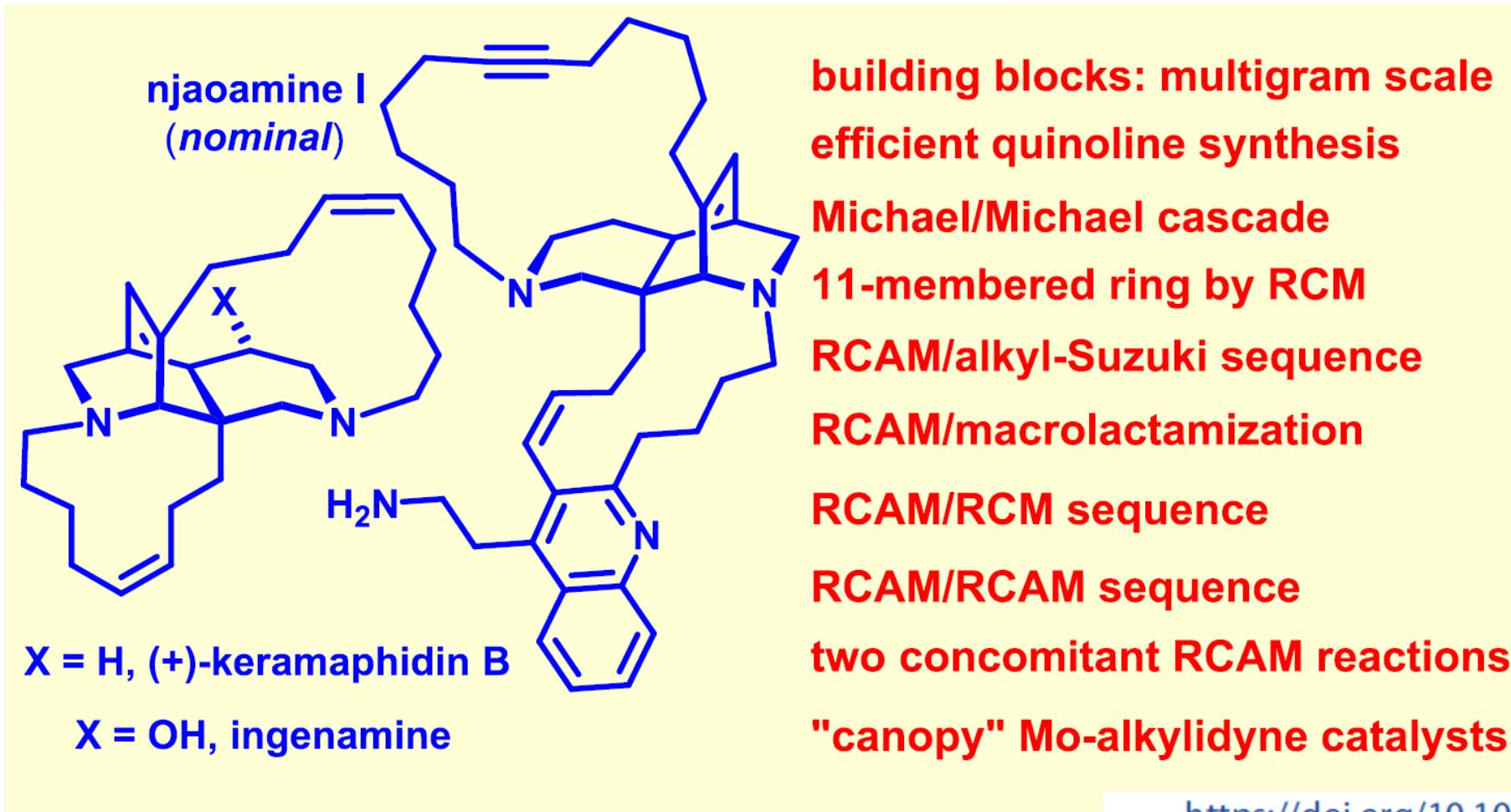
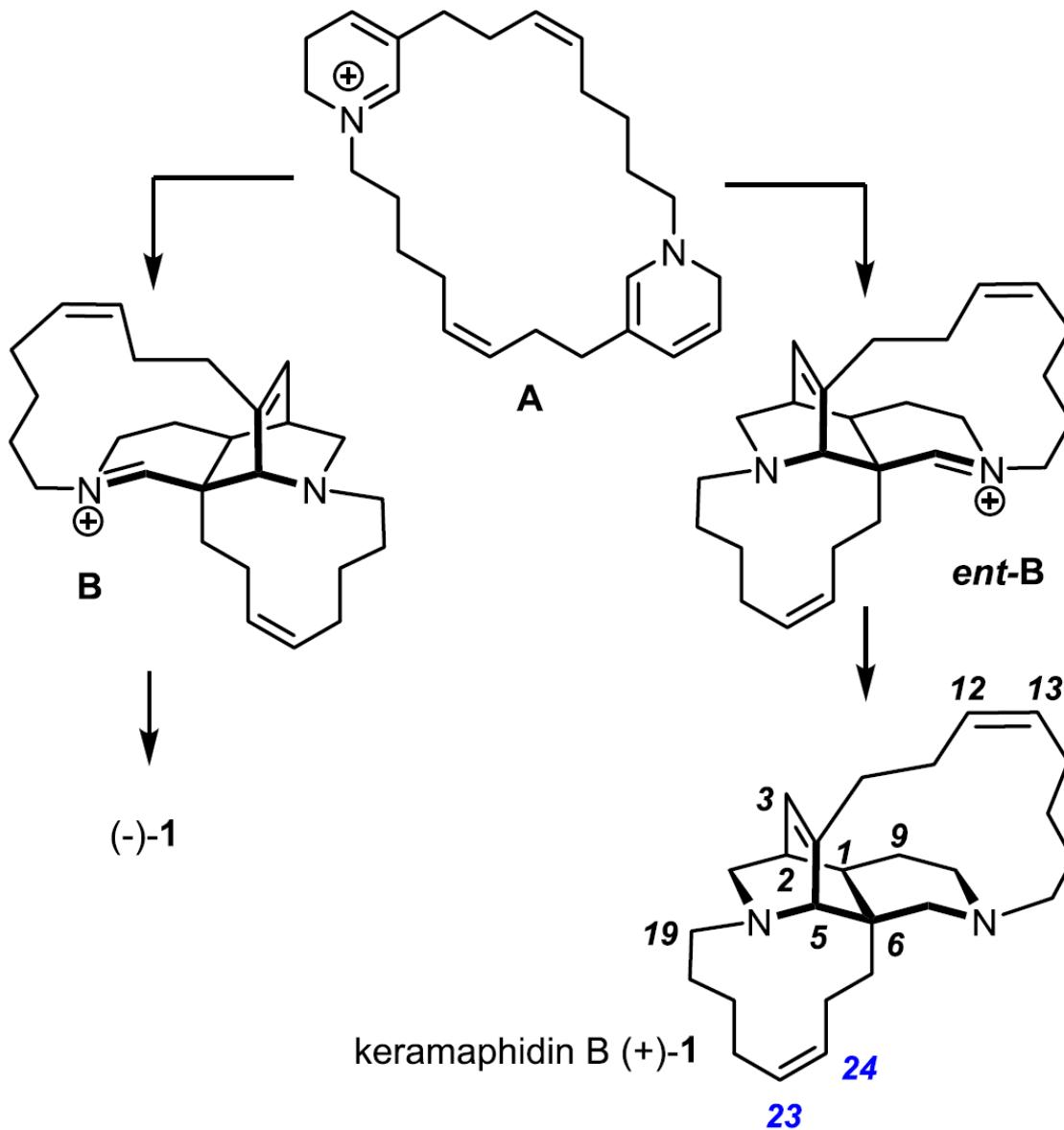


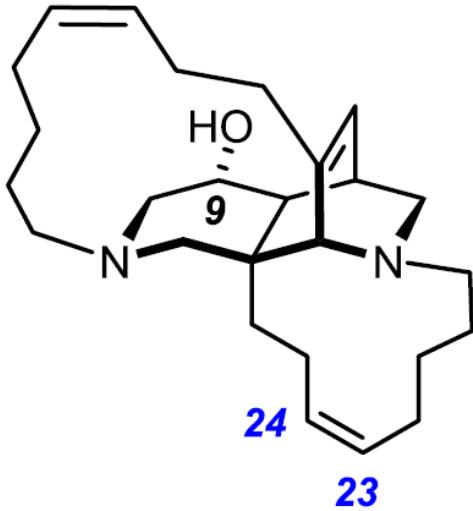
# A Unified Approach to Polycyclic Alkaloids of the Ingenamine Estate: Total Syntheses of Keramaphidin B, Ingenamine, and Nominal Njaoamine I

Zhanchao Meng,<sup>†</sup> Simon M. Spohr,<sup>†</sup> Sandra Tobegen, Christophe Farès, and Alois Fürstner\*

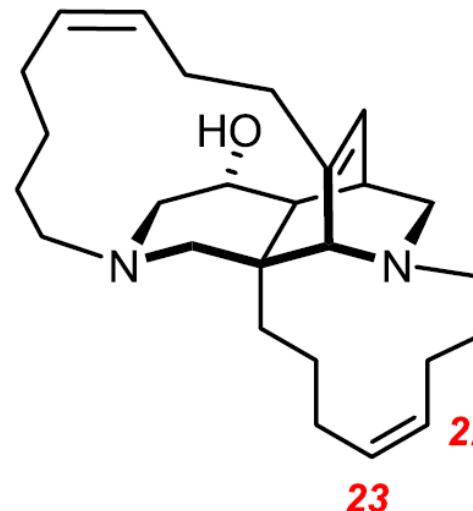


**Scheme 1. Key Step of the Proposed Biosynthesis of Keramaphidin B; Representative Alkaloids Thought To Originate from Similar Pathways**

