Highlights from Top Pre-Tenure Faculty

"Behind one door is tenure - behind the other is flipping burgers at McDonald's."

Jennifer Alleva
MacMillan Group Meeting
May 2nd 2012

Who is Pre-tenure in Chemistry in the United States

Demographics

- Who are the assistant professors in the top 50 chemistry departments?

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85% of assistant chemistry professors are male

15% are female

14% were not trained in the U.S.

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15% are female

14% were not trained in the U.S.

- Who are the assistant professors in the top 10 chemistry departments?

Currently 16 pre-tenure faculty

13 of these assistant professors are male

2 of these assistant professors were not trained in the U.S.

3 of these assistant professors are women

Where were these Assistant Professors Trained

Demographics

- Which institutions trained these current assistant faculty?

80% of assistant chemistry professors were trained at a top 10 department

Caltech Harvard MIT Berkeley UIUC Northwestern Stanford Scripps UW Madison Columbia Cornell

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Larry Overman

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- 6 Students pre-tenure as of April 2012

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Bob Grubbs
Amir Hoveyda
Patrick Walsh
Reza Ghadiri
Dave Evans
Samuel Danishefsky

- 4 Students pre-tenure as of April 2012

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95 pre-tenure faculty currently in organic chemistry

53 within Organic Synthesis and Methodology

23 Chemical Biology

19 Organic Materials

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- What are assistant professors studying at the top 10 departments?

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What does this information indicate for the future of organic chemistry?

How to select the top 5 pre-tenure faculty

- Criteria:
  - United States institutions
  - Limiting survey to organic chemists
  - Must have published papers to define the goals of their program
  - No MacMillan group alumni or Princeton Chemistry faculty

Highlights from top Pre-tenure Faculty

Sarah Reisman

Caltech

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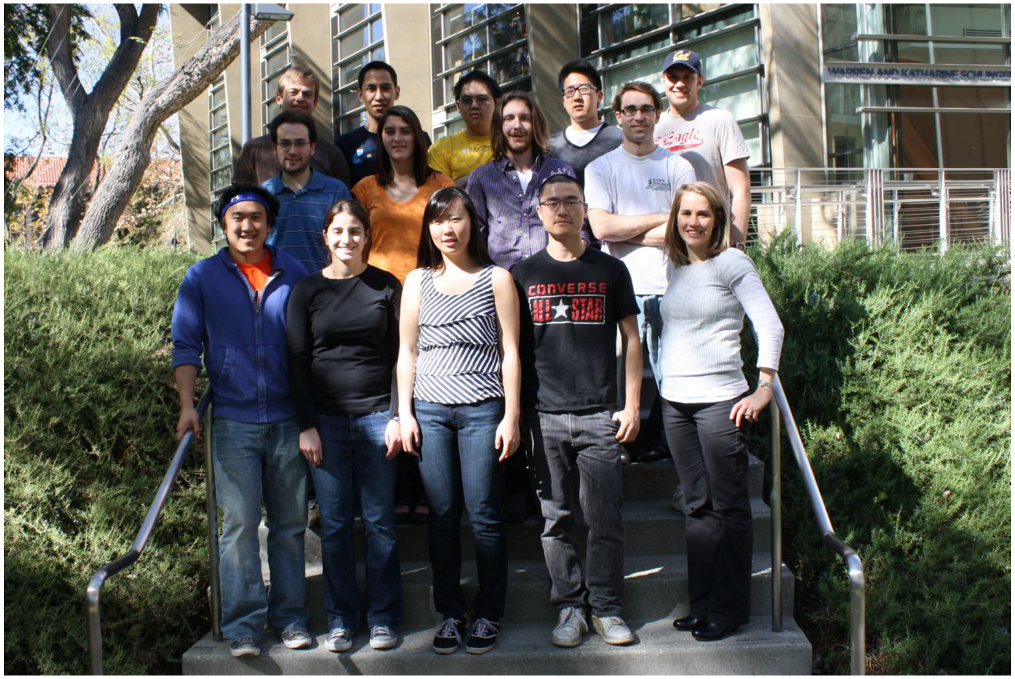
Caltech



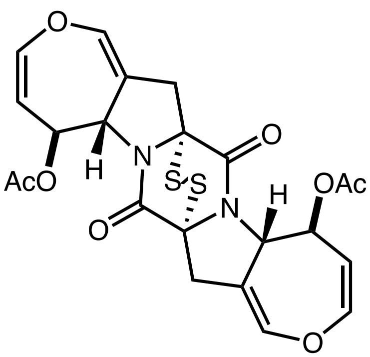
- Caltech 2008-present
- Ph.D. with John Wood on the total synthesis of Welwitindolinone A Isonitrile
- Postodoctoral studies with Eric Jacobsen on thiourea catalyzed additions to oxocarbenium ions

Reisman, S.E.; Ready, J.M.; Weiss, M.M.; Hasuoka, A.; Tamaki, K.; Ovaska, T.V.; Wood, J.L. *J. Am. Chem. Soc.* **2008**, *130*, 2087
Reisman, S.E.; Doyle, A.G.; Jacobsen, E.N. *J. Am. Chem. Soc.* **2008**, *130*, 7198

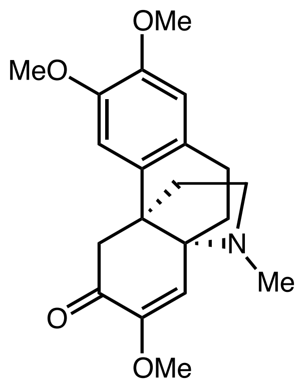
Research in the Reisman Lab

Total synthesis and synthetic methodology

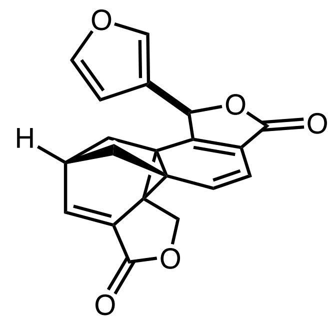
Total synthesis of complex natural products



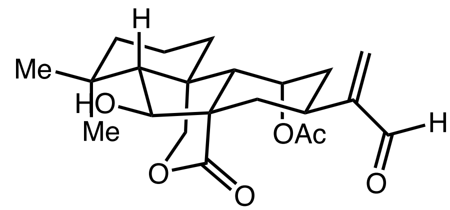
(–)-Acetylaranotin



(–)-8-Demethoxyrunanine



(+)-Salvileucalin B



(–)-Maoecrystal Z

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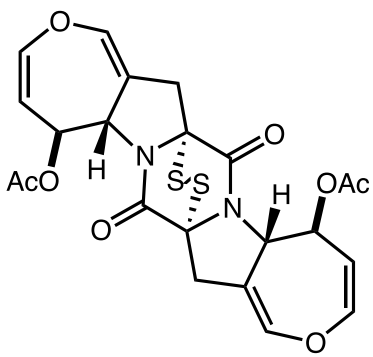

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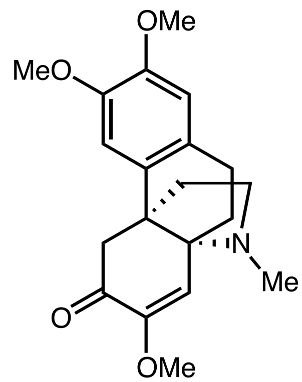

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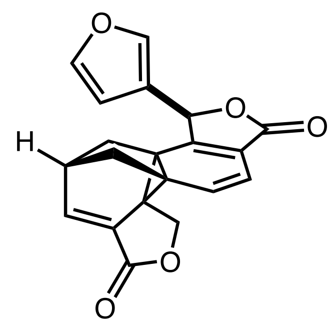

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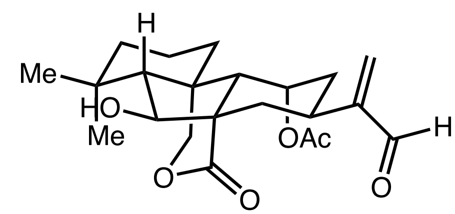

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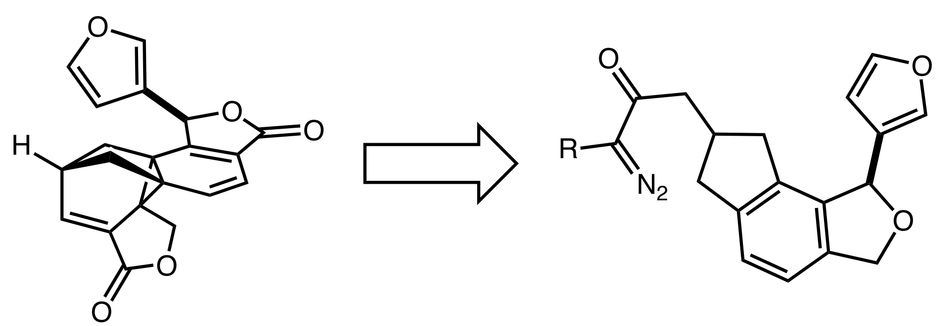
Revival of the Buchner reaction for the synthesis of cyclopropane rings



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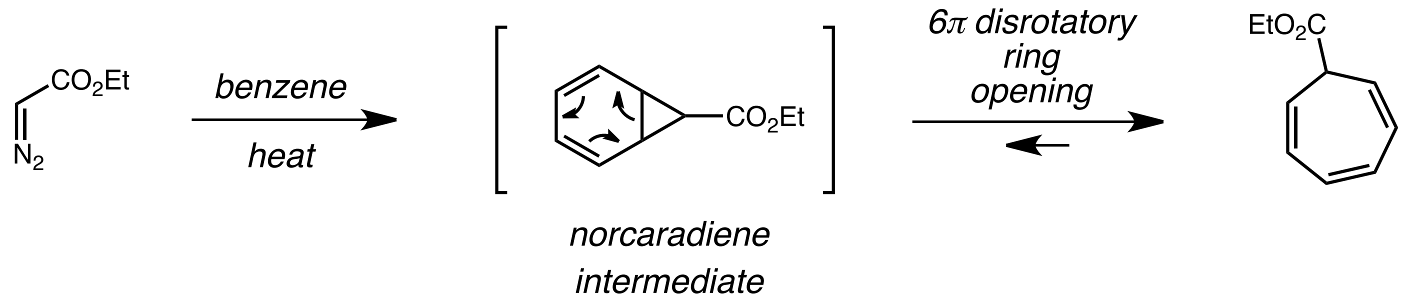
The Buchner Reaction for Natural Product Synthesis

Intercepting the norcaradiene intermediate

Buchner reaction for the formation of 7-membered rings



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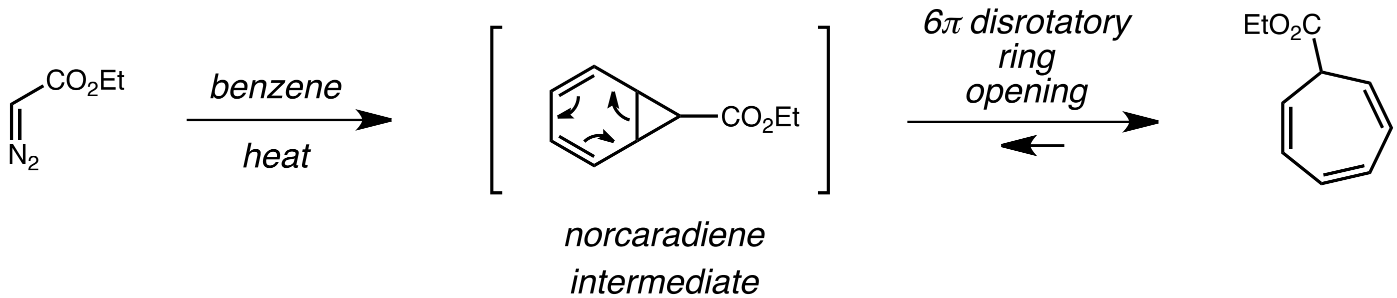
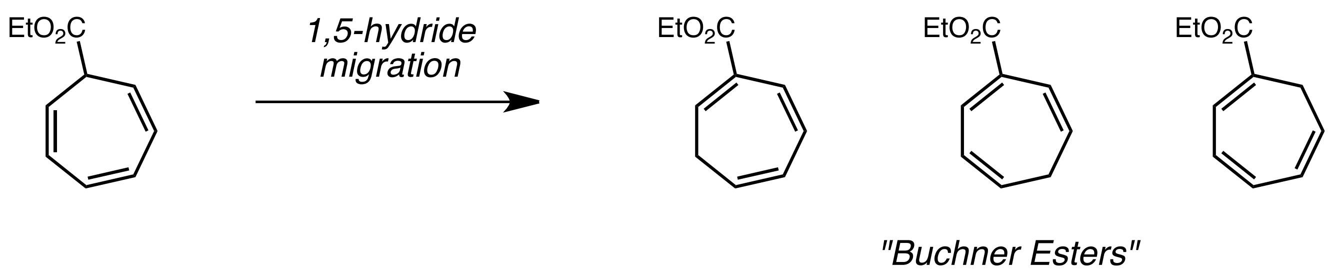


Isomerization of cycloheptatriene provides a thermodynamic mixture



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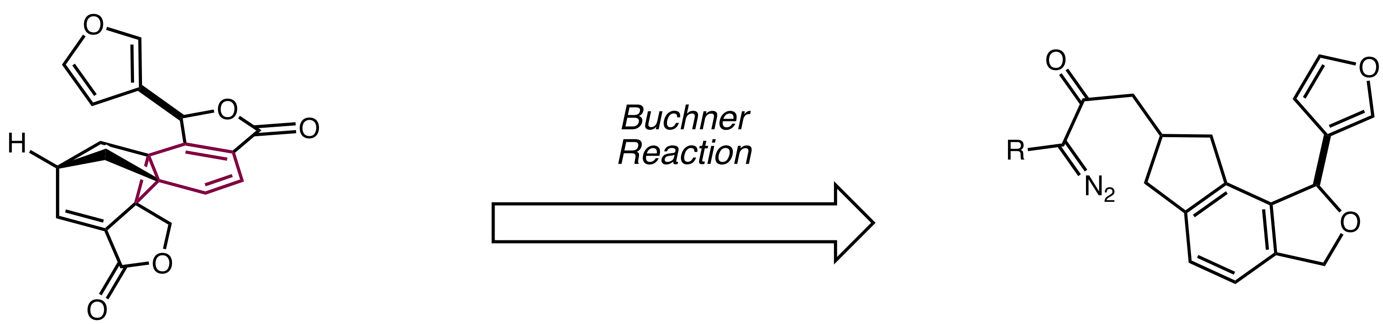
■ Retrosynthesis of Salvileucalin B



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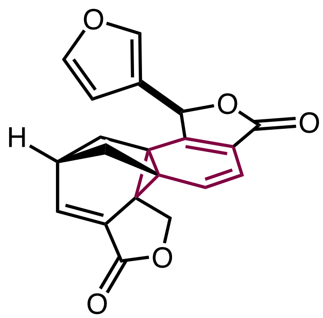

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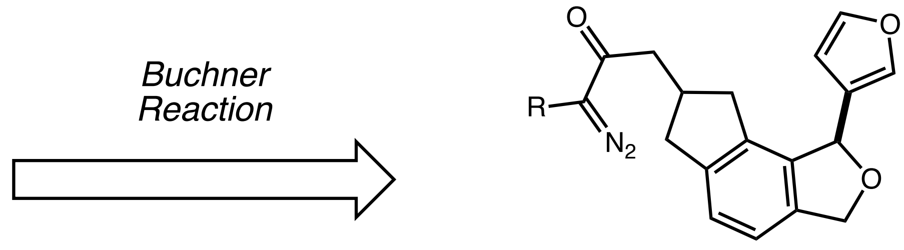

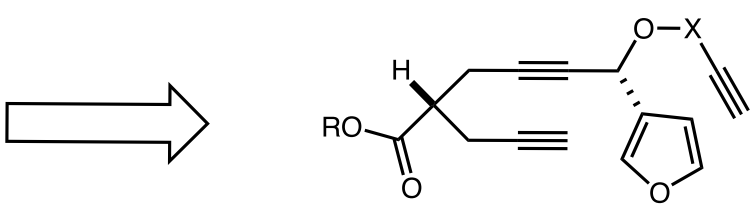

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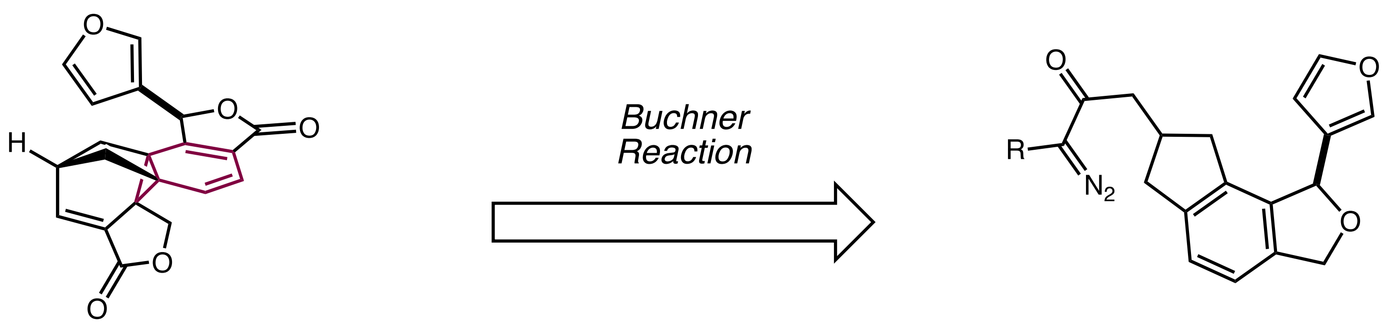

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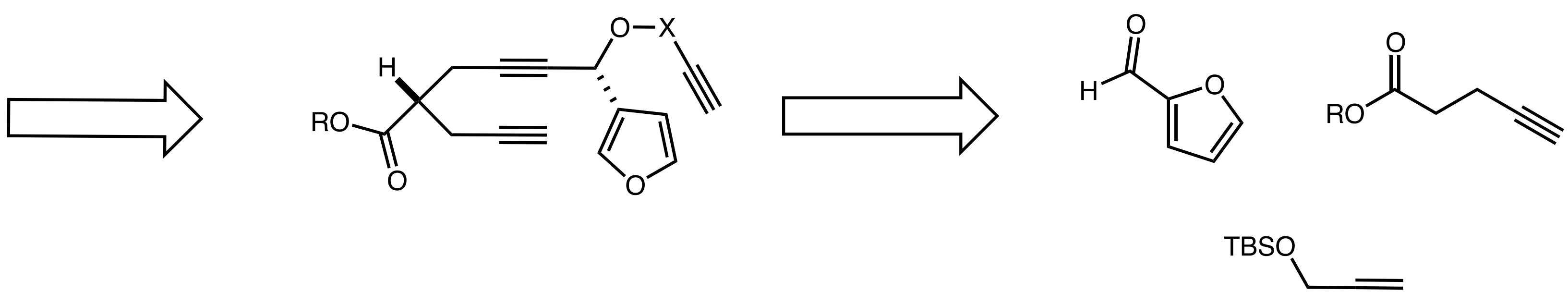

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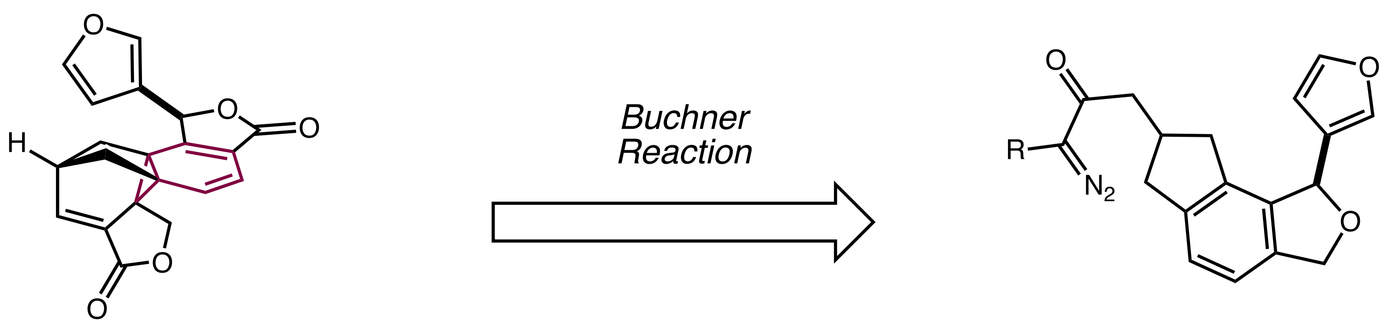

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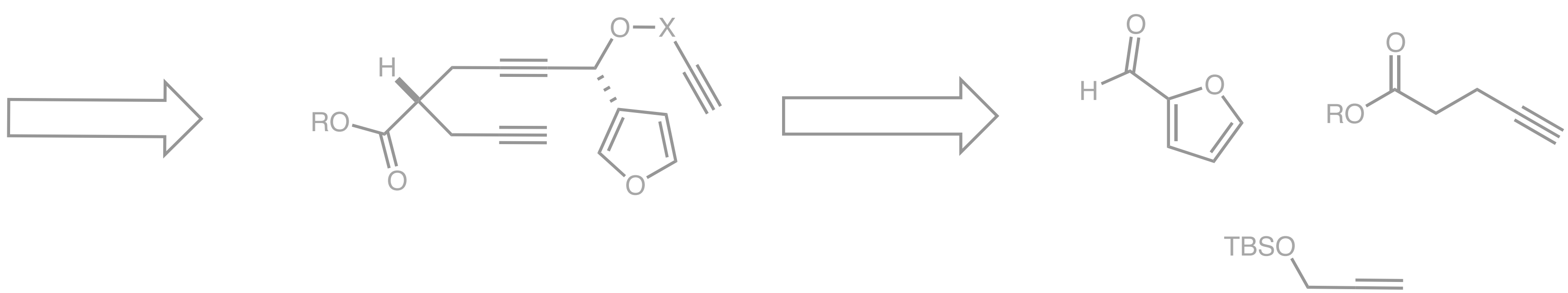

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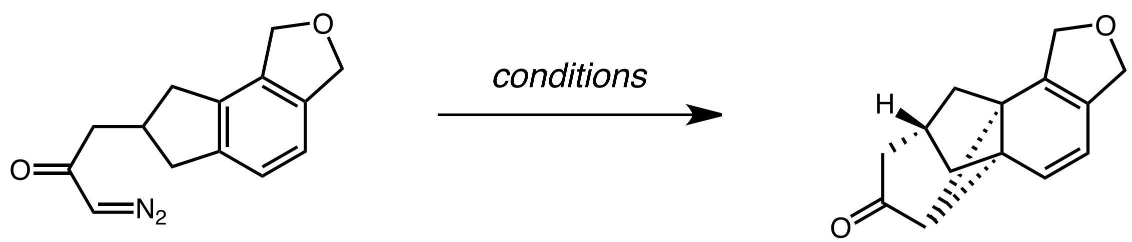

entry	catalyst	yield (%)
1	$Rh(OAc)_4$	14
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3	$Rh(tfa)_4$	5

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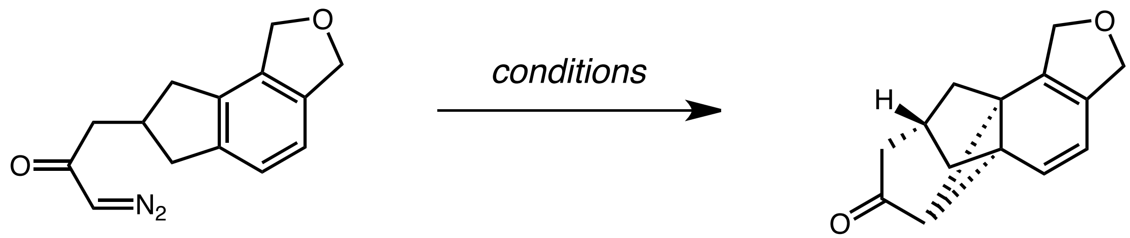

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4	$Cu(acac)_2$	30
5	$Cu(tfacac)_2$	50 (73)*
6	$Cu(hfacac)_2$	40
7	$Cu(TMHD)_2$	28
8	$Cu(TBS)_2$	11

*Isolated yield, slow addition of a-diazoketone

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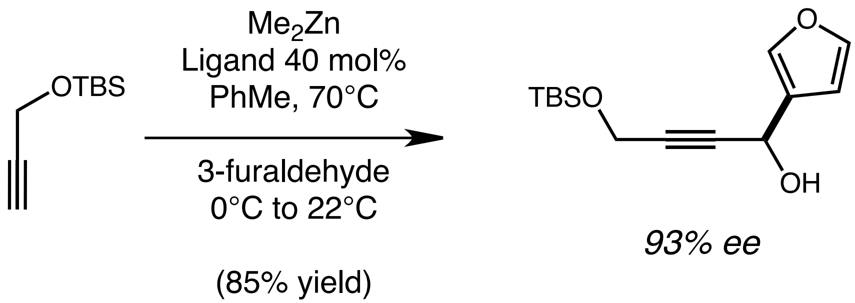
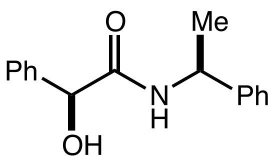
Enantioselective Total Synthesis of Salvileucalin B

Synthesis of triyne precurser

Enantioselective synthesis of cycloisomerization precurser





chiral ligand

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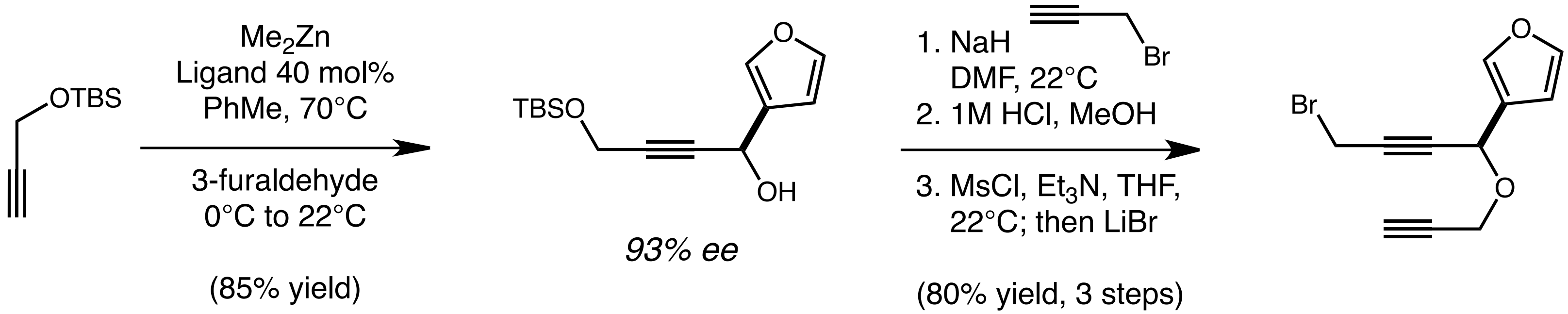

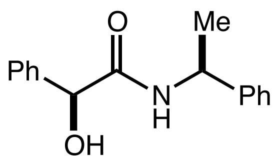

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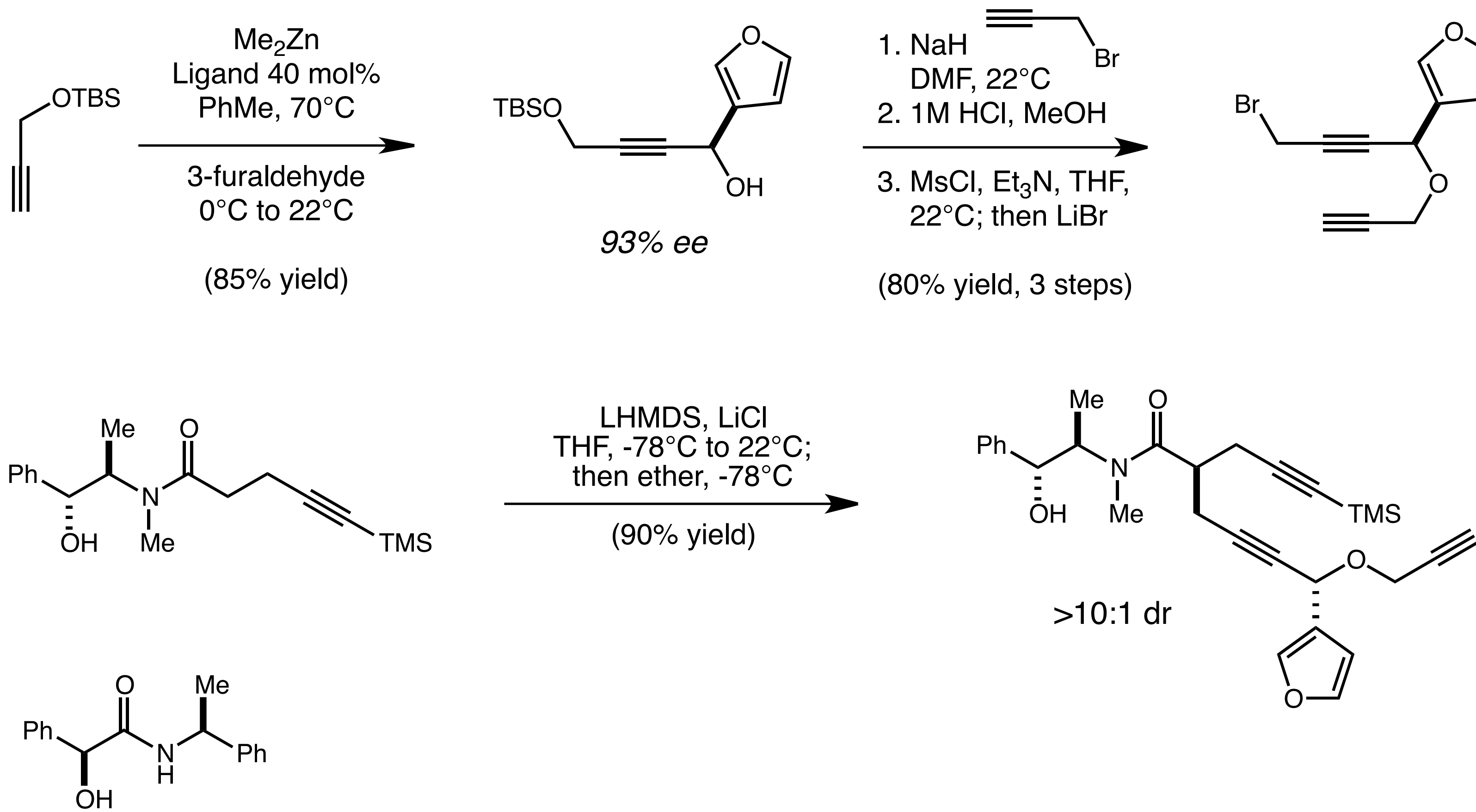

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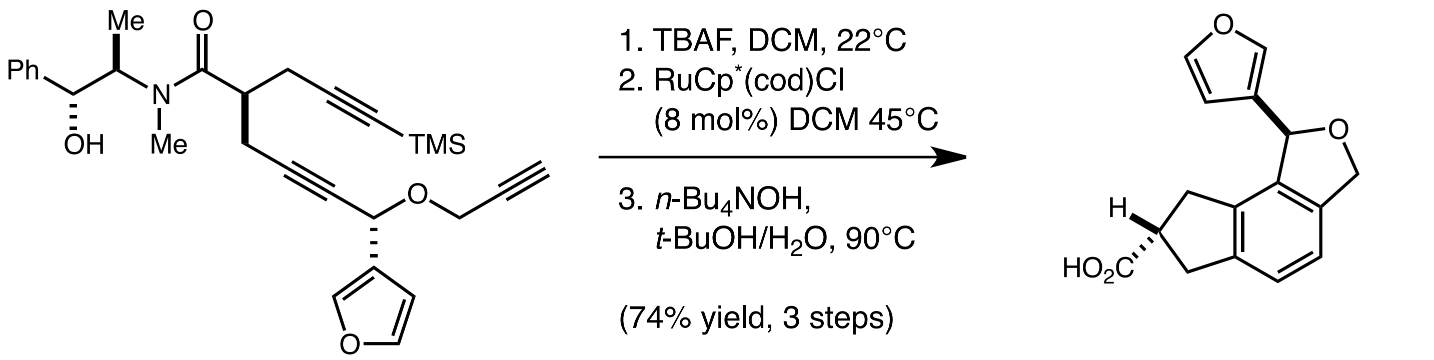

