

Total Synthesis of Taiwaniadducts B, C, and D

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Checker: Chang-Bin Yu

Date: 2014/07/15



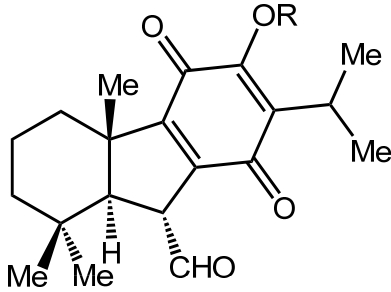
Shanghai Institute of
Organic Chemistry

Li, A. *et al* *J. Am. Chem. Soc.* **2014**, 136, 8185.

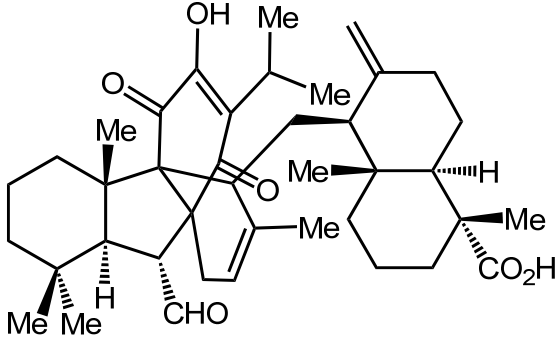
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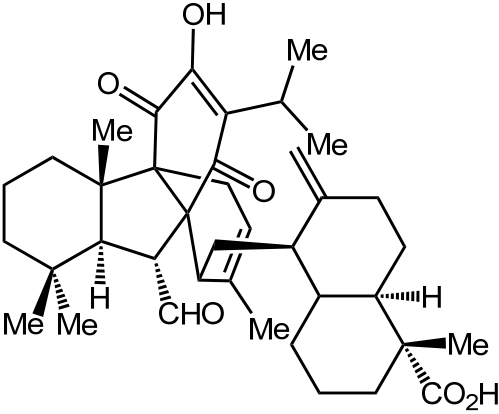
Introduction



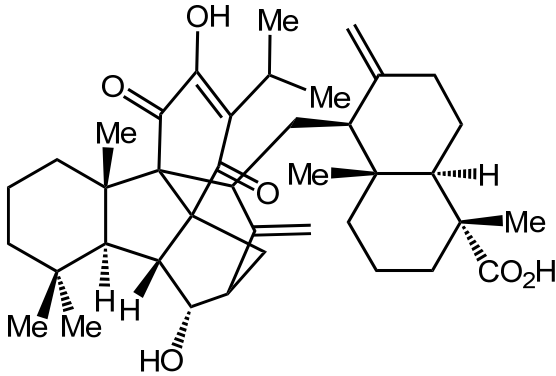
R = H, taiwaniaquinone A
R = Me, taiwaniaquinone F



