Photoredox catalysis: Light up on a shaded area

Mylène ROUDIER – Bibliographic seminar – 17th March 2016

« *Photochemistry as the key to novel structures* », Thorsten Bach, *Angew. Chem. Int. Ed*, **2015**, 11294

Outline

I. Introduction

II. Reactivity

   1) *Reductions*

   2) *Oxidations*

III. Enantioselective catalysis

IV. Conclusion

Outline

I. Introduction

I) Introduction

- Visible light photoredox catalysis

  - *"Ability of metal complexes to engage in single-electron transfer processes with organic substrates upon photo excitation with visible light "* (MacMillan, *Chem. Rev*, ***2013***, *5322).*

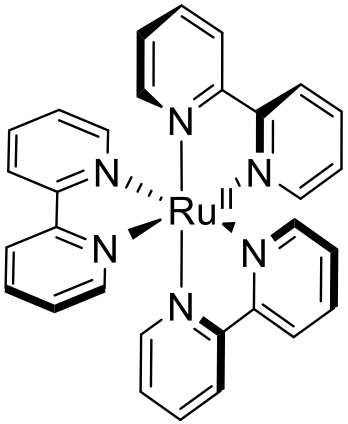
  - Extremely mild conditions: _ room temperature
    _ without highly reactive radical initiators

  - Irridiation source: typically commercial household light bulb

  - Very low catalyst loading (1 mol% or less)

I) Introduction

- Most popular photocatalyst



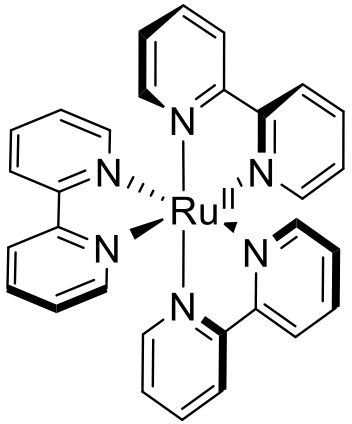
$Ru(bpy)_3^{2+}$

- 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

C. K. Prier, D. A. Rankic, D. W. C. McMillan, *Chem. Rev*, **2013**, 5322

I) Introduction

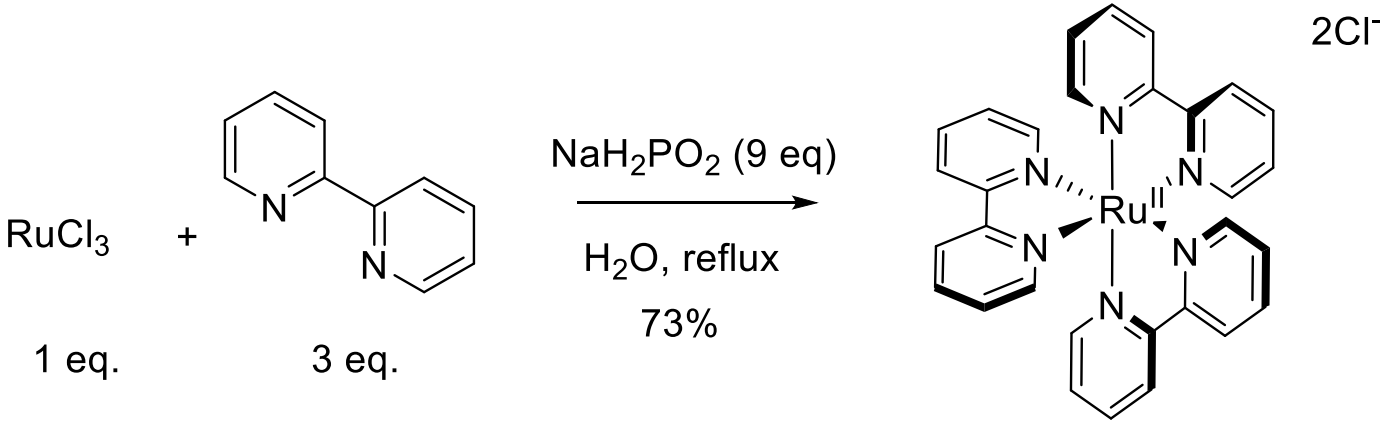
- Most popular photocatalyst



$Ru(bpy)_3^{2+}$

- 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

- Typical procedure for photocatalyst synthesis

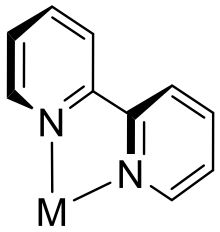


$Ru(bpy)_3Cl_2$

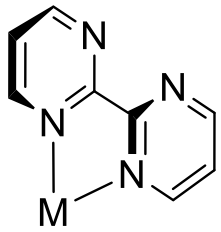
Y. Zhoa, Y. Liu, X. Du, R. Han, Y. Ding, *J. Mater. Chem. A*, **2014**, 19308

I) Introduction

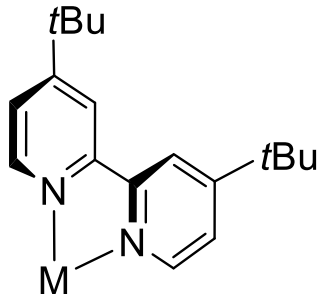
- Photocatalysts
  - Metals: ruthenium, irridium, copper
  - Ligands



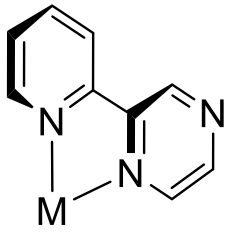
bpy



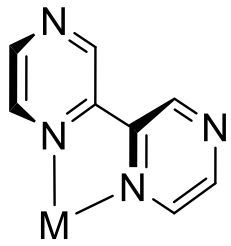
bpm



dtbbpy



ppy



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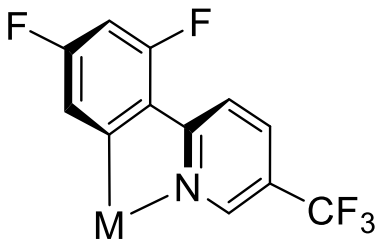
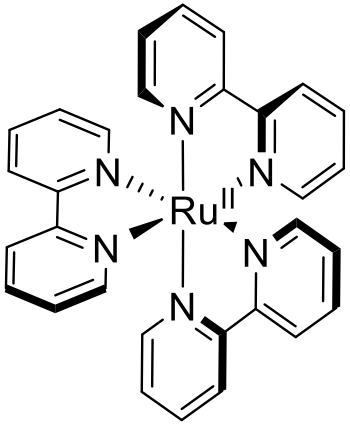


dF(CF_3)ppy

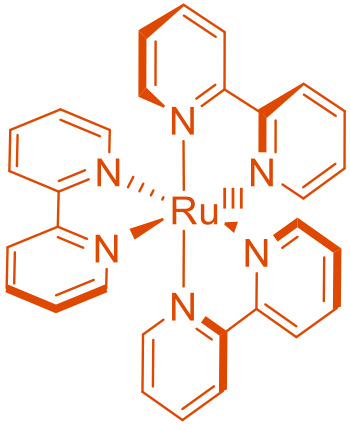
C. K. Prier, D. A. Rankic, D. W. C. McMillan, *Chem. Rev*, **2013**, 5322

I) Introduction



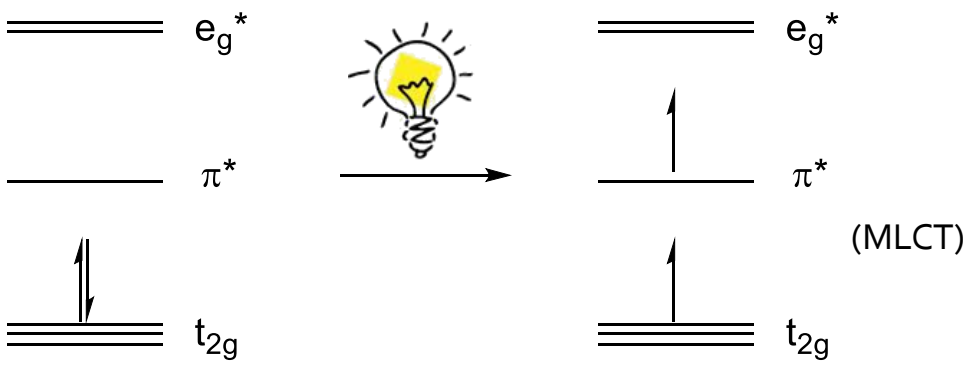
$Ru(bpy)_3^{2+}$

Ground State



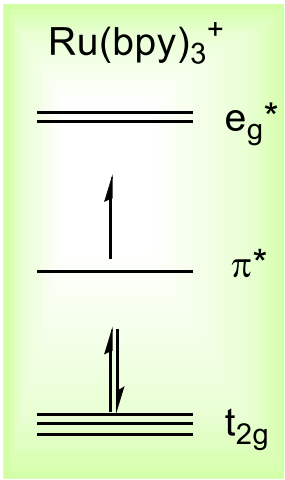
*$Ru(bpy)_3^{2+}$

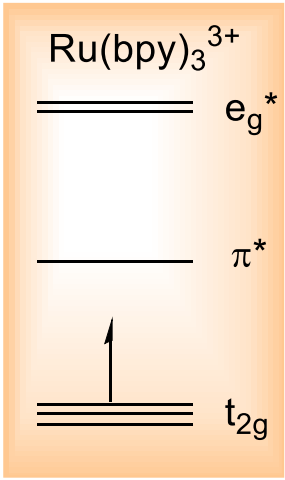
Excited State



oxidant

reductant





C. K. Prier, D. A. Rankic, D. W. C. McMillan, *Chem. Rev*, **2013**, 5322

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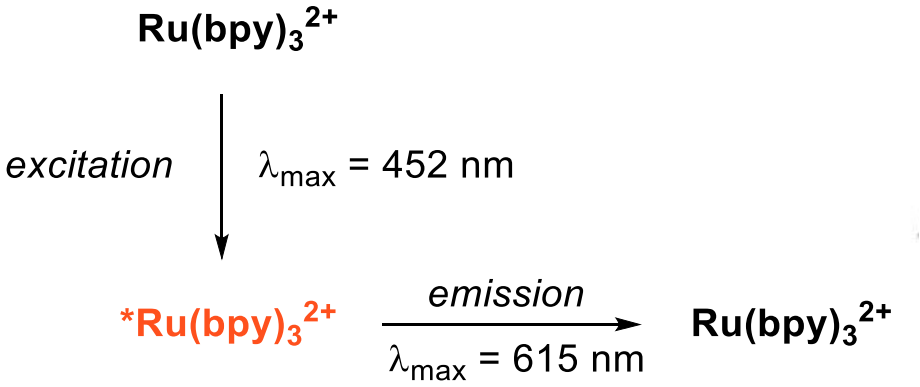

C. K. Prier, D. A. Rankic, D. W. C. McMillan, *Chem. Rev*, **2013**, 5322

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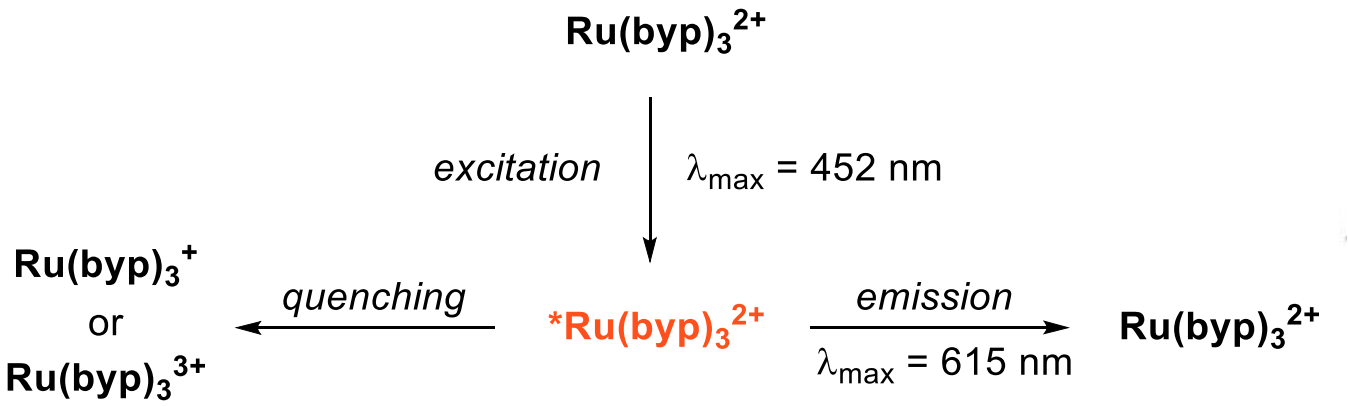

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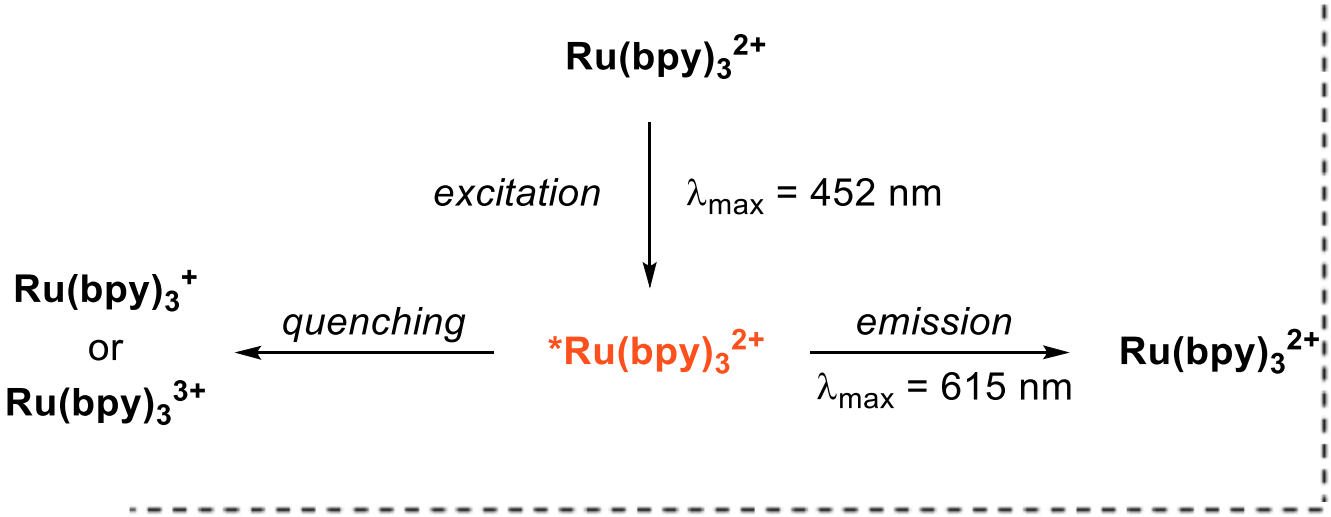
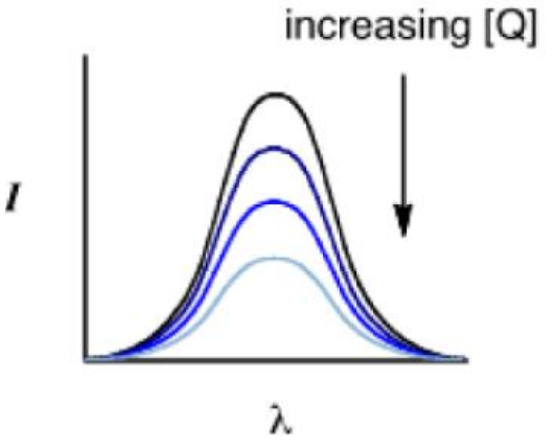




Stern-Volmer quenching studies

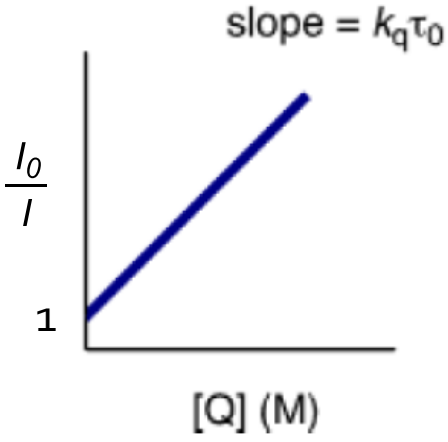
Emission intensity without quencher

Excited state lifetime without quencher

$$\frac{I_0}{I} = 1 + k_0\,\tau_0\,[Q]$$

Emission intensity with quencher

Quencher rate constante



C. K. Prier, D. A. Rankic, D. W. C. McMillan, *Chem. Rev*, **2013**, 5322

I) Introduction

- Reductive & oxidative catalyst ?
  - "*The photoexcited species has the remarkable property of being both more oxidizing and more reducing than the ground-state species* " *(MacMillan, Chem. Rev,* ***2013****, 5322).*

