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Highly efficient protection of alcohols and phenols catalysed by tin porphyrin supported on MIL-101

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The catalytic activity of 5,10,15,20-tetrakis(4-aminophenyl)porphyrinatotin(IV) trifluoromethanesulfonate, [$Sn^{IV}(TNH_2PP)(OTf)_2$], supported on chloromethylated MIL-101, was investigated in the trimethylsilylation of alcohols and phenols with hexamethyldisilazane (HMDS) and also their tetrahydropyranylation with 3,4-dihydro-2H-pyran. Excellent yields, mild reaction conditions, short reaction times and reusability of the catalyst without significant decrease in its initial activity are noteworthy advantages of this supported catalyst. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: metal–organic framework; tin(IV) porphyrin; MIL-101(Cr); trimethylsilylation; tetrahydropyranylation

Introduction

Protection of hydroxyl groups in alcohols and phenols is of great importance in multistep organic synthesis. A wide variety of methods such as acetylation, trimethylsilylation, methoxymethylation and tetrahydropyranylation have been reported for the protection of hydroxyl functional groups.[1,2]

For this purpose, various catalysts such as K-10 montmorillonite,[3] zirconium sulfophenylphosphonate,[4] iodine,[5] $H_3PW_{12}O_{40}$,[6] sulfonic acid-functionalized ordered nanoporous Na^+–montmorillonite,[7] sulfonic acid-functionalized nanoporous silica,[8] $ZrO(OTf)_2$,[9] $Bi(OTf)_3$,[10] [$Sn^{IV}(TPP)(BF_4)_2$],[11] nanocrystalline TiO_2–$HClO_4$,[12] [Ti^{IV}(salophen)$(OTf)_2$],[13] $InBr_3$,[14] 1,3-disulfonic acid imidazolium hydrogen sulfate,[15] Ru^{III}(OTf)salophenCH_2–$NHSiO_2$–Fe,[16] alumina-supported heteropolyoxometalates,[17] $ZrCl_4$[18] and $H_{14}[NaP_5W_{29}MoO_{110}]$[19] have been introduced for the silylation of alcohols and phenols with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) as a stable, cheap and commercially available reagent. Also, various catalysts like polystyrene-supported $GaCl_3$,[20] *N*,*N*′-dibromo-*N*,*N*′-1,2-ethanediylbis(benzene sulfonamide),[21] $La(NO_3)_3{\cdot}6H_2O$,[22] ferric perchlorate,[23] vanadyl(IV) acetate,[24] activated carbon-supported sulfuric acid,[25] {[K.18-crown-6]Br_3}$_n$,[26] tungstosilicate salts,[27] silica–alumina-supported heteropoly acids,[28] sulfonic acid-functionalized carbon catalyst from glycerol pitch,[29] aniline–terephthalaldehyde resin *p*-toluenesulfonic acid salt,[30] $Al(OTf)_3$,[31] *p*-toluenesulfonic acid,[32] $Ru(CH_3)_3$(triphos)]$(OTf)_2$[33] and $K_5CoW_{12}O_{40}{\cdot}3H_2O$[34] have been developed for the tetrahydropyranylation of alcohols and phenols. Because of the importance of these reactions, development of efficient and versatile catalytic systems for the protection of alcohols and phenols is still expedient.

Electron-deficient metalloporphyrins are excellent Lewis acid catalysts in the protection of alcohols and phenols.[35–41] However, the major drawback of these expensive biomimetic homogeneous catalysts is that they cannot be recovered and reused. To overcome this problem, immobilization and anchoring of them onto solid supports have been considered.

