

**Organic Chemistry Portal**  
**Reactions >> Name Reactions**

**Further Information**

[Literature](#)

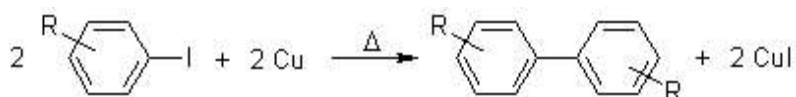
**Related Reactions**

[Buchwald-Hartwig Coupling](#)

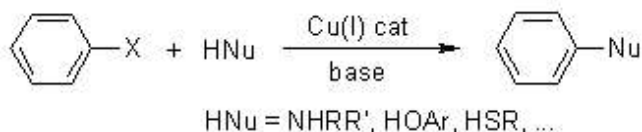
[Chan-Lam Coupling](#)

[Rosenmund-von Braun Reaction](#)

**Ullmann Reaction**

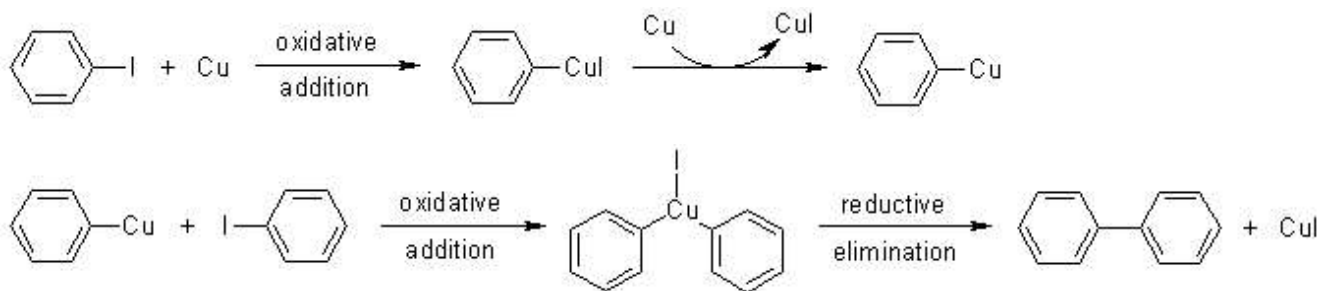


There are two different transformations referred as the Ullmann Reaction. The "classic" Ullmann Reaction is the synthesis of symmetric biaryls via copper-catalyzed coupling. The "Ullmann-type" Reactions include copper-catalyzed Nucleophilic Aromatic Substitution between various nucleophiles (e.g. substituted phenoxides) with aryl halides. The most common of these is the Ullmann Ether Synthesis.

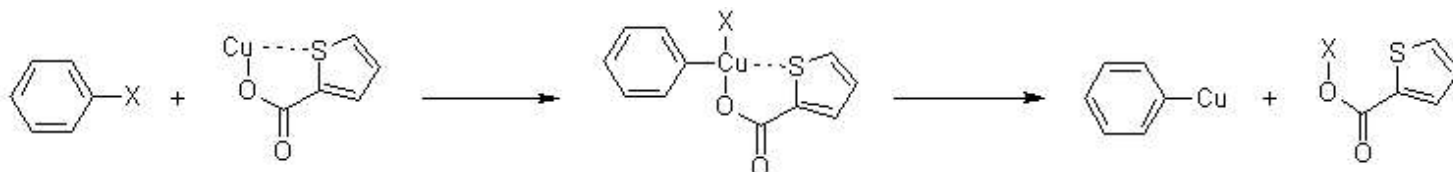


**Mechanism of the Ullmann Reaction**

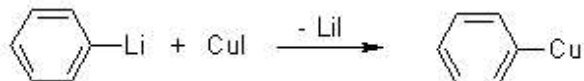
Biaryls are available through coupling of the aryl halide with an excess of copper at elevated temperatures (200 °C). The active species is a copper(I)-compound which undergoes oxidative addition with the second equivalent of halide, followed by reductive elimination and the formation of the aryl-aryl carbon bond.



The organocopper intermediate can be generated at a more moderate 70 °C using a novel thiophenecarboxylate reagent. The reaction otherwise follows the same reaction path as above.

