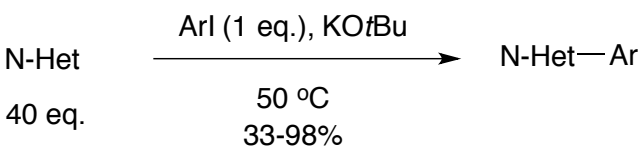
KO*t*Bu: A Privileged Reagent for Electron Transfer Reactions?

J. Am. Chem. Soc. 2016, **138**, 7401-7410.

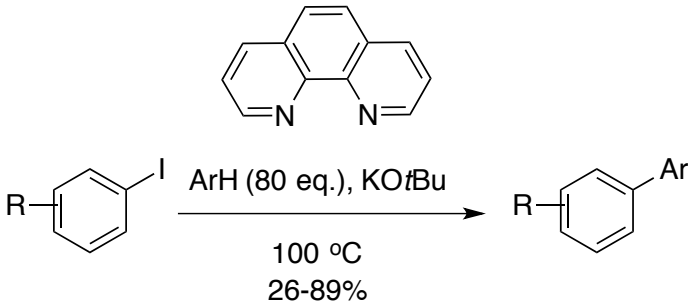
6/18/16

Mike Frasso

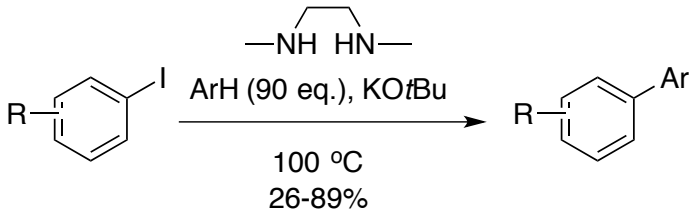
Transition Metal Free Couplings



Org. Lett **2008**, *10*, 4673-4676.



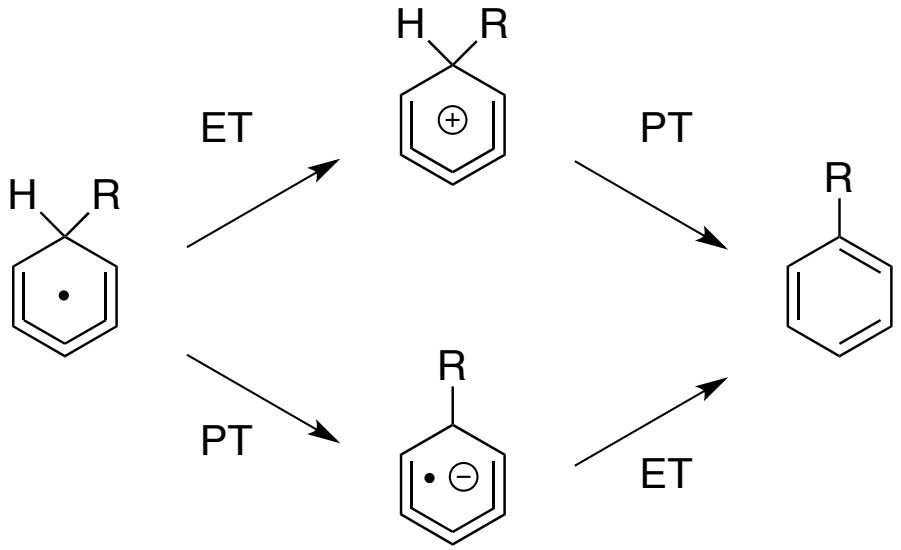
Nat. Chem. **2010**, *2*, 1044-1049.



J. Am. Chem. Soc. **2010**, *132*, 16737-16739.

- Extensive purification/trace metal analysis performed
- All suggest radical mechanisms
- $K_H/K_D = 1.29$

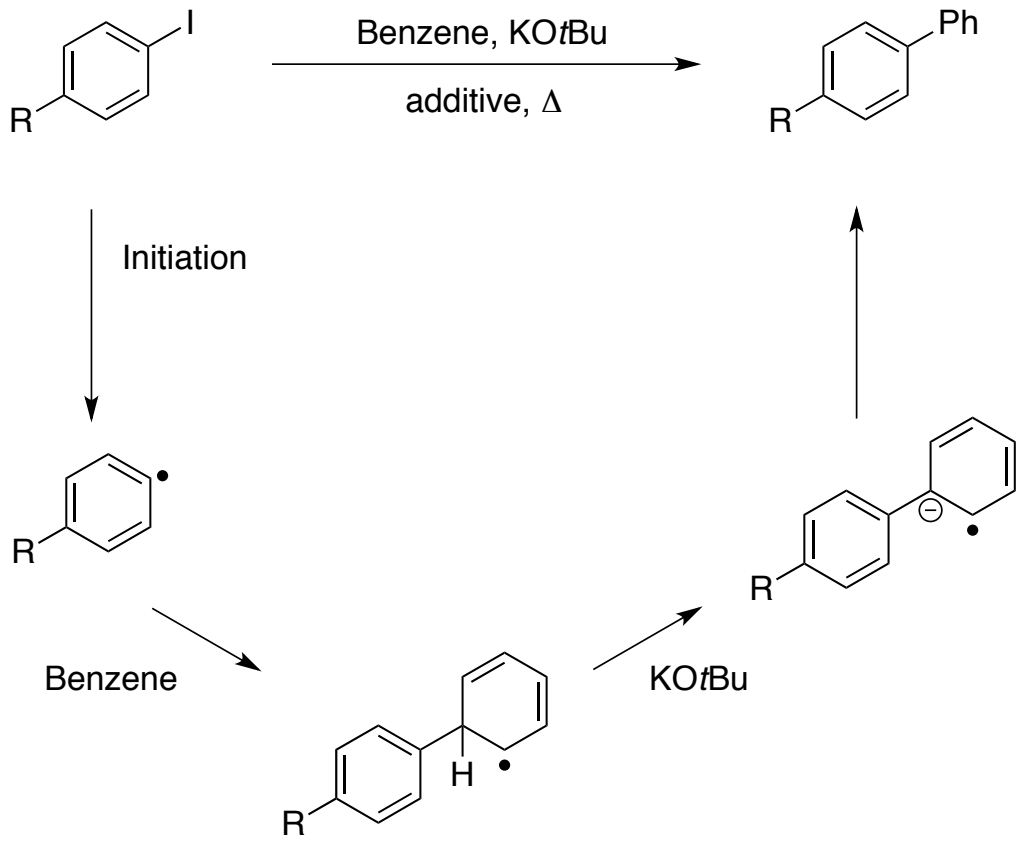
Possibilities Following Radical Addition



- Proton Transfer (PT) most likely favored due to strongly basic conditions

Angew. Chem. Int. Ed. **2011**, *50,* 5018-5022.

