Metalloradical Catalysis for Stereoselective Nitrogen Transfer Reactions

Prof. X. Peter Zhang's Research Group

Department of Chemistry, Merkert Center, Boston College, Chestnut Hill, MA 02467

Nitrogen Transfer via Co(II)-Based Metalloradical Catalysis

Aminyl radicals have been demonstrated as one type of highly reactive intermediates that are able to undergo various radical-type transformations for synthesis of nitrogen-containing compounds. While "free" aminyl radicals have been shown to have a rich chemistry, their applications for organic synthesis still remain largely underdeveloped due to the difficulty with the control of reactivity and selectivity. To address the formidable challenges of nitrogen-centered radicals, our group has introduced the concept of Co(II)-based metalloradical catalysis (MRC) for catalytic generation of a new class of metal-stabilized aminyl radicals, namely α-metalloaminyl radicals (also known as α-Co(III)-nitrene radicals) for developments of stereoselective nitrogen transfer processes. These new α-metalloaminyl radical intermediates have been demonstrated as the key intermediates in the radical olefin aziridination and C–H amination reactions, providing versatile approaches to amino compounds from the abundant olefin and hydrocarbon sources through an unique stepwise radical process.

Aminyl Radical & Metalloradical Catalysis (MRC)

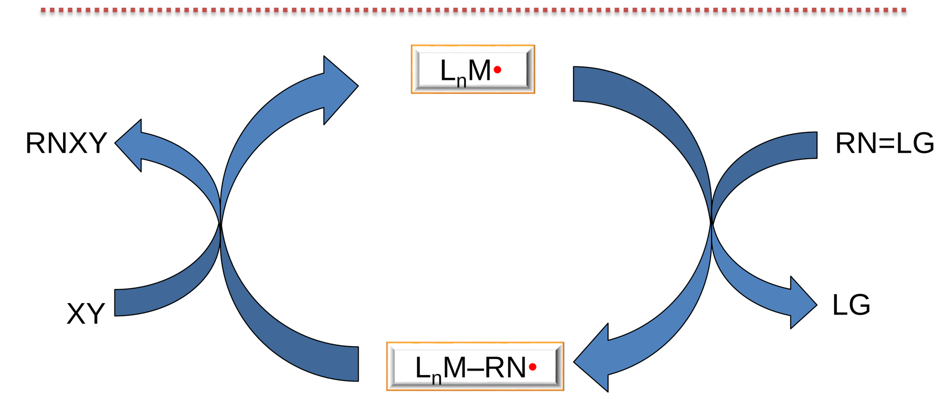
Types of Radical Reactions

- Radical Substitution
- Radical Addition
- Radical Elimination

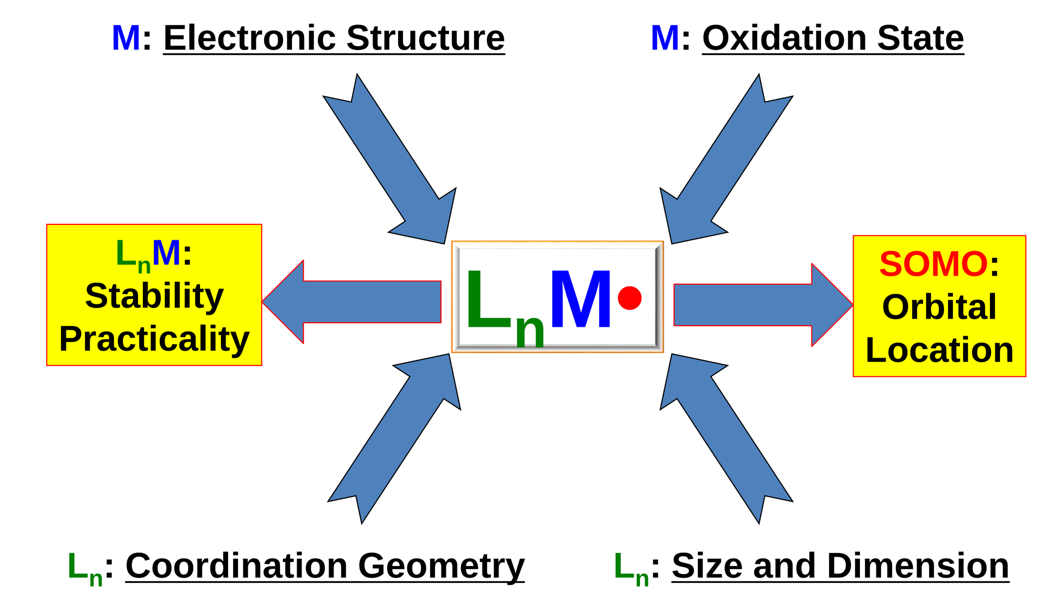
$R_2N\bullet$

Challenges of Radical Reactions

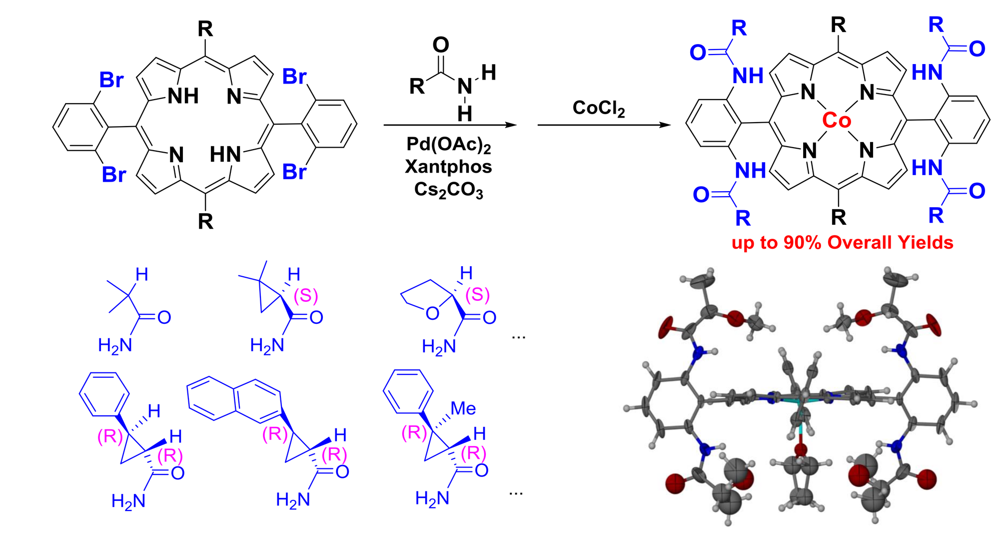
- Generation of Radicals
- Control of Radical Reactivity
- Control of Radical Selectivities



Design of Metalloradical Catalysts for MRC

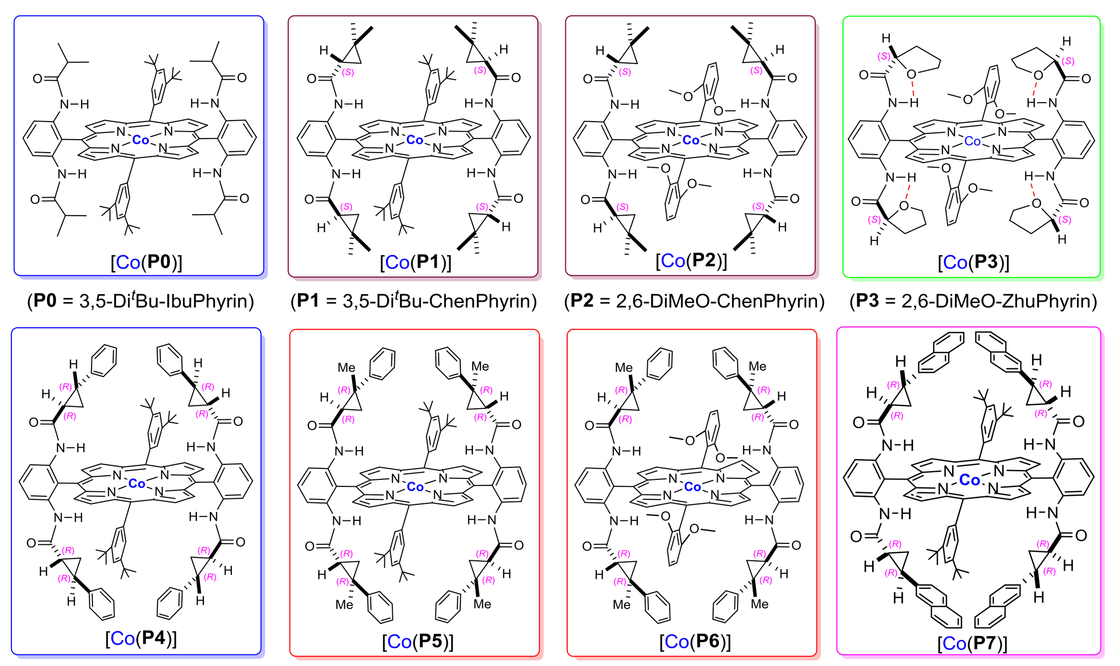


Co(II)(Por)-Based Metalloradical Catalysts



J. Am. Chem. Soc. **2004**, *126*, 14718;
J. Am. Chem. Soc. **2008**, *130*, 5042;
J. Am. Chem. Soc. **2011**, *133*, 15292;
Angew. Chem. Int. Ed. **2013**, *52*, 5309.

