

Silver Natural Asphalt Sulfonate (NA-SO₃Ag): Fabrication and Utilization as a New Heterogeneous, Carbonaceous, and Retrievable Nanocatalyst for C(sp²)-X (X = C, S, and Se) Bond Formation

Touba Zolfaghari, Mohammad Soleiman-Beigi,* and Homa Kohzadi



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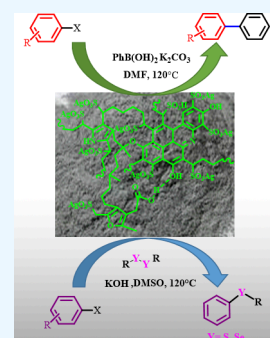
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ABSTRACT: Silver-based catalysts are valuable catalysts in various areas of the chemical industry, organic syntheses, and transformations, and from a chemical and industrial point of view, their recycling is very important. Herein, silver natural asphalt sulfonate (NA-SO₃Ag) was fabricated via the grafting of Ag(I) on the surface of the solid natural asphalt sulfonate as a novel and efficient recoverable silver nanocatalyst. Natural asphalt is one of the hydrocarbons that are found in mineral veins. The structure of NA-SO₃Ag was characterized by diverse microscopic and spectroscopic techniques including Fourier-transform infrared (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), and inductively coupled plasma optical emission spectroscopy (ICP-OES) techniques. The NA-SO₃Ag nanocatalyst was utilized for C–Se and C–S bond formation via coupling reactions of aryl halides and organic disulfides/diselenides to afford a wide variety of diaryl sulfides/selenides in good to excellent yields. Additionally, the utilization of NA-SO₃Ag in C–C bond formation was examined in Suzuki coupling reactions successfully. For at least 6 trials, this heterogeneous catalyst can be separated and reused without any activity reduction.



INTRODUCTION

One important aspect of any organic reaction is the catalyst, which can improve the process and chemical reactions. A catalyst is a specific aspect of organic reactions. Most of the chemical processes for the synthesis of biological compounds are performed with catalysts.^{1,2} Therefore, the choice of a suitable catalyst that accords with the principles of green chemistry is an important challenge.³ Today, the design of heterogeneous catalytic systems that have high activity and low toxicity has attracted specific attention. In this regard, different substrates have been used as catalyst support.^{4–6} Among chemical substrates, carbon is distinct because it is found in dramatically various forms. Carbon, due to its valence, exists in various allotropic forms such as carbon black, diamond, fullerenes, graphene, and carbon nanotubes. Carbonaceous compounds are used in various catalytic processes because of their unique features, such as chemical inertness, high surface area and porosity, suitable mechanical properties, and low cost.^{7–9} Natural asphalt is a type of carbonaceous mineral compound that includes 70–80% of carbon, 15% of hydrogen, and a trace amount of nitrogen.¹⁰ Solid natural asphalt with its features such as excellent stability, low cost, high thermal stability, large specific surface area, and high carbon contents is a suitable candidate for the preparation of various nanocatalysts in organic reactions. Solid natural asphalt can be functionalized and linked with different metals such as copper, palladium, and silver. In our previous studies, we succeeded in synthesizing different catalysts

based on natural asphalt, and we investigated their catalytic activity in various reactions.^{11,12}

In the last few decades, silver, due to its features such as low price, abundance, and low toxicity in comparison to transition metals such as ruthenium, platinum, palladium, and iridium, attracted special attention for the synthesis of nanocatalysts. Silver-based catalysts as one straightforward and powerful catalyst used in organic reactions such as cycloaddition reactions,¹³ cyclizations,¹⁴ coupling reactions,¹⁵ C–H functionalization,¹⁶ etc. Transition-metal-catalyzed formation of C–C, C–S, and C–Se bonds by cross-coupling reactions is a powerful tool for the preparation of numerous important products in pharmaceutical, biological, and agrochemicals products. Suzuki cross-coupling has attracted the greatest attention because of readily accessible, nontoxic, and stable aryl boronic acids and aryl halides.¹⁷ Diaryl sulfides are a common component of natural products and are frequently utilized as crucial building blocks in organic transformations since they are biologically active compounds.^{18–20} So far, various methods have been reported for the synthesis of diaryl sulfides. During the last decades, various transition metals, including palladium, cobalt,

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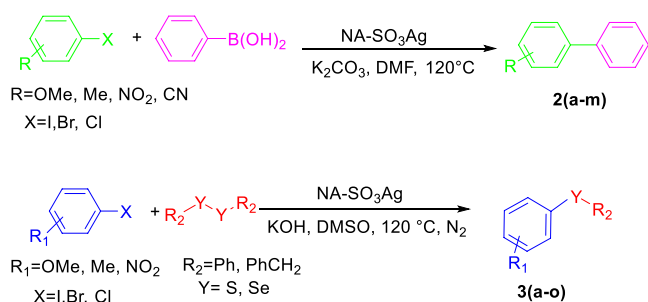
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indium, rhodium, and nickel, have been reported in this reaction. Cross-coupling aromatic halides and thiols in the presence of transition metals is the most common method for the synthesis of diaryl sulfides. In this regard, to overcome some problems with sulfur agents, such as malodor, toxicity, and volatility, new sulfur-transfer agents that are stable and odorless have been introduced, such as potassium ethyl xanthogenate, potassium thiocyanate, amino thiourea benzothiazole, etc.^{21–23}

In this work, we used natural asphalt for the synthesis of new and efficient silver-based catalysts. The reaction was carried out in the presence of disulfides as ArS donor agents. Herein, we report silver natural asphalt sulfonate (NA-SO₃Ag) as an efficient and reusable nanocatalyst for the Suzuki C–C coupling reaction, C–S, and C–Se coupling (Scheme 1). NA-SO₃Ag contains features such as easy preparation and separation, high chemical and physical stability, eco-friendliness, and reusability.

Scheme 1. NA-SO₃Ag-Catalyzed C-X (X = C, S, and Se) Bond Formation via Coupling Reactions



RESULTS AND DISCUSSION

At the first, in order to prepare the catalyst, aromatic, vinyl, and benzylic moieties that exist in the structure of natural asphalt are sulfonated in the presence of concentrated sulfuric acid. The proposed structure of the natural asphalt sulfonic acid is shown in Figure 1.

