



Tetrahydropyranlation of alcohols and phenols catalyzed by a new polystyrene-bound tin(IV) porphyrin

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ABSTRACT

In the present work, tetrahydropyranlation of alcohols and phenols with 3,4-dihydro-2H-pyran (DHP) catalyzed by *tetrakis(p-aminophenyl)porphyrinatotin(IV) trifluoromethanesulfonate*, [Sn^{IV}(TNH₂PP)(OTf)₂], supported on chloromethylated polystyrene is reported. The prepared catalyst was characterized by elemental analysis, FT-IR and diffuses reflectance UV–Vis spectroscopic methods. This new heterogenized catalyst was found as efficient and reusable catalyst for tetrahydropyranlation of primary, secondary and tertiary alcohols as well as phenols at room temperature.

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1. Introduction

There is an increasing demand in catalysis for developing systems that allow the recovery and reuse of the catalyst. Environmental concerns together with economic considerations make necessary and convenient this recovery [1–3]. Since transition-metal complexes are often expensive to purchase or prepare, their immobilization on a support offer a several advantages over their homogeneous counterparts. Supported catalysts can be recovered from reaction mixtures by simple filtration, they do not contaminate the product solution, they can be recycled, and they can increase selectivity [4].

Polystyrene is one of the most popular polymeric supports used in synthetic organic chemistry because of its inexpense, ready availability, mechanical robustness, chemical inertness, and facile functionalization.

The importance of selective introduction and removal of protecting groups in organic synthesis is well established. These protections are necessary during the course of various transfor-

mations in a synthetic sequence, especially in the synthesis of fine chemicals and natural products. Amongst them, tetrahydropyranlation is one of the most frequently used methods for the protection of hydroxyl groups in synthetic organic chemistry, in particular natural product chemistry, because of its easy installation, general stability to most nonacidic reagents, and easy removal under mild acidic conditions [5,6].

A variety of catalysts including protonic and Lewis acid catalysts such as *p*-toluene sulfonic acid (PTSA) [7], *bis*[trimethylsilyl]sulfate [8], (CH₃)₃SiI [9], CuCl₂ [10], DDQ [11], Ru(CH₃)₃(triphos)](OTf)₂ [12], I₂ [13], AlCl₃·6H₂O [14], In(OTf)₃ [15], ZrCl₄ [16], K₅CoW₁₂O₄₀·3H₂O [17], ionic liquids [18], Bu₄N⁺Br₃⁻ [19], and LiOTf [20], K-10 clay [21], alumina impregnated with ZnCl₂ [22], silica chloride [23], AlCl₃@PS [24], silica-based sulfonic acid [25,26], H₆P₂W₁₈O₆₂ [27], PdCl₂(CH₃CN)₂ [28], vanadyl(IV) acetate [29] and [Sn^{IV}(TPP)(OTf)₂] [30] have been developed for tetrahydropyranlation of alcohols and phenols.

Although these procedures provide an improvement, many of these catalysts or activators need long reaction times, drastic reaction conditions or tedious workups, moisture sensitive or expensive of the catalyst. Hence, introduction of new procedures to circumvent these problems is still in demand.

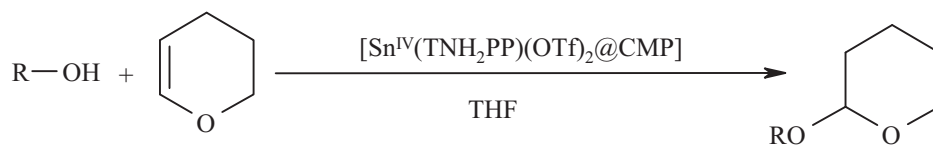
Electron-deficient metalloporphyrins have been used as mild Lewis acids catalysts [31–34]. Suda group has reported the use of chromium and iron porphyrins in organic synthesis. They used Cr(tpp)Cl for regioselective [3,3] rearrangement of

