

Silica supported perchloric acid ($\text{HClO}_4\text{-SiO}_2$): A highly efficient and reusable catalyst for the protection of hydroxyl groups using HMDS under mild and ambient conditions

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Abstract

Various alcohols, phenols, naphthols, and oximes were effectively converted into their corresponding trimethylsilyl ethers with hexamethyldisilazane in the presence of solid silica supported perchloric acid under very mild conditions at room temperature with short reaction time in good to excellent yields. The notable advantages of this protocol are: work up procedure is easy and the catalyst can be recovered by simple filtration and reused.

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1. Introduction

Trimethylsilylation of organic compounds having labile hydrogen atoms such as alcohols, phenols, and carboxylic acids is an important organic transformation [1–3]. It is a frequently used protection method in several chemical conversions and synthesis of natural products due to the enhanced stability under a variety of conditions, solubility in non-polar solvents, thermal stability and the ease of removal protecting group which is simply accomplished by acid or base induced hydrolysis giving only unreactive siloxane as by-product. It is also used in analytical chemistry to prepare silyl ethers as volatile derivatives for gas chromatography and mass spectrometry [1–5].

The preparation of silyl ethers can be done by dehydrogenative silylation of hydroxyl groups with hydrosilanes [6,7] and also by the treatment of alcohols with silyl chlorides or silyl triflates in the presence of an organic base [8,9]. However, some of these methods 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, giving NH_3 as the only by-product. Even though the handling of this reagent is easy, but the low silylation power of HMDS is the main drawback to its application; therefore, there are a variety of catalysts for activating of this reagent, such as $(\text{CH}_3)_3\text{SiCl}$ [10], K-10 montmorillonite [11], sulfonic acids [12], zirconium sulfophenyl phosphonate [13], ZnCl_2 [14], Envirocat EPZGO [15], tungstophosphoric acid [16], iodine [17], lithium perchlorate [18], cupric sulfate pentahydrate [19], H- β zeolite [20], MgBr_2 [21], lithium perchlorate supported on silica gel [22], $\text{Al}(\text{HSO}_4)_3$ [23], $\text{Al}(\text{OTf})_3$ [24], magnesium triflate [25], copper triflate [26], and trichloroisocyanuric acid [27].

However, in most of these cases a long reaction time, drastic reaction conditions, or tedious workup is needed. In addition, many of these reagents are moisture sensitive or expensive. The lack of a facile and effective synthetic methodology for the silylation of hydroxyl groups prompted us to develop a convenient and practical procedure for the protection of hydroxyl groups in the presence of heterogeneous catalyst under solvent-free conditions. The use of heterogeneous catalysts under solvent-free conditions is becoming very popular as it has many advantages: reduced pollution, reusability, high selectivity, low cost, and simplicity in process and in handling. These factors are especially important in industry. In the present research for functional group transformation, we wish to describe a new protocol for the

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mild and rapid trimethylsilylation of a wide variety of hydroxyl groups using HMDS and a catalytic amount of silica supported perchloric acid as a recyclable solid Brønsted acid catalyst. This catalyst is safe, moisture stable, non-toxic, easy to handle, environmentally benign and presents fewer disposal problems. Silica supported perchloric acid as a recyclable solid acid catalyst was prepared from the reaction of silica gel with perchloric acid [28]. Silica supported perchloric acid has been used in some organic reactions, such as direct conversion of acetals to acetates [29], formation of 1,3-dithiolane/dithiane [30], synthesis of acylals from aldehydes [31], synthesis of 2,3-unsaturated-*o*-glucosides [32], and geminal diacylation of aldehydes [28].

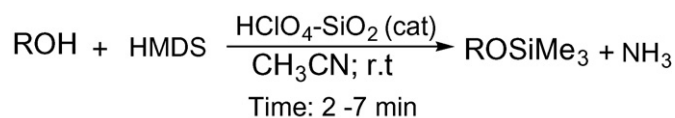
2. Results and discussion

The trimethylsilylation of hydroxyl groups is easily carried out at room temperature under mild conditions in the presence of silica supported perchloric acid as active acid catalyst (Scheme 1).

First, we tried to convert benzyl alcohol (1 mmol) to its corresponding benzylsilylether with HClO₄-SiO₂ (0.05 g, equal to 0.025 mmol of H⁺) and HMDS (0.8 mmol) in the presence of various solvents (Table 1). The results in Table 1 show that amongst these solvents, acetonitrile was the solvent of choice in terms of time and product yield.

