Journal Pre-proofs

Exploration of the mechanism and scope of the CuI/DABCO catalysed C-S coupling reaction

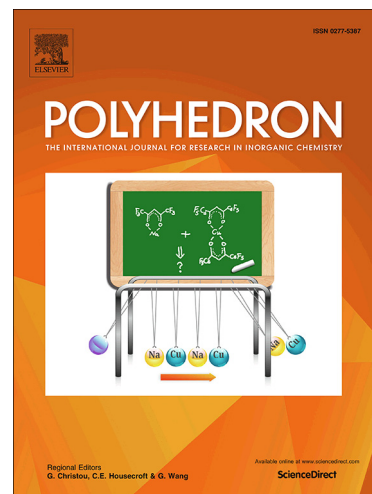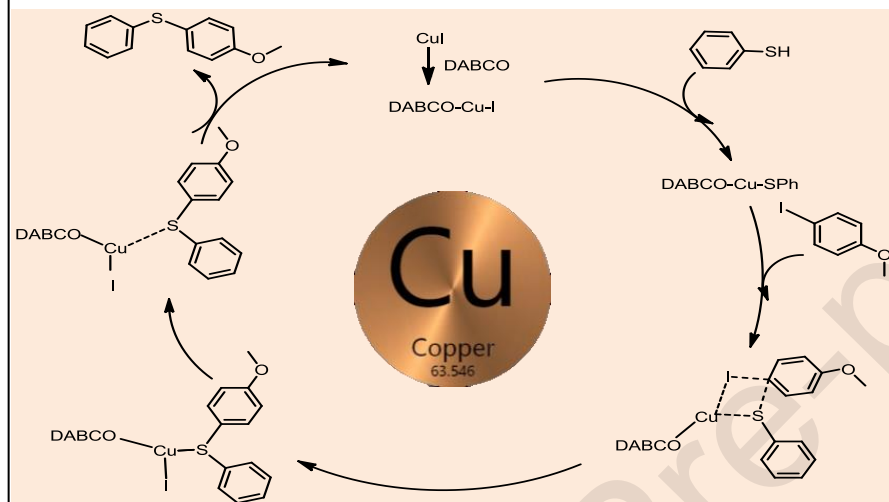Anns Maria Thomas, D.R. Sherin, Sujatha Asha, T.K. Manojkumar, Gopinathan Anilkumar

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Graphical Abstract

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Anns Maria Thomas, Sherin D. R., Sujatha Asha,
Manojkumar T. K.* and Gopinathan Anilkumar*

Polyhedron

Exploration of the mechanism and scope of the CuI/DABCO catalysed C-S coupling reaction

Anns Maria Thomas,[a,b] Sherin D. R.,[c] Sujatha Asha,[a,d] Manojkumar T. K.*[c] and Gopinathan Anilkumar*[a,e]

[a] School of Chemical Sciences, Mahatma Gandhi University, Priyadarsini Hills P O, Kottayam, Kerala, INDIA 686560.

[b] Nirmala College, Muvattupuzha P.O, Ernakulam, INDIA, 686661.

[c] Indian Institute of Information Technology and Management-Kerala, Trivandrum, INDIA.

[d] Govt. Polytechnic College, Thannurkara P.O, Chelakkara, Thrissur, Kerala, INDIA.

[e] Advanced Molecular Materials Research Center(AMMRC), Mahatma Gandhi University, Priyadarsini Hills P O, Kottayam, Kerala, INDIA 686560.

ARTICLE INFO

ABSTRACT

A cost effective and easily available CuI/DABCO catalytic system has been developed for the C–S cross-coupling reaction. This method is extremely useful for the thioetherification of aryl and heteroaryl halides, providing excellent yields and good chemoselectivity. We have also explored the mechanism of the reaction using DFT studies.

