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Recyclable Imidazolium Ion tagged Nickel Catalyst for Microwave Assisted C-S Cross-Coupling in Water using Sulfonyl hydrazide as a Sulfur Source

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A facile and convenient synthesis of aryl sulfides through sulfenylation of alkyl halides with arylsulfonyl hydrazides, catalyzed by a simple and water-soluble Ni(II) complex has been reported. Nickel complex based on the imidazolium ion tagged salen architecture was synthesized and well characterized using various analytical techniques. Greener solvent, water was used as solvent media and moderate to good yields of aryl sulfides were obtained by using 5 mol% of the catalyst under microwave irradiation. Incorporation of ion tag functionality helped in the recycling of catalyst and successful reuse up to five runs without appreciable change in its activity.

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1. Introduction

Ubiquitous distribution of organosulfur functionalities in nature and biological system represents its essential role for the maintenance and growth of life.[1] Organosulfur motifs widely exist in natural bioactive products and synthetic drugs, leading to their application in pharmaceuticals industry.[2] Traditional protocol for their synthesis utilises coupling between a nucleophilic sulfur source and an electrophilic carbon of an organic halides/triflates/boronic acid using metal catalysts.[3] The catalyst systems are based on palladium, nickel, copper, cobalt, iron or indium metals[4] and different sulfenylating agents are thiols, disulfides, thioamides, N-thioimides and 2-thiobenzamides.[5] Use of volatile and foul-smelling sulfur sources lead to serious environmental and health issues.[6] The other limitations associated with these methodologies are catalyst deactivation through sulfur moieties, oxidative S-S coupling (disulfide formation) and difficult handling of substrates.[7] In search of developing efficient synthetic methodologies, another sulfur source, aryl/alkyl sulfonyl hydrazide which is readily available, free of offensive odor and compatible with moisture has been used. Many metal-based catalytic systems utilizing sulfonyl hydrazides to give desired C-S coupled products in good yield have been reported.[8]

In recent years, methods using efficient catalytic systems, greener solvents and other form of heating sources (microwave, ultrasonic) targeting the green chemistry concepts have been developed.[9] The advantages of using water as the reaction medium are its non-toxicity, low cost, wide availability and compatibility with homogeneous and heterogeneous catalytic systems, simplified workup procedures and enabling recycling of catalyst.[10] Nickel based catalytic systems are widely explored for carbon-sulfur transformation since nickel is abundant, cheap, environment friendly, but most of these systems require zinc to reduce nickel to its desirable oxidation state for sulfenylation.[11]

Typically used classical homogeneous metal catalysts work well for organic synthesis transformations, but they suffer from the problem of recyclability, product isolation, and purification. Various methodologies have been developed to overcome these problems and use of ion tagged catalysts have emerged as alternatives to conventional catalysts addressing eco-friendly concerns and economic demands.[12] The ion tagged catalysts are designed not only to exhibit good catalytic activities but also for efficient recycling.[13] The anions in ion tags are either organic or inorganic moieties that facilitate water miscibility of catalyst to provide better recycling without diminishing catalytic efficiency.[14] By keeping above mentioned shortcomings in mind and in continuation to our efforts to develop green methodologies, a water-soluble imidazolium ion tagged salen Ni(II) complex was synthesized and used as a catalyst for the C-S coupling reaction. This protocol does not require reducing agent and introduction of imidazolium ion tag allowed, improved catalyst recovery and use of water as a solvent.

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Electronic Supplementary Information (ESI) available: [IR, UV-vis, ^{1}H and ^{13}C NMR, and mass spectrometry data for the ion tagged ligand and its Ni complex, and ^{1}H and ^{13}C NMR data for isolated products and ESI-MS spectra of *in situ* generated species].
Electronic supplementary information (ESI) available. See DOI: 10.1039/x0xx00000x

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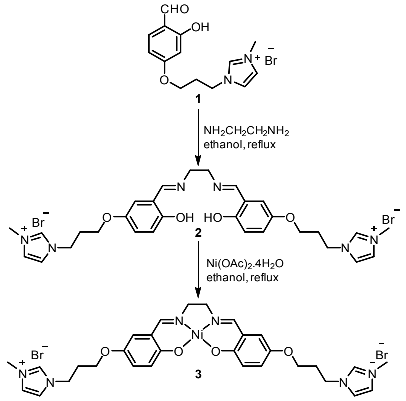


Scheme 1 Synthesis of ligand **2** and complex **3**

2. Result and Discussions

In the present study, the synthetic route for the formation of the imidazolium ion tagged salen ligand **2** and its Ni(II) **3** complex was devised (**Scheme 1)**. Both the ligand and complex were stable in air and completely soluble in highly polar solvents (DMF, DMSO, MeOH, EtOH, water etc.). The structures of the both **2** and **3** were well established using FT-IR, UV-visible, ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. Several trials failed to obtain suitable crystals of both **2** and **3** for single-crystal XRD.

