Cooperative Catalysis

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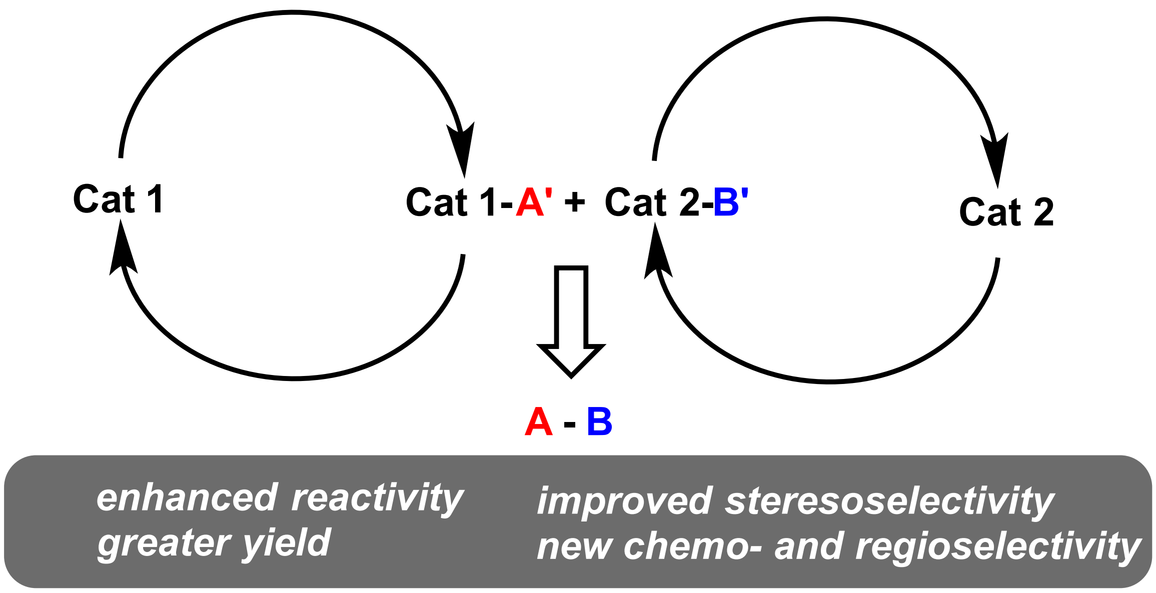
Cooperative Catalysis and Activation with N-Heterocyclic Carbenes

*Michael H. Wang and Karl A. Scheidt**



Reporter: Yang Li

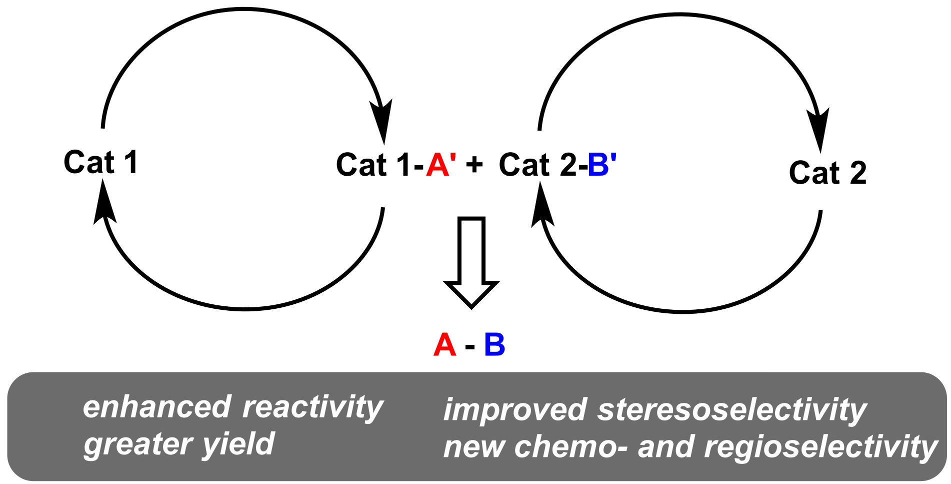
Supervisor: Prof. Yong Huang

Mar. 27th, 2017

Outline:

1. Introduction
2. NHC Cooperative Catalysis
    - 2.1 NHC/Lewis Acid Cooperative Catalysis
    - 2.2 Oxidative NHC Catalysis
    - 2.3 Oxidative NHC/Lewis Acid Cooperative Catalysis
    - 2.4 NHC/Brønsted Acid Cooperative Catalysis
    - 2.5 NHC/Brønsted Base Cooperative Catalysis
3. Summary and Outlook
4. Ackonwledgement

1.Introduction:



In cooperative (synergistic) systems, two distinct catalysts independently activate separate substrates to generate products with remarkable efficiency and selectivity that are unobtainable through single-catalyst systems

In many of the following examples, rigorous kinetic studies are not readily available to examine the impact of cocatalyst additives on reaction rate; however, addition of this second species led to observable improve- ments (e.g., yield, stereoselectivity), which arise owing to the enhanced rates of the favored pathways.

