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Regioselective *Ortho*-C—H sulfenylation of free phenols catalyzed by Co(II)-immobilized on silica-coated magnetic nanoparticles

Sepideh Khaef[a,b], Abed Rostami[c], Vahid Khakyzadeh[d,*], Mohammad Ali Zolfigol[b], Avat Arman Taherpour[a], Meysam Yarie[b]

[a] Department of Organic Chemistry, Faculty of Chemistry, Razi University, Kermanshah, Iran
[b] Department of Organic Chemistry, Faculty of Chemistry, Bu Ali Sina University, Hamedan, Iran
[c] Vice Chancellor for Food and Drug, Kurdistan University of Medical Sciences, Sanandaj, Iran
[d] Department of Chemistry, K. N. Toosi University of Technology, P.O. Tehran, Iran

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ABSTRACT

Fe_3O_4@SiO_2-UT@Co^{II} is prepared by the silica-coated magnetic nanoparticles, urea-triazole, and $CoCl_2$. This organic-inorganic hybride composite showed a good to excellent catalytic activity toward regioselective *ortho*-sulfenylation of free phenols and naphthols using pivalic anhydride as a directing group, also $K_2S_2O_8$ and PPh_3 were employed as oxidant and additive respectively. The newly synthesized catalyst was fully characterized by using different techniques such as FT-IR, TGA, DTG, TEM, SEM, EDS, ICP and VSM analyses. The competitive price, accessibility and lower toxicity of cobalt compared to expensive transition metals using for C—H bond activation and functionalization constitute precious advantages for this method. Moreover, this heterogeneous catalyst could be magnetically recovered and reused without significant loss of its catalytic activity after five cycles.

Introduction

The C—H functionalization processes play an important role in organic chemistry by using transition metals due to its versatile and efficient applications in the synthesis of aryl-containing chemicals and resolve the problems of prefunctionalization with halogens or reactivity troubles with lighter halogens [1–5]. These processes can significantly simplify the synthesis of pharmaceuticals, natural products, polymers, and feedstock commodity chemicals [6–8]. Among C—H functionalization processes, C—H functionalization of phenols is an essential because these compounds are common structural motifs found in many bioactive natural products and medicine [9–12]. Typically, phenols are modified with an appended directing group including silyl [13], acyl [14], 2-pyridyl [15], carboxylate [16], silanol [17], carbamat [17], pyridyl/pyrimidyl [18–24] and ester groups [25] in order to promote regioselective *ortho*- C—H bond activation and overcomes their poor directing abilities. However, noble transition metals such as palladium and rhodium are essential in most cases.

A derivative aryl sulfenyl phenols exist in a diversity of natural products and medicines. For example; 2-sulfanylphenols were applied as a drug for the treatment of cancer, HIV, heart disease, allergy, and obesity [26–28]. Hence, regioselective *ortho*-sulfenylation of phenol as one of the most powerful protocols have attracted considerable attention [29,30]. Traditionally, aryl sulfenyl phenols have been synthesized from cross-coupling reaction of 2-halophenols with thiols in the presence of transition metals (Scheme 1, **path A**) [31–34]. Takaki and coworkers have reported an alternative method for the sulfenylation of phenols using a stoichiometric amount of $FeCl_3$ under an oxygen atmosphere (Scheme 1, **path B**) [35]. Migita-type cross-coupling between aryl halides and aryl thiols followed by selective hydroxylation of aryl thioethers were applied for the synthesis of arylsulfenylphenols (Scheme 1, **path C**) [36]. Cyclohexanone has been used as a substrate for the synthesis of arylsulfenylphenols through successive dehydrogenation of two saturated carbon-carbon bonds of the six-membered ring by using molecular oxygen as a hydrogen acceptor (Scheme 1, **path D**) [37–39].

Numerous methods have been recently introduced for the sulfenylation of 2-naphthols. At first, iodine was introduced as a catalyst by Huang for the thiolation of aryl 2-naphthols with arylsulfonyl hydrazides *via* C—H bond functionalization (Scheme 1, **path E**) [40], Then the application of iodine as a catalyst has been developed for the direct sulfenylation of 2-naphthols with aryl thiols in DMSO solvent (Scheme 1, **path F**) [41]. Afterward, Xiao et al. reported the reaction of sodium sulfinates with aryl 2-naphthols in the presence of iodine catalyst for

* Corresponding author.
E-mail address: v.khakyzadeh@kntu.ac.ir (V. Khakyzadeh).

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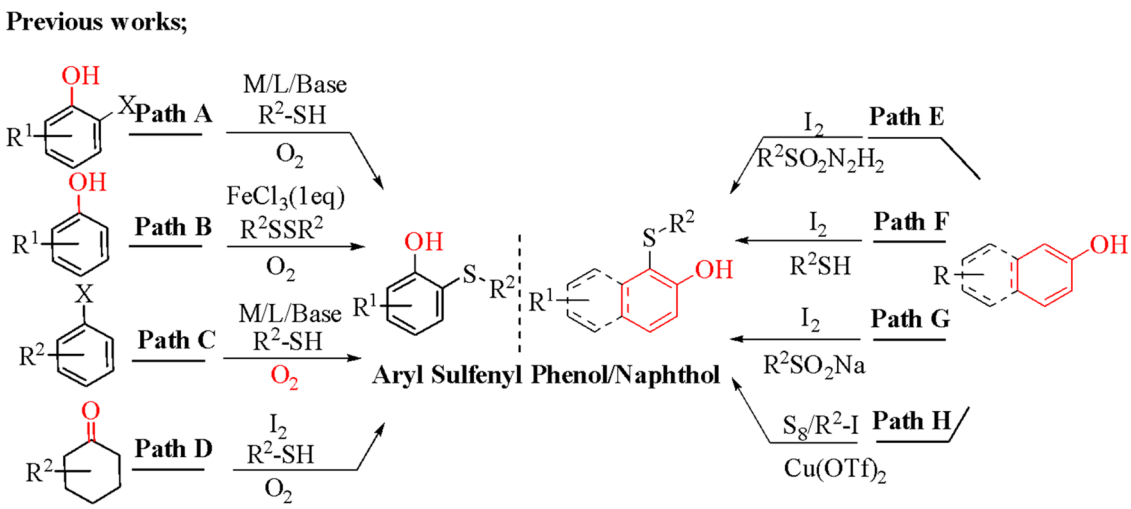


