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Preparation, characterization and application of succinimidinium hydrogensulfate ([H-Suc]HSO_4) as an efficient ionic liquid catalyst for the *N*-Boc protection of amines†

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In this work, succinimidinium hydrogensulfate ([H-Suc]HSO_4), as a novel Brønsted acidic ionic liquid is prepared and characterized by studying its FT-IR, ^{1}H NMR, ^{13}C NMR, mass and SEM. This reagent can be used as an efficient catalyst for the *N*-Boc protection of amines at room temperature and neat conditions. This new method consistently has the advantages of excellent yields and short reaction times. Further, this ionic liquid can be recovered and reused for several times.

Introduction

As a host of reviews indicates ionic liquids (ILs) have gained considerable interest because of their unique properties such as negligible volatility, non-flammability, good thermal stability, great chemical and electro-chemical stability and high conductivity.[1] They have been used in a broad variety of synthesis,[2–4] catalysis,[5–7] separation,[8–11] and biotechnology,[12] especially as promising "green" electrolytes for electrochemical devices such as dye-sensitized solar cells,[13–15] lithium ion batteries,[16,17] supercapacitors,[18,19] and fuel cells.[20,21]

Ionic liquids (ILs), being accepted as environmentally benign media, have been widely applied in many reactions as catalysts or dual catalyst-solvent due to their low vapor pressure, reusability and high thermal and chemical stability.[22,23]

Introduction of Brønsted-acidic functional groups into cations or anions of the ILs, especially the SO_3H-functional groups, obviously increase their acidities and water solubilities.[24–27] Hence, Brønsted-acidic ILs can be used as highly efficient acid catalysts and have been attracting great interest as green substitutes for H_2SO_4, HF, and $AlCl_3$ catalysts in chemical processes.[28] In point of fact, the use of Brønsted-acidic ILs as catalysts is an area of persistent activity. Nevertheless, development and exploration of these catalysts are currently in the preliminary stage.

Protection and deprotection of organic functions play an essential role in the elegant art of multistep organic synthesis.[29] The choice of a suitable protecting group often determines which method will be chosen, on grounds of simplicity, highest yields of desired products, and ease of work up/separation. This choice in turn determines the overall cost of at the industrial level. The presence of an amine function in so many biologically active compounds makes its protection a frequently needed exercise in synthetic/medicinal chemistry.

Protection of amines as *N*-*tert*-butylcarbamate is an important technique in multistep organic synthesis.[30] Among different methods, the *N*-*tert*-butoxycarbonyl (*N*-Boc) protection has been widely used for the amino acids during peptide synthesis due to their resistance towards racemization.[31]

Among the different available groups for the *N*-Boc protection such as Boc_2O, $BocONH_2$, $BocN_3$, BocON=N(CN)Ph and 1-(*tert*-butoxycarbonyl) benzotriazole,[32] the di-*tert*-butoxypyrocarbonate is the most popular because of its commercial availability, low cost and stability and efficiency.

There are limited numbers of reports on the use of *Lewis* acid catalysts to effect the above transformation. These include yttria-zirconia,[33] $Zn(ClO_4)_2 \cdot 6H_2O$,[34] $LiClO_4$,[35] $ZrCl_4$,[36] $Cu(BF_4)_2 \cdot XH_2O$,[37] $HClO_4/SiO_2$,[38] Montmorillonite K10 or KSF,[39] succinimide sulfonic acid (SuSA),[40] *N*-sulfonic acid poly-(4-vinylpyridinium) chloride,[41] $H_3PW_{12}O_{40}$,[42] sulfamic acid,[43] and indium(III) halides.[44] However, long reaction times, unsatisfactory yields, and limited applicabilities are drawbacks in several methods. The recovery of the catalysts is also a problem. Moreover, though various catalysts have been employed, the utility of a catalyst having Brønsted acid character for the preparation of *N*-Boc derivatives has not yet been properly explored.

Herein, we report an efficient method for the chemoselective *N*-*tert*-butyloxycarbonylation of amines which relies exclusively on hydrogen bonding for carbonyl activation.

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Experimental section

Reagents and materials

Chemicals were purchased from Fluka, Merck, Aldrich and Southern Clay Products Chemical Companies. Yields refer to isolated products. Products were characterized by their physical constants, comparison with authentic samples and IR and NMR spectroscopy. The purity determination of the substrate and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates.

