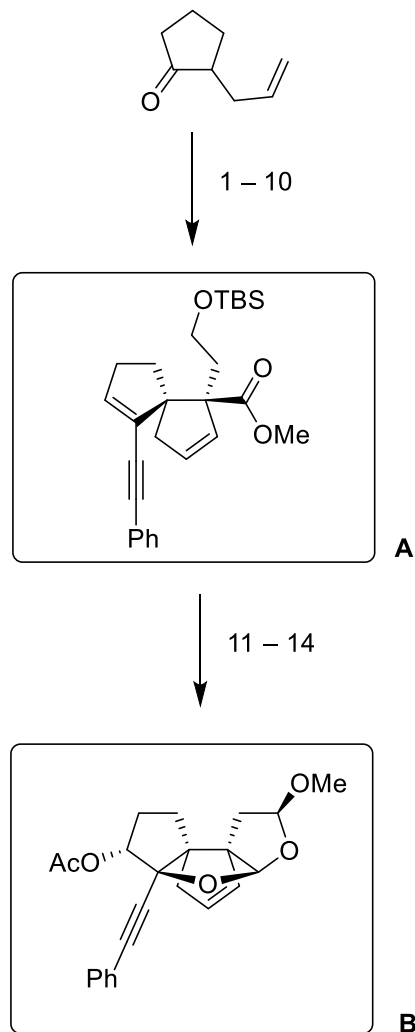


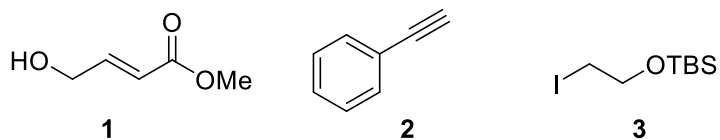
Total Synthesis of Ginkgolide C and Formal Syntheses of Ginkgolides A and B

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J. Am. Chem. Soc. **2022**, *144*, 17792-17796.



1. Amberlyst 15, CH(OMe)₃, MeOH, reflux
2. Propionic acid (cat.), **1**, 150 °C
3. Grubbs II, CH₂Cl₂, reflux
4. DBU, PhMe, 80 °C
5. PhNTf₂, LHMDS, THF, –45 °C
6. Pd(PPh₃)₂Cl₂, **2**, CuI, Et₃N, 60 °C
7. KHMDS, 18-Crown-6, THF, –78 °C then **3**
8. *m*-CPBA, CH₂Cl₂, r.t.
9. Ac₂O, Et₃N, DMAP, CH₂Cl₂, r.t. then MeOH, TBAF, 65 °C
10. AcOK, DMSO, 145 °C

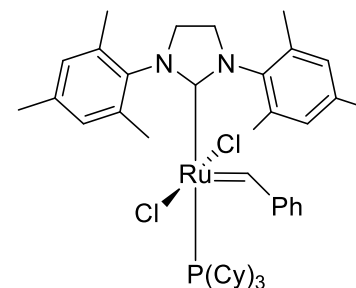


11. DMP, CH₂Cl₂, r.t.
12. Amberlyst 15, CH(OMe)₃, MeOH, CH₂Cl₂, 65 °C
13. DIBAL-H (5 eq.), THF, –78 °C → 0 °C
14. HCl (4M in dioxane), THF, r.t. then Et₃N, DMAP, Ac₂O, r.t.

Step 2: Please, name the reaction.

Claisen rearrangement

Step 3: Please, show the structure of Grubbs II catalyst



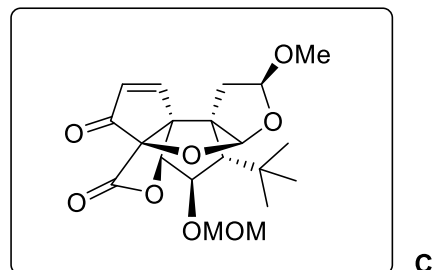
Step 6: Please, name the reaction.