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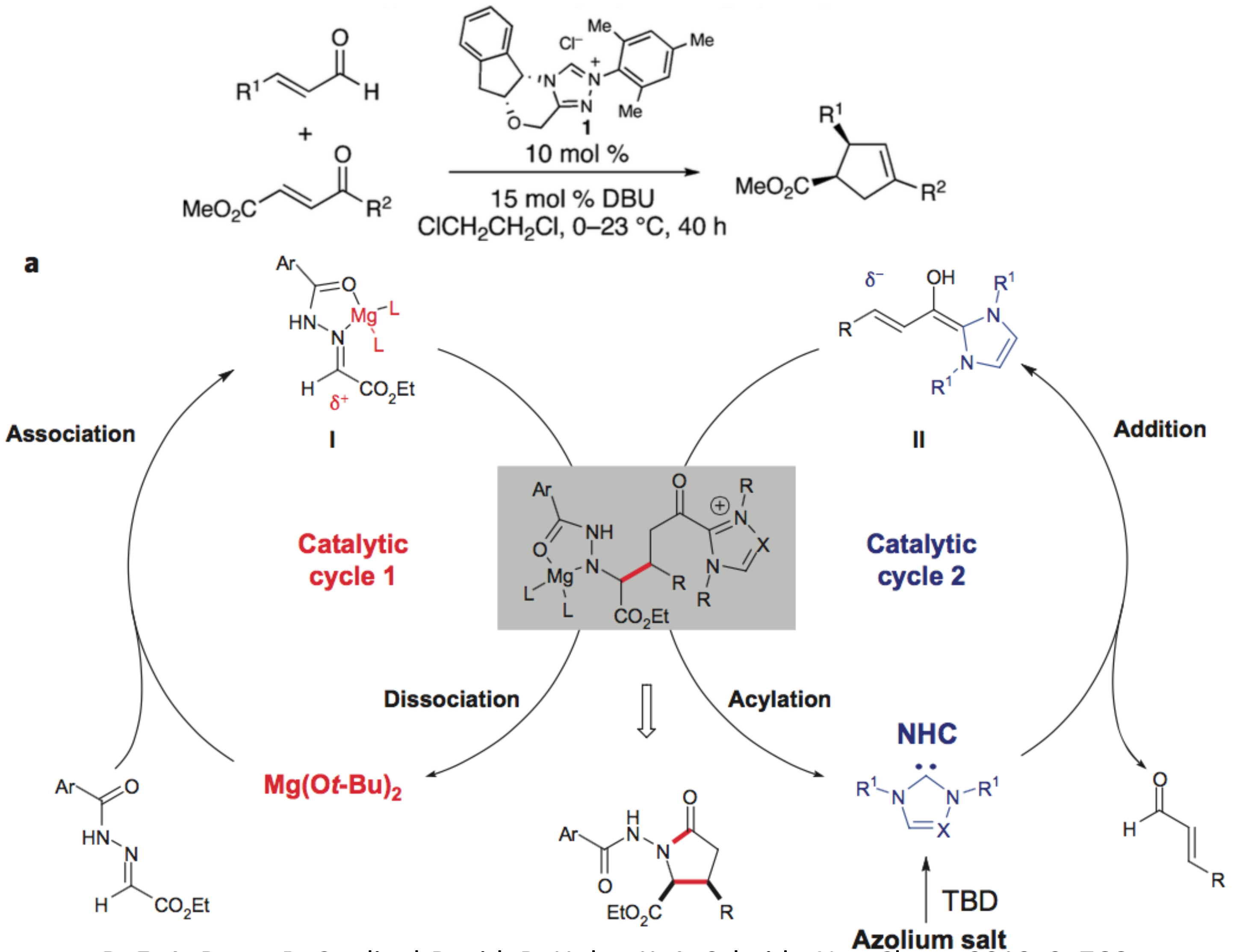
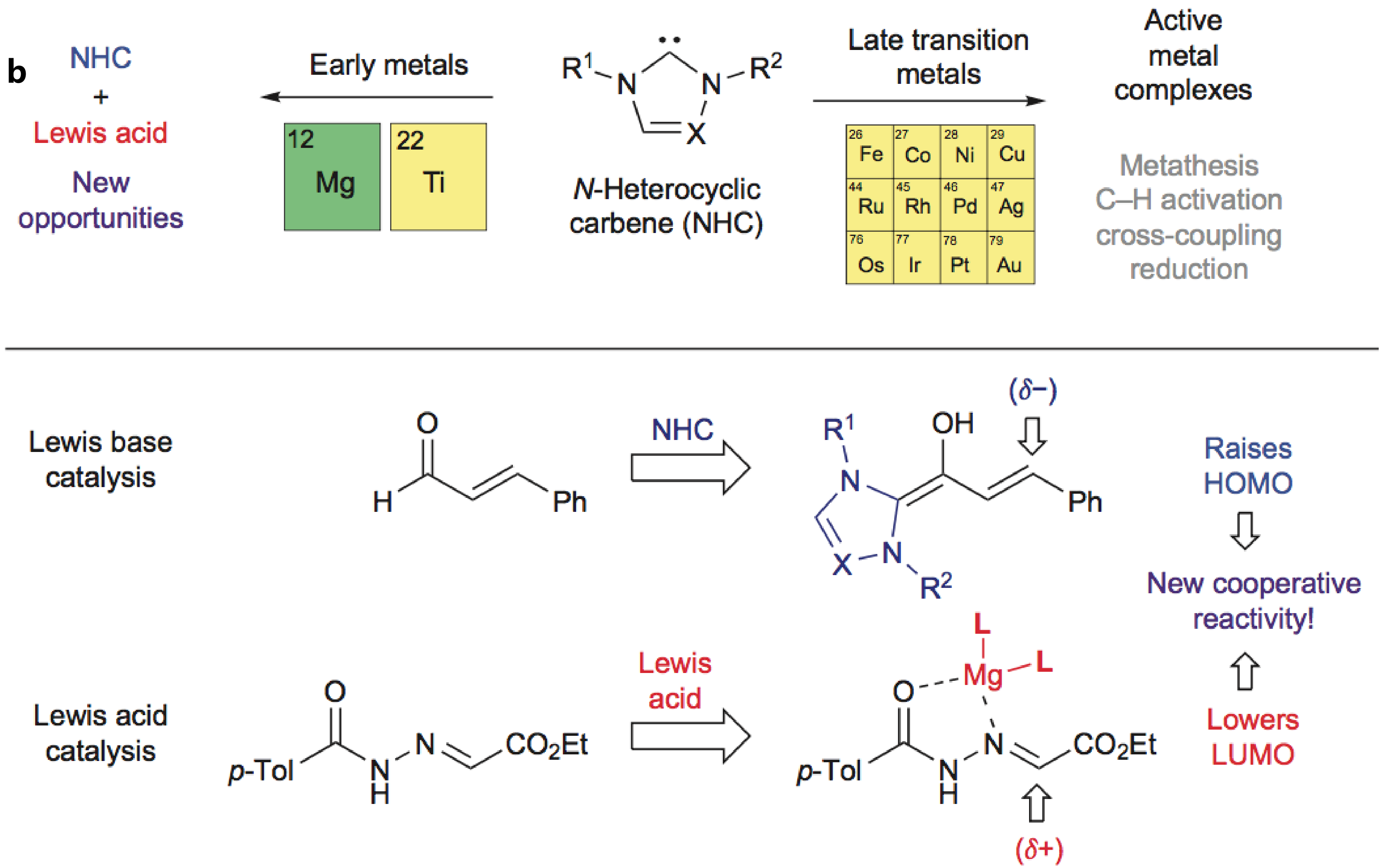
2.1 NHC/Lewis Acid Cooperative Catalysis

Enhanced reactivity by cooperative catalysis :



D. E. A. Raup, B. Cardinal-David, D. Holte, K. A. Scheidt, Nat. Chem. 2010, 2, 766.

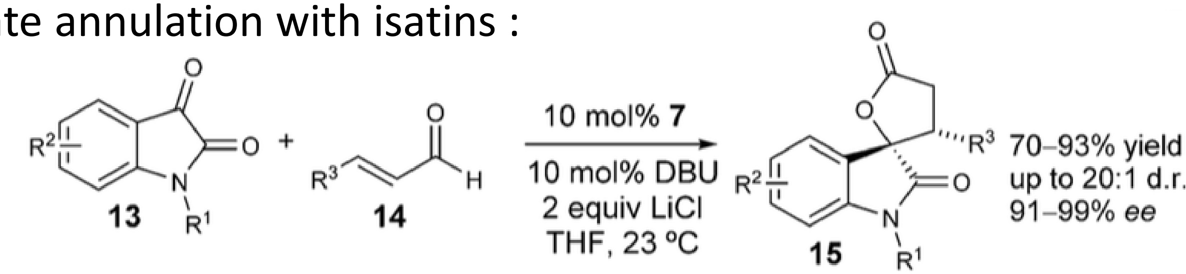
2.1 NHC/Lewis Acid Cooperative Catalysis

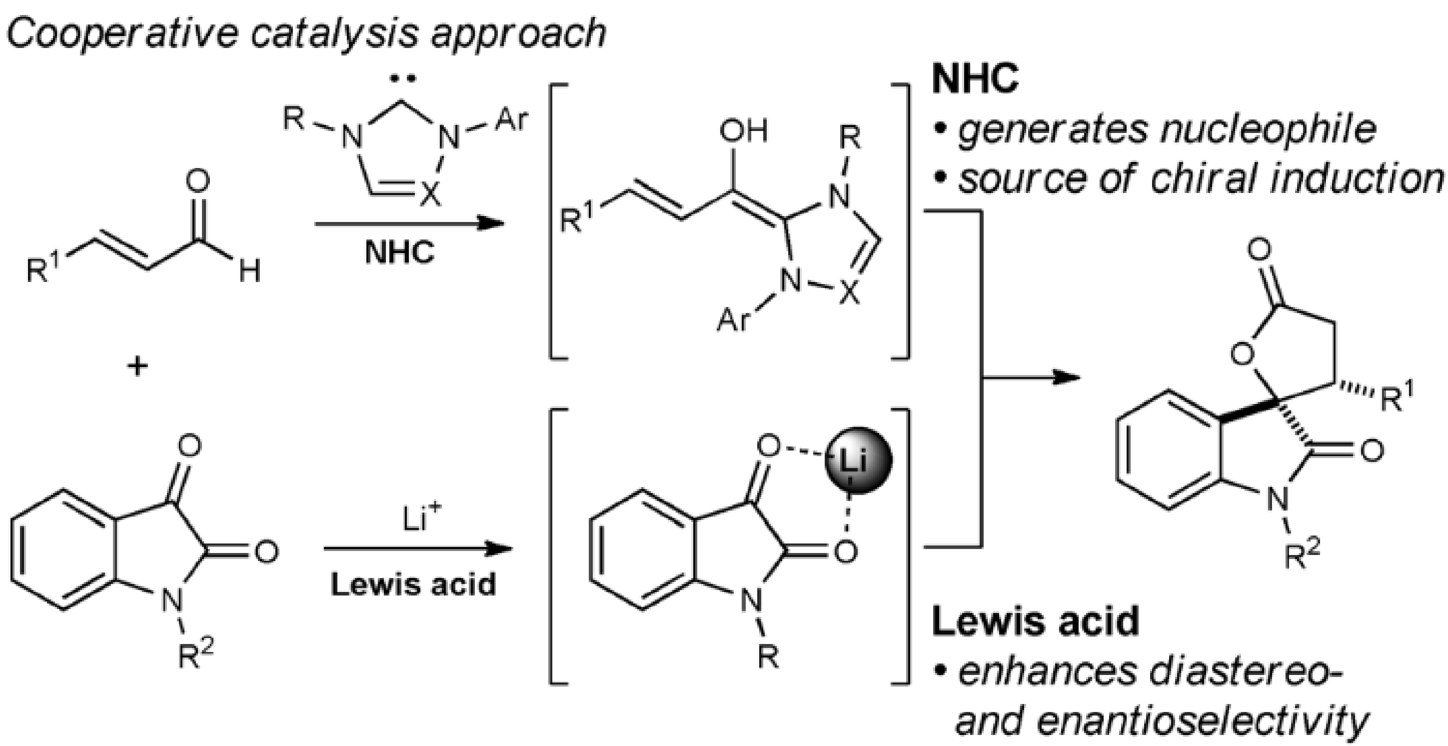


D. E. A. Raup, B. Cardinal-David, D. Holte, K. A. Scheidt, Nat. Chem. 2010, 2, 766.

2.1 NHC/Lewis Acid Cooperative Catalysis

Homoenolate annulation with isatins :