Characterization

The IR spectra were run on a Perkin-Elmer bio-spectrometer and *Bruker Vector 22*. The ^{1}HNMR (400 MHz) and ^{13}CNMR (100 MHz) were run on a Bruker AVANCE^{III}-400 spectrometer in $CDCl_3$ using TMS as an internal reference (δ in ppm). Micro-analyses were performed on a Perkin-Elmer 240-B micro-analyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

Catalyst preparation of the ionic liquid ([H-Suc]HSO_4)

In a round-bottomed flask, 0.53 mL sulfuric acid (98%, $d = 1.84$) was added drop wise to a mixture of succinimide (0.99 g, 10 mmol) in 50 mL of dichloromethane on an ice bath. The reaction mixture was stirred at room temperature for 30 min, and then the solvent was evaporated under reduced pressure. The solid residue was washed with 2 × 5 mL ether and dried under vacuum. After this process [H-Suc]HSO_4 was obtained as a cream solid (1.94 g, 97%) (m.p. 78 °C) (Scheme 1).

General procedure for the *N*-Boc protection of amines

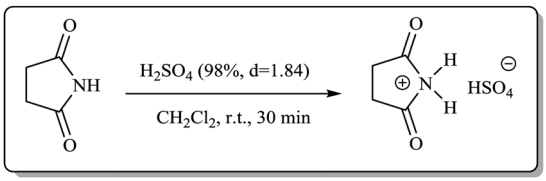
The substrate (1 mmol) was added to a magnetically stirred mixture of [H-Suc]HSO_4 (2 mol%) and $(Boc)_2O$ (1 mmol, 0.218 g) at room temperature. After completion of the reaction (TLC), the mixture was diluted with EtOAc (10 mL) and the catalyst was decanted. Evaporation of the solvent followed by column chromatography (silica-gel) eluting with EtOAc in *n*-hexane (5–15%) gave the desired product in good to high yields.

The spectral data of the selected and new compounds are as follow:

***Tert*-Butyl (3-phenylpropyl) carbamate (o).** Colorless oil, IR (neat): ν = 3370, 2990, 1680, 1240, 1160; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.47 (s, 9H), 1.79–1.87 (q, J = 7.6 Hz, 2H), 2.64–2.68 (t, J = 7.6 Hz, 2H), 3.15–3.19 (t, J = 7.6 Hz, 2H), 4.58 (br s, NH) 7.19–7.32 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.43, 31.76, 33.14, 40.24, 79.14, 125.93, 128.38, 128.43, 141.58, 155.98 ppm.

Di-*tert*-butyl ethane-1,2-diyldicarbamate (dd). Out-white solid, m.p. 144 °C; IR (KBr, cm^{-1}): 3379, 2985, 1685, 1164; ^{1}H-NMR (400 MHz, $CDCl_3$): 1.45 (s, 18H), 3.24 (s, 4H), 4.89 (s, NH) ppm, ^{13}C-NMR (100 MHz, $CDCl_3$): 28.38, 40.83, 79.45, 155.11 ppm.

Di-*tert*-butyl hexane-1,6-diyldicarbamate (ee). White solid, m.p. 97 °C; IR (KBr, cm^{-1}): 3373, 2979, 1689, 1172; ^{1}H-NMR (400 MHz, $CDCl_3$): 1.32–1.50 (m, 26H), 3.07–3.13 (t, J = 8 Hz, 4H), 4.57 (s, NH) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): 26.34, 28.43, 29.99, 40.38, 79.06, 156.02 ppm.



Scheme 1 Preparation of [H-Suc]HSO_4.

Results and discussion

Catalyst characterization

The graphical ^{1}H NMR spectra of succinimidinium hydrogensulfate ([H-Suc]HSO_4) is displayed in Fig. 1. The important peak of ^{1}HNMR spectra of [H-Suc]HSO_4 is related to the acidic hydrogen (HSO_4) which is observed in 11.06 ppm that not observed in the succinimide ^{1}HNMR spectra.

Fig. 2 shows the FTIR spectra of succinimide and succinimidinium hydrogensulfate ([H-Suc]HSO_4). The strong absorptions at 1180.22, 1071.07, 883.49 and 579.8 cm^{-1} in the ionic liquid are assigned to the asymmetric and symmetric stretching and bending S–O vibrations of hydrogensulfate group, that are absent in succinimide.[45]

The broad band at 2937–3500 cm^{-1}, can be typically seen in the spectra of the catalyst due to the stretching vibrations of O–H bond. The SO_2 asymmetric vibrations are found at 1404 and 1295 cm^{-1} and the symmetric SO_2 stretching vibration

