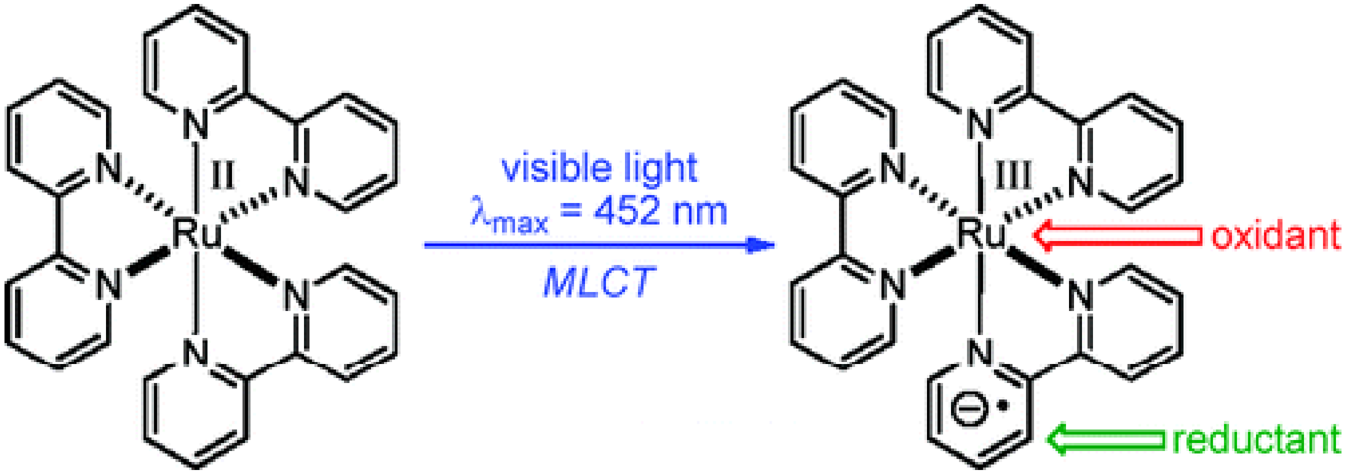
Visible Light Photoredox Catalysis with Transition Metal Complexes: Application in Organic Synthesis

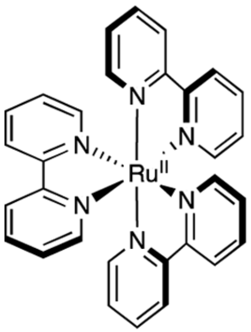


Penghao Chen

Dong Group Seminar

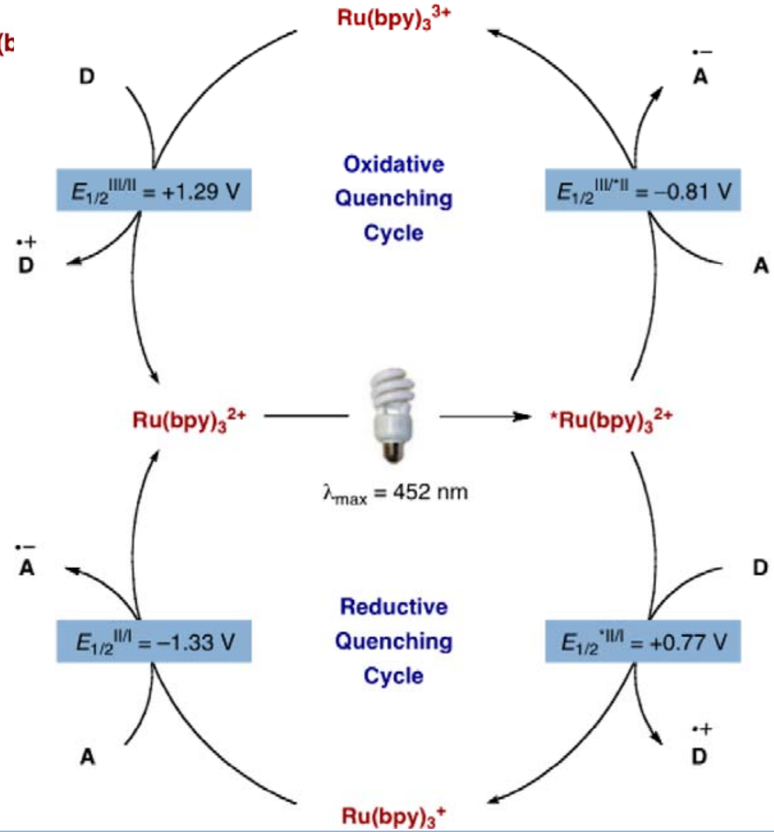
April, 10th, 2013

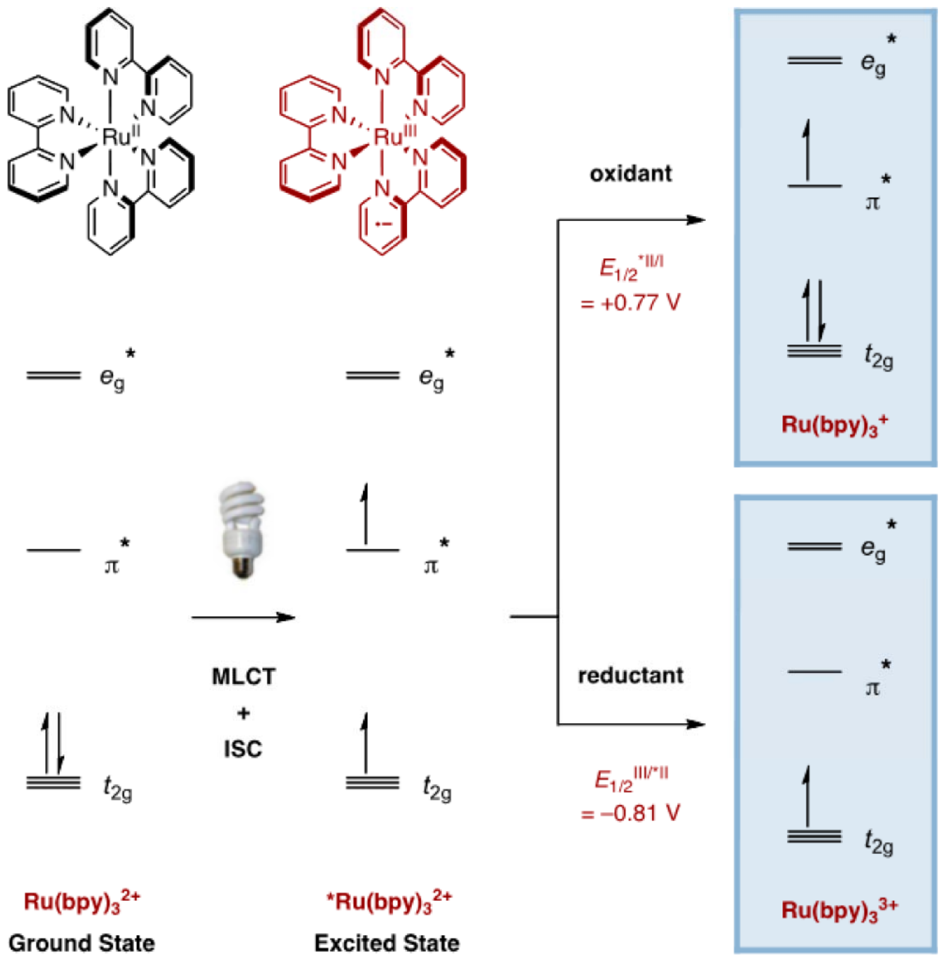
Introduction



Ru(b

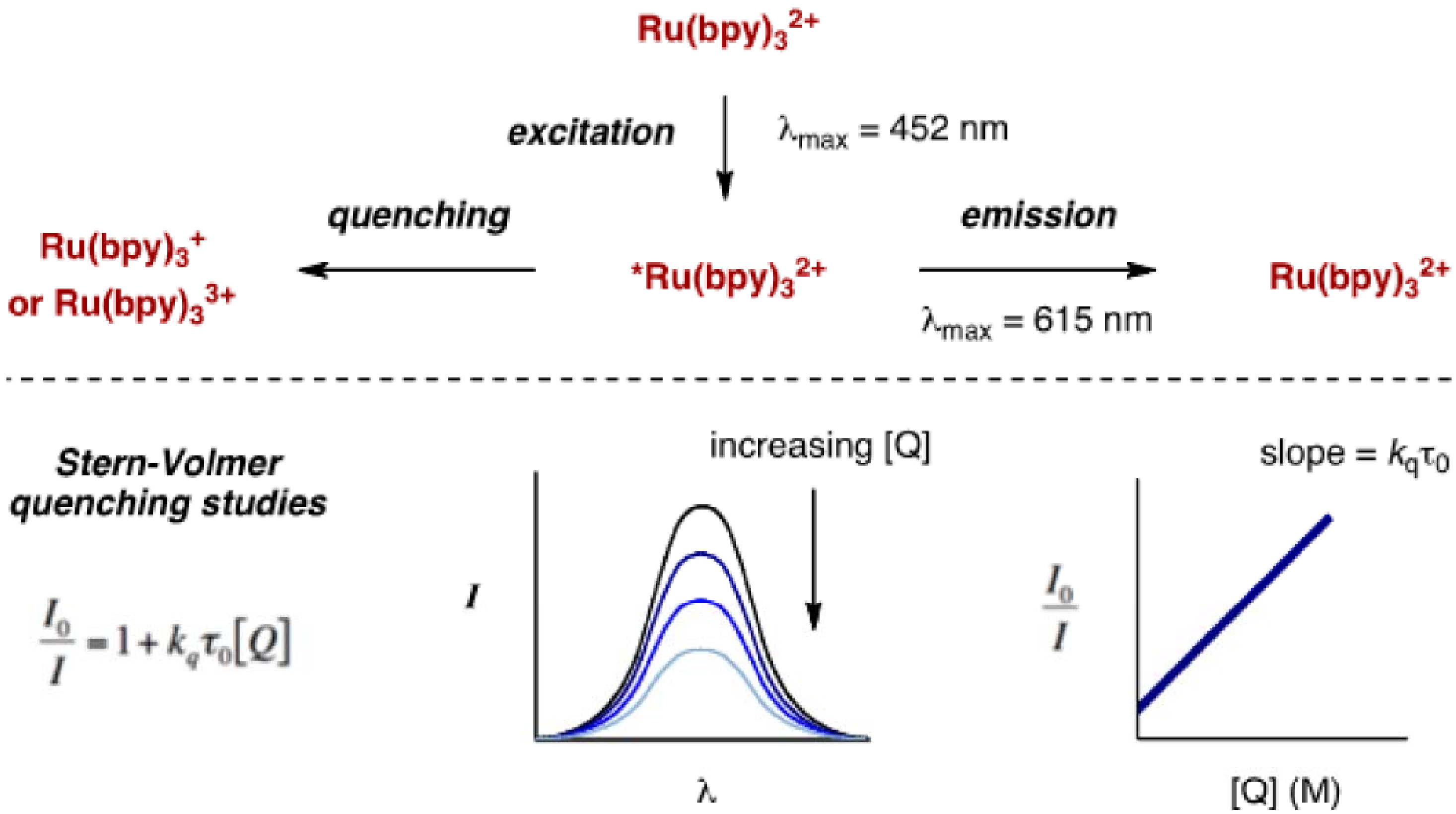
- Absorption at 452 nm (visible light)
- Stable, long-lived excited state (τ = 1100 ns)
- Single electron transfer (SET) catalyst
- Effective excited state oxidant and reductant





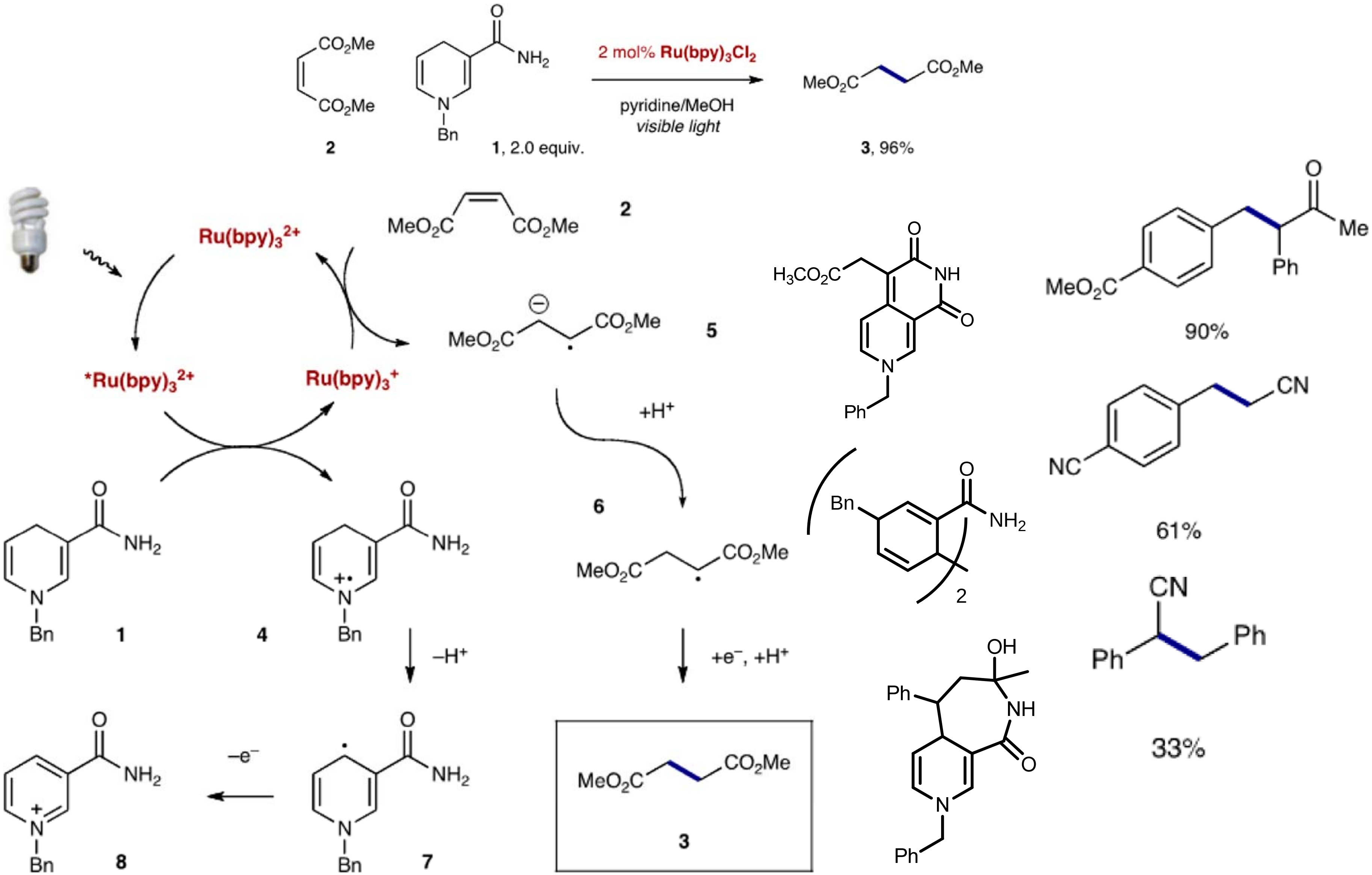
Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, 46, 159

Introduction *Stern-Volmer Relationship*



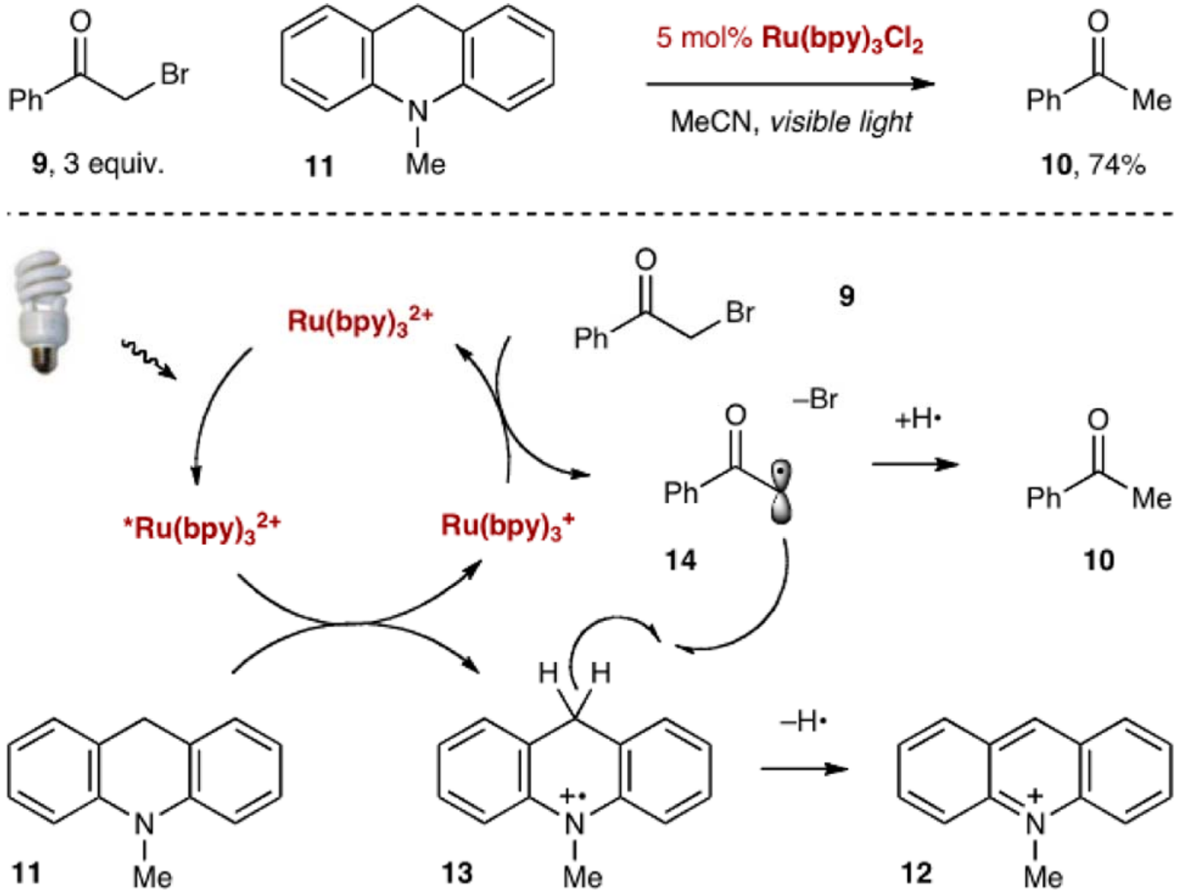
Turro, N. J. Modern Molecular Photochemistry; Benjamin/Cummings: Menlo Park, CA, **1978**.

