



# Polystyrene resin-supported CuI-cryptand 22 complex: a highly efficient and reusable catalyst for the formation of aryl–sulfur bonds in aqueous media



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## ABSTRACT

The air and moisture stable polystyrene resin-supported copper(I) iodide-cryptand-22 complex (PS-C22-CuI) behaves as an efficient and robust heterogeneous catalyst in the cross-coupling reaction of aryl halides and thiols in aqueous media. Moreover, the heterogeneous catalyst can be easily recovered by filtration and reused for five cycles without significant loss in activity.

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## Introduction

The formation of C–S bonds has received much attention from the chemical community because various substituted aryl sulfides are of great significance to the pharmaceutical industry.<sup>1,2</sup> Transition metal-catalyzed cross-coupling reactions for the formation of C<sub>aryl</sub>–sulfur bonds are one of the most powerful organometallic transformations applied to the synthesis of various aryl sulfides and their derivatives. These compounds are of interest in pharmaceutical and material science.<sup>3–5</sup> Among these, the coupling of aryl halides with aryl- or alkyl thiols represents the most successful method for the formation of aryl–sulfur bonds; however, harsh reaction conditions such as high temperatures, polar solvents, and strong bases are often required.<sup>6</sup>

Compared to the well-established methodologies for C–C, C–O, and C–N bond formation, metal-catalyzed S-arylation has been less explored due to the complications associated with thiols undergoing oxidative coupling to disulfides; furthermore, organic sulfur compounds have been shown to bind to transition metal catalysts, leading to catalyst deactivation.<sup>7</sup> Typical, C<sub>aryl</sub>–sulfur bond formation proceeds by cross-coupling between aryl halides and thiols in the presence of various transition metals, including Pd,<sup>7,8</sup> Ni,<sup>9</sup> Fe,<sup>10,11</sup> Co,<sup>12</sup> Zn,<sup>13</sup> In,<sup>14</sup> and Cu.<sup>15–18</sup> Copper(I) catalysts are partic-

ularly attractive because they represent an environmentally friendly and cost-effective alternative to the aforementioned transition metals. However, they suffer from inherent thermodynamic instability, which results in their oxidation to Cu(II) and/or disproportionation to Cu(0) and Cu(II). Previously, we have demonstrated that complexes of Cu(I) and Pd(II) with the commercially available diazacrown ether 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (Kryptofix® 22 or cryptand 22) operate as active homogeneous catalysts under aerobic conditions.<sup>19–22</sup> We postulated that the macrocyclic and chelating effect of such flexible N- and O-containing ligands may assist in stabilizing the reactive palladium and copper intermediates allowing catalysis. In an effort to find an efficient catalyst for the S-arylation reaction, we herein report the cross-coupling between aryl halides and various thiols catalyzed using the heterogeneous, reusable, heat-, and air-stable catalyst, PS-C22-CuI. Anchoring homogeneous catalysts and converting them into heterogeneous catalytic systems can have advantages, such as increased surface area resulting in higher loading of the active sites, simpler isolation of the reaction products, and recycling of the catalyst systems by filtration.<sup>23,24</sup> For the preparation of heterogeneous catalysts using precious metals, the complexes of transition metals can be grafted on various inorganic and organic supports such as mesoporous silica,<sup>25</sup> ionic liquids,<sup>26,27</sup> and polymer surfaces.<sup>28,29</sup> Polymer-supported catalysts offer many advantages for industrial applications due to their versatile processing capabilities and ease of separation and recycling. Among

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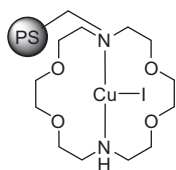


Figure 1. Heterogeneous PS-C22-CuI catalyst.

