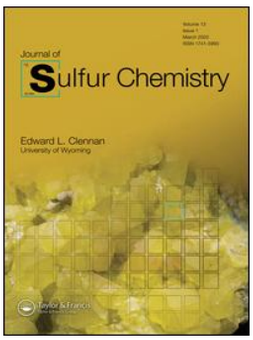

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Iron-promoted sulfur sequestration for the substituent-dependent regioselective synthesis of tetrazoles and guanidines

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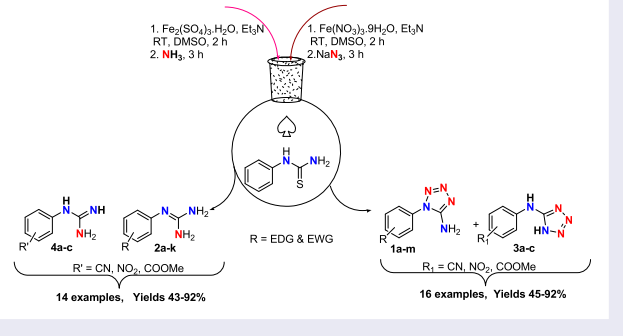
ABSTRACT

We have established a facile and versatile synthetic methodology for the construction of tetrazoles and guanidines in the presence of an eco-friendly, inexpensive, easily available iron reagent. Aromatic thioureas with electron-donating substituents produced their respective target products in quantitative yield. In contrast, when electron-withdrawing substituted aromatic thioureas were used, the expected products were obtained in reduced yield. However, the desired products were obtained in good yield at moderate temperature. In addition, mechanistic studies revealed that the synthetic route involved iron-based subsequent reactions of addition and removal of sulfur.



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Sulfur-extracting reagent iron; room temperature; tetrazoles; guanidines; desulfurization

Introduction

The conversion of a simple substrate into diverse libraries of more complex molecules constitutes a great challenge in modern organic synthesis from both academic and industrial standpoints [1,2]. Recently, multicomponent reactions have emerged as important synthetic approaches involving at least three or more than three variable components

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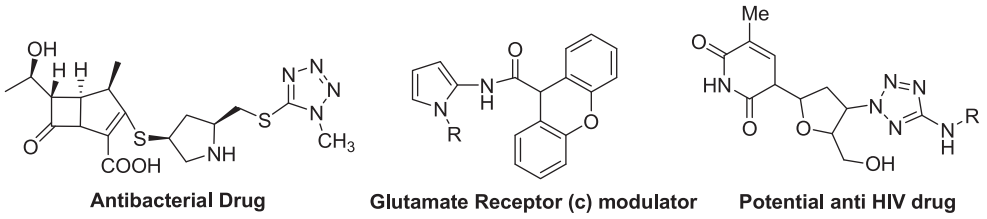


Figure 1. Examples of biological important tetrazole compounds.

participating in such a way that to provide a single product [3–9]. Multicomponent reactions provide a valuable and convenient methodology to create several natural, bioactive, and non-bioactive organic molecules. Over the past few decades, these MCRs have had a significant impact due to their huge advantages such as speed, efficiency, green reaction conditions, and atom economy. Based on the better productivity and considerable process time reduction of MCRs compared to the classical techniques, MCRs have become popular in organic chemistry [10–15].

Tetrazoles are an interesting class of heterocyclic compound, and they are resistant to metabolic degradation as well as towards chemical oxidants [16] and as structural components of many biological important molecules [17]. In this regard, a few examples of tetrazoles, such as bearing anti-bacterial drug [18], receptor modulator [19], and anti-HIV [20,21] activity, are shown in Figure 1.

Initially, the synthesis of substituted tetrazole has been developed using traditional methods, such as the addition of $NaNO_2$ to aminoguanidine [22], the addition of NaN_3 to carbodiimides or cyanamides [23–26], the reaction of amines with a leaving group in tetrazoles 5-position [27,28], and nucleophilic substitution by N_3^- of chlorine in α-chloroformamidines [29]. Later the traditional methods of tetrazole syntheses were replaced by modern methods that have used various transition metals like copper [30,31], mercury [32,33], lead salts [34], zinc salts [35–41], and cobalt sources [42]. Furthermore, tetrazoles have also been constructed in the presence of TBAF [43] and iodine [44].

