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$[Sn^{IV}(TPP)(BF_4)_2]$: An efficient and reusable catalyst for chemoselective trimethylsilylation of alcohols and phenols with hexamethyldisilazane

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Tin(IV)tetraphenylporphyrinato tetrafluoroborate, $[Sn^{IV}(TPP)(BF_4)_2]$, was used as an efficient catalyst for trimethylsilylation of alcohols and phenols with hexamethyldisilazane (HMDS). High-valent $[Sn^{IV}(TPP)(BF_4)_2]$ catalyzes trimethylsilylation of primary, secondary and tertiary alcohols as well as phenols, and the corresponding TMS-ethers were obtained in high yields and short reaction times at room temperature. While, under the same reaction conditions $[Sn^{IV}(TPP)Cl_2]$ is less efficient to catalyze these reactions. One important feature of this catalyst is its ability in the chemoselective silylation of primary alcohols in the presence of secondary and tertiary alcohols and phenols. The catalyst was reused several times without loss of its catalytic activity.

1. Introduction

The protection of functional groups is often necessary during the course of various transformations in a synthetic sequence, especially in the synthesis of fine chemicals and natural products [1–3]. Hydroxy functional group, which is a versatile functional group, can be protected by a wide variety of methods such as tetrahydropyranylation, acetylation, methoxymethylation and trimethylsilylation. Commonly, silyl ethers are prepared by treatment of hydroxyl compounds with silyl chlorides or silyl triflates in the presence of bases such as imidazole [4], 4-(*N*,*N*-dimethylamino)pyridine [5], *N*,*N*-diisopropylethylamine [6] and Li_2S [7]. However, some of these silylation methods suffer from disadvantages such as the lack of reactivity or the difficulty in removal of amine salts derived during the silylation reaction. To overcome these problem, 1,1,1,3,3,3-hexamethyldisilazane (HMDS), which is a stable, commercially available and cheap reagent, is used for preparation of silyl ethers from hydroxyl compounds. This silylation method does not need special precautions and produces ammonia as by-product, but silylation in the absence of a suitable catalyst needs forceful conditions and long reaction times [8]. In order to increase the silylating power of HMDS, a variety of catalysts including trichloroisocyanuric acid (TCCA) [9], silica supported perchloric acid ($HClO_4$–SiO_2) [10], $ZrCl_4$ [11], K-10 montmorilonite [12], $LiClO_4$ [13], $H_3PW_{12}O_{40}$ [14], iodine [15], $InBr_3$ [16], zirconium sulfophenyl phosphonate [17], $CuSO_4 \cdot 5H_2O$ [18], sulfonic acid-functionalized nanoporous silica [19], $MgBr_2 \cdot OEt_2$ [20], $LaCl_3$ [21], poly(*N*-bromobenzene-1,3-disulfonamide) and *N*,*N*,*N*′,*N*′-tetrabromobenzene-1,3-disulfonamide [22], $Fe(TFA)_3$ [23], Fe_3O_4 [24], $(n\text{-}Bu_4N)Br$ [25] and $ZrO(OTf)_2$ [26] have been reported. Although these procedures provide an improvement, but many of these catalysts 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 [27–32]. Recently, chromium and iron porphyrins have been used for organic transformations. Chromium(III) tetraphenylporphyrinato chloride, Cr(tpp)Cl, has been applied for regio-selective [3,3] rearrangement of aliphatic allyl vinyl ethers and for Claisen rearrangement of simple aliphatic allyl vinyl ethers. Iron(III)tetraphenylporphyrinato triflate, Fe(tpp)OTf, has been used for rearrangement of α,β-epoxy ketones into 1,2-diketones and chromium(III)tetraphenylporphyrinato triflates, Cr(tpp)OTf, has been reported for highly regio- and stereoselective rearrangement of epoxides to aldehydes [33–36].

