Note

# Preparation of Silica Supported Tin Chloride: As a Recyclable Catalyst for the Silylation of Hydroxyl Groups with HMDS

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Silica-supported tin chloride [$SiO_2$-$Sn(Cl)_{4-n}$] has been prepared by mixing tin chloride with activated silica gel in toluene under refluxing conditions for one day. A range of primary, secondary, and tertiary alcohols as well as phenolic hydroxyl groups were converted into their corresponding trimethylsilyl ethers with hexamethyldisilazane in the presence of catalytic amounts of silica-supported tin chloride at room temperature. An excellent chemoselective silylation of hydroxyl groups in the presence of other functional groups was also observed. This catalyst could be recycled and reused fifteen times without loss of efficiency.

**Keywords:** Silylation; Silica-supported tin chloride; Hydroxyl groups; Alcohols; Catalyst.

## INTRODUCTION

In recent years, the search for environmentally benign chemical processes or methodologies has received much attention.[1] Heterogenization of homogeneous catalysts has been an interesting area of research from the industrial point of view; this combines the advantages of homogeneous catalysts (high activity and selectivity, etc.) with the engineering advantages of heterogeneous catalysts (easy catalyst separation, long catalytic life, easy catalyst regenerability, thermal stability and recyclability).[2] Therefore, attachment of Lewis acids on solid supports has received much attention. One way to convert corrosive, strong Lewis acids into environmentally friendlier catalysts is by supporting them on high-surface-area solids, such as graphite, $Al_2O_3$, $SiO_2$, zeolites, clays, etc. The support has to be thermally and chemically stable during the reaction process and has to provide accessibility and a good dispersion of the active sites.[2,3]

Protection and deprotection of functional groups are inevitable processes for the synthesis of poly-functional compounds. Silylation of alcohols and polyols is one of the most commonly used methods for their protection.[4] Trimethylsilylation is a classic way to produce volatile derivatives of alcohols and polyols, as required for their vapor phase chromatography/mass spectrometric analysis.[5] Another application is conversion of trimethylsilyl ethers into the corresponding dialkyl ethers.[6] Generally, the formation of trimethylsilyl ethers has been carried out by treatment of alcohols with trimethylsilyl chloride or trimethylsilyl triflate in the presence of a base,[7] $Li_2S$,[8] and sometimes a non-ionic superbase catalyst.[9] However, some of these methods have frequently suffered from drawbacks, such as lack of reactivity or the difficulty in removal of amine salts. 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) is a stable, commercially available, and cheap reagent for trimethylsilylation of hydrogen-labile substrates,[10] giving ammonia as the only by-product. On the other hand, silylation, using this silazan-type reagent, is nearly neutral and does not require any special precautions. However, the weak silylating ability of HMDS is the main drawback for this application which in many instances needs forceful conditions and long reaction times. A variety of catalysts such as $(CH_3)_3SiCl$,[11] tungstophosphoric acid,[12] H-β zeolite,[13] $B(C_6F_5)_3$,[14] $LiClO_4$,[15] 1,3-dibromo-5,5-dimethylhydantoin,[16] silica-supported perchloric acid,[17] tribromomelamine,[18] 1,3-dibromo-5,5-diethylbarbituric acid,[19] $LaCl_3$,[20] tribromoisocyanuric acid and DABCO-$Br_2$,[21] vanadium hydrogen sulfate,[22] $Fe(HSO_4)_3$,[23] $ZrO(OTf)_2$,[24] $ZnO$[25] and tetrabutylammonium bromide[26] have been reported for the silylation of hydroxyl groups using HMDS. In addition to the previously reported procedures, the facile and general synthetic methodology for the silylation of alcohols under

essentially neutral conditions is in demand, so this encouraged us to develop an efficient, convenient, and practical procedure for the protection of hydroxyl groups under mild and heterogeneous conditions.

## RESULTS AND DISCUSSION

Along the line of our studies in application of solid acid catalysts in chemical transformations,[27,28] herein we wish to describe the preparation of silica-supported tin chloride as illustrated in Fig. 1, and its use as a catalyst for the conversion of alcohols into the corresponding trimethylsilyl ethers. Silica-supported tin chloride ($SiO_2$-$SnCl_{4-n}$) has been prepared by the reaction of tin tetrachloride with activated silica gel which was proved to be a solid acid of super acid strength.