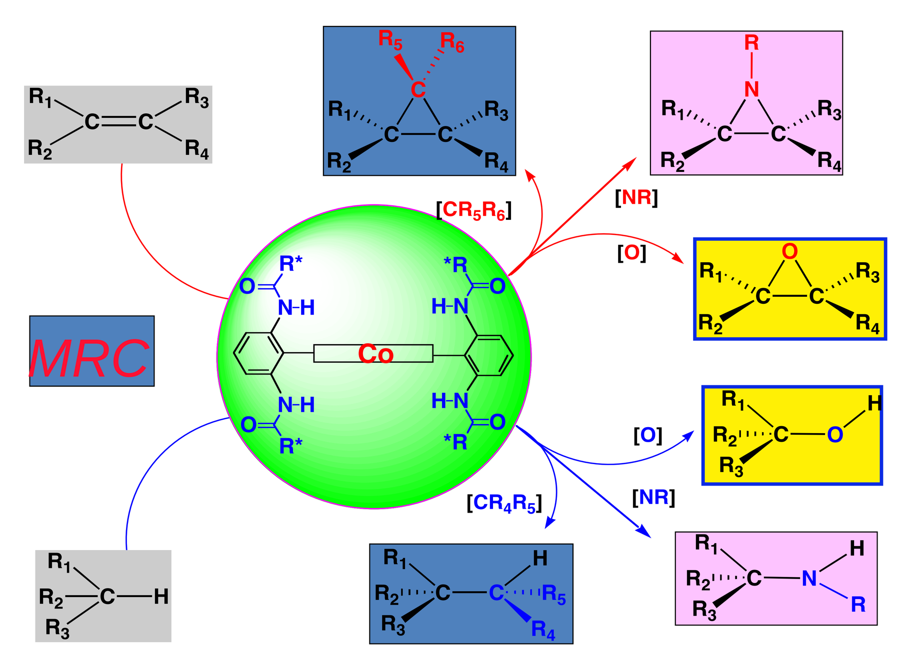
A Typical Toolbox of Catalysts



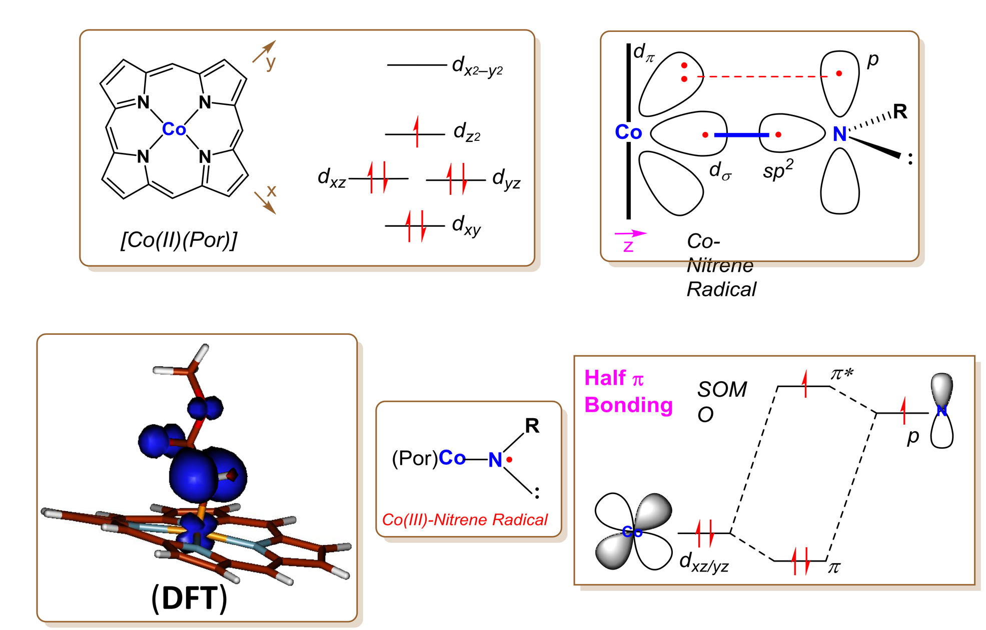
(P0 = 3,5-Di^{t}Bu-IbuPhyrin) (P1 = 3,5-Di^{t}Bu-ChenPhyrin) (P2 = 2,6-DiMeO-ChenPhyrin) (P3 = 2,6-DiMeO-ZhuPhyrin)

