Group Topic

Photoredox Catalysis from Tomislav Rovis Group

Junchun Zhang

2023.2.24

Contents of the presentation

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- Phtotoredox Catalysis without Metal-Catalysis
- Phtotoredox Catalysis with Metal-Catalysis
- Os Phtotoredox Catalysis

Group Introduction

Tomislav Rovis

Samuel Latham Mitchill Professor

简历:

1986-1990年 多伦多大学（University of Toronto）获得学士学位

1993-1998年 多伦多（University of Toronto）大学获得博士学位（Prof. Mark Lautens）

1998-2000年 哈佛大学（Harvard University）NSERC博士后研究员（Prof. David A. Evans）

2000-2005年 科罗拉多州立大学（,Colorado State University）化学系助理教授

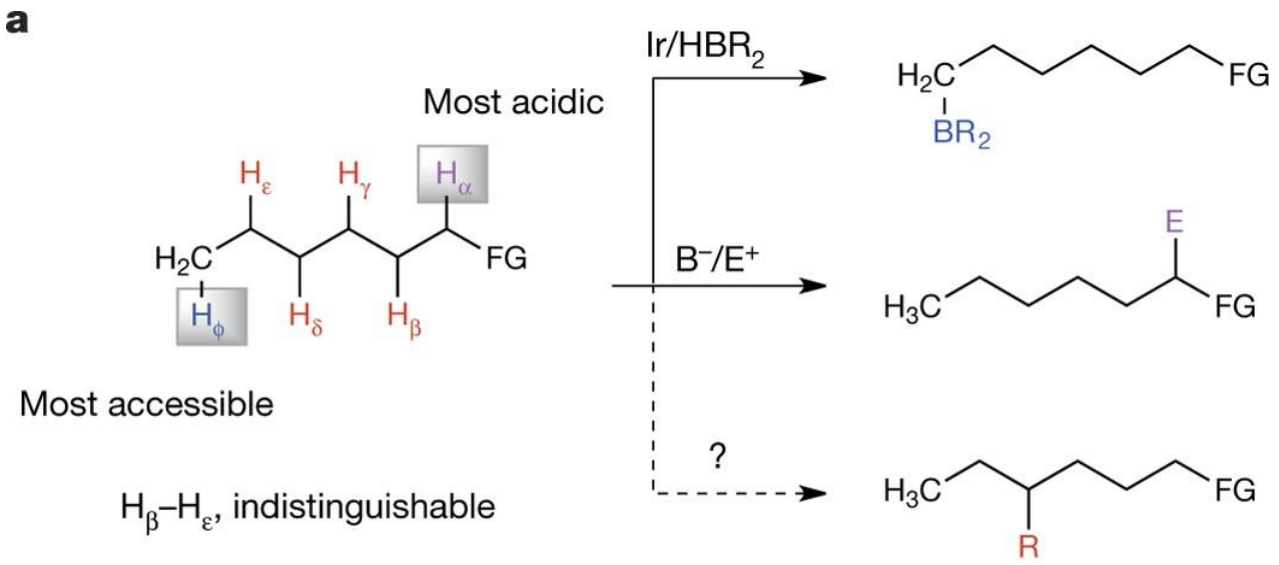
2005-2008年 科罗拉多州立大学（ Colorado State University）副教授

2008-2016年 科罗拉多州立大学（,Colorado State University）教授

2016- 哥伦比亚大学（Columbia University）化学系教授

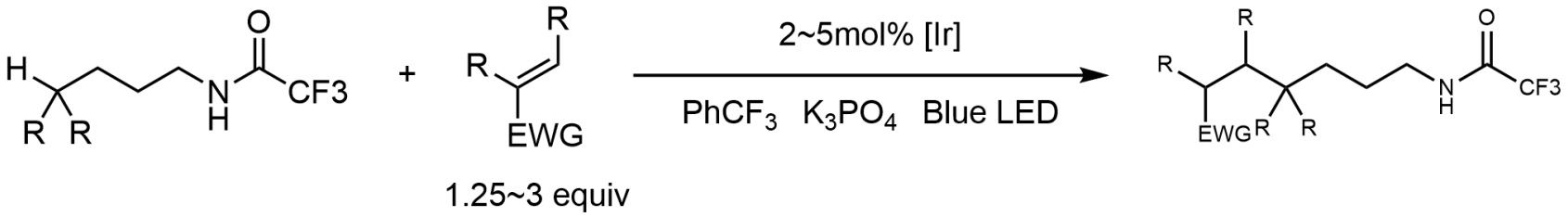
Phtotoredox Catalysis without Metal-Catalysis

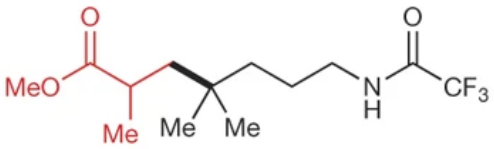
Reaction 1 Background



Chu, John C. K.; Rovis, Tomislav, *Amide-directed photoredox-catalysed C–C bond formation at unactivated sp3 C–H bonds. Nature* ***539****, 272–275 (2016)*

Reaction 1





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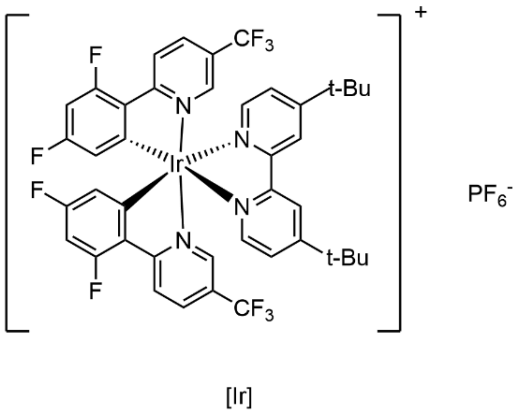

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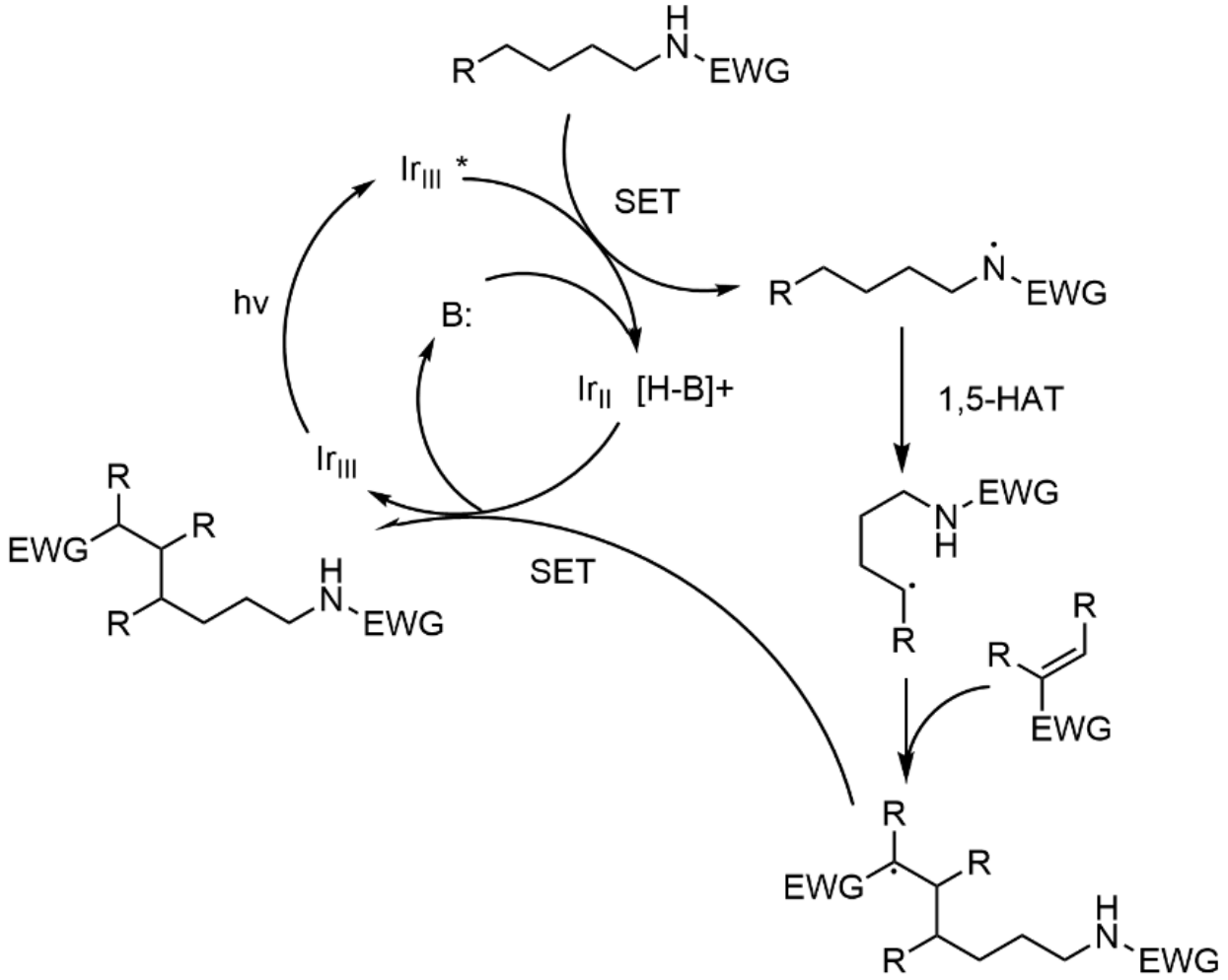
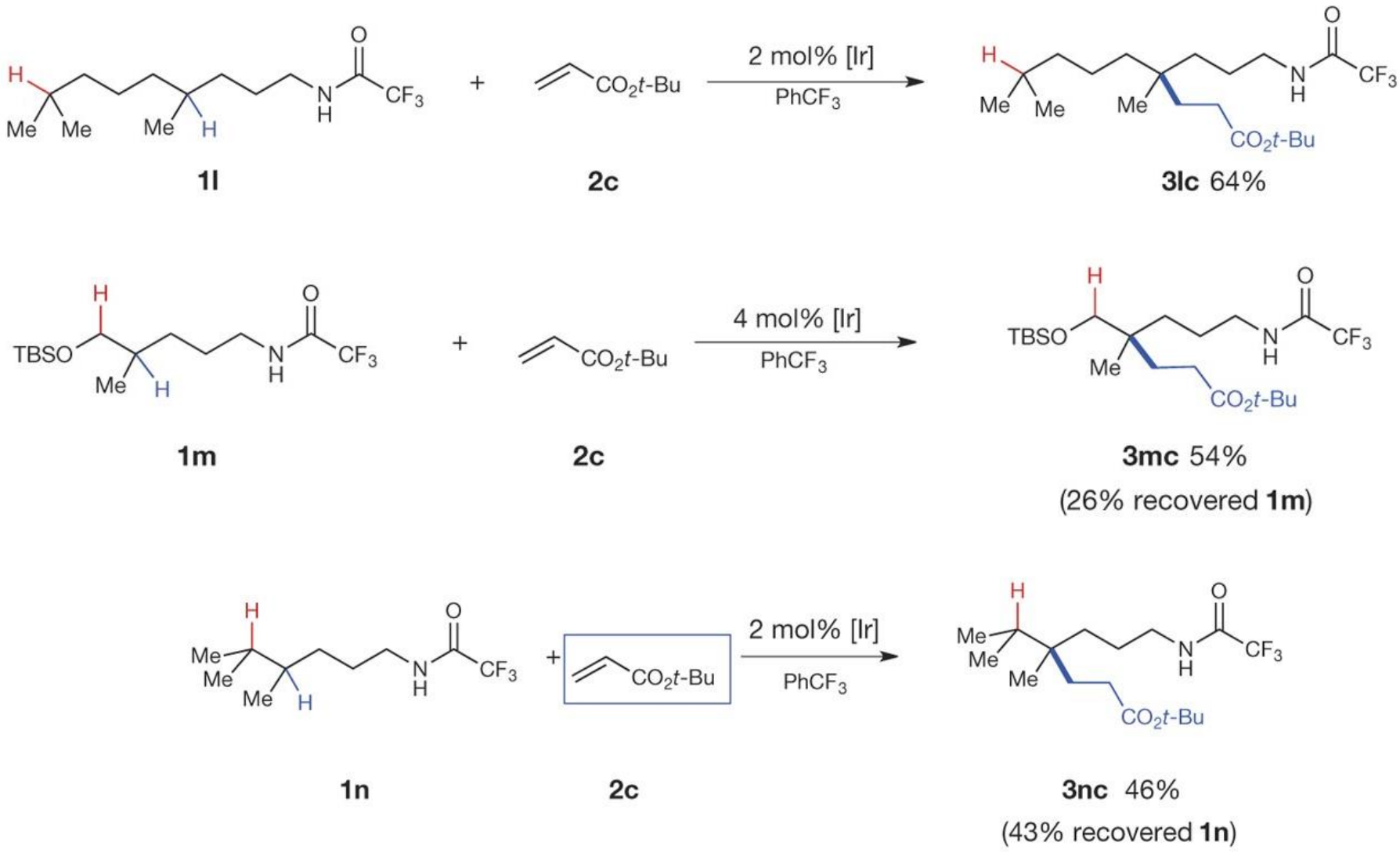
Chu, John C. K.; Rovis, Tomislav, *Amide-directed photoredox-catalysed C–C bond formation at unactivated sp3 C–H bonds. Nature* ***539****, 272–275 (2016)*

Reaction 1 Mechanism



Chu, John C. K.; Rovis, Tomislav, *Amide-directed photoredox-catalysed C–C bond formation at unactivated sp3 C–H bonds. Nature* ***539****, 272–275 (2016)*

Reaction1 Site-Selective



Chu, John C. K.; Rovis, Tomislav, *Amide-directed photoredox-catalysed C–C bond formation at unactivated sp3 C–H bonds. Nature* ***539****, 272–275 (2016)*

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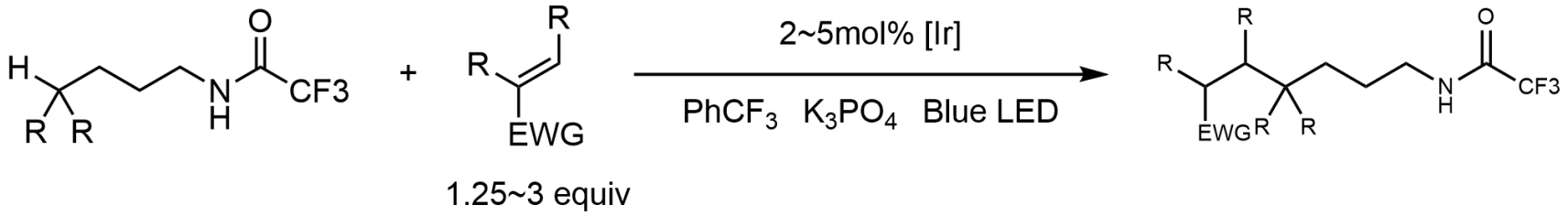
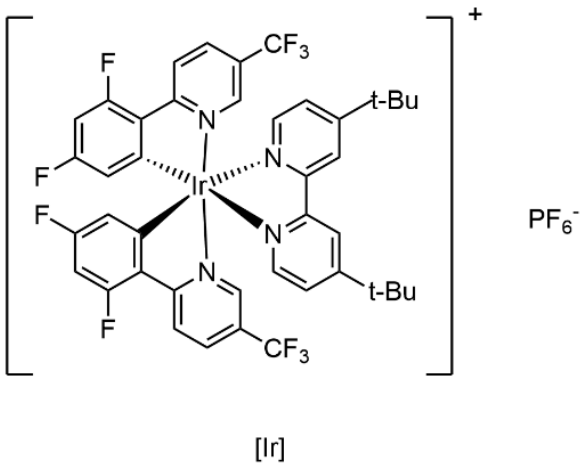
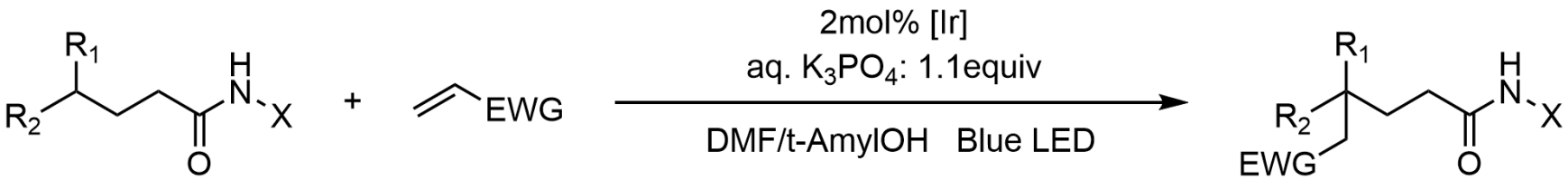
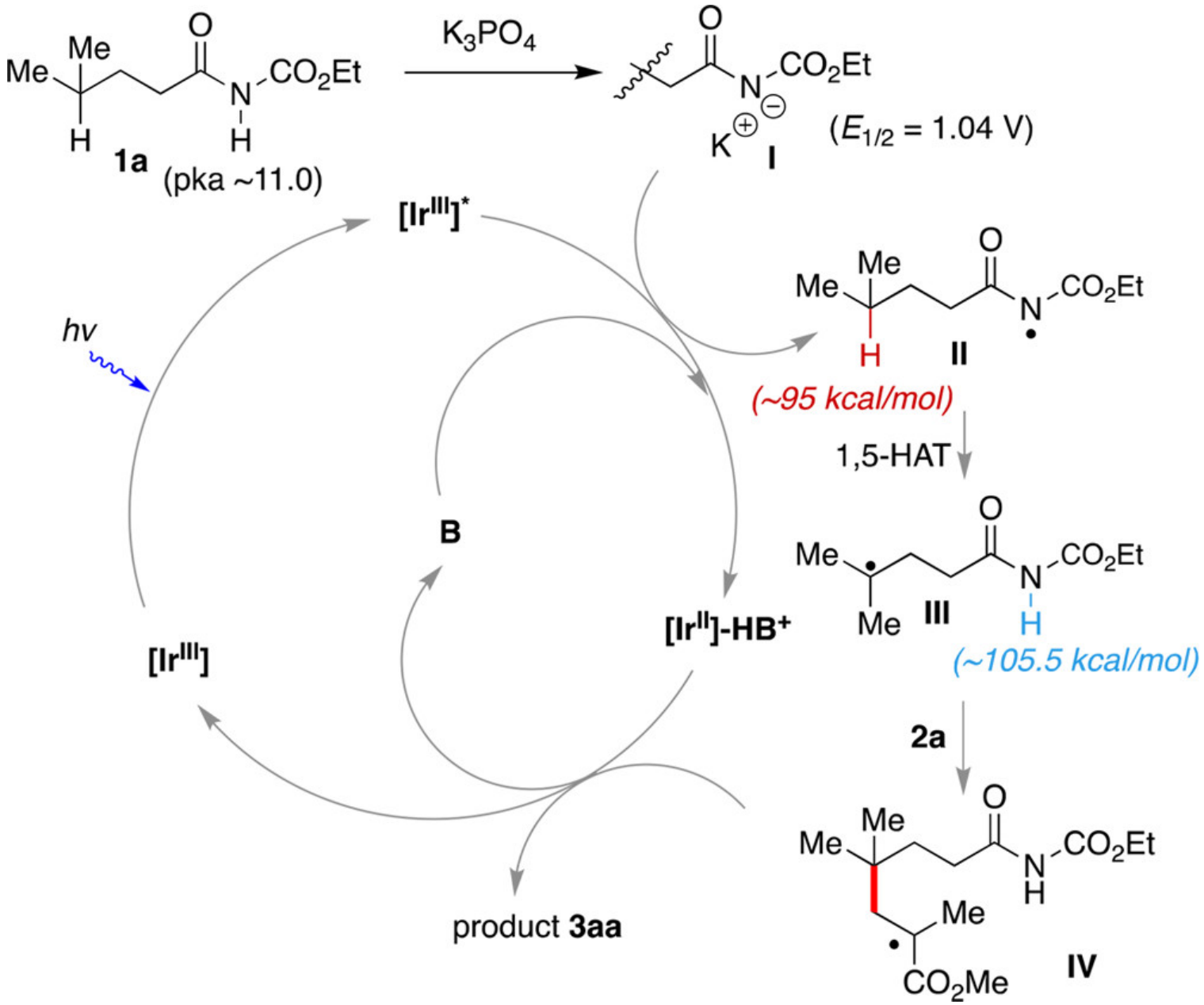






Dian-Feng Chen, John C. K. Chu, and Tomislav Rovis, *Directed γ-C(sp3)–H Alkylation of Carboxylic Acid Derivatives through Visible Light Photoredox Catalysis. J. Am. Chem. Soc. 2017, 139, 42, 14897–14900*

Reaction 2 Mechanism



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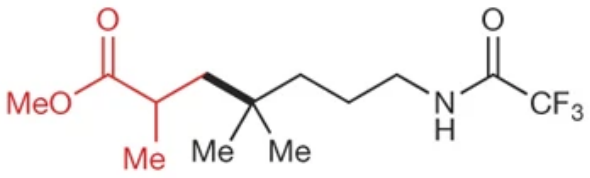
Reaction 1 Scope



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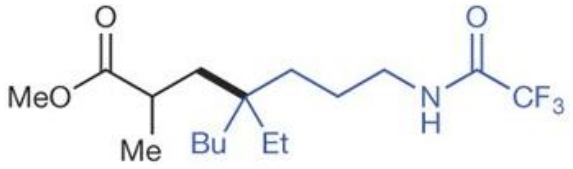
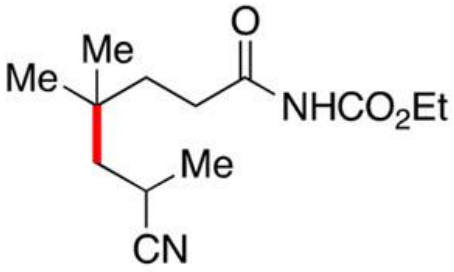


3ca 80%, 1:1 d.r.

Chu, John C. K.; Rovis, Tomislav, *Amide-directed photoredox-catalysed C–C bond formation at unactivated sp3 C–H bonds. Nature* ***539****, 272–275 (2016)*

Reaction 2 Scope



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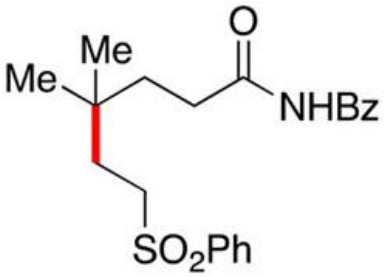
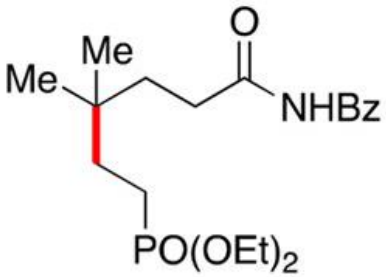


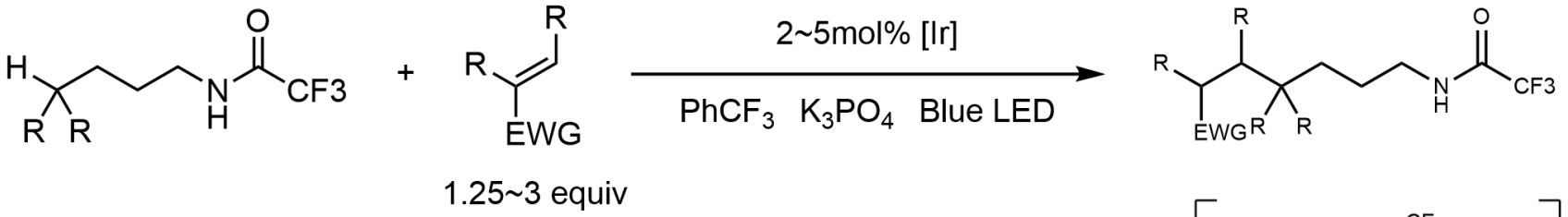
3bk: 55%



3bl: 78%

Dian-Feng Chen, John C. K. Chu, and Tomislav Rovis, *Directed γ-C(sp3)–H Alkylation of Carboxylic Acid Derivatives through Visible Light Photoredox Catalysis. J. Am. Chem. Soc. 2017, 139, 42, 14897–14900*

Reaction 3



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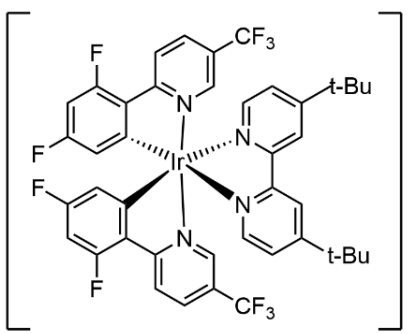
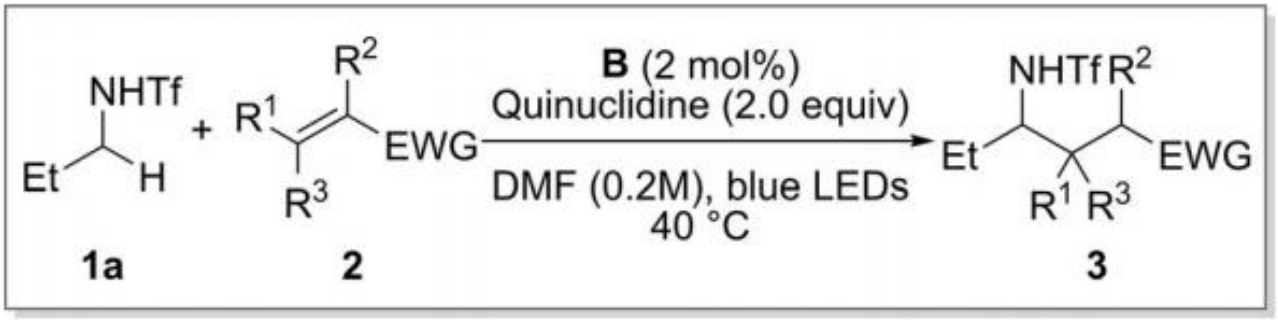
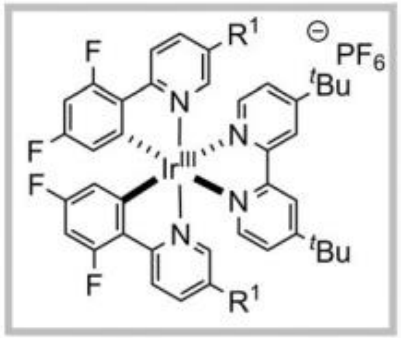




