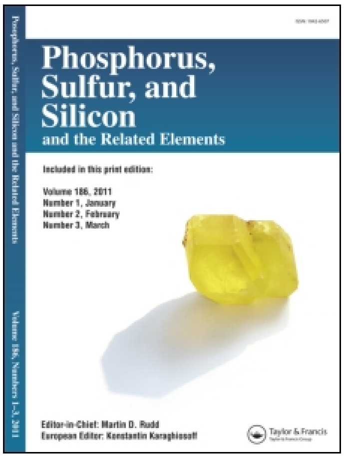

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Silica-Supported Ferric Chloride (Silica-$FeCl_3$): A Reusable, Easily Controllable Catalyst for the Protection of Hydroxyl Groups under Mild and Ambient Conditions

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Silica-Supported Ferric Chloride (Silica-$FeCl_3$): A Reusable, Easily Controllable Catalyst for the Protection of Hydroxyl Groups under Mild and Ambient Conditions

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Diverse alcohols, phenols, and naphthols were converted into their corresponding trimethylsilyl ether effectively with hexamethyldisilazane in the presence of silica-$FeCl_3$ under solvent-free and ambient conditions with short reaction time in good to excellent yields. Work up procedure is easy, and the catalyst can be recovered by simple filtration and reused.

Keywords Alcohols; Hexamethyldisilazane; Phenols; Silica-$FeCl_3$; Trimethylsilylation

INTRODUCTION

Solid-phase organic synthesis (SPOS) has become increasingly important in synthesizing large numbers of combinatorial and parallel compound collections.[1–5] Acidic catalysts have been used, mainly in industry, for producing more than 1 × 10^8 Mt/year of products.[6] Among acidic catalysts, the most commonly used are HF, H_2SO_4, $HClO_4$, and H_3PO_4. Solid acids have many advantages such as ease of handling, decreasing reactor and plant corrosion problems, and environmentally safe disposal.[6,7] Also, wastes and by-products can be minimized or avoided by developing cleaner synthesis routes.[8] Green chemistry has been defined as a set of principles that reduce or eliminate the use or generation of hazardous substances. In addition, there is current research and general interest in heterogeneous systems because of their importance in industry and in developing technologies.[9] Heterogeneous organic

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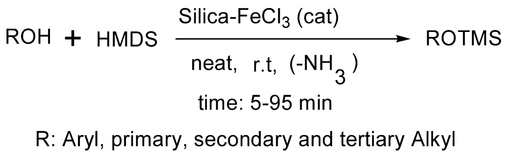
reactions have proven useful to chemists in the laboratory as well as in the industrial context. These reactions are effected by the reagents immobilized on the porous solid supports and have advantages over the conventional solution phase reactions because of the good dispersion of active reagent sites, associated selectivity and easier work-up.[10]

The preparation of silylethers could carry out by treatment of alcohols with silyl chlorides or silyl triflates in the presence of an organic base.[11–14] However, some of these methods frequently suffered from drawbacks such as lack of reactivity or the difficulty in removal of amine salts.[15] 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 byproduct.[15–17] 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 $(CH_3)_3SiCl$,[18] K-10 montmorillonite,[19] sulfonic acids,[20] zirconium sulfophenyl phosphonate,[21] $ZnCl_2$,[22] Envirocat EPZGO,[23] tungstophosphoric acid,[24] iodine,[25] lithium perchlorate,[26] cupric sulfate pentahydrate,[27] $MgBr_2$,[28] lithium perchlorate supported on silica gel,[29] $Al(HSO_4)_3$,[30] $Al(OTF)_3$,[31] magnesium triflate,[32] copper triflate,[33] and silica-$HClO_4$.[34]

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. In the present research for functional group transformation, we wish to describe a new protocol for the mild and rapid trimethylsilylation of a wide variety of hydroxyl groups using HMDS and a catalytic amount of silica-$FeCl_3$ as a recyclable solid Lewis acid catalyst. This reagent is safe, easy to handle, environmentally benign and presents fewer disposal problems. Silica-$FeCl_3$ as a recyclable solid acid catalyst was prepared from the reaction of silica gel with ferric chloride.[35,36] The trimethylsilylation is easily carried out at room temperature under solvent-free conditions (Scheme 1).

RESULTS AND DISCUSSION

A wide range of structurally diverse and functionalized alcohols, phenols and naphthols underwent silylation by this procedure to provide the corresponding TMS ethers in good to excellent isolated yields as shown in Table I (entries 1–22).



