



Highly efficient chemo- and regioselective silylation of –OH groups and cyanosilylation of aldehydes promoted by $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ as a new recyclable catalyst

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ABSTRACT

$\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ as an easy handling recyclable catalyst was applied for trimethylsilylation of diethyl α -hydroxyphosphonates, alcohols and phenols with high selectivity using HMDS as a silylating agent. Cyanotrimethylsilyl ethers were also obtained in excellent yields from treatment of aldehydes with TMSCN in the presence of this catalyst.

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1. Introduction

Functional group protection is an unavoidable process during the multi-step synthesis. One of the most popular reactions for masking hydroxyl functional groups is their transformation to silyl ethers [1]. Preparation of silyl ethers is usually carried out by the reaction of alcohols with silyl halides in the presence of stoichiometric amount of an organic base. The most familiar bases used for this purpose are: imidazole [2], 4-(*N,N*-dimethylamino)pyridine [3], and *N,N*-diisopropylethylamine [4]. In these methods, separation of ammonium salts is a time consuming process.

Reaction of hydroxyl functional groups with $\text{R}_3\text{Si-H}$ catalyzed by dirhodium(II) perfluorooctanoate $\{\text{Rh}_2(\text{PFO})_4\}$ [5], $\text{Ph}_2\text{P-SiEt}_3$ /diethyl azodicarboxylate (DEAD)/pyridinium *p*-toluenesulfonate (PPTS) system [6] and with hexamethyldisilane using $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2\text{-PPh}_3$ [7] have also provided silyl ethers. Preparation of silyl ethers from allylsilane and silyl enol ethers in the presence of catalytic amount of *p*-toluenesulfonic acid [8,9], I_2 [10], trifluoromethanesulfonic acid [11] or $\text{Sc}(\text{OTf})_3$ [12] are also appeared in the literature. Although these procedures provide improvements, they suffer from expensive silylating agents and catalysts, using

hazardous and not available chemicals such as DEAD, moisture sensitive compounds and using organic solvents.

Hexamethyldisilazane (HMDS) as an inexpensive and easy available compound has been used for the preparation of trimethylsilyl ethers from hydroxyl compounds. The only by product of this reaction is NH_3 gas, which is a notable advantage for the method. The main drawback of HMDS is its poor silylating property [13]. However, this difficulty is overwhelmed by using various acid catalysts such as ZnCl_2 [14], K-10 montmorillonite [15,16], I_2 [17], $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [18], $\text{Cu}(\text{OTf})_2$ [19], LiClO_4 [20], $\text{Mg}(\text{OTf})_2$ [21], $\text{Al}(\text{OTf})_3$ [22] and lithium perchlorate dispersed on silica gel [23]. Compounds carrying activated N–Br bonds; 1,3-dibromo-5,5-diethylbarbituric acid and *N,N,N',N'*-tetrabromobenzene-1,3-disulfo- namide [24,25], LaCl_3 [26], sulfonic acid-functionalized ordered nanoporous silica [27], iron(III) trifluoroacetate [28] and zirconyl triflate [29] have been used to activate HMDS for silylation reaction.

Although silylation ability of HMDS has been improved by these methods, yet some problems such as long reaction times, drastic reaction conditions and sometimes, a tedious work-up should still be overcome. However, introduction of new protocols using stable, cost effective, recyclable and non-corrosive catalysts with high efficiency are of great demand, especially for large-scale operations.

α -Hydroxy nitriles or cyanohydrins are interesting compounds in both chemistry and biology [30]. Cyanohydrins are precursors

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of a number of valuable synthetic intermediates such as α -hydroxy acids, α -amino acids and β -amino alcohols [31–35]. Cyanohydrins have also been used as starting materials in the synthesis of pharmaceuticals and natural products such as diltiazem, glycoside amygdalin, and fenvalerate [36]. Because of their importance in organic synthesis, preparation of cyanohydrins has been extensively studied. Traditionally, cyanohydrins are prepared by the addition of highly toxic hydrogen cyanide to carbonyl compounds, which is an equilibrium process [37–39]; while addition of base increases the rate of the reaction [40]. Transhydrocyanation from acetone cyanohydrin to the carbonyl compounds is another method of cyanohydrin preparation [41–45]. Reaction has been mediated under basic conditions [41,42], or using lanthanide(III) alkoxides [43], titanium-, zirconium-, and aluminum-based [44,45] reagents as catalysts.

