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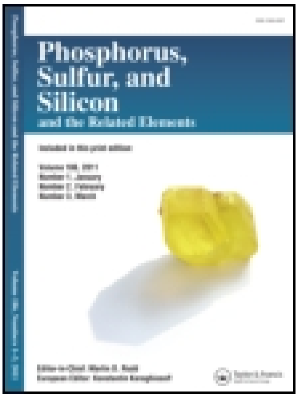

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Rice Husk Ash: A New, Cheap, Efficient, and Reusable Reagent for the Protection of Alcohols, Phenols, Amines, and Thiols

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RICE HUSK ASH: A NEW, CHEAP, EFFICIENT, AND REUSABLE REAGENT FOR THE PROTECTION OF ALCOHOLS, PHENOLS, AMINES, AND THIOLS

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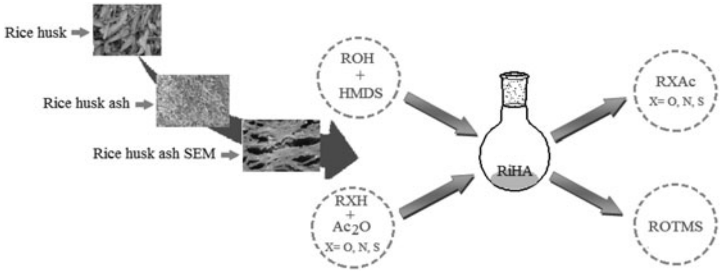
GRAPHICAL ABSTRACT



Abstract *A mild, efficient, and eco-friendly protocol for the protection of alcohols and phenols as trimethylsilyl ethers has been developed using rice husk ash as a reagent. This reagent is also able to catalyze the acetylation of alcohols, phenols, thiols, and amines with acetic anhydride. All reactions were performed under mild conditions in good to high yields.*

[Supplementary materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements *for the following free supplemental files: Additional text, tables, and figures.]*

Keywords Rice husk ash (RiHA); heterogenous reagent; trimethylsilylation; acetylation; protection; mild reaction conditions

INTRODUCTION

Protection and deprotection of organic functions are important processes during multistep organic synthesis.[1,2] The choice of a method that is used for the functional group transformations depends on its simplicity, high yields of the desired products, short reaction times, low cost of the process, and ease of the work-up procedures.

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Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gpss.

Trimethylsilylation of organic compounds having labile hydrogen atoms is an important organic transformation.[1,3] This protection method is frequently used in multistep synthesis of natural products due to the enhanced stability of the silyl derivatives under a variety of conditions, their solubility in nonpolar solvents, and the thermal stability and ease of the removal of the silyl groups. Silylation is also extensively used for the derivatization of hydroxy compounds in order to increase their volatility for gas chromatography (GC) and mass spectrometry.[4] A wide variety of methods using silylating agents, such as chlorotrimethylsilane and a base,[5] bis-(trimethylsilyl)trifluoro acetamide,[6] allylsilanes together with an acid,[7] and bistrimethylsilyl ether,[8] have been reported for this purpose. However, these reagents require the addition of bases, and the difficulty in removing the ammonium salts is frequently encountered. A longer reaction time is an additional disadvantage of these reagents.

Hexamethyldisilazane (HMDS) is one of the most widely used reagents for this purpose. Although, its handling does not require special precautions and the work-up is not time consuming, the low silylation power of HMDS is the main drawback to its application, which needs forceful conditions and long reaction times.

Among the many protecting groups for alcohols, phenols, amines, and thiols, acetate is used with high frequency. The acetylation is typically performed using acetic anhydride in the presence of either basic[9–12] or acidic catalysts.[13–18] Although various acetylation methods are available, most have one or more drawbacks including long reaction times, harsh conditions, harmful organic solvents, and tedious work-up procedures. One of the most promising solutions to these problems seems to use green and insoluble catalysts or using eco-friendly solvent-free conditions. When an insoluble catalyst is used, it can be separated easily by filtration and recycled. Also, solvent-free synthetic methods are valuable for environmental and economical reasons.[19–21]

The major goals of "Green chemistry" are to increase process selectivity, maximize the use of starting materials, and to replace hazardous and stoichiometric reagents with eco-friendly reagents in order to facilitate easy separation of the final reaction mixture, including recovery of the promotor.