However, these methods require either toxic reagents or harsh reaction conditions such as high temperature. They also lack regioselectivity [45], suffer from unavailable starting materials, lower yields, and are limited to aryl substituents. Furthermore, many of the reports have focused on the formation of tetrazoles from cyanides and cyanamides. On the other hand, very few reports [44] are available for the synthesis of tetrazole from thiourea. Therefore, we initiated research to develop the formation of tetrazoles from thiourea using 'sulfur-extracting reagent iron' as a reagent. The proposed reaction involves desulfurization, nucleophilic substitution, and electrocyclization. In addition, we would like to confirm that no report is available for the synthesis of tetrazole using an iron reagent.

In extension, we wish to report the synthesis of substituted guanidines, which have biological and medicinal importance (Figure 2) [46,47]. Recently, Izdebski and co-workers have synthesized protected guanidines from amine using DMAP at room temperature [48,49]. Later, Giacomelli [50] have used cyanuric chloride (TCT) to prepare di-Boc-guanidines instead of classical $HgCl_2$ to avoid heavy-metal waste. In this century, Mack [51] has developed a methodology for the preparation of protected guanidines from the

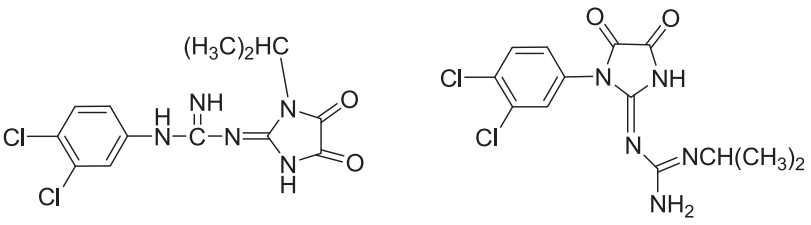


Figure 2. Examples for biological important guanidine molecules.

treatment of protected imines and amines in the presence of acetonitrile under mild reaction conditions. In addition, recently Yanina Lamberti group has reported novel guanidines from acyl thiourea, and they found the good biological activity of those compounds [52].

Furthermore, the existed methods have some other drawbacks like (i) the use of toxic reagents; (ii) extremely alkaline conditions; (iii) the use of expensive reagents; (iv) the use of high reaction temperature; (v) low yields involving tedious purification procedures; and (vi) the need for longer reaction time. To the best of our knowledge, no report is available for the synthesis of guanidines from thiourea in the presence of iron reagents. Therefore, we would like to report the synthesis of substituted guanidines from thiourea using cheap, readily available, and air-stable iron reagents under mild reaction conditions.

Experimental materials and methods

General information

Aniline, CS_2, $FeCl_3$, $Fe(NO_3)_3.H_2O$, $Fe_2(SO_4)_3.H_2O$, $FeCl_2$, Et_3N, pyridine, sodium bicarbonate, sodium acetate, and sodium hypo phosphate are purchased from Aldrich and used without further purification. The solvents are purchased and dried according to the standard procedure prior to use.^{1}H NMR (400 MHz) spectra are recorded with a Varian 400 spectrometer. Infrared (IR) spectra are recorded as a Perkin Elmer Spectrum on FT-IR spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on either Varian or Bruker Advance spectrometer. We have used Perkin Elmer Spectrum One FT-IR spectrometer for recording the IR spectra. CHNS analyzer (Perkin Elmer) has been used for analyzing the elemental analysis.

Representative experimental procedure for the synthesis of phenylamino tetrazole

Substituted thiourea (2 mmol, 304 mg) was completely dissolved in the DMSO (3 mL) at room temperature. To this, Et_3N (2 mmol, 202 mg) and catalyst were added slowly at room temperature. The resulting reaction mixture was stirred at room temperature for 2 h. After that, NaN_3 (2 mmol, 130 mg) was added, and stirring was further continued for 3 h. The development of the reaction was examined by TLC (30% ethyl acetate in hexane). The black color solid, which was observed during the reaction, separated using the centrifugation process. The clear reaction mixture extracted with ethyl acetate (2 × 10 mL), and the organic layer was washed with brine (1 × 5 mL) and water (2 × 5 mL). Drying and evaporation of the solvent gave a residue that was purified by column chromatography using 30% ethyl acetate in hexane as eluent to obtain phenyl aminotetrazole as a solid.

