Overriding Stereochemical Outcomes in Cyclase Phase Total Synthesis: Enantioselective Synthesis of Habiterpenol and Dasyscyphin A

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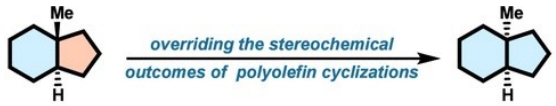
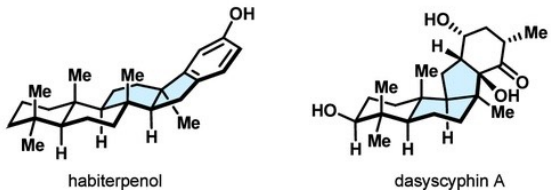
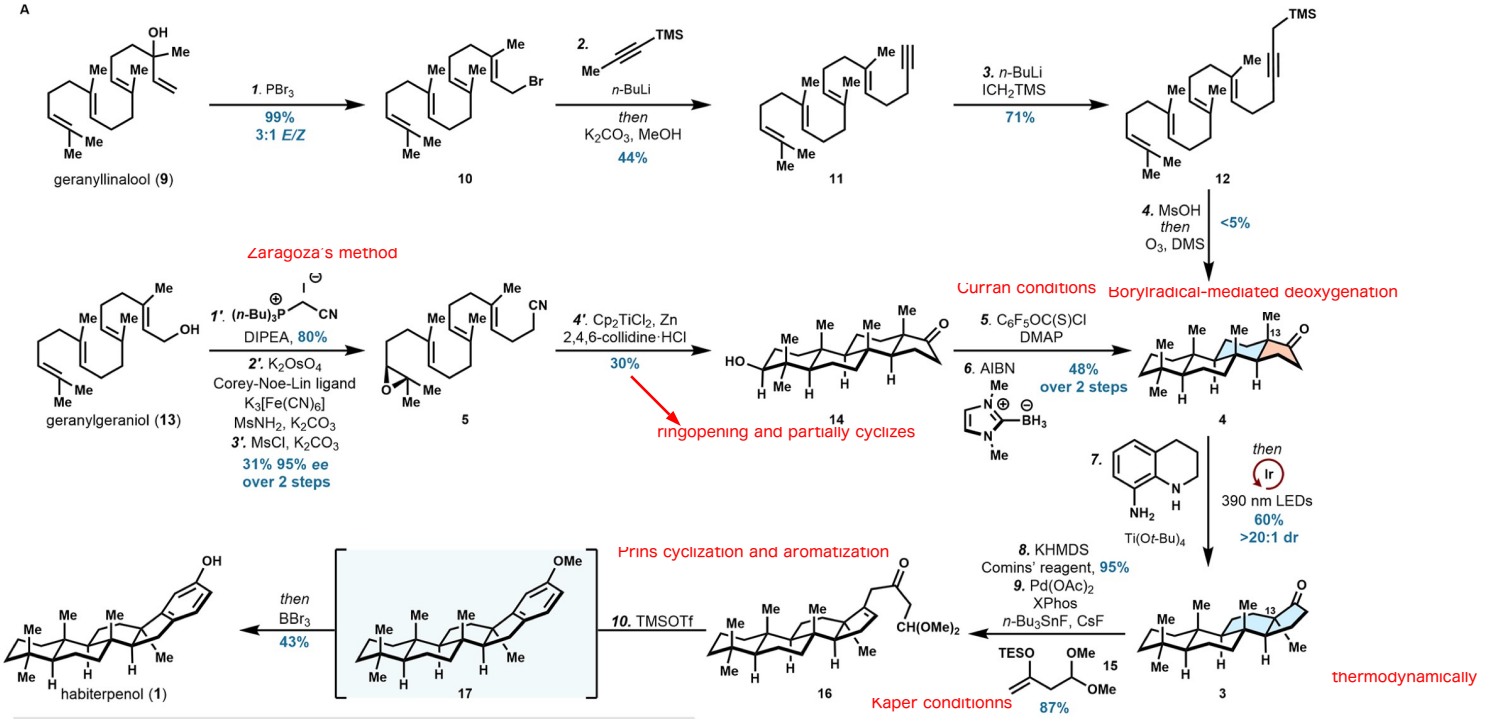




