Organic Electron Donors

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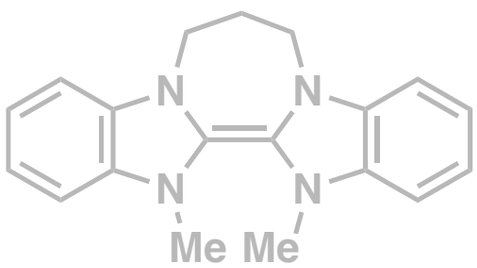
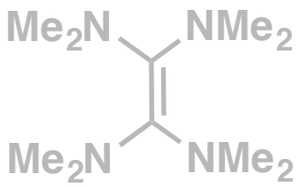
Department of Chemistry and Biochemistry

University of California, Santa Barbara

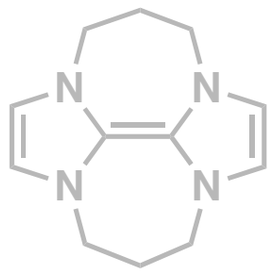
11/15/2018



TAF1

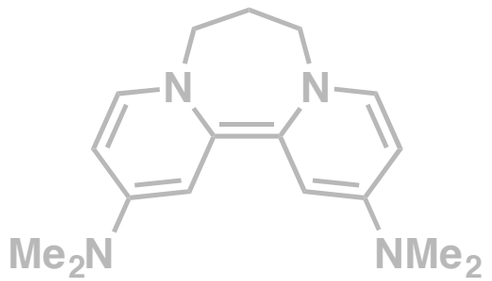


TDAE



TAF2

TTF



BPL

Outlines

Organic Electron Donors

Background

Organic reactions with electron transfers

Common electron donor reagents and reduction potentials

Typical organic electron donors

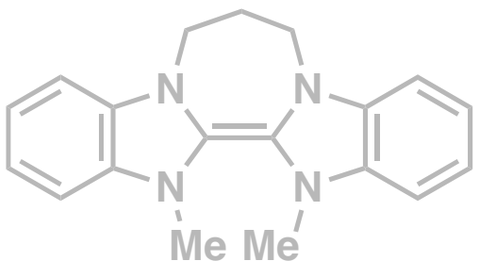
Early development (TTF, TDAE)

‘Super electron donors’ (TAFs, bispyridinylidene)

Application in organic synthesis

Application in mechanism studies

Transition metal free reaction w/ DMEDA



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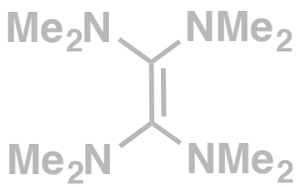

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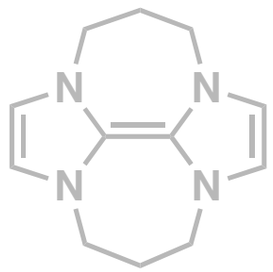

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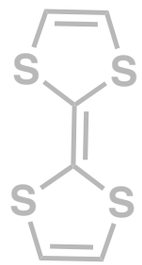
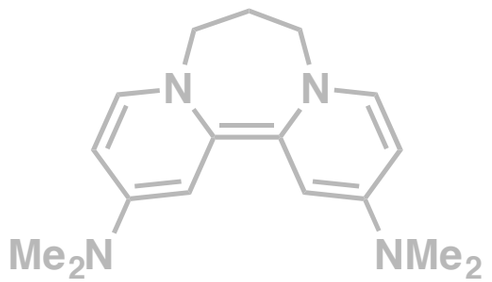


TTF



BPL

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Organic Electron Donors

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- Organic reactions with electron transfers
- Common electron donor reagents and reduction potentials

Typical organic electron donors

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- ‘Super electron donors’ (TAFs, bispyridinylidene)
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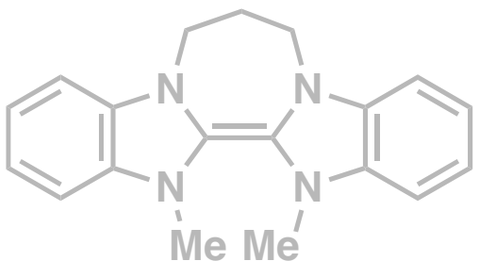

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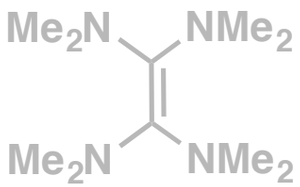
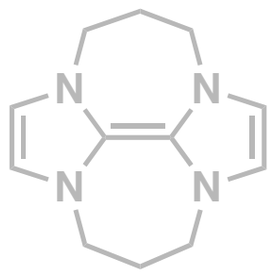


TDAE



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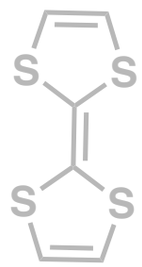
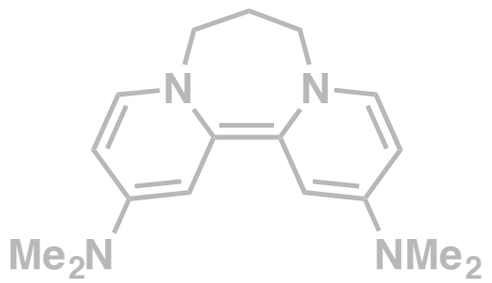


TTF

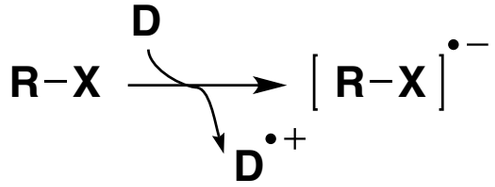


BPL

Background

Organic reactions with electron transfers

Single electron transfer (SET) is an important process in various redox- and radical-type organic reactions.



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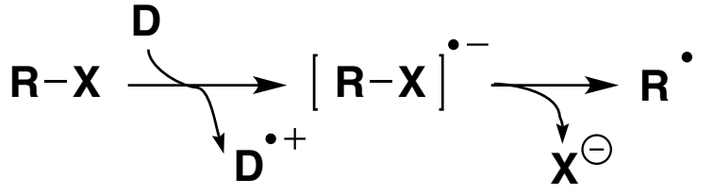

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Organic reactions with electron transfers

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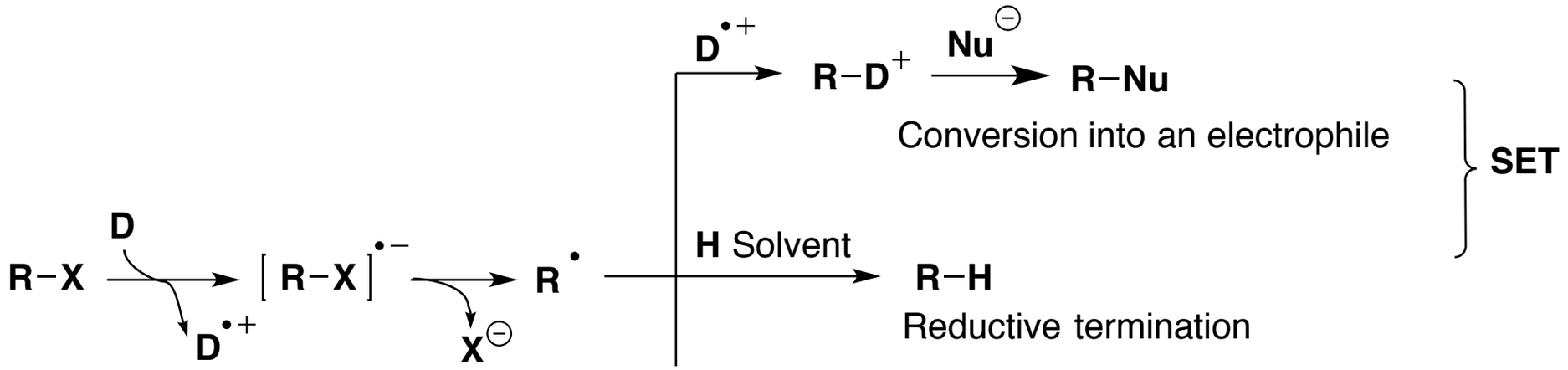

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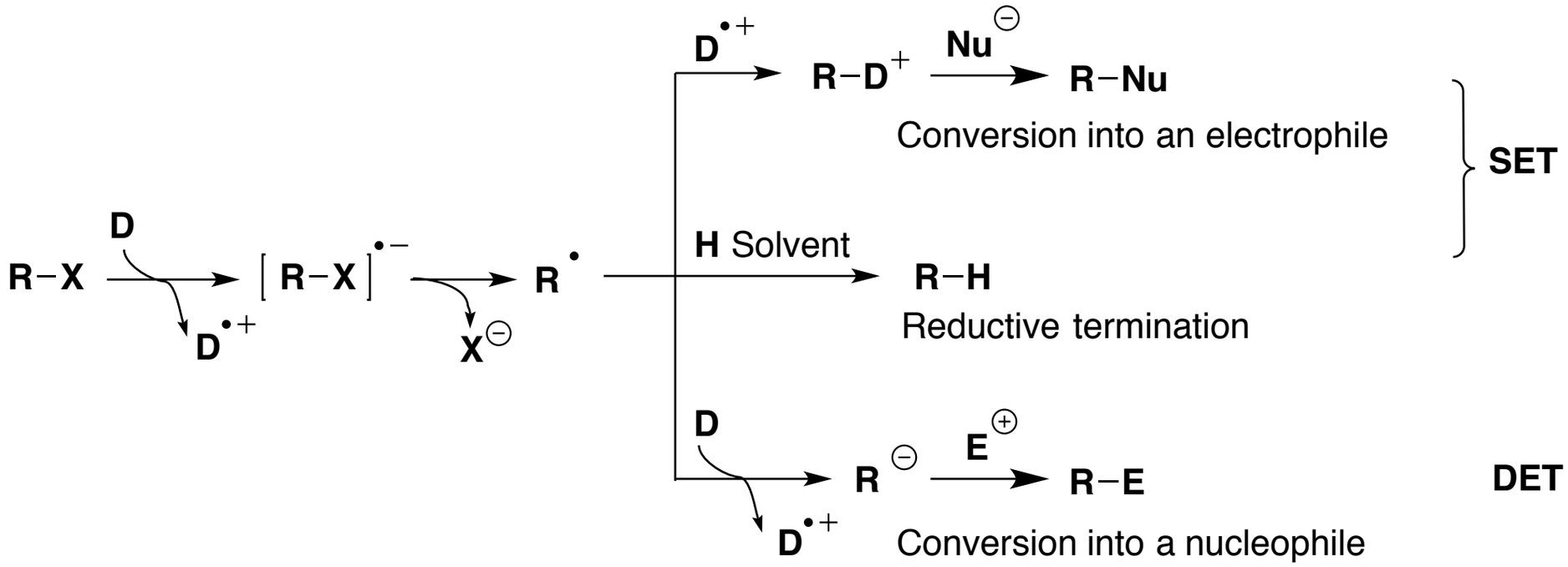
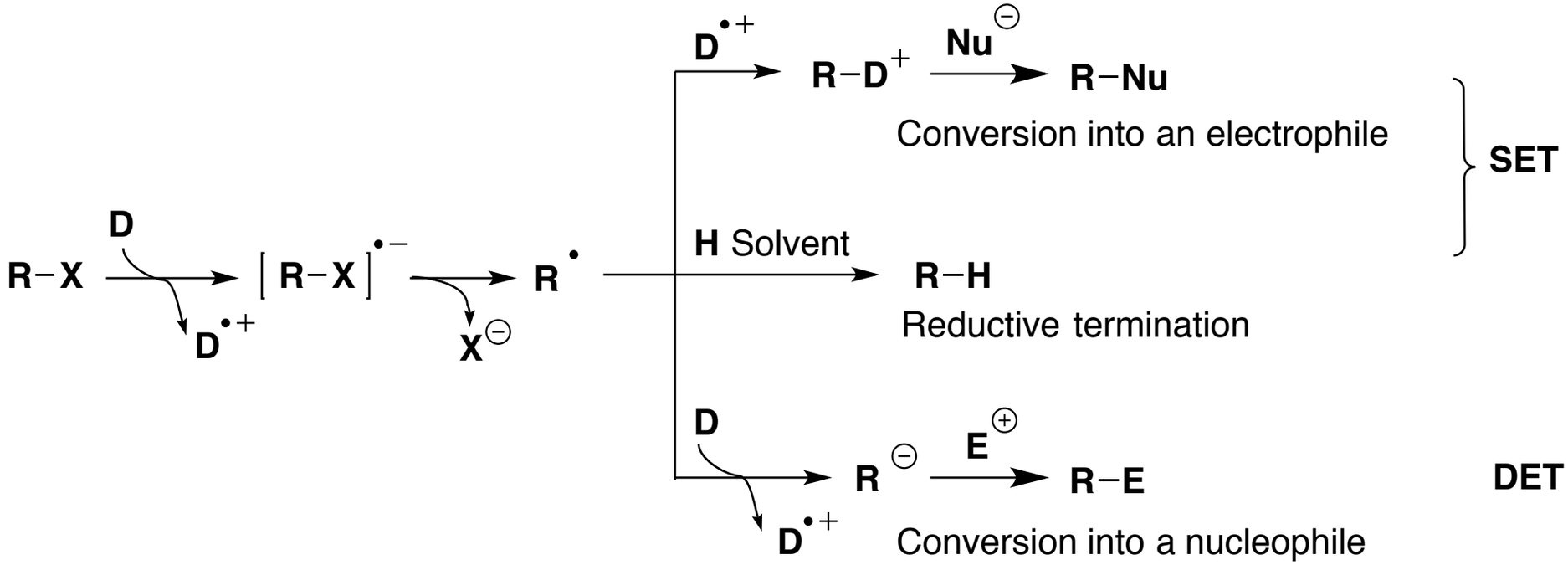
Single electron transfer (SET) is an important process in various redox- and radical-type organic reactions.



