Organic Super Electron Donors

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Supervisor: Prof. Quan Cai

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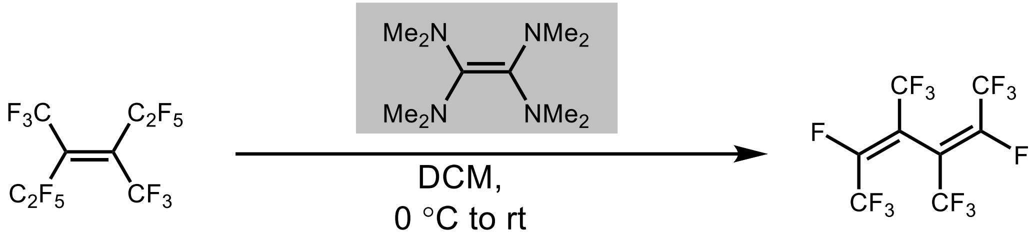
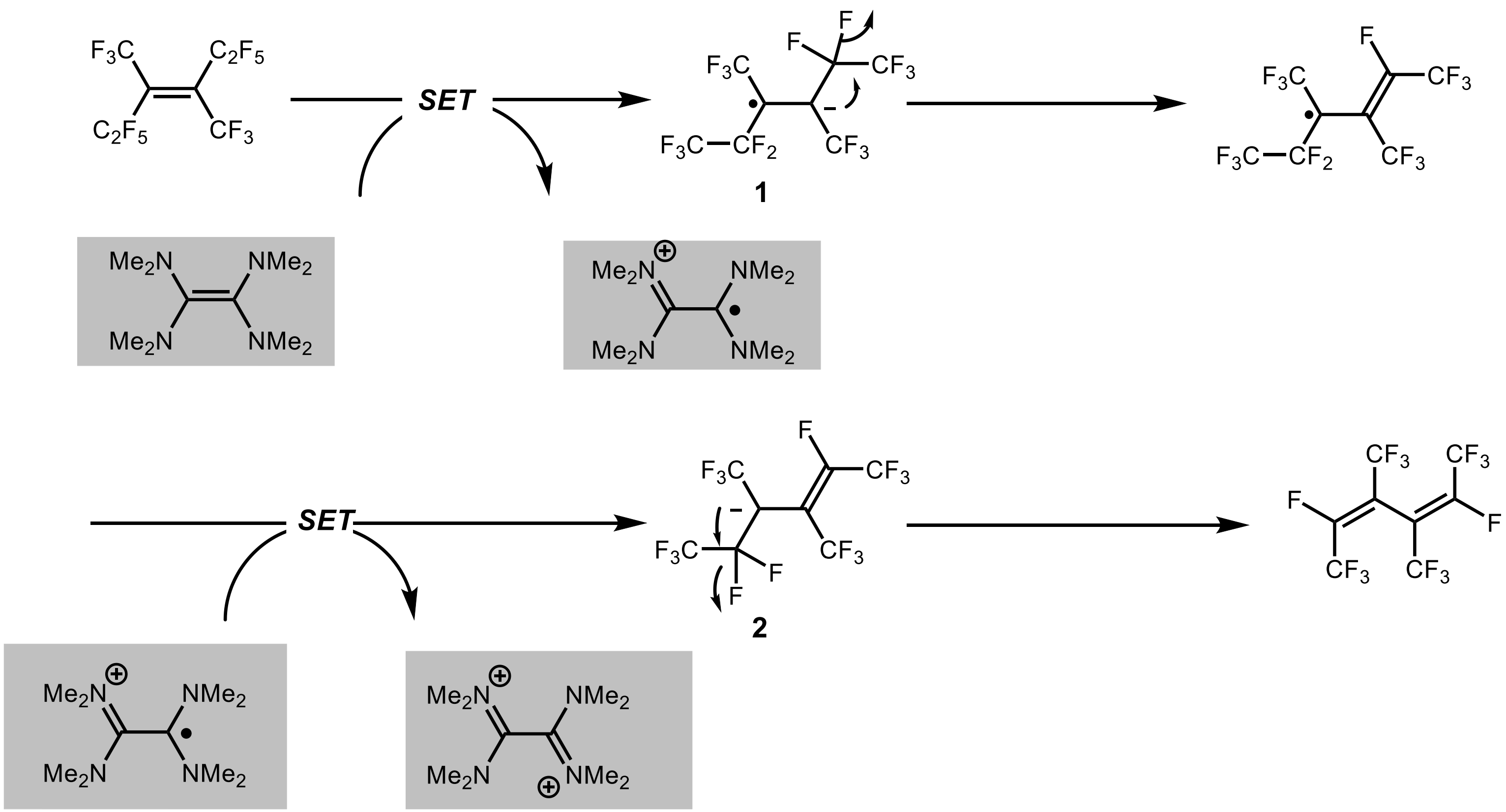
Discovery

Electron-Donor

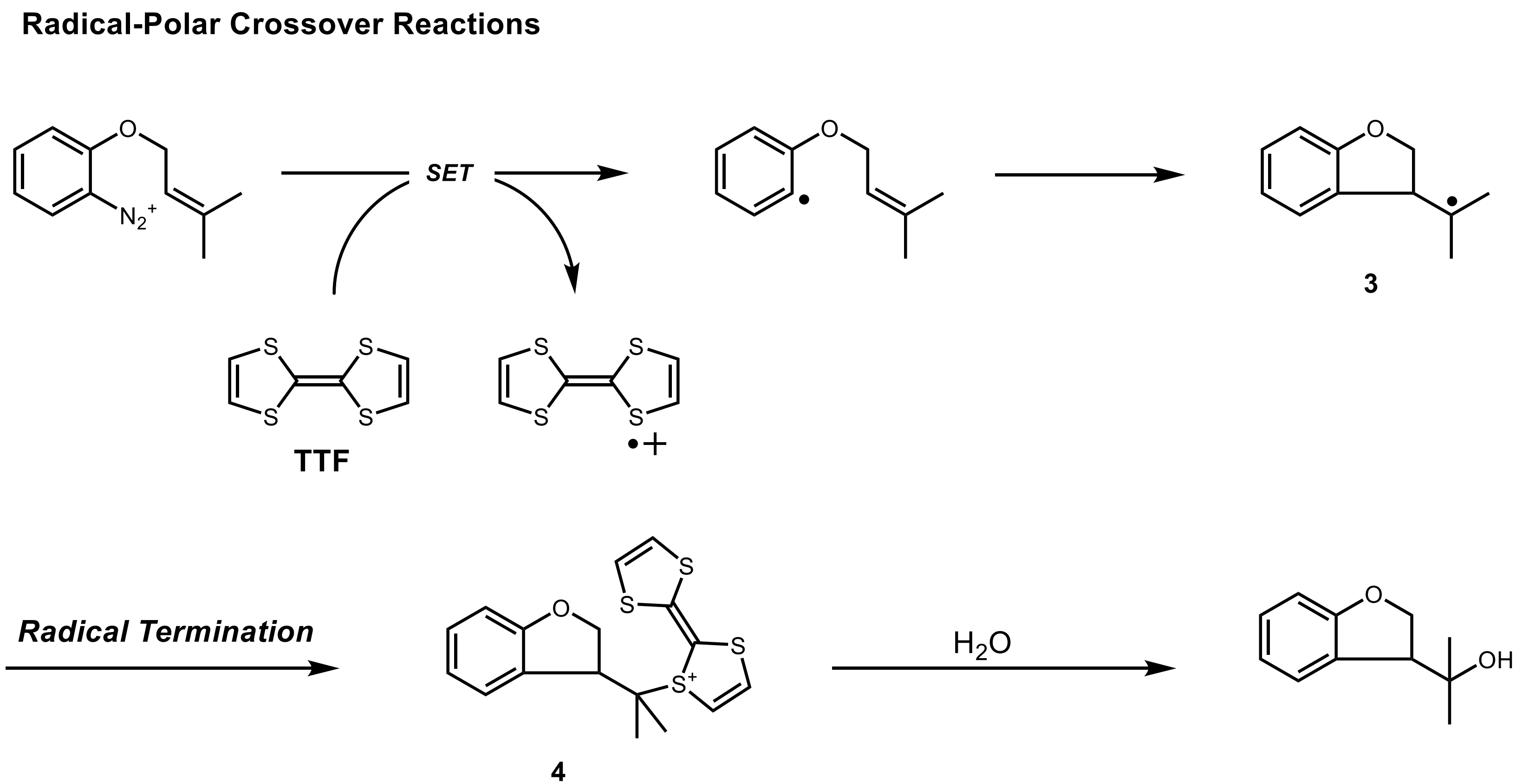




Lafferty, R. H., Jr. et al. *J. Am. Chem. Soc*. **1950**, *72*, 3646
Drakesmith, F. G. et al. *J. Chem. Soc., Perkin Trans. 1* **1994**,3115.

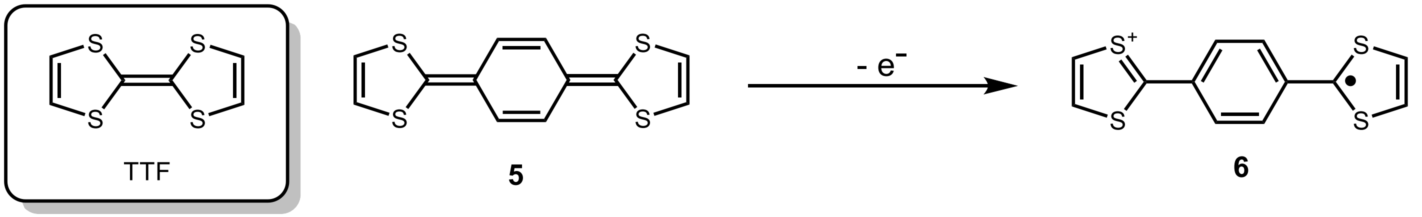
Discovery

Electron-Donor



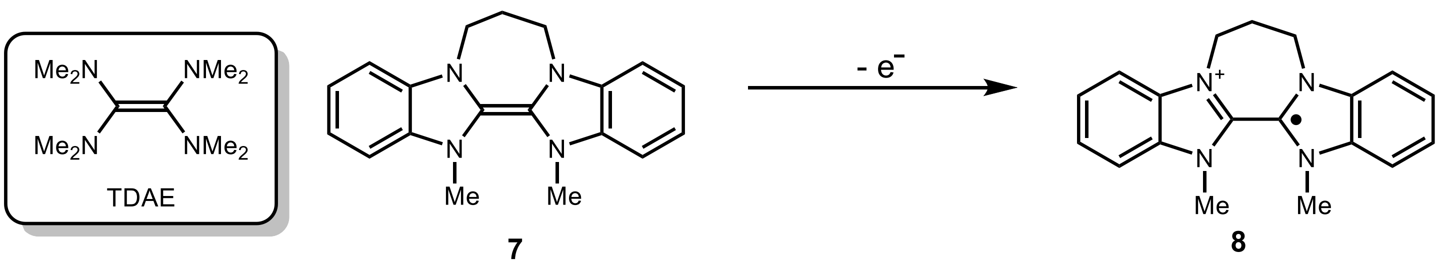
J. A. Murphy, et al. *J. Chem. Soc. Chem. Commun.*, **1993**, 295.

Discovery



Aromatic driving force

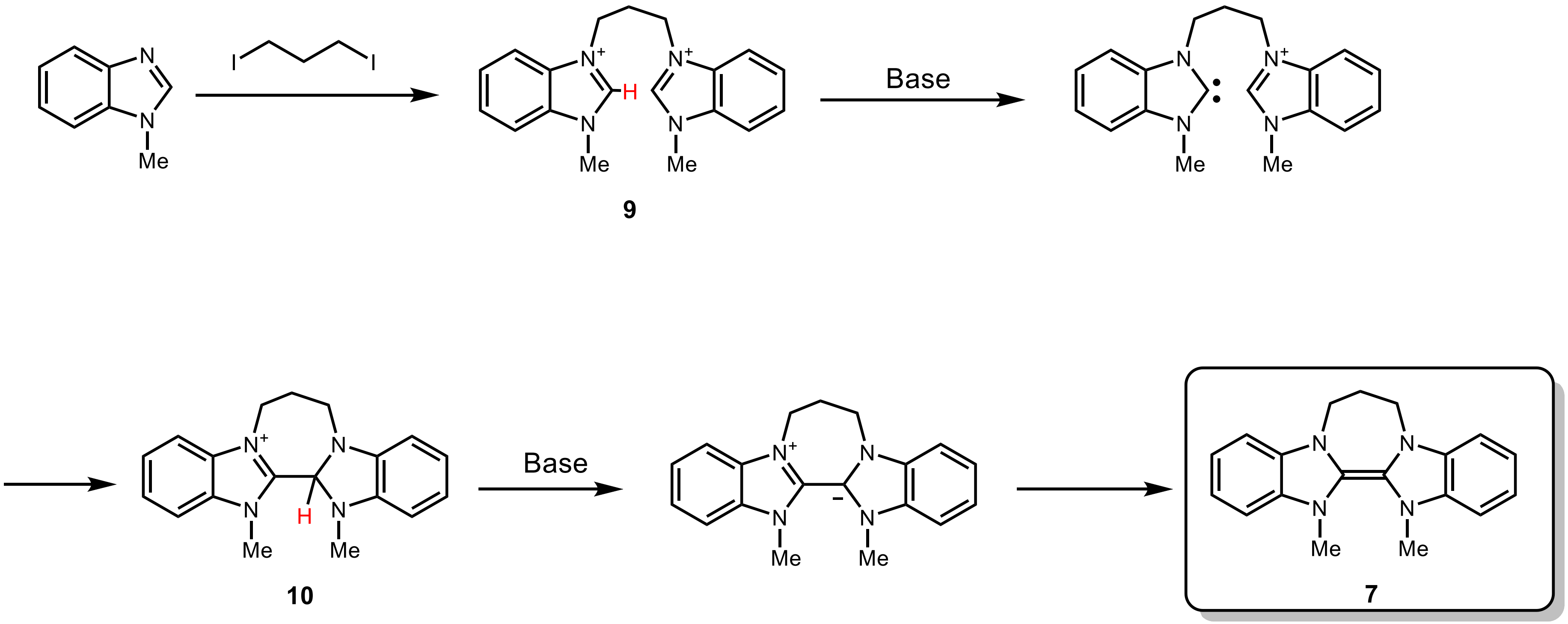
Yamashita Y.; Kobayashi. Y.; Miyashi T. *Angew. Chem., Int. Ed.* **1989**, *28*, 1052



J. A. Murphy, et al. *Angew. Chem., Int. Ed*. **2005**, *44*, 1356

Discovery

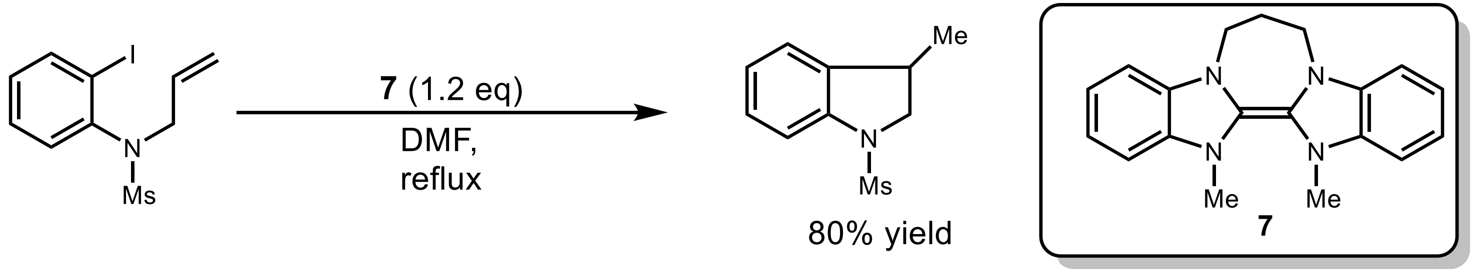
The method to prepare **7**



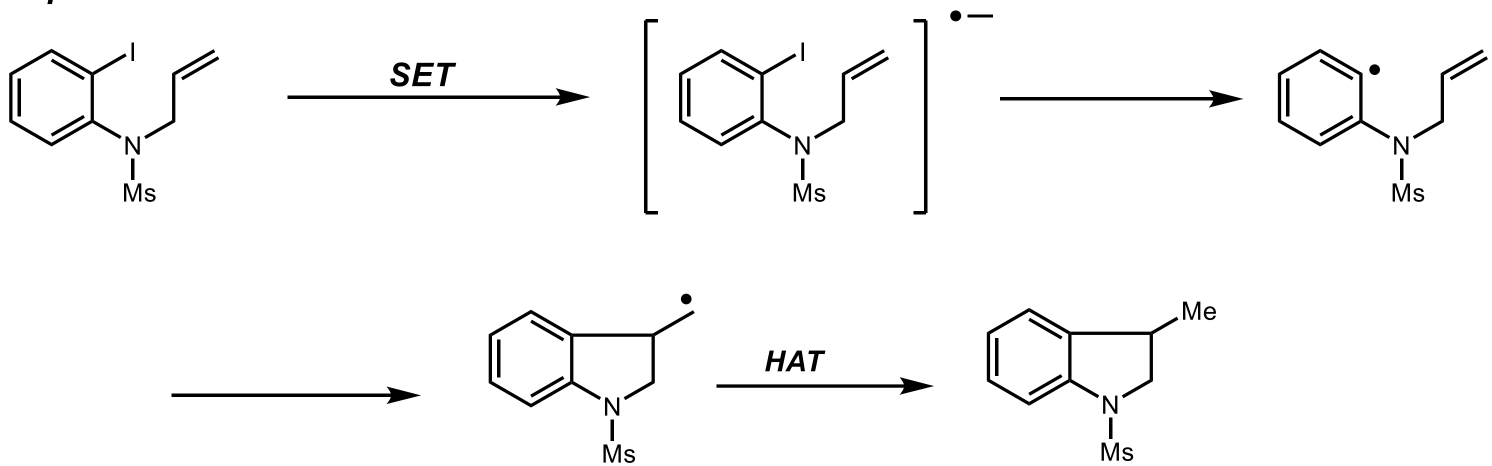
J. A. Murphy, et al. *Angew. Chem., Int. Ed*. **2005**, *44*, 1356

Discovery

The application of **7**



Proposed Mechanism

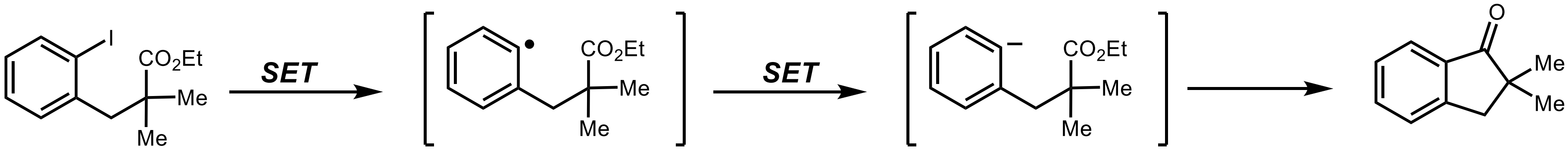


7 is the first neutral organic molecule to form aryl radicals from iodoarenes !