2.1 IR Spectra

An IR peak observed at 1623 cm^{-1} due to ν(C═N) stretching in the spectrum of **2** shifted towards lower frequency (1605 cm^{-1}) in the spectrum of **3**, suggesting coordination through the two azomethine groups. In the spectrum of **2,** a broad band due to the intra-molecular hydrogen-bonded O–H group was observed at 3250–3500 cm^{-1}, which disappeared in **3** due to the deprotonation upon complexation. Shifting of the phenolic C-O stretching peak at 1172 cm^{-1} in the spectrum of **2** to 1124 cm^{-1} further confirmed coordination[15] (**Fig. S1** ESI†).

2.2 Electronic spectra

In solid state **2** and **3** were bright yellow and brown coloured bench stable solids respectively. Solvent state UV-visible spectral studies were performed in DMSO solvent (**Fig. S2a** ESI†). In **2** intense absorption bands appeared at 278 and 308 nm due to the excitation of π-electrons of the aromatic ring and the third band at 393 nm attributed to the *n*- *π** transition of C=N groups. In **3** along with these three absorption bands, a band at 438 nm appeared due to the charge transfer transitions and characteristic broad band with weak intensity (540-560 nm) due to *d*-*d* transitions. This broad band was further confirmed by solid-state UV-visible spectra and its presence apparently suggested the formation of square planar complexes[16] (**Fig. S2b** ESI†).

2.3 NMR spectral studies

The ^{1}H NMR spectrum of **2** showed resonance signals at *δ* 8.45 assigned to azomethine proton and a downfield singlet at 13.79 ppm due to two phenolic -OH protons. Shifting of H-C=N- protons to *δ* 7.81 and absence of –OH signals indicated deprotonation of the hydroxyl group of **2** and confirmed the bonding of oxygen to the metal ions (C–O–M). In the ^{1}H NMR spectrum of **3**, the presence of only one sharp singlet for the –CH═N proton clearly indicated that the magnetic environment is equivalent for both the protons, suggesting the planar arrangement of the ligand around metal centre. The ^{13}C NMR spectrum of **2** showed a strong NMR signal at *δ* 163.2 which may reasonably be assigned to azomethine carbon, after getting coordinated with nickel metal it shifted downfield at *δ* 165.8 ppm. (**Fig. S3** and **S4** ESI†). All other peaks are well justifying the proposed structure.[17] The absence of any other proton signal confirmed the proposed environment around the nickel centre.

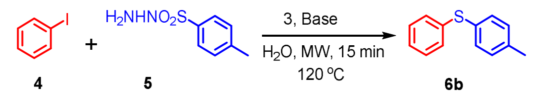
2.4 Mass spectral studies

The High-resolution mass spectra of **2** showed a peak of *m*/*z* (*z* = 2) at 273.1487 (found), (273.1472 calculated) corresponding to $[C_{30}H_{38}N_6O_4 - Br]^{2+}$ and for **3,** a peak of *m*/*z* at 301.1069 (found), (301.1071 calculated), due to $[C_{30}H_{38}N_6NiO_4 - Br]^{2+}$ (**Fig. S5** ESI†). These peaks further supported the structures and the absence of other coordinating groups.

2.5 Catalytic activity of the catalyst for C-S cross-coupling reaction

Initially, the C-S cross-coupling of *p*-tolyl-sulfonyl hydrazide **5** and iodobenzene **4** in the presence of catalyst **3** was selected as a model reaction for the optimization of the reaction conditions. The influence of base, temperature, and catalyst was investigated to find out the most suitable condition for this transformation (**Table 1**). After these trials, it was concluded that when **3** (5 mol%) was applied as a catalyst along with NEt$_3$ (2 equiv.) in water under microwave irradiation (MW) at 120 ℃, gave the desired product in good yield (86%, entry 6) after 15 min.

Table 1 Optimization of the reaction conditions[a]



S. No	Catalyst (mol %)	Base (equiv)	T (□)	Yield (%)
1	10	DBU (3)	120	60
2	10	K_2CO_3 (3)	120	21
3	10	Cs_2CO_3 (3)	120	23
4	10	NEt_3 (3)	120	82
5	5	NEt_3 (3)	120	86
6	**5**	**NEt_3 (2)**	**120**	**86**
7	5	NEt_3 (1)	120	40
8	4	NEt_3 (2)	120	65
9	5	NEt_3 (2)	130	53
10	5	NEt_3 (2)	110	-
11	-	NEt_3 (2)	120	-
12	-	-	120	-

[a] *Reaction condition:* **4** (1 mmol), **5** (2 mmol), **3** (5 mol%), water (3 ml).