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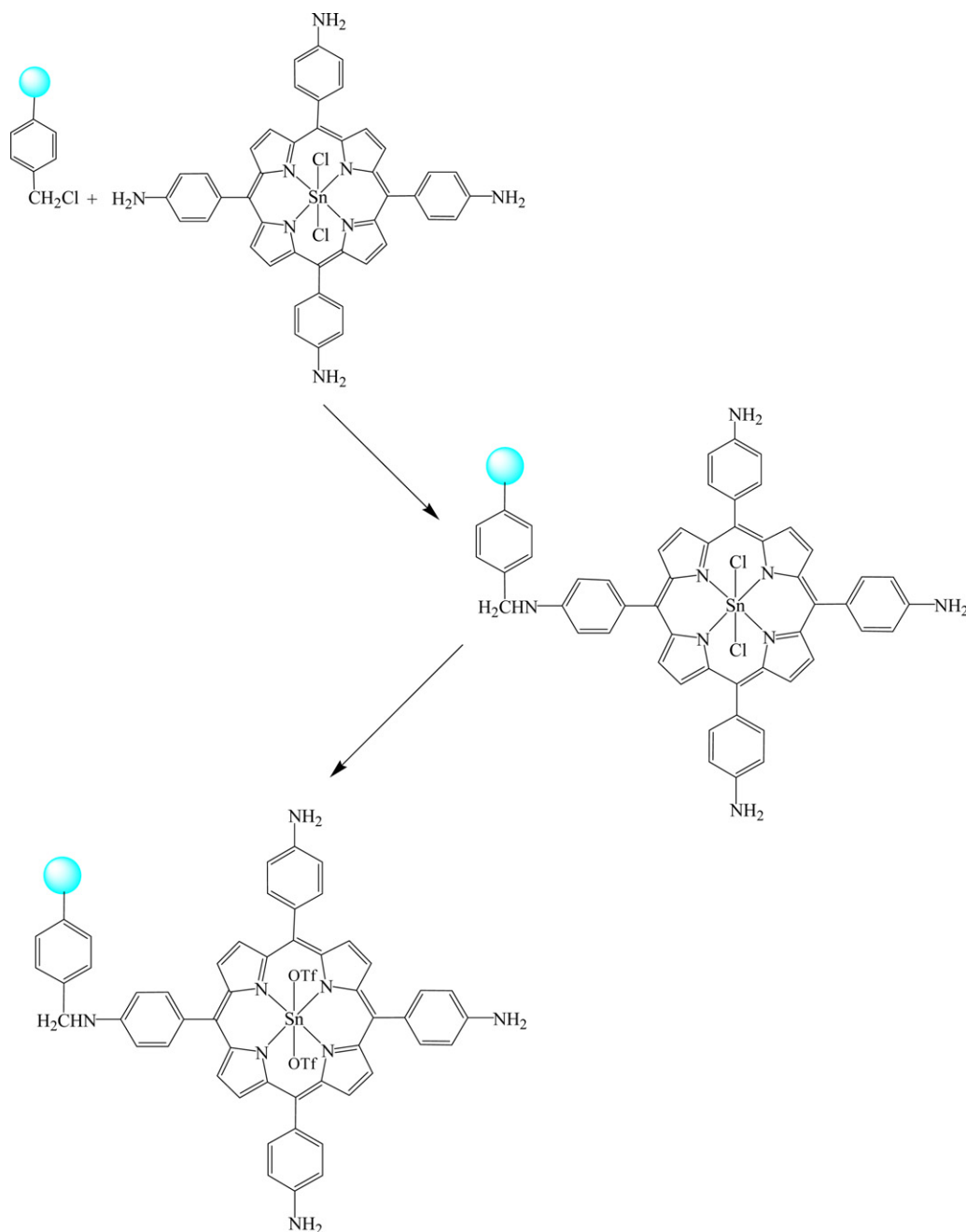
Scheme 1. Tetrahydropyranylation of alcohols and phenols with DHP catalyzed by $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$.

aliphatic allyl vinyl ethers and for Claisen rearrangement of simple aliphatic allyl vinyl ethers, $\text{Fe}(\text{tpp})\text{OTf}$ for rearrangement of α,β -epoxy ketones into 1,2-diketones and $\text{Cr}(\text{tpp})\text{OTf}$ for highly regio- and stereoselective rearrangement of epoxides to aldehydes [35–38].

Recently, we have reported the use of tetraphenylporphyrinatotin(IV) perchlorate [39,40], tetraphenylporphyrinatotin(IV) trifluoromethanesulfonate [30,41–44], and tetraphenylporphyrin-

natotin(IV) tetrafluoroborate [45–47] in organic transformations.