The rice husk ash (RiHA), as a product of combustion of rice husk, is considered to be the most economical source of silica.[22] As we know, over the years, silica powders and gels have been widely used in industry as fillers, adsorbents, chromatographic agents, catalyst, and as catalytic supports. Several researchers have utilized RiHA to prepare zeolites and mesoporous silica.[23] Some utilize RiHA as an adsorbent to adsorb metal ions such as Cd^{2+}, Zn^{2+}, and Ni^{2+}, and heavy metals such as lead and mercury from aqueous solution.[24] Some organic matters, such as Congo red, vacuum pump oil, palmytic acid, Indigo Carmine dye, Brilliant Green dye and so on, can also be adsorbed by RiHA.[25,26] However, the final disposal of the RiHA after adsorption has not been reported.

RESULTS AND DISCUSSION

Very recently, we have reported the applicability of rice husk in the promotion of the silylation of hydroxyl groups, *N*-boc protection of amines, acetylation of hydroxyl groups, amines, and thiols,[27a] and synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[α] xanthen-11-one and quinoxaline derivatives.[27b] In continuation of these studies, we were interested to investigate the applicability of RiHA, as a source of amorphous silica,[28] in the promotion of the protection of alcohols, phenols, amines, and thiols.

Initially, we studied the standardization of the silylation reaction conditions with investigating the effect of different molar ratio of reactants and different solvents (CH_2Cl_2, *n*-hexane, acetone, $CHCl_3$, Et_2O, CCl_4, H_2O, and CH_3CN) on the reaction in terms of time and product yield. Our investigations clarified that the best results can be obtained under the conditions shown in Scheme 1.

$$\mathrm{ROH} \xrightarrow[\mathrm{CH_3CN,\ r.t.}]{\mathrm{HMDS\ (0.75\ mmol),\ RiHA\ (0.02\ g)}} \mathrm{ROSiMe_3}$$

Scheme 1

After optimization of the reaction conditions, different types of alcohols were subjected to trimethylsilylation using this method (Table 1). Trimethylsilylation of benzylic alcohols including different types of substituents proceeded efficiently with high isolated yields (Table 1, entries 1–16). Primary and less hindered secondary aliphatic alcohols were also successfully converted to the corresponding silyl ethers in almost quantitative yields at room temperature (Table 1, entries 17–21). This method was also found to be useful for trimethylsilylation of allylic alcohols, diols, and acyloins (Table 1, entries 22 and 23). No elimination and rearrangement byproducts were observed at all. Phenols also undergo silylation easily using this method, and their corresponding silyl ethers can be isolated in good to high yields (Table 1, entries 24–33).

As shown in Table 1, more hindered secondary and tertiary alcohols, amines, and thiols are resistant to RiHA and remain intact in the reaction mixture (Table 1, entries 34–43). Therefore, this methodology shows selectivity, and is suitable for the selective trimethylsilylation of benzylic and primary and less hindered secondary aliphatic alcohols and phenols in the presence of the above-mentioned substrates (Table 1, entries 44–46).

To illustrate the efficiency of the proposed method, Table 2 compares our results obtained from the silylation of benzyl alcohol with HMDS catalyzed by RiHA with other results reported in the literature. This comparison clarifies that all the catalysts require more reaction times than RiHA. In addition, as it can be seen alumina-supported $H_2PMo_{11}VCuO_{40}$ and RiH are able to catalyze this type of reactions, but in higher amounts than there are in RiHA. As reported in the literature, 0.1 g of alumina-supported $H_2PMo_{11}VCuO_{40}$ and 0.08 g of RiH are needed for the promotion of the silylation of hydroxyl functional groups (Table 2, entries 3 and 6). On the other hand catalysts such as H-β zeolite and alumina-supported $H_2PMo_{11}VCuO_{40}$ need higher reaction times (Table 2, entries 1 and 3) and catalysts such as H-β zeolite, phenyltrimethylammonium tribromide, alumina-supported $H_2PMo_{11}VCuO_{40}$, and nanoporous solid silica sulfonic acid need toxic solvents such as toluene and CH_2Cl_2 (Table 2, entries 1– 4).

After the above-mentioned reactions, we have tried to extend the applicability of RiHA in organic transformations by studying the role of this reagent in the promotion of the acetylation reactions. Our investigations clarified that RiHA is also efficiently able to catalyze the acetyl protection of alcohols, phenols, thiols, and amines with Ac_2O. All reactions are performed under mild reaction conditions in good to high yields (Scheme 2, Table 3).

