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Nafion® SAC-13: heterogeneous and reusable catalyst for the activation of HMDS for efficient and selective O-silylation reactions under solvent-free condition

Gurusamy Rajagopal [†], Hanbin Lee, Sung Soo Kim [*]

Department of Chemistry, Inha University, Incheon 402-751, South Korea

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ABSTRACT

Nafion SAC-13 effectively activates hexamethyldisilazane (HMDS) for the efficient and selective silylation of alcohols. Primary, secondary, and tertiary alcohols and phenols are efficiently converted to their corresponding silylethers in short reaction times (4–8 min) with excellent yield at rt under solvent-free condition. Simple and clean reactions, high yield of the products and efficient recycling of the catalyst are the salient features of this methodology.

1. Introduction

There has been considerable interest in the development of stable, reusable, and highly active heterogeneous solid acids that is environmentally benign replacement for their homogeneous counter part.[1] Even though liquid acids are important in their own right, the industrial applications are limited due to the difficulties associated with their toxicity, handling, and disposal of acidic wastes. Heterogeneous catalysis is an important area in organic synthesis as it provides not only an alternative to homogeneous catalysis but also has the advantages of easy catalyst recovery, recycling, mild reaction condition. The introduction of solid acid catalysts such as sulfated zirconia,[2] heteropoly acids,[3] acidic polymers,[4] clays, and zeolites[5] has stimulated the development of replacement of liquid acid catalysts for organic transformations. Acidic ion-exchange polymer resins represent one class of potential solid acid material. In particular, Nafion resin, a perfluorosulfonic acid resin, has been shown to be an effective catalyst for a wide range of acid catalyzed reactions.[6] Thermal stability, chemical resistance, and possible regeneration make Nafion as a safe and valued solid acid catalyst. It exhibits an acidic character comparable to that of 100% sulfuric acid.[7] These unique properties have led to the application of Nafion as a multi-purpose heterogeneous catalyst to a wide variety of organic reactions such as Friedel–Crafts type electrophilic reactions, synthesis of esters, ethers, and various rearrangements reactions.[8] Nafion-H has been reported to catalyze variety of major organic reactions such as alkylation, olefin isomerization, olefin oligomerization, acylation, esterification, hydration, dehydration, nitration, and Fries rearranagement.[9] Catalytic activity of Nafion-H for Strecker reaction and for the synthesis of fluorinated benzimidazolines, benzothiozolines, and benzoxazolines has been reported.[10] Nafion-H-catalyzed MW assisted Ritter reaction and Biginelli condensation reaction have been also studied recently.[11] The preparation of Nafion-H silica nanocomposites, that is, the immobilization of Nafion into silica matrix has been investigated by Harmer and co-workers.[12] Outstanding catalytic performance was found for commercially available silica supported Nafion-H (Nafion-H SAC-13) in various organic transformations.[13]

Protection of hydroxyl functional group is an important process in multi-step synthesis.[14] One of the popular methods for this purpose is to transfer hydroxyl group into their corresponding silylether. Generally, the formation of silylether was carried out by the treatment of alcohols with silylchlorides or silyl triflayes under the influence of basic condition.[15] However, these methods frequently suffered from drawbacks such as lack of reactivity and the difficulty in removal of ammonium salts. Polymer supported silylating reagent was introduced by Noyori and Murata.[16]

Hexamethyldisilazane (HMDS) is a cheap and commercially available compound that can be used for the preparation of trimethylsilylethers from hydroxyl compound. O-Silylation of alcohol using HMDS is an attractive alternative, since the only by-product of the reaction is ammonia. Even though the handling of this reagent is easy, its main drawback is its poor silylating power, which needs forceful condition and long reaction time.[17] A variety of catalysts have been reported for the activation of HMDS in the literature. Trichloroisocyanuric acid (TCCA),[18] zirconium sulfophenyl phosphonate,[19] $ZnCl_2$,[20] Envirocat EPZGO,[21] tungstophosphoric acid,[22] K-10 montmorillonite,[23] iodine,[24] lithium perchlorate,[25] cupric sulfate pentahydrate,[26] H-β zeolite,[27] $MgBr_2$,[28] lithium perchlorate supported on silica gel,[29] sulfonic acid-functionalized

* Corresponding author. Tel.:+82 32 860 7678; fax: +82 32 867 5604.
E-mail address: sungsoo@inha.ac.kr (S.S. Kim).
† Permanent address: Dept of Chemistry, Govt. Arts College (Men), Nandanam, Chennai 600035, India.

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silica,[30] magnesium triflate,[31] $InBr_3$,[32] zirconium triflate,[33] $ZrCl_4$[34] NBS,[35] iron(III) trifluoroacetate,[36] silica supported perchloric acid ($HClO_4/SiO_2$),[37] Fe_3O_4,[38] poly(*N*-bromobenzene-1,3-disulfonamide),[39] barbutric acid,[40] and $Al(H_2PO_4)_3$[41] are important systems. Although these procedures provide improvement, many of these catalysts or activators require long reaction time and drastic reaction condition.

Solvent-free reactions have attracted considerable attention in chemical processes for different reasons.[42] In continuation of our work on solvent-free catalytic systems,[43] we herein report the use of Nafion SAC-13 as a reusable and heterogeneous catalyst for efficient and selective O-silylation of wide variety of alcohols and phenols.