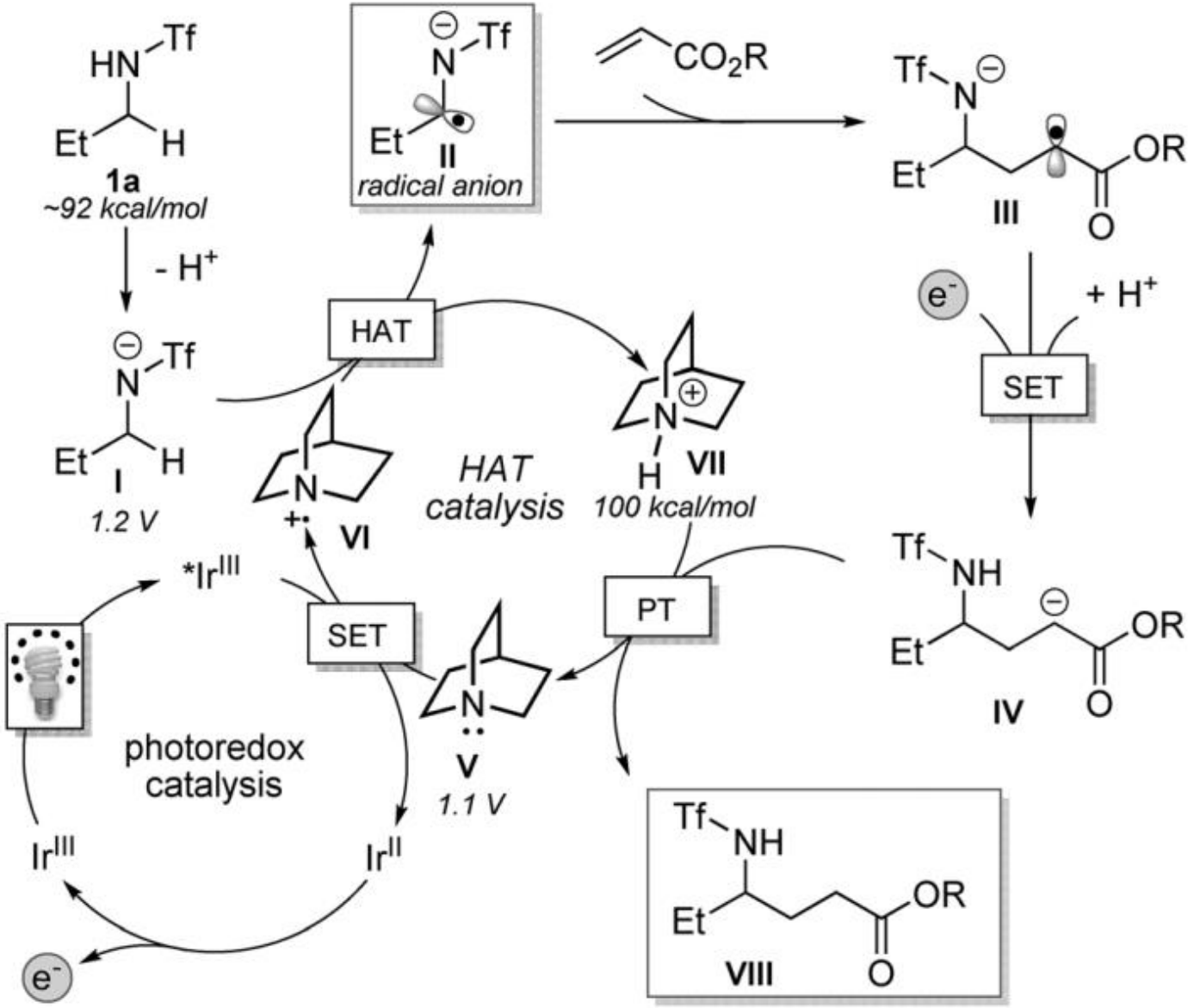
Ashley, Melissa A.; Yamauchi, Chiaki; Chu, John C. K.; Otsuka, Shinya; Yorimitsu, Hideki ; Rovis, Tomislav , *Photoredox-Catalyzed Site-Selective α-C(sp3)-H Alkylation of Primary Amine Derivatives. Angew. Chem. Int. Ed.2019, 58, 4002-4006.*



A: Ir(dF-CF_3) $R^1 = CF_3$

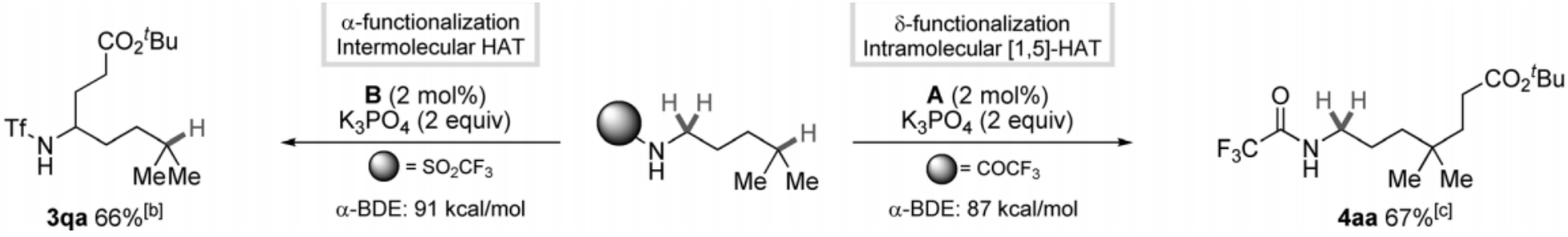
B: Ir(dF-Me) $R^1 = Me$

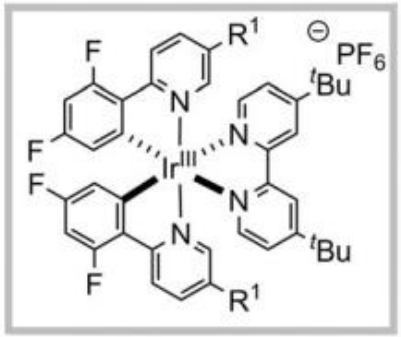
Reaction 3 Mechanism



Ashley, Melissa A.; Yamauchi, Chiaki; Chu, John C. K.; Otsuka, Shinya; Yorimitsu, Hideki ; Rovis, Tomislav , *Photoredox-Catalyzed Site-Selective α-C(sp3)-H Alkylation of Primary Amine Derivatives. Angew. Chem. Int. Ed.2019, 58, 4002-4006.*

Reaction 3 Application





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B: Ir(dF-Me) R^1 = Me

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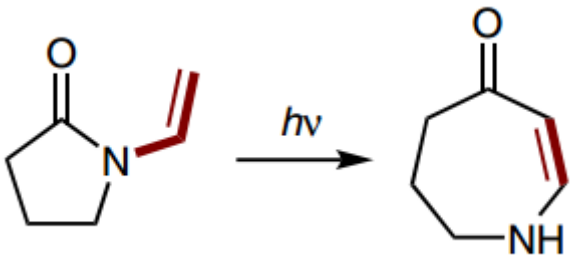
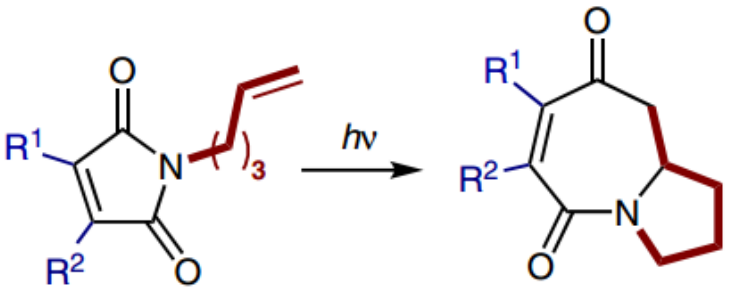
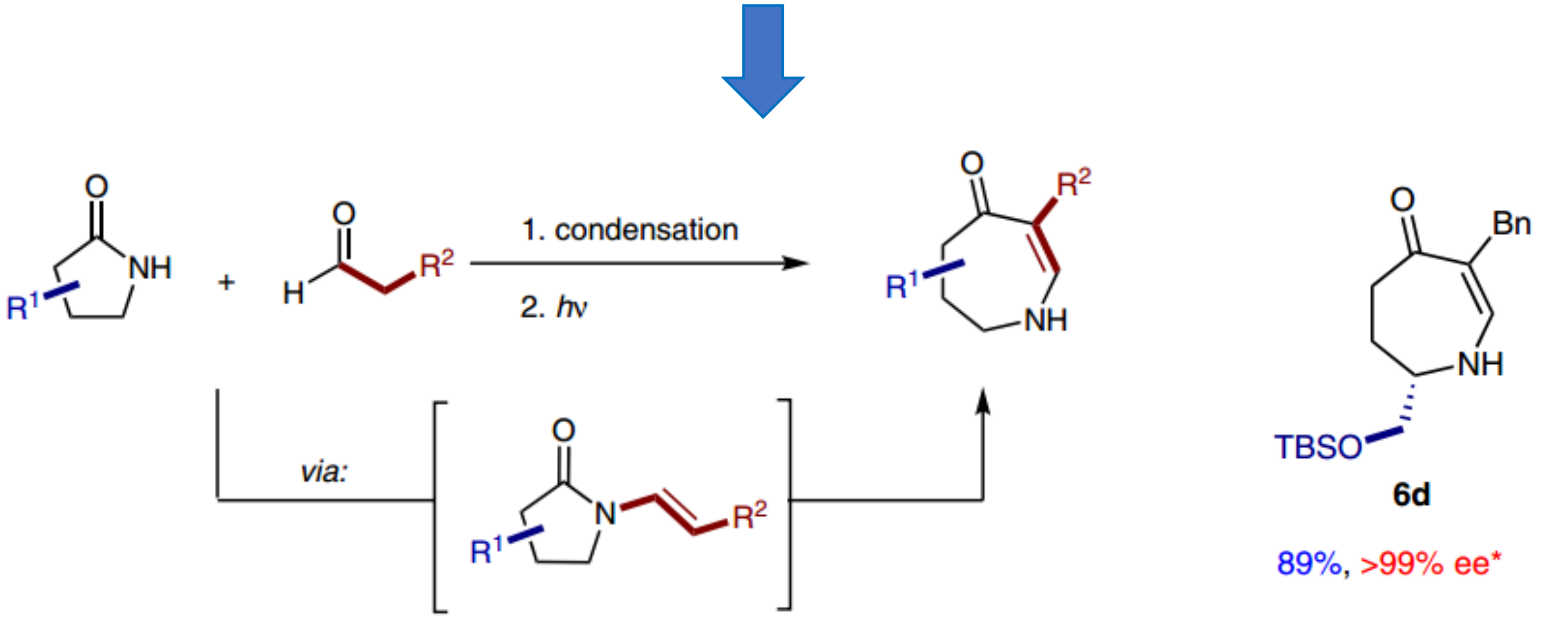
Reaction 4



Buhr, G. *DE 2013761, 1970.*

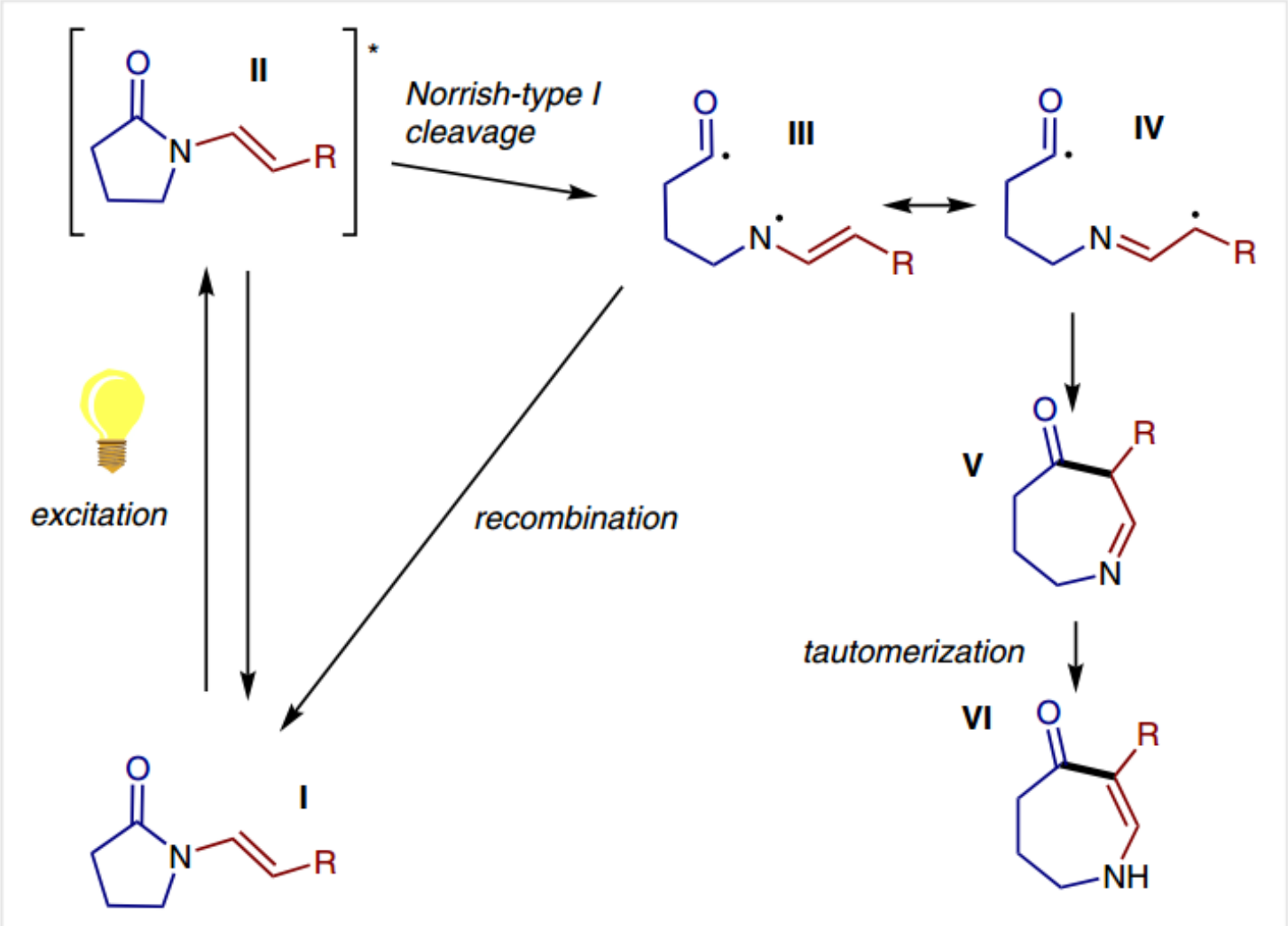


Booker-Milburn, K. I.; Anson, C. E.; Clissold, C.; Costin, N. J.;Dainty, R. F.; Murray, M.; Patel, D.;Sharpe, A. Eur. J. *Org. Chem.2001, 1473.*



Thullen, Scott M.; Rubush, David M.; Rovis, Tomislav , *A Photochemical Two-Step Formal [5+2] Cycloaddition: A Condensation-Ring-Expansion Approach to Substituted Azepanes. Synlett.* 2017; 28(20): 2755-2758

Reaction 4 Mechanism



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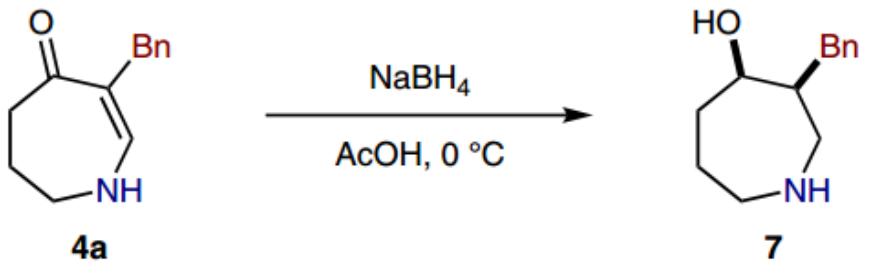
Reaction 4 Application

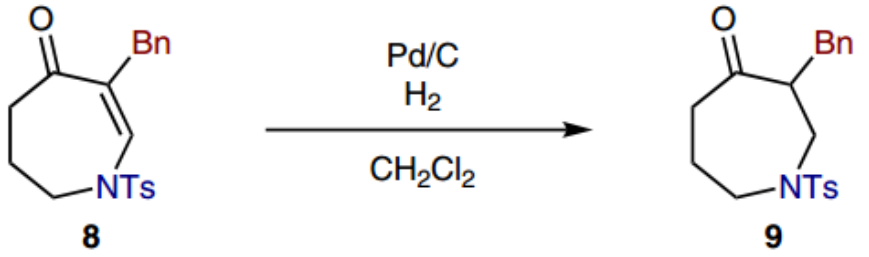
Global reduction:



4a **7**

99%
4:1 dr

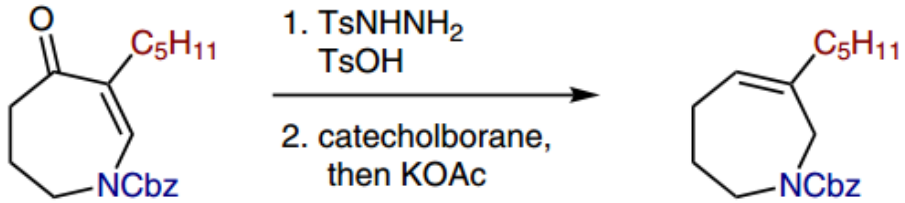
Hydrogenation:



8 **9**

99%

Wolff–Kishner:

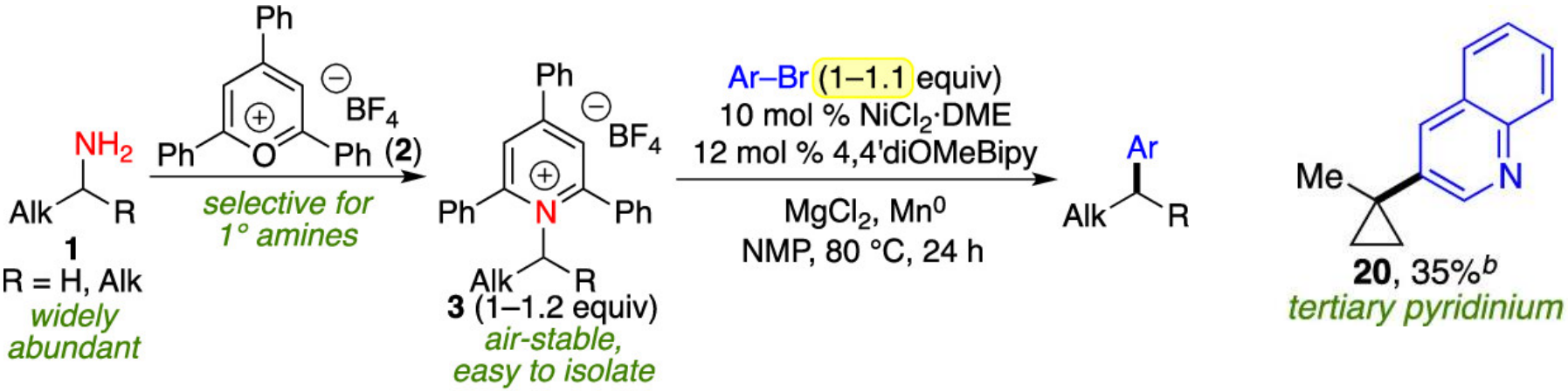


10 **11**

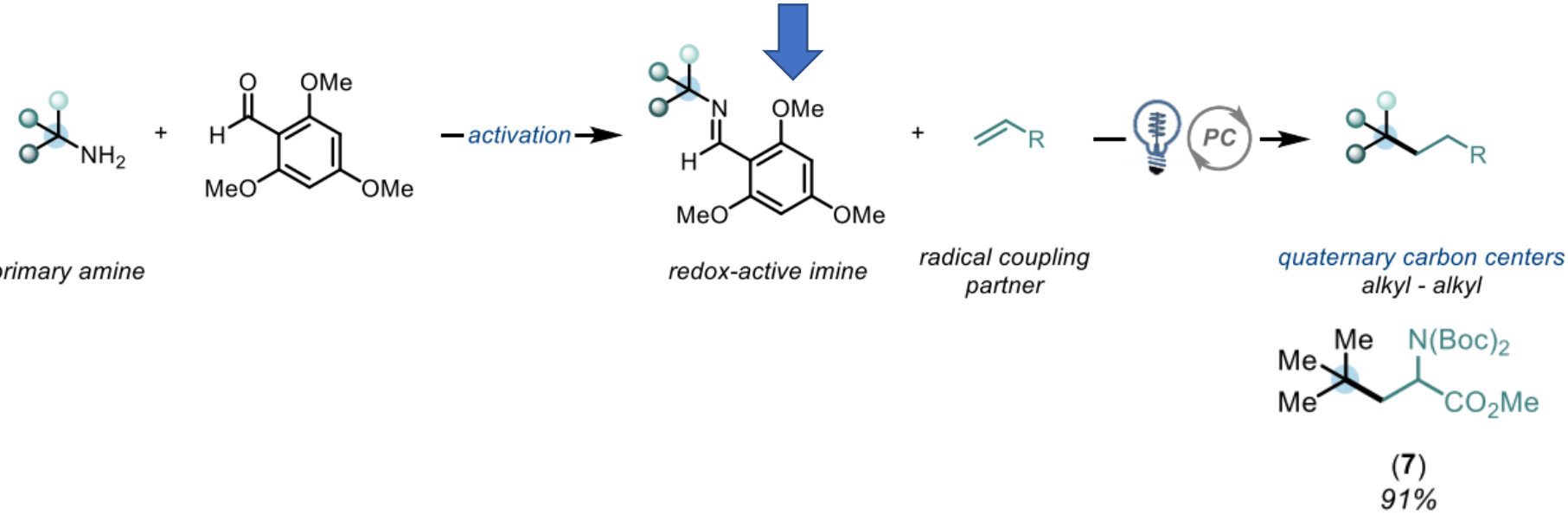
76%

Thullen, Scott M.; Rubush, David M.; Rovis, Tomislav *, A Photochemical Two-Step Formal [5+2] Cycloaddition: A Condensation-Ring-Expansion Approach to Substituted Azepanes. Synlett.* 2017; 28(20): 2755-2758

Reaction 5

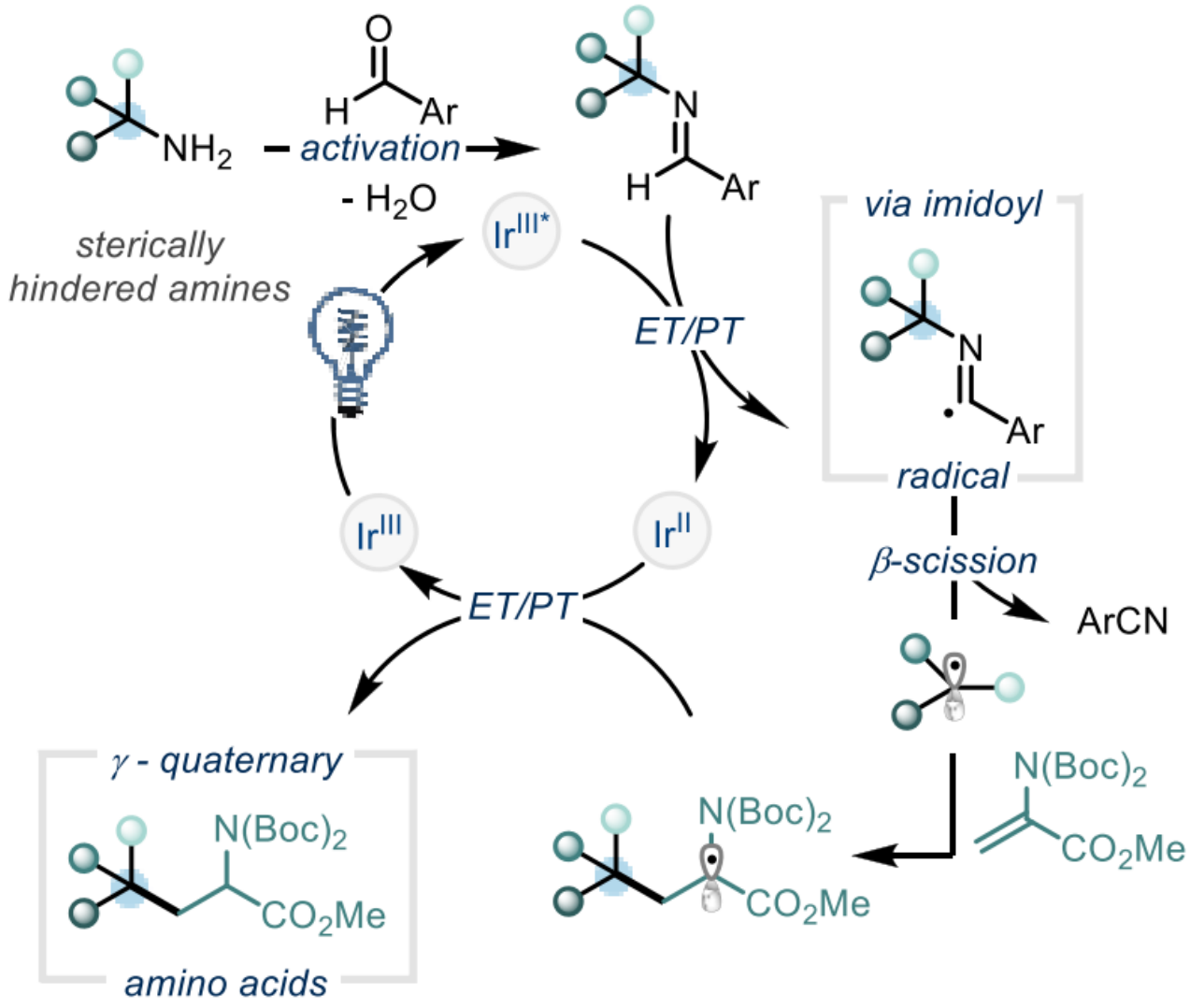


Liao, J.; Basch, C. H.; Hoerrner, M.E.; Talley, M. R.; Boscoe, B. P.; Tucker, J. W.; Garnsey, M. R.;Watson, M. P. *Deaminative Reductive Cross-Electrophile Couplings of Alkylpyridinium Salts and Aryl Bromides. Org. Lett. 2019, 21,2941−2946.*



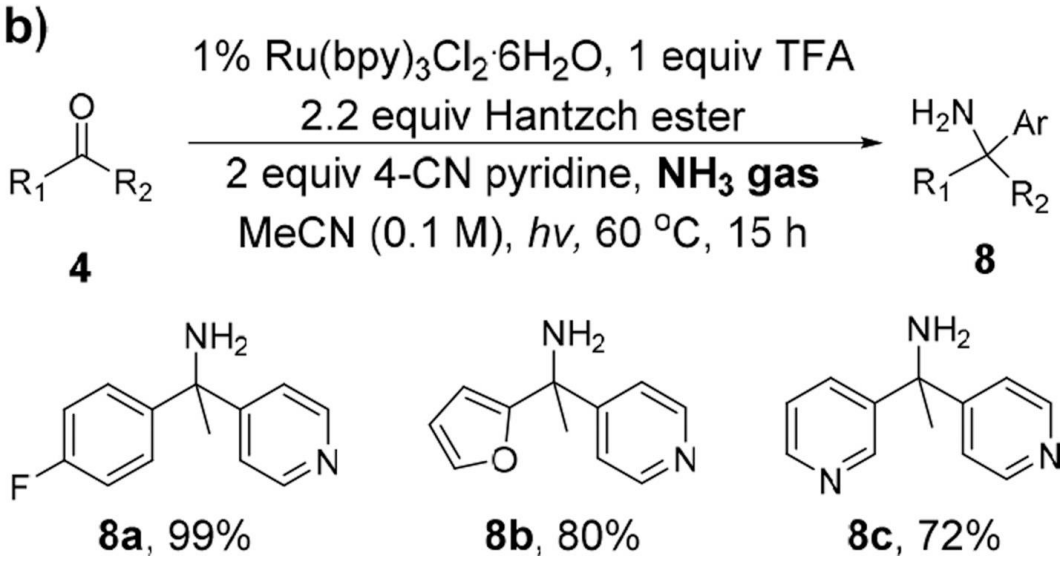
Ashley, Melissa A.; Rovis, Tomislav, *Photoredox-Catalyzed Deaminative Alkylation via C–N Bond Activation of Primary Amines. J. Am. Chem. Soc.* 2020, 142, 43, 18310−18316.

