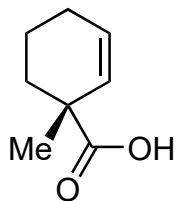


Tandem Decarboxylative Cyclization/Alkenylation Strategy for Total Syntheses of (+)-Longirabdiol, (-)-Longirabdolactone, and (-)-Effusin

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



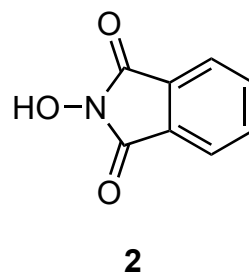
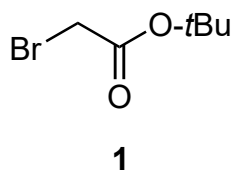
1-4



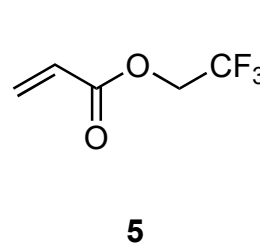
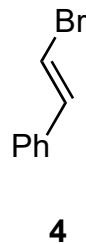
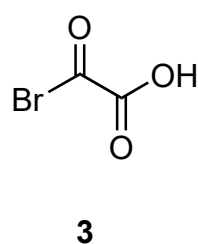
5-11



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



5. $RuCl_3$, $NaIO_4$
6. Boc_2O , DMAP, t-BuOH
7. LDA, BOMCI
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**



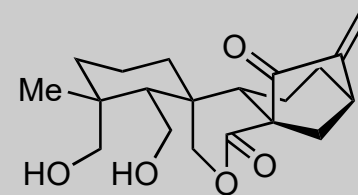
4. Draw a mechanism for the cyclization step and classify it using Baldwin's rules.

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.

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

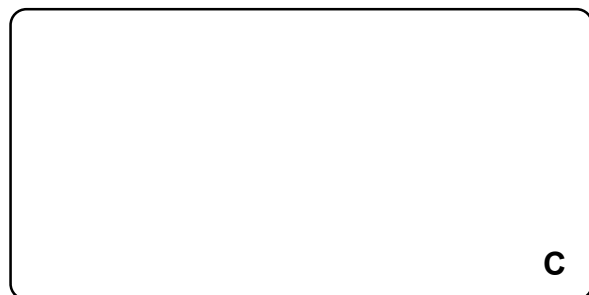


(+)-longirabdiol

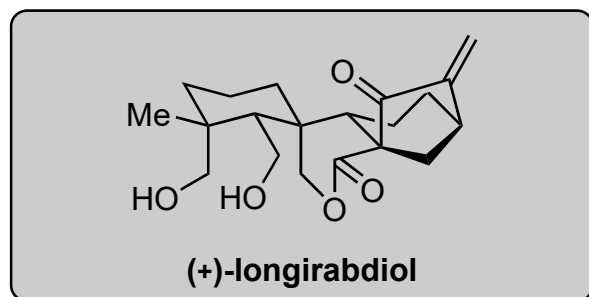
B



12-15



16-20



12. H_2 , Pd/C
13. $(\text{PhSeO})_2\text{O}$
14. allylMgBr, $\text{CuBr}\cdot\text{Me}_2\text{S}$, LiBr then allyl iodide
15. HG-II

16. LDA, 2,3-dibromopropene
17. Et_3B , $n\text{-Bu}_3\text{SnH}$
18. SeO_2 , $t\text{-BuOOH}$
19. DMP, NaHCO_3
20. LiBF_4

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.

18. Name this reaction.