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# Deprotection of *tert*-butyldimethylsilyl (TBDMS) ethers using efficient and recyclable heterogeneous silver salt of silicotungstic acid catalyst under mild reaction condition

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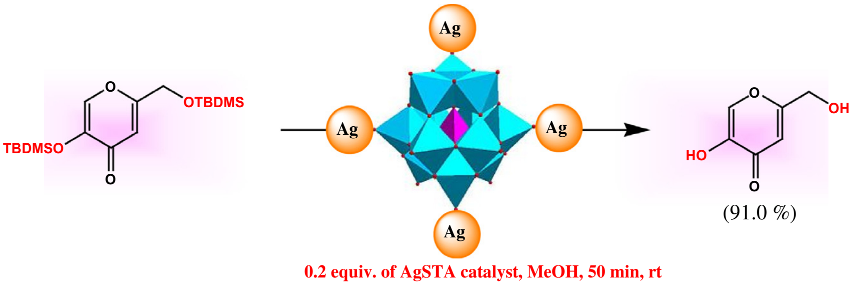
## HIGHLIGHTS

- Deprotection of various substituted alkyl & phenolic TBDMS ethers at room temperature.
- Silver exchanged silicotungstic acid found to be efficient catalyst in desilylation.
- 0.2 equiv. of AgSTA catalyst showed tremendous catalytic activity.
- Alkyl and phenolic TBDMS ethers were cleaved in methanol under mild condition.
- 100% conversion of reactant and up to 92.0% yield of respective alcohol in 40 min.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Deprotection of various substituted alkyl and phenolic TBDMS ethers were carried out using prepared silver exchanged silicotungstic acid (AgSTA) salt as heterogeneous catalyst in methanol at room temperature. The Brönsted acidic protons of silicotungstic acid were substituted by Lewis acidic silver molecule and prepared heterogeneous AgSTA catalyst which characterized using different spectroscopic and analytical methods. 0.2 equiv. of AgSTA catalyst showed tremendous catalytic activity in the desilylation of alkyl and phenolic TBDMS ethers under mild reaction condition in methanol to produce respective alcohol in excellent yield. On screening, 100% conversion of reactants and up to 92.0% yield of respective alcohol in 40 min reaction time was achieved using 0.2 equiv. of AgSTA catalyst. The solid AgSTA catalyst was separated from the reaction mixture by simple filtration process at the end of reaction and reused for several times without significant loss of catalytic activity. The present eco-friendly catalytic system is found to be very convenient, high yielding, fast and clean method for desilylation of alkyl as well as phenolic silyl ethers even in existence of other sensitive organic functional groups such as aldehyde, methoxy, and acetate under mild reaction condition.

## 1. Introduction

Since a hydroxyl group can contribute in numerous organic transformations under mild reaction conditions, a central problem in organic synthesis is to ensure that a hydroxyl function in a multifunctional molecule is protected from unwanted reactions altogether or until such time as it's intrinsic reactivity is required. Protective groups suitable for contemporary synthesis should ensure efficiency of preparation, selective removal and stability

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under the intended reaction conditions [1–4]. The *tert*-butyldimethylsilyl (TBDMS) group is used widely for the protection of hydroxyl group in synthetic organic chemistry due to their ease of installation, stability towards various conditions such as Grignard reaction, Wittig reaction, and reduction reaction, and finally deprotect easily without affecting other organic functional groups [1–7].

Momentous research in silylation chemistry has been reported in the development of various types of desilylation reactions [4–7]. It is well-known that the deprotection reaction of alkyl and phenolic TBDMS ethers to form respective alcohols using fluoride containing compounds in THF has been used commonly for the removal of TBDMS [8–10]. However, such type of reactions can lead to side reactions and formation of byproducts due to its strong basicity, and restrict the wide application of this reagent for the deprotection of TBDMS ether groups. Therefore, various alternative research methods in silylation chemistry have been resulted in the progress of deprotection of TBDMS ethers. Generally, the acidic reagents such as $CF_3COOH/H_2O$, $CH_3COOH,^4HF$, $SbCl_5$, $SnCl_2$, have been reported for desilylation [8–12]. In addition to that, the basic reagents namely $NaOH/Bu_4NHSO_4$, TBATB, $K_2CO_3$, $Cs_2CO_3$, were also utilized for the deprotection of silyl ethers [13–16]. Oxidizing reagents DDQ, $KMnO_4$, $BaMnO_4$, and reducing agents DIBAL–H, $LiAlH_4$, NaH, have also been reported for desilylation [17–21]. However, most of these procedures have difficulties such as longer reaction time, harsh reaction conditions, use of expensive and corrosive reagents as well as cumbersome work-up procedures.