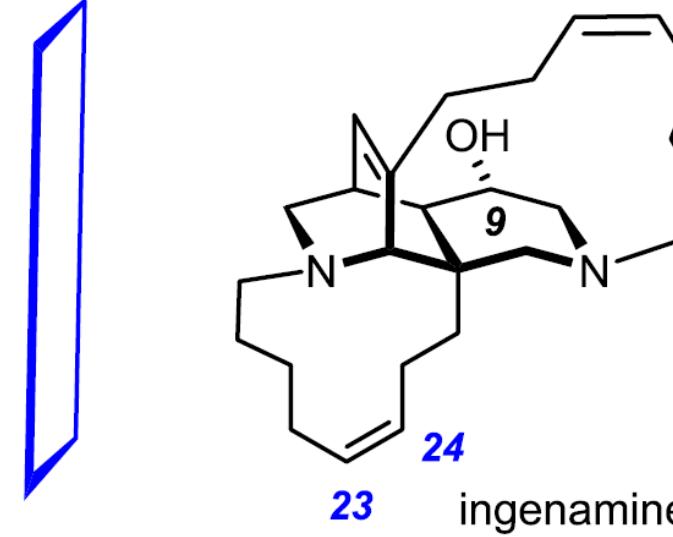




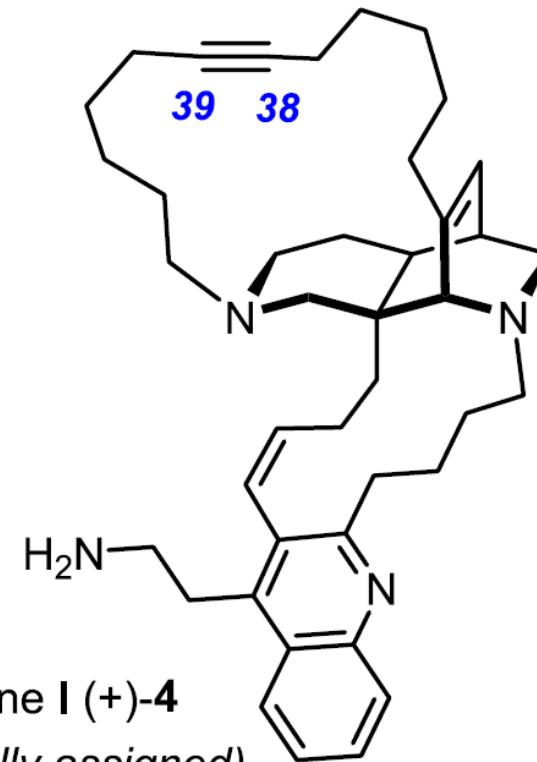
xestocyclamine A (-)-2  
*(revised structure)*



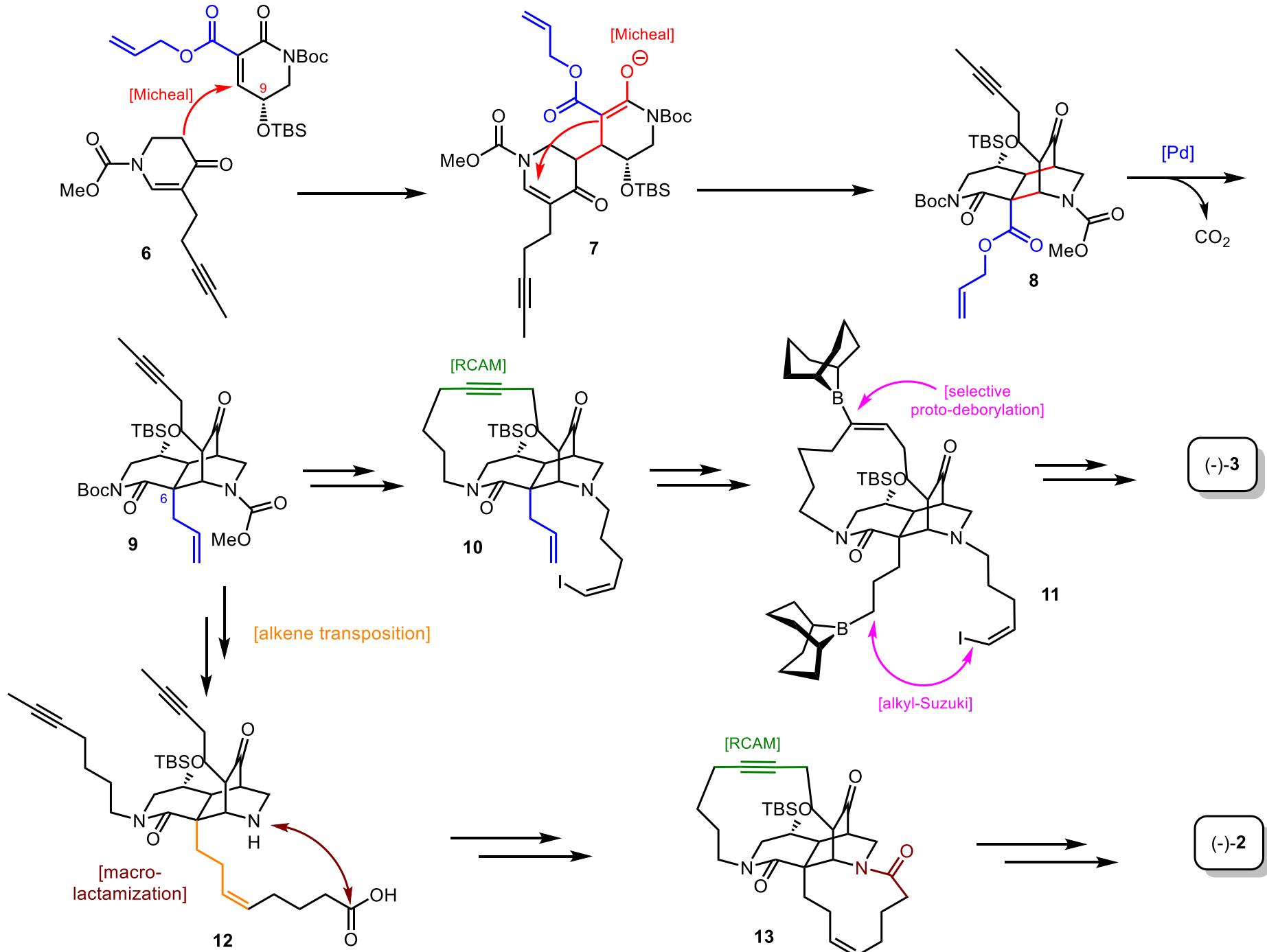
nominal xestocyclamine A (-)-3  
*(as originally assigned)*

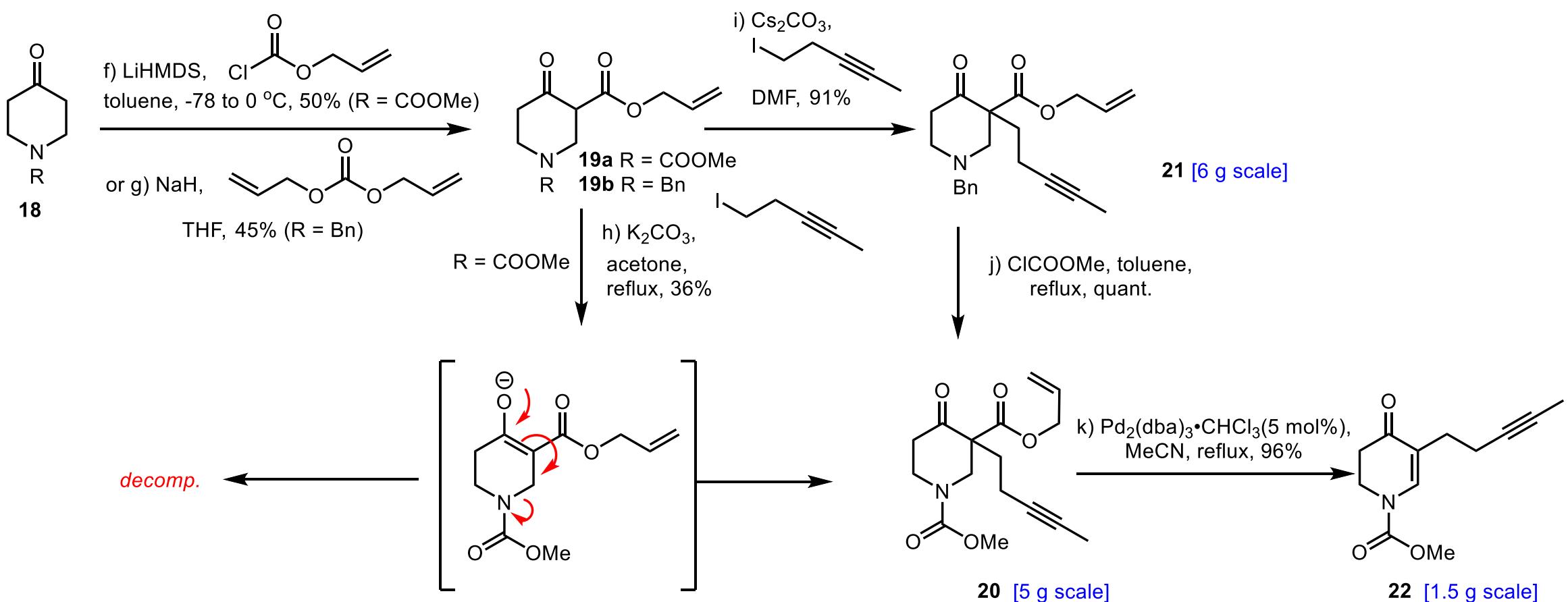
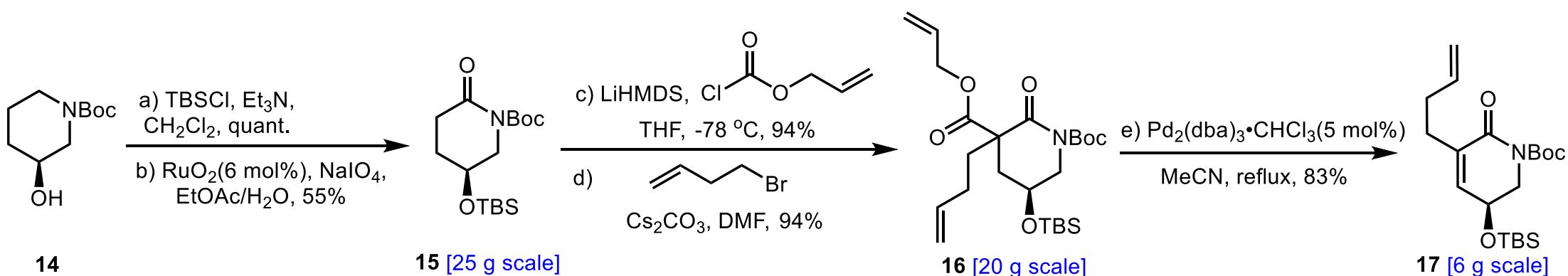


