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Polystyrene-bound electron-deficient tin(IV) porphyrin: A new, highly efficient, robust and reusable catalyst for acetylation of alcohols and phenols with acetic anhydride

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ABSTRACT

In the present work, tetrakis(p-aminophenyl)porphyrinatotin(IV) trifluoromethanesulfonate, $[Sn^{IV}(TNH_2PP)(OTf)_2]$, supported on chloromethylated polystyrene was prepared and characterized by elemental analysis, FT IR and diffuse reflectance UV-Vis spectroscopic methods. This new heterogenized catalyst was used for acetylation of alcohols and phenols with acetic anhydride in short reaction times and high yields. The catalyst is of high reusability and stability in the acetylation reactions and was recovered several times without loss of its initial activity and catalyst leaching.

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1. Introduction

The development of environmentally benign synthesis has attracted much attention in recent years. Therefore, development of polymer-bound catalysts and reagents with high activity and selectivity is of great importance in organic synthesis [1–3]. Since most of metal complexes are often expensive to purchase or prepare, the immobilization of these complexes on a support can provide catalysts which are easier to handle, and may exhibit improved selectivities and activities because of the support environment [4].

From synthetic point of view, polystyrene is one of the most popular polymeric supports used in synthetic organic chemistry because of its low cost, ready availability, mechanical robustness, chemical inertness, and facile functionalization.

The protection of hydroxyl groups is often necessary during the course of various transformations in a synthetic sequence, especially in the synthesis of fine chemicals and natural products. Several methods such as acetylation, tetrahydropyranylation, methoxymethylation and tri-methylacetylation have been reported for protection of hydroxyl groups [5,6]. A variety of procedures using homogeneous or heterogeneous catalysts such as iodine [7], p-toluenesulfonic acid [8], alumina [9], zinc chloride [10], cobalt chloride [11], montmorillonite K-10 and KSF [12], zeolite HSZ-360 [13], zirconium sulfophenyl phosphonate [14], $Sc(OTf)_3$ [15], $TaCl_5$ [16], $TMSOTf$ [17], $Cu(OTf)_2$ [18], $In(OTf)_3$ [19], magnesium bromide [20], bismuth(III) salts [21], ferric perchlorate adsorbed on silica-gel [22], $RuCl_3$ [23], $InCl_3$ [24], $Ce(OTf)_3$ [25], $Mg(ClO_4)_2$ [26], $ZrCl_4$ [27], Cp_2ZrCl_2 [28], $ZrOCl_2 \cdot 8H_2O$ [29], $Al(OTf)_3$ [30], $NaHSO_4 \cdot SiO_2$ [31], $La(NO_3)_3 \cdot 6H_2O$ [32], $NbCl_5$ [33], $Gd(OTf)_3$ [34], Alumina supported MoO_3 [35], cerium polyoxometalate [36], $Zn(ClO_4)_2 \cdot 6H_2O$ [37], $Mg(NTf_2)_2$ [38], $Cu(BF_4)_2$ [39], $BiO(ClO_4)_2$ [40], $HClO_4$-SiO_2 [41], HBF_4-SiO_2 [42], electron-deficient tin [IV] porphyrins [43–45] and $ZrO(OTf)_2$ [46] have been routine-

ly reported for acetylation of alcohols and phenols with Ac_2O. Although these procedures provide an improvement, many of these catalysts or activators need long reaction times, drastic reaction conditions or tedious work-up and are moisture-sensitive or expensive in terms of the catalyst. Hence, the introduction of new procedures to circumvent these problems is still in demand.

Electron-deficient metalloporphyrins have been used as mild Lewis acid catalysts [47–50]. The Suda group has reported the use of chromium and iron porphyrins in organic synthesis. They used Cr(tpp)Cl for regioselective [3,3] rearrangement of aliphatic allyl vinyl ethers and for Claisen rearrangement of simple aliphatic allyl vinyl ethers, Fe(tpp)OTf for rearrangement of α,β-epoxy ketones into 1,2-diketones and Cr(tpp)OTf for highly regio- and stereo-selective rearrangement of epoxides to aldehydes [51–54].

