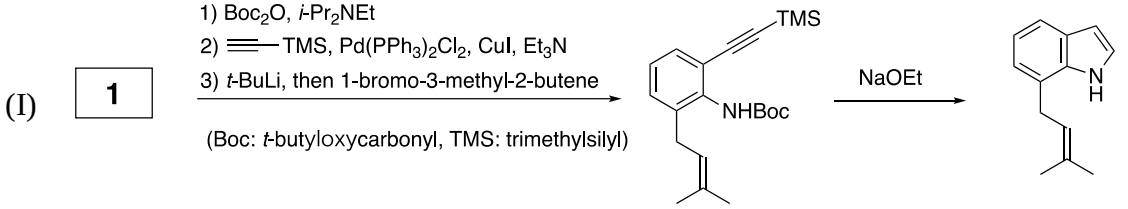
［有機化学標準］

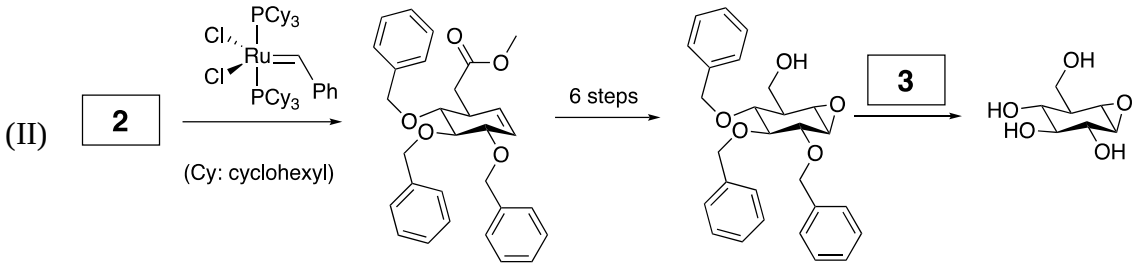
以下の問（１）～（３）に答えよ．各スキームでは反応溶媒の表記は省略されている．

（１） 次に示すスキーム(I)～(IV)は天然有機化合物の合成経路の一部である．以下の問(a)~(c)に答えよ．

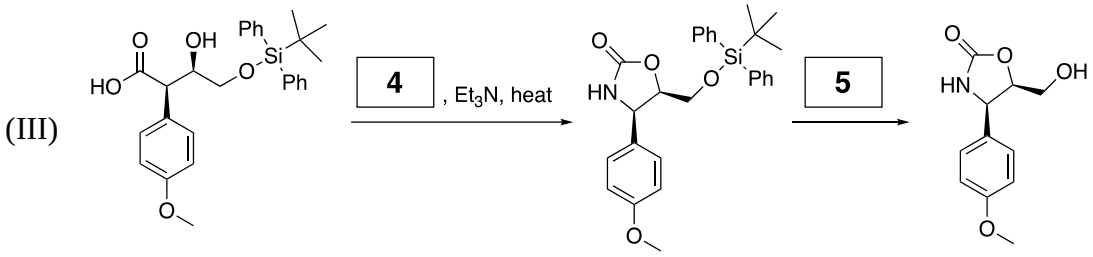
(I)



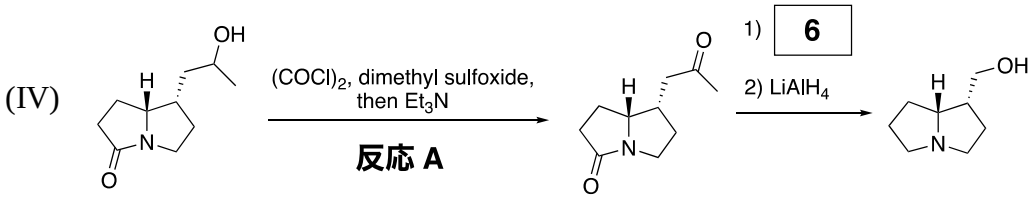
(II)



(III)



(IV)



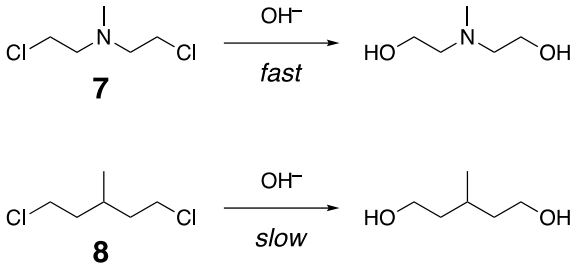
(a) 化合物 **1** および **2** として利用可能な化合物の構造式をそれぞれ一つ描け．**2** については，全てのキラル中心の立体化学を明示して描くこと．

