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Construction and characterization of a magnetic nanoparticle-supported Cu complex: a stable and active nanocatalyst for synthesis of heteroaryl-aryl and di-heteroaryl sulfides†

Yutong Fang,^a Songlin Chen^{*bc} and Li-Yuan Chang^{†d}

Diaryl and di-heteroaryl sulfides exist in the structure of many drugs and important biological compounds, also these compounds are well-known in medicinal chemistry due to important biological and pharmaceutical activities. Therefore, the development of novel, ecofriendly and efficient catalytic systems for the preparation of diaryl and di-heteroaryl sulfides is a very attractive and important challenge in organic synthesis. In this attractive methodology, we wish to introduce Fe₃O₄-supported 3-amino-4-mercaptobenzoic acid copper complex (Fe₃O₄@AMBA-CuI) nanomaterials as a novel and efficient magnetically recoverable catalyst for the preparation of heteroaryl-aryl and di-heteroaryl sulfides with high yields through reaction of heteroaryl halides with aryl or heteroaryl boronic acids and S₈ as the sulfur source under ecofriendly conditions. This catalytic system was very efficient and practical for a diverse range of heteroaryl substrates including benzothiazole, benzoxazole, benzimidazole, oxadiazole, benzofuran, and imidazo[1,2-*a*]pyridine, because the desired diaryl and di-heteroaryl sulfides were prepared with high yields. The reusability-experiments revealed that the Fe₃O₄@AMBA-CuI nanocatalyst can be magnetically separated and reused at least six times without a significant decrease in its catalytic activity. VSM and ICP-OES analyses confirmed that despite using the Fe₃O₄@AMBA-CuI nanocatalyst 6 times, the magnetic properties and stability of the catalyst were still maintained. Although all the obtained heteroaryl-aryl and di-heteroaryl sulfide products are known and previously reported, the synthesis of this number of heteroaryl-aryl and di-heteroaryl sulfides has never been reported by any previous methods.

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Introduction

Catalysts are one of the key factors or reagents of most chemical transformations.¹ Most industrial and chemical processes and almost all chemical reactions require catalysts.^{2–4} Generally, catalysts are divided into two large categories, homogeneous and heterogeneous catalysts.^{5,6} Homogeneous catalysts show more activity than heterogeneous catalysts due to their high dispersion.^{7–10} But the main problem in homogeneous catalysts is their difficult separation from the reaction mixture, often associated with the production of large amounts of waste and high energy consumption.^{11–13} But in heterogeneous catalysis

systems, the problem of catalyst separation can be solved by simple methods such as centrifugation.¹⁴ Therefore, the best catalytic system is one that has the advantages of both homogeneous and heterogeneous catalysts.¹⁵ Stabilization of the desired catalyst on a solid substrate was considered as an ideal solution to prepare efficient and green catalysts.^{16–19} In the new century, all eyes turned towards nanotechnology in catalyst science because nanoparticles have valuable properties.^{20–22} In the last decade, the immobilization of transition metals on nanoparticles to prepare an environmentally friendly, separable and efficient catalyst has been used as a popular catalytic system.^{23–25} Heterostructure/hybrid catalysts offer a compelling array of advantages, prominently characterized by their ability to amalgamate the distinctive merits of individual components.^{26,27} By fusing different materials into a heterostructure, these catalysts harness a synergistic effect that enhances overall performance. One key advantage lies in the combination of complementary properties, allowing for the optimization of catalytic activity through the cooperative interaction of diverse components.^{28,29} This integration facilitates improved reactivity, efficient charge transfer, and, consequently, heightened

^aSinopec Research Institute of Petroleum Processing, Beijing 100089, China

^bDepartment of Basics, Naval University of Engineering, Wuhan 430030, Hubei, China. E-mail: chensonglin0170@163.com

^cSchool of Resource and Environmental Engineering, Wuhan University of Science and Technology, Wuhan 430070, Hubei, China

^dInstitute of Chemical and Nanotechnology Research, Shanghai, China. E-mail: liyuanchang839@gmail.com

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catalytic efficiency.^{30,31} Heterostructure catalysts, exemplified by their capacity to merge the strengths of varied materials, transcend the limitations of traditional catalysts.^{32,33} The versatility inherent in these catalysts enables their customization for specific reactions, contributing to their applicability across a wide range of chemical processes.^{34–36} In essence, the advantages of heterostructure/hybrid catalysts lie in their ability to go beyond the capabilities of individual components, offering a versatile and efficient platform for catalyzing diverse reactions in the realm of materials science and chemical engineering.

Among nanomaterials, magnetic nanoparticles have attracted the attention of many researchers in catalysis processes due to their unique characteristics.^{37,38} During the last decade, the research on catalytic application of magnetic nanoparticles has been studied significantly and it is due to its simple synthesis, low cost and relatively high sensitivity.^{39–42} An outstanding feature of the catalysts immobilized on the magnetic nanoparticles is that they are easily separated from the reaction environment by applying an external magnetic field.^{43,44} Surface modification of magnetic nanoparticles is usually done easily and the synthesized nanomagnetic-catalyst has high stability and efficiency and is easily separated from the reaction mixture.^{45–47}

Research on coupling reactions is always a very attractive and ideal challenge for chemists because these reactions are usually difficult and under harsh conditions.^{48,49} One of the most popular reactions in this field is research on the formation of sulfur-carbon bonds (sulfides) through C–S coupling reactions.^{50,51} Sulfides are organic compounds that have a wide variety of applications in organic chemistry, medicine, and biochemistry.^{52–54} In addition, many natural compounds, amino acids and enzymes of living organisms either have C–S bonds or are used for the synthesis of sulfides.⁵⁵ Diaryl and di-heteroaryl sulfides are an important category of compounds containing

C–S bonds that have important medicinal properties such as anti-inflammatory, treatment of diabetes, Alzheimer's, Parkinson's disease or as an inhibitor for the treatment of human immunodeficiency virus, asthma, obstructive pulmonary disease, platelet aggregation inhibitors or anti-cancer.^{56–59} Diaryl and heteroaryl sulfides exist in the structure of many drugs and important biological compounds, some examples of which are shown in Fig. 1.^{59–62} So far, many methods have been reported for the preparation of diaryl sulfides, but most of these methods, despite their advantages, also have a series of disadvantages, such as the use of expensive catalysts, toxic solvents, difficult reaction conditions, and long time.

As Cu based catalysts are the most efficient catalysts in this process, in this attractive methodology, we wish to introduce AMBA-CuI functionalized Fe_3O_4 nanomaterials as a novel and efficient magnetically recoverable catalyst for the preparation of heteroaryl-aryl and di-heteroaryl sulfides with high yields through reaction of heteroaryl halides with aryl or heteroaryl boronic acids and S_8 as sulfur source under ecofriendly conditions.

Result and discussion

Preparation of Fe_3O_4 @AMBA-CuI nanocatalyst

The stepwise preparation of Fe_3O_4 @AMBA-CuI nanocatalyst is shown in Scheme 1. First, magnetic Fe_3O_4 nanoparticles coated with 3-amino-4-mercaptobenzoic acid (AMBA) in order to fabricate Fe_3O_4 @AMBA nanomaterial as ligand. Then, CuI was immobilized on the Fe_3O_4 @AMBA ligand at refluxing ethanol to construct Fe_3O_4 @AMBA-CuI nanocatalyst.

Characterization of Fe_3O_4 @AMBA-CuI nanocatalyst

The structure of Fe_3O_4 @AMBA-CuI nanocatalyst was well characterized with a number of spectroscopic techniques.

