



Synthesis of Novel Polyunsaturated Odd-Carbon Dicarboxylic Acids as New Polymer Feedstocks

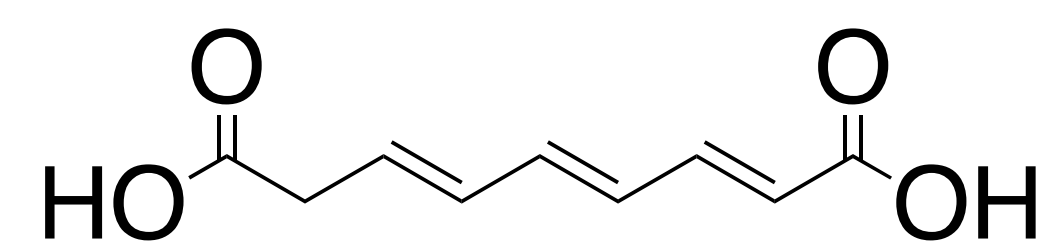
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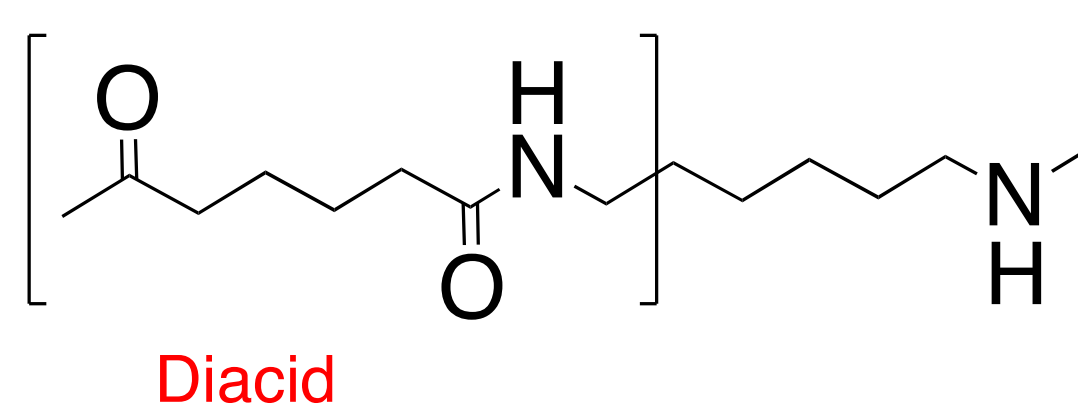
OVERALL GOAL

The goal of our research is to synthesize polyunsaturated odd-carbon dicarboxylic acids, which can be used as precursors for creating new types of functionalized polymers. Our initial goal is to prepare the first of these new diacids, 2,4,6-nonatriene-1,9-dioic acid, via chemical synthesis.



