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Cross-linked poly(4-vinylpyridine/styrene) copolymer-supported bismuth(III) triflate: an efficient heterogeneous catalyst for silylation of alcohols and phenols with HMDS

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Cross-linked poly(4-vinylpyridine/styrene) copolymer-supported bismuth(III) triflate (³⁰P/S-Bi) effectively activates hexamethyldisilazane (HMDS) for the silylation of alcohols and phenols. By the use of this heterogeneous catalytic system, a wide range of alcohols as well as phenols are converted into their corresponding trimethylsilyl ethers in high yield under mild reaction conditions. The catalyst was reused more than 10 times without significant loss of its catalytic activity. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: silylation; polymer-supported Lewis acid; alcohol; phenol; HMDS

Introduction

Silylation is an important and useful transformation for the protection of alcohol and phenol moieties.^[1] It is also used to prepare volatile derivatives of alcohols and phenols for GC and GC-MS analyses.^[2] In general, formation of silvl ether is carried out using various silylating agents, such as allylsilane,^[3] hexamethyldisiloxane^[4] and chlorotrimethylsilane,^[5] with a variety of alcohols. 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) is an inexpensive, commercially available alternative reagent and gives ammonia as the only by-product for the silulation of hydrogenlabile substrate. Activation of HMDS was done using a variety of catalysts such as various metal salts^[6] and heterogeneous catalysts.^[7] Along with various catalytic systems, silylation was also promoted in nitromethane as a solvent.^[8] Although these catalytic methods enhanced the activity of HMDS for silylation, some of the catalysts still required a long reaction time,^[6p] high reaction temperature^[6h,7d] and an excess amount of reagent.^[7i]

Heterogeneous catalysis is one of the hottest issues in organic synthesis owing to the awareness of society and industry of the need for 'green' chemistry, in terms of the removal of toxic metals from the waste stream as well as the potential to control costs via catalyst recovery and recycling.^[9] Significant efforts have been made towards this objective in an attempt to develop a homogeneous catalyst that is anchored to polymer support.^[10]

Recently, lanthanide triflates have received considerable attention as mild, water-stable Lewis acids in a wide range of organic transformations.^[11] So far, these catalysts have been mainly utilized in homogeneous reaction conditions in most applications. Polymer-supported lanthanide triflates have been also reported by Koyabashi and Janda's group.^[12,13] However, lanthanide triflates are expensive, and thus, their use in large-scale synthesis is limited. Therefore, cheaper and more efficient catalysts are desirable. Compared with lanthanide triflates, bismuth triflate is less expensive, remarkably non-toxic and easily prepared even on a multi-gram scale from commercially available bismuth oxide and triflic acid.^[14] In addition, immobilization of these triflates will provide more practical, reusable and cost-effective catalytic system.

Our group has developed cross-linked poly(4-vinylpyridine/styrene) copolymer-supported ytterbium(III) triflate (³⁰P/S-Yb) as an efficient heterogeneous catalyst for the synthesis of β -amino ketones.^[15] In continuation of our research on supported Lewis acids, we report efficient and reusable heterogeneous poly(4-vinylpyridine/styrene) copolymer-supported bismuth(III) triflate (³⁰P/S-Bi) for the trimethylsilylation of alcohols and phenols.

Experimental

All the glassware was silanized by treating with Sigmacote[®] or 10% dichlorodimethylsilane in toluene followed by dry methanol. FT-IR spectra were recorded using a Jasco 4100 spectrometer equipped with a diamond single-reflection attenuated total reflectance accessory. ¹H NMR (400 MHz) spectra were recorded with Varian INOVA-399. Chemical shifts were reported in ppm in CDCl₃ with tetramethylsilane as the internal standard. ¹³C NMR data were collected on a Varian Inova-399 (100 MHz) or Varian VNS600 (150 MHz). Mass data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high-resolution mass spectrometer.

