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DFT Studies and Crystal Structure of Synthesized 1,3-bis(2-thiophenylmethyl)-4,5-dihydroimidazolidinium hexafluorophosphate Salt

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Abstract: The synthesized compound **5**, ($C_{13}H_{15}N_2S_2$)[PF_6], was fully characterized with X-ray diffraction method. In this compound, the asymmetric unit contains a 1,3-(2-thiophenylmethyl)-4,5-dihydroimidazolidinium cation and a hexafluorophosphate anion. Due to an 180° rotation about the thiophene-CH_2 bonds, the thiophene rings in the cation are disordered [site-occupancy factors = 0.903(4)/0.097(4) and 0.837(5)/0.163(5), respectively]. The short C—N bond lengths [1.303(4) and 1.287(4) Å] in the imidazolidine ring display partial electron delocalization within the N—C—N fragment. Anion and cations are connected through intermolecular C—H...F hydrogen bonds and three π-π stacking interactions [centroid-centroid distances = 3.890(3), 3.852(5) and 3.816(7) Å] between the thiophene rings of the adjacent cations, forming layers parallel to (011). Furthermore, we studied theoretical studies of this compound, too. Geometry optimization was carried out in gas phase by Density Functional Theory (DFT) method with B3LYP applying 6-311++G** basis set. The obtained results from experimental and theoretical structural properties of compound **5** had been compared to each other.

Keywords: Imidazolidinium salt, synthesis, crystal structure, DFT, C—H...F hydrogen bonds, π-π stacking interactions.

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INTRODUCTION

Heterocyclic salts are significant in terms of being used as a carbene ancillary ligand in catalytic reactions. Complexes containing heterocyclic groups have high catalytic activities for many useful organic transformations such as C—C and C—N cross-coupling reactions, C—H bond activation and metathesis [1-7]. The catalytic activity can be changed with the substituents on the N atom of the salts such as imidazolium, imidazolidinium or bis-benzimidazolium [5, 8]. Carbon-carbon cross-coupling reactions, which play an important role in the synthesis of natural products, drug design and industrially important starting materials, have been an area of interest for organic chemists for a long time [9-11].

To estimate the structural properties of the compounds, *ab initio* methods such as DFT in the computational chemistry are significant tools. Some chemical and physical properties of the chemical compounds and materials are extensively investigated due to *ab initio* calculations based on the quantum mechanics [12]. DFT is the most widely used for "*ab initio*" calculations of the structure of molecules, atoms, surfaces, crystals and their interactions [13].

Herein, we prepared a heterocyclic salt (**5**) containing thiophene moiety (Scheme 1). The crystalline structure of 1,3-bis(2-thiophenylmethyl)-4,5-dihydroimidazolidinium hexafluorophosphate salt (**5**) was reported in this study. Moreover, we studied the compound's theoretical structural properties with DFT software.

EXPERIMENTAL SECTION

General Method for the Preparation of the Imidazolidinium Salt

The study was made according to method defined in the literature [14, 15]. To a solution of diamine **1** (15 mmol) in toluene (20 mL), heteroaryl-2-carbaldehyde **2** (29 mmol) was added at ice bath temperature. After the obtained mixture was stirred at 0 ºC for 18 h, the solvent in the medium was removed *in vacuo*. The formed Schiff base **3** was crystallized from diethyl ether/hexane (1:2) mixture at 25 °C. To a solution of Schiff base **3** (24 mmol) in methyl alcohol (40 mL), $NaBH_4$ (48 mmol) was added. After the mixture was stirred for 24 h, the solvent was removed. The heteroaryl-substituted diamine **4** as the product was crystallized from a mixture of dichloromethane/diethyl ether (1:1). Ammonium hexafluorophosphate (NH_4PF_6) (1.0 mmol) was added to a solution of heteroaryl-substituted diamine **4** (1.0 mmol) in $CH(OEt)_3$ (5 mL) and the reaction mixture was heated for 12 h at 80 °C. A solid was seen to precipitate. Then the heteroaryl-substituted heterocyclic salt **5** was crystallized from ethyl alcohol/diethyl ether (1:2) mixture. Results of ^1H NMR, ^{13}C NMR (by using Bruker AC300P FT spectrometer operating) and melting point (by using an Electrothermal 9200 melting point apparatus) can be found in a previous study [15].

