FULL PAPER

Graphene oxide-bound electron-deficient tin(IV) porphyrin: a highly efficient and selective catalyst for trimethylsilylation of alcohols and phenols with hexamethyldisilazane

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Majid Moghadam and Valiollah Mirkhani, Department of Chemistry, Catalysis Division, University of Isfahan, Isfahan 81746-73441, Iran. Email: moghadamm@sci.ui.ac.ir; mirkhani@sci.ui. ac.ir The catalytic activity of graphene oxide-bound tetrakis(*p*-aminophenyl)porphyrinatotin (IV) trifluoromethanesulfonate, $[Sn^{IV}(TNH_2PP)(OTf)_2]$, in the trimethylsilylation of alcohols and phenols with hexamethyldisilazane (HMDS) is reported. The prepared catalyst was characterized using inductively coupled plasma analysis, scanning electron microscopy, transmission electron microscopy, and Fourier transform infrared and diffuse reflectance UV–visible spectroscopies. This heterogeneous catalyst was used for selective trimethylsilylation of various alcohols and phenols with HMDS in short reaction times and high yields. Also, the catalyst is of high reusability and stability, in that it was recovered several times without loss of its initial activity. The chemoselectivity of this catalytic system in the silylation of primary alcohols in the presence of secondary and tertiary alcohols and also phenols was investigated.

KEYWORDS

alcohols, graphene oxide, phenols, silylation, tin(IV) porphyrin

1 | INTRODUCTION

Protection of hydroxyl functional groups by their conversion to silvl ether groups is a common and often used method in synthetic organic chemistry. The protection of such functional groups is often necessary during the course of various transformations in a synthetic sequence, especially in the synthesis of fine chemicals and natural products.^[1–3] Commonly, silvl ethers are prepared by treatment of hydroxyl compounds with silvl chlorides or silvl triflates in the presence of bases such as imidazole,^[4] 4-(N,N-dimethylamino)pyridine,^[5] N, *N*-diisopropylethylamine^[6] and Li₂S.^[7] However, some of these silvlation methods suffer from disadvantages such as lack of reactivity or the difficulty in removal of amine salts derived during the silvlation reaction. To solve these problems, 1,1,1,3,3,3-hexamethyldisilazane (HMDS), a stable, commercially available and cheap reagent, is used as a source of trimethylsilyl groups. By using HMDS, ammonia is produced as a by-product but the disadvantage of HMDS is its low silvlating ability in the absence of a suitable catalyst which increases the reaction times.^[8] To enhance the

silvlating power of HMDS, a variety of catalysts, including trichloroisocyanuric acid,^[9] silica-supported perchloric acid,^[10] $ZrCl_4$,^[11] K-10 montmorillonite,^[12] LiClO₄,^[13] H₃PW₁₂O₄₀,^[14] iodine,^[15] InBr₃,^[16] zirconium sulfo phenylphosphonate,^[17] CuSO₄·5H₂O,^[18] sulfonic acid-functionalized nanoporous silica,^[19] MgBr₂OEt₂,^[20] LaCl₃,^[21] poly(N-bromobenzene-1,3-disulfonamide) and N,N,N',N'tetrabromobenzene-1,3-disulfonamide,^[22] Fe(TFA)₃.^[23] Fe₃O₄,^[24] (*n*-Bu₄N)Br,^[25] ZrO(OTf)₂,^[26] [Sn^{IV}(TNH₂PP) (OTf)₂]/CM-MIL-101,^[27] [Sn^{IV}(TNH₂PP)(OTf)₂]@CMP,^[28] $[Sn^{IV}(TPP)(OTf)_2],^{[29]}$ $[Sn^{IV}(TPP)(BF_4)_2],^{[30]}$ $[V^{IV}(TPP)$ (OTf)₂],^[31] Ru^{III}(OTf)SalophenCH₂-NHSiO₂-Fe^[32] and [Ti^{IV}(salophen)(OTf)₂],^[33] have been reported. Although these procedures provide an improvement, many of these catalysts need long reaction times, severe drastic reaction conditions or tedious workups, are moisture sensitive or are expensive. Hence, introduction of new procedures to circumvent these problems is still in demand.