Using this method, different types of benzylic (including a variety of substituents) and primary, secondary, and tertiary aliphatic alcohols and phenols were converted to their corresponding acetates in quantitative yields (Table 3, entries 1–22). This method is also very useful for the effective acetylation of amines and thiols (Table 3, entries 23–33). No elimination and rearrangement byproducts were observed at all.

Table 1 Trimethylsilylation of alcohols and phenols catalyzed by RiHA[a,b]

Entry	Product	Time (min)	Yield (%)	Ref.
1	$PhCH_2OSiMe_3$	3	90	29
2	$2\text{-}ClC_6H_4CH_2OSiMe_3$	10	80	30
3	$4\text{-}ClC_6H_4CH_2\ OSiMe_3$	5	84	30
4	$3,4\text{-}Cl_2C_6H_3CH_2OSiMe_3$	8	82	31
5	$4\text{-}BrC_6H_4CH_2OSiMe_3$	12	89	32
6	$2\text{-}BrC_6H_4CH_2OSiMe_3$	13	87	33
7	$2\text{-}NO_2C_6H_4CH_2OSiMe_3$	23	84	34
8	$4\text{-}NO_2C_6H_4CH_2OSiMe_3$	15	83	30
9	$2\text{-}MeC_6H_4CH_2OSiMe_3$	21	82	33
10	$4\text{-}Me_2CHC_6H_4CH_2OSiMe_3$	5	85	35
11	$3\text{-}MeOC_6H_4CH_2OSiMe_3$	8	82	31
12	$4\text{-}MeOC_6H_4CH_2OSiMe_3$	18	89	36
13	2,3-Dihydro-1*H*-inden-1-$OSiMe_3$	7	83	31
14	9*H*-fluoren-9-$OSiMe_3$	10	88	31
15	1-Phenylpropan-1-$OSiMe_3$	10	84	37
16	$(Ph)_2CHOSiMe_3$	25	80	29
17	$PhCH_2CH_2OSiMe_3$	11	81	38
18	$PhCH(Me)CH_2OSiMe_3$	5	82	33
19	$PhCH_2NHCH_2CH_2OSiMe_3$	12	80	39
20	Cyclohexan$OSiMe_3$	9	82	29
21	2-Isopropyl-5-methylcyclohexan-$OSiMe_3$	30	81	29
22	$PhCH = CHCH_2OSiMe_3$	8	83	37
23	$Ph(CO)CH(OSiMe_3)Ph$	17	70	38
24	$PhOSiMe_3$	13	86	29
25	Naphthalen-2-$OSiMe_3$	4	90	40
26	Naphthalen-1-$OSiMe_3$	6	83	29
27	$2,4\text{-}Me_2C_6H_3OSiMe_3$	7	87	37
28	$3,5\text{-}Me_2C_6H_3OSiMe_3$	4	91	41
29	$4\text{-}Me_2CHC_6H_4OSiMe_3$	5	90	42
30	$2\text{-}PhC_6H_4OSiMe_3$	17	89	40
31	2-Vinyl$C_6H_4OSiMe_3$	11	81	40
32	$C_6H_{4\text{-}}1,4\text{-}(OSiMe_3)_2$	3	80[c]	43
33	$2\text{-}MeO\text{-}4\text{-}MeC_6H_3OSiMe_3$	12	82	36
34	1,7,7-Trimethylbicyclo[2.2.1]heptan-2-$OSiMe_3$	120	0[d]	—
35	Adamantan-2-$OSiMe_3$	120	0[d]	—
36	Adamantan-1-$OSiMe_3$	180	0[d]	—
37	$PhCH_2NHSiMe_3$	120	0[d]	—
38	$PhNHSiMe_3$	150	0[d]	—
39	$PhN(SiMe_3)Me$	120	0[d]	—
40	Cyclohexan-$NHSiMe_3$	120	0[d]	—
41	$PhSSiMe_3$	120	0[d]	—
42	Naphthalen-2-$SSiMe_3$	120	0[d]	—
43	2-((trimethylsilyl)sulfanyl)benzo[*d*]$SSiMe_3$	120	0[d]	—
44	$PhCH_2OSiMe_3$ + Adamantan-1-$OSiMe_3$	4	100[d] + 0[d]	—
45	$PhCH_2CH_2OSiMe_3$ + $PhN(SiMe_3)Me$	12	100[d] + 0[d]	—
46	$4\text{-}ClC_6H_4CH_2OSiMe_3$ + $PhSSiMe_3$	10	100[d] + 0[d]	—

[a] Products were identified spectroscopically, comparison with authentic samples and also by the conversion of the products to their starting materials.