(P4 = 3,5-Di^{t}Bu-XuPhyrin) (P5 = 3,5-Di^{t}Bu-QingPhyrin) (P6 = 2,6-DiMeO-QingPhyrin) (P7 = 3,5-Di^{t}Bu-Xu(2'-Naph)Phyrin)

Asymmetric Atom/Group Transfer Reactions

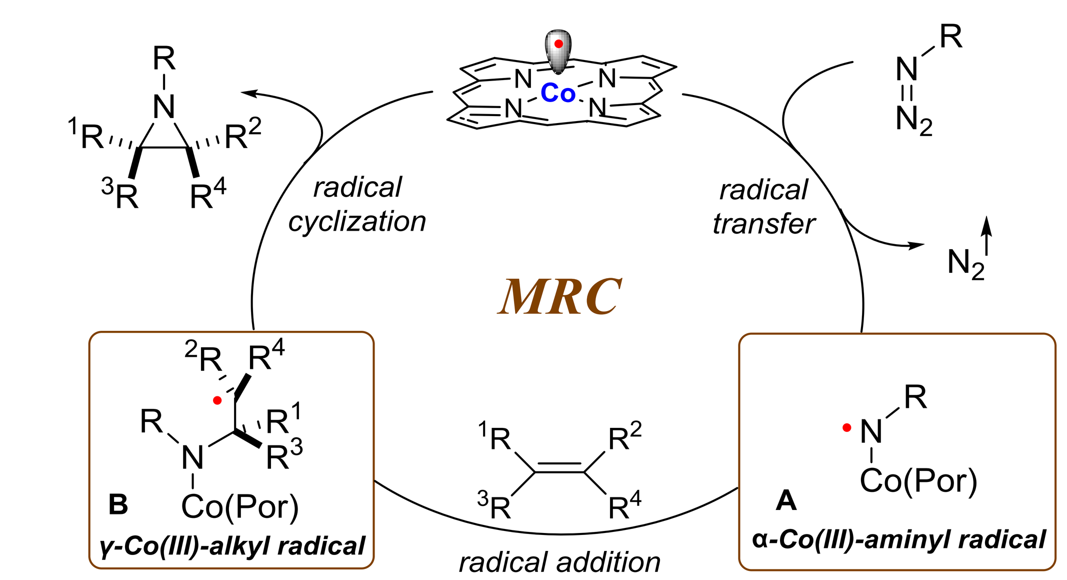


Co(II) Porphyrins as Metalloradical Catalysts



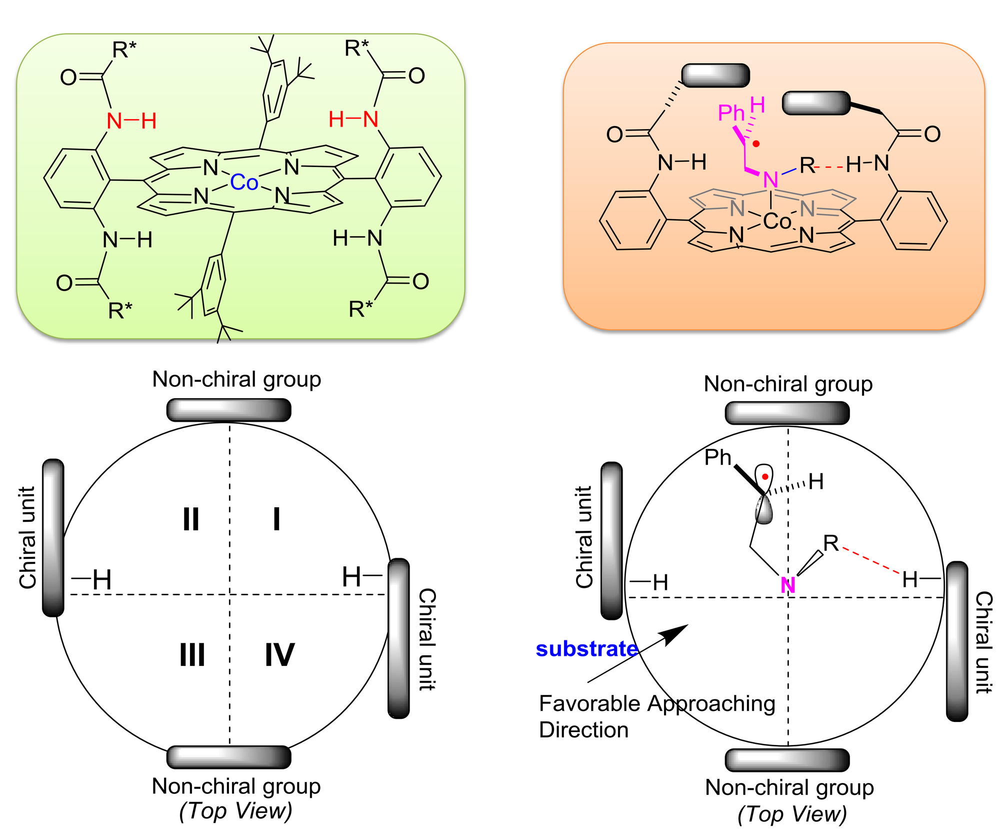
J. Am. Chem. Soc. **2011**, *133*, 8518.

