

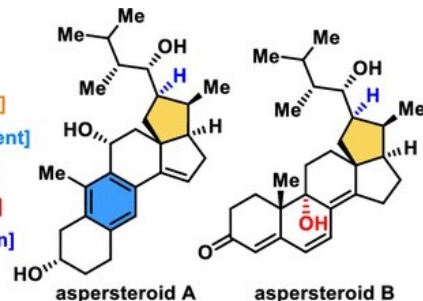
ergostane-type 18,22-cyclosterols

regioselective, divergent late-stage oxidations

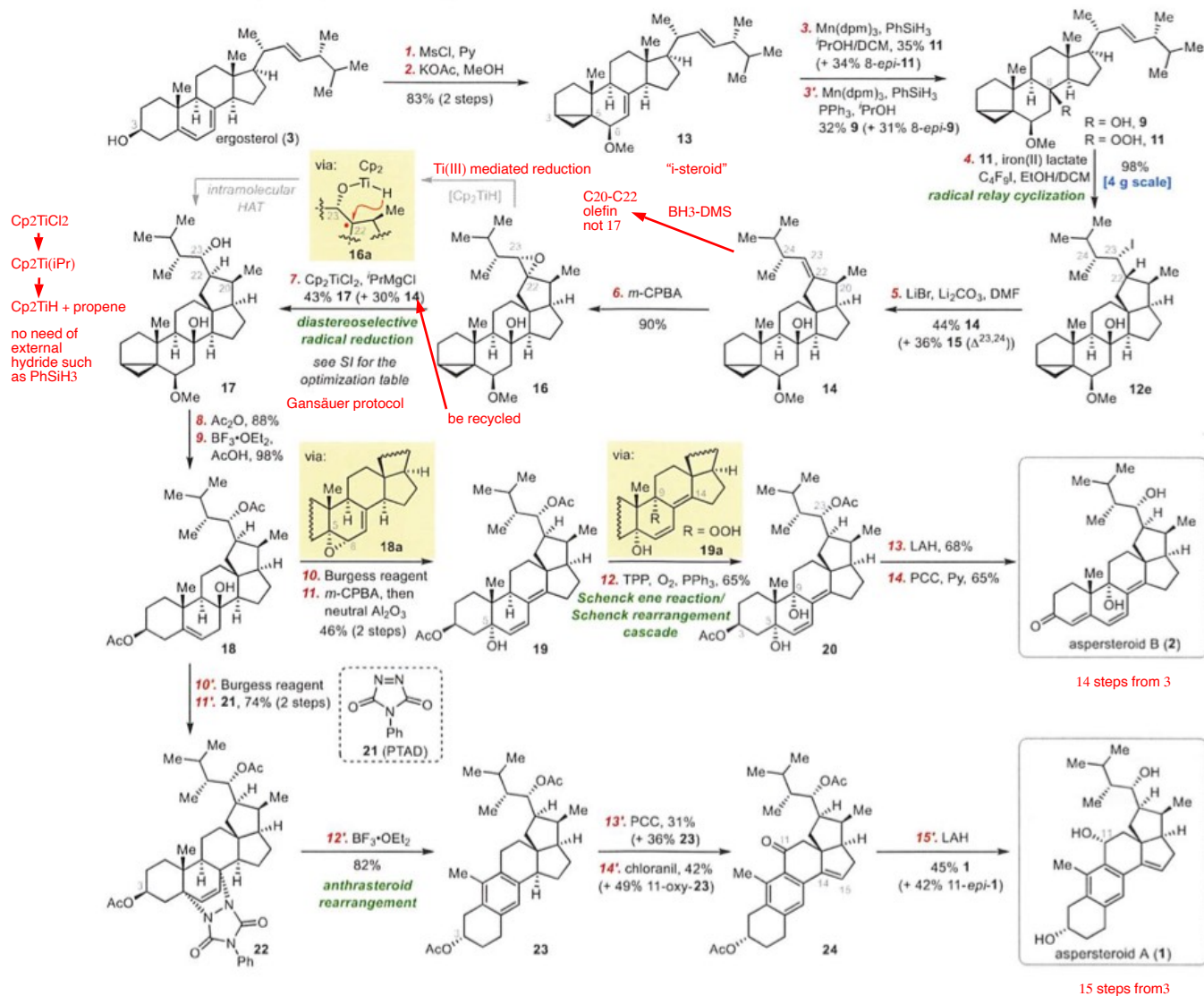
a thermodynamically unfavorable cis-substituted cyclopentane motif

a 1(10→6) abeo-steroid

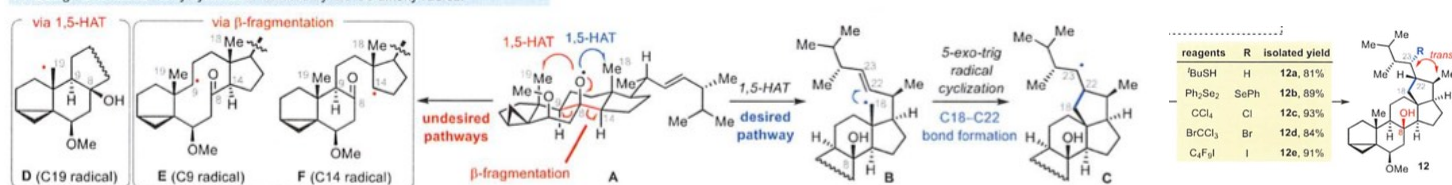
[14~15 steps]
 [radical relay cyclization]
 [anthrasteroid rearrangement]
 [Schenck ene/Schenck
 rearrangement cascade]
 [epoxide radical reduction]



Scheme 3. Bioinspired Synthesis of Aspersteroids A and B



A. Design of a radical relay cyclization initiated by the C8 alkoxy radical



Scheme S1. The Mechanism of the Anthrasteroid Rearrangement

