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


1. K$_2$CO$_3$, 1
2. TFA
3. 2, DIC, DMAP
4. Zn (3 eq), CuCl$_2$ (cat.), DavePhos, 3, 4

5. RuCl$_3$, NaIO$_4$
6. Boc$_2$O, 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$_4$)$_2$·6H$_2$O (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.*

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

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.

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

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