Introduction

Transition metal catalysed C–S bond forming reactions are widely applied in organic synthesis for the production of key moieties in biological, pharmaceutical or material fields.[1] The traditional methods, which require high temperature, polar solvents or strong reducing agents, can be replaced by this protocol.[2] Pioneering work on transition metal catalysed C-S coupling reactions was reported by Migita and co-workers.[3] Unfortunately Pd catalysts are expensive and have low turnover numbers. In addition to this, Pd catalysts are usually combined with phosphine ligands, requiring tedious procedures for their preparation, and they are moisture sensitive too. As a result of these constraints, improved alternatives were sought for large scale applications and eventually transition metal catalysed C–S coupling reactions emerged.[4] We have recently reported Zn and Fe-catalysed C–S coupling reactions.[4d,4i] In continuation of our efforts to develop a more affordable catalyst with better yield and functional group tolerance, we focused on Cu catalysts.[5] Copper has certain desirable features, such as low toxicity, less cost and is it compatible with many readily available and cheap ligands. Moreover, it has many stable variable oxidation states suitable for a catalytic cycle. Driven by these facts, we focussed on the C-S coupling reaction employing Cu as the catalytic system. To our delight we found that the combination of CuI and DABCO is well suited for the C-S coupling reaction, with wide scope and

good yields. Furthermore, the excellent chemoselectivity of this method enabled the synthesis of 4-(4-nitrophenylsulfanyl)phenylamine, which is otherwise difficult to obtain using metal-catalysed coupling reactions. 4-(4-Nitrophenylsulfanyl)phenylamine can be used as a precursor for the synthesis of Dapsone, a drug for the treatment of leprosy.[6]

Results and Discussions

The reaction between 4-iodoanisole and thiophenol was chosen as the model reaction to examine the scope of the Cu-catalysed reaction. It is known that addition of a ligand to a metal catalyst increases the solubility and enhances the catalytic action. Inspired by this idea, we screened different N,N- and N,O-bidentate ligands for the C-S coupling reaction. The results are shown in Table 1.

Table 1: Ligand screening [a]
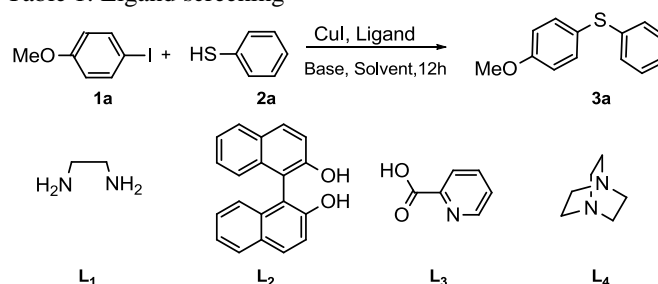
		(° C)	
1	Ethylene diamine (L₁)	80	8
2	BINOL (L₂)	80	32
3	Picolinic acid (L₃)	80	12
4	DABCO (L₄)	80	34
5	DABCO (L₄)	120	98
6	DABCO (L₄)	RT	-

a) Reaction conditions: 1a (0.6 mmol), 2a (0.5 mmol), CuI (10 mol%), ligand (20 mol%), base - K_2CO_3 (2 equiv.), solvent - DME, N_2, b): isolated yield, RT - room temperature

On examining different ligands, we found that the N,N-bidentate ligand DABCO was the most effective one for this coupling reaction, giving 34% yield and on increasing the temperature to 120 °C, we got a maximum yield of 98%.

Table 2: Base and solvent optimization

MeO—⟨ ⟩—I + HS—⟨ ⟩   CuI, DABCO / solvent, Base, 120 °C, 12 h, N_2 → MeO—⟨ ⟩—S—⟨ ⟩
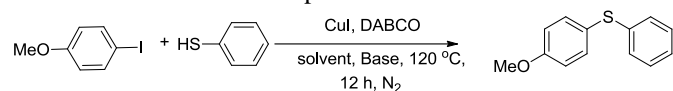
Entry	Solvent	Base	Temperature (°C)	Yield (%)ᵇ
1	CH₃CN	K₂CO₃	120	93
2	Water	K₂CO₃	120	31
3	Toluene	K₂CO₃	120	45
4	DMF	K₂CO₃	120	53
5	THF	K₂CO₃	120	93
6	DMSO	K₂CO₃	120	59
7	t-BuOH	K₂CO₃	120	65
8	DME	K₂CO₃	120	98
9	DME	Na₂CO₃	120	85
10	DME	K₃PO₄	120	80
11	DME	NaOᵗBu	120	81
12	DME	KOᵗBu	120	96
13	DME	TEA	120	96
14	DME	_	120	69ᶜ
15	DME	K₂CO₃	120	85

