Organic & Biomolecular Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/obc

Journal Name

RSCPublishing

ARTICLE

One Molecule of Ionic Liquid and *tert*-Alcohol on Polystyrene-Support as Catalysts for Efficient Nucleophilic Substitution Including Fluorination

Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

Sandip S. Shinde* and Sunil N. Patil

The *tert*-alcohol and ionic liquid solvents in one molecule ([mim-^{t}OH][OMs], Fig 1) was immobilized on polystyrene reported to be a highly efficient catalyst in aliphatic nucleophilic substitution using alkali metal salts. Herein, we investigated catalytic activity of new structurally modified polymer-supported *tert*-alcohol functionalized imidazolium salt catalyst in nucleophilic substitution of 2-(3-methanesulfonyloxypropyoxy)naphthalene as model substrate with various metal nucleophiles. The *tert*-alcohol moiety of IL with hexyl chain distance from polystyrene had better catalytic activity compared to the other resin which lack alkyl linker and *tert*-alcohol moiety. We found that the maximum [mim-^{t}OH][OMs] loading had the best catalytic efficacy among the tested PSIL in nucleophilic fluorination. The catalytic efficiency of the PS[him-^{t}OH][OMs] as PTC was determine by carrying out various nucleophilic substitution using the corresponding alkali metal salts from third to sixth periodic in CH_3CN or *tert*-BuOH media. The scope this protocol with primary and secondary polar substrates containing many heteroatoms are also reported. This PS[him-^{t}OH][OMs] catalyst not only enhances the reactivity of alkali metal salts and reduces the formation of by-products but also affording high yield with easy isolation.

Introduction

Nucleophilic displacement reaction using alkali metal salts is commonly and widely applicable method because their easily availability, abundant in nature and potent sources of nucleophiles. However, the low solubility and reactivity in organic solvent make nucleophilic substitutions under harsh conditions and is one of the major obstacle in applications at industrial process.[1] Phase transfer catalysts (PTCs) such as Tetraalkylammonium, tetraalkylphosphonium salts, and crown ether derivatives in combination with alkali metal salts are conventionally used in numerous nucleophilic substitution reactions to enhance the reactivity of nucleophile.[2] However, PTCs are ineffective in case of metal salts having tight ion pair, and selectivity decreases when employing in fluorination reaction because "naked" fluoride not only act as nucleophile but also as a base.[3] Characteristic feature of best PTC is that enhance the interphase migration of a reactant in heterogeneous solid–liquid and liquid–liquid systems from one phase into another where reaction can take place. Imidazolium-based ionic liquids (ILs) were reported to exhibit catalytic activity when used as a PTC or reaction media in several chemical transformations.[4] They are generally defined as organic/inorganic salts with liquid at room temperature, which have a good chemical stability and low flammability, insignificant vapor pressure and high ionic conductivity.[5] A unique attribute of ILs their modularity, they can be tailored to meet specific needs by making simple structural modification on their the cation or anion component.[6] Particularly, 1,3-Dialkylimdaolium-based salts are representative of tailor-made ILs. However, in spite of their well reorganized advantages, a series of drawbacks, such as their high cost, low biodegradability, and toxicological properties have restricted their wide application.[7] ILs can cause problems in product separation and recovery of ILs, especially when the product is polar or somewhat soluble in water.

Recently, an economic and environmental points of view, the heterogenization of homogeneous catalytic reactions has attracted great attention from a wide range of organic chemists.[8] The supported catalyst based on well-defined catalytic unit tethered to an insoluble matrix have become the subject of intense research activity.[9] Amongst the various approaches used for the synthesis of solid supported IL catalysts, the covalent attachment of ILs to the polystyrene resin offer benefits to minimizes the possibility of leaching thereby avoiding the

necessity of catalyst activity loss and reuse of expensive and toxic catalysts.[10] The immobilized ILs into polystyrene-based (PSILs) showed sufficient catalytic activity in various nucleophilic substitution reactions[11] and facilitated the isolation of product.[12] Recently, we reported a *tert*-alcohol functionalized, imidazolium-based IL [mim-^{t}OH][OMs] (Fig. 1) possessing *tertiary* alcohol moiety, which provided remarkable reactivity and selectivity in nucleophilic fluorination by reducing the basicity of the fluoride ion due to the polar hydroxyl group of [mim-^{t}OH][OMs] is believed to elevate the solubility and reactivity of anion in various nucleophilic substitutions.[13] The catalytic activity of [mim-^{t}OH][OMs] was not limited to homogeneous condition but also shown superior PTC activity in various nucleophilic substitution with alkyl sulfonate and alkyl halides under heterogeneous protocols methods.[14] Due to its many practical benefits, facile and short synthesis, and liquid at room temperature attracted our interest, we report herein catalytic activity of structurally-modified PSIL (Fig. 1) in various nucleophilic substitutions reactions.

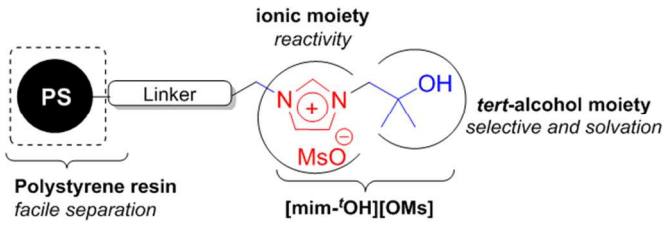
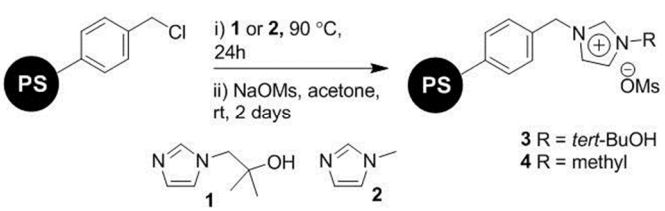


Fig 1. Polystyrene-supported *tert*-alcohol functionalized ionic liquids

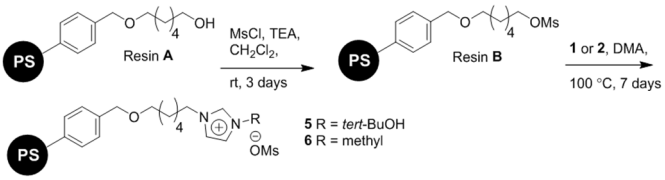
Results and discussion,

Four structurally-modified PSIL systems with non-alkyl or hexyl-chain as linkers, and various loading levels of ionic liquid portion with counteranion mesylate [OMs] from polystyrene resins were prepared. The PS[im-^{t}OH][OMs] PS=polymer support; (im-^{t}OH =1-1-(2-hydroxy-2-methylpropyl)imidazolium cation), and PS [mim][OMs] (mim =1-methylimidazolium cation) both has no alkyl chain as a linker, was prepared using the procedure, as shown in Scheme 1. Merrifield resin (1% divinylbenzene, 4.0 mmol Cl/g) was reacted with 1-methylimidazole or 1-(2-hydroxy-2-methylpropyl)imidazole at 90 °C for 24 h to obtain PS[mim][Cl], and PS[im-^{t}OH][Cl] respectively . A further treatment of these PSIL with NaOMs afforded OMs anion exchanged PS[mim] [OMs], and PS[im-^{t}OH] [OMs] (2.2 mmol and 1.9 mmol of IL portion/g of polymer-supported product afforded respectively).



