Boron-Doped Polycyclic Aromatic Hydrocarbons

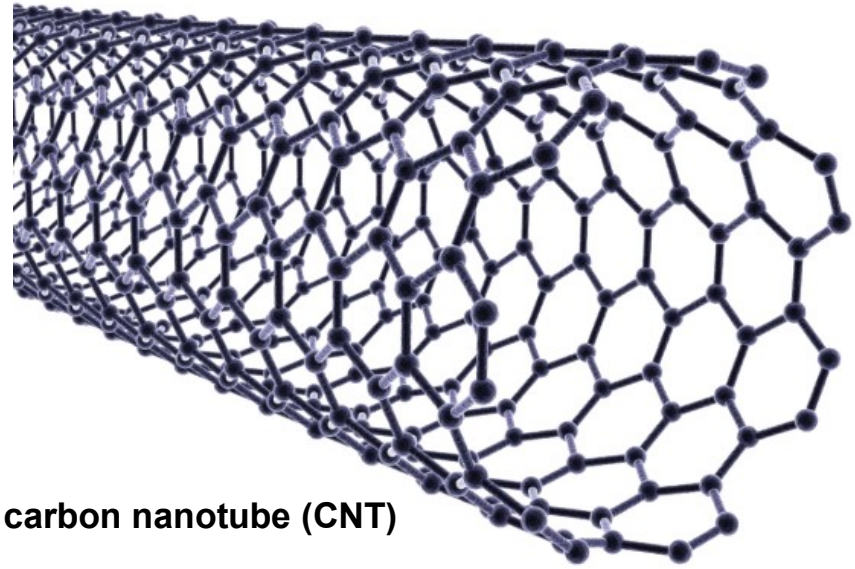
2024.12.12. Literature Seminar

D2 Wataru Shigematsu

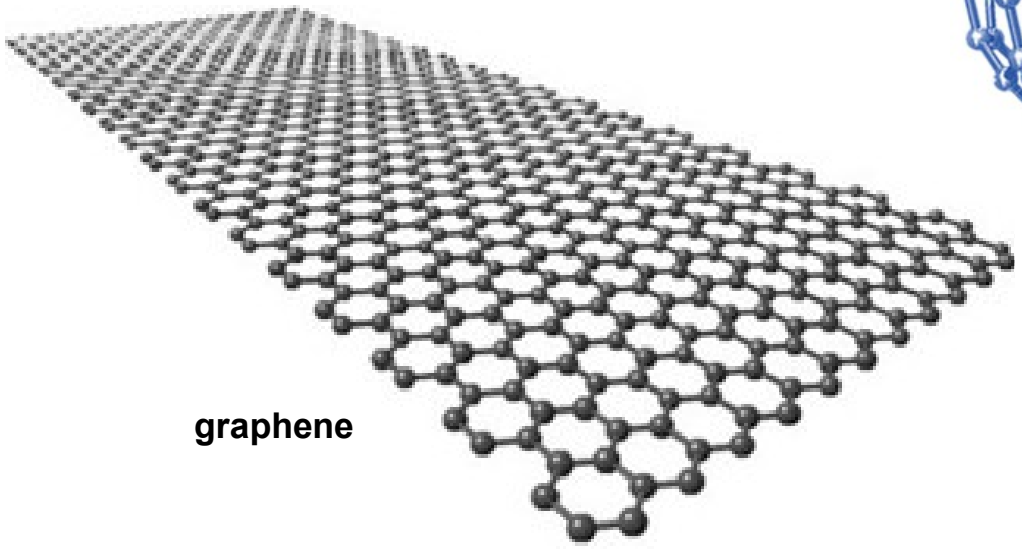
Contents

Contents

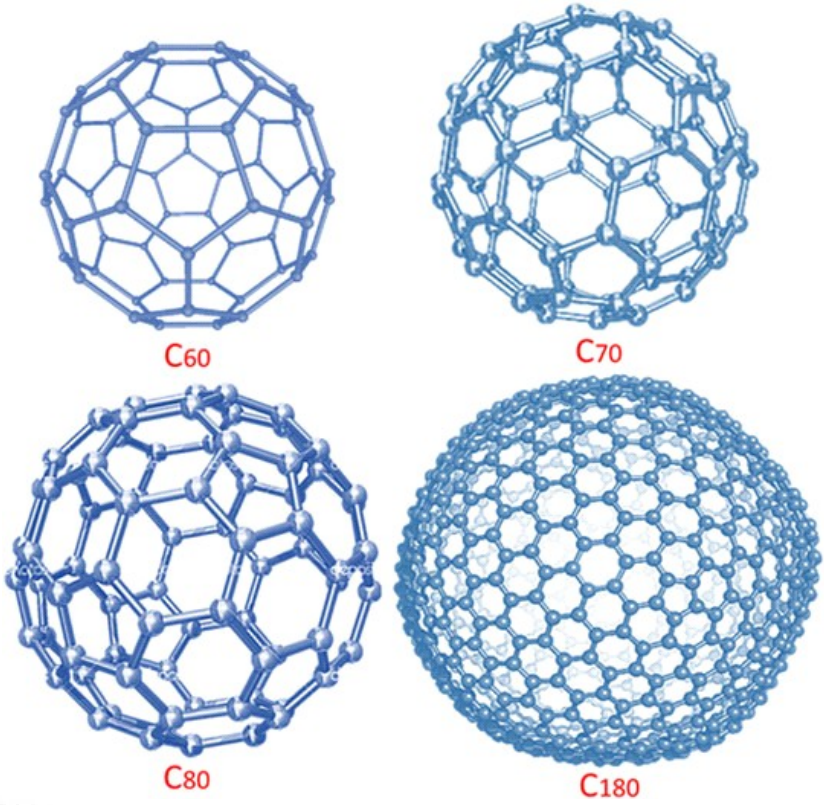
Polycyclic Aromatic Hydrocarbons



carbon nanotube (CNT)

