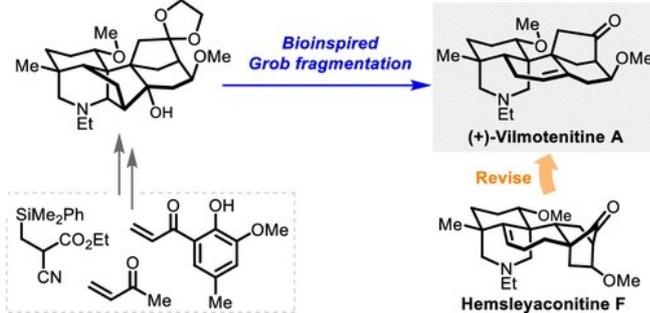


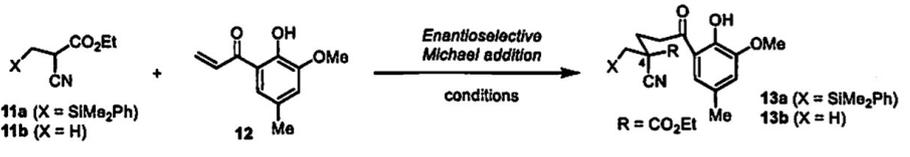
Asymmetric Total Synthesis of Vilmotenitine A and Structural Revision of Hemsleyaconitine F

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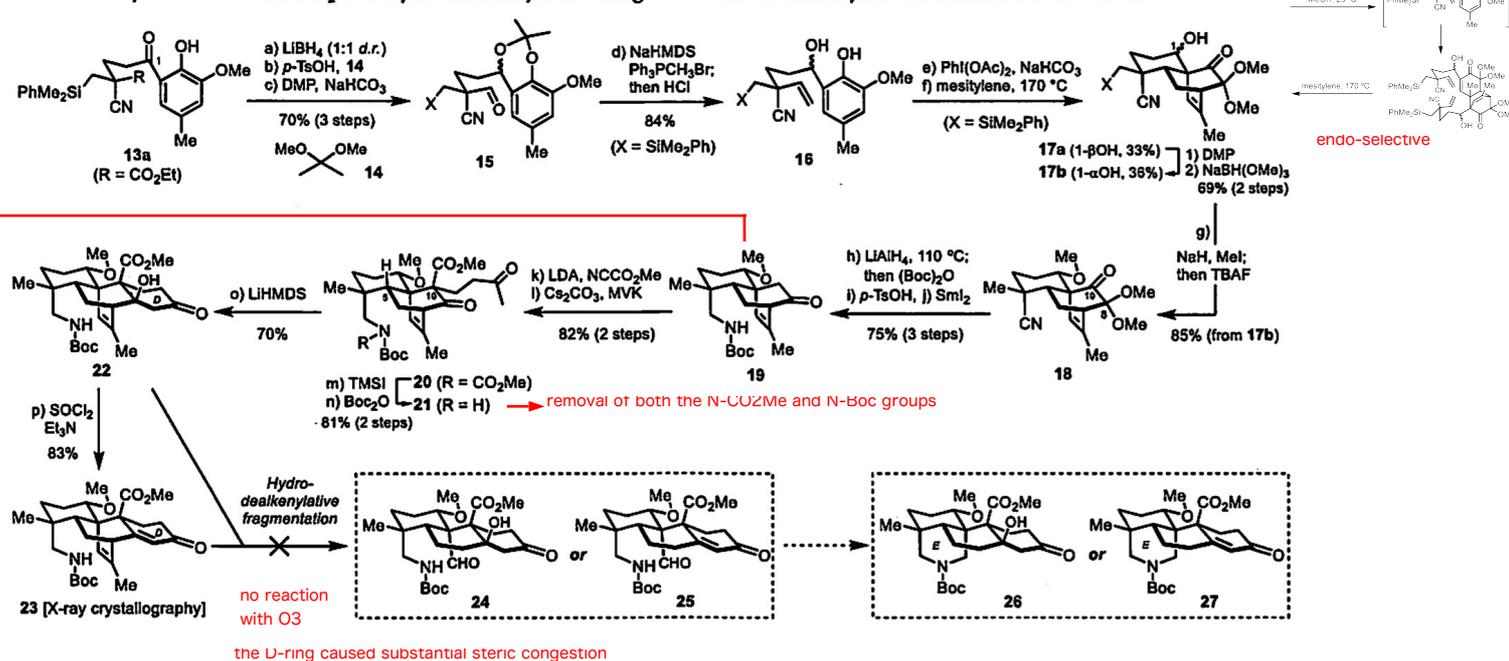