a) Reaction conditions: 1a (0.6 mmol), 2a (0.5 mmol), CuI (10 mol%), ligand (20 mol%), base (2 equiv.), 120 °C, 12 h, N_2, b): isolated yield, c): 2.2 equiv. of DABCO was used

We then examined the influence of different solvents and found that DME was the most effective one (Table 2). Non-polar solvents were found to decrease the yield of the reaction. Next we studied the effect of different bases on the outcome of the reaction. The cheap inorganic base K_2CO_3 was found to be the most effective one for this reaction. Since the efficiency of the metal catalysed reaction greatly depends upon the catalyst loading, next we set out to optimize the catalyst loading. Different ratios of ligand and catalysts were tried and we found that a combination of 5 mol% of CuI and 10 mol% of DABCO was the most efficient catalyst loading for this reaction.

We conducted several control experiments to find the different factors which limit the reaction (Table 3). First, we have carried out the reaction in the absence of CuI and found that no product was formed. This proves that presence of the Cu catalyst is essential for this reaction. In the absence of the ligand DABCO we got only a trace amount of the product. Next we checked whether the ligand DABCO, which is an unhindered nucleophile, could act as the ligand by conducting the reaction in the absence of K_2CO_3 and we found that the yield of the product was reduced to 69%. Carrying out the reaction under an aerobic atmosphere enhanced the homocoupling of the thiols and the required product was obtained in small amounts. Lowering the time or
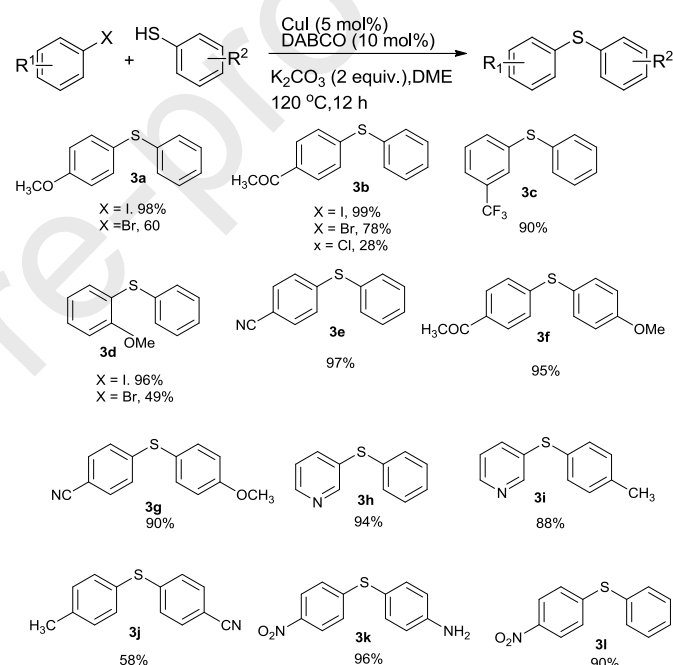
product.

Table 3: Control experiments

Entry	CuI	DABCO	K₂CO₃	N₂	Yieldᵇ
1	✓	✓	✓	✓	98
2		✓	✓	✓	-
3	✓		✓	✓	Trace
4	✓	✓		✓	69
5	✓	✓	✓		Trace

a) Reaction conditions: ArX (0.6 mmol), thiol (0.5 mmol), CuI (5 mol%), ligand (10 mol%), base (2 equiv.), 120 °C, N_2, b) isolated yield.

On screening different substrates, we found that both electron rich and electron deficient substrates gave excellent yields for the reaction. First, we coupled aryl halides and aryl thiols. (Scheme 1). More importantly heterocyclic halides also gave very good yields. Sterically hindered substrates usually provide a challenging task to synthetic chemists in coupling reactions. To our delight, sterically hindered reactants like 2-iodoanisole also gave good yields for the reaction.