J. A. Murphy, et al. *Angew. Chem., Int. Ed*. **2005**, *44*, 1356

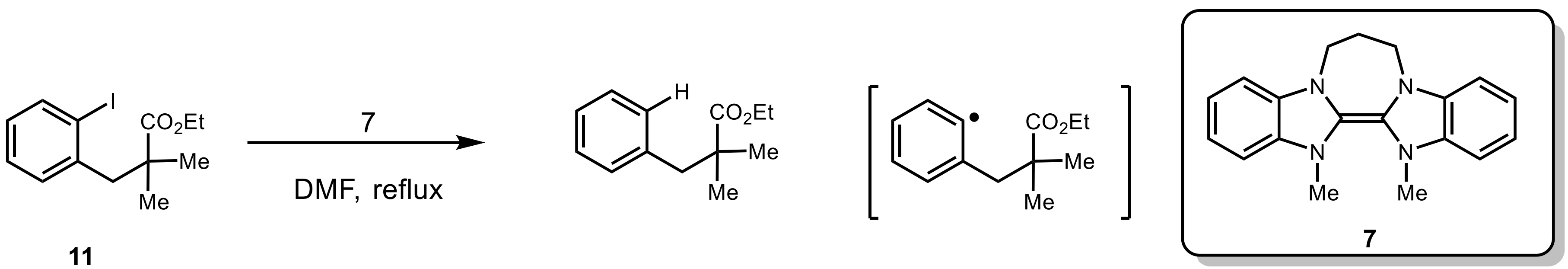
Discovery

Hypothesis



11 12

Aryl radical Aryl anion



11 7

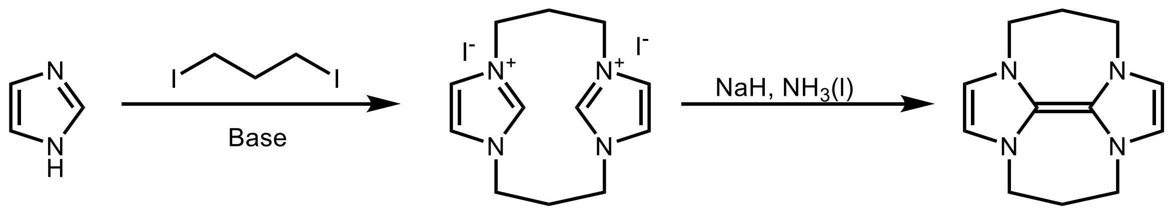
Aryl radical

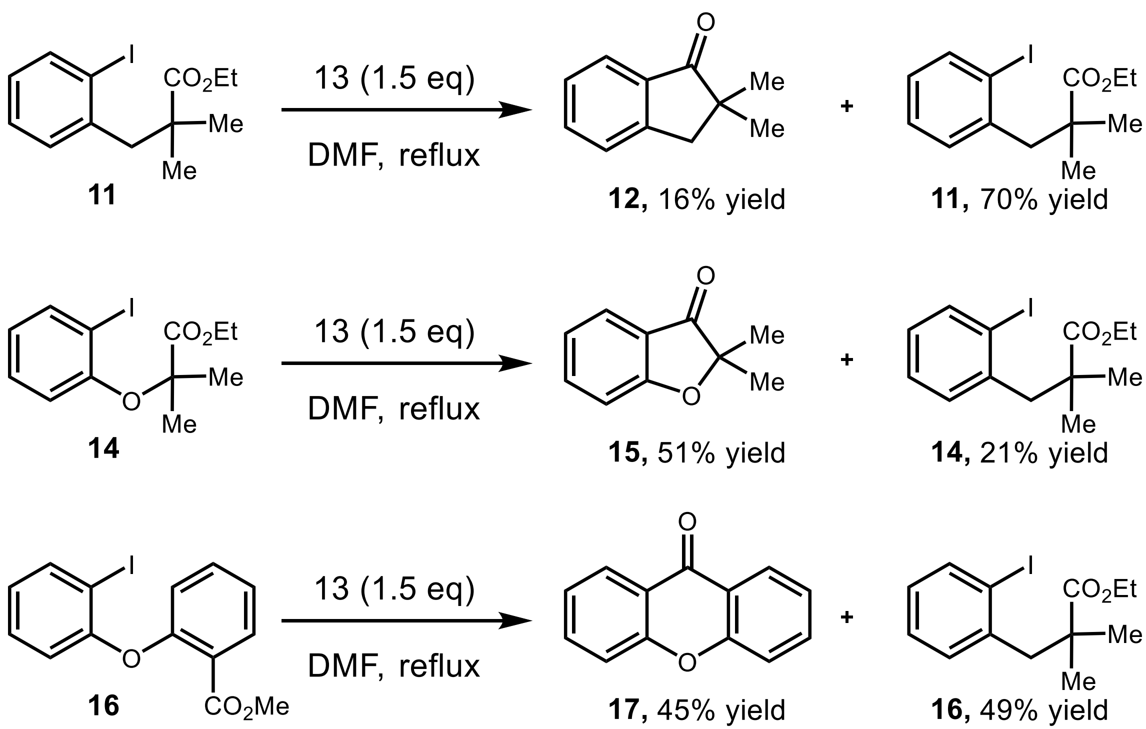
We need a more-reactive Organic Electron Donor !

J. A. Murphy; T. Tuttle; et al. *Angew. Chem., Int. Ed*. **2007**, *46*, 5178

Discovery

The electron donor 13

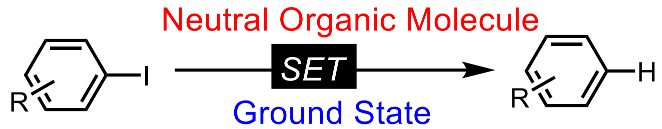


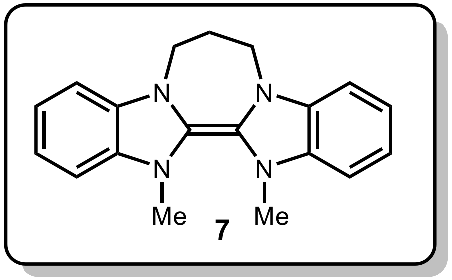


J. A. Murphy, T. Tuttle, et al. *Angew. Chem., Int. Ed*. **2007**, *46*, 5178

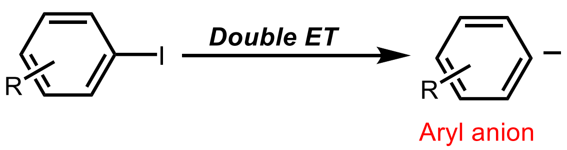
Super-electron Donors

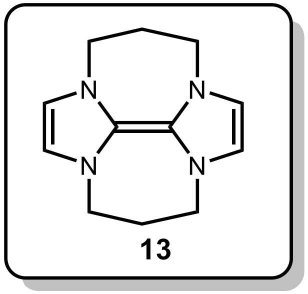
Concept





The first neutral organic molecule
to form aryl *radicals* from iodoarenes





The first neutral organic molecule
to form aryl *anions* from iodoarenes

J. A. Murphy, et al. *Angew. Chem., Int. Ed*. **2005**, *44*, 1356

J. A. Murphy, T. Tuttle, et al. *Angew. Chem., Int. Ed*. **2007**, *46*, 5178

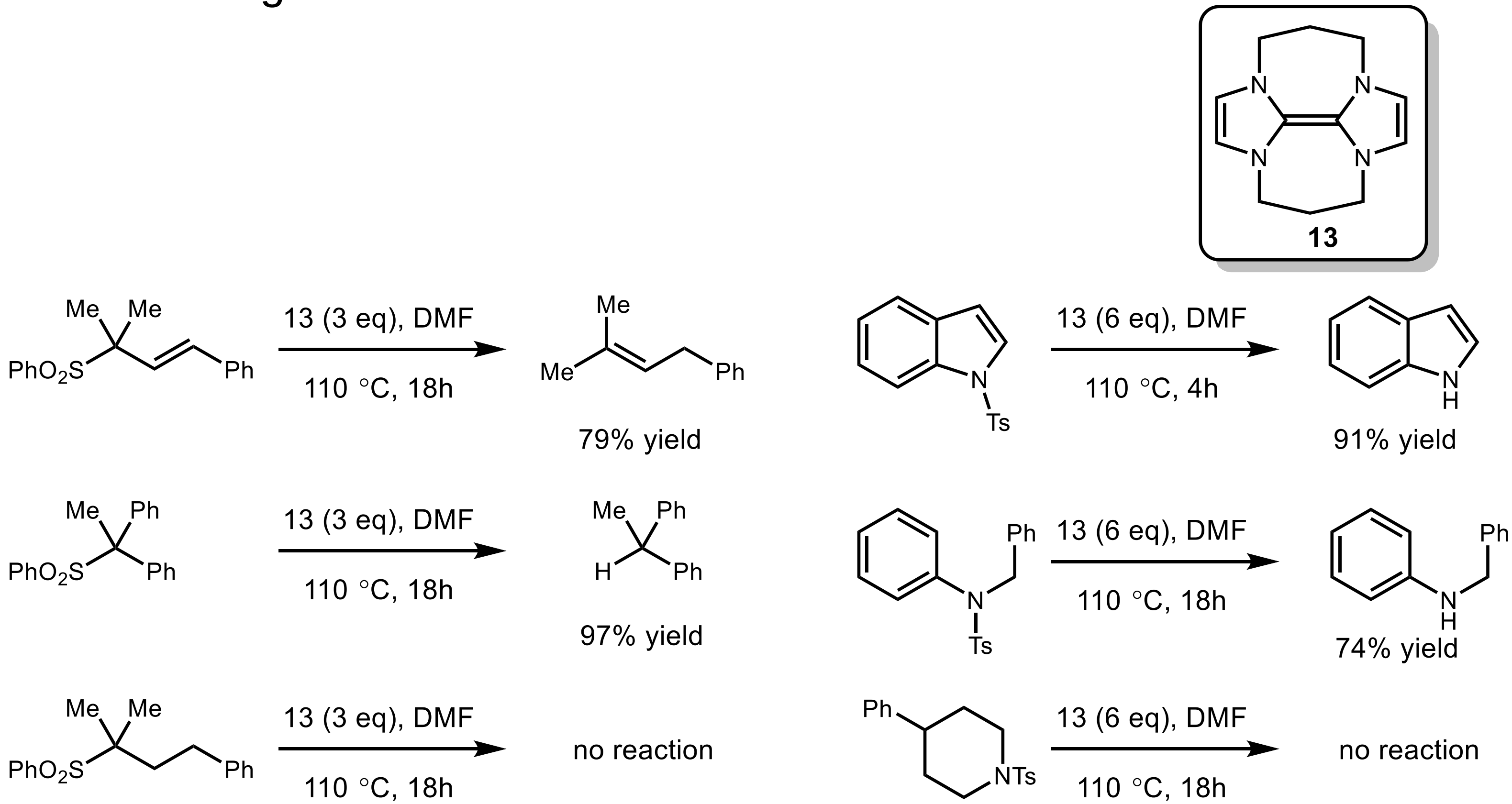
Super-electron Donors

Advantages

- Under very mild conditions because of their neutrality
- In the absence of metal ions
- With wider applicability than in the case of photochemically assisted reactions

Super-electron Donors

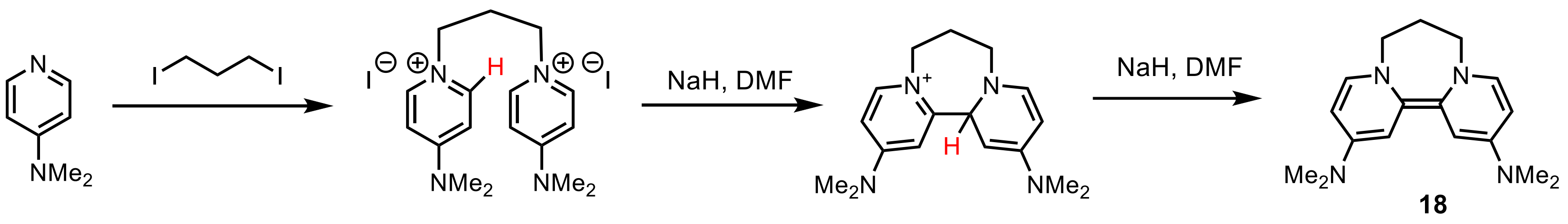
Reductive Cleavage of Sulfones and Sulfonamides

