Silica-bonded *S*-sulfonic acid as a recyclable catalyst for the silylation of hydroxyl groups with hexamethyldisilazane (HMDS)

Khodabakhsh Niknam, Dariush Saberi, Hajar Molaee, and Mohammad Ali Zolfigol

Abstract: Silica-bonded *S*-sulfonic acid (SBSSA) was prepared by the reaction of 3-mercaptopropylsilica (MPS) and chlorosulfonic acid in *tert*-butylmethyl ether, and used as a catalyst for the silylation of hydroxyl groups. A good range of primary, secondary alcohols and phenolic hydroxyl groups were effectively converted into their corresponding trimethylsilyl ethers with hexamethyldisilazane (HMDS) in the presence of catalytic amounts of SBSSA under mild conditions at room temperature with short reaction times and in good-to-excellent yields. An excellent chemoselective silylation of hydroxyl groups in the presence of other functional groups was also observed. The heterogeneous catalyst was recycled for 30 runs upon the reaction of benzyl alcohol with HMDS without lossing its catalytic activity.

Key words: silylation, silica-bonded *S*-sulfonic acid, hydroxyl groups, alcohols, catalyst.

Résumé : On a préparé de l'acide *S*-sulfonique lié à de la silice par (ASSLS) par réaction du 3-mercaptopropylsilicium (MPS) et de l'acide chlorosulfonique dans le éther de *tert*-butylméthyle et on l'a utilisé comme catalyseur pour la silylation de groupes hydroxyles. On a ainsi pu transformer un ensemble représentatif de groupes hydroxyles d'alcools primaires et secondaires et phénoliques en éthers triméthylsilyles correspondants par réaction avec de l'hexaméthyldisilazane (HMDS) en présence de quantités catalytiques d'acide *S*-sulfonique lié à de la silice, dans des conditions douces, à la température ambiante, avec des courts temps de réaction et avec des rendements allant de bons à excellents. On a pu aussi observer une excellent silylation chimiosélective de groupes hydroxyles en présence d'autres groupes fonctionnels. Le catalyseur hétérogène a pu être recyclé au moins trente fois, sans perte d'activité, pour la réaction de l'alcool benzylique avec le HMDS.

Mots-clés : silylation, acide *S*-sulfonique lié à de la silice, groupes hydroxyles, catalyseur.

[Traduit par la Rédaction]

Introduction

In recent years, there has been much attention on the search for environmentally benign chemical processes or methodologies, because they are essential for the conservation of the global ecosystem. The development of heterogeneous catalysts for fine chemical synthesis has become a major area of research, as the potential advantages of these materials (facile recovery and reusability; the potential for incorporation in continuous reactors and micro reactors) over homogeneous systems can lead to novel environmentally benign chemical procedures for academia and industry.[1] Application of solid acids in organic transformations is desirable, owing to their simplicity in handling, decreased reactor and plant corrosion problems, and more environmentally safe disposal.[2–10] Green chemistry not only requires the use of environmentally benign reagents and solvents, but also requires the use of recyclable catalysts. One way to overcome the problem of recyclability of the traditional acid catalysts is to chemically anchor their reactive center onto an inorganic solid carrier with a large surface area to create new organic–inorganic hybrid catalyst.[5,6] The reactive centers in these solid-supported catalysts are highly mobile similar to homogeneous catalysts, and at the same time have the advantage of recyclability like heterogeneous catalysts. In this view, several types of solid sulfonic-acid-functionalized silica (both amorphous and ordered) have been synthesized and applied as an alternative to traditional sulfonic acid resins and homogeneous acids in catalyzing chemical transformations.[5,7]

Herein, we wish to describe the preparation of silica-bonded *S*-sulfonic acid (SBSSA) as illustrated in Scheme 1, and its use as catalyst for the conversion of alcohols into corresponding trimethylsilyl ethers. Sulfur content of SBSSA by conventional elemental analysis was 16.12%. Typically, a loading at ~0.35 mmol/g is obtained. On the other hand, when the washed sulfonated product **2** was placed in an aqueous NaCl solution, the pH of the solution dropped virtually instantaneously to pH 1.85, as ion exchange occurred between protons and sodium ions (proton exchange capacity: 0.33 mmol/g of sulfonic acid **2**), which is in good agreement with the result obtained from TGA and titration.

