Synthesis of phenols by using aryldiazonium silica sulfate nanocomposites

Amin Zarei, Leila Khazdooz, Hamidreza Aghaei, Mohammad Mehdi Gheisari, Shahrzad Alizadeh, Laleh Golestanifar

PII: S0040-4020(17)31094-3

DOI: 10.1016/j.tet.2017.10.057

Reference: TET 29060

To appear in: *Tetrahedron*

Received Date: 16 August 2017

Revised Date: 16 October 2017

Accepted Date: 20 October 2017

Please cite this article as: Zarei A, Khazdooz L, Aghaei H, Gheisari MM, Alizadeh S, Golestanifar L, Synthesis of phenols by using aryldiazonium silica sulfate nanocomposites, *Tetrahedron* (2017), doi: 10.1016/j.tet.2017.10.057.

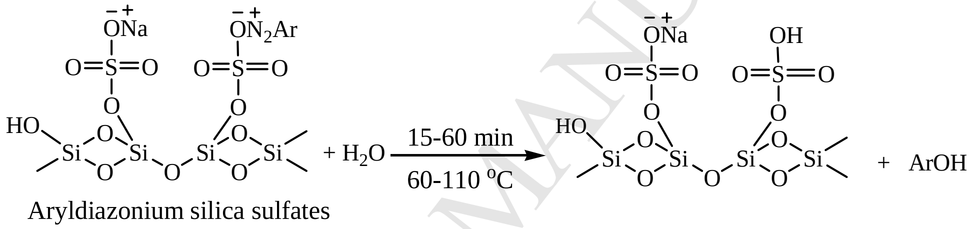
Graphical Abstract

Synthesis of phenols by using aryldiazonium silica sulfate nanocomposites

Amin Zarei,[a]* Leila Khazdooz,[b] Hamidreza Aghaei,[c]
Mohammad Mehdi Gheisari,[b] Shahrzad Alizadeh[c]
and Laleh Golestanifar[c]

[a] *Department of Science, Fasa Branch, Islamic Azad University, PO Box No. 364, Fasa 7461713591, Fars.*
[b] *Department of Science, Isfahan (Khorasgan)) Branch, Islamic Azad University, Isfahan 81595-158, Iran.*
[c] *Department of Chemistry, Shahreza Branch, Islamic Azad University, Shahreza 311-86145, Isfahan, Iran.*

Leave this area blank for abstract info.



Tetrahedron
journal homepage: www.elsevier.com

Synthesis of phenols by using aryldiazonium silica sulfate nanocomposites

Amin Zarei, [a]*, Leila Khazdooz, [b] Hamidreza Aghaei, [c] Mohammad Mehdi Gheisari, [b] Shahrzad Alizadeh [c] and Laleh Golestanifar [c]

[a] *Department of Science, Fasa Branch, Islamic Azad University, PO Box No. 364, Fasa 7461713591, Fars.*
[b] *Department of Science, Isfahan (Khorasgan) Branch, Islamic Azad University, Isfahan 81595-158, Iran.*
[c] *Department of Chemistry, Shahreza Branch, Islamic Azad University, Shahreza 311-86145, Isfahan, Iran.*

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Phenols
Nanocomposite
Hydrolysis
Aryldiazonium silica sulfate
Solvent-free conditions

ABSTRACT

Type your Abstract text here

2009 Elsevier Ltd. All rights reserved.

The hydrolysis of a new type of diazonium salt immobilized on the surface of silica sulfuric acid was studied in this work. By using diazonium salt nanocomposites, a number of phenol derivatives were synthesized in good yields. In contrast to the previous works, the present procedure was conveniently carried out under mild and solvent-free conditions. The effects of solvent and temperature were studied on the dediazoniation products. The notable advantages of this methodology were operational simplicity, availability of reactants, short reaction time and easy work-up.

1. Introduction

In comparison with aryl halides and triflates, arenediazonium salts ($ArN_2^+X^-$) have a greater reactivity and wider availability from inexpensive aromatic amines. Therefore, these salts have been prepared and studied as useful intermediates in classical and modern organic synthesis.[1] Moreover, arenediazonium salts are used for the modification of conducting surfaces in materials science, which has led to a wide range of applications in biochemical sensors, microelectronics and in the biomedical industry.[2] These salts have been prepared by a wide variety of methods. One of the oldest and commonly used methods involves the diazotization of aromatic amines with sodium nitrite in a highly acidic aqueous solution.[3] Moreover, diazonium salts can be formed in organic solvents by the reaction between aromatic amines and an alkyl nitrite in the presence of an acid. It is notable that the counterion (X^-), determined by the choice of the acid, has an important role for both stability and reactivity of the diazonium salt.[4] For example, aryldiazonium chlorides ($ArN_2^+Cl^-$) are usually unstable above 0 °C and some of them are explosive. Furthermore, because of this instability, subsequent reactions with diazonium salts must be carried out under the same conditions that these salts are formed. Thus, aryldiazonium salts with higher stability and versatility that are not explosive are desirable and necessary. Recent developments have shown that the stability of the aryldiazonium cation can be modulated by changing its counterion. Among arenediazonium salts, arenediazonium tetrafluoroborates are much used because of their stability and availability. [5] Moreover, aryldiazonium salts with disulfonimides, [6] carboxylates, [7] tosylates, [8] and tetrachloroaurate [9] counterions have been synthesized and reported to good stability. Diazotization reactions of these anhydrous aryl diazonium salts are carried out in an appropriate organic solvent, and it is necessary to add Et_2O into the reaction mixture to precipitate the corresponding diazonium salt. Also, in most of these procedures, it is required to control the reaction at low temperatures. Recently, diazonium ions have been immobilized on silica nanoparticles (Figure 1).[10] Although these nanocomposites are suitable for deposition on a metal surface, they are not useful for consequent organic syntheses because diazonium groups are directly linked to the surface of the SiO_2. Moreover, the synthesis of these kinds of diazonium salts is time-consuming and expensive.

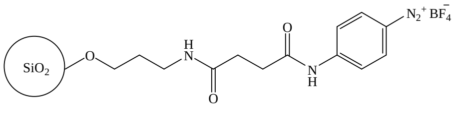


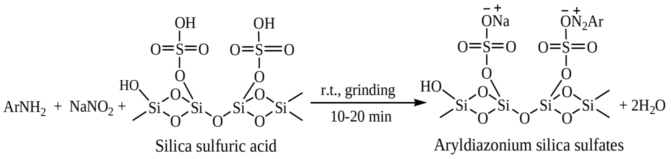
Figure 1. Silica nanoparticles functionalized with diazonium groups.

Recently, we have reported a new method for the preparation of anhydrous and stable aryldiazonium ions on the surface of

---

* Corresponding author. Tel: +989171302528, Fax: +983132289113, Email: aj_zarei@yahoo.com, aminzarei@iaufasa.ac.ir

silica sulfuric acid (SSA), named aryldiazonium silica sulfates ($ArN_2^{+-}OSO_3$-SiO_2). These aryldiazonium salts are easily synthesized by using aromatic amines, sodium nitrite and silica sulfuric acid as an inexpensive and safe solid acid (Scheme 1).[11] It is notable that these reactions are carried out in a few minutes under solvent-free conditions. Contrary to the reported methods, diazotization reactions of these salts are conducted at room temperature in one step and there is no need to maintain the reactions at low temperatures.