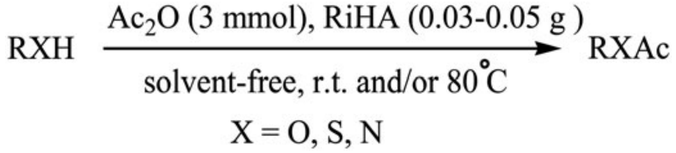
[b] Isolated yield.

[c] 0.04 g of RiHA was used.

[d] Identified by TLC or GC.

Table 2 Comparison of some of the results obtained by the silylation of benzyl alcohol with HMDS in the presence of RiHA, with some of other reported catalysts

Entry	Catalyst	Conditions	Time (min)	Yield (%)	Ref.
1	H-β zeolite (10% w/w)	Toluene, 80°C	300	95	44a
2	Phenyltrimethylammonium tribromide (0.05 mmol)	CH_2Cl_2, r. t.	30	91	36
3	Alumina-supported $H_2PMo_{11}VCuO_{40}$ (0.1 g)	Toluene, 85°C	60	95	44b
4	Nanoporous solid silica sulfonic acid (2 mol%)	CH_2Cl_2, r. t.	80	100	34
5	Al_2O_3-SO_3H (0.025 g, 0.075 mmol of H^+)	Solvent-free, r. t.	2	98	44c
6	RiH (0.08 g)	CH_3CN, r. t.	5	94	27a
7	RiHA (0.02 g)	CH_3CN, r. t.	3	90	This work



Scheme 2

In order to show the merit of the catalyst, Table 4 compares our results obtained from the acetylation of benzyl alcohol with acetic anhydride catalyzed by RiHA with some other results reported in the literature. This comparison clarifies that all the catalysts require more reaction times than RiHA. In addition, some of these catalysts ($FePO_4$ and [bis(2-hydroxyanil) acetylacetonato]manganese (III) chloride) need higher reaction times (Table 4, entries 1 and 2) and some of them ([Bis(2-hydroxyanil) acetylacetonato]manganese (III) chloride) need harsh solvents such as CH_3NO_2 (Table 4, entry 2).

It is very important to note that although Ai-, Si-, and Fe-based reagents are able to catalyze the above-mentioned reactions (Table 2, entries 1, 3–6 and Table 4, entries 1, 4–7), yet the amounts of the catalysts are higher than the available amounts of Fe, Al, and Si in RiHA. So, we can say that the observed efficiency of RiHA may be due to the synergistic effect between the components of this reagent and this is under further consideration in our laboratory.

From the context of green approach, the reusability of the reagent was tested in the silylation and acetylation of 4-chlorobenzyl alcohol. After completion of the reaction, the reagent was washed well with acetonitrile, acetone, and water, then dried at 100°C prior to used and tested for its activity in subsequent run and fresh reagent was not added. It was seen that the reagent displayed very good reusability (Figure 1).

In conclusion, we have developed a mild efficient and high yielding method for the *O*-silyl protection of alcohols and phenols, and acetylation of alcohols, phenols, thiols, and amines, using RiHA as the promotor. In contrast to some existing methods using potentially hazardous reagents/additives, this new method offers the following advantages: (i) low cost, availability and reusability of the reagent, (ii) avoids the use of any base, metal, or Lewis acid catalysts, (iii) relatively short reaction times, (iv) easy and clean work-up, (v) high yields, and (vi) no side reactions. We are exploring further applications of RiHA for the other types of organic reactions in our laboratory.

Table 3 Acetylation of alcohols, phenols, thiols[a], and amines[b] in the presence of RiH[c]