(b) 反応剤 **3**～**6** として適する試薬をそれぞれ答えよ．必要であれば，複数の試薬を組み合わせてもよい．

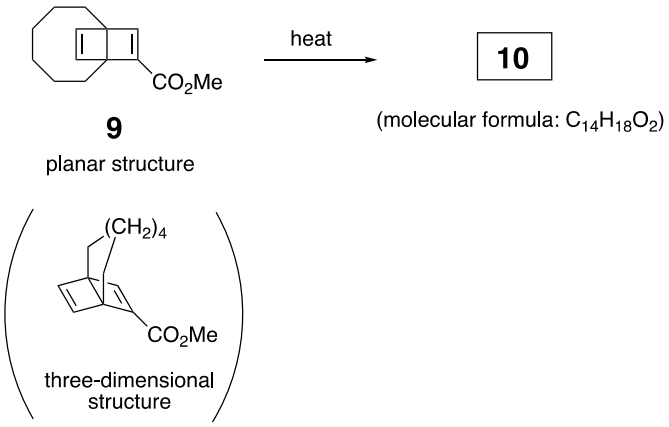
(c) **反応 A** の反応機構を，中間体の構造を示しつつ電子の移動を表す巻矢印表記法を用いて示せ．反応に関与しない部分の構造は“R–”と省略してよい．

（２） 以下の問(d)に答えよ．

(d) 化合物 **7** および **8** と水酸化物イオンとの反応では，化合物 **7** の反応の方が速い．この反応速度の違いが生じる理由を簡潔に説明せよ．



（３） 化合物 **9** を加熱条件下で反応させたところ，分子式が $C_{14}H_{18}O_2$ である主生成物 **10** を与えた．生成物 **10** の ^{1}H NMR 測定では，7〜8 ppm の領域に水素原子 3 個分のシグナルが観測されたほか，高磁場領域（−1〜0 ppm）にも複数のシグナルが観測された．以下の問(e)〜(h)に答えよ．



(e) 生成物 **10** の分子構造式を描け．

(f) この反応は電子環状反応によるシクロブテン環の開環とみなすことができるが，この反応は熱反応条件では禁制反応である．なぜ本反応が禁制反応と判断できるかを，「同旋的」あるいは「逆旋的」のいずれかの単語を用いて簡潔に説明せよ．

(g) 禁制であるにもかかわらず，実際にはこの電子環状反応が進行する理由を簡潔に説明せよ．

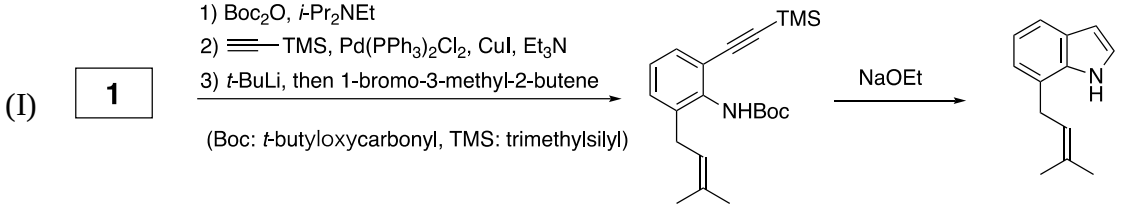
(h) 生成物 **10** の ^{1}H NMR 測定で高磁場領域（−1〜0 ppm）に観測された特徴的な水素原子について，このように高磁場領域にシグナルを与える理由を簡潔に説明せよ．

[Organic Chemistry: Standard]

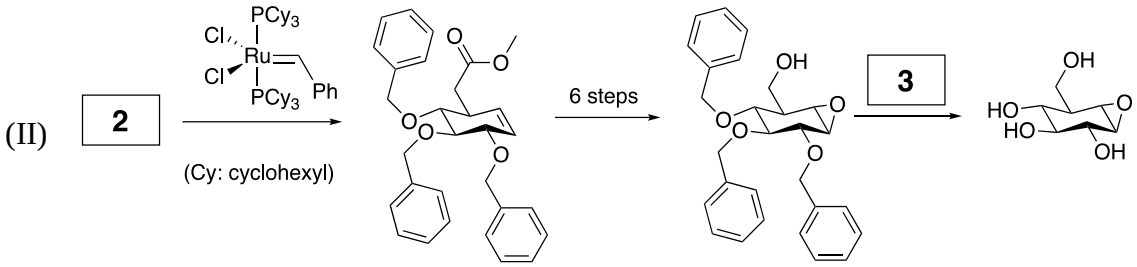
Answer problems (1) through (3). The reaction solvents are omitted in each scheme.

(1) The following schemes (I)–(IV) are parts of synthetic pathways of natural organic compounds. Answer the following problems (a) through (c).