Recently, we have reported the use of tetraphenylporphyrinatotin(IV) perchlorate [43,55], tetraphenylporphyrinatotin(IV) trifluoromethanesulfonate [44,56–59], and tetraphenylporphyrinato- tin(IV) tetrafluoroborate [45,59–61] in organic transformations.

In the present work, we report the preparation, characterization and investigation of catalytic activity of *tetrakis(p-aminophenyl)porphyrinatotin(IV)* trifluoromethanesulfonate, $[Sn^{IV}(TNH_2PP)(OTf)_2]$, supported on chloromethylated polystyrene in the acetylation of alcohols and phenols with acetic anhydride (Scheme 1).

2. Experimental

Chemicals were purchased from Merck or Fluka chemical companies. Chloromethylated polystyrene (cross-linked with 2% divinylbenzene, 4–5% Cl content, 1.14–1.40 mmol/g Cl) was purchased from Fluka. FT IR spectra were obtained with potassium bromide pellets in the range 400–4000 cm^{-1} with a Nicolet Impact 400D spectrometer. Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2-m column packed with silicon DC-200 or Carbowax 20 m. In the GC experiments, *n*-decane was used as an internal standard. ^1H NMR spectra were recorded on a Bruker-Avance AQS 400 MHz spectrometer. Tetra(4-aminophenyl)porphyrin was prepared according to the literature [62]. The $[Sn^{IV}(TNH_2PP)Cl_2]$ catalyst was prepared according to the procedure reported for metallation of porphyrins [63]. In this manner, tetra(4-aminophenyl)porphyrin was reacted with $SnCl_2\cdot2H_2O$ in refluxing DMF.

2.1. Supporting of $[Sn^{IV}(TNH_2PP)Cl_2]$ on chloromethylated polystyrene, $[Sn^{IV}(TNH_2PP)Cl_2]@CMP$

To a solution of $[Sn^{IV}(TNH_2PP)Cl_2]$ (0.5 g) in DMF (50 mL), were added chloromethylated polystyrene (2.5 g) and triethylamine (3 mL). The mixture was heated at 100 °C
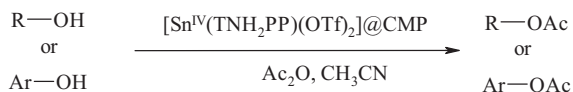
for 72 h. After cooling to room temperature, the green solids were filtered, washed with Et_2O and acetone and dried.

2.2. Conversion of $[Sn^{IV}(TNH_2PP)Cl_2]@CMP$ to $[Sn^{IV}(TNH_2PP)(OTf)_2]@CMP$

To a suspension of $[Sn^{IV}(TNH_2PP)Cl_2]@CMP$ (2 g) in THF (50 mL) was added NaOTf (1 g) and stirred at 60 °C for 8 h, after which the catalyst was filtered and washed with THF.

2.3. General procedure for acetylation of alcohol and phenols with Ac_2O catalyzed by $[Sn^{IV}(TNH_2PP)(OTf)_2]@CMP$

To a solution of alcohol or phenol (1 mmol) and Ac_2O (3 mmol per OH group) in CH_3CN (0.5 mL) was added $[Sn^{IV}(TNH_2PP)Cl_2]@CMP$ (70 mg, 0.01 mmol) and stirred at room temperature for appropriate time. The progress of the reaction was monitored by GC. After completion of the reaction, Et_2O (10 mL) was added and the catalyst was filtered. The filtrates were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to afford the crude product.