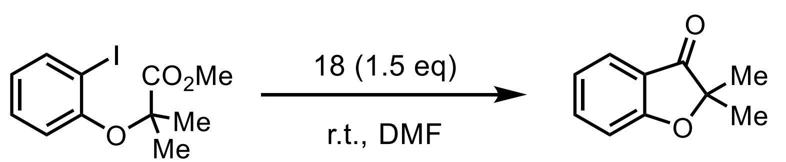


J. A. Murphy; T. Tuttle, et al. *J. Am. Chem. Soc*. **2007**, *129*, 13368

Super-electron Donors

A new *Super-electron-donor* derived from DMAP





14

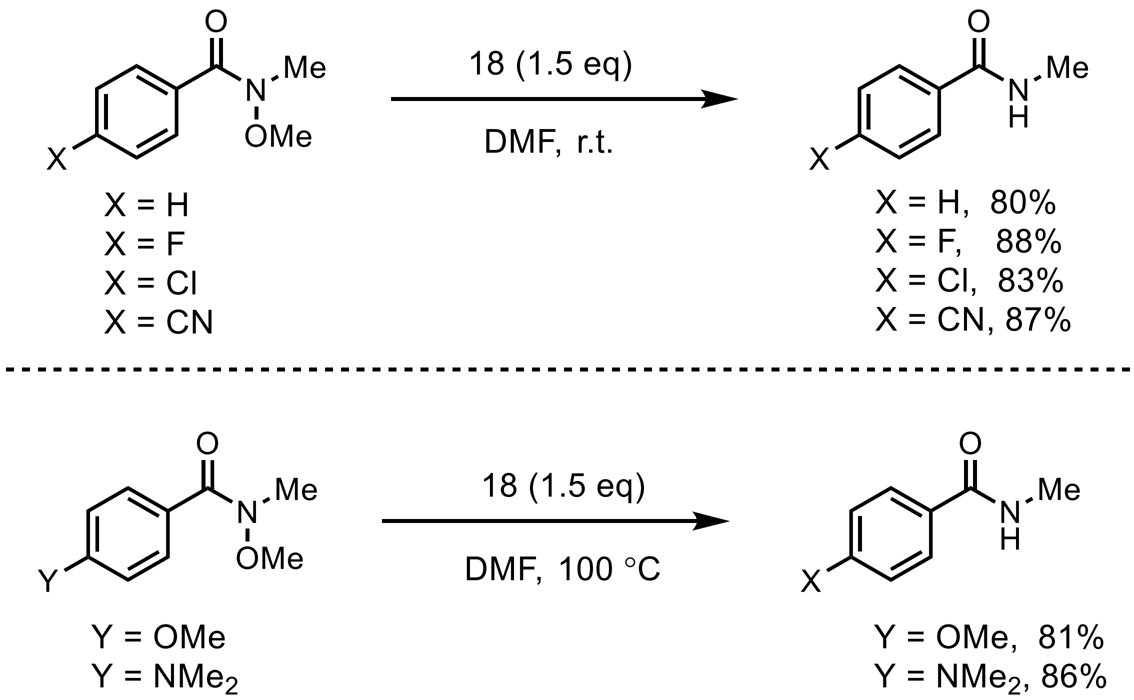
15, 83% yield

18 is a more-reactive *Super-electron donor*

J. A. Murphy. et al. *Synlett,* **2008**, *14*, 2132

Super-electron Donors

Reductive Cleavage of N–O Bonds in Weinreb Amides

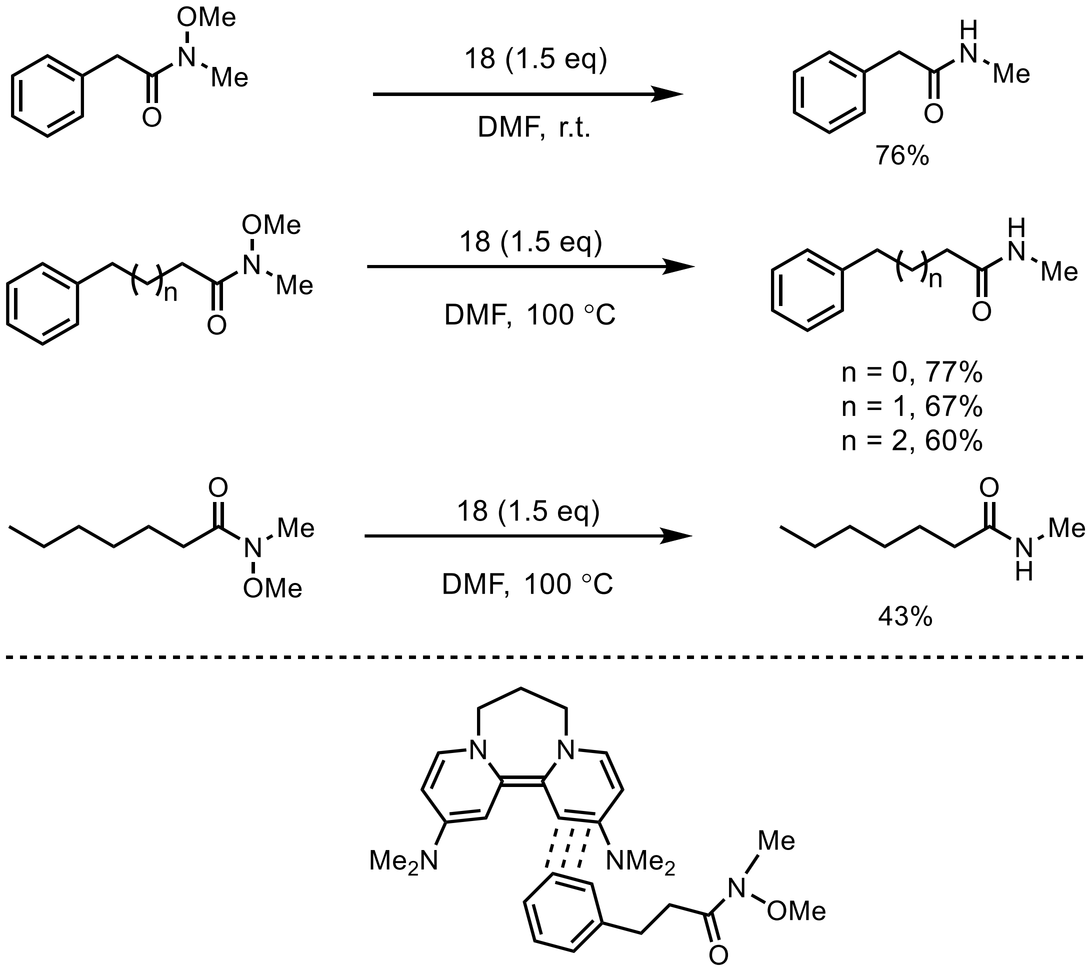


Neighbouring-group electron-transfer effect

J. A. Murphy. et al. *Synlett*, **2008**, *14*, 2132

Super-electron Donors

Reductive Cleavage of N–O Bonds in Weinreb Amides

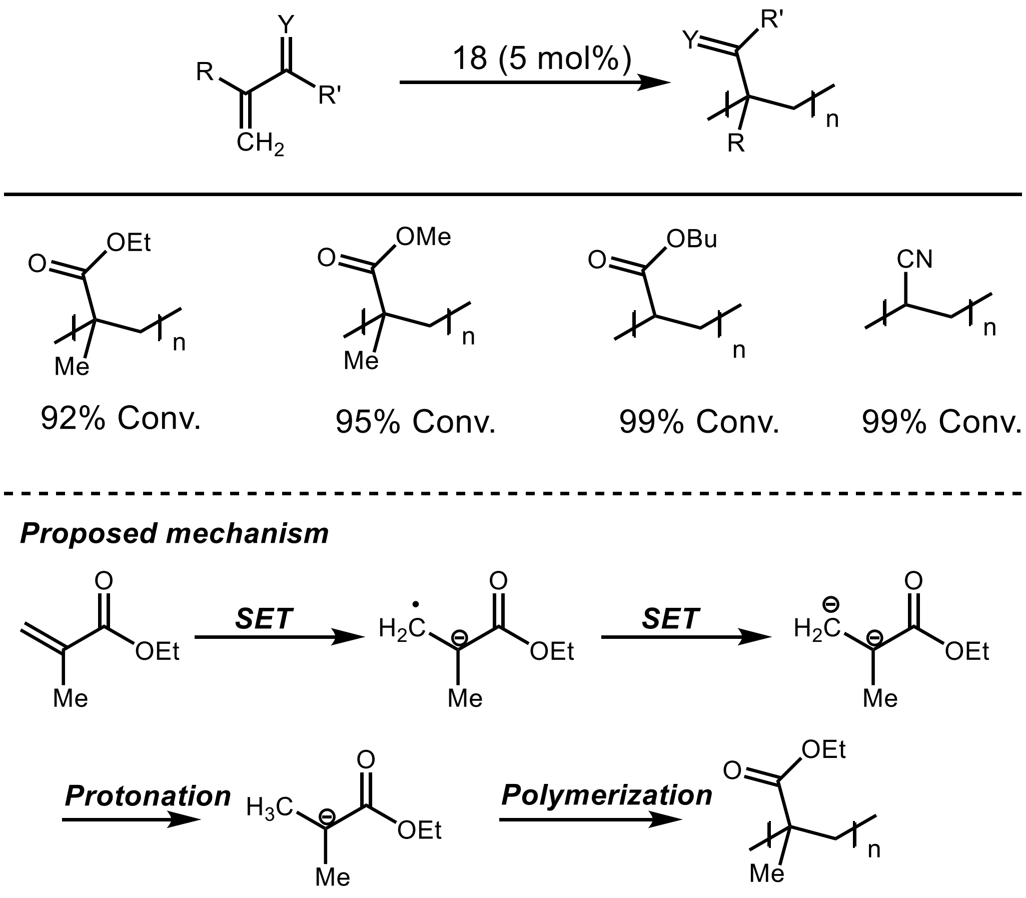


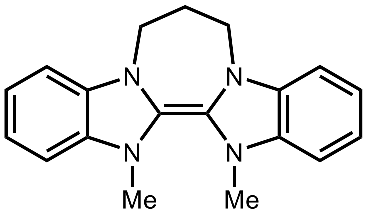
π-stacking interaction

J. A. Murphy. et al. *Synlett*, **2008**, *14*, 2132

Super-electron Donors

Polymerization Initiated by *SED*



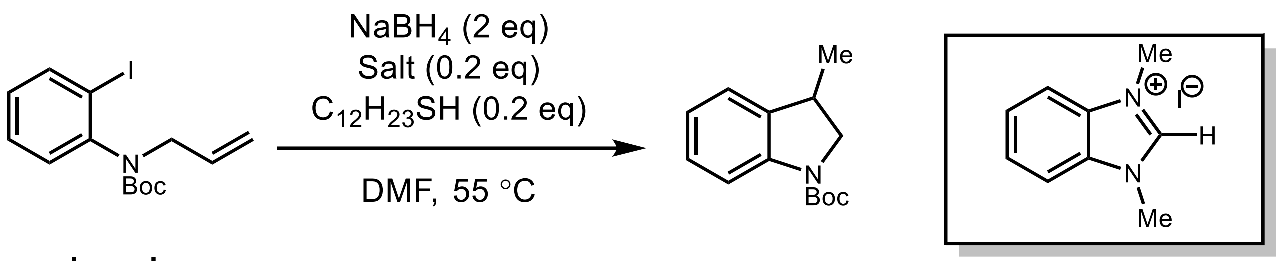


18

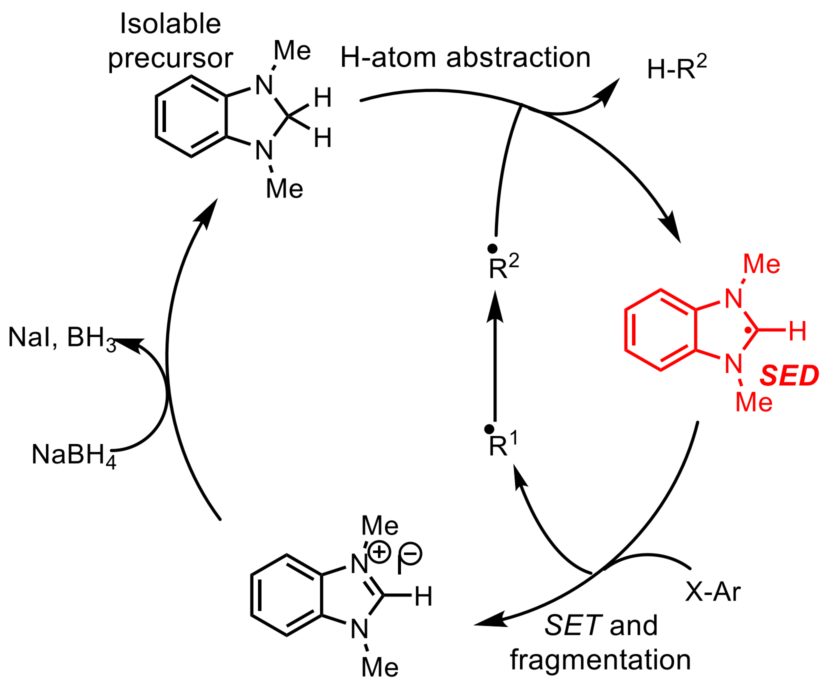
Vanelle P. et. al. *Angew. Chem., Int. Ed*. **2016**, *55*, 5994

Super-electron Donors

SEDs catalyze radical chain reactions



Plausible mechanism

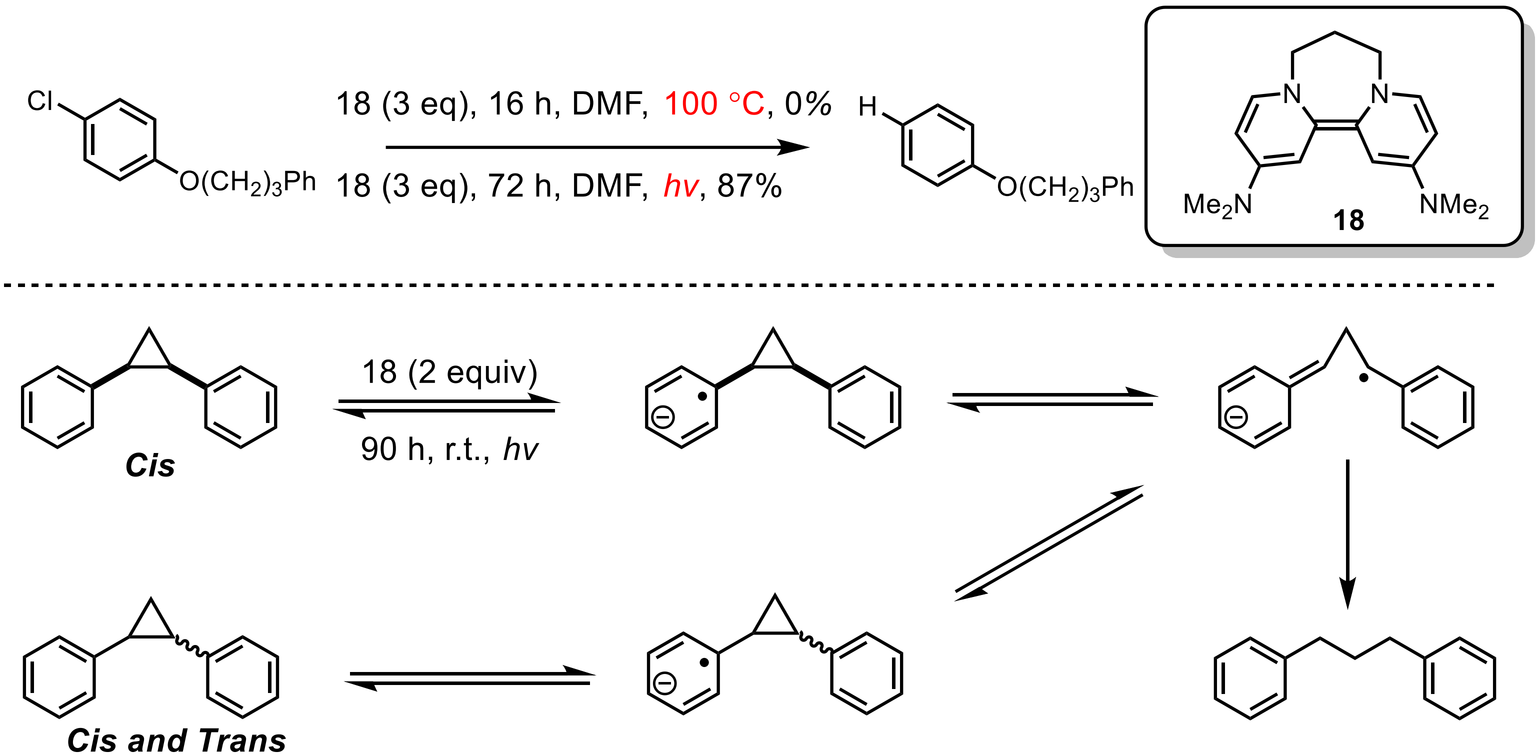


J. A. Murphy; T. Tuttle, et al. *Angew. Chem., Int. Ed*. **2019**, *131*, 11576

Photoactivation of *SEDs*

Activating Benzenes by photoactivated *SEDs*

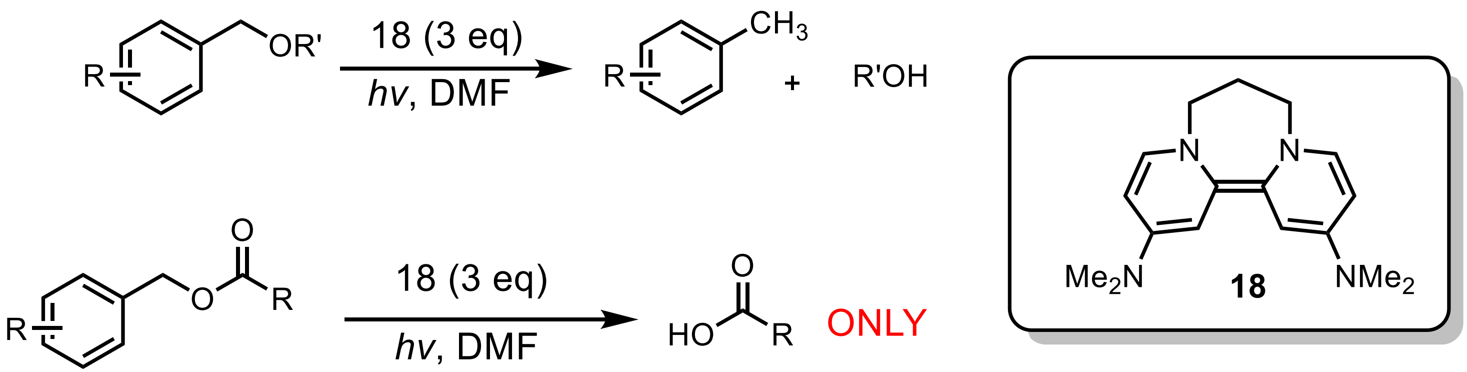
Absorption maxima at 260, 345, and 520 nm