Acidic hydrolysis of cyanotrimethylsilyl ethers is further route to obtain cyanohydrins [46,47]. These compounds are prepared from the reaction of carbonyl compounds with TMSCN, and many catalysts and reagents have been introduced to achieve this goal. Various Lewis acids [48–66], base catalysts [67–70], solid catalysts [71–74], organocatalysts [75–81], ionic liquids [82,83] and bifunctional catalysts [84–87] have been employed to furnish cyanosilylation of carbonyl compounds with TMSCN. Although many promising catalysts and reagents have been introduced to promote this reaction, there is much room for the design and preparation of new catalysts, which offer short reaction time, easier work-up and can be recycled simply without considerable loss of their catalytic abilities.

Titanium tetrachloride (TiCl_4) as a powerful Lewis acid has found many applications in organic synthesis and industry. However, this compound is a liquid and highly aggressive material that creates clouds of HCl when is exposed to air and moisture. Therefore, its handling needs serious precautions. Recently, we have introduced $\text{TiCl}_3(\text{OTf})$ as a potential solid substitute for fuming liquid TiCl_4 in a number of organic reactions [88–91].

Herein, we report $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ as a silica bound Ti(IV) based compound which is used for selective trimethylsilylation of diethyl α -hydroxyphosphonates, alcohols and phenols with (HMDS) at room temperature. This catalyst has been also applied for efficient preparation of cyanotrimethylsilyl ethers from the reaction of aldehydes with TMSCN.

2. Experimental

2.1. General remarks

Chemicals were purchased from Merck and Fluka Chemical Companies. IR spectra were run on a Shimadzu model 8300 FT-IR spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-250. The purity of the products and the progress of the reactions were accomplished by TLC on silica gel polygram SILG/UV254 plates or GC. ICP analysis was performed by a VARIAN VISTA-PRO CCD Simultaneous ICP-OES.

2.2. Preparation of the catalyst

$\text{TiCl}_3(\text{OTf})$ was prepared according to the literature from the reaction between TiCl_4 and TfOH [92]. The catalyst [$\text{TiCl}_2(\text{OTf})\text{-SiO}_2$] was prepared by adding $\text{TiCl}_3(\text{OTf})$ (0.61 g, 2 mmol) to dry silica gel (70–230 mesh, 6 g) in dry CH_2Cl_2 (15 mL) under nitrogen atmosphere at room temperature. The reaction was performed immediately by the evolution of HCl gas. After evaporation of the solvent, the solid silica bound Ti(IV) catalyst was obtained in 6.53 g. The amount of the evolved HCl gas was measured by back titration method. The weight increase of silica gel and the amounts

of liberated HCl gas were in accord with the formation of $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$.

2.3. General procedure for the preparation of trimethylsilyl ethers catalyzed by $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$

To the stirring mixture of HMDS (97 mg, 0.6 mmol) and an alcohol, phenol or α -hydroxyphosphonate (1 mmol), $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ (30 mg, 0.01 mmol) was added at room temperature (alcohols and phenols are soluble in HMDS; whereas, α -hydroxyphosphonates appeared as a heterogeneous mixture). The reaction completed after appropriate time (monitoring by TLC or GC). EtOAc or Et_2O (5 mL) was added to the reaction mixture and filtered. The catalyst separated and washed with another portion of EtOAc or Et_2O (5 mL). To the combined resulting filtrates, H_2O (5 mL) was added. The organic layer decanted and dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent afforded the almost pure products. In a few cases, further purification performed by short pad of

Table 1


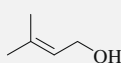
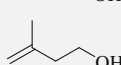
Trimethylsilylation of α -hydroxyphosphonates catalyzed by solid $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ with HMDS under neat conditions at room temperature.^a