Next, we prepared a range of silylethers under the following reaction conditions: hydroxyl compound (1 eq), HMDS (0.8 eq), HClO₄-SiO₂ (0.05 eq), and acetonitrile (2 mL) (Table 2).

A wide range of various alcohols and oximes underwent silylation by this procedure to provide the corresponding TMS ethers in good to excellent isolated yields as shown in Table 2 (entries 1–25). Benzylic alcohols, phenols, and primary alcohols generally are faster than secondary and tertiary alcohols. Trimethylsilylation of aldoxime and ketoxime also produce the corresponding trimethylsilylated compounds at these conditions



R= primary, secondary, tertiary Alkyl, Aryl and oxime

Scheme 1.

Table 1
Silylation of benzyl alcohols with HMDS in the presence of HClO₄-SiO₂ as heterogeneous catalyst at room temperature

Entry	Solvent ^a	Molar ratio, substrate/HMDS	Time (min)	GC yield (%)	Yield ^b (%)
1	Dichloromethane	1/0.8	180	100	89
2	Chloroform	1/0.8	200	100	91
3	Ethyl acetate	1/0.8	200	80	75
4	<i>n</i> -Hexane	1/0.8	200	55	50
5	Diethyl ether	1/0.8	200	70	60
6	Acetonitrile	1/0.8	2	100	98

^a The amount of solvent was chosen 2 mL.

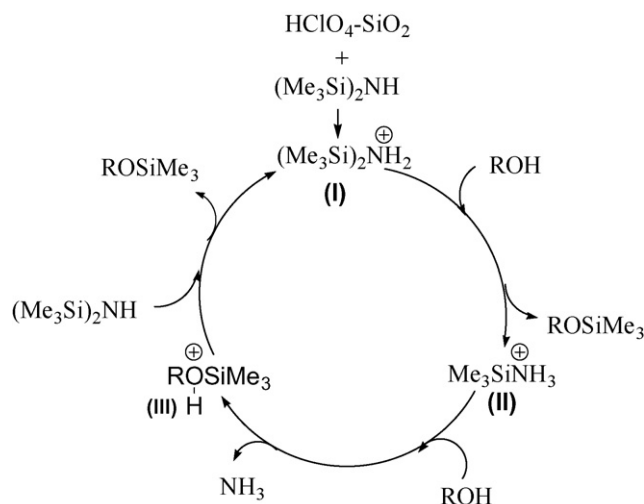
^b Isolated yield and the product gave satisfactory IR and NMR spectra.

(Table 2, entries 23–25), whereas thiophenol, 1,3-propane dithiol (Table 2, entries 26 and 27), aniline and phthalimide (Table 2, entries 28 and 29) and remained unaffected under the reaction conditions. Generally, in all cases of benzyl, primary, secondary, and tertiary alcohols the reactions were completed within less than 7 min in acetonitrile as solvent accompanied by evolution of NH₃ gas from the reaction mixture. Inspection of the data in Table 2 clearly shows that different types of hindered secondary and tertiary alcohols were successfully converted to the corresponding silyl ethers (Table 2).

We also investigated selective silylation of different binary mixture of alcohols and also alcohols in the presence of phenol, amine, amide, and thiols (Table 3). This method was shown to be highly selective for primary alcohols such as benzyl alcohols and 1-octanol (Table 3, entries 1–3). The primary alcohols were completely converted to the corresponding silyl ethers, while the secondary alcohols and phenols were converted to the corresponding silylated products with 3–10% yield. Excellent selectivity was also observed for the conversion of primary and secondary alcohols in the presence of tertiary alcohols such as adamantanol (Table 3, entries 4 and 5). We also explored the chemoselectivity of silica supported perchloric acid in the silylation method. Table 3 clearly shows that alcohols and phenols in the presence of an amine, amide and thiols were completely converted to the corresponding trimethylsilyl ethers as sole product (Table 3, entries 7–10).

To show the efficiency of the HClO₄-SiO₂ in comparison with reported results in the literature, Table 4 compares some of our results with trichloroisocyanuric acid [27], Mg(OTf)₂ [25], H-β zeolite [20] and molecular iodine [17] respect to reaction times, yields of the obtained products.