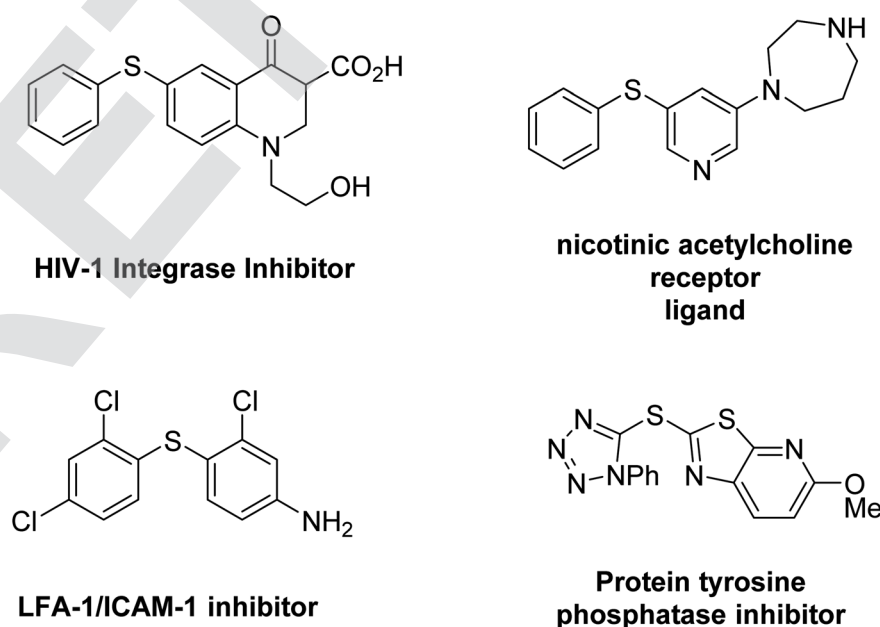
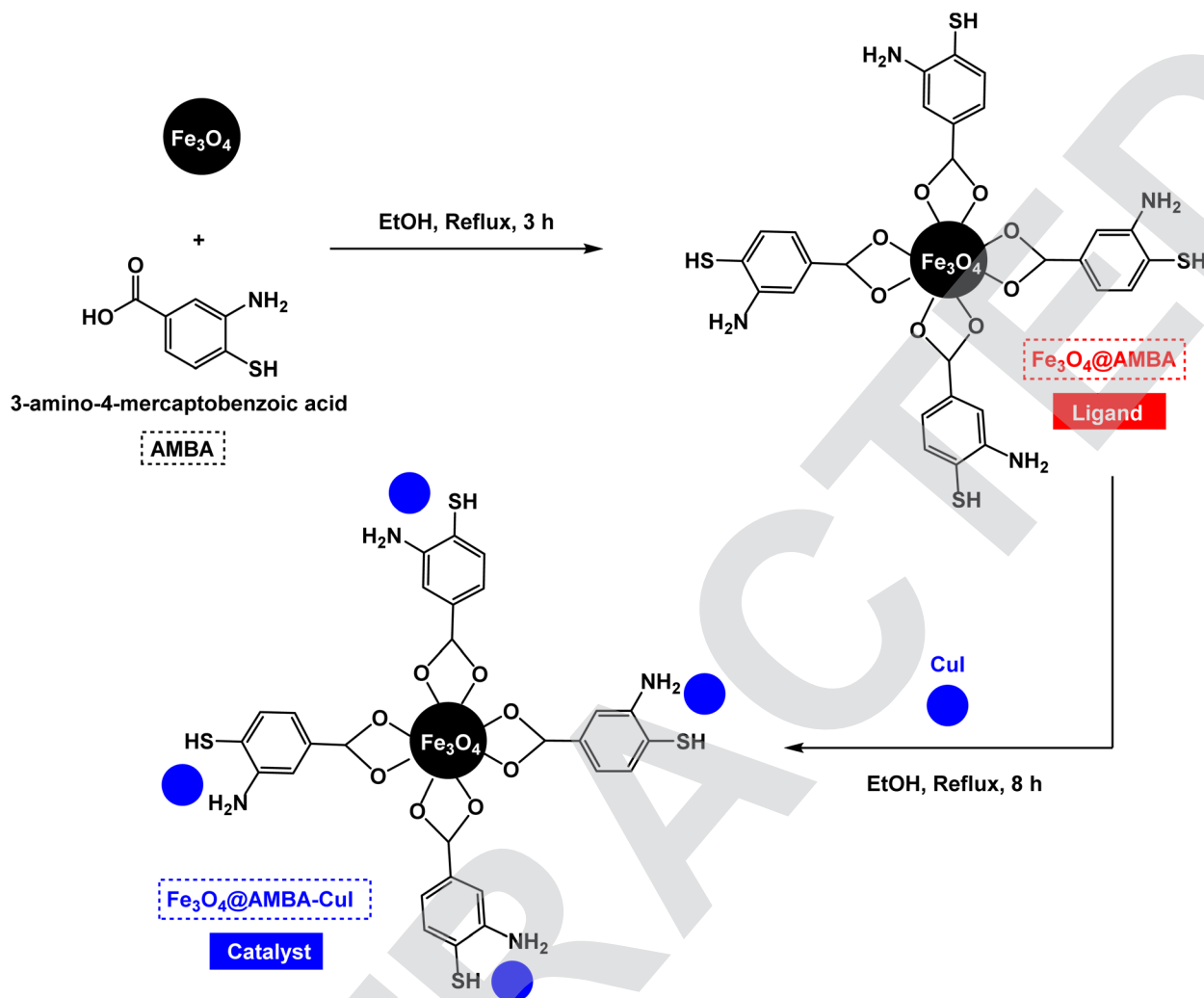


Fig. 1 Valuable biological and bioactive molecules with diaryl or heteroaryl sulfide structure.





Scheme 1 General schematic for fabrication of $\text{Fe}_3\text{O}_4@AMBA\text{-CuI}$ nanocatalyst.

FT-IR spectroscopy. In order to understand functional groups supported on magnetic nanoparticles, FT-IR spectra of $\text{Fe}_3\text{O}_4@AMBA$ ligand and $\text{Fe}_3\text{O}_4@AMBA\text{-CuI}$ nanocatalyst was taken. As shown in Fig. 2, the presence of a specific peak in the

region of 580 cm^{-1} confirms the iron-oxygen bond. The presence of hydroxyl groups was determined by the broad peak in the region of approximately 3400 cm^{-1} . Also, the presence of a broad peak in the region of $2800\text{--}3000\text{ cm}^{-1}$ is related to C-H

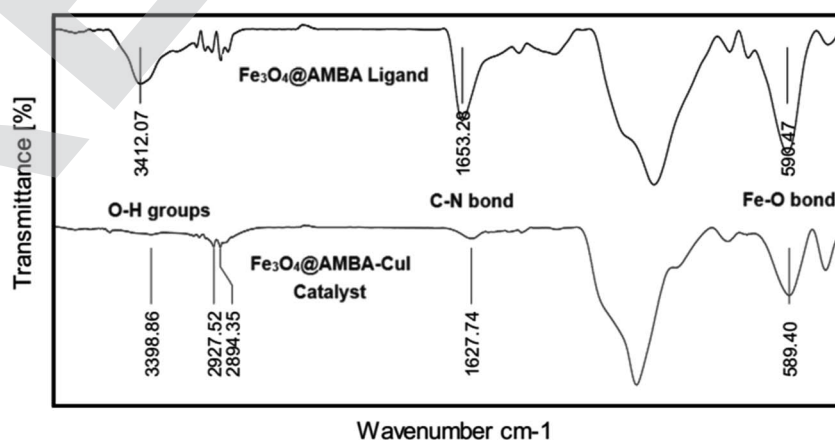


Fig. 2 FT-IR spectra of $\text{Fe}_3\text{O}_4@AMBA$ ligand and $\text{Fe}_3\text{O}_4@AMBA\text{-CuI}$ nanocatalyst.



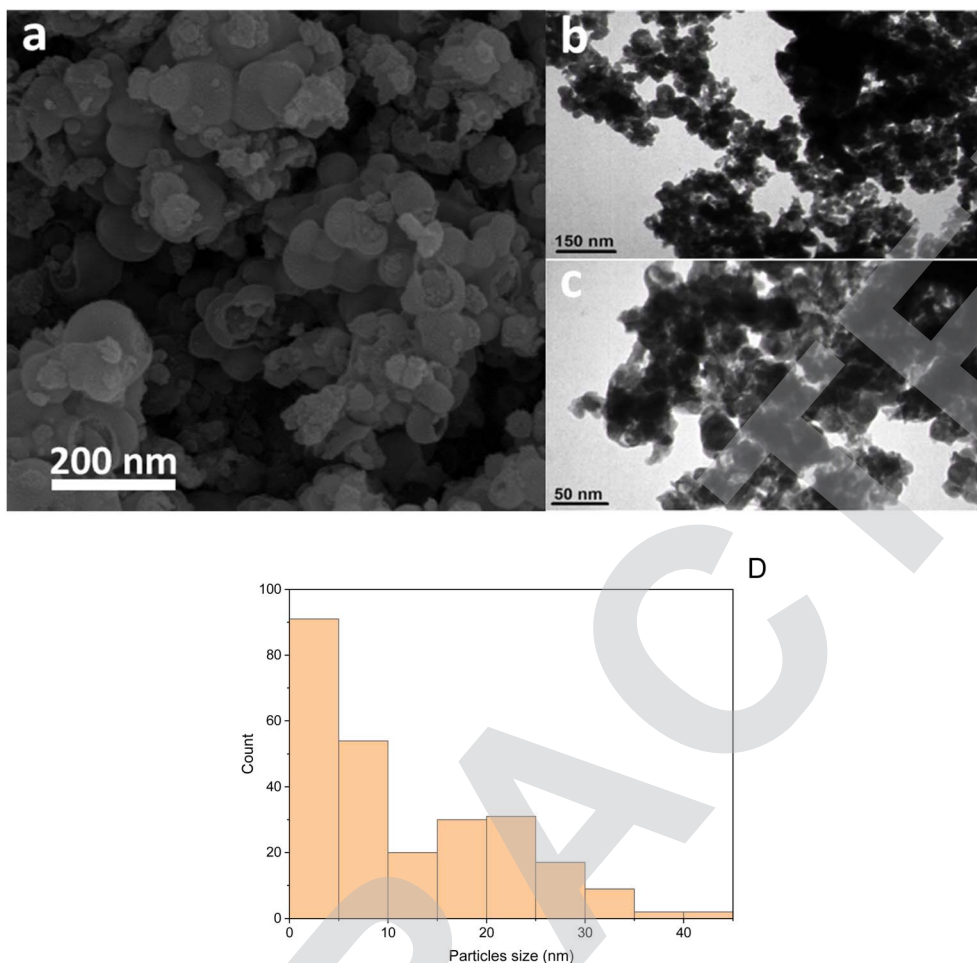


Fig. 3 (a) SEM, (b and c) TEM images of $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ nanocatalyst at different magnifications and (d) particles distribution histogram.

