



Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: https://www.tandfonline.com/loi/gpss20

Silica-coated Fe₃O₄ magnetic nanoparticlessupported sulfonic acid as a highly active and reusable catalyst in chemoselective deprotection of tert-butyldimethylsilyl (TBDMS) ethers

Sayed Hossein Javadi, Daryoush Zareyee, Azam Monfared, Khadijeh Didehban & Sayed Ahmmad Mirshokraee

To cite this article: Sayed Hossein Javadi, Daryoush Zareyee, Azam Monfared, Khadijeh Didehban & Sayed Ahmmad Mirshokraee (2019): Silica-coated Fe₃O₄ magnetic nanoparticlessupported sulfonic acid as a highly active and reusable catalyst in chemoselective deprotection of tert-butyldimethylsilyl (TBDMS) ethers, Phosphorus, Sulfur, and Silicon and the Related Elements, DOI: 10.1080/10426507.2019.1576680

To link to this article: <u>https://doi.org/10.1080/10426507.2019.1576680</u>



View supplementary material 🖸

| -0 | _ | 1 |
|----|---|---|
| | | Г |
| | | Γ |
| | | Ľ |
| _ | _ | - |

Published online: 28 Sep 2019.



Submit your article to this journal 🕑



View related articles



View Crossmark data 🗹

Taylor & Francis Taylor & Francis Group

Check for updates

Silica-coated Fe₃O₄ magnetic nanoparticles-supported sulfonic acid as a highly active and reusable catalyst in chemoselective deprotection of tertbutyldimethylsilyl (TBDMS) ethers

Sayed Hossein Javadi^a, Daryoush Zareyee^b, Azam Monfared^a, Khadijeh Didehban^a, and Sayed Ahmmad Mirshokraee^a

^aChemistry Department, Payam-e-Nour University, Tehran, Iran; ^bDepartment of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran

ABSTRACT

Anchored propyl sulfonic acid on the surface of silica-coated magnetic nanoparticles $(Fe_3O_4@SiO_2@PrSO_3H)$ was successfully employed in the deprotection of TBDMS ethers. The prepared magnetically separable nanocatalyst exhibited efficient catalytic activity with high conversion and selectivity in cleavage of TBDMS ethers. TBDMS ethers are efficiently cleaved to the corresponding hydroxyl compounds in methanol solution containing 2 mol% magnetic nano-catalysts. Good to excellent yields of products, simple work-up and product separation, selective cleavage of TBDMS ethers in the presence of TBDPS ethers, easy recycling of the catalyst with external magnet with no loss in its activity (7 reaction cycles) are important features of this new protocol.

ARTICLE HISTORY

Received 11 December 2018 Accepted 28 January 2019

KEYWORDS

Silyl ether; TBDMS ether; selective deprotection; magnetic nanoparticles; heterogeneous acid catalyst

GRAPHICAL ABSTRACT



Introduction

Silvl ether formation is not only a fundamental process in the synthesis of functional organosilicon compounds but also an important technique for protection of reactive hydroxyl groups during multistep organic syntheses.^[1-3] The tert-Butyldimethylsilyl (TBDMS) ethers are among the most frequently used protective groups for alcohols, because of ease of introduction, stability to a variety of reagents, and ease of selective deprotection.^[4-6] Although, the major goal of such a protection is usually to prevent unfavorable reactions of hydroxyl groups, in many cases it is often necessary to convert selectively the silvl ethers to their corresponding

parent alcohols.^[7,8] Many methods have been developed to remove silvl-protecting groups. Tetrabutylammonium fluoride (TBAF) is the most typical desilylating reagent,^[9,10] but it has no selectivity and has possible side-reactions caused by the nucleophilicity of fluoride ion. Thus, many alternative and mild protocols have been reported for the deprotection of silyl ethers.^[11-33] However, while acknowledging the pioneering advances in this area, some of these methods suffer from limitations such as prolonged reaction times,^[22,23,31] troublesome work-up steps,^[12,23] and the use of non-recyclable and sensitive catalysts,^[12-15,18,21,24,25,28,31,33] so, it is still of great interest to devise new methods for selective cleavage of TBDMS ethers.

CONTACT Daryoush Zareyee 🔊 zareyee@gmail.com 🝙 Department of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran; Azam Monfared (admonfared@gmail.com) Chemistry Department, Payam-e-Nour University, Tehran, Iran. Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gpss.

Supplemental data for this article can be accessed https://doi.org/10.1080/10426507.2019.1576680.

