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# **Copper-catalyzed C-N coupling reaction of tosylhydrazones**

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### **1** | INTRODUCTION

Tosylhydrazones are a class of useful organic reagents with high reactivities.<sup>[1-3]</sup> They are used in synthesis of alkenes with two name reactions, such as Shapiro reaction<sup>[4-7]</sup> and the Bamford-Stevens reaction.<sup>[8-10]</sup> Recently tosylhydrazones have been found to be applied in more and more new organic reactions.<sup>[11,12]</sup> Especially, it is found that tosylhydrazones are a new kind of reagents in palladium-catalyzed coupling reactions with aryl halides, sulfonates or boronic acids for synthesis of

Tosylhydrazones are a kind of labile and highly reactive compounds, which are apt to be transformed into reactive diazo compounds and then into extremely reactive carbenes under the basic condition. In order to fulfil the valuable C-N coupling reaction, diaryliodonium salts are evaluated and prove to be a class of efficient electrophiles. The reaction with ligand-free copper salt as catalyst shows a wide range of substrate scope. A plausible mechanism is proposed.

### KEYWORDS

C-N coupling, copper catalysis, diaryliodonium salts, tosylhydrazones

polysubstituted olefins<sup>[11–19]</sup> and multi-arylmethanes<sup>[20]</sup> with excellent structural diversities (Figure 1).

Highly reactive and labile tosylhydrazones under basic catalytic conditions make their C-N coupling reaction become an unresolved problem, although the C-N coupling reaction has achieved great progress.<sup>[21-27]</sup> Inspired by our recent study of diaryliodonium salts and amino acid amides,<sup>[28]</sup> we thought that diaryliodonium salts may act as a class of suitable electrophiles for the C-N coupling reaction. As we known, diaryliodonium salts are a kind of highly electron-deficient aromatic

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compounds with mildness, nontoxicity, stability and facile preparation, and they have been widely applied in organic synthesis.<sup>[29–32]</sup> As our on-going study on C-N cross coupling reactions,<sup>[28–37]</sup> we planned to explore the reaction of diaryliodonium salts and tosylhydrazones (Figure 1).

The C-N coupling product sulfonamides are widely applied in pharmaceuticals,<sup>[38]</sup> bioactive compounds,<sup>[39,40]</sup> dyes and herbicides.<sup>[41,42]</sup> As an important buiding block of drugs, it has been developing for decades.<sup>[43–45]</sup> The traditional sulfonamide drugs are obtained through the reaction of amine and sulfonyl chloride.<sup>[46]</sup> But sulfonyl chloride is troublesome in the reaction process, because it is corrosive, hydrolysable easily and hazardous.<sup>[47,48]</sup> Taking into account these unfavorable factors, a mild and highly efficient method to synthesize sulfonamides is highly concerned.

Sulfonamides and indazoles are important building blocks for pharmaceuticals and bioactive compounds. For example, ionidamine is an anticancer drug; YC-1 is reported to exhibit anticancer activity; YD-3 is an



FIGURE 1 Some reactions related to tosylhydrazones



angiogenic drug; and WXL-1 is a potent antimicrobial agent, newbouldine and neuro-transmitter inhibitors (Figure 2).<sup>[49–51]</sup>

### 2 | EXPERIMENTAL

#### 2.1 | General

All reactions were carried out under argon atmosphere in dried glassware. The glassware used were dried in an electric oven at 120°C. Chemicals were purchased from Aladdin, Adamas, Aldrich, Alfa Aesar, and Kelong Chemical Company, and used without further treatment. Petroleum ether refers to the fraction boiling in the 60–90°C range. <sup>1</sup>H NMR spectra were determined on a Bruker Avance 300 MHz instrument or on a Bruker Avance III 400 MHz instrument. <sup>1</sup>H NMR data are reported in  $\delta$  units (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm), DMSO (2.50 ppm) or acetone (2.05 ppm) in the deuterated solvent, unless otherwise stated. <sup>13</sup>C NMR spectra are reported in (ppm) relative to deuterochloroform (77.2 ppm), DMSO-d<sub>6</sub> (39.5 ppm) or acetone-d<sub>6</sub> (206.7 ppm for C=O) unless otherwise stated, and all were obtained with <sup>1</sup>H decoupling. High-resolution mass spectra were recorded on a Shimadzu LCMS-IT-TOF instrument in the ESI mode. IR spectra were taken on a Thermo Nicolet NEXUS 670 FTIR infrared spectrometer using a Nicolet Omnic workstation.

