

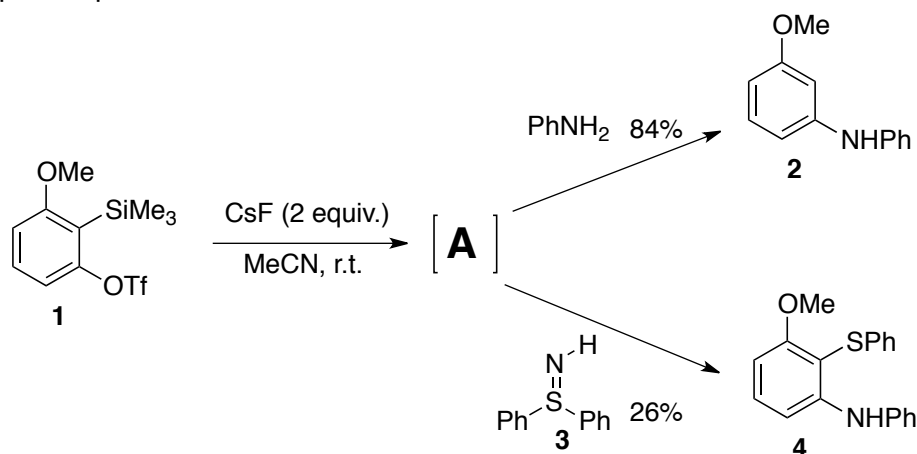
Cumulative Examination Organic Chemistry

By: Vladimir Gevorgyan
(November 3, 2016)

- Try to answer all questions. Partial credits will be given for incomplete answers. Extra credits will be given for detailed answers.
- Pay attention to the quality of your drawings. Points will be deducted if the drawings are unclear or sloppy.

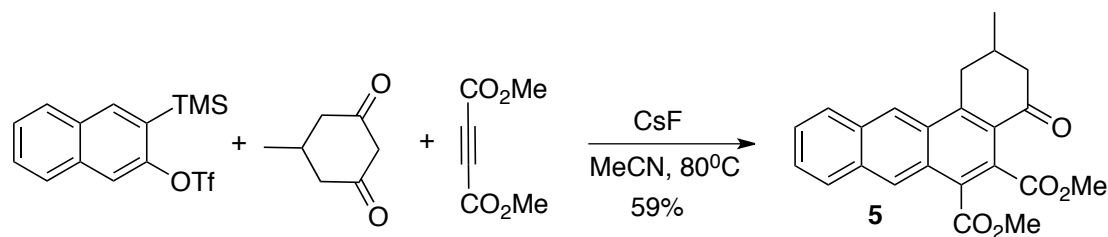
1 (20 pts)* Larock and co-workers shown (*Org. Lett.* **2003**, 5, 4673) that compound **1** when treated with CsF and aniline, produces arylamine **2** in good yield. Later, Hosoya and co-workers reported (*J. Am. Chem. Soc.* **2015**, 137, 14071) a reaction of **1** with sulfimine **3**, which under otherwise identical conditions leads to thioaniline **4**, albeit in low yield.

- 1a (5 pts)** Draw the structure of intermediate **A**, and provide mechanism for its formation.
1b (5 pts) Provide the mechanism for transformation **A**→**2**, and explain the observed regiochemistry.
1c (10 pts) Propose a plausible mechanism for transformation **A**→**4**.