© 2019 Taylor & Francis Group, LLC

To avoid major environmental hazards and to satisfy growing stringent global environmental regulations, it is imperative to develop a truly catalytic process with minimal waste production. Consequently much attention has now been paid to design of strong heterogeneous acid catalysts that can replace the conventional hazardous liquid- or traditional waste generating Lewis-acid catalysts.^[34-40] However, to maintain economic viability, a suitable heterogeneous system must not only minimize the production of waste, but should also exhibit high stability, activities, and selectivities comparable or superior to the existing homogeneous routes. Toward this aim, many support materials^[41-52] are often used for immobilization of sulfuric acid, which can be separated by conventional separation techniques such as centrifugation and filtration. However, over recent decades, magnetic nanoparticles have aroused remarkable interest and they are a good candidate for consolidation of homogeneous catalysts such as sulfuric acid.^[53–59]

Considering that magnetic separation is more efficient and attractive than traditional centrifugation or filtration, very recently, we reported synthesis and application of heterogeneous sulfonated core-shell magnetic nanoparticles (SMNPs) (Fe₃O₄@SiO₂@PrSO₃H) as a renewable and reusable strong solid acid catalyst in some organic transformations.^[60–61] So in the present study, in our continuing



Scheme 1. Deprotection of TBDMS ethers using $Fe_3O_4@SiO_2@PrSO_3H$ in methanol at ambient temperature.

quest for new applications of $Fe_3O_4@SiO_2@PrSO_3H$, we wish to report the use of heterogeneous $Fe_3O_4@SiO_2@PrSO_3H$ in selective deprotection of TBDMS ethers (Scheme 1).

Results and discussion

We started to study the desilvaltion of various types of TBDMS ethers catalyzed by Fe₃O₄@SiO₂@PrSO₃H catalyst by examining the condition for cleavage of benzyloxy(tertbutyl)dimethyl silane. A summary of the optimization experiments is provided in Table 1. Results of the reaction pointed to an optimized performance of 2 mol% of Fe₃O₄@SiO₂@PrSO₃H, which furnish the corresponding benzyl alcohol in methanol as solvent in 98% yield at room temperature after 2 h. As can be seen, the reaction did not proceed within 120 min in the absence of a catalyst (Table 1, entry 8), indicating a catalyst must be needed for the deprotection reaction. Additionally, though 2 mol% of catalyst is enough to allow the cleavage of benzyloxy(tert-butyl)dimethyl silane in a short reaction time, increasing the amount of SMNPs to more than 2 mol% resulted in only a slightly decreased reaction time (Table 1, entry 10).

Under the optimized synthetic conditions, we next studied the scope of this reaction (Table 2). We have found that a series of TBDMS ethers such as primary (Table 2, entries 1-7, 11), secondary (entries 8-10, 12-14) and allylic (entry 13) TBDMS ethers were converted into the corresponding alcohols in high yields following the above procedure. As indicated in Table 2, the use of either aromatic or aliphatic TBDMS ethers in this reaction could generate the hydroxyl groups and because of the mildness of reaction conditions, different functionalities such as halogens, alkyl, nitro and C = C double bond remained intact (entries 2-5, 13). These results demonstrate the high performance and activity of the designed catalyst for the cleavage of different TBDMS ethers bearing different functional groups. In order to assess its generality, the same reaction was investigated for deprotection of more sterically demanding TBDMS-protected tertiary alcohols under the standardized conditions (entry 15). Although the procedure is very dependent on steric factors, interestingly, we found that a modest yield of the corresponding tertiary alcohol was also obtained with longer reaction times.

| Table 1. Fe ₃ O ₄ @SiO ₂ @PrSO ₃ H catalyzed cleavage of benzyloxy (<i>tert</i> -butyl)dimethyl silane under different reaction condit |
|---|
|---|

| | | O ₄ @SiO ₂ @PrSO ₃ H (mol%) | ОН | |
|-------|--|--|------------|--------------------------|
| | | Solvent, rt | • | |
| Entry | Fe ₃ O ₄ @SiO ₂ @PrSO ₃ H (mol%) | solvent | Time (min) | Yield ^[a] (%) |
| 1 | 2 | H ₂ O | 120 | 28 |
| 2 | 2 | CH₃CN | 120 | 25 |
| 3 | 2 | Toluene | 120 | trace |
| 4 | 2 | CH ₂ Cl ₂ | 120 | trace |
| 5 | 2 | THF | 120 | 20 |
| 6 | 2 | EtOH | 120 | 45 |
| 7 | 2 | CH₃OH | 120 | 98 |
| 8 | 0 | CH₃OH | 120 | trace |
| 9 | 1 | CH₃OH | 120 | 58 |
| 10 | 3 | CH₃OH | 100 | 98 |

