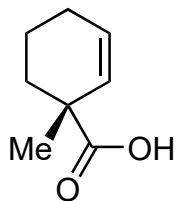
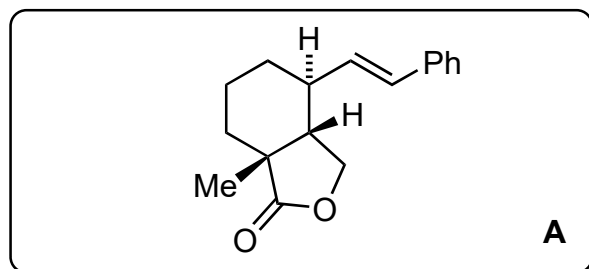


Tandem Decarboxylative Cyclization/Alkenylation Strategy for Total Syntheses of (+)-Longirabdiol, (-)-Longirabdolactone, and (-)-Effusin

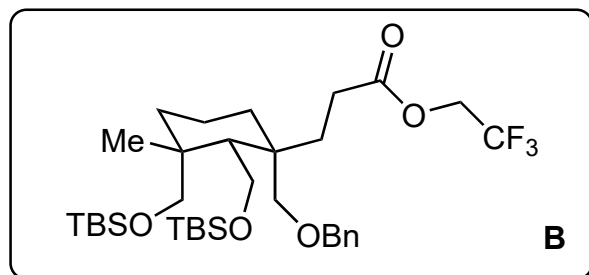
J. Zhang, Z. Li, J. Zhuo, Y. Cui, T. Han, C. Li
J. Am. Chem. Soc. **2019**, *141*, 8372–8380.



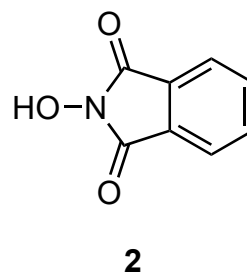
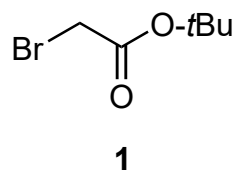
1-4



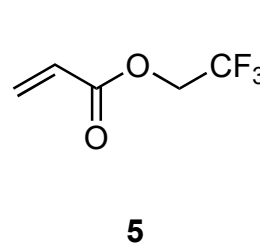
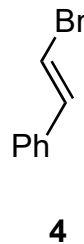
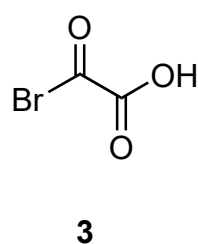
5-11



1. K_2CO_3 , **1**
2. TFA
3. **2**, DIC, DMAP
4. Zn (3 eq), $CuCl_2$ (cat.), DavePhos, **3**, **4**



5. $RuCl_3$, $NaIO_4$
6. Boc_2O , DMAP, t-BuOH
7. LDA, BOMCl
8. $LiBH_4$
9. TBSOTf, 2,6-lutidine then TESOTf, citric acid
10. **2**, DIC
11. Zn (2 eq), $Ni(ClO_4)_2 \cdot 6H_2O$ (cat.), LiCl, **5**



4. Draw a mechanism for the cyclization step and classify it using Baldwin's rules.

(see mechanism below) 5-exo-trig

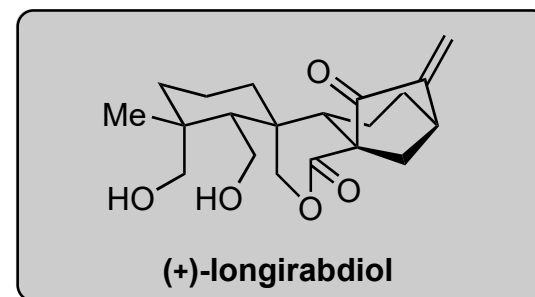
4. Hint: cyclization then metal-catalyzed alkenylation occurs to form a cis-fused heterocycle. **3** is a non-participating additive.

5. Hint: oxidative olefin cleavage

11. Name this reaction.

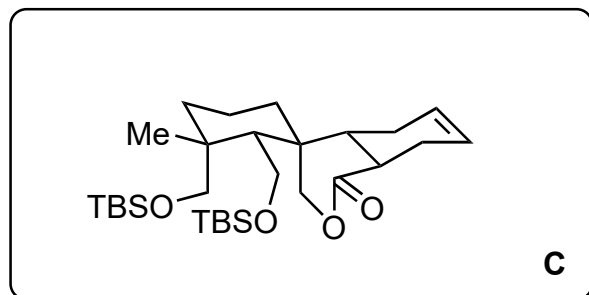
Giese reaction

Hint: C-C bond cleavage, then C-C bond formation.

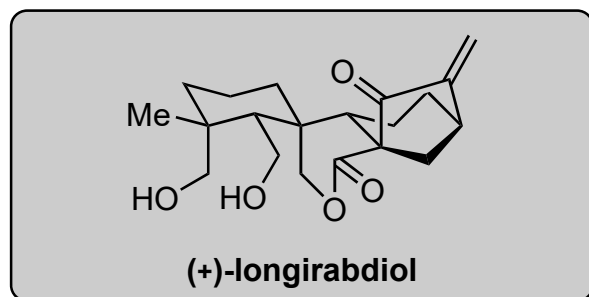


B

12-15



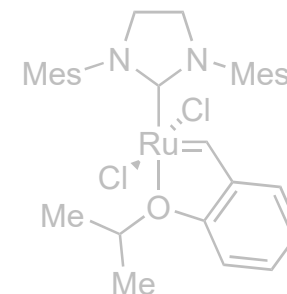
16-20



12. H₂, Pd/C
13. (PhSeO)₂O
14. allylMgBr, CuBr•Me₂S, LiBr then allyl iodide
15. HG-II

16. LDA, 2,3-dibromopropene
17. Et₃B, *n*-Bu₃SnH
18. SeO₂, *t*-BuOOH
19. DMP, NaHCO₃
20. LiBF₄

12. *Hint: after the transformation, a spontaneous lactonization occurs.*
- 13: *Hint: an α,β -unsaturated lactone is formed*
15. Draw the structure of HG-II.



17. Using the nomenclature of bridged bicyclic molecules, name the ring formed.
bicyclo[3.2.1]octane
18. Name this reaction.
Riley oxidation