2.4. Catalyst reusability

At the end of each reaction, the catalyst was filtered, washed thoroughly with Et_2O, dried and reused.
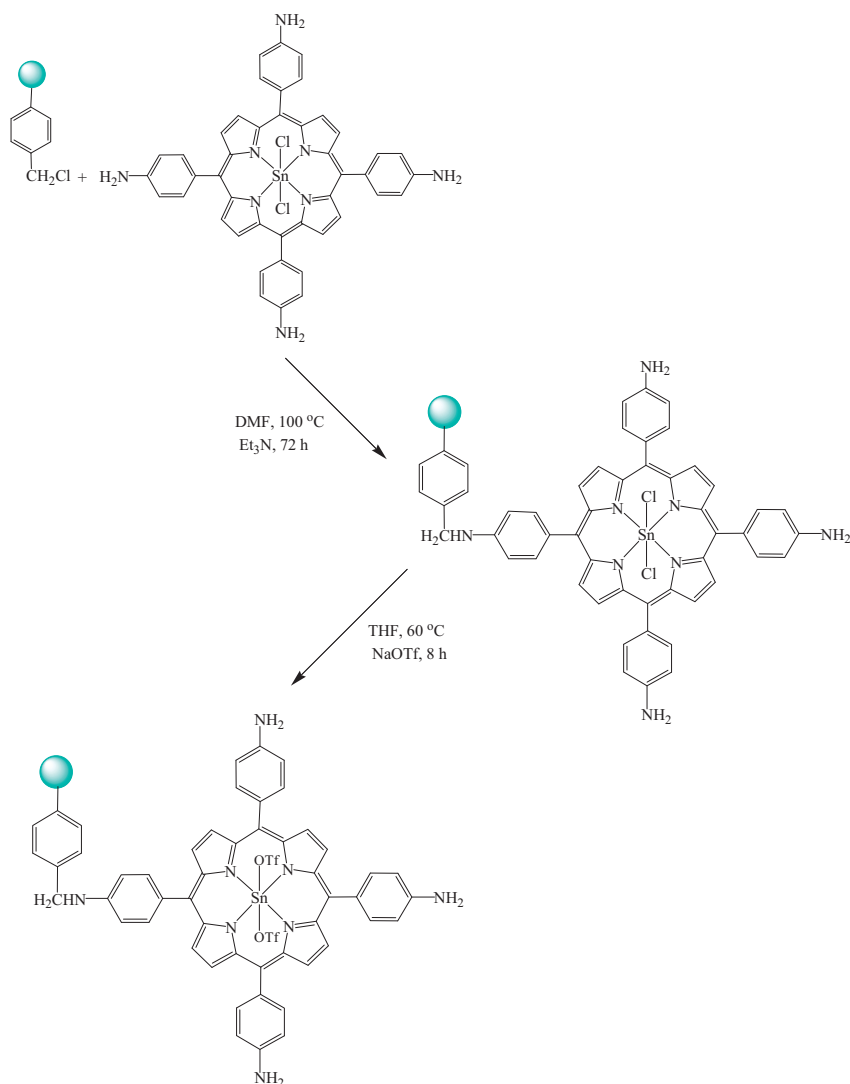
3. Results and discussion

3.1. Preparation and characterization of $[Sn^{IV}(TNH_2PP)(OTf)_2]@CMP$

Scheme 2 shows the preparation route for $[Sn^{IV}(TNH_2PP)(OTf)_2]@CMP$. First, chloromethylated polystyrene (cross-linked with 2% divinylbenzene, 4–5% Cl content, 1.14–1.40 mmol/g Cl) was reacted with $[Sn^{IV}(TNH_2PP)Cl_2]$ to afford the $[Sn^{IV}(TNH_2PP)Cl_2]@CMP$. Then, the chlorines were substituted by OTf^- by the reaction of $[Sn^{IV}(TNH_2PP)Cl_2]@CMP$ with NaOTf. This substitution increases the electron-deficiency of tin(IV).

The prepared catalyst was characterized by elemental analysis, FT IR and UV-Vis spectroscopic methods. The nitrogen content of the catalyst, measured by CHNS analysis, was obtained as 1.64% (1.17 mmol/g). According to this value, the amount of porphyrin introduced to polystyrene was calculated as 0.146 mmol/g. The Sn content of the catalyst was also determined by ICP (0.143 mmol/g) which was in accordance with the data obtained by CHNS analysis.

The evidence for attachment of tin(IV) porphyrin on the polystyrene was obtained from FT IR spectra of chloromethylated polystyrene and $[Sn^{IV}(TNH_2PP)(OTf)_2]@CMP$. The sharp C-Cl peak (due to -CH_2Cl groups) at 1264 cm^{-1} in the starting polymer (Fig. 1A) was practically absent or seen as a weak band after introducing of tin(IV) porphyrin on the polymer (Fig. 1B). A peak at 1622 cm^{-1} assigned to C = N and a peak at 1175 cm^{-1} assigned to C-N stretching modes also appeared, which confirmed the supporting of tin(IV) porphyrin on the support.