The FT-IR spectrum of the catalyst (Fig. 2) shows the absorption range of O-Sn asymmetric stretching modes around 500-550 cm$^{-1}$.[29]

Powder X-ray diffraction was run and the strongest peaks of the XRD pattern correspond to the $SiO_2$ plane with the other peaks indexed as the (35), (53), and (67) planes of supported tin chloride (Fig. 3).

The trimethylsilylation of hydroxyl groups is easily carried out at room temperature under mild conditions in
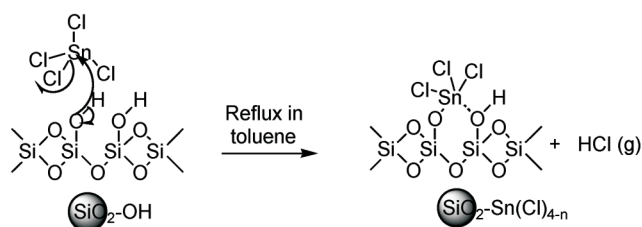
the presence of silica-supported $Sn(Cl)_{4-n}$ as catalyst (Scheme I). First, we tried to convert benzyl alcohol (1 mmol) as a model reaction, to its corresponding silylether with HMDS in the presence of different catalytic amounts of silica-supported $Sn(Cl)_{4-n}$ (Table 1).

**Scheme I** Conversion of different kinds of hydroxyl groups into corresponding silyl ethers in the presence of silica-supported $Sn(Cl)_{4-n}$ as catalyst



$$ROH + HMDS \xrightarrow[CH_3CN; \ rt]{SiO_2-OSnCl_{4-n}} ROSiMe_3 + NH_3$$
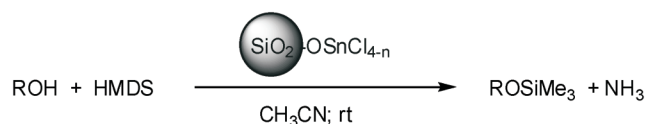
R = primary, secondary, and tertiary alkyl, and aryl

As shown in Table 1, the optimal amount of silica-supported $Sn(Cl)_{4-n}$ was 0.015 g per 1 mmol of benzyl alcohol and 0.8 mmol of HMDS.

Also, to optimize the reaction conditions, the model reaction was employed to screen suitable solvents (Table 2). The results in Table 2 show that amongst these solvents, acetonitrile was the solvent of choice in terms of reaction time and product yield.

Next, we prepared a range of silylethers under the following reaction conditions: hydroxyl compound (1 mmol), HMDS (0.8 mmol), silica-supported $Sn(Cl)_{4-n}$ (0.015 g), and acetonitrile (2 mL) (Table 3). A wide range of various alcohols underwent silylation by this procedure to provide the corresponding TMS ethers in good to excellent yields. Benzylic, primary and secondary alcohols, and also phenols generally react faster than tertiary alcohols. Trimethyl-
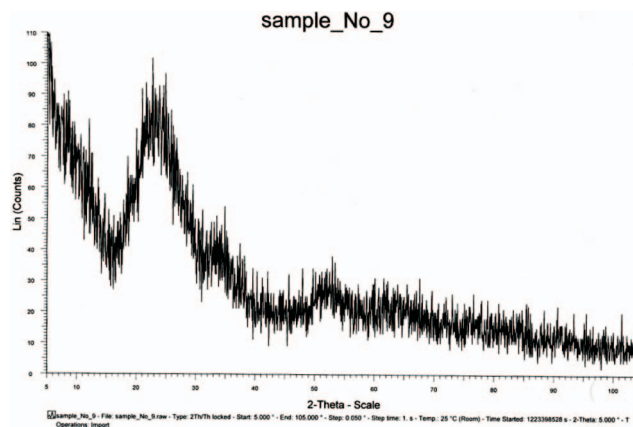


Fig. 1. Probable structure of covalently anchored silica-supported tin chloride.



Fig. 2. FT-IR spectra of silica-supported $Sn(Cl)_{4-n}$.



Fig. 3. XRD of silica-supported $Sn(Cl)_{4-n}$.

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Table 1. Silylation of benzyl alcohols with HMDS in the presence of different catalytic amounts of silica-supported $Sn(Cl)_{4-n}$ in acetonitrile at room temperature[a]

| Entry | The amounts of catalyst (g) | Time (min) | Conversion (%) |
|---|---|---|---|
| 1 | 0.005 | 60 | 50 |
| 2 | 0.01 | 30 | 90 |
| 3 | 0.015 | 5 | 100 |
| 4 | 0.03 | 5 | 100 |

[a] The molar ratios of substrate: HMDS were used as follows 1: 0.8 mmol respectively.