X-ray Crystal Structure

Single-crystal diffraction data were gathered by a STOE IPDS II diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), in the rotation method, at 25 °C. All data were made accurate for polarization, Lorentz and absorption effects [16]. Crystal structure was solved by direct methods using program SHELXS97 and refined by the full-matrix least-squares method for all F^2 data using the SHELXL97 [17] programs. With the anisotropic displacement parameters, all non-hydrogen atoms were refined. All H atoms were positioned geometrically and were refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$. The fluorine atoms of the hexafluorophosphate anion are disordered over two sites with occupancies of 0.588(13) and 0.412(13). The crystallographic data and the refinement procedure details for the title compound are summarized in Table 1. The list of selected geometric parameters is given in Table 2.

Table 1. The crystallographic data and the refinement procedure details for **5**

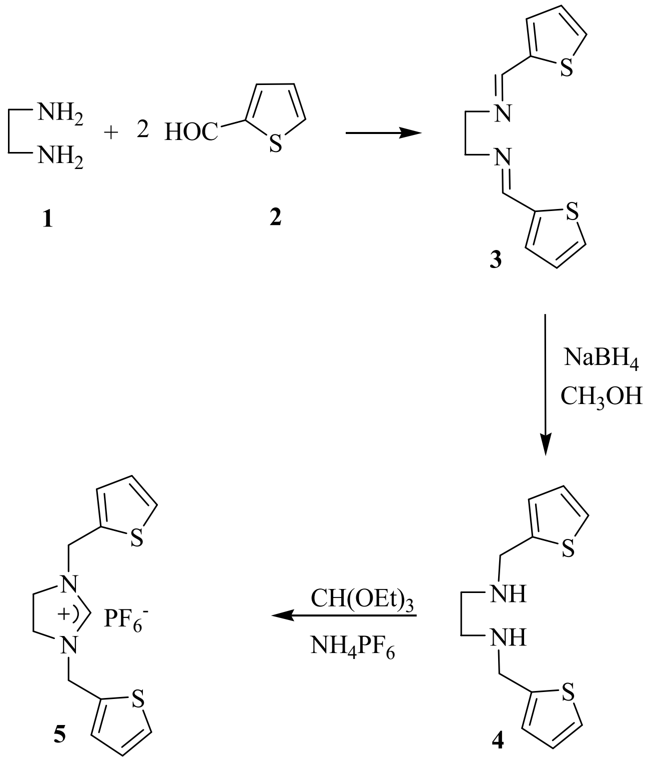
Chemical formula	$C_{13}H_{15}F_6N_2PS_2$
M_r	408.36
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	20.3151 (12), 6.0059 (3), 14.9112 (9)
β (°)	109.987 (4)
V (Å^3)	1709.74 (17)
Z	4
μ (MoKα) (mm^{-1})	0.46
Crystal size (mm)	0.50 × 0.45 × 0.39
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10743, 3743, 2447
R_{int}	0.026
θ values (°)	$\theta_{max} = 27.1$, $\theta_{min} = 2.1$
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.642
Range of h, k, l	$h = -25 \rightarrow 25$, $k = -7 \rightarrow 6$, $l = -18 \rightarrow 18$
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.060, 0.182, 1.08
No. of reflections	3743
No. of parameters	262
No. of restraints	40
H-atom treatment	H-atom parameters constrained
$(\Delta/\sigma)_{max}$	< 0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.62, -0.48

The computations were carried out at 6-311++G** levels using the SPARTAN 10 software package [18], with operating density functional methods. The calculations were done for the optimized structures in the gas phase. SPARTAN software [19] is a molecular modeling and computational chemistry application from wavefunction.

RESULTS AND DISCUSSION

Characterization of the Heteroaryl-substituted Heterocyclic Salt

In a previous study, the structure of 1,3-bis(2-thiophenylmethyl)imidazolidinium salt was determined by elemental analysis, ^{1}H and ^{13}C NMR [15]. Furthermore, the structure of this compound was completely characterized with X-ray studies. The ^{1}H NMR spectrum of the salt assigned the structures. The resonance for C(2)-H was observed as a sharp singlet 8.71 ppm [15]. The imino carbon atom was observed at 158.0 ppm in ^{13}C NMR.



Scheme 1. Synthesis of imidazolidinium salt [15].

Single crystal and molecular structure

A single crystal of the imidazolidinium salt, which is adequate for X-ray diffraction, was acquired by slow diffusion of dichloromethane into diethyl ether solutions at 25 °C. The molecular view of compound is represented in Figs. 1 and 2.