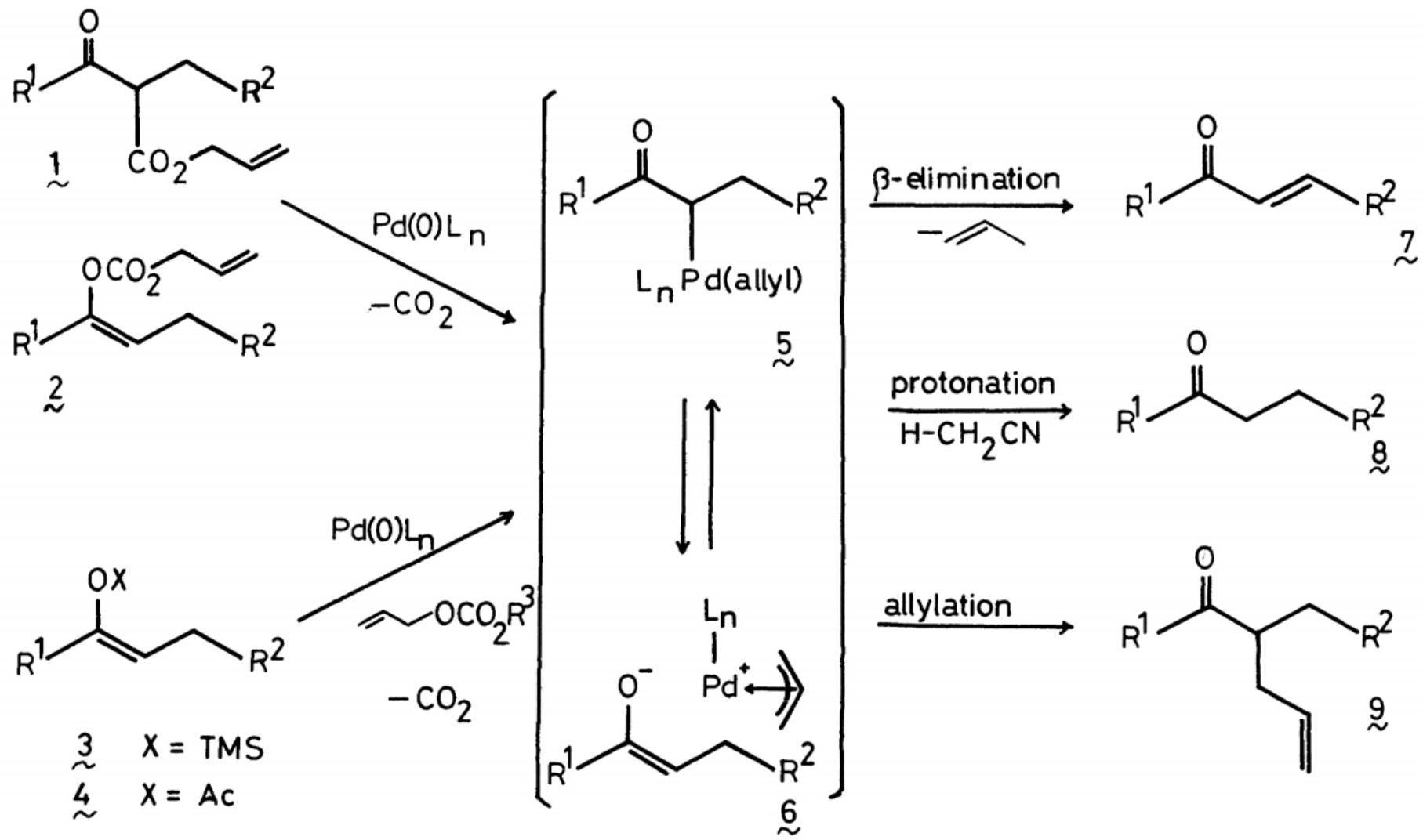
ingenamine (+)-2

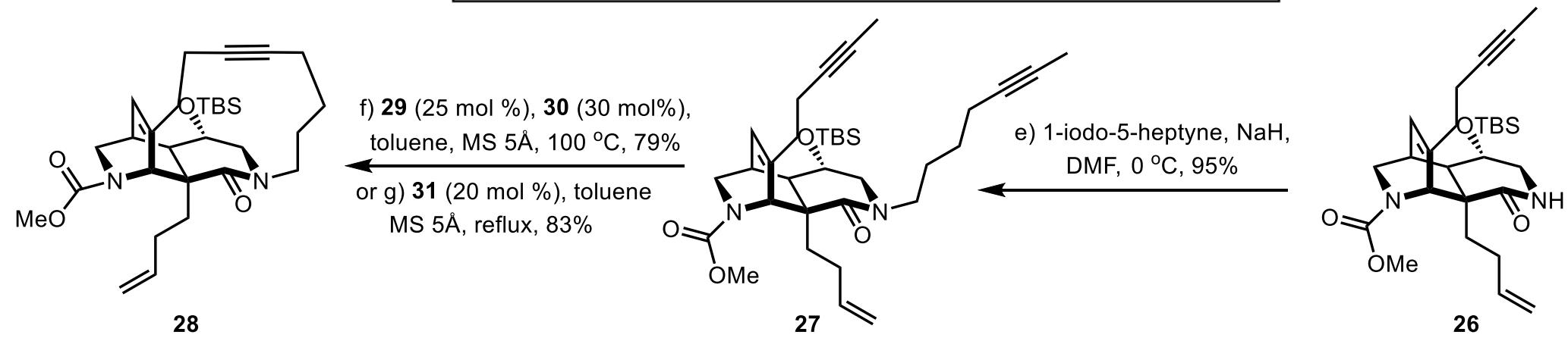
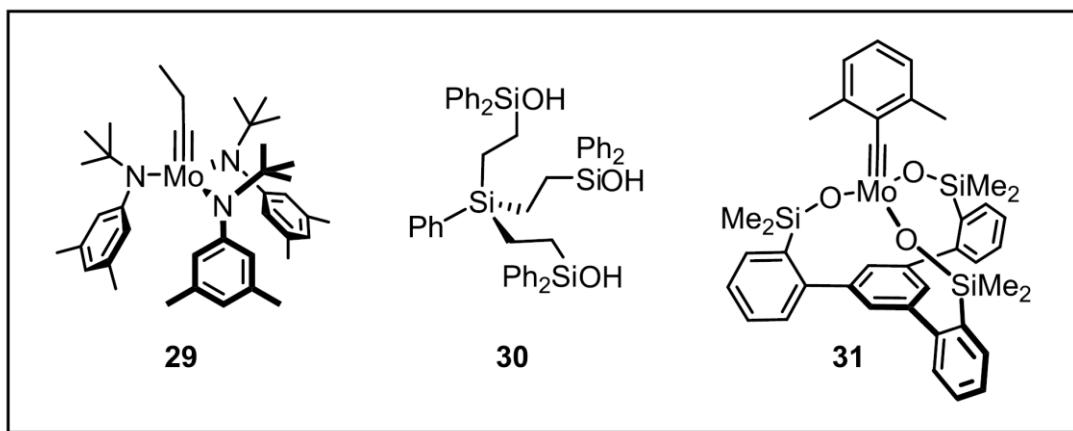
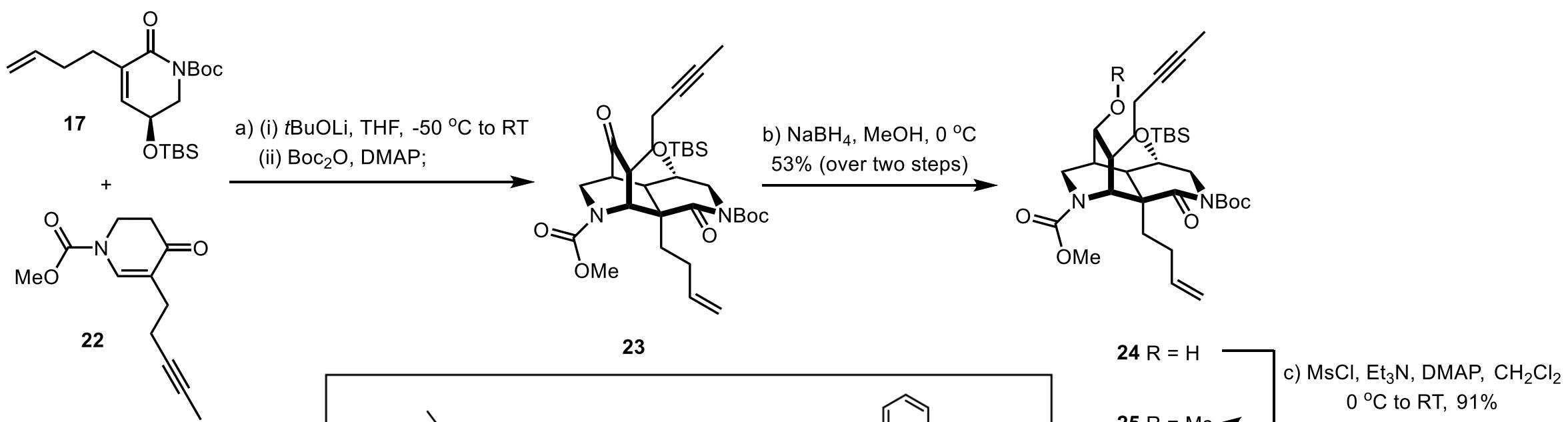