Protection and deprotection of functional groups are in-

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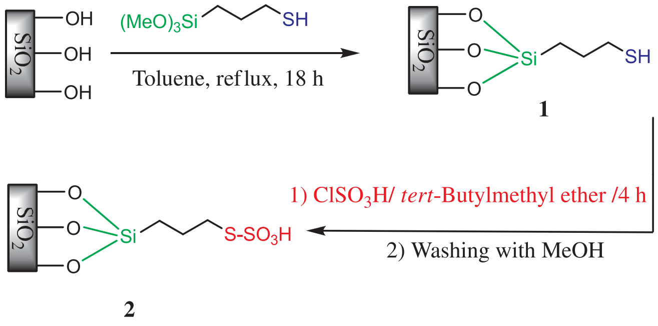
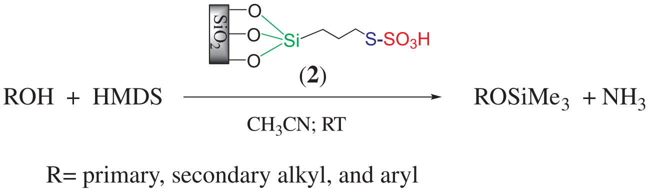
Scheme 1. Preparation of silica-bonded *S*-sulfonic acid.



Scheme 2. Conversion of different kinds of hydroxyl groups into corresponding silyl ethers



evitable processes for the synthesis of polyfunctional compounds. Silylation of alcohols and polyols is one of the most commonly used methods for their protection.[11] Trimethylsilylation is a classic way to produce volatile derivatives of alcohols and polyols, as required for their vapor-phase chromatography/mass spectrometric analysis.[12] Another application is the conversion of trimethylsilyl ethers into the corresponding ethers.[13] 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,[14] Li_2S,[15] and sometimes a nonionic super base catalyst.[16] However, some of these methods have frequently suffered from drawbacks, such as lack of reactivity or the difficulty in removal of amine salts derived from the reaction of by-produced acid and co-bases during the silylation reaction. 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) is a stable, commercially available, and inexpensive reagent for trimethylsilylation of hydrogen-labile substrates,[17] giving ammonia as the only byproduct. On the other hand, silylation, using this silazan-type reagent, is nearly neutral and does not need any special precautions. However, the weak silylating ability of HMDS is a main drawback for its application, which needs forceful conditions and long reaction times in many instances. A variety of catalysts, such as $(CH_3)_3SiCl$,[18] silica chloride,[19] $ZnCl_2$,[20] $LiClO_4$,[21] H-β zeolite,[22] tungestophosphoric acid,[23] poly(*N*-bromobenzene-1,3-disulfonamide),[24] ultrasound,[25] $CuSO_4{\cdot}5H_2O$ and $Cu(OTf)_2$,[26] $Al(HSO_4)_3$,[27] KBr,[28] silica-supported perchloric acid,[29] sulfonic-acid-functionalized silica,[30] silica sulfuric acid,[31] 1,3-dibromo-5,5-diethylbarbituric acid,[32] tribromoisocyanuric acid and DABCO-Br_2,[33] $Fe(F_3CCO_2)_3$,[34] tetrabutylammonium bromide,[35] tribromomelamine,[36] and alumina sulfuric acid[37] 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 desirable, so this subject encouraged us to develop an efficient, convenient, and practical procedure for the protection of hydroxyl groups under mild and heterogeneous conditions.

Results and discussion

The trimethylsilylation of hydroxyl groups is easily carried out at room temperature under mild conditions in the presence of SBSSA as a catalyst (Scheme 2). First, we studied the reaction of 4-bromobenzyl alcohol with HMDS in the presence of SBSSA in CH_3CN at room temperature. The optimal amount of the catalyst was 0.015 g per 1 mmol of 4-bromobenzyl alcohol and 0.8 mmol of HMDS. Next, we prepared a range of silylethers under the following reaction conditions: hydroxyl compound (1 mmol), HMDS (0.8 mmol), SBSSA (0.015 g), and acetonitrile (2 mL) (Table 1). A wide range of alcohols underwent silylation by this procedure to provide the corresponding TMS ethers in good-to-excellent yields. Generally, benzylic alcohols, phenols, and primary and secondary alcohols are faster than tertiary alcohols. Trimethylsilylation of hydroxyl groups produce corresponding trimethylsilylated compounds under these conditions, whereas substituted thiophenol, 1-butantiol (Table 1, entries 8, 25, and 26), aniline derivatives, aliphatic amines (Table 1, entries 22–24), and *N*-phenyl acetamide (Table 1, entry 27) remained intact under the reaction conditions. 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 1, entry 19).

