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# Introduction

Acid catalyzed Hosomi–Sakurai allylation is one of the most important carbon–carbon bond forming reactions which is a key step in natural product synthesis, *e.g.* concise synthesis of nematocidal oxylipid<sup>1</sup> and heliespirone A and C having inhibitory activity in the coleoptile bioassay (Fig. 1).<sup>2</sup> Homoallyl ethers (HAEs) synthesized by the reaction of acetals with allyltrimethylsilane are also used as starting materials for many organic transformations.<sup>3*a*-*e*</sup>

Initially, Hosomi and Sakurai reported the allylation of acetals with titanium chloride as a catalyst.<sup>4</sup> Thereafter, conventional Lewis acids in stoichiometric or catalytic quantities were studied which included TMSNTf<sub>2</sub>,<sup>5</sup> Sc(OTf)<sub>3</sub>,<sup>6</sup> diphenylboryl triflate,<sup>7</sup> TMSOTf,<sup>8a-c</sup> Bi(OTf)<sub>3</sub>,<sup>9</sup> AlBr<sub>3</sub>/CuBr,<sup>10</sup> TMSI,<sup>11</sup> NbCl<sub>5</sub>/AgClO<sub>4</sub>,<sup>12</sup> CuBr/microwave,<sup>13</sup> liquid SO<sub>2</sub>,<sup>14</sup> trityl perchlorate,<sup>15</sup> FeCl<sub>3</sub>,<sup>16</sup> and BiBr<sub>3</sub>,<sup>17</sup> AlCl<sub>3</sub>, BF<sub>3</sub>·Et<sub>2</sub>O,<sup>18,19</sup> TiCp<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>,<sup>20</sup> and TMSN(SO<sub>2</sub>F)<sub>2</sub>.<sup>21</sup> All these catalysts suffered from cumbersome work-up procedures due to unwanted salt formation. Exceptionally, a few Brønsted acids have been studied for the allylation of acetals such as sulfonimides with good yields but about 50% loss of the catalyst was observed up to 3rd recycling run and simultaneously needed aqueous work-up.<sup>22</sup> List et al. screened different sulfonic acids among which 2,4-dinitrobenzenesulfonic acid

# Highly efficient triphenyl(3-sulfopropyl)phosphonium functionalized phosphotungstic acid on silica as a solid acid catalyst for selective mono-allylation of acetals<sup>†</sup>

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Silica supported phosphotungstic acid functionalized with triphenyl(3-sulfopropyl)phosphonium (PW-Si/TPSP) was developed as a solid acid catalyst for C–C bond formation *via* Hosomi–Sakurai allylation of acetals. Functionalization of PW as well as its binding to silica was confirmed by solid state <sup>31</sup>P-NMR and <sup>29</sup>Si-NMR, respectively. Among the various catalysts prepared, the 30% PW loaded (30PW-Si/TPSP) catalyst gave an excellent yield of homoallyl ethers (HAEs) *via* selective mono-allylation of acetals with allyltrimethylsilane. A plausible reaction pathway has also been proposed in which the strong Brønsted acid sites of 30PW-Si/TPSP play an important role in activating the acetals to form the corresponding oxonium cations. The versatility of our catalyst was demonstrated for the allylation of a wide variety of acetals while its stability was established in five successful recycling runs.

> gave excellent activity but again compromising the recovery of the catalyst.<sup>23</sup> Silicomolybdic acid supported on silica facilitated the allylation of acetals and aldehydes to HAEs but the activity diminished to 15% in the 3rd recycling run.<sup>24</sup> It is very important for a greener approach that the catalyst should be stable for subsequent reuse for several times without compromising the activity under the reaction conditions. Thus, there exists a scope to design a catalyst for allylation of acetals which does not undergo any leaching of the active component and can be recycled several times without losing its activity.

> Heteropolyanion based 1-methyl-3-(3-sulfopropyl)imidazolium, 1-(3-sulfopropyl)pyridinium and triphenyl(3-sulfopropyl)phosphonium (TPSP) salts were well reported for acid-catalyzed esterification due to their self-induced phase separation properties.<sup>25–27</sup> Despite their self-separation nature, synthetic utility of these catalysts for new organic transformations is restricted due to



Fig. 1 Nematocidal oxylipid and heliespirones



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their high solubility in polar solvents like alcohols, acetonitrile, *etc.* Therefore, more efforts are desired to develop new strategies for these catalytic systems to render them truly heterogeneous for their easy and wide range of applications in transformations of practical significance.

In the continuation of our previous work on the heterogeneous povidone (PVP) based phosphotungstic acid catalyst system,<sup>28</sup> we report here the silica supported triphenyl(3sulfopropyl)phosphonium salt of phosphotungstic acid (PW-Si/TPSP) as a novel heterogeneous and recyclable acid catalyst for the selective mono-allylation of acetals by the Hosomi-Sakurai reaction (Scheme 1).