njaoamine I (+)-4  
*(as originally assigned)*



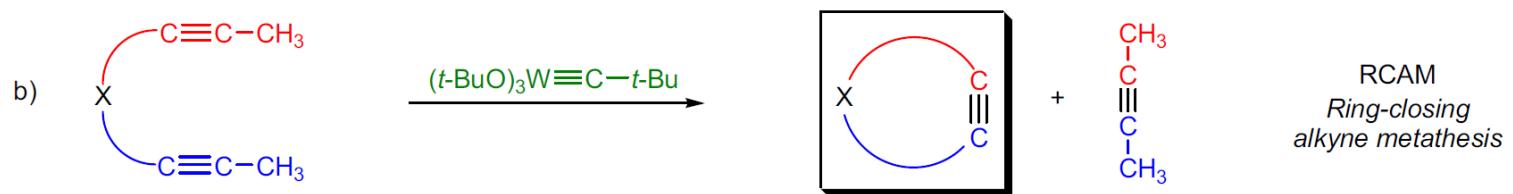
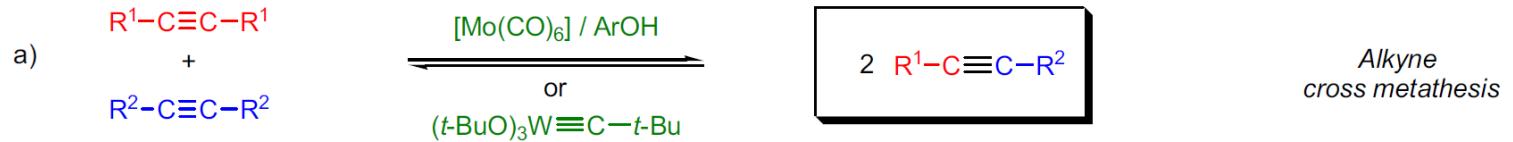




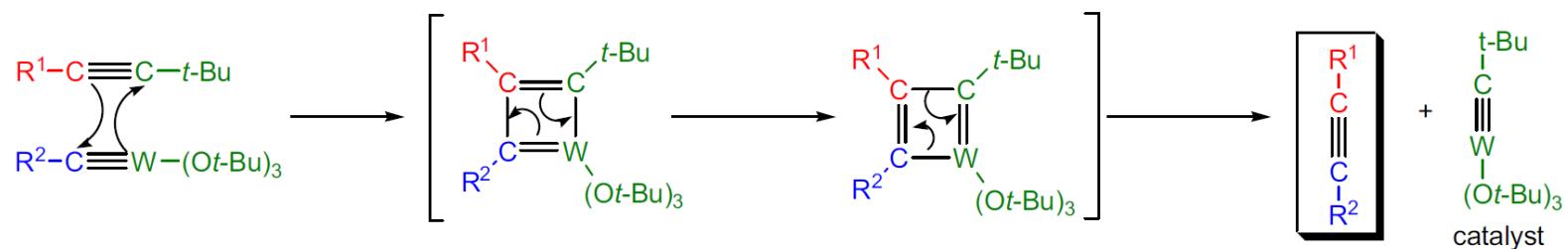
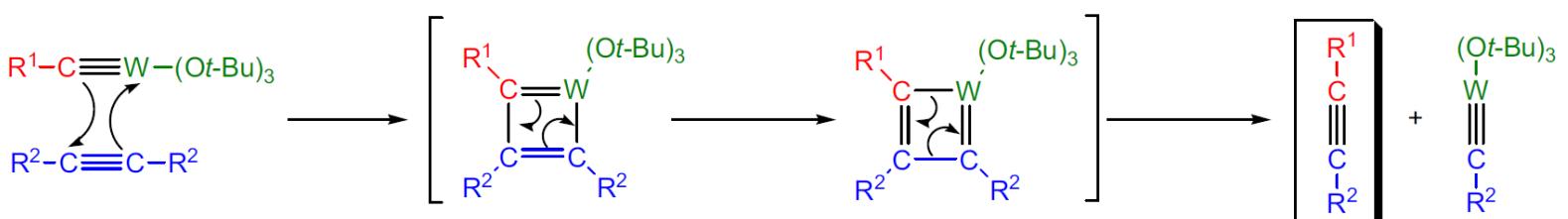
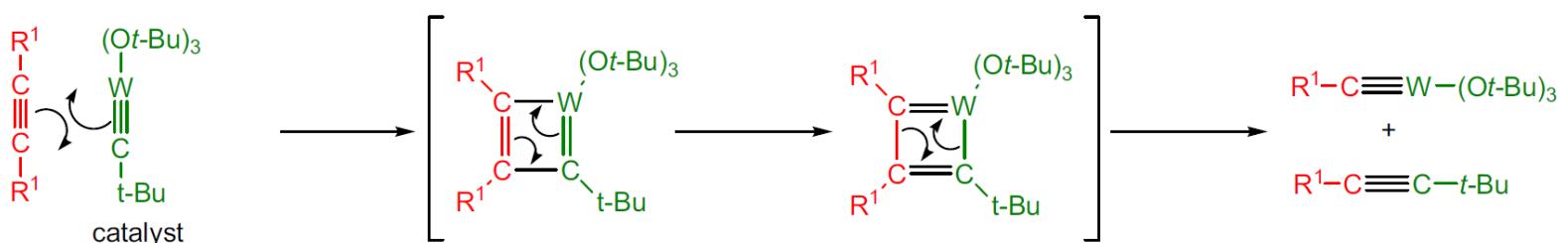


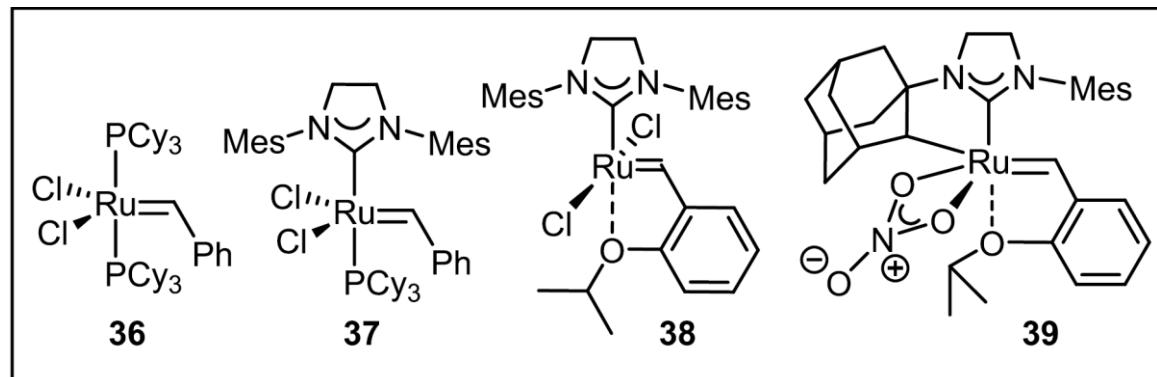
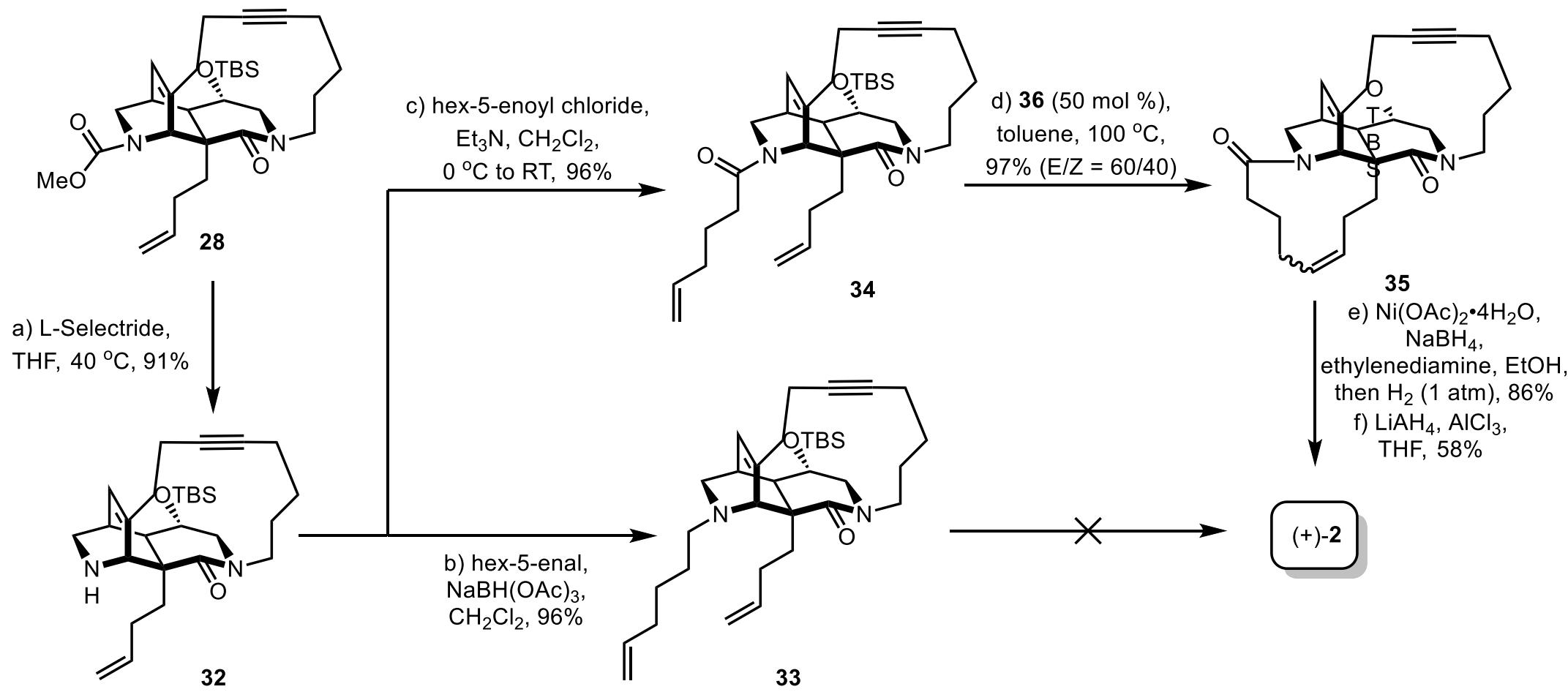
# ALKYNE METATHESIS

