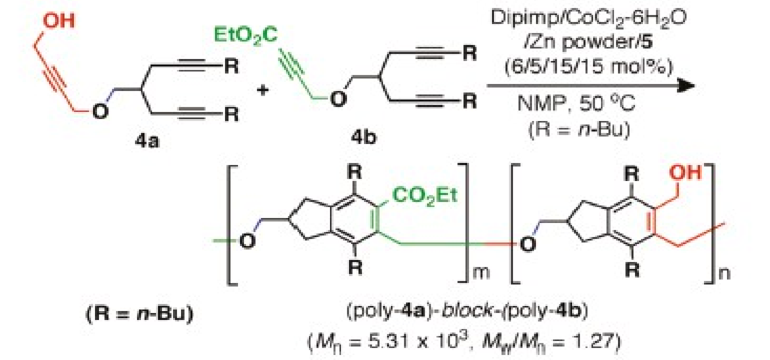
[2+2+2] Cycloaddition Polymers

By: Robert B. Login   rloginconsulting.com

I recently acquired the 2013 monumental book "Transition Metal -Mediated Aromatic Ring Construction", a 796pp review, Ed. K. Tanaka, which is a wonderful review of this subject. It led me to think about the application of this chemistry to the synthesis of polymers. What seemed obvious was to di-functionalize the components of the [2+2+2] reaction to generate repeat units and hence to build polymers.

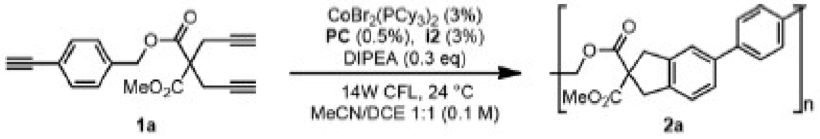
Scheme 3. Polymerization of Triyne Monomer 4a

Scheme 4. Polymerization of a Mixture of Monomers 4a and 4b



Sugiyama, Y. K., Kato, R., Sakurada, T., & Okamoto, S. (2011). Chain-Growth Cycloaddition Polymerization via a Catalytic Alkyne [2+ 2+ 2] Cyclotrimerization Reaction and Its Application to One-Shot Spontaneous Block Copolymerization. *Journal of the American Chemical Society*, *133*(25), 9712-9715.

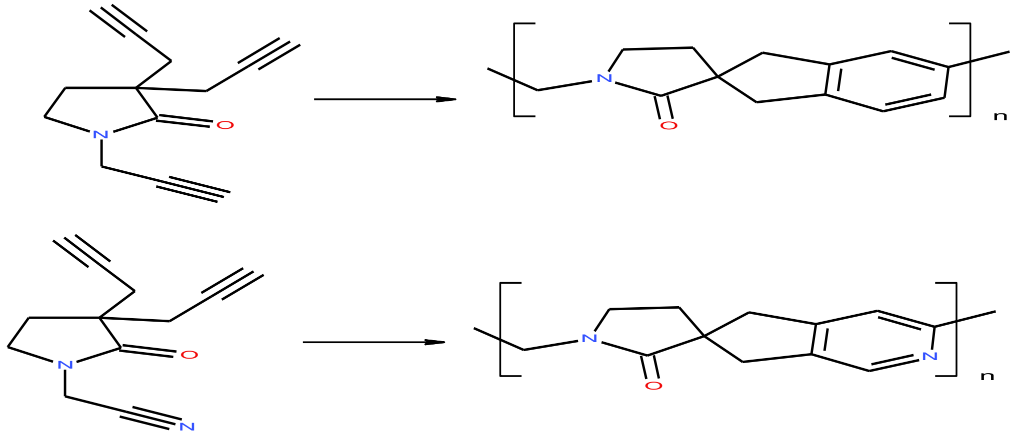
Okamoto, S., & Sugiyama, Y. K. (2013). From the Development of Catalysts for Alkyne and Alkyne–Nitrile [2+ 2+ 2] Cycloaddition Reactions to Their Use in Polymerization Reactions. *Synlett*, *24*(09), 1044-1060.