Representative experimental procedure for the synthesis of phenylguanidines

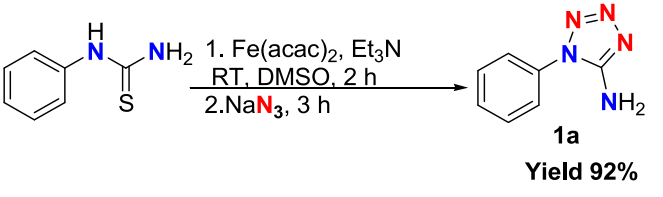
Et_3N (2 mmol, 202 mg), catalyst (50 mol %), and thiourea (2 mmol) were stirred in DMSO at room temperature, and the reaction mixture was stirred for 2 h. After that, Aq NH_3 (2 mL) was added, and further stirring was continued for 3 h. The progress of the reaction was monitored by TLC using 30% ethyl acetate in hexane as eluent. After completion of the reaction, the target reaction mixture was centrifuged for 10 min by using a centrifugation machine to separate the black color solid. The clear solution mixture extracted with ethyl acetate (2 × 10 mL), and the organic layer was washed with brine (1 × 5 mL) and water (2 × 5 mL). Drying and evaporation of the solvent gave a residue that was purified by column chromatography using 30% ethyl acetate in hexane as eluent to obtain phenyl aminoguanidine as a solid.

Results and discussion

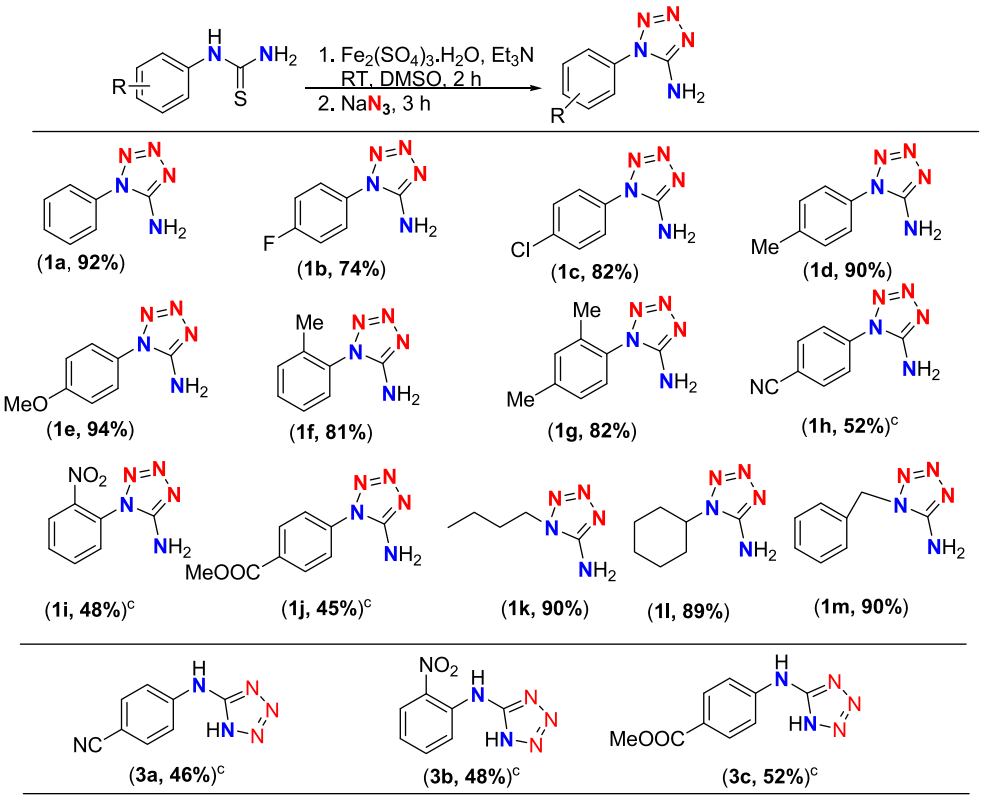
First, reaction conditions were optimized using readily available *N*-phenyl thiourea and sodium azide as model substrates, together with different iron reagents, bases, and solvents. The reactions were also carried out at room temperature. Initially, solvent optimization was carried out using Et_3N as a base and ferric sulfate as a catalyst. In this connection, the formation of tetrazole was more efficient when using DMSO as solvent compared to the use of other solvents (Acetone, CH_3CN, DMF, EtOH, MeOH, H_2O, *n*-hexane, and *n*-heptane). The control experiment confirmed that the reaction did not give the target product in the absence of solvent. Since thiourea does not dissolve in nonpolar solvents like *n*-hexane and *n*-heptane, the reaction could not give the target product. No tetrazole formation was observed in the presence of other solvents, which would not make complex with the iron reagent.