Because of prominent properties of metal–organic frameworks, especially MIL-101 ($Cr_3X(H_2O)_2O(bdc)_3$; X = F, OH; bdc = benzene-1,4-dicarboxylate), such as high surface area, high chemical and hydrothermal stability, tuneability and large pores, they can be used as both catalyst and support.[42–49]

Goesten *et al*. reported a mild and safe route for the chloromethylation of aromatic rings of MIL-101(Cr) with methoxyacetyl chloride in the presence of aluminium chloride.[50] The chlorine atoms can be replaced by metalloporphyrins bearing nucleophilic groups in their structure, and in this way these expensive catalysts can be heterogenized.[51]

Previously, we reported the immobilization of [$Sn^{IV}(TNH_2PP)(OTf)_2$] on chloromethylated MIL-101 (CM-MIL-101) and investigated its catalytic activity in the cycloaddition of carbon dioxide to epoxides.[52] The high catalytic activity of this heterogeneous catalyst in carbon dioxide fixation prompted us to explore its catalytic activity in the trimethylsilylation and tetrahydropyranylation of alcohols and phenols. In the present paper, highly efficient, rapid and selective protection of alcohols and phenols with HMDS and 3,4-dihydro-2H-pyran (DHP) catalysed by [$Sn^{IV}(TNH_2PP)(OTf)_2$]/CM-MIL-101 at room temperature is reported (Scheme 1). Also, the stability and reusability of this catalyst were investigated in these reactions.

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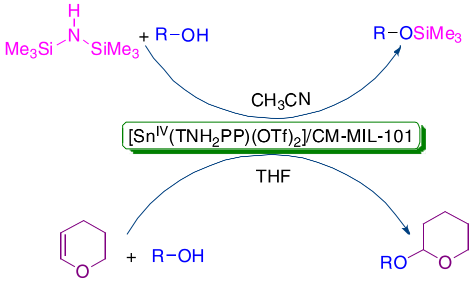
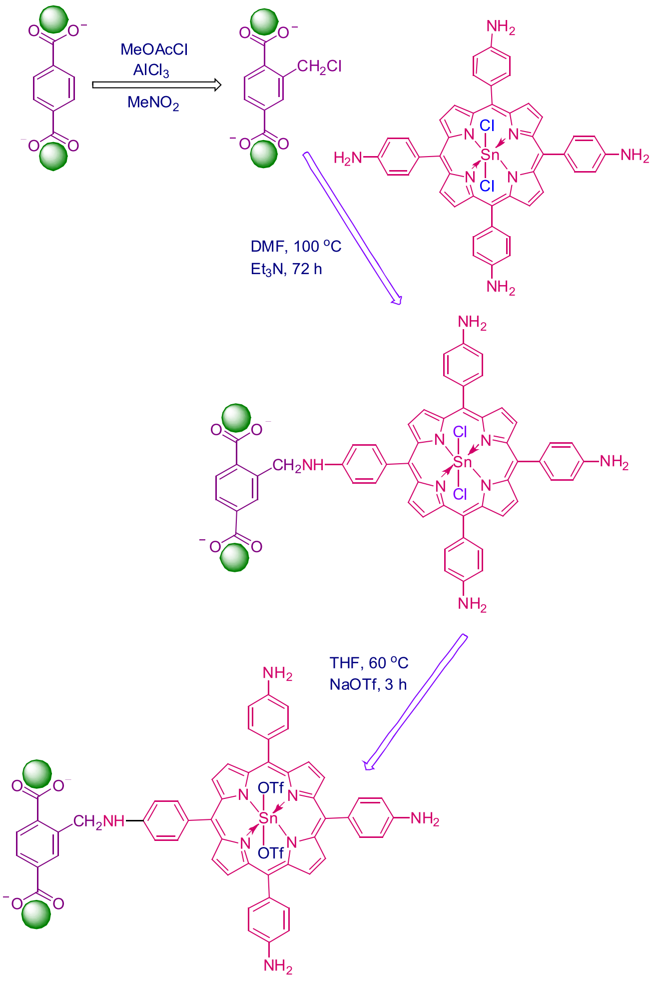


Scheme 1. Catalytic protection of alcohols and phenols using $[Sn^{IV}(TNH_2PP)(OTf)_2]$/CM-MIL-101.