In all reactions, we have studied, fast evolution of ammonia gas was observed. We were also able to isolate HClO₄-SiO₂ from the reaction mixture and reused it for the similar reaction without observable loss of its catalytic activity. With these observations we have proposed a mechanism in which the generation of NH₃ and the catalytic role of HClO₄-SiO₂ in a catalytic cycle are clarified (Scheme 2).



Scheme 2.

Table 2
Silylation of alcohols, phenols, naphthols, and oximes with HMDS in the presence of $\text{HClO}_4\text{-SiO}_2$ as heterogeneous catalyst (0.05 g) at room temperature

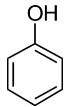
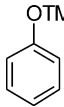
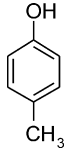
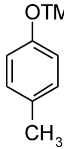
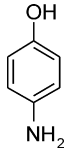
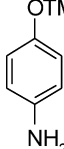
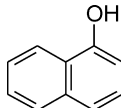
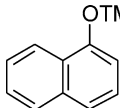
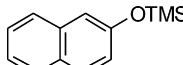
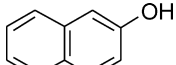
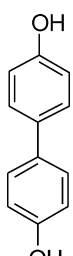
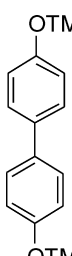
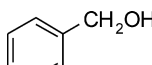
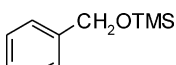
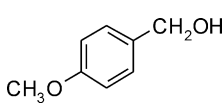
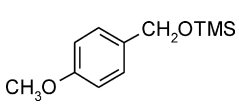
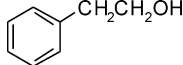
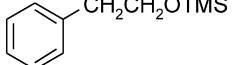
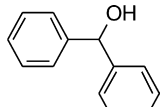
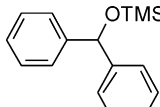
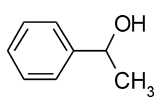
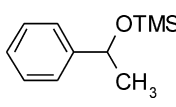


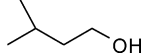
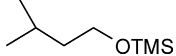
Entry	Substrate	Product	Molar ratio, substrate/HMDS	Time (min)	GC yield (%)	Yield ^a (%)
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2			1/0.8	3	100	97
3			1/0.8	3	100	91
4			1/0.8	4	100	92
5			1/0.8	4	100	91
6			1/1.7	4	100	95
7			1/0.8	2	100	98
8			1/0.8	2	100	95
9			1/0.8	2	100	97
10			1/0.8	4	100	89
11			1/0.8	4	100	91
12			1/0.8	2	100	85
13			1/0.8	2	100	87

Table 2 (Continued)

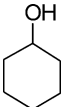
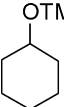
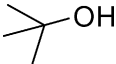
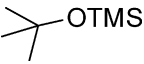
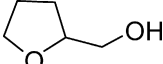
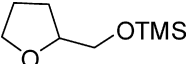
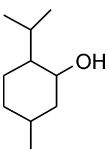
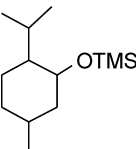
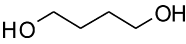
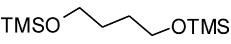
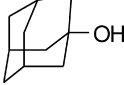
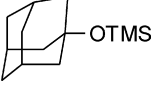
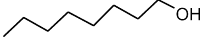
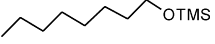
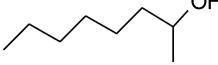
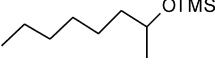
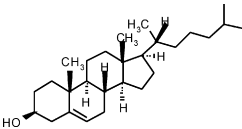
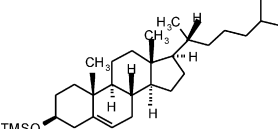
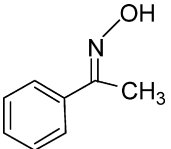
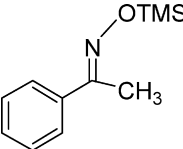
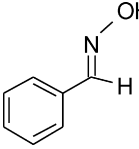
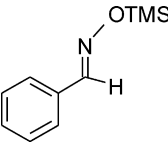
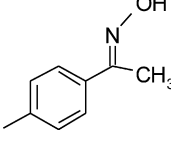
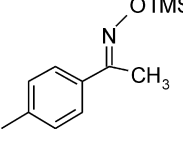
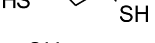

