An Investigation of Organic Radicals for Magnetic Polymers

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RISE est. 1996

SEFEROS RESEARCH GROUP

A History of Magnets

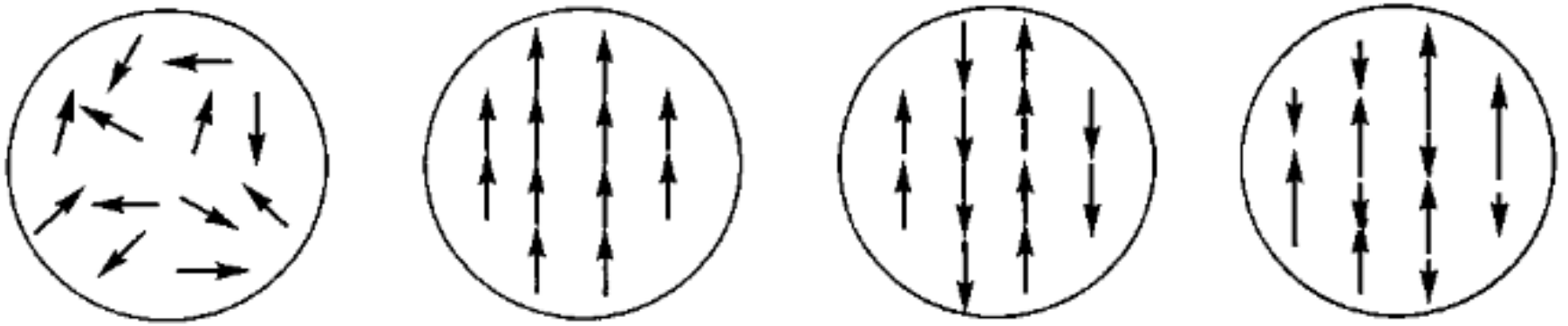
- Ancient people discovered lodestones that attract metals. Composition: mostly Fe_3O_4
- Around 2500 years ago, magnets were applied as compasses for navigation in Europe, China and elsewhere
- Nowadays, magnets have become a part of our life




Schmidl, P. S. Journal of Arabic and Islamic Studies 2017, 1, 81.

Why is a Compound Magnetic?

- If two electrons are paired together in an orbital, they are diamagnetic elections (total spin = 0).
- If electrons are not paired, they exhibit paramagnetism
- Types of magnetism

