Organic Cumulative Exam (February 1, 2018) Daesung Lee

1. (15 Points) The following ring closure reactions can occur either under thermal conditions or in the presence of a non-metal catalyst. Draw the mechanism of each reaction by drawing intermediates and arrows for electron movement.

Adv. Synth. Catal. 2016, 358,1566

Org. Lett. 2017, 19, 5597

(c)
$$O CO_2Et$$
 $O CO_2Et$ $O CO_2Et$ $O CO_2Et$

2. (40 Points) Consider the following oxidation-induced ring-forming reactions. Except the reaction in (a), the other transformations in (B)–(d) involve a [1,2] carbon–carbon bond-shift to deliver the indicated products. Provide the mechanism of each transformation by drawing the key intermediates and electron movement with arrows.

J. Am. Chem. Soc. 2016, 138, 14868

Org. Lett. 2018, 20, 84

(d)
$$\begin{array}{c} \text{Rh}_2(\text{esp})_2 \text{ (2.5 mol\%), PhI(OPiv)}_2 \\ \hline \text{CaO (2.6 equiv), CH}_2\text{CI}_2, \text{ rt, 87\%} \\ \end{array}$$

3. (15 points) The synthesis and structural revision of Dichrocephones A and B involves the following transformations.

Angew. Chem. Int. Ed. 2018, 57, DOI: 10.1002/anie.201711766

- (a) (5 Points) Draw a reasonable mechanism for the conversion of 8 to 9.
- (b) (5 Points) Draw a reasonable mechanism for the conversion of 7 to 10.
- (c) (5 Points) Provide any catalyst that can transform 11 to 6 in a single step.

4. (30 points) Consider the following transformations, which is a part of the total synthesis of Periconianone A (*J. Am. Chem. Soc.* **2017**, *139*, 16096).

(b)
$$N_2$$
 OTBS $Rh_2(OAc)_2 CH_2Cl_2, rt,$ $Rh_2(OAc)_2 CH_2Cl_2, rt,$

(c)
$$N_2$$
 OTBS $Rh_2(OAc)_2 CH_2Cl_2, rt,$

- (a) (10 Points) Draw a reasonable mechanism for the conversion of 7 to 8 in (a).
- (b) (10 Points) Draw the structure of a transition state (TS 9) that leads to the structure and stereochemistry of product 9 (in (b).
- (c) (10 points) By changing the geometry of the reacting crotyl alcohol, product 10 will be generated through a transition state closely related to TS 9. Draw the structure of 10 unambiguously.