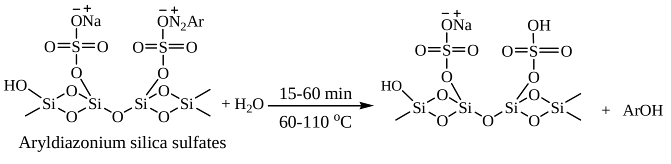


Scheme 1. Immobilization of aryldiazonium ion on SSA.

By using these new arenediazonium salts, a number of compounds can be synthesized efficiently under mild and heterogeneous conditions.[11] It is noteworthy that some of these syntheses are easily carried out under solvent-free conditions and the corresponding products are isolated by simple extraction.[11] Moreover, in some of these reactions, the used solid support can be recycled after completion of the reaction. These significant capabilities of aryldiazonium silica sulfates are in accordance with the green chemistry principles, and make them more attractive than the other arenediazonium salts.

Phenols and their derivatives are widely used as intermediates in organic chemistry, and are found in natural products, polymers, materials, and biological and medicinal compounds.[12] Functional phenols are commonly prepared by direct hydroxylation of aryl halides with strong basic hydroxide salts, or by metal-catalyzed hydroxylation of aryl halides.[13] Thermal decomposition of aryldiazonium salts in a highly acidic aqueous solution or copper-catalyzed transformation of aryldiazonium salts can be the other routes for the preparation of phenol derivatives.[14] Recently, the synthesis of phenols has been followed by oxidative hydrolysis of aryl boronic acids.[15] Although some of these methods have convenient protocols with good to high yields, the majority of these methods are associated with limitations such as: the use of strong basic and acidic reaction conditions, high reaction temperature, long reaction time, low yield of the product, using excess amount of expensive reagents, using toxic solvents and the use of expensive catalysts and additives. Therefore, the introduction of an efficient, convenient and cost-effective method for the synthesis of phenols under mild and neutral conditions is desirable.

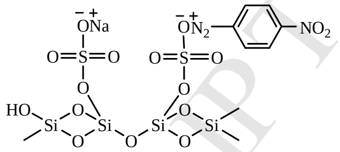
In continuation of our ongoing program to develop environmentally benign methods in organic synthesis, herein we report an efficient method for the synthesis of phenol derivatives by using aryldiazonium silica sulfates under mild, heterogeneous and solvent-free conditions (Scheme 2).



Scheme 2. Synthesis of phenols by using aryldiazonium silica sulfates.

2. Results and discussion

As mentioned, modification of surfaces using diazonium salts is an ongoing area of research in materials and organic chemistry.[2,16] Therefore, the synthesis of aryldiazonium salts with good stability is necessary to follow this purpose. In this area of research, aryldiazonium silica sulfates can be introduced as one of the most important classes of the stable aryldiazonium salts with the simplest synthesis procedure. In the present work, we study the reasons of the stability of aryldiazonium silica sulfates by surface study of 4-nitrophenyl diazonium silica sulfate as a model (Scheme 3).



Scheme 3. 4-nitrophenyl diazonium silica sulfate.

First, to demonstrate the formation of the arenediazonium ion on the surface of silica sulfuric acid, The FT-IR spectrum of 4-nitrophenyl diazonium silica sulfate was studied and compared with the spectrum of silica sulfuric acid (Figure 2). Two spectra show a broad stretching vibration of the hydroxyl groups around 3400 cm^{-1}. The other broad peaks that are almost common between the two spectra refer to asymmetric and symmetric O=S=O stretching from 1300-1000 cm^{-1} that overlap with the asymmetric and symmetric stretching bands of Si-O-Si. [17] Moreover, the S-O stretching bands around 581 cm^{-1} are almost alike between the two spectra.[17] It is notable that the main peaks that can support the formation of the 4-nitrophenyl diazonium group on the surface of silica sulfuric acid are clearly observed at 2292, 1545 and 1354 cm^{-1}. These stretching bands are respectively attributed to $N{\equiv}N^+$, and the asymmetric and symmetric vibrations of NO_2.[10,17] It should be mentioned that the adsorbed water band overlapping with aromatic C=C stretching band appears at 1635 cm^{-1}. Also, a peak at 851 cm^{-1} is observed which is corresponding to the C-H bending vibrations in the para substitution of aromatic ring.[17]

To further study the formation of the diazonium salt on the surface of silica sulfuric acid, X-Ray Photoelectron Spectroscopy (XPS) data of 4-nitrophenyl diazonium silica sulfate were considered. As shown in Figure 3, the presence of Si, S and O are demonstrated by appearance of three peaks at ~103, ~164 and ~533 eV respectively.[2] There are two main peaks which are indicative of the formation of the 4-nitrophenyl diazonium ion on SSA. The first peak that appears at ~285 eV is attributed to the C 1s XP spectrum,[2] because of the presence of a phenyl group in the structure of 4-nitrophenyl diazonium silica sulfate. The second XP spectrum assigned to $N{\equiv}N^+$ and NO_2 appears at ~406 eV as a small peak (N1s).[2] Moreover, the presence of the Na 1s XP spectrum at ~1073 eV indicates that the protons of SSA have been exchanged with sodium cations of $NaNO_2$ during the diazotization process.

After the formation of the 4-nitrophenyl diazonium salt on the surface of silica sulfuric acid, the morphology of this salt was studied and compared with SiO_2 and SSA. It should be mentioned that silica sulfuric acid is synthesized by using amorphous silica according to our previous works.[18] In order to study the surface of these materials, the XRD spectra of SiO_2, SSA and 4-nitrophenyl diazonium silica sulfate were compared. As shown in Figure 4, both silica and silica sulfuric acid indicate similar amorphous peaks centered at $2\Theta = 23°$ (Figure 4, (a, b)). It means that by modification of the amorphous SiO_2 surface with

