

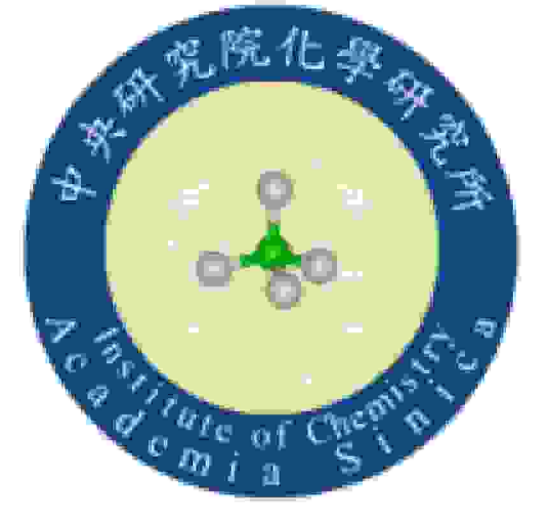


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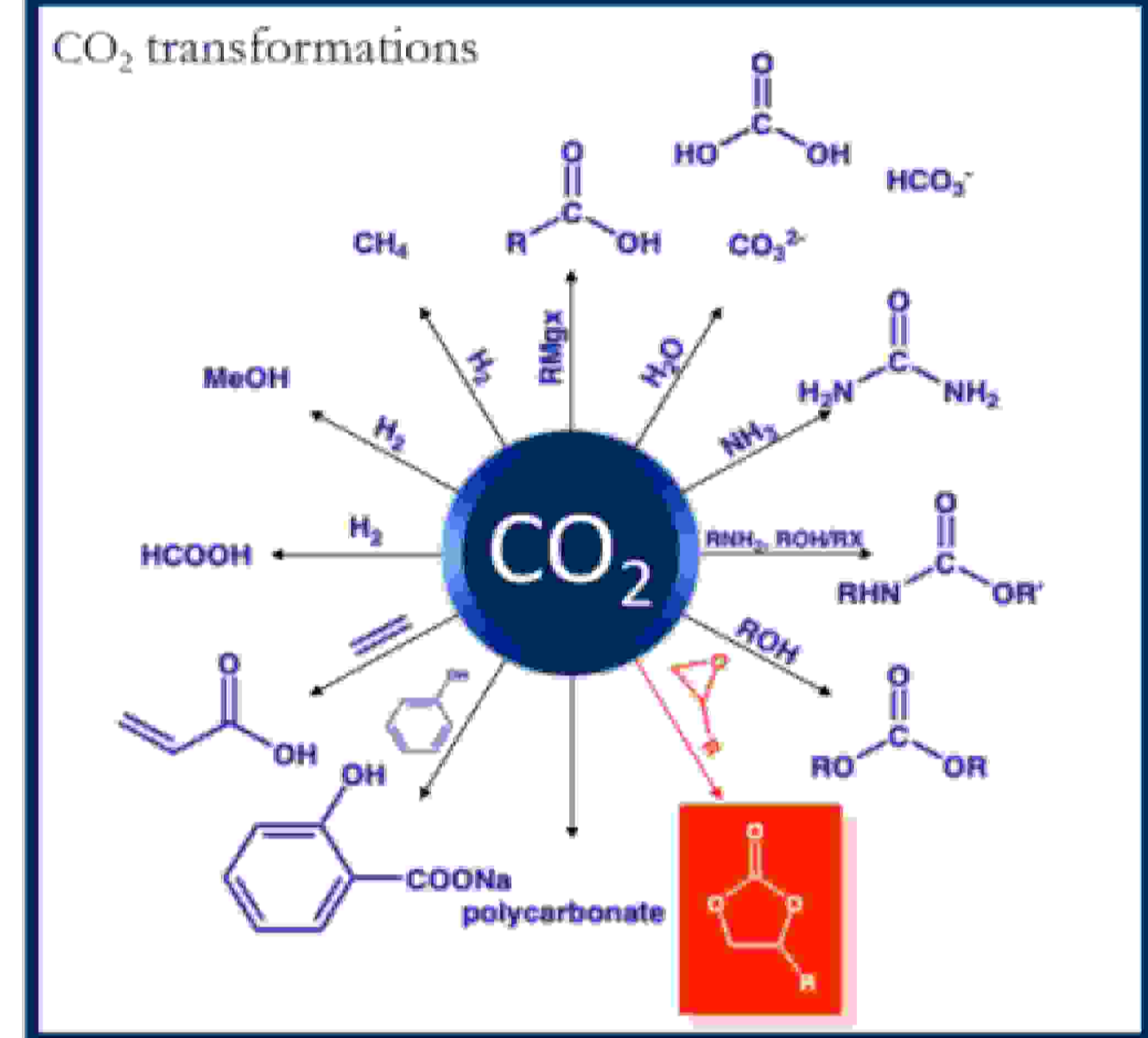
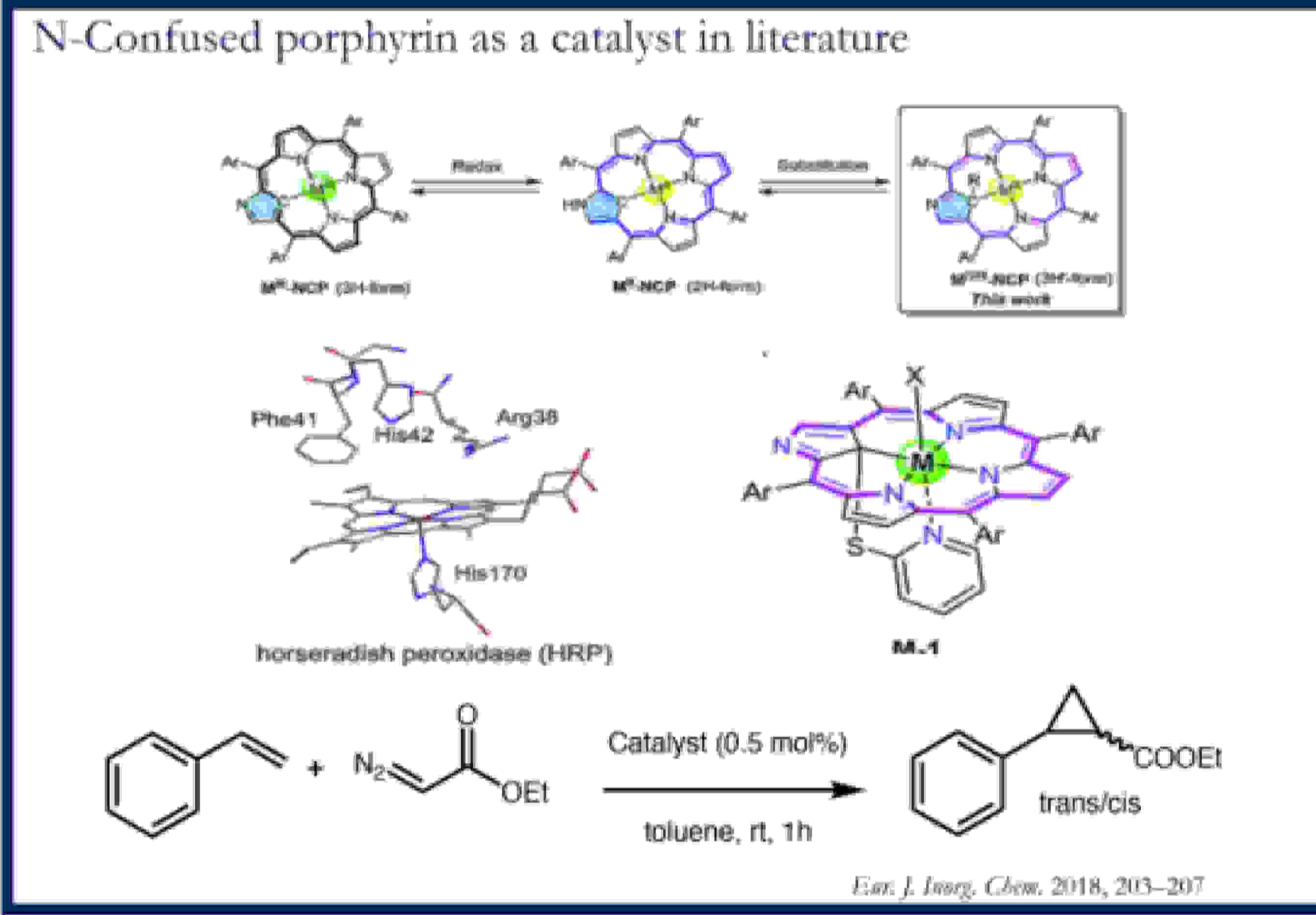
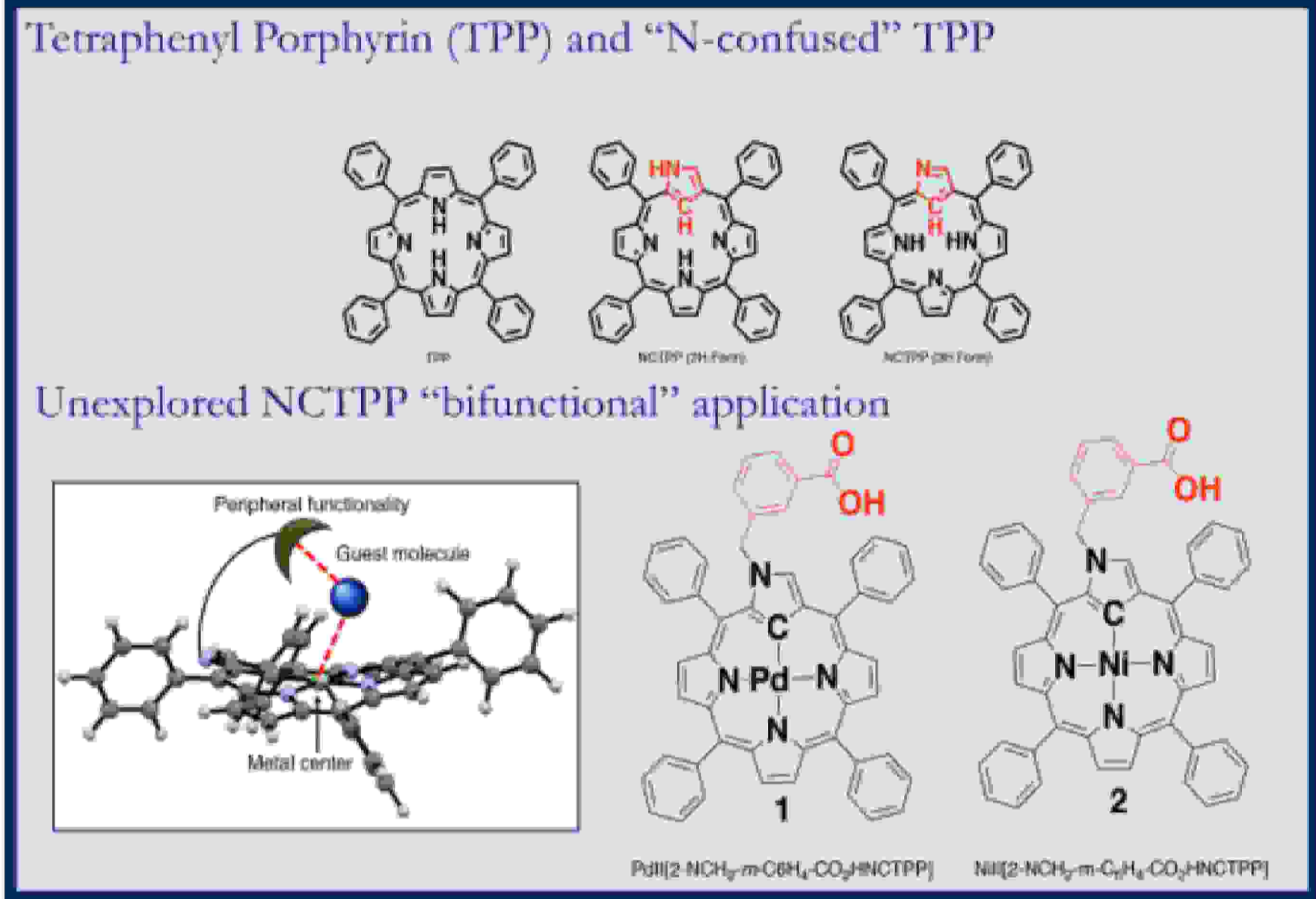
From Confusion to Fixation: Designing bifunctional N-Confused Porphyrin complexes as catalysts for CO₂ fixation[†]