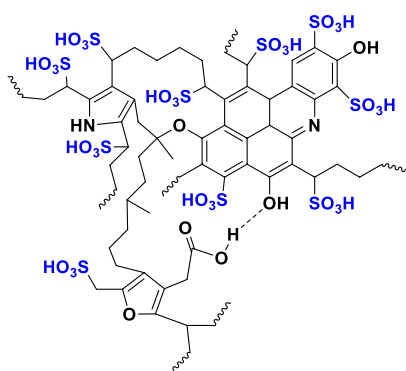
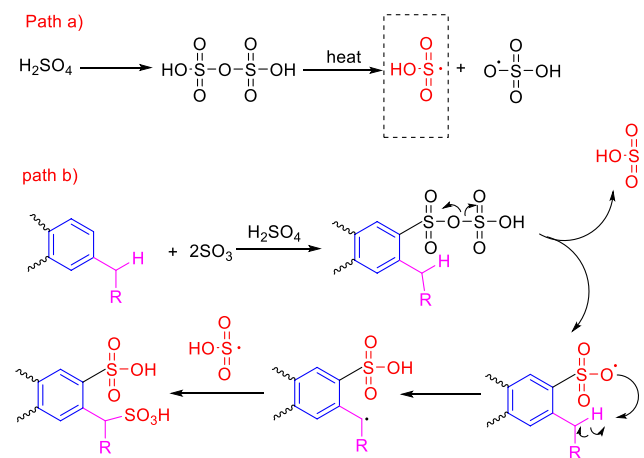


Figure 1. Part of the natural asphalt sulfonic acid structure.

Natural asphalt consists of aromatic and polycyclic rings with different carbon chains, which can be sulfonated in the presence of concentrated sulfuric acid at a high temperature. Sulfonation of natural asphalt occurs on aromatic rings and benzylic position, due to the formation of stable radicals according to the following mechanism.^{24,25} As shown in the mechanism, there are two paths for the generation of SO₃H radicals. In path a, the SO₃H radical is generated by heating concentrated sulfuric acid (oleum) at high temperature, and in path b, it is produced by

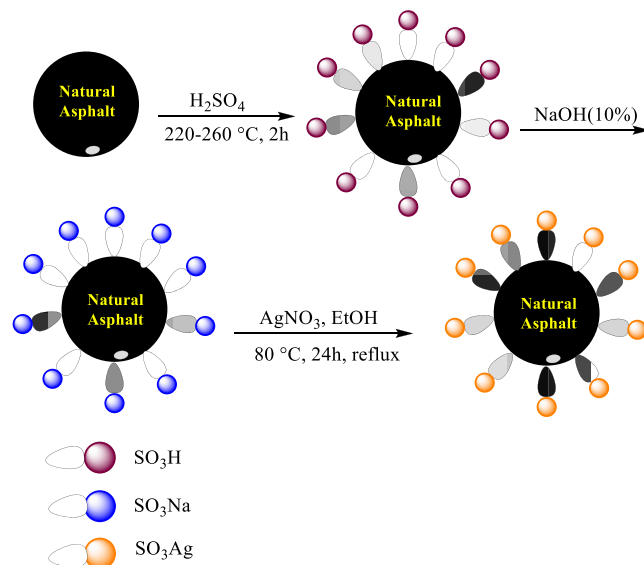
the reaction between SO₃ (2 equiv) and aryl moiety of natural asphalt under acidic conditions and at high temperatures (Scheme 2).

Scheme 2. Proposed Mechanism for Aliphatic Carbon Sulfonation



The general route for the synthesis of NA-SO₃Ag is demonstrated in Scheme 3. This nanocatalyst was prepared in

Scheme 3. General Route for the Synthesis of NA-SO₃Ag



three steps and characterized by Fourier-transform infrared (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), EDS, inductively coupled plasma (ICP), Brunauer–Emmett–Teller (BET), and X-ray diffraction (XRD) techniques.

FTIR Analysis. FTIR spectra of NA (a), NA-SO₃Na (b), and NA-SO₃Ag (c) have been shown in Figure 2. According to Figure 2a, the peaks at 3435 cm⁻¹ are related to the O–H and N–H groups, the stretching vibrations at 2851–2922 cm⁻¹ belong to the aliphatic C–H, and the peak at 1455 cm⁻¹ is attributed to the aromatic rings; also the peak at 1267 cm⁻¹ belongs to the S=O bond and approved the synthesis of NA-SO₃Na which suggested that the natural asphalt has been sulfonated successfully. Shifting some peaks such as 1730–1703

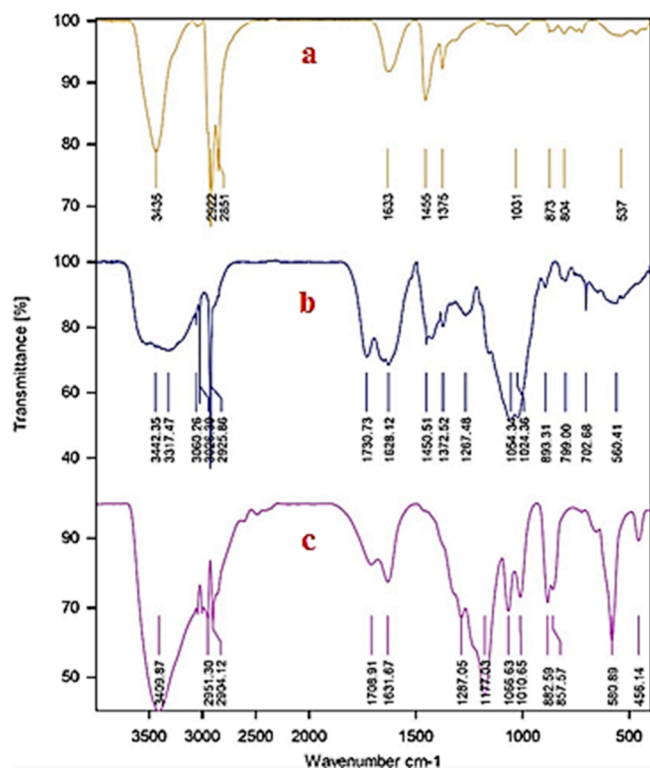


Figure 2. FTIR spectra of NA (a), NA-SO₃Na (b), and NA-SO₃Ag (c).

cm⁻¹ in Figure 2b signify the replacement of Ag with sodium in NA-SO₃Na.