Table 2. Silylation of benzyl alcohols with HMDS in the presence of silica-supported $Sn(Cl)_{4-n}$ as catalyst at room temperature in different solvents[a]

| Entry | Solvent[b] | Time (min) | Conversion (%) |
|---|---|---|---|
| 1 | n-Hexane | 300 | 80 |
| 2 | Dichloromethane | 300 | 90 |
| 3 | Chloroform | 300 | 25 |
| 4 | Ethyl acetate | 100 | 82 |
| 5 | Diethyl ether | 300 | 68 |
| 6 | Acetonitrile | 5 | 100 |
| 7 | Acetone | 300 | 75 |

[a] The molar ratios of substrate: HMDS: Cat. were used as follows 1: 0.8: mmol and 0.015 g, respectively.
[b] The amount of solvent chosen was 2 mL.

silylation of hydroxyl groups produce corresponding trimethylsilylated compounds under these conditions, whereas substituted thiophenol, 1-butantiol (Table 3, entries 17, and 29, 30), aniline and aliphatic amines derivatives (Table 3, entries 26-28) and *N*-phenyl acetamide (Table 3, entry 31) remained intact under the reaction conditions. Allylic and propargylic alcohols such as cinnamyl, allyl and propargyl alcohols converted to unidentified polymeric material under these conditions (Table 3, entry 25-27).[12] It is worth mentioning that in the case of *p*-aminophenol only the phenolic group reacted under these conditions and the amino group remains intact (Table 3, entry 6).

We investigated selective silylation of mixtures of alcohols in the presence of amine, amide, and thiol functionalities. This method was shown to be highly selective for the primary alcohols such as benzyl alcohol and 2-phenylethanol. The primary alcohols were completely converted to the corresponding silyl ethers, while tertiary alcohols were untouched (Scheme II, Table 3, entries 6 and 17). Excellent chemoselectivity was also observed for the conversion of secondary alcohols and phenols in the presence of

**Scheme II** Chemoselectivity between primary, secondary alcohols and phenols in the presence of tertiary alcohols and amides using silica-supported $Sn(Cl)_{4-n}$ with HMDS
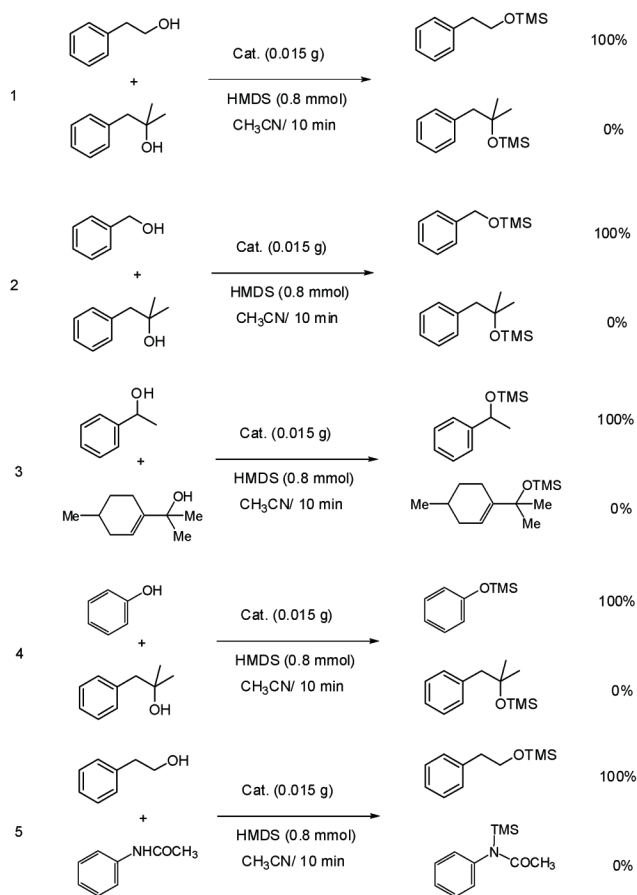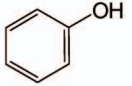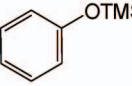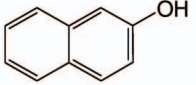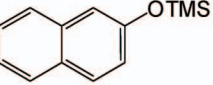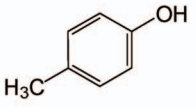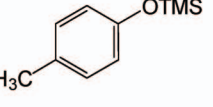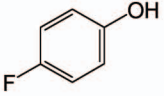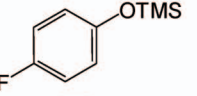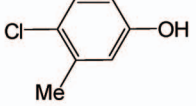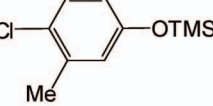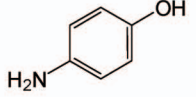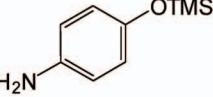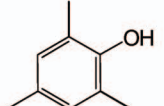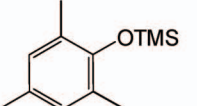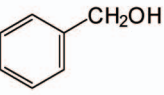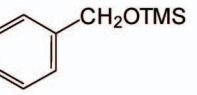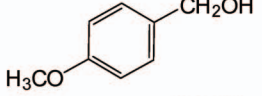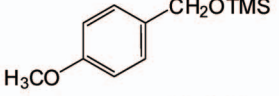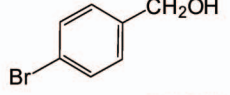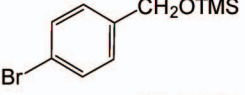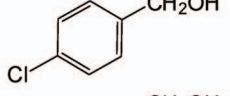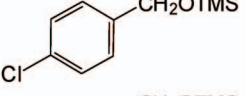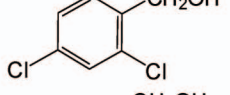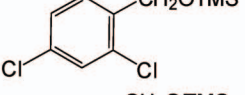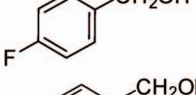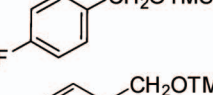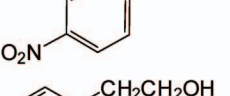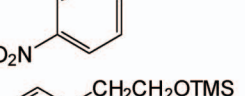


