Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron 60 (2004) 4087–4096
Tetrahedron

Oxidation of allylic alcohols, amines, and sulfides mediated by assembled triphase catalyst of phosphotungstate and non-cross-linked amphiphilic copolymer

Yoichi M. A. Yamada, Hidetsugu Tabata, Masato Ichinohe, Hideyo Takahashi and Shiro Ikegami*

Faculty of Pharmaceutical Sciences, Teikyo University, Sagamiko, Kanagawa 199-0195, Japan

Received 26 January 2004; accepted 19 February 2004

Abstract—A novel catalyst PWAA, an assembled complex of phosphotungstic acid ($H_3PW_{12}O_{40}$) and a non-cross-linked copolymer of *N*-isopropylacrylamide with an ammonium, was developed. It is an amphiphilic, cross-linked, and supramolecular insoluble complex and showed catalytic activity on oxidation with aqueous hydrogen peroxide. PWAA, used in 2.7×10^{-5}–2.0×10^{-3} mol equiv., catalyzed oxidation of allylic alcohols, amines, and sulfides efficiently. The turnover number (TON) of PWAA reached up to 35,000. PWAA showed a good stability in organic/aqueous media and was reused three to five times.

1. Introduction

A development of phase-transfer solid-phase catalyst that mediates aqueous–organic biphase reactions is one of the most important issues for recent synthetic organic chemistry and industrial engineering.[1,2] Using such triphase catalysts enables effective reactions between organic substrates and water-soluble reagents.[2] In addition to this, these solid-phase catalysts are easily separated by filtration or decantation from the system and are reused without any treatments. Hence, this catalytic system can enhance economy of the reaction and decrease environmental pollution under ideal conditions.

In order to realize this triphase catalytic oxidation system, one may say that using water-soluble oxidants such as hydrogen peroxide is suitable.[1] Although many toxic reagents such as Cr(VI), Mn(VII), Os(VIII) and Pb(IV) have been utilized for oxidation, such heavy metal species are stoichiometric or substoichimetric oxidants, and thus many toxic wastes must be disposed. On the contrary, hydrogen peroxide is sustainable and economical; it is a cheap and clean oxidant transformed into harmless water.[1c] Thus, the oxidation system promoted by triphase catalysts with hydrogen peroxide can fulfill all the requirements of economy, efficiency, and safety.

Over the past few decades, a considerable number of studies have been made on triphase catalysts which were immobilized with cross-linked polystyrene resins, silica gels or metals. These catalytic systems, however, generally resulted in lower catalytic activity compared with their soluble counterparts, and were often obliged to use hazardous chlorohydrocarbon solvents.[3] Besides, reuse of these catalysts was often difficult owing to the gradual decline of the catalytic activity. These problems made them less practical. Therefore, we decided to concentrate on developing triphase catalysts that were highly active and reusable.

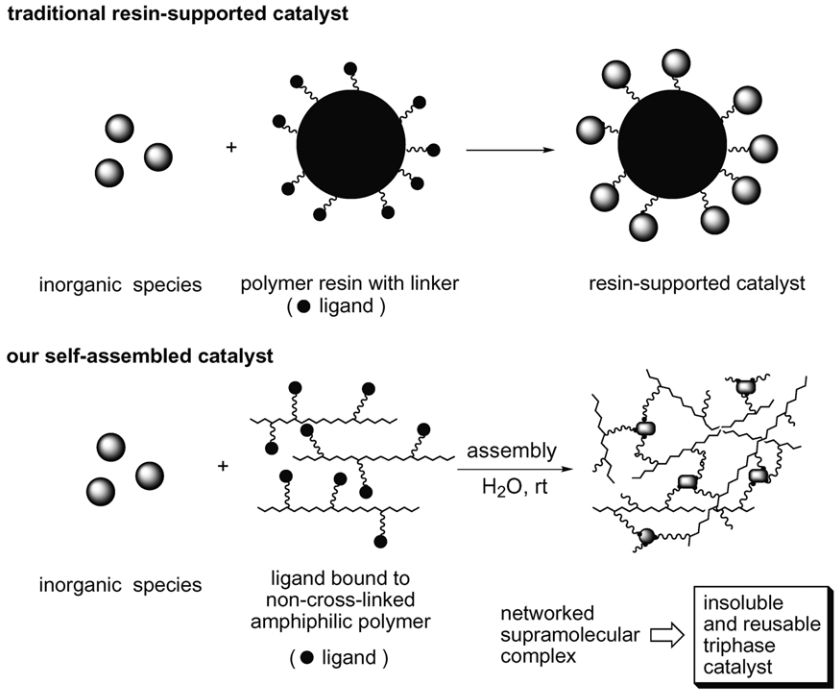
In traditional triphase catalysts, as we have mentioned before, a catalytic species was anchored to a linker that was immobilized to a polymer resin or silica gel (Scheme 1, above). In our approach, however, the insoluble catalysts were constructed from self-assembly process of non-cross-linked amphiphilic copolymer ligands and inorganic species.[4] This process would promote the cross-linking of the copolymer by the inorganic species to provide networked, supramolecular, and insoluble complexes (Scheme 1, below). They might possess many mesopores where the inorganic species would be tightly supported by many ligands not to be dissociated. We expected such complexes should act as highly active catalysts based on the following points: (1) the complexes have a characteristic high-to-volume ratio to react with a substrate and a reagent, (2) they can capture these reagents effectively by their mesopores, and (3) the amphiphilic copolymers and the inorganic species might construct effective catalytic sites

---

Keywords: Catalysis; Oxidation; Polymer support; Self-assembly; Tungsten and compounds.

* Corresponding author. Tel.: +81-426-85-3728; fax: +81-426-85-1870; e-mail address: shi-ike@pharm.teikyo-u.ac.jp

0040–4020/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2004.02.072



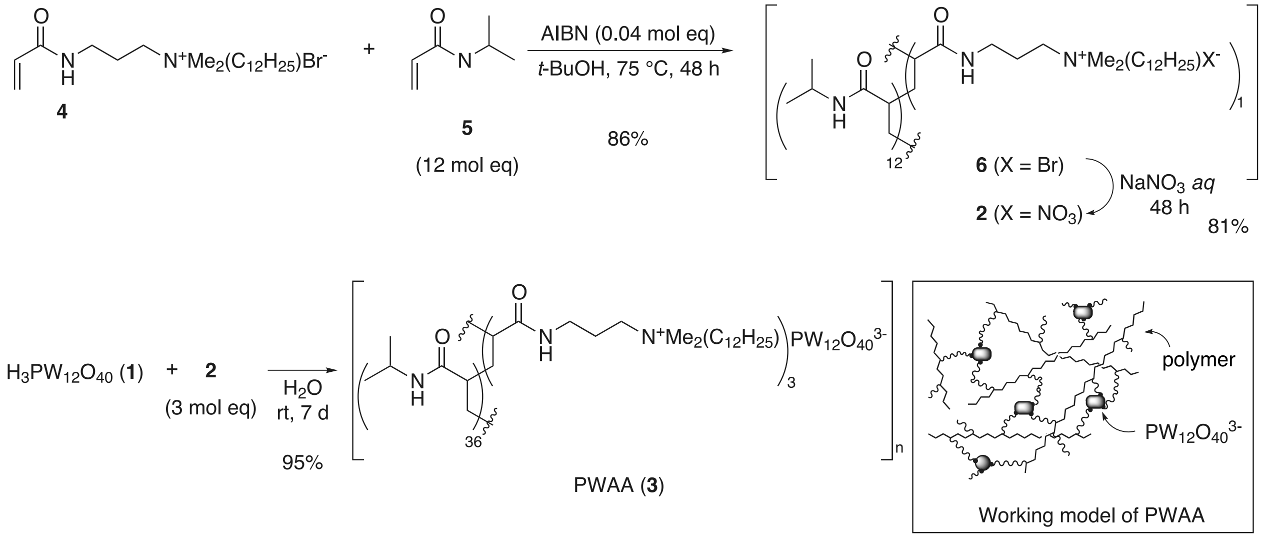
Scheme 1. Hypothesis of formation of a self-assembled complex for an insoluble oxidation catalyst.

with high affinity to both hydrophobic and hydrophilic reagents.