Experimental

Reagents and Methods

All materials were of commercial reagent grade and were obtained from Merck or Fluka. Diffuse reflectance UV–visible spectra were recorded with a solid UV–visible JASCO model V-670 spectrophotometer. FT-IR spectra were obtained with potassium bromide pellets in the range 400–3500 cm^{-1} with a JASCO 6300 spectrophotometer. X-ray diffraction patterns were recorded using a Bruker D_8 Advance X-ray diffractometer with nickel monochromatized Cu K_{α} radiation ($\lambda = 1.5406$). Gas chromatography (GC) experiments were performed using an Agilent 6890 instrument equipped with a flame ionization detector using a 6FT3H OV-101 column. In the GC experiments, *n*-decane was used as the internal standard. Tetra(4-aminophenyl)porphyrin was prepared according to the literature.[53] The $[Sn^{IV}(TNH_2PP)Cl_2]$ catalyst was prepared according to the procedure reported for metallation of porphyrins.[54] The hybrid catalyst was prepared based on a reported procedure (Scheme 2).[52]



Scheme 2. Preparation of the catalyst.

Table 1. Optimization of reaction parameters in trimethylsilylation of benzyl alcohol with HMDS

Entry	Catalyst (mg)	HMDS (mmol)	Solvent	Time (min)	Yield (%)[a]
1	40	0.7	CH_3CN	1	83
2	50	0.7	CH_3CN	1	91
3	60	0.7	CH_3CN	1	100
4	70	0.7	CH_3CN	1	100
5	60	2	CH_3CN	1	100
6	60	1	CH_3CN	1	100
7	60	0.7	CH_3CN	1	100
8	60	0.5	CH_3CN	1	95
9	60	0.7	THF	1	74
10	60	0.7	CH_2Cl_2	1	63
11	60	0.7	*n*-Hexane	1	56

[a] GC yield.

General Procedure for Trimethylsilylation of Alcohols and Phenols with HMDS in the Presence of $[Sn^{IV}(TNH_2PP)(OTf)_2]$/CM-MIL-101

A solution of alcohol or phenol (1 mmol) and HMDS (0.7 mmol) in CH_3CN (1 ml) was prepared. $[Sn^{IV}(TNH_2PP)(OTf)_2]$/CM-MIL-101 (60 mg, 0.008 mmol) was added to this solution and stirred at room temperature. The progress of the reaction was monitored using GC. After completion of the reaction, Et_2O (10 ml) was added and the catalyst was filtered. The filtrate was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to afford the crude product.

Table 2. Optimization of reaction parameters in tetrahydropyranylation of benzyl alcohol with DHP

Entry	Catalyst (mg)	DHP (mmol)	Solvent	Time (min)	Yield (%)[a]
1	60	2	THF	3	69
2	70	2	THF	3	86
3	80	2	THF	3	98
4	90	2	THF	3	98
5	100	2	THF	3	98
6	80	1.5	THF	3	75
7	80	1	THF	3	63
8	80	2	CH_3CN	3	71
9	80	2	CH_2Cl_2	3	60
10	80	2	*n*-Hexane	3	21

[a] GC yield.

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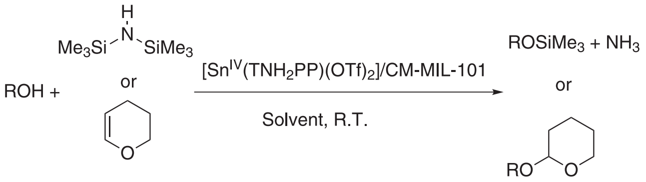
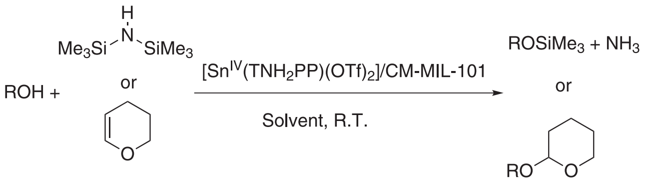
Table 3. Trimethylsilylation and tetrahydropyranylation of alcohols catalysed by $[Sn^{IV}(TNH_2PP)(OTf)_2]$/CM-MIL-101 at room temperature[a]