However, a high yield of tetrazole was observed when using Et_3N and pyridine instead of inorganic bases (NaOAc, NaOH, and Na_2HPO_4). Organic bases like Et_3N and Pyridine complex with iron salts that increase their solubility, which leads to an increase in the yield of tetrazole product. Among the inorganic bases, sodium acetate is better than others. It might be reasoned that NaOAc may produce $Fe(OAc)_2$, which is more soluble than other iron sources. To confirm, we have performed the control experiment with an organosoluble iron source like $Fe(acac)_2$, and it gave tetrazole product in good yield (Scheme 1). In the case of disodium phosphate and sodium hydroxide, we could observe tetrazole product along with some other undetermined spots, which are in TLC (bond might be broken in the presence of strong bases).

Both Iron (II) and iron (III) sources ($FeCl_2$, $Fe_2(SO_4)_3.H_2O$, $Fe(NO_3)_3.9H_2O$, $FeCl_3$) exhibited similar levels of activity and selectivity. Reaction with lower amounts of iron



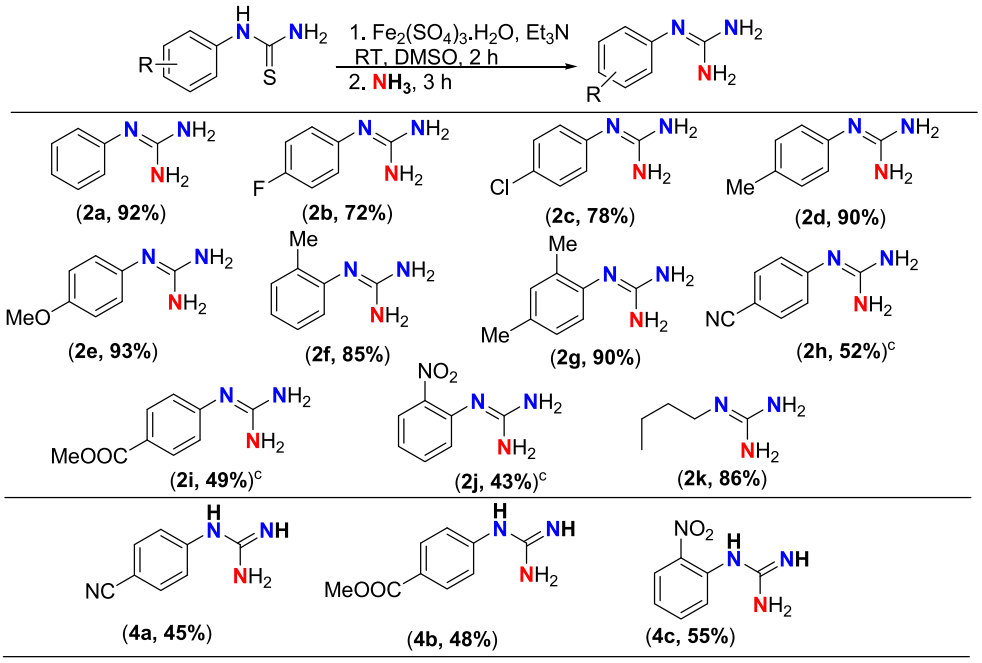
Scheme 1. Synthetic route for the synthesis of 1-alkyl-5-amino tetrazoles.



Scheme 2. Substrate scope for the synthesis of tetrazoles[a]. [a] Reaction conditions: substituted thiourea (2 mmol), $Fe_2(SO_4)_3.H_2O$ (50 mol %), Et_3N (1 eq), DMSO, room temperature, 2 h, then NaN_3 (1 eq), rt, 3 h. [b] Isolated yield. [c] K_2CO_3 (1 eq) was used.

source (25 mol %) gave lower yields of tetrazole. In a control reaction in which an iron source was absent, the tetrazole was not formed, and the starting material was recovered intact.

