

Correction to Synthesis of *N*-Alkenyl 2-Pyridonyl Ethers via a Au(I)-Catalyzed Rearrangement of 2-Propargyloxypyridines

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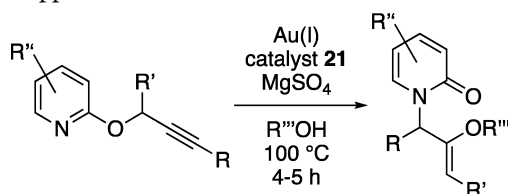
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Supporting Information

It was recently brought to our attention that the regiochemistry of ether product **8/26** was incorrectly assigned in this report. The correct structure contains a 1,1-disubstituted alkene, rather than the 1,2-disubstituted alkene that was originally proposed. This change impacts the proposed reaction mechanism, as the actual product results from a 6-*endo* addition of the cyclic nitrogen onto the activated alkyne, rather than a 5-*exo* addition as previously thought.

The graphical abstract, Schemes 4 and 6, and the graphical component of Tables 1, 3, and 4 were affected. The corrected versions appear below.



In addition, this change alters the mechanism that is proposed in Scheme 5. An alternate graphic and updated text for the Results and Discussion (page 9896) appear below.

While unselective and inefficient, the AuCl-catalyzed process represents the first observation of compounds **8**, **9**, and **10** being formed from 2-propargyloxypyridines **7**. The greater Lewis acidity and oxophilicity of Au(I), relative to Au(III), may account for this observation, as the activation of ketone **4** by Au(I) is expected to lead to the formation of intermediate **14**, which is poised to generate compounds **8**, **9**, and **10** (Scheme 5).

In addition, footnote b in Tables 1, 2, and 4 incorrectly indicates that the reported selectivity ratio is between 5-*exo* and 6-*endo* addition. As all products of this transformation are actually derived from the 6-*endo* pathway, these footnotes should simply report the “selectivity ratio” for compound **8** relative to the combination of compounds **4**, **9**, and **10**.

^bSelectivity ratio = 8/(4 + 9 + 10)

It also is necessary to update the abstract and conclusion to eliminate the mention of 5-*exo* and 6-*endo* selectivity.

Abstract: *N*-Alkyl 2-pyridones and other enolizable heterocycles are important synthetic constructs, due to their prevalence

in natural products and pharmaceutical targets and their capacity to serve as models for a number of biological and chemical processes. The disclosed Au(I)-catalyzed reaction utilizes 2-propargyloxypyridines to access *N*-alkylated 2-pyridone products derived from addition of the ring nitrogen to the pendent alkyne. After extensive optimization, biaryl Au(I) catalyst **21** was found to provide the highest combination of selectivity and yield for the 1,1-disubstituted ether product **8**. Herein, we report the application of this new Au(I)-catalyzed C–N bond formation for the preparation of a variety of 2-pyridonyl ether analogues, which have the potential to serve as an entry point for the synthesis of complex *N*-alkyl 2-pyridone-containing frameworks.

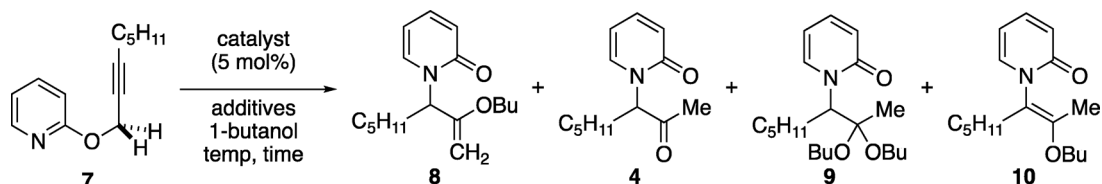
Conclusion: After extensive optimization, biaryl catalyst **21** has been found to facilitate the selective formation of 1,1-disubstituted ethers **8** and **26**. While the isolated yields of *N*-alkyl 2-pyridonyl ethers **8** and **26** remain modest (12 examples, 22–58% yield), the usefulness of this class of compounds as an entry point for the installation of *N*-alkyl 2-pyridones into a range of complex scaffolds is significant, rendering this method an important step toward the inclusion of this motif into targets of interest.

In light of this structural reassignment, the names for compounds **8a–d**, **26a–c**, and **26f–h** in the Experimental Section should appear as follows.