Electron-deficient metalloporphyrins have been used as mild Lewis acids catalysts.^[34–39] Suda's group has reported the use of chromium and iron porphyrins in organic

synthesis. They used Cr(tpp)Cl for regioselective [3] rearrangement of aliphatic allyl vinyl ethers and for Claisen rearrangement of simple aliphatic allyl vinyl ethers, Fe(tpp) OTf for rearrangement of α , β -epoxy ketones into 1,2-diketones and Cr(tpp)OTf for highly regio- and stereoselective rearrangement of epoxides to aldehydes.^[40–43] Recently, we have

$$\begin{array}{c} \mathsf{R}\text{-}\mathsf{OH} \ + \ \ \mathsf{Me}_3\mathsf{Si}^{/\overset{\mathsf{N}}{\mathsf{N}}}\mathsf{SiMe}_3 \\ & \overbrace{\mathsf{CH}_3\mathsf{CN}}^{\mathsf{I}^\mathsf{V}}(\mathsf{TNH}_2\mathsf{PP})(\mathsf{OTf})_2]@\mathsf{GO} \\ & \mathsf{R}\text{-}\mathsf{OSiMe}_3 + \mathsf{NH}_3 \end{array}$$

SCHEME 1 Trimethylsilylation of alcohols and phenols with HMDS catalysed by $[Sn^{IV}(TNH_2PP)(OTf)_2]@GO.$



reported the use of tin(IV)tetraphenylporphyrinato perchlorate, tin(IV)tetraphenylporphyrinato trifluoromethanesulfonate, tin (IV)tetraphenylporphyrinato tetrafluoroborate and V(IV) tetraphenylporphyrinato trifluoromethanesulfonate in the ring opening of epoxides, protection of alcohols and phenols, fixation of CO₂, olefination of aldehydes and cyclopropanation of ole-fins.^[27–31,44–55]

Graphene, a very recent rising star in materials science, with an atomically thin two-dimensional structure that consists of sp^2 -hybridized carbons, exhibits remarkable electronic and mechanical properties. Functionalization and dispersion of graphene sheets are of crucial importance for their applications.^[56-60] Carbon materials such as carbon nanotubes, carbon black and graphite are some of the most widely used supports for the preparation of catalysts.^[61] However, graphene is chemically inert and has no surface functionalization and therefore it is difficult to support catalytic active species on its surface.^[62,63] Epoxy, carboxyl and hydroxyl functional groups can be introduced on the surface of graphene nanosheets by oxidation with strong oxidants.^[64,65]

In this paper, we report a rapid and highly efficient method for the trimethylsilylation of alcohols and phenols with HMDS catalysed by high-valent $[Sn^{IV}(TNH_2PP)(OTf)_2]$ supported on graphene oxide (GO) nanosheets at room temperature (Scheme 1).



FIGURE 1 FT-IR spectra of (A) GO-COOH and (B) [Sn^{IV}(TNH₂PP) (OTf)₂]@GO.

2 | EXPERIMENTAL

Chemicals were purchased from Merck and Sigma Aldrich chemical companies. Fourier transform infrared (FT-IR) spectra were obtained with potassium bromide pellets in the range 400-4000 cm⁻¹ using a JASCO 6300 spectrophotometer. Diffuse reflectance UV-visible spectra were recorded with a JASCO V-670 spectrophotometer. Inductively coupled plasma (ICP) analyses were carried out with a PerkinElmer Optima 7300 DV spectrometer. Field-emission scanning electron microscopy (FE-SEM) images of [Sn^{IV}(TNH₂PP)(OTf)₂]@GO were obtained with a Philips Sigma FE-SEM instrument. An EM10C-100 KV transmission electron microscopy (TEM) instrument was used for recording the TEM images. The reaction progress was monitored using a Shimadzu GC-16 A instrument with a flame ionization detector using silicon DC-200 or Carbowax 20M column and n-decane was used as internal standard. Tetra(4-aminophenyl)porphyrin was prepared and metallated according to the literature.^[66,67] The GO according to a modified Hummers prepared was method.[68,69]



2.1 | Preparation of GO-supported tin porphyrin: [Sn^{IV}(TNH₂PP)(OTf)₂]@GO

2.1.1 | Chlorination of GO-COOH

In a 100 ml round-bottomed flask equipped with a condenser and a magnetic stirrer bar, GO-COOH (1 g) and SOCl₂ (30 ml) were mixed and refluxed for 12 h. After this,





FIGURE 2 (A) UV-visible spectrum of homogeneous $[Sn^{IV}(TNH_2PP)$ (OTf)₂] and (B) diffuse reflectance UV-visible spectrum of $[Sn^{IV}(TNH_2PP)(OTf)_2]@GO$.





