


Cite this: *RSC Adv.*, 2022, 12, 34730

Acidic tributyl phosphonium-based ionic liquid: an efficient catalyst for preparation of diverse pyridine systems *via* a cooperative vinylogous anomeric-based oxidation†

Sepideh Jalali-Mola, Morteza Torabi, Meysam Yarie 
and Mohammad Ali Zolfigol *

In this study, an acidic phosphonium-based ionic liquid, namely tributyl(3-sulfopropyl)phosphonium trifluoroacetate, was designed and synthesized *via* a facile and green route. From an accurate perspective, the structure of the prepared ionic liquid was investigated using FT-IR, ¹H NMR and ¹³C NMR spectroscopies, and EDX, elemental mapping and TGA/DTG analysis. In this intensive research, catalytic application of tributyl(3-sulfopropyl)phosphonium trifluoroacetate was explored for the preparation of diverse pyridine systems such as triaryl pyridines, 2-amino-3-cyanopyridines and indolyl pyridines *via* a cooperative vinylogous anomeric-based oxidation (CVABO). The observed results proved that prepared acidic phosphonium-based ionic liquid is a effective catalyst for the multicomponent synthesis of pyridines.

Received 25th July 2022
Accepted 17th November 2022

DOI: 10.1039/d2ra04631h

rsc.li/rsc-advances

Introduction

Ionic liquids (ILs), as remarkable class of chemical compounds, have attracted a tremendous deal of interest.^{1–3} Many of researchers in modern sciences are engaged in exploration of the exceptional properties of these versatile systems.^{4,5} These materials, due to irreplaceable privileges such as suitable chemical and thermal stability, controlled miscibility, tunability, designability, low vapor pressure, high ionic conductivity, *etc.*, are an integral part of catalysis, biotechnology, medical sciences, energetic materials, separation and extraction processes, electrochemistry, surfactants and functional materials.^{2,6–12} In subsequent and intensive study, acidic ILs have been investigated in catalytic processes such as multicomponent reactions and CO₂ fixation, biomass processing, and electrolytes.^{13,14}

The cationic section of ILs plays a decisive role in viscosity, solubility, melting point, density and other characteristic properties of ionic liquids.¹⁵ Among varied type ILs, phosphonium-based ionic liquid (PILs) are more thermal and chemical stable and less viscous than other ILs.^{16,17} PILs due to environment compatibility, low cost and simplicity of synthesis, have an excellent potential for academic and industrial chemical processes.^{18–26} It goes without saying that there are several

reports for variety applications of PILs. Wittig reagents,²⁶ catalytic applications,²⁷ desulfurization and denitrogenation of liquid fuels,^{18,28} extraction of phenolic compounds from water²⁹ and recovery of metals³⁰ are a selection of applications of PILs. In recent years, catalytic applications of PILs have received much attentions.¹⁶ These systems, have a good catalytic response to multicomponent reactions,¹⁶ CO and CO₂ fixation,^{31–33} Mukaiyama-aldol reaction,³³ hydroformylation acetalization³⁴ and Heck reactions.³⁵ A number of catalytic applications of PILs are shown in Scheme 1.

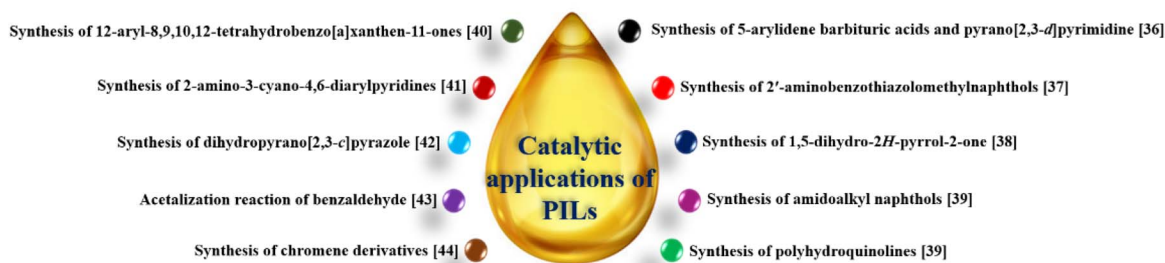
Triaryl pyridines and nicotinonitriles as the most important subunits of pyridine families are ubiquitous subsets of pyridine families.^{36–40} Triaryl pyridines are popular building blocks in supramolecular chemistry,⁴¹ advanced devices as components of OLEDs,⁴² sensors⁴³ and photo sensitizers⁴⁴ and have good medicinal potentials such as antidepressant, anticancer and antimicrobial activities.^{45,46} Noticeably, nicotinonitrile derivatives by pharmaceutical and medicinal functions, have a crucial role and created new insights in the design of anticancer compounds, antihistaminic, antimicrobial and *etc.*^{47–49} Multi-component strategy for the synthesis of pyridine families has a fundamental attitude of synthetic efficiency, utility high atom economy and selectivity.^{50–52} A number of pharmaceutical applications of triaryl pyridines and nicotinonitriles are sketched in Scheme 2.

In this study, we devoted our focus on the design and synthesis of tributyl(3-sulfopropyl)phosphonium trifluoroacetate and its catalytic application in the preparation of triaryl pyridines, indolyl pyridines and nicotinonitriles

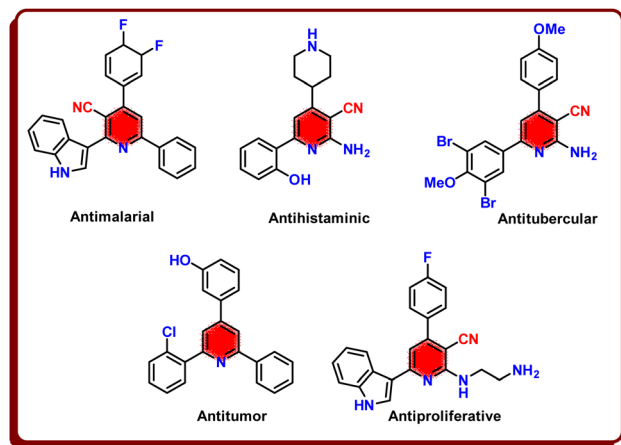
Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran. E-mail: mzolfigol@yahoo.com

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d2ra04631h>





Scheme 1 Catalytic applications of PILs in organic reactions.



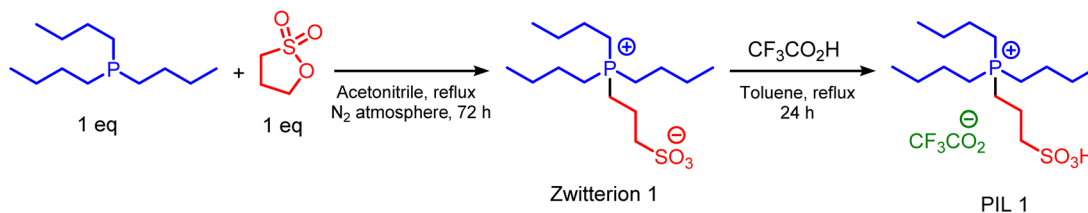
Scheme 2 Selected pharmaceutical applications of triaryl pyridines and nicotinonitriles.