After having optimized reaction conditions in hand, the scope and versatility of this method was extended to the reaction of phenyl-, *p*-tolyl, *p*-nitrophenyl, benzyl, *p*-tertiary butyl, and napthyl sulfonyl

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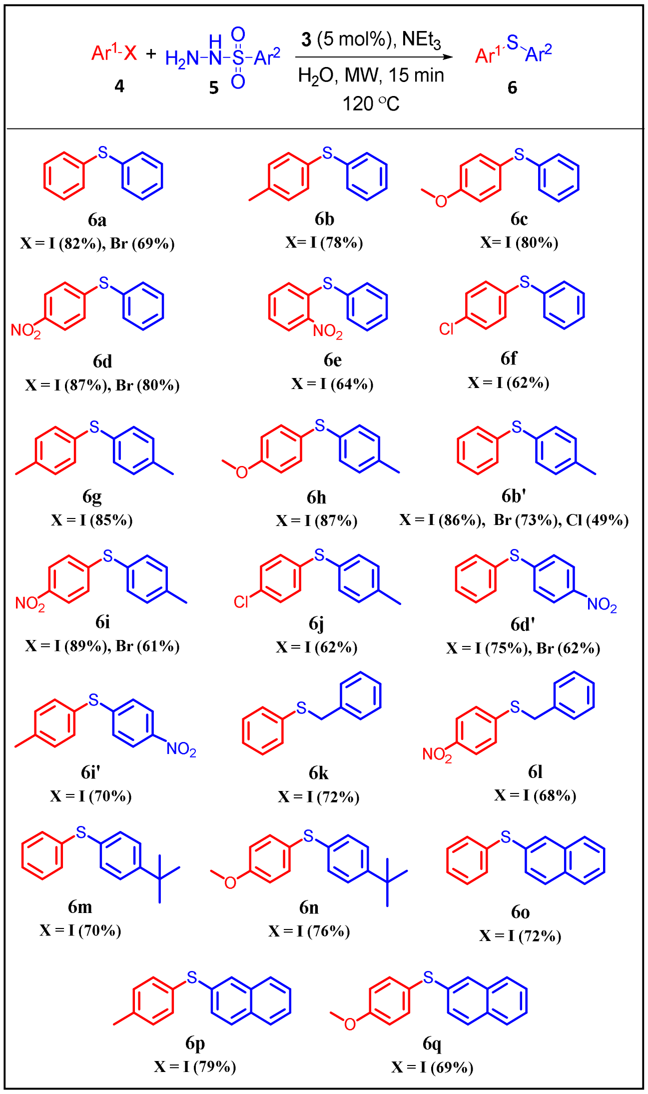
hydrazides with different aryl halides. A diverse range of unsymmetrical diaryl sulfides **6a-q** were obtained in moderate to good yields under MW for 15 min (**Table 2**). Both electron donating and withdrawing groups at different positions of reactants were well tolerated during the reaction. Both reactants having electron donating group at the *para* position provided a good yield of diaryl sulfides (**Table 2** entry **6b**, **6c**, **6g**, **6h** and **6b'**). Aryl halides derivatives with electron withdrawing group at *para* position (**Table 2** entry **6d** and **6i**) were more reactive as compared to similarly substituted sulfonyl hydrazides derivatives (**Table 2** entry **6i'** and **6l**). Less reactive *o*-nitro aryl iodide (**Table 2**, entry **6e**) was also reacted under these reaction conditions. Sterically hindered and bulky sulfonyl hydrazides also reacted well to provide desired thioether (**Table 2** entry **6m, 6n, 6o, 6p,** and **6q**). Only bromobenzene and *p*-nitrobromobenzene reacted and trials failed for other derivatives of bromobenzene. Chlorobenzene only reacted with *p*-tolyl sulfonyl hydrazide and gave only 49% yield of the product (**Table 2** entry **6b'**).