2. Results and discussion

Nafion SAC-13 is a porous nanocomposite, which contains 10–20% Nafion-H polymer on amorphous silica (SiO_2).[12a,13a,e] In order to show the catalytic activity of Nafion catalyst, we have studied the catalytic activities of Nafion-H,[10a] Nafion SAC-13, and Nafion NR-50 and the results are summarized in Table 1. Primarily as a model reaction, silylation of benzyl alcohol with HMDS was performed under various reaction conditions. The optimization reaction was carried out with various solvents. CH_2Cl_2 is proved to be a suitable solvent for the present catalytic system (entry 1). Due to basic nature of CH_3CN, THF, and toluene, they interact with acidic catalyst and reduce catalytic activity in terms of reaction time and yield (entries 2–4). In order to reduce the solvent waste we have tested the silylation reaction under solvent-free condition. All the three Nafions catalyzed the reaction giving comparable yield under similar conditions (entries 5–7). It has been observed that the reaction time for Nafion-H and Nafion NR-50 is higher compared to Nafion SAC-13 (entries 6 and 7). This is probably due to the enhancement of bulk acidity caused by better accessibility of the sulfonic acid group on the higher surface area of Nafion SAC-13. Decrease of catalyst amount from 50 mg to 25 mg slightly alters reaction time (entry 9). Further increase of catalyst amount hardly influences the reaction yield (entry 10).

We have chosen entry 5 of Table 1 as a standard condition for our investigations. O-Silylation of various primary alcohols including electron-donating or electron-withdrawing groups proceeds efficiently with remarkable isolated yield (entries 1–12). Strongly electron-withdrawing nitro group barely affect the yield and reaction time (entries 8 and 9). This method is also suitable for allylic alcohols (entries 13 and 14). No elimination or rearrangement by-product was observed at all. Alipahtic (entries 15–17) and heterocyclic (entry 18) primary alcohols smoothly undergo trimethylsilylation reaction with remarkable yield.

We extend our methodology to secondary, tertiary alcohols, and phenols (Table 3). We have also found that various benzylic secondary alcohols react smoothly with HMDS under mild condition to produce excellent yield (entries 1–4). Very good yields were obtained for *ortho*-methoxy 1-phenylethanol and α-cyclobenzyl alcohols (entries 5 and 6). The change of phenyl to napthyl group (entries 7 and 8) hardly influences the reactivity and gives the excellent comparable yield. Benzhydrol (entry 9) and *para*-substituted benzhydrol (entry 10) underwent smooth trimethylsilylation reaction. Aliphatic secondary alcohols also give excellent yield (entries 11 and 12). Tertiary alcohol takes a little longer reaction time with good yield (entry 13).

The silylation of a variety of phenols with HMDS is also investigated. Phenol and substituted phenols were silylated easily and their corresponding silylethers were isolated in excellent yield (entries 14–17). 2-Naphthol is also silylated under similar reaction condition with 98% yield within 5 min (entry 18). Cyclohexanols (entries 19 and 20) and sterically hindered adamentanol (entry 21) produce silylethers in excellent yield.

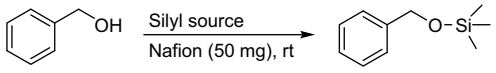
Nafion SAC-13 is not only a stable solid but also can be recycled. Nafion SAC-13 is reused five consecutive times without any special treatment. It has been found that the catalytic efficiency remains almost unchanged in terms of reaction time and yield (Table 4).

Table 5 shows the efficiency of Nafion SAC-13 in comparison with reported results in the literature. Higher temperature, long reaction time, low yield, and limitation of substrate applicability make our system as a better choice.

We have investigated selective silylation of different binary mixture of alcohols. As shown in Table 6, primary benzylic alcohol is favorably produced in the presence of secondary benzylic alcohol with the ratio of 90:10 [Eq. 1]. A secondary benzylic alcohol is predominantly formed with the ratio of 85:15 [Eq. 2] and the ratio increases to 97:3 with tertiary alcohol [Eq. 3].

The plausible reaction pathway is as follows (Scheme 1). Generation of ammonia gas was observed (odor and litmus paper) in all reactions. Nafion SAC-13 as a Bronsted acid, reacts with HMDS to produce **I**. This in turn reacts with alcohol to produce silylating species **II**. Irreversible cleavage of **II** leads to the fast evolution of ammonia and formation of **III**. The catalytic cycle can be completed after the release of H^+ from **III**.

Table 1
Optimization of O-silylation of benzyl alcohol using Nafion catalysts



Entry	Catalyst	Solvent	Silyl Source	Reaction time (min)	Yield[a] (%)
1	Nafion SAC-13	CH_2Cl_2	HMDS	10	99
2	Nafion SAC-13	CH_3CN	HMDS	20	80
3	Nafion SAC-13	THF	HMDS	25	85
4	Nafion SAC-13	Toluene	HMDS	20	83
5	Nafion SAC-13	No solvent	HMDS	4	99
6	Nafion-H	No solvent	HMDS	10	98
7	Nafion NR-50	No solvent	HMDS	20	97
8	Nafion SAC-13	No solvent	TMSCN	15	98
9	Nafion SAC-13	No solvent	HMDS	10	97[b]
10	Nafion SAC-13	No solvent	HMDS	4	98[c]

[a] Isolated yields.
[b] Catalyst (25 mg) used.
[c] Catalyst (100 mg) used.

3. Conclusions

We have introduced a new catalytic application of Nafion SAC-13 as the activator of HMDS for the efficient protection of variety of alcohols and phenols under solvent-free condition. Short reaction time, excellent yield, easy work-up, and selectivity are noteworthy advantages of this method. The catalyst is heterogeneous, recyclable, non-corrosive, and environmentally benign compound. The present method clearly manifests the future potential of Nafion SAC-13 for many other organic transformations.

