

# SYNLETT Spotlight 368

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

## Copper(I) Bromide

Compiled by Dexuan Xiang

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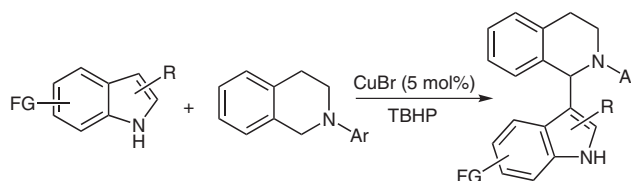
### Introduction

Copper(I) bromide (CuBr) is a white crystalline powder with a melting point of 504 °C, a boiling point of 1345 °C, and a specific gravity of 4.72 g/cm<sup>3</sup>. It is slightly soluble in cold water and decomposes in hot water, and becomes dark blue when exposed to sunlight. CuBr can be prepared

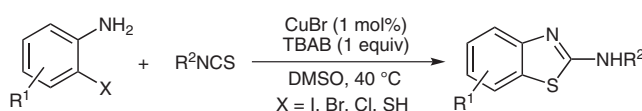
by the reduction of cupric salts with sulfite in the presence of bromide,<sup>1</sup> and is commercially available. It is a very useful reagent and widely used as catalyst in many organic synthetic reactions, for example in cross-dehydrogenative couplings (CDC),<sup>2,3</sup> aminations,<sup>4</sup> Sandmeyer,<sup>5</sup> click<sup>6</sup> and multi-component reactions<sup>7</sup> as well as for the synthesis of a variety of types of organic compounds.

### Abstract

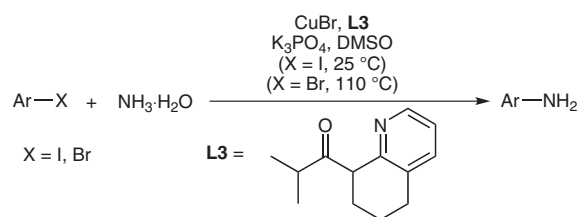
(A) Li et al. developed a novel and efficient C–C bond formation method via the CDC reaction of indoles and tetrahydroisoquinolines catalyzed by copper bromide in the presence of the oxidizing reagent TBHP.<sup>8</sup>



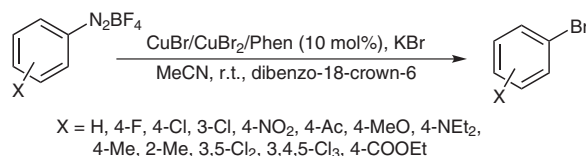
(B) Guo et al. described a mild and efficient tandem method for the synthesis of 2-aminobenzothiazoles. In the presence of CuBr and TBAB, a variety of 2-halobenzenamines underwent the tandem reaction with isothiocyanates in moderate to excellent yields.<sup>9</sup>



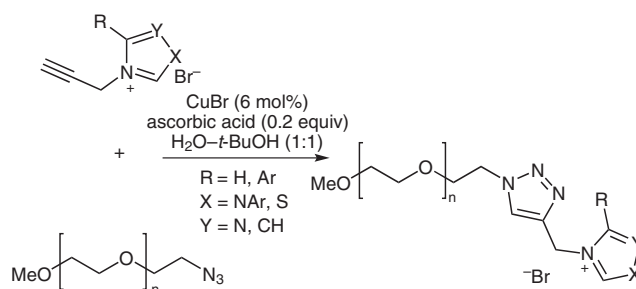
(C) The copper(I) bromide/1-(5,6,7,8-tetrahydroquinolin-8-yl)-2-methylpropan-1-one (CuBr/L3) combination catalyzed the cross-coupling reactions between aryl or heteroaryl halides and aqueous ammonia with high yields to produce primary aromatic or heteroaromatic amines at room temperature or under mild conditions.<sup>4</sup>



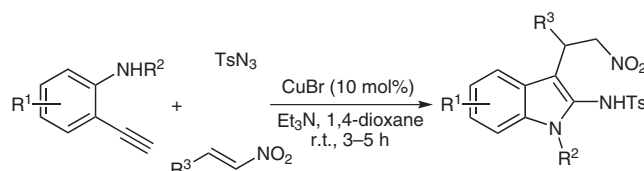
(D) Beletskaya et al. provided a catalytic version of the Sandmeyer bromination reaction employing a Cu(I)/Cu(II)/phen catalytic system. This synthetic protocol seems to be highly useful for the preparation of various aryl bromides and dibromides in excellent yields.<sup>5</sup>