Entry	Ar-	Isolated yield (%)
1	$\text{C}_6\text{H}_5\text{-}$	90
2	$p\text{-OCH}_3\text{-C}_6\text{H}_4\text{-}$	90
3	$o\text{-Cl-C}_6\text{H}_4\text{-}$	94
4	$p\text{-NO}_2\text{-C}_6\text{H}_4\text{-}$	95
5	$m\text{-NO}_2\text{-C}_6\text{H}_4\text{-}$	98
6	$p\text{-Cl-C}_6\text{H}_4\text{-}$	92
7	$2,6\text{-Cl}_2\text{C}_6\text{H}_4\text{-}$	90

^a The equivalent ratios of substrate:HMDS:catalyst was 1:0.6:0.01.

Table 2

Trimethylsilylation of alcohols and phenols catalyzed by $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ with HMDS under neat conditions at room temperature.^a

Entry	Substrate	Time (min)	Isolated yield (%)
1	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	5	92
2	$p\text{-NO}_2\text{-C}_6\text{H}_4\text{CH}_2\text{OH}$	5	90
3	$p\text{-MeO-C}_6\text{H}_4\text{CH}_2\text{OH}$	5	94
4	Ph_2CHOH	30	92
5		25	95
6		10	94
7		15	92
8	$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$	30	90
9	$\text{PhCH}_2\text{CH}_2\text{OH}$	5	94
10	$\text{PhCH}_2\text{CH}_2\text{CH}_2\text{OH}$	10	92
11	$\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{OH})\text{CH}_3$	90	88
12	Menthol	90	93
13	Adamantanol	240	90
14	Phenol	30	87
15	2-Hydroxynaphthalene	30	85
16	Cholesterol	10	95 ^b
17	$\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$	48 h	nr
18	$\text{C}_6\text{H}_5\text{CH}_2\text{SH}$	48 h	nr

^a The equivalent ratios of substrate:HMDS:catalyst was 1:0.6:0.01.

^b The reaction was performed in CH_2Cl_2 as a solvent.

silica gel using the appropriate solvent and the desired products were obtained in 90–98% (Table 1) and 85–95% (Table 2) isolated yields.

2.4. General procedure for cyanosilylation of aldehydes catalyzed by $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$

$\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ (60 mg, 0.02 mmol) was added to a mixture of an aldehyde (2 mmol) and TMSCN (0.30 mL, 2.4 mmol). The resulting mixture stirred at room temperature. After completion of the reaction (as monitored by TLC or GC), EtOAc or any other appropriate organic solvent (5 mL) was added to the reaction mixture and the solid $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ was filtered. The solid residue washed with another portion of the solvent (5 mL) and filtered. The filtrates combined and the solvent evaporated on a rotary evaporator to isolate the crude product. Purification by a short column chromatography on silica gel afforded the pure products in 85–94% isolated yields (Table 5).

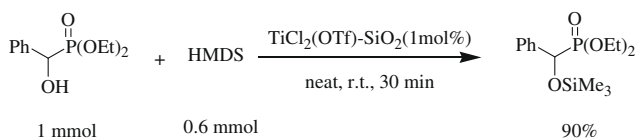
3. Results and discussion

First, $\text{TiCl}_3(\text{OTf})$ was immobilized on silica gel surface by the addition of $\text{TiCl}_3(\text{OTf})$ to a stirring suspension of dried silica gel in dry CH_2Cl_2 . Evaporation of the solvent provided $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ as an air and moisture stable compound. This compound was applied as a catalyst for the preparation of trimethylsilyl and trimethylcyanosilyl ethers.

3.1. Trimethylsilylation of α -hydroxyphosphonates, alcohols and phenols

α -Trimethylsilyloxyphosphonates are useful precursors for the preparation of organic compounds which are attractive in biology and in industry [93]. α -Acidic hydrogen of α -trimethylsilyloxyphosphonates can be deprotonated with strong bases to generate α -carbanionic species in the reaction mixture [94]. However, the *in situ* generated α -carbanionic species become important synthons, which are equivalent to acyl anions and can take part in carbon-carbon bond forming reactions. β,γ -Unsaturated ketones, carboxylic acids, and unsymmetrical ketones can be prepared by alkylation of the carbanionic species [95,96]. α -Trimethylsilyloxyphosphonates are also easily converted to α -hydroxy ketones after alkaline hydrolysis of Si-O bond followed by elimination of dialkyl phosphate [97]. By consideration of the vast applications, the importance of silylation of α -hydroxyphosphonates becomes relevant in organic synthesis.