Background

Organic reactions with electron transfers



Common electron donors reagents:

Active metals: alkali metals, alkali earth metals

Low valent metallic reagents: SmI_2, $TiCl_3$

Organic metallic reagents: Sodium naphthaline, CpTiIII

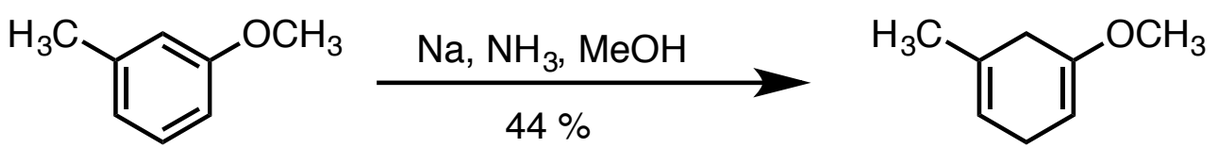
J. Broggi, et al. *Angew. Chem. Int. Ed.* **2014**, ***53***, 384–413

L. Zhang, L. Jiao, *Chem. Sci.* **2018**, ***9***, 2711-2722

Background

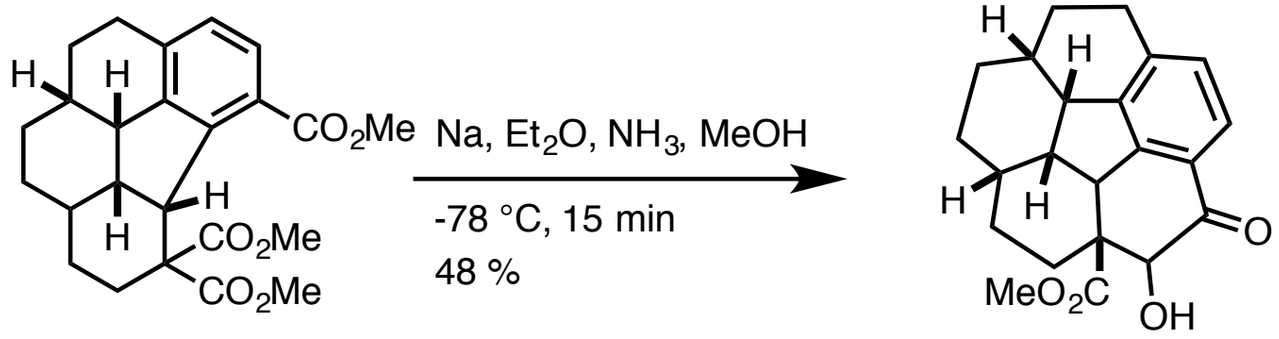
Classic reactions involved electron donors:

Birch reduction



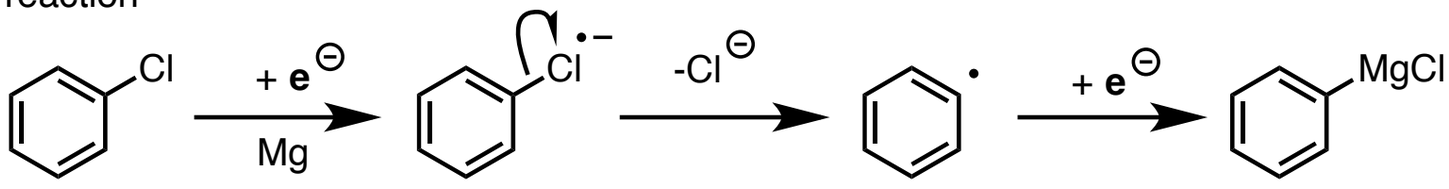
Birch, A. J. J. Chem. Soc. 1944, 430-436

Acyloin condensations



Lawton, R. G. J. Am. Chem. Soc. 1971, 93, 1730

Grigard reaction



J. Broggi, et al. *Angew. Chem. Int. Ed.* **2014**, ***53***, 384–413
L. Zhang, L. Jiao, *Chem. Sci.* **2018**, ***9***, 2711-2722

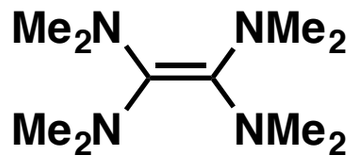
Background

Organic electron donors

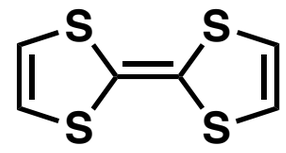
OEDs: neutral, ground state organic molecules that reduce substrates by single electron transfer.

Advantages: tunable reducing ability, mild reaction conditions

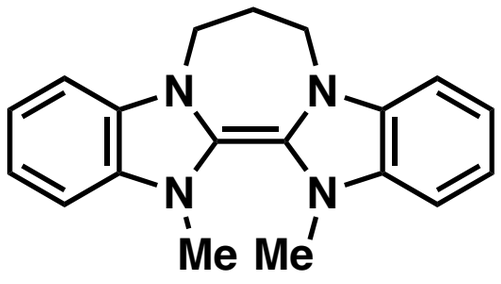
Common organic electron donors



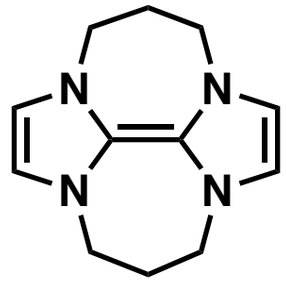
Tetrakis(demethylamine)ethlyene **(TDAE)**



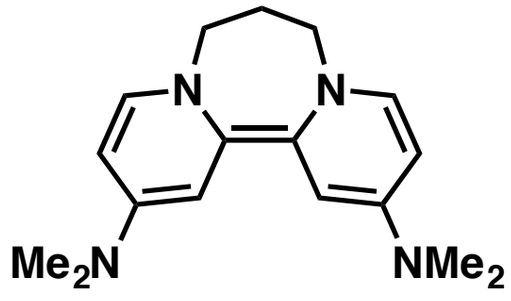
Tetrathiafulvalene **(TTF)**



Dibenzo-Tetraazafulvalene
Dibenzo-TAF
TAF1



Diimidazo-Tetraazafulvalene
Diimidazo-TAF
TAF2

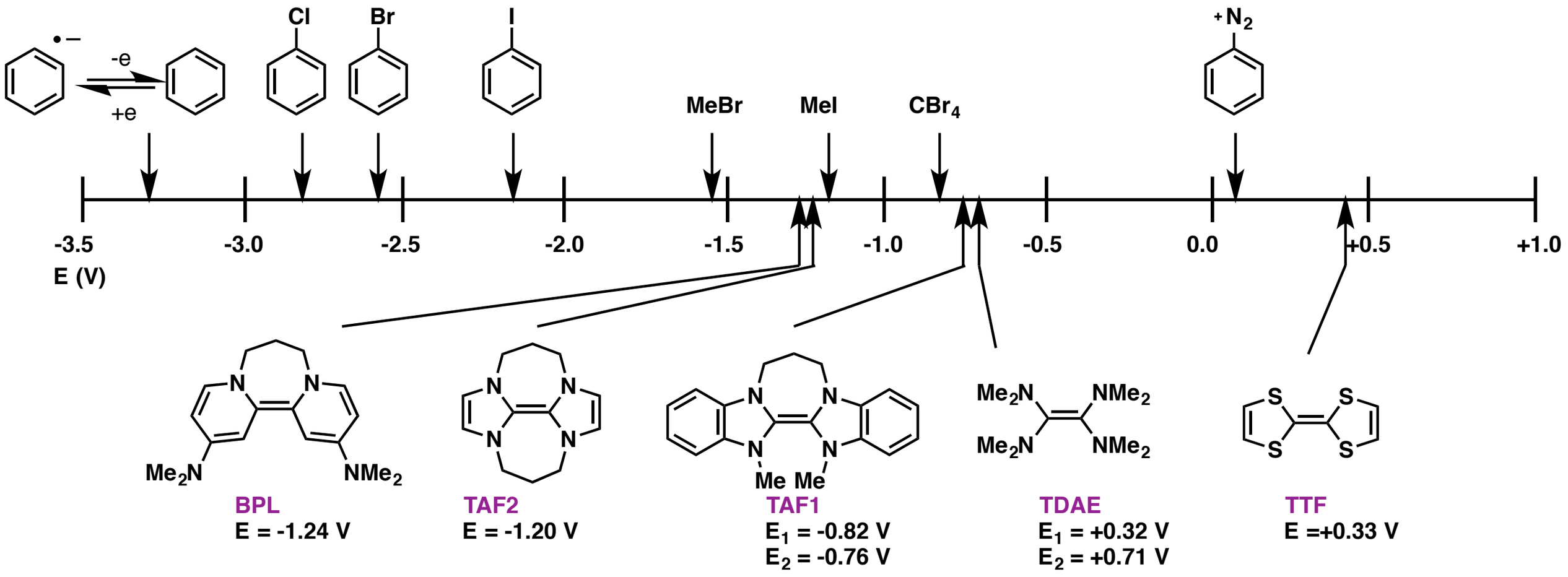


Bispyridinylidene
BPL

J. Broggi, et al. *Angew. Chem. Int. Ed.* **2014**, ***53***, 384–413

Background

Reduction potential



BPL
E = -1.24 V

TAF2
E = -1.20 V

TAF1
E_1 = -0.82 V
E_2 = -0.76 V

TDAE
E_1 = +0.32 V
E_2 = +0.71 V

TTF
E =+0.33 V

Reduction potential reflects ability to donate electrons

Which functional group can accept the electron

Outlines

- **Organic Electron Donors**
- **Background**
  - Organic reactions with electron transfers
  - Common electron donor reagents and reduction potentials
- **Typical organic electron donors**
  - Early development (TTF, TDAE)
  - ‘Super electron donors’ (TAFs, bispyridinylidene)
  - Application in organic synthesis
- **Application in mechanism studies**
  - Transition metal free reaction w/ DMEDA

