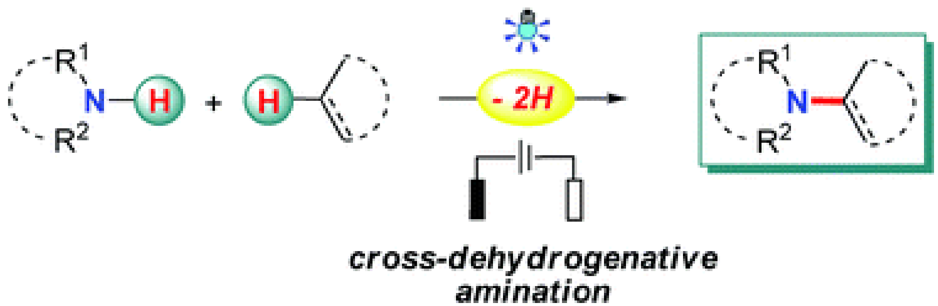
Recent advances in radical-based C–N bond formation via photo-/electrochemistry

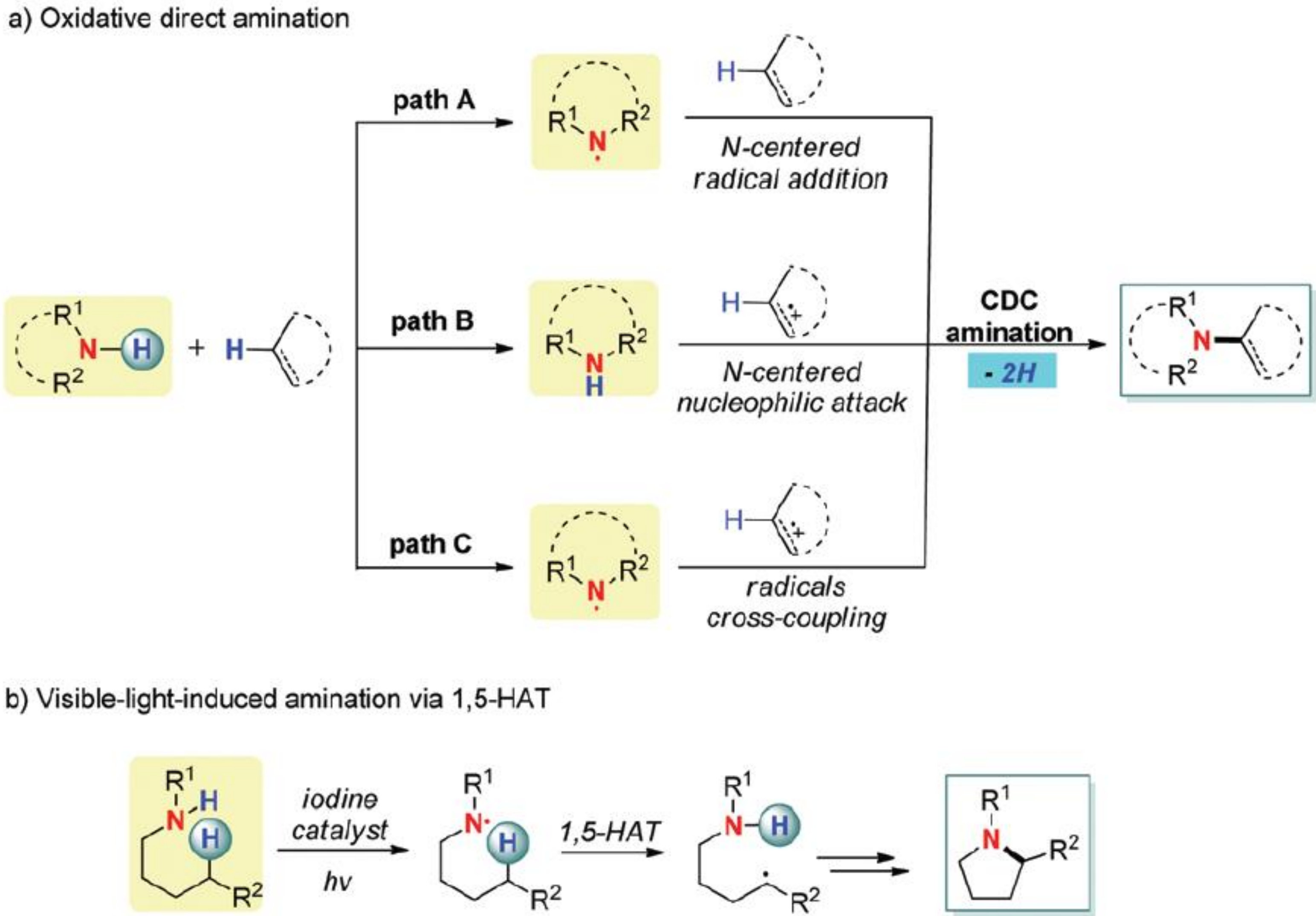


Reporter: Pengfei Yuan
Supervisor: Prof. Yong Huang

Date: Jul. 9th, 2018

Content

1. Introduction



Wu. Xia, *Chem. Soc. Rev.* **2018**, *47*, 2591.

2. C–N bond formation via N-radical species addition

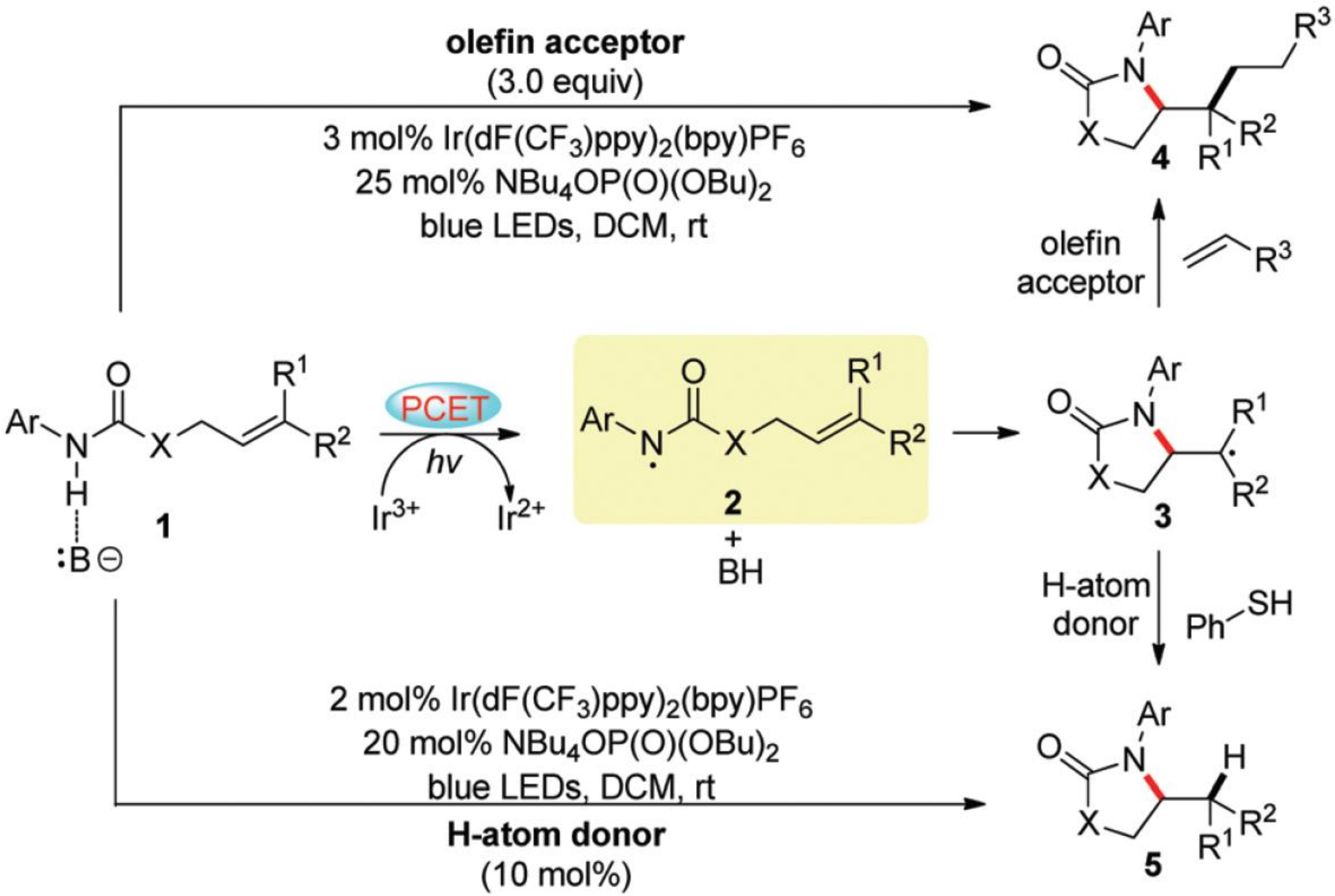
2.1 Radical addition to C–C double/triple bonds