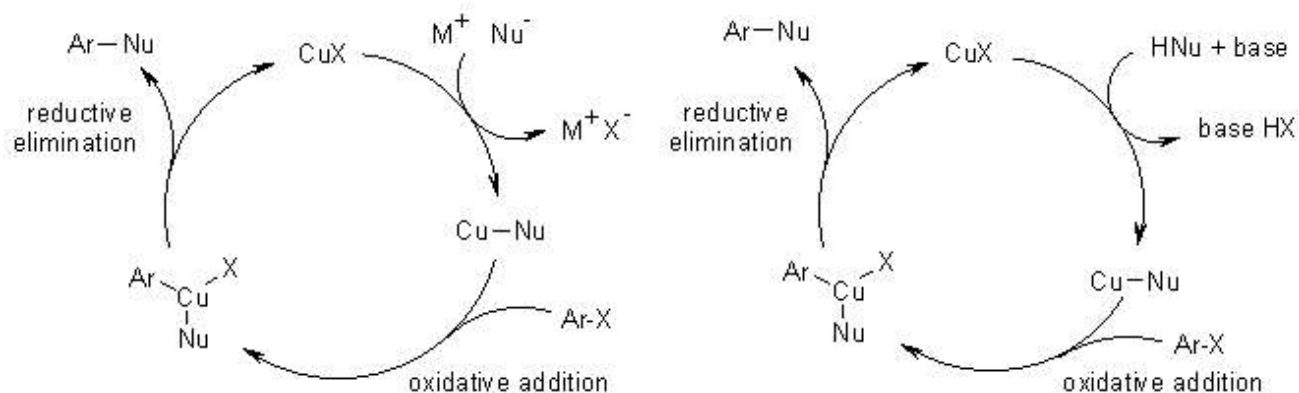


Another possibility is the use of Cu(I) for the oxidative coupling of aryllithium compounds at low temperatures. This method can also be used to generate asymmetric biaryls, after addition of the appropriate halide.

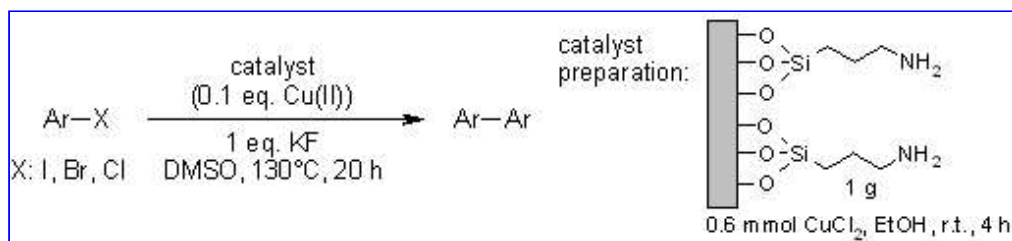


Ullmann-type reactions proceed through a catalytic cycle, and in one mechanism the copper is postulated to undergo oxidation to Cu(III). As some Cu(III) salts have been prepared, the suggestion for the mechanism is intriguing (see also [Chan-Lam](#)

Coupling):

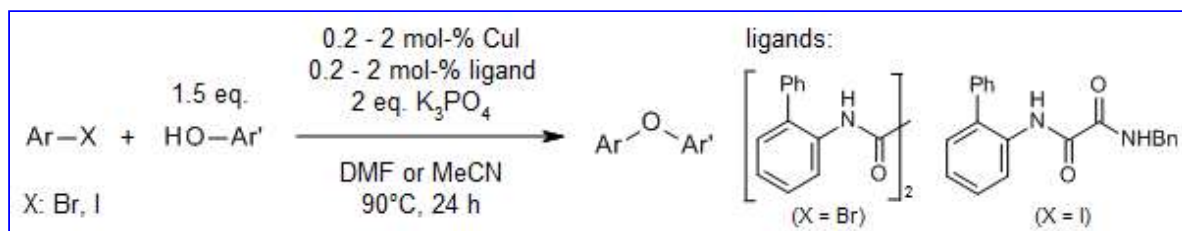


## Recent Literature



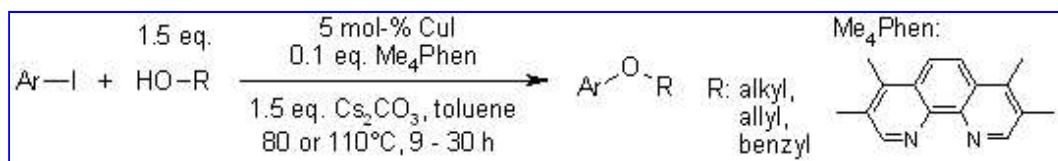
Immobilization of Copper(II) in Organic-Inorganic Hybrid Materials: A Highly Efficient and Reusable Catalyst for the Classic Ullmann Reaction