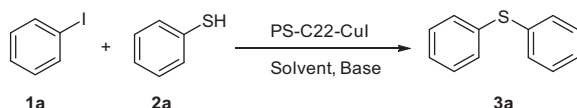
several kinds of polymers, chloromethylated polystyrene has attracted particular attention as a support for transition metal complexes due to its thermal stability, chemical inertness, low cost, and availability. Polystyrene-supported ligands, such as ethylenediamine,<sup>30</sup> *N*-heterocyclic carbenes,<sup>31</sup> and macrocyclic Schiff base,<sup>32</sup> that can form effective complexes with certain transition metals, have also been utilized in heterogeneous systems for cross-coupling reactions.

We have previously reported the efficient synthesis of 1,4-disubstituted 1,2,3-triazoles in water at room temperature using the air/moisture stable, heterogeneous, polystyrene resin-supported copper(I) iodide cryptand-22 complex, PS-C22-CuI (Fig. 1).<sup>33</sup> In order to establish other heterogeneous copper-catalyzed C–S cross-coupling reactions using this catalyst, we herein report the application of this catalyst in the S-arylation of thiols under aerobic condition in aqueous media.

## Results and discussion

The C22-functionalized polystyrene resin-supported CuI complex (PS-C22-CuI) was prepared according to an earlier report by our group.<sup>33</sup> The copper loading of the polymer-anchored Cu(I) complex, as determined by inductively coupled plasma (ICP) was 1.1% (0.17 mmol/g). Optimization of the reaction conditions including solvent, base, temperature, and catalyst loading were

Table 1  
Screening of reaction conditions for the Cu-catalyzed coupling of iodobenzene and thiophenol<sup>a</sup>



| Entry           | Catalyst (mol%) | Solvent                    | Base                            | Yield <sup>b</sup> (%) |
|-----------------|-----------------|----------------------------|---------------------------------|------------------------|
| 1               | 0.4             | —                          | K <sub>2</sub> CO <sub>3</sub>  | 38                     |
| 2               | 0.4             | Toluene                    | K <sub>2</sub> CO <sub>3</sub>  | 42                     |
| 3               | 0.4             | MeCN                       | K <sub>2</sub> CO <sub>3</sub>  | 70                     |
| 4               | 0.4             | DMSO                       | K <sub>2</sub> CO <sub>3</sub>  | 83                     |
| 5               | 0.4             | H <sub>2</sub> O           | K <sub>2</sub> CO <sub>3</sub>  | 65                     |
| 6               | 0.4             | DMF                        | K <sub>2</sub> CO <sub>3</sub>  | 96                     |
| 7               | 0.4             | H <sub>2</sub> O/DMF (1:1) | K <sub>2</sub> CO <sub>3</sub>  | 84                     |
| 8               | 0.4             | H <sub>2</sub> O/DMF (1:2) | K <sub>2</sub> CO <sub>3</sub>  | 96                     |
| 9               | 0.4             | H <sub>2</sub> O/DMF (1:2) | KOH                             | 91                     |
| 10              | 0.4             | H <sub>2</sub> O/DMF (1:2) | Cs <sub>2</sub> CO <sub>3</sub> | 72                     |
| 11              | 0.4             | H <sub>2</sub> O/DMF (1:2) | KO <sup>t</sup> Bu              | 83                     |
| 12              | 0.4             | H <sub>2</sub> O/DMF (1:2) | DIPEA                           | 51                     |
| 13              | 0.4             | H <sub>2</sub> O/DMF (1:2) | Et <sub>3</sub> N               | 74                     |
| 14 <sup>c</sup> | 0.4             | H <sub>2</sub> O/DMF (1:2) | K <sub>2</sub> CO <sub>3</sub>  | 87                     |
| 15 <sup>d</sup> | 0.4             | H <sub>2</sub> O/DMF (1:2) | K <sub>2</sub> CO <sub>3</sub>  | 96                     |
| 16              | 0.3             | H <sub>2</sub> O/DMF (1:2) | K <sub>2</sub> CO <sub>3</sub>  | 82                     |
| 17              | 0.5             | H <sub>2</sub> O/DMF (1:2) | K <sub>2</sub> CO <sub>3</sub>  | 95                     |
| 18              | 0.6             | H <sub>2</sub> O/DMF (1:2) | K <sub>2</sub> CO <sub>3</sub>  | 94                     |

<sup>a</sup> Reaction conditions: iodobenzene (1.0 mmol), thiophenol (1.2 mmol), base (2.0 mmol), solvent (1.5 mL), 90 °C, 6 h, PS-C22-CuI.