These catalysts were prepared by sequential loading of phosphotungstic acid  $(PW/H_3PW_{12}O_{40})$  in the range of 10–30% on silica (w/w) followed by abstraction of protons by TPSP (Scheme 2).

The catalysts were well characterized and their activities were tested for allylation of acetals with allyltrimethylsilane to synthesize homoallyl ethers. New motifs were synthesized after the selective mono-allylation of *o*-allylated phenolic acetals which can be further extended to polymer synthesis. Again, due to the well-defined solid acid nature, these catalysts will be useful for important acid-catalyzed organic transformations to resolve the problems of conventional acid systems like recovery, solubility, recyclability *etc*.

### Results and discussion

#### Catalyst characterization

Fig. 2 shows the FT-IR spectra of PW-TPSP (A), 30PW-Si/TPSP (B) and recovered 30PW-Si/TPSPR (C) catalyst samples. Four peaks observed at 1075 cm<sup>-1</sup> (P-O), 972 cm<sup>-1</sup> (W=O) (terminal), 892 cm<sup>-1</sup> (W-O<sub>b</sub>-W) (corner-sharing) and 807 cm<sup>-1</sup> (W-Oc-W) (edge-sharing) exactly matched with those of parent PW confirming the intact Keggin unit of phosphotungstate in PW/TPSP (Fig. 2, A).<sup>29,30</sup> However, a slight blue shift was observed for the peaks of 30PW-Si/TPSP and recovered 30PW-Si/TPSPR samples (Fig. 2, B and C) which confirmed the interaction between silica and the TPSP salt. The poorly visible peaks at 1640 cm<sup>-1</sup>, 1587 cm<sup>-1</sup> and 1485 cm<sup>-1</sup> could be due to the stretching vibrations of C=C, in accordance with the aromatic C-H bending vibrations as evidenced by the presence of peaks at 725 cm<sup>-1</sup> and 687 cm<sup>-1</sup>. The peaks due to asymmetric and symmetric stretching of O=S=O appeared at 1193 cm<sup>-1</sup> and 1037 cm<sup>-1</sup>, respectively. P-Ar and P-C bond formation with the phosphonium cation was confirmed by the peaks at 1437 cm<sup>-1</sup> and 742 cm<sup>-1</sup> (broad,



Scheme 1 Hosomi–Sakurai mono-allylation of acetals using 30PW-Si/TPSP.





merged), respectively.<sup>27</sup> Thus, the IR study provided clear evidence of structural characterization of the phosphonium cation and sulfonic acid and retention of the Keggin unit present in the prepared catalysts.

The Keggin structure of the catalysts was also confirmed by XRD as shown in Fig. 3. The broad peak at  $2\theta = 21.71^{\circ}$  was attributed to silica showing its amorphous nature (Fig. 3, A) while the sharp peaks at  $2\theta = 20.3^{\circ}$ , 26.3°, 28.38° and 36.27° were assigned to the Keggin structure of PW (Fig. 3, B).<sup>31,32</sup>

These characteristic reflection peaks were also observed for 30PW-Si at  $2\theta = 20.8^{\circ}$ , 26.1°, 28°, and 35° confirming the presence of well-dispersed PW on silica (Fig. 3, C). Among the four peaks, two small peaks at  $2\theta = 21.38^{\circ}$  and 26.1° for the 30PW-Si/TPSP catalyst sample also indicated that the Keggin structure was retained but intensities of the peaks decreased due to the exchange of protons with TPSP cations as evidenced by the decrease in crystallite size of the cubic



Fig. 2 FT-IR of (A) PW-TPSP, (B) 30PW-Si/TPSP and (C) 30PW-Si/TPSPR.



Fig. 3 X-ray diffraction analysis of (A) silica, (B) PW, (C) 30PW-Si and (D) 30PW-Si/TPSP.

heteropolyanion resulting in shrinking of lattice cells (Fig. 3, D).<sup>33a,b,34</sup>

The solid-state magic-angle spinning CP-29Si-NMR study revealed the incorporation of PW onto the silica surface (Fig. 4a) while CP-<sup>31</sup>P-NMR confirmed the presence of phosphonium cations in the catalyst and was also useful to understand the surrounding environment of 'P' (Fig. 4b). <sup>29</sup>Si-MAS NMR of 30PW-Si and 30PW-Si/TPSP showed the peaks at -112.54 and -112.27 ppm for Q<sub>4</sub>-[Si(OSi<sub>4</sub>)] SiO<sub>2</sub> with 63.15% and 64.70% and at -104.01 and -105.96 ppm for Q<sub>3</sub>-[Si(OSi<sub>3</sub>)OH] with 36.15% and 35.9%, respectively (Fig. 4a, A and B). The amount of the dominant Q4 in silica decreased while that of Q3 increased in the 30PW-Si/TPSP catalyst due to the incorporation of PW into silica matrix. Thus, the ratio of Q<sub>4</sub>/Q<sub>3</sub> was lowered up to 1.764 in 30PW-Si/TPSP as compared to that in the parent silica. This lowering of the Q<sub>4</sub>/Q<sub>3</sub> ratio was clearly due to bonding of heteropolyacid molecules to silicon atoms near the surface, thus decreasing the number of silicon atoms having 4 Si neighbours.34,35