SEM Analysis. SEM was used to estimate the morphology and the particle size of the nanoparticles. The SEM images of

NA-SO₃Ag are illustrated in Figure 3. According to these images, these nanoparticles have a spherical shape, and the particle sizes are on the nanometer scale of 66 nm.

EDX Analysis and ICP. Energy dispersive X-ray (EDX) analysis is one of the suitable techniques for the characterization of the elements in the structure of nanocatalysts. EDX analysis and EDS mapping of NA-SO₃Ag shown in Figures 4 and 5

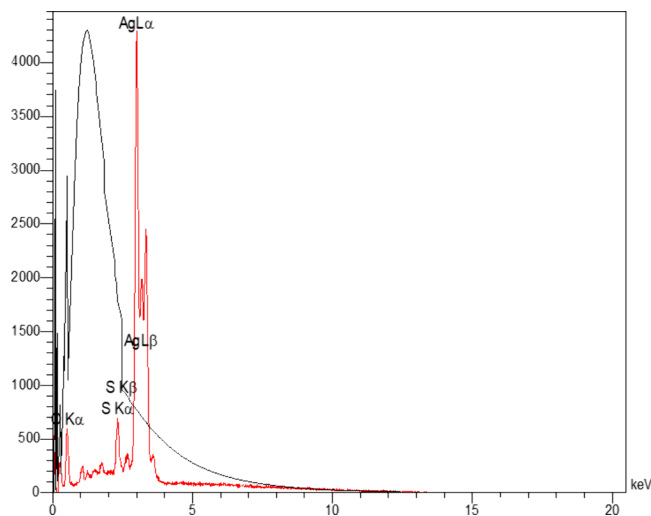


Figure 4. EDX spectrum of NA-SO₃Ag.

confirm the existence of S, O, N, and Ag elements in the structure of the synthesized catalyst. Also, the ICP analysis found the exact amount of silver loaded on the catalyst to be $1.95 \times 10^{-3} \text{ mol g}^{-1}$.

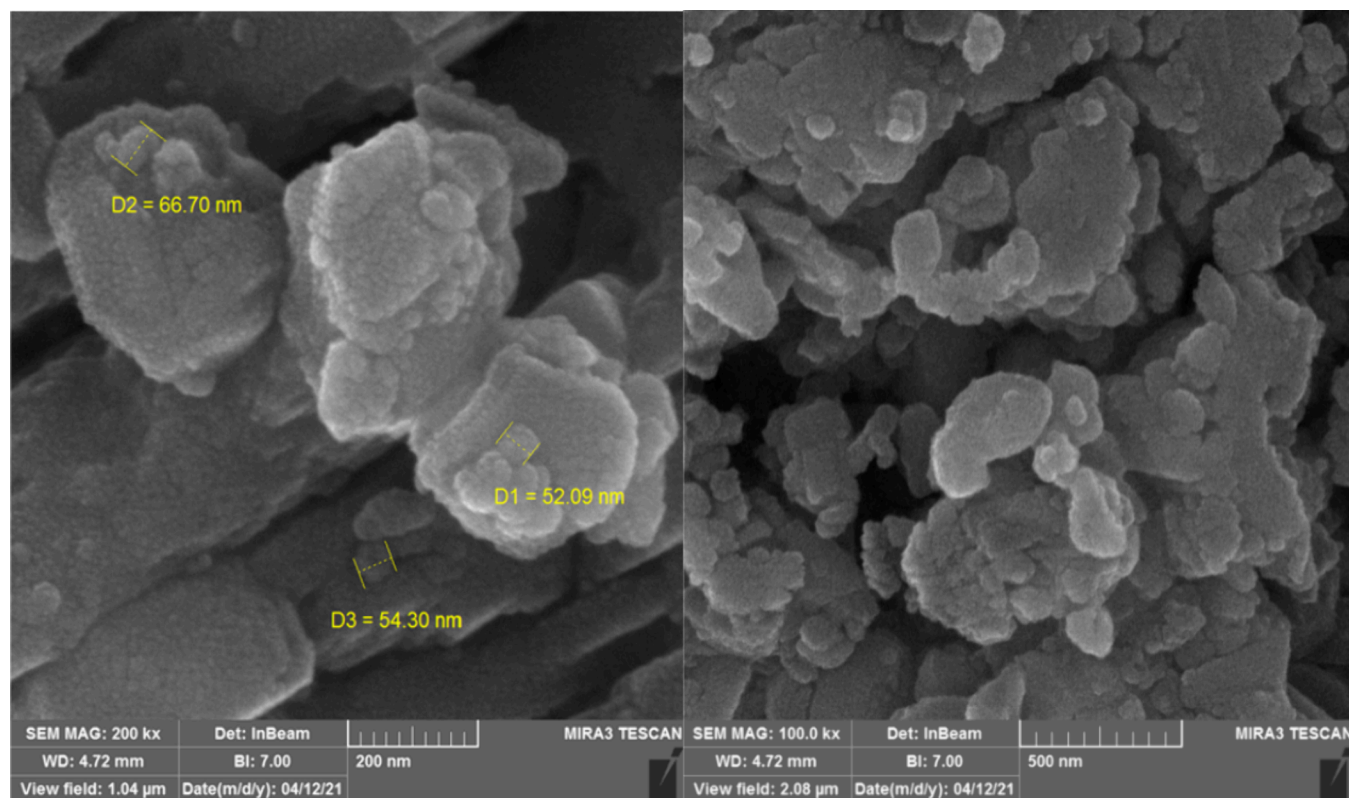


Figure 3. SEM images of NA-SO₃Ag.