Entry	ROH	Trimethylsilylation			Tetrahydropyranylation		
		Time (min)	Yield (%)[b]	TOF (h^{-1})	Time (min)	Yield (%)[b]	TOF (h^{-1})
1	$PhCH_2OH$	1	100	7692	3	98	1960
2	$PhCH_2CH_2OH$	1	100	7692	3	98	1960
3	$PhCH_2CH_2CH_2OH$	1	100	7692	3	97	1940
4	$4\text{-}ClC_6H_4CH_2OH$	1	100	7692	4	94	1403
5	$4\text{-}O_2NC_6H_4CH_2OH$	1	98	7538	6	79	790
6	$2\text{-}MeOC_6H_4CH_2OH$	2	100	3846	4	95	1418
7	$4\text{-}MeOC_6H_4CH_2OH$	1	100	7692	3	93	1860
8	$4\text{-}t\text{-}BuC_6H_4CH_2OH$	2	100	3846	4	91	1358
9	$2\text{-}MeC_6H_4CH_2OH$	2	100	3846	3	90	1800
10	$1\text{-}C_7H_{15}OH$	1	100	7692	3	92	1840
11	$1\text{-}C_8H_{17}OH$	1	100	7692	3	90	1800
12	$C_6H_{13}CH(Me)OH$	2	100	3846	4	95	1418
13	1-Adamantanol	4	95	1792	6	90	900
14	Me_3COH	3	98	2450	5	89	1072

[a] Reaction conditions: alcohol (1 mmol), HMDS (0.7 mmol), CH_3CN (0.5 ml) and $[Sn^{IV}(TNH_2PP)(OTf)_2]$/CM-MIL-101 (60 mg) for trimethylsilylation; alcohol (1 mmol), DHP (2 mmol), THF (0.5 ml) and $[Sn^{IV}(TNH_2PP)(OTf)_2]$/CM-MIL-101 (80 mg) for tetrahydropyranylation.
[b] GC yield.

Table 4. Trimethylsilylation and tetrahydropyranylation of phenols catalysed by $[Sn^{IV}(TNH_2PP)(OTf)_2]$/CM-MIL-101 at room temperature[a]



Entry	ROH	Trimethylsilylation			Tetrahydropyranylation		
		Time (min)	Yield (%)[b]	TOF (h^{-1})	Time (min)	Yield (%)[b]	TOF (h^{-1})
1	C_6H_5OH	1	97	7461	4	95	1418
2	$4\text{-}ClC_6H_4OH$	1	96	7385	4	96	1433
3	$4\text{-}O_2NC_6H_4OH$	2	98	3769	6	75	750
4	$4\text{-}MeC_6H_4OH$	2	100	3846	4	95	1418
5	1-Naphthol	3	100	2500	5	91	1096

[a] Reaction conditions: alcohol (1 mmol), HMDS (0.7 mmol), CH_3CN (0.5 ml) and $[Sn^{IV}(TNH_2PP)(OTf)_2]$/CM-MIL-101 (60 mg) for trimethylsilylation; alcohol (1 mmol), DHP (2 mmol), THF (0.5 ml) and $[Sn^{IV}(TNH_2PP)(OTf)_2]$/CM-MIL-101 (80 mg) for tetrahydropyranylation.
[b] GC yield.

General Procedure for Tetrahydropyranylation of Alcohols and Phenols with DHP in the Presence of $[Sn^{IV}(TNH_2PP)(OTf)_2]$/CM-MIL-101

A mixture of alcohol or phenol (1 mmol), $[Sn^{IV}(TNH_2PP)(OTf)_2]$/CM-MIL-101 (80 mg, 0.01 mmol) and DHP (2 mmol) in THF (1 ml) was prepared and stirred at room temperature. The progress of the reaction was monitored using GC. After completion of the reaction, the solvent was evaporated, *n*-hexane (10 ml) was added and the catalyst was filtered. The filtrate was concentrated under reduced pressure to afford the crude product.