Metalloradical Catalysis for Asymmetric Aziridination

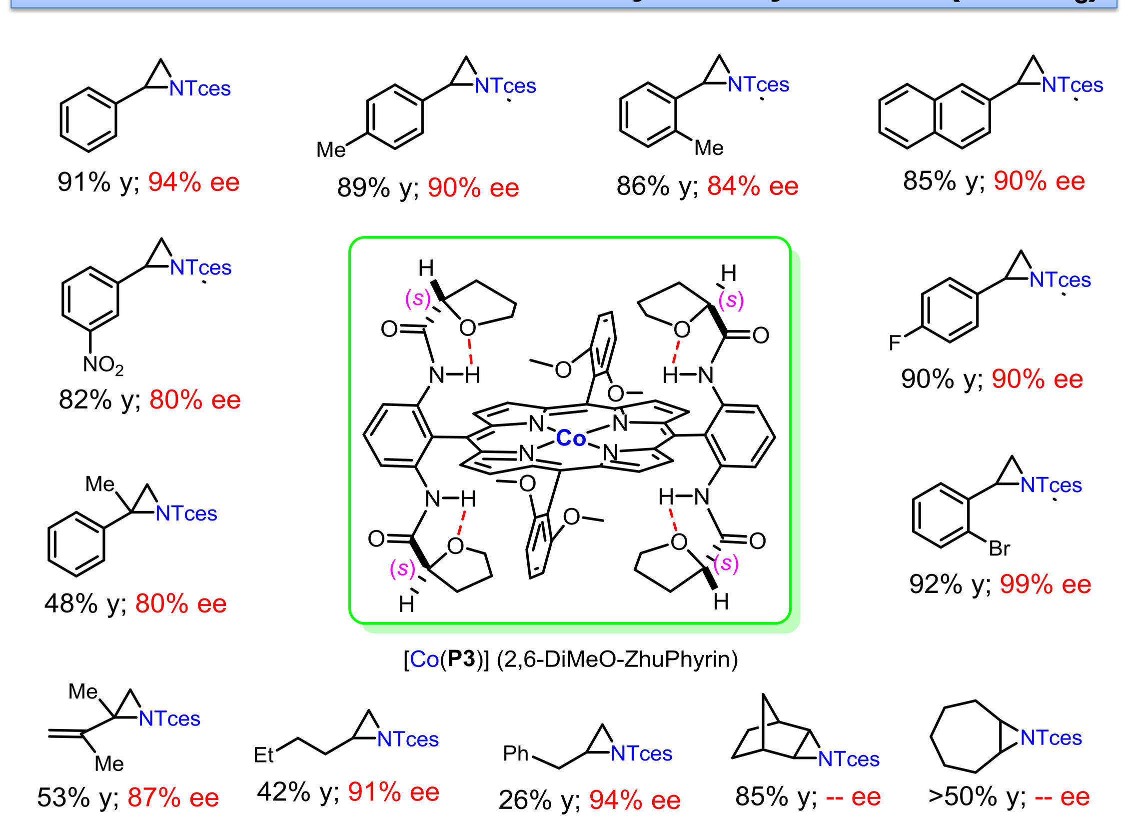


Dalton Trans. **2011**, *40*, 5697.

