COMMUNICATION

A C G publications

Org. Commun. XX:X (2025) X-XX

organic communications

Regioselective pyrrole *C*–benzylation using hexaethylene glycolic ionic liquids as a recyclable catalyst

Yogesh R. Jorapur [1*], Gurusamy Rajagopal [2] and Rajendra Kankariya [1]

[1]*Department of Chemistry, Pratibha College of Commerce & Computer Studies, Chinchwad, Pune 411019, Maharashtra, India*
[2] *Department of Chemistry, Government Arts College (Autonomous), Coimbatore, 641018, Tamil Nadu, India*

(Received May 17, 2025; Revised July 15, 2025; Accepted July 18, 2025)

Abstract: We have thoroughly investigated the *C*-benzylation of pyrrole (**1**) using different second and third generation ionic liquids (ILs). The pyrrole *C*-benzylation is achieved with benzyl halides, mesylate, and tosylate selectively at C2 position in good yield. Moreover, minimal byproducts under relatively mild conditions in hexaethylene glycol substituted imidazolium based ILs (hexaEGILs) have been observed. 2-Benzyl pyrrole (**3**) was synthesized in high yield from pyrrole (**1**) and benzyl bromide (**2a**) in the presence of [hexaEGmim][OMs] and [dihexaEGim][OMs] as two different tailor-made ILs as catalysts (10 mol%) in MeCN at 80 °C within an hour.

Keywords: Pyrrole benzylation, benzyl bromide, ionic liquids, ethylene glycols, green chemistry;

1. Introduction

The conventional nucleophilic substitution (S_N) reactions utilize the polar aprotic solvents particularly, "tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), hexamethylphosphoric triamide (HMPA)" etc.[1-6] However, from the green chemistry point of view, their adverse environmental impact make these solvents an unsuitable reaction media.[7,8]

Over the past two decades, ILs (Figure 1a) are found to be favorable media for S_N2 reactions due to their highly charged yet non-coordinating nature.[9-21] Because of negligible vapor pressure and magnificent thermal stabilities of ILs, it could be a potential candidate to supplant the conventional organic solvents used till today. However, the biphasic framework requires the use of stoichiometric amount of ILs. This brings up concerns regarding ILs price and their biodegradability data.[22-24] The alternative to this problem is to develop some new protocols where ILs can act as a catalyst and not as

* Corresponding author: E-mail: dryogeshrjorapur@gmail.com

The article was published by ACG Publications
http://www.acgpubs.org/journal/organic-communications © Month-Month 2025 EISSN:1307-6175
DOI: http://doi.org/10.25135/acg.oc.192.2505.3516
Available online: July 28, 2025

the reaction solvent. This is often conceivable by centering the consideration of wide scientific community on the third generation tailor-made ILs.[25]

2. Background

Recently, Kim *et al*. has designed and prepared [hexaEGILs] (Figure 1b) and developed a new catalytic system for nucleophilic fluorination reactions.[26,27a] Binder *et. al.* used glycol based ILs in copper catalyzed microwave-assisted azide/alkyne "click" reaction.[27b] Further, amino-polystyrene supported hexaethylene glycol-bridged IL catalyst was found to be remarkably efficient at catalyzing the selective nucleophilic hydroxylation of alkyl halides.[27c] "Eco-friendly protocol from epoxide to cyclic carbonates using tri-s-triazine terminal-linked ILs" was recently reported by Sun and coworkers.[28]

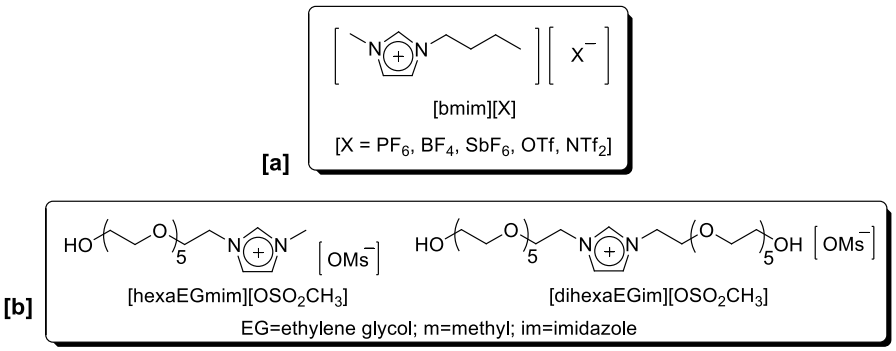
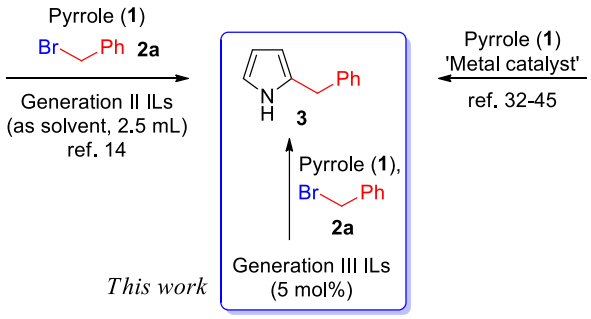


