



# Mild and efficient silylation of alcohols and phenols with HMDS using $\text{Bi}(\text{OTf})_3$ under solvent-free condition

Santosh T. Kadam, Sung Soo Kim \*

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

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## ABSTRACT

A very efficient and mild silylation of alcohols and phenols with hexamethyldisilazane (HMDS) at rt is developed using  $\text{Bi}(\text{OTf})_3$  as the catalyst. Primary, secondary and tertiary alcohols as well as phenols are excellently converted into corresponding TMS ethers in a very short reaction time. This procedure can also be applied to large scale silylation for industrial application.

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## 1. Introduction

Functional group protection is the heart of multifunctional synthesis of target molecules. Protection of alcohols and phenols represents one of the most ubiquitous steps [1]. Formation of silyl ether from hydroxyl group is one of the most popular and widely used method. Silylation of hydroxyl group is also used in analytical chemistry to prepare volatile derivatives of alcohols and phenols for GC and GC–MS analyses [2]. Silylation enhances solubility in non-polar solvent and increases thermal stability as well. Many silylating agents, such as chlorotrimethylsilane [3], hexamethyldisiloxane [4], and allylsilane [5], have been used for the introduction of silyl group into a variety of alcohols. However, most of the methods suffer from disadvantages such as long reaction time and difficulties in the removal of amine salt formed as a by-product. An alternative reagent for the silylation of hydroxyl compound is 1,1,1,3,3,3-hexamethyldisilazane (HMDS) which is an inexpensive, commercially available reagent and gives ammonia as the only by-product. The weak silylation power of HMDS (it usually requires relatively high catalyst loading) is the main drawback to its application. Various catalysts have been developed such as  $\text{InBr}_3$  [6],  $\text{I}_2$  [7],  $\text{LiClO}_4$  [8],  $\text{LaCl}_3$  [9], K-10 montmorillonite [10], sulfonic acid-functionalized nanoporous silica [11], zirconium sulfophenyl phosphate [12]  $(\text{CH}_3)_3\text{SiCl}$  [13], zirconyl triflate [14] and iron (III) trifluoroacetate [15] for the activation of HMDS. Even though these catalytic systems enhance the ability of HMDS for the silylation, still some of the catalysts require long reaction time [16], high

temperature [17] and excess amount of reagent [18]. The lack of facile and general synthetic methodology under essentially mild reaction condition has prompted us to develop an efficient, convenient and practical procedure for the silylation of alcohols and phenols under solvent-free conditions.

With increasing environmental concern the need for solvent-free and environmentally benign method has become of significant importance. According to the principle of green chemistry, synthetic method should be designed to use substances that exhibit little or no toxicity to human health and environment [19]. In this regard, bismuth salts have recently attracted considerable attention because bismuth salts are remarkably non-toxic [20,21], stable and cost less.  $\text{Bi}(\text{OTf})_3$  has been a specially favourable candidate because it is commercially available and can also be easily prepared from commercially available compounds [22]. Accordingly  $\text{Bi}(\text{OTf})_3$  have been used as an effective catalyst for various organic reactions such as benzylation of pentanediones [23], allylation of aldehydes [24], synthesis of trisubstituted quinolines [25], Friedel–Craft reaction [26] and Sakuri–Prins–Ritter reaction [27].

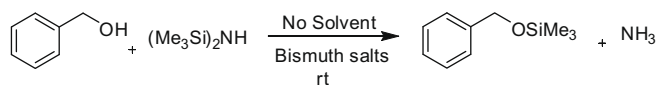
## 2. Results and discussion

In continuation of our interest on solvent-free catalytic method [28,29], we herein report a simple, mild and efficient method for the synthesis of trimethylsilyl ether of alcohols and phenols under solvent-free condition (Scheme 1).

We have examined the potential of HMDS for silylation of alcohol in presence of various bismuth salts without using solvent at rt as shown in Table 1.