We herein report the full detail of our approach: a development of a highly active triphase catalyst PWAA (**3**), formed from phosphotungstic acid ($H_3PW_{12}O_{40}$) (**1**) and poly{[3-(*a*cryloylamino)propyl]dodecyldimethylammonium nitrate}-*co*-(*N*-isopropyl*a*crylamide)$_{12}$} (**2**) and its application to oxidation of allylic alcohols, amines and sulfides.[5] It was found that PWAA has a good catalytic activity on oxidation in both aqueous and organic solvent. It should be noted that the turnover number (TON=mol of a product/mol of a catalyst) of PWAA reached up to 35,000.

2. Preparation of a triphase catalyst PWAA

PWAA was prepared as shown in Scheme 2. Ammonium salt **4** was synthesized from commercially available *N*-[3-(dimethylamino)propyl]acrylamide with 1-bromododecane in 92% yield. Random copolymerizations of **4** with 12 mol equiv. of **5** were performed in the presence of 0.04 mol equiv. of AIBN in *t*-BuOH at 75 °C for 48 h, resulting in that non-cross-linked polymer **6** was formed. It was an amphiphilic polymer that was soluble in water, *t*-BuOH, and CH_2Cl_2. The ratio of the *N*-isopropylacryl amide unit to the ammonium unit to be 12/1 was determined by ^1H NMR. The bromide **6** was ion-exchanged to the



Scheme 2. Preparation of a novel triphase catalyst PWAA with the structure **3**.

nitrate **2**.[6] The molecular weight of **2** was wide-ranging (thousands to tens of thousands) as a result of gel-permeation chromatography relative to polystyrene standards. Thus, complexation to form PWAA was carried out according to the procedure for the preparation of $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3PW_{12}O_{40}$.[7] A self-assembly process of **1** with **2** (3 mol equiv. as an ammonium unit) in water at room temperature resulted in the formation of white insoluble precipitates simultaneously. After stirring for 7 days at the same temperature, the resulted precipitate was washed and dried to give PWAA as white lumps.[8] PWAA were insoluble in H_2O and organic solvents such as MeOH, EtOH, *i*-PrOH, AcOEt, Me_2CO, CH_2Cl_2, toluene, Et_2O and hexane.

To elucidate the structure of PWAA, several spectroscopic measurements were examined. The elementary analysis showed that one complex unit of $\mathbf{3}\cdot 22H_2O$. The infrared spectrum of PWAA exhibited strong vibrations at 1080 (P=O), 978 (W=O), 897 and 818 cm^{-1}, while that of **1** exhibited them at 1080, 982, 893 and 808 cm^{-1}. Viewed in this light, the structure of the phosphotungstic acid unit of PWAA can be regarded as that of **1**.

Furthermore, we analyzed PWAA by gel-phase ^{31}P NMR; a broad singlet peak was detected at −13 ppm (Fig. 1). Since it was reported that the signals of $H_3PW_{12}O_{40}$ and $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3PW_{12}O_{40}$ were observed at the similar frequency (−14.7 ppm[9] and −14.5 ppm,[10] respectively), it would be supported that phosphotungstate in PWAA maintained the heteropolyacidic structure such as the Keggin type ($PW_{12}O_{40}^{3-}$).[11]

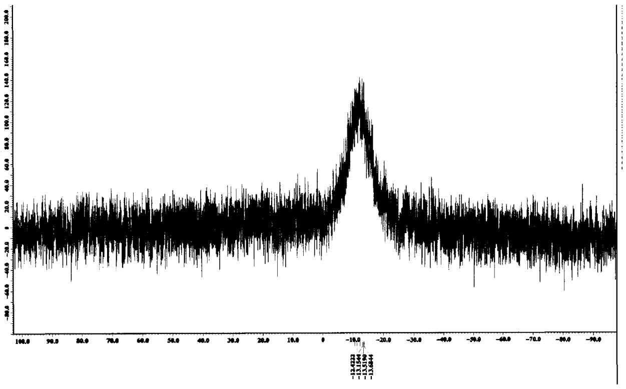


Figure 1. A gel-phase ^{31}P NMR chart of PWAA.

A scanning electron microscope (SEM) of PWAA was also investigated (Fig. 2). PWAA was treated with gold vapor by the sputter-coating method. It was observed that PWAA possessed many pores, whose diameter was about 1–10 μm (left) and hundreds nanometer or less (center). Further magnification (×50,000) showed many projections those lengths were less than 100 nm (right); all these things make it clear that PWAA has a high surface-to-volume ratio and many reactive sites. The further structural investigation of the catalyst is now under the way.

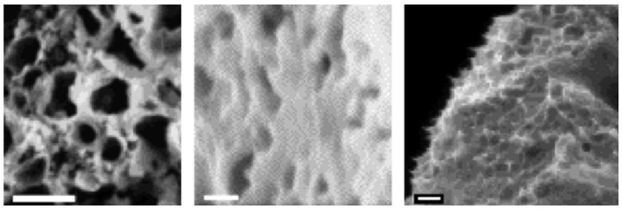
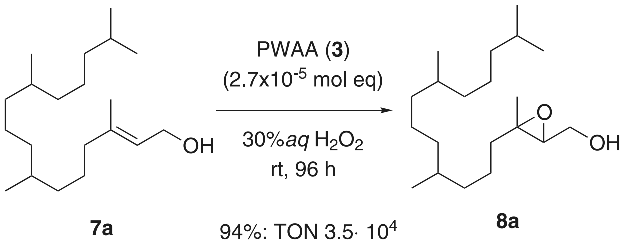


Figure 2. Scanning electron micrographs (SEM) of PWAA; (left): scale bar: 10 μm; (center): scale bar: 500 nm; (right): scale bar: 100 nm.

3. Epoxidation of allylic alcohols catalyzed by PWAA

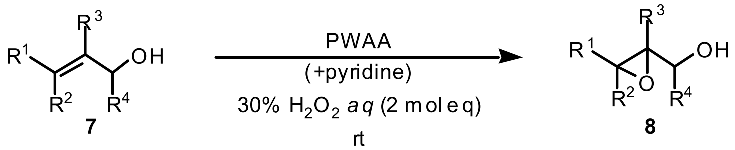
With the insoluble complex PWAA in hand, the epoxidation of allylic alcohols with aqueous H_2O_2 under the organic solvent-free conditions was examined.[12,13] We were pleased to find that PWAA showed a very high catalytic activity on epoxidation. In the presence of 2.7×10^{-5} mol equiv. of PWAA, the reaction of phytol (**7a**) with 2 mol equiv. of 30% aqueous H_2O_2 resulted in the corresponding epoxy alcohol **8a** in 94% yield (Scheme 3). TON of PWAA was approximately 35,000. This result showed that PWAA has a excellent catalytic activity among the precedent.

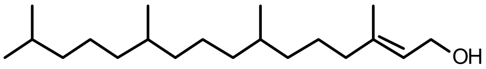
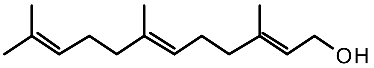
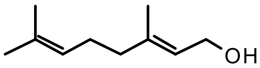
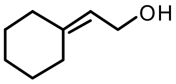
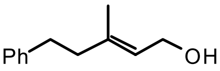
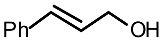
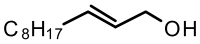
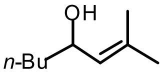
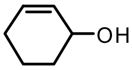
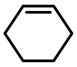
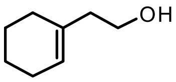
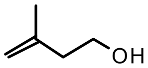


Scheme 3. Epoxidation of phytol (**7a**) promoted by PWAA.

