[40,41,42] $ClO_4$,[43] 1/2 $SO_4$,[44] $NO_3$, [44] $PF_6$,[45,46] $BF_4$,[47,48], $AgCN_2$[49]).

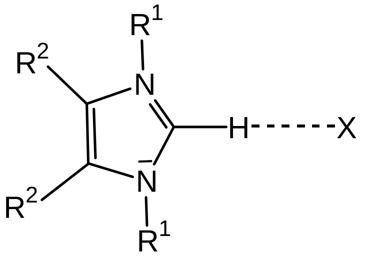
The nature of the hydrogen bonds apparently depends on the properties of the counterions, and appears to be weaker with hard and less basic counterions. With stable imidazolium ions and corresponding alcohol and amines, the stable adducts **15** (R1=Mes, R2=H),[50] **16** (R1=Mes, R2=H) and **17** (R1=Mes, R2=H) are formed.[51]



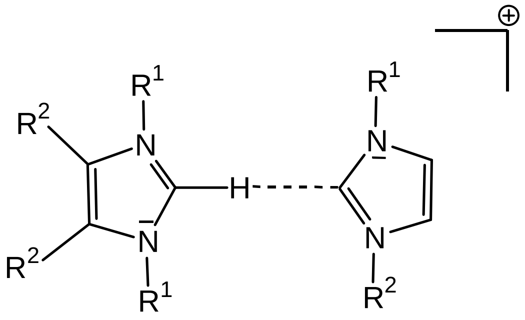
**12**



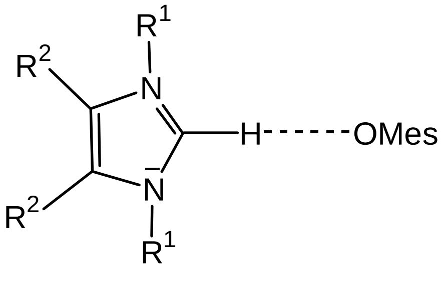
**13**



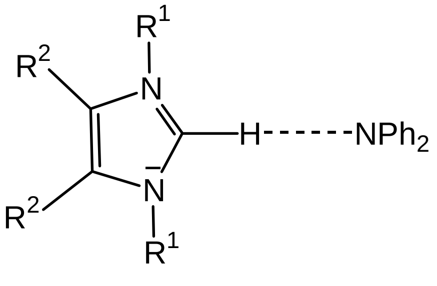
**14**



**15**



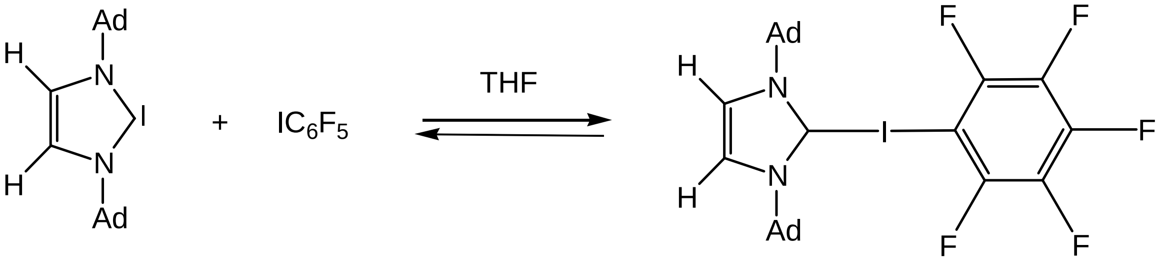
**16**



**17**

#### 1.2.2.2.2 Reactions with fluorine compounds

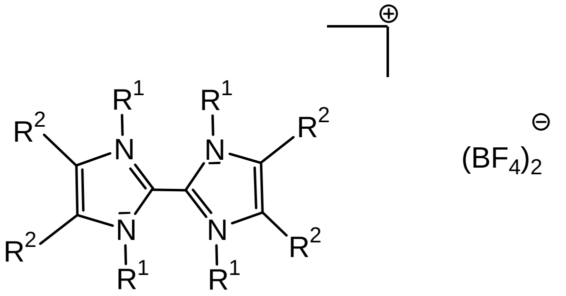
The recent availability of polyfluoroaromatic compounds has initiated much research on this interesting class of compounds. Nucleophilic aromatic substitutions ($S_NAr$) of haloarenes with amines are generally difficult to achieve and are limited to fluorides having a strongly electron-withdrawing group, such as a nitro group at the *para* position.[52,53] Nucleophilic aromatic substitution reactions with imidazole of haloarenes having strongly electron-withdrawing groups were studied under ultrasonic and microwave irradiations. The course of the $S_NAr$ reactions was found to be strongly dependent on the electron-withdrawing properties of the substituents as well as on the leaving ability of the halogen atom. Although some pentafluorobenzene was obtained as the solution of the ylide aged, that product was not displacement by a carbene carbon moiety.[52] Arduengo et al. reported that a stable diaminocarbenes reacts with iodopentafluorobenzene to afford an ylide **18**, by attack of the carbene at iodide (scheme 6).[54]



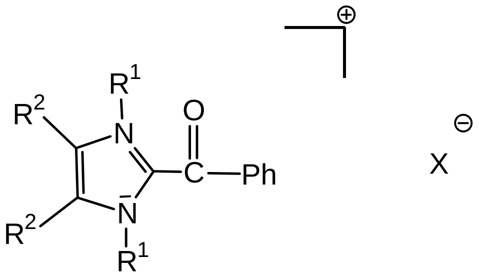
**18**

**Scheme 6. Arduengo stable diaminocarbenes reacts with iodopentafluorobenzene**

Numerous imidazolium compounds are known in which substituents are linked to the 2-position through C-C bonds. With 2-fluoro-1,3-diisopropyl-4,5-dimethylimidazolium tetrafluoroborate, **13** gives the dicationic salt **19** (R1=*i*-Pr, R2=Me) [55] after addition of $BF_3.Et_2O$. Acylation of **13** occurs with PhC(O)F to give the fluoride salt **20** (R1=*i*-Pr, R2=Me), which gives the corresponding complex salt on addition of $BF_3$, $PhSiF_3$ and $PhSnF_3$.[56]

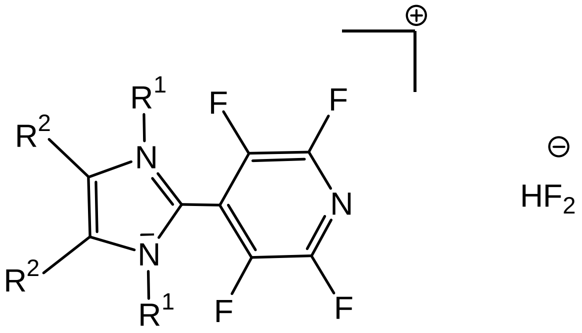


**19**

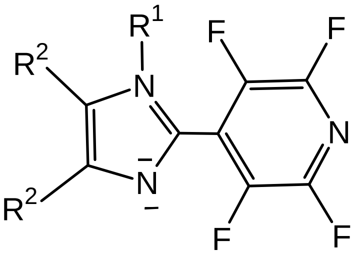


**20**

Nucleophilic aromatic substitution of fluorine substituents has also been reported elsewhere. With pentafluoropyridine, **13** reacts to give the $HF_2$ salts **21** (R1=Me, *i*-Pr, R2=Me) from which the imidazol **22** is obtained through thermolysis.[57]



**21**



**22**

## 1.3 Aim of Study

The object of this work is to clarify nucleophilic properties of diaminocarbenes; the nucleophilicity of diaminocarbenes is presumably a consequence of delocalization in the carbene itself and, probably to a great extent, of the conjugative delocalization in the transition state for attack by the carbene on an electrophilic substrate.[58]

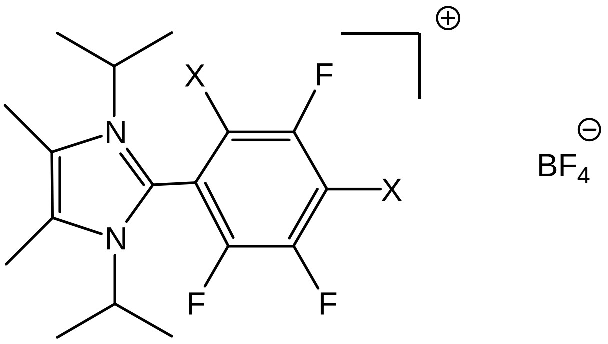
The carbon-fluorine bond is commonly found in pharmaceuticals, fluorine-containing aromatics have been incorporated into drugs (analgesic, antibacterial). Recently, nucleophilic aromatic substitution of haloarenes with different nucleophilic center became very important. We are interested to obtain more information on the scope of such reactions, we have now investigated that 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** attack polyfluoroaromatic compounds in which fluoride displaced by the carbene carbon to afford different types of imidazolium adducts **23**.

It has been reported that protonation of nonstabilized phosphorus ylides with organic acids such as phenols provide a facile route to hydrogen-bonded organic phosphonium salts.[59] Given the considerable recent interest in the structure and chemistry of stable N-heterocyclic carbenes, and their similar basicity to that of nonstabilized ylides, we felt it would be interesting to employ a similar route for the synthesis of hydrogen-bonded imidazolium aryl oxide salts **24**.

The possibility of 2H-imidazolium ions to form stable C-H…X bonds [60,61] have been reported recently, suggesting that C-H…X hydrogen bonds may act as an additional stabilizing factor in their crystal structures. So our current research efforts also continue to focus on design and synthesis of new structures of imidazolium salts **25** containing ion pairs linked by C-H…X (X = O, S, N) hydrogen bonds.

The new derivatives can be classified into:

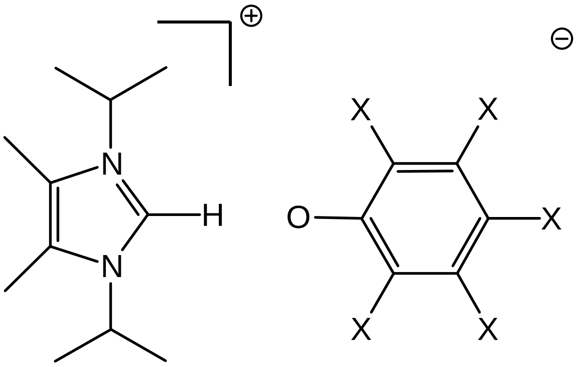
### 1.3.1 Nucleophilic aromatic substitution with 2,3-dihydroimidazole-2- ylidenes.



X = F, CN

**23**

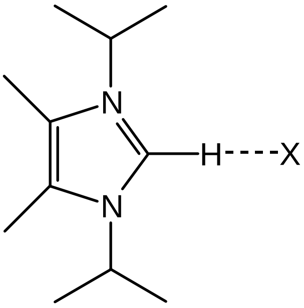
### 1.3.2 Imidazolium aryl oxide adducts of the types of 2,3-dihydroimidazole-2-ylidenes.



X = H, Cl, F

**24**

### 1.3.3 Salt derivatives of 2,3-dihydroimidazole-2-ylidenes.



**25**

# Results & 2

# Discussion

# 2. Results and Discussion

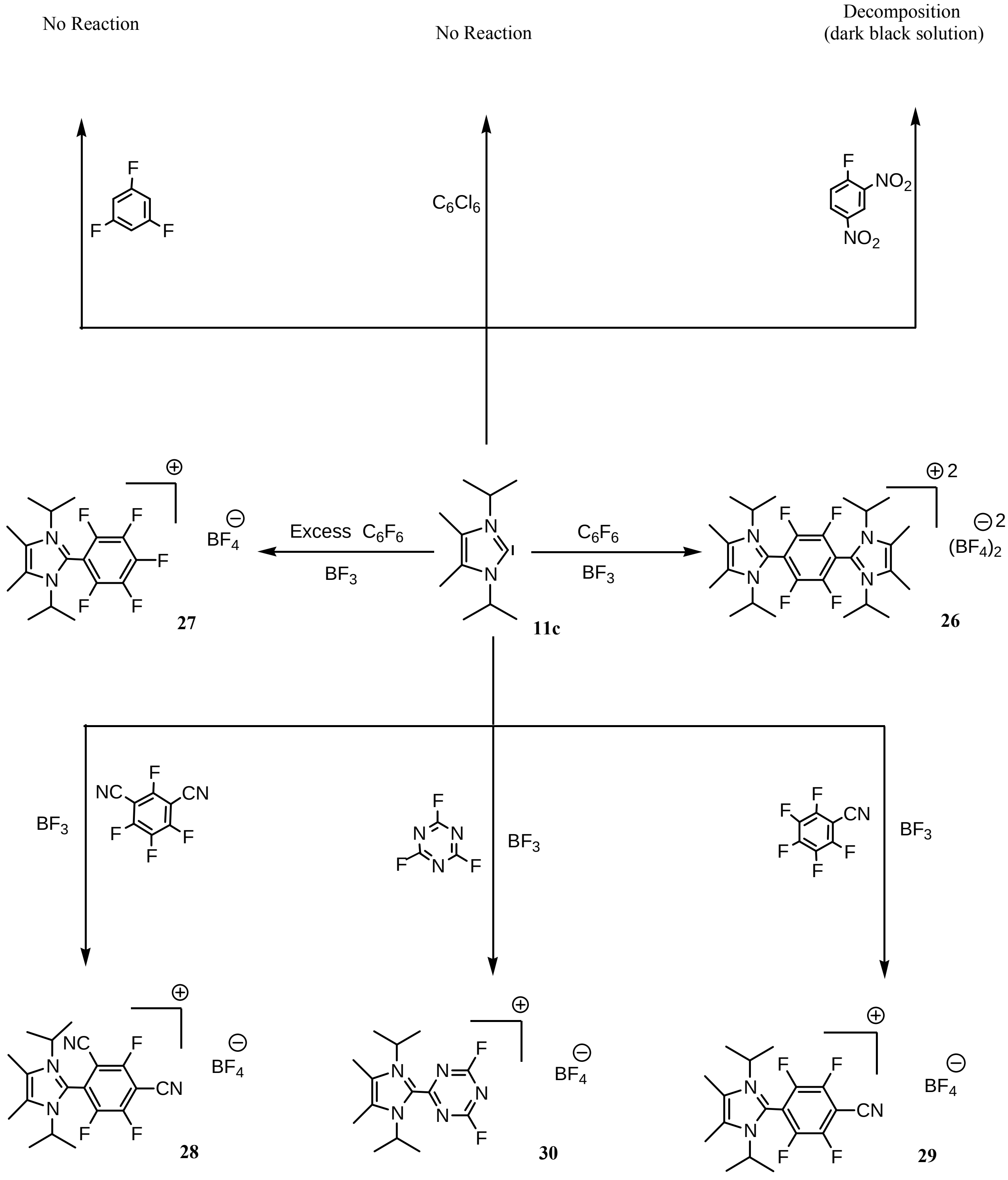
## 2.1 Nucleophilic aromatic substitution ($S_NAr$) with 2,3-dihydroimidazole-2- ylidenes

Owing to the basic and nucleophilic character of heterocyclic carbenes, 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene **11c** reacted with different kinds of polyfluoroaromatic compounds to give interesting results. $S_NAr$ reactions occur via an addition-elimination mechanism, it is most likely that the addition of a nucleophile is a rate determining step, the most remarkable feature in $S_NAr$ that fluorine is the best leaving group.[62] Inductive effect of fluorine atoms decreases the electron density at the carbon to which they are attached to facilitate nucleophilic aromatic substitution.[63]

Reaction of hexafluorobenzene with **11c** depends on the reaction conditions and stoichiometry; **11c** reacted with hexafluorobenzene in 2:1 molar ratio to give the disubstituted salt **26** in very good yield, also 1:1 molar ratio gave the same result but with low yield, while adding a drop-wise of **11c** solution to an excess amount of hexafluorobenzene gave the mono substituted salt **27**, after standing NMR tube of **27** for one week at RT, the $^{19}F$ NMR spectra showed new signal due to the presence of disubstituted salt. Since the inductive effect of fluorine is much stronger than that of chlorine,[63] the reaction of hexachlorobenzene with **11c** has not been occurred. This result follows that the fluoro compounds underwent $S_NAr$ reactions much easier than their chloro analogues.[53] Activation of the chloro groups by electron-withdrawing groups on the ring is necessary for the substitution to occur.[64] In addition, cyanuric trifluoride is much more susceptible to nucleophilic attack than is hexafluorobenzene,[65] it was reacted immediately with **11c** to give the stable salt **30** in very good yield.

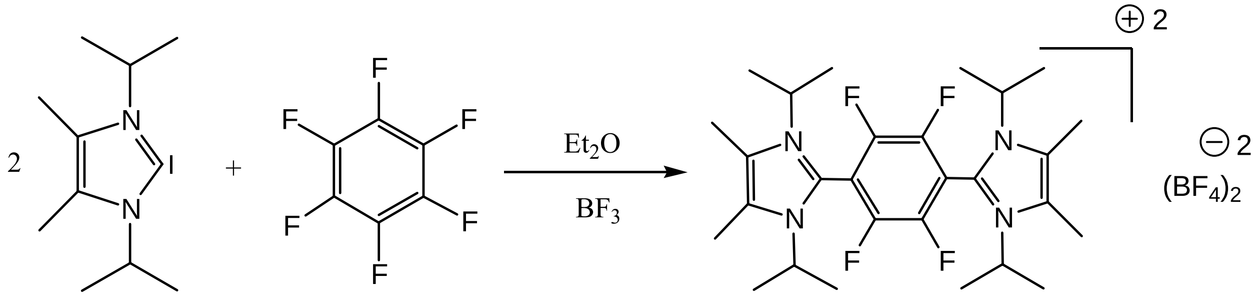
Furthermore, this work exploring polyfluoroaromatic compounds substituted by electron-withdrawing groups which enable $S_NAr$ to proceed smoothly; **11c** was reacted with tetrafluoroisophthalonitrile and Pentafluorobenzonitrile to give salts **28** and **29** respectively, in high yield. However, aromatic compounds substituted by $NO_2$ as an electron-withdrawing group at positions ortho and para to a leaving group undergo nucleophilic substitution smoothly,[66] but in our case the decomposition has been occurred immediately after the reaction of **11c** with 1-fluoro-2,4-dinitrobenzene (Sanger's reagent), this observation might be attributed to the presence of very strong withdrawing groups ($NO_2$) which offer a very fast and uncontrolled reaction and it might be reacted with **11c** even at very low temperature.

All of the above mentioned reactions were carried out in dry diethyl ether at -70 $^{o}$C and gave stable salts in very good yields, these reactions are outlined in scheme 7 and the results confirmed by NMR, mass spectroscopy, elemental analysis and single crystal X-ray diffraction.



**Scheme 7. Nucleophilic aromatic substitution reactions of 2,3-dihydroimidazole-2- ylidenes**

### **2.1.1** 1,3-Diisopropyl-4,5-dimethyl-2,2-(pentafluorophenylimidazolium) tetrafluoroborate (**26**)



**11c** **26**

The X-ray crystal structure of **26** is depicted in figure 1. Single crystals were grown from diethyl ether vapor diffuse into an acetonitrile solution at RT. The crystal crystallizes in the monoclinic space group $p2_1$/c. Selected bond lengths and angles are summarized in table 1. The structure exhibits the imidazolium ion are coordinated at the para position of the benzene ring and forming a C-C bond, where the $C_1$-$C_4$ bond distance [1.476 Å] is similar to that found in 1,3-diisopropyl-4,5-dimethyl-2-tetrafluoropyridylimidazolium chloride [1.489 Å].[57,67] We observed that all of C-F bond distances are equivalent [1.335 Å] , The dihedral angle between $N_1$ $N_2$ $C_4$ $C_5$ $C_6$ / $C_1$ $C_2$ $C_3$ is 111.9°.

The structure of **26** has also been confirmed obviously from the $^{19}$F NMR spectrum, two distinct fluorine signals were detected, one of them was assigned to the tetrafluoroborate anion and the second is for the symmetrical fluorine atoms at the phenyl ring.

**Table 1. Selected bond lengths (Å) and angles (deg) for $C_{32}H_{46}B_2F_{12}N_6$ (26).**

| | |
|---|---|
| C(1)-C(2) | 1.380(2) |
| C(1)-C(3) | 1.389(3) |
| C(1)-C(4) | 1.476(2) |
| C(2)-F(1) | 1.335(2) |
| C(4)-N(2) | 1.335(2) |
| C(4)-N(1) | 1.340(2) |
| B(1)-F(5) | 1.338(4) |
| C(15)-C(16) | 1.414(5) |
| C(16)-N(3) | 1.132(4) |
| | |
| C(2)-C(1)-C(3) | 115.86(16) |
| C(2)-C(1)-C(4) | 121.71(15) |
| C(3)-C(1)-C(4) | 122.43(15) |
| C(2)#1-C(3)-C(1) | 122.02(16) |
| N(2)-C(4)-N(1) | 108.79(15) |
| N(2)-C(4)-C(1) | 126.17(16) |
| N(1)-C(4)-C(1) | 125.03(15) |
| C(4)-N(1)-C(5) | 108.41(15) |
| F(6)-B(1)-F(5) | 106.5(3) |
| F(6)-B(1)-F(4) | 111.0(2) |
| N(3)-C(16)-C(15) | 178.4(4) |

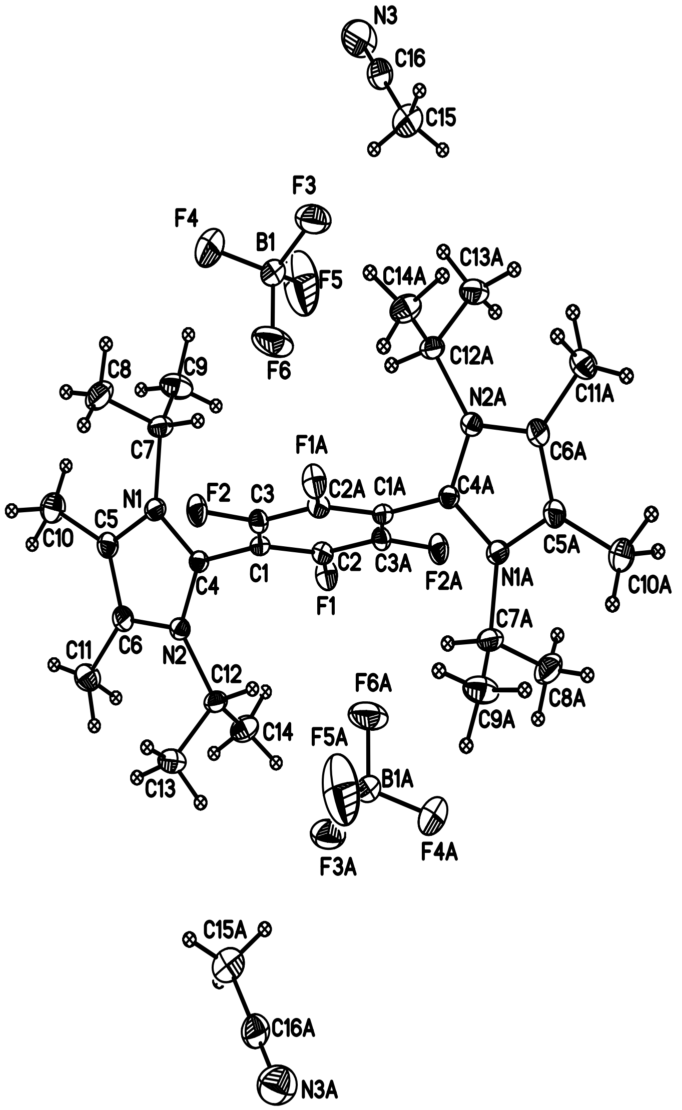
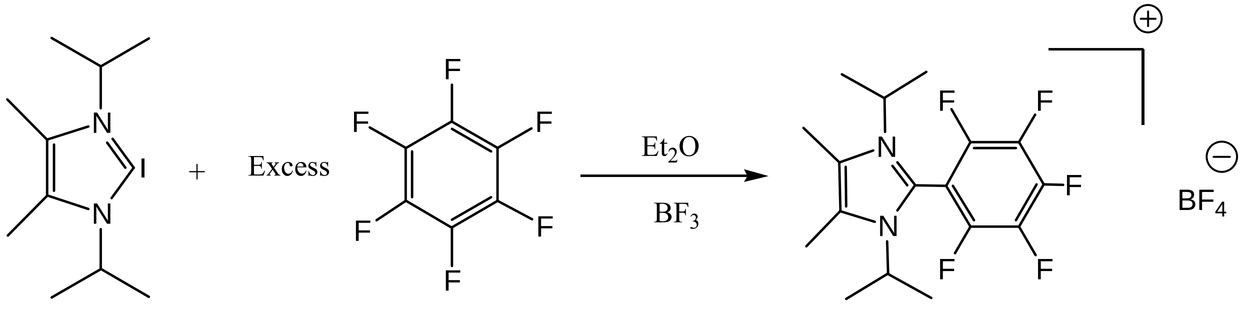


**Figure 1. The crystal structure of $C_{32}H_{46}B_2F_{12}N_6$ (26)**

### **2.1.2** 1,3-Diisopropyl-4,5-dimethyl-2-pentafluorophenylimidazolium tetrafluoroborate **(27)**



**11c** **27**

Single crystals of **27** that were suitable for X-ray crystal structure analysis were obtained by allowing diethyl ether vapor diffuse into an acetonitrile solution at RT. Its X-ray crystal structure is depicted in figure 2. The crystal crystallizes in the monoclinic space group $p2_1/n$. Selected bond lengths and angles are summarized in table 2. The imidazolium ion is coordinated to the benzene ring and forming a C-C bond, where the $C_1$-$C_7$ bond distance [1.473 Å] is similar to that found in **26** and in 1,3-diisopropyl-4,5-dimethyl-2-tetrafluoropyridylimidazolium chloride [1.489 Å].[57,67] We observed that all of C-F bond distances are equivalent [1.332 Å] and similar to those found in **26** , The dihedral angle between $C_7$ $C_8$ $C_9$ $N_1N_2$ / $C_1$ $C_2$ $C_3$ $C_4$ $C_5$ $C_6$ is 63.2°. After standing NMR tube of **27** for one week at RT, the $^{19}F$ NMR spectra showed new signal due to the presence of disubstituted salt.

**Table 2. Selected bond lengths (Å) and angles (deg) for $C_{17}H_{20}BF_9N_2$ (27).**

| | |
|---|---|
| C(1)-C(6) | 1.387(3) |
| C(1)-C(2) | 1.396(3) |
| C(1)-C(7) | 1.473(2) |
| C(2)-F(1) | 1.335(2) |
| C(7)-N(1) | 1.340(2) |
| C(7)-N(2) | 1.348(2) |
| B(1)-F(7) | 1.361(3) |
| | |
| C(6)-C(1)-C(2) | 117.5(2) |
| C(6)-C(1)-C(7) | 122.0(2) |
| C(2)-C(1)-C(7) | 120.5(2) |
| F(5)-C(6)-C(1) | 119.7(2) |
| N(1)-C(7)-N(2) | 108.9(2) |
| N(1)-C(7)-C(1) | 126.1(2) |
| N(2)-C(7)-C(1) | 124.9(2) |
| C(7)-N(1)-C(8) | 108.3(2) |
| C(7)-N(1)-C(10) | 123.8(2) |
| C(8)-N(1)-C(10) | 127.9(2) |
| C(9)-C(8)-N(1) | 107.2(2) |
| N(1)-C(8)-C(13) | 124.9(2) |
| C(8)-C(9)-N(2) | 107.5(2) |
| N(2)-C(9)-C(14) | 124.7(2) |
| C(7)-N(2)-C(9) | 108.1(2) |
| F(8)-B(1)-F(7) | 110.0(2) |
| F(8)-B(1)-F(6) | 114.5(2) |

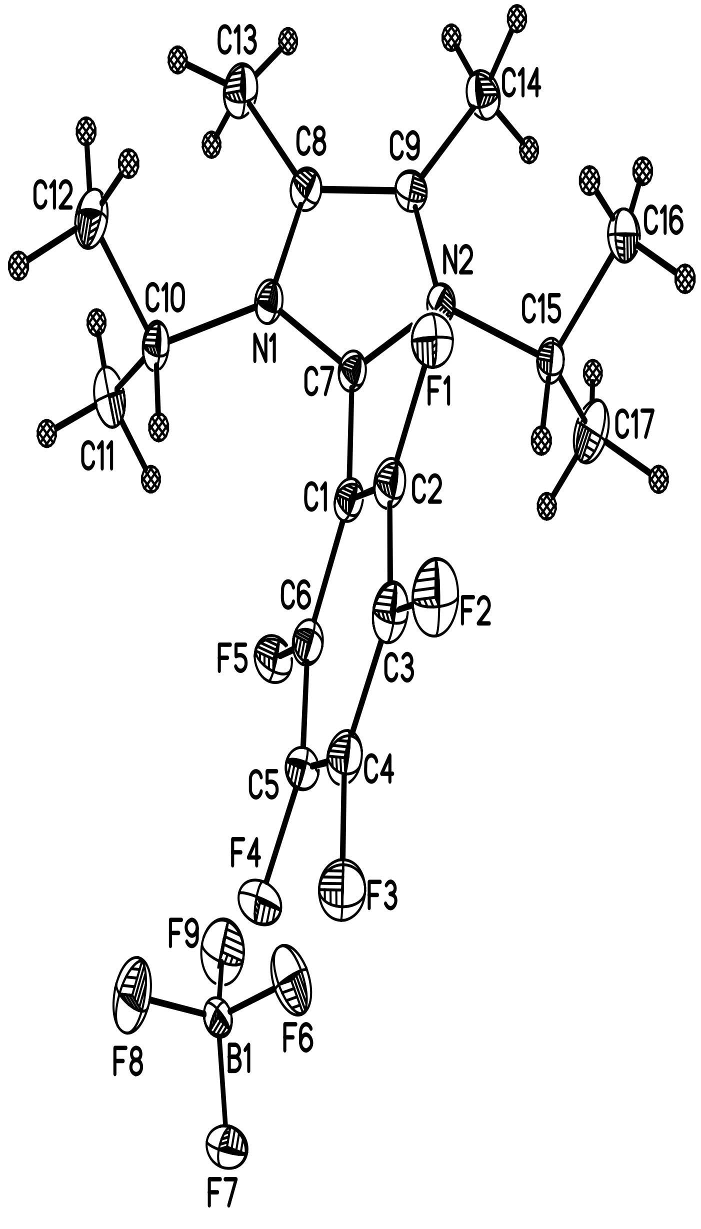
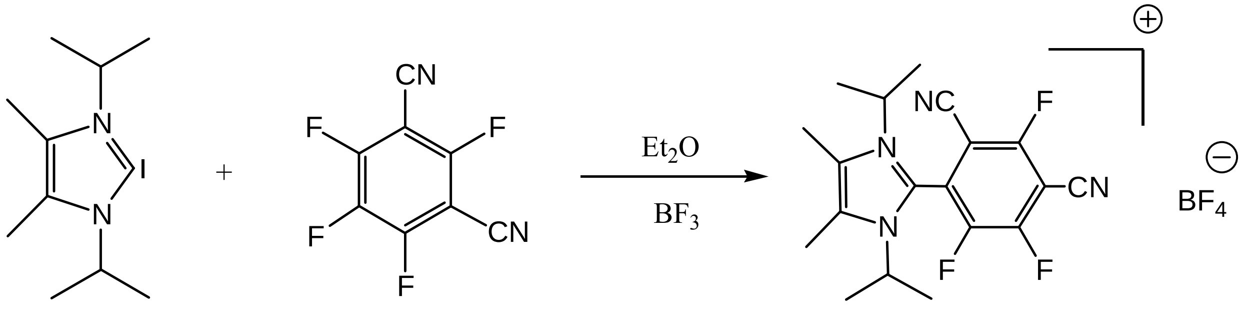


**Figure 2. The crystal structure of $C_{17}H_{20}BF_9N_2$ (27).**

### **2.1.3** 4-(1,3-Diisopropyl-4,5-dimethylimidazolium)-2,5,6-trifluoro-isophthalonitrile tetrafluoroborate **(28)**



**11c** **28**

The X-ray structure for **28** is depicted in figure 3; single crystals of **28** were obtained by allowing diethyl ether vapor diffuse into an acetonitrile solution at RT, only the picture of **28** is present because structure refinement gave high R values. As expected the $C_2$-imidazolium ion is coordinated to the tetrafluoroisophthalonitrile at the para position of the one of electron withdrawing groups (CN) and forming a C-C bond, this observation has also been assigned by $^{13}C$ and $^{19}F$ NMR spectroscopy, where in the fluorine spectrum four distinct signals were detected for **28**, one of them was assigned to the tetrafluoroborate anion, the molecular weight of the product has been confirmed by mass spectroscopy and the analytical data (C, H, and N) are consistent with the expected formulation of the salt. The spectroscopic data of **28** are given in the experimental section.

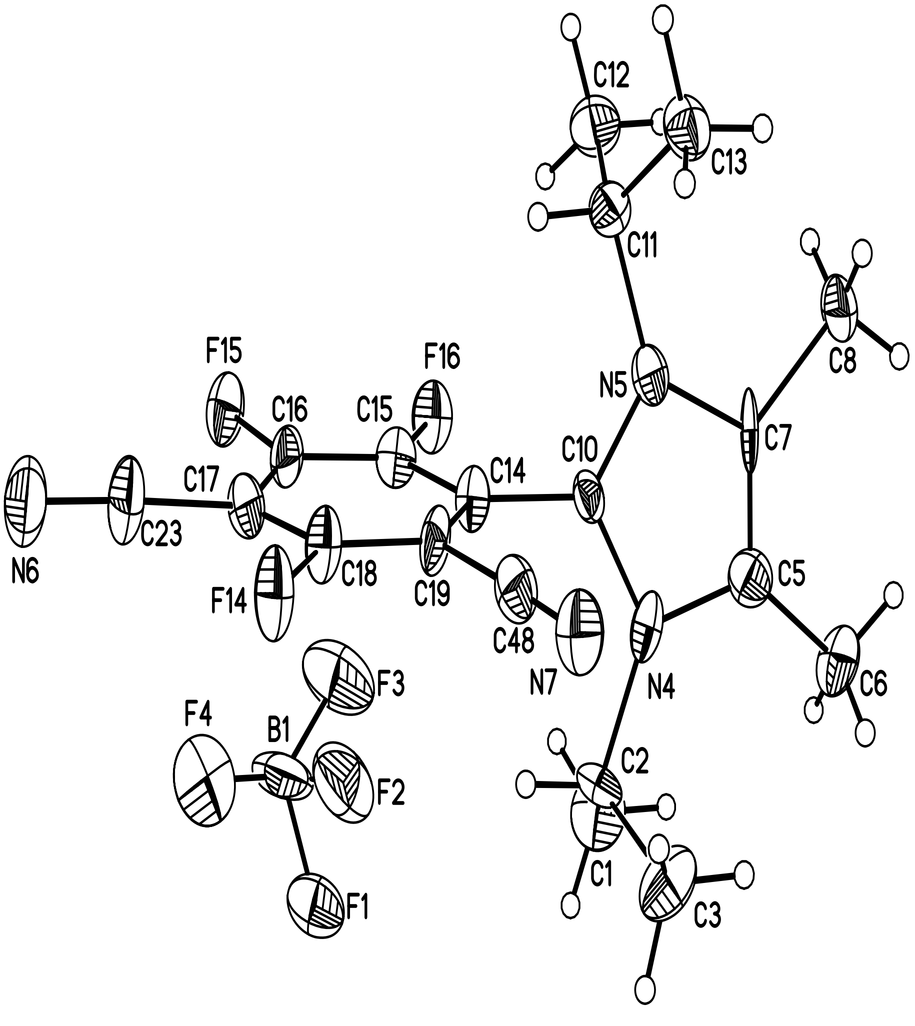
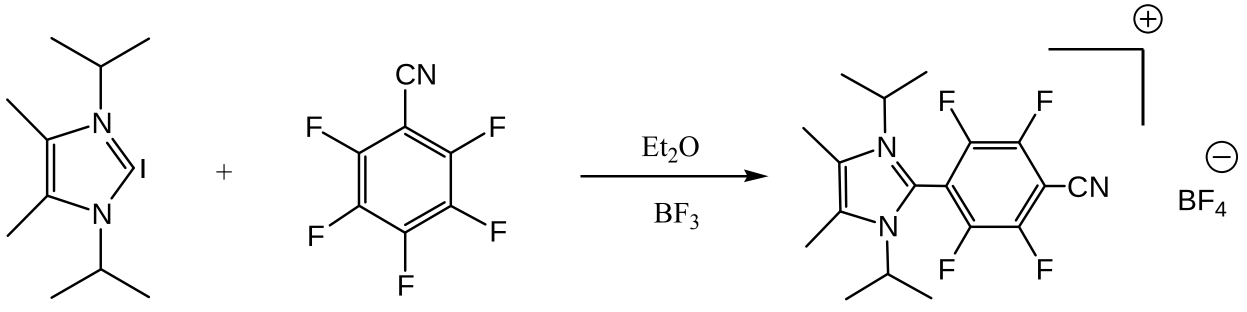


**Figure 3. The crystal structure of $C_{19}H_{20}BF_7N_4$ (28).**

### **2.1.4** 4-(1,3-Diisopropyl-4,5-dimethylimidazolium)- 2,3,5,6-tetrafluoro-benzonitrile tetrafluoroborate **(29)**



**11c** **29**

Single crystals of **29** that were suitable for X-ray crystal structure analysis were obtained by allowing diethyl ether vapor diffuse into an acetonitrile solution at RT. Its X-ray crystal structure is depicted in figure 4. The crystal crystallizes in the orthorhombic space group $p2_12_12_1$. The imidazolium ion is coordinated to the benzene ring and forming a C-C bond, where the $C_1$-$C_{11}$ bond distance [1.476 Å] is similar to that found in **26** and **27**. We observed that all of C-F bond distances are equivalent [1.343 Å] and also similar to those found in **26** and **27**. As expected the $C_2$-imidazolium ion is coordinated to the pentafluorobenzonitrile at the para position of the electron withdrawing group (CN), this observation has also been assigned by $^{13}C$ and $^{19}F$ NMR spectroscopy, where in the fluorine spectrum three distinct signals were detected for **29**, one of them was assigned to the tetrafluoroborate anion.

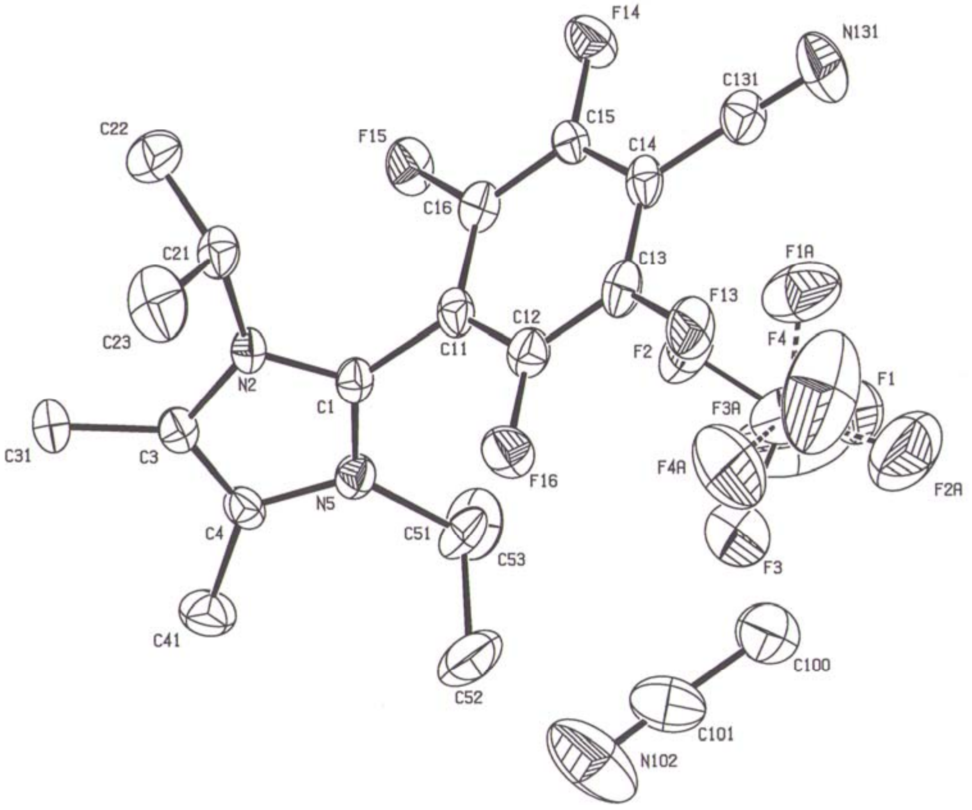
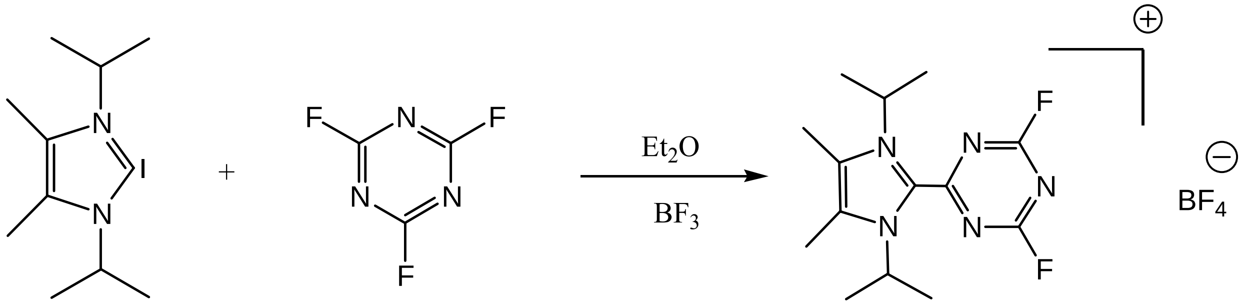


**Figure 4. The crystal structure of $C_{18}H_{20}BF_8N_3$ (29).**

### **2.1.5** 2-(1,3-Diisopropyl-4,5-dimethylimidazolium)-4, 6-difluoro-[1, 3, 5] triazine tetrafluoroborate **(30)**



**11c** **30**

The X-ray structure for **30** is depicted in figure 5; single crystals of **30** were obtained by allowing diethyl ether vapor diffuse into an acetonitrile solution at RT, only the picture of **30** is present because structure refinement gave high R values. As expected the $C_2$-imidazolium ion is coordinated to the cyanuric fluoride through C-C bond, this observation has also been assigned by $^{13}C$ and $^{19}F$ NMR spectroscopy, where in the fluorine spectrum two distinct signals were detected for **30**, one of them was assigned to the tetrafluoroborate anion, the molecular weight of the product has been confirmed by mass spectroscopy and the analytical data (C, H, and N) are consistent with the expected formulation of the salt. The spectroscopic data of **30** are given in the experimental section.