Having the optimal conditions in our hand, the scope of the protocol was next explored (Scheme 2). The process was found to be generally applicable; various aryl- and alkyl-substituted thioureas have reacted with sodium azide to provide the corresponding tetrazoles **1a–m** in moderate to good yield. Aryl thiourea having electron-donating substituents on the phenyl ring (4-Me, 4-OMe, and 2,4-diMe) were more reactive than those hold electron-withdrawing substituents on the aryl ring (4-F, 4-CN, 2-NO_2, and 4-COOMe groups). In addition, aryl thioureas were partially more reactive than alkyl thioureas. The thiourea having strong electron-withdrawing groups like 4-CN, 2–NO_2, and 4-COOMe on phenyl ring gave the corresponding tetrazoles in less yield under optimized reaction conditions. Therefore, we have carried out further optimization to improve the yield of the products. In this connection, they were tested using a strong base (anhydrous potassium carbonate (K_2CO_3)), and they gave their respective target products **1h–j** in moderate yield. On the other hand, the thioureas contain strong EWG like 4-CN, 2–NO_2, and 4-COOMe on phenyl ring provided other isomeric products **3a–c** in 46%, 48%, and 52% yields, respectively.

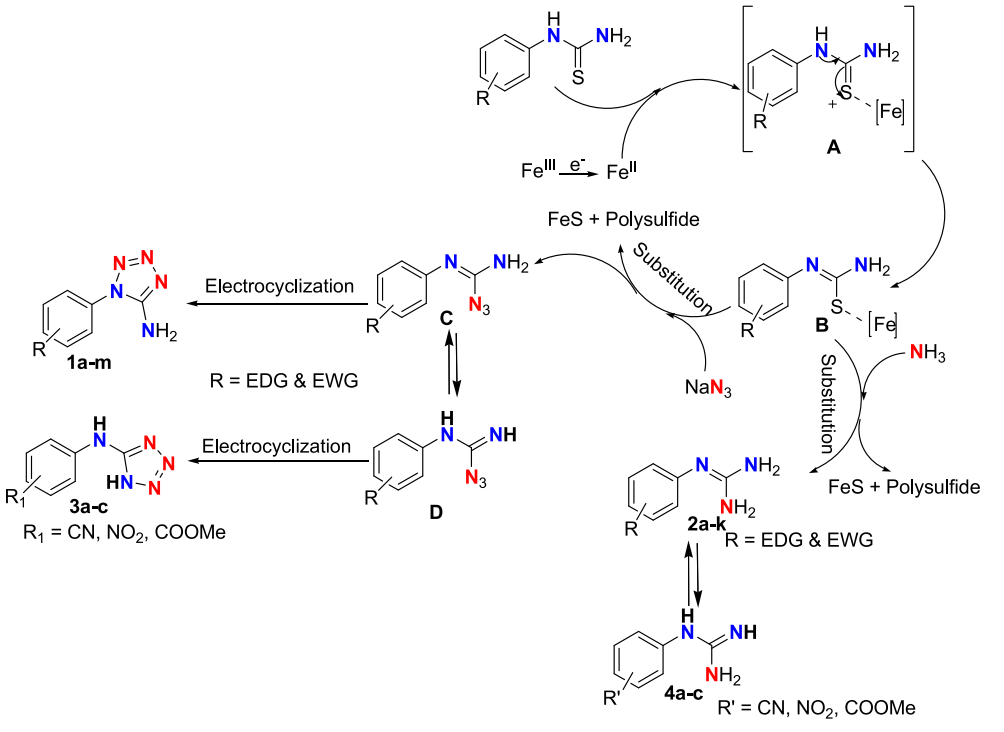


Scheme 3. Substrate scope for the synthesis of *N*-aryl/alkyl guanidines[a]. [a] Reaction conditions: substituted thiourea (2 mmol), $Fe_2(SO_4)_3.H_2O$ (50 mol %), Et_3N (1 eq), DMSO, room temperature, 2 h, then Aq NH_3 (1 eq), rt, 3 h. [b] Isolated yield. [c] K_2CO_3 (1 eq) was used.

