



# SO<sub>3</sub>H-functionalized ionic liquids as efficient and recyclable catalysts for the synthesis of pentaerythritol diacetals and diketals

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## ABSTRACT

The efficient, simple and environmentally friendly synthesis of pentaerythritol diacetals and diketals using SO<sub>3</sub>H-functionalized ionic liquids (ILs) as catalysts was reported. The ILs showed high catalytic activities and reusabilities with good to excellent yields of the desired products. *H*<sub>0</sub> (Hammett function) values and the minimum-energy geometries of SO<sub>3</sub>H-functionalized ILs were determined and the results revealed that the acidities and catalytic activities of ILs in acetalization were related to their structures. The IL [PSPy][OTf] with the shortest H–O bond distance had the strongest acidity and the highest catalytic activity in the synthesis of pentaerythritol diacetals and diketals.

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## 1. Introduction

Acetals are biologically important due to their role in the chemistry of carbohydrates [1–3]. Also, in the fragrance and pharmaceutical industries, acetals are employed as both intermediates and end products [4,5]. Pentaerythritol acetals in general are applied as plasticizers and vulcanizers for various polymeric materials, raw materials for the production of valuable resins and lacquers, physiologically active substances and defoamers for washing solution defoamers for washing solution containing anionic surfactants [6,7]. They can be used as potential protective groups for aldehydes and ketones as well as important derivatives of carbonyl compounds, since most are crystalline substances and have sharp melting points. Several publications have described the preparation of pentaerythritol diacetals under acidic conditions [8–10]. However, many of these reported methods suffer from drawbacks such as harsh reaction conditions, unsatisfactory yields, cumbersome product isolation procedures, great excess of aldehyde (ketones), volatile and hazardous organic solvents, which have to be recovered, treated and disposed of. Therefore, the design and synthesis of highly active catalysts aimed at overcoming these limitations become a significant challenging task.

During the past decades, ionic liquids (ILs) have received considerable attention as environmentally friendly and effective reaction media for a wide variety of organic reaction and other applications

in chemistry [11–14]. The introduction of specific functionality has led to the identification of functionalized ionic liquids (FILs, or task-specific ionic liquids, TSILs) [15]. Among different kinds of FILs, SO<sub>3</sub>H-functionalized ILs have been intensively studied over the past five years, because the existence of SO<sub>3</sub>H-functional groups can obviously enhance their acidities and water solubilities [16–20]. We have reported the efficient acetalization of aromatic aldehydes with diols using FILs based on benzimidazolium cations as catalysts [21]. As an extension to our previous work on FILs catalysis, we investigate the synthesis of pentaerythritol diacetals and diketals promoted by SO<sub>3</sub>H-functionalized ILs (Fig. 1), which possess good recyclabilities and reusabilities. As far as we know, this is the first example of synthesis of pentaerythritol diacetals and diketals in ILs.

## 2. Experimental

### 2.1. Chemicals and instruments

All chemicals were analytical grade and used as received. The melting points were determined on Sanyo Gallenkamp MPD350 apparatus. <sup>1</sup>H NMR spectra were recorded on Bruker DRX-500 spectrometer. FT-IR measurements were performed using KBr disc on a NEXUS 670 FT-IR infrared spectrometer (Nicolet).

### 2.2. Synthesis of SO<sub>3</sub>H-functionalized ILs

SO<sub>3</sub>H-functionalized ILs based on trimethylamine, 1-methylimidazole and pyridine were prepared according to the procedures reported by Cole et al. [22], Li et al. [23] and Dai

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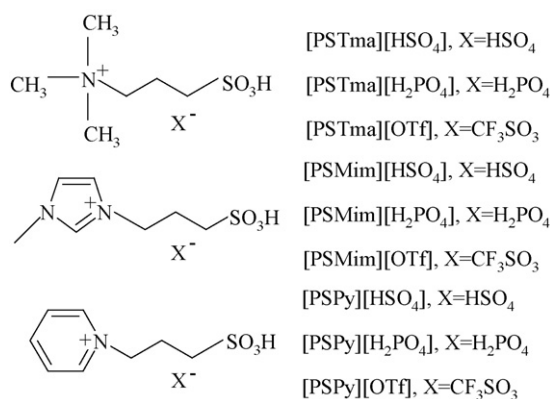


Fig. 1. Structures of SO<sub>3</sub>H-functionalized ILs used in this paper.

**Table 1**  
Synthesis of dibenzalpenpentaerythritol catalyzed by various SO<sub>3</sub>H-functionalized ILs.

Entry	ILs	Yield (%) <sup>a</sup>
1	[PSTma][HSO <sub>4</sub> ]	88
2	[PSTma][H <sub>2</sub> PO <sub>4</sub> ]	86
3	[PSTma][OTf]	90
4	[PSMim][HSO <sub>4</sub> ]	88
5	[PSMim][H <sub>2</sub> PO <sub>4</sub> ]	86
6	[PSMim][OTf]	90
7	[PSPy][HSO <sub>4</sub> ]	89
8	[PSPy][H <sub>2</sub> PO <sub>4</sub> ]	86
9	[PSPy][OTf]	93
10	H <sub>2</sub> SO <sub>4</sub> (98%) <sup>b</sup>	65
11	H <sub>2</sub> SO <sub>4</sub> (98%) <sup>c</sup>	84

<sup>a</sup> Yield refers to isolated pure products: pentaerythritol (10 mmol), benzaldehyde (20 mmol), SO<sub>3</sub>H-functionalized IL (3 mmol), T = 100 °C, t = 1.5 h.

<sup>b</sup> Solvent free.

<sup>c</sup> Solvent: benzene.

and co-workers [24], respectively. The obtained ILs were identified by <sup>1</sup>H NMR and IR analysis.

### 2.3. UV–vis acidity evaluation

Dichloromethane solutions of the ILs were prepared from anhydrous CH<sub>2</sub>Cl<sub>2</sub> and the ILs (dried under vacuum at 70 °C for 2 h). All spectra were obtained with an Agilent B453 spectrophotometer.