Amidyl radical ddition
Hydrazonyl radical addition
Aminium radical cation addition

2.2 Radical species addition to aromatic rings

2.1 Radical addition to C–C double/triple bonds

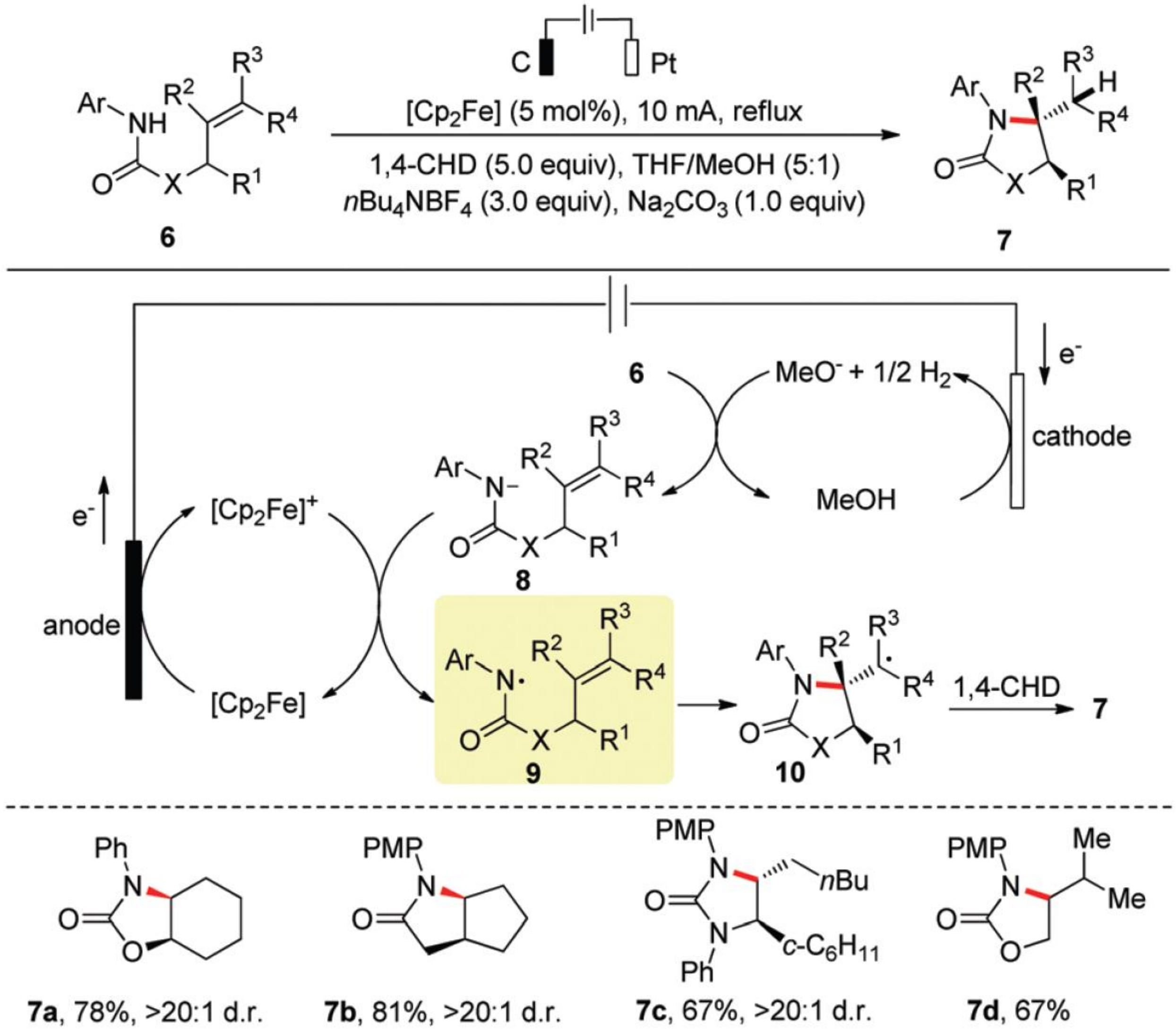
Amidyl radical addition:



