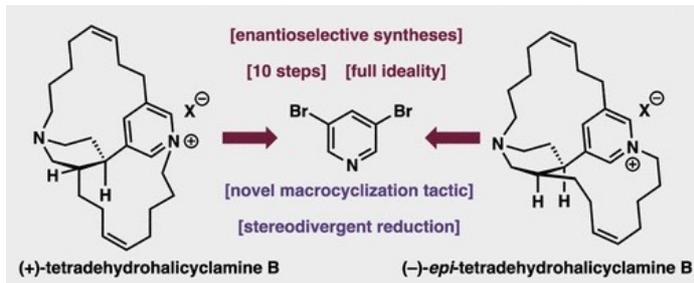
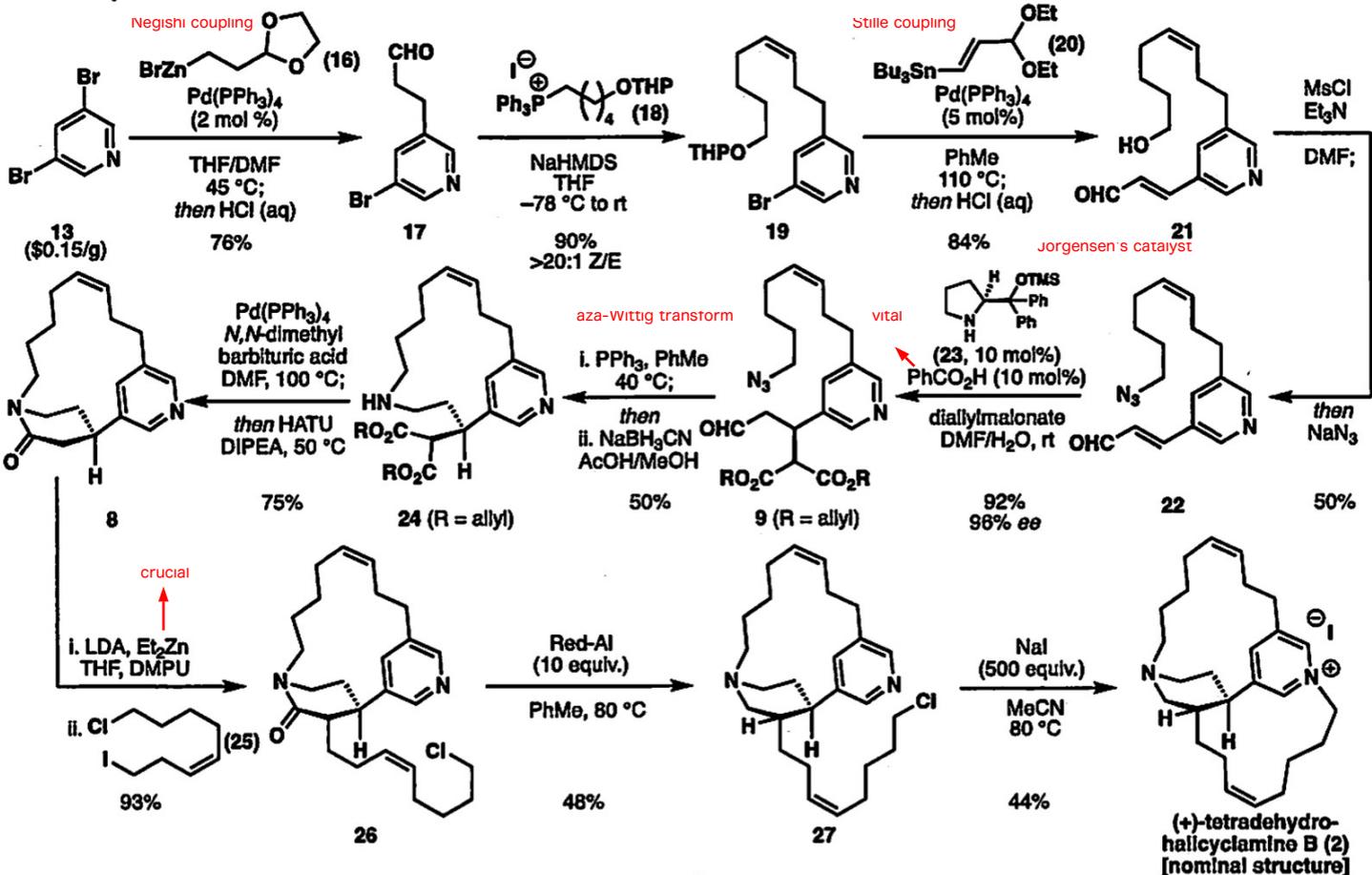


macrocyclic diamine alkaloids

zero extraneous redox, protecting group manipulations, or functional group



### Total Synthesis of (+)-tetradehydrohalicyclamine B



not structurally identical to the natural

#### A. Data Comparison for Isolated and Synthetic Samples of 2

Position	Natural <sup>a</sup>	Synthetic A (ppm)
4	143.1	140.3, 2.8
15	49.7	40.0, 9.7
16	40.5	22.0, 18.5
8	29.9	25.9, 9.6

Position	Natural <sup>a</sup>	Synthetic A (ppm)
8 (H <sup>1</sup> )	1.32	0.35, 0.97
8 (H <sup>1</sup> )	2.09	1.50, 0.59
16	2.54	2.12, 0.42
27	8.99	9.00, 0.11

COZY: — HMBC: —

#### B. Putative Biogenesis of halicyclamines

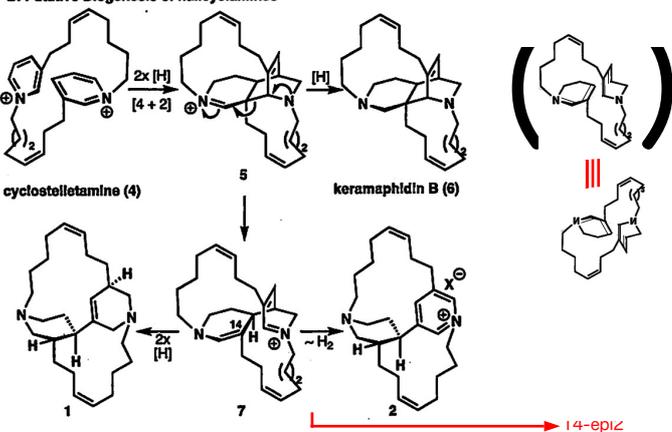


Figure 1. (A) Halicyclamine B and its closely related aromatic congeners. (B) Proposed biosynthetic origins of the featured halicyclamine natural products.

#### B. Total Synthesis of (-)-epi-tetradehydrohalicyclamine B