Figure 1. Second (a) and third (b) generation ILs.

The synthesis and reactions of five-membered aromatics have attracted researcher's interest for over a century because of their medicinal and pharmacological significance.[29-31] The "*C*-alkylations of pyrrole on C2 and C5 positions from reactive halide moieties such as allyl, benzyl, and acetate" have been reported.[32-38] The photocatalytic C2 alkylation with diazo esters was recently reported by Gryko *et al*.[39] Hintermann recently reported "hydrogen auto-transfer alkylation of substituted pyrroles by alkali alkoxides in alcohols at elevated temperature".[40] The aluminum,[41] cobalt,[42] and copper-catalyzed[43,44] direct alkylation of pyrrole using activated alkyl substituents have also been independently reported. The "role of hexameric resorcinarene capsule as a hydrogen bonding catalyst" towards the addition of heteroarenes has also been documented.[45] We have also reported highly efficient nucleophilic substitution reactions in ILs, including "pyrrole *C*-alkylation at C2 and C5 positions with various alkyl halides and mesylates" (Scheme 1).[14]

However, to the best of our understanding, no reports have been published on the regioselective benzylation of pyrrole using alkyl halides with IL as either catalysts or solvents. In this study, we present that by employing a custom-designed IL as a catalyst, significant rate enhancement of the *C*-benzylation of pyrrole on second position can be accomplished from benzyl halides or mesylates. In this methodology preferential introduction of a benzyl group at the second position of pyrrole can be achieved with minimizing the formation of other products including dibenzylated product (Scheme 1).[46-48]



Scheme 1. Schematic representation of previous and this work

3. Experimental

3.1. Chemicals and Apparatus

The ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer at RT and the chemical shifts are reported in δ units (ppm) relative to tetramethylsilane (TMS). TLC analysis was performed on 0.25 mm silica gel 60 aluminium sheets containing F_{254}. Column chromatography was performed using 200–400 mesh silica gel. All other known compounds including the IL, [bmim][Cl] were commercially available. Tailor-made ILs [hexaEGmim][OMs] and [dihexaEGim][OMs] were synthesized according to the reported procedure[26, 27a] and was duly characterized before use.

3.2. Typical Procedure for Pyrrole C-Benzylation in IL (Table 2)

In a pre-dried pressure vial benzyl halides/mesylate/tosylate (**2a**, 171 mg; **2b**, 127 mg; **2c**, 218 mg; **2d**, 186 mg; **2e**, 262 mg; 1.0 mmol), pyrrole (**1**; 0.14 mL, 2.0 mmol), $NaHCO_3$ (84 mg, 1.0 mmol) and [hexaEGmim][OMs] (45 mg, 0.1 mmol) or [dihexaEGim][OMs] (70 mg, 0.1 mmol) in 3.0 mL of anhydrous MeCN was heated at 80 °C in oil bath. Reaction was monitored using TLC, after completion the reaction mixture was extracted from IL phase with ethyl ether (10 mL x 3). The organic layer was dried over anhydrous Na_2SO_4, evaporated under reduced pressure and was purified by column chromatography (5% EtOAc/hexanes) to obtain of 2-benzyl-*1H*-pyrrole (**3**) as colorless oil.

*2-Benzyl-1H-pyrrole (**3**)*: Yield (133 mg, 85%); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 3.97 s (2H, CH_2), 5.98-6.00 m (1H, H_{arom}), 6.13-6.15 m (1H, H_{arom}), 6.65-6.66 m (1H, H_{arom}), 7.18-7.31 m (5H, H_{arom}), 7.80 bs (NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 34.0, 106.4, 108.3, 116.9, 126.4, 128.6, 128.7, 130.6, 139.5; MS (EI) 157 $[M]^+$, 80 (100). HR MS (EI) Calcd for $C_{11}H_{11}N$ $[M]^+$ 157.0891, found 157.0891; CAS Registry No. 33234-48-9.