“Base-Promoted Homolytic Aromatic Substitution”



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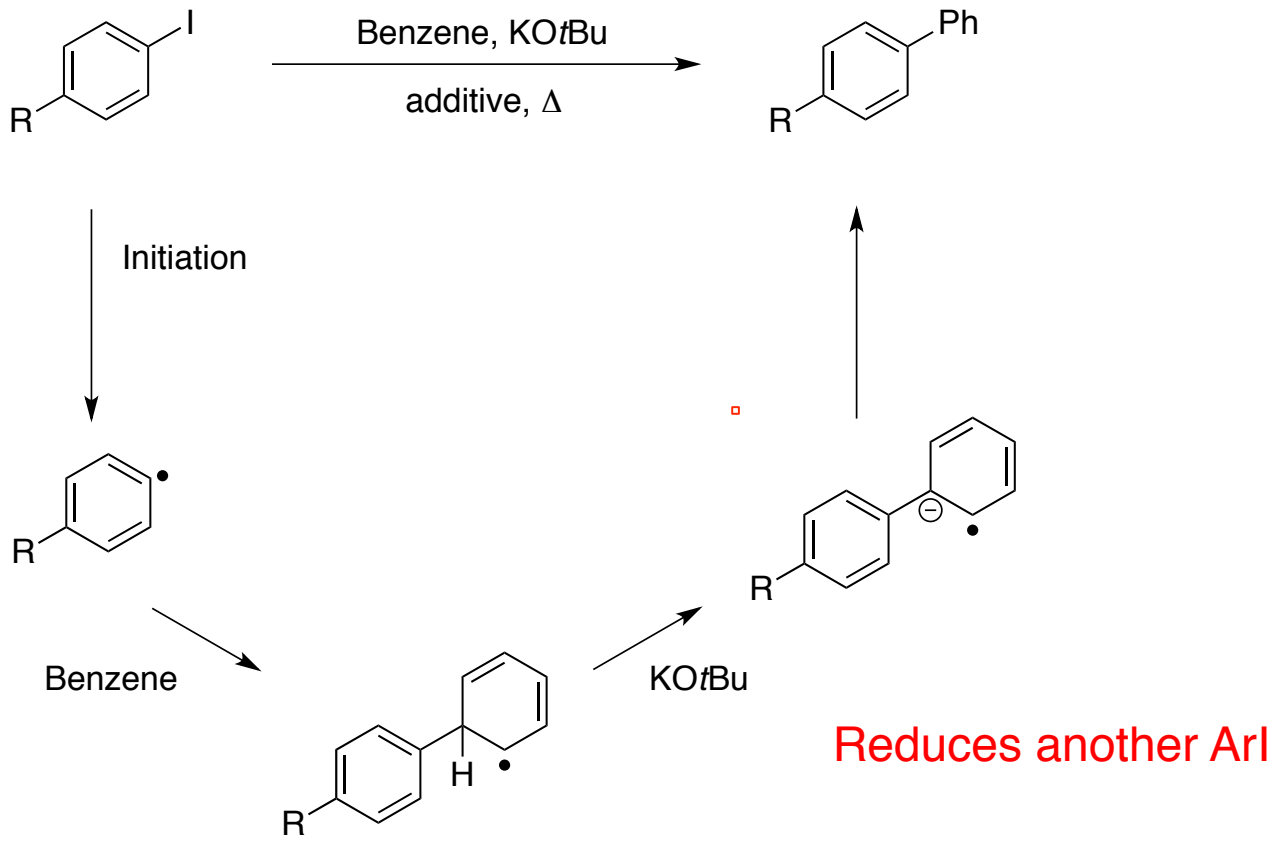
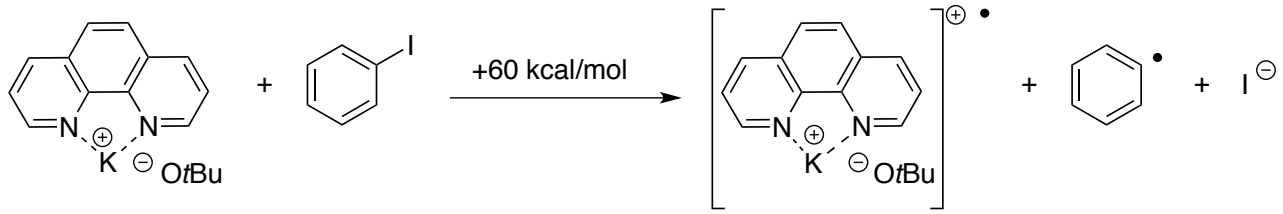
“Base-Promoted Homolytic Aromatic Substitution”