J. A. Murphy, et al. *Angew. Chem., Int. Ed*. **2012**, *51*, 3673

Photoactivation of *SEDs*

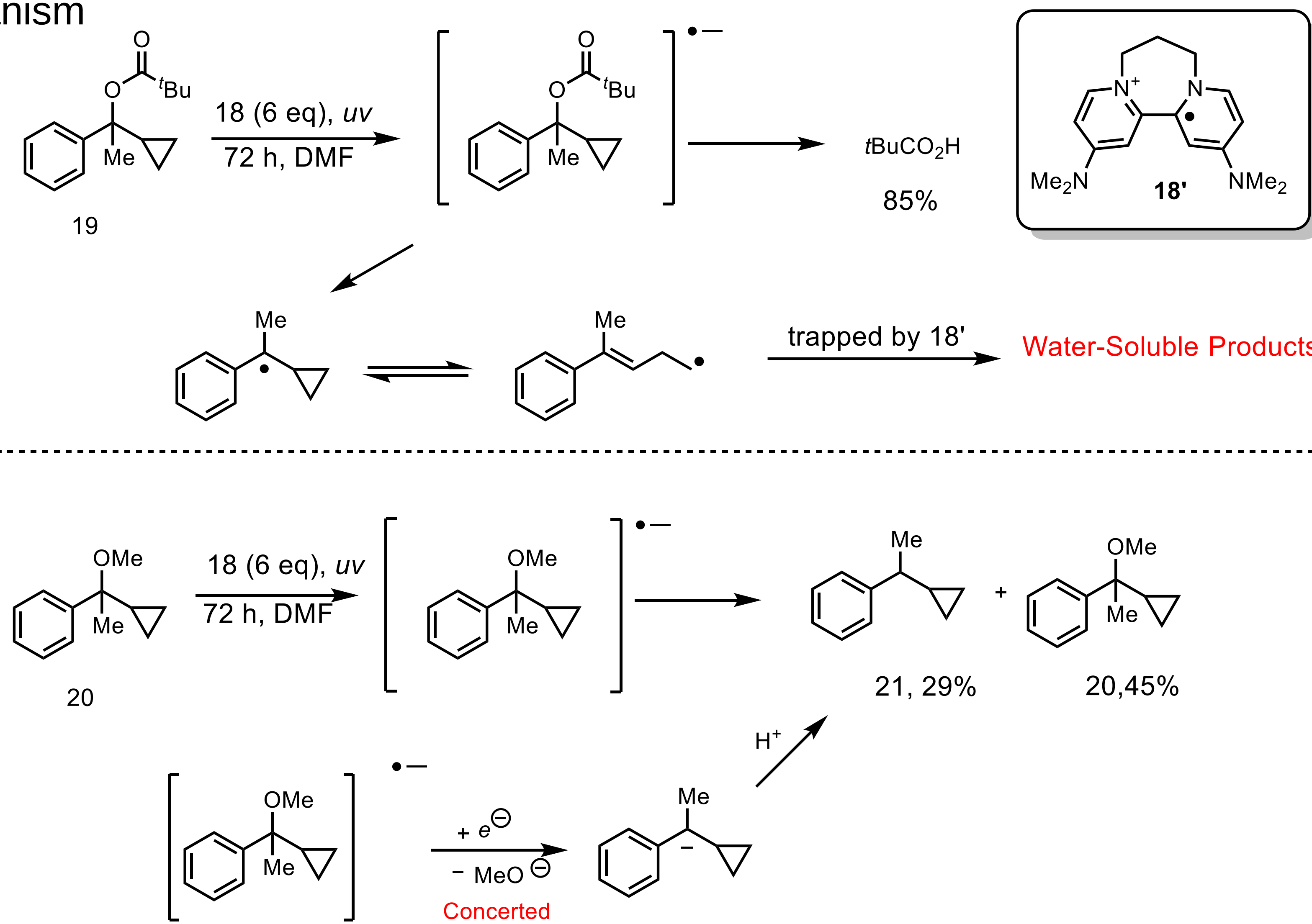
Reductive Cleavage of Benzylic Esters and Ethers



J. A. Murphy, et al. *Angew. Chem., Int. Ed.* **2013**, *52*, 2239

Photoactivation of *SEDs*

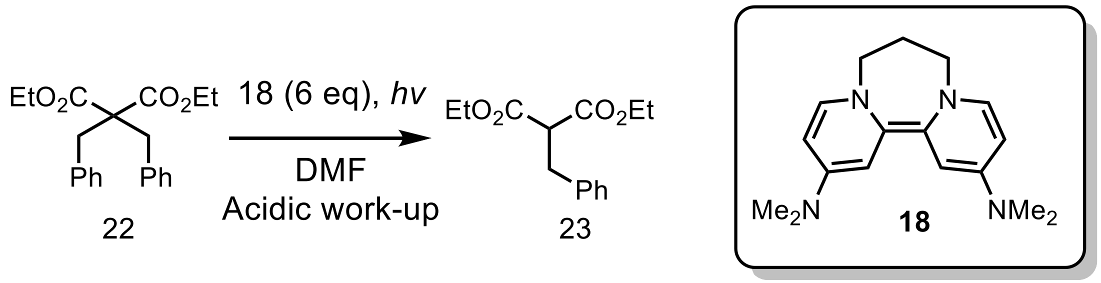
Mechanism



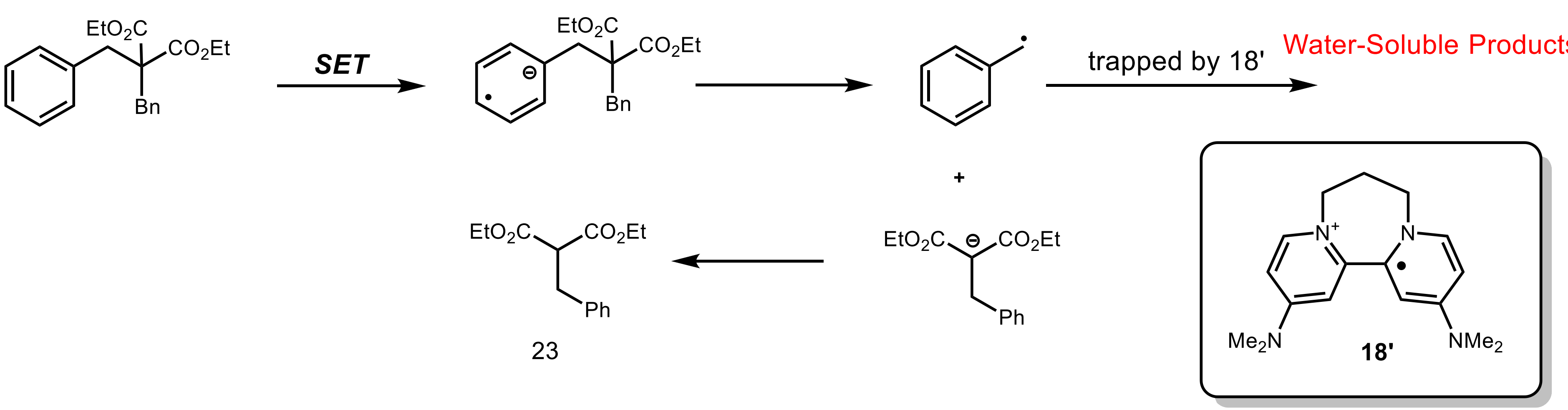
J. A. Murphy, et al. *Angew. Chem., Int. Ed.* **2013**, *52*, 2239

Photoactivation of *SEDs*

Reduction of Arenes by photoactivated *SEDs*



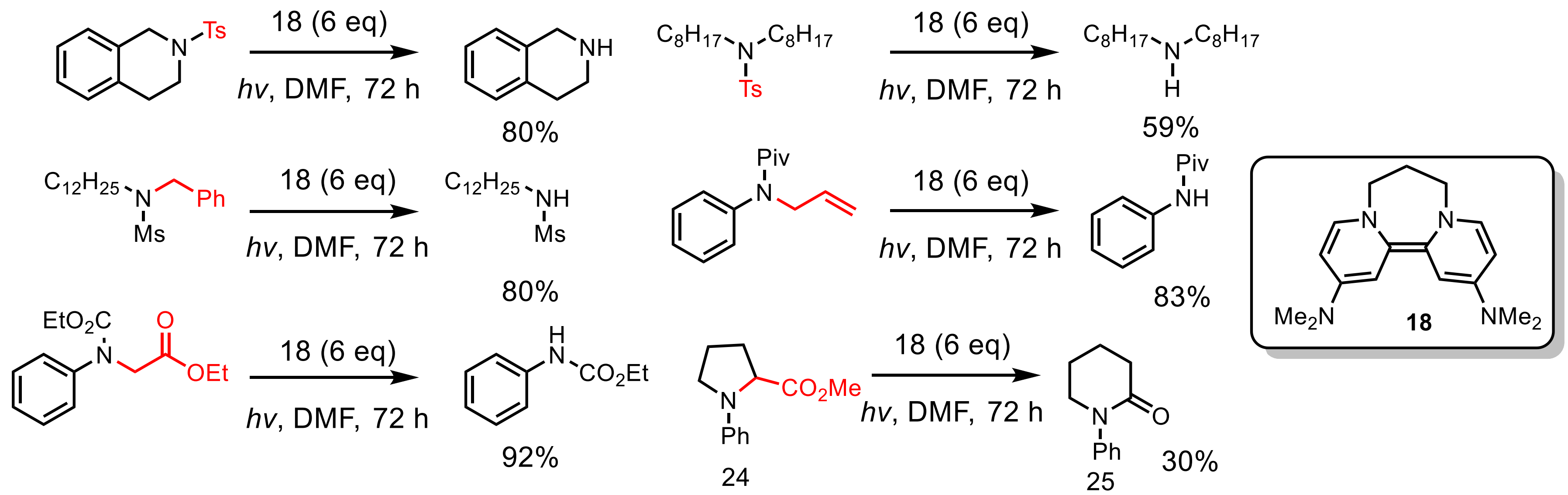
Proposed mechanism



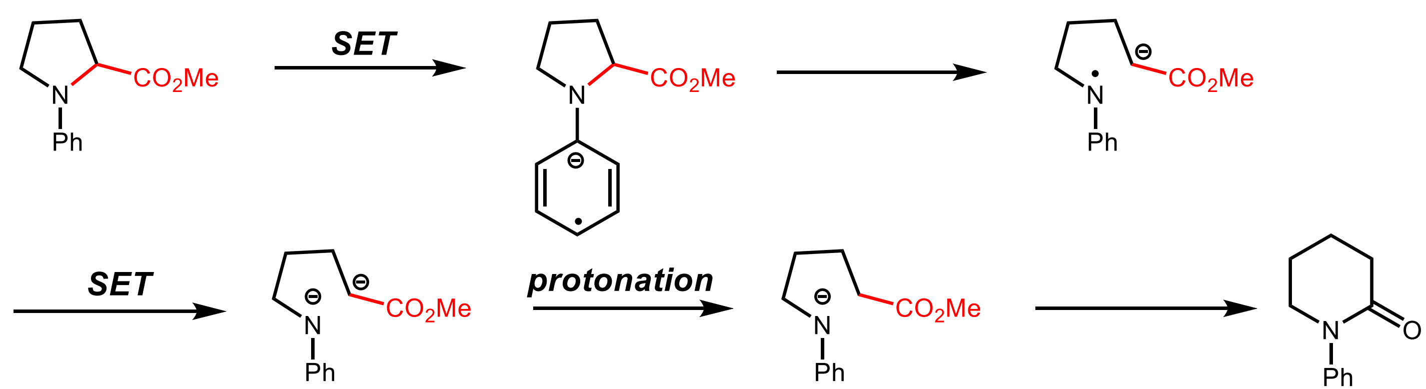
J. A. Murphy, et al. *J. Am. Chem. Soc*. **2013**, *135*, 10934

Photoactivation of *SEDs*

Reductive Cleavage of C-N and S-N



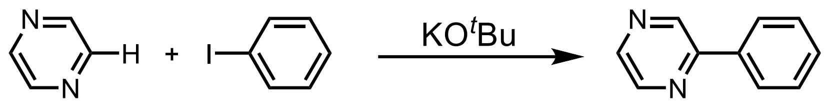
Proposed mechanism



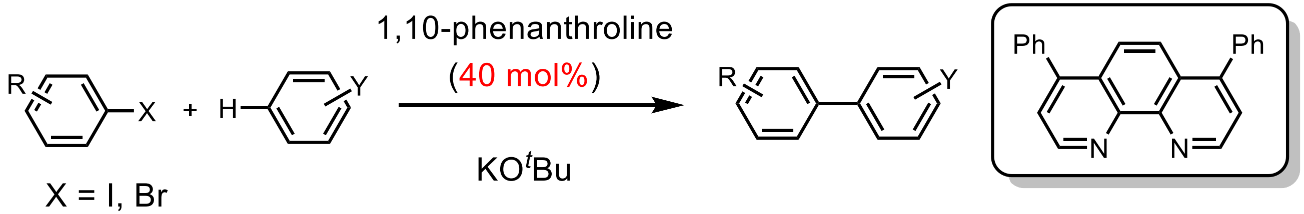
J. A. Murphy. et al, *Angew. Chem., Int. Ed*. **2014**, *53*, 474

SEDs as initiators in Haloarene–Arene Coupling

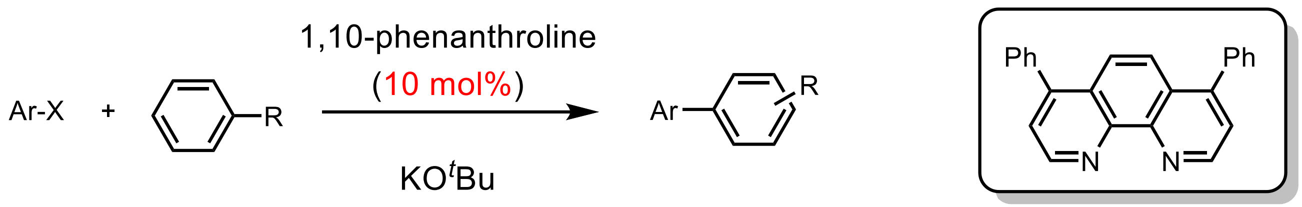
Background



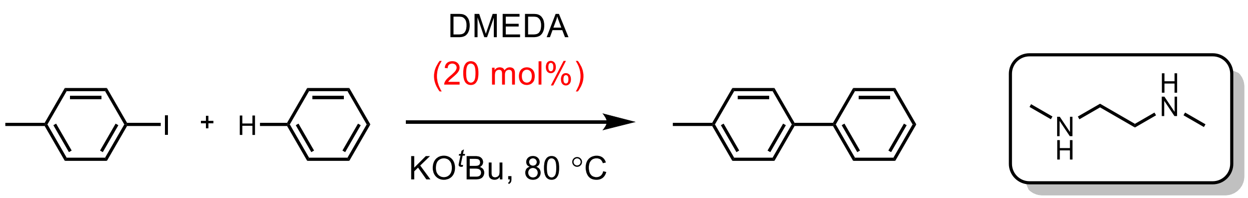
T. Itami, et al. *Org. Lett*. **2008**, *10*, 4673.



Shi, Z. J. et al. *Nat. Chem*. **2010**, *2*, 1044



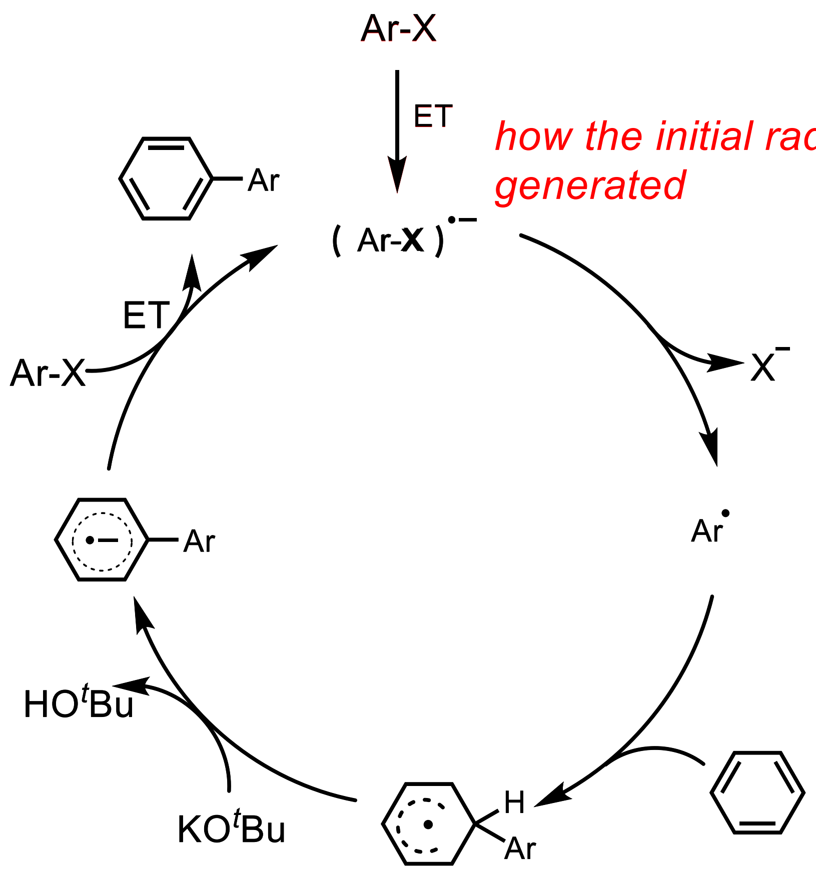
T. Hayashi, et al. *J. Am. Chem. Soc.* **2010**, *132*, 15537



Lei, A. W. et al. *J. Am. Chem. Soc.* **2010**, *132*, 16737

SEDs as initiators in Haloarene–Arene Coupling

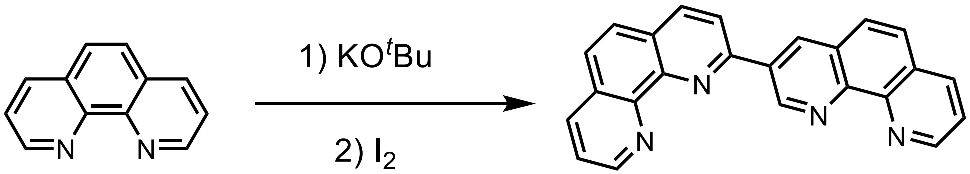
Base-promoted homolytic aromatic substitution (**BHAS**) reactions