Net Reductive Reaction 1. *Reduction of Electron Poor Olefin*



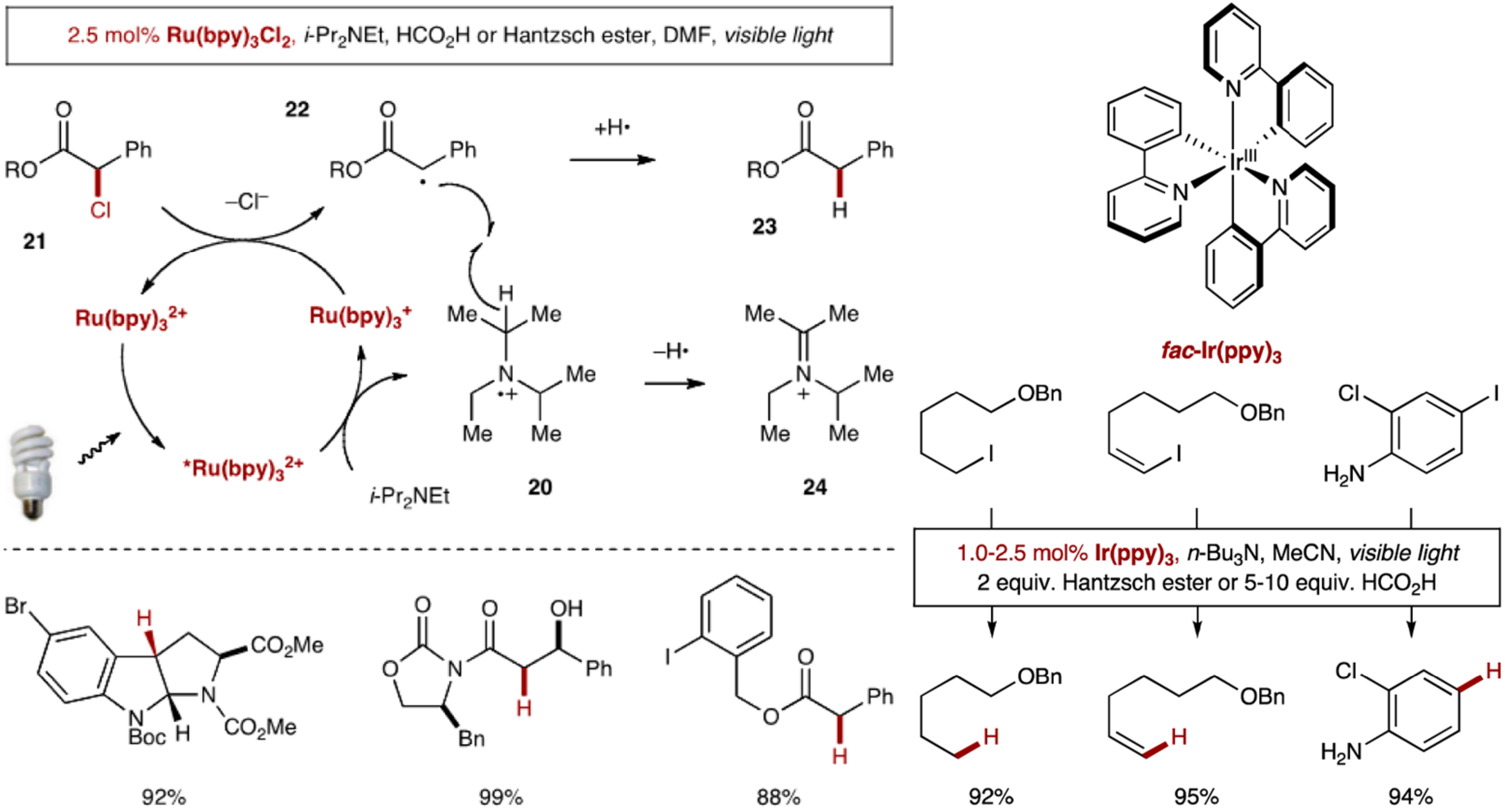
Pac, C. *et. al., J. Am. Chem. Soc.* **1981**, 103, 6495

Net Reductive Reaction 2. Reductive Dehalogenation



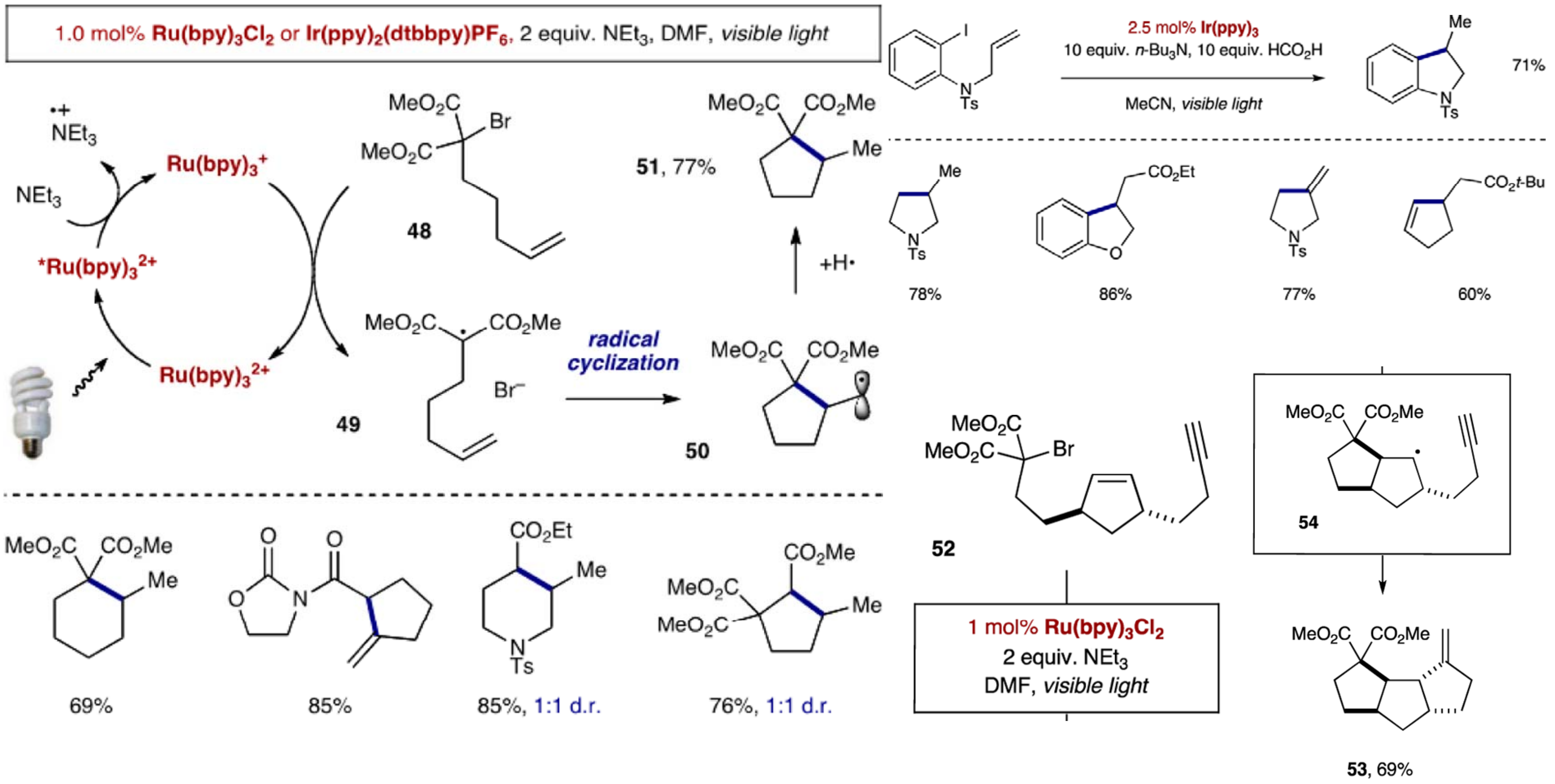
Fukuzumi, S. *et. al., J. Phys. Chem.* **1990**, 94, 722.

Net Reductive Reaction *2. Reductive Dehalogenation*



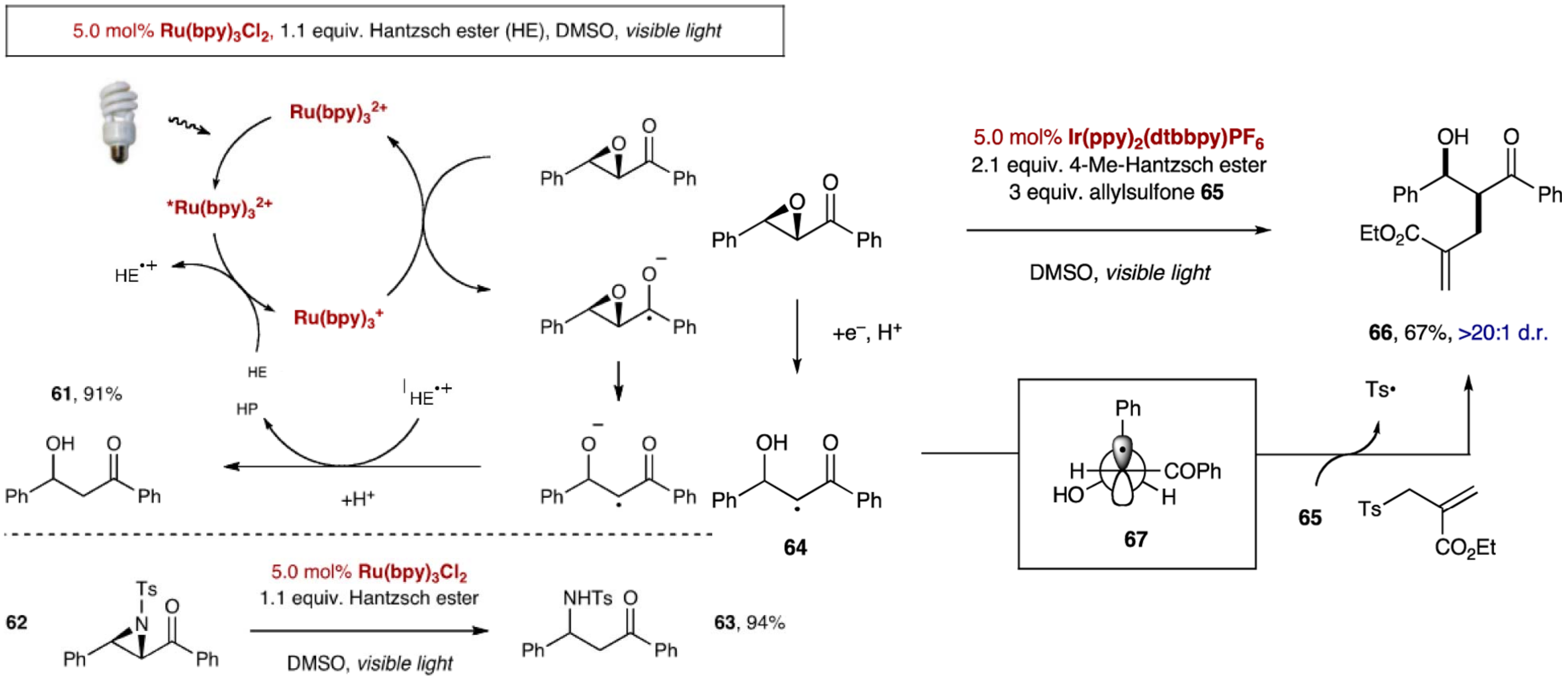
Stephenson, C. R. J. *et. al., J. Am. Chem. Soc.* **2009**, 131, 8756.
Stephenson, C. R. J. *et. al., Nature Chem.* **2012**, 4, 854

Net Reductive Reaction 3. Radical Cyclization



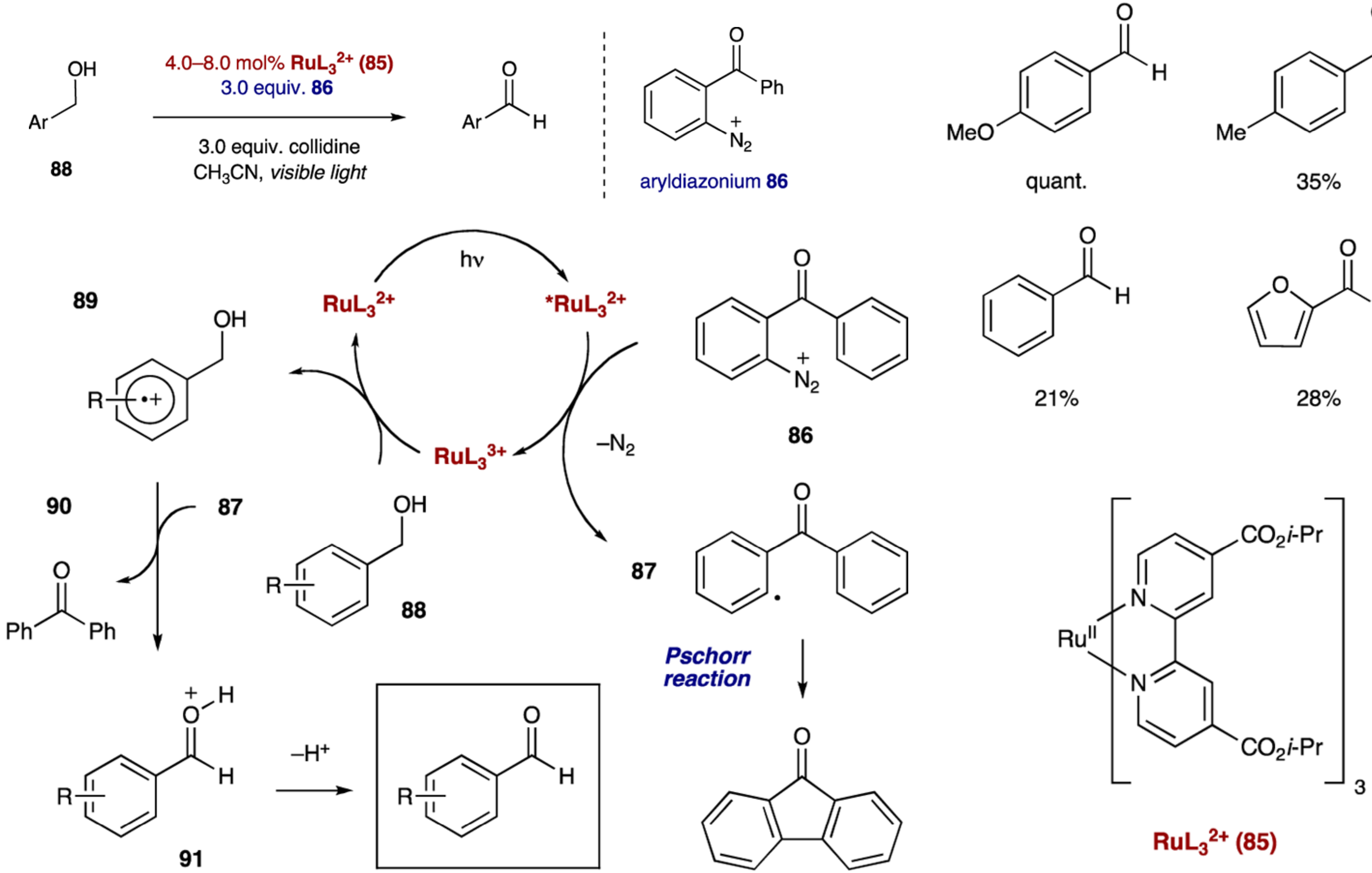
Stephenson, C. R. J. *et. al., Chem. Commun*. **2010**, 46, 4985
Stephenson, C. R. J. *et. al., Nature Chem.* **2012**, 4, 854

Net Reductive Reaction 4. Epoxide and Aziridine Opening



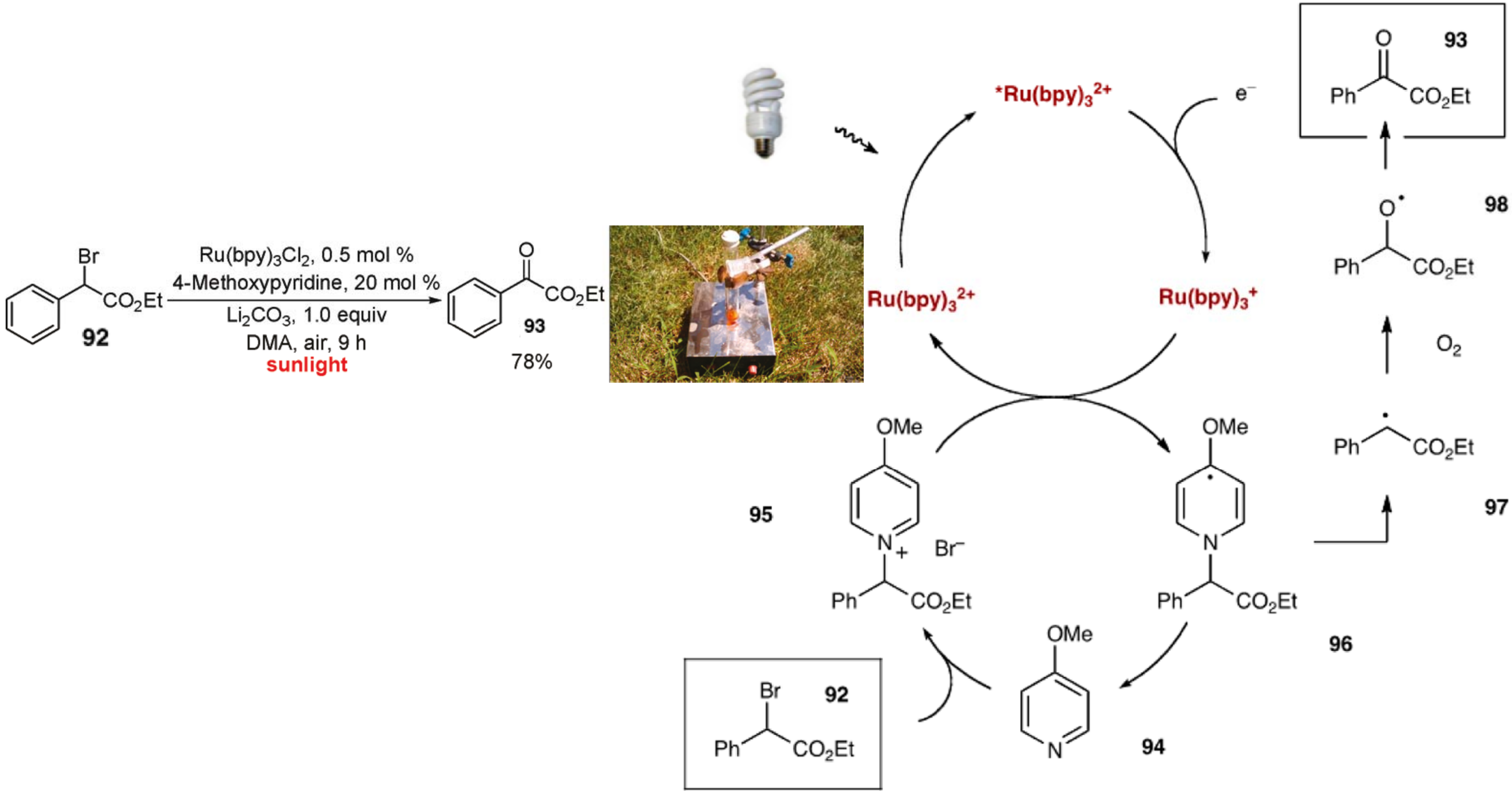
Fensterbank, L. *et. al., Angew. Chem., Int. Ed.* **2011**, 50, 4463
Hasegawa, E. *et. al., Tetrahedron* **2006**, 62, 6581
Guindon, Y. *et. al., Synlett* **1998**, 213 Guindon, Y. *et. al., Synlett* **1995**, 449