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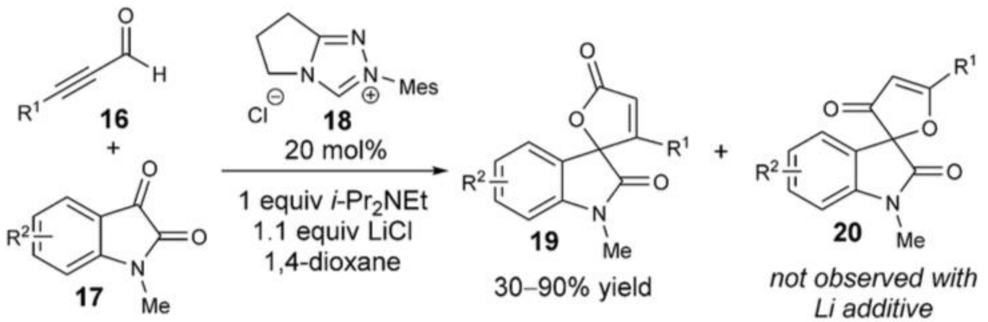
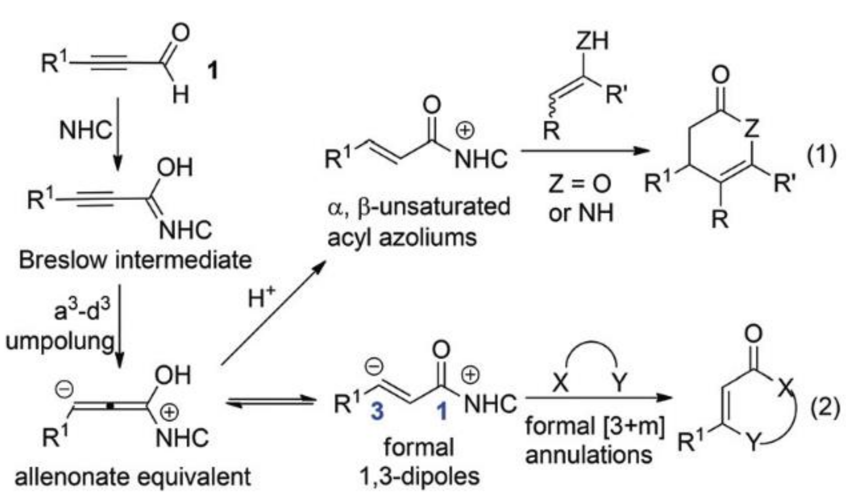
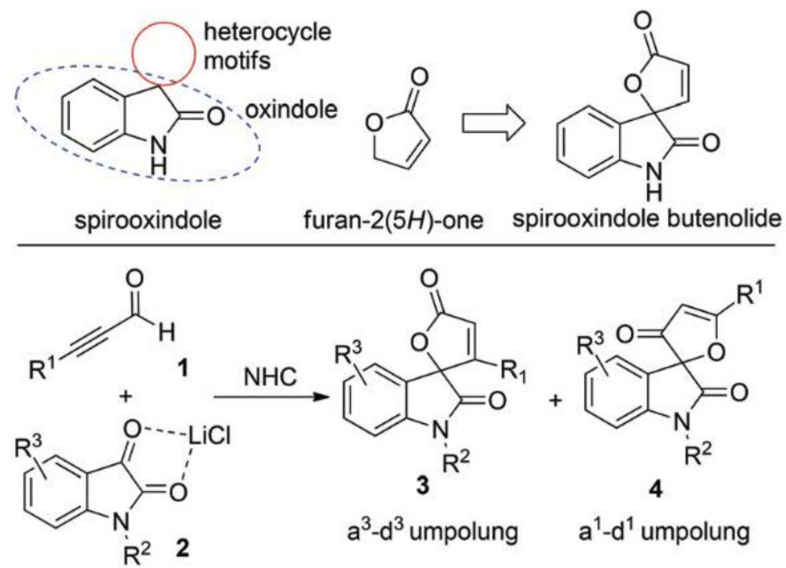
2.1 NHC/Lewis Acid Cooperative Catalysis

Annulation of ynals and isatins :