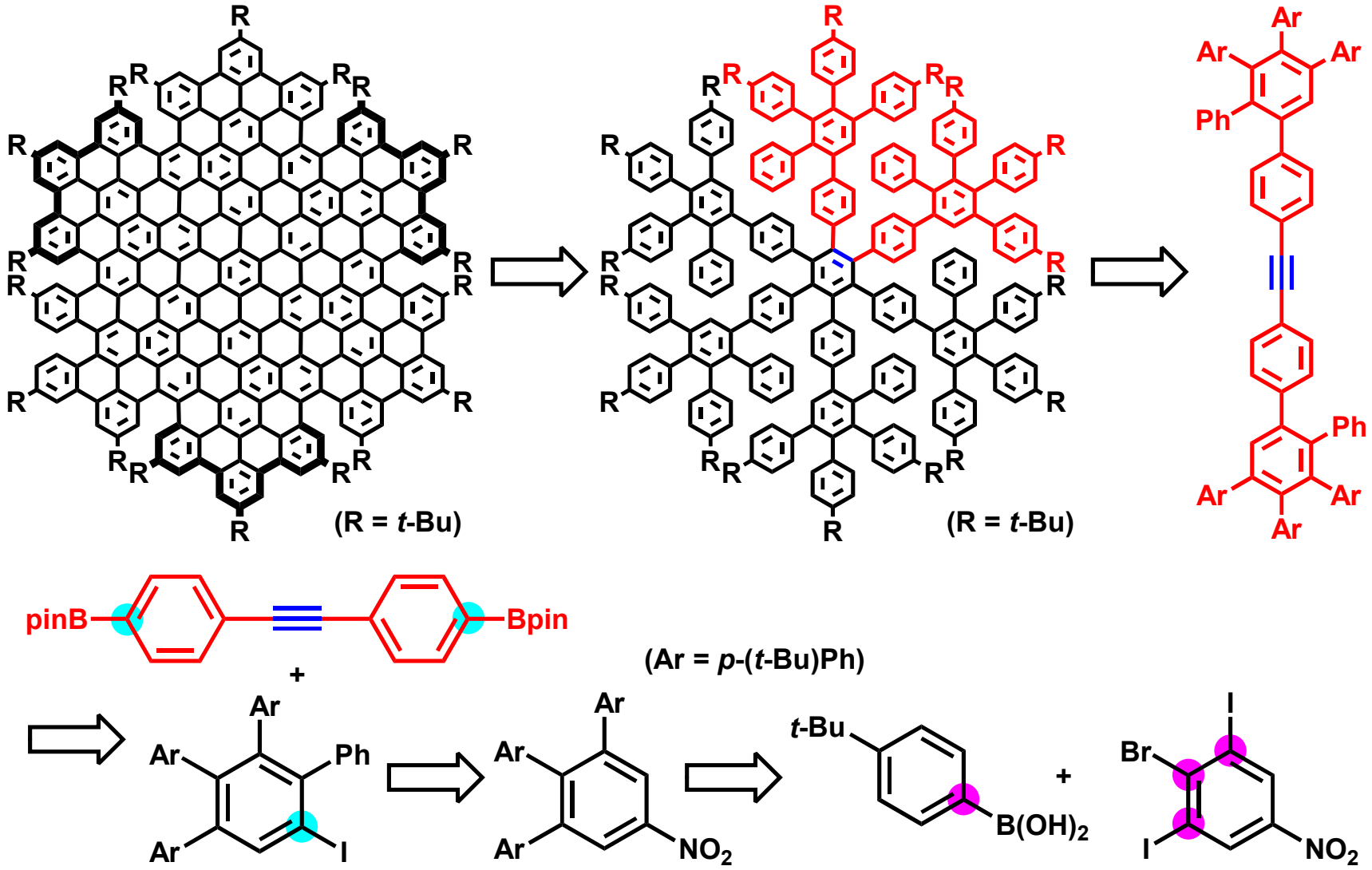


graphene



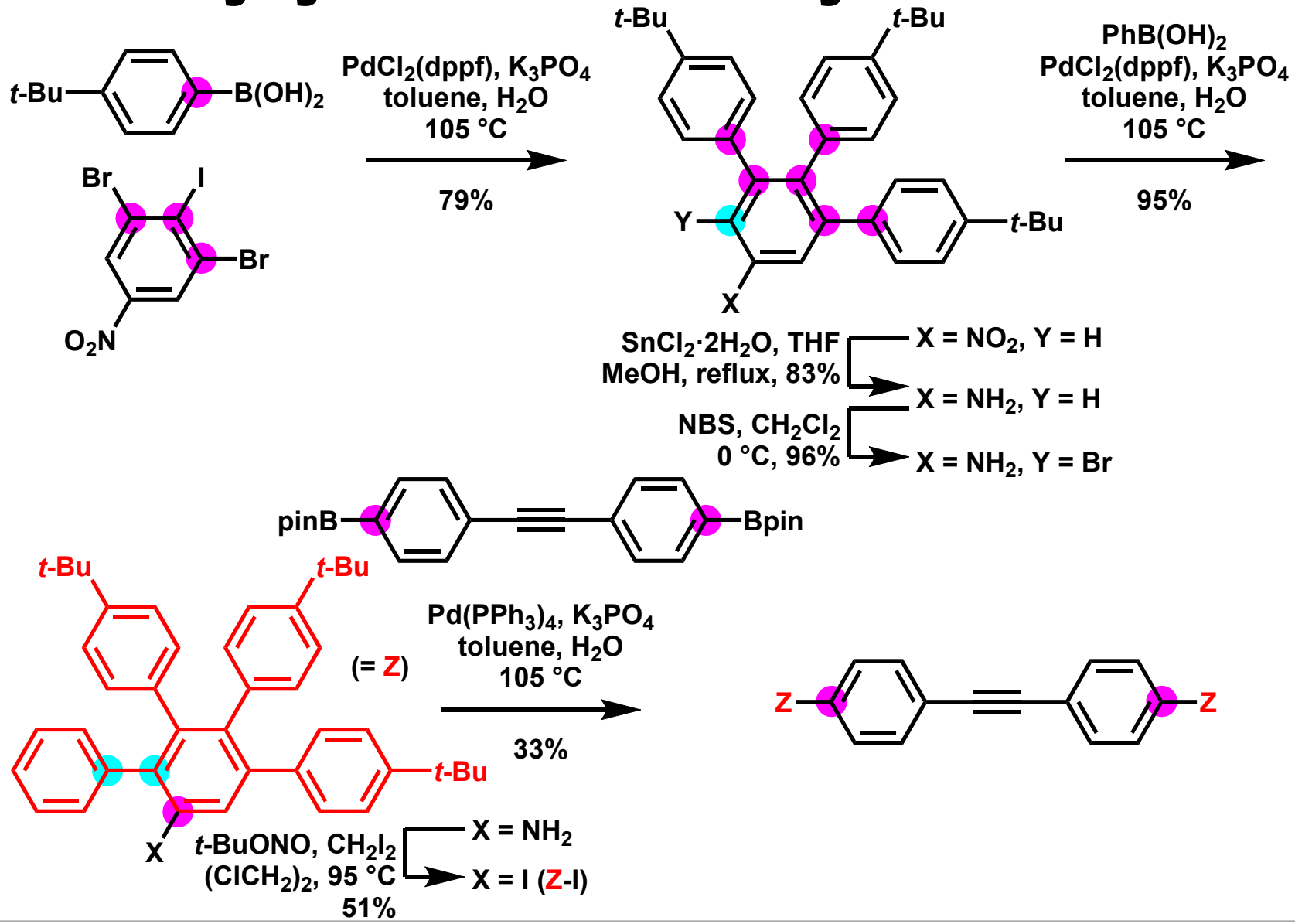
frallene

Synthetic Strategy for C222 nanographene



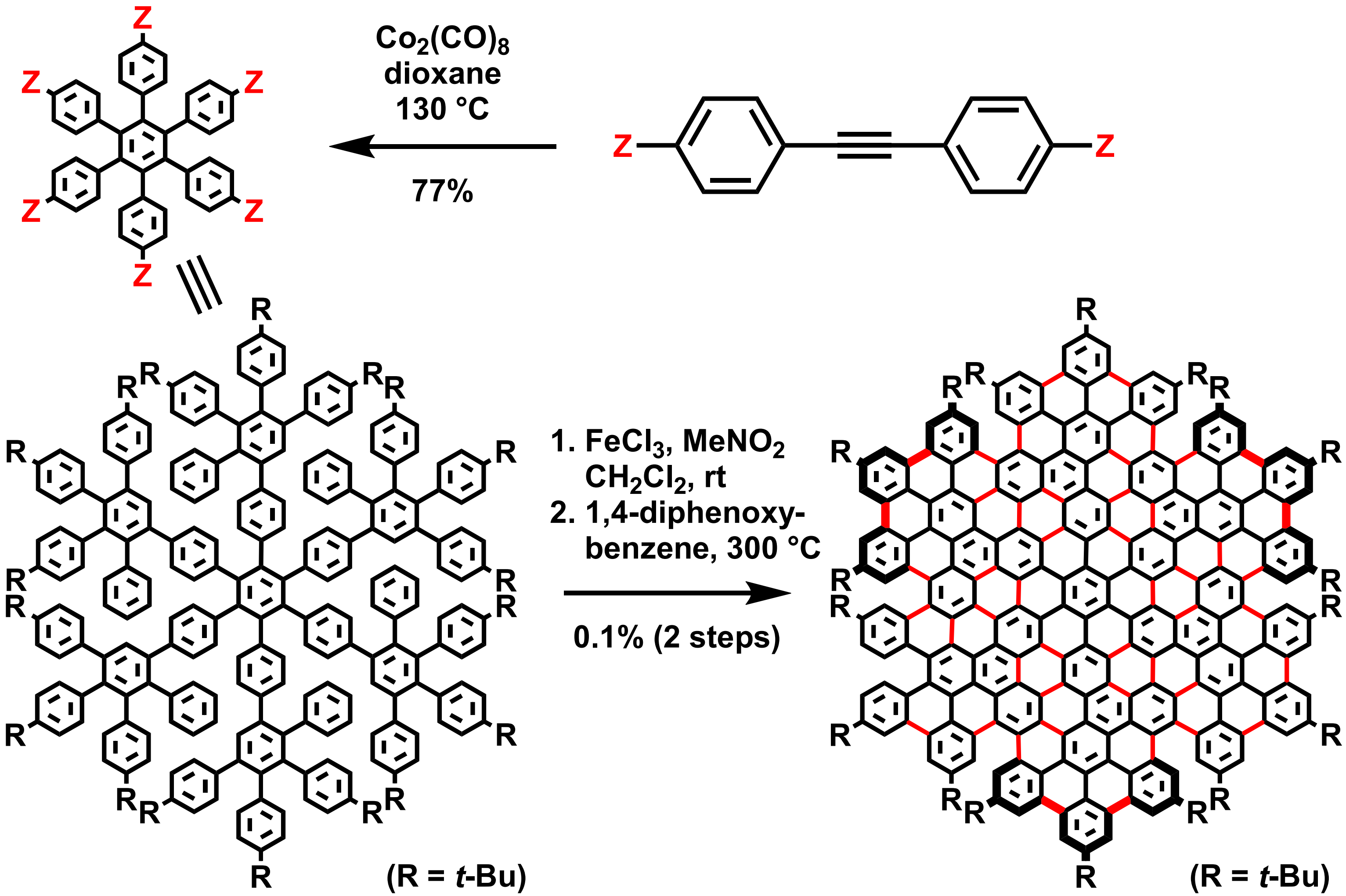
1) Zhang, Z.; Zhu, H.; Gu, J.; Shi, H.; Hirose, T.; Jiang, L.; Zhu, Y.; Zhong, D.; Wang, J. *J. Am. Chem. Soc.* **2024**, *146*, 24681.

Polycyclic Aromatic Hydrocarbon



1) Zhang, Z.; Zhu, H.; Gu, J.; Shi, H.; Hirose, T.; Jiang, L.; Zhu, Y.; Zhong, D.; Wang, J. *J. Am. Chem. Soc.* **2024**, *146*, 24681.

Synthesis of C222 nanographene



1) Zhang, Z.; Zhu, H.; Gu, J.; Shi, H.; Hirose, T.; Jiang, L.; Zhu, Y.; Zhong, D.; Wang, J. *J. Am. Chem. Soc.* **2024**, *146*, 24681.

Contents

1. Introduction

2. Synthesis of π-Extended 9b-Boraphenalenes and Their Physical Characters

pubs.acs.org/JACS Article

π-Extended 9b-Boraphenalenes: Synthesis, Structure, and Physical Properties

Prof. Takuji Hatakeyama

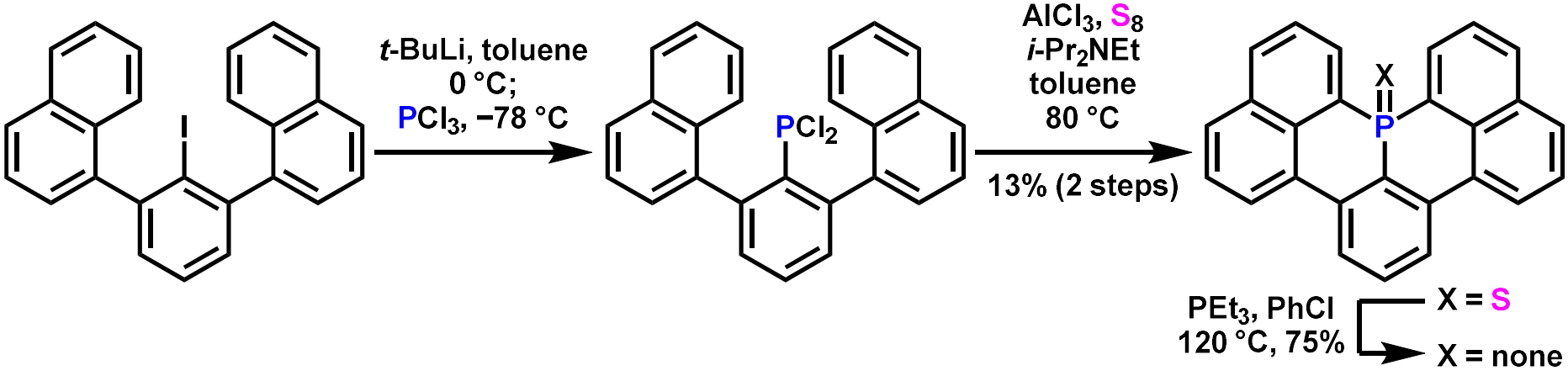
-2000 B.S. @The University of Tokyo
-2005 Ph.D. @The University of Tokyo
(Prof. Eiichi Nakamura)
2005- postdoc @University of Chicago
(Prof. R. F. Ismagilov)
2006- assistant @Kyoto University
(Prof. Masaharu Nakamura)
2007- assistant professor @Kyoto University
(Prof. Masaharu Nakamura)
2013- associate professor @Kwansei Gakuin University
2018- professor @Kwansei Gakuin University
2022- professor @Kyoto University

Research Topics

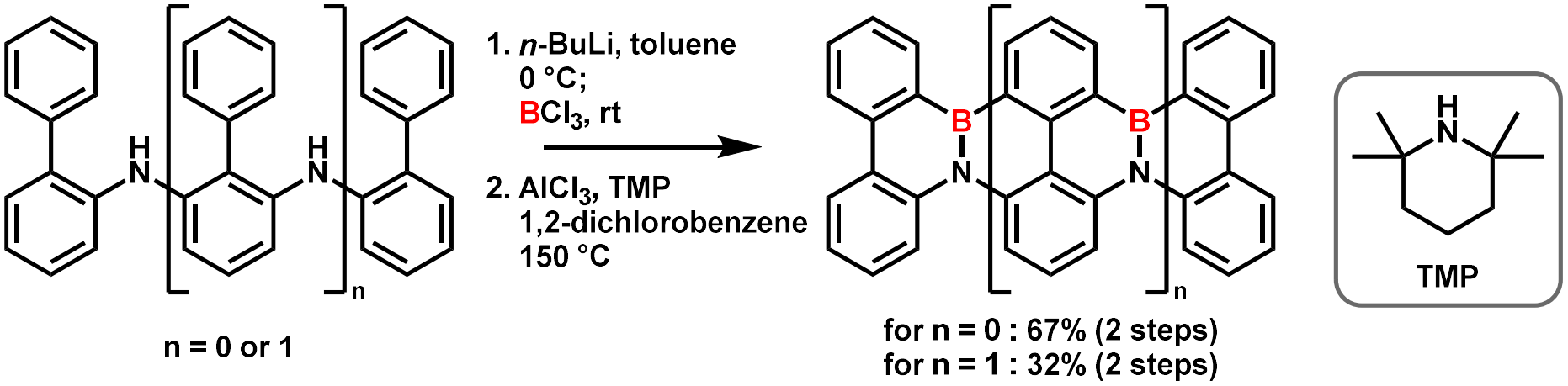
- Development of tandem hetero-Friedel-Crafts reactions toward giant π-conjugated systems with heteroatoms
- Development of narrow-band emitters based on multiple resonance effect

Tandem Hetero-Friedel-Crafts Reactions

1. Tandem phospha-Friedel-Crafts reaction



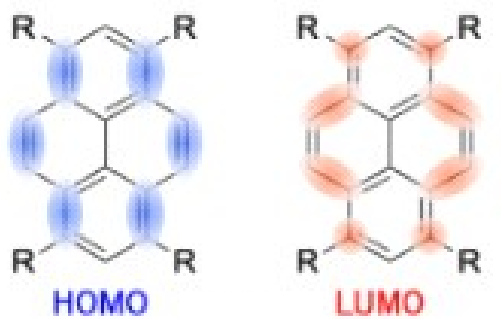
2. Synthesis of BN-fused polycyclic aromatic hydrocarbone



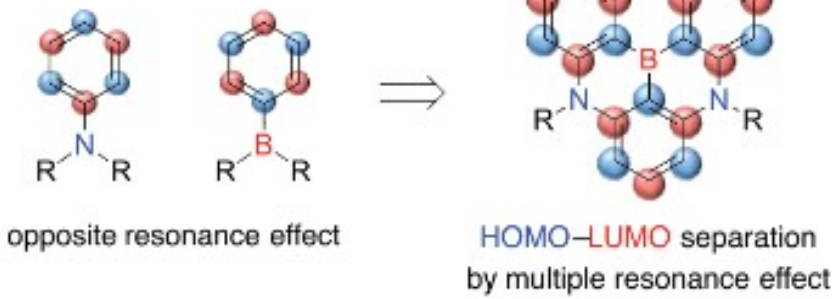
1) Hatakeyama, T.; Hashimoto, S.; Nakamura, M. *Org. Lett.* **2011**, *13*, 2130.
2) Hatakeyama, T.; Hashimoto, S.; Seki, S.; Nakamura, M. *J. Am. Chem. Soc.* **2011**, *133*, 18614.