Scheme 1. Preparation of polymer-supported ionic liquids

Scheme 2 shown the preparation of PSIL system of both ILs with having hexyl chain as a linker such as PS[him-^{t}OH][OMs] and PS[hmim][OMs] (him-^{t}OH =1-*n*-hexyl-3-(2-hydroxy-2-methylpropyl)imidazolium, and hmim=1-*n*-hexyl-3-methylimidazolium respectively) were prepared according to our previously reported procedure.[14]

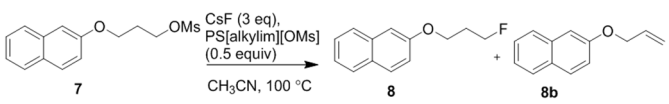


Scheme 2. Preparation of polymer-supported hexyl-linker ionic liquids.

Hexanol-branched polystyrene resin was treated with methanesulfonyl chloride in the presence of triethylamine in CH_2Cl_2 using a shaker to obtain mesylate polymer. Subsequently, this mesylate polymer were treated with 1-(2-hydroxy-2-methylpropyl)imidazole, or N-methylimidazole in DMA for a week to afford the corresponding ionic polymers, that is, PS[him-^{t}OH][OMs], and PS[hmim][OMs] respectively. These were analyzed by elemental analysis to quantify the percentage loading of the ammonium moieties by measuring the nitrogen content, giving 1.7 mmol/g for PS[him-^{t}OH][OMs], and 1.6 mmol/g for PS[hmim][OMs]. These free flowing structurally-modified polystyrene-supported ionic liquids used to investigate their catalytic activity in nucleophilic substitution reactions. The catalytic activities of these four PSIL for nucleophilic fluorination reaction according to the hexyl chain as a linker and *tert*-alcohol moiety in the PSIL system were examined by carrying out the nucleophilic fluorination of a model substrate, 2-(3-methanesulfonyloxypropyloxy)-naphthalene (**7**), using 3 equiv of CsF in the presence of 0.5 equiv of the PSIL systems at 100 °C under the same conditions described in our previous report of this nucleophilic substitutions reaction as shown in Table 1. Whereas the same reaction with CsF in presence of PS[him-^{t}OH][OMs] was proceed at an unprecedented fast rate and completed in 1.5 h to afford the 2-(3-fluoropropyl)-naphthalene (**8**) in excellent yields (98%) without forming any appreciable amount of by-products (entry 5). Same fluorination reaction in absence of any catalyst didn't proceed at all (entry 1). Entries 2 and 3 indicate that fluorination using PS[mim][OMs] and PS[hmim][OMs], which has non-alkyl and hexyl as linker alkyl chain respectively, affording fluorinated product **8**, in good

yield (89% and 92% yield respectively) along with formation of alkene by-product.

Table 1. Nucleophilic Fluorination of Mesylate **7** with CsF using PS[him-^{t}OH][OMs] or the Stated Alternative Catalyst.[a]



Entry	PS[alkylim][OMs] (0.5 equiv)	Temp (°C)	Time (h)	**7**	Yield of product[b] (%)	
					8	Comments
1	-	100	24	98		
2	PS[mim]	100	6	-	89,	6% alkene, trace alcohol[c]
3	PS[hmim]	100	2.8	-	92	7% alkene
4	PS[mim-^{t}OH]	100	5	-	94	trace alkene[c]
5	PS[him-^{t}OH]	100	1.5	-	98	
6	PS[him-^{t}OH]	35	24	95	trace[c]	
7	[bmim]	100	2.5	18	76	trace alcohol[c]
8	[18]crown-6 (2)	100	6	trace[c]	90	6% alkene

[a] All reactions were carried out on a 1.0 mmol scale of mesylate **7** in 5 mL CH_3CN. [b] Isolated yield. [c] Determined by ^{1}H NMR

Interestingly, when using same amount of PS[mim-^{t}OH][OMs] as catalyst (entry 4), fluorination reaction was completed in 5h, affording desire fluoroalkane in high selectivity than that using same amount of IL (entry 7) or the 2 equiv of [18]-crown-6 as the phase transfer catalytic system (entry 8). These results indicate that the PSIL system, PS[mim- ^{t}OH][OMs] with no-alkyl chain linker shows slightly lower catalytic activity compared with PS[him-^{t}OH][OMs]. However, these PSIL system with *tert*-alcohol moiety had superior catalytic activity with enhance fluoride nucleophilicity and reducing by-product formation than among tested other resin and PTC.

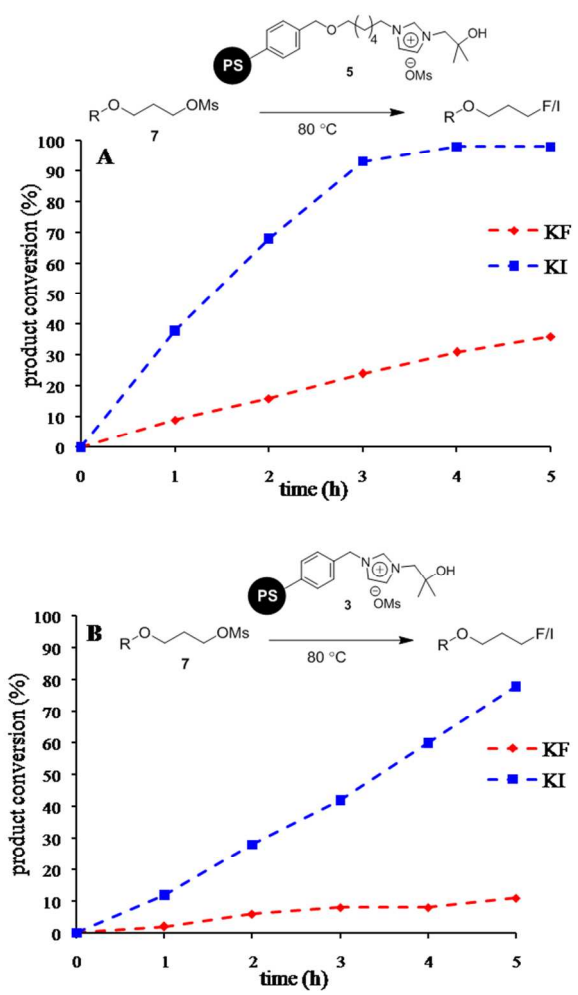


Fig.2 Linker of catalyst dependence the reactivity of KF and KI in nucleophilic substitution reactions