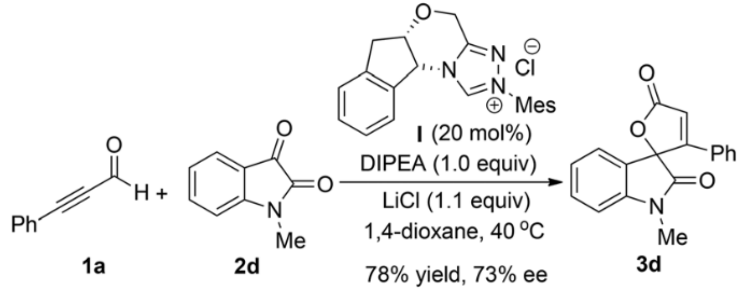


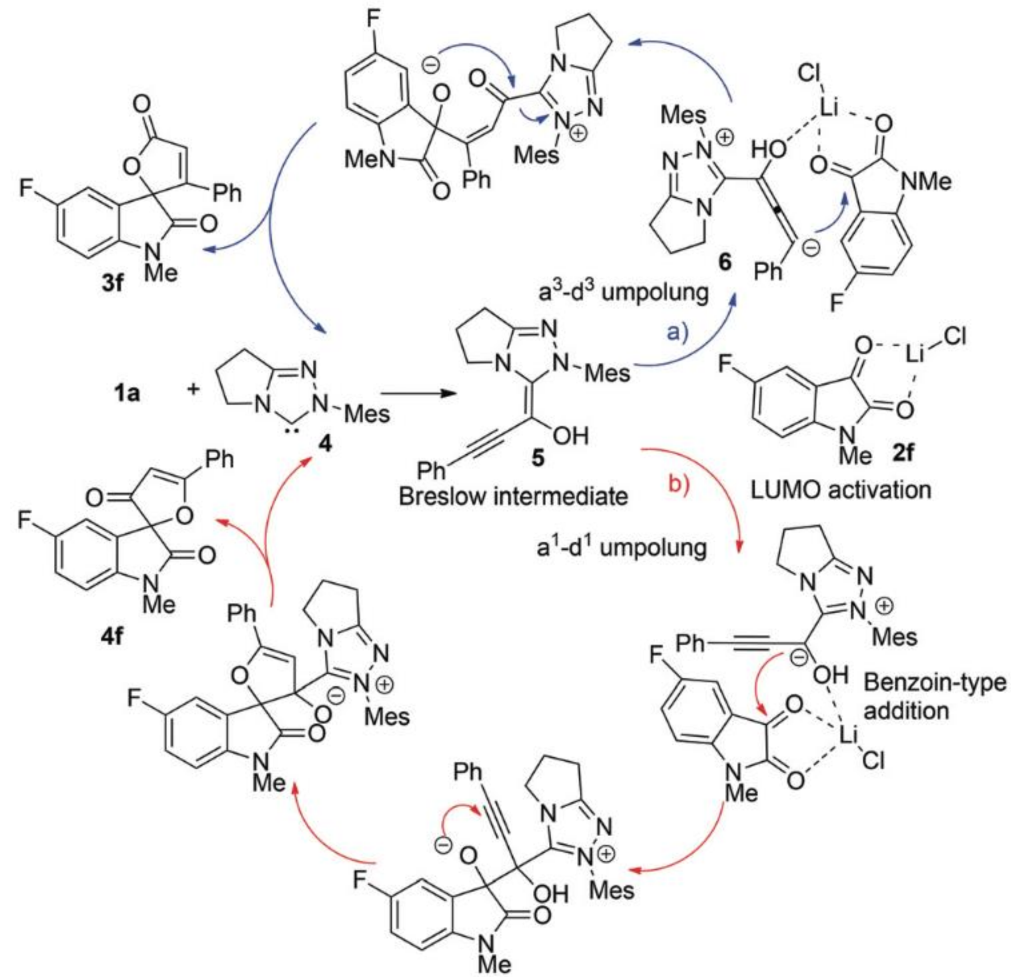




Y. Zhang, Y. Lu, W. Tang, T. Lu, D. Du, Org. Biomol. Chem. 2014, 12, 3009

2.1 NHC/Lewis Acid Cooperative Catalysis

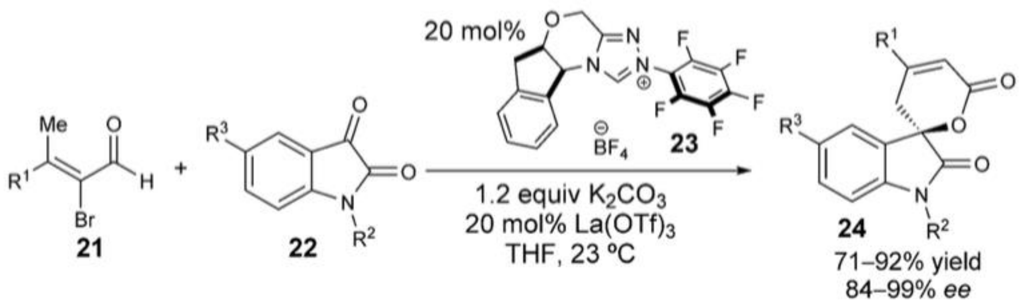


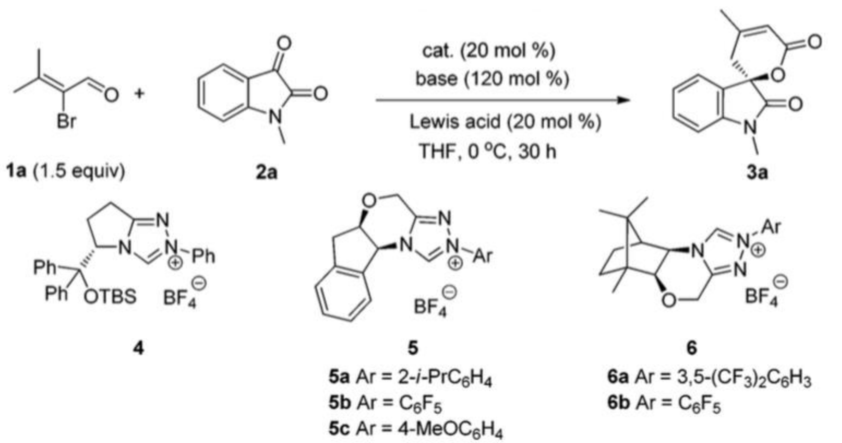


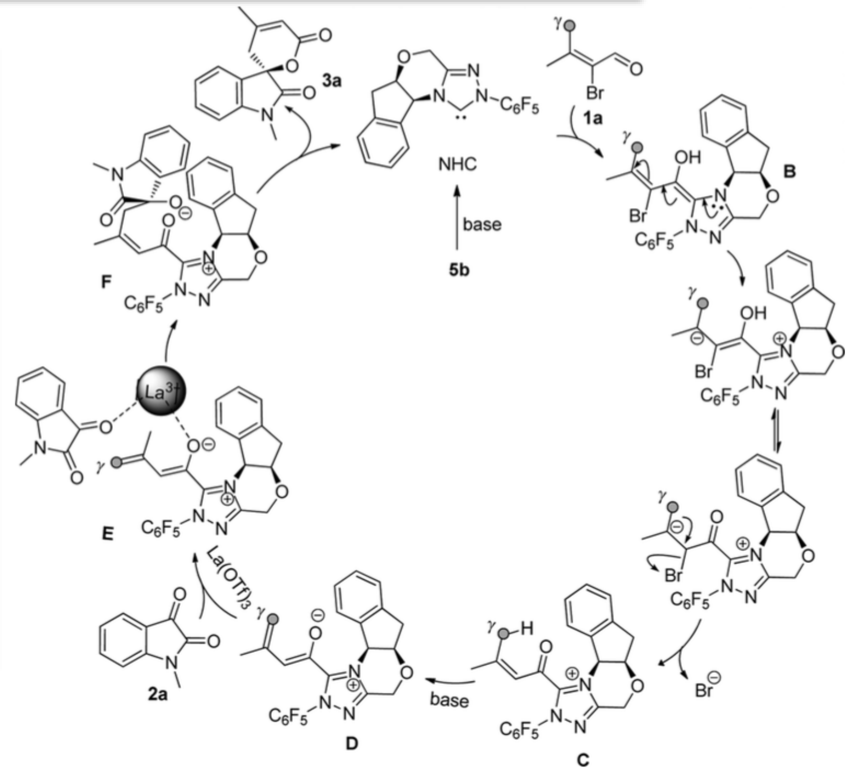
Y. Zhang, Y. Lu, W. Tang, T. Lu, D. Du, Org. Biomol. Chem. 2014, 12, 3009

2.1 NHC/Lewis Acid Cooperative Catalysis

Synthesis of oxindole–dihydropyranone spirocycles :



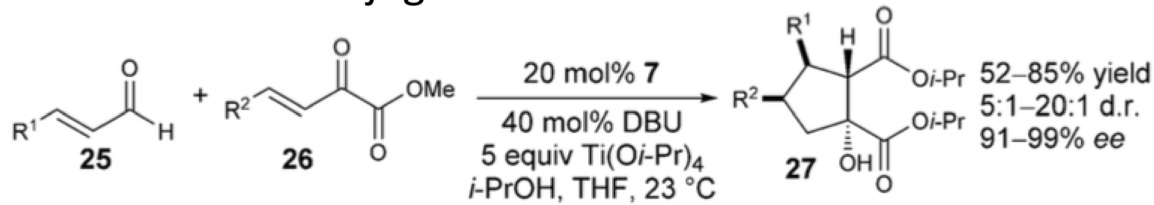


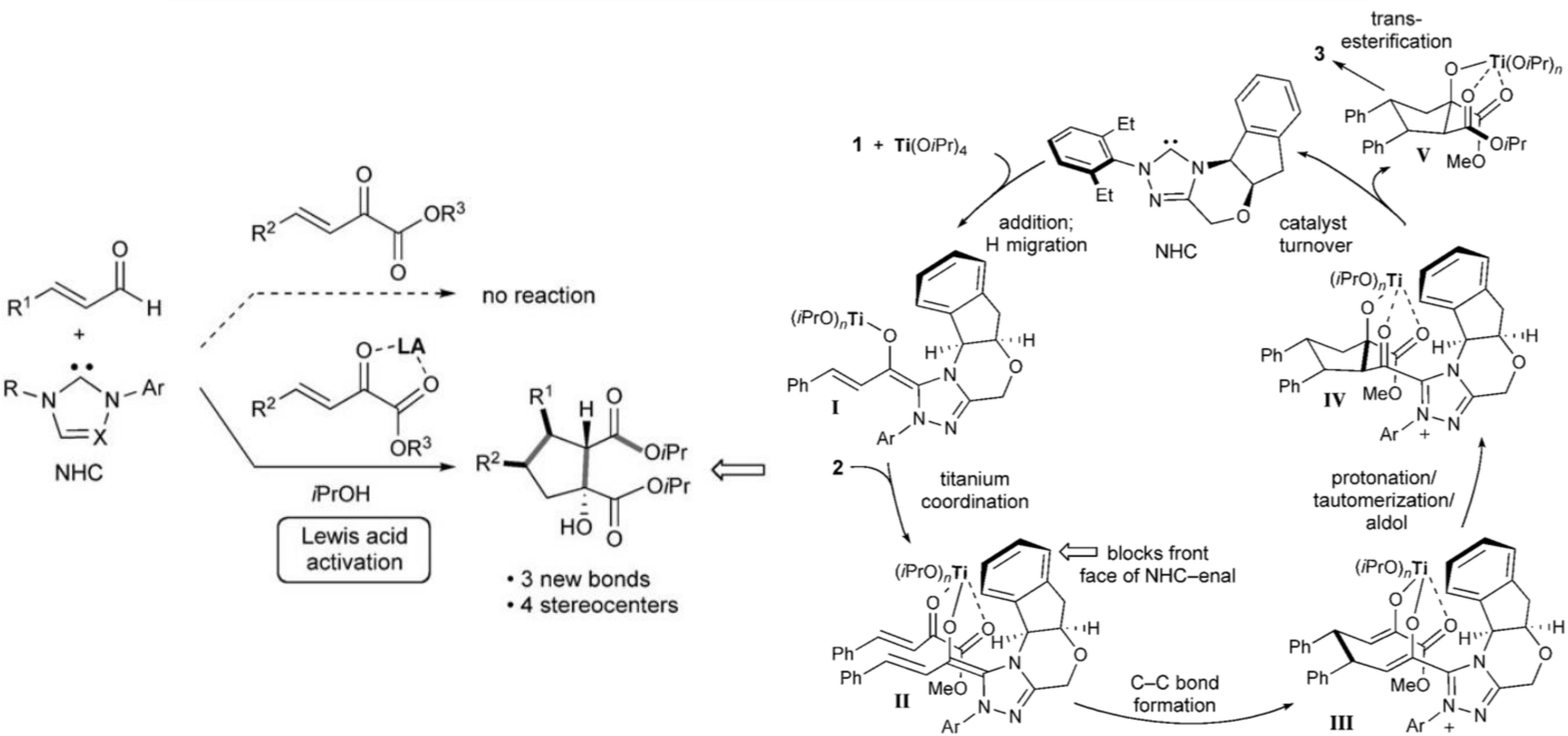


Z. Xiao, C. Yu, T. Li, X.-S. Wang, C. Yao, Org. Lett. 2014, 16, 3632

2.1 NHC/Lewis Acid Cooperative Catalysis

NHC/Lewis acid homoenolate conjugate addition:





D. T. Cohen, B. Cardinal-David, K. A. Scheidt, Angew. Chem. Int. Ed. 2011, 50, 1678

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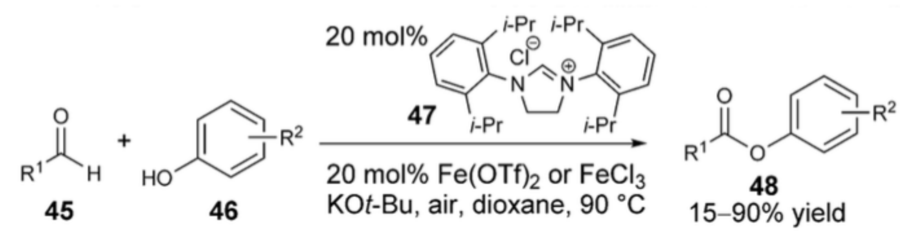
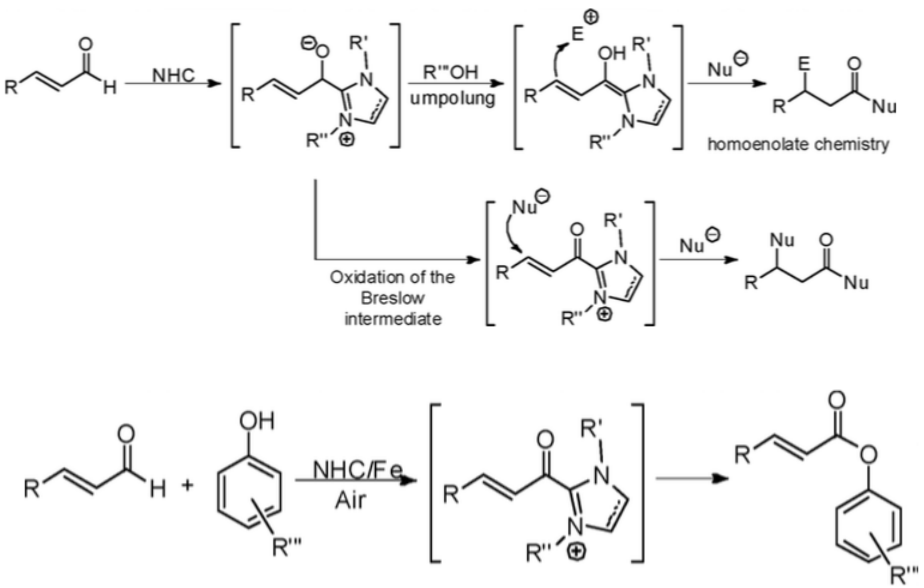
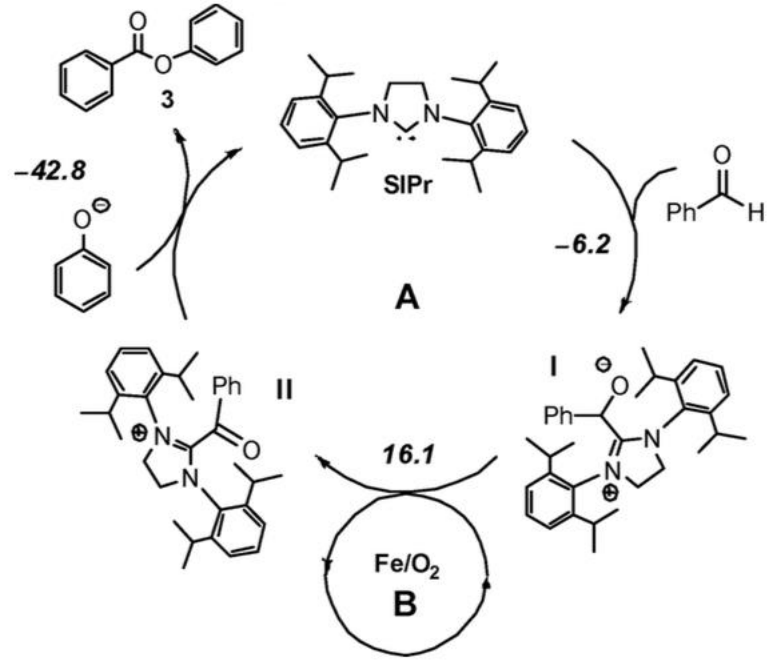
2.2 Oxidative NHC Catalysis

NHC/iron-catalyzed esterification :







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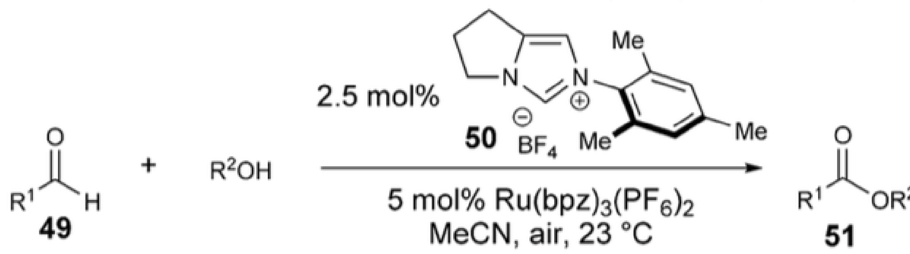
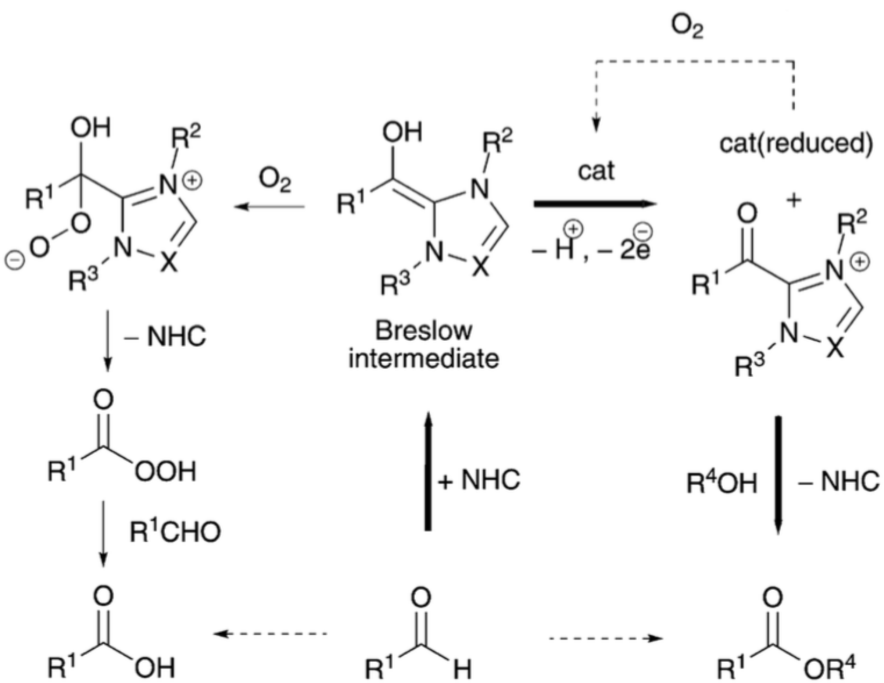
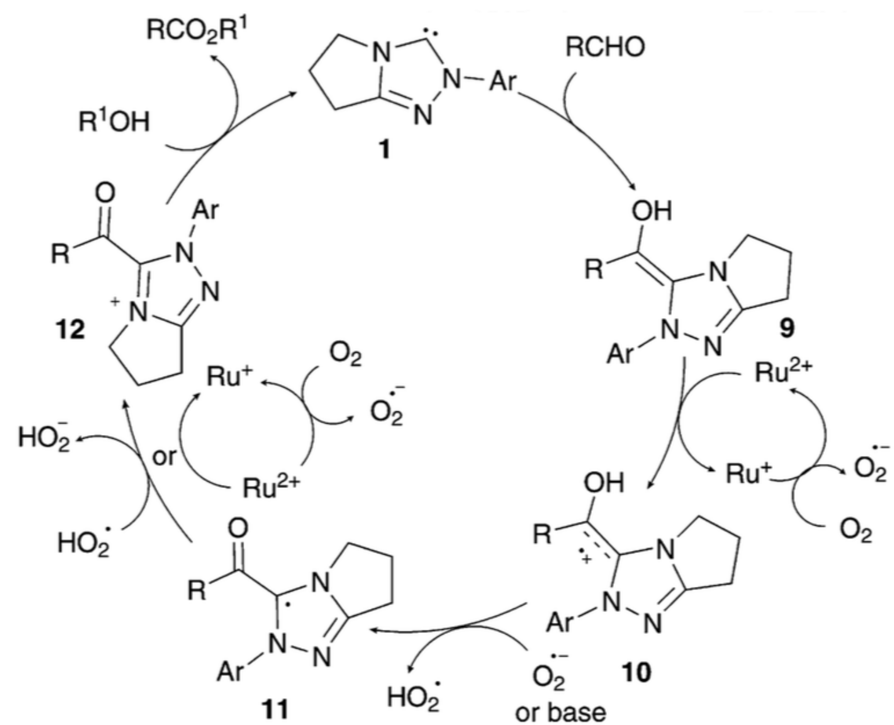
2.2 Oxidative NHC Catalysis