Simple Model for Stereoselectivity

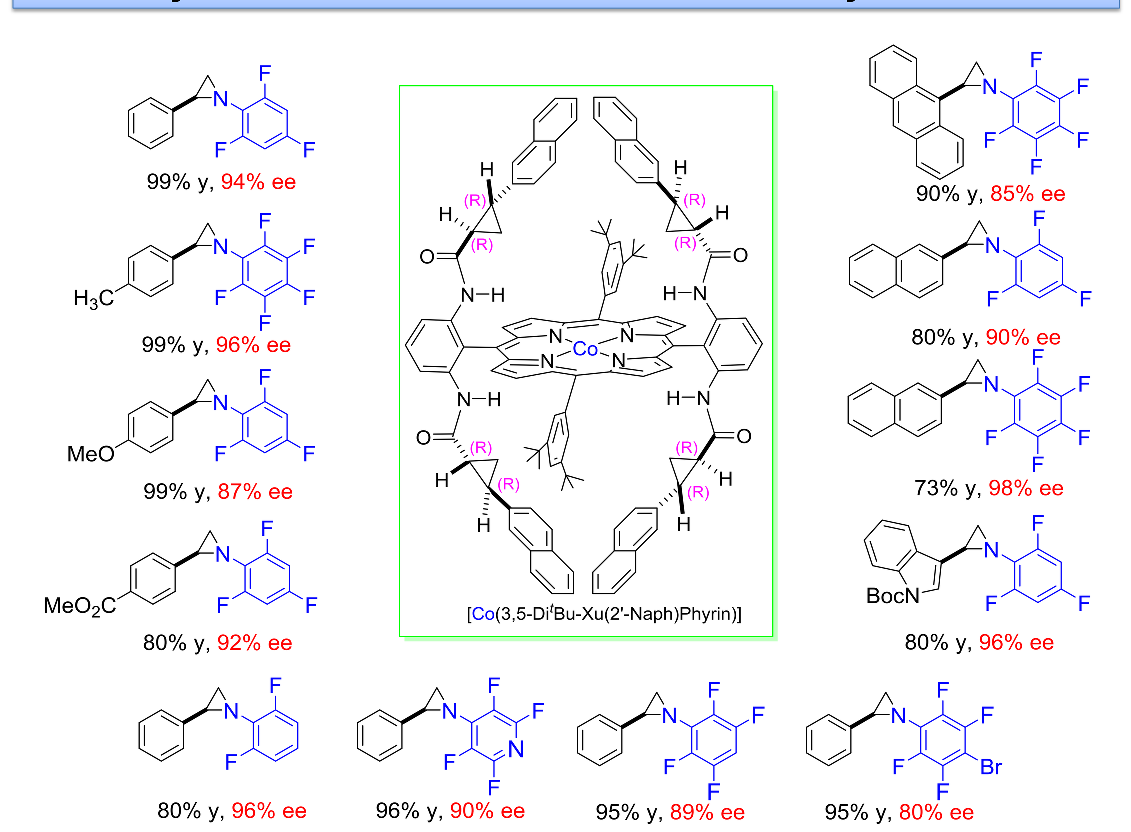


Aziridination with Trichloroethoxysulfonyl Azides ($TcesN_3$)



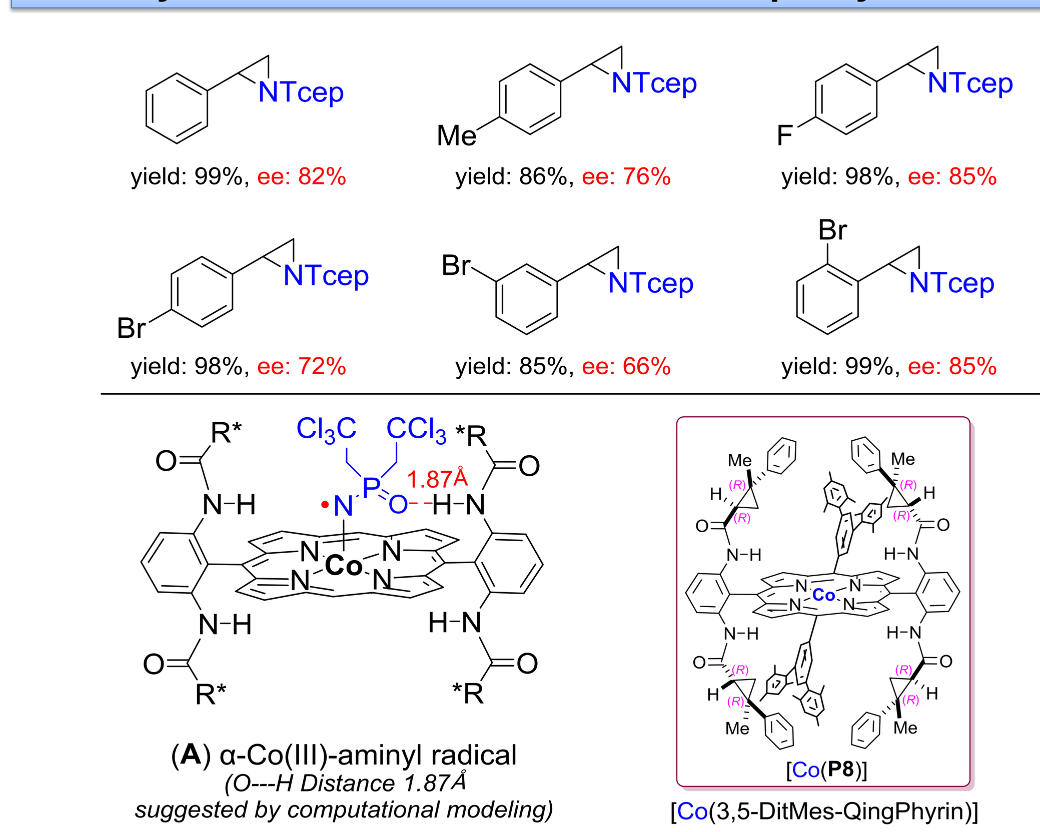
Chem. Comm. **2009**, *28*, 4266.