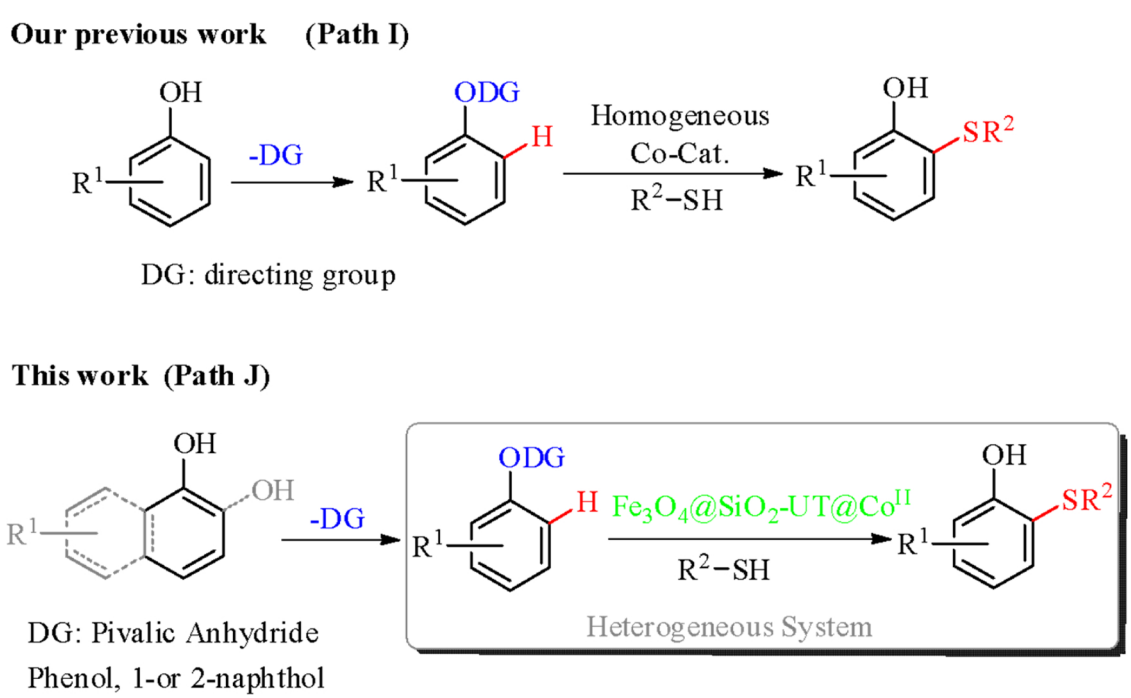
Scheme 1. Previous strategies toward synthesis of aryl sulfenyl phenol/naphthol.

the synthesis of arylsulfenylnaphtols (Scheme 1, **path G**) [42]. Sulfenylation of aryl 2-naphthols with iodohydrocarbons and sulfur powder in the presence of a copper-based catalyst was performed for the synthesis of arylsulfenylnaphtols (Scheme 1, **Path H**) [43].

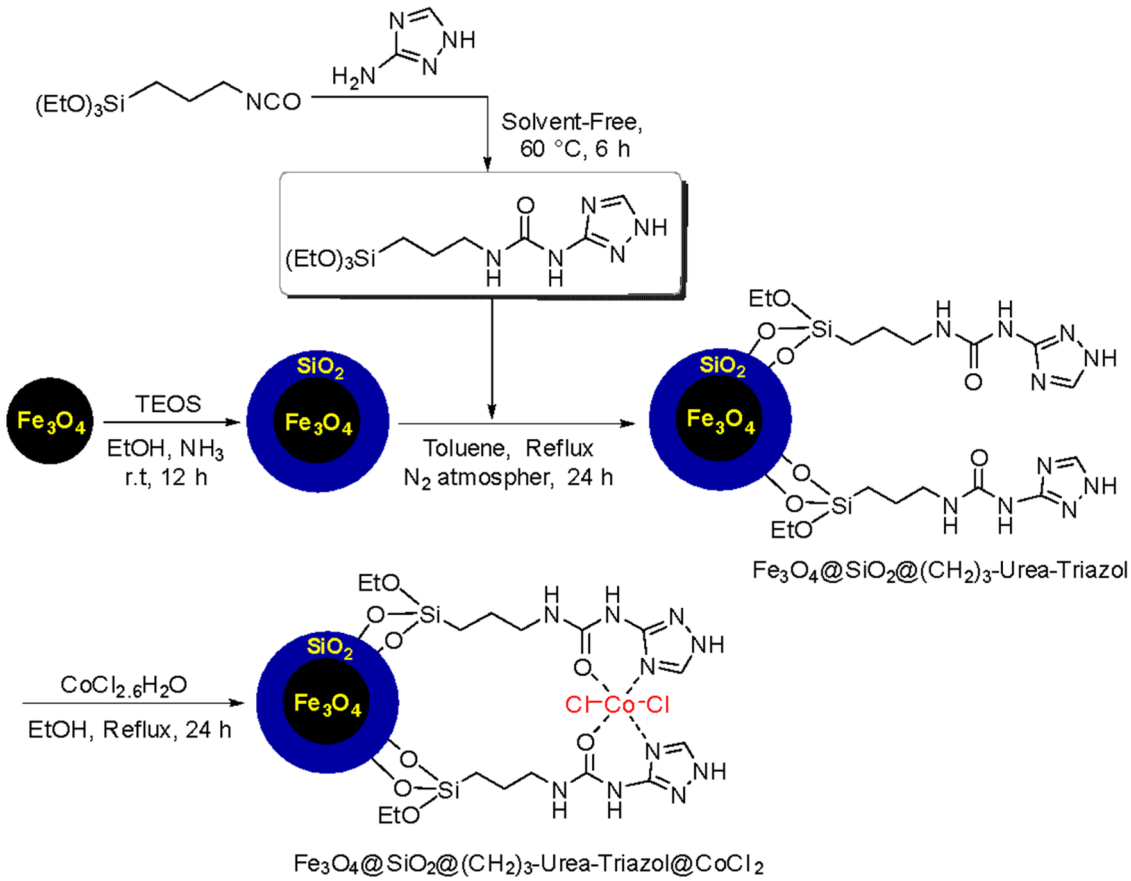
Employing heterogeneous catalysts has numerous advantages for fine chemical synthesis. They can undoubtedly exhibit high specific surface area to volume ratio, which heightens the contact between reactants and catalyst support and consequently raises the catalytic activity and easily separate out of the reaction mixture [44–46]. In this regard, magnetically separable catalysts have attracted a great deal of attention. These elegant alternatives can improve the efficiency of the catalyst separation from the reaction mixture upon reaction completion by applying an external magnet [47–51]. Also, magnetic nanoparticles (MNPs) can be applied as valuable structures for the immobilization of both inorganic and organic catalytic active molecules [52–58]. Natural and biochemical compounds like urea/thiourea can be used as a ligand for MNPs. As a part of our continuous efforts for the synthesis of aryl sulfides [59–67] and arylsulfenyphenols (Scheme 2, **Path I**) [68], we dedicate a useful, clean and simple protocol for the synthesis of sulfenylphenols/naphtols *via* Fe_3O_4@SiO_2-UT@Co^{II} catalyzed CH− bond activation and subsequent functionalization of phenols/naphthols with thiols in the presence of pivalic anhydride as a directing group, $K_2S_2O_8$ and PPh_3 as oxidant and additive respectively (Scheme 2, **path v**).

Results and discussion

In the beginning, Fe_3O_4 nanoparticles were prepared by the methods of previous works [69]. Then, the surface Fe_3O_4 nanoparticles were modified by a layer of SiO_2 through the reaction with tetraethylorthosilicate (TEOS) [34]. In the Following step, 1 g of the Fe_3O_4@SiO_2 and urea-based ligand (5 mmol) in 80 ml of dry toluene were refluxed under a nitrogen atmosphere for 24 h. The synthesized nanoparticles (Fe_3O_4@SiO_2@ $(CH_2)_3$-Urea-Triazole) were separated and washed thoroughly with *n*-hexane and air-dried. Finally, $CoCl_2.6H_2O$ (5 mmol, 1.190 g) was added to a mixture of 1 g of the magnetic nanoparticles (Fe_3O_4@SiO_2@ $(CH_2)_3$-Urea-Triazole) in ethanol and refluxed



Scheme 2. Strategies for the sulfenylation of *ortho*-phenols/naphthols situation and our work.



