Total syntheses of (–)-macrocalyxoformins A and B and (–)-ludongnin C

Zichen Cao, Wenxuan Sun, Jingfu Zhang, Junming Zhuo, Shaoqiang Yang, Xiaocui Song, Yan Ma, Panrui Lu, Ting Han & Chao Li

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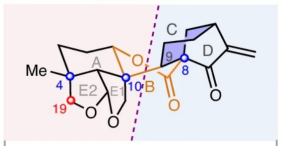
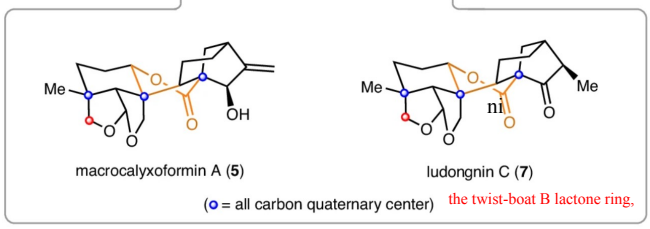
decarboxylative Giese & lactonization



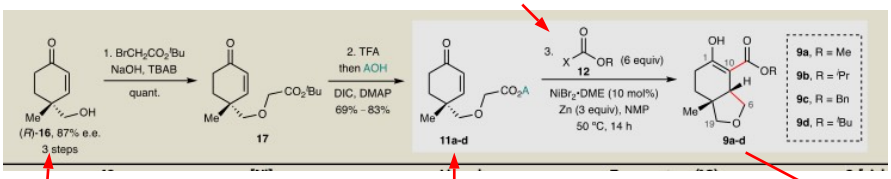
macrocalyxoformin B (6)



macrocalyxoformin A (5) ludongnin C (7)

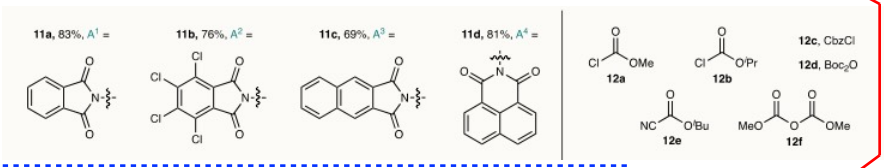
(o = all carbon quaternary center) the twist-boat B lactone ring,

reductive decarboxylative cyclization/reductive radical-polar crossover (RRPCO)

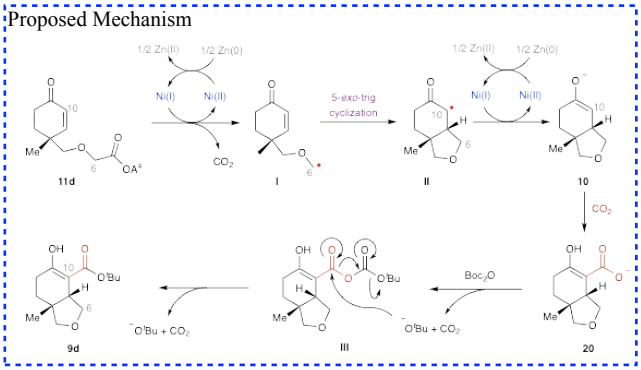


Rawal's procedure

redox-active ester (RAE)