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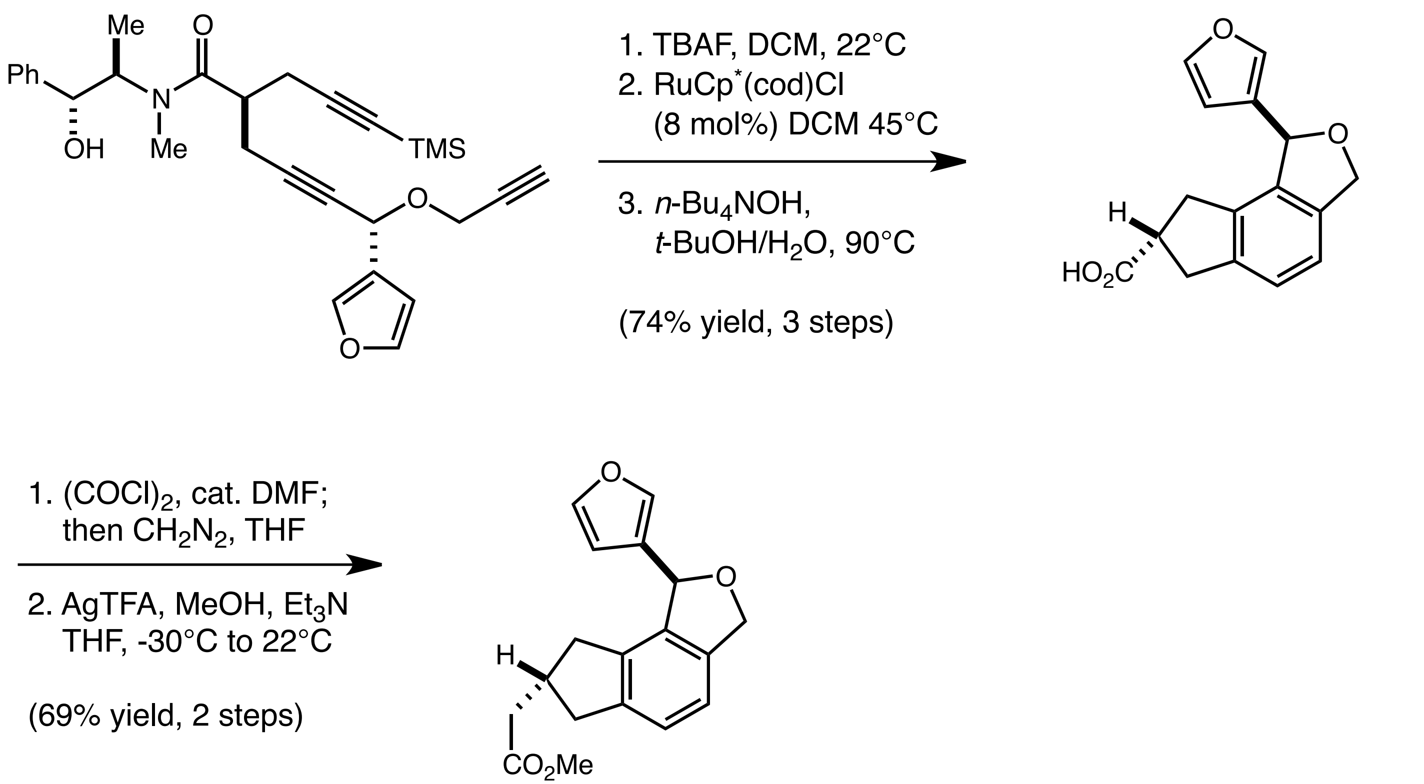

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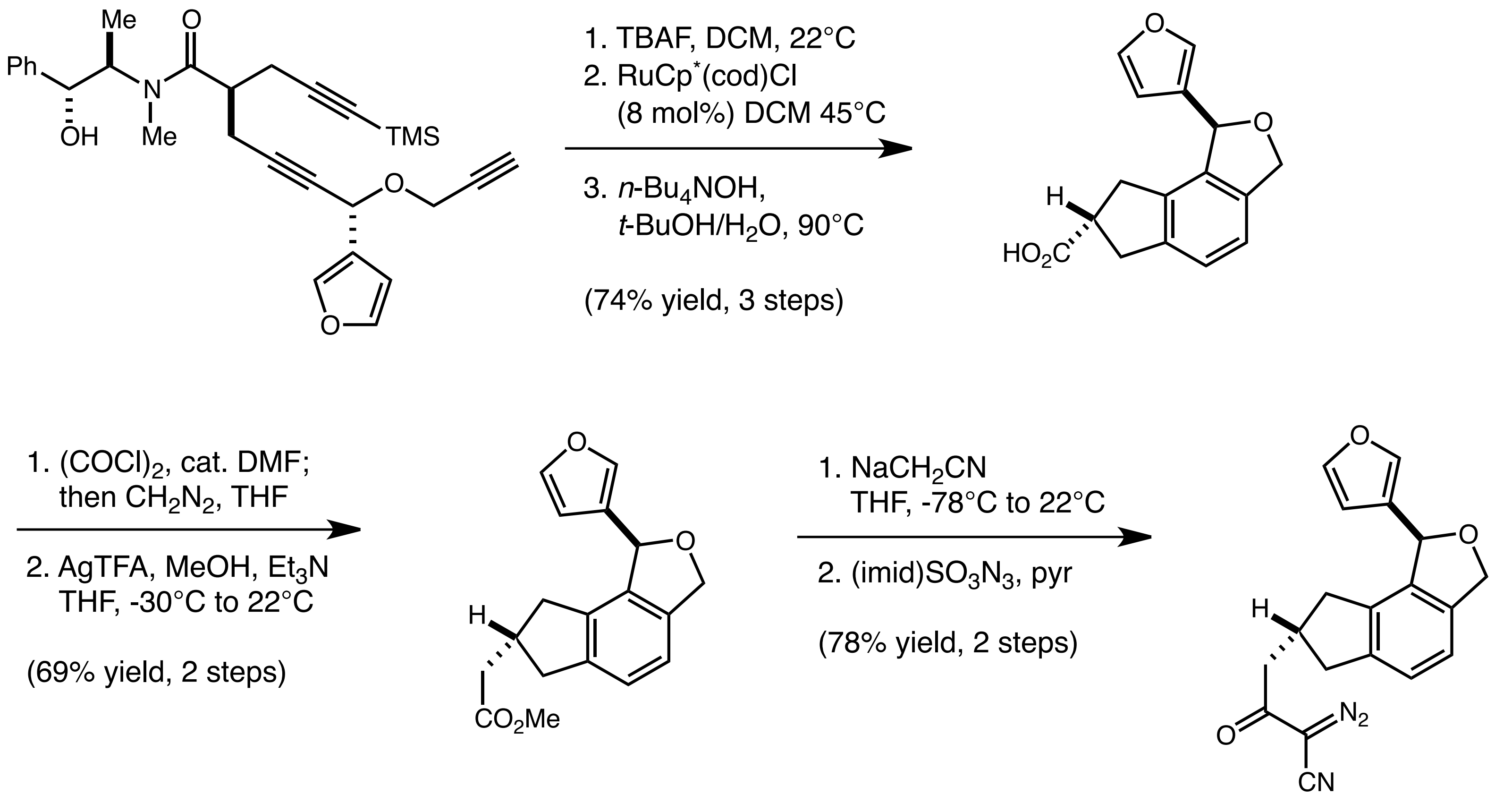

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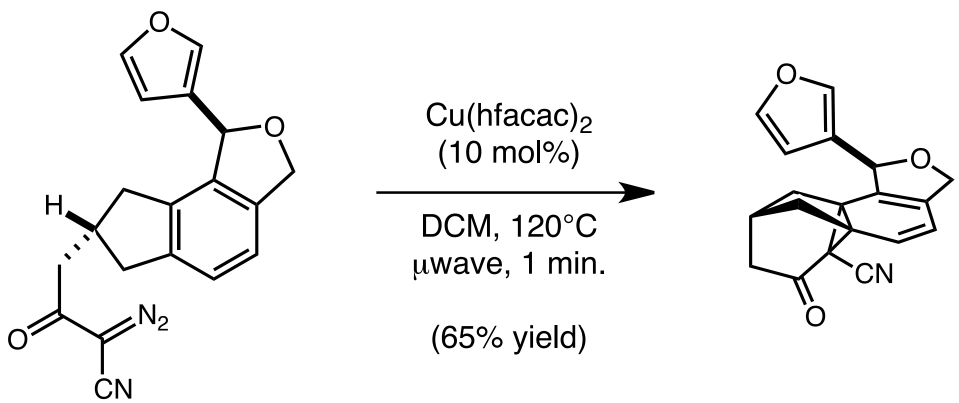
Synthesis of Norcaradiene Core

■ Application of Cu-mediated Buchner reaction



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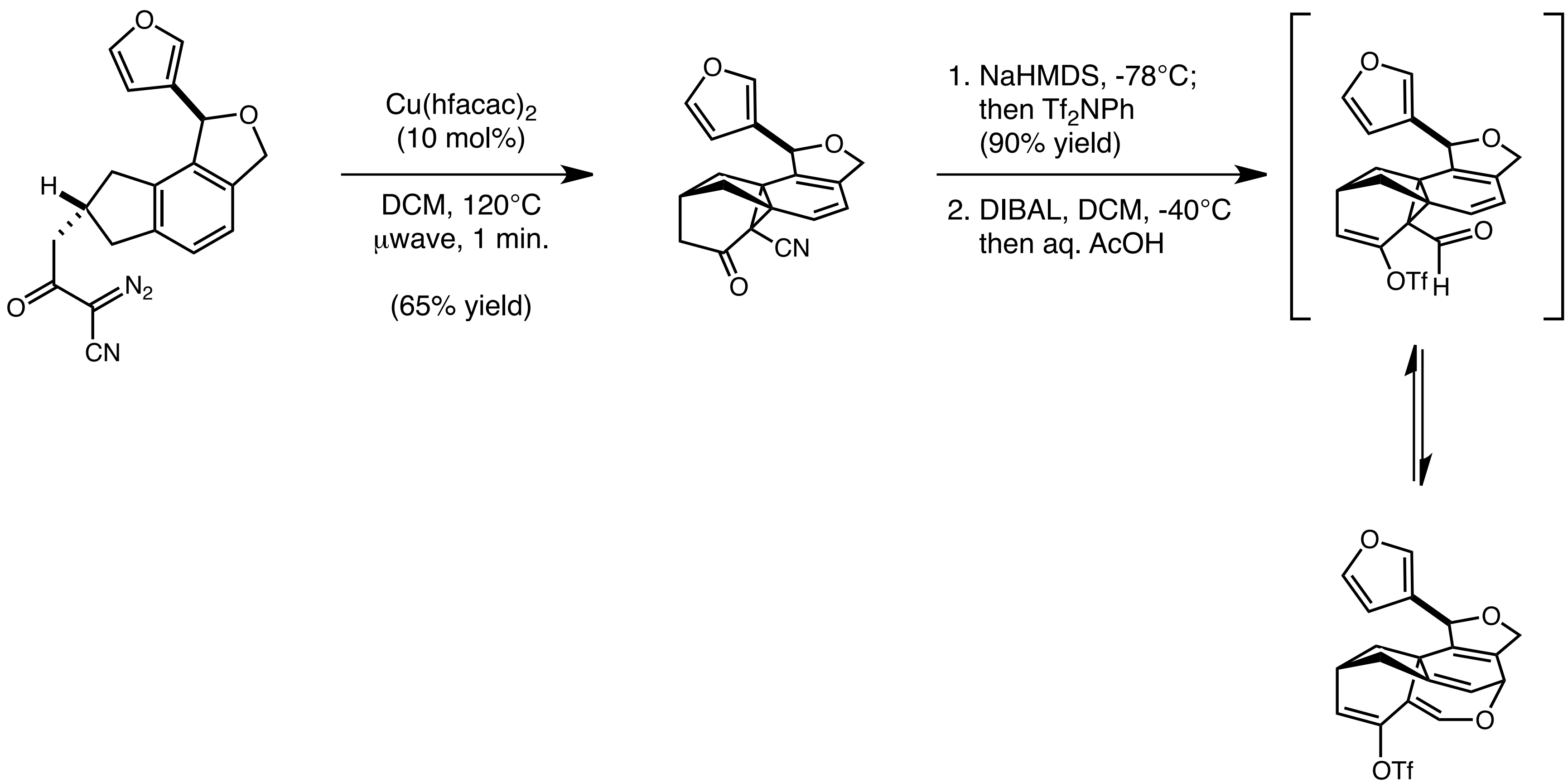

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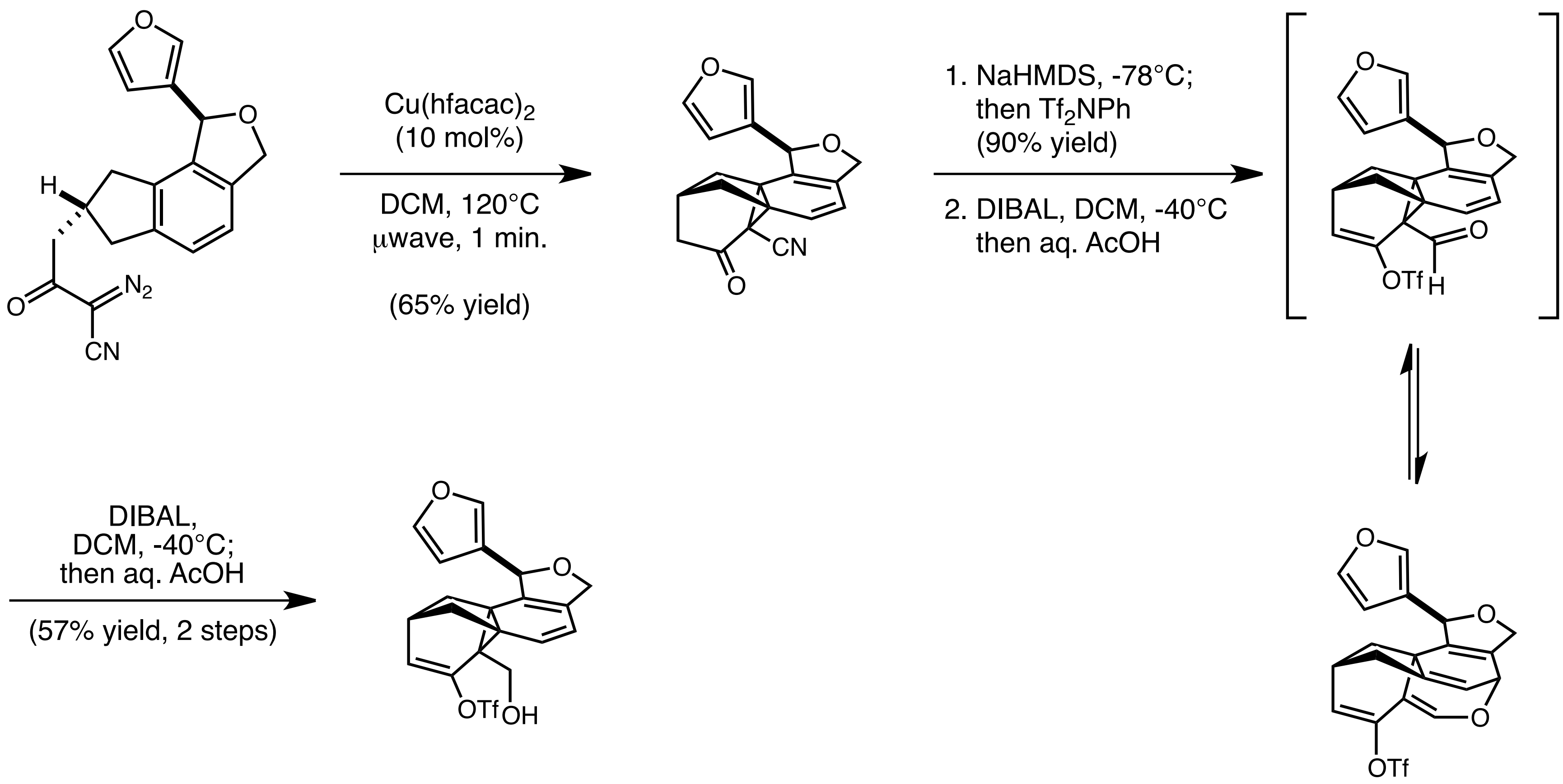

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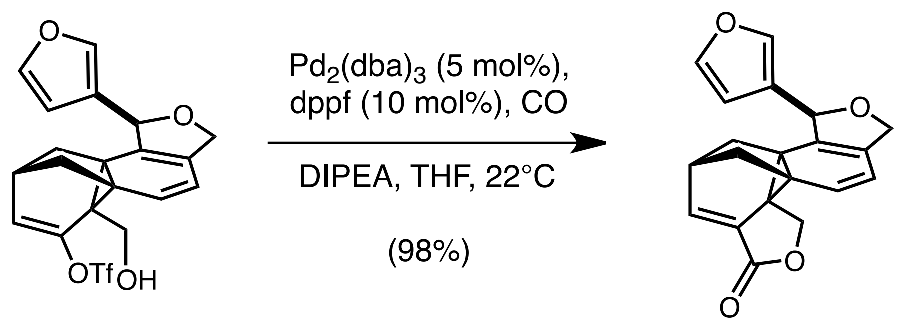
Enantioselective Total Synthesis of Salvileucalin B

End game

Synthesis of lactone and oxidation of tetrahydrofuran



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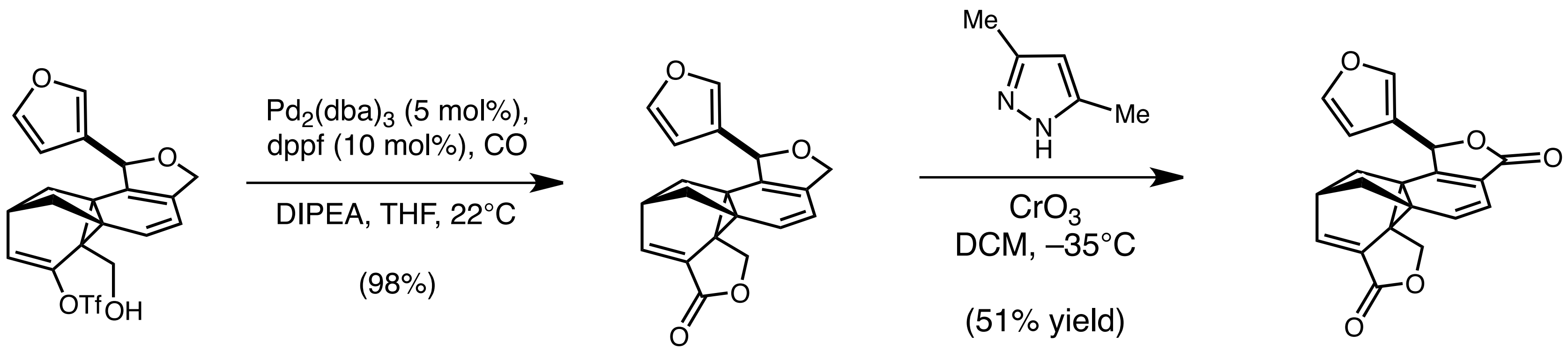

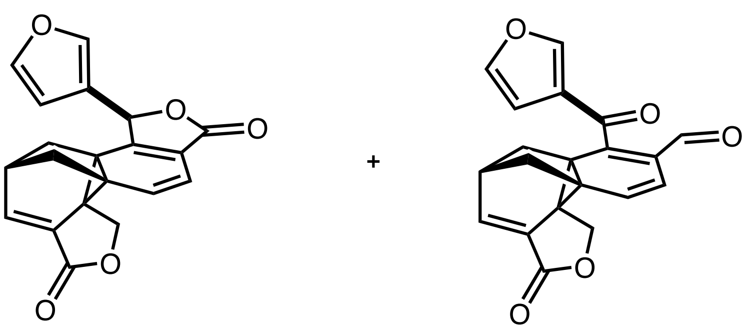

1:2 ratio

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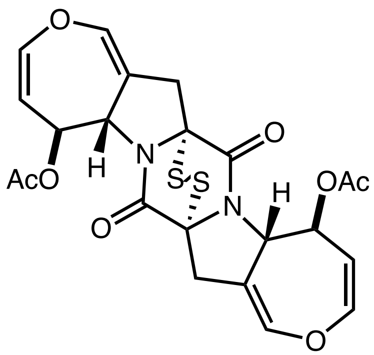

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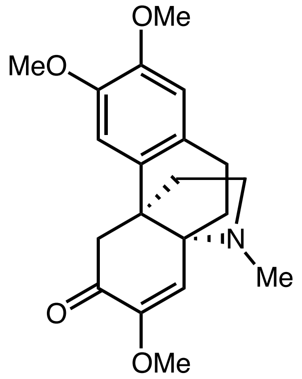

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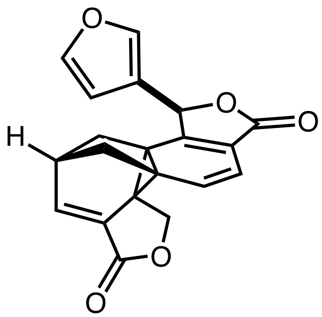

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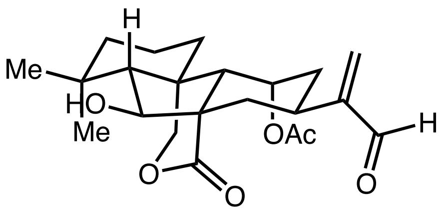

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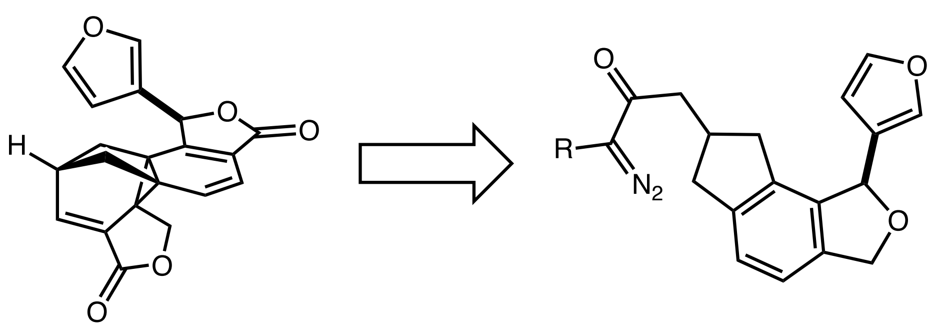

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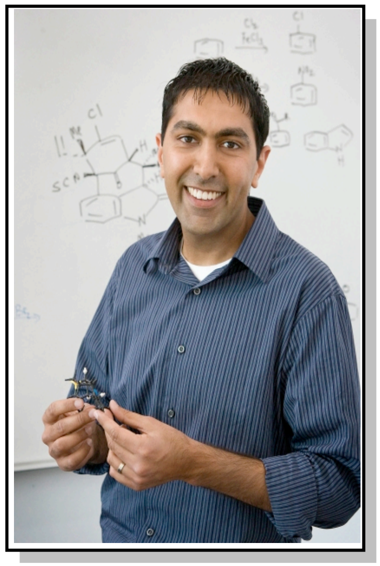
Sarah Reisman

Caltech

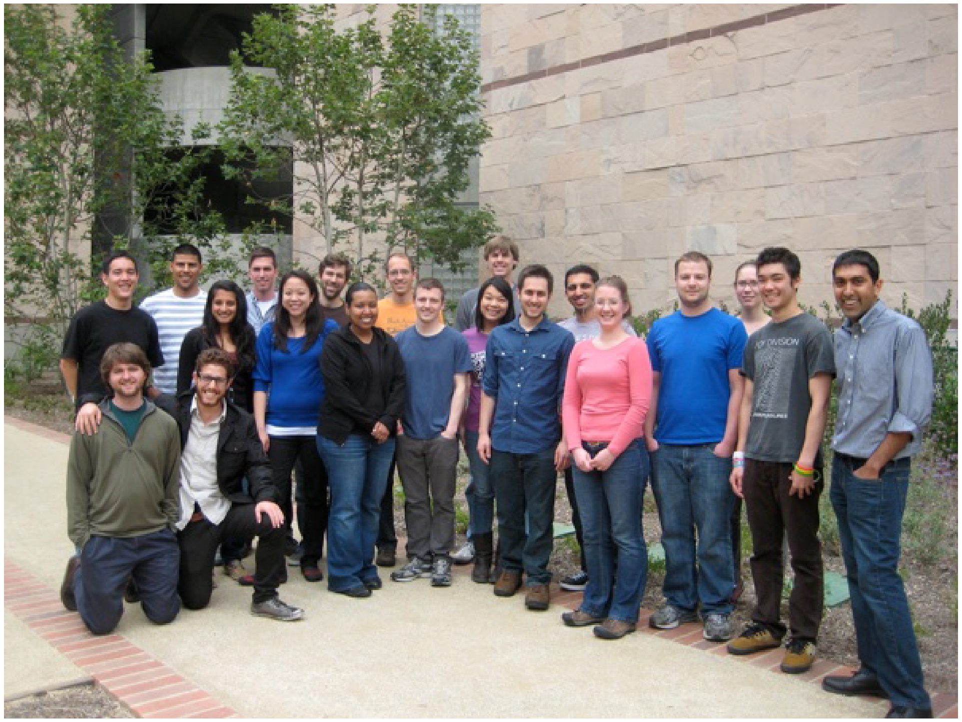


Neil Garg

UCLA

Neil Garg

UCLA



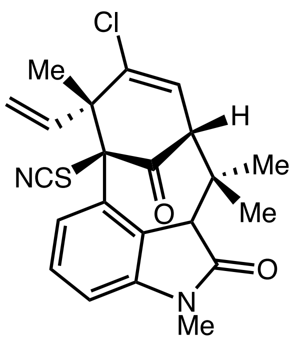
- Assistant Professor at UCLA 2007-present
- Ph.D. with Brian Stoltz on the total synthesis of Dragmacidin D and F
- Postdoctoral work with Larry Overman on the total synthesis of (–)-Sarain A

Garg, Neil, K; Hiebert, Sheldon; Larry E. Overman. *Angew. Chem. Int. Ed.* **2006**, *45*, 2912.
Garg, Neil, K; Caspi, Daniel D.; Brian M. Stoltz. *J. Am. Chem. Soc.* **2004**, *126*, 9552.
Garg, Neil, K; Sarpong, R.; Brian M. Stoltz. *J. Am. Chem. Soc.* **2002**, *124*, 13179.

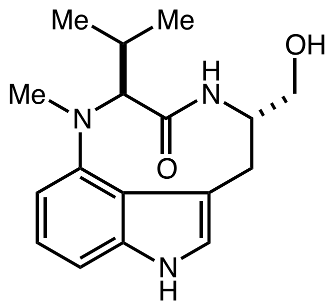
Research in the Garg Lab

UCLA

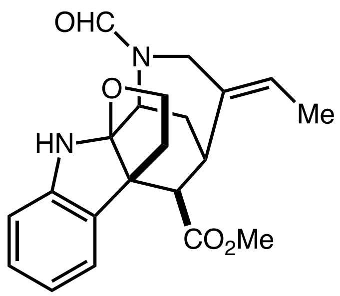
Synthesis of complex natural products



N-Methylwelwitindolinone C Isothiocyanate



Indolactam V

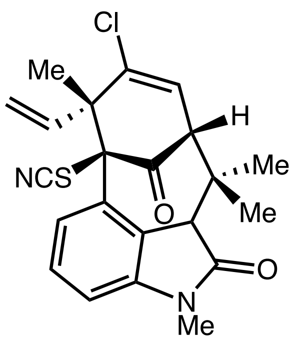


Aspidophylline A

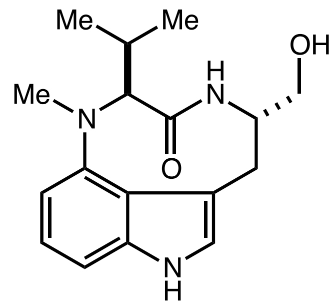
Research in the Garg Lab

UCLA

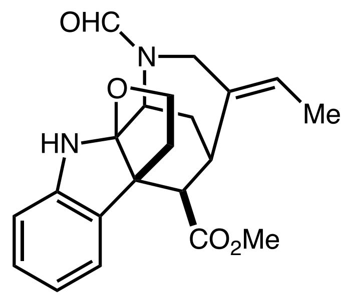
Synthesis of complex natural products



N-Methylwelwitindolinone C Isothiocyanate

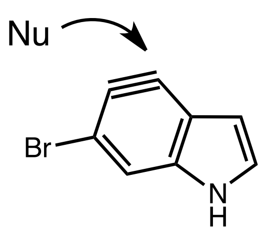


Indolactam V

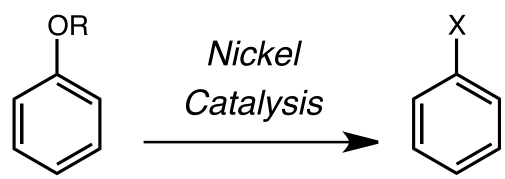


Aspidophylline A

Development of novel synthetic methods



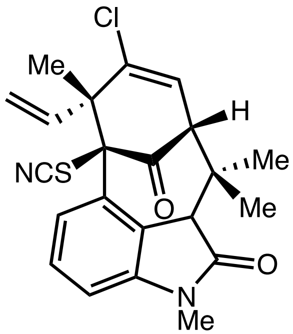
Intercepting Indolyne



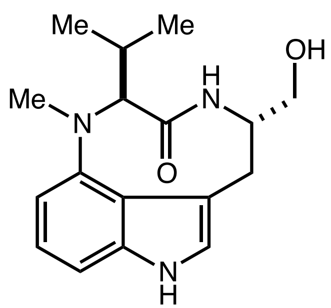
Research in the Garg Lab

UCLA

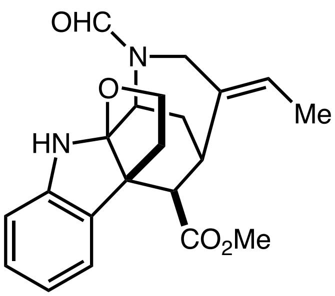
■ Synthesis of complex natural products



N-Methylwelwitindolinone C Isothiocyanate

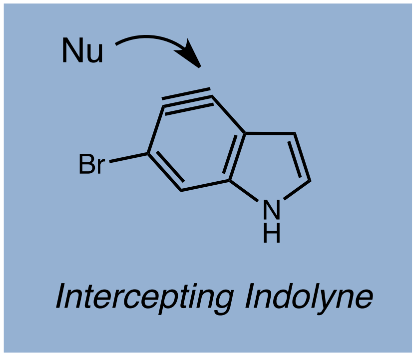


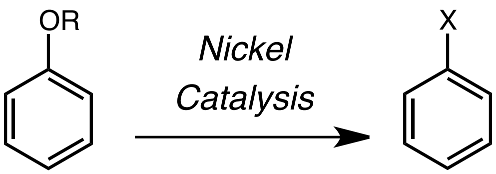
Indolactam V



Aspidophylline A

■ Development of novel synthetic methods

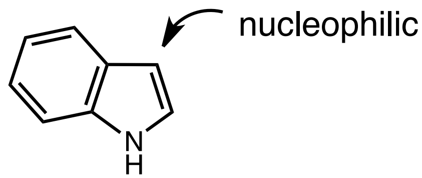




Regioselectivity in Nucleophilic Additions to Indolyne

Experimental and Computational Study

Umpolong of the Indole heterocycle



Indole

Regioselectivity in Nucleophilic Additions to Indolyne

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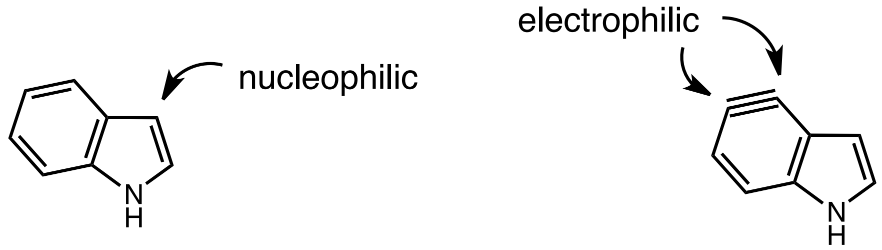

Indole

Indolyne

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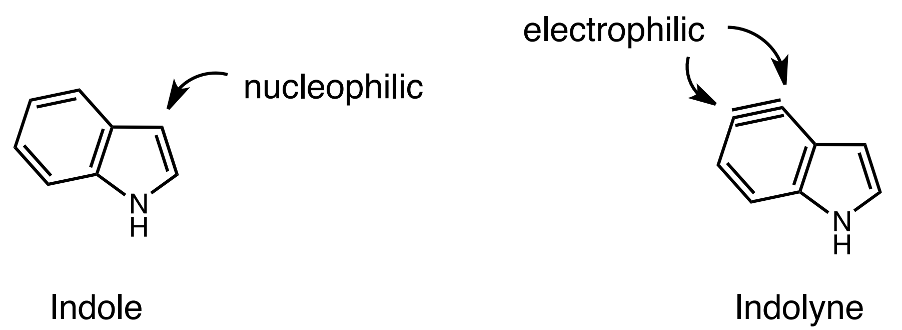