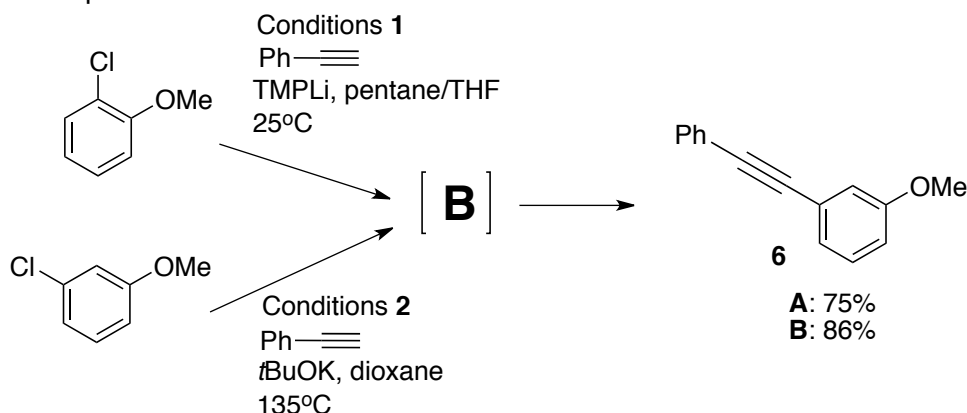


***note:** This question is taken from one of the previous cumes (11.05.2015)

2 (15 pts) Recently, Shu, Wu, and co-workers reported a three-component transition metal-free annulation reaction [*Org. Lett.* **2016**, 18, 3762]. Provide detailed mechanism for formation of **5**.



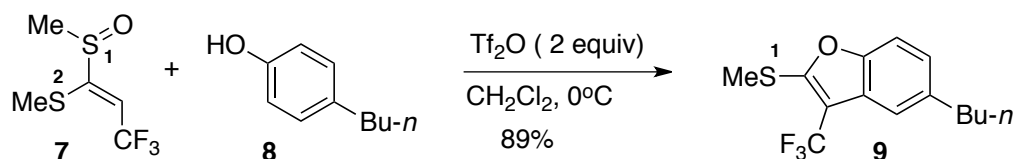
3 (15 pts) Daugulis group reported a metal-free version of Sonogashira reaction [*Org. Lett.* **2011**, *13*, 4172]. Regardless of the regioisomer of arylchloride used, the same product **6** has been obtained, which presumes involvement of the same intermediate **B**.



3a (5 pts) Rationalize formation of intermediate **B** from both arylchloride regioisomers.

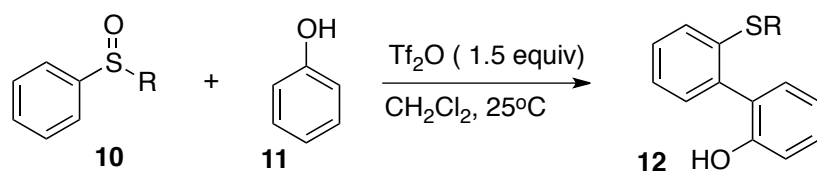
3b (10 pts) Propose a plausible mechanism for transformation **B**→**6**.

4 (15 pts) Provide detailed mechanism for “extended Pummerer reaction” toward **9** [Yorimitsu, Oshima, *et al*, *J. Am. Chem. Soc.* **2010**, *132*, 11838].

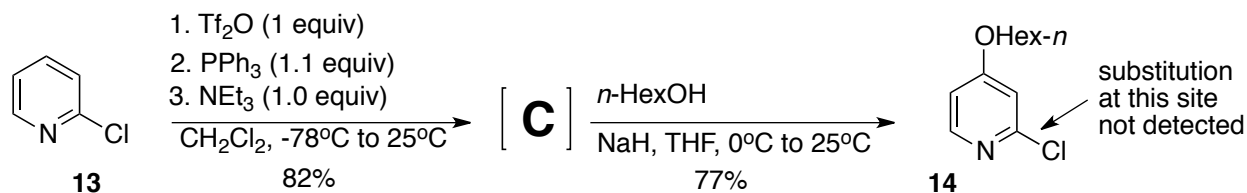


Hint: pay attention to sulfur atoms labeling

5 (15 pts) The same research group recently extended this metal free strategy toward biphenyls **12** [Yorimitsu, *et al*, *J. Am. Chem. Soc.* DOI: 10.1021/jacs6b10278]. Provide detailed mechanism for this transformation.



6 (20 pts) Very recently, McNally reported a metal-free *para*-selective C–H oxygenation of pyridines [*J. Am. Chem. Soc.* DOI: 10.1021/jacs6b08662]. Provide detailed mechanism for this transformation. Also, provide reasoning, why substitution of chloride at the C-2 position did not occur.



Hint: intermediate **C** is stable isolable compound