The reflectance spectrum of the polymer-bound porphyrin resembles solution counterpart spectrum with only

R—OH
or
Ar—OH

$\xrightarrow[\text{$Ac_2O$, CH_3CN}]{\text{$[Sn^{IV}(TNH_2PP)(OTf)_2]@CMP$}}$

R—OAc
or
Ar—OAc

Scheme 1. Acetylation of alcohols and phenols with Ac_2O catalyzed by $[Sn^{IV}(TNH_2PP)(OTf)_2]@CMP$.

Scheme 2. The preparation route for [Sn^{IV}(TNH$_2$PP)(OTf)$_2$]@CMP.

a slight red shift, and the Soret band was appeared at 445 nm and the Q bands observed at 558 and 619 nm. These observations clearly proved the presence of metalloporphyrin on the polystyrene (Fig. 2).

3.2. Acetylation of alcohols and phenols with Ac$_2$O catalyzed by [Sn^{IV}(TNH$_2$PP)(OTf)$_2$]@CMP

First, the amount of catalyst was optimized in the acetylation of 4-chlorobenzyl alcohol with Ac$_2$O. The results, which are summarized in Table 1, showed that in the presence of 0.01 mmol (70 mg) of [Sn^{IV}(TNH$_2$ PP)(OTf)$_2$]@CMP the highest yield was obtained. Then, the amount of Ac$_2$O was also optimized. The results showed that in the presence of 3 mmol of Ac$_2$O, the reaction was completed (Table 2).

In order to show the effect of OTf groups on the catalytic activity of tin (IV) porphyrin, the catalytic activity of [Sn^{IV}(TNH$_2$PP)Cl$_2$]@CMP (1 mol%) was also investigated in

the acetylation of 4-chlorobenzyl alcohol with Ac$_2$O. In this case, only 23% of the corresponding acetate was obtained while in the presence of [Sn^{IV}(TNH$_2$PP)(OTf)$_2$]@CMP, the reaction was completed after 6 min. These observations indicated that the presence of OTf groups is necessary for catalytic activity of tin(IV) porphyrin. The OTf groups increases the electron-deficiency of tin(IV) porphyrin which in turn increases the activity of the catalyst.

The optimized conditions, which were obtained for acetylation of 4-chlorobenzyl alcohol, were alcohol, Ac$_2$O and catalyst in a molar ratio of 100: 300: 1. Under these conditions, a wide variety of alcohols were subjected to acetylation with Ac$_2$O. The obtained results showed that different primary, secondary (including aliphatic and aromatic alcohols) and tertiary alcohols were acetylated successfully at room temperature (Table 3). As can be seen, in benzylic alcohols the nature of substituent (electron-withdrawing or electron-releasing) has no significant effect on the product yield. In the absence of catalyst only
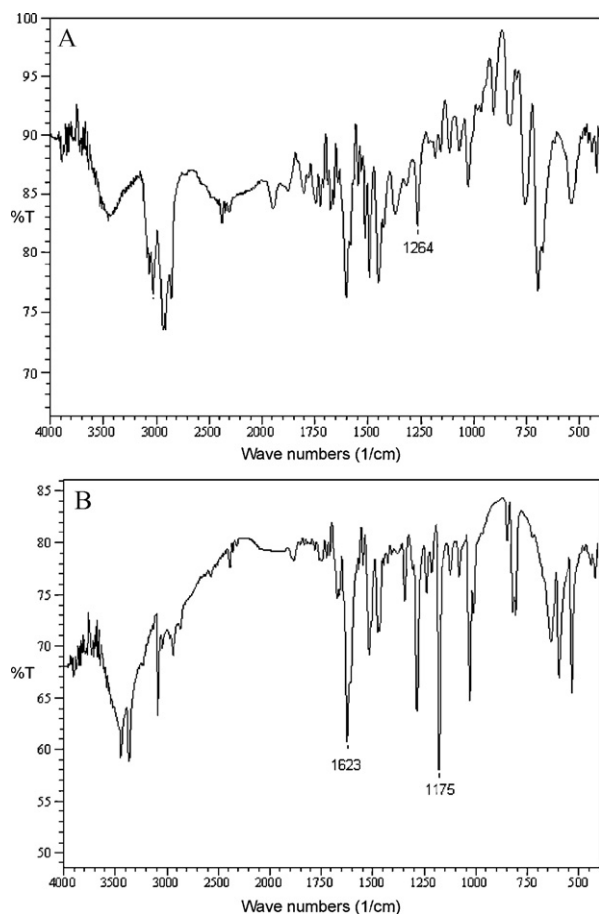
Fig. 1. The FT IR spectrum of (A) chloromethylated polystyrene and (B) $[Sn^{IV}(TNH_2PP)(OTf)_2]$@CMP.