SCHEME 1

Generally, in the all cases the reactions of primary, secondary, and tertiary alcohols were completed within less than 95 min, in solvent-free conditions at room temperature accompanied by evolution of NH_3 gas from the reaction mixture. Inspection of the data in Table I clearly shows that different types of hindered secondary and tertiary alcohols were successfully converted to the corresponding silylethers (Table I). The catalyst could be recycled by filtering it from the reaction mixture and then washing the solid reagent by ethyl acetate followed by draying in an oven at 100°C for 30 min.

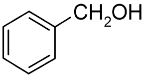
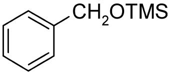
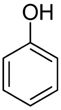
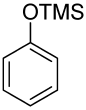
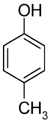
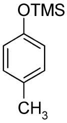
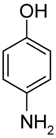
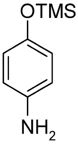
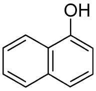
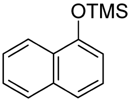
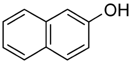
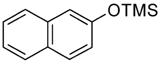
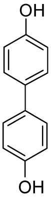
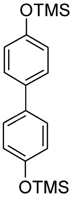
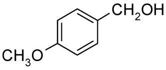
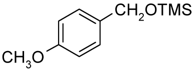
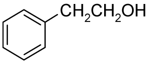
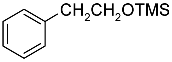
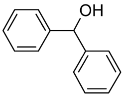
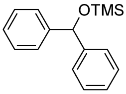
Silica-$FeCl_3$ can act as Brønsted and Lewis acid catalysts, as illustrated in Scheme 2.

The effect of catalyst and their abilities to acts as a Brønsted or Lewis acid in this reactions is unknown. in this suggested mechanism, however, according to the evolution of NH_3 in the reaction conditions, we have proposed, that an acid-base interaction between empty π orbital of Fe in silica-$FeCl_3$ as 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 ROTMS and also formation of the unstable complexes of silica-$FeCl_3$ with ammonia (**III**). Cleavage of this complex with HMDS, leading to the fast evolution of NH_3. Release of silica-$FeCl_3$ as catalyst from intermediate (**III**), reenters catalytic cycle (Scheme 3).

CONCLUSION

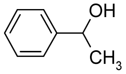
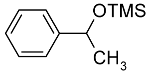
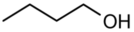
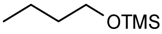
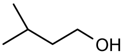
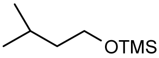
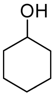
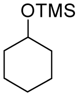
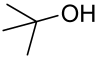
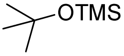
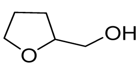
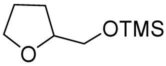
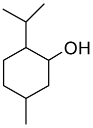
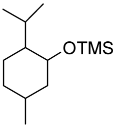
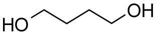
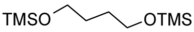
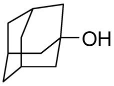
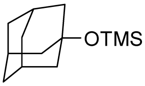
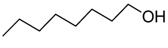
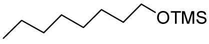
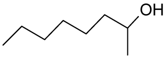
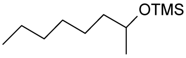
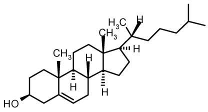
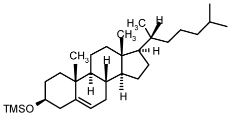
In conclusion, we have demonstrated that silica-$FeCl_3$ is a new, efficient and heterogeneous catalyst for trimethylsilylation of a variety of hydroxyl groups using HMDS under solvent-free conditions. The reactions were carried out at room temperature with short reaction time and produce the corresponding timethylsilyl ethers in good to excellent yields. This method is important from an environmental point of view and economic considerations, because it produces little waste. It also has excellent activity on an industrial scale and in all cases, the

TABLE I Silylation of Alcohols, Phenols and Naphthols with HMDS in the Presence of Solid SIlica-FeCl$_3$ as Catalyst (0.05 g) under Solvent-Free Condition at Room Temperature

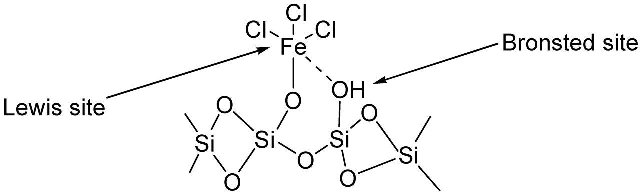
Entry	Substrate	Product	Molar Ratio Substrate/HMDS	Time (min)	Yield[a] (%)
1			1/0.7	5	95
2			1/0.7	5	95
3			1/0.7	4	96
4			1/1.3	4	90
5			1/0.7	6	93
6			1/0.7	5	94
7			1/1.3	5	96
8			1/0.7	6	94
9			1/0.7	15	93
10			1/0.7	20	95