*2,5-Dibenzyl-1H-pyrrole (**4**)*: light brown solid; T_{mp} 74-76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 3.89 s (4H, $2CH_2$), 5.85 d (J = 2.4 Hz, 2CH), 7.16-7.21 m (6H, H_{arom}), 7.24-7.29 m (4H, H_{arom}), 7.45 bs (NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 34.1, 106.6, 126.3, 128.5, 128.6, 130.0, 139.7; MS (EI) 247 $[M]^+$, 156 (100). HR MS (EI) Calcd for $C_{18}H_{17}N$ $[M]^+$ 247.1361, found 247.1362; CAS Registry No. 850662-64-5.

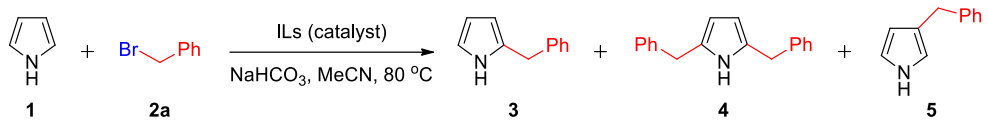
*3-Benzyl-1H-pyrrole (**5**)*: colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 3.89 s (2H, CH_2), 6.10-6.12 m (1H, H_{arom}), 6.54-6.56 m (1H, H_{arom}), 6.73-6.25 m (1H, H_{arom}), 7.19-7.35 m (5H, H_{arom}), 8.02 s (NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 33.3, 108.9, 115.3, 117.9, 123.1, 125.6, 128.2, 128.6, 142.2; MS (EI) 157 $[M]^+$ (100), 156 (83). HR MS (EI) Calcd for $C_{11}H_{11}N$ 157.0891 $[M]^+$ (100), found 157.0888 $[M]^+$ (100); CAS Registry No. 33234-57-0.

*1-Benzyloxycarbonylpyrrole (**6**)*: colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 5.25 s (2H, CH_2), 6.12 t (2H, H_{arom}, J = 2.6 Hz), 7.18 t (2H, H_{arom}, J = 2.6 Hz), 7.25-7.32 m (5H, H_{arom}); MS (EI) 201 $[M]^+$, 91 (100). HR MS (EI) Calcd for $C_{12}H_{11}O_2N$ 201.0790 $[M]^+$ (100), found 201.0791 $[M]^+$; CAS Registry No. 56857-08-0.

4. Present Study

To begin the investigation, we first performed the blank reaction with benzyl bromide (**2a**) as the model compound in MeCN as reaction media (Scheme 2, Table 1, entry 1). The reaction was found to be very slow and reached to completion after 36 h at 80 °C providing 65, 8, and 5% of 2-benzyl-*1H*-pyrrole (**3**), 2,5-bis-*1H*-pyrrole (**4**), and 3-benzyl-*1H*-pyrrole (**5**) respectively together with 4% of 1-benzyloxycarbonyl pyrrole (**6**).

Regioselective pyrrole *C*–benzylation



Scheme 2. Pyrrole *C*-benzylation with benzyl bromide catalyzed by hexaethylene glycolic ILs.

Table 1. Optimization of pyrrole *C*-benzylation with benzyl bromide (**2a**).[a]

entry	ILs (equiv)	yield of product (%)[b] after 30 min		yield of product (%)[b] after time (h)			
		3	**4**	**time (h)**	**3**	**4**	**5**
1[c]	[blank]	-	-	36	65	8	5
2	[bmim][BF_4] (0.11)	-	-	22	72	6	7
3[d]	[bmim][BF_4] (0.11)	6	traces[g]	18	68	5	5
4	[bmim][BF_4] (1.1)	11	traces[g]	12	74	5	5
5[e]	[bmim][OMs] (0.1)	14	traces[g]	6	76	4	-
6	[bmim][OMs] (1.0)	35	traces[g]	90 min	78	4	-
7	[hexaEGmim][OMs] (0.05)	38	-	3	85	3	-
8	[hexaEGmim][OMs] (0.10)	46	-	2	85	4	-
9	[hexaEGmim][OMs] (1.0)	80	6	30 min	80	6	-
10[f]	[hexaEGmim][OMs] (1.0)	76	8	30 min	76	8	-
11	[dihexaEGim][OMs] (0.05)	36	-	3	84	4	-
12	[dihexaEGim][OMs] (0.10)	46	-	2	85	3	-