Asymmetric Aziridination with Fluoroaryl Azides



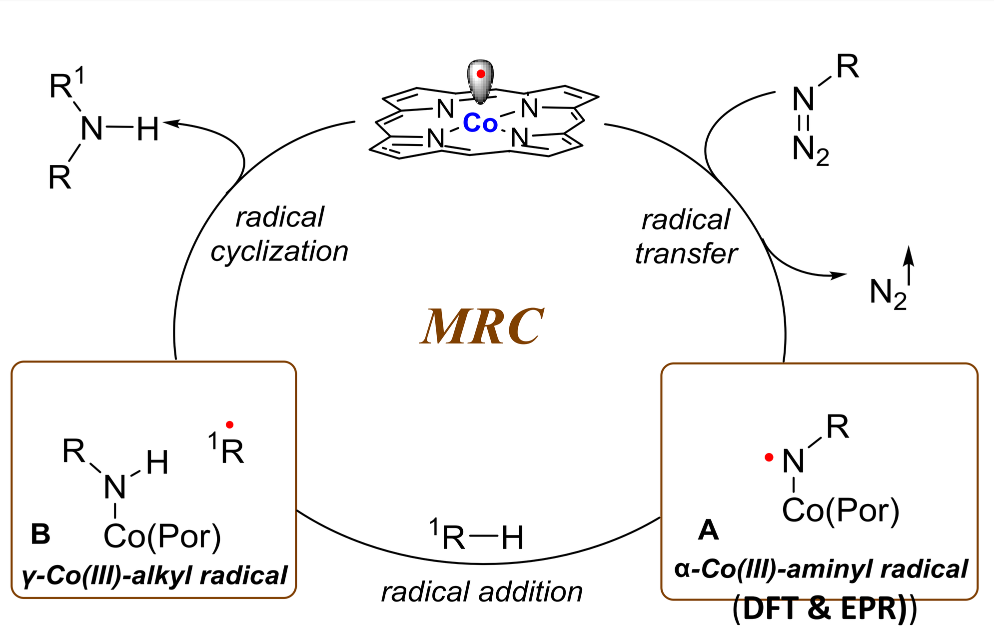
Angew. Chem. Int. Ed. **2013**, *52*, 5309.

Asymmetric Aziridination with Phosphoryl Azides



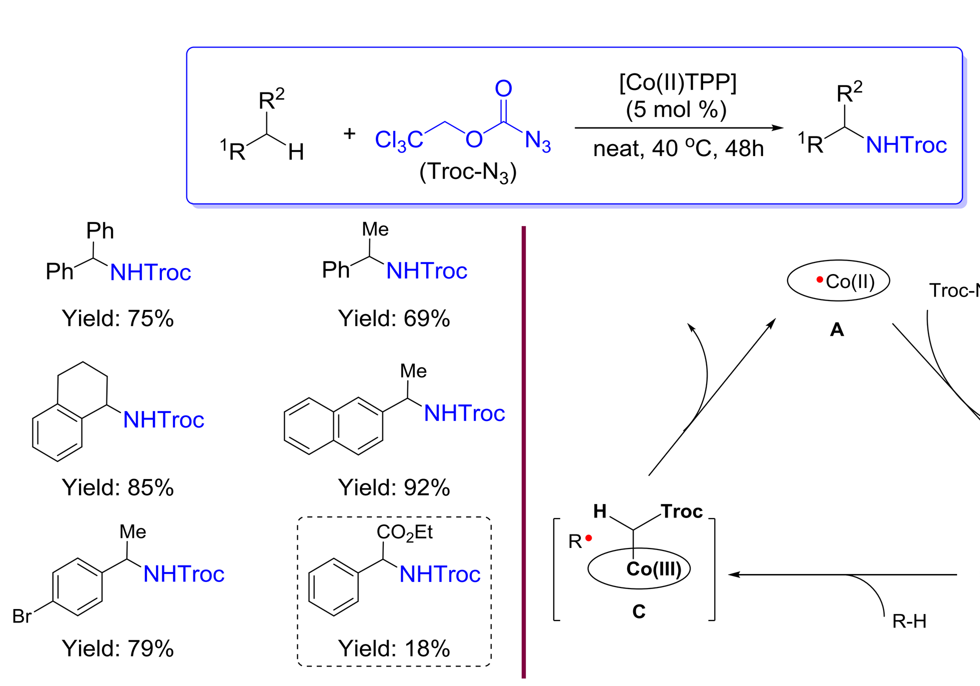
Beilstein J. Org. Chem. **2014**, 10,1282.