R. R. Knowles, *Acc. Chem. Res.* **2016**, *49*, 1546.

2.1 Radical addition to C–C double/triple bonds

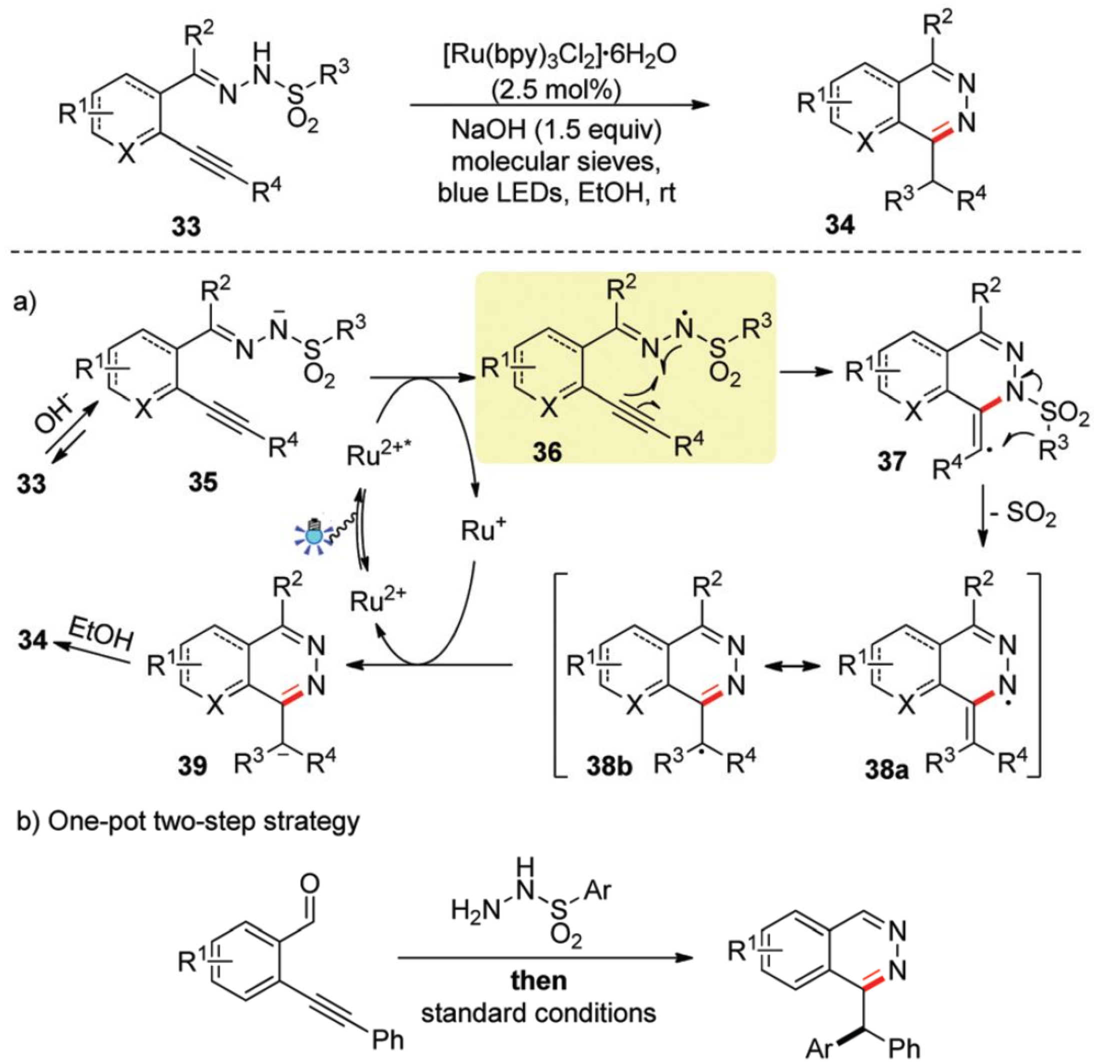
Amidyl radical addition:



H. C. Xu, *Angew. Chem. Int. Ed.* **2016**, *55*, 2226.

2.1 Radical addition to C–C double/triple bonds

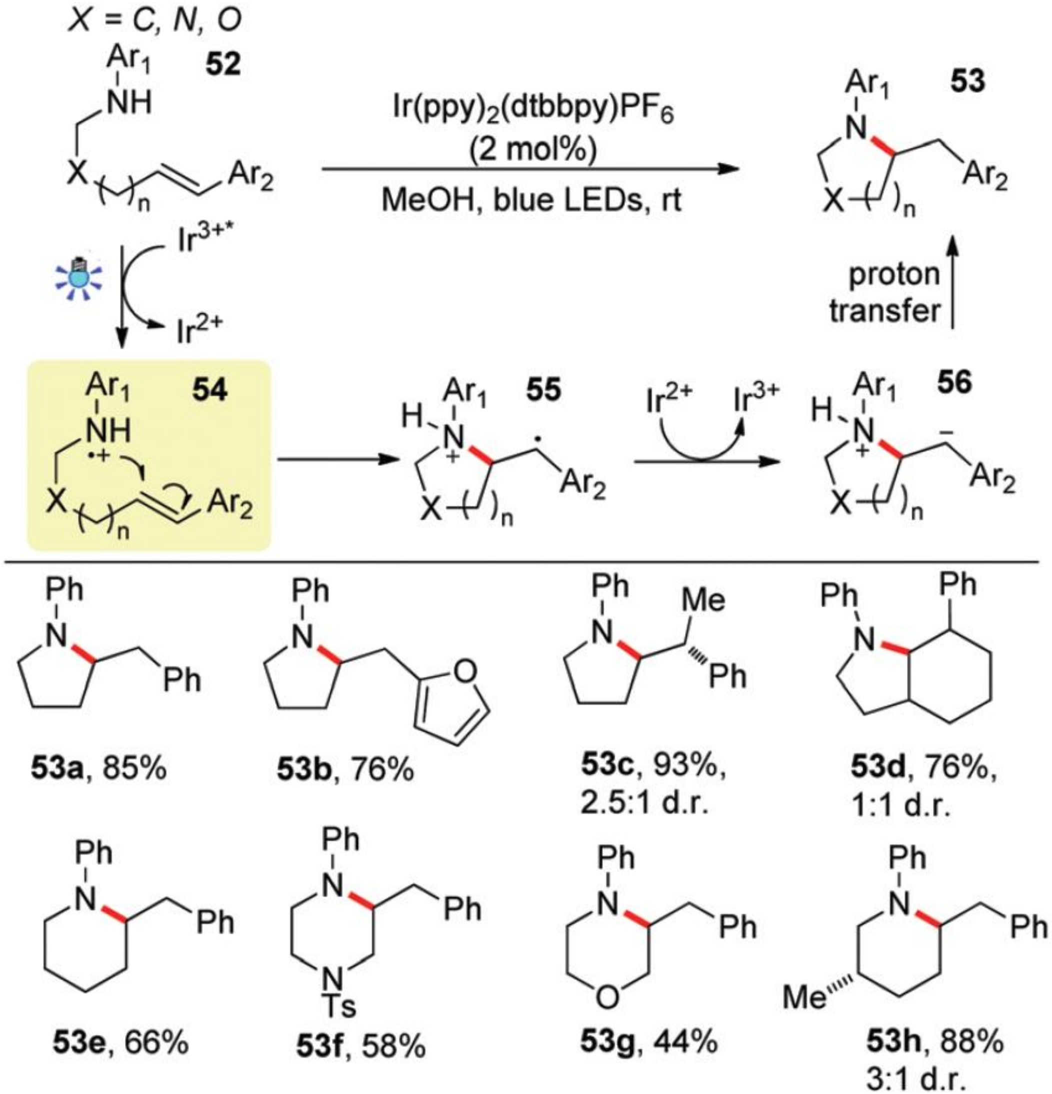
Hydrazonyl radical addition:



P. Belmont, *Chem. Sci.* **2016**, *7*, 5002.

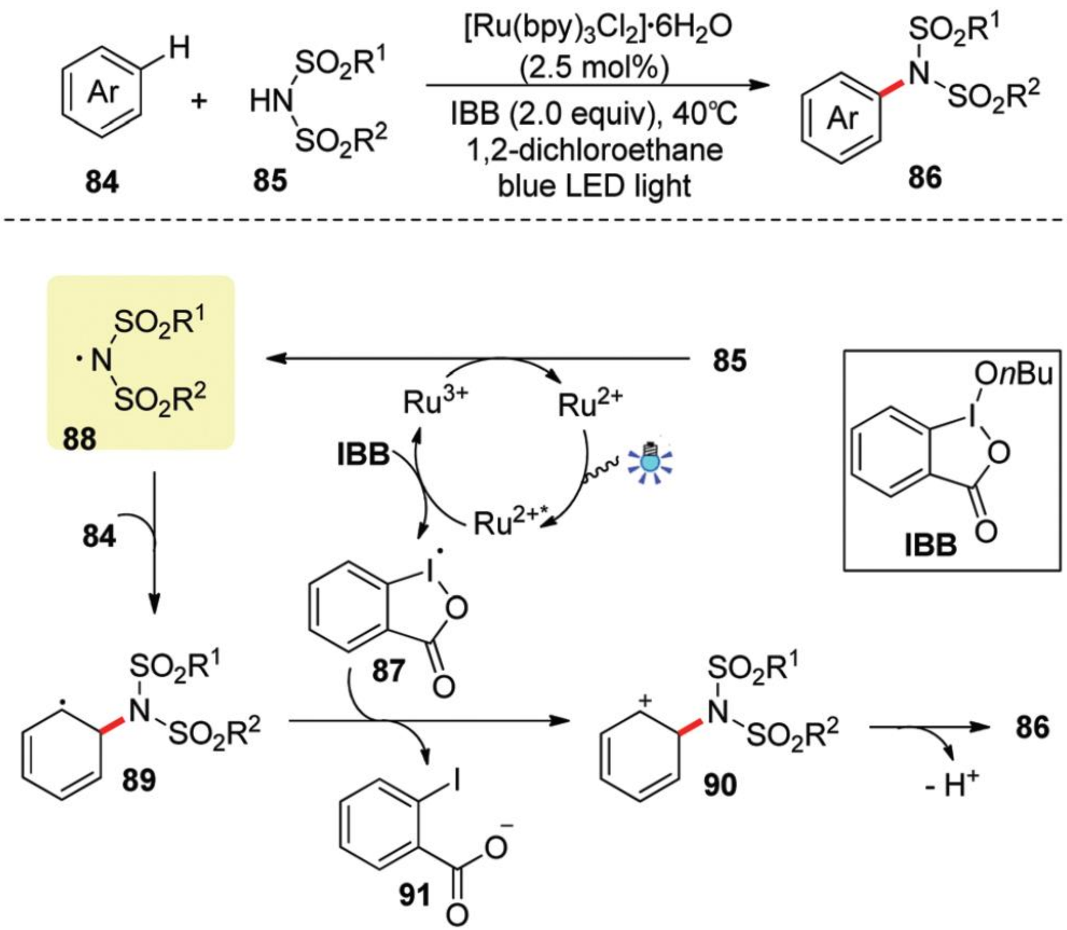
2.1 Radical addition to C–C double/triple bonds

Aminium radical cation addition：



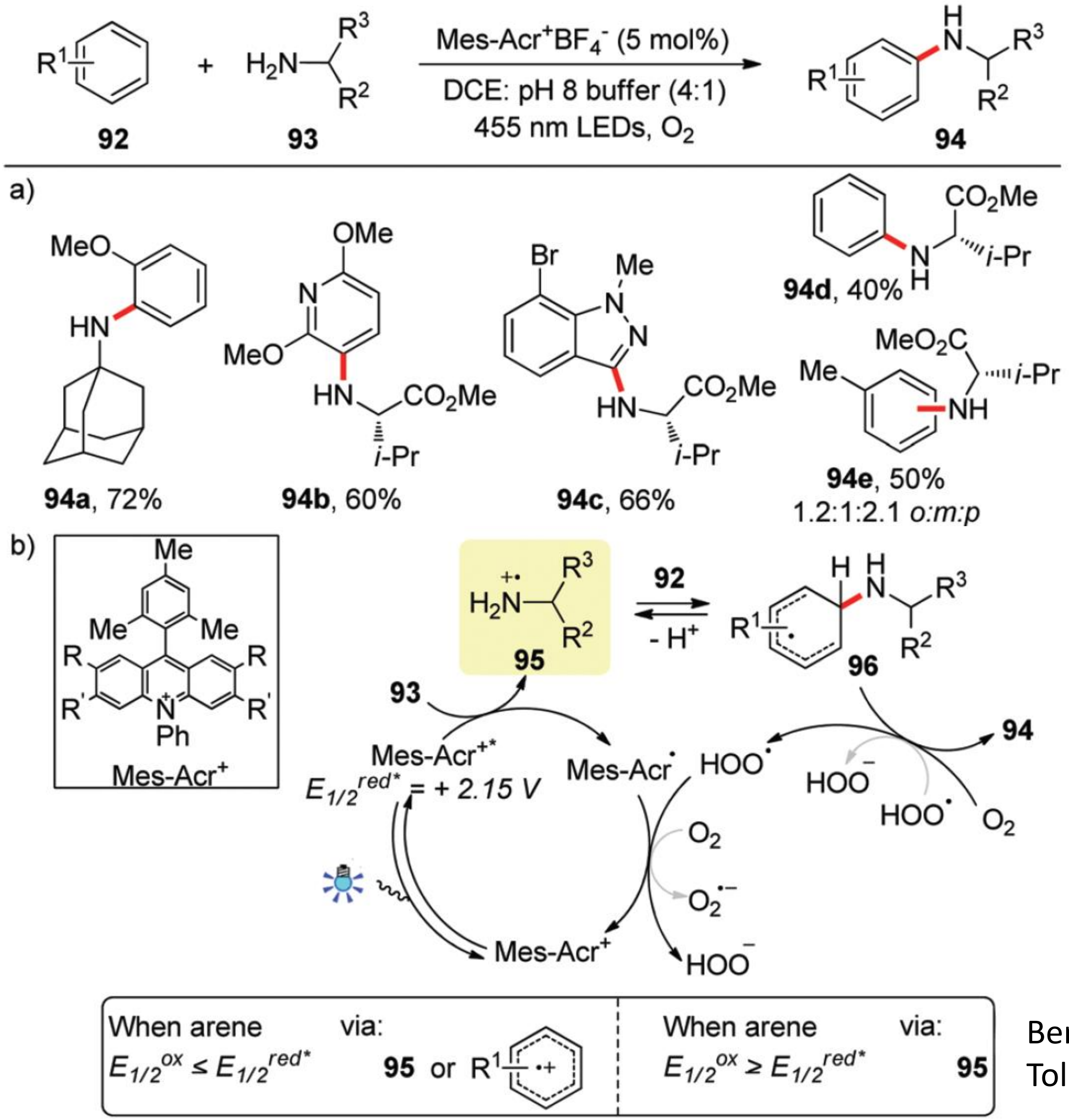
R. R. Knowles, *J. Am. Chem. Soc.* **2014**, *136*, 12217.