bonds in aromatic ring. The peak related to the C–N bond was observed in the region of 1630 cm^{-1} . Compared to the spectrum of the $\text{Fe}_3\text{O}_4\text{@AMBA}$ ligand, the C–N peak in the catalyst shifted to the lower region (1627 cm^{-1}), which indicates the fixation of copper metal on the ligand.

SEM and TEM analysis. The morphology and structure of particles in $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ nanocatalyst was studied by SEM and TEM photographs. The SEM and TEM images clearly showed that the formed particles are spherical and uniform and their size is in the range of nanometers. TEM images and histogram shown that the particles have a size in the range of 20 nm Fig. 3.

EDX, elemental mapping and ICP-OES analysis. In order to understand the elements in the $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ nanocatalyst structure, EDX and elemental mapping techniques were used (Fig. 4 and 5). These techniques confirmed the presence of Fe (47.31 wt%), and O (32.34 wt%), as the main elements of Fe_3O_4 catalytic support, in addition the presence of C (12.81 wt%), N (3.54 wt%), S (2.73 wt%) and Cu (1.27 wt%) in the structure confirm the formation of $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ nanocatalyst. It is worth to mention that the distribution pattern of Cu species is in excellent with the nitrogen and sulfur species on catalyst surface that confirm their correlation and complexation. ICP-

OES analysis was used to find out the amount of copper in the structure of the $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ nanocatalyst, and the results showed that the amount of Cu in the structure of the nanocatalyst is $14.32 \times 10^{-5}\text{ mol g}^{-1}$ which confirm the presence of copper in structure and successful complexation of surface functionalities with the Cu ions.

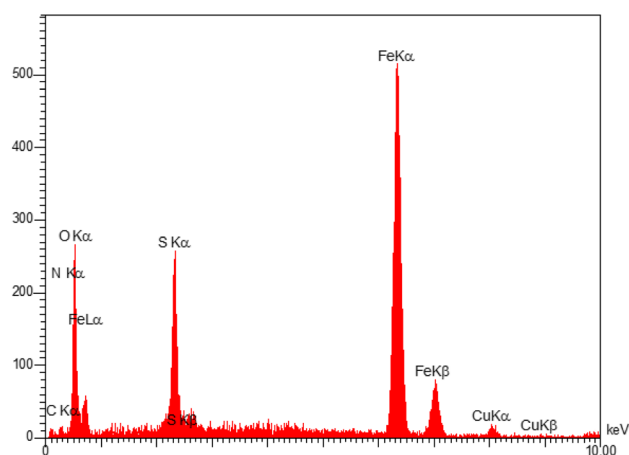


Fig. 4 EDX analysis of $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ nanocatalyst.



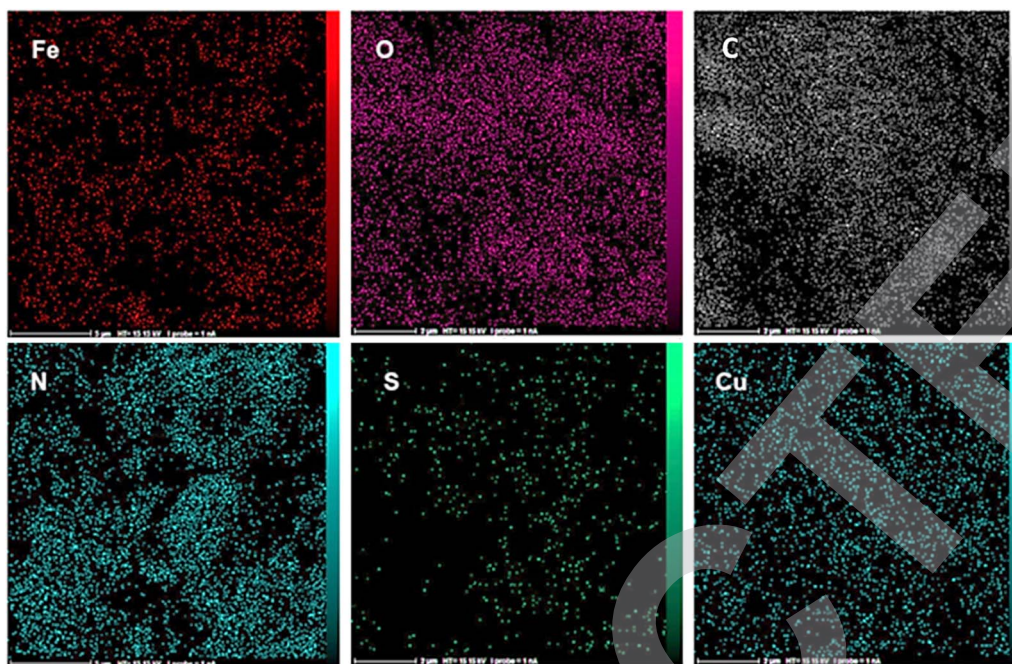


Fig. 5 The X-ray map analysis of $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ nanocatalyst.

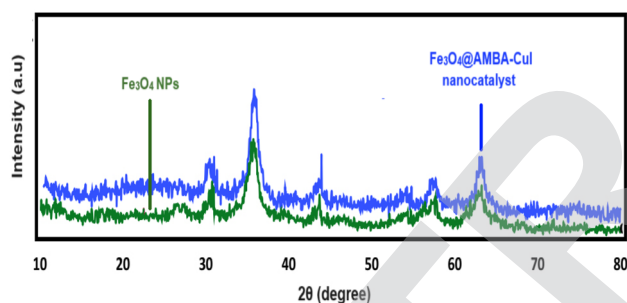


Fig. 6 XRD analysis of Fe_3O_4 NPs and $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ nanocatalyst.

XRD analysis. In order to study the structure and nature of Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ nanocatalyst, XRD analysis were used. XRD spectra of Fe_3O_4 NPs and $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ nanocatalyst are shown in Fig. 6. As was found in XRD analysis, the first inner layer “ Fe_3O_4 ” core was properly synthesized which its cubic pattern of the crystallography, is in agreement with standard magnetic XRD spectra and “9 005 840” COD. The XRD patterns shows peaks in 30.35° , 35.535° , 37.26° , 43.33° , 47.20° , 53.50° , 57.15° , 62.8° and 64.90° which are assigned by miller indices 220, 311, 222, 400, 331, 422, 511, 440, and 531 respectively.⁶³ As you can see in the X-ray analysis, the spectra of the $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ nanocatalyst and the magnetic Fe_3O_4 nanoparticles completely coincide, which indicates that the nature of the $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ catalyst has not changed despite the immobilization of the 3-amino-4-mercaptobenzoic acid (AMBA) and CuI on the surface of magnetic Fe_3O_4 nanoparticles.

TGA analysis. To assess the thermal stability of the $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ nanocatalyst, we employed Thermogravimetric Analysis (TGA) with air as the oxygen atmosphere. The TGA

spectra of the $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ nanocatalyst are illustrated in Fig. 7. A discernible decrease in weight, approximately 5%, was observed below 225°C . This phenomenon is ascribed to the elimination of physically or chemically adsorbed water from the catalyst surface, aligning with findings from previous Fe_3O_4 TGA studies.^{64,65} Consistent with literature reports, the TGA curve for bare Fe_3O_4 tends to stabilize above 200°C , denoting the completion of primary thermal events.^{65–67} The residual mass signifies the presence of remaining iron oxide products or any inert material within the sample.^{68,69} Notably, the TGA analysis of the $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ nanocatalyst revealed an additional substantial weight loss between 225 and 600°C . This aligns with expectations for the region where organic contaminants or impurities undergo decomposition through aerobic pyrolysis.⁷⁰ In this instance, the weight loss is attributed to the degradation of AMBA moieties on the surface of Fe_3O_4 MNPs, validating the successful synthesis of the target complex *via* post-modification methods.