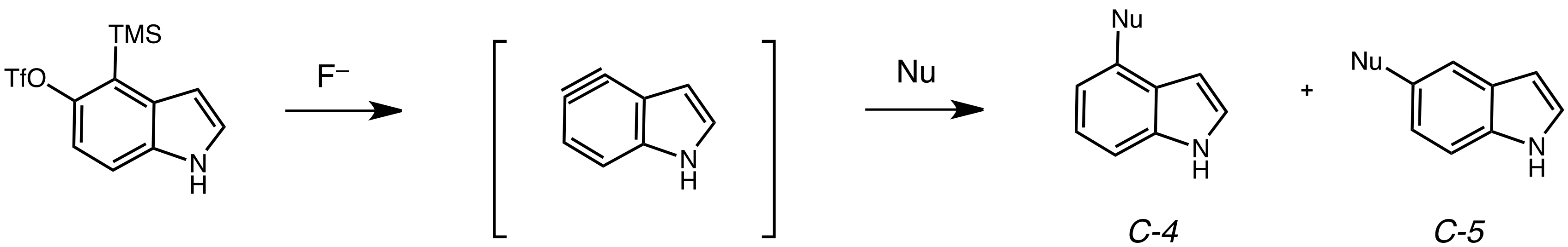

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Experimental and Computational Study

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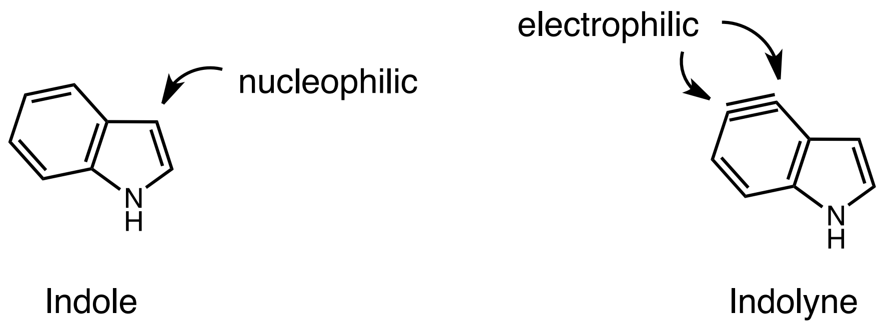
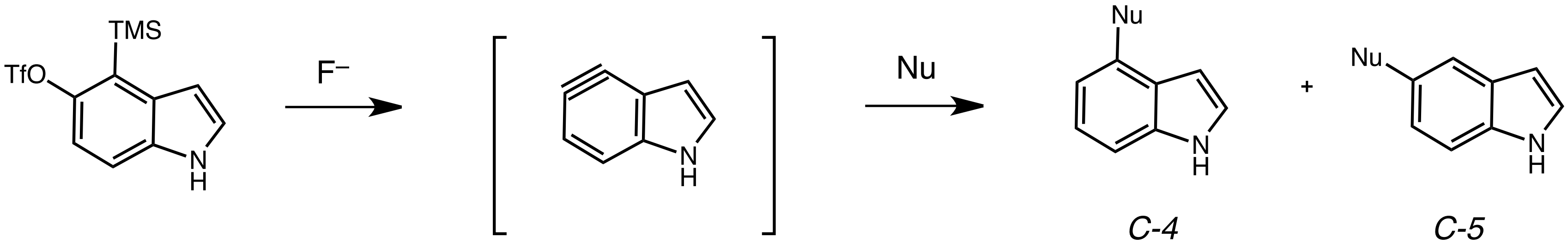


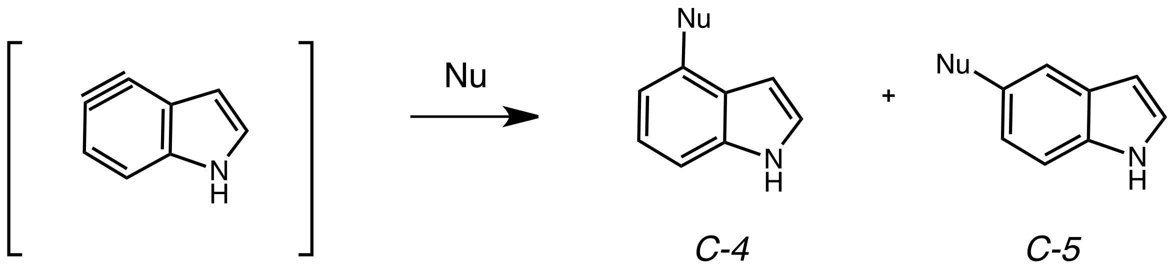


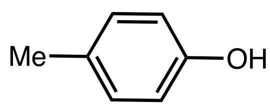
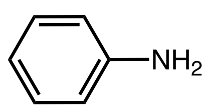
Preference for C-5 attack of nucleophile observed experimentally

Regioselectivity in Nucleophilic Additions to Indolyne

Experimental and Computational Study

Experimental regioselectivity compares to computational prediction



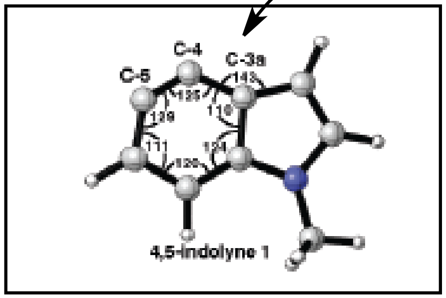
Nucleophile	Yield, Ratio (C-5/C-4)	Computed
	80%, 3:1	$\Delta\Delta G^{\ddagger}$ =2.8 115:1
	91%, 12.5:1	$\Delta\Delta G^{\ddagger}$ =3.0 160:1
N_3—Bn	86%, 2.4:1	$\Delta\Delta G^{\ddagger}$ =0.6 2.5:1
KCN	85%, 3.3:1	C-5 preferred

Garg, Neil, K. et al. *J. Am. Chem. Soc.* **2010**, *132*, 1267.

Regioselectivity in Nucleophilic Additions to Indolyne

Experimental and Computational Study

- Favored TS has the lower distortion energy



C-3a bond angle distorted:
θ_{ccc}=110° (pyrrole= 126°)

Garg, Neil, K. et al. *J. Am. Chem. Soc.* **2010**, *132*, 1267.

Regioselectivity in Nucleophilic Additions to Indolyne

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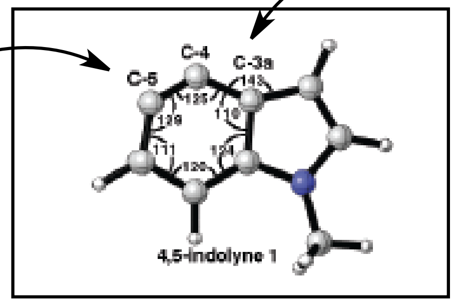

Nu attack at C-5 relieves strain:
θ_{ccc} opens to 118°

Garg, Neil, K. et al. *J. Am. Chem. Soc*. **2010**, *132*, 1267.

Regioselectivity in Nucleophilic Additions to Indolyne

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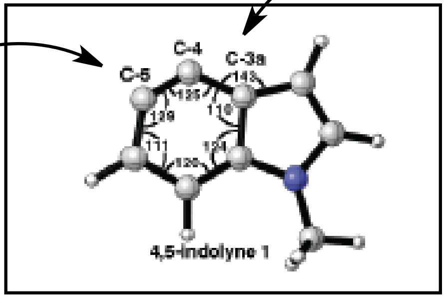

Nu attack at C-4 increases unfavorable distortion: θ_{ccc} becomes 108°

Garg, Neil, K. et al. *J. Am. Chem. Soc.* **2010**, *132*, 1267.

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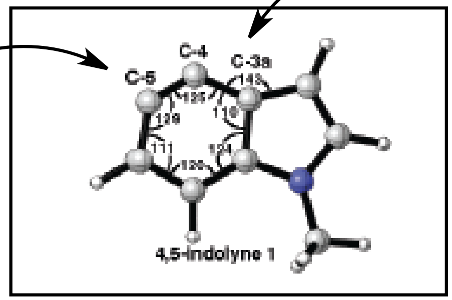
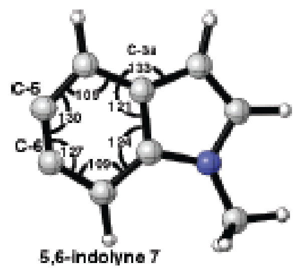
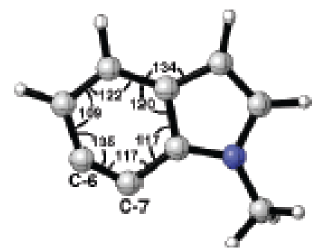


Nu attack at C-4 increases unfavorable distortion: θ_{ccc} becomes 108°



preference for C-5 attack diminished
C-5 and C-6 have similar θ



C-6 attack exclusively

Garg, Neil, K. et al. *J. Am. Chem. Soc.* **2010**, *132*, 1267.

Reversing the Regioselectivity in Nucleophilic Additions to Indolyne

Application to the synthesis of Indolactam V

- Lessons learned from computation:

more planar site is preferred for nucleophilic attack

more electropositive carbon is preferred site for nucleophilic attack

Bronner, S.M.; Goetz, A. E.; Garg, Neil, K. et al. *J. Am. Chem. Soc.* **2011**, *133*, 3832.

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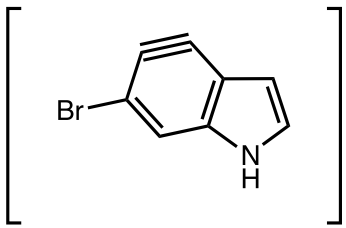

Can inclusion of a C-6 bromine direct nucleophilic attack to C-4?

Bronner, S.M.; Goetz, A. E.; Garg, Neil, K. et al. *J. Am. Chem. Soc.* **2011**, *133*, 3832.

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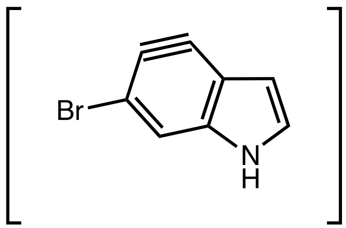


Can inclusion of a C-6 bromine direct nucleophilic attack to C-4?

C-4 θ_{ccc} = 130°

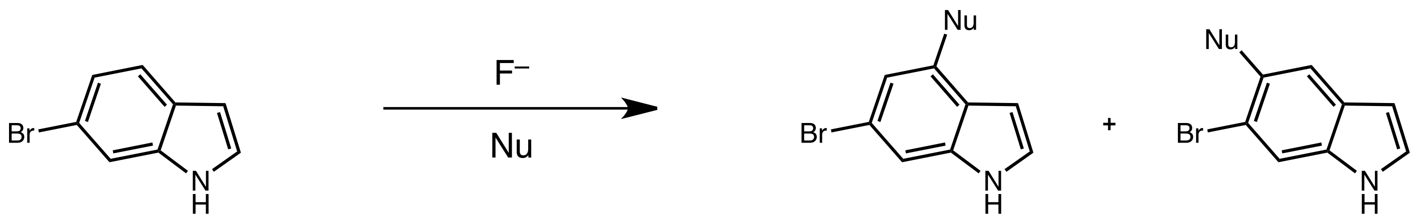
C-5 θ_{ccc} = 124°

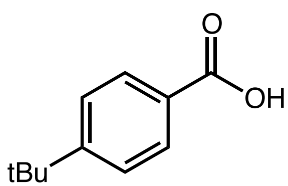
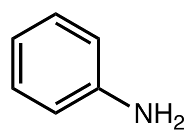
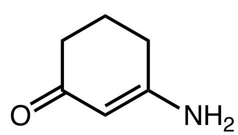
Bronner, S.M.; Goetz, A. E.; Garg, Neil, K. et al. *J. Am. Chem. Soc.* **2011**, *133*, 3832.

Reversing the Regioselectivity in Nucleophilic Additions to Indolyne

Application to the synthesis of Indolactam V

■ Bromine reverses selectivity of nucleophilic addition for a variety of nucleophiles



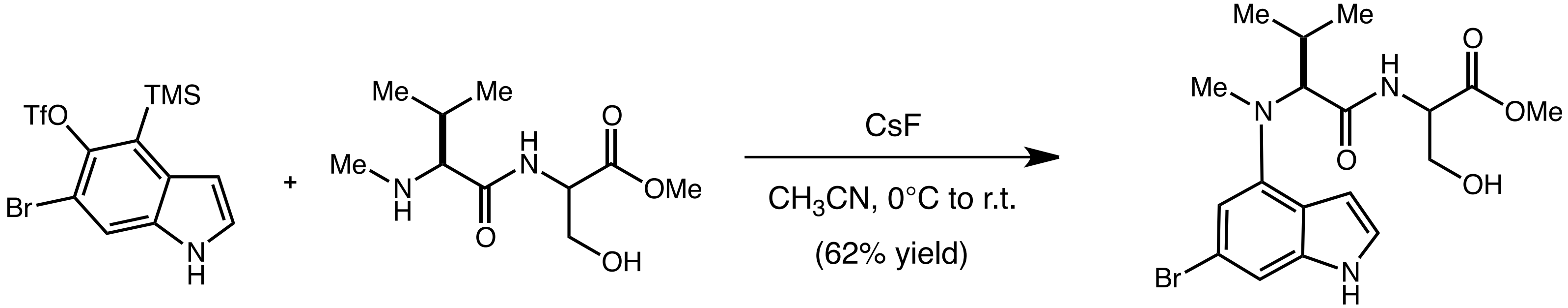
Nucleophile	Yield	Ratio C-5 : C-4
	58%	1:13
	70%	1:14
	68%	1:20

Bronner, S.M.; Goetz, A. E.; Garg, Neil, K. et al. *J. Am. Chem. Soc*. **2011**, *133*, 3832.

Reversing the Regioselectivity in Nucleophilic Additions to Indolyne

Application to the synthesis of Indolactam V

Synthesis of Indolactam V



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Reversing the Regioselectivity in Nucleophilic Additions to Indolyne

Application to the synthesis of Indolactam V

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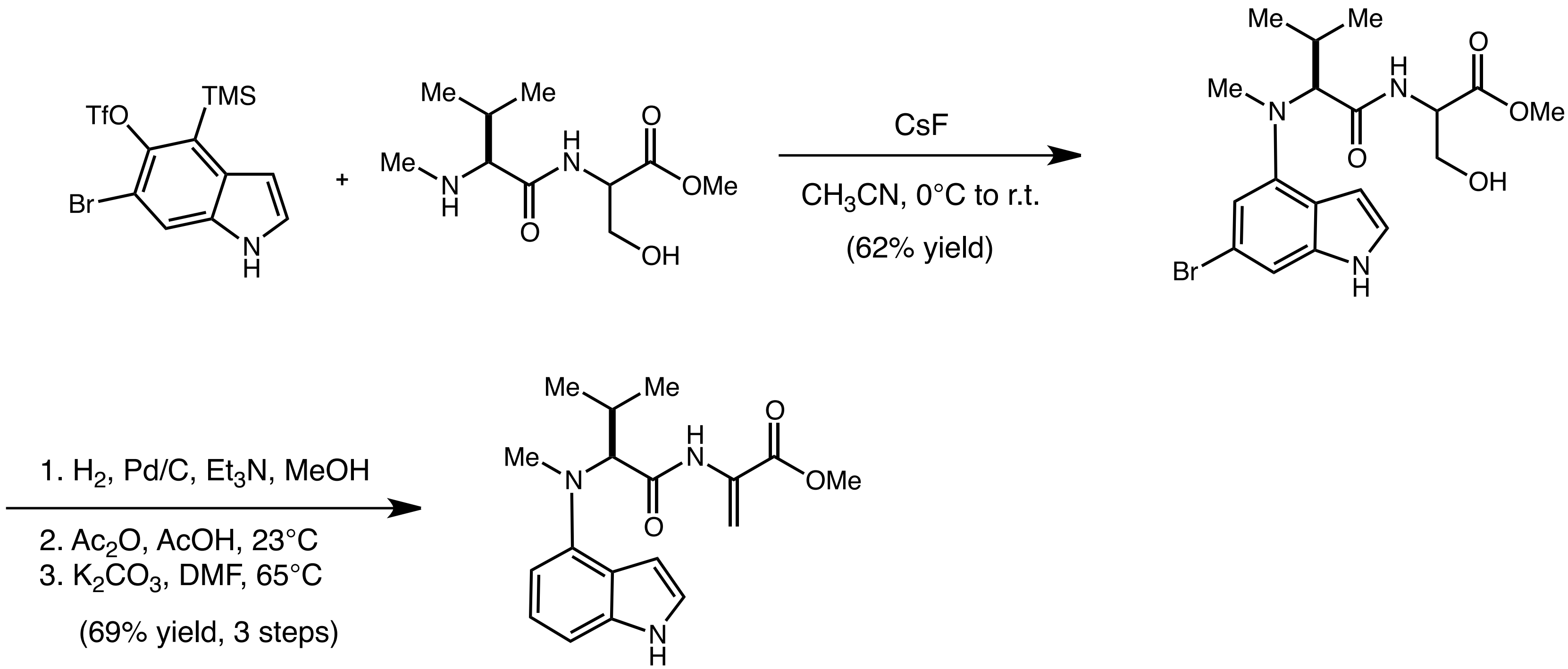

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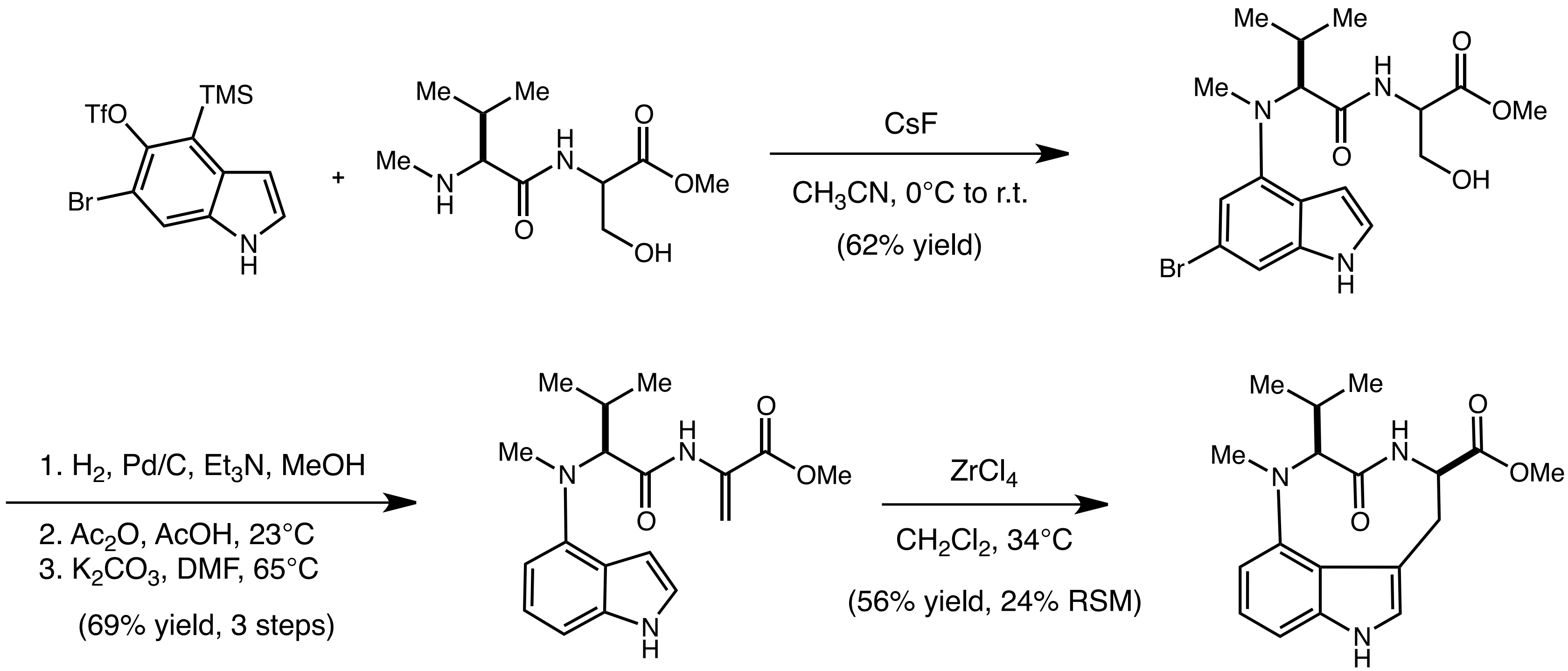
Reversing the Regioselectivity in Nucleophilic Additions to Indolyne

Application to the synthesis of Indolactam V

■ Synthesis of Indolactam V



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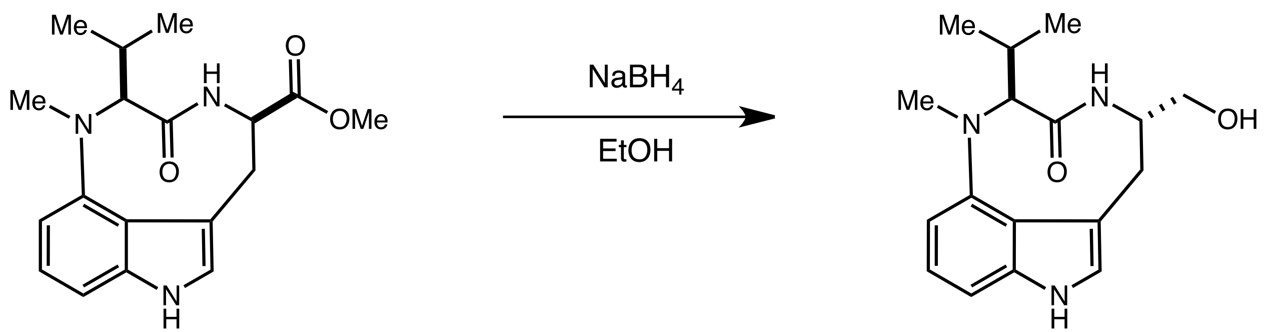


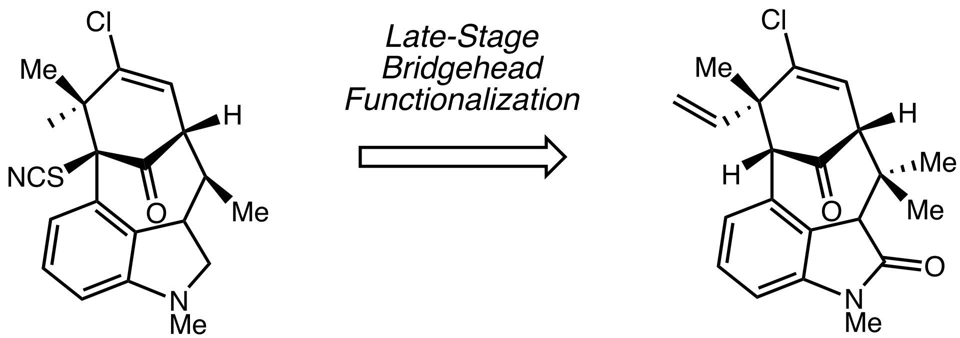
Indolactam V

Bronner, S.M.; Goetz, A. E.; Garg, Neil, K. et al. *J. Am. Chem. Soc.* **2011**, *133*, 3832.

Reversing the Regioselectivity in Nucleophilic Additions to Indolyne

Application to the synthesis of N-MethylWelwitindolinone C Isothiocyante

Assembly of [4.3.1] bicycle through indolyne cyclization



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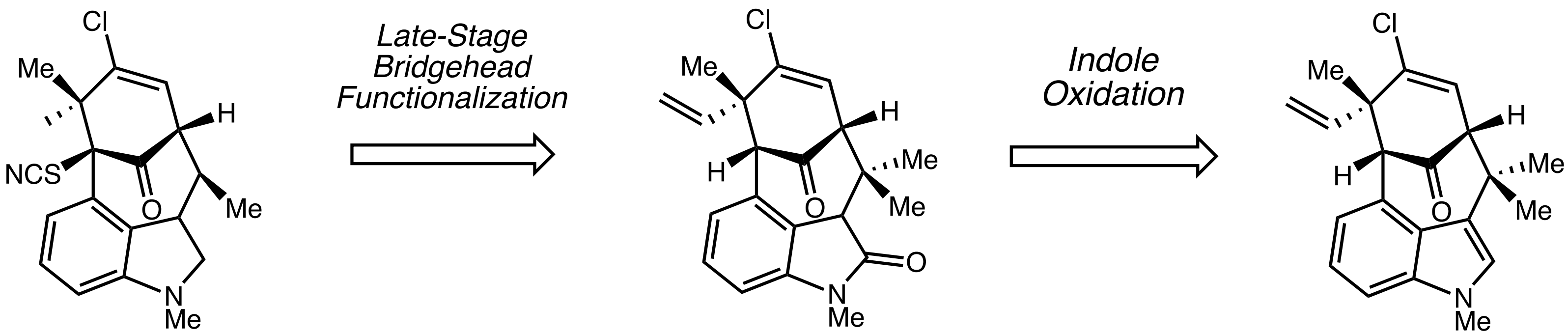

Huters, A. D..; Quasdorf, K. W.; Styduhar, E. D.; Garg, Neil, K. *J. Am. Chem. Soc.* **2011**, *133*, 3832.

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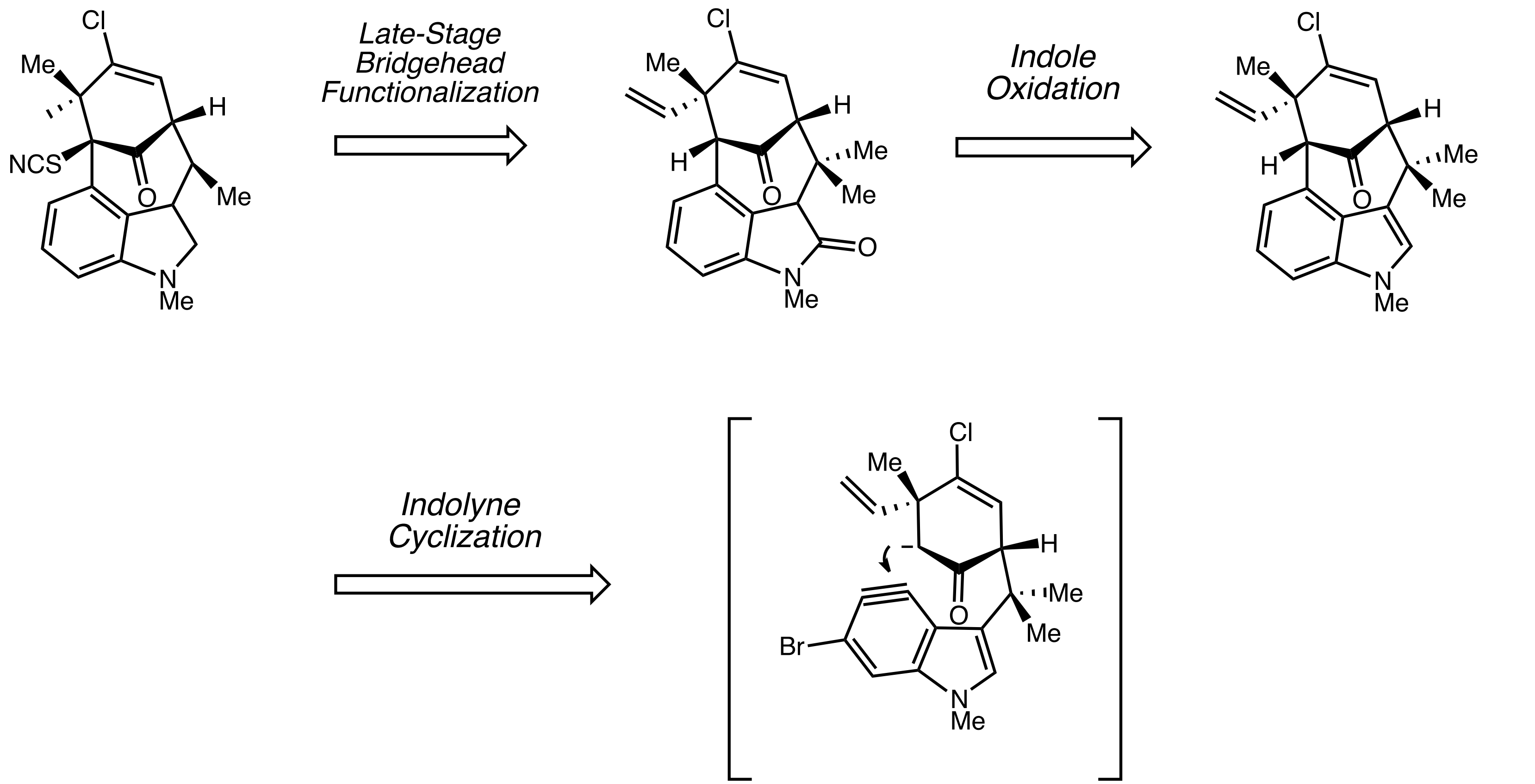

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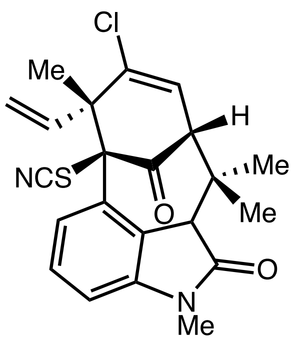
Research in the Garg Lab

UCLA

Synthesis of complex natural products



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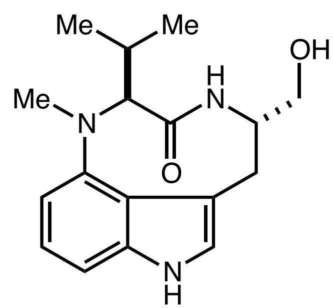
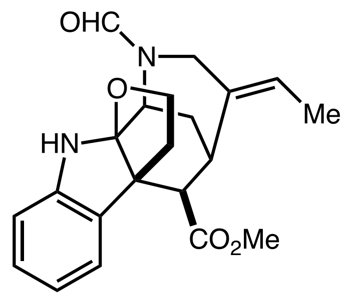


Indolactam V



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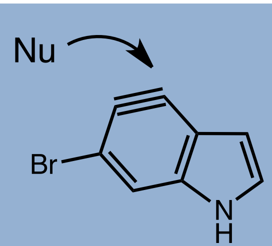

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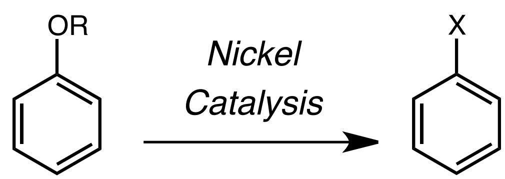
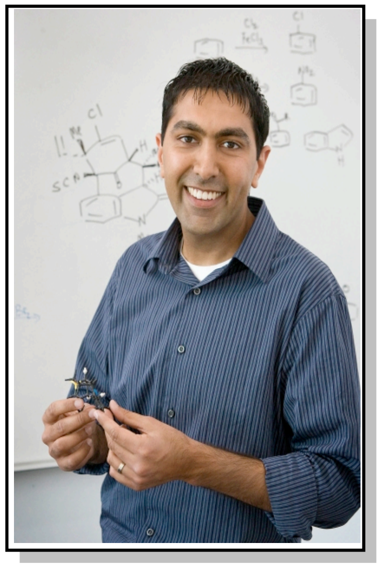


Highlights from top Pre-tenure Faculty

Sarah Reisman

Caltech



Neil Garg

UCLA

Gojko Lalic

University of Washington

Gojko Lalic

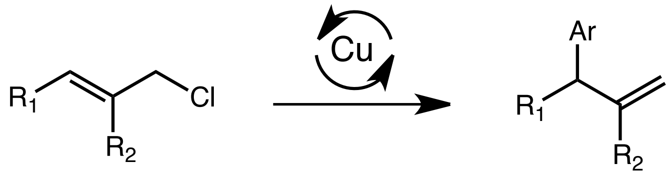
University of Washington

- Assistant Professor, University of Washington 2008-present
- Postdoctoral fellow with E. J. Corey on the synthesis of Platensimycin
- Postdoctoral fellow with R. Bergman studying the reactions of zirconium complexes
- Ph.D. with Matt Shair studying the metal catalyzed thioester aldol and Mannich reactions