taiwaniadduct B

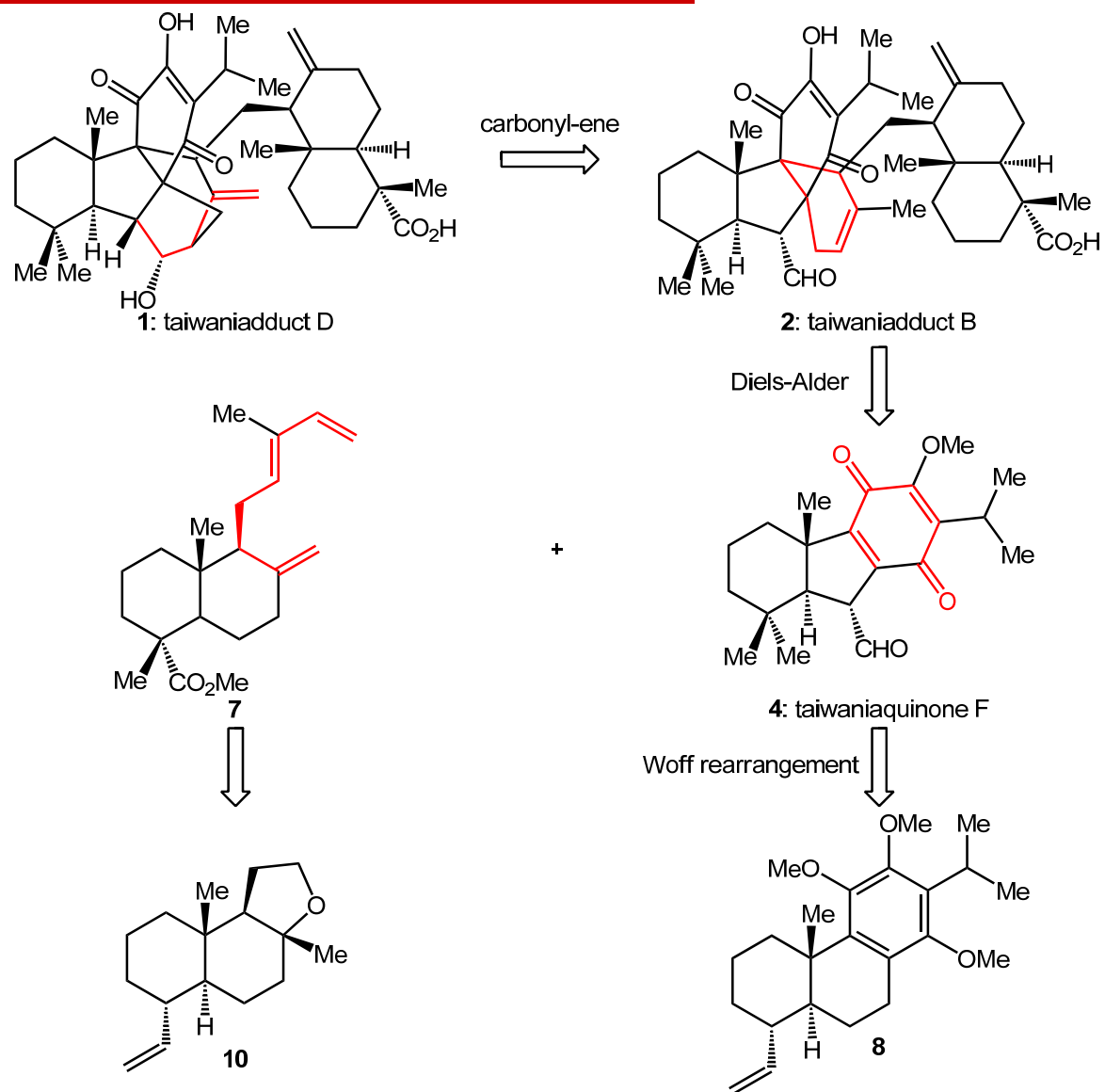


taiwaniadduct C

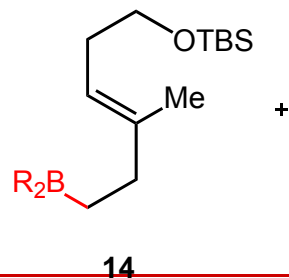
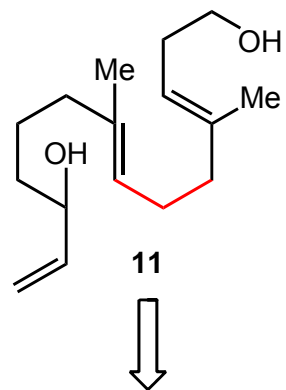
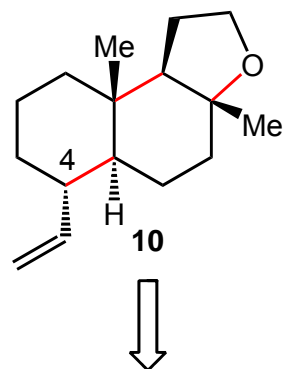


taiwaniadduct D

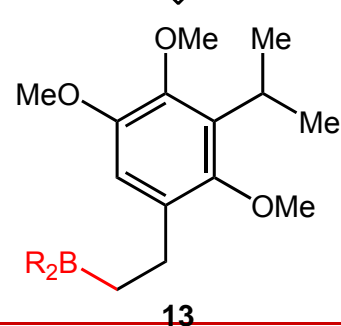
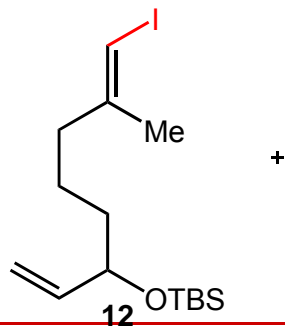
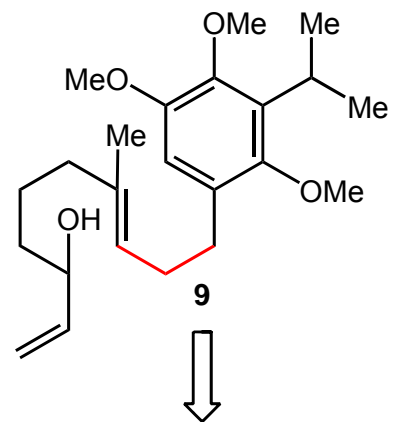
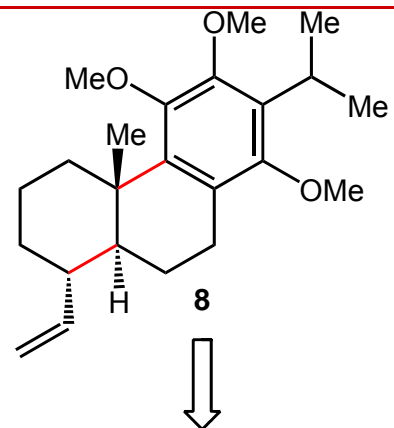
Retrosynthetic Analysis