<sup>31</sup>P-NMR of TPSP showed a sharp peak at 22.70 ppm for 'P' (Fig. 4b, A) which was slightly shifted to 23.46 ppm in Si/ TPSP, indicating the existence of some interactions of TPSP with the silica surface (Fig. 4b, B). However, the presence of a broad peak at a still further downfield position at 24.03 ppm for the 30PW-Si/TPSP sample (Fig. 4b, A and C) evidenced the interaction of TPSP with PW.<sup>36</sup> Similarly, a sharp peak at -14.91 ppm for the 30PW-Si sample was due to the tetrahedral 'P' atom of the Keggin structure while shifting of this peak to -15.28 ppm for the 30PW-Si/TPSP sample proved the interactions of heteropolyanions with triphenylphosphine and silica (Fig. 4b, B and C).<sup>37–39</sup>

The thermal stability and characteristic decomposition patterns of silica (A), PW-TPSP (B), 30PW-Si/TPSP (C) and 30PW-Si (D) samples were determined using thermogravimetric analysis (TGA) (Fig. 5). The silica support was thermally stable with a total weight loss of only about 3% up to 700 °C (Fig. 5, A).



**Fig. 4** (a) Solid-state MAS CP-<sup>29</sup>Si NMR of (A) 30PW-Si and (B) 30PW-Si/TPSP samples. (b) Solid-state MAS CP-<sup>31</sup>P NMR of (A) TPSP, (B) Si/TPSP, (C) 30PW-Si/TPSP and (D) 30PW-Si samples.

At 100–105 °C, the PW-TPSP and 30PW-Si/TPSP samples showed 3% weight loss while 8% weight loss was observed for the 30PW-Si sample due to physically adsorbed water (Fig. 5, B, C and D). Beyond 104 °C, sequential thermal decomposition was observed in the range of 280–300 °C, as evidenced by 7% weight loss for PW-TPSP (Fig. 5, B) while only 2% weight loss for the 30PW-Si/TPSP sample (Fig. 5, C) was detected. Further decomposition of PW to form metal oxides and water was also observed beyond 460–500 °C with a maximum weight loss of 9% for PW-TPSP (Fig. 5, B) while only 5% and 5.5% weight losses were observed for 30PW-Si/ TPSP and 30PW-Si samples (Fig. 5, C and D), respectively.<sup>40,41</sup> In summary, high thermal stability was attained due to strong ionic interactions of PW with silica and TPSP.



Fig. 5 TGA profiles of (A) Si, (B) PW-TPSP, (C) 30PW-Si/TPSP and (D) 30PW-Si samples.

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Fig. 6 NH<sub>3</sub>-TPD of (A) silica, (B) PW, (C) PW-TPSP and (D) 30PW-Si/TPSP samples.

Since the acidity of the catalysts play an important role in the allylation of acetals, the acid strengths of various samples were compared by measuring the temperature programmed desorption of ammonia ( $NH_3$ -TPD) and the results are shown in Fig. 6.

NH<sub>3</sub>-TPD of the silica, PW and 30PW-Si/TPSP samples showed the first peak in the region of 100–200 °C (Fig. 6, A, B and D) due to weak acidity. Peaks in the region of 550–650 °C in the PW sample indicated the presence of strong acid sites (Fig. 6, B),<sup>42,43</sup> while the peaks in the region of 250–550 °C for the PW-TPSP and 30PW-Si/TPSP samples (Fig. 6, C and D) indicated the presence of strong acid sites at lower temperature. These peaks could be due to the newly created acid sites by the total exchange of protons from silica supported PW to TPSP in the 30PW-Si/TPSP sample forming sulfonic acid. The order of the acid amount of various



Fig. 7 Pyridine-FTIR of (A) PW, (B) PW-TPSP and (C) 30PW-Si/TPSP.

samples was found to be PW (0.3983 mmoles NH<sub>3</sub> per g) > PW-TPSP (0.2381 mmoles NH<sub>3</sub> per g) > 30PW-Si/TPSP (0.176 mmoles NH<sub>3</sub> per g) > silica (0.011191 mmoles NH<sub>3</sub> per g) (ESI† Table S1). Although the 30PW-Si/TPSP sample showed lower acidity as compared to PW-TPSP, the distribution of acid sites on silica played an important role in enhancing the product yields. The BET surface area of the 30PW-Si/TPSP (110.69 m<sup>2</sup> g<sup>-1</sup>) and 30PW-Si (116.70 m<sup>2</sup> g<sup>-1</sup>) catalysts and that of the silica support (232.57 m<sup>2</sup> g<sup>-1</sup>) were also evidence for the increase in active sites due to the smooth distribution of PW which has only a surface area of 5 m<sup>2</sup> g<sup>-1</sup> (ESI† Fig. S1).