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Heterogenizaton of Bismuth Triflate on Cross-linked Poly(4vinylpyridine/styrene) Copolymer with 30% Pyridine Functionality (³⁰P/S-Bi)

As previously reported,^[12] cross-linked poly(4-vinylpyridine/ styrene) copolymer with 30% pyridine functionality was prepared by radical suspension copolymerization of 4-vinylpyridine (30 mol%), styrene (70%) and 1 mol% of the 1,4-bis(4vinylphenoxy)butane as a flexible cross-linker. A 500 mg aliquot of ³⁰P/S resin was placed in a 20 ml vial containing 150 mg of Bi(OTf)₃. A 10 ml aliquot of methanol–dichloromethane (1 : 1) cosolvent was added to the vial. After being tightly capped, these vials were shaken for 24 h at room temperature. The resultant resin was collected in plastic syringe equipped with a polystyrene frit and washed with methanol–dichloromethane (1 : 1) solvent several times, then dried under reduced pressure to give Bi(OTf)₃immobilized resin [578 mg, loading level: 0.2 mmol Bi(OTf)₃/g resin] as pale yellow solid.

General Procedure for Trimethylsilylation of Alcohols and Phenols

³⁰P/S-Bi (50 mg, corresponding to 0.01 mmol Bi, 1 mol%) was added to the mixture of alcohol or phenol (1.0 mmol) and HMDS (0.8 mmol) in CH₂Cl₂ (4 ml). The reaction mixture was stirred at room temperature for the appropriate time (see Tables 2 and 3) and the progress of the reaction was monitored by TLC. The reaction mixture was filtered through a plastic syringe with a polyethylene frit and washed with dichloromethane. Concentration of the organic layer under vacuum gave a crude mass, which was purified by flash chromatography on silica gel to give the desired product. A reusability test of ³⁰P/S-Bi catalyst was performed using the recovered catalyst from the previous run for a successive 10 times after simple filtration, washing and drying under vacuum. All the reactions in Tables 2 and 3 were performed using the recovered catalyst from the previous reaction. ¹H and ¹³C NMR data for known products were the same as the literature values.^[6e,j,p,7c,19] Spectral data for new products are given below (Table 2, entries 2, 3, 8, 13, 14 and Table 3, entries 5, 9, 13, 15).



(3,5-Dimethylbenzyloxy)trimethylsilane (Table 2, entry 2)

IR (neat): 3017, 2956, 2898, 1608, 1459, 1249, 1093, 870, 836 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 0.02 [s, 9H, -Si(CH₃)₃], 2.14 (s, 6H, 2 × -CH₃), 4.45 (s, 2H, -CH₂Ar), 6.72 (s, 1H, Ar–H), 6.77 (s, 2H, Ar–H). ¹³C NMR (100 MHz, CDCl₃): 0.0 [-Si(CH₃)₃], 21.6 (2 × –CH₃), 65.0 (-CH₂Ar), 125.0 (Ar–C), 129.1 (Ar–C), 138.1 (Ar–C), 141.0 (Ar–C). HRMS (FAB): m/z [M]⁺ calcd for C₁₂H₂₀OSi: 208.1283; observed: 208.1281.



Trimethyl(3,4,5-trimethoxybenzyloxy)silane (Table 2, entry 3)

IR (neat): 2955, 2898, 2838, 1590, 1457, 1249, 1126, 1097, 871, 837, 751 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 0.00 (s, 9H, -Si(CH₃)₃), 3.65 (s, 6H, $2 \times -OCH_3$), 3.68 (s, 3H, -OCH₃), 4.45 (s, 2H, -CH₂Ar), 6.38 (s, 2H, Ar-H). ¹³C NMR (100 MHz, CDCl₃): 0.0 [-Si(CH₃)₃], 56.3 (-OCH₃), 61.1 (-OCH₃), 65.1 (-CH₂Ar), 104.0 (Ar-C), 137.0 (Ar-C), 137.3 (Ar-C), 153.5 (Ar-C). HRMS (FAB): m/z [M]⁺ calcd for C₁₃H₂₂O₄Si: 270.1287; observed: 270.1285.



