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# Novel ionic liquid 1,3-disulfonic acid imidazolium hydrogen sulfate {[Dsim]HSO<sub>4</sub>} efficiently catalyzed *N*-boc protection of amines

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## KEYWORDS

Ionic liquid;  
1,3-Disulfonic acid  
imidazolium hydrogen  
sulfate {[Dsim]HSO<sub>4</sub>};  
*N*-boc protection;  
Amine.

**Abstract** A simple and highly efficient method for the protection of amines from their corresponding *N*-boc derivatives is reported. It is interesting that only 0.1 mol % of novel ionic liquid 1,3-disulfonic acid imidazolium hydrogen sulfate {[Dsim]HSO<sub>4</sub>} can efficiently catalyze the reaction. Clean reaction, very short reaction times, high yields, easy preparation and high TOF (turn over frequency) values of the catalyst in comparison with reported catalysts are some advantages of this work.

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## 1. Introduction

Ionic Liquids (ILs) have received considerable interest as eco-friendly solvents, catalysts and reagents in the context of green synthesis, because of their unique properties, such as low volatility, non-flammability, high thermal stability, negligible vapor pressure and ability to dissolve a wide range of materials. Among them, ILs exhibiting a Brønsted acid character possess useful characteristics of solid acids and mineral liquid acids. Such ILs have been designed to replace traditional mineral liquid acids, like sulfuric acid and hydrochloric acid, in a range of chemical transformations [1,2]. In continuation of our ongoing program on the synthesis and applications of acidic ILs in organic synthesis, we have recently introduced a new category of ionic liquids, namely Sulfonic Acid Functionalized Imidazolium Salts (SAFIS) [3–6]. This class of ILs has been used as an efficient catalyst and reagent in organic transformations,

such as synthesis of bis(indolyl)methans [3], preparation of *N*-sulfonyl imines [4], nitration of phenols [5], synthesis of 1-amidoalkyl-2-naphthols [6], preparation of benzimidazoles [7], and chemoselective trimethylsilyl protection of hydroxyl groups [8]. In this work, we synthesize another analogue of SAFIS, namely, 1,3-disulfonic acid imidazolium hydrogen sulfate {[Dsim]HSO<sub>4</sub>} (as an ionic liquid), via the reaction of 1,3-disulfonic acid imidazolium chloride {[Dsim]Cl}, with H<sub>2</sub>SO<sub>4</sub> (99.99%), which exhibits many interesting properties (Scheme 1).

Functional group protection and deprotection methods are important in the synthesis of the target molecule. The protection of amines is one of the most fundamental and useful transformations in organic synthesis, especially in peptide synthesis [9,10].

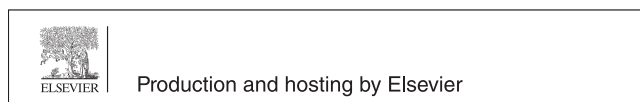
Several reagents and methods have been used for *N*-*tert*-butoxycarbonylation of amines [11–13]. These methodologies suffer from a variety of drawbacks, such as long reaction times, low yields, high toxicity and the use of expensive reagents. Commercially available *di-tert*-butyl dicarbonate (*diboc*) is an efficient reagent for clean and rapid introduction of the boc-protecting group [14–17].

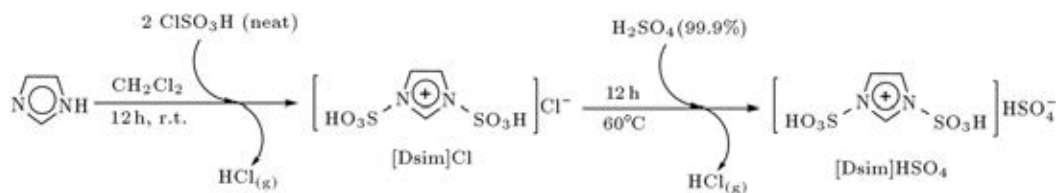
Herein, we report the selective *tert*-butoxycarbonylation of various amines, using *diboc* catalyzed by 1,3-disulfonic acid imidazolium hydrogen sulfate {[Dsim]HSO<sub>4</sub>} as a novel

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Scheme 1: The preparation of 1,3-disulfonic acid imidazolium hydrogen sulphate.