Net Oxidative Reaction 1. Functional Group Reactions



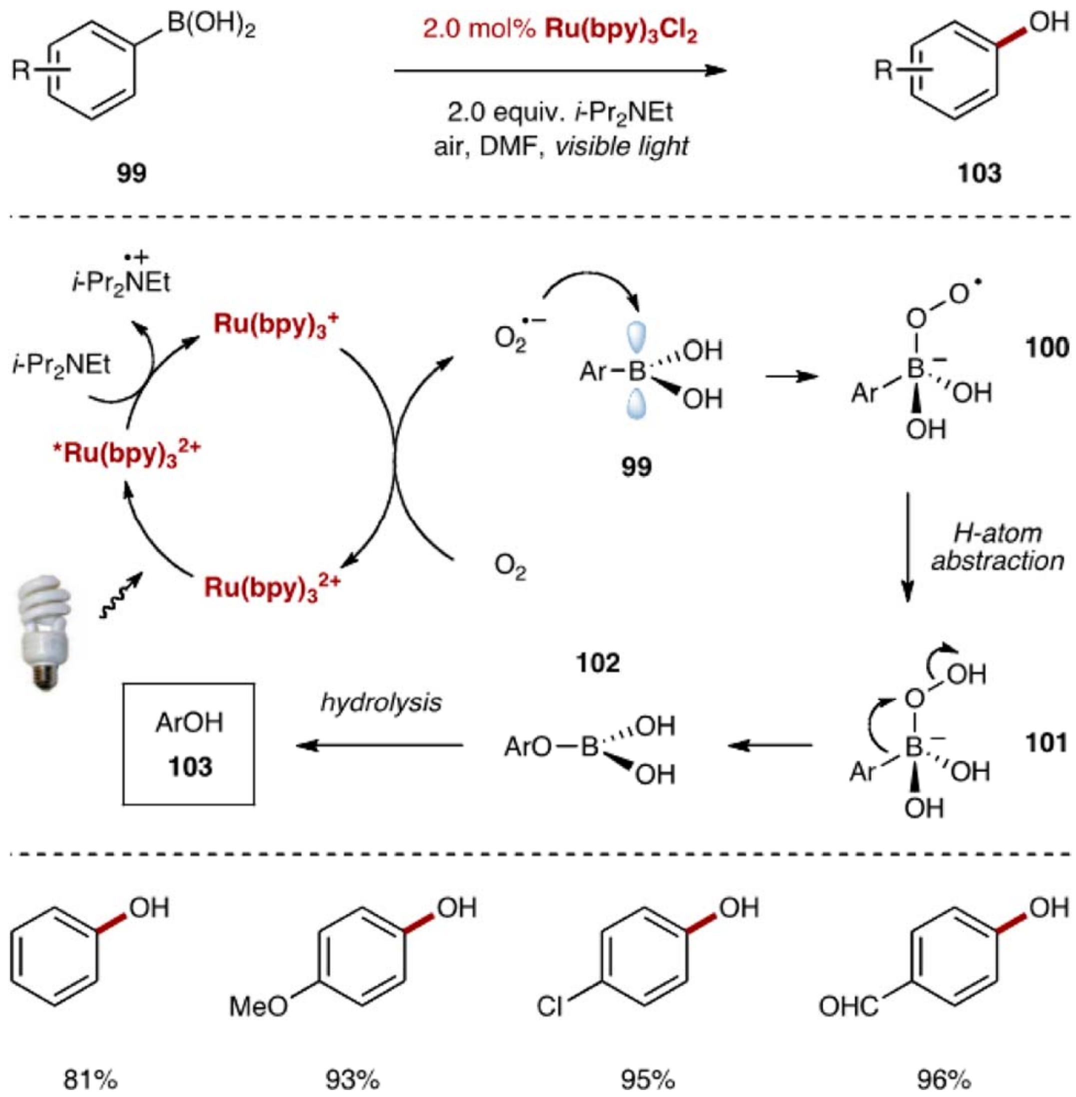
Cano-Yelo, H.; Deronzier, A. *Tetrahedron Lett.* **1984**, 25, 5517

Net Oxidative Reaction 1. *Functional Group Reactions*



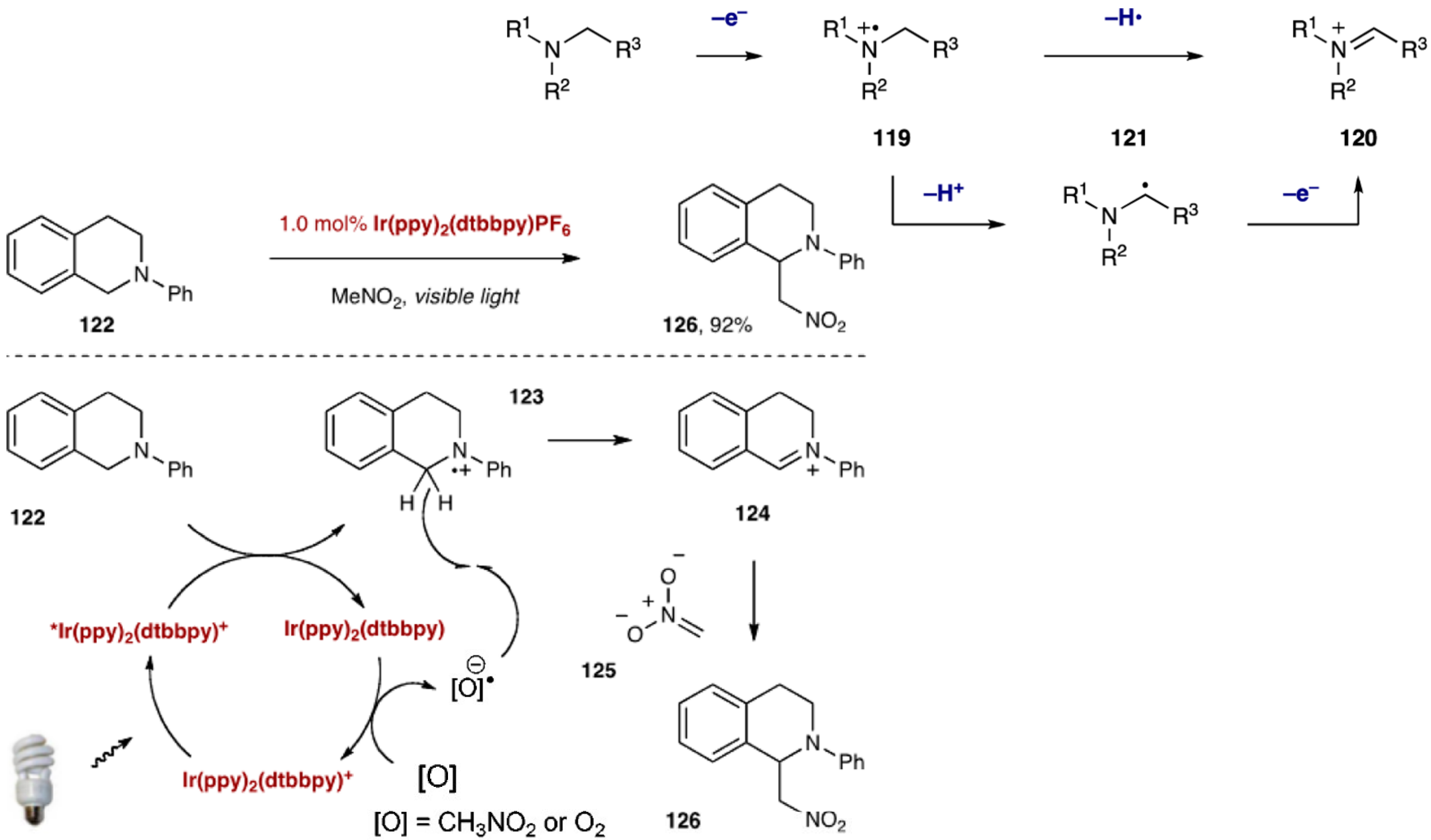
Jiao, N. *et. al., Org. Lett.* **2011**, 13, 2168

Net Oxidative Reaction 1. Functional Group Reactions



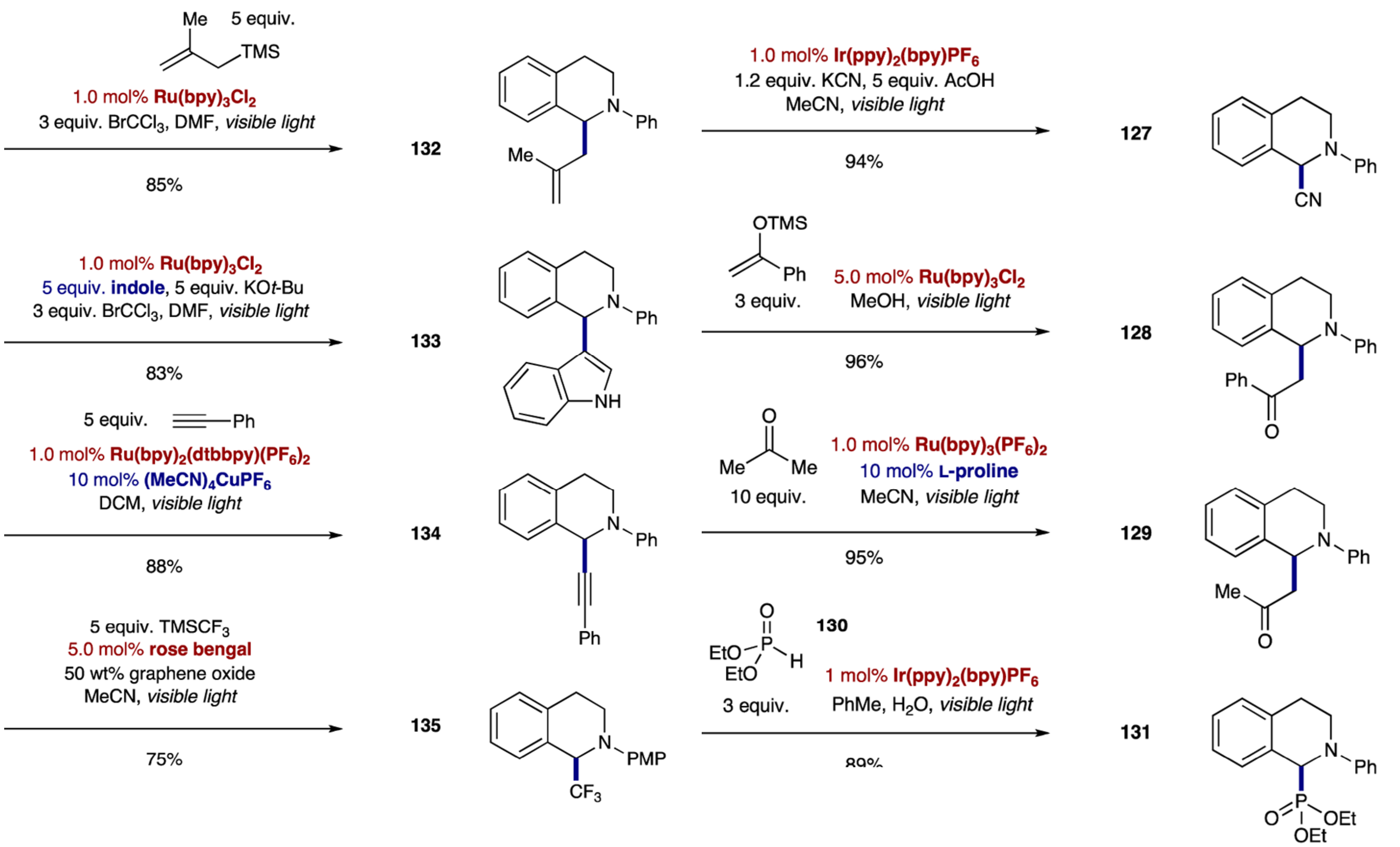
Jørgensen, K. A.; Xiao, W.-J. *Angew. Chem., Int. Ed.* **2012**, 51, 784

Net Oxidative Reaction 2. Oxid. Generation of Iminium Ions

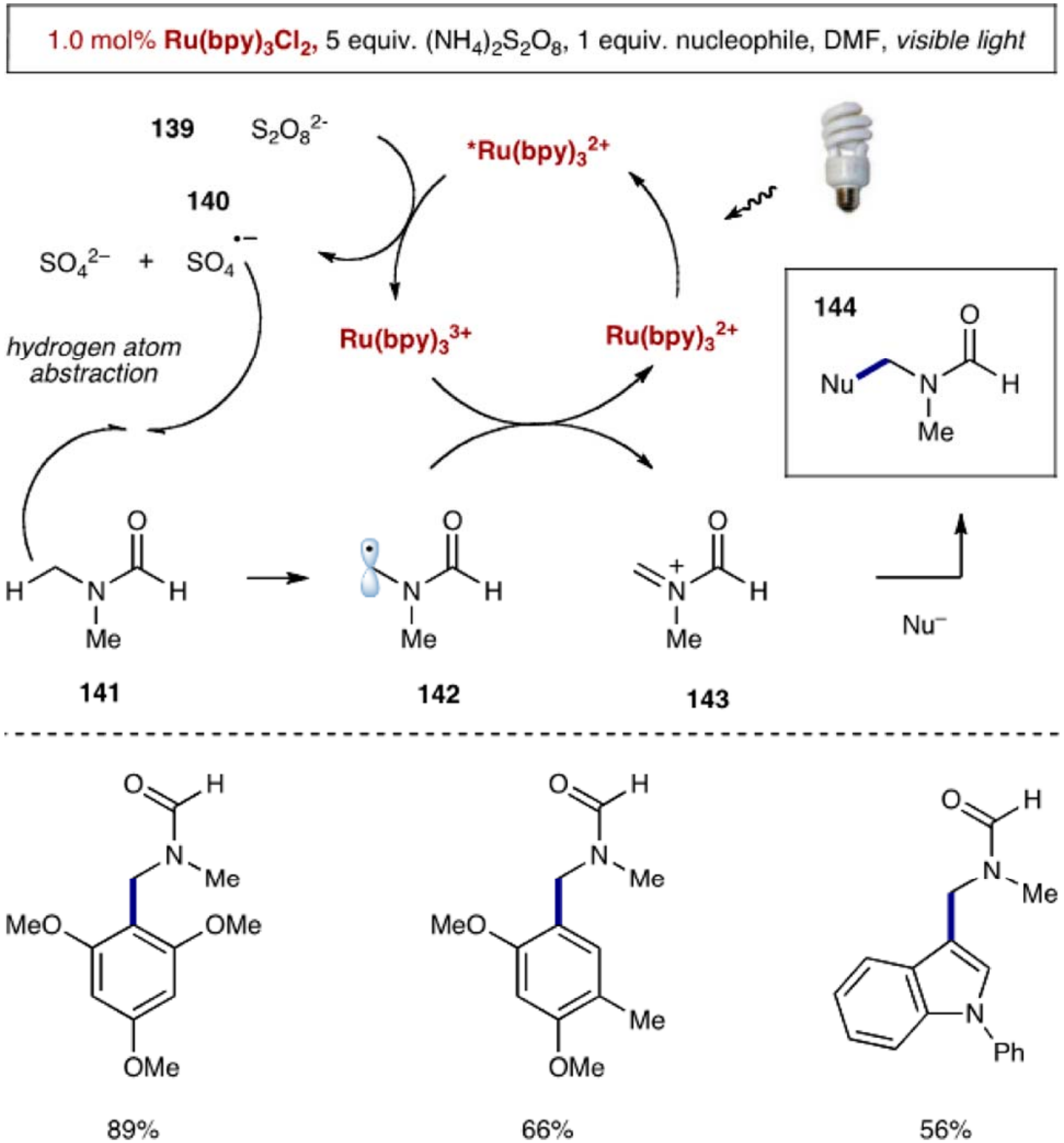


Stephenson, C. R. J. *et. al., J. Am. Chem. Soc.* **2010**, 132, 1464

Net Oxidative Reaction 2. Oxid. Generation of Iminium Ions

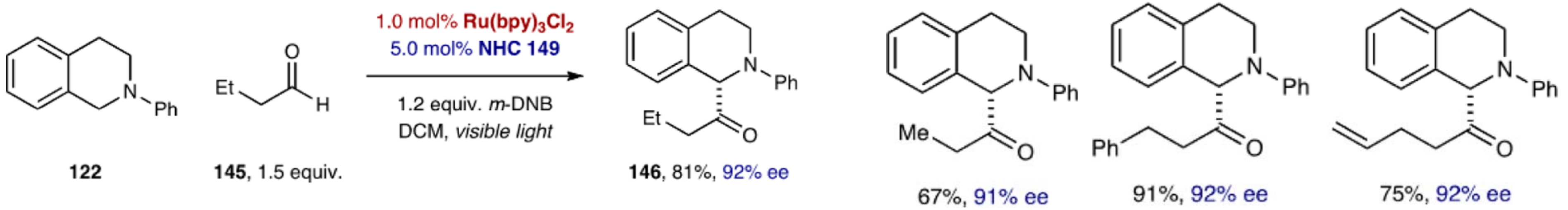


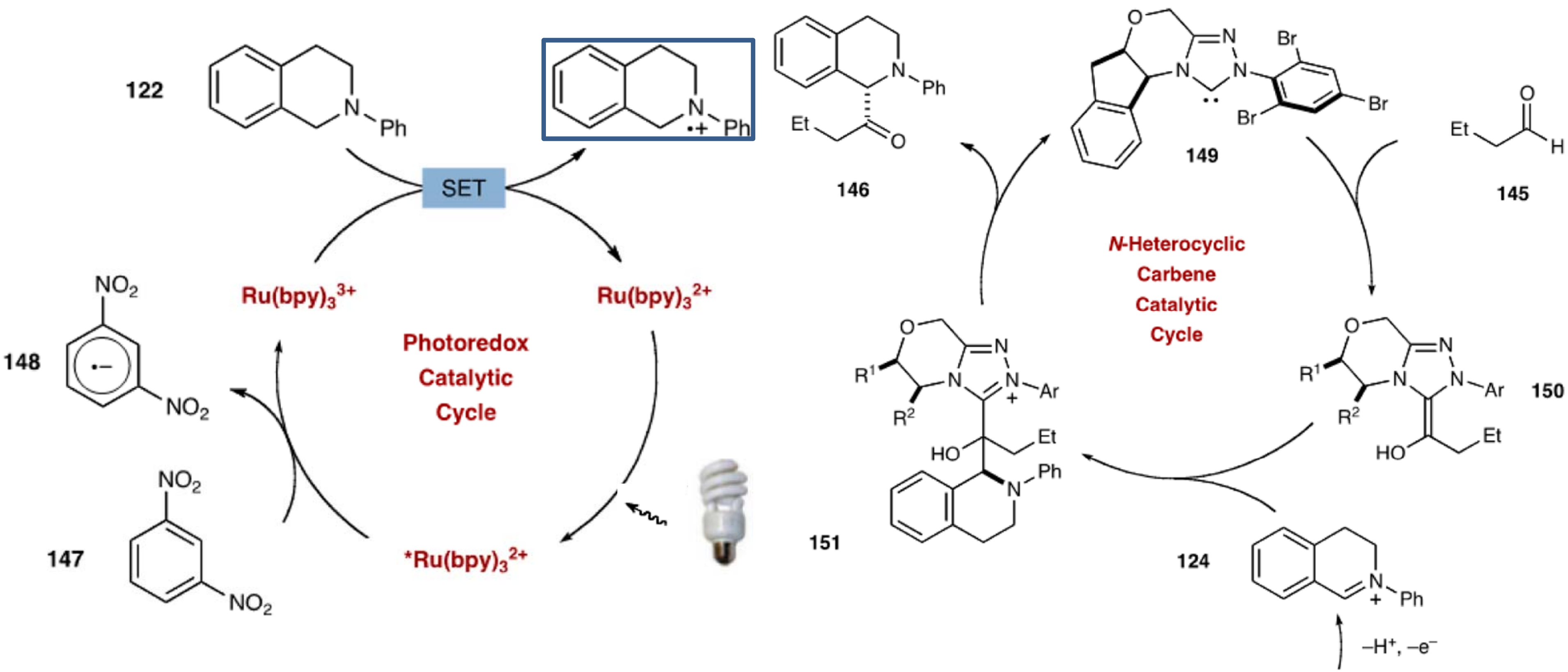
Net Oxidative Reaction 2. Oxid. Generation of Iminium Ions