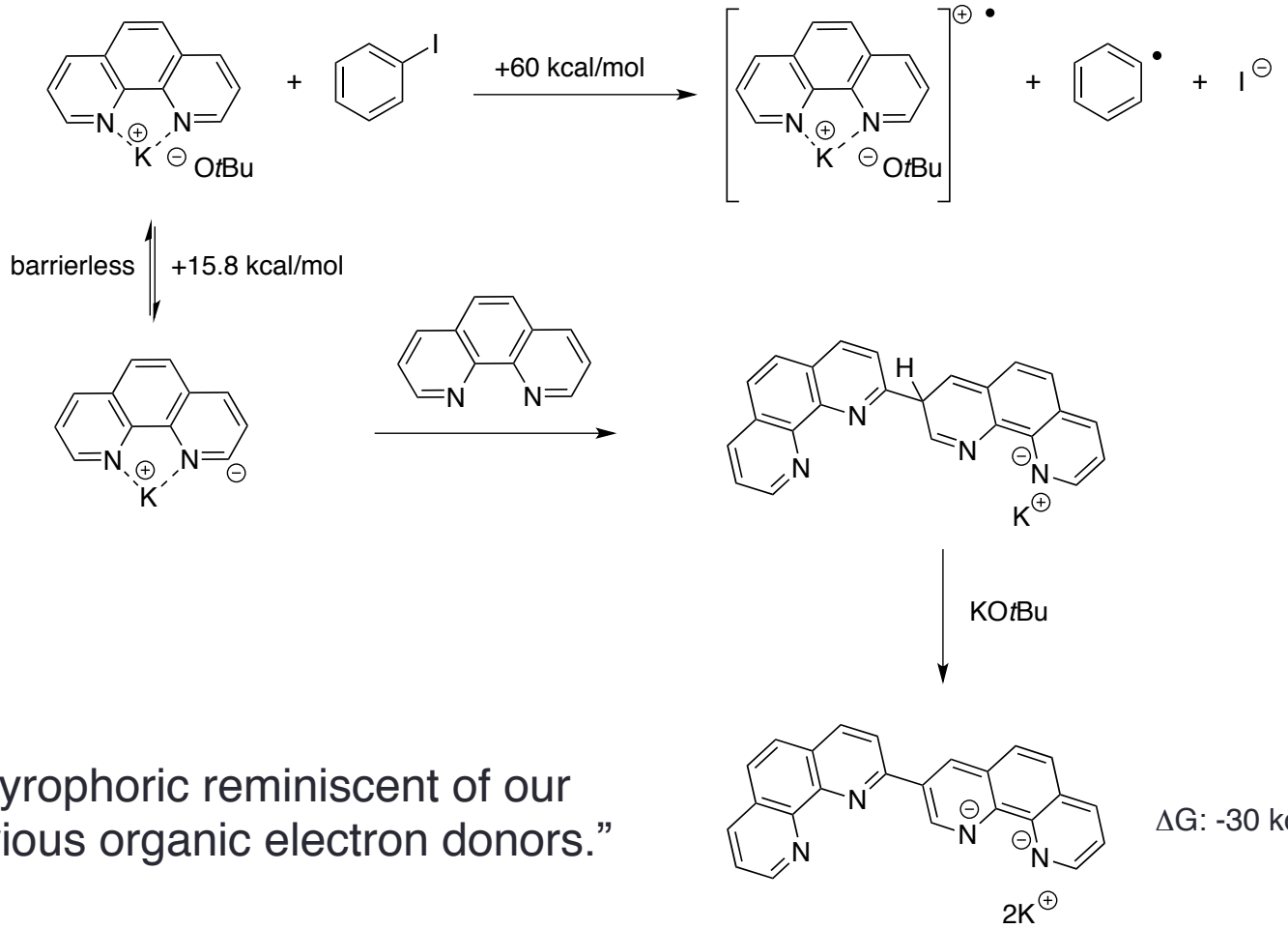
J. Am. Chem. Soc. 2016, **138**, 7401-7410.
Angew. Chem. Int. Ed. **2011**, *50,* 5018-5022.

A Different Proposal for Initiation



J. Am. Chem. Soc. 2016, **138***,* 7401-7410.
Chem. Sci. **2014***, 5,* 476-482.

A Different Proposal for Initiation

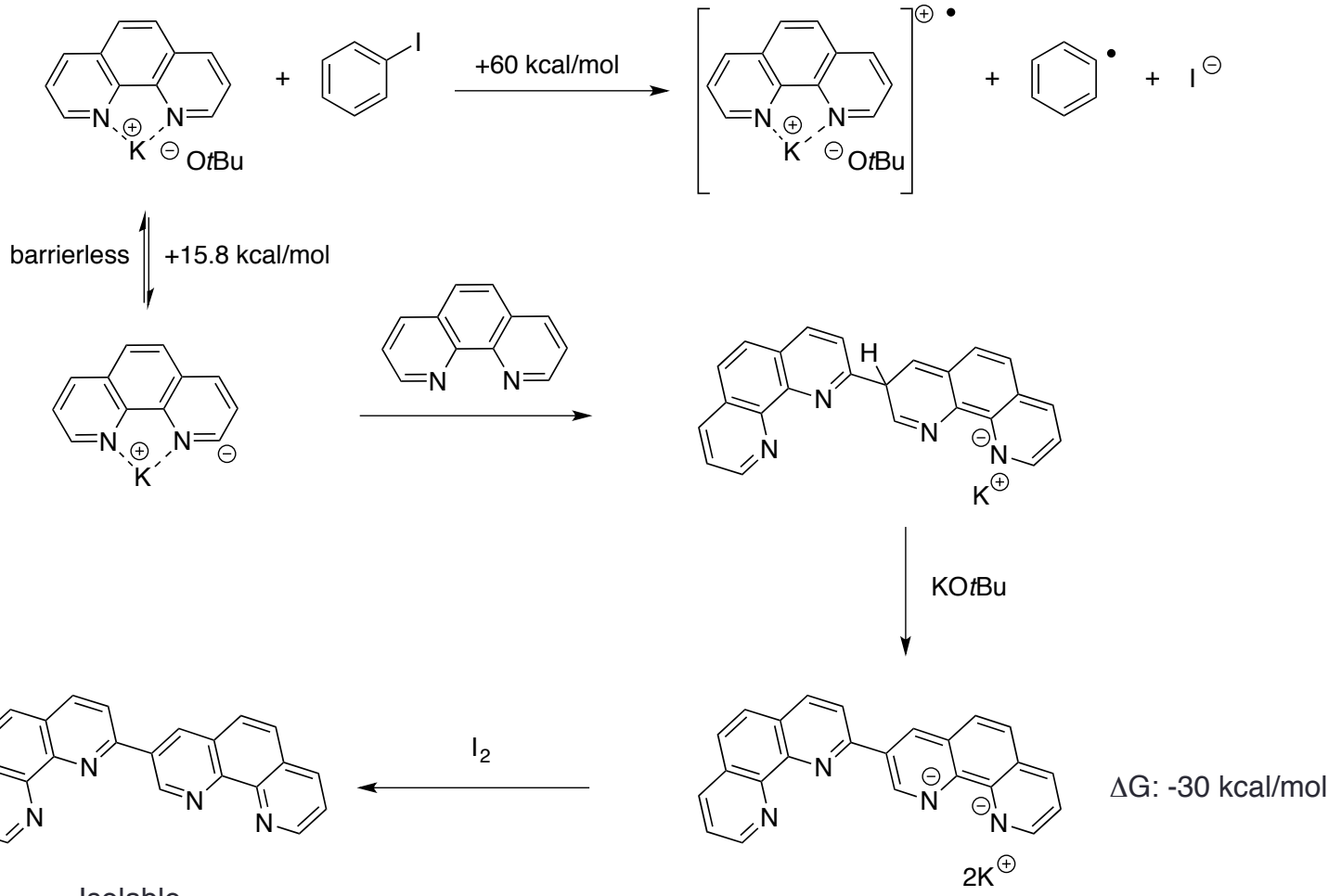


"…pyrophoric reminiscent of our previous organic electron donors."

