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Functional Ionic Liquids as Efficient and Recyclable Catalysts for the Methylation of Formaldehyde with Aromatics

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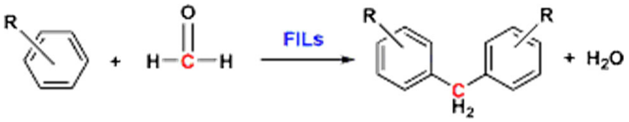
Abstract Methylation of formaldehyde with various aromatics under functional ionic liquids catalysis has been developed. Among the ionic liquids investigated, triphenyl-(4-sulfobutyl)-phosphonium triflate ([TTPBs][CF_3SO_3]) showed high activity and afforded excellent yields of diarylmethane derivatives. A mechanism for the catalytic performance of [TTPBs][CF_3SO_3] is proposed. Besides, the catalyst can simply be separated from the reaction mixture by centrifugation and be recycled ten times without noticeable loss of activity.

Graphical Abstract Diarylmethane derivatives were successfully synthesized from the methylation of formaldehyde with aromatics using efficient and recyclable functional ionic liquids as catalysts, excellent yields and selectivities were obtained under solvent free conditions. The catalyst was reused at least ten consecutive recycles without noticeable loss in its catalytic activity. Meanwhile, the usability of catalyst was explored.



Keywords Formaldehyde · Methylation · Diarylmethane · Ionic liquids

1 Introduction

The methylation reaction of formaldehyde with aromatics is one of the powerful carbon–carbon bond-forming reactions in organic synthesis for the production of diarylmethane derivatives, which are useful in organic synthesis and polymer synthesis [1–4]. Diarylmethane moiety exists in many organic compounds and also shows interesting physiological activity [5–8]. It has already been reported that diarylmethane derivatives can be synthesized by the methylation of formaldehyde with aromatics in the presence of a liquid protonic acid (e.g., sulphuric acid, phosphoric acid, hydrochloric acid, etc.) [9–13] or a Lewis acid (e.g., $InCl_3 \cdot 4H_2O$, [14] $FeCl_3$, [15] etc.). However, heavy corrosion, difficulty in separation and recovery, disposal of the spent catalyst are the disadvantages associated with the reported methods involving methylation of formaldehyde with aromatics. In order to solve the above problems, the more environmentally friendly and easily separable solid acids, such as montmorillonite KSF [16], heteropoly acids [17], molecular sieves [18, 19] have been employed in the methylation reaction of formaldehyde with phenol. Recently, based on biomass conversion, Zhang and coauthors [20, 21] reported a series of solid-acid as catalysts for the alkylation between furan and carbonyl compounds and

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found that Nafion-212 resin is the best catalyst given 67 % yield at 50 °C for 2 h. Nevertheless, the rapid deactivation of solid acids might be the major drawbacks from the viewpoint of industrial application.

Ionic liquids (ILs) have attracted interest as a novel catalyst because of their favorable properties. ILs possess the advantageous characteristics of both homogenous and heterogeneous catalysts, such as high acid or alkali density, uniform catalytic active centers, easy separation and recyclability [22]. Therefore, they had been widely used in the catalytic processes such as material synthesis, organic reaction and the recent biomass conversion [23–26]. However, it has not yet seen in the literature reports about the methylation of formaldehyde with arenes under the catalysis of functionalized ILs (FILs). In our previous work concerning the application of acid-functionalized ILs in esterification, [27] cyclotrimerization, [28] carbonylation [29, 30] and other acid catalyzed reactions, we found that they especially those with an alkane sulfuric acid group are advanced alternatives to traditional liquid acid catalysts. This promoted us to explore the potential applications of such SO_3H-functionalized ILs (Scheme 1) in the methylation of formaldehyde with aromatics. Moderate to good yields were obtained for the methylation of arenes containing various groups with formaldehyde in the presence of [TTPBs][CF_3SO_3] catalyst. Moreover, the recyclability of the catalyst system was also examined. Finally, a possible reaction mechanism for this reaction system was discussed based on the experimental results.

2 Experimental

2.1 ILs Preparation

ILs were prepared according to the previous literature [31]. A stoichiometric amount of 1,4-butane sultone, 1,3-propane sultone, or bromobutane was added dropwise to a solution of triphenylphosphine, *N*-methyl imidazole or pyridine in toluene, and then the mixture was stirred at 60 °C for 12 h. The white solid zwitterion was washed repeatedly with toluene to remove non-ionic residues and dried in vacuo. Then the zwitterion and CF_3SO_3H or H_2SO_4 were mixed in a molar ratio of 1:1 in anhydrous toluene, and stirred magnetically at 60 °C for 8 h, followed by washing with toluene and drying in vacuo to obtain the final ILs. When using *p*-toluenesulfonic acid as source of anion, the preparation of FIL was conducted by water as solvent and the system was at reflux for 8 h. The mixture was dried in vacuo to form corresponding ILs. The ^1H NMR spectra and ^{13}C NMR spectra in CD_3OD or D_2O were recorded on an Avance TM III-400 MHz NMR spectrometer using tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in parts per million (ppm, δ) and referenced to D_2O (d = 4.79) or CD_3OD (d = 3.31). Elementary analyses were obtained with an Elementar Vario EL cube instrument.