Stephenson, C. R. J. *et. al., J. Org. Chem.* **2012**, 77, 4425

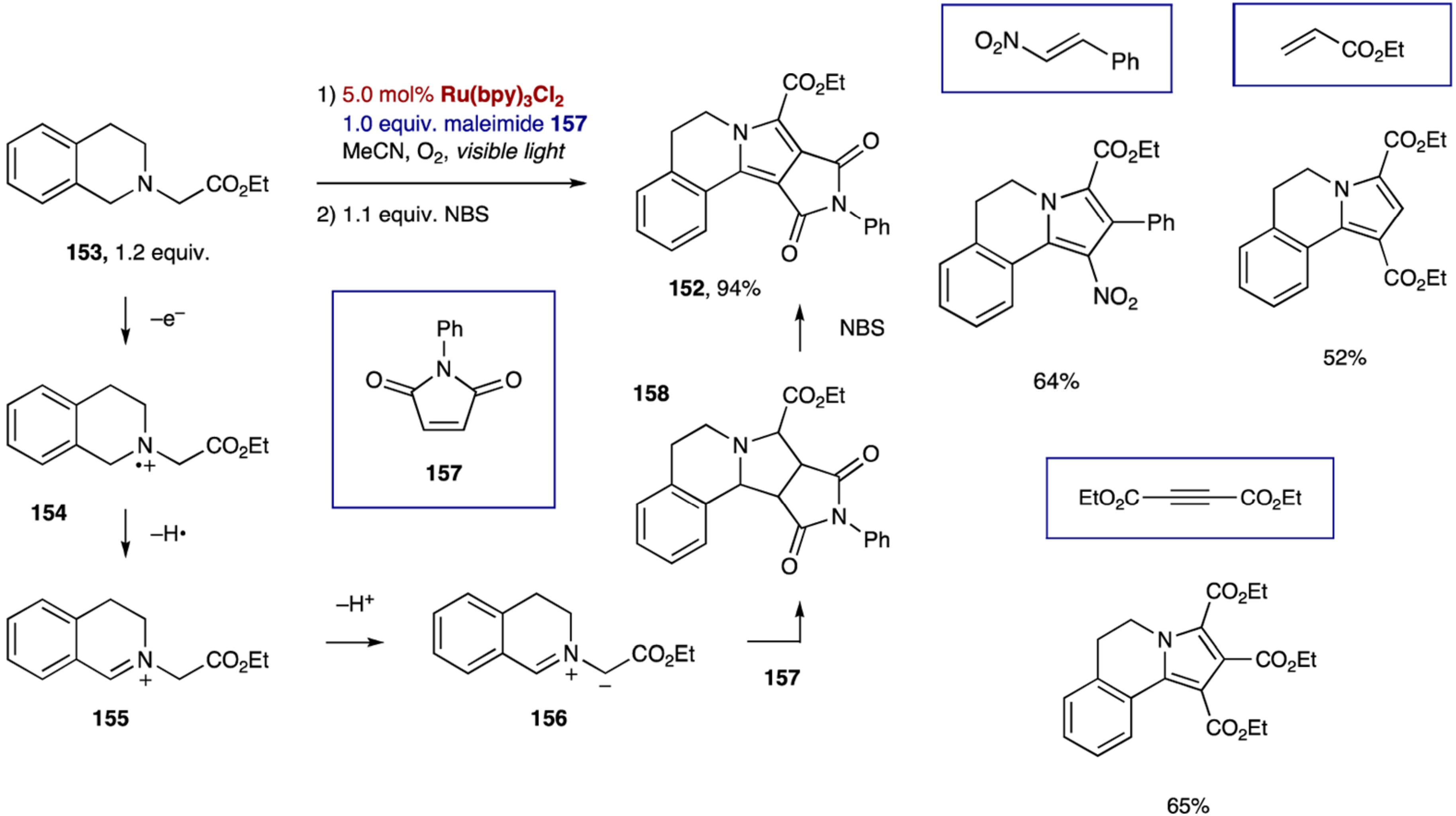
Net Oxidative Reaction 2. Oxid. Generation of Iminium Ions





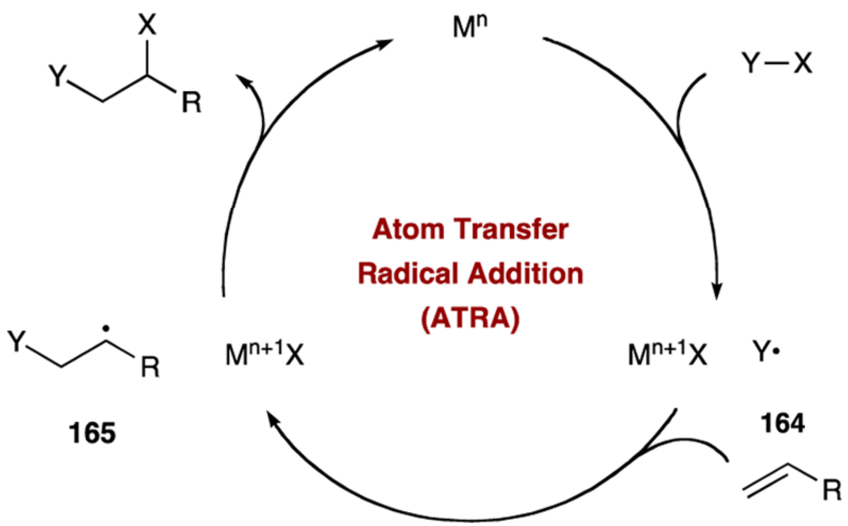
DiRocco, D. A.; Rovis, T. *J. Am. Chem. Soc.* **2012**, 134, 8094

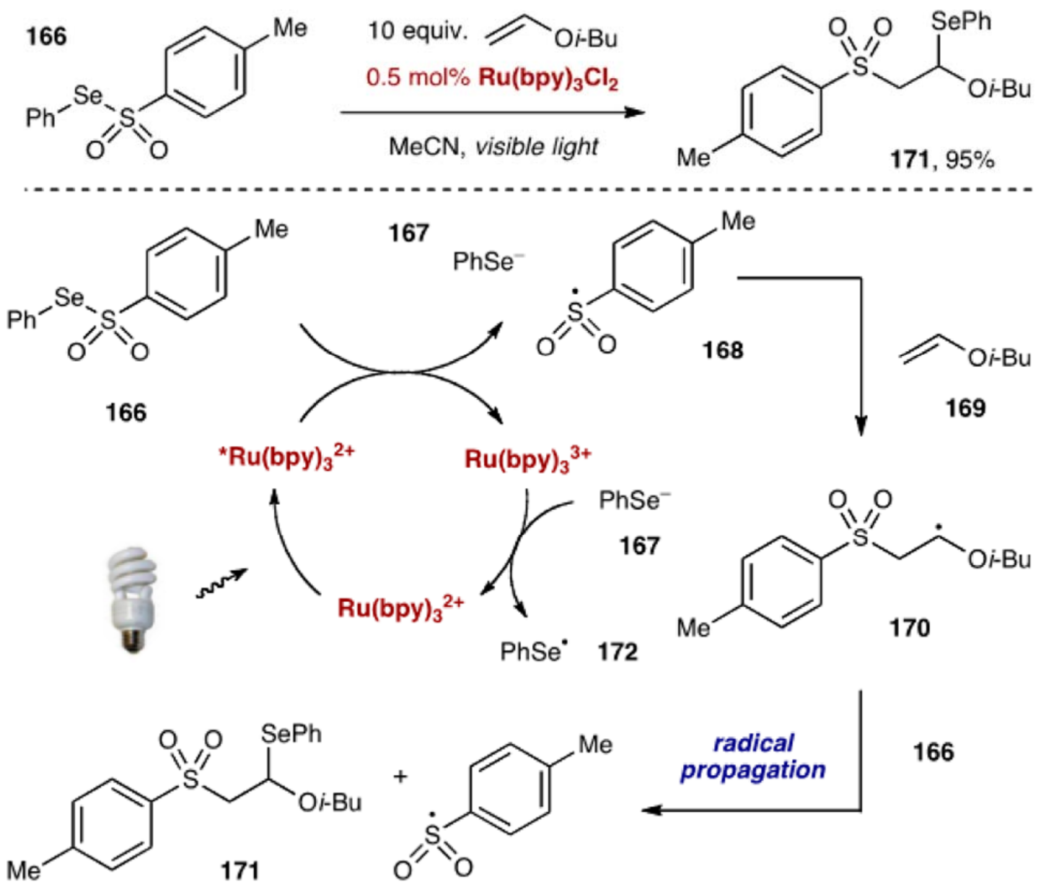
Net Oxidative Reaction 3. Azomethine Ylide [3+2] C.-A.



Xiao, W.-J. *et. al., Angew. Chem., Int. Ed.* **2011**, 50, 7171

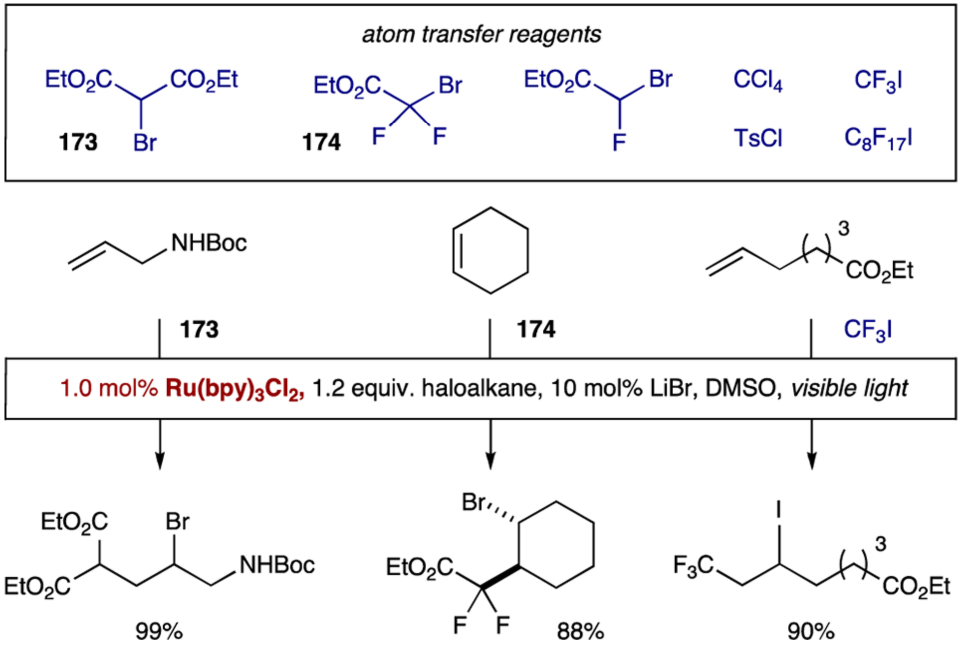
Redox Neutral Reactions *1. Atom Transfer Radical Addition*

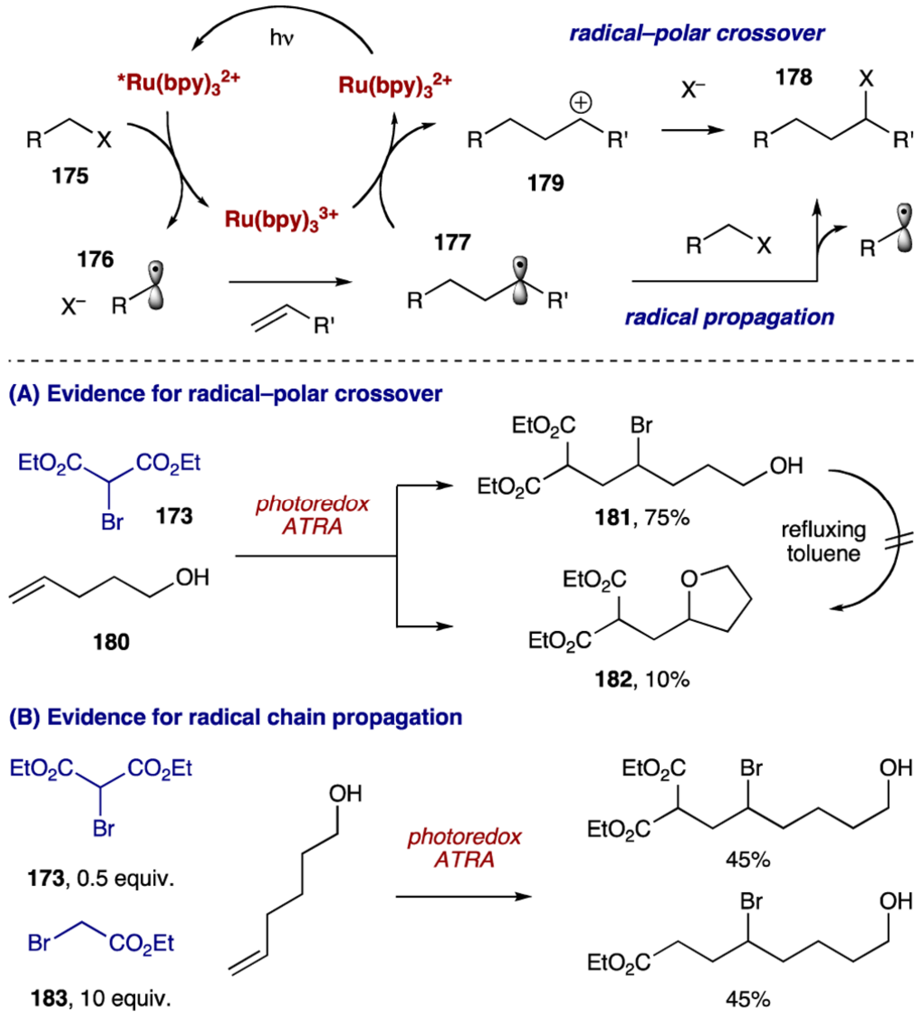




Barton, D. H. R. *et. al., Tetrahedron Lett.* **1994**, 35, 2869

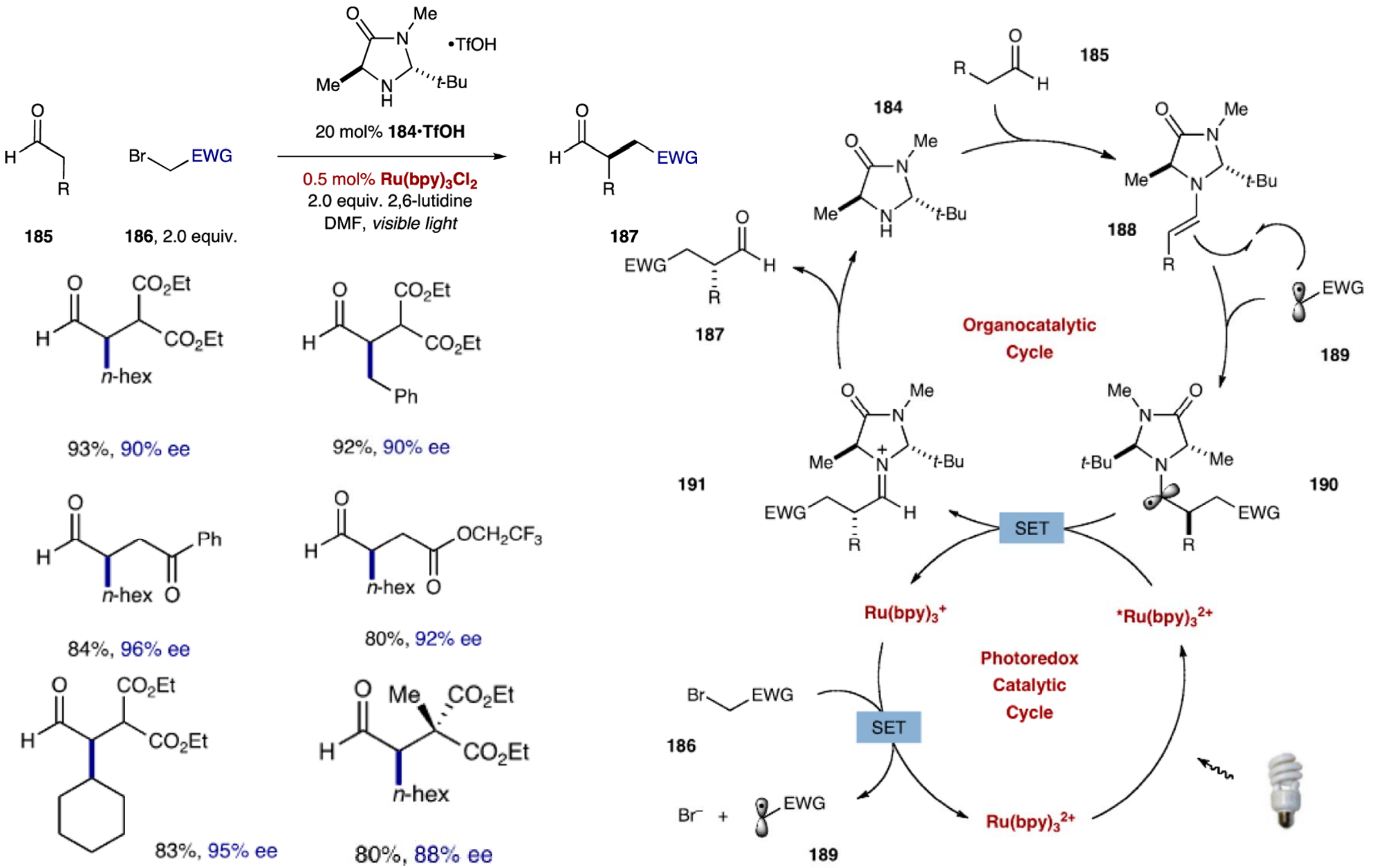
Redox Neutral Reactions *1. Atom Transfer Radical Addition*





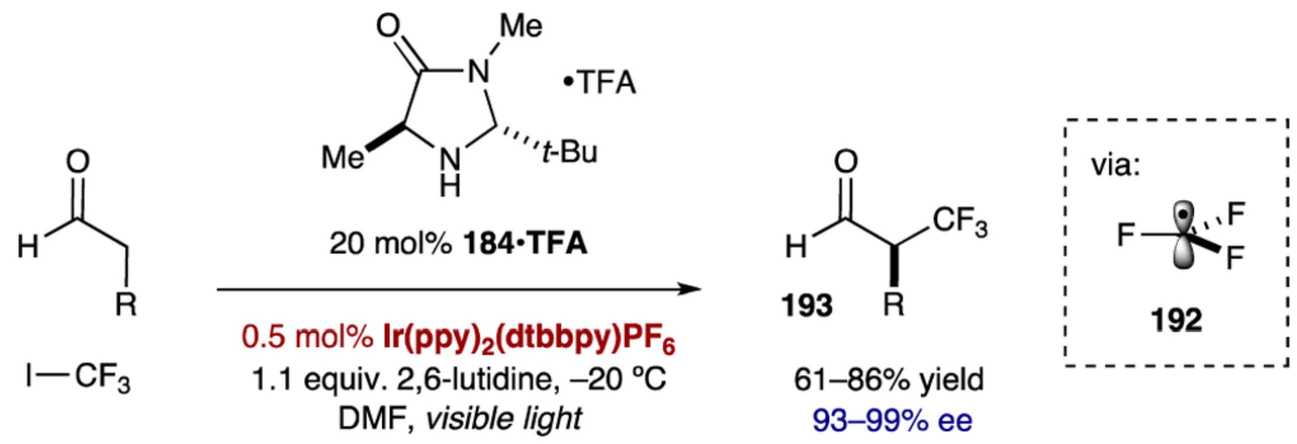
Stephenson, C. R. J. *et. al., J. Am. Chem. Soc.* **2011**, 133, 4160
Stephenson, C. R. J. *et. al., J. Am. Chem. Soc.* **2012**, 134, 8875

