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# Imidazole, pyrimidine and diazepine containing heteroarylsubstituted heterocyclic salts as efficient ligand precursors for Mizoroki–Heck coupling reaction: synthesis, structural characterization and catalytic activities

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Abstract The nine new heteroaryl-substituted imidazolidinium (1a-c), pyrimidinium (2a-c) and diazepinium (3a-c) salts as N-heterocyclic carbene (NHC) precursors were synthesized in good yields and entirely characterized using elemental analyses and conventional spectroscopic methods. In situ formed complexes from heterocyclic salts (1-3), Pd(OAc)<sub>2</sub> and in the presence of KOBu<sup>t</sup> as a base were tested as catalysts for the Mizoroki-Heck coupling reaction in an aqueous media and very high yields were achieved. 1,3-Di(5-methylthiophen-2-ylmethyl)pyrimidinium hexafluorophosphate salt (2b) was structurally characterized by single-crystal X-ray diffraction. In the 2b compound  $(C_{16}H_{21}N_2S_2)^+[PF_6]^-$ , the terminal thiophene rings are twisted with a dihedral angle of 72.8(3)°. In the pyrimidine ring, the three successive C atoms between the N atoms are disordered over two positions [occupancy ratio 0.753(12):0.247(12)]. In the crystal, neighboring molecules are linked by C-H...F hydrogen bonds, running along the b axis.

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M. N. Tahir Department of Physics, Sargodha University, Sargodha, Pakistan **Keywords** Imidazolidinium salt · Pyrimidinium salt · Diazepinium salt · Mizoroki–Heck coupling reaction · Catalyst · X-ray diffraction

## Introduction

Transition metal-catalyzed carbon-carbon coupling reactions are very powerful tools in numerous organic transformations. In modern organic synthesis, the Mizoroki-Heck reaction, which consists of the coupling of an alkene with a halo compound, has become a corner stone [1]. This significance reaction has become a subject of major interest at industrial level and its applications in the laboratory [2, 3]. In recent years, sterically hampered carbene ligands, NHCs and electron rich alkyl phosphines have received increasing interest [4-10]. Diverse NHC ligands have been prepared in short time and some of them, for a variety of palladium-catalyzed transformations, have been used successfully [11-15]. However, industrial applications of Mizoroki-Heck reactions are rare, chiefly due to the following two problems [16, 17]: Firstly, palladium is costly and pollution of the product by palladium has to be firmly controlled. Secondly, many phosphine ligands are even more expensive and they are not appropriate to work with as they are subject to P-C bond degradation at elevated temperature, are poisonous and air sensitive [18].

Recently, the advantages brought to fine chemistry by means of the easy substitution of a phosphine ligand by a nucleophilic heterocyclic diaminocarbene, such as imidazolidine and benzimidazolidine ligands, have brought important advancements in catalytic activity. Illustrative instances are found in Mizoroki–Heck coupling reactions [19–21], cyclopropanation [22], hydrogenation [23, 24],



Scheme 1 Synthesis of heteroaryl-substituted imidazolidinium (1a-c), pyrimidinium (2a-c) and diazepinium (3a-c) salts

ruthenium catalysts for the formation of furans [25], methathesis [26], hydrosilylation [27] and rhodium catalysts for arylation [28]. A number of significant roles in homogeneous catalysis, such as controlling activity and providing a stabilizing effect as well as selectivity by altering electronic and steric parameters, are provided by the ancillary ligand coordinated to the metal center. In tuning the catalytic activity, the position, number and nature of the substituents on the N atom(s) and/or NHC ring play a crucial role.

Herein, to find efficient palladium catalysts we prepared a series of new heterocyclic salts (1-3) containing furan, thiophene and pyrrol moieties (Scheme 1). The crystal structure of 1,3-di(5-methylthiophen-2-ylmethyl)imidazolidinium hexafluorophosphate salt (1b) is reported here. We also reported the use of in situ formed catalytic system consisting of Pd(OAc)<sub>2</sub> as palladium source, 1-3 as carbene precursors and KOBu<sup>t</sup> as a base for the coupling of styrene with different aryl bromides in aqueous media. New heteroaryl-substituted imidazolidin-2-ylidene, pyrimidin-2-ylidene and diazepin-2-ylidene palladium(II) systems exhibited quite high catalytic activity.