2.1.1 *[TTPBs][CF_3SO_3]*

^1H NMR (400 MHz, CD_3OD): *δ* 1.86 (h, J = 7.8 Hz, 2H), 2.00 (h, J = 8.3 Hz, 2H), 2.86 (t, J = 3.5 Hz, 2H), 3.44 (t, J = 7.5 Hz, 2H), 7.72–7.77 (m, J = 5.5 Hz, 9H), 7.80 (t, J = 2.2 Hz, 3H), 7.87 (t, J = 4.7 Hz, 3H), ^{13}C NMR (100 MHz, CD_3OD): δ 20.84, 25.33, 47.18, 47.28, 47.82, 48.24, 49.70, 118.99 ($J_{C\sim F}$ = 315.1 Hz), 130.13, 133.50, 134.74. Anal. Calcd for $C_{23}H_{24}F_3O_6PS_2$: C, 50.36; H, 4.41; O, 17.50. Found: C, 49.91; H, 4.39; O, 17.91.

2.1.2 *[TTPBs][HSO_4]*

^1H NMR (400 MHz, CD_3OD): *δ* 1.87 (h, J = 7.8 Hz, 2H), 1.98 (h, J = 7.2 Hz, 2H), 2.86 (t, J = 3.6 Hz, 2H), 3.44 (t, J = 7.6 Hz, 2H), 7.72–7.77 (m, J = 5.5 Hz, 9H), 7.80 (t, J = 2.1 Hz, 3H), 7.86 (t, J = 4.1 Hz, 3H), ^{13}C NMR (100 MHz, CD_3OD): δ 19.89, 25.43, 47.18, 47.39, 47.60, 47.82, 48.03, 130.0, 133.50, 134.87. Anal. Calcd for $C_{22}H_{25}O_7PS_2$: C, 53.21; H, 5.08; O, 22.56. Found: C, 53.12; H, 5.12; O, 22.63.

2.1.3 *[TTPBs][Ts-OH]*

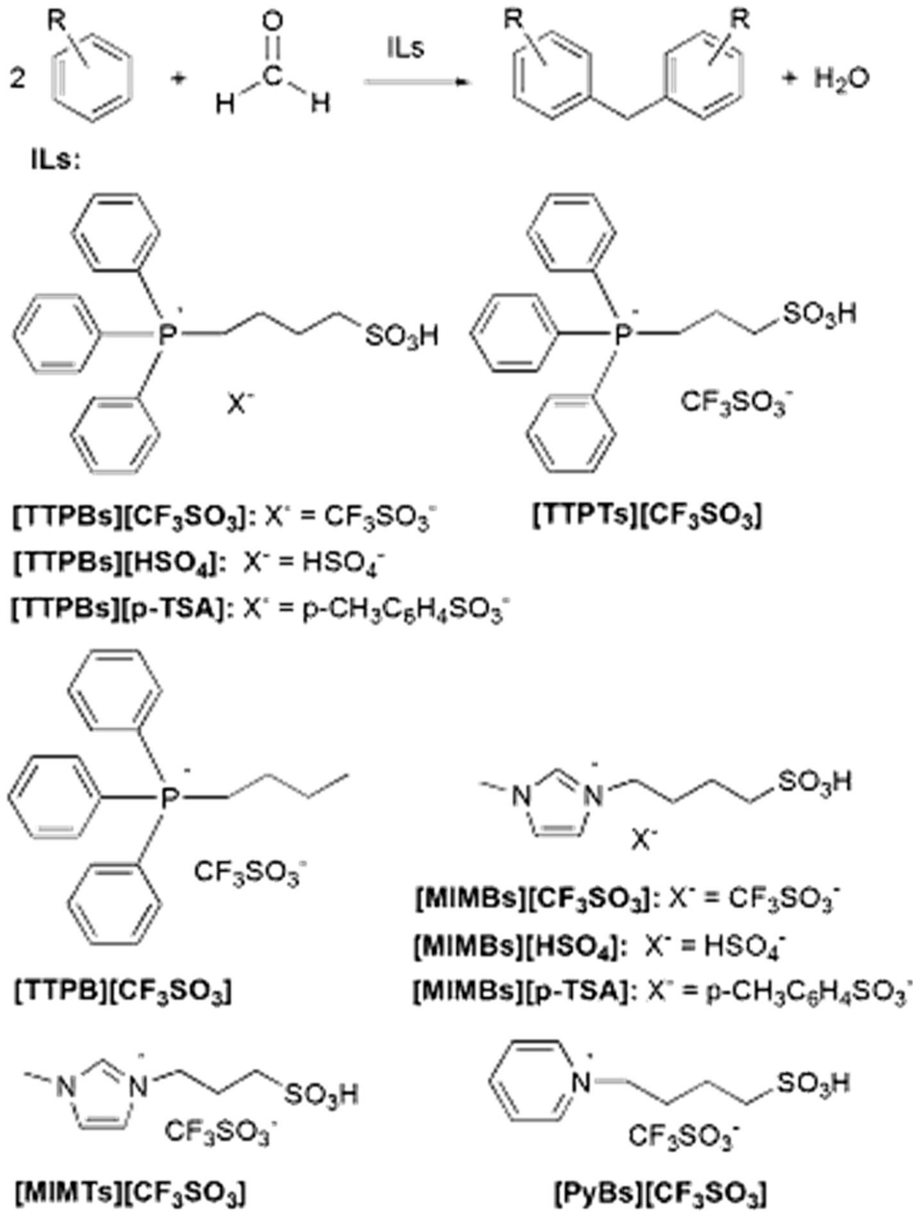
^1H NMR (400 MHz, CD_3OD): *δ* 1.87 (h, J = 7.9 Hz, 2H), 2.01 (h, J = 7.2 Hz, 2H), 2.36 (s, 3H), 2.86 (t, J = 3.6 Hz, 2H), 3.44 (t, J = 7.5 Hz, 2H), 7.24(d, J = 2.0 Hz, 2H), 7.71(d, J = 1.1 Hz, 2H), 7.72–7.77 (m, J = 3.5 Hz, 9H), 7.80 (t, J = 2.8 Hz, 3H), 7.87 (t, J = 4.0 Hz, 3H), ^{13}C NMR (100 MHz, CD_3OD): δ 19.89, 21.0, 25.43, 46.97, 47.18, 47.39, 47.60, 47.82, 48.03, 48.24, 125.60, 128.45, 130.18, 133.40. Anal. Calcd for $C_{29}H_{31}O_6PS_2$: C, 61.04; H, 5.48; O, 16.82. Found: C, 60.93; H, 5.60; O, 16.90.