FIGURE 3 SEM images of (A) GO and (B) [Sn^{IV}(TNH₂PP)(OTf)₂]@GO. (C) Energy-dispersive X-ray spectrum of [Sn^{IV}(TNH₂PP)(OTf)₂]@GO.

the reaction mixture was cooled and the SOCl₂ was evaporated. The resulting precipitate was chlorinated GO (GO-COCl).

2.1.2 | Supporting of [Sn^{IV}(TNH₂PP)Cl₂] on GO-Cl

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To a solution of $[Sn^{IV}(TNH_2PP)Cl_2]$ (0.5 g) in dimethylformamide (DMF; 50 ml) were added GO-COCl (2.5 g) and triethylamine (5 ml). The mixture was heated at 100° C for 72 h. After cooling to room temperature, the black solids were filtered, washed with DMF, EtOH and acetone, and dried.

2.1.3 | Conversion of $[Sn^{IV}(TNH_2PP)Cl_2]$ @GO to $[Sn^{IV}(TNH_2PP)(OTf)_2]$ @GO

To a suspension of $[Sn^{IV}(TNH_2PP)Cl_2]@GO (2 g)$ in tetrahydrofuran (THF; 50 ml) was added NaOTf (1 g) and the resulting mixture was stirred at 60°C for 8 h. After this, the catalyst was filtered and washed with THF.^[55]

2.2 | General Procedure for Trimethylsilylation of Alcohols and Phenols

A suspension of alcohol or phenol (1 mmol), $[Sn^{IV}(TNH_2PP)$ (OTf)₂]@GO (40 mg, 0.01 mmol) and HMDS (0.5 mmol per OH group) in CH₃CN (1 ml) was prepared and stirred at room temperature for the appropriate time (2–4 min). The progress of the reaction was monitored by GC. After completion of the reaction, Et₂O (30 ml) was added and the catalyst was filtered. The filtrates were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure to afford the crude product.

3 | RESULTS AND DISCUSSION

3.1 | Preparation and characterization of [Sn^{IV} (TNH₂PP)(OTf)₂]@GO

Scheme 2 shows the preparation route for $[Sn^{IV}(TNH_2PP) (OTf)_2]@GO.$ First, GO was prepared by a modified Hummers method.^[69] Then carboxylic acid groups were converted to acyl chloride in order to increase the reactivity of GO-COOH. In the next step, $[Sn^{IV}(TNH_2PP)Cl_2]$ was reacted with GO-COCl to obtain the catalyst. Finally, the chlorines were exchanged with OTf⁻ by the reaction of $[Sn^{IV}(TNH_2PP)Cl_2]@GO$ with NaOTf. This increases the electron deficiency of tin(IV).

The prepared catalyst was characterized using ICP analysis, FT-IR spectroscopy, diffuse reflectance UV–visible spectrophotometry, TEM and FE-SEM.

The FT-IR spectra of GO and [Sn^{IV}(TNH₂PP)Cl₂]@GO are shown in Fig. 1. In the spectrum of pure GO, the strong

band at 1726 cm⁻¹ corresponds to carboxylic acid groups and the bands at 1051, 1223 and 1618 cm⁻¹ are attributed to the C–O (epoxy), C–OH and C=C bonds in GO, respectively. In addition, a broad band at 3429 cm⁻¹, attributed to the stretching mode of O–H bonds, reveals the presence of many hydroxyl groups.

Homogeneous $[Sn^{IV}(TNH_2PP)(OTf)_2]$ showed absorption peaks at 430 nm (Soret band) and 562 and 620 nm (Q bands) (Fig. 2(A)). The reflectance spectrum of $[Sn^{IV}(TNH_2PP)(OTf)_2]$ @GO resembles the solution counterpart spectrum with only a slight shift and a Soret band at 435 nm and Q bands at 580 and 635 nm, which clearly indicates the presence of metalloporpyhrin on the polystyrene (Fig. 2(B)).