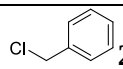
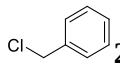
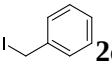
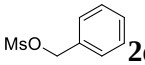
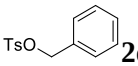
[a]All reactions with 1.0 mmol reaction scale of benzyl bromide (**2a**, 171 mg) with pyrrole (**1**, 0.14 mL, 2.0 mmol) and $NaHCO_3$ (84 mg, 1.0 mmol) in acetonitrile (3.0 mL) at 80 °C. [b]Isolated yield. [c]1-Benzyloxycarbonylpyrrole (**6**) was obtained (8.0 mg, 4% yield). [d]Potassium carbonate (138 mg, 1.0 mmol) used and 1-benzyloxycarbonylpyrrole (**6**) was obtained (20 mg, 10% yield). [e]Potassium carbonate (138 mg, 1.0 mmol) used and 1-benzyloxycarbonylpyrrole (**6**) was obtained (24 mg, 12% yield). [f]In the absence of MeCN. [g]Observed on TLC.

To check the catalytic behavior of IL, we conducted the reaction with approximately 10 mol% of [bmim][BF_4]. The reaction completed after 22 h to yield desired product (**3**) (72% yield) together with (**4**) (6% yield) and (**5**) (7% yield) (entry 2). Subsequently, in the presence of potassium carbonate, the reaction has taken similar lengths of time for completion with the good regioselectivity (entry 3). The shift of counter anion from [BF_4] to [OMs] improved the reaction time; 18 h for entry 3 and 6 h for entry 5. The objective of this report was to achieve enhanced reactivity and regioselectivity using the tailor-made ILs, so we next performed several experiments with [hexaEGmim][OMs] and [dihexaEGim][OMs]. As a catalytic amount (5-10 mol%), tailor-made IL gave desired product in short reaction time (within 2 h) than the conventional [bmim][BF_4]. With excess of ILs (1.0 equiv) without any co-solvent, the reaction was found to be much more rapid than the conventional ILs (entry 10). Subsequently, comparison was made between the two tailor-made ILs; both the ILs, [hexaEGmim][OMs] and [dihexaEGim][OMs] found to have almost similar reaction time and selectivity (entries 8 and 12).

In an effort to examine a novel method for synthesizing *C*-benzylated pyrrole, we have analyzed the benzylation of pyrrole using various benzyl halides or mesylates. The results reported in Table 2 shows that this approach is very successful. The yields for the 2-benzyl-*1H*-pyrrole (**3**) product vary between 70% and 85%. The benzylation of pyrrole with various good leaving groups such as chloro-, iodo-, mesylate-, and tosylate- under these conditions provided (**3**) in good yield (70, 80, 84, and 72%, entries 1, 3-5 respectively). Chlorides as a leaving group found to show sluggish behavior in comparison to iodo-, mesylate- and tosylate. However, use of KI (0.1 mmol) enhances the reaction rate by *in-situ* exchange of chloro to iodo; iodide is a better leaving group than chloride because it is larger and more polarizable (entry 2). The leaving group ability significantly impacts

reaction rates in nucleophilic substitution. Iodide is the best leaving group within the halides (entry 3); both mesylate and tosylate groups are superior to halides (entries 4 and 5). Presumably, stronger acids (with lower *pKa* values) form weaker conjugate bases, which are more stable and therefore better leaving groups.

Table 2. Benzylation of pyrrole with various benyl halides/mesylate/tosylate in [hexaEGmim][OMs].[a]

entry	compound	time (h)	yield (%)[b]	
			3	**4**
1	 **2b**	24	70	10
2[c]	 **2b**	2	82	6
3	 **2c**	1.5	80	6
4[d]	 **2d**	45 min	84	5
5[d]	 **2e**	30 min	72	9

[a]All reactions with 1.0 mmol reaction scale of benzyl halides/mesylate (OMs)/tosylate (OTs) (**2**), pyrrole (**1**, 0.14 mL, 2.0 mmol), $NaHCO_3$ (84 mg, 1.0 mmol) and [hexaEGmim][OMs] (45 mg, 0.1 mmol) in MeCN (3.0 mL) at 80 °C. [b]Isolated yield. [c]KI (17 mg, 0.1 mmol) was used. [d]Reaction temp. (70 °C).