Scheme 3. Synthesis of Fe_3O_4@SiO_2@ $(CH_2)_3$-Urea-Triazole@$CoCl_2$.

for 24 h. Finally, the desired catalyst was separated and washed thoroughly with ethanol and air-dried (Scheme 3). The structure of catalyst was fully identified by FT-IR, TGA, DTG, TEM, SEM, EDS, ICP, and VSM analyses.

Fig. 1 investigated the FT-IR spectra of the applied materials for the synthesis of the desired catalyst in a comparative mode. The peak appeared at 1650 cm^{-1} can be described to the stretching vibration mode of C═O that affirmed existence of urea moiety within the structure of catalyst. The broad peak discerned at around 2900–3600 cm^{-1} can be ascribed to the overlapping of N—H and un-coated O—H stretching bands.

As depicted in Fig. 2, the EDX analysis verified all expected elements which exist within the structure of the novel prepared magnetically recoverable catalyst. These elements are iron, silicon, oxygen, carbon, nitrogen, and cobalt.

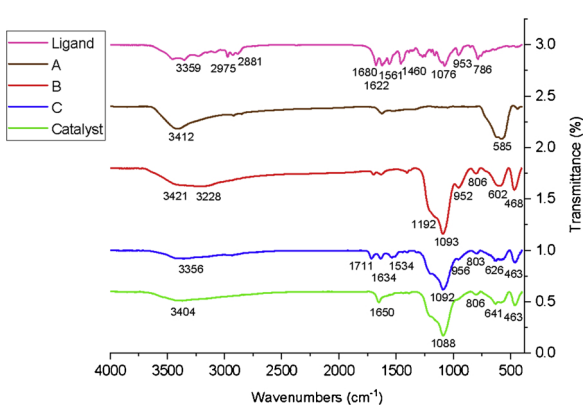


Fig. 1. FT-IR spectra of the ligand, Fe_3O_4 (A), Fe_3O_4@SiO_2 (B), Fe_3O_4@SiO_2@$(CH_2)_3$-Urea-Triazole (C) and the Catalyst (Fe_3O_4@SiO_2-UT@Co^{II}).

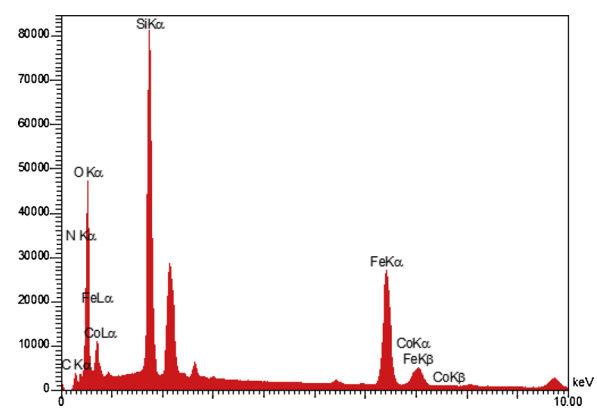


Fig. 2. EDX analysis of the novel prepared catalyst (Fe_3O_4@SiO_2-UT@Co^{II}).

The morphology of the prepared catalyst was also investigated by using SEM analysis. The resulting images illustrated in Fig. 3 (a–b) shows the nanosized structure of the prepared catalyst. Particle size distribution histogram based on SEM images is shown in Fig. 4. According to this histogram, the most particle sizes are 20 – 25 nm and the average size of the catalyst particles is almost 22 nm. The average size of the catalyst particles is almost 23 nm. Also, in order to study the morphology and size of the catalyst in more detail, TEM analysis was also used. The resulting images are portrayed in Fig. 3 (c–d). These images confirmed the obtained data from SEM images and the core-shell structure of nanoparticles.

The thermal behavior of the prepared catalyst was investigated by using TG/DTG analyses. The resulting plots are illustrated in Fig. 5. The weight loss from room temperature to around 150 °C is related to the

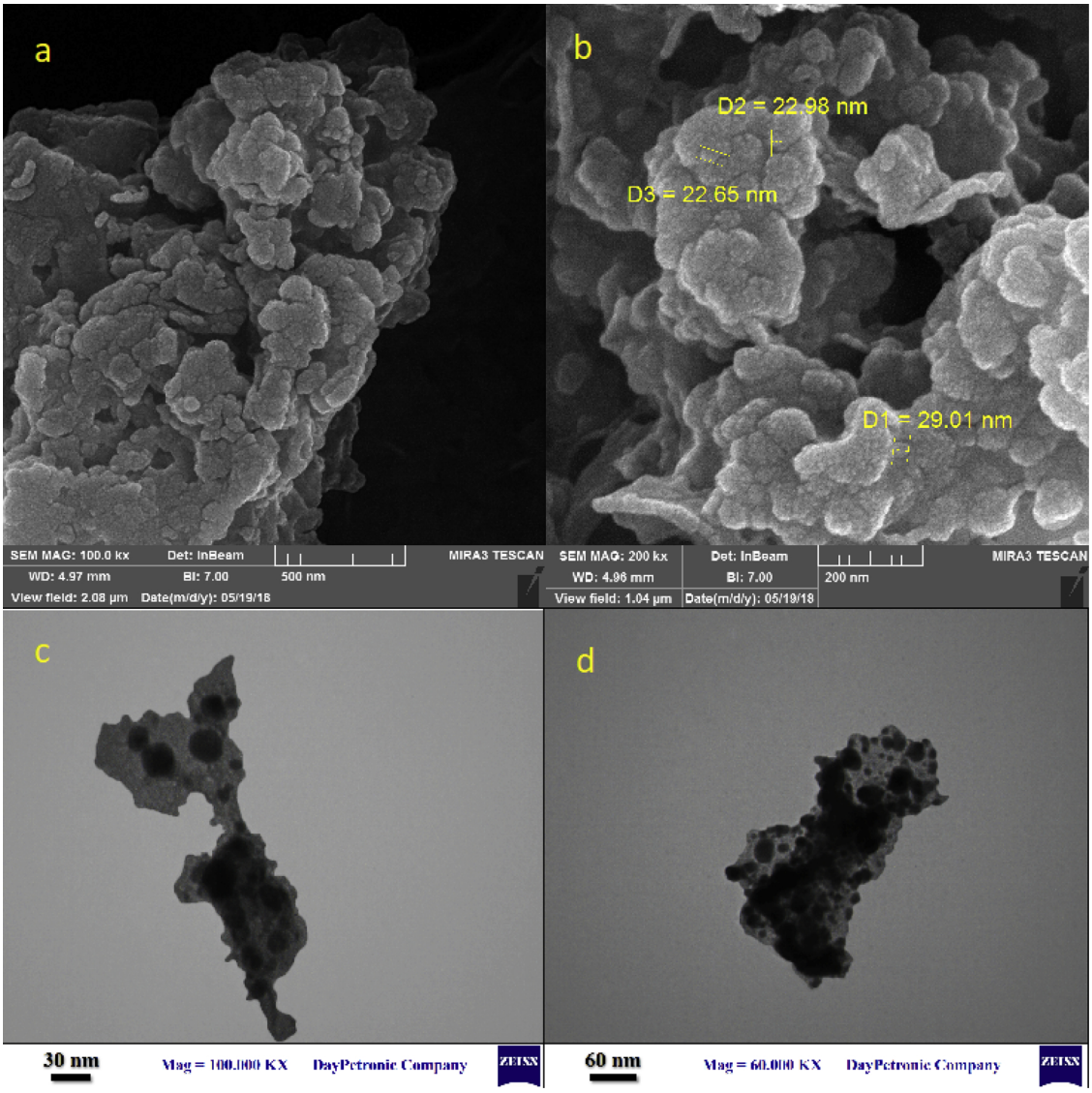


Fig. 3. SEM images (low magnification (a)- high magnification (b)) and TEM images (high magnification c–d) of the novel prepared catalyst (Fe_3O_4@SiO_2-UT@Co^{II}).