Ruthenium-catalyzed oxidation of Breslow intermediates :







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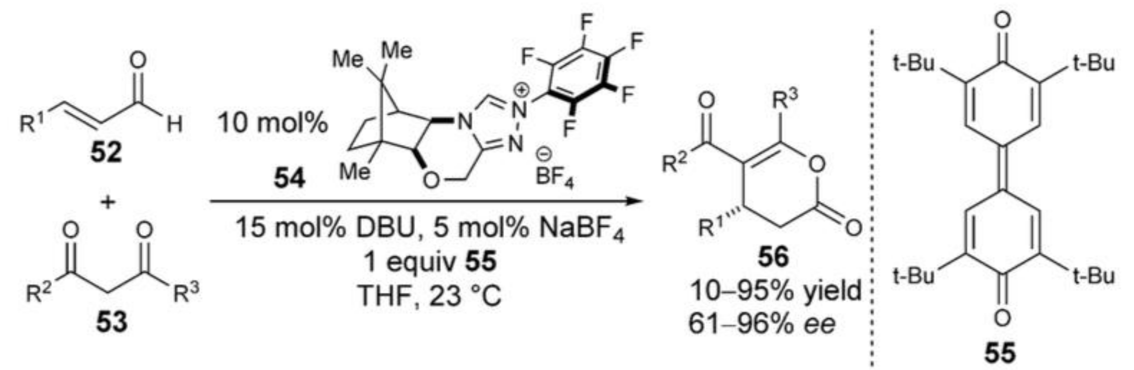
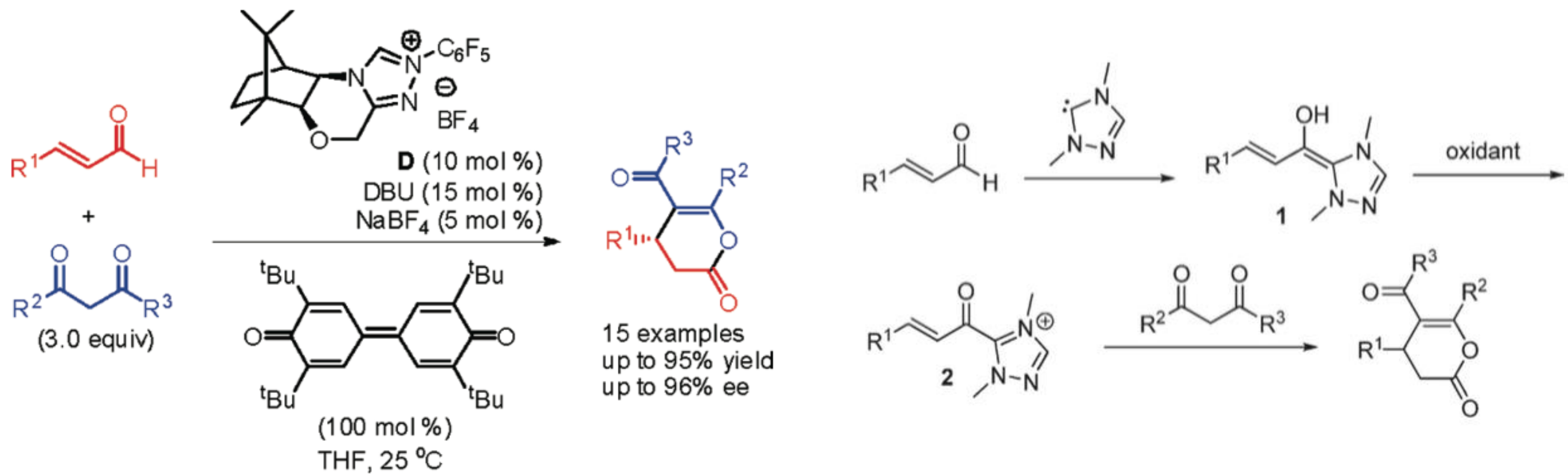
Outline:

2.3 Oxidative NHC/Lewis Acid Cooperative Catalysis

Oxidative NHC/Lewis acid catalyzed annulation :





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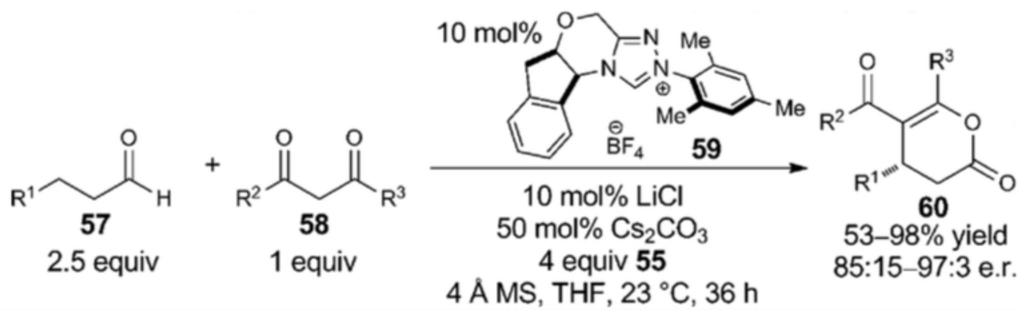
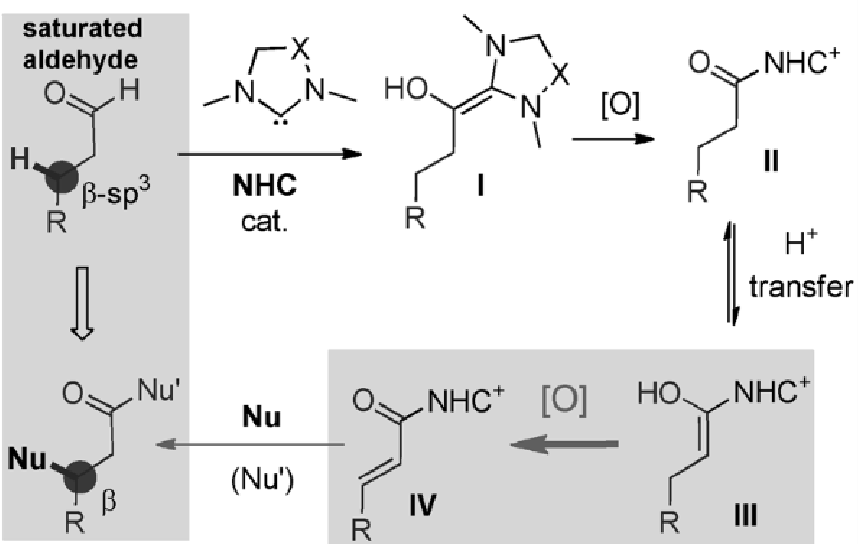
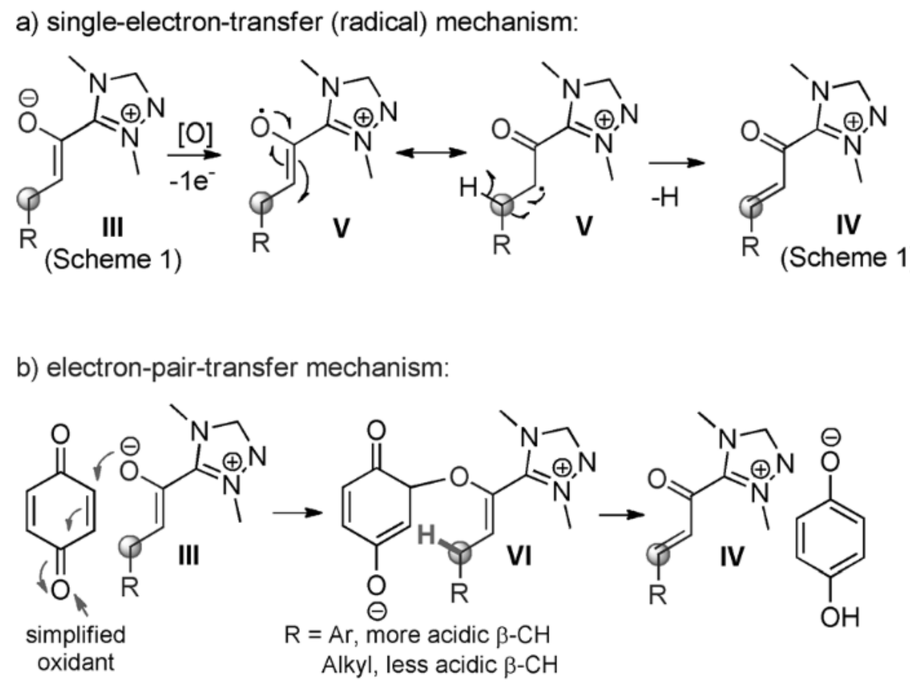
2.3 Oxidative NHC/Lewis Acid Cooperative Catalysis