^[a]Isolated yields.

| Entry | Substrate | Product | Time (min/h) | Yield ^[a,b,c] (%)[ref.] |
|-------|---------------------------|-----------------------|--------------|------------------------------------|
| 1 | OTBDMS | ОН | 120 | 98 ^[26] |
| 2 | CI | СІ | 140 | 95 ^[33] |
| 3 | | CI | 150 | 90 ^[33] |
| 4 | OTBDMS | ОН | 120 | 92 ^[30] |
| 5 | O ₂ N OTBDMS | O ₂ N OH | 150 | 90 ^[20] |
| 6 | OTBDMS | OH | 100 | 94 ^[26] |
| 7 | OTBDMS | ОН | 100 | 95 ^[12] |
| 8 | CH3 | OH CH ₃ | 180 | 89 ^[12] |
| 9 | OTBDMS CH ₃ | OH CH ₃ | 180 | 91 ^[16] |
| 10 | OTBDMS | ОН | 200 | 93 ^[30] |
| 11 | OTBDMS | ОН | 120 | 100 ^[30] |
| 12 | OTBDMS | ОН | 240 | 88 ^[30] |
| 13 | OTBDMS | OH | 220 | 85 ^[30] |
| 14 | OTBDMS | ОН | 300 | 89 ^[26] |
| 15 | Me | Ме | 300 | 55 ^[31] |
| 16 | OTBDMS | ОН | 10h | NR ^[26] |
| 17 | OTBDPS | ОН | 10h | NR ^[26] |

Table 2. Deprotection of TBDMS ethers to the corresponding alcohols using 2 mol% Fe₃O₄@SiO₂@PrSO₃H in methanol at room temperature.

^[a]Reaction condition: TBDMS ether (1 mmol), $Fe_3O_4@SiO_2@PrSO_3H$ (2 mol%), solvent: CH₃OH, room temperature.

^[b]Isolated yields.

^[c]Some products were characterized from spectral (¹H NMR) data and by direct comparison with the parent alcohols.

It is noteworthy that the reaction seems to be unsuitable for deprotection of phenolic TBDMS ethers and tert-butyldiphenylsilyl (TBDPS) ethers (entries 16, 17) even with increasing the time of reaction. Under the reaction conditions, phenolic TBDMS ethers and TBDPS ethers remained unreacted and were recovered unchanged, indicating that the reaction could be selective for the deprotection of alcoholic TBDMS ethers in the presence of either TBDPSprotected alcohols or phenolic TBDMS ethers in competitive experiments (Scheme 2).

The prepared magnetic nanocatalyst was easily recovered by separation with an external magnet after the reaction and was subsequently recycled under the same reaction conditions. Therefore, finally, we checked the reusability of the $Fe_3O_4@SiO_2@PrSO_3H$ catalyst in the cleavage of benzyloxy(*tert*-butyl)dimethylsilane in methanol under the optimized conditions. After the completion of the reaction, insoluble catalyst was separated from the reaction mixture by an external magnet and was washed with methanol several times and then directly reused for further reaction. The results of seven runs showed that the recovered catalyst retains its activity in terms of yields of 98%, 96%, 98%, 95%, 94%, 90% and 88%, respectively (Figure S 1 Supplemental Materials).

The suggested mechanism of the $Fe_3O_4@SiO_2@PrSO_3H$ catalyzed deprotection of TBDMS ethers (Scheme 3) involve complexation of the silyl ether oxygen with acidic proton of catalyst weakens the silyl ether bond precipitating the formation of a methoxy silyl ether and a proton, and then the catalytic species is regenerated.

