

Synthesis of Conjugated Linear and Cyclic Polyynes by Alkyne Metathesis

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- **Martes 11 de Agosto a las 14 horas**
- **Aula: RFP 3er piso DQIAQF/INQUIMAE**
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Resumen

The controlled synthesis of conjugated polyynes with an odd number of carbon–carbon triple bonds remains a significant challenge in organic and organometallic chemistry. Conventional approaches typically rely on irreversible C–C bond-forming reactions, which operate under kinetic control and often suffer from limited selectivity and functional-group tolerance.

In this lecture, I will discuss our recent work on molybdenum-catalyzed alkyne metathesis as a complementary strategy for the synthesis of linear and cyclic carbon-rich architectures. Through reversible $C\equiv C$ bond cleavage and formation, alkyne metathesis enables thermodynamic control and provides selective access to conjugated triynes from diyne substrates. The key to this transformation is the fine-tuning of catalyst structure and substrate sterics, which governs the selectivity toward triyne products over competing diyne formation [1].

Triyne intermediates serve as versatile building blocks for the synthesis of more complex acetylenic systems, including stable cumulenes and extended conjugated polyynes such as pentaynes and heptaynes, accessible through the strategic use of dicobalt masking groups. In addition, the reversible nature of alkyne metathesis is particularly advantageous for macrocyclization reactions, allowing the formation of dehydrobenzannulene macrocycles containing triyne units under thermodynamic control [2].

Overall, this work highlights alkyne metathesis as a powerful tool for the construction of well-defined carbon-rich molecular architectures and opens new opportunities for the design of carbyne analogues, functional π -conjugated frameworks, and molecular materials.

References

- [1] H. Ehrhorn, M. Tamm, “Well-Defined Alkyne Metathesis Catalysts: Developments and Recent Applications”, *Chem. Eur. J.* 2019, 25, 3190-3208.
[2] J. Escudero et al., “Synthesis of Conjugated Linear and Cyclic Polyynes by Selective Alkyne Metathesis”, *Angew. Chem. Int. Ed.*, 2026, e202523344.