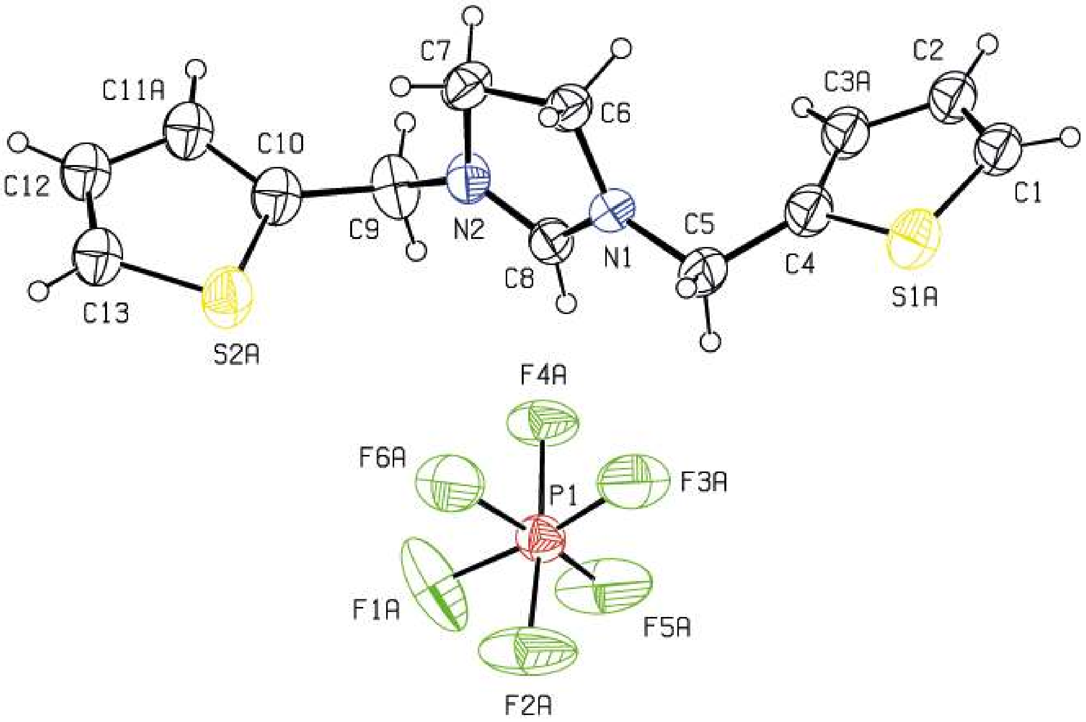


Figure 1. An ORTEP plot [20] of the molecular structure of **5**. At the 30 % probability level, displacement ellipsoids for non-H atoms are drawn. Only major disorder component is shown.

In compound **5** (Figure 1), 1,3-bis(2-thiophenylmethyl)-4,5-dihydroimidazolidinium cation has a thiophenyl-ring flip disorder. Two positions of both thiophene rings in the cation are obtained by an 180° rotation about the thiophene-CH_2 bonds.

A similar thiophene ring disorder has been observed in a thiophene derivative, 1,3-bis(2-thiophenylmethyl)-4,5-dihydroimidazolidinium trichlorido([eta]6-*p*-cymene)ruthenate(II)

[21]. The bond lengths and angles in **5** were found to be similar to those reported for the structures of the related compounds with furfuryl or thenyl moities [22, 23].

The imidazolidine ring (N1/N2/C6–C8) is essentially planar [maximum deviations = -0.008(2) Å for N1 and 0.007(3) Å for C8]. Because of the *π*-electron delocalization on the imidazolium ring, the N1—C8 and N2—C8 bond lengths of 1.303(4) and 1.287(4) Å in the imidazolidine ring are shorter than the average single C—N bond length of 1.48 Å. This case shows double bond character in these C—N bonds and demonstrates a partial electron delocalization within the N1—C8—N2 fragment.