VSM analysis. The magnetic property of the $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ nanocatalyst was measured by vibrating-sample magnetometer (VSM) analysis. As shown in Fig. 8, VSM analysis showed that the $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ catalyst has a magnetic property of 46.721 emu g^{-1} , which confirms that despite the immobilization of 3-amino-4-mercaptobenzoic acid (AMBA) and CuI on the surface of the magnetic nanoparticles, it still has a high magnetic property.

Catalytic investigation in heteroaryl-aryl and di-heteroaryl sulfide products

After identifying the structure of the $\text{Fe}_3\text{O}_4\text{@AMBA-CuI}$ catalyst, we decided to investigate its catalytic activity in the C–S coupling reactions. First, one-pot three-component reaction of



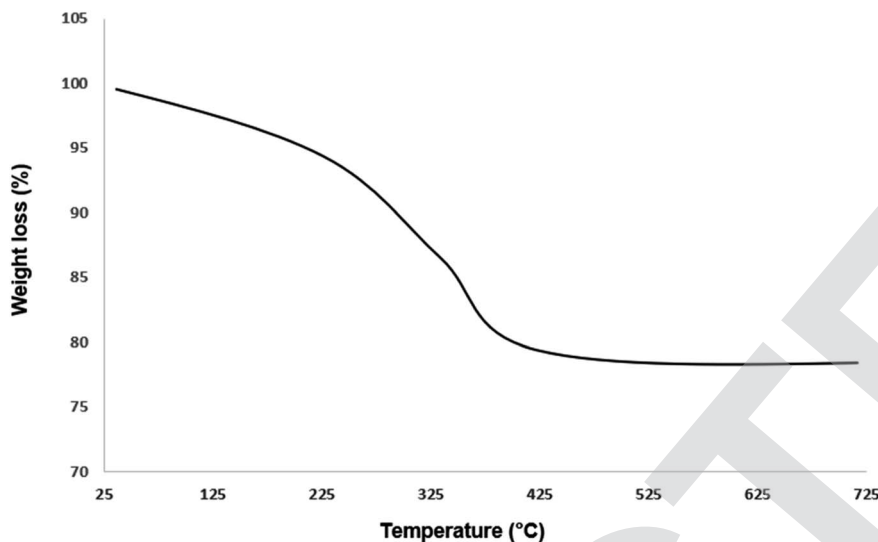


Fig. 7 TGA analysis of Fe₃O₄@AMBA-CuI nanocatalyst.

2-iodobenzo[d]thiazole with phenyl boronic acid and S₈ as sulfur source was optimized under different conditions. In the absence of catalyst, the model reaction was not performed using NaOH as base in DMF (Table 1, entry 1). With introduction of Fe₃O₄@AMBA-CuI catalyst, the 2-(phenylthio)benzo[d]thiazole (**product 4a**) was synthesized with good yields; and by standardizing the amount of Fe₃O₄@AMBA-CuI catalyst, the amount of 8 mol% was chosen as the optimal amount for C-S coupling reactions (Table 1, entry 6).

The presence of base for the synthesis of heteroaryl-aryl and di-heteroaryl sulfides was very vital because the 2-(phenylthio)benzo[d]thiazole (**product 4a**) was not formed in the absence of base (Table 2, entry 1). To find the best base, a number of conventional bases was tested and the results confirmed that potassium acetate (KOAc) is the most efficient base for the synthesis of the 2-(phenylthio)benzo[d]thiazole (**product 4a**) (Table 2, entry 6). Finally, in order to select the best medium reaction, a number of solvents were tested under the optimized amount of Fe₃O₄@AMBA-CuI

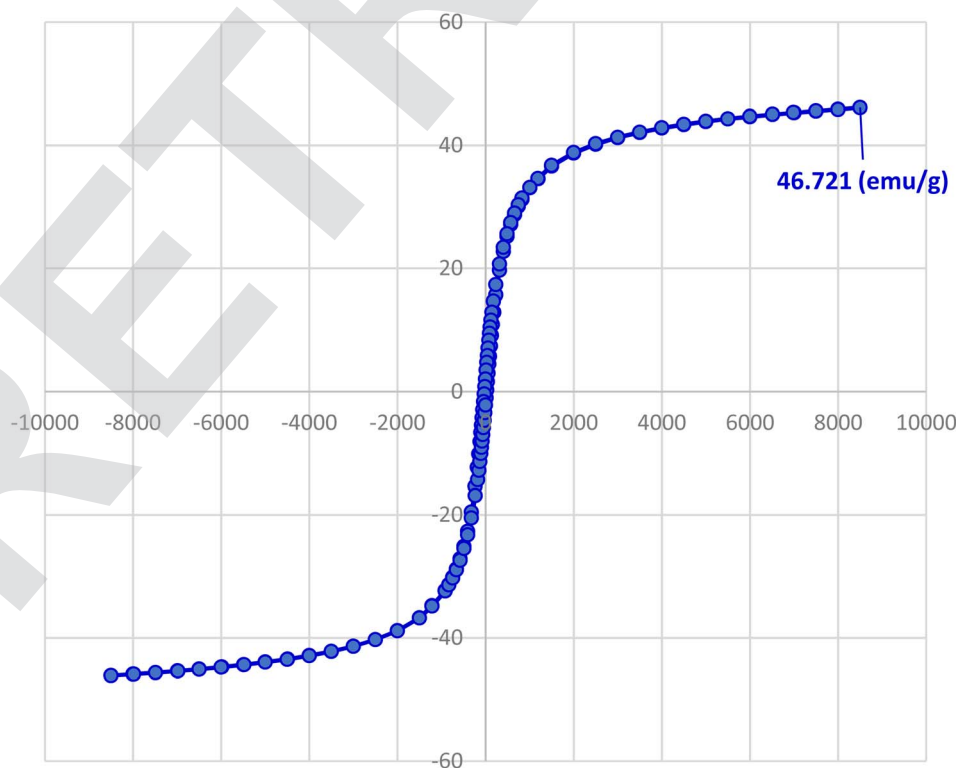


Fig. 8 VSM analysis of Fe₃O₄@AMBA-CuI nanocatalyst.

Table 1 Effect of catalyst on the preparation of 2-(phenylthio)benzo[d]thiazole (product 4a)

Entry	Catalyst (mol%)	Time (h)	Yield% ^a
1	No catalyst	24	×
2	Fe ₃ O ₄ (5 mol%)	24	11%
3	Fe ₃ O ₄ @AMBA-CuI (5 mol%)	6	69%
4	Fe ₃ O ₄ @AMBA-CuI (6 mol%)	6	75%
5	Fe ₃ O ₄ @AMBA-CuI (7 mol%)	6	73%
6	Fe₃O₄@AMBA-CuI (8 mol%)	6	86%
7	Fe ₃ O ₄ @AMBA-CuI (9 mol%)	6	86%
8	Fe ₃ O ₄ @AMBA-CuI (10 mol%)	6	86%

^a Yields referred to isolated products.

nanocatalyst in the presence of KOAc as base. The results confirmed that PEG is the best solvent for C–S coupling reactions. It is worth mentioning that when the reaction temperature increased from 100 to 120 °C, the yield of the obtained product increased (from 93% to 95%) and the reaction time decreased (from 6 h to 5 h) (Table 3, entry 8). But the temperature above 120 °C did not affect the progress of the reaction.

In next stage of experimental works, we decide to study the scope of heteroaryl iodides and aryl or heteroaryl boronic acids for synthesis of heteroaryl-aryl and di-heteroaryl sulfides catalyzed by Fe₃O₄@AMBA-CuI nanomaterial (8 mol%) in the presence of KOAc in PEG at 120 °C for 5 h (Table 4). As seen in Table 4, most of the heteroaryl-aryl and di-heteroaryl sulfide products were synthesized with excellent yields and the

Table 2 Effect of several base on the preparation of 2-(phenylthio)benzo[d]thiazole (product 4a)

Entry	Base	Time (h)	Yield% ^a
1	No base	24	×
2	NaOH	6	86%
3	KOH	6	79%
4	<i>t</i> -BuOK	6	22%
5	Pyridine	6	17%
6	KOAc	6	90%
7	Et ₃ N	6	63%
8	K ₂ CO ₃	6	87%
9	CsF	6	84%
10	DBU	6	30%

^a Yields referred to isolated products.