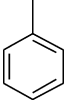
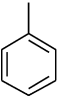
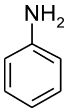
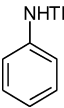
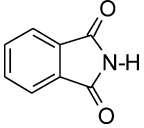
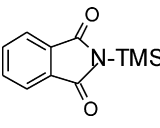
Entry	Substrate	Product	Molar ratio, substrate/HMDS	Time (min)	GC yield (%)	Yield ^a (%)
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15			1/0.8	7	100	85
16			1/0.8	2	100	91
17			1/0.8	6	100	95
18			1/1.7	2	100	90
19			1/0.8	7	100	95
20			1/0.8	2	100	95
21			1/0.8	3	100	93
22			1/0.8	7	100	97
23			1/0.8	4	100	95
24			1/0.8	4	100	90
25			1/0.8	4	100	89
26			1/1.7	10	–	–
27			1/0.8	10	–	–

Table 2 (Continued)

Entry	Substrate	Product	Molar ratio, substrate/HMDS	Time (min)	GC yield (%)	Yield ^a (%)
28			1/0.8	10	–	–
29			1/0.8	10	–	–

^a Yields refer to the pure isolated products. All known products have been reported previously in the literature and were characterized by comparison of IR and NMR spectra with authentic samples [11–27].

Table 3
Selective *O*-trimethylsilylation of alcohols in the presence of HMDS and HClO₄–SiO₂ as catalyst at room temperature

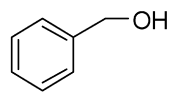
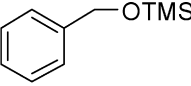
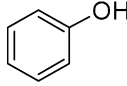
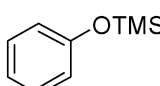
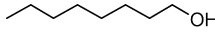
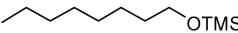
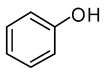
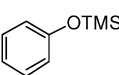
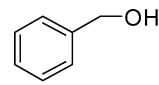
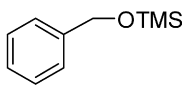
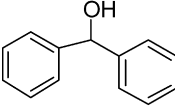
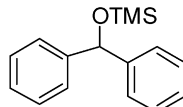
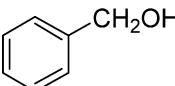
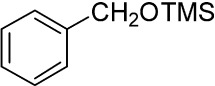
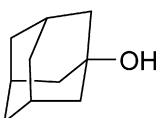
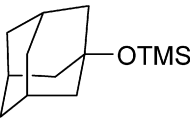
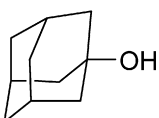
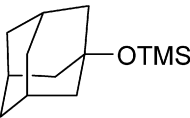
Entry	Substrate	Product binary mixture	Molar ratio, substrate 1/substrate 2/HMDS/catalyst	Time (min)	GC yield (%)
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					3
2			1/1/0.8/0.025 (0.05 gr)	7	88
					10
3			1/1/0.8/0.025 (0.05 gr)	7	100
					10
					
4			1/1/0.8/0.025 (0.05 gr)	7	100
					8

Table 3 (Continued)

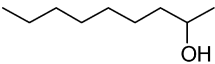
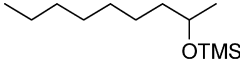
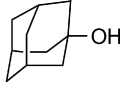
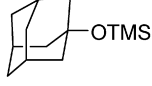
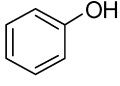
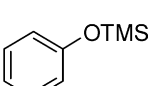
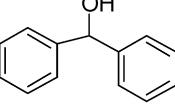
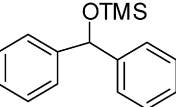
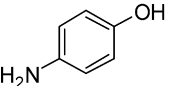
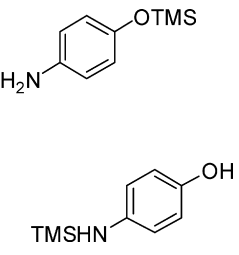
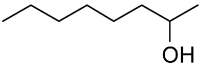
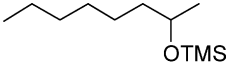
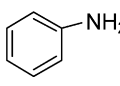
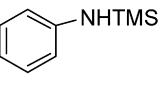
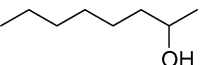
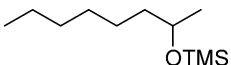
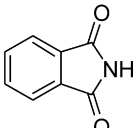
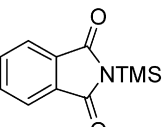
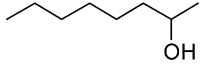
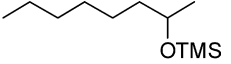
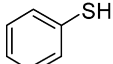
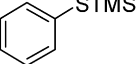
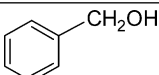
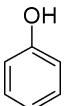
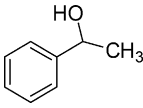
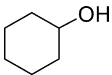
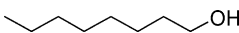
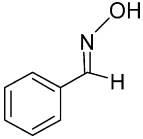
Entry	Substrate	Product binary mixture	Molar ratio, substrate 1/substrate 2/HMDS/catalyst	Time (min)	GC yield (%)
5			1/1/0.8/0.025 (0.05 gr)	7	100
					3
6			1/1/0.8/0.025 (0.05 gr)	7	75
					10
7			1/1/0.8/0.025 (0.05 gr)	10	100
					0
8			1/1/0.8/0.025 (0.05 gr)	10	100
					0
9			1/1/0.8/0.025 (0.05 gr)	10	100
					0
10			1/1/0.8/0.025 (0.05 gr)	10	100
					0