Entry	Product	Time (min)	Yield (%)[d]	Ref.
1	$PhCH_2OAc$	15	91	45
2	4-$ClC_6H_4CH_2OAc$	14	93	18
3	4-$BrC_6H_4CH_2OAc$	20	90	46
4	2-$BrC_6H_4CH_2OAc$	20	93	47
5	4-$Me_2CHC_6H_4CH_2OAc$	30	94	13
6	(Anthracen-10-yl)methan-OAc	40	94	48
7	$(Ph)_2CHOAc$	100	92	46
8	PhCH(Me)OAc	45	91	18
9	CyclopentylOAc	30	90	49
10	2-Isopropyl-5-methylcyclohexan-OAc	60	93	46
11	$PhCH(OAc)CH_2OAc$	50	90[e]	47
12	Ph(CO)CH(OAc)Ph	180	80	18
13	1,7,7-Trimethylbicyclo[2.2.1]heptan-2-OAc	35	89	50
14	Adamantan-2-OAc	45	90	47
15	Adamantan-1-OAc	120	89	51
16	PhOAc	5	96	52
17	Naphthalen-2-OAc	8	96	45
18	Naphthalen-1-OAc	15	94	18
19	2,4-$Me_2C_6H_3OAc$	12	97	17
20	4-$Me_2CHC_6H_4OAc$	15	95	46
21	2-PhC_6H_4OAc	75	93	52
22	C_6H_4–1,4-$(OAc)_2$	10	92[e]	18
23	$PhCH_2SAc$	8	90	53
24	4-BrPhSAc	10	92	16
25	4-MePhSAc	8	91	45
26	Naphthalen-2-SAc	20	90	15
27	$PhCH_2NHAc$	<1	97	50
28	PhNHAc	<1	96	54
29	4-BrPhNHAc	<1	96	49
30	4-$NO_2PhNHAc$	15	92	54
31	3-MeOPhNHAc	10	96	14
32	Naphthalen-1-NHAc	<1	98	49
33	$(Ph)_2NAc$	40	91	49

[a] Alcohols, phenols, and thiols are acetylated at 80°C.

[b] Amines are acetylated at room temperature.

[c] Products were identified spectroscopically, comparison with authentic samples and also by the conversion of the products to their starting materials.

[d] Isolated yield.

[e] 0.1 g of RiHA was used.

EXPERIMENTAL

General

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. All yields refer to the isolated products. Products were characterized by their physical constants and comparison with authentic samples. The purity determination of the substrate and reaction monitoring were accompanied by thin layer chromatography (TLC) on silica-gel polygram SILG-UV 254 plates.

Table 4 Comparison of some of the results obtained by the acetylation of benzyl alcohol in the presence of RiHA, with some of the reported catalysts

Entry	Catalyst	Ac_2O (mmol)	Conditions	Time (h)	Yield (%)	Ref.
1	$FePO_4$ (0.05 mmol)	2.5	Solvent-free, r.t.	10	92	55a
2	[Bis(2-hydroxyanil) acetylacetonato]manganese (III) chloride (0.01 mmol)	2	CH_3NO_2, r.t.	5	97	55b
3	$Bi(TFA)_3$ (0.05 mmol)	1.5	CH_3CN, r. t.	1	96	55c
4	$HClO_4$–SiO_2 (1 mol%)	1.5	Solvent-free, r. t.	1	96	55d
5	Zeolite H-FER (0.015 g)	1.5	Solvent-free, 75°C	1.5	99	55e
6	HBF_4–SiO_2 (1 mol%)	1	Solvent-free, r.t.	1	94	55f
7	Alumina-supported MoO_3 (1 mol%)	2	Solvent-free, r.t.	0.33	99	55g
8	RiH (0.3 g)	3	Solvent-free, 80°C	1	94	27a
9	RiHA (0.05 g)	3	Solvent-free, 80°C	0.25	93	This work

Instrumentation

The IR spectra were run on a Perkin-Elmer bio-spectrometer (PerkinElmer, USA) and Bruker Vector 22 (Bruker, Germany). The 1H NMR (400 MHz) and 13C NMR (100 MHz) were run on a Bruker AVANCEIII-400 spectrometer (Bruker, Germany) in CDCl3 using tetramethylsilane (TMS) as an internal reference (δ in ppm). Microanalyses were performed on a Perkin-Elmer 240-B microanalyzer (PerkinElmer, USA). Melting points were recorded on a Büchi B-545 (Büchi Corporation, USA) apparatus in open capillary tubes. The characterization of rice husk was obtained using scanning electron microscopy (SEM-Philips XL30, FEI Company, North America) with field emission gun and energy dispersive spectroscopy (EDS). Prior to placing into the microscope, the rice husk particles were coated with gold under vacuum (SCD 005 sputter coater, Bal-Tec, Swiss) and examined at an acceleration voltage of 17 KV. X-ray diffrac- tometry (XRD) diagrams of the samples were

