

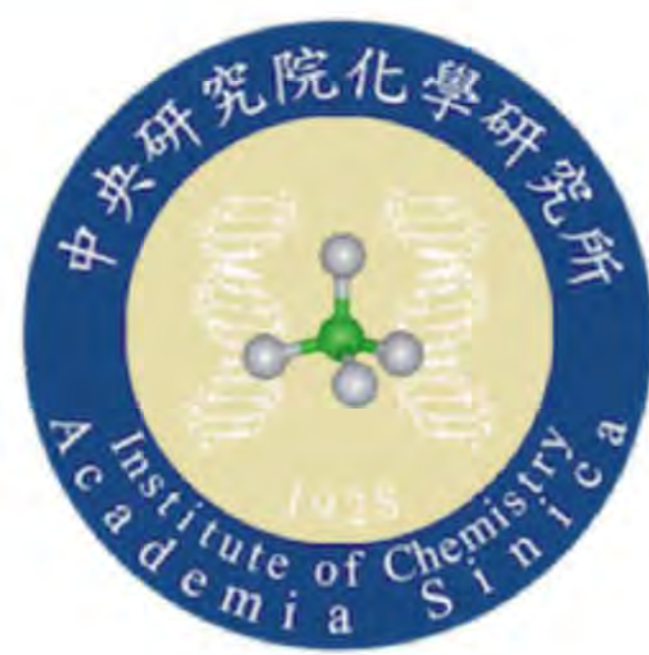


2021「中技社科技獎學金」

2021 CTCI Foundation Science and Technology Scholarship

境外生研究獎學金

Research Scholarship for International Graduate Students



The Green Approach for Chemical Synthesis: Enzymatic Mimic Reactivity Promoted by Frustrated Lewis Pair-like of Carbene



Yi-Chen Chan^{a,b,c}, Wen-Ching Chen^a and Tiow-Gan Ong^{a*}

^aInstitute of Chemistry, Academia Sinica, No. 128, Sec. 2, Academia Road, Nangang, Taipei 11529, Taiwan, R.O.C.

^bDepartment of Applied Chemistry, National Chiao Tung University, No. 1001, Ta Hsueh Road, Hsinchu 300, Taiwan, R.O.C.