ΔG: -30 kcal/mol

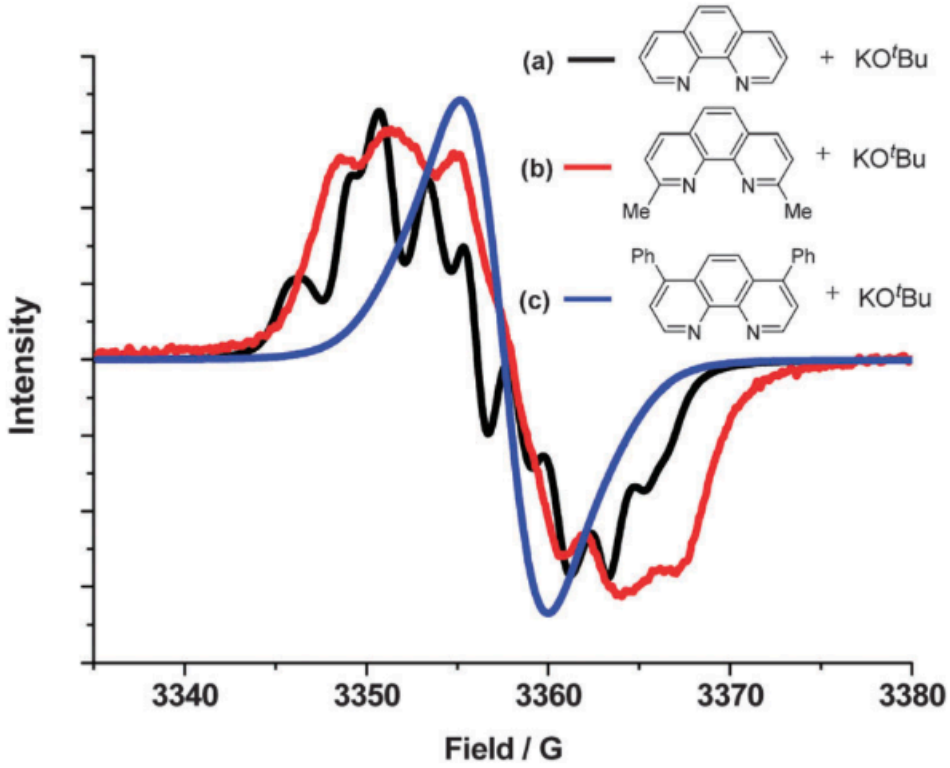
J. Am. Chem. Soc. 2016, **138**, 7401-7410.
Chem. Sci. **2014**, *5,* 476-482.

A Different Proposal for Initiation



J. Am. Chem. Soc. 2016, **138***,* 7401-7410.
Chem. Sci. **2014***, 5,* 476-482.

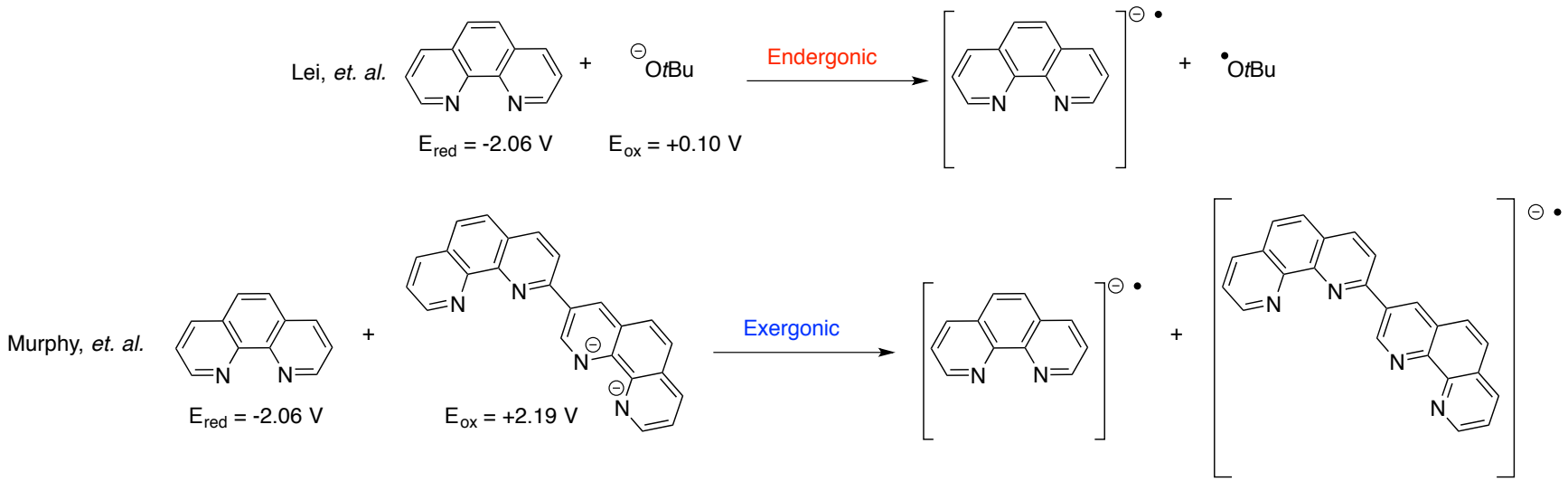
EPR Evidence



- In DMF, 100 °C
- Black trace is not symmetric
- May be a superposition of 2 similar radicals