Reaction 5 Mechanism



Ashley, Melissa A.; Rovis, Tomislav, *Photoredox-Catalyzed Deaminative Alkylation via C–N Bond Activation of Primary Amines. J. Am. Chem. Soc.* 2020, 142, 43, 18310−18316.

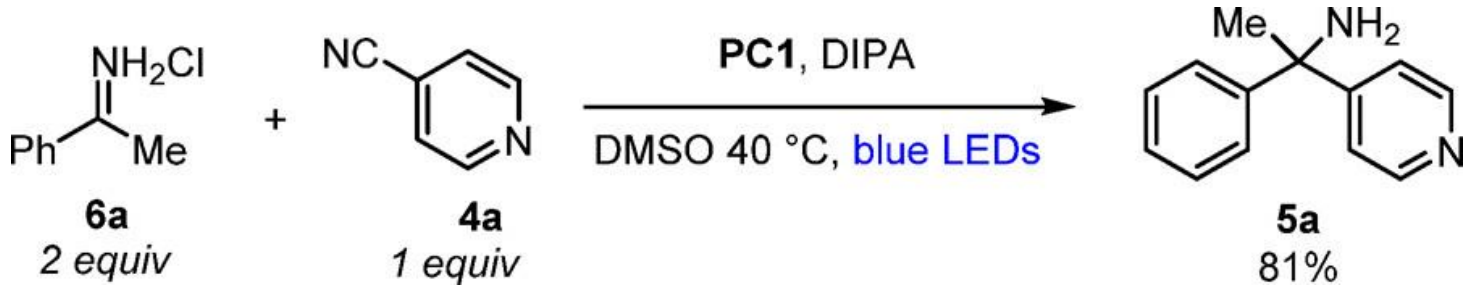
Reaction 6 Background

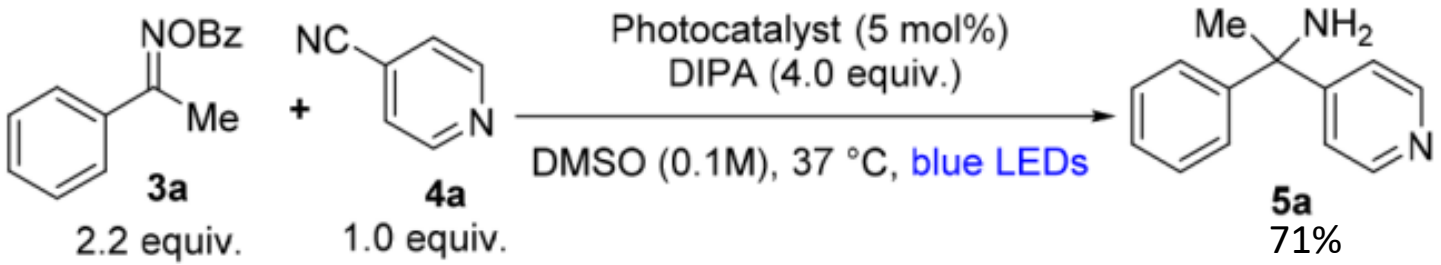


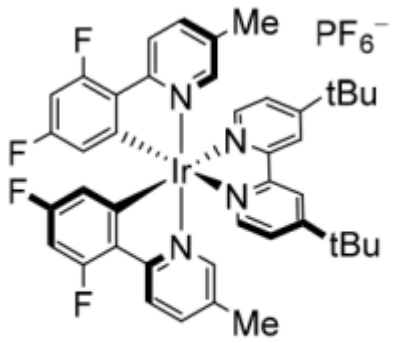
Rong, J.; Seeberger, P. H.; Gilmore, K. *Chemoselective Photoredox Synthesis of Unprotected Primary Amines Using Ammonia. Org. Lett. 2018, 20, 4081−4085.*

Nicastri, Michael C. ; Lehnherr, Dan ; Lam, Yu-hong ; DiRocco, Daniel A.; Rovis, Tomislav, *Synthesis of Sterically Hindered Primary Amines by Concurrent Tandem Photoredox Catalysis. J. Am. Chem. Soc.* 2020, 142, 2, 987−998.

Reaction 6

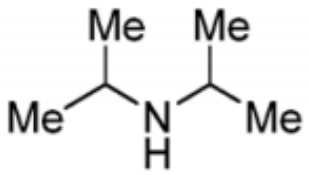






Ir[dF(Me)ppy]$_2$(dtbbpy)PF$_6$

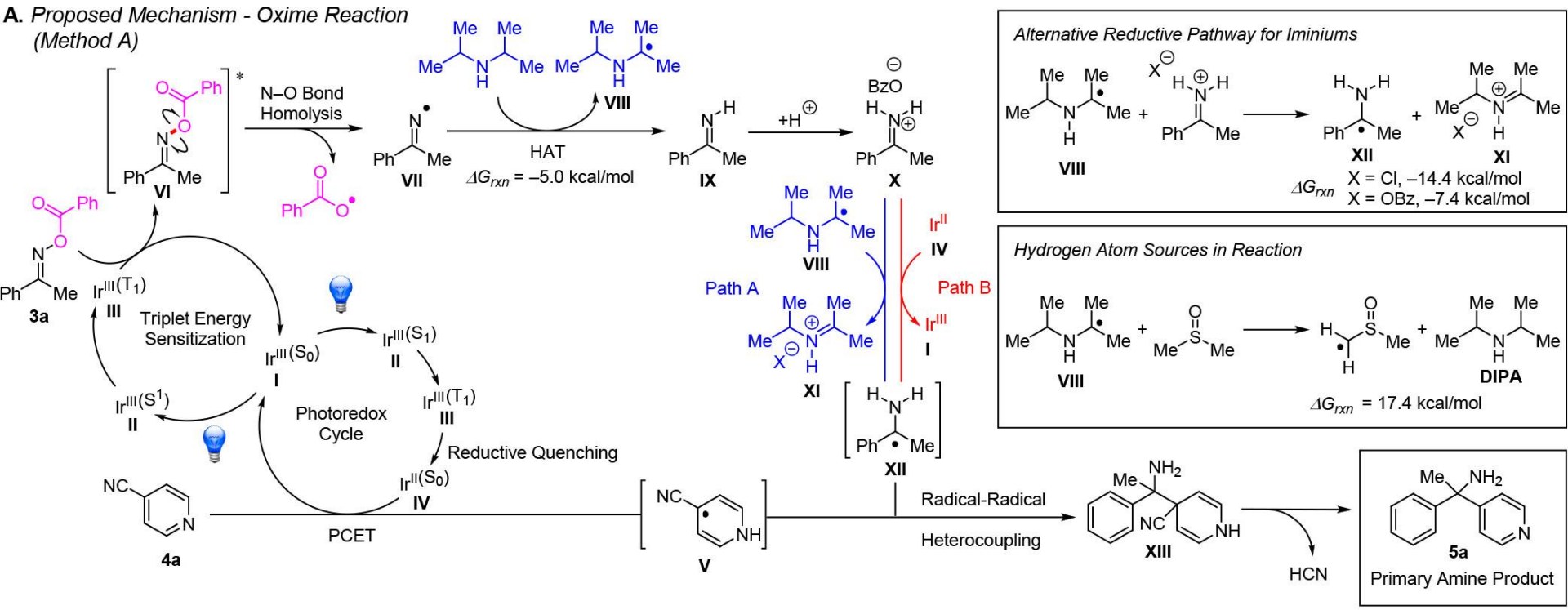
PC1



DIPA

Nicastri, Michael C. ; Lehnherr, Dan ; Lam, Yu-hong ; DiRocco, Daniel A.; Rovis, Tomislav, *Synthesis of Sterically Hindered Primary Amines by Concurrent Tandem Photoredox Catalysis. J. Am. Chem. Soc.* 2020, 142, 2, 987−998.

Reaction 6 Mechanism



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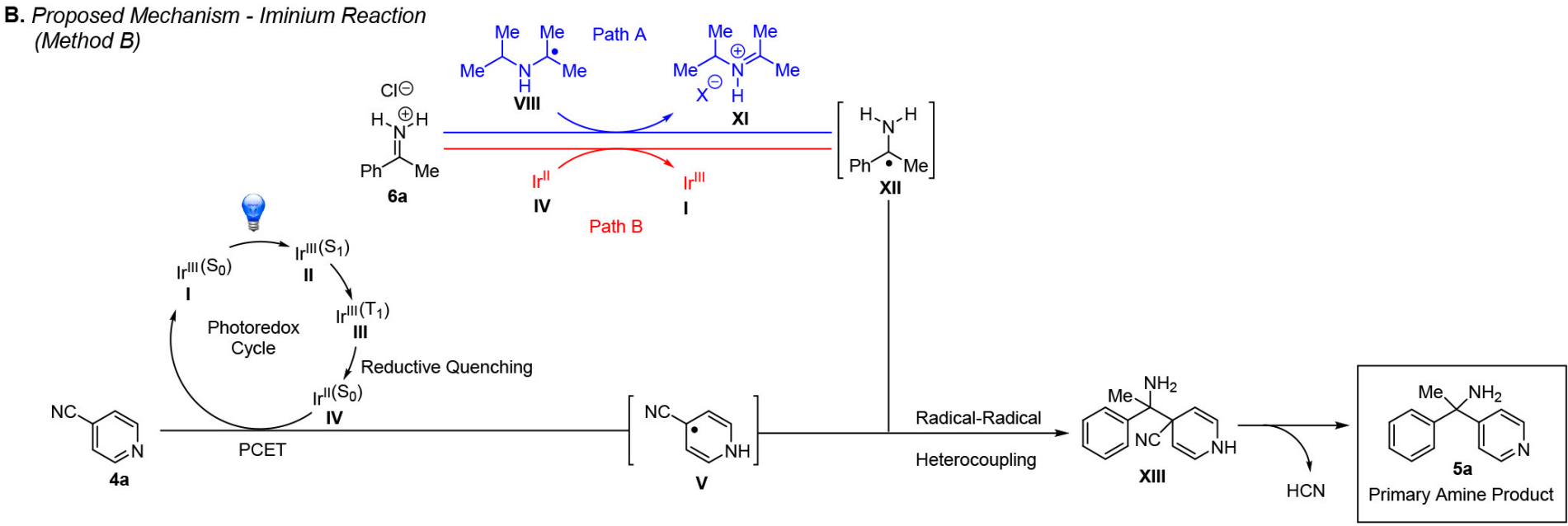
Reaction 6 Mechanism



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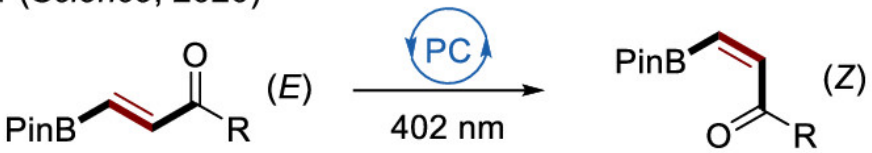
Reaction 7

Weaver (*JACS*, 2014) and Gilmour (*JACS*, 2015)

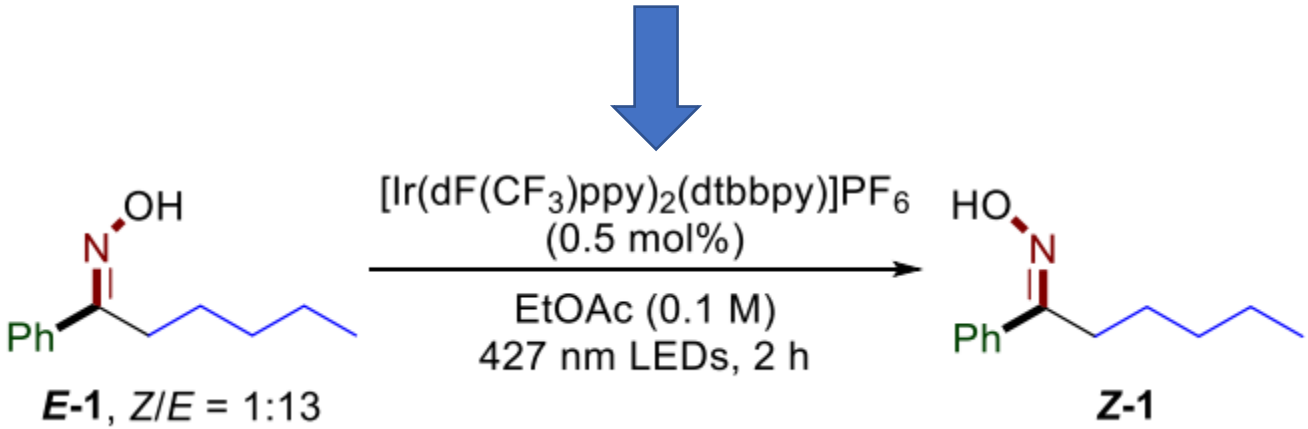
Gilmour (*Science*, 2020)



Singh, K.; Staig, S. J.; Weaver, J. D. *Facile Synthesis of ZAlkenes via Uphill Catalysis. J. Am. Chem. Soc. 2014, 136, 5275−5278.*

Metternich, J. B.; Gilmour, R. *A Bio-Inspired, Catalytic E → Z Isomerization of Activated Olefins. J. Am. Chem. Soc. 2015, 137, 11254−11257.*

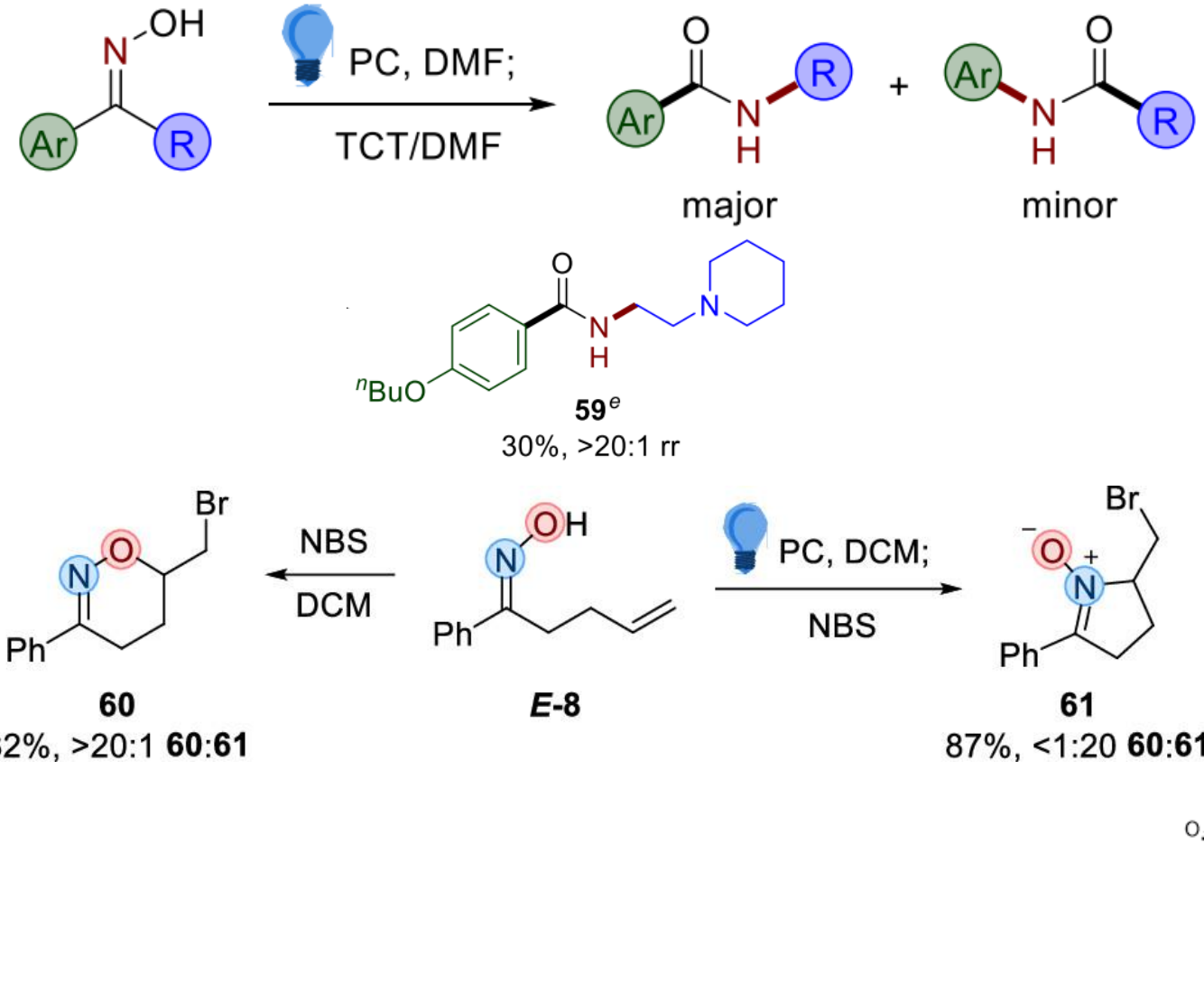
Molloy, J. J.; Schäfer, M.; Wienhold, M.; Morack, T.; Daniliuc, C. G.; Gilmour, R. *Boron-Enabled Geometric Isomerization of Alkenes via Selective Energy-Transfer Catalysis. Science 2020, 369, 302−306.*



***E*-1**, *Z*/*E* = 1:13 **Z-1**

Zhang, Xiao ; Rovis, Tomislav , *Photocatalyzed Triplet Sensitization of Oximes Using Visible Light Provides a Route to Nonclassical Beckmann Rearrangement Products. J. Am. Chem. Soc.* 2021, 143, 50, 21211−21217.

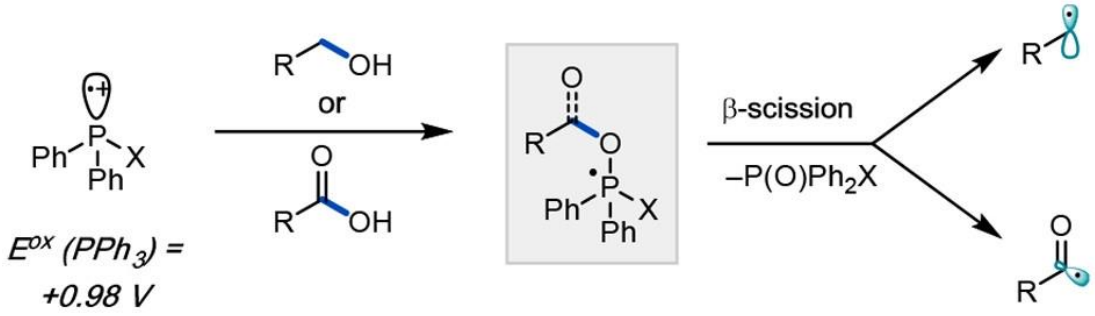
Reaction 7 Application



Zhang, Xiao ; Rovis, Tomislav , *Photocatalyzed Triplet Sensitization of Oximes Using Visible Light Provides a Route to Nonclassical Beckmann Rearrangement Products. J. Am. Chem. Soc.* 2021, 143, 50, 21211−21217.

Reaction 8

C. This Work – phosphine radical mediator (X = Ph or OEt)

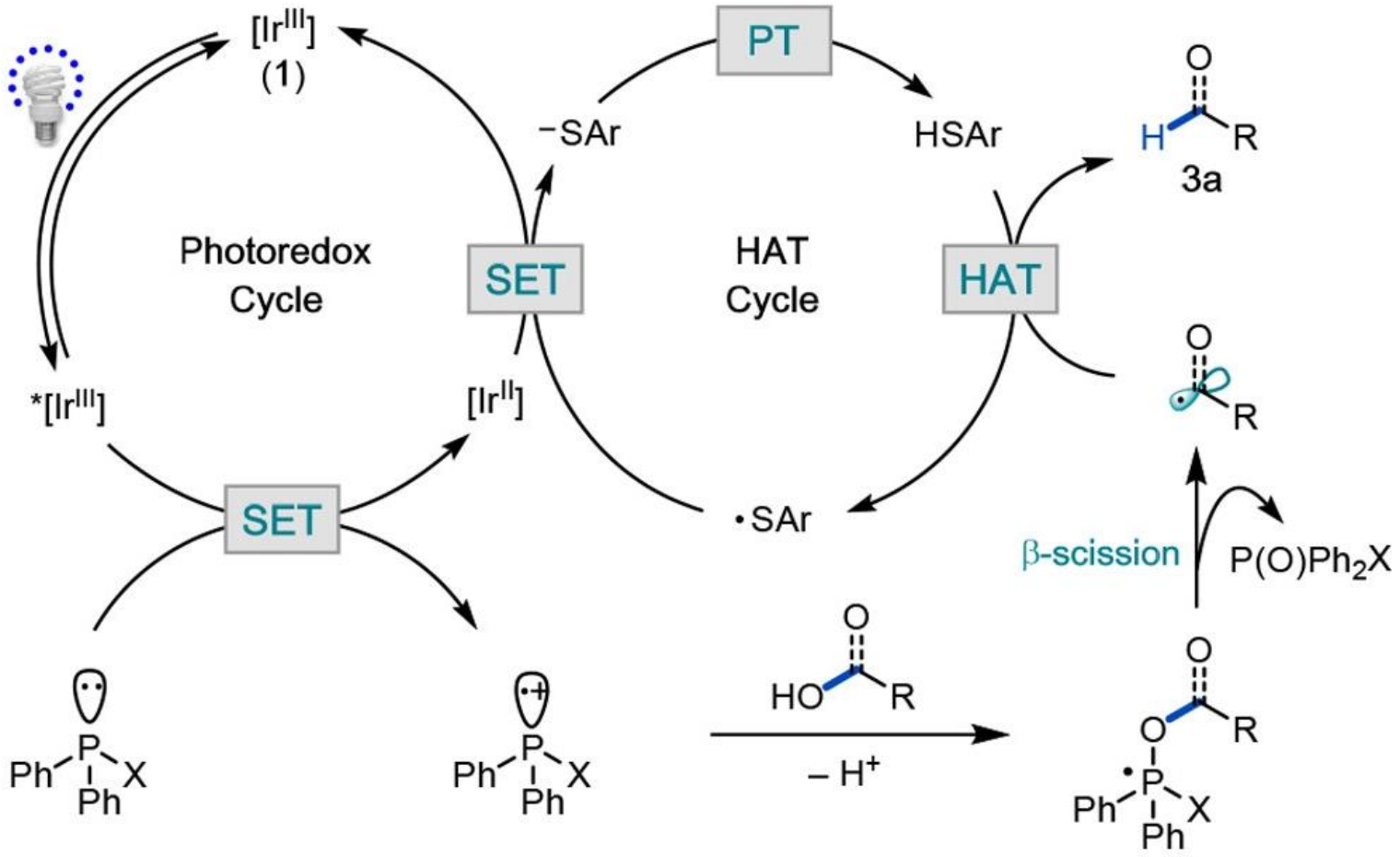


R=Alkyl ⟶ X=OEt

R=Ar ⟶ X=Ph

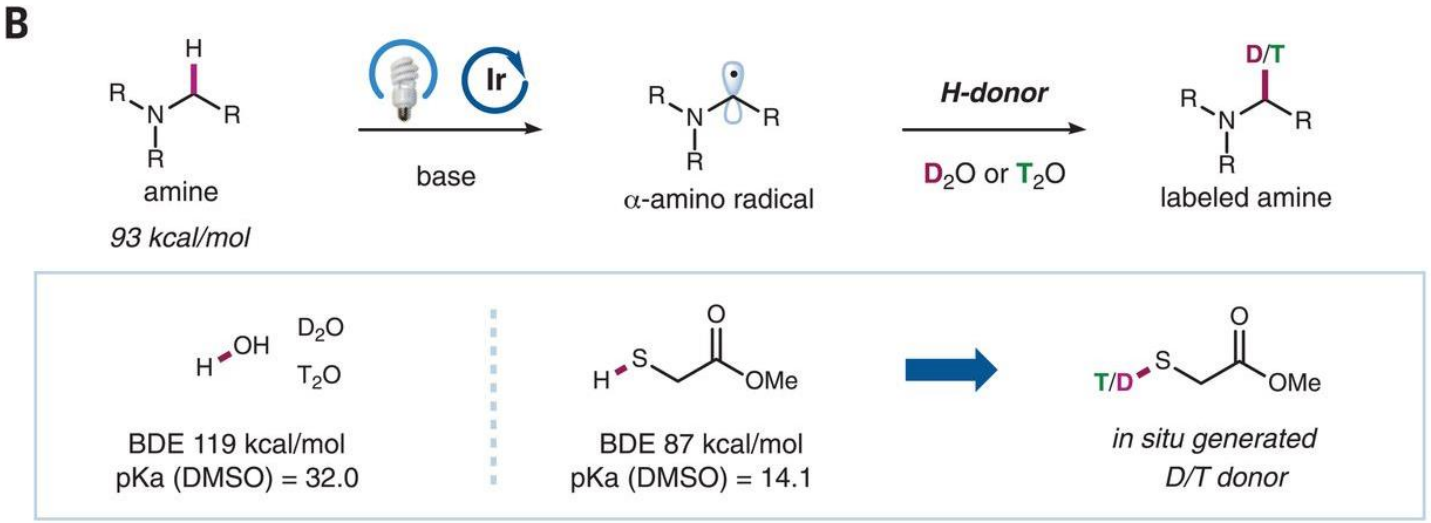
Stache, Erin E.; Ertel, Alyssa B.; Rovis, Tomislav ; Doyle, Abigail G., *Generation of Phosphoranyl Radicals via Photoredox Catalysis Enables Voltage-Independent Activation of Strong C-O Bonds. ACS Catal.* 2018, 8, 12, 11134−11139.