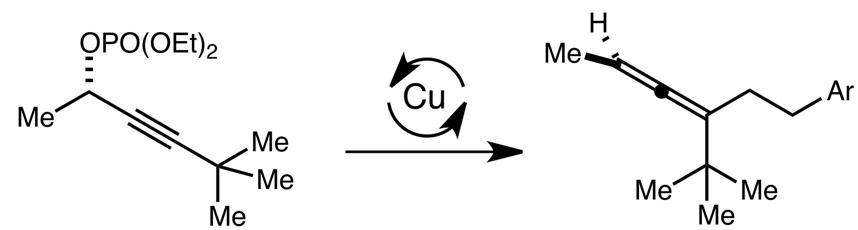
Research in the Lalic Lab

Organic Synthesis and Synthetic Methodology

■ Novel methods in copper catalysis



Catalytic S_N2' reactions with Boronic Esters

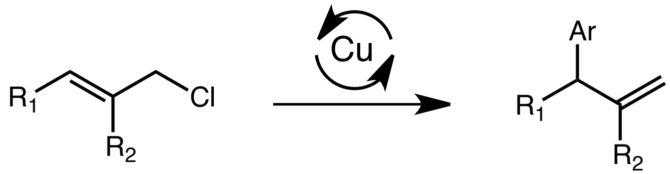


Asymmetric Synthesis of Trisubstituted Allenes

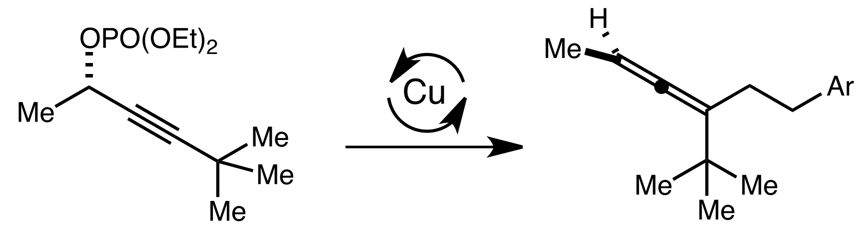
Research in the Lalic Lab

Organic Synthesis and Synthetic Methodology

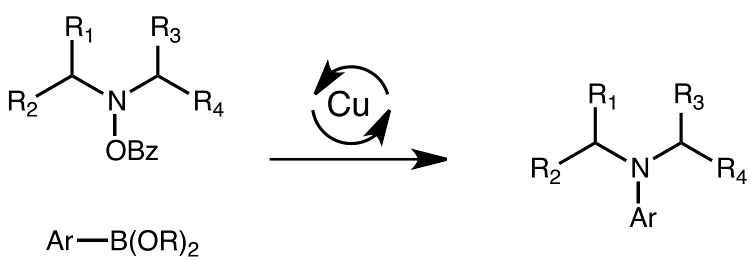
■ Novel methods in copper catalysis



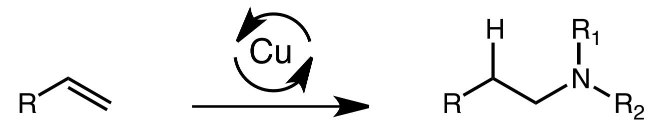
Catalytic S_N2' reactions with Boronic Esters



Asymmetric Synthesis of Trisubstituted Allenes



Synthesis of Hindered Anilines

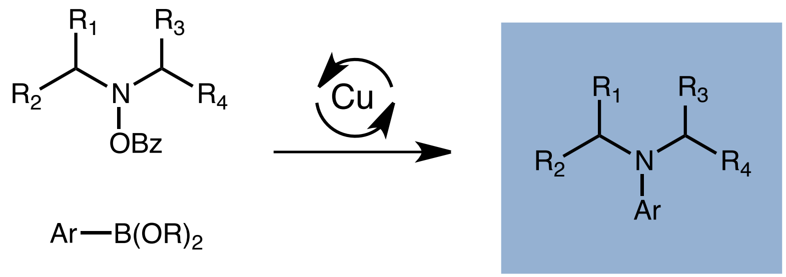


Anti-Markovnikov Hydroamination

Copper-Catalyzed Electrophilic Amination of Aryl Boronic Esters

Synthesis of Hindered Anilines

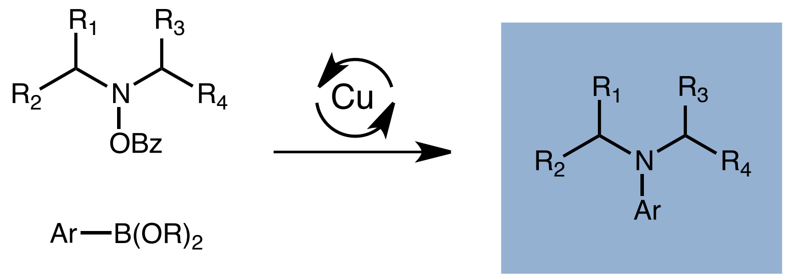
- *N*-Aryl structural motif highly prevalent in medicinal agents



Copper-Catalyzed Electrophilic Amination of Aryl Boronic Esters

Synthesis of Hindered Anilines

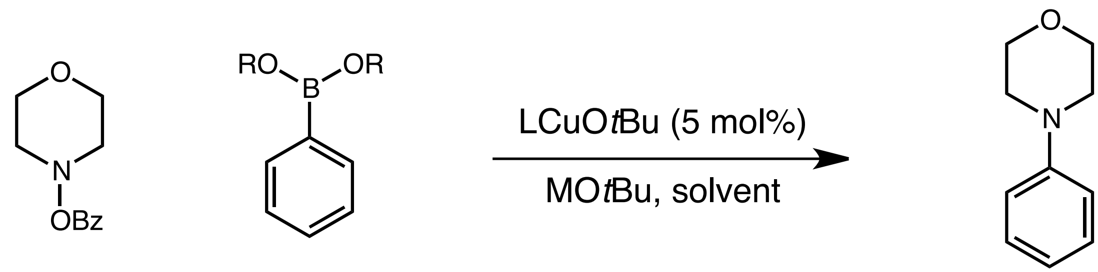
- *N*-Aryl structural motif highly prevalent in medicinal agents



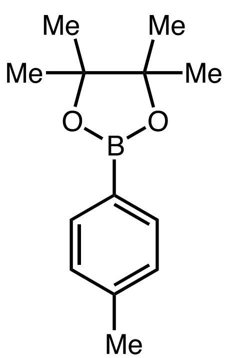
- No method of direct synthesis of a product prefunctionalized with –I or –Br
- Most methods require excess of one coupling partner
- Chan-Lam amination is incompatable with hindered substrates

Copper-Catalyzed Electrophilic Amination of Aryl Boronic Esters

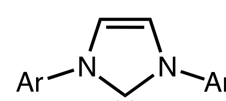
Synthesis of Hindered Anilines



$Ar–B(OR)_2$	L	M	Solvent	Yield (%)
1	IMes	Na	THF	<5



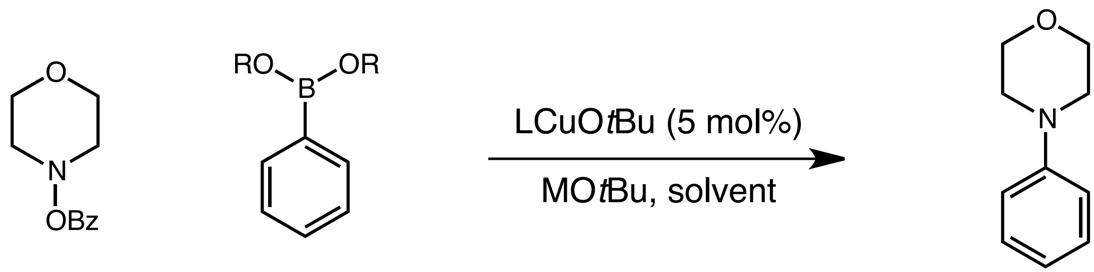
1



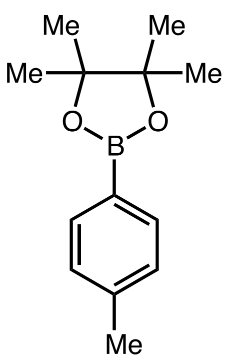
IMes

Copper-Catalyzed Electrophilic Amination of Aryl Boronic Esters

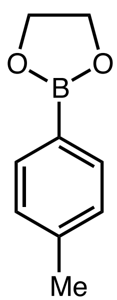
Synthesis of Hindered Anilines



Ar–B(OR)$_2$	L	M	Solvent	Yield (%)
1	IMes	Na	THF	<5
2	IMes	Na	THF	16
3	IMes	Na	THF	72



1



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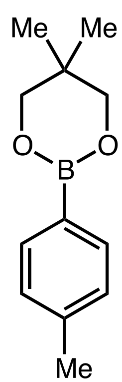

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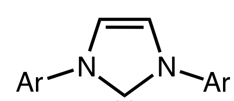
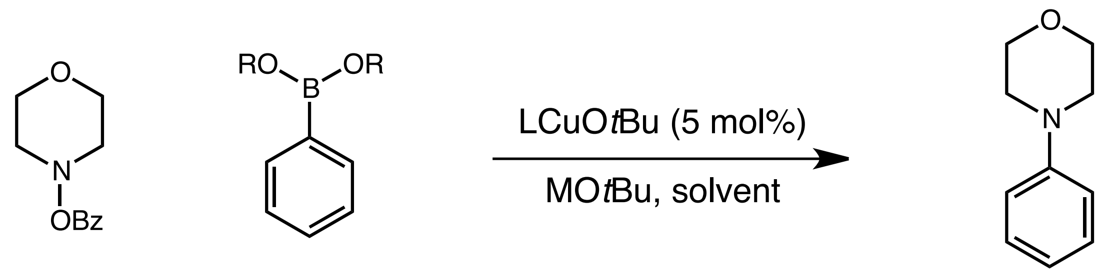


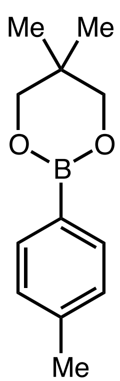
IMes

Copper-Catalyzed Electrophilic Amination of Aryl Boronic Esters

Synthesis of Hindered Anilines



$Ar–B(OR)_2$	L	M	Solvent	Yield (%)



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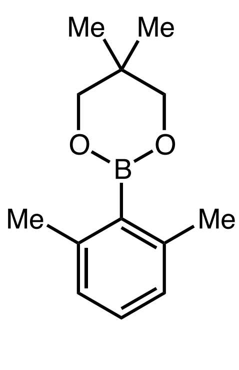

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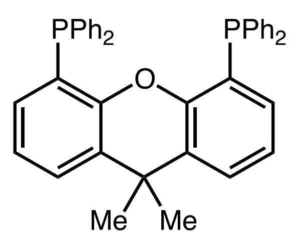
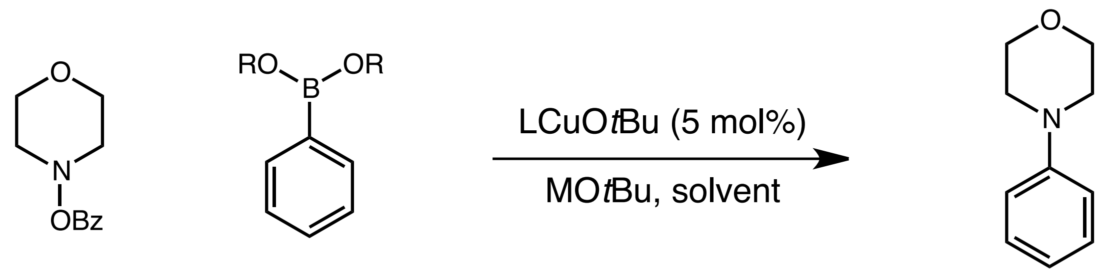
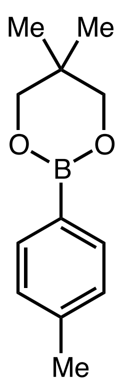


Copper-Catalyzed Electrophilic Amination of Aryl Boronic Esters

Synthesis of Hindered Anilines



$Ar–B(OR)_2$	L	M	Solvent	Yield (%)
3	Xantphos	Na	1,4-dioxane	99
4	Xantphos	Na	1,4-dioxane	8
4	Xantphos	Li	1,4-dioxane	56



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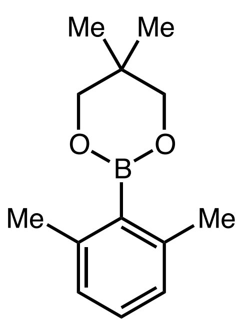

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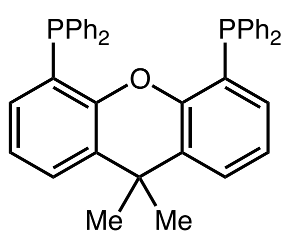
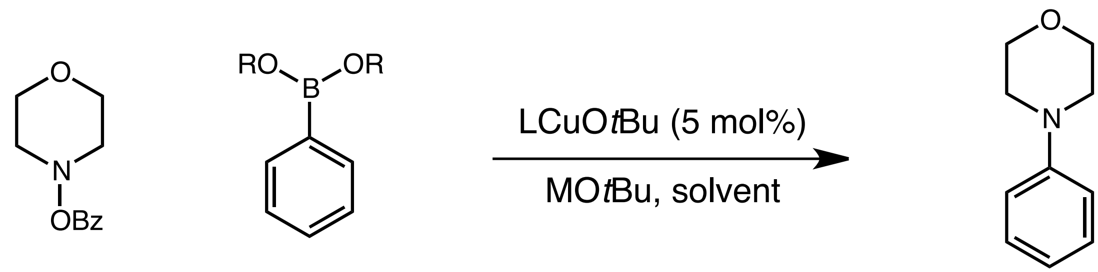
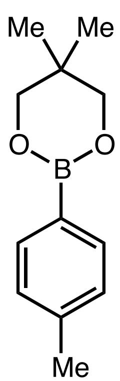


Copper-Catalyzed Electrophilic Amination of Aryl Boronic Esters

Synthesis of Hindered Anilines



Ar–B(OR)$_2$	L	M	Solvent	Yield (%)	
3	Xantphos	Na	1,4-dioxane	99	
4	Xantphos	Na	1,4-dioxane	8	
4	Xantphos	Li	1,4-dioxane	56	
4	Xantphos	Li	PhMe	74	
4	Xantphos	Li	PhMe	81	45°C
4	Xantphos	Li	PhMe	94	60°C



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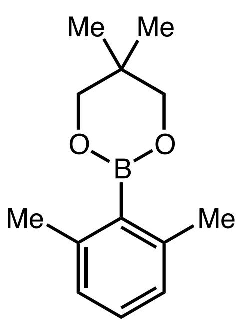

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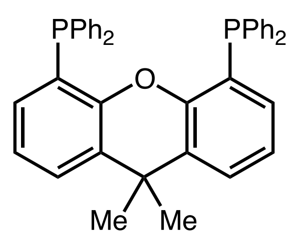
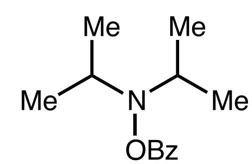
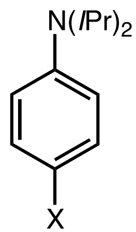


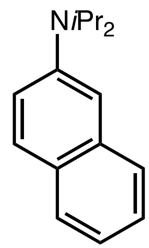


Copper-Catalyzed Electrophilic Amination of Aryl Boronic Esters

Substrate Scope



X	
OMe	85%
Cl	82%
Br	84%
I	82%
CHO	94%
CO_2Me	89%



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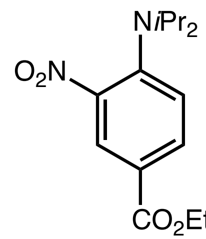

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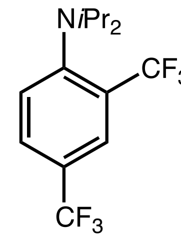

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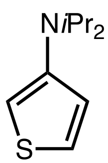

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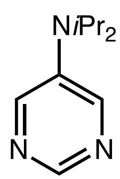

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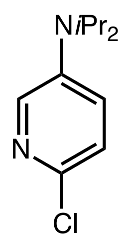

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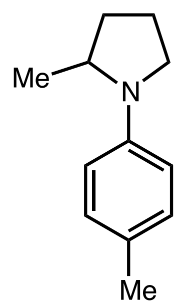

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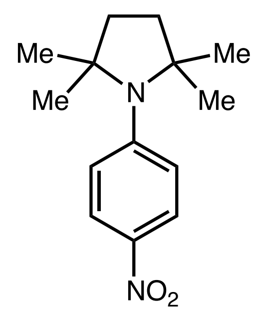

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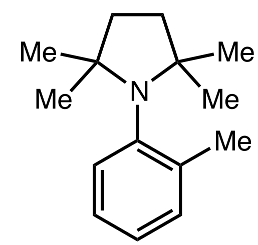

60%

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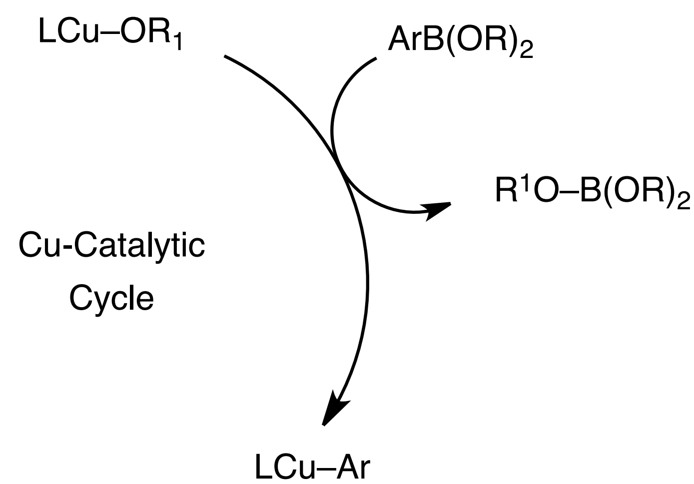
Copper-Catalyzed Electrophilic Amination of Aryl Boronic Esters

Proposed Mechanism



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Copper-Catalyzed Electrophilic Amination of Aryl Boronic Esters

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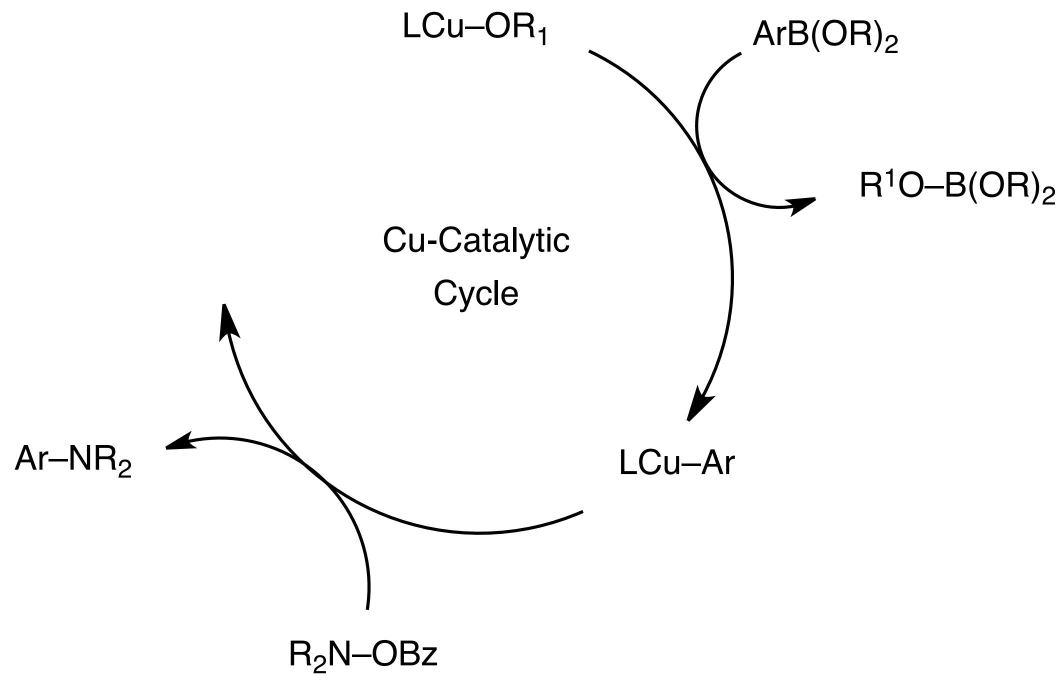

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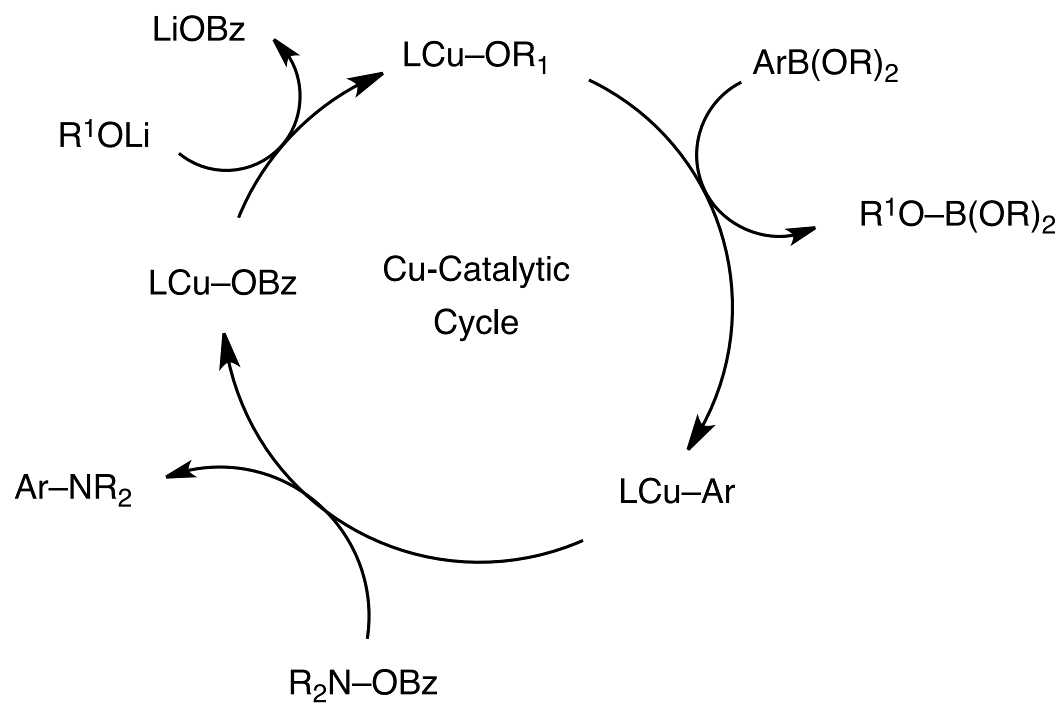

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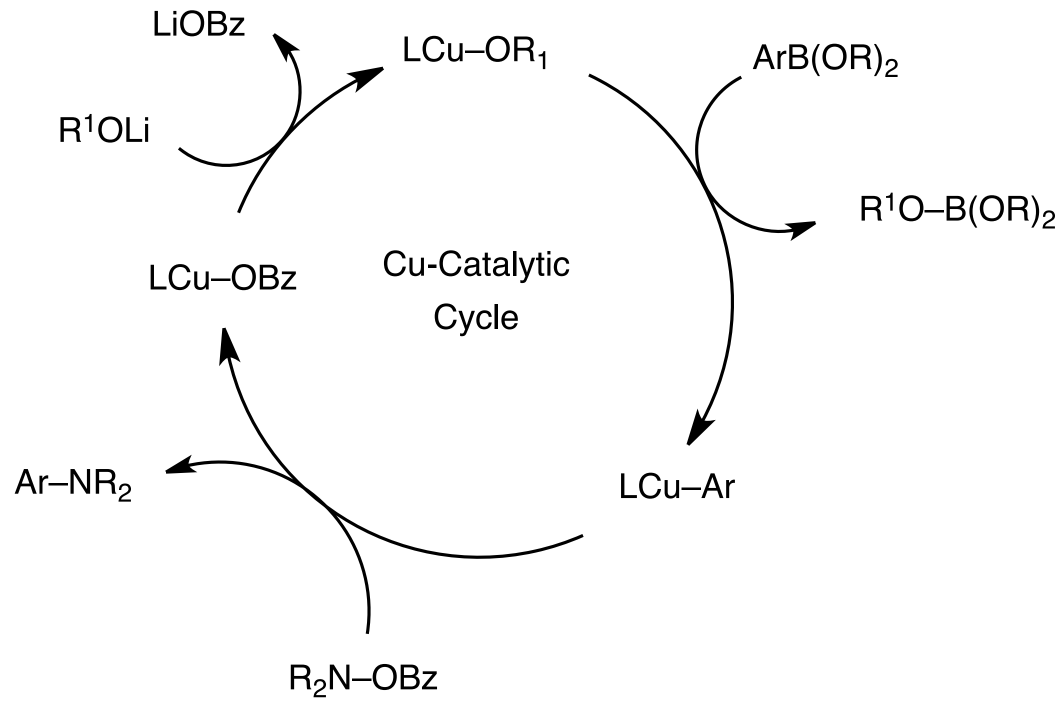
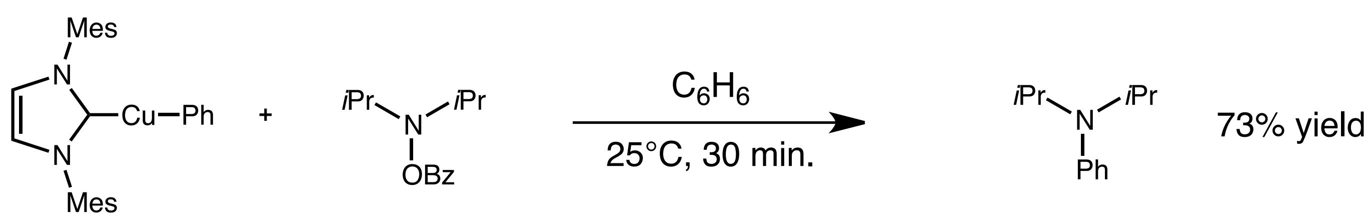
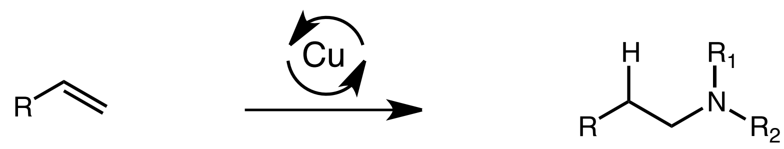




Rucker, R. P.; Whittaker, A. M.; Fang, H.; Gojko Lalic *Angew. Chem. Int. Ed.* **2012**, *51*, 3953.

Copper-Catalyzed Alkene Hydroamination with Alkyl Boranes

Synthesis of Tertiary Alkyl Amines



simple olefin

Single Regioisomer of Tertiary Alkylamine

Rucker, R. P.; Whittaker, A. M.; Dang, H.; Gojko Lalic *J.* Am. Chem. Soc. **2012**, *134*, 6571.

Copper-Catalyzed Alkene Hydroamination with Alkyl Boranes

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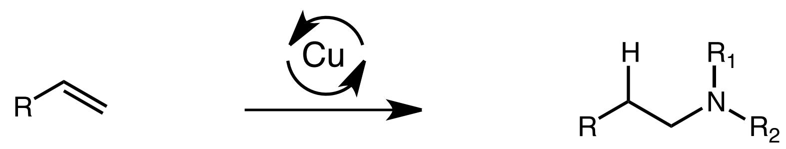
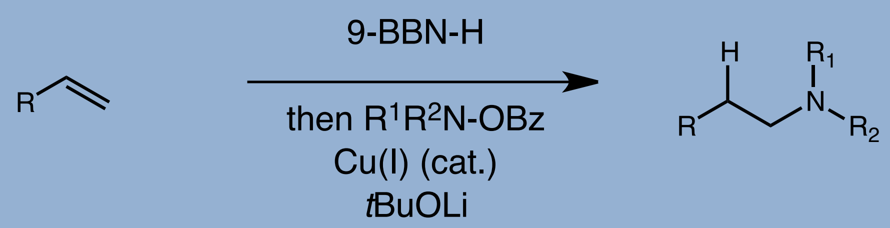


simple olefin

Single Regioisomer of Tertiary Alkylamine



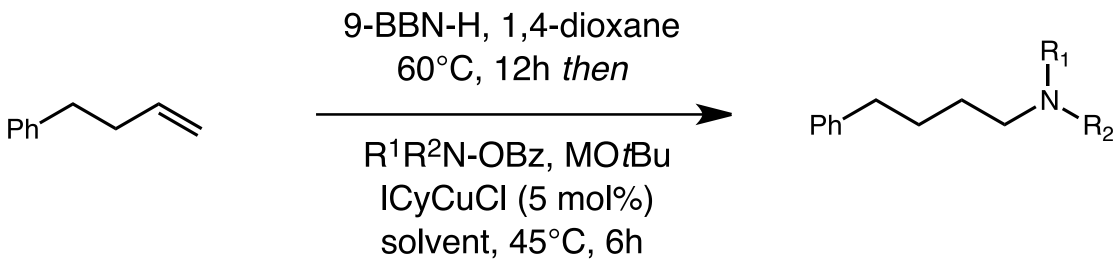
Can this be achieved through a novel hydroboration-amination procedure?

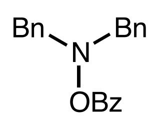
Rucker, R. P.; Whittaker, A. M.; Dang, H.; Gojko Lalic *J*. Am. Chem. Soc. **2012**, *134*, 6571.

Copper-Catalyzed Alkene Hydroamination with Alkyl Boranes

Synthesis of Tertiary Alkyl Amines

Initial Studies



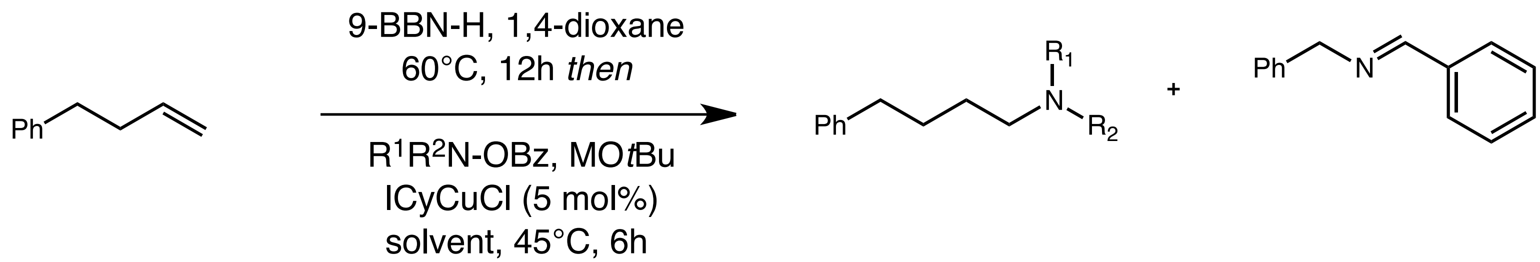
Entry	R_2N–OBz	M	Cosolvent	Yield
1		Na	1,4-dioxane	16%
2		K	1,4-dioxane	11%

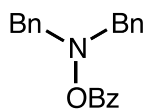
Rucker, R. P.; Whittaker, A. M.; Dang, H.; Gojko Lalic *J.* Am. Chem. Soc. **2012**, *134*, 6571.

Copper-Catalyzed Alkene Hydroamination with Alkyl Boranes

Synthesis of Tertiary Alkyl Amines

Initial Studies



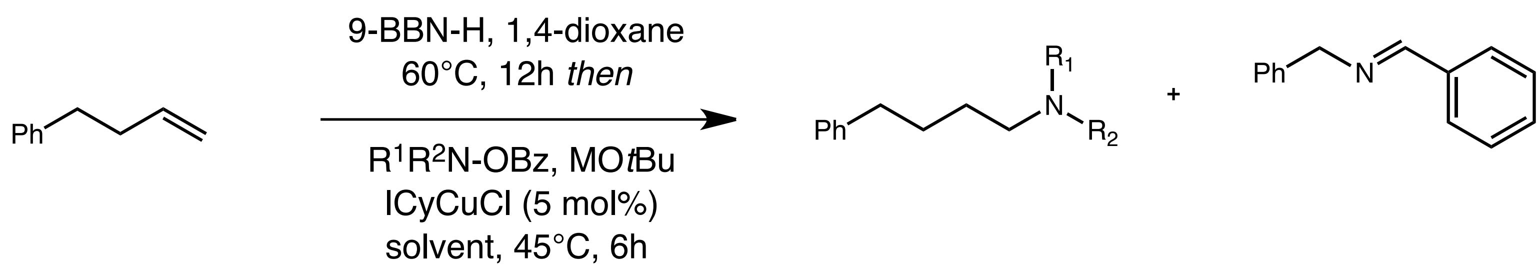
Entry	R_2N–OBz	M	Cosolvent	Yield
1		Na	1,4-dioxane	16%
2		K	1,4-dioxane	11%

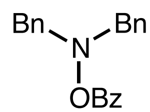
Rucker, R. P.; Whittaker, A. M.; Dang, H.; Gojko Lalic *J.* Am. Chem. Soc. **2012**, *134*, 6571.