We investigated the selective silylation of different binary mixture of alcohols and also alcohols and phenols in the presence of amine, amide, and thiols. This method was shown to be highly selective for primary alcohols, such as benzyl alcohol and 2-phenylethanol. Primary alcohols were completely converted to the corresponding silyl ethers, while tertiary alcohols were converted to the corresponding silylated products with 0% yield (Scheme 3).

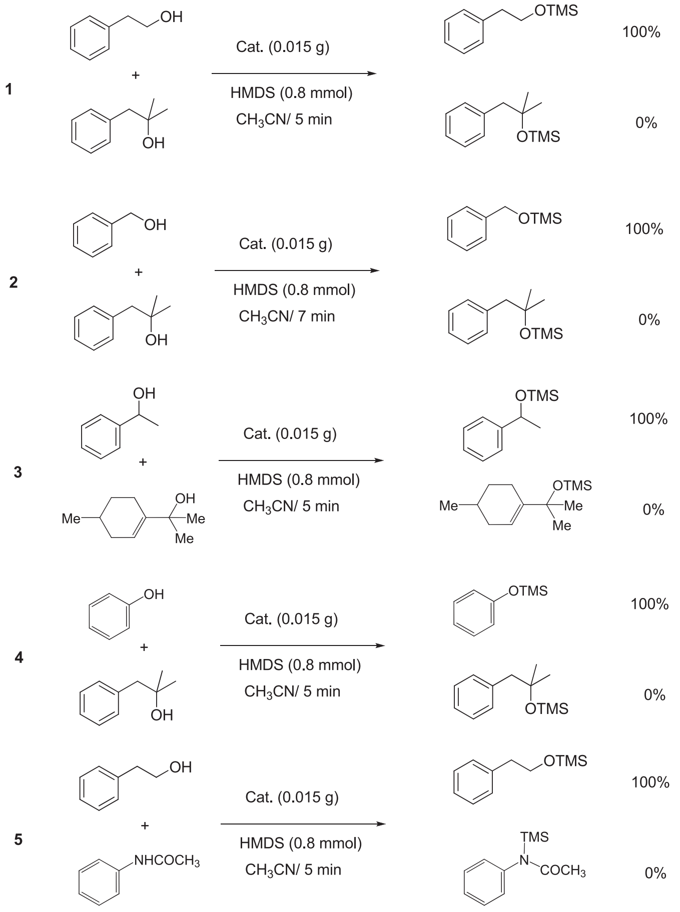
Excellent chemoselectivity was also observed for the conversion of secondary alcohols and phenols in the presence of tertiary alcohols such as α-terpinene, 1-phenyl-2-methyl-2-propanol (Scheme 3). We also explored the chemoselectivity of SBSSA in the silylation method. Alcohols and phenols in the presence of an amine, amide, and thiols were completely converted to the corresponding trimethylsilyl ethers as sole product.

To show the efficiency of the SBSSA in comparison with previously reported procedures, Table 2 compares some of our results with $LiClO_4$'/SiO_2,[21] H-β zeolite,[22] $HClO_4$/SiO_2,[29] sulfonic-acid-functionalized silica,[30] silica sulfuric acid,[31] and alumina sulfuric acid[37] with respect to reaction times and yields of obtained products. It is clear from the results shown in Table 2, that silylation reactions carried out with SBSSA require shorter reaction times and lower catalyst loading.

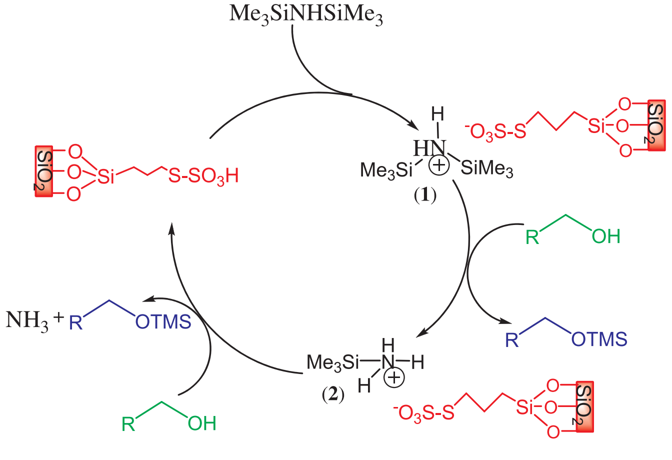
In all reactions studied, fast evolution of ammonia gas was observed (HMDS is stronger base than NH_3). With this observation, we have proposed a mechanism in which the generation of NH_3 and catalytic role of SBSSA in a catalytic cycle is clarified (Scheme 4).[29,34]