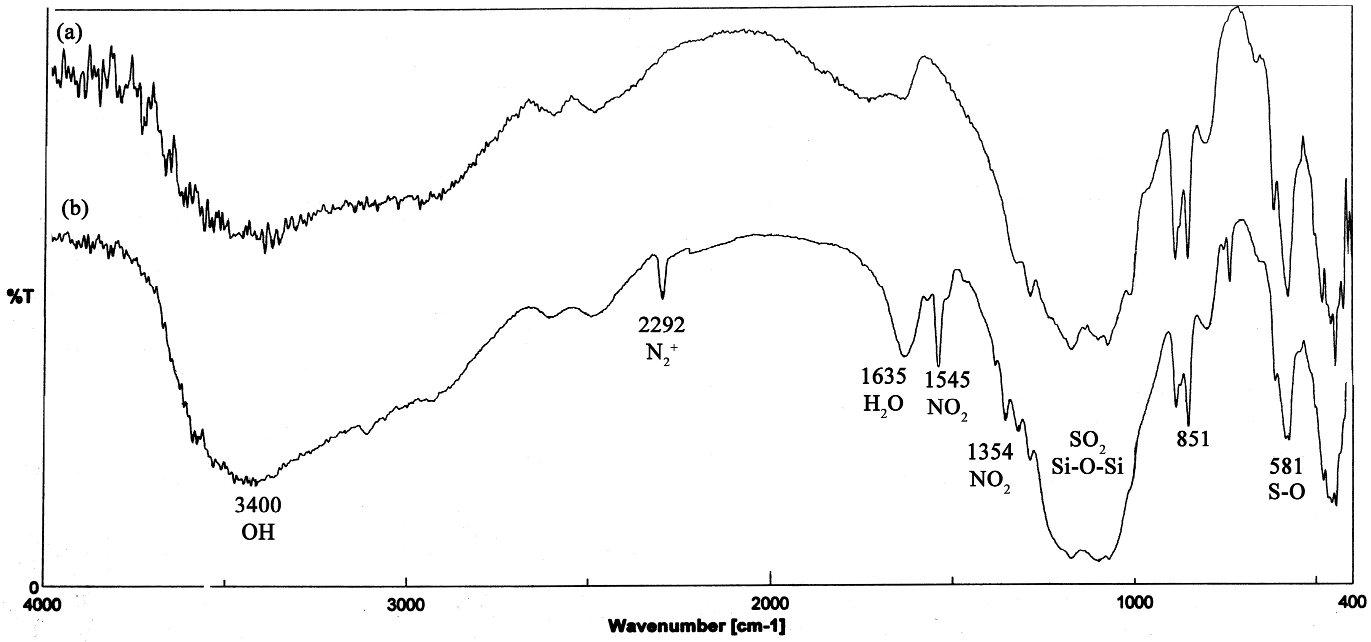


Figure 2. (a) FT-IR spectra of SSA. (b) FT-IR spectra of 4-nitrophenyl dizonium silica sulfate.

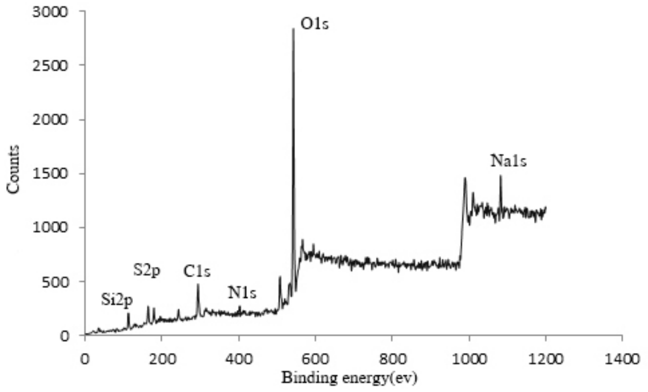


Figure 3. XPS spectra of 4-nitrophenyl diazonium silica sulfate.

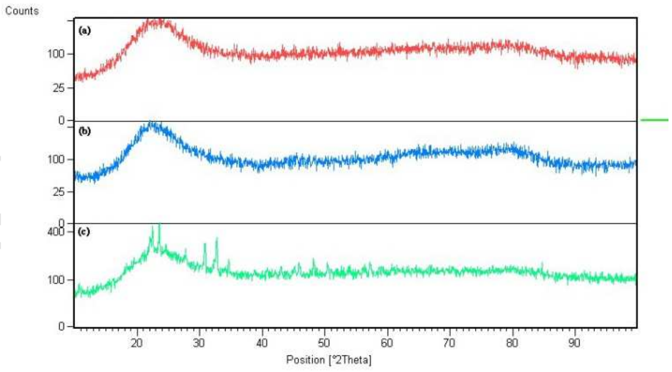


Figure 4. (a) XRD pattern of amorphous silica. (b) XRD pattern of silica sulfuric acid. (c) XRD pattern of 4-nitrophenyl diazonium silica sulfate.

SO_3H, no change in its morphology is observed. However, the XRD pattern of 4-nitrophenyl diazonium silica sulfate shows the crystalline phases specially at 2ϴ = 22°, 24°, 28°, 31°, 33°, 35° and 48° (Figure 4, (c)). We think that by immobilization of the corresponding diazonium salt on SSA, the ionic structures and crystalline phases on the surface increase.

To further investigate the morphology of the present materials, the SEM images of amorphous SiO_2, SSA and 4-nitrophenyl diazonium silica sulfate were studied (Figure 5). The findings demonstrate that no substantial difference was observed between the morphology of silica and silica sulfuric acid (Figure 5, (a, b)). These results are in agreement with the XRD patterns of these materials. It is notable that the SEM images of 4-nitrophenyl diazonium silica sulfate indicate the new phases of the corresponding diazonium ions which are irregularly formed on the surface of SSA (Figure 5, (c)). In the present procedure the diazotization process is carried out under solvent-free conditions, therefore the particle size distribution of these new phases is different (Figure 5, (d-f)).

To better illustrate the morphology of the present diazonium salt, the TEM images of 4-nitrophenyl diazonium silica sulfate were studied. As shown in Figure 6, 4-nitrophenyl diazonium ions are agglomerated on the surface of silica sulfuric acid in various nanometer sizes. It should be mentioned that by increasing the nano phases of the diazonium salts on SSA, the active sites of the present nanocomposite increase so that the next reactions can easily be carried out under solvent-free conditions.[11]

It is known that one of the most important restrictions when using diazonium salts is their instability at room temperature. However, by immobilization of these salts on the surface of silica sulfuric acid, their stabilities increase so that some of these salts can be kept at ambient conditions for days. In the present work, for the first time, we examined the stability of these salts at higher temperature by studying the thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of 4-nitrophenyl diazonium silica sulfate nanocomposite (Figure 7, 8). The TGA curve indicates that the decomposition of the present nanocomposite with 30% of the total weight loss is done in several steps (Figure 7).