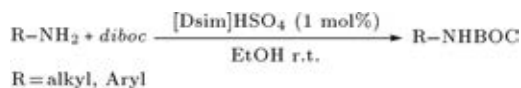
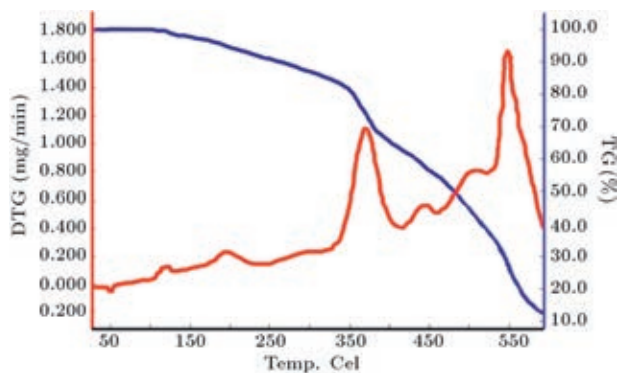
Scheme 2: Selective *tert*-butoxycarbonylation of various amines using *diboc* catalyzed by [Dsim]HSO<sub>4</sub>.

Figure 1: TG/DTG diagrams of the catalyst.

ionic liquid, at room temperature with high yields and very short reaction times. Interestingly, this method has none of the above-mentioned drawbacks for the N-boc protection of amines at all (Scheme 2).

## 2. Results and discussion

The structure of 1,3-disulfonic acid imidazolium hydrogen sulfate was identified by IR, <sup>1</sup>H and <sup>13</sup>C NMR and mass spectra.

The IR spectrum of the catalyst shows a broad peak at 3100–3400 cm<sup>-1</sup> related to the OH in the SO<sub>3</sub>H group. Moreover, the two peaks observed at 1085 cm<sup>-1</sup> and 1285 cm<sup>-1</sup> correspond to vibrational modes of the N–SO<sub>2</sub> bond.

The <sup>1</sup>H NMR spectrum of [Dsim]HSO<sub>4</sub> show the unmistakable acidic hydrogen (SO<sub>3</sub>H) peaks at 13.55 and 11.95 ppm. To prove that this peak is really related to the hydrogen of SO<sub>3</sub>H in the compound, we also run <sup>1</sup>H NMR of [Dsim]Cl and H<sub>2</sub>SO<sub>4</sub> in DMSO – d<sub>6</sub>. In these spectra, the peaks of the two acidic hydrogen groups of [Dsim]HSO<sub>4</sub>, [Dsim]Cl and H<sub>2</sub>SO<sub>4</sub> were observed at 13.55 and 11.95, 13.34, and 12.54 ppm, respectively. This observation showed that [Dsim]HSO<sub>4</sub> was exactly synthesized. Other details regarding the NMR signals are provided in the experimental section.

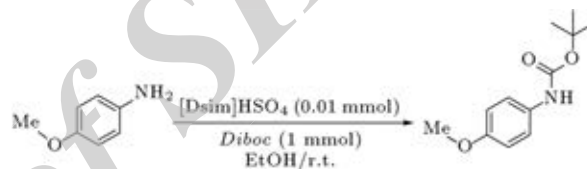
The mass spectrum of the compound gave the correct molecular ion peak at 326. The thermogram analysis of the catalyst was studied at a range of temperatures between 25 to 600 °C. The thermogram (TG) of the catalyst shows two weight losses (Figure 1). The first strong weight loss was observed after 350 °C and the second strong weight loss appears after 540 °C. Therefore, the molecular decomposition occurred for this catalyst after 350 °C.

To optimize the reaction conditions, as a model, the reaction of 4-methoxyaniline with *diboc* (Scheme 3) was tested in

Table 1: Effect of different amounts of the catalyst on the reaction of 4-methoxyaniline with *diboc*.

Catalysts	Mol% of catalyst	Temp. (°C)	Time (min)	Yield <sup>a</sup> (%)
–	–	r.t.	60	20
H <sub>2</sub> SO <sub>4</sub>	0.1	r.t.	60	23
H <sub>2</sub> SO <sub>4</sub>	1	r.t.	60	31
[Dsim]Cl	0.1	r.t.	15	88
[Dsim]Cl	1	r.t.	10	90
[Dsim]HSO <sub>4</sub>	0.1	r.t.	5	98
[Dsim]HSO <sub>4</sub>	1	r.t.	5	98

<sup>a</sup> Isolated yield.