Catalyst Reusability

The reusability of the catalyst was investigated in the repeated trimethylsilylation and tetrahydropyranylation of benzyl alcohol. The reactions were carried out as described above. At the end of

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each reaction, the catalyst was filtered and washed with Et_2O, acetonitrile and ethanol, successively, then dried and reused.

Results and Discussion

Trimethylsilylation and Tetrahydropyranylation of Alcohols and Phenols Catalysed by [$Sn^{IV}(TNH_2PP)(OTf)_2$]/CM-MIL-101

First, the reaction parameters were optimized for the trimethylsilylation of benzyl alcohol with HMDS. As evident from Table 1, the best results are obtained in the presence of 0.008 mmol (60 mg) of [$Sn^{IV}(TNH_2PP)(OTf)_2$]/CM-MIL-101 and the best solvent is acetonitrile in the presence of 0.7 mmol of HMDS.

In the tetrahydropyranylation of benzyl alcohol with DHP, the optimized reaction conditions are 80 mg (0.01 mmol) of [$Sn^{IV}(TNH_2PP)(OTf)_2$]/CM-MIL-101 and DHP (2 mmol) in THF (1 ml) (Table 2).

In order to show the effect of OTf groups on the electron deficiency of tin(IV) porphyrin, the model reaction was carried out using [$Sn^{IV}(TNH_2PP)Cl_2$]/CM-MIL-101 as catalyst (0.008 mmol) at room temperature. The results show that the amount of the corresponding silyl ether is 23% after 1 min, while in the presence of [$Sn^{IV}(TNH_2PP)(OTf)_2$]/CM-MIL-101 catalyst, the reaction is completed.

Also, the same reaction was designed for the tetrahydropyranylation of benzyl alcohol in the presence of 0.01 mmol of [$Sn^{IV}(TNH_2PP)Cl_2$]/CM-MIL-101. The results show that only 14% of the tetrahydropyranyl (THP) ether is produced after 3 min, while, by substitution of Cl^- by OTf^- groups, the reaction is almost completed (98% yield).

Under the optimized reaction conditions, a wide variety primary, secondary (including aliphatic and aromatic alcohols) and tertiary alcohols were subjected to trimethylsilylation with HMDS and tetrahydropyranylation with DHP. The corresponding trimethylsilyl (TMS) ethers and THP ethers are produced in good to excellent yields. The results are given in Table 3. As is evident, the reaction times are lower in the case of trimethylsilylation compared to tetrahydropyranylation, and the turnover frequencies (TOFs) are higher for trimethylsilylation. Also, in the trimethylsilylation and tetrahydropyranylation reactions, the nature of the substituents on the benzylic alcohols (electron-withdrawing or electron-donating) has no significant effect on the product yield.

Blank experiments in the absence of catalyst were carried out and only small amounts of the corresponding TMS or THP ethers are produced. Also, the catalytic activity of MIL-101 as support was investigated in these reactions under the same conditions described for [$Sn^{IV}(TNH_2PP)(OTf)_2$]/CM-MIL-101. The results show only 15% of the corresponding TMS ether and 9% of the corresponding THP ether are produced.

The protection of phenols in the presence of [$Sn^{IV}(TNH_2PP)(OTf)_2$]/CM-MIL-101 was also investigated under the same conditions as described for alcohols. As evident from Table 4, all hydroxyl groups are converted to their corresponding TMS and THP ethers in excellent yields at room temperature.