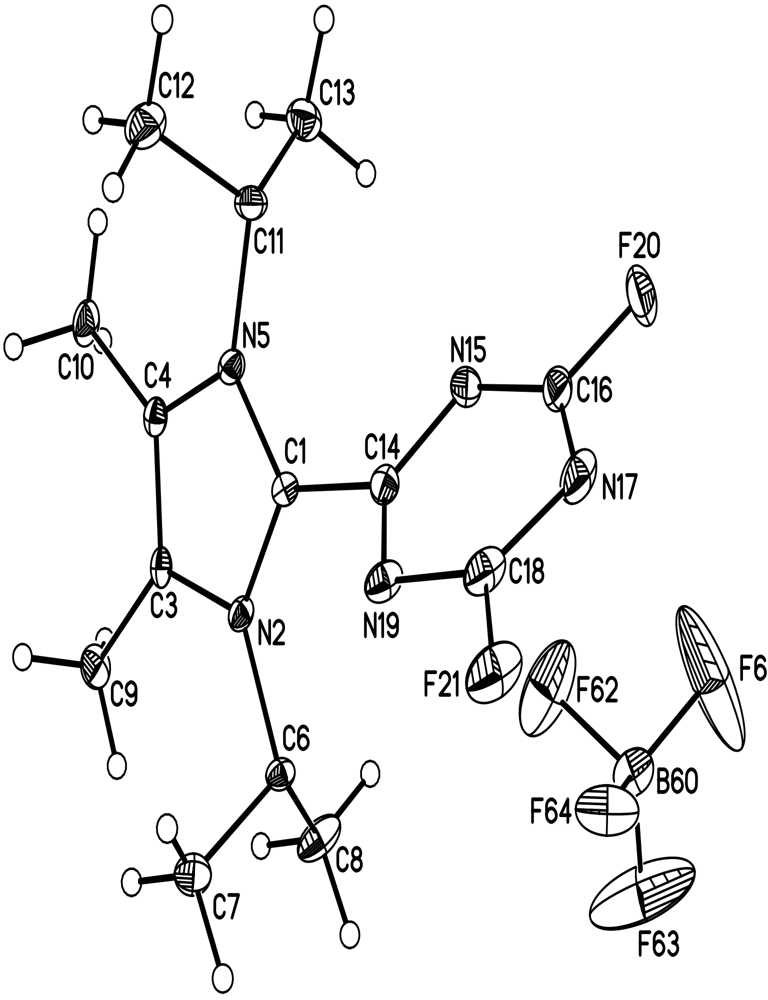
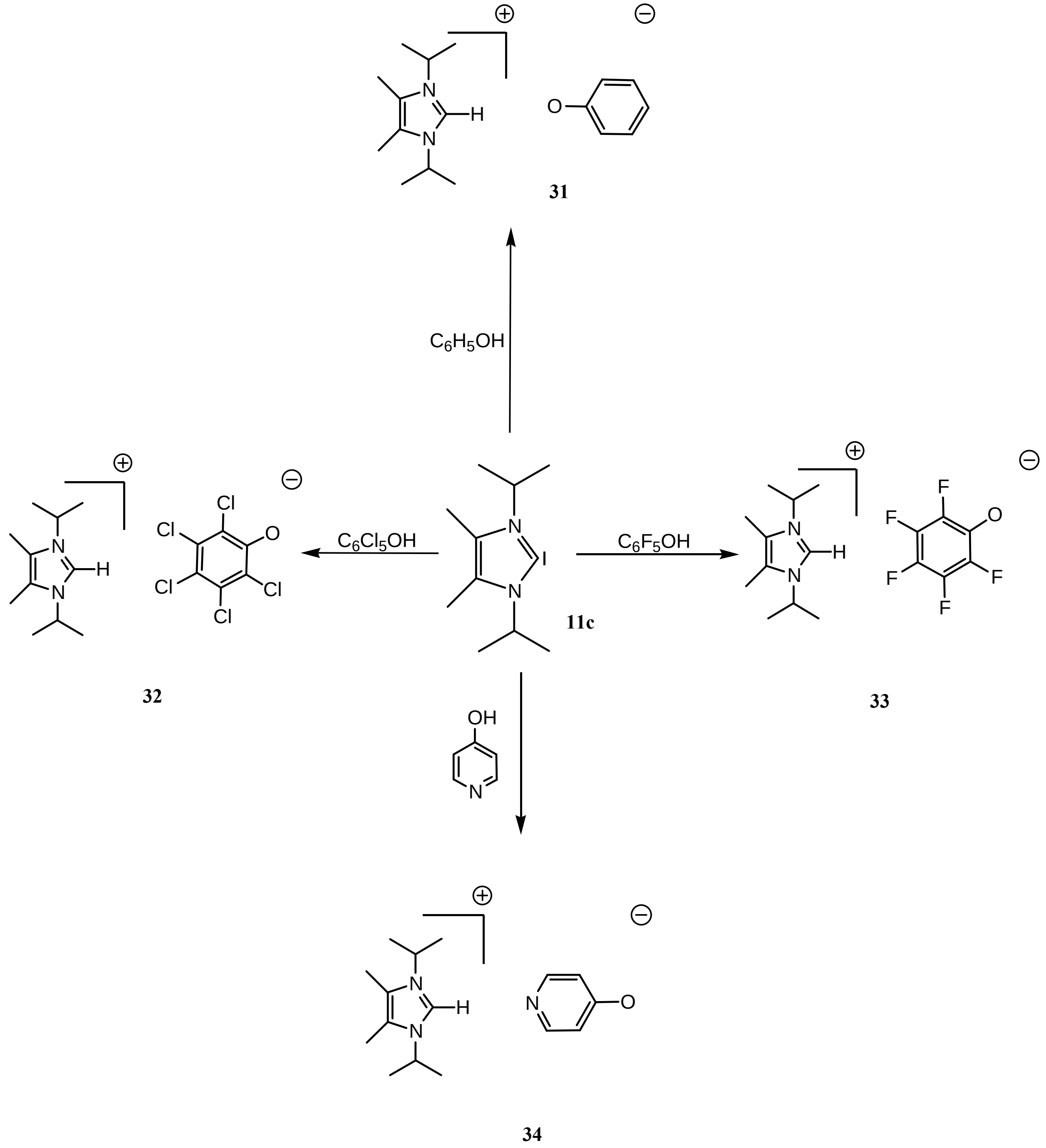


**Figure 5. The crystal structure of $C_{14}H_{20}BF_6N_5$ (30).**

## 2.2 Imidazolium aryl oxide adducts of the types of 2,3-dihydroimidazole-2-ylidenes

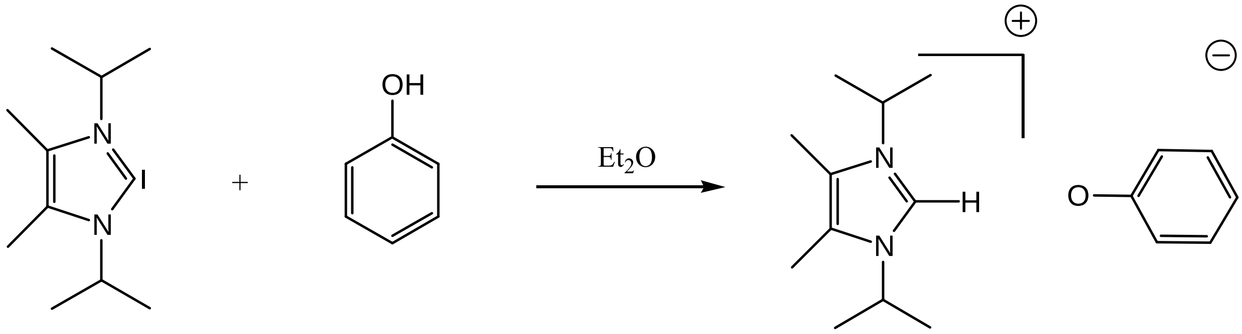
1,3-Diisopropyl-4,5-dimethylimidazolium phenolate **31**, 1,3-diisopropyl-4,5-dimethylimidazolium pentachlorophenolate **32** and 1,3-diisopropyl-4,5-dimethylimidazolium pentafluorophenolate **33** were obtained from 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene **11c** and the corresponding phenols derivatives as stable crystals in excellent yields. The crystal structure analyses of these compounds reveal the presence of ion pairs linked by almost linear C-H-O hydrogen bonds, where the H…O distances are in the range of [1.998-2.273] Å. These distances do not correlate with the base strength of their phenolate ions. Thus, packing effects seem to predominate. With 4-hydroxypyridine, the carbene **11c** gives 1,3-diisopropyl-4,5-dimethylimidazolium 4-pyridinolate **34** whose crystal structure analysis indicates the ions to be connected in the solid state by a C-H-N bond. The characterization of these structures can be viewed as a structural model for the proton transfer from an acidic group to a basic C atom which is significant in relation to the use of stable carbenes as a strong bases.[51]

All of the above mentioned reactions were carried out in dry diethyl ether at -50 $^{o}$C to give stable imidazolium alcoholates salts, these reactions are outlined in scheme 8 and the results confirmed by NMR, mass spectroscopy, elemental analysis and single crystal X-ray diffraction.



**Scheme 8. Imidazolium aryl oxide adducts of 2,3-dihydroimidazole-2-ylidenes**

### **2.2.1** 1,3-diisopropyl-4,5-dimethylimidazolium phenolate **(31)**



**11c** **31**

Single crystals of **31** that were suitable for X-ray crystal structure analysis were obtained by allowing diethyl ether vapor diffuse into an acetonitrile solution at RT. The salt crystallizes in the monoclinic space group $p2_1$/c. The X-ray crystal structure is depicted in figure 6 and it reveals the presence of an ion pair linked by C-H…O hydrogen bond [$C_1$-$H_1$ 0.967, $H_1$···$O_{17}$ 1.998 Å; $C_1$-$H_1$-$O_{17}$ 178.7°]. A view on the interionic distances reveals the presence of separated ions in the unit cell. Selected bond lengths and angles are given in table 3. Several noteworthy features are evident in the X-ray structure of **31**, it exhibits an approximately linear C-H…O interaction [$C_1$-$H_1$-$O_{17}$ 178.7°], the $O_{17}$…$H_1$ bond distance [1.998 Å] is longer and the $C_{11}$-$O_{17}$ [1.2881 Å] bond distance is shorter than that found in the previously reported data by John A *etal.* [O…H 1.88 Å, $C_{11}$-$O_{17}$ 1.306 Å].[51] This significant lengthening and shortening in $O_{17}$…$H_1$ and $C_{11}$-$O_{17}$ bond distances respectively, might be attributed to the bulky substituents on the phenol ring. The dihedral angle between imidazolium ion and phenoxide is 104.2°.

**Table 3. Selected bond lengths (Å) and angles (deg) for $C_{17}H_{26}N_2O$ (31).**

| | |
|---|---|
| N(5)-C(1) | 1.320(2) |
| N(5)-C(4) | 1.388(2) |
| N(2)-C(3) | 1.388(2) |
| C(3)-C(4) | 1.338(2) |
| C(1)-N(2) | 1.322(2) |
| C(11)-C(16) | 1.415(2) |
| C(11)-O(17) | 1.288(2) |
| C(11)-C(12) | 1.410(2) |
| C(12)-C(13) | 1.381(2) |
| C(13)-C(14) | 1.374(2) |
| C(14)-C(15) | 1.374(2) |
| C(15)-C(16) | 1.375(2) |
| | |
| C(1)-N(5)-C(4) | 109.8(1) |
| N(5)-C(1)-N(2) | 107.2(1) |
| C(1)-N(2)-C(3) | 110.1(1) |
| C(4)-C(3)-N(2) | 106.2(1) |
| C(3)-C(4)-N(5) | 106.8(1) |
| O(17)-C(11)-C(12) | 122.8(1) |
| O(17)-C(11)-C(16) | 122.2(1) |
| C(12)-C(11)-C(16) | 115.0(1) |
| C(13)-C(12)-C(11) | 121.4(1) |
| C(14)-C(13)-C(12) | 121.8(1) |
| C(13)-C(14)-C(15) | 118.4(1) |
| C(14)-C(15)-C(16) | 120.7(1) |
| C(15)-C(16)-C(11) | 122.7(1) |

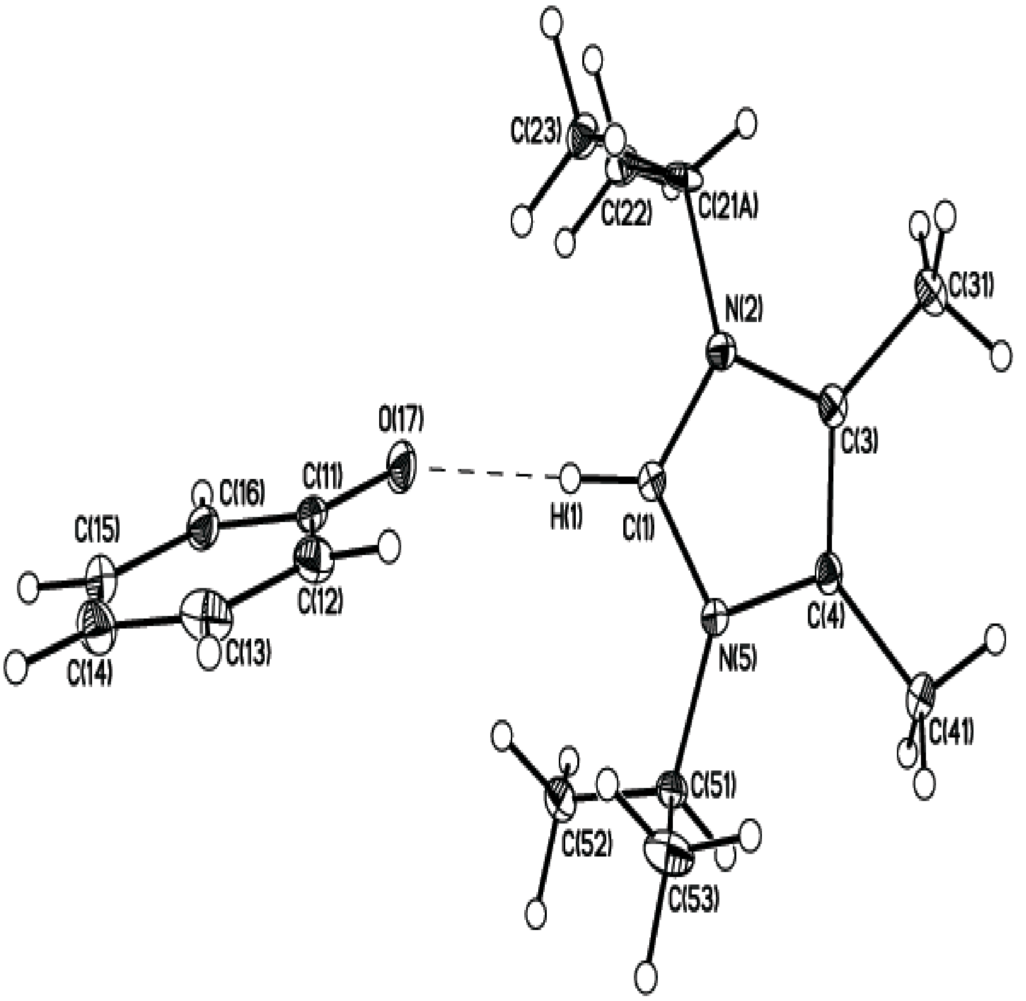
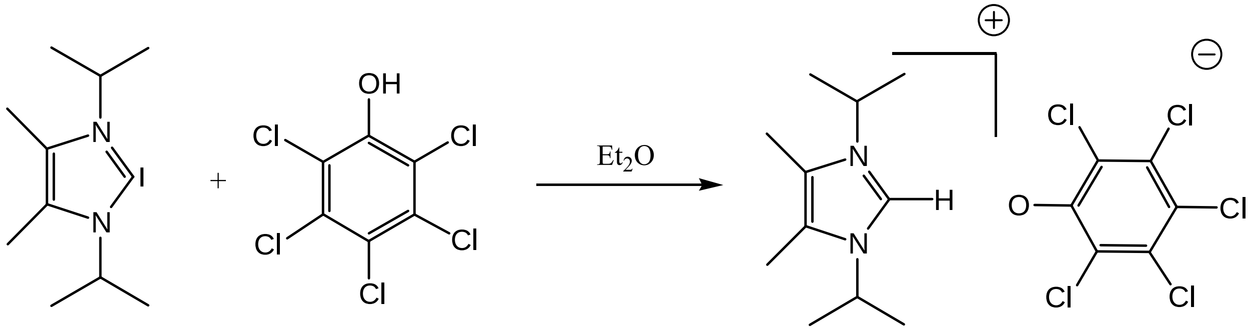


**Figure 6. View of the ion pair of $C_{17}H_{26}N_2O$ (31) in the crystal.**

### **2.2.2** 1,3-Diisopropyl-4,5-dimethylimidazolium 2,3,4,5,6-pentachloro phenolate **(32)**



**11c**

**32**

Single crystals of **32** that were suitable for X-ray crystal structure analysis were obtained by allowing diethyl ether vapor diffuse into an acetonitrile solution at RT. The salt crystallizes in the orthorhombic space group $p2_12_12_1$. The X-ray crystal structure is depicted in figure 7 and it reveals the presence of an ion pair linked by C-H…O hydrogen bond [$C_1$-$H_1$ 0.843, $H_1 \cdots O_{26}$ 2.273 Å; $C_1$-$H_1$-$O_{26}$ 176.5°]. A view on the interionic distances reveals the presence of separated ions in the unit cell. Selected bond lengths and angles are given in table 4. Several noteworthy features are evident in the X-ray structure of **32**, it exhibits an approximately linear C-H…O interaction [$C_1$-$H_1$-$O_{26}$ 176.5°], the $O_{26}$…$H_1$ bond distance [2.273 Å] is longer and the $C_{20}$-$O_{26}$ bond distance [1.263 Å] is slightly shorter than that found in **31**, it might be attributed to the packing effect and to the substituted chloro atoms on the phenol ring. The C-C-Cl angles in the anion are not equal; the [$C_{20}$-$C_{21}$-$Cl_{27}$ 116.02°] angle is too close to the $C_{20}$-$O_{26}$ bond so it is shorter than [$C_{21}$-$C_{22}$-$Cl_{28}$ 120.08°] angle. The dihedral angle between imidazolium ion and pentachloro phenoxide is 100.4°.

**Table 4. Selected bond lengths (Å) and angles (deg) for $C_{17}H_{21}Cl_5N_2O$ (32).**

| | |
|---|---|
| C(1)-N(2) | 1.334(2) |
| C(1)-N(5) | 1.334(2) |
| N(2)-C(3) | 1.386(2) |
| C(3)-C(4) | 1.354(2) |
| C(4)-N(5) | 1.390(2) |
| C(20)-O(2) | 1.263(2) |
| C(20)-C(25) | 1.434(2) |
| C(20)-C(21) | 1.436(2) |
| C(21)-C(22) | 1.384(2) |
| C(21)-Cl(27) | 1.737(2) |
| C(22)-C(23) | 1.393(2) |
| C(22)-Cl(28) | 1.731(2) |
| C(23)-C(24) | 1.399(2) |
| C(23)-Cl(29) | 1.728(2) |
| C(24)-C(25) | 1.385(2) |
| C(24)-Cl(30) | 1.727(2) |
| C(25)-Cl(31) | 1.731(2) |
| | |
| N(2)-C(1)-N(5) | 108.4(2) |
| C(1)-N(2)-C(3) | 108.8(1) |
| C(4)-C(3)-N(2) | 107.2(1) |
| C(3)-C(4)-N(5) | 106.8(1) |
| C(1)-N(5)-C(4) | 108.8(1) |
| O(26)-C(20)-C(25) | 123.6(2) |
| O(26)-C(20)-C(21) | 123.5(2) |
| C(25)-C(20)-C(21) | 112.9(1) |
| C(22)-C(21)-C(20) | 123.7(2) |
| C(21)-C(22)-C(23) | 120.7(2) |
| C(22)-C(23)-C(24) | 118.3(2) |
| C(25)-C(24)-C(23) | 120.8(2) |

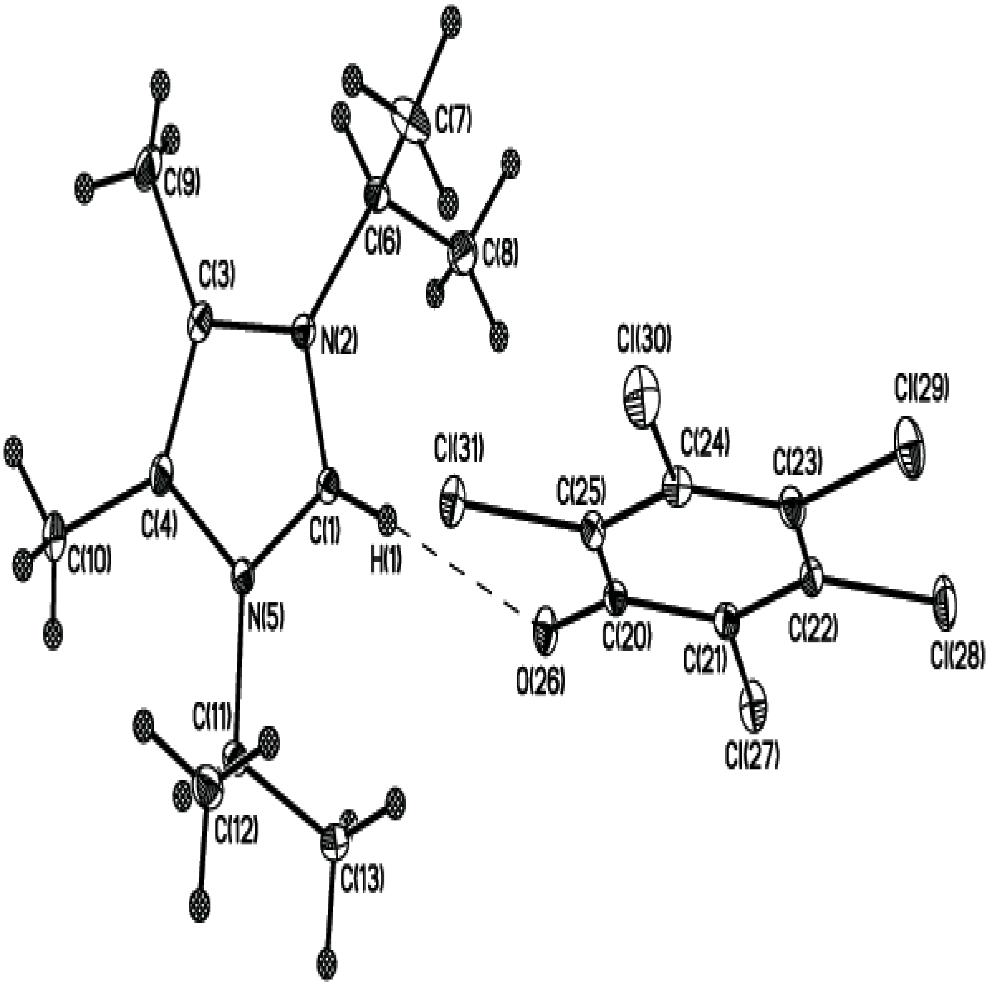
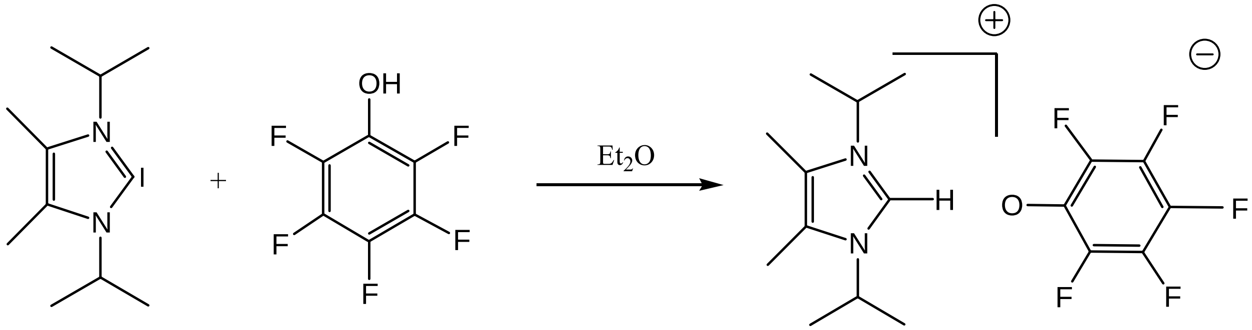


**Figure 7. View of the ion pair of $C_{17}H_{21}Cl_5N_2O$ (32) in the crystal.**

### **2.2.3** 1,3-Diisopropyl-4,5-dimethylimidazolium 2, 3, 4, 5,6-pentafluoro phenolate **(33)**



**11c** **33**

Single crystals of **33** that were suitable for X-ray crystal structure analysis were obtained by allowing diethyl ether vapor diffuse into an acetonitrile solution at RT. The salt crystallizes in the orthorhombic space group $p2_12_12_1$. The X-ray crystal structure is depicted in figure 8 and it reveals the presence of an ion pair linked by C-H…O hydrogen bond [$C_{20}$-$H_{20}$ 0.930, $H_{20}\cdots O_7$ 2.071 Å; $C_{20}$-$H_{20}$-$O_7$ 171.7°]. A view on the interionic distances reveals the presence of separated ions in the unit cell. Selected bond lengths and angles are given in table 5. Several noteworthy features are evident in the X-ray structure of **33**, it exhibits a near linear C-H…O interaction [$C_{20}$-$H_{20}$-$O_7$ 171.7°], the $O_7$…$H_{20}$ [2.071 Å] and the $C_1$-$O_7$ [1.276 Å] bond distances are in agreement with those observed in **31**, moreover fluoro atoms make a weak H-F hydrogen bonds [ $F_{10}$-$H_{26c}$ 2.620, $F_9$-$H_{31c}$ 2.880, $F_8$-$H_{29a}$ 2.703, $F_{11}$-$H_{28a}$ 2.667, $F_{12}$-$H_{27b}$ 2.682] Å. The dihedral angle between imidazolium ion and pentafluoro phenoxide is 160.9°.

**Table 5. Selected bond lengths (Å) and angles (deg) for $C_{17}H_{21}F_5N_2O$ (33).**

| | |
|---|---|
| C(1)-O(7) | 1.276(5) |
| C(1)-C(2) | 1.409(6) |
| C(1)-C(6) | 1.413(7) |
| C(2)-F(8) | 1.364(5) |
| C(2)-C(3) | 1.376(6) |
| C(3)-F(9) | 1.351(5) |
| C(3)-C(4) | 1.376(7) |
| C(4)-F(10) | 1.357(5) |
| C(4)-C(5) | 1.371(7) |
| C(5)-F(11) | 1.349(6) |
| C(5)-C(6) | 1.368(7) |
| C(6)-F(12) | 1.354(5) |
| C(20)-N(24) | 1.324(5) |
| C(20)-N(21) | 1.328(5) |
| N(21)-C(22) | 1.391(5) |
| C(22)-C(23) | 1.356(6) |
| C(23)-N(24) | 1.388(5) |
| | |
| O(7)-C(1)-C(2) | 124.1(4) |
| O(7)-C(1)-C(6) | 123.6(4) |
| C(2)-C(1)-C(6) | 112.3(4) |
| C(3)-C(2)-C(1) | 124.3(4) |
| C(4)-C(3)-C(2) | 120.2(4) |
| C(5)-C(4)-C(3) | 118.2(4) |
| C(6)-C(5)-C(4) | 121.0(4) |
| C(5)-C(6)-C(1) | 123.9(4) |

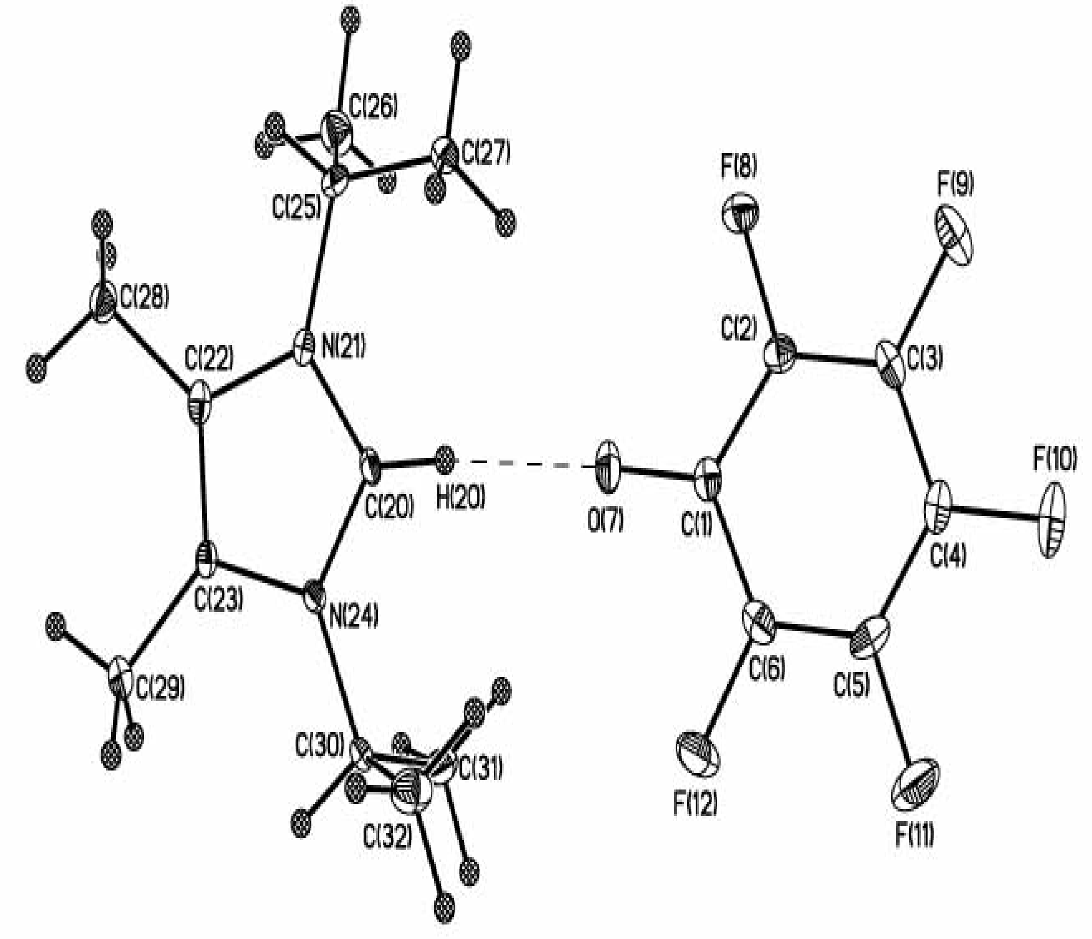
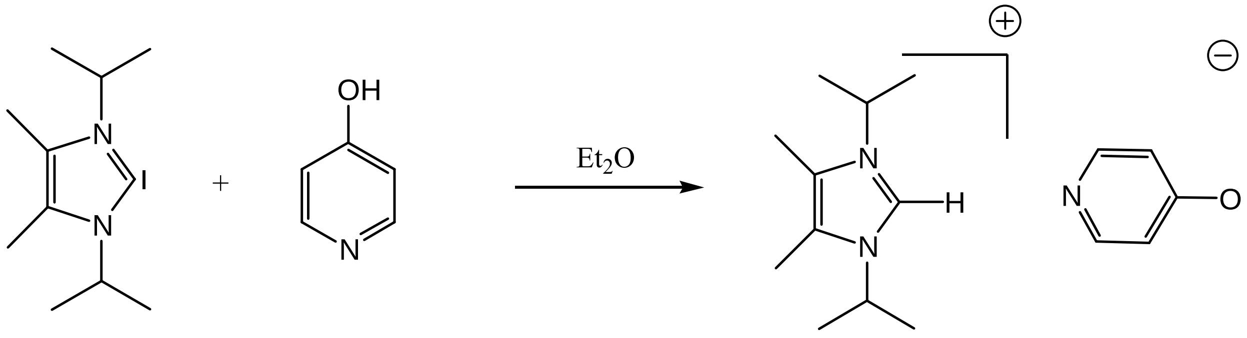


**Figure 8. View of the ion pair of $C_{17}H_{21}F_5N_2O$ (33) in the crystal.**

### **2.2.4** 1,3-Diisopropyl-4,5-dimethylimidazolium 4-pyridinolate **(34)**



**11c** **34**

Single crystals of **34** that were suitable for X-ray crystal structure analysis were obtained by allowing diethyl ether vapor diffuse into an acetonitrile solution at RT. The salt crystallizes in the orthorhombic space group *C*mcm. The X-ray crystal structure is depicted in figure 9 and it reveals the presence of an ion pair linked by C-H…N hydrogen bond [$C_{10}$-$H_{10}$ 0.933, $H_{10}$···$N_4$ 2.225 Å; $C_{10}$-$H_{10}$-$N_4$ 180.0°]. A view on the interionic distances reveals the presence of separated ions in the unit cell. Selected bond lengths and angles are given in table 6. Several noteworthy features are evident in the X-ray structure of **34**, it exhibits a linear C-H…N interaction [$C_{10}$-$H_{10}$-$N_4$ 180.0°], in addition we observed weak contacts between the pyridinolate oxygen atom and methyl protons of a neighboured cation [$H_{15A}$···$O_5$ 2.479 Å]. The $C_1$-$O_5$ [1.268 Å] bond distance is a bit shorter compared with this length in **31**. The dihedral angle between ions is perpendicular to each other [90.0°].

**Table 6. Selected bond lengths (Å) and angles (deg) for $C_{16}H_{25}N_3O$ (34).**

| | |
|---|---|
| C(1) – O(5) | 1.268(4) |
| C(1) – C(2) | 1.422(4) |
| C(2) – C(3) | 1.371(4) |
| C(3) – N(4) | 1.341(3) |
| C(10) – N(11) | 1.329(2) |
| N(11) – C(12) | 1.387(3) |
| C(12) – C(12)#2 | 1.353(4) |
| | |
| O(5) – C(1) – C(2) | 123.5(2) |
| C(2) – C(1) – C(2)#2 | 113.0(3) |
| C(3) – C(2) – C(1) | 120.7(3) |
| N(4) – C(3) – C(2) | 126.0(3) |
| C(3) - N(4) – C(3)#1 | 113.4(3) |
| C(10) - N(11) – C(12) | 109.1(2) |
| C(10) - N(11) – C(13) | 124.4(2) |
| C(12) - N(11) – C(13) | 126.5(2) |
| C(14) - C(13) – C(14)#1 | 113.1(2) |
| N(11) - C(13) – C(14)#1 | 110.0(1) |
| N(11) – C(12) – C(15) | 122.6(2) |
| N(11) – C(13) – C(14) | 110.0(1) |

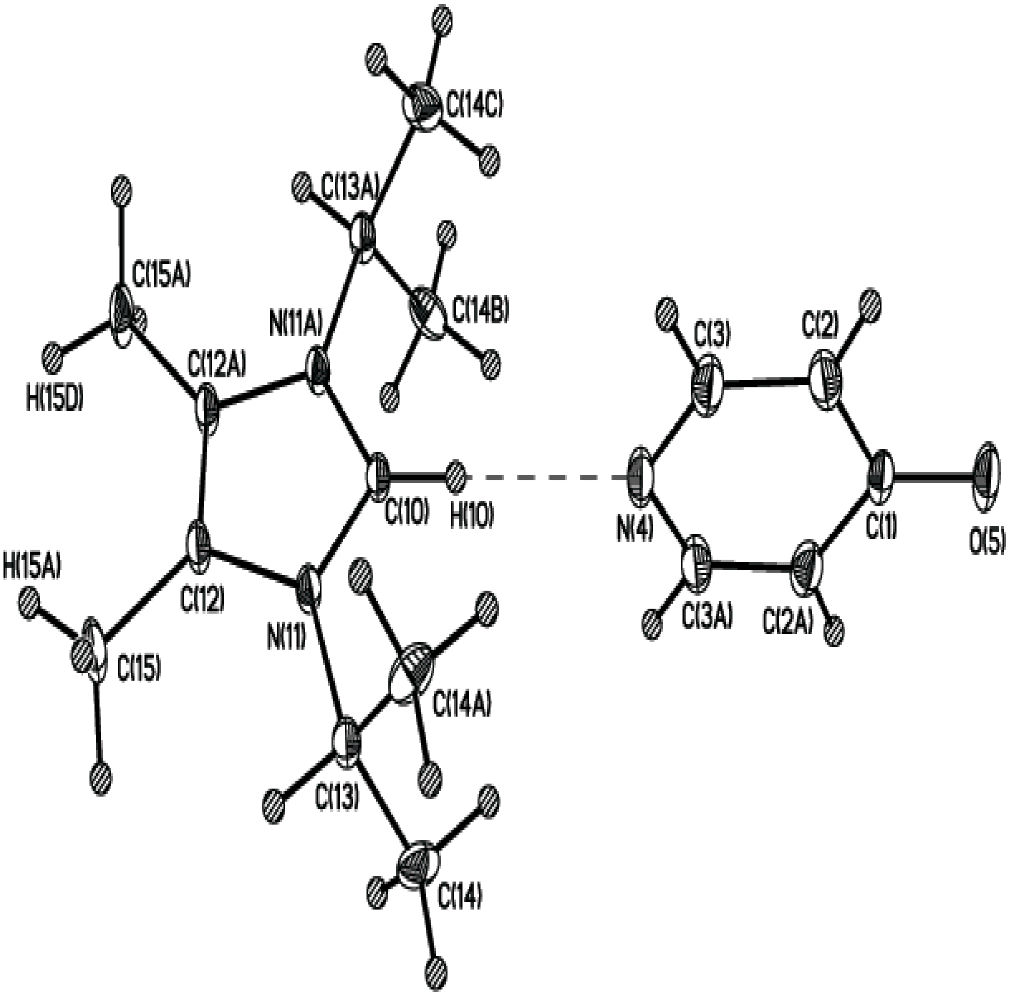


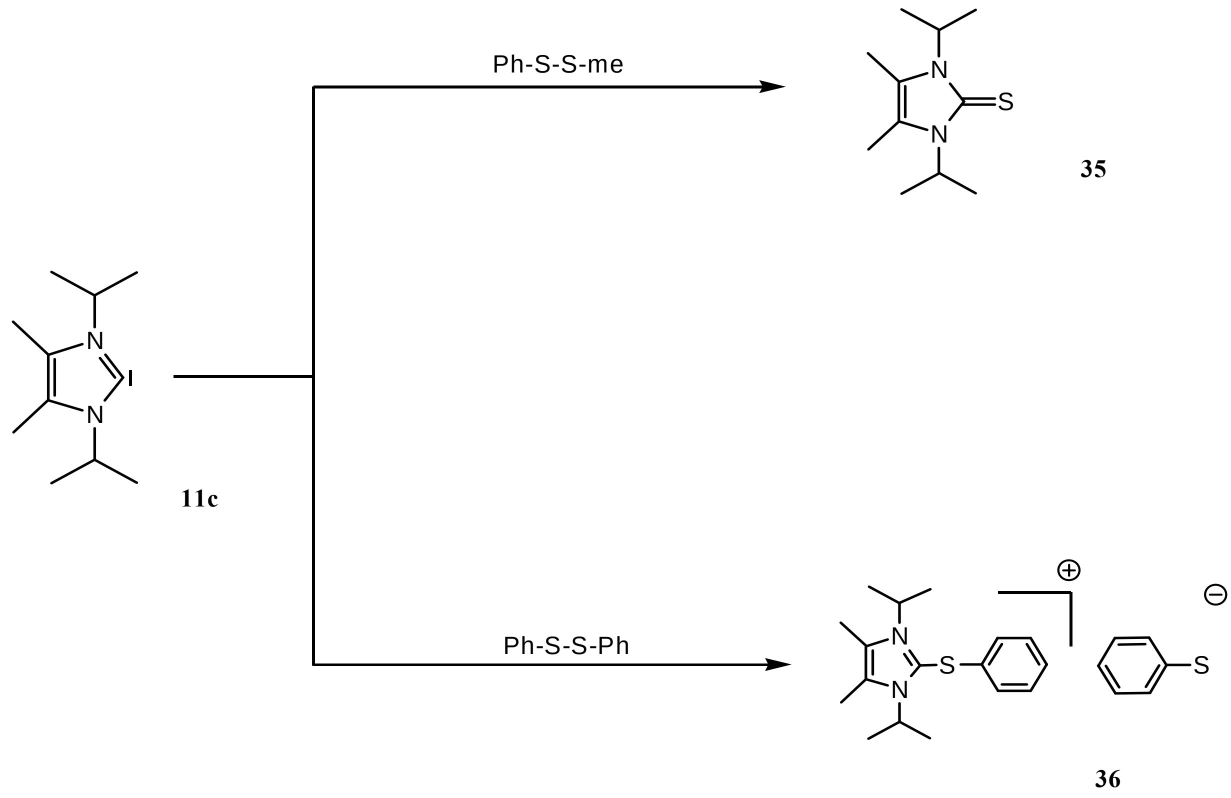
**Figure 9. View of the ion pair of $C_{16}H_{25}N_3O$ (34) in the crystal.**

### 2.3 Further derivatives of 2,3-dihydroimidazole-2-ylidenes

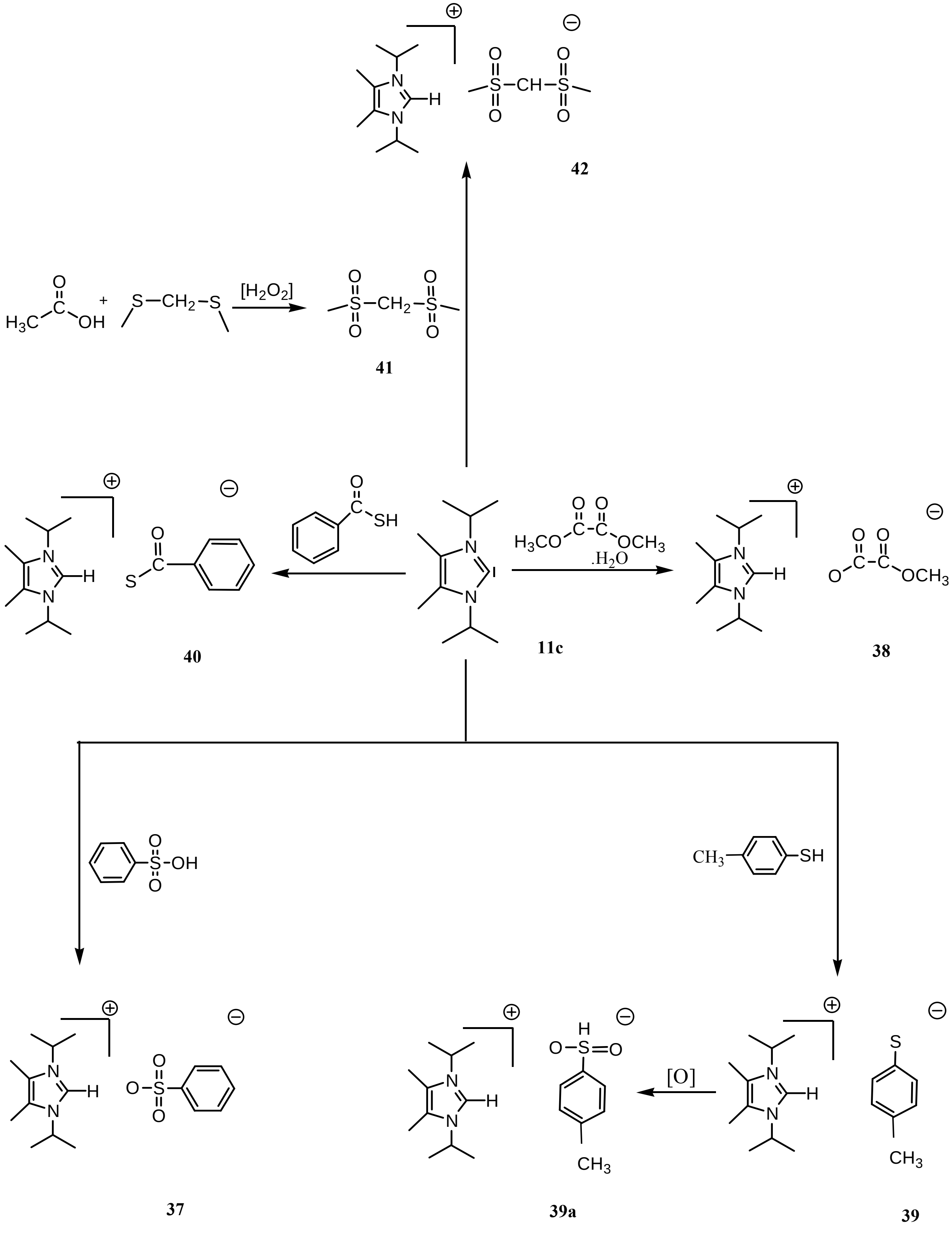
Owing the strongly basic character of heterocyclic carbenes, **11c** was reacted smoothly with disulfide compounds, the sulfur-sulfur bond in organic disulphides is readily cleaved by such nucleophiles as cyanide, phosphines, thiols, amines and hydroxide,[68] this cleavage has been observed in the reaction of diphenyl disulfide with **11c** to give **36**, furthermore **11c** was reacted with methyl phenyl disulfide to give the corresponding adduct **35** which afford a new synthetic route for 2,3-dihydro-imidazole-2-thione.[26]

On the other hand, **11c** was reacted with benzenesulfonic acid, 4-Methylbenzenethiol and thiobenzoic acid respectively in diethyl ether at -50 $^{o}$C to give the salts **37**, **39** and **40** in good yield. While the reaction of **11c** with bis-methane sulfone was carried out at RT to give the salt **42**. The formation of **38** needs vigorous condition, where **11c** reacted with dimethyl oxalate at 85 $^{o}$C as solid-solid reaction for about 2 h, the starting dimethyl oxalate contains water, so we observed the signal for 2H-imidazolium ion in $^{1}$H NMR spectra. These reactions revealed that the hydrogen atom bound to oxygen or sulfur atoms to form classical hydrogen bonds. Apparently their properties are influenced by interionic interactions which have been detected mainly in their 2H-derivatives as hydrogen bonds. The C-H…X interaction is typically weak and it acts as an additional stabilizing factor in their crystal structures.[69]

The above mentioned reactions are outlined in scheme 9 and 10, the results confirmed by NMR, mass spectroscopy, elemental analysis and single crystal X-ray diffraction.