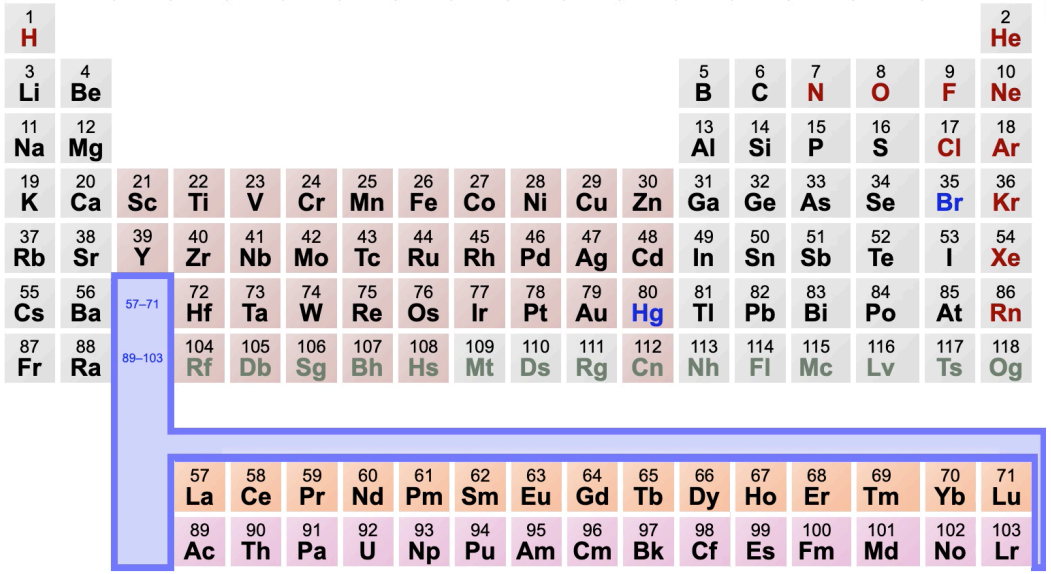


Paramagnetism Ferromagnetism Antiferromagnetism Ferrimagnetism

M. Kamachi, Journal of Macromolecular Science Part C- Polymer Reviews, 2002.

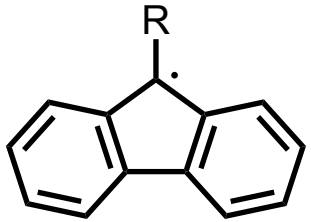
Traditional Magnets

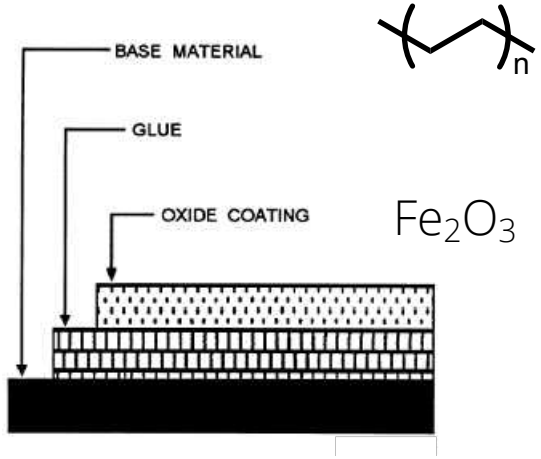
- Spin-containing molecules (unpaired electrons in d-, f- orbitals)
  - Transition, lanthanide, and actinide metals
    - e.g. Cobalt
  - Oxidized Metal
    - e.g. Fe_3O_4



Hankache, J.; Wenger, O. S. Organic Mixed Valence. ChemInform, 2011, 42(43).

Organic Magnets

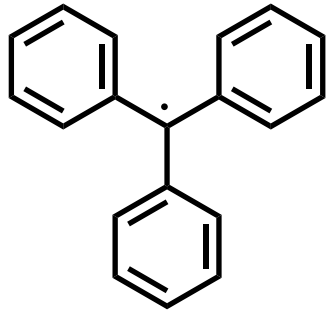
- Metal-containing organic polymers
  - Not themselves magnetic
  - e.g. Magnetic tape, magnetic gum
- Paramagnetic small molecules and polymers
  - Polycarbenes 
  - Free radicals 



Rajca, A. Magnetic Ordering in an Organic Polymer. *Science,* 2001, *294*(5546), 1503–1505.
Integrated Publishing, Inc. http://electronicstechnician.tpub.com/14091/css/Magnetic-Tape-Construction-234.htm

Radical Species

- Organic radicals often appear as reaction intermediates
- Featured with short life time and high reactivity
- Stable organic radical
  - Not air/moisture sensitive
  - Can be stored/handled under ambient conditions
    - Unpaired electron delocalized throughout conjugated system
    - Sterical hindrance that prevents radicals from reacting

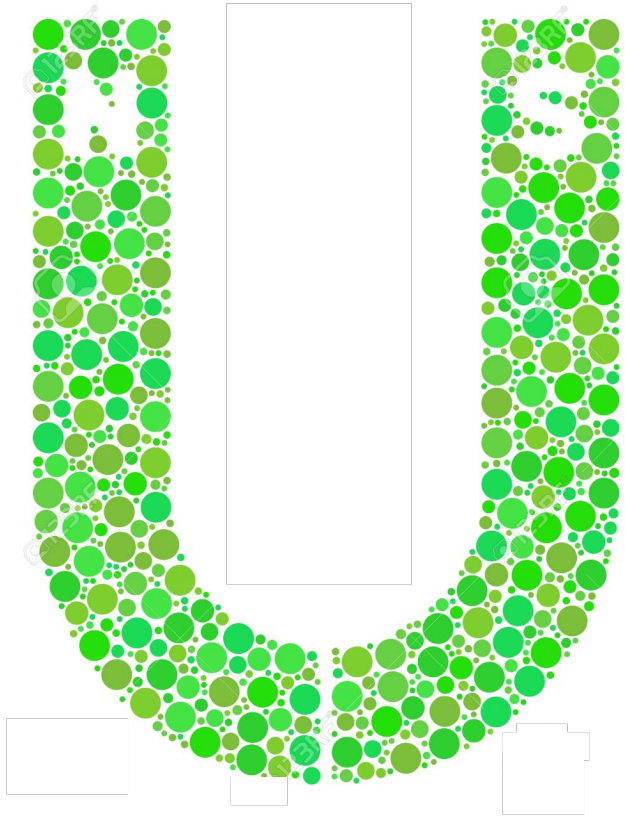


Triphenylmethyl radical
first carbon centered stable radical
discovered by Gomberg in 1900

Zhang, K.; Monteiro, M. J.; Jia, Z. Stable Organic Radical Polymers: Synthesis and Applications. Polymer Chemistry 2016, 7(36), 5589–5614.

Organic Magnets Have Potential for New Applications

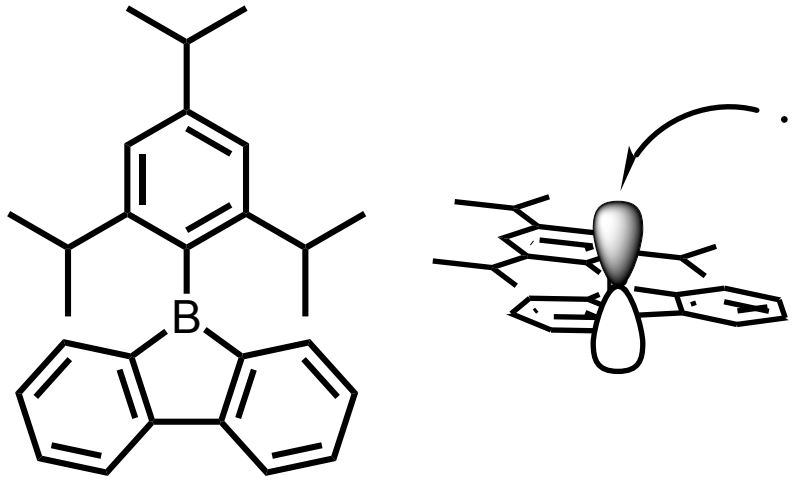
- Magnetic properties
  - Attraction and repulsion through space
- Polymer properties
  - Crystalline
  - Optically active
  - Stretchable