Reaction 8 Mechanism

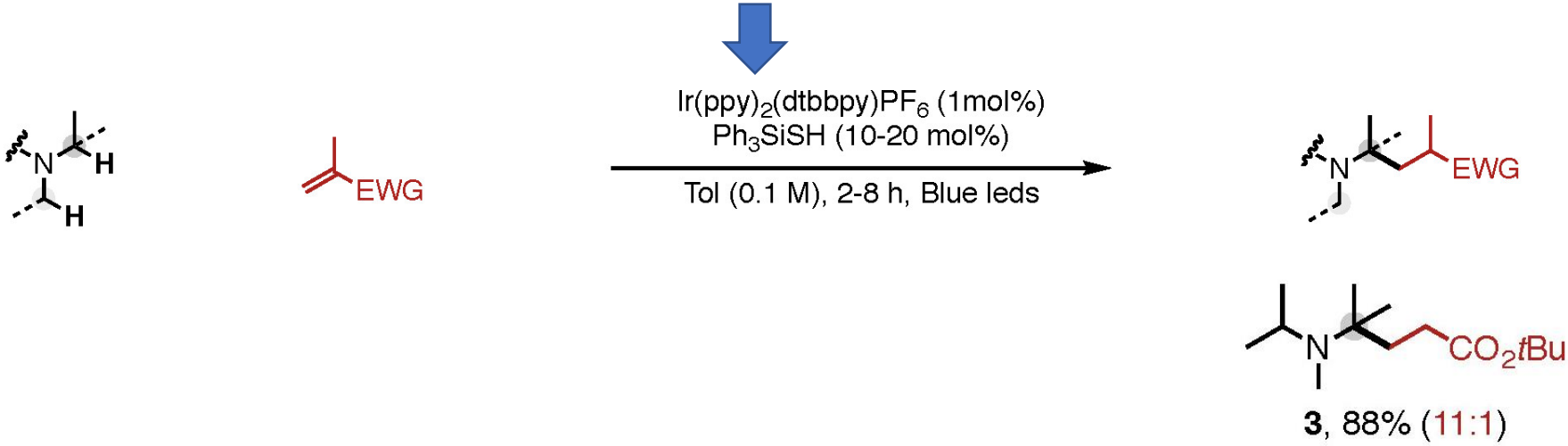


Stache, Erin E.; Ertel, Alyssa B.; Rovis, Tomislav ; Doyle, Abigail G., *Generation of Phosphoranyl Radicals via Photoredox Catalysis Enables Voltage-Independent Activation of Strong C-O Bonds. ACS Catal.* 2018, 8, 12, 11134−11139.

Reaction 9

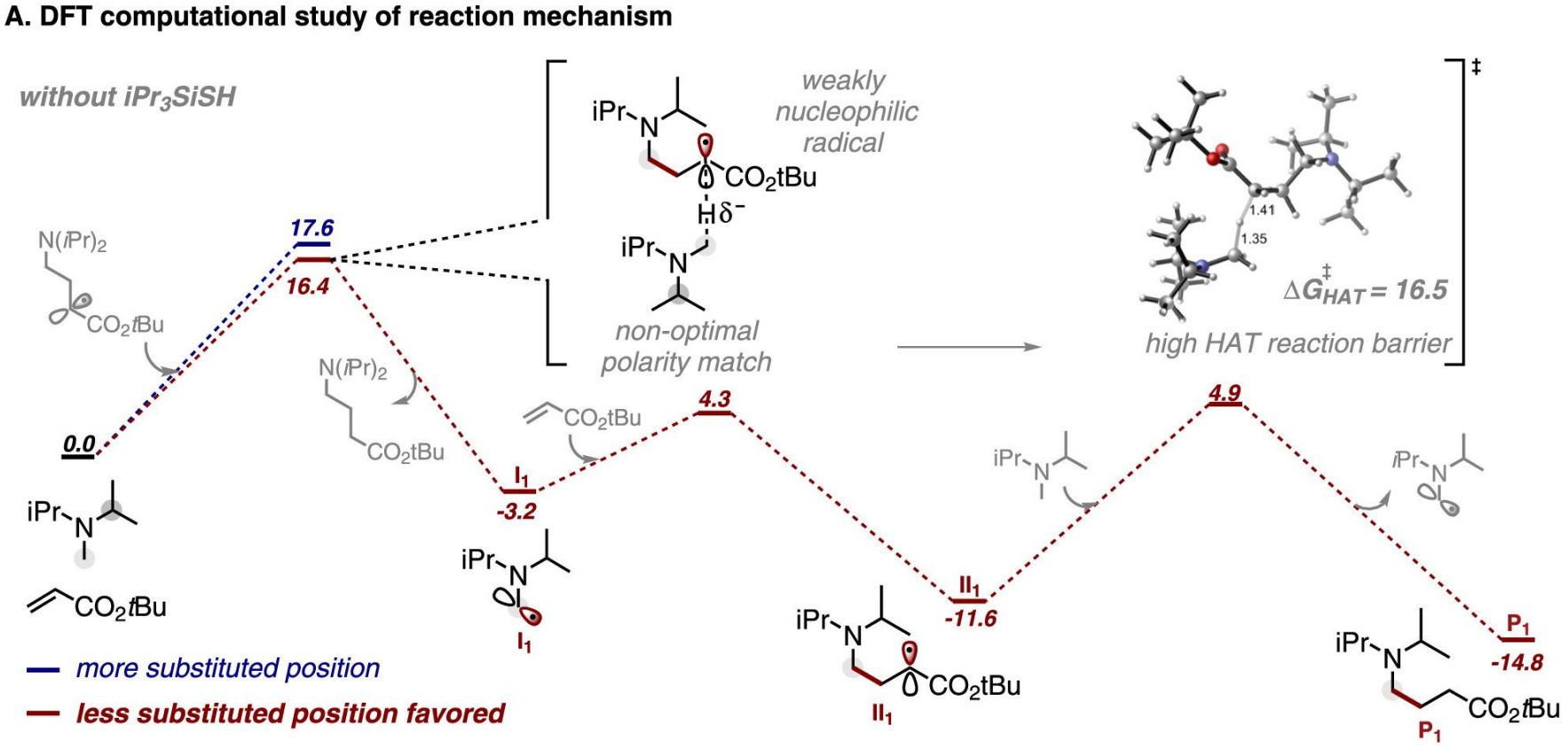


Loh, Y. Y.; Nagao, K.; Hoover, A. J.; Hesk, D.; Rivera, N. R.; Colletti, S. L.; Davies, I. W.; MacMillan, D. W. C. *PhotoredoxCatalyzed Deuteration and Tritiation of Pharmaceutical Compounds. Science 2017, 358, 1182–1187*



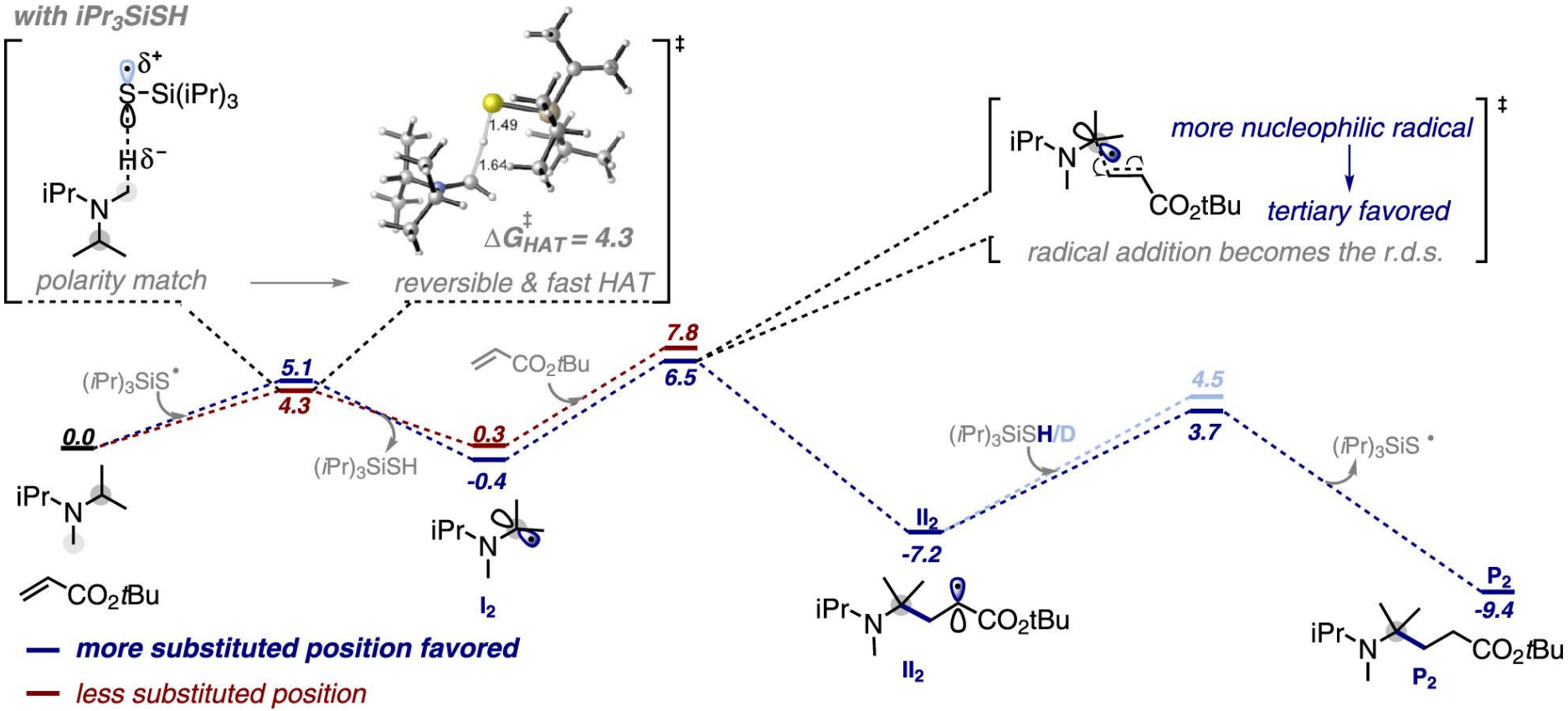
Shen, Yangyang ; Funez-Ardoiz, Ignacio; Schoenebeck, Franziska; Rovis, Tomislav , *Site-Selective α-C–H Functionalization of Trialkylamines via Reversible Hydrogen Atom Transfer Catalysis. J. Am. Chem. Soc.* 2021, 143, 45, 18952−18959.

Reaction 9 Mechanism



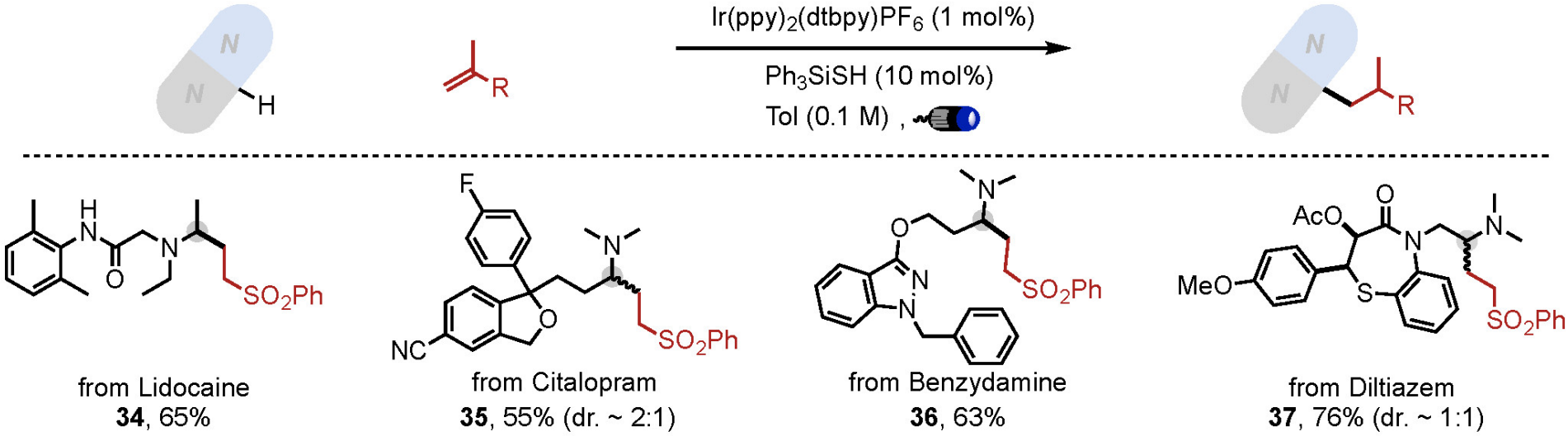
Shen, Yangyang ; Funez-Ardoiz, Ignacio; Schoenebeck, Franziska; Rovis, Tomislav , *Site-Selective α-C–H Functionalization of Trialkylamines via Reversible Hydrogen Atom Transfer Catalysis. J. Am. Chem. Soc.* 2021, 143, 45, 18952−18959.

Reaction 9 Mechanism



Shen, Yangyang ; Funez-Ardoiz, Ignacio; Schoenebeck, Franziska; Rovis, Tomislav , *Site-Selective α-C–H Functionalization of Trialkylamines via Reversible Hydrogen Atom Transfer Catalysis. J. Am. Chem. Soc.* 2021, 143, 45, 18952−18959.

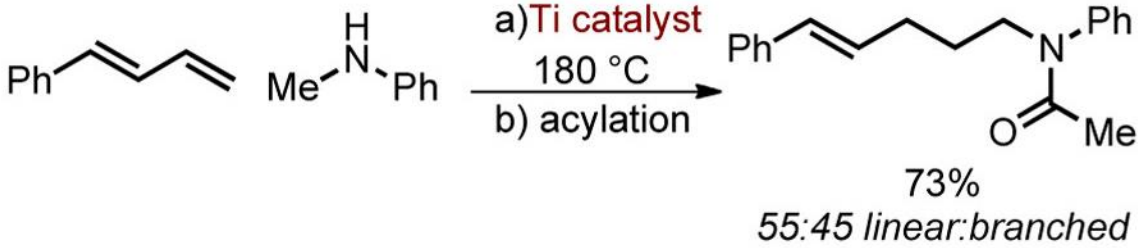
Reaction 9 Application



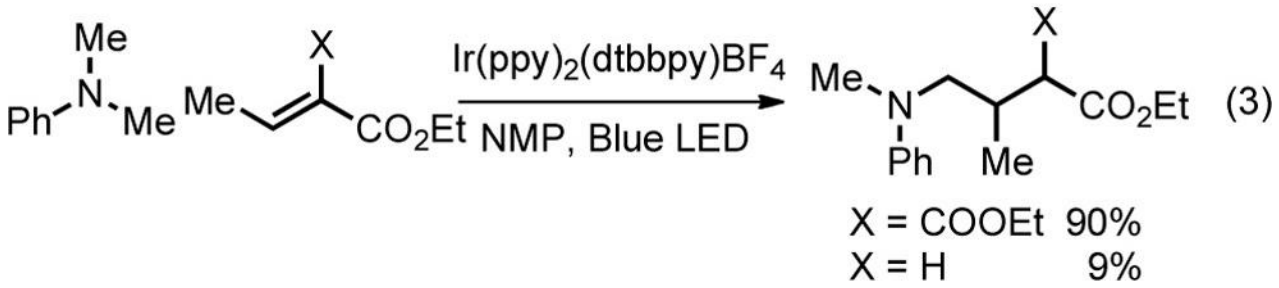
Shen, Yangyang ; Funez-Ardoiz, Ignacio; Schoenebeck, Franziska; Rovis, Tomislav , *Site-Selective α-C–H Functionalization of Trialkylamines via Reversible Hydrogen Atom Transfer Catalysis. J. Am. Chem. Soc.* 2021, 143, 45, 18952−18959.

Phtotoredox Catalysis with Metal-Catalysis

Reaction 10



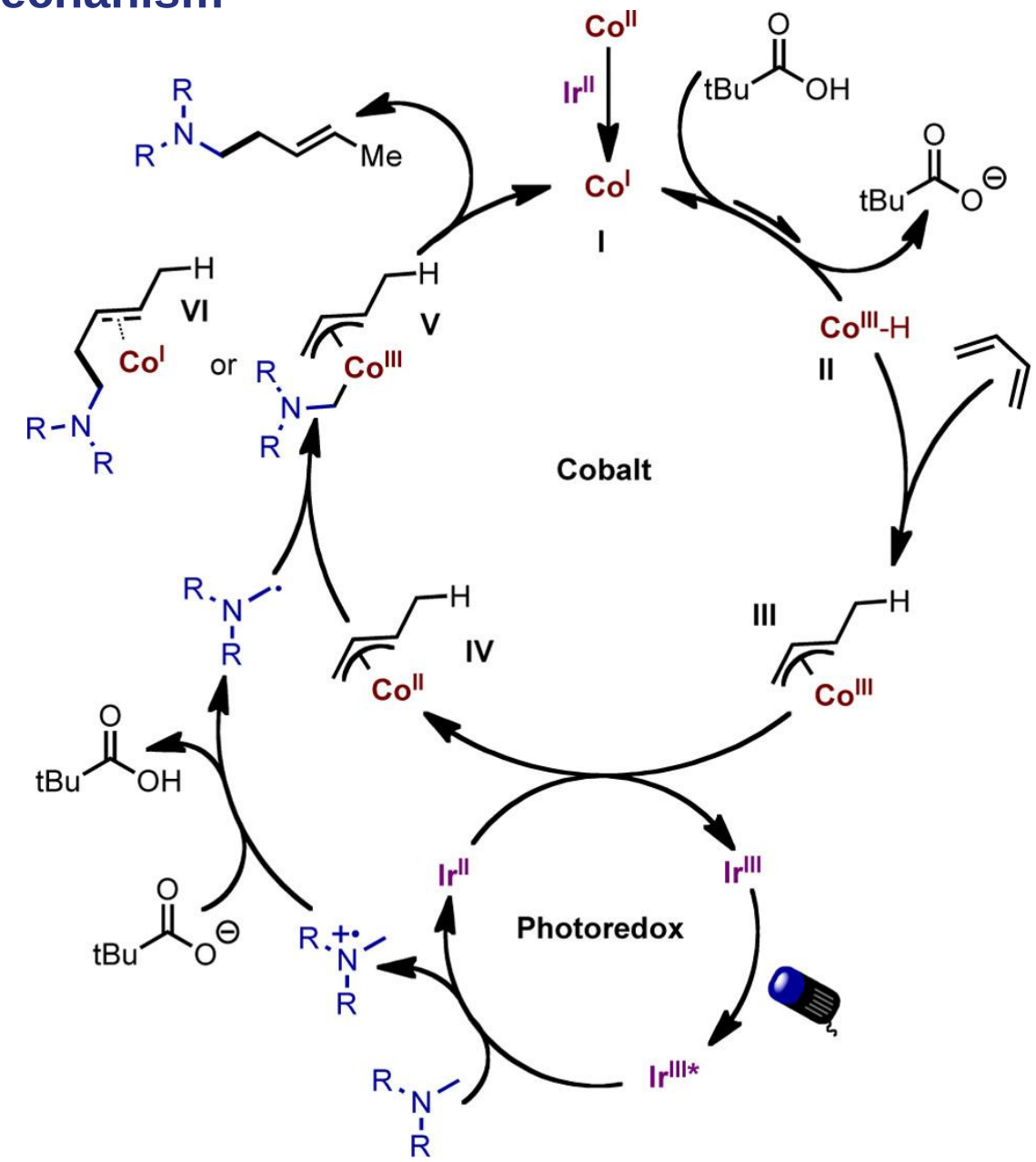
Dörfler, J.; Preuß, T.; Brahms, C.; Scheuer, D.; Doye, S. *Dalton Trans. 2015, 44, 12149−12168.*



Miyake, Y.; Nakajima, K.; Nishibayashi, Y. *J. Am. Chem. Soc. 2012, 134, 3338−3341.*

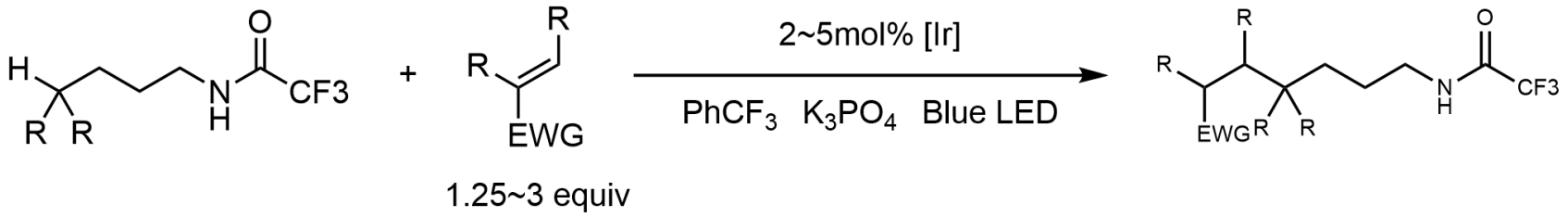
Thullen, Scott M.; Rovis, Tomislav, *A Mild Hydroaminoalkylation of Conjugated Dienes Using a Unified Cobalt and Photoredox Catalytic System. J. Am. Chem. Soc.* 2017, 139, 43, 15504−15508.

Reaction 10 Mechanism



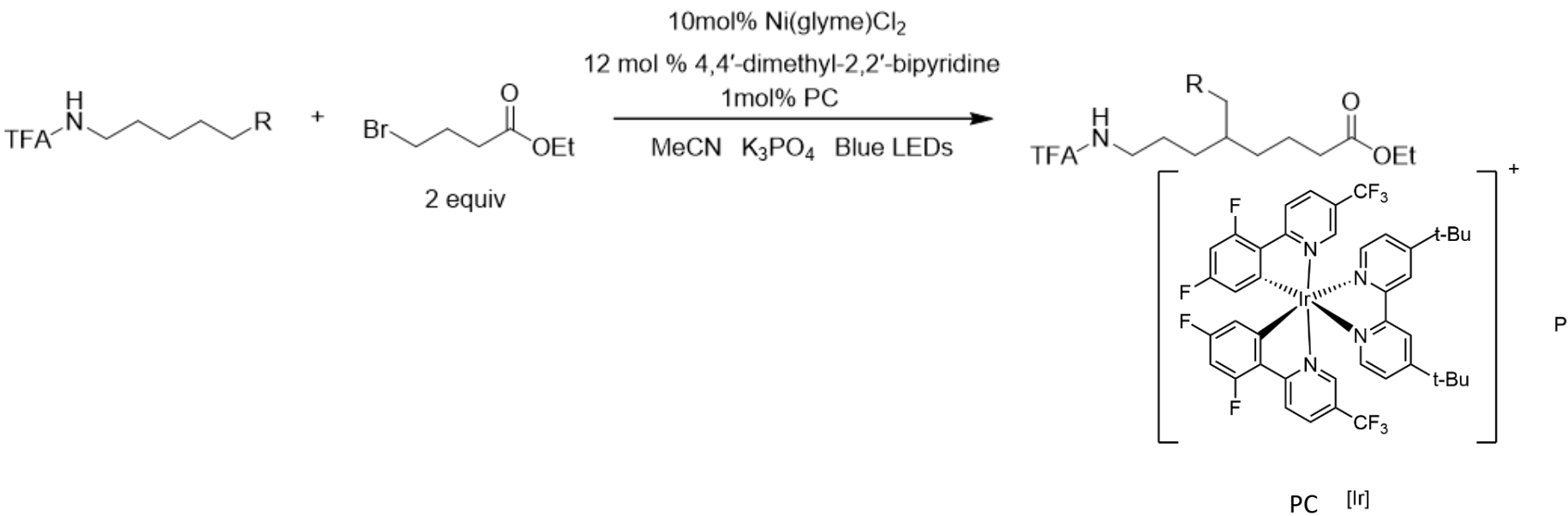
Thullen, Scott M.; Rovis, Tomislav, *A Mild Hydroaminoalkylation of Conjugated Dienes Using a Unified Cobalt and Photoredox Catalytic System. J. Am. Chem. Soc.* 2017, 139, 43, 15504−15508.