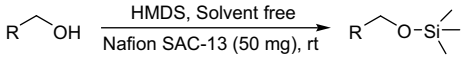
4. Experimental section

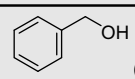
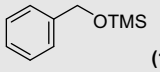
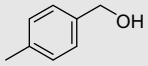
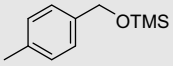
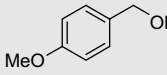
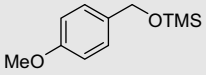
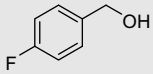
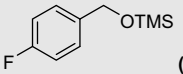
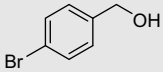
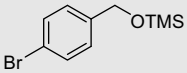
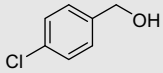
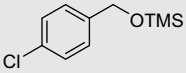
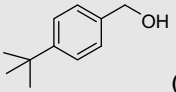
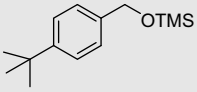
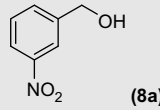
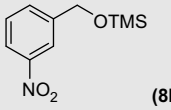
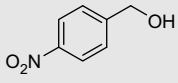
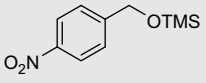
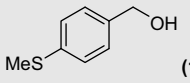
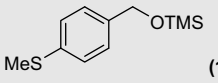
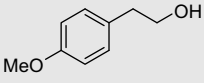
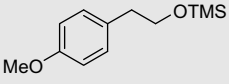
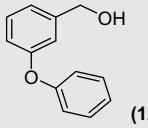
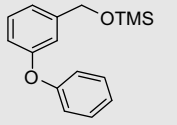
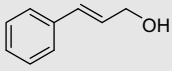
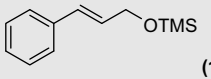
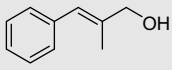
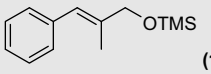
4.1. General

4.1.1. Instrumentation

In all the cases the ^1H NMR spectra were recorded with Varian Gemini 200 or 400 MHz instrument. Chemical shifts are reported in parts per million in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR data were collected on Varian Gemini 200 or 400 MHz instrument (50or 100 MHz).

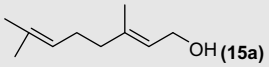
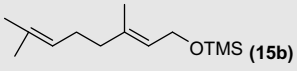
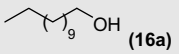
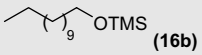
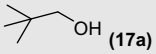
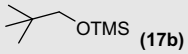
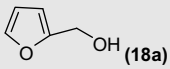
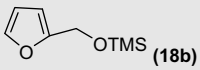
Table 2
O-Silylation of primary alcohols with HMDS in the presence of Nafion SAC-13 as a heterogeneous catalyst



Entry	Substrate	Product	Reaction time (min)	Yield[a] (%)
1	 **(1a)**	 **(1b)**	4 4	99 100[b]
2	 **(2a)**	 **(2b)**	4	98
3	 **(3a)**	 **(3b)**	3 3	99 100[b]
4	 **(4a)**	 **(4b)**	4	98
5	 **(5a)**	 **(5b)**	4	97
6	 **(6a)**	 **(6b)**	4	98
7	 **(7a)**	 **(7b)**	5	97
8	 **(8a)**	 **(8b)**	5	97
9	 **(9a)**	 **(9b)**	5	97
10	 **(10a)**	 **(10b)**	4	98
11	 **(11a)**	 **(11b)**	5	98
12	 **(12a)**	 **(12b)**	5	98
13	 **(13a)**	 **(13b)**	5	96
14	 **(14a)**	 **(14b)**	5	95

(*continued on next page*)

Table 2 (*continued*)

Entry	Substrate	Product	Reaction time (min)	Yield[a] (%)
15	 OH **(15a)**	 OTMS **(15b)**	5	96
16	 OH **(16a)**	 OTMS **(16b)**	4	95
17	 OH **(17a)**	 OTMS **(17b)**	4	98
18	 OH **(18a)**	 OTMS **(18b)**	5	96

[a] Isolated yields.
[b] GC yields.

4.2. Experimental procedure

4.2.1. General procedure for O-silylation of alcohols/phenols

To a stirred solution of alcohol/phenol (1 mmol) and HMDS (1 mmol) was added Nafion SAC-13 (50 mg) and the mixture was stirred at room temperature for the time mentioned in the tables. After completion of the reaction (monitored by TLC, *n*-hexane/EtOAc, 9:1), *n*-hexane(5 ml) was added and the catalyst was recovered by filtration. The filtrate was washed with CH_2Cl_2 and acetone, and then dried. The filtrate was washed with water (10 ml) and the organic layer was dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave the highly pure product without further purification. The desired pure products were characterized by comparison of their NMR data with those of known compounds.[19,23,37,44] The spectral data of some representative trimethylsilylethers are given below.

4.2.2. Characterization data

4.2.2.1. Trimethyl(benzyloxy)silane (Table 2, ***1b****)*[37]. ^{1}H NMR ($CDCl_3$) δ 7.32–7.34 (m, 5H), 4.73 (s, 2H), 0.13 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 138.32, 128.36, 127.45, 127.35, 67.85, 0.29. HRMS *m*/*z* calcd for $C_{10}H_{16}OSi$ $[M+H]^+$ 186.0970, found 186.0979.