Stock Photo from http://www.123rf.com

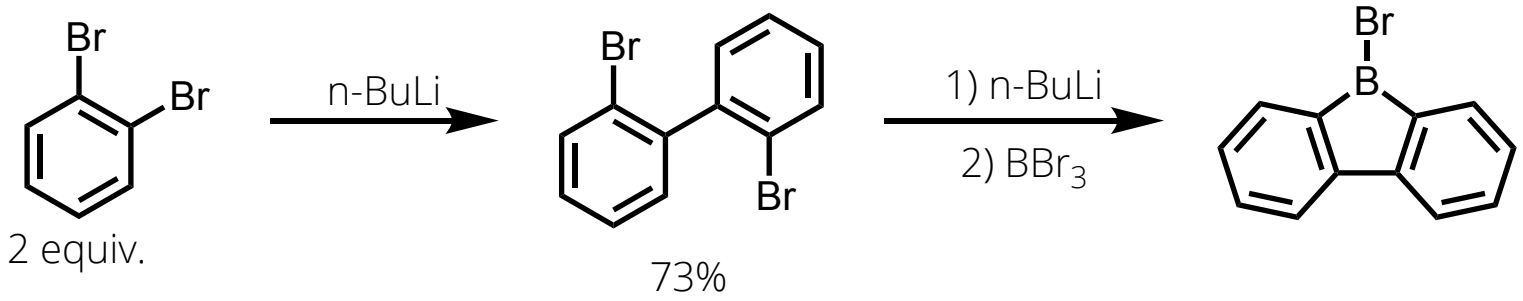
Reaction Target: TipBF

- Rationale
  - Delocalization achieved by the π-conjugated system
  - Empty p-orbital on boron
  - Retain planar molecular structure and aromaticity



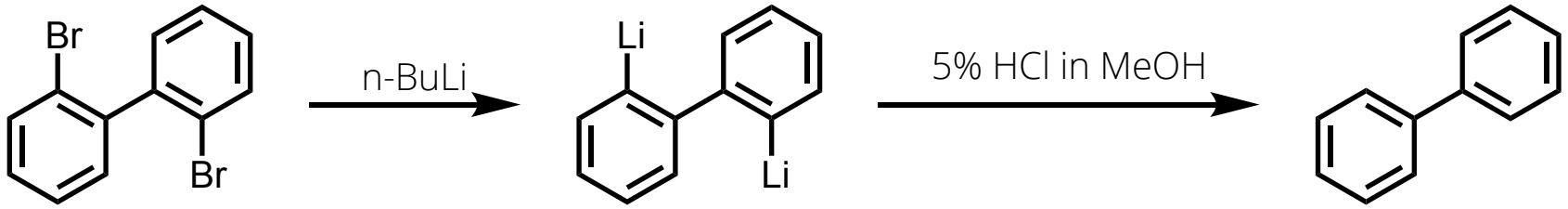
TipBF = 2,4,6-tris(triisopropyl)phenyl borafluorene

Attempted Synthesis of 9-Bromoborafluorene

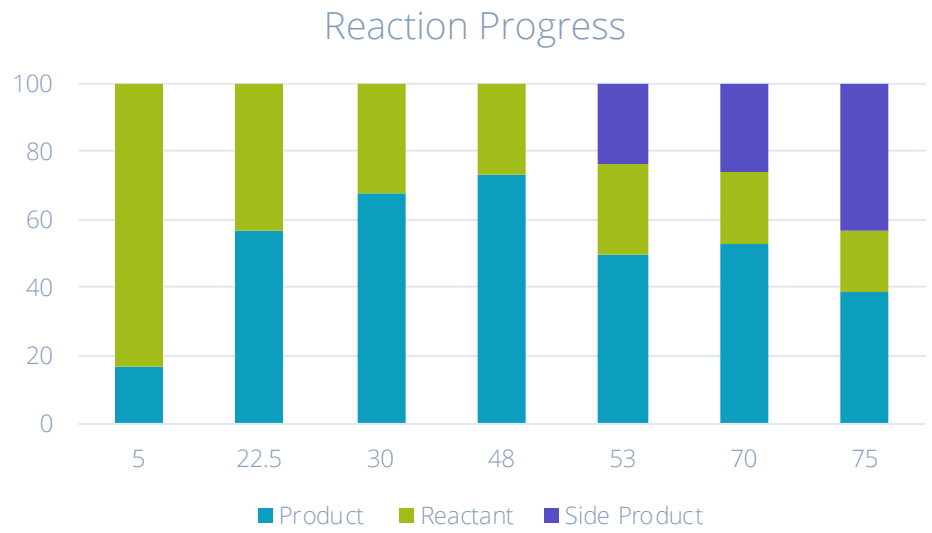


- 2,2'-Dibromobiphenyl was successfully synthesized
- Second step after purification yielded brown powder (a lot of side products)