Scheme 2. Total Synthesis of Habiterpenol



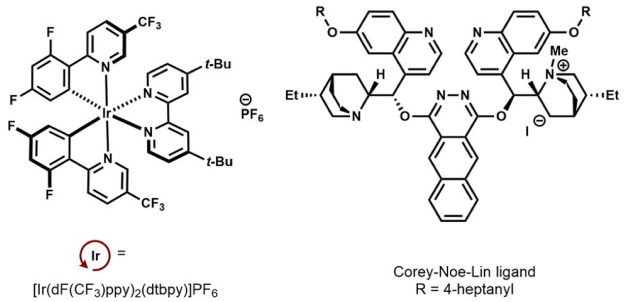
B

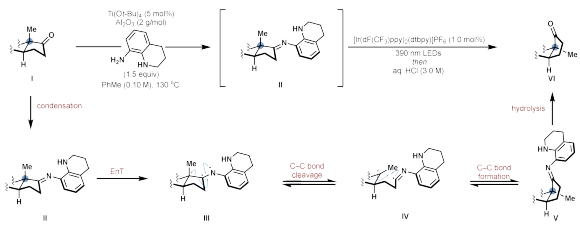
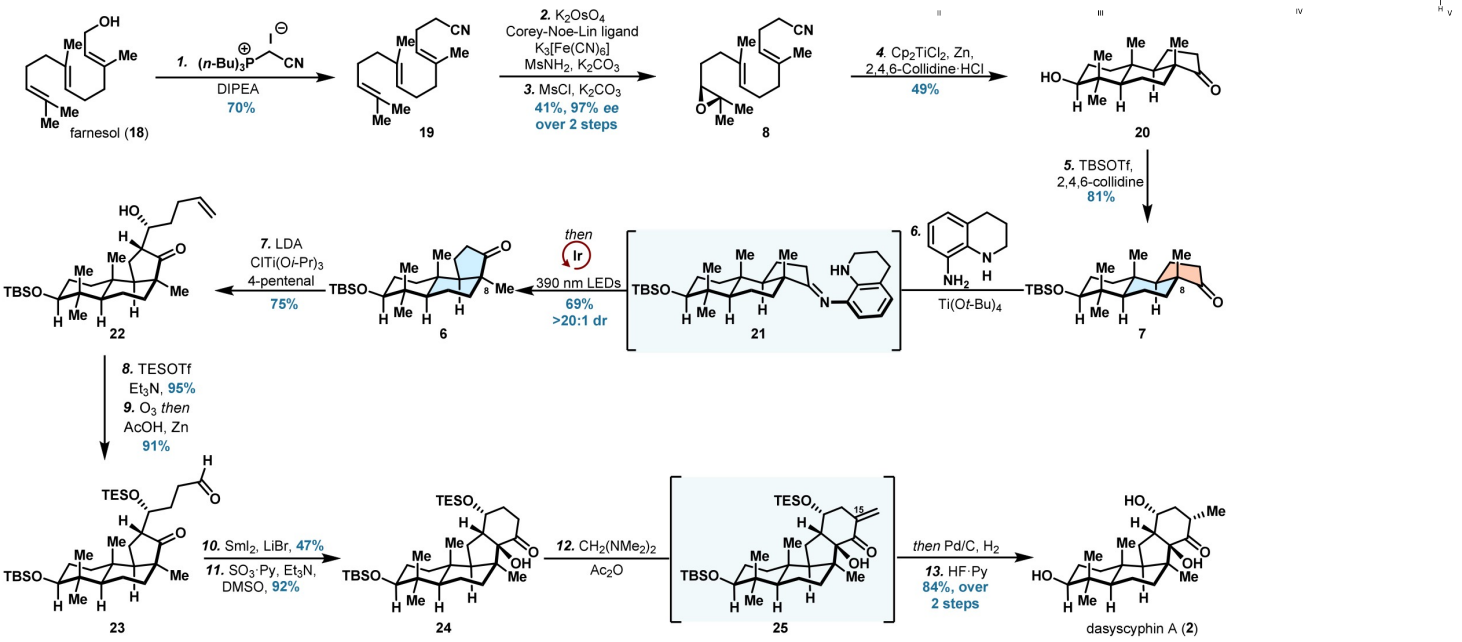
Cp_2TiCl_2 (3.3 equiv), Zn (6.6 equiv) → THF (0.10 M), 25 °C, 3 h

entry	variation from standard conditions	yield (%)[a]
1	none [*ref.* 15]	0
2	60 °C	28
3	2,4,6-collidine·HCl (2.0 equiv)	39
	catalytic polyolefin cyclization with 10 mol% Cp_2TiCl_2	
4	2,4,6-collidine·HCl (2.0 equiv)	42
5	2,4,6-collidine·TFA (2.0 equiv)	22
6	2,4,6-collidine·TfOH (2.0 equiv)	8
7	2,4,6-collidine·HCl (2.0 equiv), Mn (6.0 equiv)	57

[a]Reactions performed on a 0.10 mmol scale and the yields was determined by ^{1}H NMR spectroscopy of the crude reaction mixtures utilizing CH_2Br_2 as the internal standard.

stabilizes the active Ti(III) species





Scheme 3. Total Synthesis of Dasyscyphin A