4.2.2.2. Trimethyl(4-methylbenzyloxy)silane (Table 2, ***2b****)*[37]. ^{1}H NMR ($CDCl_3$) δ 7.21–7.26 (d, *J*=7.3 Hz, 2H), 7.11–7.19 (d, *J*=7.3 Hz, 2H), 4.75 (s, 2H), 2.38 (s, 3H), 0.09 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 137.9, 136.6, 128.9, 126.6, 64.5, 21.0, −0.38. HRMS *m*/*z* calcd for $C_{11}H_{18}OSi$ $[M+H]^+$ 194.1127, found 194.1135.

4.2.2.3. (4-Methoxybenzyloxy)trimethylsilane (Table 2, ***3b****)*[37]. ^{1}H NMR ($CDCl_3$) δ 7.21–7.24 (d, *J*=8.0 Hz, 2H), 6.82–6.85 (d, *J*=8.0 Hz, 2H), 4.62 (s, 2H), 3.81 (s, 3H), 0.07 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 159.0, 133.0, 128.5, 113.8, 64.7, 55.1, −0.48. HRMS-EI$^+$ *m*/*z* calcd for $C_{11}H_{18}O_2Si$ $[M+H]^+$: 210.1076, found 210.1073.

4.2.2.4. (4-Fluorobenzyloxy)trimethylsilane (Table 2, ***4b****).* ^{1}H NMR ($CDCl_3$) δ 7.49–7.56 (m, 2H), 7.25 (t, *J*=7.2 Hz, 2H), 4.89 (s, 2H), 0.39 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 163.2, 160.8, 128.2, 128.1, 115.1, 114.9, 63.9, −0.42. HRMS-EI$^+$ *m*/*z* calcd for $C_{10}H_{15}FOSi$: 198.0876, found 198.0869.

4.2.2.5. (4-Bromobenzyloxy)trimethylsilane (Table 2, ***5b****).* ^{1}H NMR ($CDCl_3$) δ 7.27 (d, *J*=10 Hz, 2H), 7.01 (d, *J*=8.8 Hz, 2H), 4.46 (s, 2H), 0.01 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 137.9, 136.6, 128.9, 126.6, 64.5, 21.0, 0.32. HRMS *m*/*z* calcd for $C_{10}H_{15}BrOSi$ $[M+H]^+$ 258.0076, found 258.0083.

4.2.2.6. (4-Chlorobenzyloxy)trimethylsilane (Table 2, ***6b****).* ^{1}H NMR ($CDCl_3$) δ 7.25 (d, *J*=8.6 Hz, 2H), 7.05 (d, *J*=10 Hz, 2H), 4.49 (s, 2H), 0.05 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 138.9, 135.6, 127.9, 125.6, 65.5, 20.0, 0.21. HRMS *m*/*z* calcd for $C_{10}H_{15}ClOSi$ $[M+H]^+$ 214.0581, found 214.0587.

4.2.2.7. (4-tert-Butylbenzyloxy)trimethylsilane (Table 2, ***7b****).* ^{1}H NMR ($CDCl_3$) δ 7.35 (dd, *J*=7.1 Hz, 2H), 7.25 (d, *J*=7.1 Hz, 2H), 4.64 (s, 2H), 1.29 (s, 9H), 0.13 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 150.0, 137.9, 126.4, 125.1, 64.4, 34.4, 31.3, −0.38. HRMS-EI$^+$ *m*/*z* calcd for $C_{14}H_{24}OSi$:236.1596, found 236.1599.

4.2.2.8. Trimethyl(3-nitrobenzyloxy)silane (Table 2, ***8b****).* ^{1}H NMR ($CDCl_3$) δ 8.20(s, 1H), 8.10 (d, *J*=7.4 Hz, 1H), 7.65 (d, *J*=7.4 Hz, 1H), 7.32–7.53 (m, 1H), 4.77 (s, 2H), 0.18 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 148.3, 143.2, 132.1, 129.1, 122.0, 121.0, 63.3, −0.55. HRMS-EI$^+$ *m*/*z* calcd for $C_{10}H_{15}NO_3Si$ 225.3165, found 225.3159.

4.2.2.9. Trimethyl(4-nitrobenzyloxy)silane (Table 2, ***9b****)*[19]. ^{1}H NMR ($CDCl_3$) δ 7.20 (d, *J*=8.6 Hz, 2H), 7.14 (d, *J*=10 Hz, 2H), 4.41 (s, 2H), 0.03 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 139.9, 137.6, 127.9, 125.6, 64.5, 22.0, 0.22.

4.2.2.10. Trimethyl(4-(methylthio)benzyloxy)silane (Table 2, ***10b****).* ^{1}H NMR ($CDCl_3$) δ 7.25 (s, 5H), 4.66 (s, 2H), 2.48 (s, 3H), 0.17 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 137.9, 136.9, 127.1, 126.7, 64.2, 16.0, −0.42. HRMS *m*/*z* calcd for $C_{11}H_{18}OSSi$:226.0848, found 198.0832.

4.2.2.11. (4-Methoxyphenethoxy)trimethylsilane (Table 2, ***11b****).* ^{1}H NMR ($CDCl_3$) δ 7.27 (d, *J*=7.3 Hz, 2H), 7.00 (d, *J*=7.3 Hz, 2H), 3.91 (s, 3H), 3.86 (t, *J*=7.1 Hz, 2H), 2.93 (t, *J*=7.1 Hz, 2H), 0.23 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 158.0, 130.9, 129.9, 113.6, 64.0, 55.1, 38.5, −0.57. HRMS-EI$^+$ *m*/*z* calcd for $C_{12}H_{20}O_2Si$ $[M+H]^+$ 224.1233, found 224.1227.