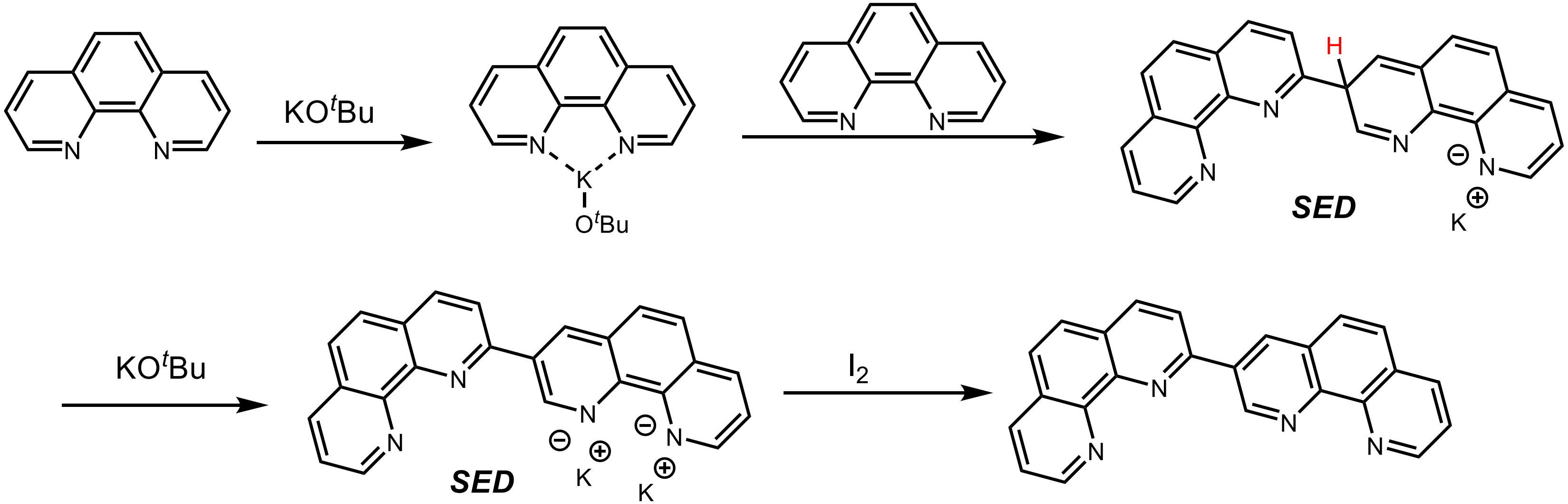
A. Studer; D. P. Curran, *Angew. Chem., Int. Ed.* **2011**, *50*, 5018

SEDs as initiators in Haloarene–Arene Coupling

Initiation with phenanthrolines as additives



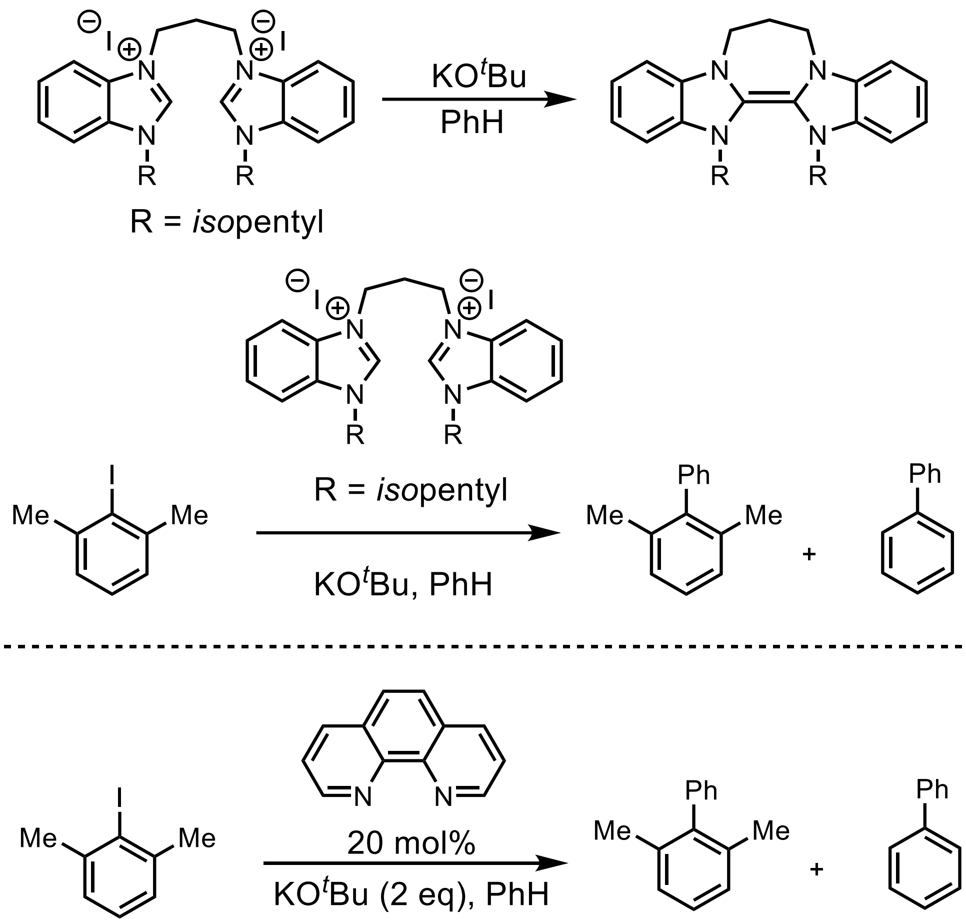
Proposed mechanism



John A. Murphy, et al. *Chem. Sci*., **2014**, *5*, 476

SEDs as initiators in Haloarene–Arene Coupling

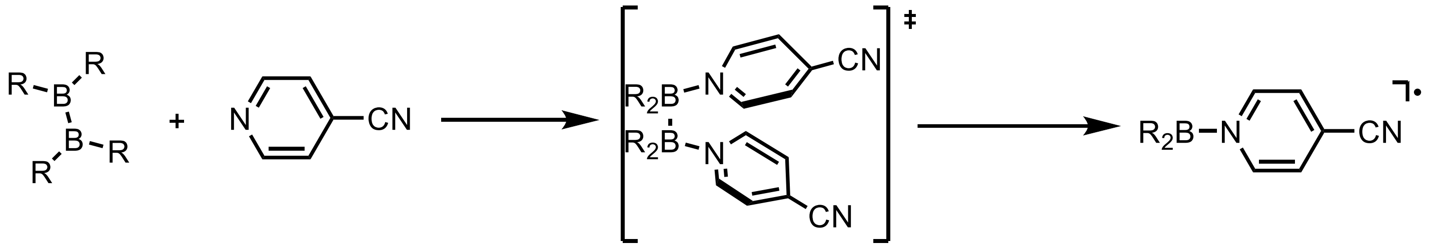
Initiation with phenanthrolines as additives



John A. Murphy, et al. *Chem. Sci*. **2014**, *5*, 476

SEDs derived from diborons

Background



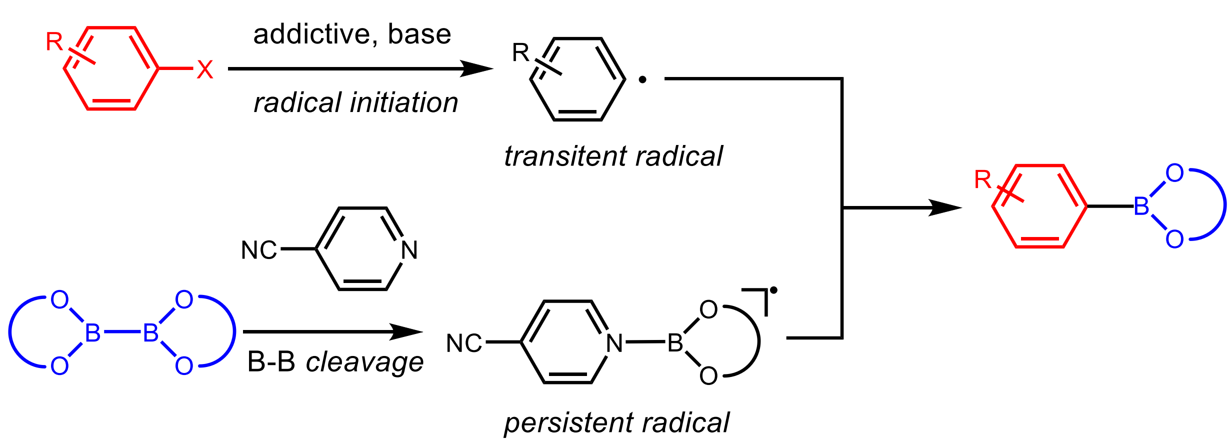
Cooperative activation

Captodatively stabalized boryl radical

Li, S. H. et al. *Angew. Chem., Int. Ed*. **2016**, *55*, 5985

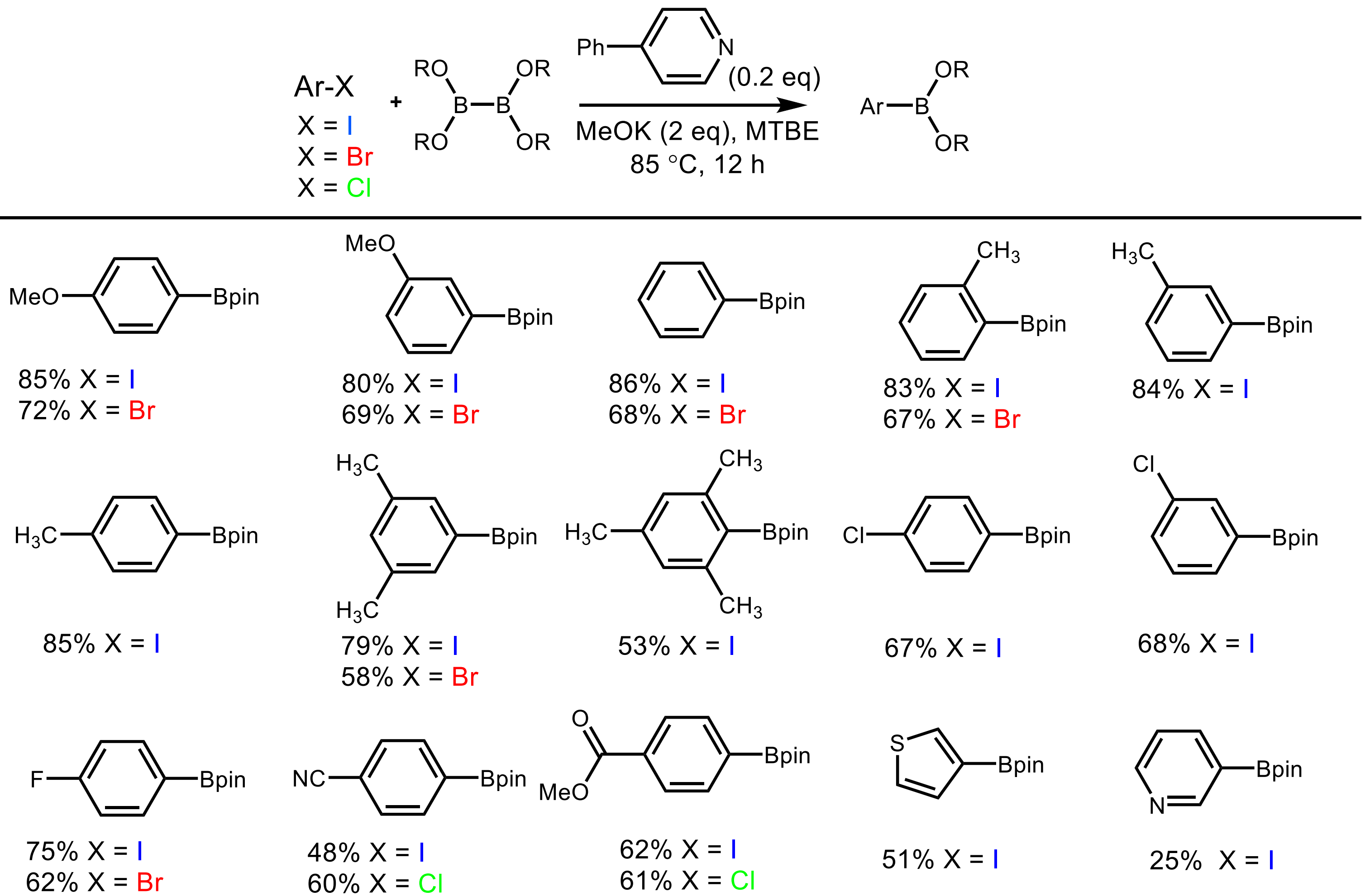
SEDs derived from diborons

Jiao's idea: Radical Borylation of Aryl Halides



Zhang L.; Jiao L. *J. Am. Chem. Soc*. **2017**, *139*, 607

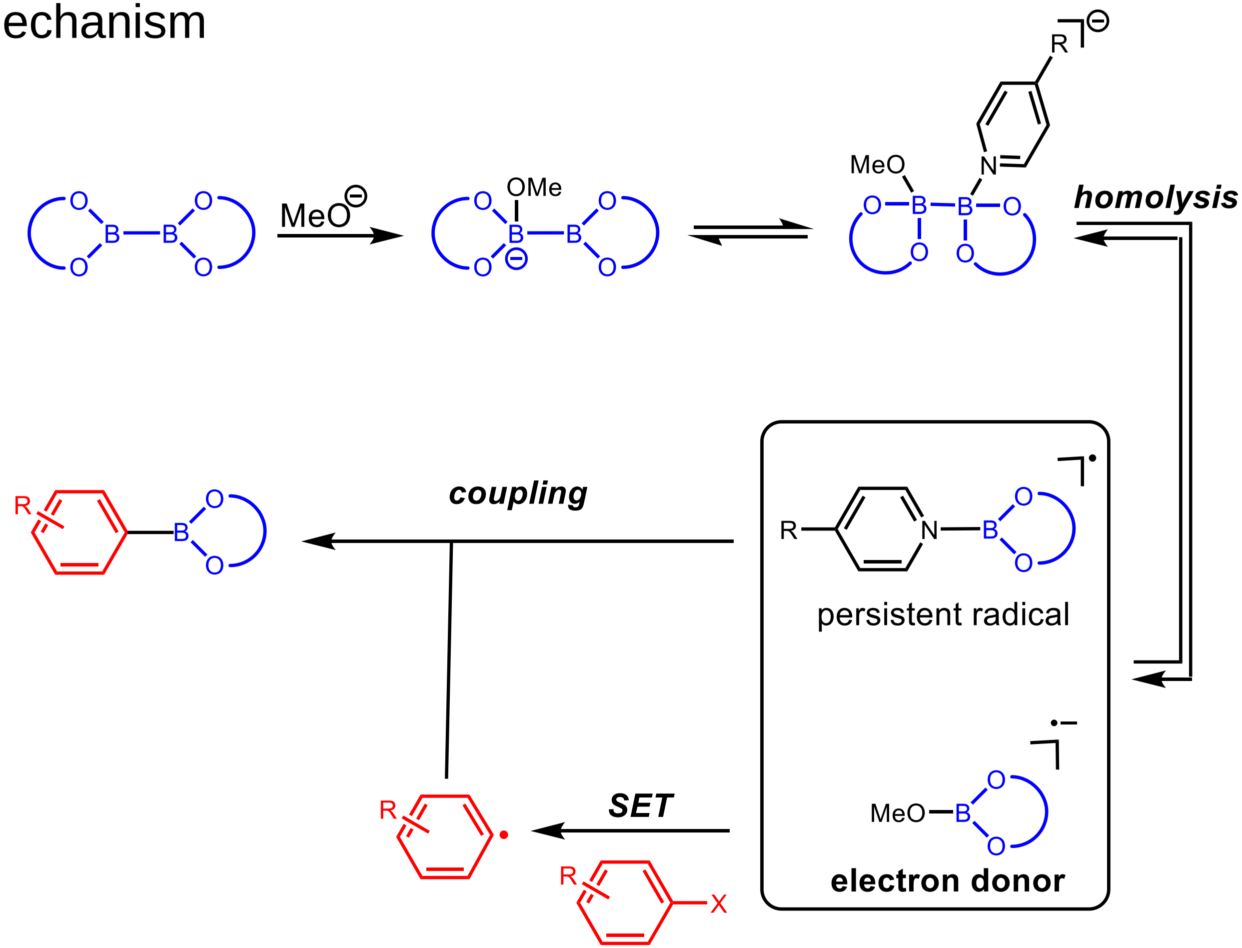
SEDs derived from diborons



Zhang L.; Jiao L. *J. Am. Chem. Soc*. **2017**, *139*, 607

SEDs derived from diborons

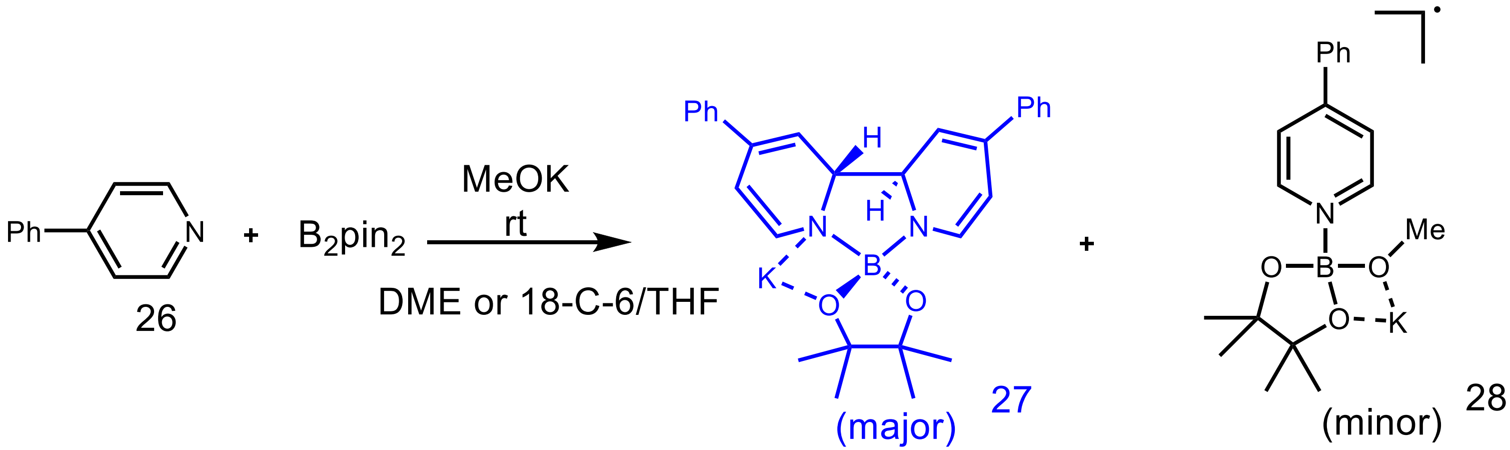
Proposed mechanism



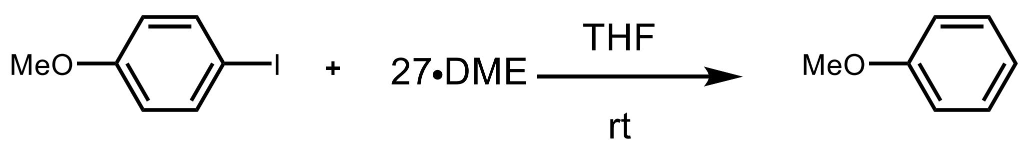
Zhang L.; Jiao L. *J. Am. Chem. Soc*. **2017**, *139*, 607