R^1⟨ ⟩—X + HS—⟨ ⟩—R^2 CuI (5 mol%) / DABCO (10 mol%) / K_2CO_3 (2 equiv.),DME / 120 °C,12 h → R_1⟨ ⟩—S—⟨ ⟩—R^2

3a H₃CO—⟨ ⟩—S—⟨ ⟩
X = I. 98%
X = Br, 60

3b H₃COC—⟨ ⟩—S—⟨ ⟩
X = I, 99%
X = Br, 78%
x = Cl, 28%

3c ⟨ ⟩—S—⟨ ⟩ CF₃
90%

3d ⟨ ⟩—S—⟨ ⟩ OMe
X = I. 96%
X = Br, 49%

3e NC—⟨ ⟩—S—⟨ ⟩
97%

3f H₃COC—⟨ ⟩—S—⟨ ⟩—OMe
95%

3g NC—⟨ ⟩—S—⟨ ⟩—OCH₃
90%

3h ⟨N⟩—S—⟨ ⟩
94%

3i ⟨N⟩—S—⟨ ⟩—CH₃
88%

3j H₃C—⟨ ⟩—S—⟨ ⟩—CN
58%

3k O₂N—⟨ ⟩—S—⟨ ⟩—NH₂
96%

3l O₂N—⟨ ⟩—S—⟨ ⟩
90%

a) Reaction conditions: ArX (0.6 mmol), thiol (0.5 mmol), CuI (5 mol%), ligand (10 mol%), base (2 equiv.), 120 °C, N_2, b) Isolated yield, c) 1.6 equiv. of thiophenol was used and the reaction was carried out for 24 h. d) The reaction was carried out for 17 h.

Scheme.1: Substrate scope of Cu-catalysed C-S cross-coupling between aryl iodides and aryl thiolsᵃ

Another significant feature of this reaction is that the product 4-((4-nitrophenyl)thio)aniline can be used as a precursor of the drug dapsone (Scheme 2).
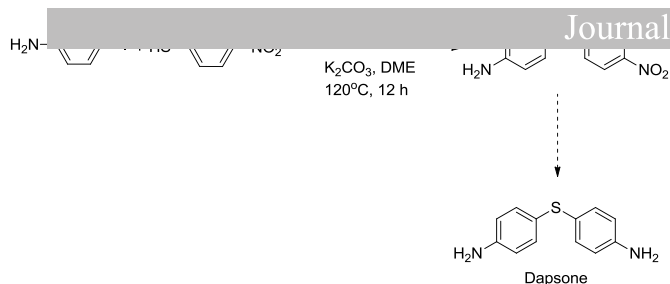
Scheme 2: Synthetic route to the drug Dapsone

We then applied this rich chemistry for the coupling of aryl halides with alkyl thiols, giving excellent yields of the products (Scheme 3).

R^2 = alkyl

3m
97%

3n
CF₃
99%

3o
H₃CO
89%

3p
95%

3q
H₃C
91%

3r
O₂N
86%

3s
MeO
60%
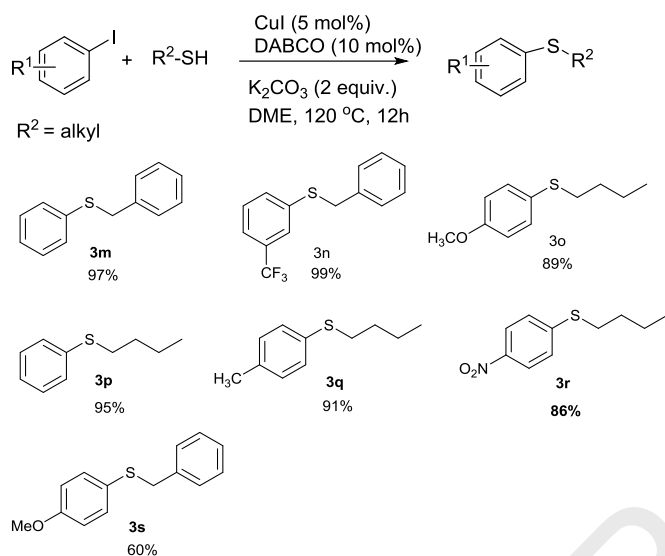
a) Reaction conditions: ArX (0.6 mmol), alkyl thiol (0.5 mmol), CuI (5 mol%), ligand (10 mol%), base (2 equiv.), 120 °C, N₂, b) isolated yield.