Copper-Catalyzed Alkene Hydroamination with Alkyl Boranes

Synthesis of Tertiary Alkyl Amines

Initial Studies



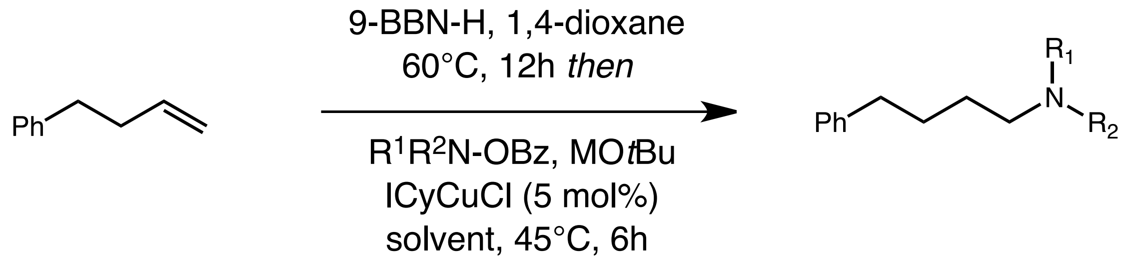
Entry	R_2N–OBz	M	Cosolvent	Yield
1		Na	1,4-dioxane	16%
2		K	1,4-dioxane	11%
3		Li	1,4-dioxane	56%
4		Li	pentane	97%

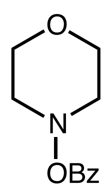
Rucker, R. P.; Whittaker, A. M.; Dang, H.; Gojko Lalic *J.* Am. Chem. Soc. **2012**, *134*, 6571.

Copper-Catalyzed Alkene Hydroamination with Alkyl Boranes

Synthesis of Tertiary Alkyl Amines

Initial Studies



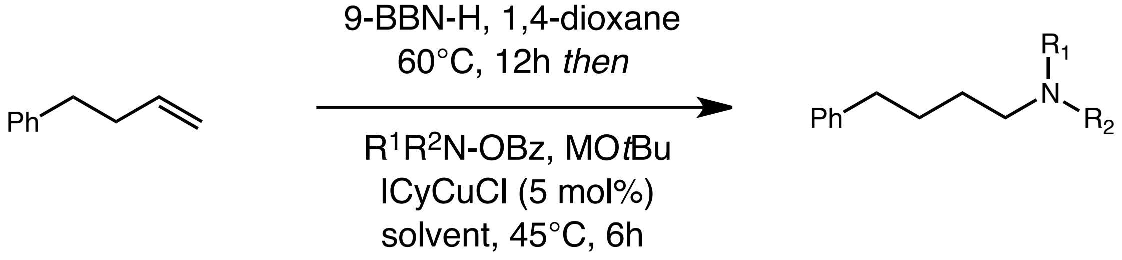
Entry	R_2N–OBz	M	Cosolvent	Yield
5		Li	pentane	<5%

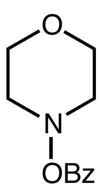
Rucker, R. P.; Whittaker, A. M.; Dang, H.; Gojko Lalic *J.* Am. Chem. Soc. **2012**, *134*, 6571.

Copper-Catalyzed Alkene Hydroamination with Alkyl Boranes

Synthesis of Tertiary Alkyl Amines

Initial Studies



Entry	R_2N–OBz	M	Cosolvent	Yield
5		Li	pentane	<5%
6[1]		Li	pentane	52%

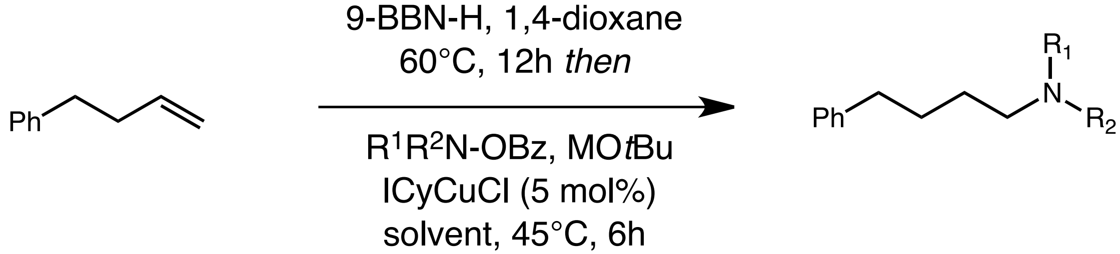
[1]Electrophile added over 6 hours

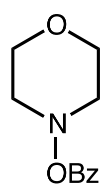
Rucker, R. P.; Whittaker, A. M.; Dang, H.; Gojko Lalic *J.* Am. Chem. Soc. **2012**, *134*, 6571.

Copper-Catalyzed Alkene Hydroamination with Alkyl Boranes

Synthesis of Tertiary Alkyl Amines

Initial Studies



Entry	R_2N–OBz	M	Cosolvent	Yield
5		Li	pentane	<5%
6[1]		Li	pentane	52%
7[2]		Li	toluene	86%
8[3]		Li	toluene	99%

[1]Electrophile added over 6 hours

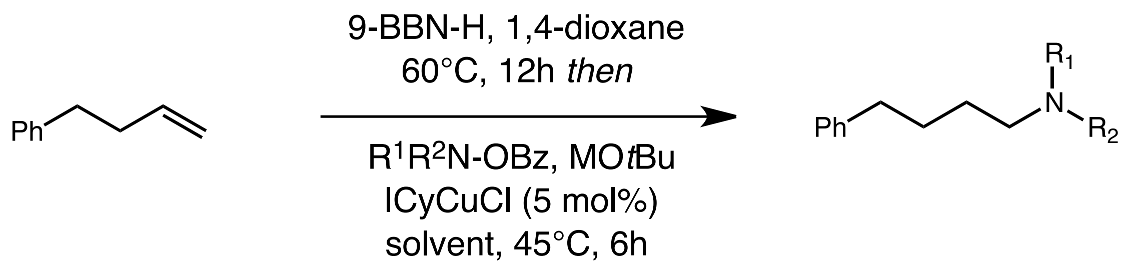
[2]Electrophile added over 3 hours

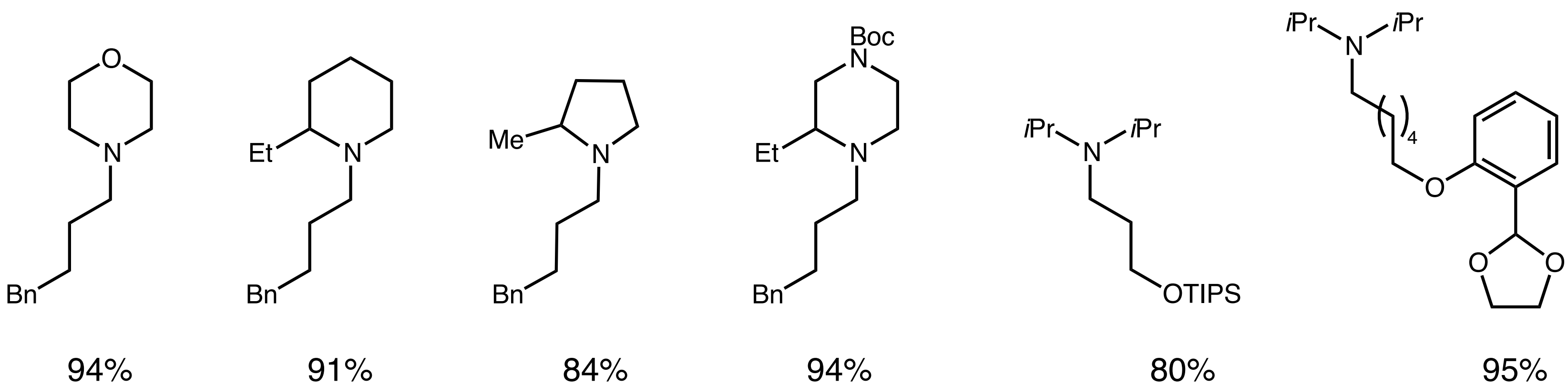
[3]60°C

Rucker, R. P.; Whittaker, A. M.; Dang, H.; Gojko Lalic *J.* Am. Chem. Soc. **2012**, *134*, 6571.

Copper-Catalyzed Alkene Hydroamination with Alkyl Boranes

Substrate Scope





Rucker, R. P.; Whittaker, A. M.; Dang, H.; Gojko Lalic *J.* Am. Chem. Soc. **2012**, *134*, 6571.

Copper-Catalyzed Alkene Hydroamination with Alkyl Boranes

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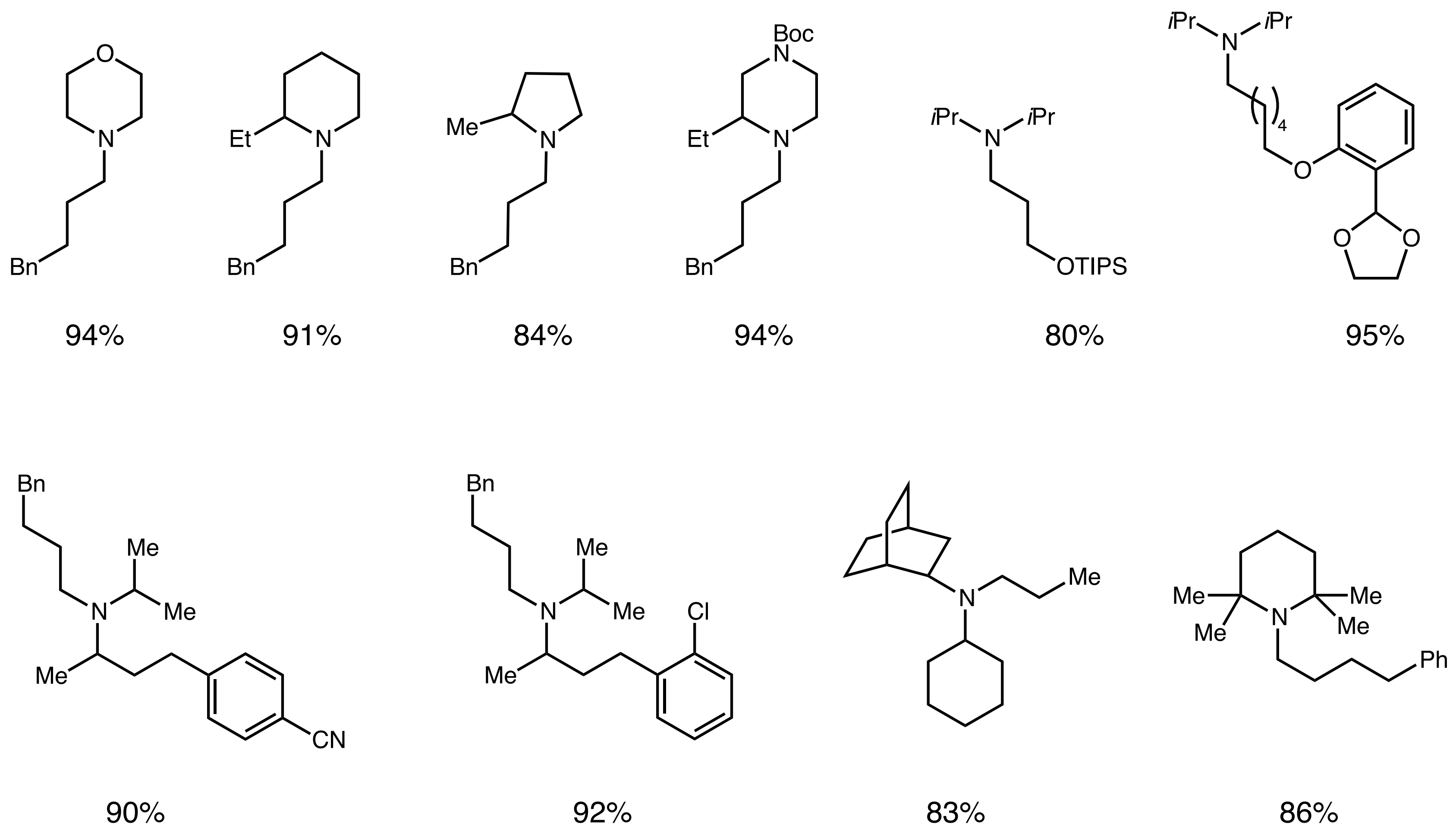
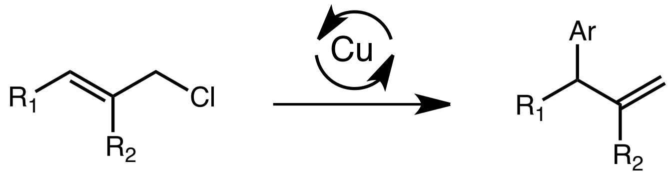


Rucker, R. P.; Whittaker, A. M.; Dang, H.; Gojko Lalic *J. Am. Chem. Soc.* **2012**, *134*, 6571.

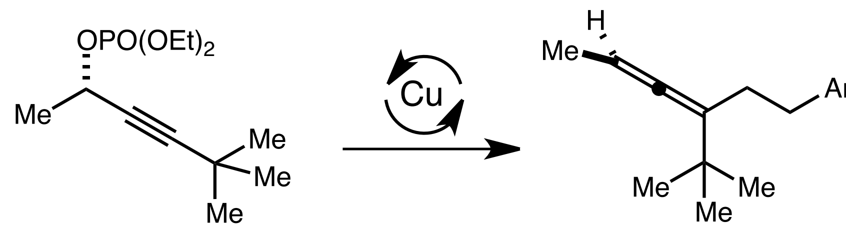
Research in the Lalic Lab

Organic Synthesis and Synthetic Methodology

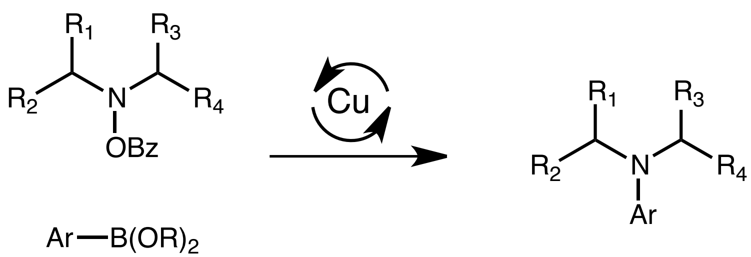
■ Novel methods in copper catalysis



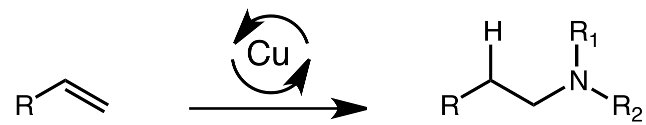
Catalytic S_N2' reactions with Boronic Esters



Asymmetric Synthesis of Trisubstituted Allenes



Synthesis of Hindered Anilines

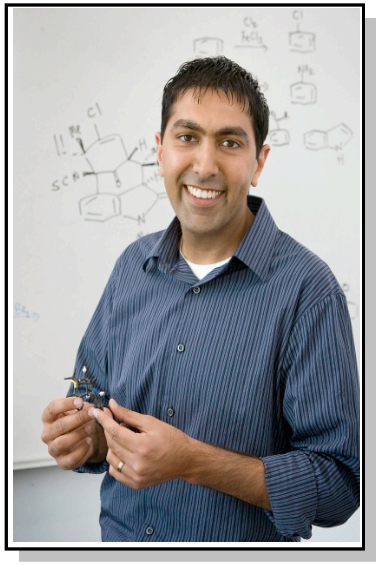


Anti-Markovnikov Hydroamination

Highlights from top Pre-tenure Faculty

Sarah Reisman

Caltech



Neil Garg

UCLA

Gojko Lalic

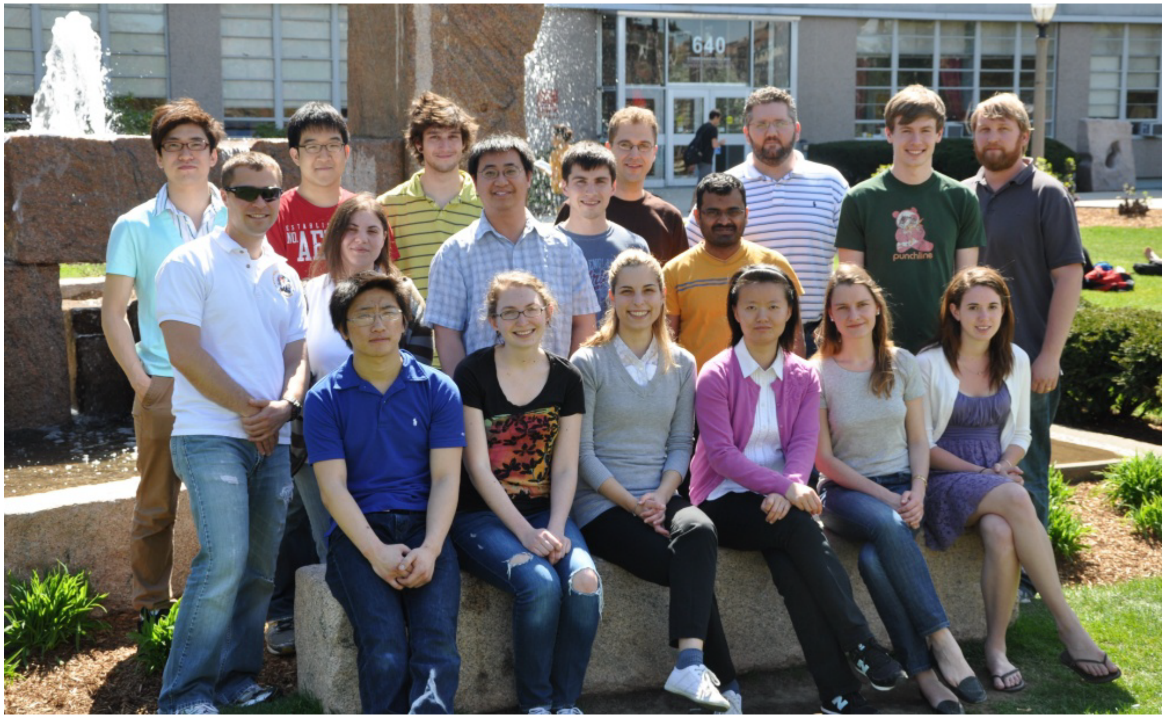
University of Washington

Corey Stephenson

Boston University

Corey Stephenson

Boston University

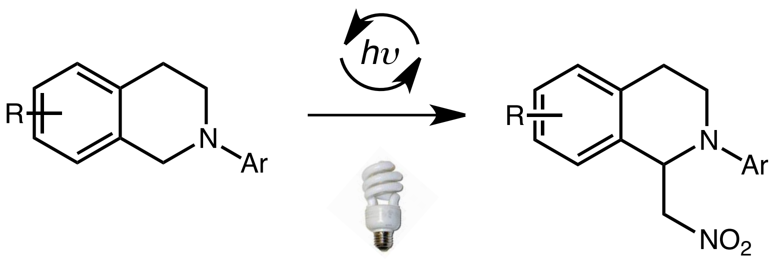


- Assistant Professor at Boston University 2007-present
- Ph.D. with Peter Wipf on the development of alkylzirconocene catalyzed C-C bond formations
- Postdoctoral work with Erick Carreira in asymmetric catalysis using chiral diene ligands

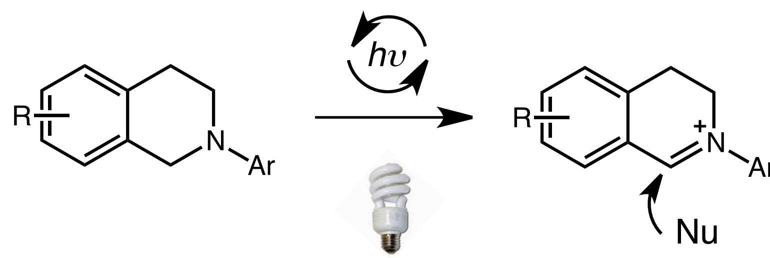
Research in the Stephenson Group

Photoredox Catalysis

Photoredox catalysis

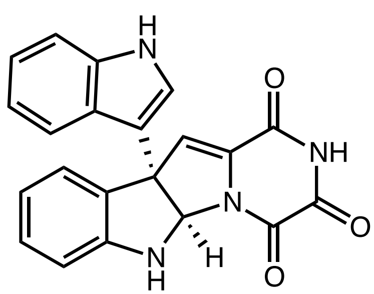


Photoredox Aza-Henry

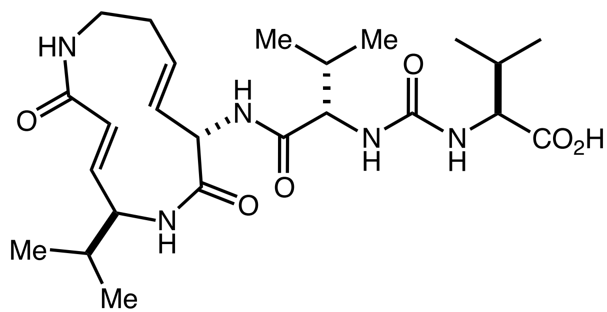


Nucleophilic trapping of iminiums generated through photoredox

Complex molecule synthesis



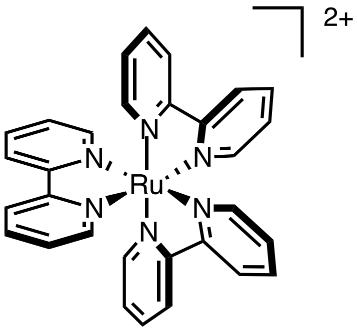
gliocladin C

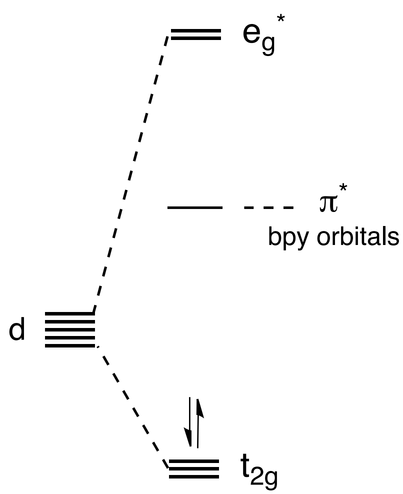


syringolin A

Research in the Stephenson Group

Photoredox Catalysis





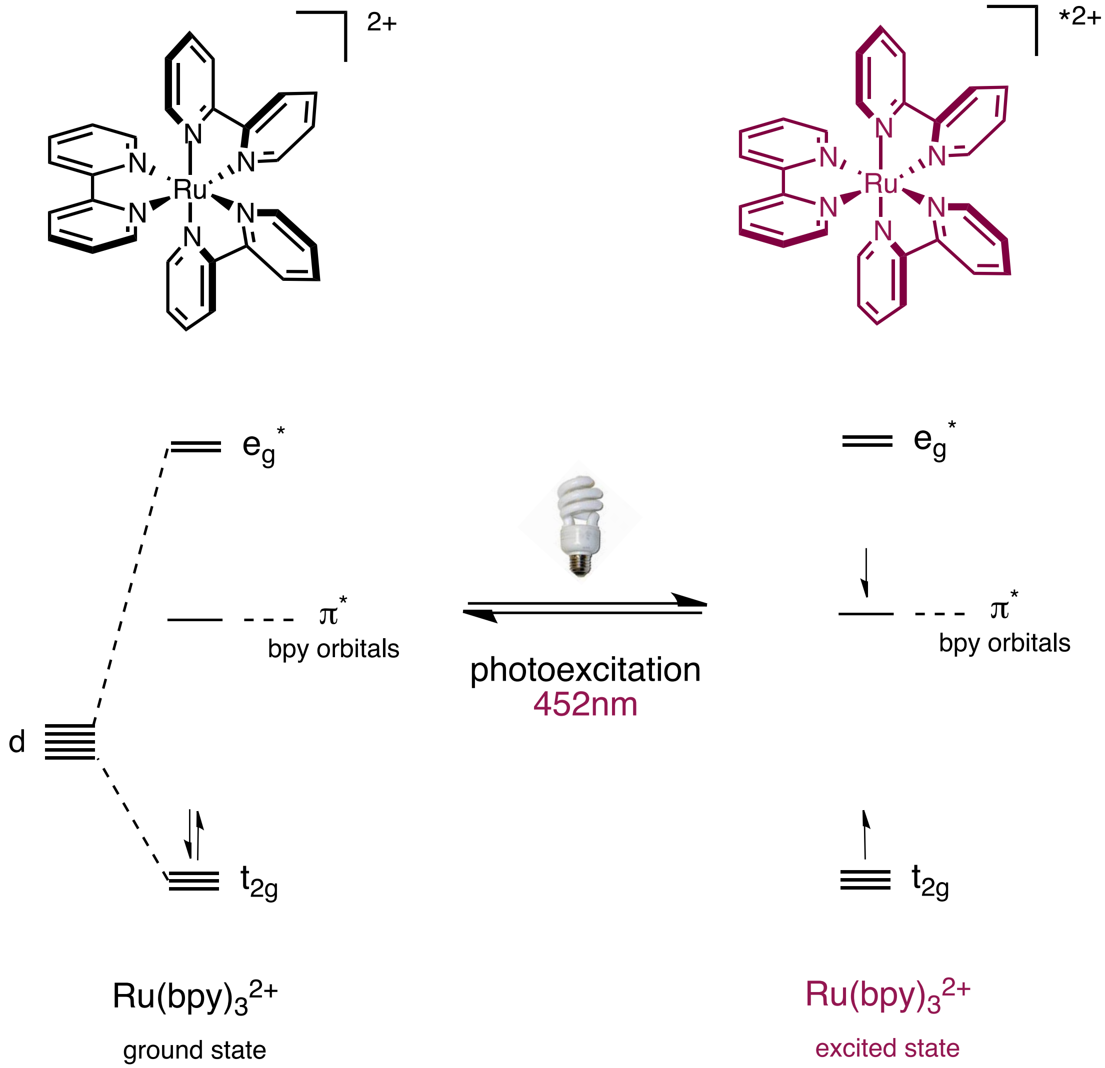
$Ru(bpy)_3^{2+}$

ground state

Coord. Chem. Rev. **1988**, *84*, 85.

Research in the Stephenson Group

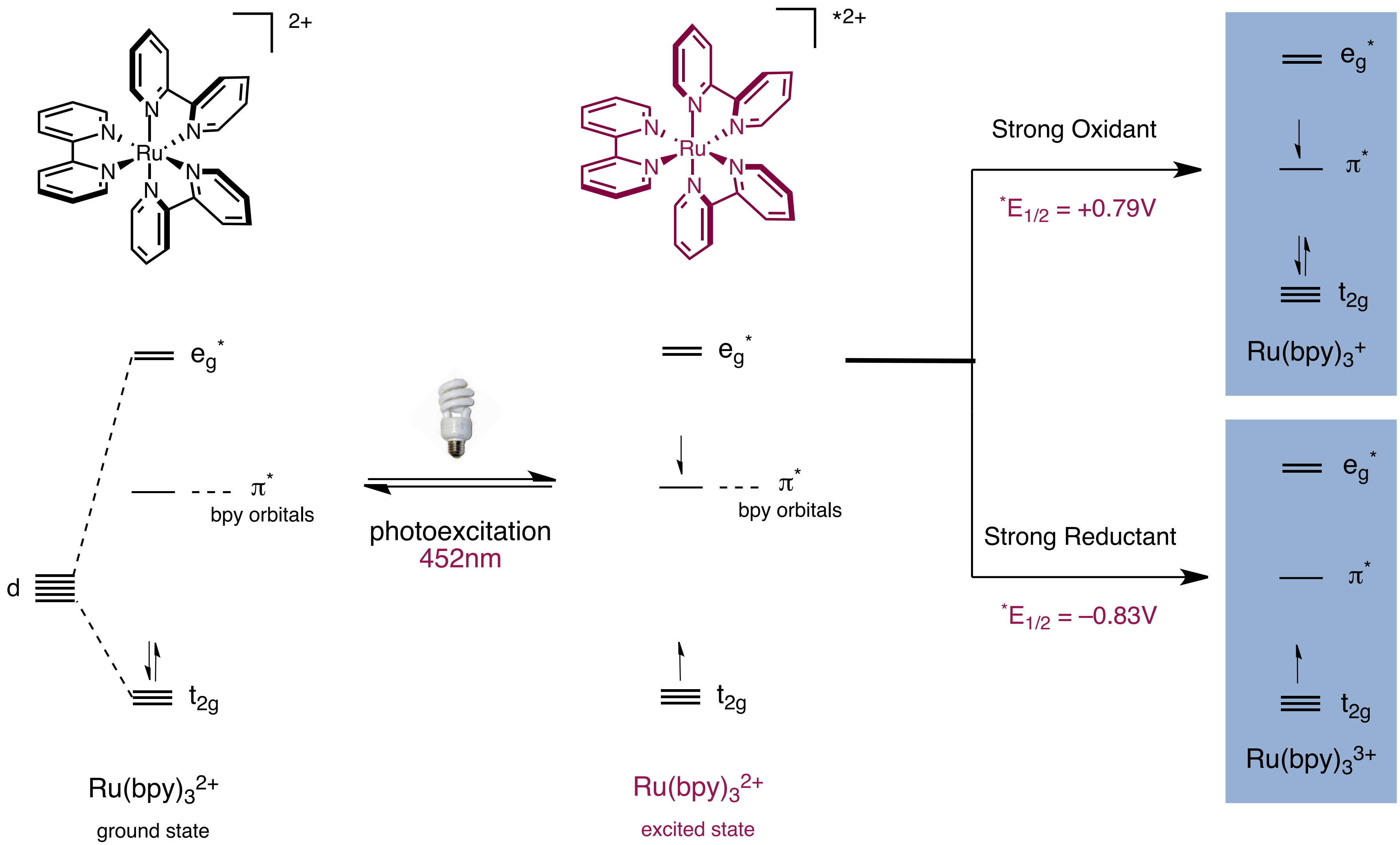
Photoredox Catalysis



Coord. Chem. Rev. **1988**, *84*, 85.

Research in the Stephenson Group

Photoredox Catalysis

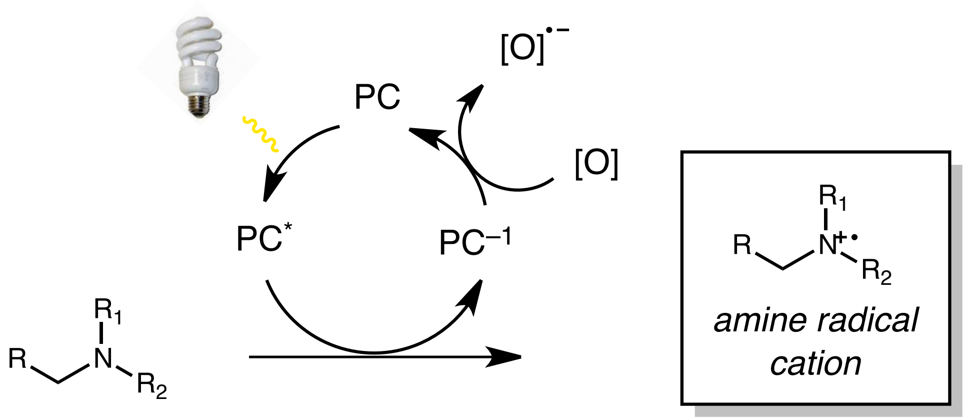


Coord. Chem. Rev. **1988**, *84*, 85.