The tin porphyrin content of the catalyst was determined by measuring the Sn content of the heterogeneous catalyst using ICP analysis. The results showed a value of about 237 µmol g⁻¹ of the catalyst. The surface morphologies of GO and [Sn^{IV}(TNH₂PP)Cl₂]@GO were studied using FE-SEM. As shown in Fig. 3(A), there are large flakes of GO with macroscopic wrinkling. Compared to GO sheets, the FE-SEM image of [Sn^{IV}(TNH₂PP)Cl₂]@GO (Fig. 3(B))



FIGURE 4 TEM images of [Sn^{IV}(TNH₂PP)(OTf)₂]@GO.

 TABLE 1
 Optimization of amounts of catalyst and HMDS in trimethylsilylation of 4-chlorobenzyl alcohol^a

Entry	Catalyst, mg (mmol)	HMDS (mmol)	Time (min)	Yield (%) ^b
1	0	0.5	2	12
2	30 (0.007)	0.5	2	58
3	40 (0.009)	0.5	2	74
4	50 (0.011)	0.5	2	100
5	50 (0.011)	0.7	2	100
6	50 (0.011)	1	2	100
7	60 (0.014)	0.5	2	100

^aReaction conditions: 4-chlorobenzyl alcohol (1 mmol), HMDS, catalyst, CH_3CN (1 ml).

^bGC yield.

exhibited an agglomerated layered structure containing tin porphyrin. Also, the energy-dispersive X-ray spectrum clearly shows the presence of Sn in the catalyst texture (Fig. 3 (C)). The TEM image of $[Sn^{IV}(TNH_2PP)(OTf)_2]@GO$ (Fig. 4) clearly indicates that tin porphyrin has been supported on the GO. The light regions belong to GO and the dark parts are the tin porphyrin.

3.2 | Trimethylsilylation of Alcohols and Phenols Catalysed by [Sn^{IV}(TNH₂PP)(OTf)₂]@GO

First, the amount of catalyst was optimized in the silvlation of 4-chlorobenzyl alcohol with HMDS. In this manner, different amounts of catalyst were used and the best results were obtained in the presence of 0.01 mmol (40 mg) of [Sn^{IV} (TNH₂PP)(OTf)₂]@GO (Table 1). In order to investigate the effect of the OTf groups on the electron deficiency of the tin(IV) porphyrin, the silvlation of 4-chlorobenzyl alcohol with HMDS was performed in the presence of 1 mol% of the [Sn^{IV}(TNH₂PP)Cl₂]@GO catalyst at room temperature. The results showed that the amount of the corresponding silvl ether in the presence of [Sn^{IV}(TNH₂PP)Cl₂]@GO was 45% after 10 min, while in the presence of [Sn^{IV}(TNH₂PP)(OTf) ₂]@GO, the reaction was completed in 2 min. It seems that the OTf groups increase the electron deficiency of the Sn centre and, due to the non-coordinative nature of OTf groups, they provide a vacant coordination site for attachment of HMDS. Then, the amount of HMDS was optimized in the trimethylsilylation of 4-chlorobenzyl alcohol. As evident

 TABLE 2
 Effect of solvent on trimethylsilylation of 4-chlorobenzyl alcohol with HMDS^a

Entry	Solvent	Time (min)	Yield (%) ^b
1	CH ₃ CN	2	100
2	CH_2Cl_2	2	48
3	CHCl ₃	2	69
4	THF	2	75

^aReaction conditions: 4-chlorobenzyl alcohol (1 mmol), HMDS (0.5 mmol), catalyst (50 mg, 1 mol%), solvent (1 ml).



TABLE 3 Trimethylsilylation of alcohols and phenols with HMDS catalysed by [Sn^{IV}(TNH₂PP)(OTf)₂]@GO at room temperature^a