## **Results and discussion**

Characterization of the heteroaryl-substituted heterocyclic salts, 1–3

1,3-Dialkylimidazolidinium (1a-c), 1,3-dialkylpyrimidinium (2a-c) and 1,3-dialkyldiazepinium (3a-c) salts are NHC precursors. The synthesis of salts containing furan, thiophene and pyrrol moieties was achieved by the reaction of N, N'-dialkylethane-1,2-diamine, N, N'-dialkylpropane-1,3-diamine and N,N'-dialkylbutane-1,4-diamine with ammonium hexafluorophosphate in triethyl orthoformate for 1-3, respectively (Scheme 1). The resulting imidazolidinium, pyrimidinium and diazepinium salts were obtained in very good yields of 75-95 %. The structures of salts 1-3 were determined by spectroscopic methods (<sup>1</sup>H NMR, <sup>13</sup>C NMR and FT-IR) and elemental analyses. Also, 1,3-di(5-methylthiophen-2-ylmethyl)pyrimidinium hexafluorophosphate salt (2b) was structurally characterized by single-crystal X-ray diffraction method. The <sup>1</sup>H NMR spectra of the heterocyclic salts containing furan, thiophene and pyrrol moieties further supported the assigned



Fig. 1 The molecular structure of the 2b compound with 30 % probability displacement ellipsoids for non-H atoms. Only the major disorder component is shown



Fig. 2 The crystal packing and hydrogen bonding of the 2b compound along the *b* axis. H atoms not involved in hydrogen bonding and the minor disordered component are omitted for clarity

structures; the resonances for C(2)-H were observed as sharp singlets at 8.00, 8.67, 8.01, 7.96, 8.75, 8.51, 7.80, 7.90 and 7.62 ppm, respectively, for the heterocyclic salts **1–3**. <sup>13</sup>C NMR chemical shifts were consistent with the proposed structure; the imino carbon atom appeared as a typical singlet in the <sup>1</sup>H-decoupled mode at 156.7, 157.4, 155.8, 154.0, 153.1, 152.4, 157.7, 157.1 and 156.6 ppm, respectively, for **1–3**. The NMR values are similar to those found for 1,3-dialkylheterocyclic salts. The heterocyclic salts (**1–3**) showed FT-IR absorption at 1,561.17, 1,525.26, 1,504.49, 1,504.60, 1,561.53, 1,550.04, 1,563.31, 1,574.01 and 1,585.99 cm<sup>-1</sup>, respectively, which are assigned to v(C=N). These values are slightly lower than the normal

v(C=N) value because of the  $\pi$ -electron delocalization in the heterocyclic ring.

Single crystal and molecular structure

A single crystal of the heteroaryl-substituted salt **2b**, which is suitable for X-ray diffraction, was obtained by slow diffusion of dichloromethane into diethylether solutions at ambient temperature. There is not appear lattice held organic solvent molecules such as dichloromethane and diethylether in the unit cells of the determined structure in **2b**. The molecular view of compound **2b** is represented in Figs. 1 and 2.

The terminal thiophene rings (S1/C1–C4 and S2/C12–C15) of the title compound make a dihedral angle of 72.8(3)° with each other. In the pyrimidine ring, the three successive C7-C8-C9 atoms between the N1 and N2 atoms are disordered over two positions with the occupancies of [0.753(12) and 0.247(12)]. The N1/N2/C7A-C9A/C10 ring of the major component adopts an envelope conformation [Puckering parameters [29] are  $Q_{\rm T} = 0.415(11)$  Å,  $\theta = 54.0(12)^{\circ}$  and  $\phi = 118.8(16)^{\circ}$ ]. The other ring with the minor component is puckered with the puckering parameters of  $Q_{\rm T} = 0.36(3)$  Å,  $\theta = 60(5)^{\circ}$  and  $\phi = 227(5)^{\circ}$ . All bond lengths and angles are normal [30].

Mizoroki-Heck coupling reaction

It has been observed that the palladium-catalyzed coupling of aryl bromides with styrene carries on under various conditions. A wide range of bases (K<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub> and KOBu<sup>t</sup>) and solvents (DMF, H<sub>2</sub>O and dioxane), as well as catalysts, in situ formed from Pd(OAc)<sub>2</sub> and carbene precursors 1-3, has been employed with varying degrees of success according to the substrates. A series of experiments have been performed with styrene and 4-bromoacetophenone as model compounds to find optimum conditions. As a base, KOBu<sup>t</sup> was the best choice in DMF/H<sub>2</sub>O systems. In addition, the reactions were performed in air. After determining the optimized coupling reaction conditions, the efficiencies of the salts and reach of the reaction were evaluated by investigating the coupling of various psubstituted aryl bromides with styrene. The results are given in Table 1.