\* Corresponding author. Fax: +82 32 867 5604.

E-mail address: [sungsoo@inha.ac.kr](mailto:sungsoo@inha.ac.kr) (S.S. Kim).



**Scheme 1.** Silylation of benzyl alcohol with HMDS.

**Table 1**

Silylation of benzyl alcohol with HMDS using bismuth salts at rt without solvent.

Entry	Catalyst (mol%)	Time (min)	Yield (%) <sup>a</sup>
1	Bismuth chloride (0.5)	20	67
2	Bismuth nitrate (0.5)	40	48
2	Bismuth triflate (0.5)	4	99
4	Bismuth oxide (0.5)	60	20
5	Bismuth bromide (0.5)	30	55

Upon addition of bismuth triflate to the mixture of an alcohol and HMDS, the silyl ether is formed in excellent yield in short reaction time. Therefore, bismuth triflate is found to be an effective catalyst for the silylation. The optimal molar ratio of alcohol, HMDS and bismuth triflate is found to be 1.0 mmol: 1.0 mmol and 0.5 mol%, respectively. The efficiency of Bi(OTf)<sub>3</sub> as the catalyst for the silylation of aliphatic, aromatic, primary, secondary, hindered alcohols is shown in Table 2.

Various benzyl alcohols having electron-donating and electron-withdrawing substituents undergo smooth silylation with excellent yield (entries 1–6). The catalyst may be equally applicable for large scale (10.0 mmol and 0.1 mol) silylation of benzyl alcohol and the reaction proceeds rapidly (entry 1). Isolation of larger scale (0.1 mol) reaction was performed by distillation (bp: 206–210 °C). Strongly electron-withdrawing nitro group affects the corresponding silylation with quite high yield (entry 5). The “relatively” longer reaction time (12 min) may indicate that slight substituent effects are in operation for the reaction. *trans*-2-methyl-3-phenyl-2-propen-1-ol needs “relatively” prolonged reaction time (entry 7). The catalytic system is also applicable to heterocyclic alcohol such as furfuryl alcohol and gives corresponding silyl ether in high yield (entry 8). Numerous secondary alcohols give corresponding silyl ethers with remarkably high yield (entries 9–14). 1-(2-Methoxyphenyl)-1-propanol exhibits neither steric nor electronic effects on reactivity (entry 13). Sterically hindered 4,4'-difluorobenzhydryl produces silyl ether in excellent yield with a very short reaction time (entry 14). 3-Methyl-1-phenyl-1-propanol and 2-adamantanol also underwent silylation under present conditions (entries 15 and 16). The method tolerates the acid sensitive alcohols having double bond like geraniol (entries 18). The catalyst is also able to convert the primary, secondary and neopentyl alcohol into corresponding silyl ether in good yield (entries 19–22).

Interestingly, phenols too undergo the silylation in presence of Bi(OTf)<sub>3</sub> to produce silyl ether in considerably high yield (entries 23–26). Relative to 4-methoxyphenol, 3-methoxyphenol has lower yield and longer reaction time (entries 24 and 25). This may suggest that slight electronic effect could reduce the yield and lengthen the reaction time. Present catalytic system cannot produce any silyl compounds from thiols and amines (entries 27 and 28). Benzenethiol and benzylamine gave no silylation product at all even by increasing the catalyst amount up to 2 mol% after 3 h. This is because oxophilicity of silicon atom towards alcoholic OH may be strong enough to overcome the reactivities of HMDS with N–H and S–H bonds of amines and thiols, respectively. The possible chemoselective protection of alcohol in the presence of thiol and amine is demonstrated as shown in Scheme 2.

The generality and the excellence of Bi(OTf)<sub>3</sub> in terms of catalyst loading, short reaction time and solvent-free condition can be easily understood from the comparison of the data with literature results as shown in Table 3.