In the present work, preparation, characterization and investigation of catalytic activity of *tetrakis(p-aminophenyl)porphyrinatotin(IV) trifluoromethanesulfonate*, $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]$, supported on chloromethylated polystyrene in the tetrahydropyranylation of alcohols and phenols with 3,4-dihydro-2H-pyran is reported (Scheme 1).



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

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 and metallated according to the literature [48,49].

2.1. Supporting of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]$ on chloromethylated polystyrene, $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]\text{@CMP}$

To a solution of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]$ (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 ethanol and acetone and dried.

2.2. Conversion of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]\text{@CMP}$ to $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]\text{@CMP}$

To a suspension of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]\text{@CMP}$ (2 g) in THF (50 mL) was added NaOTf (1 g) and stirred at 60 °C for 8 h. After, the catalyst was filtered and washed with ethanol.

2.3. General procedure for tetrahydropyranylation of alcohol and phenols catalyzed by $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]\text{@CMP}$

A mixture of alcohol or phenol (1 mmol), $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]\text{@CMP}$ (70 mg, 0.01 mmol) and DHP (2 mmol per OH group) in THF (0.5 mL) was prepared 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 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 $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]\text{@CMP}$

Scheme 2 shows the preparation route for $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]\text{@CMP}$. First, chloromethylated polystyrene (cross-linked with 2% divinylbenzene, 4–5% Cl content, 1.14–1.40 mmol/g Cl) was reacted with $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]$ to obtain the $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]\text{@CMP}$. Then, the chlorines were substituted by OTf^- by the reaction of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]\text{@CMP}$ with NaOTf. This 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 was measured to be 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 evidence for attachment of tin(IV) porphyrin on the polystyrene was obtained