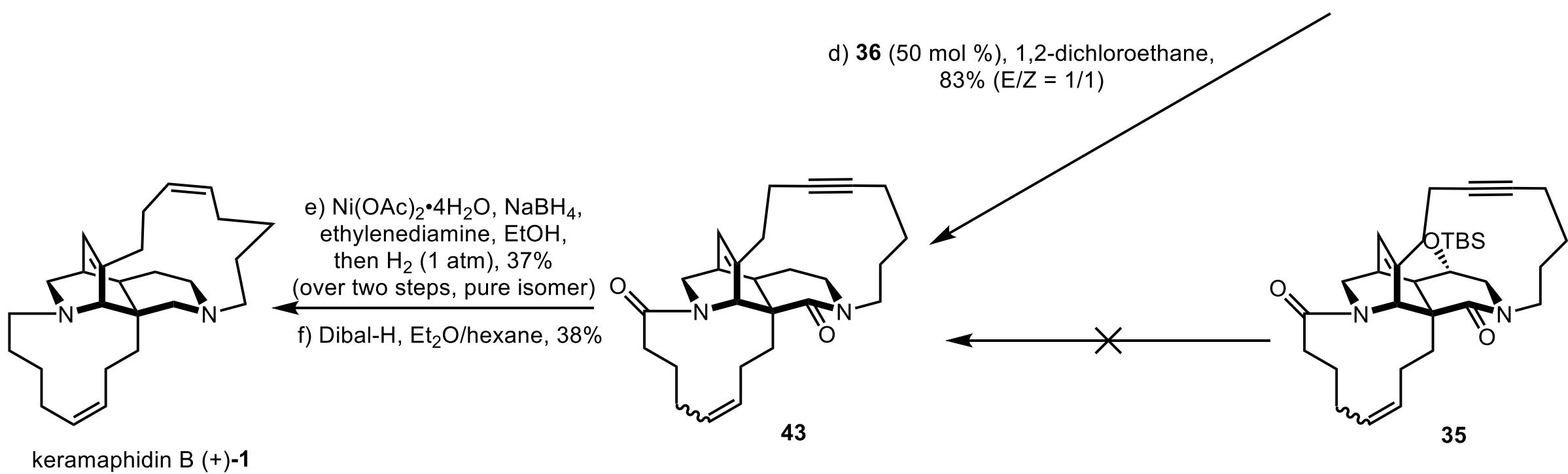
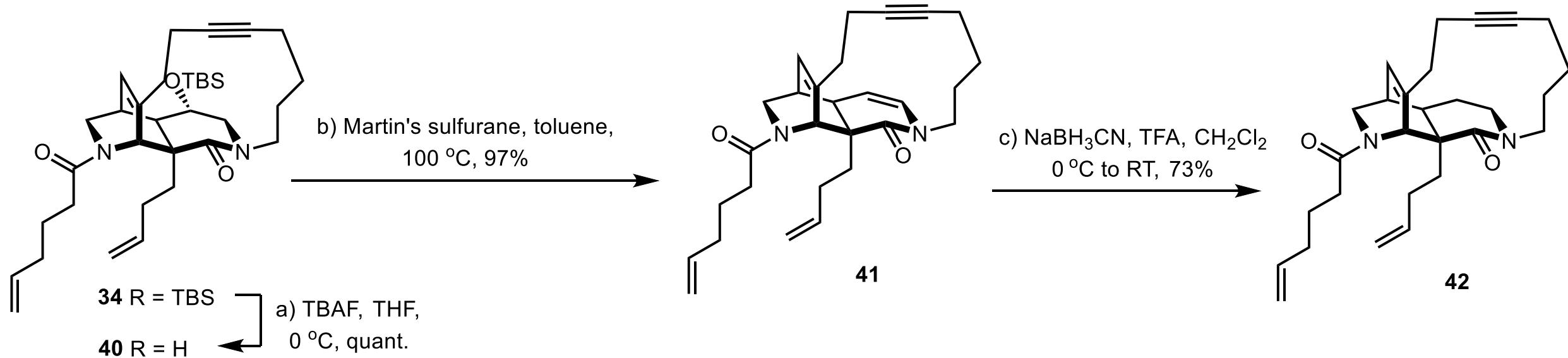
(References are on page 536)



Mechanism:







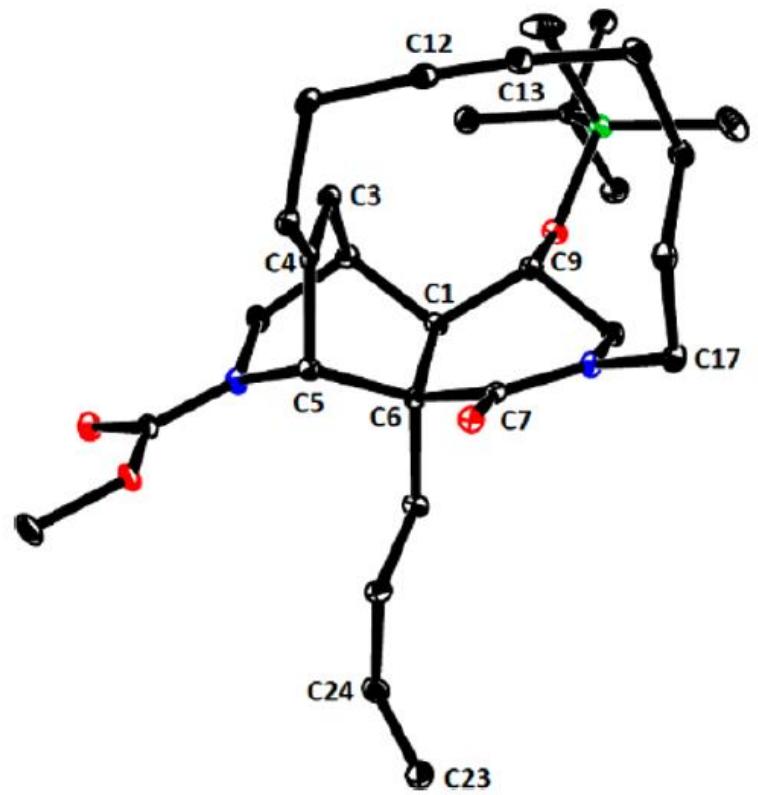


Figure 1. Structure of cycloalkyne **28** in the solid state.