Oxidative NHC/Lewis acid catalyzed annulation with satu- rated aldehydes :







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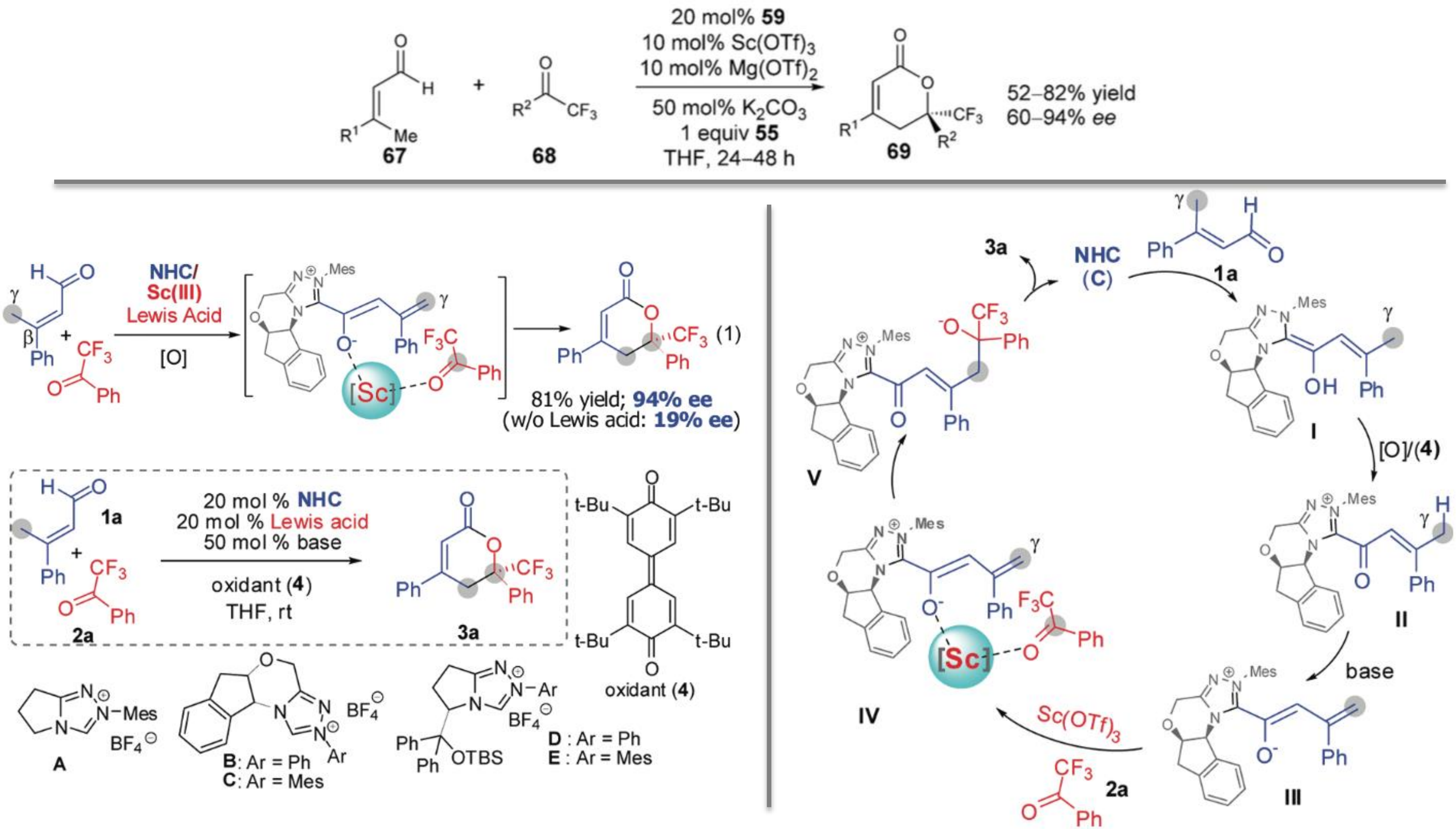
2.3 Oxidative NHC/Lewis Acid Cooperative Catalysis

Oxidative NHC/Lewis acid catalyzed γ-addition :



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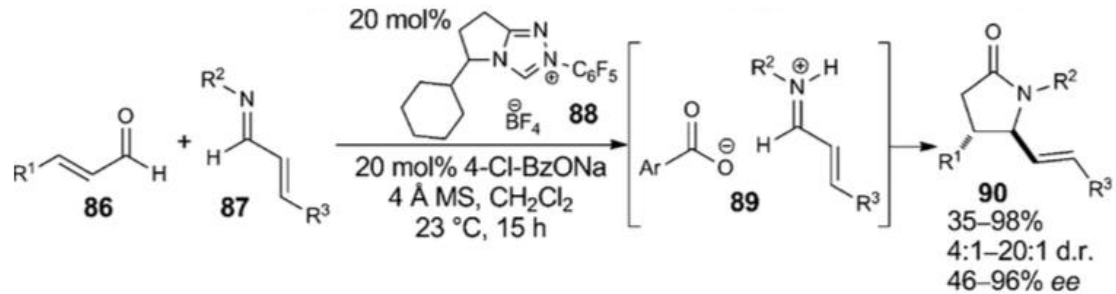
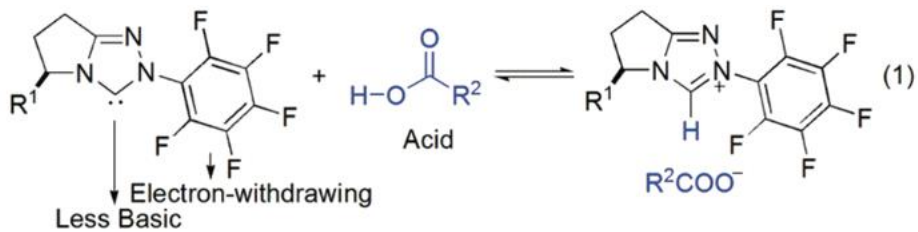
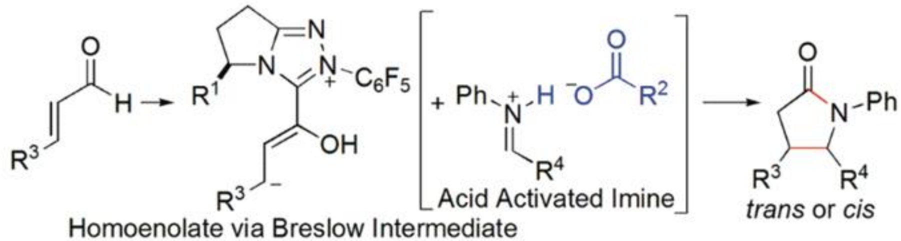
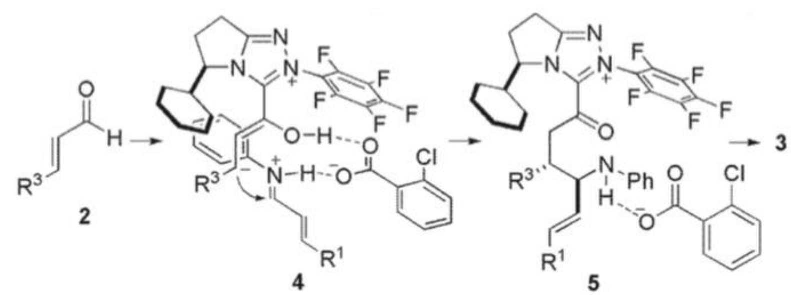
2.4 NHC/Brønsted Acid Cooperative Catalysis

NHC/Brønsted acid cooperative catalysis :









