Journal of Molecular Catalysis A: Chemical 349 (2011) 63–70

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Preparation, characterization and use of 3-methyl-1-sulfonic acid imidazolium hydrogen sulfate as an eco-benign, efficient and reusable ionic liquid catalyst for the chemoselective trimethylsilyl protection of hydroxyl groups

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ARTICLE INFO

Article history:
Received 1 August 2011
Received in revised form 23 August 2011
Accepted 23 August 2011
Available online 31 August 2011

Keywords:
Ionic liquid catalyst
Protection
Green chemistry
Trimethylsilanes
Hydroxyl compounds

ABSTRACT

New and novel ionic liquid (3-methyl-1-sulfonic acid imidazolium hydrogen sulfate) is a recyclable and eco-benign catalyst for the chemoselective trimethylsilyl protection of hydroxyl groups under solvent-free conditions to afford trimethylsilanes in excellent yields (92–100%) and in very short reaction times (1–8 min). The catalyst was characterized by FT-IR, ^{1}H NMR and ^{13}C NMR studies. All the products were extensively characterized by ^{1}H NMR, IR, GC–MS and melting point analyses. A mechanism for the catalytic activity is proposed. The catalyst can be recovered and reused without loss of activity. The work-up of the reaction consists of a simple separation, followed by concentration of the crude product and purification.

1. Introduction

Ionic liquids (based imidazolium or other organic cations) have received considerable interest as eco-friendly solvents, catalysts and reagents in green synthesis because of their unique properties, such as low volatility, nonflammability, high thermal stability, negligible vapor pressure and ability to dissolve a wide range of materials [1–9]. Among them, Brønsted acidic ionic liquids have designed to replace solid acids and traditional mineral liquid acids like sulfuric acid and hydrochloric acid in chemical procedures [10–14]. As mentioned imidazolium salts having a Brønsted acidic group are of importance, and they have been successfully utilized as catalyst in organic synthesis. These subjects encouraged us to synthesize functionalized imidazolium salt, with Brønsted acidic property, including ionic liquid 3-methyl-1-sulfonic acid imidazolium hydrogen sulfate {[Msim]HSO_4}. We wish to use it as catalyst for different organic transformations.

Transformation of hydroxyl groups to their trimethylsilyl ethers is of value from different views [15]. This conversion enhances solubility of the compounds in non-polar solvents, increases thermal stability, and used extensively to increase volatility of the compounds for gas chromatography and mass spectrometry as well. Moreover, protection of hydroxyl groups and their transformation to the corresponding silyl ethers is of vital importance in the total synthesis of complex organic molecules. For these vast applications of silyl ethers presentation of new methods, using new catalysts is of demand from industries and academia. Generally, the formation of silylethers was carried out by the treatment of alcohols with silylchlorides or silyl triflates under the influence of basic conditions [16]. However, some of these methods frequently suffered from drawbacks such as lack of reactivity and the difficulty in removing amine salts derived from the reaction of produced acids and bases during the course of the reaction. Hexamethyldisilazane (HMDS) is a cheap and commercially available reagent that can be used for the preparation of trimethylsilyl ethers from hydroxyl compounds. O-Silylation of alcohols using HMDS is an attractive alternative, since the only by-product of the reaction is ammonia which is easily removed from the reaction mixture. However, its main drawback is its poor silylating power, which needs forceful conditions and long reaction times [17]. A variety of catalysts have been reported for the activation of HMDS; of them trichloroisocyanuric acid (TCCA) [18], zirconium sulfophenyl phosphonate [19], $ZnCl_2$ [20], Envirocat EPZGO [21], tungstophosphoric acid [22], K-10 montmorillonite [23], iodine [24], lithium perchlorate [25], cupric sulfate pentahydrate [26], H-β zeolite [27], $MgBr_2$ [28], lithium perchlorate supported on silica gel [29], sulfonic acid-functionalized silica [30], magnesium triflate [31], $InBr_3$ [32], zirconium triflate [33], $ZrCl_4$ [34], NBS [35], iron(III) trifluoroacetate [36], silica supported perchloric acid [37], Fe_3O_4 [38], poly(N-bromobenzene-1,3-disulfonamide)

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doi:10.1016/j.molcata.2011.08.021

[39], barbutric acid [40], $Al(H_2PO_4)_3$ [41], tetrabutylammonium phtalimide-N-oxyl (TBAPINO) [42], $TiCl_3(OTf)$ [43], Nafion® SAC-13 [44] and Bu_4NBr [45] are ones. Although the silylation ability of HMDS has been promoted in the presence of these catalysts, yet some of the presented methods suffer from long reaction times, low yields, and drastic reaction conditions and sometimes, a tedious workup is required. In addition, in most of the reported methods, selectivity of the protocols is either poor or is not reported properly. Consequently, a new procedure that addresses these drawbacks is desirable.

2. Experimental

Chemicals were purchased from Merck, Aldrich and Fluka Chemical Companies and used without further purification. The purity determination of the products was accomplished by TLC on silica gel polygram SIL G/UV 254 plates. The MS were measured under GC (70 eV) conditions. The FTIR spectra were recorded on a PerkinElmer 781 Spectrophotometer. In all the cases the ^1H NMR spectra were recorded with Bruker Avance 300 MHz instrument. Chemical shifts are reported in parts per million in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR data were collected on Bruker Avance 75 MHz instrument.

