

Fast and selective bisurea catalysts for ring opening polymerization: insights from DFT mechanistic studies

Rachele Zunino,^{1,2} Jia Zhang³, Niklas Warlin,³ Robert M. Waymouth³ and Giovanni Talarico^{1,2}



¹Scuola Superiore Meridionale, Largo San Marcellino 10, 80138 Naples, Italy.

²Department of Chemical Sciences, University of Naples Federico II, Via Cintia, I-80126 Naples, Italy.

³Department of Chemistry, Stanford University, Stanford, California 94305-5080, United States.

rachele.zunino@unina.it



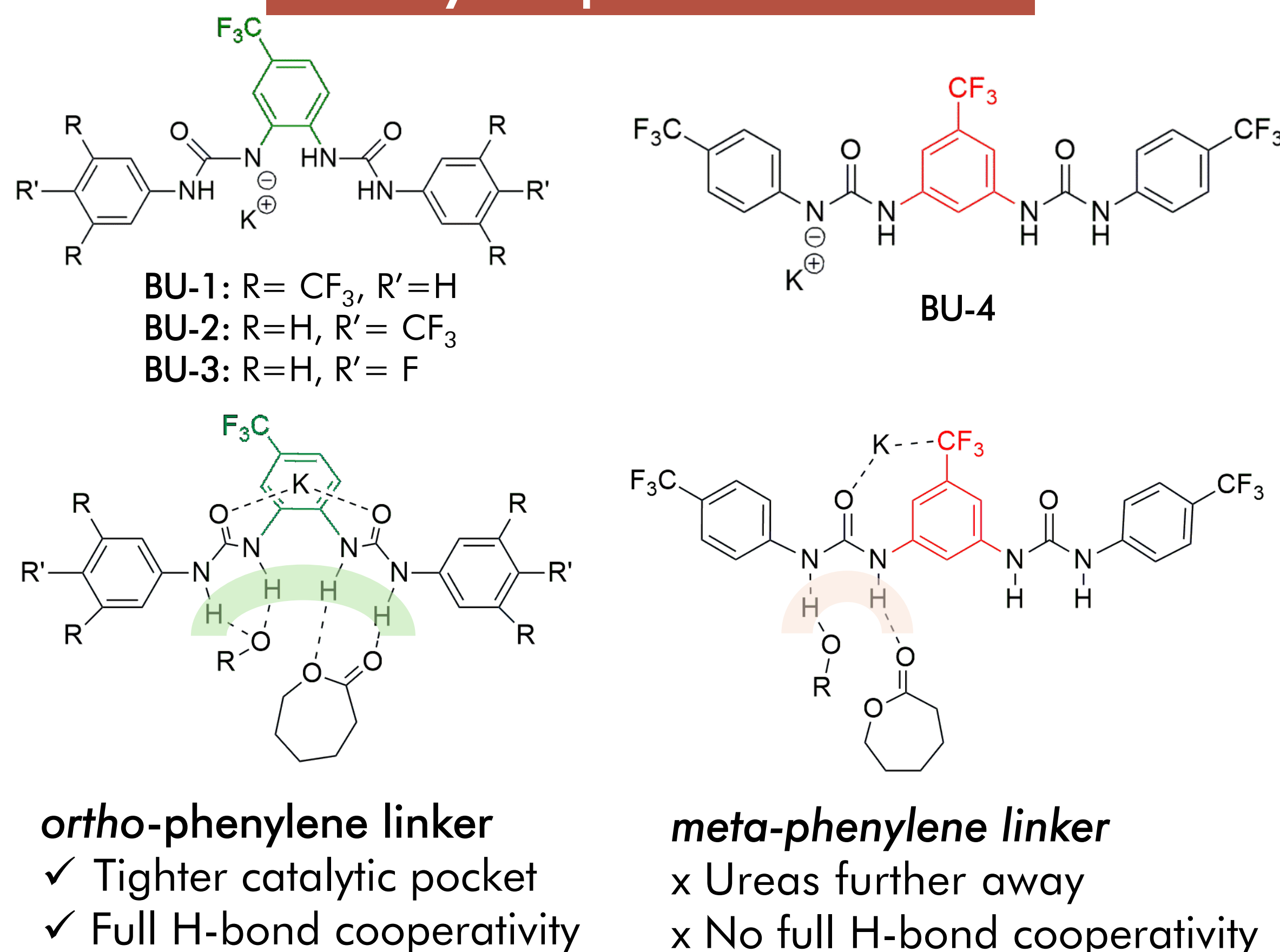
Introduction

Organocatalyzed ring-opening polymerization (ROP) is a versatile technique for synthesizing biodegradable polymers^{1,2}.

We introduce **bisurea** (BU) anions as a novel class of **organocatalysts** that are **fast**, **easily tunable**, and **exceptionally selective**. BU catalysts facilitate the ROP of various monomers, achieving **high conversions** (>95%) **in seconds to minutes**, producing polymers with precise molecular weights and **very low dispersities** ($\mathcal{D} \approx 1.01$)³.