Reaction 1



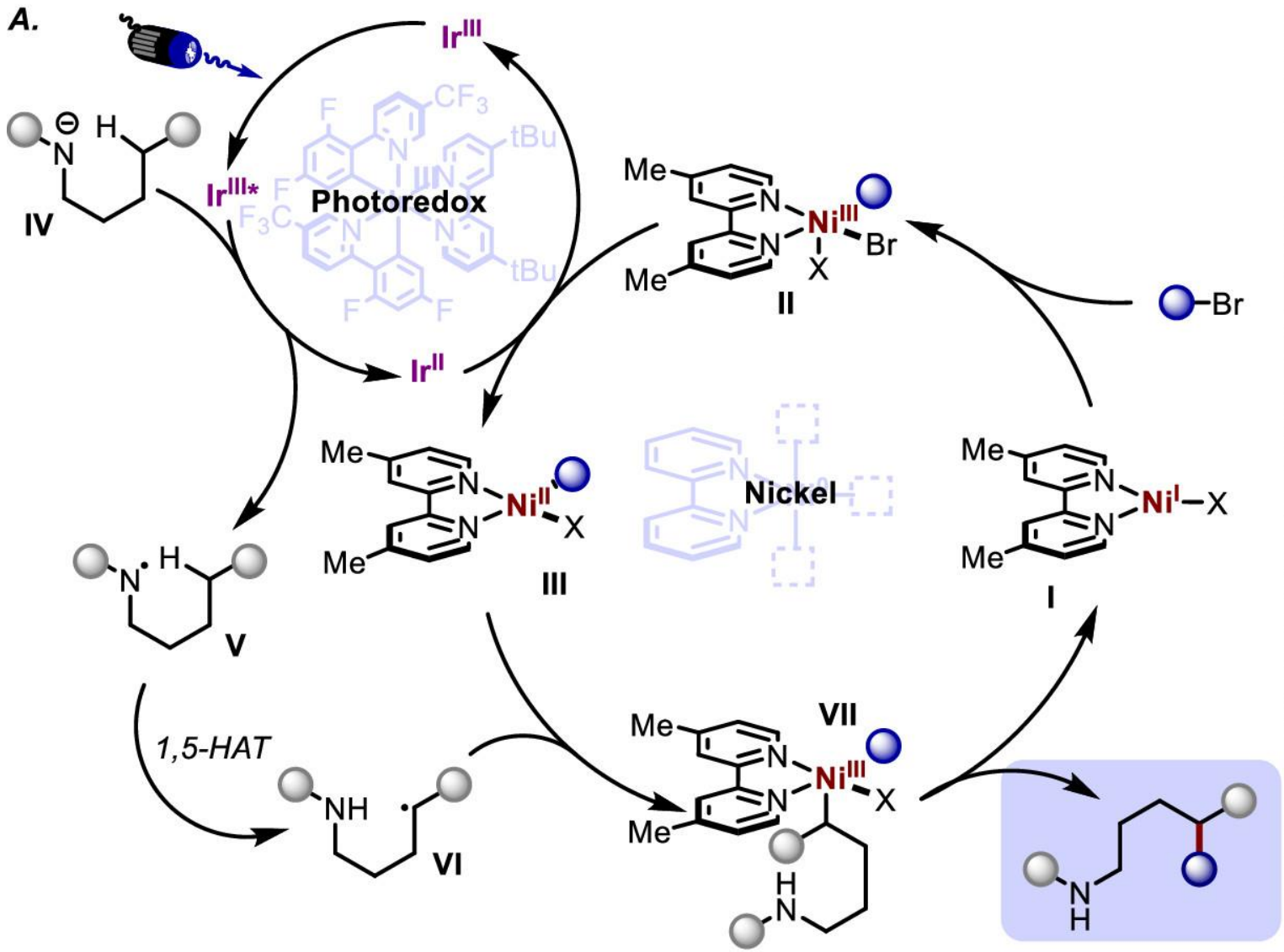
Chu, John C. K.; Rovis, Tomislav, *Amide-directed photoredox-catalysed C–C bond formation at unactivated sp3 C–H bonds. Nature* ***539****, 272–275 (2016)*

Reaction 11



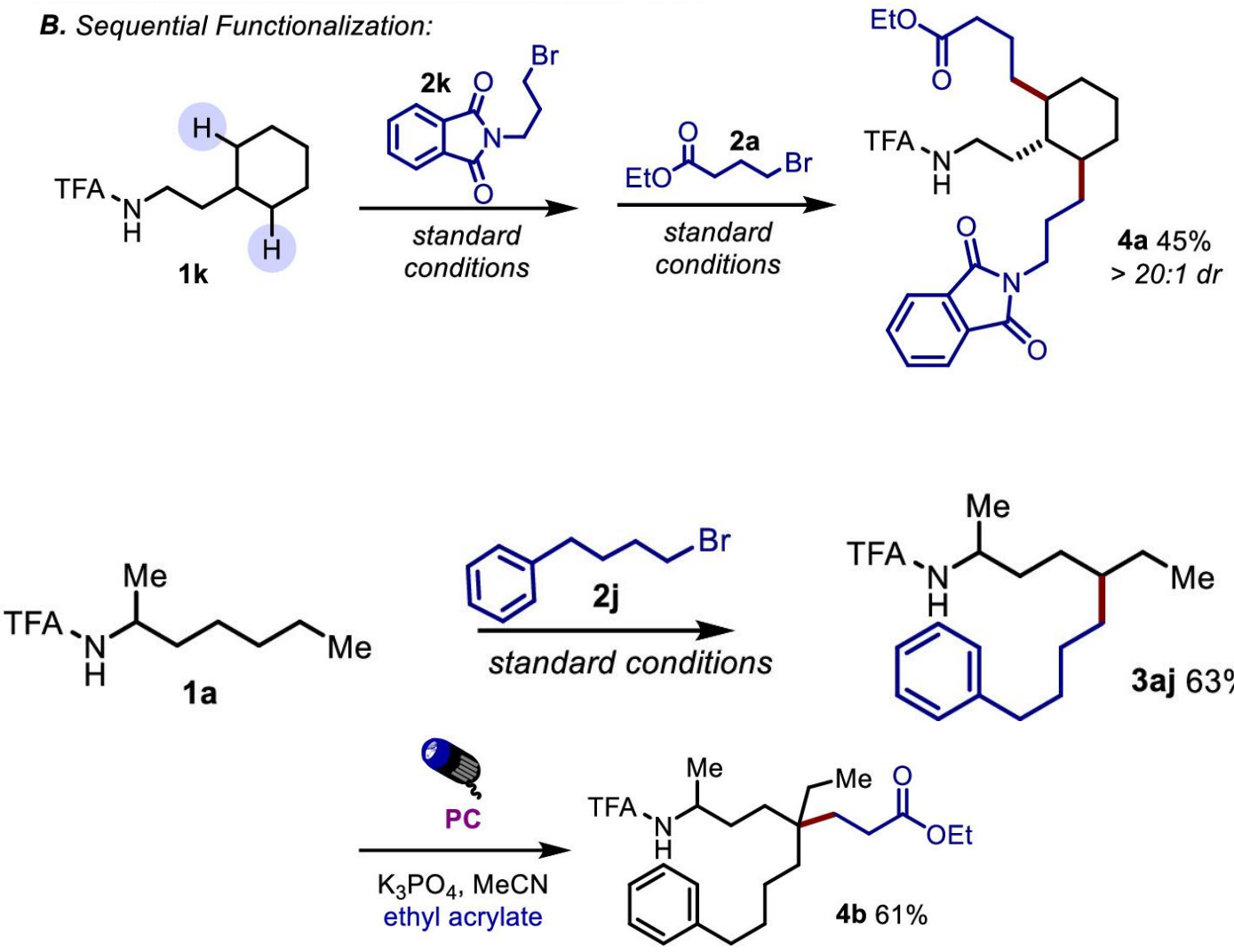
Thullen, Scott M.; Treacy, Sean M.; Rovis, Tomislav, *Regioselective Alkylative Cross-Coupling of Remote Unactivated C(sp3)-H Bonds. J. Am. Chem. Soc.* 2019, 141, 36, 14062−14067.

Reaction 11 Mechanism



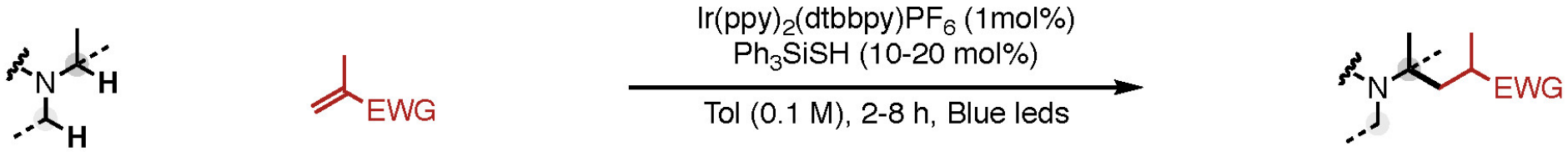
Thullen, Scott M.; Treacy, Sean M.; Rovis, Tomislav, *Regioselective Alkylative Cross-Coupling of Remote Unactivated C(sp3)-H Bonds. J. Am. Chem. Soc.* 2019, 141, 36, 14062−14067.

Reaction 11 Application



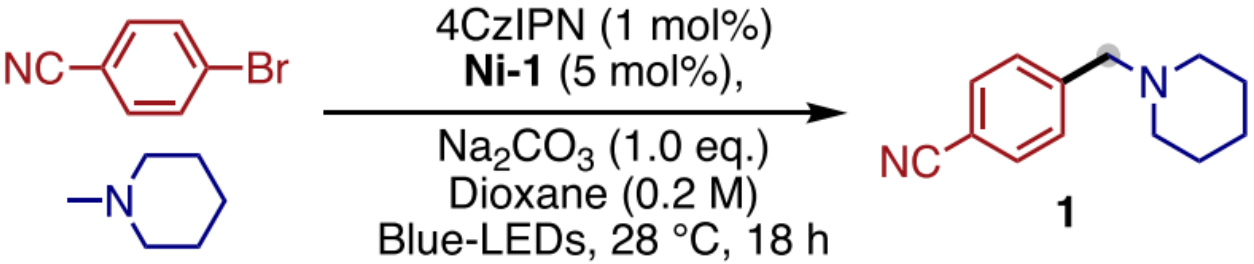
Thullen, Scott M.; Treacy, Sean M.; Rovis, Tomislav, *Regioselective Alkylative Cross-Coupling of Remote Unactivated C(sp3)-H Bonds. J. Am. Chem. Soc.* 2019, 141, 36, 14062−14067.

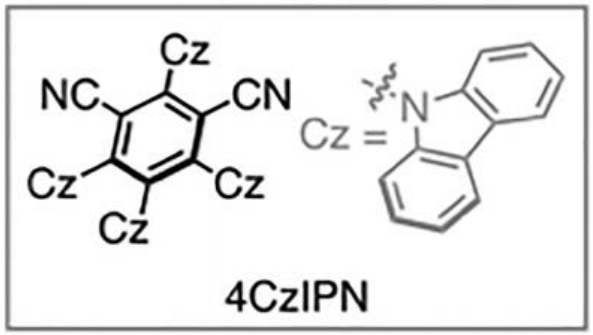
Reaction 9

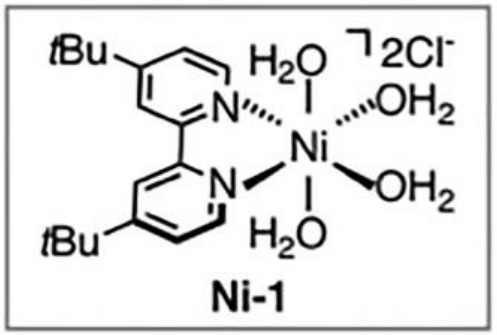


Shen, Yangyang ; Funez-Ardoiz, Ignacio; Schoenebeck, Franziska; Rovis, Tomislav , *Site-Selective α-C–H Functionalization of Trialkylamines via Reversible Hydrogen Atom Transfer Catalysis. J. Am. Chem. Soc.* 2021, 143, 45, 18952−18959.

Reaction 12

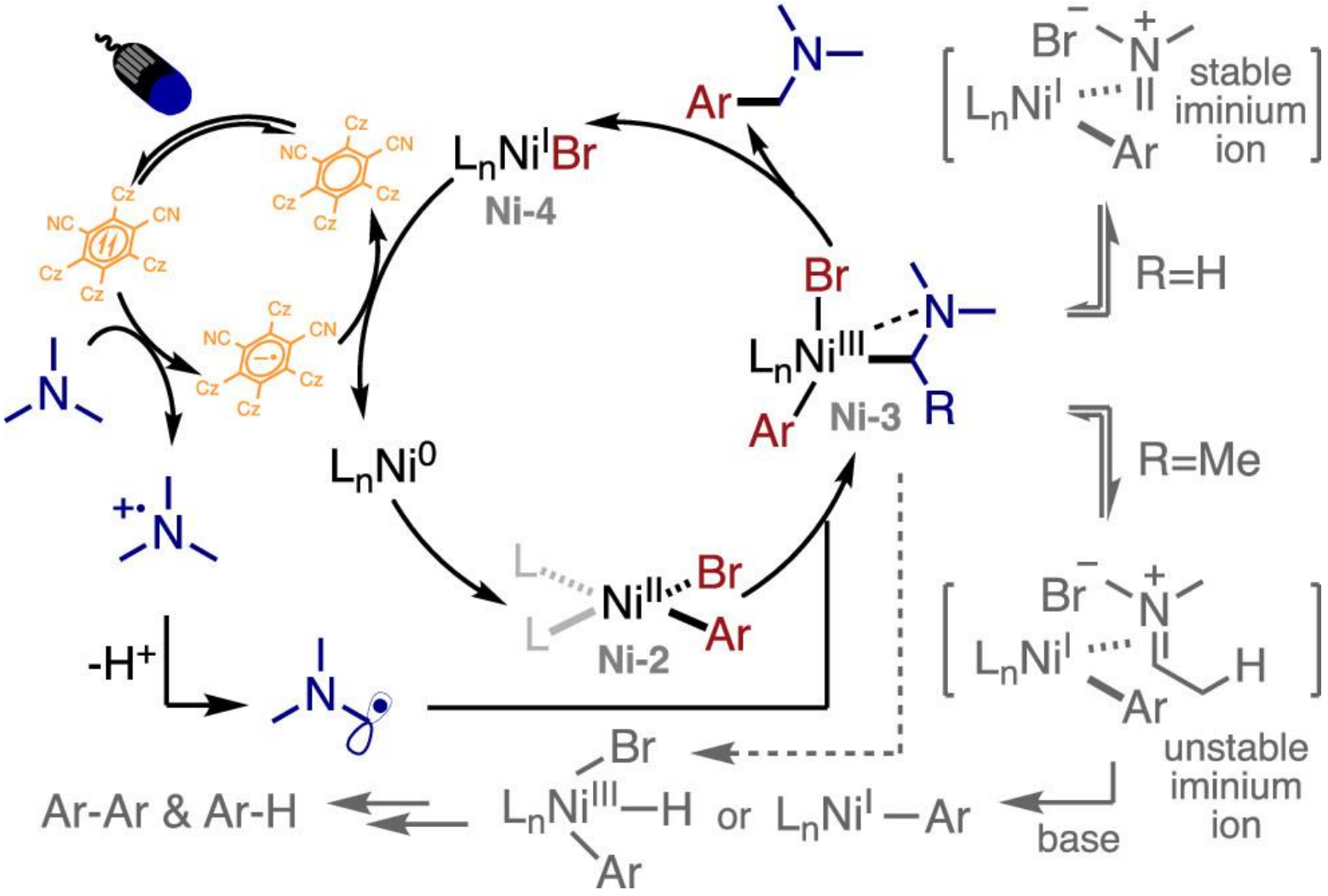






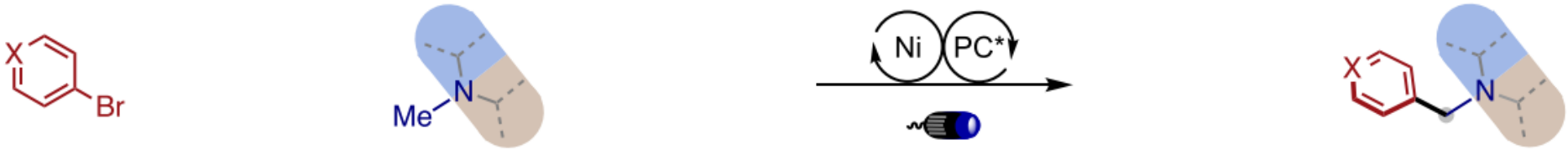
Shen, Yangyang ; Rovis, Tomislav , *Late-Stage N-Me Selective Arylation of Trialkylamines Enabled by Ni/Photoredox Dual Catalysis. J. Am. Chem. Soc.* 2021, 143, 40, 16364−16369.

Reaction 12 Mechanism

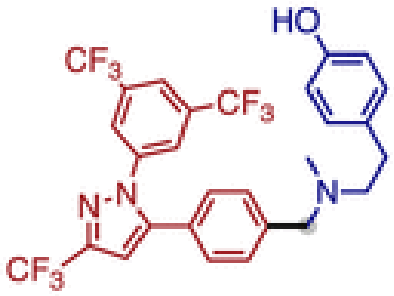


Shen, Yangyang ; Rovis, Tomislav , *Late-Stage N-Me Selective Arylation of Trialkylamines Enabled by Ni/Photoredox Dual Catalysis. J. Am. Chem. Soc.* 2021, 143, 40, 16364−16369.

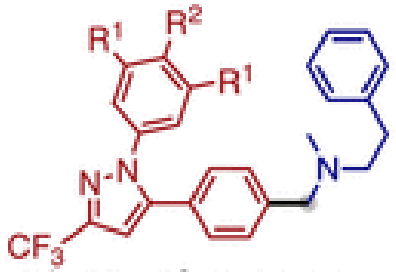
Reaction 12 Late-Stage N-Me Selective Arylation



22, 61%
from Tropinone



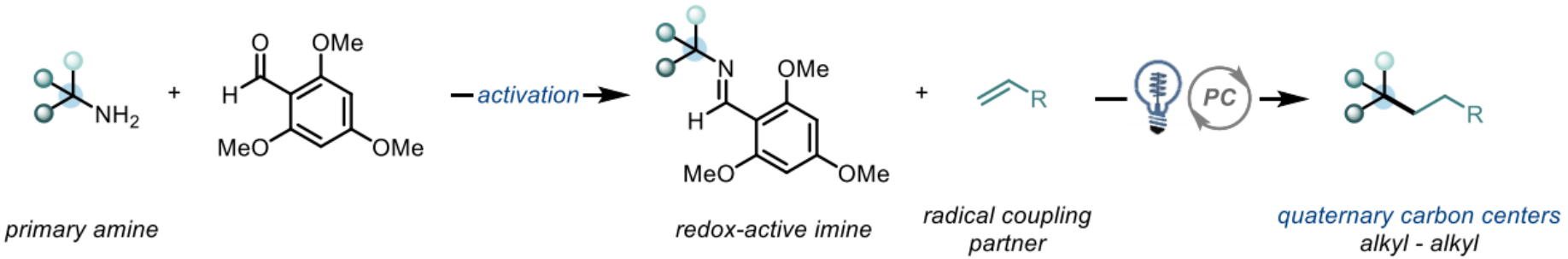
23, 74%
from Hordenine



R^1=CF_3, R^2=H, **24**, 84%
R^1=H, R^2=SO_2NH_2, **25**, 65%
from *N,N*-DMPEA

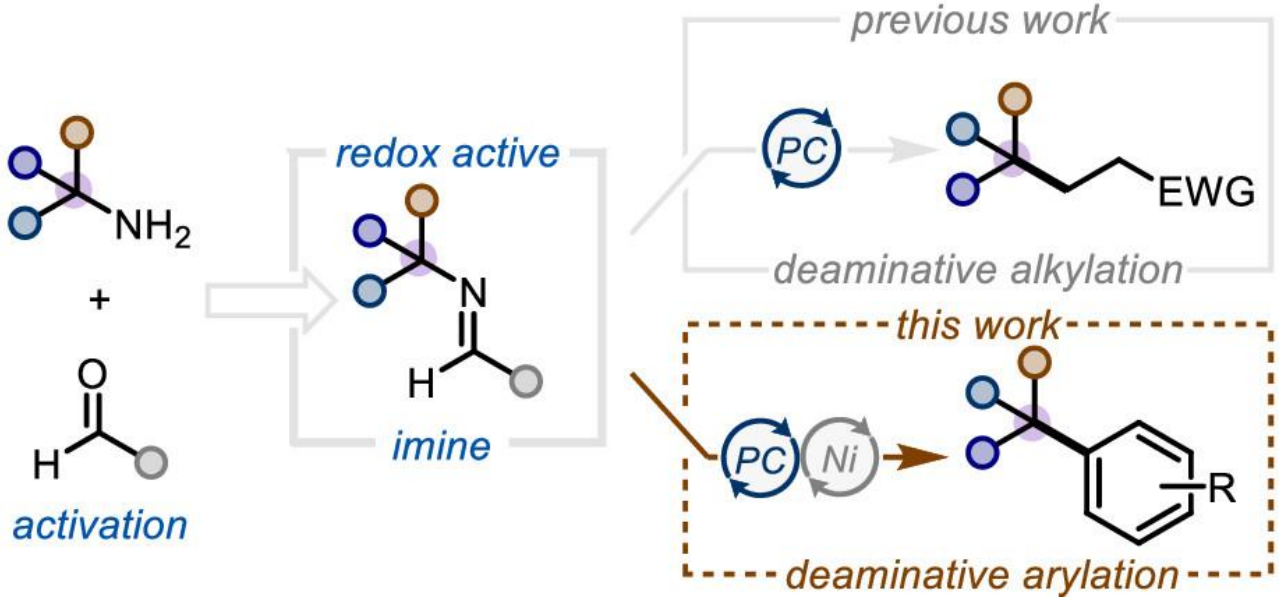
Shen, Yangyang ; Rovis, Tomislav , *Late-Stage N-Me Selective Arylation of Trialkylamines Enabled by Ni/Photoredox Dual Catalysis. J. Am. Chem. Soc.* 2021, 143, 40, 16364−16369.

Reaction 5



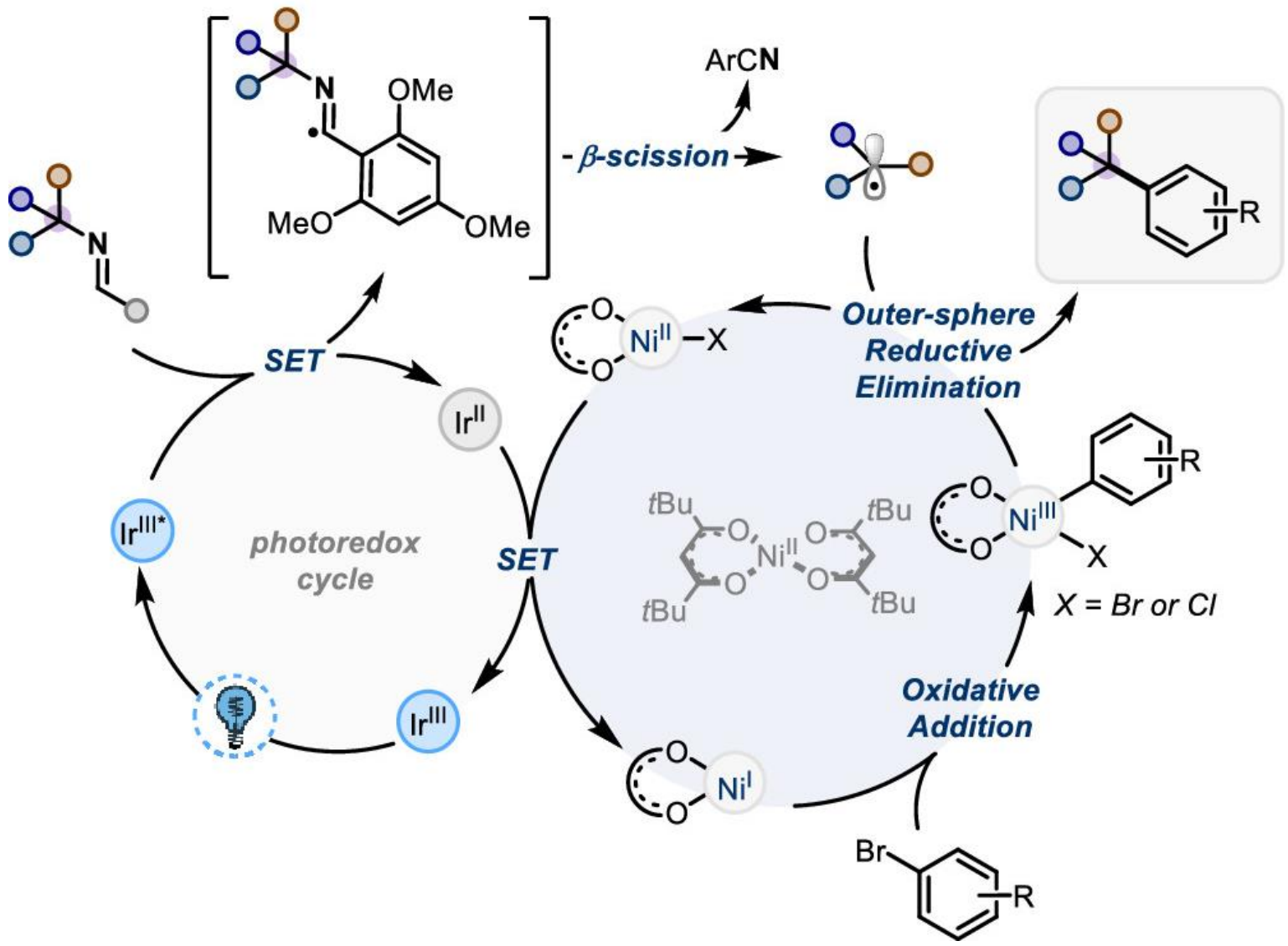
Ashley, Melissa A.; Rovis, Tomislav, *Photoredox-Catalyzed Deaminative Alkylation via C–N Bond Activation of Primary Amines. ACS Catal.* 2020, 142, 43, 18310−18316.