2.2 Radical species addition to aromatic rings



K. Itami, *Chem*, **2017**, *2*, 383.

2.2 Radical species addition to aromatic rings

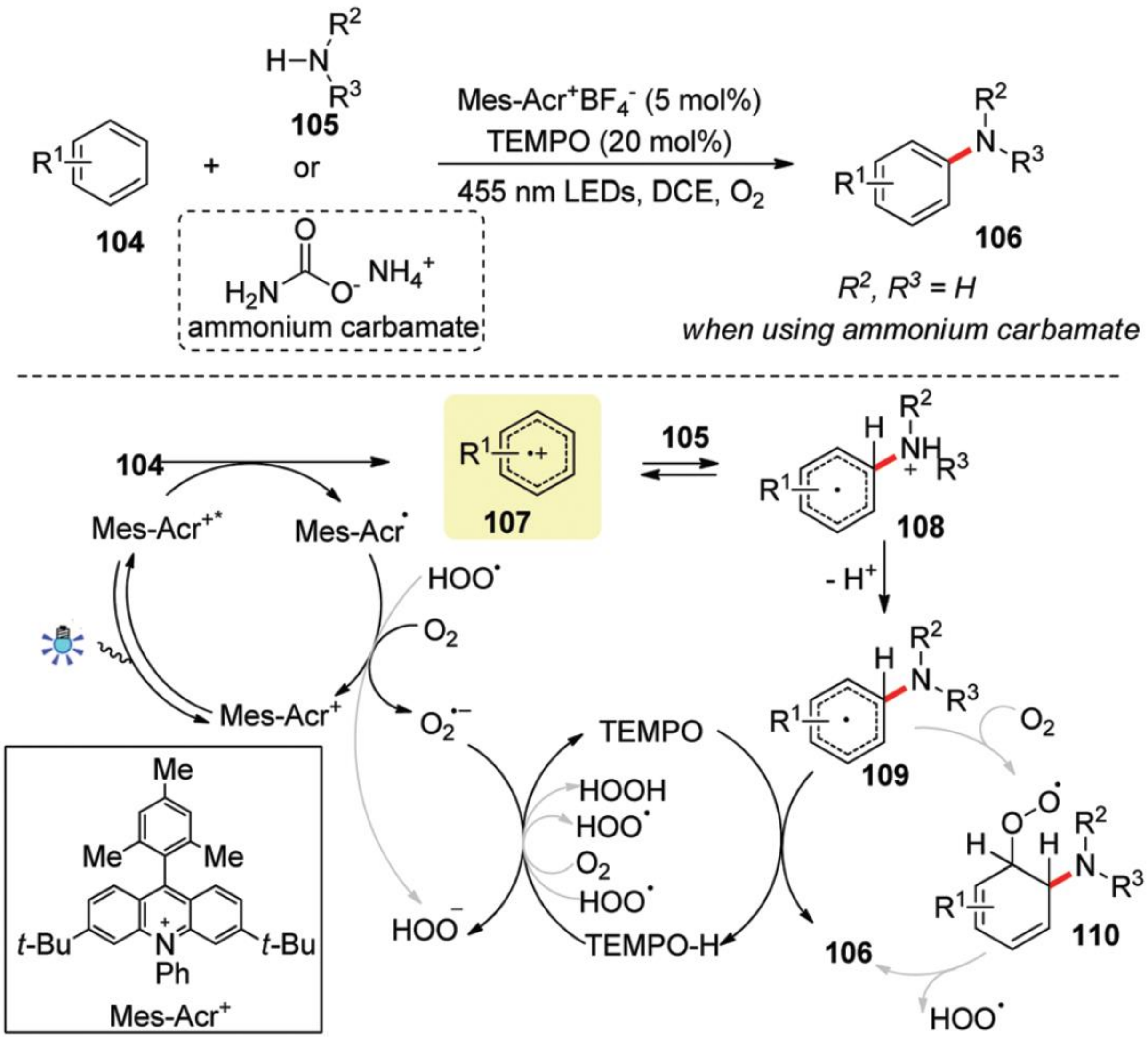


Benzene ($E_{1/2}ox$ = +2.75 V)
Toluene ($E_{1/2}ox$ = +2.42 V)