Quite active catalytic processes that are both stable towards moisture and oxidant variations and easy to handle are still being sought today. It is environmentally and economically advantageous to use water as solvent for chemical reactions, because it is nonflammable, economical, abundant, nonpoisonous and easily separable from organic compounds [31]. Therefore, we used water together with DMF as solvent in our study. Also, a number of Table 1 The Mizoroki-Heck coupling reaction of styrene with various aryl bromides

+ R 
$$\longrightarrow$$
 Br  $\frac{\text{KOBu}^{t}, \text{LHX}, \text{Pd}(\text{OAc})_{2}}{80 \,^{\circ}\text{C}, 1 \text{ h}}$ 

 $\frown$ 

Entry	R	LHX	Yield (%) <sup>a, b, c</sup>
1	COCH <sub>3</sub>	1a	96
2	COCH <sub>3</sub>	1b	89
3	COCH <sub>3</sub>	1c	89
4	COCH <sub>3</sub>	2a	76
5	COCH <sub>3</sub>	2b	81
6	COCH <sub>3</sub>	2c	81
7	COCH <sub>3</sub>	3a	95
8	COCH <sub>3</sub>	3b	78
9	COCH <sub>3</sub>	3c	95
10	СНО	1a	99
11	СНО	1b	99
12	СНО	1c	96
13	СНО	2a	99
14	СНО	2b	95
15	СНО	2c	98
16	СНО	<b>3</b> a	99
17	СНО	3b	94
18	СНО	3c	98
19	OCH <sub>3</sub>	1a	64
20	OCH <sub>3</sub>	1b	73
21	OCH <sub>3</sub>	1c	89
22	OCH <sub>3</sub>	2a	87
23	OCH <sub>3</sub>	2b	84
24	OCH <sub>3</sub>	2c	98
25	OCH <sub>3</sub>	<b>3</b> a	92
26	OCH <sub>3</sub>	3b	84
27	OCH <sub>3</sub>	3c	99
28	CH <sub>3</sub>	1a	97
29	CH <sub>3</sub>	1b	95
30	CH <sub>3</sub>	1c	79
31	CH <sub>3</sub>	2a	61
32	CH <sub>3</sub>	2b	97
33	CH <sub>3</sub>	2c	94
34	CH <sub>3</sub>	<b>3</b> a	97
35	CH <sub>3</sub>	3b	98
36	CH <sub>3</sub>	3c	99
37	Н	1a	94
38	Н	1b	75
39	Н	1c	87
40	Н	2a	95
41	Н	2b	93
42	Н	2c	92
43	Н	<b>3</b> a	92
44	Н	3b	92

Table 1   continued					
Entry	R	LHX	Yield (%) <sup>a, b, c</sup>		
45	Н	30	98		

<sup>a</sup> Reaction conditions: aryl bromide (1.0 mmol), styrene (1.5 mmol), Pd(OAc)<sub>2</sub> (1.0 mmol %), KOBu<sup>t</sup> (2.0 mmol), 1–3 (2.0 mmol %), H<sub>2</sub>O (3 mL)-DMF(3 mL), temperature 80 °C, 1 h

<sup>b</sup> Purity of compounds is checked by GC and NMR spectroscopy

<sup>c</sup> Yields are based on aryl bromide

reports show that water has been used as solvent in palladium-mediated Mizoroki–Heck reactions [4, 5, 32, 33].

As the control experiment showed, the Mizoroki-Heck coupling reaction in the absence of 1-3 did not occur. Under the optimized reaction conditions, a diversity of aryl bromides bearing electron-withdrawing or electron-donating groups reacted with styrene, affording the coupled products in good to excellent yields. As expected, electrondeficient bromides for the conversions proved to be beneficial. According to these results, the in situ formed complexes from imidazolidinium, pyrimidinium and diazepinium with Pd(OAc)<sub>2</sub> were tested as catalysts for Mizoroki-Heck coupling reactions in H<sub>2</sub>O-DMF mixture. The influence of the heteroaryl substituents on N atoms was investigated under the same conditions in this coupling reaction. All salts (1-3) exhibited very good catalytic activities.

In the crystal structure, C–H...F hydrogen bonds connect the neighboring molecules along the *b* axis. In addition,  $\pi$ - $\pi$  and C–H... $\pi$  interactions are not observed. The selected bond lengths and angles are given in Table 2.

H atoms bound to C atoms were positioned geometrically and refined using a riding model, with C–H = 0.93-0.97 Å and  $U_{iso}(H) = 1.2$  or  $1.5U_{eq}(C)$ . In the pyrimidine ring, the three successive C atoms between the N atoms are disordered over two sites, with approximate occupancies of 0.753(12) and 0.247(12).