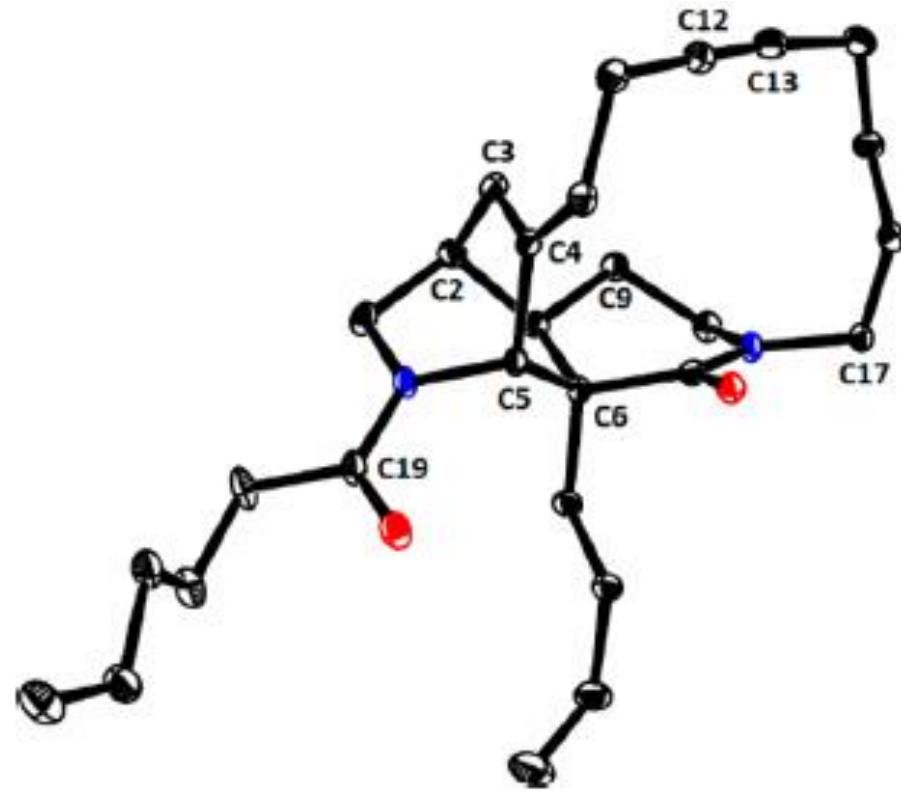
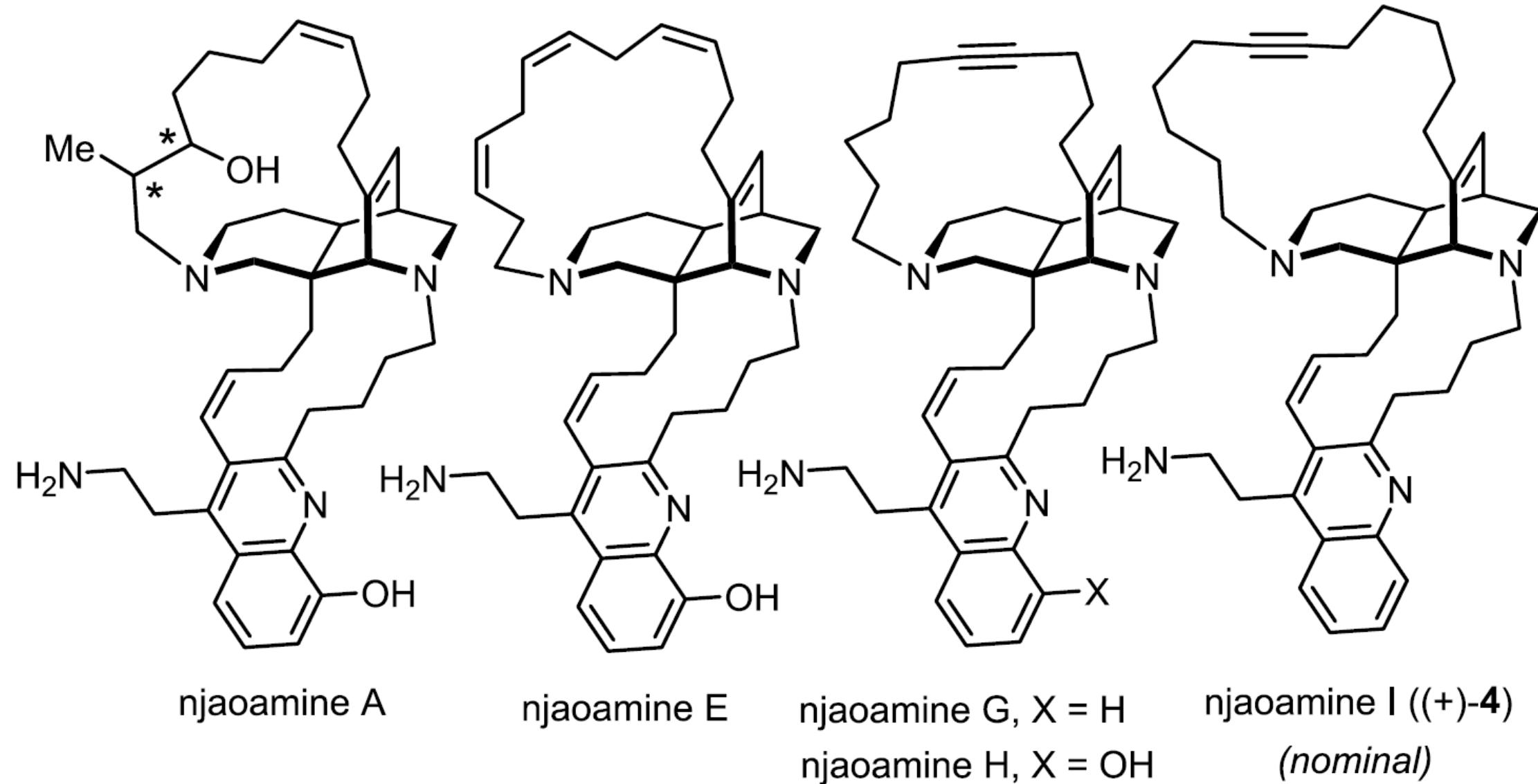
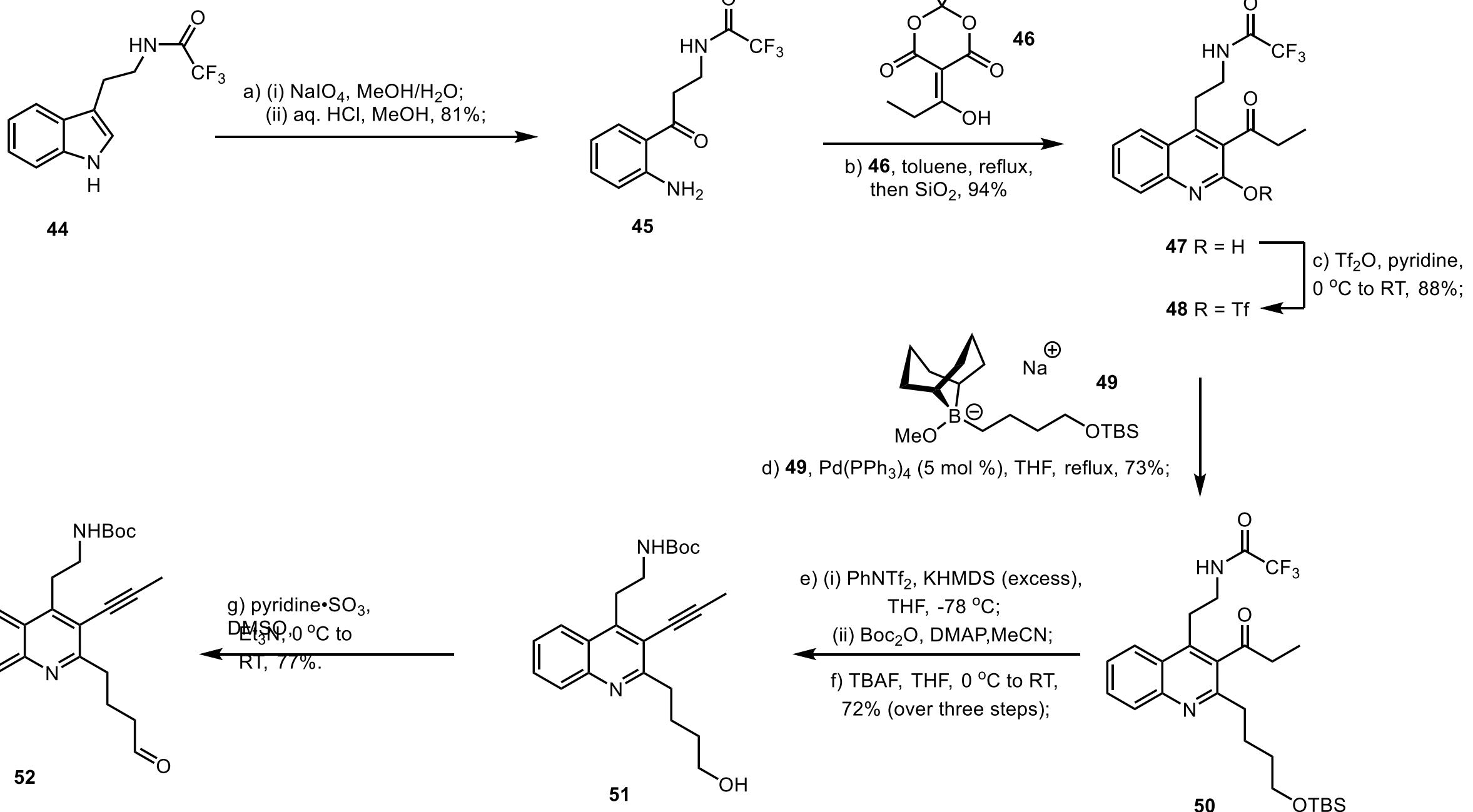
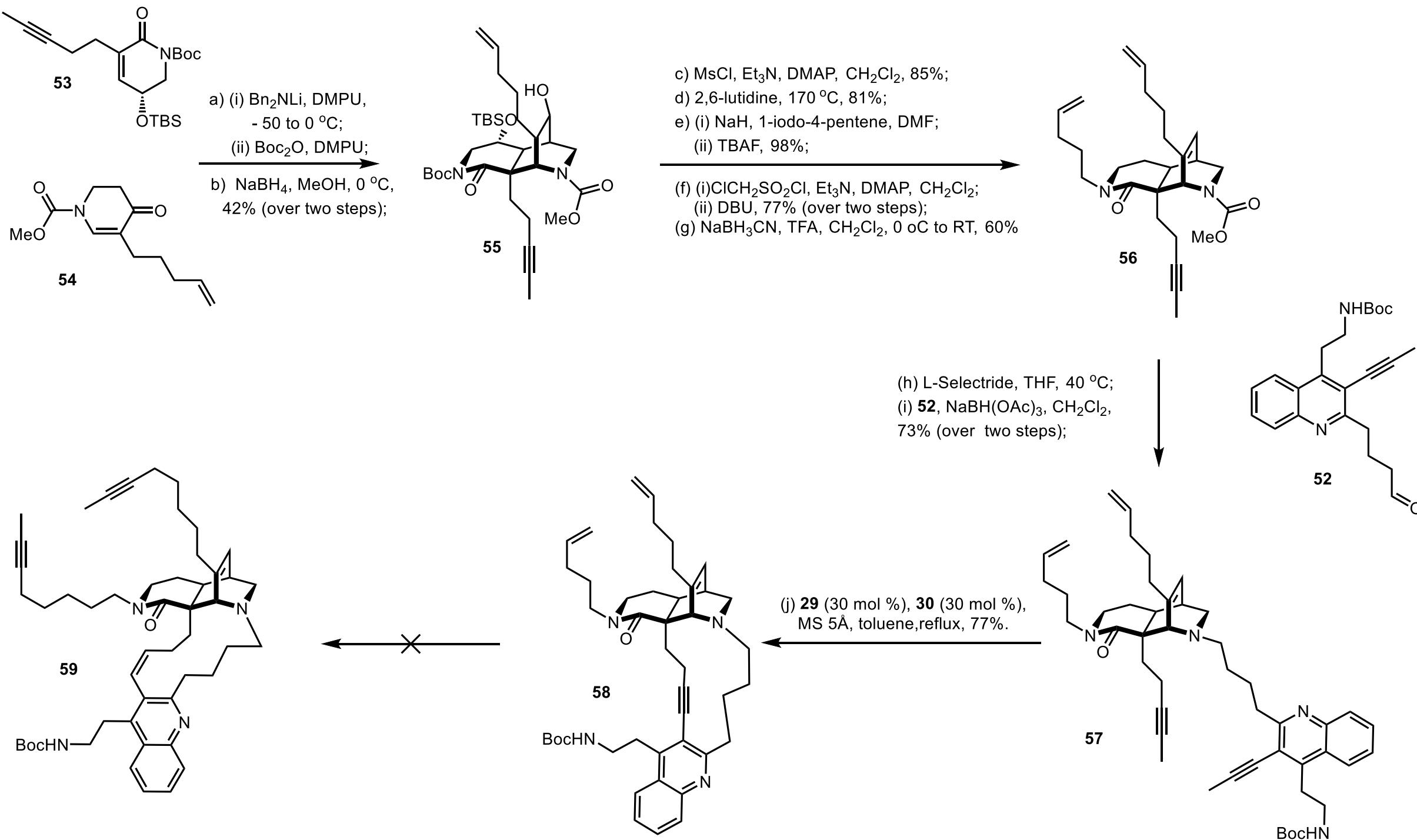