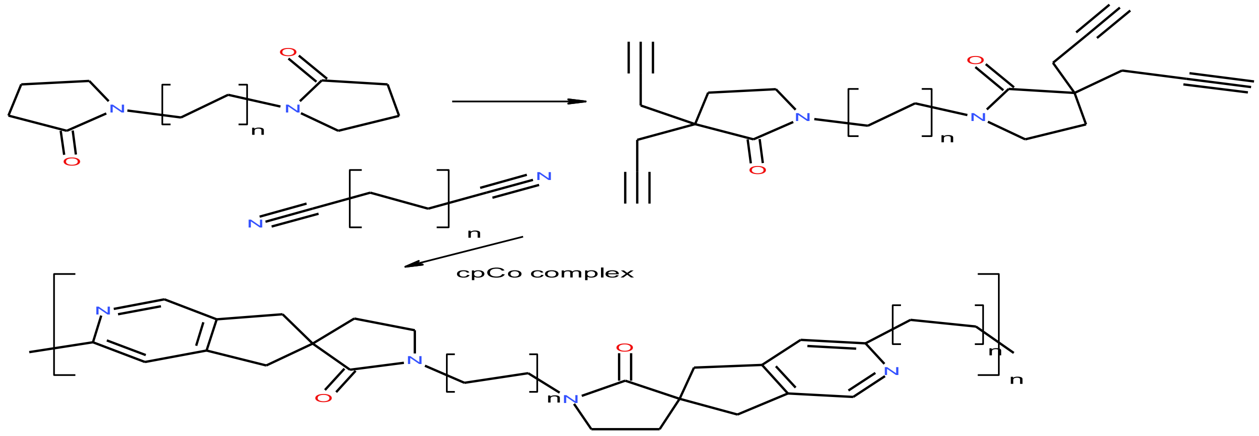
Ravetz, B. D., Ruhl, K. E., & Rovis, T. (2018). External Regulation of Cobalt-Catalyzed Cycloaddition Polymerization with Visible Light. *ACS Catalysis*, *8*, 5323-5327.

Apparently there are few references to polymerization but the above show the possibilities.

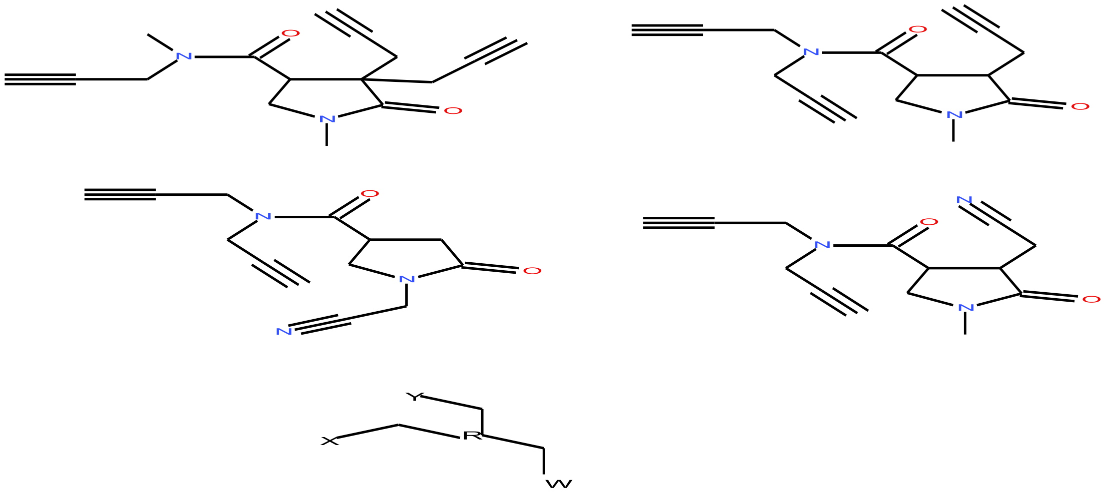
I previously published proposals concerning acetylenic pyrrolidone derivatives, “The Chemistry of Acetylenic Derivatives of Pyrrolidone” on my web page rloginconsulting.com. Please take a look as it will enhance the following proposals.