SEDs derived from diborons

The structure of the electron donor



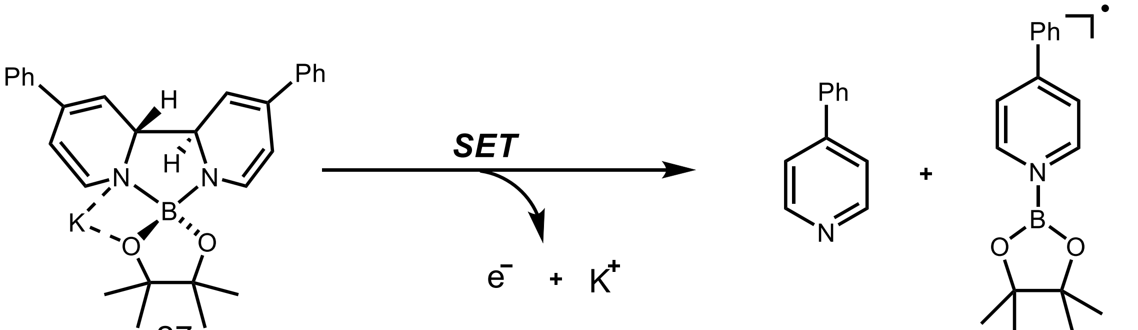
Pyridine- and boron-containing complexes as super electron donors



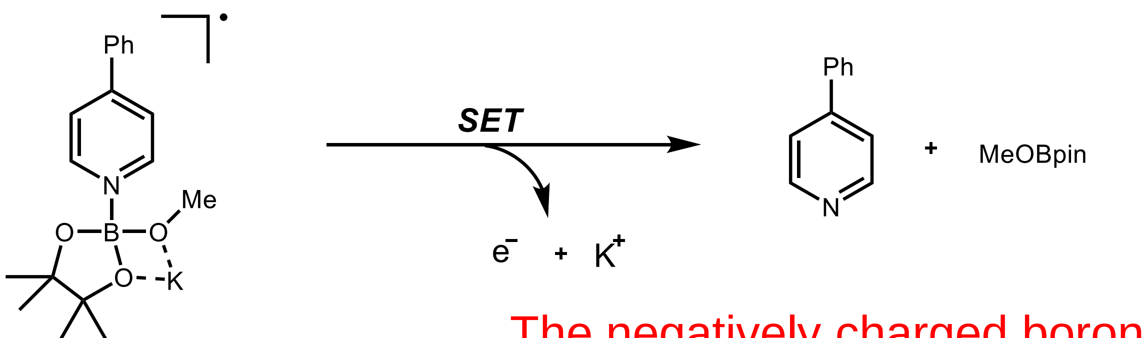
Zhang L.; Jiao L. *Chem. Sci*. **2018**, *9*, 2711

SEDs derived from diborons

Driving force



27



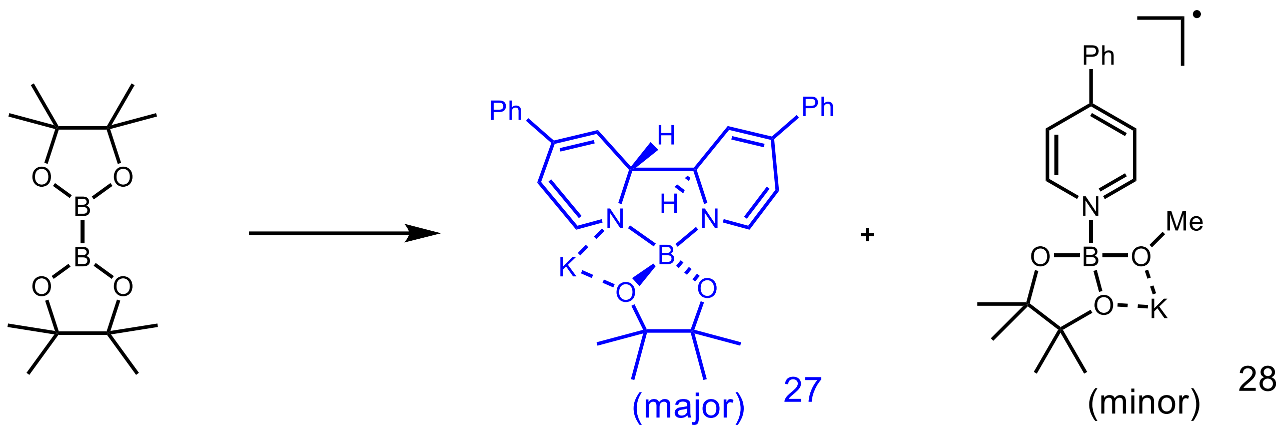
28

The negatively charged boron center

The aromaticity of the pyridine ring

Zhang L.; Jiao L. *Chem. Sci*. **2018**, *9*, 2711

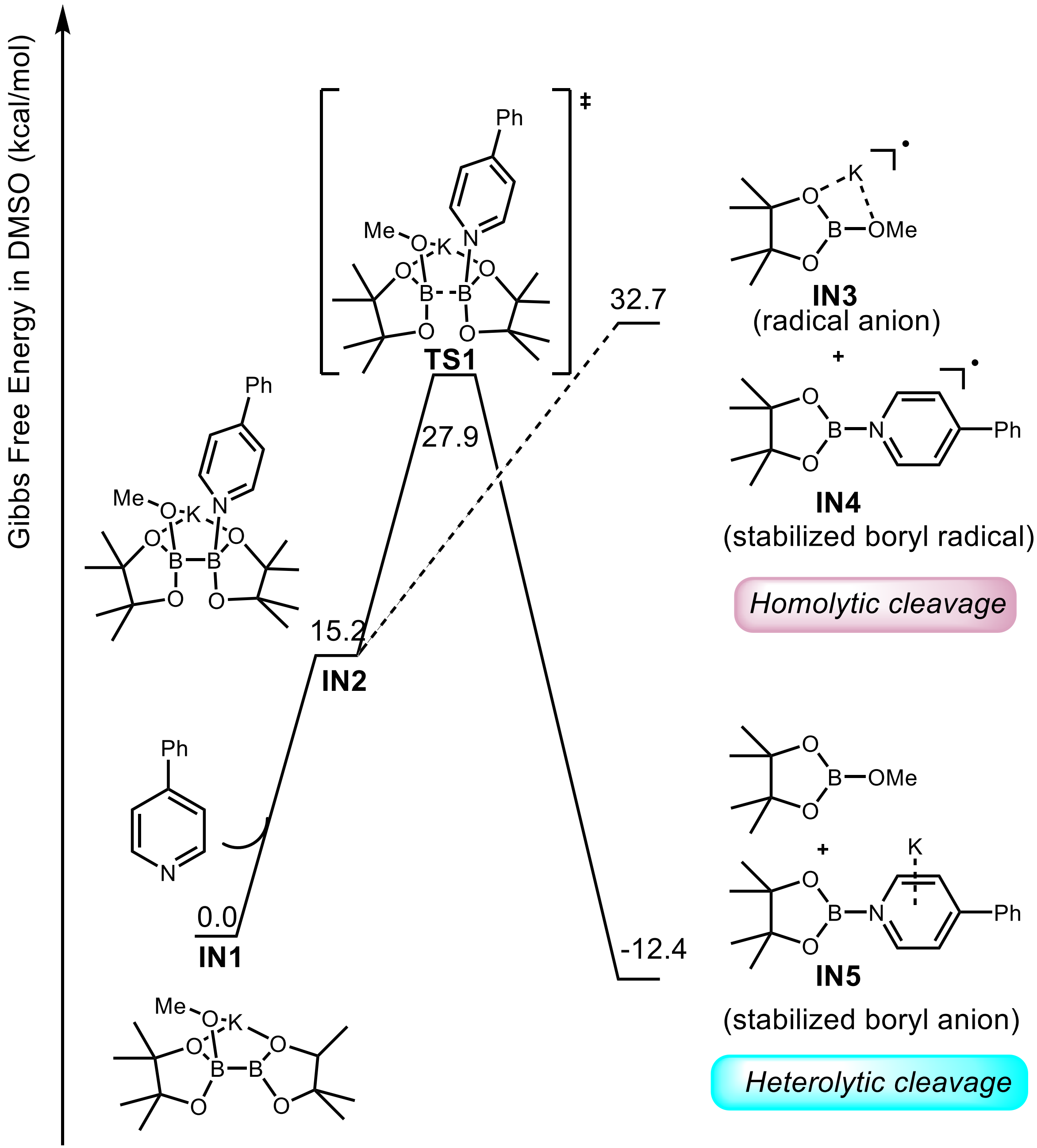
SEDs derived from diborons



Two questions

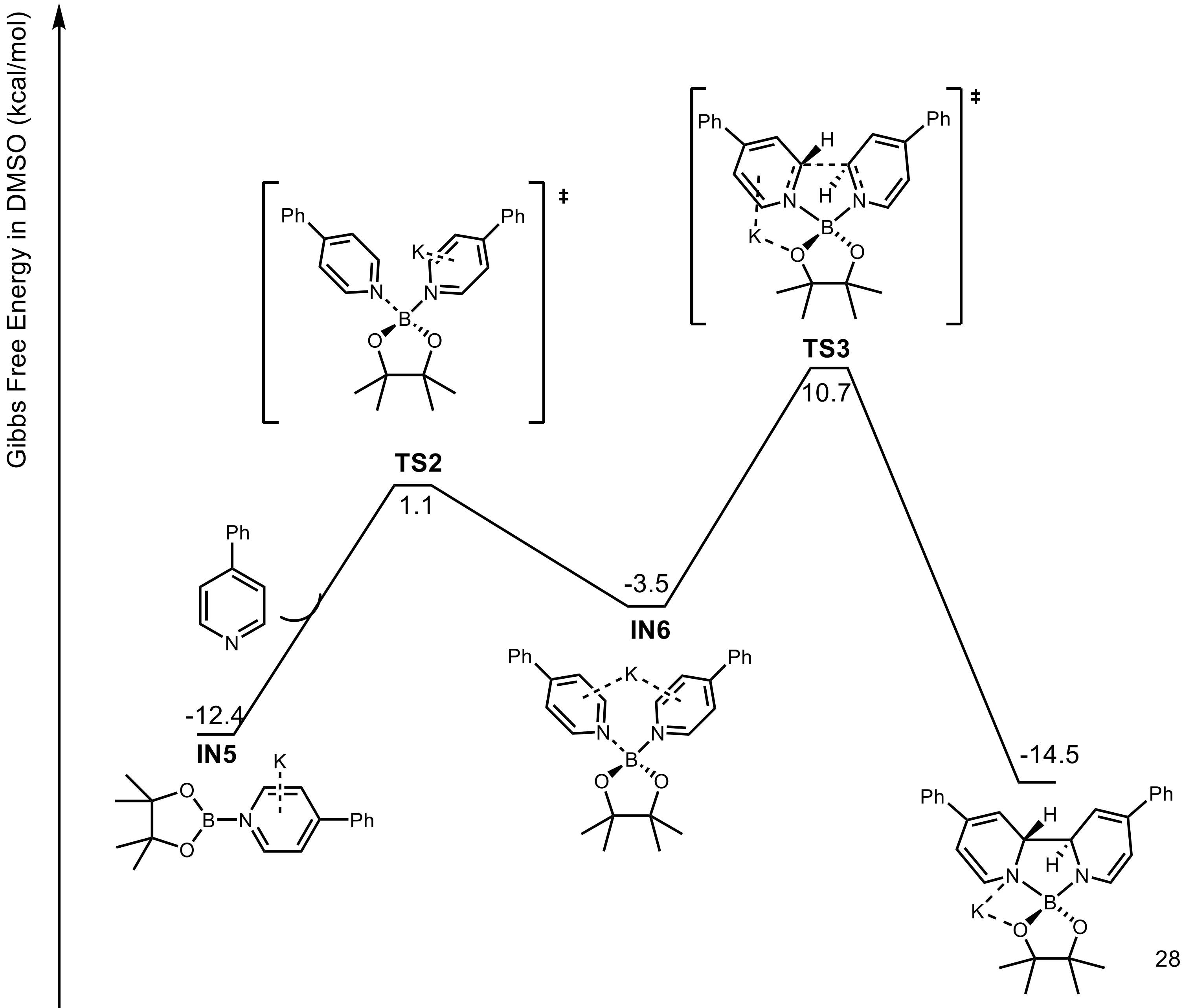
? The mode of boron–boron bond cleavage

? Mechanism for the formation of super-electron-donors



Gibbs free energy profile for the homolytic and heterolytic cleavage pathways of diboron.