Silylation of α -hydroxyphosphonates in the presence of catalytic amounts of $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ with HMDS was investigated. For this purpose and optimization of the reaction conditions, we have studied the reaction of diethyl α -hydroxy (phenylmethyl)phosphonate as a model compound with HMDS under solvent-free conditions in the presence of $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ as a catalyst at room temperature. We have found that the optimized molar ratio of substrate:HMDS:catalyst was 1:0.6:0.01 as presented in Scheme 1.



Scheme 1. Optimization conditions for silylation of α -hydroxyphosphonates upon the reaction of diethyl α -hydroxy (phenylmethyl)phosphonate with HMDS in the presence of $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ as a catalyst.

Then, we applied this ratio to structurally diverse α -hydroxyphosphonates for their conversion to the corresponding α -trimethylsilyloxyphosphonates effectively and the corresponding desired products were isolated in excellent yields (88–98%) in short reaction times (Table 1). Separation of the catalyst from the reaction mixture performed very easily by a simple filtration, which after drying was recycled for the subsequent reactions without observable loss of its catalytic activity.

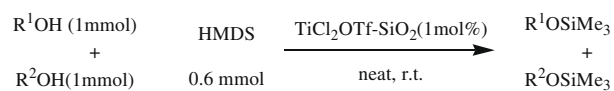
Then, we applied the optimized ratio from the preceding section for silylation reactions of different alcohols and phenols under similar reaction conditions. In the presence of this catalyst, benzylic alcohols were readily transformed into their corresponding trimethylsilyl ethers in excellent yields (Table 2, entries 1–4). Allyl, homoallyl and acid sensitive alcohols were also reacted under similar reaction conditions without the formation of any rearrangement or dehydration side products (Table 2, entries 5–7 and 12). Reaction of primary alcohols in the presence of this catalyst proceeded smoothly in short reaction times in excellent yields (Table 2, entries 8–10). However, this catalyst was also effective for conversion of -OH groups of secondary and tertiary alcohols to their trimethylsilyl ethers in excellent yields without formation of any dehydration or rearranged side products (Table 2, entries 11–13). Silylation of phenolic substrates (Table 2, entries 14 and 15) with HMDS under similar conditions was also performed smoothly and cleanly in high yields. Conversion of cholesterol to its trimethylsilyl ether in the absence of solvent was not a clean and a straightforward reaction. Then, this reaction was performed in CH_2Cl_2 at room temperature with success and the silylated product was isolated in a high yield within a short reaction time (Table 2, entry 16). Trimethylsilylation of amines and thiols under similar reaction conditions did not proceed at all (Table 2, entries 17 and 18).

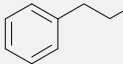
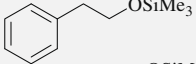
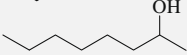
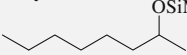
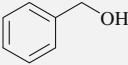
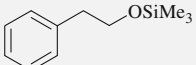
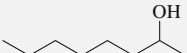
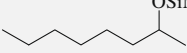
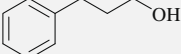
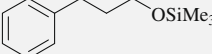
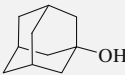
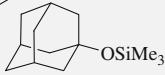
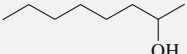
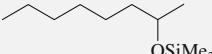
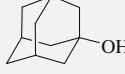
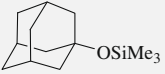
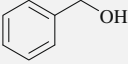
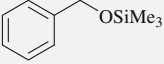
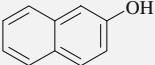
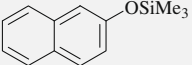
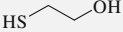
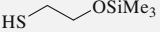
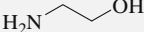
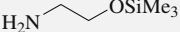
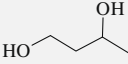
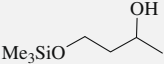
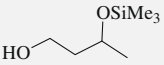
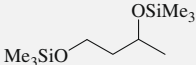
Selectivity of the catalysts for chemical transformations is important, especially, when the catalyst is used in multi-step synthesis. We have found that in the presence of this catalyst, silylation of different -OH groups proceeded with high selectivity as summarized in Table 3.

