

Total Synthesis of Keramaphidin B and Ingenamine by Base-Catalyzed Diels–Alder Reaction Using Dynamic Regioselective Crystallization

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Cite this: J. Am. Chem. Soc. 2024, 146, 16, 11054–11060

dynamic crystallization can be an alternative when the selectivity is not controlled by either kinetic or thermodynamic approaches in solution

regioselective cleavage of the TIPS during chromat.

Scheme 3. Total Synthesis of (±)-Keramaphidin B and (±)-Ingenamine

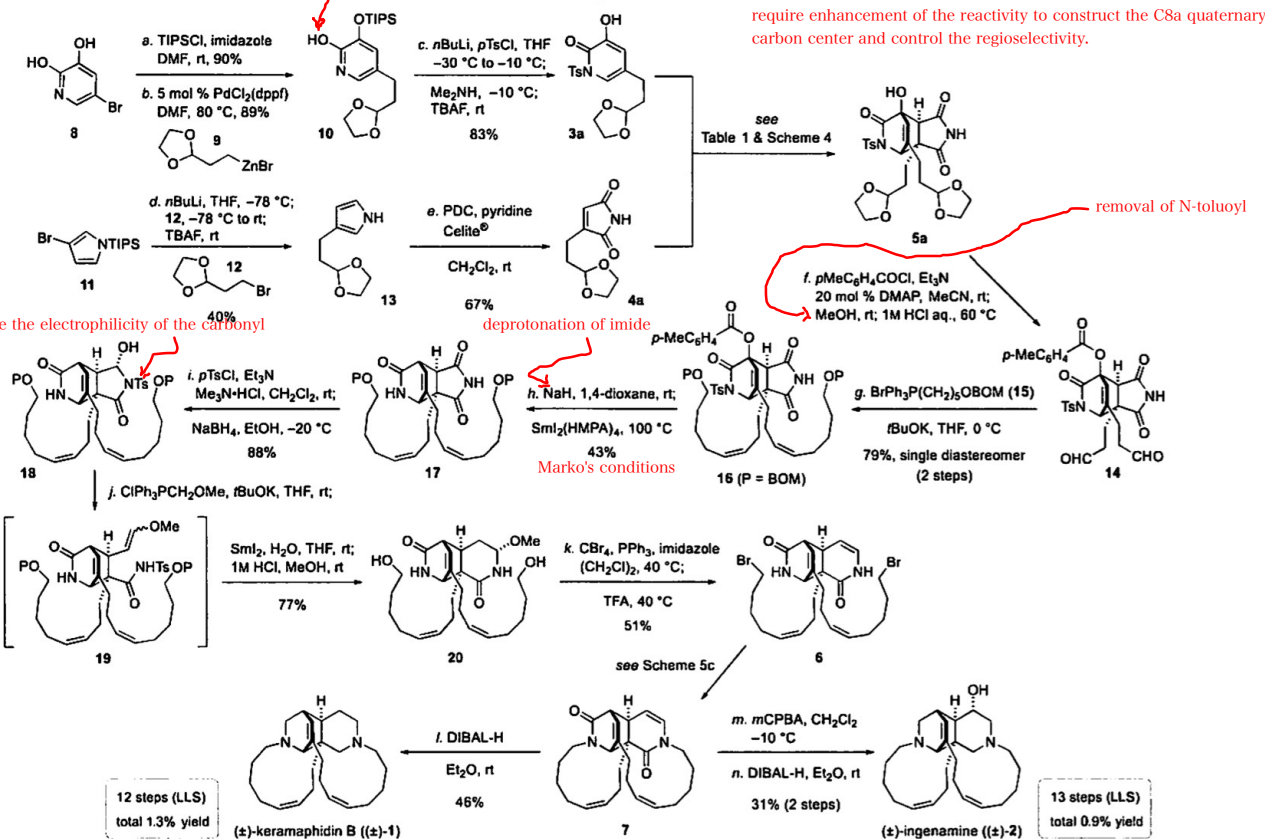


Table 1. DMAP-Catalyzed Diels–Alder Reaction between 3-Hydroxy-2-pyridone and Maleimide^a

all soluble in the solvent
To clarify the mechanism

No exo-product was observed

entry	SM	additive	yields ^b		
			5b	21b	3b
1	3b+4b	none	5%	14%	55%
2	3b+4b	LiCl	39%	20%	8%
3	5b	none	98%	0%	0%
4	21b	none	0%	97%	0%
5	5b	LiCl	38%	15%	12%
6	21b	LiCl	27%	11%	11%

^a3b (1 equiv), 4b (1.2 equiv), DMAP (10 mol %), additive (1 equiv), CH₂Cl₂/C₆H₆ = 1 (0.2 M), 40 °C, 3 days. ^bYields were determined by ¹H NMR using mesitylene as an internal standard.

,the addition of LiCl render the Diels–Alder reaction reversible

Scheme 4. Dynamic Regioselective Crystallization in Base-Catalyzed Diels–Alder Reaction