Research in the Stephenson Group

Photoredox Catalysis for Amine Functionalization

■ Oxidative functionalization of tertiary amines

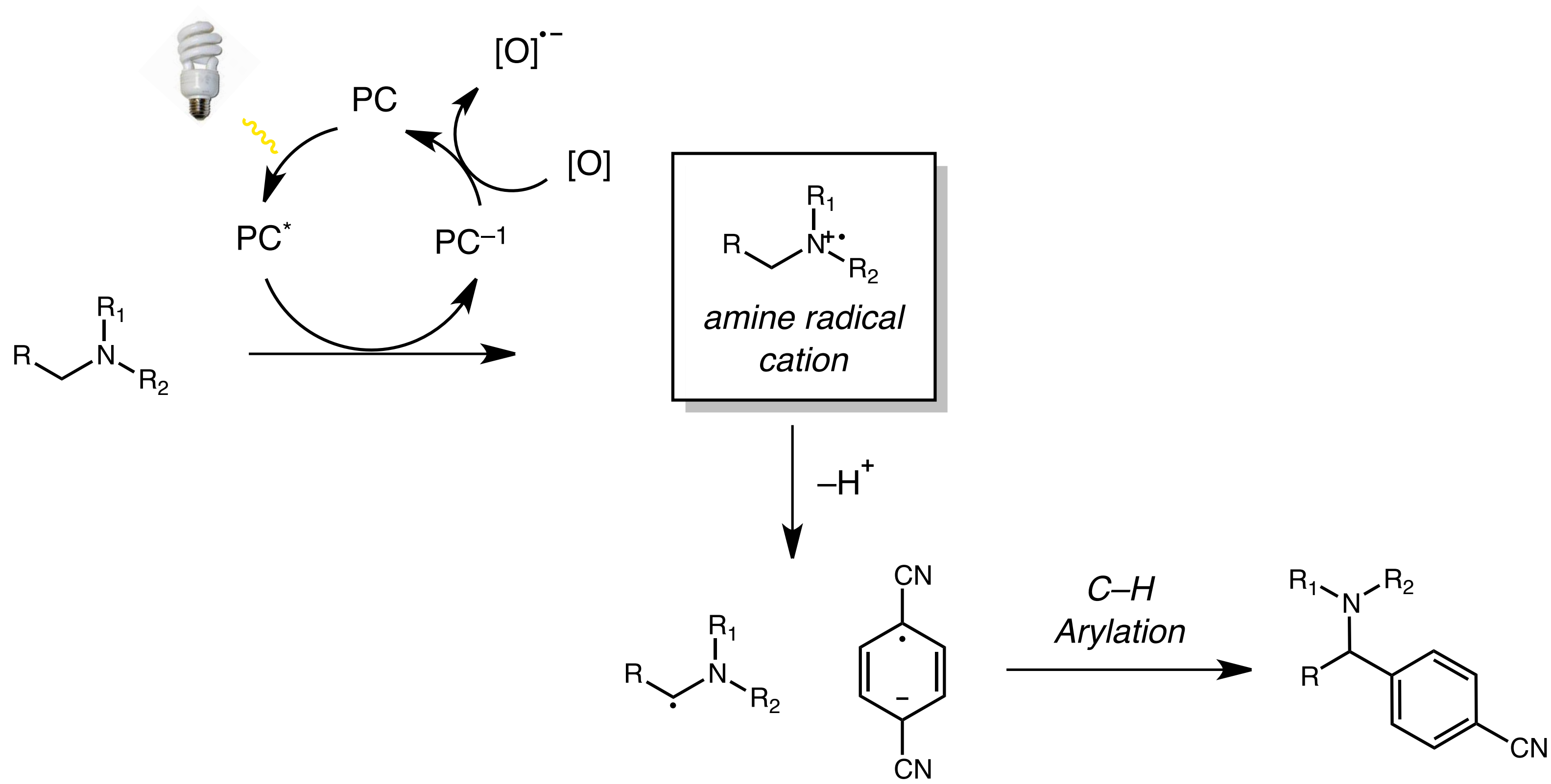


Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem* **2012**, *77,* 1617.
McNally, A.; Prier, C. K.; MacMillan, D. W. C. *Science*, **2011**, *334, 1114.*

Research in the Stephenson Group

Photoredox Catalysis for Amine Functionalization

■ Oxidative functionalization of tertiary amines



Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem* **2012**, *77,* 1617.
McNally, A.; Prier, C. K.; MacMillan, D. W. C. *Science*, **2011**, *334, 1114.*

Research in the Stephenson Group

Photoredox Catalysis for Amine Functionalization

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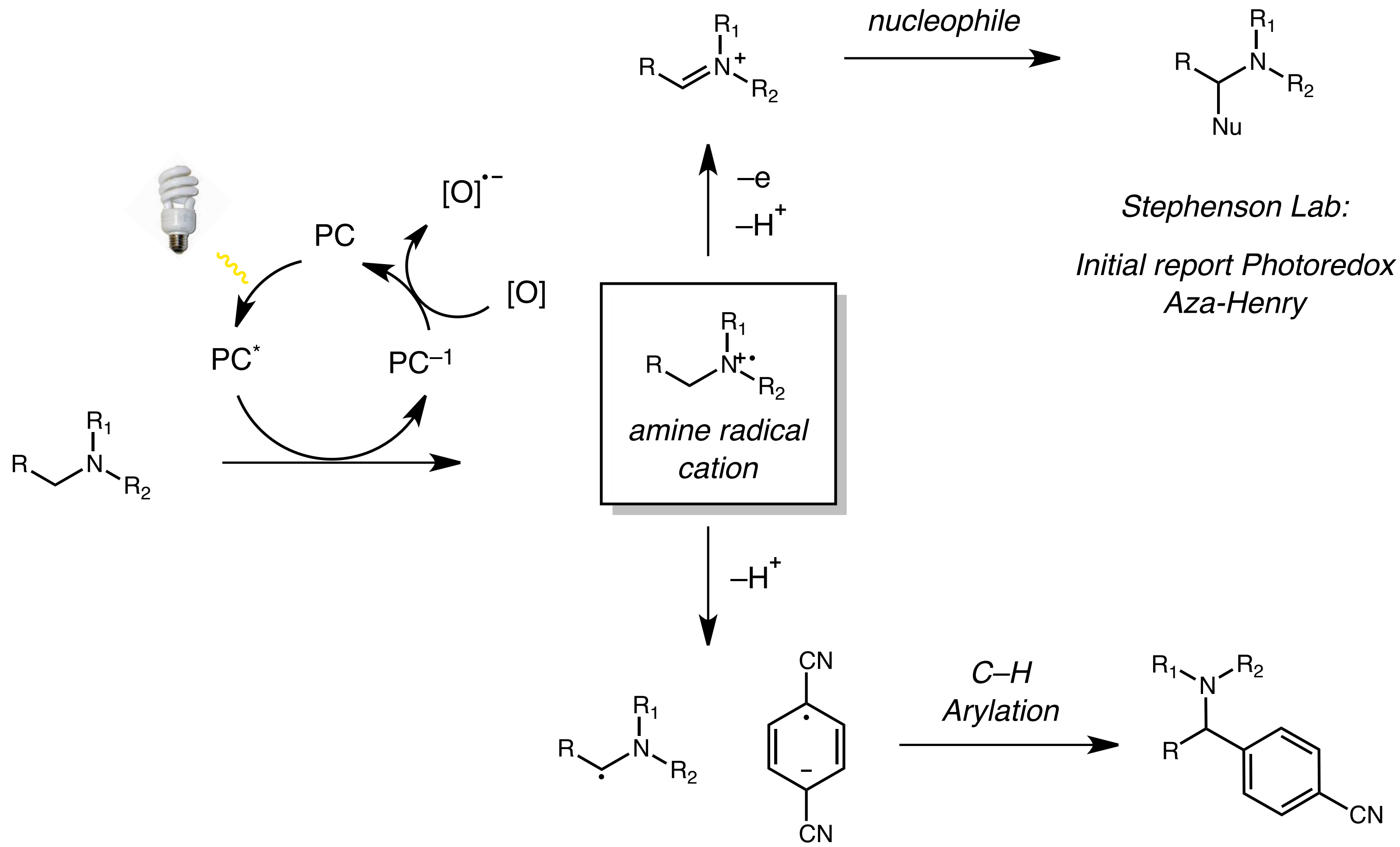

Stephenson Lab:

Initial report Photoredox Aza-Henry

Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem* **2012**, *77,* 1617.
McNally, A.; Prier, C. K.; MacMillan, D. W. C. *Science*, **2011**, *334, 1114.*

Research in the Stephenson Group

Photoredox Catalysis for Amine Functionalization

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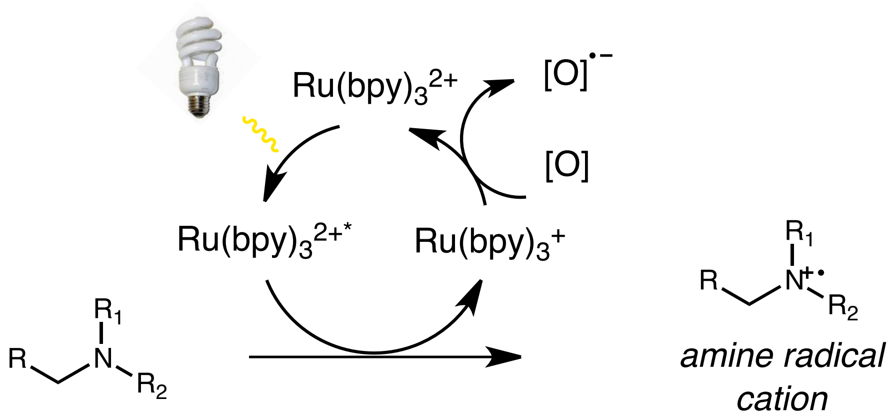
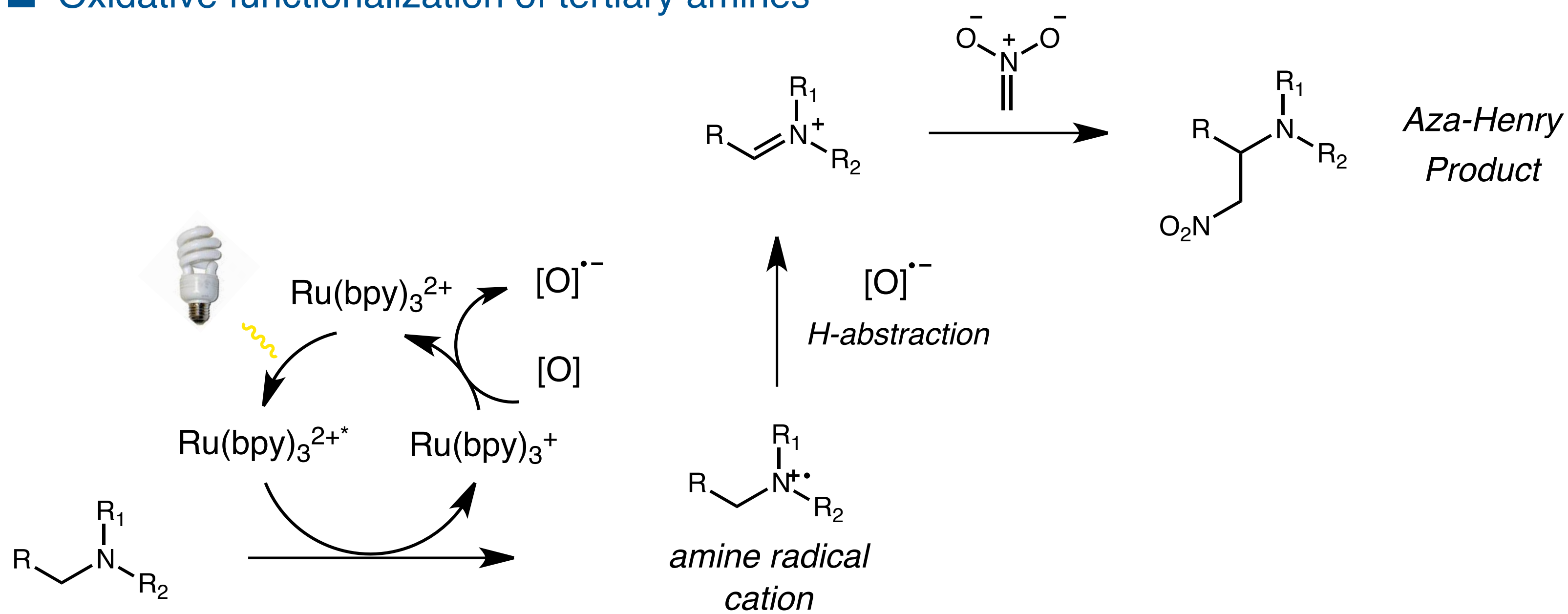


Research in the Stephenson Group

Photoredox Catalysis for Amine Functionalization

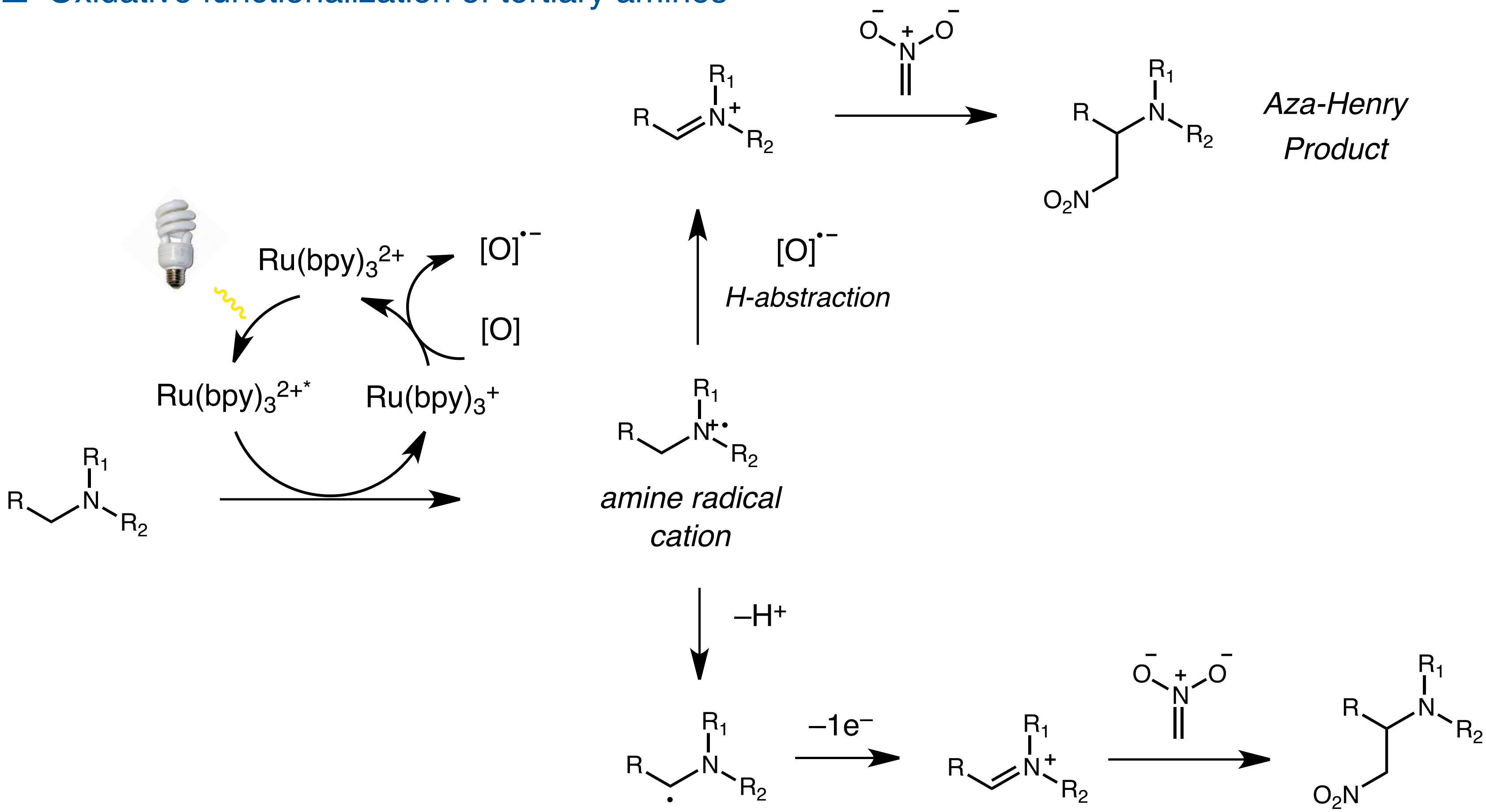
■ Oxidative functionalization of tertiary amines



Research in the Stephenson Group

Photoredox Catalysis for Amine Functionalization

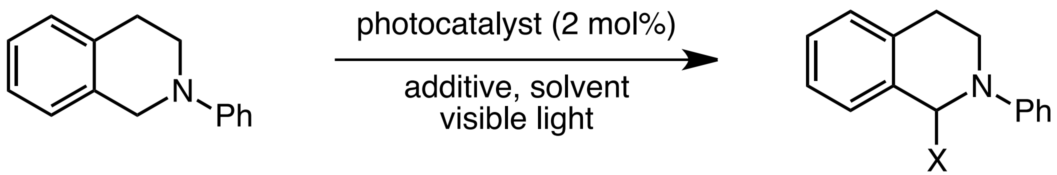
Oxidative functionalization of tertiary amines



Photoredox Catalyzed Aza-Henry Reaction

Photoredox Catalysis for Amine Functionalization

Initial Studies



Photocatalyst	Oxidant	Solvent	Nucleophile	Yield
$Ru(bpy)_3^{2+}$	$(EtO_2C)_2CHBr$	DMF	OMe	73%
$Ru(bpy)_3^{2+}$	$(EtO_2C)_2CHBr$	MeOH	OMe	100%*

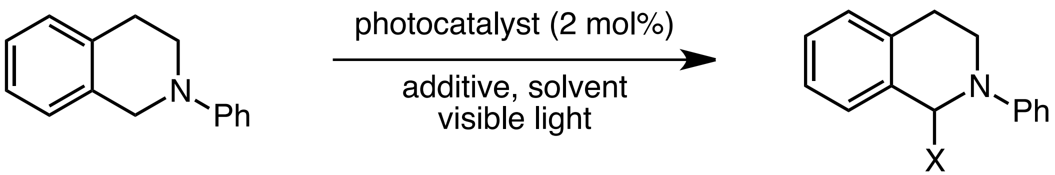
* percent conversion

Condie, A. G.; Gonzalez-Gomez, J. C.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2010**, *132*, 1464

Photoredox Catalyzed Aza-Henry Reaction

Photoredox Catalysis for Amine Functionalization

Initial Studies



Photocatalyst	Oxidant	Solvent	Nucleophile	Yield
$Ru(bpy)_3^{2+}$	$(EtO_2C)_2CHBr$	DMF	OMe	73%
$Ru(bpy)_3^{2+}$	$(EtO_2C)_2CHBr$	MeOH	OMe	100%*
$Ru(bpy)_3^{2+}$	no additive	MeOH	OMe	100%*
$Ru(bpy)_3^{2+}$	no additive	CH_3NO_2	CH_3NO_2	81%
$Ru(bpy)_3^{2+}$	degassed	CH_3NO_2	CH_3NO_2	76%

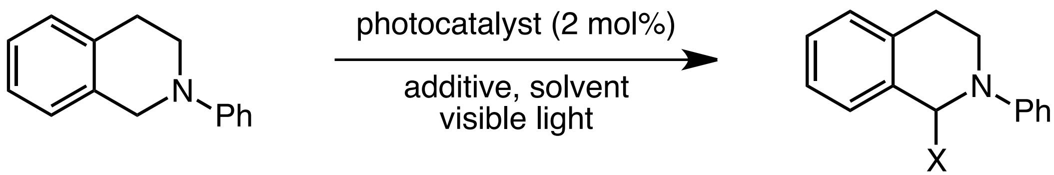
* percent conversion

Condie, A. G.; Gonzalez-Gomez, J. C.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2010**, *132*, 1464

Photoredox Catalyzed Aza-Henry Reaction

Photoredox Catalysis for Amine Functionalization

Initial Studies



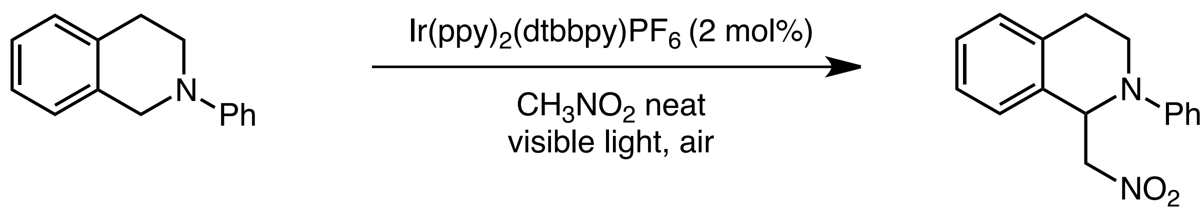
	Photocatalyst	Oxidant	Solvent	Nucleophile	Yield
	$Ru(bpy)_3^{2+}$	$(EtO_2C)_2CHBr$	DMF	OMe	73%
	$Ru(bpy)_3^{2+}$	$(EtO_2C)_2CHBr$	MeOH	OMe	100%*
	$Ru(bpy)_3^{2+}$	no additive	MeOH	OMe	100%*
	$Ru(bpy)_3^{2+}$	no additive	CH_3NO_2	CH_3NO_2	81%
	$Ru(bpy)_3^{2+}$	degassed	CH_3NO_2	CH_3NO_2	76%
	$Ir(ppy)_2(dtbbpy)PF_6$	O_2	CH_3NO_2	CH_3NO_2	92%
no light	$Ir(ppy)_2(dtbbpy)PF_6$	O_2	CH_3NO_2	CH_3NO_2	0%*
	no catalyst: 7.5 days	O_2	CH_3NO_2	CH_3NO_2	83%*

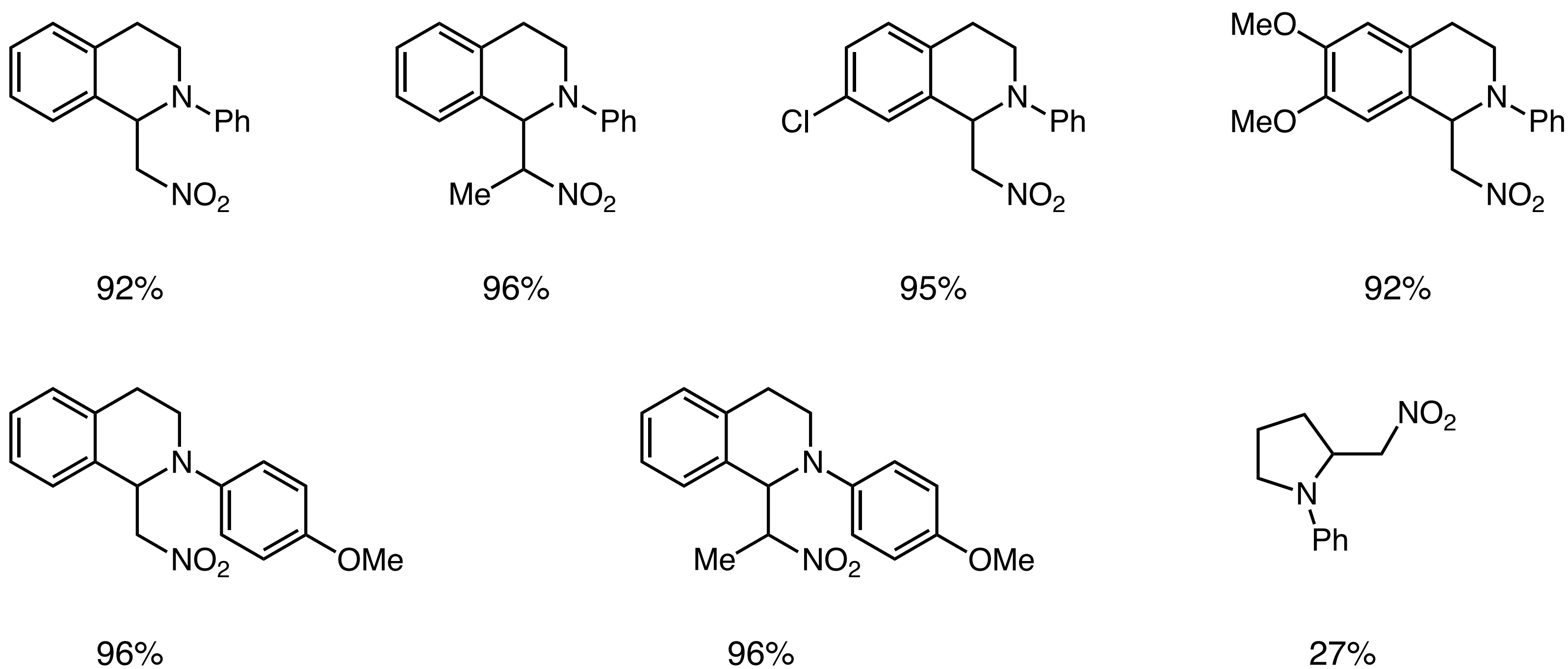
* percent conversion

Condie, A. G.; Gonzalez-Gomez, J. C.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2010**, *132*, 1464

Photoredox Catalyzed Aza-Henry Reaction

Substrate Scope

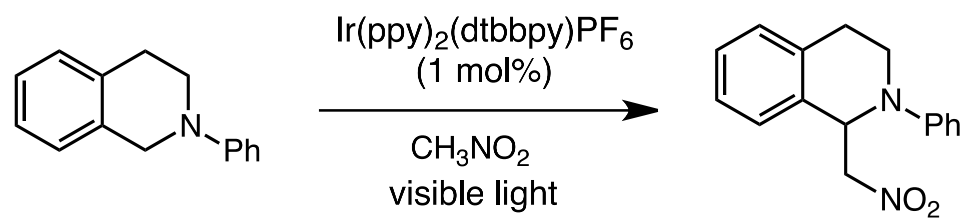


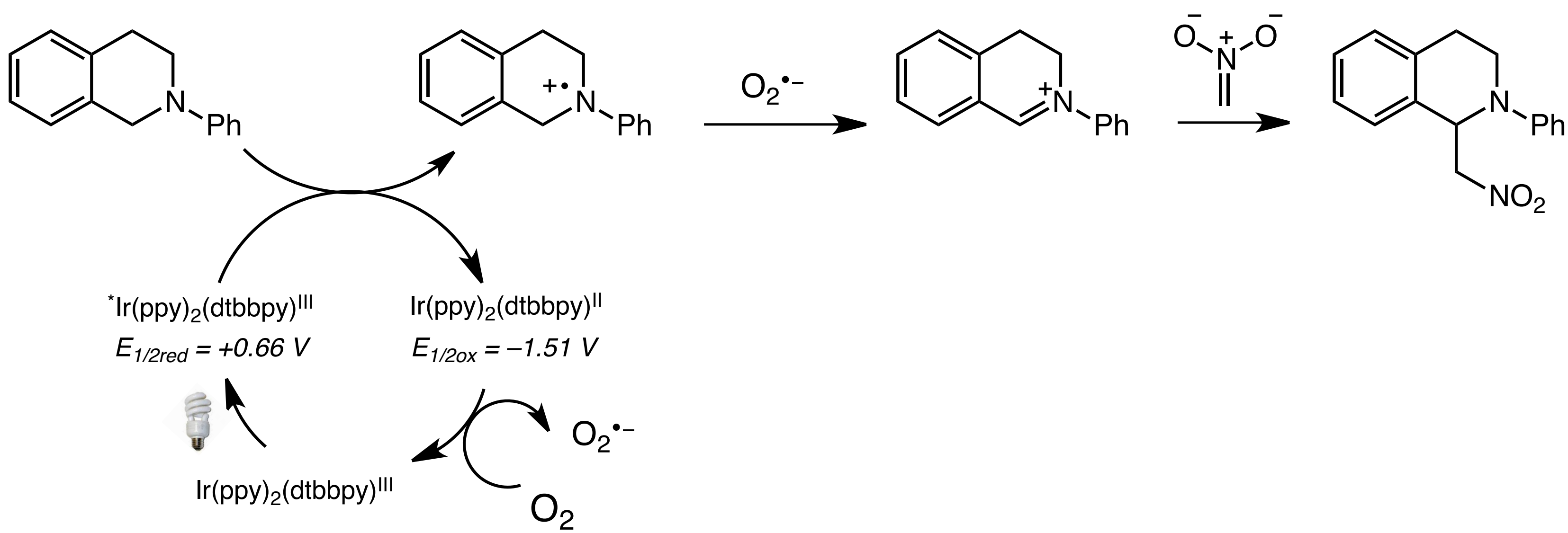


Condie, A. G.; Gonzalez-Gomez, J. C.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2010**, *132*, 1464

Photoredox Catalyzed Aza-Henry Reaction

Proposed Mechanism

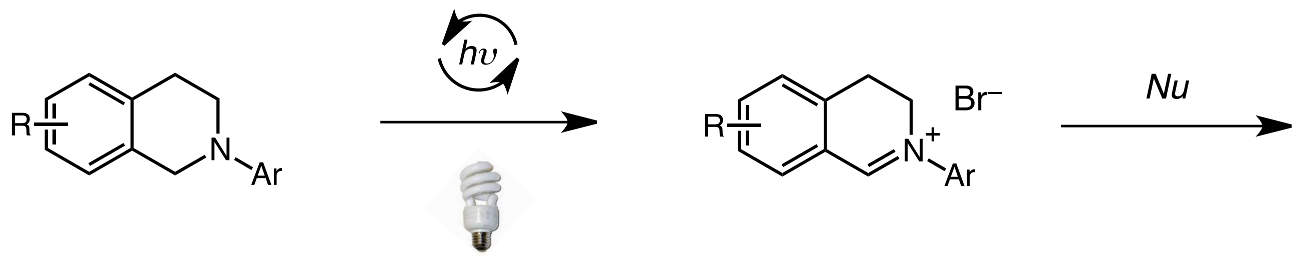




Condie, A. G.; Gonzalez-Gomez, J. C.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2010**, *132*, 1464

Nucleophilic Trapping of Iminium Intermediates

Photoredox Catalysis

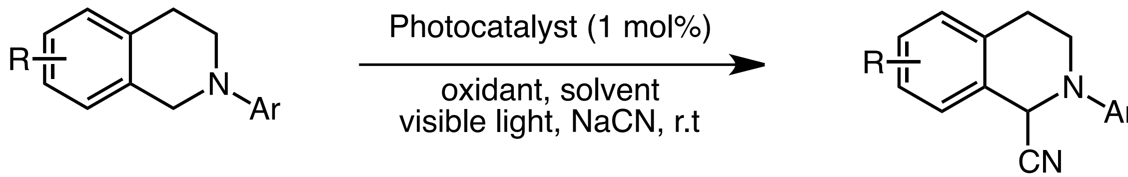


Enolates
Strecker
Alkynylation
Mannich
Sakurai
Friedel-Crafts

Freeman, D. B.; Furst, L.; Condie, A. G.; Stephenson, C. R. J. *Org. Lett.* **2012**, *14*, 94.

Nucleophilic Trapping of Iminium Intermediates

Photoredox Catalysis

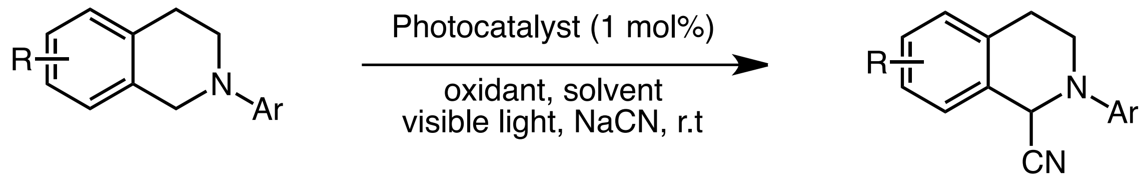


Photocatalyst	Oxidant	Solvent	Yield
$Ir(ppy)_2(dtbbpy)PF_6$	$(EtO_2C)_2CHBr$	DMF	36%
$Ru(bpy)_3^{2+}$	$(EtO_2C)_2CHBr$	DMF	95%

Freeman, D. B.; Furst, L.; Condie, A. G.; Stephenson, C. R. J. *Org. Lett.* **2012**, *14*, 94.

Nucleophilic Trapping of Iminium Intermediates

Photoredox Catalysis

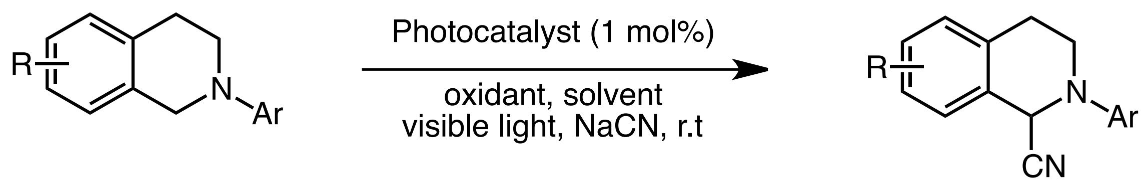


Photocatalyst	Oxidant	Solvent	Yield
$Ir(ppy)_2(dtbbpy)PF_6$	$(EtO_2C)_2CHBr$	DMF	36%
$Ru(bpy)_3^{2+}$	$(EtO_2C)_2CHBr$	DMF	95%
$Ru(bpy)_3^{2+}$	CCl_4/DMF 1:1	DMF	36%
$Ru(bpy)_3^{2+}$	CCl_4	CH_3CN	53%
$Ru(bpy)_3^{2+}$	$BrCCl_3$	DMF	60%

Freeman, D. B.; Furst, L.; Condie, A. G.; Stephenson, C. R. J. *Org. Lett.* **2012**, *14*, 94.