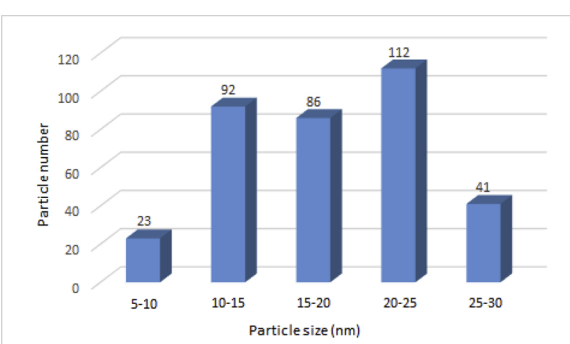


Fig. 4. Particle size distribution histogram.

evaporation of the physically absorbed solvent during the catalyst preparation pathway. The catalyst shows high thermal stability up to 300 °C. At this stage the weight losses are beginning which related to the decomposition of the organic-inorganic tags anchored to the surface of Fe_3O_4@SiO_2 nanoparticles. 80 % residual weight up to 600 °C shows thermal stability of Fe_3O_4 and SiO_2.

The magnetic properties of all prepared material in the way of the desired catalyst were explored by VSM analysis. The resulting magnetic curves were illustrated in Fig. 6. The achieved data indicated that the modification of the surface of Fe_3O_4 nanoparticles leads to the reducing of magnetic properties of each step. The data predict high magnetic properties (around 27 emu/g) for desired catalyst which verified the facile separation of the catalyst from the reaction mixture.

SEM of the catalyst after a cycle of reaction which shows in Fig. 7, portrays that the average size of the catalyst particles remains almost 18 nm after the reaction.

The amount of Co species in the prepared catalyst was investigated by inductively coupled plasma (ICP) analysis (Table 1). ICP data showed that the Co content in Fe_3O_4@SiO_2-UT@Co^{II} compound was 2.77×10^{-4} mol gr^{-1} (row 1). ICP Mass analysis of recovered catalyst after a cycle of the reaction (row 2), revealed that Co leaching from the surface of the catalyst was about 4.94 %, this means that synthesized catalyst has stability in the reaction conditions.

To further study on the metal leaching of the synthesized catalyst, hot filtration test was performed. The reaction of *p*-cresol with thiophenol was stopped after 10 h, and then the catalyst was separated by an external magnet from the reaction mixture. While the solution was still hot, the reaction mixture investigated by GC after 20 h. The results indicated that the reaction didn't progress after the separation of catalyst.

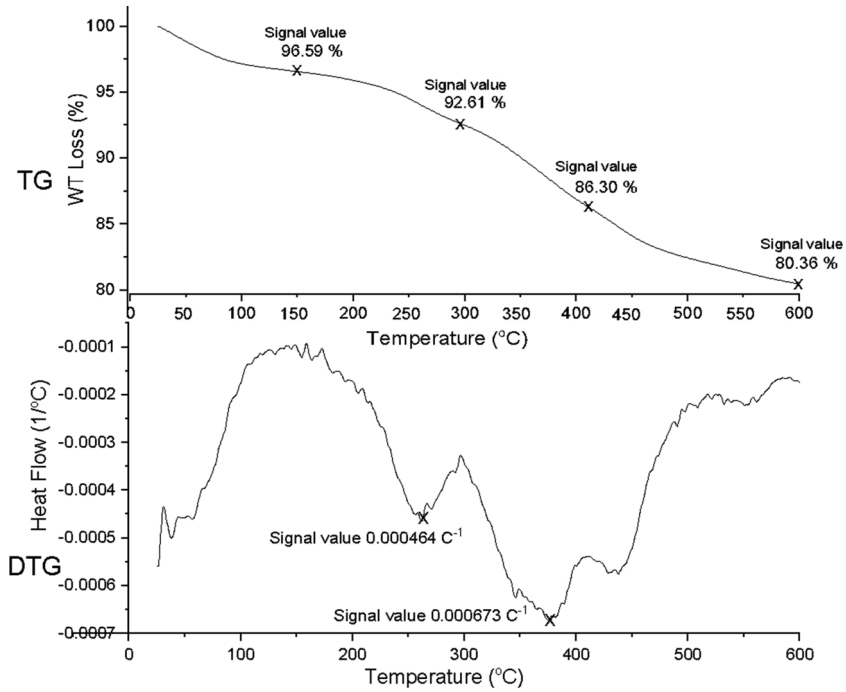


Fig. 5. TG/DTG plots of the novel prepared catalyst (Fe_3O_4@SiO_2-UT@Co^{II}).

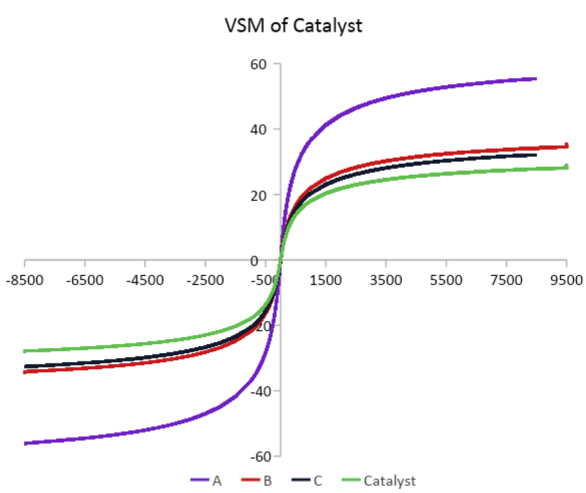


Fig. 6. VSM curves Fe_3O_4 (A), Fe_3O_4@SiO_2 (B), Fe_3O_4@SiO_2@ $(CH_2)_3$-Urea-Triazole (C), Catalyst: Fe_3O_4@SiO_2@ $(CH_2)_3$-Urea-Triazole@$CoCl_2$.

