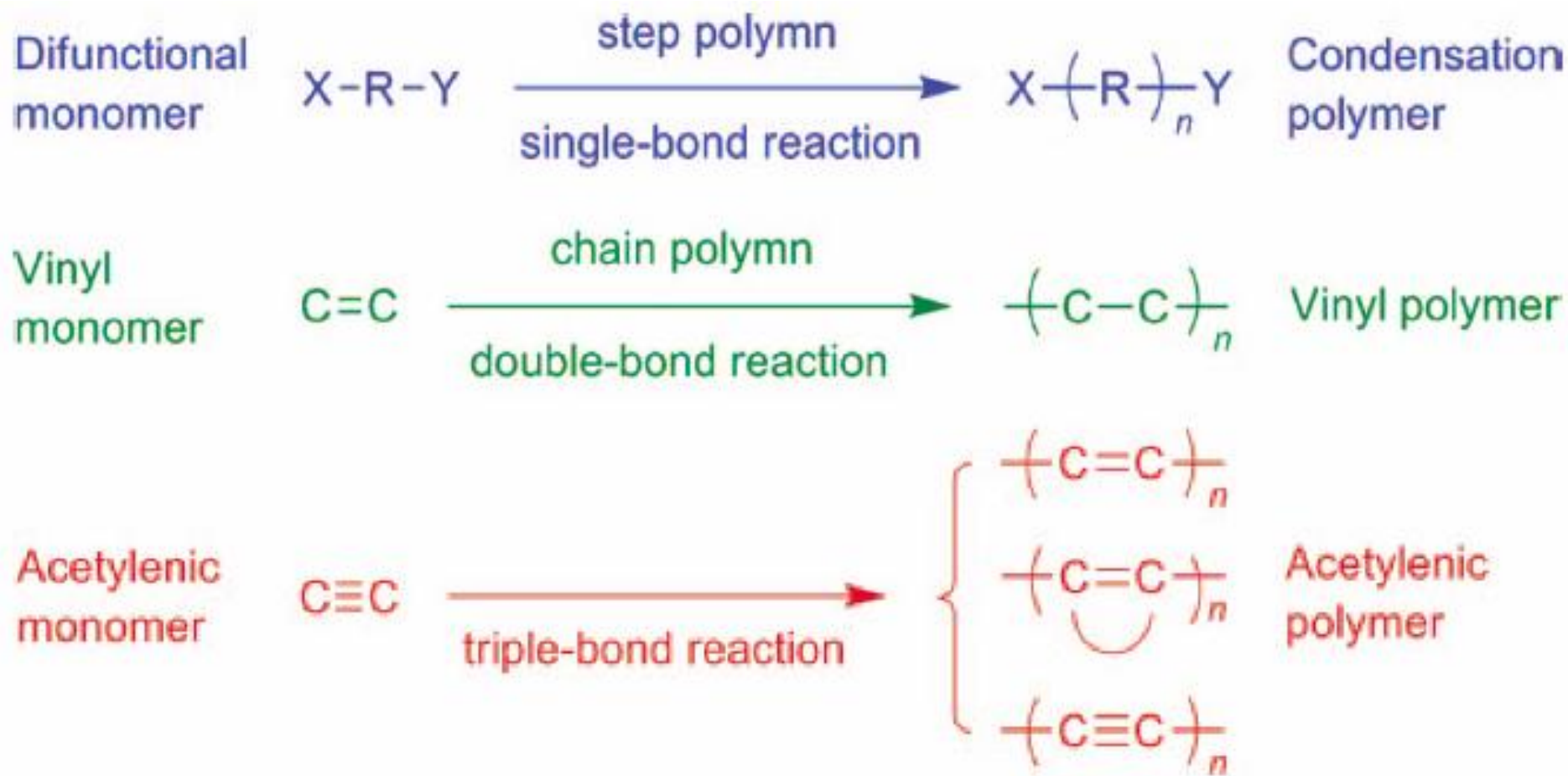


Metal-Catalyzed Alkyne Polymerization

Chris Johnson

Traditional Polymerizations



Polyacetylene



Heeger



MacDiarmid



Shirikawa

Polyacetylene

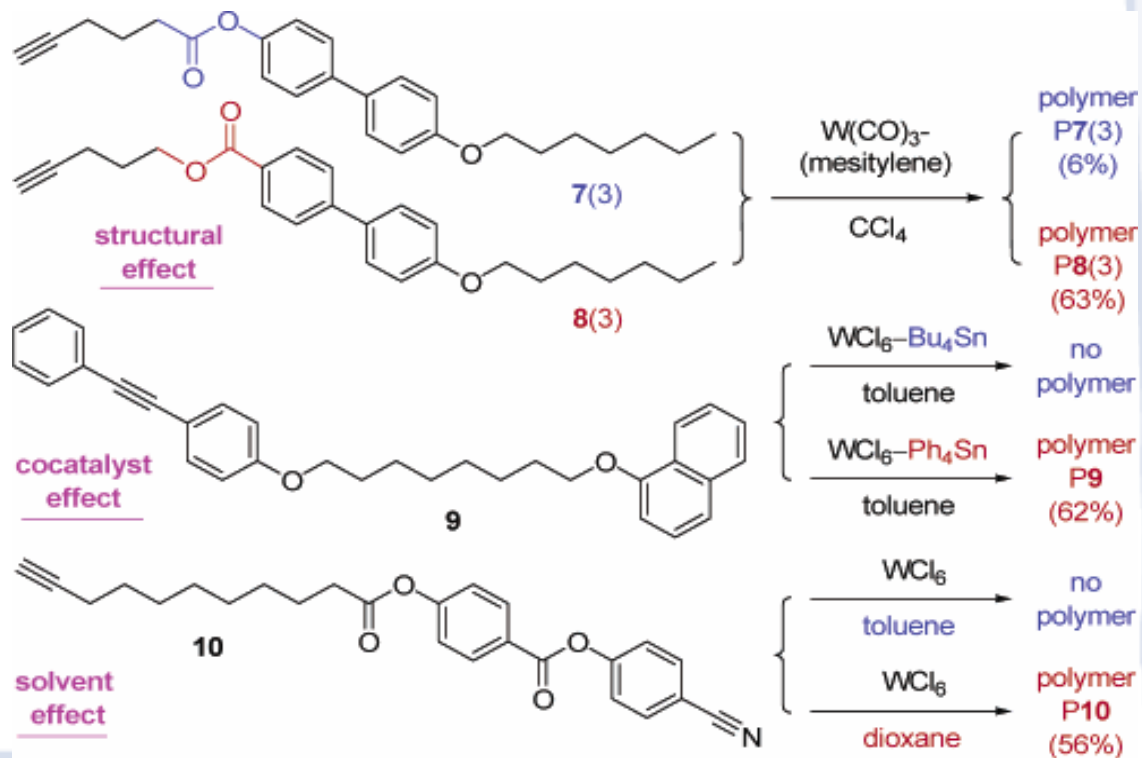
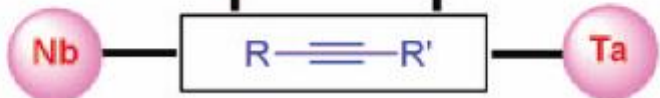
Unsubstituted acetylene