2.1. General procedure for the preparation of ionic liquid [Msim]HSO_4 (Scheme 1)

A round-bottomed flask (50 ml) was charged with 1-methylimidazole (0.492 g, 6.0 mmol) in dry CH_2Cl_2 (10 ml), and then chlorosulfonic acid (0.700 g, 6.0 mmol) was added dropwise over a period of 10 min at ice-bath. After the addition was completed, the reaction mixture was stirred for 40 min, then sulfuric acid 96% (0.588 g, 6.0 mmol) was added dropwise over a period of 3 min at room temperature. The reaction mixture was stirred for 8 h under pressure of nitrogen (to remove the produced HCl), heat for 60 min at 45 °C, and the CH_2Cl_2 was decanted. The residue was washed with dry CH_2Cl_2 (3×20 ml) and dried under vacuum to give [Msim]HSO_4 as a viscous pale yellow oil in 95% yield, 1.691 g.

2.1.1. Spectral data of ionic liquid [Msim]HSO_4

Viscous pale yellow oil: FT-IR (liquid film): 3419, 1639, 1510, 1288, 1171, 1063, 1011, 881, 881 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ (ppm) 3.74 (s, 3H, CH3), 7.43 (s, 1H), 7.50 (s, 1H), 8.81 (s, 1H), 12.24 (s, 1H), 13.92 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 36.5, 120.6, 124.2, 136.6; MS: m/z = 261 (M^++1), 260 (M^+), 245 (M^+-CH_3), 179 (M^+-SO_3H), 164 (M^+-CH_3SO_3H), 148 (M^+-CH_3SO_4H), 67 (M^+-$CH_3SO_3HSO_4H$).

2.2. General procedure for O-silylation of alcohols and phenols with HMDS in the presence of [Msim]HSO_4 ionic liquid

Ionic liquid [Msim]HSO_4 (5 mg, ~0.02 mmol) was added to a stirred mixture of alcohol, phenol or naphthol (1.0 mmol) and HMDS (97 mg, 0.6 mmol), and the mixture was stirred at room temperature under solvent-free conditions for the time mentioned in Tables 2 and 3. After completion of the reaction (monitored by TLC), the ionic liquid was recovered by decanted and washed with Et_2O (2×5 ml). The product was extracted with Et_2O, washed with water then dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure gave the highly pure product without further purification. The desired pure products were characterized by comparison of their IR and NMR data as well as boiling point with those of known compounds [5,9,10,23,30,41,44,45].

3. Results and discussion

3.1. Characterization of catalyst

Fig. 1 presents the graphical FTIR spectra of starting 1-methyl imidazole and 3-methyl-1-sulfonic acid imidazolium hydrogen sulfate. Asymmetric and symmetric SO_2 stretching vibrations appeared as strong absorptions at 1325.01 (asy SO_2), 1172.64 (sy SO_2), respectively, that were absent in 1-methyl imidazole [46]. The

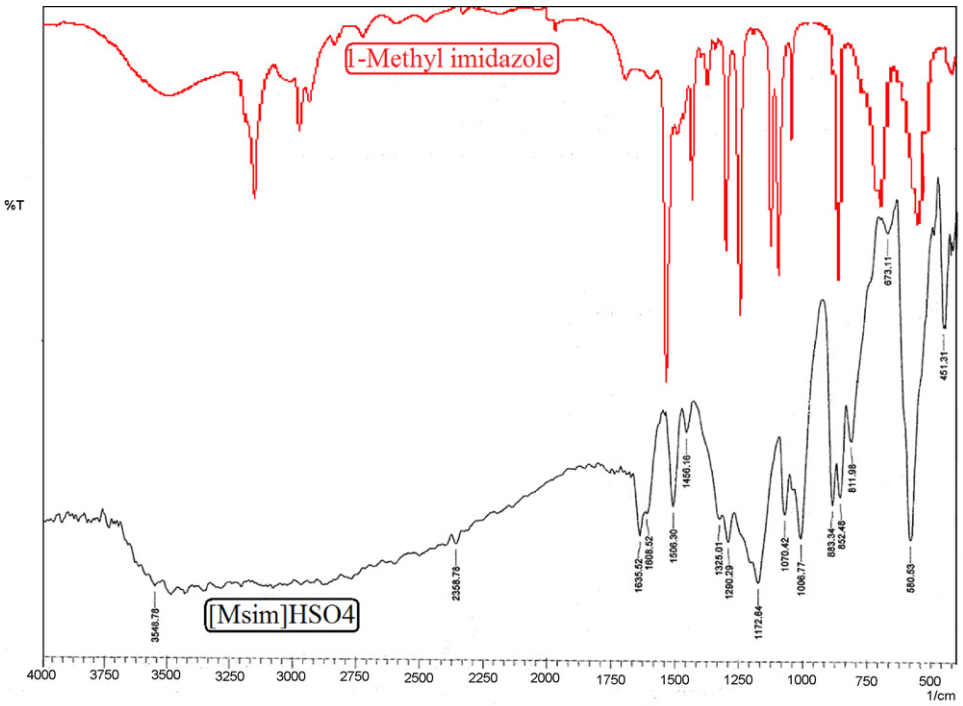


Fig. 1. FTIR spectra of 1-methyl imidazole (upper) and 3-methyl-1-sulfonic acid imidazolium hydrogen sulfate (bottom){[Msim]HSO_4}.