The possibility of recycling the catalyst was examined. For this purpose, the reaction of benzyl alcohol and HMDS

Scheme 3. Chemoselectivity between primary, secondary alcohols, and phenols in the presence of tertiary alcohols and amides using SBSSA with HMDS.

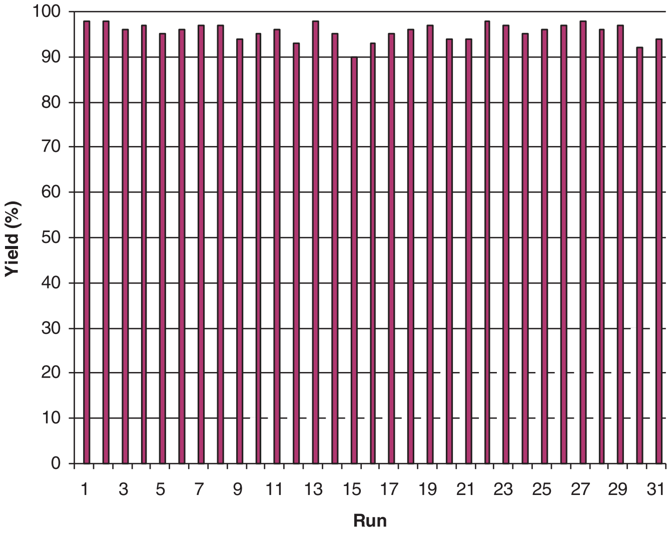


Scheme 4. Proposed mechanism for the conversion of alcohols into the corresponding silyl ether by using SBSSA.



was studied in acetonitrile at room temperature in the presence of SBSSA. When the reaction was complete, the mixture was filtered and the solid was washed with dichloromethane, and the recycled catalyst was saved for the next reaction. The recycled catalyst could be directly reused 30 times without any treatment. No observation of appreciable loss in its catalytic activities was noticed (Fig. 1).

Fig. 1. Recyclability of solid silica-bonded *S*-sulfonic acid 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. One major advantage of our described method is using very low molecular ratio of the catalysts in comparison with the reported procedures in the literature. Therefore, we think that this method can be a useful addition to the present methodologies for the silylation of hydroxy groups.

Experimental

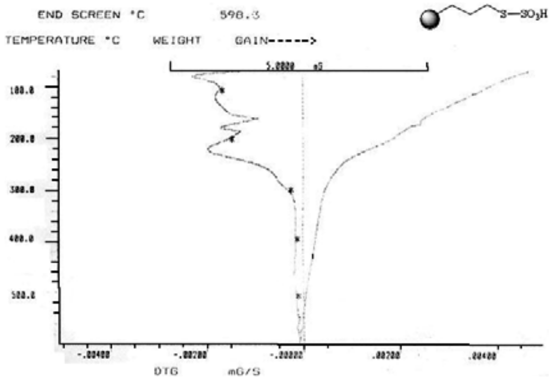
General

Chemicals were purchased from Merck, Fluka, and Aldrich Chemical Companies. IR spectra were run on a Shimadzu IR-435 FTIR spectrophotometer. ^{1}H NMR was run on JEOL NMR spectrometer (FX 90Q) and Bruker Avance (DRX 500 MHz). Melting points were recorded on a Melting Point SMP1 apparatus in open capillary tubes and are uncorrected. The progress of reaction was followed with TLC, using silica gel SILG/UV 254 plates. All the products are known and were characterized by comparison of their spectral (IR, ^{1}H NMR), TLC, and physical data with those reported in the literature.[22–36] 3-Mercaptopropylsilica **1** (MPS) was prepared according to the previously reported procedure.[5a]