Fig. 7 shows the pyridine-FTIR characterization of various catalyst samples carried out at 50 °C in order to distinguish between Lewis and Brønsted acid sites. Bare PW showed strong peaks at 1542 cm<sup>-1</sup>, 1636 cm<sup>-1</sup> and 1611 cm<sup>-1</sup> due to the pyridinium ion bonded to hydrogen confirming its strong Brønsted acidity and a peak at 1490 cm<sup>-1</sup> attributed to unspecifically adsorbed pyridine.

Interestingly, no peak was observed at 1450 cm<sup>-1</sup>, indicating the absence of any Lewis acid sites (Fig. 7).<sup>44</sup> In the case of PW-TPSP and 30PW-Si/TPSP samples, the peaks at 1544 cm<sup>-1</sup> and 1590 cm<sup>-1</sup> could be attributed to Brønsted acid sites and the peak at 1490 cm<sup>-1</sup> was assigned to unspecifically adsorbed pyridine but a new peak appearing at 1440 cm<sup>-1</sup> was due to pyridine bonded to phosphonium cations (Fig. 7, B and C).<sup>45</sup> This again clearly confirmed the presence of phosphonium cations and thus the exchange of protons from PW to the sulfate, imparting the Brønsted acidic nature to the 30PW-Si/TPSP catalyst. The concentration of the acid sites determined from the area under the curve showed the order of acidity as follows: PW > PW-TPSP > 30PW-Si/TPSP (ESI† Table S2, Fig. S2, A–C).



Fig. 8 Plausible reaction mechanism for the H–S reaction of acetals with allyl-TMS over 30PW-Si/TPSP catalyst.

#### Reaction optimization study

Table 1 shows the studies on catalyst screening and the effect of solvents to achieve the optimum reaction conditions for allylation of acetals with allyl-TMS.

Initially, benzaldehyde dimethyl acetal (BDMA) was reacted without a catalyst and also in the presence of the triphenyl(3-sulfopropyl)phosphonium salt or zwitterion (TPSP) alone, showing no formation of any products which indicates that acid sites are needed to catalyze the reaction (Table 1, entries 1 and 2). A commercially available acid catalyst, Amberlyst 15, was found to give only 40% of homoallyl ethers (HAEs) but mainly favoured the deprotection of BDMA to benzaldehyde (Table 1, entry 3). Heteropolyacid/PW (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·*x*H<sub>2</sub>O) alone and that supported on silica gave higher product yields of 74% and 80%, respectively, than Amberlyst 15. However, the remaining product formed was again benzaldehyde (Table 1, entries 4 and 5).

Triphenyl(3-sulfopropyl)phosphonium hydrogen sulfate showed still lower activity (Table 1, entry 6) but when PW was used as the anion with zwitterions of 1-methyl-3-(3sulfopropyl)imidazolium (PW-MIMBS) and triphenyl(3sulfopropyl)phosphonium (PW-TPSP), the yield of the product increased up to 81% and 84%, respectively (Table 1, entries 7 and 8). This is because the heteropolyanion plays a vital role in stabilizing the intermediate carbocation.<sup>46</sup> Hence, to obtain an excellent product yield using PW and at the same time to overcome the drawback of the solubility of

 Table 1
 Reaction optimization for allylation of benzaldehyde via the

 Hosomi–Sakurai reaction<sup>a</sup>
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Entry	Catalysts	Solvent	Conversion <sup>c</sup> (%)
1	Without catalyst	Acetonitrile	_
2	TPSP	Acetonitrile	_
3	Amberlyst 15	Acetonitrile	$40^b$
4	$H_{3}PW_{12}O_{40}(PW)$	Acetonitrile	$74^b$
5	30PW-Si	Acetonitrile	$80^b$
6	H <sub>2</sub> SO <sub>4</sub> -TPSP	Acetonitrile	24
7	PW-MIMBS	Acetonitrile	81
8	PW-TPSP	Acetonitrile	84
9	A. 10PW-Si/TPSP	Acetonitrile	53
	B. 20PW-Si/TPSP		86
	C. 30PW-Si/TPSP		>99
	D. 50PW-Si/TPSP		>99
10	30PW-Si/TPSP	Acetonitrile	61
	A. 0.025 g		
	B. 0.050 g		>99
	C. 0.100 g		>99
11	30PW-Si/TPSP	NEAT	$60^e$
12	30PW-Si/TPSP	Water	$30^b$
13	30PW-Si/TPSP	Methanol	$<\!\!5$
14	30PW-Si/TPSP	Toluene	50
15	30PW-Si/TPSP	Dichloromethane	83
16	30PW-Si/TPSP	Acetonitrile	$>99^d$
17	30PW-Zr/TPSP	Acetonitrile	$81^b$