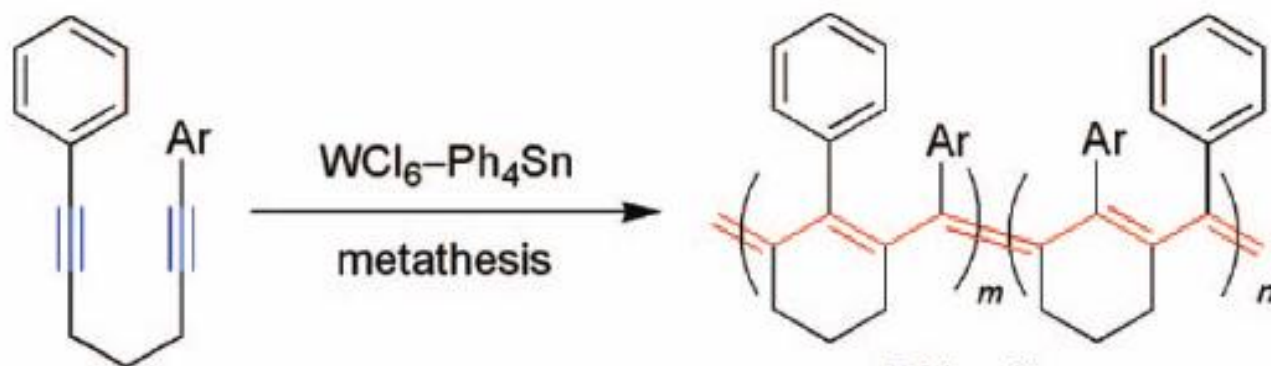
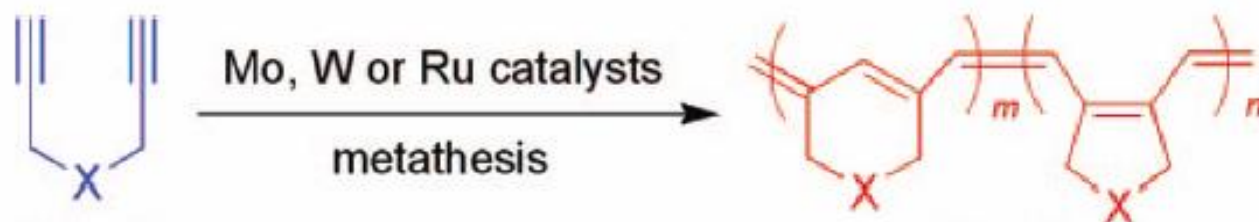
Monosubstituted acetylene



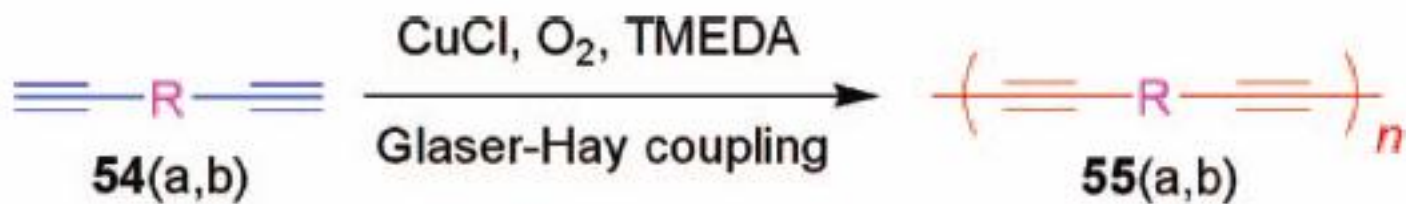
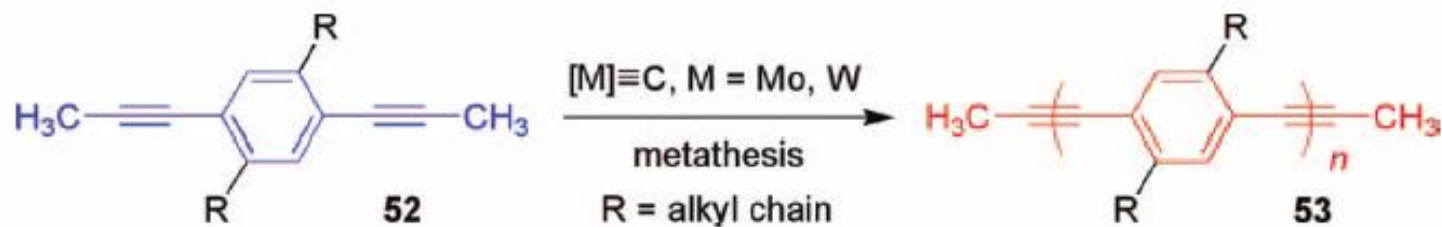
Disubstituted acetylene



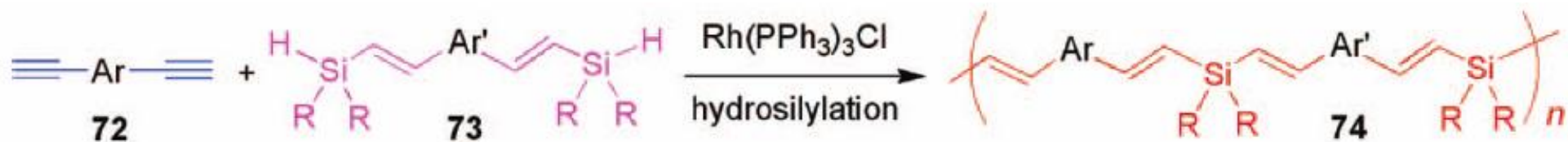
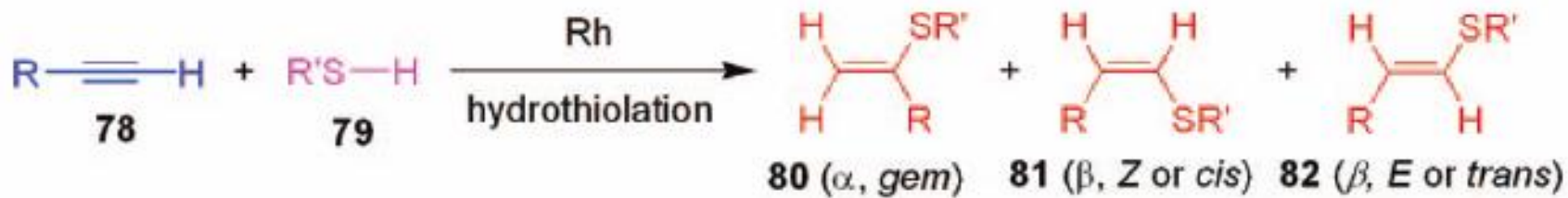
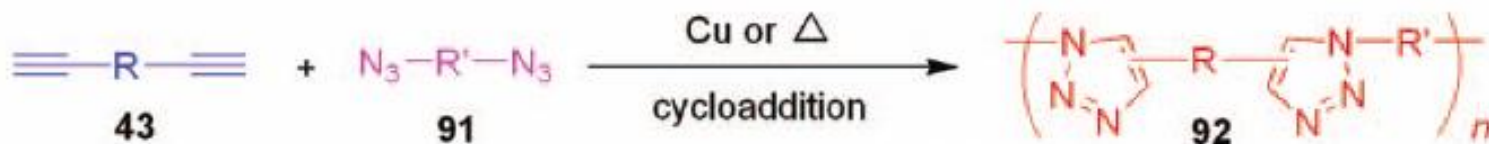
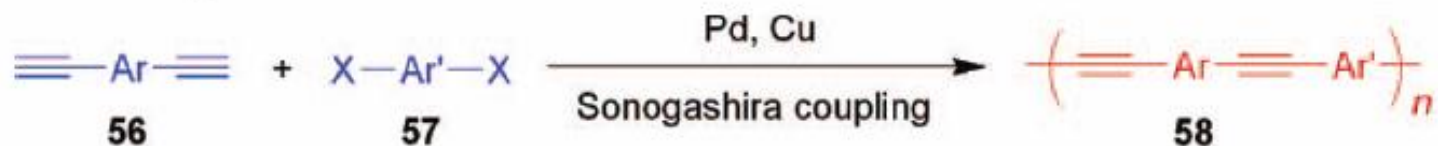
Diyne Polymerization