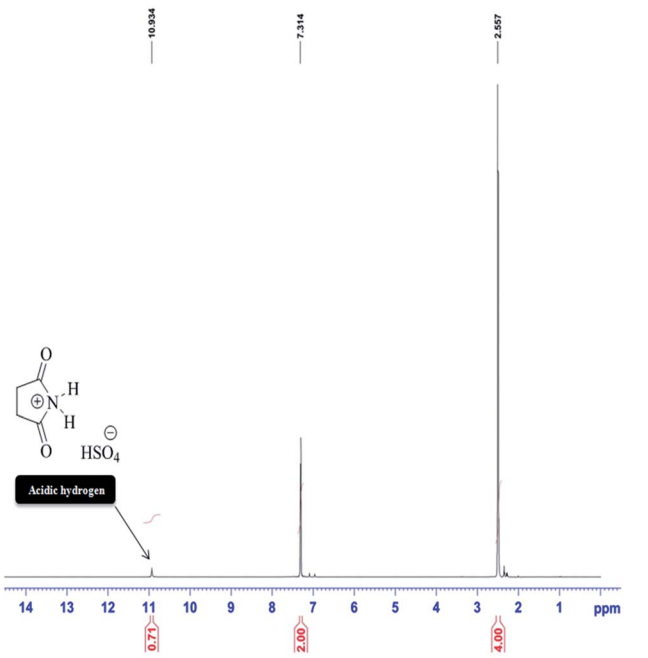


Fig. 1 ^{1}H NMR spectra of the succinimidinium hydrogensulfate ([H-Suc]HSO_4).

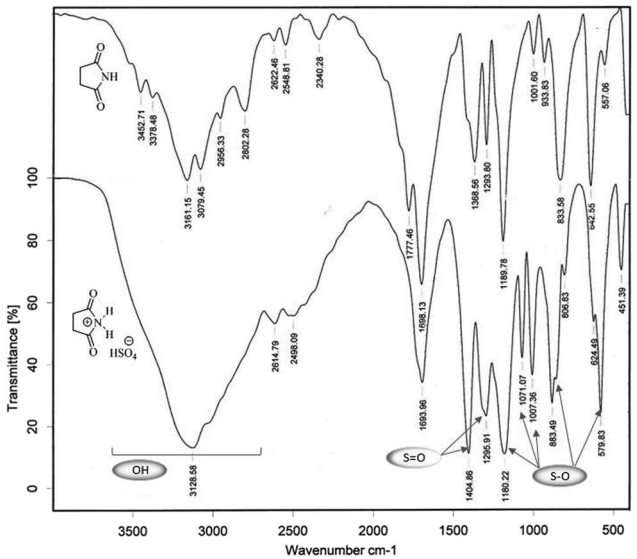


Fig. 2 FT-IR spectra of succinimide (up), and succinimidinium hydrogensulfate ([H-Suc]HSO_4) (down).

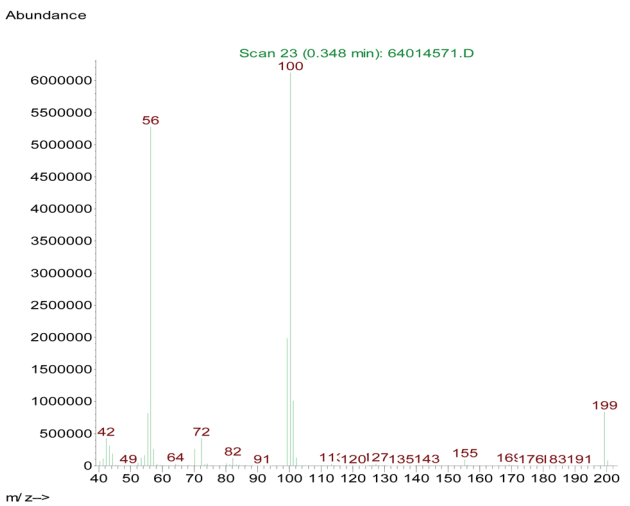


Fig. 3 Mass spectra of succinimidinium hydrogensulfate ([H-Suc]-HSO_4).

appears around 1180 cm^{-1}.[46] The band at 1071 cm^{-1} is assigned to the SOH bending vibration. The bands at 1698 and 1777 cm^{-1} in the succinimide arise from resonance of the nitrogen with C=O groups, but the carbonyl group in the ionic liquid is typically at 1693 cm^{-1}. The reason is, here the nitrogen has positive charge and can't resonance with carbonyl groups.