Reaction 13



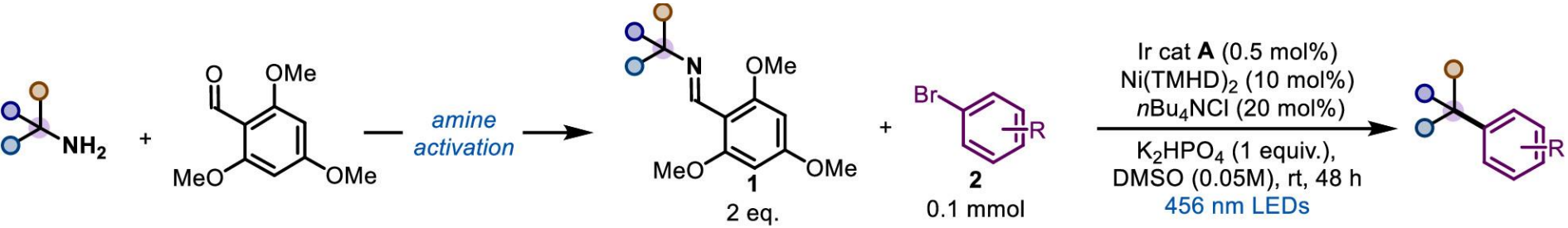
Dorsheimer, Julia R. ; Ashley, Melissa A.; Rovis, Tomislav , *Dual Nickel/Photoredox-Catalyzed Deaminative Cross-Coupling of Sterically Hindered Primary Amines. J. Am. Chem. Soc.* 2021, 143, 46, 19294−19299.

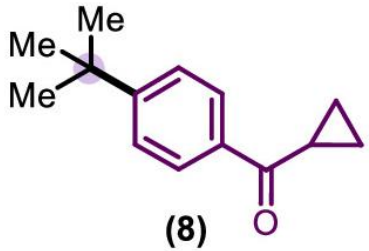
Reaction 13 Mechanism



Dorsheimer, Julia R. ; Ashley, Melissa A.; Rovis, Tomislav , *Dual Nickel/Photoredox-Catalyzed Deaminative Cross-Coupling of Sterically Hindered Primary Amines. J. Am. Chem. Soc.* 2021, 143, 46, 19294−19299.

Reaction 13 Scope



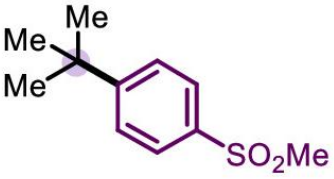


(8)

92%

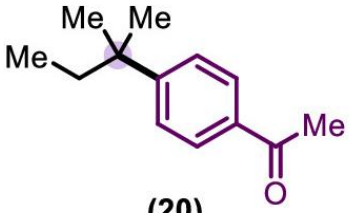
(12)

75%



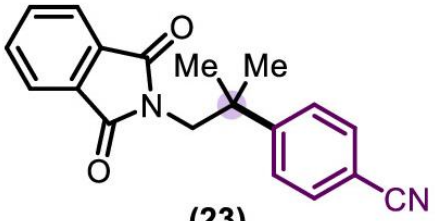
(5)

86%



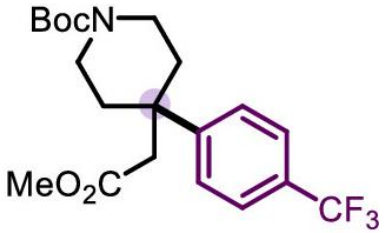
(20)

84%



(23)

70%

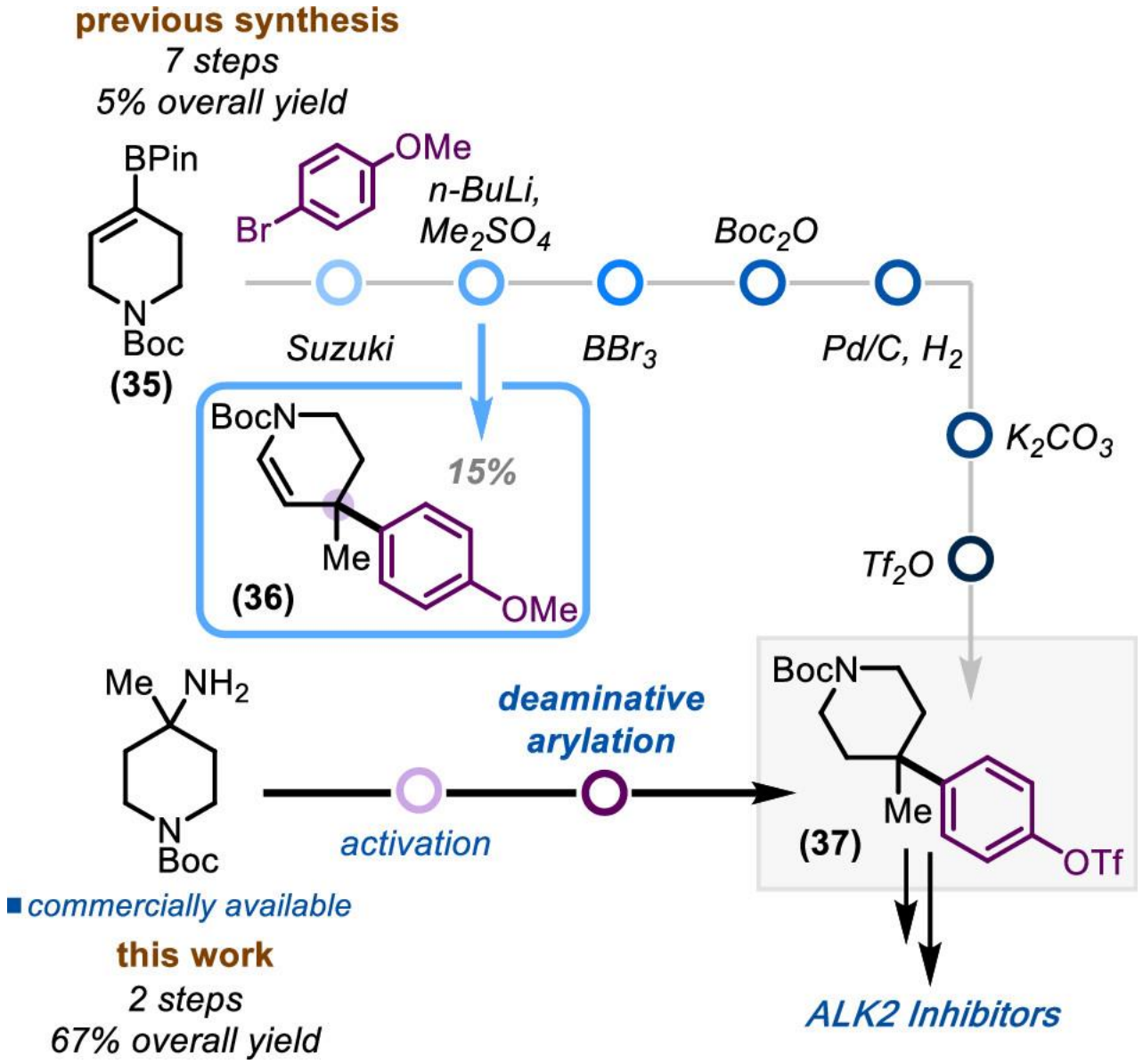


(34)

65%

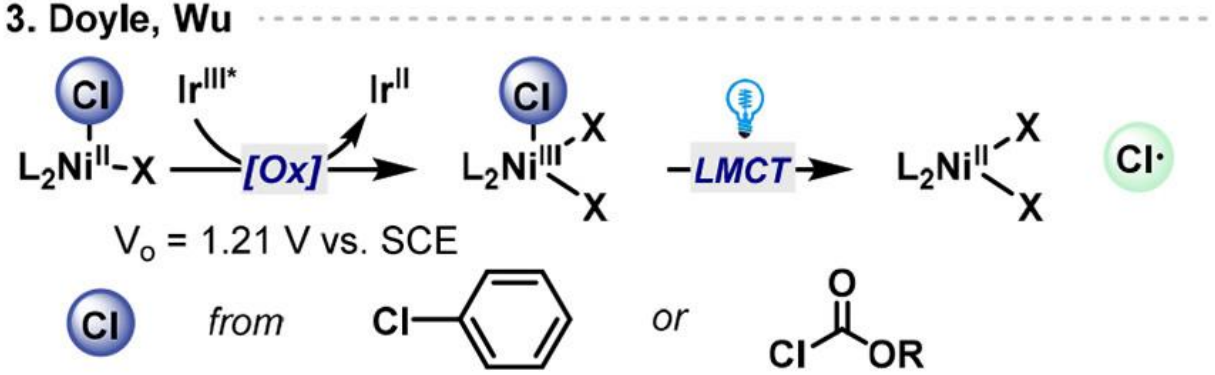
Dorsheimer, Julia R. ; Ashley, Melissa A.; Rovis, Tomislav , *Dual Nickel/Photoredox-Catalyzed Deaminative Cross-Coupling of Sterically Hindered Primary Amines. J. Am. Chem. Soc.* 2021, 143, 46, 19294−19299.

Reaction 13 Application



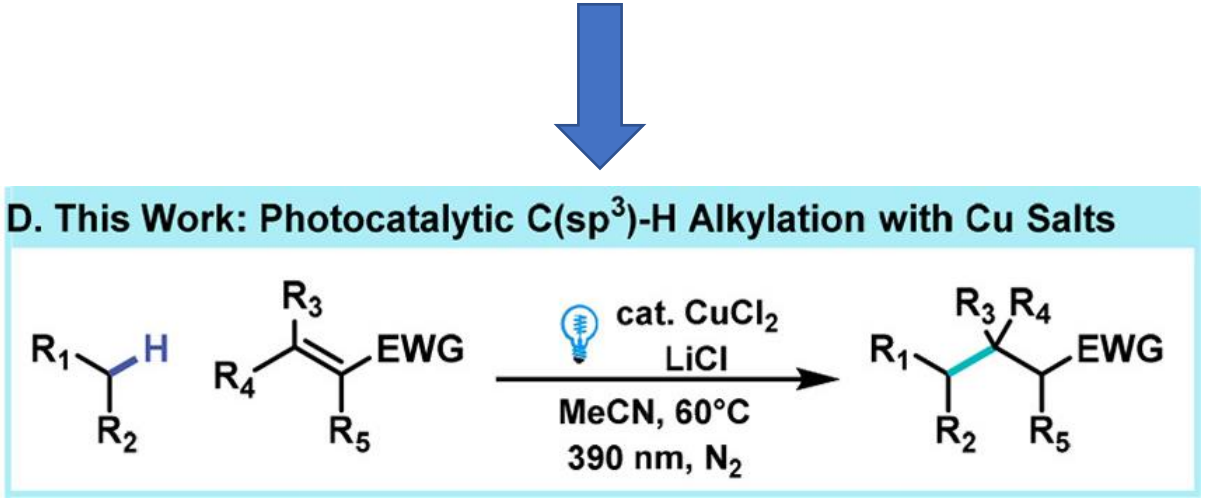
Dorsheimer, Julia R. ; Ashley, Melissa A.; Rovis, Tomislav , *Dual Nickel/Photoredox-Catalyzed Deaminative Cross-Coupling of Sterically Hindered Primary Amines. J. Am. Chem. Soc.* 2021, 143, 46, 19294−19299.

Reaction 14 Background



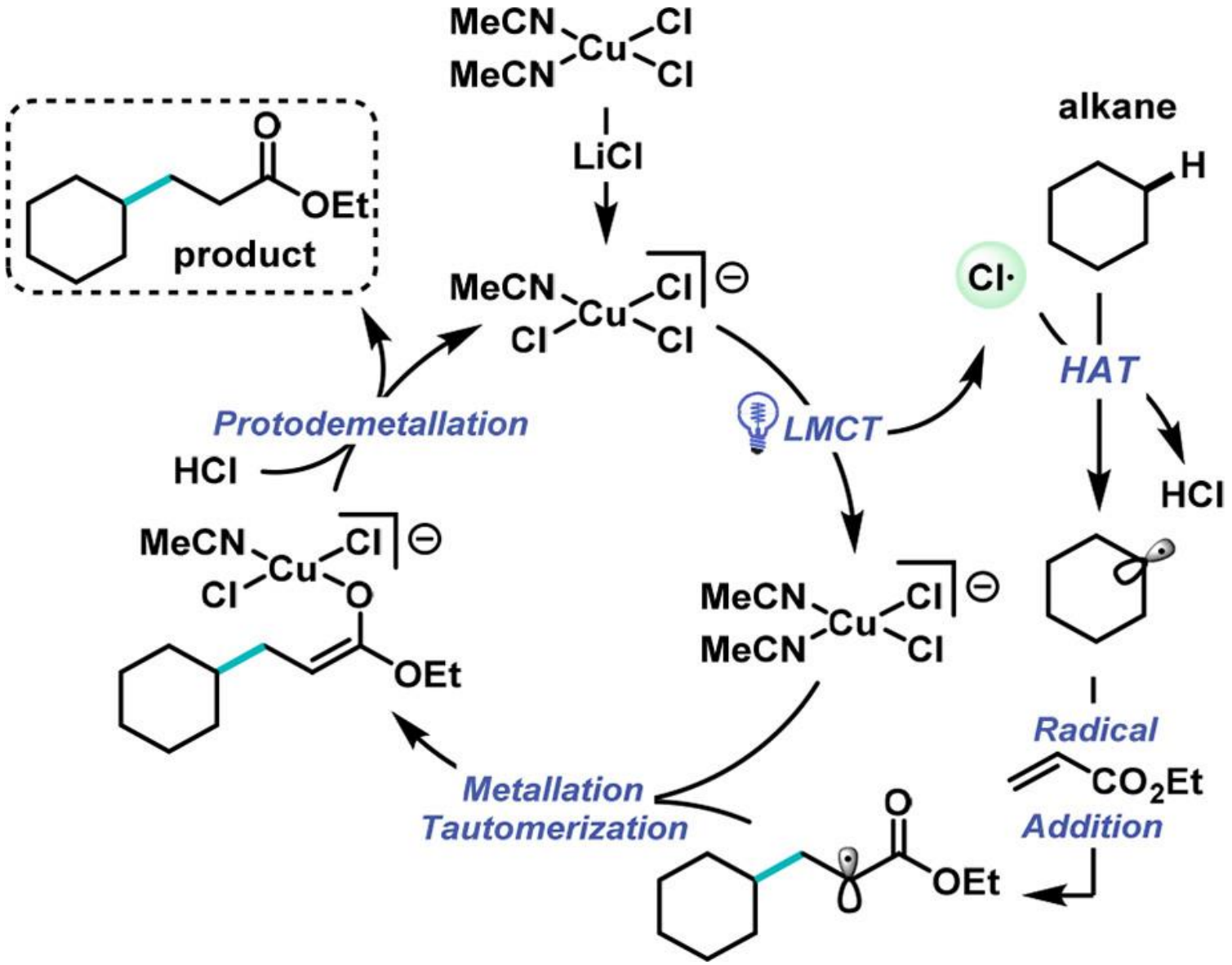
Deng, H. P.; Fan, X. Z.; Chen, Z. H.; Xu, Q. H.; Wu, J. *Photoinduced Nickel-Catalyzed Chemo- and Regioselective Hydroalkylation of Internal Alkynes with Ether and Amide α-Hetero C(sp3)-H Bonds. J. Am. Chem. Soc. 2017, 139, 13579−13584.*

Ackerman, L. K. G.; Martinez Alvarado, J. I.; Doyle, A. G. *Direct C-C Bond Formation from Alkanes Using Ni-Photoredox Catalysis. J. Am. Chem. Soc. 2018, 140, 14059−14063*



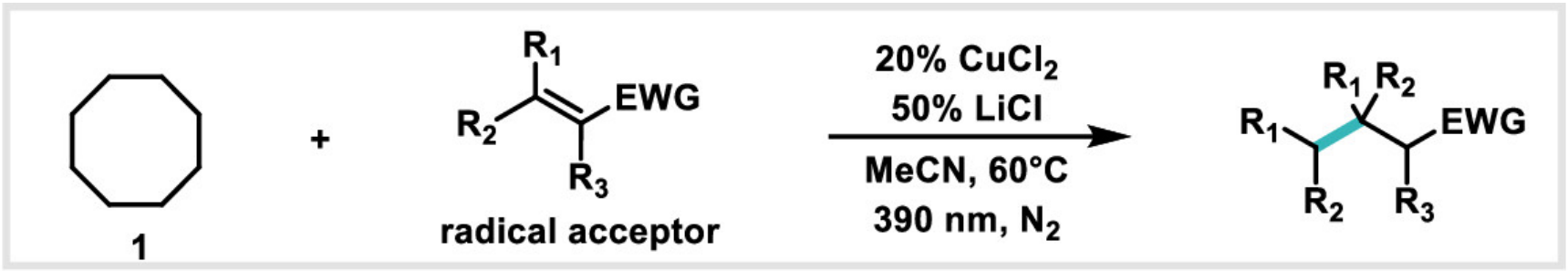
Treacy, Sean M.; Rovis, Tomislav , *Copper Catalyzed C(sp3)–H Bond Alkylation via Photoinduced Ligand-to-Metal Charge Transfer. J. Am. Chem. Soc.* 2021, 143, 7, 2729−2735

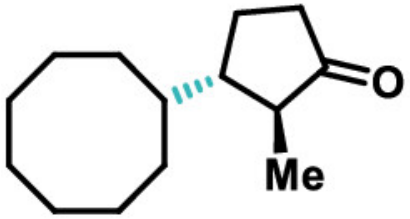
Reaction 14 Mechanism



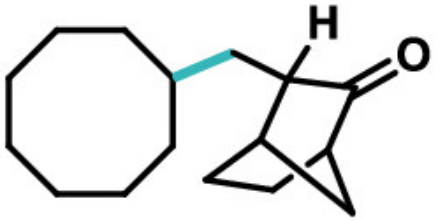
Treacy, Sean M.; Rovis, Tomislav , *Copper Catalyzed C(sp3)–H Bond Alkylation via Photoinduced Ligand-to-Metal Charge Transfer. J. Am. Chem. Soc.* 2021, 143, 7, 2729−2735

Reaction 14 Scope

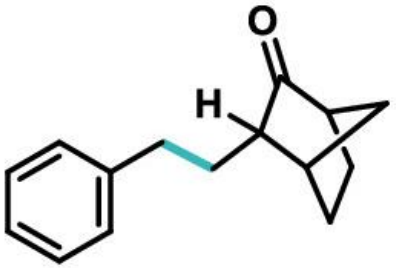




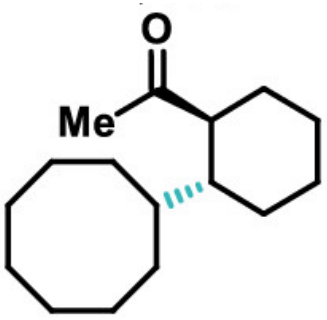
43, 83%, >20:1 dr



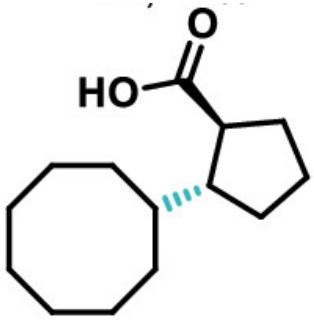
44, 72%, 10:1 dr



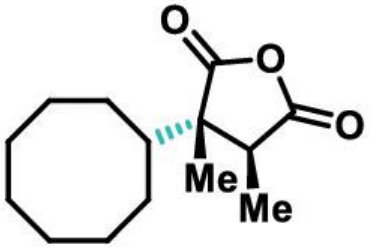
45, 70%, >20:1 dr



46, 57% 15:1 dr[b]



47, 75%, >20:1 dr

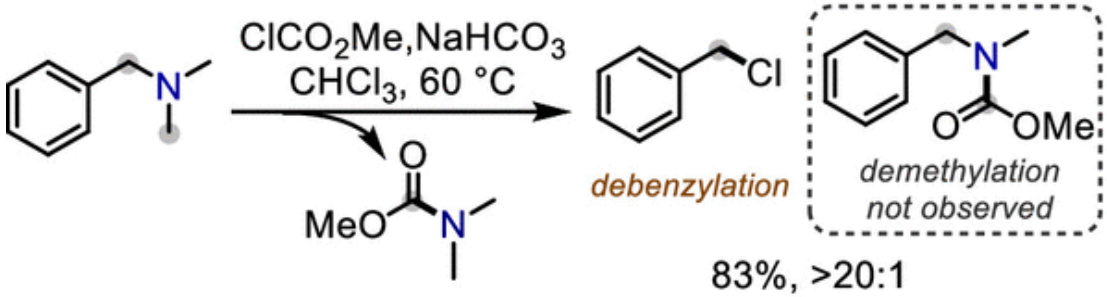


48, 67%, >20:1 dr

Treacy, Sean M.; Rovis, Tomislav , *Copper Catalyzed C(sp3)–H Bond Alkylation via Photoinduced Ligand-to-Metal Charge Transfer. J. Am. Chem. Soc.* 2021, 143, 7, 2729−2735

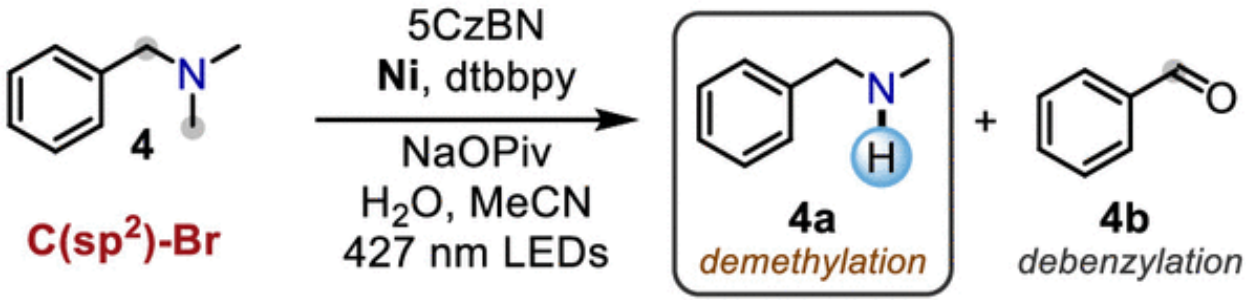
Reaction 15

A. Classical approach for *N*-demethylation[34]



Brine, G. A.; Boldt, K. G.; Hart, C. K.; Carroll, F. I. *The N-Demethylation of Morphine and Codeine Using Methyl Chloroformate. Org. Prep. Proced. Int. 1976, 8 (3), 103−106.*

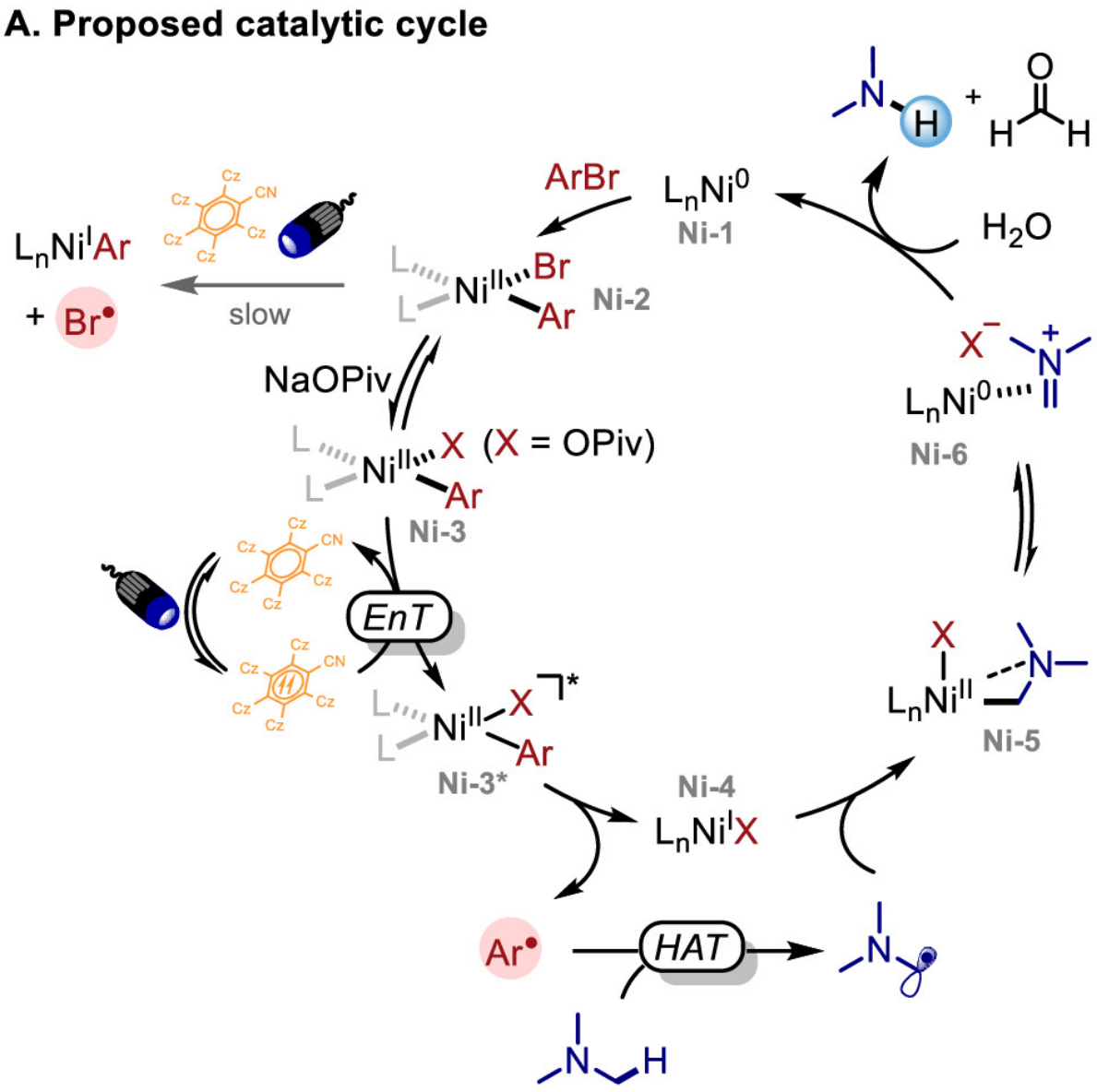
B. This work for selective *N*-demethylation



