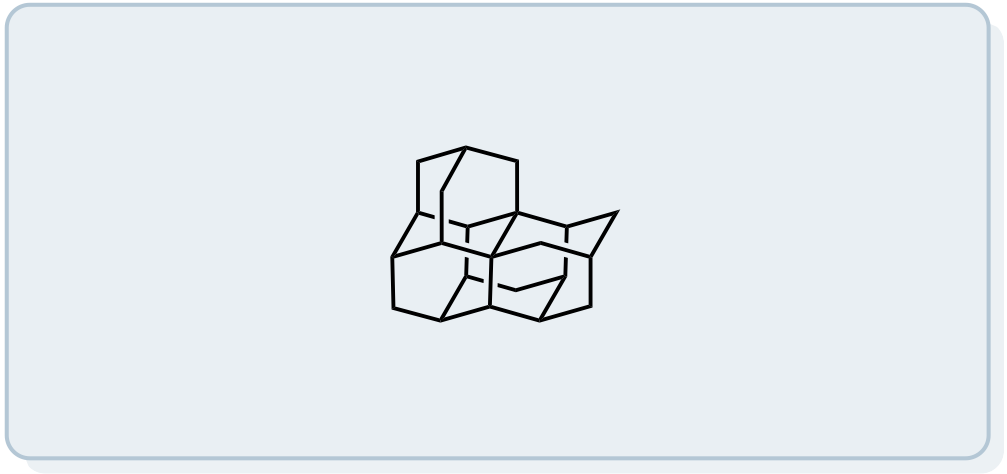


Stereoselective Total Synthesis of* Skew-*tetramantane

Biegasiewicz Group Meeting

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nature chemistry

Article

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Stereoselective total synthesis of *skew*-tetramantane

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Xiao-Yu Li & Christof Sparr

Diamond's elementary chiral constituent—*skew*-tetramantane—features

Author Introduction



First Author: Xiaoyu Li

- PhD Candidate in the Sparr Lab, University of Basel
- Recognized for outstanding work in Chemistry by the Camille and Henry Dreyfus Foundation (2026)

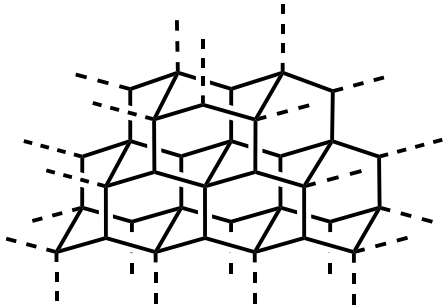


Corresponding Author: Christof Sparr

- Associate Professor at University of Basel, Switzerland
- Received PhD from ETH Zurich (Advisor: Ryan Gilmour)
- Post-doctoral fellowship at University of Cambridge (Advisors: Deiter Seebach and Steven Ley)

Overview of Tetramantanes

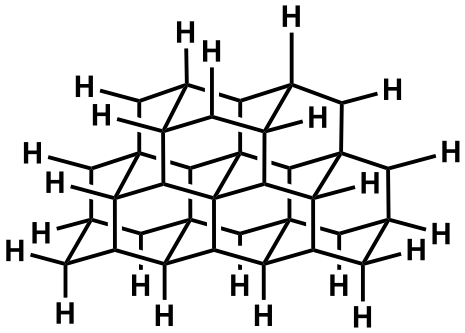
The Diamond Lattice:



An endless sp^3 C crystal that is very hard, and very inert

Overview of Tetramantanes

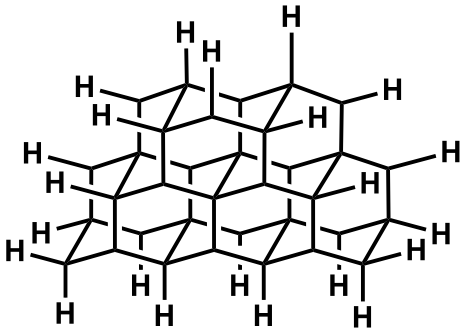
Diamondoids are different!



Smaller molecules, 'hydrogen-terminated' diamondoid scaffolds are physically and synthetically more interesting

Overview of Tetramantanes

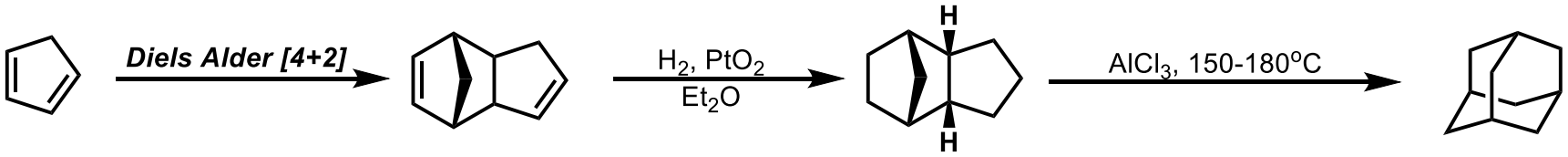
Diamondoids are different!



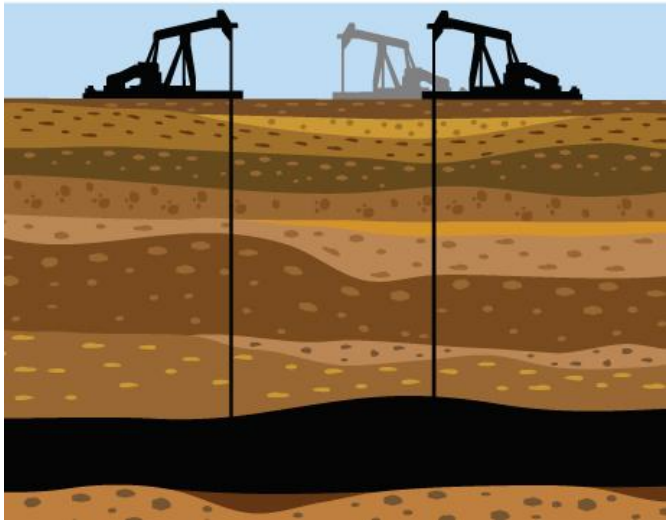
Smaller molecules, 'hydrogen-terminated' diamondoid scaffolds are physically and synthetically more interesting

How Do We Get Diamondoids?

Schleyer Method:

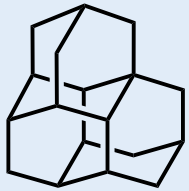


Synthetic Scope is Limited to Lower Diamondoids

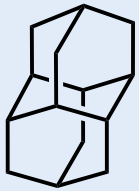


Overview of Tetramantanes

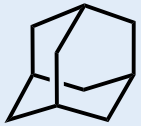
"Lower" Diamondoids



Triamantane

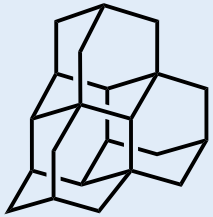


Diamantane

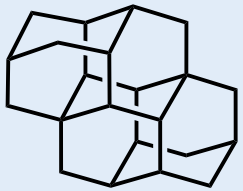


Adamantane

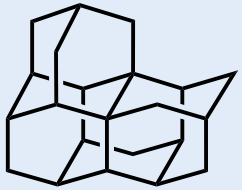
Tetramantane Isomers



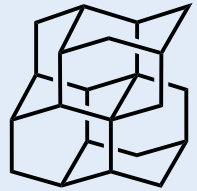
iso-Tetramantane



anti-Tetramantane



(P)-skew-Tetramantane



(M)-skew-Tetramantane

Gaining a Functional handle on Diamondoids has implications in many areas:



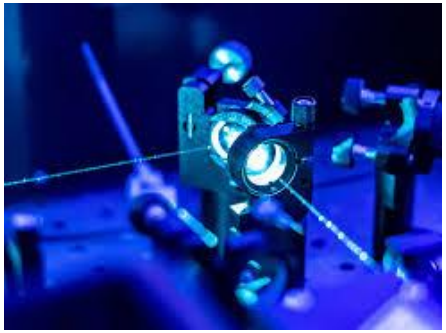
Quantum Computing



Pharmaceuticals



Synthetic Diamonds



Optics

Central Question to Address

"Lower" Diamondoids



Triamantane



Diamantane

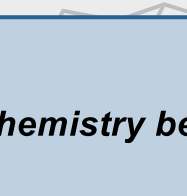


Adamantane

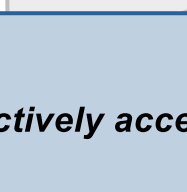
Tetramantane Isomers



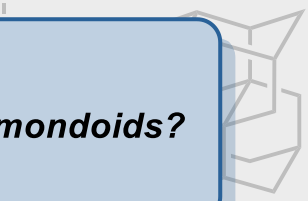
iso-Tetramantane



anti-Tetramantane



(P)-skew-Tetramantane



(M)-skew-Tetramantane

How can synthetic chemistry be used to selectively access higher diamondoids?

Gaining a Functional handle on Diamondoids has implications in many areas:

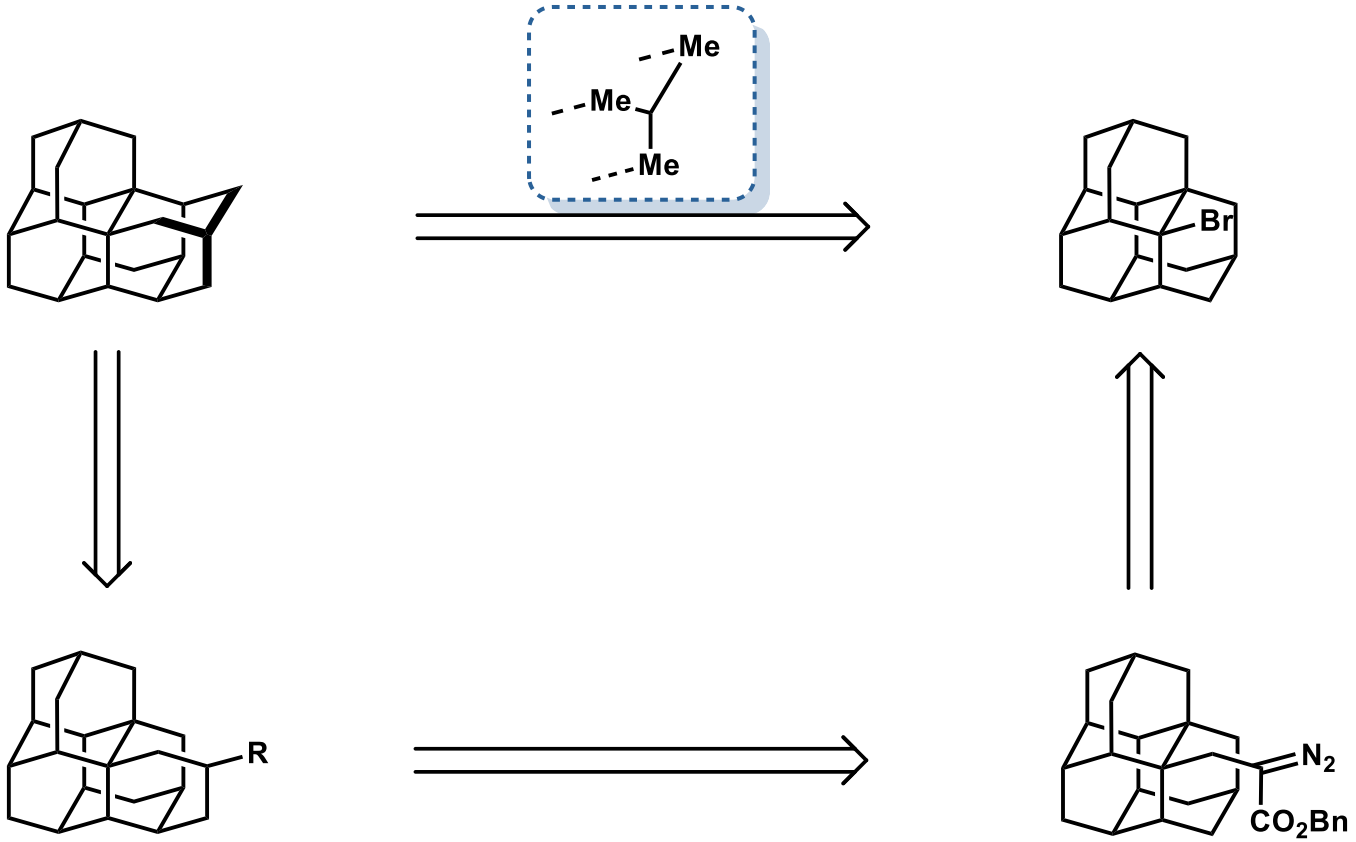
Quantum Computing

Pharmaceuticals

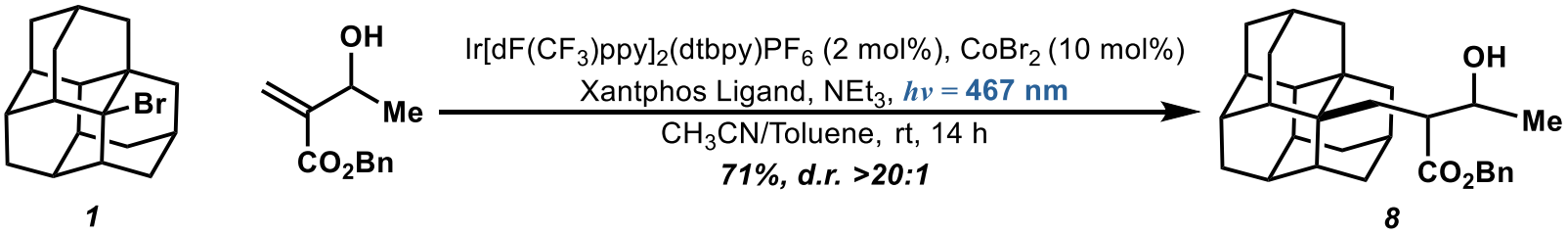
Synthetic Diamonds

Optics

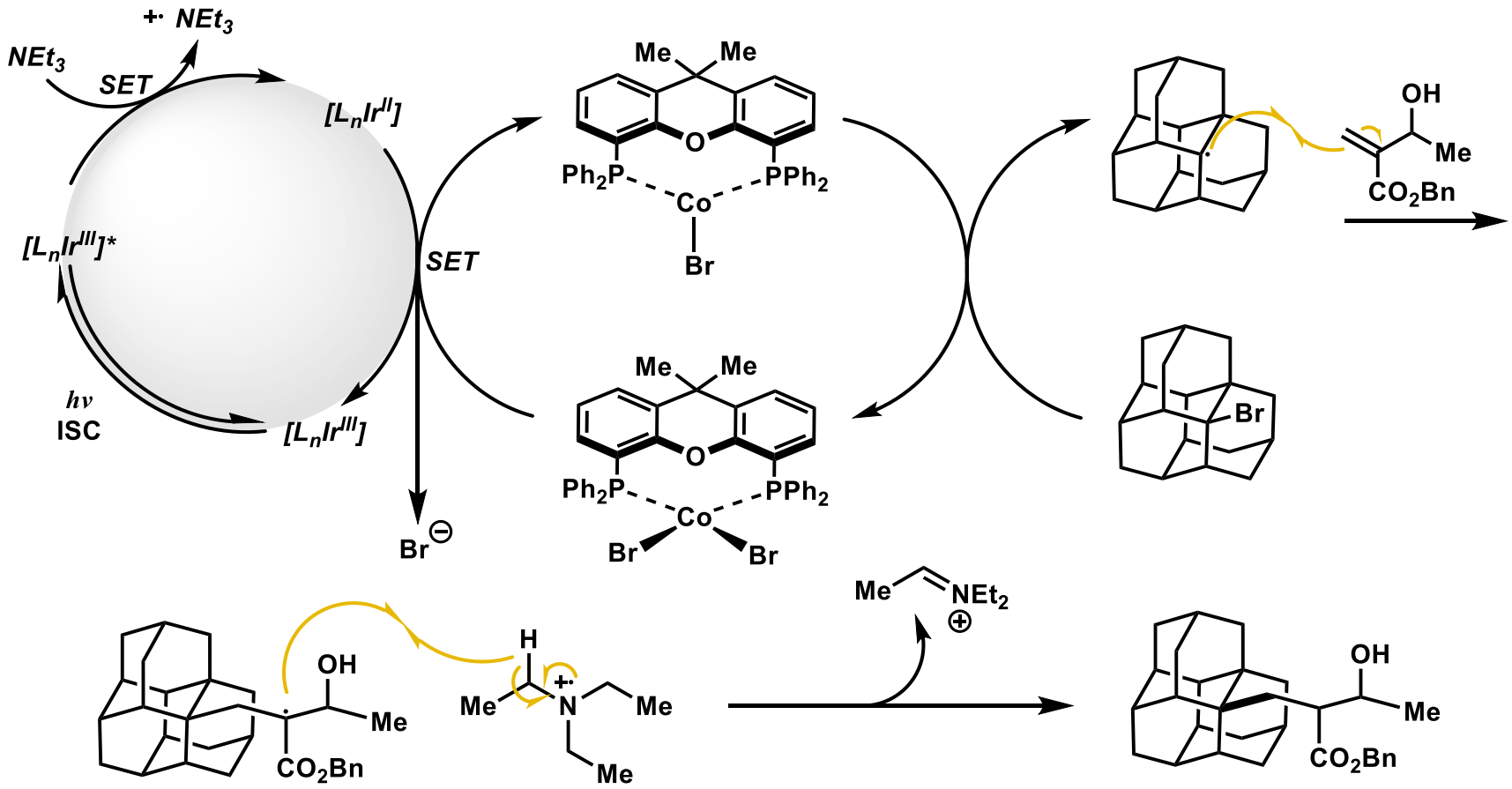
Retrosynthetic Overview



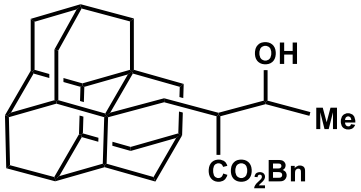
Iridium-Cobalt Giese Reaction



1 8



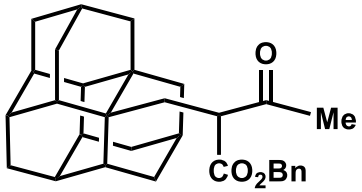
Forward Synthesis I



8

PCC (2 eq), CH_2Cl_2, ***92%***

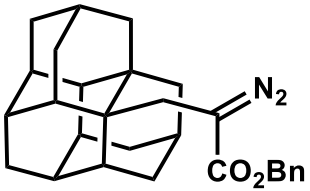
Corey-Suggs Oxidation



9

p-ABSA (1.5 eq), DBU (10 eq)
THF, ***95%***

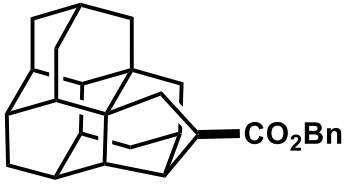
Deacetylative Regitz Diazo Transfer



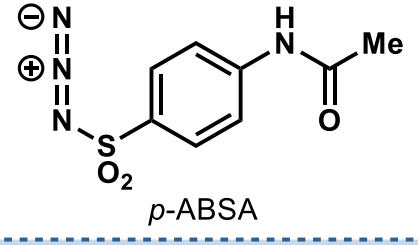
6

Rh_2(*R*-TCPTAD)$_4$ (1 mol%)
CH_2Cl_2, -80°C, ***97%, d.r.>20:1***

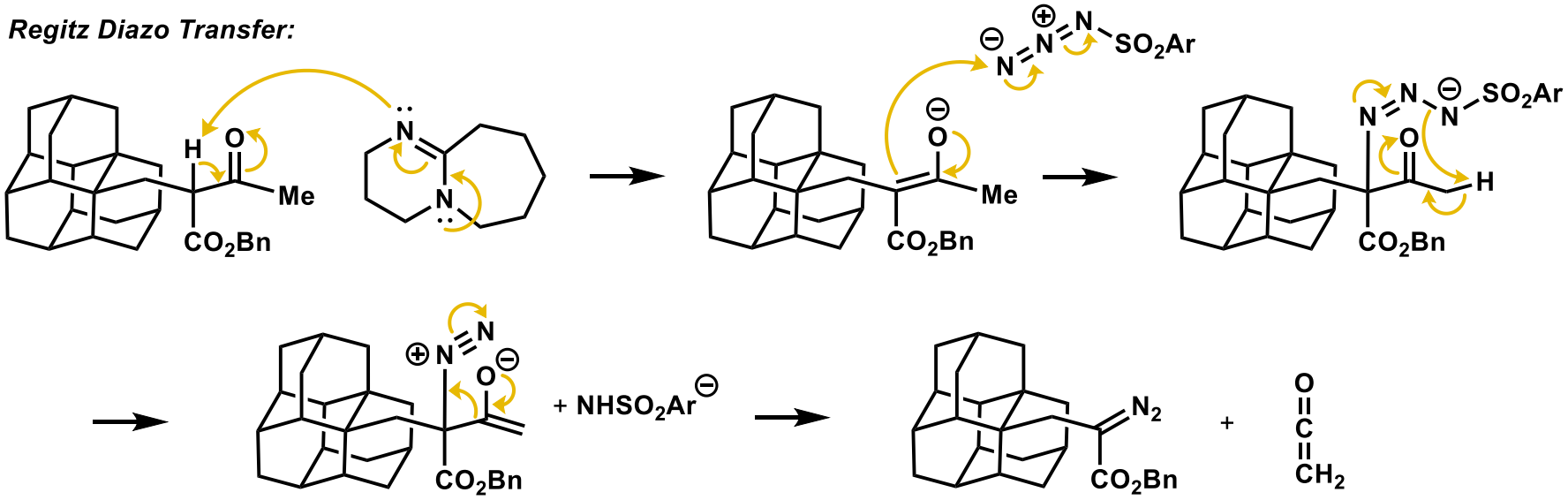
Davies Rh Catalysis



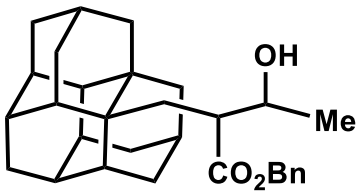
7a



Regitz Diazo Transfer:



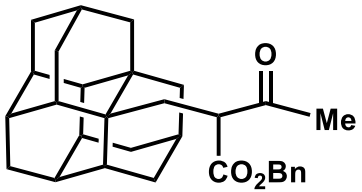
Forward Synthesis I



8

PCC (2 eq), CH_2Cl_2, ***92%***

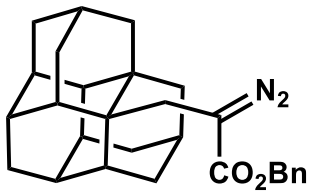
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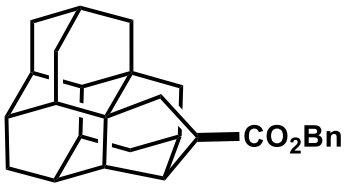
Deacetylative Regitz Diazo Transfer



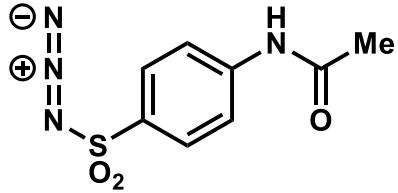
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Davies Rh Catalysis

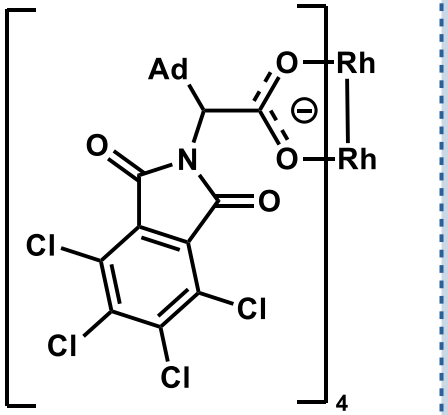


7a

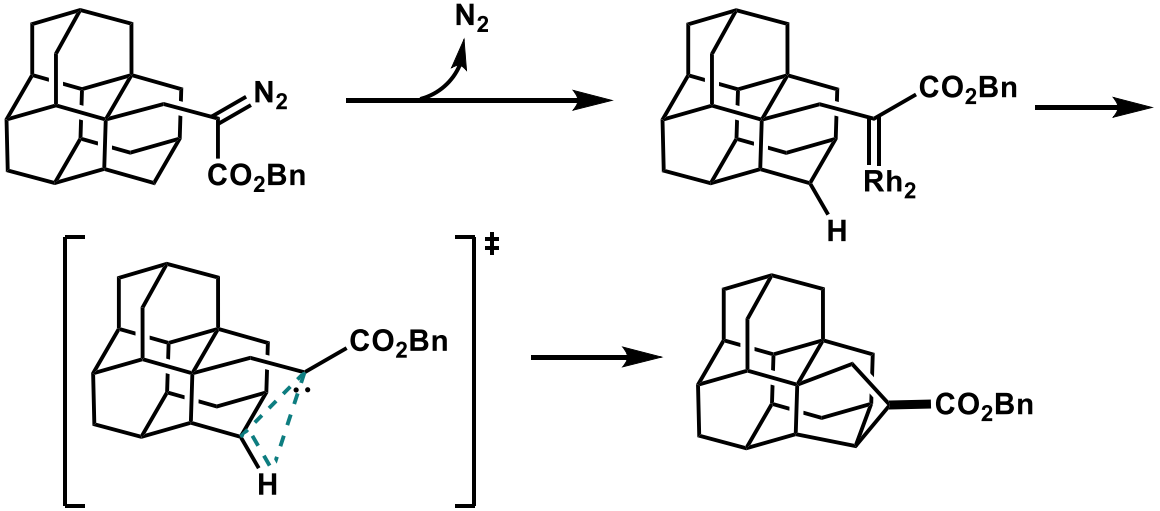


p-ABSA

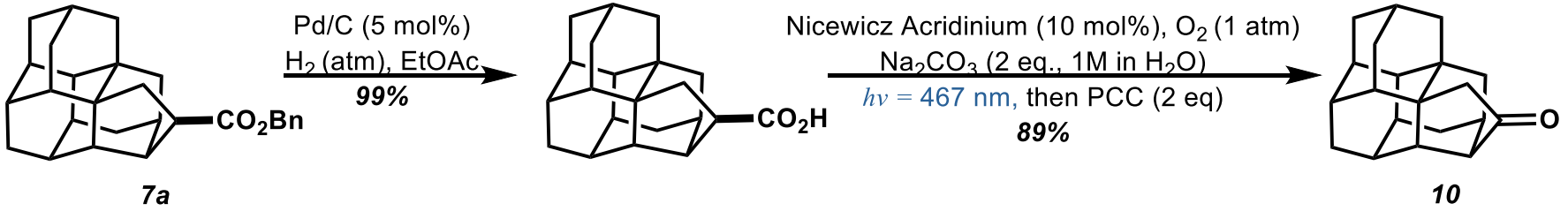
Davies Rhodium Catalysis: C-H Insertion



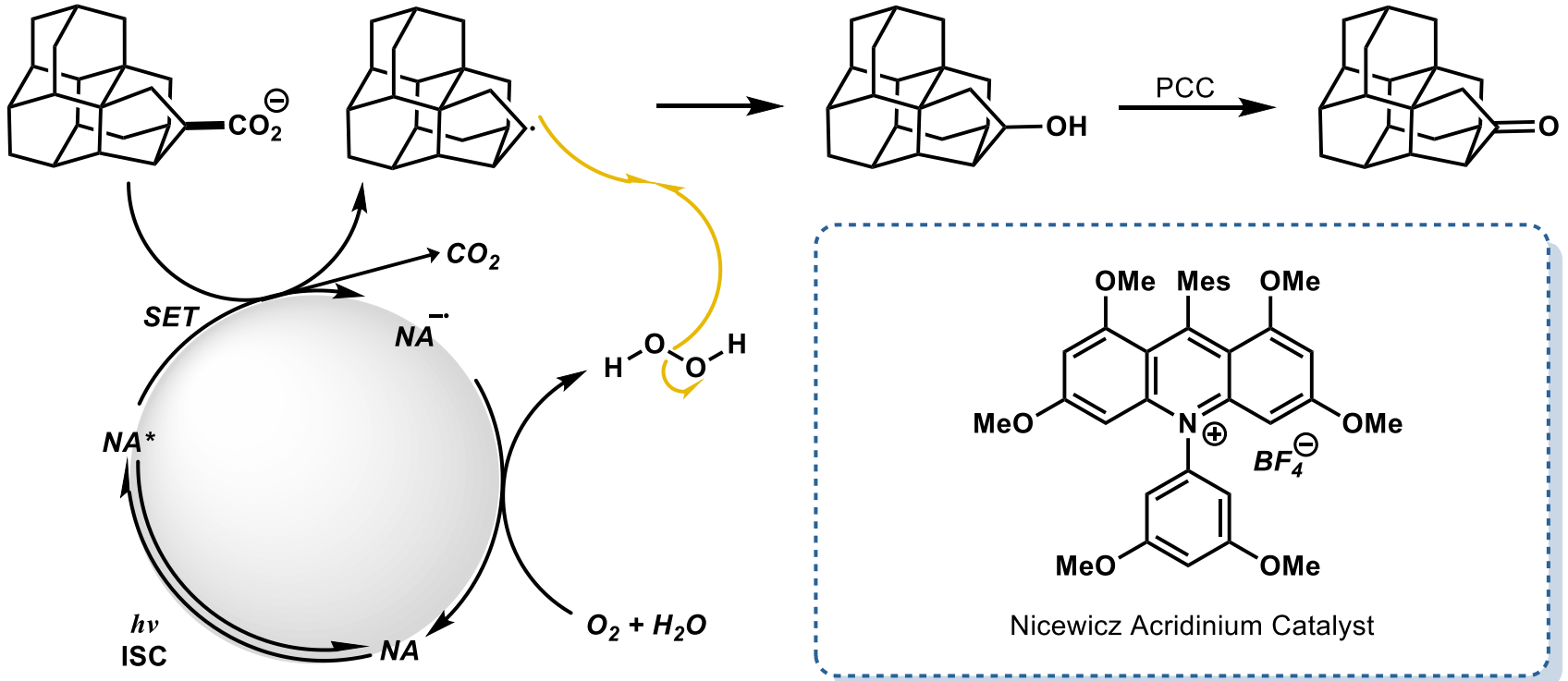
Rh_2(*R*-TCPTAD)$_4$



Decarboxylative Oxidation

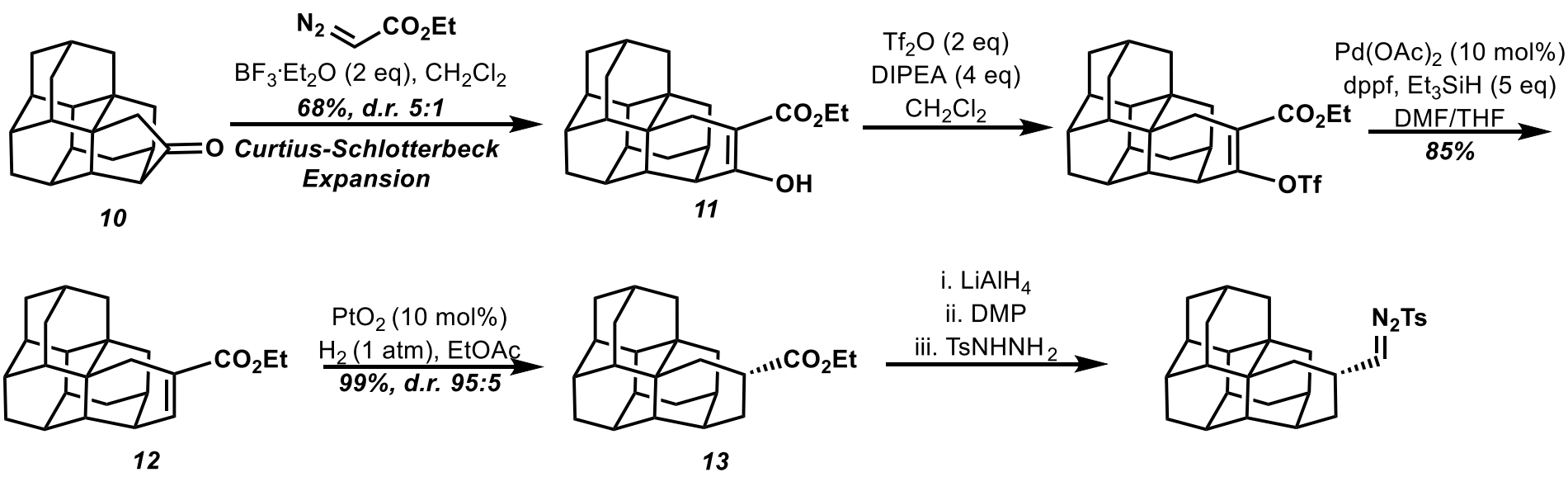


Decarboxylative Oxidation