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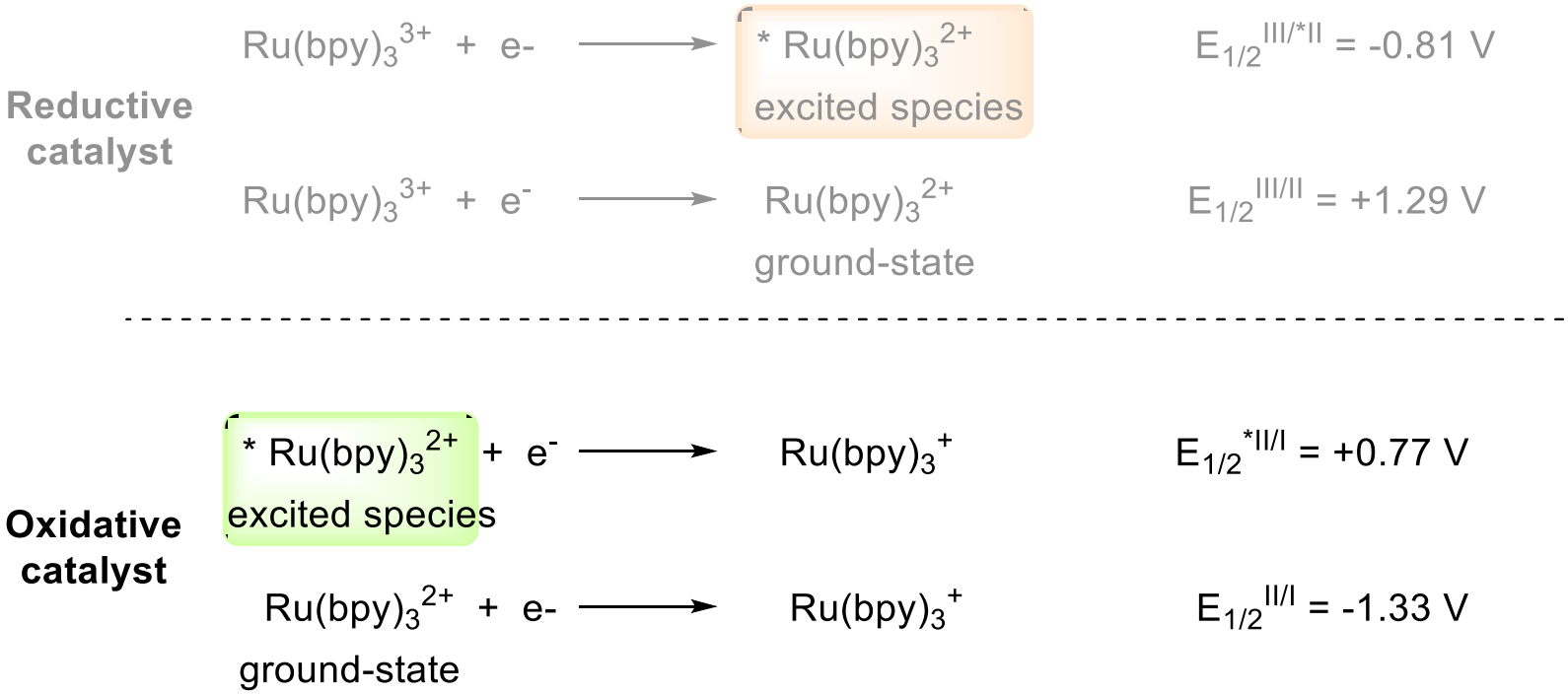
Reductive catalyst

$Ru(bpy)_3^{3+} + e^- \longrightarrow {}^*Ru(bpy)_3^{2+}$ (excited species) $\quad E_{1/2}^{III/*II} = -0.81\ V$

$Ru(bpy)_3^{3+} + e^- \longrightarrow Ru(bpy)_3^{2+}$ (ground-state) $\quad E_{1/2}^{III/II} = +1.29\ V$

I) Introduction

- Reductive & oxidative catalyst ?
  - "*The photoexcited species has the remarkable property of being both more oxidizing and more reducing than the ground-state species*" (MacMillan, Chem. Rev, **2013**, 5322).



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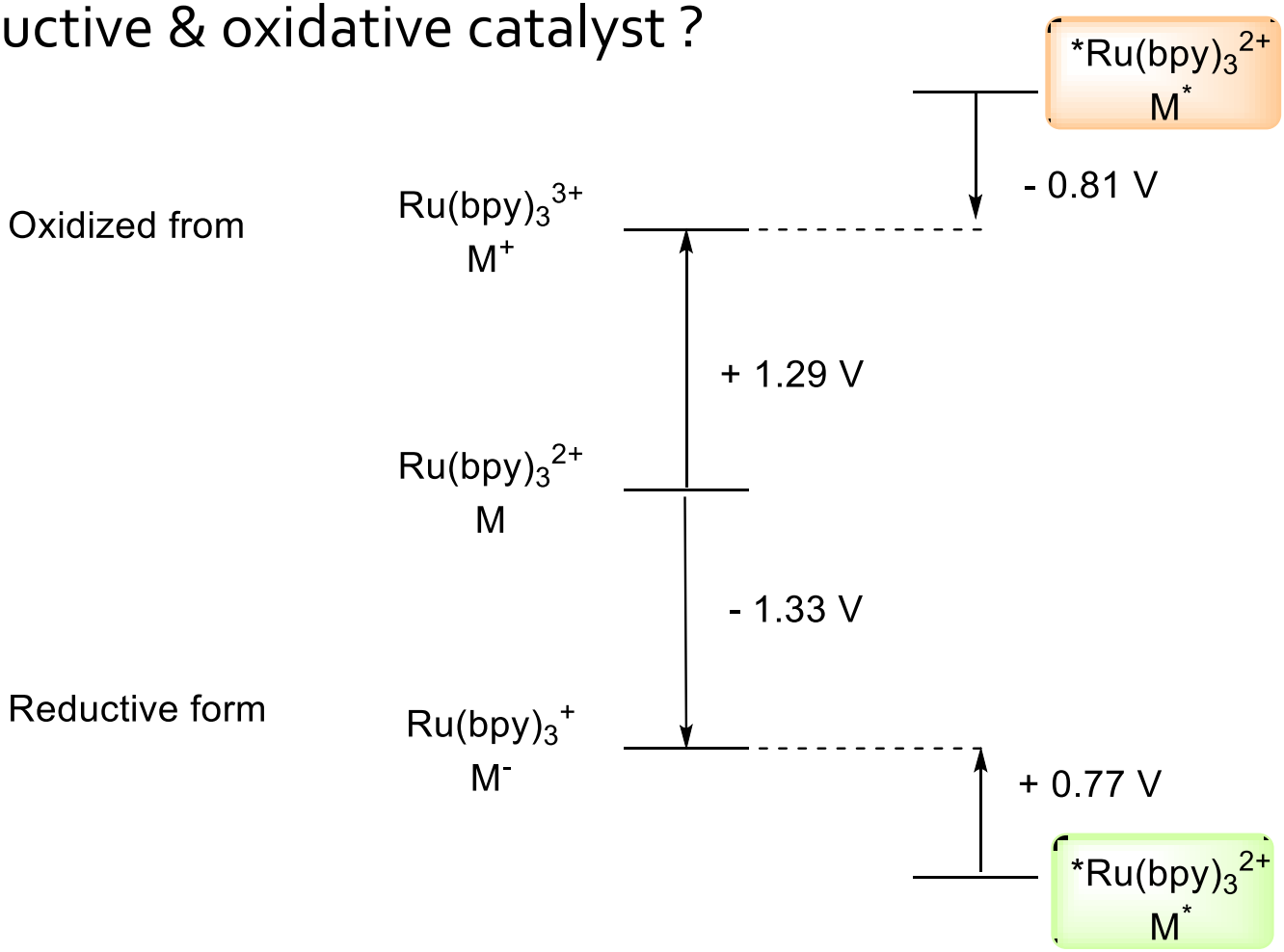


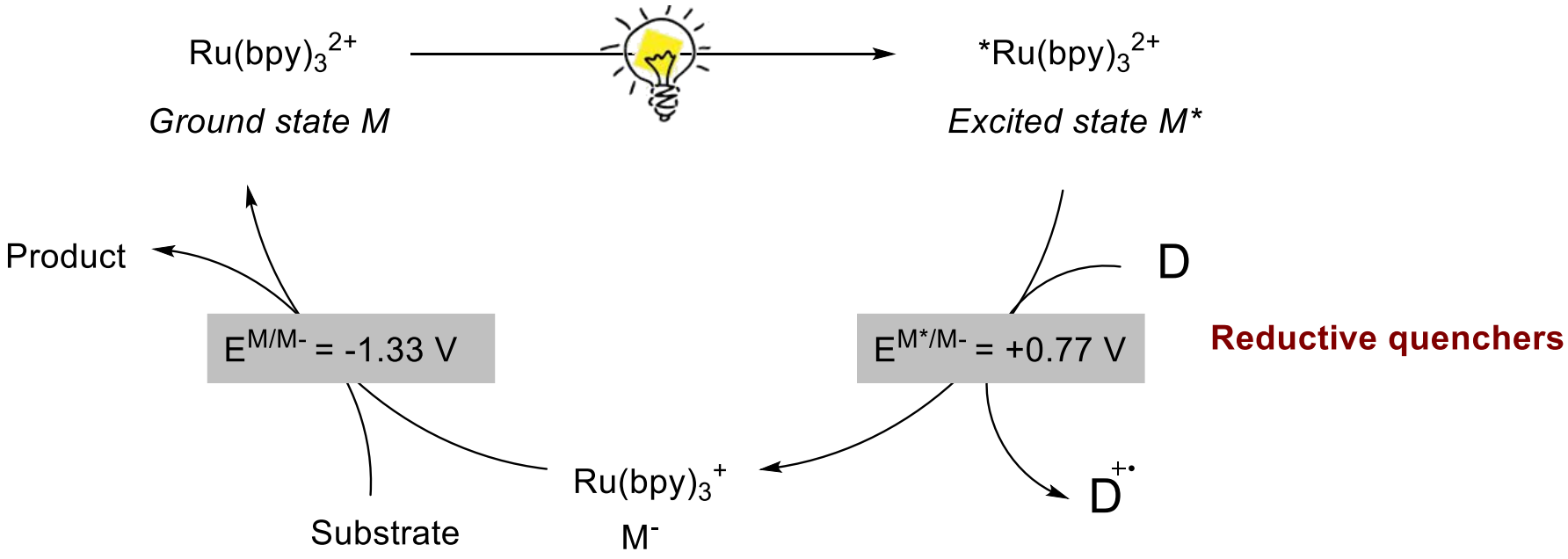
I) Introduction

I. Introduction

II. Reactivity

1) Reductions

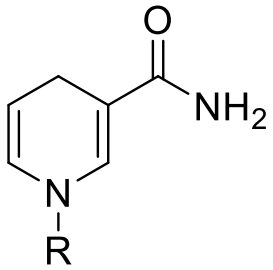
II) Reactivity - Reductions

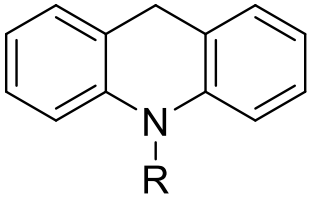


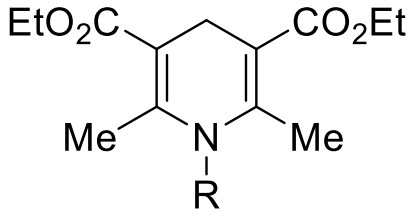
C. K. Prier, D. A. Rankic, D. W. C. McMillan, *Chem. Rev*, **2013**, 5322

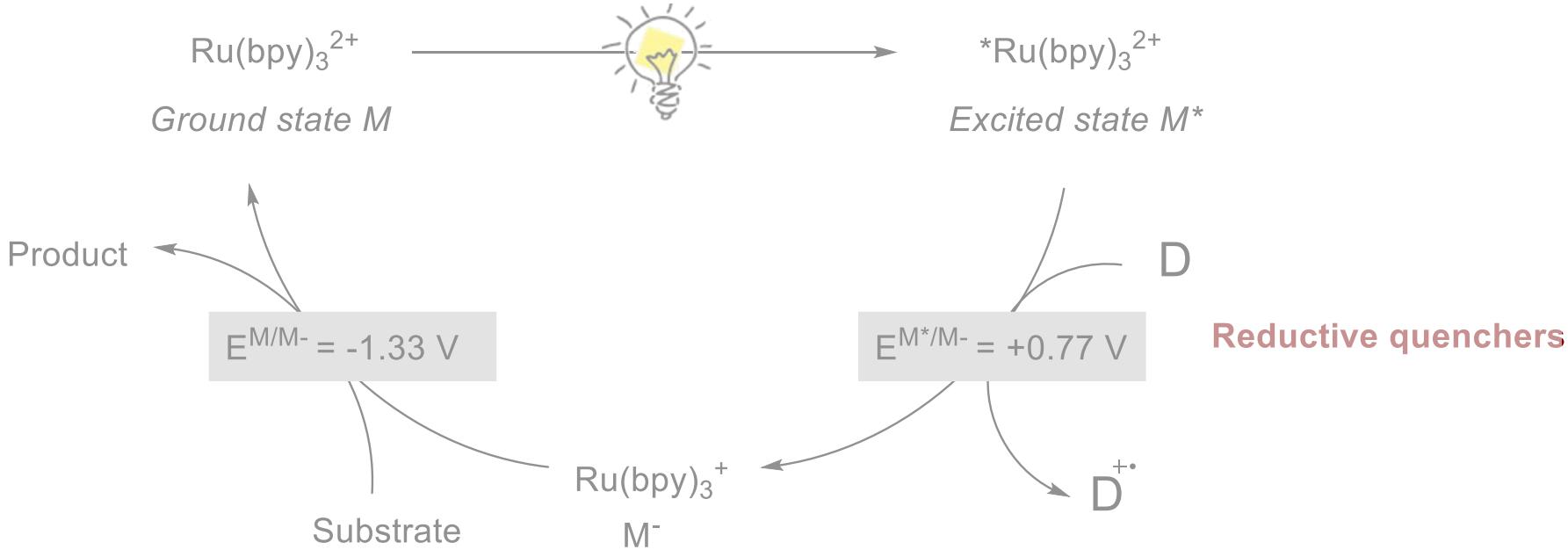
II) Reactivity - Reductions

Reductive quenchers (tertiary amines)









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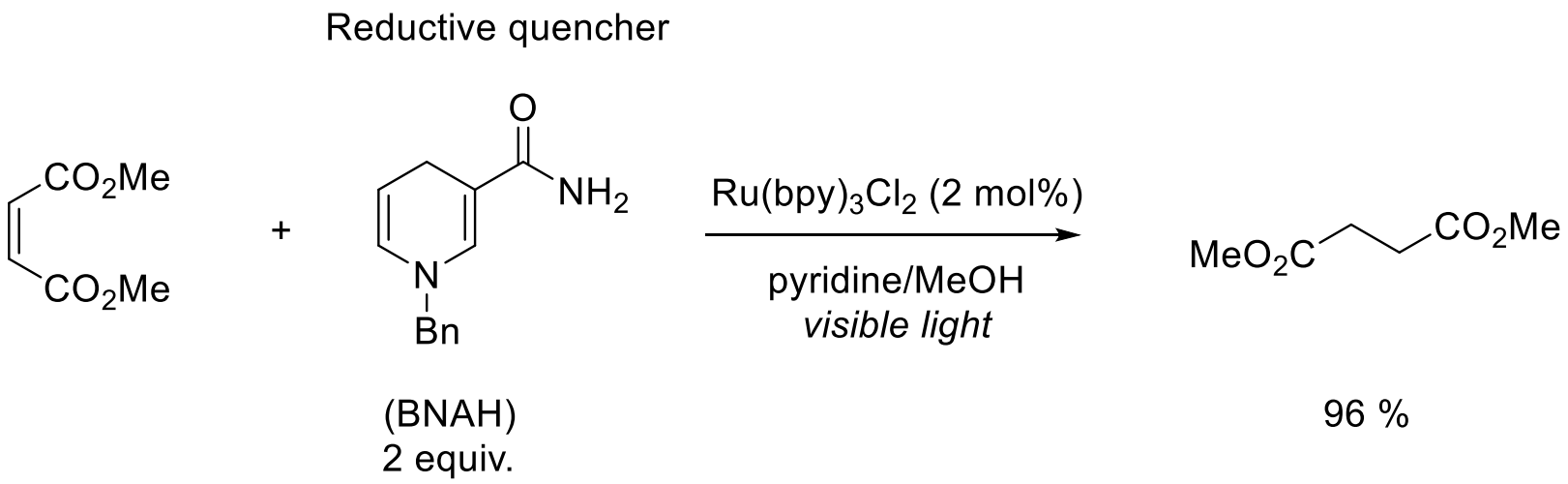
II) Reactivity - Reductions