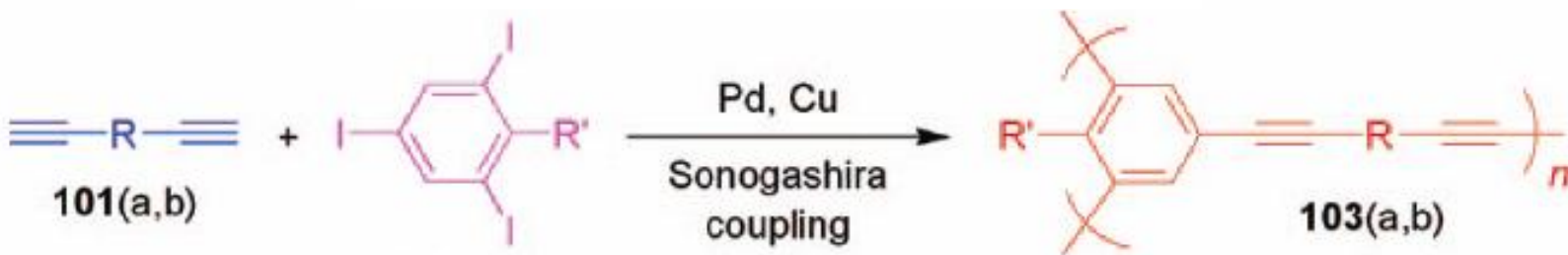
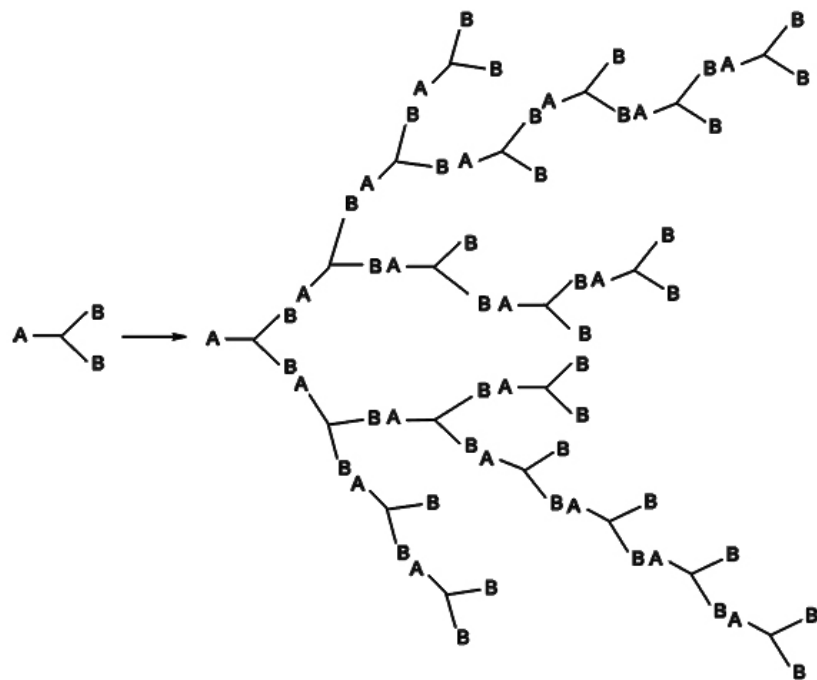
Diyne Polymerization



A-A B-B Polymerization

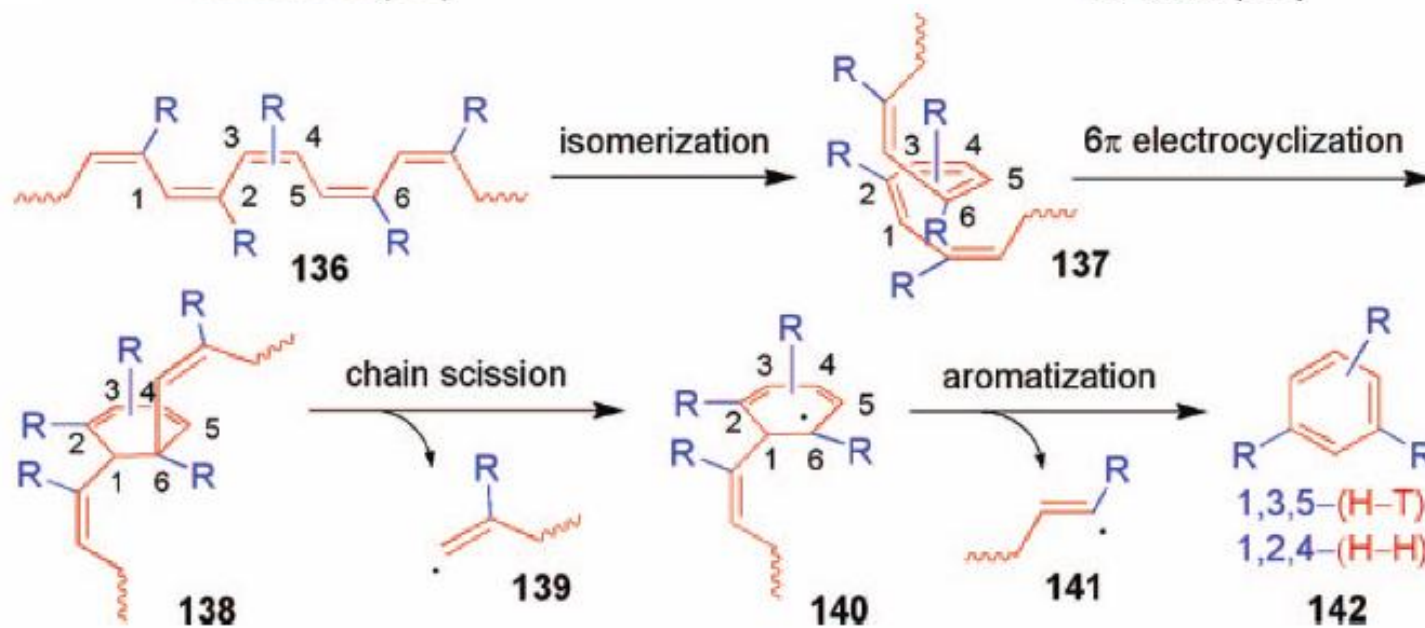
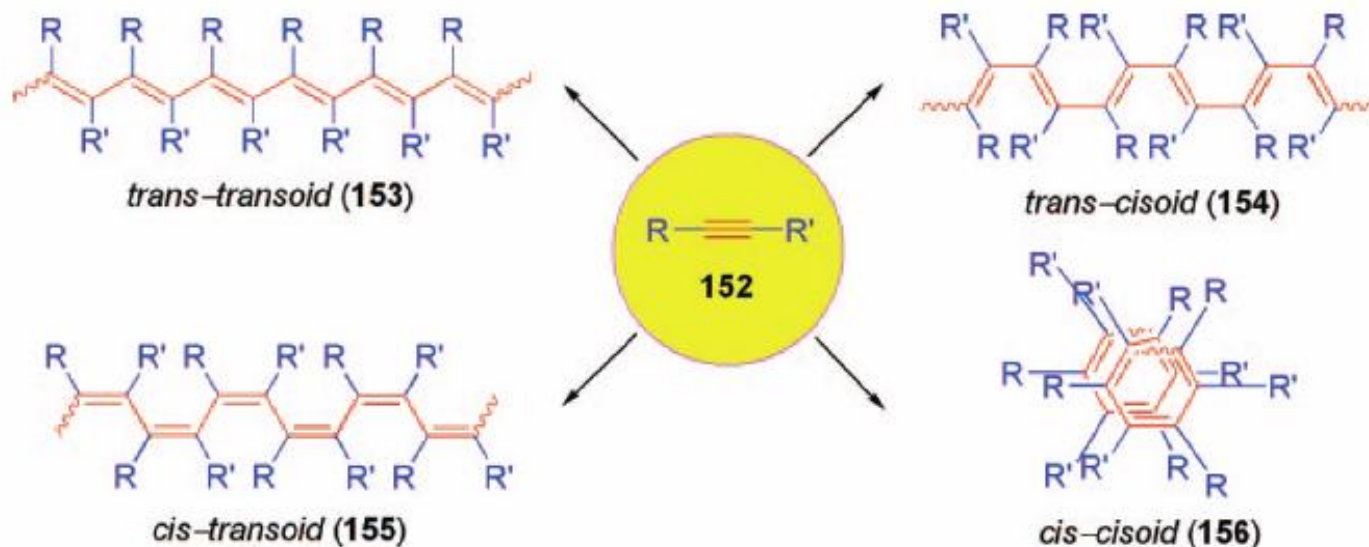