(Schemes 3 and 4). In turn, a cooperative vinylogous anomeric-based oxidation was investigated to justify the mechanism of synthesis of pyridines.^{53–56}

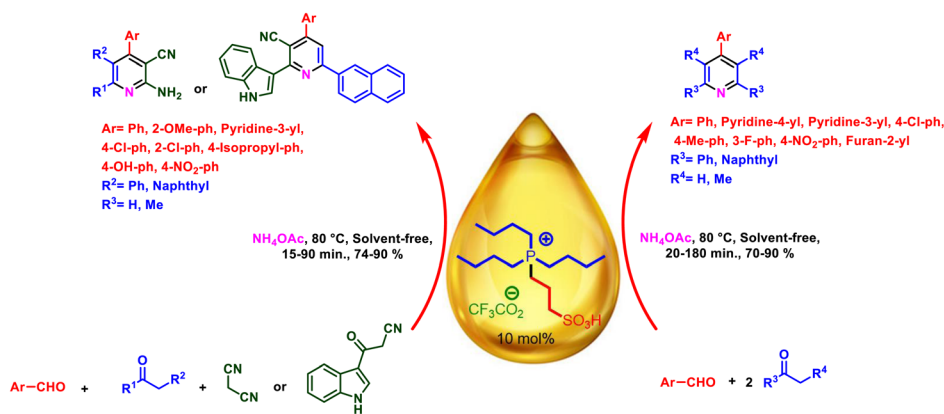
Results and discussion

As it is discussed in detail below, several techniques were applied for determination and characterization of the tributyl(3-sulfopropyl)phosphonium trifluoroacetate.

In FT-IR spectrum of **PIL 1**, emergence of broad pick at 3479 cm^{-1} , indicates the acidic functional group and the stretching band of aliphatic C–H groups are observed at 2966 cm^{-1} . The characteristic peak at 1760 was confirmed the existence of carbonyl group of trifluoroacetate anion. The diagnostic stretching bond of $\text{S}=\text{O}$ was appeared at 1158 cm^{-1} .



Scheme 3 Experimental routes for the synthesis of acidic tributyl phosphonium-based ionic liquid.



Scheme 4 Experimental procedure for the synthesis of triaryl pyridines, indolyl pyridines and nicotinonitriles.

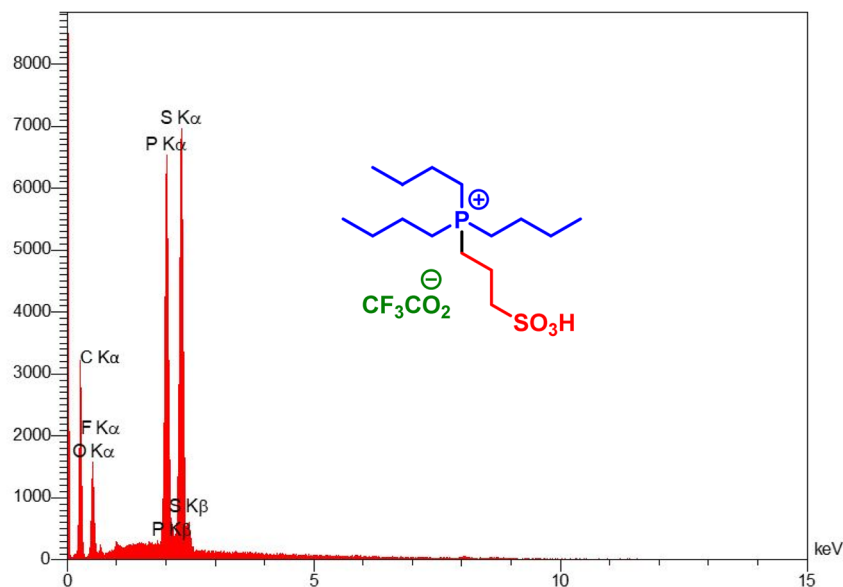


Fig. 1 EDX analysis of PIL 1.

Also, ¹H NMR and ¹³C NMR spectra are well consistent with the structure of the catalyst (see ESI†).

Elemental composition of target catalyst was evaluated by using EDX analysis. According to the observed results, the

expected elements in the structure of tributyl(3-sulfopropyl)phosphonium trifluoroacetate including C, S, P, O and F are approved (Fig. 1). In addition, elemental mapping analysis was used for further confirmation of the obtained data from EDX

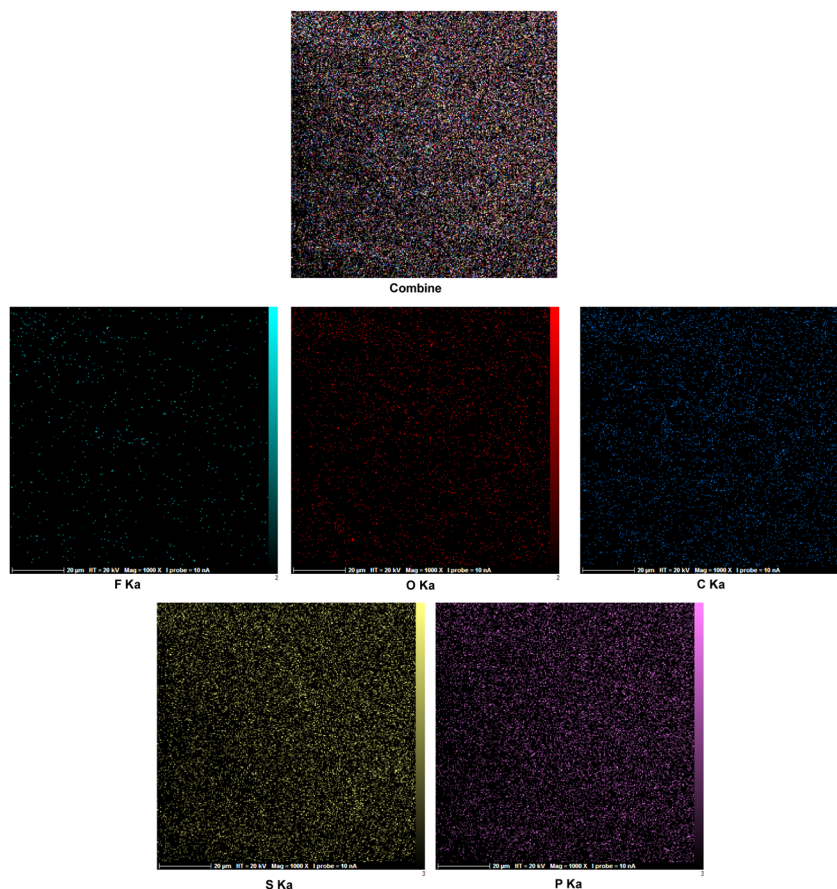


Fig. 2 Elemental mapping analysis of PIL 1.



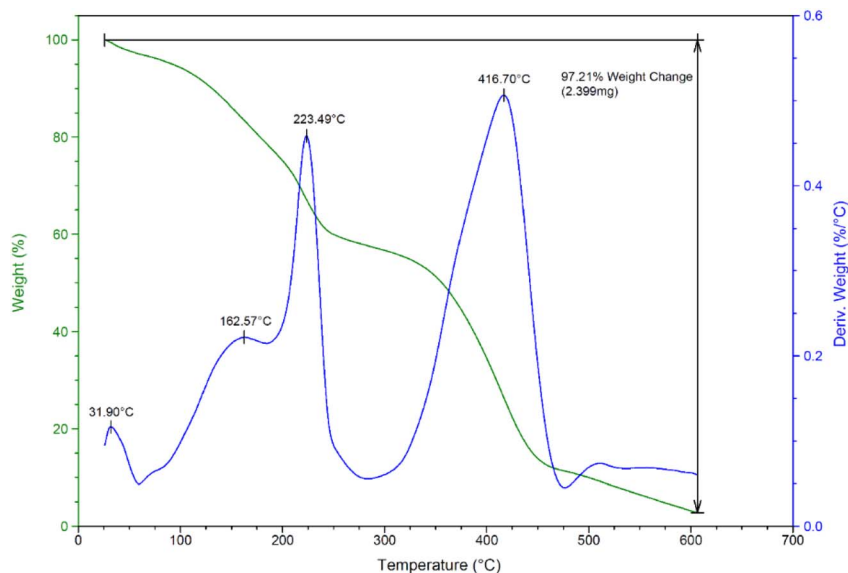


Fig. 3 TGA/DTG curves of PIL 1.

analysis. Also, due to this technique, scattering of elements are well observed (Fig. 2).