Figure 2 illustrates in details the alkyl chain linker of PSIL dependence of the reactivity of KF and KI in nucleophilic halogenations of alkyl mesylate **7** were carried out in the presence of PSIL system, which has methyl and hexyl chain as linker between polystyrene backbone and IL portion ([mim-^{t}OH] and [him-^{t}OH]) in CH_3CN at 80 °C to determine the previous illustrated the key role of the alkyl chain length as a linker between polystyrene resin and ionic liquid to facile nucleophilic substitution. Figure 2A indicates that the both the nucleophilic fluorination and iodination in the presence of hexyl linker PS[hmim-^{t}OH][OMs], proceeds the much faster compared to that of using PS[mim-^{t}OH][OMs], which has no linker (Figure 2B). These results clearly suggest that the solvation of metal halides accelerated in presence of PS[hmim-^{t}OH][OMs] due to immobilized ILs [mim-^{t}OH][OMs] portion easily approach to the alkali metal salts, presumably it makes it a potent nucleophile. We believe that this different morphology of non alkyl and hexyl chain linker of PSIL effect may be the most important factor in the reactivity enhancing in this reaction. Over all, the long distance between the polystyrene

resin and the ionic liquid portion of the PSIL allowed the reagents to approach the ionic liquid portion easily.

Table 2. Nucleophilic substitution of the mesylate **7** with CsF using various loading levels of PS[him-^{t}OH][OMs].

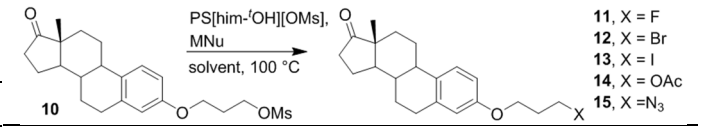
Entry	Loading level of **5** (mmol/g) (0.5 equiv)	Time (h)	Yield of product (%)[a]		
			7	**8**	**8b**
1	0[b]	4	93	trace[c]	
2	0.4	3.8		89	7
3	1.1	2.5		90	trace[c]
4	1.7	1.5		97	

[a] Isolated yield. [b] 200 mg resin **A** were used. [c]Determined by ^{1}H NMR

Table 2 illustrate the catalytic efficiency of the PS[him-^{t}OH][OMs] according to its ionic liquid loading on the polystyrene support was investigated using nucleophilic fluorination reactions in the presence of PS[him-^{t}OH][OMs] at various concentrations, 1.7, 1.1, and 0.4 mmol/g, which were obtained from mesylated resin, in CH_3CN under the same condition as shown entry 5 in Table 1. A comparison of entries 2-4 shows that nucleophilic fluorination using CsF in the presence of PS[him-^{t}OH][OMs], which possesses a higher ionic liquid loading (1.7 mmol/g), showed a faster reaction rate, converting mesylate **7** into the corresponding fluoroalkane product **8**, almost quantitatively (97% yield). However, this fluorination using PS[him-^{t}OH][OMs] containing a lower ionic liquid loading formed a significant amount of alkene by-product by an elimination side reaction due to the lack of fluorine-hydrogen bonding. However, the polystyrene resin **A** with no ionic liquid portion had no catalytic activity in this fluorination reaction.

Based on the swelling properties of PS[him-^{t}OH][OMs] in *t*-BuOH or CH_3CN solvent,[13] Table 3 shown the nucleophilic substitution reaction using various nucleophile in presence of PS[him-^{t}OH][OMs] was carried out in either *t*-BuOH or CH_3CN. As expected, fluorination using RbF in *t*-BuOH as reaction media showed a slightly faster rate (2h, entry 2) than when using CH_3CN (3h, entry 1), affording desire fluoroalkane **2** along with new by-product ether. Fluorination using KF in *tert*-BuOH was incomplete even after 12h, afforded fluoroalkane 2 in 10% yield (entry 3). Interestingly, same reaction using KF in presence of higher loading catalyst, reaction was sluggish and completed after 12 h, affording fluoroalkane 76% along with alkene by-product 16% (entry 4). Entry 5 indicates that nucleophilic fluorination in presence of PS[him-^{t}OH][OMs] with CsF, which has higher periodic alkali metal fluorides among those tested, proceeded the fastest, affording the fluoroalkane product 3 along with new by-product alkoxyether 5% . Although, fluorination was fastest in *tert*-BuOH but selectivity were obtained using CH_3CN as reaction media.

Table 3. Nucleophilic substitution of the mesylate **10** with MNu using PS[him-^{t}OH][OMs] in various solvents.[a]



entry	MNu	Solvent	Time (h)	Yield (%)[b]	Comments
1	RbF	CH_3CN	3	90	5% alkene
2	RbF	*t*-BuOH	2	89	7% ether
3	KF	*t*-BuOH	12	10	88% SM
4	KF	CH_3CN	12	76	16% alkene
5	CsF	*t*-BuOH	1	92	5% ether
6	KBr	CH_3CN	80 (min)	84,	11% alkene
7	CsBr	CH_3CN	50 (min)	98	
8	CsI	CH_3CN	30 (min)	89	5 % alkene
9	KOAc	CH_3CN	1	99	
10	NaN_3	CH_3CN	4	96	

[a] All reactions were carried out on a 1.0 mmol scale of mesylate **10**, 3 mmol MNu in 5 mL CH_3CN at 100 °C. [b] Isolated yield.

Entries 6-7 shows that both the reactivity of the bromination and iodination using KBr, CsBr, and CsI, in the reaction of alkyl mesylate **1** to the corresponding alkyl halides (**3**, and **4**, respectively) in CH_3CN. In this representative dipolar aprotic solvent at 100 °C, the reaction rate is inversely dependent on the strength of their ionic bonding: the weaker the ionic bonding of the cesium halide, the higher the reactivity.

Table 4. Study of recyclability of PS[him-^{t}OH][OMs] as Catalyst.[a]

entry	PS[him-^{t}OH][OMs]	yield (%)
1		98
2	1st cycle	98
3	2nd cycle	97
4	3rd cycle	96
5	4th cycle	96

[a] Reaction carried out under the same condition as entry 7 of Table 3.

