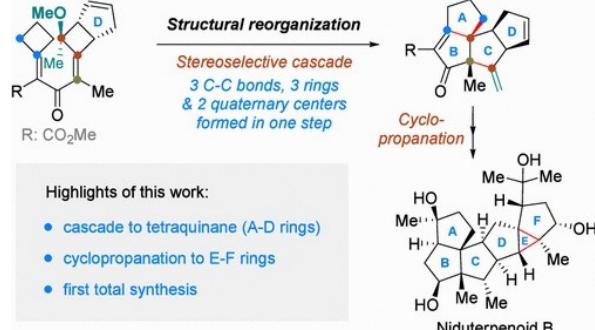
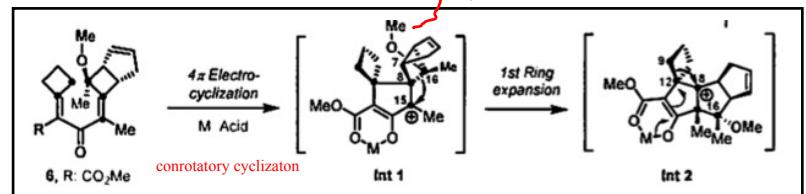


Total Synthesis of the Hexacyclic Sesterterpenoid Niduterpenoid B via Structural Reorganization Strategy

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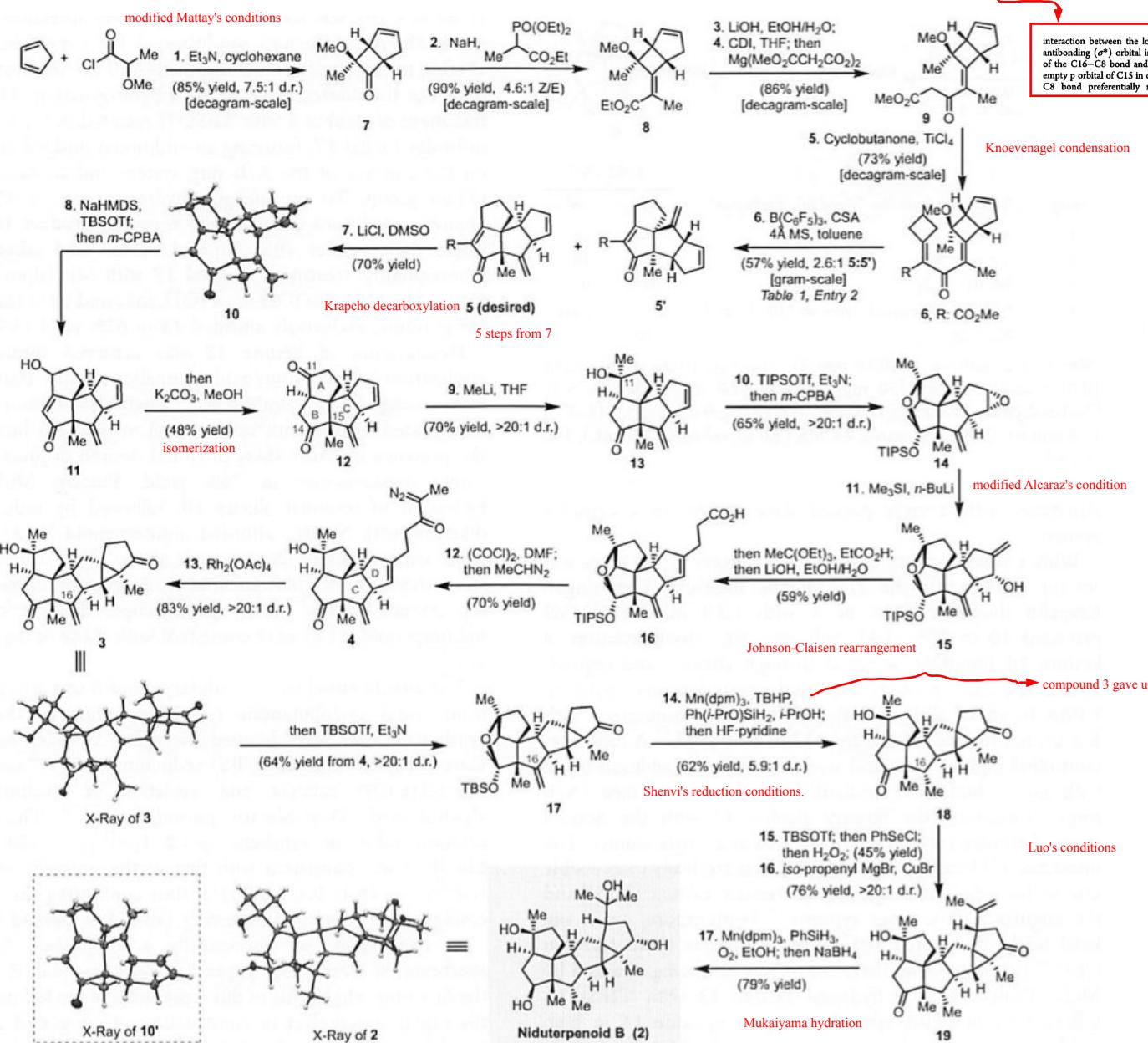


Highlights of this work:

- cascade to tetraquinane (A-D rings)
- cyclopropanation to E-F rings
- first total synthesis

a tandem Nazarov cyclization and double ring expansions of 1,3-

The n-σ* noncovalent interaction between the lone pair of OMe and the C16-C8 antibonding (σ*) orbital increases the HOMO orbital energy of the C16-C8 bond and lowers the energy barrier with the empty p orbital of C15 in carbocation Int 1, making the C16-C8 bond preferentially migrate.



acid sensitive: systemic optimization of various reaction

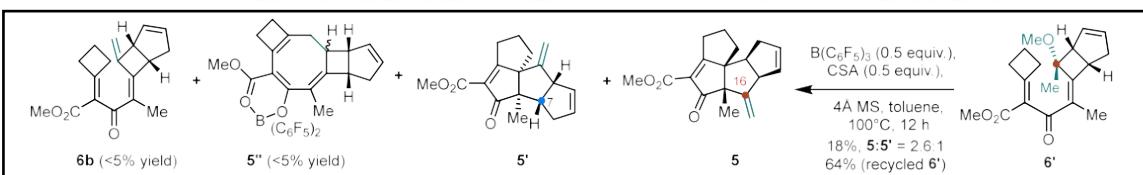
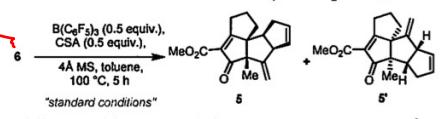


Table 1. Cascade Reaction Discovery and Optimization



Entry	Variations from the *standard conditions*	Yield (%) ^b	
		5	5'
1	none	36	14
2 ^c	3 g-scale of 6	41	16
3	No B(C ₆ F ₅) ₃	0	0
4	B(C ₆ F ₅) ₃ (1 equiv.), toluene, 120 °C, 12 h	8	trace
5	No CSA	10	<5

^aReaction conditions: 6 (0.10 mmol), B(C₆F₅)₃ (0.05 mmol), CSA (0.05 mmol), 4 Å MS (50 mg), toluene (1.0 mL), 100 °C, 5 h.

^bIsolated yields. ^cReaction conditions: 6 (3.0 g, 9.6 mmol), B(C₆F₅)₃ (5.9 mmol), CSA (6.5 mmol), 4 Å MS (3.0 g), toluene (100 mL), 100 °C, 5 h.

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