Table 3 Influence of solvent and temperature on the preparation of 2-(phenylthio)benzo[d]thiazole (product 4a)

Entry	Solvent (°C)	Time (h)	Yield% ^a
1	DMF (100 °C)	6	90%
2	EtOH (reflux)	6	85%
3	Toluene (100 °C)	6	34%
4	DMSO (100 °C)	6	87%
5	Water (reflux)	6	42%
6	PEG (100 °C)	6	93%
7	PEG-400 (110 °C)	5	93%
8	PEG-400 (120 °C)	5	95%
9	PEG-400 (130 °C)	5	95%
10	Solvent-free (100 °C)	5	93%
11	PEG-400 (120 °C)	12	8%

^a Yields referred to isolated products.

presence of different functional groups on the phenyl ring did not have much effect on the yield of the sulfide products. This catalytic system was very efficient and practical for a diverse range of heteroaryl iodides including benzothiazole, benzoxazole, benzimidazole, oxadiazole, benzofuran, imidazo[1,2-*a*]pyridine, because the desired diaryl and di-heteroaryl sulfides were prepared with high yields. Although all the obtained heteroaryl-aryl and di-heteroaryl sulfide products are known and previously reported, but synthesis of this number of heteroaryl-aryl and di-heteroaryl sulfides has never been reported by any methods.

Based on methods reported for preparation of diaryl sulfides in the presence of copper catalysts, we presented a plausible mechanistic-pathway for synthesis of heteroaryl-aryl and di-heteroaryl sulfides through three-component reaction of heteroaryl halides with aryl or heteroaryl boronic acids and S₈ as sulfur source catalyzed by Fe₃O₄@AMBA-CuI nanomaterial. In this respect, one-pot three-component reaction of 2-iodobenzo[d]thiazole with phenyl boronic acid and S₈ as sulfur source for the synthesis of **product 4a** was considered as the model reaction (Scheme 2). First, copper disulfide was prepared from the reaction of Fe₃O₄@AMBA-CuI nanocatalyst with potassium disulfide (formed the reaction of KOAc with S₈). The oxidative-addition of phenyl boronic acid to copper disulfide led to form aryl organocopper (intermediate **A**), which may convert to intermediate **B**. Then, the reaction of 2-iodobenzo[d]thiazole with intermediate **B** led to form key intermediate **C**, which followed a reduction-elimination process in order to prepare the 2-(phenylthio)benzo[d]thiazole (**Product 4a**).

Catalyst recovery

One of the most important and valuable factors in catalytic systems is the simple separation of the catalyst and the study of its reusability. In this regard, the reusability of Fe₃O₄@AMBA-CuI nanocatalyst in three-component reaction of heteroaryl halides with aryl or heteroaryl boronic acids and S₈ as sulfur source for the synthesis of **product 4a** was evaluated as a sample reaction. After the completion of the reaction, the Fe₃O₄@AMBA-CuI nanocatalyst was readily recovered through magnetic separation, washed with ethanol absolute several times, and reused for next runs. As shown in Fig. 9, the Fe₃O₄@AMBA-CuI nanocatalyst can be reused at least six runs with constant catalytic activity. As shown in Fig. 10, VSM analysis showed that the recovered Fe₃O₄@AMBA-CuI catalyst (after 6 runs) has a magnetic property of 38.047 emu g⁻¹, which confirms that despite the separation and reusability of Fe₃O₄@AMBA-CuI nanocatalyst, it still has a high magnetic property. ICP-OES analysis was used to find out the amount of copper in the structure of the recovered Fe₃O₄@AMBA-CuI nanocatalyst after 6 runs, and the results showed that the amount of Cu in the structure of the nanocatalyst is 14.25 × 10⁻⁵ mol g⁻¹.

Comparison

To highlight the superior performance of the Fe₃O₄@AMBA-CuI nanocatalyst in comparison to previously documented catalytic systems, we opted to examine its efficacy in synthesis of 2-(phenylthio)benzo[d]thiazole as the model reaction. As depicted in Table 5, conventional methods in the literature often necessitated prolonged reaction times under harsh conditions, resulting in



Heteroaryl—I + S_8 + $Ar-B(OH)_2$

(8 mol%) $Fe_3O_4@AMBA-CuI$
 KOAc, PEG, 120 °C, 5 h

Heteroaryl—S—Ar

0.5 mmol (1) 0.5 mmol (2) 0.6 mmol (3)

21 Examples
 Yield: 84-97%
 Products 4a-u

Heteroaryl: Benzothiazole, Benzoxazole, Benzimidazole, Oxadiazole, Benzofuran, imidazo[1,2-a]pyridine

Ar: Phenyl and Heteroaryl Heteroaryl: Pyridine, Furan, Thiophene, Benzothiazole

Functional Groups on Phenyl Ring : Me, OMe, NO_2 , CN, CF_3 , H

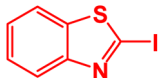
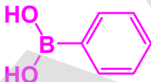
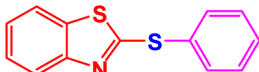
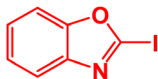
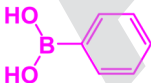
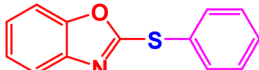
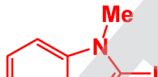
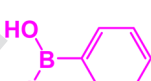

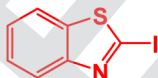
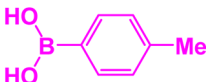
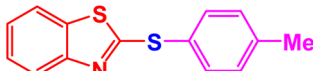
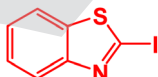
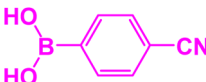
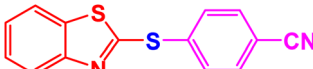
Entry	Heteroaryl halide	Aryl boronic acid	Product (sulfide)
1			 95% Product 4a
2			 94% Product 4b
3			 92% Product 4c
4			 96% Product 4d
5			 92% Product 4e

Table 4 (Contd.)

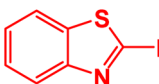
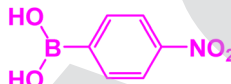
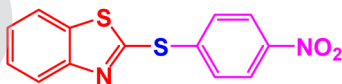
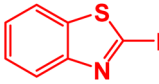
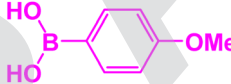
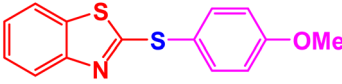
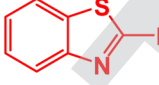
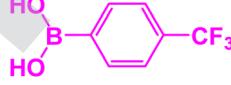
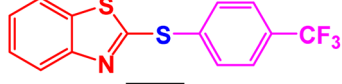
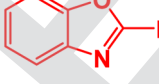
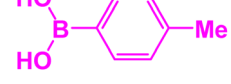

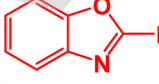
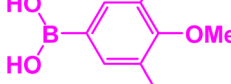
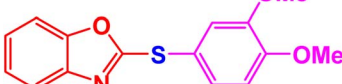
<div><div><div><div><div>Heteroaryl-I</div><div>0.5 mmol</div><div>1</div></div><div><div>S₈</div><div>0.5 mmol</div><div>2</div></div><div><div>Ar-B(OH)₂</div><div>0.6 mmol</div><div>3</div></div></div><div><div>Heteroaryl</div><div>Benzothiazole, Benzoxazole, Benzimidazole, Oxadiazole, Benzofuran, imidazo[1,2-a]pyridine</div><div>Ar: Phenyl and Heteroaryl</div><div>Functional Groups on Phenyl Ring : Me, OMe, NO₂, CN, CF₃, H</div></div><div><div>(8 mol%)</div><div>Fe₃O₄@AMBA-CuI</div><div>KOAc, PEG, 120 °C, 5 h</div></div><div><div>Heteroaryl-S-Ar</div><div>21 Examples</div><div>Yield: 84-97%</div><div>Products 4a-u</div></div></div></div>			
Entry	Heteroaryl halide	Aryl boronic acid	Product (sulfide)
6			 91% Product 4f
7			 97% Product 4g
8			 86% Product 4h
9			 96% Product 4i
10			 93% Product 4j

Table 4 (Contd.)

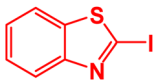
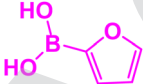
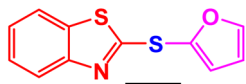
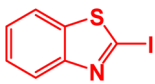
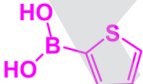
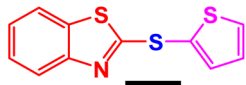
<p style="text-align: center;"> </p> <p> Heteroaryl-I 1 2 3 </p> <p> Heteroaryl Benzothiazole, Benzoxazole, Benzimidazole, Oxadiazole, Benzofuran, imidazo[1,2-a]pyridine Ar: Phenyl and Heteroaryl Heteroaryl: Pyridine, Furan, Thiophene, Benzothiazole Functional Groups on Phenyl Ring : Me, OMe, NO₂, CN, CF₃, H </p>			
Entry	Heteroaryl halide	Aryl boronic acid	Product (sulfide)
11			 91% Product 4k
12			 85% Product 4l
13			 92% Product 4m
14			 86% Product 4n
15			 84% Product 4o



Table 4 (Contd.)