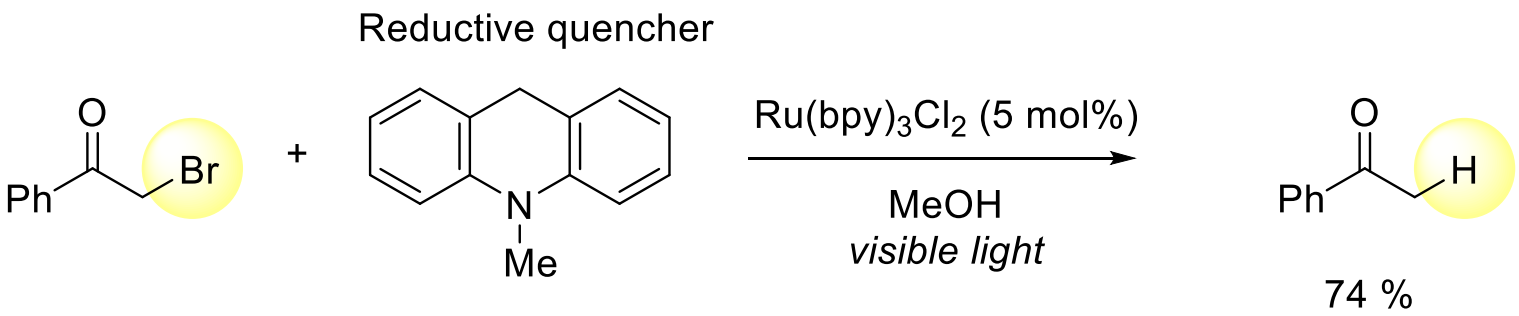
- Reductions
  - First reaction demonstrating the potential of visible light
  - Earliest report by Pac and co-workers in 1981
  - Reduction of electron-deficient olefins



C. Pac, M. Ihama, M. Yasuda, Y. Miyauchi, H. Sakurai, *J. Am. Chem. Soc.*, **1981**, 6495

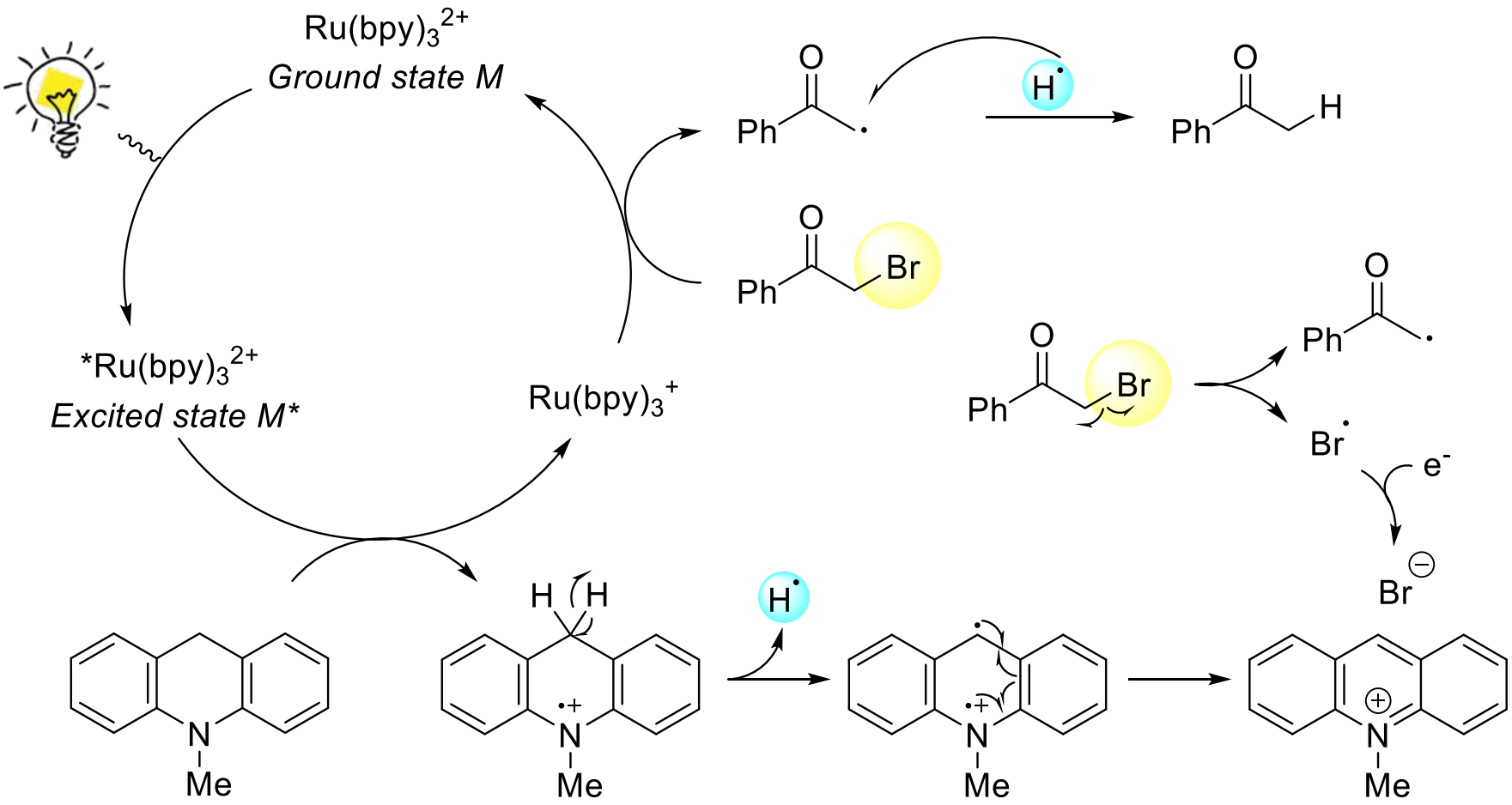
II) Reactivity - Reductions

- Reductive dehalogenations
  - Since 1990 reductive dehalogenations started to be studied



S. Fukuzumi, S. Mochizuki, T. Tanaka, *J. Phys. Chem. Soc.*, **1990**, 722

II) Reactivity - Reductions



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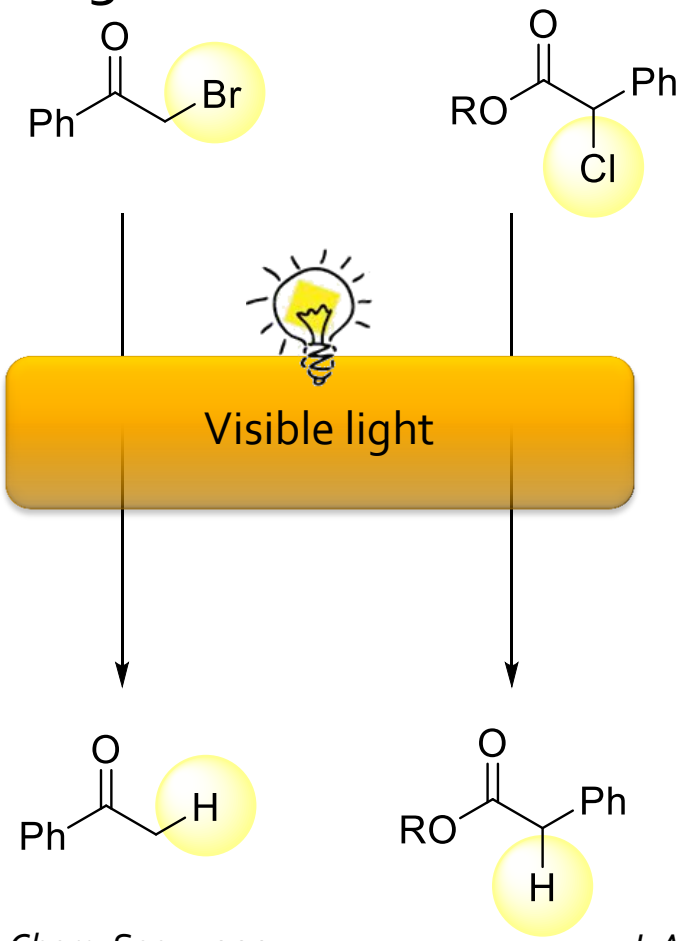
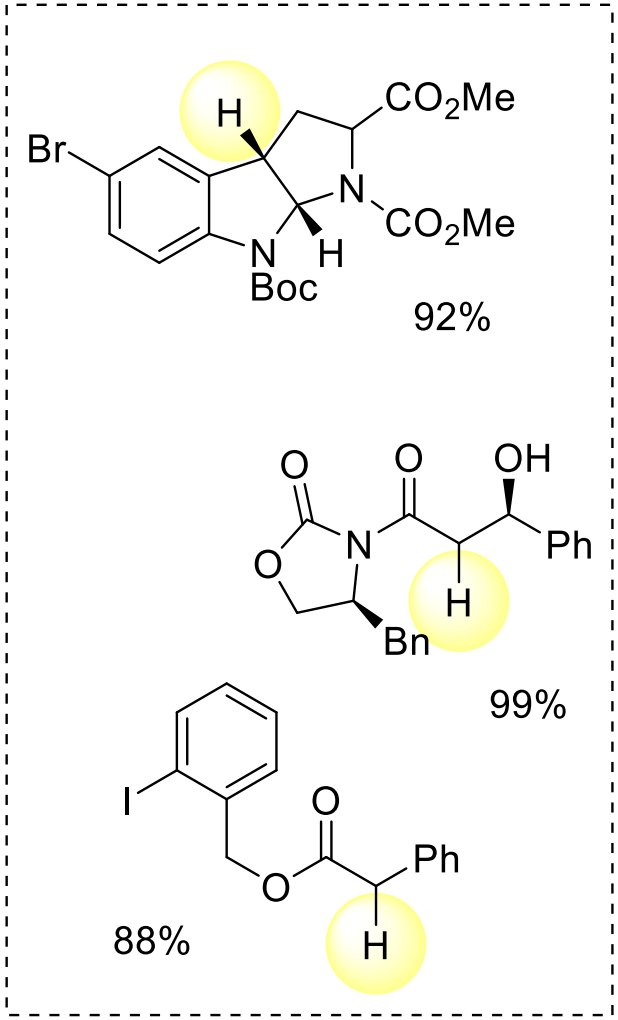
II) Reactivity - Reductions

- Reductive dehalogenations

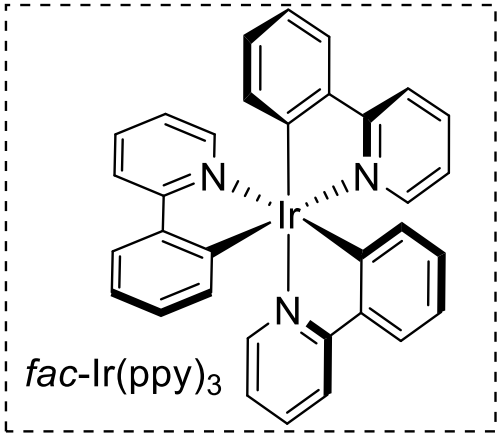


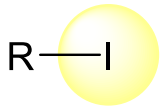


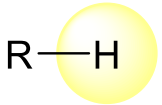
J. Phys. Chem. Soc., **1990**, 722

J. Am. Chem. Soc., **2009**, 8756

II) Reactivity - Reductions



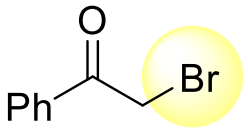


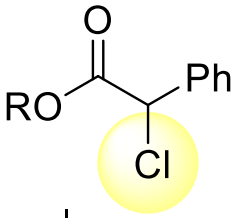


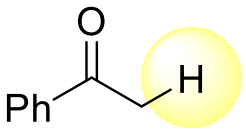
R = alkyl, alkenyl or aryl

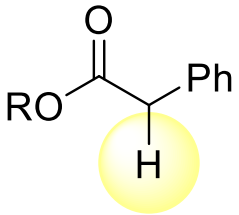
82-97%

Nature Chem., **2012**, 854







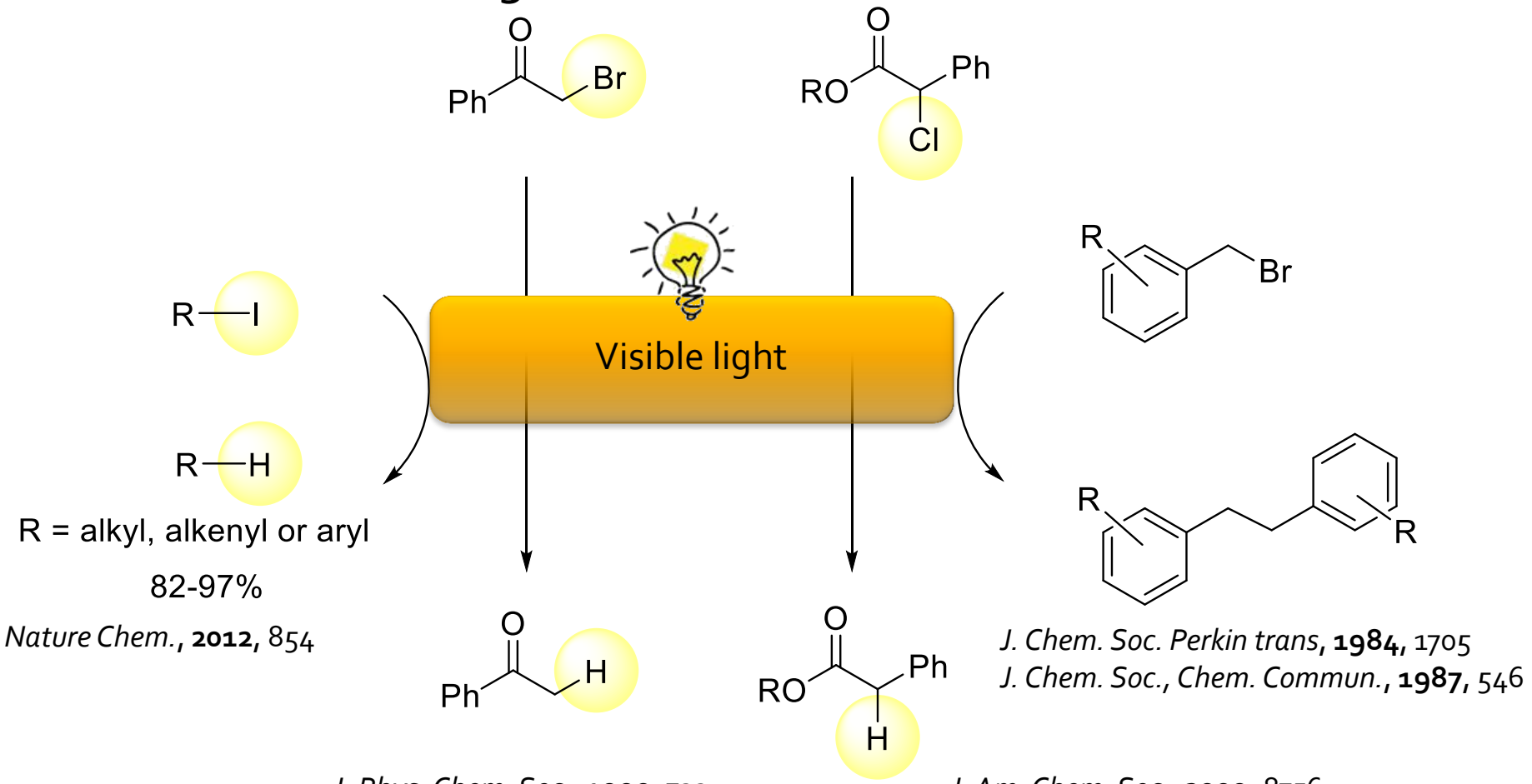


J. Phys. Chem. Soc., **1990**, 722

J. Am. Chem. Soc., **2009**, 8756

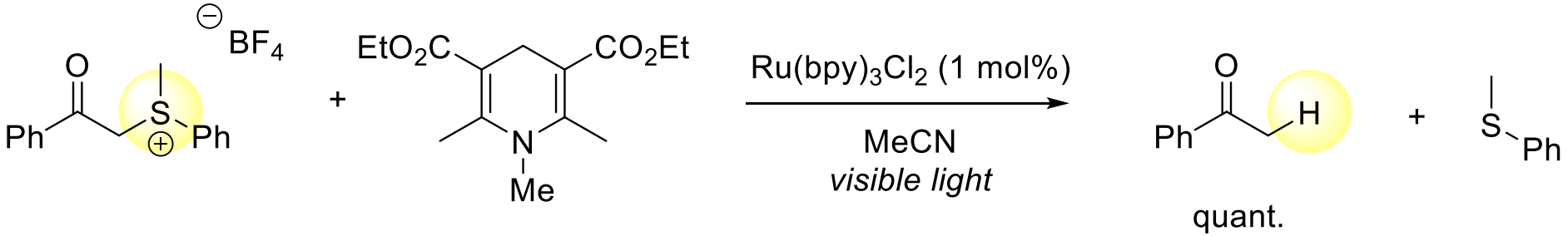
II) Reactivity - Reductions

- Reductive dehalogenations

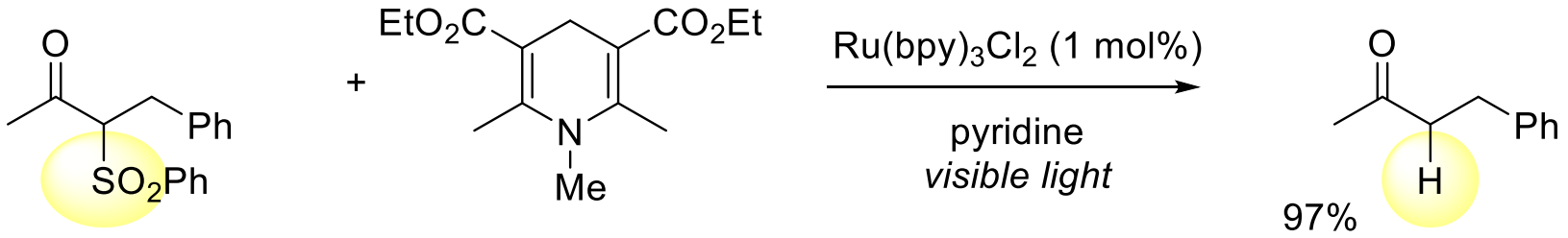


II) Reactivity - Reductions

- Reductive cleavage of sulfonium and sulfonyl groups



D. M. Hedstrand, W. M. Kruizinga, R. M. Kellogg, *Tetrahedron Lett.*, **1978**, 1255



K. Nakamura, M. Fujii, H. Mekata, S. Oka, A. Ohno, *Chem. Lett.*, **1986**, 87

II) Reactivity - Reductions

- Reductions
  - Reduction of nitro to amines
  - Reduction of azydes to amines
  - Reductive epoxide opening
  - Reduction aziridine opening
  - Radical cyclization
  - Reduction of protecting groups
  - …