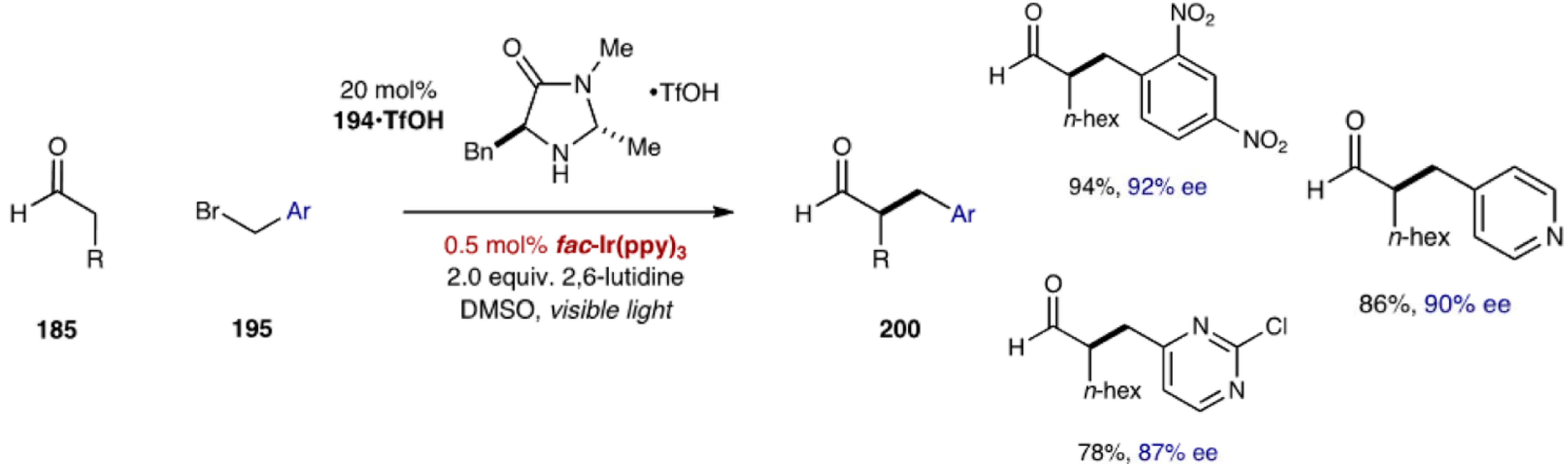
Redox Neutral Reactions *2. Photoredox Organocatalysis*



MacMillan, D. W. C. *Nature* **2008**, 455, 304

Redox Neutral Reactions *2. Photoredox Organocatalysis*

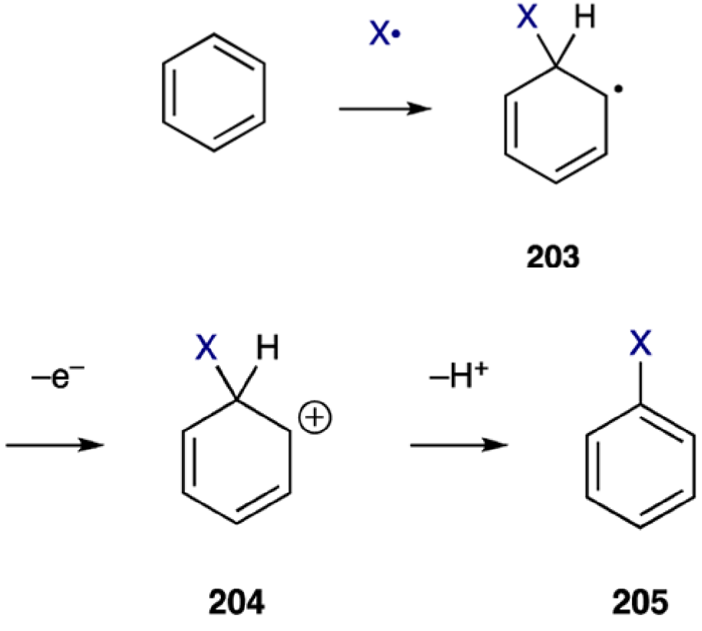


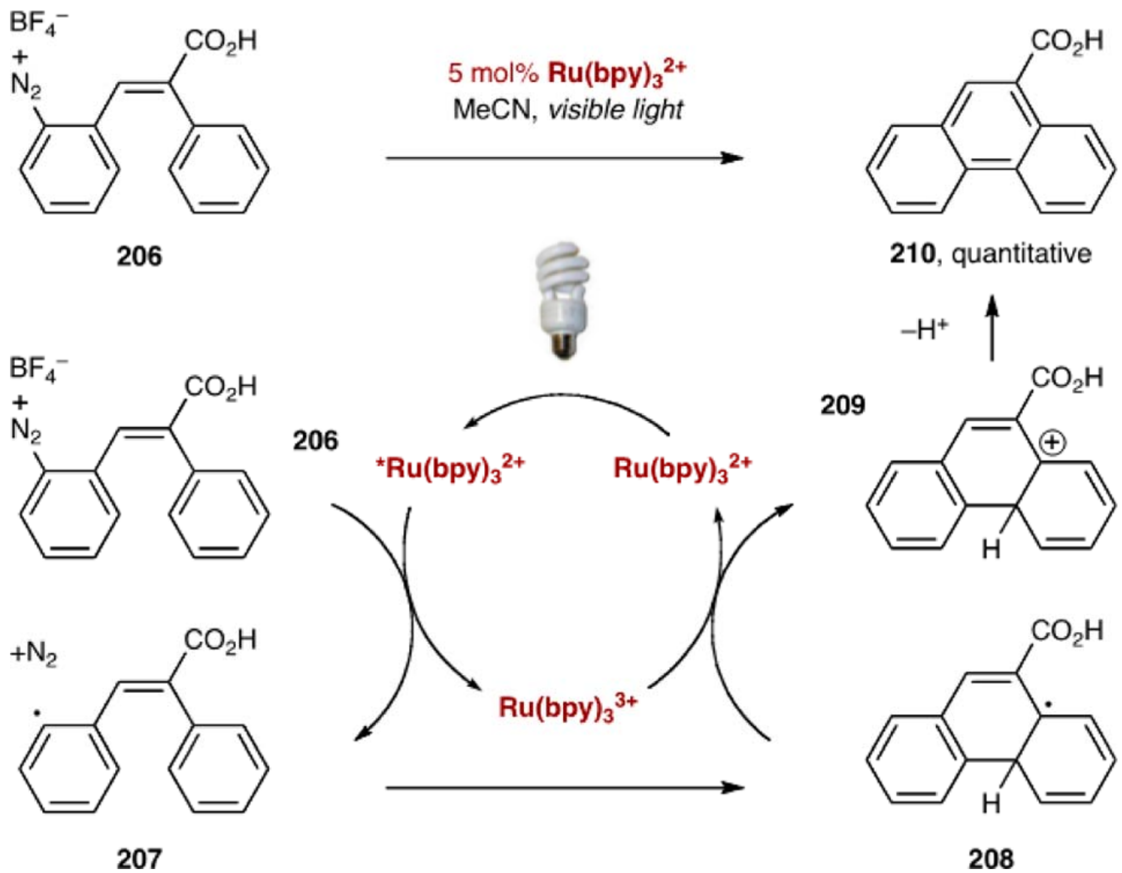


MacMillan, D. W. C. *et. al., J. Am. Chem. Soc.* **2009**, 131, 10875
MacMillan, D. W. C. *et. al., J. Am. Chem. Soc.* **2010**, 132, 13600

Redox Neutral Reactions 3. *Radical Additions to Arene*

3. 1 *Arylation of Arenes: Diazonium Salts*





Cano-Yelo, H.; Deronzier, A. *J. Chem. Soc., Perkin Trans.* 2 **1984**, 1093
Cano-Yelo, H.; Deronzier, A. *J. Photochem.* **1987**, 37, 315

Redox Neutral Reactions 3. *Radical Additions to Arene*

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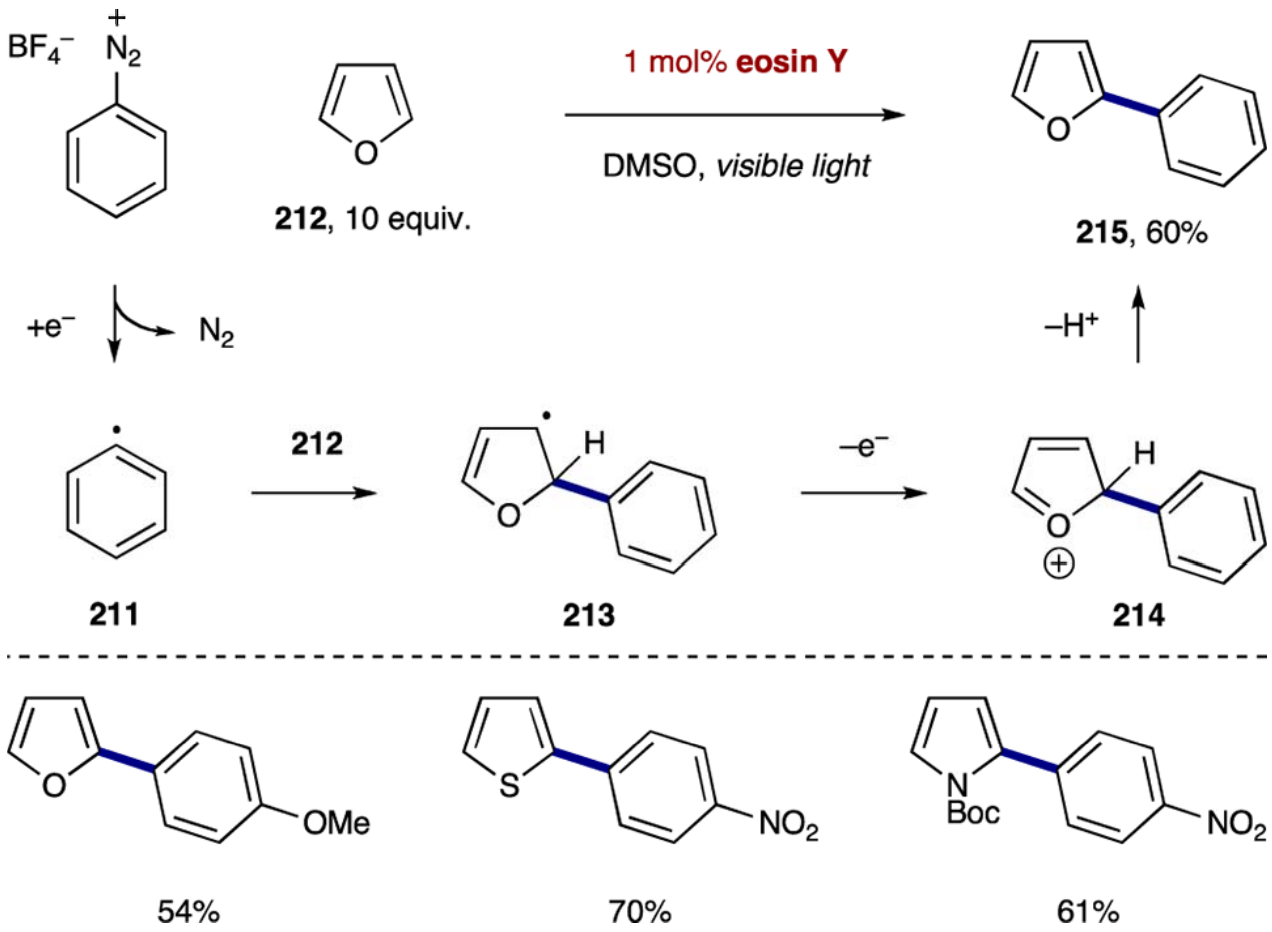
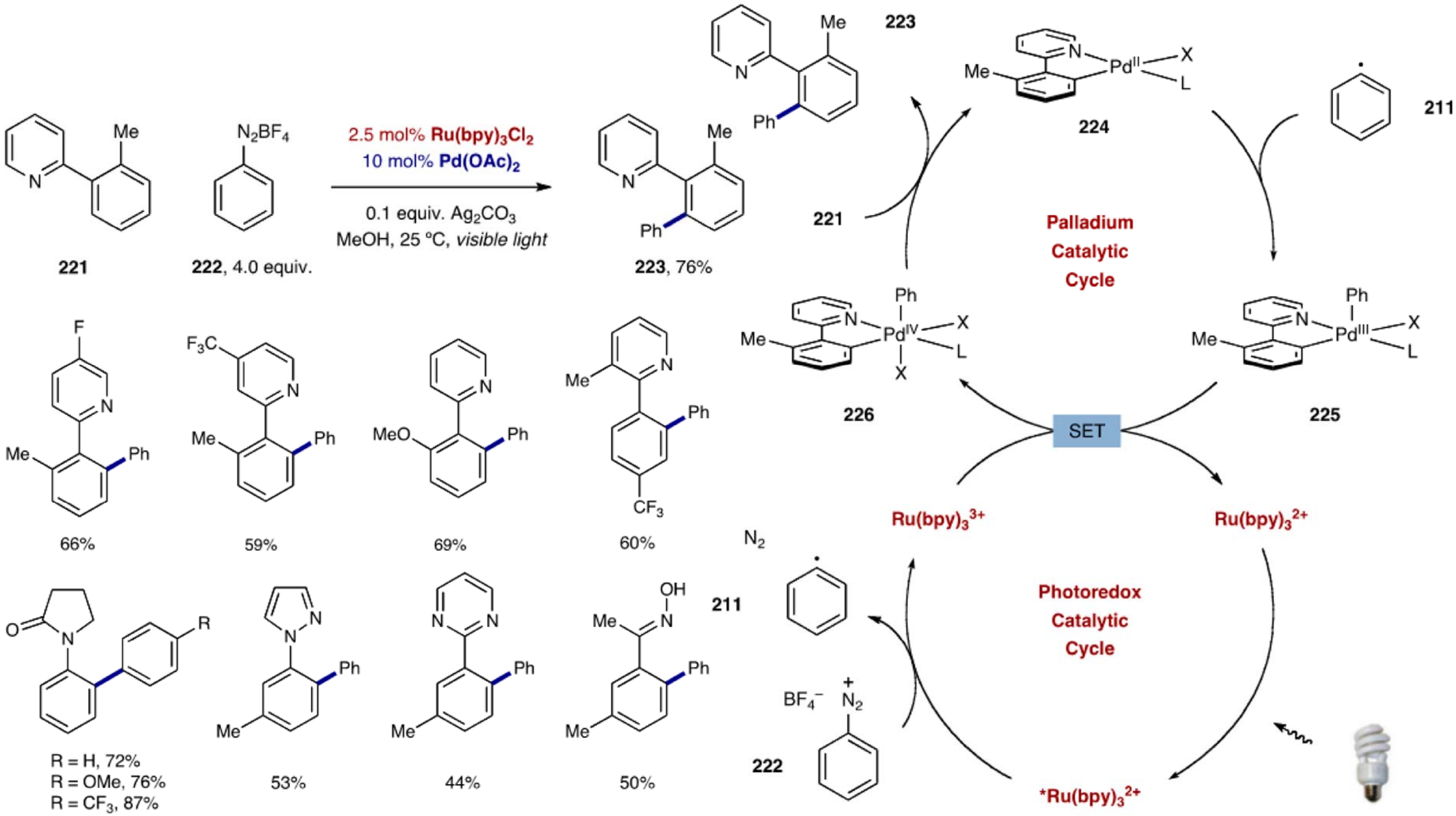


König, B. *J. Am. Chem. Soc.* **2012**, 134, 2958

Redox Neutral Reactions 3. *Radical Additions to Arene*

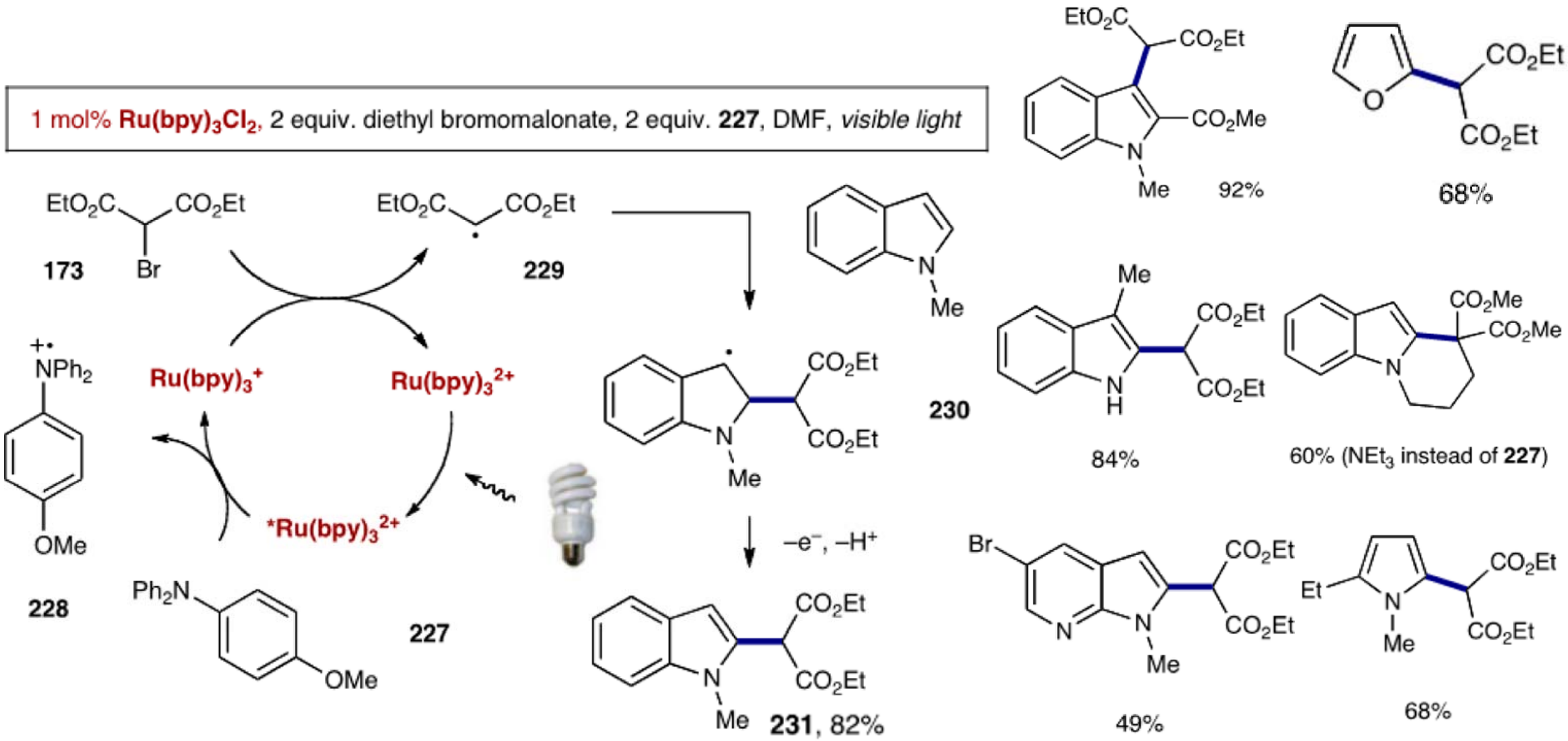
3. 1 *Arylation of Arenes: Diazonium Salts*