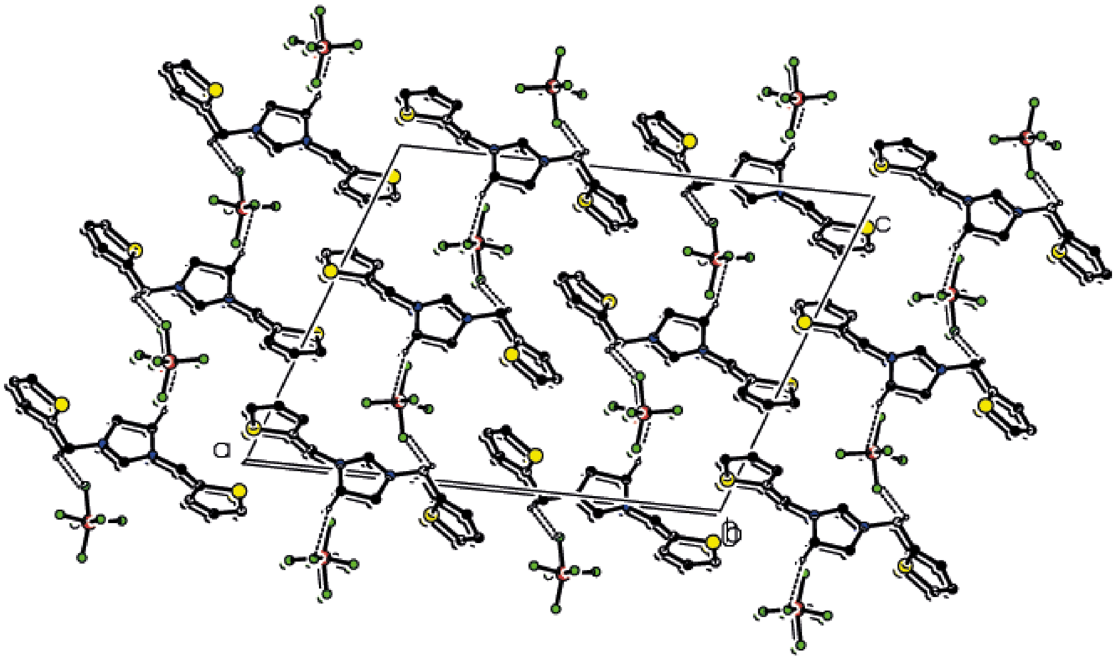


Figure 2. View of the hydrogen bonding and molecular packing of **5** in the unit cell. H atoms not involved in H bonding are omitted for clarity and only major disorder component is shown.

In the crystal structure of compound **5**, adjacent anion and cations are connected by C—H···F hydrogen bonds and slipped π–π inter actions [*Cg2*...*Cg2*^{i}= 3.890(3) Å; where *Cg*2 is the centroid of the S2A/C10/C11A/C12/C13 thiophene ring; symmetry code (i): 1-x, 1-y, 1-z], with an interplanar distance of 3.660(2) Å and resulting a slipping distance of 1.320Å, forming a three-dimensional network (Table 1 and Figure 2).

Table 2. Selected geometric parameters (Å, º) for **5**

C1—C2	1.330 (5)	C10—S2B	1.616 (11)
C1—C3B	1.492 (19)	C10—S2A	1.704 (4)
C1—S1A	1.679 (4)	C11A—C12	1.420 (9)
C2—C3A	1.389 (7)	S2A—C13	1.667 (4)
C2—S1B	1.544 (13)	C11B—C13	1.518 (18)
C3A—C4	1.402 (7)	S2B—C12	1.566 (10)
S1A—C4	1.709 (4)	C12—C13	1.317 (5)
C3B—C4	1.526 (16)	F1A—P1	1.511 (8)
S1B—C4	1.544 (13)	F2A—P1	1.548 (9)
C4—C5	1.494 (5)	F3A—P1	1.605 (7)
C5—N1	1.455 (4)	F4A—P1	1.593 (6)
C6—N1	1.471 (4)	F5A—P1	1.544 (7)
C6—C7	1.529 (4)	F6A—P1	1.562 (7)
C7—N2	1.465 (4)	F1B—P1	1.507 (12)
C8—N2	1.287 (4)	F2B—P1	1.534 (11)
C8—N1	1.303 (4)	F3B—P1	1.433 (13)
C9—N2	1.454 (4)	F4B—P1	1.484 (13)
C9—C10	1.497 (5)	F5B—P1	1.514 (12)
C10—C11A	1.420 (8)	F6B—P1	1.512 (8)
C10—C11B	1.519 (16)		
C1—S1A—C4	92.45 (17)	C8—N1—C6	109.5 (3)
C4—S1B—C2	98.3 (6)	C5—N1—C6	123.9 (3)
N2—C8—N1	114.5 (3)	C8—N2—C9	125.2 (3)
C13—S2A—C10	92.74 (19)	C8—N2—C7	110.4 (3)
C12—S2B—C10	94.9 (4)	C9—N2—C7	123.8 (3)
C8—N1—C5	126.3 (3)		
C4—C5—N1—C8	-119.8 (4)	C10—C9—N2—C8	-125.8 (4)

Table 3. Hydrogen-bond parameters (Å, °) for **5**

	D—H	H...A	D...A	D—H...A
C6—H6A···F2Ai	0.97	2.48	3.413 (9)	162
C8—H8···F3A	0.93	2.38	3.266 (10)	159
C9—H9A···F6Aii	0.97	2.55	3.231 (11)	128

Symmetry codes: (i) x, 1/2-y, 1/2+z; (ii) x, 1+y, z.

