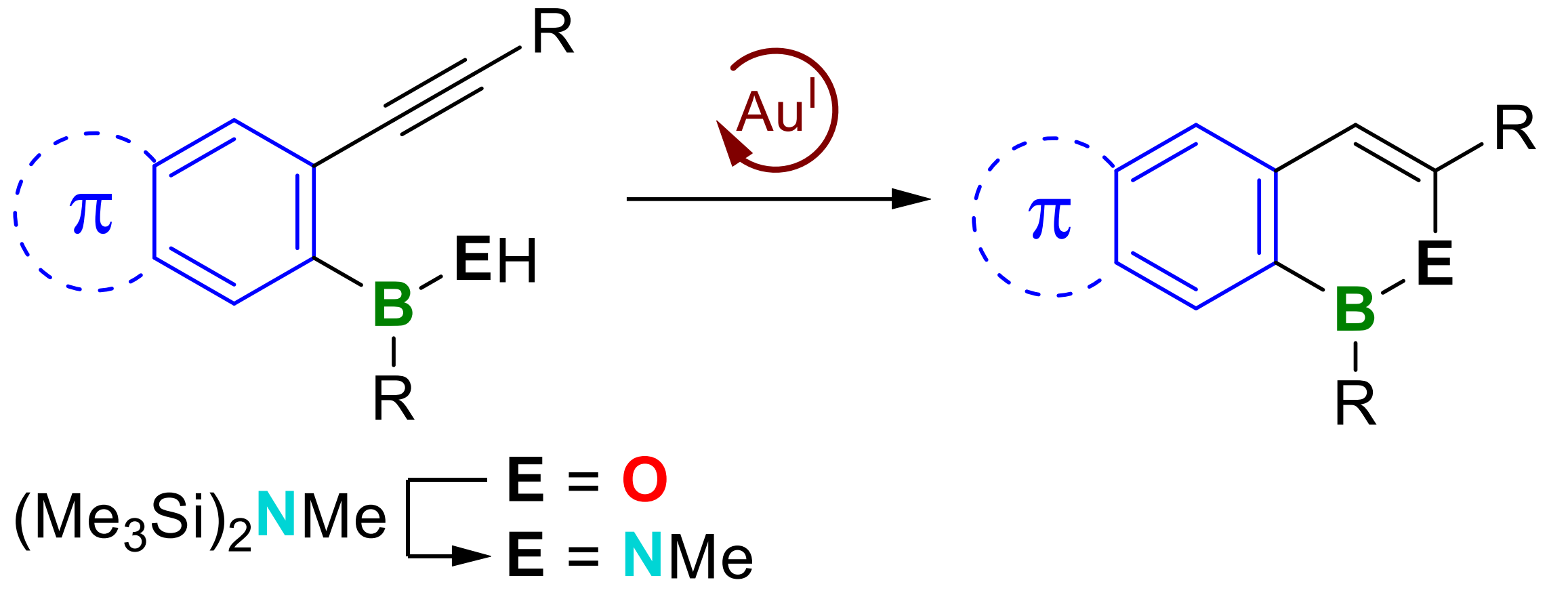
Synthesis of highly luminescent B,E-doped polycyclic aromatic hydrocarbons (E = N, O)

Simon M. Mittag, Eugenia Peresypkina, Alexander Virovets, Hans-Wolfram Lerner, Matthias Wagner*
Institute of Inorganic and Analytical Chemistry, Goethe-University Frankfurt am Main, Max-von-Laue Str. 7, 60438 Frankfurt am Main, Germany