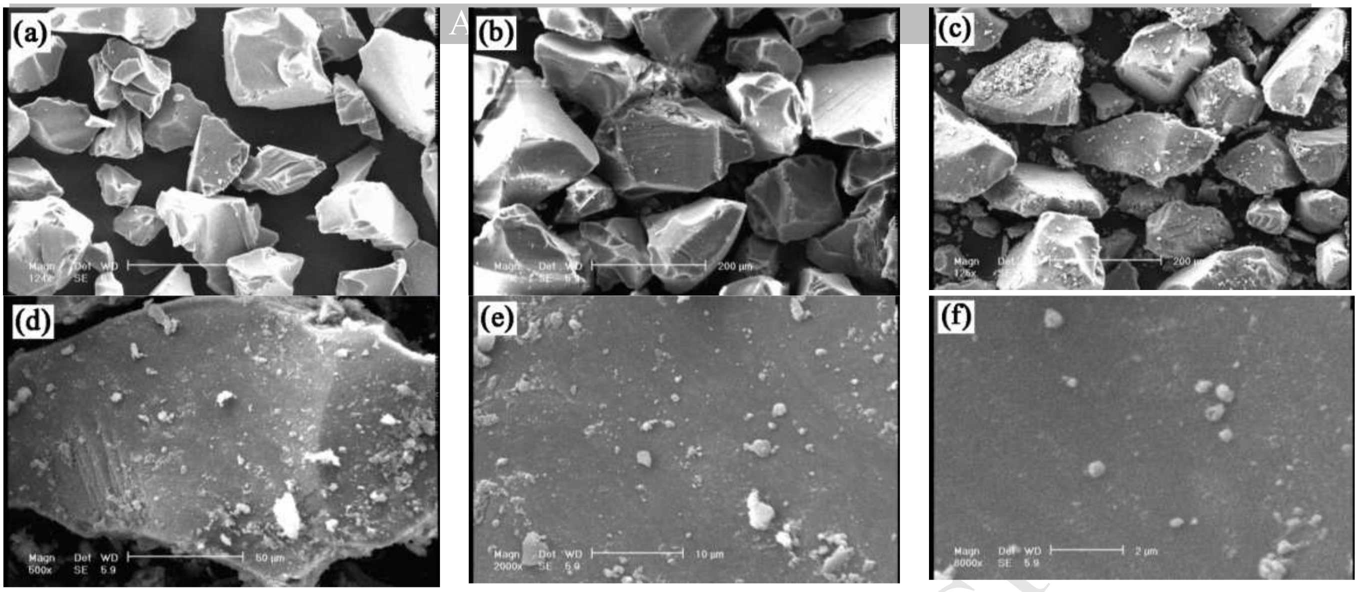


Figure 5. (a) SEM image of amorphous SiO_2 in 200 µm scale. (b) SEM image of SSA in 200 µm scale. (c) SEM image of 4-nitrophenyl diazonium silica sulfate in 200 µm scale. (d) SEM image of 4-nitrophenyl diazonium silica sulfate in 50 µm scale. (e) SEM image of 4-nitrophenyl diazonium silica sulfate in 10 µm scale. (f) SEM image of 4-nitrophenyl diazonium silica sulfate in 2 µm scale.

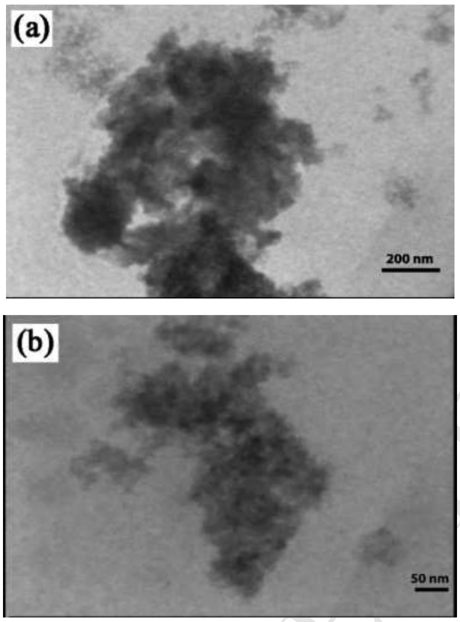


Figure 6. (a) TEM images of 4-nitrophenyl diazonium silica sulfate in 200 nm scale. (b) TEM images of 4-nitrophenyl diazonium silica sulfate in 50 nm scale.

At first, the physically absorbed water is removed from the nanocomposite in the range of 37-108 °C. At higher temperature (148-157 °C), decomposition of the diazonium salt takes place by exhaust of N_2 molecule from the surface of the nanocomposite. This step is in agreement with the DSC analysis by appearance of an exothermic peak at ~145 °C (Figure 8). By increasing the temperature (231-276 °C), the support (SSA) is decomposed and converted to silica by exhaust of SO_3 from the surface of silica sulfuric acid.[19] The result completely coincides with the DSC measurement by emergence of an exothermic peak at ~250 °C (Figure 8). Finally, the last peak appears in the range of 300-311 °C (Figure 7). It may be due to the decomposition of the phenyl group of 4-nitrophenyl diazonium silica sulfate. As a whole, the present diazonium salt nanocomposite is stable not only at room temperature but also at higher temperature so that its decomposition point is almost at 145 °C. Moreover, by knowing the decomposition point of each aryl diazonium silica sulfate, we are able to adjust the best temperature for the progress of the reaction without decomposition of the corresponding diazonium salt.

After studying the morphology of these types of diazonium salts immobilized on the surface of silica sulfuric acid, their application for the synthesis of functional phenols was studied. As cited in the literature, the usual method for the conversion of an aryldiazonium salt to the corresponding phenol is thermal decomposition of the diazonium salt in a highly acidic aqueous solution. [14a] It should be mentioned that the use of high acidity conditions is required to prevent the ionization of the resulting phenol to phenoxide which couples easily with unreacted diazonium ion to form the azo compound. Another side reaction encountered during thermal decomposition of a diazonium ion is the reaction of an aryl cation (formed by losing N_2 from an aryldiazonium ion) with the phenolic product to produce an arylphenol or a diaryl ether.[14a] Moreover, to obtain a high yield of phenol uncontaminated with azo compound, addition of a solution of the diazonium salt to a boiling sulfuric acid solution with simultaneous removal of the phenol product by steam distillation is usually required. [14a]

In this work, these difficulties were reduced by thermal decomposition of aryldiazonium silica sulfates under neutral and solvent-free conditions. First, the synthesis of phenol was studied by using phenyldiazonium silica sulfate ($PhN_2^{+-}OSO_3$-SiO_2) under different conditions (Table 1). The completion of the reactions was monitored by the 2-naphtholate test (absence of azo coupling with 2-naphtholate). It should be mentioned that the reactions carried out at 25 and 35 °C were not complete after the time specified in Table 1. But, the corresponding reactions carried out at 50 and 60 °C were complete after the time indicated in Table 1. By comparison of the findings, the best result was obtained when the reaction was carried out at 60 °C under solvent-free conditions (Table 1, entry 5). In all reactions carried out in water, the phenol product was isolated by an acidic