<sup>*a*</sup> Reaction conditions: benzaldehyde dimethyl acetal (1 mmol): allyl-TMS (1.5 mmol), solvent (2 mL), catalyst (0.050 g), temperature (RT), N<sub>2</sub>, reaction time (1 h). <sup>*b*</sup> The remaining product is benzaldehyde. <sup>*c*</sup> Yields on GC. <sup>*d*</sup> Reaction time: 0.5 h. <sup>*e*</sup> Tarry product formed. the above catalysts, the silica supported hydrophobic triphenyl(3-sulfopropyl)phosphonium salt of phosphotungstic acid (PW-Si/TPSP) with different loadings of PW was used. This proved to be a successful strategy and the yield of the product obtained was in the ascending order of PW loading ranging from 10-50%, giving 53% and 86% yields for 10% (10PW-Si/TPSP) and 20% (20PW-Si/TPSP) loadings, respectively (Table 1, entries 9(A) and (B)). For both 30% (30PW-Si/ TPSP) and 50% (50PW-Si/TPSP) loadings, more than 99% yields of the products were obtained (Table 1, entries 9(C) and (D)); hence, 30% PW loading was considered to be the optimum for complete conversion of acetals. The quantity of the 30PW-Si/TPSP catalyst also dramatically influenced the yield of the product. With 0.025 g of the catalyst, 61% product yield was obtained while with 0.050 g and 0.1 g of the catalyst, more than 99% yields were achieved (Table 1, entries 10(A)-(C)).

The solvent studies showed very interesting trends. The reaction without any solvent yielded only 60% of the product, however, it was accompanied with the formation of some tarry material (Table 1, entry 11). When water was used as a solvent, only 30% product yield was obtained with benzaldehyde (70%) formed as the major product as the deprotection of acetals is well known to occur in the presence of water and an acid catalyst (Table 1, entry 12). In the presence of methanol, the product yield was almost completely suppressed to the extent of only 5% (Table 1, entry 13). This was due to the rapid degradation of allyl-TMS by methanol to form alkoxy-TMS, thus, allyl-TMS is unavailable to attack on the oxonium cation which is a driving force to facilitate the reaction. Solvents like toluene and DCM gave moderate to good yields of about 50% and 83%, respectively (Table 1, entries 14 and 15). Acetonitrile served as the best solvent giving more than 99% yield in a very short time of 0.5 h (Table 1, entry 16). Therefore, acetonitrile was used as the solvent in further studies. Silica, when replaced with zirconia (ZrO<sub>2</sub>) as the support, adversely affected the product yield up to 81% with benzaldehyde as the by-product (Table 1, entry 17).

#### Substrate scope

After having achieved the best catalyst and optimized reaction conditions, the scope of our catalyst was further extended by screening a variety of acetals for the Hosomi– Sakurai allylation reaction and the results are presented in Table 2.

BDMA reacted with allyl-TMS to give 99% product yield (Table 2, entry 1). Mono- and di-methoxy substituted compounds having electron donating effects also reacted rapidly to give 96% and 98% product yields, respectively (Table 2, entries 2 and 3). *Ortho-* and *para*-substitutions in chloro-dimethyl acetals did not affect the allylation reaction resulting in 96% and 97% product yields, respectively (Table 2, entries 4 and 5). Piperonaldehyde dimethyl acetal also gave 99% yield in a very short time (Table 2, entry 6). Not only 1-naphthaldehyde dimethyl acetal but also the corresponding

diethyl acetal reacted to give 99% product yield (Table 2, entries 7 and 8). The presence of an electron withdrawing substituent on dimethyl and diethyl acetals retarded the rate of reaction as indicated by four-fold longer reaction times to achieve the same level of product yield (Table 2, entries 9–13).

Aliphatic acetals like 3,3-dimethoxypropylbenzene also reacted with allyl-TMS to give 97% product yield in 3 h (Table 2, entry 14).  $\alpha,\beta$ -Unsaturated cinnamaldehyde dimethyl and diethyl acetals smoothly reacted to achieve product yields of 95% and 98%, respectively (Table 2, entries 15 and 16). The 30PW-Si/TPSP catalyst was also successfully applied to the allylation of *o*-allylated phenolic acetals showing 93–99% product yield (Table 2, entries 17–21). This demonstrates very well the versatility and efficiency of the new catalyst developed for the Hosomi–Sakurai reaction of different functional groups. These new double allylated moieties will be further extended to polymerization reactions.

#### Reaction pathway

A plausible reaction mechanism is proposed to explain the pathway for allylation of acetals by the H–S reaction over the PW-Si/TPSP catalyst. The catalytic cycle was initiated by strong Brønsted acid sites of 30PW-Si/TPSP, activating the acetal to form the corresponding oxonium cation **A**, which further reacted with allyl-TMS to form the silica-stabilized carbocation **B**. This was followed by the removal of volatile alkoxy-TMS by the attack of methanol, generated in the initial step, to give the desired homoallyl ether **C** and the catalyst was regenerated for the subsequent cycle (Fig. 8).