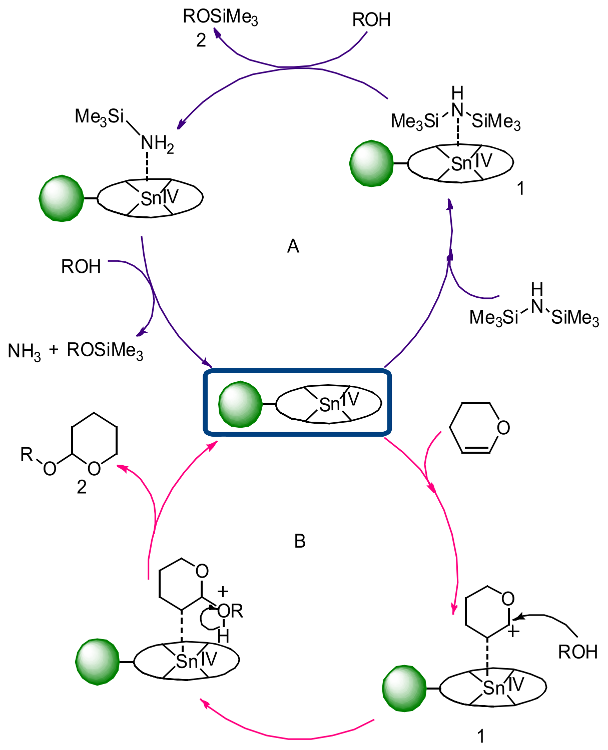
Table 5. Selective trimethylsilylation and tetrahydropyranylation of alcohols and phenols catalysed by [$Sn^{IV}(TNH_2PP)(OTf)_2$]/CM-MIL-101 at room temperature[a]

$$R'OH + ROH + \begin{matrix}HMDS\\ \text{or}\\ DHP\end{matrix} \xrightarrow[\text{Solvent, R.T.}]{[Sn^{IV}(TNH_2PP)(OTf)_2]/CM\text{-}MIL\text{-}101} \begin{matrix}\text{TMS-ethers}\\ \text{or}\\ \text{THP-ethers}\end{matrix}$$

Entry	ROH	Trimethylsilylation		Tetrahydro-pyranylation	
	R'OH	Time (min)	Yield (%)[b]	Time (min)	Yield (%)[b]
1	$C_6H_5CH_2OH$	1	100	3	98
	C_6H_5OH		8		3
2	$C_6H_5CH_2OH$	1	100	3	98
	$C_8H_{17}OH$		19		8
3	$C_6H_5CH_2OH$	1	100	3	98
	1-Adamantanol		0		0

[a] Reaction conditions: each alcohol (1 mmol), HMDS (0.7 mmol), CH_3CN (0.5 ml) and [$Sn^{IV}(TNH_2PP)(OTf)_2$]/CM-MIL-101 (60 mg) for trimethylsilylation; each alcohol (1 mmol), DHP (2 mmol), THF (0.5 ml) and [$Sn^{IV}(TNH_2PP)(OTf)_2$]/CM-MIL-101 (80 mg) for tetrahydropyranylation.

[b] GC yield.



Scheme 3. Proposed mechanisms for trimethylsilylation and tetrahydropyranylation of alcohols and phenols catalysed by [$Sn^{IV}(TNH_2PP)(OTf)_2$]/CM-MIL-101.

In order to investigate the selectivity of this catalytic system, trimethylsilylation and tetrahydropyranylation of binary mixtures of primary, secondary and tertiary alcohols or phenols were carried out (Table 5). The results show that the trimethylsilylation and tetrahydropyranylation of benzyl alcohol are much easier than of phenol. This is due to the resonance between the lone pair electrons on the oxygen with the aromatic ring that reduces the nucleophilicity of phenol. In the competing reactions of benzyl alcohol and 1-octanol, benzyl alcohol is converted to its corresponding TMS ether and DHP ether in higher yields (Table 5, entry 2).

The proposed mechanisms for trimethylsilylation and tetrahydropyranylation of alcohols and phenols are shown in

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Scheme 3.[55,56] A plausible mechanism for these reactions is that the protective agent (DHP or HMDS) is first activated by tin(IV) porphyrin to afford **1**. Nucleophilic attack of alcohol to **1** and consequent proton transfer produces final product **2** and releases the catalyst for the next run (Scheme 3).