Fig. 2. The DR UV-Vis spectrum of $[Sn^{IV}(TNH_2PP)(OTf)_2]$@CMP.

small amounts of the corresponding acetates were produced. In the case of tertiary alcohols such as 1-adamantol and 2-methyl-1-phenyl-2-propanol (entries 17 and 18) no elimination product was observed.

In order to show the advantage of the presented method in the acetylation reactions, we have compared the obtained results in the acetylation of benzyl alcohol with acetic anhydride catalyzed by $[Sn^{IV}(TNH_2PP)(OTf)_2]$@CMP with some of those reported in the literature (Table 4). It is clear that the method presented is superior in terms of reaction time, catalyst amount, or product yield. Recently,

Table 1
Optimization of catalyst amount in the acetylation of 4-chlorobenzyl alcohol with Ac$_2$O[a].

Entry	Time (min)	Catalyst amounts (mmol, mg)	Yield (%)[b]
1	6	40 mg (0.006 mmol)	31
2	6	50 mg (0.0071 mmol)	54
3	6	60 mg (0.0086 mmol)	88
4	6	70 mg (0.010 mmol)	100
5	6	80 mg (0.011 mmol)	100

[a] Reaction conditions: alcohol (1 mmol), Ac$_2$O (3 mmol), catalyst, CH$_3$CN (1 mL).
[b] GC yield.

Table 2
Optimization of Ac$_2$O amount in the acetylation of 4-chlorobenzyl alcohol[a].

Entry	Time (min)	Ac$_2$O (mmol)	Yield (%)[b]
1	6	0.5	18
2	6	1.0	38
3	6	1.5	55
4	6	2.0	81
5	6	2.5	92
6	6	3.0	100
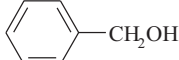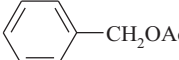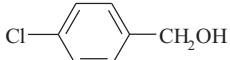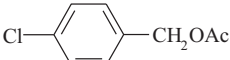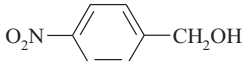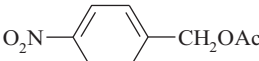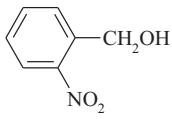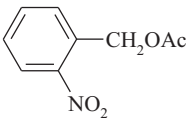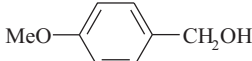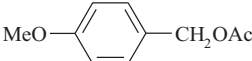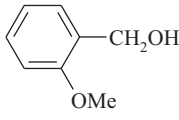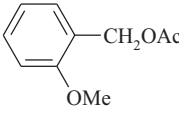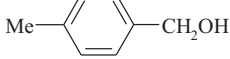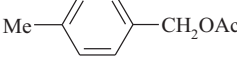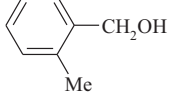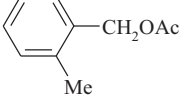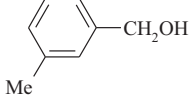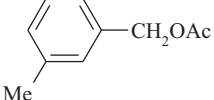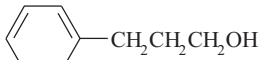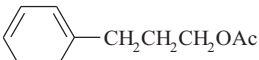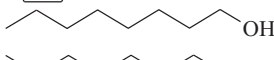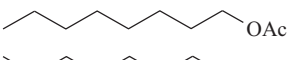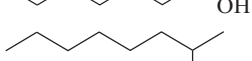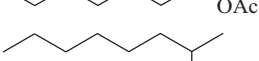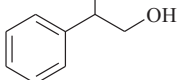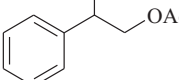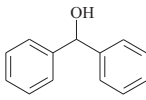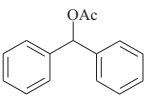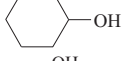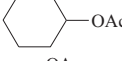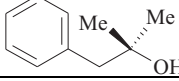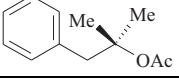
[a] Reaction conditions: alcohol (1 mmol), Ac$_2$O, catalyst (1 mol%), CH$_3$CN (1 mL).
[b] GC yield.