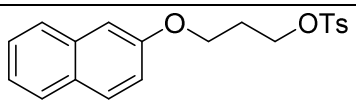
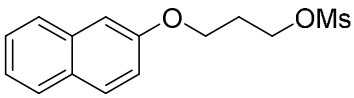
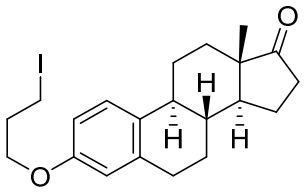
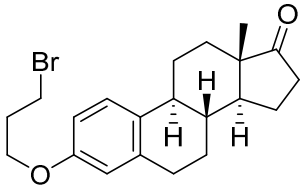
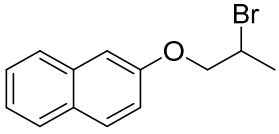
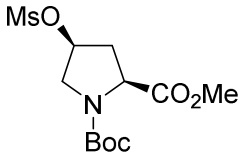
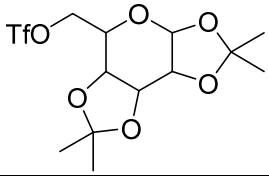
Table 4 illustrate that the bromination reactions repeatedly were performed under the same condition given entry 7 in Table 3 to verify the catalytic validity of PS[him-^{t}OH][OMs]. It is noteworthy that catalyst could certainly be reused repeatedly without the loss of its catalytic efficiency. In each cycle, desired product **12** was afforded in quantitative yield (96-98%).

Scope of other metal nucelophilies such as KOAc and NaN_3 were also afforded corresponding acetoxylation and azidation product (5 and 6, entry 9 and 10 respectively), almost quantitatively. Moreover, CH_3CN was found to be the best reaction media for nucleophilic substitution using the combination of PS[him-^{t}OH][OMs] and metal nucleophile.

Extending the scope of leaving group, Table 5 illustrates the nucleophilic substitution of various primary and secondary halide or sulfonate as leaving groups with alkali metal salts in the presence of PS[him-^{t}OH][OMs] as a catalyst. Entry 1, tosylate substrates smoothly reacted with CsF using 0.5 equiv of PS[him-^{t}OH][OMs] to give desired 2-(3-fluoropropoxy)-

naphthalene (**8**) in quantitatively. Azidation reaction of third periodic metal salt NaN_3 with 2-(3-methanesulfonyloxypropoxy)-naphthalene was gave 98% yield (entry 2). Nucleophilic fluorination with base sensitive iodo-substrates (entry 3) with KCl was converted moderately to desire 3-*O*-(3-chloro-*n*-propyl)estrone in 90% yield after reaction run for 14 h at 80 °C. Entry 4 and 5, both primary and secondary bromo substrate with KCN and CsF gave good to moderate conversion into corresponding desire product cyano and fluoroalkane respectively. Nucleophilic substitution with polar substrates secondary mesylateproline and triflatesugar (entry 6 and 7), which are difficult to extract from the ionic liquids due to their solubility in the liquid salts. Reaction of these substrates with NaN_3 and CsF using catalyst PS[him-^{t}OH][OMs] not only proceeded in high yield to affording corresponding azidopyrolidine and fluorosugar respectively, but also allowed products to be isolated and purified easily. Moreover, the PSIL system, PS[him-^{t}OH][OMs] with hexyl-chain as linker shown slightly higher PTC activity compared to PS[mim-^{t}OH][OMs].

Table 5. Nucleophilic substitution with various substrates under various reaction conditions.[a]

entry	substrate	MNu	Time	temp	Yield (%) [b]
1		CsF	4	100	93
2		NaN_3	2	100	98
3		KCl	14	80	90
4		KCN	2	100	96
5		CsF	6	60	74
6		NaN_3	12	80	92
7		CsF	1	80	93

[a]Unless otherwise noted, all reactions were carried out on a 1.0 mmol scale substrate with 3.0 equiv of MNu and 0.5 equiv of PS[him-^{t}OH][OMs] in CH_3CN.
[b]Isolated yield.

Experimental

Materials and General Method

All chemicals were obtained from commercial suppliers and were used without further purification unless otherwise stated. Flash chromatography was carried out using Merck silica gel 60 (230-400 mesh). Analytical thin layer chromatography (TLC) was performed with Merck Silica gel F-254 glass-backed plates. Visualization on TLC was monitored by UV light. ^{1}H and ^{13}C NMR spectra were recorded using both Varian (200 MHz) and Varian UNITY-INOVA 400 (400 MHz) and calibrated using residual undeuterated solvent or tetramethylsilane as an internal reference. High-resolution mass spectra were recorded using Jeol-JMS 700 and low-resolution mass spectra were obtained using VK Quattro II GC-MS/MS spectrometer (ESI or EI). Melting points were checked using OptiMelt apparatus (Stanford research systems).

Scheme 1.

Polystyrene-Supported 11-(2-hydroxy-2-methylpropyl)imidazolium Mesylate (3, PS[mim-^{t}OH][OMs]).

Merrifield peptide resin (4.0 g, 16.0 mmol, 1.0 equiv., 1% DVB, 4.0 mmol Cl/g) in 1-(2-hydroxy-2-methylpropyl)imidazole (22.5 g, 160 mmol, 10 equiv) was stirred for more than 24 h at 90 °C. The mixture was then cooled to room temperature. The resin was filtered and washed successively with dichloromethane, methanol, and finally acetone, and added to NaOMs (15.0 g, 128 mmol, 8 equivs.) in acetone (250 mL). The resulting mixture was stirred for more than 2 days at 25 °C. After filtration, the resin was washed repeatedly with acetone, acetone-water (1:1), water, acetone-water (1:1), acetone, and finally diethyl ether. After drying under high vacuum, PS[mim][OMs] was obtained and identified by elemental analysis; yield: 5.2 g; ^{13}C (100 Hz, DMSO-D_6 and $CDCl_3$) δ 26.2, 62.68, 126.44, 143.42; Anal. Found: N, 5.3 (1.9 mmol/g of 1-(2-hydroxy-2-methylpropyl) imidazolium salt).

Polystyrene-Supported 1-Methylimidazolium Mesylate (4, PS[mim][OMs]). Prepared according to the procedure used for 3 except for the use of 1-methylimidazole (250 mL) instead of 1-(2-hydroxy-2-methylpropyl)imidazole. After drying under high vacuum, 6.1 g of PS[mim][OMs] was obtained; 5.9 g. 13C (100 Hz, DMSO-D6 and CDCl3) δ 35.68, 62.56, 125.40; Anal. Found: N, 6.2 (2.2 mmol/g of imidazolium salt).

