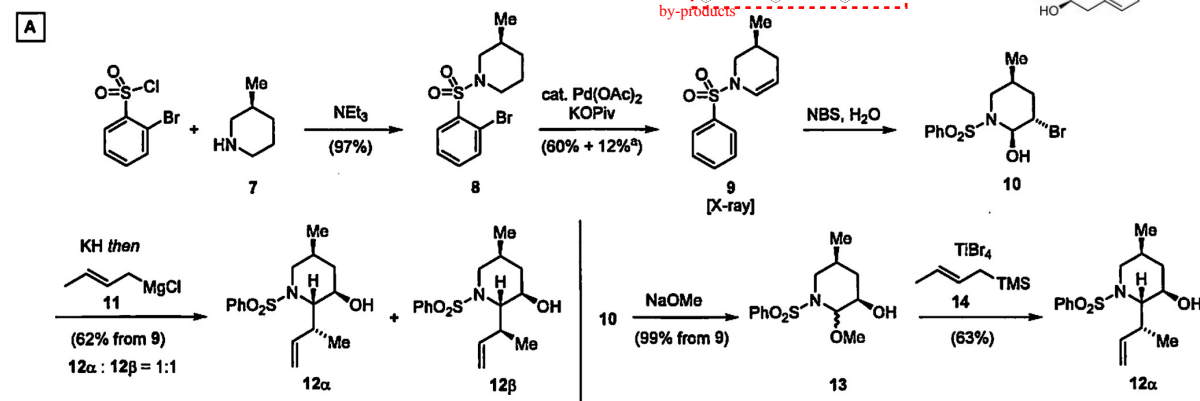


# Concise Synthesis of (-)-Veratramine and (-)-20-iso-Veratramine via Aromatic Diels-Alder Reaction

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isosteroidal alkaloids  
transition-metal catalyzed intramolecular Diels-Alder cycloaddition-aromatization cascade

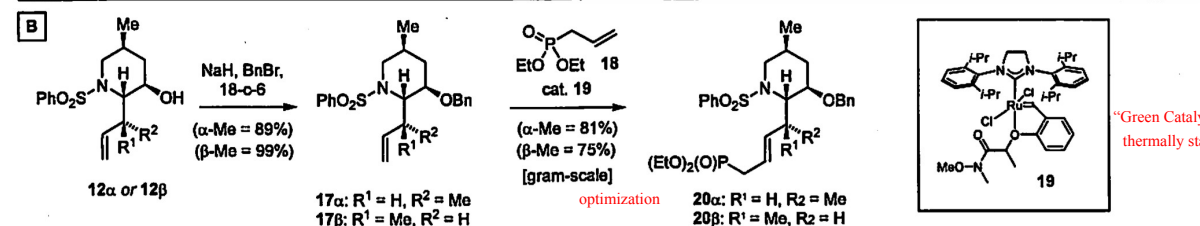
## Scheme 3. Assembly and Linkage of the Key Building Blocks<sup>a</sup>



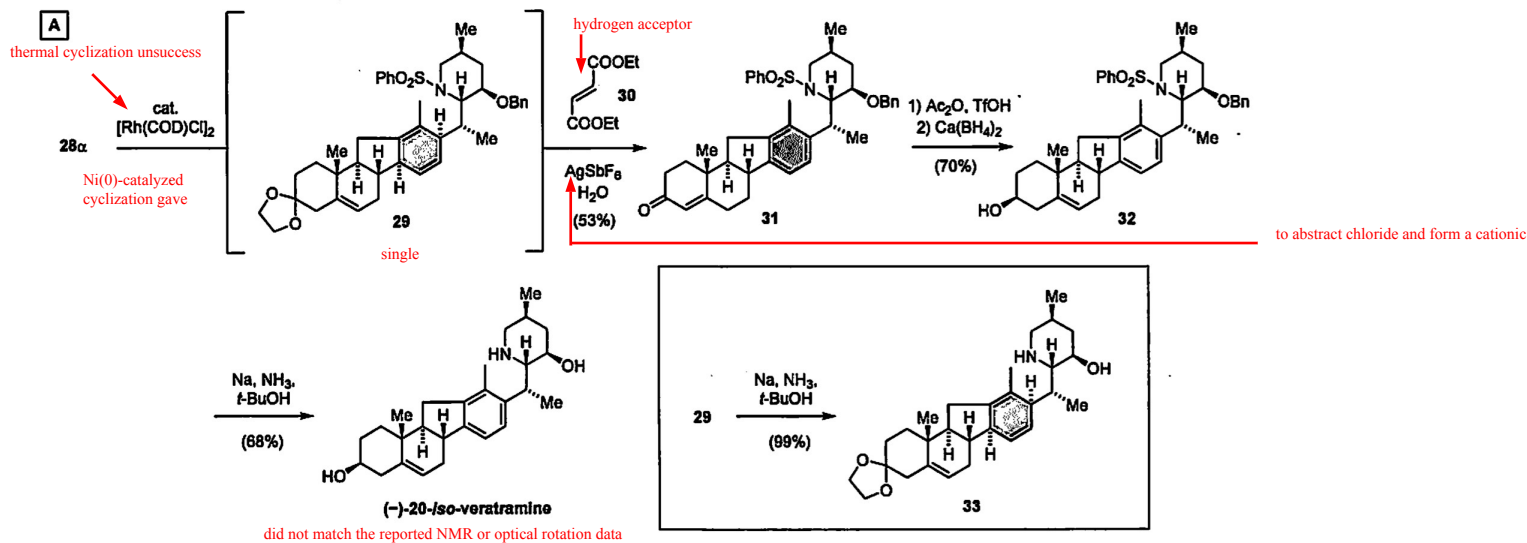
Scheme 4. Reaction Design and Optimization for the Diastereoselective Crotylation of *N,O*-Acetal 13<sup>a</sup>

Lewis Acid	NMR Yield 12α (%)	12α:16	RSM (% <sup>b</sup> )
TiCl <sub>4</sub> (1.1 equiv)	28	1.9:1	12
TiCl <sub>4</sub>	47	5.3:1	10
BF <sub>3</sub>	6	2.1:1	11
B <sub>4</sub> O <sub>7</sub>	8	0.4:1	0
Sn(OTf) <sub>2</sub>	0	0	26
Cp*TiCl <sub>3</sub>	0	0	63
Ti(OAc) <sub>4</sub>	0	0	75
TiBr <sub>4</sub>	65 <sup>c</sup>	13:1	0

<sup>a</sup>14 (2.0 equiv), Lewis acid (2.2 equiv), DCM (0.05 or 0.1 M), -78 °C. <sup>b</sup>The sum of 13 and its hydrolyzed *N,O* hemiacetal analogue. <sup>c</sup>Isolated yield.



## Scheme 5. Construction of the D Ring and Completion and Corroborating X-ray Diffraction Analysis<sup>a</sup>



standard conditions (e.g., TsNHNH/AcOH) resulted in tosylhydrazine condensation with

to abstract chloride and form a cationic