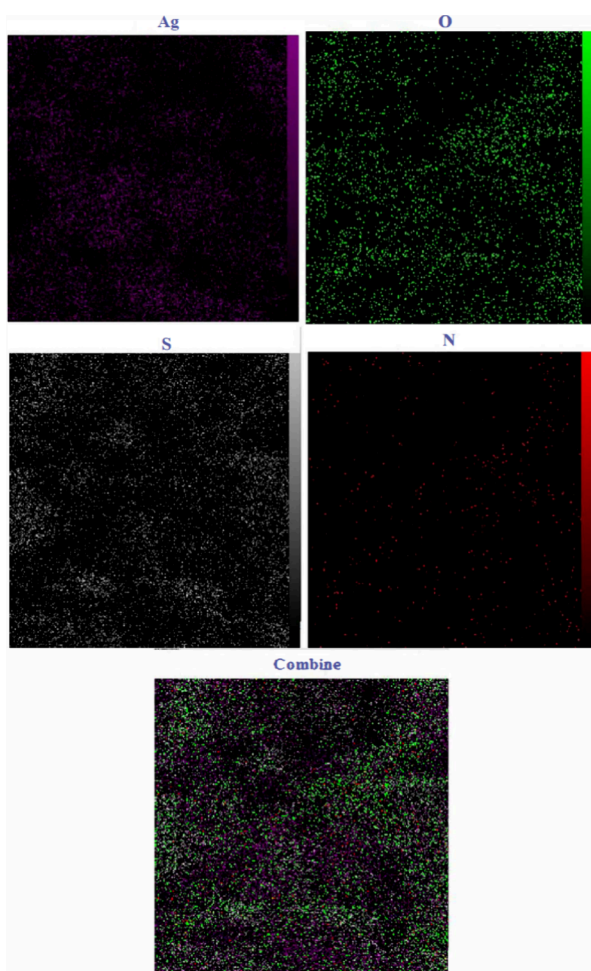


Figure 5. Elemental mapping of NA-SO₃Ag.

XRD Analysis. XRD analysis was applied to study the crystalline structures of nanocatalysts. The XRD pattern of NA-SO₃Ag is shown in Figure 6. This curve shows eight peaks at $2\theta = 19.23, 22.53, 31.03, 32.13, 39.43, 45.68, 65.93,$ and 78.98 that are in good match with the standard pattern.²⁶

TGA Analysis. The thermal stability of NA-SO₃Ag was studied by TGA analysis. The TGA curve of NA-SO₃Ag, which

is illustrated in Figure 7, shows weight losses. The weight loss below 150 °C related to the removal of physically adsorbed solvents on the surface of the catalyst, and the next weight loss appeared upper than 150 °C related to the decomposition of organic groups such as R-SO₃ in the catalyst. As shown in the TGA analysis, the synthesized catalyst has retained about 88% of its initial mass at 700 °C, which indicates its high thermal stability.

BET Analysis. BET analysis was used for the investigation of the structural properties of NA-SO₃Ag. According to the IUPAC classification, the sample exhibited type III curves. The BET curve of NA-SO₃Ag is shown in Figure 8 and shows the surface area of $6.72 \text{ m}^2\text{g}^{-1}$, and the pore diameter is 1.88 nm.

Catalytic Activity. After the synthesis and characterization of NA-SO₃Ag, its application in the C–C, C–S, and C–Se coupling reactions was studied. Herein, organic disulfides have been used to synthesize aryl sulfides instead of using aryl thiols due to aryl thiols have disadvantages such as malodor, volatile, and toxic problems.

Initially, the prepared catalyst was applied to the Suzuki cross-coupling reaction. For this purpose, the reaction of iodobenzene with phenylboronic acid was selected as a model reaction to gain optimum conditions. First, the effect of the catalyst amount on the model reaction was studied. When the model reaction was examined in the absence of NA-SO₃Ag, the reaction did not occur, and the best results were obtained with 20 mg of NA-SO₃Ag in dimethylformamide (DMF). Moreover, the selected reaction was tested under various conditions to find the efficient solvent, base, and temperature, as the best result was obtained in DMF in the presence of NA-SO₃Ag (20 mg) via using K₂CO₃ at 120 °C (the results are shown in Table 1). It is worth mentioning that this reaction was tested under optimal conditions in the presence of some silver(I) salts such as AgNO₃, AgCl, AgSO₄, and AgCrO₄ (Table 1, entries 19–22). After optimum conditions were found, some derivatives of biaryl were synthesized (Table 2)^{27–32}. Based on the results of Table 2, the aryl iodides were more reactive than aryl bromides and chlorides.

In the second part of our study, the synthesis of sulfides and selenides was studied. Therefore, to reach the optimum conditions, the reaction of iodobenzene and diphenyl disulfide was chosen as a model reaction and tested under different

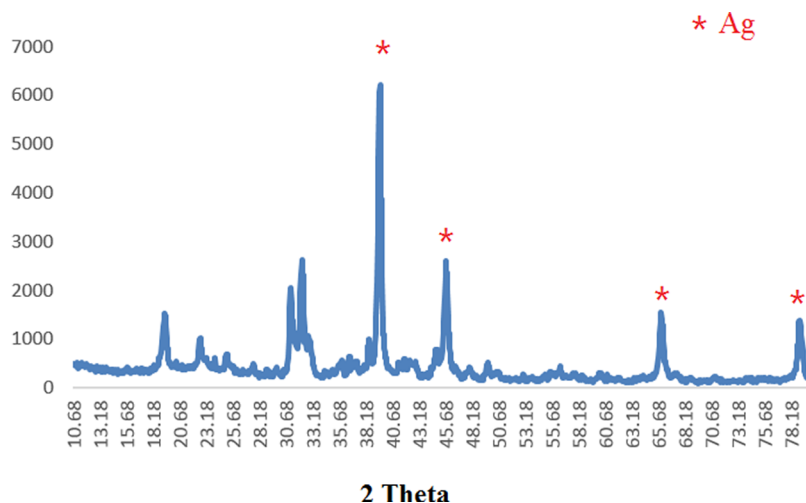


Figure 6. XRD spectrum of NA-SO₃Ag.

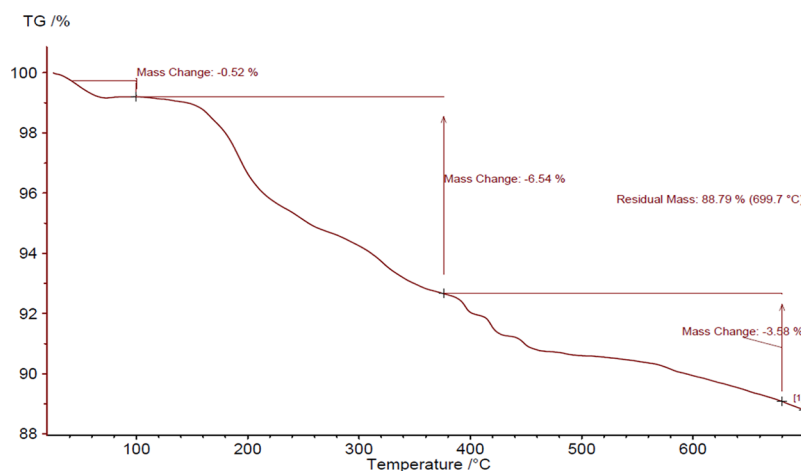


Figure 7. TGA curve of NA-SO₃Ag.