### 2.4. Computational methods

The minimum-energy geometries of SO<sub>3</sub>H-functionalized ILs and isolated [PSPy]<sup>+</sup>, [PSMim]<sup>+</sup>, [PSTma]<sup>+</sup> cations were determined

**Table 3**  
The geometry parameters of isolated cations and SO<sub>3</sub>H-functionalized ILs.

	[PSTma]	[PSTma][HSO <sub>4</sub> ]	[PSTma][H <sub>2</sub> PO <sub>4</sub> ]	[PSTma][OTf]	[PSMim]	[PSMim][HSO <sub>4</sub> ]
H–O bond distance (Å)	H <sub>14</sub> –O <sub>13</sub> = 0.956	H <sub>11</sub> –O <sub>10</sub> = 0.981	H <sub>14</sub> –O <sub>13</sub> = 0.992	H <sub>14</sub> –O <sub>13</sub> = 0.970	H <sub>14</sub> –O <sub>13</sub> = 0.952	H <sub>14</sub> –O <sub>13</sub> = 0.970
Distance between the anion and sulfonic acid group (Å)		H <sub>11</sub> ···O <sub>14</sub> = 1.676	H <sub>14</sub> ···O <sub>15</sub> = 1.538	H <sub>14</sub> ···O <sub>15</sub> = 1.758		H <sub>14</sub> ···O <sub>18</sub> = 1.739
Other hydrogen bonds in ILs (Å)		H <sub>24</sub> ···O <sub>12</sub> = 2.294 H <sub>19</sub> ···O <sub>15</sub> = 2.611 H <sub>19</sub> ···O <sub>12</sub> = 2.417 H <sub>5</sub> ···O <sub>15</sub> = 2.438	H <sub>20</sub> ···O <sub>26</sub> = 1.900 H <sub>5</sub> ···O <sub>16</sub> = 2.038	H <sub>33</sub> ···O <sub>18</sub> = 2.331 H <sub>26</sub> ···O <sub>18</sub> = 2.375 H <sub>5</sub> ···O <sub>18</sub> = 2.276		H <sub>5</sub> ···O <sub>18</sub> = 2.308 H <sub>29</sub> ···O <sub>18</sub> = 2.560 H <sub>29</sub> ···O <sub>15</sub> = 2.046
H–O bond distance (Å)	[PSMim][H <sub>2</sub> PO <sub>4</sub> ] H <sub>14</sub> –O <sub>13</sub> = 0.969	[PSMim][OTf] H <sub>14</sub> –O <sub>13</sub> = 0.965	[PSPy] H <sub>25</sub> –O <sub>24</sub> = 0.950	[PSPy][HSO <sub>4</sub> ] H <sub>25</sub> –O <sub>24</sub> = 0.976	[PSPy][H <sub>2</sub> PO <sub>4</sub> ] H <sub>30</sub> –O <sub>23</sub> = 0.994	[PSPy][OTf] H <sub>25</sub> –O <sub>24</sub> = 0.963
Distance between the anion and sulfonic acid group (Å)	H <sub>14</sub> ···O <sub>16</sub> = 1.962	H <sub>14</sub> ···O <sub>18</sub> = 1.814		H <sub>25</sub> ···O <sub>28</sub> = 1.700	H <sub>30</sub> ···O <sub>26</sub> = 1.556	H <sub>25</sub> ···O <sub>26</sub> = 1.732
Other hydrogen bonds in ILs (Å)	H <sub>30</sub> ···O <sub>15</sub> = 2.737 H <sub>27</sub> ···O <sub>15</sub> = 1.631 H <sub>5</sub> ···O <sub>15</sub> = 2.480	H <sub>27</sub> ···O <sub>15</sub> = 2.057 H <sub>5</sub> ···O <sub>18</sub> = 2.326 H <sub>27</sub> ···O <sub>18</sub> = 2.644 H <sub>30</sub> ···O <sub>15</sub> = 2.455		H <sub>8</sub> ···O <sub>26</sub> = 2.001 H <sub>8</sub> ···O <sub>29</sub> = 2.492 H <sub>19</sub> ···O <sub>26</sub> = 2.386 H <sub>16</sub> ···O <sub>28</sub> = 2.608	H <sub>16</sub> ···O <sub>26</sub> = 2.754 H <sub>8</sub> ···O <sub>28</sub> = 2.265	H <sub>8</sub> ···O <sub>29</sub> = 2.270 H <sub>16</sub> ···O <sub>29</sub> = 2.415

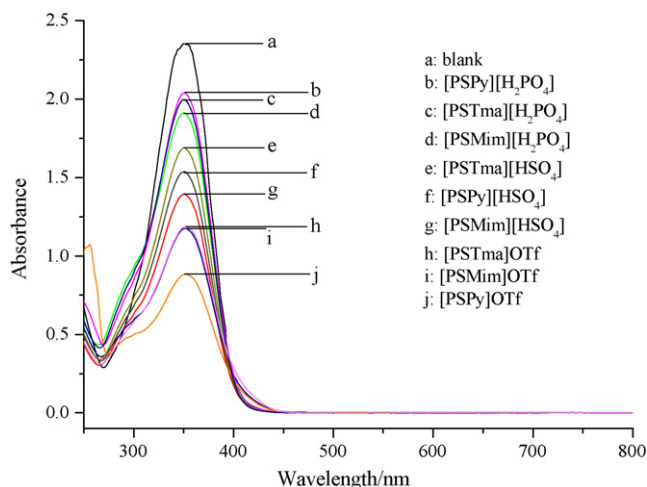


Fig. 2. Absorbance spectra of 4-nitroaniline for various SO<sub>3</sub>H-functionalized ILs in CH<sub>2</sub>Cl<sub>2</sub>.

**Table 2**  
Calculation and comparison of H<sub>0</sub> values of different SO<sub>3</sub>H-functionalized ILs in CH<sub>2</sub>Cl<sub>2</sub> (20 °C).

Entry	ILs	A <sub>max</sub>	[I] (%)	[IH <sup>+</sup> ] (%)	H <sub>0</sub>
1	–	2.353	100.0	0	–
2	[PSTma][HSO <sub>4</sub> ]	1.689	71.8	28.2	1.40
3	[PSTma][H <sub>2</sub> PO <sub>4</sub> ]	1.996	84.8	15.2	1.74
4	[PSTma][OTf]	1.184	50.3	49.7	1.00
5	[PSMim][HSO <sub>4</sub> ]	1.393	59.2	40.8	1.15
6	[PSMim][H <sub>2</sub> PO <sub>4</sub> ]	1.912	81.3	18.7	1.63
7	[PSMim][OTf]	1.173	49.8	50.2	0.99
8	[PSPy][HSO <sub>4</sub> ]	1.537	65.3	34.7	1.26
9	[PSPy][H <sub>2</sub> PO <sub>4</sub> ]	2.038	86.6	13.4	1.80
10	[PSPy][OTf]	0.882	37.5	62.5	0.77

Indicator: 4-nitroaniline.

by performing ab initio geometry optimizations at the RHF/6-31(d, p) level using the Gaussian03 program [25]. A vibrational analysis was performed to ensure the absence of negative frequencies and verify the existence of a true minimum.