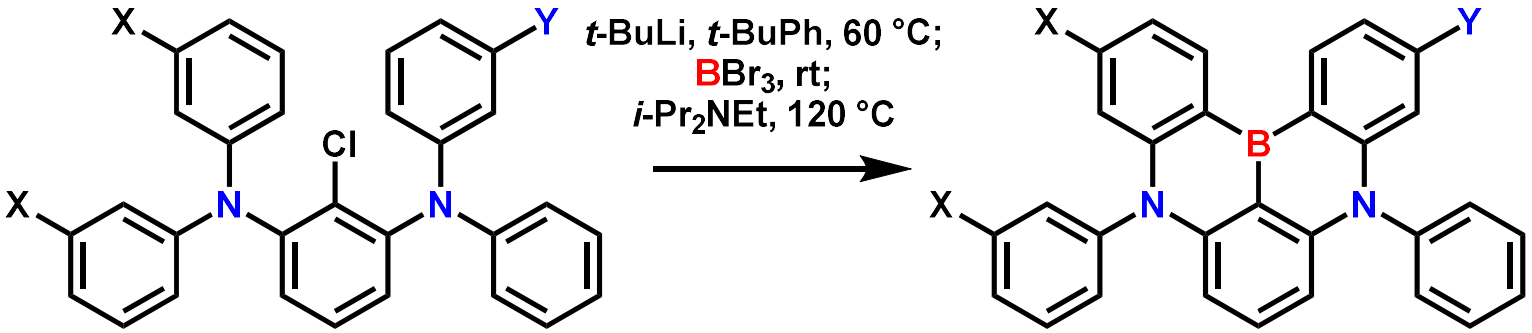
Development of Narrow-band Emitter “DABNA”

HOMO and LUMO of pyrene



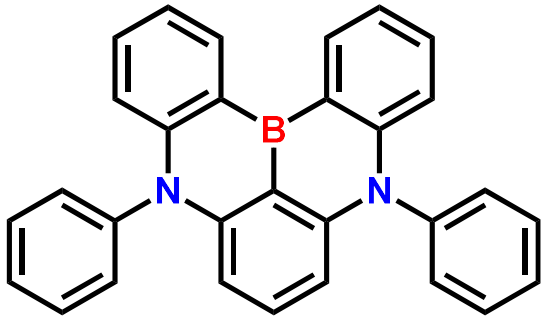
(b) new TADF molecule



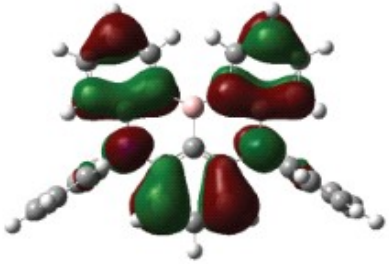


1) Hatakeyama, T.; Shiren, K.; Nakajima, K.; Nomura, S.; Nakatsuka, S.; Ni, J.; Ono, Y.; Ikuta, T. *Adv. Mater* .**2016**, *28*, 2777.

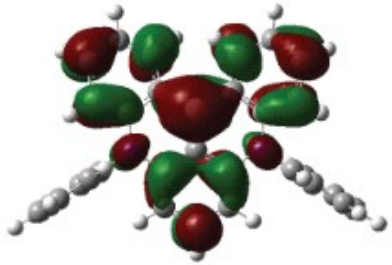
“Atom Localized” HOMO and LUMO



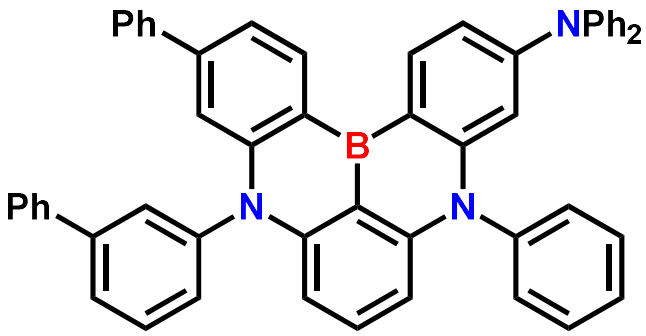
DABNA-1



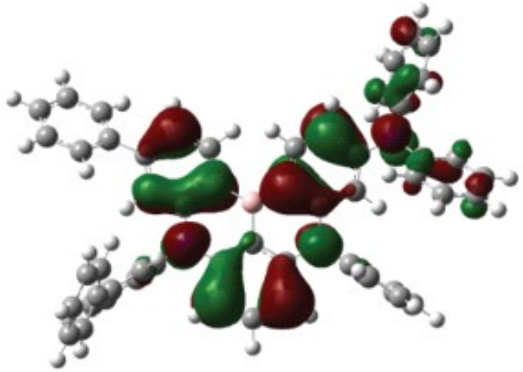
HOMO (–4.74 eV)



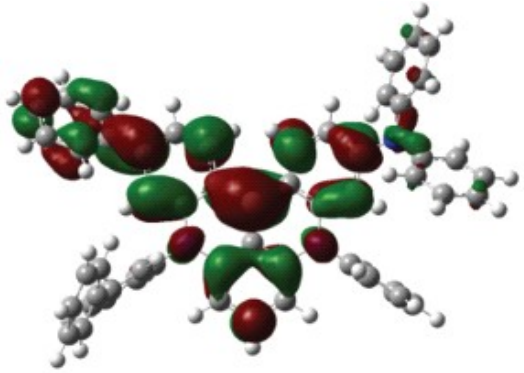
LUMO (–1.08 eV)



DABNA-2



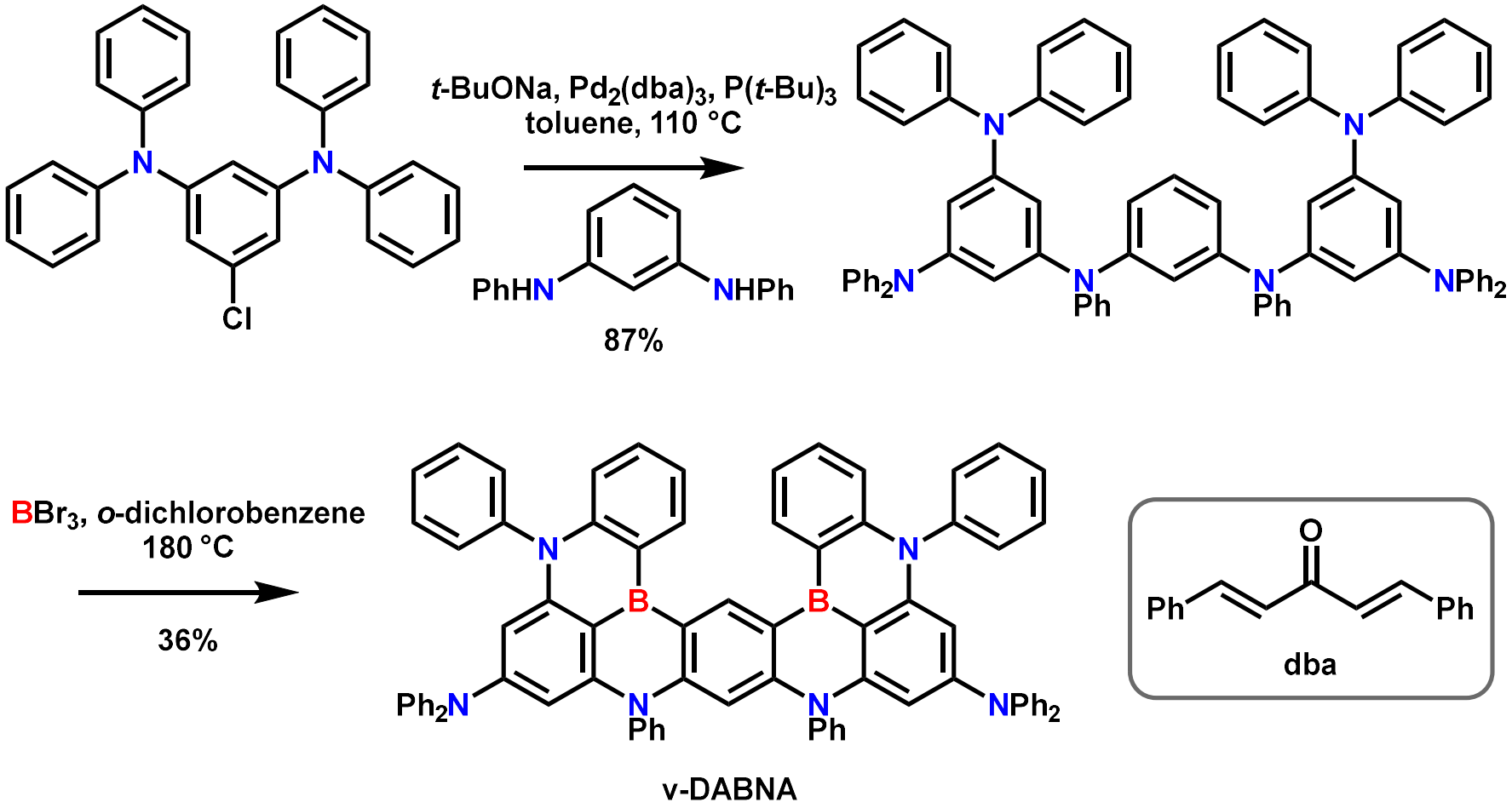
HOMO (–4.69 eV)



LUMO (–1.21 eV)

1) Hatakeyama, T.; Shiren, K.; Nakajima, K.; Nomura, S.; Nakatsuka, S.; Ni, J.; Ono, Y.; Ikuta, T. *Adv. Mater* .**2016**, *28*, 2777.

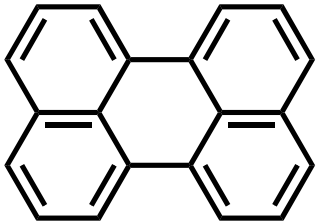
Synthesis of new DABNA “v-DABNA”

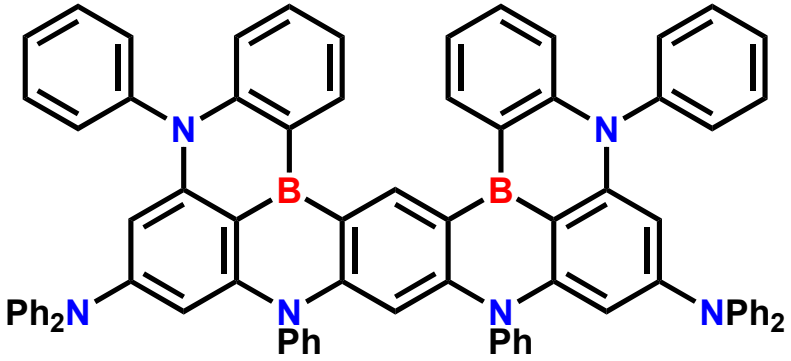


1) Kondo, Y.; Yoshiura, K.; Kitera, S.; Nishi, H.; Oda, S.; Gotoh, H.; Sasada, Y.; Yanai, M.; Hatakeyama, T. *Nat. Photonics* **2019**, *13*, 678.

v-DABNA as a New Organic LED

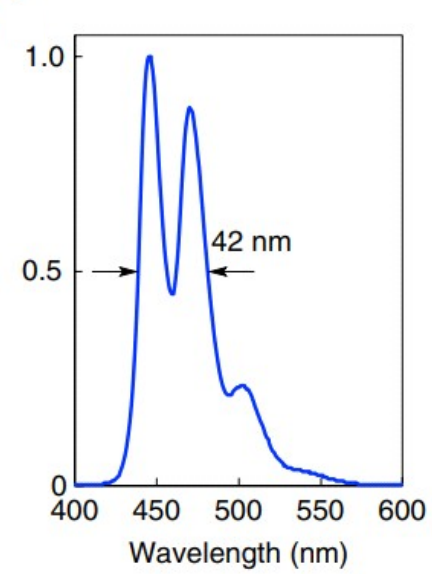
compound

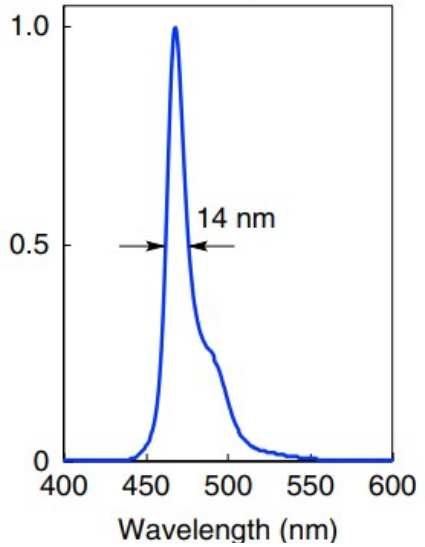




perylene **v-DABNA**

PL spectra





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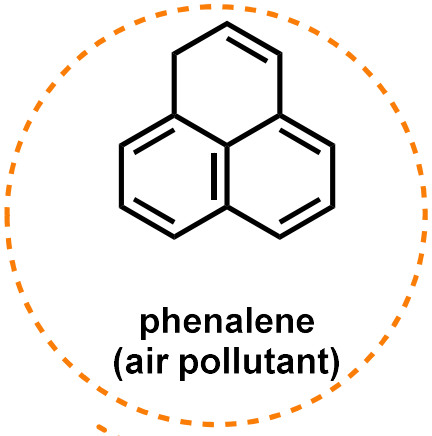
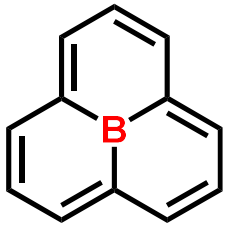
9b-Boraphenalene

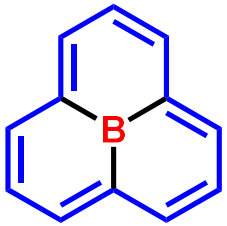


phenalene
(air pollutant)