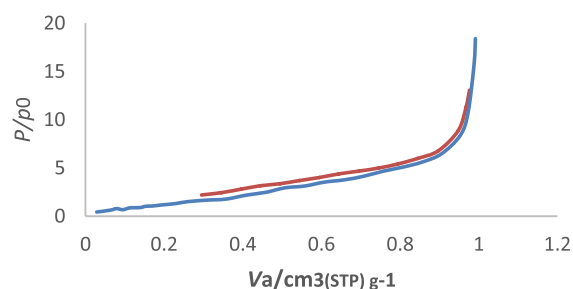


Figure 8. BET curve of NA-SO₃Ag.

conditions in the presence of various bases. The results show the best yield was obtained in dimethyl sulfoxide (DMSO) solvent using KOH and (30 mg) of NA-SO₃Ag at 120 °C (Table 3).

After finding optimum reaction conditions, we synthesized some derivatives of sulfides and selenides by using a range of different aryl halides (Table 4)^{33–36}.

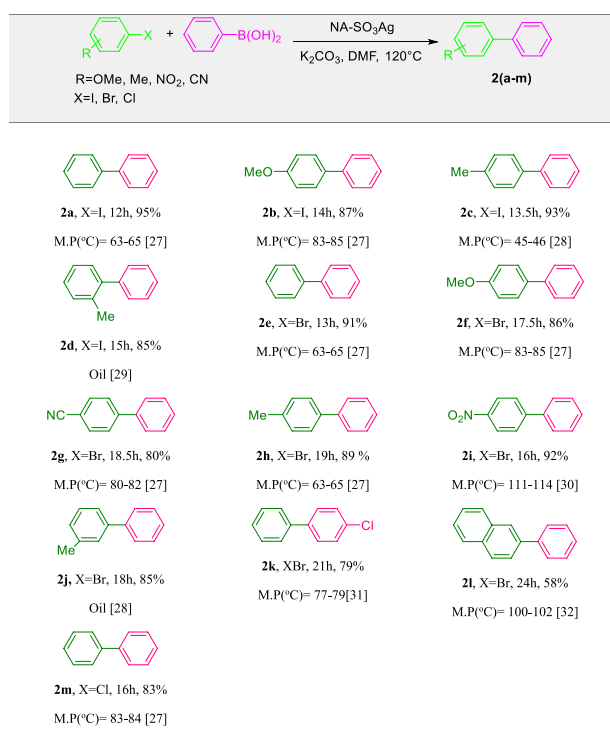
Proposed Mechanism. A mechanism for the C–S coupling is suggested in Scheme 4. Initially, intermediate (I) is formed by the oxidative addition of silver(I) to the aryl halide. Then, intermediate (II) in the presence of diphenyl disulfide is transformed to intermediate (III) by transmetalation. Afterward, intermediate (III) was formed by attacking the halide group and

Table 1. Optimization of the Reaction Conditions for the Suzuki Cross-Coupling Using NA-SO₃Ag^a

entry	temp (°C)	solvent	base	catalyst	amount of catalyst (mg)	yield ^b (%)
1	120	DMF	K ₂ CO ₃			
2	120	DMF	K ₂ CO ₃	NA-SO ₃ Ag	5	63
3	120	DMF	K ₂ CO ₃	NA-SO ₃ Ag	10	76
4	120	DMF	K ₂ CO ₃	NA-SO ₃ Ag	15	81
5	120	DMF	K ₂ CO ₃	NA-SO ₃ Ag	20	95
6	reflux	EtOH	K ₂ CO ₃	NA-SO ₃ Ag	20	52
7	reflux	H ₂ O	K ₂ CO ₃	NA-SO ₃ Ag	20	
8	reflux	toluene	K ₂ CO ₃	NA-SO ₃ Ag	20	48
9	120		K ₂ CO ₃	NA-SO ₃ Ag	20	
10	120	DMSO	K ₂ CO ₃	NA-SO ₃ Ag	20	90
11	120	DMF	KOH	NA-SO ₃ Ag	20	60
12	120	DMF	NaOH	NA-SO ₃ Ag	20	58
13	120	DMF	(CH ₃) ₃ COK	NA-SO ₃ Ag	20	43
14	120	DMF	TBAOH	NA-SO ₃ Ag	20	trace
15	r. t.	DMF	K ₂ CO ₃	NA-SO ₃ Ag	20	trace
16	40	DMF	K ₂ CO ₃	NA-SO ₃ Ag	20	61
17	60	DMF	K ₂ CO ₃	NA-SO ₃ Ag	20	73
18	90	DMF	K ₂ CO ₃	NA-SO ₃ Ag	20	85
19	120	DMF	K ₂ CO ₃	AgNO ₃	20	50
20	120	DMF	K ₂ CO ₃	AgCl	20	40
21	120	DMF	K ₂ CO ₃	AgSO ₄	20	50
22	120	DMF	K ₂ CO ₃	AgCrO ₄	20	N.R. ^c

^aReaction conditions: phenylboronic acid (1.2 mmol), iodobenzene (1 mmol), and base (3 mmol), cat, temp (°C), in 2 mL of solvent for 12 h.

^bIsolated yields. ^cNo reaction.

Table 2. NA-SO₃Ag-Catalyzed Biaryl Synthesis via Suzuki Reaction^a

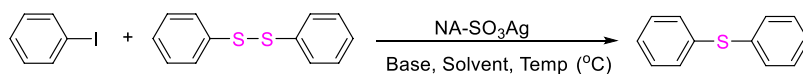
^aReaction conditions: phenylboronic acid (1.2 mmol), arylhalide (1 mmol), K₂CO₃ (3 mmol), and NA-SO₃Ag (20 mg) at 120 °C in 2 mL of DMF.

the exit of the PhSX group. Finally, reductive elimination of the previous intermediate is led to the formation of diaryl disulfide.