2.1.4 *[TTPTs][CF_3SO_3]*

^1H NMR (400 MHz, CD_3OD): *δ* 2.13 (h, J = 6.7 Hz, 2H), 2.99 (t, J = 3.5 Hz, 2H), 3.63 (t, J = 7.6 Hz, 2H), 7.72–7.80 (m, J = 7.5 Hz, 9H), 7.82 (t, J = 3.2 Hz, 3H), 7.88 (t, J = 4.0 Hz, 3H), ^{13}C NMR (100 MHz, CD_3OD): δ 18.61, 47.18, 47.38, 47.60, 47.82, 48.03, 118.84 ($J_{C\sim F}$ = 315.1 Hz), 130.25, 133.61, 134.92. Anal. Calcd for $C_{22}H_{22}F_3O_6PS_2$: C, 49.44; H, 4.15; O, 18.0. Found: C, 49.32; H, 4.21; O, 18.87.

2.1.5 *[TTPB][CF_3SO_3]*

^1H NMR (400 MHz, CD_3OD): *δ* 0.96 (t, J = 3.6 Hz, 3H), 1.58 (m, J = 12.2 Hz, 4H), 3.38 (t, J = 7.3 Hz, 2H),



Scheme 1 Methylation of formaldehyde with aromatics catalyzed by acidic ionic liquids

7.72–7.76 (m, J = 5.2 Hz, 9H), 7.81 (t, J = 3.1 Hz, 3H),7.88 (t, J = 4.0 Hz, 3H), ^{13}C NMR (100 MHz, CD_3OD): δ18.48, 20.18, 20.70, 47.18, 47.39, 47.60, 47.82, 48.03, 118.75 ($J_{C\sim F}$ = 315.1 Hz), 130.25, 133.61. Anal. Calcd for $C_{23}H_{24}F_3O_3PS$: C, 58.97; H, 5.16; O, 10.25. Found: C, 58.99; H, 5.16; O, 10.30.

2.1.6 *[MIMBs][CF_3SO_3]*

^{1}H NMR (400 MHz, D_2O): δ 1.29 (h, J = 7.8 Hz, 2H), 1.56 (h, J = 7.5 Hz, 2H), 2.48 (t, J = 7.6 Hz, 2H), 3.43 (s, 3H), 3.78 (t, J = 7.2 Hz, 2H), 6.98 (d, J = 3.6 Hz, 1H), 7.03 (d, J = 4.0 Hz, 1H), 8.26 (s, 1H). ^{13}C NMR (100 MHz, D_2O): δ 20.91, 28.07, 35.61, 48.84, 50.06, 118.05 ($J_{C\sim F}$ = 315.1 Hz), 122.11, 123.61, 135.83. Anal. Calcd for $C_9H_{15}N_2F_3O_6S_2$: C, 29.35; H, 4.10; N, 7.61. Found: C, 29.32; H, 4.21; N, 7.56.

2.1.7 *[MIMBs][HSO_4]*

^{1}H NMR (400 MHz, D_2O): δ 1.58 (h, J = 4.8 Hz, 2H), 1.85 (h, J = 7.8 Hz, 2H), 2.78 (t, J = 7.6 Hz, 2H), 3.72 (s, 3H), 4.08 (t, J = 7.0 Hz, 2H), 7.26 (d, J = 3.6 Hz, 1H), 7.32 (d, J = 3.6 Hz, 1H), 8.57 (s, 1H). ^{13}C NMR (100 MHz, D_2O): δ 20.86, 28.04, 35.62, 48.85, 55.36, 122.08, 123.67, 135.94. Anal. Calcd for $C_8H_{16}N_2O_7S_2$: C, 30.37; H, 5.10; N, 8.86. Found: C, 29.53; H, 5.20; N, 8.78.

2.1.8 *[MIMBs][Ts-OH]*

^{1}H NMR (400 MHz, D_2O): δ 1.56 (h, J = 7.7 Hz, 2H), 1.84 (h, J = 7.5 Hz, 2H), 2.23 (s, 3H), 2.77 (t, J = 7.6 Hz, 2H), 3.70 (s, 3H), 4.05 (t, J = 7.0 Hz, 2H), 7.19 (d, J = 6.4 Hz, 2H), 7.24 (d, J = 3.6 Hz, 1H), 7.30 (d, J = 3.6 Hz, 1H), 7.51 (d, J = 8.4 Hz, 2H), 8.54 (s, 1H). ^{13}C NMR (100 MHz, D_2O): δ 20.39, 20.82, 27.99, 35.53, 48.79, 49.95, 122.03, 123.53, 125.23, 129.34, 135.79, 139.34, 142.35. Anal. Calcd for $C_{15}H_{22}N_2O_6S_2$: C, 46.02; H, 5.66; N, 7.16. Found: C, 45.96; H, 5.72; N, 7.15.