Nucleophilic Trapping of Iminium Intermediates

Photoredox Catalysis

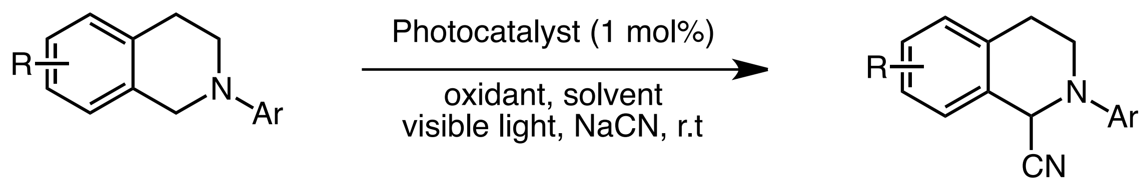


	Photocatalyst	Oxidant	Solvent	Yield	
	$Ir(ppy)_2(dtbbpy)PF_6$	$(EtO_2C)_2CHBr$	DMF	36%	
	$Ru(bpy)_3^{2+}$	$(EtO_2C)_2CHBr$	DMF	95%	
	$Ru(bpy)_3^{2+}$	CCl_4/DMF 1:1	DMF	36%	
	$Ru(bpy)_3^{2+}$	CCl_4	CH_3CN	53%	
	$Ru(bpy)_3^{2+}$	$BrCCl_3$	DMF	60%	
	$Ru(bpy)_3^{2+}$	$BrCCl_3$	DMF	85%	*iminium pre-generated*
Bu_4NCN as Nu	$Ru(bpy)_3^{2+}$	$BrCCl_3$	DMF	17%	*iminium pre-generated*

Freeman, D. B.; Furst, L.; Condie, A. G.; Stephenson, C. R. J. *Org. Lett.* **2012**, *14*, 94.

Nucleophilic Trapping of Iminium Intermediates

Photoredox Catalysis

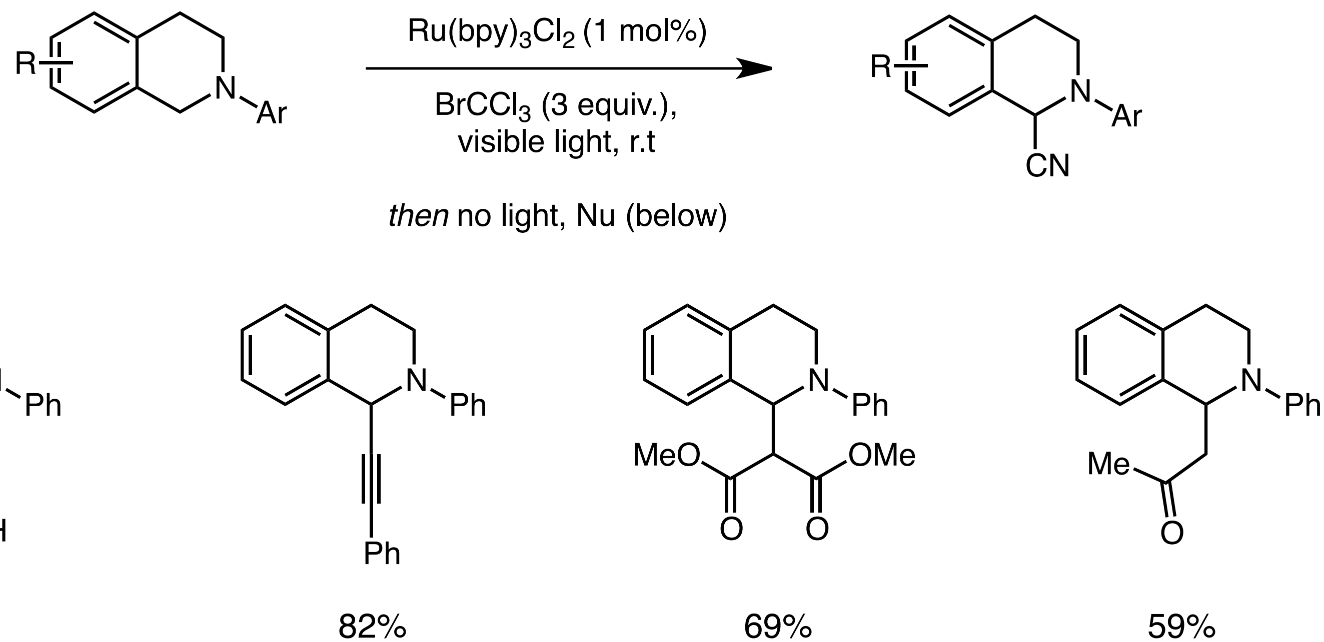


	Photocatalyst	Oxidant	Solvent	Yield	
	$Ir(ppy)_2(dtbbpy)PF_6$	$(EtO_2C)_2CHBr$	DMF	36%	
	$Ru(bpy)_3^{2+}$	$(EtO_2C)_2CHBr$	DMF	95%	
	$Ru(bpy)_3^{2+}$	CCl_4/DMF 1:1	DMF	36%	
	$Ru(bpy)_3^{2+}$	CCl_4	CH_3CN	53%	
	$Ru(bpy)_3^{2+}$	$BrCCl_3$	DMF	60%	
	$Ru(bpy)_3^{2+}$	$BrCCl_3$	DMF	85%	*iminium pre-generated*
Bu_4NCN as Nu	$Ru(bpy)_3^{2+}$	$BrCCl_3$	DMF	17%	*iminium pre-generated*
	$Ru(bpy)_3^{2+}$	$BrCCl_3$	THF	NR	*iminium pre-generated*
	$Ru(bpy)_3^{2+}$	$BrCCl_3$	2:1 THF/H_2O	83%	*iminium pre-generated*

Freeman, D. B.; Furst, L.; Condie, A. G.; Stephenson, C. R. J. *Org. Lett.* **2012**, *14*, 94.

Nucleophilic Trapping of Iminium Intermediates

Photoredox Catalysis



Freeman, D. B.; Furst, L.; Condie, A. G.; Stephenson, C. R. J. *Org. Lett.* **2012**, *14*, 94.

Nucleophilic Trapping of Iminium Intermediates

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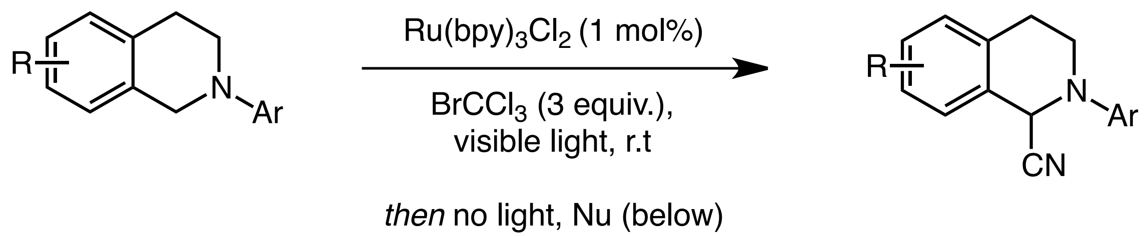

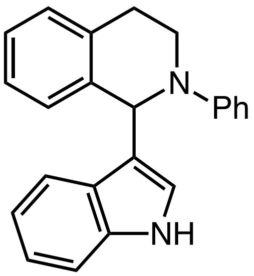

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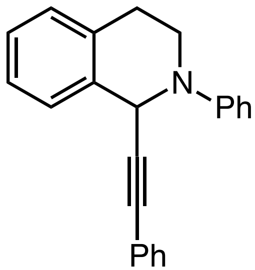
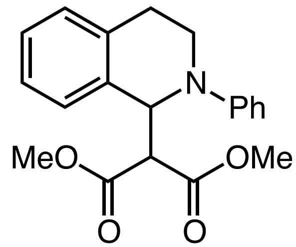
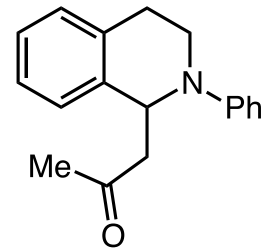


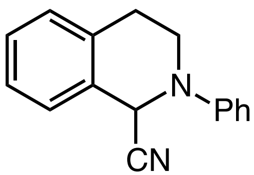
82%



69%



59%



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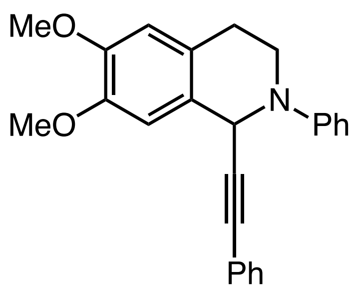
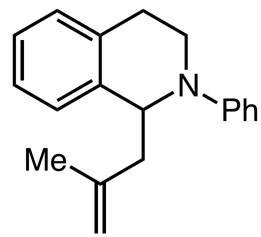
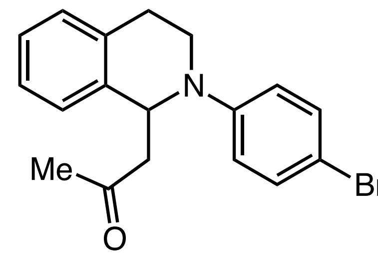


89%



85%



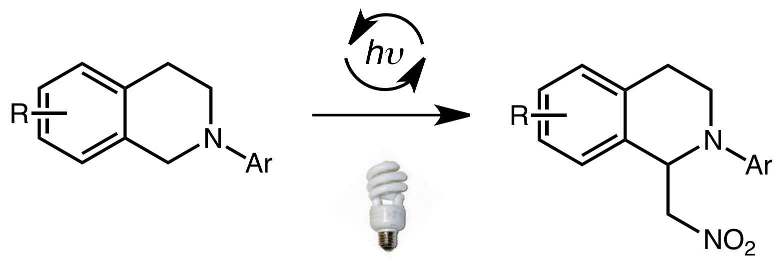
65%

Freeman, D. B.; Furst, L.; Condie, A. G.; Stephenson, C. R. J. *Org. Lett.* **2012**, *14*, 94.

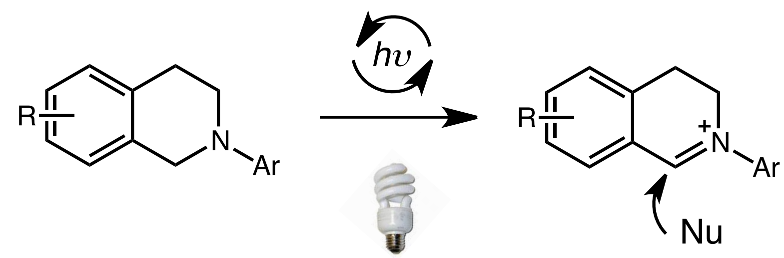
Research in the Stephenson Group

Photoredox Catalysis

Photoredox catalysis

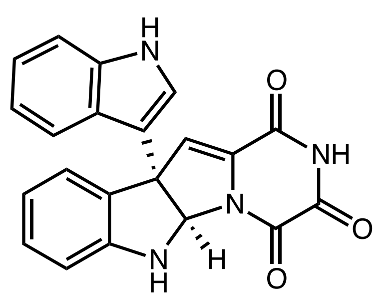


Photoredox Aza-Henry

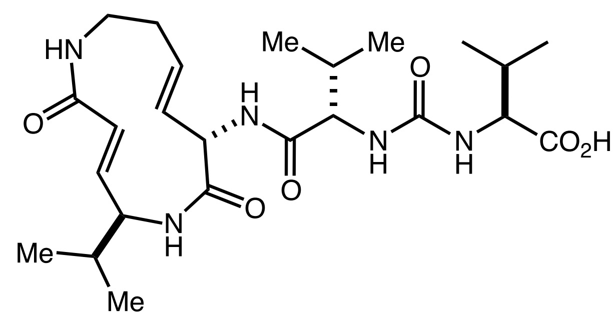


Nucleophilic trapping of iminiums generated through photoredox

Complex molecule synthesis



gliocladin C

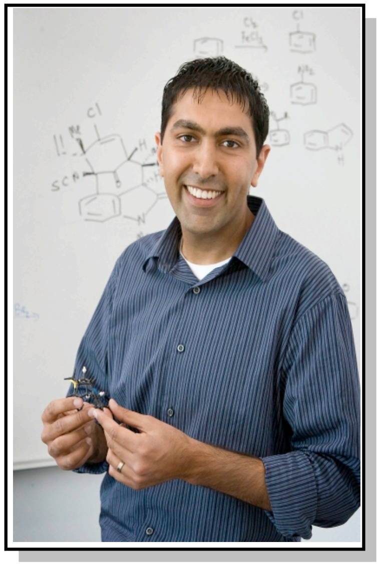


syringolin A

Highlights from top Pre-tenure Faculty

Sarah Reisman

Caltech



Neil Garg

UCLA

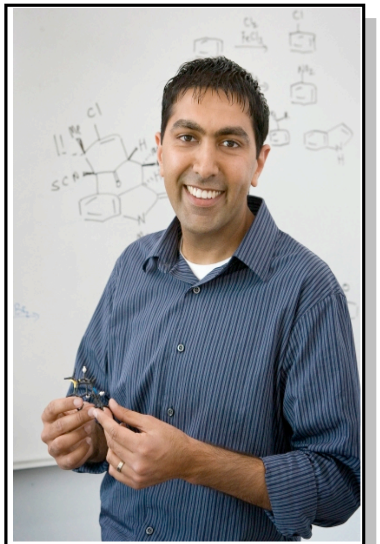
Gojko Lalic

University of Washington

Corey Stephenson

Boston University

Highlights from top Pre-tenure Faculty



Sarah Reisman

Caltech

Neil Garg

UCLA

Gojko Lalic

University of Washington

Corey Stephenson

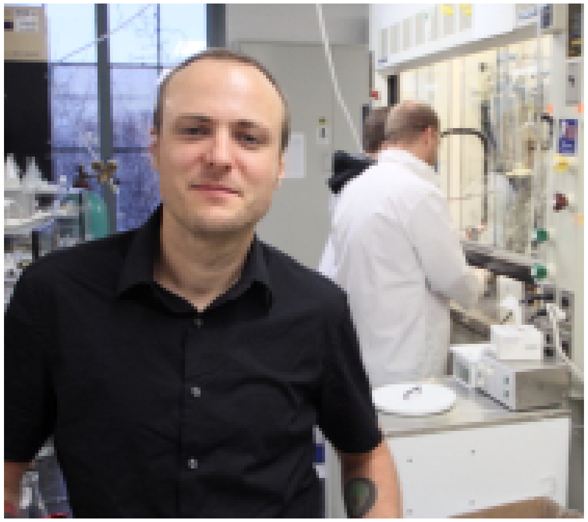
Boston University

Regan Thomson

Northwestern

Regan Thomson

Northwestern University

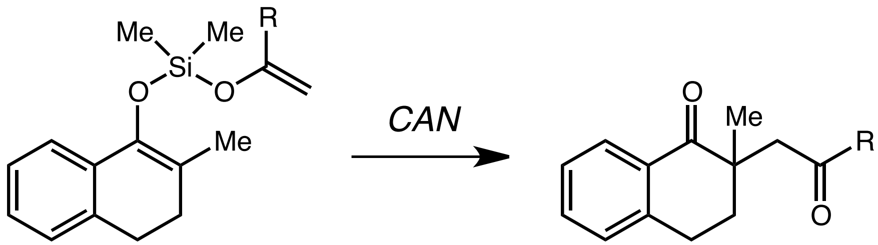


- Assistant Professor at Northwestern 2007-present
- Ph.D. with Prof. L. Mander, total synthesis of *Sordaricin*
- Postdoctoral work with Prof. Dave Evans developing enantioselective *Ni* catalyzed methods

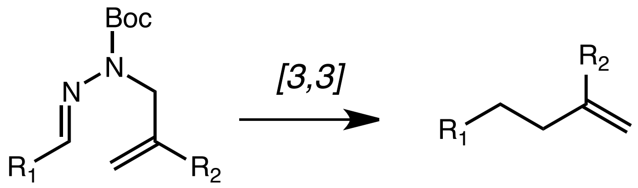
Research in the Thomson Group

Organic Synthesis and Synthetic Methodology

Novel methods for C–C bond construction



Oxidative Couplings of Silyl Enol Ethers

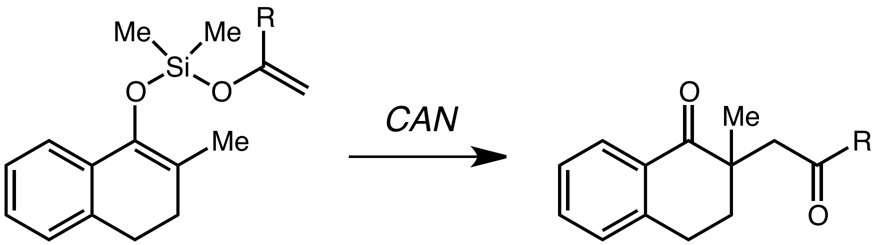


Traceless Reaction Development

Research in the Thomson Group

Organic Synthesis and Synthetic Methodology

■ Novel methods for C–C bond construction



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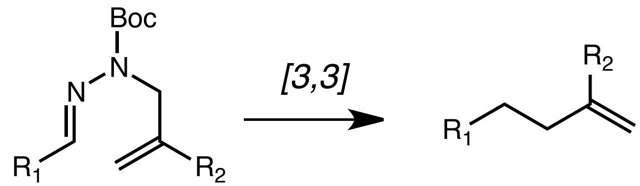
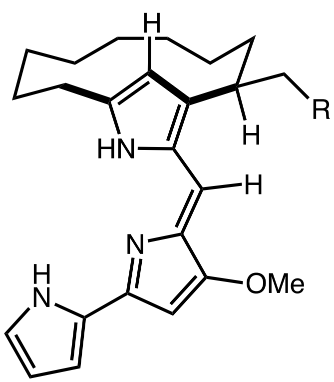
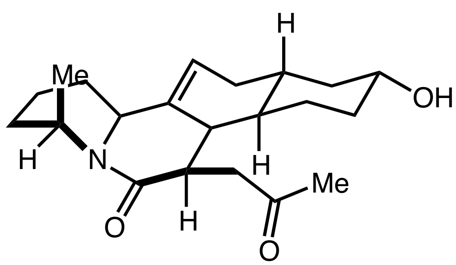


Traceless Reaction Development

■ Total synthesis of complex natural products



Prodigiosin R1 (R=iPr)



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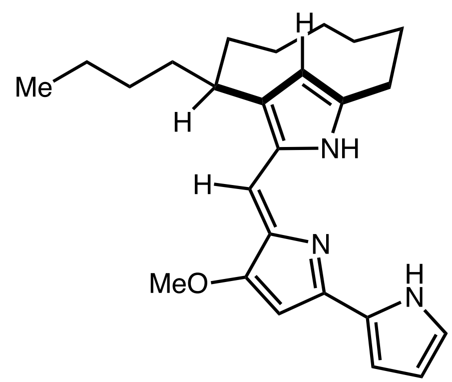
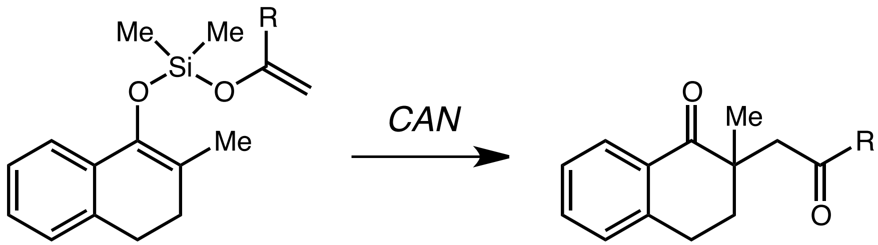


Streptorubin B

Research in the Thomson Group

Organic Synthesis and Synthetic Methodology

Novel methods for C–C bond construction



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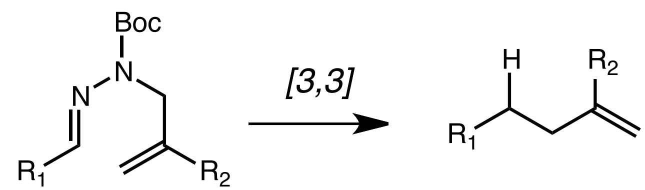

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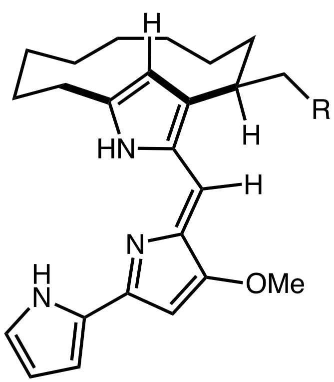

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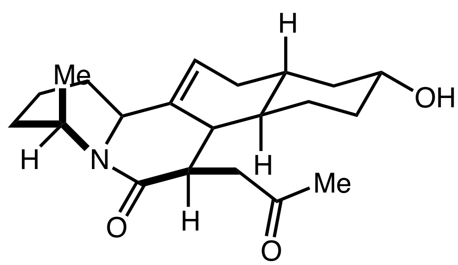

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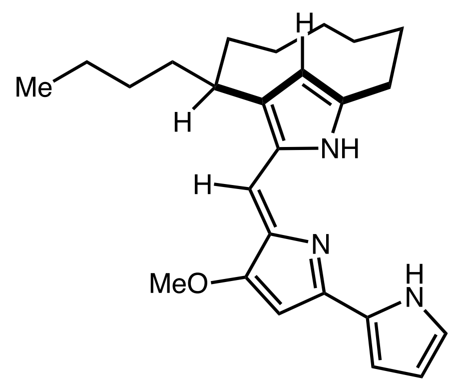
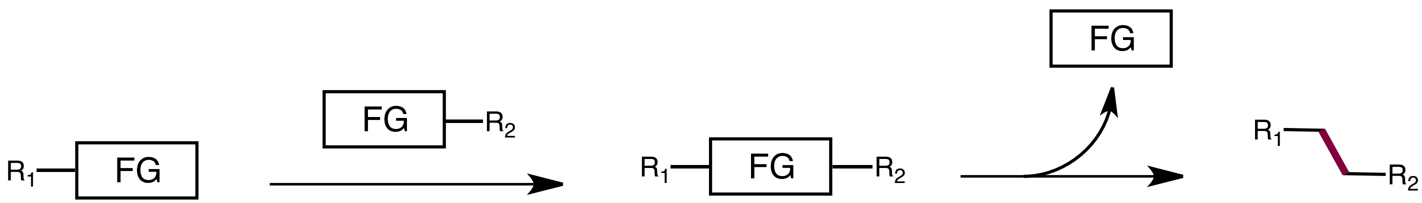


Streptorubin B

Traceless Bond Construction

Bond Formation without an Obvious Retron

■ Formation of a new σ-bond without extrusion of a functional handle



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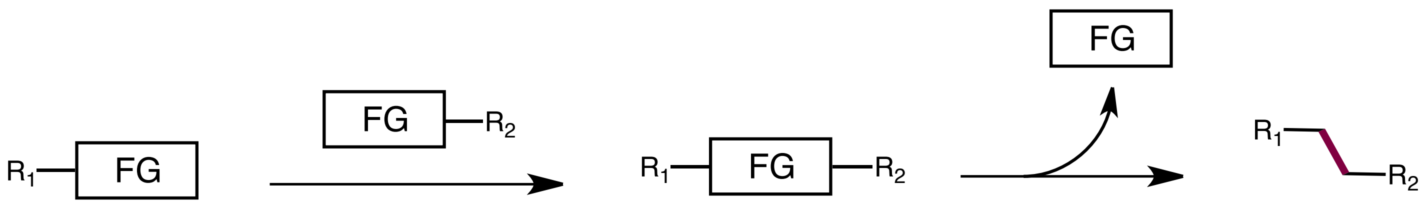
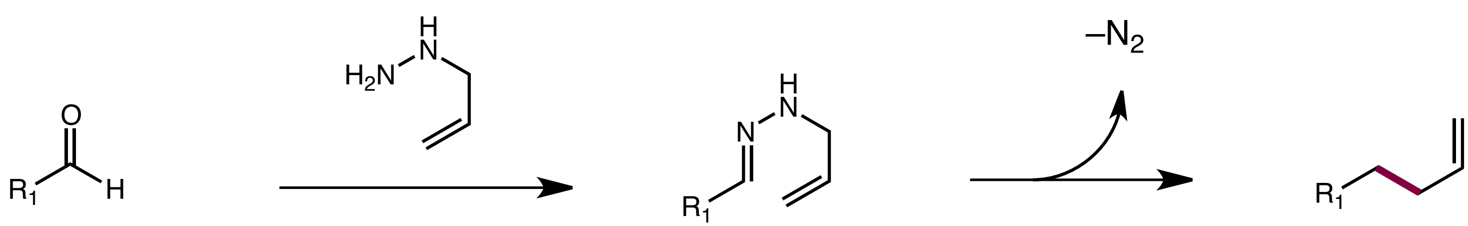


■ Steven's thermal rearrangement of *N*-allylhydrazones



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Cu(II) Promoted [3,3] Sigmatropic Rearrangement

Tandem C–C and C–Cl Bond Formation

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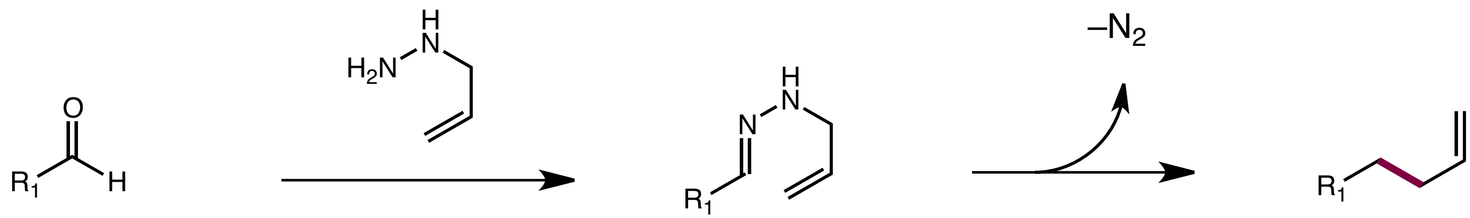

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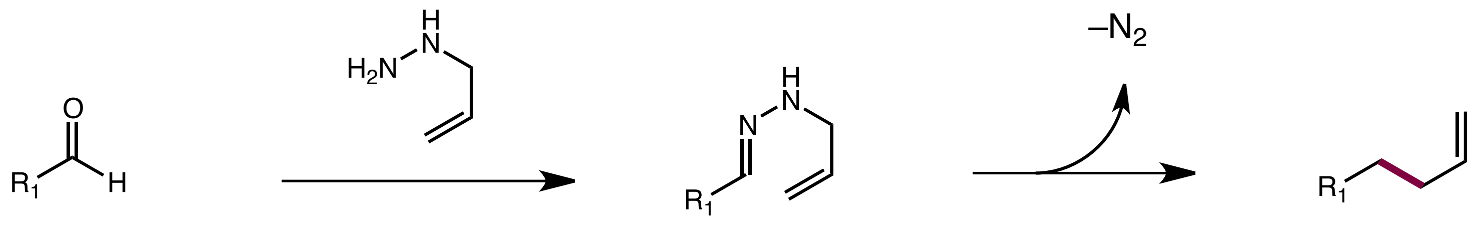
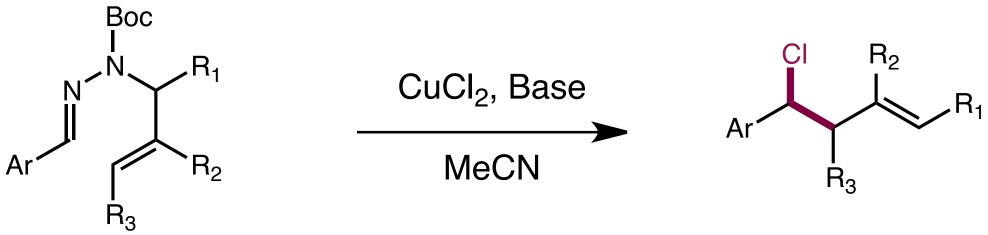


■ Utilizing *N*-allylhydrazones in Synthesis



Mundal, D. A.; Lee, J. L.; Thomson, R. J. *J. Am. Chem. Soc.* **2008,** *130*, 1148.
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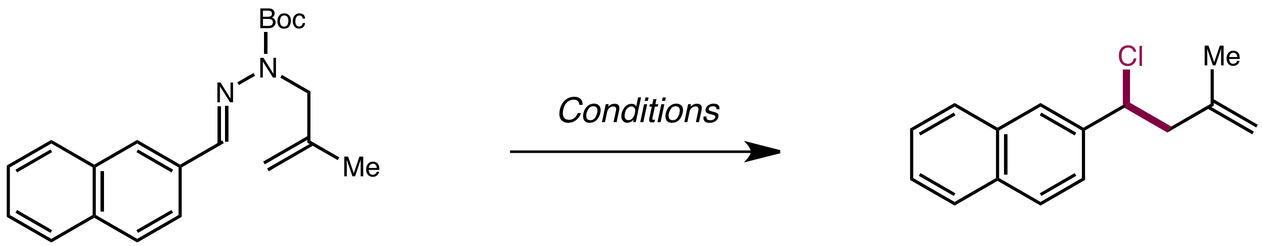
Tandem C–C and C–Cl Bond Formation

■ Optimization of Cu promoted rearrangement



Entry	Solvent	Temp (°C)	$CuCl_2$ (equiv)	time (h)	Conversion (%)
1	PhMe	110	0	24	0
2	PhMe	23	1	24	0

Mundal, D. A.; Lee, J. L.; Thomson, R. J. *J. Am. Chem. Soc.* **2008,** *130*, 1148.