### 2.5. General procedure for the synthesis of pentaerythritol diacetals and diketals

A mixture of pentaerythritol (10 mmol), aldehyde (ketone) (10 mmol) and IL (3 mmol) was placed into a round bottom flask of 25 mL capacity. The flask was fitted with a condenser and flushed with nitrogen gas. A nitrogen balloon was fitted at the top of the

condenser to maintain inert atmosphere. The acetalization was typically proceed for 1.5–4 h with vigorous stirring at 100 °C. After the reaction, the reaction mixture was cooled to room temperature and the layers separated. The crude product was isolated by distillation and purified by recrystallization with ethanol as a solvent to give the title compound, which was characterized by FT-IR and  $^1\text{H}$  NMR. The IL phase contained the produced water, could be easily recovered and reused in the next run after heat treatment under vacuum at 70 °C for 2 h.

IR spectra and  $^1\text{H}$  NMR spectra data for products **1–12** (Table 4) are shown as follows:

(1): M.p. (°C): 43–45. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2958, 2930, 2871, 1110, 1075, 990, 722.  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6$ -acetone)  $\delta$  0.90 (t, 6H,  $2\text{CH}_3$ ), 1.20–1.69 (m, 8H,  $2(\text{CH}_2)_2$ ), 3.24–3.41 [m, 6H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 4.41 (t, 2H, 2CH), 4.65 [d, 2H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ].

(2): M.p. (°C): 159–160. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3120, 2987, 2864, 1610, 1504, 1675, 1114, 1087, 1022, 781, 743.  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6$ -acetone)  $\delta$  3.51–3.92 [m, 6H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 4.82 [d, 2H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 5.55 (s, 2H, 2ArCH), 6.32–6.53 (m, 4H,  $\beta$ -H), 7.42 (d, 2H,  $\alpha$ -H).

(3): M.p. (°C): 155–156. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3034, 2958, 2857, 1496, 1468, 1373, 1160, 1115, 1078, 1030, 1021, 747.  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6$ -acetone)  $\delta$  3.49–3.93 [m, 6H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 4.80 [d, 2H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 5.41 (s, 2H, 2PhCH), 7.19–7.58 (m, 8H, 2Ph).

(4): M.p. (°C): 141–142. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2970, 2856, 1575, 1477, 1384, 1073, 960, 710.  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6$ -acetone)  $\delta$  3.61–3.82 [m, 6H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 4.83 [d, 2H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 5.48 (s, 2H, 2 PhCH), 7.25–7.48 (m, 8H, 2Ph).

(5): M.p. (°C): 201–202. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2980, 2862, 1596, 1490, 1382, 1201, 1162, 1076, 816, 680.  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6$ -acetone)  $\delta$  3.63–3.85 [m, 6H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 4.82 [d, 2H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 5.50 (s, 2H, 2 PhCH), 7.26–7.50 (m, 8H, 2Ph).

(6): M.p. (°C): 183–184. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3008, 2828, 1610, 1517, 1460, 1396, 1063, 1034, 830.  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6$ -acetone)  $\delta$  3.18 (s, 6H,  $2\text{OCH}_3$ ), 3.87–4.01 [m, 6H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 4.32 [d, 2H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 4.56 (s, 2H, 2PhCH), 6.81–7.78 (m, 8H, 2Ph).

(7): M.p. (°C): 212–213. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2973, 2860, 1618, 1470, 1384, 1075, 806.  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6$ -acetone)  $\delta$  2.35 (s, 6H,  $2\text{CH}_3$ ), 3.63–3.83 [m, 6H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 4.56 [d, 2H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 5.43 (s, 2H, 2PhCH), 7.18–7.36 (m, 8H, 2Ph).

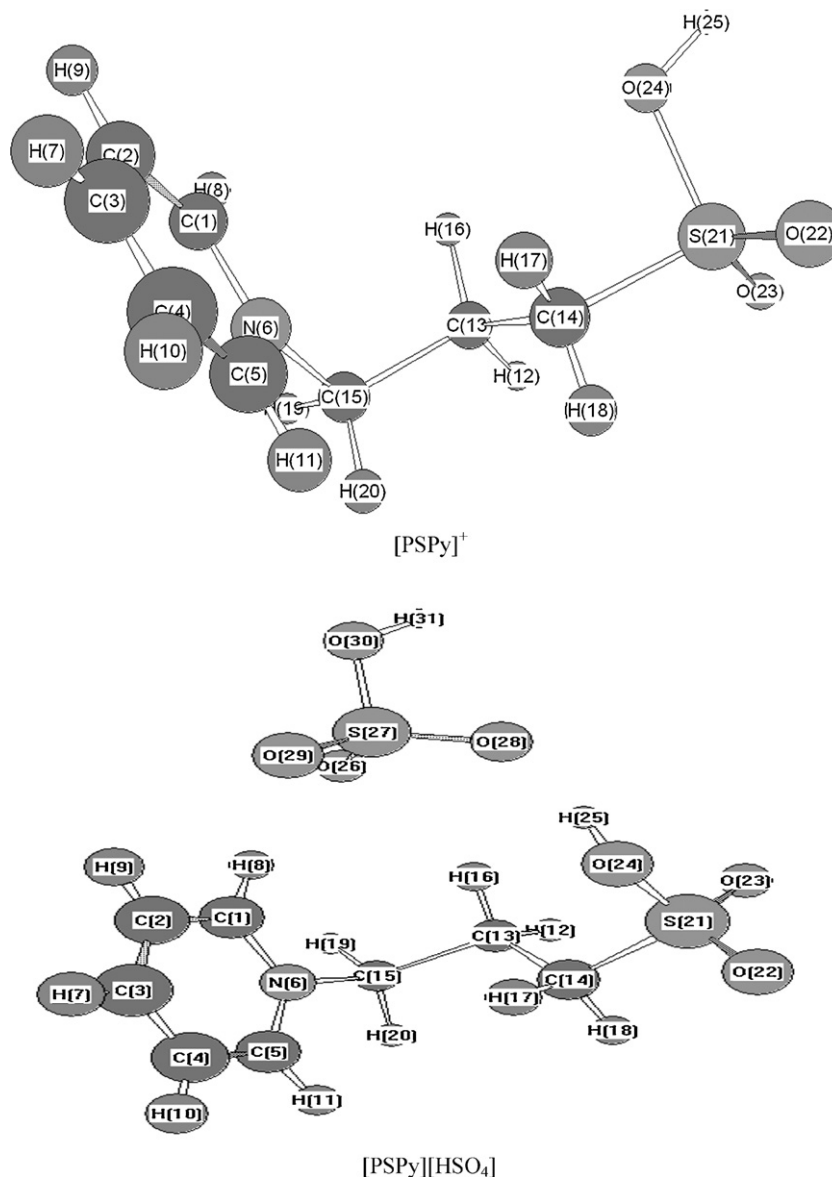


Fig. 3. Molecular structures of isolated [PSPy]<sup>+</sup> cation and ILs based on [PSPy]<sup>+</sup> cation.