**Table 2**

Silylation of variety of alcohols and phenols with HMDS catalyzed by Bi(OTf)<sub>3</sub> without solvent<sup>a</sup>.

Entry	Product	Time (min)	Yield (%) <sup>b</sup>
1		4 7 <sup>c</sup>	99 92 <sup>c</sup>
2		5 <sup>d</sup> 5	91 <sup>d</sup> 94
3		6	95
4		8	91
5		12	90
6		4	99
7		20	98
8		20	90
9		5	94
10		2	99
11		4	98
12		2	96
13		2	99
14		3	99
15		45	83

Table 2 (continued)

Entry	Product	Time (min)	Yield (%) <sup>b</sup>
16		15	90
17		4	95
18		5	95
19		35	84
20		10	87
21		15	85
22		35	90
23		6	93
24		5	98
25		8	91
26		7	95
27		3 h	NR
28		3 h	NR
29		6 <sup>e</sup>	94 <sup>e</sup>

<sup>a</sup> Reaction condition: alcohol (1.0 mmol), HMDS (1.0 mmol), Bi(OTf)<sub>3</sub> (0.5 mol%).

<sup>b</sup> Isolated yield.

<sup>c</sup> 10.00 mmol of benzyl alcohol, 10.00 mmol of HMDS.

<sup>d</sup> Benzyl alcohol (0.1 mol); HMDS (0.1 mol).

<sup>e</sup> 2.0 mmol of benzyl alcohol and 1.0 mmol of HMDS were used.

A plausible mechanism has been shown in Scheme 3. Lewis acid–base interaction between the bismuth triflate and nitrogen of HMDS polarizes the N–Si bond to produce the reactive silylating agent (I), which rapidly reacts with alcohol to give the corresponding silyl compounds and complex (II). This complex (II) reacts with another molecule of alcohol to produce the corresponding silyl derivative. Finally the complex (III) collapses to the formation of

ammonia and liberation of the catalyst. The evolution of ammonia was confirmed by its strong, pungent odor and using the red Litmus paper which turns to blue. The silylation reaction using 2:1/ alcohol: HMDS molar ratio was performed and it produce corresponding silyl compound with high yield (entry 29).

In conclusion, we have demonstrated that Bi(OTf)<sub>3</sub> is a highly efficient chemoselective catalyst for silylation of alcohols and phenols under solvent-free condition at rt. The catalyst is also capable of large scale silylation. The major advantage of this method is that: operational simplicity at rt within a short reaction time and low catalyst loading (0.5 mol%). This reaction may require the lowest catalyst quantity of all the previous studies in recent years (Table 3). The use of relatively non-toxic and inexpensive catalyst add to the versatility of this method.

### 3. Experimental

In all cases the <sup>1</sup>H NMR (200 MHz) spectra were recorded with Varian Gemini 200. Chemical shifts were reported in ppm in CDCl<sub>3</sub> with tetramethylsilane as the internal standard. <sup>13</sup>C NMR data were collected on a Varian Gemini 400 (100 MHz). Some compounds were also identified by HRMS (EI) with Jeol DMX 303 and GCMS (EI 70 eV). Data were collected through 1200L Single Quadrupole GC/MS system with 3800GC/Varian.

#### 3.1. Trimethylsilylation of alcohols and phenols

Bi(OTf)<sub>3</sub> (0.5 mol%) was added to the mixture of alcohol or phenol (1.0 mmol) and HMDS (1.0 mmol). The reaction mixture was stirred at rt for the appropriate time (see Table 2). The progress of reaction was monitored by TLC. The reaction mixture was diluted with EtOAc. Concentration of the organic layer under vacuum gave crude mass, which was purified by column chromatography with silica gel.

<sup>1</sup>H and <sup>13</sup>C NMR data for known products are the same with literature values [8,14,33–36]. Spectral data and HRMS values for new products are given below (entries 6, 7, 9, 11, 13–15, 18–22 and 26).