Recently, we have reported the use of tin(IV)tetraphenylporphyrinato perchlorate [37,38], tin(IV)tetraphenylporphyrinato trifluoromethanesulfonate [39,40], and tin(IV)tetraphenylporphyrinato tetrafluoroborate [41,42] in organic synthesis.

In this paper, we wish to report a rapid and highly efficient method for trimethylsilylation of alcohols and phenols with hexamethyldisilazane catalyzed by high-valent $[Sn^{IV}(TPP)(BF_4)_2]$ at room temperature (Scheme 1).

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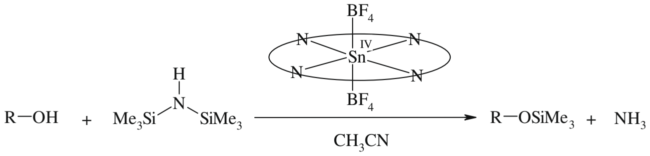


Scheme 1. Trimethylsilylation of alcohols and phenols with HMDS catalyzed by $[Sn^{IV}(TPP)(BF_4)_2]$.

2. Experimental

Chemicals were purchased from Merck chemical company. ^1H NMR spectra were recorded in $CDCl_3$ solvent on a Bruker AM 80 MHz or a Bruker AC 400 MHz spectrometer using TMS as an internal standard. Infrared spectra were run on a Philips PU9716 or Shimadzu IR-435 spectrophotometer. All analyses were performed on a Shimadzu GC-16A instrument with a flame ionization detector using silicon DC-200 or Carbowax 20M columns and *n*-decane was used as internal standard. The tetraphenylporphyrin was prepared and metallated according to the literature [43,44]. The $[Sn^{IV}(TPP)(BF_4)_2]$ catalyst was prepared as reported previously [40].

Table 1
Investigation of catalytic activity of different metalloporphyrin catalysts in the trimethylsilylation of 4-chlorobezyl alcohol with HMDS.[a]

Entry	Catalyst	Time (min)	Yield (%)[b]
1	$[Sn^{IV}(TPP)(BF_4)_2]$	1	100
2	$[SnIV(TPP)Cl_2]$	1	21
3	$[Fe^{III}(TPP)(BF_4)]$	1	77
4	$[Mn^{III}(TPP)(BF_4)]$	1	43
5	$[Fe^{III}(TPP)Cl]$	1	26
6	$[Mn^{III}(TPP)Cl]$	1	17
7	$[Cu(TPP)]$	1	8

[a] Reaction conditions: 4-chlorobenzyl alcohol (1 mmol), HMDS (0.5 mmol), catalyst (1 mol%), CH_3CN (0.5 ml).
[b] GC yield.

2.1. General procedure for the silylation of alcohols and phenols with HMDS catalyzed by $[Sn^{IV}(TPP)(BF_4)_2]$

A mixture of alcohol or phenol (1 mmol), $[Sn^{IV}(TPP)(BF_4)_2]$ (10 mg, 0.01 mmol) and HMDS (0.5 mmol per OH group) in CH_3CN (1 mL) was prepared and stirred at room temperature for appropriate time (Table 1). The progress of the reaction was monitored by GC and TLC in 30 s intervals. After completion of the reaction, the

Table 2
Trimethylsilylation of alcohols with HMDS catalyzed by $[Sn^{IV}(TPP)(BF_4)_2]$ at room temperature.[a]