Thermogravimetric/differential thermogravimetric analysis displayed that **PIL 1** was stable up to 223 °C. Fiddling weight

loss up to 163 °C is related to the separation of trapped solvents. Also, it seems that the two extreme weight loss respectively in 223 and 416 °C which indicate the decomposition of $-(CH_2)_3-SO_3H$ and butyl chains of the catalyst⁵⁷ (Fig. 3).

Table 1 Optimizing of the reaction conditions for the synthesis of **1j**^a

Entry	Solvent	Temperature (°C)	Catalyst loading (mol%)	Time (min)	Yield ^b (%)
1 ^c	—	80	10	15	85
2	—	80	20	15	85
3	—	80	40	15	75
4	—	80	—	60	45
5	—	90	10	10	85
6	—	70	10	45	62
7	—	60	10	45	56
8	—	40	10	60	Trace
9	—	Room temperature	10	120	Trace
11	H ₂ O	Reflux	20	60	57
12	EtOH	Reflux	20	60	85
13	<i>n</i> -Hexane	Reflux	20	60	75
14	EtOAc	Reflux	20	60	Trace
15	CHCl ₃	Reflux	20	60	80

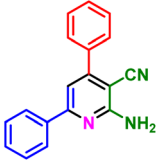
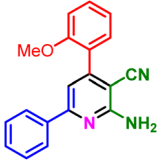
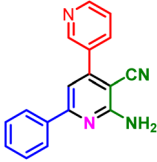
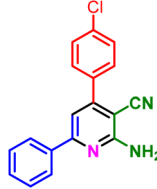
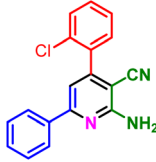
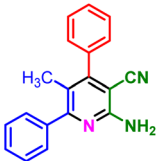
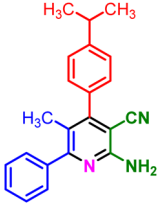
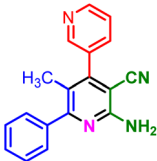
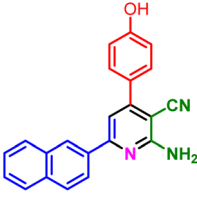
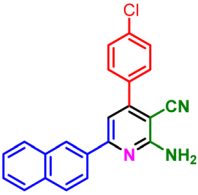
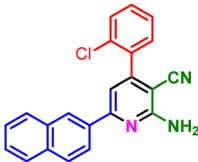
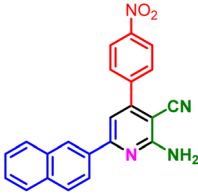
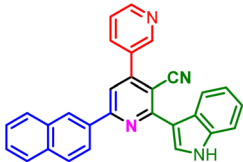
^a Reaction conditions: 4-chlorobenzaldehyde (1 mmol, 0.140 g), 1-(naphthalen-2-yl)ethan-1-one (1 mmol, 0.170 g), malononitrile (1 mmol, 0.066 g) and ammonium acetate (1 mmol, 0.078 g). ^b Related to isolated yields. ^c Data for the model reaction.

In a deliberate study, after characterization of **PIL 1**, its catalytic application was investigated for the synthesis of diverse pyridine systems. In this respect, 4-chlorobenzaldehyde, 1-(naphthalen-2-yl)ethan-1-one, malononitrile and ammonium acetate as typical compounds were selected for the optimization of the reaction conditions. Initially, the role of temperature was examined and several temperatures consist of 40, 60, 70, 80 and 90 °C were exerted for the model reaction. The obtained experimental data proved that 80 °C is the best operational temperature. After that, the reaction was performed in the presence of different solvents including polar (protic and aprotic) and nonpolar solvents. The reaction has a substantial yield by using EtOH and CHCl₃ as solvent. Then, the different amounts of catalyst were used in model reaction that due to the observed results, 10 mol% of catalyst gives the desired product by good yield. As confirmed by the obtained data, the best results for the model reaction achieved by the performing of the reaction in the presence of 10 mol% of catalyst and solvent free conditions at 80 °C (Table 1).

In a discrete study, to expand the substrate scope for the desired molecules, different electron-poor or electron-rich aromatic aldehydes, aromatic ketones, malononitrile or 3-(1*H*-indol-3-yl)-3-oxopropanenitrile have been used. By using malononitrile or 3-(1*H*-indol-3-yl)-3-oxopropanenitrile as starting materials nicotinonitrile derivatives were successfully synthesized (Table 2) and in the same conditions without malononitrile or 3-(1*H*-indol-3-yl)-3-oxopropanenitrile and by using 2 equivalents of ketones triaryl pyridine derivatives were achieved (Table 3).

The plausible mechanistic route for the synthesis of nicotinonitrile derivatives is revealed in Scheme 5. Firstly, activated 1-(naphthalen-2-yl)ethan-1-one by catalyst was reacted by ammonia (from NH₄OAc) and leads to imine intermediate. Likewise, Knoevenagel intermediate was achieved by reaction of 4-chlorobenzaldehyde and malononitrile. In the second step, these two intermediates were reacted with each other to produce intermediate **a**. Then, through an intermolecular cyclization and subsequent tautomerization processes, the intermediate **d** was produced. After that, in the key step, with the participation of a cooperative vinylogous anomeric-based

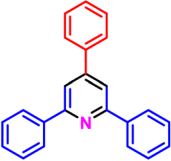
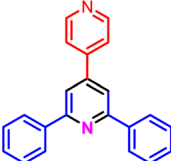
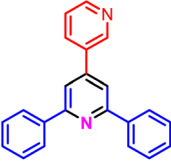
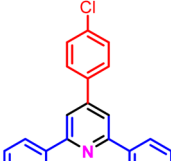
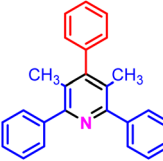
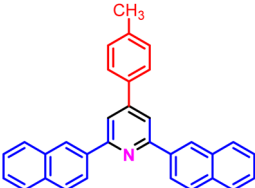
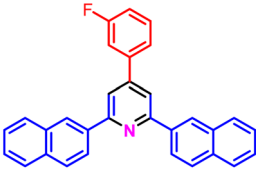
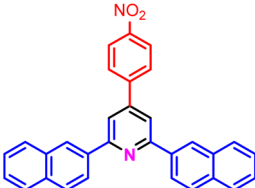
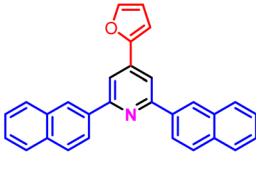
Table 2 Synthesis of nicotinonitrile derivatives in the presence of **PIL 1** as catalyst^a

 <p>1a, 30 min, 80% MP: 179–181 °C [180]⁵⁶ White solid</p>	 <p>1b, 15 min, 85% MP: 195–197 °C [198–201]⁵⁸ White solid</p>	 <p>1c, 30 min, 80% MP: 199–202 °C [206–210]⁵⁹ Yellow solid</p>	 <p>1d, 80 min, 85% MP: 198–202 °C [188–190]⁵⁸ White solid</p>	 <p>1e, 90 min, 88% MP: 184–186 °C [192]⁵⁶ White solid</p>
 <p>1f, 25 min, 75% MP: 198–202 °C [205]⁵⁶ White solid</p>	 <p>1g, 15 min, 75% MP: 239–241 °C [New] White solid</p>	 <p>1h, 25 min, 82% MP: 221–223 °C [>300]⁵⁶ Yellow solid</p>	 <p>1i, 15 min, 80% MP: 265–267 °C [New] White solid</p>	
 <p>1j, 15 min, 85% MP: 205–208 °C [218–220]⁵⁹ White solid</p>	 <p>1k, 15 min, 75% MP: 166–170 °C [New] White solid</p>	 <p>1l, 20 min, 90% MP: 193–196 °C [204–206]⁶⁰ Brown solid</p>	 <p>1m, 45 min, 75% MP: >300 °C [New] Yellow solid</p>	

^a Reaction conditions: 1-(naphthalen-2-yl)ethan-1-one (1 mmol, 0.170 g), malononitrile (1 mmol, 0.066 g) or 3-(1*H*-indol-3-yl)-3-oxopropanenitrile (1 mmol, 0.184), ammonium acetate (1 mmol, 0.078 g), aromatic aldehyde (1 mmol), catalyst (10 mol%), solvent-free, 80 °C.