Catalyst preparation

To a magnetically stirred mixture of 3-mercaptopropylsilica **1** (5 g) in *tert*-buylmethyl ether (20 mL), chlorosulfonic acid (1.00 g, 9 mmol) was added dropwise at 0 °C for 2 h. After addition was complete, the mixture was stirred for 2 h until HCl gas evolution was stopped. Then, the mixture was filtered and washed with methanol (30 mL) and dried at room temperature to obtain silica-bonded functionalized sulfonic acid **2** (SBSSA) as cream powder (5.22 g). Sulfur content of the samples was 16.12% by conventional elemental analysis. TGA analysis of SBSSA shows a first mass loss due to the desorption of water below 100 °C (Fig. 2). This

Fig. 2. TGA diagram for a sample of silica-bonded *S*-sulfonic acid under nitrogen stream.



is followed by a second mass loss starting at 140 °C, corresponding to the loss of the covalently bound organic group. From this mass loss, it is calculated that the loading of the organic group bound to silica surface was 1.78 mmol g^{-1}.

pH analysis of the SBSSA

To an aqueous suspension of 0.1 g SBSSA, NaOH (1.8 mL, 0.1 mol/L) was added. This is equal to a loading of 1.8 mmol SO_3H g^{-1}. So, all of the SH functional groups in 3-mercaptopropylsilica **1** were sulfonated. According to previous reports,[5] the loading of 3-mercaptopropylsilica **1** is 0.33 mmol/g.

General procedure for the silylation of alcohols

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

Trimethyl(benzyloxy)silan (Table 1, entry 1)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[29] bp 212 °C/760 torr (1 torr = 133.322 Pa). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: 0.19 (s, 9H), 4.72 (s, 2H), 7.35–7.36 (m, 5H).

Trimethyl(4-methoxybenzyloxy)silan (Table 1, entry 2)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[29] bp 257–258 °C/760 torr. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: 0.18 (s, 9H), 3.81 (s, 3H), 4.66 (s, 2H), 6.91 (d, 2H, *J* = 8.5 Hz), 7.44 (d, 2H, *J* = 8.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 0.30, 55.21, 64.41, 113.75, 128.13, 133.16, 158.90.

Trimethyl(4-bromobenzyloxy)silan (Table 1, entry 3)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[36] bp 250 °C/760 torr. ^{1}H NMR (90 MHz, $CDCl_3$, ppm) δ: 0.17 (s, 9H), 4.65 (s, 2H), 7.20 (d, 2H, *J* = 8.4 Hz), 7.46 (d, 2H, *J* = 8.6 Hz).

Trimethyl(4-chlorobenzyloxy)silan (Table 1, entry 4)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[36] bp 228 °C/760 torr. ^{1}H NMR (90 MHz, $CDCl_3$, ppm) δ: 0.19 (s, 9H), 4.68 (s, 2H), 7.28–7.30 (m, 4H).

Trimethyl(4-nitrobenzyloxy)silan (Table 1, entry 5)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[25] bp > 300 °C/760 torr. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: 0.22 (s, 9H), 4.83 (s, 2H), 7.52 (d, 2H, *J* = 8.8 Hz), 8.22 (d, 2H, *J* = 8.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: –0.10, 63.95, 123.95, 127.00, 147.49, 149.16.

Trimethyl(2-phenylethoxy)silan (Table 1, entry 6)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[29] bp 230 °C/760 torr. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: 0.11 (s, 9H), 2.87 (t, 2H, *J* = 7.3 Hz), 3.81 (t, 2H, *J* = 7.3 Hz), 7.23–7.33 (m, 5H).

Trimethyl(3-phenylpropyloxy)silan (Table 1, entry 7)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[25] bp 245 °C/760 torr. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: 0.22 (s, 9H), 1.92–1.98 (m, 2H), 2.77 (t, 2H, *J* = 7.8 Hz), 3.70 (t, 2H, *J* = 6.4 Hz), 7.26–7.29 (m, 3H), 7.35–7.38 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 0.03, 32.60, 34.70, 62.36, 126.17, 128.75, 128.91, 142.58.

Trimethyl(2-mercaptoethoxy)silan (Table 1, entry 8)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[38] bp 146 °C/760 torr. ^{1}H NMR (90 MHz, $CDCl_3$, ppm) δ: 0.06 (s, 9H), 1.43 (t, 1H, *J* = 8.1 Hz), 2.44–2.82 (m, 2H), 3.49–3.82 (m, 2H).