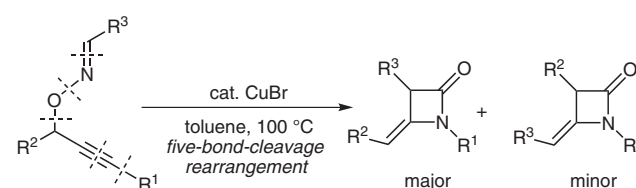
(E) Zeitler et al. reported a new and efficient, atom-economic immobilization of various heterazolium salts, which could conveniently prepared via copper-catalyzed [3+2] cycloaddition. The high catalytic activity of their corresponding carbene derivatives was demonstrated in both intramolecular Stetter reactions and redox esterifications.<sup>6</sup>



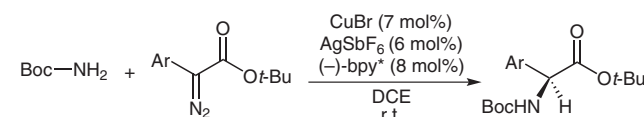
(F) Chen et al. developed a copper-catalyzed three-component reaction of 2-ethynylaniline, sulfonyl azide, and nitroolefins. This reaction generates functionalized indoles in good yields and proceeds smoothly under mild conditions.<sup>10</sup>



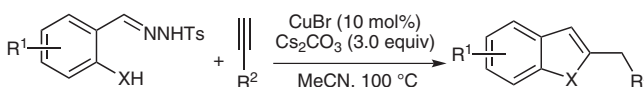
(G) Nakamura et al. revealed a drastic skeletal rearrangement of readily accessible and fairly stable *O*-propargyl oximes to β-lactam derivatives catalyzed by copper bromide. The rearrangement is highly useful as an entirely new approach for synthesizing β-lactam derivatives in an efficient manner.<sup>11</sup>



(H) Lee et al. reported a Cu/bpy\*-catalyzed method for the asymmetric insertion of (*R*)-diazocarbonyl compounds into the N–H bonds of carbamates to generate an array of easily deprotected arylglycines in good enantiomeric excess.<sup>12</sup>



(I) Zhou et al. described a new method for the synthesis of benzofurans and indoles via CuBr-catalyzed coupling–allenylation–cyclization of terminal alkynes with *N*-tosylhydrazone derivatives.<sup>13</sup>



## References

- (1) Hartwell, J. L. *Org. Synth. Coll. Vol. 3*; John Wiley & Sons: London, **1955**, 185.
- (2) Li, Z.; Li, C. *J. Am. Chem. Soc.* **2006**, *128*, 56.
- (3) Yang, F.; Li, J.; Xie, J.; Huang, Z. *Org. Lett.* **2010**, *12*, 5214.
- (4) Wang, D.; Cai, Q.; Ding, K. *Adv. Synth. Catal.* **2009**, *351*, 1722.
- (5) Beletskaya, I. P.; Sigeev, A. S.; Peregudov, A. S.; Petrovskii, P. V. *Synthesis* **2007**, 2534.
- (6) Zeitler, K.; Mager, I. *Adv. Synth. Catal.* **2007**, *349*, 1851.
- (7) Zhang, K.; Huang, Y.; Chen, R. *Tetrahedron Lett.* **2010**, *51*, 5463.
- (8) Li, Z.; Li, C. *J. Am. Chem. Soc.* **2005**, *127*, 6968.
- (9) Guo, Y.; Tang, R.; Zhong, P.; Li, J. *Tetrahedron Lett.* **2010**, *51*, 649.
- (10) Chen, Z.; Zheng, D.; Wu, J. *Org. Lett.* **2011**, *13*, 848.
- (11) Nakamura, I.; Araki, T.; Terada, M. *J. Am. Chem. Soc.* **2009**, *131*, 2804.
- (12) Lee, E. C.; Fu, G. C. *J. Am. Chem. Soc.* **2007**, *129*, 12066.
- (13) Zhou, L.; Shi, Y.; Xiao, Q.; Liu, Y.; Ye, F.; Zhang, Y.; Wang, J. *Org. Lett.* **2011**, *13*, 968.