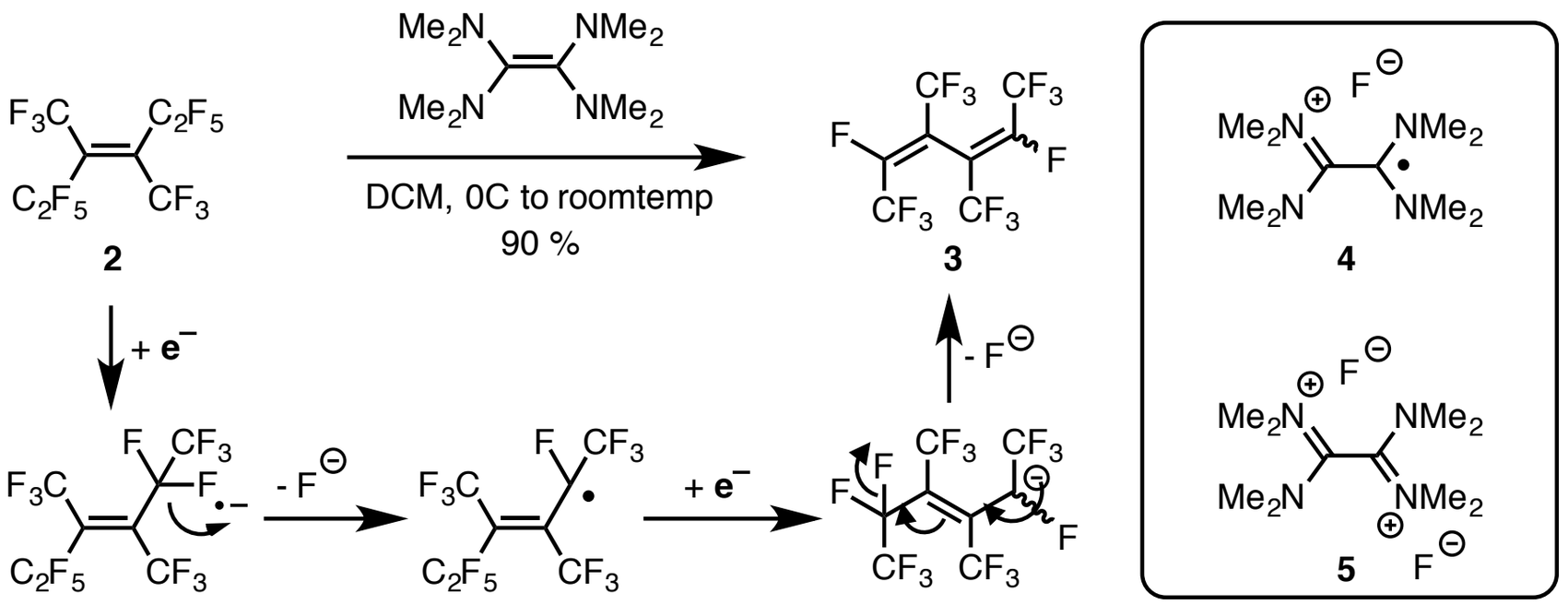
Discovery of Organic electron donors

TDAE as an electron donor

In 1950, discovery of tetrakis(dimethylamino)ethene (**TDAE**) in industry

Its ability to reduce electron poor perfluoro substrates

Industrial application of TDAE reduction



Lafferty, R. H., Jr. *J. Am. Chem. Soc.* **1950**, ***72***, 3646

TDAE oxidized to its radical anion **4** and di-anion **5**

Electron rich ethene & heteroatoms as OEDs

Discovery of Organic electron donors

TTF as organic electronic material

In 1970, inspired by powerful electron donating properties of **TDAE**, Fred Wudl applied Tetrathiafulvalene (**TTF**) to organic electronics.

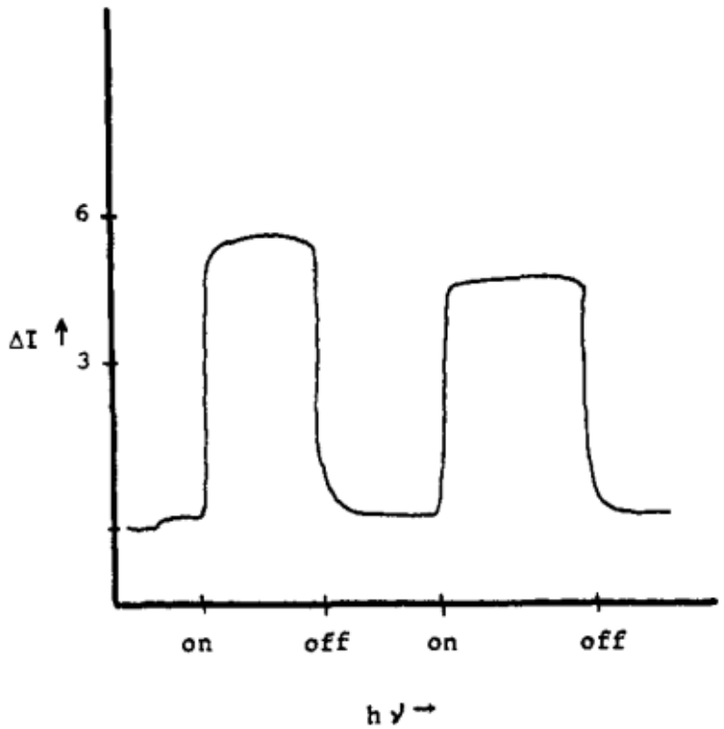
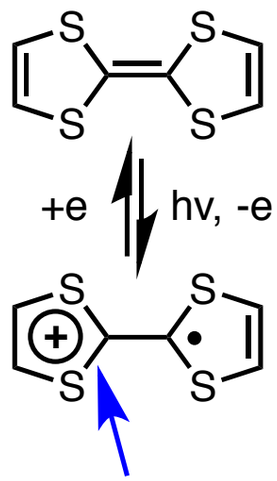


Figure 1. ΔI = photocurrent (10^{-12} A).



$\rho = 10^{12}\ \Omega$ cm

+e ⇌ hv, -e

Cl^- $\rho = 3.7 \pm 1\ \Omega$ cm

(4n + 2) π electrons

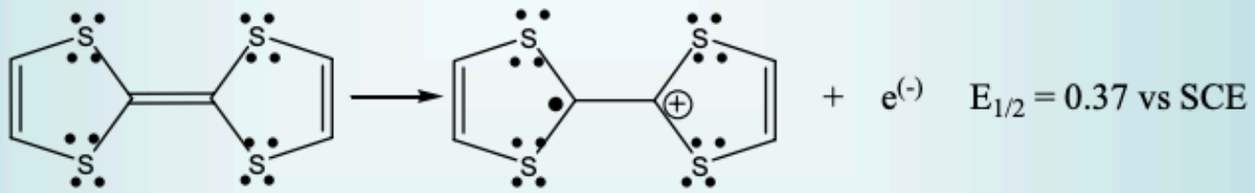
"**TTF** as an excellent organic solid semiconductor." - F. Wuld

Aromatic stabilization energy

F. Wudl, et al. *J. Am. Chem. Soc.* **1972**, ***94***, 670–672.
F. Wudl, et al. *Chem. Commun.* **1970**, 1453

Discovery of Organic electron donors

The Marriage of TTF & TCNQ



Alternating Stack

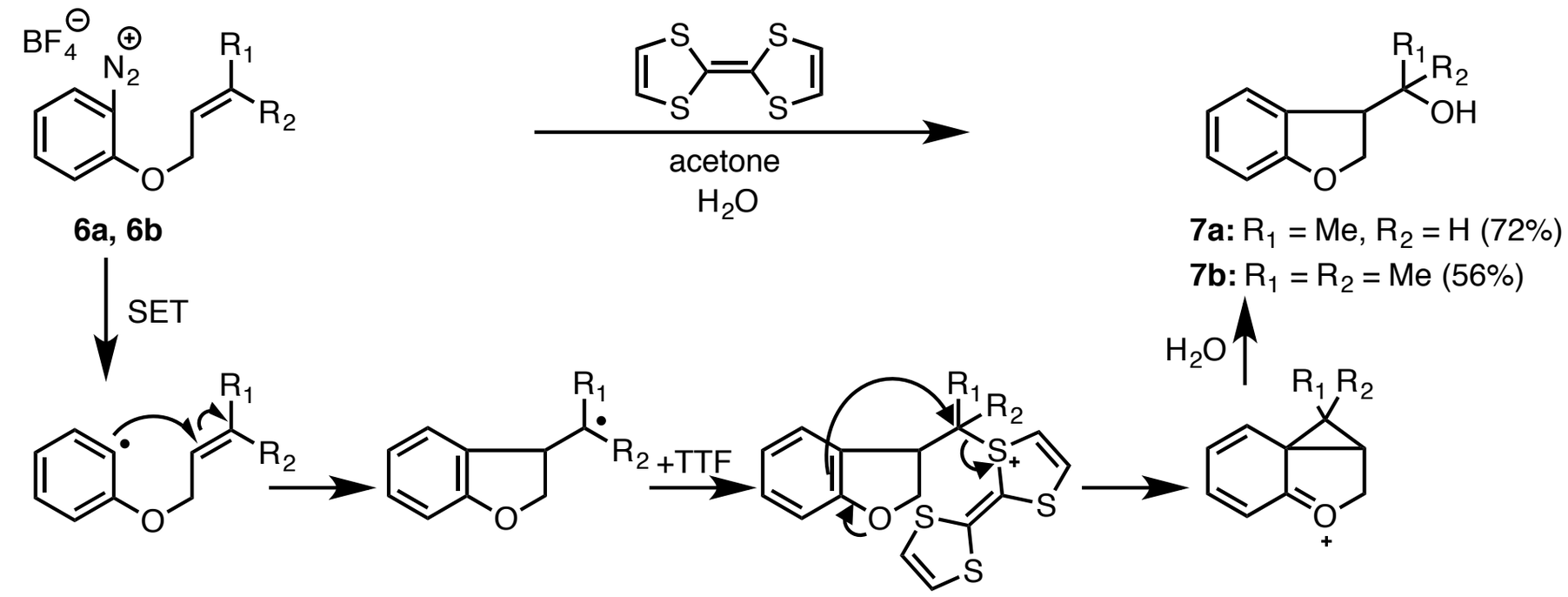
Segregated Stack

Discovery of Organic electron donors

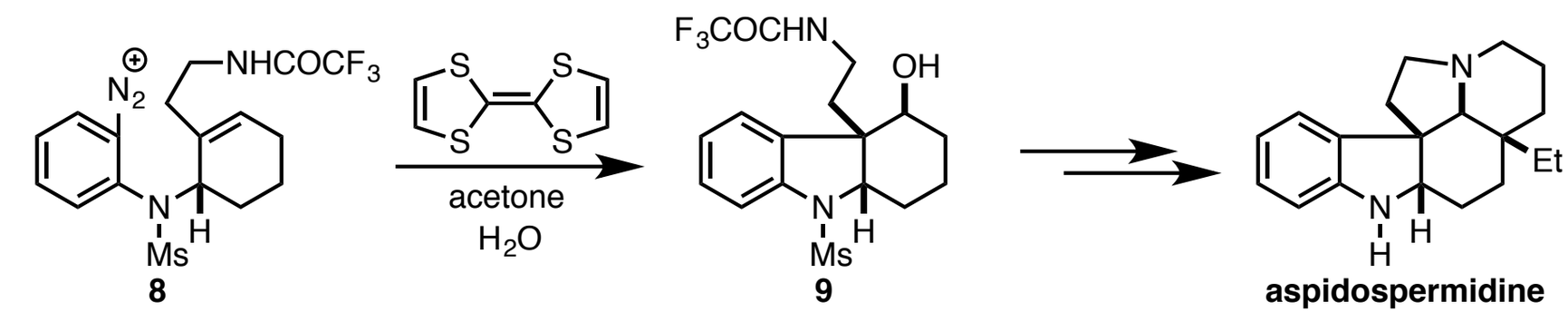
TTF as organic donor

In 1990s, J. A. Murphy used alkene to trap the benzyl radical generated when treating arenediazonium with TTF.