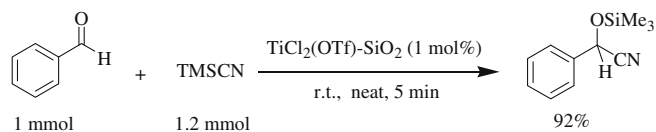
Recycling of the catalyst was explored upon silylation of benzyl alcohol with HMDS in the presence of $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ as a model reaction. After completion of the reaction, CH_2Cl_2 was added to the solvent less reaction mixture and the solid catalyst was simply separated by filtration. The isolated catalyst dried in oven and re-used for the similar reaction for six consecutive runs without observable loss in its catalytic activity. The level of Ti leaching into the liquid phase was determined by inductively coupled plasma atomic emission spectroscopy (ICP). The results showed that the amount of leached Ti was 5.38 ppm after the reaction, corresponding to a loss of 4.2% of the initially added catalyst.

In order to show the merit of the catalyst, we have compared the results of silylation of diethyl α -hydroxy (phenylmethyl)phosphonate using HMDS with some other catalysts such as different metal triflates, silica gel and silica gel wetted with HCl solution (Table 4). As it is evident from the results tabulated in the table, the reaction in the presence of Cu, Al and Mg triflates is faster than that has been performed using LiOTf and $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$. However, the reaction in the presence of $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ required much less molar equivalent of the catalyst. In addition, the heterogeneity of $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ facilitates its separation and recycling process. The catalytic activity of $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ has also been compared with silica gel and silica gel moist with HCl, which their reactions were completely failed.

The catalyst was stored in a moisture ambient for two weeks and after then, it was applied for the silylation reaction of benzyl alcohol with HMDS. However, we observed that there was no change in the catalytic activity of $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ in this reaction.

Table 3Competitive silylation reactions of alcohols using HMDS in the presence of solid $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ at room temperature under solvent-free conditions.

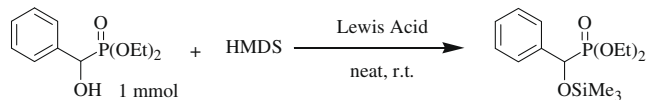
Entry	Substrate	Time (min)	Product	GC yield (%)
1		10		84
				16
2		10		87
				11
3		10		100
				0
4		90		85
				17
5		10		100
				0
6		10		100
7		10		100
8		5		78
				17
				5



Scheme 2. Optimization conditions for cyanosilylation of aldehydes upon the reaction of benzaldehyde with TMSCN in the presence of $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ as a catalyst.

Table 4

Comparison between $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ and some other promoters for silylation reaction of diethyl α -hydroxybenzylphosphonate with HMDS.



Entry	Lewis acid	Time	Yield (%) ^a	Reference
1	$\text{Cu}(\text{OTf})_2$ (11 mol%)	15 min	97 ^b	[19]
2	$\text{Mg}(\text{OTf})_2$ (10 mol%)	Immediately	96	[21]
3	$\text{Al}(\text{OTf})_3$ (10 mol%)	Immediately	97	[22]
4	LiOTf (10 mol%)	90 min	100 ^c	[22]
5	$\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ (1 mol%)	30 min	90	–
6	Silica gel (30 mg)	3 h	Negligible	–
7	Silica gel (30 mg) wetted with HCl (0.03 mmol)	3 h	Negligible	–

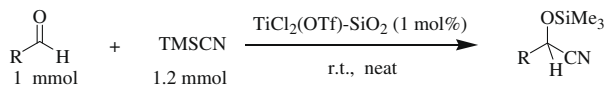
^a Isolated yield.

^b The reaction has been carried out in CH_3CN as solvent.

^c % Conversion based on ^1H NMR.