### 2.2 | General procedure

To an oven-dried 25 ml test tube with standard ground joint equipped with a stir bar was added 0.5 mmol N-tosylhydrazones, 0.7 mmol diphenyliodonium triflate, 0.1 mmol anhydrous CuI, 0.5 mmol  $Cs_2CO_3$ , 5 ml dioxane. The test tube was sealed with a sleeve rubber stopper

**FIGURE 2** Representative bioactive indazoles and sulfonamide derivatives

and evacuated and refilled with argon for three cycles. The mixture was stirred under room temperature for 24 hrs. And then the reaction mixture was quenched with water, added with 2 ml saturated NaCl solution, and extracted with ethyl acetate (20 ml) for three times. The combined organic layer was dried with anhydrous  $MgSO_4$ , and condensed in vacuum on a rotary evaporator. The residual was purified on a silica gel chromatograph column by means of gradient elution (eluent: petroleum ether/ethyl acetate) to give the desired product.

### **3** | **RESULTS AND DISCUSSION**

During the primary experimentation, many reaction conditions were screened. Finally, in the presence of CuI and  $Cs_2CO_3$ , the reaction afforded a product, which was verified to be the C-N coupling product N'-benzylidene-4methyl-N-phenylbenzenesul-fonohydrazide. Therefore we found a C-N coupling protocol for the highly reactive tosylhydrazones, and we investigated the C-N coupling reaction in detail in the following (Scheme 1).

Benzaldehyde tosylhydrazones **1a** and diphenyliodonium triflate **2a** were selected as the model substrates to establish an optimized reaction condition, and the selected results were listed in Table 1.

Initially, since there were several catalyst-free C-N coupling reactions reported, the reaction was performed at 60°C under the catalyst-free condition, but only trace of the product was detected on TLC (entry 1). While Pd  $(OAc)_2$  was used as a catalyst for this reaction, no product 3a was obtained (entry 2). Next, given that the C-N coupling reactions in the presence of I2 had been reported, [52,53] I<sub>2</sub> was used as catalyst, but the reaction gave no desired product 3a (entry 3). Therefore, various copper salts, such as CuBr, CuCl, CuI, Cu (OAc)<sub>2</sub>, and CuCl<sub>2</sub>, were used in the C-N coupling reaction. The different cuprous and cupric salts had significantly effect on the yield of product **3a** (entries 4–8). When cupric salts was took part in the coupling reaction, the yield of product **3a** increased greatly. The yields of the coupling reactions with Cu (OAc)<sub>2</sub> and CuCl<sub>2</sub> as catalyst are 88% and 71%, respectively (entries 7-8). Compared with the catalyst cupric salts, cuprous salts offered much higher yields. Both CuBr and CuCl obtained higher yields of 86% and 80% (entries 4 and 6). Surprisingly, CuI exhibited an excellent catalytic result with the highest yield of 94% (entry 5).

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First of all, diphenyliodonium triflate and Lphenylalaninamide were adopted as the model substrates (Table 1). Given that several catalyst-free C-N coupling reactions with diaryliodonium salts were reported, the two reactants were performed at room temperature under the catalyst-free condition, but only trace product was detected on TLC (entry 1). When Pd (OAc)<sub>2</sub> was used as catalyst for this reaction, the yield was very low (Entry 2).

To investigate suitable reaction temperatures, a series of temperatures were screened including RT, 40°C, 60°C, 90°C. When temperature was lower than 60°C, the higher temperature, the higher yield. But while the temperature was higher than 60°C, the yield did not improve as expected (entries 20–22 vs. 5). It seemed that high temperature causes tosylhydrazones to decompose. Shortening the reaction time resulted in lower yields (entries 23–25), but too long time was unnecessary (entry 26).

Under the optimized reaction conditions, tosylhydrazones with various substituents were evaluated to react with diphenyliodonium triflate (Table 2). Particularly, tosylhydrazones with all kinds of substituents could react with diphenyliodonium triflate (entries 1–14).

Reaction of benzaldehyde tosylhydrazones and diaryliodonium triflate gave product **3a** with 94% yield (entry 1). The structure of **3a** was further confirmed by single-crystal X-ray structure analysis (Figure 3). Tosylhydrazones both with electron-rich and -deficient functional groups at the para-position of the aryl ring afforded the desired products in good yields (entries 2–8). In addition, when acetophenone tosylhydrazones was employed as the substrate, the corresponding product **3i** was obtained with a high yield (entry 9). 2,2,2-Trifluoro-1-phenylethan-1-one tosylhydrazones was also a suitable substrate, the desired coupling product **3j** was obtained in 88% yield (entry 10).