Table 3 Synthesis of triaryl pyridines by using PIL 1 as a catalyst^a

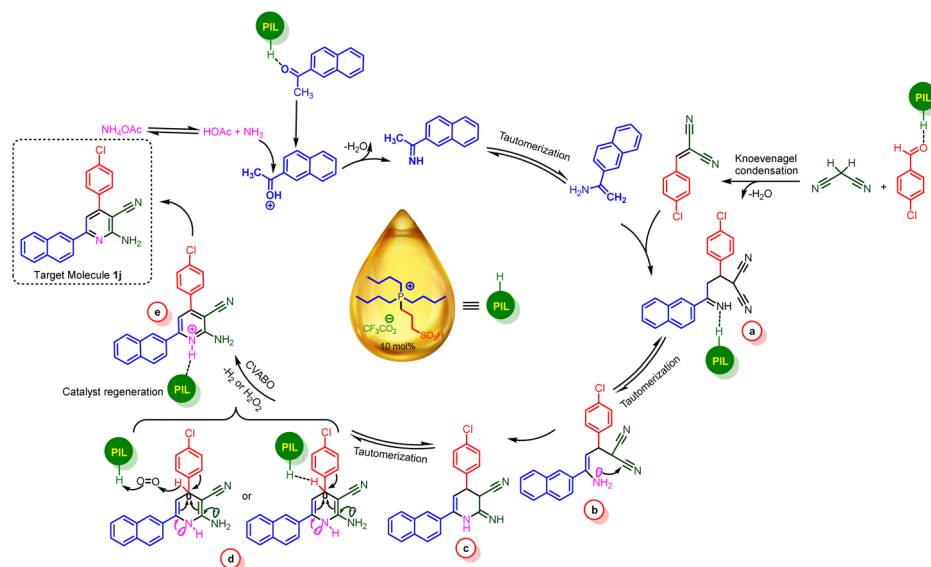
				
2a , 180 min, 75% MP: 117–120 °C [136–138] ⁶¹ White solid	2b , 30 min, 75% MP: 232–236 °C [187–190] ⁶² White solid	2c , 60 min, 70% MP: 140–143 °C [Not reported] ⁶³ White solid	2d , 180 min, 83% MP: 112–116 °C [133–135] ⁶⁴ White solid	2e , 45 min, 70% MP: 125–127 °C [130–133] ⁶⁵ White solid
				
2f , 120 min, 75% MP: 150–154 °C [Not reported] ⁶⁶ White solid	2g , 120 min, 80% MP: 149–152 °C [New] White solid	2i , 20 min, 90% MP: 193–196 °C [231–233] ⁶⁶ Brown solid	2j , 30 min, 72% MP: 215–217 °C [220–221] ⁶⁷ Brown solid	

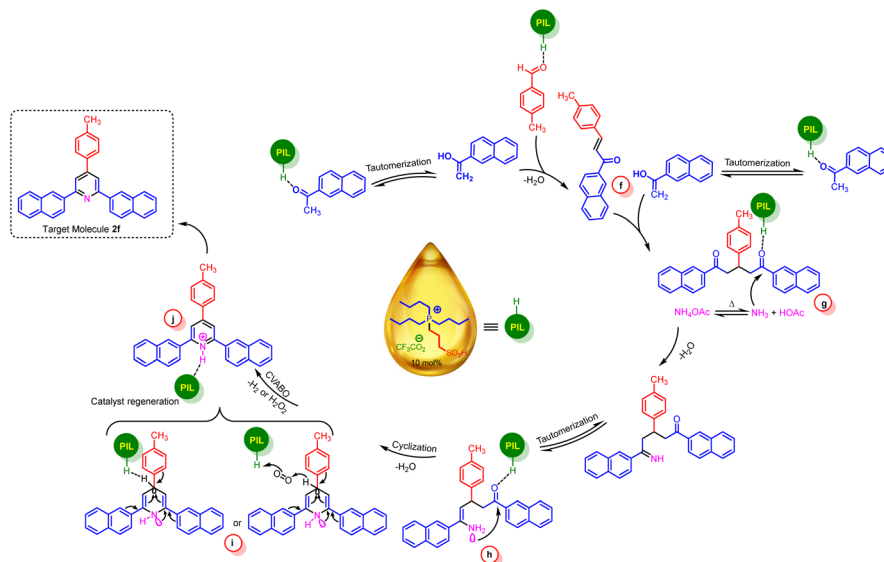
^a Reaction conditions: 1-(naphthalen-2-yl)ethan-1-one (2 mmol, 0.340 g), ammonium acetate (1 mmol, 0.078 g), aromatic aldehyde (1 mmol), catalyst (10 mol%), solvent-free, 80 °C.

oxidation and releasing of H₂O₂ in air condition or releasing of H₂ under inert atmosphere (N₂ or argon), dihydropyridine structure is oxidized to target pyridine product.

Similarly, we suggested a plausible mechanism for the synthesis of triaryl pyridine systems (Scheme 6). At the first step, 1-(naphthalen-2-yl)ethan-1-one was activated by catalyst and converted to enolic form and reacted by 4-methylbenzaldehyde that leads to intermediate **f**. Then, due to Michael addition of enolic form of ketone to intermediate **f**,

intermediate **g** was produced. In the next step, ammonia attacked to intermediate **g** and by removing one molecule of H₂O and tautomerization processes, the enamine **h** is produced. After this, by intermolecular cyclization reaction and removing of H₂O, dihydropyridine intermediate was achieved. Finally, CVABO leads to removing of H₂O₂ under air condition or H₂ in inert atmosphere and desired target molecule was produced.

Scheme 5 Plausible mechanism for the synthesis of **1j** by using PIL 1 as catalyst.



Scheme 6 Plausible mechanism for the synthesis of **2f** in the presence of **PIL 1**.

Experimental section

General experimental procedure for the synthesis of **PIL 1**

At the first, zwitterion **1** was synthesized according to the reported procedure.¹⁵ Hereupon, tributyl phosphine (5 mmol, 1.01 g), 1,2-oxathiolane 2,2-dioxide (5 mmol, 0.61 g) and acetonitrile as solvent were successively added into a 50 mL round-bottomed flask and refluxed under N₂ atmosphere for 72 h. After completing of the reaction, the solvent was removed and the remained oil was washed with diethyl ether to gives the oily product. In the second step, zwitterion **1** (5 mmol, 1.62 g) and trifluoro acetic acid (5 mmol, 0.57 g) and 30 mL of toluene as catalyst were added into a 50 mL round-bottomed flask and the mixture of reaction was refluxed at 110 °C for 24 h. After that, the oily product was separated from solvent by using extraction with *n*-hexane to gives **PIL 1** as desired product.