2.1.9 *[MIMTs][CF_3SO_3]*

^{1}H NMR (400 MHz, D_2O): δ 2.23 (h, J = 7.3 Hz, 2H), 2.84 (t, J = 7.6 Hz, 2H), 3.81 (s, 3H), 4.28 (t, J = 7.0 Hz, 2H), 7.36 (d, J = 3.6 Hz, 1H), 7.43 (d, J = 3.6 Hz, 1H), 8.67 (s, 1H). ^{13}C NMR (100 MHz, D_2O): δ 24.99, 35.60, 47.10, 47.63, 117.97 ($\mathrm{J}_{\mathrm{C}\sim\mathrm{F}}$ = 315.1 Hz), 122.10, 123.67, 136.09. Anal. Calcd for $C_8H_{13}N_2F_3O_6S_2$: C, 27.12; H, 3.70; N, 7.91. Found: C, 27.46; H, 3.08; N, 7.92.

2.1.10 *[PyBs][CF_3SO_3]*

^{1}H NMR D_2O (δ ppm): 1.64 (h, J = 7.8 Hz, 2H), 2.03 (h, J = 7.6 Hz, 2H), 2.82 (t, J = 7.6 Hz, 2H), 4.51 (t, J = 7.6 Hz, 2H), 7.92 (t, J = 7.2 Hz, 2H), 8.42 (t, J = 4.6 Hz, 1H), 8.73 (d, J = 5.6 Hz, 2H); ^{13}C NMR D_2O (δ ppm): 20.78, 29.24, 49.85, 61.11, 117.96 ($J_{C\sim F}$ = 315.4 Hz CF_3), 128.21, 144.16, 145.59; Anal. Calcd for $C_{10}H_{14}NF_3O_6S_2$: C, 32.88; H, 3.86; N, 3.83. Found: C, 32.71; H, 3.73; N, 3.87.

2.2 General Procedure for the Methylation of Formaldehyde and Aromatics

The reaction was carried out using a 25 mL round-bottomed flask equipped with a magnetic stirrer. In a typical experiment, substituted aromatics (80 mmol), formaldehyde (10 mmol) and IL (1.8 mmol) were charged into the flask, then the flask was sealed up and the reaction was performed at 140–170 °C for 2–12 h. After reaction, the flask was cooled to room temperature and the IL was separated from the reaction mixture by centrifugation. The final products were identified and quantitatively analyzed by gas chromatography/mass spectrometry (GC/MS) (Agilent 7890A/5975C) and GC (Agilent 6890 equipped with a SE-54 capillary column), respectively. A known amount of *n*-heptane was added as an internal standard to the product mixture before the GC analysis. For the recycling of catalyst, the IL was extracted with *n*-hexane (5 mL × 3) and dried in a vacuo for 8 h before reusing.

3 Results and Discussion

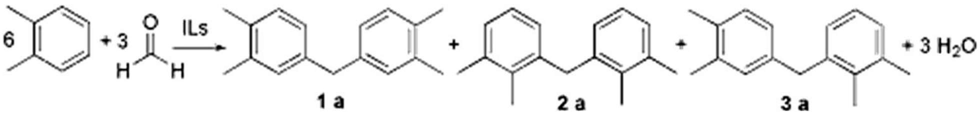
Initially, a probe reaction of trioxane (10 mmol) and *o*-xylene (60 mmol) was carried out at 160 °C under solvent-free conditions catalyzed by these ILs (2 mol %) and the results are shown in Table 1. Besides the main product bis(dimethylphenyl)methane, small amount of 1,1,2-tris(dimethylphenyl)ethane was also detected in the reaction mixture. It is obviously to see that the catalytic activities of ILs with the same cations were mainly affected by the anions. ILs with $CF_3SO_3^-$ as anion appeared to be superior to those of the corresponding ILs with HSO_4^- or *p*-$(CH_3)C_6H_5SO_3^-$ as anion (Table 1, entries 1–3 and entries 6–8). This may be due to the strong acidity of ILs with $CF_3SO_3^-$ compared with other anions when possessing the same cation [29]. Those of [CF_3SO_3]-type ILs bearing one alkyl sulfonic acid group on cations exhibited better activity than the one without –SO_3H group on cation (Table 1, entries 1, 4, 6, 9, 10 vs. entry 5), and the carbon chain length between –SO_3H group and cation core has only a slight effect on catalytic efficiency (Table 1, entries 1, 4 vs. entries 6, 9). Among the ten ILs investigated, –SO_3H functionalized phosphonium based IL, [TTPBs][CF_3SO_3] appeared to be the best catalyst with 89.3 % total yield of bis(dimethylphenyl)methanes (Table 1, entry 1).

Methylation of formaldehyde with aromatics mostly proceeds via a two-step conversion, that is hydroxymethylation of formaldehyde with aromatics to produce benzyl alcohol followed by subsequent alkylation of benzyl alcohol with aromatics [16, 20, 21, 32, 33]. The hydroxymethylation step requires a strong acid to protonate formaldehyde because of its low proton affinity, in addition alkylation of benzyl alcohol and aromatic is also a typical acid-catalyzed reaction. So SO_3H-functionalized ILs with strong acidity can be suitable catalysts for the aimed reaction.