Radical-Polar crossover reaction using **TTF**



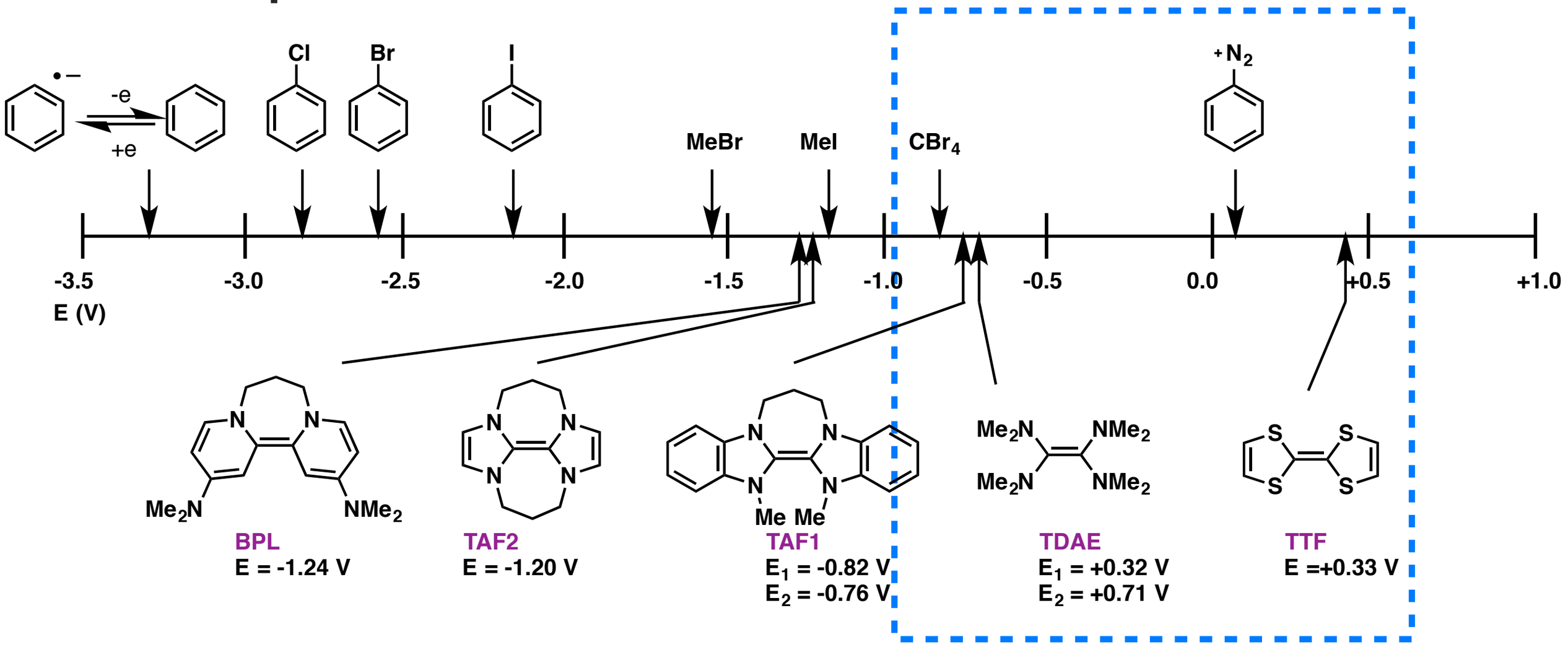
Application in total synthesis



Chem. Commun. **1993**, 295−297.

Background

Reduction potential



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TAF2
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TAF1
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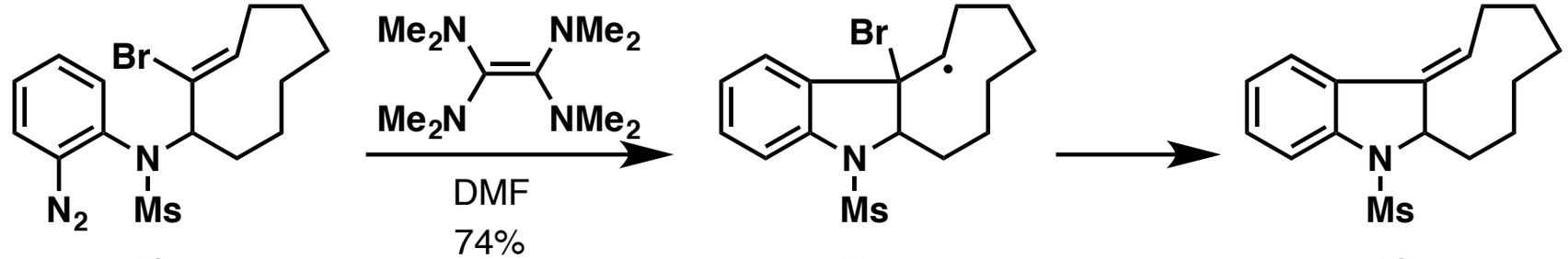
TTF
E =+0.33 V