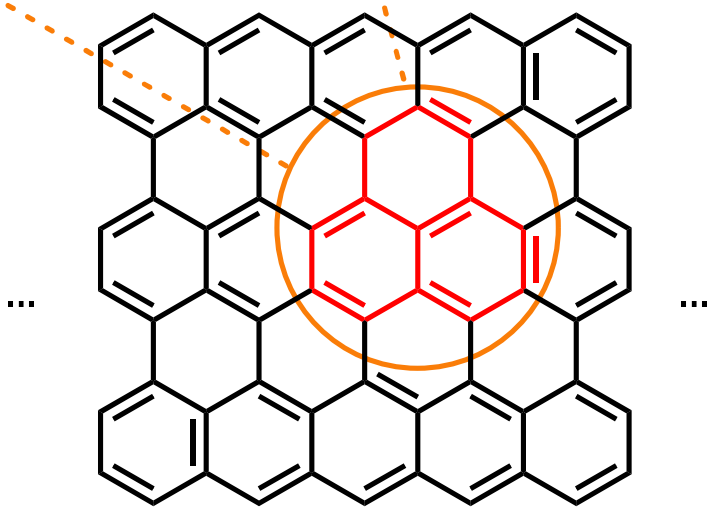


9b-boraphenalene
(no reports)

≡



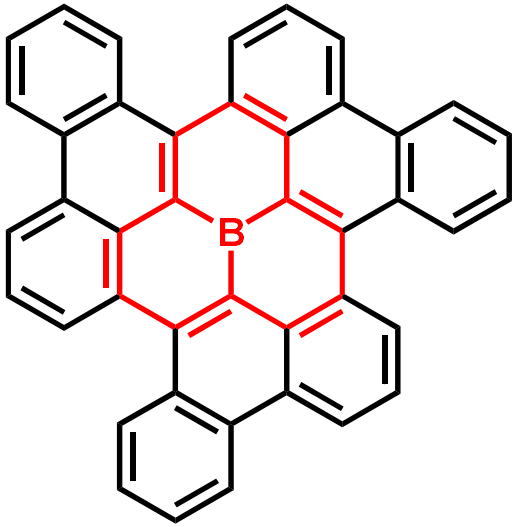
12π-antiaromaticity



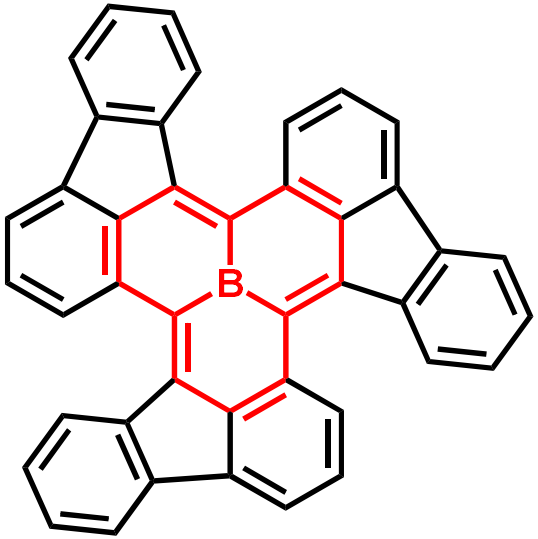
... graphene ...

- 9b-Boraphenalene can be a boron-doped nanographene fragment.
- However, synthetic method of 9b-boraphenalene hasn't been reported.

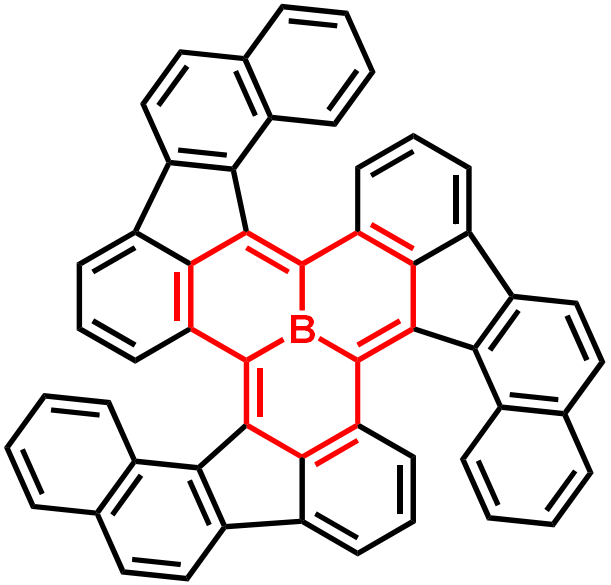
π-Extended 9b-Boraphenalenes



BP-Phen



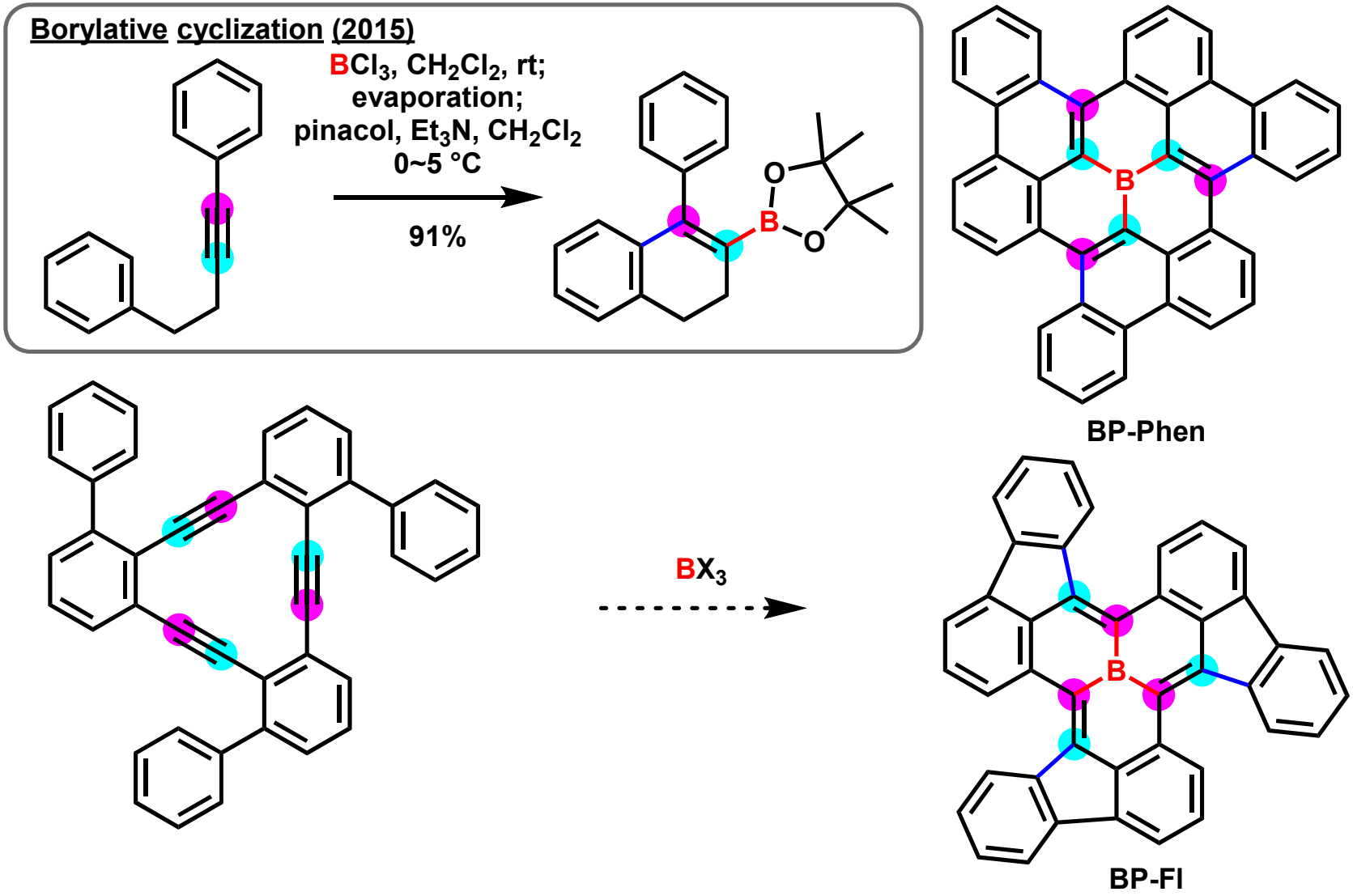
BP-Fl



BP-BnFl

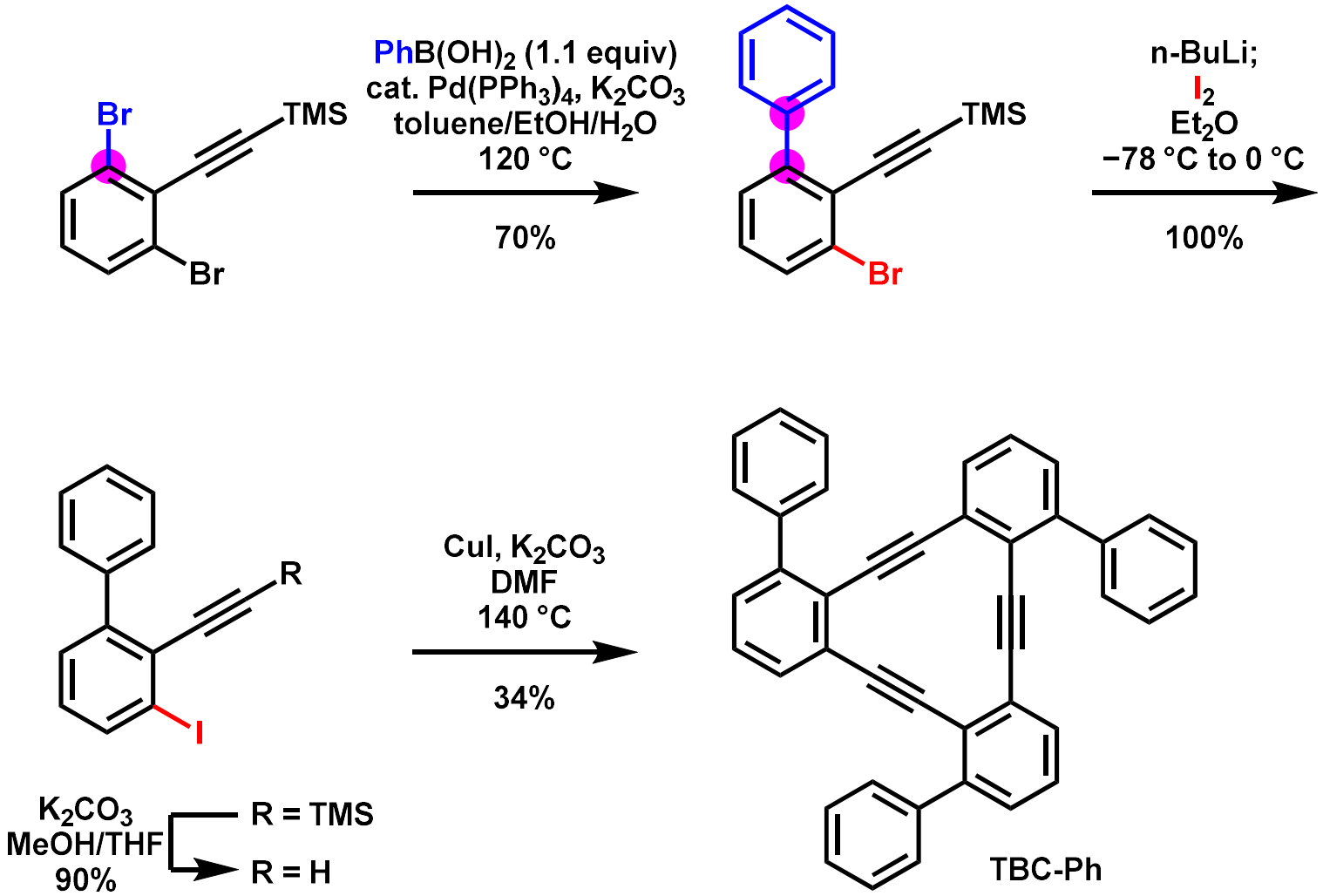
1) Ikeno, A.; Hayakawa, M.; Sakai, M.; Tsutsui, Y.; Nakatsuka, S.; Seki, S.; Hatakeyama, T. *J. Am. Chem. Soc.* **2024**, *146*, 17084.