Scheme 1: Pyrrolidone is known to react with electrophiles when activated by strong bases. Selected transition metal catalysts are then required to effect polymerization. The above references clearly show that this type of monomer can be readily polymerized.



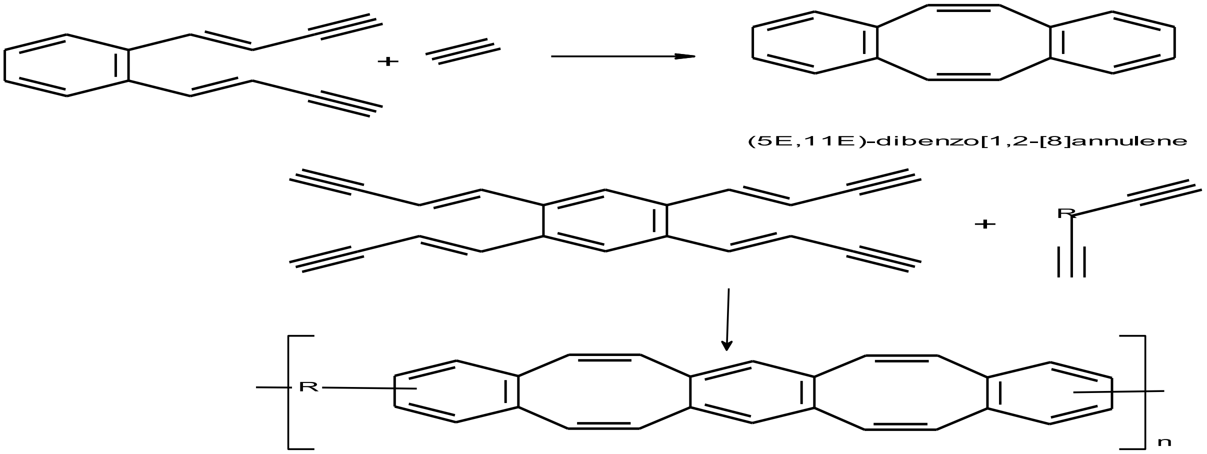
Scheme 2: Separation of the components is also feasible.



Scheme 3: Examples based on pyrrolidone derivatives. In general X,Y and Z are the moieties that would result in [2+2+2] reactions with the proviso that X,Y and Z cannot react internally to form non-polymeric derivatives.