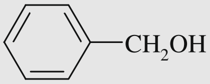
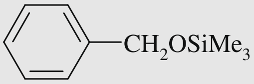
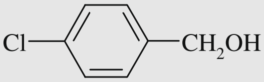
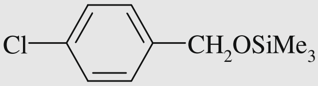
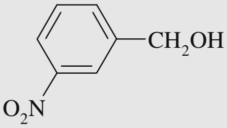
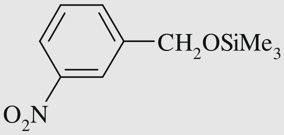
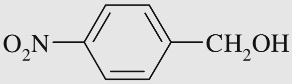
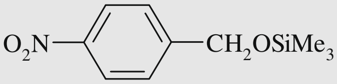
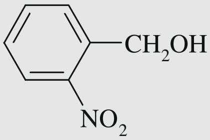
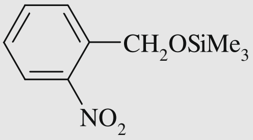
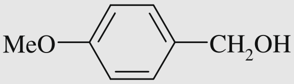
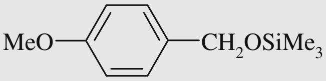
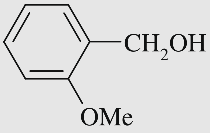
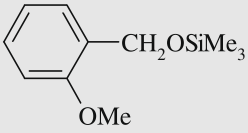
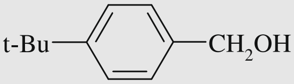
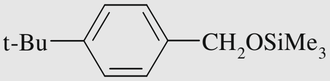
Entry	Hydroxy compound	TMS-ether	Time (min)	Yield (%)[b]
1			1	100
2			1	100
3			2	100
4			2	100
5			2	100
6			1	100
7			2	100
8			1	100

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Table 2 (*continued*)

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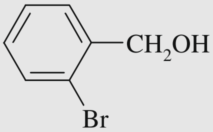
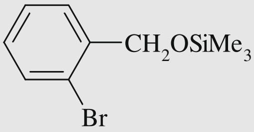
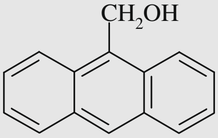
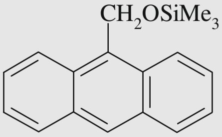
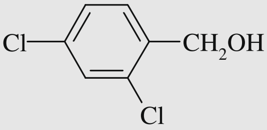
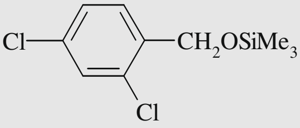
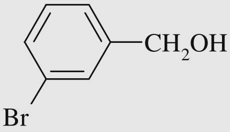
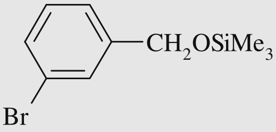
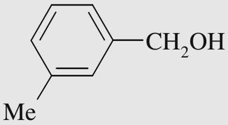
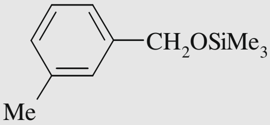
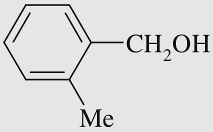
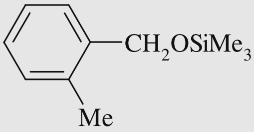
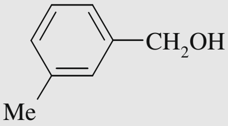
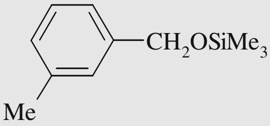
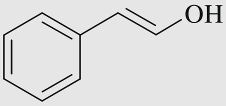
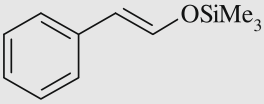
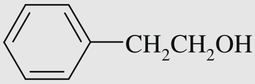
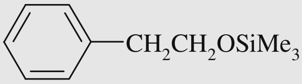
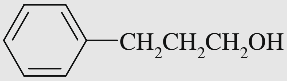
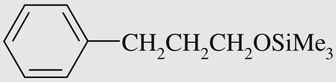
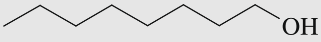
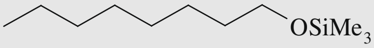
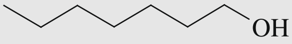
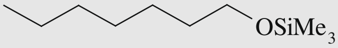
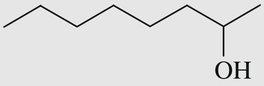
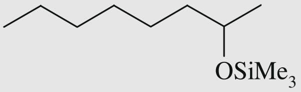
9			1	100
10			1	100
11			1	100
12			1	100
13			1	100
14			1	100
15			1	100
16			1	100
17			1	100
18			1	100
19			1	100
20			1	100
21			2	100