Synthetic Strategy



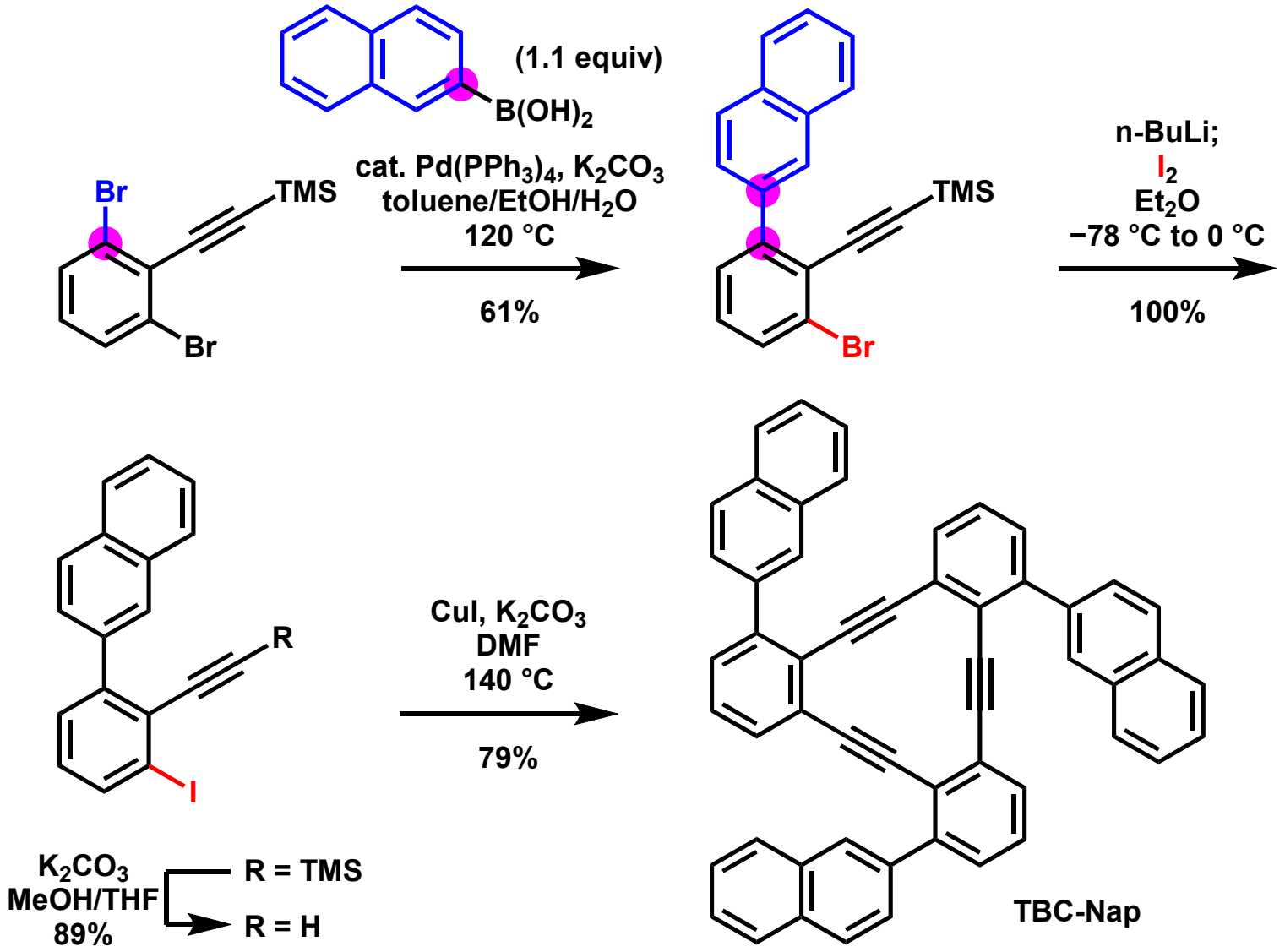
1) Warner, A. J.; Lawson, J. R.; Fasano, V.; Ingleson, M. J. *Angew. Chem., Int. Ed.* **2015**, *54*, 11245.
2) Ikeno, A.; Hayakawa, M.; Sakai, M.; Tsutsui, Y.; Nakatsuka, S.; Seki, S.; Hatakeyama, T. *J. Am. Chem. Soc.* **2024**, *146*, 17084.

Synthesis of Cyclization Precursor TBC-Ph



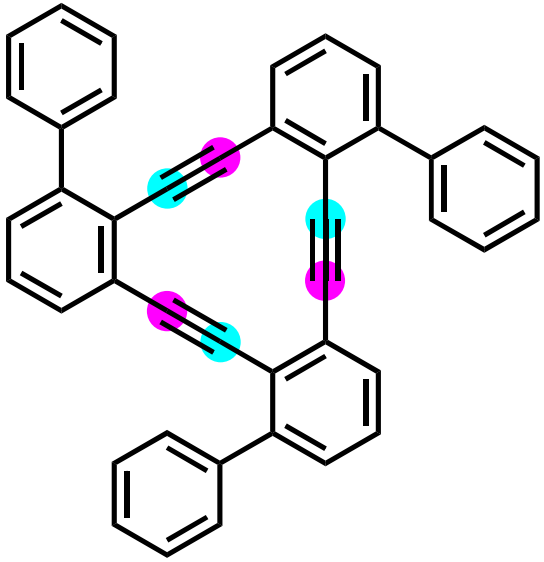
1) Ikeno, A.; Hayakawa, M.; Sakai, M.; Tsutsui, Y.; Nakatsuka, S.; Seki, S.; Hatakeyama, T. *J. Am. Chem. Soc.* **2024**, *146*, 17084.

Synthesis of Cyclization Precursor TBC-Nap

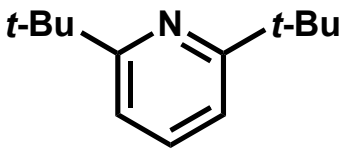


1) Ikeno, A.; Hayakawa, M.; Sakai, M.; Tsutsui, Y.; Nakatsuka, S.; Seki, S.; Hatakeyama, T. *J. Am. Chem. Soc.* **2024**, *146*, 17084.

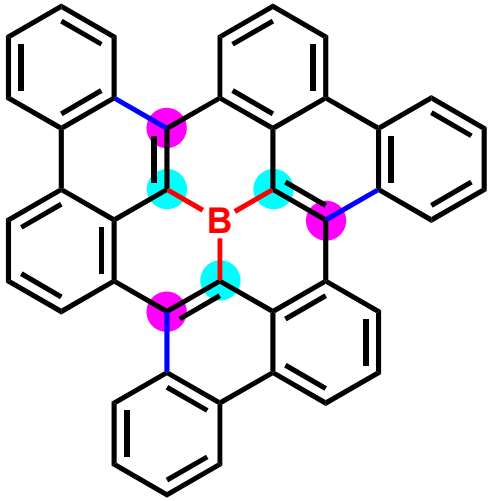
Borylative Cyclization from TBC-Ph



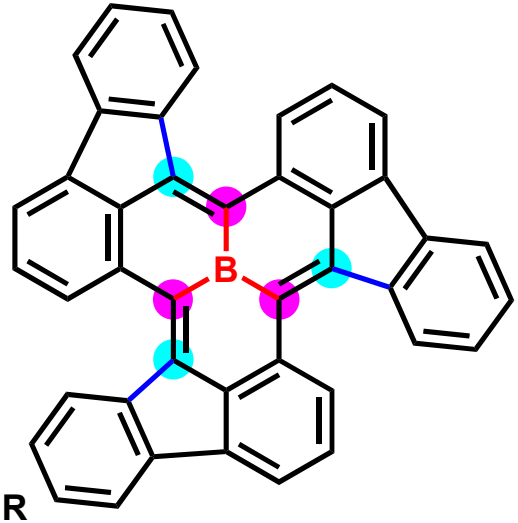
TBC-Ph



BI_3
1,2,4-trichlorobenzene
150 °C



BP-Phen : 14%[a] (16%[b])

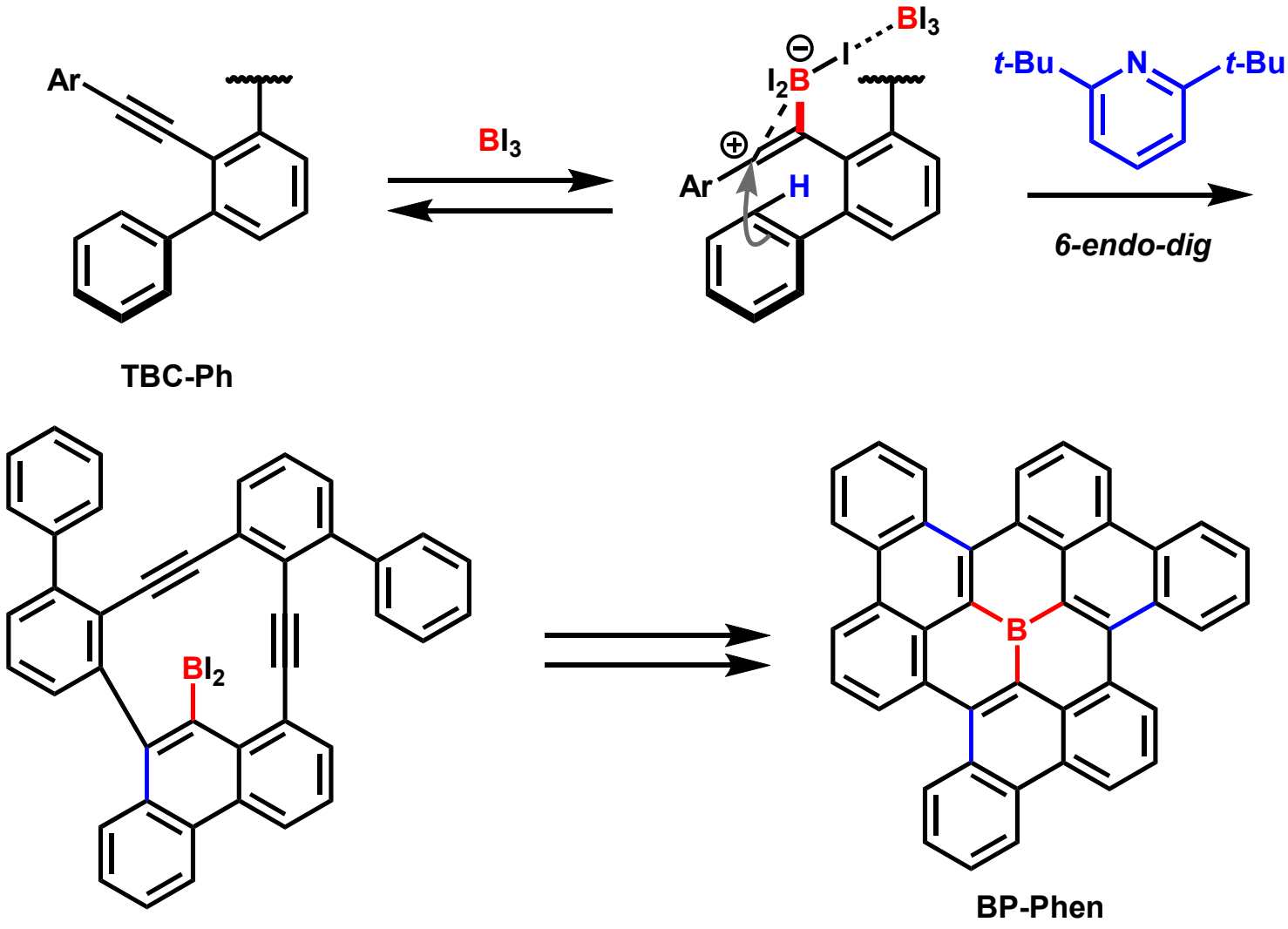


BP-Fl : 10%[a] (10%[b])