Scheme 3: Cu-catalysed coupling of aryl halides with alkyl thiols

DFT Studies to explore the mechanism

To explore the mechanism, the reaction between 4-iodoanisole and thiophenol was modelled (Scheme 4).
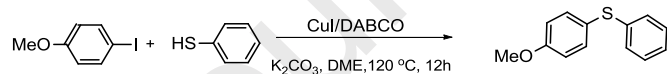
a): Reaction conditions: 4-iodoanisole (0.6 mmol), thiophenol (0.5 mmol), CuI (5 mol%), DAcBCO (10 mol%), base (2 equiv.), N₂.

Scheme 4: Cu-catalysed C-S coupling reaction

The computational calculations were performed using DFT theory using the hybrid B3LYP functional and the Gaussian-09 software package.[7] Chemcraft visualization software was used to construct the input molecular structure.[8] In geometry optimization studies, the stationary point may be a minimum, transition state or a higher order saddle point. Locating the stationary point and calculating its geometry and energy is called geometry optimization. Determining the minimum is called minimization and determining the transition state is referred to as transition state optimization. Once a transition point is found, vibrational analysis is carried out to find whether the transition point is a minimum (zero imaginary frequency) or a transition

and frequency calculations were performed using the SDD basis set. Solvent effects were taken into consideration using the polarizable continuum (PCM) model, taking DME as the solvent.[9] The Gibbs free energies of all the optimized structures were calculated.

Results and discussion

Geometry optimizations were done using density functional theory to locate the stationary points in the potential energy curve of reaction profiles and their nature was confirmed using computed vibrational frequencies.
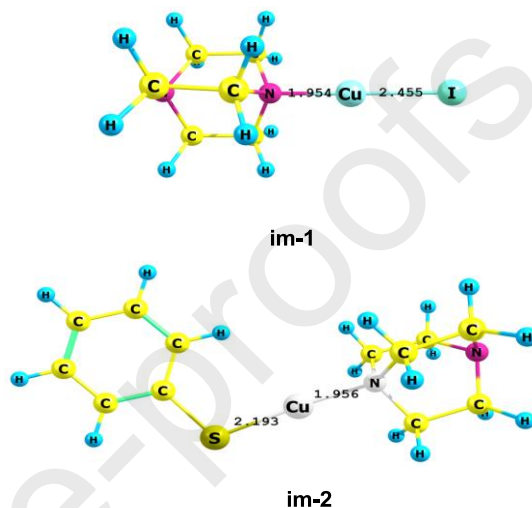

Figure 1: Structures of intermediates im-1 and im-2

The possible steps involved in the catalytic cycle are as follows:

1). Formation of the Cu-DABCO complex (im-1)

According to the computational studies, the first step is CuI salt coordinate formation with the ligand, forming a Cu(I) DABCO complex. The optimized geometry shows that a linear complex exists with a coordination bond between CuI and the ligand. This complex may exist as part of an equilibrium between the biligated and monoligated metal complexes. This is supposed to be the active catalytic species in the reaction pathway. In addition to Cu(I) complexes, other copper sources like Cu(0), Cu(II) have also been reported for C-heteroatom coupling reactions.[4b] However, it has been experimentally confirmed and reported that from all these complexes, the active catalytic species generated that provides the highest reaction rate is Cu(I) based.[10] The geometry of the Cu(I) DABCO complex was optimized and the result is shown in Figure 1 (im-1). This type of DABCO-Cu-I polymeric complex has already been reported.[11] The Cu-N bond length in the complex was computed to be 1.954 Å and the Cu-I bond length was 2.455 Å.