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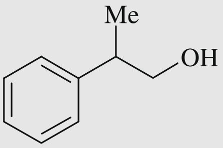
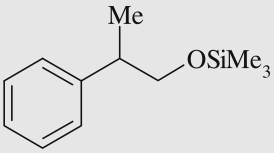
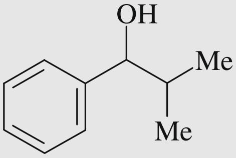
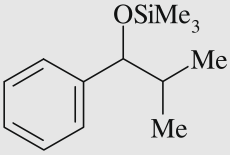
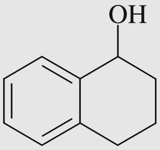
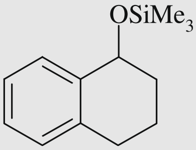
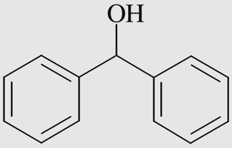
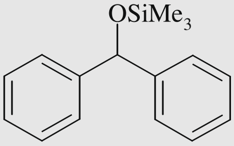
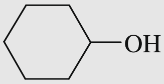
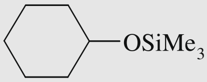
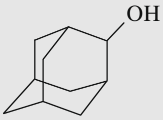
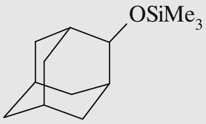
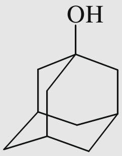
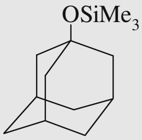
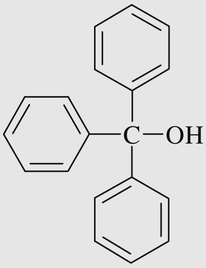
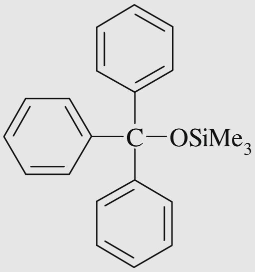
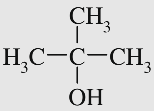
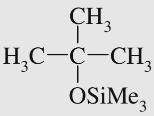
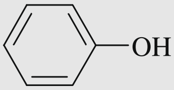
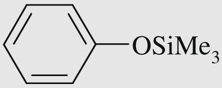
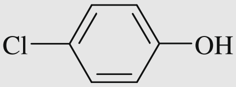
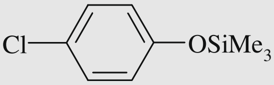
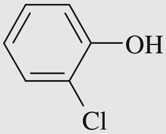
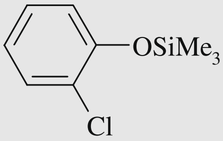
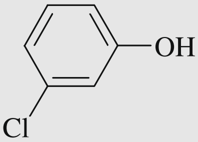
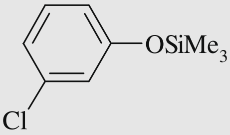
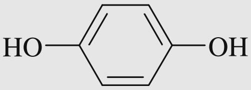
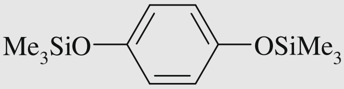
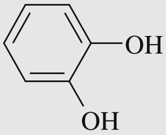
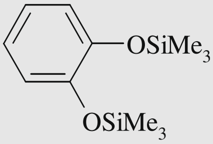
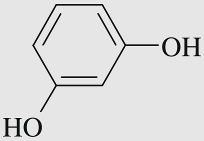
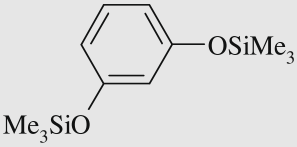
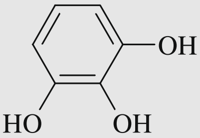
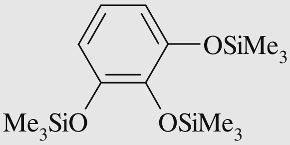
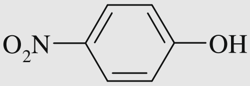
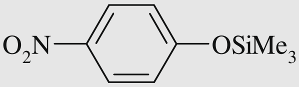
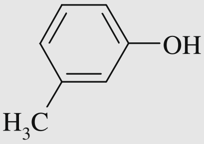
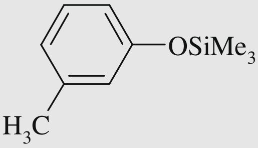
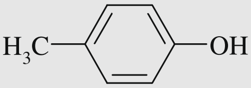
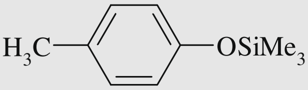
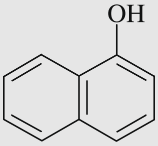
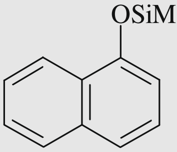
22			1	100
23			1.5	100
24			1	100
25			1	100
26			2	95
27			2	100
28			5	99
29			2	97
30	 $H_3C-\overset{CH_3}{\underset{OH}{C}}-CH_3$	 $H_3C-\overset{CH_3}{\underset{OSiMe_3}{C}}-CH_3$	1	97