Sanford, M. S. *et. al., J. Am. Chem. Soc.* **2009**, 131, 11234

Redox Neutral Reactions 3. *Radical Additions to Arene*

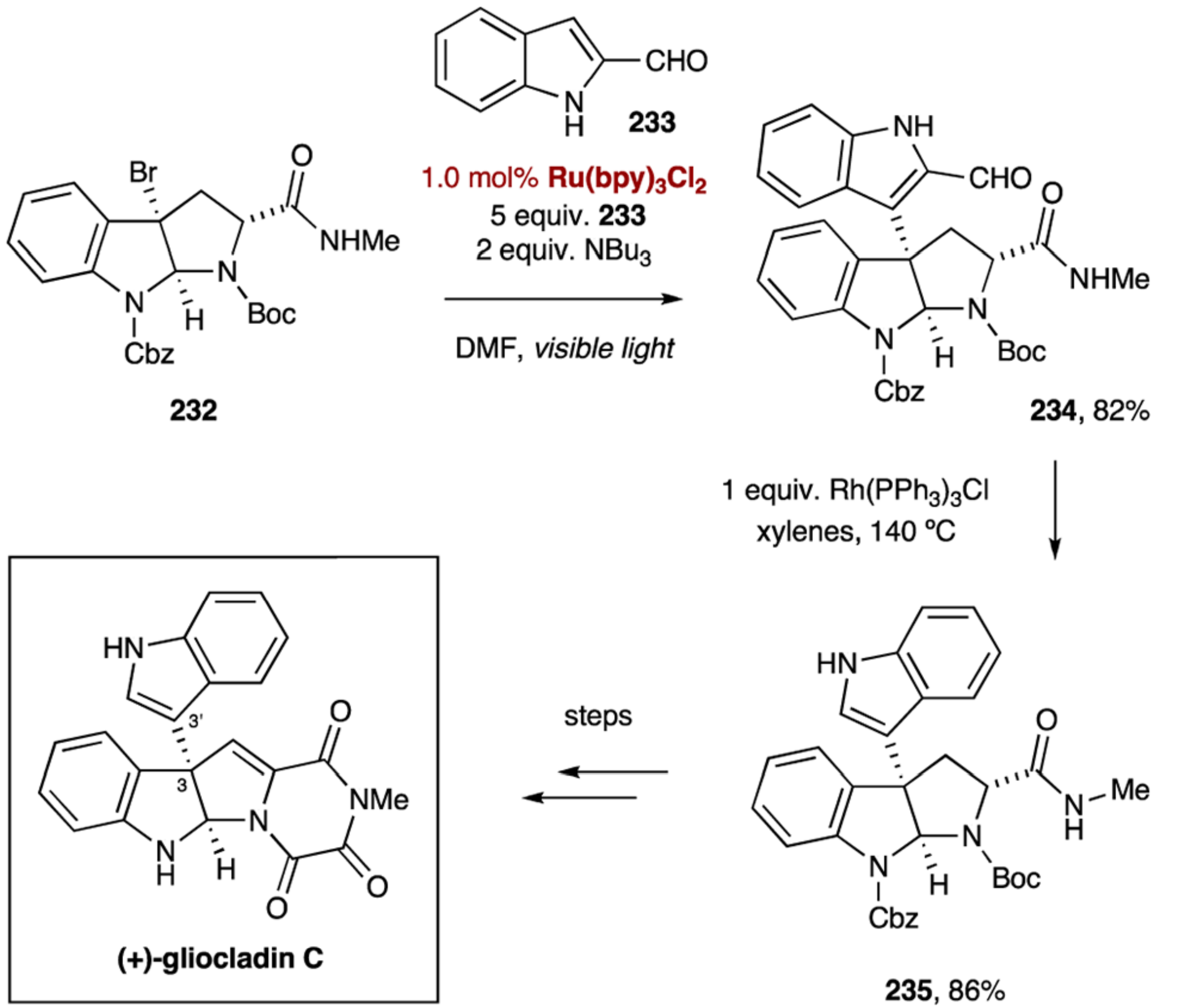
3. 2 *Alkylation of Arenes*



Stephenson, C. R. *et. al., J. Org. Lett.* **2010**, 12, 368
Stephenson, C. R. *et. al., J. Org. Lett.* **2010**, 12, 3104

Redox Neutral Reactions 3. Radical Additions to Arene

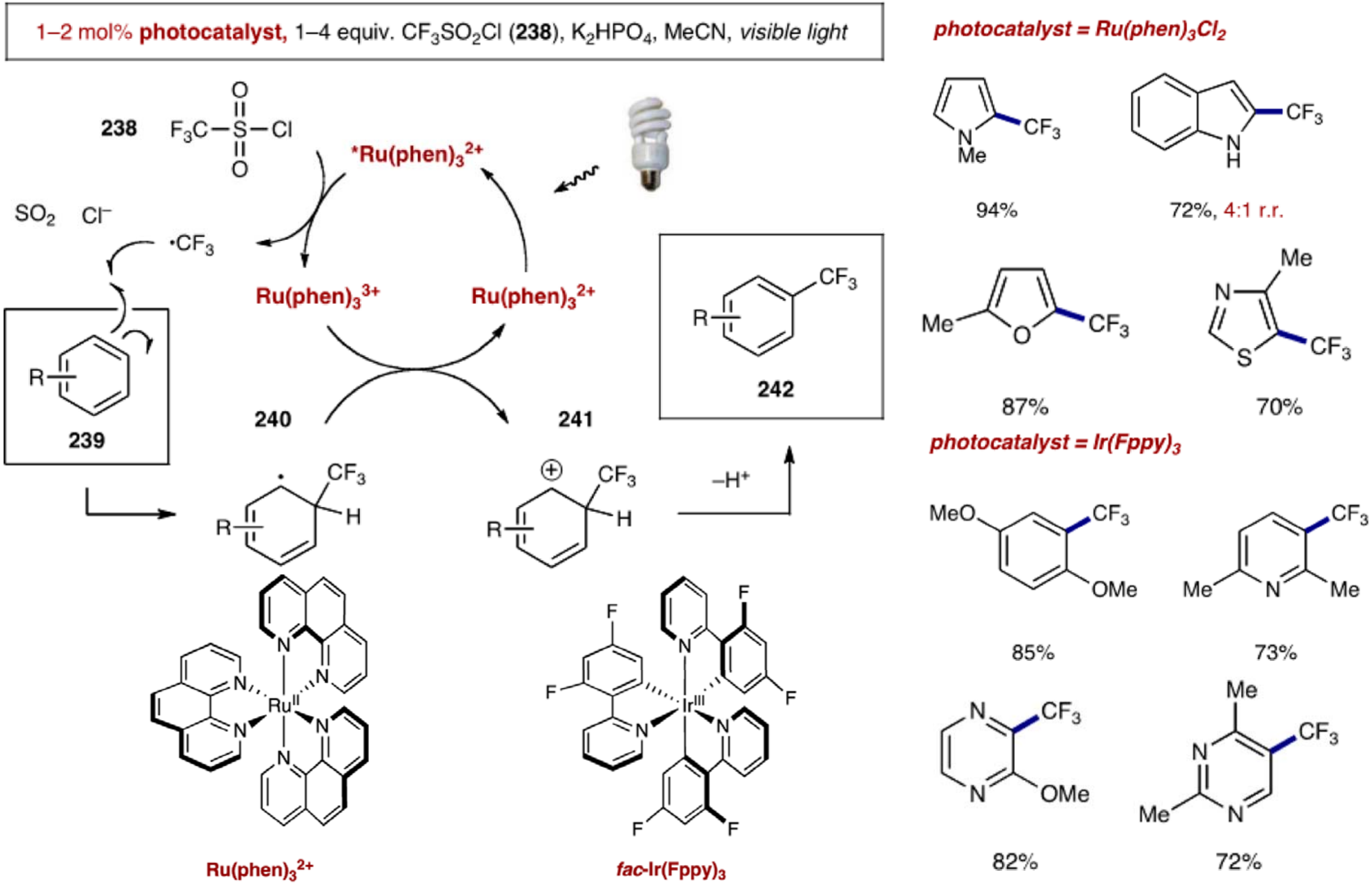
3. 2 Alkylation of Arenes



Stephenson, C. R. J. *et. al., Angew. Chem., Int. Ed.* **2011**, 50, 9655

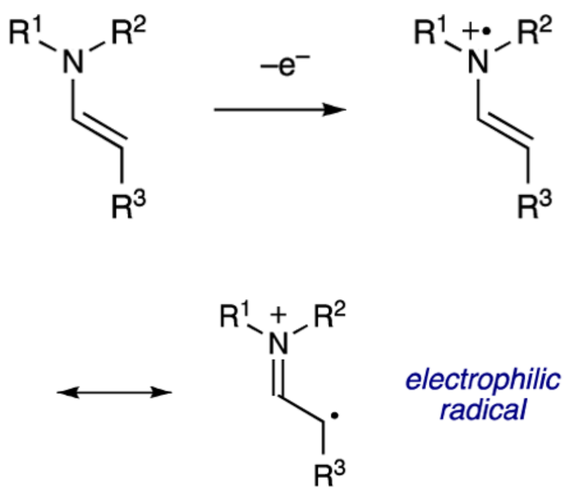
Redox Neutral Reactions 3. *Radical Additions to Arene*

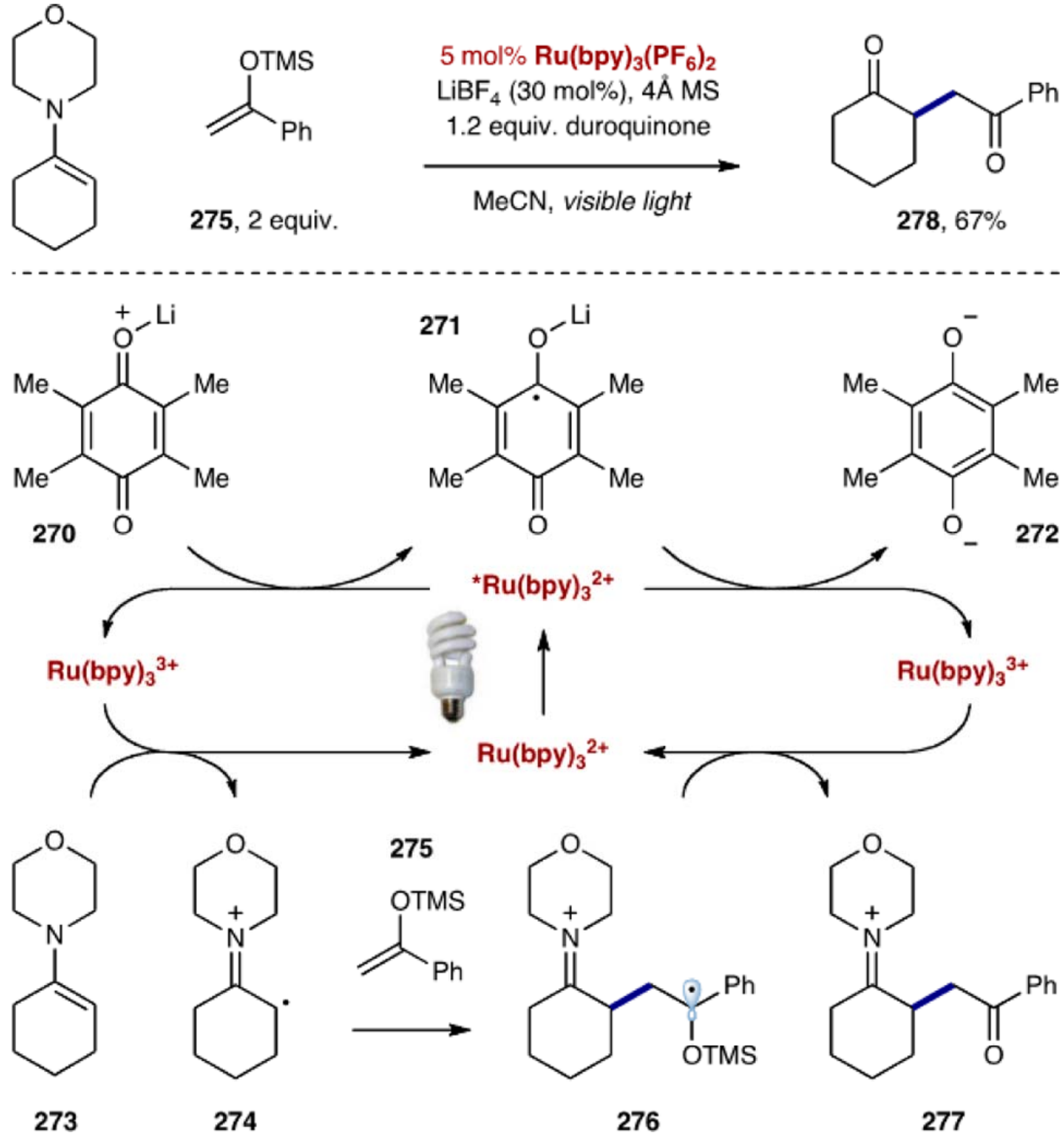
3. 2 *Alkylation of Arenes*



MacMillan, D. W. C. *Nature* **2011**, 480, 224

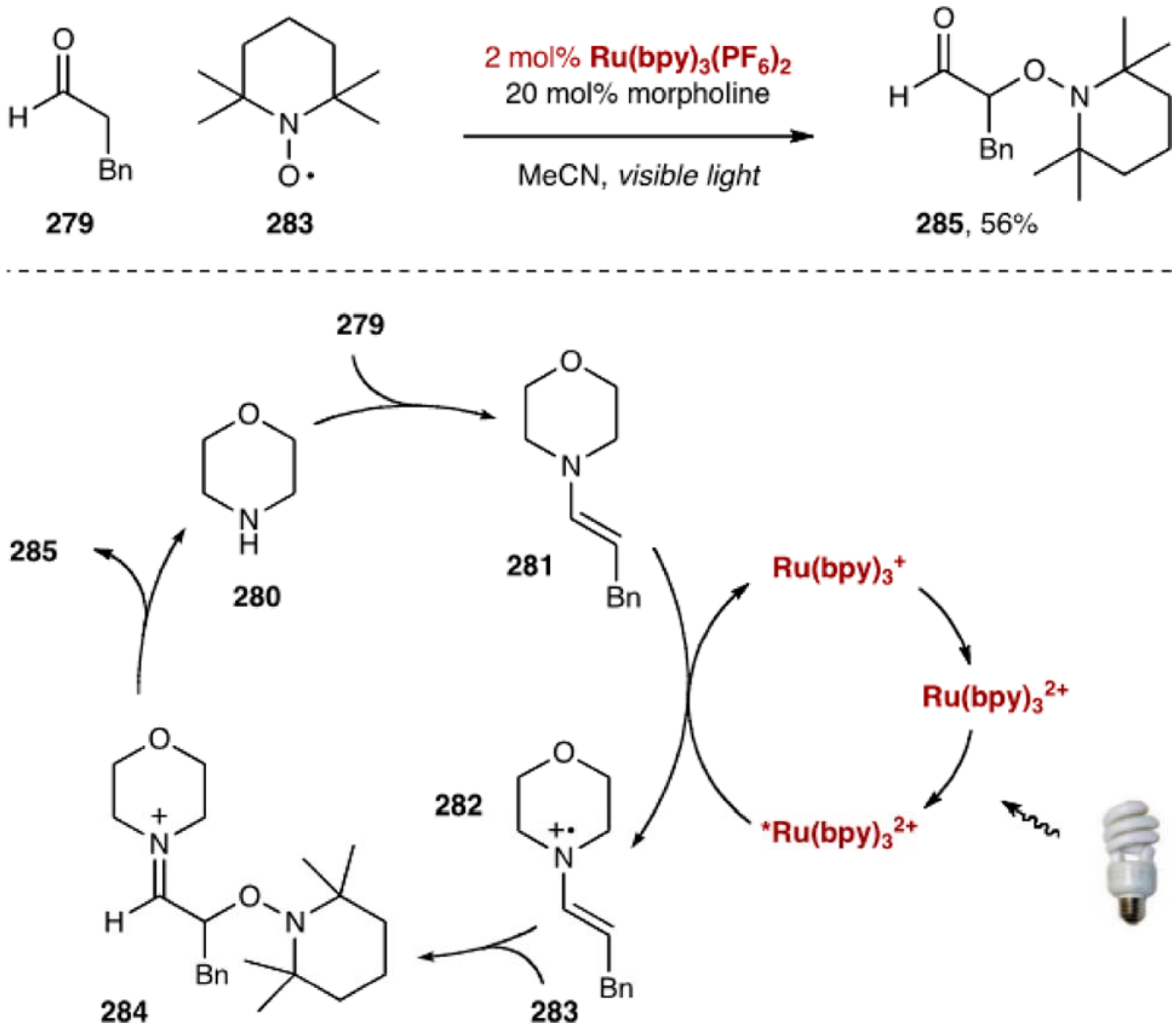
Redox Neutral Reactions 4. Rxn of Enamine Radical Cations





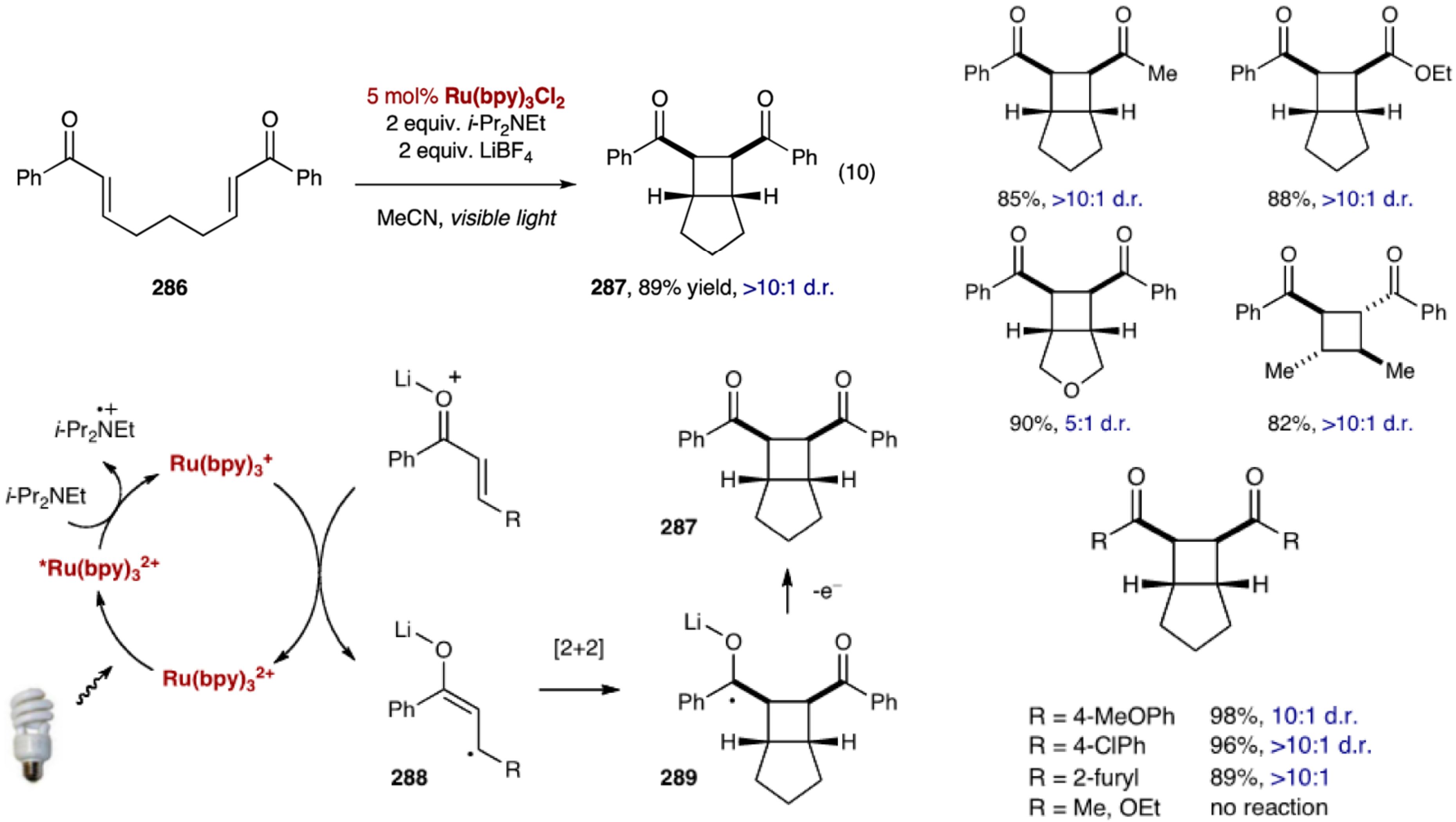
Akita, M. *et. al., Chem. Commun.* **2012**, 48, 5355