The mass spectra of succinimidinium hydrogensulfate ionic liquid is presented in Fig. 3. The important peaks of MS spectrum of the ionic liquid were related to the $[M^+ + 2] = 199$ and $[M^+ - SO_4H] = 100$.[47]

The titration method is used to determine the number of protic protons of the prepared catalyst. In this experiment a solution of the ionic liquid was titrated with NaOH. The titration curve for the reaction of 20 mL of 0.090 M ionic liquid with

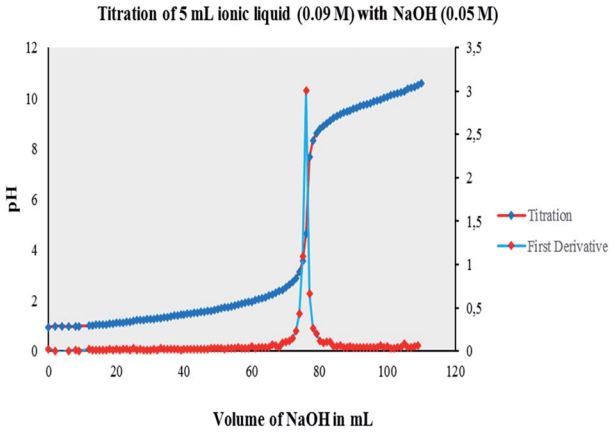


Fig. 4 Titration and its first derivative curves of the ionic liquid with NaOH.

0.050 M NaOH is given in Fig. 4. This figure clearly shows that, when 76.5 mL of the basic solution is added, all the acidic protons are neutralized. On the other hand eqn (1), shows that for the neutralization of each of the acidic protons 36 mL of the basic solution is needed. On the basis of these studies it can be concluded that this ionic liquid has two protic protons with almost the same acidic power.

$$M\,(\text{acid}) \times V\,(\text{acid}) = M\,(\text{base}) \times V\,(\text{base})\ 0.09\ (\text{molar}) \times 20\ (\text{mL}) = 0.05\ (\text{molar}) \times V\,(\text{base}) \quad (1)$$

$$V\,(\text{base}) = 36\ \text{mL}$$

The samples of succinimide and [H-Suc]HSO_4 were also analyzed by scanning electron microscopy (SEM), as represented in Fig. 5. These images clearly show the aggregation of the product after modification of succinimide with sulfuric acid. This aggregation can be caused by hydrogen bonding sites and nearby the positive and negative sides.

There are several methods for the evaluation of the acidity of Brønsted ionic liquids. One of these methods is UV-visible spectrophotometry technique. In this technique, various concentrations of the ionic liquid are prepared in CCl_4 as a solvent. 4-Nitroaniline is utilized as a basic indicator ($pK_a = 0.99$) to capture the dissociative proton. Then the Hammett function and the acidity are determined.[48]

The acidity of the Brønsted ionic liquids were measured by evaluating the protonation extent of uncharged indicator base (named I) in the SFILs, interms of the measurable ratio $[I]/[IH^+]$. The Hammett function (H_0) is defined as:

$$H_0 = pK_{(I)_{aq}} + \log([I]_s/[IH^+]_s)$$

where $pK_{(I)_{aq}}$ is the pK_a value of the indicator in an aqueous solution. $[IH^+]_s$ and $[I]_s$ are the molar concentrations of the protonated and unprotonated forms of the indicator in the solvent, respectively.