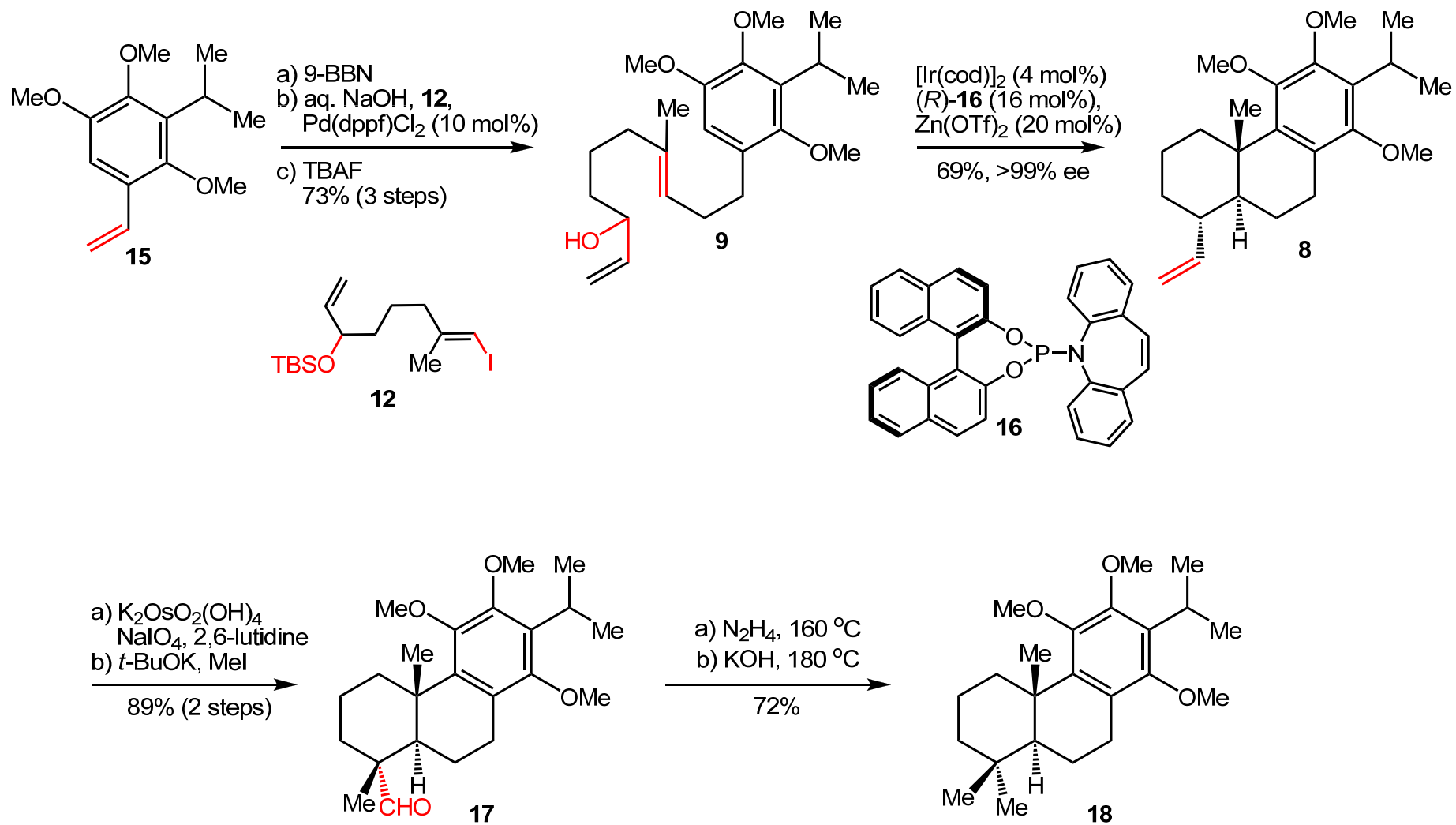
Retrosynthetic Analysis



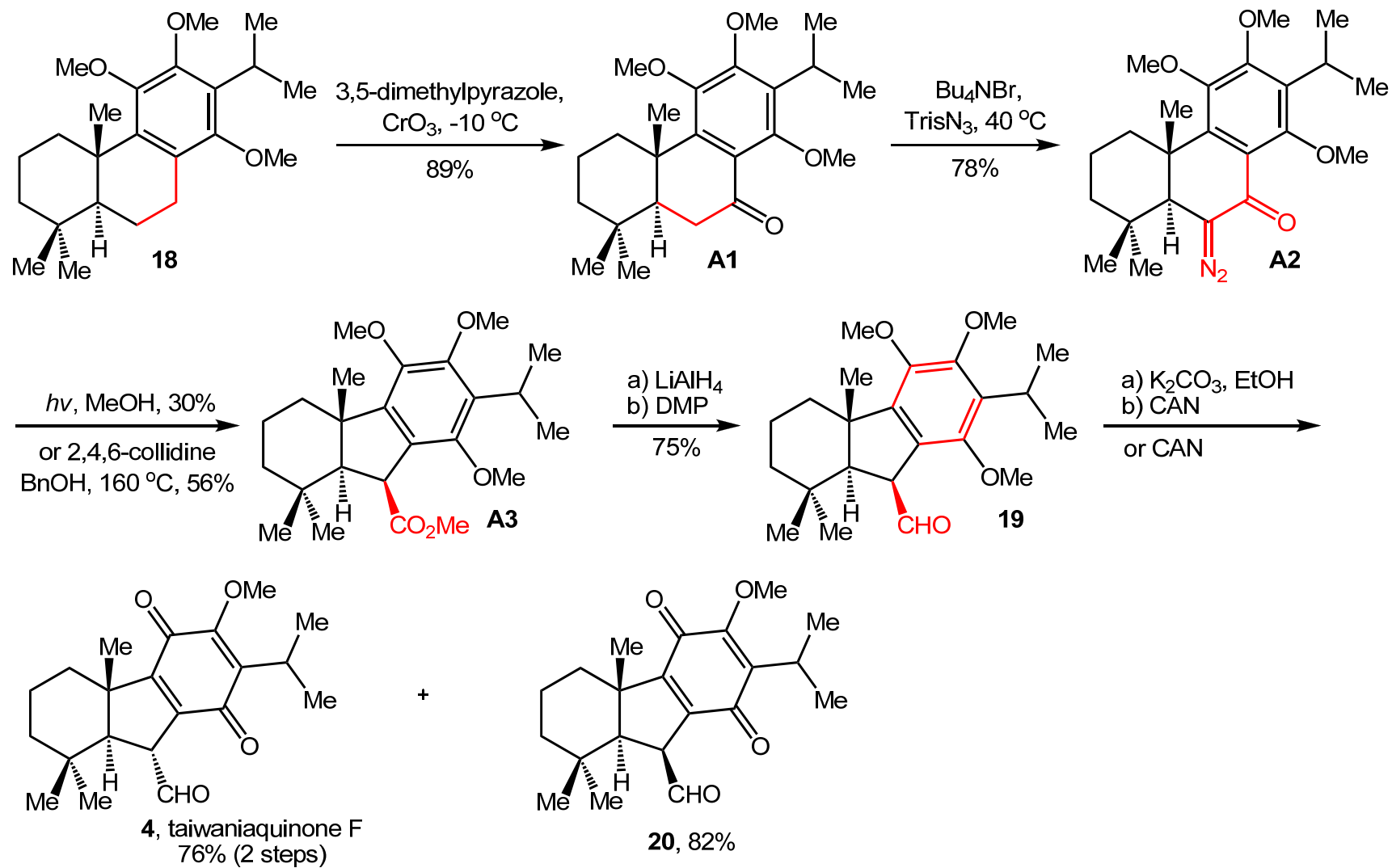
Ir-catalyzed asymmetric
polyene cyclization