Table 2, Entry 6: (4-Methoxyphenethoxy)trimethylsilane: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.28 (s, 9H), 2.78 (t, J = 16 Hz, 2H), 3.74 (t, J = 16 Hz, 2H), 3.78 (s, 3H), 6.84 (d, J = 8 Hz, 2H), 7.13 (d, J = 8 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 0.58, 38.53, 55.14, 64.07, 113.67, 129.91, 130.95, 158.04. HRMS-EI +: m/z Calcd for C<sub>12</sub>H<sub>20</sub>O<sub>2</sub>Si: 224.1233; found: 224.1217.

Table 2, Entry 7: (E)-Trimethyl-(2-methyl-3-phenylallyloxy)silane: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.12 (s, 9H), 1.80 (s, 3H), 4.11 (s, 2H), 6.47 (s, 1H), 7.24–7.27 (m, 5H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 0.36, 15.09, 68.35, 124.42, 126.20, 128.05, 128.89, 137.23, 137.23, 37.91. HRMS-EI +: m/z Calcd for C<sub>13</sub>H<sub>20</sub>O<sub>2</sub>Si: 220.1283; found: 220.1292.

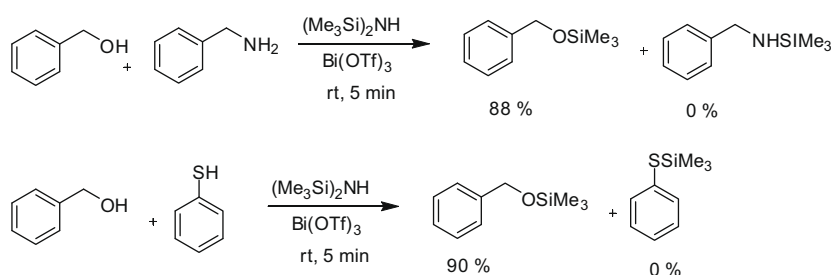
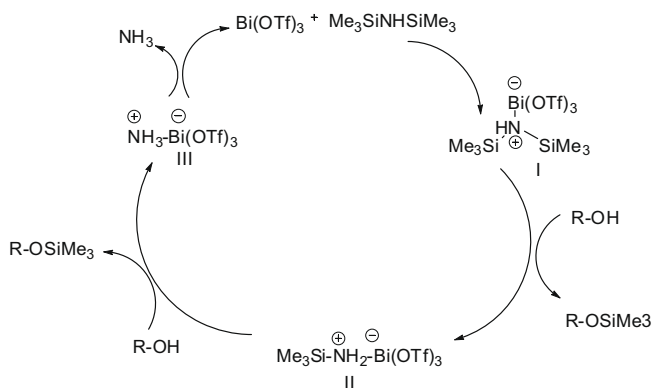
Table 2, Entry 9: (Cyclopropyl(phenyl)methoxy)trimethylsilane: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.02 (s, 9H), 0.19–0.44 (m, 4H), 1.05 (d, J = 7.6 Hz, 1H), 3.99 (d, J = 6.8 Hz, 1H), 7.13–7.29 (m, 5H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 0.23, 2.80, 3.56, 80.25, 125.95, 127.00, 128.05, 15.18. HRMS-EI +: m/z Calcd for C<sub>13</sub>H<sub>20</sub>O<sub>2</sub>Si: 220.1283; found: 220.1279.

Table 2, Entry 10: Trimethyl(1-phenylethoxy)silane: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.39 (s, 9H), 1.45 (d, J = 8 Hz, 3H) 4.87 (q, J = 20 Hz, 1H), 7.30–7.35 (m, 5H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 0.06, 25.14, 26.83, 70.58, 125.33, 125.35, 126.81, 127.42, 128.11, 146.42. HRMS-EI +: m/z Calcd for C<sub>11</sub>H<sub>18</sub>O<sub>2</sub>Si: 194.1127; found: 194.1131.

