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

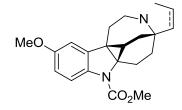
Reported total syntheses of Lundurine A and B were lengthy and involve over 20 linear synthetic steps

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



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Synthetic approach





(+/-)-**13**, 91% (-)-**13**, 7

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Mechanistic explanation



Synthesis of alcohol 20

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Synthesis of azo compound 21

Mechanism

Ε

Mechanism



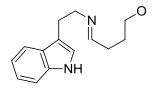
Enantioselective Claisen Rearrangement

Basic conditions are necessary to avoid Picket-Spengler type reaction

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

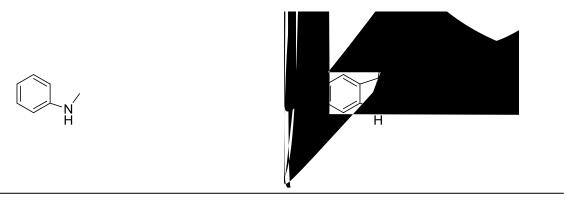


Ohira-Bestmann reagent



Mechanism

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



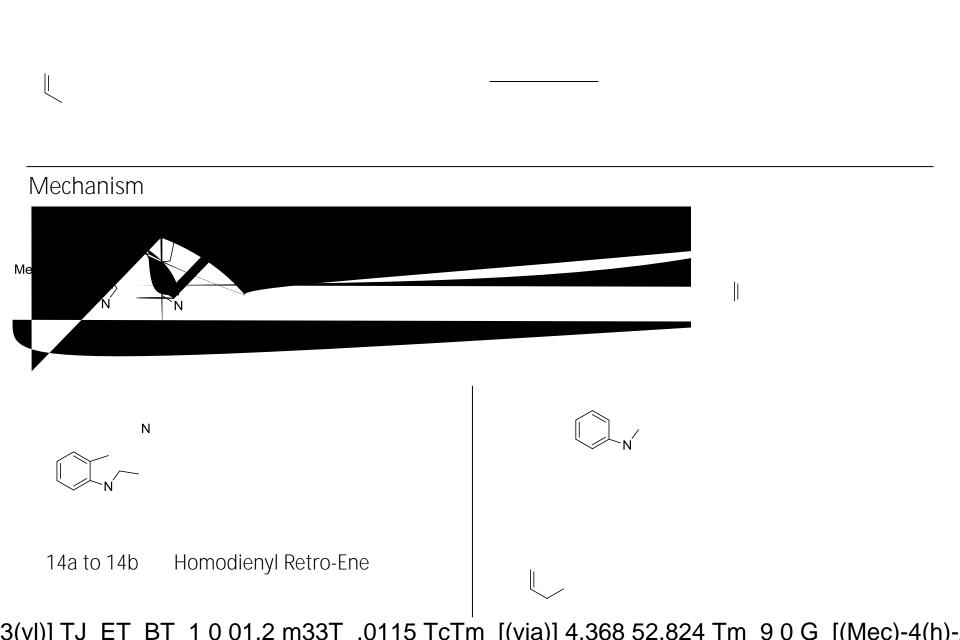
Mechanism

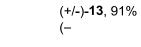
Overall, an 8-endo-dig reaction? Known to be catalysed by Au(III)catalysts in the presence of Ag salts No explanation has been provided why Au(I) catalyzes the reaction

Johnson-Lemiex cleavage

Mechanism

$$\bigcap_{\mathsf{R}'}^{\mathsf{R}'} \longrightarrow$$





BF