Theoretical studies

Molecular structure and physical properties of the molecule can be predicted accurately by the help of computational methods based on DFT. The theoretical and experimental structural properties of compound **5** were examined. Experimental geometric parameters (bond angles and lengths) were compared with computed values from density functional theory with B3LYP 6-311++G** basis set. The lowest energy conformation of compound **5** was used in theoretical calculations. Theoretical calculation results were obtained in good agreement with experimental data.

Table 4. Experimental and calculated selected geometric parameters for **5**

Bond Lengths (Å)	**Experimental**	**Calculated(Vacuum)**
C1—C2	1.330 (5)	1.364
S1A—C4	1.709 (4)	1.748
C4—C5	1.494 (5)	1.497
C5—N1	1.455 (4)	1.473
C6—N1	1.471 (4)	1.482
C6—C7	1.529 (4)	1.548
C7—N2	1.465 (4)	1.479
C8—N1	1.303 (4)	1.317
C9—N2	1.454 (4)	1.475
C9—C10	1.497 (5)	1.500
C10—S2A	1.704 (4)	1.748
C11A—C12	1.420 (9)	1.425
C12—C13	1.317 (5)	1.366
F3A—P1	1.605 (7)	1.652
Bond Angles (°)		
C1—S1A—C4	92.45 (17)	91.54
C8—N1—C6	109.5 (3)	109.17
C5—N1—C6	123.9 (3)	122.59
N2—C8—N1	114.5 (3)	114.36
C13—S2A—C10	92.74 (19)	91.53
C8—N2—C9	125.2 (3)	125.34
C8—N2—C7	110.4 (3)	109.90
C9—N2—C7	123.8 (3)	124.73

CONCLUSIONS

In this work, the synthesized salt was characterized by using single crystal X-ray diffraction method. The molecular structures were theoretically investigated by the DFT calculations. The obtained geometrical parameters of the optimized geometries were in agreement with X-ray structure results.

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SUPPORTING INFORMATION

CCDC 1014061 contains the supplementary crystallographic data for this paper. These data can be obtained, free of charge, from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/deposit.

REFERENCES

1. Akkoc S, Gok Y. Synthesis and characterization of 1-phenyl-3-alkylbenzimidazol-2-ylidene salts and their catalytic activities in the Heck and Suzuki cross-coupling reactions. Journal of Coordination Chemistry. 2013 Apr;66(8):1396–404. DOI: 10.1080/00958972.2013.786053.

2. Winkelmann OH, Riekstins A, Nolan SP, Navarro O. A Comparative Study on (NHC)Pd(acac)Cl Complexes (NHC = N-heterocyclic carbene): Indications for the Origin of the Different Reactivity of Saturated and Unsaturated NHC in Cross-Coupling Reactions. Organometallics. 2009 Oct 12;28(19):5809–13. DOI: 10.1021/om900677v.

3. Akkoç S, Gök Y, Akkurt M, Tahir MN. Catalytic activities in the direct C5 arylation of novel palladium N-heterocyclic carbene complexes containing benzimidazol-2-ylidene nucleus. Inorganica Chimica Acta. 2014 Mar;413:221–30. DOI: 10.1016/j.ica.2014.01.015.

4. Ritter T, Day MW, Grubbs RH. Rate Acceleration in Olefin Metathesis through a Fluorine−Ruthenium Interaction. Journal of the American Chemical Society. 2006 Sep;128(36):11768–9. DOI: 10.1021/ja064091x.

5. Yılmaz Ü, Şireci N, Deniz S, Küçükbay H. Synthesis and microwave-assisted catalytic activity of novel bis-benzimidazole salts bearing furfuryl and thenyl moieties in Heck and Suzuki cross-coupling reactions. Applied Organometallic Chemistry. 2010;n/a-n/a.