Organic electron donors

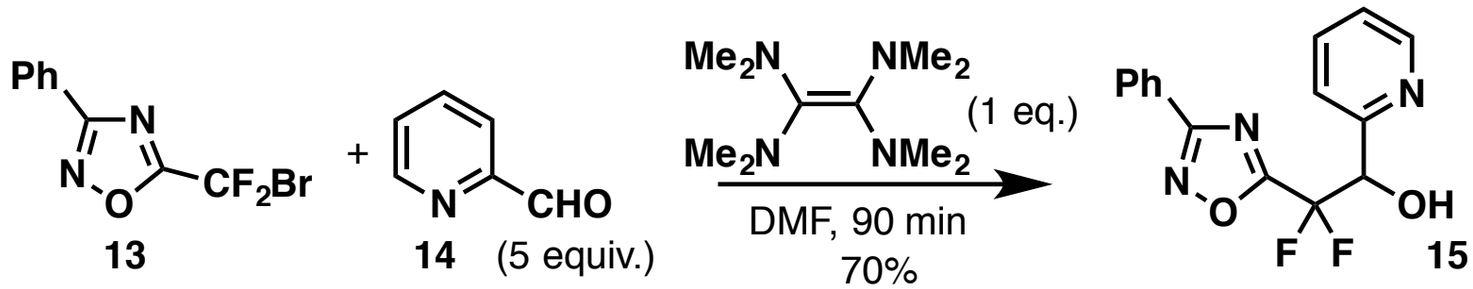
TDAE: a moderate electron donor

Radical cyclization from benzodiazonium with TDAE

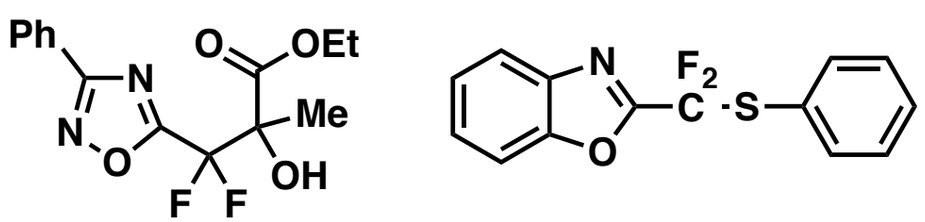


J. A. Murphy, *Beilstein J. Org. Chem.* **2009**, 19

Radical difluoroalkyl addition to electrophiles



M. Medebielle *J. Org. Chem.* **1998**, 5385

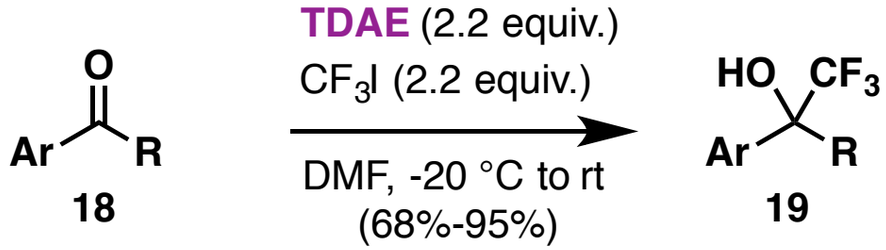


M. Medebielle, *tetrahedron lett.* **2001**, 3463

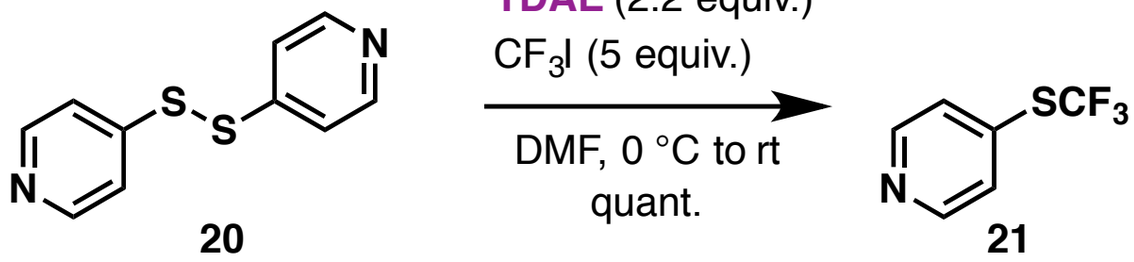
Organic electron donors

TDAE: a moderate electron donor

Radical trifluoromethyl addition to electrophiles



W. R. Dolbier, *Org. Lett,* **2001**, 4271

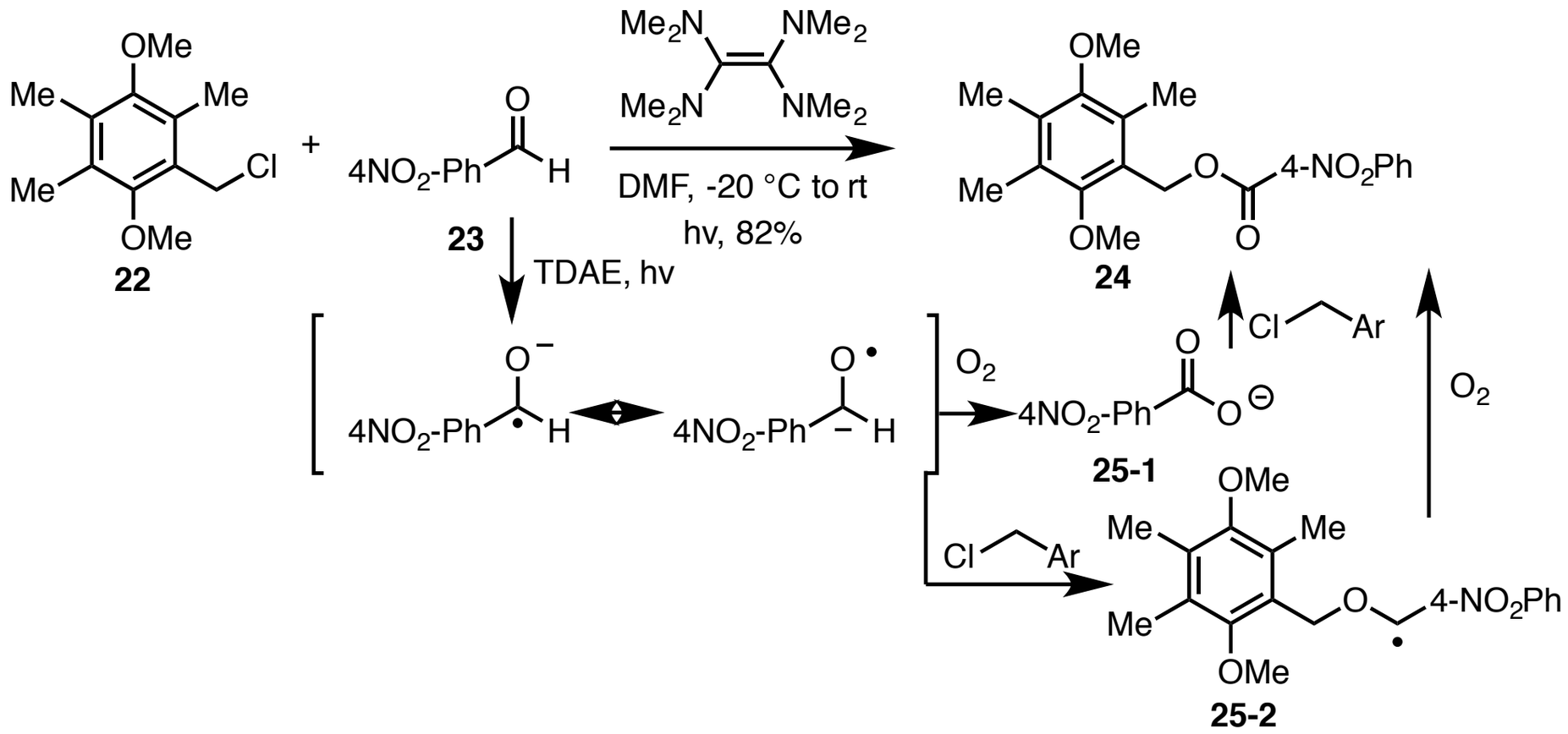


W. R. Dolbier, *Org. Lett*, **2004**, 301

Organic electron donors

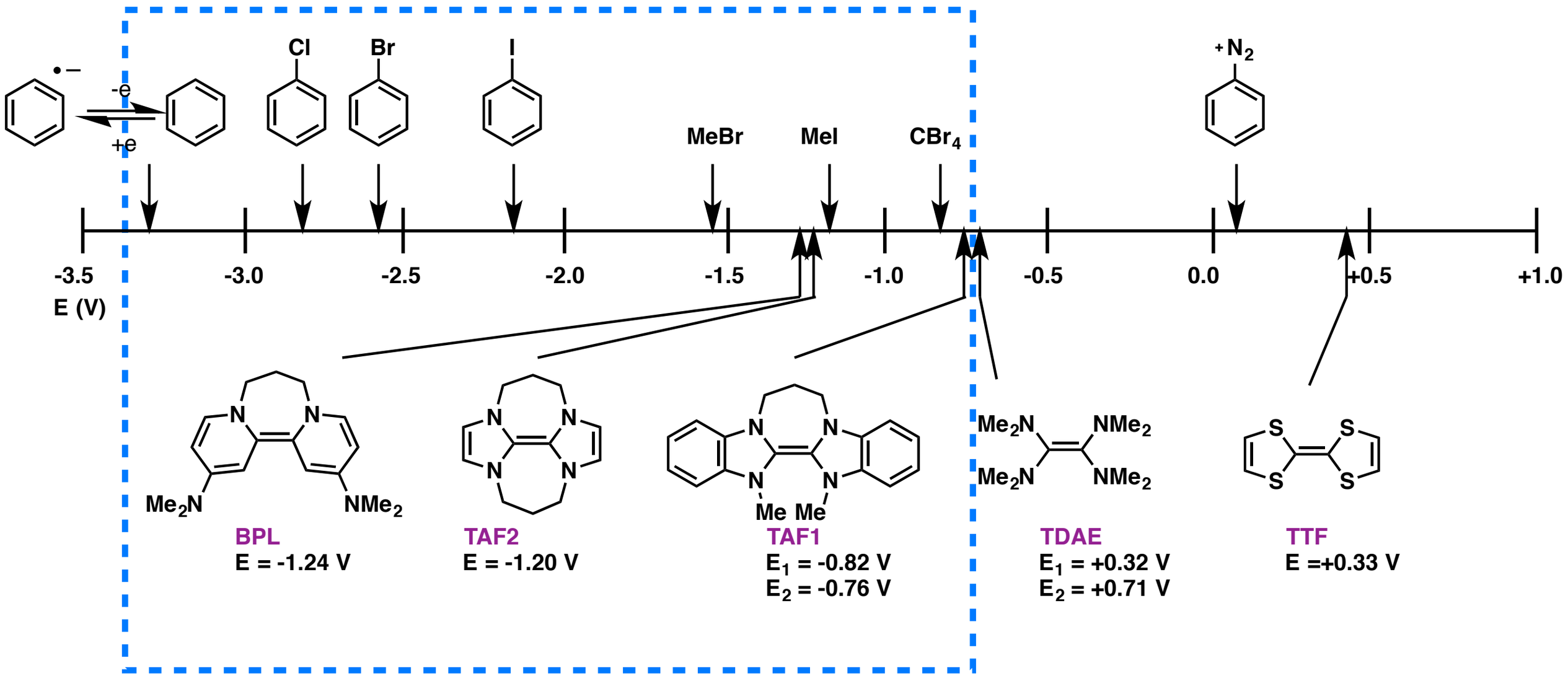
TDAE: a moderate electron donor

SET to aldehyde by light



Background

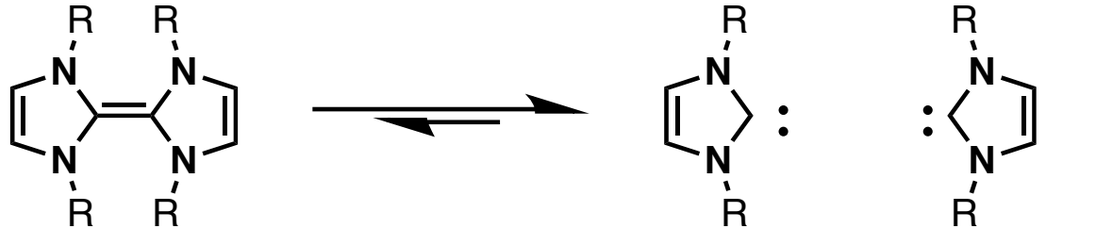
Reduction potential



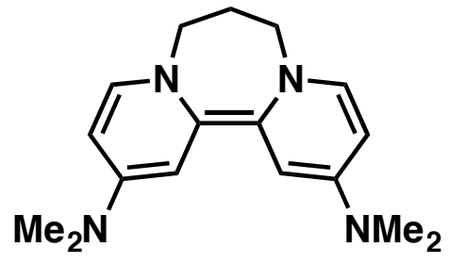
Organic electron donors

Super electron donors : TAFs and bispyridinylidene

Tetraazafulvalene or NHC?

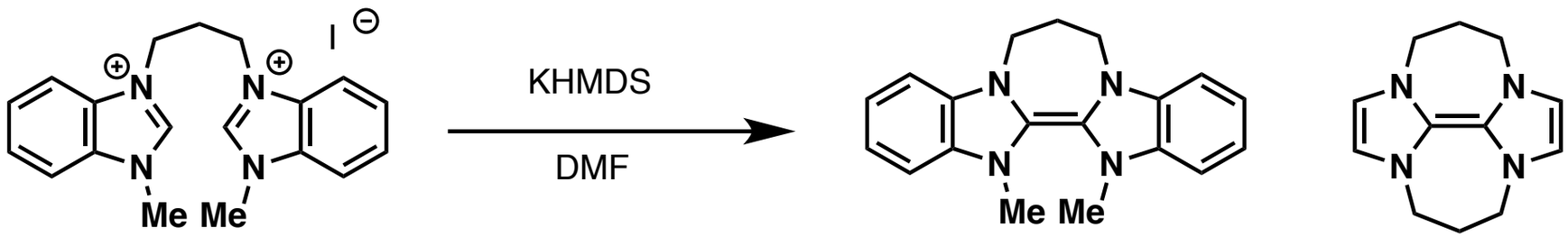


tetraazafulvalene — Strongly favor **NHC** carbene



BPL
E = -1.24 V

Earliest TAFs by J.A. Murphy contained methylene bridges



26

TAF1
E_1 = -0.82 V
E_2 = -0.76 V

TAF2
E = -1.20 V

J. A. Murphy, *Angew. Chem. Int. Ed.* **2005**, 1356
J. A. Murphy, *Angew. Chem. Int. Ed.* **2007**, 5178
J. A. Murphy, *Org. Lett.* **200**8, 1227

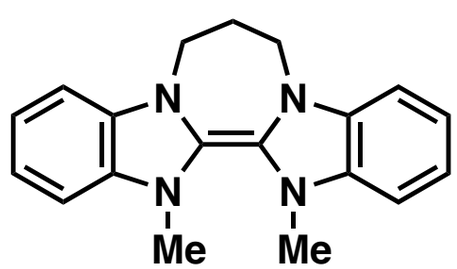
Features: Neutral organic molecules

Low reduction potential: SET to benzyl iodi

(**TAF2** and **BPL**) DET and anionic cyclization

Organic electron donors

Super electron donors : SET v.s. DET



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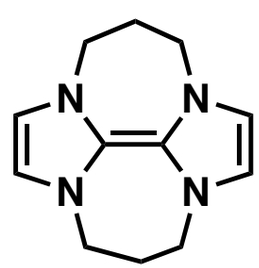
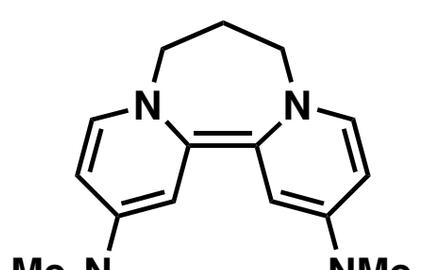
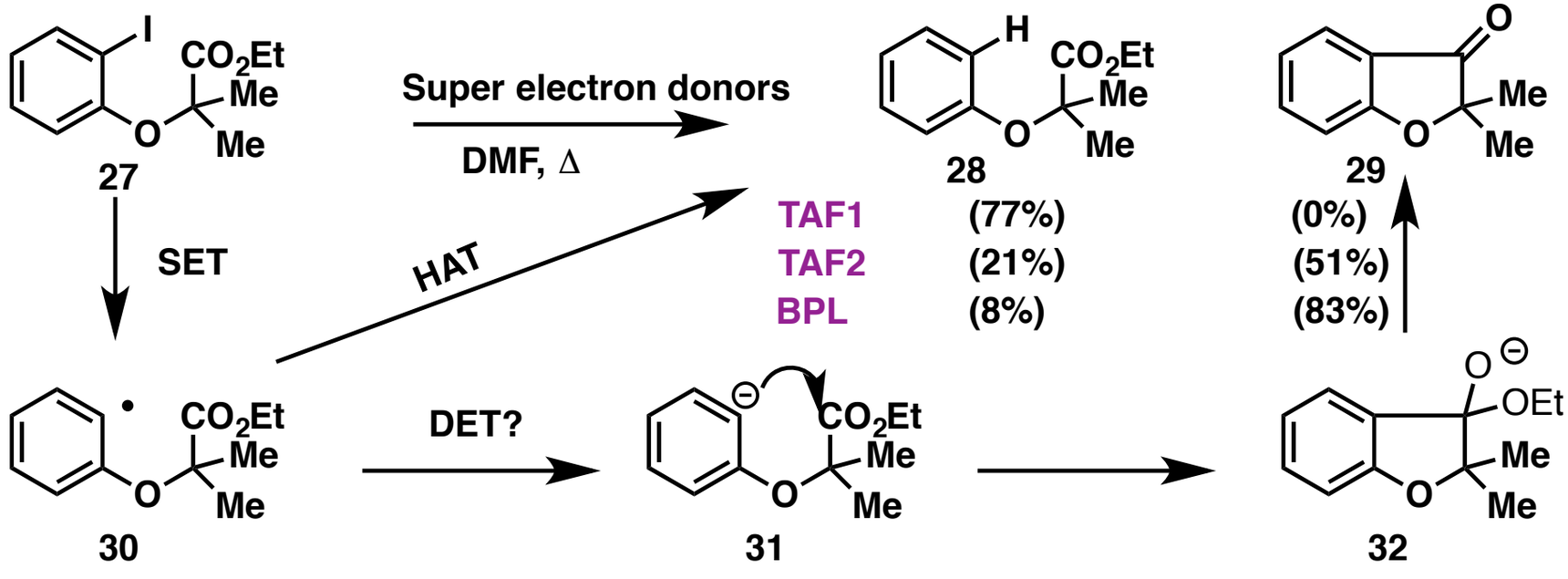