D. A. Nicewicz, *Angew. Chem. Int. Ed.* **2017**, *56*, 15644.

3. CDC amination via N-atom nucleophilic addition

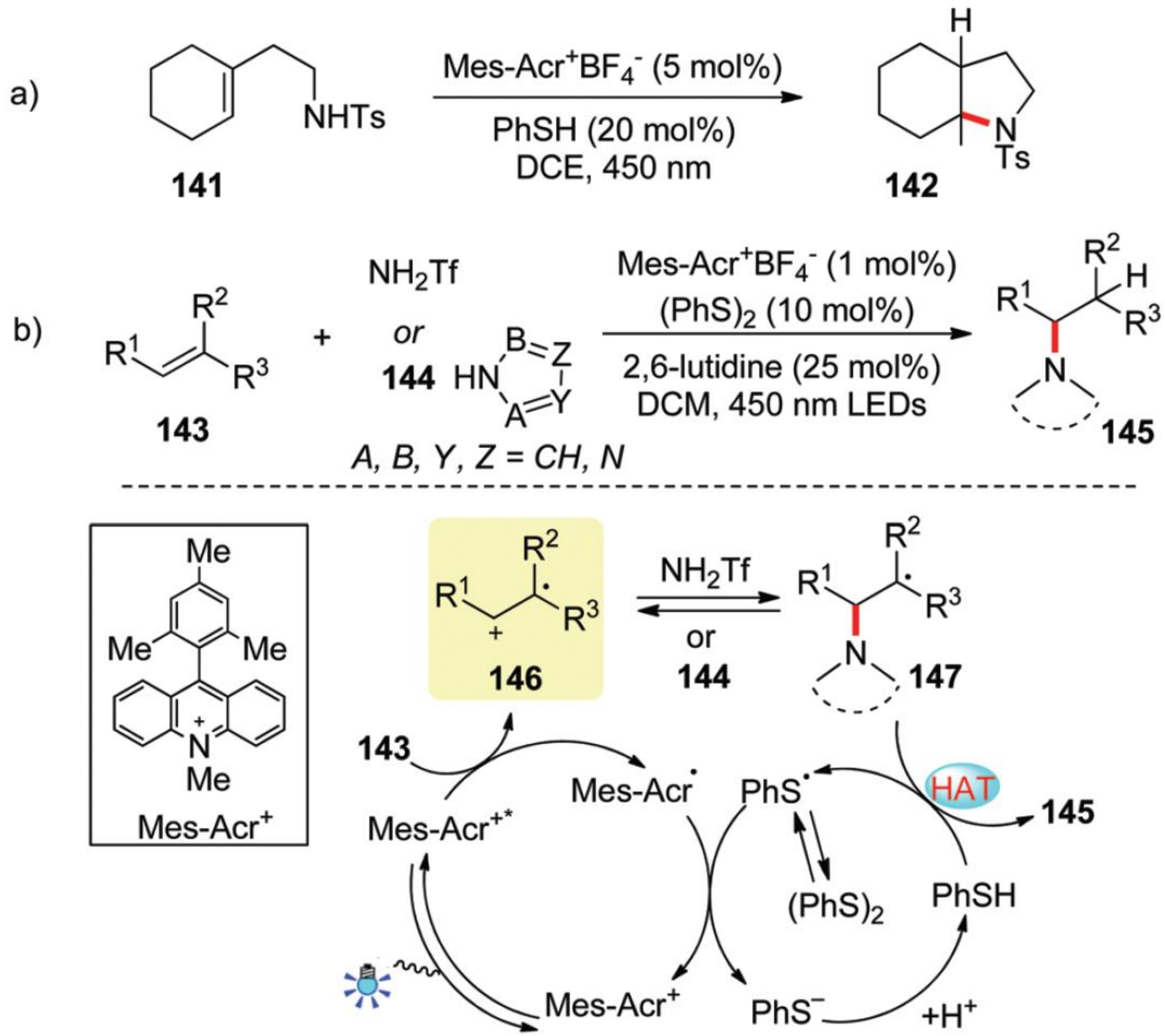
Aromatic C(sp2)–H bonds amination



D. A. Nicewicz, *Science*, **2015**, *349*, 1326.

3. CDC amination via N-atom nucleophilic addition

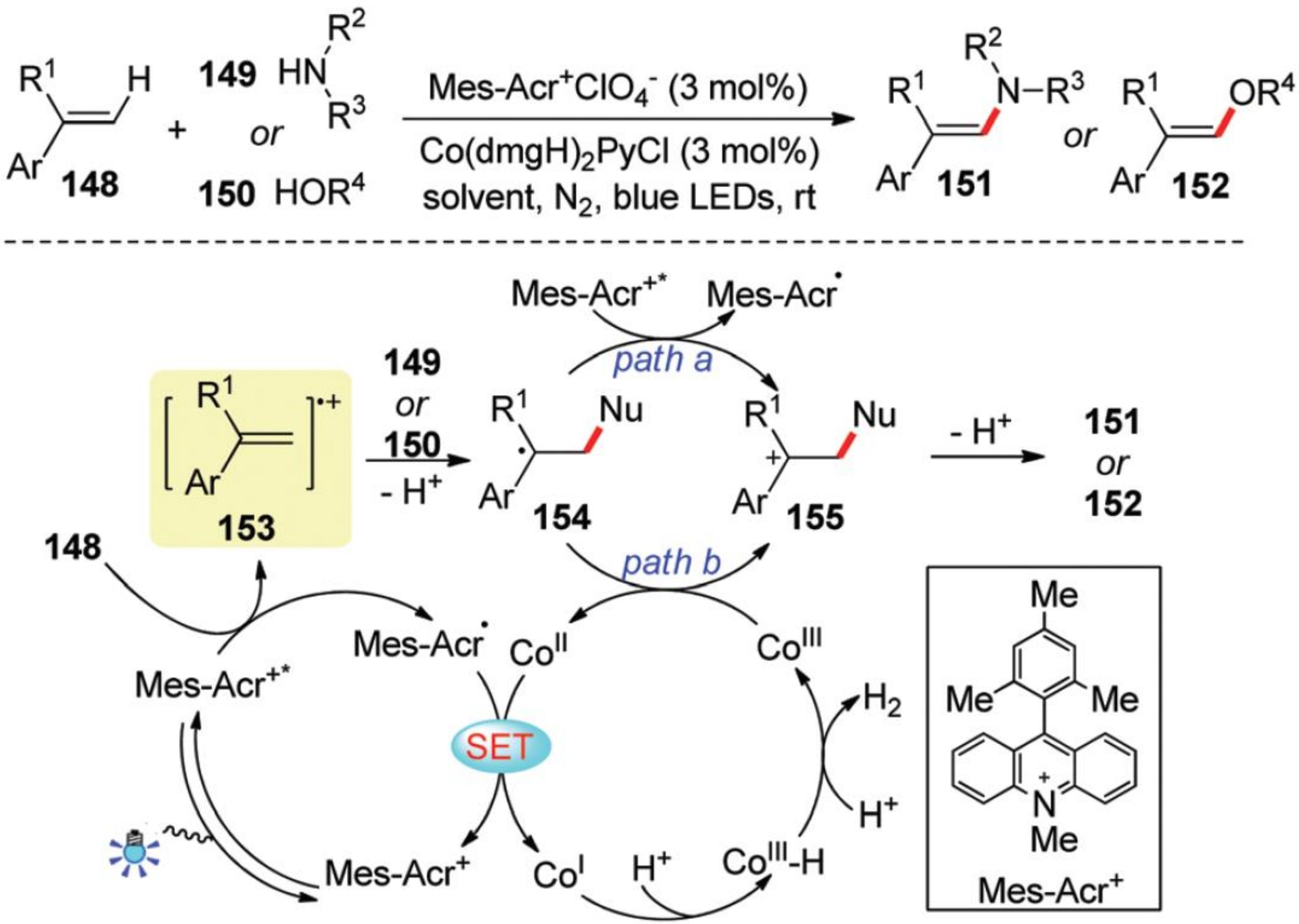
Olefinic C(sp2)–H bond amination



1) D. A. Nicewicz, *J. Am. Chem. Soc.* **2013**, *135*, 9588.
2) D. A. Nicewicz, *Angew. Chem. Int. Ed.* **2014**, *53*, 6198.

