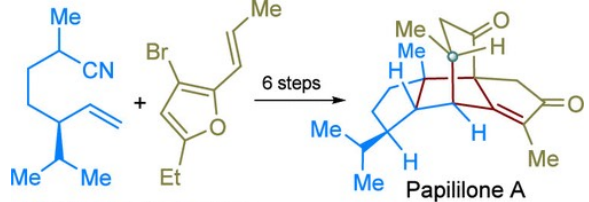


Convergent Total Synthesis of Papillone A via Pd-Catalyzed Alkenylation/
Cyclization Cascade

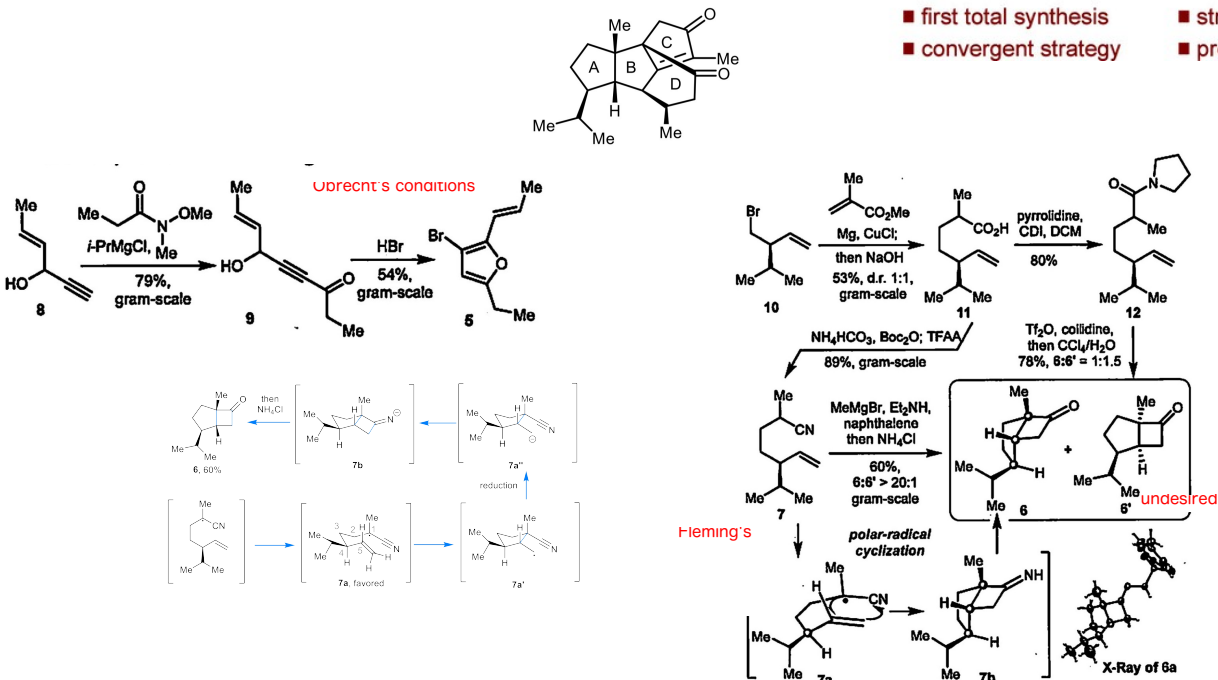
Xing-Qian Shan, Xiang Zhang, Peng-Fei Lian, Bao-Kuan Guo, Yong-Qiang Tu, and



the first total synthesis in a nine step LLS without the use of a protecting group

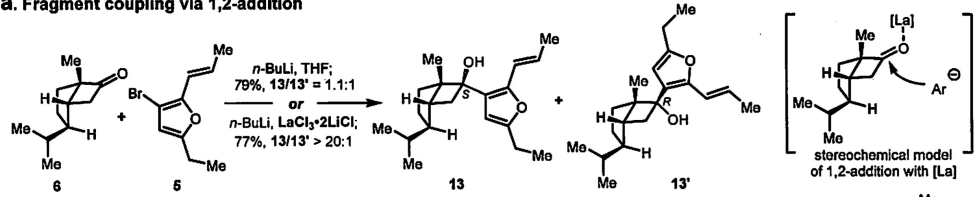
Highlights of this work:

- first total synthesis
- structural revision
- convergent strategy
- protecting group free