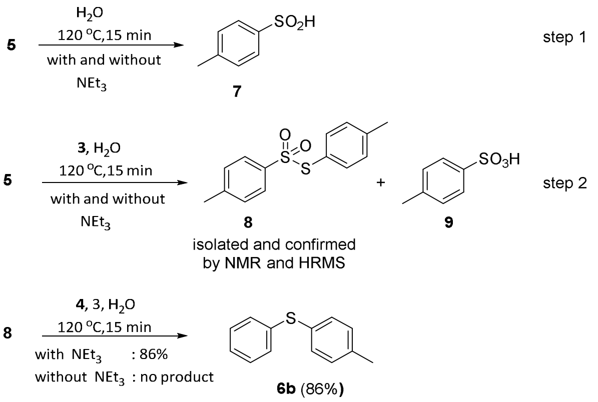
Table 2 Substrate scope for sulfenylation reaction using 3[a, b]



[a]*Reaction condition:* aryl halide (1 mmol), sulfonyl hydrazide (2 mmol), **3** (5 mol%), NEt$_3$ (2 equiv.), water (3 ml). [b]Isolated yield.

2.6 Mechanism studies of the C-S Cross-Coupling Reaction

To investigate the possible mechanism for this arylthiolation, a series of control reactions with *p*-toluenesulfonyl hydrazide under different reaction condition was carried out and reaction mixtures were analysed using mass spectra (**Scheme 2** step 1 and 2). **5** in the presence or absence of base gave only sulfinic acid **7** when 5 mol% of **3** was added, thiosulfonate **8** (59%) was obtained along with sulfonic acid **9**, indicating that base has no role in the formation of **8**. Isolated **8** on further treatment with iodobenzene under standard reaction conditions provided desired product in 86% yield. No coupling was observed in the absence of a base, whereas desired product was obtained when the base was present, suggesting the necessity of base for the effective removal of halide. Therefore, a plausible mechanistic pathway based on above control experiments and the evidence shown in literature precedent[18] was proposed (**Scheme 3**). With the aid of catalyst **3** and air oxidative decomposition of sulfonyl hydrazides, **5** takes place into sulfur source **8** with the release of N$_2$ and H$_2$O. In catalytic cycle oxidative addition of aryl halide to **3** gives nickel species **10**, which on reaction with sulfur source **8** gives nickel species **11**. Finally, on reductive elimination, coupling product was formed and again **3** was regenerated and used for next catalytic cycle. Few species involved in the reaction were identified with the help of mass spectra (**Fig. S6-S9**, ESI†), **8** was also confirmed by NMR and HRMS spectra (**Fig. S10** ESI†).



Scheme 2 Control experiments

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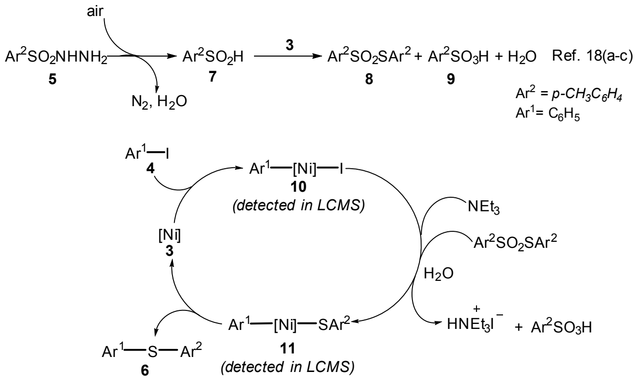

Scheme 3 Plausible mechanistic pathway

2.7 Recyclability of catalyst 3

The reusability of the aqueous catalytic system is very important from the practical and economic viewpoints. Therefore, the reusability test of **3** was done, the use of this water-soluble nickel catalytic system enabled easy separation of the catalyst from the organic phase. As shown in **Fig. 1** the catalyst can be recycled up to 5th cycle and the further gradual loss of activity of catalyst was due to the successive extraction or deactivation of the catalyst.

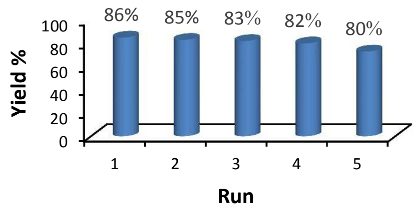

Fig. 1 Recyclability of catalyst

3. Experimental section

3.1 Reagents and materials

Imidazolium ion tagged aldehyde **1** was synthesized according to our previously reported methods.[19] Sulfonyl hydrazides were prepared according to the literature procedure.[20] All other chemicals were purchased from Alfa Aesar, Sigma-Aldrich and Spectrochem and used without purification. The solvents used were purchased from Merck (India). The melting points were determined in open capillary tubes on an MPA120- automated melting point apparatus and are uncorrected. Reactions were monitored using thin layer chromatography (TLC) on 0.2 mm silica gel F254 plates (Merck). The IR spectra were recorded on ABB Bomen MB 3000 FTIR spectrophotometer using KBr pellets. The electronic spectra were recorded on Shimadzu UV-1800 and Shimadzu UV-2450 UV-Vis spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Ascend™ 400 MHz spectrometer using $CDCl_3$ and DMSO-d_6 as solvents and the chemical shifts are expressed in ppm. The mass spectra were recorded on 6545 Q-TOF LC/MS spectrometer. Microwave reactions were performed in a microwave synthesis reactor Monowave 300 (Anton Paar, Austria) with 10- mL standard vial and teflon-coated magnetic stir bar.