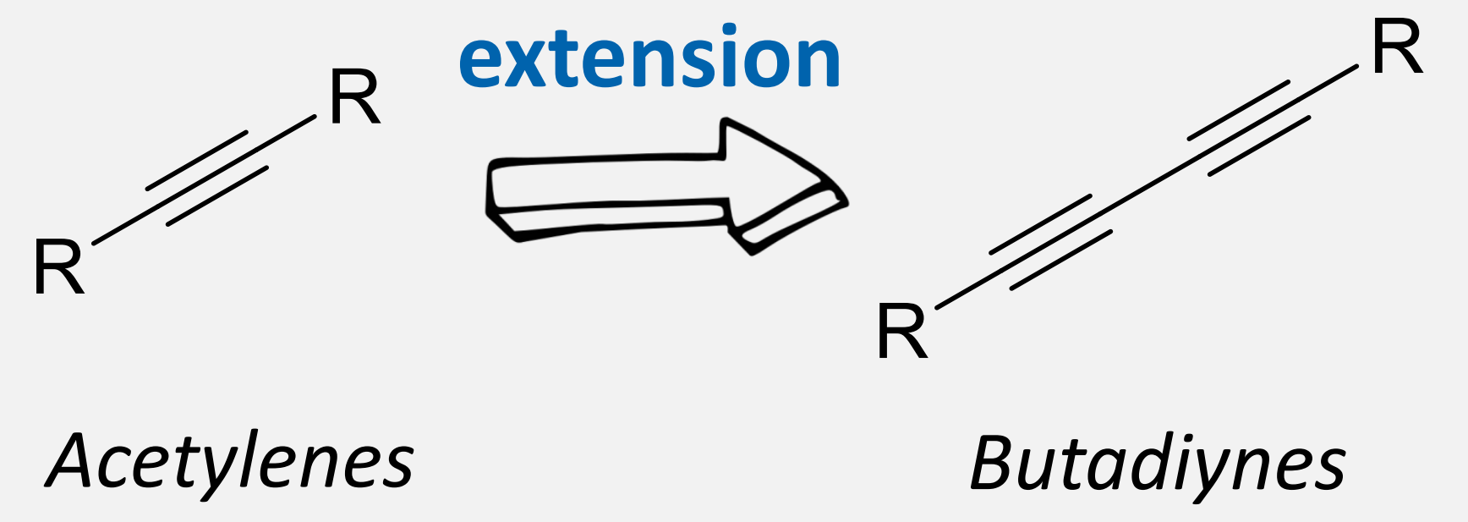
Introduction

- **Luminescence:** Doping of polycyclic aromatic hydrocarbons (PAHs) with p-block elements such as B (π-electron acceptor) and N or O (π-electron donors) provides access to materials (B,E-PAHs) tailored for use in organic light-emitting diodes (OLEDs)[1]
- **Synthesis:** Commonly used E-directed electrophilic borylation reactions often require harsh reaction conditions (*e.g.*, BBr_3, Δ)[2,3]
  → In contrast, transition-metal-catalyzed cyclization reactions provide greater functional group compatibility [2,3]

Previous work:



Task:



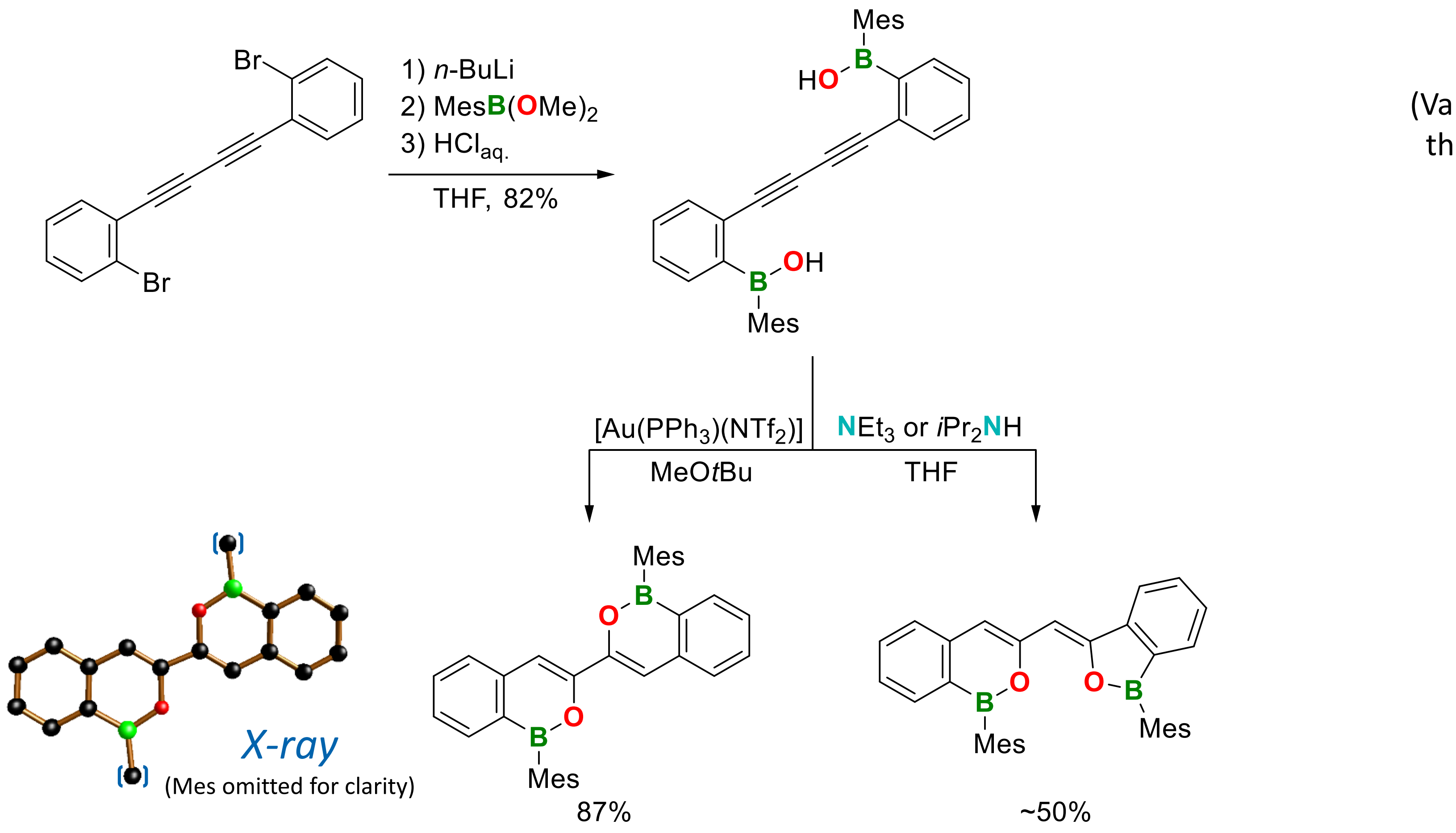
Acetylenes *Butadiynes*

Butadiynes are much more reactive than acetylenes!