	[Sn ^{IV} (TNH₂P	→ R-OSiMe ₃ + NH ₃		
	R-OH CH ₃ C			
Entry	R	Time (min)	Yield (%) ^b	TOF (h^{-1})
1	PhCH ₂	2	98	2672
2	4-ClPhCH ₂	2	100	2727
3	2,4-Cl ₂ PhCH ₂	2	100	2727
4	4-MeOPhCH ₂	2	100	2727
5	2-MeOPhCH ₂	2	98	2672
6	2-BrPhCH ₂	2	96	2618
7	4-BrPhCH ₂	2	98	2672
8	3-BrPhCH ₂	2	98	2672
9	3-NO ₂ PhCH ₂	3	90	1636
10	3-NO ₂ PhCH ₂	3	92	1672
11	9-Anthracenyl-CH2	3	97	1763
12	<i>n</i> -C ₈ H ₁₇	2	90	2454
13	<i>n</i> -C ₇ H ₁₅	2	93	2536
14	Cyclohexyl	2	97	2654
15	2-Adamantyl	3	92	1672
16	1-Adamantyl	5	90	981
17	Triphenylmethyl	3	94	1709
18	Ph	2	96	2618
19	4-ClPh	2	90	2454
20	2-ClPh	2	93	2536
21	4-NO ₂ Ph	2	90	1227

 aReaction conditions: alcohol or phenol (1 mmol), HMDS (0.5 mmol), catalyst (1 mol%), CH_3CN (1 ml).

^bGC yield.

from Table 1, the best results were obtained with 0.5 mmol of HMDS. In order to choose the reaction medium, various solvents such as dichloromethane, chloroform, THF and acetonitrile were used. The best results were obtained in acetonitrile (Table 2). The optimized conditions obtained for the silylation of 4-chlorobenzyl alcohol were alcohol, HMDS and catalyst in a molar ratio of 100:50:1.

Under the optimized reaction conditions, a wide variety of alcohols were converted to their corresponding silyl

 $\label{eq:selective trimethyl silvation of alcohols and phenols catalysed by $$ [Sn^{IV}(TNH_2PP)(OTf)_2]@GO in CH_3CN^a$$ $$ CM_3^2(TNH_2PP)(OTf)_2]@GO in CH_3CN^a$$ $$ CM_3^2(TNH_2PP)(OTf)_2]@GO in CH_3CN^a$$ $$ CM_3^2(TNH_2PP)(OTf)_2]@GO in CH_3CN^a$$ $$ CM_3^2(TNH_2PP)(OTf)_2]@GO in CH_3CN^a$$ $$ CM_3^2(TNH_2PP)(OTf)_2]$ $$ CM_3^2$

R-OH [Sn ^{IV} (TNH ₂ PP)(OTf) ₂]@GO R-OSiMe ₃					
	R'-OH	CH_3CN , HMDS	R'-OSiMe ₃		
Entry	R	R'	Time (min)	Yiel	d (%) ^b
5)	R	R'
1	4-ClPhCH ₂	Cyclohexyl	2	97	0
2	4-ClPhCH ₂	Adamantyl	2	94	0
3	4-ClPhCH ₂	$n-C_8H_{17}$	2	95	5
4	4-ClPhCH ₂	Ph	2	90	0

 aReaction conditions for a binary mixture: 1 mmol of each alcohol or phenol, HMDS (0.5 mmol), catalyst (1 mol%), CH_3CN (1 ml).

OH Catalyst OSiMe ₃							
Entry	Catalyst	HMDS (mmol)	Catalyst (mol%)	<i>T</i> (°C)	Time (min)	Yield (%)	Ref.
1	[Sn ^{IV} (TNH ₂ PP)(OTf) ₂]@GO	0.5	1	RT	2	98	This work
2	HClO ₄ –SiO ₂	0.8	2.5	RT	2	98	[10]
3	ZrCl ₄	0.8	2	RT	1	95	[11]
4	$H_{3}PW_{12}O_{40}$	0.8	1	55-60	23	90	[14]
5	Iodine	0.8	1	RT	2	98	[15]
6	CuSO ₄ ·5H ₂ O	0.7	1	RT	12	98	[18]
7	Sulfonic acid@ nanoporous silica	0.6	3	RT	55	99	[19]
8	$MgBr_2 \cdot OEt_2$	0.6	5	RT	5	98	[20]
9	LaCl ₃	0.7	10	RT	3 h	91	[21]
10	Poly(N-bromobenzene-1,3-disulfonamide)	1.4	0.02 g	RT	90	90	[22]
11	N,N,N',N'-tetrabromobenzene-1,3-disulfonamide	1.4	4	RT	30	90	[22]
12	Fe(TFA) ₃	0.7	2.5	RT	5	92	[23]
14	Fe ₃ O ₄	1	10	RT		98	[24]
15	ZrO(OTf) ₂	2	0.5	RT	1	92	[26]
16	[Sn ^{IV} (TNH ₂ PP)(OTf) ₂]/CM-MIL-101	0.7	1	RT	1	100	[27]
17	[Sn ^{IV} (TNH ₂ PP)(OTf) ₂]@CMP	0.5	1	RT	2	100	[28]
18	[Sn ^{IV} (TPP)(OTf) ₂]	0.5	1	RT	1	100	[29]
19	[Sn ^{IV} (TPP)(BF ₄) ₂]	0.5	1	RT	1	100	[30]
20	[V ^{IV} (TPP)(OTf) ₂]	0.6	1	RT	1	100	[30]
21	[Ti ^{IV} (Salophen)(OTf) ₂]	0.7	1	RT	1	100	[31]
22	Ru ^{III} (OTf)SalophenCH2-NHSiO2-Fe	0.7	4	RT	1	100	[32]