## **Experimental section**

### Materials and methods

All reactions for the preparation of heterocyclic salts (1–3) containing furan, thiophene and pyrrol moieties were carried out under argon in flame-dried glassware using standard Schlenk type flasks. Test reactions for the catalytic activities of catalysts in the Mizoroki–Heck coupling reaction were carried out in air. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Bruker AC300P FT spectrometer operating at 300.13 MHz (<sup>1</sup>H) and 75.47 MHz (<sup>13</sup>C). Chemical shifts ( $\delta$ ) were given in ppm relative to tetramethylsilane, coupling constant (*J*) in Hz. Melting points

Table 2 Hydrogen-bond parameters (Å, °) for C<sub>16</sub>H<sub>21</sub>N<sub>2</sub>S<sub>2</sub>·F<sub>6</sub>P (2b)

	D–H	HA	DA	<i>D</i> –H… <i>A</i>
C8A–H8A2F6 <sup>i</sup>	0.97	2.41	3.264 (8)	146
C10–H10…F4 <sup>ii</sup>	0.93	2.36	3.224 (7)	155
Symmetry codes: (i)	1 - x, 1	-v, 1-z;	(ii) $1 - x, -y$	z, 1 - z

were measured in open capillary tubes with an Electrothermal 9200 melting point apparatus. Elemental analyses were preformed by the TUBITAK Microlab.

General procedure for the preparation of the heteroarylsubstituted heterocyclic salts, 1–3

To a solution of diamine A (15 mmol) in toluene (20 mL), heteroaryl-2-carbaldehyde B (29 mmol) was added slowly at ice bath temperature and the resulting mixture was stirred at 0 °C for 18 h. Then, the solvent was removed in vacuo. The formed Schiff bases C as crude products were crystallized from diethylether/hexane (1:2) at room temperature. To a solution of schiff bases C (24 mmol) in methyl alcohol (40 mL), NaBH<sub>4</sub> (48 mmol) was added slowly at room temperature and the resulting mixture was stirred for 24 h. Then, the solvent was removed in vacuo, and the obtained heteroaryl-substituted diamines D as product were crystallized from a mixture of dichloromethane/diethylether (1:1). Ammonium hexafluorophosphate (NH<sub>4</sub>PF<sub>6</sub>) (1.0 mmol) was added to a solution of heteroaryl-substituted diamine **D** (1.0 mmol) in CH(OEt)<sub>3</sub> (5 mL) and the reaction mixture was heated for 12 h at 80 °C. A solid was precipitated. Then, the precipitated heteroaryl-substituted heterocyclic salts E were crystallized from ethyl alcohol/diethyl ether (1:2) at room temperature.

1,3-Di(5-methylfurfuryl)imidazolidinium hexafluorophosphate, 1a

Yield: 76 %; m.p.: 30-31 °C; IR: v(C=N): 1,561.17 cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>),  $\delta$  2.26 (s, 6 H, CH<sub>3</sub>); 3.89 (s, 4 H, NCH<sub>2</sub>CH<sub>2</sub>N); 4.57 (s, 4 H, NCH<sub>2</sub>C<sub>4</sub>H<sub>2</sub>OCH<sub>3</sub>); 5.89, 6.61 (d, 4 H, J 2.9 Hz, J 3.0 Hz, NCH<sub>2</sub>C<sub>4</sub>H<sub>2</sub>OCH<sub>3</sub>);

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8.00 (s, 1 H, 2-CH). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>),  $\delta$  13.5 (CH<sub>3</sub>); 44.7 (NCH<sub>2</sub>CH<sub>2</sub>N); 48.3 (NCH<sub>2</sub>C<sub>4</sub>H<sub>2</sub>OCH<sub>3</sub>); 106.7, 112.4, 143.9 and 153.9 (NCH<sub>2</sub>C<sub>4</sub>H<sub>2</sub>OCH<sub>3</sub>); 156.7 (2-CH). Anal. Calcd. for C<sub>15</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>PF<sub>6</sub>: C, 44.56; H, 4.74; N, 6.93. Found: C, 44.48; H, 4.79; N, 6.95 %.