Table 4
Comparison result of HClO₄-SiO₂ (1) with trichloroisocyanuric acid (2) [27], Mg(OTf)₂ (3) [25], H-β zeolite (4) [20], and molecular iodine (5) [17] in the synthesis of trimethylsilyl ether using HMDS

Entry	Substrate	Time (min)/yield (%)				
		1	2	3	4	5
1		2/98	240/90	38/95	300/95	2/98
2		3/97	108/92	60/70	600/87	–
3		4/91	–	–	–	3/96
4		3/91	90/85	–	700/95	–
5		2/95	240/87	50/95	–	3/92
6		4/90	–	–	–	–

In this mechanism, we have suggested that an acid–base interaction between catalyst and nitrogen in HMDS polarizes N–Si bond of HMDS to produce a reactive silylating agent (I). A rapid reaction with alcohol then ensues, leading to the ammonium silylating species (II) with concomitant release of the corresponding silyl ether. Irreversible cleavage of (II) with alcohol, leading to the fast evolution of NH₃ and also formation of the unstable protonated silyl ether (III). Release of H⁺ as catalyst from intermediate (III), re-enters catalytic cycle (Scheme 2).

3. Experimental

All reagents were purchased from Merck and Aldrich and used without further purification. Silica supported perchloric acid was prepared according to the reported procedure [28]. All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples and by spectroscopy data (IR, ¹H NMR spectra). The NMR spectra were recorded on a Bruker Avance DPX 300 and 500 MHz instrument. The spectra were measured in CDCl₃ relative to TMS (0.00 ppm). GC analysis was run with Shimadzu GC-14A. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. TLC was performed on Silica-gel polygram SIL G/UV 254 plates.

3.1. General procedure: silica supported perchloric acid [28] catalyzed silylation of alcohols and oximes in the presence of HMDS

To a stirred solution of alcohol (1 mmol) and HMDS (0.8 mmol) was added silica supported perchloric acid (0.05 g,

equal to 0.025 mmol of H⁺) and the mixture was stirred at room temperature for the time specified in Table 2. The reaction was followed by TLC (*n*-hexane–EtOAc, 9:1). After completion of the reaction, the mixture was diluted with *n*-hexane. The resulting mixture was passed through a short pad of silica gel. Then, the pad column was washed with *n*-hexane (2 × 10 mL). Evaporation of the solvent under reduced pressure gave pure product(s) (Tables 1 and 2).

The desired pure product(s) was characterized by comparison of their physical data with those of known compounds [11–27]. The spectral data of some representative trimethylsilyl ethers are given below.

3.1.1. Trimethylphenoxy silane (entry 1, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 7.31 (t, 2H, *J* = 8.0 Hz), 7.02 (t, 1H, *J* = 7.3 Hz), 6.90 (d, 2H, *J* = 7.8 Hz), 0.34 (s, 9H) ppm; IR (CCl₄): 3039, 2960, 1596, 1492, 1252, 1164, 1070, 1024, 1002, 918, 843, 759, 692 cm⁻¹.

3.1.2. Trimethyl(4-methyl phenoxy) silane (entry 2, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 7.09 (d, 2H, *J* = 8.0 Hz), 6.81 (d, 2H, *J* = 8.1 Hz), 2.33 (s, 3H), 0.32 (s, 9H) ppm; IR (CCl₄): 2960, 1613, 1509, 1251, 1168, 1103, 916, 846, 754 cm⁻¹.