Since the catalytic activity of PWAA was evaluated, a series of epoxidation of several allylic alcohols was performed in the presence of 5.0×10^{-4} mol equiv. of PWAA (Table 1). Hydrophobic substrates of **7a** and farnesol (**7b**) were converted to the corresponding epoxides in high yields. Epoxidation of **7a** proceeded in 7 h at room temperature to give **8a** in 96% yield with TON reaching approximately 2000 (entry 1). In the reaction of **7b**, 2,3-epoxy alcohol **8b** was obtained in 84% yield (entry 2). In this case, other trialkylsubstituted alkene moieties were intact. The epoxidation of less hydrophobic geraniol (**7c**) was messy to afford **8c** in 12% yield owing to acidic hydrolysis of the epoxide (entry 3). We found that the addition of a trace amount of pyridine was effective to reduce an acidity in this system and thus to prevent the epoxide-opening reactions.[14] The reaction of **7c** in the presence of PWAA and 6.0×10^{-3} mol equiv. of pyridine for 15 h resulted in the formation of **8c** in 80% yield (entry 4), where the C(6)–(7) double bond was not affected. Under identical conditions, trisubstituted allylic alcohols such as an exocyclic allylic alcohol **7d** and a linear one **7e** provided the corresponding epoxides in high yields (entries 5 and 6). Although disubstituted allylic alcohols were less reactive, they were converted to the corresponding epoxides in quantitative yields by using 2.0×10^{-3} mol equiv. of PWAA (entries 7 and 8). Besides, the diasteroselective epoxidation of 2-methyl-2-octen-4-ol (**7h**) furnished the *threo*-selective

Table 1. Epoxidation of allylic alcohols promoted by PWAA



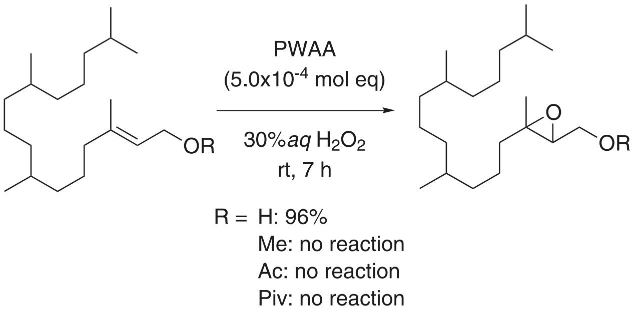
Entry	Substrate		**3b** (mol equiv.)	Pyridine (mol equiv.)	Time (h)	Yield (%)[a]
1		**7a**	5.0×10^{-4}	—	7	**8a**:96
2		**7b**	5.0×10^{-4}	—	13	**8b**:84
3		**7c**	5.0×10^{-4}	—	37	**8c**:12
4		**7c**	5.0×10^{-4}	6.0×10^{-3}	15	**8c**:80
5		**7d**	5.0×10^{-4}	6.0×10^{-3}	12	**8d**:83
6		**7e**	5.0×10^{-4}	6.0×10^{-3}	13	**8e**:96
7		**7f**	2.0×10^{-3}	9.6×10^{-2}	30	**8f**:quant
8		**7g**	2.0×10^{-3}	2.4×10^{-2}	33	**8g**:quant
9		**7h**	2.0×10^{-3}	9.6×10^{-2}	85	**8h**:73 (threo/erythro=91:9)
10		**7i**	2.0×10^{-3}	2.4×10^{-2}	—	[b]
11		**7j**	2.0×10^{-3}	2.4×10^{-2}	24	[c]
12		**7k**	2.0×10^{-3}	2.4×10^{-2}	—	[b]
13		**7l**	2.0×10^{-3}	2.4×10^{-2}	—	[b]

[a] Isolated yields.
[b] The product was not isolated because the reaction was messy.
[c] No reaction.

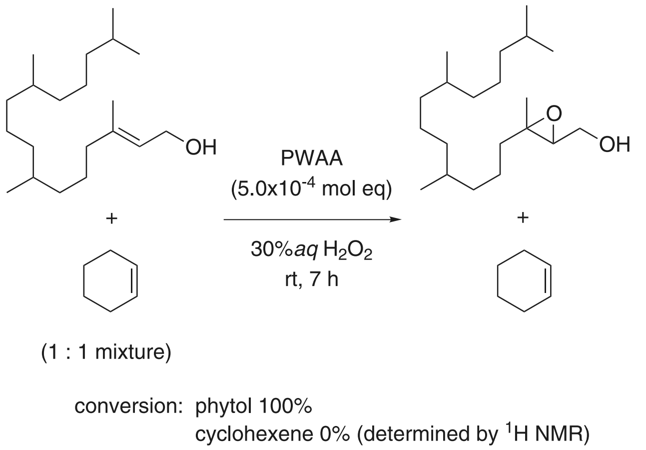
epoxy alcohol **8h** in 73% yield (*threo*/*erythro* (91:9)) (entry 9).

We further investigated the oxidation of cyclic allylic alcohol. In the case of 2-cyclohexen-1-ol (**7i**), decomposition of the product was so fast that the reaction was messy. This result might suggest that PWAA was not able to activate a *s-trans* allylic alcohol efficiently. In respect of chemoselectivity, cyclohexene (**7j**), an unmodified alkene, was not converted to cyclohexene oxide at all. Moreover, the epoxidation of homoallylic alcohols **7k** and **7l** was also slow and did not provide the corresponding products. These results indicated that hydroxyl group at allylic position was essential to proceed the epoxidation efficiently.

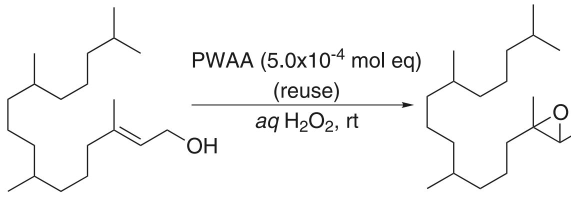
For reasons mentioned above, we investigated the proximity effect of allylic alcohol (Scheme 4). Epoxidation of a phytol-methyl ether, a phytol-acetyl ester and a phytol-pivaloyl ester under identical conditions did not proceed at all. Besides, the mixture of phytol (**7a**) and cyclohexene (**7j**) resulted in the quantitative conversion of phytol and the no reaction of cyclohexene under the identical conditions



Scheme 4. The epoxidation of phytol derivatives.



Scheme 5. Epoxidation of the mixture of phytol and cyclohexene promoted by PWAA.



7a

8a

Scheme 6. Epoxidation of phytol (**7a**) catalyzed by recycled PWAA.

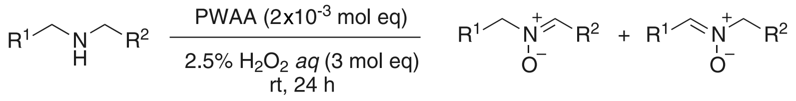
(Scheme 5). Considered these results, epoxidation was promoted by the interaction of hydroxyl group of allylic alcohol with PWAA which is similar to early transition metal catalyses.[15]

Moreover, recycling of PWAA in case of **7a** was examined as shown in Scheme 6. It was found that PWAA was reused three times; in the first to third cycle runs, the product **8a** was given in 96, 93, and 97% yields, respectively. The activity of PWAA was unchanged under the oxidation conditions through the consecutive runs, although PWAA was pulverized through runs.