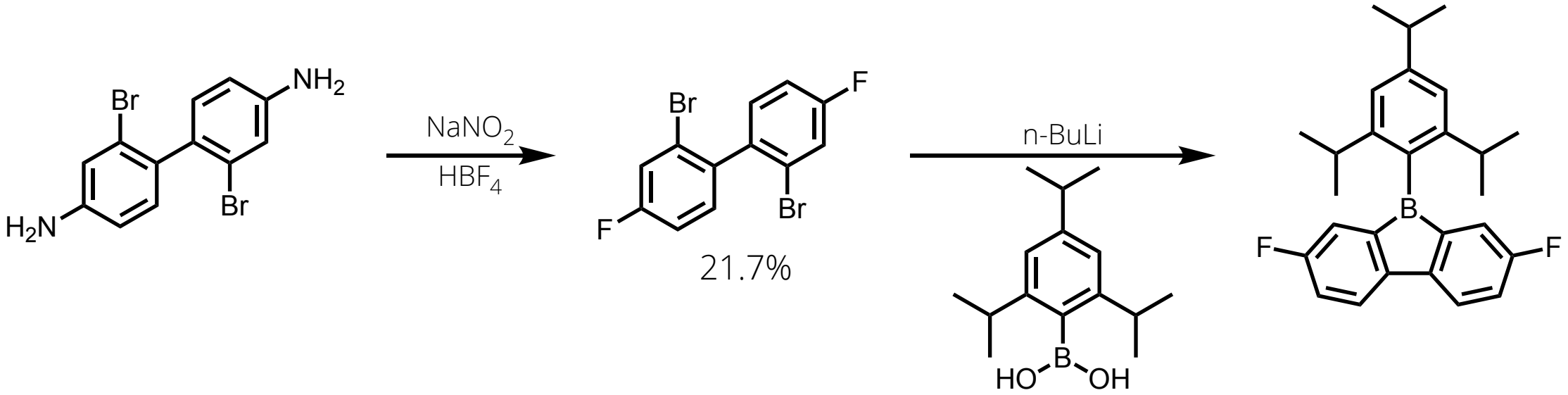
Lithiation Test



- Taking aliquots every few hours
- Work-up using acid
- Characterized by NMR



Attempted Synthesis of TipBF



- No product observed in second step

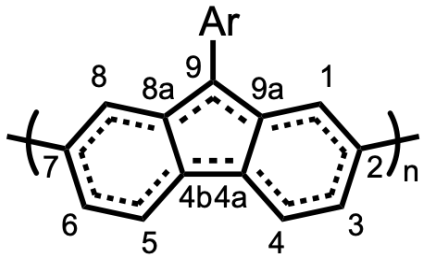
TipBF = 2,4,6-tris(triisopropyl)phenyl borafluorene

Summary for 9-Borafluroenes Derivatives

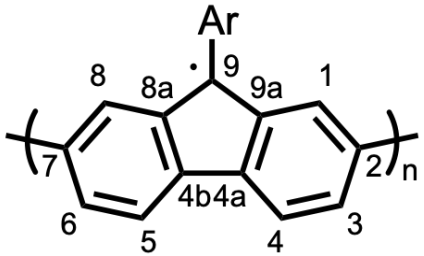
- Pros
  - Stabilization through π-conjugated system
  - Retain planar molecular structure and aromaticity
- Cons
  - Extremely air unstable
  - Difficult to synthesize and purify

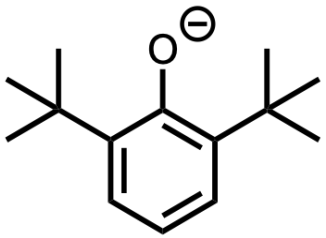
Fluorene Derivatives

- Rationale
  - Fluorenes are π-conjugated planer structure
  - Mostly air stable, easy to handle
  - Well delocalize the 9-position radical with two aromatic system aside