Zhang L.; Jiao L. *Chem. Sci*. **2018**, *9*, 2711

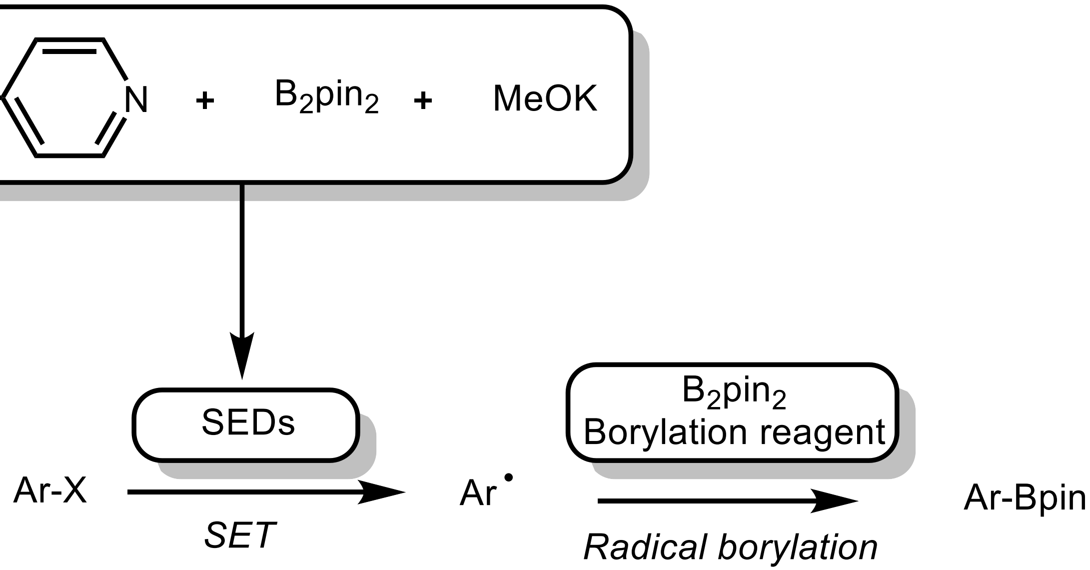


Gibbs free energy profile for the formation of the complex

Zhang L.; Jiao L. *Chem. Sci*. **2018**, *9*, 2711

SEDs derived from diborons

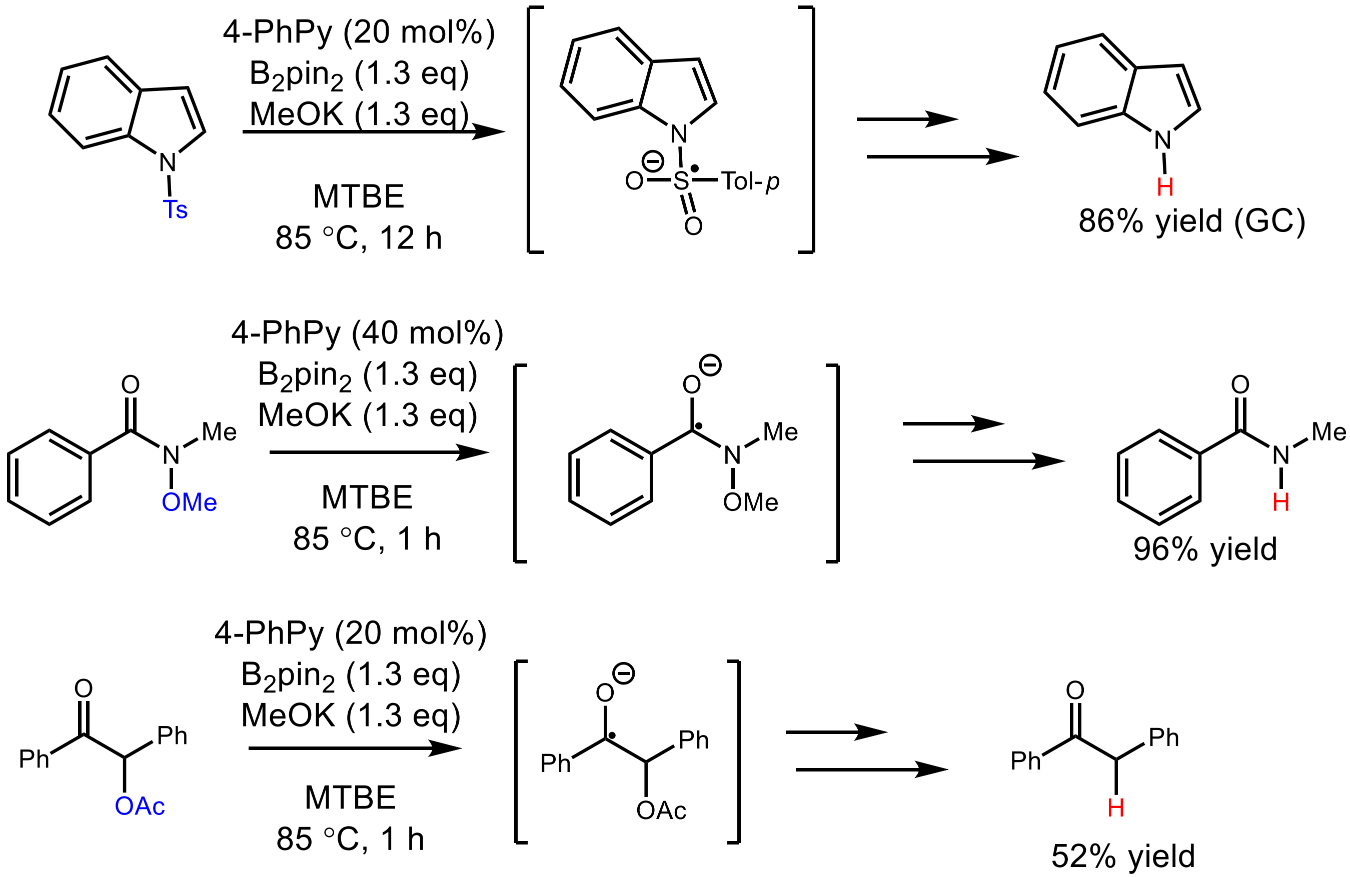
Revised radical borylation mechanism



Zhang L.; Jiao L. *Chem. Sci*. **2018**, *9*, 2711

SEDs derived from diborons

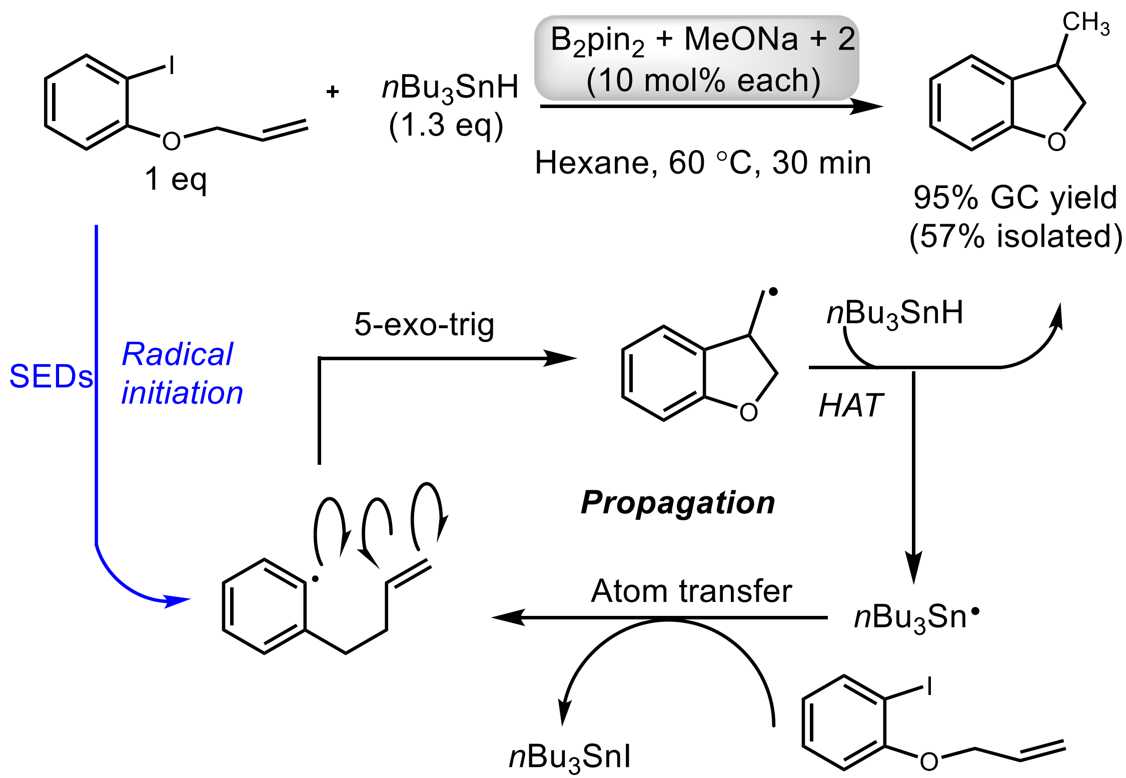
Reductive Cleavage of S-N, N-O and C-O



Zhang L.; Jiao L. *Chem. Sci*. **2018**, *9*, 2711

*SED*s derived from diborons

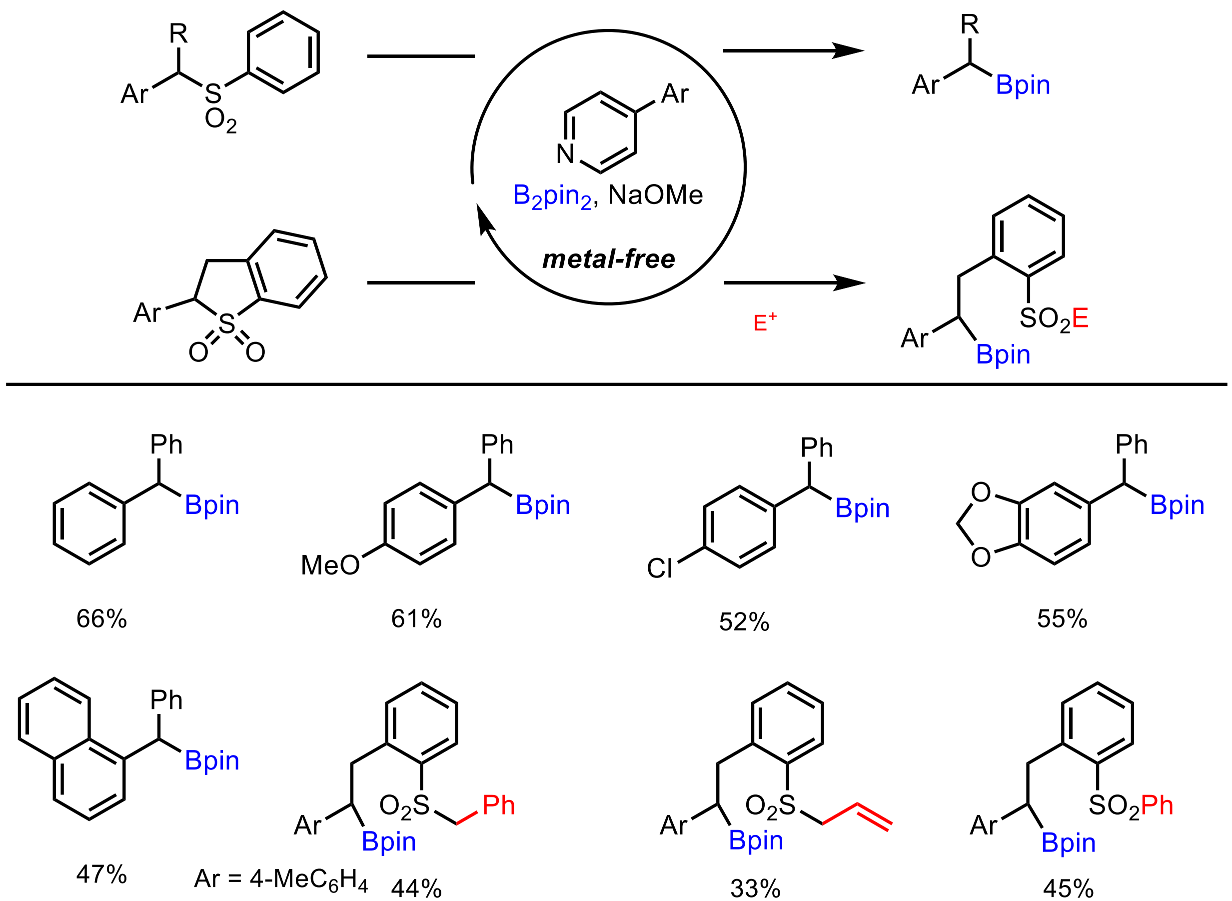
*SED*s mixture as the radical initiator



Zhang L.; Jiao L. *Chem. Sci*. **2018**, *9*, 2711

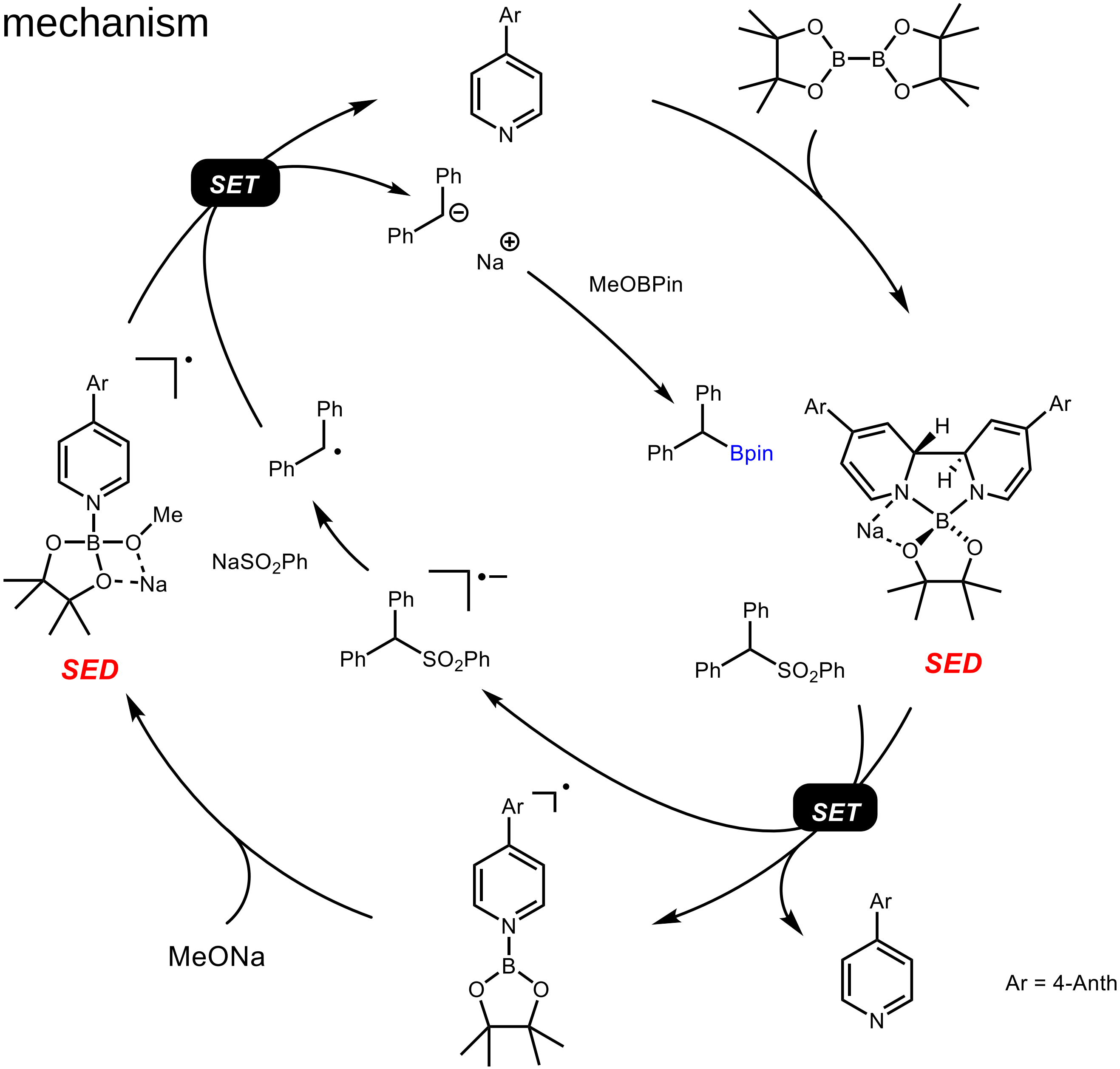
SEDs derived from diborons

Desulfonative borylation of benzyl sulfones



C. M. Crudden. et al. *Org. Biomol. Chem*. **2019**, *17*, 7300

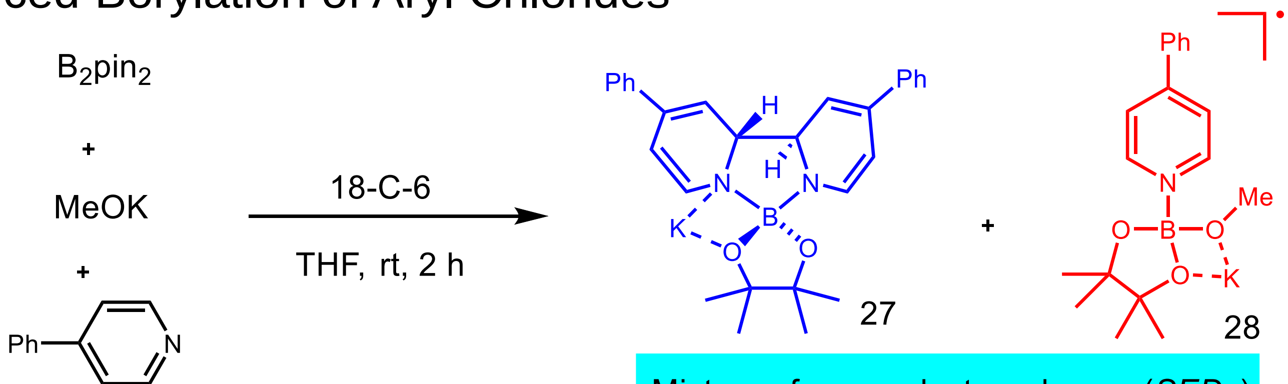
Proposed mechanism



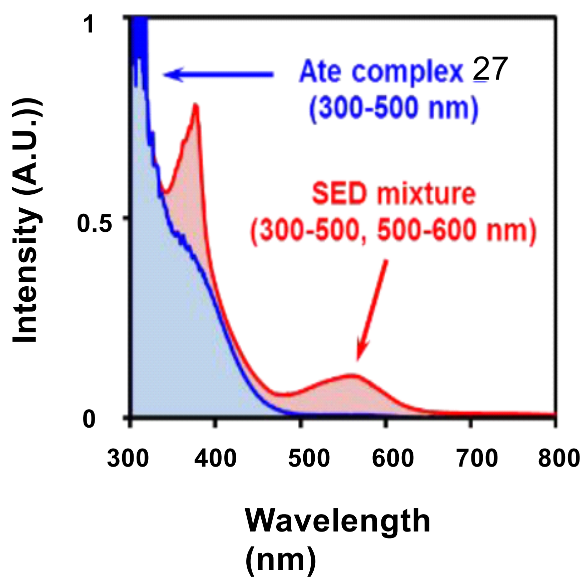
C. M. Crudden. et al. *Org. Biomol. Chem*. **2019**, *17*, 7300

SEDs derived from diborons

Visible-Light-Induced Borylation of Aryl Chlorides



Mixture of super electron donors (*SEDs*)



Complex 27 Absorption band 300−500 nm

Complex 28 Absorption band 500−600 nm

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SEDs derived from diborons

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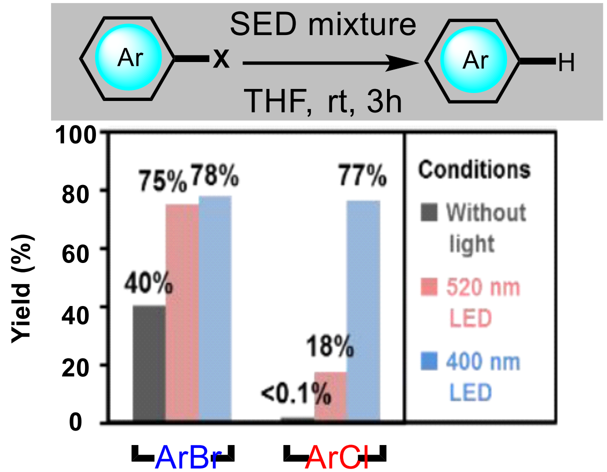
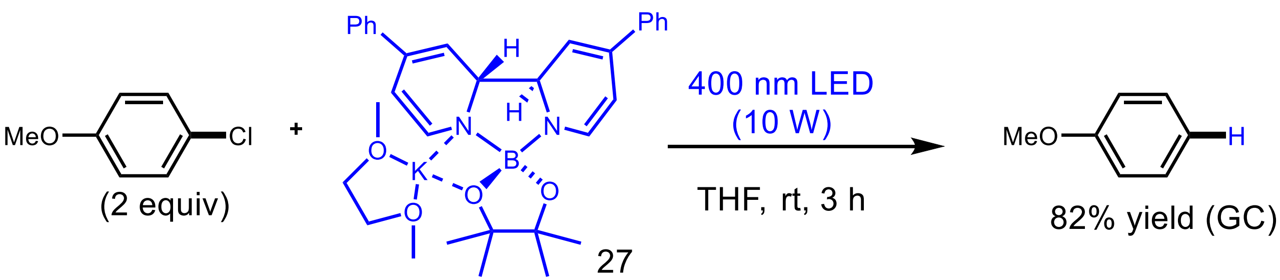


(Ar = 4-MeOPh)



27

Complex 27 exhibits a superior reactivity!