Redox Neutral Reactions 4. Rxn of Enamine Radical Cations



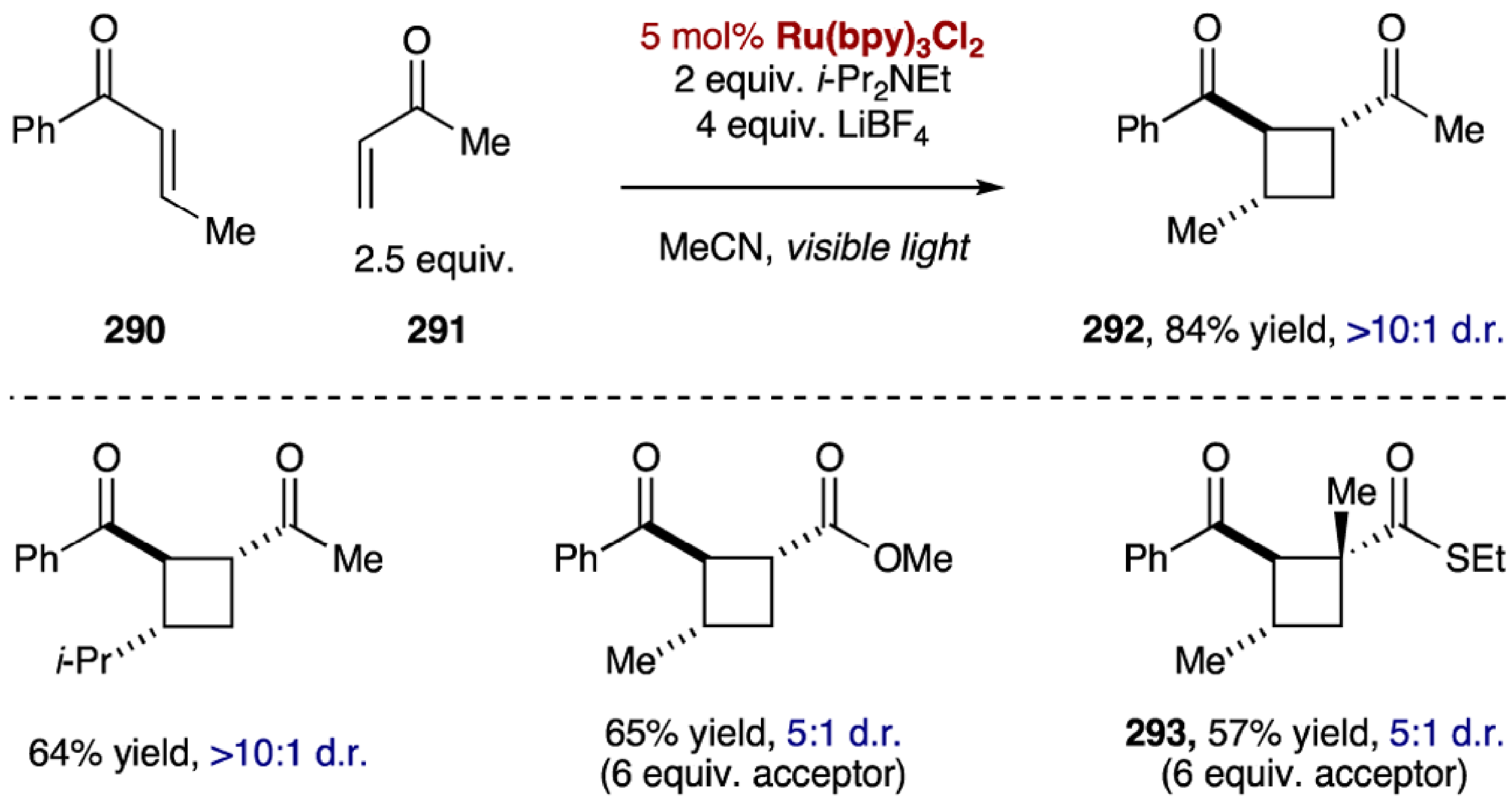
Akita, M. *et. al., Chem. Lett.* **2009**, 38, 166

Redox Neutral Reactions 5. *[2+2] C.-A.*



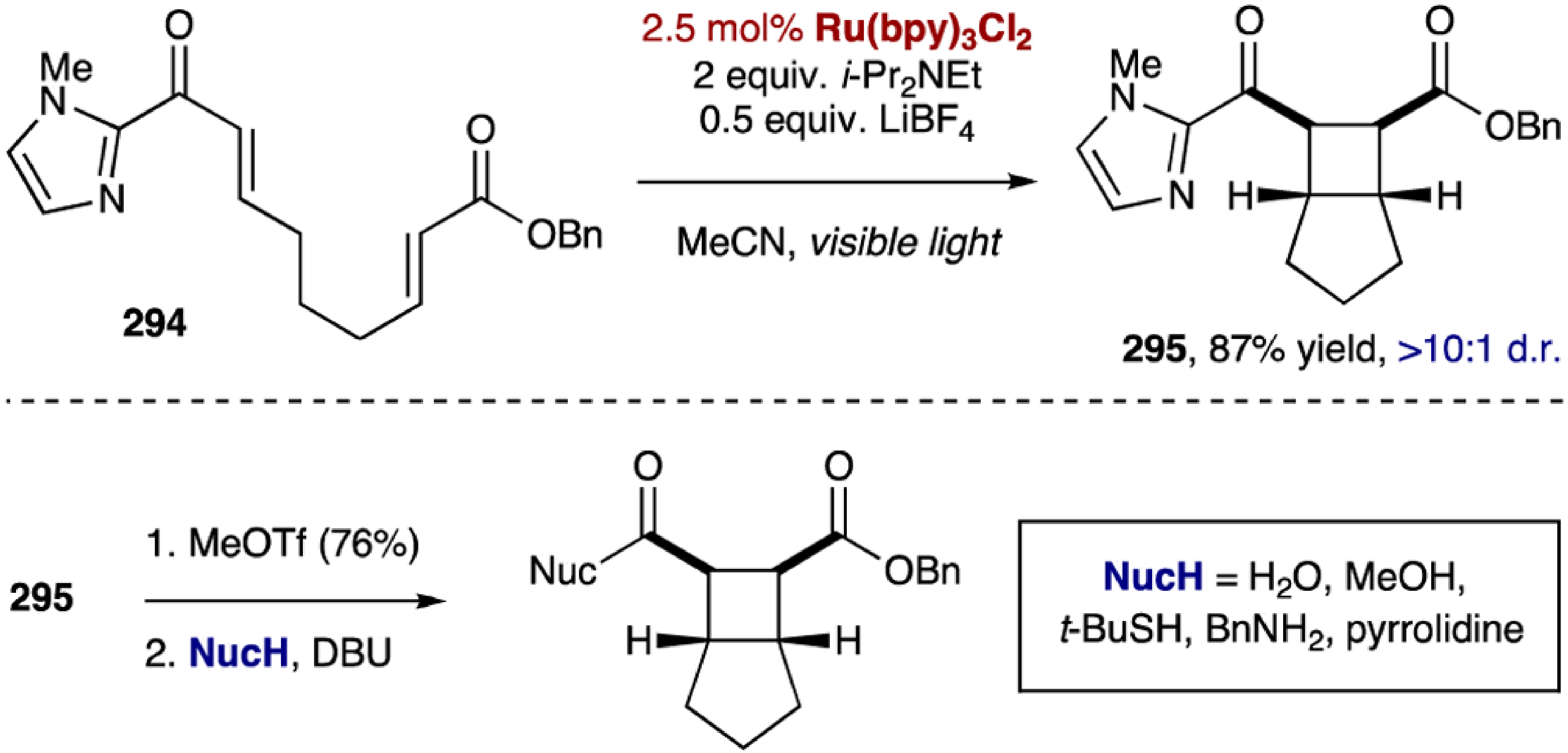
Yoon, T. P. *et. al., J. Am. Chem. Soc.* **2008**, 130, 12886

Redox Neutral Reactions *5. [2+2] C.-A.*



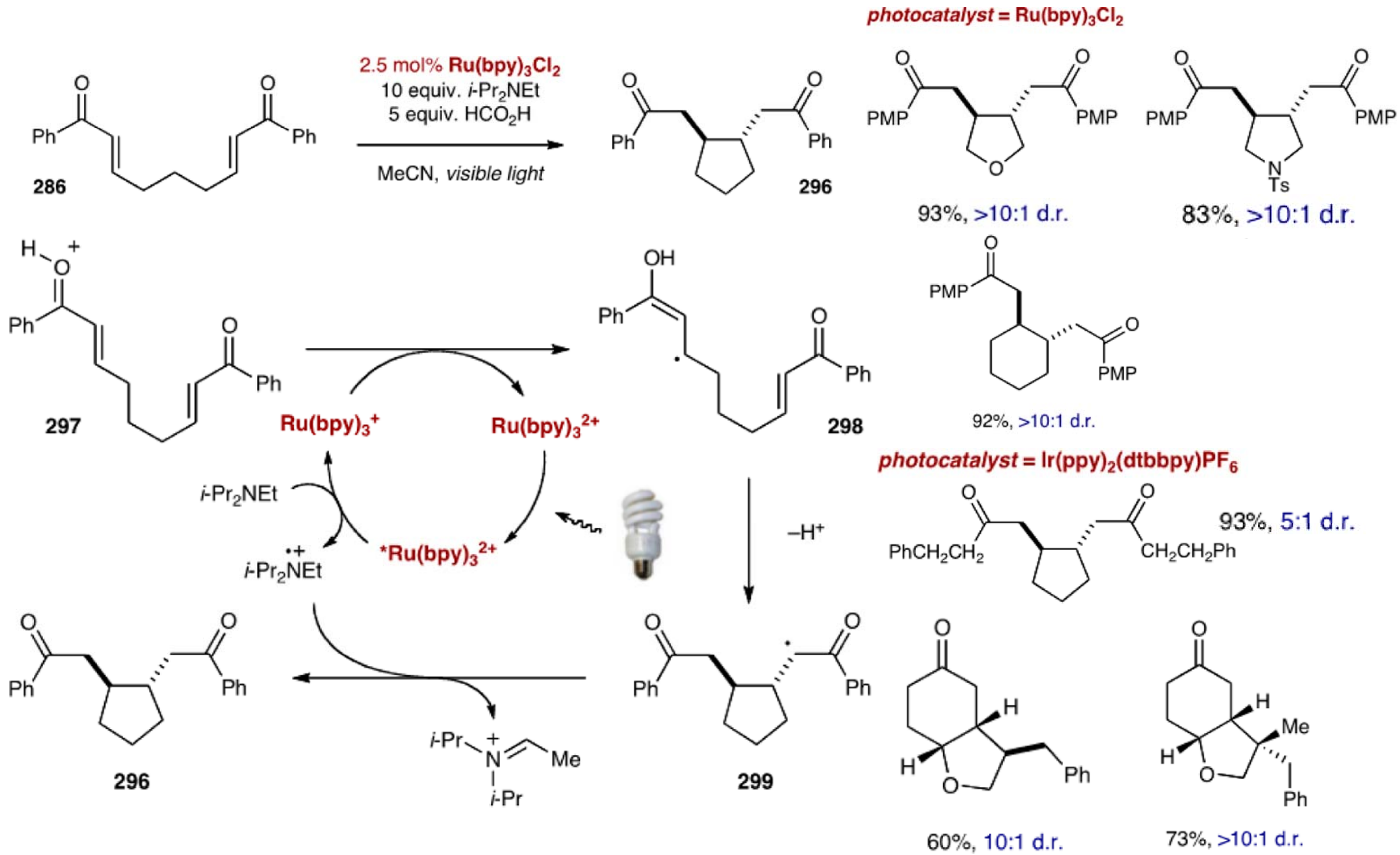
Yoon, T. P. *et. al., J. Am. Chem. Soc.* **2009**, 131, 14604

Redox Neutral Reactions 5. *[2+2] C.-A.*



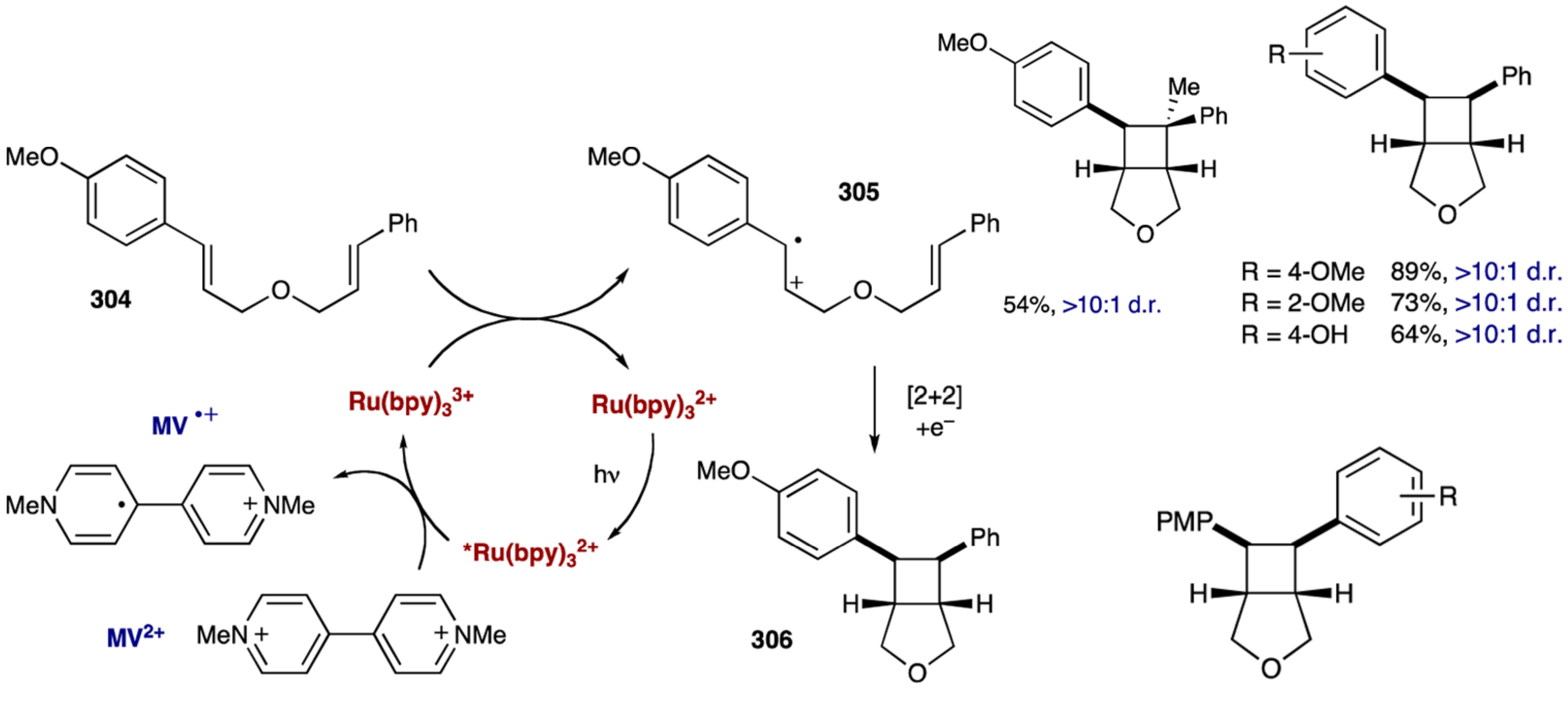
Yoon, T. P. *et. al., Org. Lett.* **2012**, 14, 1110

Redox Neutral Reactions *5. [2+2] C.-A.*



Yoon, T. P. *et. al., Chem. Sci.* **2011**, 2, 2115

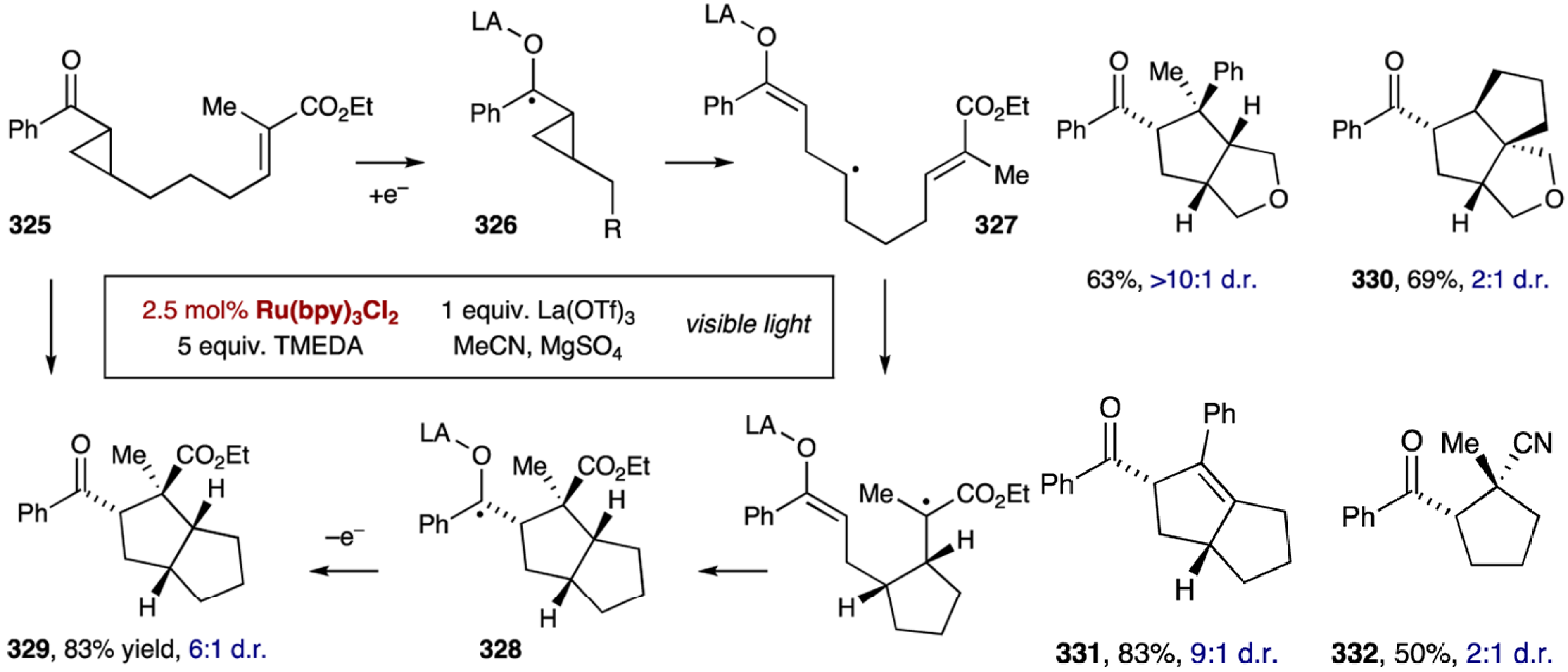
Redox Neutral Reactions *5. [2+2] C.-A.*



Conditions: 1-5 mol% **$Ru(bpy)_3(PF_6)_2$**, 15 mol% $MV(PF_6)_2$, $MgSO_4$, $MeNO_2$, visible light