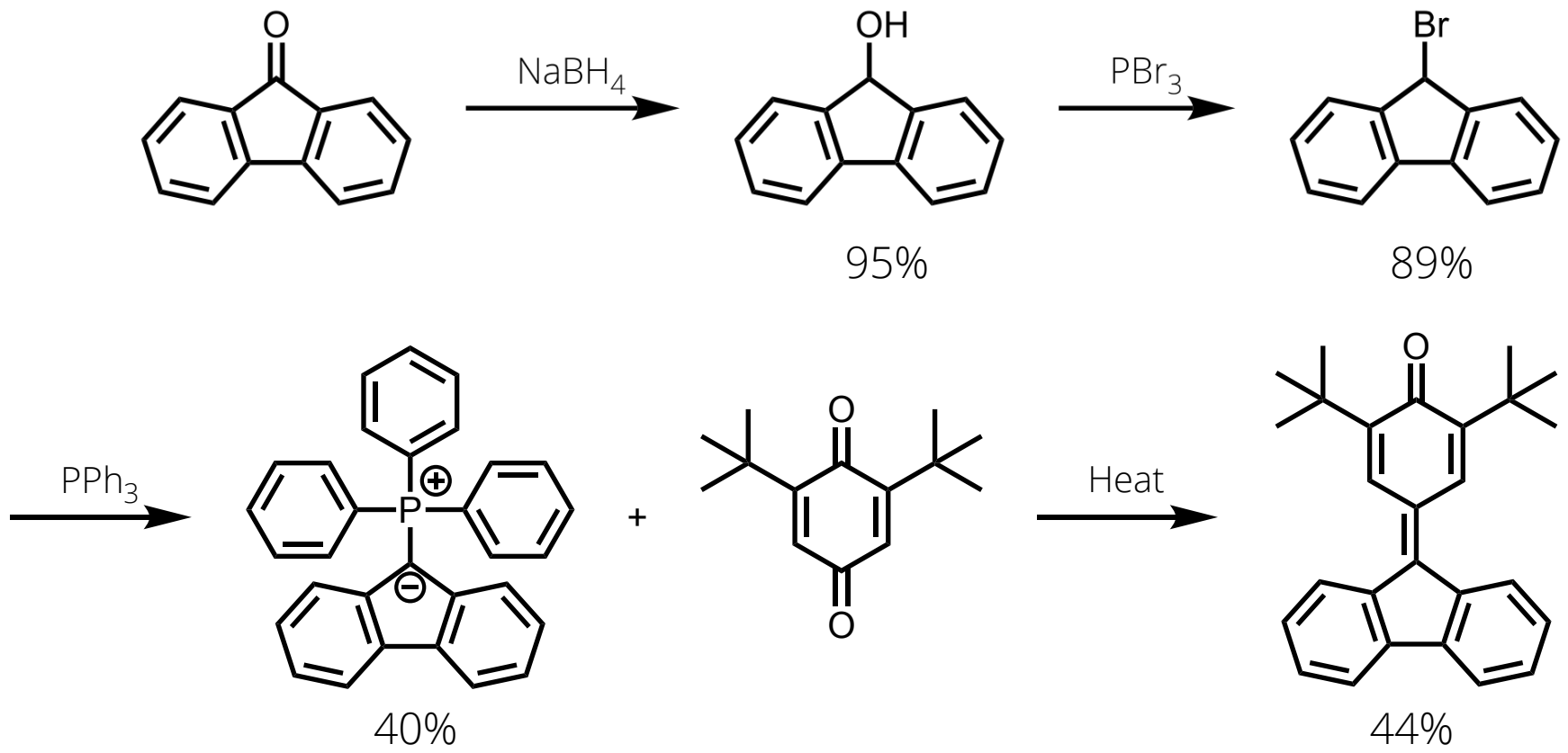


- Targeting Molecule



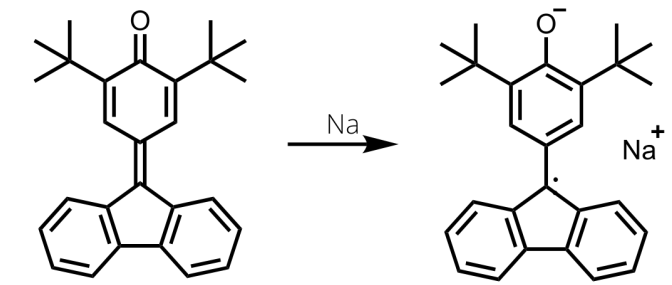


Synthetic Route



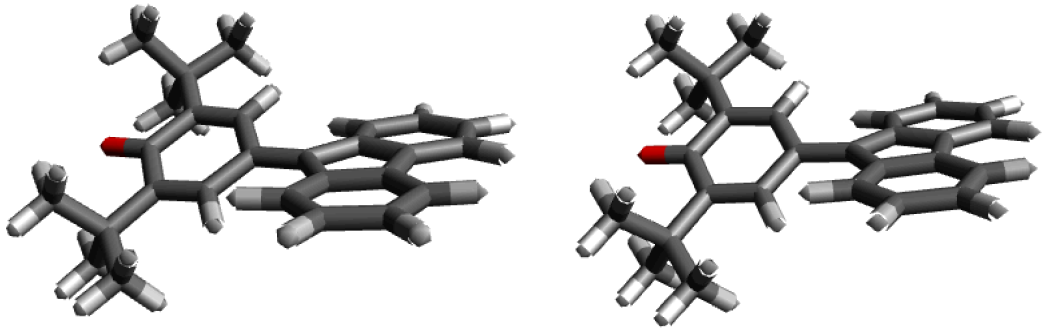
Testing Radical Formation

- Driving Force
  - Increase of aromaticity
- Countering Force
  - Formation of a free radical
  - Increase of formal charge