Trimethyl[(2-methylbiphenyl-3-yl)methoxy]silane (Table 2, entry 8)

IR (neat): 3063, 3034, 2956, 2900, 1707, 1599, 1477, 1250, 1121, 1066, 883, 835, 755 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 0.03 (s, 9H, -Si(CH₃)₃), 1.20 (s, 3H, -CH₃), 4.54 (s, 2H, -CH₂Ar), 6.96–7.23 (m, 8H, Ar–*H*). ¹³C NMR (100 MHz, CDCl₃): -0.1 (-Si(CH₃)₃), 16.0 (-CH₃), 63.6 (-CH₂Ar), 125.6 (Ar–*C*), 126.4 (Ar–*C*), 127.0 (Ar–*C*), 128.2 (Ar–*C*), 129.2 (Ar–*C*), 129.6 (Ar–*C*), 133.1 (Ar–*C*), 139.4 (Ar–*C*), 142.4 (Ar–*C*), 142.6 (Ar–*C*). HRMS (FAB): m/z [M]⁺ calcd for C₁₇H₂₂OSi: 270.1440; observed: 270.1436.



Trimethyl[3-(trifluoromethyl)phenethoxy]silane (Table 2, entry 13)

IR (neat): 2956, 2899, 2864, 1597, 1323, 1492, 1323, 1251, 1162, 1093, 838, 798, 701 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 0.02 [s, 9H, -Si(CH₃)₃], 2.85 (t, J = 6.8 Hz, 2H, -CH₂Ar), 3.75 [t, J = 6.8 Hz, 2H, -CH₂OSi(CH₃)₃], 7.30–7.50 (m, 4H, Ar–*H*). ¹³C NMR (125 MHz, CDCl₃): -0.7 [-Si(CH₃)₃], 39.0 (-CH₂Ar), 63.2 [-CH₂OSi(CH₃)₃], 123.7 (q, ³J_{C-F} = 3.8 Hz, Ar–C), 124.3 (q, ¹J_{C-F} = 270.6 Hz, -CF₃), 125.9 (q, ³J_{C-F} = 3.8 Hz, Ar–C), 128.6 (Ar–C), 130.6 (q, ²J_{C-F} = 31.9 Hz, Ar–C), 132.5 (q, ⁴J_{C-F} = 1.3 Hz, Ar–C), 140.2 (Ar–C). HRMS (FAB): m/z [M + H]⁺ calcd for C₁₂H₁₈F₃OSi, 263.1079; observed, 263.1075.



Trimethyl[2-(phenylthio)ethoxy]silane (Table 2, entry 14)

IR (neat): 3074, 2955, 2897, 1584, 1481, 1249, 1081, 871, 837, 736 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 0.02 [s, 9H, -Si(CH₃)₃], 2.97 (t, J = 7.2 Hz, 2H, -SCH₂Ar), 3.66 [t, J = 7.2 Hz, 2H, -CH₂OSi(CH₃)₃], 7.04–7.24 (m, 5H, Ar–H). ¹³C NMR (100 MHz, CDCl₃): -0.2 [-Si(CH₃)₃], 36.0 (-SCH₂Ar), 61.8 [-CH₂OSi(CH₃)₃], 126.2 (Ar–C), 129.1 (Ar–C), 129.3 (Ar–C), 136.4 (Ar–C). HRMS (FAB): m/z [M]⁺ calcd for C₁₁H₁₈OSSi, 226.0848; observed, 226.0849.



Table 1. ³⁰ P/S-Bi catalyzed silylation of benzyl alcohol with HMDS ^a			
Entry	Catalyst (mg)	Si) ₂ NH $Catalyst$ CH ₂ Cl ₂ , rt Time (min)	OSiMe ₃ + NH ₃ Yield (%) ^b
1	None	60	23
2	³⁰ P/S resin (30)	60	NR
3	Pyridine ^c	60	NR
4	³⁰ P/S-Bi (10)	45	56
5	³⁰ P/S-Bi (30)	30	62
6	³⁰ P/S-Bi (50)	10	92
7	³⁰ P/S-Bi (70)	10	92
8 ^[6i]	Bi(OTf) ₃ ^d	4	99
^a Reaction conditions: alcohol (1.0 mmol), HMDS (0.8 mmol) in CH ₂ Cl ₂ (4 ml). ^b Isolated yield. ^c 1.0 mmol. ^d 0.5 mol%.			

