Lundurines A, B & C

Lundurines A, B and C - isolated from , a plant native to north of Borneo

Show interesting cytotoxicity properties

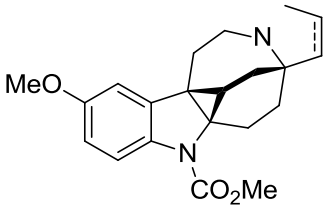
These alkaloids feature a unique polyhydropyrroloazocine and cyclopropyl moiety fused to the indoline ring

Reported total syntheses of Lundurine A and B were lengthy and involve over 20 linear synthetic steps

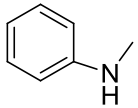
Thus difficult to synthesize useful quantities of final targets to study broad biological assays

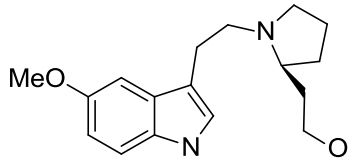
In this paper, a more efficient total synthesis (12-14 steps) of Lundurine A, B and the first total synthesis of Lundurine C (racemic and enantiopure) were reported

Retrosynthesis

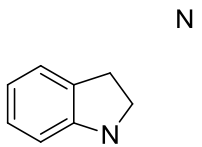


Synthetic approach





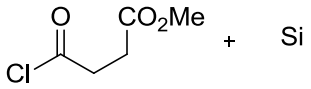
(+/-)-**13**, 91%
(–)-**13**, 7


N
N

Mechanistic explanation

Synthesis of alcohol 20

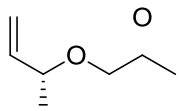
Synthesis of azo compound 21



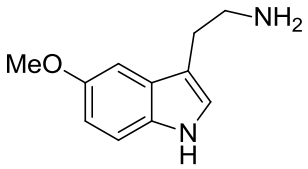
Mechanism

E

Mechanism



Enantioselective Claisen Rearrangement



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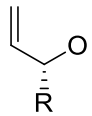
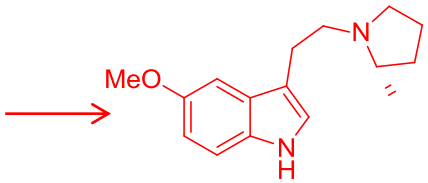
Basic conditions are necessary to avoid Picket-Spengler type reaction





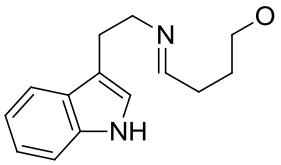
minor

major

Both - and - isomers are stable even at 100 °C for several hours

Curtin-Hammett principle is not applicable

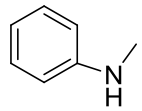
Picket-Spengler type reaction: under acidic conditions

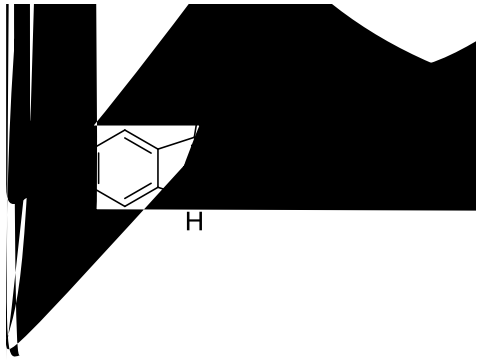


Ohira-Bestmann reagent

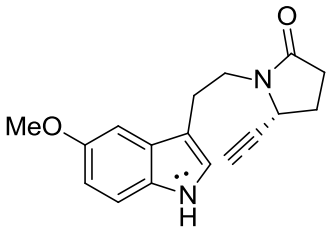
Mechanism

Rare 8-endo-dig gold(I) catalyzed hydroarylation



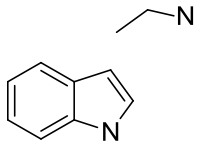


Mechanism

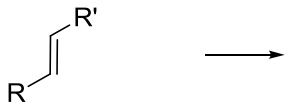


Overall, an 8-endo-dig reaction?
Known to be catalysed by Au(III)catalysts in the presence of Ag salts
No explanation has been provided why Au(I) catalyzes the reaction

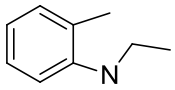
Johnson-Lemiex cleavage

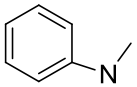


Mechanism



Mechanism





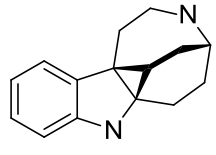
14a to 14b Homodienyl Retro-Ene

3(yl)] TJ ET BT 1 0 01.2 m33T .0115 TcTm [(via)] 4.368 52.824 Tm 9 0 G [(Mec)-4(h)-

(+/-)-**13**, 91%
(–

BF

2) AcOH, 0 to
25 °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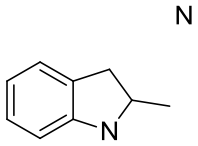
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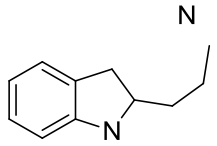
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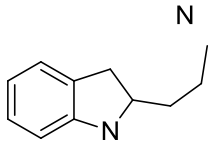
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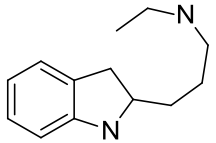
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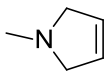
N


NaBH4
N
N