<div><div><div><div><div>Heteroaryl-I</div><div>0.5 mmol</div><div>1</div></div><div><div>S_8</div><div>0.5 mmol</div><div>2</div></div><div><div>Ar-B(OH)₂</div><div>0.6 mmol</div><div>3</div></div></div><div><div>Heteroaryl</div><div>Benzothiazole, Benzoxazole, Benzimidazole, Oxadiazole, Benzofuran, imidazo[1,2-a]pyridine</div><div>Ar: Phenyl and Heteroaryl</div><div>Functional Groups on Phenyl Ring : Me, OMe, NO₂, CN, CF₃, H</div></div></div><div><div>(8 mol%)</div><div>$Fe_3O_4@AMBA-CuI$</div><div>KOAc, PEG, 120 °C, 5 h</div></div><div><div>Heteroaryl-S-Ar</div><div>21 Examples</div><div>Yield: 84-97%</div><div>Products 4a-u</div></div></div>			
Entry	Heteroaryl halide	Aryl boronic acid	Product (sulfide)
16			<div>88%</div> <div>Product 4l</div>
17			<div>88%</div> <div>Product 4q</div>
18			<div>90%</div> <div>Product 4r</div>
19			<div>87%</div> <div>Product 4s</div>

Table 4 (Contd.)

<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <p>Heteroaryl—I</p> <p>0.5 mmol</p> <p>1</p> </div> <div style="text-align: center;"> <p>S₈</p> <p>0.5 mmol</p> <p>2</p> </div> <div style="text-align: center;"> <p>Ar—B(OH)₂</p> <p>0.6 mmol</p> <p>3</p> </div> </div> <div style="text-align: center; margin-top: 10px;"> <p>(8 mol%)</p> <p>Fe₃O₄@AMBA-CuI</p> <p>KOAc, PEG, 120 °C, 5 h</p> </div> <div style="text-align: center;"> <p>Heteroaryl—S—Ar</p> <p>21 Examples</p> <p>Yield: 84-97%</p> <p>Products 4a-u</p> </div>			
<p>Heteroaryl</p> <p>Benzothiazole, Benzoxazole, Benzimidazole, Oxadiazole, Benzofuran, imidazo[1,2-a]pyridine</p> <p>Ar: Phenyl and Heteroaryl Heteroaryl: Pyridine, Furan, Thiophene, Benzothiazole</p> <p>Functional Groups on Phenyl Ring : Me, OMe, NO₂, CN, CF₃, H</p>			
Entry	Heteroaryl halide	Aryl boronic acid	Product (sulfide)
20			 <p>91%</p> <p>Product 4t</p>
21			 <p>92%</p> <p>Product 4u</p>

^a Yields referred to isolated sulfide products.

the product being synthesized with only moderate to good efficiency. In contrast, our approach utilized an environmentally friendly solvent and achieved the model reaction in just 5 hours, yielding the desired product with an outstanding efficiency of 95%. Furthermore, the Fe₃O₄@AMBA-CuI nanocatalyst demonstrated complete stability and adherence to the principles of green chemistry.

Conclusion

In this attractive and highly efficient, we shown that Fe₃O₄@AMBA-CuI nanomaterial can be successfully catalyzed one-pot three-component reaction of heteroaryl halides with aryl or heteroaryl boronic acids and S₈ as sulfur source under eco-friendly conditions in order to synthesize heteroaryl-aryl and di-heteroaryl sulfides. Under this catalytic system, a broad spectrum of heteroaryl-aryl and di-heteroaryl sulfides were synthesized with high to excellent yields in less than 5 h. The reusability-experiments revealed that the Fe₃O₄@AMBA-CuI nanocatalyst can be magnetically separated and reused at least six runs without significant decrease in its catalytic

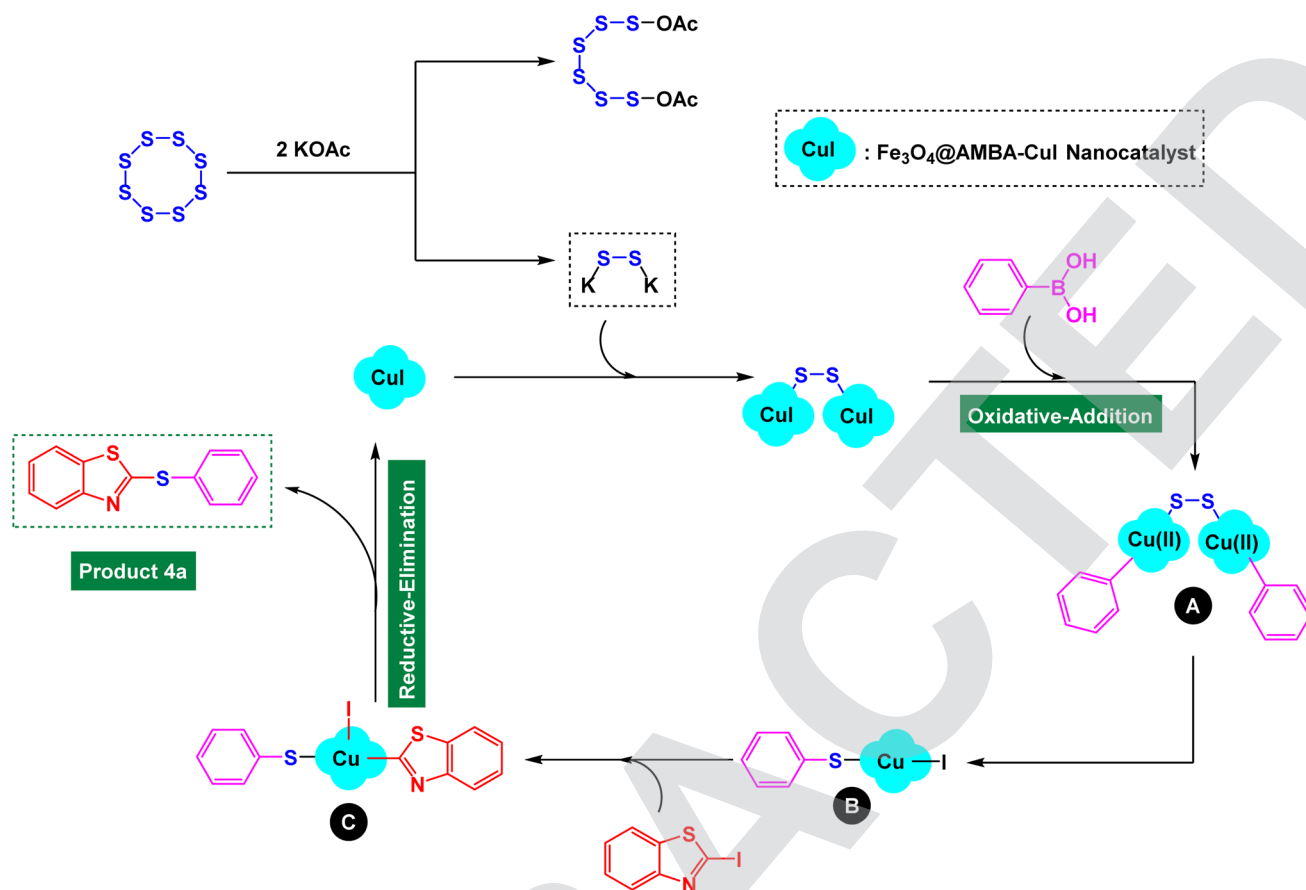
activity. VSM and ICP-OES analyzes confirmed that despite using the Fe₃O₄@AMBA-CuI nanocatalyst 6 times, the magnetic properties and stability of the catalyst were still maintained. Although all the obtained heteroaryl-aryl and di-heteroaryl sulfide products are known and previously reported, but synthesis of this number of heteroaryl-aryl and di-heteroaryl sulfides has never been reported by any methods.

Experimental

Synthesis of Fe₃O₄@AMBA-CuI nanocatalyst

At the first step the Fe₃O₄ was prepared according to previous report.⁷⁶ In the next step 1 g of Fe₃O₄ was dispersed in 50 mL of ethanol for 30 min and, then, 4 mmol of 3-amino-4-mercaptobenzoic acid (AMBA) was added to the reaction mixture and stirred under reflux conditions for 3 h. After the mixture was cooled, the synthesized Fe₃O₄@AMBA MNPs were accumulated using an external magnet, washed with water and ethanol and dried at 80 °C. Afterwards, 2 g of Fe₃O₄@AMBA was dispersed in 100 mL of ethanol for 30 minutes. Then, it was treated with 2.5 mmol of CuI and stirred under reflux





Scheme 2 Mechanistic pathway for synthesis of heteroaryl-aryl and di-heteroaryl sulfides through three-component reaction of heteroaryl halides with aryl or heteroaryl boronic acids and S_8 as sulfur source catalyzed by $Fe_3O_4@AMBA-CuI$ nanomaterial.