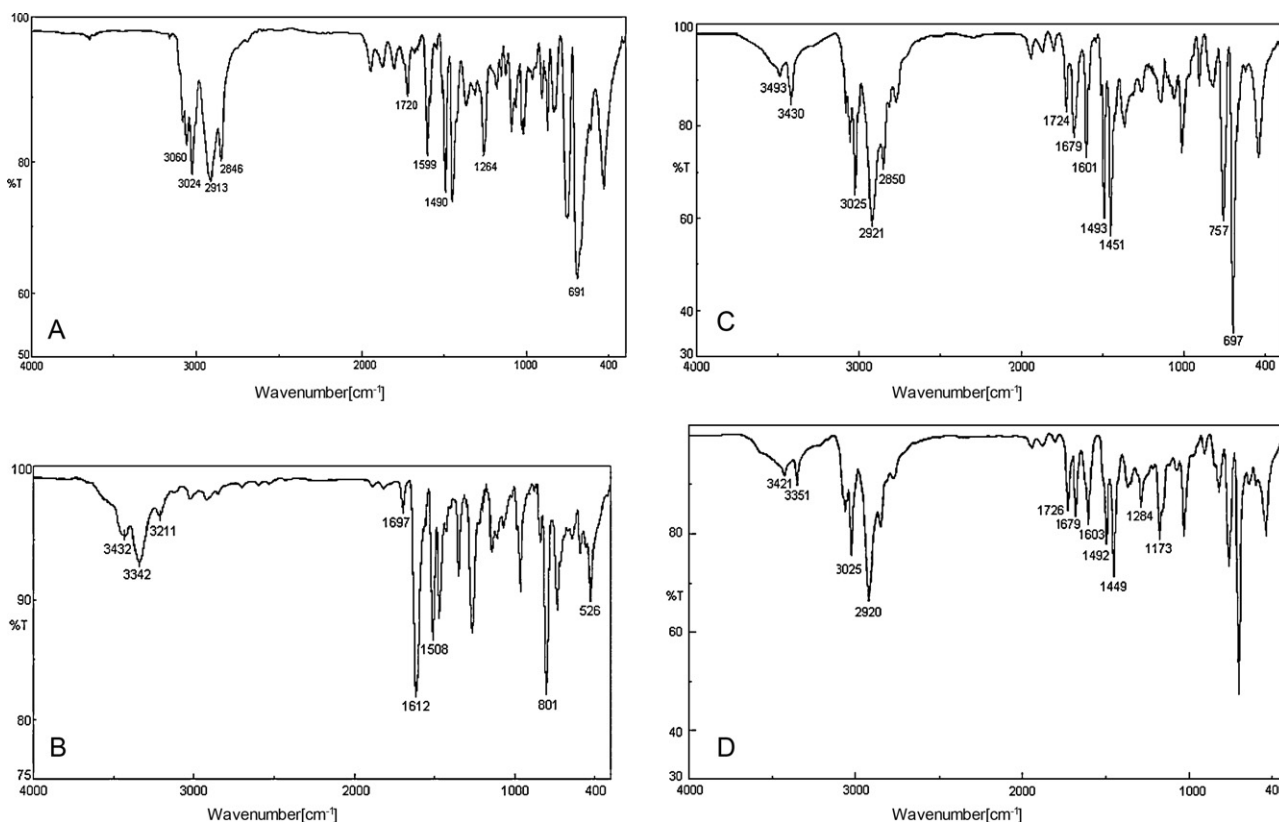


Fig. 1. The FT IR spectrum of (A) chloromethylated polystyrene; (B) $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]$; (C) $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]\text{@CMP}$ and (D) $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]\text{@CMP}$.

Table 1
Optimization of catalyst amount in the acetylation of 4-chlorobenzyl alcohol with DHP catalyzed by $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$.

Entry	Time (min)	Catalyst amounts (mmol, mg)	DHP (mmol)	Solvent	Yield (%) ^a
1	6	40 mg (0.006 mmol)	2	THF	22
2	6	50 mg (0.0071 mmol)	2	THF	61
3	6	60 mg (0.0086 mmol)	2	THF	84
4	6	70 mg (0.010 mmol)	2	THF	100
5	6	80 mg (0.011 mmol)	2	THF	100
6	6	70 mg (0.010 mmol)	2	CH_3CN	88
7	6	70 mg (0.010 mmol)	2	CH_2Cl_2	58
8	6	70 mg (0.010 mmol)	2	CHCl_3	44
9	6	70 mg (0.010 mmol)	2	<i>n</i> -Hexane	17
10	6	70 mg (0.010 mmol)	1	THF	51
11	6	70 mg (0.010 mmol)	1.5	THF	76

^a GC yield.

from FT IR spectra of chloromethylated polystyrene (Fig. 1A), $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]$ (Fig. 1B), $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]@\text{CMP}$ (Fig. 1C) and $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$ (Fig. 1D). The bands at 2920 cm^{-1} and 2850 cm^{-1} in the FT-IR spectrum of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]@\text{CMP}$ and the bands at 2919 cm^{-1} and 2850 cm^{-1} in the FT-IR spectra of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$ are attributed to stretching vibrations of aliphatic C–H bond. These bands which do not present in the homogeneous $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]$ are an indication for attachment of porphyrin on the polystyrene. The presence of the band at 1724 cm^{-1} in the FT-IR spectrum of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]@\text{CMP}$ and 1725 cm^{-1} in the FT-IR spectrum of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$ are attributed to bending vibrations of N–H secondary amine which does not present in the FT-IR spectrum of the $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]$. An indication for conversion of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]@\text{CMP}$ to $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$ is the appearance of bands at 1284 cm^{-1} and 1173 cm^{-1} that are related to stretching vibrations of C–F and S=O bonds, respectively.

The bands at 3493 cm^{-1} and 3429 cm^{-1} in FT-IR spectrum of the $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]@\text{CMP}$ and the bands at 3421 cm^{-1} and 3350 cm^{-1} of in FT-IR spectrum of the $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$ are attributed to stretching vibrations of N–H primary and secondary amines. The bands at 1678 cm^{-1} in the FT-IR spectrum of the $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]@\text{CMP}$ and 1679 cm^{-1} in the FT-IR spectrum of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$ are attributed to bending vibrations of N–H primary amine. Since these bands do not present in the chloromethylated polystyrene, it is clear that the porphyrin has been attached to polystyrene. The sharp C–Cl peak (due to $-\text{CH}_2\text{Cl}$ groups) at 1264 cm^{-1} in the starting polymer was practically omitted or seen as a weak band after introducing of tin(IV) porphyrin on the polymer.