symmetric S–N stretching vibration also appeared at 883.34 cm^{-1}. This special IR peaks indicated that sulfonic and sulfate groups were successfully introduced in the 1-methyl imidazole molecule. On the other hand, the presence of an sulfonic acid group on the imidazole nitrogen in the [Msim]HSO_4 ionic liquid increased the number of vibrational modes and brought completely different FTIR spectrum. The strong band at 1639.38 cm^{-1} arising from the sulfonated imidazole ion appears and The CH-aromatic bands at 3091.68 and 3161.11 cm^{-1} become very weak. In imidazole ring, the electrons of carbon atoms and that of nitrogen atoms are delocalized to form aromatic rings. The observed effect may be therefore ascribed to "some changes in aromatic ring" as a consequence of the sulfonated imidazole formation. By comparison with SOH bending frequencies in sulfuric acid and other sulfonic acids, the band at 1070.42 cm^{-1} is assigned to SOH bend [47]. The Broad and strong band at 3200–3550 cm^{-1} arising from the hydroxyl groups in the [Msim]HSO_4 ionic liquid.

The corresponding spectral data have been reported in Section 2. Moreover, the graphical ^1H and ^{13}C NMR spectra of the [Msim]HSO_4 ionic liquid are presented in Fig. 2. The important peaks of ^1H NMR spectra of ionic liquid 3-methyl-1-sulfonic acid imidazolium hydrogen sulfate were related to the acidic hydrogen

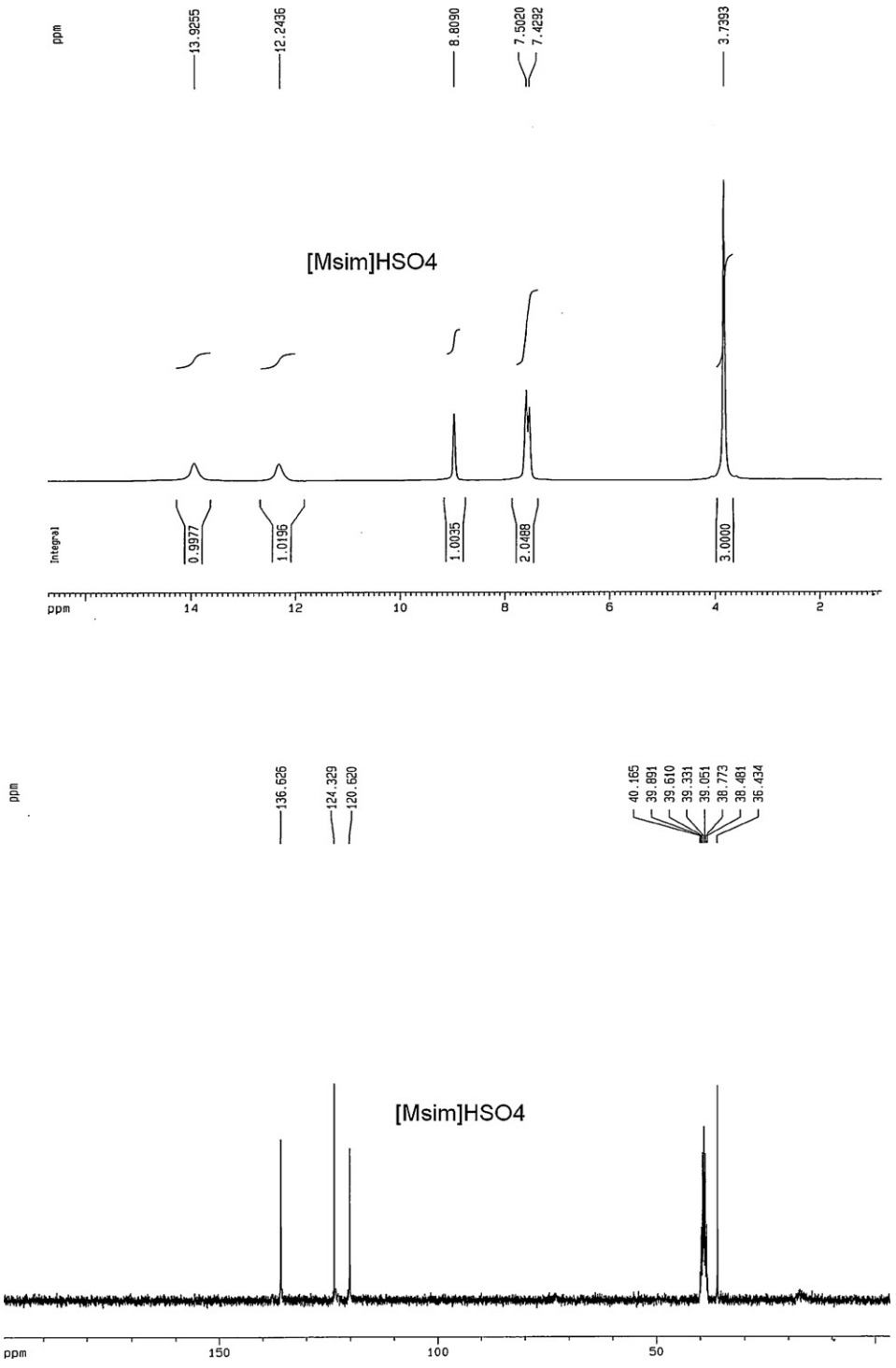


Fig. 2. ^1H NMR and ^{13}C NMR of 3-methyl-1-sulfonic acid imidazolium hydrogen sulfate [Msim]HSO_4 ionic liquid.

