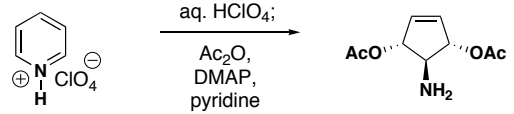
Due Date: Monday, May 1st.
Points: 150

Please delineate reasonable mechanisms for the following transformations. (5 points each)

1



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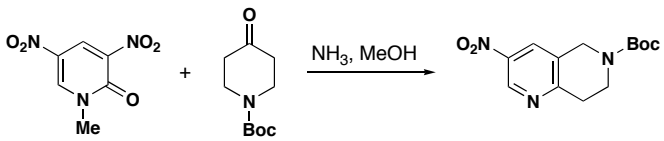

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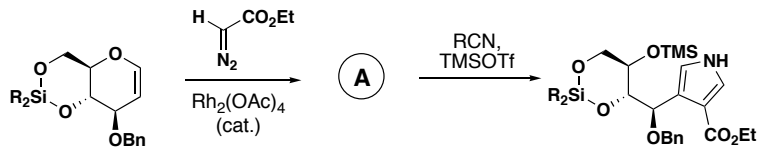

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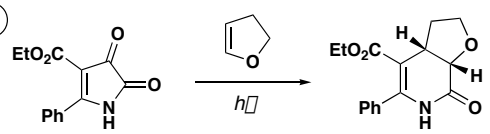

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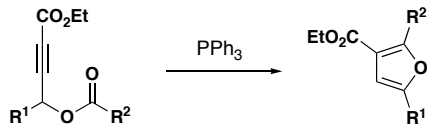

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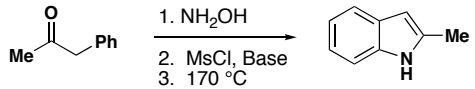

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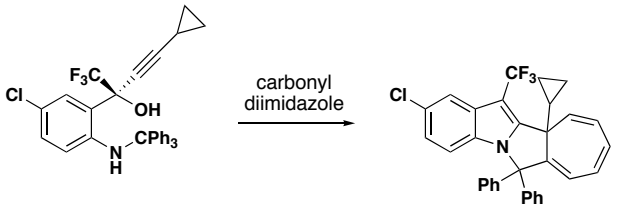

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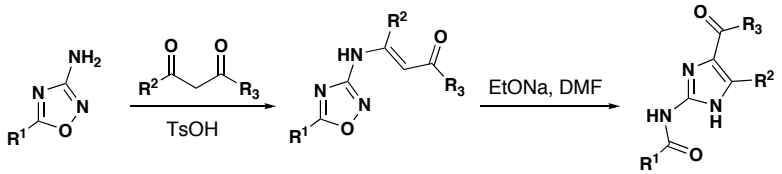

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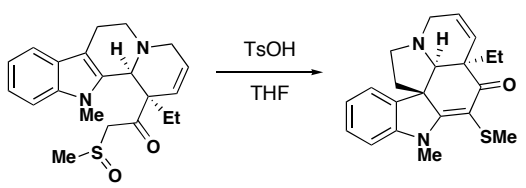

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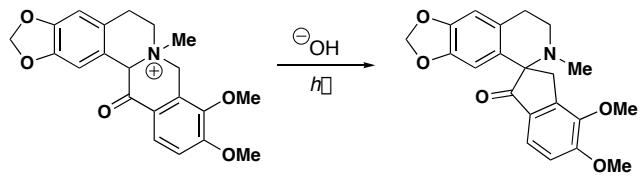

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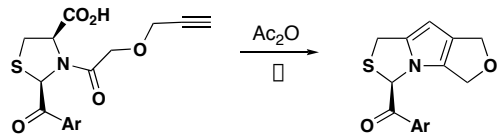

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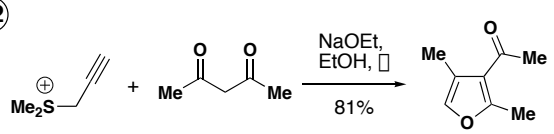
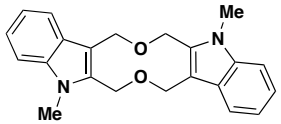


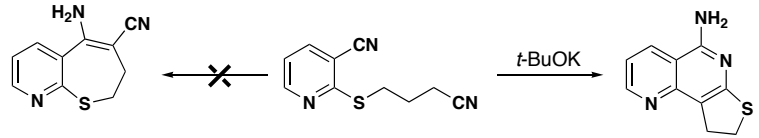
Advanced problems in heterocyclic chemistry (10 points each).

1 Treatment of *N*-methylaniline with 4-chlorobut-2-yn-1-ol in acetone at reflux temperature in the presence of anhydrous K_2CO_3 gave the expected tertiary amine in 91% yield. Room temperature oxidation of a dilute solution of this amine with *m*-CPBA resulted in formation of a colorless crystalline solid in 56% yield, which was shown to have the structure **1**. Please deduce a mechanism for the formation of **1**.



1

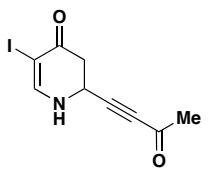
2 Japanese workers recently designed a synthesis of 5-amino-2,3-dihydrothiepino[2,3-*b*]pyridine-4-carbonitrile **2** based on Thorpe-Ziegler cyclization of 2-(3-cyanopropylthio)pyridine-3-carbonitrile **1**. Treatment of **1** with potassium *t*-butoxide however, did not give **2**, but produced the thieno-[2,3-*h*][1,6]naphthyridine **3** in 82% yield. Suggest a mechanism for the transformation of **1** to **3**.



2 **1** **3**

Provide simple syntheses for the following compounds. (5 points each) ***You may not use Pd or other similar metals that achieve cross-coupling.*** Most syntheses are possible in 1–3 steps.

1



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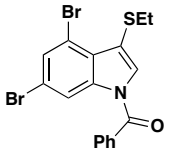

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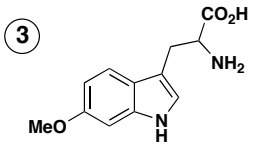

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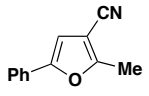

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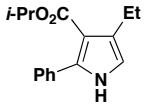

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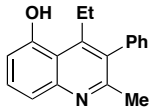

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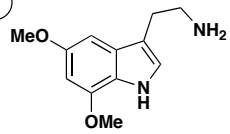

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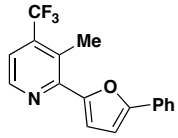

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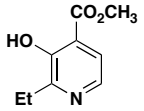

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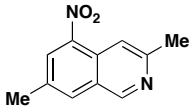

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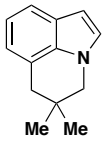

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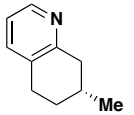

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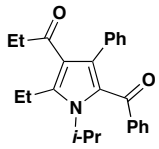

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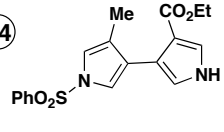

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