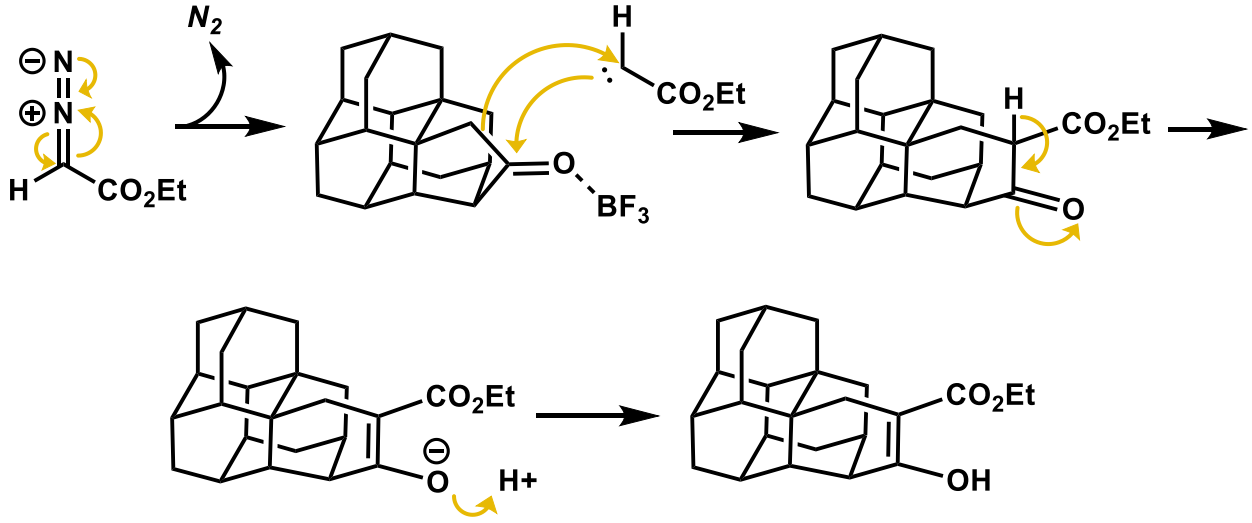


Nicewicz Acridinium Catalyst

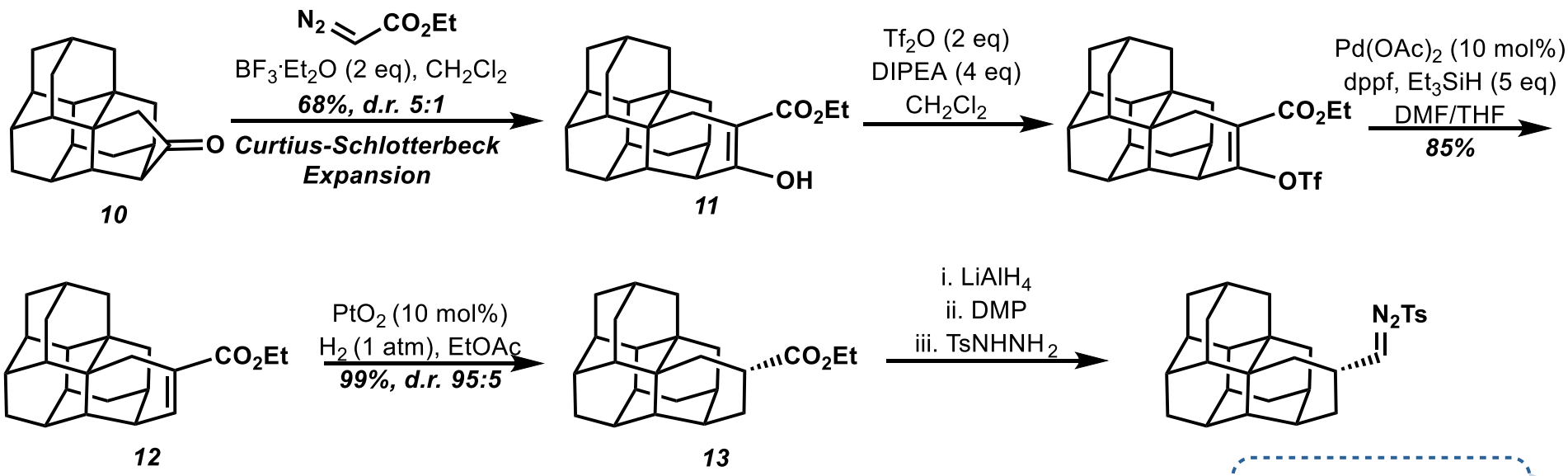
Forward Synthesis II



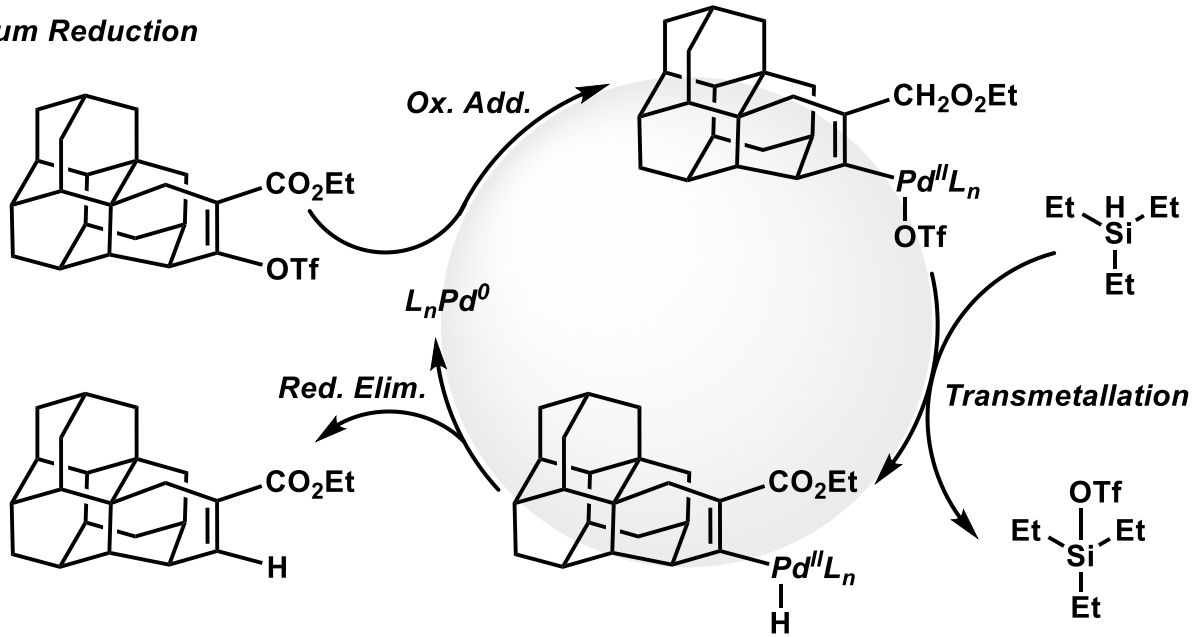
Curtius-Schlotterbeck Ring Expansion

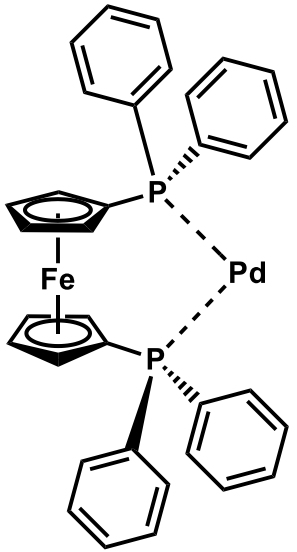


Forward Synthesis II



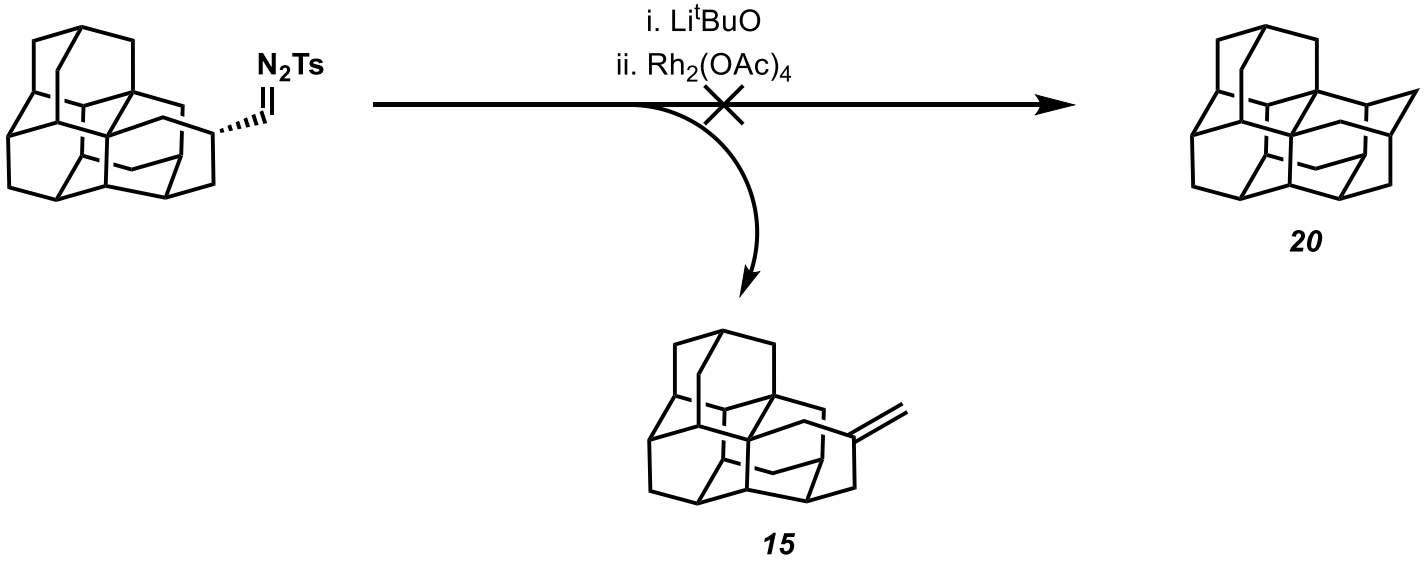
Palladium Reduction



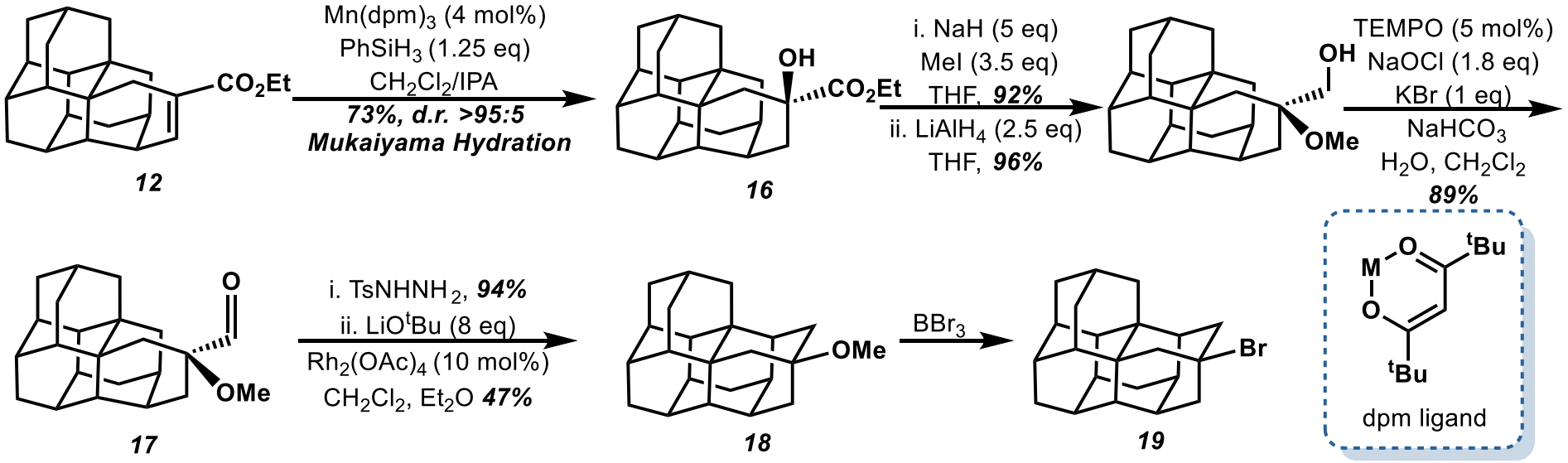