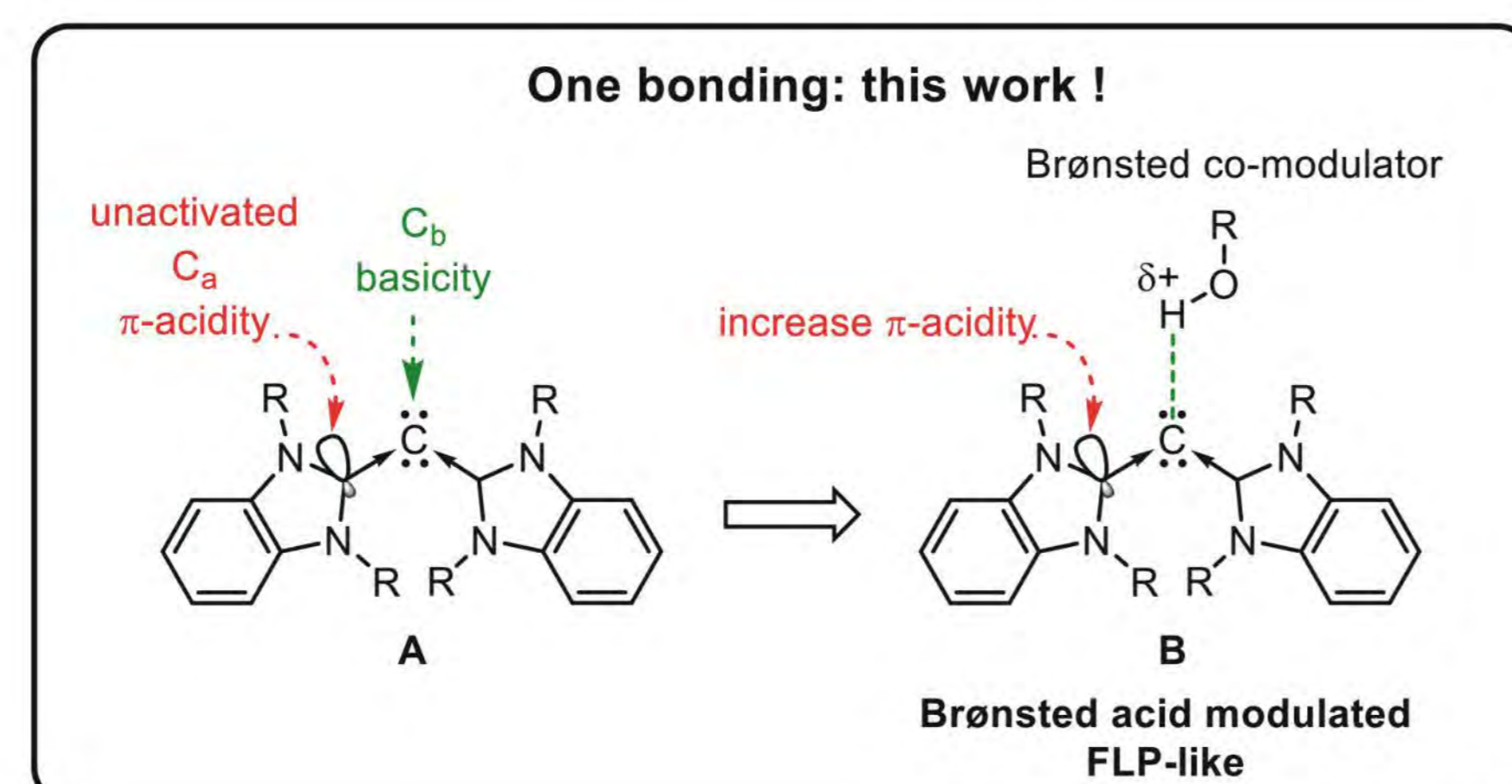
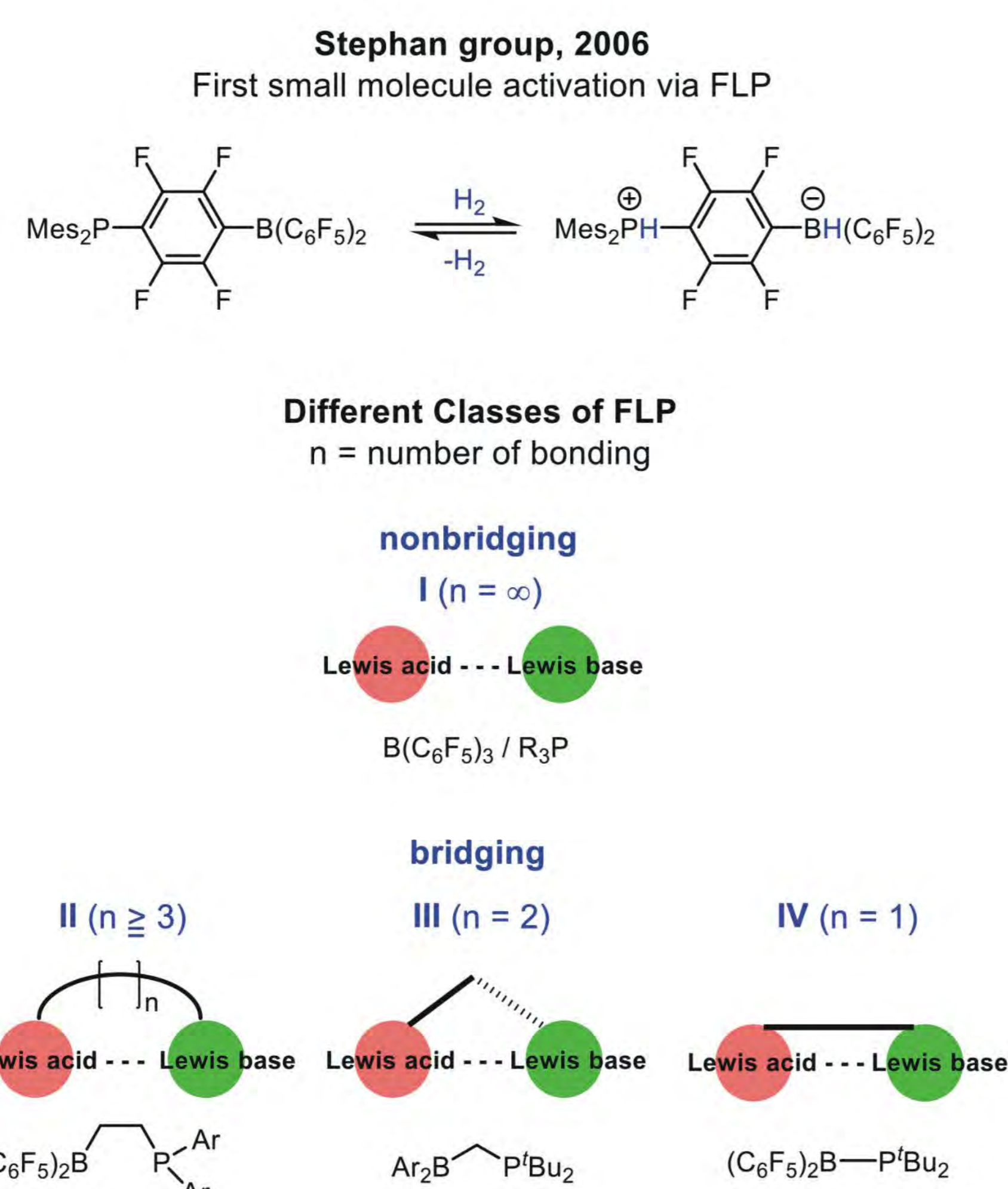
^cSustainable Chemical Science and Technology, Taiwan International Graduate Program, Academia Sinica and National Chiao Tung University, Taiwan, R.O.C.