Experimental route for the synthesis of nicotinonitrile derivatives

Aromatic aldehyde derivatives (1 mmol), malononitrile (1 mmol, 0.066 g) or 3-(1*H*-indol-3-yl)-3-oxopropanenitrile (1 mmol, 0.184), 1-(naphthalen-2-yl)ethan-1-one (1 mmol, 0.170 g), ammonium acetate (1 mmol, 0.078 g) and 10 mol% of **PIL 1** were charged into a 10 mL round-bottomed flask. The mixture of reaction was stirred at 80 °C. After completing of each of reactions as indicated by TLC technique (*n*-hexane/ethylacetate, 6/4), 10 mL of H₂O was poured into the mixture of reaction to separate the catalyst. After that, hot EtOH was added to the mixture of reaction and remained solid washed three times and dried at 80 °C to give pure products.

General experimental procedure for the synthesis of triaryl pyridine derivatives

Aromatic aldehydes (1 mmol), 1-(naphthalen-2-yl)ethan-1-one (2 mmol, 0.340 g), ammonium acetate (1 mmol, 0.078 g) and

10 mol% of **PIL 1** were added into a 10 mL round-bottomed flask and reacted at 80 °C. Then, reaction progress was checked by TLC techniques (*n*-hexane/ethylacetate, 6/4). After completing of reaction, 10 mL of H₂O was added to the flask and the catalyst was separated. After that, the remained solid was washed with hot EtOH and dried at 80 °C to gives a pure product.

Spectral data

Tributyl(3-sulfopropyl)phosphonium trifluoroacetate **PIL 1**.

FT-IR (KBr, ν , cm⁻¹): 3479, 2966, 1760, 1467, 1157, 1038. ¹H NMR (301 MHz, DMSO-d₆) δ_{ppm} 5.04 (s, 1H), 2.61 (t, *J* = 7.0 Hz, 2H), 2.52–2.36 (m, 2H), 2.33–2.17 (m, 6H), 1.95–1.72 (m, 2H), 1.63–1.39 (m, 12H), 0.98 (t, *J* = 7.2 Hz, 9H). ¹³C NMR (76 MHz, DMSO-d₆) δ_{ppm} 159.5, 159.0, 158.5, 158.0, 121.1, 117.3, 113.5, 109.7, 51.4, 23.8, 23.6, 23.1, 23.0, 18.1, 17.4, 13.4.

2-Amino-4-(2-methoxyphenyl)-6-phenylnicotinonitrile (**1b**).

Mp = 195–197 °C. FT-IR (KBr, ν , cm⁻¹): 3482, 3342, 2226, 1622, 1583. ¹H NMR (301 MHz, DMSO-d₆) δ_{ppm} 8.12–8.09 (m, 2H, aromatic), 7.51–7.49 (3, 4H, aromatic), 7.37 (dd, *J* = 9, 1.8 Hz, 1H, aromatic), 7.23–7.11 (m, 2H, aromatic), 7.14–7.08 (m, 1H, aromatic), 6.94 (s, 2H, NH₂), 3.82 (s, 3H, CH₃). ¹³C NMR (76 MHz, DMSO-d₆) δ_{ppm} 160.6, 158.8, 156.5, 153.4, 138.1, 131.4, 130.5, 130.5, 129.2, 127.6, 126.6, 121.1, 117.2, 112.2, 110.7, 89.6, 56.0.

2'-Amino-6'-phenyl-[3,4'-bipyridine]-3'-carbonitrile (**1c**).

Mp = 199–202 °C. FT-IR (KBr, ν , cm⁻¹): 3465, 3311, 2205, 1635, 1582, 1483. ¹H NMR (301 MHz, DMSO-d₆) δ_{ppm} 8.90 (dd, *J* = 3, 0.9 Hz, 1H, aromatic), 8.76 (dd, *J* = 4.9, 1.6 Hz, 1H, aromatic), 8.19–8.13 (m, 3H, aromatic), 7.64–7.60 (m, 1H, aromatic), 7.53–7.51 (m, 3H, aromatic), 7.40 (s, 1H, aromatic), 7.16 (s, 2H, NH₂). ¹³C NMR (76 MHz, DMSO-d₆) δ_{ppm} 161.3, 159.4, 152.2, 150.9, 149.2, 137.9, 136.6, 133.3, 130.7, 129.2, 127.8, 124.1, 117.3, 109.8, 87.1.

2-Amino-4-(4-chlorophenyl)-6-phenylnicotinonitrile (**1d**).

Mp = 198–202 °C. FT-IR (KBr, ν , cm⁻¹): 3486, 3362, 2215, 1630,



2215, 1630, 1573, 1546. ^1H NMR (301 MHz, DMSO-d_6) δ_{ppm} 8.15 (dd, $J = 6.7, 3.0$ Hz, 2H, aromatic), 7.74 (d, $J = 6$ Hz, 2H, aromatic), 7.65 (d, $J = 6$ Hz, 2H, aromatic), 7.53–7.50 (m, 3H, aromatic), 7.31 (s, 1H, aromatic), 7.11 (s, 2H, NH_2). ^{13}C NMR (76 MHz, DMSO-d_6) δ_{ppm} 161.3, 159.2, 154.1, 137.9, 136.3, 135.0, 130.8, 130.7, 129.3, 129.1, 127.8, 117.4, 109.6, 86.9.

2-Amino-4-(2-chlorophenyl)-6-phenylnicotinonitrile (1e). Mp = 184–186 °C. FT-IR (KBr, ν , cm^{-1}): 3489, 3344, 2229, 1596, 1622, 1478. ^1H NMR (301 MHz, DMSO-d_6) δ_{ppm} 8.15–8.12 (m, 2H, aromatic), 7.69–7.66 (m, 1H, aromatic), 7.58–7.49 (m, 6H, aromatic), 7.24 (s, 1H, aromatic), 7.15 (s, 2H, NH_2). ^{13}C NMR (76 MHz, DMSO-d_6) δ_{ppm} 160.6, 159.1, 153.6, 137.8, 136.7, 131.7, 131.4, 131.2, 130.7, 130.2, 129.2, 128.0, 127.7, 116.6, 110.2, 88.9.

2-Amino-5-methyl-4,6-diphenylnicotinonitrile (1f). Mp = 198–202 °C. ^1H NMR (301 MHz, DMSO-d_6) δ_{ppm} 7.56–7.38 (m, 10H, aromatic), 6.79 (s, 2H, NH_2), 1.84 (s, 3H, CH_3). ^{13}C NMR (76 MHz, DMSO-d_6) δ_{ppm} 161.9, 158.5, 155.7, 140.5, 137.6, 129.3, 129.2, 129.1, 128.9, 128.8, 128.4, 117.1, 117.1, 89.6, 17.2.

2-Amino-4-(4-isopropylphenyl)-5-methyl-6-phenylnicotinonitrile (1g). Mp = 239–241 °C. FT-IR (KBr, ν , cm^{-1}): 3429, 3307, 2211, 1646, 1584. ^1H NMR (301 MHz, DMSO-d_6) δ_{ppm} 7.50–7.32 (m, 9H), 7.24–7.21 (m, 2H), 2.92 (hept, $J = 7.0$ Hz, 1H), 1.54 (s, 3H), 1.23 (d, $J = 7.0$ Hz, 6H). ESI-MS (m/z) = calcd for $\text{C}_{22}\text{H}_{21}\text{N}_3$ (M^+) 327.43, found: 328.024.

2'-Amino-5'-methyl-6'-phenyl-[3,4'-bipyridine]-3'-carbonitrile (1h). Mp = 221–223 °C. FT-IR (KBr, ν , cm^{-1}): 3466, 3292, 2213, 1634, 1557, 1456. ^1H NMR (301 MHz, DMSO-d_6) δ_{ppm} 8.72 (dd, $J = 6, 1.6$ Hz, 1H, aromatic), 8.66 (d, $J = 2.3$, 1H, aromatic), 7.93 (dt, $J = 9, 3$ Hz, 1H, aromatic), 7.63–7.58 (m, 1H, aromatic), 7.56–7.45 (m, 5H, aromatic), 6.90 (s, 2H, NH_2), 1.87 (s, 3H, CH_3). ^{13}C NMR (76 MHz, DMSO-d_6) δ_{ppm} 162.2, 158.6, 152.3, 150.3, 149.2, 140.2, 136.8, 133.5, 129.3, 129.0, 128.5, 124.1, 117.4, 117.0, 89.5, 17.2.