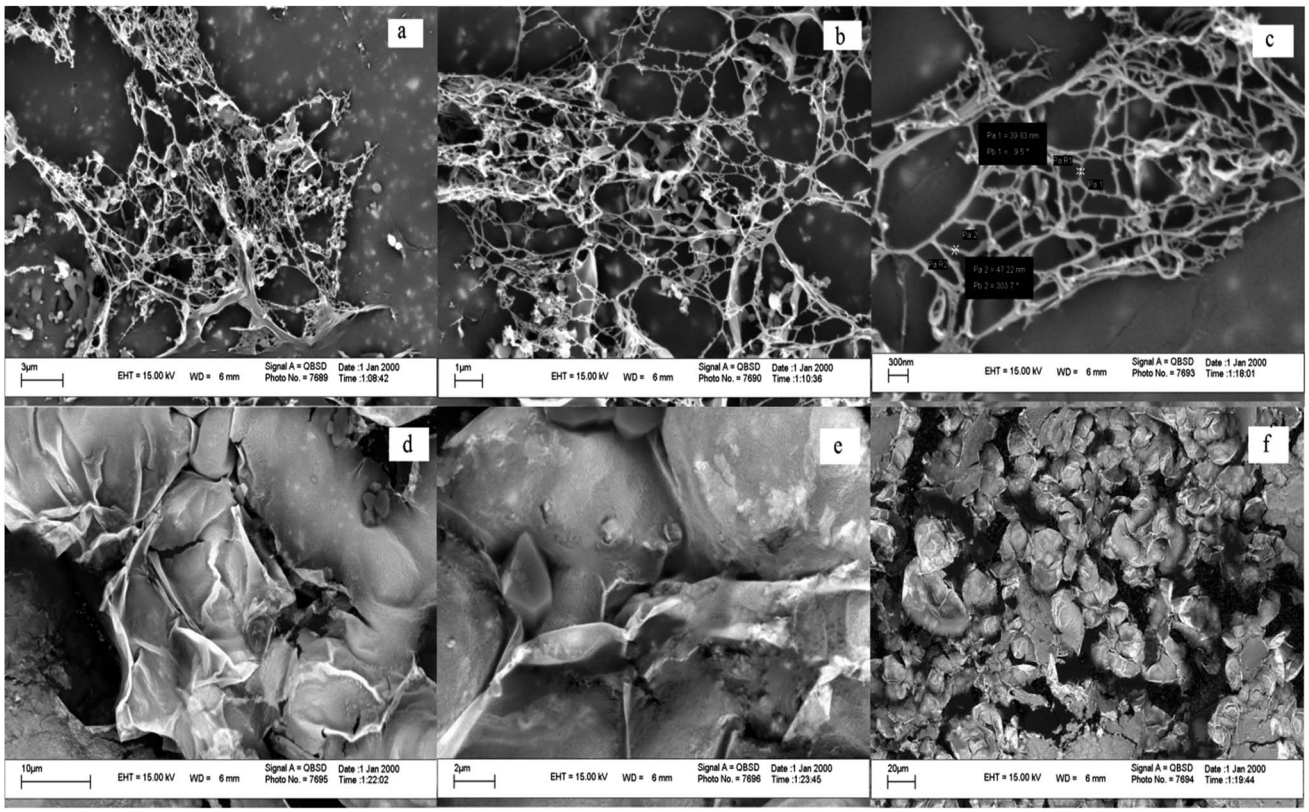


Fig. 5 SEM micrographs of succinimide (a–c) and [H-Suc]HSO_4 (d–f).

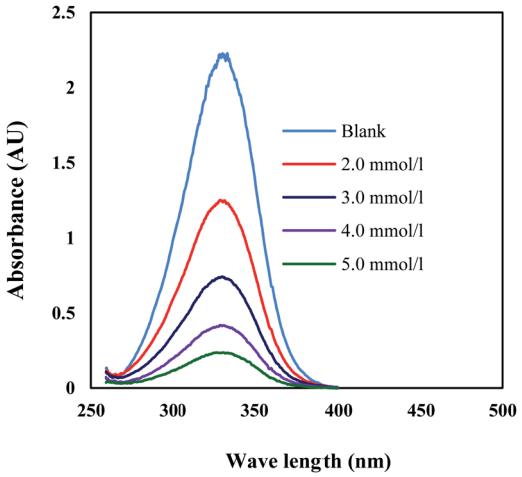


Fig. 6 Absorption spectra of 4-nitroaniline (indicator) and [H-Suc]HSO_4 (catalyst) in CCl_4.

The maximum absorbance of the blank solution (indicator in CCl_4) was observed at 329 nm. Fig. 6 compares the absorbance of different concentrations of the ionic liquid solutions.

As shown in Fig. 7 in comparison to the blank solution (which revealed that the indicator is partially in the [IH^+] form) the absorbance of the unprotonated form of the indicator in [H-Suc]HSO_4 was weak. The obtained results which are listed in Table 1, show the acidity strength of [H-Suc]HSO_4 (Fig. 8).

Catalytic activity

On the basis of the information obtained from the above mentioned studies, we anticipated that this ionic liquid could be used as an efficient catalyst for the promotion of the reactions which need the use of an acidic catalyst to speed-up. Therefore, we were interested to investigate the applicability of this reagent in the *N*-Boc protection of amines.

At first and in order to optimize the reaction conditions the *N*-Boc protection of aniline was chosen as a probe reaction.

Investigation of the effect of different factors (including the temperature, solvent and/or solvent-free conditions, amount of the catalyst and amount of the protecting agent) on the reaction rate and also the yield of the product clarified that the best results can be obtained under the conditions shown in Scheme 2.

After optimization of the reaction conditions various aromatic, heteroaromatic, aliphatic (cyclic and acyclic) and heterocyclic amines were treated with $(Boc)_2O$ under the selected conditions and the results are summarized in Table 2.