To compare the performance of $Fe_3O_4@SiO_2@PrSO_3H$ with some reported protocols, the desilylation of tert-butyldimethyl(phenethoxy)silane in the presence of $Sc(OTf)_3$,^[12]

 Table 3. Comparison of the efficiency of catalysts in cleavage of tertbutyldimethyl(phenethoxy)silane.

| Í | OTBDMS | catalyst (x mo | ol%) ➡► | | ∕ОН |
|-------|---|-------------------------------------|------------|-------------------|------------------------|
| | | Solvent, r | t. | | |
| Entry | Catalyst (mol%) | Solvent | T (°C) | Time (min/[h]) | Yield (%) |
| 1 | $Fe_3O_4@SiO_2@PrSO_3H$ (2) | Methanol | rt | 100 | 94 ^a |
| 2 | $Fe(OTs)_3.6H_2O(2)$ | Methanol | rt | 105 | 77 ^{[13],b,c} |
| 3 | $Sc(OTf)_3$ (0.1) | CH ₃ CN/H ₂ O | rt | 60 | 98 ^{[12],b} |
| 4 | [tetraEG(mim) ₂][OMs] ₂ (0.2 eq.) | Methanol | rt | 80 | 91 ^{[28],b} |
| 5 | NIS (5) | Methanol | rt | [18] | 92 ^{[31],b,d} |

^aPresent work.

^bNon-recoverable catalyst. ^cLow yield of product.

^dLong reaction time.

 $Fe(OTs)_{3.}6H_2O$,^[13] [tetraEG(mim)₂][OMs]₂^[28] and NIS^[31] with respect to the reusability, reaction times and yields of the products is shown (Table 3). Entry 2 shows deprotection using $Fe(OTs)_{3.}6H_2O$ in methanol proceeded very sluggish and provided only 77% of the corresponding 2-phenyl ethanol after 105 min. In addition, some protocols used non-recoverable catalyst,^[12,13,28,31] or had a long reaction time.^[31]

Experimental section

Procedure for deprotection of TBDMS ethers

Catalyst (0.03 g, 2 mol %) was added to TBDMS ethers (1 mmol) in methanol (5 mL) at ambient temperature and the mixture was stirred for appropriate time indicated in Table 2 until the reaction was completed as monitored by



Scheme 3. The plausible reaction mechanism for the deprotection of TBDMS ethers.



Scheme 2. Selective cleavage of benzylic TBDMS ethers in the presence of a, c) phenolic TBDMS ethers and b) tert-butyldiphenylsilyl (TBDPS) ethers.

gas chromatography and thin-layer chromatography. After the completion of reaction, the catalyst was separated by an external magnet and after the evaporation of methanol, the product was isolated by rapid filtration through a short pad of silica gel.

Conclusions

In conclusion, we have demonstrated a mild and convenient route for the deprotection of a variety of TBDMS ethers. The catalyst showed outstanding results with a number of advantages including excellent yields and short reaction times, low catalyst loading, reusability of the catalyst and ease of operation and workup, making it a potentially useful and attractive approach to industrial production. The results revealed that the reaction is selective for deprotection of alcoholic TBDMS ethers in the presence of either TBDMS or TBDPS-protected of phenols ethers alcohols. Furthermore, the catalyst can be collected easily by a magnet and reused seven times with only a very slight loss of catalytic activity.