tertiary alcohols such as α-terpinene, 1-phenyl-2-methyl-2-propanol.

We also explored the chemoselectivity of silica-supported $Sn(Cl)_{4-n}$ in the silylation method. Alcohols and phenols in the presence of an amine, amide and thiols were completely converted to the corresponding trimethylsilyl ethers as the sole product.

To show the efficiency of the silica-supported $Sn(Cl)_{4-n}$ in comparison with some previously reported procedures, Table 4 compares some of our results with H-β zeolite,[13] $LiClO_4$-$SiO_2$,[15] $LaCl_3$,[20] $Fe(HSO_4)_3$,[23] $ZrO(OTf)_2$,[24] and $ZnO$[25] with respect to reaction times and yields.

In all the reactions we have studied, fast evolution of ammonia gas was observed. With this observation we have proposed a mechanism in which the generation of $NH_3$ and the role of silica-supported $Sn(Cl)_{4-n}$ in a catalytic cycle is clarified (Scheme III).[17,22]

Table 3. Silylation of alcohols, phenols, and naphthols with HMDS in the presence of silica-supported $Sn(Cl)_{4-n}$ as catalyst at room temperature[a]

| Entry | Substrate | Product | Time (min) | Yield[b] % |
|-------|-----------|---------|------------|------------|
| 1 | phenol (OH) | phenol (OTMS) | 4 | 95 |
| 2 | naphthol (OH) | naphthol (OTMS) | 4 | 88 |
| 3 | 4-methylphenol ($H_3C$, OH) | 4-methylphenol ($H_3C$, OTMS) | 5 | 90 |
| 4 | 4-fluorophenol (F, OH) | 4-fluorophenol (F, OTMS) | 5 | 88 |
| 5 | chloro-methyl phenol (Cl, Me, OH) | chloro-methyl phenol (Cl, Me, OTMS) | 3 | 90 |
| 6 | 4-aminophenol ($H_2N$, OH) | 4-aminophenol ($H_2N$, OTMS) | 5 | 89 |
| 7 | trimethylphenol (OH) | trimethylphenol (OTMS) | 5 | 88 |
| 8 | benzyl alcohol ($CH_2OH$) | benzyl ($CH_2OTMS$) | 5 | 92 |
| 9 | $H_3CO$, $CH_2OH$ | $H_3CO$, $CH_2OTMS$ | 6 | 92 |
| 10 | Br, $CH_2OH$ | Br, $CH_2OTMS$ | 6 | 90 |
| 11 | Cl, $CH_2OH$ | Cl, $CH_2OTMS$ | 3 | 92 |
| 12 | Cl, Cl, $CH_2OH$ | Cl, Cl, $CH_2OTMS$ | 4 | 94 |
| 13 | F, $CH_2OH$ | F, $CH_2OTMS$ | 10 | 91 |
| 14 | $O_2N$, $CH_2OH$ | $O_2N$, $CH_2OTMS$ | 8 | 90 |
| 15 | $CH_2CH_2OH$ | $CH_2CH_2OTMS$ | 6 | 95 |