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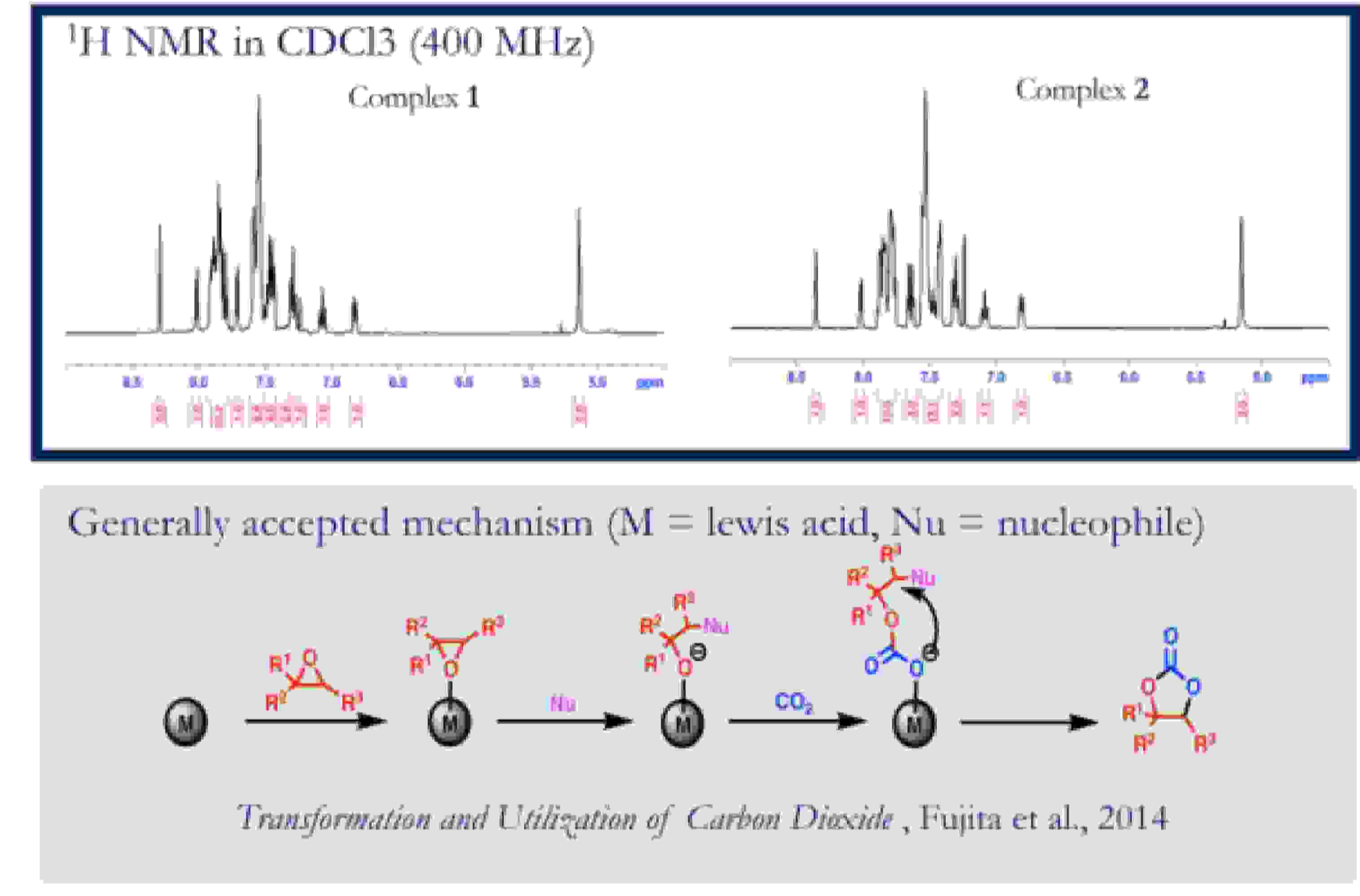
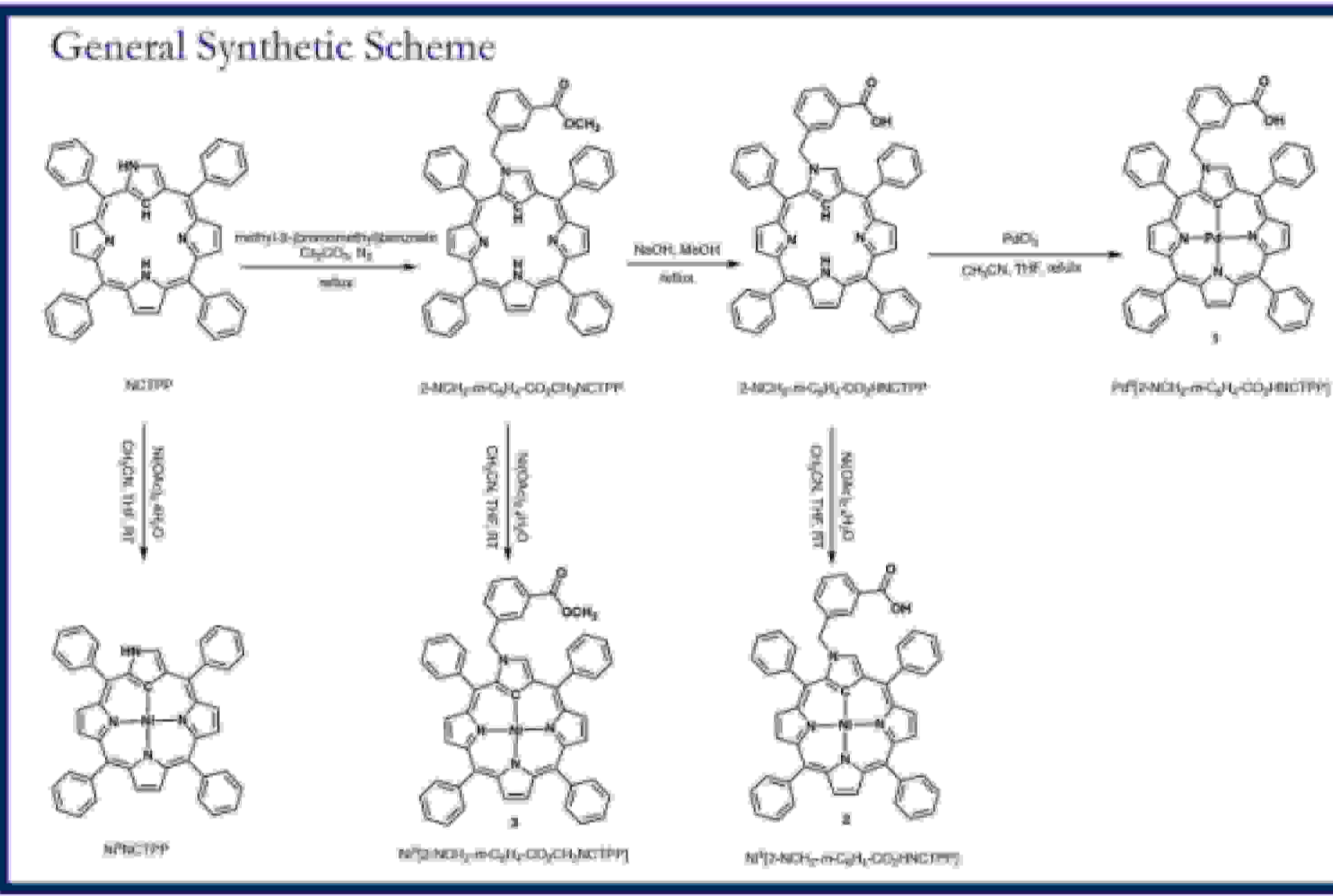
Abstract