3.1.3. Trimethyl(4-amino phenoxy) silane (entry 3, Table 2)

¹H NMR (CDCl₃, 500MHz): δ = 6.61 (d, 2H, *J* = 8.5 Hz), 6.51 (d, 2H, *J* = 6.5 Hz), 3.34 (s, 2H), 0.22 (s, 9H) ppm; ¹³C NMR

(CDCl₃, 125 MHz): δ = 140.4, 120.6, 116.2, 96.1, 0.2 ppm; IR (CCl₄): 3357, 2952, 1624, 1509, 1244, 1120, 911, 846, 754 cm⁻¹.

3.1.4. Trimethyl(1-naphthalenoxy) silane (entry 4, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 8.25 (dd, 1H, J = 3.4 Hz), 7.88 (dd, 1H, J = 3.4 Hz), 7.54 (m, 3H), 7.41 (t, 1H, J = 7.7 Hz), 6.97 (d, 1H, J = 7.4 Hz), 0.44 (s, 9H) ppm; IR (CCl₄): 3050, 2959, 1579, 1507, 1461, 1390, 1272, 1154, 1093, 1051, 1015, 914, 848, 796, 771 cm⁻¹.

3.1.5. Trimethyl(2-naphthalenoxy) silane (entry 5, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 7.85 (d, 1H, J = 8.1 Hz), 7.82 (d, 1H, J = 8.8 Hz), 7.7 (d, 1H, J = 8.2 Hz), 7.5 (t, 1H, J = 5.0 Hz), 7.41 (t, 1H, J = 6.9 Hz), 7.31 (d, 1H, J = 2.1 Hz), 7.18 (dd, 1H, J = 2.3 Hz), 0.41 (s, 9H) ppm; IR (CCl₄): 3057, 2959, 1631, 1598, 1508, 1468, 1349, 1254, 1173, 1122, 978, 926, 855, 746 cm⁻¹.

3.1.6. Bistrimethyl(4,4'-biphenoxy) silane (entry 6, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 7.45 (d, 2H, J = 8.6 Hz), 6.92 (d, 2H, J = 8.5 Hz), 0.32 (s, 9H) ppm; ¹³C NMR (CDCl₃): δ = 154.3, 134.2, 127.7, 120.2, 0.28 ppm; IR (CCl₄): 2960, 1603, 1490, 1255, 1169, 1102, 923, 841, 759 cm⁻¹.

3.1.7. Trimethyl(benzyloxy) silane (entry 7, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 7.367.35 (5H, m), 4.72 (2H, s), 0.18 (9H, s) ppm; IR (CCl₄): 2957, 1496, 1454, 1377, 1250, 1207, 1096, 1027, 842, 727, 695 cm⁻¹.

3.1.8. Trimethyl(4-methoxybenzyloxy) silane (entry 8, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 7.29 (2H, d, J = 8.3 Hz), 6.91 (2H, d, J = 8.4 Hz), 4.66 (2H, s), 3.81 (3H, s), 0.18 (9H, s) ppm; ¹³C NMR (CDCl₃, 125 MHz): δ = 158.9, 133.1, 128.1, 113.7, 64.4, 55.2, -0.3 ppm; IR (CCl₄): 2999, 2959, 2901, 2836, 1613, 1587, 1512, 1464, 1376, 1300, 1248, 1171, 1085, 1037, 840, 751, 688 cm⁻¹.

3.1.9. Trimethyl(2-phenylethoxy) silane (entry 9, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 7.31 (2H, t, J = 7.7 Hz), 7.24 (3H, m), 3.81 (2H, t, J = 7.2 Hz), 2.87 (2H, t, J = 7.2 Hz), 0.11 (9H, s) ppm; IR (CCl₄): 3064, 3028, 2955, 2899, 1604, 1479, 1474, 1454, 1383, 1250, 1207, 1094, 1030, 928, 842, 740, 698 cm⁻¹.

3.1.10. Trimethyl(diphenylmethoxy) silane (entry 10, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 7.41 (4H, d, J = 7.5 Hz), 7.34 (2H, t, J = 7.3 Hz), 7.24 (4H, t, J = 7.1 Hz), 5.80 (1H, s), 0.11 (9H, s) ppm; IR (CCl₄): 3063, 3027, 2957, 2863, 1598, 1492, 1453, 1354, 1303, 1251, 1187, 1090, 1061, 1027, 917, 885, 740, 700, 602 cm⁻¹.