Sonogashira cross-coupling

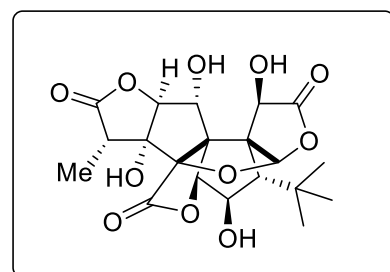
Hint step 8: Two products are formed. Step 9 converts one of them into **A** and step 10 converts the other into **A**.

B

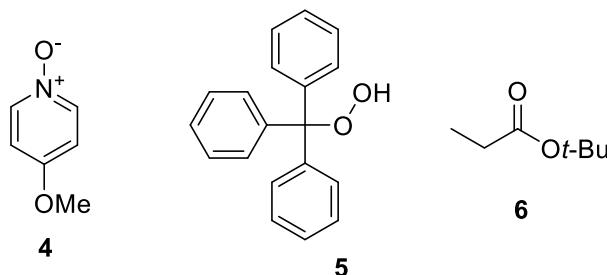
↓
15 – 21



↓
22 – 28

**Ginkgolide C**

15. SeO₂, 1,4-dioxane, 110 °C *then* DMP, CH₂Cl₂, 60 °C
16. *t*-BuLi, CuCN, THF, -78 °C *then* TMSI, -78 °C *then* TBAF, r.t. *then* NaOH, MeOH, THF, H₂O, 75 °C
17. KHMDS, Davis' oxaziridine, THF, -78 °C → r.t.
18. MOMBr, DIPEA, TBAI, CH₂Cl₂, 55 °C
19. RuCl₃, NaIO₄, CCl₄, MeCN, H₂O, 50 °C
20. NaBH₄, THF, H₂O, r.t. *then* NaOH, 50 °C *then* AcOH, r.t.
21. IBX (8 eq.), **4** (8 eq.), DMSO, 75 °C



22. PPTS, pyr, Ac₂O, PhCl, 135 °C
23. DBU, **5**, CH₂Cl₂, -25 °C
24. LDA, **6** *then* SM, THF, HMPA, -78 °C → -30 °C
25. CSA, CH₂Cl₂, r.t.
26. DMDO, acetone, r.t.
27. Br₂, NaOAc, AcOH, H₂O, r.t.
28. K₂CO₃, MeOH, r.t.

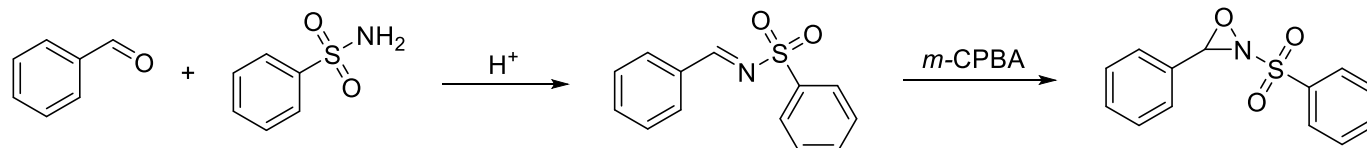
Step 15: Please name the first reaction which takes place and show the mechanism

Riley oxidation

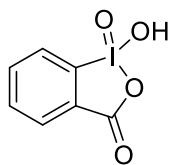
Step 16: Please, categorize the occurring cyclization according to the Baldwin rules.

5-endo-dig

Step 17: Please, show the structure of Davis' oxaziridine. How would you prepare this reagent?



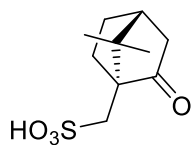
Step 21: Please, show the structure of IBX.



Step 22: Same conditions without Ac_2O led only to several sideproducts and no desired product. Why is Ac_2O essential?

MOM-group is cleaved under reaction conditions which leads to formation of several acetals.
 Ac_2O replaces the MOM-group which prevents formation of undesired acetals.

Step 25: Please, show the structure of CSA.



Step 26: How would you generate DMDO?