Ni:$NiCl_2$

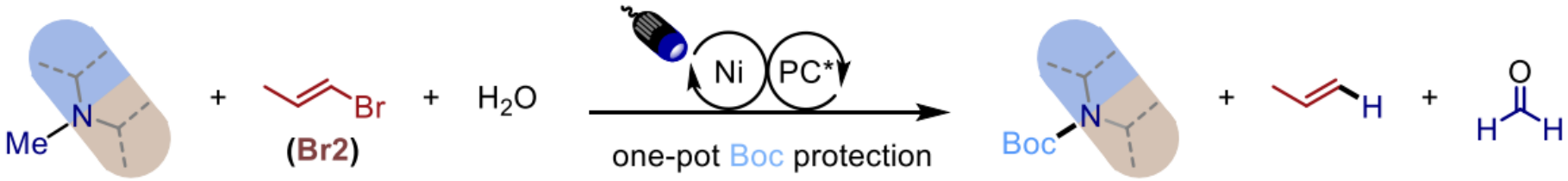
Zhang, Xiao ; Shen, Yangyang; Rovis, Tomislav, *Photoinduced Nickel-Catalyzed Selective N-Demethylation of Trialkylamines Using C(sp2)−Bromides as HAT Reagents. J. Am. Chem. Soc. 2023, 145, 6, 3294–3300*

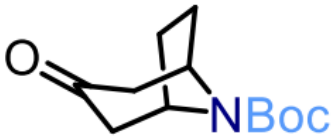
Reaction 15 Mechanism



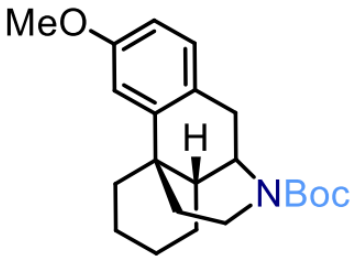
Zhang, Xiao ; Shen, Yangyang; Rovis, Tomislav, *Photoinduced Nickel-Catalyzed Selective N-Demethylation of Trialkylamines Using C(sp2)–Bromides as HAT Reagents. J. Am. Chem. Soc. 2023, 145, 6, 3294–3300*

Reaction 15 Late-Stage Application

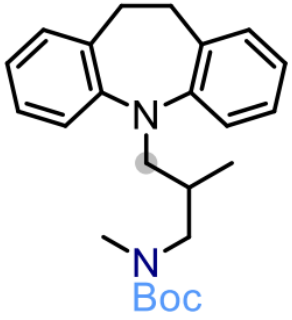




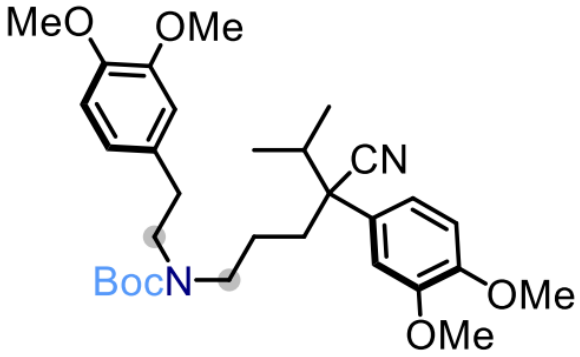
23, 61%
from Tropinone



27, 60%
from Dextromethorphan



29, 59% (4:1)[c,d]
from Trimipramine

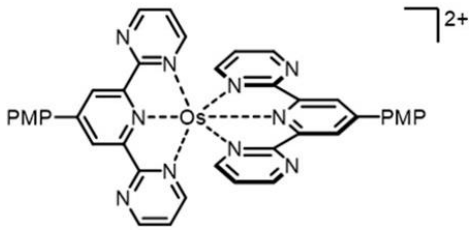


30, 64% (6:1:1)[c,d]
from Verapamil

Zhang, Xiao ; Shen, Yangyang; Rovis, Tomislav, *Photoinduced Nickel-Catalyzed Selective N-Demethylation of Trialkylamines Using C(sp2)–Bromides as HAT Reagents. J. Am. Chem. Soc. 2023, 145, 6, 3294–3300*

Os Phtotoredox Catalysis

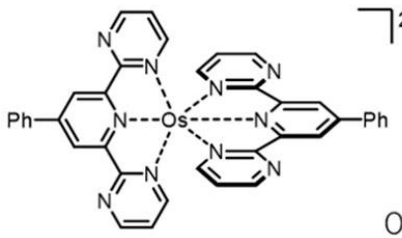
Reaction 16



$Os(bpm(pMeO)ppy)_2(PF_6)_2$
Os1

[Os(II)*]/[Os(I)]: 1.24V
[Os(II)]/[Os(I)]: -0.59V

[Os(II)*]/[Os(III)]: -0.42V
[Os(II)]/[Os(III)]: 1.37V

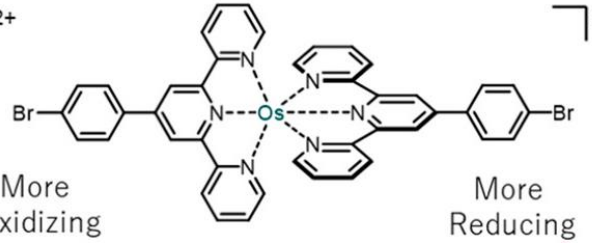


$Os(bpmppy)_2(PF_6)_2$
Os2

[Os(II)*]/[Os(I)]: 1.01V
[Os(II)]/[Os(I)]: -0.77V

[Os(II)*]/[Os(III)]: -0.52V
[Os(II)]/[Os(III)]: 1.25V

More Oxidizing

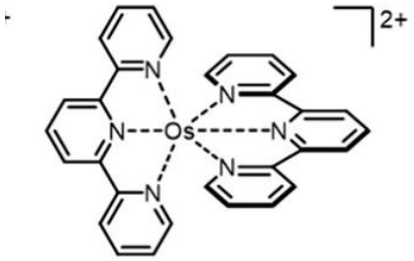


More Reducing

$Os(bptpy)_2(PF_6)_2$
Os3

[Os(II)*]/[Os(I)]: 0.93V
[Os(II)]/[Os(I)]: -0.82V

[Os(II)*]/[Os(III)]: -0.67V
[Os(II)]/[Os(III)]: 1.08 V



$Os(tpy)_2(PF_6)_2$
Os4

[Os(II)*]/[Os(III)]: -0.79V
[Os(II)]/[Os(III)]: 0.98V

[Os(II)*]/[Os(I)]: 0.57V
[Os(II)]/[Os(I)]: -1.20V

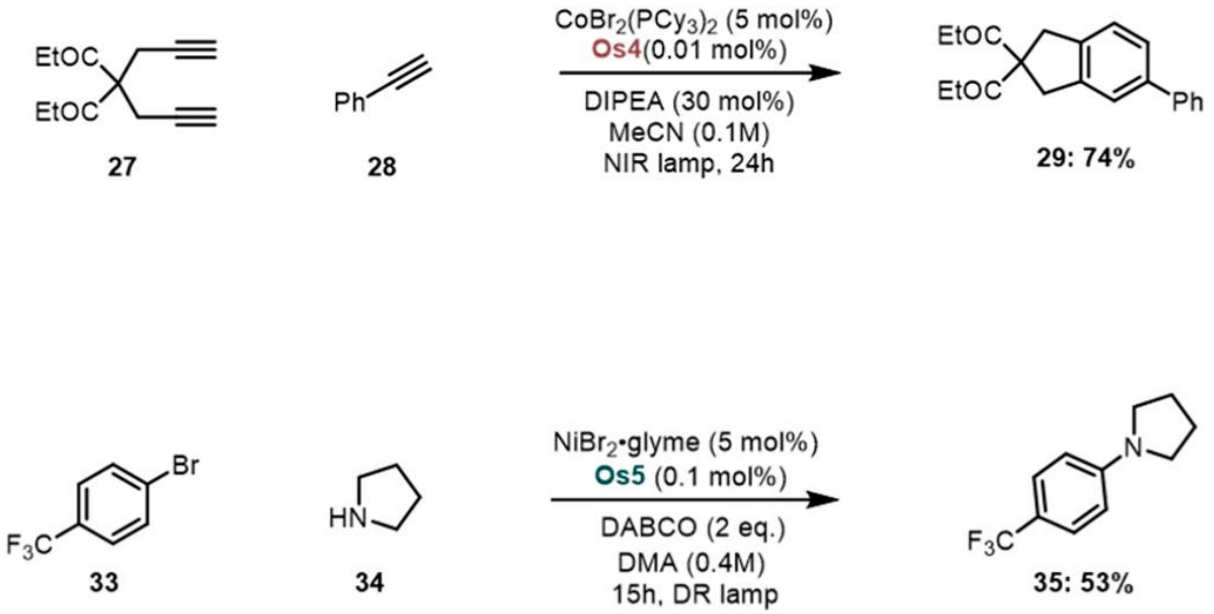
$Os(phen)_3(PF_6)_2$
Os5

[Os(II)*]/[Os(III)]: -0.90V
[Os(II)]/[Os(III)]: 0.90V

[Os(II)*]/[Os(I)]: 0.42V
[Os(II)]/[Os(I)]: -1.38V

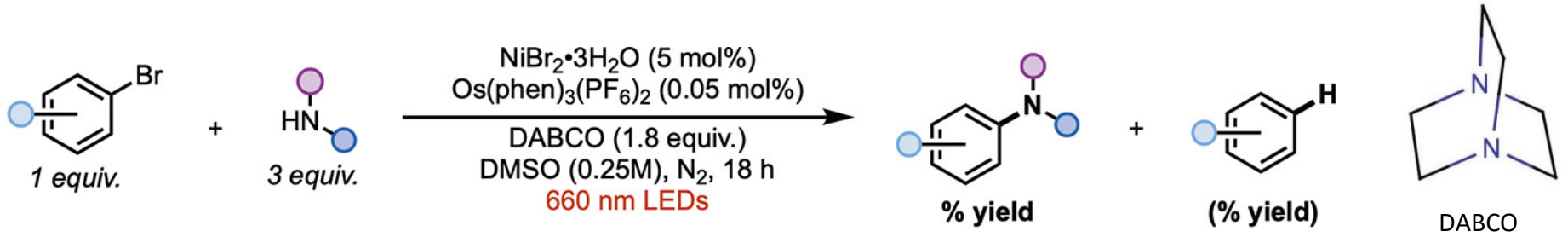
Ravetz, Benjamin D.; Tay, Nicholas E. S.; Joe, Candice L. ; Sezen-Edmonds, Melda ; Schmidt, Michael A. ; Tan, Yichen; Janey, Jacob M. ; Eastgate, Martin D. ; Rovis, Tomislav , *Development of a Platform for Near-Infrared Photoredox Catalysis. ACS Cent. Sci.* 2020, 6, 11, 2053−2059

Reaction 16 Application

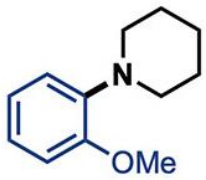


Ravetz, Benjamin D.; Tay, Nicholas E. S.; Joe, Candice L. ; Sezen-Edmonds, Melda ; Schmidt, Michael A. ; Tan, Yichen; Janey, Jacob M. ; Eastgate, Martin D. ; Rovis, Tomislav *, Development of a Platform for Near-Infrared Photoredox Catalysis. ACS Cent. Sci.* 2020, 6, 11, 2053−2059

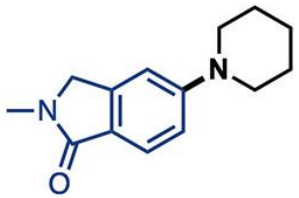
Reaction 17



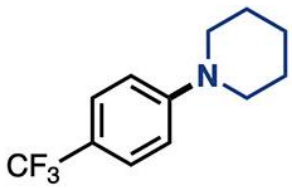
(2)
92% (n.d.)



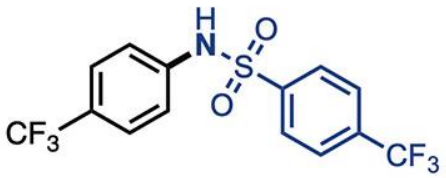
(16)
50% (n.d.)



(18)
97% (n.d.)



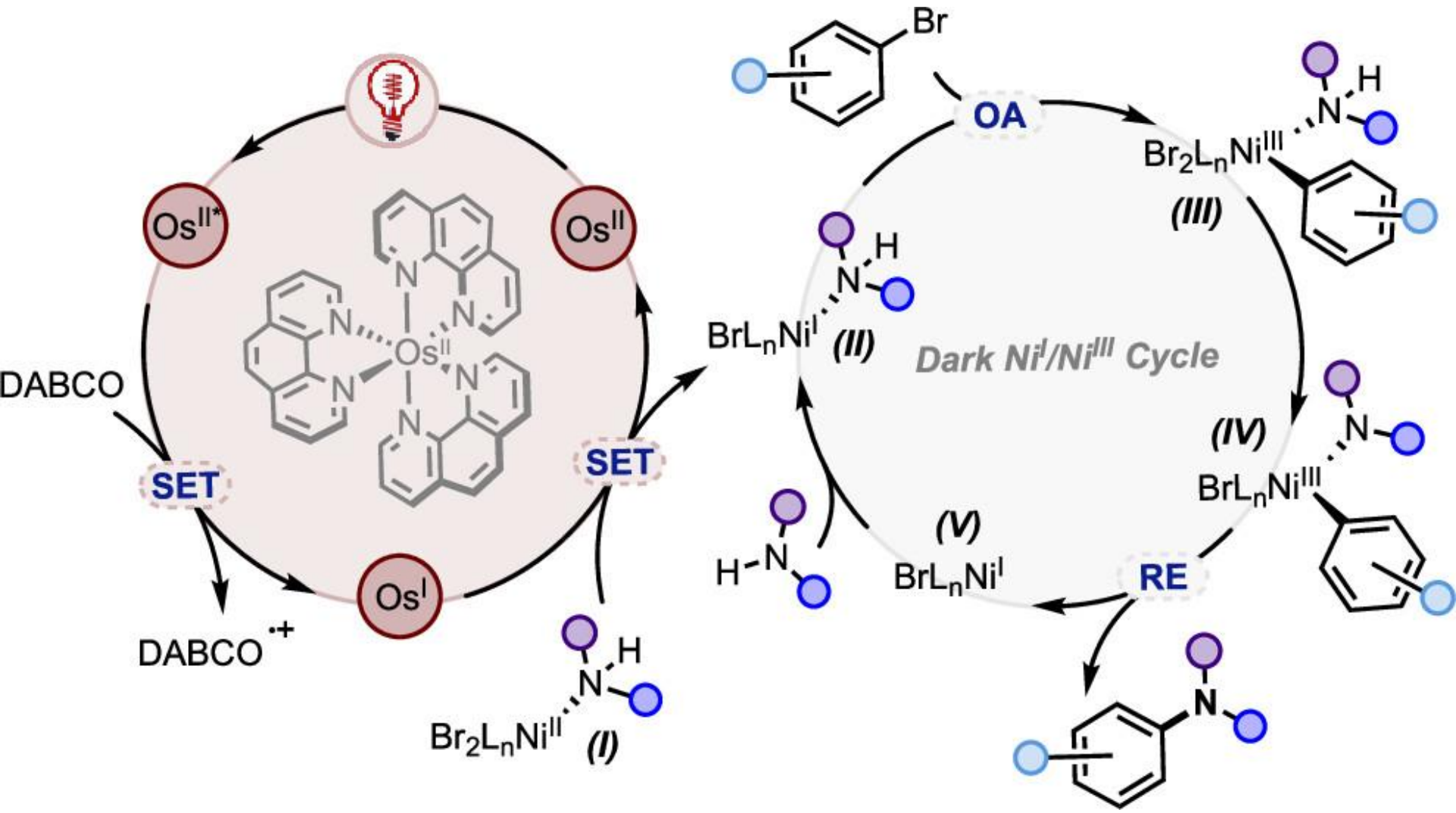
(28)
72% (n.d.)



(41)
60%[e] (n.d.)

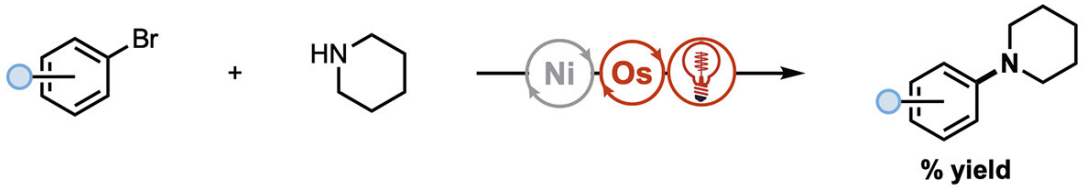
Goldschmid, Samantha L.; Soon Tay, Nicholas Eng; Joe, Candice L. ; Lainhart, Brendan C.; Sherwood, Trevor C. ; Simmons, Eric M. ; Sezen-Edmonds, Melda ; Rovis, Tomislav , *Overcoming Photochemical Limitations in Metallaphotoredox Catalysis: Red-Light-Driven C–N Cross-Coupling. J. Am. Chem. Soc.* 2022, 144, 49, 22409−22415

Reaction 17 Mechanism

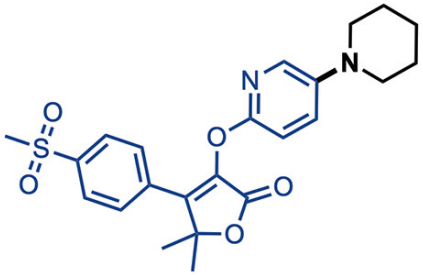


Goldschmid, Samantha L.; Soon Tay, Nicholas Eng; Joe, Candice L. ; Lainhart, Brendan C.; Sherwood, Trevor C. ; Simmons, Eric M. ; Sezen-Edmonds, Melda ; Rovis, Tomislav , *Overcoming Photochemical Limitations in Metallaphotoredox Catalysis: Red-Light-Driven C–N Cross-Coupling. J. Am. Chem. Soc.* 2022, 144, 49, 22409−22415

Reaction 17 Application



drug-like scaffolds



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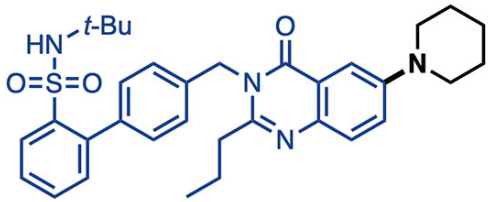

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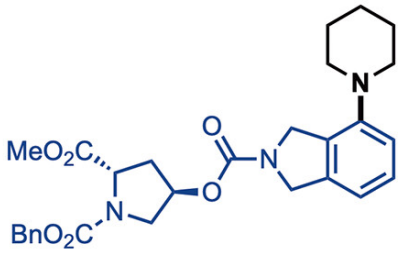
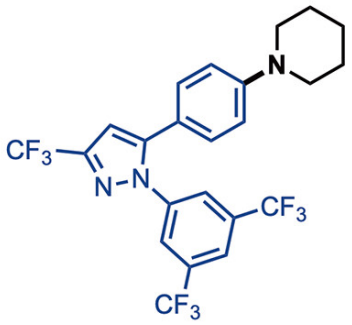


(45)
41%



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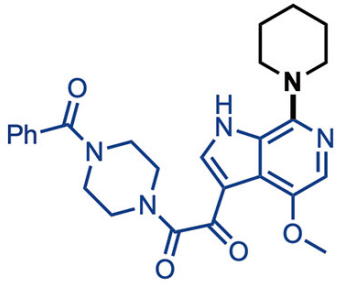

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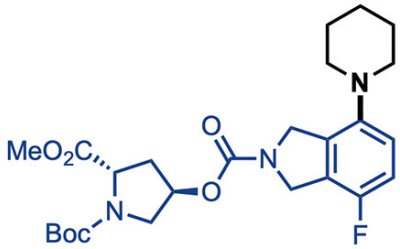

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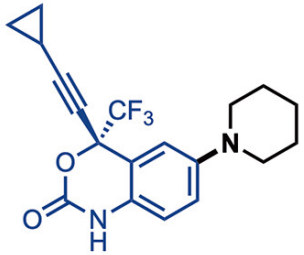

(49)
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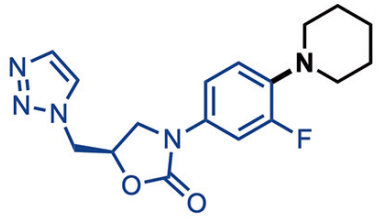
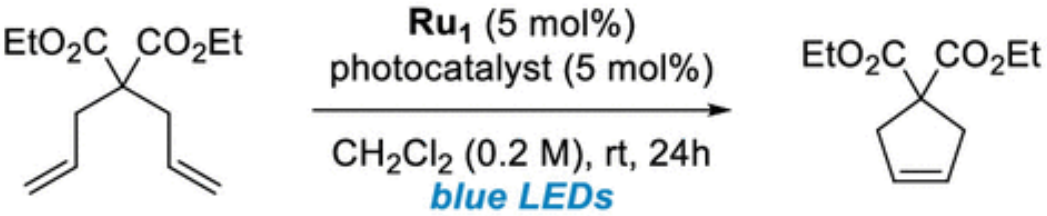


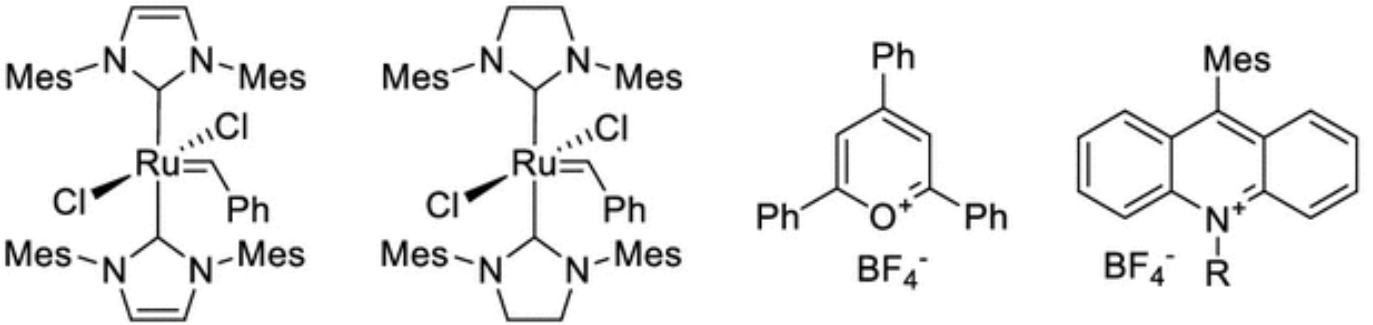
(50)
27%

Goldschmid, Samantha L.; Soon Tay, Nicholas Eng; Joe, Candice L. ; Lainhart, Brendan C.; Sherwood, Trevor C. ; Simmons, Eric M. ; Sezen-Edmonds, Melda ; Rovis, Tomislav , *Overcoming Photochemical Limitations in Metallaphotoredox Catalysis: Red-Light-Driven C–N Cross-Coupling. J. Am. Chem. Soc.* 2022, 144, 49, 22409−22415

Reaction 18 Background

(a) Reaction optimization





$RuCl_2(CHPh)(IMes)_2$ (**Ru_1**)

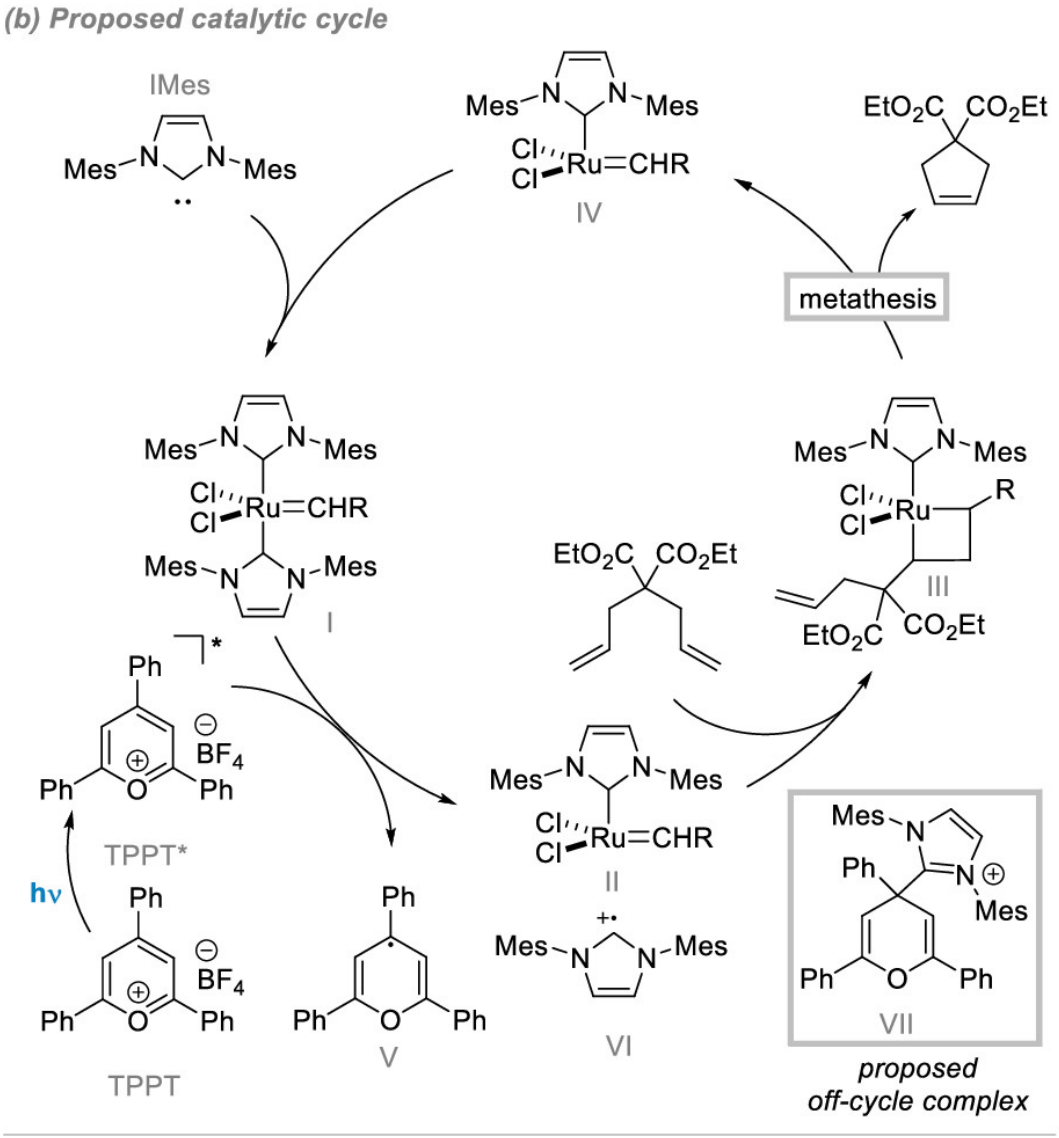
$RuCl_2(CHPh)(SIMes)_2$ (**Ru_2**)

TPPT

MesAcrPh (R=Ph)
MesAcrMe (R=Me)

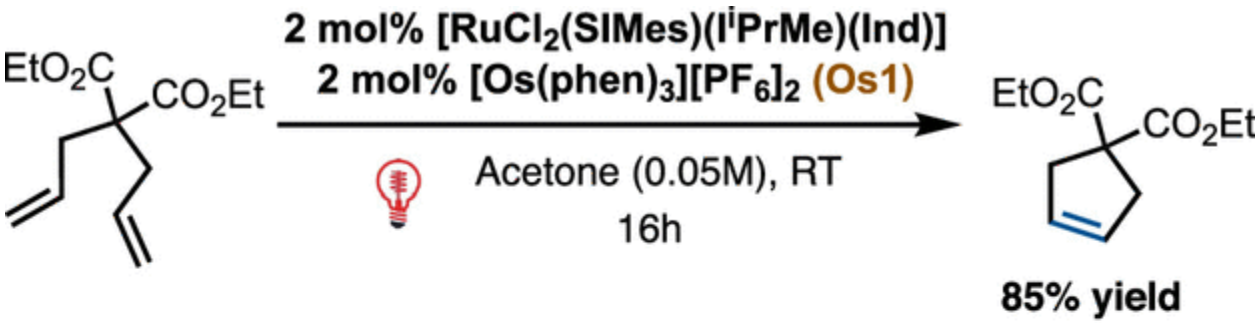
Theunissen, Cedric; Ashley, Melissa A.; Rovis, Tomislav, *Visible-light-controlled ruthenium-catalyzed olefin metathesis. J. Am. Chem. Soc.* 2019, 141, 17, 6791−6796.