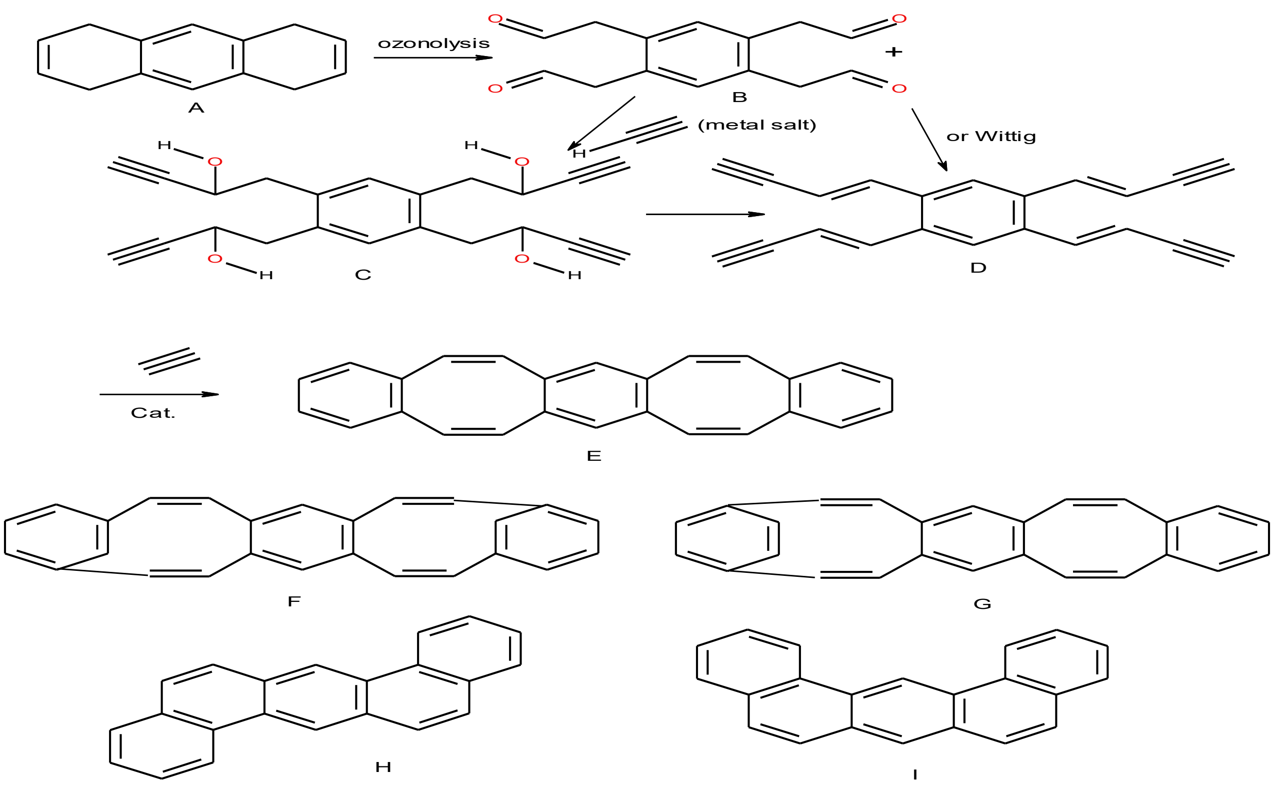
I'm suggesting these examples based on using pyrrolidone derivatives but obviously other possibilities can be envisaged.

Other [2+2+2] proposals: (see chap. 10, 14 and 16 of the Tanaka book)

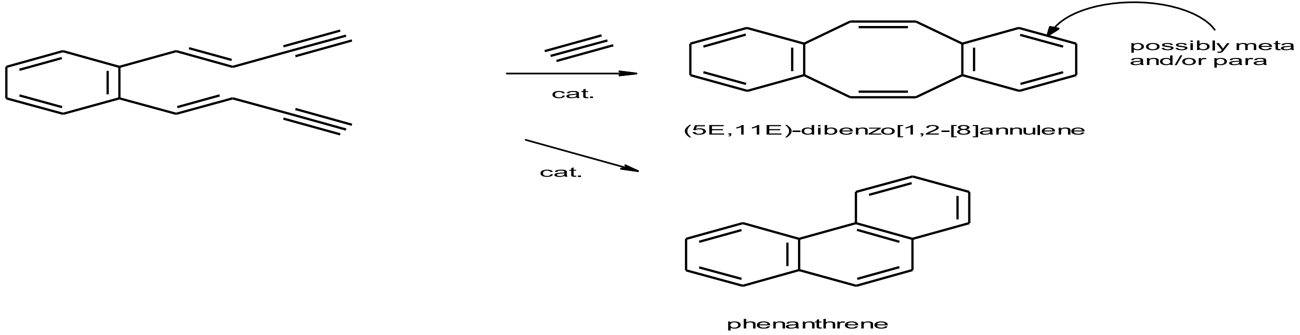


Scheme 4: Annulene compound and possible polymer.