(*Continued on next page*)

TABLE I Silylation of Alcohols, Phenols and Naphthols with HMDS in the Presence of Solid SIlica-FeCl$_3$ as Catalyst (0.05 g) under Solvent-Free Condition at Room Temperature (*Continued*)

Entry	Substrate	Product	Molar Ratio Substrate/HMDS	Time (min)	Yield[a] (%)
11			1/0.7	9	93
12			1/0.7	45	83
13			1/0.7	47	85
14			1/0.7	55	92
15			1/0.8	55	88
16			1/0.8	46	91
17			1/0.7	93	96
18			1/1.3	45	94
19			1/0.7	90	93
20			1/0.7	80	95
21			1/0.7	91	90
22			1/0.7	51	98

[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 ^{1}H NMR spectra with authentic samples.[20–34]

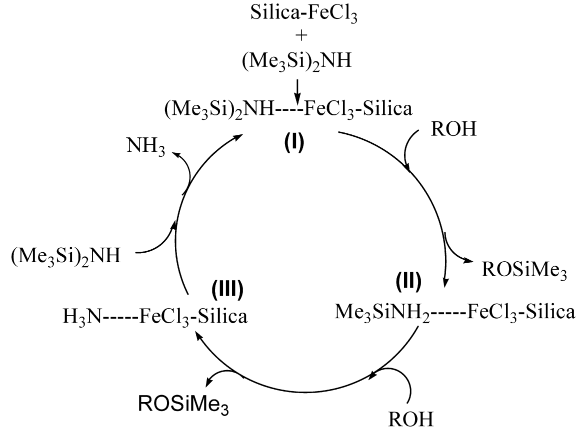


SCHEME 2 Brønsted acidity arising from inductive effect of Lewis acid center-coordinated to a silica support.[37,38]

catalyst can be recovered from reaction mixtures and reused. 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.

EXPERIMENTAL

All reagents were purchased from Merck and Aldrich and used without further purification. Silica-$FeCl_3$ was prepared according to the reported procedure.[35,36] 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 $CDCl_3$ 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.



SCHEME 3

General Procedure for Silylation of Alcohols Using HMDS Catalyzed with Silica-$FeCl_3$

To a stirred solution of alcohol (1 mmol) and HMDS (0.7 mmol) was added silica-$FeCl_3$ (0.05 g) and the mixture was stirred at room temperature for the time specified in Table I. The reaction was followed by GC and TLC (*n*-Hexane-EtOAc, 9:1). After completion of the reaction, the heterogeneous catalyst was filtered and 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) (Table I). The desired pure product(s) was characterized by comparison of their physical data with those of known compounds.[20–34] The spectral data of some representative trimethylsilyl ethers are given below:

Trimethyl(benzyloxy) Silane (Entry 1, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 7.36 \times 7.35$ (m, 5H), 4.72 (s, 2H), 0.19 (s, 9H) ppm; IR (CCl_4): 3050, 2957, 1496, 1454, 1377, 1250, 1207, 1096, 1027, 842, 727, 695 cm^{-1}.

Trimethylphenoxy Silane (Entry 2, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 7.31$ (t, 2H, $J = 8.0$ Hz), 7.02 (t, 1H, $J = 7.3$ Hz), 6.92 (d, 2H, $J = 7.8$ Hz), 0.34 (s, 9H) ppm; IR (CCl_4): 3039, 2960, 1596, 1492, 1252, 1164, 1070, 1024, 1002, 918, 843, 759, 692 cm^{-1}.

Trimethyl(4-methyl phenoxy) Silane (Entry 3, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 7.08$ (d, 2H, $J = 8.0$ Hz), 6.80 (d, 2H, $J = 8.1$ Hz), 2.33 (s, 3H), 0.32 (s, 9H) ppm; IR (CCl_4): 2960, 1613, 1509, 1251, 1168, 1103, 916, 846, 754 cm^{-1}.

Trimethyl(4-amino phenoxy) Silane (Entry 4, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 6.61$ (d, 2H,$J = 8.5$ Hz), 6.51 (d, 2H, $J = 6.5$ Hz), 3.34 (s, 2H), 0.22 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 147.6$, 140.4, 120.6, 116.7, 0.2 ppm; IR (CCl_4): 3357, 2952, 1624, 1509, 1244, 1120, 911, 846, 754 cm^{-1}.