ethers. The results obtained for the silylation of various primary, secondary and tertiary alcohols showed that the all reactions were completed in 2–5 min at room temperature (Table 3). As can be seen, for benzylic alcohols, the nature of the substituents (electron-withdrawing or electron-releasing) has no significant effect on the product yield. In the absence of catalyst only small amounts of the corresponding silyl ethers were produced. The activity of $[Sn^{IV}(TNH_2PP)(OTf)_2]@GO$ was also investigated in the silylation of phenols with HMDS. The silylation of phenols with HMDS. The silylation of alcohols with HMDS. The results showed that all reactions were completed in 2–6 min for all phenols and the desired silyl ethers were obtained in excellent yields at room temperature (Table 3).

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The selectivity of this method was investigated using binary mixtures of primary, secondary and tertiary alcohols and phenols (Table 4). The results showed that primary alcohols were selectively converted to their corresponding silyl ethers in the presence of secondary or tertiary alcohols, or phenols.

The result obtained using this catalytic system in the trimethylsilylation of benzyl alcohol with HMDS was compared with some of those recently reported in the literature (Table 5). As can be seen, the present method is superior in terms of reaction time and/or amount of catalyst, or product yield.

3.3 | Catalyst Reuse and Stability

The stability of the [Sn^{IV}(TNH₂PP)(OTf)₂]@GO catalyst was monitored using multiple sequential silylation of 4chlorobenzyl alcohol with HMDS. For each of the repeated reactions, the catalyst was filtered, washed exhaustively with methanol and acetonitrile, and then dried before using with fresh 4-chlorobenzyl alcohol and HMDS. The catalyst was consecutively reused five times without any detectable catalyst leaching or any significant loss of its activity (Table 6). After each run the filtrates were used for determination of catalyst leaching. No Sn was detected in the filtrates using elemental analysis. This is not surprising because the reaction times are short. The catalytic activity of separated liquid was also checked. In this manner, the catalyst was filtered,

TABLE 6 Reusability of $[Sn^{IV}(TNH_2PP)(OTf)_2]@GO in the silvlation of4-chlorobenzyl alcohol with HMDS^a$

Entry	Time (min)	Yield (%) ^b	Sn leached (%)
1	2	97	0
2	2	94	0
3	2	90	0
4	2	90	0
5	2	87	0

^aReaction conditions: 4-chlorobenzyl alcohol (1 mmol), HMDS (0.5 mmol), catalyst (1 mol%), CH_3CN (1 ml).

^bGC yield.

fresh 4-chlorobenzyl alcohol and HMDS were added to the filtrates and the reaction mixture was stirred for 1 h. The results showed that no silyl ether was produced. The nature of the recovered catalyst was monitored using FT-IR spectrophotometry. No change was observed in the FT-IR spectrum of the catalyst, which indicates the stability and robustness of the catalyst.

4 | CONCLUSIONS

A stable and heterogeneous Sn(IV) compound was prepared and characterized for the first time. This new electron-deficient tin(IV) porphyrin, [Sn^{IV}(TNH₂PP)(OTf)₂]@GO, was used for the rapid and efficient silylation of primary, secondary and tertiary alcohols, and phenols with HMDS. Short reaction times, excellent yields and easy workup, and the reusability and stability of the catalyst are noteworthy advantages of this method.

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