TAF2



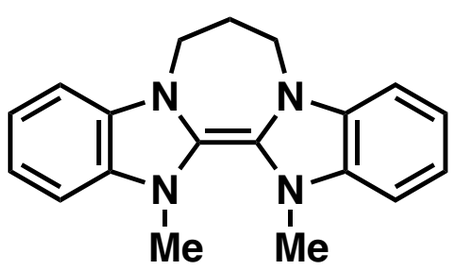
BPL



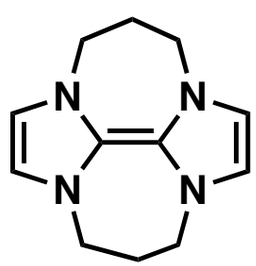
J. A. Murphy, *Angew. Chem. Int. Ed.* **2007,** 5178

Organic electron donors

Super electron donors : SET v.s. DET



TAF1



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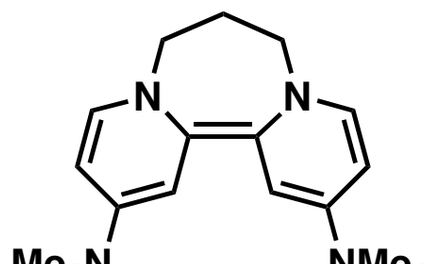

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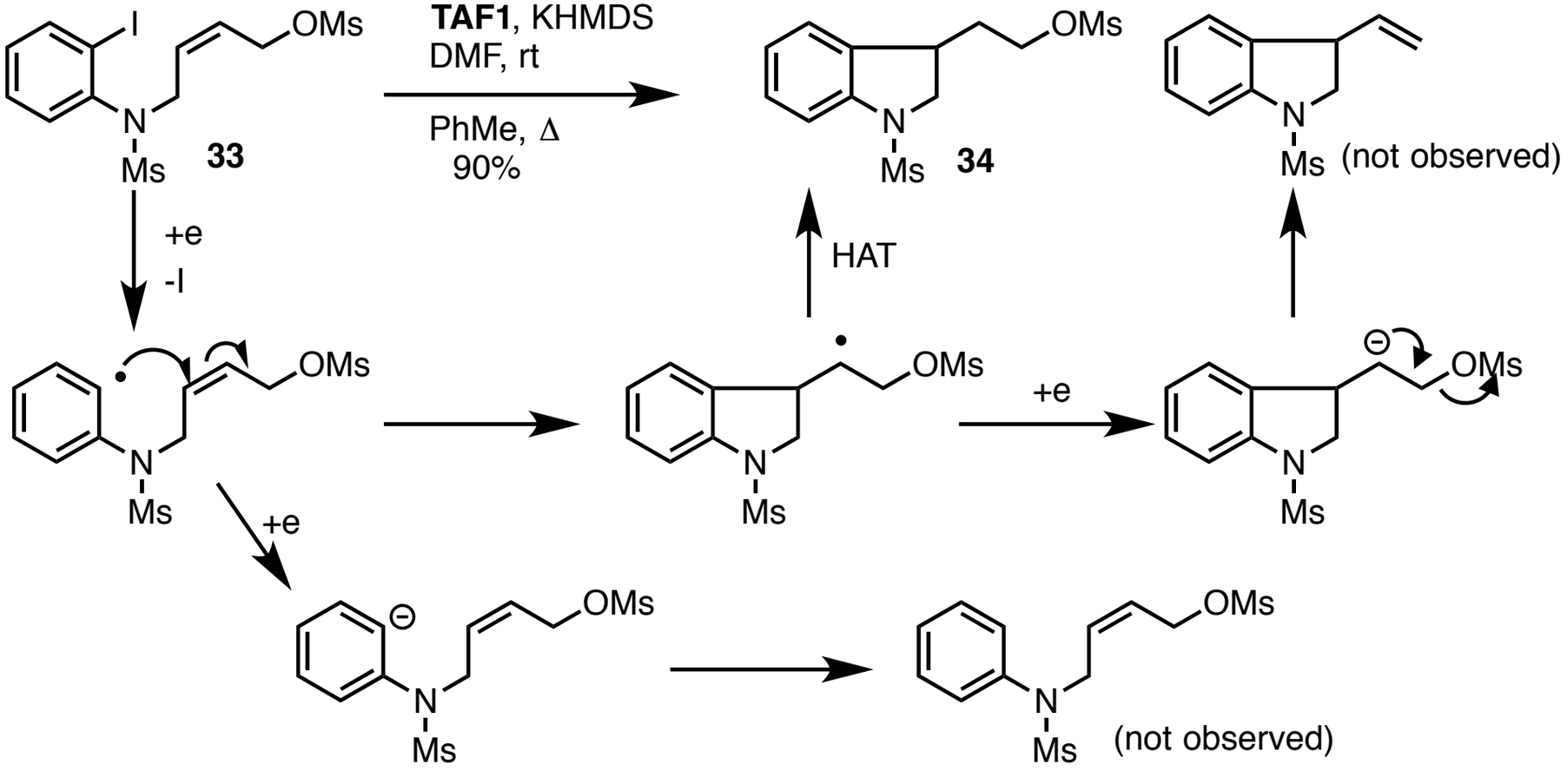
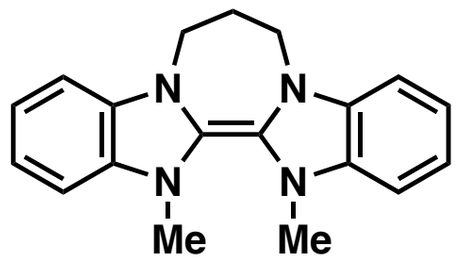


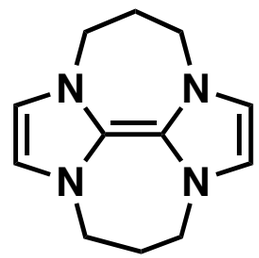
J. A. Murphy, *Angew. Chem. Int. Ed.* **2005**, 1356

Organic electron donors

Super electron donors : Reactions of Diimidazol-TAF



TAF1



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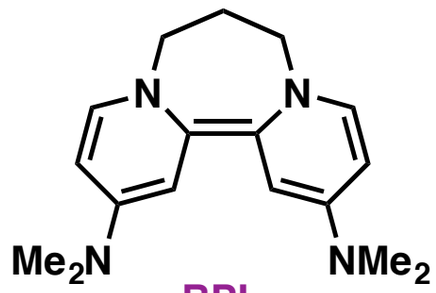

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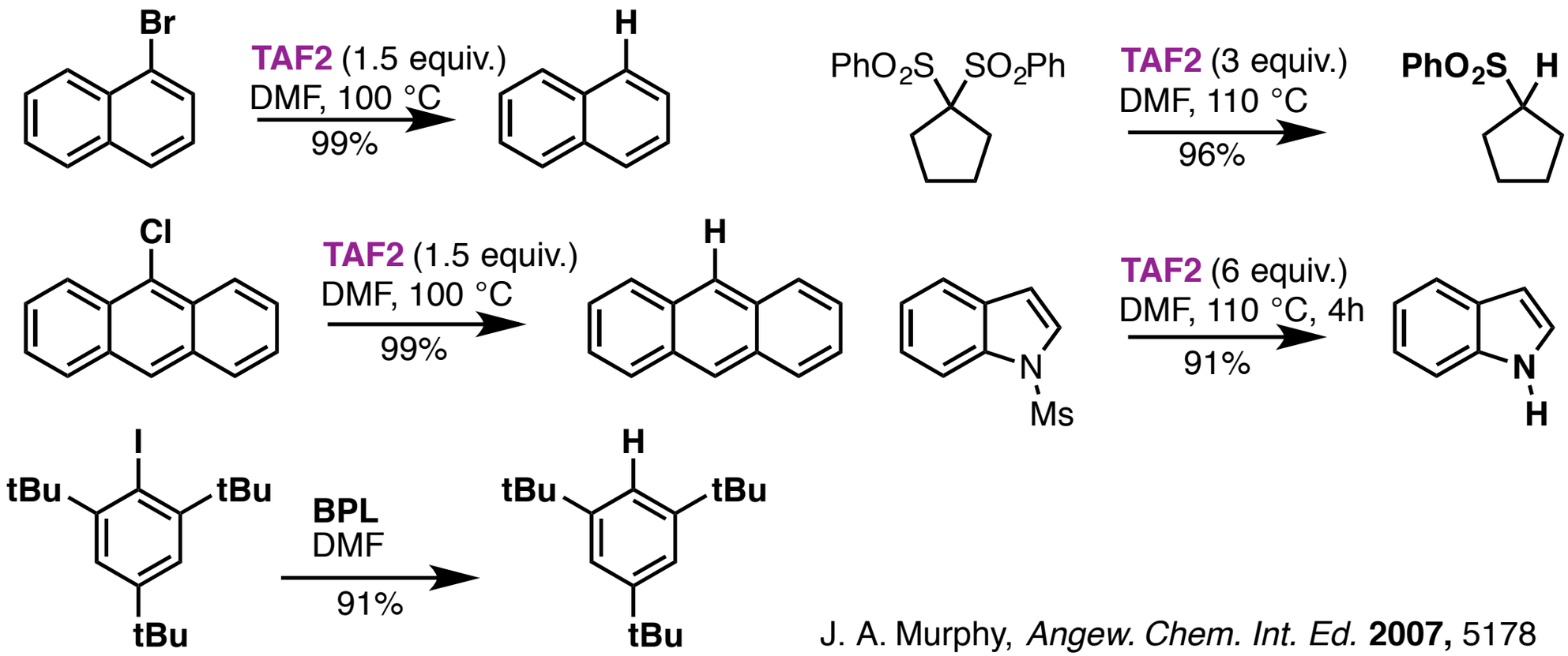


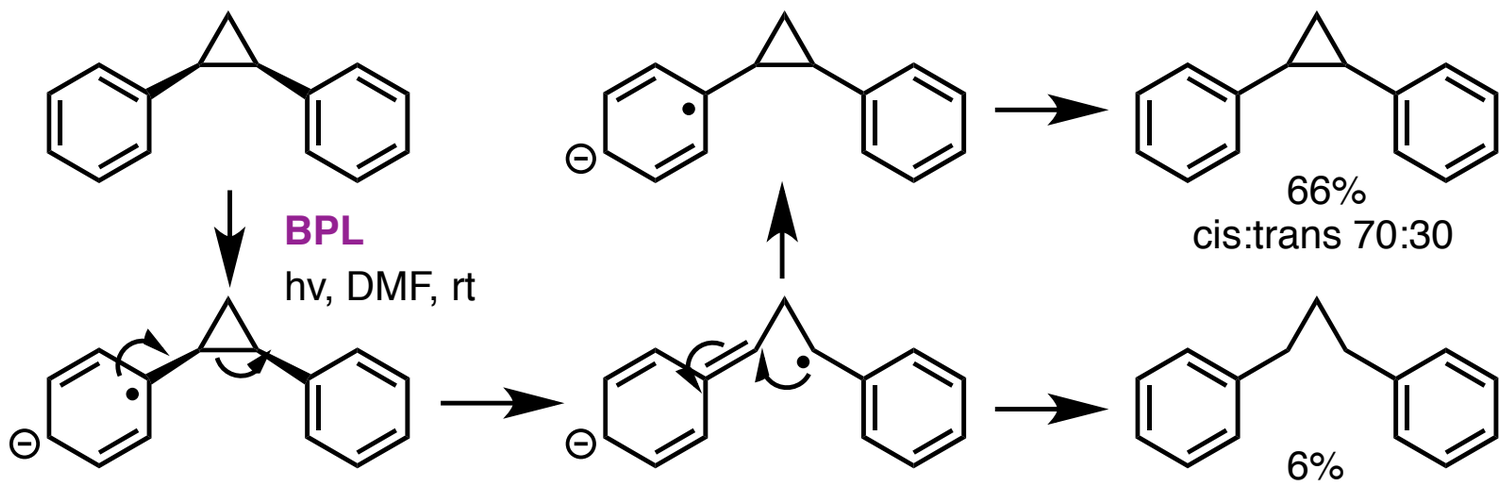
J. A. Murphy, *Angew. Chem. Int. Ed.* **2007,** 5178