3.1.11. Trimethyl(α -methylbenzyloxy) silane (entry 11, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 7.38 (3H, m), 7.28 (1H, t, J = 6.9 Hz), 4.93 (1H, q, J = 6.3 Hz), 1.51 (3H, d, J = 6.3 Hz), 0.15 (9H, s) ppm; IR (CCl₄): 3063, 3027, 2972, 2927, 2868, 1688, 1603, 1492, 1450, 1369, 1250, 1206, 1090, 1032, 999, 959, 841, 757, 699 cm⁻¹.

3.1.12. Trimethyl butoxy silane (entry 12, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 3.58 (2H, t, J = 6.5 Hz), 1.52 (2H, qui, J = 6.5 Hz), 1.33 (2H, six, J = 5.4 Hz), 0.92 (3H, t, J = 7.3 Hz), 0.11 (9H, s) ppm; IR (CCl₄): 2959, 1384, 1250, 1095, 900, 792 cm⁻¹.

3.1.13. Trimethyl isopentyloxy silane (entry 13, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 3.59 (2H, t, J = 6.8 Hz), 1.69 (1H, sep, J = 6.7 Hz), 1.42 (2H, q, J = 6.8 Hz), 0.91 (6H, d, J = 6.6 Hz), 0.10 (9H, s) ppm; IR (CCl₄): 2959, 1464, 1385, 1250, 1092, 991, 794 cm⁻¹.

3.1.14. Trimethyl cyclohexyloxy silane (entry 14, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 3.57–3.51 (1H, m), 1.79–1.70 (4H, m), 1.53–1.50 (1H, m), 1.29–1.21 (4H, m), 1.13 (1H, m), 0.10 (9H, s) ppm; IR (CCl₄): 2933, 2857, 1450, 1375, 1249, 1092, 1049, 996, 887, 839, 748 cm⁻¹.

3.1.15. Trimethyl (tert-butoxy) silane (entry 15, Table 2)

¹H NMR (CDCl₃, 300 MHz): δ = 1.23 (9H, s), 0.11 (9H, s) ppm; ¹³C NMR (CDCl₃, 75 MHz): δ = 58.1, 31.1, 1.4 ppm; IR (CCl₄): 2977, 1363, 1250, 1051, 794 cm⁻¹.

3.1.16. Trimethyl(tetrahydro-2-furylmethoxy) silane (entry 16, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 3.87 (1H, m), 3.76 (1H, m), 3.67 (1H, m), 3.46 (2H, t, J = 4.9 Hz), 1.82 (3H, m), 1.54 (1H, m), 0.02 (9H, s) ppm; ¹³C NMR (CDCl₃, 125 MHz): δ = 79.4, 68.1, 65.1, 27.6, 25.5, -0.6 ppm; IR (CCl₄): 2933, 1450, 1375, 1249, 1092, 1049, 996, 887, 839, 748 cm⁻¹.

3.1.17. Trimethyl[5-methyl-2-(1-methylethyl) cyclohexyl]oxy silane (entry 17, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 3.39 (1H, six, J = 4.3 Hz), 2.14 (1H, six, J = 2.2 Hz), 1.84 (1H, dd, J = 4.4 Hz), 1.5 (2H, m), 1.36 (1H, m), 1.13 (1H, m), 0.94 (1H, m), 0.89 (6H, d, J = 6.6 Hz), 0.73 (3H, d, J = 6.8 Hz), 0.10 (9H, s) ppm; ¹³C NMR (CDCl₃, 125 MHz): δ = 72.4, 50.0, 45.4, 34.5, 31.6, 25.2, 22.9, 22.2, 21.2, 15.9, 0.5 ppm; IR (CCl₄): 2955, 1455, 1249, 1069, 931, 886, 839 cm⁻¹.

3.1.18. Bistrimethyl(1,4-butanedioxy) silane (entry 18, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 3.59 (4H, t, J = 5.7 Hz), 1.55 (4H, qui, J = 3.0 Hz), 0.10 (18H, s) ppm; IR (CCl₄): 2956, 1250, 1094, 840 cm⁻¹.