[6] Akkoç S, Gök Y, İlhan İ Ö, Kayser V. N-Methylphthalimide substituted benzimidazolium salts and PEPPSI Pd-NHC complexes: synthesis, characterization and catalytic activity in carbon-carbon bond forming reactions. Beilstein Journal of Organic Chemistry. 2016 Jan; 12: 81-8. DOI:10.3762/bjoc.12.9

[7] Akkoç S, Gök Y, İlhan İ Ö, Kayser V. In situ generation of efficient palladium N-heterocyclic carbene catalysts using benzimidazolium salts for the Suzuki-Miyaura cross-coupling reaction. Current Organic Synthesis. 2016; 13. DOI: 10.2174/1570179413666151218200334

[8] Durap F, Metin Ö, Aydemir M, Özkar S. New route to synthesis of PVP-stabilized palladium(0) nanoclusters and their enhanced catalytic activity in Heck and Suzuki cross-coupling reactions. Applied Organometallic Chemistry. 2009 Oct; 23: 498–503. DOI: 10.1002/aoc.1555

[9] Aktaş A, Akkoç S, Gök Y, Palladium catalyzed Mizoroki-Heck and Suzuki-Miyaura reactions using napthalenomethyl-substituted imidazolidin-2-ilidene ligands in aqueous media. Journal of Coordination Chemistry. 2013 Aug; 66: 2901-9. DOI: 10.1080/00958972.2013.819092.

[10] Resch V, Schrittwieser J H, Siirola E, Kroutil W. Novel carbon-carbon bond formations for biocatalysis. Current Opinion in Biotechnology. 2011 Feb; 22: 793-9. DOI: 10.1016/j.copbio.2011.02.002.

[11] Minto R E, Blacklock B J. Biosynthesis and function of polyacetylenes and allied natural products. Progress in Lipid Research. 2008 Jul; 47(4): 233-306. DOI: 10.1016/j.plipres.2008.02.002.

[12] Kart H H, Özdemir Kart S, Karakuş M, Kurt M. Ab initio/DFT calculations of butyl ammonium salt of O,O'-dibornyl dithiophosphate. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2014 Aug; 129: 421–8. DOI: 10.1016/j.saa.2014.03.076.

[13] Argaman N, Makov G. Density functional theory: An introduction, American Journal of Physics. 68 (2000) 69-79. DOI.org/10.1119/1.19375.

[14] Akkoç S, Gök Y, Akkurt M, Tahir M N, Imidazole, pyrimidine and diazepine containing heteroaryl-substituted heterocyclic salts as efficient ligand precursors for Mizoroki-Heck coupling reaction: synthesis, structural characterization and catalytic activities, Journal of the Iranian Chemical Society. 2014 Mar; 11: 1767-74. DOI: 10.1007/s13738-014-0449-z.

[15] Ozdemir İ, Gurbuz N, Gok Y, Cetinkaya B. *N*-functionalized azolin-2-ylidene-palladium-catalyzed heck reaction. Heteroatom Chemistry. 2008 Jan; *19(1)*: 82-6. DOI: 10.1002/hc.20415.

[16] Stoe & Cie (2002). *X-AREA* and *X-RED32*. Stoe & Cie, Darmstadt, Germany.

[17] Sheldrick G M. A short history of *SHELX*. Acta Crystallographica Section A. 2008; A64: 112–122. DOI:10.1107/S0108767307043930.

[18] Spartan'10; Wavefunction, Inc.: Irvine, CA, 2011.

[19] Young D. Computational Chemistry. Wiley-Interscience, 2001. Appendix A. A.1.6 pg 330, SPARTAN.

[20] Farrugia L J. WinGX and ORTEP for Windows: an update. Journal of Applied Crystallography. 2012 Jun; 45: 849–54. ISSN: 0021-8898.

[21] Arslan H, VanDerveer D, Özdemir I, Gürbüz N, Gök Y, Çetinkaya B. 1,3-bis(2-thienylmethyl)-4,5-dihydroimidazolium trichlorido(6-p-cymene)ruthenate(II). Acta Crystallographica Section E. 2009; E65: 165–6. ISSN: 1600-5368.

[22] Yıldırım S Ö, Akkurt M, Şireci N, Küçükbay H, Kazak C. 2-[(2-Furylmethyl)sulfanyl]-1*H*-3,1-benzimidazol-3-ium chloride dihydrate. Acta Crystallographica Section E. 2007; E63: 2433. ISSN: 1600-5368.

[23] Akkurt M, Şireci N, Deniz S, Küçükbay H, Büyükgüngör O. 1,3-Difurfuryl-benzimidazolium chloride monohydrate. Acta Crystallographica Section E. 2009; E65: 2037–8. ISSN: 1600-5368.