As we can see using this method different types of aromatic, benzylic, primary and secondary aliphatic amines were reacted instantaneously and gave the corresponding *N*-Boc products in excellent yields during short reaction times (Table 2, entries 1–22). The protocol could also equally work with heterocyclic amines (Table 2, entries 23–25). Indole was also quantitatively converted to its *N*-Boc protected derivative under the selected conditions (Table 2, entry 26). The method could also be used

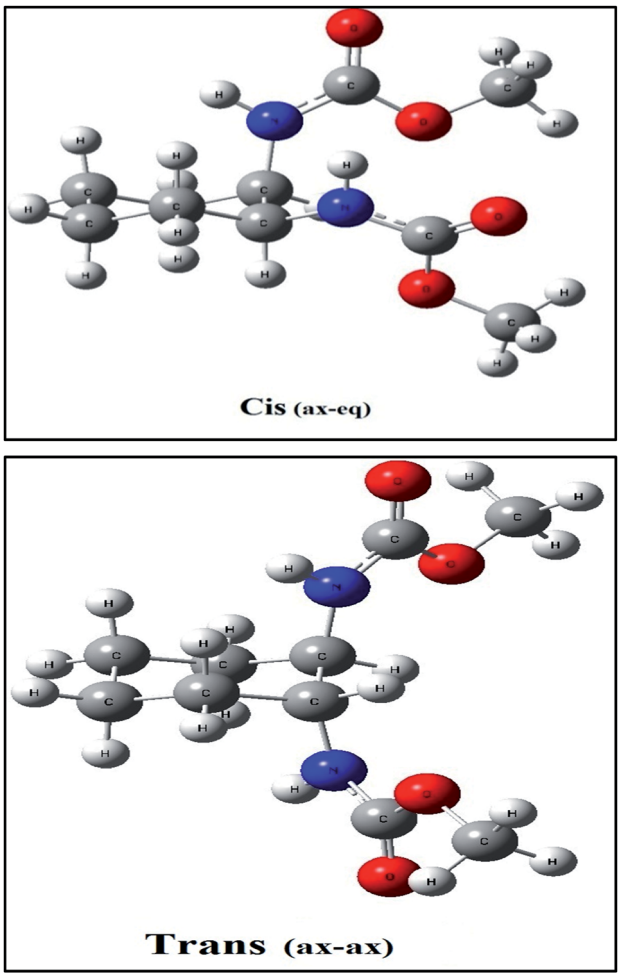


Fig. 7 *Cis* and *trans* di-*tert*-butyl cyclohexane-1,2-diyldicarbamate conformations.

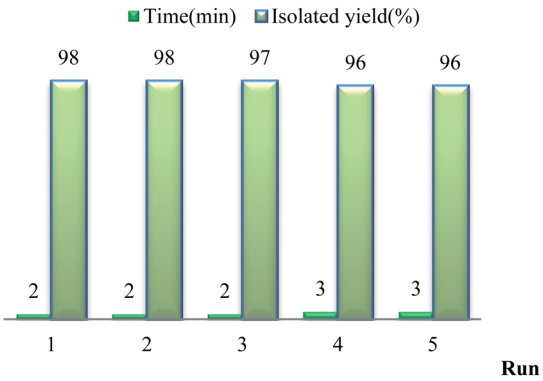
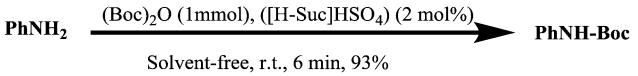


Fig. 8 Reusability of [H-Suc]HSO_4 in the *N*-Boc protection of aniline (Table 1, entry 1).



Scheme 2 *N*-Boc protection of aniline.

be for the *N*-Boc protection of 2-cyclohexenylethane amine. The double bond remains intact under these conditions (Table 2, entry 27). Aliphatic and aromatic amines containing two amine functional groups have also changed to their *N*-Boc derivatives under the applied reaction conditions (Table 2, entries 28–31). The chemoselectivity of this IL was also estimated by performing the *N*-Boc protection of amines in bifunctional compounds (Table 2, entries 2, 10 and 33–35). Excellent chemoselectivity was obtained for amines containing OH and/or SH functionalities, providing *N*-Boc derivatives as the major products, and no significant *O*/*S*-*tert* butoxy carbonylation took place.

It should be mentioned that GC-mass information of di-*tert*-butyl cyclohexane-1,2-diyldicarbamate (Table 2, entry 29) shows a mixture of the products with percentages of 33 and 67. This result clarifies that we have *cis* and *trans* isomers. A series of molecular density functional theory calculations were carried out for these two stable isomers (ax-ax and ax-eq). Calculations were performed with the Gaussian 03 set of programs,[49] on a personal computer (Pentium 4). Geometry optimization were done both at the DFT level with analytic gradients and with the 6-311++G (d,p) basis set in the gas phase and solvent (chloroform). The results are demonstrated that in the both of phases the optimization energy of the *trans* conformer is greater than *cis* conformer (2.50 and 2.55 kcal mol^{-1} respectively). The structures of two conformations of stereoisomers are shown in Fig. 7.

