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Stereoselective total synthesis of *skew*-tetramantane, diamond's chiral core

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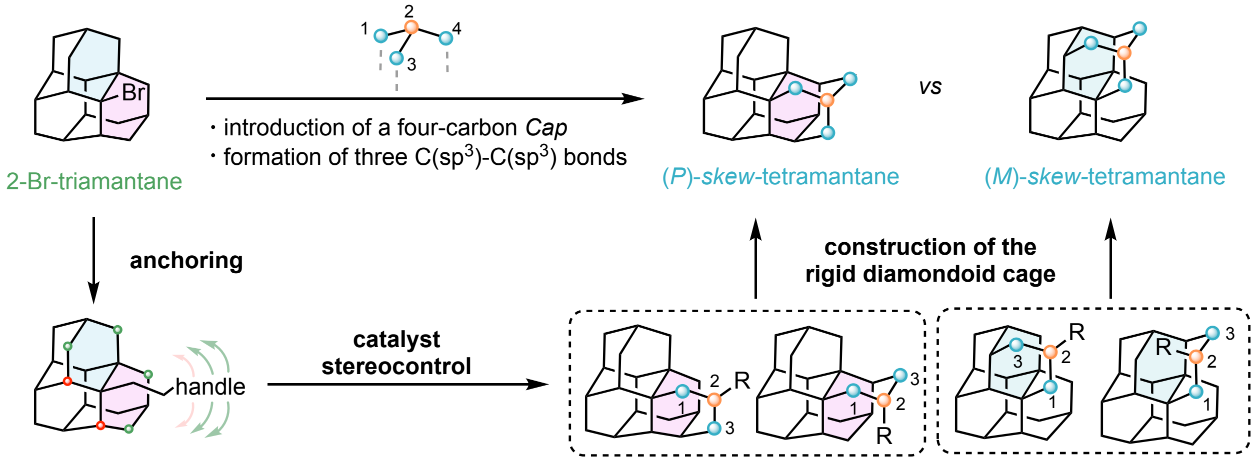
Diamond's elementary chiral constituent – *skew*-tetramantane – features extreme rigidity, stability and a precisely defined geometry, epitomizing the parent structure of a σ-helicene. While *skew*-tetramantane is naturally occurring in trace fractions in fossil fuels, efforts over several decades for its selective synthesis remained unfruitful. With the recent advances in photo- and transition metal catalysis to tame radical and carbene species, we now devised a targeted total synthesis of *skew*-tetramantane by means of a **stereoselective adamantalogous cage-extension**. A first cap attachment was thereby effected by a **photocatalytic Giese reaction**, while remarkable regio-, diastereo- and enantiocontrol were achieved by an **intramolecular C(sp^3)–H insertion** using Davies' chiral rhodium catalysts. **Density functional theory** (**DFT**) calculations elucidate the origin of this high selectivity, revealing a stereoelectronically biased transition state governed by catalyst–substrate interactions. The fusion to the adamantine *skew*-tetramantane structure was completed after a **Buchner–Curtius–Schlotterbeck ring expansion** and a **stereoselective Mukaiyama hydration** by an **intramolecular C(sp^3)–H insertion of a nonstabilized carbenoid**. Overall, this approach provides access to synthetic *skew*-tetramantane in isomerically pure form with σ-helicity defined by catalyst-control, marking a selective pathway to higher diamondoids.



[1] **X.-Y. Li,** C. Sparr. Stereoselective Total Synthesis of *skew*-Tetramantane. *Nat. Chem.* ***2025**, 17, In print. ChemRxiv* **2025**, 10.26434/chemrxiv-2025-bp807.

[2] **X.-Y. Li,** C. Sparr. Streamlined synthesis of triamantane from readily available starting materials. *Helvetica Chimica Acta*. Manuscript in Preparation.

[3] **X.-Y. Li,** C. Sparr. Stereoselective total synthesis of *skew*-tetramantane, diamond's chiral core**.** *Eur. Pat. Appl.* EP 25185320.6, filed June 2025.