Trimethyl(2-phenylpropan-2-yloxy)silane (Table 3, entry 5)

IR (neat): 3087, 3063, 2978, 1601, 1493, 1249, 1174, 1031, 835, 760, 698 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 0.02 [s, 9H, -Si(CH₃)₃], 1.97 (s, 6H, $2 \times -CH_3$), 7.04–7.24 (m, 5H, Ar–H). ¹³C NMR (100 MHz, CDCl₃): 0.0 [-Si(CH₃)₃], 30.1 ($2 \times -CH_3$), 72.8 [-C(CH₃)₂OSi(CH₃)₃], 122.3 (Ar–*C*), 124.0 (Ar–*C*), 125.5 (Ar–*C*), 147.6 (Ar–*C*). HRMS (FAB): *m/z* [M – CH₃]⁺ calcd for C₁₁H₁₇OSi: 193.1049; observed: 193.1050.



(4'-Bromobiphenyl-4-yloxy)trimethylsilane (Table 3, entry 9)

IR (neat): 3040, 2956, 1598, 1476, 1251, 1199, 1078, 914, 835, 752 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 0.02 [s, 9H, -Si(CH₃)₃], 6.81–6.85 (m, 4H, Ar–*H*), 7.38–7.47 (m, 4H, Ar–*H*). ¹³C NMR (100 MHz, CDCl₃): 0.4 [-Si(CH₃)₃], 116.0 (Ar–*C*), 121.0 (Ar–*C*), 128.4 (Ar–*C*), 131.5 (Ar–*C*), 132.0 (Ar–*C*), 133.4 (Ar–*C*), 140.0 (Ar–*C*), 155.3 (Ar–*C*). HRMS (FAB): m/z [M]⁺ calcd for C₁₅H₁₇BrOSi, 320.0232; observed, 320.0234.



2-[3-(Trimethylsilyloxy)phenyl]acetic acid (Table 3, entry 13)

IR (neat): 3035, 2959, 2899, 1708, 1602, 1487, 1270, 1252, 1157, 983, 840 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 0.02 [s, 9H, -Si(*CH*₃)₃], 3.32 (s, 2H, -*CH*₂COOH), 6.45–6.55 (m, 2H), 6.62 (d, *J* = 7.2 Hz, 1H, Ar–*H*), 6.92 (t, *J* = 7.8 Hz, 1H, Ar–*H*), 11.2 (brs, 1H, -COOH). ¹³C NMR (100 MHz, CDCl₃): 0.4 [-Si(CH₃)₃], 41.2 (-CH₂COOH), 121.4 (Ar–*C*), 122.6 (Ar–*C*), 129.8 (Ar–*C*), 155.5 (Ar–*C*), 178.2 (-COOH). HRMS (FAB): *m/z* [M + H]⁺ calcd for C₁₁H₁₇O₃Si, 225.0947; observed, 225.0949.



4-(Trimethylsilyloxy)butan-2-one (Table 3, entry 15)

IR (neat): 2958, 2898, 1715, 1358, 1250, 1169, 1098, 877, 837, 749 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 0.04 [s, 9H, -Si(CH₃)₃], 2.08 (s, 3H, CH₃CO-), 2.5 (t, J = 6.4 Hz, 2H, -COCH₂-), 3.7 [t, J = 6.4 Hz, 2H, -CH₂OSi(CH₃)₃]. ¹³C NMR (100 MHz, CDCl₃): 0.4 [-Si(CH₃)₃], 30.8 (CH₃CO-), 46.5 (-COCH₂-), 58.1 [-CH₂OSi(CH₃)₃], 207.8 (-CO-). HRMS (FAB):m/z [M + H]⁺ calcd for C₇H₁₇O₂Si, 161.0998; observed, 161.0996.

Results and Discussion

By considering the excellence of poly(4-vinylpyridine/styrene) copolymer (P/S resins) as an effective supporting material for immobilization of Lewis acid previously reported by our group,^[15] we decided to use P/S resin as a support for the heterogenization of bismuth triflate.

The immobilization was done by the treatment of bismuth triflate with ³⁰P/S resin (the superscript 30 indicates the percentage pyridine content) in a mixture of methanol and dichloromethane by a previously reported method.^[12] The swelling property of cross-linked resin in organic solvents is an important factor for effective solid-phase reactions.^[16] ³⁰P/S-Bi catalyst showed outstanding swelling in dichloromethane, hence dichloromethane was chosen as the solvent system for this conversion. We have examined the potential of ³⁰P/S-Bi as a heterogeneous catalyst for silylation of benzyl alcohol as a model substrate with HMDS at room temperature, as shown in Table 1.