1,3-Di(5-methylthiophen-2-ylmethyl)imidazolidinium hexafluorophosphate, 1b

Yield: 83 %; m.p.: 159–160 °C; IR:  $\nu$ (C=N): 1,525.26 cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13 MHz, DMSO),  $\delta$  2.44 (s, 6 H, CH<sub>3</sub>); 3.78 (s, 4 H, NCH<sub>2</sub>CH<sub>2</sub>N); 4.79 (s,4 H, NCH<sub>2</sub>C<sub>4</sub>H<sub>2</sub>SCH<sub>3</sub>); 6.75–6.99 (m, 4 H, thiophene-*H*); 8.67 (s, 1 H, 2-CH). <sup>13</sup>C NMR (75.47 MHz, DMSO),  $\delta$  15.5 (CH<sub>3</sub>); 45.9 (NCH<sub>2</sub>CH<sub>2</sub>N); 48.0 (NCH<sub>2</sub>C<sub>4</sub>H<sub>2</sub>SCH<sub>3</sub>); 126.1, 129.5, 133.4 and 141.6 (thiophene-*C*); 157.4 (2-CH). Anal. Calcd. for C<sub>15</sub>H<sub>19</sub>N<sub>2</sub>S<sub>2</sub>PF<sub>6</sub>: C, 41.28; H, 4.39; N, 6.42. Found: C, 41.36; H, 4.28; N, 6.39 %.

1,3-Di(*N*-methylpyrrol-2-ylmethyl)imidazolidinium hexafluorophosphate, 1c

Yield: 80 %; m.p.: 103–104 °C; IR:  $\nu$ (C=N): 1,547.70 cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>),  $\delta$  3.62 (s, 6 H, CH<sub>3</sub>); 3.80 (s, 4 H, NCH<sub>2</sub>CH<sub>2</sub>N); 4.66 (s, 4 H, CH<sub>2</sub>-C<sub>4</sub>H<sub>3</sub>NCH<sub>3</sub>); 6.07–6.68 (m, 6 H, pyrrol-*H*); 8.01 (s, 1 H, 2-CH). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>),  $\delta$  33.7 (CH<sub>3</sub>); 43.7 (NCH<sub>2</sub>CH<sub>2</sub>N); 47.7 (NCH<sub>2</sub>C<sub>4</sub>H<sub>3</sub>NCH<sub>3</sub>); 107.6, 111.8, 122.2 and 124.9 (pyrrol-*C*); 155.8 (2-CH). Anal. Calcd. for C<sub>15</sub>H<sub>21</sub>N<sub>4</sub>PF<sub>6</sub>: C, 44.78; H, 5.26; N, 13.93. Found: C, 44.66; H, 5.35; N, 13.91 %.

1,3-Di(5-methylfurfuryl)pyrimidinium hexafluorophosphate, 2a

Yield: 85 %; m.p.: 170–171 °C; IR:  $\nu$ (C=N): 1,561.53 cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>),  $\delta$  2.09 (p, 2 H, *J* 5.9 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 2.29 (s, 6 H, CH<sub>3</sub>); 3.39 (t, 4 H, *J* 5.9 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 4.57 (s, 4 H, NCH<sub>2</sub>-furan); 5.96–6.42 (m, 4 H, furan-*H*); 7.96 (s, 1 H, 2-CH). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>),  $\delta$  13.4 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 18.6 (CH<sub>3</sub>); 42.5 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 51.5 (NCH<sub>2</sub>-furan); 106.9, 112.8, 144.1 and 152.5 (furan-*C*); 154.0 (2-CH). Anal. Calcd. for C<sub>16</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>PF<sub>6</sub>: C, 45.94; H, 5.06; N, 6.70. Found: C, 45.87; H, 5.13; N, 6.71 %.

1,3-Di(5-methylthiophen-2-ylmethyl)pyrimidinium hexafluorophosphate, 2b

Yield: 78 %; m.p.: 182–183 °C; IR:  $\upsilon$ (C=N): 1,504.49 cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13 MHz, DMSO),  $\delta$  1.88 (p, 2 H, J 5.4 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 2.44 (s, 6 H, CH<sub>3</sub>); 3.26 (t, 4 H, J 5.6 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 4.78 (s, 4 H,

NCH<sub>2</sub>C<sub>4</sub>H<sub>2</sub>SCH<sub>3</sub>); 6.76–7.01 (m, 4 H, thiophene-*H*); 8.75 (s, 1 H, 2-C*H*). <sup>13</sup>C NMR (75.47 MHz, DMSO),  $\delta$  15.5 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 18.8 (*C*H<sub>3</sub>); 40.1 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 52.9 (NCH<sub>2</sub>-thiophene); 106.1, 129.3, 134.1 and 141.6 (thiophene-*C*); 153.1 (2-CH). Anal. Calcd. for C<sub>16</sub>H<sub>21</sub>N<sub>2</sub>. S<sub>2</sub>PF<sub>6</sub>: C, 42.66; H, 4.70; N, 6.22. Found: C, 42.77; H, 4.60; N, 6.26 %.

