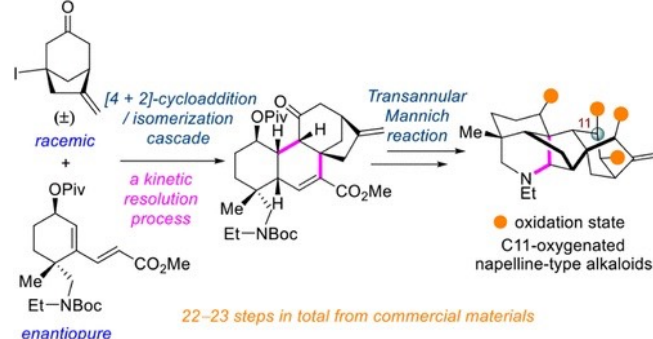
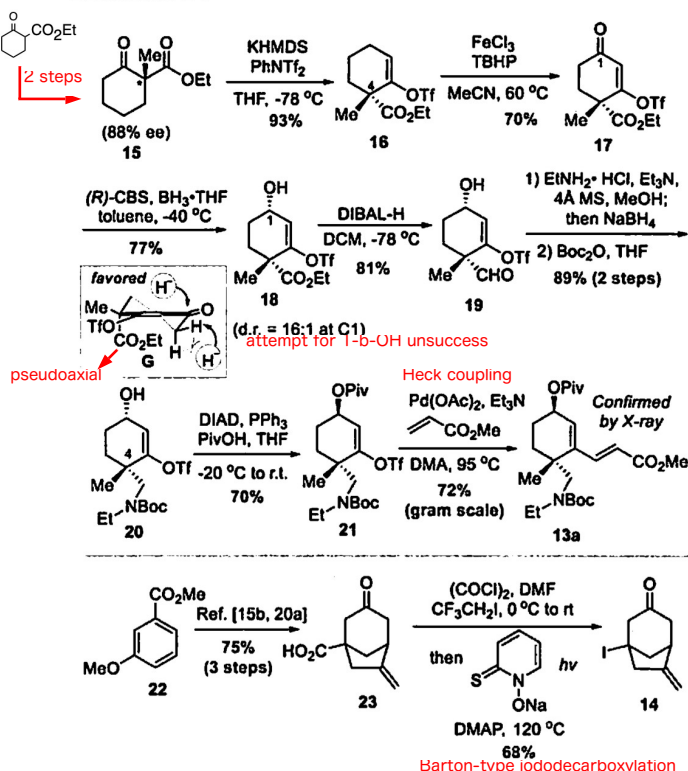
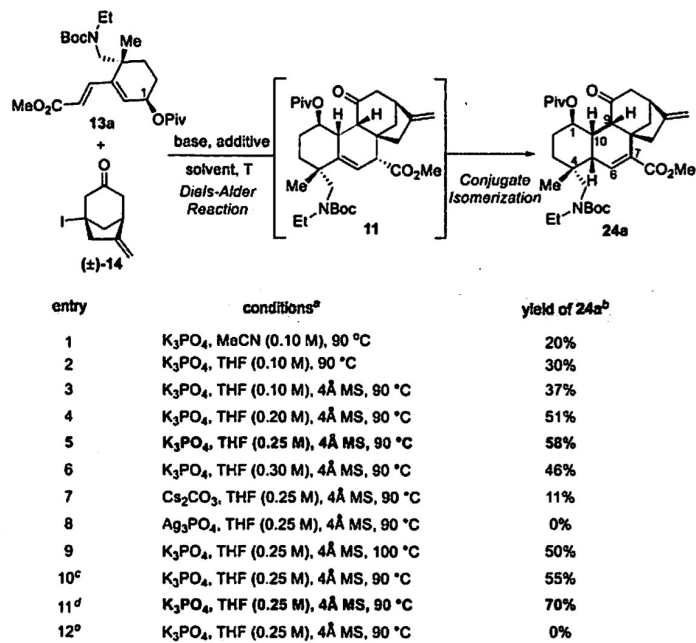




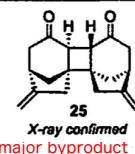
## Scheme 2. Preparation of Chiral Diene 13a and Dienophile Precursor 14



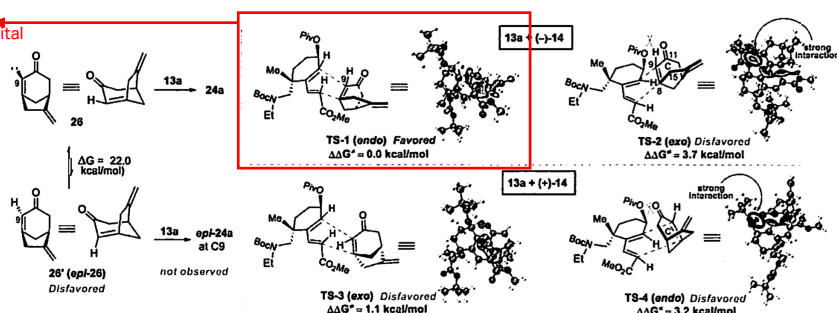
a.



<sup>a</sup>Unless stated otherwise, the reactions were performed with 13a (100mg, 0.23 mmol), 14 (180 mg, 0.69 mmol), base (2.74 mmol), solvent, 4A MS (280 mg) until 13a was completely consumed by the analysis of TLC. <sup>b</sup>Isolated yield. <sup>c</sup>Gram scale: 13a (1.00 g, 2.28 mmol), 14 (1.8 g, 6.84 mmol), K<sub>3</sub>PO<sub>4</sub> (9.14 g, 27.42 mmol), THF (9.2 mL), 4A MS (2.80 g). <sup>d</sup>performed with (-)-14. <sup>e</sup>performed with (+)-14.



from the back side of the OPiv  
in an endo manner (secondary orbital  
interaction)



hetero-[2 + 2]-cycloaddition  
between 13a and 14 was  
not observed

## Scheme 3. Completion of the Total Syntheses of C11-Oxygenated Napelline Alkaloids: (+)-Pendulumine I and (+)-Aconicarmichinium C