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| Entry | Substrate | Product | Time (min) | Yield (%) |
|---|---|---|---|---|
| 16 | PhCH₂CH₂CH₂OH | PhCH₂CH₂CH₂OTMS | 6 | 92 |
| 17 | HS–CH₂CH₂–OH | HS–CH₂CH₂–OTMS | 5 | 88 |
| 18 | cyclohexanol (OH) | cyclohexyl–OTMS | 5 | 89 |
| 19 | Ph₂CH–OH | Ph₂CH–OTMS | 3 | 93 |
| 20 | PhCH(OH)CH₃ | PhCH(OTMS)CH₃ | 5 | 91 |
| 21 | 1-indanol (OH) | 1-indanyl–OTMS | 3 | 91 |
| 22 | PhCH₂C(Me)₂OH | PhCH₂C(Me)₂OTMS | 360 | 72 |
| 23 | Me-cyclohexenyl-C(Me)₂OH | Me-cyclohexenyl-C(Me)₂OTMS | 360 | 71 |
| 24 | furfuryl–OH | furfuryl–OTMS | 10 | 88 |
| 25 | cinnamyl–OH | cinnamyl–OTMS | 10 | –[c] |
| 26 | allyl–OH | allyl–OTMS | 10 | –[c] |
| 27 | propargyl–OH | propargyl–OTMS | 10 | –[c] |
| 28 | Ph–NH₂ | Ph–NHTMS | 180 | No Reac. |
| 29 | PhCH₂–NH₂ | PhCH₂–NHTMS | 180 | No Reac. |
| 30 | Ph–NH–Ph | Ph–N(TMS)–Ph | 180 | No Reac. |
| 31 | n-Bu–SH | n-Bu–STMS | 180 | No Reac. |
| 32 | 4-Br–C₆H₄–SH | 4-Br–C₆H₄–STMS | 180 | No Reac. |
| 33 | Ph–NHCOCH₃ | Ph–N(TMS)COCH₃ | 180 | No Reac. |

[a] The molar ratios of substrate: HMDS: Cat. were used as follows 1: 0.8 and 0.015 (g), respectively. [b] Isolated Yield. [c] Unidentified polymeric material was isolated.

Table 4. Comparison of the results of silica-supported Sn(Cl)$_{4-n}$ (**I**)[a] with H-β zeolite (**II**)[b] [13], LiClO$_4$-SiO$_2$ (**III**)[c] [16], LaCl$_3$ (**IV**)[d] [28], Fe(HSO$_4$)$_3$ (**V**)[e] [31], ZrO(OTf)$_2$ (**VI**)[f] [32], and ZnO (**VII**)[g] [33] in the synthesis of trimethylsilyl ether using HMDS

| Entry | Substrate | Time (min)/Yield (%)[h] | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | I | II | III | IV | V | VI | VII |
| 1 | ![benzyl alcohol] CH$_2$OH | 5/92 | 300/95 | 5/98 | 180/91 | 13/90[i] | 1/100[j] | 5/95 |
| 2 | ![naphthol] OH | 4/88 | 20h/67 | 120/84 | - | - | 4/100[j] | 5/93 |
| 3 | ![cyclohexanol] OH | 5/89 | 700/95 | 5/96 | - | 20/80[i] | 1/100[j] | 120/91 |
| 4 | ![1-phenylethanol] OH | 5/91 | - | 30/89 | 180/94 | 24/80[i] | 4/100[j] | 7/89 |
| 5 | ![phenethyl alcohol] CH$_2$CH$_2$OH | 6/95 | - | - | 240/88 | - | 1/100[j] | 11/92 |