2-Amino-4-(4-hydroxyphenyl)-6-(naphthalen-2-yl)nicotinonitrile (1i). Mp = 265–267 °C. FT-IR (KBr, ν , cm^{-1}): 3474, 3383, 3055, 1638, 1571. ^1H NMR (301 MHz, DMSO-d_6) δ_{ppm} 10.02 (s, 1H, OH), 8.80–8.72 (m, 1H), 8.29 (dd, $J = 8.7, 1.8$ Hz, 1H), 8.07–7.97 (m, 3H), 7.63–7.58 (m, 4H), 7.44 (s, 1H), 6.99–6.95 (m, 4H). ^{13}C NMR (76 MHz, DMSO-d_6) δ_{ppm} 161.5, 159.4, 158.68, 155.3, 135.6, 134.1, 133.3, 130.4, 129.2, 128.5, 128.0, 128.0, 127.64, 127.47, 127.07, 125.03, 117.97, 115.99, 109.76, 86.78. ESI-MS (m/z) = calcd for $\text{C}_{22}\text{H}_{15}\text{N}_3\text{O}$ (M^+) 337.38, found: 337.969.

2-Amino-4-(2-chlorophenyl)-6-(naphthalen-2-yl)nicotinonitrile (1k). Mp = 206–209 °C. FT-IR (KBr, ν , cm^{-1}): 3493, 3439, 2222, 1622, 1596, 1551. ^1H NMR (301 MHz, DMSO-d_6) δ_{ppm} 8.76 (s, 1H), 8.31 (dd, $J = 9, 3$ Hz, 1H, aromatic), 8.06–7.97 (m, 3H, aromatic), 7.78 (d, $J = 9$ Hz, 2H), 7.67 (d, $J = 6$ Hz, 2H, aromatic), 7.61–7.58 (m, 2H, aromatic), 7.49 (s, 1H, aromatic), 7.16 (s, 2H, NH_2). ^{13}C NMR (76 MHz, DMSO-d_6) δ_{ppm} 161.4, 159.1, 154.2, 136.3, 135.3, 135.0, 134.2, 133.3, 130.8, 129.3, 128.6, 128.1, 127.7, 127.7, 127.1, 125.0, 117.4, 110.0, 87.0. ESI-MS (m/z) = calcd for $\text{C}_{22}\text{H}_{14}\text{ClN}_3$ (M^+) 355.83, found: 355.918.

2'-(1H-Indol-3-yl)-6'-(naphthalen-2-yl)-[3,4'-bipyridine]-3'-carbonitrile (1m). Mp > 300 °C. FT-IR (KBr, ν , cm^{-1}): 3443, 3133, 2223, 1592, 1567, 1531. ^1H NMR (301 MHz, DMSO-d_6) δ_{ppm} 11.91 (s, 1H), 8.98 (s, 1H), 8.54–8.49 (m, 2H), 8.44–8.43 (m, 1H), 8.17–

8.15 (m, 2H), 8.13–8.09 (m, 1H), 8.05–8.01 (m, 1H), 7.89–7.86 (m, 2H), 7.66–7.60 (m, 5H), 7.31–7.28 (m, 2H). ^{13}C NMR (76 MHz, DMSO-d_6) δ_{ppm} 158.6, 157.9, 155.6, 137.4, 136.9, 135.4, 134.3, 133.5, 130.2, 129.5, 129.4, 129.2, 129.1, 128.1, 128.0, 127.3, 126.6, 124.9, 122.9, 121.8, 121.3, 119.4, 117.2, 113.5, 112.6, 102.0. (m/z) = calcd for $\text{C}_{29}\text{H}_{18}\text{N}_4$ (M^+) 422.49, found: 423.100.

2,4,6-Triphenylpyridine (2a). Mp = 117–120 °C. FT-IR (KBr, ν , cm^{-1}): 3063, 1692, 1578, 1548, 1494. ^1H NMR (301 MHz, DMSO-d_6) δ_{ppm} 8.38–8.34 (m, 4H, aromatic), 8.20 (s, 2H, aromatic), 8.07–8.04 (m, 2H, aromatic), 7.62–7.47 (m, 9H, aromatic). ^{13}C NMR (76 MHz, DMSO-d_6) δ_{ppm} 157.0, 150.1, 139.3, 138.2, 129.8, 129.7, 129.6, 129.2, 127.8, 127.5, 117.1.

4-(4-Chlorophenyl)-2,6-diphenylpyridine (2d). Mp = 112–116 °C. FT-IR (KBr, ν , cm^{-1}): 3067, 1601, 1544, 1491, 1384. ^1H NMR (301 MHz, DMSO-d_6) δ_{ppm} 8.37–8.33 (m, 4H, aromatic), 8.21 (s, 2H, aromatic), 8.11 (d, $J = 9$ Hz, 2H, aromatic), 7.64–7.49 (m, 8H). ^{13}C NMR (76 MHz, DMSO-d_6) δ_{ppm} 157.1, 148.7, 139.2, 137.0, 134.7, 129.8, 129.7, 129.5, 129.2, 127.5, 116.9.

2,6-Di(naphthalen-2-yl)-4-(p-tolyl)pyridine (2f). Mp = 150–154 °C. FT-IR (KBr, ν , cm^{-1}): 2922, 1596, 1544, 818. ^1H NMR (301 MHz, DMSO-d_6) δ_{ppm} 8.98 (d, $J = 1.7$ Hz, 2H, aromatic), 8.61 (dd, $J = 9, 1.8$ Hz, 2H, aromatic), 8.42 (s, 2H, aromatic), 8.18–8.01 (m, 8H, aromatic), 7.64–7.60 (m, 4H, aromatic), 7.45 (d, $J = 6$ Hz, 2H, aromatic), 2.45 (s, 3H, CH_3). ^{13}C NMR (76 MHz, DMSO-d_6) δ_{ppm} 157.0, 150.0, 139.6, 136.8, 135.2, 133.9, 133.7, 130.2, 129.2, 128.7, 128.1, 127.7, 127.2, 126.9, 126.8, 125.3, 117.1, 21.4.

4-(3-Fluorophenyl)-2,6-di(naphthalen-2-yl)pyridine (2g). Mp = 149–152 °C. FT-IR (KBr, ν , cm^{-1}): 3057, 1598, 1551, 1399, 1183. ^1H NMR (301 MHz, DMSO-d_6) δ_{ppm} 9.00 (s, 2H), 8.62 (d, $J = 8.9$ Hz, 2H), 8.47 (s, 2H), 8.17–8.02 (m, 8H), 7.69–7.61 (m, 5H), 7.43 (d, $J = 9.0$ Hz, 1H). ^{13}C NMR (76 MHz, DMSO-d_6) δ_{ppm} 157.1, 148.8, 140.6, 136.5, 133.9, 133.6, 131.6, 131.5, 129.2, 128.7, 128.1, 127.3, 127.0, 126.9, 125.3, 124.1, 117.5, 116.7, 116.5, 115.0, 114.7.

