Divergent Asymmetric Synthesis of Four Pentacyclic Homoproaporphine Alkaloids via C-H Elaboration

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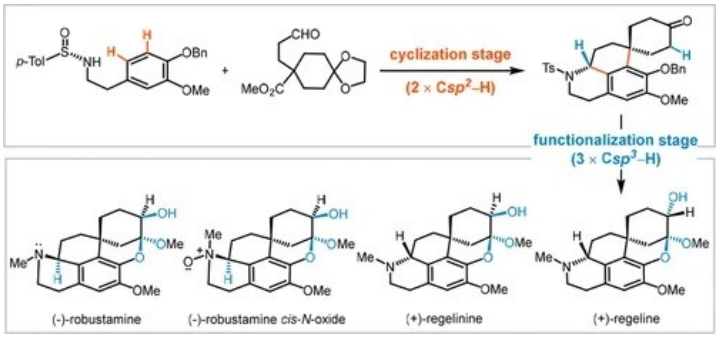
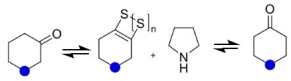


homoproaporphine family,

key reaction



Pictet-Spengler cyclization

photoredox-catalyzed decarboxylative cyclization

ketone 1,2-transposition

Davis oxidation

Rubottom oxidation

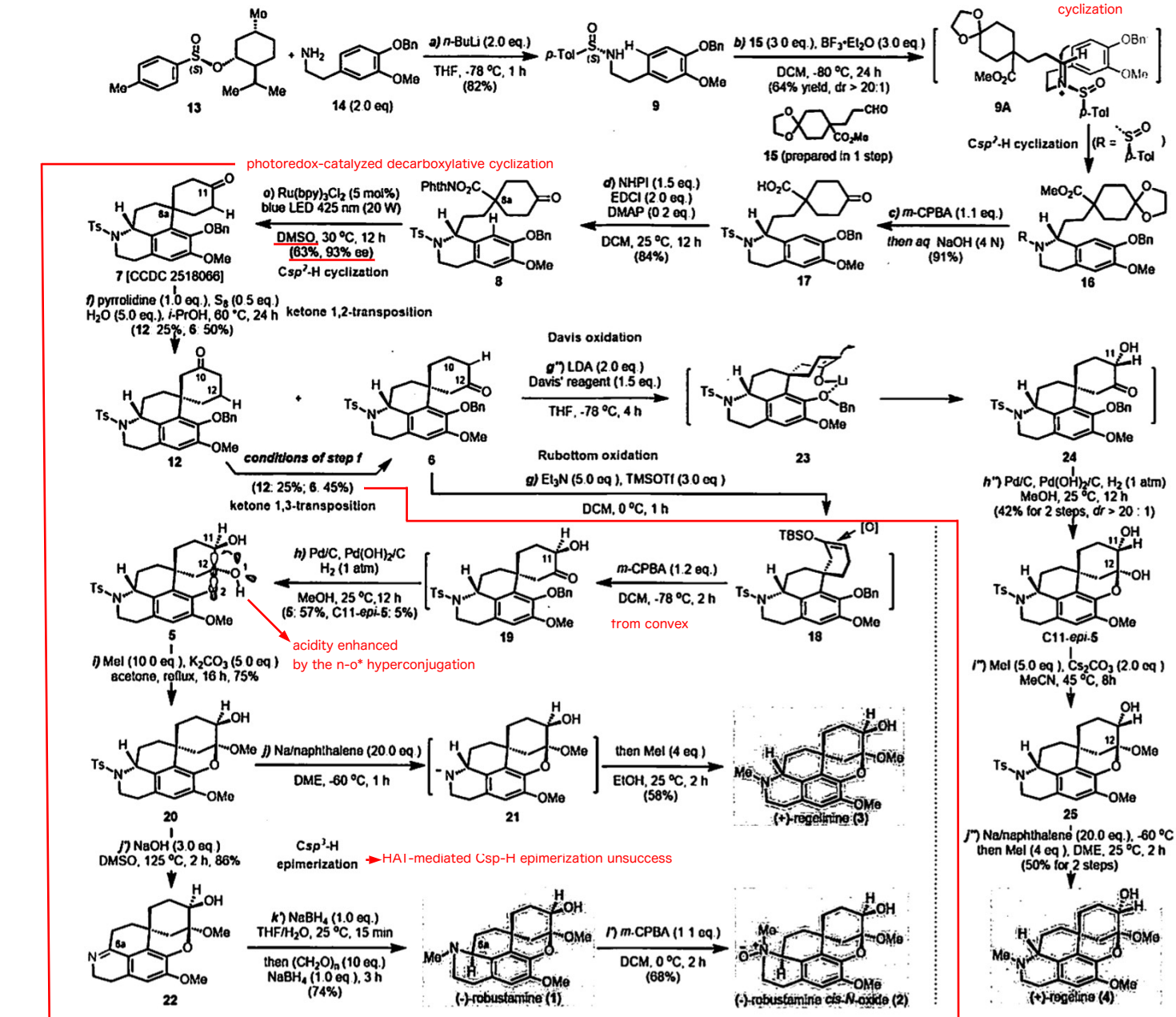
conditions of step f

ketone 1,3-transposition

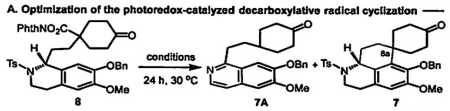
acidity enhanced by the n-σ* hyperconjugation

from convex

Csp³-H epimerization → HAT-mediated Csp-H epimerization unsuccess



A. Optimization of the photoredox-catalyzed decarboxylative radical cyclization



entry	conditions	yield (%)[a] 7A	7
1	$Ru(bpy)_3Cl_2$ (5 mol%), blue LED (425 nm), DCM	0	0[b]
2	$Ru(bpy)_3Cl_2$ (5 mol%), blue LED (425 nm), THF	0	0[b]
3	$Ru(bpy)_3Cl_2$ (5 mol%), blue LED (425 nm), MeCN	0	0[b]
4	$Ru(bpy)_3Cl_2$ (5 mol%), blue LED (425 nm), DMF	8	56
5	$Ru(bpy)_3Cl_2$ (5 mol%), blue LED (425 nm), DMSO	5	63
6	$Ir(ppy)_3$ (5 mol%), blue LED (455 nm), DMSO	38	20
7	NaI (20 mol%), PPh_3 (150 mol%), blue LED (455 nm), MeCN	20	15
8	4CzIPN (2.5 mol%), TFA (10 eq), blue LED (410 nm), DMSO	26	11

[a]Isolated yield. [b]No reaction.

standard photocatalytic conditions,