Up to several rounds of recycling and reuse of [HexaEGmim][OMs] are possible without a discernible loss in IL activity and regioselectivity. Pyrrole *C*-benzylation reaction with 10 mol% [hexaEGmim][OMs] in MeCN afforded (**3**) in high yield even after five runs (Table 3; Figure 2).

Table 3. Catalyst recycling ability.[a]

Run	0	1	2	3	4	5
yield (%)[b]	85	85	84	85	83	84

[a]All reactions with 2.0 mmol reaction scale of benzyl bromide (**2a**, 342 mg), pyrrole (**1**, 0.28 mL, 4.0 mmol), $NaHCO_3$ (168 mg, 2.0 mmole) and [hexaEGmim][OMs] (90 mg, 0.2 mmol) in MeCN (6.0 mL) at 80 °C for 2 h. [b]Isolated yield of (**3**).

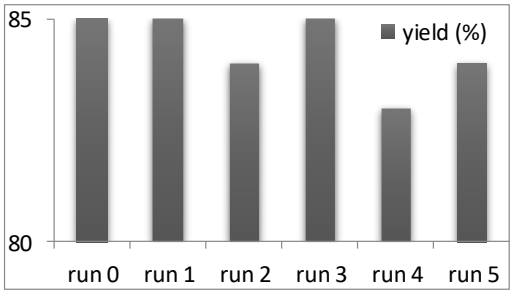
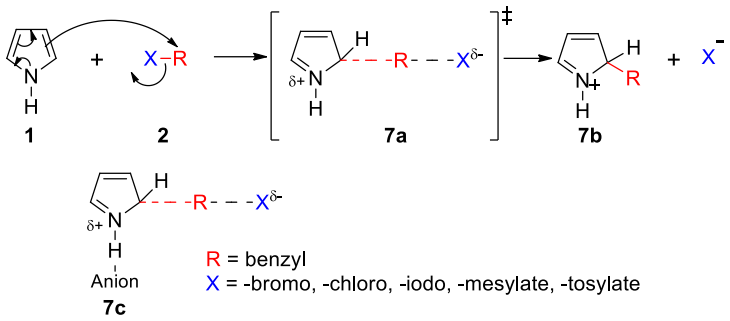


Figure 2. Catalyst recycling ability

The pyrrole *C*-benylation in the ILs media is likely caused by the following mechanism (Scheme 3). The pyrrole alkylation activated complex demonstrates that the N atom gains a positive charge as the pyrrole attacks the carbon centre, enhancing the N–H proton's capacity to donate H–bond. The positively charged species (**7b**) in turn is stabilized by the counter anion of IL.[26,27,49] The hexaethylene glycol substituted Imidazolium salt core might have a phase-transfer catalyst like

activity.[26] Further, the terminal hydroxyl group might have initial interaction by H−bonding with N–H thereby enhancing the pyrrole attack on the carbon centre.



Scheme 3. Plausible mechanism.

5. Conclusion

In summary, hexaEGILs acts as an important driving force in regioselective *C*-benzylation of pyrrole. The experimental procedure is very simple and convenient. Moreover, our methodology did not require any aqueous work-up thereby avoiding the generation of toxic waste. It is noteworthy that our procedure need not require any Lewis acid/base catalyst. Further studies on the development of more efficient green protocols (broader substrate applicability, lower reaction temperature, shorter reaction time, etc.) for *C*-benzylation of pyrrole using smart IL are in progress in our laboratories. Studies towards the development of novel IL for more effective nucleophilic substitutions are currently underway.

Acknowledgements

The author acknowledges Kamala education society, Pune, India for the support. The authors would like to express our sincere gratitude to Troyasil HPLC Column Technologies for their valuable support.