Nonlinear Polymerization



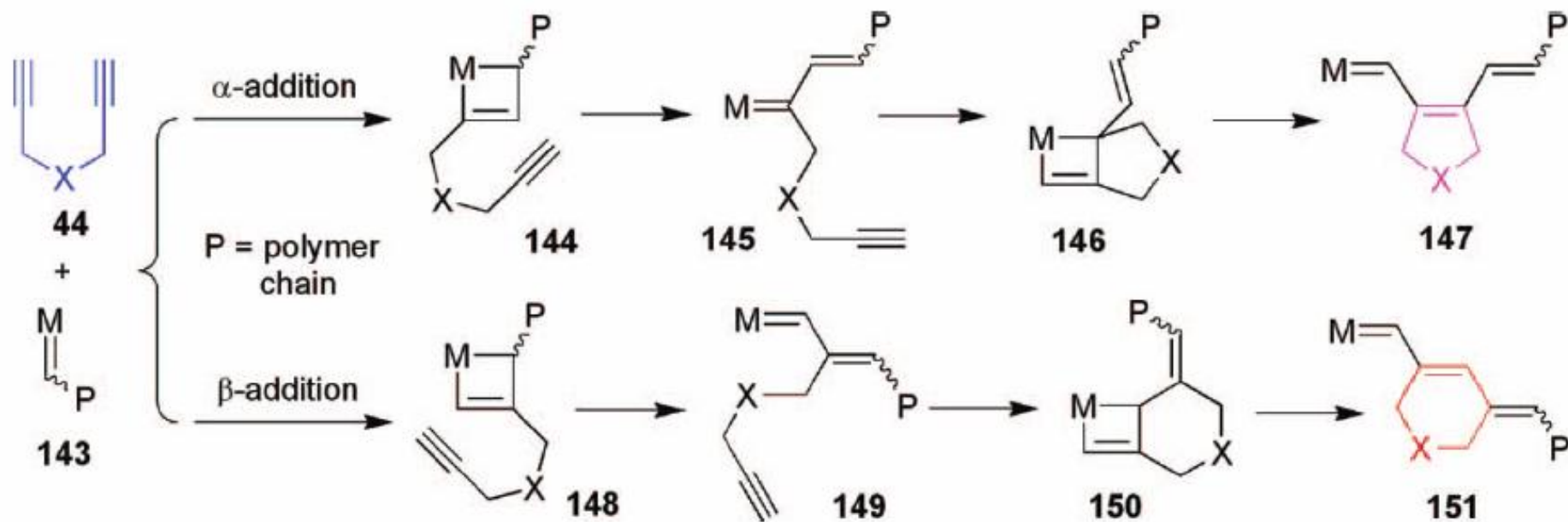
Structure

Are the repeat units arranged head-to-tail, cis/trans, R/S?



Structure

Ring size?



Structure

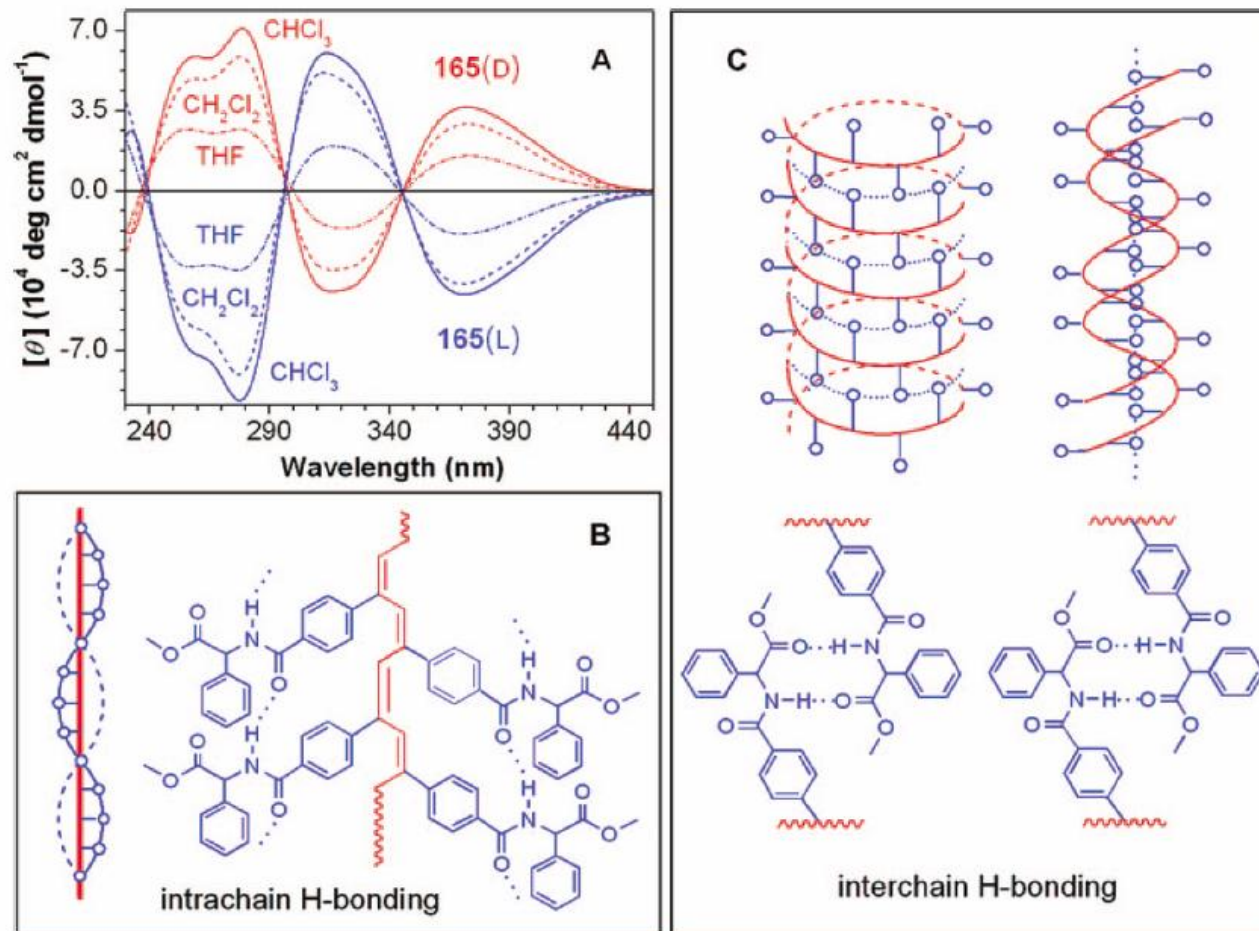


Figure 2. (A) Chain helicity of **165** determined by pendant chirality and manipulated by solvent change. Diagrammatic sketch of (B) single and (C) double helical strands of PA chains stabilized by intra- and interchain hydrogen bonds. Reproduced with permission from ref 105. Copyright 2005 American Chemical Society.