The proposed mechanistic pathway involves the initial activation of the carbonyl oxygen atoms of $(Boc)_2O$ by [H-Suc]HSO_4, followed by the nucleophilic attack of amine in one-pot, resulting the formation of the *N*-Boc protected amine. This is

Table 1 Calculation of Hammett acidity function (H_0) for [H-Suc]HSO_4[a]

Entry	Amount of catalyst	Maximum adsorptions	$[I]_S$ (%)	$[IH^+]_S$ (%)	H_0
1	—	2.2067	100	0	—
2	0.002	1.2451	56.4236	43.5764	1.10
3	0.003	0.7373	33.4118	66.5882	0.69
4	0.004	0.4137	18.7474	81.2526	0.35
5	0.005	0.2344	10.6221	89.3778	0.06

[a] Condition for UV-visible spectrum measurement: solvent: CCl_4, indicator: 4-nitroaniline ($pK_{(I)_{aq}} = 0.99$), 1.44×10^{-4} mol L^{-1} (10 mL); catalyst: [H-Suc]HSO_4, 25 °C.

Table 2 *N*-Boc protection of amines catalyzed by [H-Suc]HSO_4[a,b]

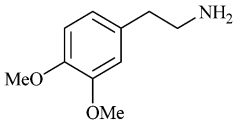
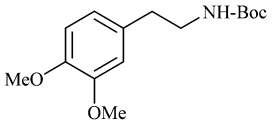
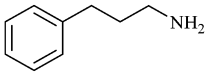
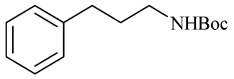
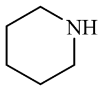
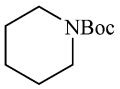
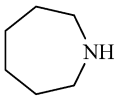
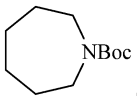
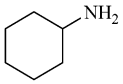
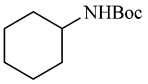
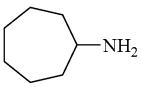
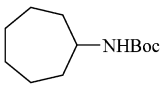
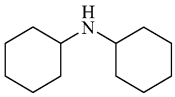
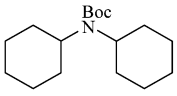
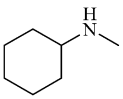
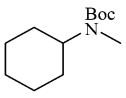
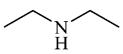
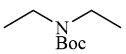
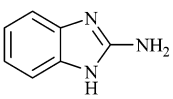
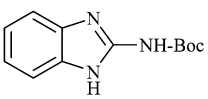
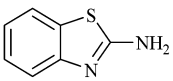
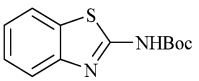
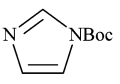
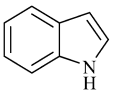
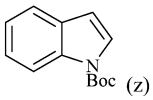
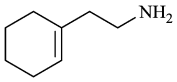
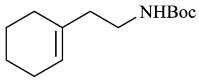
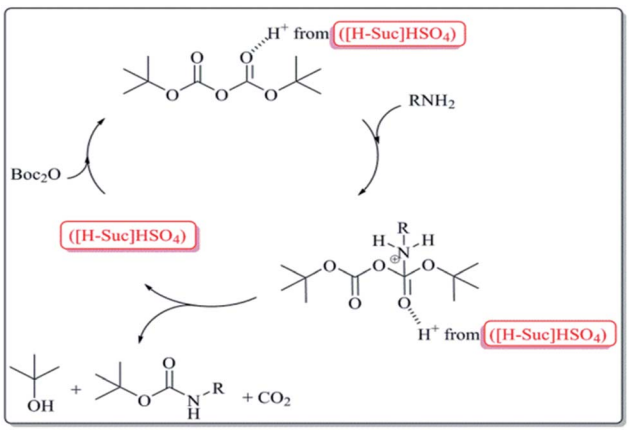
Entry	Substrate	Product	Time (min)	Yield (%)
1	$PhNH_2$	PhNH-Boc (a)	6	93
2	2-$HOC_6H_4NH_2$	2-HOC_6H_4NH-Boc (b)	8	94
3	2-$CH_3C_6H_4NH_2$	2-$CH_3C_6H_4$NH-Boc (c)	8	92
4	3-$ClC_6H_4NH_2$	3-ClC_6H_4NH-Boc (d)	7	93
5	3-$MeOC_6H_4NH_2$	3-$MeOC_6H_4$NH-Boc (e)	6	94
6	4-$BrC_6H_4NH_2$	4-BrC_6H_4NH-Boc (f)	6	93
7	4-$CH_3C_6H_4NH_2$	4-CH_3PhNH-Boc (g)	7	94
8	4-Pr-$C_6H_4NH_2$	4-Pr-C_6H_4NH-Boc (h)	8	96
9	4-$NO_2C_6H_4NH_2$	4-$NO_2C_6H_4$NH-Boc (i)	10	64
10	4-$HSC_6H_4NH_2$	4-HSC_6H_4NH-Boc (j)	10	90
11	1-Naphthyl-NH_2	1-Naphthyl-NHBoc (k)	10	93
12	$PhCH_2NH_2$	$PhCH_2$NH-Boc (l)	1	96
13	4-$CH_3PhCH_2NH_2$	4-CH_3PhCH_2NH-Boc (m)	4	97
14		 (n)	10	80
15		 (o)	15	87
16		 (p)	2	92
17		 (q)	2	91
18		 (r)	1	96
19		 (s)	10	95
20		 (t)	20	87
21		 (u)	15	88
22		 (v)	15	94
23		 (w)	3	92
24		 (x)	15	84
25		 (y)	2	92