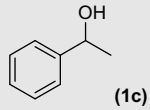
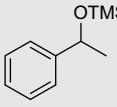
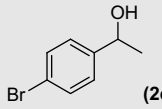
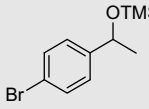
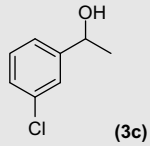
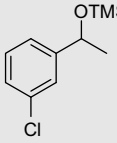
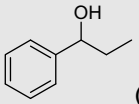
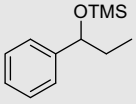
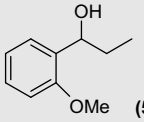
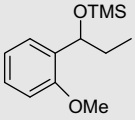
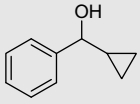
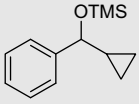
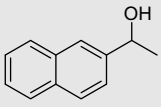
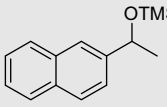
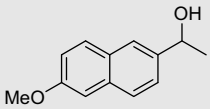
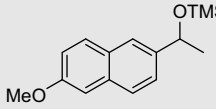
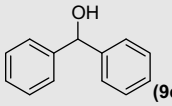
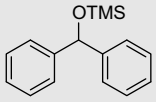
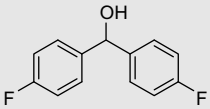
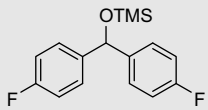
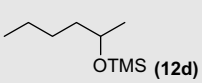
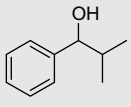
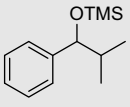
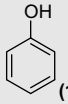
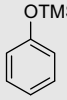
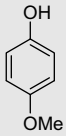
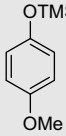
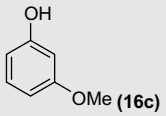
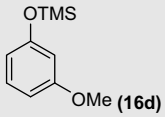
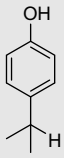
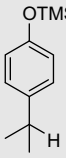
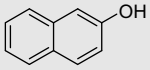
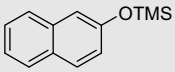
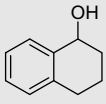
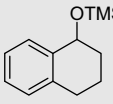
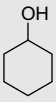
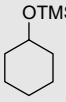
4.2.2.12. Trimethyl(4-phenoxybenzyloxy)silane (Table 2, ***12b****).* ^{1}H NMR ($CDCl_3$) δ 7.47–7.59 (m, 3H), 7.20–7.36 (m, 5H), 7.12 (dd, *J*=7.2, 1.5, 1H), 4.89 (s, 2H), 0.36 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 157.3, 157.2, 143.1, 129.6, 129.5, 123.1, 121.1, 118.9, 117.4, 116.8, 64.2, −0.43. HRMS-EI$^+$ *m*/*z* calcd for $C_{16}H_{20}O_2Si$: 272.1233, found 272.1224.

4.2.2.13. Trimethyl(3-phenylallyloxy)silane (Table 2, ***13b****)*[44]. ^{1}H NMR ($CDCl_3$) δ 7.59–7.47 (m, 3H), 7.36–7.21 (m, 5H), 7.12 (dd, *J*=2.6, 8.8 Hz, 1H), 4.89 (s, 2H), 0.36 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 137.3, 129.7, 129.2, 128.1, 127.1, 126.3, 64.2, 0.21.

4.2.2.14. (E)-Trimethyl(2-methyl-3-phenylallyloxy)silane (Table 2, ***14b****).* ^{1}H NMR ($CDCl_3$) δ 7.24–7.25 (m, 5H), 6.47 (s, 1H), 4.11(s, 2H), 1.80 (s, 3H), 0.12 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 137.9, 137.2, 128.8, 128.0, 126.2, 124.4, 68.3, 15.0, −0.36. HRMS-EI$^+$ *m*/*z* calcd for $C_{13}H_{20}OSi$: 220.1283, found 220.1290.

4.2.2.15. (E)-(3,7-Dimethylocta-2,6-dienyloxy)trimethylsilane (Table 2, ***15b****).* ^{1}H NMR ($CDCl_3$) δ 5.32 (t, *J*=3 Hz, 1H), 5.08 (t, *J*=3 Hz, 1H),

Table 3
Silylation of secondary, tertiary alcohols and phenols with HMDS in the presence of Nafion SAC-13 as a heterogeneous catalyst

Entry	Substrate	Product	Reaction time (min)	Yield[a] (%)
1	 (1c)	 (1d)	5 5	96 100[b]
2	 (2c)	 (2d)	5	98
3	 (3c)	 (3d)	5	96
4	 (4c)	 (4d)	5	95
5	 (5c)	 (5d)	6	95
6	 (6c)	 (6d)	6	94
7	 (7c)	 (7d)	5	97
8	 (8c)	 (8d)	5	98
9	 (9c)	 (9d)	6 6	96 100[b]
10	 (10c)	 (10d)	6	95
11	 (11c)	 (11d)	5	94
12	 (12c)	 (12d)	5	95
13	 (13c)	 (13d)	8	94
14	 (14c)	 (14d)	6	97
15	 (15c)	 (15d)	5	98
16	 (16c)	 (16d)	5	98
17	 (17c)	 (17d)	6	96
18	 (18c)	 (18d)	4	98
19	 (19c)	 (19d)	5	97
20	 (20c)	 (20d)	5	98
21	(21c)	(21d)	8	95

[a] Isolated yields.
[b] GC yields.