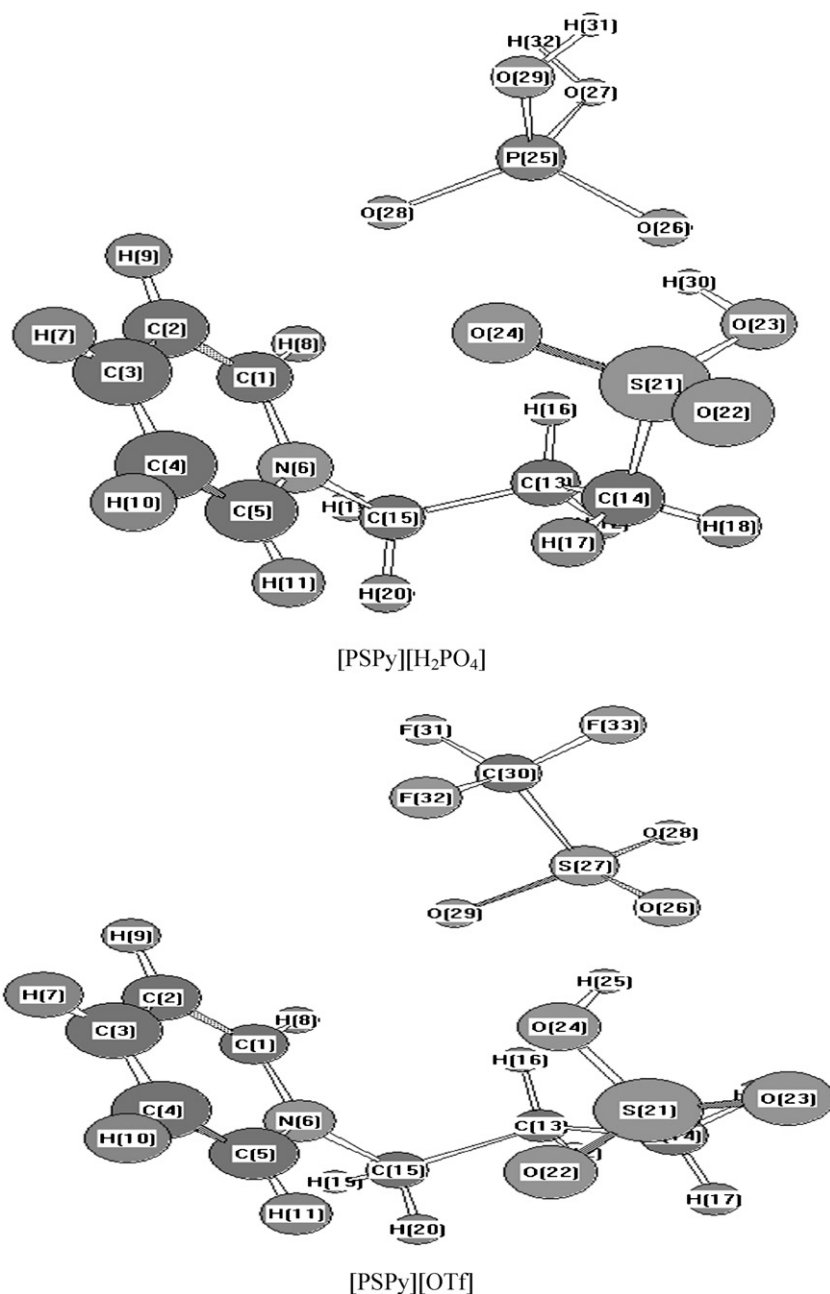


Fig. 3. (Continued).

(8): M.p. (°C): 185–186. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2983, 2904, 1615, 1534, 1354, 1078, 1005, 712, 677.  $^1\text{H}$  NMR (500 MHz,  $d_6$ -acetone)  $\delta$  3.66–3.93 [m, 6H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 4.85 [d, 2H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 5.54 (s, 2H, 2PhCH), 7.58–8.37 (m, 8H, 2Ph).

(9): M.p. (°C): 226–227. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2985, 2940, 1613, 1529, 1346, 1072, 851, 750, 697.  $^1\text{H}$  NMR (500 MHz,  $d_6$ -acetone)  $\delta$  3.73–3.94 [m, 6H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 4.85 [d, 2H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 5.53 (s, 2H, 2PhCH), 8.04–8.48 (m, 8H, 2Ph).

(10): M.p. (°C): 43–45. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2970, 2865, 1470, 1380, 1160, 1075.  $^1\text{H}$  NMR (500 MHz,  $d_6$ -acetone)  $\delta$  0.88 [s, 6H,  $2(\text{CH}_2)_5\text{CH}_3$ ], 1.28 (m, 16H,  $8\text{CH}_2$ ), 1.35 (s, 6H,  $2\text{CH}_3$ ), 1.66 (t, 4H,  $2\text{CH}_2$ ), 3.71–3.88 [m, 8H,  $\text{C}(\text{CH}_2\text{O})_4$ ].

(11): M.p. (°C): 147–148. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2980, 2900, 1468, 1378, 1250, 1171, 889, 701.  $^1\text{H}$  NMR (500 MHz,  $d_6$ -acetone)  $\delta$  1.51 (s, 6H,  $2\text{CH}_3$ ), 3.13–3.29 [m, 6H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 4.47 [d, 2H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 7.29–7.70 (m, 10H, 2Ph).

(12): M.p. (°C): 114–115. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2935, 2860, 1446, 1371, 1251, 1157, 1086, 918.  $^1\text{H}$  NMR (500 MHz,  $d_6$ -acetone)  $\delta$  1.20–2.06 [m, 20H,  $2(\text{CH}_2)_5$ ], 3.22–3.46 [m, 6H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ], 3.54 [d, 2H,  $\text{CH}_2\text{C}(\text{CH}_2)_3$ ].