BACKGROUND

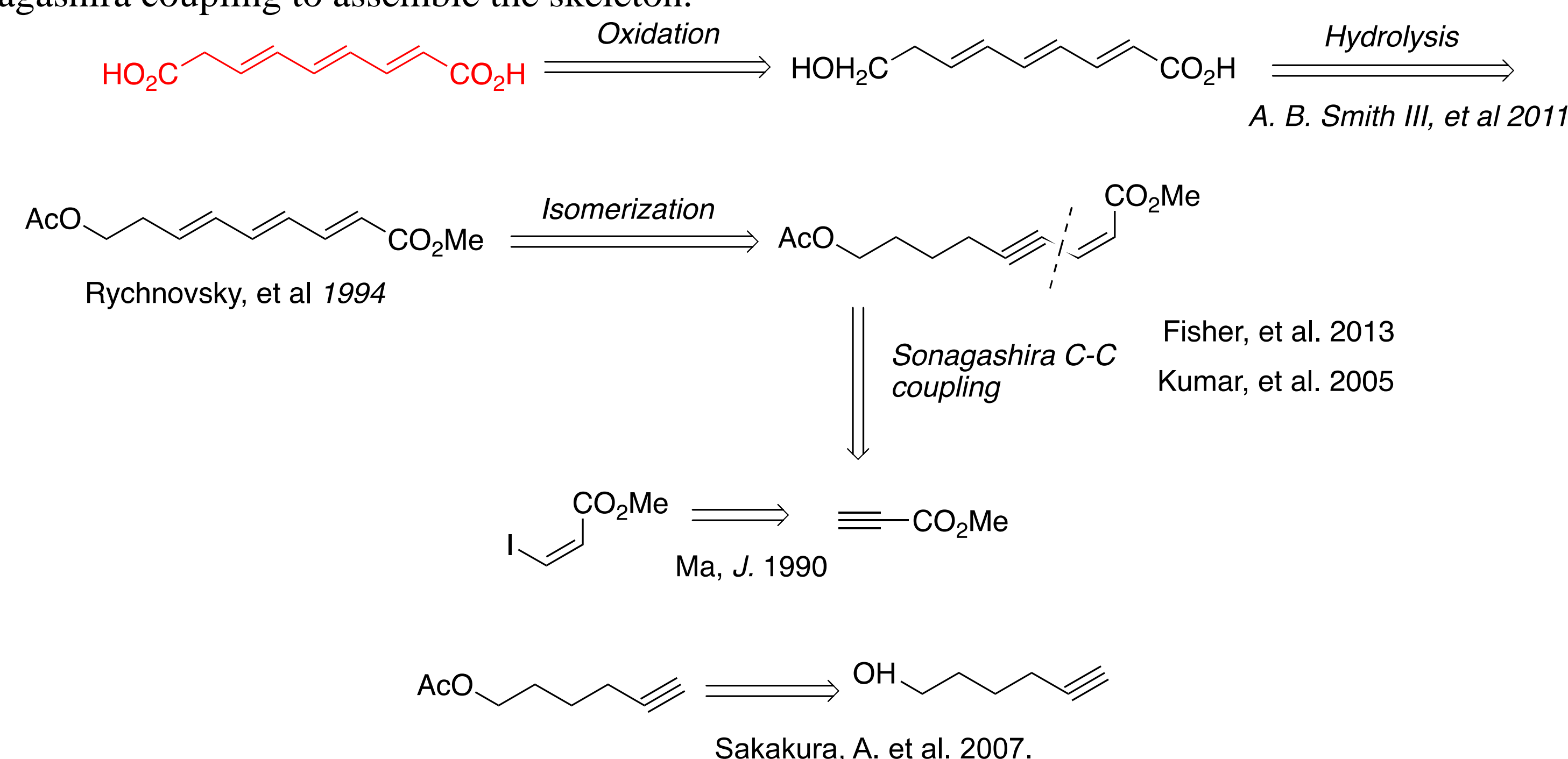
Diacids are important as polymer precursors. An example of a commercially known diacid-based polymer would be Nylon 6,6.



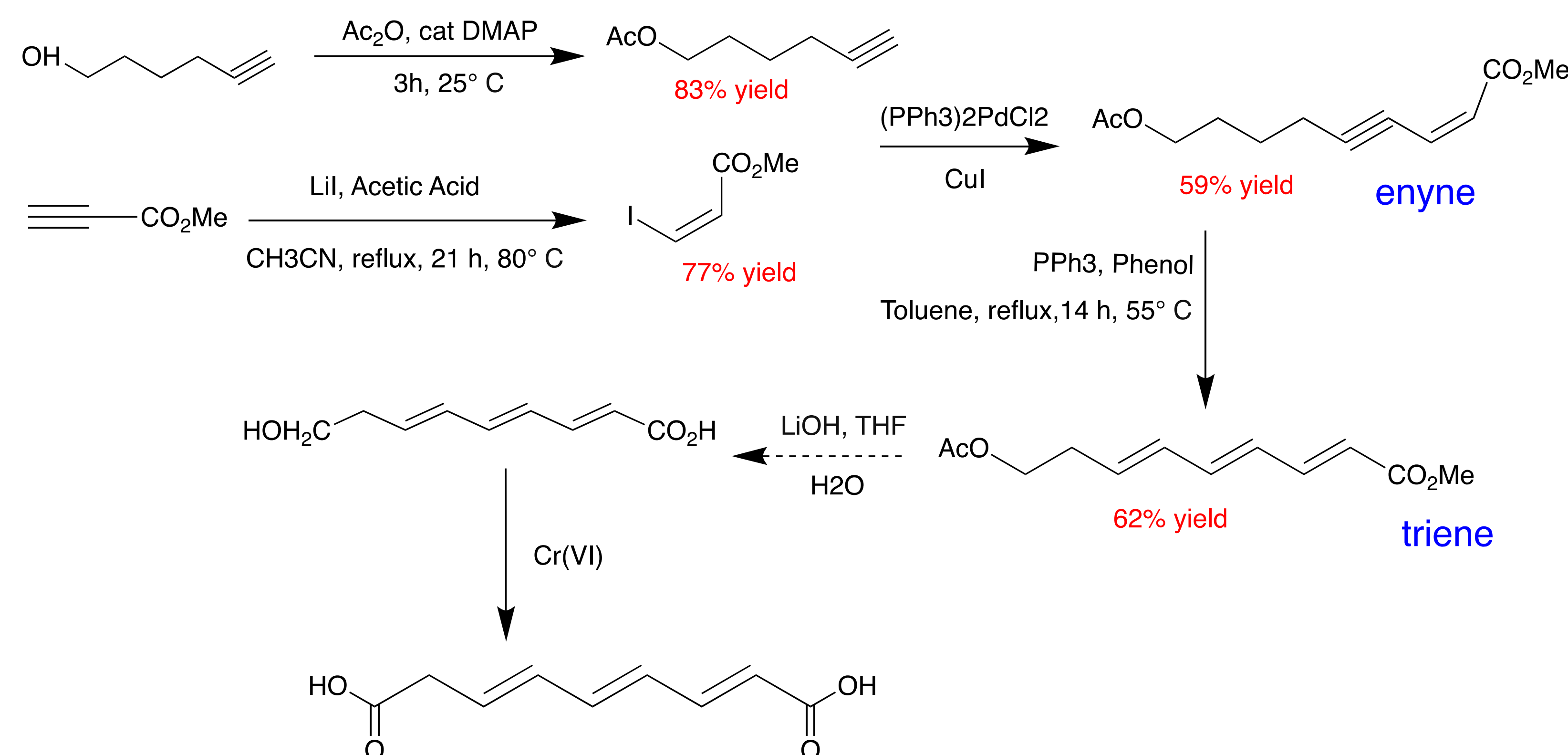
Most diacids that are commonly used as polymer precursors have an even number of carbons and lack double bonds (saturated). It would be ideal to get odd carbon precursors, both saturated and unsaturated, from renewable resources. Our collaborators in the group of Prof. Liangcheng Du (UNL Chemistry) are investigating a biosynthesis of odd chain polyunsaturated diacids. We embarked upon a chemical synthesis of 2,4,6-nonatriene-1,9-dioic acid to generate standard samples and to provide initial material for polymer studies with Prof. Yiqi Yang (UNL Textiles).