Scheme 2,

Preparation of hexanol-branched polystyrene (resin A). The aqueous phase used for the suspension polymerization reaction was prepared by dissolving acacia gum (40.0 g) and NaCl (10.0 g) in deionized water (1 L). This solution was then filtered with a tightly packed celite to remove insoluble impurities and degassed for 15 min under vacuum while being sonicated. A 1 L flange flask equipped with three-necked lid was charged with 900 mL of the aqueous solution prepared above. To this solution was added a solution of 6-(4-vinylbenzyloxy)hexanol (20.0 g, 85.4 mmol), styrene (8.89 g, 85.4 mmol), divinylbenzene (223 mg, 1.70 mmol), and benzoyl peroxide (310 mg, 1.28 mmol) in monochlorobenzene (40 mL). After the suspension was stirred at a rate of 500 rpm for 5 minutes, the spinning rate was reduced to 250 rpm. After the mixture was stirred for 12 h at 90 °C, the crude resin beads were filtered with a 400 mesh sieve, washed with warm water several times and then dried under vacuum. The resultant beads were washed by continuous extraction in Soxhlet apparatus with THF overnight, sequentially washed 50% MeOH/THF and MeOH, and dried under vacuum to give off-white resin A (28.2 g, 91%). The dried resin was sieved in four size ranges: > 50 mesh (6.12 g, 20%), 50-100 (8.94 g, 27%), 100-200 mesh (11.3 g, 36%), 200-400 mesh (900 mg, 3%).

Preparation of hexyl-O-mesylate-branched polystyrene (resin B). Hexanol-branched polystyrene (10.00 g, 38.7 mmol) and triethylamine (16.00 mL, 113.8 mmol) was suspended in CH_2Cl_2 (120 mL) by using overhead stirrer at -5 to 0 °C. Methanesulfonyl chloride (5.96 mL, 77.4 mmol) was added slowly to the suspension. After complete addition of methanesulfonyl chloride, the mixture was suspended well at 0 °C for 2 h and additional 3 days at room temperature. After filtration, the resultant resin was successively washed with CH_2Cl_2, THF, acetone and finally diethyl ether. After drying under high vacuum, 12.3 g of resin **B** was obtained.

Polystyrene-supported 1-n-Hexyl-3-(2-hydroxy-2-methylpropyl)imidazolium Mesylate (**5**, PS[him-^{t}OH][OMs]). Resin **B** (3.00 g, ca. 7.08 mmol) and 1-(2-hydroxy-2-methylpropyl)imidazole (1.20 g, 14.10 mmol) were used to obtain 3.68 g of pale yellow PS[him-^{t}OH][OMs] (5): ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6) δ 25.2, 26.3, 48.5, 58.5, 60.6, 122.0, 127.0, 136.6; FTIR vmax (cm-1) 3418, 2927, 2855, 1637, 1611, 1511, 1455, 1396, 1364, 1307, 1209, 1094, 1016. Anal. Found: N, 4. 8 (1.7 mmol/g of imidazolium salt).

Polystyrene-supported 1-n-Hexyl-3-methylimidazolium Mesylate (**6**, PS[hmim][OMs]). Resin B (1.00 g, ca. 2.36 mmol) and 1-methylimidazole (0.94 mL, 11.8 mmol) were used to obtain 1.16 g of off-white PS[hmim][OMs] (6): ^{13}C NMR (100 MHz, $CDCl_3$ and DMSO-d_6) δ 25.2, 29.2, 32.6, 45.1, 52.1, 60.6, 126.8; FTIR ν_{max} (cm^{-1}) 2924, 2853, 2361, 1654, 1637, 1571, 1511, 1457, 1421, 1363, 1103, 1044. Anal. Found: N, 4.57 (1.63 mmol/g of imidazolium salt).

Typical Procedure of the Fluorination in Table 1.
A suspension of mesylate **7** (280 mg, 1.00 mmol), CsF (454 mg, 3.00 mmol), polymer catalyst 5 (295 mg) and CH_3CN (5 mL) in a reaction vial pretreated with Sigmacote® was stirred at 100 °C. After complete reaction, the mixture was filtered and washed with EtOAc. The filtrate was concentrated by a rotary evaporator. The crude mixture was purified by flash column chromatography (20% EtOAc/hexane) to afford 2-(3-fluoropropoxy)naphthalene (8) as a colorless oil. ^{1}H NMR (200

MHz, $CDCl_3$) 2.25 (dm, J = 26.0 Hz, 2H), 4.23 (t, J = 6.2 Hz, 2H), 4.70 (dt, J = 46.8, 5.8 Hz, 2H), 7.14-7.16 (m, 2H), 7.34 (t, J = 6.8 Hz, m, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.72-7.78 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 30.4 (d, J = 19.7 Hz), 63.5 (d, J = 5.3 Hz), 80.8 (d, J = 163.0 Hz), 106.7, 118.8, 123.7, 126.4, 126.7, 127.6, 129.0, 129.4, 134.5, 156.7; HRMS (EI) calcd for $C_{13}H_{13}FO$ (M^+) 204.0950, found 204.0947.

General Procedure of Figure 2. A suspension of mesylate **7** (280 mg, 1.00 mmol), KF/KI (3.00 mmol), catalyst 3 (0.50 mmol: 100 mg)/ catalyst 5 (0.50 mmol: 295 mg) and CH_3CN (5 mL) in a reaction vial pretreated with Sigmacote® was stirred at 80 °C. After complete reaction, the mixture was filtered and washed with EtOAc. The filtrate was concentrated by a rotary evaporator. The crude mixture was purified by flash column chromatography (20% EtOAc/hexane) to afford 2-(3-fluoropropoxy)naphthalene (**8**) or 2-(3-iodopropoxy)naphthalene (**9**).

2-(3-iodopropoxy)naphthalene (**9**). CAS No.: 380363-99-5. White solid: m.p. 50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 2.32-2.38 (m, 2H), 3.43 (t, J = 6.6 Hz, 2H), 4.16 (t, J = 5.8 Hz, 2H), 7.15-7.17 (m, 2H), 7.35-7.49 (m, 2H), 7.49-7.80 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 2.7, 32.8, 67.1, 106.6, 118.8, 123.6, 126.4, 126.7, 127.6, 128.1, 129.4, 134.4, 156.5; HRMS (EI) m/z calcd for $C_{13}H_{13}OI$ (M^+) 312.0011. Found 312.0013.