2). Formation of the Cu-thiolate complex

The nucleophilic species in this reaction is the thiolate anion which is generated by the abstraction of a proton by the base K₂CO₃. The generated thiolate anion adds to the Cu complex and forms a Cu(I)-thiolate complex. The optimized geometry is shown in Figure 1 (im-2). These types of copper-thiolate complexes have already been isolated.[12] The Cu-S bond length in this complex was computed to be 2.193 Å and the Cu-N bond length was slightly increased to 1.956 Å.

For the coupling to occur, the generated Cu(I)-thiolate complex should add to the aryl iodide. This addition generates a transition state (Figure 2, ts-1). The structure was first optimized using the SDD basis set and on frequency analysis we got a single imaginary frequency confirming that it is actually a transition state. It was found that the nature of the halide ion greatly affects the oxidative addition step and the rate of the reaction. It is worth noting that in the intermediate im-2, the Cu-S bond length was 2.193 Å and the C_1-I_1 bond length in the iodoanisole was 2.156 Å, whilst in the transition state the Cu-S bond distance was increased to 2.221 Å and the C_1-I_1 distance was increased to 2.646 Å. This clearly indicates that the Cu-S and C_1-I_1 bonds start dissociating in the transition state and the C_1-S (bond distance 2.478 Å) and Cu-I_1 (bond distance 3.344 Å) bonds start forming.
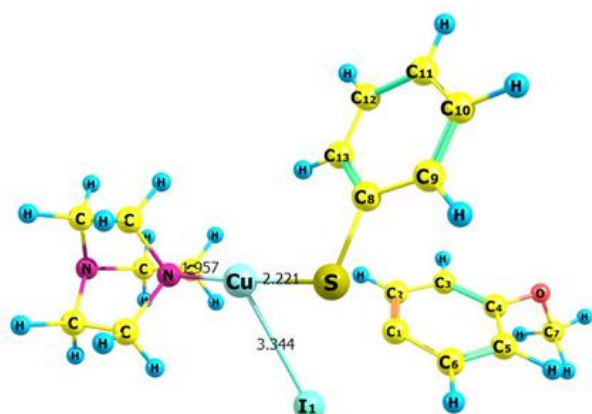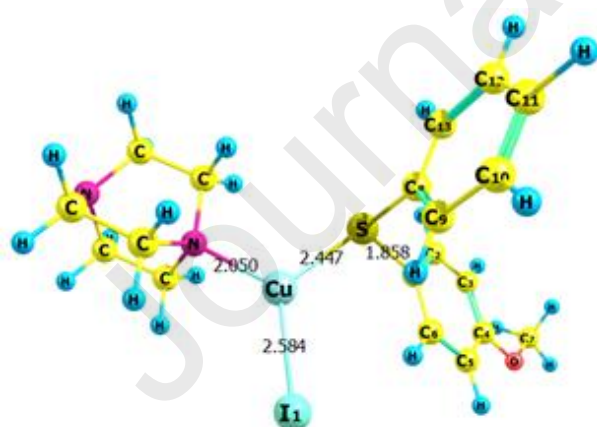

Figure 2: The structure of transition state ts-1

The mode of vibrations of the transition state clearly indicate that bond formation occurs between the C atom labelled as C_1 and the S atom. From this transition state, an intermediate is generated (Figure 3, im-3). The Cu-I_1 bond length is reduced to 2.584 Å and the S-C_1 distance to 1.858 Å, confirming the indication of initiation of bond formation.