[a] Reaction conditions: alcohol (1 mmol), HMDS (0.5 mmol), catalyst (1 mol%), CH_3CN (1 mL).

[b] GC yield.

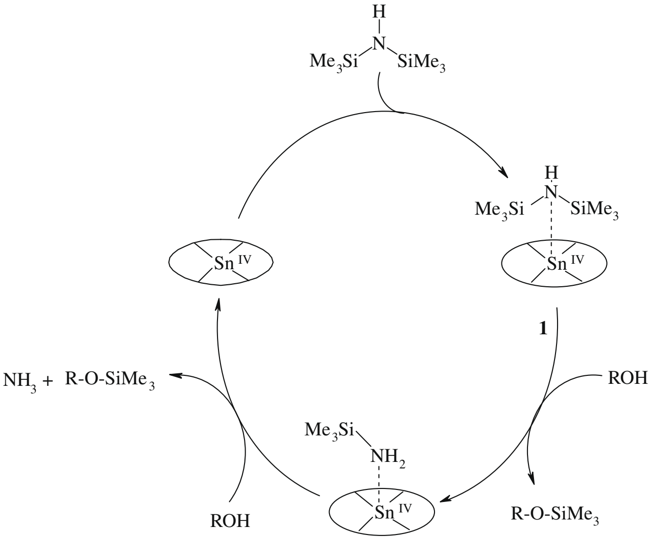
Table 3
Trimethylsilylation of phenols with HMDS catalyzed by $[Sn^{IV}(TPP)(BF_4)_2]$ at room temperature.[a]

Entry	Phenol	TMS-ether	Time (min)	Yield (%)[b]
1			1.5	100
2			2	100
3			2	100
4			2	100
5[c]			2	100
6[c]			2	100
7[c]			2	100
8[c]			2	100
9			2.5	100
10			2	100
11			2	100
12			2	100

[a] Reaction conditions: phenol (1 mmol), HMDS (0.5 mmol), catalyst (1 mol%), CH_3CN (1 mL).

[b] GC yield.

[c] Reaction was performed with 0.5 mmol of HMDS per OH group.