#### Catalyst recycling study

In order to establish the stability for reuse of our 30PW-Si/ TPSP catalyst, a recycling study was also carried out for the Hosomi–Sakurai reaction of benzaldehyde dimethyl acetal and allyl-TMS in acetonitrile and the results are shown in Fig. 9.



<sup>*a*</sup> Reaction conditions: acetals (1 mmol): allyl-TMS (1.5 mmol), acetonitrile (2 mL), 30PW-Si/TPSP (0.050 g), temperature (RT),  $N_2$ . <sup>*b*</sup> Isolated yields after column chromatography. This is because of the fact that the –I effect restricted the protonation of oxygen by acetals which slowed down the process of formation of oxonium cations and thus the rate decreased drastically.



Fig. 9 Recycling of 30PW-Si/TPSP catalyst for the Hosomi-Sakurai allylation of acetal. Reaction conditions: benzaldehyde dimethyl acetal (1 mmol): allyl-TMS (1.5 mmol), acetonitrile (2 mL), 30PW-Si/TPSP (0.050 g), temperature (RT),  $N_2$ . Yields on GC.

For this purpose, after the first run, the catalyst was filtered, recovered and charged for the subsequent run. The fresh catalyst showed a 99% yield of HAE which then marginally decreased to 94% after the fourth consecutive recycling run and remained the same for the fifth run. Thus, the developed catalyst can be reused at least up to five times under the standard reaction conditions.

The filtrates were analyzed by ICP-OES for 'W' after recovery of the 30PW-Si/TPSP catalyst which didn't show even traces of 'W' which means that the slow decrease of activities during the catalyst reusability test was due to handling.

# Conclusion

In summary, we have prepared a new triphenyl(3sulfopropyl)phosphonium (TPSP) functionalized phosphotungstic acid on a silica support as an efficient solid Brønsted acid catalyst for the selective mono-allylation of acetals via the Hosomi-Sakurai reaction. The acidity of the catalyst was systematically varied by varying the PW loading in a range of 10-30% silica. FT-IR and XRD characterization confirmed the retention of the Keggin structure of heteropolyanions. The upfield shift from 22.70 ppm to 24.03 ppm for 'P' in <sup>31</sup>P-NMR of the 30PW-Si/TPSP sample confirmed the binding of triphenyl(3-sulfopropyl)phosphonium cations to PW, while the appearance of distinct peaks at -112.54 and -104.01 ppm for Q<sub>4</sub>-[Si(OSi<sub>4</sub>)] SiO<sub>2</sub> tetrahedral sites and Q<sub>3</sub>-[Si(OSi<sub>3</sub>)OH], respectively, in <sup>29</sup>Si-NMR of 30PW-Si confirmed the incorporation of PW into the fumed silica. The acidic strength and Brønsted acidic sites of the catalyst were determined by ammonia-TPD and pyridine-FTIR and the order of acidity was observed as follows: PW > PW-TPSP > 30PW-Si/TPSP. Interestingly, the distribution of acid sites on silica of the 30PW-Si/TPSP sample played an important role in enhancing its activity for selective mono-allylation, giving 99% product yield. The versatility of our catalyst was demonstrated by achieving quantitative yields in the H-S reaction using a wide variety of substrates such as mono- and di-methoxy substituted compounds, *o*- and *p*-substituted chloro-dimethyl acetals, piperonaldehyde dimethyl acetal, and 1-naphthaldehyde dimethyl/diethyl acetals. The stability of this new heterogeneous acid catalyst was established by its successful recycling for five times.

# **Experimental section**

#### General methods

All the reactions were carried out in a flame-dried glass apparatus under inert nitrogen atmosphere using specially procured chemicals and AR-grade dried solvents from authentic suppliers like Aldrich, Alfa Aesar, Thomas Baker, *etc.* Fumed silica and heteropolyacids were purchased from Aldrich. TLC plates were purchased from Loba. 100–200 mesh silica was utilized for column chromatography using 5% ethyl acetate in pet ether as the mobile phase.