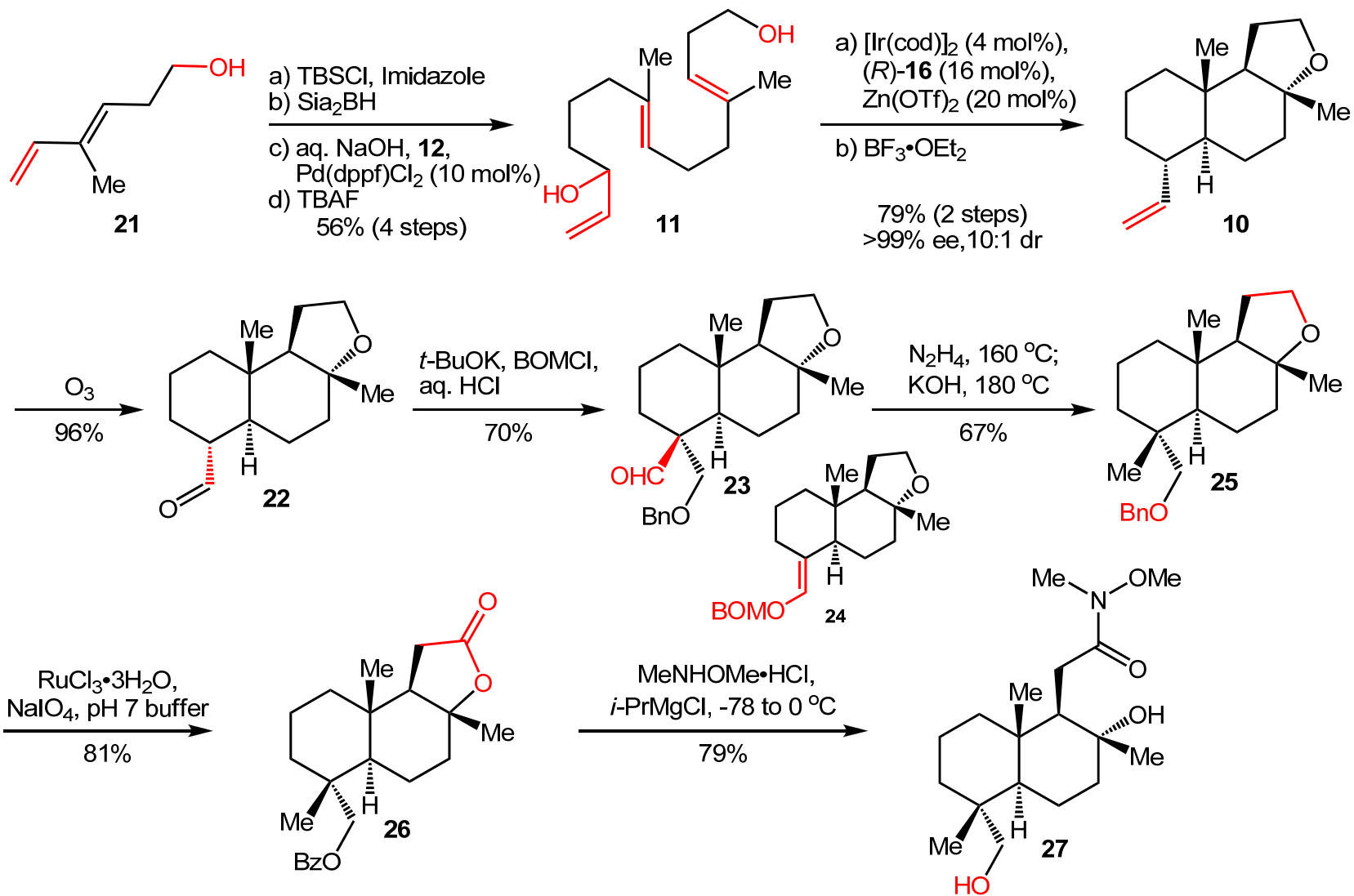
Synthesis of Dienophile



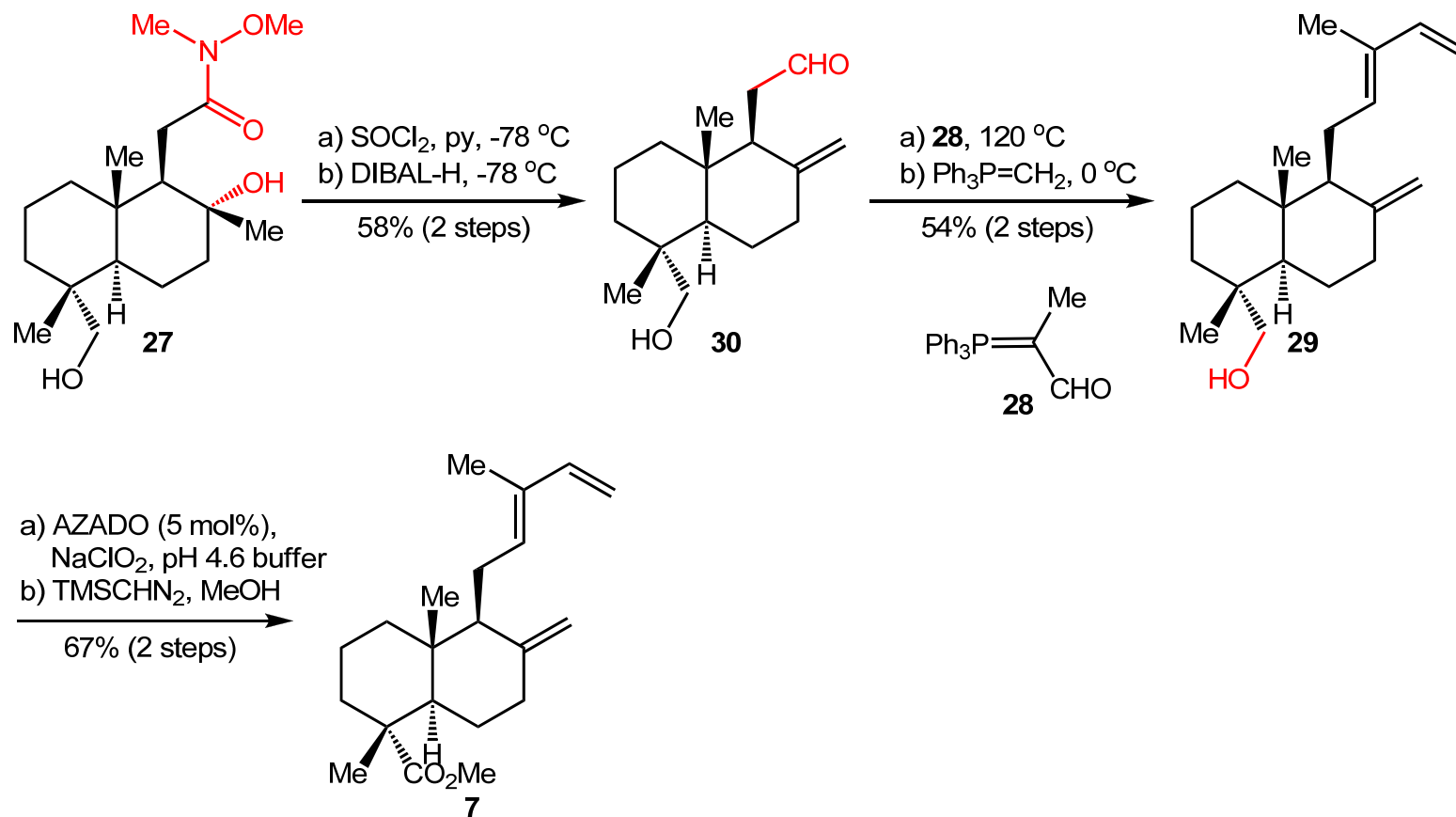
Synthesis of Dienophile