### 3. Results and discussion

#### 3.1. Synthesis of dibenzalpenpentaerythritol in different ILs

The synthesis of pentaerythritol diacetals and diketals can be catalyzed by some other inorganic Lewis acidic catalysts, of which the concentrated sulfuric acid has the highest catalytic activity. For the purpose of comparison, the same acetalization reaction was also carried out with equivalent concentrated sulfuric acid (98%) as catalyst (Table 1, entries 10, 11). The results demonstrate that the catalytic performances of the  $\text{SO}_3\text{H}$ -functionalized ILs (Table 1,

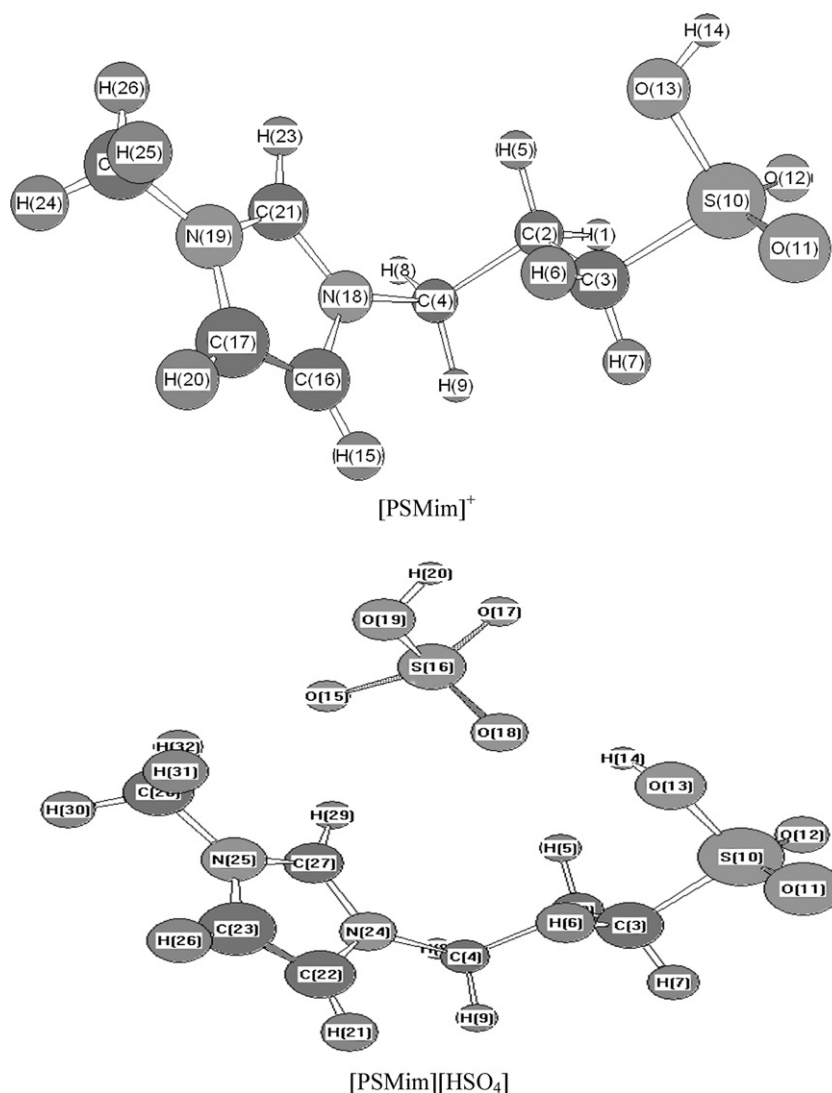


Fig. 4. Molecular structures of isolated [PSMim]<sup>+</sup> cation and ILs based on [PSMim]<sup>+</sup> cation.

entries 1–9) are better than that of the concentrated sulfuric acid (Table 1, entry 10) under the same reaction conditions. Furthermore, there are many drawbacks of using concentrated sulfuric acid catalyst system, such as heavy environmental pollution, troublesome recovery and purification of product, and difficult recovering of catalyst.

All the ILs give excellent yields of products. The reactants have good solubility in SO<sub>3</sub>H-functionalized ILs while the diacetals and diketals are almost immiscible with ILs, which facilitate the shift of the equilibrium of acetalization reaction. The acetalization started as a homogeneous process and ended as biphasic. Among all SO<sub>3</sub>H-functionalized ILs, we found that [PSPy][OTf] might be the best catalyst for the acetalization, leading to 93% yield of dibenzalpenlopentaerythritol.

### 3.2. Determination of $H_0$ values of SO<sub>3</sub>H-functionalized ILs

The measurement of the acidic scale of these SO<sub>3</sub>H-functionalized ILs was conducted on an Agilent 8453 UV-vis spectrophotometer with a basic indicator according to the literature reported previously [21,26]. With the increase of acidic scale of the acidic ILs, the absorbance of the unprotonated form of the basic indicator decreased, whereas the protonated form of the indicator could not be observed because of its small molar absorptivity and

its location, so the  $[I]/[IH^+]$  ( $I$  represents indicator) ratio could be determined from the differences of measured absorbance after the addition of Brønsted acidic ILs and Hammett function,  $H_0$ , could be calculated using Eq. (1). This value could be regarded as the relative acidity of the ILs.

$$H_0 = pK(I)_{aq} + \log \left( \frac{[I]}{[IH^+]} \right) \quad (1)$$

Under the same concentration of 4-nitroaniline (10 mg/L,  $pK_a = 0.99$ ) and ILs (5 mmol/L) in dichloromethane, we determined the  $H_0$  values of the SO<sub>3</sub>H-functionalized ILs. The maximal absorbance of the unprotonated form of the indicator was observed at 350 nm in CH<sub>2</sub>Cl<sub>2</sub>. When the IL was added, the absorbance of the unprotonated form of the basic indicator decreased. As shown in Fig. 2, the absorbance of the unprotonated form of the indicator on nine SO<sub>3</sub>H-functionalized ILs decreased as follows: [PSPy][H<sub>2</sub>PO<sub>4</sub>] > [PSTma][H<sub>2</sub>PO<sub>4</sub>] > [PSMim][H<sub>2</sub>PO<sub>4</sub>] > [PSTma][HSO<sub>4</sub>] > [PSPy][HSO<sub>4</sub>] > [PSMim][HSO<sub>4</sub>] > [PSTma][OTf] > [PSMim][OTf] > [PSPy][OTf]. After the calculation, we obtained the acidity order of the nine ILs with the following  $H_0$  values (Table 2): [PSPy][OTf] (0.77) > [PSMim][OTf] (0.99) > [PSTma][OTf] (1.00) > [PSMim][HSO<sub>4</sub>] (1.15) > [PSPy][HSO<sub>4</sub>] (1.26) > [PSTma][HSO<sub>4</sub>] (1.40) > [PSMim][H<sub>2</sub>PO<sub>4</sub>] (1.63) > [PSTma][H<sub>2</sub>PO<sub>4</sub>] (1.74) > [PSPy][H<sub>2</sub>PO<sub>4</sub>] (1.80),