References

- Lalonde, M.; Chan, T. H. Use of Organosilicon Reagents as Protective Groups in Organic Synthesis. Synthesis 1985, 1985, 817–845. DOI: 10.1055/s-1985-31361.
- [2] Greene, T. W.; Wuts, P. G. M. Protective Groups in Organic Synthesis, 4th ed.; John Wiley and Sons: NJ, 2007.
- [3] Kocienski, P. J. In *Protective Groups*; Enders, R., Noyori, R., Trost, B. M., Eds.; Thieme: Stuttgart, 1994.
- Chaudhury, S. K.; Hernandez, O. 4-Dimethylaminopyridine: An Efficient and Selective Catalyst for the Silylation of Alcohols. *Tetrahedron Lett.* 1979, 20, 99–102. DOI: 10.1016/S0040-4039(01)85893-7.
- [5] Corey, E. J.; Cho, H.; Rucker, C.; Hua, D. H. Studies with Trialkylsilyltriflates: New Syntheses and Applications. *Tetrahedron Lett.* **1981**, *22*, 3455–3458. DOI: 10.1016/S0040-4039(01)81930-4.
- [6] Lombord, L. D. An Effective Catalyst for the Introduction of the t-butyldimethylsilyl Group. *Tetrahedron Lett.* 1984, 25, 227–228. DOI: 10.1016/S0040-4039(00)99846-0.
- [7] Colvin, E. W. Silicon Reagents in Organic Synthesis; Academic: New York, 1998.
- [8] Nelson, T. D.; Crouch, R. D. Selective Deprotection of Silyl Ethers. Synthesis 1996, 1996, 1031–1069. DOI: 10.1055/s-1996-4350.
- [9] Corey, E. J.; Venkateswarlu, A. Protection of Hydroxyl Groups as Tert-butyldimethylsilyl Derivatives. J. Am. Chem. Soc. 1972, 94, 6190-6191. DOI: 10.1021/ja00772a043.
- [10] Hanessian, S.; Lavalle, P. The Preparation and Synthetic Utility of Tert-butyldiphenylsilyl Ethers. *Can. J. Chem.* 1975, 53, 2975–2977. DOI: 10.1139/v75-419.
- [11] Jadhav, V. H.; Lee, S. B.; Jeong, H.-J.; Lim, S. T.; Sohn, M.-H.; Kim, D. K. An Efficient and Chemoselective Deprotection of Tert-butyldimethylsilyl (TBDMS) ethers Using Tailor-made Ionic Liquid. *Tetrahedron Lett.* **2012**, *53*, 2051–2053. DOI: 10.1016/j.tetlet.2012.02.016.
- [12] Oriyama, T.; Kobayashi, Y.; Noda, K. Chemoselective and Practical Deprotection of Alkyl Trialkylsilyl Ethers in the Presence of Aryl Trialkylsilyl Ethers by a Catalytic Amount of Sc(OTf)₃. Synlett. **1998**, 1998, 1047–1048. DOI: 10.1055/s-1998-1890.
- [13] Bothwell, J. S.; Angeles, V. V.; Carolan, J. P.; Olson, M. E.; Mohan, R. S. A Mild and Chemoselective Method for the