-2.9439 × 10^6 KJ/mol

- 2.9442× 10^6 KJ/mol



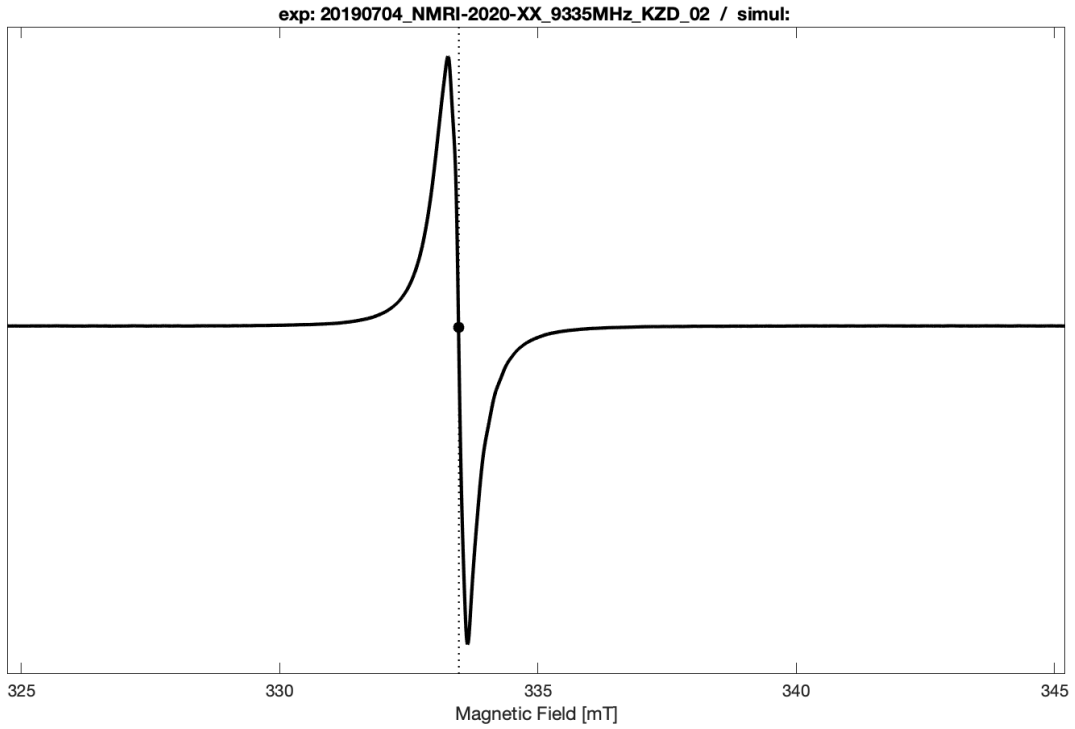
25.2°

31.8°

Basis Set: B3LYP/gen 6-311+G(d,p) SCRF=(solvent=water)

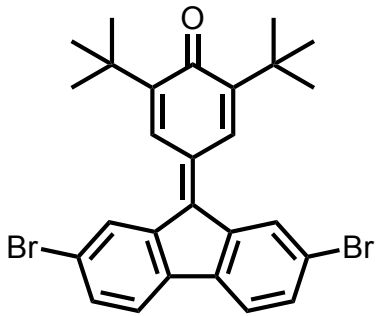
Electron Paramagnetic Resonance Analysis of Organic Radical

- Experiment Parameters
  - Field = 3334.6 Gauss
  - Frequency = 9.391 GHz
- G-factor = 2.0121

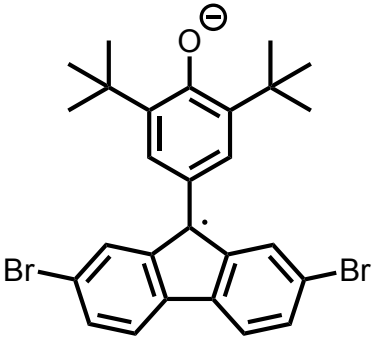


Theoretical Calculation for the Next Step

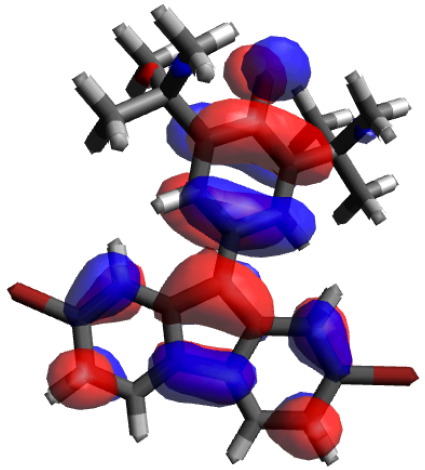
- Verified radical insertion on small molecule
- 2, 7 dibromo-functionalized group were chosen for polymerization
- HOMO of the radical form,
  and LUMO of the neutral form were calculated using Gaussian 09



