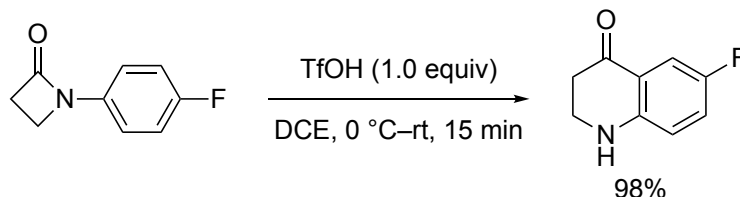


Question 1. The Fries Rearrangement is a useful method for synthesizing *o*- or *p*-ketoaniline or phenol derivatives. Shown below is an intermolecular version published by Anderson and Tepe. Provide a reasonable mechanism for this transformation and provide another name for this type of reaction.

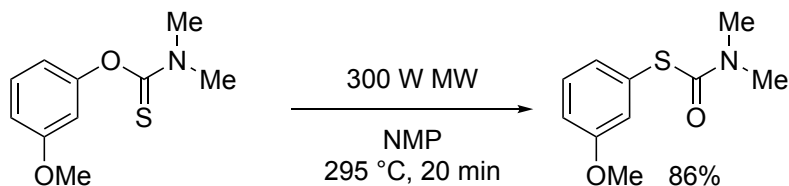


Hint: The reaction using the 4-nitroaniline derivative provides 0% yield.

Bonus. The same reaction with the *p*-anisidine derivative requires 2 equivalents of TfOH. Why?

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Question 2. Shown below is an example of the Newman-Kwart Rearrangement, which converts aryl *O*-thiocarbamates to *S*-thiocarbamates, enabling simple access to thiophenols from phenols. NKR reactions require incredibly high temperatures to occur, and as such benefit from efficient microwave heating. Shown below is an example from Moseley and Lenden. Provide an arrow pushing mechanism for this transformation.



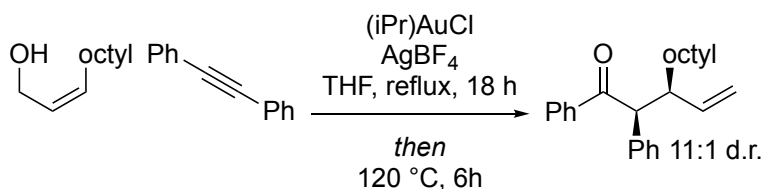
Hints: (1) Kinetic experiments show that the reaction displays first order kinetics and has a very negative entropy of activation; (2) the equivalent reaction with the 4-methoxyphenol derivative provides lower yield and requires temperatures above 300 °C for 40 minutes.

Bonus. What provides the driving force for this reaction (why does it not go the other direction)?

Bonus. This reaction only works using tertiary, *N,N*-difunctionalized *O*-thiocarbamates. Why?

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Question 3. Gold(I)-catalyzed hydrofunctionalizations, cyclizations, and rearrangements are some of the most powerful synthetic tools to emerge since the turn of the century. The ability to rapidly construct molecular complexity from simple, linear alkenes and alkynes enables robust synthetic campaigns culminating in a single, impressive reaction to construct the molecular core. Shown below is a gold-catalyzed synthesis of homoallylic ketones. Provide a reasonable mechanism for this transformation and rationalize the observed diastereoselectivity.



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