After preparation and characterization of the Fe_3O_4@SiO_2-UT@Co^{II}, we centered on design and optimized a condition reaction for C—H bond cleavage of phenols and subsequent C—S bond formation in a simple and efficient condition (Table 2). Initially, a mixture of *p*-cresol (**1a**), K_2CO_3, dimethyl sulfide (DMSO) (2 mL), and pivalic anhydride were stirred at room temperature for 2 h. Then, one-pot synthesis of sulfenylphenols/naphtols were investigated by adding thiophenol (**2a**), oxidant, additive, base, Fe_3O_4@SiO_2-UT@Co^{II} in different reaction conditions at 90 °C under air atmosphere. Toward this aim, the reaction was performed in the presence of a catalytic amount of catalyst (0.06 g) and K_2CO_3 as a base in DMSO solvent (Table2, entry 1). Under these conditions, desired product was obtained in only 20 % yield. For improving the yield of the reaction, we used different bases such as KOH, NaO^tBu, 1,4-diazabicyclo[2.2.2]octane (DABCO) and Cs_2CO_3 in this reaction (Table 2, entries 2–5). Among of them, Cs_2CO_3 was found to be the most effective base for the above said reaction (Table 2, entry 5). When the amount of catalyst was reduced, the yield of desired product decreased (Table 2, entries 6). The reaction failed in the absence of a catalyst (Table 2, entries 7). In order to study the effect of the solvents, we have conducted the reaction in PEG200, DMF, CH_3CN, and $C_2H_4Cl_2$ (DCE), but none of them displayed positive effect on the yield of product (Table 2, entries 8–11). No yield was observed when the reaction was carried out under argon atmosphere (Table 2, entry 12). Employing molecular O_2 as an oxidant had not a good effect on the efficiency of reaction (Table 2, entry 13). We used other oxidants for improving the yield. When 5 mol % of $K_2S_2O_3$ was added as oxidant to the reaction mixture, the GC yield of desired product was obtained in 79 % (Table 2, entry 14). Addition of AgCl as an oxidant to the model reaction mixture was not effective (Table 2, entry 15). Various additives such as TBAB (tetrabutylammonium bromide), TBAC (tetrabutylammonium chloride), LiBr and PPh_3 were screened to boost the yield of reaction (Table 2, entry 16–19). Surprisingly, the addition of PPh_3 to the reaction mixture caused a significantly enhanced yield, which might be due to its strong coordination effect with cobalt (Table 2, entry 19). To show the high activity of Fe_3O_4@SiO_2-UT@Co^{II} in *ortho*-regioselective sulfenylation of phenols and naphtols, $CoFe_2O_4$ MNPs and $CoCl_2$ were also tested as catalyst for the mentioned reaction (Table 2, entries 20–21) that the lower yield was obtained in the presence of them.

With the optimal conditions determined (Table 2**, entry 19**), the efficiency and applicability of Fe_3O_4@SiO_2-UT@Co^{II} were explored for the synthesis of 2-(arylthio) phenols derivatives *via ortho*-regioselective sulfenylation of phenols with aryl thiols. The results are illustrated in the Table 3. We noticed electron-donating groups on phenols dramatically promoted the reaction and gave 2-sulfenylphenols in high yields due to the fact the electron-donating groups to increase the electron density of the phenol ring (Table 3**, 3b–3i**), whereas electron-withdrawing groups slightly inhibited the transformation and moderate to low yields obtained in the reactions (**3j-3b**). There seems to be little effect of the substituent position (*ortho*, *meta* or *para*) of the phenol ring

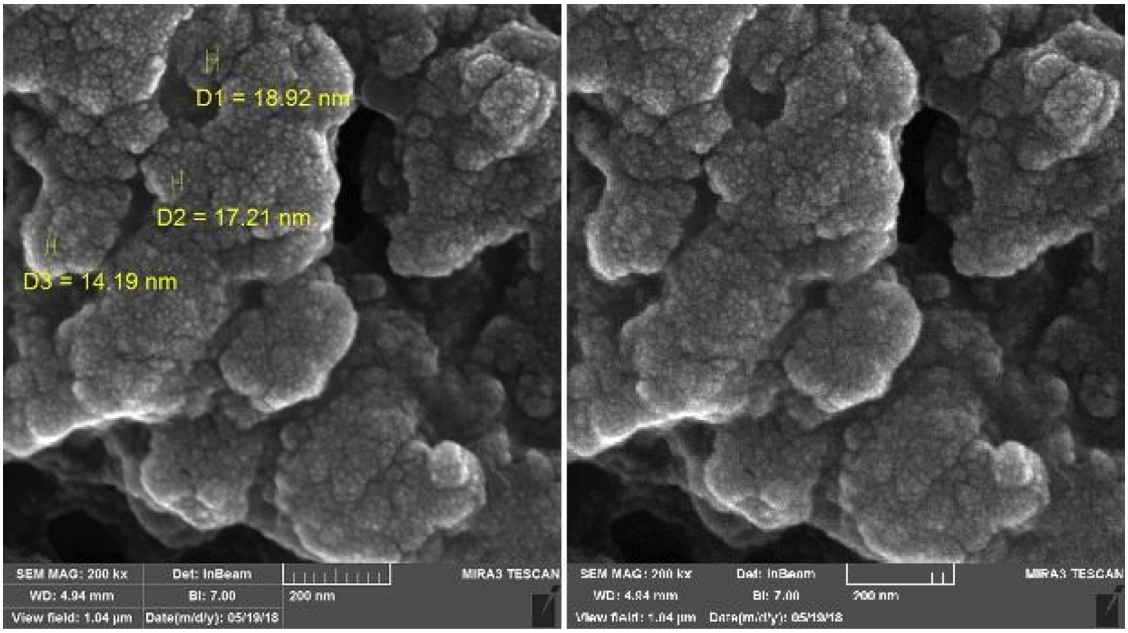


Fig. 7. SEM of the Fe_3O_4@SiO_2-UT@Co^{II} after a cycle of reaction.

Table 1
ICP Mass analysis of the Fe_3O_4@SiO_2-UT@Co^{II}.

Row	Material	Object	Result (wt. %)
1	Fe_3O_4@SiO_2-UT@Co^{II}	Co	1.6334
2[a]	Fe_3O_4@SiO_2-UT@Co^{II}	Co	1.5527

[a] (recovered catalyst).

on the reaction yield. For example, when the methyl was located at *ortho* (**3b**), *meta* (**3d**) and *para* (**3e**) position on the phenol ring, the corresponding products were obtained in 80 %, 83 %, and 95 % yields, respectively. In contrast, the pH substituent on phenol ring at an *ortho* (**3c**) and *para* (**3 g**) caused that the reaction yield partially decreased. These obtained data may be due to the phenyl rings withdrawing effect. Surprisingly, the compatibility of our catalyst with C—H bonds allows us to carry out the chemoselective sulfenylation of halophenols such as 4-Cl (**3 j**), 4-Br (**3k**) and 4-F-phenol (**3 l**) with thiophenol without changing C—X (halogen) bond. A strong electron-withdrawing group (N—O_2) on para position of phenol suppressed coupling reaction (**3 m**). Likewise, aryl thiols containing electron-rich group (**3n, 3q**) showed more reactivity than electron-poor group (**3o, 3p, 3 r** and **3 s**). Moreover, dimethyl phenol smoothly participated in the coupling with 4-methiophenol and furnished the corresponding products in excellent yield (**3 t**).

To show more synthetic applicability of the described method, generality, scop, limitations and approving the potentials of our catalyst for the sulfenylation of phenols, we have investigated the possibility of synthesis of aryl/alkyl sulfenylnaphtols using the reaction of aryl/alkyl thiols with 1 and 2-naphtol under the optimized reaction conditions (Table 2**, entry 19**).

The results in the Table 4 demonstrate that most of the aryl thiols underwent smooth transformations to afford the corresponding 1-aryl sulfenylnaphthol in good to excellent yields (**3ba- 3bd**). We further tested the described method with naphthalen-2-ol under the optimized reaction conditions. Encouragingly, the corresponding arylthiolnaphthalen-2-ol derivatives (**4ba-4bd**) were obtained in excellent yields. On the basis of the obtained results in the case of electron-rich and electron-poor aryl thiols, it was found that in the presence of electron-donating groups (**4bb**) the yield of reaction more increased than electron-withdrawing ones (**4bc and 4bd**). We have also investigated the possibility of synthesis of alkylthionaphtalen-2-ol using the reaction of alkyl thiols with 2-naphtol. Aliphatic thiols including 1-octanethiol, benzyl mercaptan, and cyclohexanethiol as sulfenylating agents were also performed successfully under present reaction conditions (**4be-4bh**).