In preliminary experiments, when the reaction was performed without any catalyst (Table 1, entry 1), the reaction was very sluggish to give only 23% silylation product after 1 h. The polymer support (30 P/S resin) itself retards the silylation reaction and gives no silylation product even after 1 h reaction time (entry 2). By considering this result, we assume that the presence of pyridine functionality of the polymer support retards the reaction. This hypothesis is supported by the same retardation of reaction mixture (entry 3). Various amounts of 30 P/S-Bi heterogeneous catalyst were tested for optimization of catalyst loading and reaction times of silylation. Accordingly 50 mg of supported 30 P/S-Bi catalyst [corresponding to 1 mol% of Bi(OTf)₃] at room temperature was chosen as the best and optimum reaction condition for silylation of alcohol with HMDS (Table 1, entry 6). The optimal



Table 2.	³⁰ P/S-Bi catalyzed silylation of benzylic and primary ali	iphatic alcohols with HMDS ^a	
	R-OH + (Me ₃ Si) ₂ NH	³⁰ P/S-Bi → R−OSiMe ₃ + NH ₃	
Entry	Products	Time (min)	Yield (%) ^b
1	OTMS	10	92
2	Me OTMS Me	10	94
3	MeO MeO OMe	10	96
4	OTMS	15	94
5	OTMS	10	88
6	CI	10	90
7	O OTMS	10	89
8	Ph	10	91
9	OTMS	40	90
10	OTMS	15	92
11	OTMS	10	91
12	MeO	10	93



molar ratio of alcohol, HMDS and ³⁰P/S-Bi was found to be 1.0 mmol-0.8 mmol-1.0 mol%, respectively. Silylation of alcohol with HMDS using unsupported bismuth triflate, in which 0.5 mol% of the catalyst was typically employed, has been also reported.^[6i] To achieve similar catalytic performance, in terms of reaction time and product yield, this heterogenized bismuth triflate was used in 1 mol%. It is accepted that immobilized catalyst shows somewhat lower catalytic activity compared with its soluble counterpart, as observed in most heterogenized catalysts.^[17] However, more importantly, heterogenization of the catalyst enables facile recovery and reuse in compensation for its lowered catalytic activity.^[18]

The catalytic activities of ³⁰P/S-Bi for the silylation of aliphatic and aromatic alcohols are shown in Tables 2 and 3. A wide range of alcohols enabled production of the corresponding trimethylsilyl ethers in excellent to good yields (Table 2). Various benzyl alcohols substituted with electron-donating and electronwithdrawing groups underwent smooth silvlation in excellent yields (Table 2, entries 1-8). Benzyl alcohol containing electronwithdrawing chlorine atoms produced the silylation product in a good yield (entry 6), and this indicates that electronic and steric effects by the chlorine atoms have no serious effect on reactivity. The silvlation of furfuryl alcohol preceded efficiently under this reaction condition (entry 9). The catalytic system was equally effective for phenethyl alcohols with electron-donating and electron-withdrawing groups on their phenyl rings (entries 10–13). In addition to benzyl and phenethyl types of alcohols, this catalytic system is also applicable for the silvlation of long-chain aliphatic alcohols (entries 14 and 15).

We extended this catalytic methodology to secondary and tertiary alcohols and phenols using the same reaction conditions (Table 3, entries 1–10). Various secondary alcohols gave corresponding silyl ethers in high yields (entries 1–4). *Sec*-1-phenethyl alcohol and 1-phenyl-2-propanol give the corresponding silylation products in high yield (entries 1 and 2). It should be noted that secondary alcohols bearing sterically demanding substituents, such as cyclopropyl ring (α -cyclopropylbenzyl alcohol) and phenyl (diphenylmethanol) also gave the corresponding silylation products in 87 and 88% yield in short reaction times, respectively (entries 3 and 4). These results indicate that the steric effect does not play a considerable role in silylation of secondary alcohols. However, in the case of tertiary alcohol (2-phenyl-2-propanol), a relatively longer reaction time (180 min) was required to obtain the product in reasonable yield (entry 5). This may be due to the steric hindrance of the two methyl groups and the benzene ring on the reaction site.