J. Am. Chem. Soc. 2016, **138**, 7401-7410.
Chem. Commun. **2015**, *51*, 545-548.

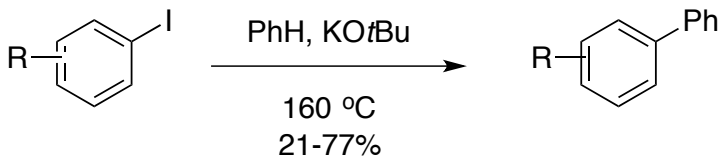
Proposed Explanation of EPR Spectrum



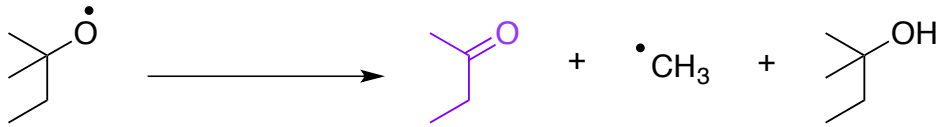
- Potentials measured by cyclic voltametry in DMF vs SCE
- Demonstrate that *t*-butoxide does not directly reduce aryl halides
  - E_{red} = -2.0 V for PhI
- Electrochemical reduction of phenanthroline inhibited by KO*t*Bu
- Conclusion: KO*t*Bu acts as a base

J. Am. Chem. Soc. 2016, **138**, 7401-7410.
Chem. Commun. **2015**, *51,* 545-548.

Is Phenanthroline Needed?



- Direct electron transfer from KO*t*Bu to ArI proposed

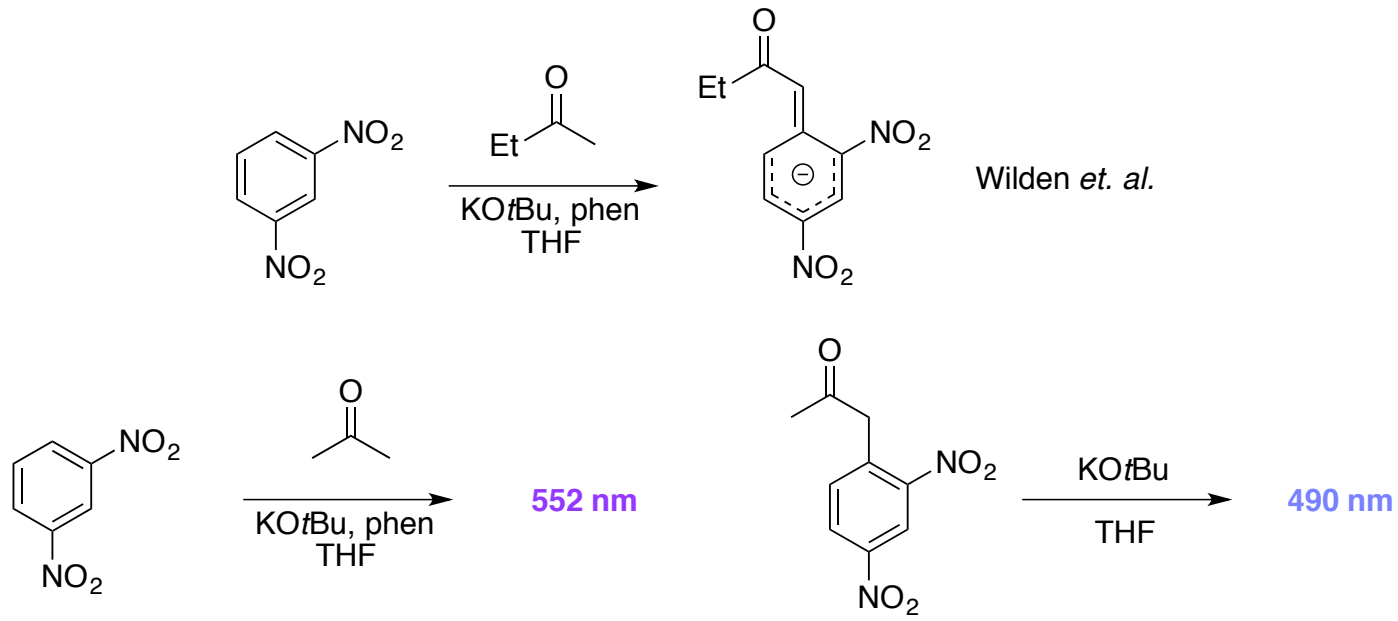


Presence confirmed
by Janovsky test

- Ketone detected by MS
- Samples were in THF

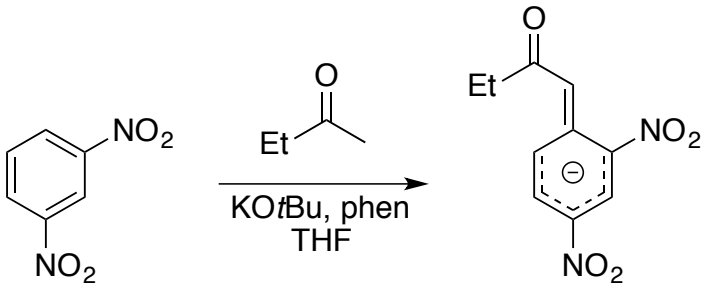
J. Am. Chem. Soc. 2016, **138**, 7401-7410.
Chem. Commun. **2014**, *50*, 2575-2578.