Proposed Pathway for trans-γ-Lactam Formation

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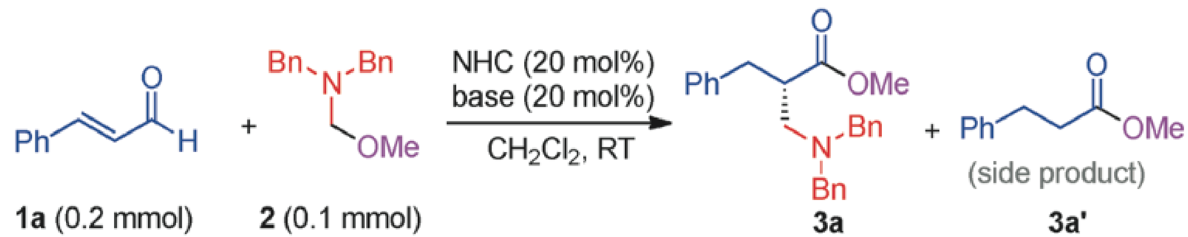
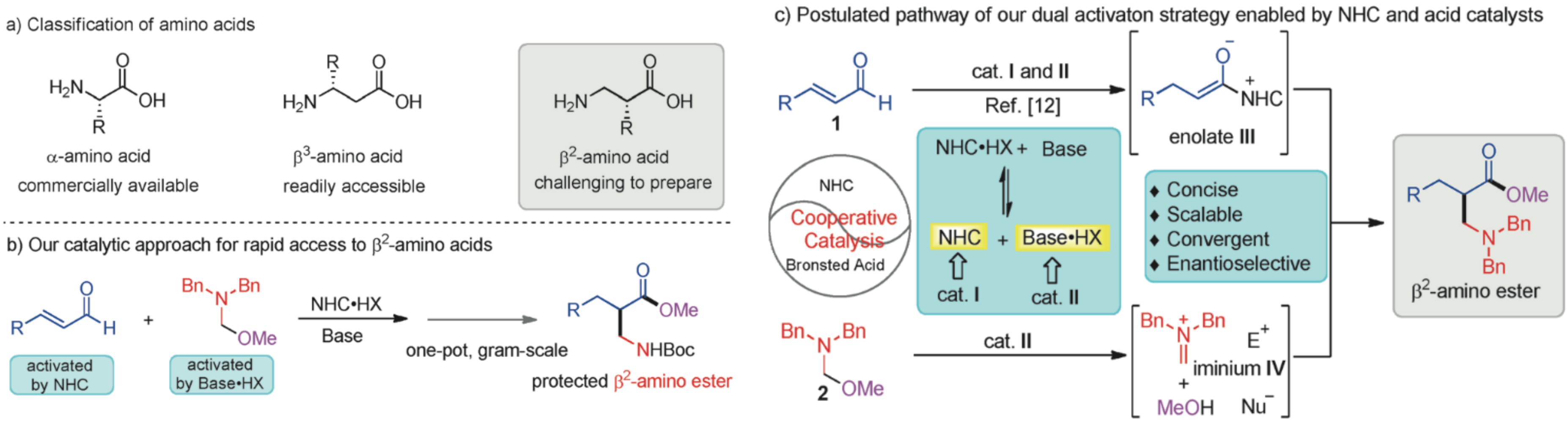
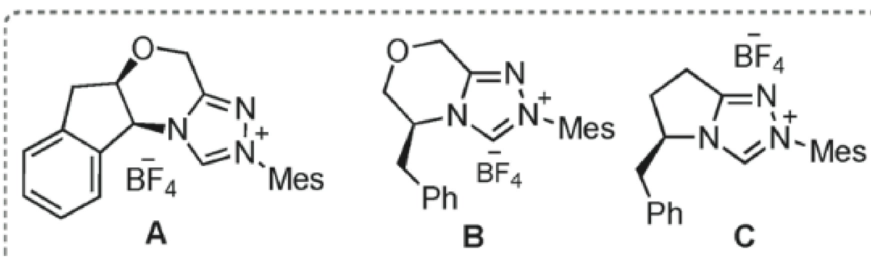
2.4 NHC/Brønsted Acid Cooperative Catalysis

Synthesis of β-amino esters :







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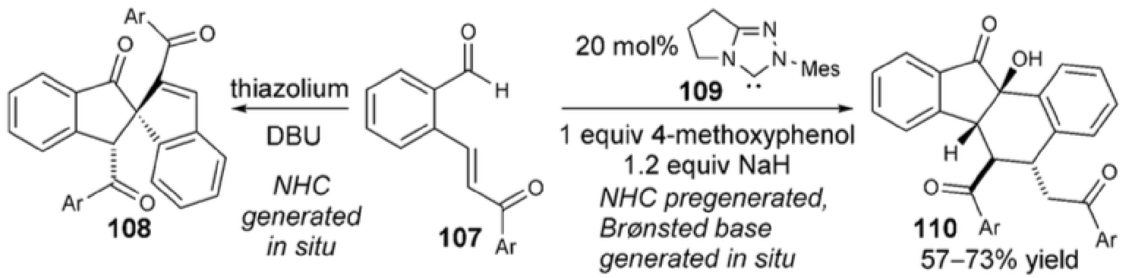
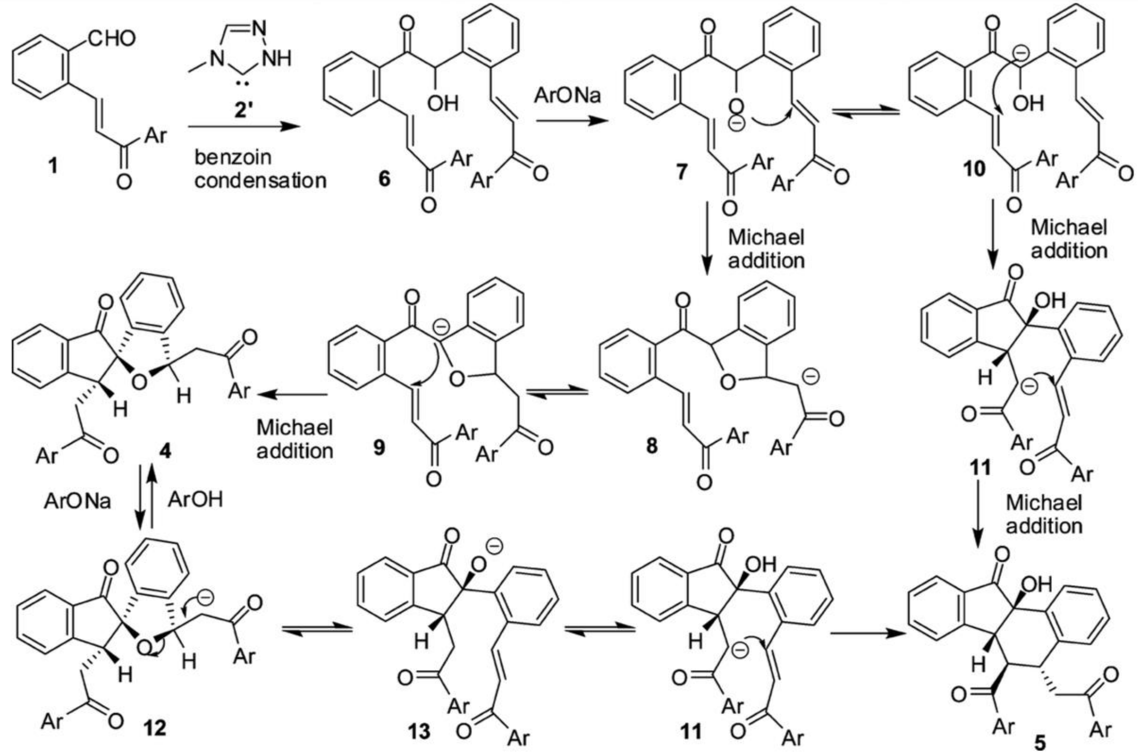
2.4 NHC/Brønsted Base Cooperative Catalysis

tandard NHC reaction conditions versus Lewis/Brønsted base activation :





Y.-f. Tong, J.-h. Mao, S. Wu, Y. Zhao, Y. Cheng, J. Org. Chem. 2014, 79, 2075

Outline:

3 Summary and Outlook

1. The field of NHC catalysis is still relatively new, and has seen enormous growth in terms of substrate scope, reaction conditions, and new modes of reactivity since 2004.

2. This last vein of research has especially revitalized interest in carbene catalysis and revealed new possible reaction types not previously available to NHC catalysis alone.

3. NHCs have been combined with Lewis acids/bases, oxidants, Brønsted acid/base. NHCs were initially isolated and studied as distinct catalysts owing to key inspiration from biological systems.

4. Continued studies by the worldwide carbene catalysis com- munity will undoubtedly provide new means of reaction discovery and development.

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4 Acknowledgement

Prof. Huang

Meng sixuan

All members in E201

Everyone here

Thanks for your attention!