Cinnamaldehyde is an essential skeleton of many biologically active organic compounds that have found wide applications in pesticides and medicines. To further investigate the potential range of the coupling reaction, tosylhydrazone with cinnamaldehyde block was researched as a substrate, giving a 68% 3 k. It is worth mentioning that the product 3 l was also obtained from the coupling reaction of naphthaldehyde tosylhydrazone and diaryliodonium triflate. 2-Chlorobenzaldehyde and 3,4-dichlorobenzaldehyde tosylhydrazones could also be used as substrates to afford the corresponding products 3 m and 3n in 83% and 88% yields, respectively.

SCHEME 1 Copper-catalyzed C-N coupling reaction of tosylhydrazones 1 and diaryliodonium salts 2



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TABLE 1 Optimization of the reaction conditions of benzaldehyde tosylhydrazones 1a and diaryliodonium triflate 2a<sup>a</sup>

|                 | OS N-NS                         |                       | catalyst, base | N C     |          |
|-----------------|---------------------------------|-----------------------|----------------|---------|----------|
| Entry           | 1a<br>Base                      | 2a<br>Catalyst        | 3a<br>Solvent  | <u></u> | Vield[%] |
| 1               |                                 |                       | 1 4-diovane    | 60      | Тгасо    |
| 2               | $C_{s_2}CO_3$                   | $Pd(\Omega \wedge c)$ | 1.4-diovane    | 60      | Trace    |
| 3               | $Cs_2CO_3$                      | I.                    | 1,4-diovane    | 60      | Trace    |
| 4               | $C_{s_2}CO_3$                   | r <sub>2</sub>        | 1.4-diovane    | 60      | 80       |
| 5               | Cs <sub>2</sub> CO <sub>3</sub> | Cul                   | 1 4-diovane    | 60      | 94       |
| 6               | Cs <sub>2</sub> CO <sub>3</sub> | CuBr                  | 1 4-dioxane    | 60      | 86       |
| 7               |                                 |                       | 1 4-dioxane    | 60      | 88       |
| 8               | Cs <sub>2</sub> CO <sub>2</sub> | CuCla                 | 1.4-dioxane    | 60      | 71       |
| 9               | C82CO2                          | CuI                   | DMSO           | 60      | 20       |
| 10              | Cs <sub>2</sub> CO <sub>3</sub> | CuI                   | DMF            | 60      | 33       |
| 11              | Cs <sub>2</sub> CO <sub>3</sub> | CuI                   | Methanol       | 60      | 76       |
| 12              | Cs <sub>2</sub> CO <sub>3</sub> | CuI                   | THF            | 60      | 71       |
| 13              | Cs <sub>2</sub> CO <sub>3</sub> | CuI                   | Toluene        | 60      | 64       |
| 14              | Na <sub>2</sub> CO <sub>3</sub> | CuI                   | 1,4-dioxane    | 60      | 73       |
| 15              | K <sub>2</sub> CO <sub>3</sub>  | CuI                   | 1,4-dioxane    | 60      | 68       |
| 16              | КОН                             | CuI                   | 1,4-dioxane    | 60      | 54       |
| 17              | NaOH                            | CuI                   | 1,4-dioxane    | 60      | 60       |
| 18              | K <sub>3</sub> PO <sub>4</sub>  | CuI                   | 1,4-dioxane    | 60      | 88       |
| 19              | NaOtBu                          | CuI                   | 1,4-dioxane    | 60      | 30       |
| 20              | Cs <sub>2</sub> CO <sub>3</sub> | CuI                   | 1,4-dioxane    | RT      | Trace    |
| 21              | Cs <sub>2</sub> CO <sub>3</sub> | CuI                   | 1,4-dioxane    | 40      | 28       |
| 22              | Cs <sub>2</sub> CO <sub>3</sub> | CuI                   | 1,4-dioxane    | 90      | 92       |
| 23 <sup>b</sup> | $Cs_2CO_3$                      | CuI                   | 1,4-dioxane    | 60      | 26       |
| 24 <sup>c</sup> | Cs <sub>2</sub> CO <sub>3</sub> | CuI                   | 1,4-dioxane    | 60      | 62       |
| 25 <sup>d</sup> | Cs <sub>2</sub> CO <sub>3</sub> | CuI                   | 1,4-dioxane    | 60      | 80       |
| 26 <sup>e</sup> | Cs <sub>2</sub> CO <sub>3</sub> | CuI                   | 1,4-dioxane    | 60      | 91       |

<sup>a</sup>Reaction conditions: tosylhydrazones (0.5 mmol), diphenyliodonium triflate (0.7 mmol), catalyst (0.1 mmol), base (0.5 mmol) in 5 ml of solvent for 24 h in argon. Reaction were performed at 60  $^{\circ}$ C, unless otherwise noted. Reaction time:

<sup>b</sup>6 h,

<sup>c</sup>12 h,

<sup>d</sup>18 h,

<sup>e</sup>30 h. Yields correspond to isolated products.