The homogeneous $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]$ showed absorption peaks at 430 (Soret band), 562 and 620 (Q bands) nm (Fig. 2A). The reflectance of the polymer-bound porphyrin resembles solution counterpart spectrum with only a slight shift and a Soret band at 435 nm and Q bands at 560 and 619 nm, which clearly indicates the presence of metalloporphyrin on the polystyrene (Fig. 2B).

3.2. Tetrahydropyranylation of alcohols and phenols catalyzed by $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$

First, the reaction parameters such as amount of catalyst, kind of solvent and amount of DHP were optimized in the tetrahydropyranylation of 4-chlorobenzyl alcohol. The results, which are summarized in Table 1, showed that the highest yield of THP-ether was obtained in the presence of 1 mol% (70 mg) of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$ with 2 mmol of DHP in THF as solvent (Table 1). Then, the catalytic activity of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]@\text{CMP}$ was also investigated in the tetrahydropyranylation of 4-chlorobenzyl alcohol. The results showed that only 21% of the corresponding THP-ether was produced. These

results clearly indicated that the presence of OTf groups is necessary for having a good catalytic activity.

Under the optimized conditions, different alcohols were subjected to tetrahydropyranylation with DHP in the presence of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]@\text{CMP}$ at room temperature (Table 2). The results showed that primary, secondary and tertiary alcohols including aromatic, aliphatic and cyclic ones were converted efficiently to their corresponding tetrahydropyranyl ethers in excellent yield. In the case of aromatic alcohols, the nature of substituents has no significant effect on the tetrahydropyranylation yield.

The ability of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})\text{Cl}_2]@\text{CMP}/\text{DHP}$ catalytic system was also investigated in the tetrahydropyranylation of phenols

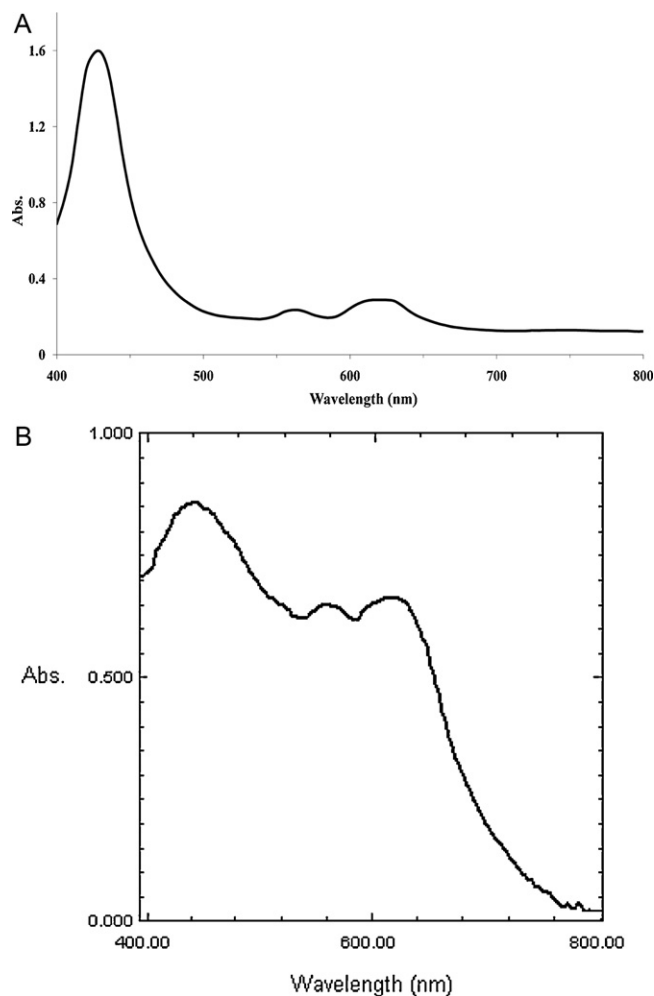
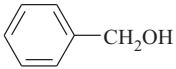
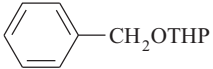
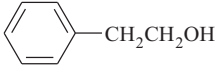
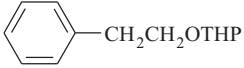
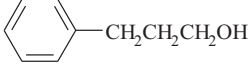