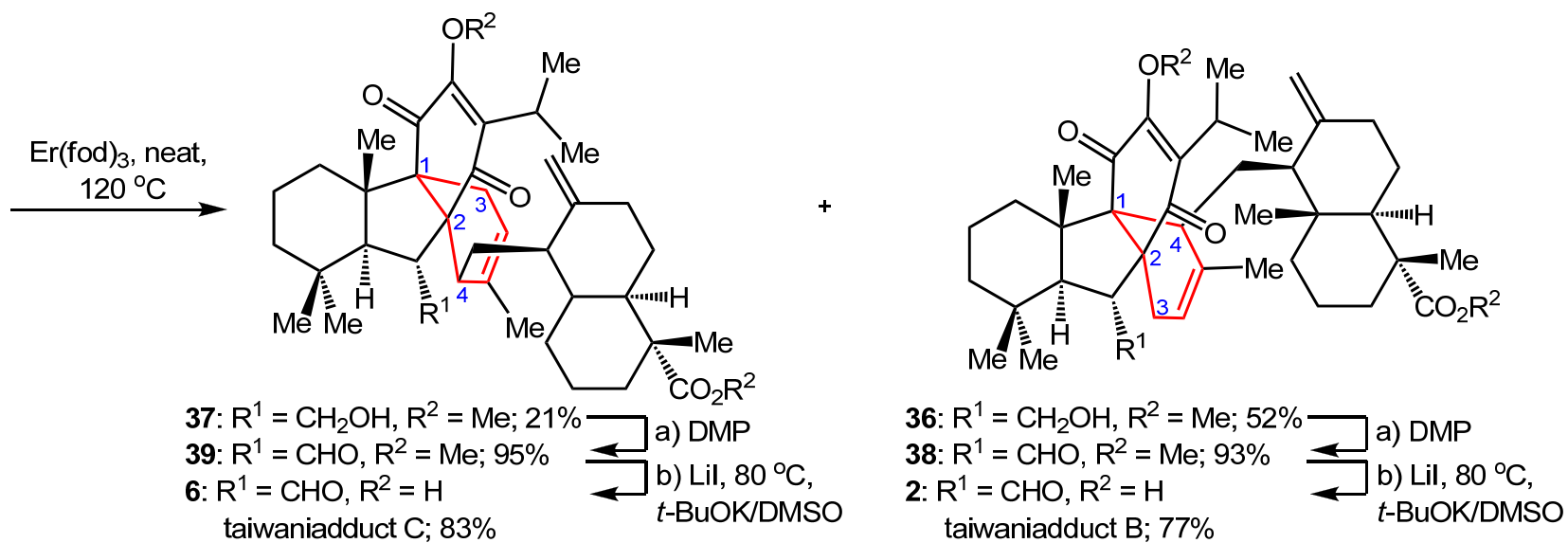
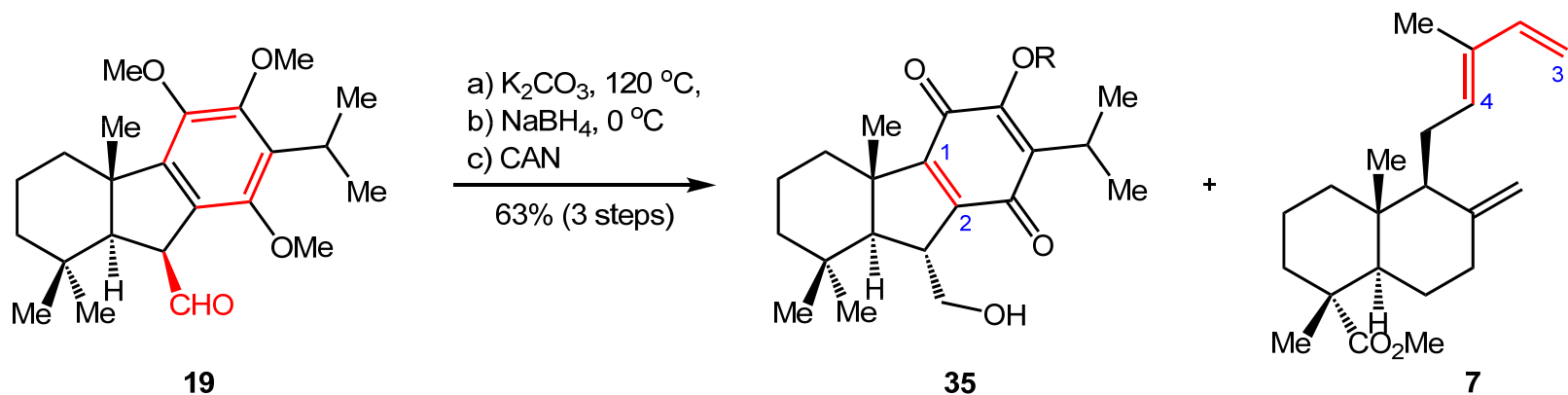
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