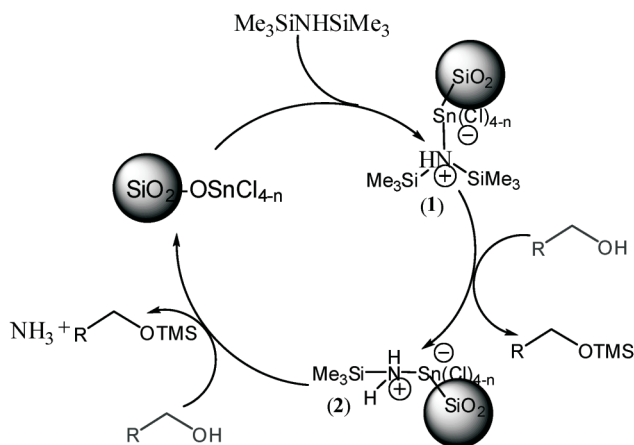The equivalent ratios of substrate/HMDS/catalyst are [a] 1/0.8/0.015 (g), [b] 1/0.6/[10%(w/w)], [c] 1/0.6/0.1 (g), [d] 1/0.7/0.2, [e] 1/1/0.25, [f] 1/2/(0.5 mol%), [g] 1/0.7/0.05 g, respectively. [h] Isolated Yield. [i] Conditions heated in an oil bath at 90-100 C. [j] GC Yields.

**Scheme III** Proposed mechanism for the conversion of alcohols into corresponding silyl ether by using silica-supported Sn(Cl)$_{4-n}$



The possibility of recycling the catalyst was examined. For this reason, the reaction of benzyl alcohol and HMDS was studied in acetonitrile at room temperature in the presence of silica-supported Sn(Cl)$_{4-n}$. When the reaction was complete, the mixture was filtered and the catalyst was washed with dichloromethane and reused. The recy-cled catalyst could be reused fifteen times without any treatment. No observation of appreciable loss in its catalytic activities was shown (Fig. 4).
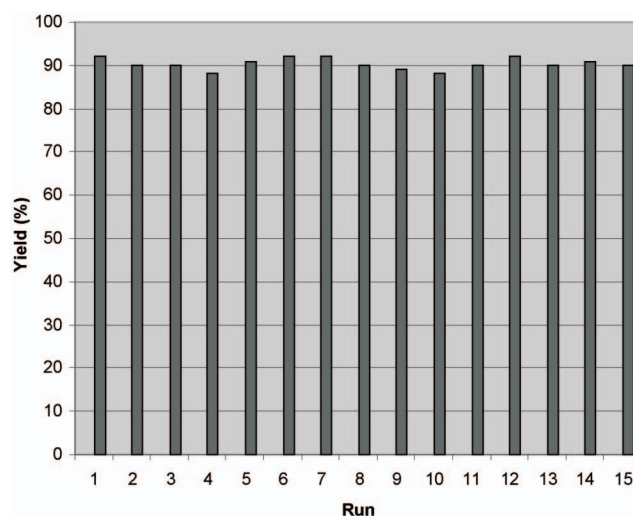


Fig. 4. Recyclability of silica-supported Sn(Cl)$_{4-n}$ (0.015 g) as catalyst in the silylation reaction of benzyl alcohol (1 mmol) and HMDS (1 mmol) at room temperature. Reaction time = 5 min.

**CONCLUSION**

In conclusion, a practical, efficient and convenient method for the silylation of hydroxyl compounds was described. Also, we prepared and introduced $SnCl_4$ supported on silica gel as an efficient and reusable catalyst. Therefore, we think that this method can be a useful addition to the present methodologies for the silylation of hydroxyl groups.

**EXPERIMENTAL SECTION**
**General**

Chemicals were purchased from Merck, Fluka and Aldrich Chemical Companies. IR spectra were run on a Shimadzu Infra Red Spectroscopy FT-IR-8000. The ^{1}H NMR were run on a JEOL NMR-Spectrometer FX 90Q and a Bruker Avance (DRX 500 MHz). Melting points were recorded on a Melting Point SMP1 apparatus in open capillary tubes and are uncorrected. With TLC using silica gel SILG/UV 254 plates the progress of reaction was followed. All of the products are known and characterized by comparison of their spectral (IR, ^{1}H-NMR), TLC and physical data with those reported in the literature.[14-22]