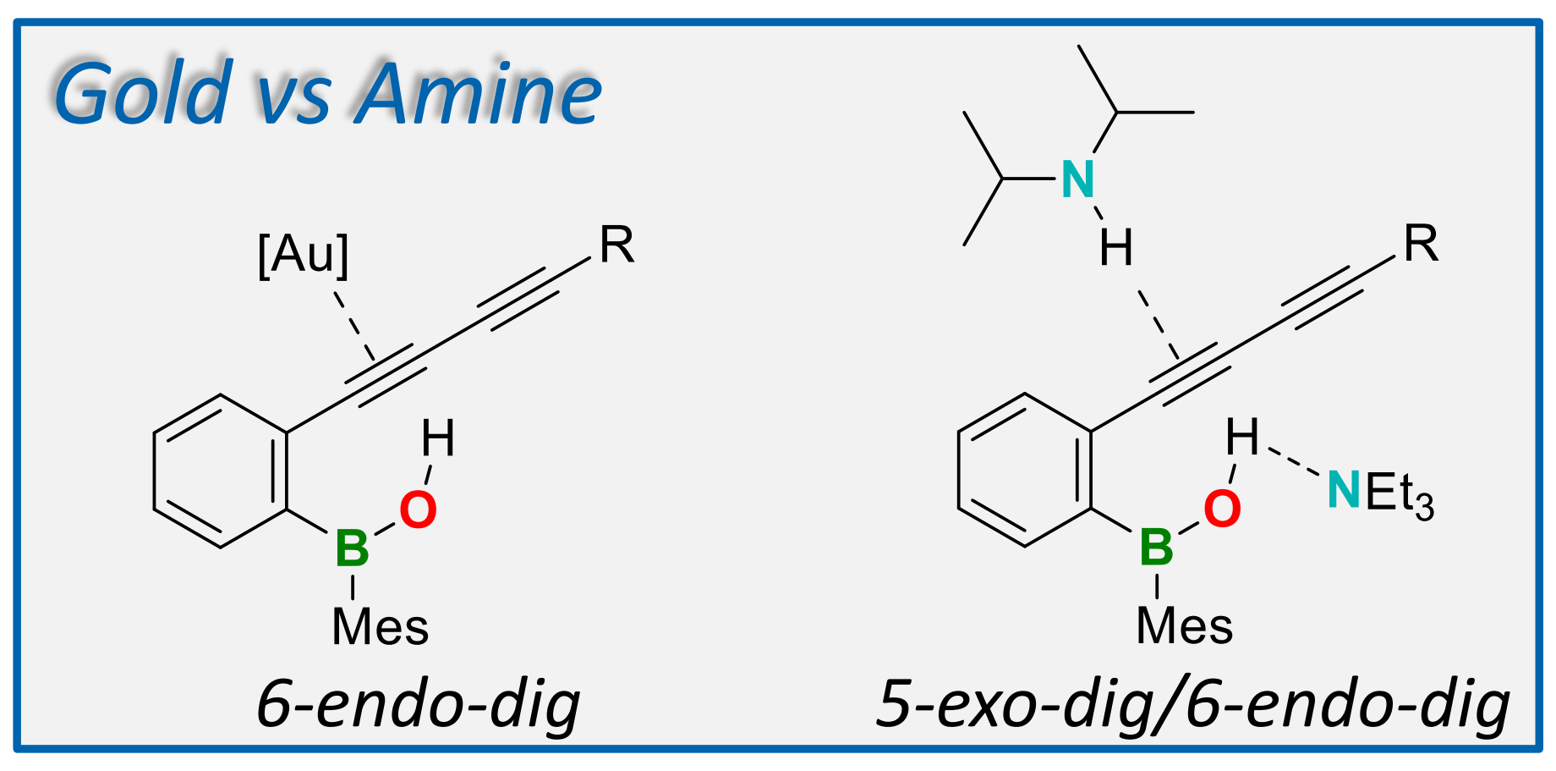
Therefore enable:

✓ New structural motifs
✓ Milder reaction conditions

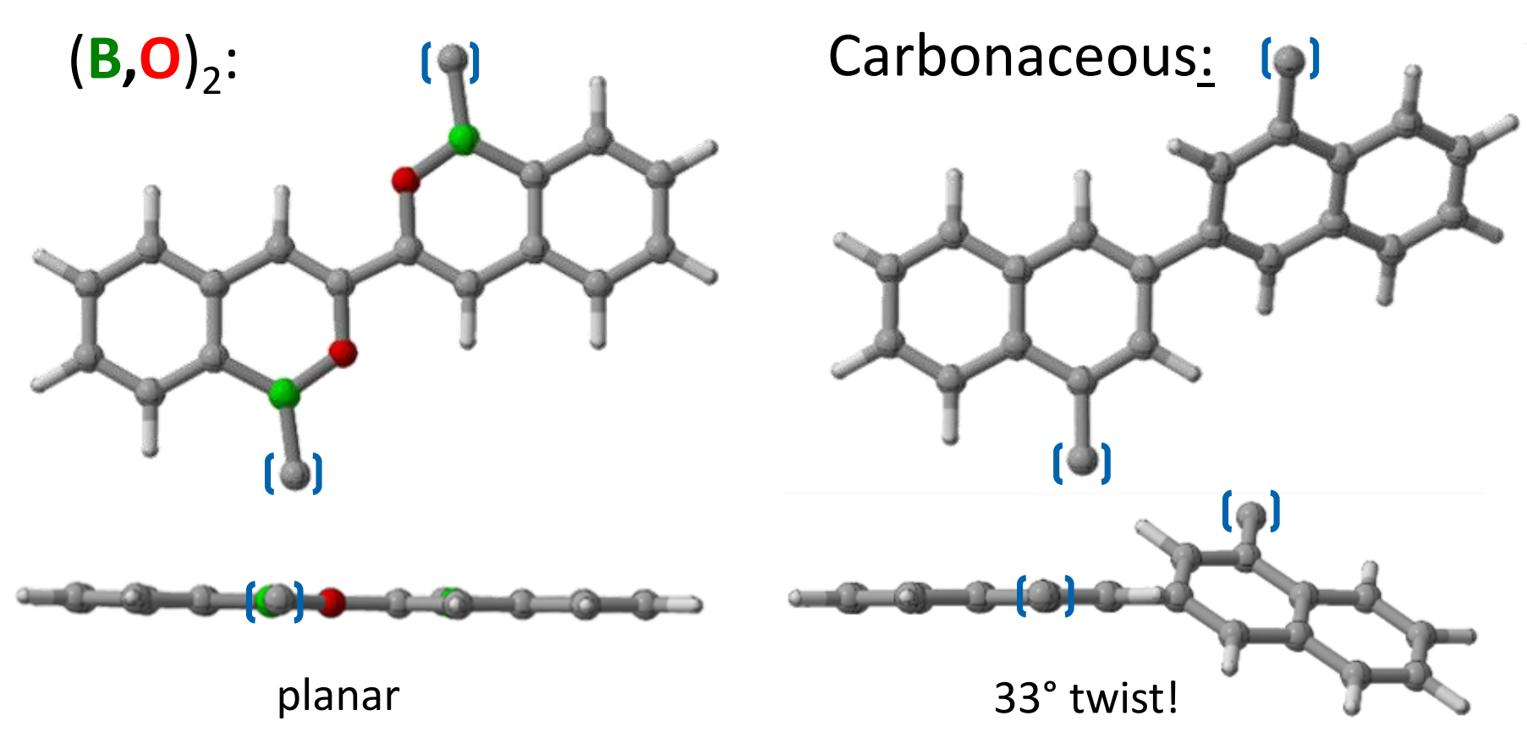
Cyclization of *o*-butadiynyl-substituted borinic acids



Reagent determines if a symmetric or asymmetric product is formed!



$(B,O)_2$-doping planarizes bay region:



Planarity increases fluorescence through:

  i. enhanced π–conjugation
  ii. intermolecular π-π-interaction

→ $(B,O)_2$-doping relieves H-H-repulsion, while maintaining π-conjugation

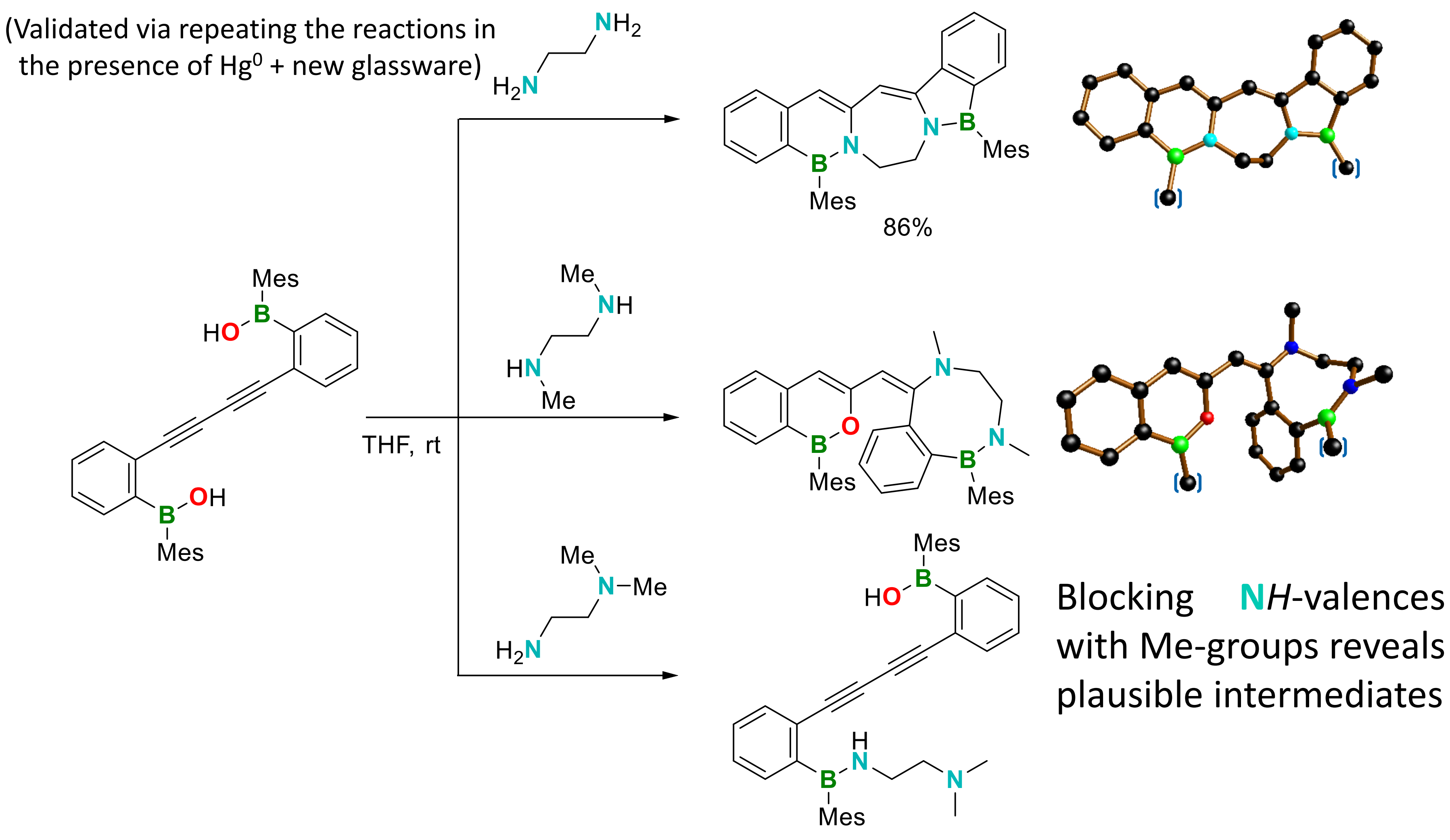
Level of theory: SMD(THF)ωB97XD/def2-TZVP

Hydroamination with ethylenediamines

No external catalyst needed!

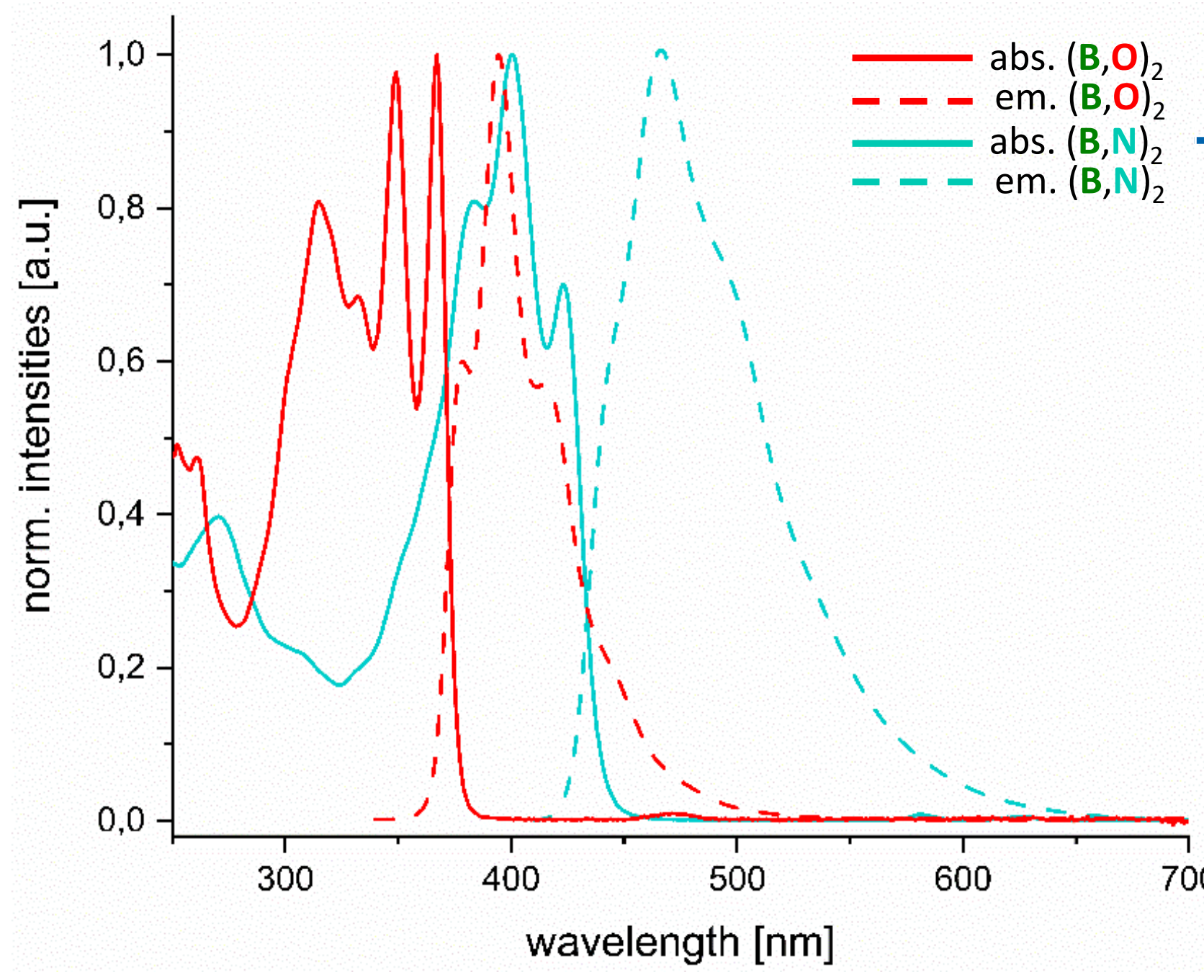
(Validated via repeating the reactions in the presence of Hg^0 + new glassware)