Janovsky Test

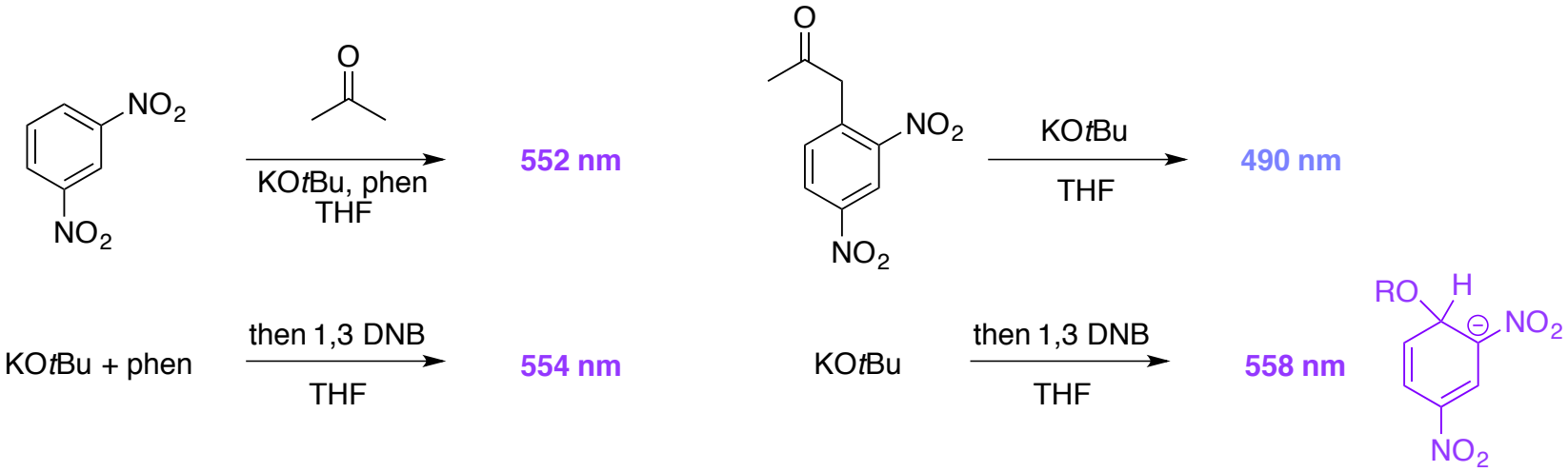


J. Am. Chem. Soc. 2016, **138**, 7401-7410.
Chem. Commun. **2014**, *50*, 2575-2578.

Janovsky Test

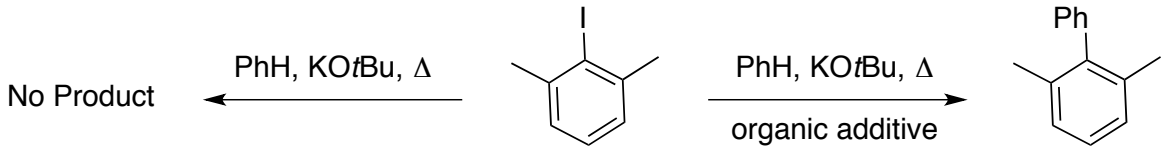


Wilden *et. al.*



J. Am. Chem. Soc. 2016, **138**, 7401-7410.
Chem. Commun. **2014**, *50*, 2575-2578.

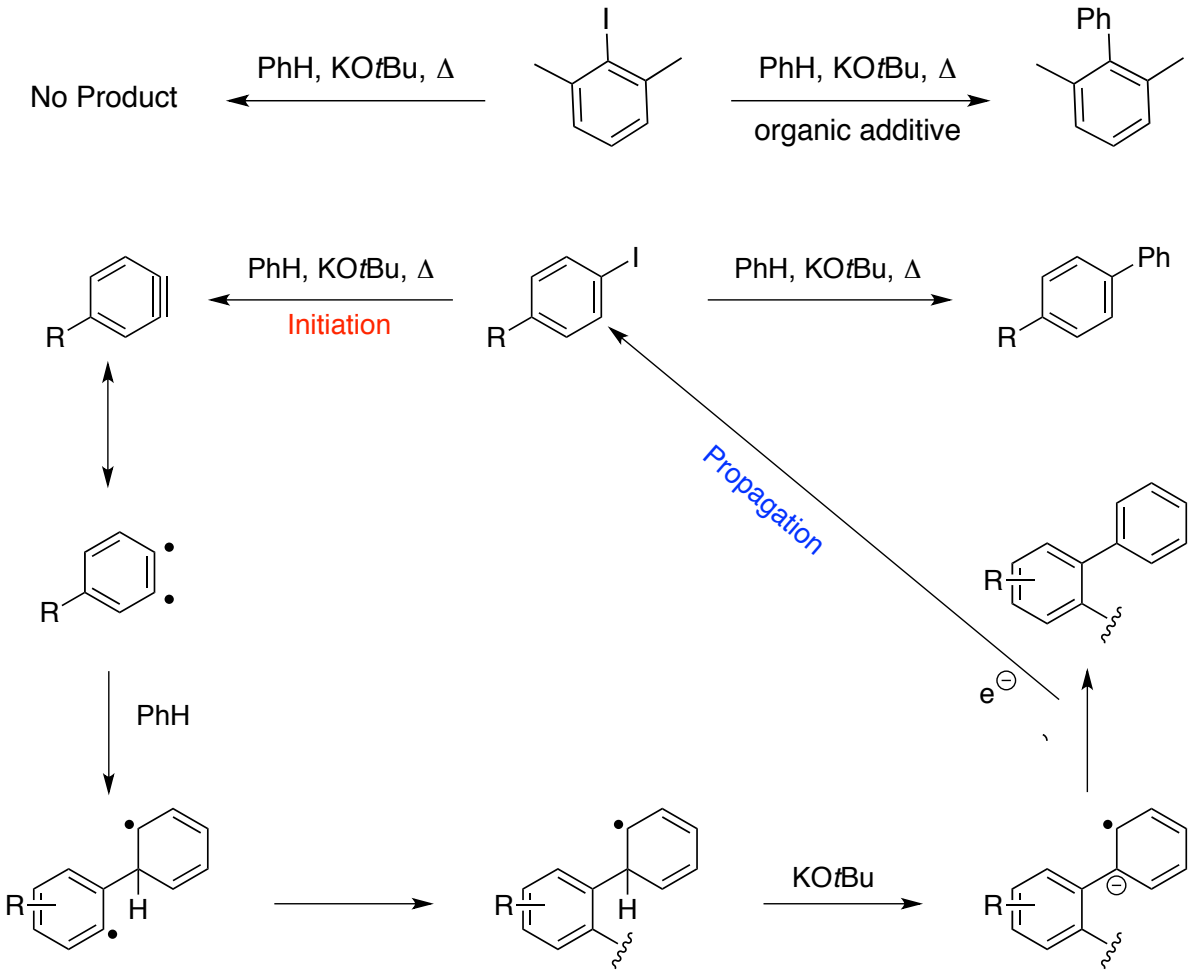
Another Alternative Proposal



- Conclusion: KO*t*Bu acts as a base in additive free reaction

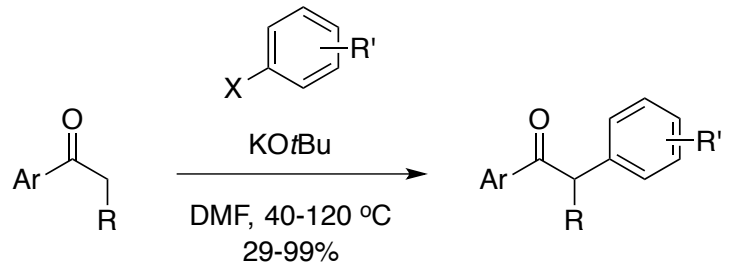
J. Am. Chem. Soc. 2016, **138**, 7401-7410.