**Catalyst preparation**

Silica gel 60 (0.063-0.200 mesh) was washed with 1 M HCl, followed by deionized water, 30% $H_2O_2$, and deionized water again. After being washed, the silica was dried overnight at 373 K in vacuum to give preconditioned silica gel.[2]

**Preparation of silica-supported tin chloride**

4.0 g of preconditioned silica was first refluxed in toluene for 2 h. Then tin chloride (5.5 mL) was added to this mixture and allowed to react for 1 day under refluxing condition. Then, the mixture was filtered and washed three times with absolute ethanol and dried at 373 K to give 5.137 g of product (0.2 g equal to 0.6 mmol $H^+$).

**FT-IR spectrum of silica-supported tin chloride**

The FT-IR spectrum of the catalyst is shown in Fig. 2. The catalyst is solid, and its solid state IR spectrum was recorded using the KBr disk technique. For silica ($SiO_2$), the major peaks are broad antisymmetric Si-O-Si stretching from 1200 to 1000 $cm^{-1}$ and symmetric Si-O-Si stretching near 802 $cm^{-1}$, and bending modes of Si-O-Si lie around 470 $cm^{-1}$. For the O-Sn-Cl group, the FT-IR absorption range of the O-Sn asymmetric stretching modes lies around 500-550 $cm^{-1}$.[29] The spectrum also shows a broad Si-OH stretching absorption from 3600-3000 $cm^{-1}$.

**X-ray diffraction (XRD) of silica-supported tin chloride**

Powder X-ray diffraction measurement was performed using a D8 Advance Diffractometer made by Bruker AXS Company in Germany. The strongest peaks of the XRD pattern correspond to the $SiO_2$ plane with the other peaks indexed as the (35), (53), and (67) planes of supported tin chloride.

**General procedure**

To a stirred solution containing the hydroxyl compound (1 mmol) and HMDS (0.8 mmol) in $CH_3CN$ (2 mL) was added silica supported $Sn(Cl)_{4-n}$ (0.015 g) and stirred at room temperature. When the reaction was complete GC (or TLC, n-hexane-EtOAc, 9:1) analysis, $CH_2Cl_2$ was added (10 mL), and silica supported $Sn(Cl)_{4-n}$ was removed by filtration. The solvent was evaporated and the trimethylsilyl ether was isolated almost as a pure product. Further purification was carried out by short column chromatography on silica gel eluting with ethyl acetate/petroleum ether, if necessary.

**REFERENCES**

1. Choudhary, D.; Paul, S.; Gupta, R.; Clark, J. H. *Green Chem*. **2006**, *8*, 479-482.
2. Li, Z.; Ma, X.; Liu, J.; Feng, X.; Tian, G.; Zhu, A. *J. Mol. Catal. A Chem*. **2007**, *272*, 132.
3. Jyothi, T. M.; Kaliya, M. L.; Herskowitz, M.; Landau, M. V. *Chem. Commun*. **2001**, 992.
4. Greene, T. W.; Wutes, P. G. M. *Greene's Protective Groups in Organic Synthesis*, 4th ed.; Wiley: New York, 2007.
5. Van Look, G.; Simchen, G.; Heberle, J. *Silylating Agents*, 2nd ed.; Fluka, Buches: Switzerland, 1995.
6. Zolfigol, M.-A.; Mohammadpoor-Baltork, I.; Habibi, D.; Mirjalili, B.-F.; Bamoniri, A. *Tetrahedron Lett*. **2003**, *44*, 8165.
7. Corey, E. J.; Sinder, B. B. *J. Am. Chem. Soc*. **1972**, *94*, 2549.
8. Olah, G. A.; Gupta, B. G. B.; Narang, S. C.; Malhotra, R. *J. Org. Chem*. **1979**, *44*, 4272.
9. Sa, B. A. D.; McLeod, D.; Verkade, J. G. *J. Org. Chem*. **1997**, *62*, 5057.
10. Lalonde, M.; Chan, T. H. *Synthesis* **1985**, 817.
11. Gauttret, P.; El-Ghamarti, S.; Legrand, A.; Coutrier, D.; Rigo, B. *Synth. Commun*. **1996**, *26*, 707.