4.15 (d, J=3.6 Hz, 2H), 4.15 (d, J=3.6 Hz, 2H), 2.00–2.10 (m, 4H), 1.59–1.67 (m, 9H), 0.06 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 139.5, 31.6, 123.8, 123.3, 29.2, 39.4, 26.3, 25.6, 17.6, 16.1, 1.8. HRMS-EI$^+$ m/z calcd for $C_{13}H_{26}OSi$: 226.1753, found 226.1774.

4.2.2.16. Trimethyl(nonan-2-yloxy)silane (Table 2, ***16b****).* ^{1}H NMR ($CDCl_3$) δ 3.73–3.70 (m, 1H), 1.39–1.24 (m, 12H), 1.10 (t, J=11 Hz, 3H), 0.85 (d, J=5.8 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 68.5, 39.6, 31.8, 29.5, 29.2, 25.9, 23.8, 22.6, 14.0, 0.18.

4.2.2.17. Trimethyl(neopentyloxy)silane (Table 2, ***17b****).* ^{1}H NMR ($CDCl_3$) δ 3.19 (s, 2H), 0.85 (s, 9H), 0.06 (s, 9H). ^{13}C NMR ($CDCl_3$) δ72.7, 26.2, 35.3, 0.53.

4.2.2.18. Trimethyl (furan-2-yl-methoxy)silane (Table 2, ***18b****).* ^{1}H NMR ($CDCl_3$) δ 7.65 (1H, d, J=4.6 Hz), 6.41–6.43 (1H, m), 6.34–6.37 (1H, m), 4.89 (2H, s), 0.23 (9H, s). ^{13}C NMR ($CDCl_3$) δ 150.2, 144.3, 109.8, 108.3, 63.4, 0.41. HRMS-EI$^+$ m/z calcd for $C_8H_{14}OSi$: 170.0763, found 170.0775.

4.2.2.19. Trimethyl-(1-phenylethoxy)silane (Table 3, ***1d****)*[37]. ^{1}H NMR ($CDCl_3$) δ 7.30–7.35 (m, 5H), 4.87 (d, J=20 Hz, 1H), 1.45 (d, J=8 Hz, 3H),

Table 4
Reusability of Nafion SAC-13 of silylation of alcohols

Substrate	Yield[a]				
	Run 1	Run 2	Run 3	Run 4	Run 5
4-Methoxybenzyl alcohol	99	99	98	98	97
1-(4-Bromophenyl)ethanol	98	96	95	95	95
Phenol	97	97	96	96	96

[a] Isolated yields.

0.39 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 146.4, 128.1, 127.4, 126.8, 125.3, 70.5, 26.8, 25.1, 0.06. HRMS-EI$^+$: *m/z* calcd for $C_{11}H_{18}OSi$: 194.1127, found 194.1131.

4.2.2.20. (1-(4-Bromophenyl)ethoxy)trimethylsilane (Table 3, ***2d****).* ^{1}H NMR ($CDCl_3$) δ 7.42–7.48 (d, *J*=7.2 Hz, 2H), 7.20–7.26 (d, *J*=7.2 Hz, 2H), 4.82 (q, *J*=7.1 Hz, 1H), 1.41 (d, *J*=7.2 Hz, 3H), 0.03 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 145.5, 131.2, 127.0, 120.4, 69.9, 26.8, 0.04. HRMS-EI *m/z* calcd for $C_{11}H_{17}BrOSi$: 272.0232, found 272.0239.

4.2.2.21. (1-(3-Chlorophenyl)ethoxy)trimethylsilane (Table 3, ***3d****).* ^{1}H NMR ($CDCl_3$) δ 7.34–7.37 (m, 1H), 7.29–7.32 (m, 3H), 4.83 (q, *J*=8.0 Hz, 1H), 1.47 (d, *J*=7.2 Hz, 3H), 0.14 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 148.7, 134.0, 129.4, 126.9, 125.5, 123.4, 69.9, 26.8, 0.04. HRMS-EI *m/z* calcd for $C_{11}H_{17}ClOSi$: 228.0737, found 228.0739.

4.2.2.22. (1-(2-Methoxyphenyl)propoxy)trimethylsilane (Table 3, ***5d****).* ^{1}H NMR ($CDCl_3$) δ 7.85(d, *J*=7.6 Hz, 1H), 7.50–7.72 (m, 1H), 7.27–7.40 (m, 1H), 7.24 (d, *J*=7.6 Hz, 1H), 5.41 (q, *J*=6.5 Hz, 1H), 4.23 (s, 3H), 2.04–2.07 (m, 2H), 1.35 (t, *J*=6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 155.5, 133.9, 127.5, 126.7, 120.4, 109.8, 69.6, 55.1, 31.7, 10.4, 0.04. HRMS-EI$^+$ *m/z* calcd for $C_{13}H_{22}O_2Si$:238.1389, found 238.1395.

4.2.2.23. (Cyclopropyl(phenyl)methoxy)trimethylsilane (Table 3, ***6d****).* ^{1}H NMR ($CDCl_3$) δ 7.13–7.27 (m, 5H), 3.98 (d, *J*=7.7 Hz, 1H), 1.02–1.06 (m, 1H), 0.22–0.44 (m, 4H), −0.06 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 145.1, 128.0, 127.0, 125.9, 78.1, 19.9, 3.5, 2.8, 0.2. HRMS *m/z* calcd for $C_{13}H_{20}OSi$ [M+H]$^+$ 220.1283, found 220.1289.