Outline

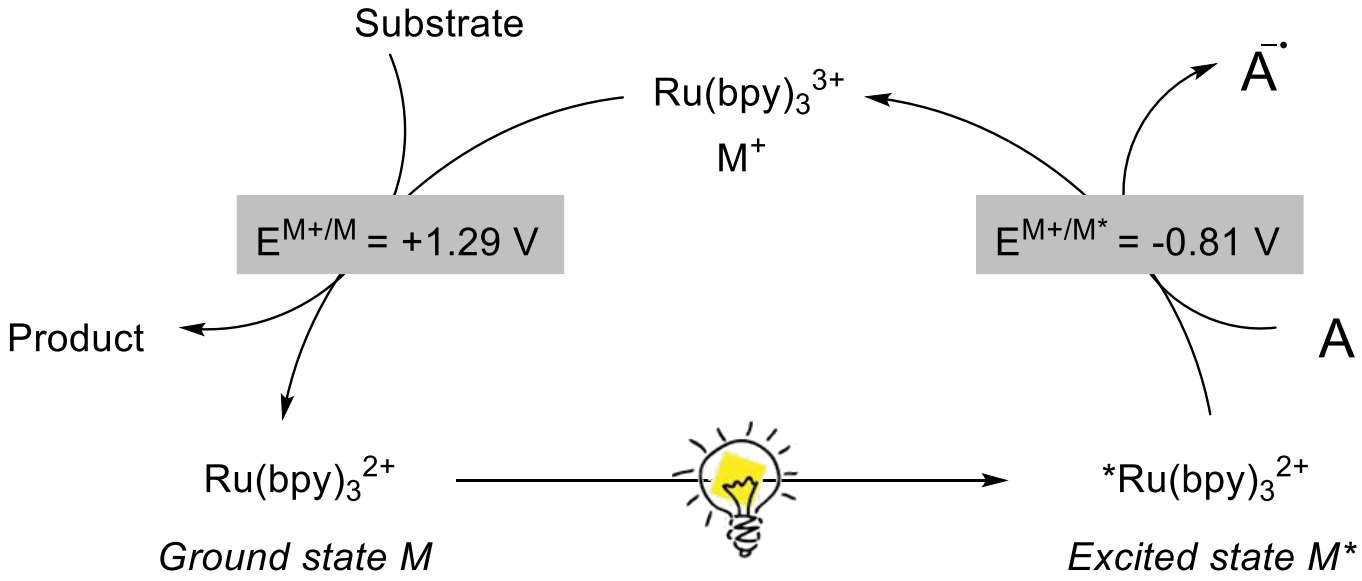
I. Introduction

II. Reactivity

1) *Reductions*

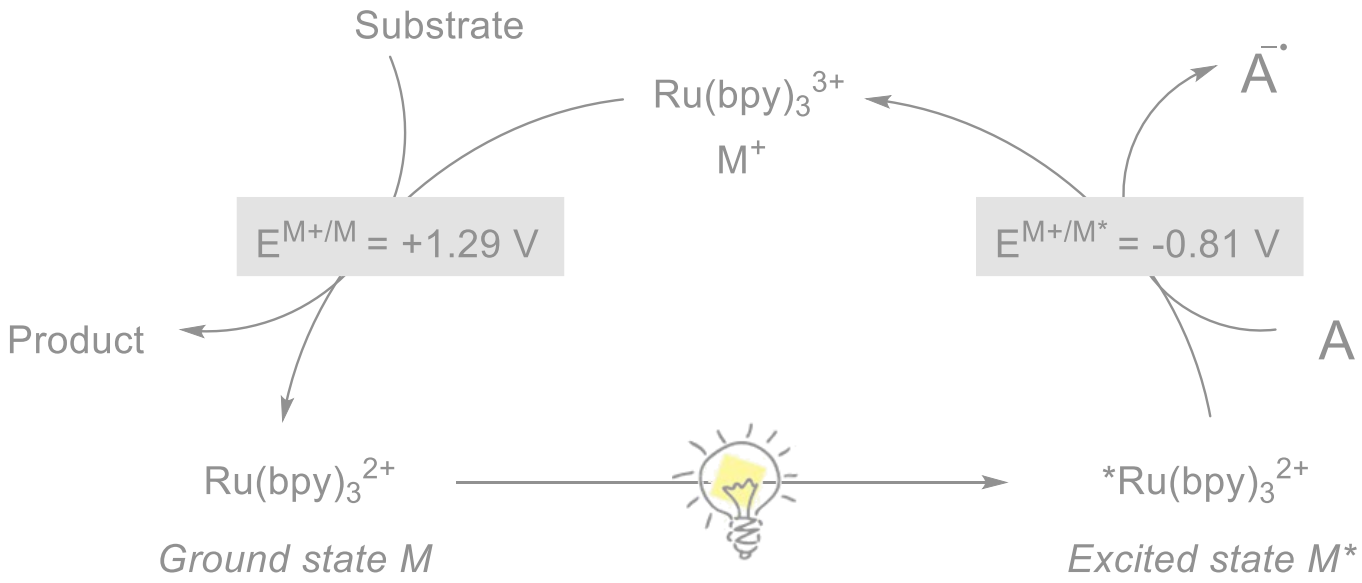
2) *Oxidations*

II) Reactivity - Oxidations

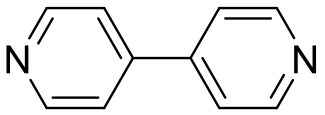


C. K. Prier, D. A. Rankic, D. W. C. McMillan, *Chem. Rev*, **2013**, 5322

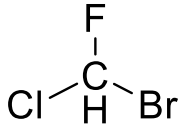
II) Reactivity - Oxidations



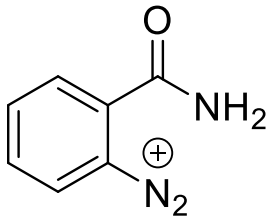
Oxidative quenchers



viologens



polyhalomethanes

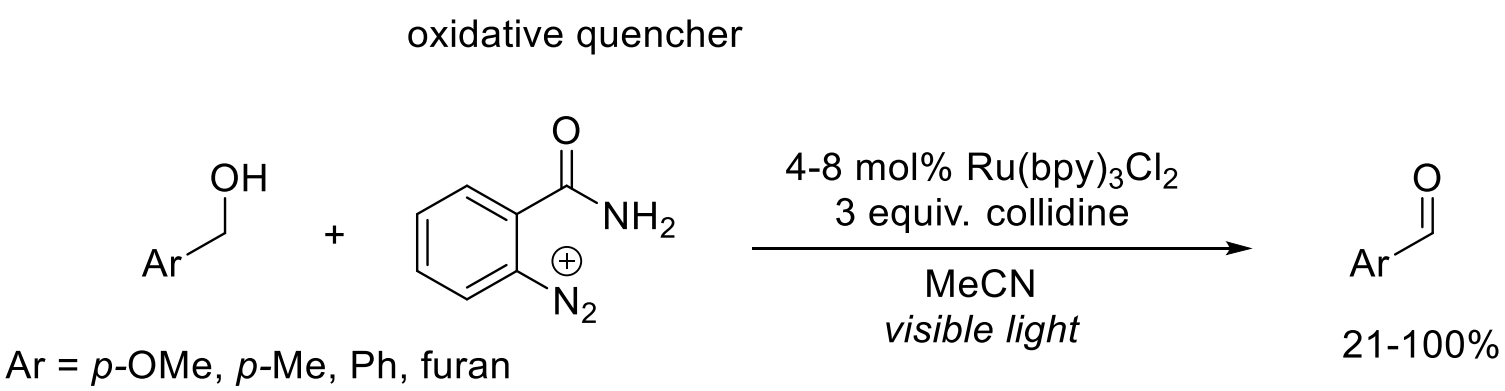


aryldiamonium salts

C. K. Prier, D. A. Rankic, D. W. C. McMillan, *Chem. Rev*, **2013**, 5322

II) Reactivity - Oxidations

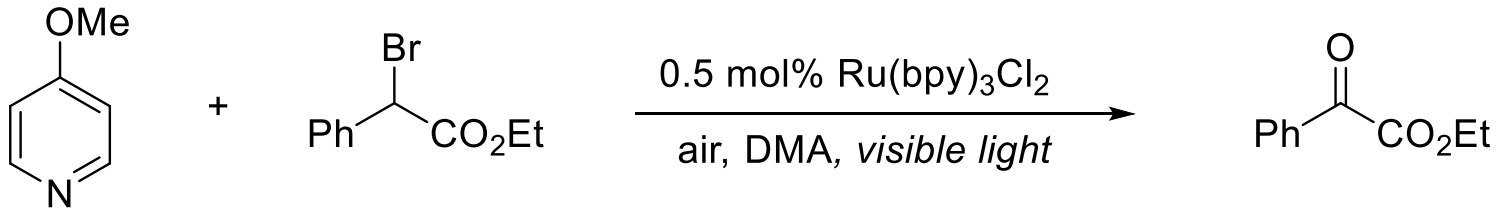
- Oxidative reactions
  - Single-electron oxidation of particulary electron-rich functional groups:
    - Electron-rich arenes
    - Electron-rich amines
  - Since 1984, oxidative reactions were studied