Scheme 2. Proposed mechanism for trimethylsilylation of alcohols and phenols with HMDS catalyzed by $[\mathrm{Sn^{IV}(TPP)(BF_4)_2}]$.

solvent was evaporated, *n*-hexane (10 mL) was added and the catalyst was filtered. The filtrates were washed with brine and dried over Na_2SO_4 and concentrated under reduced pressure to afford the crude product, which was confirmed by ^1H NMR and IR spectral data.

2.2. Catalyst recovery and reuse

The reusability of $[\mathrm{Sn^{IV}(TPP)(BF_4)_2}]$ was investigated in the repeated silylation reaction of 4-chlorobenzyl alcohol. The reactions were carried out as described above. At the end of each reaction, the solvent was evaporated and *n*-hexane was added. The catalyst was filtered, washed with *n*-hexane (10 mL) and dried before using in the next run.

3. Results and discussion

3.1. Silylation of alcohols and phenols with HMDS catalyzed by $[\mathrm{Sn^{IV}(TPP)(BF_4)_2}]$

Although metalloporphyrins are widely used as oxidation catalysts, there have been few studies on their catalytic activity as Lewis acids [27–42]. Since the metalloporphyrins are mild Lewis acids, we investigated their ability in the silylation of hydroxy compounds with HMDS. First, in order to choose the appropriate catalyst, different metalloporphyrins were used as catalysts in the silylation of 4-chlorobenzyl alcohol with HMDS. These results (Table 1) showed that amongst them, the $[\mathrm{Sn^{IV}(TPP)(BF_4)_2}]$ is the most efficient catalyst in the silylation reaction. In the case of tin

Table 4
Selective silylation of alcohols and phenols catalyzed by $[\mathrm{Sn^{IV}(TPP)(BF_4)_2}]$ in CH_3CN.[a]

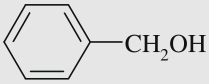
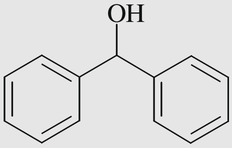
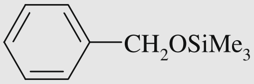
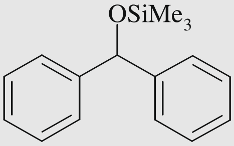
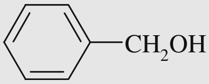
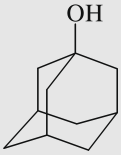
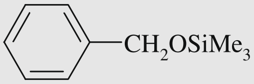
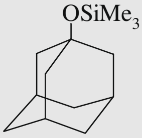
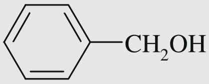
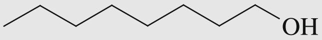
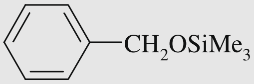
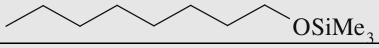
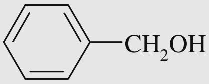
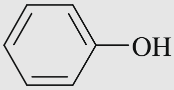
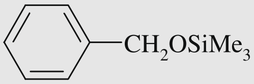
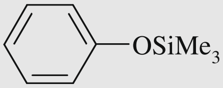
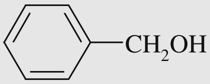
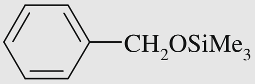
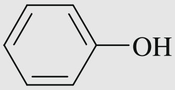
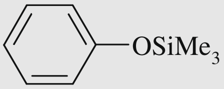
Row	ROH	Silyl ether	Time (min)	Yield (%)[b]
1	 	 	1	100 0
2	 	 	1	100 0
3	 	 	1	88 12
4	 	 	1	100 0

Table 4 (*continued*)

Row	ROH	Silyl ether	Time (min)	Yield (%)[b]
5[c]			1	100
				100

[a] Reaction conditions for a binary mixture: 1 mmol of each alcohol or phenol, HMDS (0.5 mmol), catalyst (1 mol%), CH_3CN (1 mL).