Scheme 3: The reaction of 4-methoxyaniline with *diboc* catalyzed by [Dsim]HSO<sub>4</sub>.Table 2: The effect of various solvents on the reaction of 4-methoxyaniline with *diboc* catalyzed by [Dsim]HSO<sub>4</sub>.

Entry	Solvent	Time (min)	Yield <sup>a</sup> (%)
1	EtOH	5	98
2	CH <sub>3</sub> CN	15	88
3	CHCl <sub>3</sub>	18	90
4	CH <sub>2</sub> Cl <sub>2</sub>	15	90
5	<i>n</i> -hexane	20	87
6	Acetone	12	89

<sup>a</sup> Isolated yield.

the presence of different amounts of [Dsim]HSO<sub>4</sub> at room temperature in ethanol as solvent. The results are summarized in Table 1. To prove that [Dsim]HSO<sub>4</sub> was completely synthesized, and [Dsim]Cl or H<sub>2</sub>SO<sub>4</sub> converted to [Dsim]HSO<sub>4</sub>, the model reaction was also performed in different amounts of [Dsim]Cl or H<sub>2</sub>SO<sub>4</sub>. As it can be seen in Table 1, the best results were obtained when the reaction was carried out using 0.1 mol% of [Dsim]HSO<sub>4</sub> at room temperature.

In another study, we studied the reaction of 4-methoxyaniline (1 mmol) to its corresponding N-boc protected derivative, using [Dsim]HSO<sub>4</sub> as catalyst (0.1 mol%) and *diboc* (1 mmol) in a variety of solvents, at room temperature (Table 2). The results showed that absolute ethanol is the best solvent in terms of time and product yield (Table 2).

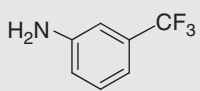
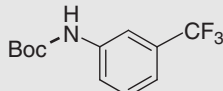
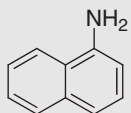
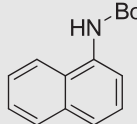
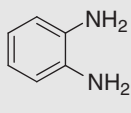
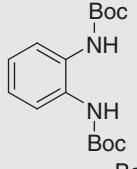
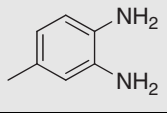
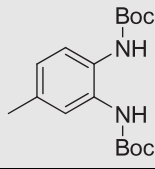
To explore the generality of the catalyst, a wide range of amines underwent N-boc protection using this procedure to provide the corresponding *tert*-butoxycarbonylated products in good to excellent yields. We also applied our reaction conditions to the N-boc protection of some aliphatic amines. The results were summarized in Table 3.

In a plausible mechanism, which is shown in Scheme 4, we suggest that the carbonyl group of *diboc* is activated by

Table 3: Protection of amines with diboc using [Dsim]HSO<sub>4</sub> as catalyst in ethanol at room temperature.

Entry	Amine	Product	Time	Yield <sup>a</sup> (%)	Ref.
1			3 min	93	[13]
2			1 min	99	[13]
3			15 min	90	[15]
4			4 min	99	[12]
5			33 min	85	[13]
6			5 min	98	[13]
7			30 min	95	[13]
8			20 min	85	[14]
9			2 h	75	[13]
10			12 min	70	[13]
11			10 min	70	[14]
12			15 min	90	[14]
13			12 h	50	[13]
14			35 min	55	[13]

Table 3 (continued)

Entry	Amine	Product	Time	Yield <sup>a</sup> (%)	Ref.
15			40 min	45	[13]
16			45 min	80	[13]
17			2 h	85	[12]
18			2 h	88	[13]