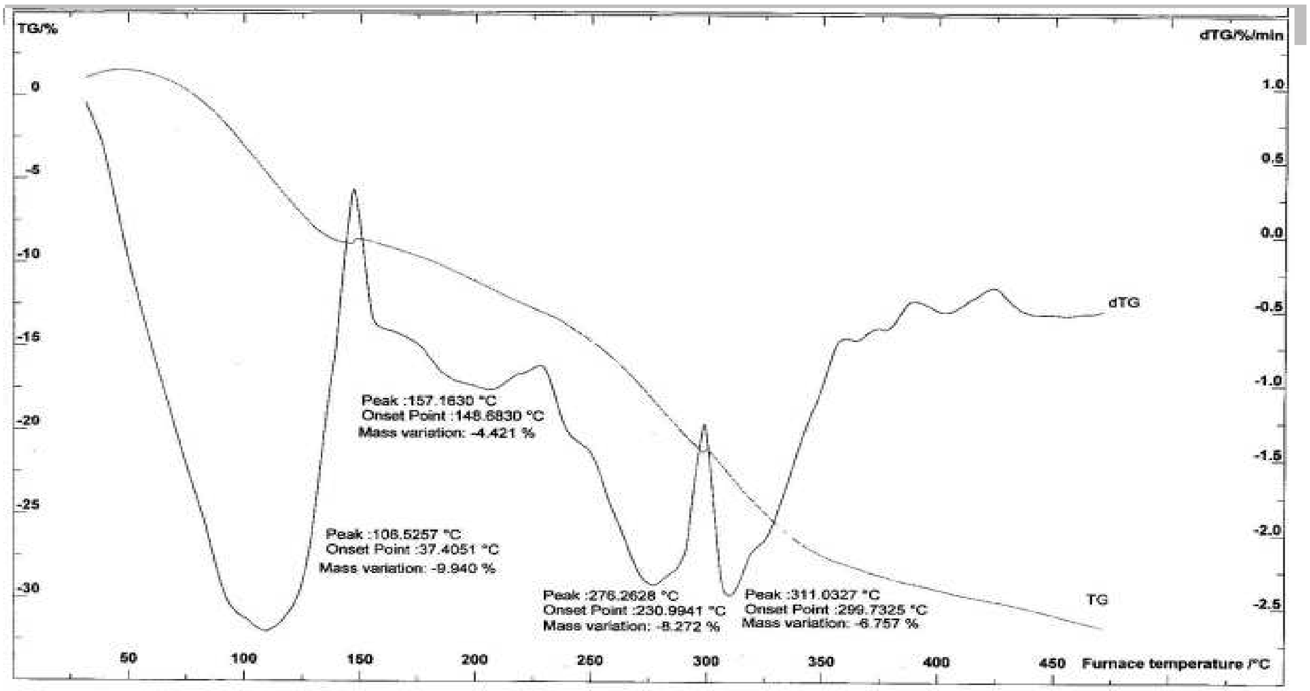


Figure 7. TGA and dTG curves of 4-nitrophenyl diazonium silica sulfate.

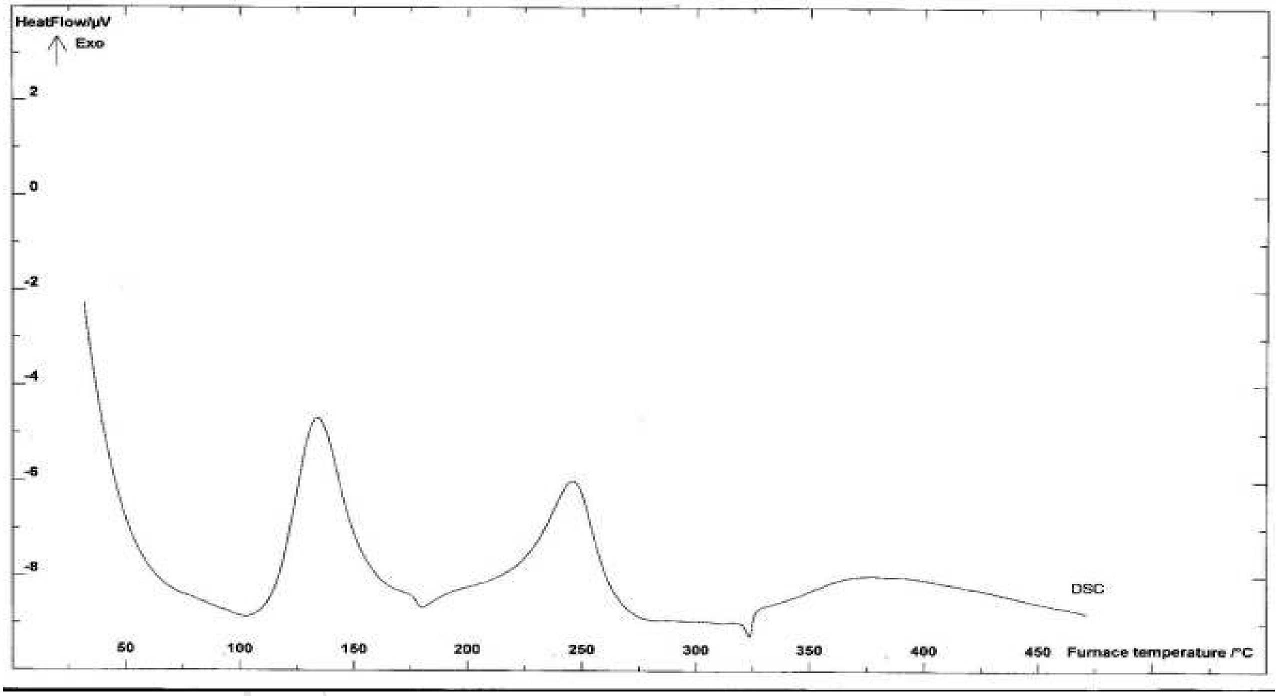


Figure 8. DSC curve of 4-nitrophenyl diazonium silica sulfate.

work-up using EtOAc as the solvent. However, when the reaction was carried out under solvent-free conditions, the phenol product was isolated by simple extraction with EtOAc. Due to the phenol solubility in water, the yield of the isolated product by acidic work-up is less than that by simple extraction. It should be cited that no by-product was observed when the reaction was carried out under solvent-free conditions at 60 ° C. However, by increasing the temperature to 70 ° C, diphenyl ether, as a side product, was obtained in 7% yield (based on GC-MS). Therefore, the best reaction conditions for the hydrolysis of phenyldiazonium silica sulfate were determined by conducting the reaction under solvent-free conditions at 60 ° C.

Table 1. Optimization of the reaction conditions for the synthesis of phenol using phenyldiazonium silica sulfate [a]

Entry	Solvent	Temperature (° C)	Time	Yield (%)[b]
1	H_2O	25	6 h	trace
2	H_2O	35	3 h	30
3	H_2O	50	1 h	68
4	H_2O	60	25 min	70
5	Solvent-free	60	15 min	81

[a] Reaction conditions: phenyldiazonium silica sulfate (1 mmol), solvent (5 mL).

[b] The yields refer to the isolated pure products.

Table 2. Synthesis of phenol derivatives by using aryldiazonium silica sulfates under solvent-free conditions.[a]

Entry	Diazonium salt	Product	Temp. (°C)	Time (min)	Yield (%)
1	$PhN_2^{+-}OSO_3$-SiO_2	Phenol	60	15	81
2	4-$MeC_6H_4N_2^{+-}OSO_3$-SiO_2	4-Methylphenol	60	25	83
3	2-$MeC_6H_4N_2^{+-}OSO_3$-SiO_2	2-Methylphenol	60	25	78
4	4-$PhC_6H_4N_2^{+-}OSO_3$-SiO_2	Biphenyl-4-ol	70	25	82
5	4-$BrC_6H_4N_2^{+-}OSO_3$-SiO_2	4-Bromophenol	80	30	74
6	3-$ClC_6H_4N_2^{+-}OSO_3$-SiO_2	3-Chlorophenol	85	30	73
7	3-$MeCOC_6H_4N_2^{+-}OSO_3$-SiO_2	3-Hydroxyacetophenone	80	30	80
8	4-$MeCOC_6H_4N_2^{+-}OSO_3$-SiO_2	4-Hydroxyacetophenone	80	30	75
9	2-$PhCOC_6H_4N_2^{+-}OSO_3$-SiO_2	2-Hydroxybenzophenone	80	30	20 [b,c]
10	4-$HOOCC_6H_4N_2^{+-}OSO_3$-SiO_2	4-Hydroxybenzoicacid	80	30	71
11	3-$NO_2C_6H_4N_2^{+-}OSO_3$-SiO_2	3-Nitrophenol	110	60	67

[a] The yields refer to the isolated pure products which were identified by FT-IR and ^{1}HNMR spectroscopy and GC-MS and compared with standard samples.