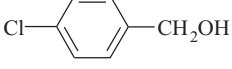
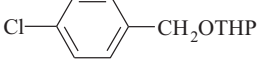
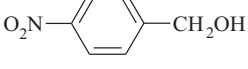
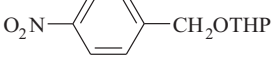
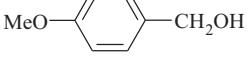
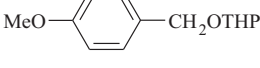
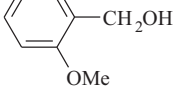
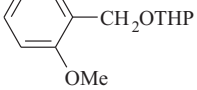
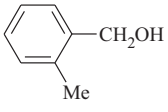
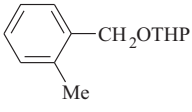

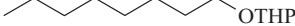
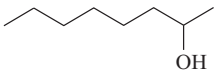
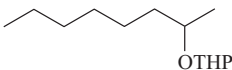
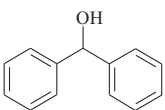
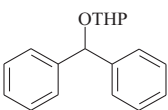
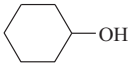
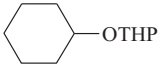
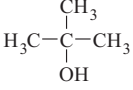
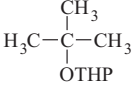
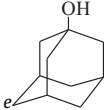
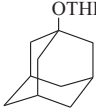


Fig. 2. The UV-Vis spectrum of (A) homogeneous $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]$ and (B) heterogeneous $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$.

Table 2
Tetrahydropyranylation of alcohols catalyzed by $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$ at room temperature.^a

Entry	Hydroxy compound	THP ether	Time (min)	Yield (%) ^b
1			4	97
2			3	95
3			3	96
4			6	99
5			6	62
6			4	95
8			4	95
9			4	94
10			4	93
11			4	90
12			4	96
13			6	94
14			6	96
15			6	93

^a Reaction conditions: alcohol (1 mmol), DHP (2 mmol), catalyst (1 mol%), THF (0.5 mL).

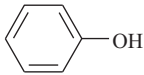
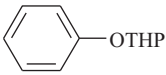
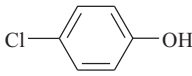
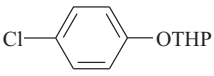
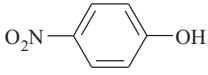
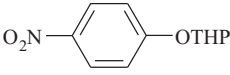
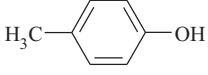
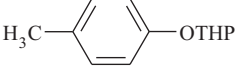
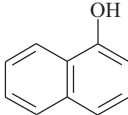
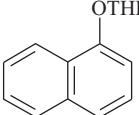
^b Isolated yield.

under the same reaction conditions described for alcohols and the corresponding THP-ethers were obtained in high yields and short reaction times (Table 3).

Since this catalytic system was active in the tetrahydropyranylation of primary, secondary and tertiary alcohols and also phenols, we decided to investigate the chemoselectivity of the presented method. In this manner, a set of competitive reactions was conducted between primary or secondary and tertiary alcohols or phenols (Table 4). The results indicated that primary alcohols are more reactive in the presence of secondary and tertiary alcohols and phenols.

Recently, we reported the use of homogeneous $[\text{Sn}^{\text{IV}}(\text{TPP})(\text{OTf})_2]$ in the tetrahydropyranylation of alcohols and phenols [30]. The reaction times in the presence of 1 mol% of the homogeneous catalyst were 3–6 min and the product yields were 60–97%. In comparison with its homogeneous counterpart [30], in the presence of 1 mol% of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$, the corresponding THP-ethers were obtained in 63–99% in 3–6 min. These observations showed that $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$, which is a heterogeneous catalyst, has reserved its catalytic activity. 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.

Table 3
Tetrahydropyranylation of phenols with DHP catalyzed by $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]\text{@CMP}$ at room temperature.^a

Entry	Phenol	THP ether	Time (min)	Yield (%) ^b
1			5	91
2			5	91
3			5	67
4			5	91
5			5	90

^a Reaction conditions: phenol (1 mmol), DHP (2 mmol), catalyst (1 mol%), THF (0.5 mL).