we reported the use of homogeneous $[Sn^{IV}(TPP)(OTf)_2]$ and $[Sn^{IV}(TPP)(BF_4)_2]$ in the acetylation of alcohols and phenols [44,45]. The reaction times in the presence of 1 mol% of homogeneous catalysts were 1–15 min and the product yields were 87–99%. In comparison with its homogeneous counterparts [44,45], in the presence of 1 mol% of $[Sn^{IV}(TNH_2PP)(OTf)_2]$@CMP, the corresponding acetates were obtained in 96–100% in 8–12 min. These observations showed that $[Sn^{IV}(TNH_2PP)(OTf)_2]$@CMP, which is a heterogeneous catalyst, in some cases the reaction times are longer for $[Sn^{IV}(TNH_2PP)(OTf)_2]$@CMP. On the other hand, the reusability of this catalyst was higher and can be separated by simple filtration in which does not contaminate the reaction product.

Under the optimized conditions, which were described for acetylation of alcohols, the acetylation of phenols with Ac$_2$O was also investigated in the presence of $[Sn^{IV}(TNH_2P-P)(OTf)_2]$@CMP. The results showed that all reactions were completed after 8 min at room temperature (Table 5). The acetylation of polyhydroxybenzenes such as hydroquinone, pyrocatechol, resorcinol and pyrogallol was also performed. The results showed that all hydroxyl groups were acetylated and the desired polyacetates were obtained in excellent yields (Table 5, entries 5–8).

Table 3
Acetylation of alcohols with Ac_2O catalyzed by $[Sn^{IV}(TNH_2PP)(OTf)_2]$@CMP at room temperature[a].

Entry	Hydroxy compound	Acetate	Time (min)	Yield (%)[b,c]
1	Ph—CH₂OH	Ph—CH₂OAc	6	100 (95)
2	Cl—C₆H₄—CH₂OH	Cl—C₆H₄—CH₂OAc	6	100 (96)
3	O₂N—C₆H₄—CH₂OH	O₂N—C₆H₄—CH₂OAc	6	100 (95)
4	(2-NO₂)C₆H₄—CH₂OH	(2-NO₂)C₆H₄—CH₂OAc	12	100 (93)
5	MeO—C₆H₄—CH₂OH	MeO—C₆H₄—CH₂OAc	6	100
6	(2-OMe)C₆H₄—CH₂OH	(2-OMe)C₆H₄—CH₂OAc	6	100
7	Me—C₆H₄—CH₂OH	Me—C₆H₄—CH₂OAc	6	100 (96)
8	(2-Me)C₆H₄—CH₂OH	(2-Me)C₆H₄—CH₂OAc	6	100
9	(3-Me)C₆H₄—CH₂OH	(3-Me)C₆H₄—CH₂OAc	6	100 (94)
10	Ph—CH₂CH₂CH₂OH	Ph—CH₂CH₂CH₂OAc	6	100
11	CH₃(CH₂)₆CH₂OH	CH₃(CH₂)₆CH₂OAc	6	100
12	CH₃(CH₂)₅CH₂OH	CH₃(CH₂)₅CH₂OAc	6	100
13	CH₃(CH₂)₅CH(OH)CH₃	CH₃(CH₂)₅CH(OAc)CH₃	6	100
14	Ph—CH(Me)—CH₂OH	Ph—CH(Me)—CH₂OAc	6	100 (95)
15	Ph₂CH—OH	Ph₂CH—OAc	6	100 (93)
16	cyclohexyl—OH	cyclohexyl—OAc	6	99
17	adamantyl—OH	adamantyl—OAc	8	96
18	Ph—CH₂—C(Me)₂—OH	Ph—CH₂—C(Me)₂—OAc	8	98 (90)