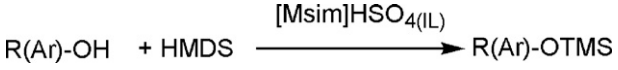
Table 1
The protection of 4-chlorobenzyl alcohol with HMDS using $[Msim]HSO_4$ ionic liquid, chlorosulfonic acid, sulfuric acid, 1-methylimidazole, 1-methylimidazolium chloride.[a]

Entry	Catalyst (2 mol%)	Time	Yield (%)[c]
1	–	6 h	N.R.
2	$[Msim]HSO_4$	1 min	98
3	[Msim]Cl	8 min	82
4	$ClSO_3H$[b]	–	N.R.
5	H_2SO_4[b]	–	N.R.
6	1-Methyl imidazole	85 min	34
7	1-Methyl imidazolium chloride	110 min	32

[a] The amounts of 4-chlorobenzylalcohol, HMDS and the catalyst in all reactions were 1 mmol, 0.6 mmol, 0.02 mmol, respectively, in room temperature under solvent-free conditions.
[b] Degradation of HMDS.
[c] Isolated and unoptimized yields.

(SO_3H) and (HSO_4) which observed in 12.24 and 13.92 ppm. To confirm that these peaks (12.24 and 13.92 ppm) were really related to the hydrogen of SO_3H and HSO_4 in the compound, not hydrogen of H_2SO_4, $ClSO_3H$ (its unreacted starting material) and HCl (formed from the reaction chloride anion with hydrogen acidic of sulfuric acid) or 1-methylimidazolium chlorosulfonate product formed from the reaction of 1-methylimidazole with $ClSO_3H$, we also run the ^1H NMR spectra of H_2SO_4, $ClSO_3H$, 1-methylimidazolium chloride (because the acidic hydrogen of 1-methylimidazolium chlorosulfonate and 1-methylimidazolium chloride are same) and intermediate 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} in DMSO-d_6. In these spectra, the peaks of the acidic hydrogen of H_2SO_4, [Msim]Cl, $ClSO_3H$ and 1-methylimidazolium chloride were observed in 14.32, 13.96, 13.45 and 8.46 ppm, respectively. The difference between the peaks of the acidic hydrogen in H_2SO_4, [Msim]Cl, $ClSO_3H$ and 1-methylimidazolium chloride confirmed that the peak observed in 12.24 and 13.92 ppm of the ^1H NMR spectra of $[Msim]HSO_4$ were correctly related to the SO_3H and HSO_4 groups of this compound. Also we examined presence and absence chloride and sulfate ions. The chloride ion was absent in the ionic liquid (checked by reaction with $AgNO_3$) whereas the sulfate ion was present (checked by reaction with $BaCl_2$).

In order to prove that the $[Msim]HSO_4$ ionic liquid was correctly synthesized, and this is responsible of the catalytic results, as a model, the protection of 4-chlorobenzyl alcohol with HMDS was examined at room temperature under solvent-free conditions in the presence of 0.02 mmol of the starting materials used for the preparation of the catalyst (i.e. 1-methylimidazole, $ClSO_3H$, H_2SO_4 and 1-methylimidazolium chloride) and intermediate [Msim]Cl. The reaction was carried out at room temperature and the catalytic results are presented in Table 1. It can be seen that 1-methylimidazole and 1-methylimidazolium chloride afforded lower yield of reaction products to those achieved over the catalyst. In the case of $ClSO_3H$ and H_2SO_4, the reaction afforded any product in the same conditions. In our opinion, some part of HMDS were degraded during the reaction. The intermediate 3-methyl-1-sulfonic acid imidazolium chloride given higher yield (82%) and at short time (8 min). However, when the reaction was carried out in the presence of $[Msim]HSO_4$, we observed higher yield (98%) at very short reaction time (1 min).



Scheme 2. The chemoselective trimethylsilyl protection of hydroxyl groups in presence of 3-methyl-1-sulfonic acid imidazolium hydrogen sulfate ionic liquid.