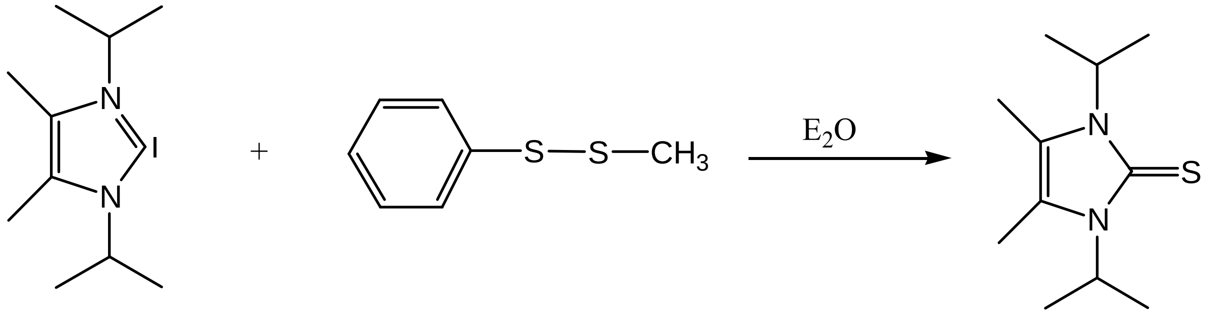


**Scheme 9. Reactions of methy phenyl disulfide and diphenyl disulfide with 11c**



Scheme 10. Salt derivatives of the types of 2,3-dihydroimidazole-2-ylidenes

### **2.3.1** 1,3-Diisopropyl-4,5-dimethyl-imidazole-2-thione **(35)**



**11c** **35**

Crystals of **35** suitable for X-ray analysis were grown as colorless prism by slow cooling of diethyl ether solution, the compound crystallizes in the monoclinic space group *C*2/c. The X-ray crystal structure of **35** is depicted in figure 10. Selected bond lengths and angles are listed in table 7. The $C_1$-$S_1$ bond length [1.698 Å] corresponds to a partial double bond[70] and it is shorter than the single bond length value of [1.81 Å] and greater than the C=S value of [1.61 Å].[71] It is representative of C-S bonding in a selection of molecules containing the grouping –N-CS-X– where X = N or C. [72,73,74] The $C_3$-$N_2$ bond length [1.395 Å] shows some shortening from the single bond value due to the presence of partial double bonds.[75] The bond length of $C_1$-$N_2$ [1.357 Å] and the angle of $N_2$-$C_1$-$N_{2A}$ [106.4°] are similar to those reported in literatures.[76]

**Table 7. Selected bond lengths (Å) and angles (deg) for $C_{11}H_{20}N_2S$ (35).**

| | |
|---|---|
| S(1)-C(1) | 1.698(3) |
| C(1)-N(2) | 1.357(2) |
| N(2)-C(3) | 1.395(3) |
| N(2)-C(4) | 1.480(3) |
| C(3)-C(3)#1 | 1.353(4) |
| C(3)-C(7) | 1.489(3) |
| C(4)-C(6) | 1.498(5) |
| | |
| N(2)-C(1)-N(2)#1 | 106.4(2) |
| N(2)-C(1)-S(1) | 126.8(1) |
| C(1)-N(2)-C(3) | 109.7(2) |
| C(1)-N(2)-C(4) | 122.4(2) |
| C(3)-N(2)-C(4) | 127.9(2) |
| C(3)#1-C(3)-N(2) | 107.1(1) |
| C(3)#1-C(3)-C(7) | 128.3(1) |
| N(2)-C(3)-C(7) | 124.6(2) |
| N(2)-C(4)-C(6) | 112.3(2) |
| C(6)-C(4)-C(5) | 111.5(3) |

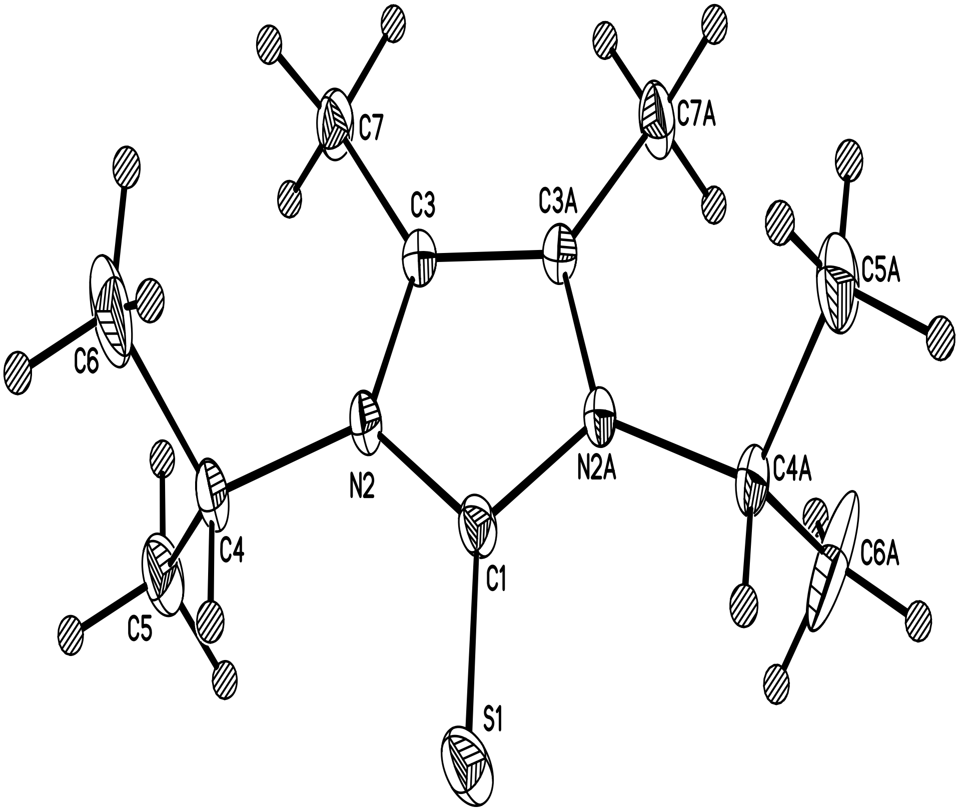
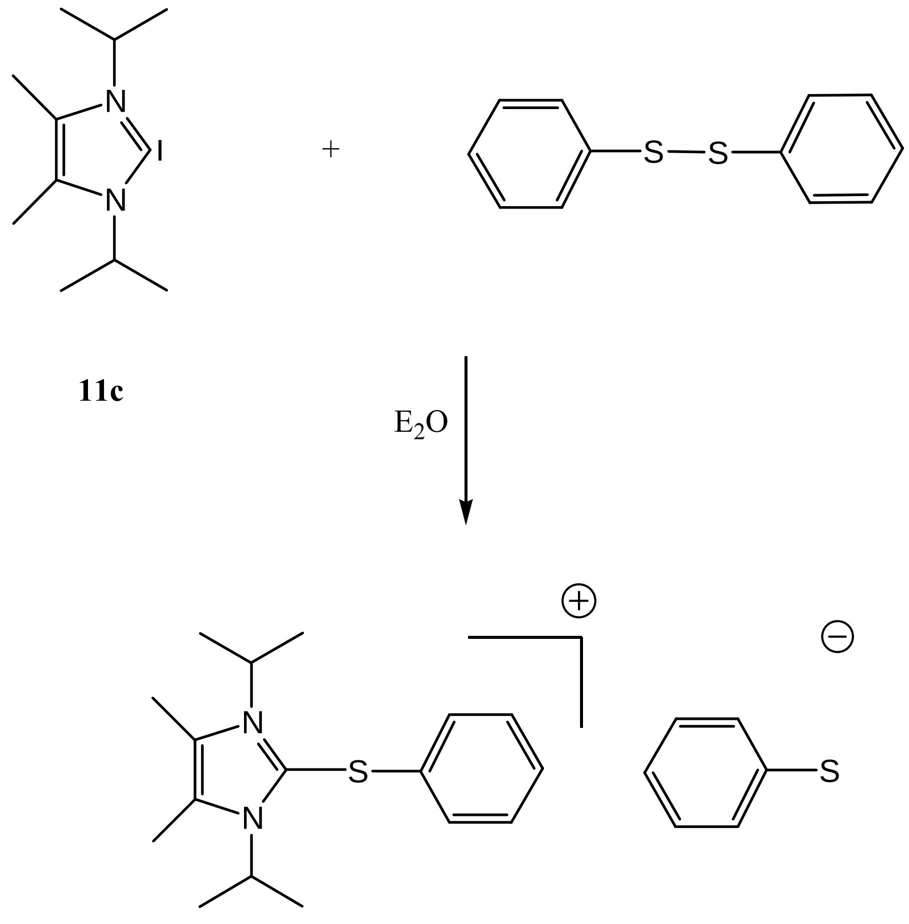


**Figure 10. The crystal structure of $C_{11}H_{20}N_2S$ (35).**

### **2.3.2** 1,3-Diisopropyl-4,5-dimethyl-2-phenylsulfanylimidazoium benzenethiol **(36)**



**11c**

**36**

The attempts to get single crystals from **36** were failed due to the very low stability and very high sensitivity of the salt toward the moisture. The structure of **36** can be assigned obviously from the NMR spectroscopy, the 2-H imidazolium ion signal has not been observed in the $^{1}$H NMR spectra, furthermore the starting diphenyl disulfide shows only four signals[77,78] in the $^{13}$C NMR spectra (figure 11) due to the presence of symmetry between phenyl groups, while in **36** the symmetry between the two phenyl rings have been disappeared (figure 12) due to the cleavage of S-S bond and formation the salt, moreover the imidazolium ion signals are all existed. The $^{1}$H and $^{13}$C NMR data of **36** imply the presence of separated ions.

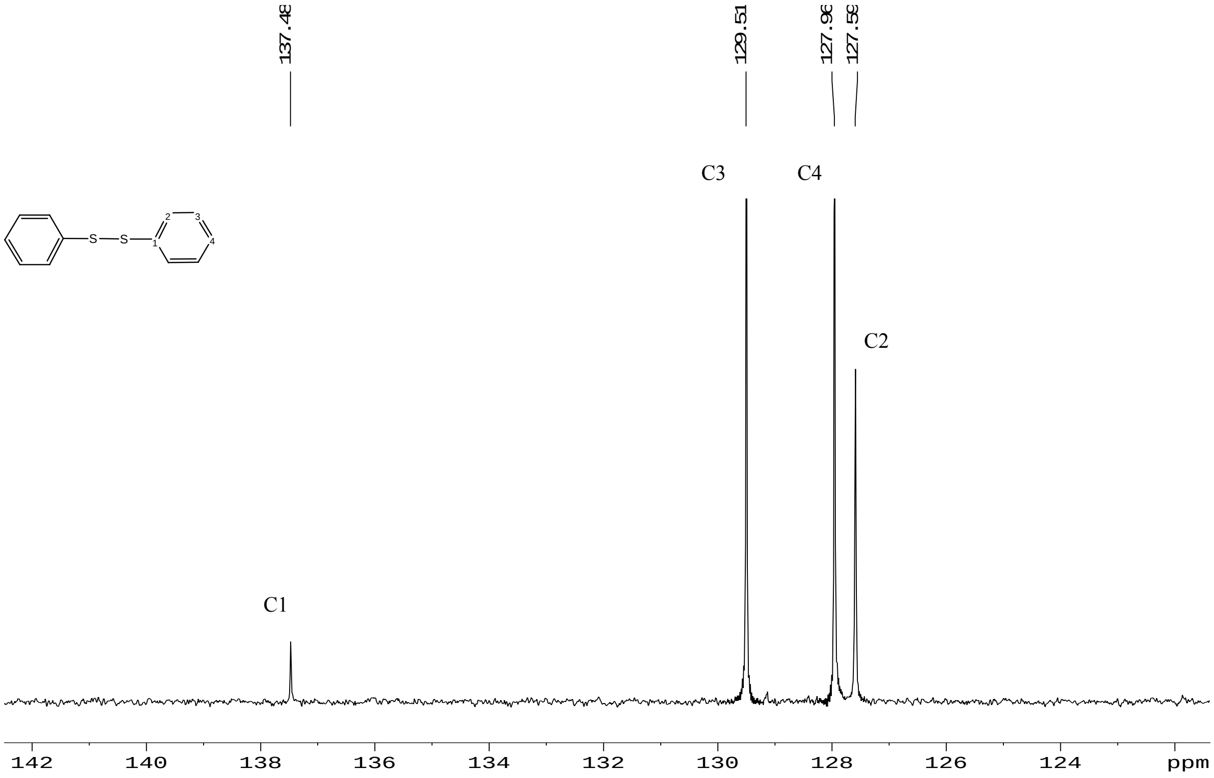


**Figure 11.** $^{13}$C NMR spectra of diphenyl disulfide in $CD_3Cl$ at 100 MHz.

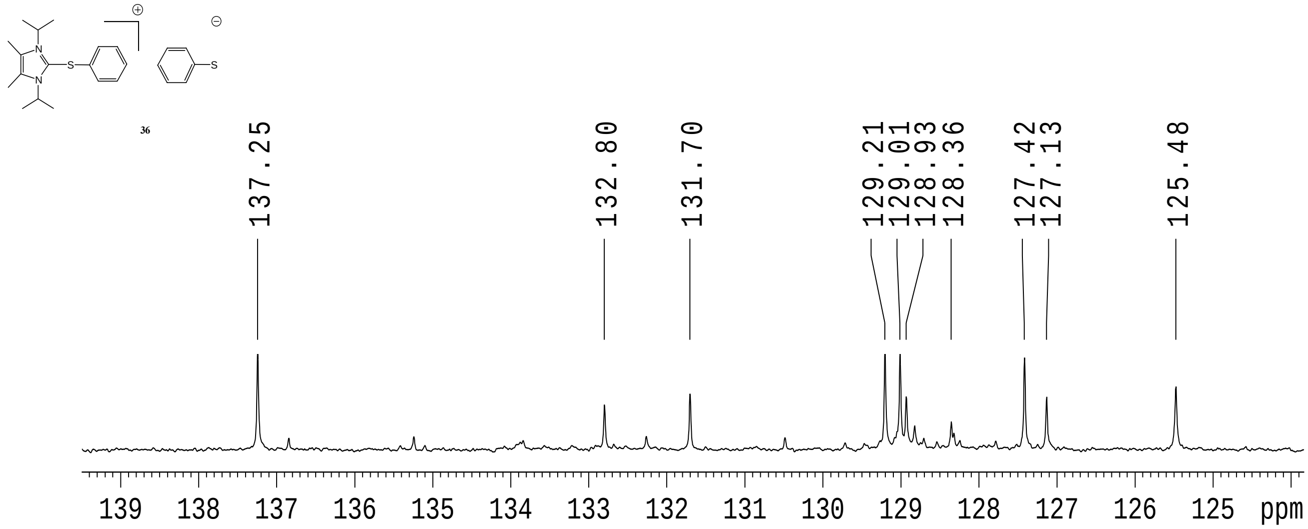
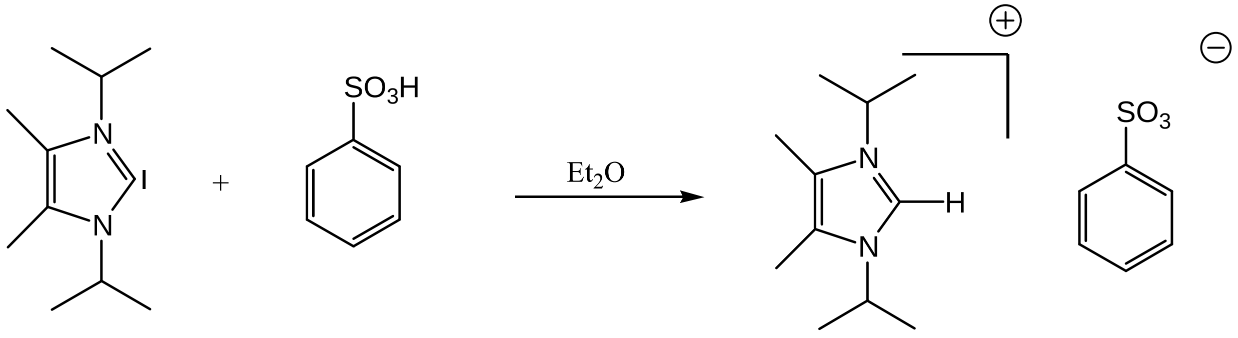


**Figure 12.** $^{13}$C NMR spectra of $C_{23}H_{30}N_2S_2$ (36) in $CD_3Cl$ at 100 MHz.

### **2.3.3** 1,3-Diisopropyl-4,5-dimethylimidazolium benzenesulfonic acid **(37)**



**11c** **37**

View of the ion pairs **37** is shown in figure 13. The two oxygen atoms of benzene sulfonate anion are linked to the imidazolium cation through two C-H…O hydrogen bonds [$C_1$-$H_1$ 0.950, $H_1$···$O_{11}$ 2.303 Å; $C_1$-$H_1$-$O_{11}$ 157.1°] and [$C_{01}$-$H_{01}$ 0.950, $H_{01}$···$O_{13}$ 2.248 Å; $C_{01}$-$H_{01}$-$O_{13}$ 140.5°]. The colorless **37** crystallizes in the triclinic space group $P\bar{1}$. Selected bond lengths and angles are provided in table 8. We observed that the S-O-H angles in **37** are not close together, where the $S_1$-$O_{11}$-$H_1$ angle is 145.0° and the $S_1$-$O_{13}$-$H_{01}$ angle is 117.3°, furthermore the bond lengths of the two hydrogen bonds are slightly different from each other by 0.055 Å, it might be attributed to the distribution of the negative charge on the benzene sulfonate anion, one oxygen atom of the benzene sulfonate ion is not involved into hydrogen bond. The bond distances and angles of the anion are in agreement with those observed in the previous reported data.[79,80]

**Table 8. Selected bond lengths (Å) and angles (deg) for $C_{17}H_{26}N_2O_3S$ (37).**

| | |
|---|---|
| H(1)-C(1) | 0.950(2) |
| H(1)-O(11) | 2.303(2) |
| H(01)-C(01) | 0.950(2) |
| H(01)-O(013) | 2.248(2) |
| S(1)-O(12) | 1.447(2) |
| S(1)-O(13) | 1.449(2) |
| S(1)-O(11) | 1.453(2) |
| S(1)-C(11) | 1.782(3) |
| S(2)-O(21) | 1.441(2) |
| S(2)-O(22) | 1.453(2) |
| S(2)-O(23) | 1.456(2) |
| S(2)-C(011) | 1.780(3) |
| | |
| C(1)-H(1)-O(11) | 157.1(2) |
| S(1)-O(11)-H(1) | 145.0(2) |
| O(13)-H(01)-C(01) | 140.5(2) |
| S(1)-O(13)-H(01) | 117.3(2) |
| O(12)-S(1)-O(13) | 112.93(13) |
| O(12)-S(1)-O(11) | 113.59(14) |
| O(13)-S(1)-O(11) | 112.67(14) |
| O(12)-S(1)-C(11) | 105.48(12) |
| O(13)-S(1)-C(11) | 105.24(13) |
| O(11)-S(1)-C(11) | 106.03(12) |
| C(12)-C(11)-S(1) | 121.0(2) |
| O(21)-S(2)-O(22) | 113.67(15) |
| O(21)-S(2)-O(23) | 113.29(14) |
| O(22)-S(2)-O(23) | 112.49(14) |
| O(21)-S(2)-C(011) | 105.70(13) |
| O(22)-S(2)-C(011) | 104.91(13) |
| O(23)-S(2)-C(011) | 105.83(13) |
| C(012)-C(011)-S(2) | 119.0(2) |

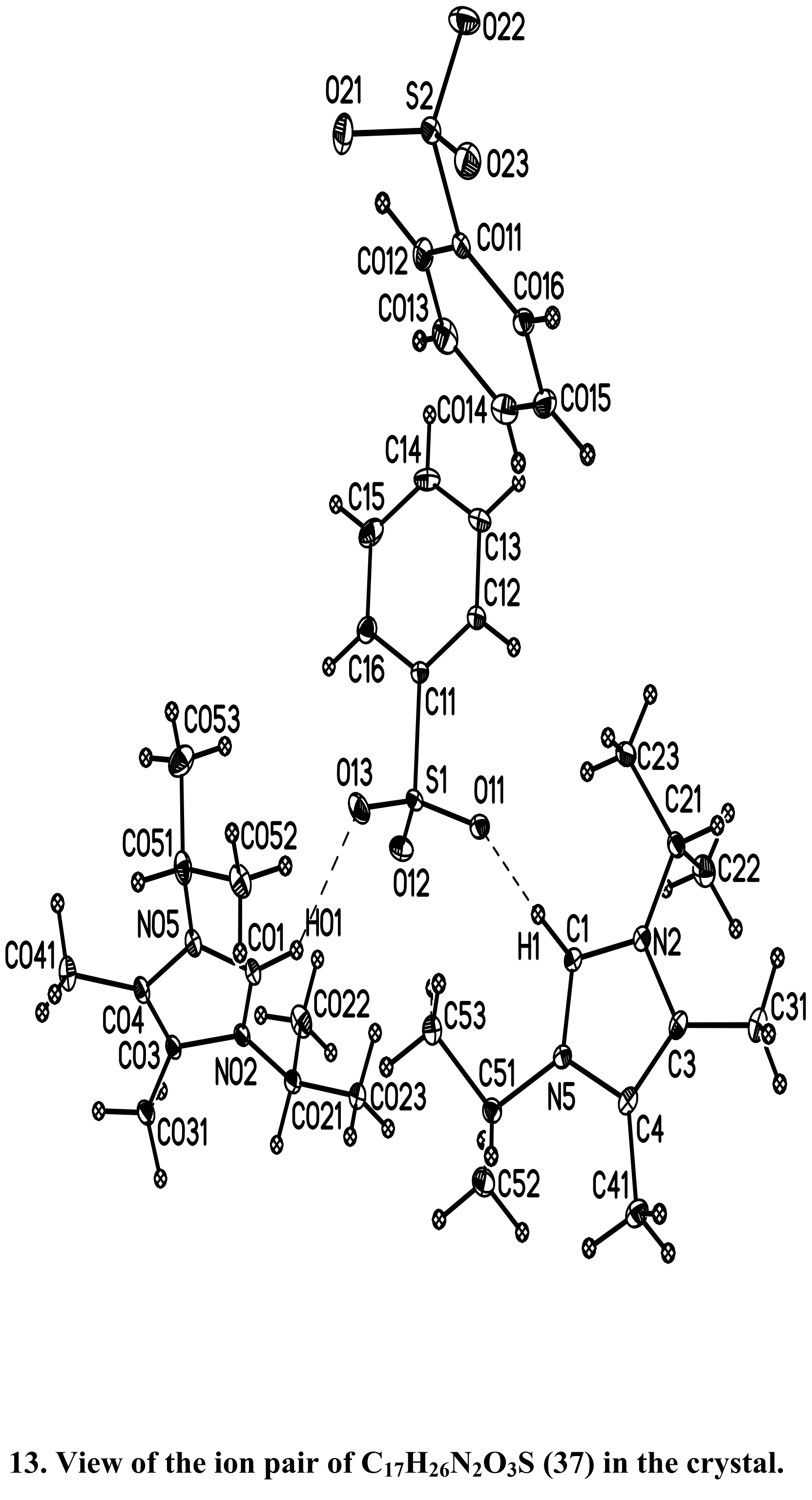
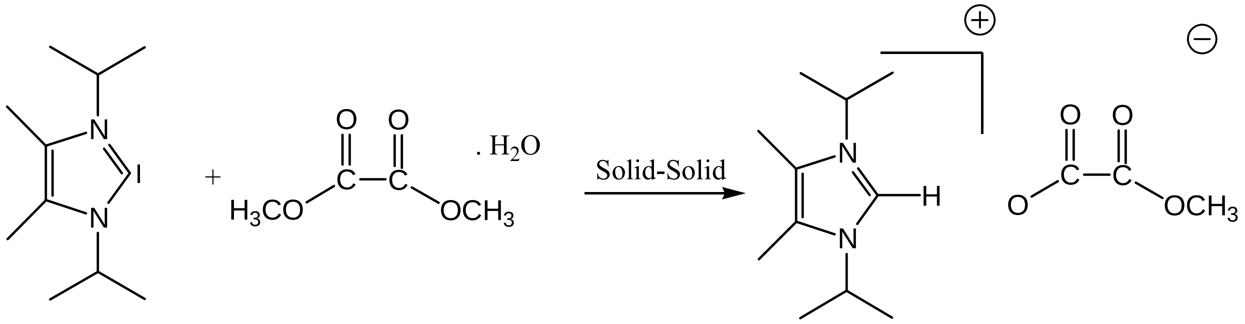


**Figure 13. View of the ion pair of $C_{17}H_{26}N_2O_3S$ (37) in the crystal.**

### **2.3.4** 1, 3-Diisopropyl-4, 5-dimethylimidazolium oxalic acid monomethyl ester **(38)**



**11c** **38**

The structure of **38** was confirmed by the results of the X-ray structure determination, the structure of this compound is shown in figure 14. Apparently, water was present in the above reaction; therefore the crystal structure analysis reveals the presence of ion pairs linked by C-H…O hydrogen bond [$C_1$-$H_1$ 0.910, $H_1{\cdots}O_{21}$ 2.253 Å; $C_1$-$H_1$-$O_{21}$ 175.0°]. The compound crystallizes in the monoclinic space group $p2_1/n$. Selected bond lengths and angles are given in table 9. The crystal structure of **38** exhibits an approximately linear C-H…O interaction [$C_1$-$H_1$-$O_{21}$ 175.0°], the flanking carbonyl $C_{22}$-$O_{20}$ bond [1.233 Å] is longer than $C_{23}$-$O_{24}$ bond [1.202 Å] as a consequence of the negative charge. This indicates that the formal negative charge is mainly delocalized at $O_{21}$-$C_{22}$-$O_{20}$, the $C_{22}$-$C_{23}$ bond length of 1.530 Å in the anion moiety is clearly indicative of a C-C single bond. [81] The bond distances and angles of the anion are in agreement with those observed in the previous reported data.[82,83] the dihedral angle between the ions ($C_1$ $N_2$ $C_3$ $C_4$ $N_5$ / $C_{22}$ $O_{20}$ $O_{21}$) is 73.1°.

**Table 9. Selected bond lengths (Å) and angles (deg) for $C_{14}H_{24}N_2O_4$ (38).**

| | |
|---|---|
| C(1)-H(1) | 0.910(2) |
| H(1)-O(21) | 2.253(2) |
| H(1)-O(22) | 2.651(2) |
| C(1)-N(5) | 1.327(2) |
| C(1)-N(2) | 1.330(2) |
| O(20)-C(22) | 1.233(2) |
| O(21)-C(22) | 1.247(2) |
| C(22)-C(23) | 1.530(3) |
| C(23)-O(24) | 1.202(2) |
| C(23)-O(25) | 1.334(2) |
| O(25)-C(26) | 1.444(3) |
| | |
| C(1)-H(1)-O(21) | 175.0(16) |
| C(22)-O(21)-H(1) | 97.2(16) |
| N(5)-C(1)-N(2) | 108.59(17) |
| O(20)-C(22)-O(21) | 128.91(19) |
| O(20)-C(22)-C(23) | 116.07(16) |
| O(21)-C(22)-C(23) | 114.96(17) |
| O(24)-C(23)-O(25) | 122.98(18) |
| O(24)-C(23)-C(22) | 125.28(17) |
| O(25)-C(23)-C(22) | 111.74(15) |
| C(23)-O(25)-C(26) | 116.97(16) |

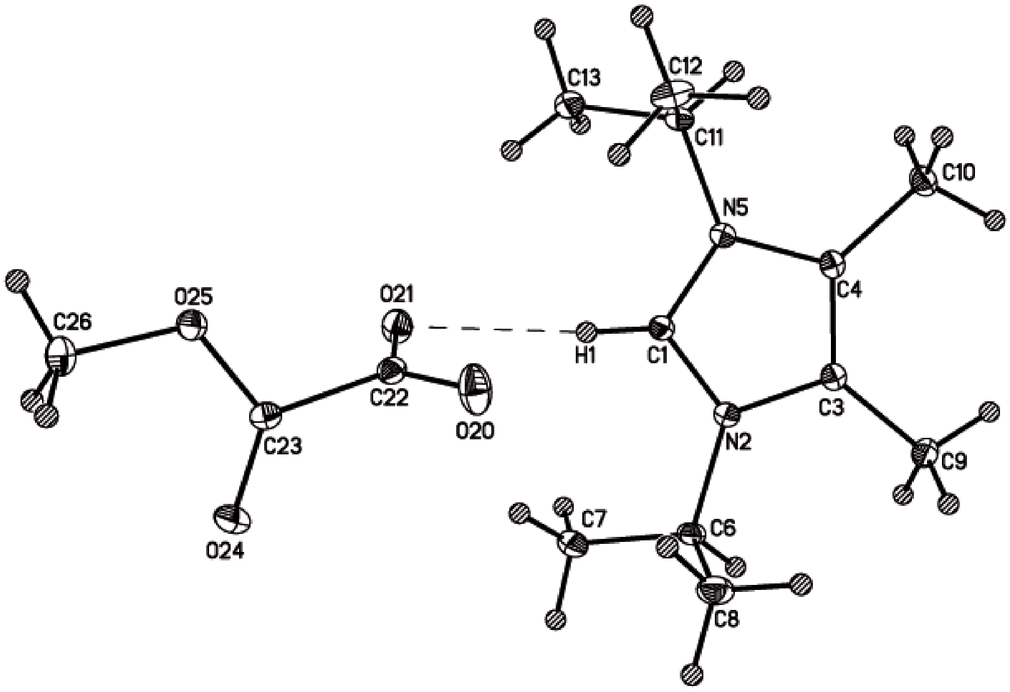
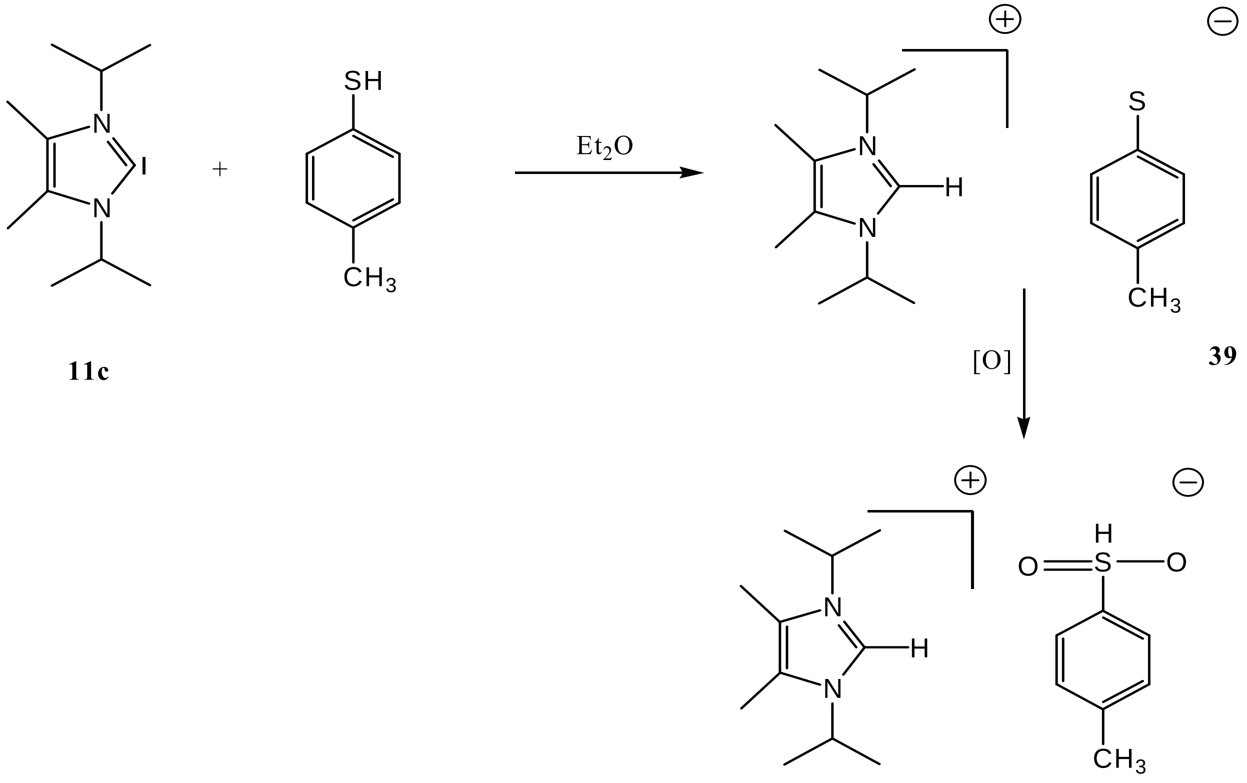


**Figure 14. View of the ion pair of $C_{14}H_{24}N_2O_4$ (38) in the crystal.**

### **2.3.5** 1,3-Diisopropyl-4, 5-dimethylimidazolium methyl benzenesulfinic acid **(39a)**



**11c**

**39**

**39a**

The salt crystallizes in the monoclinic space group $P2_1/c$. Figure 15 shows the crystal structure of **39a** with atom labeling. Single crystals of **39a** that were suitable for X-ray crystal structure analysis were obtained by allowing diethyl ether vapor diffuse into an acetone solution at RT, the product **39** was very sensitive toward atmosphere, so it enhance the oxidation probability of the methyl thio phenol ion and formed **39a** which linked by C-H…O hydrogen bond [$C_{24}$-$H_{24}$ 0.981, $H_{24}\cdots O_{02}$ 2.139 Å; $C_{24}$-$H_{24}$-$O_{02}$ 169.7°]. The selected bond lengths and angles are listed in table 10. The S-O bond lengths are approximately similar [$S_1$-$O_{02}$ 1.454, $S_1$-$O_{01}$ 1.479 Å]. Bond lengths in 4-Methylbenzenethiol anion are similar to those found in ethyl phenysulfonylacetate compound.[84] The dihedral angle between the ions is 140.5°.

**Table 10. Selected bond lengths (Å) and angles (deg) for $C_{18}H_{29}N_2O_2S$ (39a).**

| | |
|---|---|
| H(24)-C(24) | 0.981(3) |
| H(24)-O(02) | 2.139(3) |
| S(1)-O(02) | 1.454(3) |
| S(1)-O(02) | 1.454(3) |
| S(1)-O(01) | 1.479(3) |
| S(1)-C(2) | 1.809(4) |
| C(2)-C(3) | 1.380(6) |
| C(2)-C(7) | 1.389(5) |
| C(5)-C(51) | 1.513(6) |
| N(20)-C(24) | 1.329(4) |
| N(23)-C(24) | 1.332(4) |
| | |
| C(24)-H(24)-O(02) | 169.7(2) |
| S(1)-O(02)-H(24) | 130.0(2) |
| O(02)-S(1)-O(01) | 111.5(2) |
| O(02)-S(1)-C(2) | 103.47(19) |
| O(01)-S(1)-C(2) | 101.75(15) |
| C(3)-C(2)-C(7) | 119.5(4) |
| C(3)-C(2)-S(1) | 121.9(3) |
| C(7)-C(2)-S(1) | 118.6(3) |
| C(6)-C(5)-C(51) | 120.6(4) |
| C(4)-C(5)-C(51) | 121.3(4) |
| N(20)-C(24)-N(23) | 108.3(3) |

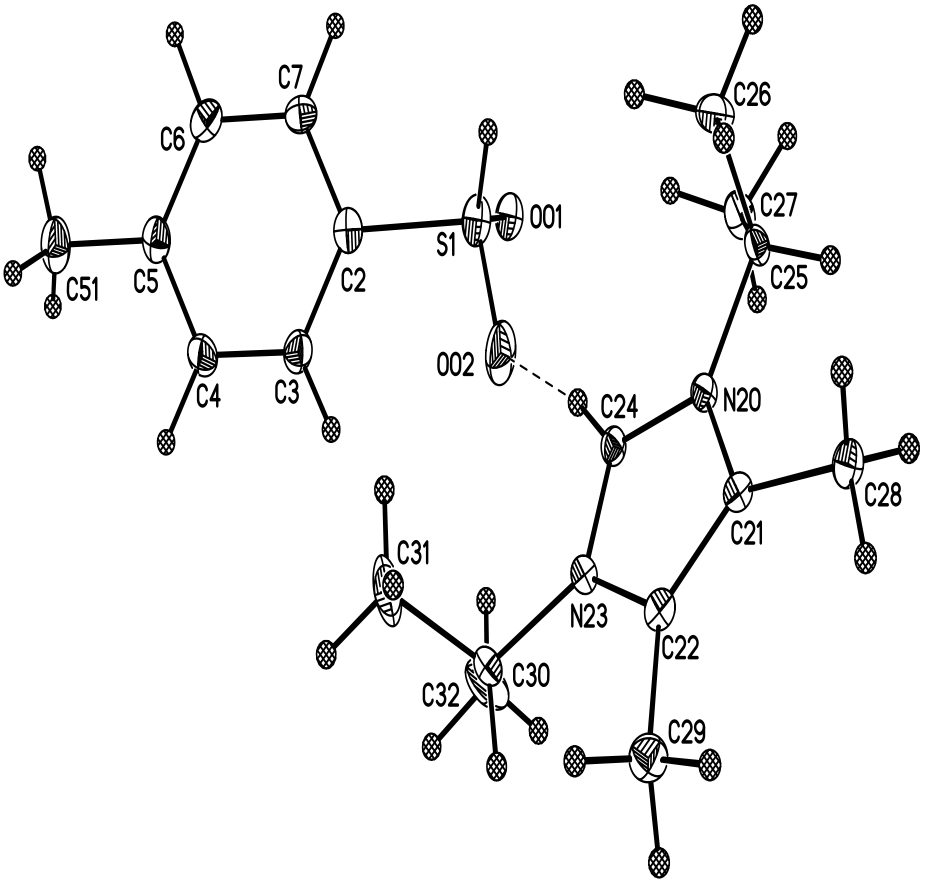
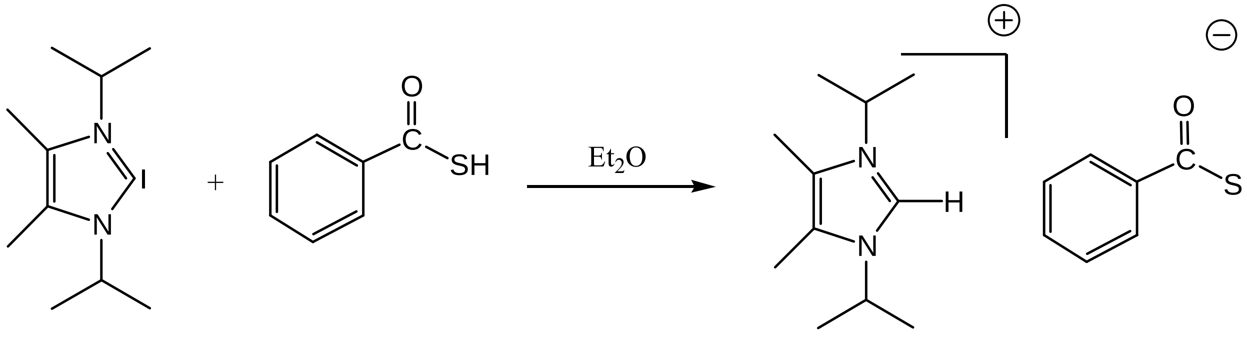


**Figure 15. View of the ion pair of $C_{18}H_{29}N_2O_2S$ (39a) in the crystal.**

### **2.3.6** 1,3-Diisopropyl-4, 5-dimethylimidazolium thiobenzoic acid **(40)**



**11c** **40**

Product **40** was characterized by X-ray crystal structure analysis and it crystallizes in the monoclinic space group $p2_1$/n. The structure of **40** is depicted in figure 16; it reveals the presence of an ion pair linked by C-H…S hydrogen bond [$C_{10}$-$H_{10}$ 0.929, $H_{10}\cdots S_1$ 2.742 Å; $C_{10}$-$H_{10}$-$S_1$ 161.4°]. In addition, there are weak hydrogen interaction between imidazolium-$C_{10}$ and carbonyl O atom [$H_{10}\cdots O_3$ 2.889 Å; $C_{10}$-$H_{10}$-$O_3$ 107.4°]. Selected bond lengths and angles are given in table 11. Several noteworthy features are evident in the X-ray structure of **40**, the $C_2$-$O_3$ and $C_2$-$S_1$ distances of the thiocarboxylate ion are 1.235 Å and 1.724 Å, respectively. The C-O bond length is slightly longer than those of common esters[85] and thioesters,[86] while the C-S distance is somewhat shorter or close compared with those in common thioesters,[87,89] suggesting that the negative charge may be localized on the less electronegative sulfur, rather than on the oxygen atom,[90] although the degree of this localization is likely to be small.[91] The interplanner angles between imidazolium ion and $S_1$-$C_2$-$O_3$ is 51.5°.

**Table 11. Selected bond lengths (Å) and angles (deg) for $C_{18}H_{26}N_2OS$ (40).**

| | |
|---|---|
| H(10)-S(1) | 2.742(3) |
| H(10)-O(3) | 2.889(3) |
| C(2)-O(3) | 1.235(3) |
| C(2)-C(4) | 1.516(4) |
| C(4)-C(9) | 1.379(5) |
| C(4)-C(5) | 1.382(5) |
| C(10)-N(11) | 1.328(4) |
| C(10)-N(14) | 1.328(4) |
| | |
| S(1)-H(10)-C(2) | 84.9(3) |
| O(3)-H(10)-C(2) | 88.2(3) |
| O(3)-H(10)-S(1) | 55.5(3) |
| C(10)-H(10)-S(1) | 161.4(3) |
| C(10)-H(10)-O(3) | 107.4(3) |
| O(3)-C(2)-C(4) | 117.7(3) |
| O(3)-C(2)-S(1) | 124.2(2) |
| C(4)-C(2)-S(1) | 118.0(2) |
| C(9)-C(4)-C(5) | 118.9(4) |
| C(9)-C(4)-C(2) | 122.7(3) |
| C(5)-C(4)-C(2) | 118.4(3) |
| N(11)-C(10)-N(14) | 108.6(3) |

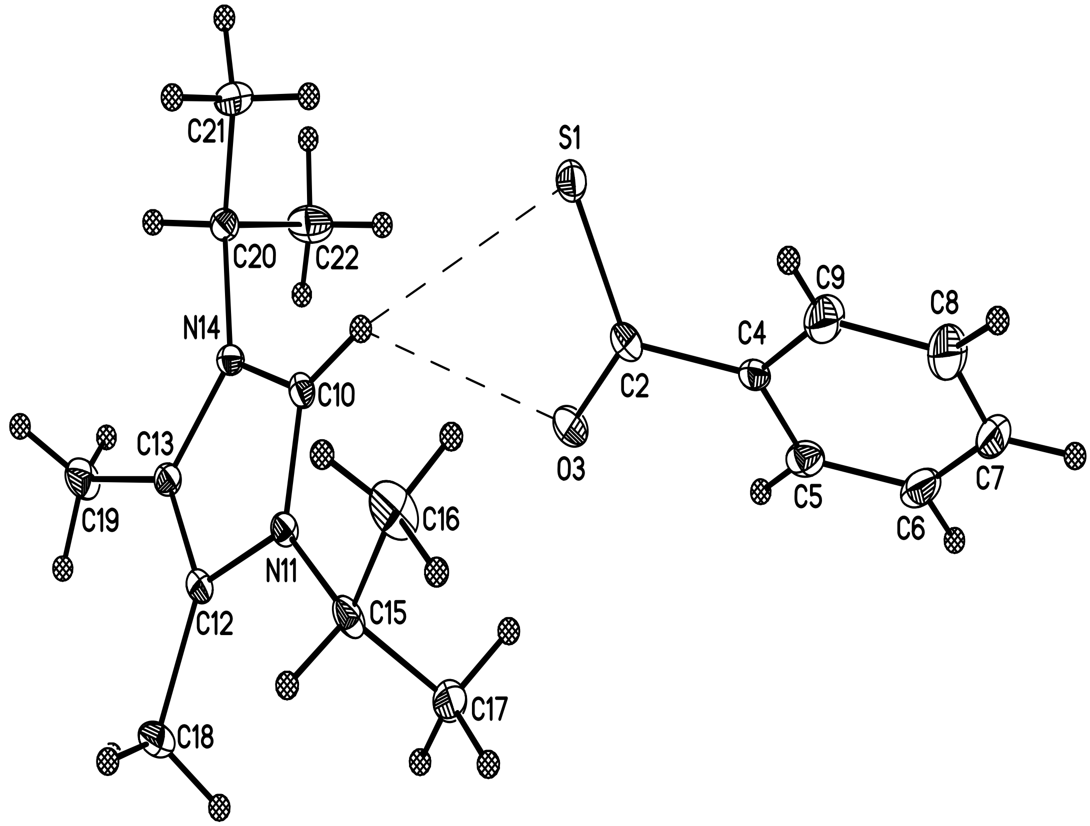
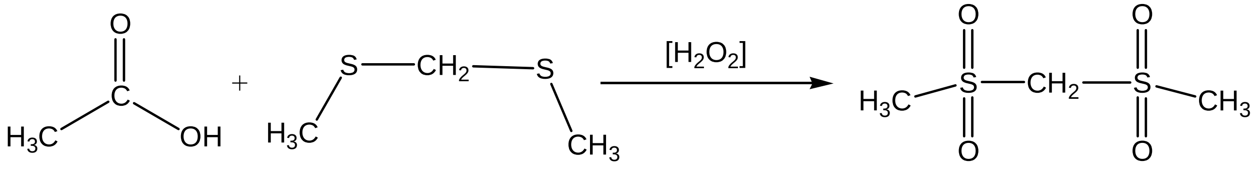


**Figure 16. View of the ion pair of $C_{18}H_{26}N_2OS$ (40) in the crystal.**

### 2.3.7 Bis-methanesulfonyl-methane (41)



**41**

The structure of **41** as determined by X-ray is shown in figure 17. Single crystals were obtained from a $CDCl_3$ solution, the colorless plate crystallizes in the monoclinic space group $p2_1/n$. Selected bond lengths and angles are provided in table 12. Several noteworthy features are evident in the X-ray structure of **41**; the conformation of this compound, with $S_1$ trans to $O_5$ and $S_2$ trans to $C_1$ is very similar to the conformations observed previously in the related bis-sulfones $(PhSO_2Br)_2CH_2$[92] and (4-methoxyphenylsulfonyl) methane.[93] The central C-S distances in **41** [1.756 Å] are very similar to the value in $(PhSO_2)_2CH_2$ [1.786 Å],[94] the $S_2$-$C_3$-$S_1$ angle is 117.20° and the two O-S-O angles are 118.02° at $S_1$ and 117.99° at $S_2$, entirely consistent with all those reported previously.[95,96] furthermore the bond distances between S-O are all equivalent [1.439 Å].