Subsequently, to investigate the scope of diaryliodonium salts, various diaryliodonium salts were examined to react with benzaldehyde tosylhydrazones (Table 3). First of all, diphenyliodonium salts with various equilibrium anions were investigated (entries 1 to 6). It is reported that the solubility and reactivity of the diaryliodonium salts was heavily affected by the

equilibrium anion  $(X^-)$ .<sup>[54]</sup> However, for our coupling reaction, the effect of equilibrium anions is not obvious. Diphenyliodonium hexafluorophosphate gave a yield of 86% (entry 2), and diphenyliodonium nitrate (entry 2) and halide anions (entries 3–5) gave slightly lower yields in a range of 74% and 82%. And diphenyliodonium triflate corresponds to 94% yield of the product (entry 1), so

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### TABLE 2 The reaction of tosylhydrazones with various substituents 1 and diphenyliodonium triflate 2a<sup>a</sup>

|       | $ \begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & $ | $\underbrace{\text{Cul, Cs}_2\text{CO}_3}_{1,4\text{-dioxane, 60°C, 24h}}$ |              |          |
|-------|--|--|--------------|----------|
| Entry | 1 2a   | Ra   | 3<br>Product | Vield[%] |
| 1     | C.H.   | H  | 39           | 0/       |
| 2     | 4-NO <sub>3</sub> C <sub>6</sub> H <sub>4</sub>  | Н  | 3b           | 73       |
| 3     | $4-\text{ClC}_6\text{H}_4$   | Н  | 3c           | 90       |
| 4     | $4\text{-BrC}_6\text{H}_4$   | Н  | 3d           | 85       |
| 5     | $4\text{-}\mathrm{CNC}_6\mathrm{H}_4$  | Н  | 3e           | 80       |
| 6     | $4-CH_3C_6H_4$   | Н  | 3f           | 85       |
| 7     | $4-CH_3OC_6H_4$  | Н  | 3 g          | 70       |
| 8     | 4-(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>   | Н  | 3 h          | 85       |
| 9     | $C_6H_5$   | Me   | 3i           | 92       |
| 10    | $C_6H_5$   | CF <sub>3</sub>  | 3ј           | 88       |
| 11    | C <sub>6</sub> H <sub>5</sub> CH=CH  | Н  | 3 k          | 68       |
| 12    | 1-Naphthyl   | Me   | 31           | 71       |
| 13    | 2-ClC <sub>6</sub> H <sub>4</sub>  | Н  | 3 m          | 83       |
| 14    | 3,4-(Cl) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>  | Н  | 3n           | 88       |

<sup>a</sup>Reaction condition: tosylhydrazones (0.5 mmol), diaryliodonium triflate salt (0.7 mmol), CuI (0.1 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.5 mmol) in 5 ml of 1, 4-dioxane for 24 h in argon at 60 °C. Yields correspond to isolated products.



FIGURE 3 Single crystal X-ray structure of 3a

TABLE 3 The reaction of benzaldehyde tosylhydrazones 1a and a variety of diaryliodonium salt 2 a