General Procedure for nucleophilic substitutions Table 3

3-O-(3-Azidopropyl)estrone (**15**): Sodium azide (325 mg, 5.0 mmol) was added to a mixture of mesylate **10** (406 mg, 1.0 mmol), catalyst **5** (0.50 mmol: 295 mg) in CH_3CN (5 mL) in a reaction vial. The mixture was stirred at 100 °C. After complete reaction, the mixture was filtered and washed with diethyl ether. Then reaction mixture was extracted with diethyl ether (10 mL × 3). The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The product conversion yield was determined by ^{1}H NMR and purified by flash column chromatography (20% EtOAc/hexane) to give 3-O-(3-Azidopropyl)estrone (**15**). White solid. m.p. 78.2-80.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 3H), 1.43-1.62 (m, 6H), 1.93-2.16 (m, 6H), 2.24 (br, 1H), 2.37-2.53 (m, 2H), 2.88 (t, J = 3.2 Hz, 2H), 3.50 (t, J = 6.4 Hz, 2H), 4.02 (t, J = 6.0 Hz, 2H), 6.64 (d, J = 2.0 Hz, 1H), 6.71 (dd, J = 8.4, 6.0 Hz, 1H), 7.19 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 21.6, 25.9, 26.5, 28.8, 29.6, 31.6, 35.8, 38.3, 43.9, 48.0, 48.6, 50.4, 64.4, 112.1, 114.5, 126.4, 132.3, 137.8, 156.7, 220.9; MS (EI) *m/z* 353([M]$^+$), 270 (100), 146; HRMS (EI) calcd for $C_{21}H_{27}N_3O_2$: [M]$^+$ 353.2103. Found 353.2100.

3-O-(3-Fluoropropyl)estrone (11). White solid: m.p. 78.3-80.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 3H), 1.43-1.62 (m, 6H), 1.96-2.19 (m, 7H), 2.38 (b 1H), 2.47 (d, J = 8.4 Hz, 1H), 2.88 (q, J = 3.6 Hz, 2H), 4.07 (t, J = 6.0 Hz, 2H), 4.63 (dt, J = 46.8, 6.0 Hz, 2H), 6.65 (d, J = 2.4 Hz, 1H), 6.71 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 21.5, 25.9, 26.5, 29.6, 30.4 (d, J = 20.0 Hz), 31.5, 35.8, 38.3, 43.9, 47.9, 50.4, 63.4 (d, J = 4.8 Hz), 80.7 (d, J = 163.0 Hz), 112.1, 114.5, 126.3, 132.2, 137.7, 156.7, 220.9. HRMS (EI) calcd for $C_{21}H_{27}FO_2$: [M]$^+$ 330.1995. Found 330.1993.

3-O-(3-Bromopropyl)estrone (12). CAS No. 975-65-5. White solid: m.p. 137.8-138.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (s, 3H), 1.39-1.69 (m, 7H), 1.92-2.19 (m, 3H), 2.26 (s, 1H), 2.29 (q, J = 6.4 Hz, 2H), 2.39 (br, 1H), 2.46-2.58 (m, 1H), 2.87-2.90 (m, 2H), 3.59 (t, J = 6.4 Hz, 2H), 4.07 (t, J = 6.0 Hz, 2H), 6.65 (d, J = 2.8 Hz, 1H), 6.71 (dd, J = 8.8, 2.8 Hz, 1H), 7.19 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 21.5, 25.9, 26.5, 29.6, 30.1, 31.5, 32.4, 35.8, 38.3, 43.9, 48.0, 50.4, 65.2, 112.1, 114.5, 126.3, 132.3, 137.8, 156.6, 220.8; MS (EI) *m/z* 390([M]$^+$, 100), 305, 266. HRMS (EI) calcd for $C_{21}H_{27}BrO_2$: [M]$^+$ 390.1194. Found 390.1197.

3-O-(3-Iodopropyl)estrone (13). CAS No. 953788-37-9. White solid: m.p. 102.3-103.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 3H), 1.43-1.61 (m, 7H), 1.93-2.15 (m, 4H), 2.24 (q, J = 6.8 Hz, 2H), 2.37 (br, 1H), 2.46-2.52 (m, 1H), 2.87-2.89 (m, 2H), 3.35 (t, J = 6.8 Hz, 2H), 4.00 (t, J = 6.0 Hz, 2H), 6.64 (d, J = 2.8 Hz, 1H), 6.71 (dd, J = 8.8, 2.8 Hz, 1H), 7.19 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 2.6, 13.7, 21.5, 25.8, 26.4, 29.6, 31.5, 33.0, 35.8, 38.2, 43.8, 48.0, 50.3, 67.0, 112.1, 114.5, 126.3, 132.2, 137.7, 156.6, 220.8; MS (EI) *m/z* 438([M]$^+$, 100), 310. HRMS (EI) calcd for $C_{21}H_{27}IO_2$: [M]$^+$ 438.1056. Found 438.1055.

3-O-(3-Acetoxypropyl)estrone (14). White solid: m.p. 72-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 3H), 1.43-1.64 (m, 7H), 1.93-2.02 (m, 2H), 2.04 (s, 3H), 2.05-2.16 (m, 4H), 2.25-2.26 (m, 1H), 2.37-2.39 (m, 1H), 2.46-2.53 (m, 1H), 2.87-2.90 (m, 1H), 4.01 (t, J = 6.0 Hz, 2H), 4.24 (t, J = 6.0 Hz, 2H), 6.63 (d, J = 2.8 Hz, 1H), 6.70 (d, J = 2.8 Hz, 1H), 7.19 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 21.0, 21.6, 26.0, 26.5, 28.6, 29.6, 31.5, 35.8, 38.3, 43.9, 48.0, 50.4, 61.3, 64.2, 112.1, 114.5, 126.3, 132.2, 137.7, 156.7, 171.1, 220.9; MS (EI) *m/z* 370([M]$^+$), 101(100). HRMS (EI) calcd for $C_{23}H_{30}O_4$: [M]$^+$ 370.2144. Found 370.2146.

Recycling Procedures of Catalyst 5, Table 4.
CsBr (1.0 g, 5.0 mmol) was added to a mixture of mesylate **10** (406 mg, 1.0 mmol), catalyst **5** (0.50 mmol: 295 mg) in CH_3CN (5 mL) in a reaction vial. The mixture was stirred at 100 °C. After complete reaction, the mixture was filtered and washed with diethyl ether. Then reaction mixture was extracted with diethyl ether (10 mL × 3). The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was purified by flash column chromatography (20% EtOAc/hexane) to give 3-O-(3-Bromopropyl)estrone (**12**). The filtered catalyst **5** was washed with water, acetone, THF, methanol, CH_2Cl_2, and finally diethyl ether and dried under vacuum. The recovered catalyst **5** was reused in the same reaction four times.