Later, we have started the optimization for the synthesis of guanidine using phenyl thiourea and Aq NH_3 as model substrates. Since Aq NH_3 is cheaper and more readily available than NaN_3, we have chosen NH_3 as nucleophile for the synthesis of guanidine derivatives. We gratifyingly confirmed that the reaction was best using $Fe_2(SO_4)_3.H_2O$ (50 mol %), Et_3N (2 mmol), and Aq NH_3 in the presence of DMSO at room temperature. All the electron-donating and electron with-drawing substituents provided their respective target products **2a–k** in 43–93% yields (Scheme 3). Similar to tetrazole formations, isomeric guanidines were also obtained in the case of strong electron-withdrawing substituents of phenyl ring. In this regard, thioureas consisting of 4-CN, 4-COOMe, and 2-NO_2 on phenyl gave guanidine products **4a–c** in 45%, 48%, and 55% yields, respectively.

To gain insight into the nature of the iron reactivity and rationalize why both Iron (II) and Iron (III) salts reacted equally well, we performed EPR experiments (see Supp.). The reaction was monitored to show that a similar iron species is generated from both $FeCl_2$ and $Fe_2(SO_4)_3.H_2O$ prepromoters. Thus, from these experiments, we strongly believe that Fe (III) may convert into Fe (II) species in the presence of substituted thiourea.

Based on experimental results and literature reports [53,54], we propose a possible catalytic cycle in Scheme 4. Iron (II) species (could be formed from Fe (III) salt) [55–60] coordinates to sulfur in thiourea followed by desulfurization (FeS was formed as byproduct and an extra sulfur might have converted into polysulfide) [61,62] and nucleophilic substitution with NaN_3 to afford the intermediate C *via* intermediates **A** and **B**. Electrocyclization then occurs depending on the electron density of the phenyl ring of the intermediate.



Scheme 4. Plausible mechanism.

While the phenyl ring contains strong electron-withdrawing groups (4-CN, 4-COOMe, or 2-NO2), it is possible to obtain the target products, substituted 5-phenylaminotetrazoles **3a–c**, *via* an intermediate **D**, otherwise phenyltetrazolamines **1a–m** are formed *via* intermediate **C**. On the other hand, desulfurization [63–69,44] of intermediate **B** and followed by nucleophilic substitution with Aq NH_3 to afford the target products **2a–k**. Whereas phenyl ring bearing strong electron-withdrawing substituents like CN, COOMe, and NO_2 to provide possible tautomeric products **4a–c**.

To confirm the formation of FeS, after completion of the reaction the solid FeS was separated *via* centrifugation, and it was subjected to Powder XRD analyses (Figure 3). The spectrum shows the peaks such as (101), (110), (102), (201), and (213) match with JCPDS XRD data for ferrous sulfide [70–73]. No other diffraction peaks appeared in the XRD pattern. Therefore, we strongly believe that ferrous sulfide has formed in the reaction medium.

Conclusion

In conclusion, a simple method for the construction of aryl/alkyl tetrazoles and guanidines has been established from thiourea under mild reaction conditions using sulfur-extracting reagent iron, which is cheap, readily available, and air-stable. In contrast to previously described methods, which frequently require unstable moisture-sensitive starting materials, such as isocyanide dichlorides, chloroformamidines, aminomethane sulfonic acids,

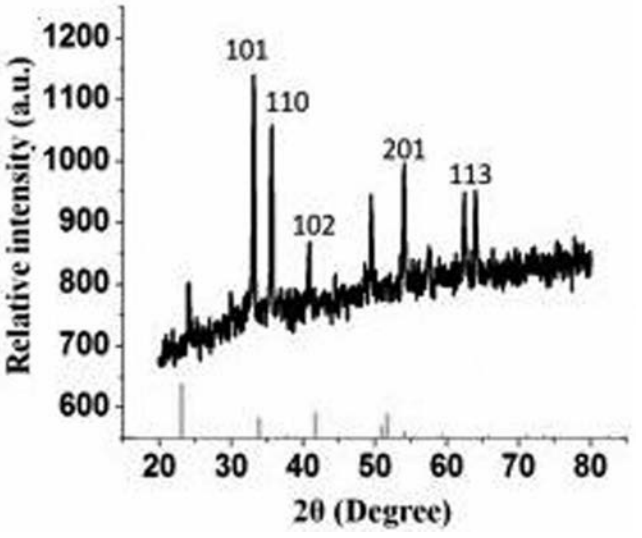


Figure 3. Powder XRD pattern for solid FeS.

and benzotriazolyl carboximidamides, our method uses stable thiourea as a starting precursor and occurs in high yields. The ease of product purification is also enhanced. Furthermore, functional group tolerance has been described in this paper. In addition, we have also conducted mechanistic studies to provide a plausible mechanism for this methodology.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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