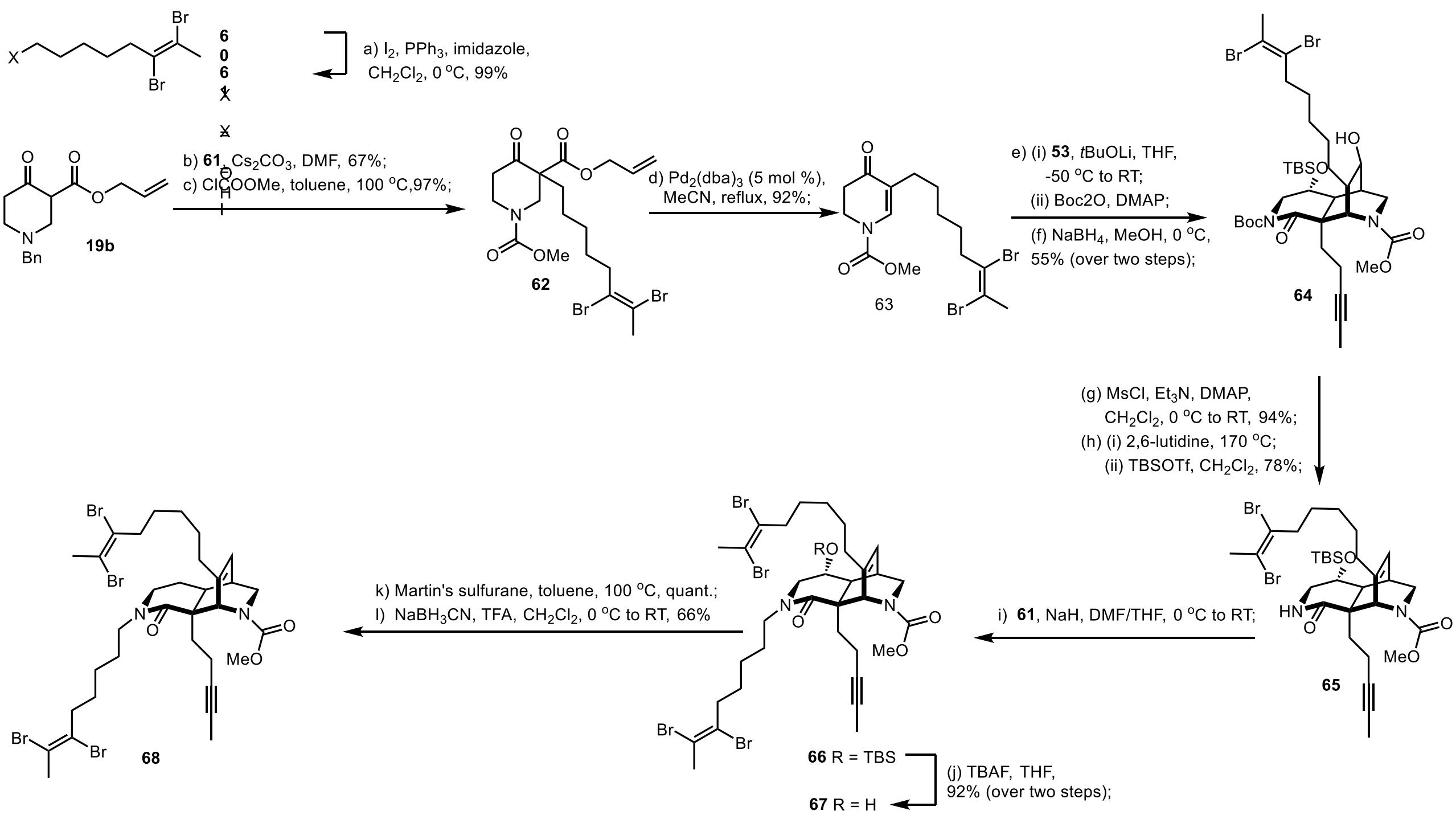
Figure 2. Structure of compound **42** in the solid state.