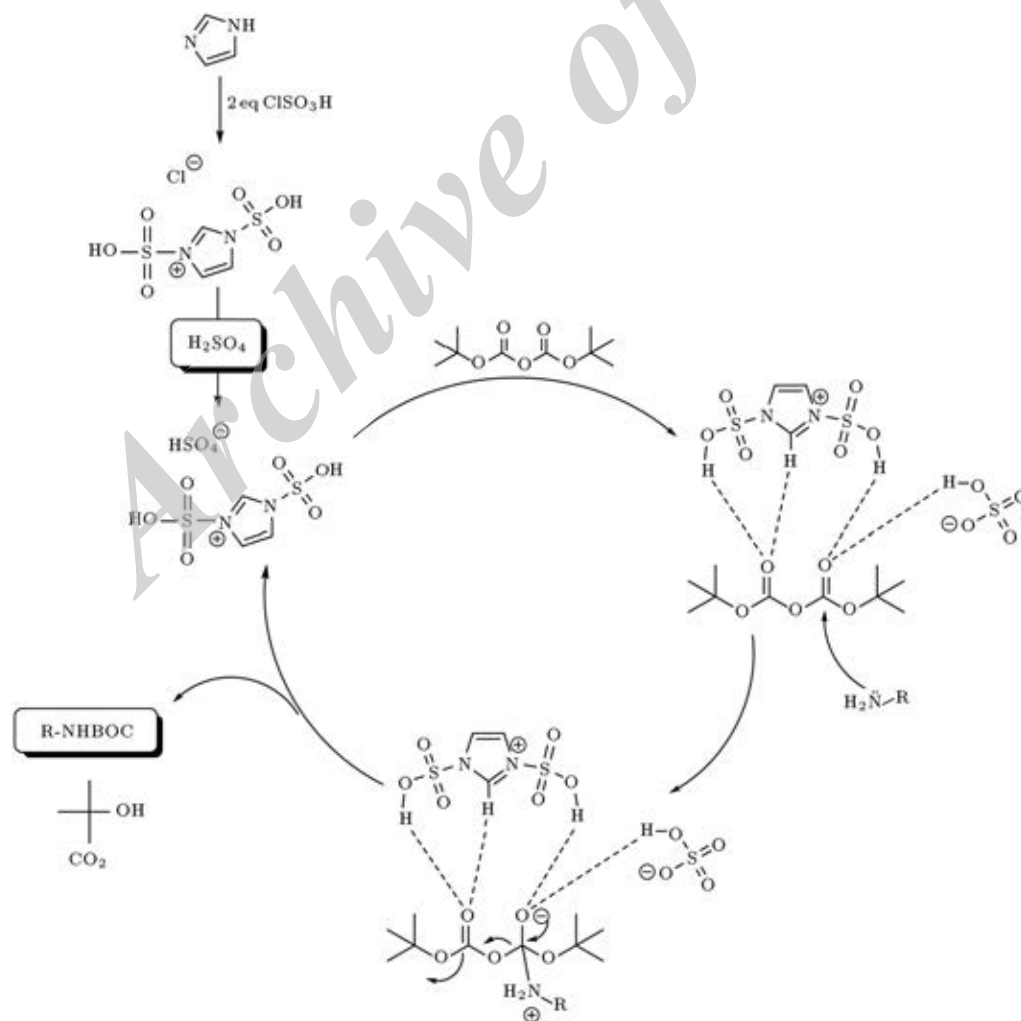
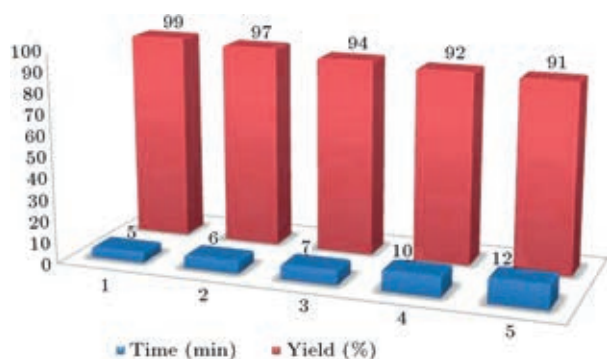
<sup>a</sup> Isolated yield.Scheme 4: The proposed mechanism for the protection of amines with *diboc* using [Dsim]HSO<sub>4</sub> as catalyst.

Table 4: Comparison of the results of the reaction of aniline with *diboc* catalyzed by [Dsim]HSO<sub>4</sub> with those obtained by the reported catalysts.

Catalyst/condition	Catalyst amount (mol%)	Time (min)	Yield <sup>a</sup> (%)	TON <sup>b</sup>	TOF <sup>c</sup> (min <sup>-1</sup> )	Ref.
[Dsim]HSO <sub>4</sub> /ethanol/r.t.	0.1	15	90	900	60	- <sup>d</sup>
Thiourea/toluene/60 °C	10	40	95	9.5	0.23	[11]
NH <sub>2</sub> SO <sub>3</sub> H/solvent-free/r.t.	5	10	96	19.2	1.92	[12]
NH <sub>2</sub> SO <sub>3</sub> H/solvent-free/r.t.	5	5	99	19.8	3.96	[12]
[H <sub>2</sub> -cryptand 222](Br <sub>3</sub> ) <sub>2</sub>	0.1	300	80	800	2.66	[13]
Cu(BF <sub>4</sub> ) <sub>2</sub> · xH <sub>2</sub> O/solvent-free/35 °C	1	5	98	98	19.6	[14]
[(HMI)BF <sub>4</sub> ]/Solvent-free/35 °C	1	15	100	100	6.66	[15]
La(NO <sub>3</sub> ) <sub>3</sub> · 6H <sub>2</sub> O/solvent-free/35 °C	5	2	100	20	10	[16]
Thiourea/toluene/60 °C	10	40	95	9.5	0.23	[17]