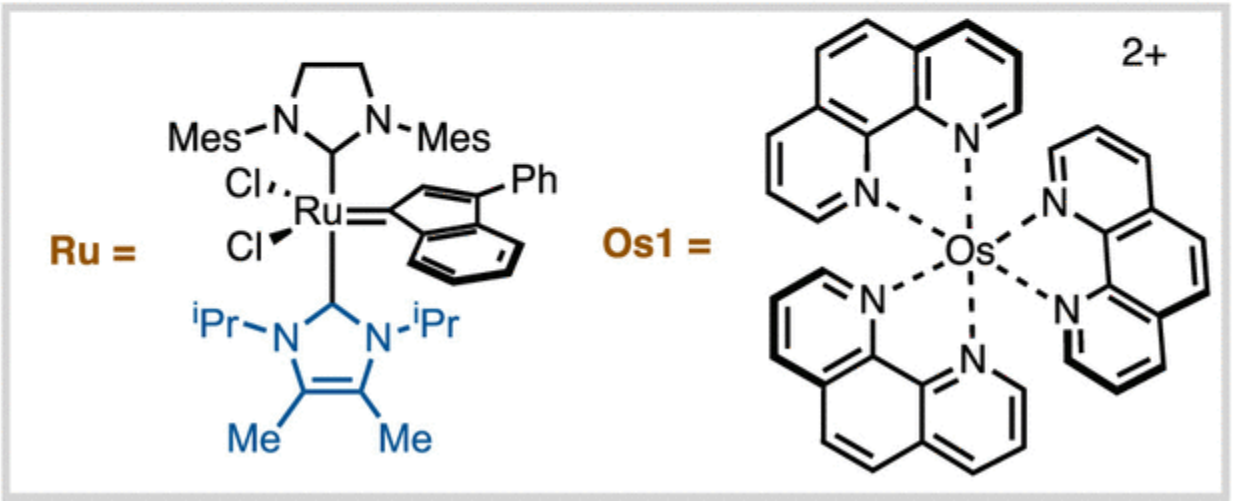
Reaction 18 Background



Theunissen, Cedric; Ashley, Melissa A.; Rovis, Tomislav, *Visible-light-controlled ruthenium-catalyzed olefin metathesis. J. Am. Chem. Soc.* 2019, 141, 17, 6791−6796.

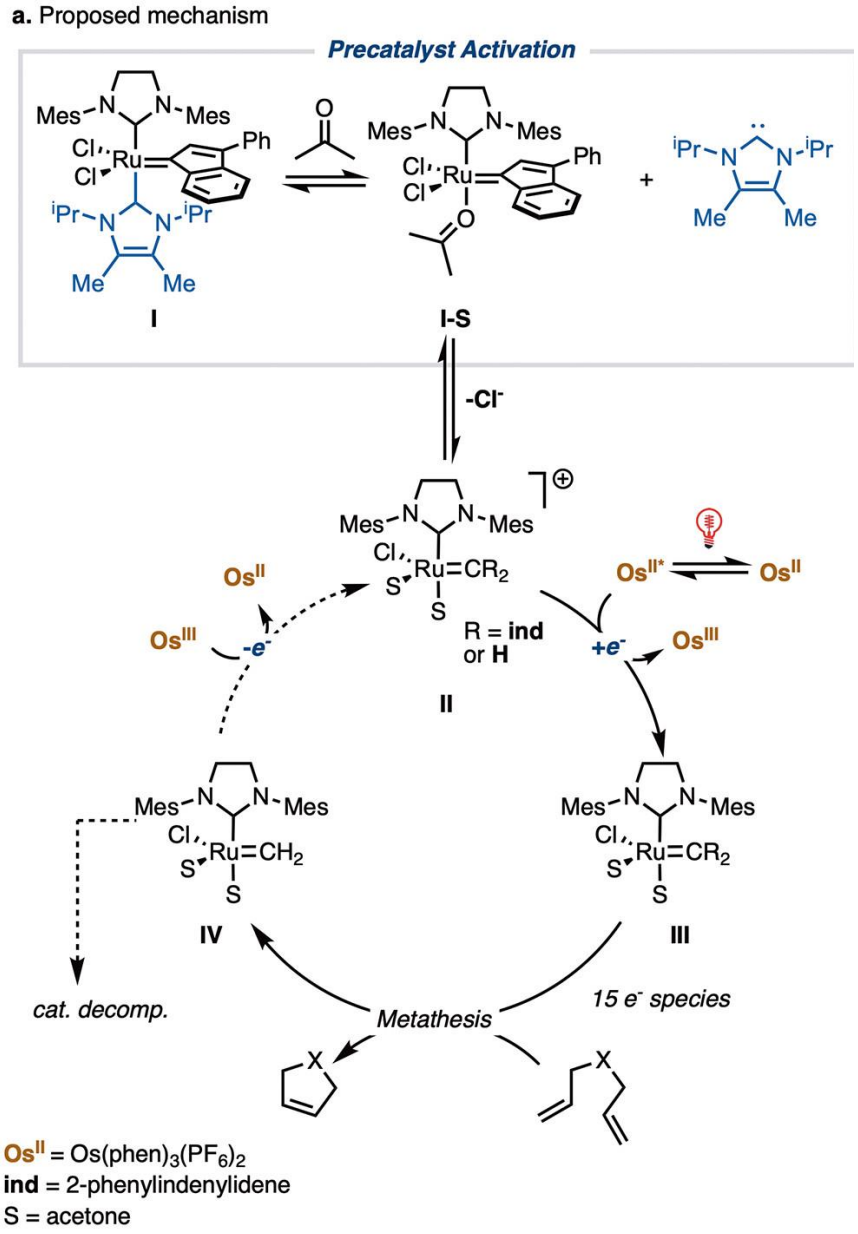
Reaction 18





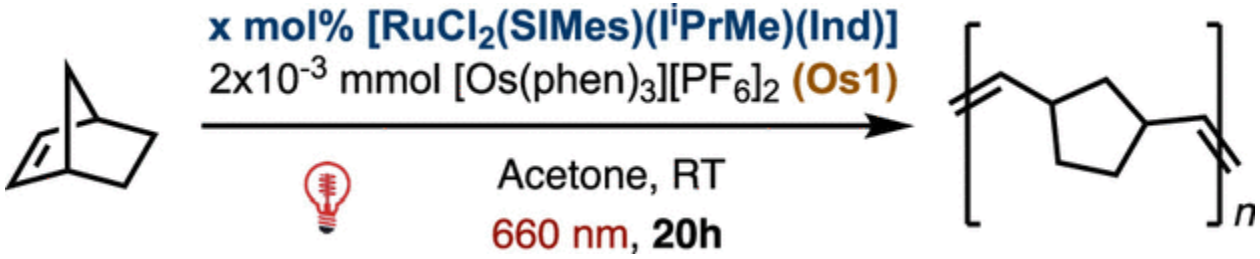
Cabanero, David C.; Nguyen, Jennifer A.; Cazin, Catherine S. J. ; Nolan, Steven P. ; Rovis, Tomislav , *Deep Red to Near-Infrared Light-Controlled Ruthenium-Catalyzed Olefin Metathesis. ACS Catal.* 2023, 13, 7, 4384−4390.

Reaction 18 Mechanism

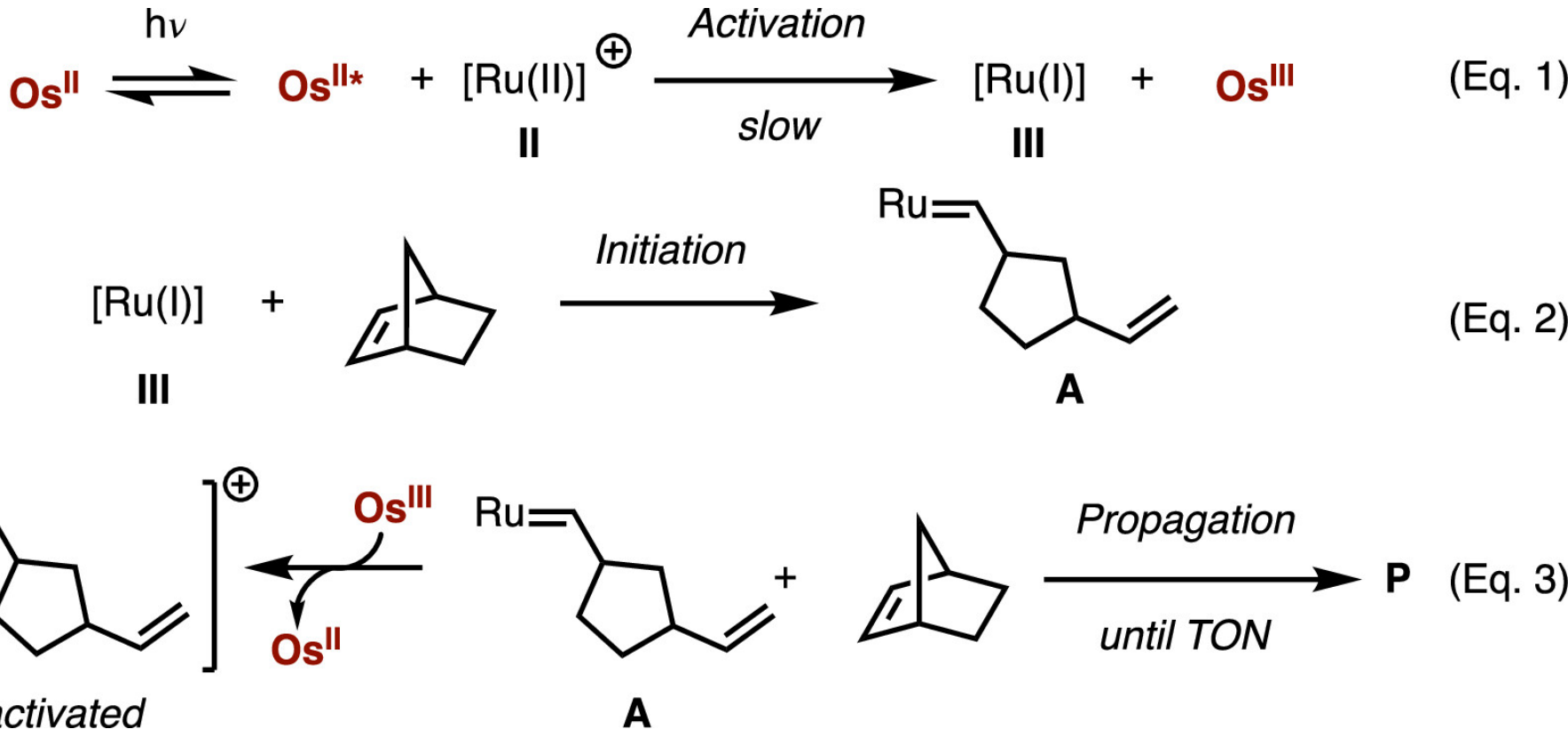


Cabanero, David C.; Nguyen, Jennifer A.; Cazin, Catherine S. J. ; Nolan, Steven P. ; Rovis, Tomislav , *Deep Red to Near-Infrared Light-Controlled Ruthenium-Catalyzed Olefin Metathesis. ACS Catal.* 2023, 13, 7, 4384−4390.

Reaction 18 Application



Mechanism



Cabanero, David C.; Nguyen, Jennifer A.; Cazin, Catherine S. J. ; Nolan, Steven P. ; Rovis, Tomislav , *Deep Red to Near-Infrared Light-Controlled Ruthenium-Catalyzed Olefin Metathesis. ACS Catal.* 2023, 13, 7, 4384−4390.

Reaction 19 Background

a

Aryl Azide

$h\nu$
(350 – 450 nm)

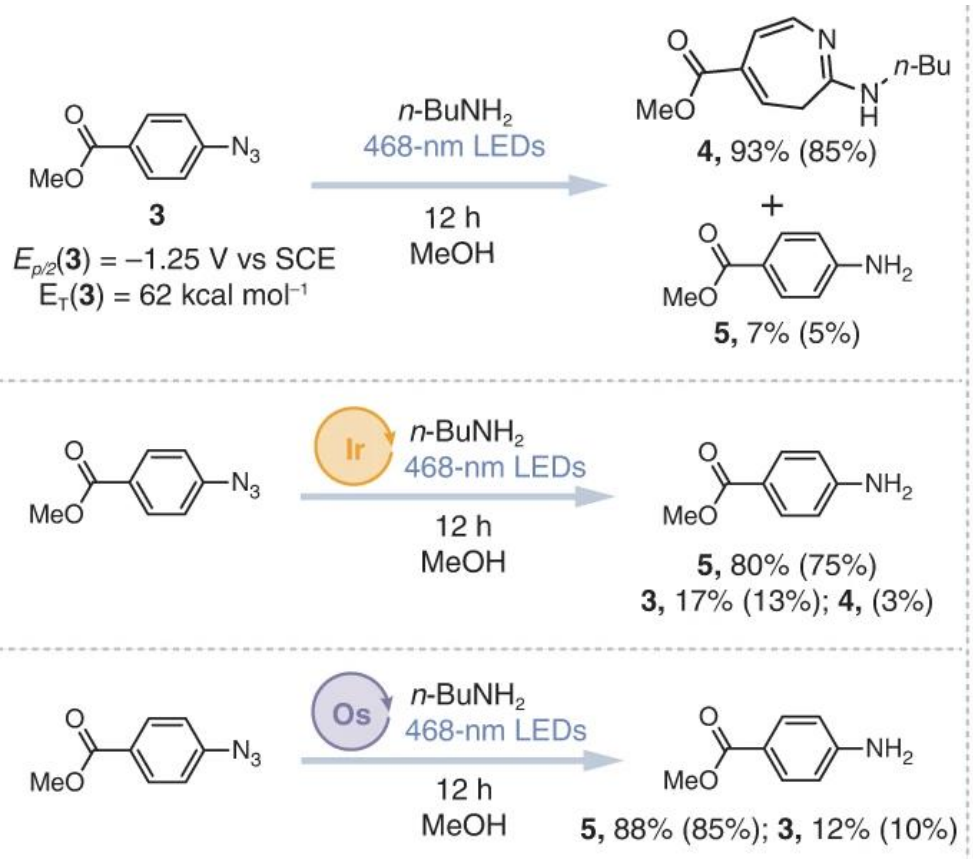
- Photoaffinity labelling
- Photo uncaging
- Photo-induced protein conjugation

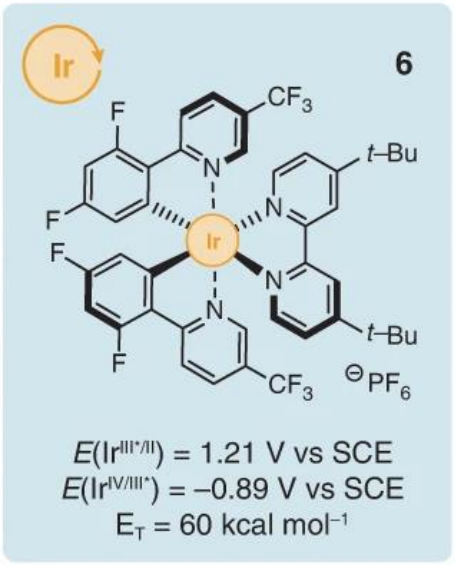
Limitations

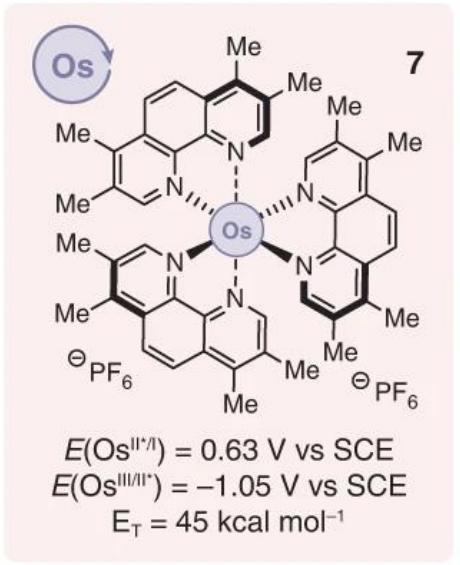
- *Non-selective labelling*
- *Requires high energy light*
- *No localized activation (i.e. biological microenvironments)*

Tay, Nicholas Eng Soon; Ryu, Keun Ah; Weber, John L.; Olow, Aleksandra K.; Cabanero, David C.; Reichman, David R.; Oslund, Rob C. ; Fadeyi, Olugbeminiyi O. ; Rovis, Tomislav , *Targeted activation in localized protein environments via deep red photoredox catalysis. Nature Chemistry*. 15, 101−109 (2023)

Reaction 19

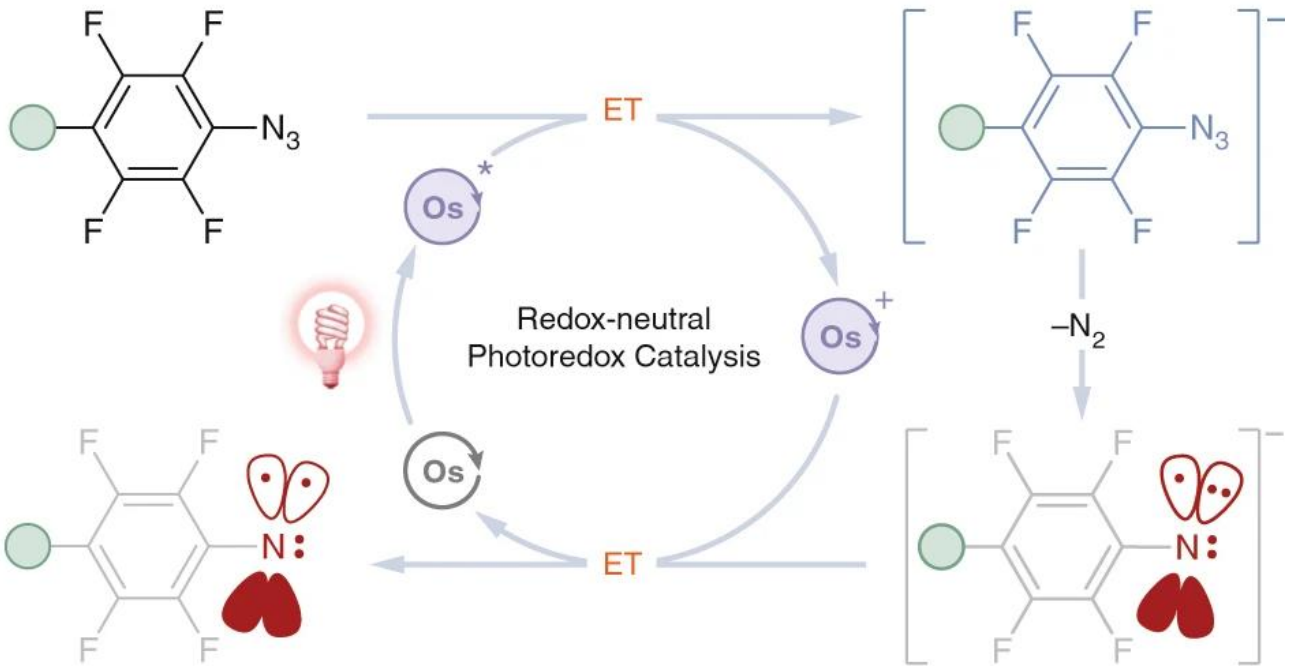






Tay, Nicholas Eng Soon; Ryu, Keun Ah; Weber, John L.; Olow, Aleksandra K.; Cabanero, David C.; Reichman, David R.; Oslund, Rob C. ; Fadeyi, Olugbeminiyi O. ; Rovis, Tomislav , *Targeted activation in localized protein environments via deep red photoredox catalysis. Nature Chemistry*. 15, 101−109 (2023)

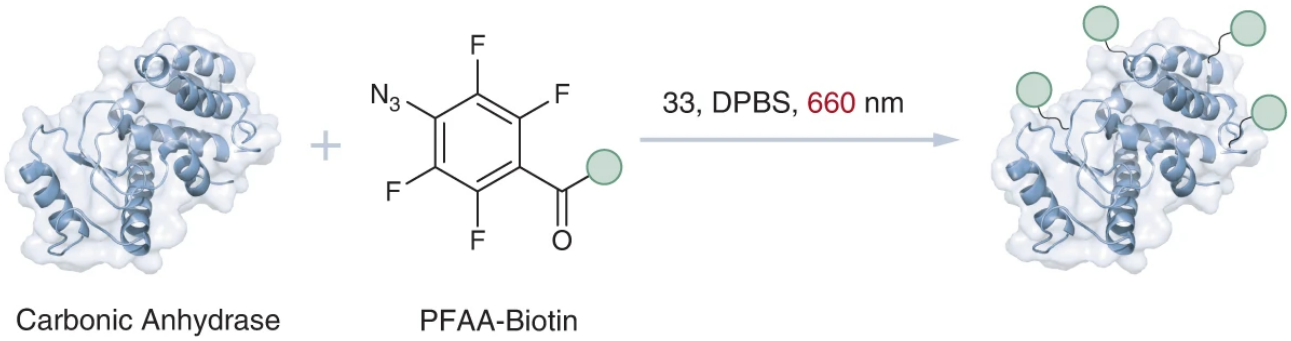
Reaction 19 Mechanism

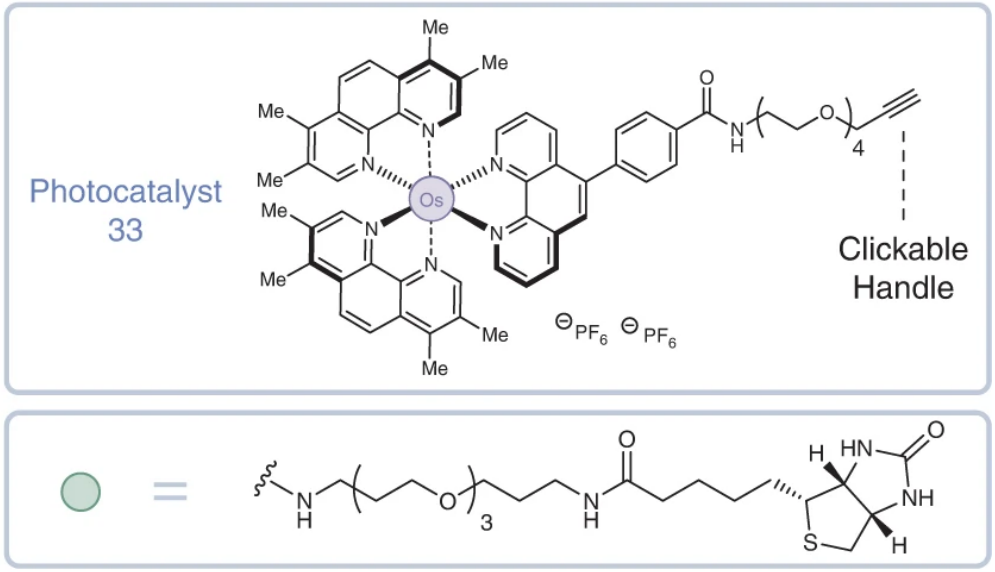


Tay, Nicholas Eng Soon; Ryu, Keun Ah; Weber, John L.; Olow, Aleksandra K.; Cabanero, David C.; Reichman, David R.; Oslund, Rob C. ; Fadeyi, Olugbeminiyi O. ; Rovis, Tomislav , *Targeted activation in localized protein environments via deep red photoredox catalysis. Nature Chemistry*. 15, 101−109 (2023)

Reaction 19 Application

a





Tay, Nicholas Eng Soon; Ryu, Keun Ah; Weber, John L.; Olow, Aleksandra K.; Cabanero, David C.; Reichman, David R.; Oslund, Rob C. ; Fadeyi, Olugbeminiyi O. ; Rovis, Tomislav , *Targeted activation in localized protein environments via deep red photoredox catalysis. Nature Chemistry*. 15, 101−109 (2023)

Thanks!