Entry	Substrate	Condition	Temperature (°C)	Solvent	Conv. (%)	Yield (%)	ee (%)
1	11a	Cl	-60	PMMA	27	17	<20
2	11a	Cl	-60	PMMA	30	18	80
3	11a	Cl	-60	PMMA	26	49	84
4	11a	Cl	-60	PMMA	13	4	84
5	11a	Cl	-60	PMMA	<5	N.D.	N.D.
6	11a	Cl	-60	PMMA	60	4	3
7	11a	Cl	-60	PMMA	65	14	41
8	11a	Cl	-20	PMMA	100	80	32
9	11a	Cl	-60	CHCl <sub>3</sub> /PMMA (1:1)	100	94	32
10	11a	Cl	-60	CHCl <sub>3</sub> /PMMA (1:1)	100	94	32
11	11a	Cl	-60	CHCl <sub>3</sub> /PMMA (1:2)	100	92	31
12	11a	Cl	-60	CHCl <sub>3</sub> /PMMA (1:3)	100	92	32
13	11a	Cl	-60	CHCl <sub>3</sub> /PMMA (1:4)	92	80	31
14	11a	Cl	-60	CHCl <sub>3</sub> /PMMA (1:5)	73	66	33

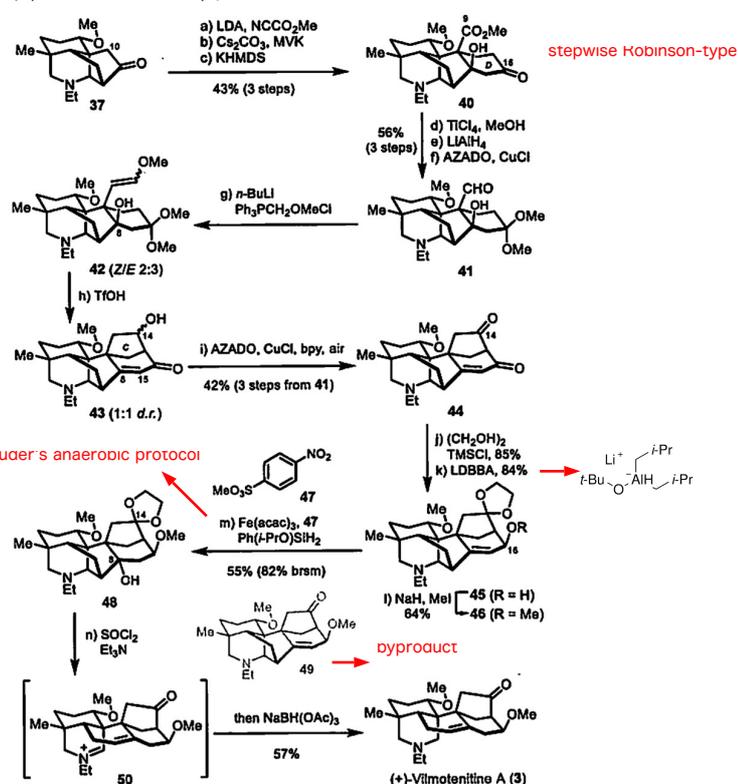
\*Solvent abbreviations: reactions were conducted with 11 (0.3 mmol), 12 (0.4 mmol), and 13 (0.4 mmol) in solvent (1 = 0.1 M). <sup>a</sup>Determined according to the isolated material. <sup>b</sup>Determined by HPLC analysis (see the Supporting Information). N.D.: not detected.



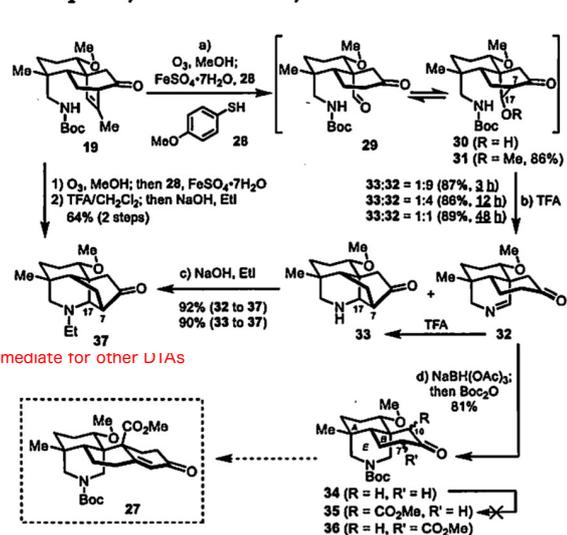
**Scheme 2. Synthesis and Attempted Hydrodealkenylative Fragmentation of Tetracyclic Intermediates 22 and 23**



**Scheme 5. Completion of the Total Synthesis of (+)-Vilmotenitine A (3)**



**Scheme 3. Hydrodealkenylative Fragmentation of 19 and Attempted Synthesis of Tetracyclic Intermediate 27**



Grob fragmentation