4.2.2.24. Trimethyl(1-(naphthalen-2-yl)ethoxy)silane (Table 3, ***7d****).* ^{1}H NMR ($CDCl_3$) δ 7.84–7.91 (m, 4H), 7.51–7.58 (m, 3H), 5.15 (q, *J*=7.7 Hz, 1H), 1.55 (d, *J*=7.7 3H), 0.18 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 143.9, 132.3, 132.7, 128.7, 127.8, 127.6, 125.8, 125.4, 124.0, 123.6, 70.7, 26.8, 0.14. HRMS *m/z* calcd for $C_{15}H_{20}OSi$ [M+H]$^+$ 244.1283, found 244.1279.

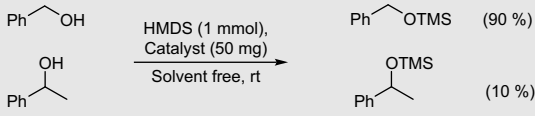
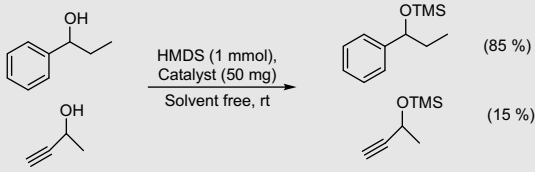
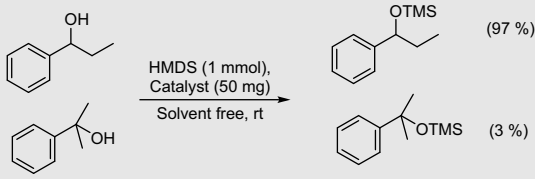
4.2.2.25. (1-(6-Methoxynaphthalen-2-yl)ethoxy)trimethylsilane (Table 3, ***8d****).* ^{1}H NMR ($CDCl_3$) δ 7.69–7.41 (m, 3H), 7.43 (dd, *J*=7.4, 1.6 Hz, 1H), 7.11–7.16 (m, 2H), 4.98 (q, *J*=7.2 Hz, 1H), 3.91 (s, 3H), 1.51 (d, *J*=7.2 Hz, 3H), 0.07 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 158.1, 141.6, 134.0, 129.3, 128.5, 126.7, 124.6, 123.5, 118.6, 105.6, 70.7, 55.2, 26.8, 0.15. HRMS *m/z* calcd for $C_{16}H_{22}O_2Si$ 274.1389, found 274.1382.

4.2.2.26. Benzhydryloxytrimethylsilane (Table 3, ***9d****)*[37]. ^{1}H NMR ($CDCl_3$) δ 7.41–7.25 (m, 10H), 5.82 (s, 1H), 0.13 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 144.8, 128.35, 128.16, 127.4, 127.2, 127, 126.5, 19.9, 0.11.

Table 5
Nafion SAC-13 catalyzed silylation of alcohols in comparison with other solvent-free and supported systems

S. No	Catalyst and conditions	Reaction time (min)	Reference
1	Nafion SAC-13, rt	4–8	Present method
2	Fe_3O_4, rt	5	38
3	Poly(*N*-bromobenzene-1,3-disulfonamide)	8–10	39
4	$LiClO_4$, rt	10–30	25
5	$H_3PW_{12}O_{40}$, 55–60 °C,	6–135	22
6	Barbutric acid, rt	60–300	40
7	$Fe(F_3CCO_2)_3$	5–120	36

Table 6
Selective O-trimethylsilylation of alcohols in the presence of HMDS with Nafion SAC-13

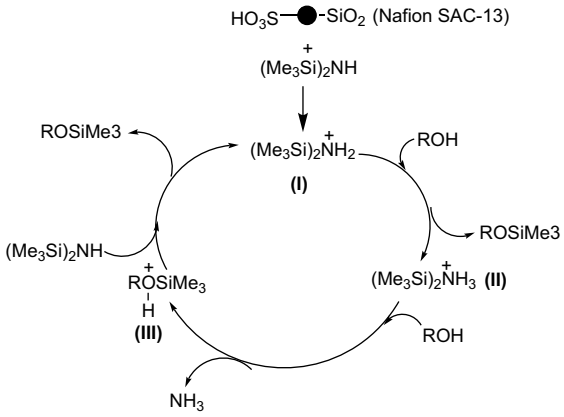
Equation	Reaction	
1		(90 %) (10 %)
2		(85 %) (15 %)
3		(97 %) (3 %)

4.2.2.27. (Bis(4-fluorophenyl)methoxy)trimethylsilane (Table 3, ***10d****).* ^{1}H NMR ($CDCl_3$) δ 7.52–7.58 (m, 4H), 7.21–7.26 (m, 4H), 5.99 (s, 1H), 0.34 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 164.4, 159.5, 140.5, 140.4, 128.1, 128.0, 115.3, 114.9, 75.2, 0.07. HRMS-EI$^+$ *m/z* calcd for $C_{16}H_{18}F_2OSi$ 292.1095, found 292.1099.

4.2.2.28. (But-3-yn-2-yloxy)trimethylsilane (Table 3, ***11d****).* ^{1}H NMR ($CDCl_3$) δ 4.7 (qd, *J*=7.1, 1.6 Hz, 1H), 2.37 (d, *J*=1.6 Hz, 1H), 1.41 (d, *J*=7.1 Hz, 3H), 0.09 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 71.4, 58.3, 25.2, 2.45, 0.07. HRMS-EI$^+$ *m/z* calcd for $C_7H_{14}OSi$:142.0814, found 142.0820.