**Table 12. Selected bond lengths (Å) and angles (deg) for $C_3H_8O_4S_2$ (41).**

| | |
|---|---|
| S(1)-O(6) | 1.4398(13) |
| S(1)-O(4) | 1.4397(14) |
| S(1)-C(1) | 1.7563(19) |
| S(1)-C(3) | 1.7889(18) |
| S(2)-O(5) | 1.4386(14) |
| S(2)-O(7) | 1.4416(15) |
| S(2)-C(2) | 1.756(2) |
| S(2)-C(3) | 1.7811(19) |
| | |
| O(6)-S(1)-O(4) | 118.02(8) |
| O(6)-S(1)-C(1) | 108.72(9) |
| O(4)-S(1)-C(1) | 109.82(10) |
| O(6)-S(1)-C(3) | 104.48(8) |
| O(4)-S(1)-C(3) | 109.10(8) |
| C(1)-S(1)-C(3) | 105.96(10) |
| O(7)-S(2)-C(2) | 109.39(11) |
| O(7)-S(2)-C(3) | 105.13(9) |
| C(2)-S(2)-C(3) | 104.87(10) |
| S(2)-C(3)-S(1) | 117.20(10) |

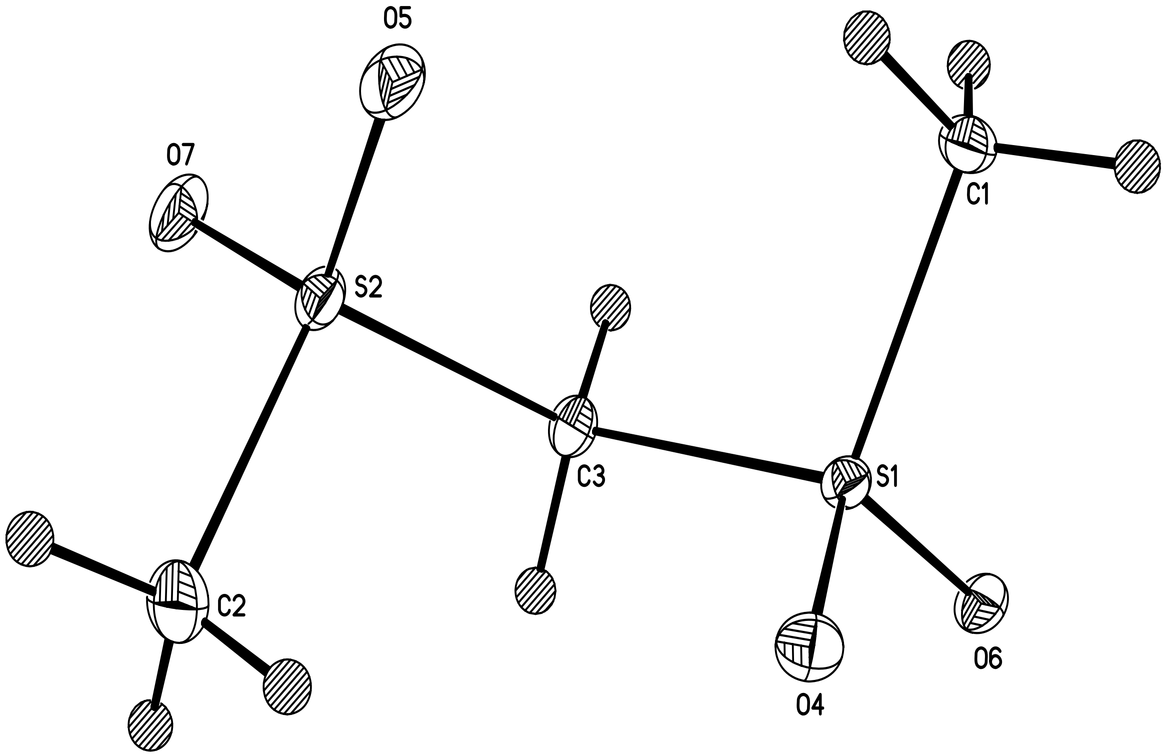
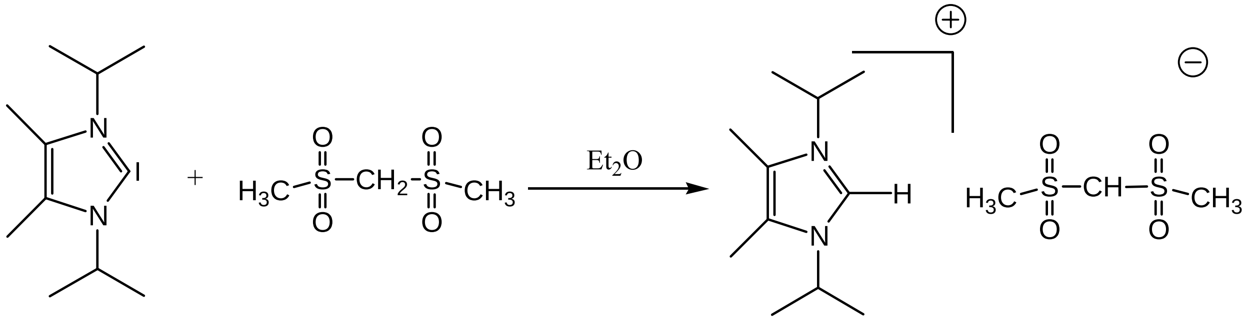


**Figure 17. The crystal structure of $C_3H_8O_4S_2$ (41).**

### **2.3.8** 1,3-Diisopropyl-4,5-dimethylimidazolium bis-methanesulfonyl-methane **(42)**



**11c** **41** **42**

All attempts to get single crystals from **42** were failed due to the very low stability of the salt and high sensitivity toward the moisture. The structure of **42** can be assigned obviously from the NMR spectroscopy, as shown in figure 19, the $^{13}$C spectra of the methyl signal for the anion of **42** ($\delta$ = 46.53 ppm), is downfield, while the CH signal ($\delta$ = 63.01 ppm) is up field, with respect to those found in **41** ($\delta$ = 41.40 ppm and $\delta$ = 70.26 ppm) respectively (figure 18). The $^{1}$H and $^{13}$C NMR spectra exhibit also the signals of the imidazolium ion in **42**. The similar chemical shift for CH of the anion in **42** have been observed after deprotonation of bis (phenylsulfonyl) methane with methyl lithium.[97] On the other hand, the corresponding imidazolium acetylacetonate (acac) salt shows a significant downfield chemical shift in $^{13}$C spectra for the $CH_{acac}$ ($\delta$ = 101.70 ppm) [98] comparing with the $CH_{sulfone}$ ($\delta$ = 63.01 ppm) in **42**, this difference in the chemical shift might be attributed to the influence of the sulfur and oxygen atoms.

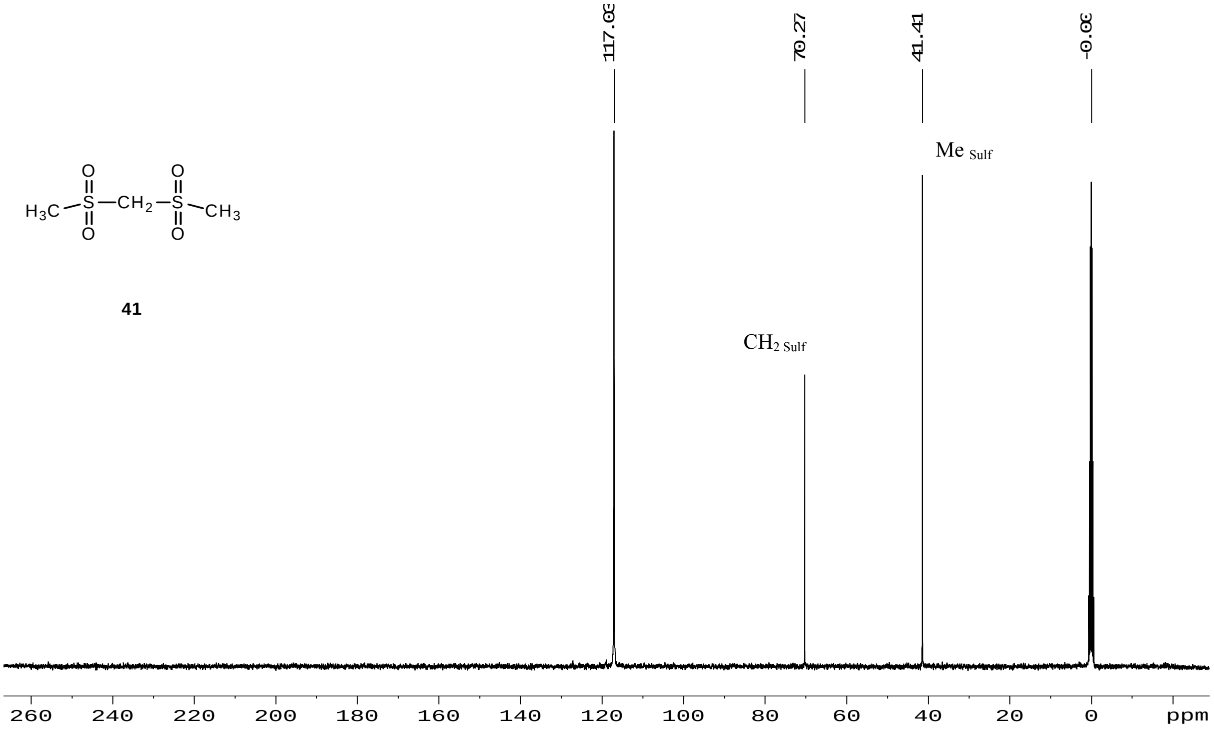


**Figure 18.** $^{13}$C NMR spectra of $C_3H_8O_4S_2$ (41) in $CD_3CN$ at 100 MHz.

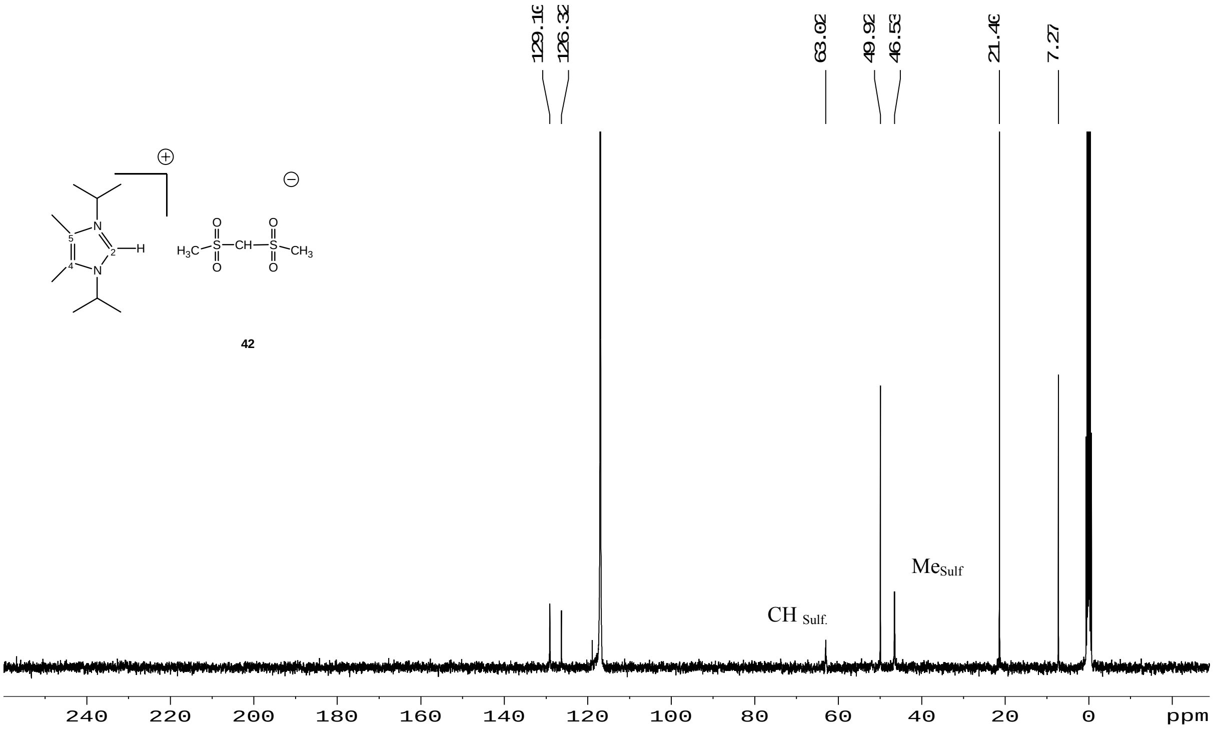


**Figure 19.** $^{13}$C NMR spectra of $C_{14}H_{28}N_2O_4S_2$ (42) in $CD_3CN$ at 100 MHz.

# Experimental 3

# Section

# 3. Experimental Section

## 3.1 Methods of analysis

### 3.1.1 Elemental analysis

The elemental analyses were measured by elemental analyzers from Carlo Erba Company, Model 1106 and HEKAtech GmbH. The accuracy was attached:

| | |
|---|---|
| Carbon: | ± 0.5% |
| Hydrogen: | ± 0.5% |
| Nitrogen: | ± 0.5% |
| Sulfur: | ± 0.5% |

### 3.1.2 Mass spectra

Mass spectra were recorded on a Finnigan Triple-Stage-Quadrupol spectrometer (TSQ-70) from Finnigan-Mat. High-resolution mass spectra were measured on a modified AMD Inectra MAT 711 A and reported as mass / charge (*m/z*). The used mass spectrometric ionization methods were electron-impact (EI) by 70 eV at 200°C or Fast-atom bombardment (FAB) by 70 eV in Nitrobenzylalcohol-Matrix at 60°C.

### 3.1.3 NMR spectra

The high resolution NMR spectra were acquired by a Bruker DRX 400 NMR spectrometer which operated at 400.13 MHz for $^{1}H$, 100.61 MHz for $^{13}C$ and 161.98 MHz for $^{19}F$ nuclei, respectively. The spectra were measured relative to TMS ($^{1}H$, $^{13}C$) and $CCl_3F$ ($^{19}F$) as an internal standards. All experiments were performed at 25 ºC. Data are reported as follows: chemical shift (multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, *J* = coupling constant (Hz) in italic form).

### 3.1.4 Crystal structure analyses

The crystals were mounted on a glass fiber with epoxy cement at room temperature. Preliminary examination and data collection were performed with a Stoe IPDS 2 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares on $F^2$ using SHELXS-97,[106] SHELXL-97[106] and SHELXTL V5.1 (NT).

### 3.2 Solvents

The solvents needed for the reactions were dried by conventional procedures and were stored over molecular sieves under argon.

### 3.3 Starting materials

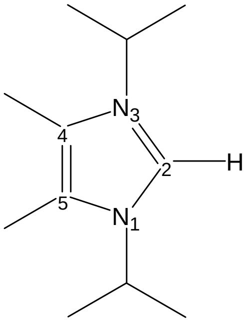
Air sensitive compounds were prepared and handled under argon by Schlenk techniques. The chemicals were purchased from the firms Adrich, Alfa Aesar, Fluka, Sigma-Aldrich and Merck. All chemicals were of reagent grade quality from commercial sources and were used without further purification. Compounds that are not described in the experimental part were synthesized according to a literature**.**

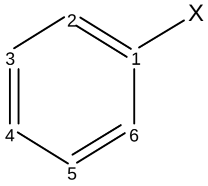
### 3.4 General comments

All reactions were carried out under an atmosphere of dry argon by using standard schlenk technique.

### 3.5 Numbering of the compounds

The compounds that analyzed by NMR spectroscopy are numbered as following:





X= O, S, Im

## 3.6 Preparation of the compounds

### **3.6.1** Synthesis of 1,3-diisopropyl-4,5-dimethyl-2,2-(pentafluorophenylimidazolium) tetrafluoroborate **(26)**

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.490 g, 2.72 mmol) in 35 mL $Et_2O$, hexafluoro benzene (0.157 ml, 1.36 mmol) was added at -70 °C and stirring overnight at room temperature, then trifluoroborate (ether complex) (0.172 ml, 1.36 mmol) was added drop-wise, then the mixture was stirred for 4 h at room temperature, the resulting precipitate was isolated, washed with $Et_2O$ and dried in vacuo. Yield: 0.928 g (56%). This solid was recrystallized from $CH_3CN$/ $Et_2O$ as needle crystals.

**$^1$H NMR ($CD_2Cl_2$):** $\delta$ = 1.52 (d, 12H, 1,3-CH*Me*$_2$, $^3$J = 6.72 Hz), 2.41 (s, 6H,4,5-Me), 4.61 (sept, 2H, 1,3-C*H*Me$_2$).

**$^{13}$C{$^1$H} NMR ($CD_2Cl_2$)**: $\delta$ = 8.96 (4,5-Me), 19.28 (1,3-CH*Me*$_2$), 52.88 (1,3-CHMe$_2$), 106.42 ($C_{Ph}^{1,4}$), 143.05, 145.59 ($C_{Ph}^{2,3,5,6}$), 126.15 ($C_{Im}^{2}$), 129.10 ($C_{Im}^{4,5}$).

**$^{19}$F{$^1$H} NMR ($CD_2Cl_2$):** $\delta$ = -153.41($BF_4$), -131.98 ($F^{1,2,3,4}$).

**$^{11}$B{$^1$H} NMR ($CD_2Cl_2$):** $\delta$ = -1.41 ($BF_4$).

**Anal. Calcd**. for $C_{28}H_{40}B_2F_{12}N_4$ (682.20 g/mol): (C, 49.29; H, 5.91; N, 8.21) %.

**Found** for $C_{28}H_{40}B_2F_{12}N_4$: (C, 49.19; H, 6.24; N, 7.84) %.

**MS (FAB pos.):** m/z (%) = 505 [10].

**MS (FAB neg.):** m/z (%) = 86.7 [100].

### **3.6.2** Synthesis of 1,3-diisopropyl-4,5-dimethyl-2-pentafluorophenylimidazolium tetrafluoroborate **(27)**

To a solution containing hexafluoro benzene (2.00 ml, 17.33 mmol) in 35 mL $Et_2O$, 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.460 g, 2.55 mmol) was added at -70 °C and stirring overnight at room temperature, trifluoroborate (ether complex) (0.32 ml, 2.77 mmol) was added drop-wise, then the mixture was stirred for 4 h at room temperature, the resulting precipitate was isolated, washed with $Et_2O$ and dried in vacuo.Yield: 0.860 g (78.10%). This solid was recrystallized from $CH_3CN$/ $Et_2O$ as plate crystals. .

**$^1$H NMR ($CD_3CN$):** $\delta$ = 1.36 (d, 12H, 1,3-CH*Me*$_2$, $^3$J = 6.62 Hz), 2.33 (s, 6H,4,5-Me), 4.37 (sept, 2H, 1,3-C*H*Me$_2$).

**$^{13}$C{$^1$H} NMR ($CD_3CN$)**: $\delta$ = 9.25 (4,5-Me), 20.04 (1,3-CH*Me*$_2$), 52.85 (1,3-CHMe$_2$), 98.86 ($C_{Ph}^{1}$), 136.63, 144.20 ($C_{Ph}^{2,6}$), 139.85 ($C_{Ph}^{4}$), 146.74 ($C_{Ph}^{3,5}$), 126.39 ($C_{Im}^{2}$), 130.30 ($C_{Im}^{4,5}$).

**$^{19}$F{$^1$H} NMR (CD$_3$CN):** $\delta$ = -152.14 (BF$_4$), -135.68, -146.99, -159.82 (F$^{1,2,3,4}$).

**$^{11}$B{$^1$H} NMR (CD$_3$CN):** $\delta$ = -1.38 (BF$_4$).

**Anal. Calcd**. for $C_{17}H_{20}BF_9N_2$ (434.15 g/mol): (C, 47.03; H, 4.64; N, 6.45) %.

**Found** for $C_{17}H_{20}BF_9N_2$: (C, 47.03; H, 4.81; N, 5.76) %.

**MS (FAB pos.):** m/z (%) = 347.1 [100].

**MS (FAB neg.):** m/z (%) = 86.7 [100].

### **3.6.3** Synthesis of 4-(1,3-diisopropyl-4,5-dimethylimidazolium)-2,5,6-trifluoro-isophthalonitrile tetrafluoroborate **(28)**

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.461 g, 2.56 mmol) in 35 mL Et$_2$O, tetrafluoroisophthalonitrile (0.511 g, 2.55 mmol) was added at -70 $^o$C and stirring overnight at room temperature, trifluoroborate (ether complex) (0.323 ml, 2.79 mmol) was added drop-wise, then the mixture was stirred for 4 h at room temperature, the resulting precipitate was isolated, washed with Et$_2$O and dried in vacuo. Yield: 0.980 g (86%). This solid was recrystallized from CH$_3$CN/ Et$_2$O as colorless crystals.

**$^1$H NMR (CD$_3$CN):** $\delta$ = 1.37 (d, 12H, 1,3-CH*Me*$_2$, $^3$J = 6.66 Hz), 2.37 (s, 6H, 4,5-Me), 4.33 (sept, 2H, 1,3-C*H*Me$_2$).

**$^{13}$C{$^1$H} NMR (CD$_3$CN)**: $\delta$ = 9.47 (4,5-Me), 20.18 (1,3-CH*Me*$_2$), 53.58 (1,3 CHMe$_2$), 99.70 (C$_{Ph}$$^6$), 101.12 (C$_{Ph}$$^4$), 106.04, 108.93 (CN), 120.10 (C$_{Ph}$$^1$), 145.64, 148.18 (C$_{Ph}$$^2$), 154.16, 156.79 (C$_{Ph}$$^3$), 159.37, 162.06 (C$_{Ph}$$^5$), 127.37 (C$_{Im}$$^2$), 131.18 (C$_{Im}$$^{4,5}$).

**$^{19}$F{$^1$H} NMR (CD$_3$CN):** $\delta$ = -152.44 (BF$_4$), -99.27, -112.13, -129.50 (F$^{1,2,3}$).

**$^{11}$B{$^1$H} NMR (CD$_3$CN):** $\delta$ = -1.34 (BF$_4$).

**Anal. Calcd**. for $C_{19}H_{20}BF_7N_4$ (448.18 g/mol): (C, 50.92; H, 4.50; N, 12.50) %.

**Found** for $C_{19}H_{20}BF_7N_4$: (C, 50.60; H, 4.48; N, 11.63) %.

**MS (FAB pos.):** m/z (%) = 361.1 [100].

**MS(FAB neg.):** m/z (%) = 86.8 [100].

### 3.6.4 Synthesis of 4-(1,3-diisopropyl-4,5-dimethylimidazolium)-2,3,5,6-tetrafluoro-benzonitrile tetrafluoroborate (29)

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.370 g, 2.05 mmol) in 35 mL $Et_2O$, pentafluorobenzonitrile (0.246 ml, 2.04 mmol) was added at -70 $^oC$ and stirring overnight at room temperature, trifluoroborate (ether complex) (0.260 ml, 2.24 mmol) was added drop-wise, then the mixture was stirred for 4 h at room temperature, the resulting precipitate was isolated, washed with $Et_2O$ and dried in vacuo. Yield: 0.780 g (86%). This solid was recrystallized from $CH_3CN$/ $Et_2O$ as plate crystals.

**$^1$H NMR ($CD_3CN$):** $\delta$= 1.58 (d, 12H, 1,3-CH*Me*$_2$, $^3J$ = 6.73 Hz), 2.55 (s, 6H,4,5-Me), 4.57 (sept, 2H,1,3-C*H*Me$_2$).

**$^{13}C\{^1H\}$ NMR ($CD_3CN$)**: $\delta$ = 9.31 (4,5-Me), 20.03 (1,3-CH*Me*$_2$), 53.14 (1,3 CHMe$_2$), 99.07 ($C_{Ph}^4$), 106.60 ($C_{Ph}^1$), 108.64 (CN), 143.54, 146.21($C_{Ph}^{2,6}$), 146.54, 149.31 ($C_{Ph}^{3,5}$), 128.64 ($C_{Im}^2$), 130.81 ($C_{Im}^{4,5}$).

**$^{19}F\{^1H\}$ NMR ($CD_3CN$):** $\delta$ = -152.24 ($BF_4$), -130.50, -133.06 ($F^{1,2,3,4}$).

**$^{11}B\{^1H\}$ NMR ($CD_3CN$):** $\delta$ = -1.33 ($BF_4$).

**Anal. Calcd**. for $C_{18}H_{20}BF_8N_3$ (441.17 g/mol): (C, 49.00; H, 4.57; N, 9.52) %.

**Found** for $C_{18}H_{20}BF_8N_3$: (C, 49.48; H, 4.60; N, 9.89) %.

**MS (FAB pos.):** m/z (%) = 354.20 [100].

**MS(FAB neg.):** m/z (%) = 87.00 [100].

### 3.6.5 Synthesis of 2-(1,3-diisopropyl-4,5-dimethylimidazolium)-4, 6-difluoro-[1, 3, 5] triazine tetrafluoroborate (30)

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.475 g, 2.63 mmol) in 35 mL $Et_2O$, cyanuric trifluoride (0.22 ml, 2.61 mmol) was added at -70 $^oC$ and stirring overnight at room temperature, trifluoroborate (ether complex) (0.334 ml, 2.91 mmol) was added drop-wise, then the mixture was stirred for 4 h at room temperature, the resulting precipitate was isolated, washed with $Et_2O$ and dried in vacuo. Yield: 0.850 g (85%). This solid was recrystallized from $CH_3CN$/ $Et_2O$ as needle crystals.

**$^1$H NMR ($CD_3CN$):**$\delta$ = 1.42 (d, 12H, 1,3-CH*Me*$_2$, $^3J$ = 6.72 Hz), 2.32 (s, 6H, 4,5-Me), 4.80 (sept, 2H, 1,3-C*H*Me$_2$).

**$^{13}C\{^1H\}$ NMR ($CD_3CN$)**: $\delta$ = 9.70 (4,5-Me), 19.94 (1,3-CH*Me*$_2$), 52.96 (1,3CHMe$_2$), 167.00 ($C_{Im-triaz}^{1}$), 170.55, 172.91 ($C_{triaz}^{3,5}$), 129.09 ($C_{Im}^{2}$), 130.79 ($C_{Im}^{4,5}$).

**$^{19}F\{^1H\}$ NMR ($CD_3CN$):** $\delta$ = -152.07 ($BF_4$), -33.45 ($F^{1,2}$).

**$^{11}B\{^1H\}$ NMR ($CD_3CN$):** $\delta$ = -1.34 ($BF_4$).

**Anal. Calcd**. for $C_{14}H_{20}BF_6N_5$ (383.14 g/mol): (C, 43.89; H, 5.26; N, 18.28) %.

**Found** for $C_{14}H_{20}BF_6N_5$: (C, 43.93; H, 5.60; N, 18.04) %.

**MS (FAB pos.):** m/z (%) = 296 [100].

**MS(FAB neg.):** m/z(%) = 86.9 [100].

### **3.6.6** Synthesis of 1,3-diisopropyl-4,5-dimethylimidazolium phenolate **(31)**

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.465 g, 2.58 mmol) in 30 mL $Et_2O$, phenol (0.243 g, 2.58 mmol) was added at -50 °C. After stirring overnight at room temperature, the precipitate was filtered off, washed with $Et_2O$ and dried in vacuo. Yield: 0.670 g (95%). This solid was recrystallized from $CH_3CN$/ $Et_2O$ as colorless crystals.

**$^1H$ NMR ($CD_2Cl_2$):** $\delta$ = 1.58 (d, 12H, 1,3-CH*Me*$_2$, $^3J$ = 6.80 Hz), 2.15 (s, 6H, 4,5-Me), 4.41 (sept, 2H, 1,3-C*H*Me$_2$), 7.01-7.22 (m, 5 H, Ph), 10.58 (s, 1 H, $C_{Im}^{2}$).

**$^{13}C\{^1H\}$ NMR ($CD_2Cl_2$)**: $\delta$ = 7.70 (4,5-Me), 21.88 (1,3-CH*Me*$_2$), 50.19 (1,3-CHMe$_2$), 115.59 ($C_{Ph}^{4}$), 121.60 ($C_{Ph}^{2,6}$), 128.76 ($C_{Ph}^{3,5}$), 156.15 ($C_{Ph}^{1}$), 124.77 ($C_{Im}^{2}$), 133.16 ($C_{Im}^{4,5}$).

**Anal. Calcd**. for $C_{17}H_{26}N_2O$ (274.40 g/mol): (C, 74.41; H, 9.55; N, 10.21) %.

**Found** for $C_{17}H_{26}N_2O$: (C, 75.25; H, 10.07; N, 10.21) %.

**MS (FAB neg.):** m/z (%) = 93 [100].

### **3.6.7** Synthesis of 1,3-diisopropyl-4,5-dimethylimidazolium 2,3,4,5,6-pentachloro phenolate **(32)**

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.560 g, 3.11 mmol) in 30 mL $Et_2O$, pentachlorophenol (0.828 g, 3.10 mmol) was added at -50 $^oC$. After stirring overnight at room temperature, the precipitate was filtered off, washed with $Et_2O$ and dried in vacuo. Yield: 1.27 g (91%). This solid was recrystallized from $CH_3CN$/ $Et_2O$ as colorless crystals.

**$^1$H NMR ($CDCl_3$):** $\delta$ = 1.49 (d, 12H,1,3-CH*Me*$_2$, $^3$J = 6.80 Hz), 2.15 (s, 6H,4,5-Me), 4.41(sept,2H,1,3-C*H*Me$_2$), 10.37 (s, 1 H, $C_{Im}^2$).

**$^{13}$C{$^1$H} NMR ($CDCl_3$)**: $\delta$ = 8.73 (4,5-Me), 22.39 (1,3-CH*Me*$_2$), 51.16 (1,3-CHMe$_2$), 108.89($C_{Ph}^4$), 122.11($C_{Ph}^{2,6}$), 129.15 ($C_{Ph}^{3,5}$), 161.43 ($C_{Ph}^1$), 125.77 ($C_{Im}^2$), 134.25 ($C_{Im}^{4,5}$).

**Anal. Calcd**. for $C_{17}H_{21}Cl_5N_2O$ (446.62 g/mol): (C, 45.72; H, 4.74; N, 6.27) %.

**Found** for $C_{17}H_{21}Cl_5N_2O$: (C, 45.87; H, 4.51; N, 6.21) %.

**MS (FAB neg.):** m/z (%) = 264.7 [100].

### **3.6.8** Synthesis of 1,3-diisopropyl-4,5-dimethylimidazolium 2, 3, 4, 5,6-pentafluoro phenolate **(33)**

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.547 g, 3.03 mmol) in 30 mL $Et_2O$, pentafluorophenol (0.560 g, 3.04 mmol) was added at -50 $^oC$. After stirring overnight at room temperature, the precipitate was filtered off, washed with $Et_2O$ and dried in vacuo. Yield: 0.920 g (84%). This solid was recrystallized from $CH_3CN$/ $Et_2O$ as colorless crystals.

**$^1$H NMR ($CD_3CN$):** $\delta$ = 1.50 (d, 12H, 1,3-CH*Me*$_2$, $^3$J = 6.72 Hz), 2.23 (s, 6H,4,5-Me), 4.49 (sept, 2H,1,3-C*H*Me$_2$), 9.34 (s, 1 H, $C_{Im}^2$).

**$^{13}$C{$^1$H} NMR ($CD_3CN$)**: $\delta$ = 7.24 (4,5-Me), 21.40 (1,3-CH*Me*$_2$), 49.89 (1,3-CHMe$_2$), 137.70 ($C_{Ph}^4$), 140.08 ($C_{Ph}^{2,6}$), 142.39 ($C_{Ph}^{3,5}$), 147.60 ($C_{Ph}^1$), 125.94 ($C_{Im}^2$), 130.90 ($C_{Im}^{4,5}$).

**$^{19}$F{$^1$H} NMR ($CD_3CN$):** $\delta$ = -173.51, -196.84, -196.90.

**Anal. Calcd**. for $C_{17}H_{21}F_5N_2O$ (364.35 g/mol): (C, 56.04; H, 5.81; N, 7.69) %.

**Found** for $C_{17}H_{21}Cl_5N_2O$: (C, 55.42; H, 5.59; N, 7.31) %.

**MS (FAB neg.):** m/z (%) = 182.9 [100].

### **3.6.9** Synthesis of 1,3-diisopropyl-4,5-dimethylimidazolium 4-pyridinolate **(34)**

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.680 g, 3.77 mmol) in 30 mL $Et_2O$, 4-hydroxy pyridine (0.360 g, 3.79 mmol) was added at -50 $^oC$. After stirring overnight at room temperature, the precipitate was filtered off, washed with $Et_2O$ and dried in vacuo. Yield: 0.550 g (55%). This solid was recrystallized from $CH_3CN$/ $Et_2O$ as colorless crystals.

**$^1$H NMR ($CD_3CN$):** $\delta$ = 1.55(d, 12H,1,3-CH*Me*$_2$, $^3J$ = 6.68 Hz), 2.22 (s, 6H,4,5-Me), 4.48 (sept, 2H,1,3-C*H*Me$_2$), 6.00-7.64 (m, 4H, $C_6H_4NO$), 9.86 (s, 1 H, $C_{Im}^2$).

**$^{13}$C{$^1$H} NMR ($CD_3CN$)**: $\delta$ = 7.29 (4,5-Me), 21.51 (1,3-CH*Me*$_2$), 49.82(1,3-CHMe$_2$), 116.22 ($C_{Py}^{3,5}$), 148.93 ($C_{Py}^{2,6}$), 176.04 ($C_{Py}^1$), 125.72 ($C_{Im}^2$), 131.77 ($C_{Im}^{4,5}$).

**Anal. Calcd**. for $C_{16}H_{25}N_3O$ (275.39 g/mol): (C, 69.78; H, 9.15; N, 15.26) %.

**Found** for $C_{16}H_{25}N_3O$: (C, 67.77; H, 9.63; N, 14.77) %.

**MS (FAB neg.):** m/z (%) = 93.9 [100].

### **3.6.10** Synthesis of 1,3-diisopropyl-4,5-imidazole-2-thione **(35)**

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.400 g, 2.22 mmol) in 30 mL $Et_2O$, methyl phenyl disulfide (0.302 ml, 2.23 mmol) was added at room temperature. After stirring overnight, the solution was kept to stand at -35 $^oC$ for 24 h, a white crystals was formed, filtered off and dried in vacuo. Yield: 0.250 g (53%).

**$^1$H NMR ($CDCl_3$):** $\delta$ = 1.37 (d, 12H, 1,3-CH*Me*$_2$, $^3J$ = 6.65 Hz), 2.11 (s, 6H, 4,5-Me) ,5.60 (sept, 2H, 1,3-C*H*Me$_2$), 7.24 (m,3 H, Ph), 8.16 (d, 2 H, Ph), 10.13 (s, 1 H, $C_{Im}^2$).

**$^{13}$C{$^1$H} NMR ($CDCl_3$)**: $\delta$ = 10.29 (4,5-Me), 20.70 (1,3-CH*Me*$_2$), 49.30 (1,3-CHMe$_2$), 159.81 (CS), 121.40 ($C_{Im}^{4,5}$).

**Anal. Calcd**. for $C_{11}H_{20}N_2S$ (212.20 g/mol): (C, 62.22; H, 9.49; N, 13.19; S, 15.10) %.

**Found** for $C_{11}H_{20}N_2S$: (C, 62.56; H, 9.39; N, 12.99; S, 15.11) %.

**MS (EI):** m/z (%) = 212.2 [40].

**3.6.11** Synthesis of 1,3-diisopropyl-4,5-dimethyl-2-phenylsulfanylimidazoium benzenethiol **(36)**

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.240 g, 1.33 mmol) in 30 mL $Et_2O$, diphenyl disulfide (0.290 g, 1.33 mmol) was added at -50 $^oC$. After stirring overnight at room temperature, the precipitate was filtered off, washed with $Et_2O$ and dried in vacuo. Yield: 0.350 g (66%).

**$^1$H NMR ($CDCl_3$):** $\delta$ = 1.58 (d, 12H, 1,3-CH*Me*$_2$, $^3$J = 6.80 Hz), 2.19 (s, 6H,4,5-Me) ,4.44 (sept, 2H, 1,3-C*H*Me$_2$), 7.39 (m, 3 H, Ph), 7.70 (d, 2 H, Ph).

**$^{13}$C{$^1$H} NMR ($CDCl_3$)**: $\delta$ = 8.77 (4,5-Me), 22.80 (1,3-CH*Me*$_2$), 51.06 (1,3-CHMe$_2$), 125.48 ($C_{Ph}{}^4$), 127.13 ($C_{Im\text{-}Ph}{}^{2,6}$), 127.42 ($C_{Ph}{}^{3,5}$), 128.36 ($CS_{Im\text{-}Ph}$), 129.01 ($C_{Ph}{}^{2,6}$), 129.21 ($C_{Im\text{-}Ph}{}^{3,5}$), 137.25 ($CS_{Ph}$), 132.80 ($C_{Im}{}^2$),131.70 ($C_{Im}{}^{4,5}$).

**Anal. Calcd**. for $C_{23}H_{30}N_2S_2$ (398.63 g/mol): (C, 68.35; H, 7.82; N, 7.25; S, 16.59) %.

**Found** for $C_{23}H_{30}N_2S_2$: (C, 68.56; H, 7.42; N, 6.91; S, 16.54) %.

**MS (FAB pos.):** m/z (%) = 289.1 [100].

**MS (FAB neg.):** m/z (%) = 108.8 [60].

**3.6.12** Synthesis of 1,3-diisopropyl-4,5-dimethylimidazolium benzenesulfonic acid **(37)**

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.300 g, 1.66 mmol) in 30 mL $Et_2O$, benzenesulfonic acid (0.264 g, 1.66 mmol) was added at -50 $^oC$. After stirring overnight at room temperature, the precipitate was filtered off, washed with $Et_2O$ and dried in vacuo. Yield: 0.415 g (74%). This solid was recrystallized from Acetone/ $Et_2O$ as colorless crystals.

**$^1$H NMR ($CD_2Cl_2$):** $\delta$ = 1.48 (d, 12H, 1,3-CH*Me*$_2$, $^3$J = 6.67 Hz), 2.14 (s, 6H, 4,5-Me), 4.36 (sept, 2H, 1,3-C*H*Me$_2$), 7.24, 7.71 (m, 5 H, Ph), 9.39 (s, 1 H, $C_{Im}{}^2$).

**$^{13}$C{$^1$H} NMR ($CD_2Cl_2$)**: $\delta$ = 8.78 (4,5-Me), 22.56 (1,3-CH*Me*$_2$), 51.35 (1,3-CHMe$_2$), 126.24 ($C_{Ph}{}^{3,5}$), 126.38 ($C_{Ph}{}^{2,6}$), 128.15 ($C_{Ph}{}^4$), 148.14 (CS), 129.15 ($C_{Im}{}^2$), 132.65 ($C_{Im}{}^{4,5}$).

**Anal. Calcd**. for $C_{17}H_{26}N_2O_3S$ (338.46 g/mol): (C, 60.33; H, 7.74; N, 8.28; S, 9.47) %.

**Found** for $C_{17}H_{26}N_2O_3S$: (C, 59.97; H, 8.36; N, 8.21; S, 9.67) %.

**MS (FAB neg.):** m/z (%) = 156.9 [100].

### 3.6.13 Synthesis of 1, 3-diisopropyl-4, 5-dimethylimidazolium oxalic acid monomethyl ester **(38)**

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.480 g, 2.66 mmol) in 30 mL $Et_2O$, monohydrated dimethyl oxalate (0.157 g, 1.32 mmol) was added at -50 °C and stirring overnight at room temperature, insoluble crude product was filtered off, washed with $Et_2O$ and dried in vacuo. Yield: 0.196 g (52%). This solid was recrystallized from Acetone/ $Et_2O$ as colorless crystals.

**$^1$H NMR ($CD_3CN$):** $\delta$ = 1.51 (d, 12H, 1,3-CH*Me*$_2$, $^3J$ = 6.72 Hz), 2.24 (s, 6H, 4,5-Me), 4.51 (sept, 2H, 1,3-C*H*Me$_2$), 3.58 ($OCH_3$), 9.27 (s, 1 H, $C_{Im}^2$).

**$^{13}C\{^1H\}$ NMR ($CD_3CN$)**: $\delta$ = 7.27 (4,5-Me), 21.45 (1,3-CH*Me*$_2$) , 49.90 (1,3-CHMe$_2$), 49.34 ($OCH_3$) , 162.97 (CO), 167.91 (CO), 125.88 ($C_{Im}^2$), 130.89 ($C_{Im}^{4,5}$).

**Anal. Calcd**. for $C_{14}H_{24}N_2O_4$ (284.35 g/mol): (C, 59.13; H, 8.51; N, 9.85) %.

**Found** for $C_{14}H_{24}N_2O_4$: (C, 59.10; H, 8.61; N, 9.06) %.

**MS (FAB neg.):** m/z (%) = 102.9 [100].

### 3.6.14 Synthesis of 1,3-diisopropyl-4, 5-dimethylimidazolium 4-methylbenzenethiolate **(39)**

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.362 g, 2.01 mmol) in 30 mL $Et_2O$, 4-Methylbenzenethiol (0.250 g, 2.01 mmol) was added at -50 °C and stirring overnight at room temperature, insoluble crude product was filtered off, washed with $Et_2O$ and dried in vacuo. Yield: 0.500 g (74%). This solid was recrystallized from Acetone/ $Et_2O$ as colorless crystals.

**$^1$H NMR ($CD_2Cl_2$):** $\delta$ = 1.67 (d, 12H, 1,3-CH*Me*$_2$, $^3J$ = 6.71 Hz), 2.25 (s, 6H, 4,5-Me), 4.50 (sept, 2H, 1,3-C*H*Me$_2$), 2.32 (PhC*H*$_3$), 7.14 (d,2 H, $C_{Ph}^{3,5}$), 7.29 (d,2 H, $C_{Ph}^{2,6}$), 10.67 (s, 1 H, $C_{Im}^2$).

**$^{13}C\{^1H\}$ NMR ($CD_2Cl_2$)**: $\delta$ = 8.84 (4,5-Me) , 23.01 (1,3-CH*Me*$_2$), 51.30 (1,3-CHMe$_2$), 21.15 (Ph*CH*$_3$), 130.07 ($C_{Ph}^{2,6}$), 131.60 ($C_{Ph}^{3,5}$), 137.81 ($C_{Ph}^1$), 138.89 ($C_{Ph}^4$), 130.34 ($C_{Im}^2$), 134.29 ($C_{Im}^{4,5}$).

**Anal. Calcd**. for $C_{18}H_{28}N_2S$ (304.49 g/mol): (C, 71.00; H, 9.27; N, 9.20; S, 10.53) %.

**Found** for $C_{18}H_{28}N_2S$: (C, 71.65; H, 9.89; N, 8.81; S, 10.68) %.

**MS (FAB neg.):** m/z (%) = 123.0 [100].

**3.6.15** Synthesis of 1,3-diisopropyl-4, 5-dimethylimidazolium thiobenzoic acid **(40)**

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.485 g, 2.69 mmol) in 30 mL $Et_2O$, thiobenzoic acid (0.315 ml, 2.68 mmol) was added at -50 $^{o}$C. After stirring overnight at room temperature, the precipitate was filtered off, washed with $Et_2O$ and dried in vacuo. Yield: 0.750 g (87%). This solid was recrystallized from Acetone/ $Et_2O$ as colorless crystals.

**$^{1}$H NMR ($CDCl_3$):** $\delta$ = 1.57 (d, 12H, 1,3-CH*Me*$_2$, $^{3}$J = 6.73 Hz), 2.17 (s, 6H, 4,5-Me), 4.45 (sept, 2H,1,3-C*H*Me$_2$), 7.24 (m,3 H, Ph), 8.16 (d, 2 H, Ph), 10.13 (s, 1 H, $C_{Im}^{2}$).

**$^{13}$C{$^{1}$H} NMR ($CDCl_3$)**: $\delta$ = 8.71 (4,5-Me), 22.42 (1,3-CH*Me*$_2$), 51.17 (1,3-CHMe$_2$), 127.09 ($C_{Ph}^{3,5}$), 128.20 ($C_{Ph}^{2,6}$) 133.69 ($C_{Ph}^{4}$), 144.37 ($C_{Ph}^{1}$), 208.49 (CO), 125.68 ($C_{Im}^{2}$), 129.70 ($C_{Im}^{4,5}$).