3.2 Synthesis of imidazolium ion tagged ligand 2:

To an ethanolic solution of ethylenediamine (1 mmol), **1** (1 mmol) was added dropwise. The resulting solution was refluxed for 5 h and then cooled at room temperature. The solvent was evaporated under reduced pressure and washed with ether and ethyl acetate. Obtained solid was dried under vacuum and ligand **2** was obtained as bright yellow solid, yield: 92%.

3.3 Synthesis of imidazolium ion tagged nickel complex 3:

The ligand **2** (1 mmol) was stirred in ethanol and refluxed for 15 min. An ethanolic solution of $Ni(OAc)_2.4H_2O$ (1 mmol) was added to it and the mixture was kept on refluxing for 6 h. The resulting solution was evaporated under reduced pressure, washed with ether, ethyl acetate and after drying, **3** was isolated as a brown solid, yield: 95%.

3.4 General procedure for the nickel-catalyzed carbon-sulfur bond formation reaction

A mixture of aryl iodide (1 mmol), sulfonyl hydrazide (2 mmol), NEt_3 (2 equiv.) and **3** (5 mol%) in 3 ml water was stirred under microwave irradiation at 120 °C temperature for 15 min. After completion of the reaction, the mixture was extracted with ethyl acetate and concentrated under reduced pressure. The crude product was purified by column chromatography using a mixture of *n*-hexane and ethyl acetate as an eluent.

3.5 Reusability and recovery of the catalyst

After the extraction of the product, the aqueous layer containing **3** was further charged with iodobenzene, sulfonyl hydrazide, and base for the second run. The same procedure was applied for next consecutive cycles and the catalyst could be used for five times with only a slight decrease in the activity.

4. Conclusion

In summary, we have developed an imidazolium ion tagged nickel catalyst for the cross-coupling reaction of different sulfonyl hydrazides with aryl halides under microwave irradiation using water as a solvent. Sulfonyl hydrazides worked well as a sulfenylating agent for the C-S bond formation and afforded various symmetrical and unsymmetrical thioethers in moderate to good yield under mild reaction conditions. Reaction in water and recycling of catalyst makes this protocol greener and environmentally friendly.

Conflicts of interest

There are no conflicts of interest to declare.

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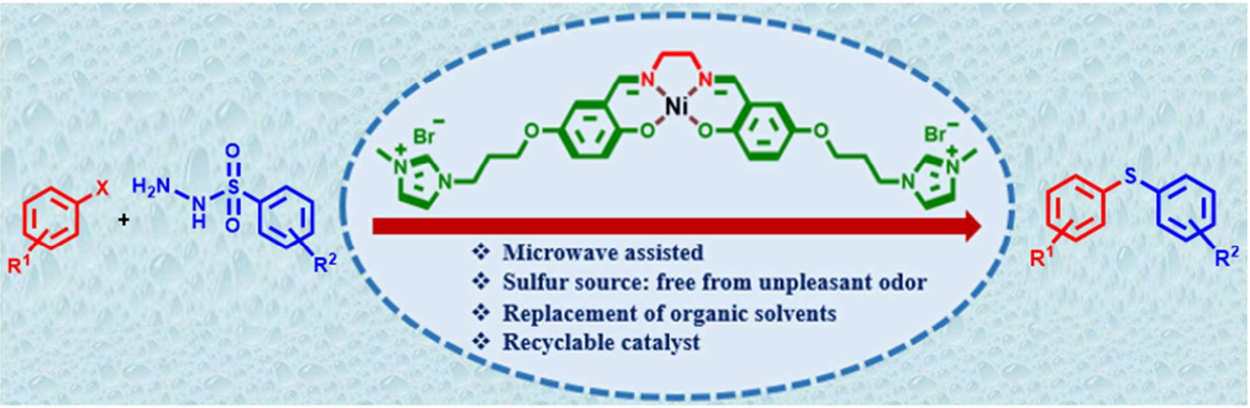
Graphical abstract

Recyclable nickel (II) catalyst promoted sulfenylation of aryl halides with sulfonyl hydrazides in water using microwave irradiation under mild conditions is reported.



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