Indeed, heterogeneous catalysts have been receiving more attention over homogeneous catalysts because of their advantages in easy recovery and recyclability in organic reactions, where catalyst is in one phase and product in another, which makes product–isolation easy and catalyst reuse convenient [22,23]. Several solid catalyst such as tetra-butyl ammonium fluoride, tri-methylsilyl chloride (TMSCl), Zn $(BF_4)_2$, Scandium triflate (Sc $(OTf)_3$), $BCl_3$, $InCl_3$, $ZnBr_2$, Cerium triflate (Ce $(OTf)_4$), $SbCl_3$, $ZrCl_4$, $Ni(II)Cl_2{\cdot}6H_2O$ and tetra-butyl ammonium tribromide (TBATB), ionic liquids, and $TiCl_4$–Lewis base complexes have been also reported for the cleavage of TBDMS ethers [1,2,24-26]. Among solid acids, sulfonic acid functionalized nanoporous silica and $NaHSO_4$ on silica have also been reported for the cleavage of TBDMS ethers [27,28]. Though, the most of these methods require hazardous reagents and difficult workup procedures that are unfavorable to the environment. Therefore, it is essential to develop a mild, eco-friendly, fast, and selective method for deprotection of alkyl and phenolic silyl ethers neither affecting on other function groups nor producing side reactions using heterogeneous catalyst in environmentally friendly reaction condition.

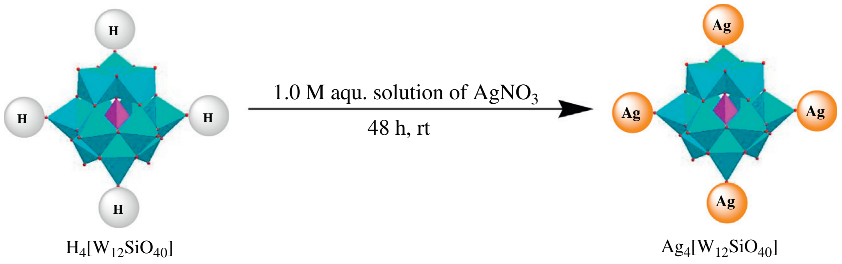
Heteropolyacids (HPAs) are known to be efficient acidic catalysts for various organic reactions. Especially, these acid catalysts have a wide range of applications in organic reactions and fine chemical synthesis [29–36]. Nevertheless, its applications are limited in the bulk form as they are soluble in water and polar solvents, possess low surface area, and low thermal stability [29,30]. In order to overcome these difficulties HPAs could be modified at a molecular level. Modification of heteropoly acids, particularly the Brønsted acidic sites to Lewis acidic site in Keggin-type is highly beneficial in organic reactions [29,37]. The Brønsted acidic protons of HPAs exchanged by large monovalent cations such as $Cs^+$, $K^+$ and $Ag^+$ could form a large range of insoluble, microporous solid Lewis acidic catalysts effective in various catalytic reactions [37]. Recently, we reported silver substituted silicotungstic acid is highly selective and extraordinary yield providing heterogeneous catalyst for the synthesis of 1,5-benzodiazepine derivatives under solvent free mild reaction condition [38]. In continuation of this work, utilization of such fabulous active mild acidic heterogamous catalyst in development of other organic reactions methodology under eco-friendly reaction condition is concentrating more attention in our laboratory.

Herein, we report the silver substituted silicotungstic acid, as a solid acid catalyst, for the deprotection of alkyl and phenolic silyl ethers in methanol at room temperature. Moreover, effect of amount of catalyst, various solvents, and comparison with other heterogeneous catalyst in desilylation reactions were also investigated as well as several TBDMS substituted derivatives were deprotected by using 0.2 equiv. of AgSTA catalyst at room temperature. In addition, recyclability of AgSTA catalyst over six cycles was also determined. Therefore, desilylation of organic compounds in mild reaction condition using modified acid sites of HPAs as solid heterogeneous catalyst without addition of an organic reagents and metal salt or mineral acid co-catalyst is highly required and such development would be safer, greener and cheaper than many of the processes in use today.

## 2. Experimental

### 2.1. Catalyst preparation

Silver exchanged silicotungstic acid (AgSTA) was prepared using precipitation method as reported in our previous method [38] and the representative reaction is shown in Scheme 1. Briefly, in a 100 ml round bottom flask 1.0 mmol of silicotungstic acid (STA) was dissolved in 10 ml deionized water. Then, the required amount of 1 M $AgNO_3$ aqueous solution was added carefully controlled by using an automatic syringe pump to the former solution of STA with vigorous stirring at room temperature. Initially, 4 ml $AgNO_3$ aqueous solution was added at a rate of 2 ml/h, and then the remaining solution was added at a rate of 10 ml/h. If the aqueous $AgNO_3$ solution was added at a constant rate of 10 ml/h from the beginning to the aqueous solution of $H_4SiW_{12}O_{40}$, fine particle size with large external surface area were formed, which had adverse effect on the catalytic activity and solubility. Therefore, the controlled addition of aqueous $AgNO_3$ solution is very important. The subsequent colloidal solution was allowed to stand for 48 h at room temperature and then, the white precipitate was separated out using centrifugation method and washed several times with deionized water to afford $Ag_4SiW_{12}O_{40}$ as a white solid. The prepared sample was dried at 120 °C in a dry oven for 12 h. The resulting AgSTA catalyst was obtained with good to efficient yield and



**Scheme 1.** Preparation of heterogeneous silver exchanged silicotungstic acid (AgSTA) using precipitation method.