Structure

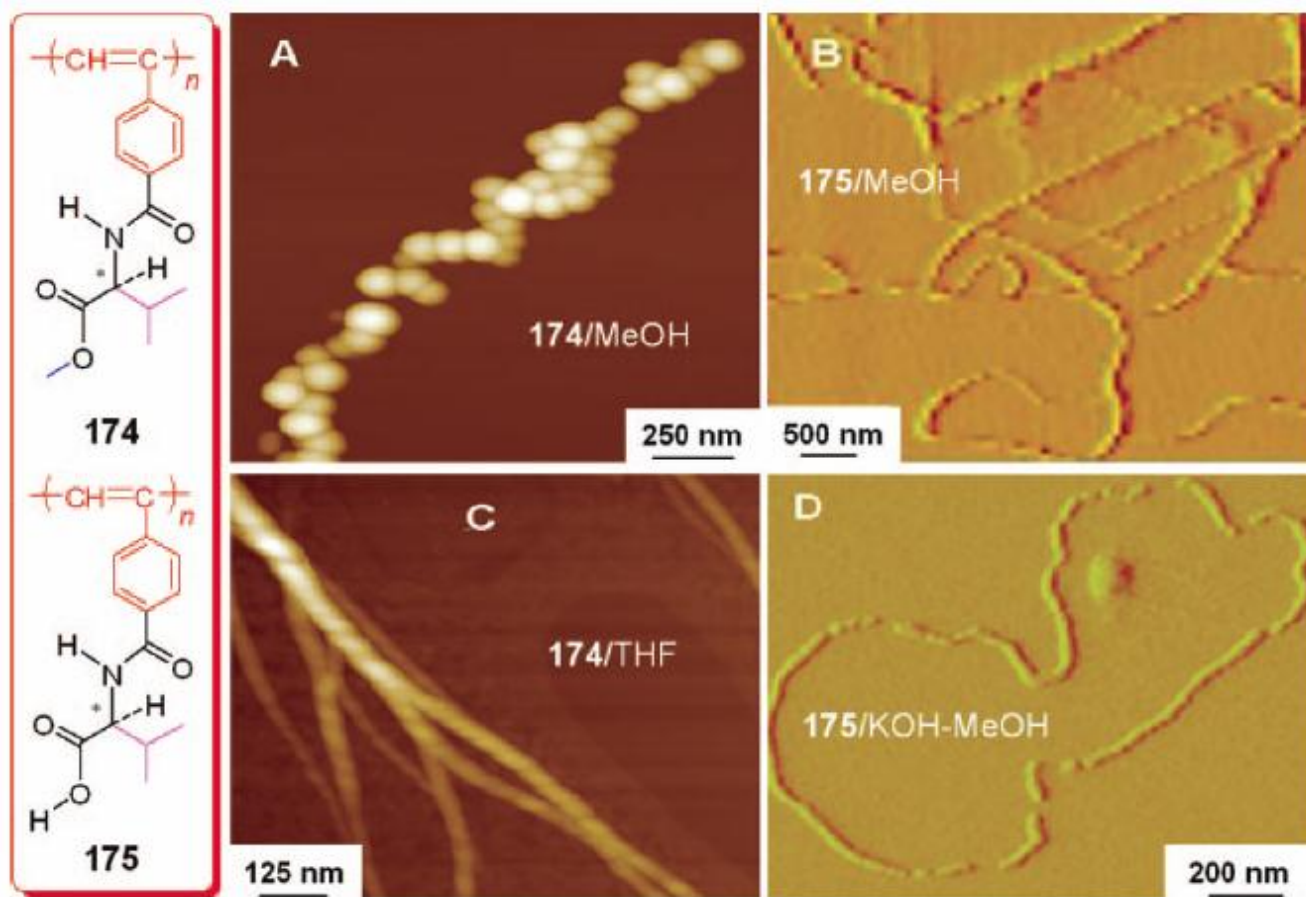
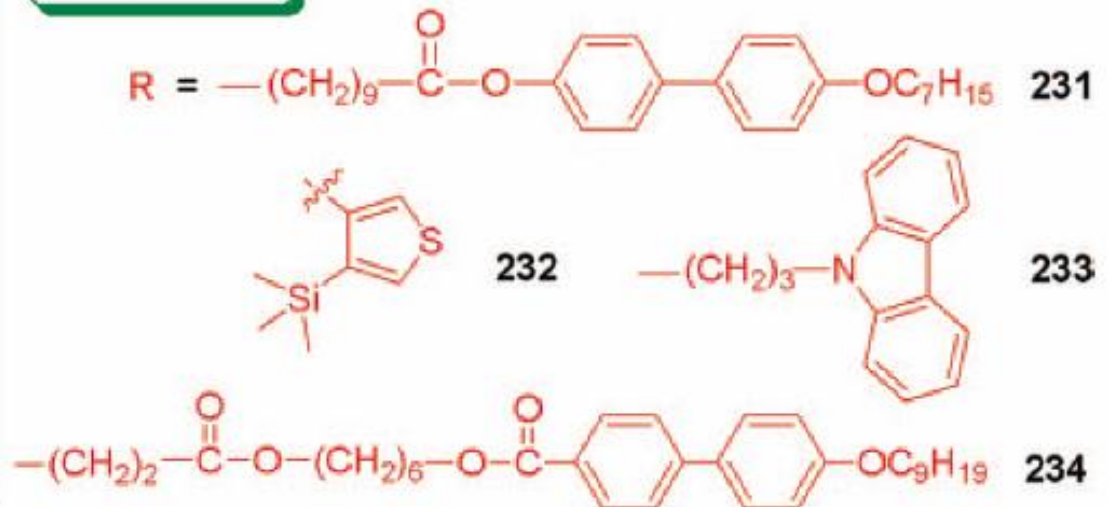
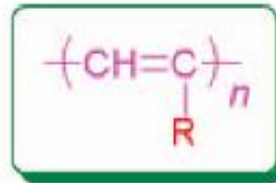
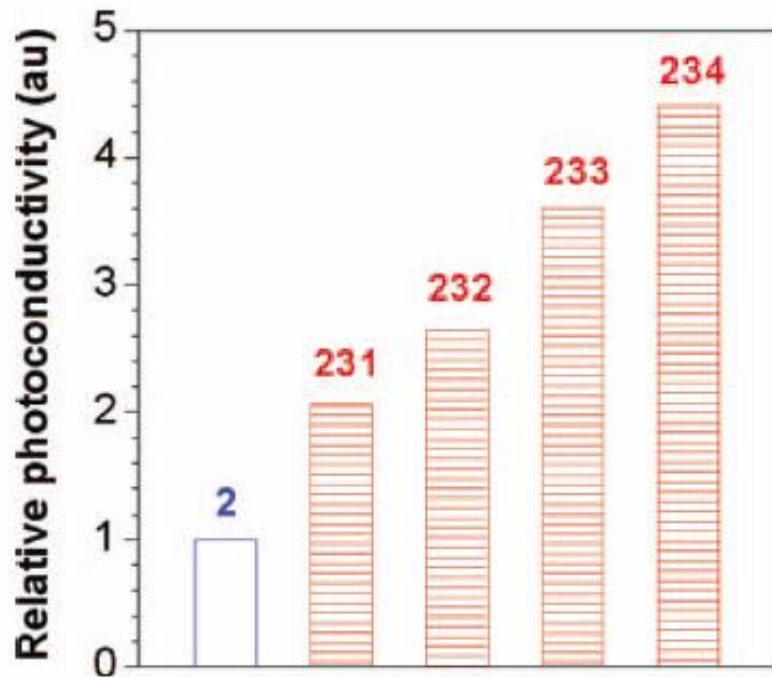


Figure 6. AFM images of supramolecular assembling structures formed by natural evaporation of the solutions of amino acid-containing PA derivatives **174** and **175**. The assembly images for **174** and **175** are reproduced with permission from refs 105 and 36. Copyright 2005 and 2001 American Chemical Society, respectively.

Photoconductivity

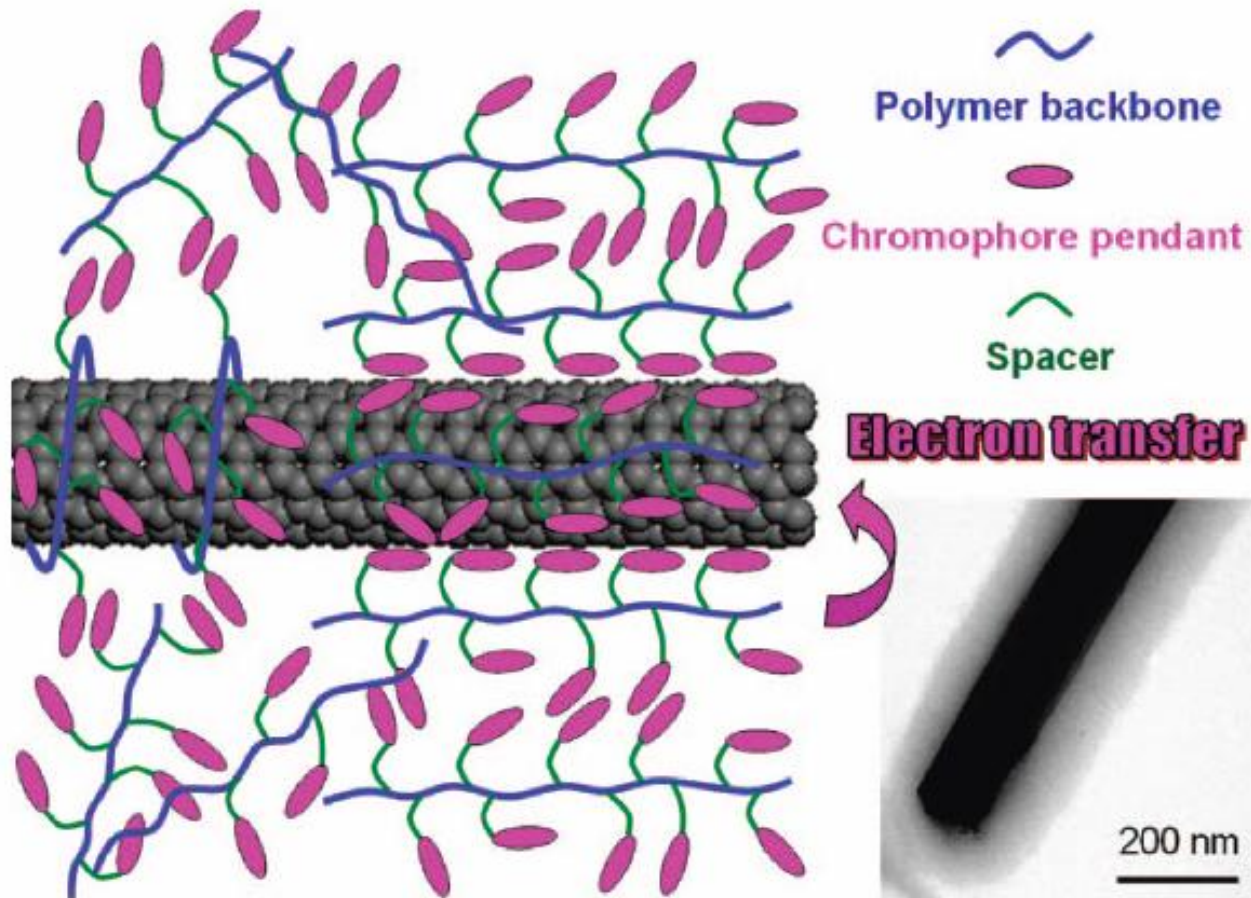
Photoconductivity increases when sidechains are:

- Electron donors
- Hole transporters
- Mesogenic and efficiently packed

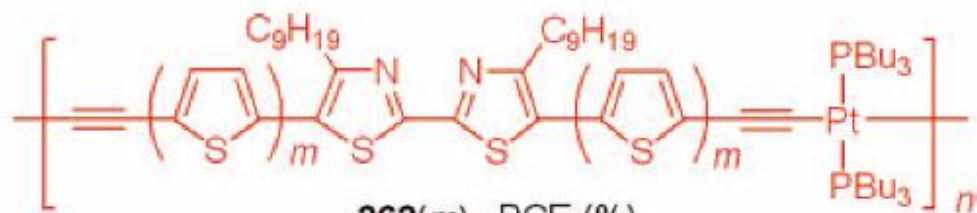


Photoconductivity

P-type PPA coil around N-type CNTs due to π - π stacking and D-A interactions while also helping to solubilize the CNTs



Photoconductivity



262(m)	PCE (%)
$m = 0$	0.21
$m = 1$	0.76
$m = 2$	2.14
$m = 3$	2.50

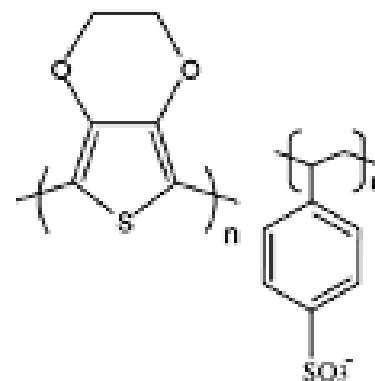
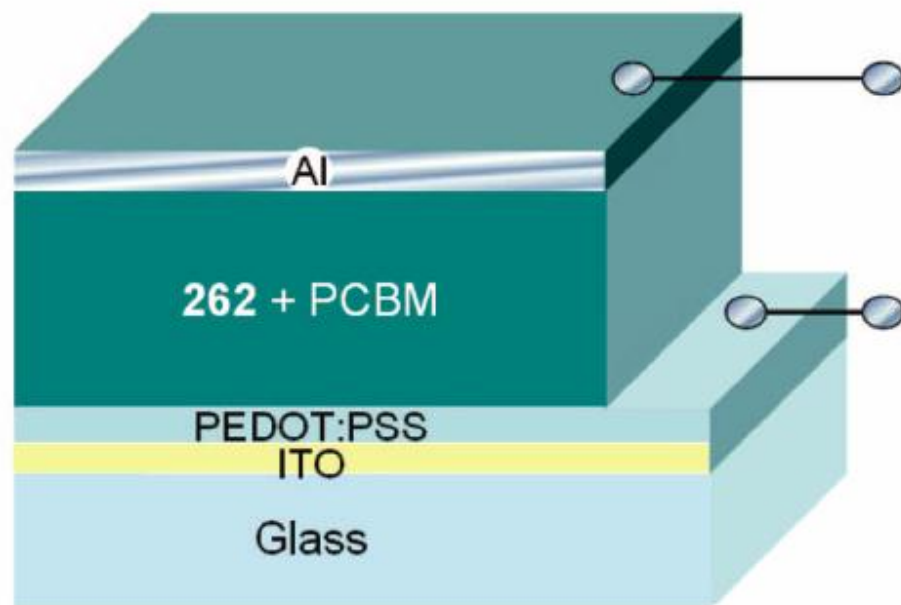
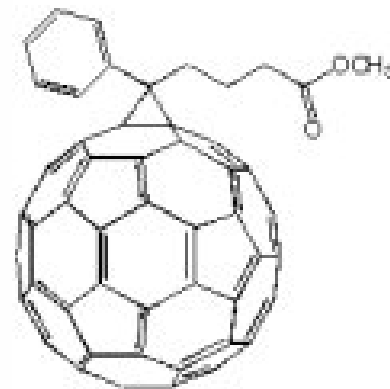


Figure 28. Power conversion efficiencies (PCEs) of poly(platinyne)-based heterojunction solar cells. Reproduced with permission from ref 509. Copyright 2007 American Chemical Society.

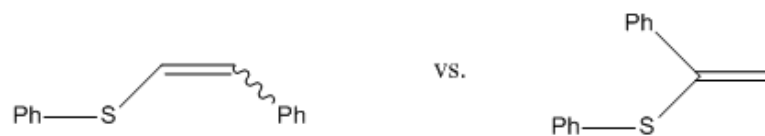
Other Applications

- Liquid Crystals
- Non-Linear Optics
- Chiral Recognition
- Fluorescence Sensing
- Ceramitization and Magnetization

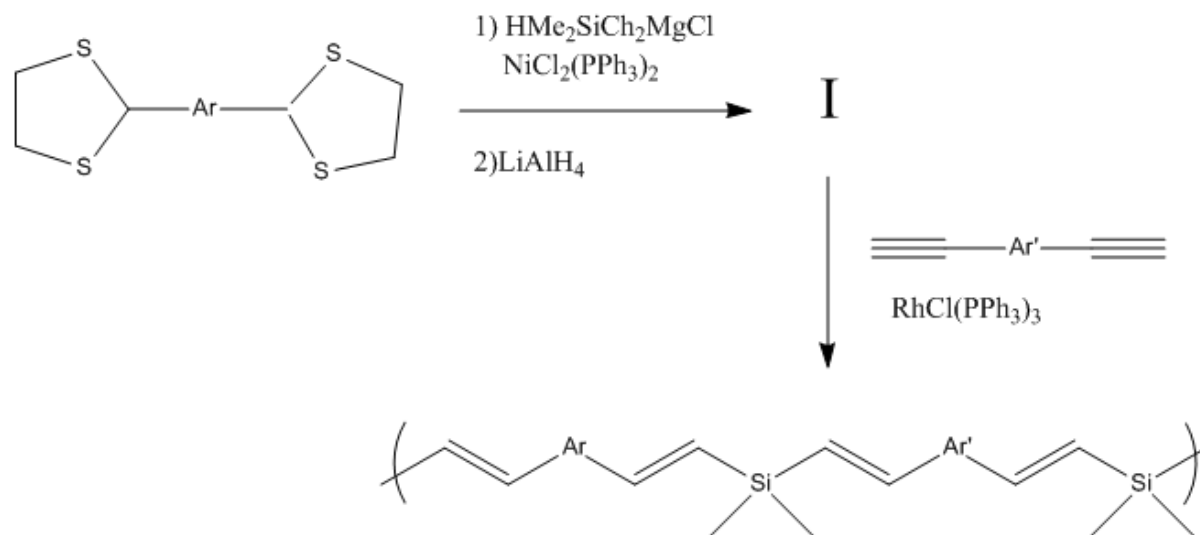
1. Provide a mechanism



2. Provide a mechanistic explanation for why $\text{RhCl}(\text{PPh}_3)_3$ provides anti-Markovnikov addition of HPh to phenylacetylene while $\text{Pd}(\text{OAc})_2$ gives Markovnikov addition.