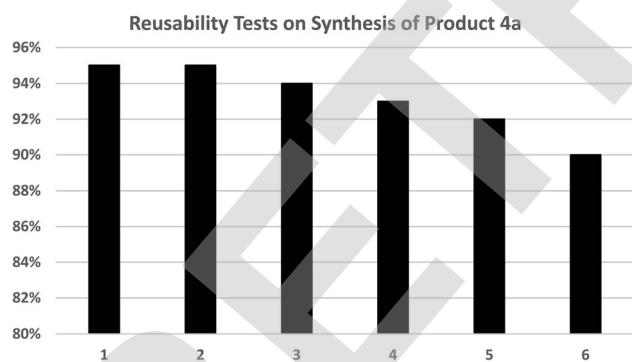


Fig. 9 Reusability tests of $Fe_3O_4@AMBA-CuI$ nanocatalyst in preparation of 2-(phenylthio)benzo[d]thiazole (Product 4a).

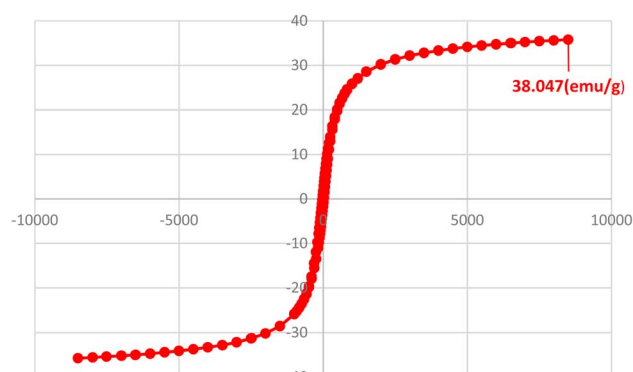


Fig. 10 VSM analysis of $Fe_3O_4@AMBA-CuI$ nanocatalyst after 6 runs.

conditions for 8 h. The obtained $[Fe_3O_4@AMBA-CuI]$ complex was collected using an external magnet, washed using water and ethanol and, finally, dried at 80 °C (Scheme 1).

General procedure for preparation of heteroaryl-aryl and di-heteroaryl sulfides catalyzed by $Fe_3O_4@AMBA-CuI$ nanocomposite

In a round bottomed flask, a mixture of heteroaryl iodides (0.5 mmol), aryl or heteroaryl boronic acids (0.6 mmol), S_8 (0.5

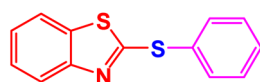
mmol) KOAc (2 equiv.) and $Fe_3O_4@AMBA-CuI$ catalyst (8 mol%) was stirred in PEG-400 at 120 °C for 5 h (the progress of the reaction was monitored by thin-layer chromatography (TLC)). After completion of the reaction, the $Fe_3O_4@AMBA-CuI$ was magnetically separated and reaction mixture was cooled to room temperature and H_2O (4 mL) was added. The product was extracted with EtOAc (3 × 4 mL) and dried over anhydrous Na_2SO_4 . The crude material was purified with chromatography column on silica gel (EtOAc/*n*-hexane) give the heteroaryl-aryl

Table 5 Comparison of the activity of this method with reported methods for the preparation of 2-(phenylthio)benzo[d]thiazole (product 4a)

Entry	Catalytic system	Conditions	Yield (%) [Ref]
1	[NiCl ₂ (PPh ₃) ₂]	EtOH, reflux, 3 h	83% ⁷¹
2	1,2-Diaminocyclohexane/CuI	DMSO, 90 °C, 4 h	86% ⁷²
3	1,10-Phenanthroline/CuI	1,4-Dioxane; rt → 90 °C; 12 h	76% ⁷³
4	Cationic 2,2'-bipyridyl/CoCl ₂ ·6H ₂ O	Water, potassium hydroxide, zinc; 24 h, 100 °C	91% ⁷⁴
5	Fe ₃ O ₄ @AMBA-CuI	PEG-400, 120 °C, 5 h	95% ⁷⁵

and di-heteroaryl sulfides products with 84–97%. All heteroaryl-aryl and di-heteroaryl sulfides products are previously reported and known.^{59,60,77–83} HNMR and CNMR were used in order to identify the structure of the heteroaryl-aryl and di-heteroaryl sulfide products.

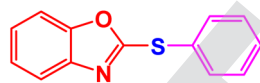
NMR data for heteroaryl-aryl and di-heteroaryl sulfide products



95%

Product 4a

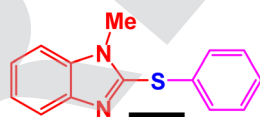
2-(Phenylthio)benzo[d]thiazole. Mp: 32–34 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.06–8.02 (m, 2H), 7.64–7.60 (m, 2H), 7.58–7.46 (m, 5H); ¹³C NMR (126 MHz, CDCl₃) δ 168.8, 155.0, 135.6, 135.1, 130.8, 130.4, 126.7, 124.5, 122.1, 120.7.



94%

Product 4b

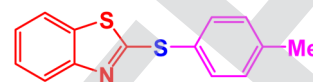
2-(Phenylthio)benzo[d]oxazole. Colorless oil, ¹H NMR (500 MHz, CDCl₃) δ 7.68–7.64 (m, 2H), 7.63–7.61 (m, 2H), 7.20–7.17 (m, 2H), 7.16–7.14 (m, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 162.8, 152.3, 142.9, 135.1, 130.3, 129.9, 127.2, 124.7, 123.8, 119.4, 110.3.



92%

Product 4c

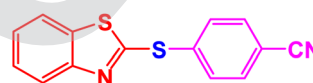
1-Methyl-2-(phenylthio)-1H-benzo[d]imidazole. Mp: 65–67 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.61–7.57 (m, 2H), 7.48–7.45 (m, 2H), 7.38 (t, *J* = 4.3 Hz, 3H), 7.23–7.21 (m, 2H), 3.78 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 146.5, 135.2, 131.5, 130.2, 129.8, 122.4, 118.6, 110.3, 32.9.



96%

Product 4d

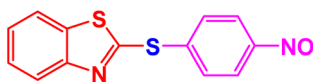
2-(p-Tolylthio)benzo[d]thiazole. Mp: 69–71 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.81 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.60–7.57 (m, 2H), 7.37–7.33 (m, 1H), 7.32–7.25 (m, 2H), 7.23–7.20 (m, 1H), 2.50 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 165.3, 153.6, 135.9, 134.1, 130.5, 130.2, 129.7, 126.3, 124.2, 121.5, 120.8, 22.5.



92%

Product 4e

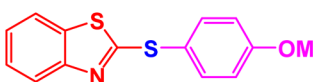
4-(Benzo[d]thiazol-2-ylthio)benzonitrile. Mp: 110–112 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.69–7.65 (m, 3H), 7.46–7.40 (m, 2H), 7.31 (d, *J* = 4.5 Hz, 1H), 7.29 (d, *J* = 4.6 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 167.2, 153.4, 136.5, 136.2, 135.7, 130.3, 128.5, 126.3, 124.6, 122.0, 120.1.



91%

Product 4f

2-((4-Nitrophenyl)thio)benzo[d]thiazole. Mp: 86–89 °C, ¹H NMR (500 MHz, CDCl₃) δ 8.00–7.95 (m, 2H), 7.65–7.63 (m, 2H), 7.45–7.41 (m, 2H), 7.20–7.14 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 161.1, 158.3, 142.8, 141.3, 139.5, 138.0, 130.2, 129.7, 128.6, 127.9, 118.4, 115.7.



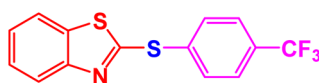
98%

Product 4g

2-((4-Methoxyphenyl)thio)benzo[d]thiazole. Mp: 55–57 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.65–7.60



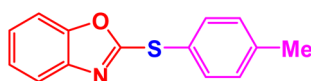
(m, 2H), 7.38–7.35 (m, 1H), 7.26 (d, $J = 7.5$ Hz, 1H), 7.22–7.00 (m, 3H), 3.89 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.2, 161.0, 154.9, 137.6, 135.7, 126.12, 124.3, 121.5, 120.8, 120.2, 115.5.



86%

Product 4h

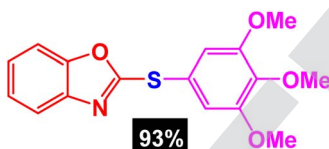
2-((4-(Trifluoromethyl)phenyl)thio)benzo[d]thiazole. Mp: 58–60 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.02 (d, $J = 7.8$ Hz, 1H), 7.85 (d, $J = 7.8$ Hz, 3H), 7.69–7.65 (m, 2H), 7.64–7.60 (m, 1H), 7.59–7.57 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 165.2, 141.0, 140.9, 139.5, 137.4, 136.5, 130.6, 129.7, 129.1, 128.7, 127.9, 127.3.