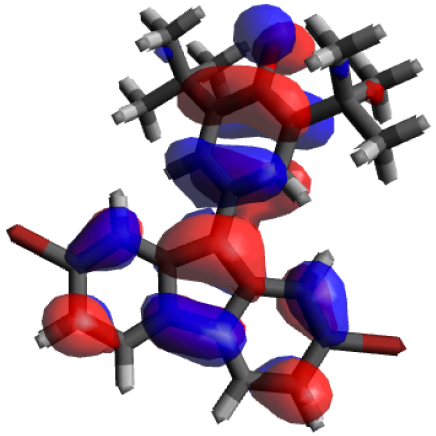
LUMO



HOMO



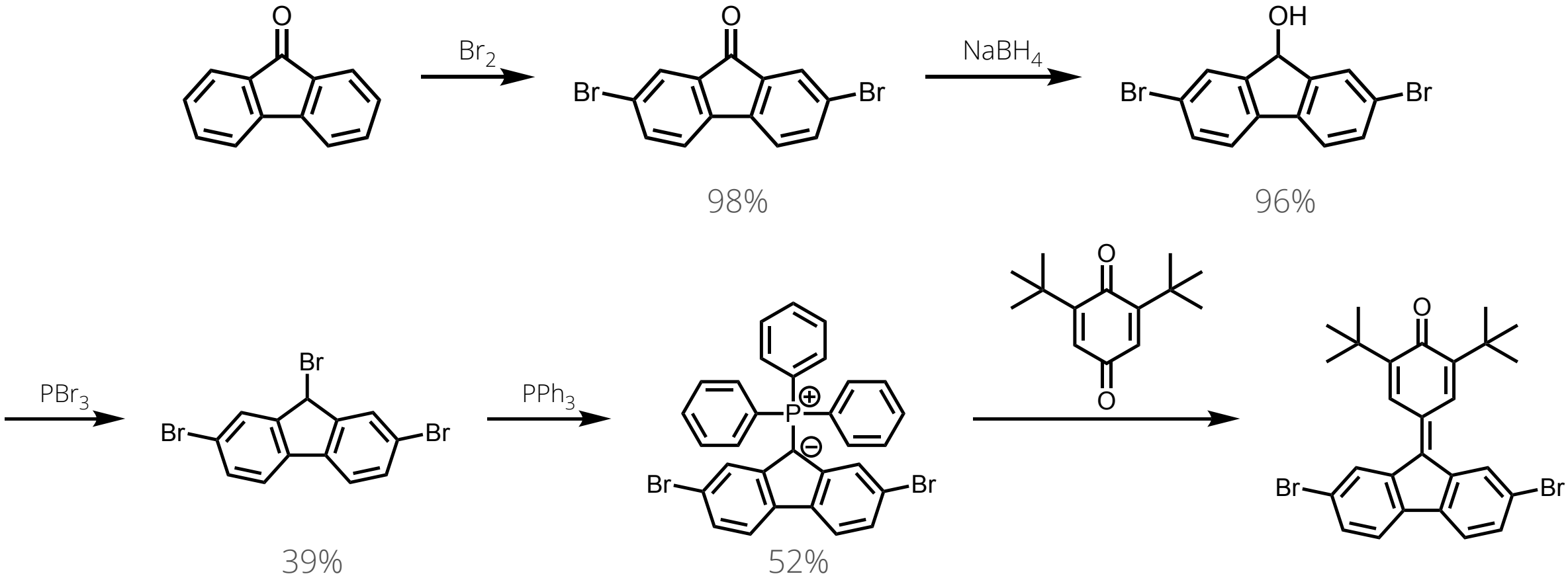
25.4°



31.9°

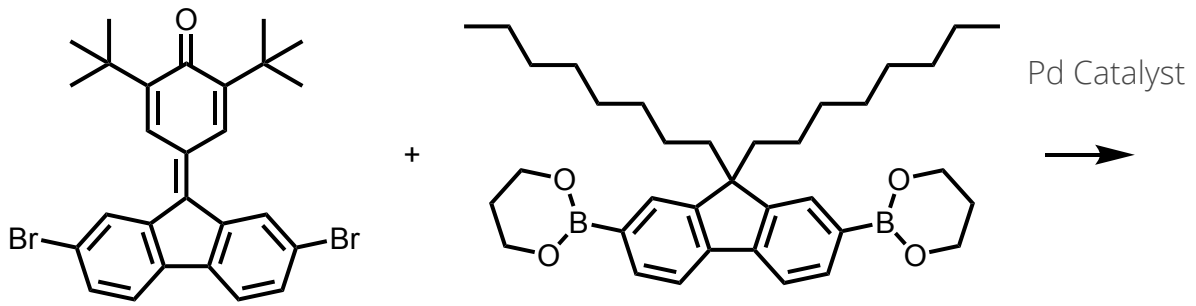
Basis Set: B3LYP/gen 6-311+G(d,p) SCRF=(solvent=water)

