

Role of Spacer Length of Tethered Cationic Molybdenum Complexes in Macrocyclization Efficiency Under Confinement

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Abstract:

Macrocyclic compounds play an important role in pharmaceutical and fragrance chemistry. For entropic reasons, oligomerization competes with macrocyclization. Several immobilization strategies have been developed and used for macrocyclization in recent years. Our group contributed with a biomimetic approach to macro (mono-) cyclization (MMC) for the synthesis of macrocyclic products¹ that entails the pore-selective immobilization of cationic olefin metathesis catalysts inside mesoporous SBA-15 materials, allowing for macrocyclization efficiencies of up to 98% employing surface organometallic chemistry.² In an effort to understand the influence of the spacer length on macrocyclization efficiency, tethered cationic molybdenum imido alkylidene *N*-heterocyclic carbene catalysts were immobilized inside the mesopores of modified SBA-15. We found that both macrocyclization efficiency and *Z*-selectivity scale with the distance of the catalyst to the pore wall, which is in line with theoretical models.

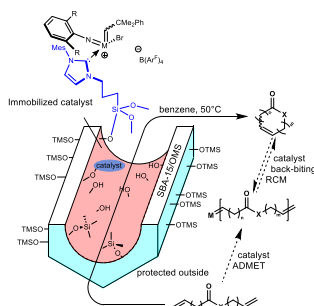


Figure 1: Tethered long-chain cationic molybdenum complexes used for macrocyclization reactions.

[1] F. Ziegler et al., *J. Am. Chem. Soc.*, 2019, **141**, 19014-19022, 10.1021/jacs.9b08776.

[2] F. Ziegler et al., *ACS Catal.*, 2021, **11**, 11570, 10.1021/acscatal.1c03057.