a) isolated yield
b) yield in crude based on NMR

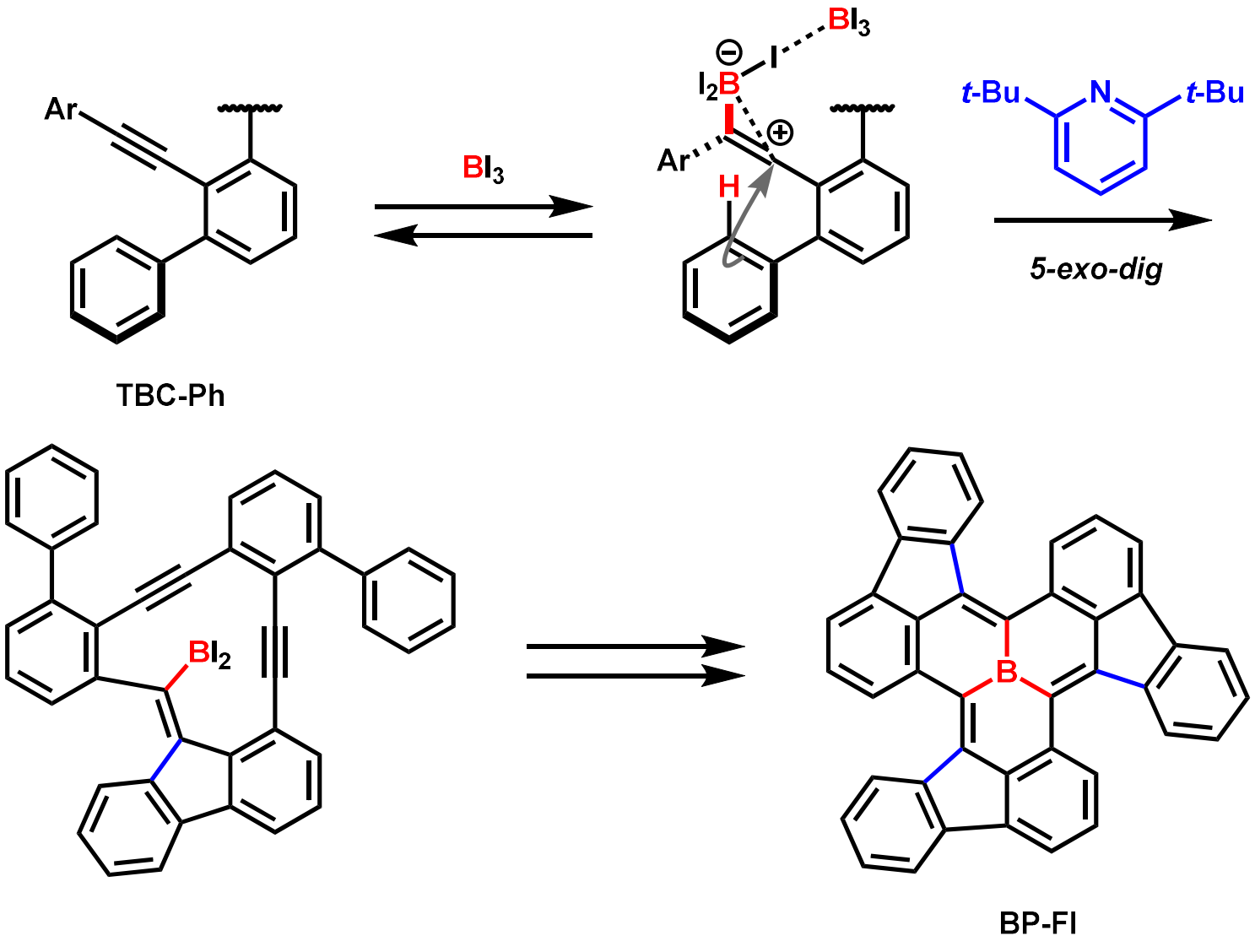
1) Ikeno, A.; Hayakawa, M.; Sakai, M.; Tsutsui, Y.; Nakatsuka, S.; Seki, S.; Hatakeyama, T. *J. Am. Chem. Soc.* **2024**, *146*, 17084.

Plausible Reaction Mechanism (BP-Phen)



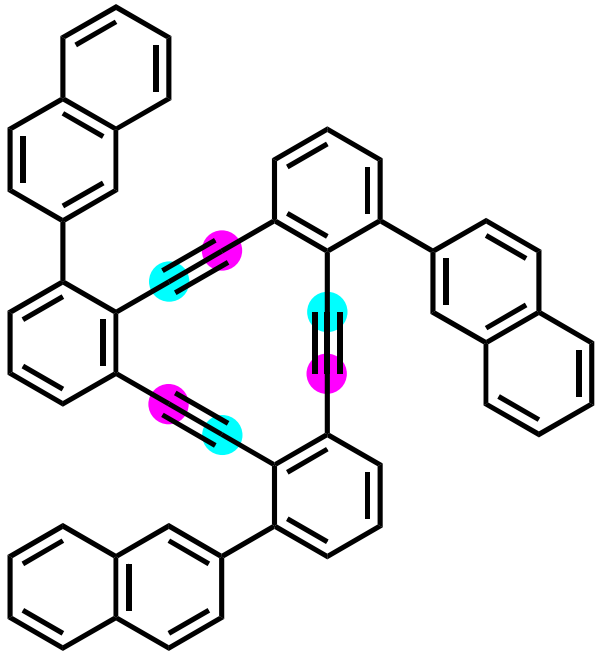
1) Ikeno, A.; Hayakawa, M.; Sakai, M.; Tsutsui, Y.; Nakatsuka, S.; Seki, S.; Hatakeyama, T. *J. Am. Chem. Soc.* **2024**, *146*, 17084.

Plausible Reaction Mechanism (BP-FI)

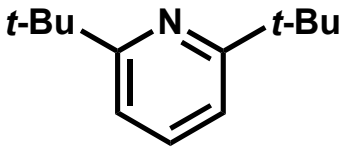


1) Ikeno, A.; Hayakawa, M.; Sakai, M.; Tsutsui, Y.; Nakatsuka, S.; Seki, S.; Hatakeyama, T. *J. Am. Chem. Soc.* **2024**, *146*, 17084.

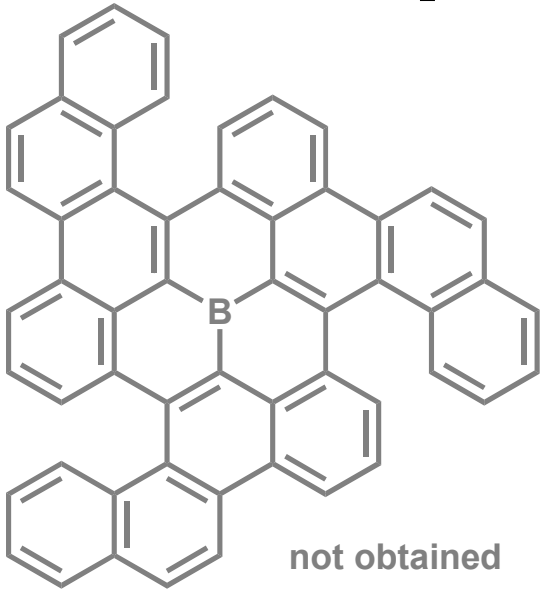
Borylative Cyclization from TBC-Nap



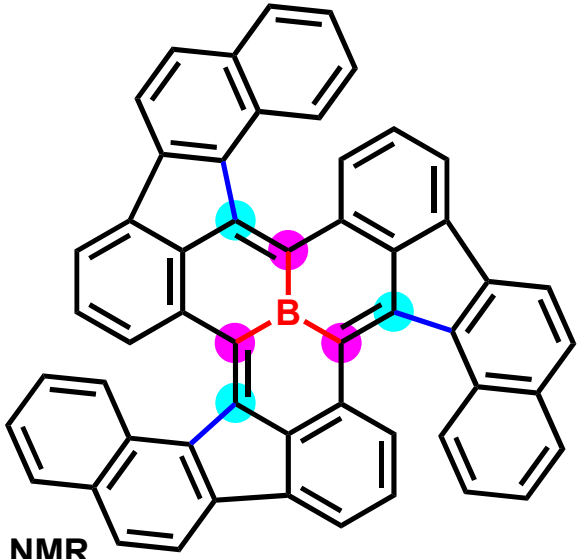
TBC-Nap



BI_3
1,2,4-trichlorobenzene
90 °C to 120 °C to 150 °C



not obtained

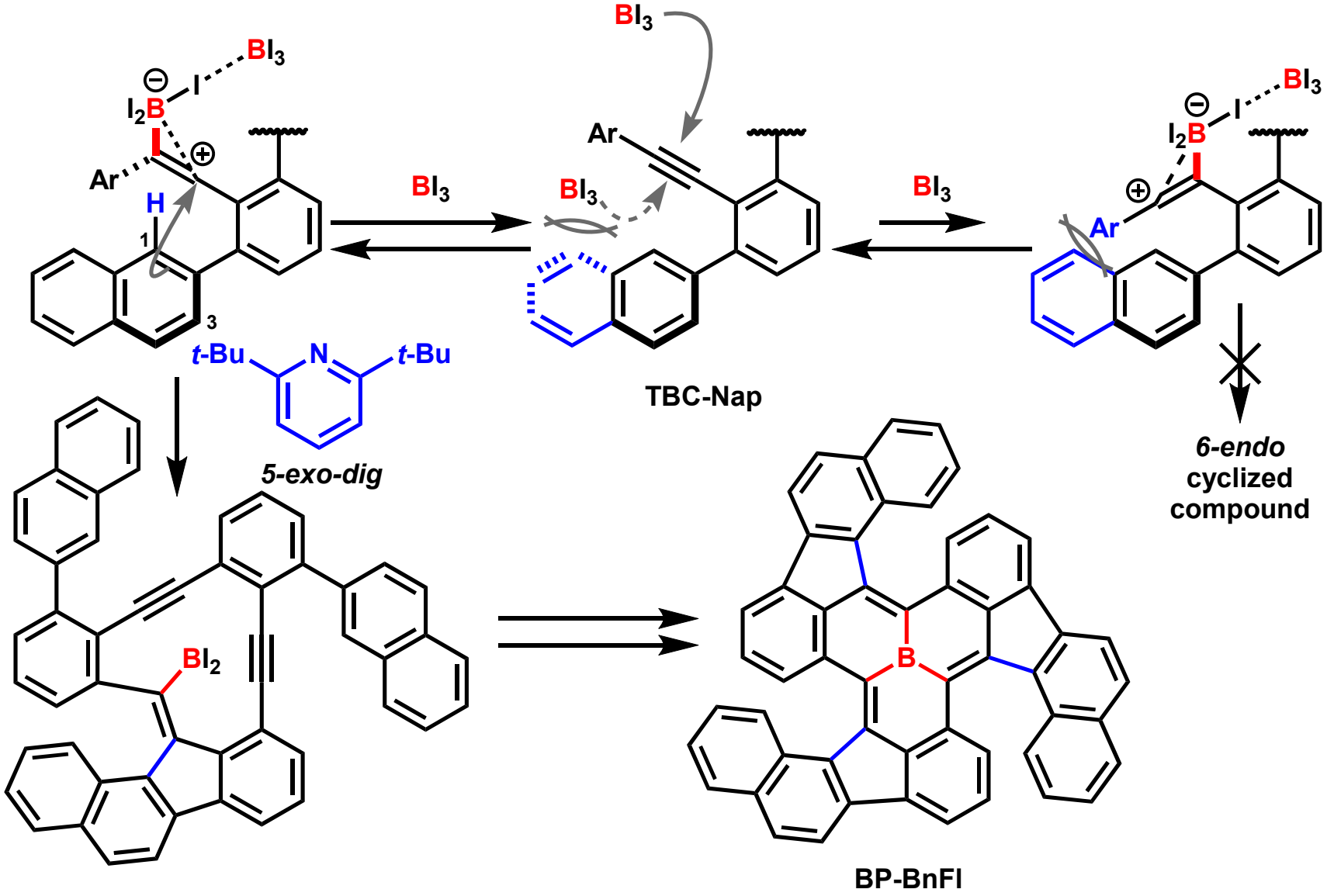


BP-BnFl : 5%[a] (15%[b])

a) isolated yield
b) yield in crude based on NMR

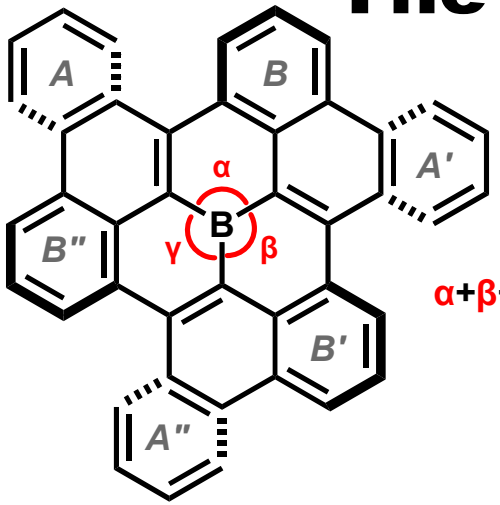
1) Ikeno, A.; Hayakawa, M.; Sakai, M.; Tsutsui, Y.; Nakatsuka, S.; Seki, S.; Hatakeyama, T. *J. Am. Chem. Soc.* **2024**, *146*, 17084.

Plausible Reaction Mechanism (my proposal)



1) Ikeno, A.; Hayakawa, M.; Sakai, M.; Tsutsui, Y.; Nakatsuka, S.; Seki, S.; Hatakeyama, T. *J. Am. Chem. Soc.* **2024**, *146*, 17084.