Deprotection of Tert-butyldimethylsilyl (TBDMS) ethers Using Iron(III) tosylate as a Catalyst. *Tetrahedron Lett.* **2010**, *51*, 1056–1058. DOI: 10.1016/j.tetlet.2009.12.076.

- [14] Calderón, D. G.; Puebla, L. J. B.; González, C. A. G.; Hernández, S. A.; Benítez, A. F.; Yáñez, E. C.; Becerril, D. C.; Romero, C. G. Selective Deprotection of TBDMS Alkyl Ethers in the Presence of TIPS or TBDPS Phenyl Ethers by Catalytic CuSO4·5H2O in Methanol. *Tetrahedron Lett.* 2013, 54, 5130–5132. DOI: 10.1016/j.tetlet.2013.07.074.
- [15] Bajwa, J. S.; Vivelo, J.; Slade, J.; Repic, O.; Blacklock, T. Selective Deprotection of Alkyl t-butyldimethylsilyl Ethers in the Presence of Aryl t-butyldimethylsilyl Ethers with Bismuth Bromide. *Tetrahedron Lett.* 2000, *41*, 6021–6024. DOI: 10.1016/ S0040-4039(00)01012-1.
- [16] Jadhav, A. H.; Chinnappan, A.; Patil, R. H.; Chung, E.-J.; Kim, H. Deprotection of Tert-butyldimethylsilyl (TBDMS) ethers Using Efficient and Recyclable Heterogeneous Silver Salt of Silicotungstic Acid Catalyst under Mild Reaction Condition. *Chem. Eng. J.* 2014, 236, 300–305. DOI: 10.1016/ j.cej.2013.09.011.
- [17] Hunter, R.; Hinz, W.; Richards, P. On the Chemoselectivity and Mechanism of Desilylation of Tert-butyldimethylsilyl Ethers with TMSOTf. *Tetrahedron Lett.* **1999**, *40*, 3643–3646. DOI: 10.1016/S0040-4039(99)00523-7.
- [18] Yadav, J. S.; Reddy, B. V. S.; Madan, C. A Mild and Selective Cleavage of Tert-butyldimethylsilyl Ethers by Indium(III) Chloride. New J. Chem. 2000, 24, 853–854. DOI: 10.1039/ b004937i.
- [19] Yang, Y. Y.; Yang, W. B.; Teo, C. F.; Lin, C. H. Regioselective Deprotection of Tert-butyldimethylsilyl Ethers by Boron Trichloride. *Synlett.* 2000, 2000, 1634–1636. DOI: 10.1055/s-2000-7942.
- [20] Khan, A. T.; Ghosh, S.; Choudhury, L. H. A Simple and Useful Synthetic Protocol for Selective Deprotection of Tert-butyldimethylsilyl (TBS) Esters. *Eur. J. Org. Chem.* 2004, 2004, 2198–2204. DOI: 10.1002/ejoc.200400031.
- [21] Zhu, J. R.; Xue, J. J.; Li, W. Z.; Chen, X. S.; Li, Y. Selective Cleavage of Phenolic Tert-butyldimethylsilyl Ethers Using Simple Organic Nitrogen Bases. *Chin. Chem. Lett.* 2010, 21, 273–276. DOI: 10.1016/j.cclet.2009.11.049.
- [22] Farras, J.; Serra, C.; Vilarrasa, J. Cleavage of Tert-butyldimethylsilyl Ethers by Chloride Ion. *Tetrahedron Lett.* **1998**, *39*, 327–330. DOI: 10.1016/S0040-4039(97)10479-8.
- [23] Hattori, K.; Sajiki, H.; Hirota, K. Undesirable Deprotection of O-TBDMS Groups by Pd/C-catalyzed Hydrogenation and Chemoselective Hydrogenation Using a Pd/C(en) Catalyst. *Tetrahedron* 2001, 57, 2109–2114. DOI: 10.1016/S0040-4020(01)00060-6.
- [24] Sharma, G. V. M.; Srinivas, B.; Krishna, P. R. A Facile Zirconium(IV) chloride Catalysed Selective Deprotection of tbutyldimethylsilyl (TBDMS) Ethers. *Tetrahedron Lett.* 2003, 44, 4689–4691. DOI: 10.1016/S0040-4039(03)01088-8.
- [25] Lipshutz, B. H.; Keith, J. Selective Deprotection of Alkyl vs. aryl Silyl Ethers. *Tetrahedron Lett.* **1998**, *39*, 2495–2498. DOI: 10.1016/S0040-4039(98)00381-5.
- [26] Das, B.; Reddy, K. R.; Thirupathi, P. A Simple, efficient and Highly Selective Deprotection of t-butyldimethylsilyl (TBDMS) ethers Using Silica Supported Sodium Hydrogen Sulfate as a Heterogeneous Catalyst. *Tetrahedron Lett.* 2006, 47, 5855–5857. DOI: 10.1016/j.tetlet.2006.06.088.
- [27] Scheidt, K. A.; Chen, H.; Follows, B. C.; Chemler, S. R.; Coffey, D. S.; Roush, W. R. Tris(dimethylamino)sulfonium Difluorotrimethylsilicate, A Mild Reagent for the Removal of Silicon Protecting Groups. J. Org. Chem. 1998, 63, 6436–6737. DOI: 10.1021/jo981215i.
- [28] Jadhav, A. H.; Kim, H. A Mild, efficient, and Selective Deprotection of Tert-butyldimethylsilyl (TBDMS) ethers Using Dicationic Ionic Liquid as a Catalyst. *Tetrahedron Lett.* 2012, 53, 5338–5342. DOI: 10.1016/j.tetlet.2012.07.108.