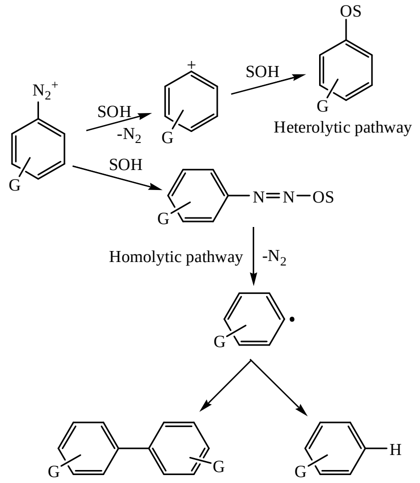
[b] Determined by GC-MS analysis.

[c] 9-Fluorenone was determined in 80% yield by GC-MS analysis.

After optimization of the reaction conditions, the generality of the present method was studied by the synthesis of various functionalized phenols. As shown in Table 2, a number of aryldiazonium silica sulfates possessing electron-withdrawing or electron-donating groups were easily converted into the corresponding phenols in good yields and short reaction time. All reactions were carried out under thermal and solvent-free conditions. In comparison with the electron-donating groups, the electron-withdrawing groups on the aromatic rings of these diazonium salts decreased the reaction rate, meaning that the reaction should be carried out at higher temperatures. In contrast to the traditional methods, in the present work, all products were isolated from the surface of silica by simple extraction without using tedious work-up. Moreover, the primary solid support was recovered according to the previous work.[11b] Contrary to the traditional methods, the azo-coupled side-products were not observed during the course of the reactions. Although arenediazonium tetrafluoroborates $(ArN_2^+BF_4^-)$ and arenediazonium chlorides $(ArN_2^+Cl^-)$ are the most common diazonium salts used for the thermal decomposition of these salts in solution, arylfluorides and arylchlorides, as side products, are formed during the course of the reactions.[20] In the present work, by immobilization of the arenediazonium salts on the surface of silica sulfuric acid, this limitation obviously decreased. It should be noted that, when 2-benzoylphenyl diazonium silica sulfate was hydrolyzed by the present procedure, 2-hydroxybenzophenone was obtained in 20% yield and 9-fluorenone, as a side product, was formed in 80% yield (Table 2, entry 9).

We changed the reaction conditions by using water as the solvent under the same reaction time and temperature. By employing these conditions, 2-hydroxybenzophenone was formed in 4% yield and 9-fluorenone was obtained in 96% yield (based on GC-MS).

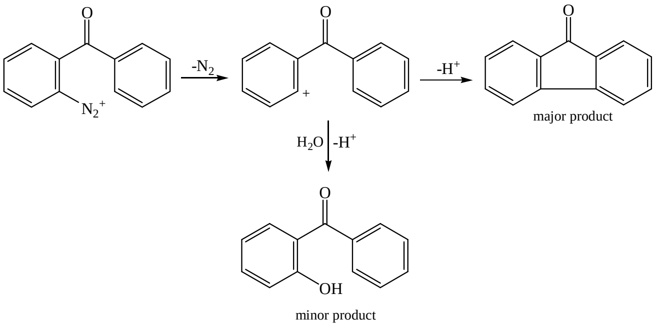
Mechanistic proposals relating to the decomposition of arenediazonium salts have been described in earlier studies.[7,14a,21] The results demonstrate that the solvolysis of arenediazonium ions occurs through two main mechanisms: heterolytic and homolytic pathways (Scheme 4).[7,21] The heterolytic solvolysis is generally carried out in solvents (SOH) with low nucleophilicity such as water or trifluoroethanol.[21] This dediazoniation is specified by losing N_2 and formation of an aryl cation as an extremely reactive intermediate. The homolytic solvolysis of arenediazonium salts takes place in solvents with better nucleophilicity such as pyridine or HMPT.[21] The formation of an aryl radical intermediate is characteristic of this pathway. MeOH, EtOH and DMSO are introduced as borderline solvents in which both mechanisms may be observed simultaneously.[21] It should be stated that electron-withdrawing substituents on the aromatic rings of arenediazonium ions make them more prone to homolytic dediazoniation.[21]



Scheme 4. Heterolytic and homolytic pathways for the solvolysis of arenediazonium ions.

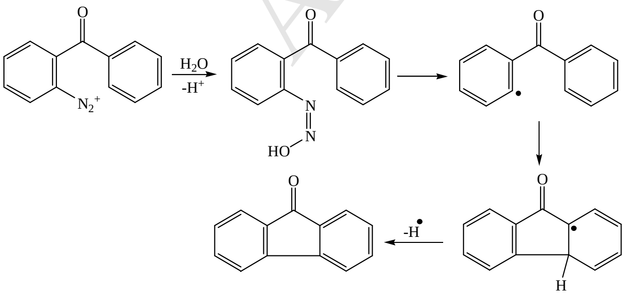
In the present work the hydrolysis of these immobilized arenediazonium ions was easily carried out under solvent-free conditions, and the phenol derivatives were obtained in good yields. Products analysis (based on GC-MS analysis) did not identify the presence of products from the homolytic pathways (e.g. ArH or biaryls) using the present procedure. Therefore, a heterolytic mechanism seems most probable.

It is known that the thermal decomposition of the diazonium salts derived from 2-aminobenzophenone in aqueous solution gives 9-fluorenone as the major product and 2-hydroxybenzophenone as the minor product.[22] The formation of 9-fluorenone and 2-hydroxybenzophenone occur readily under acidic conditions by a heterolytic mechanism (Scheme 5).[22] By following this mechanism, the ring closure reaction is carried out by an intramolecular arylation, competing with water intermolecular nucleophilic attack. It is well known that the closure of a five-membered ring usually occurs much more readily than the other intermolecular competitive reactions.[22]



Scheme 5. Proposed heterolytic mechanism for the hydrolysis of diazonium cation derived from 2-aminobenzophenone.