J. A. Murphy, *J. Am. Chem. Soc.* **2007**, ***129***, 13368

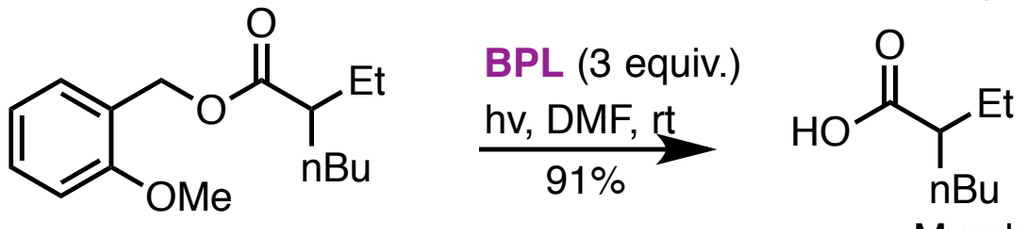
Organic electron donors

Super electron donors : bispyridinylidene

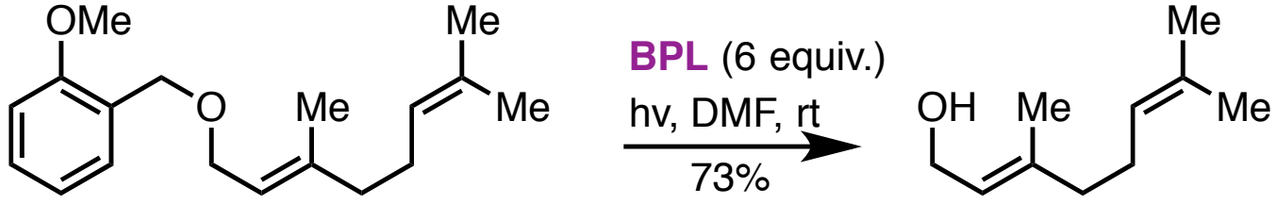
SET to benzenes



Murphy, *Angew. Chem. Int. Ed.* **2012**, 3673

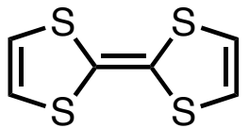
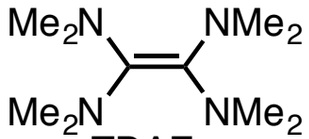
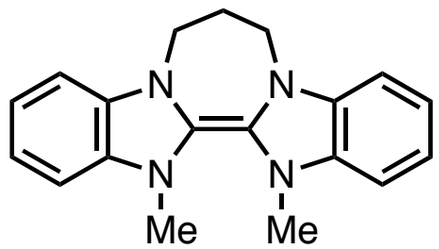
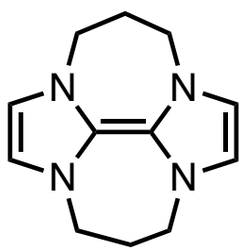
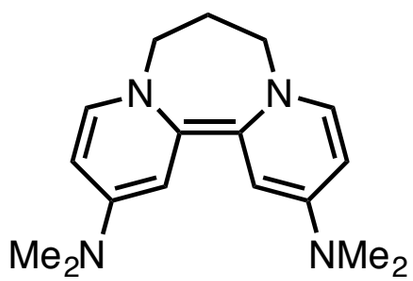


Murphy, *Angew. Chem. Int. Ed.* **2013**, 2239



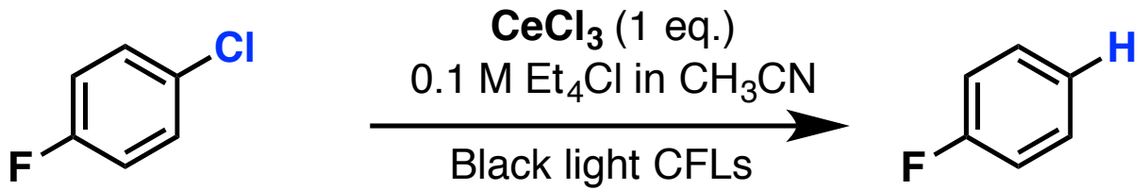
Murphy, *Angew. Chem. Int. Ed.* **2014**, 474

Synthetic applications of organic electron donors

Electron Donor	ET	Redox potential (vs SCE)	Reduced bond	Promoted reaction
 TTF	1 **e**$^-$	+0.32 V, +0.71 V (CH_3CN)	Ar-N_2^+ BF_4^-	radical cyclization radical translocation
 TDAE	1 **e**$^-$	-0.78 V, -0.61 V (CH_3CN) -0.62 V (DMF)	Ar-N_2^+ BF_4^- $ArCCl_3$ CF_3I/CF_3Br C(O)CHRBr	radical cyclization radical addition (CHO, RSSR) trifluoromethylation
	1 **e**$^-$	-0.76 V, -0.82 V (DMF)	Ar-I	radical cyclization
	2 **e**$^-$	-1.20 V (DMF)	Ar-I ArBr ArCl CSO_2Ph NTs	anionic cyclization reduction of haloarene reductive cleavage of sulfone and sulfonamide
	2 **e**$^-$	-1.24 V (DMF)	OTf NTf C(O)NOMe	anionic cyclization reduction of haloarene reductive cleavage of sulfone and sulfonamide triflate ester, Weinreb amide

More than organic electron donors

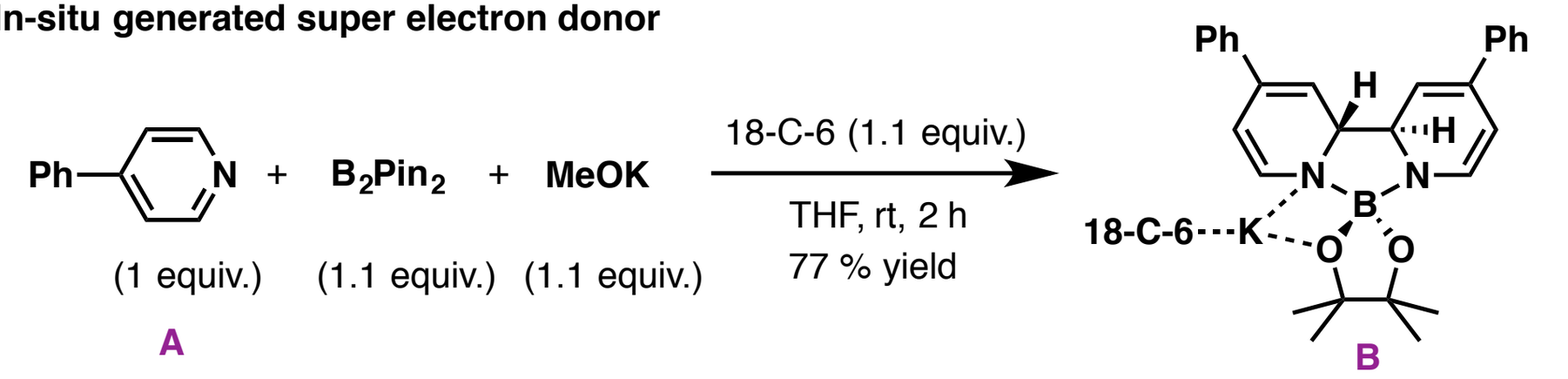
Photosynsitizer for Ar-Cl

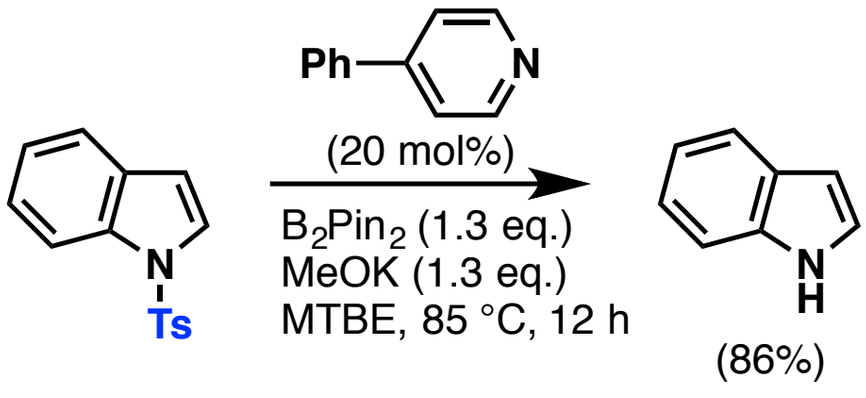


via $[CeCl_6]^{3-}$
electron donor: E = -3.45 V (Cp_2Fe)