Using [TTPBs][CF_3SO_3] as catalyst, the source of formaldehyde, i.e. solid state (trioxane and paraformaldehyde) and liquid state (50 % of aqueous solution of formaldehyde) was firstly examined and the results are shown in Table 2. We found that although similar selectivity of **1a** was obtained under different form of formaldehyde, trioxane was the best supplier of formaldehyde for the reaction that gave the product bis(dimethylphenyl)methane in high yield (91.3 %). This phenomenon may be explained in the light of better solubility of trioxane in the other reactant of *o*-xylene.

To optimize the methylation reaction conditions of trioxane with *o*-xylene, the effects of catalyst dosage, molar ratio of *o*-xylene to formaldehyde, reaction temperature, and reaction time were also investigated with

Table 1 Catalytic activities of different ILs on the methylation of formaldehyde with *o*-xylene



Entry[a]	Catalysts	Yield (%)	Selectivity (%)		
		a	1a	2a	3a
1	[TTPBs][CF_3SO_3]	89.3	86.0	1.0	3.4
2	[TTPBs][HSO_4]	71.1	93.7	1.3	3.8
3	[TTPBs][*p*-TSA]	21.4	91.7	1.8	3.3
4	[TTPTs][CF_3SO_3]	87.5	85.0	1.1	3.2
5	[TTPB][CF_3SO_3]	69.1	80.1	1.0	3.2
6	[MIMBs][CF_3SO_3]	72.2	83.5	2.1	3.4
7	[MIMBs][HSO_4]	57.1	92.9	1.3	3.8
8	[MIMBs][*p*-TSA]	41.7	94.0	1.6	4.5
9	[MIMTs][CF_3SO_3]	69.9	82.7	1.0	3.7
10	[PyBs][CF_3SO_3]	71.7	86.7	1.1	3.5

[a] Reaction conditions: amount of catalyst is 2 mol%, using trioxane as monomeric formaldehyde sources, *o*-xylene/formaldehyde = 6 (mol ratio), 160 °C, 4 h

Table 2 Influence of different monomeric formaldehyde sources on the reaction

Entry[a]	Source of formaldehyde	Yield (%)	Selectivity (%)		
		a	1a	2a	3a
1	Trioxane	91.3	87.1	1.2	3.6
2	Paraformaldehyde	81.5	86.7	1.2	3.5
3	Formalin (50 %)	76.0	87.1	2.2	3.5

[a] Reaction conditions: amount of [TTPBs][CF_3SO_3] is 2 mol%, *o*-xylene/formaldehyde = 8 (mol ratio), 160 °C, 4 h

[TTPBs][CF_3SO_3] as catalyst and the results are summarized in Table 3. The catalyst dosage had a great effect on the reaction. When molar percent content of [TTPBs][CF_3SO_3] increased from 1 to 2 mol%, (Table 3, entries 1 and 2) the total yield of products and the selectivity of **1a** increased from 72.6 and 82.9 % to 89.3 and 86.0 % respectively, and a further increase to 4 mol% resulted in decrease in yield and selectivity (Table 3, entry 3). Hence, 2 mol% of [TTPBs][CF_3SO_3] was the optimal amount to efficient production of methylation products. The increase of the molar ratio of *o*-xylene to formaldehyde is propitious for the reaction (Table 3, entries 2, 4–9) because the excess of one of the reactants makes the equilibrium shifting towards the products side. From the data of Table 3, the reaction was also influenced by reaction temperature. When the temperature increased from 140 to 160 °C, the yield of products and selectivity of **1a** increased from 87.8 to 91.3 % and 84.5 to 87.1 %, respectively (Table 3, entries 6, 10–12). Further elevate of the temperature, the yield of products decreased due to the formation of more byproducts at higher temperature. The dependence of the total yield and selectivity of **1a** on the reaction time was investigated in the range of 2–6 h (Table 3, entries 6, 13 and 14). The yield and selectivity increased with prolonging reaction time from 2 to 4 h, and then decreased slightly when the reaction proceeded, which implied occurrence of the side-reactions with time extension. When increased the dosage of [TTPBs][CF_3SO_3] and reactants to ten times, the yield of **a** and the selectivity of **1a** were still up to 90.9 and 87.3 %, respectively, which showed that methylation of formaldehyde with aromatics has good synthetic application (Table 3, entry 6 vs. entry 7).

A series of recycle experiments were conducted to investigate the recoverability and recyclability of the SO_3H-functionalized ILs. The ILs with –SO_3H functional group are hardly soluble in common organic solvents except for methanol and ethanol and have good solubility in water. [TTPBs][CF_3SO_3] dissolved in water as a separate phase could be centrifugated out from the reaction mixture at the end of the reaction. The amount of water in ILs phase is about 15 %, which is by-product of the reaction. The ILs phase was extracted by *n*-hexane (5 mL × 3) and then vacuumized for 12 h at 80 °C. After that the ILs phase was used for another cycle under the same conditions. The reusability of the recycled catalyst is shown in Fig. 1. As expected, [TTPBs][CF_3SO_3] could be reused for ten times at least and there was no obvious decrease in the

Table 3 Effects of different reaction conditions using [TTPBs][CF_3SO_3] as catalyst