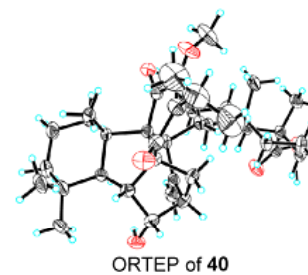
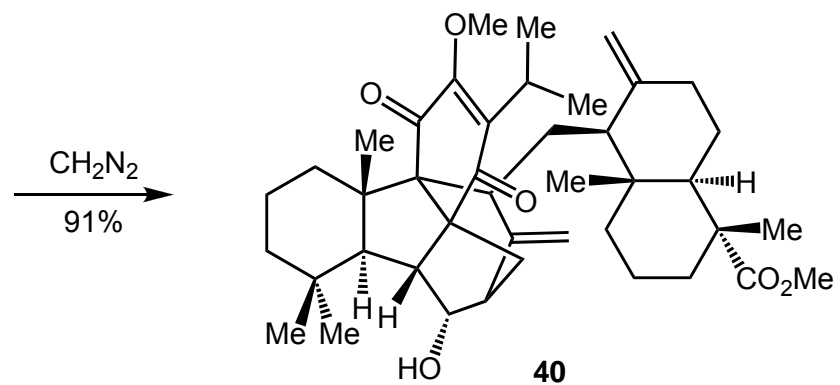
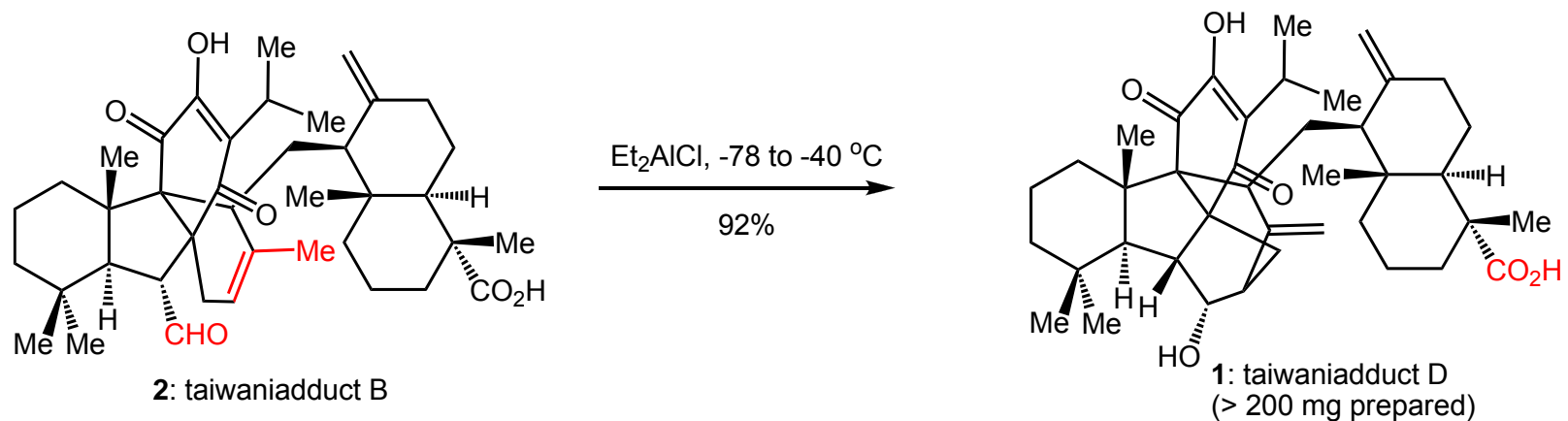
Synthesis of Diene



