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A novel copper-catalyzed C-C bond cleavage of aryl (heteroaryl) alkyl ketones for C-N bond formation

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A direct generation of amide from aryl (heteroaryl) alkyl ketones has been accomplished via copper(II) catalyzed C-C bond cleavage in the presence of diisopropylamine at moderate temperature. First, a mixture of aryl (heteroaryl) alkyl ketones (0.5 mmol) and Cu-complexes (0.1 mmol) in dimethyl sulfoxide (DMSO) (2.0 mL) was stirred at room temperature for 10 minutes. The next step was adding the sodium azide (NaN₃) (94.5 mg, 1.5 mmol) and diisopropylamine (DIPA) (0.014 mL) and the reaction mixture was heated to 120°C and stirred for 2 hours. To extend the scope of this transformation, several others alkyl aryl or heteroaryl carbonyl compounds were subjected to the same reaction conditions. It is notable that electron donating substituents on alkyl aryl ketones facilitate the reaction and the corresponding benzamides are obtained in relatively better yields. Also, to distinguish these pathways, a series of Cu(II) salts that did not contain halogens such as Cu(OAc)₂, Cu(NO₃)₂ was used to evaluate the generation of α -halo ketones, and no desired amides were observed in any case. These control experiments indicate that the ketone substrate possibly first reacts with copper(II) bromide and generate the α -bromo species and then react with sodium azide. It seems that diisopropylamine acts as a weak base, and by forming enolate allows the copper catalyst to coordinate with it, and the reductive elimination of a bromide from the copper-bound enolate was happened to form the desired α -bromocarbonyl and Cu(0). Under this reaction conditions, a diverse range of carbonyl substrates can undergo bromination at the α -position easily.

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