This work demonstrates the design of the first bifunctional catalyst that is based on N-confused tetraphenyl porphyrin (NCTPP) scaffold for the cycloaddition of epoxide to carbon dioxide to produce value added cyclic carbonates. Catalysis is achieved *via* cooperative activation of epoxide through a metal center and a peripheral benzoate moiety, together making up the molecule's bifunctional structure. Palladium complex (complex 1) facilitated percent conversion of 99% and TON = 7000. Complex 2, with a cheaper and more environmentally benign nickel center gave comparable catalytic efficiency. A second generation of catalysts, whose peripheral functionality comprises an alkylammonium bromide group shows great promise in terms of easier and step-economic preparation. Overall, the simplicity of the synthetic route towards the peripheral nitrogen modification as well as the ease of metalation can be exploited to design other bifunctional NCTPP catalytic systems using the current catalysts as model molecules.

Introduction



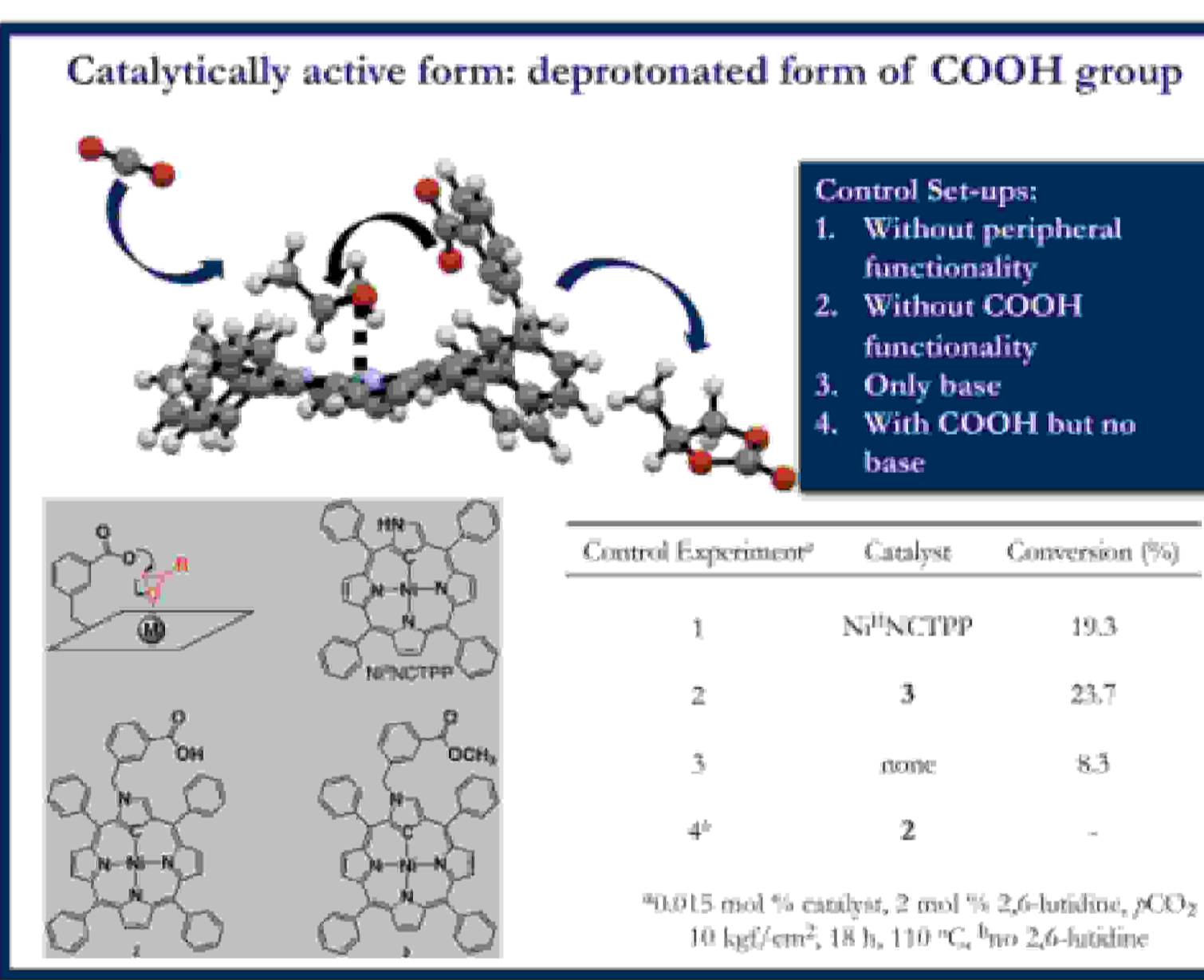
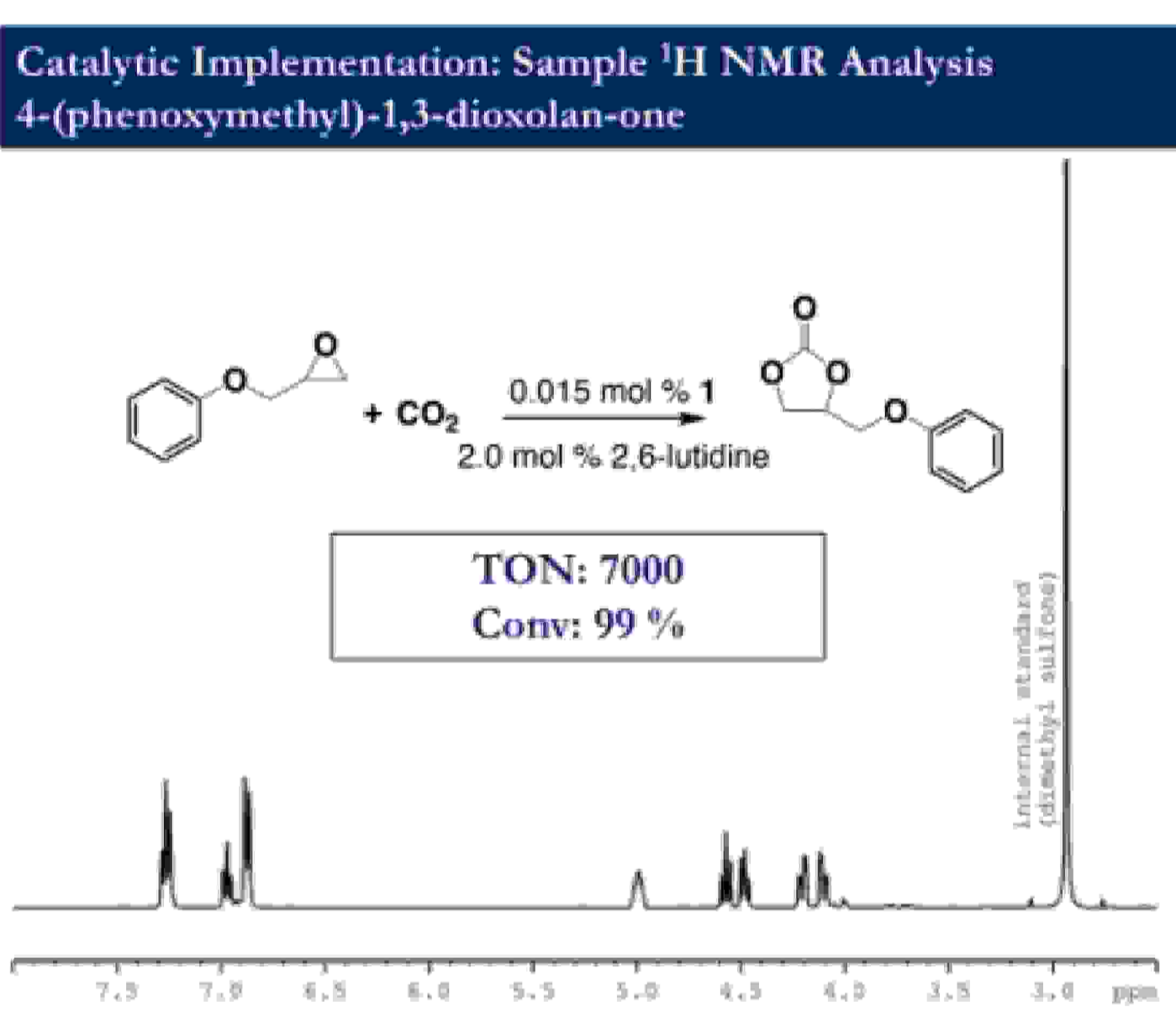
Synthetic Scheme & Characterization