Table 2 (*Contd.*)

Entry	Substrate	Product	Time (min)	Yield (%)
26		 (z)	10	90
27		 (aa)	11	88
28	Benzene-1,2-diamine	Di-*tert*-butyl 1,2-phenylenedicarbamate (bb)	12	92
29	Cyclohexane-1,2-diamine	Di-*tert*-butyl cyclohexane-1,2-diyldicarbamate (cc)	5	90
30	$NH_2(CH_2)_2NH_2$	$BocHN(CH_2)_2NHBoc$ (dd)	15	91
31	$NH_2(CH_2)_6NH_2$	$BocHN(CH_2)_6NHBoc$ (ee)	15	89
32	$PhNH(CH_2)_2NH_2$	$PhNH(CH_2)_2NHBoc$ (ff)	3	94
33	$PhCH_2NHCH_2CH_2OH$	$PhCH_2N(Boc)CH_2CH_2OH$ (gg)	2	92
34	$HO(CH_2)_2NH_2$	$HO(CH_2)_2NHBoc$ (hh)	5	92
35	$NH_2C(CH_3)_2CH_2OH$	$BocHNC(CH_3)_2CH_2OH$ (ii)	2	86

[a] Products were identified spectroscopically, comparison with authentic samples and also by the conversion of the products to their starting materials. [b] Isolated yield.



Scheme 3 The mechanistic pathway for the *N*-Boc protection of amines.

accompanied by the generation of *tert*-butanol and carbon dioxide (Scheme 3).

In order to show the merit of this method, Table 3 compares the results obtained from the *N*-Boc protection of aniline by our method with some of those reported in the literature.[33,34,40,41,50–55] As it is clear the present method is more efficient than the compared methods in terms of conditions, reaction times and/or the products yields.

We have also found that $[H\text{-Suc}]HSO_4$ can be easily recovered by decanting and washing with CH_2Cl_2 and drying at 50 °C. The reusability of this reagent is illustrated by the *N*-Boc protection of aniline in the presence of the recycled ionic liquid catalyst, which gave the requested product in 98, 98, 97, 96 and 96% yields after five runs. The average time for five consecutive runs was 2.4 min and 100% conversion for all, which clearly exhibit the practical recyclability of this catalyst Fig. 4.

In summary, we have developed an efficient methodology for the *N*-Boc protection of amines producing remarkable high

Table 3 Comparison of the results obtained from the *N*-Boc protection of aniline in the presence of various catalysts

Entry	Catalyst	Solvent	Time (min)	Yield (%)	Ref.
1	$([H\text{-Suc}]HSO_4)$	Neat	2	97	This work
2	Yttria-zirconia	CH_3CN	14 (h)	90	33
3	$Zn(ClO_4)_2 \cdot 6H_2O$	CH_2Cl_2	12 (h)	92	34
4	SuSA	Neat	2	98	40
5	NSPVPC	Neat	5	93	41
6	β-Cyclodextrine	H_2O	2.5 (h)	75	50
7	Thioglcoluril	EtOH	8	95	51
8	Saccharin sulfonic acid	*n*-Hexane	1 (h)	97	52
9	Iodine	Neat	30	95	53
10	[Py][OTf]	Neat	25	95	54
11	$[Dsim]HSO_4$	EtOH	15	90	55

yields under very mild conditions. The solvent less technique, simple operational procedure, excellent chemoselectivity and reusability of the catalyst have made our protocol not only environmentally benign but also one of the better methods for the protection of amines in organic synthesis.

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