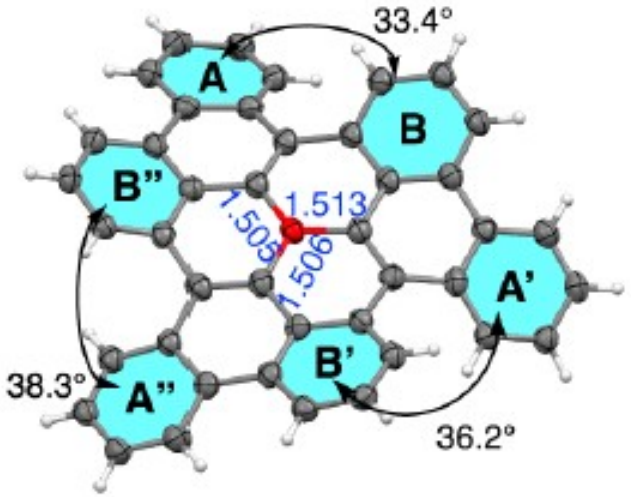
The Molecular Structures



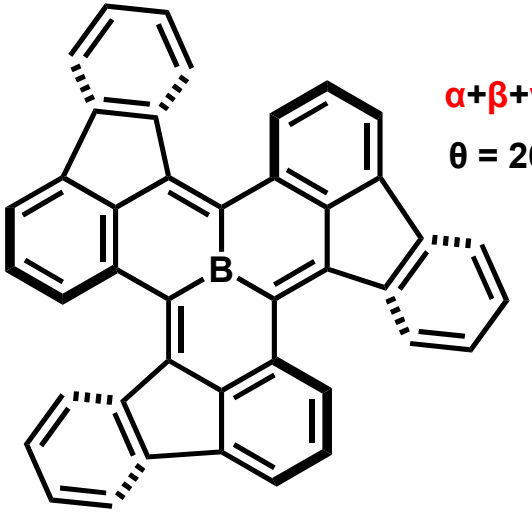
(*P*, *P*, *P*)-BP-Phen

≡

α+β+γ = 359.6°



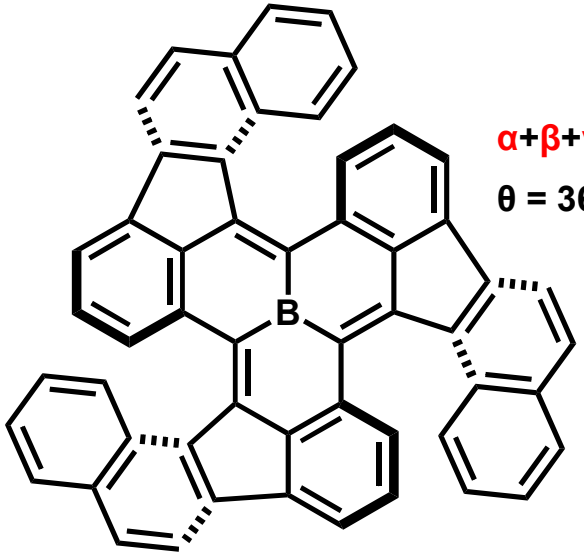
θ(A, B) = 33.4°
θ(A', B') = 36.2°
θ(A", B") = 38.3°



(*P*, *P*, *P*)-BP-Fl

α+β+γ = 359.3°

θ = 26.2°, 34.2°, 36.7°



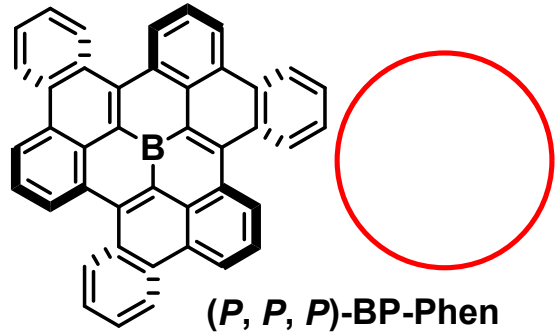
(*P*, *P*, *P*)-BP-BnFl

α+β+γ = 359.6°

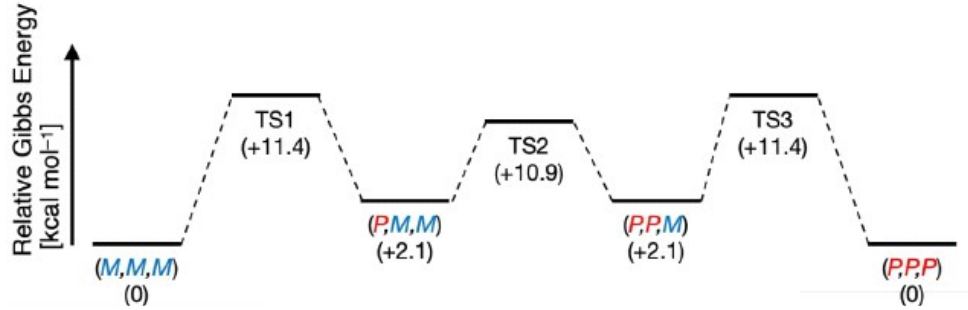
θ = 36.9°, 45.3°, 51.5°

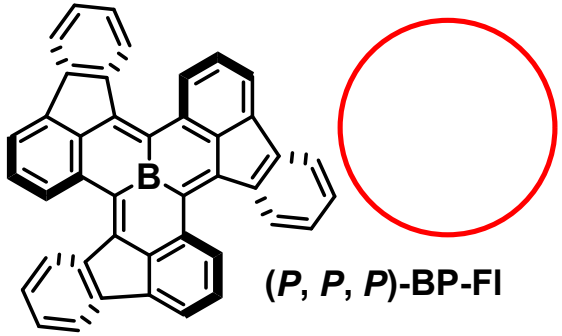
1) Ikeno, A.; Hayakawa, M.; Sakai, M.; Tsutsui, Y.; Nakatsuka, S.; Seki, S.; Hatakeyama, T. *J. Am. Chem. Soc.* **2024**, *146*, 17084.

Racemization Abilities

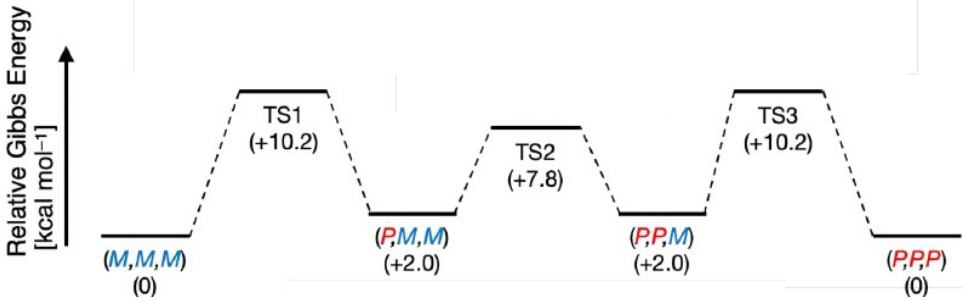


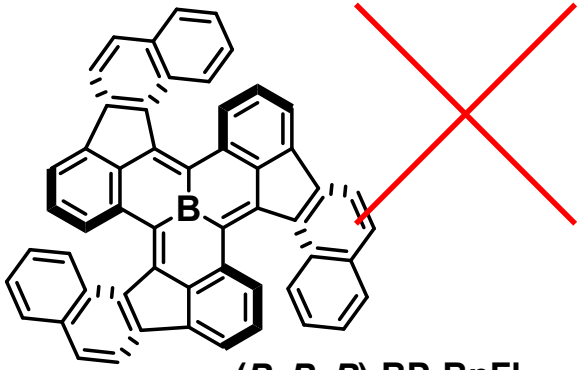
(*P*, *P*, *P*)-BP-Phen



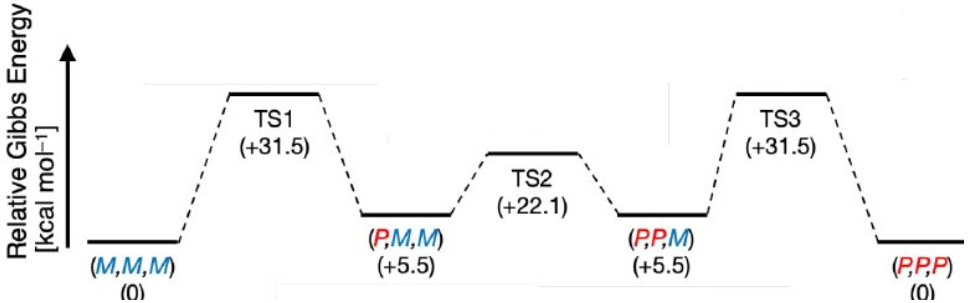


(*P*, *P*, *P*)-BP-Fl



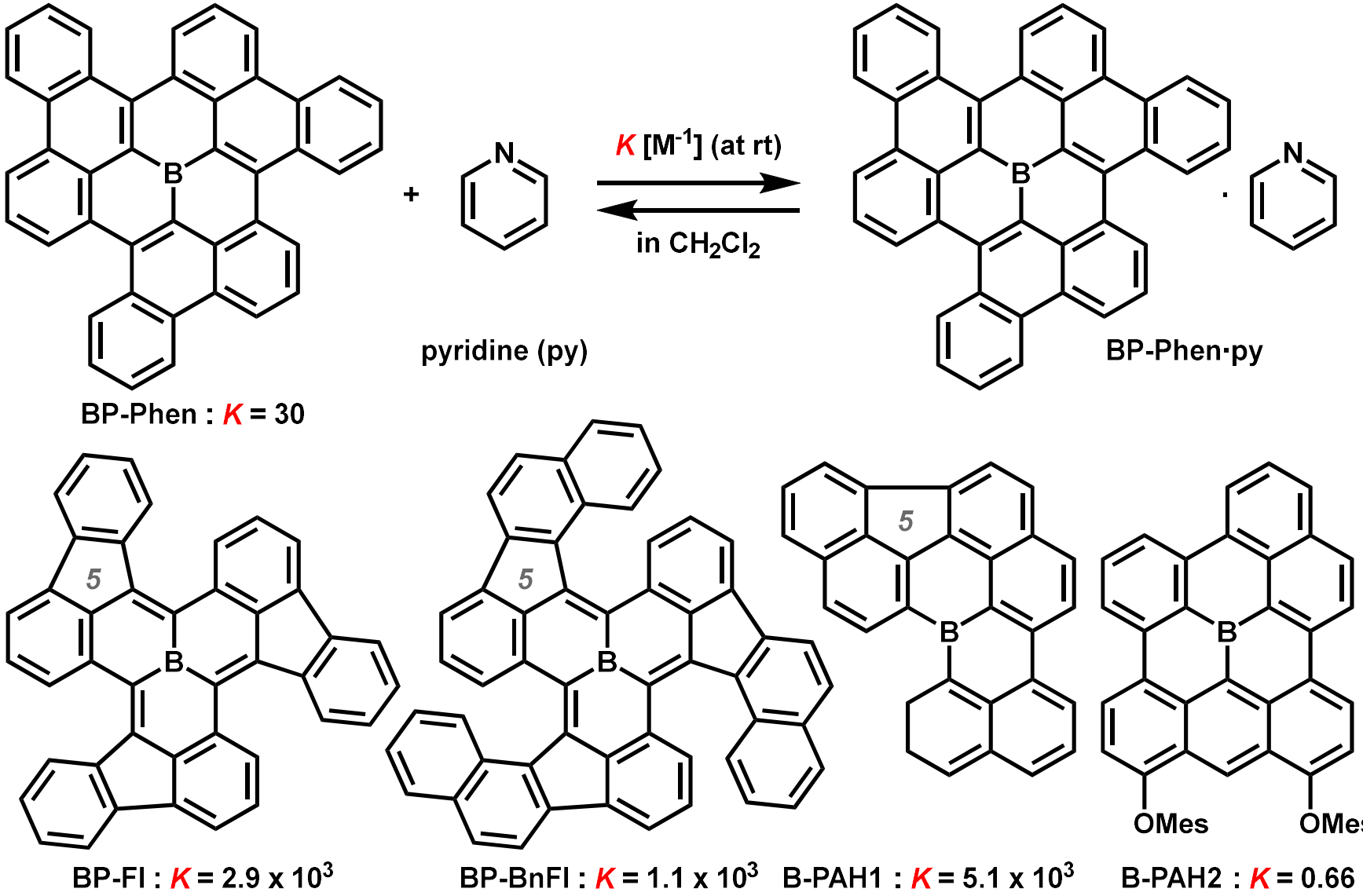


(*P*, *P*, *P*)-BP-BnFl



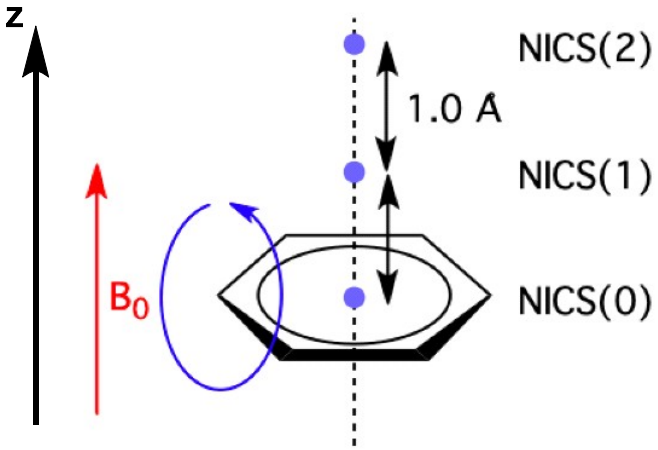
1) Ikeno, A.; Hayakawa, M.; Sakai, M.; Tsutsui, Y.; Nakatsuka, S.; Seki, S.; Hatakeyama, T. *J. Am. Chem. Soc.* **2024**, *146*, 17084.