E-mail: tgong@gate.sinica.edu.tw

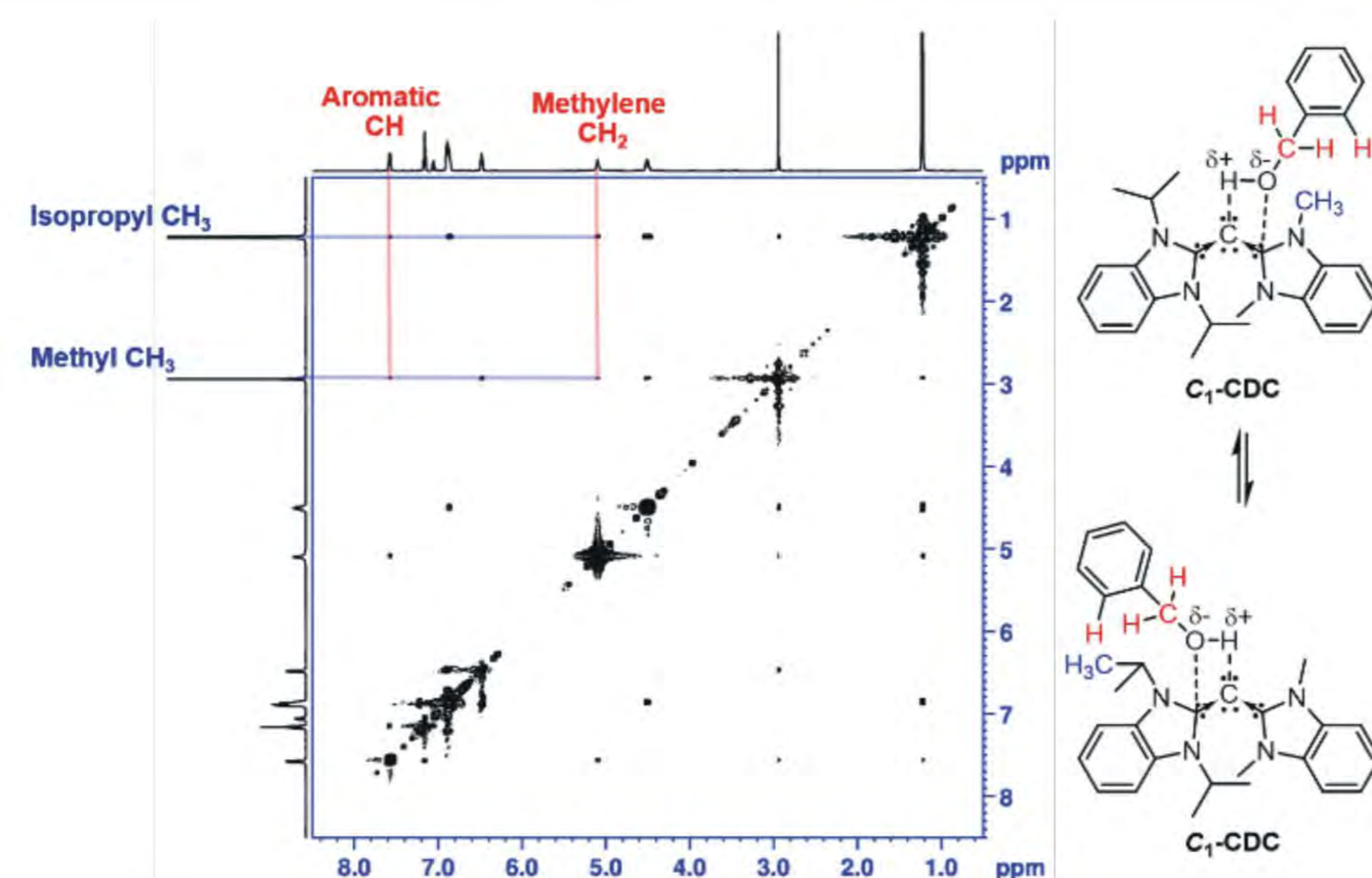
Abstract

Carbodicarbene (CDC), unique carbenic entities bearing two lone pairs of electrons are well-known for their strong Lewis basicity. We demonstrate herein, upon introducing a weak Brønsted acid benzyl alcohol (BnOH) as a co-modulator, CDC is remoulded into a Frustrated Lewis Pair (FLP)-like reactivity. DFT calculation and experimental evidence show BnOH loosely interacting with the binding pocket of CDC via H-bonding and π - π stacking. Four distinct reactions in nature were deployed to demonstrate the viability of proof-of-concept as synergistic FLP/Modulator (CDC/BnOH), demonstrating enhanced catalytic reactivity in cyclotrimerization of isocyanate, polymerization process for *L*-lactide (LA), methyl methacrylate (MMA) and dehydrosilylation of alcohols.