As discussed, by hydrolysis of 2-benzoylphenyl diazonium silica sulfate, 9-fluorenone was formed in 80% yield and 2-hydroxybenzophenone was obtained in 20% yield at 80 °C under solvent-free conditions. By using H_2O as the solvent, 9-fluorenone was obtained in 96% yield and 2-hydroxybenzophenone was formed in 4% yield at 80 °C. We think that by employing water as the solvent, the concentration of H^+ which is generated during the course of the reaction decreases and subsequently the nucleophilicity of H_2O increases. Moreover, the existence of a carbonyl group, as an electron-withdrawing group, in the structure of the corresponding diazonium salt makes it prone to partially homolytic hydrolysis according to the Scheme 6. In this mechanism, a diazohydroxide intermediate is formed by addition of water to the corresponding diazonium cation. Because of the instability of diazohydroxide group, it can undergo homolytic fragmentation to give the corresponding aryl radical.[21,22] Then, the closure of the five-membered ring occurs readily due to the proximity of the radical to the potential reaction site. Finally, 9-fluorenone is formed by losing a hydrogen radical.[22] As a whole result, by employing water as the solvent, the hydrolysis reaction of 2-benzoylphenyl diazonium silica sulfate is carried out, not only by a heterolytic mechanism but, also may be followed by a homolytic pathway. We think that the simultaneous occurrence of heterolytic and homolytic mechanisms may be a logical reason for the increase of 9-fluorenone yield in water.



Scheme 6. Proposed homolytic mechanism for the formation of 9-fluorenone by hydrolysis of diazonium cation derived from 2-aminobenzophenone.

3. Conclusions

In summary, we have developed a fast, efficient and convenient method for the synthesis of phenols in good yields. Using the present method, a number of aryldiazonium silica sulfate nanocomposites were hydrolyzed to the corresponding phenol derivations under mild and solvent-free conditions. The notable advantages of this methodology were operational simplicity, availability of reactants, short reaction time and easy work-up.

4. Experimental

4.1. General

All reagents were purchased from Merck and Aldrich and used without further purification. All yields refer to isolated products after purification. Silica sulfuric acid was synthesized according to the previous works with 4.4 mmol H+/g capacity.18 The products were characterized by comparison of physical data with those of known compounds and by spectroscopic data (FT-IR, 1HNMR and GC-MS). IR spectra were reordered on a JASCO FT-IR-680 PLUS spectrometer. 1HNMR spectra were recorded with a Bruker Avance 400 (400 MHz). The results of GC-MS were obtained by using an Agilent 7890AGC 5975C inert XLEI/CIMSD instrument. The morphology and particle size of the nanocomposite were measured by using transmission electron microscopy (TEM, Philips CM30) at 200 kV and by a scanning electron microscope (SEM, Philips XL30) operated at an acceleration voltage of 20 kV. X-ray photoelectron spectroscopy (XPS) signals were acquired by using a BESTEC 8025 system fitted with a microfocused and monochromatic Al Kα X-ray source (1486.6 eV). Phase structure analyses were determined by X-ray diffractometer (XRD, Philips Xpert) using the Ni-filtered CuKα (λCuKα=0.1542 nm, radiation at 40 kV and 30 mA). The data were collected over the 2θ range from 10° to 90° (time per step was 2.5 s and step size was 0.021°). Thermogravimetric analyses were performed in a SETARAM LABSYS instrument (SETARAM, Caluire, France) under argon atmosphere with 10°C/min heating rate.

4.2. Typical procedure for the preparation of phenyl diazonium silica sulfate

Aniline (1 mmol, 0.095 mL), silica sulfuric acid (0.75 g) and sodium nitrite (1.7 mmol, 0.12 g) were ground in a mortar witha pestle for a few minutes to obtain a homogeneous mixture. Then, four drops of water were gradually added and the mixture was ground for 10 min to give phenyl diazonium silica sulfate.

4.3. Typical procedure for the synthesis of phenol by using phenyl diazonium silica sulfate

Five drops of water were added to phenyl diazonium silica sulfate (1 mmol) and the resulting mixture was simply blended and then placed into a covered petri dish. Then, the petri dish was placed in an oven at 60 °C for 15 minutes. After that, the reaction mixture was diluted with EtOAc (15 mL) and filtered after vigorous stirring. The residue was extracted with EtOAc (2× 10 mL) and the combined organic layer was dried over anhydrous Na2SO4. The solvent was evaporated under reduced pressure to afford the crude product. Further purification was performed by flash column chromatography and the pure phenol was obtained in 81% (0.076 g).

Acknowledgments

We gratefully acknowledge the funding support received for this project from the Islamic Azad University, Fasa Branch and Khorasgan Branch.

