Cumulative Examination
Organic Chemistry

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(November 5, 2015)

•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.

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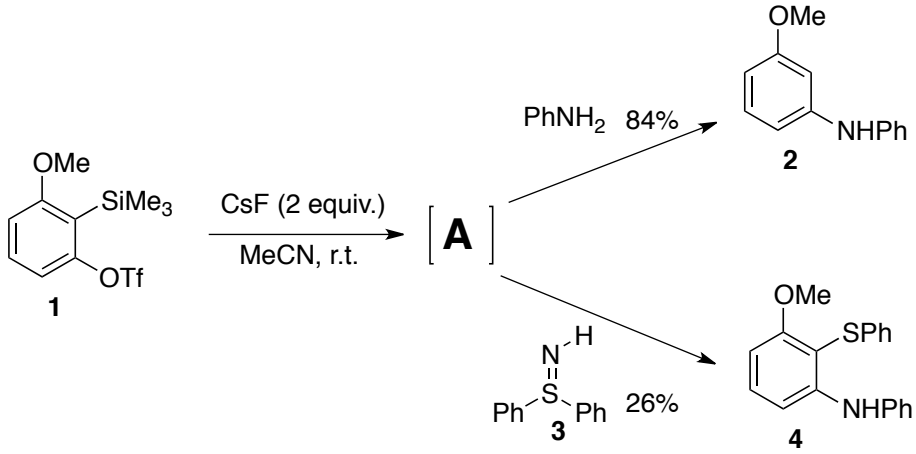
1 Larock and co-workers shown (*Org. Lett.* **2003**, *5*, 4673) that compound **1** when treated with CsF and aniline, produces arylamine **2** in good yield. Very recently, Hosoya and co-workers reported (*J. Am. Chem. Soc.* DOI:10.1021/jacs.5b10557) a reaction of **1** with sulfimine **3**, which 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.

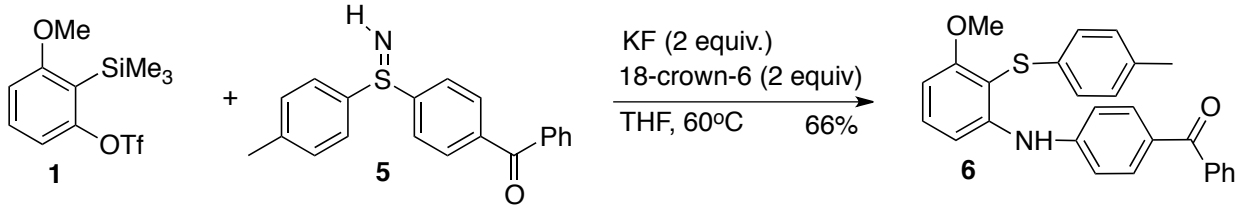
1c (**10 pts**) Propose a plausible mechanism for transformation **A**→**4**.



In the same paper from Hosoya group, it was shown that **1** upon treatment with KF/18-crown-6 reacted with unsymmetrical sulfimine **5** to produce thioaniline **6** in 66% yield.

1d (**5 pts**) Explain the role of 18-crown-6.

1e (**10 pts**) Explain the origins of the observed regiochemistry in the formation of **6**.



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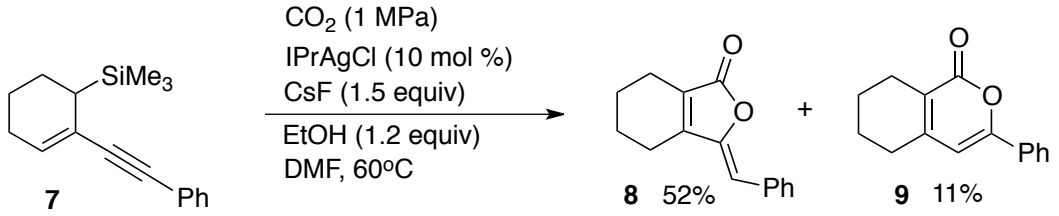
2 (**20 pts**) Provide detailed mechanism for formation of **8** and **9**; explain stereochemistry where applicable [Yamada et al, *Org. Lett.* DOI: 10.1021/acs.orglett.5b03023].



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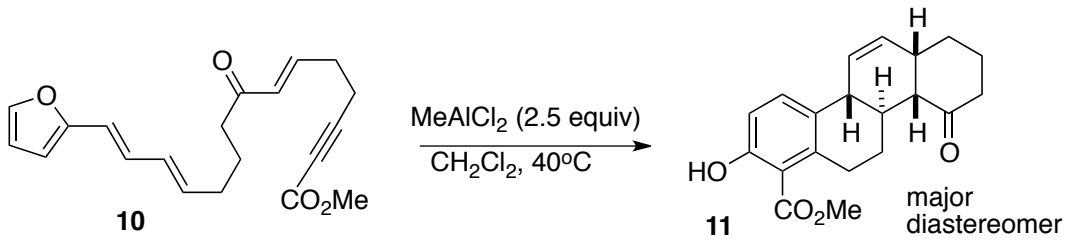
3 (**20 pts**) Provide detailed mechanism for formation of major diastereomer **11**, explain origins of diastereoselectivity [Sherburn et al, *Org. Lett.* DOI: 10.1021/acs.orglett.5b02412].



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4 (**25 pts**) Provide detailed mechanism for formation of **15**, explain the role of **14** [Dong et al, *Angew. Chem. Int. Ed.* **2015**, *54*, 12664].