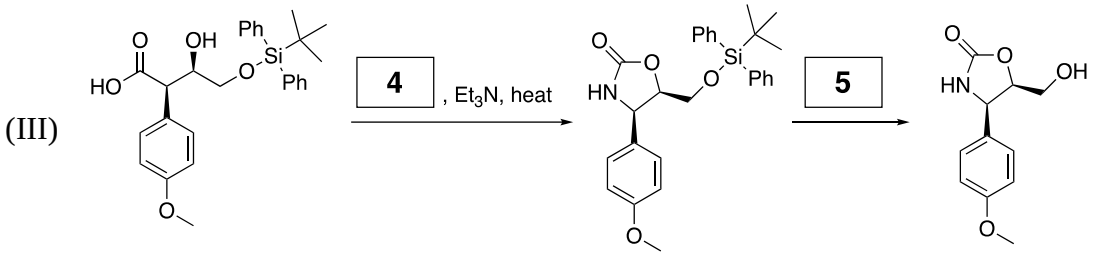
(I)



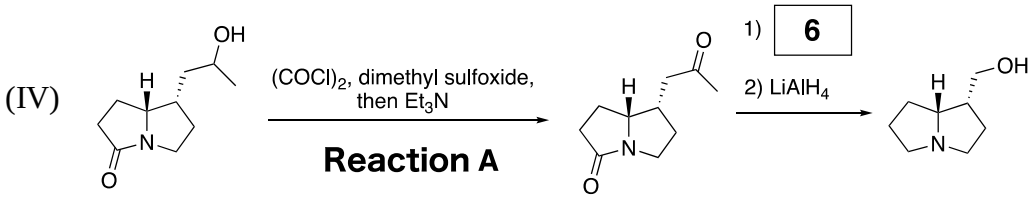
(II)



(III)



(IV)



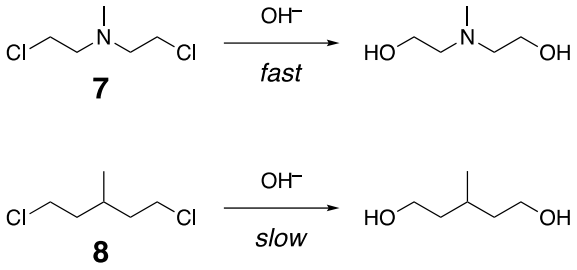
(a) Draw a compound usable for each of the starting materials **1** and **2**. For **2**, draw the structure with indication of stereochemistry of all chiral centers.

(b) Propose an appropriate reagent for each of **3**–**6**. You can propose a combination of multiple reagents if necessary.

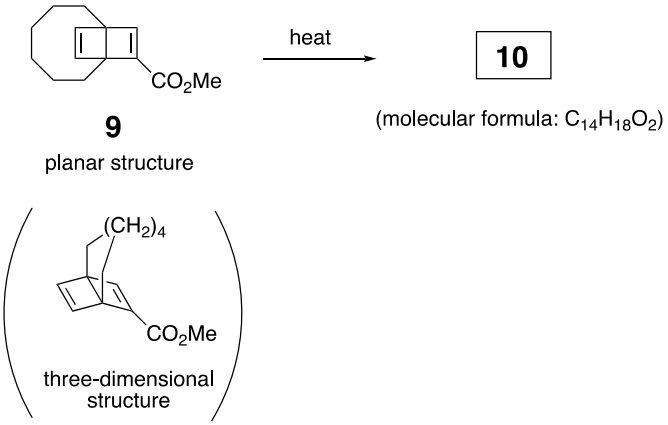
(c) Draw the mechanism of **Reaction A** by using the curved arrow formalism. A partial structure not involved in the reaction can be abbreviated as "R–".

(2) Answer the following problem (d).

(d) In the reaction with hydroxide ion, compound **7** reacts faster than compound **8**. Briefly explain the reason for the difference in the reaction rates.



(3) When compound **9** was incubated at elevated temperature, the major product **10** (molecular formula: $C_{14}H_{18}O_2$) was obtained. In the ^{1}H NMR measurement, the product **10** showed signals corresponding to three hydrogen atoms in the region of 7 to 8 ppm, and some signals were also observed in the upfield region (–1 to 0 ppm). Answer the following problems (e) through (h).



(e) Draw the molecular structure of the product **10**.

(f) This conversion can be regarded as a ring opening process of the cyclobutene moiety by an electrocyclic reaction, which is forbidden under thermal reaction conditions. Briefly explain why this reaction can be interpreted as a forbidden process using either the word “conrotatory” or “disrotatory”.

(g) Briefly rationalize the observation that this electrocyclic reaction indeed proceeded though it should be forbidden.

(h) Briefly explain why the characteristic signals in the upfield region (–1 to 0 ppm) were observed at the upfield region in the ^{1}H NMR measurement of the product **10**.