Q. Wu, L. Wang, *Synthesis*, **2008**, 2007-2012.



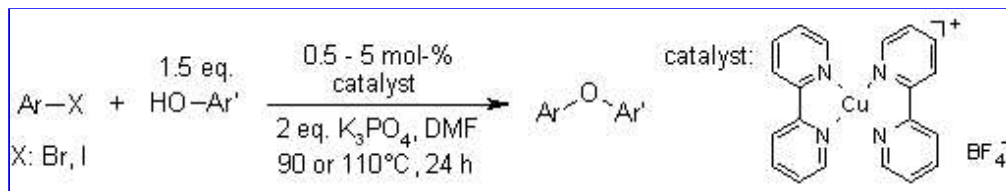
Copper-Catalyzed Diaryl Ether Formation from (Hetero)aryl Halides at Low Catalytic Loadings

Y. Zhai, X. Chen, W. Zhou, M. Fan, Y. Lai, D. Ma, *J. Org. Chem.*, **2017**, 82, 4964-4969.



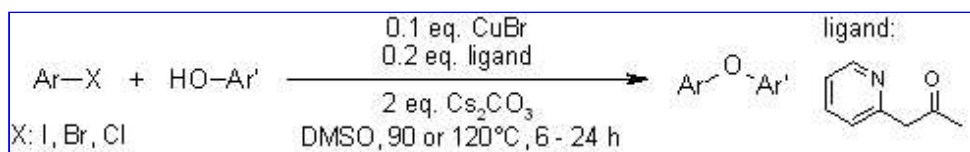
An Improved Cu-Based Catalyst System for the Reactions of Alcohols with Aryl Halides

R. A. Altman, A. Shafir, P. A. Lichtor, S. L. Buchwald, *J. Org. Chem.*, **2008**, 73, 284-286.



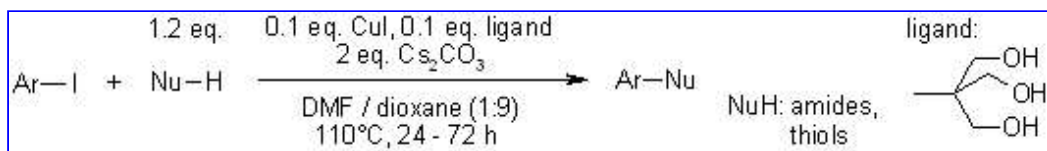
An Efficient Ullmann-Type C-O Bond Formation Catalyzed by an Air-Stable Copper(I)-Bipyridyl Complex

J. Niu, H. Zhou, Z. Li, J. Xu, S. Hu, *J. Org. Chem.*, **2008**, 73, 7814-7817.



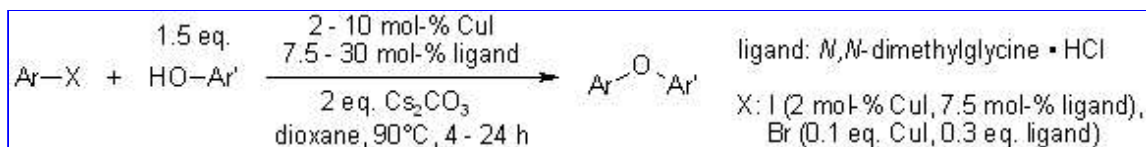
(2-Pyridyl)acetone-Promoted Cu-Catalyzed O-Arylation of Phenols with Aryl Iodides, Bromides, and Chlorides

Q. Zhang, D. Wang, X. Wang, K. Ding, *J. Org. Chem.*, **2009**, 74, 7187-7190.



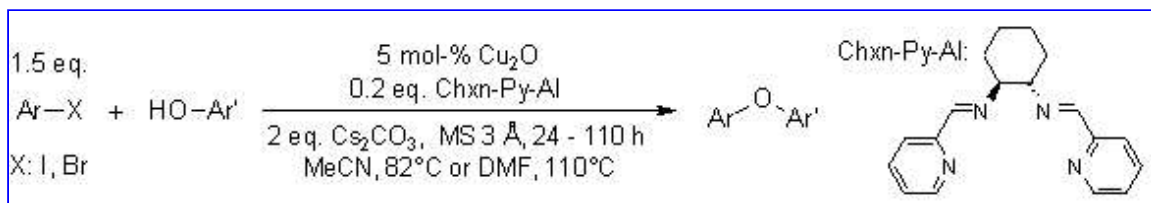
1,1,1-Tris(hydroxymethyl)ethane as a New, Efficient, and Versatile Tripod Ligand for Copper-Catalyzed Cross-Coupling Reactions of Aryl Iodides with Amides, Thiols, and Phenols

Y.-J. Chen, H.-H. Chen, *Org. Lett.*, **2006**, *8*, 5609-5612.