Table 5

Trimethylcyanosilylation of aldehydes with TMSCN in the presence of $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ (0.01 mmol) under neat conditions at room temperature.^a



Entry	Substrate	Time (min)	Isolated yield (%)
1	$\text{C}_6\text{H}_5\text{CHO}$	5	92
2	$p\text{-CH}_3\text{-C}_6\text{H}_4\text{CHO}$	5	94
3	$p\text{-OCH}_3\text{-C}_6\text{H}_4\text{CHO}$	5	92
4	$p\text{-Cl-C}_6\text{H}_4\text{CHO}$	10	87
5	$2,6\text{-}(\text{Cl})_2\text{-C}_6\text{H}_3\text{CHO}$	30	96
6	$m\text{-NO}_2\text{-C}_6\text{H}_4\text{CHO}$	60	85
7	$p\text{-NO}_2\text{-C}_6\text{H}_4\text{CHO}$	75	86
8	Furfural	5	92
9	1-Naphthaldehyde	20	85
10	2-Naphthaldehyde	30	85
11	Cinamaldehyde	5	91
12	Heptanal	5	90

^a The molar ratio of aldehyde:TMSCN:catalyst was 1:1.2:0.01.

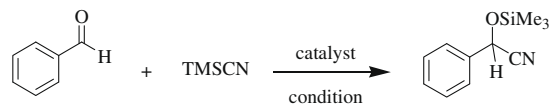
3.2. Trimethylcyanosilylation of aldehydes

Among the reported methods for the preparation of cyanohydrins, cyanosilylation of carbonyl compounds with TMSCN has been more considered. Therefore, we investigated the possibility of using $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ to catalyze cyanosilylation of carbonyl compounds with TMSCN. First, reaction of benzaldehyde with TMSCN in the presence of $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ was studied and the optimized ratio of substrate:TMSCN:catalyst for this reaction was 1 mmol:1.2 mmol:1 mol% as presented in Scheme 2.

Then, the optimized condition subjected for cyanosilylation of different aldehydes. Aromatic aldehydes with both electron-withdrawing and electron-releasing groups, aliphatic, α,β -unsaturated aldehyde and furfural as a heterocyclic aldehyde were converted to their corresponding cyanotrimethylsilyl ethers in the presence

Table 6

Reaction of benzaldehyde with trimethylsilyl cyanide in the presence of different catalysts.



Entry	Catalyst	(mol%)	Condition	Time	Yield (%)	Reference
1	AuCl_3	1	CH_2Cl_2 (solvent), r.t.	30 min	100 ^a	[64]
2	DMAP	1	CH_3CN (solvent), r.t., N_2 atmosphere	1 h	85 ^b	[69]
3	NIS	0.5	CH_2Cl_2 (solvent), r.t.	15 min	100 ^a	[79]
4	N-Heterocyclic carbenes (NHC)	0.5	THF, r.t.	10 min	91 ^b	[78]
5	$\text{TiCl}_2(\text{OTf})\text{-SiO}_2$	1	Neat, r.t.	5 min	92 ^b	–

^a Conversion yield assumed by ^1H NMR analysis.

^b Isolated yield.

of $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ in short reaction times. These results are shown in Table 5.

In order to show the advantage of the catalyst, cyanosilylation of benzaldehyde with TMSCN in the presence of $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ was compared with some of the reported methods in Table 6. As it is obvious from results of the table, the reaction in the presence of the other catalysts has been performed in solvents, whereas, in the presence of $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ non-solvent condition was employed. In addition, $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ is an easily recyclable heterogeneous catalyst, which resulted to a simple work-up of the products.

4. Conclusion

In this article, we have introduced an easy handling recyclable solid titanium(IV) based catalyst; $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$, which has been used to promote silylating ability of HMDS for the preparation of silyl ethers from α -hydroxyphosphonates, alcohols and phenols. The catalysts show high chemo- and regioselectivity between different substrates. $\text{TiCl}_2(\text{OTf})\text{-SiO}_2$ has also been used as an effective catalyst for cyanosilylation of different aldehydes. In the presence of this catalyst, reactions proceeded under solvent-free conditions and at short times in excellent yields. The strong feature of the method is easy work-up of the products and simple recycling of the heterogeneous catalyst.

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