Metalloradical Catalysis for C–H Amination



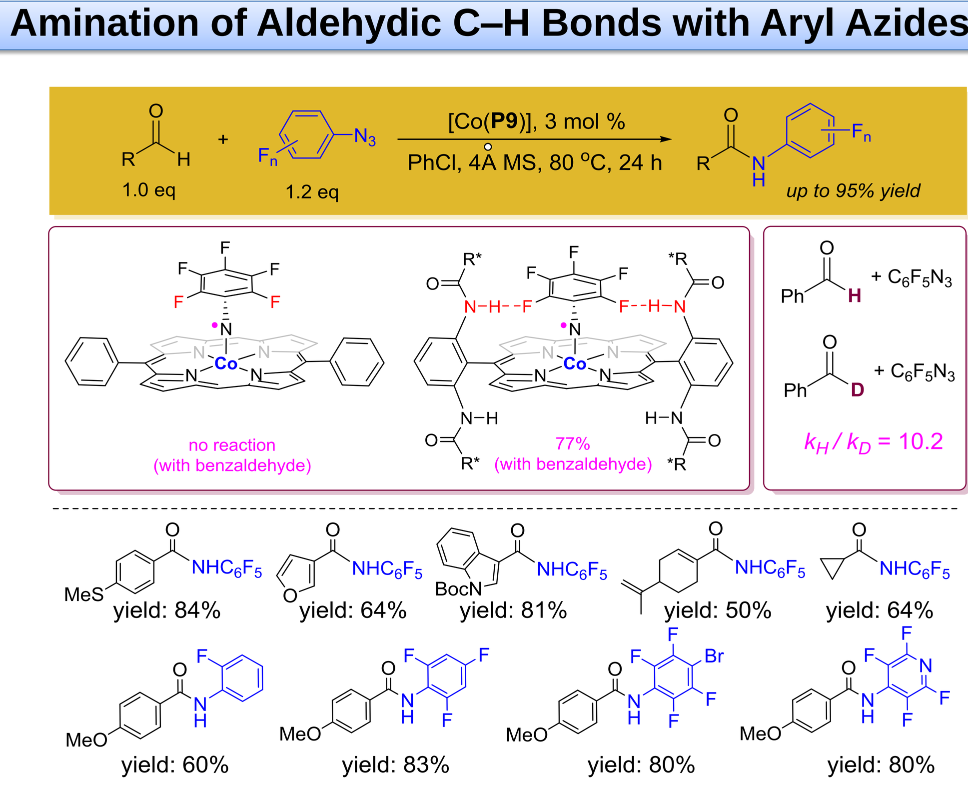
J. Am. Chem. Soc. **2011**, *133*, 12264.
J. Am. Chem. Soc. **2015**, *137*, asap.

Amination of $C(sp^3)$–H Bonds with Carbonyl Azide



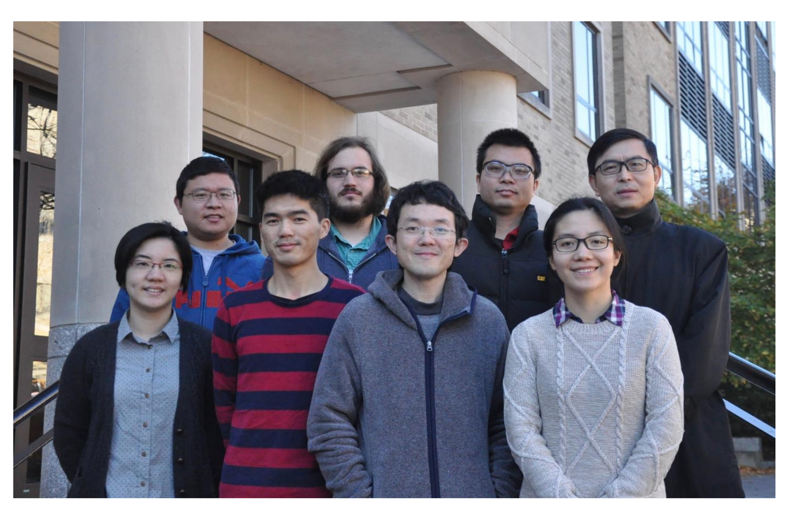
Organometallics **2009**, *29*, 389.

Amination of Aldehydic C–H Bonds with Aryl Azides



Chem. Sci. **2014**, *5*, 2422.

Acknowledgments



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