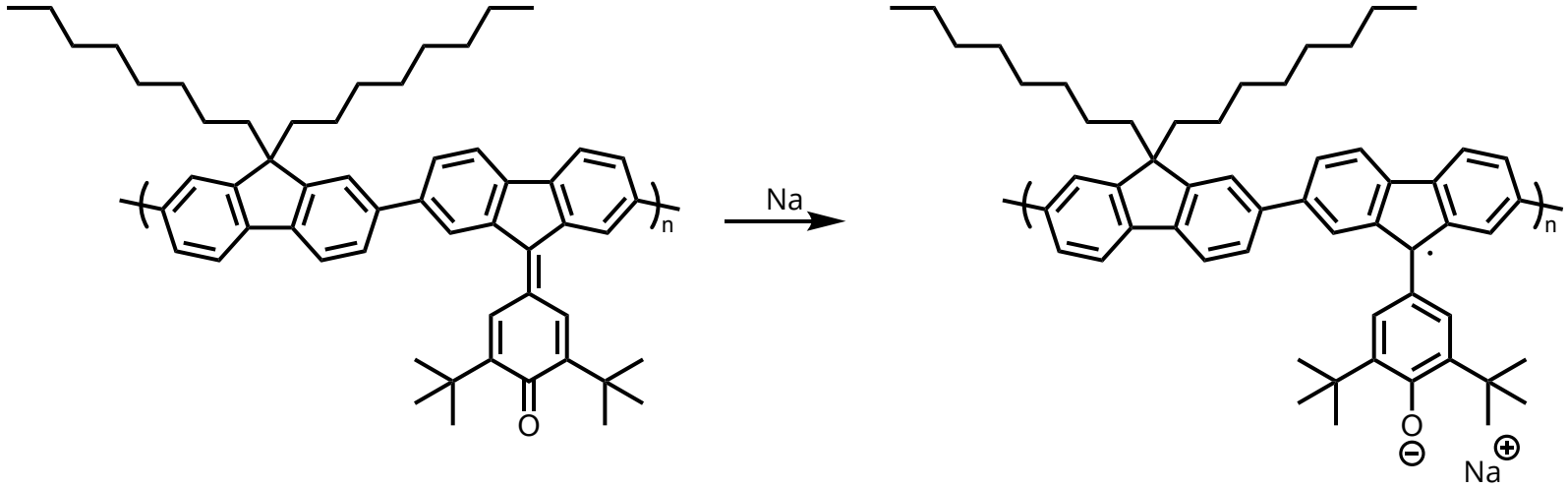
Synthetic Scheme for Fluorene Monomer



Future Work

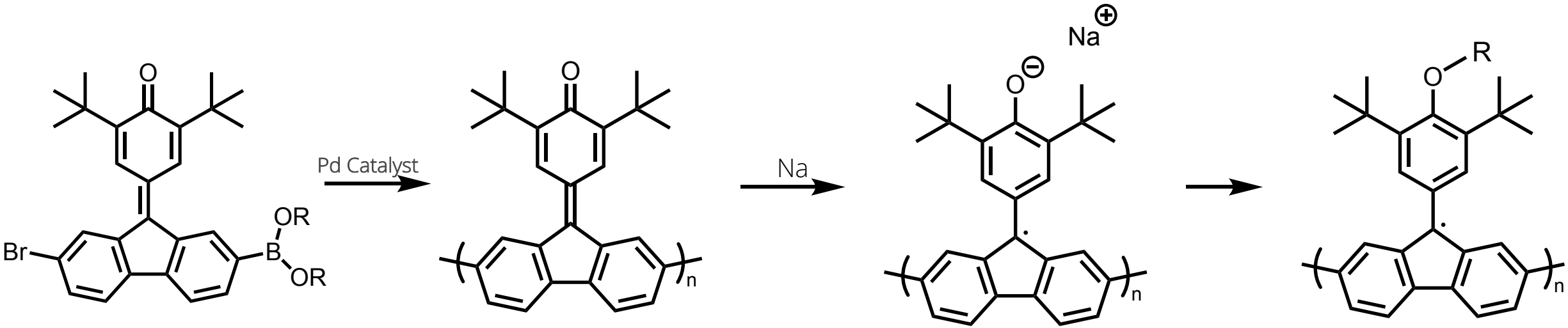
- Dibromo structure requires boronic ester functionalized coupling partner
- 9,9-dioctyl fluorene-2,7-diboronic acid bis(1,3-propanediol) ester was planned to be used to make copolymer





Future Work

- Homopolymer synthesis
- Investigate neutral radical polymers



Acknowledgments

Current Members

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Garion Hicks
Gabrielle Hoover
Dr. Charlie Jarrett-Wilkins
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George McKeown
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Nimrat Obhi
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Adam Pollit
Dr. Niradha Sachinthani
Luke Yang
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