Another Alternative Proposal

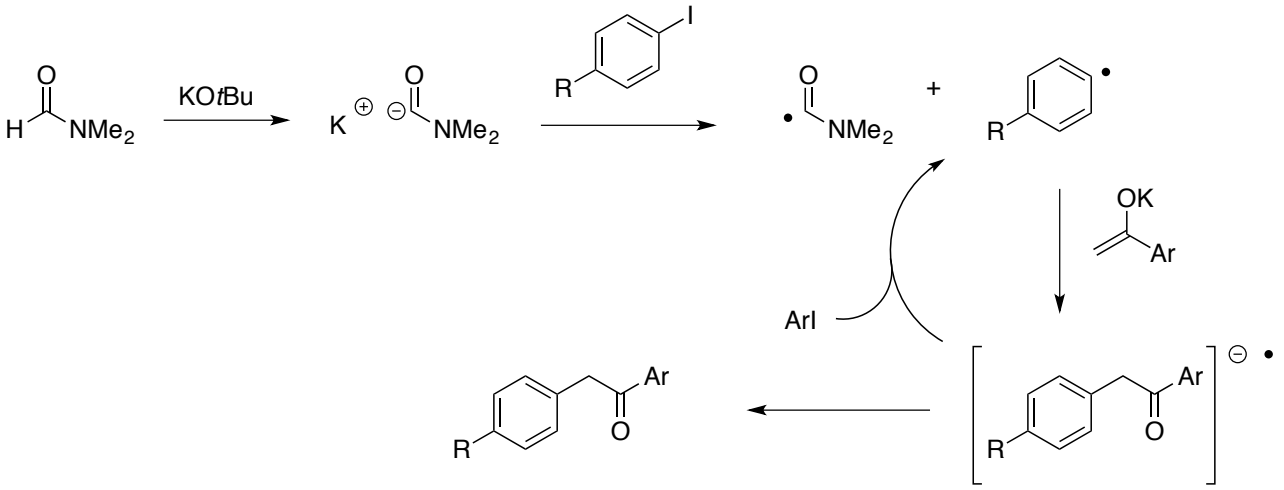


J. Am. Chem. Soc. 2016, **138**, 7401-7410.

α-Arylation of Ketones

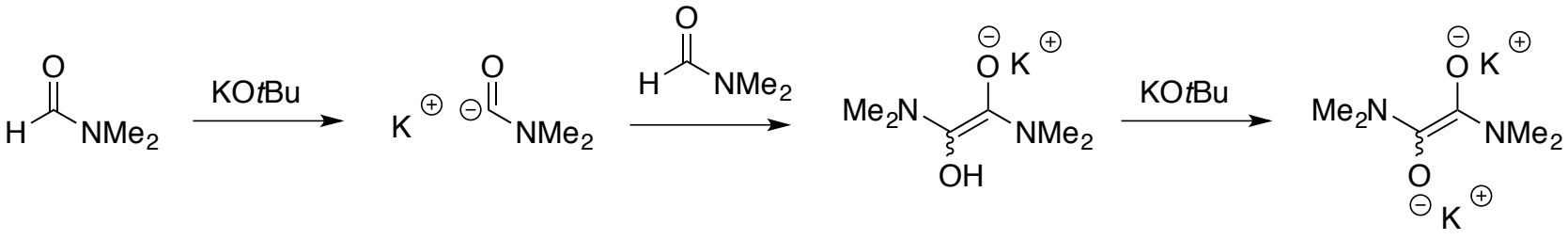


- Proceeds using 2:1 ketone to ArX
- X = I, Br, Cl
- DMF required (no dimer detected)



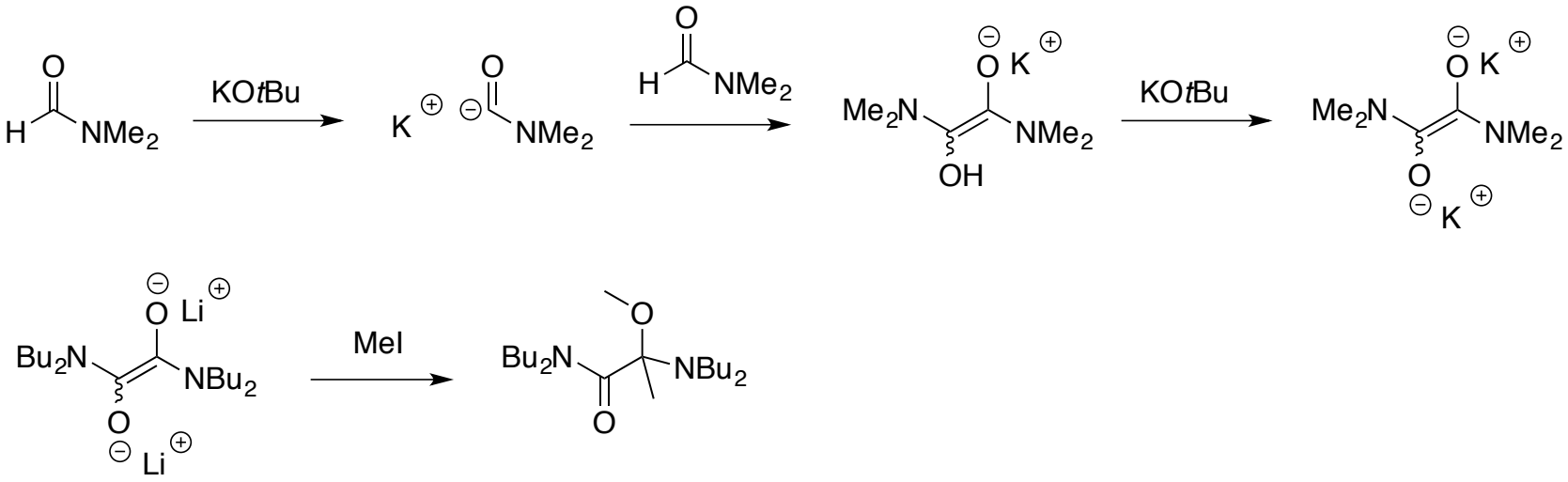
J. Am. Chem. Soc. 2016, **138***,* 7401-7410.
Angew. Chem. Int. Ed. **2015**, *54,* 10587-10591.