Trimethyl(1-naphtaleneoxy) Silane (Entry 5, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 8.25$ (dd, 1H, $J = 6.12$ and 3.4 Hz), 7.88 (dd, 1H, $J = 6.01$ and 3.4 Hz), 7.56-7.54 (m, 3H), 7.41 (t, 1H, $J = 7.7$ Hz), 6.97 (d, 1H, $J = 7.4$ Hz), 0.44(s, 9H) ppm; IR (CCl_4): 3050, 2959, 1579, 1507, 1461, 1390, 1272, 1154, 1093, 1051, 1015, 914, 848,796, 771 cm^{-1}.

Trimethyl(2-naphtaleneoxy) Silane (Entry 6, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 7.85$–7.78 (m, 3H), 7.50 (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, $J = 8.8$ and 2.3 Hz), 0.41(s, 9H) ppm; IR (CCl_4): 3057, 2959, 1631, 1590, 1508, 1460, 1349, 1254, 1173, 1122, 978, 926, 855, 746 cm^{-1}.

Bistrimethyl(4,4′-biphenoxy) Silane (Entry 7, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 7.44$ (d, 4H, $J = 8.6$ Hz), 6.91 (d, 4H, $J = 8.5$ Hz), 0.32 (s, 18H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 154.3$, 134.2, 127.7, 120.2, 0.28 ppm; IR (CCl_4): 3060, 2960, 1603, 1490, 1255, 1169, 1102, 923, 841, 759 cm^{-1}.

Trimethyl(4-methoxybenzyloxy) Silane (Entry 8, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 7.29$ (d, 2H, $J = 8.4$ Hz), 6.91 (d, 2H, $J = 8.4$ Hz), 4.66 (s, 2H), 3.81 (s, 3H), 0.18 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 158.9$, 133.1, 128.1, 113.7, 64.4, 55.2, 0.3 ppm; IR (CCl_4): 3040, 2956, 1613, 1587, 1512, 1464, 1376, 1300, 1248, 1171, 1085, 840, 751 cm^{-1}.

Trimethyl(2-phenylethoxy) Silane (Entry 9, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 7.33$–7.23 (m, 5H), 3.81 (t, 2H, $J =$ 7.3 Hz), 2.87 (t, 2H, $J = 7.3$ Hz), 0.11 (s, 9H) ppm; IR (CCl_4): 3064, 3028, 2955, 2899, 1604, 1479, 1474, 1454, 1383, 1250, 1207, 1094, 1030, 928, 842, 740, 698 cm^{-1}.

Trimethyl(diphenylmethoxy) Silane (Entry 10, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 7.41$–7.23 (m, 10H), 5.80 (s, 1H), 0.12 (s, 9H) ppm; IR (CCl_4): 3063, 3027, 2957, 2863, 1598, 1492, 1453, 1354, 1303, 1251, 1187, 1090, 1061, 1027, 917, 885, 740, 700 cm^{-1}.

Trimethyl(α-methylbenzyloxy) Silane (Entry 11, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 7.40$–7.34 (m, 4H), 7.28 (t, 1H, $J =$ 6.9 Hz), 4.93 (q, 1H, $J = 6.3$ Hz), 1.51 (d, 3H, $J = 6.3$ Hz), 0.15 (s, 9H) ppm; IR (CCl_4): 3063, 3027, 2972, 2927, 2868, 1688, 1603, 1492, 1450, 1369, 1250, 1206, 1090, 1032, 999, 959, 841, 757, 699 cm^{-1}.

Trimethyl Butoxy Silane (Entry 12, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 3.58$ (t, 2H, $J = 6.5$ Hz), 1.52 (qui, 2H, $J = 5.9$ Hz), 1.33 (six, 2H, $J = 5.4$ Hz), 0.92 (t, 3H, $J = 7.3$ Hz), 0.11 (s, 9H) ppm; IR (CCl_4): 2959, 1384, 1250, 1095, 900, 792 cm^{-1}.

Trimethyl Isopentyloxy Silane (Entry 13, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 3.59$ (t, 2H, $J = 6.8$ Hz), 1.73–1.64 (m, 1H), 1.42 (q, 2H, $J = 6.8$ Hz), 0.90 (d, 6H, $J = 6.6$ Hz), 0.10 (s, 9H) ppm; IR (CCl_4): 2959, 1464, 1385, 1250, 1092, 991, 794 cm^{-1}.