1,3-Di(*N*-methylpyrrol-2-ylmethyl)pyrimidinium hexafluorophosphate, 2c

Yield: 86 %; m.p.: 120–121 °C; IR:  $\nu$ (C=N): 1,550.04 cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>),  $\delta$  1.91 (p, 2 H, J 5.1 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 3.56 (s, 6 H, CH<sub>3</sub>); 3.21 (t, 4 H, J 6.0 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 4.66 (s, 4 H, CH<sub>2</sub>C<sub>4</sub>-H<sub>3</sub>NCH<sub>3</sub>); 5.98–6.82 (m, 6 H, pyrrol-H); 8.51 (s, 1 H, 2-CH). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>),  $\delta$  18.6 (NCH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>N); 33.9 (CH<sub>3</sub>); 42.3 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 49.9 (CH<sub>2</sub>C<sub>4</sub>H<sub>3</sub>NCH<sub>3</sub>); 107.2, 111.4, 124.2 and 124.9 (pyrrol-C); 152.4 (2-CH). Anal. Calcd. for C<sub>16</sub>H<sub>23</sub>N<sub>4</sub>PF<sub>6</sub>: C, 46.16; H, 5.57; N, 13.46. Found: C, 46.25; H, 5.49; N, 13.47 %.

1,3-Di(5-methylfurfuryl)diazepinium hexafluorophosphate, 3a

Yield: 79 %; m.p.: 110–111 °C; IR:  $\nu$ (C=N): 1,562.31 cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>),  $\delta$  1.96 (p, 4 H, *J* 2.8 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 2.29 (s, 6 H, CH<sub>3</sub>); 3.71 (t, 4 H, *J* 5.7 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 4.56 (s, 4 H, NCH<sub>2</sub>Furan); 5.97 and 6.42 (d, 4 H, *J* 2.2 Hz and *J* 3.1 Hz, furan-*H*); 7.80 (s, 1 H, 2-C*H*). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>),  $\delta$  13.6 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 24.3 (CH<sub>3</sub>); 49.5 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 106.9, 112.6, 144.7 and 153.9 (furan-*C*); 157.7 (2-*C*H). Anal. Calcd. for C<sub>17</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>PF<sub>6</sub>: C, 47.23; H, 5.36; N, 6.48. Found: C, 47.31; H, 5.33; N, 6.48 %.

1,3-Di(5-methylthiophen-2-ylmethyl)diazepinium hexafluorophosphate, 3b

Yield: 75 %; m.p.: 132–133 °C; IR:  $\upsilon$ (C=N): 1,674.01 cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>),  $\delta$  1.93 (p, 4 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 2.45 (s, 6 H, CH<sub>3</sub>); 3.69 (t, 4 H, *J* 5.7 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 4.73 (s, 4 H, NCH<sub>2</sub>-thiophene); 6.63–6.95 (m, 4 H, thiophene-*H*); 7.90 (s, 1 H, 2-C*H*). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>),  $\delta$  15.5 (NCH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 24.5 (*C*H<sub>3</sub>); 49.1 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 56.3 (NCH<sub>2</sub>-thiophene); 125.7, 129.5, 132.7 and 142.4 (thiophene-*C*); 157.1 (2-*CH*). Anal. Calcd. for C<sub>17</sub>H<sub>23</sub>N<sub>2</sub>. S<sub>2</sub>PF<sub>6</sub>: C, 43.96; H, 4.99; N, 6.03. Found: C, 44.05; H, 4.89; N, 6.06 %.

Table 3 Crystal data collection	$\overline{C_{16}H_{21}N_2S_2}\cdot F_6P$	V = 1,024.69 (8) Å <sup>3</sup>
and refinement for $C_1$ , $H_2$ , $N_2$ , $S_2$ , $F_2$ , $P_2$ , $(2h)$	$M_r = 450.46$	Z = 2
$C_{16} C_{16} $	Triclinic, $P - 1$	$D_x = 1.460 \text{ Mg m}^{-3}$
	a = 9.3159 (4) Å	Mo Ka radiation
	b = 10.9300 (5) Å	Cell parameters from 285 reflections
	c = 11.2445 (5) Å	$\theta = 3.2 - 21.4^{\circ}$
	$\alpha = 63.522 \ (2)^{\circ}$	$\mu = 0.39 \text{ mm}^{-1}$
	$\beta = 89.012 \ (2)^{\circ}$	T = 296 (2) K
	$\gamma = 89.691 \ (2)^{\circ}$	Prism, light yellow
	Bruker Kappa APEXII CCD diffractometer	2,892 reflections with $I > 2\sigma$ (I)
	$\omega$ scan	$R_{\rm int} = 0.021$
	Absorption correction: multi-scan (based on symmetry-related measurements)	$\theta_{\rm max} = 25.3^{\circ}$
	$T_{\rm min} = 0.889, T_{\rm max} = 0.913$	$h = -11 \rightarrow 10$
	13,992 measured reflections	$k = -13 \rightarrow 12$
	3,655 independent reflections	$l = -13 \rightarrow 13$
	Refinement on $F^2$	H atoms constrained to parent site
	$R[F^2 > 2\sigma(F^2)] = 0.068$	Calculated weights $w = 1/$ $[\sigma^2(F_o^2) + (0.134P)^2 + 0.7188P]$ where $P = (F_o^2 + F_c^2)/3$
	$wR(F^2) = 0.227$	$(\Delta/\sigma)_{\rm max} < 0.0001$
	S = 1.06	$\Delta  ho_{ m max} = 0.94$ e Å $^{-1}$
	3,655 reflections	$\Delta  ho_{ m min} = -0.42 \ { m e} \ { m \AA}^{-1}$
	274 parameters	Extinction correction: none