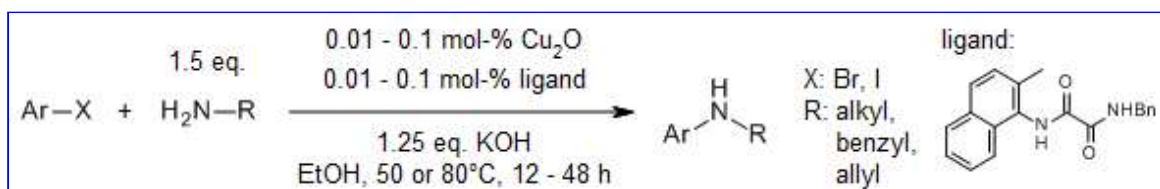
*N,N*-Dimethyl Glycine-Promoted Ullmann Coupling Reaction of Phenols and Aryl Halides

D. Ma, Q. Cai, *Org. Lett.*, **2003**, *5*, 3799-3802.



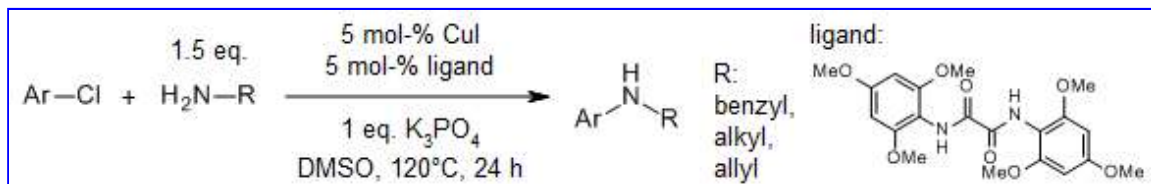
A General and Mild Ullmann-Type Synthesis of Diaryl Ethers

H.-J. Cristau, P. P. Cellier, S. Hamada, J.-F. Spindler, M. Taillefer, *Org. Lett.*, **2004**, *6*, 913-916.



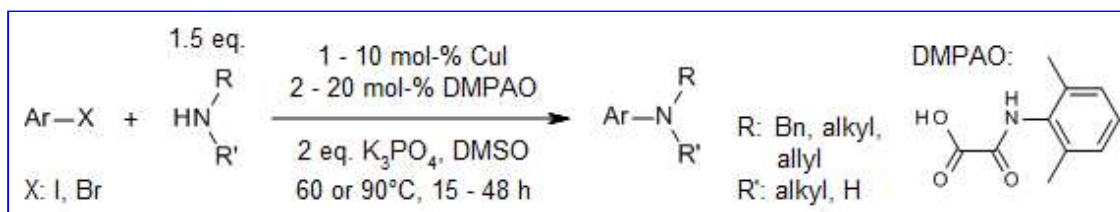
Discovery of *N*-(Naphthalen-1-yl)-*N'*-alkyl Oxalamide Ligands Enables Cu-Catalyzed Aryl Amination with High Turnovers

J. Gao, S. Bhunia, K. Wang, L. Gan, S. Xia, D. Ma, *Org. Lett.*, **2017**, *19*, 2809-2812.



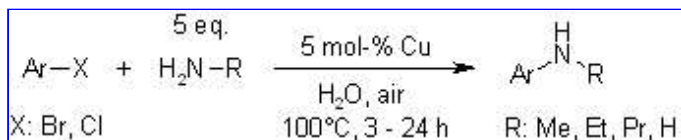
CuI/Oxalic Diamide Catalyzed Coupling Reaction of (Hetero)Aryl Chlorides and Amines