<sup>b</sup> Isolated yields.

<sup>c</sup> Reaction run at 80 °C.

<sup>d</sup> Reaction run at 100 °C.

Table 2  
PS-C22-CuI catalyzed coupling of aryl halides and thiols<sup>a</sup>

| ArX + RSH       |  | PS-C22-CuI (0.4 mol%)  |           | ArSR     |                          |
|-----------------|--|--|-----------|----------|--------------------------|
| 1               | 2  | DMF/H <sub>2</sub> O, K <sub>2</sub> CO <sub>3</sub> , 90 °C | 3         |          |                          |
| Entry           | ArX  | R  | Product   | Time (h) | Yield <sup>b,c</sup> (%) |
| 1               | PhI  | Ph   | <b>3a</b> | 6        | 96 <sup>17</sup>         |
| 2               | 4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> I  | Ph   | <b>3b</b> | 5        | 97 <sup>34</sup>         |
| 3               | 4-MeOC <sub>6</sub> H <sub>4</sub> I               | Ph   | <b>3c</b> | 7        | 92 <sup>17</sup>         |
| 4               | 1-Iodonaphthalene                                  | Ph   | <b>3d</b> | 8        | 93 <sup>35</sup>         |
| 5               | PhI  | 4-MeOC <sub>6</sub> H <sub>4</sub>                           | <b>3e</b> | 7        | 91 <sup>17</sup>         |
| 6               | PhBr   | Ph   | <b>3a</b> | 10       | 90 <sup>17</sup>         |
| 7               | 4-MeCOC <sub>6</sub> H <sub>4</sub> Br             | Ph   | <b>3f</b> | 9        | 92 <sup>36</sup>         |
| 8               | 4-NCC <sub>6</sub> H <sub>4</sub> Br               | Ph   | <b>3g</b> | 10       | 91 <sup>36</sup>         |
| 9               | 4-MeC <sub>6</sub> H <sub>4</sub> Br               | Ph   | <b>3h</b> | 12       | 87 <sup>37</sup>         |
| 10              | 4-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> Br | Ph   | <b>3i</b> | 16       | 86 <sup>35</sup>         |
| 11              | 2-Bromopyridine                                    | Ph   | <b>3j</b> | 13       | 81 <sup>38</sup>         |
| 12              | 2-MeOC <sub>6</sub> H <sub>4</sub> Br              | Ph   | <b>3k</b> | 12       | 70 <sup>8</sup>          |
| 13              | PhBr   | 4-MeC <sub>6</sub> H <sub>4</sub>                            | <b>3h</b> | 12       | 85 <sup>37</sup>         |
| 14              | 4-MeC <sub>6</sub> H <sub>4</sub> Br               | 4-MeC <sub>6</sub> H <sub>4</sub>                            | <b>3l</b> | 12       | 83 <sup>39</sup>         |
| 15              | 4-MeOC <sub>6</sub> H <sub>4</sub> Br              | 4-ClC <sub>6</sub> H <sub>4</sub>                            | <b>3m</b> | 14       | 82 <sup>38</sup>         |
| 16              | 4-MeC <sub>6</sub> H <sub>4</sub> Br               | 4-ClC <sub>6</sub> H <sub>4</sub>                            | <b>3n</b> | 14       | 80 <sup>40</sup>         |
| 17              | PhBr   | 2-ClC <sub>6</sub> H <sub>4</sub>                            | <b>3o</b> | 14       | 84 <sup>41</sup>         |
| 18              | PhBr   | 4-BrC <sub>6</sub> H <sub>4</sub>                            | <b>3p</b> | 14       | 85 <sup>38</sup>         |
| 19              | PhBr   | 2-Naphthyl   | <b>3q</b> | 14       | 83 <sup>40</sup>         |
| 20              | 4-MeC <sub>6</sub> H <sub>4</sub> Br               | 2-Naphthyl   | <b>3r</b> | 14       | 81 <sup>40</sup>         |
| 21              | PhBr   | Benzyl   | <b>3s</b> | 20       | 84 <sup>42</sup>         |
| 22              | 4-MeCOC <sub>6</sub> H <sub>4</sub> Br             | C <sub>6</sub> H <sub>13</sub>                               | <b>3t</b> | 20       | 83 <sup>42</sup>         |
| 23              | 4-MeC <sub>6</sub> H <sub>4</sub> Br               | C <sub>6</sub> H <sub>13</sub>                               | <b>3x</b> | 20       | 80 <sup>42</sup>         |
| 24              | 4-MeOC <sub>6</sub> H <sub>4</sub> Br              | C <sub>8</sub> H <sub>17</sub>                               | <b>3y</b> | 20       | 81 <sup>43</sup>         |
| 25 <sup>c</sup> | PhCl   | Ph   | <b>3a</b> | 24       | 31 <sup>17</sup>         |
| 26 <sup>c</sup> | 4-HOCC <sub>6</sub> H <sub>4</sub> Cl              | Ph   | <b>3z</b> | 24       | 35 <sup>12</sup>         |
| 27 <sup>c</sup> | 4-MeCOC <sub>6</sub> H <sub>4</sub> Cl             | Ph   | <b>3f</b> | 24       | 36 <sup>36</sup>         |