1,3-Di(*N*-methylpyrrol-2-ylmethyl)diazepinium hexafluorophosphate, 3c

Yield: 80 %; m.p.: 92–93 °C; IR:  $\nu$ (C=N): 1,585.99 cm<sup>-1</sup>. <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>),  $\delta$  1.94 (p, 4 H, *J* 5.5 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 3.55 (s, 6 H, CH<sub>3</sub>); 3.67 (t, 4 H, *J* 5.4 Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 4.61 (s, 4 H, CH<sub>2</sub>C<sub>4</sub>H<sub>3</sub>. NCH<sub>3</sub>); 6.06–6.67 (m, 6 H, pyrrol-*H*); 7.62 (s, 1 H, 2-CH). <sup>13</sup>C NMR (75.47 MHz, CDCl<sub>3</sub>),  $\delta$  24.5 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>. CH<sub>2</sub>N); 33.8 (CH<sub>3</sub>); 48.6 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 52.7 (CH<sub>2</sub>C<sub>4</sub>H<sub>3</sub>NCH<sub>3</sub>); 107.7, 112.4, 122.9 and 125.2 (Pyrrol- *C*); 156.6 (2-CH). Anal. Calcd. for C<sub>17</sub>H<sub>25</sub>N<sub>4</sub>PF<sub>6</sub>: C, 47.44; H, 5.86; N, 13.02. Found: C, 47.51; H, 5.79; N, 13.00 %.

General procedure for the Mizoroki-Heck coupling reaction

Heterocyclic salts 1–3 (2.0 mmol),  $Pd(OAc)_2$  (1.0 mmol), aryl bromide (1.0 mmol), styrene (1.5 mmol),  $KOBu^t$ (2.0 mmol), H<sub>2</sub>O (3 mL) and DMF (3 mL) were added to a small Schlenk tube and the mixture was heated to 80 °C for 1 h. After the reaction was completed, the mixture was extracted with ethylacetate, and purified by flash chromatography on silica gel. The purity of the compounds was checked by NMR and GC. Yields are based on aryl bromide. X-ray crystallographic studies

A suitable crystal of **2b** for X-ray diffraction was obtained by slow diffusion of dichloromethane into diethylether solutions at room temperature. Data collection: APEX2 [34]; cell refinement: SAINT [34]; data reduction: SAINT [29]. Program(s) used to solve structure: SHELXS97 [35]. Program(s) used to refine structure: SHELXL97 [35]. Molecular graphics: ORTEP-3 for Windows [36] and PLATON [37]. Software used to prepare material for publication: WinGX [38] and PLATON [37]. The data collection, details of the X-ray structure determination and refinement for **2b** are given in Table 3.

## Conclusions

In this work, newly designed heteroaryl-substituted heterocyclic salts were successfully synthesized and fully characterized. Also, using single-crystal X-ray diffraction, we determined the structures in the solid state of compound **2b**. An easy to handle, highly effective and environmentally benign process was developed for palladium-mediated Mizoroki–Heck coupling reactions. In addition, the newly synthesized nine salts were successfully used in this coupling reaction. A significant influence of the reaction temperature and time was observed on the catalytic activity of the synthesized salts. The best results were obtained for the salt 3c while all of the salts were found to be catalytically active.