W. Zhou, M. Fan, J. Yin, Y. Jiang, D. Ma, *J. Am. Chem. Soc.*, **2015**, *137*, 11942-11945.



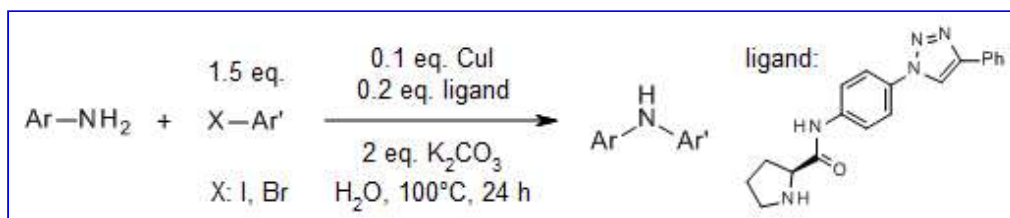
CuI/DMPAO-Catalyzed *N*-Arylation of Acyclic Secondary Amines

Y. Zhang, X. Yang, Q. Yao, D. Ma, *Org. Lett.*, **2012**, *14*, 3056-3059.



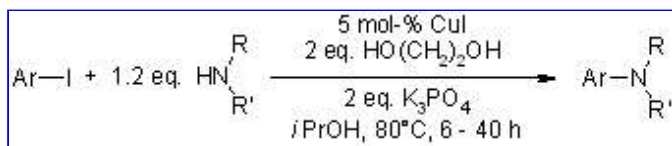
A Facile and Practical Copper Powder-Catalyzed, Organic Solvent- and Ligand-Free Ullmann Amination of Aryl Halides

J. Jiao, X.-R. Zhang, N.-H. Chang, J. Wang, J.-F. Wei, X.-Y. Shi, Z.-G. Chen, *J. Org. Chem.*, **2011**, *76*, 1180-1183.



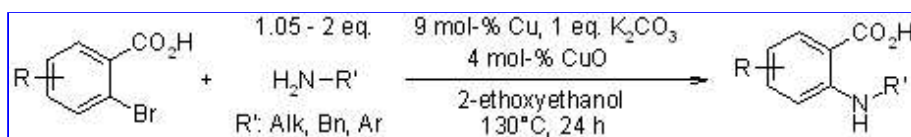
"On Water" Promoted Ullmann-Type C-N Bond-Forming Reactions: Application to Carbazole Alkaloids by Selective N-Arylation of Aminophenols

G. Chakraborti, S. Paladhi, T. Mandal, J. Dash, *J. Org. Chem.*, **2018**, 83, 7347-7359.



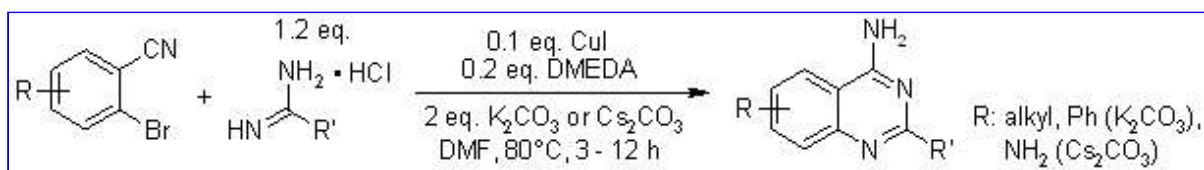
Copper-Catalyzed Coupling of Alkylamines and Aryl Iodides: An Efficient System Even in an Air Atmosphere

F. Y. Kwong, A. Klapars, S. L. Buchwald, *Org. Lett.*, **2002**, 4, 581-584.



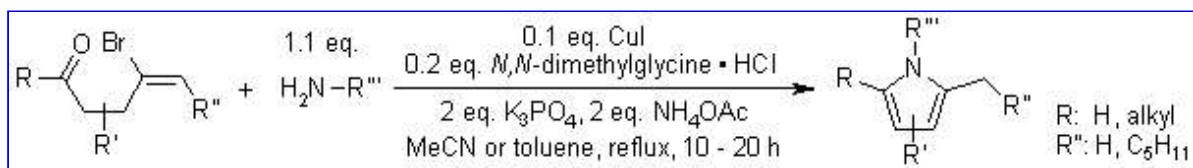
Regioselective Copper-Catalyzed Amination of Bromobenzoic Acids Using Aliphatic and Aromatic Amines