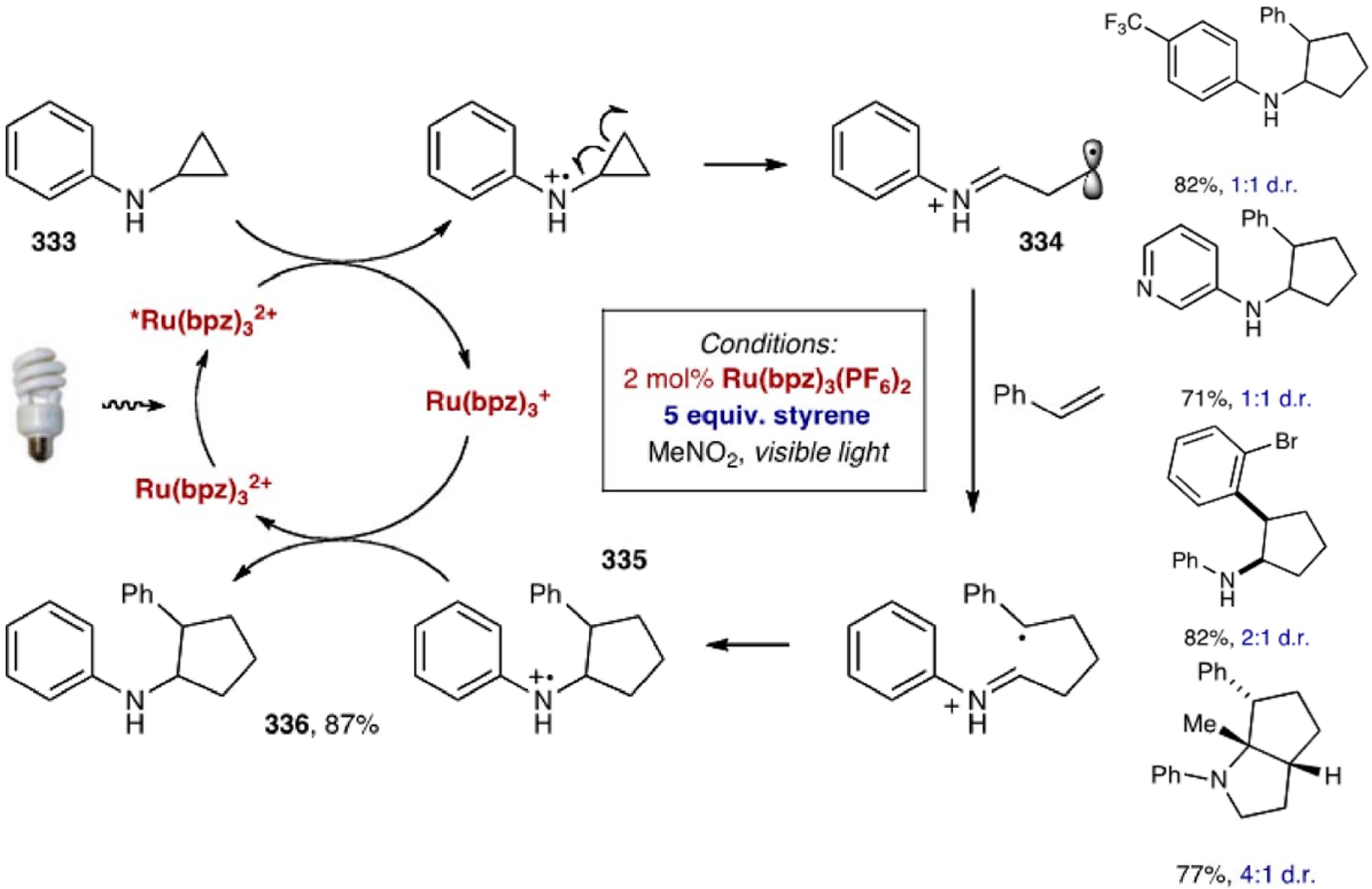
Yoon, T. P. *et. al., J. Am. Chem. Soc.* **2010**, 132, 8572

Redox Neutral Reactions *6. [3+2] C.-A. : C.-P. Ring Opening*



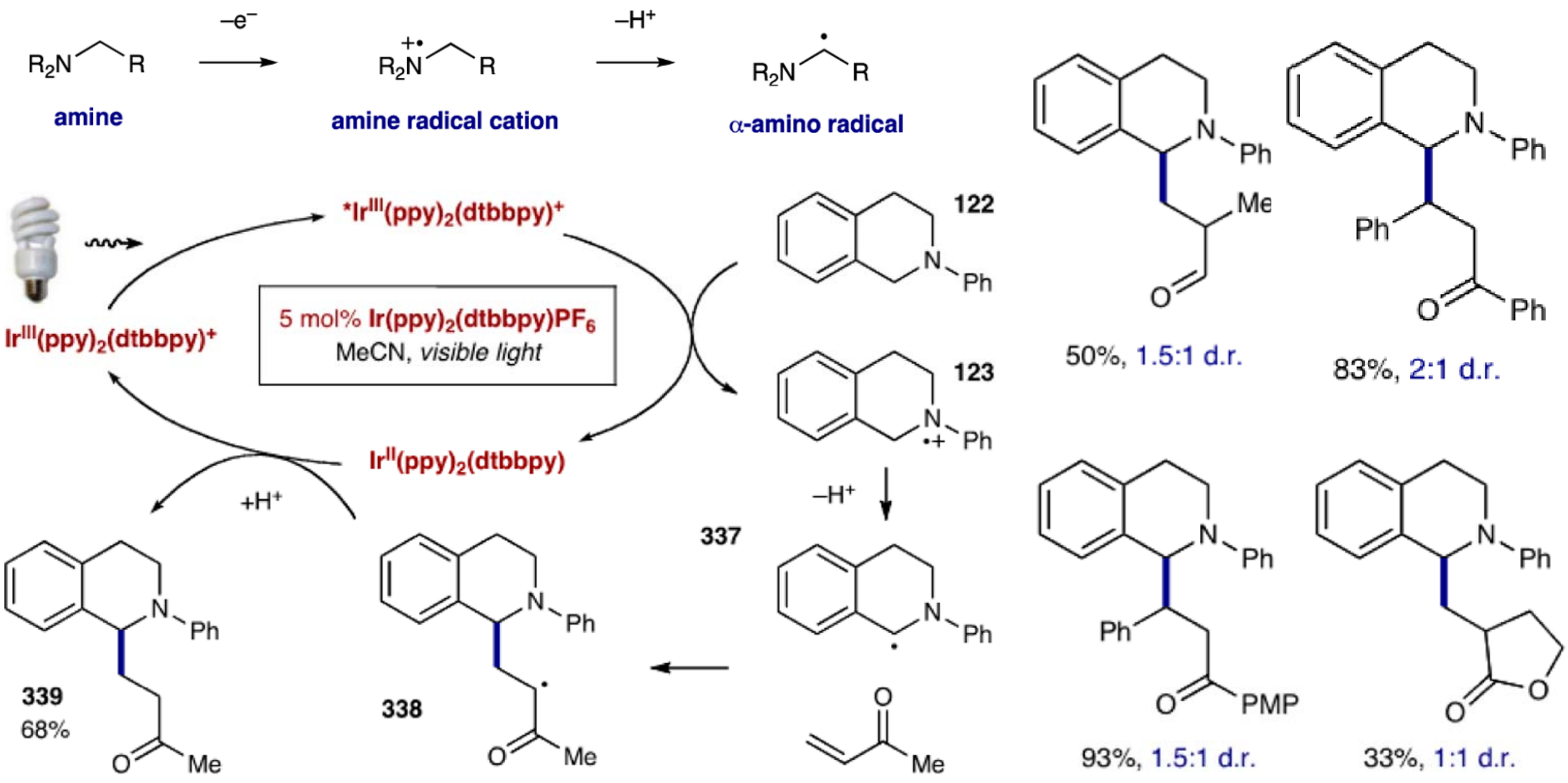
Yoon, T. P. *et. al., J. Am. Chem. Soc.* **2011**, 133, 1162

Redox Neutral Reactions 6. *[3+2] C.-A. : C.-P. Ring Opening*



Zheng, N. *et. al., Angew. Chem., Int. Ed.* **2012**, 51, 222

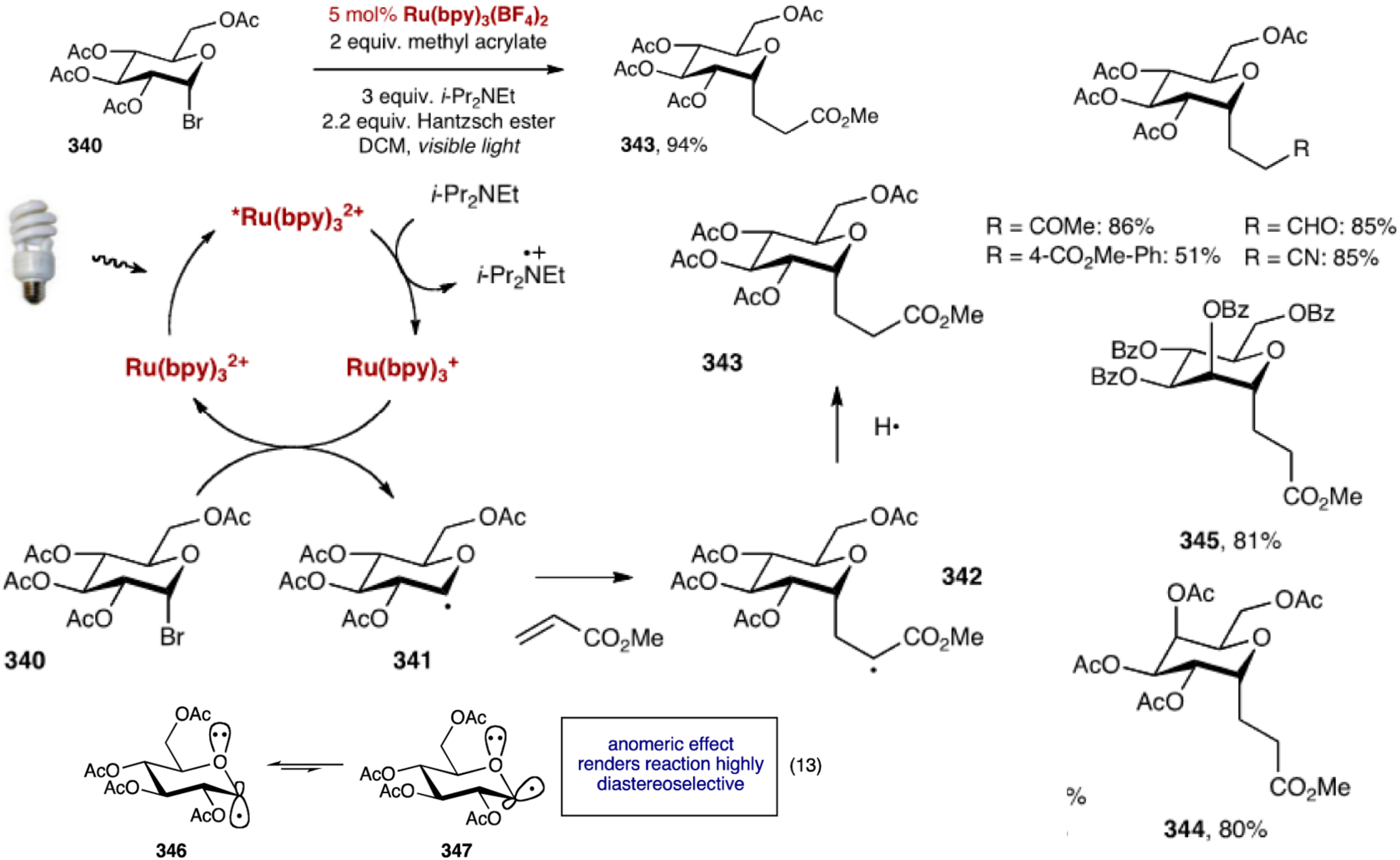
Redox Neutral Reactions 7. Radical Conjugate Addition Rxn



Pandey, G.; Reiser, O. *et. al., Org. Lett.* **2012**, 14, 672
Renaud, P. *et. al., Synthesis* **1996**, 913

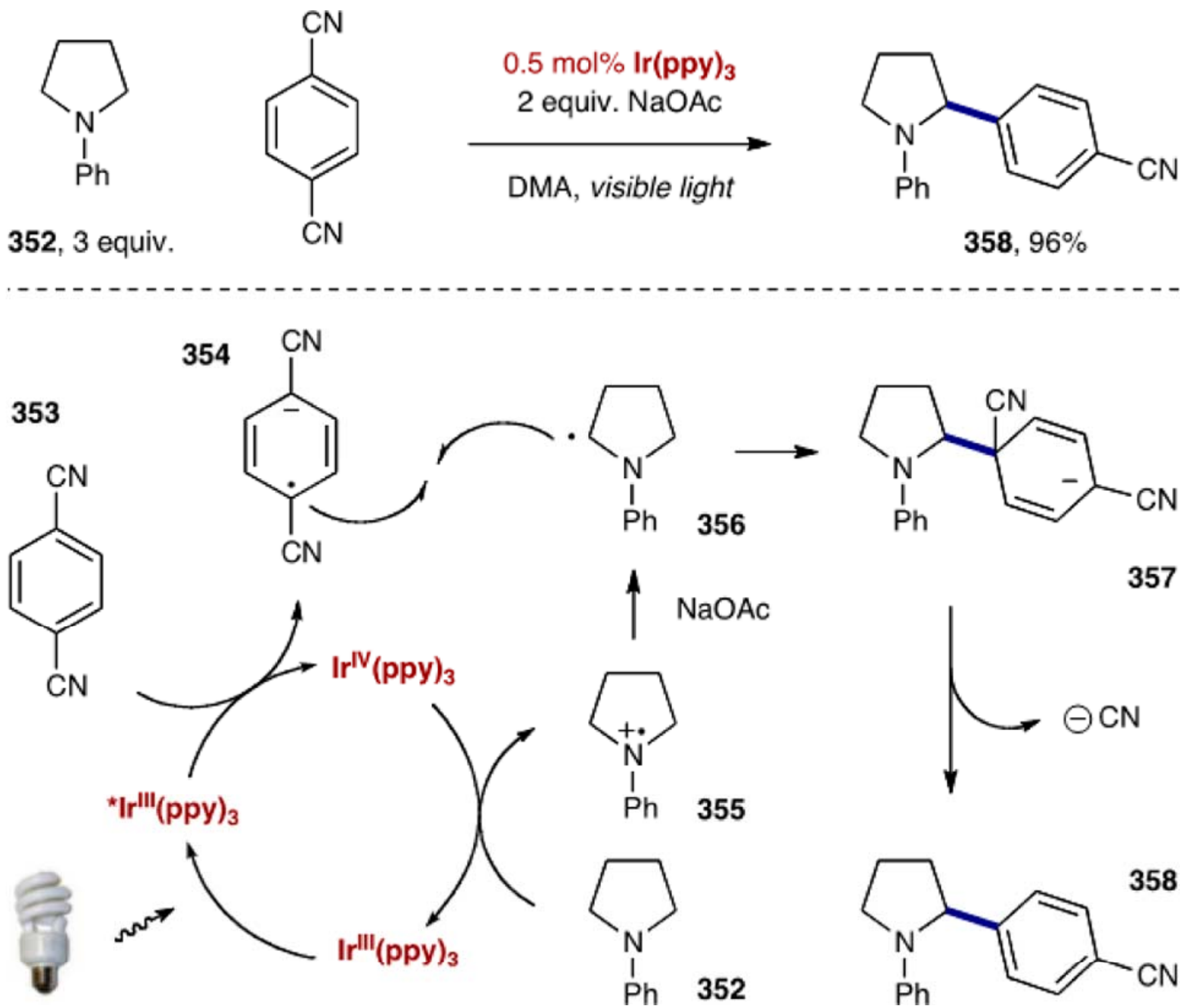
For α-amino radical:
Chow, Y. L. *et. al., Chem. Rev.* **1978**, 78, 243

Redox Neutral Reactions 7. Radical Conjugate Addition Rxn



Gagné, M. R. *et. al., Angew. Chem., Int. Ed.* **2010**, 49, 7274
Gagné, M. R. *et. al., Org. Lett.* **2011**, 13, 2406

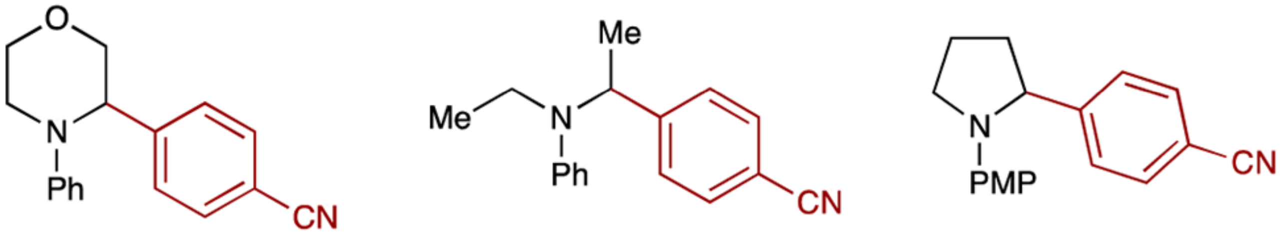
Redox Neutral Reactions 8. α-Arylation of Amines



MacMillan, D. W. C. *et. al., Science* **2011**, 334, 1114

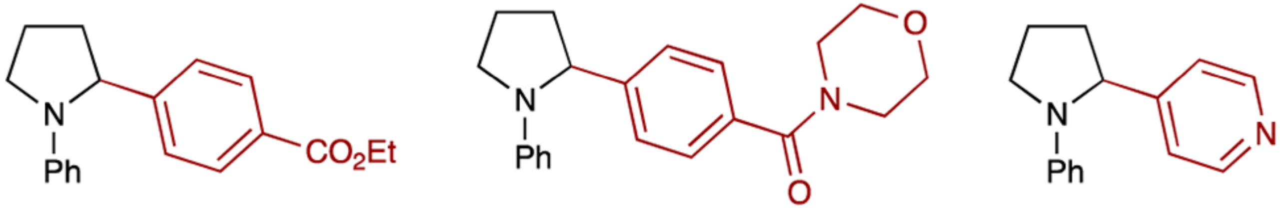
Redox Neutral Reactions *8. α-Arylation of Amines*

(A) Amine scope *Conditions:* 0.5-1.0 mol% $Ir(ppy)_3$, 2 equiv. NaOAc, DMA, *visible light*



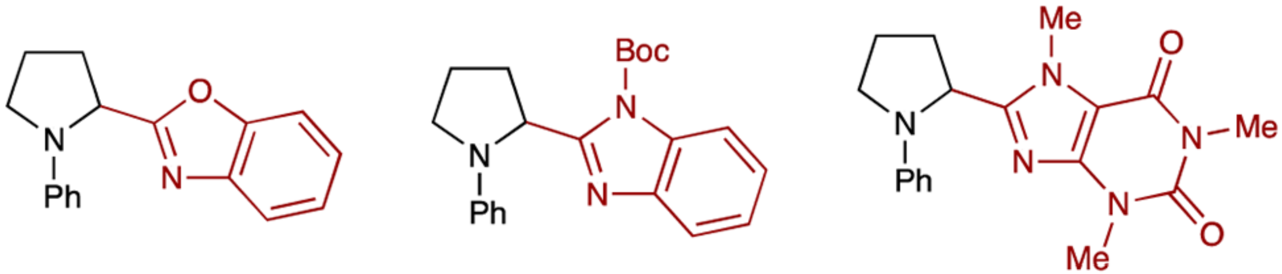
96% 94% 88%

(B) Arene scope: aryl nitriles *Conditions:* 1.0 mol% $Ir(ppy)_3$, NaOAc, DMA, *visible light*



80% 64% 72%

(C) Arene scope: aryl chlorides 1.0 mol% $Ir(ppy)_2(dtbbpy)PF_6$, NaOAc, DMA, *visible light*



91% 92% 66%

MacMillan, D. W. C. *et. al., Science* **2011**, 334, 1114

Conclusion

- *Low Temperature*
- *Different Reactivity*
- *Low-loading of Transition Metal*
- *Green Energy Source.*

Acknowledge