Trimethyl Cyclohexyloxy Silane (Entry 14, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 3.57$-3.51 (m, 1H), 1.79-1.70 (m, 4H), 1.53-1.50 (m, 1H), 1.29-1.13 (m, 5H), 0.10 (s, 9H) ppm; IR (CCl_4): 2933, 2857, 1450, 1375, 1249, 1092, 1049, 996, 887, 839, 748 cm^{-1}.

Trimethyl (Tert-butoxy) Silane (Entry15, Table I)

^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.23$ (s, 9H), 0.05 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 58.1$, 31.1, 1.4 ppm; IR (CCl_4): 2977, 1363, 1250, 1051, 794 cm^{-1}.

Trimethyl(tetrahydro-2-furylmethoxy) Silane (Entry 16, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 3.91$–3.83 (m, 1H), 3.79–3.73 (m, 1H), 3.70–3.63 (m, 1H), 3.46 (t, 2H, $J = 4.9$ Hz), 1.84–1.73 (m, 3H), 1.59–1.50 (m, 1H), 0.02 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta =$ 79.4, 68.1, 65.1, 27.6, 25.5, 0.6 ppm; IR (CCl_4): 2933, 1450, 1375, 1249, 1092, 1049, 996, 887, 839, 748 cm^{-1}.

Trimethyl[5-methyl-2-(1-methylethyl)cyclohexyl]oxy Silane (Entry 17, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 3.39$ (six, 1H, $J = 4.3$ Hz), 2.14 (six, 1H, $J = 2.2$ Hz), 1.85-1.83 (m, 1H), 1.64–1.56 (m, 2H), 1.43–1.32 (m, 1H), 1.17–1.11 (m, 1H), 1.06–0.93 (m, 2H), 0.89 (d, 6H, $J = 6.7$ Hz), 0.86–0.76 (m, 1H), 0.72 (d, 3H, $J = 6.8$ Hz), 0.10 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 72.4$, 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}.

Bistrimethyl(1,4-butanedioxy) Silane (Entry 18, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 3.59$ (t, 4H, $J = 5.7$ Hz), 1.55 (qui, 4H, $J = 3.0$ Hz), 0.10(s, 18H) ppm; IR (CCl_4): 2956, 1250, 1094, 840 cm^{-1}.

Trimethyl(tricyclo[3,3,1,1^{3,7}] doc-1-yloxy) Silane (Entry 19, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 2.10$ (s, 3H), 1.76 (d, 6H, $J = 2.9$ Hz), 1.60 (d, 6H, $J = 2.5$ Hz), 0.13(s, 9H), ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 71.3$, 46.0, 36.2, 30.9, 3.0 ppm; IR (CCl_4): 2908, 1453, 1353, 1304, 1240, 1132, 1093, 1016, 964, 871, 837, 752 cm^{-1}.

Trimethyl(1-octyloxy) Silane (Entry 20, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 3.56$ (t, 2H, $J = 6.7$ Hz), 1.52 (qui, 2H, $J = 6.8$ Hz), 1.31–1.28 (m, 10H), 0.88 (t, 3H, $J = 6.5$ Hz), 0.10 (s, 9H) ppm; IR (CCl_4): 2928, 2857, 1250, 1099, 840, 746 cm^{-1}.

Trimethyl[(1-methylheptyl)oxy] Silane (Entry 21, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 3.75$ (six, 1H, $J = 5.7$ Hz), 1.44–1.26 (m, 10H), 1.12 (d, 3H, $J = 6.0$ Hz), 0.88 (t, 3H, $J = 6.6$ Hz), 0.10 (s, 9H) ppm; IR (CCl_4): 2958, 2929, 2858, 1458, 1375, 1249, 1135, 1084, 1049, 956, 830, 794, 747 cm^{-1}.

Trimethyl[(3β)-Choest-4-en-3-yl]oxy Silane (Entry 22, Table I)

^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 5.32$ (t, 1H, $J = 2.2$ Hz), 3.51–3.45 (m, 1H), 2.29–0.86 (m, 40H), 0.67 (s, 3H), 0.12 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 141.4$, 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, 31.9, 28.2, 28.0, 24.2, 23.8, 22.7, 22.5, 21.0, 19.3, 18.7, 11.8, 0.2 ppm; IR (KBr): 2950, 1466, 1380, 1249, 1085, 958, 897, 840, 754 cm^{-1}.

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