[a] Reaction conditions: alcohol (1 mmol), Ac_2O (3 mmol), catalyst (1 mol%), CH_3CN (1 mL).
[b] GC yield.
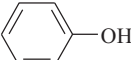[c] Yields in the parentheses refer to isolated products.
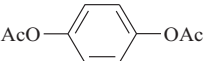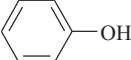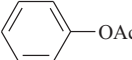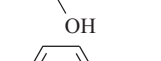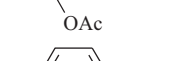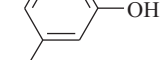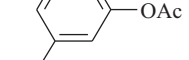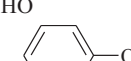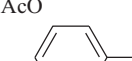
Table 4
Comparison of the results obtained for the acetylation of benzyl alcohol catalyzed by [Sn^{IV}(TNH$_2$PP)(OTf)$_2$]@CMP with those obtained by the recently reported catalysts.

Entry	Catalyst	Catalyst (mol%)	Temperature	Time (min)	Yield (%)	Ref.
1	[Sn^{IV}(TNH$_2$PP)(OTf)$_2$]@CMP	1	RT	6	100	–
2	I$_2$	10	RT	1	99	[7]
3	CoCl$_2$	0.5	RT	240	98	[11]
4	Montmorillonite KSF	20 mg	RT	60	90	[12]
5	Zeolite HSZ-360	20 mg	60 °C	60	84	[13]
6	TaCl$_5$	10 mg	RT	–	77	[16]
7	Cu(OTf)$_2$	2	RT	30	97	[18]
8	In(OTf)$_3$	0.1	RT	15	97	[19]
9	BiCl$_3$	10	RT	35	98	[21]
10	Bi(TFA)$_3$	5	RT	60	96	[21]
11	Bi(OTf)$_3$	1	RT	5	99	[21]
12	RuCl$_3$	5	RT	10	95	[23]
13	InCl$_3$	0.1	RT	30	85	[24]
14	Ce(OTf)$_3$	1	RT	12	98	[25]
15	Mg(ClO4)$_2$	1	RT	15	100	[26]
16	Cp$_2$ZrCl$_2$	1	RT	600	93	[28]
17	[Sn^{IV}(TPP)(OTf)$_2$]	1	RT	1	99	[44]
18	[Sn^{IV}(TPP)(BF$_4$)$_2$]	1	RT	1	99	[45]

Table 5
Acetylation of phenols with Ac$_2$O catalyzed by [Sn^{IV}(TNH$_2$PP)(OTf)$_2$]@CMP at room temperature[a].

Entry	Phenol	Acetate	Time (min)	Yield (%)[b,c]
1			8	100 (96)
2			8	100 (95)
3			8	100 (93)
4			8	100 (95)
5[d]			8	100 (94)
6[d]			8	100
7[d]			8	100
8[d]			8	100
9			8	100 (94)

[a] Reaction conditions: phenol (1 mmol), Ac$_2$O (3 mmol), catalyst (1 mol%), CH$_3$CN (1 mL).
[b] GC yield.
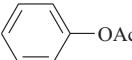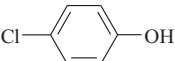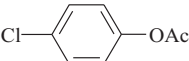[c] Yields in the parentheses refer to isolated products.
[d] Reaction was performed with 2 mmol of Ac$_2$O per OH group.
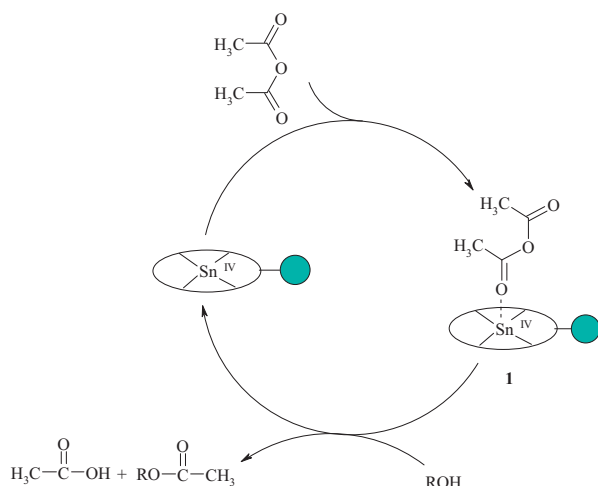
Scheme 3. The proposed mechanism.