|       | V + Ar <sub>2</sub> lX Cul, Cul, Cul, Cul, Cul, Cul, Cul, Cul,    | s <sub>2</sub> CO <sub>3</sub><br>b, 60 °C, 24h | L N          |          |
|-------|---|---|--------------|----------|
| Entry | 1a 2<br>Ar  | X-  | 3<br>Product | Yield[%] |
| 1     | C <sub>6</sub> H <sub>5</sub>                                     | OTf   | 3a           | 94       |
| 2     | C <sub>6</sub> H <sub>5</sub>                                     | PF <sub>6</sub> -                               | 3a           | 86       |
| 3     | C <sub>6</sub> H <sub>5</sub>                                     | NO <sub>3</sub> <sup>-</sup>                    | 3a           | 82       |
| 4     | C <sub>6</sub> H <sub>5</sub>                                     | Cl <sup>-</sup>                                 | 3a           | 80       |
| 5     | C <sub>6</sub> H <sub>5</sub>                                     | Br <sup>-</sup>                                 | 3a           | 74       |
| 6     | C <sub>6</sub> H <sub>5</sub>                                     | I-  | 3a           | 77       |
| 7     | $4-CH_3C_6H_4$  | OTf⁻  | 30           | 83       |
| 8     | $4$ -t- $C_4H_9C_6H_4$  | OTf <sup>-</sup>                                | 3p           | 85       |
| 9     | 3,4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> | OTf <sup>-</sup>                                | 3q           | 68       |
| 10    | 2,4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> | OTf <sup>-</sup>                                | 3r           | 93       |
| 11    | 2,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> | OTf <sup>-</sup>                                | 3 s          | 88       |
| 12    | $2-CH_3-5-t-C_4H_9C_6H_3$   | OTf <sup>-</sup>                                | 3 t          | 74       |
| 13    | 2-CH <sub>3</sub> -5-BrC <sub>6</sub> H <sub>3</sub>              | OTf <sup>-</sup>                                | 3u           | 78       |
| 14    | Diphenyleneiodonium $(Ar_2I^+)$                                   | OTf <sup>-</sup>                                | 3v           | 98       |

<sup>a</sup>Reaction conditions: benzaldehyde tosylhydrazones (0.5 mmol), diaryliodonium salt (0.7 mmol), CuI (0.1 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.5 mmol) in 5 ml of 1, 4-dioxane for 24 hr in argon. Reaction were performed at 60 °C. Yields of the isolated products are given.

triflate was the best equilibrium anion for the C–N coupling reaction.

Diaryliodonium triflates of *para*-substituted alkyl groups gave the products in high yields (entries 7–8). Di (3,4-dimethylphenyl) iodonium triflate afforded the corresponding C–N coupling products in yield of 68% (entries 9). All of the bulky ortho-substituted di (2,4-dimethylphenyl) iodonium triflate, di (2,5-dimethylphenyl) iodonium triflate and di (2-methyl-5-tert-butylphenyl) iodonium triflate afforded pretty high yields (entry 10–13), as suggests that the steric hindrance of diaryliodonium triflates has little or no effect on the reaction. Di (2-methyl-5-bromo) iodonium triflate with electron-poor aryl group gave the corresponding product with a similar yield to that of diaryliodonium triflates with electron-rich groups (entry 13 vs. 7–12).

In surprise, diphenyleneiodonium triflate which has an amazing iodo-containing five-membered ring structure can perform a similar reaction and offered a product **3v** with an extremely high yield of 98% (entry 14).

At the beginning of this study, we use classical and cheaper iodobenzene to carry out the C-N coupling reaction instead of diaryliodonium salts. However, experiments showed that the reaction of benzaldehyde tosylhydrazones 1a and iodobenzene couldn't give the product 3a under the same condition. We think that the reason is the lower activity of iodobenzene than diaryliodonium salts. The product 3v (entry 14) with the structure of iodobenzene confirms the speculation (Scheme 2).

Based on the above experimental results, a plausible mechanism of copper-catalyzed C-N coupling reaction of diphenyliodonium salts and tosylhydrazones is proposed (Scheme 3). First, copper (I) salt (CuX, X = I, Br, Cl, etc.) and the tosylhydrazone **1** forms a complex **4**. Under the basic condition, the proton and the X of complex **4** is removed by Cs<sub>2</sub>CO<sub>3</sub>. Then an active complex **5** with two empty coordination sites is formed. The Cu (I) complex **5** undergoes oxidative addition with the diphenyliodonium salt. And a Cu (III) complex **6** is



**SCHEME 2** The reaction of benzaldehyde tosylhydrazones **1a** and diphenyleneiodonium triflate **2v** 



SCHEME 3 A plausible mechanism.

produced, and at the same time, aryl iodide is released. Consequently, reductive elimination of the bulky Cu (III) complex **6** affords the product **3** and the catalyst CuX is restored.

### 4 | CONCLUSION

In summary, a new protocol for ligand-free cuprous iodidecatalyzed C–N coupling reaction of tosylhydrazones and diaryliodonium salts under mild conditions was realized. The protocol provides a simple and feasible approach for the high-yield preparation of a wide range of N-aryl tosylhydrazones. This is the first time that tosylhydrazones were arylated with diaryliodonium salts as the aromatic electrophile.

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### SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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