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

II) Reactivity - Oxidations

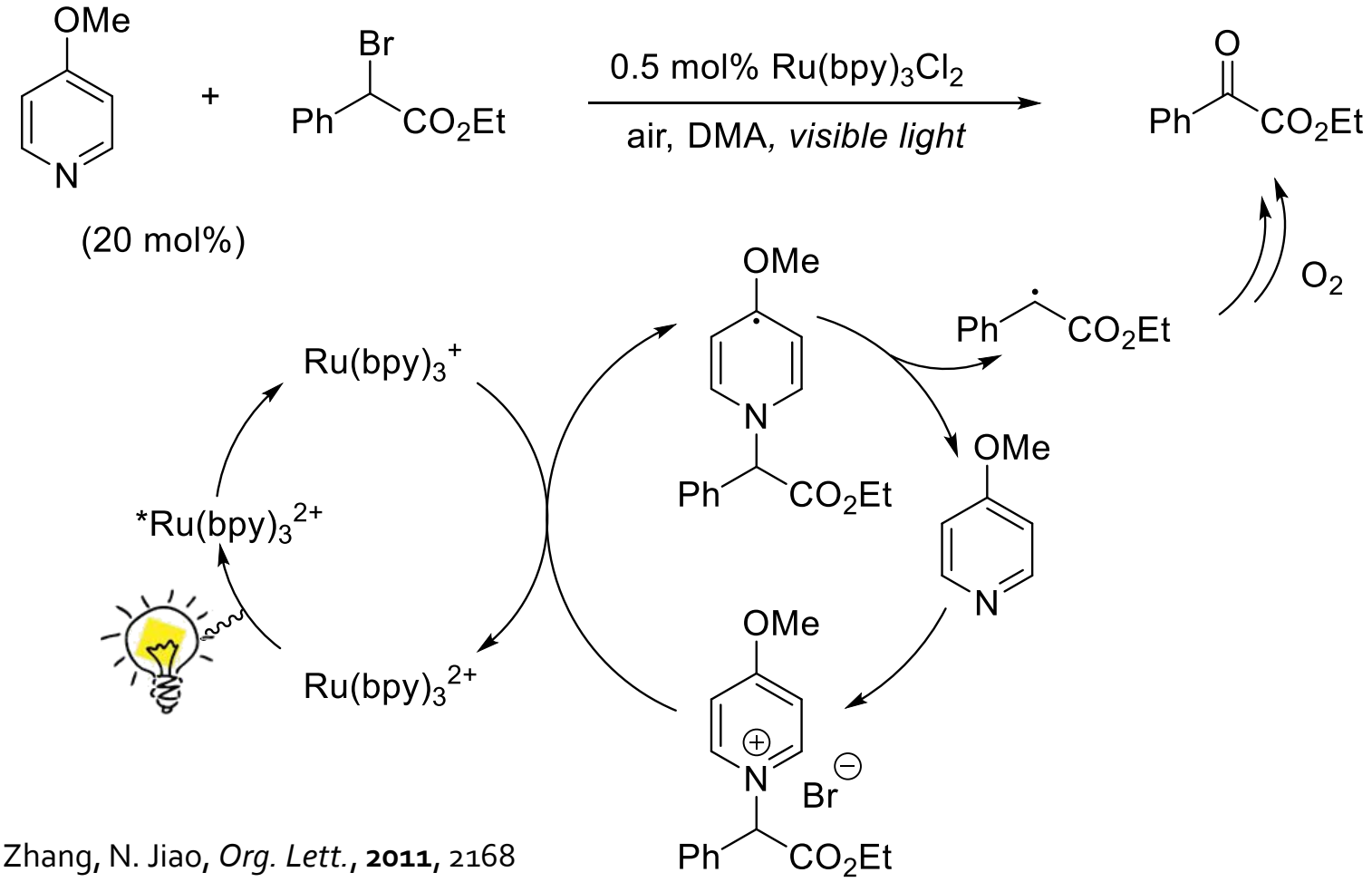
- Aerobic oxidation of benzylic halides



Y. Su, L. Zhang, N. Jiao, *Org. Lett.*, **2011**, 2168

II) Reactivity - Oxidations

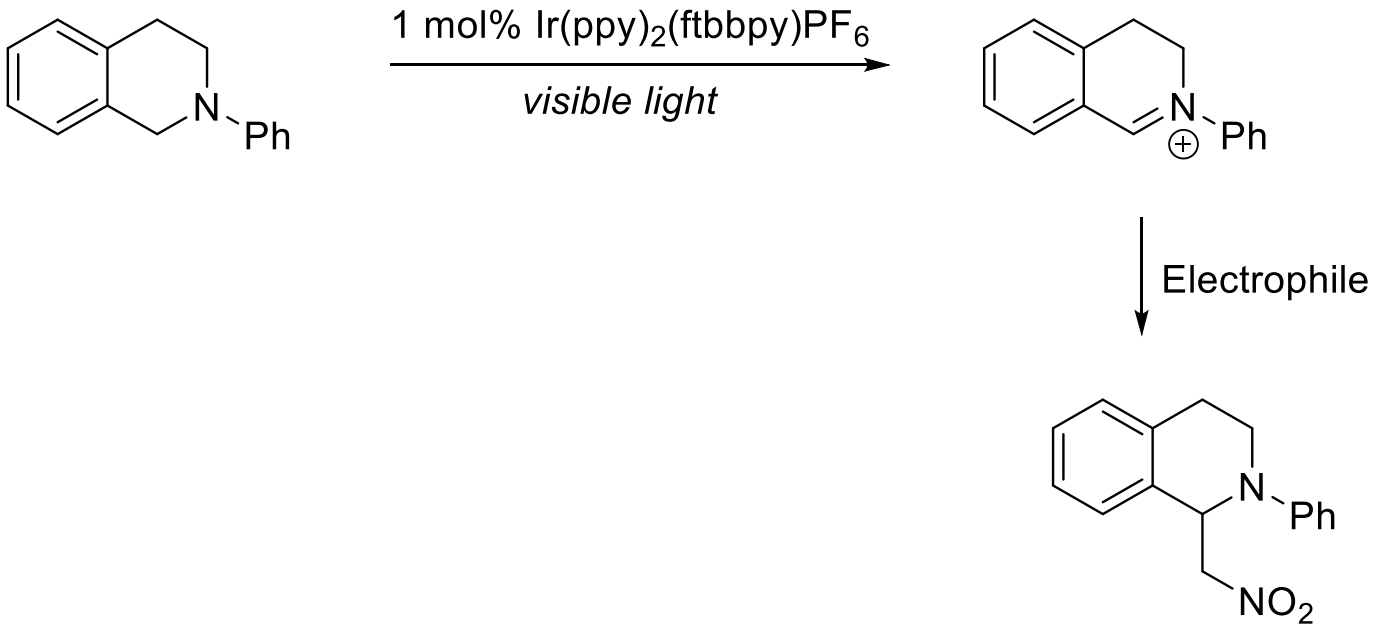
- Aerobic oxidation of benzylic halides



Y. Su, L. Zhang, N. Jiao, *Org. Lett.*, **2011**, 2168

II) Reactivity - Oxidations

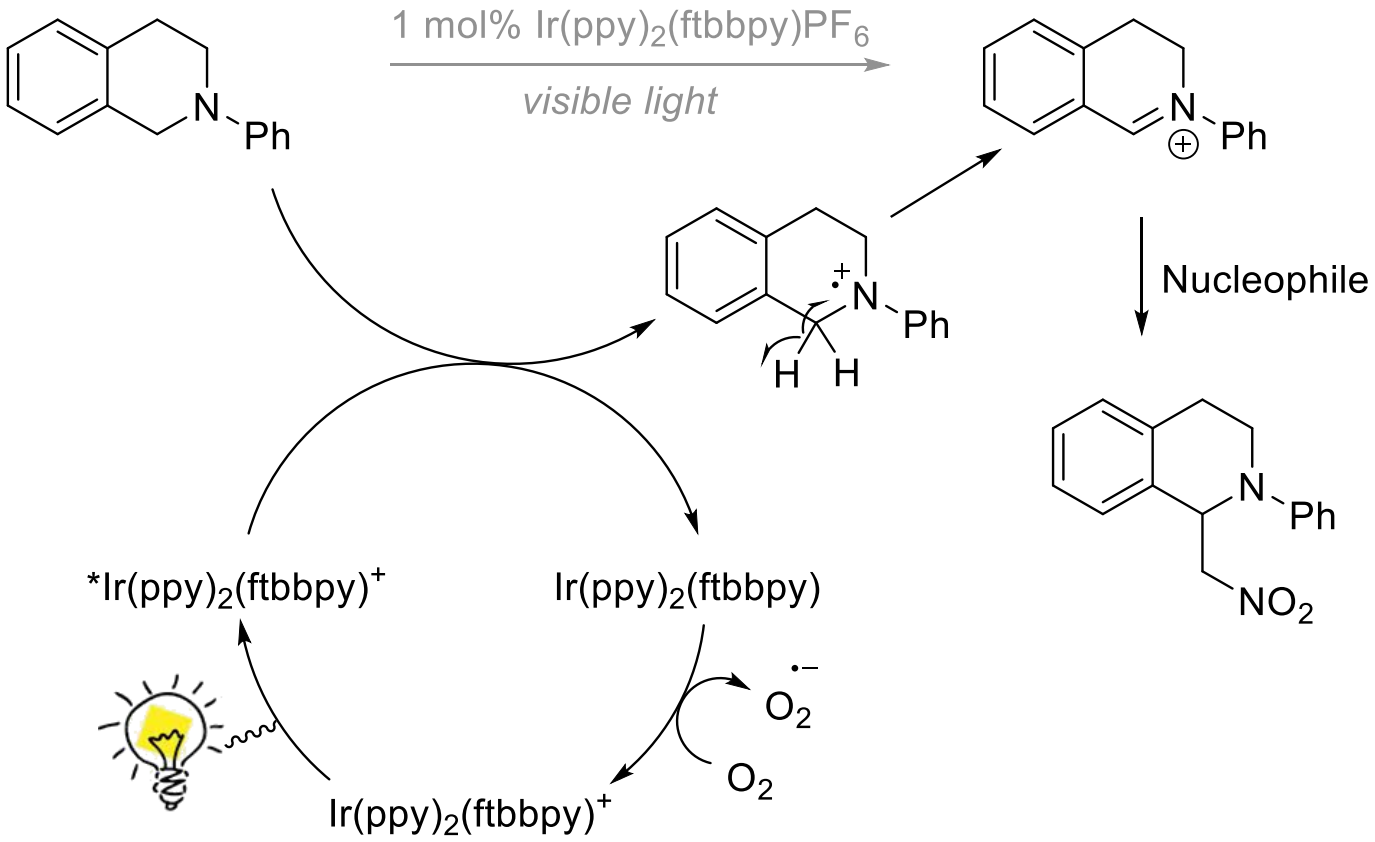
- Amine oxidation to iminium ions



A. G. Condie, J. C. Gonzalez-Gomez, C. R. J. Stephenson, *J. Am. Chem. Soc.*, **2010**, 1464

II) Reactivity - Oxidations

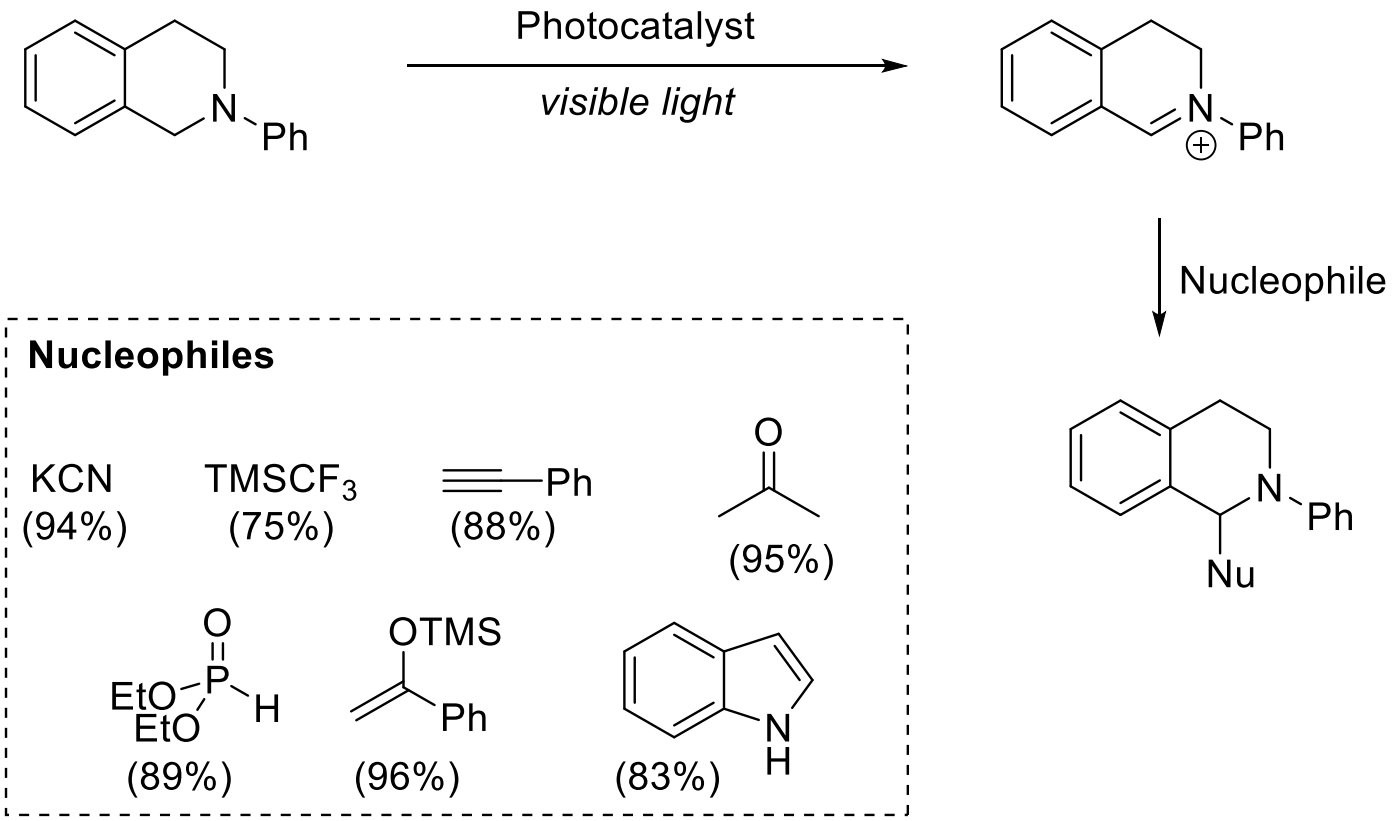
- Amine oxidation to iminium ions



A. G. Condie, J. C. Gonzalez-Gomez, C. R. J. Stephenson, *J. Am. Chem. Soc.*, **2010**, 1464

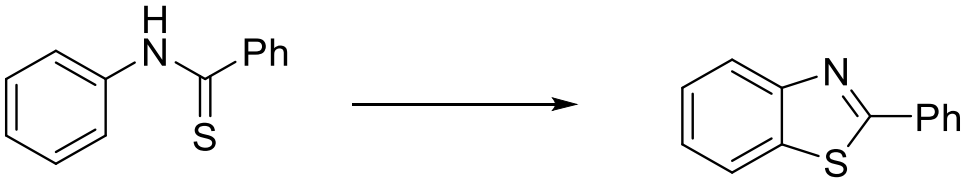
II) Reactivity - Oxidations

- Amine oxidation to iminium ions



II) Reactivity - Oxidations

- Oxidations
  - Oxidative biaryl coupling
  - Oxidative conversion of thiobenzanilides to benzothiazoles



  - α-arylation of amides
  - Oxidative deprotection of PMB
  - …

II) Reactivity - Oxidations

I. Introduction

II. Reactivity

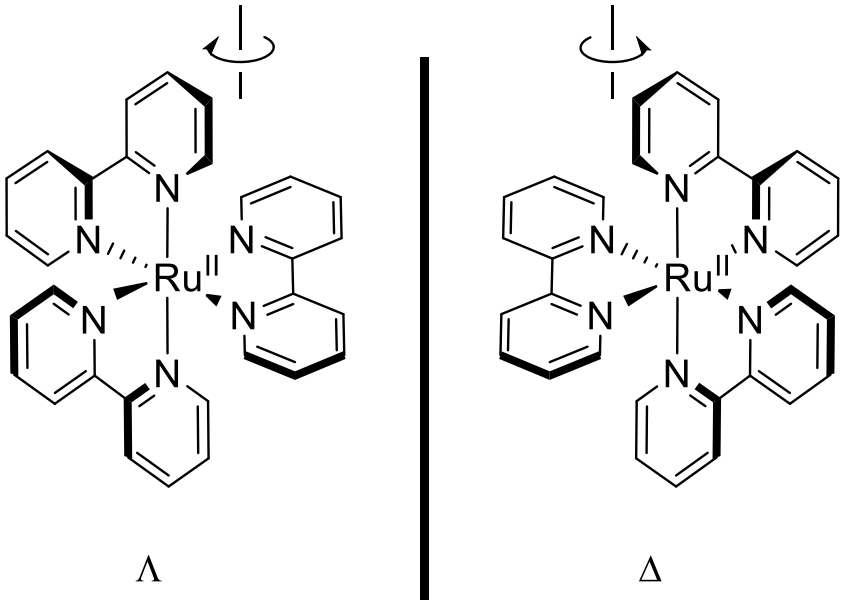
1) *Reductions*

2) *Oxidations*

III. Enantioselective catalysis

III) Enantioselective catalysis

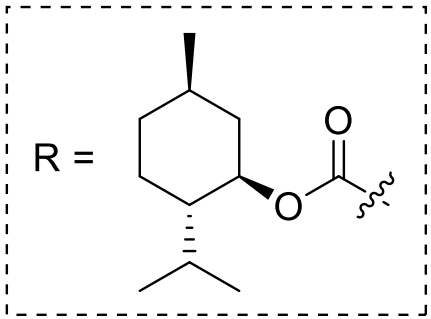
- Enantiomeric forms of $Ru(bpy)_3^{2+}$

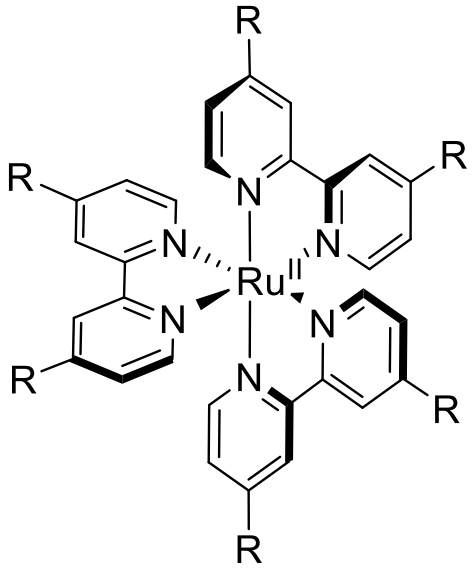


- Octahedral metal complexes
- C_3 symmetry axis
- Induce enantioselectivity ?

III) Enantioselective catalysis

- $Ru(menbpy)_3^{2+}$ used for enantioselective synthesis ?
  - Prepared as mixture of Δ and Λ forms
  - Diastereomers with R substituents
  - Simply to separe by column chromatography



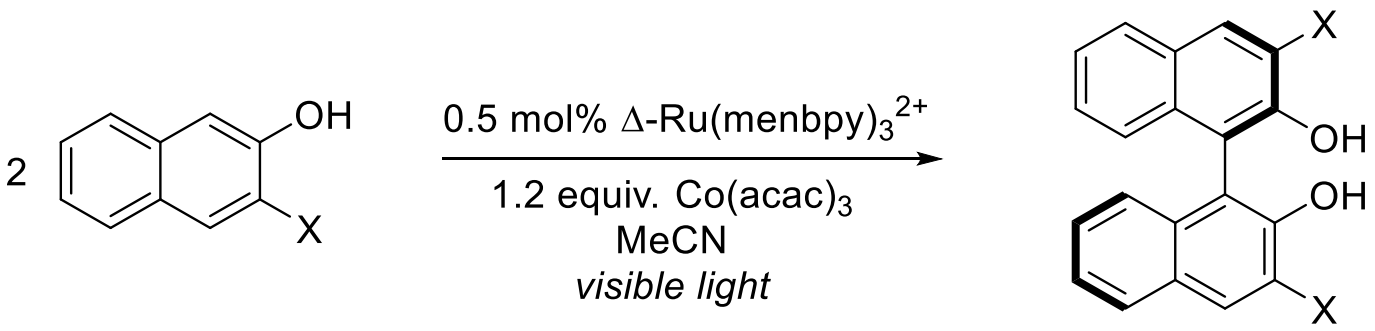


Δ-$Ru(menbpy)_3^{2+}$

T. Hamada, H. Ishida, S. Usui, Y. Watanabe, K. Tsumura, K. Ohkubo, , *J. Chem. Soc., Chem. Commun.*, **1993**, 909

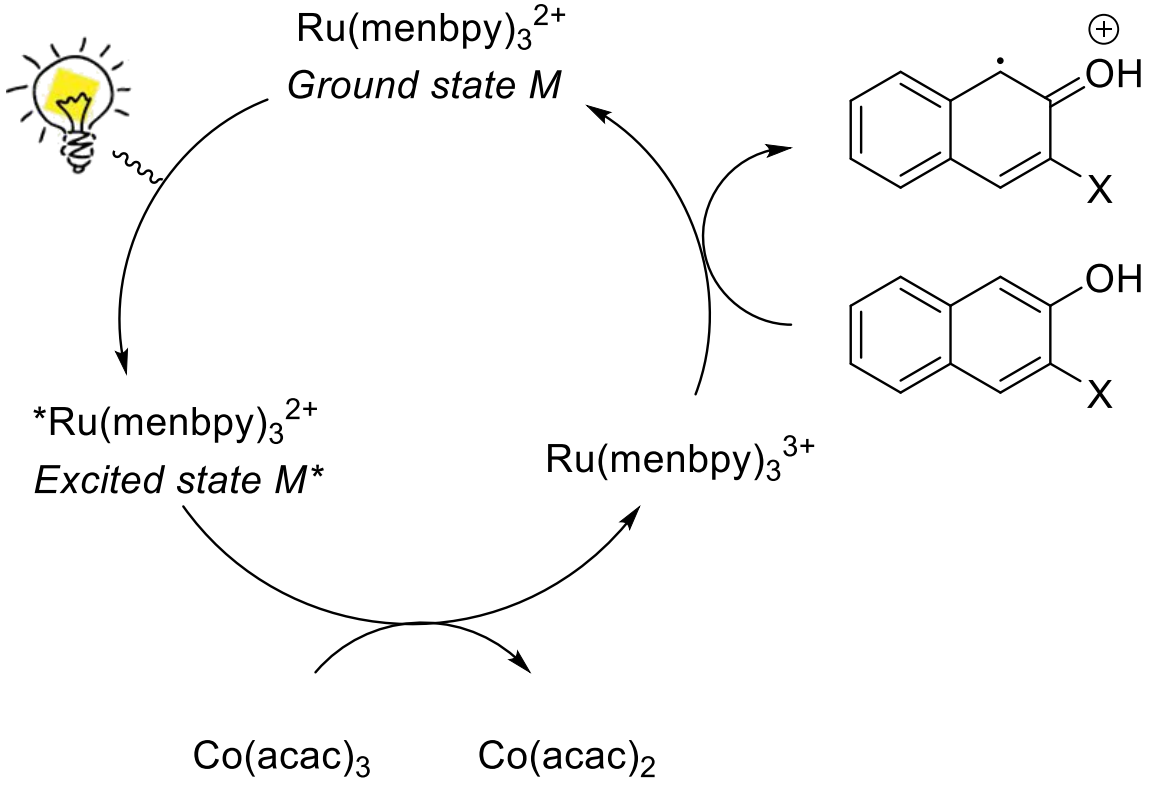
III) Enantioselective catalysis

- Ru(menbpy)$_3^{2+}$ used for enantioselective synthesis ?