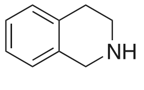
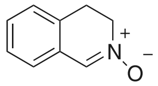
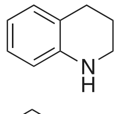
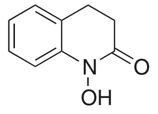
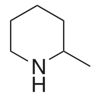
4. Oxidation of amines catalyzed by PWAA

Since PWAA efficiently promoted the epoxidation of allylic alcohols, we applied this oxidation to heteroatoms: secondary amines and sulfides.[16,17] Oxidation of secondary amines is the most straightforward method and the direct route to prepare nitrones, which are important substrates for the synthesis of nitrogen-containing bioactive compounds. It was beforehand confirmed that no oxidation of dibenzylamine (**9a**) with hydrogen peroxide was observed at room temperature. On the contrary, addition of 2×10^{-3} mol equiv. of PWAA to this reaction system proceeded oxidation to give the corresponding nitrone (**10a**) in 86% yield (Table 2, entry 1).[18] Bis(p-substituted benzyl)amines were also converted to the corresponding oximes under similar conditions. The reaction of bis[(4-trifluoromethyl)benzyl]amine (**9b**) proceeded smoothly to afford **10b** in 90% yield. TON of PWAA in this oxidation reached 450. However, bis(4-chlorobenzyl)amine (**9c**) and

Table 2. Oxidation of secondary amines by PWAA



9 10 10'

Entry	Amines	R^1	R^2	Temperature (°C)	Time (h)	Nitrone	Yield (%)[a]
1	**9a**	Ph	Ph	rt	24	**10a**	89
2	**9b**	p-CF$_3$–C$_6$H$_4$	p-CF$_3$–C$_6$H$_4$	rt	24	**10b**	90
3	**9c**	p-Cl–C$_6$H$_4$	p-Cl–C$_6$H$_4$	rt	24	**10c**	56
4	**9d**	p-MeO–C$_6$H$_4$	p-MeO–C$_6$H$_4$	rt	48	**10d**	62
5	**9e**	p-MeO–C$_6$H$_4$	p-CF$_3$–C$_6$H$_4$	rt	24	**10e**+**10e′**	94 (**10e**+**10e′**=1.7/1)
6	**9f**	Ph	p-CF$_3$–C$_6$H$_4$	rt	24	**10f**+**10f′**	80 (**10f**+**10f′**=1.3/1)
7	**9g**	Ph	p-CN–C$_6$H$_4$	40	24	**10g**+**10g′**	71 (**10g**+**10g′**=1.5/1)
8	**9h**	(CH$_3$)$_3$	Ph	rt	24	**10h**	34
9	**9i**	 NH		rt	12	**10i**  N+ O−	70
10	**9j**	 N H		rt	12	**10j**  N O OH	30
11	**9k**	 N H		rt	12	—	[b]

[a] Isolated yields.

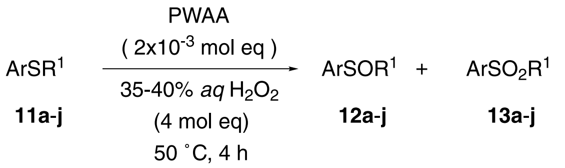
[b] The product was not isolated because the reaction was messy.

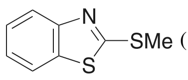
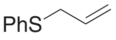
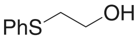
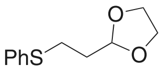
bis(4-methoxybenzyl)amine (**9d**) were converted to **10c** and **10d** in moderate yields. We further examined the regioselective oxidations of bis(*p*-substituted benzyl)amines. Although it seemed reasonable that the deprotonation took place at more acidic benzylic position selectively, the reactions gave nitrones in 71–94% yield albeit with low regioselectivity (1.3/1–1.7/1) (entries 5–7).[19] Turning to cyclic secondary amines, tetrahydroisoquinoline (**9i**) was converted to **10i**, which is the useful substrate for the synthesis of isoquinoline alkaloids, in 70% yield (entry 9).[16c] Oxidation of tetrahydroquinoline (**9j**) provided **10j** instead of the corresponding nitrone.[16d] (entry 10). The reaction of cyclic aliphatic amine **9k** was so messy because of the side reactions such as oxidative dimerization so that the corresponding product was not isolated (entry 11).

5. Oxidation of sulfides catalyzed by PWAA

Next, we turned our attention to oxidation of sulfides to sulfones (Table 3).[20,21] Sulfones have been utilized as the syntons for total synthesis of bioactive natural compounds. As depicted in parenthesis in Table 3, oxidation of **11a–k** with hydrogen peroxide in the absence of PWAA proceeded sluggishly to give mainly the corresponding sulfoxides **12a–k** in low to moderate yields[22] rather than sulfones **13a–k**. Meeting our expectations, PWAA efficiently proceeded the oxidation of sulfides to give sulfones under similar conditions. In the presence of 2×10^{-3} mol equiv. of PWAA, **11a** was converted into **13a** in 97% yield (entry 1). TON of PWAA reached approximately 500. The substituted aryl methyl sulfides were also converted to the corresponding sulfones in high yields (84–90%) (entries 3, 5 and 7). Similarly, oxidation of alkyl thiophenols also provided the corresponding sulfones in high yields (entries 9, 15, 17 and 19). It is notable that the catalytic system tolerates a wide variety of functional group. For example, methylthio benzothiazole (**11f**) that is a useful nucleophile for the Julia olefination[23] was converted to the sulfone **13f** in 78% yield (entry 11). In this reaction, benzothiazole ring was unaffected through the reaction. The chemoselective oxidation of methylthiobenzaldehyde (**11g**) proceeded to give **13g** in 86% yield with intactness of formyl group (entry 13). Besides, the oxidation of **11h** and **11i** proceeded efficiently to give **13h** and **13i** in high yields, where the olefin and alcohol were tolerated and β-elimination of the alcohol was not observed (entries 15 and 17). Sulfide **11j** with a cyclic acetal in the structure was converted to **13j**, which was the substrate for the preparation of the prostaglandin analogue, in 71% yield (entry 19).[24] On the other hand, the reaction of diphenyl sulfide **11k** hardly proceeded (entry 21).

Table 3. Oxidation of sulfides to sulfones with and without PWAA



Entry	11	Catalyst	12 (%)[a]	13 (%)[a]
1[b]	PhSMe (**11a**)	PWAA	3	97
2[b]	**11a**	—	(74)	(26)
3	*p*-Me–C_6H_4SMe (**11b**)	PWAA	9	90
4	**11b**	—	(71)	(22)
5	*p*-Br–C_6H_4SMe (**11c**)	PWAA	12	87
6	**11c**	—	(70)	(15)
7	*p*-MeO–C_6H_4SMe (**11d**)	PWAA	6	84
8	**11d**	—	(76)	(24)
9	PhSEt (**11e**)	PWAA	3	91
10	**11e**	—	(75)	(17)
11[c]	 (**11f**)	PWAA	17	78
12[c]	**11f**	—	(9)	(0)
13	*p*-CHO–C_6H_4SMe (**11g**)	PWAA	—	86
14	**11g**	—	(53)	(33)
15[c]	 (**11h**)	PWAA	3	81
16[c]	**11h**	—	(80)	(10)
17	 (**11i**)	PWAA	—	Quant
18	**11i**	—	(80)	(13)
19	 (**11j**)	PWAA	11	71
20	**11j**	—	(54)	(trace)
21	PhSPh (**11k**)	PWAA	10	6
22	**11k**	—	4	(0)

The yields of the oxidations without PWAA were in parentheses.

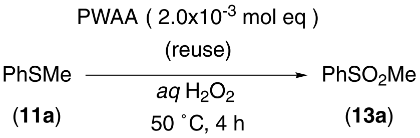
[a] Isolated yields.

[b] 3 mol equiv. of H_2O_2 was used.