3. CDC amination via N-atom nucleophilic addition

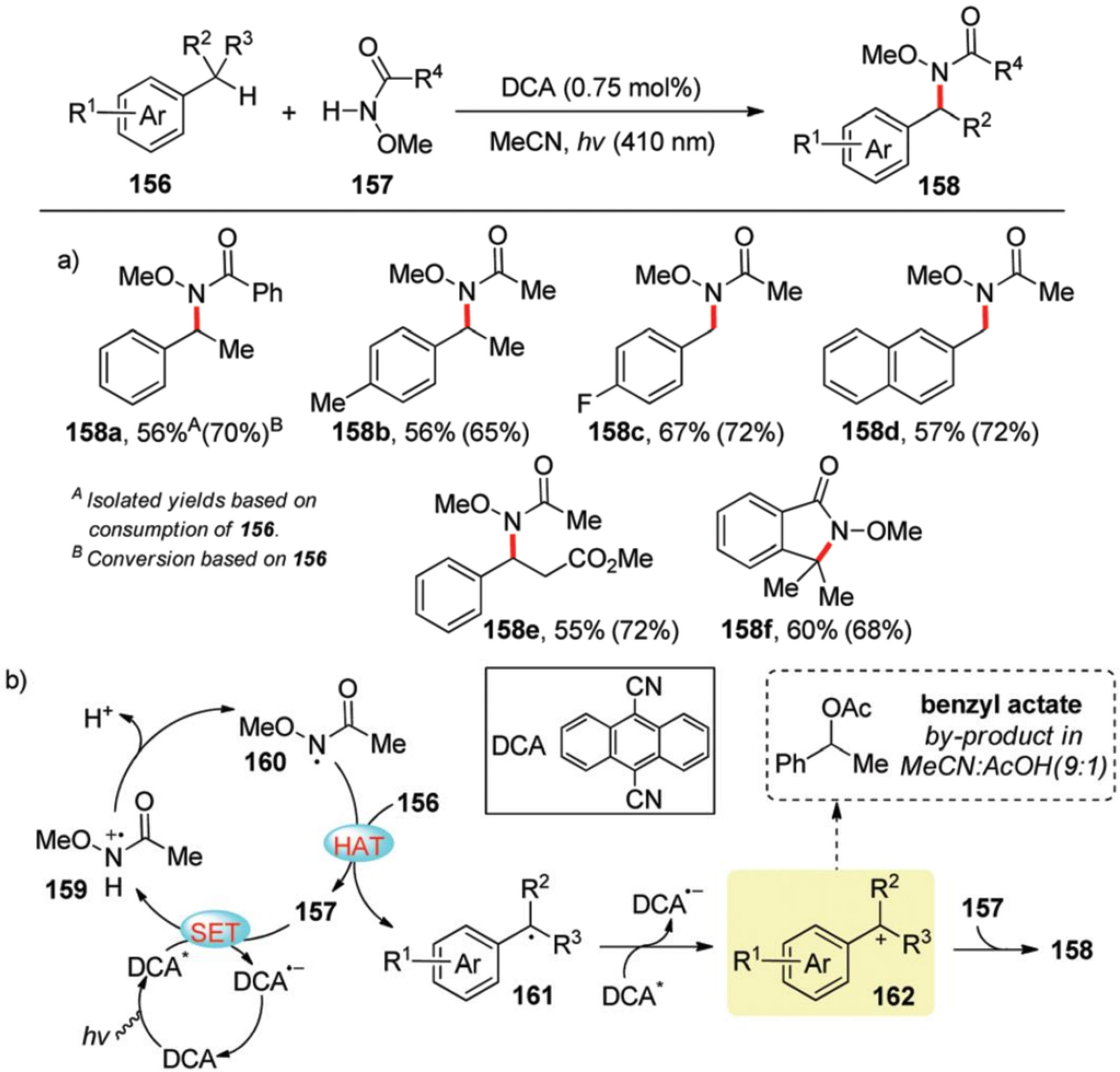
Olefinic C(sp2)–H bond amination



A. Lei, *Angew. Chem. Int. Ed.* **2017**, *56*, 1120.

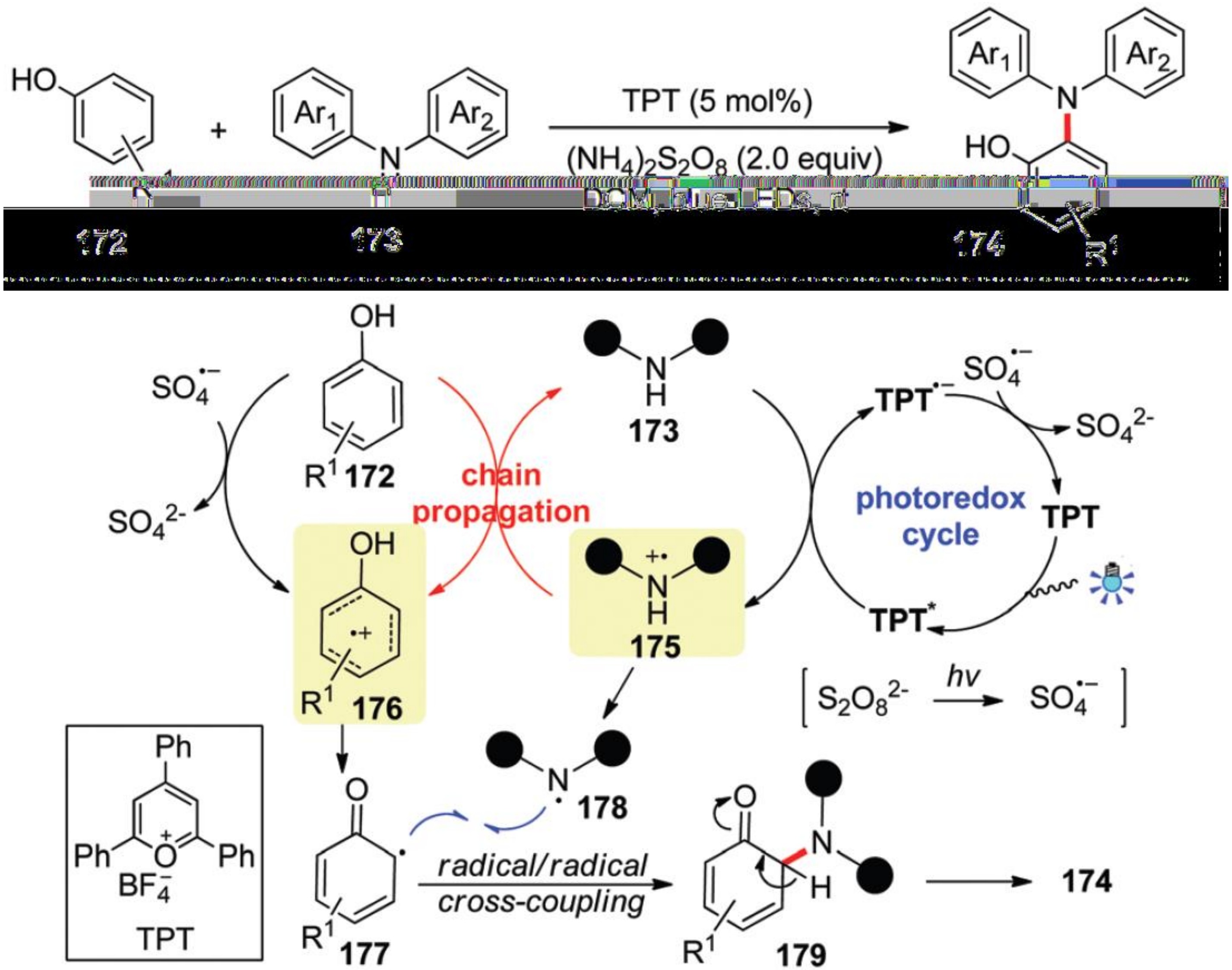
3. CDC amination via N-atom nucleophilic addition

Benzylic C(sp3)–H bond amination



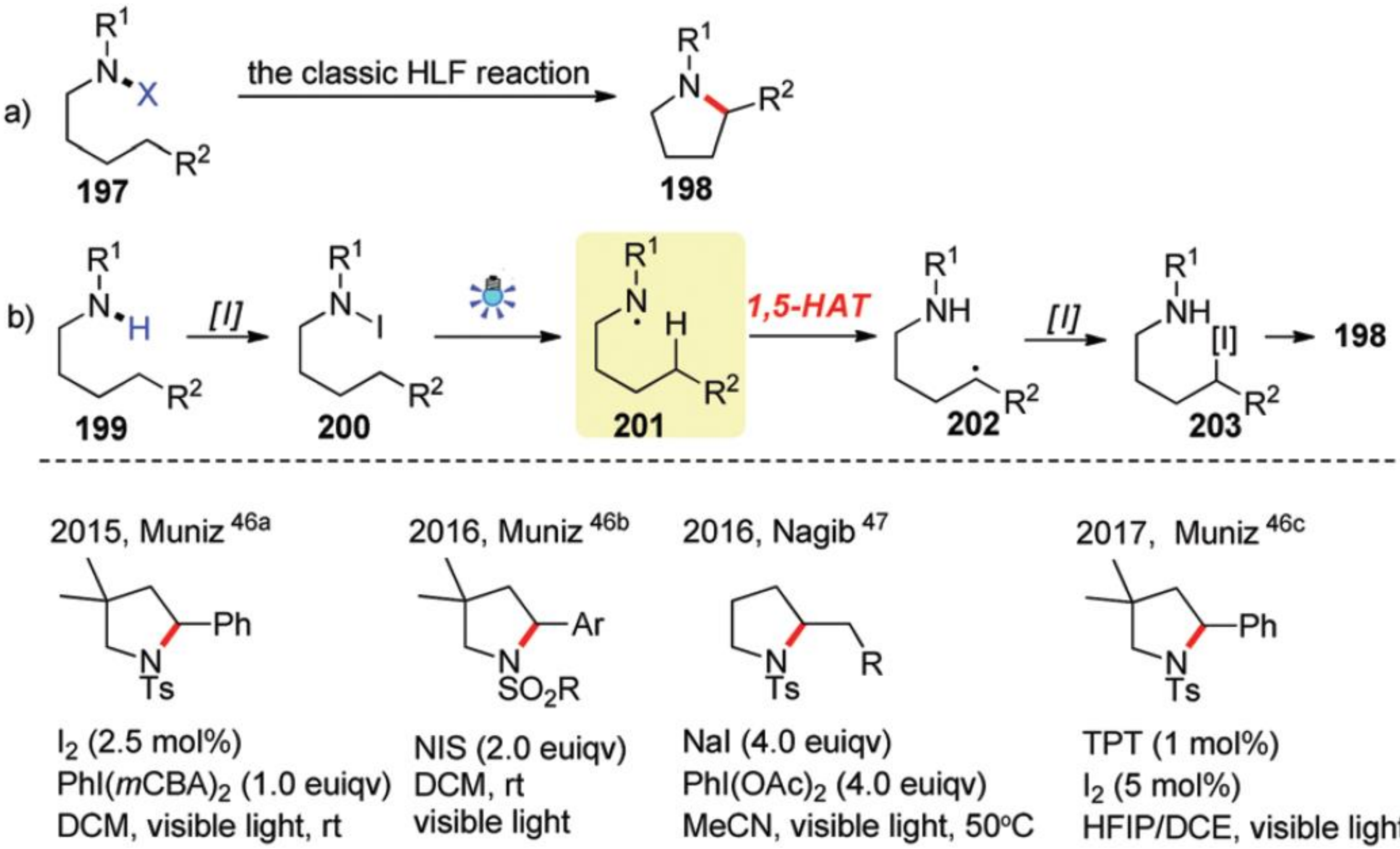
R. Laha, *Angew. Chem. Int. Ed.* **2015**, *54*, 14875.