Entry[a]	Amount of catalyst (mol%)	O-xylene: formaldehyde (mol ratio)	Temp. (°C)	Time (h)	Yield (%)	Selectivity (%)		
					a	**1a**	**2a**	**3a**
1	1	6	160	4	72.6	82.9	1.1	4.9
2	2	6	160	4	89.3	86.0	1.0	3.4
3	4	6	160	4	82.6	82.3	1.1	3.7
4	2	2	160	4	43.3	67.4	0.9	2.4
5	2	4	160	4	70.1	78.7	1.6	3.2
6	2	8	160	4	91.3	87.1	1.2	3.6
7[b]	2	8	160	4	90.9	87.3	1.3	3.1
8	2	10	160	4	93.1	91.3	1.1	3.4
9	2	12	160	4	98.6	93.9	1.9	3.7
10	2	8	140	4	87.8	84.5	2.4	3.3
11	2	8	150	4	90.6	87.3	1.2	3.5
12	2	8	170	4	89.4	86.0	1.1	3.6
13	2	8	160	2	91.0	86.2	1.1	3.4
14	2	8	160	6	83.6	83.6	1.1	3.4

[a] Reaction conditions: using trioxane as monomeric formaldehyde sources

[b] The dosage of *o*-xylene is 0.8 mol, formaldehyde is 0.1 mol, [TTPBs][CF_3SO_3] is 0.018 mol

yield of products and selectivity of **1a**, which indicated that [TTPBs][CF_3SO_3] was stable in the reaction system.

The applicability of this catalytic system for the reaction of various aromatics with formaldehyde was also studied and the results were summarized in Table 4. The results indicated that aromatics containing electron donating substituents such as –OCH_3 and –CH_3 gave corresponding methylation products in excellent yields within 4–8 h at 160 °C, and no significant effect was observed by changing the number and the position of the –CH_3 group in the benzene ring (Table 4, entries 1–3, 6, 8). Astonishingly, benzene which does not have any substituent also affords methylation product in 31.1 yield and 76.0 % selectivity (Table 4, entry 7). The methylation of aromatics substituted with an electron-withdrawing group such as –Cl and –Br was also successful using 4 mol % [TTPBs][CF_3SO_3] as catalyst. The yield of bis(2-methoxyl-5-chlorophenyl)methane was found to be 87.3 % under 160 °C for 12 h, as well as 100 % of selectivity to the corresponding products (Table 4, entry 4). As for the *p*-bromoanisole, the yield and selectivity were 76.7 and 98.7 %, respectively (Table 4, entry 5). Thus, the feasibility of the FILs catalyzed methylation reaction of formaldehyde with aromatics, is dependent on the nucleophilicity of the respective aromatics. To obtain more insight into the catalytic possibilities of FILs, we also investigated the reaction of *N*,*N*-dimethylaniline with formaldehyde for synthesis of 4,4′-methylenebis(*N*,*N*-dimethylaniline), 68.2 yield and 96.2 % selectivity were obtained under 160 °C for 12 h (Table 4, entry 10).

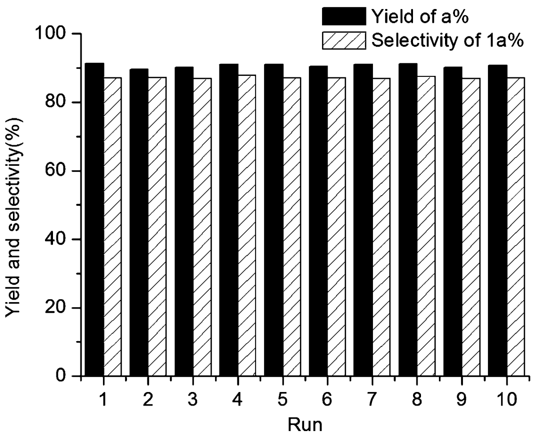
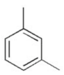
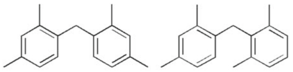
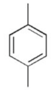
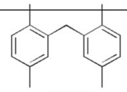
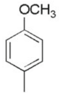
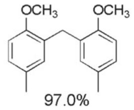
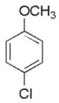
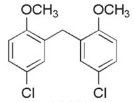
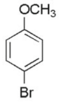
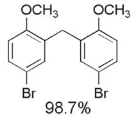
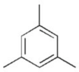
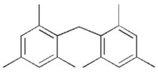
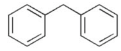
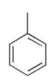
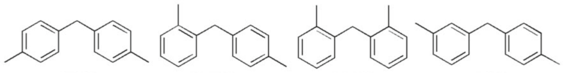
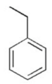
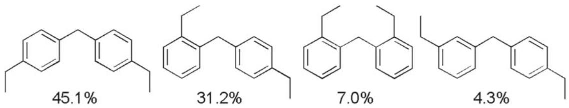
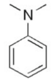
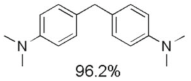


Fig. 1 Recycling of [TTPBs][CF_3SO_3] in the methylation reaction of formaldehyde with *o*-xylene. Reaction conditions: amount of [TTPBs][CF_3SO_3] is 2 mol%, *o*-xylene/formaldehyde = 8 (mol ratio), 160 °C, 4 h