The plausible mechanism for the Suzuki cross-coupling reaction has been reported in the literature, as shown in Scheme 5. Herein, intermediate (II) is produced from oxidative addition of aryl halide to silver (I). Then, intermediate II is transformed to intermediate (III) by transmetalation and X replacement by Ph. Finally, biaryl is synthesized by reductive elimination of the intermediate (III) and separation of nanocatalyst.

To study and investigate the capability of the recovery and reusability of the NA-SO₃Ag, the synthesis of biphenyl (**2a**) and diphenyl sulfide (**3a**) was studied. For this purpose, after completion of the reaction, the catalyst was separated from the reaction mixture using filtration, washed with ethanol, dried, and reused for the next runs; results show that the catalyst can be reused six times while maintaining its catalytic activity (Figure 9). Also, the XRD spectrum, SEM image, and FTIR spectrum of the catalyst before and after recovery (Figures 10,11,12) were found in good similarity due to the stability of NA-SO₃Ag under reaction conditions and after recovery. In addition, the ICP result after recovery is $1.7 \times 10^{-3} \text{ mol g}^{-1}$, which indicates the strong stabilization of silver on the surface of natural asphalt sulfate.

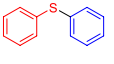
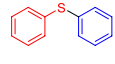
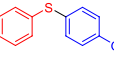
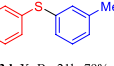
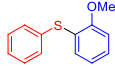
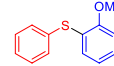
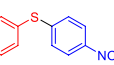
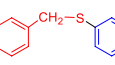
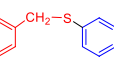
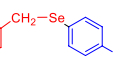
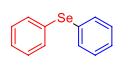
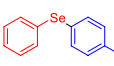
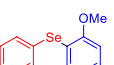
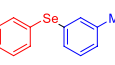
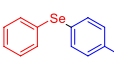
Comparison of the Catalyst Activity. The efficiency of NA-SO₃Ag as a catalyst was demonstrated by comparing it to those of the catalysts reported in the literature. Table 5 presents the results associated with the coupling of iodobenzene and diphenyl disulfide/diselenide in order to synthesize **3b** and **3k**. As shown in Table 5, NA-SO₃Ag catalyzed the reaction and better than other reported catalysts.

Table 3. Seeking Optimization Reaction Conditions: NA-SO₃Ag-Catalyzed Coupling Reaction of Iodobenzene with Diphenyl Disulfide^a

entry	temperature (°C)	solvent	base	catalyst	amount of catalyst (mg)	yield ^b (%)
1	120	DMSO	KOH	NA-SO ₃ Ag		
2	120	DMSO	KOH	NA-SO ₃ Ag	5	40
3	120	DMSO	KOH	NA-SO ₃ Ag	10	60
4	120	DMSO	KOH	NA-SO ₃ Ag	15	63
5	120	DMSO	KOH	NA-SO ₃ Ag	20	79
6	120	DMSO	KOH	NA-SO ₃ Ag	30	91
7	reflux	toluene	KOH	NA-SO ₃ Ag	30	trace
8	120	DMF	KOH	NA-SO ₃ Ag	30	79
9	reflux	EtOH	KOH	NA-SO ₃ Ag	30	63
10	reflux	H ₂ O	KOH	NA-SO ₃ Ag	30	55
11	120	DMSO	K ₂ CO ₃	NA-SO ₃ Ag	30	50
12	120	DMSO	NaOH	NA-SO ₃ Ag	30	59
13	120	DMSO	Me ₃ COK	NA-SO ₃ Ag	30	42
14	120	DMSO	TBAOH	NA-SO ₃ Ag	30	trace
15	r. t.	DMSO	KOH	NA-SO ₃ Ag	30	trace
16	40	DMSO	KOH	NA-SO ₃ Ag	30	50
17	60	DMSO	KOH	NA-SO ₃ Ag	30	60
18	90	DMSO	KOH	NA-SO ₃ Ag	30	82
19	120	DMSO	KOH	AgNO ₃	30	30
20	120	DMSO	KOH	AgCl	30	30
21	120	DMSO	KOH	AgSO ₄	30	40
22	120	DMSO	KOH	AgCrO ₄	30	N. R ^c

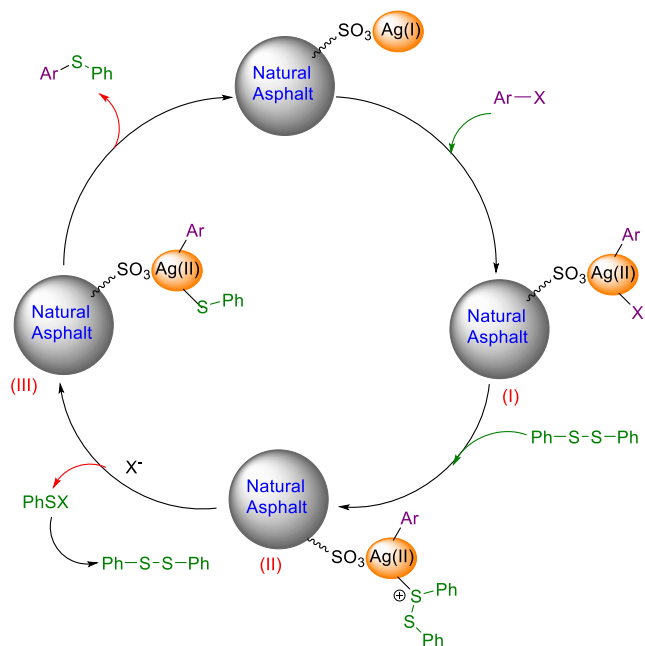
^aReaction conditions: iodobenzene (2.2 mmol), diphenyl disulfide (1 mmol), and base (3 mmol), in 2 mL of solvent for 16 h. ^bIsolated yields. ^cNo reaction.