3. Show the mechanism and intermediate I



References

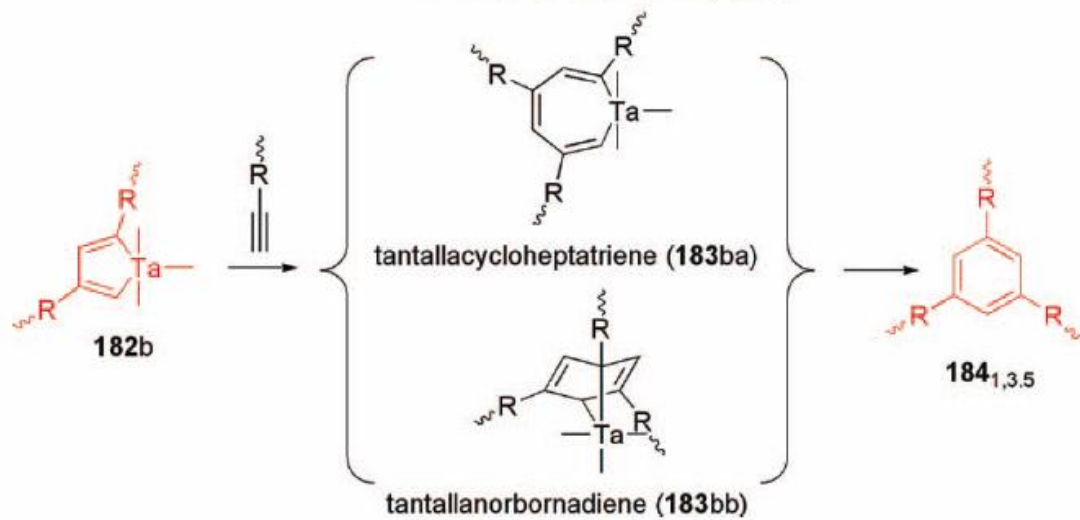
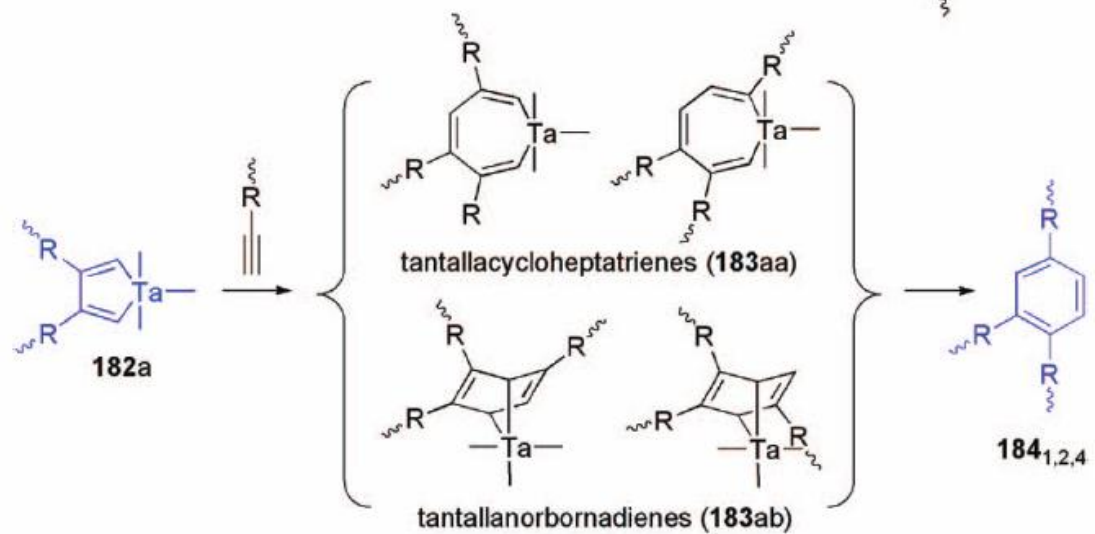
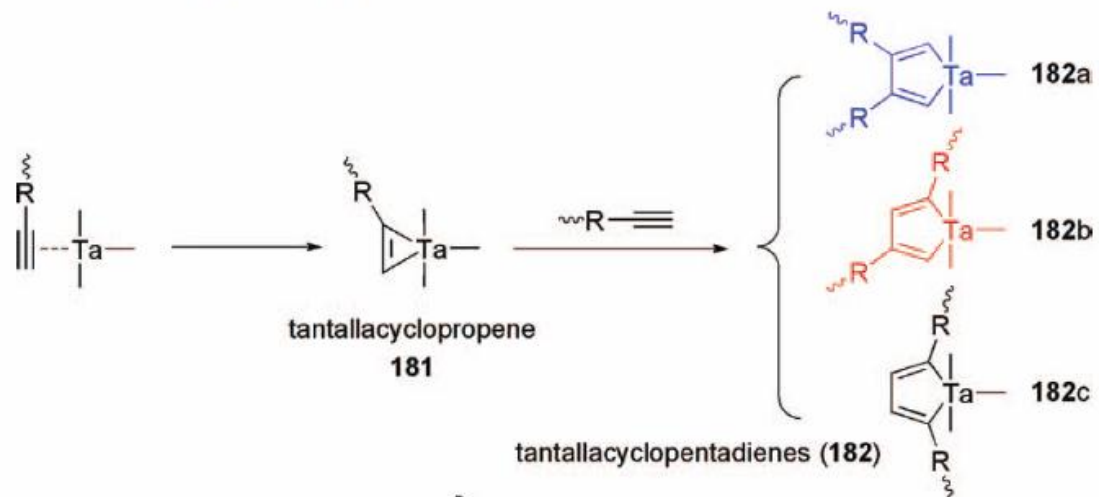
Lam, J. W. Y.; Tang, B. Z. *Chem. Rev.* **2009**, 109, 5799.