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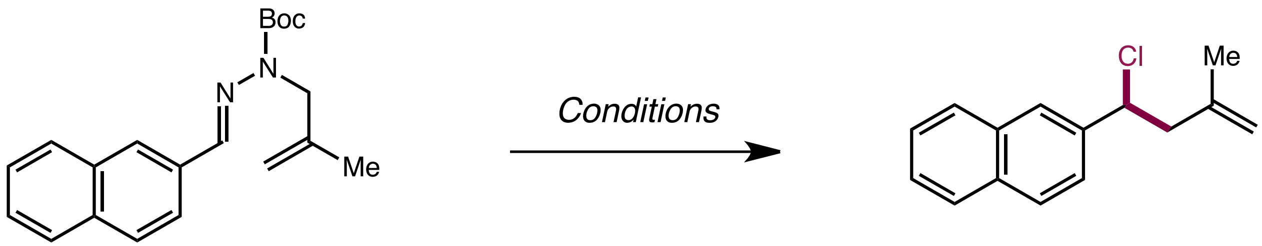

Entry	Solvent	Temp (°C)	$CuCl_2$ (equiv)	time (h)	Conversion (%)
1	PhMe	110	0	24	0
2	PhMe	23	1	24	0
3	THF	23	1	24	0
4	MeOH	23	1	24	0
5	DCM	23	1	24	25

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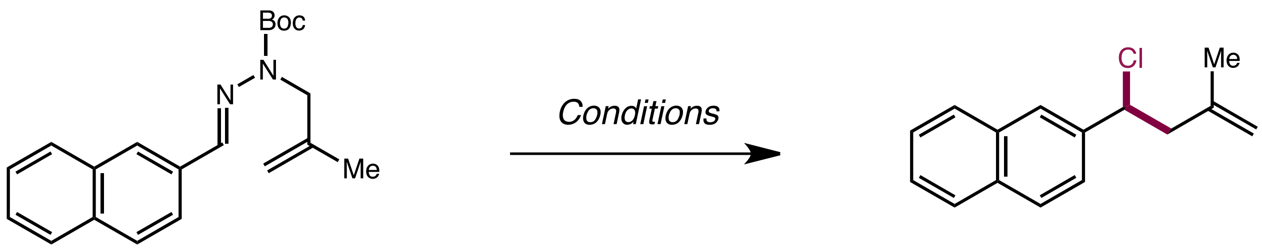

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5	DCM	23	1	24	25
6	MeCN	23	1	24	28
7	MeCN	23	4	16	100

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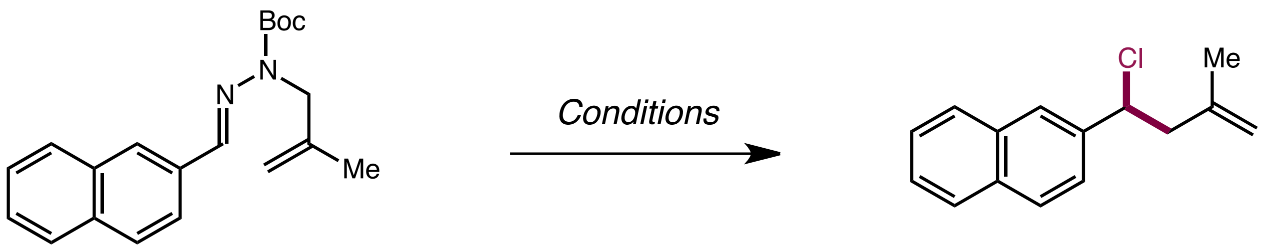

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4	MeOH	23	1	24	0
5	DCM	23	1	24	25
6	MeCN	23	1	24	28
7	MeCN	23	4	16	100
8	MeCN	82	4	0.3	100

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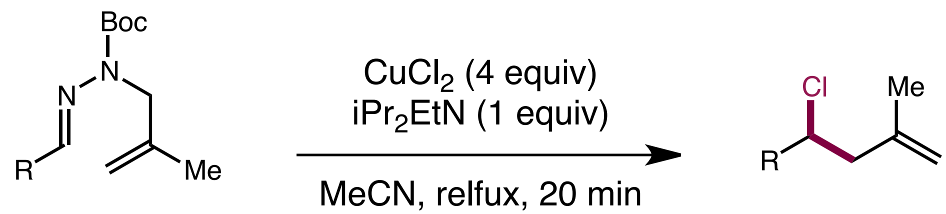
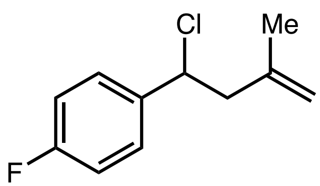
Cu(II) Promoted [3,3] Sigmatropic Rearrangement

Tandem C–C and C–Cl Bond Formation

■ Reaction substrate scope





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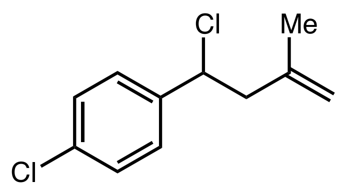

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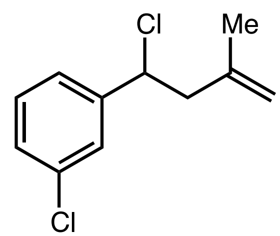

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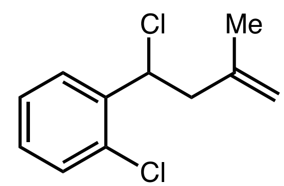

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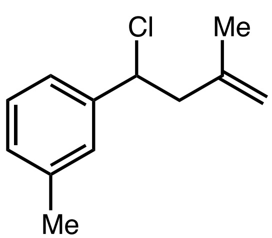

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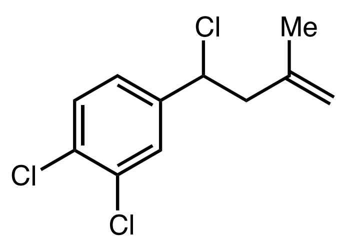

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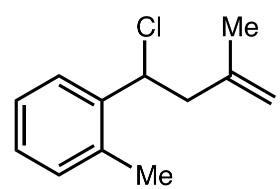

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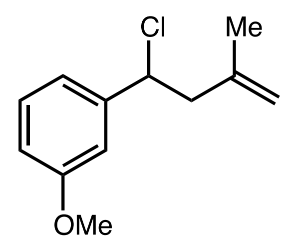

47%

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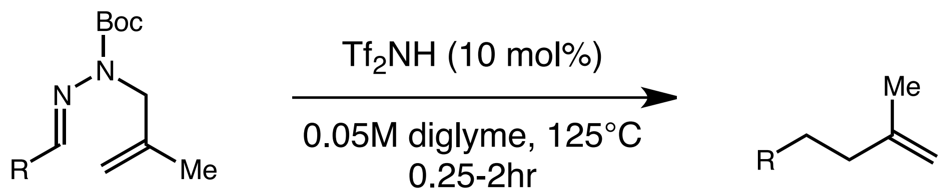
Triflamide Catalyzed Sigmatropic Rearrangement of N-Allylhydrazones

Traceless Bond Construction

■ New approach broadens substrate scope



■ $Hf(OTf)_4$ yields product at 125°C

■ Controls reveal HOTf catalyzes reaction

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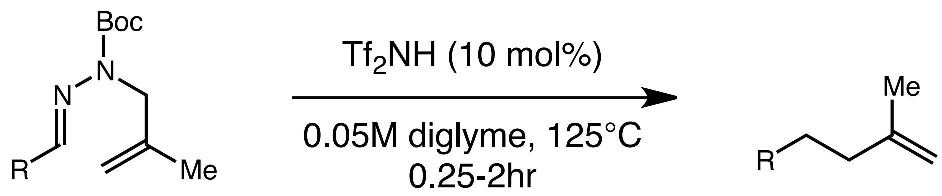

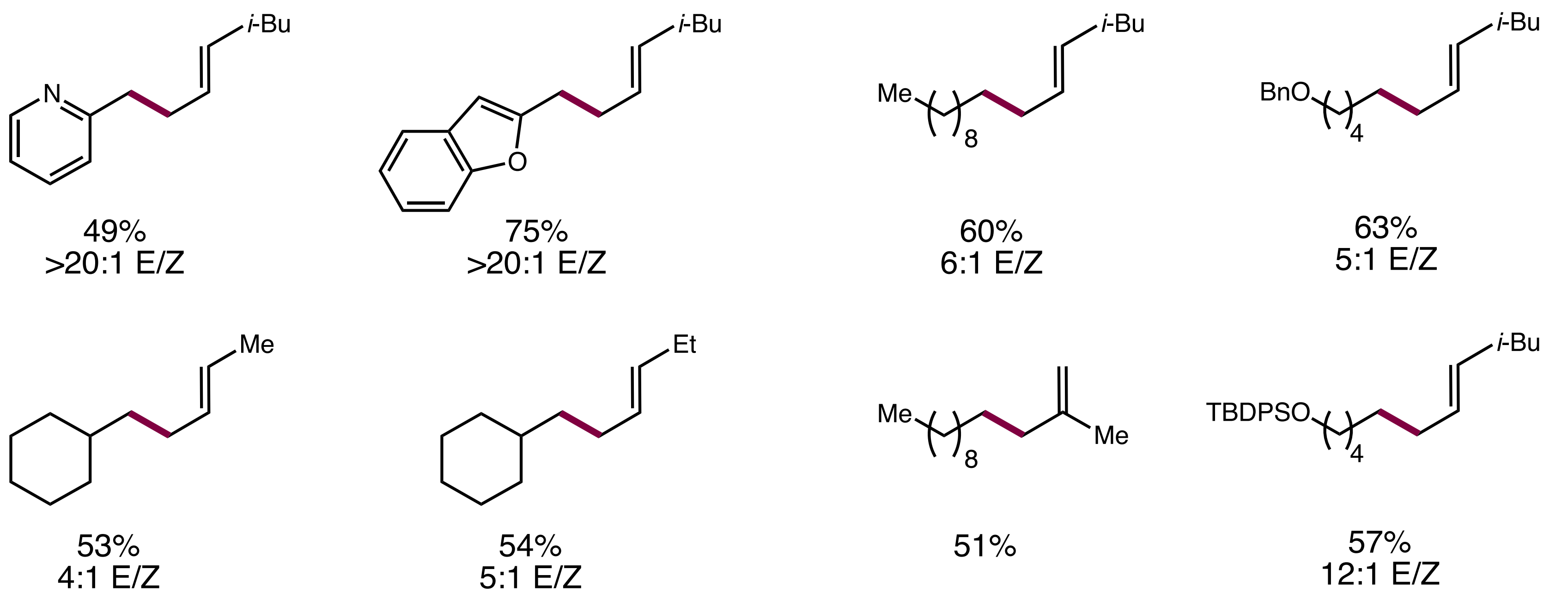

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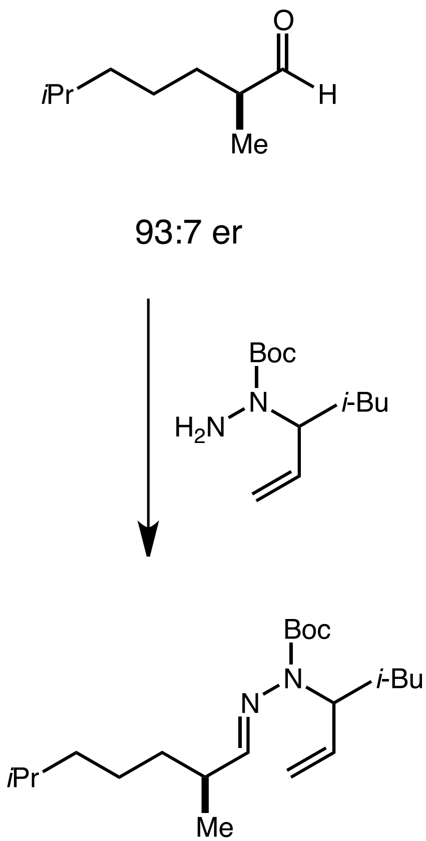

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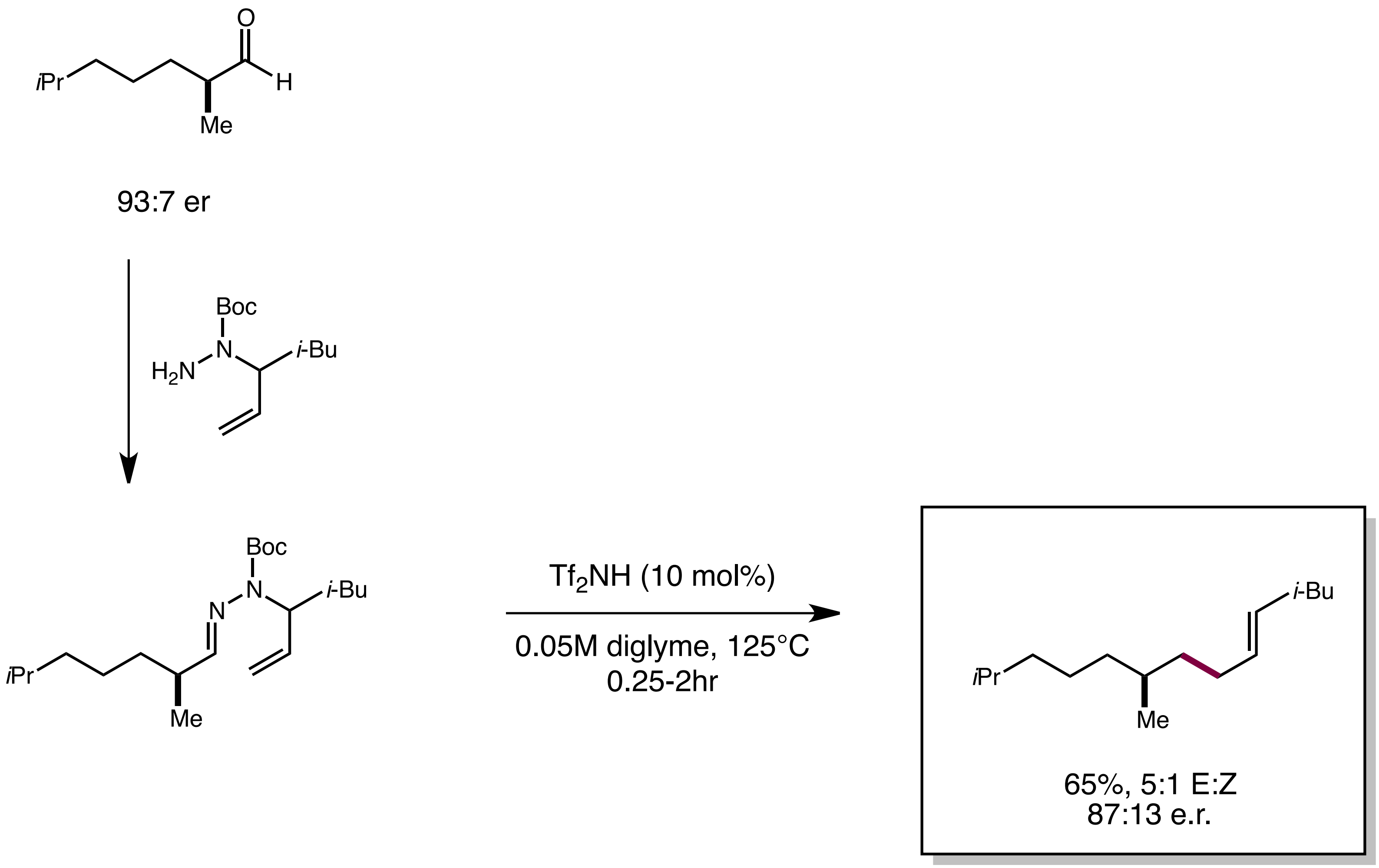

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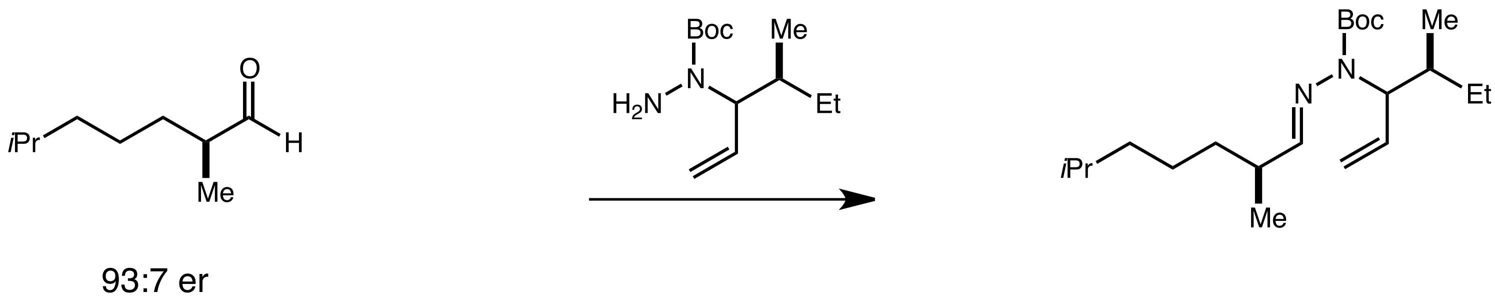

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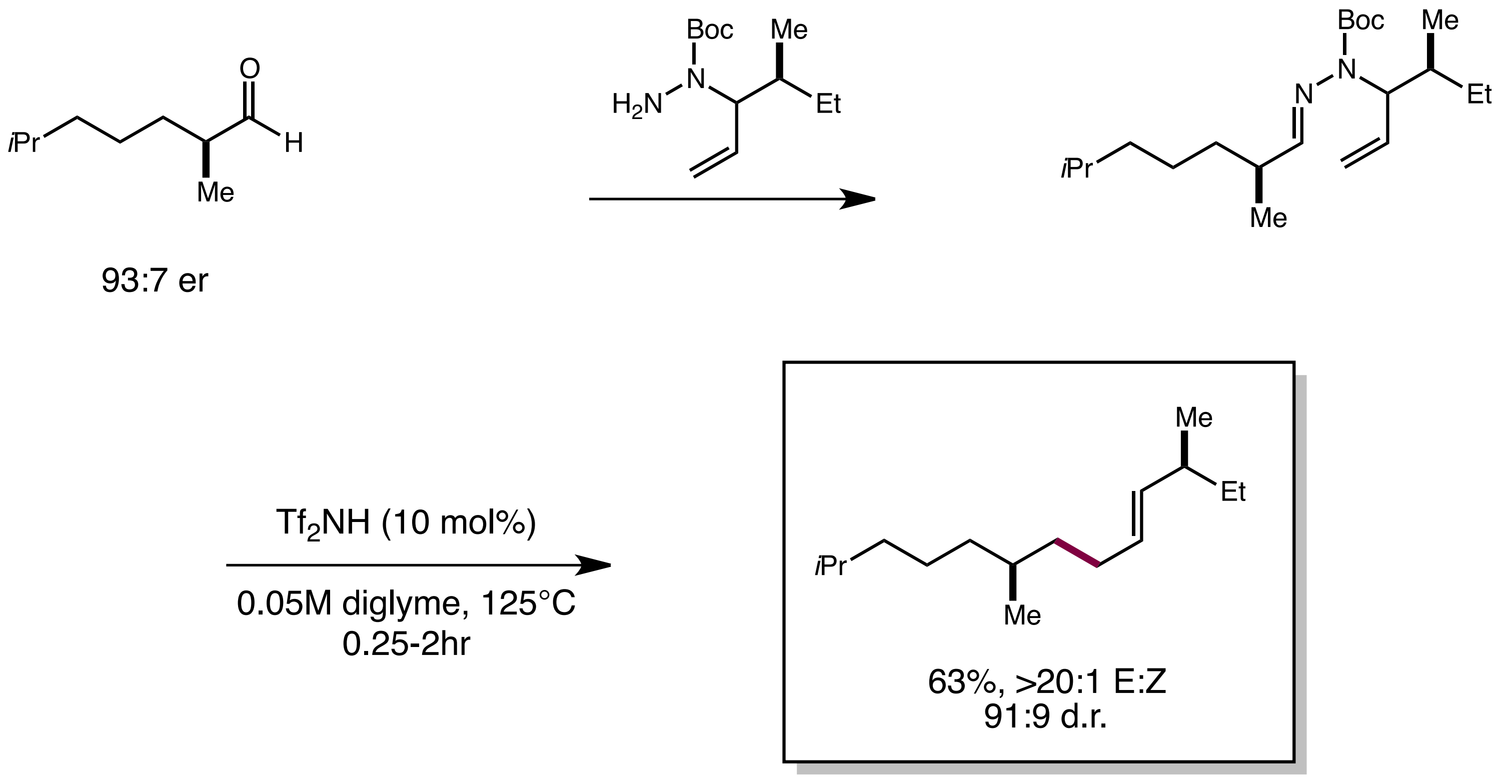

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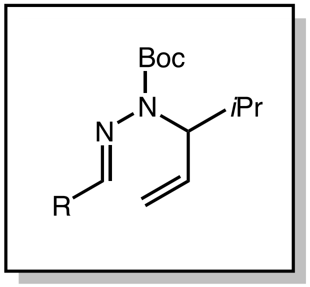
Proposed Mechanism



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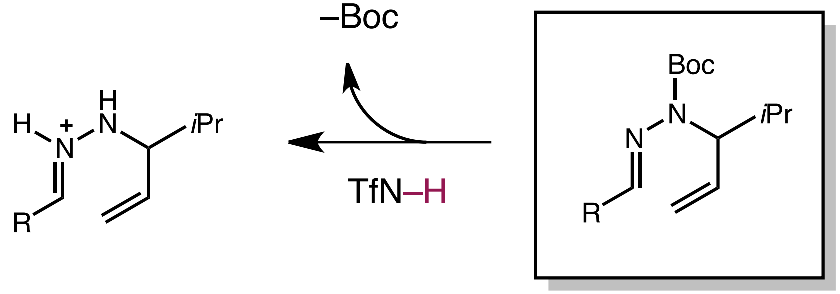

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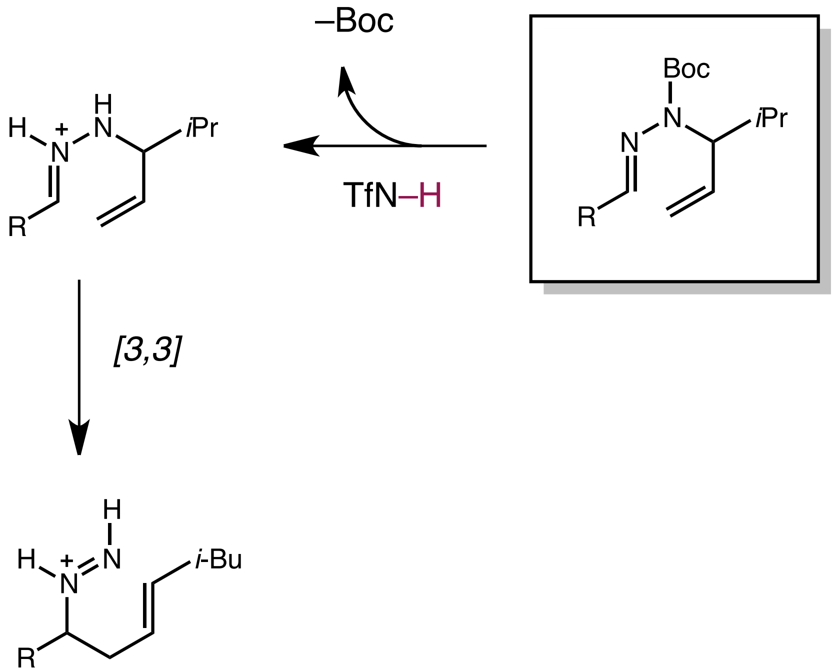

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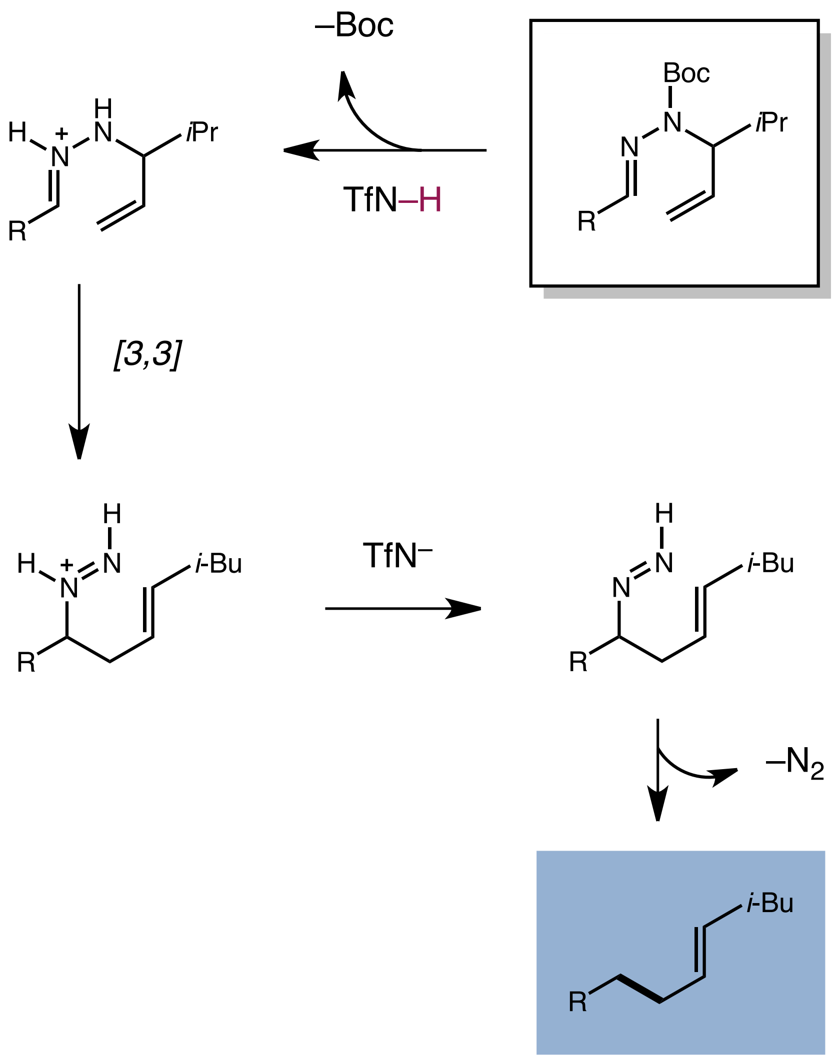

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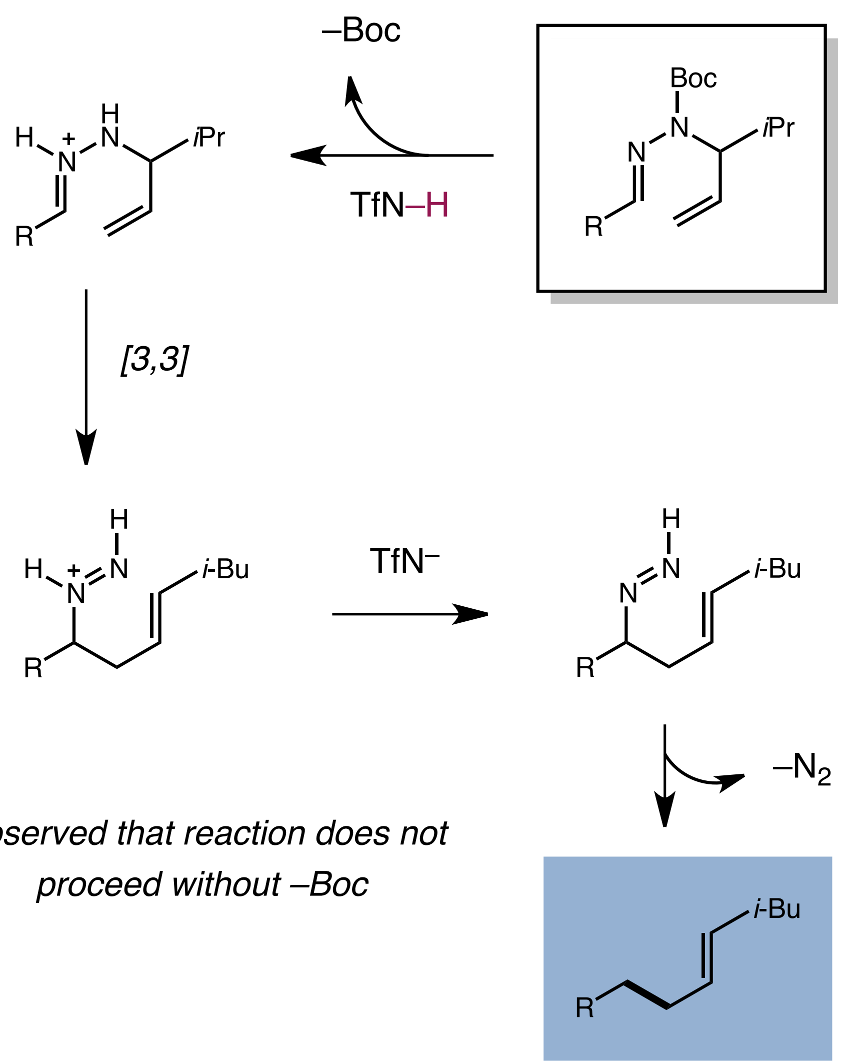

Observed that reaction does not proceed without –Boc

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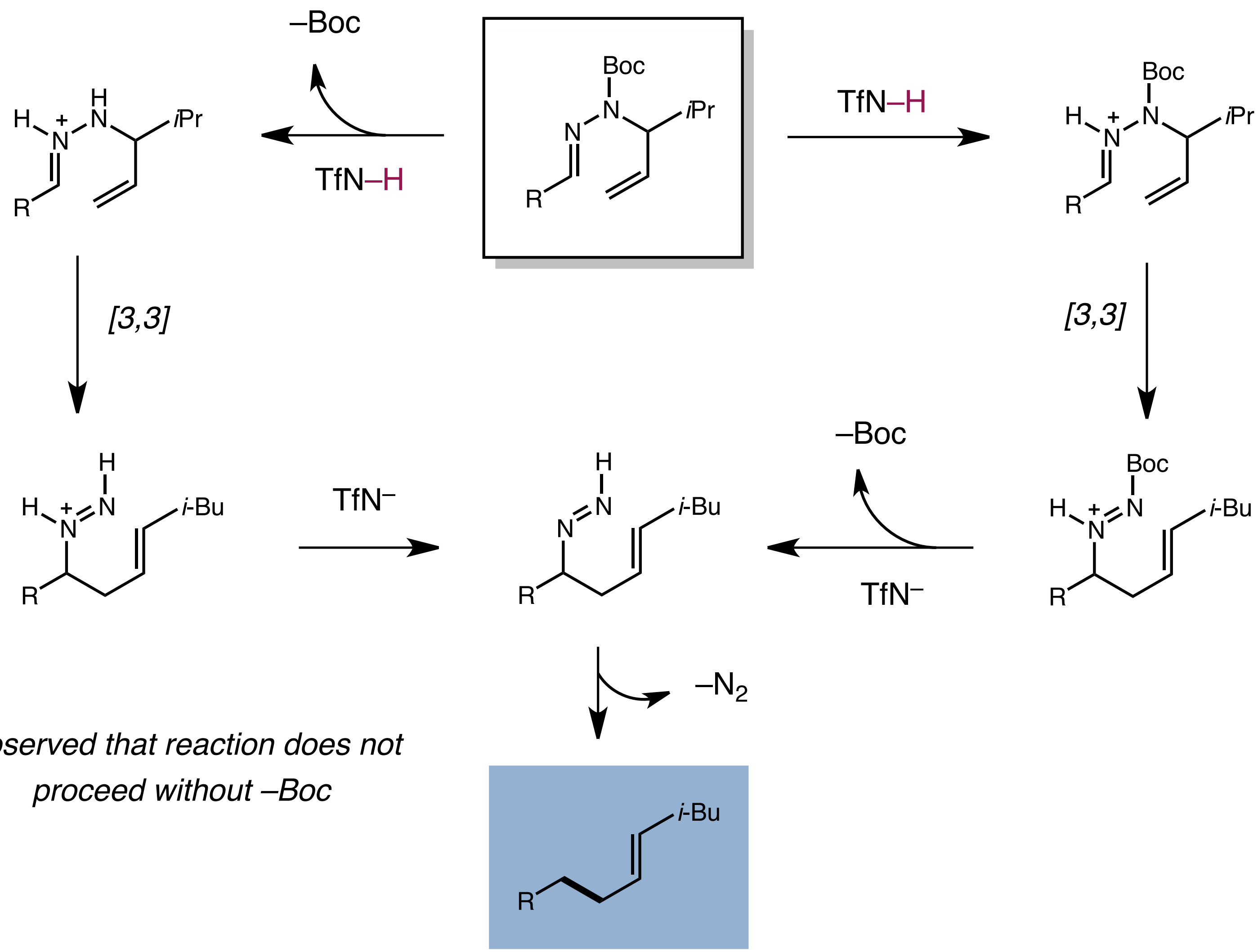

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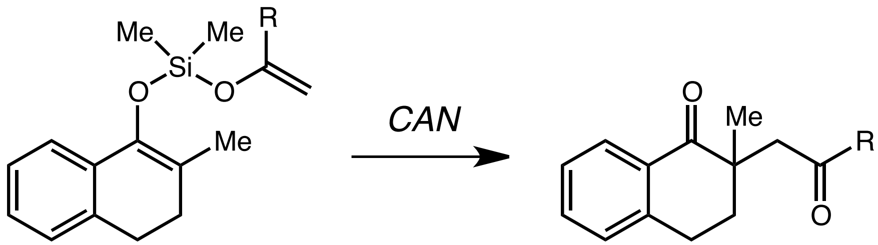

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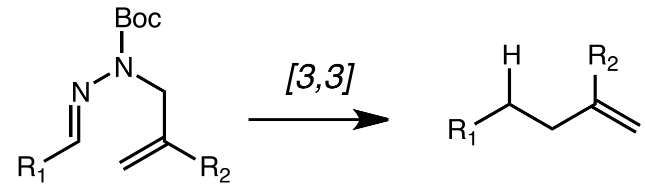
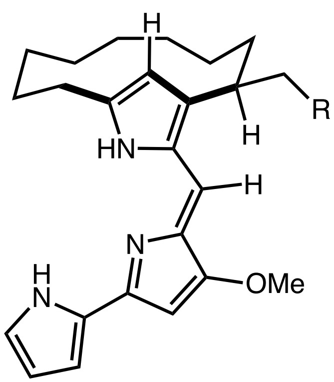
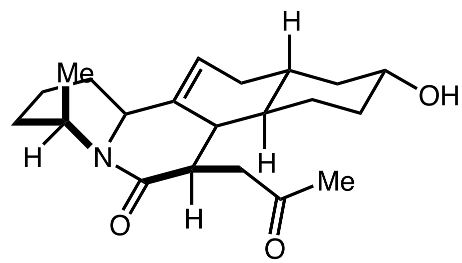


Traceless Reaction Development

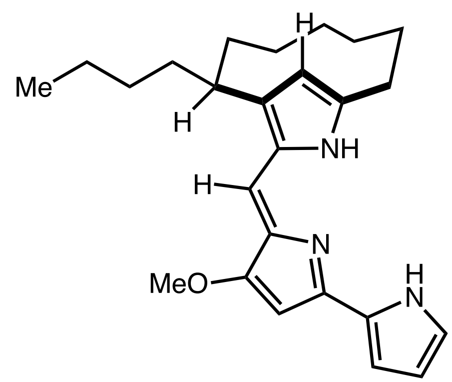
Total synthesis of complex natural products



Prodigiosin R1 (R=iPr)



GB17

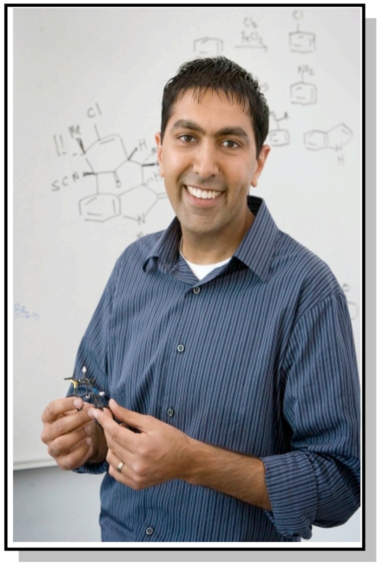


Streptorubin B

Highlights from top Pre-tenure Faculty

Sarah Reisman

Caltech



Neil Garg

UCLA

Gojko Lalic

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Corey Stephenson

Boston University

Regan Thomson

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