Conclusion

In conclusion, we reported the tributyl(3-sulfoethyl)phosphonium trifluoroacetate as a new phosphonium-based ionic liquid with acidic moiety. The prepared ionic liquid was characterized by using FT-IR, ^1H NMR and ^{13}C NMR spectroscopies, EDX, elemental mapping and TGA/DTG analysis. After that, **PIL 1** has been shown good potential as an efficient catalyst for the multicomponent synthesis of triaryl pyridines, 2-amino-3-cyanopyridines and indolyl pyridine. In this work, we used diverse starting materials such as different ketones and aldehydes that leads to formation of varied pyridine systems. Moreover, most of synthesized pyridine derivatives have a relatively good yields and short reaction times. In a separate study, a plausible mechanism based on a cooperative vinylogous anomeric-based oxidation was suggested for the synthesis of pyridine derivatives.

Conflicts of interest

There are no conflicts to declare.



Acknowledgements

We thank the Bu-Ali Sina University and Iran National Science Foundation [(INSF), Grant Number: 98001912] for financial support to our research group.

References

- 1 S. Zhang, J. Zhang, Y. Zhang and Y. Deng, *Chem. Rev.*, 2017, **117**, 6755.
- 2 K. S. Egorova, E. G. Gordeev and V. P. Ananikov, *Chem. Rev.*, 2017, **117**, 7132.
- 3 B. Wang, L. Qin, T. Mu, Z. Xue and G. Gao, *Chem. Rev.*, 2017, **117**, 7113.
- 4 Z. Lei, B. Chen, Y. M. Koo and D. R. MacFarlane, *Chem. Rev.*, 2017, **117**, 6633.
- 5 F. Ren, J. Wang, F. Xie, K. Zan, S. Wang and S. Wang, *Green Chem.*, 2020, **22**, 2162.
- 6 Y. Tao, R. Dong, I. V. Pavlidis, B. Chen and T. Tan, *Green Chem.*, 2016, **18**, 1240.
- 7 E. Sebastiao, C. Cook, A. Hu and M. Murugesu, *J. Mater. Chem. A*, 2014, **2**, 8153.
- 8 S. K. Singh and A. W. Savoy, *J. Mol. Liq.*, 2020, **297**, 112038.
- 9 P. Sun, S. Zhang, J. Pang, Y. Tan, D. Sun, C. Xia, X. Cheng and X. Xin, *J. Mol. Liq.*, 2018, **272**, 180.
- 10 G. R. Zhang and B. J. Etzold, *J. Energy Chem.*, 2016, **25**, 199.
- 11 A. J. Greer, J. Jacquemin and C. Hardacre, *Molecules*, 2020, **25**, 5207.
- 12 (a) M. Kharazi, J. Saien, M. Yarie and M. A. Zolfigol, *J. Pet. Res.*, 2021, **31**, 113; (b) M. Kharazi, J. Saien, M. Yarie and M. A. Zolfigol, *J. Pet. Sci. Eng.*, 2020, **195**, 107543; (c) M. Kharazi, J. Saien, M. Yarie and M. A. Zolfigol, *J. Mol. Liq.*, 2019, **296**, 111748; (d) J. Saien, M. Kharazi, M. Yarie and M. A. Zolfigol, *Ind. Eng. Chem. Res.*, 2019, **58**, 3583.
- 13 A. S. Amarasekara, *Chem. Rev.*, 2016, **116**, 6133.
- 14 T. Wang, D. Zheng, J. Zhang, B. Fan, Y. Ma, T. Ren, L. Wang and J. Zhang, *ACS Sustainable Chem. Eng.*, 2018, **6**, 2574.
- 15 (a) D. Dupont, S. Raiguel and K. Binnemans, *Chem. Commun.*, 2015, **51**, 9006–9009; (b) M. Chen, B. T. White, C. R. Kasprzak and T. E. Long, *Eur. Polym. J.*, 2018, **108**, 28.
- 16 S. Khazalpour, M. Yarie, E. Kianpour, A. Amani, S. Asadabadi, J. Y. Seyf, M. Rezaeivala, S. Azizian and M. A. Zolfigol, *J. Iran. Chem. Soc.*, 2020, **17**, 1775.
- 17 D. Wei-Li, J. Bi, L. Sheng-Lian, L. Xu-Biao, T. Xin-Man and A. Chak-Tong, *Appl. Catal., A*, 2014, **470**, 183.
- 18 E. Kianpour, S. Azizian, M. Yarie, M. A. Zolfigol and M. Bayat, *Chem. Eng. J.*, 2016, **295**, 500.
- 19 N. Noroozi-Shad, M. Gholizadeh and H. Sabet-Sarvestani, *J. Mol. Struct.*, 2022, **1257**, 132628.
- 20 H. Shirota, K. Takahashi, M. Ando and S. Kakinuma, *J. Chem. Eng. Data*, 2019, **64**, 4701.
- 21 K. J. Fraser and D. R. MacFarlane, *Aust. J. Chem.*, 2009, **62**, 309.
- 22 J. Chen, M. Li, M. Li, X. Lin and T. Qiu, *ACS Sustainable Chem. Eng.*, 2020, **8**, 6956.
- 23 M. Stalpaert, N. Peeters and D. De Vos, *Catal. Sci. Technol.*, 2018, **8**, 1468.
- 24 A. H. T. Hang, T. L. H. Nguyen, D. K. N. Chau and P. H. Tran, *RSC Adv.*, 2018, **8**, 11834.
- 25 M. Chen, B. T. White, C. R. Kasprzak and T. E. Long, *Eur. Polym. J.*, 2018, **108**, 28.
- 26 (a) H. B. Phan, Q. B. T. Nguyen, C. M. Luong, K. N. Tran and P. H. Tran, *Mol. Catal.*, 2021, **503**, 111428; (b) H. B. Phan, C. M. Luong, L. P. Nguyen, B. T. Bui, H. T. Nguyen, B. V. Mai and P. H. Tran, *ACS Sustainable Chem. Eng.*, 2022, **10**, 8673; (c) D. S. Firaha, A. V. Gibalova and O. Holloczki, *ACS Omega*, 2017, **2**, 2901.
- 27 M. Stalpaert, K. Janssens, C. Marquez, M. Henrion, A. L. Bugaev, A. V. Soldatov and D. De Vos, *ACS Catal.*, 2020, **10**, 9401.
- 28 (a) E. Mosayebi, S. Azizian, M. Yarie and M. A. Zolfigol, *J. Mol. Liq.*, 2021, **326**, 115326; (b) F. R. Moghadam, E. Kianpour, S. Azizian, M. Yarie and M. A. Zolfigol, *R. Soc. Open Sci.*, 2020, **7**, 200803; (c) F. R. Oghadam, S. Azizian, M. Bayat, M. Yarie, E. Kianpour and M. A. Zolfigol, *Fuel*, 2017, **208**, 214; (d) F. R. Moghadam, S. Azizian, E. Kianpour, M. Yarie, M. Bayat and M. A. Zolfigol, *Chem. Eng. J.*, 2017, **309**, 480.
- 29 E. Skoronski, M. Fernandes, F. J. Malaret and J. P. Hallett, *Sep. Purif. Technol.*, 2020, **248**, 117069.
- 30 H. Mahandra, F. Faraji and A. Ghahreman, *Sustain. Chem. Eng.*, 2021, **9**, 8179.
- 31 J. Steinbauer, C. Kubis, R. Ludwig and T. Werner, *ACS Sustainable Chem. Eng.*, 2018, **6**, 10778.
- 32 F. Liu, Y. Gu, H. Xin, P. Zhao, J. Gao and M. Liu, *ACS Sustainable Chem. Eng.*, 2019, **7**, 16674.
- 33 T. Werner, *Adv. Syn. Catal.*, 2009, **351**, 1469.
- 34 P. Wang, X. Chen, D. L. Wang, Y. Q. Li and Y. Liu, *Green Energy Environ.*, 2017, **2**, 419.
- 35 D. Rauber, F. Philippi and R. Hempelmann, *J. Fluorine Chem.*, 2017, **200**, 115.
- 36 C. Allais, J. M. Grassot, J. Rodriguez and T. Constantieux, *Chem. Rev.*, 2014, **114**, 10829.
- 37 J. A. Bull, J. J. Mousseau, G. Pelletier and A. B. Charette, *Chem. Rev.*, 2012, **112**, 2642.
- 38 J. S. Carey, D. Laffan, C. Thomson and M. T. Williams, *Org. Biomol. Chem.*, 2006, **4**, 2337.
- 39 R. S. Rohokale, B. Koenig and D. D. Dhavale, *J. Org. Chem.*, 2016, **81**, 7121.
- 40 M. Torabi, M. Yarie, S. Baghery and M. A. Zolfigol, *Recent advances in catalytic synthesis of pyridine derivatives*, Elsevier Inc., 2023, pp. 503–580, ISBN: 978-0-323-91221-1.
- 41 Z. Zarnegar, J. Safari and M. Borjian-Borujeni, *Chem. Heterocycl. Compd.*, 2015, **50**, 1683.
- 42 L. F. B. Fontes, R. N. da Silva, A. M. S. Silva and S. Guieu, *ChemPhotoChem*, 2020, **4**, 5312.
- 43 A. G. Fang, J. V. Mello and N. S. Finney, *Tetrahedron*, 2004, **60**, 11075.
- 44 M. K. Dhinakaran and T. M. Das, *Org. Biomol. Chem.*, 2012, **10**, 2077.
- 45 D. Ashok, M. R. Reddy, R. Dharavath, N. Nagaraju, K. Ramakrishna, S. Gundu and M. Sarasija, *J. Chem. Sci.*, 2021, **133**, 1.