12. Firouzabadi, H.; Iranpoor, N.; Amani, K.; Nowrouzi, F. *J. Chem. Soc. Perkin Trans 1* **2002**, 2601.

13. Tillu, V. H.; Jadhav, V. H.; Borate, H. B.; Wakharkar, R. D. *Arkivoc* **2004**, *14*, 83.

14. Shinke, S.; Tsuchimoto, T.; Kawakami, Y. *Silicon Chem*. **2005**, *3*, 243.

15. Azizi, N.; Yousefi, R.; Saidi, M. R. *J. Organomet. Chem*. **2006**, *691*, 817.

16. Khazaei, A.; Rostami, A.; Mahboubifar, M. *J. Chin. Chem. Soc*. **2007**, *54*, 483-487.

17. Shaterian, H. R.; Shahrekipoor, F.; Ghashang, M. *J. Mol. Catal. A Chem*. **2007**, *272*, 142.

18. Ghorbani-Choghamarani, A.; Zolfigol, M. A.; Hajjami, M.; Jafari, S. *J. Chin. Chem. Soc*. **2008**, *55*, 1208-1213.

19. Khazaei, A.; Zolfigol, M. A.; Tanbakouchian, Z.; Shiri, M.; Niknam, K.; Saien, J. *Catal. Commun*. **2007**, *8*, 917.

20. Narsaiah, A. V. *J. Organomet. Chem*. **2007**, *692*, 3614.

21. Niknam, K.; Zolfigol, M. A.; Chehardoli, G.; Dehghanian, M. *Chin. J. Catal*. **2008**, *29*, 901.

22. Shirini, F.; Zolfigol, M. A.; Abedini, M.; Sakhaei, A. R. *J. Chin. Chem. Soc*. **2008**, *55*, 943-946.

23. Shirini, F.; Zolfigol, M. A.; Abri, A. *Monatsh. Chem*. **2008**, *139*, 17.

24. Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Chahardahcheric, S.; Tavakoli, Z. *J. Organomet. Chem*. **2008**, *693*, 2041.

25. Shaterian, H. R.; Ghashang, M. *Phosphorus, Sulfur Silicon Relat. Elem*. **2008**, *183*, 194.

26. Shirini, F.; Abedini, M. *J. Iran. Chem. Soc*. **2008**, *5*, S87.

27. (a) Zolfigol, M.-A.; Niknam, K.; Nazari, F. *J. Chin. Chem. Soc*. **2006**, *53*, 669-676. (b) Zolfigol, M.-A.; Bagherzadeh, M.; Niknam, K.; Shirini, F.; Mohammadpoor-Baltork, I.; Choghamarani, A.-G.; Baghbanzadeh, M. *J. Iran. Chem. Soc*. **2006**, *3*, 73-80. (c) Niknam, K.; Zolfigol, M.-A.; Khoramabadi-Zad, A.; Zare, R.; Shayegh, M. *Catal. Commun*. **2006**, *7*, 494-498. (d) Zolfigol, M.-A.; Niknam, K.; Bagherzadeh, M.; Choghamarani, A.-G.; Koukabi, N.; Hajjami, M.; Kolvari, E. *J. Chin. Chem. Soc*. **2007**, *54*, 1115-1118. (e) Niknam, K.; Fatehi-Raviz, A. *J. Iran. Chem. Soc*. **2007**, *4*, 438-443. (f) Zolfigol, M. A.; Ghaemi, E.; Madrakian, E.; Niknam, K. *J. Chin. Chem. Soc*. **2008**, *55*, 704-711. (g) Zolfigol, M. A.; Chehardoli, G.; Dehghanian, M.; Niknam, K.; Shirini, F.; Khoramabadi-Zad, A. *J. Chin. Chem. Soc*. **2008**, *55*, 885-889.

28. (a) Niknam, K.; Zolfigol, M.-A.; Sadabadi, T.; Nejati, A. *J. Iran. Chem. Soc*. **2006**, *3*, 318-322. (b) Niknam, K.; Zolfigol, M.-A.; Shayegh, M.; Zare, R. *J. Chin. Chem. Soc*. **2007**, *54*, 1067-1073. (c) Niknam, K.; Zolfigol, M.-A.; Sadabadi, T. *J. Iran. Chem. Soc*. **2007**, *4*, 199-204. (d) Niknam, K.; Zolfigol, M.-A.; Tavakoli, Z.; Heidari, Z. *J. Chin. Chem. Soc*. **2008**, *55*, 1373-1378.

29. Kawakami, K.; Okawara, R. *J. Organomet. Chem*. **1966**, *6*, 249.