The catalytic activity of ³⁰P/S-Bi was also investigated for silylation of phenols (entries 6-10). Phenols with various substituents underwent silvlation in high yield (entries 6-10). However, compared with aliphatic alcohols, aromatic alcohol substrates needed somewhat longer reaction times to obtain the silylation products in reasonable yield. For example, 2-naphthol offered 74% yield in 55 min reaction time (entry 10). Unfortunately, the present heterogeneous catalytic system was unable to catalyze the silylation of other types of hydrogen-labile substrates such as amine and thiol. 4-Methoxybenzenethiol and benzylamine gave no silylation product at all under the present reaction conditions (entries 11 and 12). The lack of reactivity was due to the higher affinity of silicon atom of HMDS towards the oxygen of the hydroxyl group than the nitrogen and sulfur of amine and thiol, respectively.^[20] This heterogeneous catalytic protocol was utilized successfully in the selective silylation of hydroxyl group in the presence of other functional groups in the same molecule (entries 13-15). The present method tolerates the presence of carboxylic acid (entry 13), amine (entry 14) and enolizable carbonyl group (entry 15). We also investigated the selective silvlation of benzyl alcohols over tertiary and phenolic hydroxyl groups (Scheme 1). When an equimolar mixture of benzyl alcohol and 2-phenyl-2-propanol (Scheme 1a) or 2-naphthol (Scheme 1b) was reacted with 0.8 mmol of HMDS under the same reaction conditions, only the benzyl alcohol converted predominantly to silulation products.

³⁰P/S-Bi is not only a stable, efficient and water-tolerant solid catalyst, but it can also be recycled and reused without losing its activity. The reusability of this catalyst was examined using trimethylsilylation of benzyl alcohol with HMDS as a model reaction for 10 consecutive times. It was found that the catalytic efficiency

$\begin{array}{c c c c c c c c c c} & 1 & 2988 & 3988 & 38866 & 3886 & 3886 & 38866 & 38866 & 38866 & 38866 & 38866 & 38866 &$	Table 3. ³⁰ P/S-Bi catalyzed silylation of secondary, tertiary alcohols and phenols with HMDS ^a			
IntyProductsTime (min)Yield (%) ¹ 1 $\int_{f} \int_{f} \int$		R−OH + (Me ₃ Si) ₂ NH ³⁰P/S-Bi CH ₂ Cl ₂ , rt	→ R−OSiMe ₃ + NH ₃	
$1 \qquad \qquad$	Entry	Products	Time (min)	Yield (%) ^b
$ \begin{array}{c c} & \downarrow & \downarrow \\ \downarrow & \downarrow \\ 1 \\ 2 \\ 2 \\ \downarrow & \downarrow \\ \downarrow$	1	OTMS	10	90
2 $\int_{C} \int_{C} \int_$				
3 $\int_{c} \int_{c} \int_$	2	OTMS	10	86
$ \begin{array}{c c} & & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & \\ & & \\ & $	3	отмs	10	87
$\begin{array}{c cccc} 4 & & & & & & & & & & & & & & & & & & $				
$ \begin{array}{c c} & & & & & & & & & & & & \\ & & & & & & $	4	OTMS	15	88
5 $\downarrow \downarrow \downarrow$ OTMS 180 78 6 $\downarrow \downarrow \downarrow \downarrow$ OTMS 20 86 7 $\downarrow \downarrow \downarrow \downarrow \downarrow$ OTMS 15 83 8 $\downarrow \downarrow \downarrow \downarrow \downarrow$ OTMS 20 76 9 $\downarrow \downarrow \downarrow \downarrow \downarrow$ OTMS 20 76 10 $\downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow$ OTMS 55 71 11 $\downarrow \downarrow \downarrow \downarrow \downarrow \downarrow \downarrow$ OTMS 55 74 12 $\downarrow \downarrow \downarrow \downarrow$ NHTMS 180 NR				
$i \qquad i \qquad$	5	OTMS	180	78
$\begin{bmatrix} 6 & & & & & & & & & & & & & & & & & & $				
7 $\int_{Br} OTMS$ 15 83 8 $\int_{Br} OTMS$ 20 76 9 $Br + \int_{Cl} OTMS$ 25 71 10 $\int_{Cl} OTMS$ 55 74 11 $\int_{MeO} OTMS$ 180 NR 12 $\int_{MeO} NR$ 180 NR	6	OTMS	20	86
8 F_{r} 9 F_{r} F_{r	7	OTMS	15	83
8 $\downarrow \downarrow \downarrow$		Br		
Br + Cl $Br + Cl$ $Br + Cl$ $Br + Cl + OTMS$ $I0$ $I0 + Cl + OTMS$ $I1 + Cl + OTMS$ $I1 + Cl + OTMS$ $I1 + Cl + OTMS$ $I2 + Cl + OTMS$ $I30 + NR$ $I2 + Cl + OTMS$ $I30 + NR$	8	OTMS	20	76
9 Br $ -$ OTMS 25 71 10 $ -$ OTMS 55 74 11 $ -$		Br		
10Image: OTMS557411Image: STMS180NR12Image: NHTMS180NR	9	BrOTMS	25	71
11 STMS 180 NR 12 NHTMS 180 NR	10	OTMS	55	74
12 NHTMS 180 NR	11	STMS	180	NR
	12	NHTMS	180	NR