The other case for the mixing of 1-methylimidazole with $ClSO_3H$ and H_2SO_4 in dry CH_2Cl_2, is formation of a separate phase (H_2SO_4 and $ClSO_3H$ dissolved in 1-methylimidazole). To recognize that this physical phenomenon can not be achieved in these conditions, we noticed to the ^1H NMR spectral data of the product obtained from the mixing, with those in 1-methylimidazole, $ClSO_3H$, H_2SO_4 and the intermediate 3-methyl-1-sulfonic acid imidazolium chloride separately. The ^1H NMR spectral data include:

3-Methyl-1-sulfonic acid imidazolium hydrogen sulfate: ^1H NMR (300 MHz, DMSO-d_6): δ (ppm) 3.74 (s, 3H, CH_3), 7.43 (s, 1H), 7.50 (s, 1H), 8.81 (s, 1H), 12.24 (s, 1H), 13.92 (s, 1H).
3-Methyl-1-sulfonic acid imidazolium chloride: ^1H NMR (300 MHz, DMSO-d_6): δ (ppm) 3.77 (s, 3H, CH_3), 7.46 (s, 1H), 7.51 (s, 1H), 8.84 (s, 1H), 13.96 (s, 1H).
1-Methylimidazole: ^1H NMR (300 MHz, DMSO-d_6): δ (ppm) 3.61 (s, 3H, CH_3), 7.02 (s, 1H), 7.11 (s, 1H), 7.64 (s, 1H).
$ClSO_3H$: ^1H NMR (300 MHz, DMSO-d_6): δ (ppm) 13.45 (s, 1H).
H_2SO_4: ^1H NMR (300 MHz, DMSO-d_6): δ (ppm) 14.32 (s, 1H).

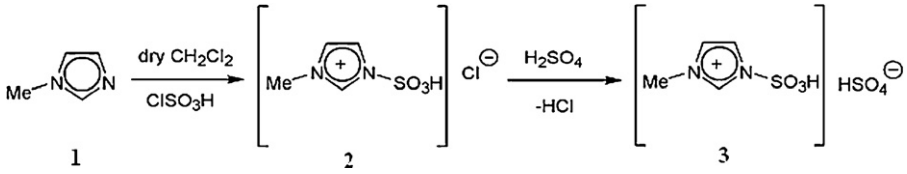
As it can be seen, the ^1H NMR data of the product were different with those in 1-methylimidazole, $ClSO_3H$ and the intermediate [Msim]Cl. Moreover, 1-methylimidazole and $ClSO_3H$ were easily dissolved in CH_2Cl_2; however, the intermediate [Msim]Cl solid and $[Msim]HSO_4$ ionic liquid were insoluble in CH_2Cl_2.

3.2. The protection of alcohols and phenols

Recently and in continuation of our ongoing research program on the development of new methods for the protection of hydroxyl groups, we decided to the preparation of novel 3-methyl-1-sulfonic acid imidazolium hydrogen sulfate ionic liquid (Scheme 1) and investing the silylation reaction of hydroxyl groups with HMDS in the presence of this ionic liquid (Scheme 2).

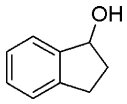
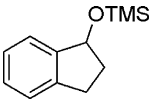
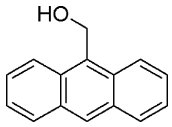
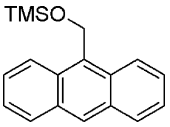
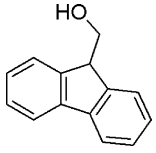
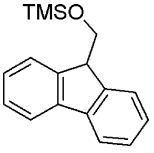
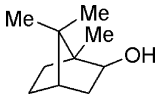
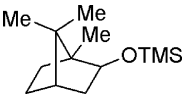
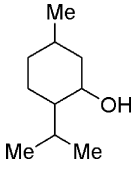
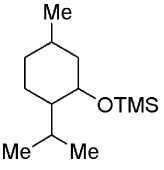
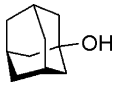
Optimization of the reaction conditions showed that the best results were obtained when the reaction was performed at room temperature under solvent-free conditions, while the relative ratio of the substrate/HMDS/$[Msim]HSO_4$ was 1.0 mmol/0.6 mmol/0.02 mmol, respectively. After that, different types of alcohols were subjected to trimethylsilylation under the determined conditions (Table 2).

O-Silylation of benzylic alcohols including acid sensitive, electron-donating or electron-withdrawing groups proceeds efficiently with high isolated yield (Table 2, entries 1–16). Primary and secondary aliphatic alcohols were also efficiently converted to their corresponding trimethylsilyl ethers under the same reaction conditions (Table 2, entries 17–24). This method was found to be useful for the protection of hindered secondary and tertiary alcohols (Table 2, entries 25–28). This method is also useful for the silylation of diols and acyloins (Table 2, entries 29–31). No elimination



Scheme 1. The synthesis of 3-methyl-1-sulfonic acid imidazolium hydrogen sulfate ionic liquid.

Table 2
The silylation of alcohols with HMDS in the presence of $[Msim]HSO_4$ at room temperature under solvent-free conditions.[a,b]