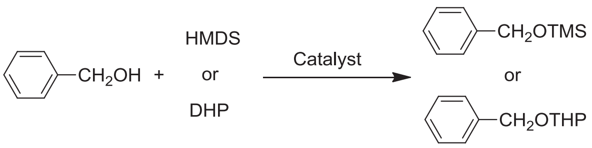
In continuation of our study to show the effectiveness of the catalyst under investigation in the protection of alcohols and phenols, the results of trimethylsilylation of benzyl alcohol with HMDS catalysed by $[Sn^{IV}(TNH_2PP)(OTf)_2]/CM\text{-}MIL\text{-}101$ are compared with some of those reported in the literature (Table 6). The results show that this catalyst is superior in terms of reaction time, product yield, catalyst amount and also reusability.

Catalyst Reusability and Stability

The reusability of the $[Sn^{IV}(TNH_2PP)(OTf)_2]/CM\text{-}MIL\text{-}101$ catalyst was studied using multiple sequential trimethylsilylation and tetrahydropyranylation of benzyl alcohol with HMDS and DHP, respectively. For each of the repeated reactions, the catalyst was filtered, washed exhaustively with Et_2O, acetonitrile and ethanol successively, and dried before being used in the next catalytic experiment. The catalyst was consecutively reused seven times without detectable catalyst leaching or a significant loss of its activity (Table 7).

The nature of the recovered catalyst was monitored using diffuse reflectance UV–visible spectrophotometry and FT-IR spectroscopy. No change is observed in these spectra (Figs. 1 and 2) which indicates the strong bond between tin(IV) porphyrin and the support.

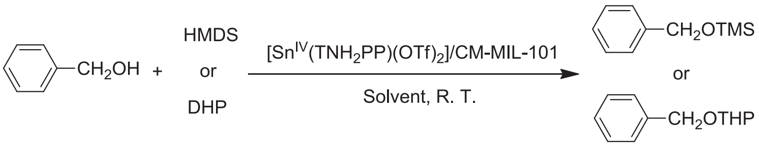
Table 6. Comparison of the catalytic activity of $[Sn^{IV}(TNH_2PP)(OTf)_2]/CM\text{-}MIL\text{-}101$ in the trimethylsilylation and tetrahydropyranylation of benzyl alcohol with that of some recently reported catalysts



Entry	Catalyst	Temp.[a]	HMDS (mmol)	DHP (mmol)	Time (min)	Yield (%)	TOF (h^{-1})	Ref.
1	$[Sn^{IV}(TNH_2PP)(OTf)_2]/CM\text{-}MIL\text{-}101$	r.t.	0.7	—	1	100	7692	Present work
2	$Ru^{III}(OTf)salophenCH_2\text{–}NHSiO_2\text{–}Fe$	r.t.	0.7	—	1	100	1425	[16]
3	$[Sn^{IV}(TNH_2PP)(OTf)_2]@CMP$	r.t.	0.5	—	2	100	3000	[38]
4	$[Ti^{IV}(salophen)(OTf)_2]$	r.t.	0.7	—	1	100	6000	[13]
5	$ZrO(OTf)_2$	r.t.	2	—	1	92	11040	[9]
6	$[Sn^{IV}(TNH_2PP)(OTf)_2]/CM\text{-}MIL\text{-}101$	r.t.	—	2	3	98	1960	Present work
7	$[Sn^{IV}(TPP)(OTf)_2]@CMP$	r.t.	—	2	4	97	1448	[57]
8	$Al(OTf)_3$	r.t.	—	5	480	87	109	[31]
9	$CMK\text{-}5\text{-}SO_3H$	r.t.	—	1.5	30	100	100	[58]
10	$PS/GaCl_3$	r.t.	—	1.1	25	98	23	[20]

[a] Temperature: r.t., room temperature.