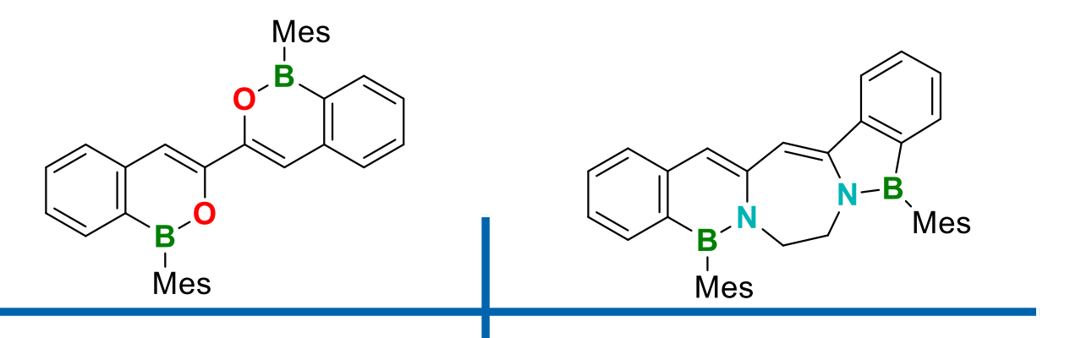
X-ray structures
(Mes omitted for clarity)



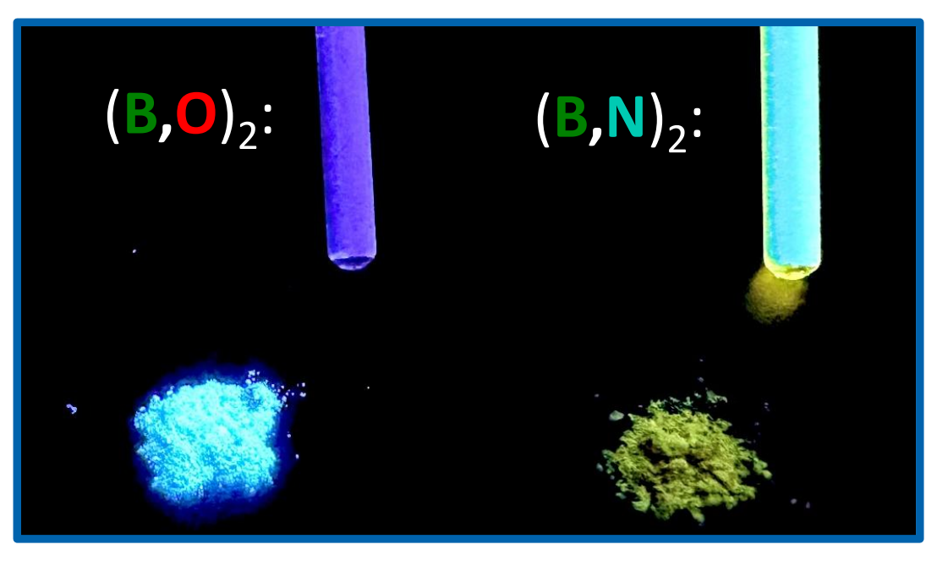
Blocking NH-valences with Me-groups reveals plausible intermediates

Optoelectronic properties:

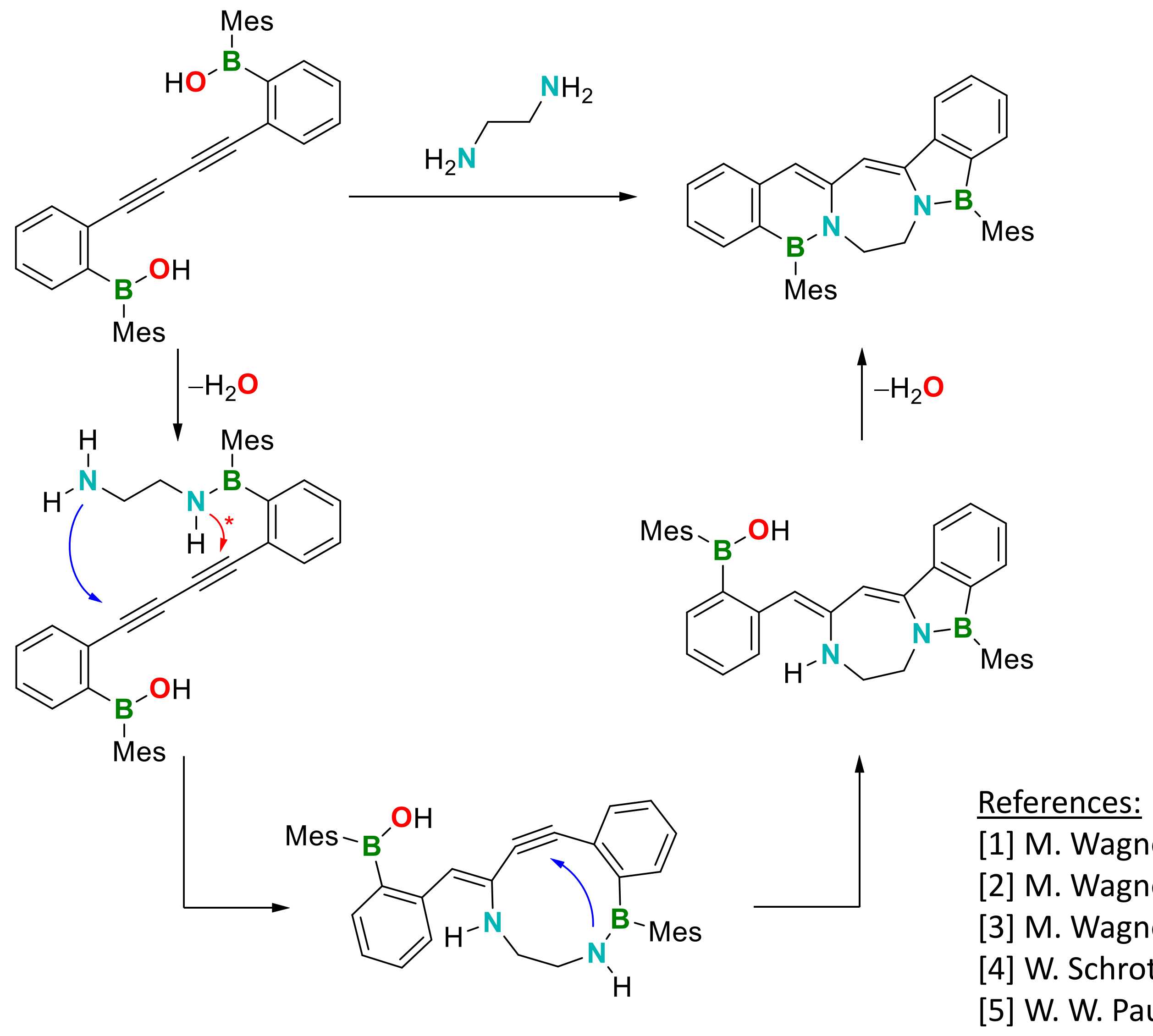




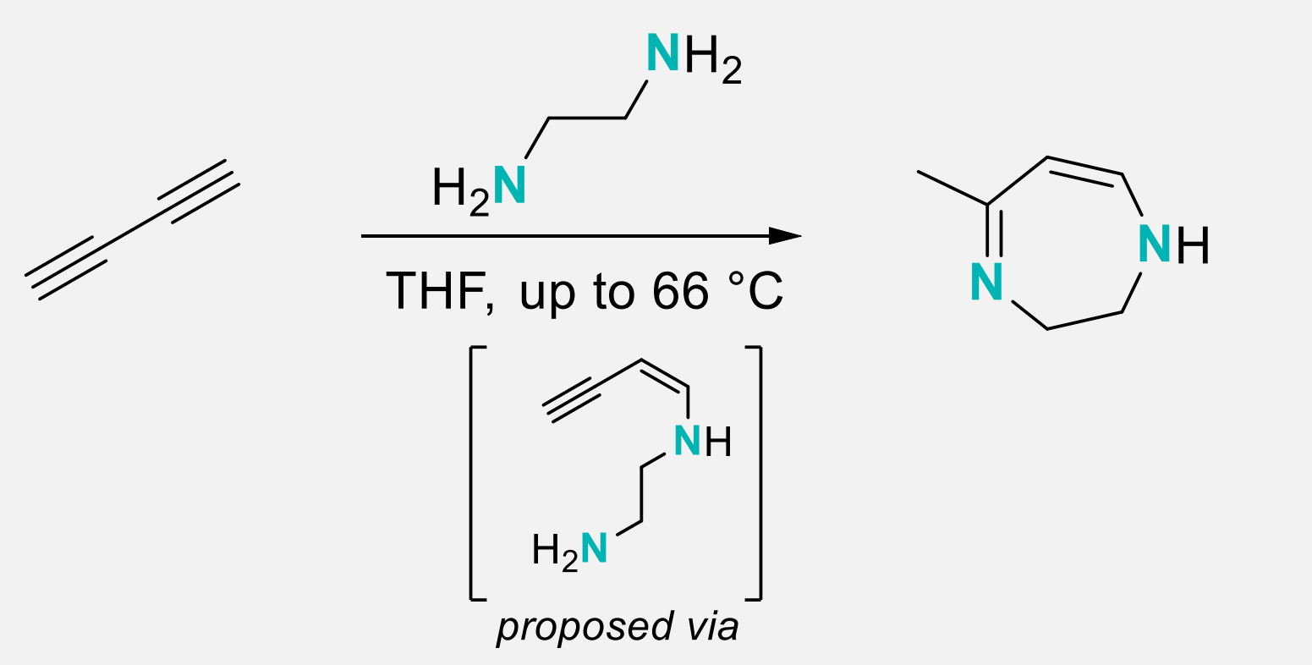
$\lambda_{em, max}$	395 nm	465 nm
Φ_{PL}(*c*-hexane)	70%	99%
FWHM	3006 cm^{-1} (0.38 eV)	3260 cm^{-1} (0.41 eV)
$E_{1/2}$	−2.61 V	−2.43 V



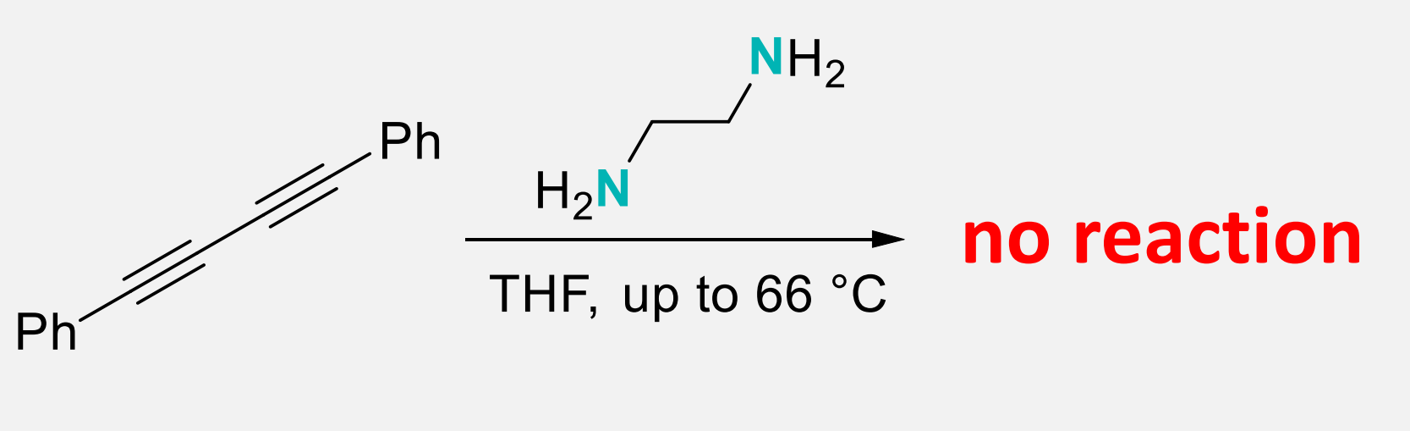
Mechanistic proposal for a autocatalyzed hydroamination reaction



W. Schroth et al. (**1969**), *W. W. Paudler et al.* (**1969**):[4,5]



Reactivity of aryl substituted butadiynes:



- Hydroamination does not occur in the absence of B, indicating that preactivation is necessary
- A hydroamination reaction at the *ortho*-positioned C≡C bond of the boronamine is not feasible (red arrow*)
- Strained 10-membered ring enables second hydroamination

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References:
[1] M. Wagner *et al.*, *Asian J. Org. Chem.* **2018**, *7*, 37–53.
[2] M. Wagner *et al.*, *Angew. Chem. Int. Ed.* **2019**, *58*, 11379–11384.
[3] M. Wagner *et al.*, *Chem. Sci.* **2021**, *12*, 5898–5909.
[4] W. Schroth *et al.*, *Z. Chem.* **1969**, *9*, 143.
[5] W. W. Paudler *et al.*, *J. Org. Chem.* **1969**, *34*, 999-1001.

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