Entry	Substrate	Product	Time (min)	Yield (%)
1	$C_6H_5CH_2OH$	$C_6H_5CH_2OTMS$	1	96
2	$2\text{-}ClC_6H_4CH_2OH$	$2\text{-}ClC_6H_4CH_2OTMS$	1	97
3	$2\text{-}BrC_6H_4CH_2OH$	$2\text{-}BrC_6H_4CH_2OTMS$	1	96
4	$2\text{-}MeC_6H_4CH_2OH$	$2\text{-}MeC_6H_4CH_2OTMS$	1	94
5	$2\text{-}O_2NC_6H_4CH_2OH$	$2\text{-}O_2NC_6H_4CH_2OTMS$	12	87
6	$4\text{-}ClC_6H_4CH_2OH$	$4\text{-}ClC_6H_4CH_2OTMS$	1	98
7	$4\text{-}BrC_6H_4CH_2OH$	$4\text{-}BrC_6H_4CH_2OTMS$	1	97
8	$4\text{-}O_2NC_6H_4CH_2OH$	$4\text{-}O_2NC_6H_4CH_2OTMS$	10	92
9	$4\text{-i-}PrC_6H_4CH_2OH$	$4\text{-i-}PrC_6H_4CH_2OTMS$	1	96
10	$2\text{-}(PhO)C_6H_4CH_2OH$	$2\text{-}(PhO)C_6H_4CH_2OTMS$	2	97
11	$3,4\text{-}Cl_2C_6H_3CH_2OH$	$3,4\text{-}Cl_2C_6H_3CH_2OTMS$	1	98
12	$C_6H_5CH(Me)OH$	$C_6H_5CH(Me)OTMS$	5	90
13	$C_6H_5CH(OH)CH(Me)_2$	$C_6H_5CH(OTMS)CH(Me)_2$	5	90
14			5	92
15	$(C_6H_5)_2CHOH$	$(C_6H_5)_2CHOTMS$	1	96
16			2	98
17	$C_6H_5CH_2CH_2OH$	$C_6H_5CH_2CH_2OTMS$	2	96
18	$C_6H_5CH_2CH_2CH_2OH$	$C6H5CH_2CH_2CH_2OTMS$	2	96
19	$C_6H_5CH(Me)CH_2OH$	$C_6H_5CH(Me)CH_2OTMS$	3	95
20	$C_6H_5CH_2NHCH_2CH_2OH$	$C_6H_5CH_2NHCH_2CH_2OTMS$	10	92
21			3	95
22	$(Me)_2CHOH$	$(Me)_2CHOTMS$	4	94
23	$(CH_2)_4CHOH$	$(CH_2)_4CHOTMS$	5	92
24	$(CH_2)_5CHOH$	$(CH_2)_5CHOH$	5	94
25			5	90
26			7	87
27	$C_6H_5CH_2C(OH)(Me)_2$	$C_6H_5CH_2C(OTMS)(Me)_2$	10	87
28			12	91
29	$C_6H_5CH_2CH(OH)CH_2OH$	$C_6H_5CH_2CH(OTMS)CH_2OTMS$	4	90[c]
30	$C_6H_5(CO)CH(OH)C_6H_5$	$C_6H_5(CO)CH(OTMS)C_6H_5$	4	98
31	$4\text{-}Me\text{-}C_6H_5(CO)CH(OH)C_6H_5\text{-}Me\text{-}4'$	$4\text{-}Me\text{-}C_6H_5(CO)CH(OTMS)C_6H_5\text{-}Me\text{-}4'$	4	98

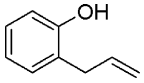
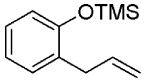
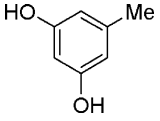
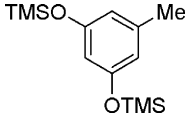
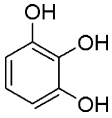
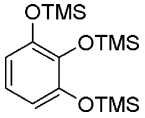
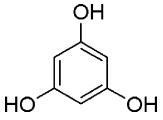
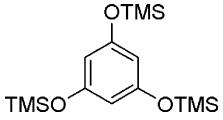
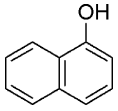
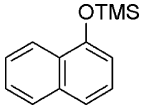
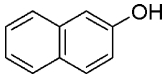
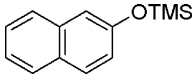
[a] Products were characterized by their physical constants, comparison with authentic samples, and IR, ^1H NMR, ^{13}C NMR spectroscopy.
[b] Isolated yields.
[c] HMDS 1.2 mmol is used.

or rearrangement by-product was observed during the course of the reaction.

In order to show the generality of the method, we also applied the optimized condition for silylation of the structurally different phenols and some naphthols (Table 3). Phenol and substituted phenols were silylated easily and their corresponding silylethers were isolated in excellent yields. The change of phenyl to napthyl group (Table 3, entries 19 and 20) hardly influences the reactivity and gives the excellent comparable yields. We have also applied this method for silylation of two amines and thiols. The reactions did not proceed after a long reaction times and the starting materials were isolated intact (Table 3, entries 21–24).