Supporting Information

Supporting information accompanies this paper on http://www.acgpubs.org/journal/organic-communications

ORCID
Yogesh R. Jorapur: 0000-0002-2683-1641
Gurusamy Rajagopal: 0000-0002-6396-5112
Rajendra Kankariya: 0009-0009-9408-0198

References

[1] For a monograph on this subject, see: Hartshorn, S. R. *Aliphatic nucleophilic substitution*, Cambridge University, Press: Cambridge, 1973.
[2] Smith, M. D.; March, J. *Advanced Organic Chemistry* 5th ed., Wiley-Interscience: New York, 2001, 389-674.
[3] For review, see: Katritzky, A. R.; Brycki, B. E. The mechanisms of nucleophilic substitution in aliphatic compounds. *Chem. Soc. Rev.* **1990**, *19*, 83-105.
[4] Sowinski, A. F.; Whitesides, G. M. S_N2 displacements and reductive coupling of ketones with olefins in *N*, *N*-diethylacetamide and *N*-ethylpyrrolidone. *J. Org. Chem.* **1979**, *44*, 2369-2376.

[5] Martin, H. D.; Weise, A.; Niclas, H.–J. The solvent dimethyl sulfoxide. *Angew. Chem. Int. Ed.* **1967**, *6*, 318-334.
[6] Parker, A. J. Protic-dipolar aprotic solvent effects on rates of bimolecular reactions. *Chem. Rev.* **1969**, *69*, 1-32.
[7] Welles, W. L.; Wilburn, R. E.; Ehrlich, J. K.; Floridia, C. M. New York hazardous substances emergency events surveillance: learning from hazardous substances releases to improve safety. *J. Hazard. Mater.* **2004**, *115*, 39-49.
[8] (a) Tsai, J.–H.; Hsu, Y.–C.; Yang, J.–Y. The relationship between volatile organic profiles and emission sources in ozone episode region−a case study in Southern Taiwan. *Sci. Total Environ.* **2004**, *328*, 131-142. (b) Sulochana, M.; Ram Babu; Thakur, S.; Mahalle, P. R.; Jorapur, Y.; Nakkella, A. K. Green Chemistry Innovations for Sustainable Development. *Afr. J. Biol. Sci.*, **2024**, *6*, 5524–5541.
[9] Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. Chemical and biochemical transformations in ionic liquids. *Tetrahedron* **2005**, *61*, 1015-1060.
[10] Jorapur, Y. R.; Chi D. Y. Ionic liquids: an environmentally friendly media for nucleophilic substitution reactions. *Bull. Korean Chem. Soc.* **2006**, *27*, 345-354.
[11] Tang, S.; Baker, G. A.; Zhao, H. Ether-and alcohol-functionalized task-specific ionic liquids: attractive properties and applications. *Chem. Soc. Rev.* **2012**, *41*, 4030-4066.
[12] Dai, C.; Zhang, J.; Huang, C.; Lei, Z. Ionic liquids in selective oxidation: catalysts and solvents. *Chem. Rev.*, **2017**, *117*, 6929–6983.
[13] Al-Saidi, H. M.; Emara, A. A. A. The recent developments in dispersive liquid–liquid micro extraction for pre-concentration and determination of inorganic analytes. *J. Saudi Chem. Soc.*, **2014**, *18*, 745-761.
[14] Jorapur, Y. R.; Lee, C.–H.; Chi, D. Y. Mono-and dialkylations of pyrrole at C2 and C5 positions by nucleophilic substitution reaction in ionic liquid. *Org. Lett.*, **2005**, *7*, 1231-1234.
[15] Jorapur, Y. R.; Chi, D. Y. Synthesis of symmetrical organic carbonates via significantly enhanced alkylation of metal carbonates with alkyl halides/sulfonates in ionic liquid. *J. Org. Chem.*, **2005**, *70*, 10774-10777.