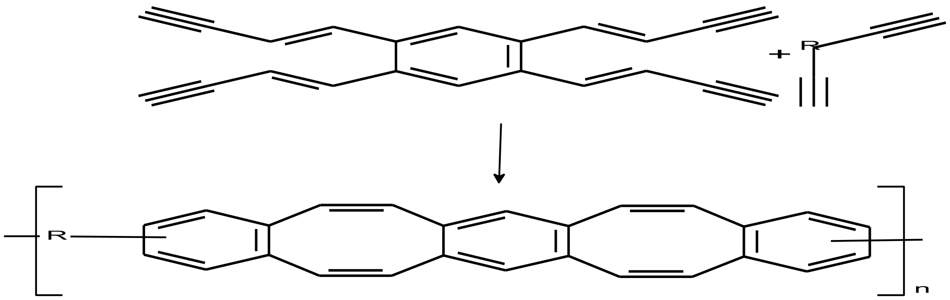
After studying this chemistry, I found that Scheme 4 maybe to simple and wishful thinking? Scheme 5 maybe more likely.



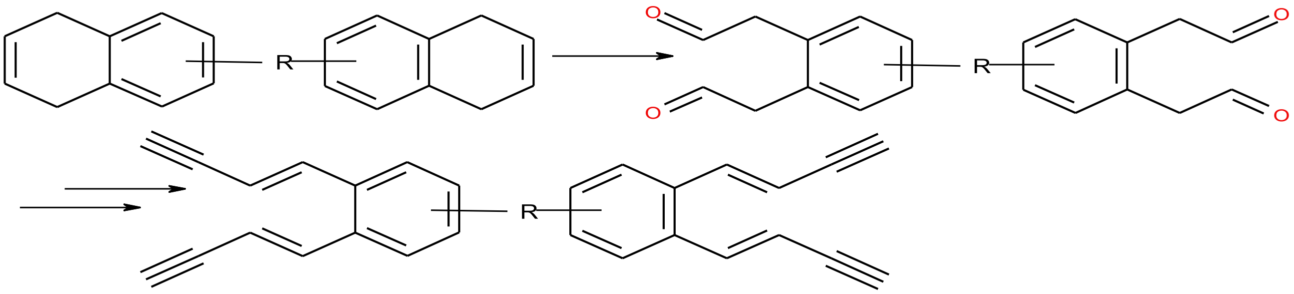
Scheme 5: E is the desired product but F and G are other possible aromatic substitutions. Other possibilities for aromatic substitution besides F & G are not shown. H & I are where the external acetylenic is not involved but the reaction is internal.



Scheme 6: It might be easier to visualize the above.



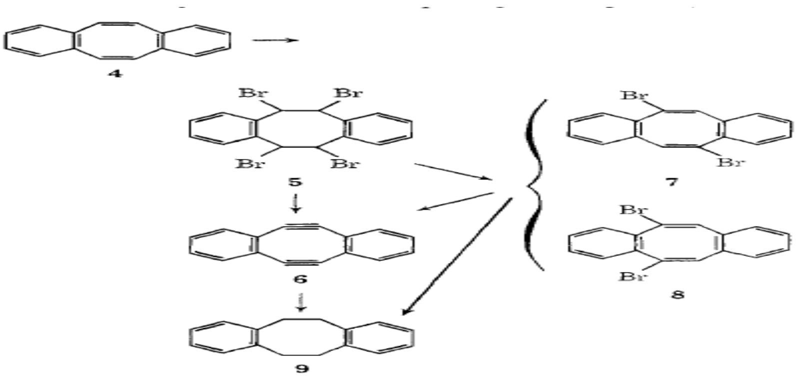
Scheme 7: This would be a very interesting polymer. Depending on the R group, it could be completely conjugated.