Due to the important of the selectivity in synthetic organic chemistry, competitive reactions were designed to evaluate the chemoselectivity of the protocol. The results summarized in Table 4, clearly indicate that primary alcohols were easily protected

Table 3
The silylation of phenols and naphthols with HMDS in the presence of $[Msim]HSO_4$ at room temperature under solvent-free conditions.[a,b]

Entry	Substrate	Product	Time (min)	Yield (%)
1	C_6H_5OH	C_6H_5OTMS	1	99
2	4-FC_6H_4OH	4-FC_6H_4OTMS	1	98
2	4-EtC_6H_4OH	4-EtC_6H_4OTMS	1	98
3	3-MeC_6H_4OH	3-MeC_6H_4OTMS	1	98
4	3,4-$(Me)_2C_6H_3OH$	3,4-$(Me)_2C_6H_3OTMS$	2	95
5	2,4-$(Me)_2C_6H_3OH$	2,4-$(Me)_2C_6H_3OTMS$	1	96
6	4-i-PrC_6H_4OH	4-i-PrC_6H_4OTMS	2	98
7	2-PhC_6H_4OH	2-PhC_6H_4OTMS	4	98
8	$C_6H_5CH_2C_6H_4OH$	$C_6H_5CH_2C_6H_4OTMS$	2	98
9			2	98
10	2-$NH_2C_6H_4OH$	2-$NH_2C_6H_4OTMS$	5	95[c]
11	4-$NH_2C_6H_4OH$	4-$NH_2C_6H_4OTMS$	2	96[c]
12	1,2-$(OH)_2C_6H_4$	1,2-$(OTMS)_2C_6H_4$	5	98[c]
13	1,4-$(OH)_2C_6H_4$	1,4-$(OTMS)_2C_6H_4$	5	98[c]
14	4-HOC_6H_4-C_6H_4OH-4′	4-$TMSOC_6H_4$-C_6H_4OTMS-4′	4	98[c]
15			5	96[c]
16	2-$(OH)C_6H_4CH_2OH$	2-$(OTMS)C_6H_4CH_2OTMS$	3	94[c]
17			40	85[d]
18			15	88[d]
19			2	91
20			5	89
21	$C_6H_5CH_2NH_2$	$C_6H_5CH_2NHTMS$	120	0
22	$C_6H_5CH_2SH$	$C_6H_5CH_2STMS$	120	0
23	4-$MeC_6H_4CH_2NH_2$	4-$MeC_6H_4CH_2NHTMS$	120	0
24	4-$MeC_6H_4CH_2SH$	4-$MeC_6H_4CH_2STMS$	120	0

[a] Products were characterized by their physical constants, comparison with authentic samples, and IR, ^1H NMR, ^{13}C NMR spectroscopy.
[b] Isolated yields.
[c] HMDS 1.2 mmol is used.
[d] HMDS 1.8 mmol is used.

in the presence of secondary ones with very high chemoselectivity (entry 1). This was not the case when secondary alcohols were subjected to react with HMDS in the presence of the tertiary alcohols with low chemoselectivity (entry 2). Under similar conditions alcohols and phenols can be protected preferentially in the presence of amines and thiols (entries 3–5).

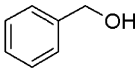
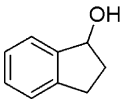
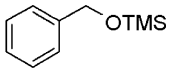
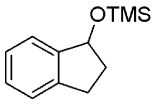
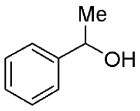
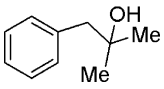
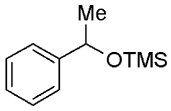
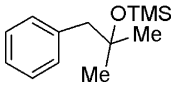
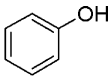
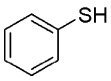
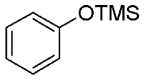
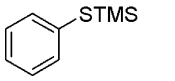
3.3. Comparison of the efficiency of the catalyst with the recently reported catalysts for the protection hydroxyl groups

To compare the applicability and the efficiency of our catalyst with the reported catalysts for the protection hydroxyl groups, we have tabulated the results of this catalyst to perform the silylation of benzhydrol with HMDS in Table 5. As it is shown in Table 5, the $[Msim]HSO_4$ ionic liquid remarkably improved the silylation of benzhydrol in different terms, for example higher temperature, longer reaction times, lower yields, and limitation of the substrate applicability in other methods, make our system as a better choice. The reaction times were shorter, and the yields were higher when the $[Msim]HSO_4$ catalyst were utilized.

3.4. Proposed mechanism

The mechanism of the reaction is not clear, but the fast evolution of NH_3 gas from the reaction mixture (indicated by odor and litmus paper) and the reusability of the catalyst, directed to accept the mechanism that is shown in Scheme 3 as the most probable one. On the basis of this mechanism, $[Msim]HSO_4$ reacts with HMDS to produce the reactive silylating agent (I), this in turn reacts with the substrate to produce the requested silyl ether and $[Msim]HSO_4$–NH_3+ (II). Irreversible cleavage of (II) leads to the fast evolution of NH_3 and release of the reactive silylating agent (I), which re-enters to the catalytic cycle.

Table 4
Chemoselectivity of O-trimethylsilylation reactions in the presence of ionic liquid [Msim]HSO_4.[a]

Entry	Substrates	Products	Conversion (%)[b]	Time (min)
1	 + 	 + 	100 0	10
2	 + 	 + 	100 48	10
3	$C_6H_5CH_2NHCH_2CH_2OH$	$C_6H_5CH_2NHCH_2CH_2OTMS$	92	10
4	2-$NH_2C_6H_4OH$	2-$NH_2C_6H_4OTMS$	95	10
5	 + 	 + 	100 0	10

[a] The reaction conditions: equivalent ratios of substrate/HMDS/catalyst are: 1 mmol/0.6 mmol/0.02 mmol, at room temperature under solvent-free conditions.
[b] GC yield.