To understand the origin of their exceptional performance, we investigated the ROP of ϵ -CL using Density Functional Theory calculations.

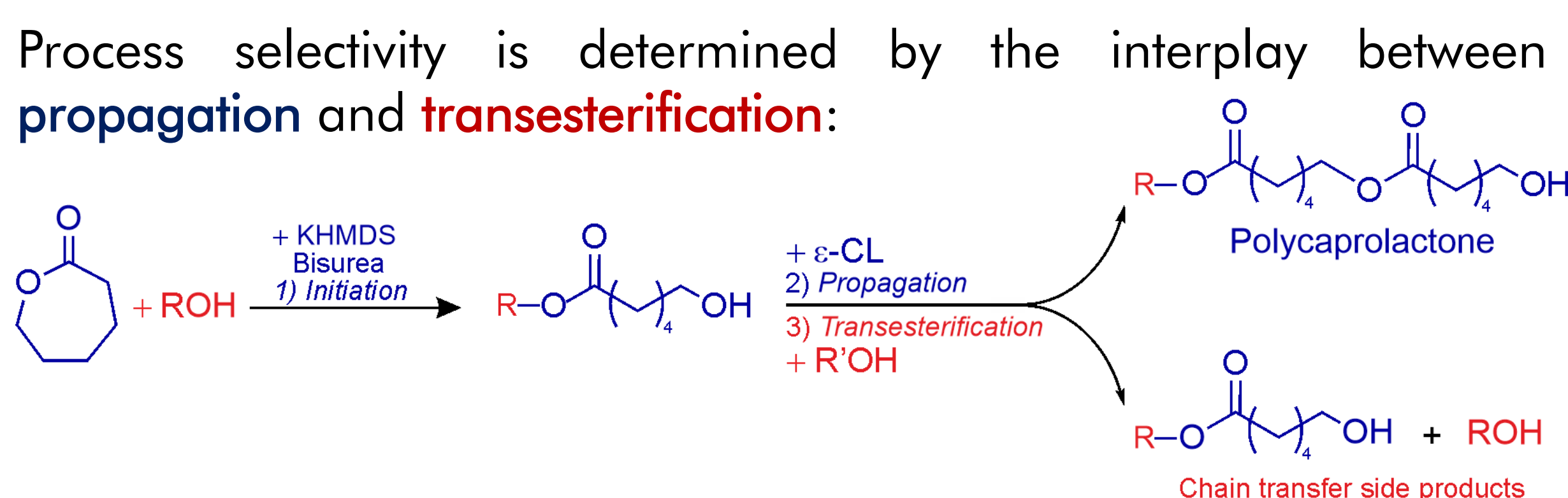
Catalytic species and RCs



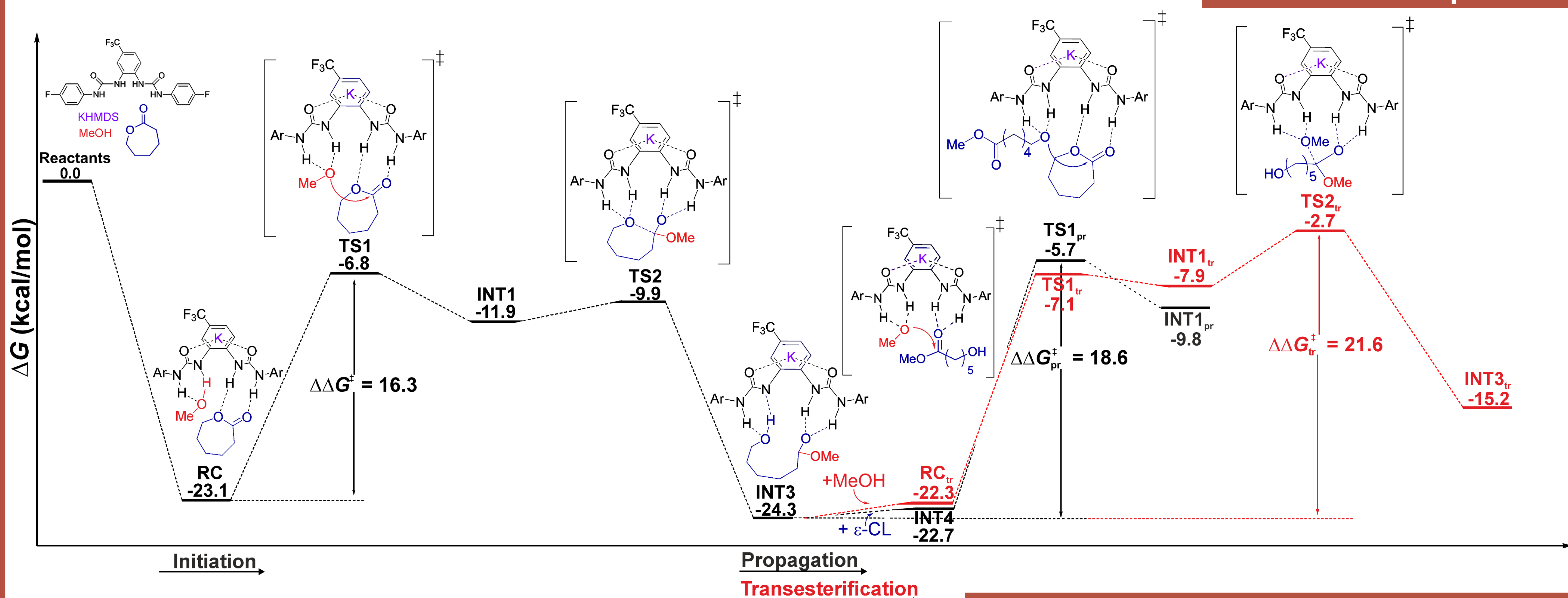
Kinetic and Activation parameters

catalyst	k_p	$\Delta\Delta G_{pr}^\ddagger$	k_p/k_{tr}	$ \Delta\Delta G_{tr}^\ddagger - \Delta\Delta G_{pr}^\ddagger $
BU-1	290	19.5	5714	3.4
BU-2	252	19.9	3350	2.3
BU-3	580	18.6	3803	3.0
BU-4	196	22.4	347	0.9

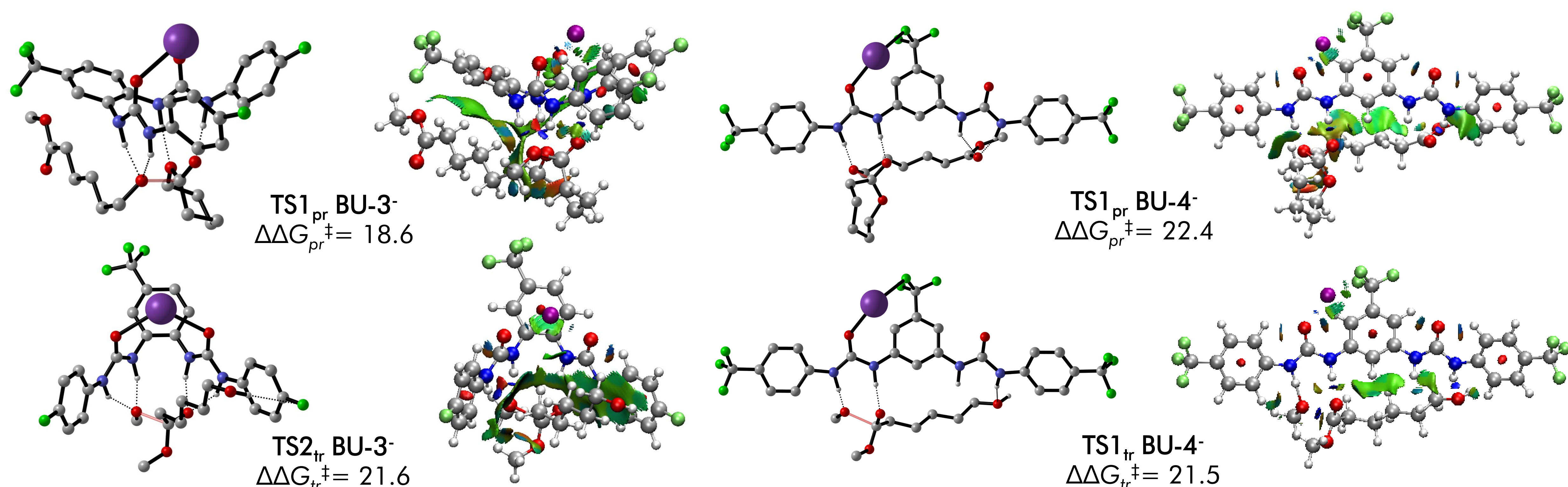
ortho-phenylene BUs display superior activity and selectivity!



DFT reaction pathway



Structures of RDSs and NCI analysis



Conclusions

DFT calculations revealed that the **remarkable activity** and **selectivity** of BUs arise from the **cooperativity of H-bonding sites**, which is fully enabled only when an *ortho*-phenylene linker brings the urea groups into close proximity and electronic conjugation.

Moreover, the semi-rigid linker plays a key role in shaping a **catalytic pocket** that is both **tight** and **flexible**, efficiently promoting ϵ -CL ROP, while suppressing competitive transesterification thus ensuring high process selectivity.

¹Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M. *Macromolecules* 2010, 43, 2093–2107.

²Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. *Chem. Rev.* 2007, 107 (12), 5813–5840.

³Zhang, J.; Lui, K.H.; Zunino, R.; Jia, Y.; Morodo, R.; Warlin, N.; Hedrick, J. L.; Talarico, G.; Waymouth, R.M. *J. Am. Chem. Soc.* 2024, 146 (32), 22295–22305