Table 3. (Continued)

•			
	R-OH + (Me ₃ Si) ₂ NH	\sim CH ₂ Cl ₂ , rt	R-OSiMe ₃ + NH ₃
Entry	Products	Time (min)	Yield (%) ^b
13	OH OTMS	20	88
14	OTMS NH ₂	10	92
15	Отмя	12	90

^a Reaction conditions: alcohol or phenol (1.0 mmol), HMDS (0.8 mmol), ³⁰P/S-Bi (50 mg, corresponding to 0.01 mmol Bi, 1 mol%) in CH₂Cl₂ (4 ml). ^b Isolated yield.



Scheme 1. ³⁰P/S-Bi catalyzed selective silylation of benzyl alcohol over tertiary and phenolic alcohols.

Table 4. ³⁰ P/S-Bi catalyzed silylation of alcohols in comparison with other literature				
No.	Catalyst (mg)	HMDS (mmol)	Time (min)	Reference
1	³⁰ P/S-Bi (50)	0.8	10-55	Present method
2	$SO_{3}H - SiO_{2}$ (19)	0.6	35-420	[7c]
3	HClO ₄ -SiO ₂ (50)	0.8	3-10	[7a]
4	[Sn ^{IV} (TPP)(OTf) ₂] (10)	0.5	1-6	[7h]
5	H- β zeolite (19)	0.6	5–30 h	[7d]
6	$TiCl_2(OTf) - SiO_2$ (60)	0.6	5-30	[7j]
7	LiClO ₄ -SiO ₂ (1000)	0.6	5-120	[7i]
^a All reactions were conducted at room temperature. The reaction of entry 5 was carried out at 80 $^{\circ}$ C.				



remained almost unchanged in terms of reaction yield (92, 90 and 91% yield for first, fifth and tenth cycles, respectively). The catalytic efficiency of ³⁰P/S-Bi was compared with reported heterogeneous catalytic systems as shown in Table 4. The yields and reaction times of present methods were comparable with those of reported methods.

Scheme 2. Plausible mechanism for silylation of an alcohol with HMDS.

The evolution of ammonia was confirmed by its pungent odor and using red litmus paper, which turned blue. The evolution of ammonia suggests a plausible reaction path, as shown in Scheme 2. Lewis acid-base reaction between the 30 P/S-Bi and the nitrogen of HMDS induces the polarization of the N–Si bond to give the reactive silylating agent (I), which rapidly interacts 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, complex (III) releases the ammonia and catalyst for completion of the catalytic cycle.

Conclusions

We have demonstrated the catalytic activity and reusability of poly(4-vinylpyridine/styrene) copolymer-supported Bi(OTf)₃ (³⁰P/S-Bi) to be highly efficient, non-corrosive and environmentally benign for the silylation of alcohols and phenols at room temperature. Various types of alcohols, including benzyl, secondary, tertiary and aromatic alcohols, are able to give silylation products in good to excellent yield. ³⁰P/S-Bi is also able to selectively silylate the hydroxyl group in the presence of carboxylic acid, amine and enolizable carbonyl groups in good yield. ³⁰P/S-Bi is not only an efficient stable solid catalyst but can also be reused without considerable loss of activity.

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