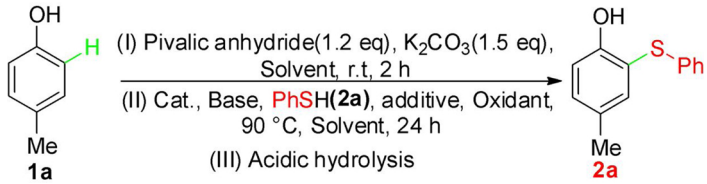
Control experiments were carried out to gain preliminary insights into the mechanism of the catalytic procedure. In this regard, we explore the roles of pivalic anhydride, O_2, and catalyst on the path of reaction. Under the standard conditions without the addition of pivalic anhydride, phenol (**1a**) did not convert to the desired product (**3a**), leaving the starting material intact and disulfide (**4a**) obtained in 10 % yield (Scheme 4**a**).

The reaction of phenol ester (instead of the phenol/ pivalic system) with thiophenol (**2a**) in the reaction, desired product (**3a**) obtained with 73 % yield (Scheme 4**b**).

In the presence of N_2 gas as without oxygen condition was not found any product (Scheme 4**c**). Using disulfide (**4a**) instead of thiophenol (**2a**), the product **3a** was formed in only 5 % yield under the standard reaction condition (Scheme 4**d**). In a control experiment in the absence of phenol substrates, thiophenol (**2a)** underwent dimerization to afford disulfide (**4a**) in 5 % yield (Scheme 4**e**).

According to our above control experiments and related references, a plausible reaction pathway for the reaction of thiols with phenols and naphtols in the presence of pivalic anhydride as directing group and Fe_3O_4@SiO_2-UT@Co^{II} as a catalyst has been illustrated in Scheme 5. It is known that phenol reacts with pivalic anhydride to produce phenolic ester (**I**) [59–67]. Then, cobalt coordinate to oxygen atom (**II**) leading to a directed *ortho*-metalation by a radical pathway and provide the key intermediate **III** [14,59]. Intermediate **III,** furnishes the **IV** *via* aromatization and Cobalt reduction in the presence of $K_2S_2O_8$ (possible reactions were proposed in the red circle). In continue, the intermediate **IV** reacts with the thiol to generate **V**, which undergoes reductive elimination and RS immigration gives **VI**. Finally, the desired product

Table 2
Optimization of catalyst, base, solvent, temperature, and additives.



Entry	Solvent	Base	Additive (5 mol %)	Oxidant (5 mol %)	GC Yield (%)
1	DMSO	K_2CO_3	–	air	20
2	DMSO	KOH	–	air	5
3	DMSO	KO^tBu	–	air	55
4	DMSO	DABCO	–	air	10
5	DMSO	Cs_2CO_3	–	air	60
6	DMSO	Cs_2CO_3	–	air	45[b]
7	DMSO	Cs_2CO_3	–	air	0[c]
8	PEG	Cs_2CO_3	–	air	0
9	DMF	Cs_2CO_3	–	air	38
10	CH_3CN	Cs_2CO_3	–	air	0
11	$C_2H_4Cl_2$	Cs_2CO_3	–	air	10
12	DMSO	Cs_2CO_3	–	Ar	0[d]
13	DMSO	Cs_2CO_3	–	O_2	40[e]
14	DMSO	Cs_2CO_3	–	$K_2S_2O_3$	79
15	DMSO	Cs_2CO_3	–	AgCl	45
16	DMSO	Cs_2CO_3	TBAB	$K_2S_2O_8$	90
17	DMSO	Cs_2CO_3	TBAC	$K_2S_2O_8$	87
18	DMSO	Cs_2CO_3	LiBr	$K_2S_2O_8$	80
19	DMSO	Cs_2CO_3	PPh_3	$K_2S_2O_8$	95
20	DMSO	Cs_2CO_3	PPh_3	$K_2S_2O_8$	60[f]
21	DMSO	Cs_2CO_3	PPh_3	$K_2S_2O_8$	75[g]

[a]Condition: **1a** (1 mmol), **2a** (1.2 mmol), catalyst (0.06 g, 0.166 mmol), Cs_2CO_3 (3 mmol), DMSO (2 mL), $K_2S_2O_8$ (5 mol %), PPh_3 (5 mol %), 90 °C, 24 h.
[b] The reaction carried out in the presence of 0.04 g of the catalyst.
[c] Without catalyst.
[d] Under argon atmosphier.
[e] Under O_2 atmosphier.
[f] $CoFe_2O_4$ (0.04 g) was used.
[g] $CoCl_2$ (10 mol%) was used.

results from **VI** and release fresh catalyst for a new reaction cycle.

The reusability of the synthesized nanomagnetic catalyst was investigated for C—S bond coupling *via* C—H bond activation reaction of *p*-cresol with thiophenol for five runs under the optimized reaction conditions. The data are depicted in Fig. 8. After completion of each run, ethyl acetate was added to the reaction mixture for dissolving the desired product, unreacted starting materials and separation of heterogenous nanomegnetic catalyst. Then the catalyst was separated from the reaction mixture by using an external magnet, repeatedly it was washed with ethyl acetate, dried and reused in the next run. The obtained data show that the performance of the catalyst smoothly decreases after five sequential runs.

Conclusion

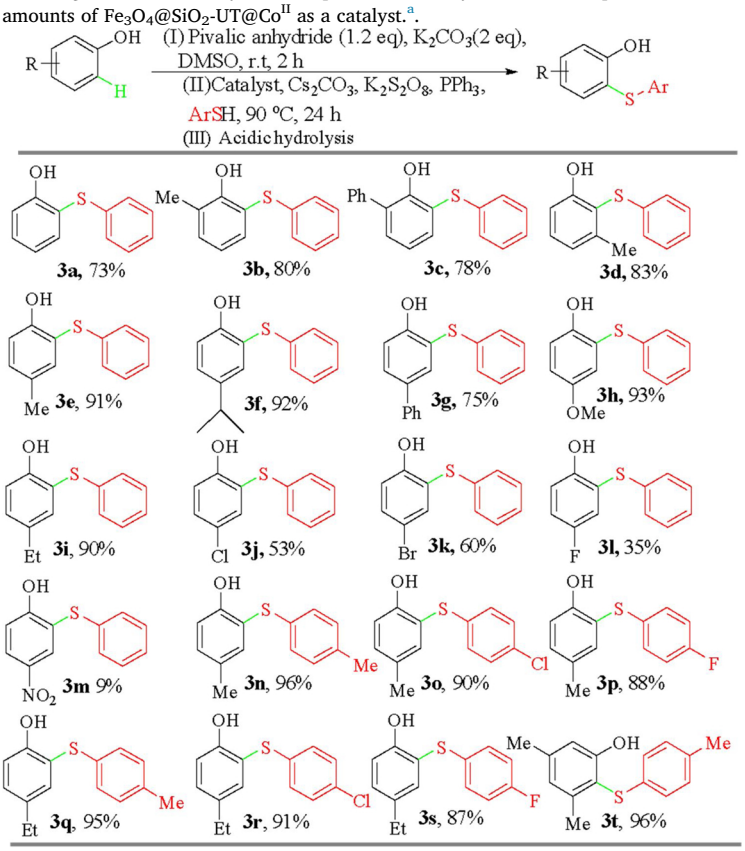
In conclusion, we have developed Fe_3O_4@SiO_2-UT@Co^{II} as new magnetically catalytic system for the synthesis of 2-arylsulfenylphenol from free-phenols, aryl/alkyl sulfides, and pivalic anhydride as a directing group *via* CH— bond activation. Significant advantages of the introduced system are as follows: (i) A one-pot synthesis approach, which offers a more straightforward and practical method and (ii) the use of cheap, commercially available, easy-to-handle and chemically stable starting substances and catalyst. More applications regarding the introduced system are under development. We think that the present work can open up a new and promising insight for designing and synthesis of various kinds of sulfides. Development of described method for cross-coupling of phenols and/or arenes with sulfur agents in other useful transformations is under investigation in our laboratory.