**Anal. Calcd**. for $C_{18}H_{26}N_2OS$ (318.47 g/mol): (C, 67.88; H, 8.23; N, 8.88; S, 10.07) %.

**Found** for $C_{18}H_{26}N_2OS$: (C, 67.47; H, 8.52; N, 8.79; S, 10.91) %.

**MS (FAB neg.):** m/z (%) = 136.9 [100].

**3.6.16** Synthesis of bis-methanesulfonyl-methane **(41)**

To a solution containing acetic acid (16.00 ml, 279.76 mmol), and then (2.00 ml, 19.58 mmol) of Bis (methylthio) methane was added with stirring at 0 $^{o}$C for 15 min. After that (17.00 ml, 720 mmol) of hydrogen peroxide was added drop wise at room temperature, and then the mixture was heated for 3 h at 55 $^{o}$C, the white precipitate was formed, washed with methanol and dried in vacuo. Yield: 2.72 g (82%).

**$^{1}$H NMR ($CD_3CN$):** $\delta$ = 3.09 ($CH_3$), 4.67 ($CH_2$).

**$^{13}$C{$^{1}$H} NMR ($CD_3CN$)**: $\delta$ = 41.40 ($CH_3$), 70.26 ($CH_2$).

**$^{13}$C NMR** (MAS): $\delta$ = 44.21 ($CH_3$), 73.01 ($CH_2$).

**Anal. Calcd**. for $C_3H_8O_4S_2$ (172.00 g/mol): (C, 20.92; H, 4.68; S, 37.16) %.

**Found** for $C_3H_8O_4S_2$: (C, 20.52; H, 4.58; S, 37.17) %.

**MS (EI.):** m/z (%) = 172.00 [10].

**3.6.17** Synthesis of 1,3-diisopropyl-4,5-dimethylimidazolium bis-methanesulfonyl-methane **(42)**

To a solution containing 1,3-diisopropyl-4,5-dimethyl-4,5-dimethylimidazol-2-ylidene **11c** (0.320 g, 1.77 mmol) in 30 mL $Et_2O$, bis-methane sulfone (0.307 g, 1.78 mmol) was added at room temperature. After stirring for about 48 h, the resulting precipitate was isolated, washed with $Et_2O$ and dried in vacuo. Yield: 0.520 g (83%).

**$^1$H NMR ($CD_3CN$):** $\delta$ = 1.41 (d, 12H, 1,3-CH*Me*$_2$, $^3$J = 6.72 Hz), 2.15 (s, 6H, 4,5-Me), 4.41 (sept, 2H, 1,3-C*H*Me$_2$), 2.73 ($CH_{3\ \mathrm{sulfone}}$), 3.41 ($CH_{\mathrm{sulfone}}$), 8.36 (s, 1 H, $C_{Im}^2$).

**$^{13}$C{$^1$H} NMR ($CD_3CN$)**: $\delta$ = 7.27 (4,5-Me), 21.40 (1,3-CH*Me*$_2$), 49.92 (1,3-CHMe$_2$), 46.53 ($CH_{3\ \mathrm{sulfone}}$), 63.01 ($CH_{\mathrm{sulfone}}$), 126.31 ($C_{Im}^2$), 129.10 ($C_{Im}^{4,5}$).

**$^{13}$C NMR** (MAS): $\delta$ = 10.00, 11.16 (4,5-Me), 24.43,26.78 (1,3-CH*Me*$_2$), 52.29 ($Me_{\mathrm{sulfone}}$), 49.08 (1,3-*C*HMe$_2$), 65.46 ($CH_{\mathrm{sulfone}}$), 127.97 ($C_{Im}^2$), 133.02 ($C_{Im}^{4,5}$).

**Anal. Calcd**. for $C_{14}H_{28}N_2O_4S_2$ (352.51 g/mol): (C, 47.70; H, 8.01; N, 7.95; S, 18.19) %.

**Found**: (C, 47.41; H, 7.88; N, 7.11; S, 17.81) %.

**MS (FAB neg.):** m/z (%) = 170.8 [100].

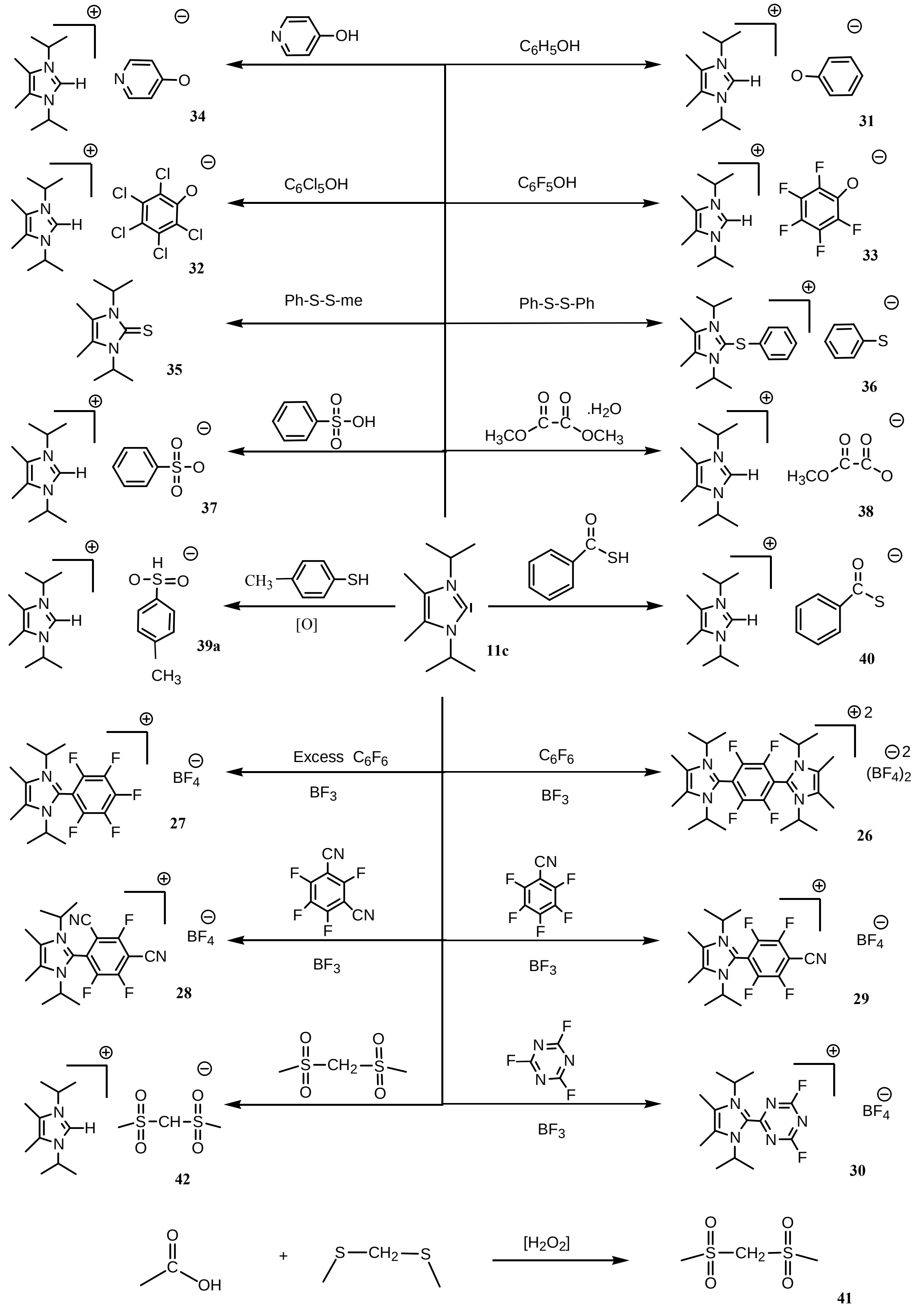
# 4. Summary and Conclusions

New different types of 2,3-dihydroimidazole-2-ylidenes have successfully synthesized on the route to possible drugs (scheme 11). The resulting compounds are classified into nucleophilic aromatic substitution, imidazolium aryl oxide and salt derivatives.

As expected, the reactions of polyfluoroaromatic compounds with **11c** are more reactive than their corresponding polychloroaromatic compounds,[99] because of the unique position of fluorine in the periodic system; it is the smallest possible mono-anion with the largest negative charge density.[100] $S_NAr$ reactions of polyfluoroaromatic compounds occur via an addition-elimination mechanism,[62] where the carbene **(11c)** attack the carbon atoms linked to fluorine, and thus a nonaromatic" meisenheimer intermediate" is formed in the rate-determining step of the reaction. Rearomatization is a strong driving force ejecting the fluoride leaving groups in a subsequent fast step[63] forming compounds **26**, **27**, **28**, **29** and **30**. In compound **26** the second nucleophilic replacement occurred in the position para to the first substitution, which is most favored than the ortho position due to the steric factor.[100] $^{19}F$ NMR data of **27** reveal the presence of hexafluorobenzene signal, which was used in excess to afford the monosubstituted salt. The nucleophilic substitution of polyfluoroaromatic compounds occurred mainly at the para position to the electron-withdrawing group (CN) and the corresponding adducts **28** and **29** were obtained. Both the inductive and resonance electron-withdrawing groups facilitated the nucleophilic substitution. The resonance effect contributes to the orientation of the replaced fluorine.[101] The nitrogen heterocyclic compounds perfluoropyridine, perfluoropyridazine, and cyanuric fluoride are much more susceptible to nucleophilic attack than is hexafluorobenzene,[65] thus **11c** was reacted with cyanuric fluoride and gave the stable salt **30**. Fluoroaromatics have a diverse role in biomedical applications, compounds containing carbon-fluorine bond can be potentially used in pharmaceuticals as analgesic and antibacterial agents.[102] So our future study in exploring these new fluoroaromatic derivatives (**26**, **27**, **28**, **29**, **30**) will receive much more interest for investigation in pharmaceutical field as analgesic and antibacterial agents.

Stable imidazolium alcoholates have been synthesized in good yield. As expected, the carbene **11c** was reacted readily with phenol, pentachlorophenol and pentafluorophenol in diethyl ether from which the imidazolium salts **31**, **32** and **33** respectively, precipitated as stable colourless salts. The NMR data of their solutions imply the presence of separated ions. The crystal structure analyses of compounds **31**, **32** and **33** reveal the presence of ion pairs linked by almost linear C-H…O hydrogen bonds. Similarly, the salt **34** is obtained from the carbene **11c** and 4-hydroxypyridine. In the crystal of **34** the imidazolium ions are linked by C-H…N bond from $C^2$. In addition, we observed weak contacts between the phenolate oxygen atom and methyl protons of a neighboured cation. Phenols belong to the basic compounds used in chemical industry for the synthesis of pharmaceutical products, fertilizers and pesticides.[104]

Further more **11c** was reacted with compounds contain disulfide bridge and gave the adducts **35** and **36** which linked to the imidazolium ring $C^2$ position through C-S bond. Other imidazolium salts **37**, **38**, **39a** and **40** containing ion pairs linked by hydrogen bonds have been determined by X-ray analyses; these compounds play an important role in the construction of ionic liquids,[103] which can be potentially used as pharmaceutical solvents.[4] Apparently their properties are influenced by interionic interactions which have been detected mainly in their 2H-derivatives as hydrogen bonds.[28] The close interaction of the C-H…X (X = S, O, N) hydrogen bonds have attracted considerable interest and suggested in various organic compounds to understand their crystal structures.[105] In the compound **42**, the $^{13}C$ NMR signal for the methyl groups of the anion revealed a significant deshielding in comparison with that value in **41**, this chemical shift value imply that the deprotonation has been occurred and the **42** salt was formed.



**Scheme 11. The summary of all reactions**

## 5. References

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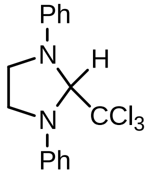
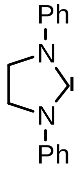
## 6.1 List of compounds



**1**

**1)** 1,3-Diphenyl-2-trichloromethyl-imidazolidine



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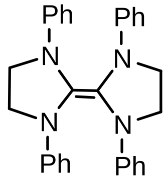
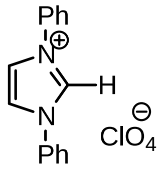
**2)** 1,3-Diphenylimidazolidin-2-ylidene



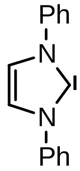
**3**

**3)** 1,3,1',3'-Tetraphenyl-[2,2'] biimidazolidinylidene



**4**

**4)** 1,3-Diphenylimidazolium perchlorate



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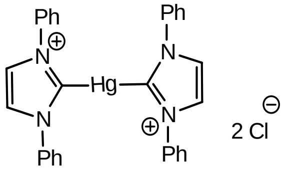
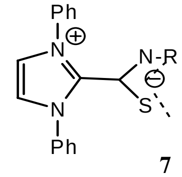
**5)** 1,3-Diphenylimidazol-2-ylidene



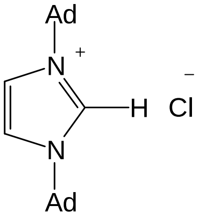
**6**

**6)** 1,3-Diphenyl-2,2-(mercuryimidazolium) chloride



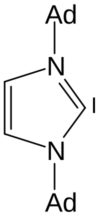
**7**

**7)** 2-(Amino-mercapto-methyl)-1,3-diphenylimidazolium salt



**8**

**8)** 1,3-Diadamantylimidazolium chloride



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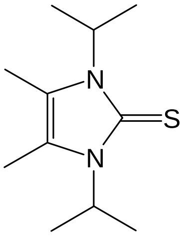
**9)** 1,3-Diadamantylimidazol-2-ylidene



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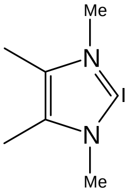
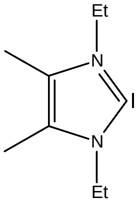
**10)** 1,3-Diisopropyl-4,5-dimethylimidazol-2-thione



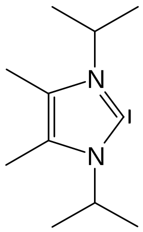
**11a**

**11a)** 1,3,4,5-Tetramethylimidazol-2-ylidene



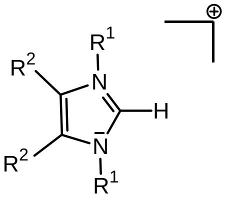
**11b**

**11b)** 1,3-Diethyl-4,5-dimethylimidazol-2-ylidene



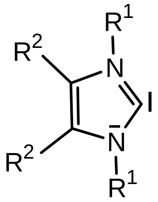
**11c**

**11c)** 1,3-Diisopropyl-4,5-dimethylimidazol-2-ylidene



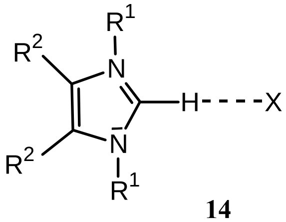
**12**

**12)** Imidazol-2-ylidene adduct



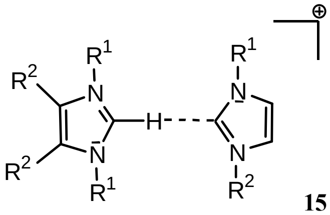
**13**

**13)** 1,3-Diethyl-4,5-dimethylimidazol-2-ylidene



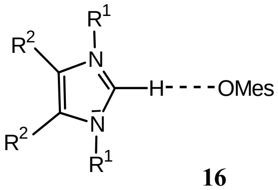
**14**

**14)** Imidazolium salt



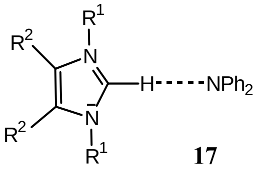
**15**

**15)** 1,3-diisopropyl-4,5-dimethyl-2- 1,3-diisopropyl imidazolium salt



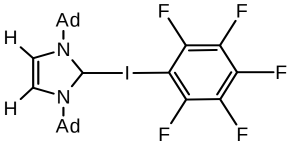
**16**

**16)** Imidazolium Alcoholate



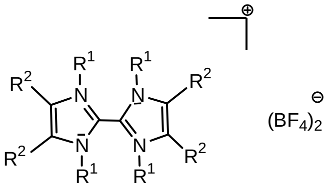
**17**

**17)** Imidazolium diphenylamine



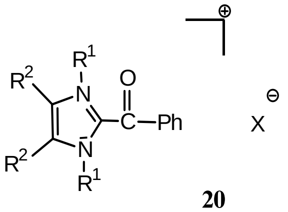
**18**

**18)** 1,3-Diadamantyl-2-iodopentafluorophenylimidazole-ylide



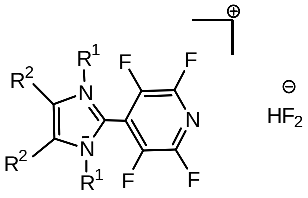
**19**

**19)** Dicationic salt of 1,3-diisopropyl-4,5-dimethylimidazolium tetrafluoroborate



**20**

**20)** Acylation of 1,3-Diisopropyl-4,5-dimethylimidazol-2-ylidene



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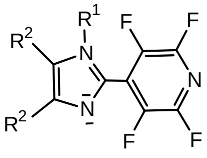
**21)** 1,3-Diisopropyl-4,5-dimethyl-2-tetrafluoropyridylimidazolium Hydrogen fluoride



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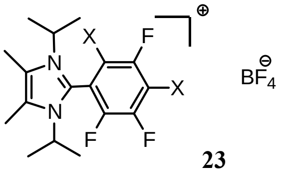
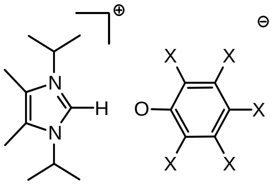
**22)** 1-isopropyl-4,5-dimethyl-2-tetrafluoropyridylimidazol-ylide



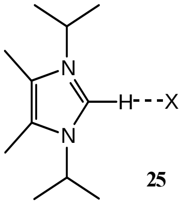
**23**

**23)** 1,3-Diisopropyl-4,5-dimethyl-2-polyfluorophenylimidazolium tetrafluoroborate



**24**

**24)** 1,3-Diisopropyl-4,5-dimethylimidazolium phenolates



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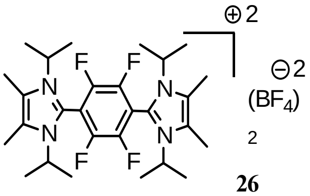
**25)** 1,3-Diisopropyl-4,5-dimethylimidazolium salt



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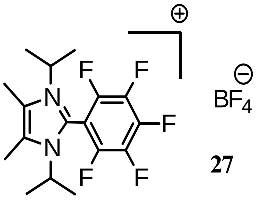
**26)** 1,3-Diisopropyl-4,5-dimethyl-2,2-(pentafluorophenylimidazolium) tetrafluoroborate



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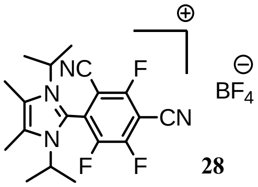
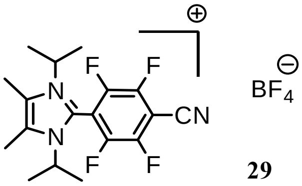
**27)** 1,3-Diisopropyl-4,5-dimethyl-2-pentafluorophenylimidazolium tetrafluoroborate



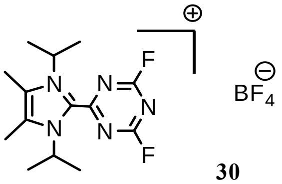
**28**

**28)** 4-(1,3-Diisopropyl-4,5-dimethylimidazolium)-2,5,6-trifluoro-isophthalonitrile tetrafluoroborate



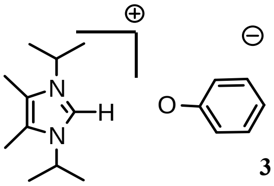
**29**

**29**) 4-(1,3-Diisopropyl-4,5-dimethylimidazolium)- 2,3,5,6-tetrafluoro-benzonitrile tetrafluoroborate



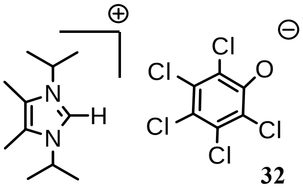
**30**

**30)** 2-(1,3-Diisopropyl-4,5-dimethylimidazolium)-4, 6-difluoro-[1, 3, 5] triazine tetrafluoroborate



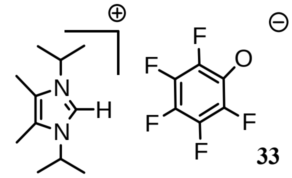
**31**

**31)** 1,3-diisopropyl-4,5-dimethylimidazolium phenolate



**32**

**32)** 1,3-Diisopropyl-4,5-dimethylimidazolium 2,3,4,5,6-pentachloro phenolate



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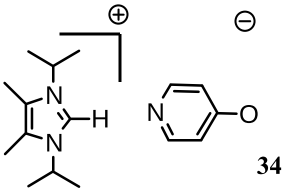
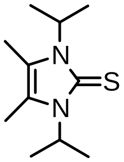
**33)** 1,3-Diisopropyl-4,5-dimethylimidazolium 2, 3, 4, 5,6-pentafluoro phenolate



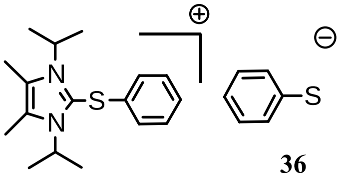
**34**

**34)** 1,3-Diisopropyl-4,5-dimethylimidazolium 4-pyridinolate



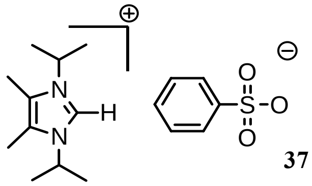
**35**

**35)** 1,3-Diisopropyl-4,5-dimethyl-1,3-dihydro-imidazole-2-thione



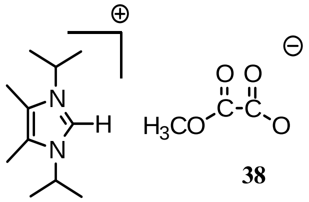
**36**

**36)** 1,3-Diisopropyl-4,5-dimethyl-2-phenylsulfanylimidazoium benzenethiol



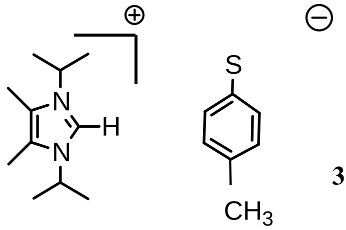
**37**

**37)** 1,3-Diisopropyl-4,5-dimethylimidazolium benzenesulfonic acid



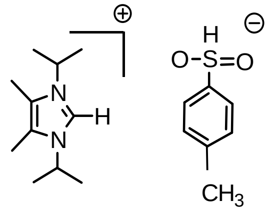
**38**

**38)** 1, 3-Diisopropyl-4, 5-dimethylimidazolium oxalic acid monomethyl ester



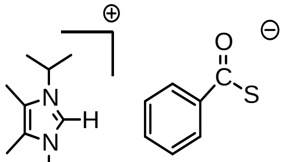
**39**

**39)** 1,3-Diisopropyl-4, 5-dimethylimidazolium 4-methylbenzenethiolate



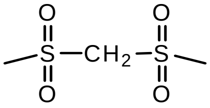
**39a**

**39a)** 1,3-Diisopropyl-4, 5-dimethylimidazolium methyl benzenesulfinic acid



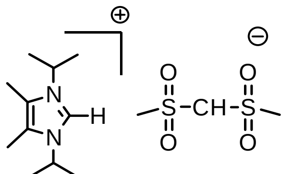
**40**

**40)** 1,3-Diisopropyl-4, 5-dimethylimidazolium thiobenzoic acid



**41**

**41)** Bis-methanesulfonyl-methane



**42**

**42)** 1,3-Diisopropyl-4,5-dimethylimidazolium bis-methanesulfonyl-methane

## 6.2 Crystal structure's tables

Table 13. Crystal data and structure refinement for $C_{32}H_{46}B_2F_{12}N_6$ (**26**).

| | | |
|---|---|---|
| Empirical formula | $C_{16}H_{23}BF_6N_3$ | |
| Formula weight | 764.37 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 14.185(2) Å | $\alpha$= 90°. |
| | b = 7.154(1) Å | $\beta$= 125.43(1)°. |
| | c = 23.128(3) Å | $\gamma$ = 90°. |
| Volume | 1912.3(4) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.327 Mg/m$^3$ | |
| Absorption coefficient | 0.120 mm$^{-1}$ | |
| F(000) | 796 | |
| Crystal size | 0.4 x 0.4 x 0.5 mm$^3$ | |
| Theta range for data collection | 2.87 to 25.94°. | |
| Index ranges | -17<=h<=17, -8<=k<=8, -28<=l<=28 | |
| Reflections collected | 20505 | |
| Independent reflections | 3677 [R(int) = 0.0491] | |
| Completeness to theta = 25.94° | 98.4 % | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 3677 / 0 / 328 | |
| Goodness-of-fit on F$^2$ | 0.894 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0531, wR2 = 0.1340 | |
| R indices (all data) | R1 = 0.0744, wR2 = 0.1443 | |
| Extinction coefficient | 0.000(2) | |
| Largest diff. peak and hole | 0.433 and -0.281 e.Å$^{-3}$ | |

Table 14. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for $C_{32}H_{46}B_2F_{12}N_6$ (**26**). U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 5714(1) | 3648(2) | 4978(1) | 34(1) |
| C(2) | 6029(1) | 5505(2) | 5126(1) | 38(1) |
| F(1) | 7031(1) | 6061(2) | 5253(1) | 54(1) |
| C(3) | 4657(2) | 3185(2) | 4849(1) | 38(1) |
| F(2) | 4275(1) | 1422(1) | 4686(1) | 52(1) |
| C(4) | 6458(1) | 2251(2) | 4955(1) | 36(1) |
| N(1) | 6208(1) | 1385(2) | 4368(1) | 42(1) |
| C(5) | 7120(2) | 204(3) | 4554(1) | 48(1) |
| C(6) | 7912(2) | 375(3) | 5265(1) | 48(1) |
| N(2) | 7490(1) | 1661(2) | 5507(1) | 40(1) |
| C(7) | 5136(2) | 1713(3) | 3644(1) | 50(1) |
| C(8) | 4460(3) | -60(5) | 3318(2) | 76(1) |
| C(9) | 5419(3) | 2718(6) | 3186(2) | 76(1) |
| C(10) | 7189(3) | -987(5) | 4052(2) | 74(1) |
| C(11) | 9052(2) | -601(5) | 5706(2) | 70(1) |
| C(12) | 8046(2) | 2287(3) | 6255(1) | 46(1) |
| C(13) | 8266(3) | 666(4) | 6738(1) | 65(1) |
| C(14) | 9123(2) | 3435(4) | 6510(2) | 66(1) |
| B(1) | 2476(2) | 4670(4) | 2614(1) | 58(1) |
| F(3) | 1433(1) | 5569(3) | 2301(1) | 101(1) |
| F(4) | 2448(2) | 3177(3) | 2251(1) | 118(1) |
| F(5) | 3213(3) | 5874(4) | 2630(3) | 196(2) |
| F(6) | 2920(2) | 4229(4) | 3276(1) | 163(1) |
| C(15) | 1389(3) | 9369(6) | 1323(2) | 84(1) |
| C(16) | 1403(2) | 9208(4) | 718(2) | 71(1) |
| N(3) | 1435(3) | 9105(5) | 242(2) | 124(1) |

Table 15. Bond lengths [Å] and angles [°] for $C_{32}H_{46}B_2F_{12}N_6$ (**26**).

| | |
|---|---|
| C(1)-C(2) | 1.380(2) |
| C(1)-C(3) | 1.389(3) |
| C(1)-C(4) | 1.476(2) |
| C(2)-F(1) | 1.335(2) |
| C(2)-C(3)#1 | 1.376(3) |
| C(3)-F(2) | 1.337(2) |
| C(3)-C(2)#1 | 1.376(3) |
| C(4)-N(2) | 1.335(2) |
| C(4)-N(1) | 1.340(2) |
| N(1)-C(5) | 1.388(2) |
| N(1)-C(7) | 1.489(2) |
| C(5)-C(6) | 1.356(3) |
| C(5)-C(10) | 1.487(3) |
| C(6)-N(2) | 1.382(3) |
| C(6)-C(11) | 1.494(3) |
| N(2)-C(12) | 1.495(2) |
| C(7)-C(8) | 1.503(4) |
| C(7)-C(9) | 1.515(4) |
| C(12)-C(13) | 1.512(3) |
| C(12)-C(14) | 1.521(3) |
| B(1)-F(6) | 1.312(3) |
| B(1)-F(5) | 1.338(4) |
| B(1)-F(4) | 1.345(3) |
| B(1)-F(3) | 1.373(3) |
| C(15)-C(16) | 1.414(5) |
| C(16)-N(3) | 1.132(4) |
| | |
| C(2)-C(1)-C(3) | 115.86(16) |
| C(2)-C(1)-C(4) | 121.71(15) |
| C(3)-C(1)-C(4) | 122.43(15) |
| F(1)-C(2)-C(3)#1 | 118.48(15) |
| F(1)-C(2)-C(1) | 119.40(16) |
| C(3)#1-C(2)-C(1) | 122.12(16) |
| F(2)-C(3)-C(2)#1 | 118.28(15) |
| F(2)-C(3)-C(1) | 119.70(16) |
| C(2)#1-C(3)-C(1) | 122.02(16) |
| N(2)-C(4)-N(1) | 108.79(15) |
| N(2)-C(4)-C(1) | 126.17(16) |
| N(1)-C(4)-C(1) | 125.03(15) |
| C(4)-N(1)-C(5) | 108.41(15) |
| C(4)-N(1)-C(7) | 124.35(16) |
| C(5)-N(1)-C(7) | 127.22(17) |
| C(6)-C(5)-N(1) | 106.80(17) |
| C(6)-C(5)-C(10) | 127.9(2) |
| N(1)-C(5)-C(10) | 125.3(2) |
| C(5)-C(6)-N(2) | 107.58(16) |
| C(5)-C(6)-C(11) | 126.5(2) |
| N(2)-C(6)-C(11) | 125.9(2) |
| C(4)-N(2)-C(6) | 108.41(15) |
| C(4)-N(2)-C(12) | 124.20(15) |
| C(6)-N(2)-C(12) | 127.37(15) |
| N(1)-C(7)-C(8) | 111.7(2) |
| N(1)-C(7)-C(9) | 110.43(19) |
| C(8)-C(7)-C(9) | 113.5(3) |
| N(2)-C(12)-C(13) | 111.72(19) |
| N(2)-C(12)-C(14) | 110.40(19) |
| C(13)-C(12)-C(14) | 113.4(2) |
| F(6)-B(1)-F(5) | 106.5(3) |
| F(6)-B(1)-F(4) | 111.0(2) |
| F(5)-B(1)-F(4) | 105.6(3) |
| F(6)-B(1)-F(3) | 111.7(2) |
| F(5)-B(1)-F(3) | 107.3(3) |
| F(4)-B(1)-F(3) | 114.1(2) |
| N(3)-C(16)-C(15) | 178.4(4) |

Table 16. Anisotropic displacement parameters (Å$^2$x 10$^3$) for $C_{32}H_{46}B_2F_{12}N_6$ (**26**). The anisotropic displacement factor exponent takes the form: $-2\pi^2$[ h$^2$ a*$^2$U$^{11}$ + ... + 2 h k a* b* U$^{12}$ ]

| | U$^{11}$ | U$^{22}$ | U$^{33}$ | U$^{23}$ | U$^{13}$ | U$^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 35(1) | 37(1) | 26(1) | 1(1) | 15(1) | 1(1) |
| C(2) | 33(1) | 40(1) | 39(1) | 3(1) | 20(1) | -2(1) |
| F(1) | 43(1) | 44(1) | 81(1) | -3(1) | 40(1) | -5(1) |
| C(3) | 40(1) | 30(1) | 40(1) | 1(1) | 21(1) | -1(1) |
| F(2) | 49(1) | 33(1) | 73(1) | -5(1) | 35(1) | -6(1) |
| C(4) | 36(1) | 35(1) | 34(1) | 1(1) | 19(1) | -1(1) |
| N(1) | 41(1) | 46(1) | 36(1) | -3(1) | 21(1) | 1(1) |
| C(5) | 50(1) | 47(1) | 50(1) | 0(1) | 31(1) | 8(1) |
| C(6) | 45(1) | 46(1) | 51(1) | 1(1) | 27(1) | 7(1) |
| N(2) | 35(1) | 42(1) | 37(1) | 0(1) | 19(1) | 3(1) |
| C(7) | 46(1) | 66(1) | 32(1) | 1(1) | 19(1) | 5(1) |
| C(8) | 62(2) | 85(2) | 59(2) | -28(2) | 23(1) | -7(1) |
| C(9) | 69(2) | 106(2) | 52(2) | 24(2) | 35(1) | 13(2) |
| C(10) | 84(2) | 78(2) | 66(2) | -7(1) | 48(2) | 20(2) |
| C(11) | 53(1) | 79(2) | 63(2) | 2(1) | 26(1) | 25(1) |
| C(12) | 40(1) | 55(1) | 33(1) | -2(1) | 15(1) | 1(1) |
| C(13) | 64(2) | 73(2) | 43(1) | 9(1) | 22(1) | 5(1) |
| C(14) | 47(1) | 80(2) | 54(1) | -13(2) | 19(1) | -14(1) |
| B(1) | 59(2) | 56(1) | 49(2) | -6(1) | 25(1) | -2(1) |
| F(3) | 74(1) | 130(2) | 67(1) | 6(1) | 23(1) | 26(1) |
| F(4) | 154(2) | 95(1) | 92(1) | -29(1) | 63(1) | 1(1) |
| F(5) | 140(2) | 100(2) | 366(5) | -22(2) | 158(3) | -31(2) |
| F(6) | 183(2) | 227(3) | 57(1) | 33(1) | 58(1) | 137(2) |
| C(15) | 85(2) | 91(2) | 76(2) | -9(2) | 47(2) | -7(2) |
| C(16) | 67(2) | 74(2) | 75(2) | -3(1) | 43(1) | 9(1) |
| N(3) | 133(3) | 153(3) | 101(2) | 11(2) | 77(2) | 41(2) |

Table 17. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for $C_{32}H_{46}B_2F_{12}N_6$ (**26**).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(7A) | 4634(16) | 2510(30) | 3718(10) | 35(5) |
| H(8A) | 4790(30) | -770(50) | 3174(18) | 90(10) |
| H(8B) | 4360(30) | -790(60) | 3620(20) | 121(15) |
| H(8C) | 3670(30) | 160(40) | 2911(17) | 82(8) |
| H(9A) | 5820(20) | 3900(40) | 3405(15) | 72(8) |
| H(9B) | 5900(30) | 1960(40) | 3088(16) | 87(9) |
| H(9C) | 4690(30) | 3140(40) | 2751(18) | 90(9) |
| H(10A) | 7010(30) | -330(60) | 3640(20) | 120(13) |
| H(10B) | 7960(40) | -1540(60) | 4310(20) | 125(13) |
| H(10C) | 6840(50) | -2330(90) | 4060(30) | 190(20) |
| H(11A) | 9660(30) | 310(50) | 5923(18) | 89(10) |
| H(11B) | 9370(50) | -670(80) | 6190(30) | 168(19) |
| H(11C) | 9280(30) | -1350(50) | 5495(19) | 102(11) |
| H(12A) | 7461(16) | 3100(30) | 6234(10) | 32(4) |
| H(13A) | 8470(30) | 1190(40) | 7170(20) | 94(10) |
| H(13B) | 7700(30) | -170(40) | 6594(15) | 73(8) |
| H(13C) | 8870(30) | -140(40) | 6803(16) | 86(9) |
| H(14A) | 9010(40) | 4330(60) | 6190(20) | 131(15) |
| H(14B) | 9830(20) | 2710(30) | 6660(12) | 58(6) |
| H(14C) | 9290(20) | 4100(30) | 6898(15) | 58(7) |
| H(15A) | 1830(40) | 10380(70) | 1610(20) | 131(14) |
| H(15B) | 570(40) | 9340(60) | 1200(20) | 136(14) |
| H(15C) | 1570(40) | 8200(70) | 1570(30) | 146(17) |

Table 18. Crystal data and structure refinement for $C_{17}H_{20}BF_9N_2$ (**27**).

| | | |
|---|---|---|
| Empirical formula | $C_{17}H_{20}BF_9N_2$ | |
| Formula weight | 434.16 | |
| Temperature | 210(2) K | |
| Wavelength | 71.073 pm | |
| Crystal system | monoclinic | |
| Space group | P 21/n | |
| Unit cell dimensions | a = 1100.3(2) pm | $\alpha$= 90°. |
| | b = 1072.1(1) pm | $\beta$= 101.03(2)°. |
| | c = 1684.1(3) pm | $\gamma$ = 90°. |
| Volume | 1.9499(5) $nm^3$ | |
| Z | 4 | |
| Density (calculated) | 1.479 $g/cm^3$ | |
| Absorption coefficient | 0.147 $mm^{-1}$ | |
| F(000) | 888 | |
| Crystal size | 0.5 x 0.5 x 0.4 $mm^3$ | |
| Theta range for data collection | 2.44 to 25.95°. | |
| Index ranges | $-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-20 \leq l \leq 20$ | |
| Reflections collected | 21093 | |
| Independent reflections | 3786 [R(int) = 0.0321] | |
| Completeness to theta = 25.95° | 99.2 % | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / parameters | 3786 / 342 | |
| Goodness-of-fit on $F^2$ | 0.980 | |
| Final R indices [I > 2$\sigma$(I)] | R1 = 0.0494, wR2 = 0.1353 | |
| R indices (all data) | R1 = 0.0650, wR2 = 0.1424 | |
| Largest diff. peak and hole | 0.654 and -0.394 e.$\AA^{-3}$ | |

Table 19. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($pm^2$x $10^{-1}$) for $C_{17}H_{20}BF_9N_2$ (**27**). U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 2450(2) | 3915(2) | 1159(1) | 33(1) |
| C(2) | 1458(2) | 4485(2) | 1423(1) | 38(1) |
| F(1) | 565(1) | 5029(1) | 887(1) | 49(1) |
| C(3) | 1384(2) | 4515(2) | 2226(1) | 48(1) |
| F(2) | 441(2) | 5082(1) | 2466(1) | 68(1) |
| C(4) | 2287(2) | 3935(2) | 2782(1) | 53(1) |
| F(3) | 2209(2) | 3942(2) | 3561(1) | 78(1) |
| C(5) | 3266(2) | 3339(2) | 2541(1) | 49(1) |
| F(4) | 4123(2) | 2771(1) | 3087(1) | 71(1) |
| C(6) | 3351(2) | 3358(2) | 1739(1) | 40(1) |
| F(5) | 4330(1) | 2817(1) | 1518(1) | 51(1) |
| C(7) | 2524(2) | 3920(2) | 295(1) | 30(1) |
| N(1) | 2461(1) | 2918(1) | -188(1) | 33(1) |
| C(8) | 2500(2) | 3324(2) | -966(1) | 36(1) |
| C(9) | 2596(2) | 4587(2) | -938(1) | 35(1) |
| N(2) | 2611(1) | 4952(1) | -148(1) | 31(1) |
| C(10) | 2360(2) | 1605(2) | 98(1) | 38(1) |
| C(11) | 3473(2) | 842(2) | -5(2) | 53(1) |
| C(12) | 1138(2) | 1022(2) | -295(2) | 54(1) |
| C(13) | 2442(3) | 2491(3) | -1684(1) | 53(1) |
| C(14) | 2671(2) | 5458(2) | -1618(1) | 47(1) |
| C(15) | 2805(2) | 6227(2) | 211(1) | 35(1) |
| C(16) | 1821(3) | 7134(3) | -202(2) | 59(1) |
| C(17) | 4113(2) | 6656(3) | 217(2) | 60(1) |
| B(1) | 273(2) | 1320(2) | 2221(1) | 45(1) |
| F(6) | 9604(2) | 2398(2) | 2158(1) | 92(1) |
| F(8) | 9589(2) | 267(2) | 2209(1) | 101(1) |
| F(9) | 911(2) | 1249(2) | 1597(1) | 96(1) |
| F(7) | 1152(2) | 1362(2) | 2909(1) | 113(1) |

Table 20. Bond lengths [pm] and angles [°] for $C_{17}H_{20}BF_9N_2$ (**27**).

| | | | |
|---|---|---|---|
| C(1)-C(6) | 138.7(3) | F(1)-C(2)-C(1) | 119.7(2) |
| C(1)-C(2) | 139.6(3) | C(3)-C(2)-C(1) | 121.5(2) |
| C(1)-C(7) | 147.3(2) | F(2)-C(3)-C(2) | 120.5(2) |
| C(2)-F(1) | 133.5(2) | F(2)-C(3)-C(4) | 120.3(2) |
| C(2)-C(3) | 137.0(3) | C(2)-C(3)-C(4) | 119.3(2) |
| C(3)-F(2) | 133.0(3) | F(3)-C(4)-C(3) | 119.6(2) |
| C(3)-C(4) | 137.6(3) | F(3)-C(4)-C(5) | 119.6(2) |
| C(4)-F(3) | 133.1(2) | C(3)-C(4)-C(5) | 120.8(2) |
| C(4)-C(5) | 137.8(3) | F(4)-C(5)-C(6) | 120.9(2) |
| C(5)-F(4) | 133.2(3) | F(4)-C(5)-C(4) | 119.9(2) |
| C(5)-C(6) | 137.1(3) | C(6)-C(5)-C(4) | 119.2(2) |
| C(6)-F(5) | 133.8(2) | F(5)-C(6)-C(5) | 118.6(2) |
| C(7)-N(1) | 134.0(2) | F(5)-C(6)-C(1) | 119.7(2) |
| C(7)-N(2) | 134.8(2) | C(5)-C(6)-C(1) | 121.7(2) |
| N(1)-C(8) | 138.9(2) | N(1)-C(7)-N(2) | 108.9(2) |
| N(1)-C(10) | 149.9(2) | N(1)-C(7)-C(1) | 126.1(2) |
| C(8)-C(9) | 135.9(3) | N(2)-C(7)-C(1) | 124.9(2) |
| C(8)-C(13) | 149.5(3) | C(7)-N(1)-C(8) | 108.3(2) |
| C(9)-N(2) | 138.4(2) | C(7)-N(1)-C(10) | 123.8(2) |
| C(9)-C(14) | 149.3(3) | C(8)-N(1)-C(10) | 127.9(2) |
| N(2)-C(15) | 149.3(2) | C(9)-C(8)-N(1) | 107.2(2) |
| C(10)-C(11) | 151.0(3) | C(9)-C(8)-C(13) | 127.9(2) |
| C(10)-C(12) | 151.5(3) | N(1)-C(8)-C(13) | 124.9(2) |
| C(15)-C(17) | 150.9(3) | C(8)-C(9)-N(2) | 107.5(2) |
| C(15)-C(16) | 152.1(3) | C(8)-C(9)-C(14) | 127.8(2) |
| B(1)-F(8) | 135.5(3) | N(2)-C(9)-C(14) | 124.7(2) |
| B(1)-F(7) | 136.1(3) | C(7)-N(2)-C(9) | 108.1(2) |
| B(1)-F(6) | 136.3(3) | C(7)-N(2)-C(15) | 123.2(1) |
| B(1)-F(9) | 137.4(3) | C(9)-N(2)-C(15) | 128.5(2) |
| | | N(1)-C(10)-C(11) | 111.1(2) |
| C(6)-C(1)-C(2) | 117.5(2) | N(1)-C(10)-C(12) | 111.2(2) |
| C(6)-C(1)-C(7) | 122.0(2) | C(11)-C(10)-C(12) | 113.4(2) |
| C(2)-C(1)-C(7) | 120.5(2) | F(8)-B(1)-F(6) | 114.5(2) |
| F(1)-C(2)-C(3) | 118.8(2) | N(2)-C(15)-C(16) | 111.5(2) |

Table 21. Anisotropic displacement parameters ($pm^2 x 10^{-1}$) for $C_{17}H_{20}BF_9N_2$ (**27**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 40(1) | 32(1) | 29(1) | -3(1) | 9(1) | -8(1) |
| C(2) | 44(1) | 35(1) | 38(1) | -3(1) | 12(1) | -7(1) |
| F(1) | 43(1) | 57(1) | 48(1) | -2(1) | 12(1) | 5(1) |
| C(3) | 63(1) | 42(1) | 45(1) | -8(1) | 27(1) | -7(1) |
| F(2) | 89(1) | 65(1) | 64(1) | -10(1) | 47(1) | 2(1) |
| C(4) | 86(2) | 44(1) | 31(1) | -5(1) | 21(1) | -15(1) |
| F(3) | 137(1) | 71(1) | 31(1) | -4(1) | 29(1) | -9(1) |
| C(5) | 69(1) | 42(1) | 32(1) | 5(1) | -2(1) | -9(1) |
| F(4) | 99(1) | 67(1) | 39(1) | 10(1) | -7(1) | 4(1) |
| C(6) | 46(1) | 36(1) | 37(1) | -2(1) | 7(1) | -7(1) |
| F(5) | 46(1) | 55(1) | 49(1) | 5(1) | 5(1) | 7(1) |
| C(7) | 32(1) | 30(1) | 30(1) | -1(1) | 7(1) | -4(1) |
| N(1) | 37(1) | 31(1) | 33(1) | -2(1) | 11(1) | -4(1) |
| C(8) | 39(1) | 40(1) | 31(1) | -2(1) | 12(1) | -3(1) |
| C(9) | 35(1) | 41(1) | 31(1) | 2(1) | 10(1) | 1(1) |
| N(2) | 33(1) | 31(1) | 30(1) | 0(1) | 8(1) | -2(1) |
| C(10) | 47(1) | 29(1) | 41(1) | -2(1) | 16(1) | -8(1) |
| C(11) | 55(1) | 39(1) | 71(2) | 9(1) | 25(1) | 5(1) |
| C(12) | 48(1) | 45(1) | 71(2) | -4(1) | 13(1) | -15(1) |
| C(13) | 78(2) | 48(1) | 39(1) | -9(1) | 23(1) | -5(1) |
| C(14) | 63(1) | 46(1) | 35(1) | 6(1) | 17(1) | 3(1) |
| C(15) | 41(1) | 28(1) | 38(1) | -1(1) | 9(1) | -3(1) |
| C(16) | 74(2) | 38(1) | 59(2) | -9(1) | -1(1) | 16(1) |
| C(17) | 54(1) | 53(2) | 78(2) | -16(1) | 25(1) | -17(1) |
| B(1) | 55(1) | 41(1) | 38(1) | 6(1) | 9(1) | 0(1) |
| F(6) | 76(1) | 75(1) | 128(2) | 28(1) | 27(1) | 29(1) |
| F(8) | 112(1) | 83(1) | 123(2) | -18(1) | 58(1) | -42(1) |
| F(9) | 114(1) | 104(2) | 87(1) | -3(1) | 63(1) | -15(1) |
| F(7) | 167(2) | 80(1) | 68(1) | 3(1) | -41(1) | 19(1) |