Some of the acetals and o-allylated acetals were prepared by the reported procedures.<sup>28</sup> Conversion of the substrates was calculated by liquid analysis using a Hewlett Packard 6890 GC (HP-5 column) and the products were characterised by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR using CDCl<sub>3</sub> (0.01% TMS) and D<sub>6</sub>-DMSO (0.01% TMS) as solvents on a 200 MHz frequency Bruker instrument. Solid-state MAS CP-NMR of the catalyst samples were carried out using a JEOL-400 MHz instrument. The products were confirmed using a QP-2010 Ultra GC-MS Shimadzu instrument with an RTX-5 column and helium as a carrier gas in EI mode at an ionization source temperature about 200 °C. A Micromeritics 2120 chemisorption instrument was used for determination of BET surface area and also NH<sub>3</sub>-TPD using helium as a carrier gas and 30% NH<sub>3</sub> in helium as an adsorbent. Functional group characterization by FT-IR of various compounds and catalysts was performed on a PerkinElmer Frontier instrument in ATR (PIKE Tech) mode at room temperature. Pyridine-FTIR was conducted using a Harrick diffuse reflectance praving mantis assembly with a temperature controller (30-850 °C) under nitrogen as a carrier gas at a flow rate of 150 mL min<sup>-1</sup>. Wide-angle X-ray diffraction (WAXRD) spectra were recorded on a PANalytical X-Pert PRO-1712 PXRD instrument using Ni filtered Cu-Ka radiation ( $\lambda = 0.154$  nm) as a source (current intensity, 30 mA; voltage, 40 kV) and an X'Celerator detector. TGA was carried out on a TGA-7 PerkinElmer instrument under N2 up to 800 °C with a heating rate of 10 °C min<sup>-1</sup>. ICP-OES and EDAX were carried out on Thermo Fisher and AMETEK instruments, respectively.

#### General procedure for catalyst preparation

Synthesis of triphenyl(3-sulfopropyl)phosphonium and related zwitterions (Scheme 2, B). To a solution of triphenylphosphine (2.6229 g, 0.1 mole) in 30 mL of toluene, 1,3-propane sultone (1.22 g, 0.1 mole) was added. Then, the mixture was refluxed at 130 °C for 48 hours, and the resultant white solid was filtered and washed with 30 mL of

toluene. The crude product residue was dried under vacuum at 120 °C and characterized using <sup>1</sup>H-NMR.

<sup>1</sup>H-NMR. <sup>1</sup>H NMR (200.17 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.2–2.18 (m, 2H), 2.97–3.04 (t, J = 7.07 Hz, 2H), 3.37–3.52 (m, 2H), 7.64–7.82 (m, 15H).

Typical procedure for the preparation of 30PW-Si/TPSP catalyst (Scheme 2, C). Triphenyl(3-sulfopropyl)phosphonium (0.0798 g, 0.000208 mole) was dissolved in 10 mL of distilled water to which 1.0 g of 30PW/Si (amount of PW: 0.3 g, 0.000104 mole) was slowly added. Then, the mixture was stirred at room temperature for 12 hours. Water was evaporated from the residue at 90 °C for 1 hour on a rotavapour and dried at 150 °C for 12 hours.

All the other catalysts (10PW-Si/TPSP, 20PW-Si/TPSP and 50PW-Si/TPSP) were prepared by using the same procedures with appropriate changes in the amount of zwitterions.

General procedure for the allylation of acetals. The 30PW-Si/TPSP catalyst (0.05 g) was added to the solution of benzaldehyde dimethyl acetal (1 mmol, 0.152 g) and allyltrimethylsilane (1.5 mmol, 0.237 mL) in acetonitrile (2 mL). The mixture was stirred at room temperature under nitrogen till the reaction was completed as monitored by TLC. Then, the catalyst was filtered and washed with 10 mL of acetonitrile. The solvent was removed from the filtrate under reduced pressure and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 9.5:0.5) to give the desired product in 99% yield.

**Procedure for catalyst recycling.** The 30PW-Si/TPSP catalyst recovered from the above mentioned procedure was dried at 150 °C and reused for the same reaction. This procedure was repeated 5 times with the same catalyst.

The amount of S and W was calculated using EDAX for the fresh and recovered 30PW-Si/TPSP catalyst which showed similar weight% of W and S which means that no leaching of the active components occurred after reaction (ESI† Table S3 and S4, Fig. S3 and S4).

#### Spectroscopic data of selected compounds

(1-Methoxybut-3-en-1-yl)benzene (Table 2, entry 1). Colorless liquid, <sup>1</sup>H NMR (200.17 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.42–2.60 (m, 2H), 3.24 (s, 3H), 4.15–4.22 (m, 1H), 2.64–2.58 (m, 1H), 2.53–2.48 (m, 1H), 2.38–2.32 (m, 1H), 1.76–1.70 (m, 1H), 1.17 (d, *J* = 6.18 Hz, 3H). <sup>13</sup>C NMR (150.92 MHz, CDCl<sub>3</sub>):  $\delta$  42.56, 56.67, 83.69, 116.89, 126.75, 127.9, 128.40, 134.84, 141.71. GC-MS: *m/z* 162.10.

1-(Allyloxy)-4-(1-methoxybut-3-en-1-yl)benzene (Table 2, entry 17). Colorless liquid, <sup>1</sup>H NMR (200.17 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.39–2.57 (m, 2H), 3.19 (s, 3H), 4.11 (t, 1H), 4.51–4.56 (d, 2H), 4.99–5.08 (m, 2H), 5.26–5.31 (m, 1H), 5.46–5.47 (m, 1H), 5.73–5.77 (m, 1H), 6.00–6.11 (m, 1H), 6.91 (d, J = 8.72 Hz, 2H), 7.17 (d, J = 8.59 Hz, 2H). <sup>13</sup>C NMR (150.92 MHz, CDCl<sub>3</sub>):  $\delta$  42.46, 56.42, 68.85, 83.19, 114.57, 116.77, 117.61, 127.93, 133.38, 133.89, 134.96, 158.17. GC-MS: m/z 218.13.