- [29] Gopinath, R.; Patel, B. K. Tetrabutylammonium Tribromide (TBATB)-meOH: An Efficient Chemoselective Reagent for the Cleavage of Tert-bButyldimethylsilyl (TBDMS) Ethers. Org. Lett. 2000, 2, 4177-4180. DOI: 10.1021/ol006720s.
- [30] Karimi, B.; Zareyee, D. A High Loading Sulfonic Acid-functionalized Ordered Nanoporous Silica as an Efficient and Recyclable Catalyst for Chemoselective Deprotection of Tert-butyldimethylsilyl Ethers. *Tetrahedron Lett.* 2005, 46, 4661–4665. DOI: 10.1016/j.tetlet.2005.04.100.
- [31] Karimi, B.; Zamani, A.; Zareyee, D. N-Iodosuccinimide (NIS) as a Mild and Highly Chemoselective Catalyst for Deprotection of Tert-butyldimethylsilyl Ethers. *Tetrahedron Lett.* 2004, 45, 9139–9141. DOI: 10.1016/j.tetlet.2004.09.157.
- [32] Shah, S. T. A.; Singh, S.; Guiry, P. J. A Novel, chemoselective and Efficient Microwave-assisted Deprotection of Silyl Ethers with Selectfluor. J. Org. Chem. 2009, 74, 2179–2182. DOI: 10.1021/jo802494t.
- [33] Bhure, M. H.; Kumar, I.; Natu, A. D.; Rode, C. V. Facile and Highly Selective Deprotection of Tert-butyldimethylsilyl Ethers Using Sulfated SnO₂ as a Solid Catalyst. *Synth. Commun.* 2008, 38, 346–353. DOI: 10.1080/00397910701767056.
- [34] Olah, G. A.; Pradeep, S. I.; Prakash, G. K. S. Perfluorinated Resinsulfonic Acid (nafion-H®) Catalysis in Synthesis. *Synthesis* 1986, 1986, 513–531. DOI: 10.1055/s-1986-31692.
- [35] Corma, A. Inorganic Solid Acids and Their Use in Acid-catalyzed Hydrocarbon Reactions. *Chem. Rev.* 1995, 95, 559–614. DOI: 10.1021/cr00035a006.
- [36] Herron, N.; Farneth, W. E. The Design and Synthesis of Heterogeneous Catalyst Systems. Adv. Mater. 1996, 8, 959–968. DOI: 10.1002/adma.19960081203.
- [37] Horsley, J. A. Producing Bulk and Fine Chemicals Using Solid Acids. CHEMTECH 1997, 27, 45–49.
- [38] Corma, A.; Garcia, H. Organic Reactions Catalyzed over Solid Acids. *Catal. Today* **1997**, *38*, 257–308. DOI: 10.1016/S0920-5861(97)81500-1.
- [39] Tanabe, K.; Holderich, W. F. Industrial Application of Solid Acid-base Catalysts. *Appl. Catal. A.* 1999, 181, 399–434. DOI: 10.1016/S0926-860X(98)00397-4.
- [40] Sheldon, R. A.; Van Bekkum, H. Fine Chemicals through Heterogeneous Catalysis. Wiley-VCH, Weinheim, 2001.
- [41] Li, Q.; Meng, F.; Zhang, B.; Tian, M.; Lian, J. Mesomorphic Phases of Main-chain Liquid-crystalline Polymers with Pendent Sulfonic Acid Groups. J. Appl. Polym. Sci. 2008, 110, 791–797. DOI: 10.1002/app.28542.
- [42] Caetano, C. S.; Guerreiro, L.; Fonseca, I. M.; Ramos, A. M.; Vital, J.; Castanheiro, J. E. Esterification of Fatty Acids to Biodiesel over Polymers with Sulfonic Acid Groups. *Appl. Catal. A: Gen.* 2009, 359, 41–46. DOI: 10.1016/ j.apcata.2009.02.028.
- [43] Fukuhara, K.; Nakajima, K.; Kitano, M.; Kato, H.; Hayashi, S.; Hara, M. Structure and Catalysis of Cellulose-Derived Amorphous Carbon Bearing SO₃H Groups. *ChemSusChem.* 2011, 4, 778–784. DOI: 10.1002/cssc.201000431.
- [44] Zareyee, D.; Serehneh, M. Recyclable CMK-5 Supported Sulfonic Acid as an Environmentally Benign Catalyst for Solvent-free One-pot Construction of Coumarin through Pechmann Condensation. J. Mol. Catal. A: Chem. 2014, 391, 88–91. DOI: 10.1016/j.molcata.2014.04.013.
- [45] Toda, M.; Takagaki, A.; Okamura, M.; Kondo, J. N.; Hayashi, S.; Domen, K.; Hara, M. Biodiesel Made with Sugar Catalyst. *Nature* 2005, 438, 178-178. DOI: 10.1038/438178a.
- [46] Zareyee, D.; Ghandali, M. S.; Khalilzadeh, M. A. Sulfonated Ordered Nanoporous Carbon (CMK-5-SO₃H) as an Efficient and Highly Recyclable Catalyst for the Silylation of Alcohols and Phenols with Hexamethyldisilazane (HMDS). *Catal. Lett.* 2011, 141, 1521–1525. DOI: 10.1007/s10562-011-0621-3.
- [47] Suganuma, S.; Nakajima, K.; Kitano, M.; Yamaguchi, D.; Kato, H.; Hayashi, S.; Hara, M. Hydrolysis of Cellulose by