Experimental section

General information

All the chemicals/reagents were purchased from E. Merck, Germany. Organic extract were dried over anhydrous sodium sulphate. Solvents were removed in a rotary evaporator under reduce pressure. Silica gel (60–120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25 mm). ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.16 ppm) and DMSO (39.52 ppm) that were obtained with 1H-decoupling and described in terms of chemical shift (δ in ppm). Data for 1H-NMR are described as following: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sx, sextet; m, multiplet; app, apparent; br, broad signal), coupling constant (Hz), integration. NMR data were given in University of Isfahan (Bruker-400 MHz) and Mashhad University of Medical Sciences (Bruker–ultrashield-300 MHz). CHNS analyses were recorded on an Agilent Leco-932 CHNS instrument (EI) at Kurdistan University.

Table 3
Ortho-regioselective sulfenylation of phenols with aryl thiols in the presence of catalytic amounts of Fe_3O_4@SiO_2-UT@Co^{II} as a catalyst.[a].



[a] ROH (1 mmol), ArSH (1.2 mmol), catalyst (0.06 g), Cs_2CO_3 (3 mmol), DMSO (2 mL), K_2S_2O8 (5 mol%), PPh_3(5 mol%), 90 °C, 24 h [b] Isolated Yield.

General procedure for the preparation the urea based ligand

To a round bottom flask (250 mL), a mixture of triethoxy(3-isocyanatopropyl)silane (5 mmol, 1.236 mL) and 3-amino-1H-1,2,4 triazole (5.2 mmol, 0.437 g) was added and stirred magnetically under solvent-free conditions at 60 °C for 6 h. After completion of the reaction, n-hexane (50 mL) was added to the mixture reaction and filtered. Then, n-hexane was evaporated and desired urea based ligand was obtained as a colorless viscose oil which characterized by FT-IR and NMR spectra. (Scheme 3)

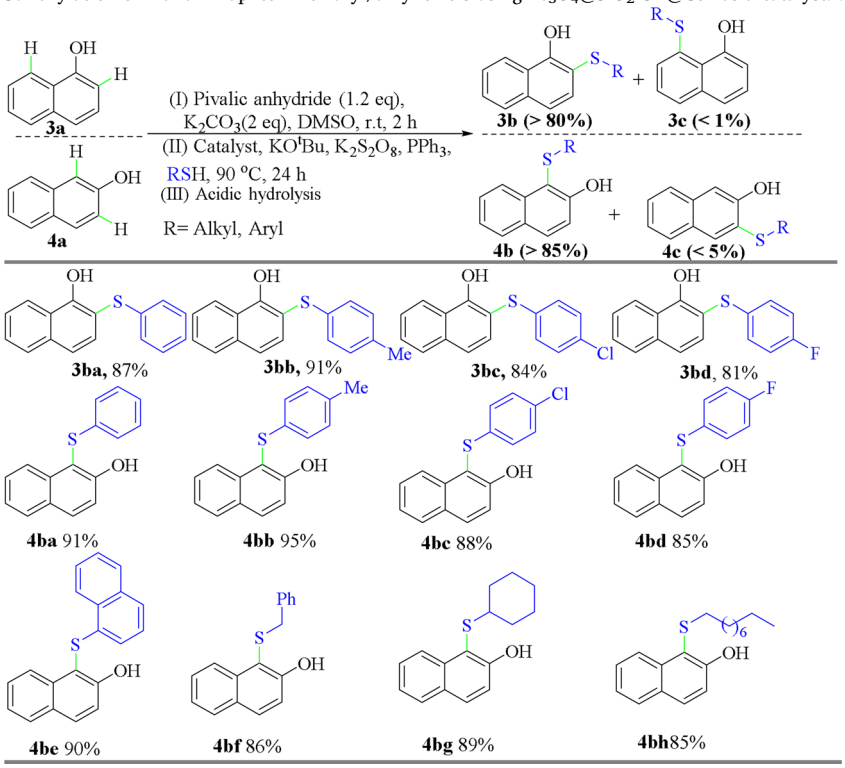
General procedure for the preparation of Co(ll)-Immobilized silica- based magnetic nano catalyst

In the beginning, Fe_3O_4 nano particles was prepared by the methods of previous works.[69] Then, the surface of Fe_3O_4 nano particles was modified by a layer of SiO_2 through the reaction with tetraethylorthosilicate (TEOS).[69] In the Following step, 1 *g* of the Fe_3O_4@SiO_2 and urea based ligand (5 mmol) in 80 ml of dry toluene were refluxed under a nitrogen atmosphere in a 150 ml round-bottom flask under mechanical stirring (600 rpm) for 24 h. Then, synthesized nanoparticles (Fe_3O_4@SiO_2@ $(CH_2)_3$-Urea-Triazole) were thoroughly washed with *n*-hexane, and dried under vacuum oven for 10 h. The reaction system was stirred for another 24 h upon the addition $CoCl_2.6H_2O$ (5 mmol, 1.190 *g*) Fe_3O_4@SiO_2@ $(CH_2)_3$-Urea-Triazole (1 *g*) in ethanol reflux. The product was obtained by centrifugation and then washed with C_2H_5OH (20 mL × 3). Finally, the obtained product was dried at 60 °C under vacuum for 10 h and stored in a desiccator (Scheme 3).