M. Anna and E. J. Schelter, *J. Am. Chem. Soc.* **2016**, 138, 16266

In-situ generated super electron donor

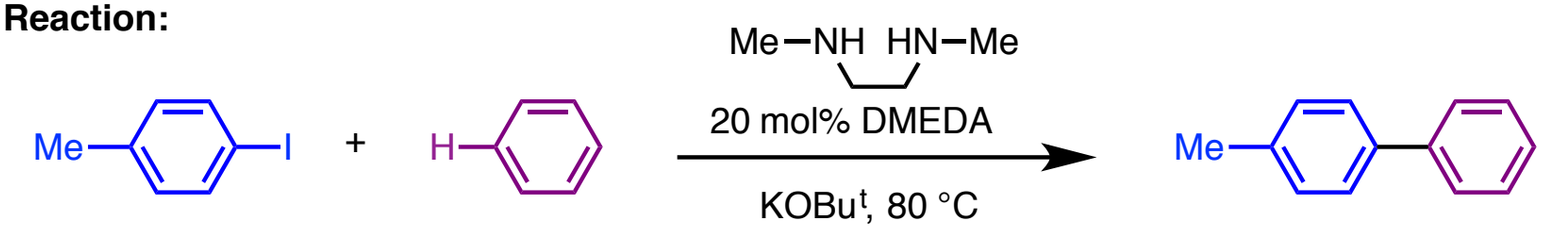




L. Zhang and L. Jiao, *Chem. Sci.* **2018**, 9, 2711

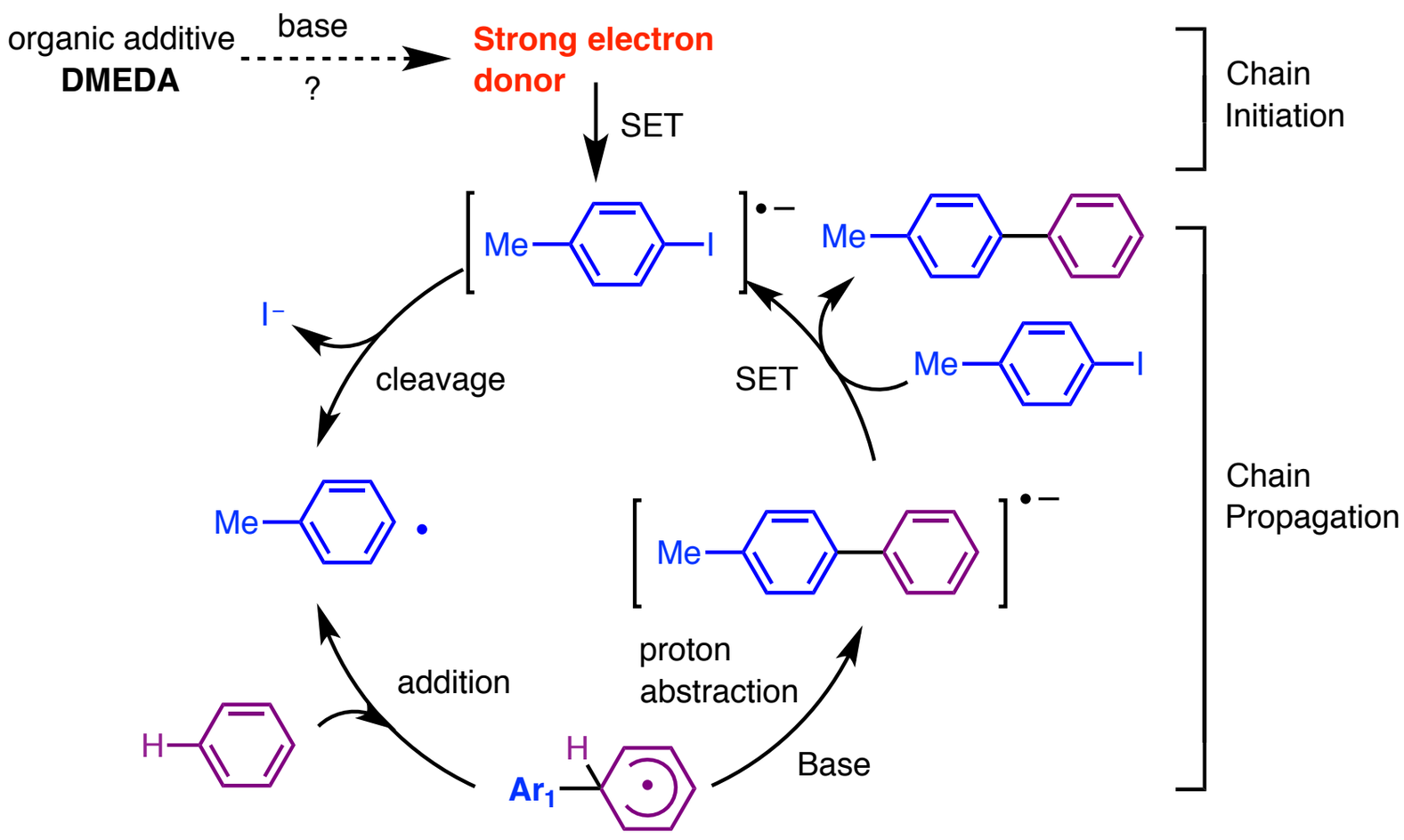
Transient electron donor

Reaction:



Lei, A. W. *J. Am. Chem. Soc.* **2012, 132**, 16737-16740

Mechanism:

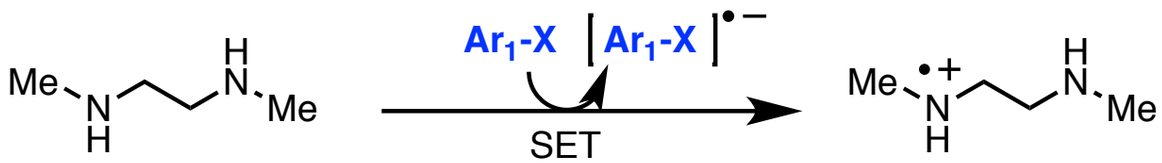


Tuttle, T., Murphy, J. A., *J. Am. Chem. Soc.* **2014**, 136, 17818

Transient electron donor

What is the Electron donor that traggers the reaction?

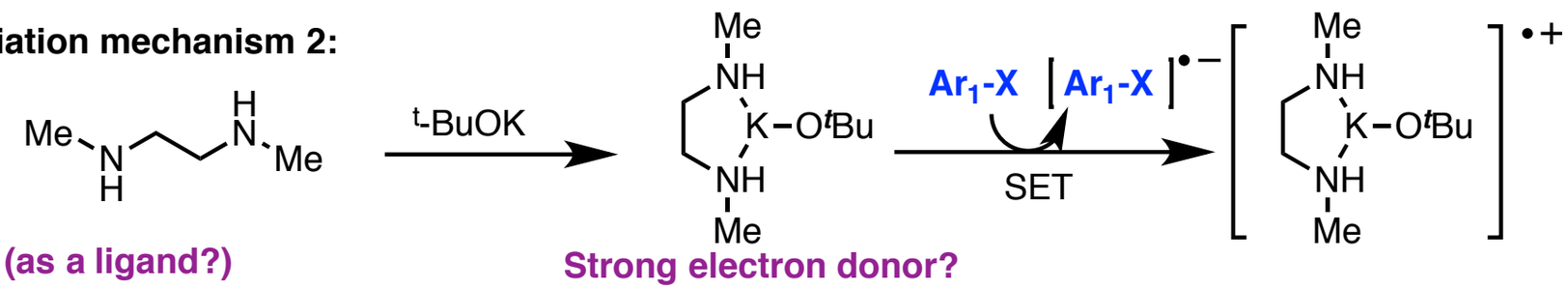
a. Initiation mechanism 1:



(as an electron donor?)

Strong electron donor?

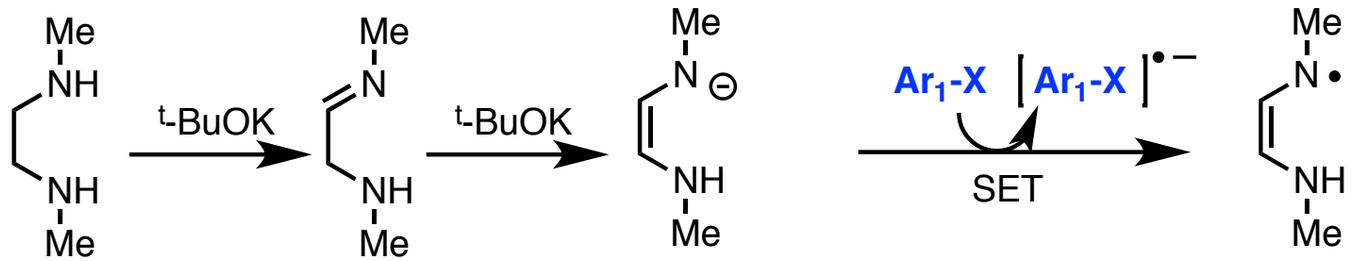
b. Initiation mechanism 2:



(as a ligand?)

Strong electron donor?

c. Initiation mechanism 3:



(as a precursor to electron donor)

Strong electron donor?

Tuttle, T., Murphy, J. A., *J. Am. Chem. Soc.* **2014**, ***136***, 17818
Jiao, L., *J. Am. Chem. Soc.* **2016**, ***138***, 7151-7160

Thank you!

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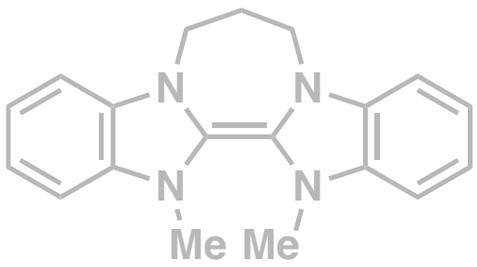
Zakarian Research Group

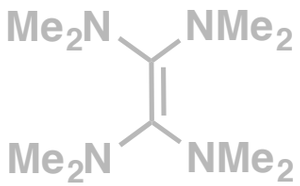
Department of Chemistry and Biochemistry

University of California, Santa Barbara

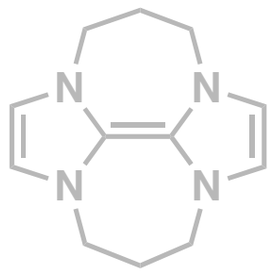
11/15/2018



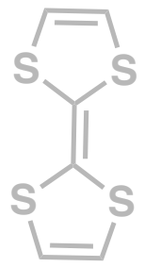
TAF1



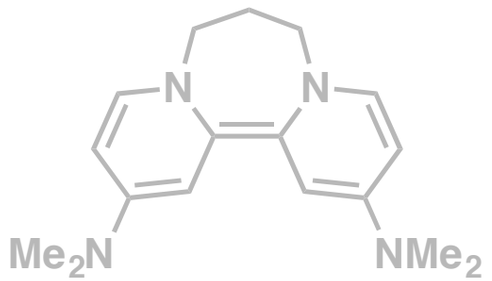
TDAE



TAF2

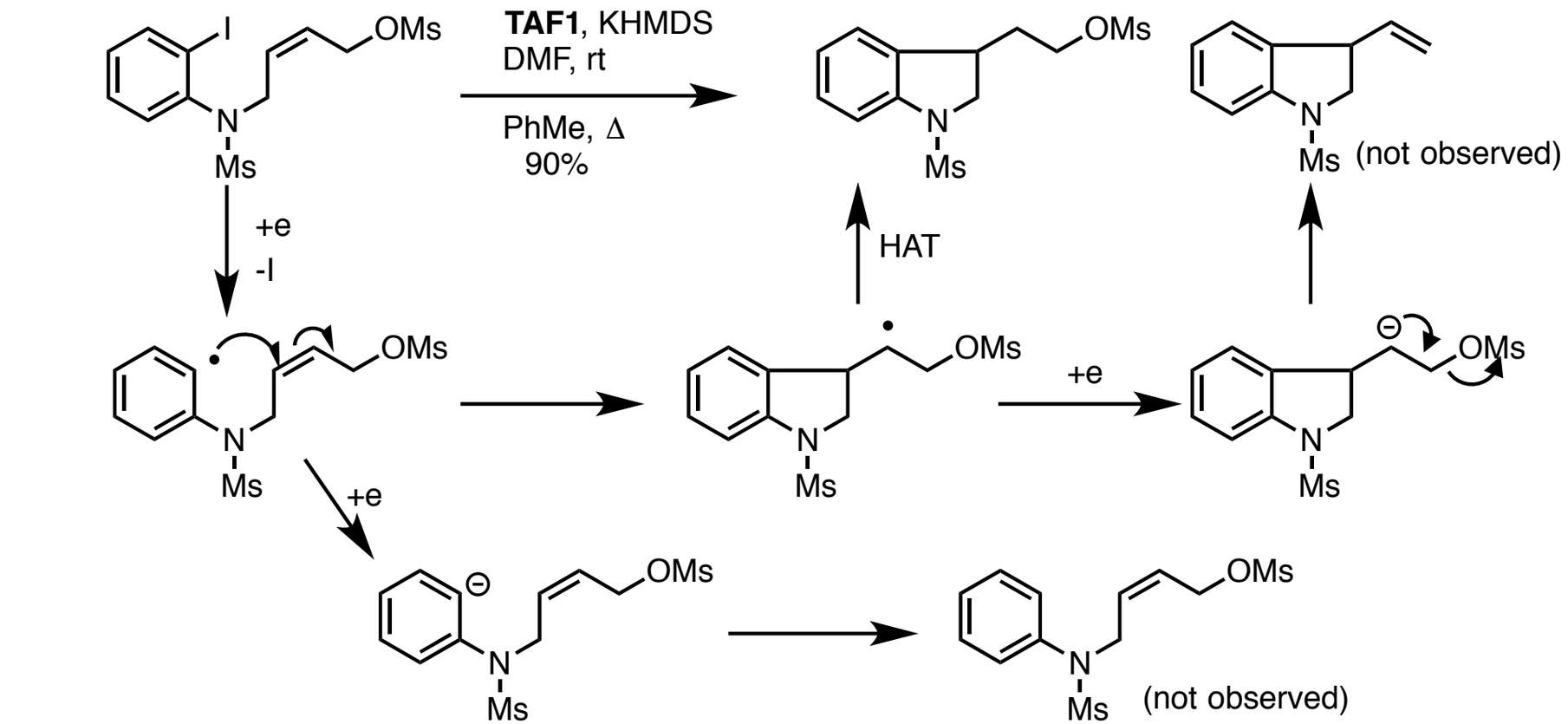


TTF



BPL

TAF1 as a one electron donor



Murphy, Angew. Chem. Int Ed. 2005, 1356