References

1. Roglans, A.; Pla-Quintana, A.; Moreno-Manas, M. *Chem. Rev.* **2006**, *106*, 4622.
2. (a) Chehimi, M. M. *Aryl Diazonium Salts: New Coupling Agents in Polymer and Surface Science*, Wiley-VCH Verlag & Co. KGaA, Boschstr. Weinheim, Germany, 2012. (b) Polsky, R.; Harper, J. C.; Dirk, S. M.; Arango, D. C.; Wheeler, D. R.; Brozik, S. M. *Langmuir* **2007**, *23*, 364. (c) Harper, J. C.; Polsky, R.; Wheeler, D. R.; Brozik, S. M. *Langmuir* **2008**, *24*, 2206. (d) Hansen, M. N.; Farjami, E.; Kristiansen, M.; Clima, L.; Pedersen, S. U.; Daasbjerg, K.; Ferapontova, E. E.; Gothelf, K. V. J. *Org. Chem*. **2010**, *75*, 2474.
3. Zollinger, H. *Diazo chemistry I, aromatic and heteroaromatic compounds*, Weinheim: Wiley VCH, 1994.
4. Felpin, F. X.; Hardy, L. N.; Callonnec, F. L.; Fouquet, E. *Tetrahedron* **2011**, *67*, 2815.
5. Taylor, J. G.; Moro, A. V.; Correia, C. R. D. *Eur. J. Org. Chem.* **2011**, 1403.
6. Barbero, M.; Crisma, M.; Degani, I.; Fochi, R.; Perracinoa, P. *Synthesis* **1998**, 1171.
7. Colas, C.; Goeldner, M. *Eur. J. Org. Chem.* **1999**, 1357.
8. Filimonov, V. D.; Trusova, M.; Postnikov, P.; Krasnokutskaya, E. A.; Lee, Y. M.; Hwang, H. Y. *Org. Lett*. **2008**, *10*, 3961.
9. Overton, A. T.; Mohamed, A. A. *Inorg. Chem*. **2012**, *51*, 5500.
10. Joselevich, M.; Williams, F. J. *Langmuir* **2008**, *24*, 11711.
11. (a) Zarei, A.; Hajipour, A. R.; Khazdooz, L.; Mirjalili, B. B. F.; Najafichermahini, A. *Dyes Pigments* **2009**, *81*, 240. (b) Zarei, A.; Hajipour, A. R.; Khazdooz, L. *Synthesis* **2009**, 941. (c) Zarei, A.; Hajipour, A. R.; Khazdooz, L.; Aghaei, H. *Tetrahedron Lett.* **2009**, *50*, 4443. (d) Zarei, A.; Hajipour, A. R.; Khazdooz, L.; Aghaei, H. *Synlett* **2010**, 1201. (e) Zarei, A.; Khazdooz, L.; Hajipour, A. R.; Aghaei, H. *Dyes Pigments* **2011**, *91*, 44. (f) Zarei, A.; Khazdooz, L.; Pirisedigh, A.; Hajipour, A. R.; Seyedjamali, H.; Aghaei, H. *Tetrahedron Lett*. **2011**, *52*, 4554. (g) Zarei, A.; Khazdooz, L.; Hajipour, A. R.; Rafiee, F.; Azizi, G.; Abrishami, F. *Tetrahedron Lett*. **2012**, *53*, 406. (h) Pirisedigh, A.; Zarei, A.; Seyedjamali, H.; Khazdooz, L.; Hajipour, A. R. *Monatsh. Chem.* **2012**, *143*, 791. (i) Zarei, A.; Khazdooz, L.; Hajipour, A. R.; Aghaei, H.; Azizi, G. *Synthesis* **2012**, 3353. (j) Zarei, A.; Khazdooz, L.; Hajipour, A. R.; Aghaei, H.; Azizi, G.; Najafichermahini, A.; Hajipour, A. R. *Dyes Pigments* **2014**, *101*, 295.
12. (a) Rappoport, Z. *The Chemistry of Phenol*, Wiley-VCH: Weinheim, 2003. (b) Tyman, J. H. P. *Synthetic and Natural Phenols*, Elsevier, New York, 1996.
13. (a) Anderson, K. W.; Ikawa, T.; Tundel, R. E.; Buchwald, S. L. *J. Am. Chem. Soc*. **2006**, *128*, 10694. (b) Schulz, T.; Torborg, C.; Schaffner, B.; Huang, J.; Zapf, A.; Kadyrov, R.; Borner, A.; Beller, M. *Angew. Chem., Int. Ed*. **2009**, *48*, 918. (c) Sergeev, A. G.; Schulz, T.; Torborg, C.; Spannenberg, A.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed*. **2009**, *48*, 7595. (d) Zhao, D.; Wu, N.; Zhang, S.; Xi, P.; Su, X.; Lan, J.; You, J. *Angew. Chem., Int. Ed*. **2009**, *48*, 8729. (e) Tlili, A.; Xia, N.; Monnier, F.; Taillefer, M. *Angew. Chem., Int. Ed*. **2009**, *48*, 8725. (f) Paul, R.; Ali, M. A.; Punniyamurthy, T. *Synlett* **2010**, 4268. (g) Song, G. L.; Zhang, Z.; Da, Y. X.; Wang, X. C. *Tetrahedron* **2015**, *71*, 8823. (h) Tan, B. Y. H.; Teo, Y. C. *Synlett* **2016**, 1814.
14. (a) Cohen, T.; Dietz, A. G.; Miser, J. R. *J. Org. Chem*. **1977**, *42*, 2053. (b) Mo, F.; Dong, G.; Zhang, Y.; Wang, J. *Org. Biomol. Chem*. **2013**, *11*, 1582.
15. (a) Prakash, G. K. S.; Chacko, S.; Panja, C.; Thomas, T. E.; Gurung, L.; Rasul, G.; Mathew, T.; Olah, G. A. *Adv. Synth. Catal*. **2009**, *351*, 1567. (b) Xu, J. M.; Wang, X. Y.; Shao, C. W.; Su, D. Y.; Cheng, G. L.; Hu, Y. F. *Org. Lett*. **2010**, *12*, 1964. (c) Hosoi, K.; Kuriyama, Y.; Inagi, S.; Fuchigami, T. *Chem. Commun*. **2010**, 1284. (d) Mulakayala, N.; Ismail, Kumar, K. M.; Rapolu, R. K.; Kandagatla, B.; Rao, P.; Oruganti, S.; Pal, M. *Tetrahedron Lett*. **2012**, *53*, 6004. (e) Zhu, C.; Wang, R.; Falck, J. R. *Org. Lett*. **2012**, *14*, 3494. (f) Gogoi, A.; Bora, U. *Synlett* **2012**, 1079. (g) Qj, H. L.; Chen, D. S.; Ye, J. S.; Huang, J. M. *J. Org. Chem*. **2013**, *78*, 7482. (h) Zou, Y. Q.; Chen, J. R.; Liu, X. P.; Lu, L. Q.; Davis, R. L.; Jorgensen, K. A.; Xiao, W. J. *Angew. Chem., Int. Ed*. **2012**, *51*, 784. (i) Chen, D. S.; Huang, J. M. *Synlett* **2013**, 499. (j) Gohain, M.; Plessis, M. D.; Tonder, J. H. V.; Bezuidenhoudt, B. C. B. *Tetrahedron Lett*. **2014**, *55*, 2082. (k) Matsui, K.; Ishigami, T.; Yamaguchi, T.; Yamaguchi, E.; Tada, N.; Miura, T.; Itoh, A. *Synlett* **2014**, 2613. (l) Paul, A.; Chatterjee, D.; Rajkamal, Haider, T.; Banerjee, S.; Yadav, S. *Tetrahedron Lett*. **2015**, *56*, 2496. (m) Yang, D. S.; An, B. J.; Wei, W.; Jiang, M.; You, J. M.; Wang, H. *Tetrahedron* **2014**, *70*, 3630. (m) Chatterjee, N.; Goswami, A. *Tetrahedron Lett*. **2015**, *56*, 1524. (n) Begum, T.; Gogoi, A.; Gogoi, P. K.; Bora, U. *Tetrahedron Lett*. **201**5, *56*, 95. (o) Mahanta, A.; Adhikari, P.; Bora, U.; Thakur, A. J. *Tetrahedron Lett*. **2015**, *56*, 1780. (p) Gupta, S.; Chaudhary, P.; Seva, L.; Sabiah, S.; Kandasamy, J. *RSC Adv*. **2015**, *5*, 89133. (q) Gupta, S.; Chaudhary, P.; Srivasava, V.; Kandasamy, J. *Tetrahedron Lett.* **2016**, *57*, 2506.
16. Belanger, D.; Pinson, J. *Chem. Soc. Rev*. **2011**, *40*, 3995.
17. Silverstein, R. M.; Webster, F. X.; Kiemle, D. J.; Bryce, D. L. *Spectrometric Identification of Organic Compounds*, 8th. Edition, Wiley, John & Sons Publisher, 2014.
18. Hajipour, A. R.; Zarei, A.; Khazdooz, L.; Mirjalili, B. B. F.; Sheikhan, N.; Zahmatkesh, S.;. Ruohoa, A. E *Synthesis* **2005**, 3644.
19. Shaterian, H. R.; Ghshang, M.; Feyzi, M. *Appl. Catal. A: Gen*. **2008**, *345*, 128.
20. (a) Canning, P. S. J.; Maskill, H.; McCrudden, K.; Sexton, B. *Bull. Chem. Soc. Jpn*. **2002**, *75*, 789. (b) Canning, P. S. J.; McCrudden, K.; Maskill, H.; Sexton, B. *Chem. Commun*. **1998**, 1971.
21. (a) Pazo-Liorente, R.; Bravo-Diaz, C.; Gonzalez-Romero, E. *Eur. J. Org. Chem*. **2004**, 3221. (b) Pazo-Liorente, R.; Bravo-Diaz, C.; Gonzalez-Romero, E. *Eur. J. Org. Chem*. **2003**, 3421.
22. DeTar, D. F. *Org. React*. **1957**, *9*, 409.