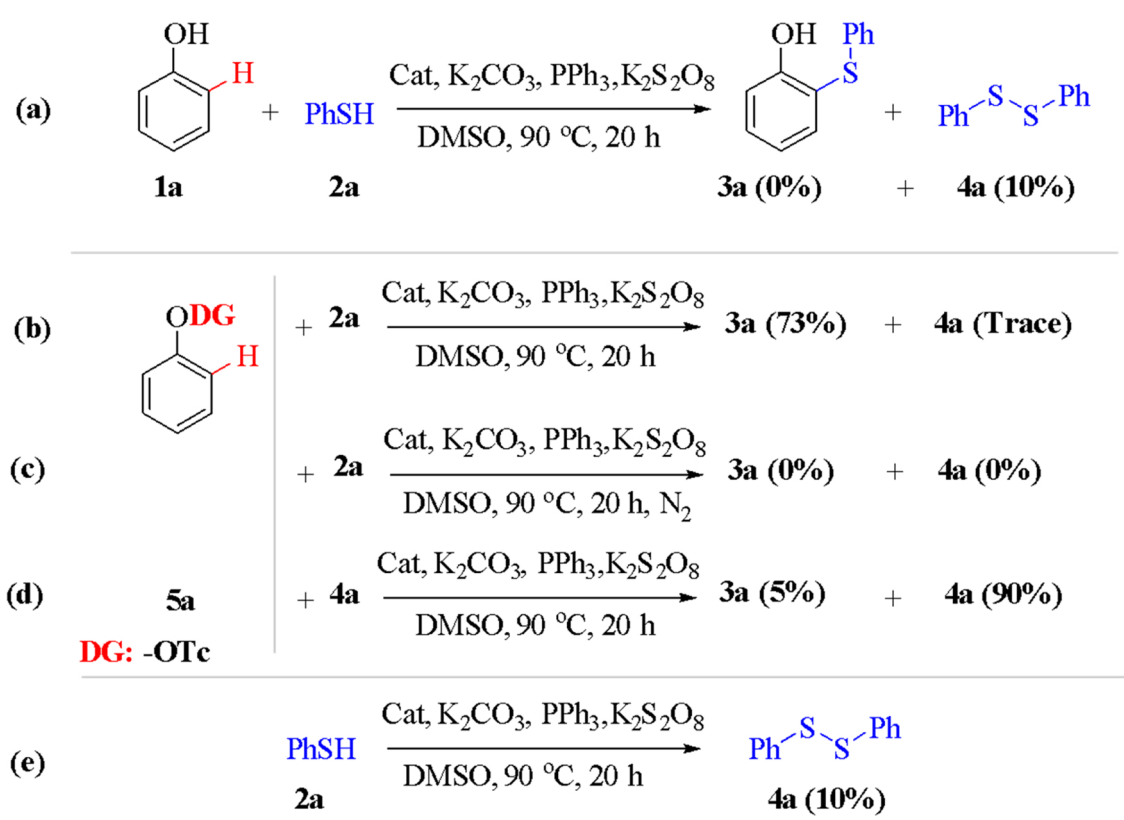
General procedure for synthesis of 2-(aryl thio) phenols

A mixture of phenol (1 mmol), Pivalic anhydride (1.2 mmol), K_2CO_3 (2 mmol) and DMSO (2 mL) was stirred at room temperature for 20–120 min. Then, catalyst (0.06 g), Cs_2CO_3 (3 mmol), PPh_3 (5 mol %), $K_2S_2O_8$ (5 mol %), thiophenol (1.2 mmol) and DMSO (2 ml) were added to the mixture which was stirred at 90 °C for 24 h. After complete conversion of phenol (TLC), HCl aq. (4.0 ml, 1 M) was added to the reaction mixture. After that, the reaction mixture was cooled to room temperature and the product was extracted with ethyl acetate (2 × 10 mL), while the catalyst was recovered under the assistance of a magnet and then washed with C_2H_5OH. The combined organic extracts were dried over anhydrous Na_2SO_4, and the solvent and volatiles were removed under vacuum to give the crude product. Further purification was performed by column chromatography on silica gel eluting with *n*-Hexane/Dichloromethane (Table 2).

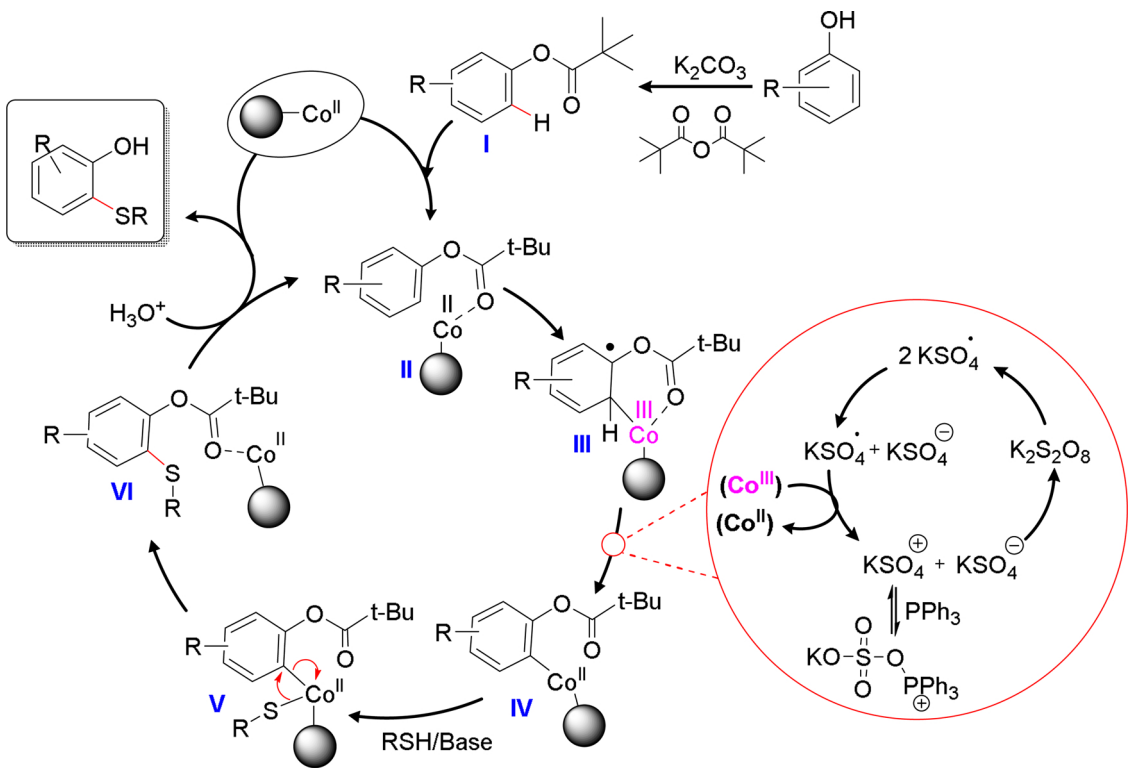
Table 4
Sulfenylation of 1 and 2-naphtol with aryl/alkyl thiols using Fe_3O_4@SiO_2-UT@Co^{II} as a catalyst.[a].



[a] ROH (1 mmol), RSH (1.2 mmol), catalyst (0.06 g), KO^tBu (3 mmol), DMSO (2 mL), $K_2S_2O_8$ (5 mol %), PPh_3(5 mol%), 90 °C, 24 h [b] Isolated Yield.



Scheme 4. Control experiment.



Scheme 5. Proposed catalytic cycle for *ortho*-regioselective sulfenylation of phenols and naphtols.

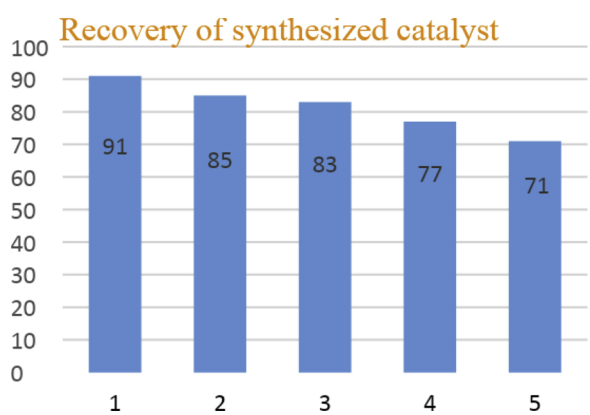


Fig. 8. Reusability of the synthesized catalyst Fe_3O_4@SiO_2-UT@Co^{II} for five reaction cycles.

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Intellectual property

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

Research ethics

We further confirm that any aspect of the work covered in this manuscript that has involved human patients has been conducted with the ethical approval of all relevant bodies and that such approvals are acknowledged within the manuscript.

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We confirm that the manuscript has been read and approved by all named authors.

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Declaration of Competing Interest

No conflict of interest exists.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.110772.

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