[c] The reaction was performed for 7 h.

The recycled activity of PWAA in the oxidation of sulfide **11a** was evaluated (Scheme 7). The oxidation of **11a** was performed under identical conditions, affording **13a** in 97% yield. In the repeated use of the recovered catalyst, PWAA mediated the second to fifth cycled runs to give **13a** in 82–88% yields. The reason to reduce yields in the second cycled run was unclear. One explanation for this may be that PWAA was pulverized and adsorbed onto the reaction vessel so that the efficiency of the reaction was reduced physically. In this respect, It was confirmed that the pulverization did not affect the intrinsic activity of PWAA: the recovered PWAA was analyzed by gel-phase ^{31}P NMR to show a broad peak at −13 ppm as well as the PWAA before use.[25]

As stated above, all the reactions were performed under organic solvent-free conditions. PWAA was insoluble and stable in both aqueous and organic solvents. We expected that PWAA should efficiently catalyze the oxidation in any media. Hence, the activity of PWAA in an organic solvent was investigated. The reactions of **11a** to **13a** were carried out with various organic solvents as depicted in Table 4. Similar to the oxidation without organic solvent completed in 4 h to give **13a** in 97% yield (entry 1), the reaction with



1st use: 97%; 2nd use: 86%; 3rd use: 83%
4th use: 88%; 5th use: 82%
(isolated yields)

Scheme 7. Oxidation of **11a** catalyzed by recycled PWAA.

Table 4. Solvent effect on the oxidation catalyzed by PWAA

$$\mathbf{11a} \xrightarrow[\text{30\% } H_2O_2 \textit{ aq}\text{, 50°C, 4 h}]{\text{PWAA } (2.0 \times 10^{-3} \text{ mol eq})} \mathbf{12a} + \mathbf{13a}$$

solvent (1.0M soln of **11a**)

Entry	Solvent	**12a**[a]	**13a**[a]
1	(Neat)	3	97
2	Toluene	3	75
3	CH_2Cl_2	8	90
4	THF	8	91
5	Et_2O	—	96
6	DMF	—	100
7	EtOH	—	99

[a] Isolated yields.

aprotic hydrophobic solvents (toluene, CH_2Cl_2, THF, and Et_2O (entries 2–5)), hydrophilic solvent (DMF (entry 6)), and protic solvent (EtOH (entry 7)) progressed smoothly to furnish **13a** in high yields. On the contrary, the reaction in toluene proceeded slower to give **13a** in 75%. It seems reasonable that both organic solvent-free and -containing systems were effective for this oxidation.

6. Summary

In conclusion, we developed a highly active and reusable solid-phase catalyst, PWAA based on our strategy: the self-assembly of phosphotungstate and an ammonium salt with a non-cross-linked amphiphilic polymer. PWAA efficiently catalyzed the oxidations of allylic alcohols, amines, and sulfides with hydrogen peroxide in both aqueous and organic media. PWAA was reused three to five times and the turnover number of PWAA reached up to 35,000. While the reusable activity and stability of PWAA should be improved, we believe our concept will be useful for creating other solid-phase catalysts.[4]

7. Experimental

7.1. General

35–40% Hydrogen peroxide and $H_3PW_{12}O_{40}$ were used without any treatment Infrared (IR) spectra were recorded on a JASCO FT/IR-8000 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL AL-400 spectrometer, opening at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR. Chemical shifts in $CDCl_3$ were reported in the δ scale relative to $CHCl_3$ (7.26 ppm for ^1H NMR and 77.00 ppm for ^{13}C NMR) as an internal reference. Gel-phase ^{31}P NMR spectra were recorded with a 600 MHz (^1H NMR) pulse Fourier transform NMR spectrometers in $CDCl_3$ suspension with 85% H_3PO_4 aqueous solution as an external standard. EIMS spectra were measured on JEOL SX-102A. Column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM).

7.1.1. [3-(Acryloylamino)propyl]dodecyldimethylammonium bromide (4). To the suspension of *N*-[3-(dimethylamino)propyl]acrylamide (1.0 mL; 6.07 mmol), Na_2CO_3 (0.161 g; 1.52 mmol) in MeOH and MeCN (12 mL each) was added $C_{12}H_{25}Br$ (2.92 mL; 12.1 mmol), and it was stirred at 60 °C for 48 h before it was filtered. The filtrate was evaporated, and purified by column chromatography (neutral silica gel; eluent: CH_2Cl_2/MeOH (gradient: 10/1–2/1 via 5/1) to afford **4** in 92% yield (2.27 g). Mp 57–70 °C; IR (KBr, cm^{-1}): 1628, 1670, 3443; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J=7.1 Hz, 3H), 1.22–1.35 (m, 18H), 1.74 (m, 2H), 2.16 (m, 2H), 3.27 (s, 6H), 3.35–3.40 (m, 2H), 3.47–3.49 (m, 2H), 3.87 (m, 2H), 5.63 (d, J=11.5 Hz, 1H), 6.33 (d, J=17.1 Hz, 1H), 6.54 (dd, J=11.5, 17.1 Hz, 1H), 8.55 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.7, 22.7, 22.9, 26.4, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 36.4, 51.0, 62.9, 64.9. 126.5, 130.7, 166.40; MS (FAB): *m/z* 326 (M^++H, base peak); HRMS (FAB): calcd for $C_{20}H_{42}ON_2$ 326.3297, found 326.3300.

7.1.2. Poly{[3-(acryloylamino)propyl]dodecyldimethylammonium bromide}-*co*-(*N*-isopropylacrylamide)$_{12}$} (6). The solution of **4** (1.46 g; 3.60 mmol), *N*-isopropylacrylamide (4.89 g; 43.2 mmol) in *t*-BuOH (70 mL) was degassed by ultrasonication for 20 min under an argon atmosphere. After AIBN (23.7 mg; 0.144 mmol) was added and again degassed for 20 min, the solution was heated at 75 °C for 48 h under an argon atmosphere, and *t*-BuOH was evaporated. The residue was purified by sedimentation from CH_2Cl_2 and Et_2O to give **6** in 86% (5.44 g). IR (KBr, cm^{-1}): 1651, 3069, 3308; ^1H NMR (600 MHz, $CDCl_3$): δ 0.88 (t, J=9.6 Hz, 3H), 0.90–2.60 (m, 133H), 3.19–4.10 (m, 24H), 6.64 (br s, 13H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 13.8, 22.4, 26.1, 29.0, 29.2, 29.3, 31.6, 41.1, 42.1, 50.5, 174.2. Elementary anal. calcd for $C_{92n}H_{187n}N_{14n}O_{20n}Br_n$ as **6**·7$n$$H_2O$: C 58.5, H 10.0, N 10.4, found: C 58.8, H 10.3, N 10.3.

7.1.3. Poly{[3-(acryloylamino)propyl]dodecyldimethylammonium nitrate}-*co*-(*N*-isopropylacrylamide)$_{12}$} (2). The mixture of **6** (1.72 g) and 0.2 M aqueous $NaNO_3$ was vigorously stirred for 41 h, followed by heated at 60 °C to precipitate **2**, and supernatant was decanted. The residue was washed with H_2O, and dried in vacuo (~0.08 mmHg) to give **2b** in 81% yield (1.38 g). IR (KBr, cm^{-1}): 1651, 3065, 3298; ^1H NMR (600 NMR, $CDCl_3$): δ 0.88 (t, J=9.6 Hz, 3H), 0.90–2.60 (m, 133H), 3.20–4.10 (m, 24H), 6.61 (br s, 13H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.0, 22.5, 22.6, 26.4, 29.2, 29.4, 29.5, 31.8, 41.2, 42.2, 50.4, 174.3. Elementary anal. calcd for $C_{92n}H_{187n}N_{15n}O_{23n}$ as **2**·7$n$$H_2O$: C 59.0, H 10.1, N 11.2, found: C 59.3, H 10.3, N 11.4.