Trimethyl(diphenylmethoxy)silan (Table 1, entry 9)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[29] bp > 300 °C/760 torr. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: 0.20 (s, 9H), 5.88 (s, 1H), 7.32 (t, 2H, *J* = 7.3 Hz), 7.40 (t, 4H, *J* = 7.6 Hz), 7.46 (t, 4H, *J* = 7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 0.65, 77.00, 127.04, 127.53, 128.68, 145.35.

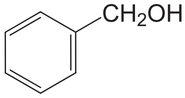
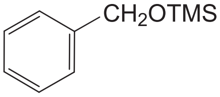
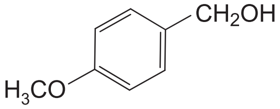
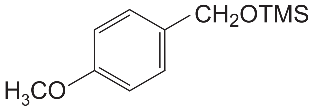
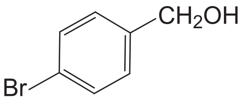
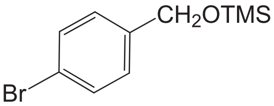
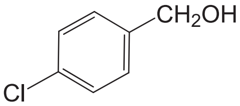
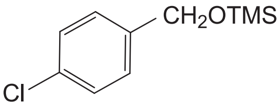
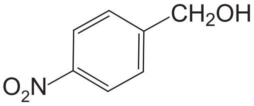
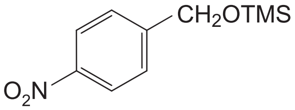
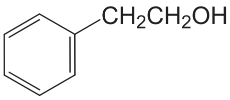
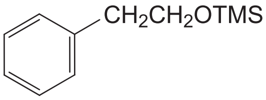
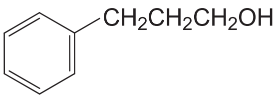
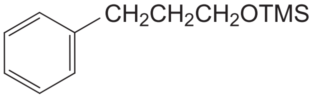
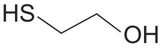
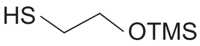
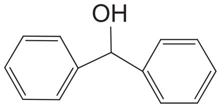
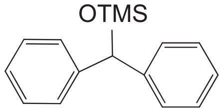
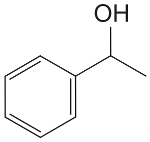
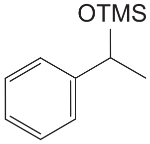
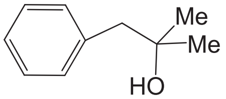
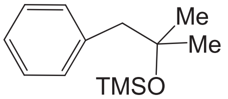
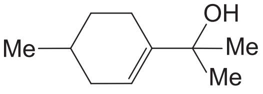
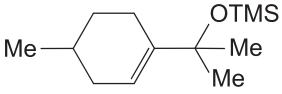
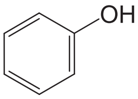
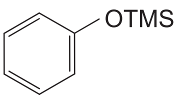
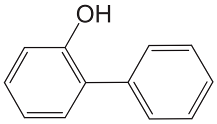
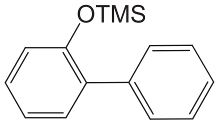
Trimethyl(1-phenylethoxy)silan (Table 1, entry 10)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[29] bp 212 °C/760 torr. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: 0.15 (s, 9H), 1.51 (d, 3H, *J* = 6.3 Hz), 4.93 (q, 1H, *J* = 6.3 Hz), 7.28 (t, 1H, *J* = 6.9 Hz), 7.34–7.40 (m, 4H).

Trimethyl(1-phenyl-2-methyl-2-propyloxy)silan (Table 1, entry 11)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[36] bp 245 °C/760 torr. ^{1}H NMR (90 MHz, $CDCl_3$, ppm) δ: 0.05 (s, 9H), 1.20 (s, 6H), 2.71 (s, 2H), 7.12–7.38 (m, 5H).

Table 1. Silylation of alcohols, phenols, and naphthols with HMDS in the presence of SBSSA as catalyst at room temperature.

