Copper-catalyzed synthesis of thiosulfonates using thiols

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A transition metal-catalyzed carbon-sulfur bond formation is an important methodology for organic synthesis. Numerous reactions have been developed to date.

In particular, thiosulfonates having sulfur-sulfone bond are employed as convenient intermediates. The synthetic methods are well investigated. To prepare thiosulfonates, an oxidation of thiols or disulfides is usually used. However, the oxidation of these requires using excess oxidants. Regrettably, a transition metal-catalyzed reaction is very restricted. Therefore, a development of a convenient method is required now.

To solve the problem, a transition metal-catalyzed synthesis of thiosulfonates via the oxidation of thiols in air was investigated. Fortunately, I found that aerobic copper-catalyzed reaction of thiols could produce the corresponding thiosulfonates in good yields. Herein, I would like to describe the developed methodology.

2x R
$$\stackrel{\square}{\longrightarrow}$$
 SH $\stackrel{\text{cat.Cul-Phen} \cdot \text{H}_2\text{O}}{\longrightarrow}$ R $\stackrel{\square}{\longrightarrow}$ S $\stackrel{\square}{\longrightarrow}$ R $\stackrel{\square}{\longrightarrow}$ S $\stackrel{\square}{\longrightarrow}$ R $\stackrel{\square}{\longrightarrow}$ 91-42%

1) P. Natarajan, *Tetrahedron Lett.*, **2015**, *56*, 4131. 2) P. K. Shyam, Y. K. Kim, C. Lee, H.-Y. Jang, *Adv. Synth. Catal.* **2016**, *358*, 56. b) Z. Zhou, H. Xu, J. Ma, X. Zeng, Y. Wei, *Green Chem.* **2024**, *26*, 4161. c) N. Iranpoor, H. Firouzabadi, A.-R. Pourali, *Tetrahedron.* **2002**, *58*, 5179.