7.1.4. Preparation of an assembled catalyst PWAA (3) from 1 with 2. When an aqueous solution of **1** (334 mg in 33 mL of H_2O; **1** was dissolved in H_2O by ultrasonication.) was added to an aqueous solution of **2** (608 mg in 116 mL H_2O; 3 mol equiv. as an ammonium unit) at room temperature, white insoluble precipitates were simultaneously yielded. After being stirred for 7 days at the same temperature, the precipitate was filtered on a glass filter, washed thoroughly with water, and dried in vacuo (~0.08 mmHg) to give **3** in 95% yield (870 mg) as white lumps: IR (KBr, cm^{-1}) 1080, 982, 893, 808; gel-phase ^{31}P NMR δ −13 (br s). Elementary anal. calcd for $C_{276n}H_{563n}N_{42n}O_{101n}P_nW_{12n}$ as PWAA·22$n$$H_2O$: C 39.8, H 6.3, N 7.1, found: C39.6, H 6.6, N 7.2.

7.2. General procedure for assembled catalyst-promoted epoxidation of allylic alcohols with hydrogen peroxide

A 25-mL flask equipped with a magnetic stirring bar was charged with 2.52 mmol of **7a**, 5.05 mmol of 30% aqueous. H_2O_2 and 1.26 μmol of PWAA. After the mixture was stirred at room temperature for 7 h, toluene (or Et_2O, AcOEt could be used.) was added, and PWAA was filtered. The organic layer was separated, washed with saturated aqueous. $Na_2S_2O_3$, dried in vacuo, and purified by flash column chromatography (SiO_2; EtOAc/hexane=1:4 to 1:2) to give the epoxy alcohol **8a** in 96% isolated yield.

7.2.1. 2,3-Epoxy-3-methyl-5-phenyl-1-pentanol (8e). Colorless oil; IR (neat, cm^{-1}) 3406, 2932, 1454, 1032, 752, 702; ^1H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 3H), 1.72–1.80 (m, 1H), 1.94–2.01 (m, 1H), 2.32 (br s, 1H), 2.64–2.79 (m, 2H), 2.88 (dd, 1H, J=4.2, 6.6 Hz), 3.63 (br dd, 1H, J=6.6, 11.6 Hz), 3.73 (br dd, 1H, J=4.2, 11.6 Hz), 7.15–7.29 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.9, 31.3, 40.3, 60.9, 61.3, 63.0, 125.9, 128.1, 128.3, 128.4, 141.0; MS (EI): *m/z* 192 (M^+), 174, 143, 131, 117, 105, 91; HRMS (EI): calcd for $C_{12}H_{16}O_2$ 192.1150, found 192.1159.

7.3. General procedure for the oxidation of amines catalyzed by PWAA

To a suspension of PWAA (40 mg; 5×10^{-3} mmol) and **9a** (2.52 mmol) was added 2.5% H_2O_2 aqueous solution (7.56 mmol) dropwise for 50 min at 0 °C. The mixture was stirred at room temperature for 24 h, before it was diluted with AcOEt and filtered through a glass filter. Brine was added to the filtrate, and it was extracted with AcOEt (×3). The extract was washed with brine, dried over Na_2SO_4, filtered, dried in vacuo, and purified by column chromatography (SiO_2; EtOAc/hexane=1:5) to give **10a** in 86% yield.

7.3.1. *N*-((*Z*)-4-Methoxybenzylidene-4′-methoxybenzyl) *N*-oxide (10d). Mp 122–125 °C; IR (KBr, cm^{-1}): 1246, 2920 cm; ^1H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H), 3.82, (s, 3H), 4.95 (s, 2H), 6.88–6.94 (m, 4H), 7.26 (s, 1H), 7.37–7.41 (m, 2H), 8.17–8.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 55.3, 70.1, 113.6, 114.2, 123.3, 125.3, 130.4, 130.6, 133.2, 159.8, 160.8; MS (EI): *m/z* 271 (M^+), 121 (M^+−N(O)=CHArOMe, base peak); HRMS (EI): calcd for $C_{16}H_{17}O_3N$ 271.1208, found 271.1205.

7.3.2. *N*-4-Methoxybenzyl-*N*-4-trifluoromethylbenzylamine (9e). To a solution of 5% Pd/C (80 mg) in methanol (27 mL) under H_2 atmosphere was added 4-trifluoromethylbenzaldehyde (1.23 mL; 9 mmol) and 4-methoxybenzaldehyde (1.08 mL; 9.9 mmol), and the resulting mixture was stirred at rt for 5 h. After the substrate was consumed (checked by TLC), the suspension was filtered. The filtrate was evaporated, purified by column chromatography (SiO_2; MeOH/CH_2Cl_2=1:100) to give **9e** in 72% yield (1.73 g; 6.50 mmol). Mp 29–30 °C; IR (neat, cm^{-1}): 1327, 3337; ^1H NMR (400 MHz, $CDCl_3$): δ 1.73 (br s, 1H), 3.73 (s, 2H), 3.79 (s, 3H), 3.84 (s, 2H), 6.87 (d, J=8.5 Hz, 2H), 7.25 (d, J=8.5 Hz, 2H), 7.45 (d, J=8.1 Hz, 2H), 7.57 (d, J=8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.8, 52.9, 55.6, 114.1, 123.1, 125.4, 125.4, 125.4, 125.5, 125.8, 128.5, 129.1, 129.5, 132.2, 144.6, 158.9; MS (EI): *m/z* 295 (M^+), 159 (M^+−$NHCH_2ArOCH_3$), 121 (M^+−$NHCH_2ArOCF_3$, base peak); HRMS (EI): calcd for $C_{16}H_{16}ONF_3$ 295.1184, found 295.1180.

7.3.3. *N*-(*Z*)-4-Methoxybenzyl-*N*-4-(trifluoromethyl)-benzylidene *N*-oxide (10e). Mp 124–129 °C; IR (KBr, cm^{-1}): 1327, 3072 cm; ^1H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3H), 5.02 (s, $CH_3OArC\mathit{H_2}N(O){=}CHArCF_3$, 2H), 6.93–6.96 (m, 2H), 7.39–7.41 (m, 3H), 7.63 (d, J=8.3 Hz, 2H), 8.30 (d, J=8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 71.1, 114.4, 122.3, 124.6, 125.0, 125.1, 125.2, 128.4, 130.8, 131.1, 131.5, 132.2, 133.4, 160.1; MS (EI): *m/z* 309 (M^+), 121 (M^+−N(O) =$CHArCF_3$, base peak); HRMS (EI): calcd for $C_{16}H_{14}O_2NF_3$ 309.0977, found 309.0971.

7.3.4. *N*-(*Z*)-4-Methoxybenzylidene-*N*-4-(trifluoromethyl)benzyl *N*-oxide (10e′). Mp 124–128 °C; IR (KBr, cm^{-1}): 1327, 3082; ^1H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 5.07 (s, $CH_3OArCH{=}N(O)C\mathit{H_2}ArCF_3$, 2H), 6.93 (d, J=8.8 Hz, 2H), 7.42 (s, $CH_3OArC\mathit{H}{=}N(O)CH_2ArCF_3$, 1H), 7.61 (d, J=8.3 Hz, 2H), 7.66 (d, J=8.3 Hz, 2H), 8.22 (d, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz NMR, $CDCl_3$): δ 55.4, 70.0, 113.8, 123.0, 125.6, 125.7, 129.1, 130.5, 131.0, 134.2, 137.2, 161.1; MS (EI): *m/z* 309 (M^+), 159 (M^+−N(O)=$CHArOCH_3$, base peak); HRMS (EI): calcd for $C_{16}H_{14}O_2NF_3$ 309.0977, found 309.0978.