Products of Table 5,

Entry 2 in Table 5: 2-(3-Azidopropoxy)naphthalene. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.09-2.15 (m, 2H), 3.56 (t, *J* = 6.8 Hz, 2H), 4.17 (t, *J* = 6.0 Hz, 2H), 7.13-7.15 (m, 2H), 7.22-7.25 (m, 1H), 7.41-7.45 (m, 1H), 7.71-7.78 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.8, 48.4, 64.5, 106.6, 118.7, 123.6, 126.3, 126.6, 127.5, 129.0, 129.3, 134.4, 156.4; MS (EI) *m/z* 227([M]$^+$), 169, 143(100), 115. HRMS (EI) calcd for $C_{13}H_{13}N_3O$: [M]$^+$ 227.1059. Found 227.1060.

Entry 3 in Table 5: 3-O-(3-Chloropropyl)estrone. White solid. m.p. 102-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 3H), 1.43-1.64 (m, 6H), 1.93-2.24 (m, 7H), 2.37-2.39 (m, 1H), 2.46-2.53 (m, 1H), 2.87-2.90 (m, 2H), 3.73 (t, *J* = 6.4 Hz, 2H), 4.08 (t, *J* = 5.6 Hz, 2H), 6.65 (d, *J* = 2.8 Hz, 1H), 6.71 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 21.6, 25.9, 26.5, 29.6, 31.6, 32.3, 35.8, 38.3, 41.5, 44.0, 48.0, 50.4, 64.2, 112.1, 114.5, 126.4, 132.3, 137.8, 156.7, 220.9; MS (EI) *m/z* 346([M]$^+$, 100), 261, 222. HRMS (EI) calcd for $C_{21}H_{27}ClO_2$: [M]$^+$ 346.1700. Found 346.1702.

Entry 4 in Table 5: 3-O-(3-Cyanopropyl)estrone. as a white solid: m.p. 119-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43-169 (m, 10H), 1.93-2.16 (m, 7H), 2.46-2.53 (m, 1H), 2.57 (t, J = 7.2 Hz, 2H), 2.87-2.90 (m, 2H), 4.05 (t, J = 6.0 Hz, 2H), 6.63 (d, J = 2.4 Hz, 1H), 6.70 (dd, J = 8.4, 2.4 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 14.1, 21.5, 25.5, 25.8, 26.4, 29.6, 31.5, 35.8, 38.2, 43.9, 48.0, 50.3, 65.2, 112.0, 114.5, 119.1, 126.4, 132.6, 138.0, 156.3, 220.8; MS (EI) m/z 337([M]$^+$, 100), 252, 213. HRMS (EI) calcd for $C_{22}H_{27}NO_2$: [M]$^+$ 337.2042. Found 337.2042.

Entry 5 in Table 5: 2-(2-Fluoro-n-propoxy)naphthalene. Colorless liquid; ^{1}H NMR (400 MHz,$CDCl_3$) δ 1.50 (dd, *J* = 23.6, 6.4 Hz, 3H), 4.09-4.24 (m, 2H), 5.00-5.16 (m, 1H), 7.13-7.46 (m,4H), 7.71-7.78 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5 (d, *J* = 22.0 Hz), 70.7 (d, *J* =23.5 Hz), 88.3 (d, *J* = 167.5 Hz), 106.7, 118.7, 123.7, 126.3, 126.6, 127.5, 129.0, 129.4, 134.3,156.3; MS (EI) 204 (M+), 144 (100), 115. HRMS (EI) calcd for $C_{13}H_{13}FO$ (M+) 204.0950, found 204.0947.

Entry 6 in Table 5: N-BOC-cis-4-azido-L-proline methyl ester. CAS No. 84520-68-3; as a yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.41 (s, 9H), 1.46 (s, 9H), 2.14 (t, *J* = 4.4 Hz, 1H), 2.17 (t, *J* = 4.4 Hz, 1H), 2.41-2.51 (m, 2H), 3.42-3.50 (m, 2H), 3.66-3.79 (m, 8H), 4.12-4.15 (m, 2H), 4.31 (dd, *J* = 8.8, 4.4 Hz, 1H), 4.42 (dd, *J* = 8.8, 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.1, 28.3, 35.0, 35.9, 50.7, 51.2, 52.2, 52.3, 57.2, 57.6, 58.2, 59.1, 80.5, 153.3, 171.8, 172.2. HRMS (EI) calcd for $C_{11}H_{18}N_4O_4$ (M+) 270.1328, found 270.1327.

Entry 7 in Table 5: 1,2 : 3,4-di-O-isopropylidene-6-fluoro-6-deoxy-β-D-galactopyranose. CAS No. 2021-97-8; obtained 246 mg (94%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 6H), 1.43 (s, 3H), 1.53 (s, 3H), 4.02-4.09 (m, 1H), 4.24-4.26 (m, 1H),4.32-4.34 (m, 1H), 4.43-4.52 (m, 1H), 4.55-4.64 (m, 2H), 5.53 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 24.3, 24.8, 25.8, 25.9, 66.5 (d, *J* = 22.8 Hz), 70.3, 70.4 (d, *J* = 6.1 Hz), 70.4, 82.0 (d, *J* = 167.6 Hz), 96.1, 108.7, 109.5 HRMS (EI) calcd for $C_{12}H_{19}FO_5$ (M+) 262.1217, found 262.1220.

Conclusions

In summary, we have prepared the various morphological polystyrene-supported *tert*-alcohol functionalized imidazolium salts that act as highly efficient heterogeneous catalysts for nucleophilic substitution reactions using alkali metal salts as a nucleophilic source. PS[him-^{t}OH][OMs] having hexyl chain as a linker was shown better catalytic activity among the tested, which convert various haloalkanes and sulfonyloxyalkanes to their corresponding substituted products. Moreover, a higher ionic liquid [him-^{t}OH][OMs] loading catalyst have high catalytic activities in nucleophilic fluorination with better selectivity. Furthermore, this PSIL enhance the reactivity of alkali metal salts in various reaction such as azidation, cyanation, iodination, bromination, chlorination, acetylation and fluorination, indicating that hydroxyl group of PS[him-^{t}OH][OMs] may offer a great benefit on certain nucleophilic substitution reactions, specially fluorine as nucleophile. In practical merits: product recovery, purification is simple and catalyst recovery and reuse could be useful in industrial chemical process.

Acknowledgements

S.S.Shinde would like to thank Department of Science and Technology (DST) Government of India for the Young scientist project Fast Track and Ramanujan fellowship scheme for is gratefully acknowledged. Thanks to Director CSIR-NCL for constant support, the CSIR for providing junior research fellowship to S.P.