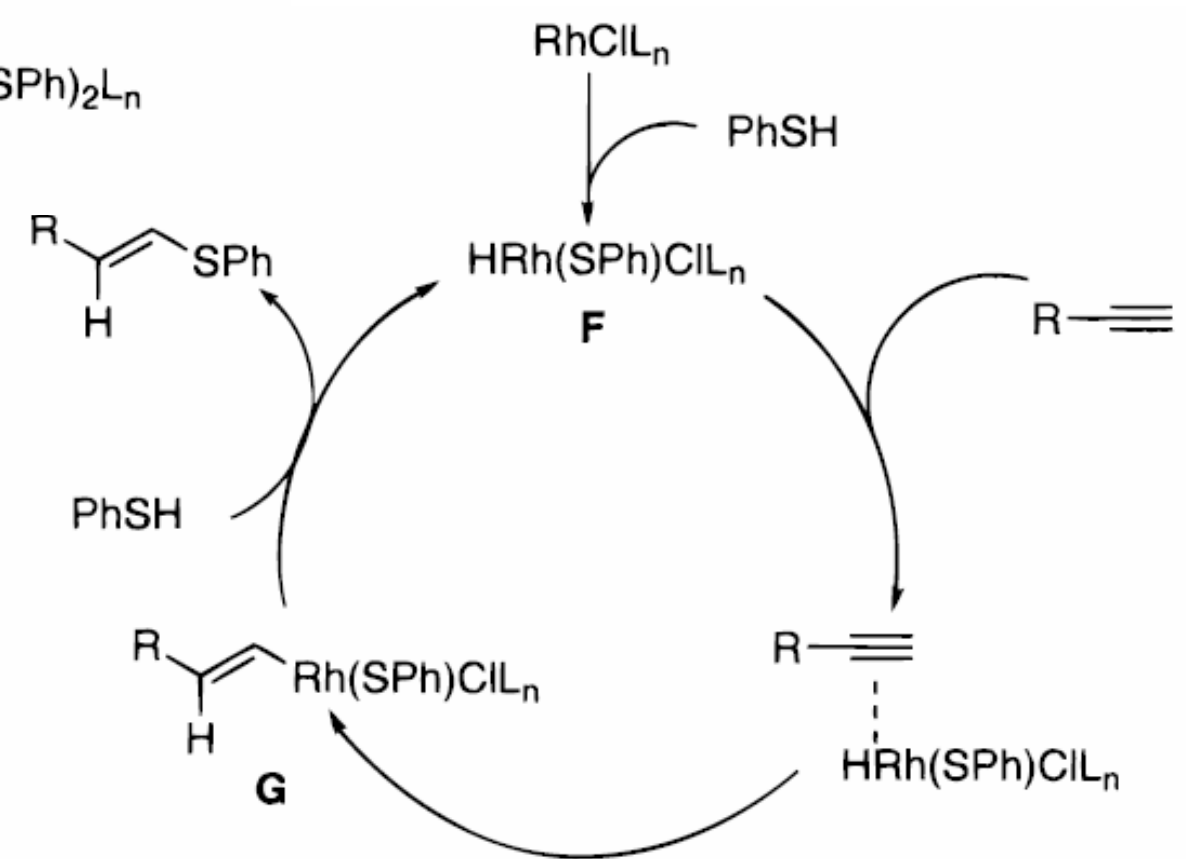
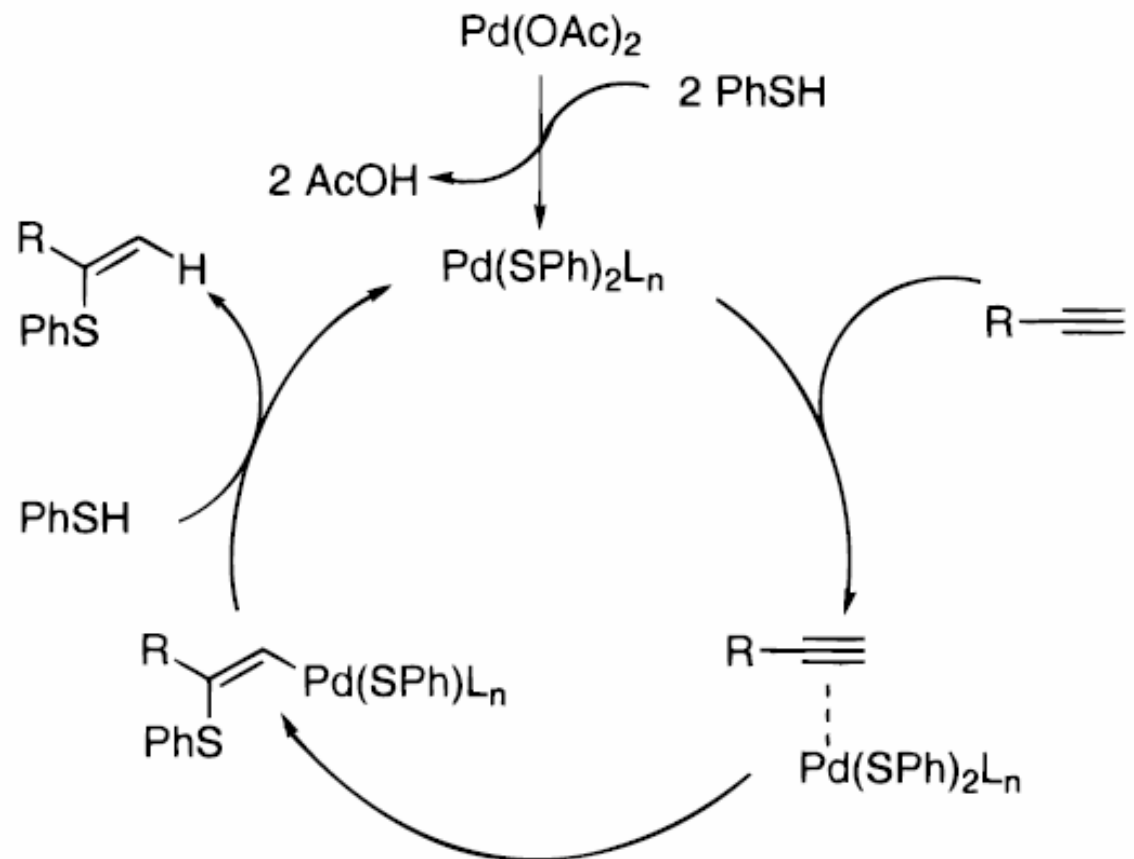
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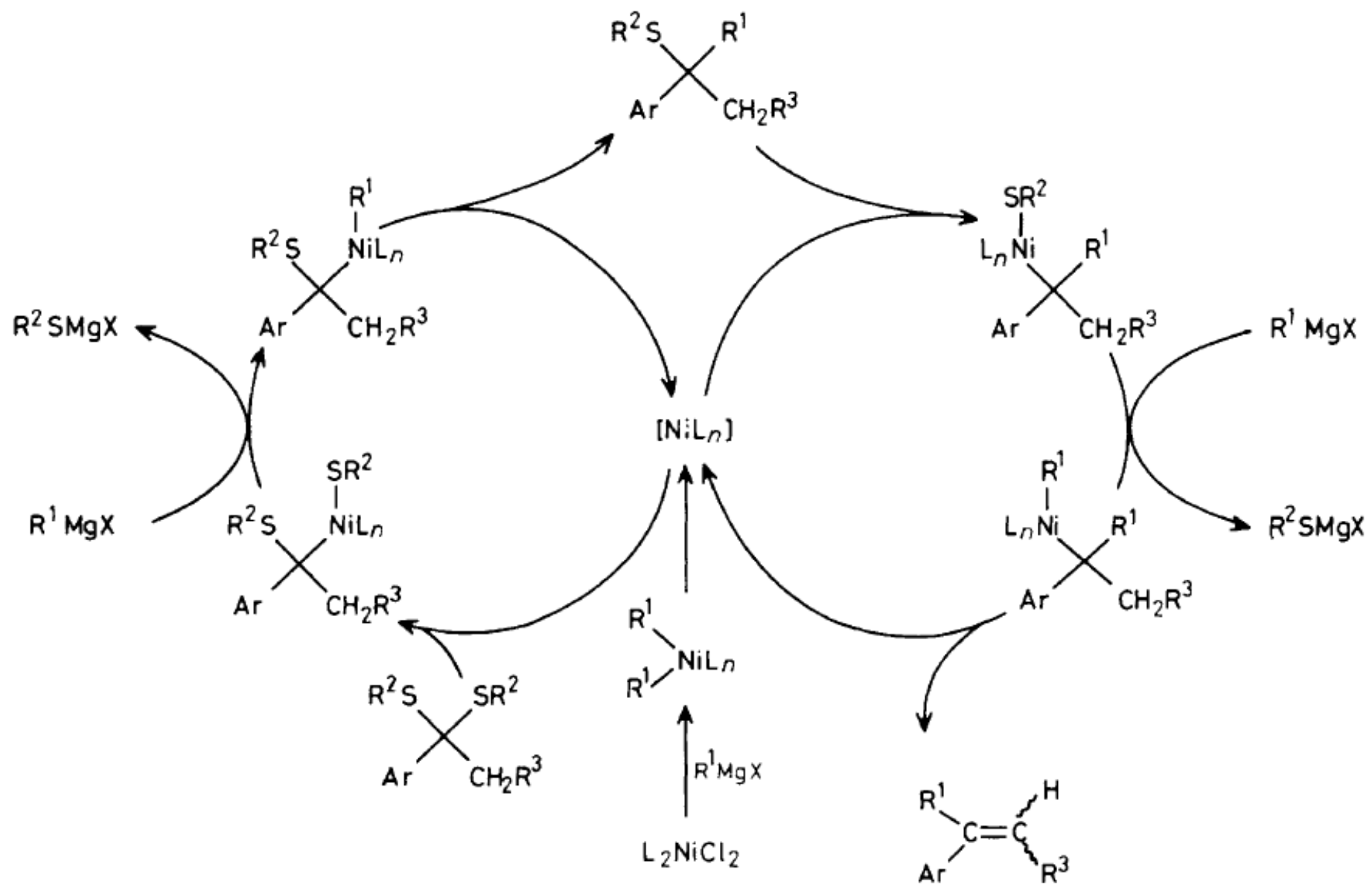
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Scheme 1