Table 7. Recyclability of $[Sn^{IV}(TNH_2PP)(OTf)_2]/CM\text{-}MIL\text{-}101$ in trimethylsilylation and tetrahydropyranylation of benzyl alcohol[a]



Run	Trimethylsilylation after 2 min		Tetrahydropyranylation after 5 min	
	Yield (%)[b]	Sn leached (%)[c]	Yield (%)[b]	Sn leached (%)[c]
1	100	0	98	0
2	100	0	98	0
3	100	0	98	0
4	100	0	98	0
5	100	0	98	0
6	100	0	97	0
7	98	0	96	0

[a] Reaction conditions: alcohol (1 mmol), HMDS (0.7 mmol), CH_3CN (0.5 ml) and $[Sn^{IV}(TNH_2PP)(OTf)_2]/CM\text{-}MIL\text{-}101$ (60 mg) for trimethylsilylation; alcohol (1 mmol), DHP (2 mmol), THF (0.5 ml) and $[Sn^{IV}(TNH_2PP)(OTf)_2]/CM\text{-}MIL\text{-}101$ (80 mg) for tetrahydropyranylation.

[b] GC yield.

[c] Determined by ICP.

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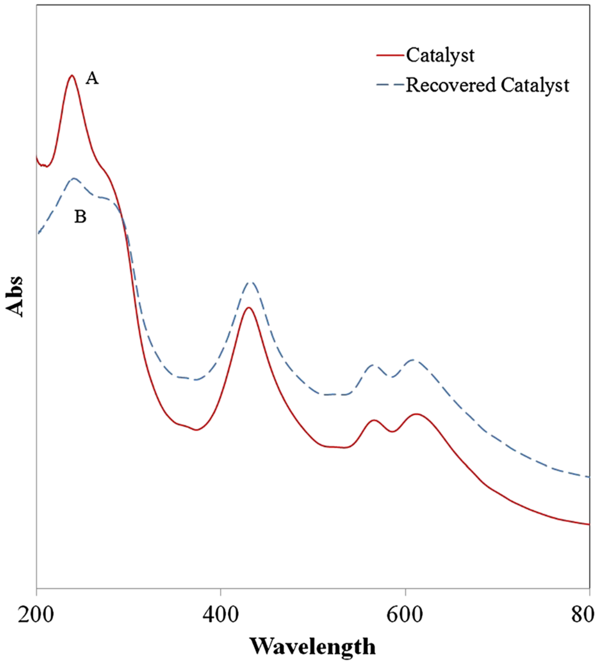

Figure 1. Diffuse reflectance UV–visible spectra of (A) $[Sn^{IV}(TNH_2PP)(OTf)_2]$/CM-MIL-101 and (B) recovered catalyst.

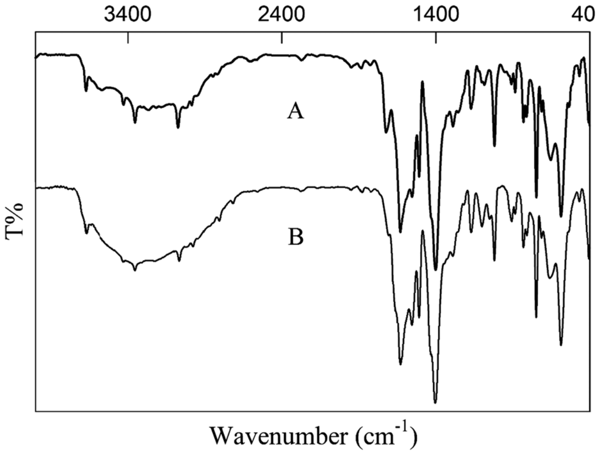

Figure 2. FT-IR spectra of (A) $[Sn^{IV}(TNH_2PP)(OTf)_2]$/CM-MIL-101 and (B) recovered catalyst.

Conclusions

We have reported a rapid and efficient catalytic system for trimethylsilylation and tetrahydropyranylation of alcohols and phenols with HMDS and DHP, respectively. The results showed that this system catalysed the protection of primary, secondary and tertiary alcohols, as well as phenols in very short reaction times and with high yields under mild conditions (room temperature). Finally the catalyst could be reused several times without any noticeable catalyst leaching.

Acknowledgement

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