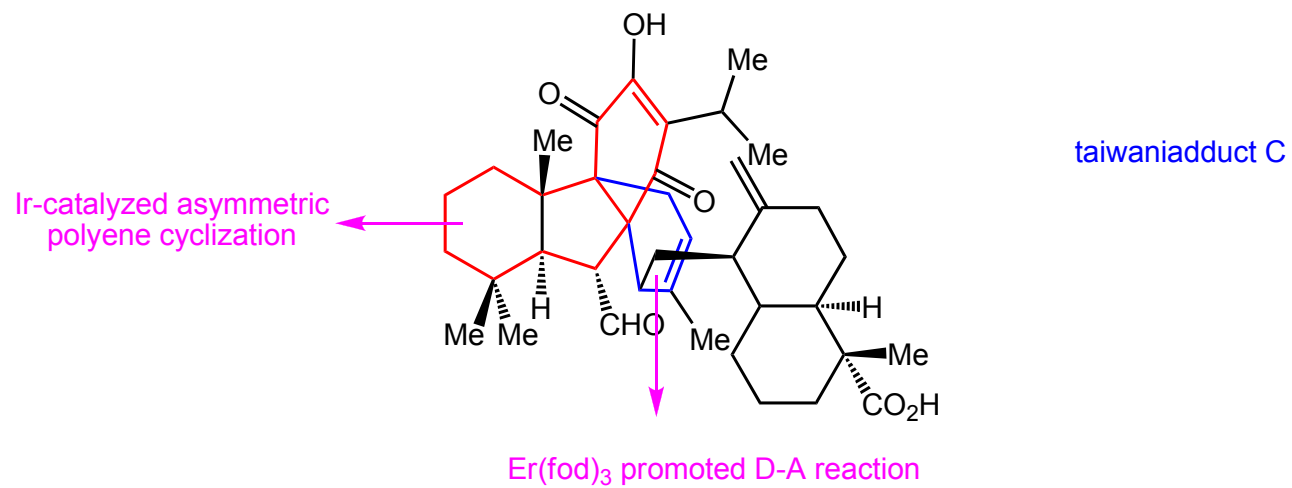
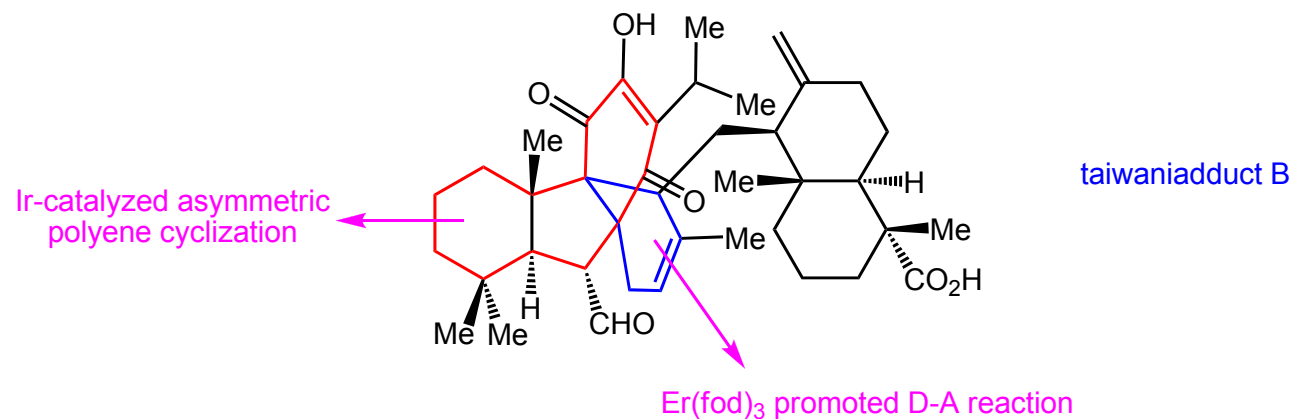
Total Synthesis of Taiwaniadducts