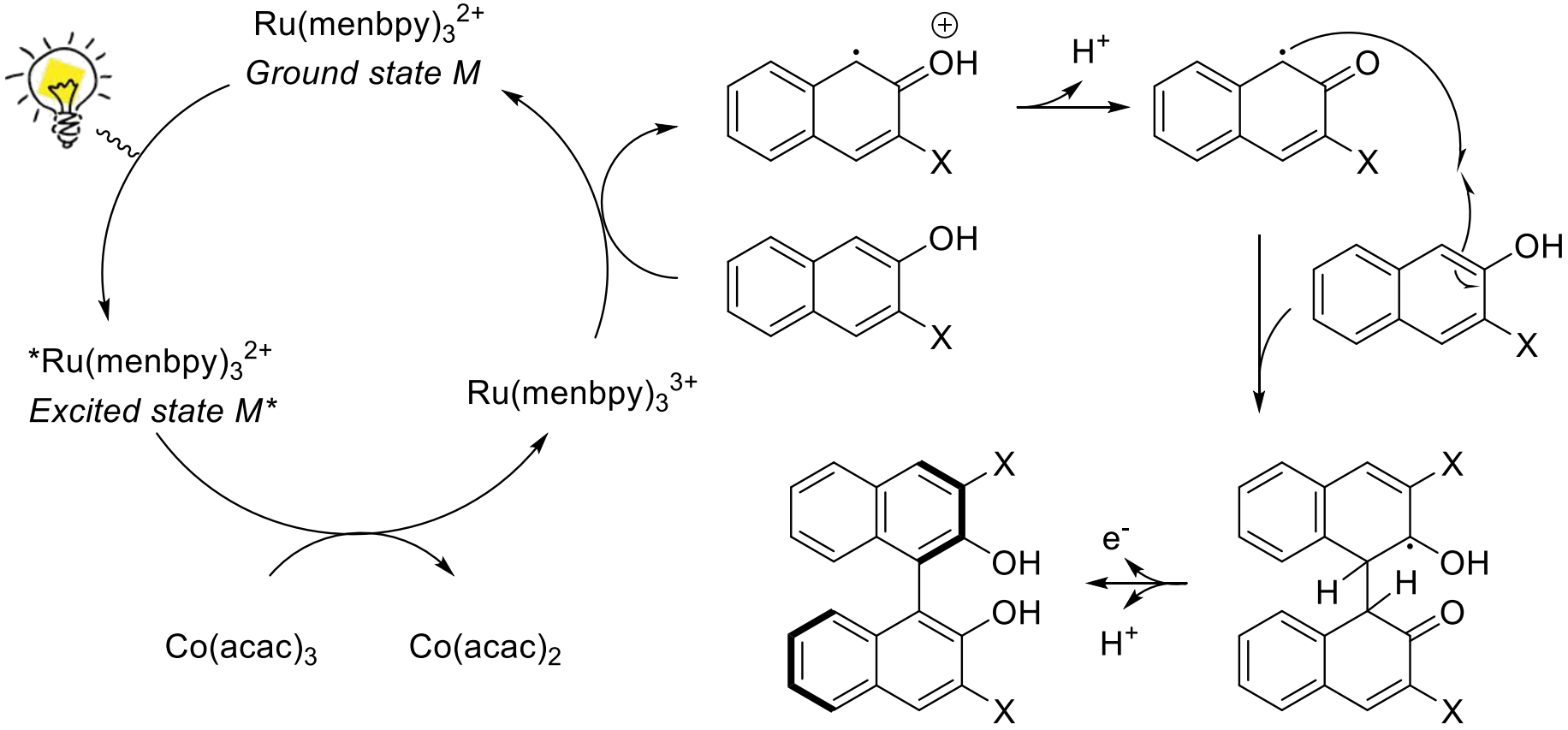


T. Hamada, H. Ishida, S. Usui, Y. Watanabe, K. Tsumura, K. Ohkubo, , *J. Chem. Soc., Chem. Commun.*, **1993**, 909

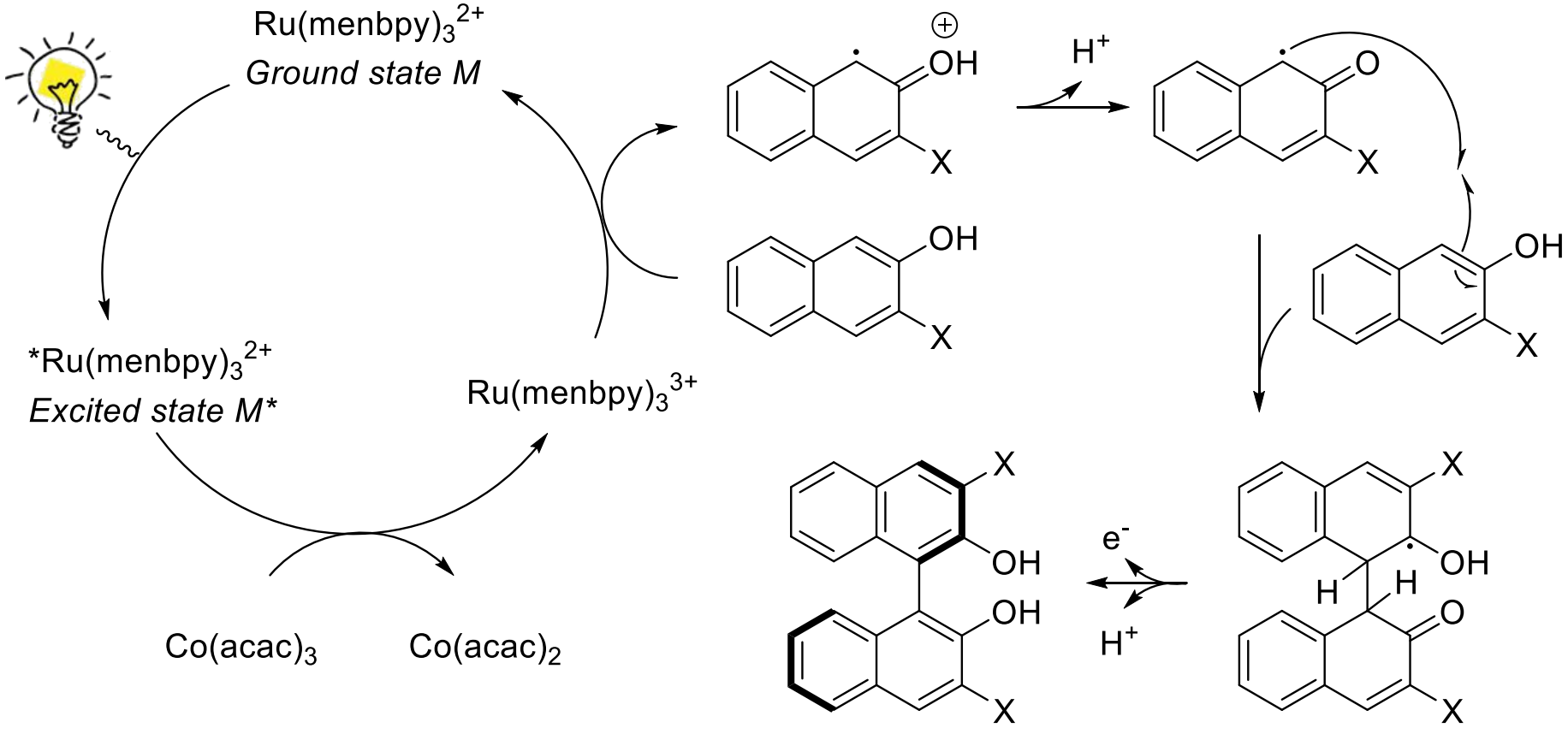
III) Enantioselective catalysis



III) Enantioselective catalysis



III) Enantioselective catalysis

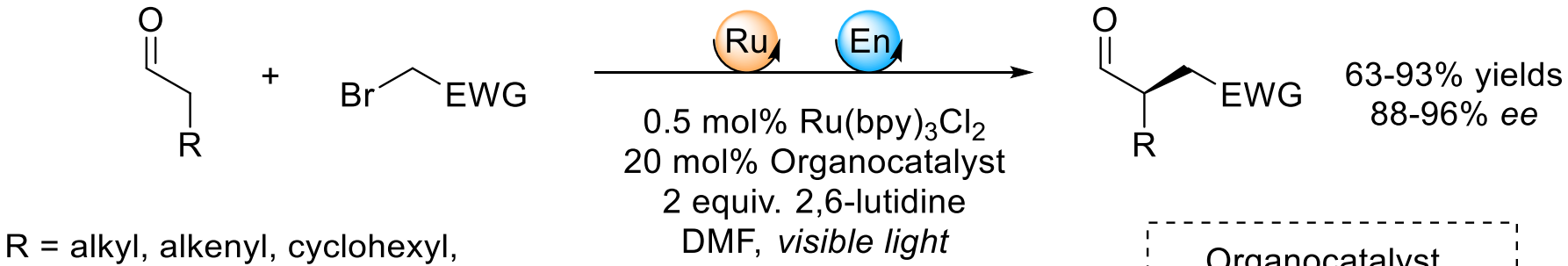


III) Enantioselective catalysis

- Low enantioselectivities reflect:
  - Catalyst:
    - Only generates reactive radical species
    - Catalyst does not serve for bond-formation
    - Not present in the transition-state
    - No effect on the stereochemical outcome
- Low enantioselectivities highlight:
  - Enantioselectivity challenge

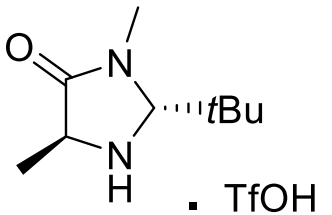
III) Enantioselective catalysis

- Enantioselective α-alkylation of aldehydes by visible-light
  - In 2008, first enantioselective α-alkylation of aldehydes by Nicewicz and MacMillan.
  - Dual catalysis: photoredox catalysis & enamine organocatalysis



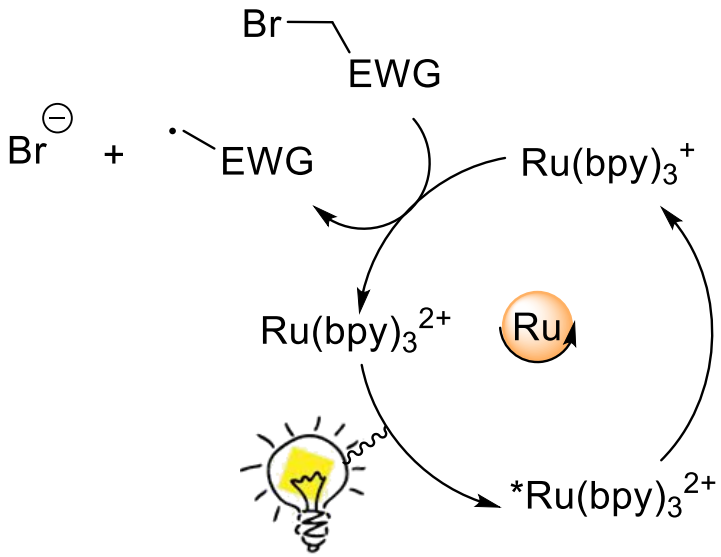
R = alkyl, alkenyl, cyclohexyl,

Organocatalyst



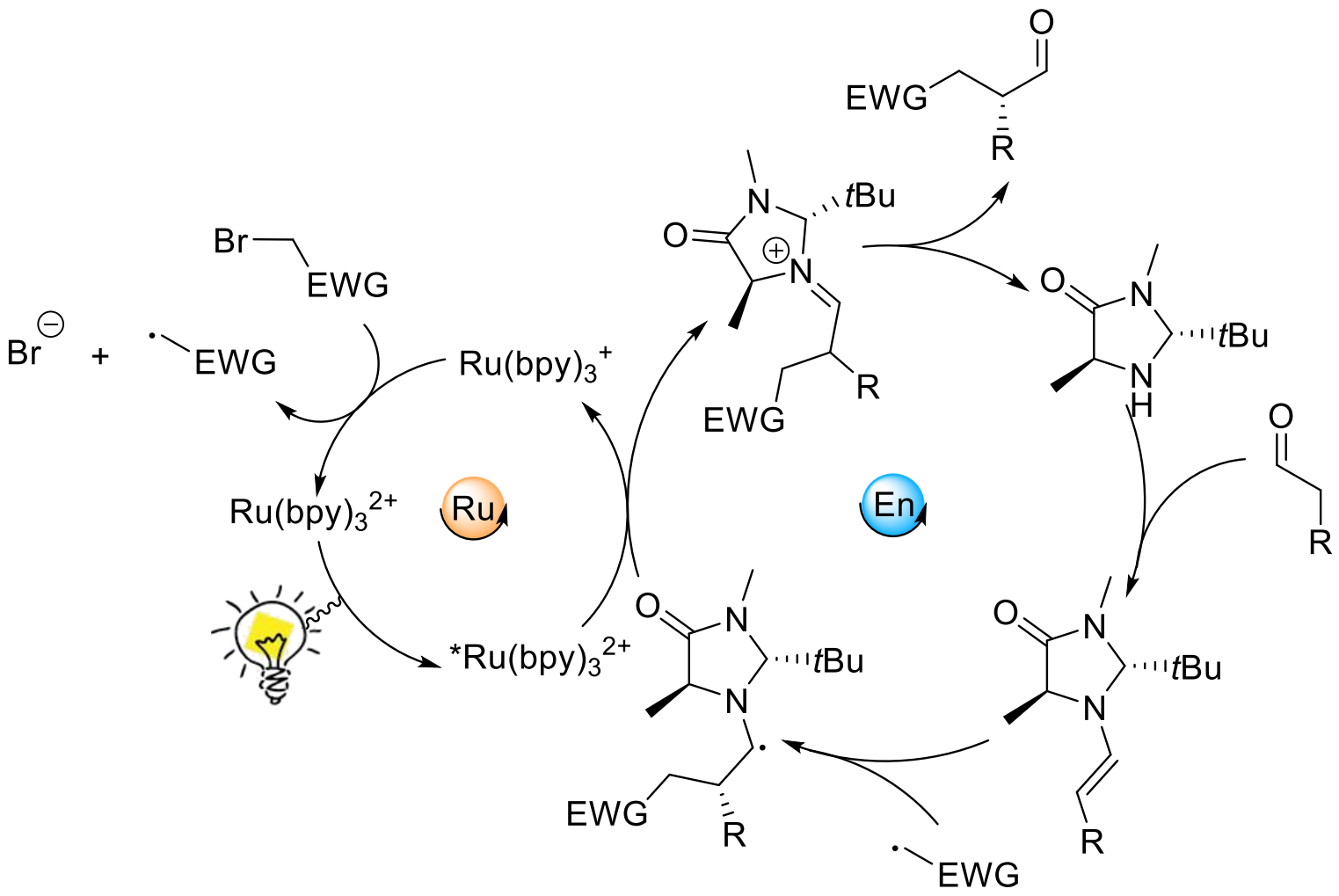
D. Nicewicz, D. W. C. MacMillan, *Science*, **2008**, 77

III) Enantioselective catalysis



D. Nicewicz, D. W. C. MacMillan, *Science*, **2008**, 77

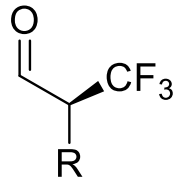
III) Enantioselective catalysis



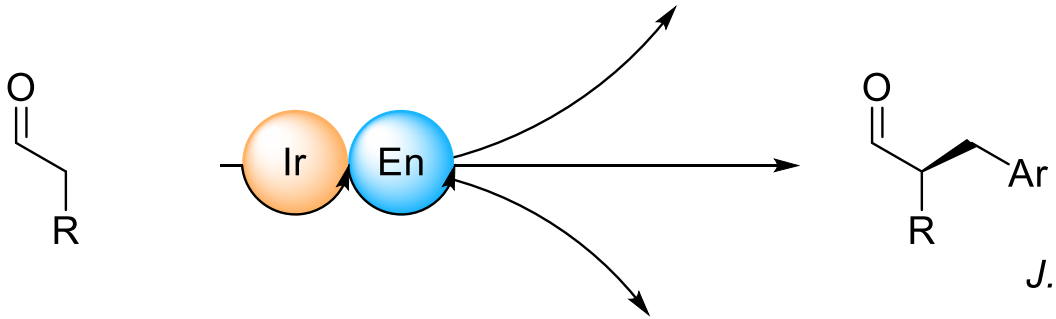
D. Nicewicz, D. W. C. MacMillan, *Science*, **2008**, 77

III) Enantioselective catalysis

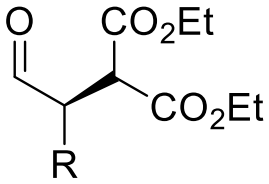
- Enantioselective α-functionalization of aldehydes