Entry	Substrate	Product	Time (min)	Yield[b](%)
1			5	94
2			3	94
3			6	96
4			6	92
5			8	91
6			3	95
7			3	96
8			5	89
9			3	90
10			3	91
11			24 h	Trace
12			24 h	<30
13			3	93
14			15	90

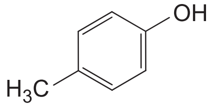
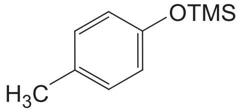
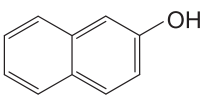
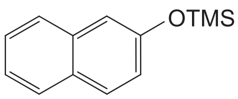
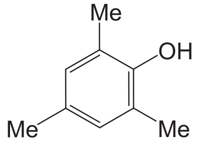
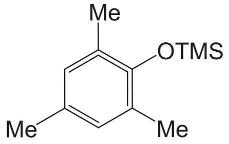
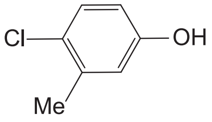
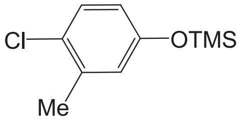
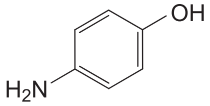
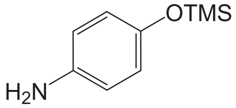
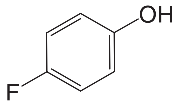
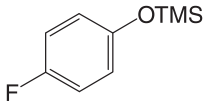
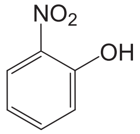
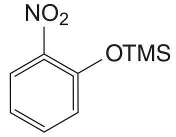
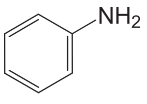
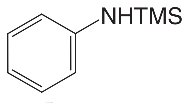
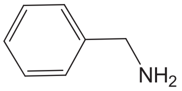
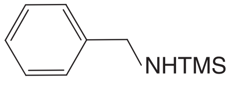
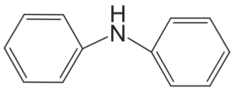
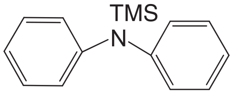
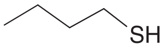
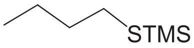
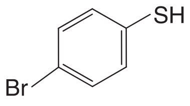
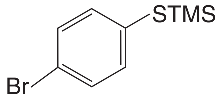
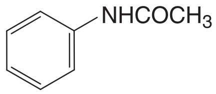
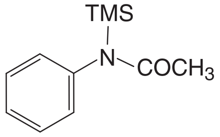
Trimethyl[1-methyl-1-(4-methyl-cyclohex-1-enyl)ethoxy]silan (Table 1, entry 12)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[32] bp 256 °C/760 torr. ^{1}H NMR (90 MHz, $CDCl_3$, ppm) δ: 0.09 (s, 9H), 0.94–2.00 (m, 16H), 5.27–5.44 (m, 1H).

Trimethylphenoxy silan (Table 1, entry 13)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[29] bp 211 °C/760 torr. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: 0.34 (s, 9H), 6.92 (d, 2H, J = 7.8 Hz), 7.02 (t, 1H, J = 7.3 Hz), 7.31 (t, 1H, J = 8.0 Hz).

Table 1. *Concluded.*

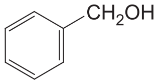
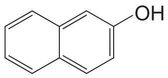
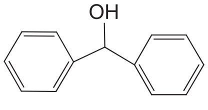
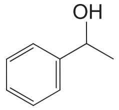
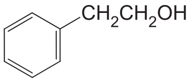
Entry	Substrate	Product	Time (min)	Yield^{b}(%)
15			6	95
16			5	93
17			2	96
18			3	96
19			5	90
20			5	91
21			24 h	NR^{c}
22			180	NR^{c}
23			180	NR^{c}
24			180	NR^{c}
25			180	NR^{c}
26			180	NR^{c}
27			180	NR^{c}

[a] Isolated yield.
[b] The yields and times of catalyst **II** are written in parenthesis.
[c] NR: No reaction.

Trimethyl(biphenyl-2-yloxy) silan (Table 1, entry 14)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[39] bp 281 °C/760 torr. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: 0.05 (s, 9H), 6.92 (dd, 1H, J_1 = 8.0 Hz, J_2 = 0.7 Hz), 7.06 (dt, 1H J_1 = 7.5 Hz, J_2 = 0.8 Hz), 7.21–7.26 (m, 1H), 7.31 (t, 1H, J = 7.4 Hz), 7.36 (dd, 1H, J_1 = 7.5 Hz, J_2 = 1.5 Hz), 7.40 (t, 2H, J = 7.5 Hz), 7.54 (d, 2H, J = 8.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 0.51, 121.03, 122.35, 127.16, 128.26, 128.81, 130.06, 133.78, 139.49, 152.73.