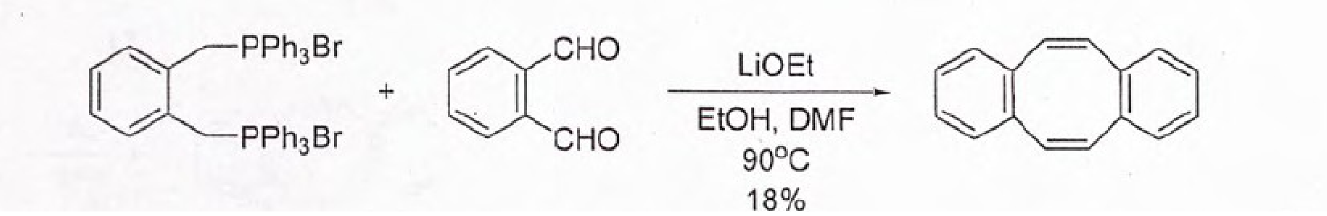


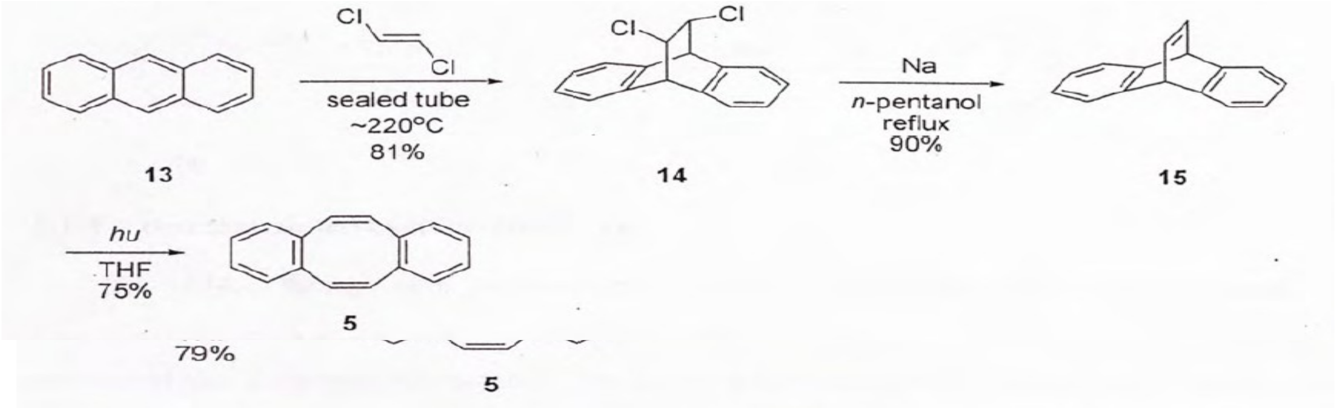
Scheme 8: Here the idea is to simplify the chemistry by dimerizing the starting monomer.

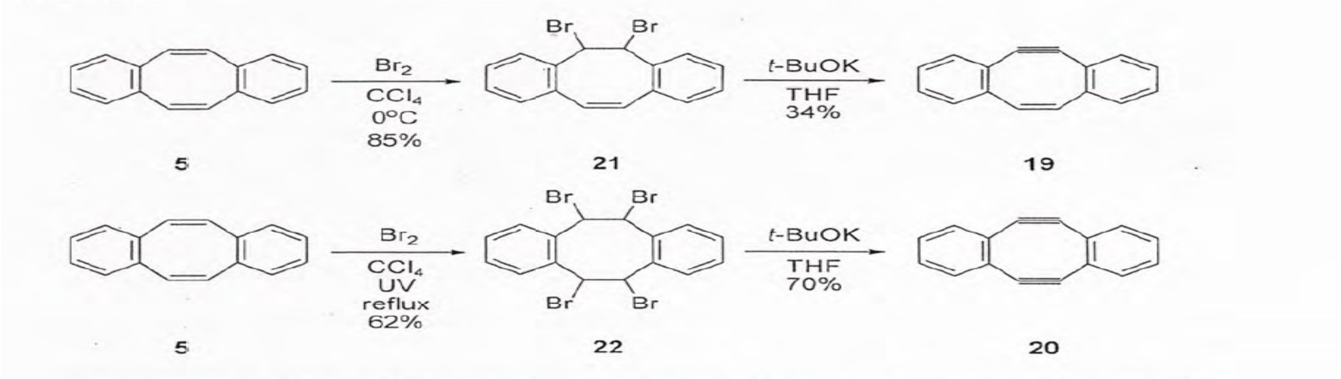
The separate alkyne that is proposed might have to be derivatised with electron withdrawing groups or other groups to make it more reactive in order to compete and overcome the internal reactions as illustrated in scheme 5 & 6.