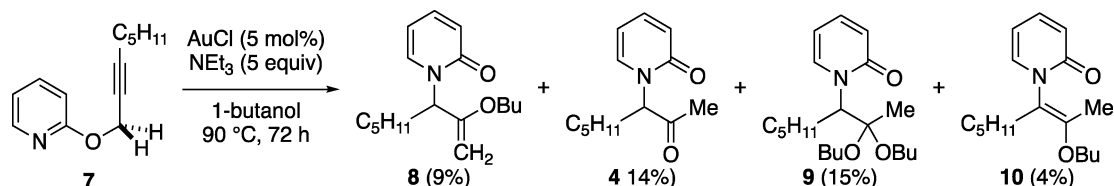
- 2-Butoxy-3-(2-pyridonyl)oct-1-ene (**8a**)
- 2-Butoxy-5-phenyl-3-(2-pyridonyl)pent-1-ene (**26a**)
- 2-Butoxy-3-cyclohexyl-3-(2-pyridonyl)prop-1-ene (**26b**)
- 2-Butoxy-3-(2-pyridonyl)-5-triisopropylsilyloxy-pent-1-ene (**26c**)
- 3-Butoxy-4-(2-pyridonyl)hex-2-ene (**26f**)
- 2-Butoxy-3-(5'-methyl-2-pyridonyl)oct-1-ene (**26g**)
- 2-Butoxy-3-(3'-methyl-2-pyridonyl)oct-1-ene (**26h**)
- 2-(3-Methylbutoxy)-3-(2-pyridonyl)oct-1-ene (**8b**)
- 2-(2-Methylpropoxy)-3-(2-pyridonyl)oct-1-ene (**8c**)
- 2-Cyclohexoxy-3-(2-pyridonyl)oct-1-ene (**8d**)

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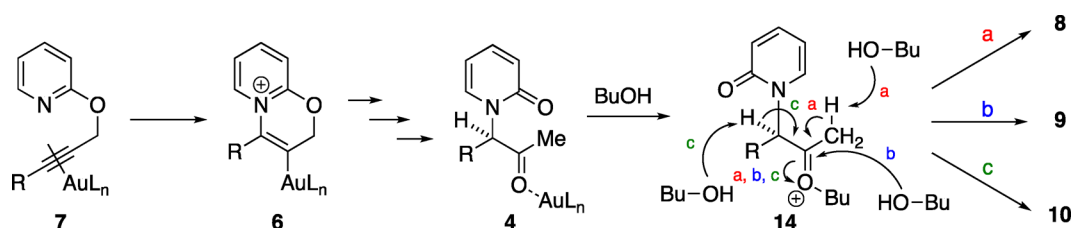
Table 1. Initial Optimization (graphic)



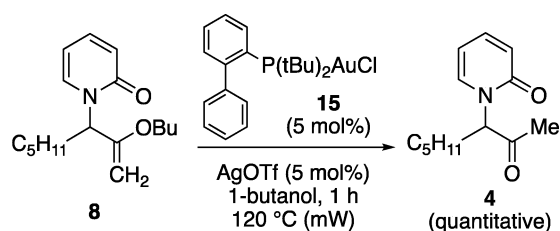
Scheme 4. Formation of 2-Pyridones 4, 8, 9, and 10



Scheme 5. Proposed Mechanisms



Scheme 6. Relative Stability



■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.0c00151>.

Complete revised file (PDF)

■ ACKNOWLEDGMENTS

We thank Professor T. Hoyer (University of Minnesota) for bringing this error to our attention.

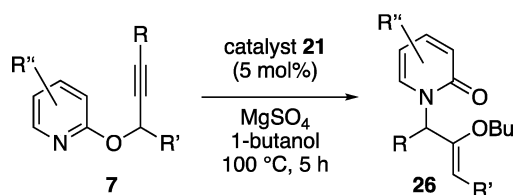
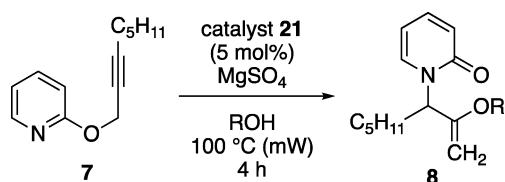
Table 3. Synthesis of *N*-Alkyl 2-Pyridones 26 (graphic)

Table 4. Synthesis of Aliphatic Ethers 8 (graphic)



Similar errors existed in the Supporting Information. As such, a new version has been provided. This updated version also contains additional 2D NMR evidence in support of the revised structure of compounds 8/26.