Table 2. Comparison of the results of SBSSA (**I**) with $LiClO_4/SiO_2$ (**II**),[21] H-β zeolite (**III**),[22] $HClO_4/SiO_2$ (**IV**),[29] sulfonic-acid-functionalized silica (**V**),[30] silica sulfuric acid (**VI**),[31] and alumina sulfuric acid (**VII**)[37] in the synthesis of trimethylsilyl ether using HMDS.

		Time (min)/ yield (%)^a						
Entry	Substrate	**I**	II	III	IV	V	VI	VII
1		5/94	5/98	300/95	2/98	80/100^b	10/93	2/98
2		5/93	120/84	20 h/67	4/100	420/80^b	5/86	4/95
3		3/90	50/87	—	4/89	60/98^b	10/85	7/89
4		3/91	30/89	—	4/91	—	15/89	8/91
5		3/95	—	—	2/97	40/100^b	—	12/97

Note: For I–VII, the equivalent ratios of substrate/ HMDS/ catalyst are 1/ 0.8/ 0.015 (g), 1/0.6/0.1 (g), 1/0.6/[10%(*w*/*w*)], 1/ 0.5/ 0.01, 1/ 0.6/ 0.003, 1/ 0.8/ 0.08 (g), 1/ 0.75/ 0.025 (g), respectively.

^{a} Isolated Yield.

^{b} GC Yield.

Trimethyl(4-methylphenoxy) silan (Table 1, entry 15)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[29] bp 206 °C/760 torr. ^1H NMR (500 MHz, $CDCl_3$, ppm) δ: 0.32 (s, 9H), 2.33 (s, 3H), 6.80 (d, 2H, *J* = 8.1 Hz), 7.08 (d, 2H, *J* = 8.0 Hz).

Trimethyl(2-naphtaleneoxy) silan (Table 1, entry 16)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[29] bp 282 °C/760 torr. ^1H NMR (500 MHz, $CDCl_3$, ppm) δ: 0.41 (s, 9H), 7.18 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.3 Hz), 7.31 (d, 1H, *J* = 2.1 Hz), 7.41 (t, 1H, *J* = 7.3 Hz), 7.50 (dt, 1H, J_1 = 7.6 Hz, J_2 = 0.8 Hz), 7.77–7.85 (m, 3H).

Trimethyl(2,4,6-thrimethylphenoxy) silan (Table 1, entry 17)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[40] bp 241 °C/760 torr. ^1H NMR (500 MHz, $CDCl_3$, ppm) δ: 0.25 (s, 9H), 2.17 (s, 6H), 2.23 (s, 3H), 6.78 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 1.37, 18.02, 20.94, 128.51, 129.47, 130.70, 150.63.

Trimethyl(4-chloro-3-methylphenoxy) silan (Table 1, entry 18)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[39] bp 243 °C/760 torr. ^1H NMR (500 MHz, $CDCl_3$, ppm) δ: 0.26 (s, 9H), 2.32 (s, 3H), 6.62 (dd, 1H, J_1 = 8.6 Hz, J_2 = 2.8 Hz), 6.72 (d, 1H, *J* = 2.8 Hz), 7.17 (d, 1H, *J* = 7.9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 0.58, 20.60, 119.13, 122.96, 127.10, 130.03, 137.42, 154.14.

Trimethyl(4-aminophenoxy) silan (Table 1, entry 19)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[29] bp 255 °C/760 torr. ^1H NMR (500 MHz, $CDCl_3$, ppm) δ: 0.22 (s, 9H), 3.34 (s, 2H), 6.51 (d, 2H, *J* = 8.5 Hz), 6.61 (d, 2H, *J* = 8.5 Hz).

Trimethyl(4-fluorophenoxy) silan (Table 1, entry 20)

Purified on short column of silica gel using petroleum ether/ethyl acetate (10:1) as eluent. Colorless liquid;[29] bp 208 °C/760 torr. ^1H NMR (500 MHz, $CDCl_3$, ppm) δ: 0.25 (s, 9H), 6.75–6.77 (m, 2H), 6.89–6.92 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ: 0.53, 116.10, 121.26, 151.52, 159.08.

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