1-(Allyloxy)-2-(1-methoxybut-3-en-1-yl)benzene (Table 2, entry 18). Colorless liquid, <sup>1</sup>H NMR (200.17 MHz, CDCl<sub>3</sub>,

TMS):  $\delta$  2.42–2.50 (m, 2H), 3.26 (s, 3H), 4.53–4.57 (CH<sub>2</sub>–O, dt, J = 1.64, 4.93 Hz, 2H), 4.72–4.78 (t, 1H), 4.98–5.11 (m, 2H), 5.23–5.31 (dq, J = 1.52, 10.61 Hz, 1H) 5.36–5.47 (dq, J = 1.64, 17.2 Hz, 1H), 5.76–6.15 (m, 2H), 6.83–6.87 (dd, J = 0.88, 8.08 Hz, 1H), 6.95–7.02 (td, J = 1.01, 7.33, 7.45 Hz, 2H), 7.17–7.26 (td, J = 1.77, 7.45, 8.08 Hz, 1H), 7.35–7.40 (dd, J = 1.77, 7.58 Hz, 1H). <sup>13</sup>C NMR (150.92 MHz, CDCl<sub>3</sub>):  $\delta$  41.09, 56.94, 68.55, 76.90, 111.50, 116.87, 120.82, 126.49, 127.99, 130.20, 133.29, 135.38, 155.85. GC-MS: m/z 218.13.

1-(Allyloxy)-2-methoxy-4-(1-methoxybut-3-en-1-yl)benzene (Table 2, entry 19). Colorless liquid, <sup>1</sup>H NMR (200.17 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.38–2.56 (m, 2H), 3.21 (s, 3H), 3.89 (s, 3H), 4.07–4.14 (m, 1H), 4.60–4.64 (m, 2H), 5.00–5.12 (m, 2H), 5.26–5.47 (m, 2H), 5.70–5.83 (m, 1H), 6.01–6.17 (m, 1H), 6.75–6.87 (m, 3H). <sup>13</sup>C NMR (150.92 MHz, CDCl<sub>3</sub>):  $\delta$  42.51, 55.99, 56.51, 69.93, 83.45, 109.74, 113.00, 116.78, 117.89, 119.23, 133.47, 134.66, 134.93, 147.51, 149.62. GC-MS: m/z 248.14.

2-(Allyloxy)-1,3-dimethoxy-5-(1-methoxybut-3-en-1-yl)benzene (Table 2, entry 20). Colorless liquid, <sup>1</sup>H NMR (200.17 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.36–2.57 (m, 2H), 3.24 (s, 3H), 3.85 (s, 6H), 4.07–4.10 (q, 1H) 4.50–4.52 (dt, J = 1.37, 6.41 Hz, 2H), 5.02–5.10 (m, 2H), 5.16–5.20 (dq, J = 1.37, 10.53 Hz, 1H), 5.28–5.34 (dq, J = 1.37, 16.94 Hz, 1H), 5.73–5.83 (m, 1H), 6.07–6.17 (m, 1H), 6.51 (s, 2H). <sup>13</sup>C NMR (150.92 MHz, CDCl<sub>3</sub>):  $\delta$  42.68, 56.17, 56.84, 74.22, 83.92, 103.39, 116.95, 117.68, 134.65, 134.93, 135.89, 137.59, 153.51. GC-MS: *m*/z 278.15.

(*E*)-1-(Allyloxy)-2-methoxy-4-(3-methoxyhexa-1,5-dien-1-yl)benzene (Table 2, entry 21). Colorless liquid, <sup>1</sup>H NMR (200.17 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.36–2.47 (m, 2H), 3.33 (s, 3H), 3.71– 3.81 (m, 1H), 3.91 (s, 3H), 4.61–4.65 (dt, *J* = 1.52, 5.31 Hz, 2H), 5.04–5.18 (m, 2H), 5.26–5.46 (m, 2H), 5.75–6.19 (m, 3H), 6.45–6.52 (d, 1H), 6.81–6.97 (m, 3H). <sup>13</sup>C NMR (150.92 MHz, CDCl<sub>3</sub>):  $\delta$  40.40, 55.97, 56.34, 69.95, 82.22, 109.35, 113.35, 117.11, 118.14, 119.63, 127.81, 130.00, 132.39, 133.29, 134.60, 141.97, 149.58. GC-MS: *m/z* 274.16.

## Abbreviations

TPSP, triphenyl(3-sulfopropyl)phosphonium zwitterion; PW, phosphotungstic acid; Si, silica; TMS, trimethylsilane; TLC, thin layer chromatography.

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