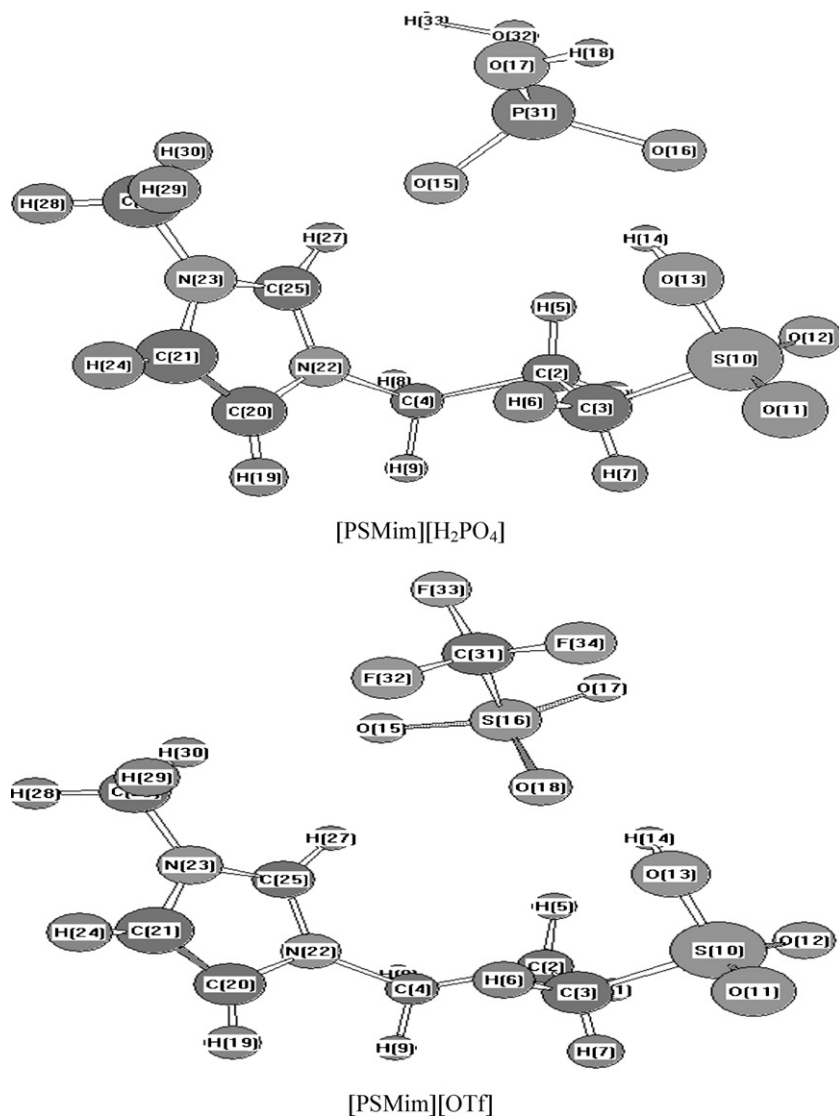


Fig. 4. (Continued).

which is in good agreement with the sequence of catalytic activity observed in acetalization. The acidities of the ILs depended both on the characteristics of the cations and anions. When the cations of the ILs were the same, the dependence of the acidities of the ILs on anions was significant. The acidities of the ILs with the conjugate base of [H<sub>2</sub>PO<sub>4</sub>]<sup>-</sup> is weaker than those of the ILs with the conjugate bases of [HSO<sub>4</sub>]<sup>-</sup> and [OTf]<sup>-</sup> (Table 2, entries 2–4).

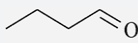

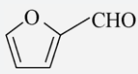
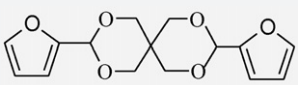
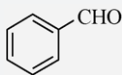

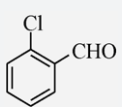
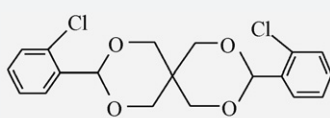
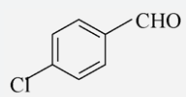
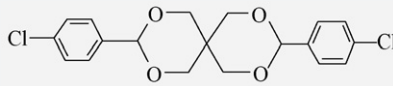
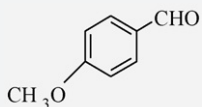
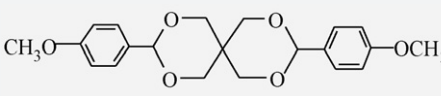
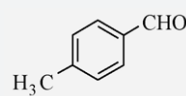
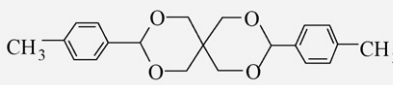
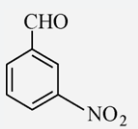
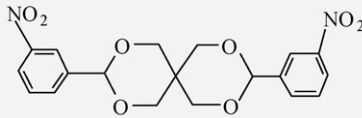
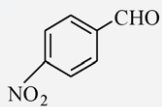
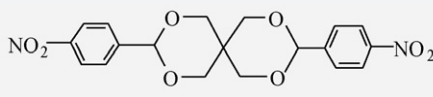
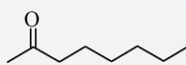

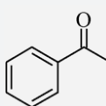
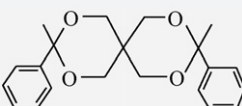