im-3

Figure 3: Optimized structure of intermediate 3, im-3

4). Formation of the product and recovery of the catalyst

From this intermediate the Cu-S bond starts dissociating to facilitate the product formation and another transition state is obtained, which is shown in Figure 4 (ts-2).
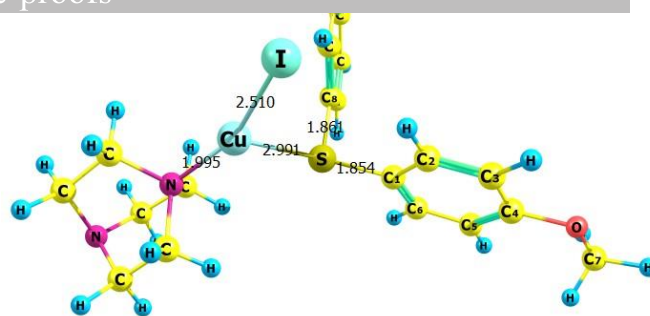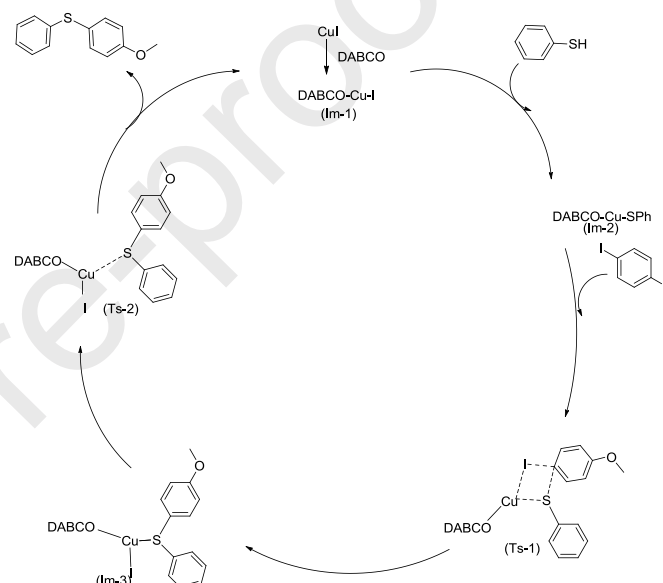

Figure 4: Structure of the transition state

Finally, dissociation of the Cu-S bond from this transition state yields the required product. The C_1-S bond length is reduced to 1.84 Å, confirming the formation of a C-S bond.

Based on the above calculations and experimental results, a plausible complete catalytic cycle is depicted in Scheme 5.

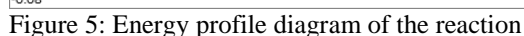Scheme 5: The complete catalytic cycle based on DFT calculations

The calculated energies of the transition states and intermediates are shown in Table 4, while the energy profile diagram of the C-S coupling reaction is shown in Figure 5.

Table 4: Energies of the transition states and intermediates

Structure	Energy (kcal)/mol
CuI	-208.8286
Dabco	-345.2708
PhSH	-630.3728
Iodoanisole	-357.5347
DABCO-Cu-I	-554.1640
DABCI-Cu-SPh	-1172.4995
HI	-12.0106
Ts-1	-1529.9773
Im-3	-1530.0603
Ts-2	-1530.0596
Product	-975.8986

The energy of all the reactants is arbitrarily fixed as zero. The complete catalytic cycle is shown below. The addition of 4-iodoanisole to the copper(I) thiolate complex is found to be the rate determining step and the activation energy barrier for this step is found to be 35.6 kcal/mol. From this complex, a copper(I)

transition state (ts-2) in which the Cu-S bond starts dissociating. Finally, the required product is formed from this transition state and the active catalyst is regenerated.

Figure 5: Energy profile diagram of the reaction

We have developed a mild and easily accessible method for the C-S coupling reaction using the mild and easily accessible CuI/DABCO catalytic system. The excellent functional group tolerance of this method enabled the synthesis of a number of sulfides and also the precursor for the drug, Dapsone. To get an insight into the mechanism of the reaction, we have carried out DFT studies and found that the possible reaction pathway involves three intermediates and two transition states.

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References and notes

Manojkumar T K: Formal analysis, data curation
Gopinathan Anilkumar: Suoervision, project administration, Fund acquisition

Graphical Abstract

Credit Author Statement

Anns Maria Thomas: Conceptualisation, methodology, investigation
Sherin D R: Software
Sujatha Asha: Methodology

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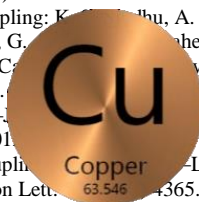
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