Notes and references

Division of Organic Chemistry, National Chemical Laboratory (CSIR-NCL), Dr. homi Bhabha Road, Pashan, Pune 411008, India. E-mail: ss.shinde@ncl.res.in

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [NMR data of all compound are available, supplementary data associated with this article can be found]. See DOI: 10.1039/b000000x/

1 (a) M. D. Smith, J. March, *Advanced Organic Chemistry*, 5th ed.; Wiley-Interscience: New York, NY, **2001**, pp 389-674; (b) O. A. Mascaretti, *Aldrichimica Acta* **1993**, *26*, 47-58; (c) T. Tajima, A. Nakajima, Y. Doi, T. Fuchigami, *Angew. Chem., Int. Ed.* **2007**, *46*, 3550-3552; (d) J. W. Lee, H. Yan, H. B. Jang, H. K. Kim, S-W. Park, S. Lee, D. Y. Chi, C. E. Song, *Angew. Chem., Int. Ed.* **2009**, 48, 7683–7686; (e) D. W. Kim, H.-J Jeong, S. T. Lim, M.-H. Sohn, J. A. Katzenellenbogen, D. Y. Chi, *J. Org. Chem.* **2008**, *73*, 957-962.

2 (a) E. V. Dehmlow, S. S. Dehmlow,*Phase Transfer Catalysis*, 3rd ed.; VCH Ltd.:New York, NY, **1993**; (b) Sun, H.; DiMagno, S. G. *J. Am. Chem. Soc.* **2005**, 127, 2050-2051; (c) D. W. Kim, H.-J Jeong, S. T. Lim, M.-H. Sohn, *Tetrahedron Lett.* **2010**, *51*, 432-434; (d) T. Ooi, K. Maruoka, *Acc. Chem. Res.* **2004**, *37*, 526-533.

3 (a) J. H. Clark, *Chem. Rev.* **1980,** *80*, 429-452. (b) A. S. Pilcher, H. L. Ammon, P. DeShong, *J. Am Chem Soc.* **1995**, *117*, 5166-5167.

4 (a) P. S. Shinde, S. S. Shinde, A. S. Renge, A. B. Rode, R. P. Pawar, *Lett. Org. Chem.,* **2009**, *6*, 8-10 (b) Y. R. Jorapur, C.-H. Lee, D. Y. Chi, *Org. Lett.* **2005**, *7*, 1231–1234; (c) Y. R. Jorapur, D. Y. Chi, *J. Org. Chem.* **2005**, *70*, 10774–10777; (d) D. W. Kim, C. E. Song, D. Y. Chi, *J. Am. Chem. Soc.* **2002**, *124*, 10278–10279; (e) D. W. Kim, C. E. Song, D. Y. Chi, *J. Org. Chem.* **2003**, *68*, 4281–4285;

5 For recent reviews on ionic liquids, see: (a) J. P. Hallett, T. Welton, *Chem Rev.* **2011**, *111*, 3508-3576; (b) R. Sheldon, *Chem. Commun.* **2001**, 2399–2407; (c) P. Wasserscheid, W. Keim, *Angew. Chem., Int. Ed.* **2000**, *39*, 3772–3789; (d) J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667–3692; (e) J. Dupont, P. A. Z. Suarez, *Phys. Chem. Chem. Phys.* **2006**, *8*, 2442–2452.

6 (a) Imperato, B. Ko¨nig, C. Chiappe, *Eur. J. Org. Chem.* **2007**, 1049-1058; (b) S.-G. Lee, *Chem. Commun.* **2006**, 1049-1063; (c) Z. Fei, T. J. Geldbach, D. Zhao, P. J. Dyson, *Chem. Eur. J.* **2006**, *12*, 2122-2130; (d) C. Chiappe, D. Pieraccini, P. Saullo, *J. Org. Chem.* **2003**, *68*, 6710-6715; (e) E. D. Bates, R. D. Mayton, I. Ntai, J. H. Davis, *J. Am. Chem. Soc.* **2002**, *124*, 926-927; (f) J. H. Devis, *Chem. Lett.* **2004**, *33*, 1072-1077.

7 (a) K. S. Eqorova, V. P. Ananikov, *ChemSusChem* **2014**, *7*, 336-360; (b) A. Riisager, B. Jørgensen, P. Wasserscheid, R. Fehrmann, *Chem. Commun.* **2006**, 994-996.

8 (a) M. Tomoi, E. Nakamura, Y. Hosokawa, H. Kakjuchi, *J. Polym. Sci. Polym. Chem. Ed.* **1985**, *23*, 49-61; (b) S. Desikan, L. K. Doraiswamy, *Ind. Eng. Chem. Res.* **1995**, *34*, 3524–3537; (c) P. McMorn, G. J. Hutchings, *Chem. Soc. Rev.* **2004**, *33*, 108–122.

9 (a) S. L. Regen, *J. Am. Chem. Soc.* **1975**, *97*, 5956–5957; (b) F. Montanari, S. Quici, P. Tundo, *J. Org. Chem.* **1981**, *46*, 2125–2130; (c) O. Arrad, Y. Sasson, *J. Org. Chem.* **1989**, *54*, 4993–4998; (d) P. Tundo, P. Venturello, *J. Am. Chem. Soc.* **1981**, *103*, 856–861.

10 For reviews on Polymer-supported catalysts, see (a) M. Benaglia, A. Puglisi, F. Cozzi, *Chem Rev.* **2003**, *103*, 3401-3429; (b) T. E. Kristensen, T. Hansen, *Eur. J. Org. Chem.* **2010**, *2010*, 3179-3204; (c) C. M. Starks, *J. Am. Chem. Soc.* **1971**, *93*, 195–199; (b) S. D. Naik, L. K. Doraiswamy, *AICHE J.* **1998**, *44*, 612–646.

11 (a) D. W. Kim, D. Y. Chi, *Angew. Chem., Int. Ed.* **2004**, *43*, 483-485; (b) D. W. Kim, D. J. Hong, K. S. Jang, D. Y. Chi, *Adv. Synth. Catal.* **2006**, 348, 1719–1727; (c) J. Jadhav, V. Gaikwad, R. Kurane, R. Salunkhe, G. Rashinkar, *Tetrahedron,* **2013**, *69*, 2920-2926.

12 For recent reviews on Solid-supported ionic liquids, see (a) Y. Gu, G. Li, *Adv. Synth. Catal.* **2009**, 351, 817–847; (b) C. P. Mehnert, *Chem. Eur. J.* **2004**, *11*, 50-56; (c) R. Giernoth, *Angew. Chem., Int. Ed.* **2010**, *49*, 2834-2839.

13 (a) S. S. Shinde, B. S. Lee, D. Y. Chi, *Org. Lett.* **2008**, *10*, 733–735. (b) S. S. Shinde, H. M. Chi, B. S. Lee, D. Y. Chi, *Tetrahedron Lett.* **2009***, 50,* 6654-6657.

14 S. S. Shinde, B. S. Lee, D. Y. Chi, *Tetrahedron Lett.* **2008***, 49,* 4245-4248.