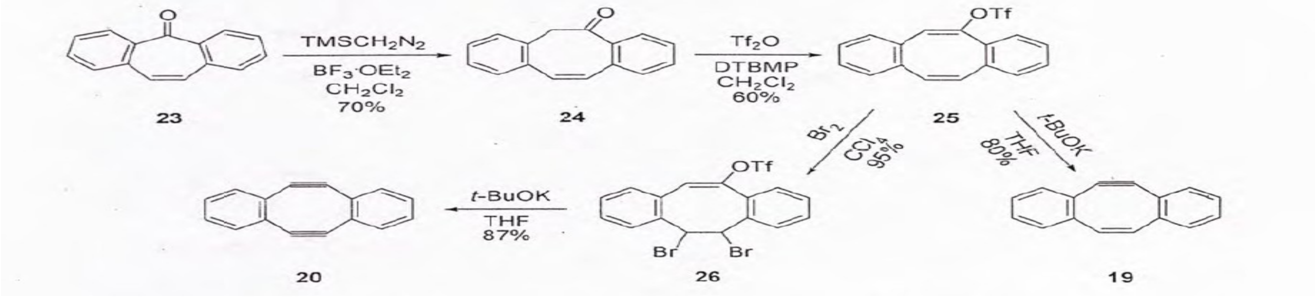
There is a substantial literature concerning alternatives to the above proposals. For example:











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Wong, H. N., Garratt, P. J., & Sondheimer, F. (1974). Unsaturated eight-membered ring compounds. XI. Synthesis of sym-dibenzo-1, 5-cyclooctadiene-3, 7-diyne and sym-dibenzo-1, 3, 5-cyclooctatrien-7-yne, presumably planar conjugated eight-membered ring compounds. *Journal of the American Chemical Society*, *96*(17), 5604-5605.

Paquette, L. A. (1975). The renaissance in cyclooctatetraene chemistry.*Tetrahedron*, *31*(23), 2855-2883. Deng, C.

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Nishinaga, T., Ohmae, T., & Iyoda, M. (2010). Recent studies on the aromaticity and antiaromaticity of planar cyclooctatetraene. *Symmetry*, *2*(1), 76-97.