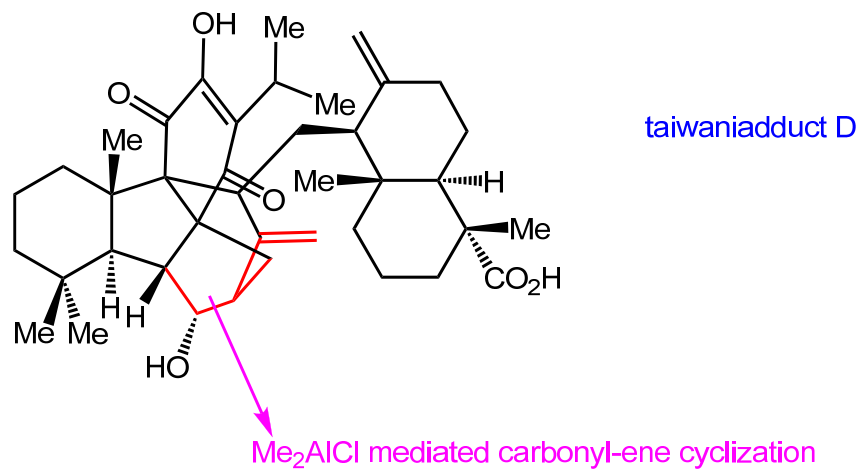
Total Synthesis of Taiwaniadducts



Summary



Summary



Taiwaniaquinoids are a class of terpenoids with impressive biological activities isolated from the endangered species *Taiwania cryptomerioides*, which have attracted remarkable attention from a synthetic perspective. A few members of this family, namely taiwaniadducts A–J, possess a characteristic Diels–Alder cycloadduct scaffold. From a biosynthetic perspective, taiwaniadduct D, the most complex molecule among them, could be derived from taiwaniadduct B through a carbonyl-ene cyclization, and taiwaniadduct B may arise from an intermolecular Diels–Alder reaction between naturally occurring taiwaniaquinone A or F and trans-ozic acid. Taiwaniadduct C is presumably the regioisomer of taiwaniaquinone A from the Diels–Alder reaction. Herein, we report the total synthesis of taiwaniadducts B, C, and D based on the above biosynthetic hypothesis.

In summary, we have accomplished the first total synthesis of taiwaniadducts B, C, and D. Ir-catalyzed asymmetric polyene cyclization was exploited to construct the scaffolds of both the diene and dienophile. Er(fod)₃ promoted intermolecular Diels–Alder and Me₂AlCl mediated carbonyl-ene reactions forged the core of **1**. The chemistry may find further applications in terpenoid synthesis.