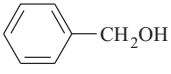
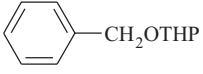
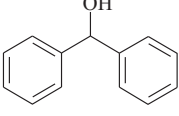
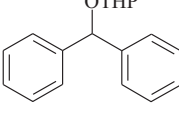
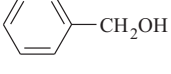
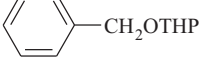
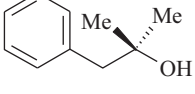
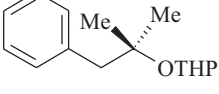
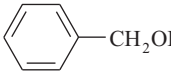
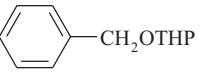

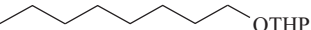
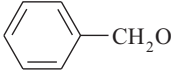
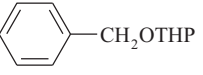
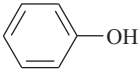
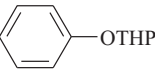
^b Isolated yield.

3.3. Catalyst reuse and stability

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

alyst was consecutively reused seven times without a detectable catalyst leaching or a significant loss of its activity (Table 5). After each run the filtrates were used for determination of catalyst leaching. No Sn was detected in the filtrates by ICP. Also, the catalytic behavior of the separated liquid was tested by addition of fresh 4-chlorobenzyl alcohol and DHP 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

Table 4
Selective tetrahydropyranylation of alcohols and phenols catalyzed by $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]\text{@CMP}$.^a

Row	ROH	THP ether	Time (min)	Yield (%) ^b
1			4	85
				21
2			4	90
				23
3			4	95
				45
4			4	92
				7

^a Reaction conditions for a binary mixture: 1 mmol of each alcohol or phenol, DHP (2 mmol), catalyst (1 mol%), THF (0.5 mL).

^b GC yield.

Table 5

Reusability of $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$ in the pyranylation of 4-chlorobenzyl alcohol with DHP.^a

Run	THP ether (%) ^b	Time (min)	Sn leached (%) ^c
1	100	6	0
2	100	6	0
3	100	6	0
4	100	6	0
5	100	6	0
6	100	6	0

^a Reaction conditions: 4-chlorobenzyl alcohol (1 mmol), DHP (2 mmol), catalyst (1 mol%), THF (0.5 mL).

^b GC yield.

^c Determined by ICP.

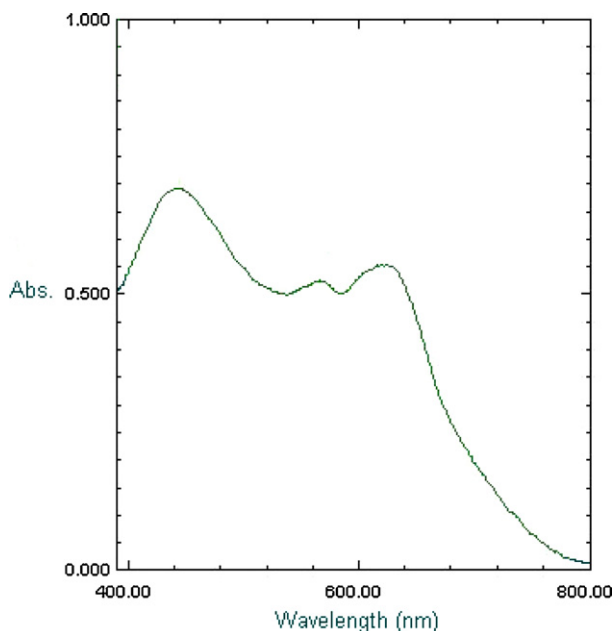


Fig. 3. The DR UV-Vis spectrum of recovered $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$.

same as blank experiments. The nature of recovered catalyst was monitored by diffuse reflectance UV-Vis spectrophotometry. 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) compound was prepared, characterized for the first time. This new electron deficient tin(IV) porphyrin, $[\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2]@\text{CMP}$, was used for efficient tetrahydropyranylation of primary, secondary and tertiary alcohols and phenols with DHP. Short reaction times, excellent yields, easy work-up and reusability and stability of the catalyst are noteworthy advantages of this method.

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