J. Am. Chem. Soc., **2009**, 10875



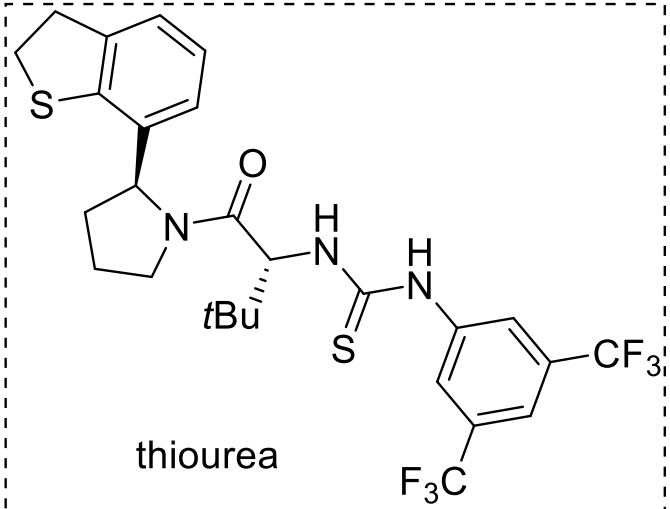
J. Am. Chem. Soc., **2010**, 13600



Angew. Chem. Int. Ed., **2011**, 951

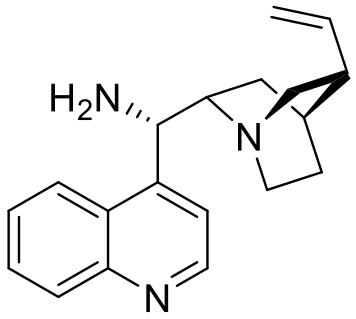
III) Enantioselective catalysis

- Organocatalyst used in combinations with photocatalysts

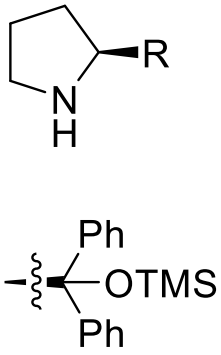


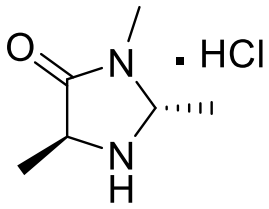
thiourea

cinchona derivates

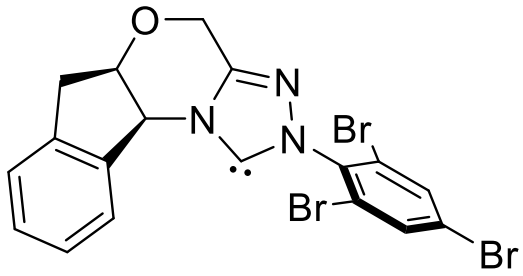


proline derivates

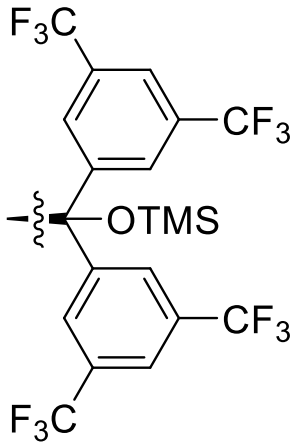




MacMillan's imidazolidinone

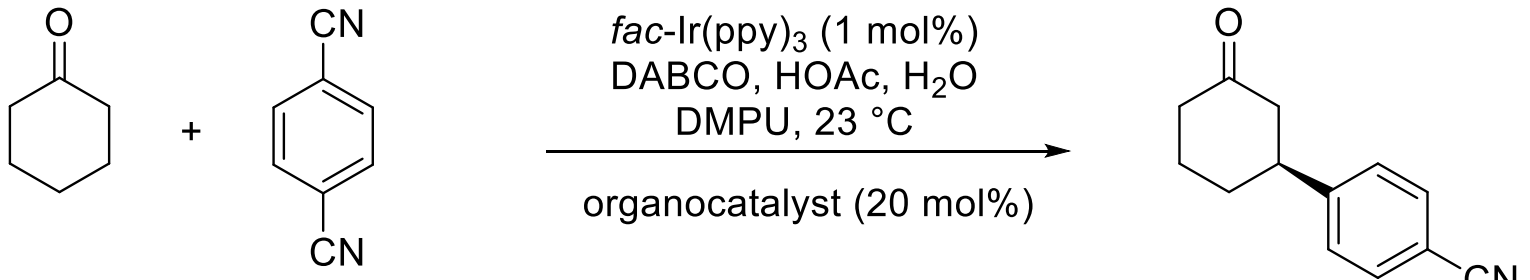


NHC

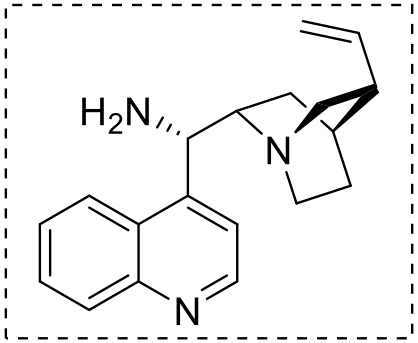


III) Enantioselective catalysis

- Enantioselective functionalization of ketones



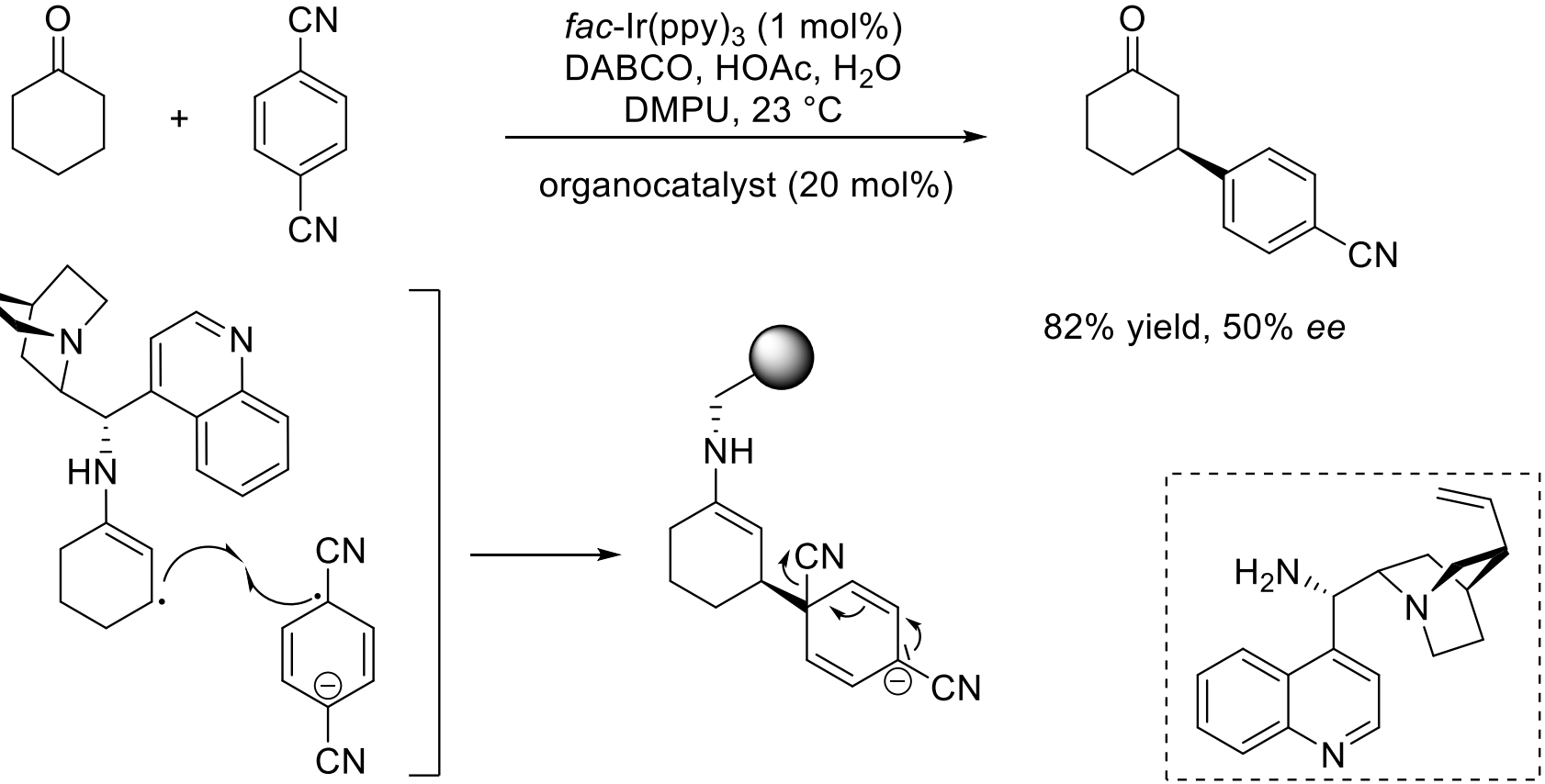
82% yield, 50% *ee*



M. T. Pirnot, D. A. Rankic, D. B. C. Martin, D. W. C. MacMillan, *Science*, **2013**, 1593

III) Enantioselective catalysis

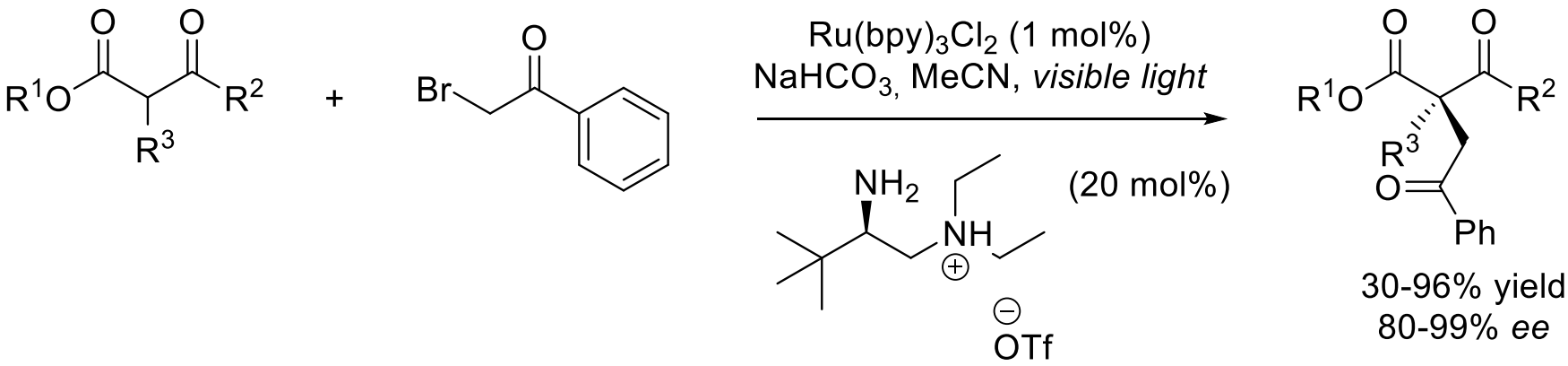
- Enantioselective functionalization of ketones



M. T. Pirnot, D. A. Rankic, D. B. C. Martin, D. W. C. MacMillan, *Science*, **2013**, 1593

III) Enantioselective catalysis

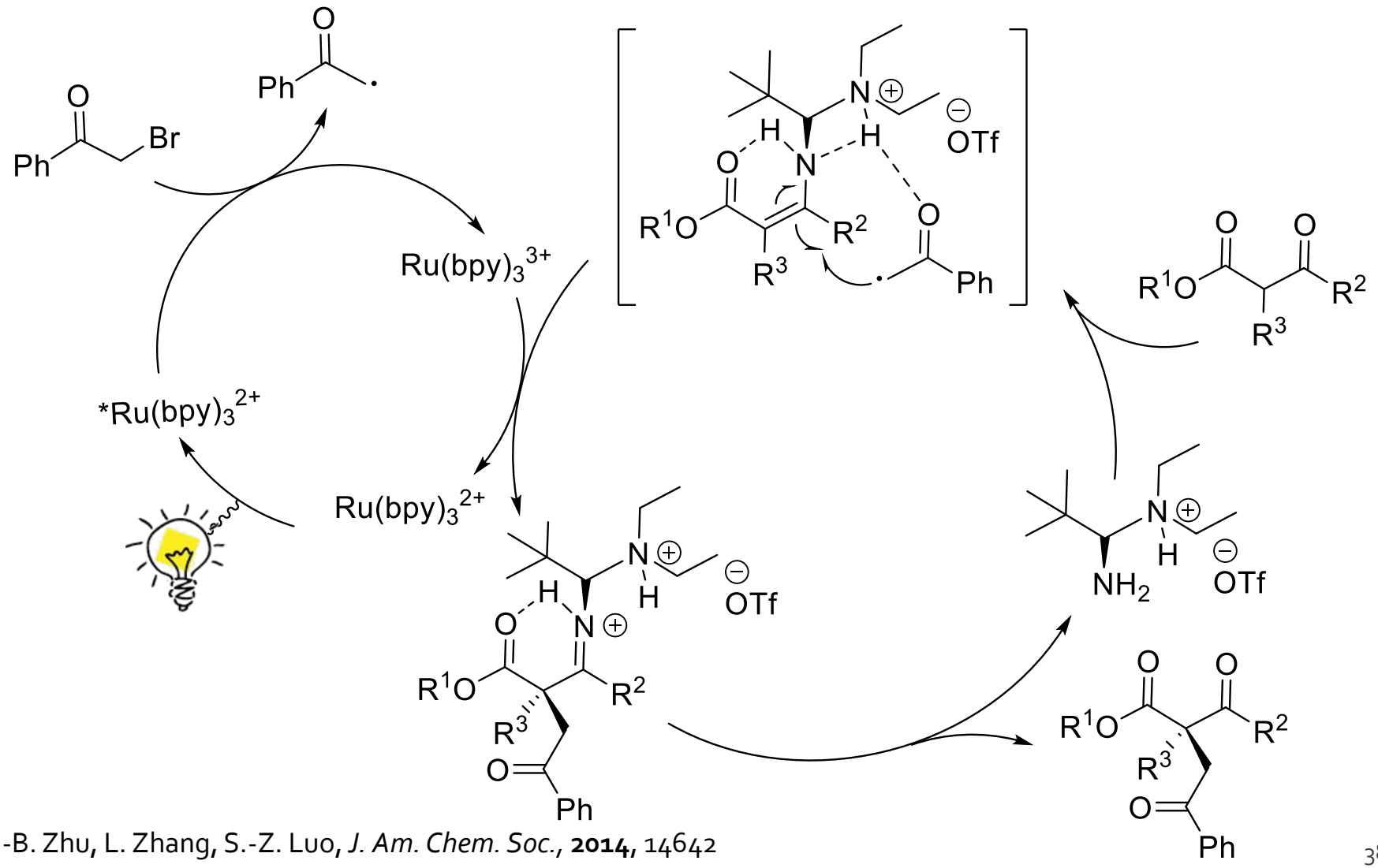
- Enantioselective functionalization of ketoesters