Table 5
Comparison of the silylation of benzhydrol in the presence of [Msim]HSO_4 with some other catalysts.

Entry	Catalyst/solvent/condition	Time (min)	Yield (%)[a]	Refs.
1	$LaCl_3$(10 mol%)/CH_2Cl_2/r.t.	210	93	[38]
2	$Al(HSO_4)_3$(3.5 mol%)/CH_3CN/r.t.	180	95	[32]
3	TCCA(10 mol%)/CH_2Cl_2/r.t.	180	95	[18]
4	$Mg(OTf)_2$(1 mol%)/neat/r.t.	120	70	[31]
5	$LiClO_4$–SiO_2 (100 mg)/CH_2Cl_2/r.t.	50	87	[29]
6	$H_3PW_{12}O_{40}$(1 mol%)/neat/55–60 °C	48	93	[22]
7	$Cu(OTf)_2$(1 mol%)/CH_3CN/r.t.	35	98	[39]
8	$TiCl_3$(OTf)-SiO_2(1 mol%)/neat/r.t.	25	95	[40]
9	n-Bu_4NBr(5 mol%)/CH_3CN/r.t.	20	90	[45]
10	$TiCl_3$(OTf)(1 mol%)/neat/r.t.	2	92	[43]
11	[Msim]HSO_4(2 mmol%)/neat/r.t.	1	96	This work

[a] Isolated Yield.

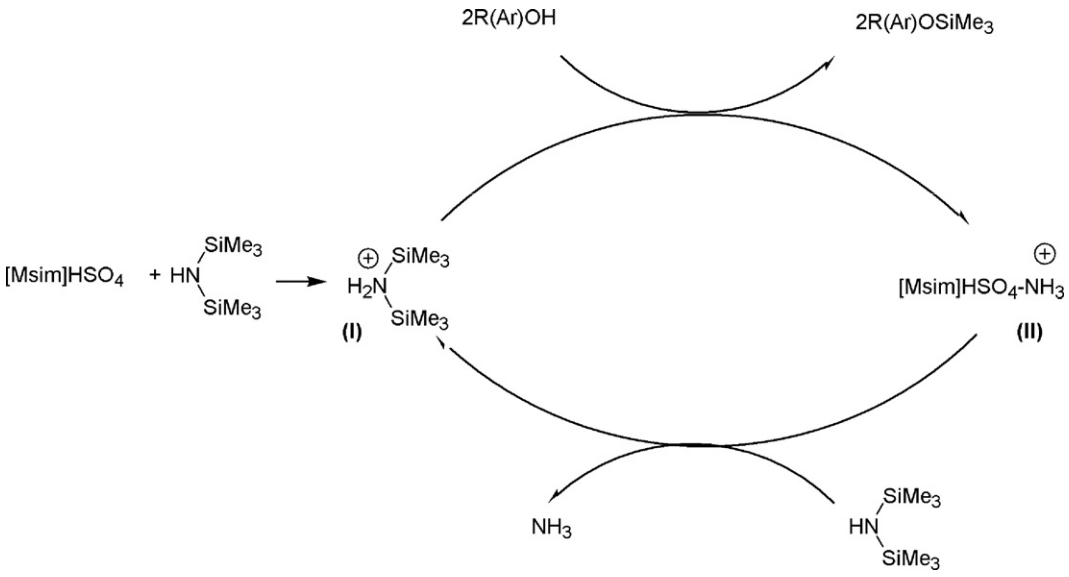
3.5. Recovering and reusing the catalyst

As previously showed, [Msim]HSO_4 was highly efficient and general for the protection of hydroxyl group. To raise the catalyst worth, recover and reuse of the ionic liquid was studied (Table 6). For this purpose, the reaction of silylation of 4-chlorobenzylalcohol and phenol with HMDS using [Msim]HSO_4 was carried out several times, and the reaction mixtures were combined. Afterward, Et_2O was added to the combined reaction mixtures, stirred for 10 min. The ionic liquid was recovered by decanted and washed with Et_2O and dried for 24 h at 50 °C. The catalytic activity of the recovered [Msim]HSO_4 was as same as the first one.

Table 6
Reusability of [Msim]HSO_4.[a]

Substrate	Time (min)/Yield (%)[b]			
	Run 1	Run 2	Run 3	Run 4
4-Chlorobenzyl alcohol	1/98	1/98	1/95	1/94
Phenol	1/98	1/97	1/96	1/96

[a] The reaction conditions: equivalent ratios of substrate/HMDS/catalyst are: 1 mmol/0.6 mmol/0.02 mmol, at room temperature under solvent-free conditions.
[b] Isilated yields.



Scheme 3. A proposed mechanism for the protection of hydroxyl group at room temperature under solvent-free conditions.

4. Conclusion

In conclusion, in this article we have reported the preparation of new and novel ion liquid (3-methyl-1-sulfonic acid imidazolium hydrogen sulfate) and its application in the promotion of the silylation of alcohols and phenols with HMDS. Mildness of the reaction conditions, short reaction times, excellent yields, easy work-up, recovery and reuse of the $[Msim]HSO_4$, and chemoselectivity were noteworthy advantages of this method.

Acknowledgement

The author is thankful to the Guilan University Research Council for partial support of this work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.08.021.

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