Table 4. Ag- NAS Catalyzed Coupling Reaction of Aryl Halides and Diaryl Disulfides/Diaryl Selenides^a

$\text{R}_1\text{-C}_6\text{H}_4\text{-X} + \text{R}_2\text{-Y-Y-R}_2 \xrightarrow[\text{KOH, DMSO, 120 }^\circ\text{C, N}_2]{\text{NA-SO}_3\text{Ag}} \text{R}_1\text{-C}_6\text{H}_4\text{-Y-R}_2$		
$\text{R}_1 = \text{OMe, Me, NO}_2$ $\text{R}_2 = \text{Ph, PhCH}_2$ $\text{X} = \text{I, Br, Cl}$ $\text{Y} = \text{S, Se}$		
 3a, X=I, 25h, 58% Oil [33]	 3b, X=I, 16h, 91% Oil [33]	 3c, X=I, 18h, 80% Oil [34]
 3d, X=Br, 21h, 79% Oil [35]	 3e, X=I, 19h, 75% Oil [33]	 3f, X=Br, 20h, 63% Oil [35]
 3g, X=Br, 22h, 88% Oil [36]	 3h, X=I, 17h, 89% Oil [33]	 3i, X=I, 16h, 75% Oil [35]
 3j, X=I, 18h, 81% Oil [34]	 3k, X=I, 16h, 83% Oil [33]	 3l, X=I, 17h, 72% Oil [32]
 3m, X=I, 19h, 58% Oil [20]	 3n, X=Br, 20h, 56% Oil [33]	 3o, X=Br, 27h, 78% Oil [20]

^aReaction conditions: aryl halide (2.2 mmol), disulfide (1 mmol), or diselenide (1 mmol) KOH (3 mmol), NA-SO₃Ag (30 mg), 120 °C, 2 mL of DMSO.

Scheme 4. Possible Mechanism for the NA-SO₃Ag-Catalyzed Coupling Reaction of Diphenyl Disulfide and Aryl Halide



EXPERIMENTAL SECTION

Apparatus and Materials. Natural asphalt was purchased from the Ghiran Shimie Javan company in Ilam, Iran, and the

Scheme 5. Possible Mechanism for the Ag-Catalyzed Suzuki Coupling Reactions

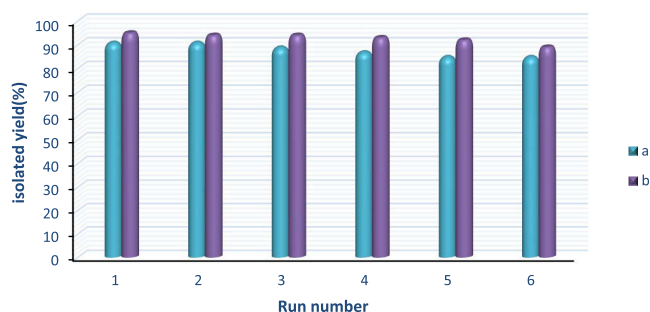
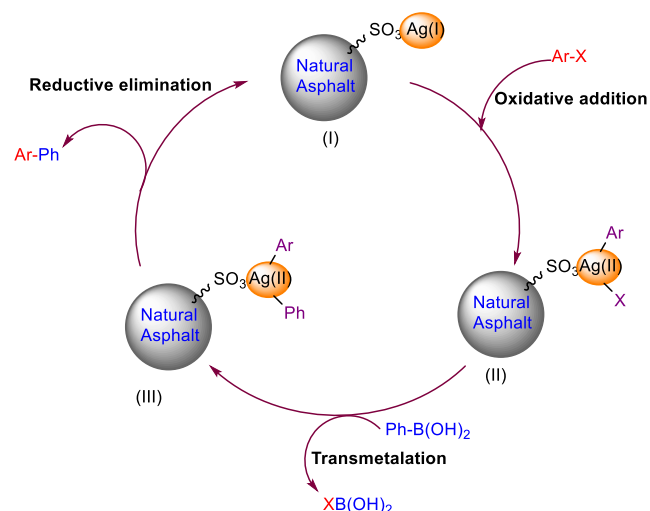


Figure 9. Recovery of NA-SO₃Ag in the synthesis of biphenyl (2a) and diphenyl sulfide (3a).

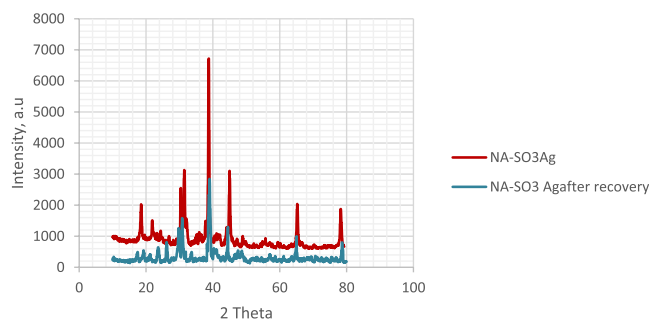


Figure 10. XRD curves of fresh NA-SO₃Ag (red) and after recovery (blue).

chemicals were from Fluka and Merck Chemical Companies. The reactions were monitored with TLC on silica-gel Polygram SILG/UV254 plates. FTIR was performed using an FTIR-8300 spectrometer made by Shimadzu. Proton nuclear magnetic resonance (¹H NMR) spectroscopy was also performed on Bruker AVANCE DPX-400 and DPX-500 spectrometers. Chemical shifts were reported in parts per million relative to TMS as the internal standard. The morphology of the catalyst was examined by performing SEM using a Mira 3-XMU. The elemental composition was determined using EDS and Mira 3-XMU. XRD was investigated by using a Holland Philips X, and the TGA curve was recorded by using a PL-STA 1500 device manufactured by Thermal Sciences.

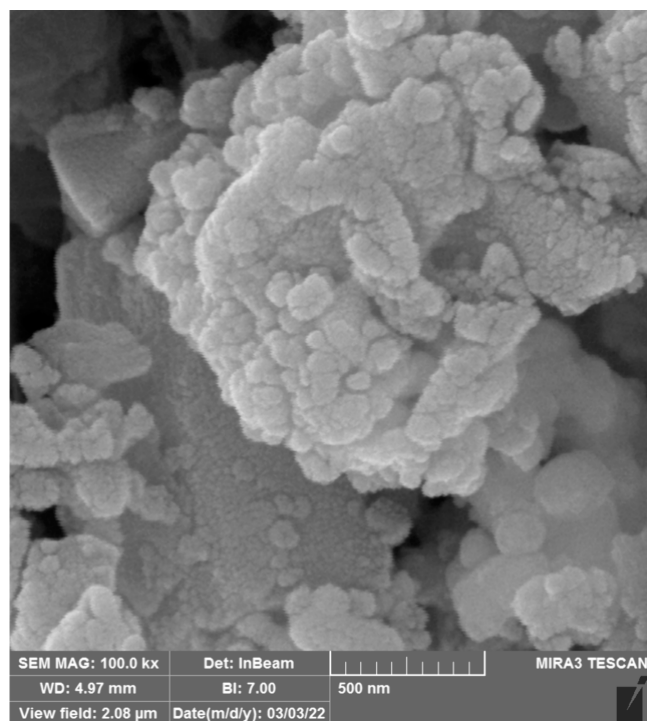


Figure 11. SEM image of NA-SO₃Ag after recovery.