Table 2, Entry 11: (1-(3-Chlorophenyl)ethoxy)trimethylsilane: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.14 (s, 9H), 1.47 (d, J = 4 Hz, 3H), 4.86 (q, J = 8 Hz, 1H), 7.29–7.32 (m, 3H), 7.35–7.38 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 0.04, 26.81, 69.98, 123.46, 125.56, 126.94, 129.44, 134.06, 148.70. HRMS-EI +: m/z Calcd for C<sub>11</sub>H<sub>17</sub>ClO<sub>2</sub>Si: 228.0737; found: 228.0729.

**Table 3**Bi(OTf)<sub>3</sub> catalyzed silylation of alcohols in comparison with other literatures.<sup>a</sup>

No.	Catalyst (mol%)	Time (min)	Solvent	Reference
1	Bi(OTf) <sub>3</sub> 0.5	Mostly less than 10	No	Present method
2	LiClO <sub>4</sub> 50	10–30	No	[8]
3	Fe(tpp)Cl 24	5–90	CH <sub>3</sub> CN	[30]
4	ZrCl <sub>4</sub> 20	1–10	CH <sub>3</sub> CN	[33]
5	Fe <sub>3</sub> O <sub>4</sub> 10	5	No	[31]
6	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> 10	6–120	No	[17]
7	Barbituric acid 10	1–5 h	No	[16]
8	Cu(OTf) <sub>2</sub> 10	5–80	CH <sub>3</sub> CN	[32]
9	Iodine 10	2–4	CH <sub>2</sub> Cl <sub>2</sub>	[7]
10	LaCl <sub>3</sub> 10	3–5 h	CH <sub>2</sub> Cl <sub>2</sub>	[9]
11	Sulfonic acid nanoporous silica 3	80–120	CH <sub>2</sub> Cl <sub>2</sub>	[11]
12	K-10 montmorillonite 100 mg	24–60	CH <sub>2</sub> Cl <sub>2</sub>	[10]
13	Zirconium sulfophenyl phosphonate 50 mg	1–20 h	CH <sub>2</sub> Cl <sub>2</sub>	[12]
14	Fe(F <sub>3</sub> CCO <sub>2</sub> ) <sub>3</sub> 5	5 min–2 h	No	[15]
15	ZrO(OTf) <sub>2</sub> 0.5	1–4	CH <sub>3</sub> CN	[14]

<sup>a</sup> All reactions were conducted at rt. The reaction of entry 6 was done at 60 °C.**Scheme 2.** Chemoselectivity of benzyl alcohol in presence of benzyl amine and benzenethiol.**Scheme 3.** Plausible mechanism for silylation of an alcohol with HMDS.

**Table 2, Entry 13:** (1-(2-Methoxyphenyl)propoxy)trimethylsilane: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.46 (s, 9H), 1.33 (t, J = 14 Hz, 3H), 2.04 (m, 2H), 4.23 (s, 3H), 5.40 (t, J = 8 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.38 (t, J = 13 Hz, 1H), 7.60 (t, J = 16 Hz, 1H), 7.86 (d, J = 7.4 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 0.04, 10.40, 31.77, 55.17, 69.62, 109.85, 120.46, 126.79, 127.51, 133.98, 155.55. HRMS-EI +: *m/z* Calcd for C<sub>13</sub>H<sub>22</sub>O<sub>2</sub>Si: 138.1389; found: 138.1381.

**Table 2, Entry 14:** ((4-Fluorocyclohexa-2,4-dienyl)(4-fluorophenyl)methoxy)trimethylsilane: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.34 (s, 9H), 5.93 (s, 1H), 7.21–7.30 (m, 4H), 7.51–7.58 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 0.07, 75.26, 114.91, 115.34, 140.53, 140.58, 159.57, 164.45.