- 46 P. Thapa, R. Karki, M. Yun, T. M. Kadayat, E. Lee, H. B. Kwon, Y. Na, W. J. Cho, N. D. Kim, B. S. Jeong, Y. Kwon and E. S. Lee, *Eur. J. Med. Chem.*, 2012, **52**, 123.
- 47 H. Tao, J. Wang, W. Lu, R. Zhang, Y. Xie, Y. C. Liu, R. Liu, L. Yue, K. Chen, H. Jiang, Y. Zhang, X. Xu and C. Luo, *RSC Adv.*, 2019, **9**, 4917.
- 48 C. S. Challa, N. K. Katari, V. Nallanchakravarthula, D. Nayakanti, R. Kapavarapu and M. Pal, *J. Mol. Struct.*, 2021, **1240**, 130541.
- 49 S. B. Goud, *Org. Biomol. Chem.*, 2022, **20**, 352.
- 50 B. H. Rotstein, S. Zaretsky, V. Rai and A. K. Yudin, *Chem. Rev.*, 2014, **114**, 8323.
- 51 T. M. Shaikh, S. Nagarajan and E. Kandasamy, *Curr. Organocatal.*, 2020, **7**, 96.
- 52 B. B. Tour and D. G. Hall, *Chem. Rev.*, 2009, **109**, 4439.
- 53 (a) F. Karimi, M. Yarie and M. A. Zolfigol, *Mol. Catal.*, 2020, **489**, 110924; (b) M. Torabi, M. Yarie, M. A. Zolfigol, S. Azizian and Y. Gu, *RSC Adv.*, 2022, **12**, 8804; (c) P. Ghasemi, M. Yarie, M. A. Zolfigol, A. Taherpour and M. Torabi, *ACS Omega*, 2020, **5**, 3207; (d) F. Karimi, M. Yarie and M. A. Zolfigol, *RSC Adv.*, 2020, **10**, 25828; (e) M. Dashteh, M. A. Zolfigol, A. Khazaei, S. Bagheri, M. Yarie, S. Makhdoomi and M. Safaiee, *RSC Adv.*, 2020, **10**, 27824; (f) F. Karimi, M. Yarie and M. A. Zolfigol, *Mol. Catal.*, 2019, **463**, 20; (g) M. Torabi, M. Yarie, M. A. Zolfigol, S. Rouhani, S. Azizi, T. O. Olomola, M. Maaza and T. A. M. Msagati, *RSC Adv.*, 2020, **11**, 3143; (h) N. Zarei, M. Torabi, M. Yarie and M. A. Zolfigol, *Polycyclic Aromat. Compd.*, 2022, **1**, DOI: [10.1080/10406638.2022.2061531](https://doi.org/10.1080/10406638.2022.2061531).
- 54 (a) M. Yarie, *Iran. J. Catal.*, 2017, **7**, 85; (b) M. Yarie, *Iran. J. Catal.*, 2020, **10**, 79; (c) M. Torabi, M. A. Zolfigol, M. Yarie and Y. Gu, *Mol. Catal.*, 2021, **516**, 110959; (d) F. Jalili, M. Zarei, M. A. Zolfigol, S. Rostamnia and A. R. Moosavi-Zare, *Microporous Mesoporous Mater.*, 2020, **294**, 109865; (e) S. Kalhor, M. Yarie, M. Torabi, M. A. Zolfigol, M. Rezaeivala and Y. Gu, *Polycyclic Aromat. Compd.*, 2021, **11**, 17456; (f) M. Torabi, M. A. Zolfigol, M. Yarie, B. Notash, S. Azizian and M. M. Azandaryani, *Sci. Rep.*, 2021, **11**, 16846.
- 55 (a) I. V. Alabugin, L. Kuhn, M. G. Medvedev, N. V. Krivoshchapov, V. A. Vil, I. A. Yaremenko, P. Mehaffy, M. Yarie, A. O. Terent'ev and M. A. Zolfigol, *Chem. Soc. Rev.*, 2021, **50**, 10253; (b) I. V. Alabugin, L. Kuhn, N. V. Krivoshchapov, P. Mehaffy and M. G. Medvedev, *Chem. Soc. Rev.*, 2021, **50**, 10212.
- 56 M. Rahmati and D. Habibi, *Res. Chem. Intermed.*, 2021, **47**, 1643.
- 57 M. Yarie, M. A. Zolfigol and M. Saeidi-Rad, *J. Mol. Liq.*, 2018, **249**, 144.
- 58 G. M. Ziarani and S. Bahar, *J. Iran. Chem. Soc.*, 2019, **16**, 365.
- 59 F. Tamaddon, S. Ghazi and M. R. Noorbala, *J. Mol. Catal. B: Enzym.*, 2016, **127**, 89.
- 60 M. Ashouri, H. Kefayati and S. Shariati, *J. Chin. Chem. Soc.*, 2019, **66**, 355.
- 61 M. A. Zolfigol, F. Karimi, M. Yarie and M. Torabi, *Appl. Organomet. Chem.*, 2018, **32**, e4063.
- 62 H. Alinezhad, M. Tajbakhsh and N. Ghobadi, *Res. Chem. Intermed.*, 2015, **41**, 9113.
- 63 H. Huang, X. Ji, W. Wu, L. Huang and H. Jiang, *J. Org. Chem.*, 2013, **78**, 3774.
- 64 J. Han, X. Guo, Y. Liu, Y. Fu, R. Yan and B. Chen, *Adv. Syn. Catal.*, 2017, **359**, 2676.
- 65 X. Zhang, Z. Wang, K. Xu, Y. Feng, W. Zhao, X. Xu, Y. Yan and W. Yi, *Green Chem.*, 2016, **18**, 2313.
- 66 H. Behmadi, S. Naderipour, S. M. Saadati, M. Barghamadi, M. Shaker and N. Tavakoli-Hoseini, *J. Heterocycl. Chem.*, 2011, **48**, 1117.
- 67 V. G. Kharchenko, N. M. Kupranets and M. N. Tilichenko, *Chem. Heterocycl.*, 1970, **4**, 10.