[16] Jorapur, Y. R.; Jeong, J. M.; Chi, D. Y. Potassium carbonate as a base for the *N*-alkylation of indole and pyrrole in ionic liquids. *Tetrahedron Lett.*, **2006**, *47*, 2435-2438.
[17] Shinde, S. S.; Lee, B. S.; Chi, D. Y. Synergistic effect of two solvents, *tert*-alcohol and ionic liquid, in one molecule in nucleophilic fluorination. *Org. Lett.* **2008**, *10*, 733-735.
[18] Hong, D. J.; Kim, D. W.; Chi, D. Y. Facile ring-closure cyclization of arenes by nucleophilic *C*-alkylation reaction in ionic liquid. *Tetrahedron Lett.* **2010**, *51*, 54-56.
[19] Oh, Y.−H.; Jang, H.−B.; Im, S.; Song, M.−J.; Kim, S.−Y.; Park, S.−W.; Chi, D. Y.; Song, C. E.; Lee, S.−Y. S_N2 Fluorination reactions in ionic liquids: a mechanistic study towards solvent engineering. *Org. Biomol. Chem.*, **2011**, *9*, 418-422.
[20] Jorapur, Y. R.; Chi, D. Y. Intramolecular cycloalkylation of pyrrole in ionic liquids and immobilized ionic liquids. *Bull. Korean Chem. Soc.*, **2011**, *32*, 3130-3132.
[21] Hawker, R. R.; Haines, R. S.; Harper, J. B. Rational selection of the cation of an ionic liquid to control the reaction outcome of a substitution reaction. *Chem. Commun.*, **2018**, *54*, 2296-2299.
[22] Gathergood, N.; Scammels, P. J.; Garcia, M. T. Biodegradable ionic liquids Part III. The first readily biodegradable ionic liquids. *Green Chem.*, **2006**, *28*, 156-160.
[23] Fukumoto, K.; Yoshizawa, M.; Ohno, H. Room temperature ionic liquids from 20 natural amino acids. *J. Am. Chem. Soc.*, **2005**, *127*, 2398-2399.
[24] Tao, G.−H.; He, L.; Liu, W.−S.; Xu, L.; Xiong, W.; Wang, T.; Kou, Y. Preparation, characterization and application of amino acid-based green ionic liquids. *Green Chem.*, **2006**, *8*, S639-646.
[25] Sawant, A. D.; Raut, D. G.; Darvatkar, N. B.; Salunkhe, M. M. Recent developments of task-specific ionic liquids in organic synthesis. *Green Chem. Lett. Rev.*, **2011**, *4*, 41-54.
[26] Jadhav, V. H.; Jeong, H.−J.; Lim, S. T.; Sohn, M. H.; Kim, D. W. Tailor-made hexaethylene glycolic ionic liquids as organic catalysts for specific chemical reactions. *Org. Lett.*, **2011**, *13*, 2502–2505.
[27] (a) Jadhav, V. H.; Kim, J. G.; Park, S. H.; Kim, D. W. Task-specific hexaethylene glycol bridged di-cationic ionic liquids as catalysts for nucleophilic fluorination using potassium fluoride. *Chem. Eng. J.*, **2017**, *308*, 664-668. (b) Zare, P.; Mahrova, M.; Tojo, E.; Stojanovic, A.; Binder, W. H. Ethylene glycol-based ionic liquids via azide/alkyne click chemistry. *J. Poly. Sci. Part A: Poly. Chem.* **2013**, *51*, 190-202. (c) Reddy, M. V.; Kang, S. M.; Yoo, S.; Woo, S. S.; Kim, D. W. Amino-polystyrene supported hexaethylene glycol-bridged ionic liquid as an efficient heterogeneous catalyst for water-mediated nucleophilic hydroxylation. *RSC Adv.* **2019**, *9*, 9435−9442.
[28] Liu, M.−S.; Lan, J.−W.; Liang, L.; Sun, J.−M.; Arai, M. Heterogeneous catalytic conversion of CO_2 and epoxides to cyclic carbonates over multifunctional tri-s-triazine terminal-linked ionic liquids. *J. Catal.*, **2017**, *347*, 138-147.