- Possibility of functionalization of β-ketoamides

Y.-B. Zhu, L. Zhang, S.-Z. Luo, *J. Am. Chem. Soc.*, **2014**, 14642

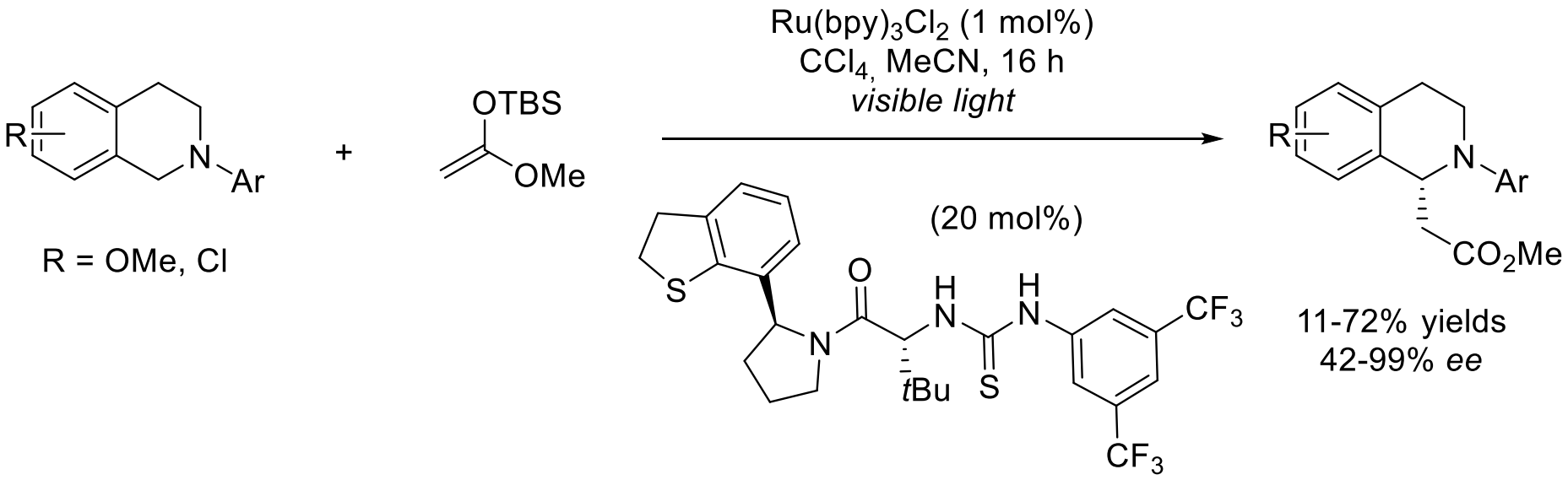
III) Enantioselective catalysis



Y.-B. Zhu, L. Zhang, S.-Z. Luo, *J. Am. Chem. Soc.*, **2014**, 14642

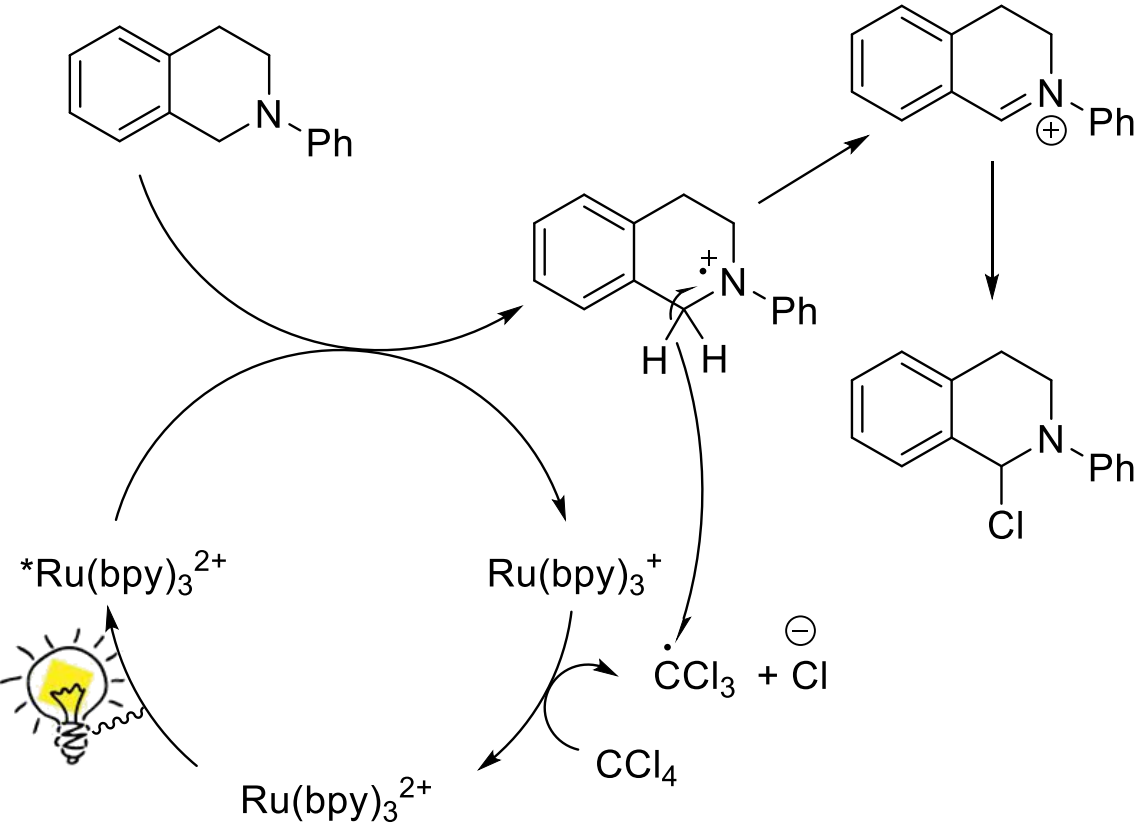
III) Enantioselective catalysis

- Enantioselective functionalization of amines
  - Stephenson, using Irridium catalyst (*JACS*, **2010**, 1464)
  - Combination of thiourea catalyst with photocatalyst



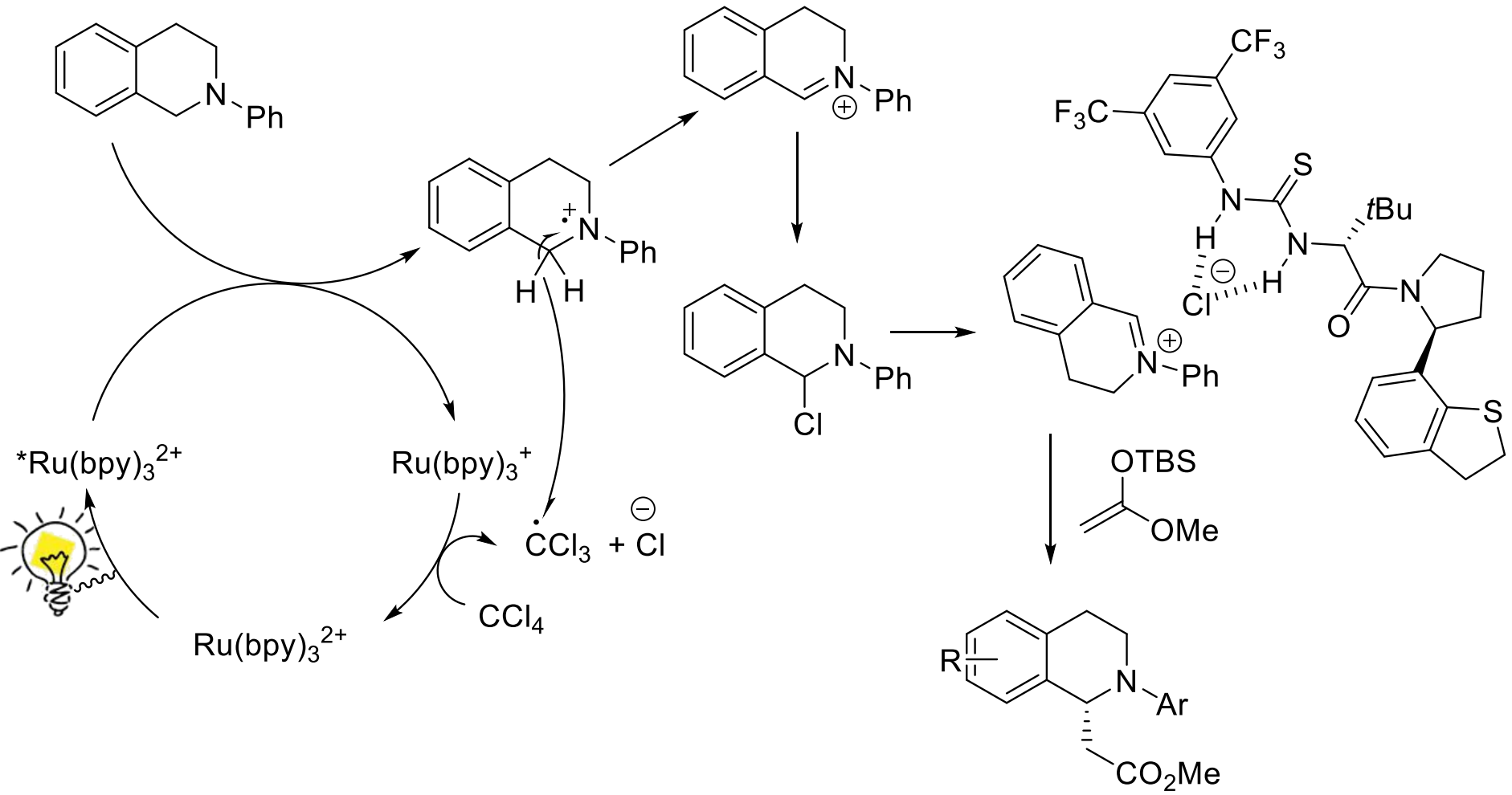
G. Bergonzini, C. S. Schindler, C.-J. Wallentin, E. N. Jacobsen, C. R. J. Stephenson, *Chem. Sci.*, **2014**, 112

III) Enantioselective catalysis



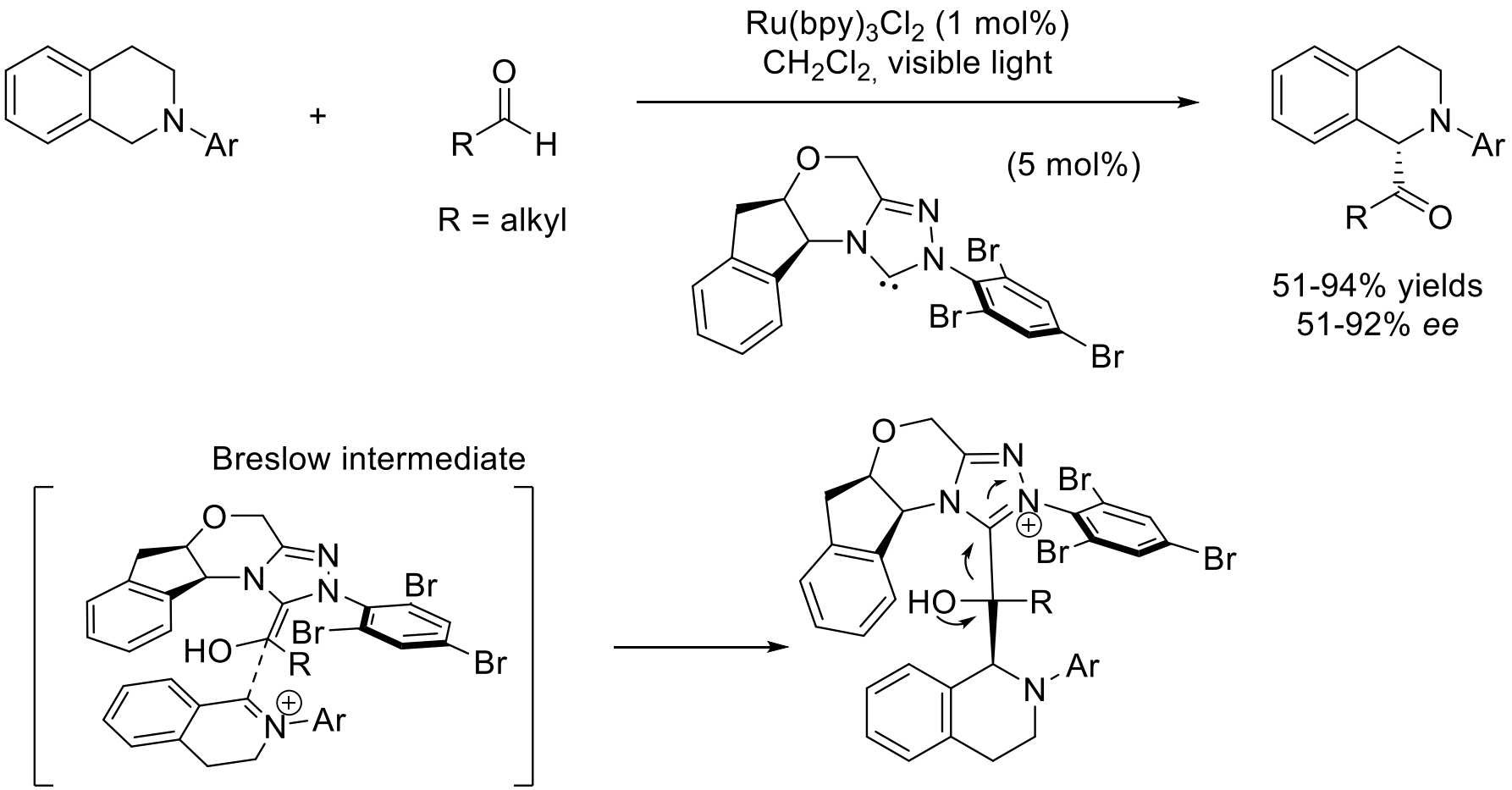
G. Bergonzini, C. S. Schindler, C.-J. Wallentin, E. N. Jacobsen, C. R. J. Stephenson, *Chem. Sci.*, **2014**, 112

III) Enantioselective catalysis



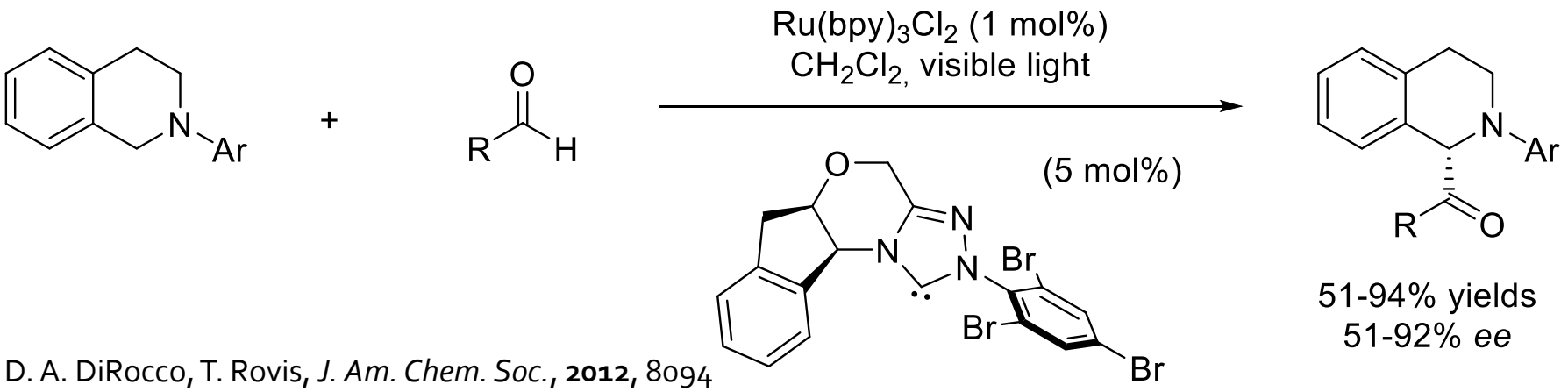
G. Bergonzini, C. S. Schindler, C.-J. Wallentin, E. N. Jacobsen, C. R. J. Stephenson, *Chem. Sci.*, **2014**, 112

III) Enantioselective catalysis

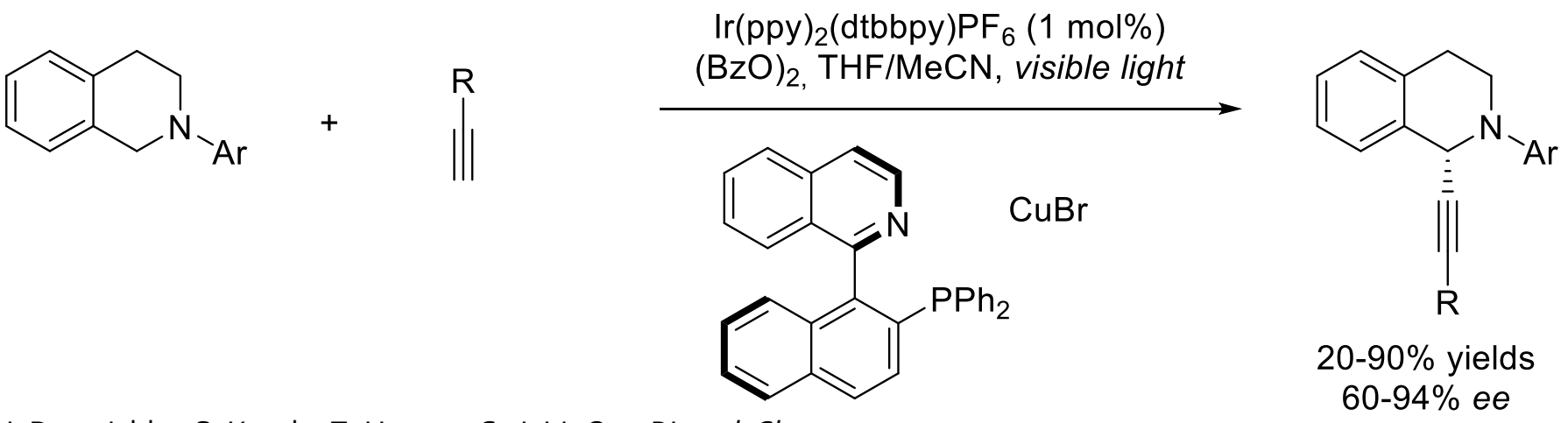


D. A. DiRocco, T. Rovis, *J. Am. Chem. Soc.*, **2012**, 8094

III) Enantioselective catalysis



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



I. Perepichka, S. Kundu, Z. Hearne, C.-J. Li, *Org. Biomol. Chem.*, **2015**, 447

III) Enantioselective catalysis

I. Introduction

II. Reactivity

1) *Reductions*

2) *Oxidations*

III. Enantioselective catalysis

IV. Conclusion

IV) Conclusion

- Photocatalysis avoid the use of stoichiometric oxidant or reductant

- Extremely mild conditions were used

- Two properties of the photocatalyst enabling reductions & oxidations

- Access in one-pot to complexes & functionalized molecules

- Variety of substrate

- Enantioselective processes well developed

- Dual catalysis: photocatalyst and metal (Cu, Ni, ..)

IV) Conclusion

Thank you for your attention

Any questions ?