### 3.3. The molecular geometries of SO<sub>3</sub>H-functionalized ILs

The minimum-energy geometries of SO<sub>3</sub>H-functionalized ILs were determined by performing ab initio geometry optimizations at the RHF/6-31(d, p) level. The fully optimized geometries of these ILs are presented in Figs. 3–5 and Table 3. It is obvious that a strong hydrogen bond network is presented in the SO<sub>3</sub>H-functionalized ILs. Taking IL [PSPy][HSO<sub>4</sub>] for example, the anion is located on the side of the propyl sulfonic acid group, and interacts with the propyl alkyl sulfonic acid group and pyridinium ring in the form of C–H...O or O–H...O type (hydrogen bonds). There are five hydrogen bonds in IL [PSPy][HSO<sub>4</sub>], which are shorter than the Van der Waals distance of 2.67 Å [27]. These include the hydrogen bonds C<sub>1</sub>–H<sub>8</sub>...O<sub>26</sub>, C<sub>1</sub>–H<sub>8</sub>...O<sub>29</sub> (bond distances are 2.001 Å, 2.492 Å) between the anion and pyridinium ring; the

hydrogen bonds C<sub>5</sub>–H<sub>19</sub>...O<sub>26</sub>, C<sub>13</sub>–H<sub>16</sub>...O<sub>28</sub> (bond distances are 2.386 Å, 2.608 Å) between the anion and alkyl sulfonic acid chain; most importantly, the strongest interaction between the anion and the sulfonic acid proton was O<sub>24</sub>–H<sub>25</sub>...O<sub>28</sub> (bond distance is 1.700 Å). The other eight SO<sub>3</sub>H-functionalized ILs also exhibit similar strong interactions between the anions and the sulfonic acid groups, which making the H–O bond of the sulfonic acid group to be lengthened with different levels compared with the one in the isolated cation. When the cations of the ILs are the same, the H–O bond distance of SO<sub>3</sub>H-functionalized ILs decreased as follows: [Cation][H<sub>2</sub>PO<sub>4</sub>] > [Cation][HSO<sub>4</sub>] > [Cation][OTf]. Taking ILs based on [PSPy]<sup>+</sup> cation as examples, the H–O bond distance of the sulfonic acid group of these ILs decreased as follows: [PSPy][H<sub>2</sub>PO<sub>4</sub>] (H<sub>30</sub>–O<sub>23</sub> = 0.994 Å) > [PSPy][HSO<sub>4</sub>] (H<sub>25</sub>–O<sub>24</sub> = 0.976 Å) > [PSPy][OTf] (H<sub>25</sub>–O<sub>24</sub> = 0.963 Å), which is reverse to their acidity sequence. The formation of hydrogen bond was a process of sharing lone electron pair of O or F atom with H atom. When the hydrogen bond was strong, the lone electron pair was shared in deep degree, and cause an increase in the electron density and stability of H atom. As a result, the acidity of H atom decreased.

The results obtained from experiments and the minimum-energy geometries of SO<sub>3</sub>H-functionalized ILs revealed that the

**Table 4**  
Synthesis of pentaerythritol diacetals and diketals catalyzed by IL [PSPy][OTf].

Entry	Aldehydes (acetones)	Product	Time (h)	Yield (%) <sup>a</sup>
1			1.5	91
2			1.5	89
3			1.5	93
4			1.5	94
5			1.5	94
6			2.5	90
7			2.0	92
8			1.5	92
9			1.5	95
10			3.0	87
11			3.0	86
12			4.0	87

<sup>a</sup> Yield refers to isolated pure products: pentaerythritol (10 mmol), aldehyde (ketone) (20 mmol), [PSPy][OTf] (3 mmol),  $T = 100^\circ\text{C}$ . All the products were characterized by FT-IR,  $^1\text{H NMR}$ .

acidities and catalytic activities of ILs were related to their structures. The  $\text{SO}_3\text{H}$ -functionalized IL with shorter H–O bond has stronger acidity and higher catalytic activity in the synthesis of pentaerythritol diacetals and diketals.

#### 3.4. Acetalization of various aldehydes (ketones) with pentaerythritol in IL [PSPy][OTf]

The rate-determining step of acetalization is the formation of a cation from the protonated hemiacetal. In order to compensate for the low rate of hemiacetal formation, the medium is sufficiently acidic to promote effective protonation of any hemiacetal that is formed and sufficiently polar to allow stabilization of the cationic intermediate. Hence in our case, the use of strongly acidic and polar  $\text{SO}_3\text{H}$ -functionalized ILs gave shorter reaction time and higher yields than the methods presented in literatures [9,10]. The acetalization of various aldehydes with pentaerythritol reported here, showed clean conversion in high yields even when moderately hindered aldehydes were used (Table 4, entries 1–9). Ketones showed lower reactivity than aldehydes for this reaction, for example in IL [PSPy][OTf], dibenzalpentapentaerythritol (Table 4, entry 3) was obtained in quantitative yield (93%) for 1.5 h, whereas acetophenone (Table 4, entry 11) provided 86% yield of product for 3.0 h. It is worth noting that the substitutional group of the reactants is crucial to the yields of products, which can be seen from entries 3 to 9 in Table 4. When 4-methoxybenzaldehyde

(Table 4, entry 6) was treated with pentaerythritol in IL, the reaction time was longer (2.5 h) and the yield of pentaerythritol di-4-methoxybenzaldehyde was lower (90%), for the strong donor methoxy group reduced the reactivity of 4-methoxybenzaldehyde. The reactivity order of aromatic aldehydes is 4-nitrobenzaldehyde > 4-chlorobenzaldehyde > benzaldehyde > 4-methylbenzaldehyde > 4-methoxybenzaldehyde, which is consistent with the report [28] that electron-withdrawing substituents could enhance the rate of acetal formation.

#### 3.5. Reusability of IL [PSPy][OTf]

Compared with the traditional acidic catalysts, easy recycling is an attractive property of the acidic ILs. Consequently, we investigated the catalytic activity of recycled [PSPy][OTf] in the synthesis of dibenzalpentapentaerythritol. After the reaction, the mixture was placed for a while in order to form two phases. The crude product was isolated by distillation and the IL phase was conveniently recovered and reused after heat treatment under vacuum at  $70^\circ\text{C}$  for 2 h. The IL maintained its structure as confirmed by  $^1\text{H}$  NMR spectroscopy. As shown in Fig. 6, [PSPy][OTf] could be reused for 8 times at least and there was no obvious decrease in the yield of dibenzalpentapentaerythritol, which indicated that [PSPy][OTf] was high efficient and recyclable catalyst for the synthesis of pentaerythritol diacetals and diketals.