Proposed Dimeric Dianion as Electron Donor



J. Am. Chem. Soc. 2016, **138**, 7401-7410.

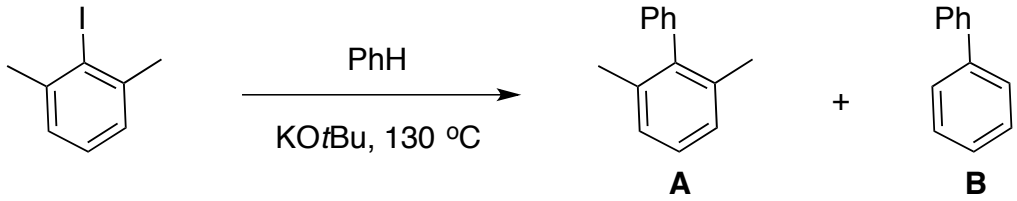
Proposed Dimeric Dianion as Electron Donor



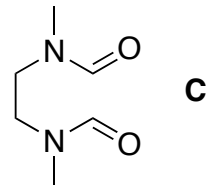
J. Org. Chem. **2000**, *65*, 1629-1635

J. Am. Chem. Soc. 2016, **138**, 7401-7410.

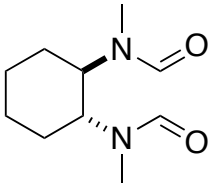
Investigating the Role of DMF



Entry	Additive	Amount	**A** + **B** (%)
1	none	---	0.5
2	DMF	1% v/v	2.6
3	DMF	0.1 mmol	0.6
4	**C**	0.05 mmol	8.0
5	**D**	0.05	16.1
6	DMF	1% v/v	0.4
7	**C**	0.5% v/v	19.6
8	**D**	0.5% v/v	31.6



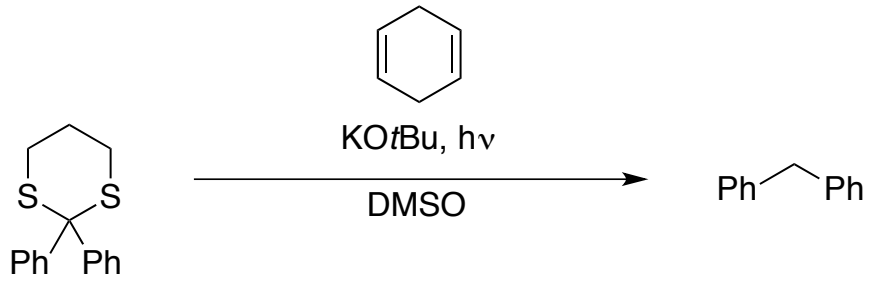
C



D

J. Am. Chem. Soc. 2016, **138**, 7401-7410.

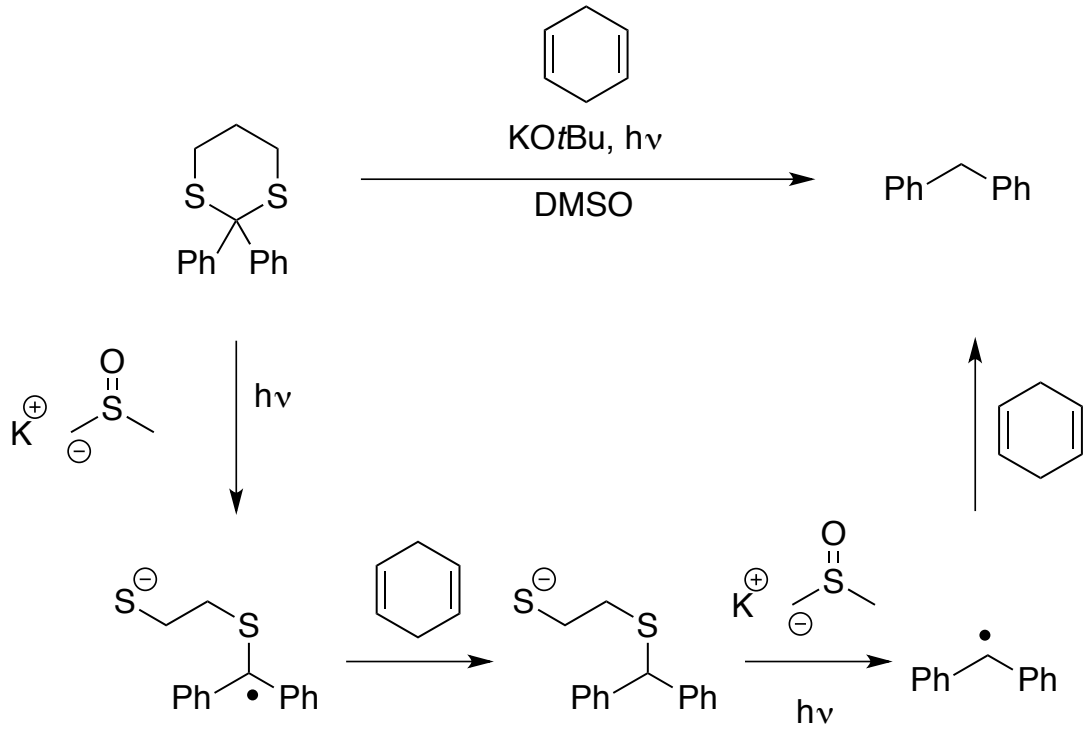
Photo-induced Cleavage of Dithiane



- Authors propose transfer from KO*t*Bu
  - "charge transfer" complex observed at 466 nm in UV/Vis spectrum
- Murphy et. al. can reproduce with KH as a base

J. Am. Chem. Soc. 2016, **138***,* 7401-7410.
Tetraheron Lett. **2013**, *54*, 1515-1518.

Photo-induced Cleavage of Dithiane



J. Am. Chem. Soc. 2016, **138***,* 7401-7410.
Tetraheron Lett. **2013**, *54*, 1515-1518.

Conclusion

- In all examined cases, KO*t*Bu acts as a base
- Electron transfer from KO*t*Bu is possible using CBr_4 as electron acceptor (E_{red} = -0.31 V)