The actual mechanism is not clear at present. However, a plausible explanation is that acetic anhydride is first activated by catalyst to afford **1**. Alcohol or phenol attacks **1** which in turn converts to the final product and releases the catalyst for the next catalytic cycle (Scheme 3).

3.3. Catalyst reuse and stability

The stability of the $[Sn^{IV}(TNH_2PP)(OTf)_2]@CMP$ catalyst was monitored using multiple sequential acetylation of 4-chlorobenzyl alcohol with Ac_2O. For each of the repeated reactions, the catalyst was filtered, washed exhaustively with water, acetonitrile and diethyl ether, respectively, and dried before using with fresh 4-chlorobenzyl alcohol

and Ac_2O. The catalyst was consecutively reused seven times without a detectable catalyst leaching or a significant loss of its activity. After each run the filtrates were used for determination of catalyst leaching. No Sn was detected in the filtrates by ICP. This is not surprising because the reaction times are short. When the same reaction was continued for 2 h, about 2% of initial Sn was leached. Also, the catalytic behavior of the separated liquid was tested by addition of fresh 4-chlorobenzyl alcohol and Ac_2O to the filtrates after each run. Execution of the acetylation reaction under the same reaction conditions, as with catalyst, showed that the obtained results were as same as blank experiments. The nature of recovered catalyst was monitored by diffuse reflectance UV-Vis spectrophotometery. No change was observed in the DR UV-Vis spectrum of the catalyst which indicates the stability and robustness of the catalyst (Fig. 3).

4. Conclusion

In conclusion, a new, robust, stable and heterogeneous tin(IV) catalyst was prepared, characterized for the first time. This new electron-deficient tin(IV) porphyrin, $[Sn^{IV}(TNH_2PP)(OTf)_2]@CMP$, was used for efficient and chemoselective acetylation of primary, secondary and tertiary alcohols and phenols with Ac_2O. Short reaction times, excellent yields, easy work-up and reusability and stability of the catalyst are noteworthy advantages of this method.

Acknowledgement

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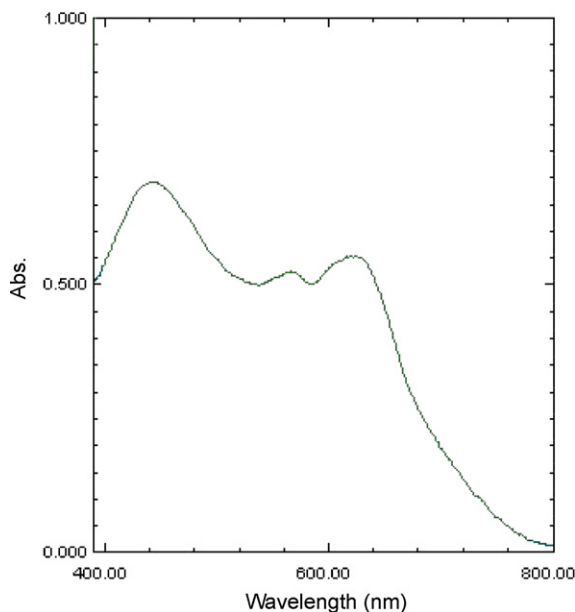[18] P. Saravanan, V.K. Singh, Tetrahedron Lett. 40 (1999) 2611.

Fig. 3. The DR UV-Vis spectrum of recovered $[Sn^{IV}(TNH_2PP)(OTf)_2]@CMP$.

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