4. CDC amination via radical cross-coupling



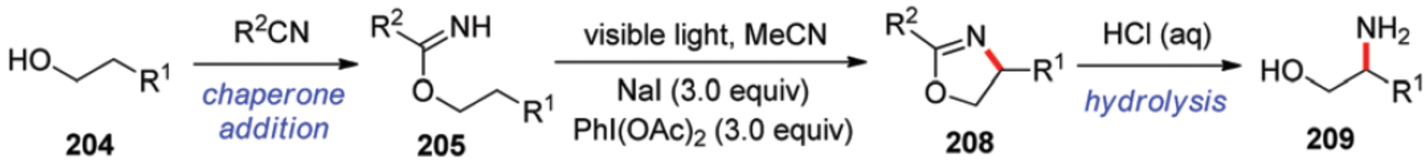
W. Xia, *ACS Catal.* **2017**, *7*, 2446.

5. CDC amination of C(sp3)–H bonds via HAT

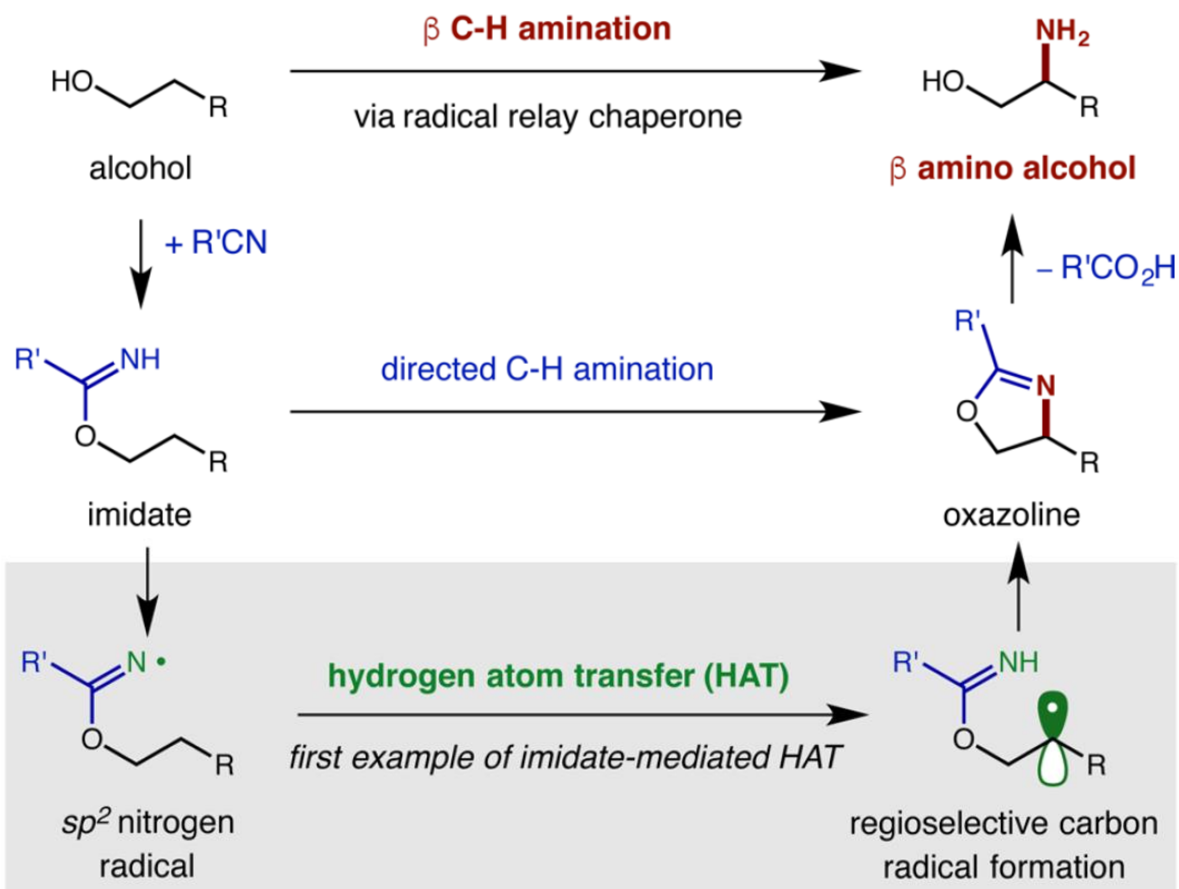


1) K. Muniz, *Angew. Chem. Int. Ed.* **2017**, *56*, 8004.
2) D. A. Nagib, *Angew. Chem. Int. Ed.* **2016**, 55, 9974.

5. CDC amination of C(sp3)–H bonds via HAT



Design of radical relay chaperone strategy for β C-H amination



D. A. Nagib, *J. Am. Chem. Soc.* **2017**, *139*, 10204.

6. Challenges and opportunities

1. N source limited to the secondary amides, carbamates, sulfonamides, diaryl amines, and azoles.
   More convenient amino sources: primary amines or secondary alkyl amines.

2. The aliphatic C(sp3)–H amination: benzylic position or α-H to a hetero atom,
   More extensive and versatile C(sp3)–H amination.

3. High enantioselectivity and selective amination at a specific position are hardly accessible in these simple radical involved reactions.

6. Acknowledgement

- **Prof. Huang**
- **Prof. Chen**
- **All members in E201**

Thanks for your attention!