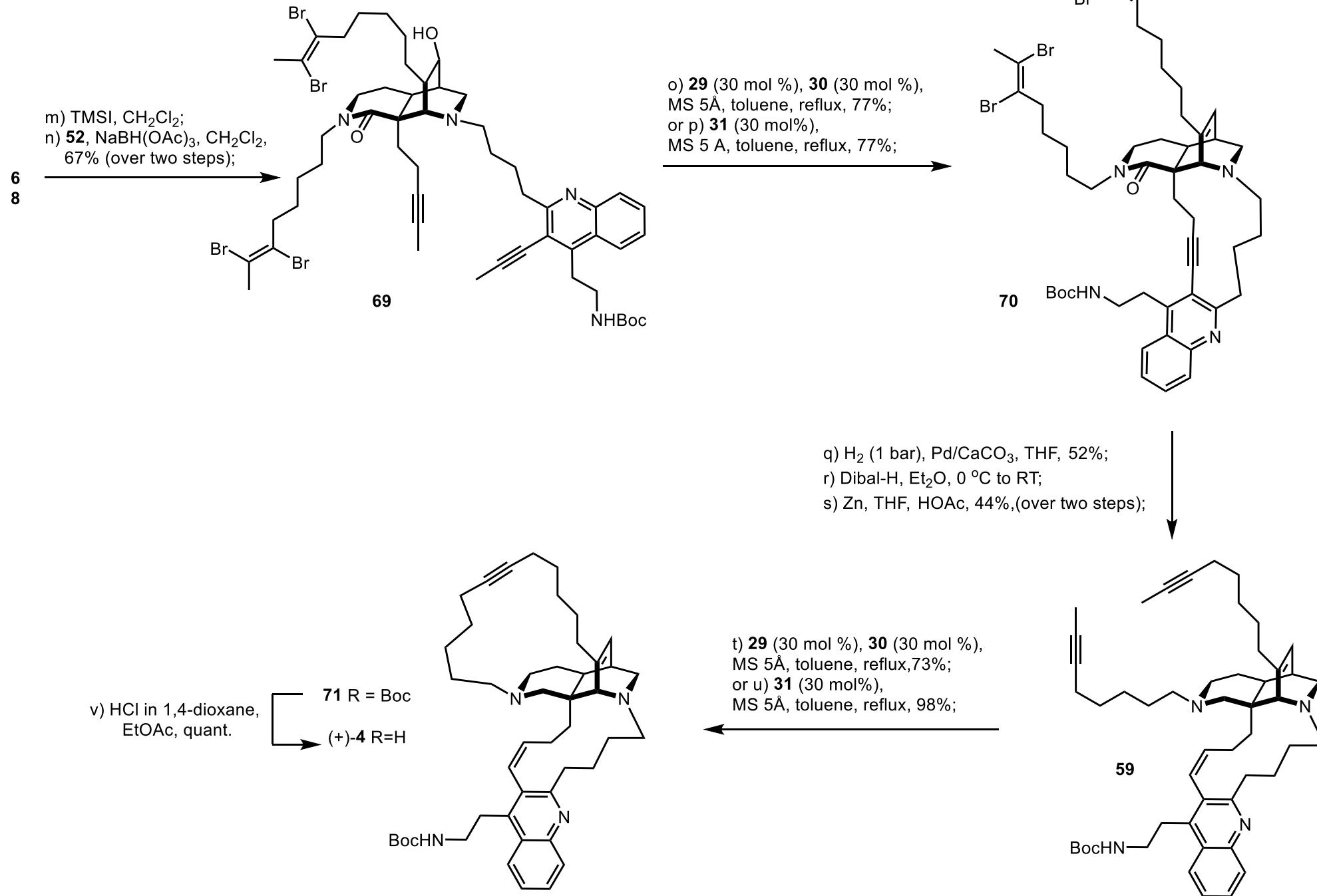


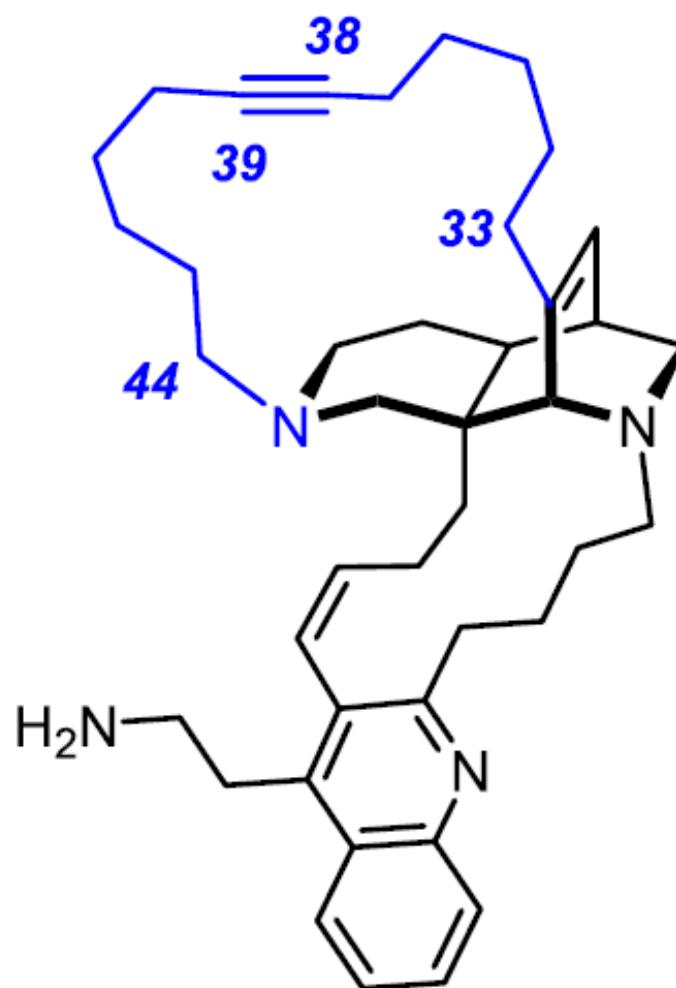
**Figure 3.** Representative members of the njaoamine family (\* stereocenters of unknown configuration).



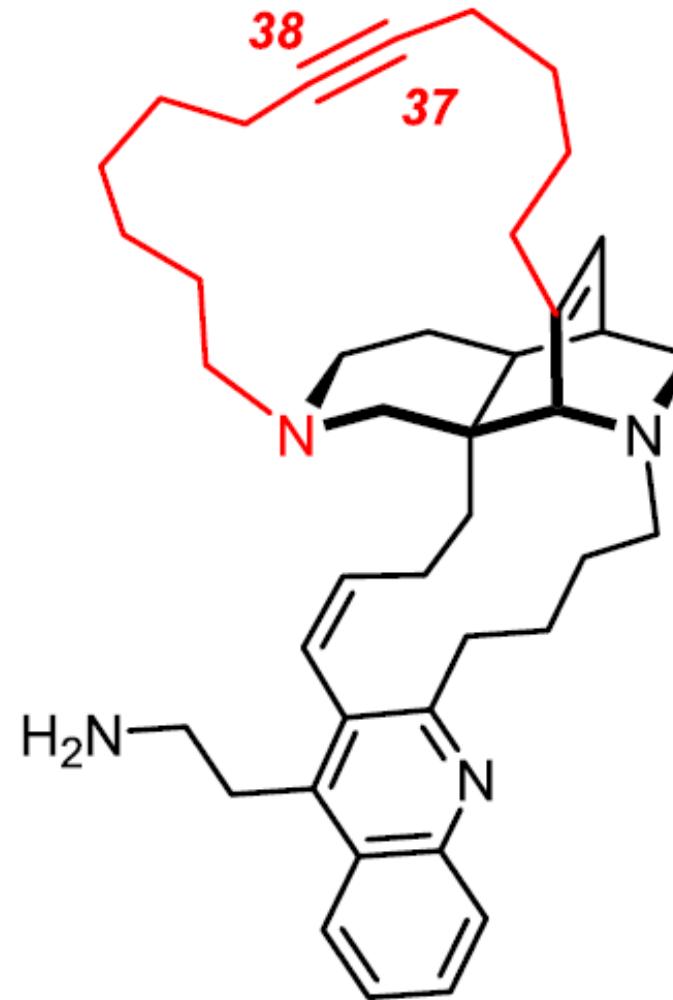






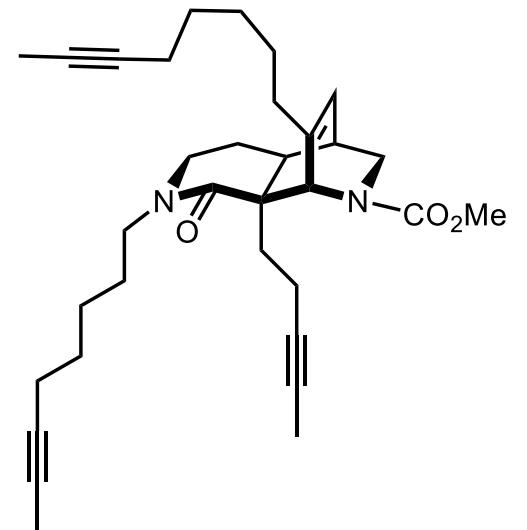


njaoamine I ((+)-4)  
*(original assignment)*

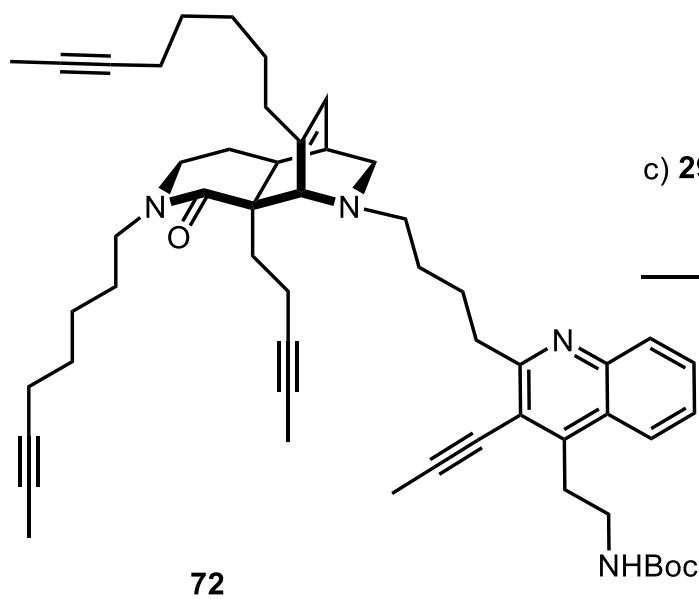
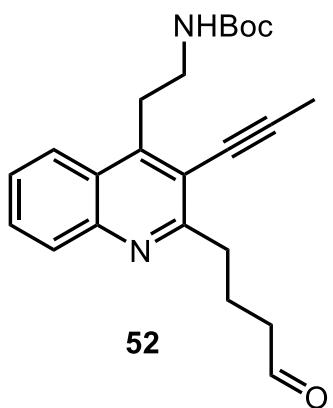


njaoamine I  
*(revised assignment)*

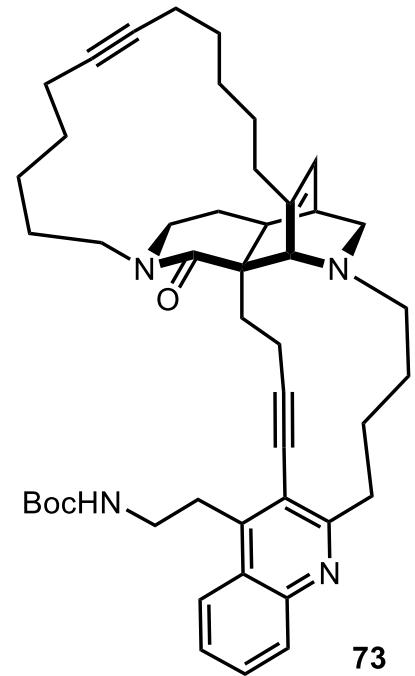
**Figure 4.** Originally assigned and revised structure of njaoamine I.



a) L-Selectride, THF, 40 °C;  
b) **52**, NaBH(OAc)<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>,  
67% (over two steps);



c) **29** (30 mol %), **30** (30 mol %),  
MS 5Å, toluene, reflux,  
35% (**73**+ 17% isomer))



**73**

**Table S1.** Statistical Analysis

Target	Macrocyclization Tactics	Step Count (LLS) <sup>a</sup>	Total Step	Overall Yield
			Count	
nominal xestocyclamine A <sup>b</sup>	RCAM / alkyl-Suzuki coupling	16	20	1.97%
actual xestocyclamine A (= <i>ent</i> -ingenamine A) <sup>b</sup>	RCAM / macrolactamization	19	23	1.94%
ingenamine A	RCAM / RCM	16	20	2.01%
keramaphidine B	RCAM / RCM	19	23	0.93%
nominal njaoamine I	RCAM / RCAM	21	32	1.14%

<sup>a</sup> starting from commercially available materials; <sup>b</sup> see ref. 2; LLS = longest linear sequence; RCAM = ring closing alkyne metathesis; RCM = ring closing olefin metathesis