<sup>a</sup> Isolated yield.<sup>b</sup> Turn-over number.<sup>c</sup> Turn-over frequency.<sup>d</sup> Our work.Figure 2: The reaction of 4-methoxyaniline with *diboc* in the presence of reused [Dsim]HSO<sub>4</sub> at room temperature.

hydrogen bond formation with the acidic hydrogens of [Dsim]HSO<sub>4</sub>. Afterward, the nitrogen of the amine attacks the carbonyl group. By opening and closing the  $\pi$  bond of the carbonyl group, the amine is protected, and one molecule of CO<sub>2</sub> and *tert*-butyl alcohol is also prepared.

In another study, recyclability of the catalyst was tested upon the reaction of the *N*-*boc* protection of 4-methoxyaniline. The reaction mixture was extracted by ethyl acetate and separated from the catalyst. Afterward, the reused catalyst was employed for another reaction. We observed that the catalytic activity of the catalyst was restored within the limits of experimental error for five successive runs (Figure 2).

Furthermore, we compared the Turn Over Number (TON) and Frequency (TOF) values of our catalyst with the reported catalysts on the reaction of aniline with *diboc* (Table 4). The TON and TOF values showed that [Dsim]HSO<sub>4</sub> was more effective than the reported catalysts.

### 3. Conclusion

In summary, we have prepared, characterized and applied a novel ionic liquid, namely; 1,3-disulfonic acid imidazolium hydrogen sulfate {[Dsim]HSO<sub>4</sub>}, as a reusable catalyst for the chemoselective *N*-*boc* protection of amines. The reaction was carried out at room temperature with high yields and very short reaction times.

### 4. Experimental

All Chemicals were purchased from Merck, Sigma-Aldrich<sup>®</sup> or Fluka Chemical Company. The products were identified by

comparison of their <sup>1</sup>H NMR, TLC and melting points with those in authentic samples. The progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. The <sup>1</sup>H NMR (300 or 90 MHz) was run on a Bruker Avance DPX FT-NMR spectrometer ( $\delta$  in ppm). Melting points were recorded on a Stuart Scientific Apparatus SMP3 (UK) in open capillary tubes.

#### 4.1. Procedure for the preparation of ionic liquid [Dsim]HSO<sub>4</sub> (Scheme 1)

Chlorosulfonic acid (1.1885 g, 10.2 mmol) was added dropwise to a round-bottomed flask (100 mL) containing imidazole (0.340 g, 5 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL), over a period of 20 min at room temperature. After the addition was completed, the reaction mixture was stirred for 12 h under pressure of nitrogen (to remove the produced HCl), stood for 5 min, and the CH<sub>2</sub>Cl<sub>2</sub> was decanted. The residue was washed with dry CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL) and dried under vacuum to give [Dsim]Cl as a viscous pale yellow oil in 95% yield, 1.257 g [6]. Then, sulfuric acid 99.99% (0.49 g, 5 mmol) was added dropwise to [Dsim]Cl (1.3233 g, 5 mmol) over a period of 5 min at room temperature under a continuous flow of nitrogen to remove the HCl gas that is produced. The resulting mixture was stirred for 12 h at 60 °C and then heated at 90 °C under powerful vacuum for 20 min to give [Dsim]HSO<sub>4</sub> as a viscous green oil in 99% yield.

#### 1,3-disulfonic acid imidazolium hydrogen sulfate {[Dsim]HSO<sub>4</sub>}:

Brown oil; IR (Nujol) 624, 1031, 1053, 1085, 1285, 1324, 3100–3400 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, DMSO - *d*<sub>6</sub>),  $\delta$  (ppm) 7.22(s, 2H), 8.44(s, 1H), 11.95(s, 1H), 13.55(s, 2H); <sup>13</sup>C NMR (75 MHz, DMSO - *d*<sub>6</sub>) :  $\delta$  (ppm) 119.5, 134.0; MS : *m/z* = 326(*M*<sup>+</sup>), 229(*M*<sup>+</sup> - HSO<sub>4</sub>), 148(*M*<sup>+</sup> - HSO<sub>4</sub>SO<sub>3</sub>H), 97(HSO<sub>4</sub>), 67(*M*<sup>+</sup> - HSO<sub>4</sub>SO<sub>3</sub>HSO<sub>3</sub>H).