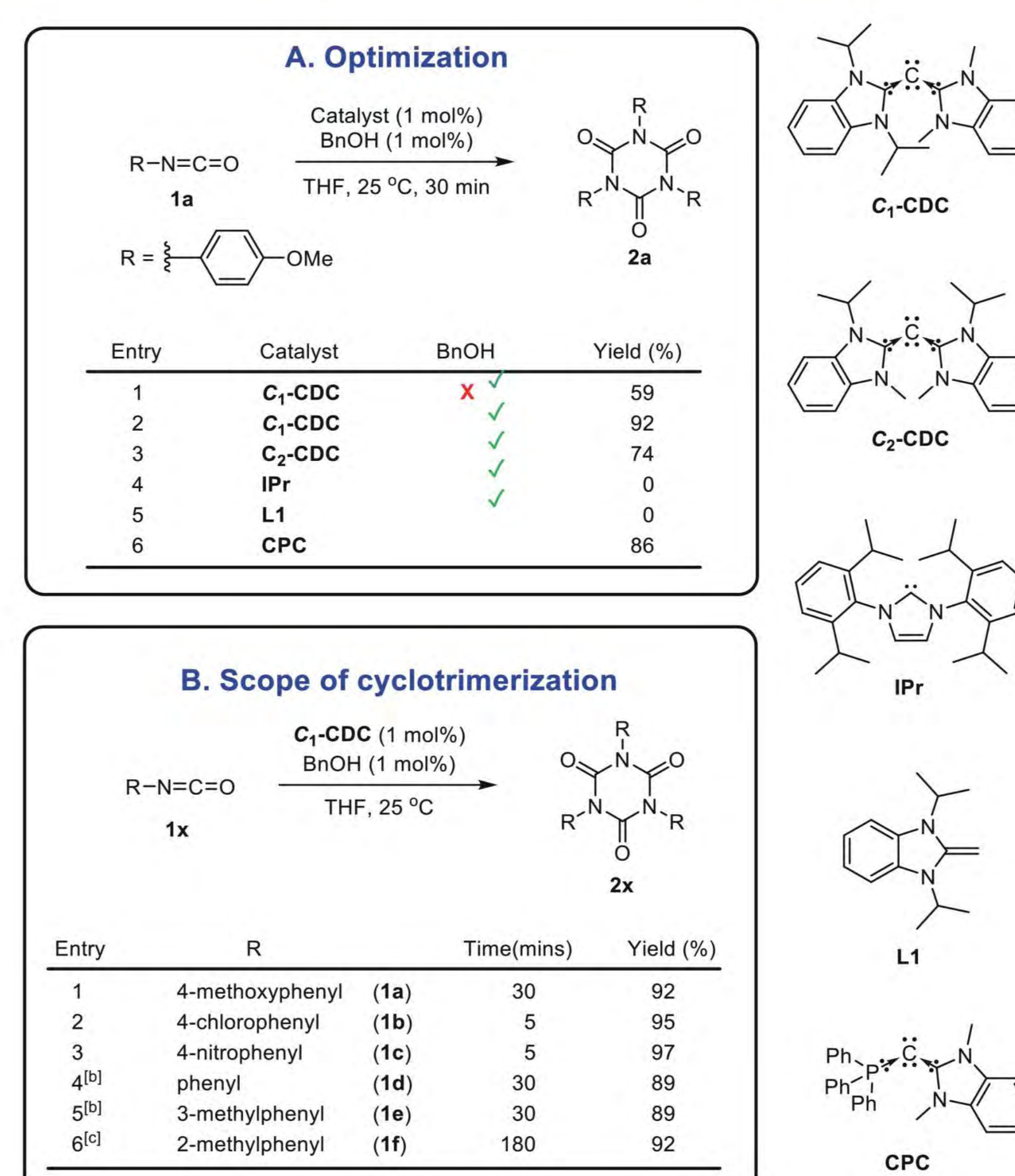
Introduction



NMR Analysis

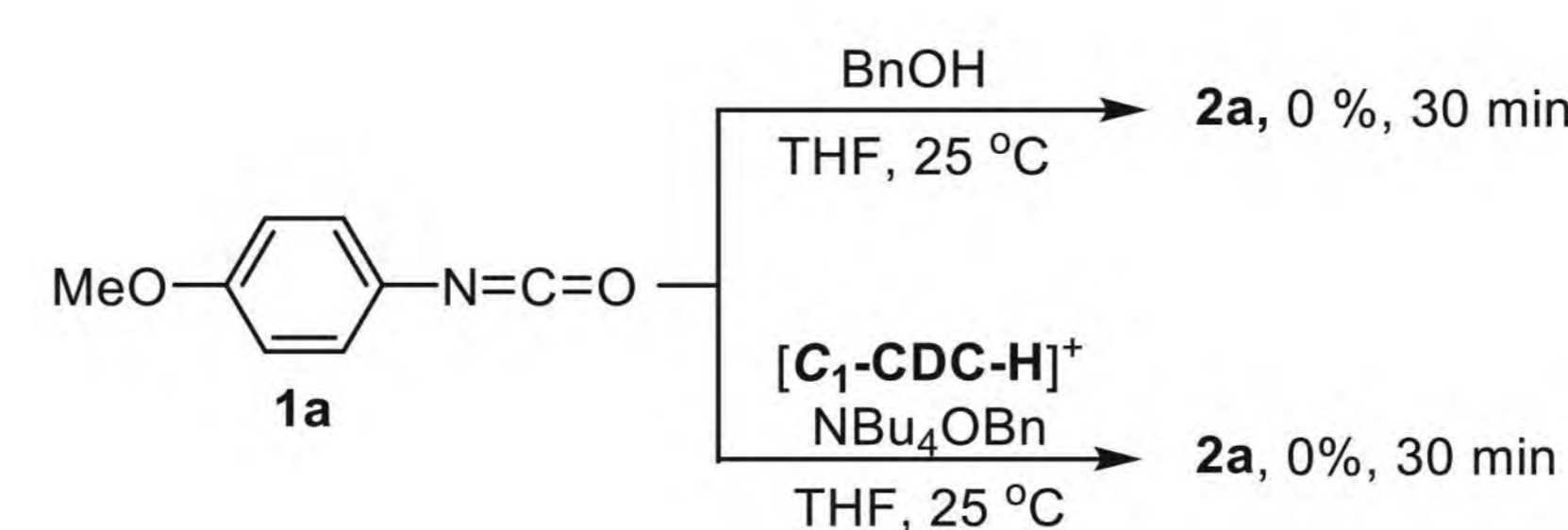


Cyclotrimerization of Isocyanates

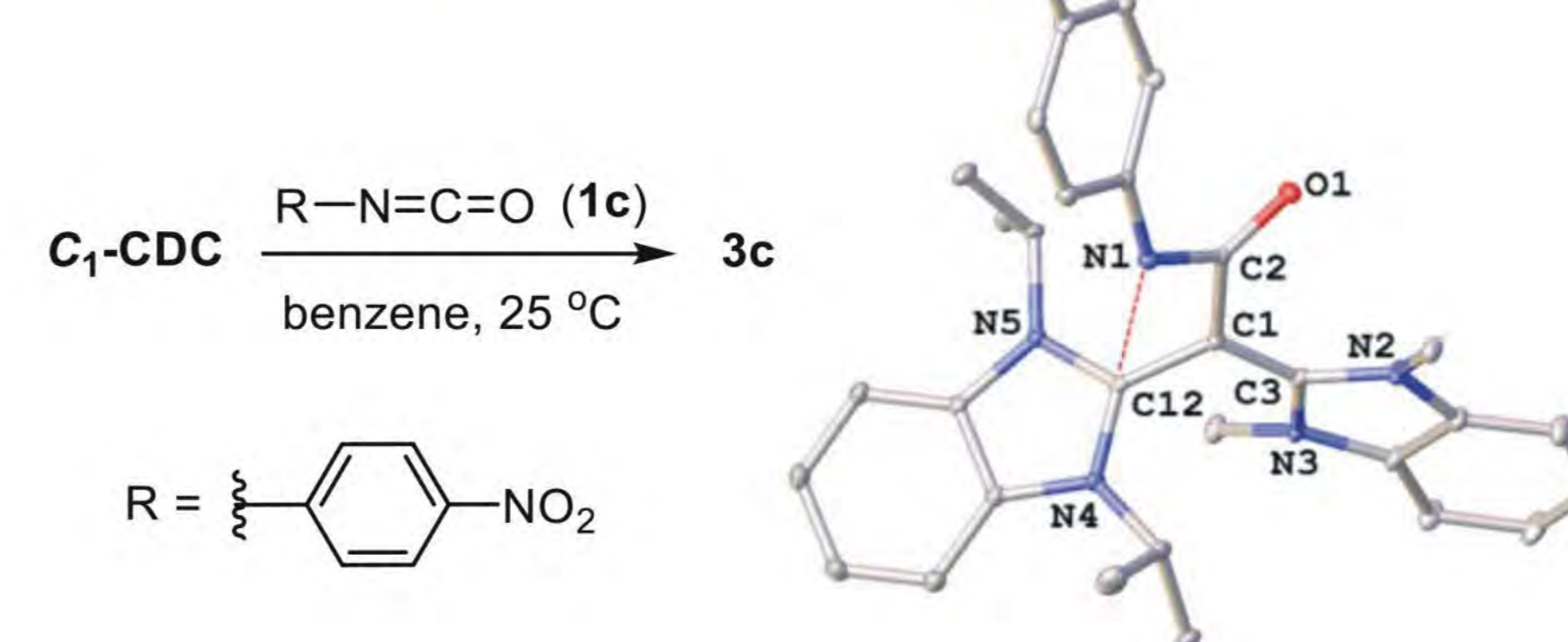


Mechanistic Study

A. Experiments for mechanism study



B. Solid structure of 3c



Conclusion

In summary, our findings bring to light a FLP-like feature in carbodicarbene attuned by a co-modulator BnOH to direct isocyanate cyclotrimerization. Moreover, this proof-of-concept could be expanded to other different catalytic reactions such as ring opening polymerization of *L*-lactide, methyl methacrylate polymerization and dehydrosilylation of alcohols. DFT calculation and NMR analysis indicated that π - π stacking and weak Brønsted acid/Lewis base pair interactions between the BnOH and CDC played a major role to generate this subtle synergistic FLP behavior in catalysis.

Reference

- Chan, Y.-C.; Bai, Y.; Chen, W.-C.; Chen, H.-Y.; Li, C.-Y.; Wu, Y.-Y.; Tseng, M.-C.; Glenn, Y. P. A.; Zhao, L.; Chen, H.-Y.; Ong, T.-G. *Angew. Chem., Int. Ed.* **2021**, *60*, 19949-19956.
- Chen, W.-C.; Shih, W.-C.; Jurca, T.; Zhao, L.; Andrada, D. M.; Peng, C.-J.; Chang, C.-C.; Liu, S.-K.; Wang, Y.-P.; Wen, Y.-S.; Yap, G. P. A.; Hsu, C.-P.; Frenking, G.; Ong, T.-G. *J. Am. Chem. Soc.* **2017**, *139*, 12830-12836.