According to the previous papers reported before, [16, 20, 21, 32, 33] a plausible mechanism for methylation of formaldehyde with aromatics catalyzed by SO_3H-functionalized ILs is shown in Scheme 2. We consider that SO_3H-functionalized ILs catalyst plays a crucial role in the decomposition process of trioxane and monomeric formaldehyde activation, which has been studied with the density functional theory (DFT) calculations [34]. That is to say, formaldehyde is firstly activated via hydrogen-bonding interaction between H atom of –SO_3H group in catalyst and O atom of CH_2O. Subsequently, a proton is transferred from catalyst to CH_2O to form the intermediate

Table 4 Methylation of formaldehyde with various aromatics catalyzed by FILs

Entry [a]	Aromatics	Time (h)	Yield (%)	Products (Selectivity)
1		8	91.7	 76.8% 14.5%
2		8	80.6	 84.3%
3		4	95.8	 97.0%
4 [b]		12	87.3	 100%
5 [b]		12	76.7	 98.7%
6		4	96.0	 99.8%
7		8	31.1	 76.0%
8		4	93.6	 47.9% 31.5% 11.2% 1.3%
9		8	66.4	 45.1% 31.2% 7.0% 4.3%
10 [b]		12	68.2	 96.2%

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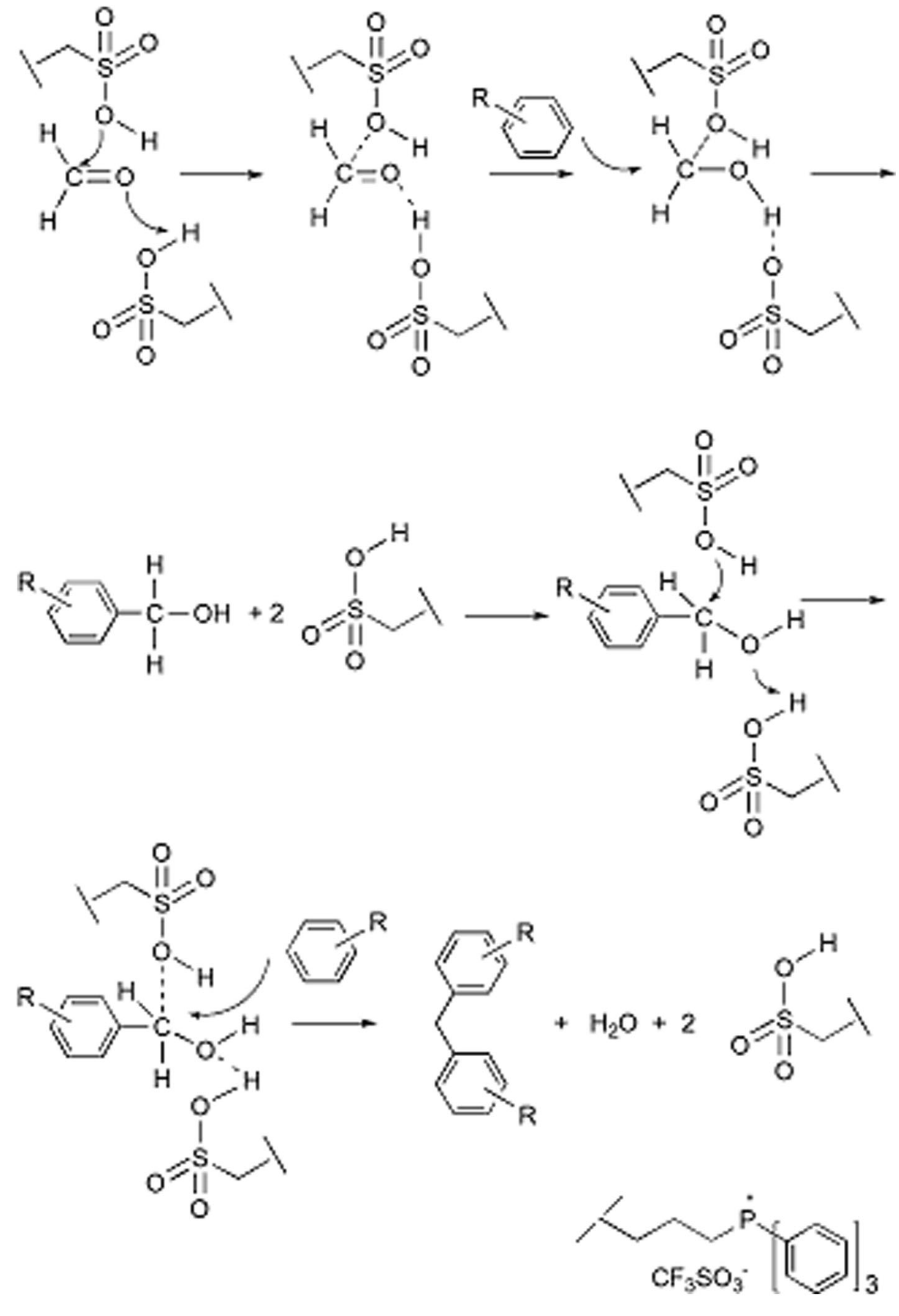
[a] Reaction conditions: amount of [TTPBs][CF_3SO_3] is 2 mol%, using trioxane as monomeric formaldehyde sources, aromatic/formaldehyde = 8 (mol ratio), 160 °C

[b] Reaction conditions: amount of [TTPBs][CF_3SO_3] is 4 mol %

methylol cation (CH_2^+OH). The electrophilic attack of methylol cation (CH_2^+OH) on aromatic ring generates a benzyl alcohol. And then hydroxymethyl group of the benzyl alcohol is further activated by the SO_3H-functionalized ILs catalyst to form hydroxyl benzyl carbocation, which reacts with the second molecule of aromatic to give diarylmethanes and eliminates a molecule of water simultaneously.