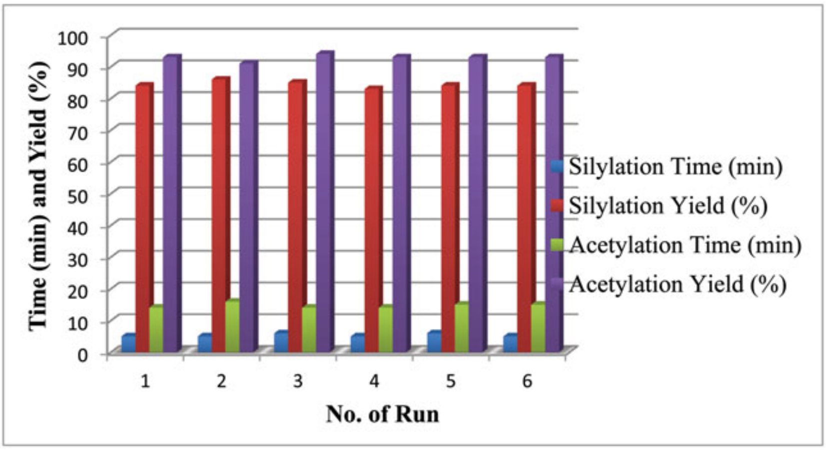


Figure 1 Reusability of RiHA in the silylation and acetylation of 4-chlorobenylalcohol (Table 1, entry 3 and Table 3, entry 2). Horizontal axes is the reusability times of the reagent and vertical axes is the time of the reaction and the yield of the product.

obtained with a diffractometer Model XRD 6000, PHILIPS Xpert pro (PANalytical formerly known as Philips Analytical Company, North America). The chemical composition of RHA was analyzed using X-ray Fluorescence (XRF) spectrometer (Model Magix Pro. Philips (PANalytical formerly known as Philips Analytical Company, North America)). Selected characterization data for the RiHA is located in the supplemental materials (Figures S1–S3 and Table S1).

Preparation of Rice Husk (RiH) and Determination of Its Components

Rice sample (named as Hassani) was obtained from Rasht (Guilan Province) in the north of Iran. Rice husk was obtained from a local mill, washed several times with distilled water to remove any adhering materials, and dried at room temperature for 48 h. The dried RiH was smashed and sieved (80–170 mesh size). Then the reagent was washed with distilled water and dried at 110°C for 4 h. The main components of the rice husk sample were determined as follows, using the reported methods in the literature[56,57]: silica (14.2%), cellulose (27.4%), hemicelluloses (18.3%), lignin (25.8%), inorganic residue (5.8%), soluble (3.5%), and moisture (5%).

Preparation of Rice Husk Ash (RiHA) and Determination of Its Components

RiHA was produced in combustion of rice husk (RiH). Since the open-field burning causes air pollution and creates a disposal problem for the large quantity of rice hull ash produced, direct soil incorporation of hulls has also been investigated. So we used a technology that has been reported in the literature.[58] The characteristics of the ash depend on the components, temperature, and time of burning. During the burning process, the carbon content is burnt off and all that remains is the silica content. The silica must be kept at a noncrystalline state in order to produce an ash with high catalytic activity. It was tested and found that the ideal temperature for producing such results is between 600°C and 700°C. If the rice husk was burnt at too high temperature or for too long period of time, the silica content will be obtained at crystalline structure. On the other hand, if the rice husk was burnt at too low temperature or for a short period of time, the RiHA will contain large amount of unburnt carbon.[59,60] The main components of RiHA sample were determined using the reported methods in the literature[46]: The RiHA contains over 80% silica by mass with a small proportion of metallic elements.

Trimethylsilylation of Alcohols and Phenols; General Procedure

To a stirring mixture of the substrate (1 mmol) and RiHA (0.08 g) in CH_3CN (3 mL), HMDS (0.75 mmol, 0.120 g) was added at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and the residue was washed with acetonitrile (5 mL). Evaporation of the solvent gave almost pure product(s). Further purification was carried out by bulb-to-bulb distillation under reduced pressure or recrystallization to afford pure silyl ether(s).

Acetylation of Alcohols, Phenols, Thiols, and Amines; General Procedure

A mixture of the substrate (1 mmol), acetic anhydride (3 mmol), and RiHA (0.3 g) was stirred at room temperature and/or 80°C. After completion of the reaction (TLC), the reaction mixture was triturated with EtOAc (15 mL) and the reagent was filtered. The organic layer was washed with saturated $NaHCO_3$ and water (3×15 mL), and dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure gave the requested products in good to high yields.

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