4.2.2.29. (Hexan-2-yloxy)trimethylsilane (Table 3, ***12d****).* ^{1}H NMR ($CDCl_3$) δ 3.70–3.78 (m, 1H), 1.24–1.34 (m, 12H), 1.10 (t, *J*=11.4 Hz, 3H), 0.85 (d, *J*=5.8 Hz, 3H), 0.10 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 68.5, 39.6, 31.8, 23.8, 22.6, 14.0, 0.18. HRMS-EI$^+$: *m/z* calcd for $C_9H_{22}OSi$: 174.1440, found 174.1458.

4.2.2.30. Trimethyl(2-methyl-1-phenylpropoxy)silane (Table 3, ***13d****).* ^{1}H NMR ($CDCl_3$) δ 7.24–7.27 (m, 5H), 4.25–4.30 (m, 1H), 1.80–1.86 (m, 1H), 0.91 (q, *J*=9.8 Hz, 3H), 0.77 (q, *J*=9.8 Hz, 3H), 0.001 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 144.4, 127.7, 126.8, 126.6, 80.4, 36.3, 19.2, 18.1, 0.09. HRMS-EI$^+$: *m/z* calcd for $C_{13}H_{22}OSi$: 222.1440, found 222.1435.



Scheme 1. Proposed reaction pathway.

*4.2.2.31. Trimethyl(phenoxy)silane (Table 3, **14d**).* ^{1}H NMR ($CDCl_3$) δ 7.30–7.26 (m, 5H), 0.31 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 152.3, 129.38, 121.4, 120.2, 0.22. HRMS-EI$^+$: *m*/*z* calcd for $C_9H_{14}OSi$: 166.0814, found 166.0821.

*4.2.2.32. 4-Methoxy(phenoxy)trimethylsilane (Table 3, **15d**)[23].* ^{1}H NMR ($CDCl_3$) δ 7.30 (d, *J*=8.6 Hz, 2H), 7.22 (d, *J*=10 Hz, 2H), 3.89 (s, 3H), 0.31 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 154.3, 148.6, 121.5, 55.8, 0.22. HRMS-EI$^+$: *m*/*z* calcd for $C_{10}H_{16}O_2Si$: 196.0920, found 196.0929.

*4.2.2.33. (3-Methoxyphenoxy)trimethylsilane (Table 3, **16d**)[23].* ^{1}H NMR ($CDCl_3$) δ 7.16 (d, *J*=9 Hz, 1H), 6.21–6.16 (m, 3H), 4.12 (s, 3H), 0.20 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 158.2, 151.6, 130.7, 114.2, 106.3, 56.8, 0.38. HRMS-EI$^+$: *m*/*z* calcd for $C_{10}H_{16}O_2Si$: 196.0920, found 196.0931.

*4.2.2.34. (4-Isopropylphenoxy)trimethylsilane (Table 3, **17d**).* ^{1}H NMR ($CDCl_3$) δ 7.03 (d, *J*=8.4 Hz, 2H), 6.74 (d, *J*=8.4 Hz, 2H), 2.77–2.91 (m, 1H), 1.20 (d, *J*=7 Hz, 6H), 0.26 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 153.0, 141.7, 127.2, 119.7, 33.3, 24.4, 0.29. HRMS-EI$^+$: *m*/*z* calcd for $C_{12}H_{20}OSi$: 208.1283, found 208.1289.

*4.2.2.35. Trimethyl(naphthalen-2-yloxy)silane (Table 3, **18d**)[37].* ^{1}H NMR ($CDCl_3$) δ 7.91–7.84 (m, 4H), 7.55–7.51 (m, 3H), 0.26 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 152.8, 134.4, 129.2, 129.3, 127.5, 126.8, 123.5, 117.7, 0.23. HRMS-EI$^+$: *m*/*z* calcd for $C_{13}H_{16}OSi$: 216.0970, found 216.0961.

*4.2.2.36. Trimethyl(1,2,3,4-tetrahydronaphthalen-1-yloxy)silane (Table 3, **19d**).* ^{1}H NMR ($CDCl_3$) δ 7.25–7.21 (m, 2H), 7.0–6.87 (m, 2H), 4.48 (t, *J*=8 Hz, 1H), 2.94 (t, *J*=6 Hz, 2H), 1.24–1.19 (m, 4H), 0.21 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 137.8, 136.4, 127.2, 125.3, 66.7, 33.7, 28.1, 19.5, 0.26. HRMS-EI$^+$: *m*/*z* calcd for $C_{13}H_{20}OSi$: 220.1283, found 220.1277.

*4.2.2.37. Cyclohexyloxytrimethylsilane (Table 3, **20d**)[37].* ^{1}H NMR ($CDCl_3$) δ 3.55–3.57 (m, 1H), 1.74–1.70 (m, 4H), 1.53–1.49 (m, 1H), 1.23–1.29 (m, 4H), 1.11–1.14 (m, 1H), 0.09 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 73.8, 35.9, 26.2, 24.6, 0.52. HRMS-EI$^+$: *m*/*z* calcd for $C_9H_{20}OSi$: 172.1283, found 172.1275.

*4.2.2.38. 2-Adamantanoltrimethylsilane (Table 3, **21d**).* ^{1}H NMR ($CDCl_3$) δ 3.79 (t, *J*=6.5 Hz), 2.12 (d, *J*=7 Hz, 2H), 1.83–1.57 (m, 12H), 1.40 (d, *J*=7 Hz, 2H), 0.10 (s, 9H). ^{13}C NMR ($CDCl_3$) δ. 74.9, 37.7, 36.6, 352, 31.1, 27.6, 27.1, 0.26.

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