Complex 1 HRMS(ESI _{neg})	
C ₅₂ H ₃₃ N ₄ O ₂ Pd ([M-H] ⁻)	
Calcd	Found
851.1638	851.1644

Complex 2 HRMS(ESI _{neg})	
C ₅₂ H ₃₃ N ₄ O ₂ Ni ([M-H] ⁻)	
Calcd	Found
803.1957	803.1967

Hypothesis & Preliminary Results



Nickel Complex 2 Activity

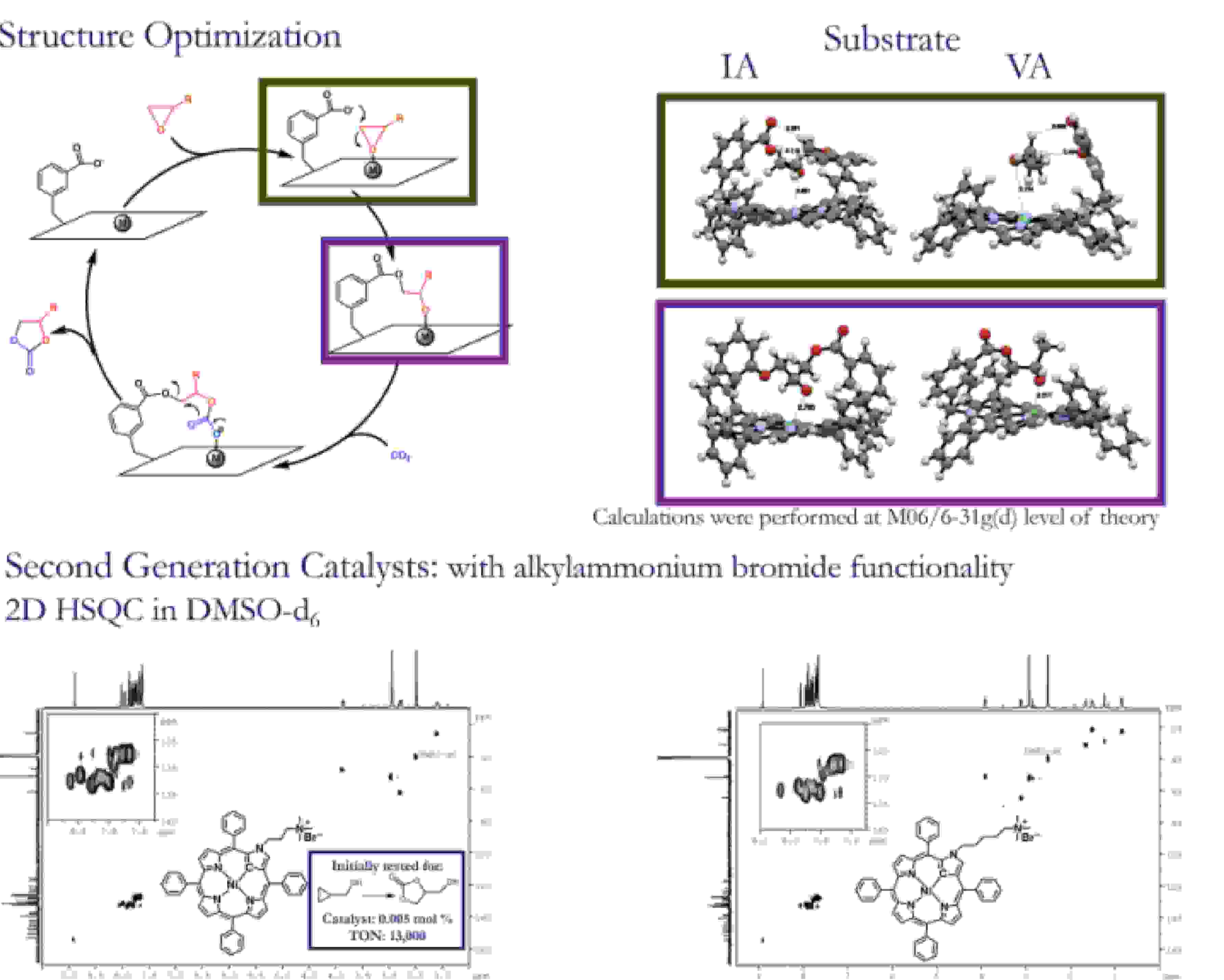
Catalyst	1	2
Reaction Conditions	• 0.015 mol % 1 • 6 mol % TEA • CO ₂ pressure: 10 kgf/cm ² • 18 h • 120 °C	• 0.015 mol % 2 • 2 mol % 2,6-lutidine • CO ₂ pressure: 10 kgf/cm ² • 18 h • 110 °C
TON	7000	6000
Conversion (%)	99	90.4

Catalytic Implementation Conclusion & Future Direction

Synthesis^a of cyclic carbonates using 2 as bifunctional catalyst

Entry	Substrate	Product	Conv (%)	TON
1	IA	IB	90.4	6000
2	IIA	IIB	98.0	6500
3	IIIA	IIIB	92.0	6100
4 ^b	IVA	IVB	89.5	3000
5	VA	VB	24.8	1600

^aReactions in stirred autoclave reactor. Conditions: pCO₂ = 0.98 MPa, T = 110 °C, 18 h, 0.015 mol % 2 and 2.0 mol % 2,6-lutidine (3.0 mol % 2,6-lutidine)



Second Generation Catalysts:

- "Step-economic" preparation
- No need for auxiliary agents (e.g., deprotonating base)
- Higher catalytic efficiency

Conclusion

- Successful synthesis of first NCTPP bifunctional catalysts
- Organic solvent-free cyclic carbonate synthesis, an important intermediate in the "green" polyurethane synthesis
- Preference towards functional epoxides as supported by theoretical calculations

Acknowledgment

Mass spectrometry analyses were performed by Mass Spectrometry facility of the Academia Sinica, Taiwan. X-Ray data collections were performed by X-Ray Laboratory of Institute of Chemistry, Academia Sinica. The financial support from Ministry of Science and Technology of Taiwan and Academia Sinica are highly appreciated.

[†]Based on our work published as a communication in Dalton Transactions in June 2019. DOI: 10.1039/C9DT00048R