[29] Fisher, H.; Orth, H. In *Die Chemie des Pyrroles* Akademische Verlag, Liepzig, 1934, vol.1-2; reproduced by Johnson Reprint Corporation, New York, 1968.
[30] Jones, R. A.; Bean G. P. *The Chemistry of Pyrroles*, Academic Press, New York, 1977, vol. 34.
[31] Livingstone, R. In Rodd's *Chemistry of Carbon Compounds*; Ansell, M. F. 2nd ed., Elsevier: Oxford, 1984, vol. 4.
[32] Jacobson, M. A.; Williard, P. G. Synthesis of 2,3-disubstituted pyrroles from 3-*N*-Dilithio-*N*-(*tert*-butyldimethylsilyl)-2-buten-1-amine. *J. Org. Chem.*, **2002**, *67*, 32-37.
[33] Nicolaou, K. C.; Claremon, D. A.; Papahatjis, D. P. A mild method for the synthesis of 2-ketopyrroles from carboxylic acids. *Tetrahedron Lett.*, **1981**, *22*, 4647-4650.
[34] Yadav, J. S.; Reddy, B. V. S.; Reddy, P. M.; Srinivas, C. Zinc-mediated Barbier reactions of pyrrole and indoles: a new method for the alkylation of pyrrole and indoles. *Tetrahedron Lett.*, **2002**, *43*, 5185-5187.
[35] Nakamura, I.; Siriwardana, A. I.; Saito, S.; Yamamoto, Y. Addition of heteroaromatics to alkylidenecyclopropanes catalyzed by palladium. *J. Org. Chem.*, **2002**, *67*, 3445-3449.
[36] Schloemer, G. C.; Greenhouse, R.; Muchowski, J. M. Highly efficient synthesis of alkyl pyrrolylacetates and dialkyl pyrrolylmalonates. *J. Org. Chem.*, **1994**, *59*, 5230-5234.
[37] Cozzi, P. G.; Zoli, L. A rational approach towards the nucleophilic substitutions of alcohols "on Water". *Angew. Chem. Int. Ed.*, **2008**, *47*, 4162-4166.
[38] (a) Zaitsev, A. B.; Gruber, S.; Plüss, P. A.; Pregosin, P. S.; Veiros, L. F.; Wörle, M. Fast and highly regioselective allylation of indole and pyrrole compounds by allyl alcohols using Ru-sulfonate catalysts. *J. Am. Chem. Soc.*, **2008**, *130*, 11604-11605. (b) For other regioselective system, refer: Boddapati, S. M.; Tamminana, R.; Alam, M. M.; Gugulothu, S.; Varala, R.; Bollikolla, H. B. Efficient Pd (II)-catalyzed regioselective ortho-halogenation of arylcyanamides. *New J. Chem.*, **2021**, *45*, 17176-17182.
[39] Ciszewski, L. W.; Durka, J.; Gryko, D. Photocatalytic alkylation of pyrroles and indoles with α-diazo esters. *Org. Lett.*, **2019**, *21*, 7028-7032.
[40] Koller, S.; Blazejak, M.; Hintermann, L. Catalytic *C*-alkylation of pyrroles with primary alcohols: Hans Fischer's alkali and a new method with iridium P, N, P-Pincer complexes. *Eur. J. Org. Chem.*, **2018**, 1624–1633.
[41] Gürdere, M. B.; Özbek, O.; Ceylan, M. Aluminum chloride–catalyzed *C*-alkylation of pyrrole and indole with chalcone and bis-chalcone derivatives. *Syn. Commun.*, **2016**, *46*, 322-331.
[42] Ghorai, J.; Chaitanya, M.; Anbarasan, P. Cp*Co (III)-catalysed selective alkylation of C–H bonds of arenes and heteroarenes with α-diazocarbonyl compounds. *Org. Biomol. Chem.*, **2018**, *16*, 7346–7350.
[43] Theunissen, C.; Wang, J.; Evano, G. Copper-catalyzed direct alkylation of heteroarenes. *Chem. Sci.*, **2017**, *8*, 3465-3470.
[44] Ozdemir, H. S.; Sahin, E.; Cakici, M.; Kilic, H. Asymmetric Friedel–Crafts alkylation of pyrrole with nitroalkenes catalyzed by a copper complex of a bisphenol A-derived Schiff base. *Tetrahedron* **2015**, *71*, 2882-2890.
[45] Gambaro, S.; De Rosa, M.; Soriente, A.; Talotta, C.; Floresta, G.; Rescifina, A.; Gaeta, C.; Neri, P. A hexameric resorcinarene capsule as a hydrogen bonding catalyst in the conjugate addition of pyrroles and indoles to nitroalkenes. *Org. Chem. Front.*, **2019**, *6*, 2339-2347.
[46] Darbeau, R. W.; White E. H. The direct alkylation of π-rich, acid-sensitive heterocyclic compounds via essentially free carbocations. *J. Org. Chem.*, **1997**, *62*, 8091-8094.
[47] Greenhouse, R.; Ramirez, C.; Muchowski, J. M. Synthesis of alkylpyrroles by the sodium borohydride reduction of acylpyrroles. *J. Org. Chem.*, **1985**, *50*, 2961-2965.
[48] Schumacher, S. S.; Hall, D. P. Tandem alkylation-reduction of 2-acylpyrroles. Convenient one-pot syntheses of 2-benzylpyrroles. *J. Org. Chem.*, **1981**, *46*, 5060-5064.
[49] Lancaster, N. L. Organic reactivity in ionic liquids: some mechanistic insights into nucleophilic substitution reactions. *J. Chem. Res.*, **2005**, 413-417.