[b] GC yield.

[c] 1 mmol of HMDS was used.

porphyrins, it is clear that introducing of BF_4 instead of Cl has increased the electron deficiency of $[Sn^{IV}(TPP)(BF_4)_2]$ which in turn increases its catalytic activity.

The optimized conditions which obtained for silylation of 4-benzyl alcohol were alcohol, HMDS and catalyst in a molar ratio of 100:50:1. Under the optimized reaction conditions, a wide variety of alcohols were converted completely to their corresponding silyl ethers. The obtained results for silylation of different primary, secondary (including aliphatic and aromatic alcohols) and tertiary alcohols showed that the reaction was immediately completed for all alcohols at room temperature and no alcohol was detected by TLC or GC (Table 2). These results showed that the nature of substituents in benzylic alcohols (electron-withdrawing or electron-releasing) has no significant effect on the yields of silyl ethers. Blank experiments in the absence of catalyst showed that only small amounts of the corresponding silyl ethers were produced.

The high catalytic activity of this catalyst in the silylation of alcohols, prompted us to investigate its ability in the silylation of phenols. In this manner, different phenols were subjected to silylation with HMDS. The reaction conditions were as described for alcohols. These results (Table 3) showed that all reactions were completed in 1–3 min for all phenols and the desired silyl ethers were obtained in excellent yields at room temperature. The silylation of polyhydroxybenzenes such as hydroquinone, pyrocatechol, resorcinol and pyrogallol was also performed. The results showed that all hydroxyl groups were silylated and the desired poly(trimethylsilyl ether) were obtained in excellent yields (Table 3, entries 5–8).

During the reactions the fast evolution of ammonia gas was observed (the evolution of NH_3 was tested by Nessler's test). On this basis, a probable mechanism has been shown in Scheme 2. In this mechanism, the Lewis acid–base interaction between porphyrin tetrafluoroborate and nitrogen in HMDS polarizes the N–Si bond of HMDS and a reactive silylating agent (**1**) is produced, which effectively silylates the hydroxyl compounds.

The selectivity of this method was also investigated. As shown in Table 4, primary alcohols were completely converted to the corresponding silyl ether in the presence of a secondary or tertiary alcohols or phenols (Table 4, entries 1, 2 and 4). Also, in a binary mixture of benzyl alcohol and 1-octanol, the benzyl alcohol was converted to the corresponding silyl ether in 88% yield, while only 12% of the corresponding silyl ether was observed for the aliphatic alcohol (Table 4, entry 3). It seems that the higher reactivity of primary in comparison with secondary and tertiary alcohols is due to the less steric hindrance of primary alcohols for attacking to silylating agent (**1**). Selective trimethylsilylation of alcohols in the presence of phenols is attributed to higher nucleophilicity of alcohols. Note that these results have been obtained in the presence of 0.5 mmol of HMDS. When, 1 mmol of HMDS was used both substrates were converted completely to their corresponding TMS-ethers.

3.2. Reusability of catalyst

The reusability of the catalyst was checked using multiple silylation of 4-chlorobenzylalcohol with HMDS. At the end of the reaction, the solvent was evaporated and *n*-hexane was added. The catalyst was filtered and used in the next run. The results showed that after reusing the catalyst for several times (four consecutive runs were checked), no change was observed in its catalytic activity.

4. Conclusion

In this paper, another application of electron deficient tin(IV)tetraphenylporphyrinato tetrafluoroborate, $[Sn^{IV}(TPP)(BF_4)_2]$, which is a stable Sn(IV) compound, is reported. This catalyst was successfully used for rapid, efficient and chemoselective silylation of primary, secondary and tertiary alcohols and phenols with 1,1,1,3,3,3-hexamethyldisilazane (HMDS). Short reaction times, excellent yields, easy work-up and stability and reusability of the catalyst are noteworthy advantages of this method.

Acknowledgement

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