7.3.5. *N*-(*Z*)-4-Benzyl-*N*-4-nitrilebenzylidene *N*-oxide (10g). Mp 143–150 °C; IR (KBr, cm^{-1}): 2224, 3034; ^1H NMR (400 MHz, $CDCl_3$): δ 5.09 (s, $ArC\mathit{H_2}$-N(O)=CHArCN, 2H), 7.40–7.49 (m, *Ar*CH2N(O)=C*H*ArCN, 6H), 7.66 (d, J=8.6 Hz, 2H), 8.29 (d, J=8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 71.9, 112.9, 118.4, 128.3, 129.0, 129.2, 132.0, 132.3, 132.4, 134.0; MS (EI): *m/z* 236 (M^+), 91 (M^+−N(O)=CHArCN, base peak); HRMS (EI): calcd for $C_{15}H_{12}ON_2$ 236.0950, found 236.0947.

7.3.6. *N*-(*Z*)-4-Benzylidene-*N*-4-nitrilebenzyl *N*-oxide (10g′). Mp 140–144 °C; IR (KBr, cm^{-1}): 2224, 3034; ^1H NMR (400 MHz, $CDCl_3$): δ 5.11 (s, $ArCH{=}N(O)C\mathit{H_2}$-ArCN, 2H), 7.39–7.44 (m, 3H), 7.51 (s, ArC*H*=N(O)-CH2ArCN, 1H), 8.29 (d, J=8.6 Hz, 2H), 8.21–8.24 (m, 2H); ^{13}C NMR (100 MHz, CDCl3): δ 70.1, 112.4, 117.9, 128.1, 128.2, 129.0, 129.6, 130.4, 132.1, 134.5, 137.9; MS (EI): *m/z* 236 (M^+), 116 (M^+−N(O)=CHAr, base peak); HRMS (EI): calcd for $C_{15}H_{12}ON_2$ 236.0950, found 236.0944.

7.4. General procedure for the oxidation of sulfides to sulfones catalyzed by PWAA

The mixture of PWAA, **11a** and 35–40% H_2O_2 aqueous solution was shaken by PetiSyther® (Shimadzu Scientific Research Inc. Japan) at 700 rpm at 50 °C for 4 h, it was diluted with AcOEt and filtered. To the filtrate was added saturated $Na_2S_2O_3$ and brine, and it was extracted with AcOEt (×3), dried over Na_2SO_4, filtered, dried in vacuo, and purified by column chromatography (SiO_2; MeOH/CH_2Cl_2=1:100) to give **13a** in 97% yield. While the shaker (PetiSyther®) for solid-phase syntheses was used in these reactions, the glassware vessel equipped with a magnetic stirrer enabled to be also used.

Acknowledgements

We thank Ms. Junko Shimode and Ms. Maroka Kitsukawa (Teikyo University) for spectroscopic measurement, and Mr. Kiyoshi Abe (Teikyo University) and Mr. Shin-ichirou Kawabata (JEOL Ltd) for SEM measurement. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Technology. Y.M.A.Y. thanks the Inoue Foundation for Science (IFS) for Inoue Research Award for Young Scientists, and Dainippon Ink and Chemicals, Inc. Award in Synthetic Organic Chemistry, Japan.

References and notes

1. (a) Anastas, P. T.; Warner, J. C. *Green chemistry: theory and practice*; Oxford University Press: Oxford, 1998. (b) In *Green chemical syntheses and processes: recent advances in chemical processing*; Anastas, P. T., Heine, L. G., Williamson, T. C., Eds.; American Chemical Society: Ohio, 2001. (c) Tundo, P.; Anastas, P.; Black, D. S.; Breen, J.; Collins, T.; Memoli, S.; Miyamoto, J.; Polyakoff, M.; Tumas, W. *Pure Appl. Chem.* **2000**, *72*, 1207–1228. (d) Noyori, R.; Aoki, M.; Sato, K. *Chem. Commun.* **2003**, 1977.
2. Regen, S. L. *Angew. Chem. Int. Ed.* **1979**, *18*, 421–429.
3. (a) Centi, G.; Cavani, F.; Trifiro, F. *Selective oxidation by heterogeneous catalysis (fundamental and applied catalysis)*; Kluwer Academic: Norwell, MA, 2000. (b) Hodnett, K. *Heterogeneous catalytic oxidation*; Wiley: New York, 2000. (c) Bunin, B. A. *The combinatorial index*; Academic: San Diego, 1998. (d) In *Reactions on polymers*; Moore, J. A., Ed.; Redel: Boston, 1973. (e) In *Solid phase synthesis*; Blossey, E. C., Neckers, D. C., Eds.; Dowden, Hutchinson and Ross: Pennsylvania, 1975. (f) Corma, A.; García, H. *Chem. Rev.* **2002**, *102*, 3837–3892.
4. (a) Yamada, Y. M. A.; Ichinohe, M.; Takahashi, H.; Ikegami, S. *Org. Lett.* **2001**, *3*, 1837–1841. (b) Yamada, Y. M. A.; Ichinohe, M.; Takahashi, H.; Ikegami, S. *Tetrahedron Lett.* **2002**, *43*, 3431–3434. (c) Yamada, Y. M. A.; Takeda, K.; Takahashi, H.; Ikegami, S. *Org. Lett.* **2002**, *4*, 3371–3374. (d) Yamada, Y. M. A.; Takeda, K.; Takahashi, H.; Ikegami, S. *J. Org. Chem.* **2003**, *68*, 7733–7741. (e) Yamada, Y. M. A.; Takeda, K.; Takahashi, H.; Ikegami, S. *Tetrahedron* **2004**, *60*, proceeding article. See doi: 10.1016/j.tet.2004.02.068. (f) Yamada, Y. M. A.; Tabata, H.; Takahashi, H.; Ikegami, S. *Synlett* **2002**, 2031–2034.
5. Partial results were reported as communications, see Refs. **4a** and **4d**.
6. Jacobs and co-workers reported the Amberlite IRA-900-supported Venturello catalyst converted into NO3- was effective for the enhancement of selectivity of epoxidation, see: Villa, A. L.; Sels, B. F.; de Vos, D. E.; Jacobs, P. A. *J. Org. Chem.* **1999**, *64*, 7267–7270.
7. Ishii, Y.; Yamawaki, K.; Ura, T.; Yamada, H.; Yoshida, T.; Ogawa, M. *J. Org. Chem.* **1988**, *53*, 3587–3593.
8. Addition of **1** to poly(*N*-isopropylacrylamide) afforded no precipitates. This result indicated that the existence of the ammonium salt units in **2** was essential for cross-linking the polymers through phosphotungstates.
9. Massart, R.; Contant, R.; Fruchart, J.-M.; Ciabrini, J.-P.; Fournier, M. *Inorg. Chem.* **1977**, *16*, 2916–2921.
10. Ishii, Y.; Tanaka, H.; Nishiyama, Y. *Chem. Lett.* **1994**, 1–4.
11. (a) Keggin, J. F.; Proc, R. *Proc. R. Soc. London, Ser. A* **1934**, *144*, 75–100. (b) Brown, G. M.; Noe-Spirlet, M.-R.; Busing, W. R.; Levy, H. A. *Acta Crystallogr. B* **1977**, *33*, 1038–1046.
12. (a) For examples of the epoxidation by homogeneous tungsten catalysts, see:Ogata, Y.; Sawaki, Y. In *Organic syntheses by oxidation with metal compounds*; Mijs, W. J., De Jonge, C. R. H. I., Eds.; Plenum Press: New York, 1986; pp 839–876. (b) Sato, K.; Aoki, M.; Noyori, R. *Science* **1998**, *281*, 1646–1647. (c) Venturello, C.; Gambaro, M. *J. Org. Chem.* **1991**, *56*, 5924–5931. (d) Venturello, C.; Gambaro, M. *Synthesis* **1989**, 295–297. (e) Bortolini, O.; Conte, V.; Di Furia, F.; Modena, G. Di Furia. *J. Org. Chem.* **1986**, *51*, 2661–2663.
13. (a) Recent attempts to improve the drawbacks on polymer-supported tungsten catalysts for the epoxidation, see: Villa, A. L.; Sels, B. F.; De Vos, D. E.; Jacobs, P. A. *J. Org. Chem.* **1999**, *64*, 7267–7270. (b) Hoegaerts, D.; Sels, B. F.; de Vos, D. E.; Verpoort, F.; Jacobs, P. A. *Catal. Today* **2000**, *60*, 209–218. (c) Gelbard, G.; Breton, F.; Quenard, M.; Sherrington, D. C. *J. Mol. Catal. A: Chem.* **2000**, *153*, 7–18. (d) Sakamoto, T.; Pac, C. *Tetrahedron Lett.* **2000**, *41*, 10009–10012. (e) Briot, E.; Piquemal, J.-Y.; Vennat, M.; Brégeault, J.-M.; Chottard, G.; Manoli, J.-M. *J. Mater. Chem.* **2000**, *10*, 953–958. (f) Ichihara, J. *Tetrahedron Lett.* **2001**, *42*, 695–697. (g) De Bos, D. E.; Wahlen, J.; Sels, B. F.; Jacobs, P. A. *Synlett* **2002**, 367–380. Also, see: Ref. 6.
14. It was reported that pH control in aqueous media was important for the tungsten-catalyzed epoxidation, see Refs. 12d, 12e and 13b.
15. Haines, A. H. *Methods for the oxidation of organic compounds*; Academic: London, 1985.
16. (a) For examples of the oxidation of amines by homogeneous tungsten catalysts; For a review, see: (a) Herrmann, W. A.; Fridgen, J.; Haider, J. J. In *Peroxide chemistry*; Adam, W., Ed.; Wiley: Weinheim, 2000; pp 406–432. (b) For examples, see: (b) Ogata, Y.; Tomizawa, K.; Maeda, H. *Bull. Chem. Soc. Jpn* **1980**, *53*, 285–286. (c) Murahashi, S.; Mitsui, H.; Shiota, T.; Tsuda, T.; Watanabe, S. *J. Org. Chem.* **1990**, *55*, 1736–1744. (d) Murahashi, S.; Oda, T.; Sugahara, T.; Masui, Y. *J. Org. Chem.* **1990**, *55*, 1744–1749. (e) Sakaue, S.; Sakata, Y.; Ishii, Y. *Chem. Lett.* **1992**, 289–292. (f) Marcantoni, E.; Petrini, M.; Polimanti, O. *Tetrahedron Lett.* **1995**, *36*, 3561–3562. (g) Ballistreri, F. P.; Barbuzzi, E. G. M.; Tomaselli, G. A. *J. Org. Chem.* **1996**, *61*, 6381–6387.
17. (a) For recent developments and improvements for the oxidation of amines, see: (a) Reddy, J. S.; Jacobs, P. A. *J. Chem. Soc. Perkin Trans. 1* **1993**, *22*, 2665–2666. (b) Joseph, R.; Sudalai, A.; Ravindranathan, T. *Synlett* **1995**, *11*, 1177–1178. (c) Joseph, R.; Ravindranathan, T.; Sudalai, A. *Tetrahedron. Lett.* **1995**, *36*, 1903–1904. (d) Delaude, L.; Laszlo, P. *J. Org. Chem.* **1996**, *61*, 6360–6370. (e) Dewkar, G. K.; Nikalje, M. D.; Ali, I. S.; Paraskar, A. S.; Jagtap, H. S.; Sudalai, S. *Angew. Chem. Int. Ed.* **2001**, *40*, 405–408.
18. The reaction oxidized by more concentrated H_2O_2 aqueous solution was less successful because dimerization of the substrates occurred. Besides, recycling of PWAA in case of **9a** was not efficient to afford **10a** in lower yield.