96%

Product 4i

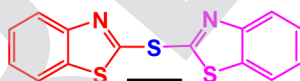
2-(p-Tolylthio)benzo[d]oxazole. Colorless oil, ^1H NMR (500 MHz, CDCl_3) δ 7.71 (d, $J = 7.7$ Hz, 2H), 7.61–7.55 (m, 2H), 7.31–7.24 (m, 2H), 7.21–7.18 (m, 2H), 2.54 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 157.0, 155.2, 143.6, 141.5, 138.7, 130.5, 129.7, 127.3, 126.1, 120.3, 115.2, 22.5.



93%

Product 4j

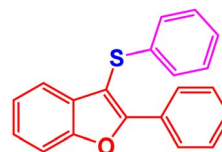
2-((3,4,5-Trimethoxyphenyl)thio)benzo[d]oxazole. Mp: 127–129 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.85 (d, $J = 8.3$ Hz, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.43 (td, $J = 7.7, 1.3$ Hz, 1H), 7.26 (td, $J = 7.5, 1.3$ Hz, 1H), 7.10 (s, 2H), 3.85 (s, 6H), 3.64 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.2, 155.3, 145.6, 141.2, 135.8, 130.7, 126.7, 125.3, 124.1, 121.0, 120.8, 58.9, 58.2.



91%

Product 4k

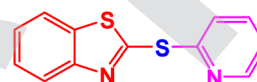
Bis(benzo[d]thiazol-2-yl)sulfane. Mp: 100–102 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.85 (dd, $J = 8.6$ Hz, 2H), 7.65–7.60 (m), 7.45–7.40 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.8, 141.6, 137.0, 135.9, 134.5, 130.2, 129.2, 127.3, 125.9.



85%

Product 4l

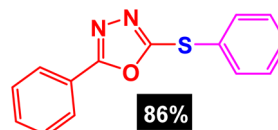
2-Phenyl-3-(phenylthio)benzofuran. Mp: 66–68 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.24 (dd, $J = 8.3$ Hz, 2H), 7.56 (d, $J = 8.2$ Hz, 1H), 7.48–7.41 (m, 5H), 7.37–7.23 (m, 5H), 7.22–7.16 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 157.8, 153.2, 136.5, 130.6, 129.7, 129.4, 129.0, 128.7, 127.3, 126.5, 125.9, 125.4, 123.4, 120.5, 111.3, 104.9.



92%

Product 4m

2-(Pyridin-2-ylthio)benzo[d]thiazole. Mp: 66–68 °C, ^1H NMR (500 MHz, CDCl_3) δ 9.26 (d, $J = 1.8$ Hz, 1H), 8.81 (dd, $J = 4.9, 1.7$ Hz, 1H), 8.29 (ddd, $J = 8.1, 2.3, 1.8$ Hz, 1H), 7.55–7.45 (m, 4H), 7.44 (ddd, $J = 8.1, 4.9, 1.8$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 161.3, 154.6, 149.7, 136.5, 135.1, 132.5, 129.8, 128.9, 126.3, 122.4.



86%

Product 4n

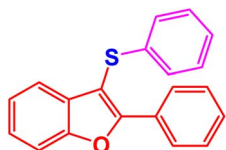
2-Phenyl-5-(phenylthio)-1,3,4-oxadiazole. Mp: 60–62 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.91 (d, $J = 7.6$ Hz, 2H), 7.70–7.64 (m, 2H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.49–7.42 (m, 5H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.9, 166.1, 133.8, 132.4, 130.8, 130.2, 129.8, 127.6, 126.4, 123.9.



84%

Product 4o

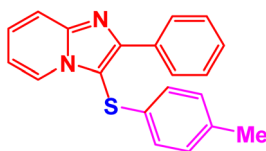
2-Phenyl-5-((3,4,5-trimethoxyphenyl)thio)-1,3,4-oxadiazole. Mp: 140–142 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.97 (d, $J = 6.7$ Hz, 2H), 7.52–7.50 (m, 3H), 6.95 (s, 2H), 3.97 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.6, 163.9, 153.2, 140.3, 132.3, 130.0, 126.4, 123.7, 121.5, 111.3, 61.7, 55.5.



88%

Product 4l

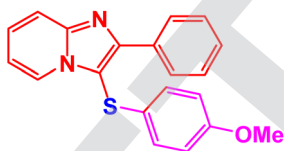
2-Phenyl-3-(phenylthio)imidazo[1,2-*a*]pyridine. Mp: 92–94 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.25 (d, 1H, J = 6.8 Hz), 8.18 (d, 2H, J = 7.6 Hz), 7.71 (d, 1H, J = 9.2 Hz), 7.45 (t, 2H, J = 7.7 Hz), 7.38 (d, 1H, J = 7.3 Hz), 7.30 (t, 1H, J = 8 Hz), 7.17 (t, 2H, J = 7.6 Hz), 7.11 (t, 1H, J = 7.6 Hz), 6.97 (d, 2H, J = 7.6 Hz), 6.85 (t, 1H, J = 6.7 Hz); ^{13}C NMR (126 MHz, CDCl_3) δ 151.0, 147.2, 133.5, 129.7, 128.5, 128.3, 127.4, 126.2, 125.6, 125.3, 124.5, 117.3, 112.2, 106.3.



88%

Product 4q

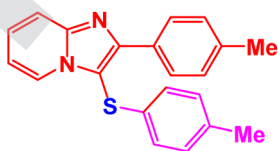
2-Phenyl-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine. Mp: 135–137 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.28 (d, 1H, J = 6.5 Hz), 8.21 (d, 2H, J = 7.5 Hz), 7.71 (d, 1H, J = 9.1 Hz), 7.46 (t, 2H, J = 7.6 Hz), 7.37 (d, 1H, J = 7.3 Hz), 7.28 (t, 1H, J = 8 Hz), 7.02 (d, 2H, J = 8 Hz), 6.95 (d, 2H, J = 8.1 Hz), 6.87 (t, 1H, J = 6.7 Hz), 2.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 152.0, 145.3, 136.8, 133.5, 131.2, 130.7, 129.7, 128.6, 128.0, 126.4, 125.7, 117.9, 112.4, 106.3, 21.3.



90%

Product 4r

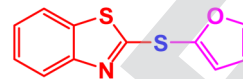
3-((4-Methoxyphenyl)thio)-2-phenylimidazo[1,2-*a*]pyridine. Mp: 112–114 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.29 (d, 1H, J = 6.1 Hz), 8.22 (d, 2H, J = 8.2 Hz), 7.71 (d, 1H, J = 8.6 Hz), 7.42–7.40 (m, 2H), 7.35 (t, 1H, J = 5.7 Hz), 7.29–7.27 (m, 1H), 6.97 (d, 2H, J = 8.3 Hz), 6.85 (t, 1H, J = 5.6 Hz), 6.75 (d, 2H, J = 8.6 Hz), 3.70 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 158.6, 150.2, 146.7, 133.6, 130.9, 129.7, 128.8, 128.6, 127.7, 126.4, 125.7, 117.7, 115.9, 112.6, 107.4, 55.3.



87%

Product 4s

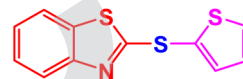
2-(*p*-Tolyl)-3-(*p*-tolylthio)imidazo[1,2-*a*]pyridine. Mp: 142–144 °C, ^1H NMR (500 MHz, CDCl_3) δ 8.24 (d, 1H, J = 6.8 Hz), 8.12 (d, 2H, J = 7.8 Hz), 7.70 (d, 1H, J = 9.1 Hz), 7.33 (t, 1H, J = 7.6 Hz), 7.25 (d, 2H, J = 8.3 Hz), 7.02 (d, 2H, J = 7.7 Hz), 6.92 (d, 2H, J = 7.7 Hz), 6.83 (t, 1H, J = 6.7 Hz), 2.38 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 151.1, 146.3, 138.7, 134.3, 130.7, 129.7, 129.1, 128.2, 126.4, 125.1, 124.4, 117.6, 112.7, 105.9, 21.3, 20.6.



91%

Product 4t

2-(Furan-2-ylthio)benzo[d]thiazole. ^1H NMR (400 MHz, CDCl_3) δ 8.03 (dd, J = 8.5 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 9.2 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.6, 161.7, 137.6, 130.5, 129.3, 119.1, 115.3, 114.5.



92%

Product 4u

2-(Thiophen-2-ylthio)benzo[d]thiazole. ^1H NMR (400 MHz, CDCl_3) δ 7.33–7.21 (m, 2H), 7.14–7.10 (m, 2H), 6.97–6.93 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.3, 149.8, 135.0, 134.7, 132.1, 130.8, 130.2, 128.3, 117.6, 116.3, 115.4.

Conflicts of interest

There are no conflicts to declare.

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