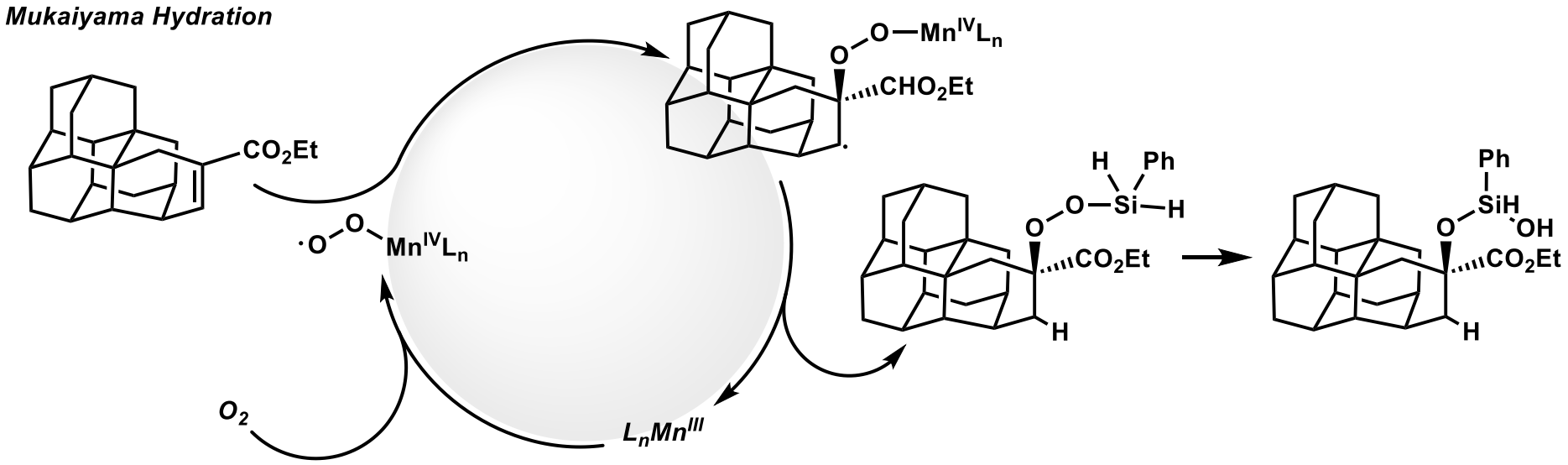
dppf ligand

Attempted Endgame Synthesis

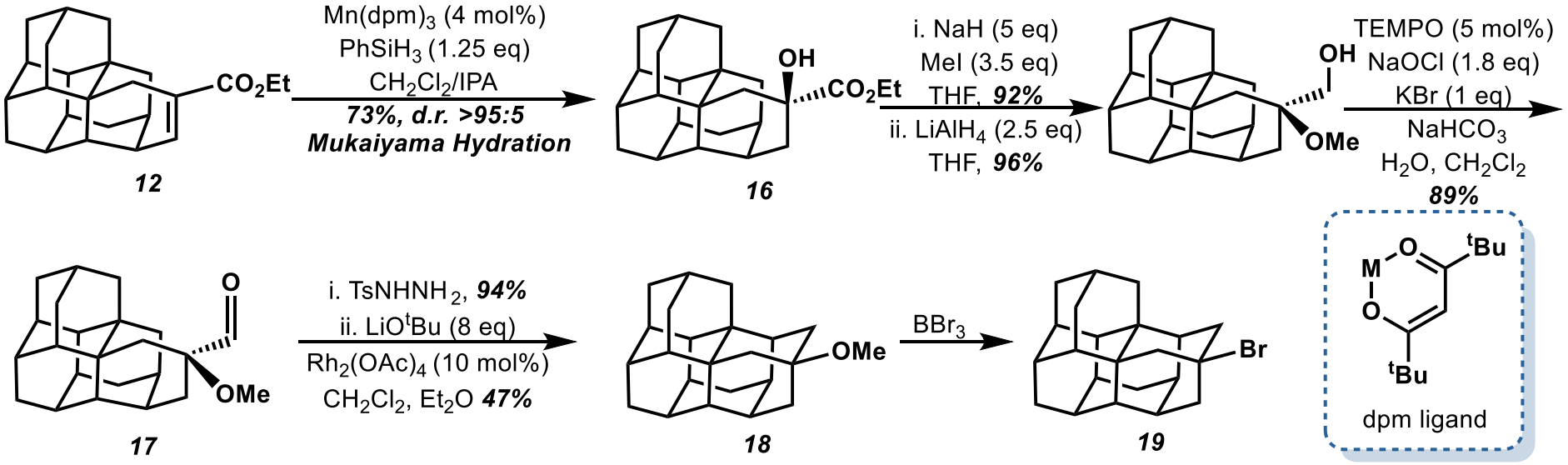


Rerouted Synthesis From Intermediate 12

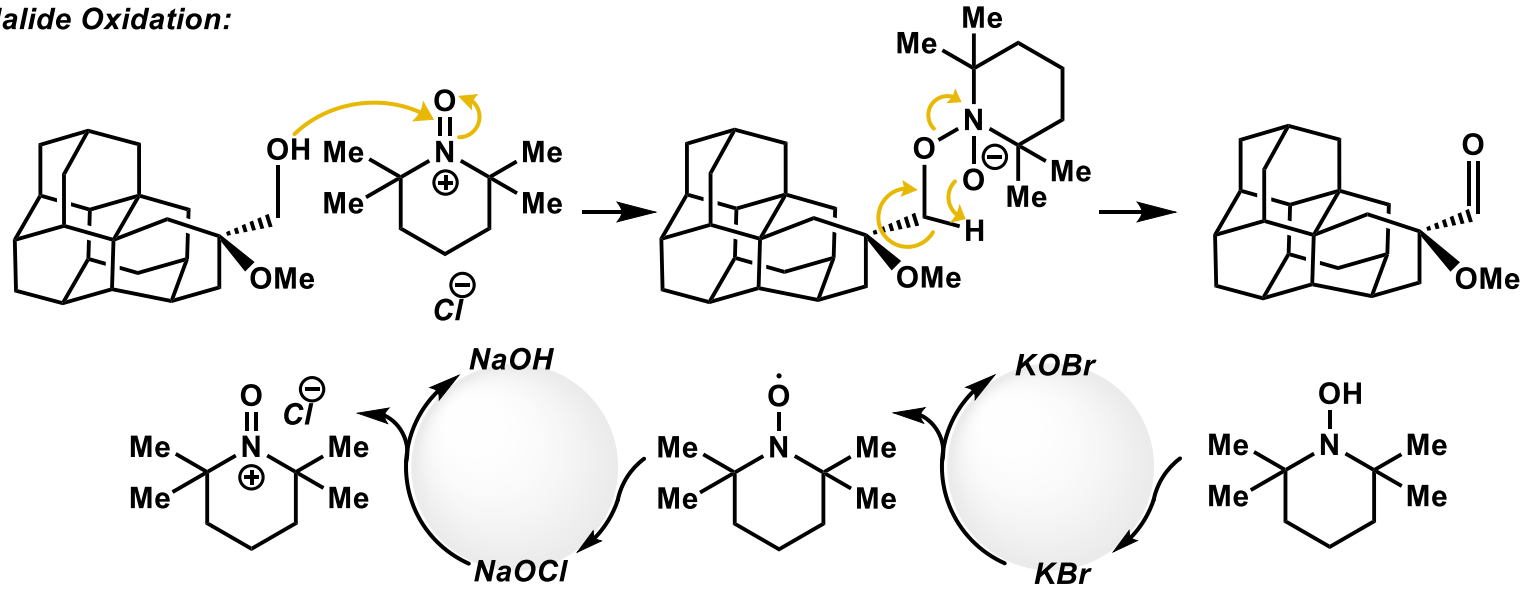




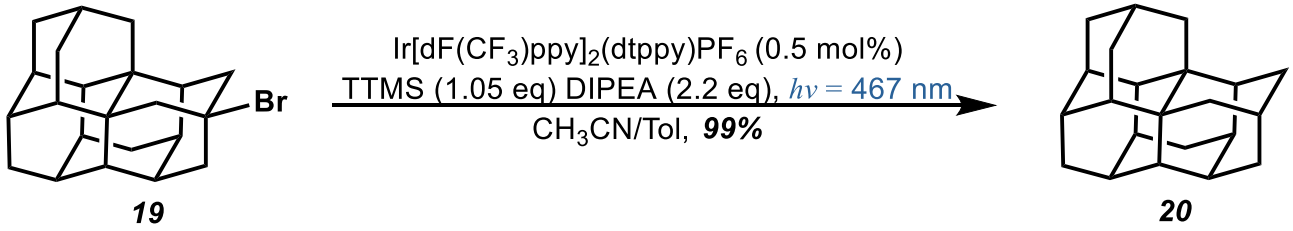
Rerouted Synthesis From Intermediate 12



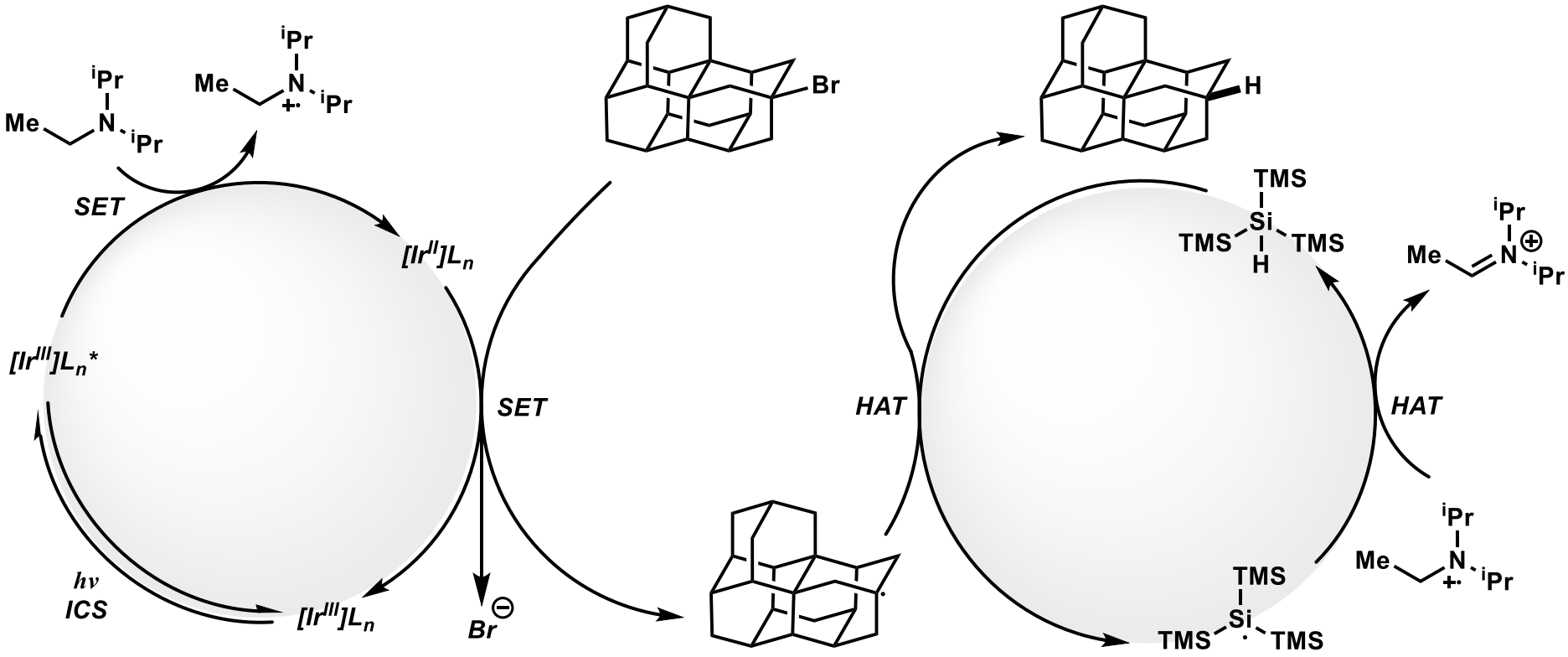
TEMPO-Halide Oxidation:



Final Step: Photocatalytic Dehalogenation



19 20



Conclusions

- The authors demonstrate a first-of-its-kind tetramantane synthesis
- 18 Step synthesis is scalable and high yielding ( )
- Showcase elegant C(sp^3)-H functionalization and metallophotoredox in a highly difficult synthesis
- Establishes a precedent for diamondoid synthesis and functionalization



Thank You for Your Attention!