#### 4.2. General procedure for the *N*-*boc* protection of amines

A solution of *diboc* (1 mmol) in ethanol (2 mL) was added to a round-bottomed flask containing [Dsim]HSO<sub>4</sub> (0.1 mol%), and the resulting solution was stirred at room temperature for 10 s. Then, amine (1 mmol) was added, and the reaction mixture was stirred at room temperature for the appropriate time (see Table 3). Afterwards, the solution of the product and the unreacted starting materials were separated from [Dsim]HSO<sub>4</sub> by decanting (the catalyst could be used for another reaction). After drying and evaporation of the solvent, the solid residue (crude product) was purified by recrystallization from *n*-hexane or ethyl acetate (5 mL) or by column chromatography on silica gel eluted with ethyl acetate/*n*-hexane (1/3).



### 4.3. Selected spectral data of the products

*Tert-butyl 4-(2-hydroxyethyl)piperazine-1-carboxylate* (1): (lit. [13]); IR (Nujol): 3450, 2976, 1700  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (90 MHz,  $\text{CDCl}_3$ ),  $\delta$  1.09(s, 9H), 2.11(m, 6H), 3.08(m, 4H), 3.30(t, 2H), 3.68(br, 1H).

*Tert-butyl 4-hydroxyphenylcarbamate* (4): (lit. [13]); IR (KBr): 3360, 2969, 1705, 1535  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (90 MHz,  $\text{CDCl}_3$ ),  $\delta$  1.48(s, 9H), 5.35(s, 1H), 6.36(s, 1H), 6.60–6.82(m, 2H), 7.02–7.35(m, 2H).

*Tert-butyl 4-methoxyphenylcarbamate* (6): (lit. [15]); IR (KBr): 3420, 2970, 1693, 1535  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (90 MHz,  $\text{CDCl}_3$ ),  $\delta$  1.47(s, 9H), 3.73(s, 3H), 6.42(s, 1H), 6.65–6.96(m, 2H), 7.15–7.32(m, 2H).

*Tert-butyl m-tolylcarbamate* (8): (lit. [14]); IR (KBr): 3327, 2960, 1698, 1533  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (90 MHz,  $\text{CDCl}_3$ ),  $\delta$  1.52(s, 9H), 2.30(s, 3H), 6.62–7.36(m, 5H).

*Tert-butyl 4,4'-methylenebis(4,1-phenylene) dicarbamate* (10): (lit. [13]); IR (KBr): 3325, 2960, 1683, 1539  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (90 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.49(s, 18H), 3.85(s, 2H), 6.42(s, 2H), 7.02–7.35(m, 8H).

*Tert-butyl 4-chlorophenylcarbamate* (11): (lit. [14]); IR (KBr): 3304, 2961, 1700, 1593  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (90 MHz,  $\text{CDCl}_3$ ),  $\delta$  1.49(s, 9H), 6.49(s, 1H), 7.19–7.35(m, 4H).

*Tert-butyl 4-bromophenylcarbamate* (12): (lit. [14]); IR (KBr): 3360, 2960, 1700, 1591  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (90 MHz,  $\text{CDCl}_3$ ),  $\delta$  1.48(s, 9H), 6.63(s, 1H), 7.26–7.43(m, 4H).

*Tert-butyl naphthalen-1-ylcarbamate* (16): (lit. [13]); IR (KBr): 3250, 2972, 1690, 1545  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (90 MHz,  $\text{CDCl}_3$ ),  $\delta$  1.55(s, 9H), 6.86(s, 1H), 7.35–7.60(m, 4H), 7.75–7.96(m, 3H).

*Tert-butyl 1,2-phenylenedicarbamate* (17): (lit. [13]); IR (KBr): 3375, 2976, 1685, 1531  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (90 MHz,  $\text{CDCl}_3$ ),  $\delta$  1.48(s, 18H), 6.71(s, 2H), 7.04–7.49(m, 4H).

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