3.1.19. *Trimethyl(tricyclo[3,3,1,1^{3,7}] doc-1-yloxy) silane* (entry 19, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 2.10 (3H, s), 1.76 (6H, d, *J* = 2.9 Hz), 1.60 (6H, d, *J* = 2.5 Hz), 0.13 (9H, s) ppm; ¹³C NMR (CDCl₃, 125 MHz): δ = 71.3, 46.0, 36.2, 30.9, 3.0 ppm; IR (CCl₄): 2908, 1453, 1353, 1304, 1240, 1132, 1093, 1016, 964, 871, 837, 752 cm⁻¹.

3.1.20. *Trimethyl(1-octyloxy) silane* (entry 20, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 3.56 (2H, t, *J* = 6.7 Hz), 1.52 (2H, t, *J* = 6.8 Hz), 1.31 (10H, m), 0.88 (3H, t, *J* = 6.5 Hz), 0.10 (9H, s) ppm; IR (CCl₄): 2928, 2857, 1250, 1099, 840, 746 cm⁻¹.

3.1.21. *Trimethyl(1-methylheptyl oxy) silane* (entry 21, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 3.75 (1H, six, *J* = 5.7 Hz), 1.44–1.26 (1H, m), 1.12 (3H, d, *J* = 6.0 Hz), 0.88 (3H, t, *J* = 6.6 Hz), 0.10 (9H, s) ppm; IR (CCl₄): 2958, 2929, 2858, 1458, 1375, 1249, 1135, 1084, 1049, 956, 830, 794, 747 cm⁻¹.

3.1.22. *Trimethyl[(3β)-cholest-4-en-3-yl]oxy silane* (entry 22, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 5.32 (1H, t, *J* = 2.2 Hz), 3.48 (1H, m), 2.29–0.86 (39H, m), 0.67 (3H, s), 0.12 (9H, s) ppm; ¹³C NMR (CDCl₃, 125 MHz): δ = 141.4, 121.3, 72.3, 56.8, 56.1, 50.2, 42.7, 42.3, 39.8, 39.5, 37.4, 36.5, 36.2, 35.7, 32.0, 31.95, 31.93, 28.2, 28.0, 24.2, 23.8, 22.7, 22.5, 21.0, 19.3, 18.7, 11.7, 0.2 ppm; IR (KBr): 2950, 1466, 1380, 1249, 1085, 958, 897, 840, 754 cm⁻¹.

3.1.23. *Trimethyl(acetophenone oxime)oxy silane* (entry 23, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 7.70 (2H, dd, *J* = 3.9 Hz), 3.87 (3H, m), 2.29 (3H, s), 0.30 (9H, s) ppm; ¹³C NMR (CDCl₃, 125 MHz): δ = 158.6, 137.0, 129.0, 128.2, 126.1, 14.1, -0.56 ppm; IR (CCl₄): 2961, 1368, 1308, 1250, 995, 924, 885, 845, 792, 758, 692 cm⁻¹.

3.1.24. *Trimethyl(benzaldehyd oxime)oxy silane* (entry 24, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 8.23 (1H, s), 7.64 (2H, dd, *J* = 3.4 Hz), 7.39 (3H, m), 0.33 (9H, s) ppm; ¹³C NMR (CDCl₃, 125 MHz): δ = 153.4, 132.6, 129.8, 128.6, 126.1, -0.67 ppm; IR (CCl₄): 3027, 2962, 1489, 1447, 1337, 1251, 1209, 1073, 948, 849, 760, 602 cm⁻¹.

3.1.25. *Trimethyl(4-methylacetophenone oxime)oxy silane* (entry 25, Table 2)

¹H NMR (CDCl₃, 500 MHz): δ = 7.70 (2H, d, *J* = 7.9 Hz), 7.27 (2H, d, *J* = 7.7 Hz), 2.46 (3H, s), 2.36 (3H, s), 0.41 (9H, s) ppm; ¹³C NMR (CDCl₃, 125 MHz): δ = 158.5, 138.9, 134.3, 129.0, 126.1, 21.2, 12.3, -0.45 ppm; IR (CCl₄): 2961, 1614, 1513, 1366, 1314, 1250, 1000, 921, 882, 845, 752 cm⁻¹.

4. Conclusion

In conclusion, we have demonstrated that silica supported perchloric acid is a new efficient catalyst for trimethylsilylation of a variety of hydroxyl groups using HMDS under mild and almost neutral conditions. This method is important from an environmental point of view and economic considerations, because it produces little waste. Simple work-up procedure, including filtering the mixture through a short pad of silica gel column followed by evaporation of the solvent is another advantage of this method.

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