C. Wolf, S. Liu, X. Mei, A. T. August, M. D. Casimir, *J. Org. Chem.*, **2006**, 71, 3270-3273.



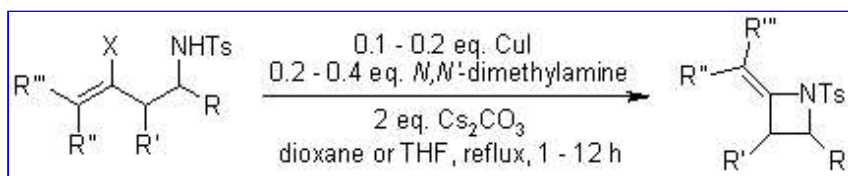
Efficient Copper-Catalyzed Synthesis of 4-Aminoquinazoline and 2,4-Diaminoquinazoline Derivatives

X. Yang, H. Liu, R. Qiao, Y. Jiang, Y. Zhao, *Synlett*, **2010**, 101-106.



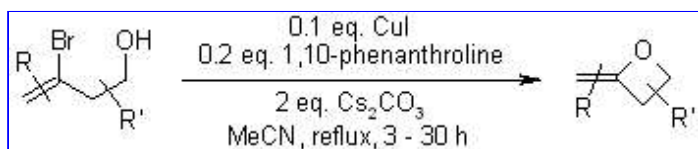
Synthesis of Pyrroles via Copper-Catalyzed Coupling of Amines with Bromoenones

Y. Pan, H. Lu, Y. Fang, X. Fang, L. Chen, J. Qian, J. Wang, C. Li, *Synthesis*, **2007**, 1242-1246.



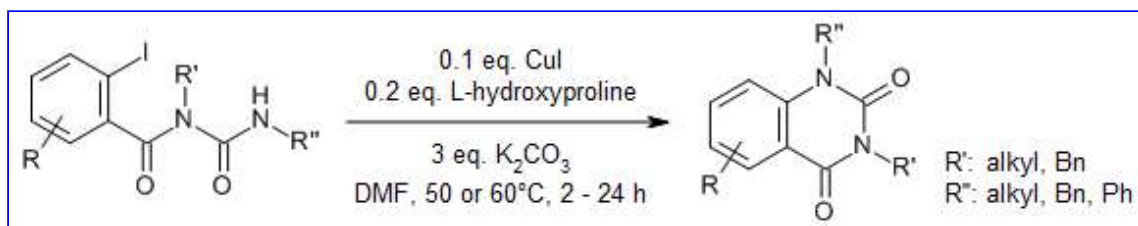
General and Highly Efficient Synthesis of 2-Alkylideneazetidines and  $\beta$ -Lactams via Copper-Catalyzed Intramolecular N-Vinylation

H. Lu, C. Li, *Org. Lett.*, **2006**, 8, 5365-5367.



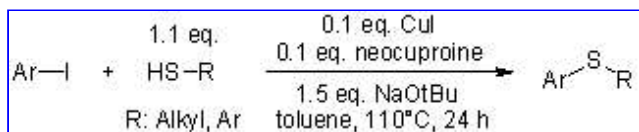
Preference of 4-exo Ring Closure in Copper-Catalyzed Intramolecular Coupling of Vinyl Bromides with Alcohols

Y. Fang, C. Li, *J. Am. Chem. Soc.*, **2007**, 129, 8092-8093.



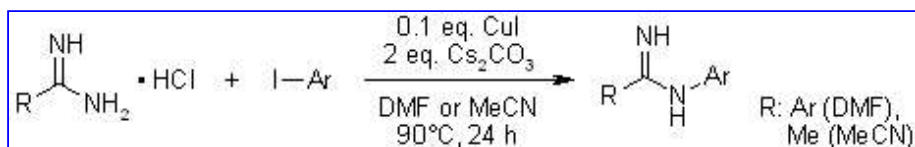
A Novel Synthesis of Disubstituted Quinazoline Diones with Differential N-Substitution via a Copper-Catalysed Cross-Coupling of Acyl Ureas

E. Durham, D. Perkins, J. S. Scott, J. Wang, S. Watson, *Synlett*, **2016**, 27, 965-968.



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C. G. Bates, R. K. Gujadhur, D. Venkataraman, *Org. Lett.*, **2002**, 4, 2803-2806.



Ligand-Free Copper-Catalyzed Arylation of Amidines

M. Cortes-Salva, C. Garvin, J. C. Antilla, *J. Org. Chem.*, **2011**, 76, 1456-1459.