19. These oxidations were controlled kinetically, and the regioselectivity for the formation of nitrones was determined at the oxidation stage of dibenzyl hydroxyamines to nitrones. It was assured by the following results: no isomerization between **10e** and **10e**′ was observed in the reaction of **10e** or **10e**′ in the presence of PWAA and 2.5% H_2O_2; the reaction of **9e** in CH_2Cl_2 at room temperature provided **10e** and **10e**′ in 95% yield with the same regioselectivity (**10e/10e**′=1.76/1); even in the reaction of **10e** or **10e**′ with CH_2Cl_2 under identical conditions, isomerizations were hardly observed.
20. (a) For examples of the oxidation of sulfides to sulfones by homogeneous tungsten catalysts, see: (a) Schultz, H. S.; Freyermuth, H. B.; Buc, S. R. *J. Org. Chem.* **1963**, *28*, 1140–1142. (b) Stec, Z.; Zawadiak, J.; Skibinski, A.; Pastuch, G. *Polish J. Chem.* **1996**, *70*, 1121–1123. (c) Neumann, R.; Juwiler, D. *Tetrahedron* **1996**, *52*, 8781–8788. (d) Gresley, N. M.; Griffith, W. P.; Laemmel, A. C.; Nogueira, H. I. S.; Perkin, B. C. *J. Mol. Catal.* **1997**, *117*, 185–198. (e) Collins, F. M.; Lucy, A. R.; Sharp, C. *J. Mol. Catal.* **1997**, *117*, 397–403. (f) Yasuhara, Y.; Yamaguchi, S.; Ichihara, J.; Nomoto, T.; Sasaki, Y. *Phosphorus Res. Bull.* **2000**, *11*, 43–46. (g) Sato, K.; Hyodo, M.; Aoki, M.; Zheng, X.-Q.; Noyori, R. *Tetrahedron* **2001**, *57*, 2469–2476, Also, see: Ref. 9.
21. (a) For recent developments and improvements for the oxidation of sulfides to sulfones, see: (a) Dell'Anna, M. M.; Mastrorilli, P.; Nobile, C. F. *J. Mol. Catal. A: Chem.* **1996**, *108*, 57–62. (b) Alcon, M. J.; Corma, A.; Iglesias, M.; Sanchez, F. *J. Mol. Catal. A: Chem.* **2002**, *178*, 253–266.
22. Noyori et al. reported that the oxidation of sulfides to sulfoxides proceeded efficiently in hydrogen peroxide without catalysts, so that we have not examined the selective oxidation to sulfoxide. See Ref. 19g.
23. Baudin, J. B.; Hareau, G.; Julia, S. A.; Ruel, O. *Tetrahedron Lett.* **1991**, *32*, 1175–1178.
24. (a) Kondo, K.; Tunemoto, D. *Tetrahedron Lett.* **1975**, *17*, 1397–1400. (b) Caton, M. P. L.; Coffee, E. C. J.; Watkins, G. L. *Tetrahedron Lett.* **1972**, *9*, 773–774.
25. Brégault et al. reported that heteropoly acidic structure easily decomposed in the presence of hydrogen peroxide under the homogeneous conditions, see: Salles, L.; Aubry, C.; Thouvenot, R.; Robert, F.; Dorémieux-Morin, C.; Chottard, G.; Ledon, H.; Jeannin, Y.; Brégault, J. *Inorg. Chem.* **1994**, *33*, 871–878On the other hand, Ishii et al. proved that $[p\text{-}C_5H_5\text{-}N^+(CH_2)_{15}CH_3]_3PW_{12}O_{40}^{3-}$ maintained the structure closed to Keggin unit after treatment with hydrogen peroxide. See Ref. 10.