<sup>a</sup> Reaction conditions: aryl halide (1.0 mmol), thiol (1.2 mmol), PS-C22-CuI (0.4 mol % of Cu), K<sub>2</sub>CO<sub>3</sub> (2.0 mmol), DMF/H<sub>2</sub>O (v/v = 2:1 (1.5 mL), 90 °C.

<sup>b</sup> Isolated yields.

<sup>c</sup> Reaction run at 120 °C.

carried out for the reaction of iodobenzene **1a** and thiophenol **2a** as model substrates. Solvents including toluene, MeCN, H<sub>2</sub>O, DMF, as well as solventless conditions were surveyed (Table 1). The reaction was significantly affected by the nature of the solvent (Table 1, entries 1–6). The highest yield was observed using DMF (entry 6, 96%); when a DMF/H<sub>2</sub>O co-solvent was selected, the same result was still attainable with DMF/H<sub>2</sub>O (v/v = 2:1) (Table 1, entry 8). Different inorganic and organic bases such as *N,N*-diisopropylethylamine (DIPEA) or triethylamine were employed at 90 °C (Table 1, entries 12 and 13). A considerable increase in product formation was observed in the presence of an inorganic base such as K<sub>2</sub>CO<sub>3</sub> in DMF/H<sub>2</sub>O (v/v = 2:1) (Table 1, entry 8). Reducing the reaction temperature from 90 °C to 80 °C had a negative effect on the product yield (Table 1, entry 14), while raising the temperature

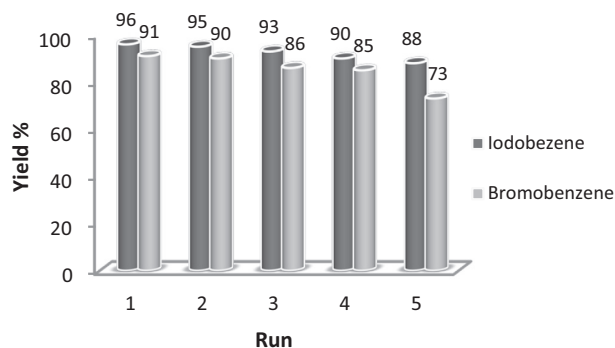


Figure 2. Recycling activity of the PS-C22-CuI catalyst in the reaction of iodobenzene with thiophenol.

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