Table 22. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (pm$^2$x 10 $^{-1}$) for $C_{17}H_{20}BF_9N_2$ (**27**).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(10A) | 2363(18) | 1690(20) | 637(14) | 37(5) |
| H(11A) | 4270(30) | 1240(30) | 286(19) | 81(9) |
| H(11B) | 3450(20) | 630(30) | -522(19) | 65(8) |
| H(11C) | 3400(20) | 110(30) | 241(15) | 54(7) |
| H(12A) | 1070(20) | 220(30) | 14(16) | 61(7) |
| H(12B) | 1110(30) | 900(30) | -880(20) | 88(10) |
| H(12C) | 430(30) | 1580(30) | -345(17) | 70(8) |
| H(13A) | 1900(30) | 1800(30) | -1698(19) | 87(10) |
| H(13B) | 2500(40) | 3050(40) | -2050(30) | 117(14) |
| H(13C) | 3180(40) | 2030(40) | -1630(20) | 109(12) |
| H(14A) | 1900(30) | 5920(30) | -1802(19) | 82(9) |
| H(14B) | 2680(30) | 5070(30) | -2060(20) | 84(10) |
| H(14C) | 3340(40) | 5980(40) | -1490(30) | 120(14) |
| H(15A) | 2688(16) | 6113(17) | 774(12) | 27(4) |
| H(16A) | 1870(20) | 7820(30) | 94(17) | 62(7) |
| H(16B) | 2020(30) | 7370(30) | -710(20) | 96(11) |
| H(16C) | 1040(30) | 6770(30) | -260(20) | 90(11) |
| H(17A) | 4200(20) | 7450(30) | 540(18) | 68(7) |
| H(17B) | 4320(30) | 6690(30) | -260(20) | 92(11) |
| H(17C) | 4710(30) | 6080(30) | 492(18) | 71(8) |

Table 23. Crystal data and structure refinement for $C_{19}H_{20}BF_7N_4$ (**28**).

| | | |
|---|---|---|
| Empirical formula | $C_{19}H_{20}BF_7N_4$ | |
| Formula weight | 448.18 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | Pbcn | |
| Unit cell dimensions | a = 18.851(4) Å | $\alpha$= 90°. |
| | b = 21.222(4) Å | $\beta$= 90°. |
| | c = 22.341(5) Å | $\gamma$ = 90°. |
| Volume | 8938(3) $Å^3$ | |
| Z | 20 | |
| Density (calculated) | 1.635 $Mg/m^3$ | |
| Absorption coefficient | 0.155 $mm^{-1}$ | |
| F(000) | 4600 | |
| Theta range for data collection | 3.03 to 27.02°. | |
| Index ranges | -23<=h<=23, -26<=k<=27, -28<=l<=28 | |
| Reflections collected | 102999 | |
| Independent reflections | 9659 [R(int) = 0.4074] | |
| Completeness to theta = 27.02° | 98.7 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 9659 / 12 / 567 | |
| Goodness-of-fit on $F^2$ | 1.142 | |
| Final R indices [I>2sigma(I)] | R1 = 0.2518, wR2 = 0.4686 | |
| R indices (all data) | R1 = 0.3834, wR2 = 0.5465 | |
| Extinction coefficient | 0.0041(9) | |
| Largest diff. peak and hole | 0.351 and -0.469 e.$Å^{-3}$ | |

Table 24. Crystal data and structure refinement for $C_{20} H_{23} B F_8 N_4$ (**29**).

| | | |
|---|---|---|
| Empirical formula | $C_{20} H_{23} B F_8 N_4$ | |
| Formula weight | 482.23 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 A | |
| Crystal system, space group | Orthorhombic, P212121 | |
| Unit cell dimensions | a = 11.1690(13) Å | α = 90°. |
| | b = 11.2614(10) Å | β = 90°. |
| | c = 18.4089(16) Å | γ = 90°. |
| Volume | 2315.4(4) A^3 | |
| Z, Calculated density | 4, 1.383 Mg/m^3 | |
| Absorption coefficient | 0.128 mm^-1 | |
| F(000) | 992 | |
| Crystal size | 0.15 x 0.10 x 0.10 mm | |
| Theta range for data collection | 3.39 to 26.82°. | |
| Index ranges | -14<=h<=14, -14<=k<=14, -23<=l<=23 | |
| Reflections collected / unique | 33734 / 4930 [R(int) = 0.1187] | |
| Completeness to 2theta = 26.82 | 99.3% | |
| Absorption correction | Difabs | |
| Max. and min. transmission | 0.772 and 0.3550 | |
| Refinement method | Full-matrix least-squares on F^2 | |
| Data / restraints / parameters | 4930 / 0 / 335 | |
| Goodness-of-fit on F^2 | 1.113 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0741, wR2 = 0.1268 | |
| R indices (all data) | R1 = 0.0976, wR2 = 0.1363 | |
| Absolute structure parameter | 0.1(11) | |
| Largest diff. peak and hole | 0.271 and -0.261 e.A^-3 | |

Table 25. Atomic coordinates ( x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $C_{20} H_{23} B F_8 N_4$ (**29**).U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 2267(3) | 5512(3) | -648(2) | 25(1) |
| C(3) | 1980(3) | 7424(3) | -880(2) | 27(1) |
| C(4) | 2604(3) | 6952(3) | -1438(2) | 27(1) |
| C(11) | 2311(3) | 4361(3) | -266(2) | 29(1) |
| C(12) | 1645(3) | 3396(3) | -487(2) | 32(1) |
| C(13) | 1711(3) | 2324(3) | -131(2) | 33(1) |
| C(14) | 2454(3) | 2196(3) | 469(2) | 30(1) |
| C(15) | 3113(3) | 3169(3) | 697(2) | 29(1) |
| C(16) | 3055(3) | 4223(3) | 329(2) | 28(1) |
| C(21) | 1022(3) | 6525(3) | 285(2) | 33(1) |
| C(22) | 1571(4) | 7292(4) | 872(2) | 49(1) |
| C(23) | -250(4) | 6840(5) | 96(3) | 55(1) |
| C(31) | 1591(4) | 8678(3) | -780(2) | 37(1) |
| C(41) | 3028(4) | 7584(4) | -2108(2) | 43(1) |
| C(51) | 3406(4) | 4832(4) | -1735(2) | 37(1) |
| C(52) | 2808(5) | 4671(5) | -2466(2) | 60(1) |
| C(53) | 4736(4) | 5081(5) | -1783(3) | 54(1) |
| C(100) | 6145(6) | 4121(5) | 2304(3) | 80(2) |
| C(101) | 5672(5) | 3094(6) | 2686(3) | 63(2) |
| C(131) | 2561(4) | 1075(3) | 834(2) | 37(1) |
| N(2) | 1773(2) | 6502(2) | -387(2) | 25(1) |
| N(5) | 2771(3) | 5757(3) | -1295(2) | 27(1) |
| N(102) | 5298(5) | 2306(6) | 2980(3) | 102(2) |
| N(131) | 2676(4) | 184(3) | 1122(2) | 58(1) |
| B(1) | -549(5) | 3550(7) | 1188(3) | 56(2) |
| F(1) | 588(7) | 3973(6) | 1274(4) | 59(2) |
| F(2) | -475(4) | 2472(4) | 755(3) | 55(2) |
| F(3) | -826(7) | 2979(5) | 1894(4) | 81(2) |
| F(4) | -1388(7) | 4207(7) | 1010(6) | 118(4) |
| F(1A) | -557(6) | 3851(7) | 417(3) | 71(3) |
| F(2A) | -726(10) | 4853(7) | 1449(4) | 103(3) |
| F(3A) | 396(11) | 3270(15) | 1442(6) | 127(6) |
| F(4A) | -1589(9) | 3184(10) | 1392(6) | 112(4) |
| F(13) | 1056(2) | 1405(2) | -355(1) | 47(1) |
| F(14) | 3827(2) | 3063(2) | 1281(1) | 41(1) |
| F(15) | 3717(2) | 5145(2) | 560(1) | 40(1) |
| F(16) | 908(2) | 3498(2) | -1060(1) | 45(1) |

Table 26. Bond lengths [A] and angles [deg] for $C_{20} H_{23} B F_8 N_4$ (**29**).

| | |
|---|---|
| C(1)-N(2) | 1.334(4) |
| C(1)-N(5) | 1.346(4) |
| C(1)-C(11) | 1.476(5) |
| C(3)-C(4) | 1.350(5) |
| C(3)-N(2) | 1.398(4) |
| C(3)-C(31) | 1.490(5) |
| C(4)-N(5) | 1.384(5) |
| C(4)-C(41) | 1.500(5) |
| C(11)-C(12) | 1.378(5) |
| C(11)-C(16) | 1.384(5) |
| C(12)-F(16) | 1.343(4) |
| C(12)-C(13) | 1.376(5) |
| C(13)-F(13) | 1.333(4) |
| C(13)-C(14) | 1.389(5) |
| C(14)-C(15) | 1.385(5) |
| C(14)-C(131) | 1.436(5) |
| C(15)-F(14) | 1.343(4) |
| C(15)-C(16) | 1.368(5) |
| C(16)-F(15) | 1.344(4) |
| C(21)-N(2) | 1.495(4) |
| C(21)-C(23) | 1.505(6) |
| C(21)-C(22) | 1.513(5) |
| C(51)-N(5) | 1.498(4) |
| C(51)-C(52) | 1.513(6) |
| C(51)-C(53) | 1.515(6) |
| C(100)-C(101) | 1.454(8) |
| C(101)-N(102) | 1.119(7) |
| C(131)-N(131) | 1.142(5) |
| B(1)-F(3A) | 1.196(12) |
| B(1)-F(4) | 1.238(8) |
| B(1)-F(4A) | 1.289(10) |
| B(1)-F(1) | 1.365(9) |
| B(1)-F(2) | 1.454(8) |
| B(1)-F(1A) | 1.460(9) |
| B(1)-F(3) | 1.483(9) |
| B(1)-F(2A) | 1.557(10) |

| | |
|---|---|
| N(2)-C(1)-N(5) | 108.7(3) |
| N(2)-C(1)-C(11) | 125.2(3) |
| N(5)-C(1)-C(11) | 126.0(3) |
| C(4)-C(3)-N(2) | 106.7(3) |
| C(4)-C(3)-C(31) | 128.1(3) |
| N(2)-C(3)-C(31) | 125.1(3) |
| C(3)-C(4)-N(5) | 107.9(3) |
| C(3)-C(4)-C(41) | 127.0(3) |
| N(5)-C(4)-C(41) | 125.1(3) |
| C(12)-C(11)-C(16) | 118.0(3) |
| C(12)-C(11)-C(1) | 122.3(3) |
| C(16)-C(11)-C(1) | 119.7(3) |
| F(16)-C(12)-C(13) | 118.8(3) |
| F(16)-C(12)-C(11) | 119.7(3) |
| C(13)-C(12)-C(11) | 121.5(3) |
| F(13)-C(13)-C(12) | 120.3(3) |
| F(13)-C(13)-C(14) | 119.6(3) |

| | |
|---|---|
| C(12)-C(13)-C(14) | 120.1(3) |
| C(15)-C(14)-C(13) | 118.5(3) |
| C(15)-C(14)-C(131) | 120.6(4) |
| C(13)-C(14)-C(131) | 120.9(3) |
| F(14)-C(15)-C(16) | 120.1(3) |
| F(14)-C(15)-C(14) | 119.2(3) |
| C(16)-C(15)-C(14) | 120.7(3) |
| F(15)-C(16)-C(15) | 119.2(3) |
| F(15)-C(16)-C(11) | 119.6(3) |
| C(15)-C(16)-C(11) | 121.2(3) |
| N(2)-C(21)-C(23) | 110.0(3) |
| N(2)-C(21)-C(22) | 111.9(3) |
| C(23)-C(21)-C(22) | 114.3(4) |
| N(5)-C(51)-C(52) | 110.8(3) |
| N(5)-C(51)-C(53) | 111.5(3) |
| C(52)-C(51)-C(53) | 113.8(4) |
| N(102)-C(101)-C(100) | 179.4(7) |
| N(131)-C(131)-C(14) | 178.3(5) |
| C(1)-N(2)-C(3) | 108.5(3) |
| C(1)-N(2)-C(21) | 123.0(3) |
| C(3)-N(2)-C(21) | 128.2(3) |
| C(1)-N(5)-C(4) | 108.1(3) |
| C(1)-N(5)-C(51) | 122.3(3) |
| C(4)-N(5)-C(51) | 129.6(3) |
| F(3A)-B(1)-F(4) | 158.2(11) |
| F(3A)-B(1)-F(4A) | 126.7(11) |
| F(4)-B(1)-F(4A) | 65.5(7) |
| F(3A)-B(1)-F(1) | 39.3(8) |
| F(4)-B(1)-F(1) | 121.8(8) |
| F(4A)-B(1)-F(1) | 156.4(8) |
| F(3A)-B(1)-F(2) | 86.8(9) |
| F(4)-B(1)-F(2) | 113.4(6) |
| F(4A)-B(1)-F(2) | 86.8(7) |
| F(1)-B(1)-F(2) | 107.6(5) |
| F(3A)-B(1)-F(1A) | 116.5(7) |
| F(4)-B(1)-F(1A) | 66.4(6) |
| F(4A)-B(1)-F(1A) | 110.6(7) |
| F(1)-B(1)-F(1A) | 92.2(6) |
| F(2)-B(1)-F(1A) | 70.2(4) |
| F(3A)-B(1)-F(3) | 74.2(8) |
| F(4)-B(1)-F(3) | 109.4(7) |
| F(4A)-B(1)-F(3) | 54.3(6) |
| F(1)-B(1)-F(3) | 104.1(6) |
| F(2)-B(1)-F(3) | 97.5(5) |
| F(1A)-B(1)-F(3) | 162.1(6) |
| F(3A)-B(1)-F(2A) | 103.9(10) |
| F(4)-B(1)-F(2A) | 54.7(5) |
| F(4A)-B(1)-F(2A) | 95.5(8) |
| F(1)-B(1)-F(2A) | 75.8(6) |
| F(2)-B(1)-F(2A) | 164.4(6) |
| F(1A)-B(1)-F(2A) | 94.6(6) |
| F(3)-B(1)-F(2A) | 96.4(5) |

Symmetry transformations used to generate equivalent atoms:

Table 27. Anisotropic displacement parameters (A^2 x 10^3) for $C_{20}H_{23}BF_8N_4$ (**29**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [ h^2 a*^2 U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| C(1) | 22(2) | 22(2) | 31(2) | -3(1) | -2(1) | 0(1) |
| C(3) | 27(2) | 23(2) | 31(2) | 1(2) | -4(1) | -1(1) |
| C(4) | 27(2) | 28(2) | 28(2) | 5(2) | -3(2) | 0(2) |
| C(11) | 28(2) | 26(2) | 33(2) | -1(2) | 7(2) | 4(2) |
| C(12) | 34(2) | 31(2) | 33(2) | -5(2) | -5(2) | -1(2) |
| C(13) | 34(2) | 22(2) | 43(2) | -8(2) | 4(2) | -4(2) |
| C(14) | 25(2) | 27(2) | 38(2) | 1(2) | 9(2) | 4(1) |
| C(15) | 31(2) | 27(2) | 29(2) | 0(2) | -5(2) | 3(2) |
| C(16) | 20(2) | 25(2) | 37(2) | -4(2) | 2(2) | -2(1) |
| C(21) | 32(2) | 30(2) | 37(2) | 0(2) | 13(2) | 2(2) |
| C(22) | 63(3) | 48(3) | 37(2) | -5(2) | 10(2) | 6(2) |
| C(23) | 33(2) | 61(3) | 72(3) | 6(3) | 14(2) | 11(2) |
| C(31) | 42(2) | 29(2) | 39(2) | 2(2) | 1(2) | 3(2) |
| C(41) | 53(3) | 45(2) | 30(2) | 5(2) | 3(2) | -4(2) |
| C(51) | 42(2) | 35(2) | 35(2) | -11(2) | 8(2) | 4(2) |
| C(52) | 70(3) | 68(4) | 42(3) | -22(2) | 1(2) | 0(3) |
| C(53) | 37(2) | 53(3) | 71(3) | -5(3) | 11(2) | 5(2) |
| C(100) | 103(5) | 84(4) | 54(3) | 2(3) | 3(3) | -34(4) |
| C(101) | 50(3) | 89(4) | 48(3) | 13(3) | 16(2) | 1(3) |
| C(131) | 41(2) | 28(2) | 42(2) | 5(2) | 7(2) | -3(2) |
| N(2) | 24(1) | 22(1) | 30(2) | -1(1) | 1(1) | 2(1) |
| N(5) | 26(2) | 27(2) | 28(2) | -2(1) | 2(1) | 2(1) |
| N(102) | 84(4) | 105(5) | 117(5) | 44(4) | 43(3) | 6(4) |
| N(131) | 64(3) | 38(2) | 71(3) | 14(2) | -6(2) | -4(2) |
| B(1) | 34(3) | 88(5) | 46(3) | -7(3) | -1(2) | 4(3) |
| F(1) | 45(3) | 70(4) | 62(4) | -11(3) | 3(3) | -31(3) |
| F(2) | 49(3) | 60(3) | 56(3) | -28(3) | 5(2) | -15(2) |
| F(3) | 108(6) | 67(4) | 69(4) | 7(3) | 23(4) | -15(4) |
| F(4) | 101(6) | 80(5) | 173(9) | -19(6) | -52(6) | 40(5) |
| F(1A) | 57(4) | 116(7) | 40(4) | -7(4) | -4(3) | -17(4) |
| F(2A) | 169(9) | 60(5) | 81(6) | -16(4) | -28(6) | 25(6) |
| F(3A) | 86(9) | 232(17) | 64(6) | -12(9) | -4(6) | 86(10) |
| F(4A) | 98(7) | 128(9) | 109(8) | 15(7) | 24(6) | -50(6) |
| F(13) | 54(1) | 27(1) | 59(2) | -5(1) | -9(1) | -13(1) |
| F(14) | 42(1) | 40(1) | 41(1) | 7(1) | -12(1) | 0(1) |
| F(15) | 39(1) | 27(1) | 53(1) | -2(1) | -14(1) | -10(1) |
| F(16) | 54(2) | 38(1) | 44(1) | 1(1) | -23(1) | -8(1) |

Table 28. Hydrogen coordinates ( x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $C_{20} H_{23} B F_8 N_4$ (**29**).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(21) | 1008 | 5695 | 478 | 40 |
| H(22A) | 2393 | 7029 | 966 | 74 |
| H(22B) | 1097 | 7223 | 1317 | 74 |
| H(22C) | 1579 | 8122 | 711 | 74 |
| H(23A) | -543 | 6302 | -282 | 83 |
| H(23B) | -281 | 7660 | -82 | 83 |
| H(23C) | -753 | 6765 | 530 | 83 |
| H(31A) | 1151 | 8752 | -322 | 55 |
| H(31B) | 1070 | 8911 | -1185 | 55 |
| H(31C) | 2295 | 9197 | -769 | 55 |
| H(41A) | 3459 | 7025 | -2421 | 64 |
| H(41B) | 3563 | 8235 | -1970 | 64 |
| H(41C) | 2337 | 7905 | -2372 | 64 |
| H(51) | 3315 | 4064 | -1468 | 45 |
| H(52A) | 1955 | 4506 | -2395 | 90 |
| H(52B) | 3182 | 4006 | -2723 | 90 |
| H(52C) | 2901 | 5398 | -2753 | 90 |
| H(53A) | 5067 | 5164 | -1292 | 80 |
| H(53B) | 4867 | 5819 | -2054 | 80 |
| H(53C) | 5135 | 4423 | -2033 | 80 |
| H(10A) | 5525 | 4735 | 2272 | 120 |
| H(10B) | 6392 | 3887 | 1814 | 120 |
| H(10C) | 6837 | 4436 | 2569 | 120 |

Table 29. Crystal data and structure refinement for $C_{14}H_{20}BF_6N_5$ (**30**)

| | | |
|---|---|---|
| Empirical formula | $C_{14}H_{20}BF_6N_5$ | |
| Formula weight | 383.14 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Unit cell dimensions | a = 10.6997(7) Å | α= 90°. |
| | b = 15.6439(13) Å | β= 90.664(5)°. |
| | c = 20.9824(13) Å | γ = 90°. |
| Volume | 3511.9(4) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.362 Mg/m$^3$ | |
| Absorption coefficient | 0.128 mm$^{-1}$ | |
| F(000) | 1412 | |
| Theta range for data collection | 3.19 to 29.27°. | |
| Index ranges | -12<=h<=14, -21<=k<=21, -28<=l<=28 | |
| Reflections collected | 48541 | |
| Independent reflections | 9488 [R(int) = 0.1365] | |
| Completeness to theta = 29.27° | 99.0 % | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 9488 / 0 / 497 | |
| Goodness-of-fit on F$^2$ | 1.112 | |
| Final R indices [I>2sigma(I)] | R1 = 0.1720, wR2 = 0.4624 | |
| R indices (all data) | R1 = 0.2112, wR2 = 0.4844 | |
| Extinction coefficient | 0.0017(12) | |
| Largest diff. peak and hole | 1.955 and -0.754 e.Å$^{-3}$ | |

Table 30. Crystal data and structure refinement for $C_{17}H_{26}N_2O$ (**31**).

| | | |
|---|---|---|
| Empirical formula | $C_{17}H_{26}N_2O$ | |
| Formula weight | 274.40 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 12.4220(9) Å | $\alpha$= 90°. |
| | b = 9.7712(9) Å | $\beta$= 107.800(5)°. |
| | c = 13.7399(15) Å | $\gamma$ = 90°. |
| Volume | 1587.9(3) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.148 Mg/m$^3$ | |
| Absorption coefficient | 0.071 mm$^{-1}$ | |
| F(000) | 600 | |
| Crystal size | 0.60 x 0.20 x 0.15 mm$^3$ | |
| Theta range for data collection | 3.06 to 26.37°. | |
| Index ranges | -15<=h<=15, -12<=k<=12, -17<=l<=16 | |
| Reflections collected | 21946 | |
| Independent reflections | 3240 [R(int) = 0.2283] | |
| Completeness to theta = 26.37° | 99.9 % | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 3240 / 0 / 285 | |
| Goodness-of-fit on F$^2$ | 1.092 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0613, wR2 = 0.0961 | |
| R indices (all data) | R1 = 0.0675, wR2 = 0.0992 | |
| Extinction coefficient | 0.000(4) | |
| Largest diff. peak and hole | 0.537 and -0.311 e.Å$^{-3}$ | |

Table 31. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $C_{17}H_{26}N_2O$ (**31**). U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| N(5) | 2750(1) | 7734(1) | 2966(1) | 24(1) |
| C(1) | 1903(1) | 8580(1) | 2900(1) | 26(1) |
| N(2) | 1092(1) | 8272(1) | 2052(1) | 26(1) |
| C(3) | 1433(1) | 7203(1) | 1550(1) | 26(1) |
| C(4) | 2475(1) | 6863(1) | 2128(1) | 25(1) |
| C(21A) | -18(2) | 8936(4) | 1732(2) | 30(3) |
| C(22) | -637(2) | 8554(3) | 2521(2) | 33(1) |
| C(23) | 156(2) | 10601(2) | 1854(2) | 31(1) |
| C(21) | -21(2) | 8933(2) | 1729(2) | 46(4) |
| C(22A) | -429(2) | 9302(2) | 2523(2) | 36(1) |
| C(23A) | -38(2) | 9942(3) | 897(2) | 43(1) |
| C(31) | 722(1) | 6617(2) | 573(1) | 35(1) |
| C(41) | 3226(1) | 5753(2) | 1993(1) | 34(1) |
| C(51) | 3850(1) | 7794(1) | 3757(1) | 29(1) |
| C(52) | 3716(1) | 8196(2) | 4774(1) | 43(1) |
| C(53) | 4609(1) | 8752(2) | 3409(1) | 49(1) |
| C(11) | 2382(1) | 3077(1) | -275(1) | 29(1) |
| C(12) | 3078(1) | 2353(2) | -737(1) | 38(1) |
| C(13) | 3634(1) | 1174(2) | -305(1) | 48(1) |
| C(14) | 3537(1) | 648(2) | 591(1) | 49(1) |
| C(15) | 2861(1) | 1324(2) | 1062(1) | 44(1) |
| C(16) | 2300(1) | 2499(1) | 644(1) | 34(1) |
| O(17) | 1852(1) | 4180(1) | -659(1) | 43(1) |

Table 32. Bond lengths [Å] and angles [°] for $C_{17}H_{26}N_2O$ (**31**).

| | | | |
|---|---|---|---|
| N(5)-C(1) | 1.3201(15) | C(31)-H(31A) | 0.986(17) |
| N(5)-C(4) | 1.3883(15) | C(31)-H(31B) | 0.970(17) |
| N(5)-C(51) | 1.4639(15) | C(31)-H(31C) | 0.981(17) |
| C(1)-N(2) | 1.3215(15) | C(41)-H(41A) | 0.989(16) |
| C(1)-H(1) | 0.967(14) | C(41)-H(41B) | 0.979(17) |
| N(2)-C(3) | 1.3880(15) | C(41)-H(41C) | 0.976(17) |
| N(2)-C(21A) | 1.464(3) | C(51)-C(53) | 1.5063(19) |
| N(2)-C(21) | 1.466(2) | C(51)-C(52) | 1.5089(19) |
| C(3)-C(4) | 1.3376(17) | C(51)-H(51) | 0.973(14) |
| C(3)-C(31) | 1.4780(17) | C(52)-H(52A) | 0.979(19) |
| C(4)-C(41) | 1.4789(17) | C(52)-H(52B) | 0.976(18) |
| C(21A)-C(22) | 1.555(4) | C(52)-H(52C) | 0.979(18) |
| C(21A)-C(23) | 1.644(5) | C(53)-H(53A) | 0.974(19) |
| C(21A)-H(21A) | 0.96(5) | C(53)-H(53B) | 0.97(2) |
| C(21A)-H(21) | 0.9257 | C(53)-H(53C) | 1.01(2) |
| C(22)-H(22A) | 0.9600 | C(11)-O(17) | 1.2881(15) |
| C(22)-H(22B) | 0.9600 | C(11)-C(12) | 1.4096(18) |
| C(22)-H(22C) | 0.9600 | C(11)-C(16) | 1.4148(18) |
| C(22)-H(22D) | 0.6228 | C(12)-C(13) | 1.381(2) |
| C(22)-H(22E) | 1.1999 | C(12)-H(12) | 0.926(17) |
| C(23)-H(23A) | 0.9600 | C(13)-C(14) | 1.374(2) |
| C(23)-H(23B) | 0.9600 | C(13)-H(13) | 0.961(19) |
| C(23)-H(23C) | 0.9600 | C(14)-C(15) | 1.374(2) |
| C(23)-H(22F) | 1.5779 | C(14)-H(14) | 0.97(2) |
| C(21)-C(22A) | 1.3829 | C(15)-C(16) | 1.3750(19) |
| C(21)-C(23A) | 1.505(3) | C(15)-H(15) | 0.991(18) |
| C(21)-H(21A) | 0.95(5) | C(16)-H(16) | 0.952(16) |
| C(21)-H(21) | 0.9210 | | |
| C(22A)-H(22D) | 0.9600 | C(1)-N(5)-C(4) | 109.78(10) |
| C(22A)-H(22E) | 0.9600 | C(1)-N(5)-C(51) | 124.72(10) |
| C(22A)-H(22F) | 0.9600 | C(4)-N(5)-C(51) | 125.29(10) |
| C(23A)-H(23D) | 0.9600 | N(5)-C(1)-N(2) | 107.15(10) |
| C(23A)-H(23E) | 0.9600 | N(5)-C(1)-H(1) | 125.8(8) |
| C(23A)-H(23F) | 0.9600 | N(2)-C(1)-H(1) | 127.0(8) |

| | |
|---|---|
| C(1)-N(2)-C(3) | 110.09(10) |
| C(1)-N(2)-C(21A) | 123.94(16) |
| C(3)-N(2)-C(21A) | 125.91(16) |
| C(1)-N(2)-C(21) | 124.10(12) |
| C(3)-N(2)-C(21) | 125.75(11) |
| C(21A)-N(2)-C(21) | 0.2(2) |
| C(4)-C(3)-N(2) | 106.22(10) |
| C(4)-C(3)-C(31) | 130.09(12) |
| N(2)-C(3)-C(31) | 123.69(11) |
| C(3)-C(4)-N(5) | 106.76(10) |
| C(3)-C(4)-C(41) | 129.88(11) |
| N(5)-C(4)-C(41) | 123.30(11) |
| N(2)-C(21A)-C(22) | 107.76(19) |
| N(2)-C(21A)-C(23) | 109.0(2) |
| C(22)-C(21A)-C(23) | 104.1(2) |
| N(2)-C(21A)-H(21A) | 103(3) |
| C(22)-C(21A)-H(21A) | 89(3) |
| C(23)-C(21A)-H(21A) | 139(4) |
| N(2)-C(21A)-H(21) | 107.6 |
| C(22)-C(21A)-H(21) | 98.4 |
| C(23)-C(21A)-H(21) | 127.9 |
| H(21A)-C(21A)-H(21) | 12.5 |
| C(21A)-C(22)-H(22A) | 109.5 |
| C(21A)-C(22)-H(22B) | 109.5 |
| H(22A)-C(22)-H(22B) | 109.5 |
| C(21A)-C(22)-H(22C) | 109.5 |
| H(22A)-C(22)-H(22C) | 109.5 |
| H(22B)-C(22)-H(22C) | 109.5 |
| C(21A)-C(22)-H(22D) | 118.1 |
| H(22A)-C(22)-H(22D) | 93.2 |
| H(22B)-C(22)-H(22D) | 115.6 |
| H(22C)-C(22)-H(22D) | 16.3 |
| C(21A)-C(22)-H(22E) | 87.9 |
| H(22A)-C(22)-H(22E) | 135.2 |
| H(22B)-C(22)-H(22E) | 27.8 |
| H(22C)-C(22)-H(22E) | 102.2 |
| H(22D)-C(22)-H(22E) | 114.9 |
| C(21A)-C(23)-H(23A) | 109.5 |
| C(21A)-C(23)-H(23B) | 109.5 |
| H(23A)-C(23)-H(23B) | 109.5 |
| C(21A)-C(23)-H(23C) | 109.5 |
| H(23A)-C(23)-H(23C) | 109.5 |
| H(23B)-C(23)-H(23C) | 109.5 |
| C(21A)-C(23)-H(22F) | 73.3 |
| H(23A)-C(23)-H(22F) | 159.0 |
| H(23B)-C(23)-H(22F) | 52.0 |
| H(23C)-C(23)-H(22F) | 88.2 |
| C(22A)-C(21)-N(2) | 114.52(8) |
| C(22A)-C(21)-C(23A) | 120.33(13) |
| N(2)-C(21)-C(23A) | 108.11(17) |
| C(22A)-C(21)-H(21A) | 114(3) |
| N(2)-C(21)-H(21A) | 103(3) |
| C(23A)-C(21)-H(21A) | 93(4) |
| C(22A)-C(21)-H(21) | 120.4 |
| N(2)-C(21)-H(21) | 107.8 |
| C(23A)-C(21)-H(21) | 80.9 |
| H(21A)-C(21)-H(21) | 12.5 |
| C(21)-C(22A)-H(22D) | 109.5 |
| C(21)-C(22A)-H(22E) | 109.5 |
| H(22D)-C(22A)-H(22E) | 109.5 |
| C(21)-C(22A)-H(22F) | 109.4 |
| H(22D)-C(22A)-H(22F) | 109.5 |
| H(22E)-C(22A)-H(22F) | 109.5 |
| C(21)-C(23A)-H(23D) | 109.5 |
| C(21)-C(23A)-H(23E) | 109.5 |
| H(23D)-C(23A)-H(23E) | 109.5 |
| C(21)-C(23A)-H(23F) | 109.5 |
| H(23D)-C(23A)-H(23F) | 109.5 |
| H(23E)-C(23A)-H(23F) | 109.5 |
| C(3)-C(31)-H(31A) | 111.2(10) |
| C(3)-C(31)-H(31B) | 110.7(9) |
| H(31A)-C(31)-H(31B) | 109.8(13) |

| | |
|---|---|
| C(3)-C(31)-H(31C) | 110.5(10) |
| H(31A)-C(31)-H(31C) | 107.6(13) |
| H(31B)-C(31)-H(31C) | 106.9(13) |
| C(4)-C(41)-H(41A) | 109.4(9) |
| C(4)-C(41)-H(41B) | 110.3(9) |
| H(41A)-C(41)-H(41B) | 107.2(13) |
| C(4)-C(41)-H(41C) | 111.0(9) |
| H(41A)-C(41)-H(41C) | 110.9(13) |
| H(41B)-C(41)-H(41C) | 108.0(14) |
| N(5)-C(51)-C(53) | 108.78(11) |
| N(5)-C(51)-C(52) | 110.85(10) |
| C(53)-C(51)-C(52) | 112.90(13) |
| N(5)-C(51)-H(51) | 105.4(8) |
| C(53)-C(51)-H(51) | 110.2(8) |
| C(52)-C(51)-H(51) | 108.5(8) |
| C(51)-C(52)-H(52A) | 111.2(10) |
| C(51)-C(52)-H(52B) | 109.6(10) |
| H(52A)-C(52)-H(52B) | 107.5(14) |
| C(51)-C(52)-H(52C) | 110.3(10) |
| H(52A)-C(52)-H(52C) | 110.4(14) |
| H(52B)-C(52)-H(52C) | 107.8(14) |
| C(51)-C(53)-H(53A) | 107.5(11) |
| C(51)-C(53)-H(53B) | 108.3(11) |
| H(53A)-C(53)-H(53B) | 109.0(15) |
| C(51)-C(53)-H(53C) | 111.4(11) |
| H(53A)-C(53)-H(53C) | 108.8(15) |
| H(53B)-C(53)-H(53C) | 111.7(16) |
| O(17)-C(11)-C(12) | 122.84(12) |
| O(17)-C(11)-C(16) | 122.17(12) |
| C(12)-C(11)-C(16) | 114.99(12) |
| C(13)-C(12)-C(11) | 121.41(14) |
| C(13)-C(12)-H(12) | 121.6(11) |
| C(11)-C(12)-H(12) | 117.0(11) |
| C(14)-C(13)-C(12) | 121.83(14) |
| C(14)-C(13)-H(13) | 119.5(11) |
| C(12)-C(13)-H(13) | 118.6(11) |
| C(13)-C(14)-C(15) | 118.41(14) |
| C(13)-C(14)-H(14) | 123.0(12) |
| C(15)-C(14)-H(14) | 118.6(12) |
| C(14)-C(15)-C(16) | 120.65(14) |
| C(14)-C(15)-H(15) | 119.6(10) |
| C(16)-C(15)-H(15) | 119.8(10) |
| C(15)-C(16)-C(11) | 122.71(13) |
| C(15)-C(16)-H(16) | 120.8(10) |
| C(11)-C(16)-H(16) | 116.4(10) |

Table 33. Anisotropic displacement parameters (Å$^2$x 10$^3$) for $C_{17}H_{26}N_2O$ (**31**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| N(5) | 21(1) | 26(1) | 25(1) | -1(1) | 6(1) | 1(1) |
| C(1) | 24(1) | 26(1) | 26(1) | -1(1) | 7(1) | 2(1) |
| N(2) | 22(1) | 30(1) | 26(1) | 2(1) | 7(1) | 2(1) |
| C(3) | 26(1) | 30(1) | 25(1) | 1(1) | 10(1) | -3(1) |
| C(4) | 26(1) | 27(1) | 25(1) | -2(1) | 10(1) | -2(1) |
| C(21A) | 19(5) | 51(7) | 18(2) | 19(3) | 2(2) | 5(4) |
| C(22) | 23(1) | 36(2) | 41(2) | 3(1) | 10(1) | 0(1) |
| C(23) | 33(1) | 24(1) | 36(1) | 2(1) | 9(1) | 4(1) |
| C(21) | 22(6) | 29(5) | 86(6) | 6(4) | 16(4) | 5(4) |
| C(22A) | 26(1) | 38(2) | 44(2) | -4(1) | 12(1) | 6(1) |
| C(23A) | 44(2) | 37(2) | 41(2) | 9(1) | 5(1) | 7(1) |
| C(31) | 33(1) | 41(1) | 27(1) | -3(1) | 5(1) | -6(1) |
| C(41) | 35(1) | 35(1) | 35(1) | -5(1) | 14(1) | 5(1) |
| C(51) | 23(1) | 29(1) | 30(1) | 0(1) | 2(1) | 2(1) |
| C(52) | 41(1) | 51(1) | 30(1) | -7(1) | -1(1) | 10(1) |
| C(53) | 28(1) | 56(1) | 55(1) | 13(1) | -1(1) | -9(1) |
| C(11) | 21(1) | 26(1) | 36(1) | 0(1) | 3(1) | -4(1) |
| C(12) | 33(1) | 47(1) | 32(1) | -7(1) | 6(1) | -3(1) |
| C(13) | 35(1) | 46(1) | 56(1) | -21(1) | 6(1) | 9(1) |
| C(14) | 40(1) | 33(1) | 64(1) | 4(1) | 1(1) | 7(1) |
| C(15) | 37(1) | 41(1) | 48(1) | 15(1) | 5(1) | -3(1) |
| C(16) | 27(1) | 33(1) | 42(1) | 2(1) | 12(1) | -1(1) |
| O(17) | 35(1) | 31(1) | 60(1) | 17(1) | 12(1) | 4(1) |

Table 34. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for $C_{17}H_{26}N_2O$ (**31**).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 1895(12) | 9304(15) | 3378(11) | 31(3) |
| H(21A) | -480(40) | 8290(60) | 1270(40) | 100(40) |
| H(22A) | -774 | 7586 | 2497 | 50 |
| H(22B) | -1344 | 9034 | 2359 | 50 |
| H(22C) | -175 | 8806 | 3194 | 50 |
| H(23A) | 534 | 10925 | 1384 | 46 |
| H(23B) | 604 | 10814 | 2540 | 46 |
| H(23C) | -568 | 11038 | 1708 | 46 |
| H(21) | -472 | 8454 | 1177 | 50(20) |
| H(22D) | -356 | 8543 | 2982 | 54 |
| H(22E) | -1210 | 9555 | 2253 | 54 |
| H(22F) | -2 | 10064 | 2884 | 54 |
| H(23D) | 272 | 9521 | 410 | 64 |
| H(23E) | 407 | 10728 | 1190 | 64 |
| H(23F) | -802 | 10220 | 560 | 64 |
| H(31A) | 567(14) | 7299(18) | 19(13) | 48(4) |
| H(31B) | 16(15) | 6273(16) | 640(12) | 45(4) |
| H(31C) | 1106(14) | 5839(17) | 371(12) | 46(4) |
| H(41A) | 2894(13) | 5322(17) | 1316(12) | 45(4) |
| H(41B) | 3963(14) | 6125(16) | 2007(12) | 44(4) |
| H(41C) | 3351(14) | 5076(17) | 2539(13) | 46(4) |
| H(51) | 4147(11) | 6866(14) | 3811(10) | 25(3) |
| H(52A) | 3423(15) | 9128(19) | 4754(13) | 57(5) |
| H(52B) | 4451(15) | 8169(18) | 5299(13) | 52(5) |
| H(52C) | 3218(15) | 7549(18) | 4971(13) | 49(5) |
| H(53A) | 4303(15) | 9670(20) | 3397(14) | 60(5) |
| H(53B) | 5354(17) | 8722(19) | 3905(15) | 66(5) |
| H(53C) | 4631(16) | 8510(20) | 2698(16) | 67(6) |
| H(12) | 3121(14) | 2683(17) | -1355(13) | 49(5) |
| H(13) | 4108(16) | 719(19) | -642(14) | 61(5) |

Table 35. Crystal data and structure refinement for $C_{17}H_{21}Cl_5N_2O$ (**32**).

| | | |
|---|---|---|
| Empirical formula | $C_{17}H_{21}Cl_5N_2O$ | |
| Formula weight | 446.61 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P2(1)2(1)2(1) | |
| Unit cell dimensions | a = 8.6782(5) Å | $\alpha$= 90°. |
| | b = 10.0603(6) Å | $\beta$= 90°. |
| | c = 23.4248(18) Å | $\gamma$ = 90°. |
| Volume | 2045.1(2) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.451 $Mg/m^3$ | |
| Absorption coefficient | 0.718 $mm^{-1}$ | |
| F(000) | 920 | |
| Crystal size | 0.30 x 0.10 x 0.10 $mm^3$ | |
| Theta range for data collection | 3.22 to 26.36°. | |
| Index ranges | -10<=h<=9, -12<=k<=12, -29<=l<=29 | |
| Reflections collected | 24012 | |
| Independent reflections | 4175 [R(int) = 0.0800] | |
| Completeness to theta = 26.36° | 99.5 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4175 / 0 / 311 | |
| Goodness-of-fit on $F^2$ | 1.100 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0237, wR2 = 0.0556 | |
| R indices (all data) | R1 = 0.0252, wR2 = 0.0562 | |
| Absolute structure parameter | -0.06(4) | |
| Extinction coefficient | 0.0011(7) | |
| Largest diff. peak and hole | 0.177 and -0.217 e.$Å^{-3}$ | |

Table 36. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for $C_{17}H_{21}Cl_5N_2O$ (**32**). U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 1672(2) | 6733(2) | 8357(1) | 22(1) |
| N(2) | 3074(2) | 6528(1) | 8572(1) | 22(1) |
| C(3) | 3981(2) | 7632(2) | 8460(1) | 26(1) |
| C(4) | 3096(2) | 8507(2) | 8168(1) | 24(1) |
| N(5) | 1652(2) | 7927(1) | 8108(1) | 21(1) |
| C(6) | 3545(2) | 5311(2) | 8892(1) | 27(1) |
| C(7) | 2931(3) | 5362(2) | 9496(1) | 44(1) |
| C(8) | 3035(3) | 4082(2) | 8570(1) | 41(1) |
| C(9) | 5608(2) | 7749(2) | 8663(1) | 40(1) |
| C(10) | 3459(3) | 9859(2) | 7942(1) | 36(1) |
| C(11) | 287(2) | 8563(2) | 7838(1) | 25(1) |
| C(12) | -518(2) | 9428(2) | 8277(1) | 33(1) |
| C(13) | -772(2) | 7502(2) | 7593(1) | 32(1) |
| C(20) | 8031(2) | 4515(2) | 8877(1) | 21(1) |
| C(21) | 7154(2) | 3305(2) | 8882(1) | 22(1) |
| C(22) | 6393(2) | 2824(2) | 9358(1) | 22(1) |
| C(23) | 6387(2) | 3541(2) | 9867(1) | 24(1) |
| C(24) | 7167(2) | 4757(2) | 9882(1) | 23(1) |
| C(25) | 7966(2) | 5215(2) | 9410(1) | 22(1) |
| O(26) | 8769(1) | 4925(1) | 8447(1) | 28(1) |
| Cl(27) | 7064(1) | 2447(1) | 8239(1) | 32(1) |
| Cl(28) | 5428(1) | 1319(1) | 9326(1) | 34(1) |
| Cl(29) | 5403(1) | 2962(1) | 10458(1) | 36(1) |
| Cl(30) | 7132(1) | 5690(1) | 10501(1) | 35(1) |
| Cl(31) | 8944(1) | 6713(1) | 9442(1) | 29(1) |

Table 37. Bond lengths [Å] and angles [°] for $C_{17}H_{21}Cl_5N_2O$ (**32**).