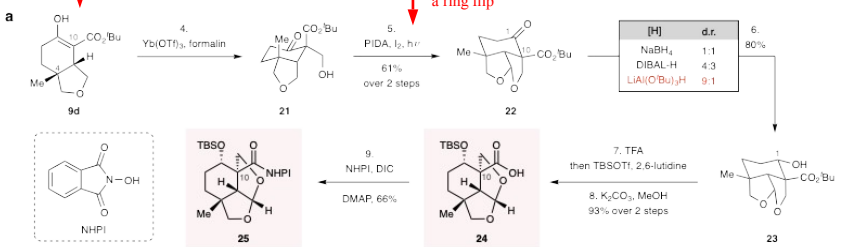


Proposed Mechanism

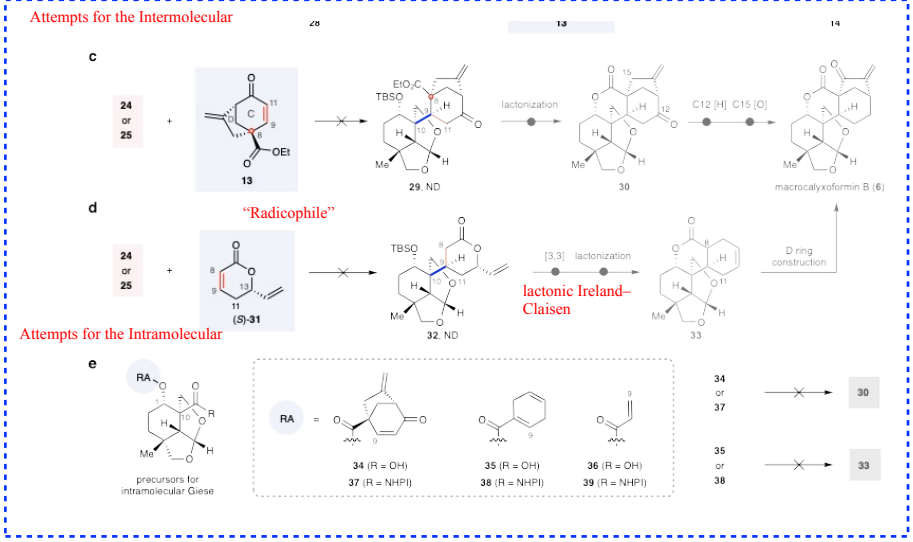


a Suárez modified Hofmann–Löffler–Freytag reaction

a ring flip



Attempts for the Intermolecular

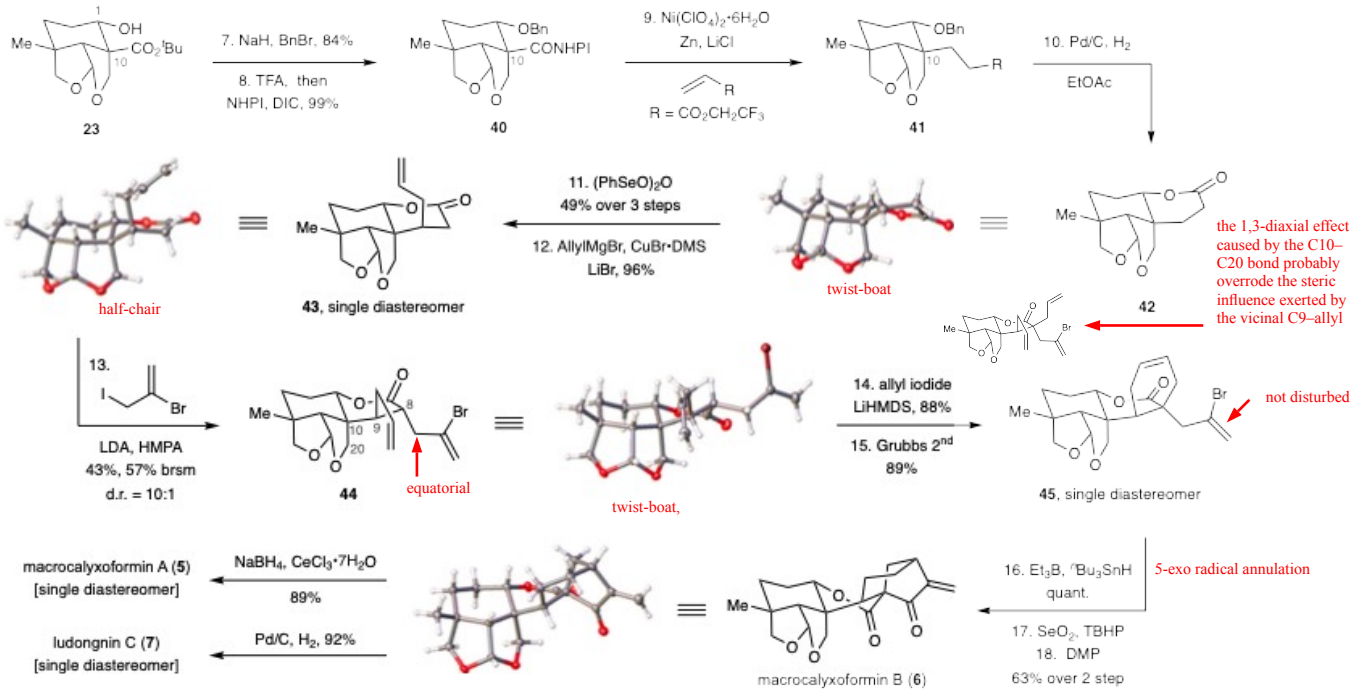


"Radicophile"

lactonic Ireland–Claisen

Attempts for the Intramolecular

Baran's decarboxylative Giese reaction conditions



half-chair

twist-boat

the 1,3-diaxial effect caused by the C10–C20 bond probably overrode the steric influence exerted by the vicinal C9–allyl

equatorial

twist-boat,

not disturbed

5-exo radical annulation