Based on the analysis of the products of the reaction of *o*-xylene with formaldehyde by using GC/MS, bis(dimethylphenyl)methane was identified as the major product and 1,1,2-tris(dimethylphenyl)ethane as byproduct, 3,4-



Scheme 2 Plausible mechanistic pathway for methylation of formaldehyde with aromatics catalyzed by [TTPBs][CF_3SO_3]

dimethylbenzyl alcohol was hardly detected in the reaction mixture. We then investigated the reaction of 3,4-dimethylbenzyl alcohol with *o*-xylene under 160 °C for 30 min, the conversion of carbinol and the yield of bis(3,4-dimethylphenyl)methane were up to 100 and 99.1 % respectively, which verifies the rate of the alkylation reaction is much higher than that of the hydroxymethylation reaction step.

4 Conclusions

In conclusion, 2 mol% [TTPBs][CF_3SO_3] was found to be an effective catalyst for methylation reaction of formaldehyde with aromatics, giving the highest yield (98.6 %) to methylation products and selectivity (93.9 %) to bis(3,4-dimethylphenyl)methane. The catalyst could simply be separated by centrifugated out from the reaction mixture. After extracted with *n*-hexane and removal of water under vacuum the catalyst could be recycled and reused for ten times without decreasing the catalytic activity. The present study shows that the SO_3H-functionalized ILs has a potential application in the procedures for C–H transformation and C–C formation of aromatics in organic synthesis.

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References

1. Ma JC, Dougherty DA (1997) Chem Rev 97:1303
2. Bruno JG, Chang MN, Choi-Sledeski YM, Green DM, McGarry DG, Regan JR, Volz FA (1997) J Org Chem 62:5174
3. Wllkinson JA, Rossington SB, Leonard J, Hussain N (2004) Tetrahedron Lett 45:5481
4. Maciejewska M, Gawdzik BJ (2005) J Appl Polym Sci 95:863
5. Stanchev S, Rakovska R, Berova N, Snatzke G (1995) Tetrahedron Asymmetry 6:183
6. Ku YY, Patel RP, Sawick DP (1996) A General. Tetrahedron Lett 37:1949
7. Prat L, Mojovic L, Levacher V, Dupas G, Queguiner G, Bourguignon J (1998) Tetrahedron Asymmetry 9:2509
8. Rische T, Eilbracht P (1999) Tetrahedron 55:1915
9. Granjon R, Fournier M (1982) US Patent 4,338,470
10. Mortimer S, Patel N, Cawse J (2012) US Patent 20,120,316, 262,A1
11. Ort MR (1983) US Patent 4,400,554
12. de la Cruz MHC, da Silva JFC, Lachter ER (2003) Appl Catal A 245:377
13. Limuro S, Ito S, Takashima T Kitamura T (1995) US Patent. 5,395,915
14. Sun HB, Huab R, Yina YG (2006) Tetrahedron Lett 47:2291
15. Li ZX, Duan Z, Wu YJ (2009) Chin Chem Lett 20:511
16. Bigi F, Conforti ML, Maggi R, Sartori G (2000) Tetrahedron 56:2709
17. Jana SK, Okamoto T, Kugita T, Namba S (2005) Appl Catal A 288:80
18. Jana SK, Kugita T, Namba S (2003) Catal Lett 90:143
19. Jana SK, Takahashi H, Nakamura M, Kaneko M, Nishida R, Shimizu H, Kugita T, Namba S (2003) Appl Catal A 245:33
20. Li GY, Li N, Wang ZQ, Li CZ, Wang A, Wang XD, Cong Y, Zhang T (2012) ChemSusChem 5:1958
21. Li GY, Li N, Li SS, Wang A, Cong Y, Wang XD, Zhang T (2013) Chem Commun 49:5727
22. Zhang X, Tu M, Paice MG (2011) Bioenerg Res 4:246
23. Pinkert A, Marsh KN, Pang SS, Staiger MP (2009) Chem Rev 109:6712
24. Zakrzewska ME, Bogel-Lukasik E, Bogel-Lukasik R (2011) Chem Rev 111:397
25. Parvulescu VI, Hardacre C (2007) Chem Rev 107:2615
26. Hallett JP, Welton T (2011) Chem Rev 111:3508
27. Liu JM, Li Z, Chen J, Xia CG (2009) Catal Commun 10:799
28. Song HY, Chen J, Xia CG, Li Z (2012) Synth Commun 42:1
29. Song HY, Li Z, Chen J, Xia CG (2012) Catal Lett 142:81
30. Song HY, Jing FX, Jin RH, Li Z, Chen J (2012) Catal Lett 144:711
31. Cole AC, Jensen JL, Ntai I, Tran KL, Weaver KJ, Forbes DC, Davis JH Jr (2002) J Am Chem Soc 124:5962
32. Garade AC, Kshirsagar VS, Rode CV (2009) Appl Catal A 354:176
33. Cai XJ, Cui SH, Qu LP, Yuan DD, Liu B, Cai QH (2008) Catal Commun 9:1173
34. Wang F, Zhu GL, Li Z, Zhao F, Xia CG, Chen J (2015) J Mol Catal A 408:228