**Table 2, Entry 15:** Trimethyl(2-methyl-1-phenylpropoxy)silane: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.01 (s, 9H), 0.77 (q, J = 9.8 Hz, 3H), 0.91 (q, J = 9.8 Hz, 3H), 1.80–1.86 (m, 1H), 4.25–4.30 (m, 1H), 7.24–7.27 (m, 5H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 0.09, 18.14,

19.26, 36.34, 80.42, 126.69, 126.80, 127.76, 144.48. HRMS-EI +: *m/z* Calcd for C<sub>13</sub>H<sub>22</sub>O<sub>2</sub>Si: 222.1440; found: 222.1438.

**Table 2, Entry 18:** (*E*)-(3,7-Dimethylocta-2,6-dienyloxy)trimethylsilane: δ 0.06 (s, 9H), 1.59–1.67 (m, 9H), 2.00–2.10 (m, 4H), 4.15 (d, J = 3.6 Hz, 2H), 5.08 (t, J = 3 Hz, 1H), 5.32 (t, J = 3 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 1.87, 16.19, 17.61, 25.60, 26.34, 39.49, 59.29, 123.31, 123.85, 131.67, 139.59. HRMS-EI +: *m/z* Calcd for C<sub>13</sub>H<sub>26</sub>O<sub>2</sub>Si: 226.1753; found: 226.1774.

**Table 2, Entry 19:** (Hexan-2-yloxy)trimethylsilane: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.10 (s, 9H), 0.85 (d, J = 5.8 Hz, 3H), 1.10 (t, J = 11.4 Hz, 3H), 1.24–1.34 (m, 12H), 3.70–3.78 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 0.18, 14.02, 22.61, 23.83, 29.29, 31.82, 39.60, 68.56. HRMS-EI +: *m/z* Calcd for C<sub>9</sub>H<sub>22</sub>O<sub>2</sub>Si: 174.1440; found: 174.1458.

**Table 2, Entry 20:** Trimethyl(undecyloxy)silane: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): 0.28 (s, 9H), 0.88 (t, J = 5.8 Hz, 3H), 1.31–1.43 (m, 14H), 1.48–1.53 (m, 4H), 3.78 (t, J = 9.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 0.52, 14.07, 22.66, 25.81, 29.44, 29.63, 31.90, 32.73, 62.70. HRMS-EI +: *m/z* Calcd for C<sub>7</sub>H<sub>18</sub>O<sub>2</sub>Si: 146.1127; found: 146.1145.

**Table 2, Entry 21:** Trimethyl(neopentyloxy)silane: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.08 (s, 9H), 0.85 (s, 9H), 3.19 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 0.53, 26.27, 34.58, 72.71.

**Table 2, Entry 22:** (But-3-yn-2-yloxy)trimethylsilane: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.09 (s, 9H), 1.41 (d, J = 7.1 Hz, 3H), 2.34 (d, J = 1.6 Hz, 1H), 4.7 (qd, J = 7.1, 1.6 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 0.07, 2.45, 25.29, 58.31, 71.45.

**Table 2, Entry 25:** (3-Methoxyphenoxy)trimethylsilane: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): 0.39 (s, 9H), 3.89 (s, 3H), 6.55–6.69 (m, 3H), 7.28 (t, J = 16 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 0.23, 55.18, 106.27, 107.05, 112.49, 129.77. HRMS-EI +: *m/z* Calcd for C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>Si: 196.0920; found: 196.0899.

**Table 2, Entry 26:** (4-Isopropylphenoxy)trimethylsilane: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 0.26, 1.20 (d, J = 7 Hz, 6H), 2.77–2.91 (m, 1H),

6.74 (d,  $J = 8.4$  Hz, 2H), 7.03 (d,  $J = 8.4$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.29, 24.24, 33.36, 119.74, 127.25, 141.70, 153.09. HRMS-EI +:  $m/z$  Calcd for  $\text{C}_{12}\text{H}_{20}\text{OSi}$ : 208.1283; found: 208.1285.

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