Amorphous Carbon Bearing SO₃H, COOH, and OH Groups. *J. Am. Chem. Soc.* **2009**, *131*, 12787–12793. DOI: 10.1021/ ja803983h.

- [48] Zareyee, D.; Moosavi, S. M.; Alaminezhad, A. Chemoselective Synthesis of Geminal Diacetates (acylals) using Eco-friendly Reusable Propylsulfonic Acid Based Nanosilica (SBA-15-Ph-PrSO₃H) under Solvent-Free. J. Mol. Catal. A: Chem. 2013, 378, 227–231. DOI: 10.1016/j.molcata.2013.07.001.
- [49] Margolese, D.; Melero, J. A.; Christiansen, S. C.; Chmelka, B. F.; Stucky, G. D. Direct Syntheses of Ordered SBA-15 Mesoporous Silica Containing Sulfonic Acid Groups. *Chem. Mater.* 2000, 12, 2448–2459. DOI: 10.1021/cm0010304.
- [50] Karimi, B.; Zareyee, D. Solvent-free Three Component Strecker Reaction of Ketones Using Highly Recyclable and Hydrophobic Sulfonic Acid Based Nanoreactors. J. Mater. Chem. 2009, 19, 8665–8670. DOI: 10.1039/b911388f.
- [51] Karimi, B.; Zareyee, D. Design of a Highly Efficient and Watertolerant Sulfonic Acid Nanoreactor Based on Tunable Ordered Porous Silica for the Von Pechmann Reaction. Org. Lett. 2008, 10, 3989–3992. DOI: 10.1021/ol8013107.
- [52] Gu, Y.; Karam, A.; Jerome, F.; Barrault, J. Selectivity Enhancement of Silica-supported Sulfonic Acid Catalysts in Water by Coating of Ionic Liquid. Org. Lett. 2007, 9, 3145–3148. DOI: 10.1021/ol071356j.
- [53] Schätz, A.; Reiser, O.; Stark, W. J. Nanoparticles as Semi-heterogeneous Catalyst Supports. *Chem. Eur. J.* 2010, 16, 8950–8967. DOI: 10.1002/chem.200903462.
- [54] Lee, J.; Lee, Y.; Youn, J. K.; Na, H. B.; Yu, T.; Kim, H.; Lee, S. M.; Koo, Y. M.; Kwak, J. H.; Park, H. G.; et al. Simple Synthesis of Functionalized Superparamagnetic Magnetite/silica Core/shell Nanoparticles and Their Application as Magnetically Separable High-performance Biocatalysts. *Small* 2008, 4, 143–152. DOI: 0.1002/smll.200700456. DOI: 10.1002/ smll.200700456.
- [55] Lu, A.; Salabas, E. L.; Schuth, F. Magnetic Nanoparticles: synthesis, protection, functionalization, and Application. *Angew. Chem. Int. Ed.* 2007, 46, 1222–1224. DOI: 10.1002/ anie.200602866.
- [56] Wang, D.; Astruc, D. Fast-growing Field of Magnetically Recyclable Nanocatalysts. *Chem. Rev.* 2014, 114, 6949–3985. DOI: 10.1021/cr500134h.
- [57] Karimi, B.; Mansouri, F.; Mirzaei, H. M. Recent Applications of Magnetically Recoverable Nanocatalysts in C-C and C-X Coupling Reactions. *ChemCatChem.* 2015, 7, 1736–1789. DOI: 10.1002/cctc.201403057.
- [58] Khazaei, A.; Sarmasti, N.; Yousefi Seyf, J. Anchoring High Density Sulfonic Acid Based Ionic Liquid on the Magnetic Nano-magnetite (Fe₃O₄), Application to the Synthesis of Hexahydroquinoline Derivatives. J. Mol. Liq. 2018, 262, 484–494. DOI: 10.1016/j.molliq.2018.04.125.
- [59] Nemati, F.; Heravi, M. M.; Saeedi Rad, R. Nano-Fe₃O₄ Encapsulated-silica Particles Bearing Sulfonic Acid Groups as a Magnetically Separable Catalyst for Highly Efficient Knoevenagel Condensation and Michael Addition Reactions of Aromatic Aldehydes with 1,3-cyclic Diketones. *Chin. J. Catal.* 2012, 33, 1825–1831. DOI: 10.1016/S1872-2067(11)60455-5.
- [60] Kabiri Esfahani, F.; Zareyee, D.; Yousefi, R. Sulfonated Coreshell Magnetic Nanoparticle (Fe3O4@SiO2@PrSO3H) as a Highly Active and Durable Protonic Acid Catalyst; synthesis of Coumarin Derivatives through Pechmann Reaction. ChemCatChem. 2014, 6, 3333-3337. DOI: 10.1002/ cctc.201402547.
- [61] Kabiri Esfahani, F.; Zareyee, D.; Shokuhi Rad, A.; Taher, -.; Bahrami, S. Sulfonic Acid Supported on Magnetic Nanoparticle as an Eco-friendly, durable and Robust Catalyst for the Synthesis of β -Amino Carbonyl Compounds through Solvent Free Mannich Reaction. *Appl. Organometal. Chem.* **2017**, *31*, e3865. DOI: 10.1002/aoc.3865.