| | |
|---|---|
| C(1)-N(2) | 1.334(2) |
| C(1)-N(5) | 1.334(2) |
| N(2)-C(3) | 1.386(2) |
| N(2)-C(6) | 1.492(2) |
| C(3)-C(4) | 1.354(2) |
| C(3)-C(9) | 1.494(2) |
| C(4)-N(5) | 1.390(2) |
| C(4)-C(10) | 1.493(2) |
| N(5)-C(11) | 1.488(2) |
| C(6)-C(8) | 1.514(3) |
| C(6)-C(7) | 1.514(3) |
| C(11)-C(12) | 1.516(3) |
| C(11)-C(13) | 1.521(3) |
| C(20)-O(26) | 1.263(2) |
| C(20)-C(25) | 1.434(2) |
| C(20)-C(21) | 1.436(2) |
| C(21)-C(22) | 1.384(2) |
| C(21)-Cl(27) | 1.737(2) |
| C(22)-C(23) | 1.393(2) |
| C(22)-Cl(28) | 1.731(2) |
| C(23)-C(24) | 1.399(2) |
| C(23)-Cl(29) | 1.728(2) |
| C(24)-C(25) | 1.385(2) |
| C(24)-Cl(30) | 1.727(2) |
| C(25)-Cl(31) | 1.731(2) |
| | |
| N(2)-C(1)-N(5) | 108.42(15) |
| C(1)-N(2)-C(3) | 108.81(14) |
| C(1)-N(2)-C(6) | 124.52(14) |
| C(3)-N(2)-C(6) | 126.66(14) |
| C(4)-C(3)-N(2) | 107.17(14) |
| C(4)-C(3)-C(9) | 130.13(18) |
| N(2)-C(3)-C(9) | 122.67(17) |
| C(3)-C(4)-N(5) | 106.78(14) |
| C(3)-C(4)-C(10) | 130.70(16) |
| N(5)-C(4)-C(10) | 122.51(16) |
| C(1)-N(5)-C(4) | 108.82(13) |
| C(1)-N(5)-C(11) | 125.63(14) |
| C(4)-N(5)-C(11) | 125.47(13) |
| N(2)-C(6)-C(8) | 109.93(15) |
| N(2)-C(6)-C(7) | 110.21(15) |
| C(8)-C(6)-C(7) | 112.98(19) |
| N(5)-C(11)-C(12) | 109.04(14) |
| N(5)-C(11)-C(13) | 109.85(14) |
| C(12)-C(11)-C(13) | 112.32(16) |
| O(26)-C(20)-C(25) | 123.61(15) |
| O(26)-C(20)-C(21) | 123.50(15) |
| C(25)-C(20)-C(21) | 112.89(14) |
| C(22)-C(21)-C(20) | 123.74(15) |
| C(22)-C(21)-Cl(27) | 120.23(12) |
| C(20)-C(21)-Cl(27) | 116.02(12) |
| C(21)-C(22)-C(23) | 120.70(15) |
| C(21)-C(22)-Cl(28) | 120.08(13) |
| C(23)-C(22)-Cl(28) | 119.21(13) |
| C(22)-C(23)-C(24) | 118.25(15) |
| C(22)-C(23)-Cl(29) | 120.83(13) |
| C(24)-C(23)-Cl(29) | 120.90(13) |
| C(25)-C(24)-C(23) | 120.81(15) |
| C(25)-C(24)-Cl(30) | 119.95(13) |
| C(23)-C(24)-Cl(30) | 119.24(13) |
| C(24)-C(25)-C(20) | 123.50(14) |
| C(24)-C(25)-Cl(31) | 119.98(13) |
| C(20)-C(25)-Cl(31) | 116.52(12) |

Table 38. Anisotropic displacement parameters ($Å^2 x 10^3$) for $C_{17}H_{21}Cl_5N_2O$ (**32**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 19(1) | 23(1) | 22(1) | 2(1) | -1(1) | -2(1) |
| N(2) | 20(1) | 23(1) | 24(1) | 0(1) | -3(1) | 2(1) |
| C(3) | 20(1) | 28(1) | 29(1) | -3(1) | 0(1) | -2(1) |
| C(4) | 24(1) | 26(1) | 24(1) | -1(1) | 2(1) | -4(1) |
| N(5) | 20(1) | 23(1) | 19(1) | 2(1) | 0(1) | -1(1) |
| C(6) | 23(1) | 23(1) | 36(1) | 2(1) | -7(1) | 4(1) |
| C(7) | 55(1) | 46(1) | 31(1) | 10(1) | -3(1) | 17(1) |
| C(8) | 44(1) | 25(1) | 55(1) | -3(1) | -15(1) | 5(1) |
| C(9) | 22(1) | 38(1) | 61(1) | 2(1) | -9(1) | -5(1) |
| C(10) | 36(1) | 29(1) | 43(1) | 7(1) | -2(1) | -11(1) |
| C(11) | 25(1) | 27(1) | 22(1) | 8(1) | -4(1) | 0(1) |
| C(12) | 31(1) | 31(1) | 37(1) | 3(1) | -2(1) | 7(1) |
| C(13) | 30(1) | 34(1) | 31(1) | 3(1) | -10(1) | -1(1) |
| C(20) | 18(1) | 22(1) | 22(1) | 4(1) | 0(1) | 1(1) |
| C(21) | 23(1) | 21(1) | 21(1) | -1(1) | -2(1) | 3(1) |
| C(22) | 20(1) | 20(1) | 26(1) | 4(1) | -1(1) | -1(1) |
| C(23) | 23(1) | 28(1) | 21(1) | 7(1) | 3(1) | 0(1) |
| C(24) | 23(1) | 26(1) | 21(1) | -1(1) | -1(1) | 4(1) |
| C(25) | 21(1) | 20(1) | 24(1) | 2(1) | -2(1) | 0(1) |
| O(26) | 32(1) | 30(1) | 22(1) | 1(1) | 6(1) | -7(1) |
| Cl(27) | 42(1) | 27(1) | 26(1) | -6(1) | 5(1) | -4(1) |
| Cl(28) | 42(1) | 25(1) | 36(1) | 4(1) | 2(1) | -11(1) |
| Cl(29) | 44(1) | 40(1) | 26(1) | 8(1) | 11(1) | -5(1) |
| Cl(30) | 46(1) | 36(1) | 23(1) | -7(1) | 6(1) | -2(1) |
| Cl(31) | 30(1) | 25(1) | 30(1) | -2(1) | 1(1) | -7(1) |

Table 39. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for $C_{17}H_{21}Cl_5N_2O$ (**32**).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 900(20) | 6230(20) | 8395(9) | 26(5) |
| H(6) | 4660(30) | 5330(20) | 8884(10) | 33(5) |
| H(7A) | 1850(30) | 5340(20) | 9490(12) | 46(7) |
| H(7B) | 3370(30) | 4630(30) | 9699(13) | 57(8) |
| H(7C) | 3260(30) | 6120(30) | 9686(13) | 56(8) |
| H(8A) | 3440(30) | 4150(30) | 8203(15) | 59(8) |
| H(8B) | 1950(30) | 4040(20) | 8538(11) | 37(6) |
| H(8C) | 3380(30) | 3220(20) | 8770(11) | 46(7) |
| H(9A) | 6210(30) | 7120(30) | 8483(13) | 59(8) |
| H(9B) | 5990(30) | 8500(30) | 8537(11) | 42(6) |
| H(9C) | 5640(30) | 7640(30) | 9047(15) | 67(9) |
| H(10A) | 2870(30) | 10560(30) | 8191(12) | 53(7) |
| H(10B) | 3140(20) | 9950(20) | 7547(10) | 32(5) |
| H(10C) | 4570(30) | 10010(30) | 7967(12) | 52(7) |
| H(11) | 690(20) | 9080(20) | 7539(10) | 32(6) |
| H(12A) | -910(30) | 8850(30) | 8578(12) | 49(7) |
| H(12B) | -1320(30) | 9840(30) | 8106(12) | 50(7) |
| H(12C) | 170(30) | 10040(30) | 8436(11) | 45(7) |
| H(13A) | -1210(20) | 6930(20) | 7903(10) | 31(5) |
| H(13B) | -1640(30) | 7960(20) | 7402(10) | 41(6) |
| H(13C) | -300(30) | 6970(30) | 7328(12) | 52(7) |

Table 40. Crystal data and structure refinement for $C_{17}H_{21}F_5N_2O$ (**33**).

| | | |
|---|---|---|
| Empirical formula | $C_{17}H_{21}F_5N_2O$ | |
| Formula weight | 364.36 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P2(1)2(1)2(1) | |
| Unit cell dimensions | a = 8.6613(12) Å | $\alpha$= 90°. |
| | b = 13.8326(14) Å | $\beta$= 90°. |
| | c = 14.7518(17) Å | $\gamma$ = 90°. |
| Volume | 1767.4(4) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.369 $Mg/m^3$ | |
| Absorption coefficient | 0.122 $mm^{-1}$ | |
| F(000) | 760 | |
| Crystal size | 0.20 x 0.15 x 0.15 $mm^3$ | |
| Theta range for data collection | 3.10 to 26.37°. | |
| Index ranges | -10<=h<=10, -17<=k<=17, -18<=l<=18 | |
| Reflections collected | 24963 | |
| Independent reflections | 3619 [R(int) = 0.1780] | |
| Completeness to theta = 26.37° | 99.8 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3619 / 0 / 307 | |
| Goodness-of-fit on $F^2$ | 1.219 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0873, wR2 = 0.1147 | |
| R indices (all data) | R1 = 0.1196, wR2 = 0.1233 | |
| Absolute structure parameter | -0.1(14) | |
| Extinction coefficient | 0.0055(9) | |
| Largest diff. peak and hole | 0.225 and -0.236 e.$Å^{-3}$ | |

Table 41. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for $C_{17}H_{21}F_5N_2O$ (**33**). U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 4083(5) | 10794(3) | 1139(3) | 28(1) |
| C(2) | 3128(5) | 10051(3) | 1476(3) | 31(1) |
| C(3) | 3028(6) | 9142(3) | 1103(3) | 33(1) |
| C(4) | 3857(6) | 8915(3) | 337(3) | 36(1) |
| C(5) | 4819(6) | 9605(4) | -19(3) | 40(1) |
| C(6) | 4933(5) | 10501(3) | 368(3) | 35(1) |
| O(7) | 4151(4) | 11642(2) | 1476(2) | 41(1) |
| F(8) | 2218(3) | 10246(2) | 2208(2) | 49(1) |
| F(9) | 2057(4) | 8481(2) | 1464(2) | 60(1) |
| F(10) | 3754(4) | 8020(2) | -35(2) | 65(1) |
| F(11) | 5673(4) | 9387(3) | -755(2) | 74(1) |
| F(12) | 5909(4) | 11145(2) | -17(2) | 60(1) |
| C(20) | 8833(5) | 1211(3) | 8340(3) | 22(1) |
| N(21) | 7846(4) | 708(2) | 7837(2) | 21(1) |
| C(22) | 8224(5) | -268(3) | 7892(3) | 25(1) |
| C(23) | 9468(5) | -329(3) | 8448(3) | 20(1) |
| N(24) | 9823(4) | 606(2) | 8720(2) | 21(1) |
| C(25) | 6559(5) | 1120(3) | 7288(3) | 27(1) |
| C(26) | 7050(7) | 1196(4) | 6301(4) | 42(1) |
| C(27) | 6063(7) | 2090(3) | 7674(4) | 38(1) |
| C(28) | 7374(6) | -1048(4) | 7413(4) | 31(1) |
| C(29) | 10359(7) | -1192(4) | 8747(4) | 34(1) |
| C(30) | 11030(5) | 903(3) | 9378(3) | 24(1) |
| C(31) | 12100(7) | 1640(4) | 8935(4) | 45(1) |
| C(32) | 10292(7) | 1287(5) | 10234(4) | 47(2) |

Table 42. Bond lengths [Å] and angles [°] for $C_{17}H_{21}F_5N_2O$ (**33**).

| | |
|---|---|
| C(1)-O(7) | 1.276(5) |
| C(1)-C(2) | 1.409(6) |
| C(1)-C(6) | 1.413(7) |
| C(2)-F(8) | 1.364(5) |
| C(2)-C(3) | 1.376(6) |
| C(3)-F(9) | 1.351(5) |
| C(3)-C(4) | 1.376(7) |
| C(4)-F(10) | 1.357(5) |
| C(4)-C(5) | 1.371(7) |
| C(5)-F(11) | 1.349(6) |
| C(5)-C(6) | 1.368(7) |
| C(6)-F(12) | 1.354(5) |
| C(20)-N(24) | 1.324(5) |
| C(20)-N(21) | 1.328(5) |
| N(21)-C(22) | 1.391(5) |
| N(21)-C(25) | 1.492(5) |
| C(22)-C(23) | 1.356(6) |
| C(22)-C(28) | 1.486(6) |
| C(23)-N(24) | 1.388(5) |
| C(23)-C(29) | 1.488(6) |
| N(24)-C(30) | 1.484(5) |
| C(25)-C(27) | 1.520(6) |
| C(25)-C(26) | 1.521(7) |
| C(30)-C(32) | 1.512(7) |
| C(30)-C(31) | 1.525(7) |

| | |
|---|---|
| O(7)-C(1)-C(2) | 124.1(4) |
| O(7)-C(1)-C(6) | 123.6(4) |
| C(2)-C(1)-C(6) | 112.3(4) |
| F(8)-C(2)-C(3) | 117.4(4) |
| F(8)-C(2)-C(1) | 118.3(4) |
| C(3)-C(2)-C(1) | 124.3(4) |
| F(9)-C(3)-C(4) | 119.7(4) |
| F(9)-C(3)-C(2) | 120.0(4) |
| C(4)-C(3)-C(2) | 120.2(4) |
| F(10)-C(4)-C(5) | 121.4(5) |
| F(10)-C(4)-C(3) | 120.4(5) |
| C(5)-C(4)-C(3) | 118.2(4) |
| F(11)-C(5)-C(6) | 119.9(5) |
| F(11)-C(5)-C(4) | 119.1(5) |
| C(6)-C(5)-C(4) | 121.0(4) |
| F(12)-C(6)-C(5) | 117.8(5) |
| F(12)-C(6)-C(1) | 118.3(4) |
| C(5)-C(6)-C(1) | 123.9(4) |
| N(24)-C(20)-N(21) | 108.8(3) |
| C(20)-N(21)-C(22) | 109.0(4) |
| C(20)-N(21)-C(25) | 125.7(3) |
| C(22)-N(21)-C(25) | 125.4(3) |
| C(23)-C(22)-N(21) | 106.4(3) |
| C(23)-C(22)-C(28) | 129.5(4) |
| N(21)-C(22)-C(28) | 124.1(4) |
| C(22)-C(23)-N(24) | 107.0(3) |
| C(22)-C(23)-C(29) | 129.9(4) |
| N(24)-C(23)-C(29) | 123.1(4) |
| C(20)-N(24)-C(23) | 108.8(3) |
| C(20)-N(24)-C(30) | 124.0(3) |
| C(23)-N(24)-C(30) | 127.1(3) |
| N(21)-C(25)-C(27) | 110.2(4) |
| N(21)-C(25)-C(26) | 109.7(4) |
| C(27)-C(25)-C(26) | 112.1(4) |
| N(24)-C(30)-C(32) | 110.2(4) |
| N(24)-C(30)-C(31) | 109.5(4) |
| C(32)-C(30)-C(31) | 112.3(5) |

Table 43. Anisotropic displacement parameters ($Å^2$x $10^3$) for $C_{17}H_{21}F_5N_2O$ (**33**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 25(2) | 27(2) | 32(3) | 2(2) | -7(2) | 3(2) |
| C(2) | 30(3) | 39(3) | 23(2) | 5(2) | 2(2) | 3(2) |
| C(3) | 31(3) | 27(2) | 39(3) | 9(2) | -11(2) | -7(2) |
| C(4) | 43(3) | 28(2) | 37(3) | -7(2) | -8(2) | 5(2) |
| C(5) | 31(3) | 59(3) | 31(3) | -4(2) | 4(2) | 15(3) |
| C(6) | 25(2) | 34(3) | 46(3) | 15(2) | -4(2) | 1(2) |
| O(7) | 43(2) | 25(2) | 54(2) | -3(2) | -5(2) | 2(2) |
| F(8) | 50(2) | 55(2) | 42(2) | -7(2) | 19(2) | -8(2) |
| F(9) | 68(2) | 47(2) | 66(2) | 10(2) | -4(2) | -26(2) |
| F(10) | 87(3) | 36(2) | 70(2) | -26(2) | -11(2) | 5(2) |
| F(11) | 77(3) | 92(3) | 55(2) | -19(2) | 29(2) | 8(2) |
| F(12) | 53(2) | 63(2) | 63(2) | 13(2) | 17(2) | -16(2) |
| C(20) | 23(2) | 15(2) | 29(2) | 2(2) | 1(2) | 2(2) |
| N(21) | 24(2) | 18(2) | 22(2) | -2(1) | 1(2) | -2(2) |
| C(22) | 28(2) | 20(2) | 28(2) | -3(2) | 9(2) | -2(2) |
| C(23) | 24(2) | 17(2) | 18(2) | -1(2) | 4(2) | -1(2) |
| N(24) | 18(2) | 18(2) | 27(2) | 3(1) | -2(2) | 1(2) |
| C(25) | 21(2) | 30(2) | 31(3) | -3(2) | -6(2) | -3(2) |
| C(26) | 49(3) | 42(3) | 36(3) | 2(3) | -2(3) | 4(3) |
| C(27) | 32(3) | 29(3) | 51(4) | -10(2) | -15(3) | 9(2) |
| C(28) | 31(3) | 27(2) | 35(3) | -6(2) | 0(2) | -1(2) |
| C(29) | 41(3) | 23(2) | 38(3) | 4(2) | -6(3) | 0(2) |
| C(30) | 26(2) | 18(2) | 29(2) | 3(2) | -5(2) | 4(2) |
| C(31) | 41(3) | 47(3) | 46(4) | 8(3) | -18(3) | -15(3) |
| C(32) | 44(3) | 62(4) | 34(3) | -10(3) | -4(3) | 13(3) |

Table 44. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for $C_{17}H_{21}F_5N_2O$ (**33**).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(20) | 8828 | 1879 | 8412 | 27 |
| H(25) | 5790(50) | 620(30) | 7320(30) | 14(10) |
| H(26A) | 7810(50) | 1650(30) | 6230(30) | 31(14) |
| H(26B) | 7330(60) | 510(40) | 6030(40) | 57(16) |
| H(26C) | 6050(90) | 1420(50) | 5970(50) | 100(20) |
| H(27A) | 7030(70) | 2620(40) | 7620(40) | 55(16) |
| H(27B) | 5710(70) | 1930(40) | 8330(40) | 62(18) |
| H(27C) | 5220(70) | 2310(40) | 7330(40) | 67(19) |
| H(28A) | 6360(50) | -960(30) | 7510(30) | 21(12) |
| H(28B) | 7540(50) | -1030(30) | 6790(30) | 19(11) |
| H(28C) | 7720(60) | -1680(40) | 7680(40) | 56(16) |
| H(29A) | 11380(70) | -1160(40) | 8600(40) | 52(17) |
| H(29B) | 10000(60) | -1740(40) | 8420(40) | 50(16) |
| H(29C) | 10310(60) | -1280(40) | 9440(40) | 71(19) |
| H(30) | 11630(40) | 310(20) | 9480(20) | 1(8) |
| H(31A) | 12910(60) | 1820(30) | 9400(30) | 34(13) |
| H(31B) | 11470(60) | 2260(40) | 8780(40) | 58(17) |
| H(31C) | 12550(70) | 1310(40) | 8390(40) | 80(20) |
| H(32A) | 9700(60) | 1880(40) | 10080(40) | 57(17) |
| H(32B) | 9630(70) | 810(40) | 10540(40) | 62(19) |
| H(32C) | 11090(70) | 1480(40) | 10720(40) | 74(19) |

Table 45. Crystal data and structure refinement for $C_{16}H_{25}N_3O$ (**34**).

| | | |
|---|---|---|
| Empirical formula | $C_{16}H_{25}N_3O$ | |
| Formula weight | 275.39 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | Cmcm | |
| Unit cell dimensions | a = 12.0238(14) Å | $\alpha$= 90°. |
| | b = 13.5371(15) Å | $\beta$= 90°. |
| | c = 9.9590(18) Å | $\gamma$ = 90°. |
| Volume | 1621.0(4) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.128 Mg/m$^3$ | |
| Absorption coefficient | 0.072 mm$^{-1}$ | |
| F(000) | 600 | |
| Crystal size | 0.30 x 0.25 x 0.20 mm$^3$ | |
| Theta range for data collection | 3.39 to 26.37°. | |
| Index ranges | -15<=h<=15, -16<=k<=16, -12<=l<=12 | |
| Reflections collected | 11310 | |
| Independent reflections | 920 [R(int) = 0.0573] | |
| Completeness to theta = 26.37° | 99.7 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 920 / 0 / 93 | |
| Goodness-of-fit on F$^2$ | 1.207 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0578, wR2 = 0.1281 | |
| R indices (all data) | R1 = 0.0634, wR2 = 0.1312 | |
| Extinction coefficient | 0.0066(13) | |
| Largest diff. peak and hole | 0.232 and -0.149 e.Å$^{-3}$ | |

Table 46. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $C_{16}H_{25}N_3O$ (**34**). U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 5000 | 2895(2) | 2500 | 42(1) |
| C(2) | 5000 | 2316(2) | 1309(3) | 47(1) |
| C(3) | 5000 | 1304(2) | 1375(3) | 48(1) |
| N(4) | 5000 | 760(2) | 2500 | 46(1) |
| O(5) | 5000 | 3832(2) | 2500 | 60(1) |
| C(10) | 0 | 3428(2) | 2500 | 32(1) |
| N(11) | 896(2) | 2852(1) | 2500 | 33(1) |
| C(12) | 563(2) | 1871(2) | 2500 | 38(1) |
| C(13) | 2062(2) | 3223(2) | 2500 | 39(1) |
| C(14) | 2283(2) | 3805(2) | 1237(2) | 48(1) |
| C(15) | 1371(2) | 1032(2) | 2500 | 54(1) |

Table 47. Bond lengths [Å] and angles [°] for $C_{16}H_{25}N_3O$ (**34**).

| | |
|---|---|
| C(1)-O(5) | 1.268(4) |
| C(1)-C(2) | 1.422(4) |
| C(1)-C(2)#1 | 1.422(4) |
| C(2)-C(3) | 1.371(4) |
| C(3)-N(4) | 1.341(3) |
| N(4)-C(3)#1 | 1.341(3) |
| C(10)-N(11)#2 | 1.329(2) |
| C(10)-N(11) | 1.329(2) |
| N(11)-C(12) | 1.387(3) |
| N(11)-C(13) | 1.489(3) |
| C(12)-C(12)#2 | 1.353(4) |
| C(12)-C(15) | 1.495(3) |
| C(13)-C(14) | 1.508(2) |
| C(13)-C(14)#1 | 1.508(2) |

| | |
|---|---|
| O(5)-C(1)-C(2) | 123.5(2) |
| O(5)-C(1)-C(2)#1 | 123.5(2) |
| C(2)-C(1)-C(2)#1 | 113.0(3) |
| C(3)-C(2)-C(1) | 120.7(3) |
| N(4)-C(3)-C(2) | 126.0(3) |
| C(3)-N(4)-C(3)#1 | 113.4(3) |
| N(11)#2-C(10)-N(11) | 108.2(3) |
| C(10)-N(11)-C(12) | 109.1(2) |
| C(10)-N(11)-C(13) | 124.4(2) |
| C(12)-N(11)-C(13) | 126.5(2) |
| C(12)#2-C(12)-N(11) | 106.8(1) |
| C(12)#2-C(12)-C(15) | 130.8(1) |
| N(11)-C(12)-C(15) | 122.6(2) |
| N(11)-C(13)-C(14) | 110.0(1) |
| N(11)-C(13)-C(14)#1 | 110.0(1) |
| C(14)-C(13)-C(14)#1 | 113.1(2) |

Table 48. Anisotropic displacement parameters ($Å^2$x $10^3$) for $C_{16}H_{25}N_3O$ (**34**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 16(1) | 23(2) | 88(3) | 0 | 0 | 0 |
| C(2) | 40(1) | 37(1) | 64(2) | 9(1) | 0 | 0 |
| C(3) | 48(2) | 33(1) | 63(2) | -6(1) | 0 | 0 |
| N(4) | 46(2) | 23(1) | 68(2) | 0 | 0 | 0 |
| O(5) | 38(1) | 23(1) | 120(3) | 0 | 0 | 0 |
| C(10) | 24(2) | 19(2) | 55(2) | 0 | 0 | 0 |
| N(11) | 19(1) | 20(1) | 60(1) | 0 | 0 | 0(1) |
| C(12) | 25(1) | 18(1) | 70(2) | 0 | 0 | 1(1) |
| C(13) | 18(1) | 25(1) | 72(2) | 0 | 0 | -1(1) |
| C(14) | 31(1) | 60(1) | 53(1) | -10(1) | 7(1) | -17(1) |
| C(15) | 31(1) | 19(1) | 112(3) | 0 | 0 | 5(1) |

Table 49. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for $C_{16}H_{25}N_3O$ (**34**).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 5000 | 2630(30) | 450(40) | 72(11) |
| H(3) | 5000 | 920(20) | 550(30) | 54(9) |
| H(10) | 0 | 4120(30) | 2500 | 34(9) |
| H(13) | 2530(30) | 2630(20) | 2500 | 52(8) |
| H(14A) | 1809(17) | 4413(16) | 1250(20) | 44(5) |
| H(14B) | 3047(19) | 3971(15) | 1200(20) | 50(6) |
| H(14C) | 2069(19) | 3414(18) | 430(30) | 65(7) |
| H(15A) | 1000(30) | 430(30) | 2500 | 66(10) |
| H(15B) | 1880(30) | 1057(19) | 1700(30) | 83(9) |

Table 50. Crystal data and structure refinement for $C_{11}H_{20}N_2S$ (**35**).

| | | |
|---|---|---|
| Empirical formula | $C_{11}H_{20}N_2S$ | |
| Formula weight | 212.35 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | C2/c | |
| Unit cell dimensions | a = 9.9437(18) Å | $\alpha$= 90°. |
| | b = 11.2057(15) Å | $\beta$= 101.715(14)°. |
| | c = 11.292(2) Å | $\gamma$ = 90°. |
| Volume | 1232.1(4) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.145 $Mg/m^3$ | |
| Absorption coefficient | 0.231 $mm^{-1}$ | |
| F(000) | 464 | |
| Crystal size | 0.25 x 0.20 x 0.15 $mm^3$ | |
| Theta range for data collection | 3.56 to 26.36°. | |
| Index ranges | -12<=h<=12, -14<=k<=14, -13<=l<=14 | |
| Reflections collected | 8600 | |
| Independent reflections | 1258 [R(int) = 0.2598] | |
| Completeness to theta = 26.36° | 99.8 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 1258 / 0 / 94 | |
| Goodness-of-fit on $F^2$ | 1.172 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0843, wR2 = 0.1275 | |
| R indices (all data) | R1 = 0.0980, wR2 = 0.1355 | |
| Extinction coefficient | 0.000(4) | |
| Largest diff. peak and hole | 0.448 and -0.244 e.$Å^{-3}$ | |

Table 51. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $C_{11}H_{20}N_2S$ (**35**). U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 0 | 2558(1) | 2500 | 52(1) |
| C(1) | 0 | 1043(3) | 2500 | 32(1) |
| N(2) | 937(2) | 317(2) | 3191(2) | 30(1) |
| C(3) | 583(2) | -873(2) | 2930(2) | 30(1) |
| C(4) | 2136(2) | 786(2) | 4063(2) | 38(1) |
| C(5) | 3478(2) | 437(3) | 3735(3) | 59(1) |
| C(6) | 2101(6) | 453(7) | 5341(3) | 108(2) |
| C(7) | 1361(3) | -1915(2) | 3537(3) | 48(1) |

Table 52. Bond lengths [Å] and angles [°] for $C_{11}H_{20}N_2S$ (**35**).

| | |
|---|---|
| S(1)-C(1) | 1.698(3) |
| C(1)-N(2) | 1.357(2) |
| C(1)-N(2)#1 | 1.357(2) |
| N(2)-C(3) | 1.395(3) |
| N(2)-C(4) | 1.480(3) |
| C(3)-C(3)#1 | 1.353(4) |
| C(3)-C(7) | 1.489(3) |
| C(4)-C(6) | 1.498(5) |
| C(4)-C(5) | 1.506(4) |
| | |
| N(2)-C(1)-N(2)#1 | 106.4(2) |
| N(2)-C(1)-S(1) | 126.8(1) |
| N(2)#1-C(1)-S(1) | 126.8(1) |
| C(1)-N(2)-C(3) | 109.7(2) |
| C(1)-N(2)-C(4) | 122.4(2) |
| C(3)-N(2)-C(4) | 127.9(2) |
| C(3)#1-C(3)-N(2) | 107.1(1) |
| C(3)#1-C(3)-C(7) | 128.3(1) |
| N(2)-C(3)-C(7) | 124.6(2) |
| N(2)-C(4)-C(6) | 112.3(2) |
| N(2)-C(4)-C(5) | 112.2(2) |
| C(6)-C(4)-C(5) | 111.5(3) |

Table 53. Anisotropic displacement parameters ($Å^2 x 10^3$) for $C_{11}H_{20}N_2S$ (**35**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 33(1) | 29(1) | 88(1) | 0 | -2(1) | 0 |
| C(1) | 22(1) | 33(2) | 39(2) | 0 | 5(1) | 0 |
| N(2) | 22(1) | 32(1) | 32(1) | -3(1) | -1(1) | 0(1) |
| C(3) | 28(1) | 31(1) | 29(1) | 1(1) | 2(1) | -1(1) |
| C(4) | 27(1) | 42(1) | 40(1) | -7(1) | -5(1) | -6(1) |
| C(5) | 29(1) | 77(2) | 66(2) | -1(2) | -1(1) | -10(1) |
| C(6) | 88(3) | 204(6) | 33(2) | -38(2) | 12(2) | -89(4) |
| C(7) | 41(1) | 37(1) | 55(2) | 8(1) | -11(1) | 3(1) |

Table 54. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2 x 10^3$) for $C_{11}H_{20}N_2S$ (**35**).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(4) | 2070(30) | 1610(30) | 3990(30) | 54(8) |
| H(5A) | 3467 | 661 | 2913 | 88 |
| H(5B) | 3602 | -410 | 3822 | 88 |
| H(5C) | 4219 | 839 | 4262 | 88 |
| H(6A) | 1300(50) | 880(40) | 5390(40) | 88(14) |
| H(6B) | 2760(40) | 870(30) | 5840(40) | 83(11) |
| H(6C) | 1740(60) | -180(50) | 5550(50) | 124(19) |
| H(7A) | 1410(30) | -1880(30) | 4380(30) | 72(10) |
| H(7B) | 2270(40) | -1980(30) | 3420(30) | 78(11) |
| H(7C) | 860(30) | -2660(30) | 3250(30) | 59(8) |

Table 55. Crystal data and structure refinement for $C_{17}H_{26}N_2O_3S$ (**37**).

| | | |
|---|---|---|
| Empirical formula | $C_{17}H_{26}N_2O_3S$ | |
| Formula weight | 338.46 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 8.8691(9) Å | $\alpha$= 87.082(8)°. |
| | b = 14.1494(15) Å | $\beta$= 88.326(8)°. |
| | c = 14.3200(14) Å | $\gamma$ = 83.988(8)°. |
| Volume | 1784.3(3) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.260 Mg/m$^3$ | |
| Absorption coefficient | 0.197 mm$^{-1}$ | |
| F(000) | 728 | |
| Crystal size | 0.40 x 0.15 x 0.15 mm$^3$ | |
| Theta range for data collection | 3.17 to 26.37°. | |
| Index ranges | -11<=h<=9, -17<=k<=17, -17<=l<=17 | |
| Reflections collected | 25481 | |
| Independent reflections | 7264 [R(int) = 0.0931] | |
| Completeness to theta = 26.37° | 99.8 % | |
| Absorption correction | None | |
| Max. and min. transmission | 0.9710 and 0.9252 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 7264 / 0 / 416 | |
| Goodness-of-fit on F$^2$ | 1.092 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0600, wR2 = 0.1469 | |
| R indices (all data) | R1 = 0.0771, wR2 = 0.1565 | |
| Extinction coefficient | 0.0047(16) | |
| Largest diff. peak and hole | 0.553 and -0.543 e.Å$^{-3}$ | |

Table 56. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $C_{17}H_{26}N_2O_3S$ (**37**). U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 4391(1) | 7507(1) | 3990(1) | 24(1) |
| N(2) | 6223(2) | 6166(2) | 6750(2) | 23(1) |
| N(5) | 4423(2) | 5777(2) | 7696(2) | 23(1) |
| O(11) | 3958(3) | 6564(2) | 3844(1) | 37(1) |
| O(12) | 3741(3) | 8232(2) | 3327(1) | 38(1) |
| O(13) | 6013(2) | 7514(2) | 4075(2) | 40(1) |
| C(1) | 5288(3) | 5506(2) | 6959(2) | 23(1) |
| C(3) | 5962(3) | 6888(2) | 7374(2) | 27(1) |
| C(4) | 4835(3) | 6638(2) | 7976(2) | 27(1) |
| C(51) | 3195(3) | 5255(2) | 8143(2) | 27(1) |
| C(11) | 3597(3) | 7829(2) | 5101(2) | 24(1) |
| C(12) | 2803(3) | 7205(2) | 5648(2) | 27(1) |
| C(13) | 2163(3) | 7477(2) | 6504(2) | 33(1) |
| C(14) | 2325(4) | 8364(2) | 6810(2) | 40(1) |
| C(15) | 3134(4) | 8986(2) | 6275(2) | 46(1) |
| C(16) | 3770(4) | 8723(2) | 5409(2) | 37(1) |
| C(21) | 7465(3) | 6106(2) | 6029(2) | 28(1) |
| C(22) | 8951(3) | 5762(3) | 6494(2) | 41(1) |
| C(23) | 7121(4) | 5475(2) | 5253(2) | 35(1) |
| C(31) | 6757(4) | 7765(2) | 7298(2) | 37(1) |
| C(41) | 4123(4) | 7138(2) | 8790(2) | 36(1) |
| C(53) | 2570(4) | 4627(2) | 7450(2) | 38(1) |
| C(52) | 3773(4) | 4692(2) | 9013(2) | 39(1) |
| S(2) | -809(1) | 7342(1) | -745(1) | 27(1) |
| O(21) | -1910(3) | 6661(2) | -722(2) | 45(1) |
| O(22) | 205(3) | 7292(2) | -1560(1) | 47(1) |
| O(23) | -1476(2) | 8309(2) | -591(2) | 38(1) |
| N(02) | 7522(2) | 9002(2) | 1783(2) | 24(1) |
| N(05) | 9096(3) | 8741(2) | 2914(2) | 27(1) |
| C(01) | 7872(3) | 8459(2) | 2546(2) | 26(1) |
| C(03) | 8560(3) | 9670(2) | 1659(2) | 24(1) |

| | | | | |
|---|---|---|---|---|
| C(04) | 9552(3) | 9512(2) | 2371(2) | 26(1) |
| C(011) | 379(3) | 7009(2) | 223(2) | 25(1) |
| C(012) | 901(4) | 6055(2) | 386(2) | 34(1) |
| C(013) | 1838(4) | 5776(2) | 1131(2) | 41(1) |
| C(014) | 2273(4) | 6453(2) | 1707(2) | 39(1) |
| C(015) | 1782(3) | 7399(2) | 1538(2) | 34(1) |
| C(016) | 825(3) | 7682(2) | 801(2) | 27(1) |
| C(031) | 8505(3) | 10381(2) | 852(2) | 31(1) |
| C(021) | 6222(3) | 8935(2) | 1167(2) | 30(1) |
| C(022) | 4897(4) | 9641(3) | 1461(2) | 42(1) |
| C(023) | 5810(4) | 7922(2) | 1184(2) | 39(1) |
| C(041) | 10884(3) | 10009(2) | 2594(2) | 37(1) |
| C(051) | 9839(3) | 8310(2) | 3782(2) | 35(1) |
| C(052) | 9770(4) | 7240(2) | 3841(2) | 37(1) |
| C(053) | 9125(5) | 8780(3) | 4630(2) | 49(1) |

Table 57. Bond lengths [Å] and angles [°] for $C_{17}H_{26}N_2O_3S$ (**37**).

| | |
|---|---|
| S(1)-O(12) | 1.447(2) |
| S(1)-O(13) | 1.449(2) |
| S(1)-O(11) | 1.453(2) |
| S(1)-C(11) | 1.782(3) |
| N(2)-C(1) | 1.330(3) |
| N(2)-C(3) | 1.388(3) |
| N(2)-C(21) | 1.486(3) |
| N(5)-C(1) | 1.335(3) |
| N(5)-C(4) | 1.390(3) |
| N(5)-C(51) | 1.490(4) |
| C(3)-C(4) | 1.363(4) |
| C(3)-C(31) | 1.489(4) |
| C(4)-C(41) | 1.485(4) |
| C(51)-C(52) | 1.517(4) |
| C(51)-C(53) | 1.518(4) |
| C(11)-C(12) | 1.384(4) |
| C(11)-C(16) | 1.386(4) |
| C(12)-C(13) | 1.392(4) |
| C(13)-C(14) | 1.373(5) |
| C(14)-C(15) | 1.382(5) |
| C(15)-C(16) | 1.398(4) |
| C(21)-C(22) | 1.517(4) |
| C(21)-C(23) | 1.518(4) |
| S(2)-O(21) | 1.441(2) |
| S(2)-O(22) | 1.453(2) |
| S(2)-O(23) | 1.456(2) |
| S(2)-C(011) | 1.780(3) |
| N(02)-C(01) | 1.329(3) |
| N(02)-C(03) | 1.389(3) |
| N(02)-C(021) | 1.486(4) |
| N(05)-C(01) | 1.327(4) |
| N(05)-C(04) | 1.394(3) |
| N(05)-C(051) | 1.496(4) |
| C(03)-C(04) | 1.361(4) |

| | |
|---|---|
| C(03)-C(031) | 1.490(4) |
| C(04)-C(041) | 1.488(4) |
| C(011)-C(016) | 1.388(4) |
| C(011)-C(012) | 1.391(4) |
| C(012)-C(013) | 1.387(5) |
| C(013)-C(014) | 1.387(5) |
| C(014)-C(015) | 1.374(5) |
| C(015)-C(016) | 1.390(4) |
| C(021)-C(023) | 1.514(4) |
| C(021)-C(022) | 1.525(4) |
| C(051)-C(053) | 1.505(5) |
| C(051)-C(052) | 1.520(4) |
| | |
| O(12)-S(1)-O(13) | 112.93(13) |
| O(12)-S(1)-O(11) | 113.59(14) |
| O(13)-S(1)-O(11) | 112.67(14) |
| O(12)-S(1)-C(11) | 105.48(12) |
| O(13)-S(1)-C(11) | 105.24(13) |
| O(11)-S(1)-C(11) | 106.03(12) |
| C(1)-N(2)-C(3) | 109.3(2) |
| C(1)-N(2)-C(21) | 126.0(2) |
| C(3)-N(2)-C(21) | 124.4(2) |
| C(1)-N(5)-C(4) | 108.9(2) |
| C(1)-N(5)-C(51) | 126.0(2) |
| C(4)-N(5)-C(51) | 125.1(2) |
| N(2)-C(1)-N(5) | 108.4(2) |
| C(4)-C(3)-N(2) | 106.6(2) |
| C(4)-C(3)-C(31) | 130.4(3) |
| N(2)-C(3)-C(31) | 122.9(3) |
| C(3)-C(4)-N(5) | 106.8(2) |
| C(3)-C(4)-C(41) | 129.8(3) |
| N(5)-C(4)-C(41) | 123.4(3) |
| N(5)-C(51)-C(52) | 110.1(2) |
| N(5)-C(51)-C(53) | 110.7(2) |
| C(52)-C(51)-C(53) | 112.1(3) |
| C(12)-C(11)-C(16) | 120.1(3) |

| | |
|---|---|
| C(12)-C(11)-S(1) | 121.0(2) |
| C(16)-C(11)-S(1) | 118.9(2) |
| C(11)-C(12)-C(13) | 120.1(3) |
| C(14)-C(13)-C(12) | 120.0(3) |
| C(13)-C(14)-C(15) | 120.3(3) |
| C(14)-C(15)-C(16) | 120.2(3) |
| C(11)-C(16)-C(15) | 119.3(3) |
| N(2)-C(21)-C(22) | 109.2(2) |
| N(2)-C(21)-C(23) | 111.1(2) |
| C(22)-C(21)-C(23) | 112.1(3) |
| O(21)-S(2)-O(22) | 113.67(15) |
| O(21)-S(2)-O(23) | 113.29(14) |
| O(22)-S(2)-O(23) | 112.49(14) |
| O(21)-S(2)-C(011) | 105.70(13) |
| O(22)-S(2)-C(011) | 104.91(13) |
| O(23)-S(2)-C(011) | 105.83(13) |
| C(01)-N(02)-C(03) | 108.7(2) |
| C(01)-N(02)-C(021) | 126.5(2) |
| C(03)-N(02)-C(021) | 124.8(2) |
| C(01)-N(05)-C(04) | 108.9(2) |
| C(01)-N(05)-C(051) | 125.2(2) |
| C(04)-N(05)-C(051) | 125.9(2) |
| N(05)-C(01)-N(02) | 109.0(2) |
| C(04)-C(03)-N(02) | 107.1(2) |
| C(04)-C(03)-C(031) | 130.6(3) |
| N(02)-C(03)-C(031) | 122.3(2) |
| C(03)-C(04)-N(05) | 106.3(2) |
| C(03)-C(04)-C(041) | 130.7(3) |
| N(05)-C(04)-C(041) | 123.0(3) |
| C(016)-C(011)-C(012) | 119.5(3) |
| C(016)-C(011)-S(2) | 121.5(2) |
| C(012)-C(011)-S(2) | 119.0(2) |
| C(013)-C(012)-C(011) | 120.3(3) |
| C(014)-C(013)-C(012) | 119.8(3) |
| C(015)-C(014)-C(013) | 120.1(3) |
| C(014)-C(015)-C(016) | 120.4(3) |

| | |
|---|---|
| C(011)-C(016)-C(015) | 120.0(3) |
| N(02)-C(021)-C(023) | 110.4(2) |
| N(02)-C(021)-C(022) | 109.3(2) |
| C(023)-C(021)-C(022) | 112.7(3) |
| N(05)-C(051)-C(053) | 110.2(2) |
| N(05)-C(051)-C(052) | 110.3(3) |
| C(053)-C(051)-C(052) | 112.2(3) |

Symmetry transformations used to generate equivalent atoms:

Table 58. Anisotropic displacement parameters (Å$^2$x 10$^3$) for $C_{17}H_{26}N_2O_3S$ (**37**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 23(1) | 27(1) | 21(1) | -1(1) | 5(1) | -2(1) |
| N(2) | 22(1) | 23(1) | 24(1) | -2(1) | -3(1) | 0(1) |
| N(5) | 24(1) | 24(1) | 22(1) | -3(1) | -2(1) | 1(1) |
| O(11) | 50(1) | 32(1) | 31(1) | -10(1) | 12(1) | -10(1) |
| O(12) | 45(1) | 42(1) | 25(1) | 5(1) | 1(1) | 5(1) |
| O(13) | 24(1) | 54(1) | 41(1) | 4(1) | 8(1) | -3(1) |
| C(1) | 24(1) | 23(1) | 22(1) | -3(1) | -3(1) | 0(1) |
| C(3) | 28(1) | 22(1) | 30(1) | -5(1) | -8(1) | 1(1) |
| C(4) | 27(1) | 25(1) | 28(1) | -6(1) | -7(1) | 2(1) |
| C(51) | 24(1) | 31(1) | 27(1) | -5(1) | 3(1) | -1(1) |
| C(11) | 23(1) | 27(1) | 20(1) | -2(1) | -1(1) | 2(1) |
| C(12) | 26(1) | 30(1) | 24(1) | -1(1) | 0(1) | 0(1) |
| C(13) | 32(2) | 42(2) | 22(1) | 2(1) | 4(1) | 5(1) |
| C(14) | 48(2) | 44(2) | 23(1) | -5(1) | 3(1) | 13(2) |
| C(15) | 65(2) | 32(2) | 41(2) | -17(1) | -3(2) | 4(2) |
| C(16) | 49(2) | 28(2) | 33(2) | -5(1) | 0(1) | -5(1) |
| C(21) | 31(1) | 25(1) | 28(1) | 0(1) | 5(1) | -5(1) |
| C(22) | 27(2) | 51(2) | 45(2) | -3(2) | 4(1) | 0(1) |
| C(23) | 45(2) | 34(2) | 26(1) | -3(1) | 8(1) | -7(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(31) | 39(2) | 30(2) | 43(2) | -6(1) | -6(1) | -8(1) |
| C(41) | 40(2) | 34(2) | 34(2) | -12(1) | 2(1) | 0(1) |
| C(53) | 35(2) | 48(2) | 34(2) | -6(1) | 2(1) | -15(1) |
| C(52) | 45(2) | 41(2) | 29(2) | 5(1) | -1(1) | -6(1) |
| S(2) | 26(1) | 36(1) | 21(1) | -3(1) | 4(1) | -9(1) |
| O(21) | 43(1) | 48(1) | 48(1) | 0(1) | -9(1) | -23(1) |
| O(22) | 37(1) | 79(2) | 23(1) | -3(1) | 7(1) | -2(1) |
| O(23) | 38(1) | 39(1) | 36(1) | 1(1) | -3(1) | -1(1) |
| N(02) | 25(1) | 24(1) | 23(1) | -1(1) | 6(1) | -4(1) |
| N(05) | 23(1) | 28(1) | 30(1) | 3(1) | 2(1) | -5(1) |
| C(01) | 25(1) | 26(1) | 28(1) | 3(1) | 3(1) | -7(1) |
| C(03) | 25(1) | 20(1) | 29(1) | -4(1) | 9(1) | -4(1) |
| C(04) | 24(1) | 21(1) | 34(1) | -2(1) | 8(1) | -3(1) |
| C(011) | 25(1) | 29(1) | 21(1) | -1(1) | 6(1) | -8(1) |
| C(012) | 42(2) | 26(1) | 36(2) | -6(1) | 4(1) | -9(1) |
| C(013) | 48(2) | 31(2) | 43(2) | 6(1) | 3(2) | 2(1) |
| C(014) | 36(2) | 49(2) | 29(2) | 2(1) | 1(1) | 4(1) |
| C(015) | 37(2) | 39(2) | 27(1) | -9(1) | 2(1) | -4(1) |
| C(016) | 32(1) | 26(1) | 24(1) | -7(1) | 6(1) | -2(1) |
| C(031) | 35(2) | 27(1) | 31(1) | -1(1) | 9(1) | -6(1) |
| C(021) | 30(1) | 39(2) | 23(1) | 0(1) | 1(1) | -10(1) |
| C(022) | 29(2) | 50(2) | 46(2) | 9(2) | -2(1) | 0(1) |
| C(023) | 45(2) | 45(2) | 31(2) | -8(1) | 4(1) | -22(2) |
| C(041) | 29(2) | 32(2) | 51(2) | 0(1) | 0(1) | -8(1) |
| C(051) | 25(1) | 38(2) | 40(2) | 10(1) | -7(1) | -8(1) |
| C(052) | 31(2) | 37(2) | 41(2) | 11(1) | 0(1) | 0(1) |
| C(053) | 62(2) | 48(2) | 36(2) | -2(2) | -16(2) | -4(2) |