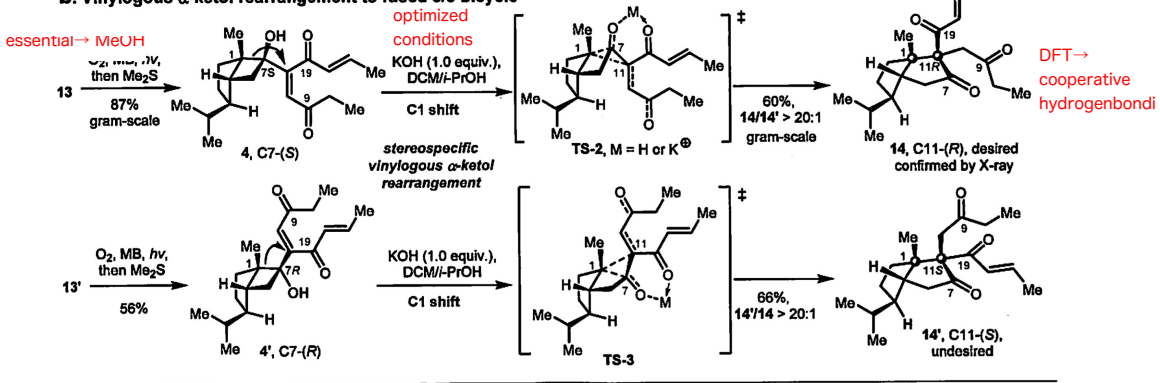


Scheme 2. Convergent Approach to Bicyclic Framework

a. Fragment coupling via 1,2-addition



b. Vinylogous α -ketol rearrangement to fused 5/5 bicycle



Scheme 3. Total Synthesis of Papillone A

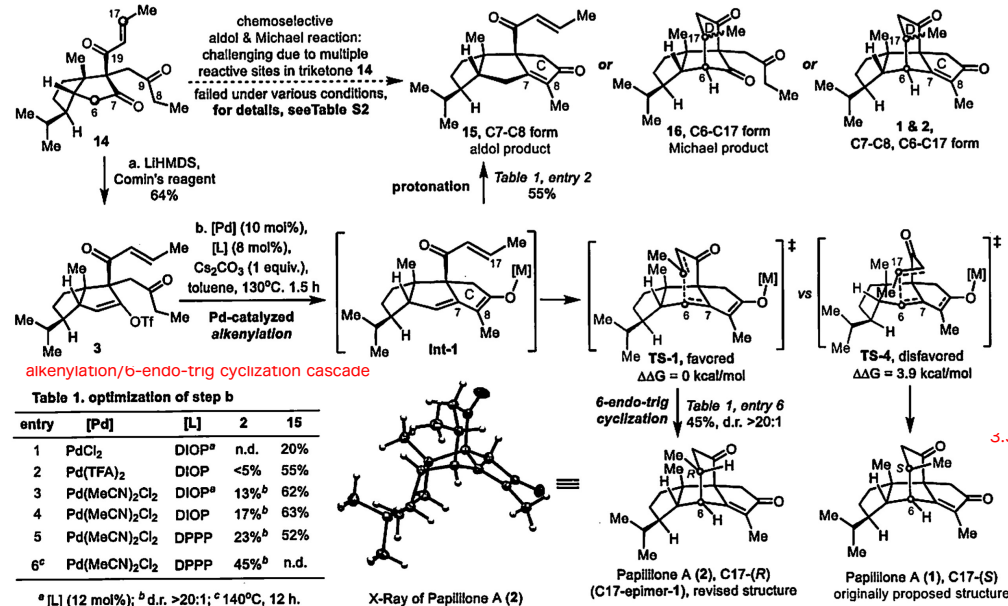


Table 1. optimization of step b

entry	[Pd]	[L]	2	15
1	PdCl ₂	DIOP ^a	n.d.	20%
2	Pd(TFA) ₂	DIOP	<5%	55%
3	Pd(MeCN) ₂ Cl ₂	DIOP ^a	13% ^b	62%
4	Pd(MeCN) ₂ Cl ₂	DIOP	17% ^b	63%
5	Pd(MeCN) ₂ Cl ₂	DPPP	23% ^b	52%
6 ^c	Pd(MeCN) ₂ Cl ₂	DPPP	45% ^b	n.d.

^a [L] (12 mol%); ^b d.r. >20:1; ^c 140°C, 12 h.

X-Ray of Papillone A (2)

Papillone A (2), C17-(R) (C17-epimer-1), revised structure

Papillone A (1), C17-(S) originally proposed structure

3.3% overall yield