Lewis Acidity of Boraphenalenes



1) Ikeno, A.; Hayakawa, M.; Sakai, M.; Tsutsui, Y.; Nakatsuka, S.; Seki, S.; Hatakeyama, T. *J. Am. Chem. Soc.* **2024**, *146*, 17084.

Introduction of NICS



Nucleus-Independent Chemical Shifts (NICS)

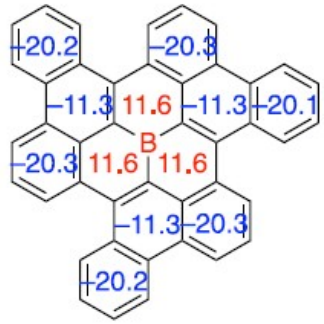
= Chemical Shifts of "dummy atom" which is located in the center of ring.
(+ : antiaromaticity, - : aromaticity)

NICS(x) : NICS value at x Å far from the center
NICS(x)$_{\pi}$: NICS(x) which comes from π (not σ)
NICS(x)$_{zz}$: z-component of NICS(x)

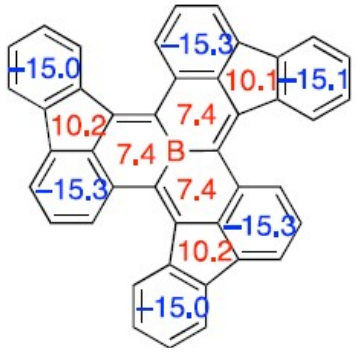
- **NICS(0)$_{\pi zz}$ is the best aromaticity index, but pre-calculation is needed.**
- **NICS(1)$_{zz}$ is the second-best index.**

1) Schleyer, P. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.
2) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. R. *Org. Lett.* **2006**, *8*, 863.

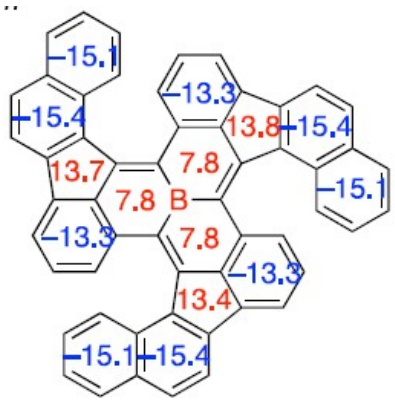
NICS(1) $_{zz}$ Values of Boraphenalenes and Their Dianions



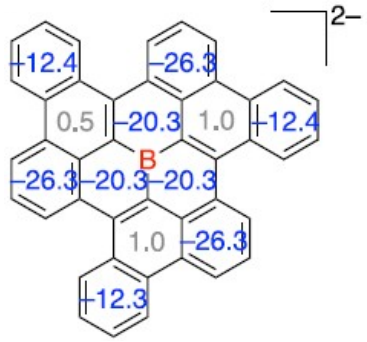
BP-Phen



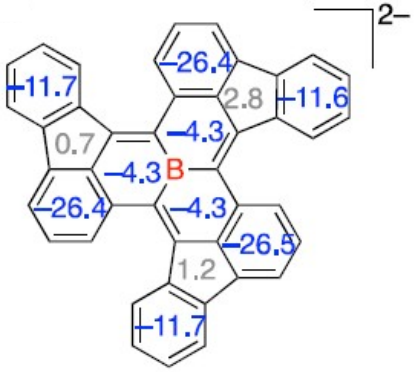
BP-FI



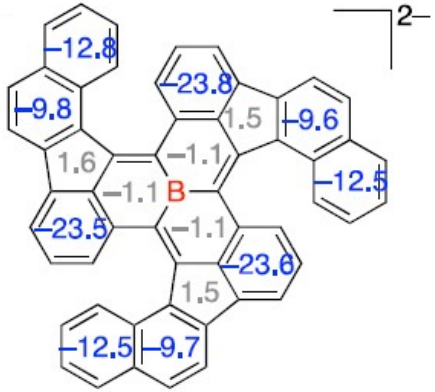
BP-BnFI



BP-Phen dianion



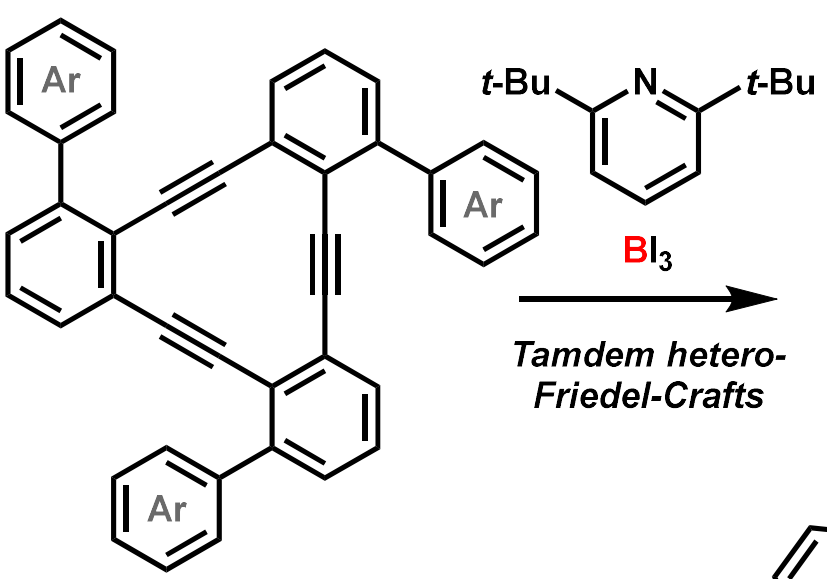
BP-FI dianion



BP-BnFI dianion

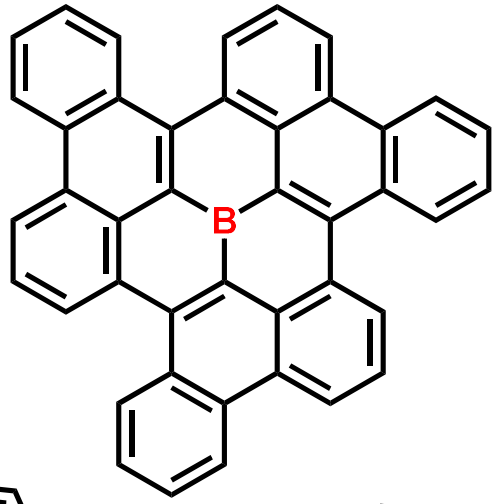
1) Ikeno, A.; Hayakawa, M.; Sakai, M.; Tsutsui, Y.; Nakatsuka, S.; Seki, S.; Hatakeyama, T. *J. Am. Chem. Soc.* **2024**, *146*, 17084.

Summary

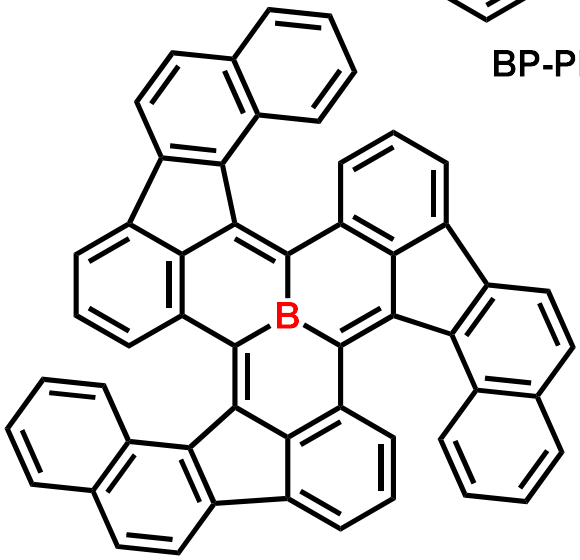


TBC-Ph (Ar = Ph)
TBC-Nap (Ar = 2-Naphthyl)

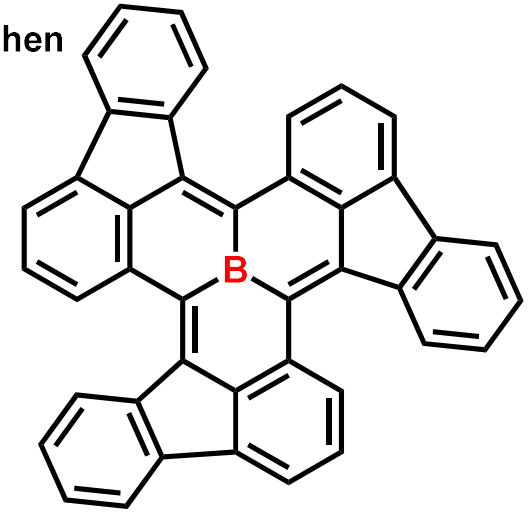
Tamdem hetero-Friedel-Crafts



BP-Phen



BP-BnFl



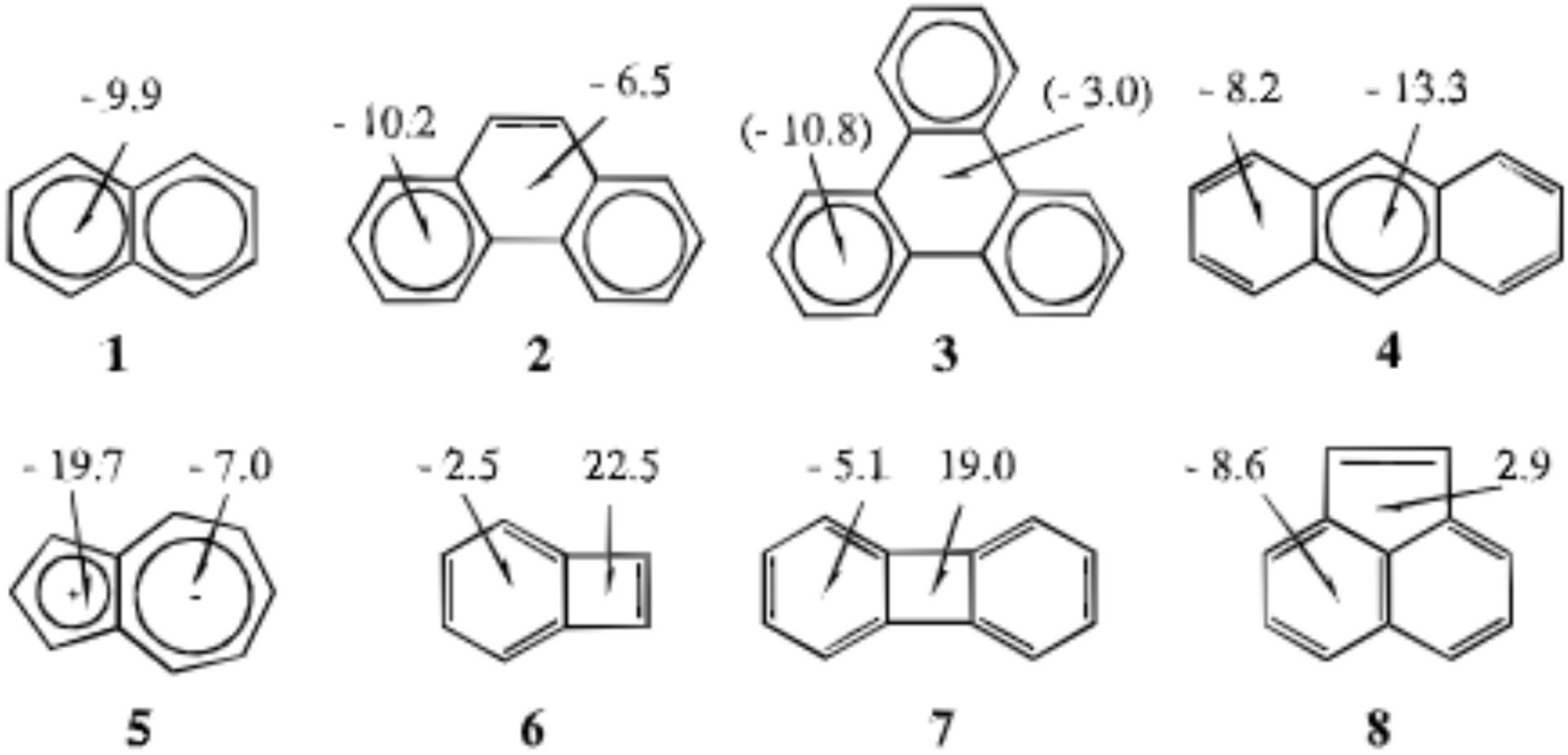
BP-Fl

- Synthesis of "new 9b-boraphenalene"
- Lewis acidity
- Aromaticity/antiaromaticity

1) Ikeno, A.; Hayakawa, M.; Sakai, M.; Tsutsui, Y.; Nakatsuka, S.; Seki, S.; Hatakeyama, T. *J. Am. Chem. Soc.* **2024**, *146*, 17084.

Appendix

Examples of NICS(0) Values



1) Schleyer, P. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.