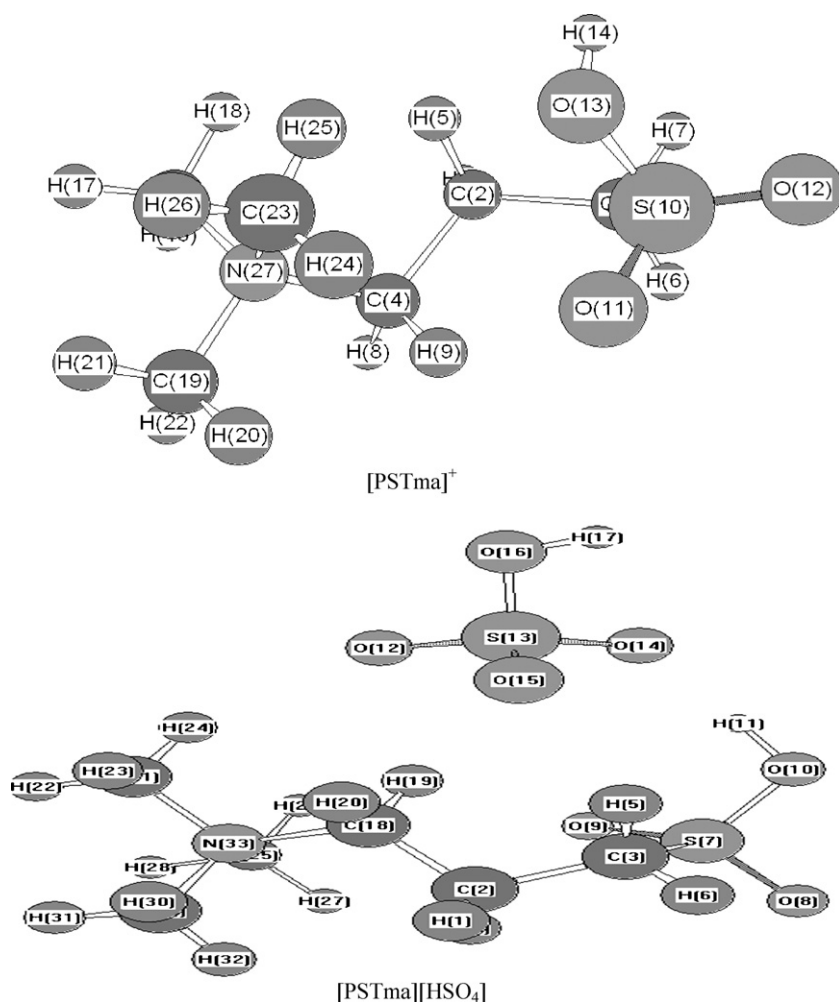


Fig. 5. Molecular structures of isolated  $[\text{PSTma}]^+$  cation and ILs based on  $[\text{PSTma}]^+$  cation.



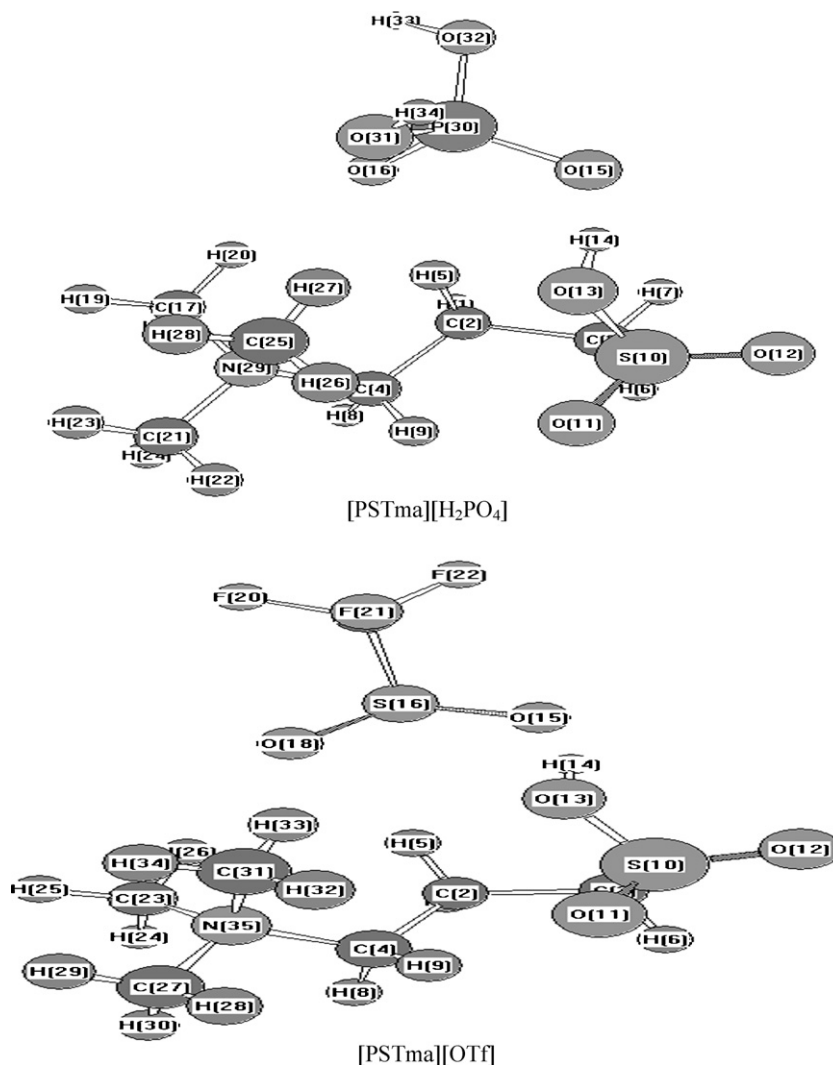


Fig. 5. (Continued).

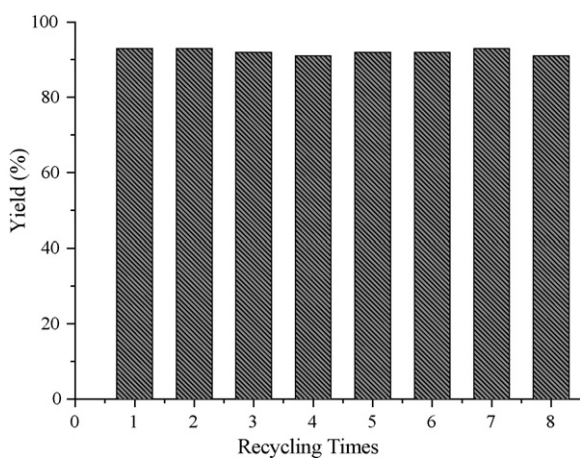


Fig. 6. Recycling of the IL [PSPy][OTf].

#### 4. Conclusions

In conclusion, a new approach to the synthesis of pentaerythritol diacetals and diketals was developed using SO<sub>3</sub>H-functionalized ILs as catalysts. This catalytic system is stable, easily separable, and

reusable. Furthermore, this series of SO<sub>3</sub>H-functionalized ILs have higher catalytic activities under mild reaction condition without the addition of any other organic solvents or catalysts. The results got from the experiments and the minimum-energy geometries of SO<sub>3</sub>H-functionalized ILs revealed that the acidities and catalytic activities of ILs in acetalization were related to their structures. The IL with shorter H–O bond distance has stronger acidity and higher catalytic activity in the synthesis of pentaerythritol diacetals and diketals.

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