Table 59. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for $C_{17}H_{26}N_2O_3S$ (**37**).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 5243 | 4938 | 6638 | 27 |
| H(51) | 2353 | 5736 | 8338 | 33 |
| H(12) | 2696 | 6590 | 5438 | 32 |
| H(13) | 1614 | 7049 | 6877 | 39 |
| H(14) | 1879 | 8551 | 7392 | 48 |
| H(15) | 3259 | 9595 | 6495 | 55 |
| H(16) | 4315 | 9153 | 5036 | 44 |
| H(21) | 7548 | 6761 | 5748 | 34 |
| H(22A) | 9131 | 6188 | 6988 | 62 |
| H(22B) | 9782 | 5758 | 6027 | 62 |
| H(22C) | 8899 | 5116 | 6767 | 62 |
| H(23A) | 6157 | 5723 | 4971 | 52 |
| H(23B) | 7049 | 4827 | 5512 | 52 |
| H(23C) | 7935 | 5469 | 4775 | 52 |
| H(31A) | 7513 | 7717 | 6785 | 55 |
| H(31B) | 7263 | 7838 | 7885 | 55 |
| H(31C) | 6018 | 8319 | 7173 | 55 |
| H(41A) | 3341 | 6769 | 9077 | 54 |
| H(41B) | 3660 | 7770 | 8580 | 54 |
| H(41C) | 4897 | 7206 | 9249 | 54 |
| H(53A) | 2200 | 5018 | 6903 | 57 |
| H(53B) | 1734 | 4314 | 7747 | 57 |
| H(53C) | 3374 | 4145 | 7252 | 57 |
| H(52A) | 4155 | 5123 | 9443 | 58 |
| H(52B) | 4593 | 4210 | 8838 | 58 |
| H(52C) | 2943 | 4380 | 9320 | 58 |
| H(01) | 7334 | 7951 | 2789 | 32 |
| H(012) | 615 | 5593 | -14 | 41 |
| H(013) | 2180 | 5123 | 1247 | 50 |
| H(014) | 2912 | 6264 | 2219 | 46 |

| | | | | |
|---|---|---|---|---|
| H(015) | 2099 | 7861 | 1927 | 41 |
| H(016) | 475 | 8335 | 694 | 32 |
| H(03A) | 7633 | 10304 | 469 | 47 |
| H(03B) | 9440 | 10281 | 473 | 47 |
| H(03C) | 8406 | 11024 | 1085 | 47 |
| H(021) | 6538 | 9119 | 512 | 36 |
| H(02A) | 5220 | 10284 | 1437 | 64 |
| H(02B) | 4562 | 9471 | 2100 | 64 |
| H(02C) | 4057 | 9623 | 1035 | 64 |
| H(02D) | 6697 | 7498 | 991 | 58 |
| H(02E) | 4984 | 7883 | 753 | 58 |
| H(02F) | 5485 | 7730 | 1819 | 58 |
| H(04A) | 11355 | 9710 | 3161 | 55 |
| H(04B) | 10553 | 10679 | 2697 | 55 |
| H(04C) | 11623 | 9966 | 2072 | 55 |
| H(051) | 10930 | 8431 | 3744 | 41 |
| H(05A) | 10252 | 6964 | 3279 | 56 |
| H(05B) | 8709 | 7104 | 3887 | 56 |
| H(05C) | 10306 | 6963 | 4395 | 56 |
| H(05D) | 9199 | 9466 | 4565 | 73 |
| H(05E) | 9656 | 8516 | 5191 | 73 |
| H(05F) | 8056 | 8663 | 4687 | 73 |

Table 60. Crystal data and structure refinement for $C_{14}H_{24}N_2O_4$ (**38**).

| | | |
|---|---|---|
| Empirical formula | $C_{14}H_{24}N_2O_4$ | |
| Formula weight | 284.35 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 8.1862(8) Å | $\alpha$= 90°. |
| | b = 10.3126(13) Å | $\beta$= 101.018(8)°. |
| | c = 18.5340(18) Å | $\gamma$ = 90°. |
| Volume | 1535.8(3) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.230 Mg/m$^3$ | |
| Absorption coefficient | 0.090 mm$^{-1}$ | |
| F(000) | 616 | |
| Crystal size | 0.25 x 0.20 x 0.10 mm$^3$ | |
| Theta range for data collection | 3.21 to 26.37°. | |
| Index ranges | -10<=h<=10, -12<=k<=12, -22<=l<=23 | |
| Reflections collected | 21417 | |
| Independent reflections | 3134 [R(int) = 0.1071] | |
| Completeness to theta = 26.37° | 99.8 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 3134 / 0 / 278 | |
| Goodness-of-fit on F$^2$ | 1.138 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0569, wR2 = 0.1019 | |
| R indices (all data) | R1 = 0.0787, wR2 = 0.1087 | |
| Extinction coefficient | 0.0062(14) | |
| Largest diff. peak and hole | 0.197 and -0.202 e.Å$^{-3}$ | |

Table 61. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for $C_{14}H_{24}N_2O_4$ (**38**). U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 8475(2) | 2624(2) | 9622(1) | 22(1) |
| N(2) | 9688(2) | 3273(1) | 9396(1) | 22(1) |
| C(3) | 11090(2) | 3275(2) | 9952(1) | 22(1) |
| C(4) | 10684(2) | 2600(2) | 10525(1) | 22(1) |
| N(5) | 9033(2) | 2216(1) | 10304(1) | 22(1) |
| C(6) | 9596(2) | 3801(2) | 8640(1) | 26(1) |
| C(7) | 7858(3) | 4246(2) | 8315(1) | 32(1) |
| C(8) | 10221(3) | 2781(2) | 8165(1) | 37(1) |
| C(9) | 12682(3) | 3908(2) | 9865(1) | 30(1) |
| C(10) | 11706(3) | 2247(2) | 11252(1) | 30(1) |
| C(11) | 8054(2) | 1376(2) | 10723(1) | 24(1) |
| C(12) | 8084(3) | -10(2) | 10445(1) | 37(1) |
| C(13) | 6309(3) | 1904(2) | 10664(1) | 33(1) |
| O(20) | 3480(2) | 9288(2) | 1694(1) | 48(1) |
| O(21) | 5173(2) | 7939(1) | 1241(1) | 34(1) |
| C(22) | 4816(2) | 8738(2) | 1692(1) | 25(1) |
| C(23) | 6214(2) | 9019(2) | 2348(1) | 24(1) |
| O(24) | 6333(2) | 8552(2) | 2950(1) | 42(1) |
| O(25) | 7316(2) | 9860(1) | 2176(1) | 34(1) |
| C(26) | 8734(3) | 10164(3) | 2743(1) | 43(1) |

Table 62. Bond lengths [Å] and angles [°] for $C_{14}H_{24}N_2O_4$ (**38**).

| | |
|---|---|
| C(1)-N(5) | 1.327(2) |
| C(1)-N(2) | 1.330(2) |
| N(2)-C(3) | 1.388(2) |
| N(2)-C(6) | 1.492(2) |
| C(3)-C(4) | 1.364(3) |
| C(3)-C(9) | 1.493(3) |
| C(4)-N(5) | 1.393(2) |
| C(4)-C(10) | 1.489(3) |
| N(5)-C(11) | 1.493(2) |
| C(6)-C(7) | 1.507(3) |
| C(6)-C(8) | 1.521(3) |
| C(11)-C(13) | 1.513(3) |
| C(11)-C(12) | 1.521(3) |
| O(20)-C(22) | 1.233(2) |
| O(21)-C(22) | 1.247(2) |
| C(22)-C(23) | 1.530(3) |
| C(23)-O(24) | 1.202(2) |
| C(23)-O(25) | 1.334(2) |
| O(25)-C(26) | 1.444(3) |
| | |
| N(5)-C(1)-N(2) | 108.59(17) |
| C(1)-N(2)-C(3) | 109.12(15) |
| C(1)-N(2)-C(6) | 124.99(16) |
| C(3)-N(2)-C(6) | 125.65(15) |
| C(4)-C(3)-N(2) | 106.72(16) |
| C(4)-C(3)-C(9) | 130.84(18) |
| N(2)-C(3)-C(9) | 122.43(16) |
| C(3)-C(4)-N(5) | 106.45(16) |
| C(3)-C(4)-C(10) | 130.66(18) |
| N(5)-C(4)-C(10) | 122.86(16) |
| C(1)-N(5)-C(4) | 109.12(15) |
| C(1)-N(5)-C(11) | 123.90(16) |
| C(4)-N(5)-C(11) | 126.77(15) |
| N(2)-C(6)-C(7) | 111.15(15) |
| N(2)-C(6)-C(8) | 109.22(16) |
| C(7)-C(6)-C(8) | 112.08(18) |
| N(5)-C(11)-C(13) | 110.31(16) |
| N(5)-C(11)-C(12) | 108.92(15) |
| C(13)-C(11)-C(12) | 112.93(19) |
| O(20)-C(22)-O(21) | 128.91(19) |
| O(20)-C(22)-C(23) | 116.07(16) |
| O(21)-C(22)-C(23) | 114.96(17) |
| O(24)-C(23)-O(25) | 122.98(18) |
| O(24)-C(23)-C(22) | 125.28(17) |
| O(25)-C(23)-C(22) | 111.74(15) |
| C(23)-O(25)-C(26) | 116.97(16) |

Table 63. Anisotropic displacement parameters (Å$^2$x 10$^3$) for $C_{14}H_{24}N_2O_4$ (**38**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 23(1) | 24(1) | 20(1) | 1(1) | 4(1) | -1(1) |
| N(2) | 24(1) | 21(1) | 21(1) | 1(1) | 4(1) | 0(1) |
| C(3) | 23(1) | 21(1) | 23(1) | -3(1) | 5(1) | 3(1) |
| C(4) | 23(1) | 21(1) | 23(1) | -4(1) | 4(1) | 4(1) |
| N(5) | 24(1) | 22(1) | 19(1) | 1(1) | 4(1) | 0(1) |
| C(6) | 30(1) | 28(1) | 21(1) | 5(1) | 6(1) | -4(1) |
| C(7) | 35(1) | 33(1) | 27(1) | 8(1) | 4(1) | 3(1) |
| C(8) | 44(1) | 43(1) | 27(1) | 2(1) | 13(1) | 5(1) |
| C(9) | 24(1) | 35(1) | 31(1) | -1(1) | 5(1) | -2(1) |
| C(10) | 29(1) | 36(1) | 25(1) | 0(1) | 1(1) | 4(1) |
| C(11) | 29(1) | 26(1) | 18(1) | 1(1) | 7(1) | -1(1) |
| C(12) | 51(1) | 26(1) | 39(1) | 0(1) | 26(1) | -4(1) |
| C(13) | 30(1) | 42(1) | 30(1) | 5(1) | 10(1) | 2(1) |
| O(20) | 33(1) | 55(1) | 53(1) | -18(1) | -3(1) | 12(1) |
| O(21) | 31(1) | 41(1) | 29(1) | -11(1) | 6(1) | -2(1) |
| C(22) | 26(1) | 24(1) | 26(1) | 1(1) | 6(1) | -3(1) |
| C(23) | 29(1) | 21(1) | 24(1) | -2(1) | 9(1) | 0(1) |
| O(24) | 46(1) | 54(1) | 26(1) | 12(1) | 3(1) | -10(1) |
| O(25) | 35(1) | 38(1) | 26(1) | 2(1) | 1(1) | -14(1) |
| C(26) | 37(1) | 51(2) | 36(1) | -4(1) | -2(1) | -16(1) |

Table 64. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for $C_{14}H_{24}N_2O_4$ (**38**).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 7450(30) | 2471(19) | 9347(11) | 24(5) |
| H(6) | 10310(20) | 4535(19) | 8696(10) | 21(5) |
| H(7A) | 7070(30) | 3530(20) | 8223(12) | 40(6) |
| H(7B) | 7470(30) | 4860(20) | 8638(12) | 35(6) |
| H(7C) | 7860(30) | 4720(20) | 7863(13) | 35(6) |
| H(8A) | 9480(30) | 2000(20) | 8145(12) | 38(6) |
| H(8B) | 11380(30) | 2510(20) | 8383(14) | 51(7) |
| H(8C) | 10180(30) | 3160(20) | 7664(13) | 41(6) |
| H(9A) | 13480(30) | 3890(20) | 10323(15) | 52(7) |
| H(9B) | 12520(30) | 4810(30) | 9730(13) | 43(6) |
| H(9C) | 13170(30) | 3470(20) | 9493(13) | 44(6) |
| H(10A) | 11830(30) | 1340(30) | 11317(13) | 47(7) |
| H(10B) | 11260(30) | 2640(20) | 11638(13) | 45(7) |
| H(10C) | 12870(30) | 2600(20) | 11290(12) | 41(6) |
| H(11) | 8620(20) | 1422(16) | 11214(10) | 12(4) |
| H(12A) | 9290(30) | -360(20) | 10540(13) | 47(7) |
| H(12B) | 7450(30) | -520(20) | 10706(13) | 40(6) |
| H(12C) | 7620(30) | -40(20) | 9917(15) | 47(7) |
| H(13A) | 5690(30) | 1840(20) | 10171(13) | 36(6) |
| H(13B) | 5730(30) | 1380(20) | 10959(13) | 46(7) |
| H(13C) | 6350(30) | 2850(30) | 10836(14) | 52(7) |
| H(26A) | 9270(40) | 9340(30) | 2934(16) | 71(9) |
| H(26B) | 8440(40) | 10550(30) | 3160(20) | 92(11) |
| H(26C) | 9450(50) | 10640(40) | 2520(20) | 100(12) |

Table 65. Crystal data and structure refinement for $C_{18}H_{29}N_2O_2S$ (**39a**).

| | | |
|---|---|---|
| Empirical formula | $C_{18}H_{29}N_2O_2S$ | |
| Formula weight | 337.49 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 14.1151(17) Å | $\alpha$= 90°. |
| | b = 8.4634(7) Å | $\beta$= 104.491(10)°. |
| | c = 16.379(2) Å | $\gamma$ = 90°. |
| Volume | 1894.4(4) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.183 Mg/m$^3$ | |
| Absorption coefficient | 0.182 mm$^{-1}$ | |
| F(000) | 732 | |
| Crystal size | 0.25 x 0.10 x 0.10 mm$^3$ | |
| Theta range for data collection | 3.26 to 26.37°. | |
| Index ranges | -17<=h<=17, -10<=k<=10, -20<=l<=20 | |
| Reflections collected | 24987 | |
| Independent reflections | 3875 [R(int) = 0.1064] | |
| Completeness to theta = 26.37° | 99.8 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 3875 / 0 / 313 | |
| Goodness-of-fit on F$^2$ | 1.152 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0851, wR2 = 0.1747 | |
| R indices (all data) | R1 = 0.1099, wR2 = 0.1864 | |
| Extinction coefficient | 0.0013(13) | |
| Largest diff. peak and hole | 0.948 and -0.421 e.Å$^{-3}$ | |

Table 66. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for $C_{18}H_{29}N_2O_2S$ (**39a**). U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 2184(1) | 4922(1) | 1863(1) | 45(1) |
| C(2) | 3415(3) | 5332(4) | 1782(2) | 36(1) |
| C(3) | 3993(3) | 6461(5) | 2276(2) | 44(1) |
| C(4) | 4907(3) | 6801(6) | 2156(2) | 48(1) |
| C(5) | 5269(3) | 6006(5) | 1553(2) | 42(1) |
| C(51) | 6264(3) | 6392(7) | 1417(3) | 61(1) |
| C(6) | 4691(3) | 4850(5) | 1078(2) | 42(1) |
| C(7) | 3769(3) | 4517(5) | 1184(2) | 38(1) |
| O(01) | 1589(2) | 5724(3) | 1105(2) | 46(1) |
| O(02) | 2129(2) | 5736(5) | 2631(2) | 70(1) |
| N(20) | 998(2) | 3643(3) | 4445(2) | 25(1) |
| C(21) | 1024(2) | 3676(4) | 5302(2) | 25(1) |
| C(22) | 1741(2) | 4696(4) | 5670(2) | 29(1) |
| N(23) | 2135(2) | 5282(3) | 5032(2) | 28(1) |
| C(24) | 1676(2) | 4619(4) | 4302(2) | 27(1) |
| C(25) | 389(2) | 2537(4) | 3828(2) | 30(1) |
| C(26) | 918(4) | 964(5) | 3892(3) | 44(1) |
| C(27) | 144(3) | 3226(6) | 2944(2) | 41(1) |
| C(28) | 339(3) | 2719(5) | 5660(2) | 33(1) |
| C(29) | 2118(3) | 5174(6) | 6569(2) | 42(1) |
| C(30) | 2951(3) | 6435(5) | 5143(3) | 39(1) |
| C(31) | 3877(4) | 5569(9) | 5146(9) | 113(4) |
| C(32) | 2699(5) | 7702(7) | 4481(4) | 65(2) |

Table 67. Bond lengths [Å] and angles [°] for $C_{18}H_{29}N_2O_2S$ (**39a**).

| | |
|---|---|
| S(1)-O(02) | 1.454(3) |
| S(1)-O(01) | 1.479(3) |
| S(1)-C(2) | 1.809(4) |
| C(2)-C(3) | 1.380(6) |
| C(2)-C(7) | 1.389(5) |
| C(3)-C(4) | 1.383(6) |
| C(4)-C(5) | 1.393(6) |
| C(5)-C(6) | 1.382(6) |
| C(5)-C(51) | 1.513(6) |
| C(6)-C(7) | 1.384(6) |
| N(20)-C(24) | 1.329(4) |
| N(20)-C(21) | 1.395(4) |
| N(20)-C(25) | 1.483(4) |
| C(21)-C(22) | 1.351(5) |
| C(21)-C(28) | 1.489(5) |
| C(22)-N(23) | 1.393(4) |
| C(22)-C(29) | 1.490(5) |
| N(23)-C(24) | 1.332(4) |
| N(23)-C(30) | 1.486(4) |
| C(25)-C(26) | 1.518(5) |
| C(25)-C(27) | 1.519(5) |
| C(30)-C(31) | 1.498(7) |
| C(30)-C(32) | 1.502(7) |

| | |
|---|---|
| O(02)-S(1)-O(01) | 111.5(2) |
| O(02)-S(1)-C(2) | 103.47(19) |
| O(01)-S(1)-C(2) | 101.75(15) |
| C(3)-C(2)-C(7) | 119.5(4) |
| C(3)-C(2)-S(1) | 121.9(3) |
| C(7)-C(2)-S(1) | 118.6(3) |
| C(2)-C(3)-C(4) | 119.8(4) |
| C(3)-C(4)-C(5) | 121.3(4) |
| C(6)-C(5)-C(4) | 118.2(4) |
| C(6)-C(5)-C(51) | 120.6(4) |
| C(4)-C(5)-C(51) | 121.3(4) |
| C(5)-C(6)-C(7) | 121.0(4) |
| C(6)-C(7)-C(2) | 120.2(4) |
| C(24)-N(20)-C(21) | 109.0(3) |
| C(24)-N(20)-C(25) | 126.3(3) |
| C(21)-N(20)-C(25) | 124.2(3) |
| C(22)-C(21)-N(20) | 106.9(3) |
| C(22)-C(21)-C(28) | 131.2(3) |
| N(20)-C(21)-C(28) | 121.9(3) |
| C(21)-C(22)-N(23) | 106.7(3) |
| C(21)-C(22)-C(29) | 131.0(3) |
| N(23)-C(22)-C(29) | 122.2(3) |
| C(24)-N(23)-C(22) | 109.1(3) |
| C(24)-N(23)-C(30) | 125.1(3) |
| C(22)-N(23)-C(30) | 125.8(3) |
| N(20)-C(24)-N(23) | 108.3(3) |
| N(20)-C(25)-C(26) | 108.4(3) |
| N(20)-C(25)-C(27) | 111.2(3) |
| C(26)-C(25)-C(27) | 113.1(3) |
| N(23)-C(30)-C(31) | 109.2(4) |
| N(23)-C(30)-C(32) | 110.1(4) |
| C(31)-C(30)-C(32) | 113.6(7) |

Table 68. Anisotropic displacement parameters (Å$^2$x 10$^3$) for $C_{18}H_{29}N_2O_2S$ (**39a**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 40(1) | 53(1) | 43(1) | 14(1) | 14(1) | 4(1) |
| C(2) | 37(2) | 39(2) | 29(2) | 14(2) | 3(1) | 5(2) |
| C(3) | 38(2) | 58(3) | 35(2) | -6(2) | 10(2) | 2(2) |
| C(4) | 41(2) | 67(3) | 35(2) | -15(2) | 4(2) | -6(2) |
| C(5) | 36(2) | 57(3) | 31(2) | 4(2) | 3(2) | 3(2) |
| C(51) | 44(2) | 94(4) | 48(3) | 0(3) | 15(2) | -2(2) |
| C(6) | 49(2) | 48(2) | 29(2) | 3(2) | 11(2) | 10(2) |
| C(7) | 48(2) | 32(2) | 35(2) | 2(2) | 9(2) | 4(2) |
| O(01) | 38(2) | 52(2) | 48(2) | 6(1) | 11(1) | 5(1) |
| O(02) | 52(2) | 111(3) | 55(2) | 1(2) | 31(2) | -10(2) |
| N(20) | 28(1) | 26(1) | 23(1) | 2(1) | 8(1) | -2(1) |
| C(21) | 29(2) | 25(2) | 21(2) | 4(1) | 7(1) | 4(1) |
| C(22) | 32(2) | 30(2) | 25(2) | 3(1) | 7(1) | 5(1) |
| N(23) | 26(1) | 28(2) | 30(1) | -2(1) | 6(1) | -2(1) |
| C(24) | 27(2) | 31(2) | 26(2) | 1(1) | 11(1) | -3(1) |
| C(25) | 29(2) | 37(2) | 25(2) | -3(1) | 9(1) | -11(2) |
| C(26) | 57(3) | 33(2) | 43(2) | -10(2) | 15(2) | -6(2) |
| C(27) | 44(2) | 55(3) | 26(2) | 1(2) | 8(2) | -13(2) |
| C(28) | 36(2) | 38(2) | 26(2) | 6(2) | 12(2) | 0(2) |
| C(29) | 47(2) | 51(3) | 26(2) | -2(2) | 5(2) | 1(2) |
| C(30) | 33(2) | 37(2) | 49(2) | -14(2) | 12(2) | -13(2) |
| C(31) | 28(3) | 71(4) | 237(12) | -46(6) | 25(4) | -13(3) |
| C(32) | 86(4) | 56(3) | 52(3) | -2(2) | 17(3) | -41(3) |

Table 69. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for $C_{18}H_{29}N_2O_2S$ (**39a**).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 2209(18) | 3480(30) | 2082(15) | 0(6) |
| H(3) | 3740(30) | 6990(50) | 2660(20) | 40(11) |
| H(4) | 5320(30) | 7630(50) | 2500(30) | 57(13) |
| H(51A) | 6387 | 5731 | 978 | 92 |
| H(51B) | 6758 | 6209 | 1929 | 92 |
| H(51C) | 6280 | 7481 | 1256 | 92 |
| H(6) | 4940(30) | 4200(60) | 650(30) | 66(14) |
| H(7) | 3370(30) | 3640(50) | 850(30) | 44(11) |
| H(24) | 1800(30) | 4840(40) | 3750(20) | 33(9) |
| H(25) | -170(30) | 2410(40) | 4010(20) | 26(9) |
| H(26A) | 530(30) | 220(50) | 3540(30) | 43(11) |
| H(26B) | 1540(30) | 1050(50) | 3700(20) | 40(11) |
| H(26C) | 1100(30) | 580(50) | 4480(30) | 40(11) |
| H(27A) | 700(30) | 3280(50) | 2710(20) | 37(10) |
| H(27B) | -380(40) | 2580(60) | 2590(30) | 72(15) |
| H(27C) | -110(30) | 4290(60) | 2940(30) | 58(14) |
| H(28A) | 510(30) | 1630(50) | 5690(20) | 35(10) |
| H(28B) | 410(30) | 3010(50) | 6230(30) | 59(13) |
| H(28C) | -310(40) | 2860(50) | 5370(30) | 60(14) |
| H(29A) | 2800(40) | 4990(50) | 6760(30) | 54(13) |
| H(29B) | 1990(30) | 6290(60) | 6690(30) | 47(12) |
| H(29C) | 1800(30) | 4590(50) | 6940(30) | 49(12) |
| H(30) | 3000(30) | 6930(50) | 5670(30) | 49(12) |
| H(31A) | 3980(50) | 4780(80) | 5620(40) | 100(30) |
| H(31B) | 3770(50) | 5120(80) | 4560(40) | 100(20) |
| H(31C) | 4420(50) | 6280(80) | 5280(40) | 100(20) |
| H(32A) | 3220(40) | 8460(60) | 4610(30) | 64(14) |
| H(32B) | 2580(40) | 7340(70) | 3960(40) | 84(19) |
| H(32C) | 2220(60) | 8150(90) | 4570(50) | 120(30) |

Table 70. Crystal data and structure refinement for $C_{18}H_{26}N_2OS$ (**40**).

| | | |
|---|---|---|
| Empirical formula | $C_{18}H_{26}N_2OS$ | |
| Formula weight | 318.47 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 8.1984(10) Å | $\alpha$= 90°. |
| | b = 15.1924(14) Å | $\beta$= 100.319(10)°. |
| | c = 14.8331(19) Å | $\gamma$ = 90°. |
| Volume | 1817.6(4) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.164 Mg/m$^3$ | |
| Absorption coefficient | 0.182 mm$^{-1}$ | |
| F(000) | 688 | |
| Crystal size | 0.20 x 0.15 x 0.15 mm$^3$ | |
| Theta range for data collection | 3.37 to 26.36°. | |
| Index ranges | -10<=h<=10, -18<=k<=18, -18<=l<=18 | |
| Reflections collected | 25176 | |
| Independent reflections | 3717 [R(int) = 0.1502] | |
| Completeness to theta = 26.36° | 99.8 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 3717 / 0 / 288 | |
| Goodness-of-fit on F$^2$ | 1.172 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0783, wR2 = 0.1087 | |
| R indices (all data) | R1 = 0.1177, wR2 = 0.1183 | |
| Extinction coefficient | 0.0017(5) | |
| Largest diff. peak and hole | 0.229 and -0.222 e.Å$^{-3}$ | |

Table 71. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for $C_{18}H_{26}N_2OS$ (**40**). U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 60(1) | 11480(1) | 2642(1) | 34(1) |
| C(2) | -264(4) | 10388(2) | 2345(2) | 27(1) |
| O(3) | -1228(3) | 10130(2) | 1660(2) | 39(1) |
| C(4) | 741(4) | 9701(2) | 2945(2) | 29(1) |
| C(5) | 1036(4) | 8903(2) | 2556(3) | 40(1) |
| C(6) | 1990(5) | 8267(3) | 3065(4) | 57(1) |
| C(7) | 2634(5) | 8416(3) | 3965(4) | 74(2) |
| C(8) | 2317(7) | 9196(4) | 4365(4) | 78(2) |
| C(9) | 1385(6) | 9844(3) | 3858(3) | 54(1) |
| C(10) | 9121(4) | 6656(2) | 3668(2) | 24(1) |
| N(11) | 10377(3) | 6128(2) | 3587(2) | 24(1) |
| C(12) | 11523(3) | 6145(2) | 4401(2) | 23(1) |
| C(13) | 10934(3) | 6710(2) | 4966(2) | 25(1) |
| N(14) | 9426(3) | 7027(2) | 4492(2) | 24(1) |
| C(15) | 10559(4) | 5595(2) | 2769(2) | 33(1) |
| C(16) | 9650(5) | 6030(3) | 1902(2) | 54(1) |
| C(17) | 9974(5) | 4669(3) | 2884(3) | 50(1) |
| C(18) | 13108(4) | 5638(3) | 4537(3) | 34(1) |
| C(19) | 11695(5) | 7018(3) | 5896(3) | 42(1) |
| C(20) | 8315(4) | 7657(2) | 4848(2) | 30(1) |
| C(21) | 7560(5) | 8293(3) | 4108(3) | 43(1) |
| C(22) | 7028(6) | 7157(3) | 5250(3) | 50(1) |

Table 72. Bond lengths [Å] and angles [°] for $C_{18}H_{26}N_2OS$ (**40**).

| | |
|---|---|
| S(1)-C(2) | 1.724(3) |
| C(2)-O(3) | 1.235(3) |
| C(2)-C(4) | 1.516(4) |
| C(4)-C(9) | 1.379(5) |
| C(4)-C(5) | 1.382(5) |
| C(5)-C(6) | 1.380(6) |
| C(6)-C(7) | 1.365(7) |
| C(7)-C(8) | 1.370(7) |
| C(8)-C(9) | 1.384(6) |
| C(10)-N(11) | 1.328(4) |
| C(10)-N(14) | 1.328(4) |
| N(11)-C(12) | 1.390(3) |
| N(11)-C(15) | 1.488(4) |
| C(12)-C(13) | 1.349(4) |
| C(12)-C(18) | 1.493(4) |
| C(13)-N(14) | 1.394(4) |
| C(13)-C(19) | 1.483(4) |
| N(14)-C(20) | 1.482(4) |
| C(15)-C(17) | 1.507(5) |
| C(15)-C(16) | 1.518(5) |
| C(20)-C(22) | 1.507(5) |
| C(20)-C(21) | 1.509(5) |

| | |
|---|---|
| O(3)-C(2)-C(4) | 117.7(3) |
| O(3)-C(2)-S(1) | 124.2(2) |
| C(4)-C(2)-S(1) | 118.0(2) |
| C(9)-C(4)-C(5) | 118.9(4) |
| C(9)-C(4)-C(2) | 122.7(3) |
| C(5)-C(4)-C(2) | 118.4(3) |
| C(6)-C(5)-C(4) | 120.7(4) |
| C(7)-C(6)-C(5) | 120.0(4) |
| C(6)-C(7)-C(8) | 119.8(4) |
| C(7)-C(8)-C(9) | 120.6(5) |
| C(4)-C(9)-C(8) | 119.9(5) |
| N(11)-C(10)-N(14) | 108.6(3) |
| C(10)-N(11)-C(12) | 108.9(2) |
| C(10)-N(11)-C(15) | 126.5(2) |
| C(12)-N(11)-C(15) | 124.6(2) |
| C(13)-C(12)-N(11) | 106.9(2) |
| C(13)-C(12)-C(18) | 130.1(3) |
| N(11)-C(12)-C(18) | 123.0(3) |
| C(12)-C(13)-N(14) | 106.8(2) |
| C(12)-C(13)-C(19) | 129.9(3) |
| N(14)-C(13)-C(19) | 123.2(3) |
| C(10)-N(14)-C(13) | 108.8(2) |
| C(10)-N(14)-C(20) | 125.1(2) |
| C(13)-N(14)-C(20) | 126.1(2) |
| N(11)-C(15)-C(17) | 109.6(3) |
| N(11)-C(15)-C(16) | 110.4(3) |
| C(17)-C(15)-C(16) | 112.6(3) |
| N(14)-C(20)-C(22) | 109.5(3) |
| N(14)-C(20)-C(21) | 110.7(3) |
| C(22)-C(20)-C(21) | 112.7(3) |

Table 73. Anisotropic displacement parameters (Å$^2$x 10$^3$) for $C_{18}H_{26}N_2OS$ (**40**). The anisotropic displacement factor exponent takes the form: $-2\pi^2$[ $h^2$ $a^{*2}U^{11}$ + ... + 2 h k a* b* $U^{12}$ ]

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 32(1) | 32(1) | 36(1) | -5(1) | -1(1) | 5(1) |
| C(2) | 20(2) | 43(2) | 22(1) | -1(1) | 10(1) | -2(1) |
| O(3) | 36(1) | 46(2) | 30(1) | -8(1) | -3(1) | -5(1) |
| C(4) | 23(2) | 29(2) | 33(2) | 3(1) | 5(1) | -8(1) |
| C(5) | 31(2) | 38(2) | 55(2) | 1(2) | 20(2) | -6(2) |
| C(6) | 40(2) | 33(2) | 102(4) | 17(2) | 26(2) | -1(2) |
| C(7) | 45(2) | 50(3) | 121(5) | 46(3) | -5(3) | -8(2) |
| C(8) | 93(4) | 68(4) | 56(3) | 28(3) | -31(3) | -19(3) |
| C(9) | 73(3) | 45(2) | 37(2) | 8(2) | -8(2) | -11(2) |
| C(10) | 21(2) | 26(2) | 24(2) | 0(1) | 1(1) | -2(1) |
| N(11) | 21(1) | 27(1) | 23(1) | -2(1) | 4(1) | 1(1) |
| C(12) | 20(1) | 27(2) | 23(2) | 3(1) | 4(1) | -1(1) |
| C(13) | 24(2) | 24(2) | 26(2) | 2(1) | 4(1) | 0(1) |
| N(14) | 23(1) | 23(1) | 25(1) | -1(1) | 4(1) | 3(1) |
| C(15) | 19(2) | 54(2) | 28(2) | -14(2) | 3(1) | 4(1) |
| C(16) | 47(2) | 93(3) | 22(2) | -12(2) | 4(2) | 13(2) |
| C(17) | 33(2) | 49(3) | 66(3) | -29(2) | 6(2) | 3(2) |
| C(18) | 29(2) | 44(2) | 28(2) | -1(2) | 1(2) | 11(2) |
| C(19) | 36(2) | 55(3) | 30(2) | -9(2) | -6(2) | 7(2) |
| C(20) | 28(2) | 29(2) | 30(2) | -11(2) | 0(1) | 5(1) |
| C(21) | 44(2) | 29(2) | 55(2) | 3(2) | 8(2) | 12(2) |
| C(22) | 48(3) | 53(3) | 57(3) | 8(2) | 31(2) | 19(2) |

Table 74. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x 10 $^3$) for $C_{18}H_{26}N_2OS$ (**40**).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(5) | 610(50) | 8800(20) | 1930(30) | 56(12) |
| H(6) | 2240(50) | 7720(30) | 2810(30) | 70(14) |
| H(7) | 3287 | 7990 | 4306 | 89 |
| H(8) | 2630(60) | 9290(30) | 5010(30) | 81(15) |
| H(9) | 1150(40) | 10370(30) | 4130(30) | 48(11) |
| H(10) | 8150(40) | 6710(20) | 3240(20) | 29(8) |
| H(15) | 11720(40) | 5620(20) | 2750(20) | 31(8) |
| H(16A) | 10069 | 6616 | 1858 | 82 |
| H(16B) | 8487 | 6056 | 1920 | 82 |
| H(16C) | 9820 | 5694 | 1379 | 82 |
| H(17A) | 10180(50) | 4340(20) | 2380(30) | 55(11) |
| H(17B) | 10550(50) | 4380(20) | 3480(30) | 53(11) |
| H(17C) | 8770(50) | 4660(20) | 2900(20) | 43(10) |
| H(18A) | 13860(50) | 5870(30) | 4190(30) | 65(13) |
| H(18B) | 12940(50) | 5030(30) | 4380(30) | 68(14) |
| H(18C) | 13630(40) | 5670(20) | 5160(30) | 44(10) |
| H(19A) | 10960(50) | 7040(20) | 6330(30) | 50(11) |
| H(19B) | 12570(50) | 6640(30) | 6160(20) | 54(11) |
| H(19C) | 12030(60) | 7600(30) | 5900(30) | 84(17) |
| H(20) | 9000(40) | 7980(20) | 5330(20) | 26(8) |
| H(21A) | 6840(50) | 7990(30) | 3640(30) | 60(12) |
| H(21B) | 6940(50) | 8700(30) | 4340(30) | 52(12) |
| H(21C) | 8430(50) | 8620(30) | 3820(30) | 74(14) |
| H(22A) | 6260(50) | 7570(30) | 5440(30) | 63(12) |
| H(22B) | 7490(50) | 6770(30) | 5740(30) | 72(14) |
| H(22C) | 6320(50) | 6840(30) | 4770(30) | 63(14) |

Table 75. Crystal data and structure refinement for $C_3H_8O_4S_2$ (**41**).

| | | |
|---|---|---|
| Empirical formula | $C_3H_8O_4S_2$ | |
| Formula weight | 172.21 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 11.0496(18) Å | $\alpha$= 90°. |
| | b = 5.793(3) Å | $\beta$= 96.77°. |
| | c = 11.0496(6) Å | $\gamma$ = 90°. |
| Volume | 702.3(3) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.629 Mg/m$^3$ | |
| Absorption coefficient | 0.703 mm$^{-1}$ | |
| F(000) | 360 | |
| Crystal size | 0.25 x 0.05 x 0.05 mm$^3$ | |
| Theta range for data collection | 3.71 to 26.33°. | |
| Index ranges | -13<=h<=13, -6<=k<=7, -13<=l<=13 | |
| Reflections collected | 9692 | |
| Independent reflections | 1441 [R(int) = 0.0737] | |
| Completeness to theta = 26.33° | 99.9 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 1441 / 0 / 115 | |
| Goodness-of-fit on F$^2$ | 1.104 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0311, wR2 = 0.0700 | |
| R indices (all data) | R1 = 0.0376, wR2 = 0.0729 | |
| Extinction coefficient | 0.0073(18) | |
| Largest diff. peak and hole | 0.419 and -0.284 e.Å$^{-3}$ | |

Table 76. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for $C_3H_8O_4S_2$ (**41**). U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 1635(1) | 10119(1) | 3553(1) | 18(1) |
| S(2) | -723(1) | 10036(1) | 1819(1) | 23(1) |
| C(1) | 1169(2) | 12396(3) | 4440(2) | 23(1) |
| C(2) | -862(2) | 7028(4) | 1665(2) | 35(1) |
| C(3) | 876(2) | 10559(3) | 2050(2) | 21(1) |
| O(4) | 1249(1) | 7950(2) | 4015(1) | 25(1) |
| O(5) | -1252(1) | 10780(3) | 2882(1) | 33(1) |
| O(6) | 2909(1) | 10408(2) | 3427(1) | 25(1) |
| O(7) | -1141(1) | 11120(3) | 671(1) | 36(1) |

Table 77. Bond lengths [Å] and angles [°] for $C_3H_8O_4S_2$ (**41**).

| | |
|---|---|
| S(1)-O(6) | 1.4398(13) |
| S(1)-O(4) | 1.4397(14) |
| S(1)-C(1) | 1.7563(19) |
| S(1)-C(3) | 1.7889(18) |
| S(2)-O(5) | 1.4386(14) |
| S(2)-O(7) | 1.4416(15) |
| S(2)-C(2) | 1.756(2) |
| S(2)-C(3) | 1.7811(19) |
| | |
| O(6)-S(1)-O(4) | 118.02(8) |
| O(6)-S(1)-C(1) | 108.72(9) |
| O(4)-S(1)-C(1) | 109.82(10) |
| O(6)-S(1)-C(3) | 104.48(8) |
| O(4)-S(1)-C(3) | 109.10(8) |
| C(1)-S(1)-C(3) | 105.96(10) |
| O(5)-S(2)-O(7) | 117.99(9) |
| O(5)-S(2)-C(2) | 109.70(11) |
| O(7)-S(2)-C(2) | 109.39(11) |
| O(5)-S(2)-C(3) | 108.90(9) |
| O(7)-S(2)-C(3) | 105.13(9) |
| C(2)-S(2)-C(3) | 104.87(10) |
| S(2)-C(3)-S(1) | 117.20(10) |

Symmetry transformations used to generate equivalent atoms:

Table 78. Anisotropic displacement parameters ($Å^2$x $10^3$) for $C_3H_8O_4S_2$ (**41**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 16(1) | 17(1) | 21(1) | 1(1) | 2(1) | 1(1) |
| S(2) | 15(1) | 29(1) | 25(1) | -1(1) | 0(1) | 2(1) |
| C(1) | 22(1) | 22(1) | 27(1) | -6(1) | 4(1) | 1(1) |
| C(2) | 24(1) | 33(1) | 48(1) | -6(1) | 3(1) | -7(1) |
| C(3) | 17(1) | 24(1) | 22(1) | 2(1) | 2(1) | -1(1) |
| O(4) | 30(1) | 20(1) | 27(1) | 4(1) | 5(1) | 0(1) |
| O(5) | 19(1) | 47(1) | 33(1) | -7(1) | 5(1) | 5(1) |
| O(6) | 14(1) | 27(1) | 33(1) | -2(1) | 2(1) | 2(1) |
| O(7) | 27(1) | 49(1) | 29(1) | 4(1) | -6(1) | 9(1) |

Table 79. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for $C_3H_8O_4S_2$ (**41**).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1A) | 330(20) | 12260(40) | 4480(20) | 34(6) |
| H(1B) | 1370(20) | 13760(40) | 4090(20) | 30(6) |
| H(1C) | 1600(20) | 12200(40) | 5240(20) | 37(6) |
| H(2A) | -520(20) | 6340(50) | 2390(20) | 41(7) |
| H(2B) | -460(30) | 6570(50) | 990(30) | 48(7) |
| H(2C) | -1660(30) | 6730(50) | 1580(20) | 49(8) |
| H(3A) | 1270(20) | 9550(40) | 1530(20) | 28(6) |
| H(3B) | 1030(20) | 12140(40) | 1858(19) | 27(6) |

## 6.3 Bibliography

**Personal Information:**

| | |
|---|---|
| Name | Eyad Mazin Mallah |
| Date of Birth | 3th of May 1979 |
| Place of Birth | Amman-Jordan |
| Nationality | Jordanian |
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**Education:**

| | |
|---|---|
| **03/2007-06/2009** | Dissertation under the guidance of Prof. Dr. Norbert Kuhn at the Faculty of Chemistry and Pharmacy, Tuebingen University-Germany, with thesis title: " Synthesis and Characterisation of Novel Cationic Imidazolium Derivatives - on the Route to Possible Drugs ". |
| **February-2004** | **M.Sc. in Applied Chemistry.**<br>Jordan University of Science and Technology (J.U.S.T), Irbid-Jordan, with thesis title "Reversed phase liquid chromatographic method for quantitation of cefaclor and its applications on dissolution and stability studies in formulations and plasma ". |
| **June-2000** | **B.Sc. in Analytical Chemistry.**<br>Jordan University of Science and Technology (J.U.S.T), Irbid-Jordan. |
| **July-1996** | **General Secondary Education Exam.**<br>Al-Hussein college, Amman- Jordan. |

## Experiences:

| | |
|---|---|
| **March/04 - March 07:** | **Staff Member**<br>Faculty of Pharmacy and Medical Technology,<br>University of Petra, Amman-Jordan. |
| **July/01 - March 07:** | **Senior Analyst and Team Leader**<br>Jordan Center for Pharmaceutical Research (**J.C.P.R)**,<br>Amman- Jordan. |
| **July/2001 - February/2004** | **Laboratory Instructor**<br>Faculty of Pharmacy and Medical Technology,<br>University of Petra, Amman- Jordan. |
| **February/2001 - June/2001** | **Teaching Assistant (TA)**<br>Department of Applied Chemistry, Jordan University of Science and Technology (J.U.S.T), Irbid-Jordan. |
| **July/2000 - June/2001** | **Analyst**<br>Jordan Center for Pharmaceutical Research (J.C.P.R),<br>Amman- Jordan. |