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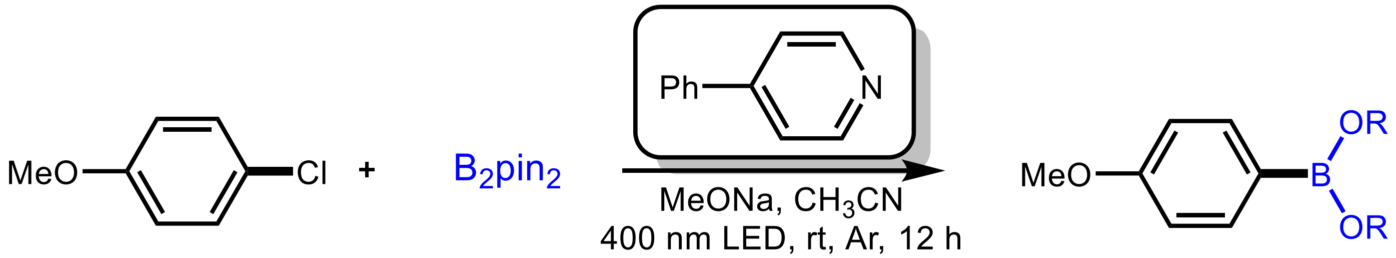
SEDs derived from diborons

Optimization of Reaction Conditions



entry	change from standard conditions	conv. (%)	yield (%)
1	none	99	92
2	365 nm LED intead of 400 nm LED	40	35
3	450 nm LED intead of 400 nm LED	66	53
4	254 nm Hg lamp (28 W) intead of 400 nm LED	6	5
5	without light	1	1
6	without 4-phenylpyridine	1	1
7	reaction set up under air	94	88

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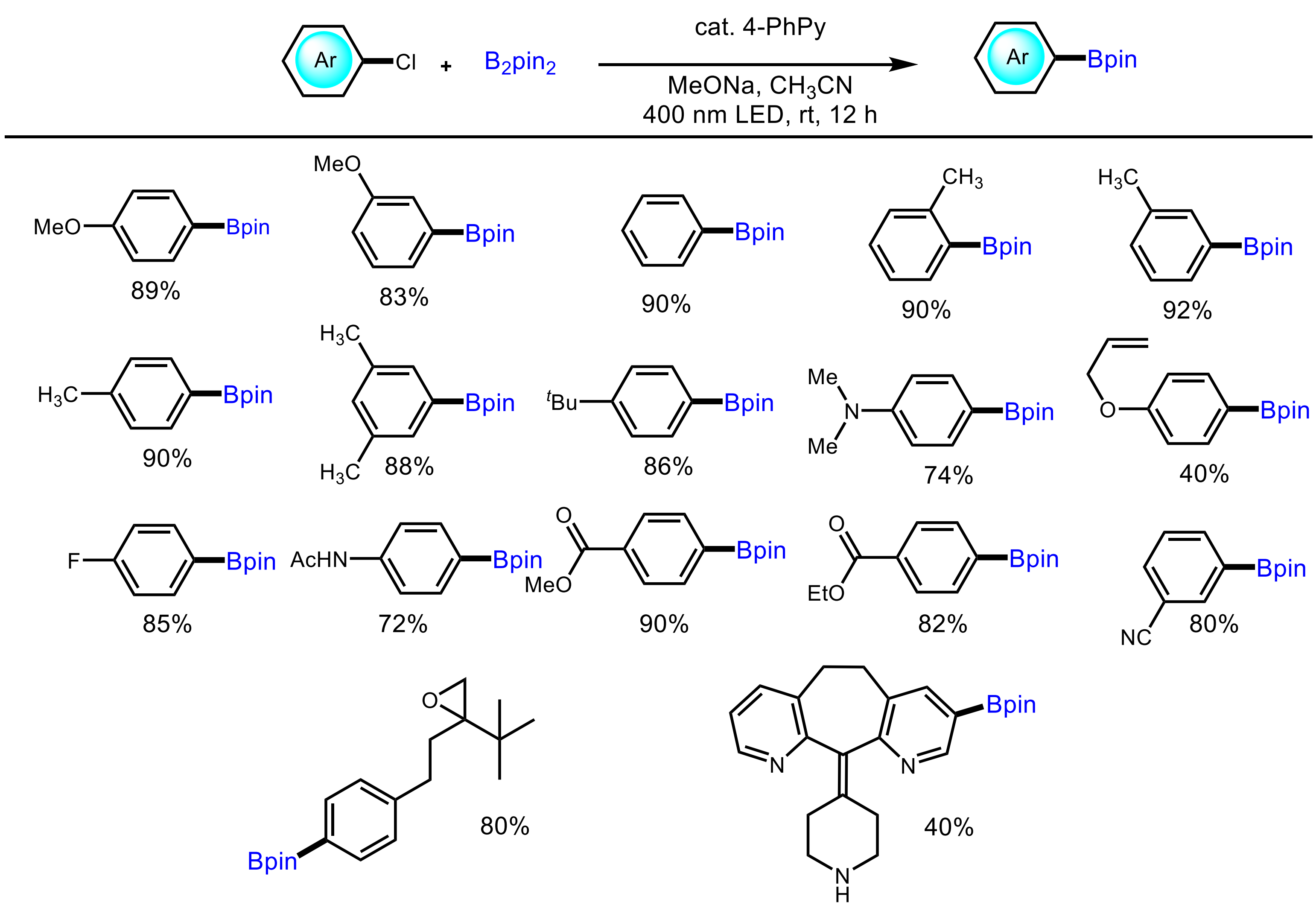
SEDs derived from diborons

Borylation of Aryl Chlorides



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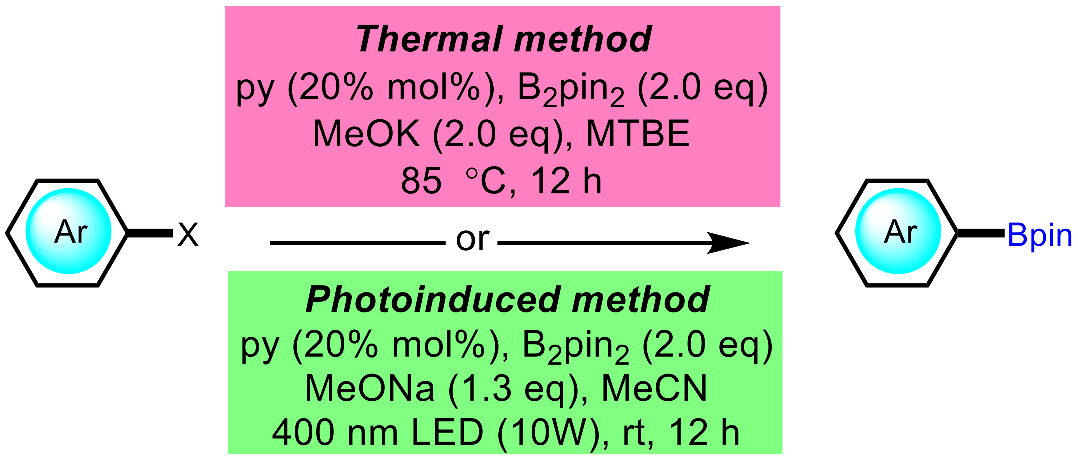
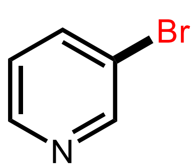
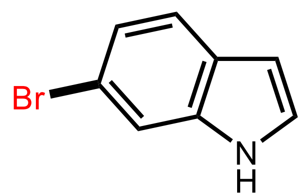
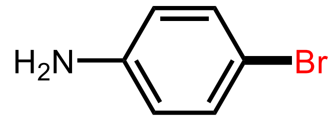
SEDs derived from diborons

Enabling Difficult Borylation Reactions



Aryl halide substrates			
Thermal method	10% yield	0% yield	0% yield
Photoinduced method	48% yield	56% yield	78% yield

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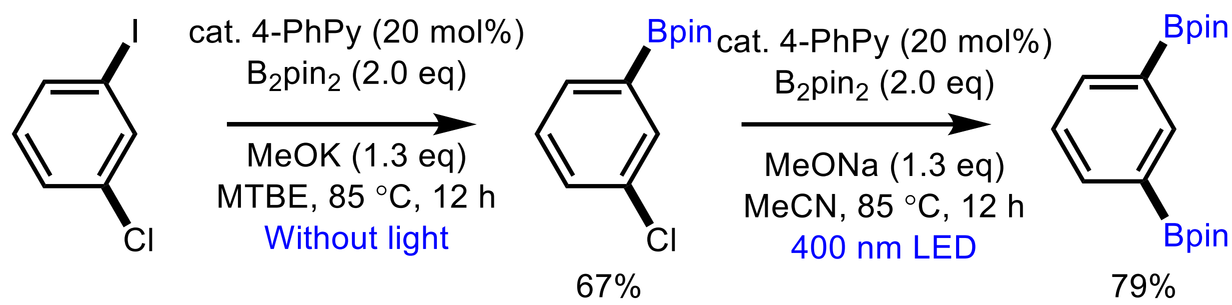
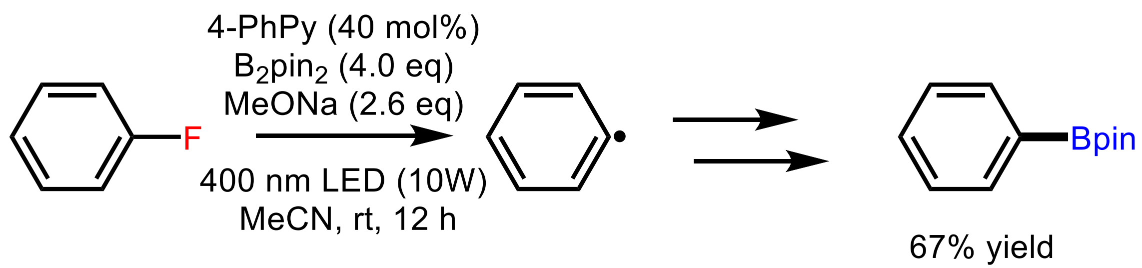
SEDs derived from diborons

Application in sequencial diborylation



Borylation of Fluorobenzene



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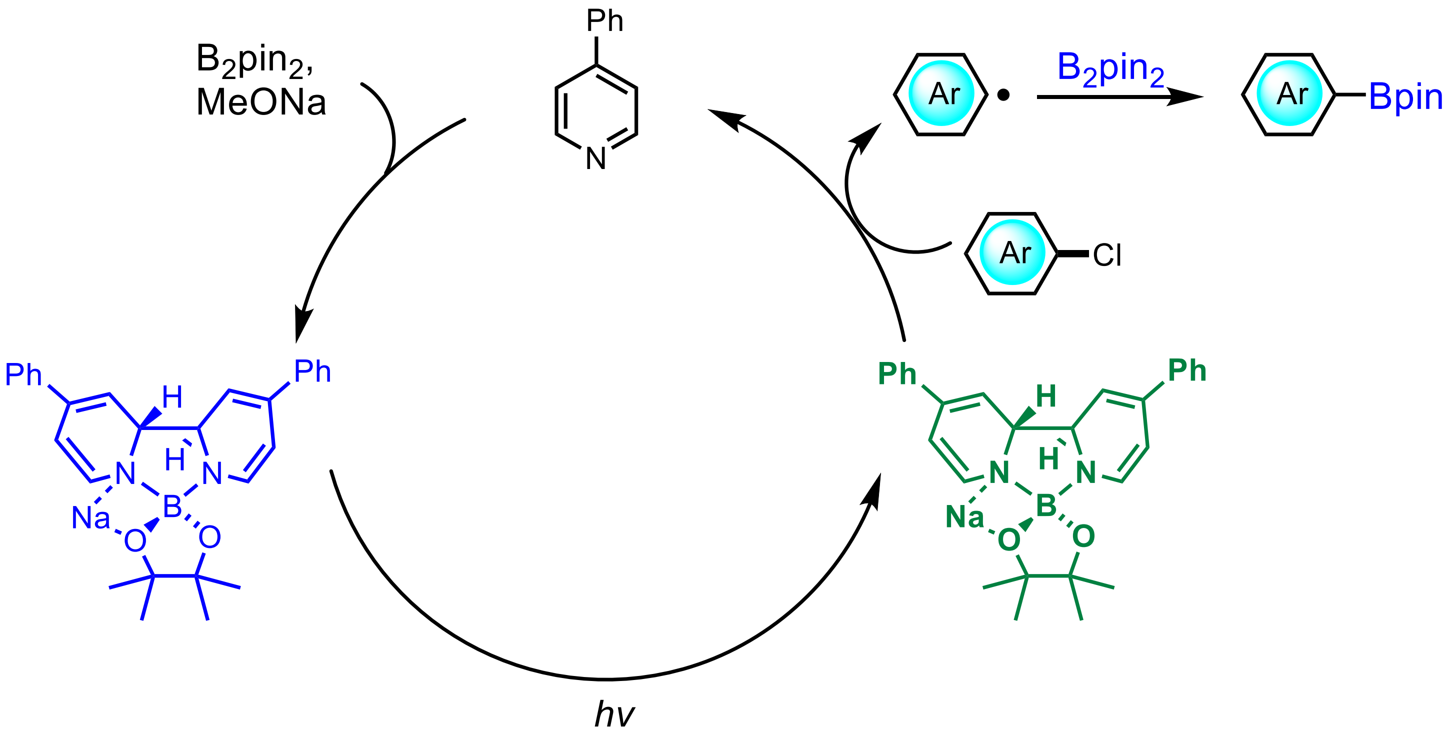
SEDs derived from diborons

Proposed mechanism



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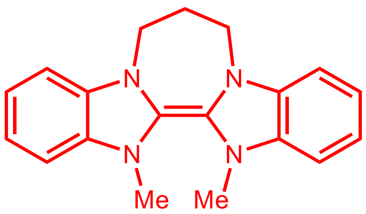
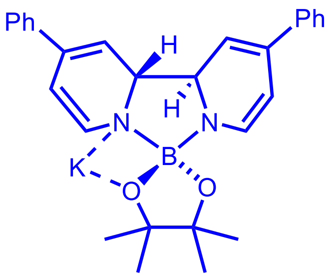
Summary



The electron-rich olefins

2005-2019

- Reactions in the ground state
- Reactions in the photo-excited state
- Haloarene–Arene Coupling



SEDs derived from diborons

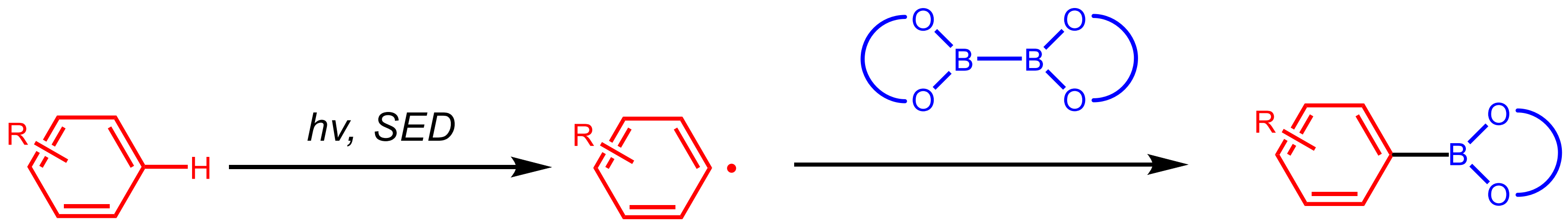
2018-2019

- Radical Borylation of Aryl Halides
- Desulfonative borylation of benzyl sulfones
- Visible-Light-Induced Borylation of Aryl Chlorides

Summary

Hypothesis

Photo-Induced Borylation of Aryl Chlorides



Thanks for your attention