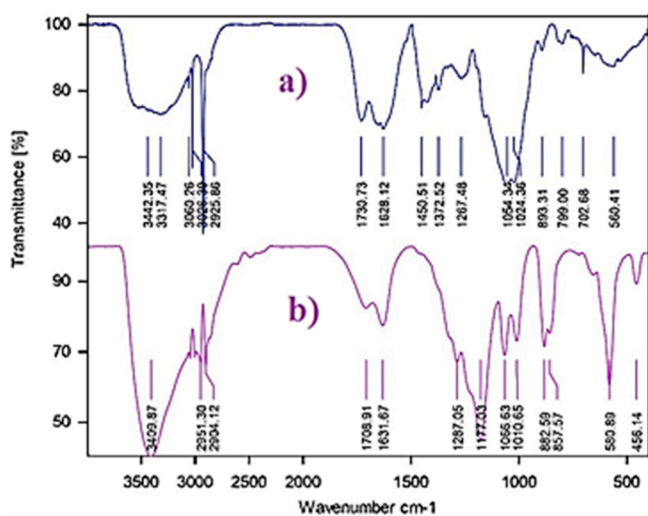


Figure 12. FTIR spectrum of fresh NA-SO₃Ag (a) and after recovery (b).

Catalyst (NA-SO₃Ag) Synthesis. *Synthesis of Natural Asphalt Sulfonic Acid.* For the synthesis of NA-SO₃, 1 g of natural asphalt was stirred in 2 mL of concentrated sulfuric acid at 220–260 °C for 2 h. After cooling the reaction mixture to room temperature, slowly add to distilled water (20 mL). Finally, in order to obtain natural asphalt sulfonic acid (NA-SO₃) the reaction mixture was filtered, washed with water, and dried at 100 °C in the oven.

Synthesis of Sodium Natural Asphalt Sulfonate (NA-SO₃Na). A mixture of NA-SO₃ (1 g) was stirred in 20 mL of NaOH solution (10%) at room temperature for 1 h. Then, the solvent was evaporated and dried at 100 °C in the oven. Finally, 1.5 g of product (NA-SO₃Na) was obtained.

Conversion of NA-SO₃Na to NA-SO₃Ag. In this step, a mixture of AgNO₃ (0.2 g) and Na-NA-SO₃ (1 g) was stirred in 20 mL of EtOH at 80 °C for 2 h. After completion, the product was separated using filtration, washed with EtOH, and dried at 70 °C in an oven.

General Procedure for the Suzuki Reaction. A mixture of aryl halide (1 mmol), phenylboronic acid (PhB(OH)₂) (1.2 mmol), K₂CO₃ (3 mmol), and NA-SO₃Ag (15 mg) was stirred at 120 °C in DMF, and the progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated using filtration, and the product was extracted with ethyl acetate. Then, the solvent was evaporated, and pure biphenyl derivatives were prepared by plate chromatography in good to excellent yields.

General Procedure for the Synthesis of Sulfides/Selenide. A mixture of aryl halide (2.2 mmol), organic disulfide/diselenide (1 mmol), KOH (3 mmol), and NA-SO₃Ag (30 mg) was stirred at 120 °C in DMSO, and the progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by using filtration, and the product was extracted with ethyl acetate. Then, the solvent was evaporated, and pure sulfide and selenide compounds were prepared by plate chromatography.

CONCLUSIONS

In this work, NA-SO₃Ag was utilized and characterized with various techniques in order to develop and introduce a new and mineral carbonaceous class compound. Then, the activity of NA-SO₃Ag in the C–S, C–Se, and C–C coupling reactions was studied. The results obtained from ICP analysis for fresh NA-SO₃Ag and after recovery confirmed that the silver was attached to the natural asphalt sulfonate well. Also, TGA results showed that the synthesized catalyst has high thermal stability and is suitable for high-temperature reactions. In this work, a variety of aromatic sulfides and selenides, and biaryls, including different functional groups, were successfully converted into correspond-

Table 5. Comparison Results of NA-SO₃Ag with Other Catalysts in the Synthesis of 3b and 3k Products

entry	catalyst	conditions	product	time (h)	yield (%)	[ref]
1	Ni(II)Br ₂ -bpy-Zn	DMF, 110 °C	3b	18	81	37
2	CuFe ₂ O ₄	KOH, DMSO, 120 °C	3k	18	98	38
3	Cu ₂ O-bpy-Mg	DMF, 120 °C	3k	30	94	39
4	Cu ₂ O-bpy-Mg	DMF, 120 °C	3b	18	90	39
5	Cu(I)bipyridyl-Mg	DMF, microwaves, 200 °C	3b	6	60	40
6	Cu(I)bipyridyl-Mg	DMF, microwaves, 200 °C	3k	6	62	40
7	CuFe ₂ O ₄	CS ₂ CO ₃ , DMSO, 100 °C	3b	24	98	41
8	NA-SO ₃ Ag	KOH, DMSO, 120 °C	3b	16	91	this work
9	NA-SO ₃ Ag	KOH, DMSO, 120 °C	3k	16	83	this work

ing products in good to excellent yields. Among the advantages of this work, we can mention the use of a diphenyl disulfide (as an ArS transfer agent), which is stable and odorless.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c04447>.

Selected spectral data and ^1H and ^{13}C NMR of some of compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Mohammad Soleiman-Beigi – Department of Chemistry, Basic of Sciences Faculty, Ilam University, 69315-516 Ilam, Iran;
orcid.org/0000-0002-7805-5066;
Email: m.soleimanbeigi@ilam.ac.ir, SoleimanBeigi@yahoo.com

Authors

Touba Zolfaghari – Department of Chemistry, Basic of Sciences Faculty, Ilam University, 69315-516 Ilam, Iran
Homa Kohzadi – Department of Chemistry, Basic of Sciences Faculty, Ilam University, 69315-516 Ilam, Iran

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.3c04447>

Notes

The authors declare no competing financial interest.

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