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CCDC 927101 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

#### References

- 1. B. Cornils, W.A. Herrmann (Eds). Applied homogeneous catalysis with organometallic compounds, vol. 2, (Wiley-VCH Verlag GmbH, Federal Republic of Germany, 2002) (Chapter 3)
- 2. A.M. Rouhi, Chem. Eng. News 82, 49 (2004)
- 3. A.B. Donnay, L.E. Overman, Chem. Rev. 103, 2945 (2003)
- 4. S. Akkoc, Y. Gök, J. Coord. Chem. 66, 1396 (2013)
- 5. A. Aktaş, S. Akkoç, Y. Gök, J. Coord. Chem. 66, 2901 (2013)
- 6. Y. Gök, S. Akkoç, S. Albayrak, M. Akkurt, M.N. Tahir, Appl. Organometal. Chem. (2014). doi:10.1002/aoc.3116
- 7. D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, Chem. Rev. 100, 39 (2000)
- 8. R. Corberán, E. Mas-Marzá, E. Peris, Eur. J. Inorg. Chem. 1700 (2009)
- 9. C. Xu, X.Q. Hao, Z. Li, X.M. Dong, L.M. Duan, Z.Q. Wang et al., Inorg. Chem. Commun. 17, 34 (2012)
- 10. F.E. Hahn, Angew. Chem. Int. Ed. 45, 1348 (2006)
- 11. T.Y. Zhang, H. Zhang, Tetrahedron Lett. 43, 193 (2002)
- 12. J.M. Lu, H. Ma, S.S. Li, D. Ma, L.X. Shao, Tetrahedron 66, 5185 (2010)
- 13. J. Cheng, M.L. Trudell, Org. Lett. 3, 1371 (2001)
- 14. T. Liu, X. Zhao, Q. Shen, L. Lu, Tetrahedron 68, 6535 (2012)

- 15. D. Munz, C. Allolio, K. Döring, A. Poethig, T. Doert, H. Lang et al., Inorg. Chim. Acta 392, 204 (2012)
- 16. V. Farina, Adv. Synth. Catal. 346, 1553 (2004)
- 17. İ. Özdemir, N. Gürbüz, Y. Gök, B. Çetinkaya, Heteroatom Chem. 19, 82 (2008)
- 18. W.A. Herrmann, B. Cornils, W.A. Herrmann, Applied homogeneous catalysis with organometallic compounds (Wiley-VCH, Weinheim, 1996)
- 19. C.S. Lee, Y.B. Lai, W.J. Lin, R.R. Zhuang, W.S. Hwang, J. Organomet. Chem. 724, 235 (2013)
- 20. M. Bagherzadeh, M. Amini, A. Ellero, L.K. Woo, Inorg. Chim. Acta 383, 46 (2012)
- 21. İ. Özdemir, M. Yiğit, E. Cetinkaya, B. Cetinkaya, Appl. Organometal. Chem. 20, 187 (2006)
- 22. B. Çetinkaya, İ. Özdemir, P.H. Dixneuf, J. Organomet. Chem. 534, 153 (1997)
- 23. Y. Kondo, K. Inamoto, M. Uchiyama, T. Sakamoto, Chem. Commun. 2704 (2001)
- 24. M. Yiğit, B. Yiğit, İ. Özdemir, E. Çetinkaya, B. Çetinkaya, Appl. Organomet. Chem. 20, 322 (2006)
- 25. İ. Özdemir, B. Yiğit, B. Çetinkaya, D. Ülkü, M.N. Tahir, C. Arıcı, J. Organomet. Chem. 633, 27 (2001)
- 26. R.D. Savka, H. Plenio, J. Organomet. Chem. 710, 68 (2012)
- 27. P.V. Chouthaiwale, V. Rawat, A. Sudalai, Tetrahedron Lett. 53, 148 (2012)
- 28. M. Yiğit, İ. Özdemir, E. Çetinkaya, B. Çetinkaya, Trans. Met. Chem. 32, 536 (2007)
- 29. D. Cremer, J.A. Pople, J. Am. Chem. Soc. 97, 1354 (1975)
- 30. F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans. 2, 1 (1987)
- 31. C. Li, T.H. Chan, Organic reactions in aqueous media (Wiley, New York, 1997)
- 32. A. Slamani, S. Demir, İ. Özdemir, Catal. Commun. 29, 141 (2012)
- 33. M. Bakherad, A. Keivanloo, B. Bahramian, S. Jajarmi, J. Organomet. Chem. 724, 206 (2013)
- 34. Bruker APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA (2009)
- 35. G.M. Sheldrick, Acta Crystallogr. A64, 112 (2008)
- 36. L.J. Farrugia, J. Appl. Crystallogr 30, 565 (1997)
- 37. A.L. Spek, Acta Crystallogr. D65, 148 (2009)
- 38. L.J. Farrugia, J. Appl. Crystallogr. 32, 837 (1999)