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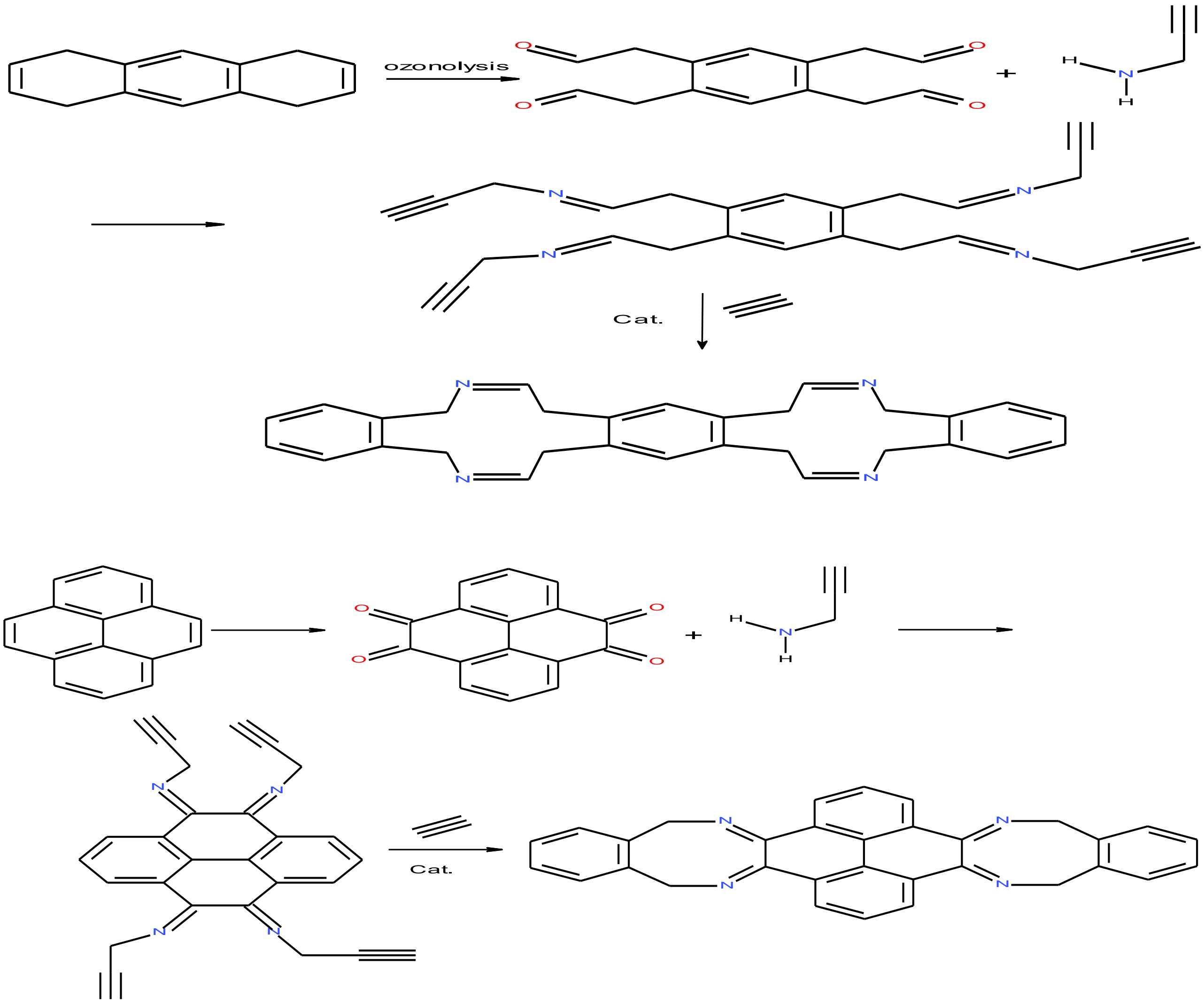
Raviola, C., Protti, S., Ravelli, D., & Fagnoni, M. (2016). (Hetero) aromatics from dienynes, enediynes and enyne–allenes. *Chemical Society Reviews*, *45*(15), 4364-4390.

Imines can also be considered:



Scheme 9: Considering all the caveats, can imines be utilized? These example only show the compounds I would hope results from this chemistry but as scheme 5 cautions this might not be the case?

Also nitriles can be substituted for acetylenes to afford pyradines(not shown). Also the free acetylene that is shown reacting with the enynes benzene derivatives can be substituted with electron withdrawing groups like carboxy esters to make them more reactive in the above proposed reactions.

Polymeric examples of scheme 9 are not shown but implied.

Thank you for looking at these proposals.
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