OVERALL RETROSYNTHESIS

Our synthetic plan presented illustrates a retrosynthesis (working backwards) including 6 convergent steps. The two key steps include: the isomerization of an enyne (double bond, triple bond) to a triene and the use of a Sonagashira coupling to assemble the skeleton.



RESULTS

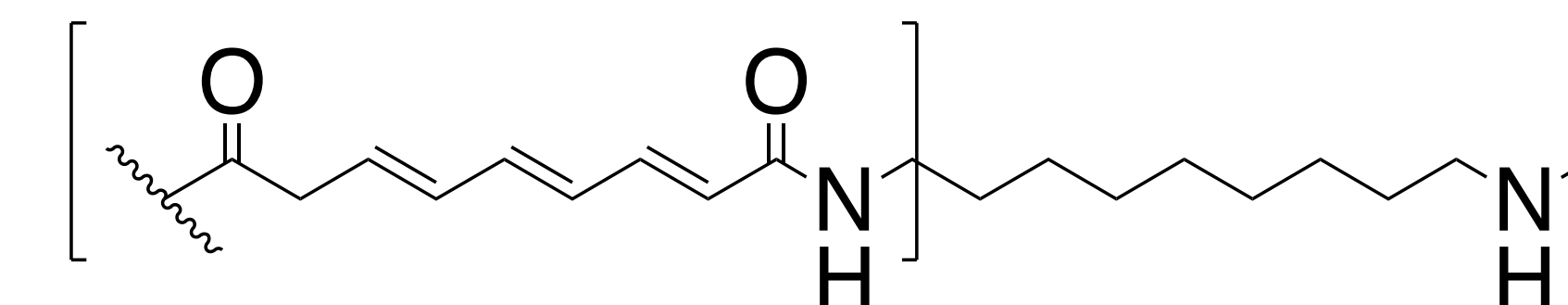


The first two steps of my synthesis protect the alcohol of 5-hexyn-1-ol and convert the alkyne of methyl propynoate into an iodine-substituted alkene. The resulting two intermediates underwent a Sonagashira C-C coupling reaction to create an enyne possessing all of the carbons of the desired product. The enyne is then isomerized to a triene (three double bonds) in what has proved a challenging step. After this, we only require two simple reactions to get to our target molecule: hydrolysis to deprotect the acetate and methyl ester; and, oxidation to convert the resulting primary alcohol to a carboxylic acid.

CONCLUSION

The first four steps of the synthesis proceeded in good yields. The Sonagashira reaction had a somewhat lower yield than expected but did give the correct enyne. The key isomerization reaction clearly proceeded to give the desired framework, although in a moderate yield and containing more than one isomer according to NMR. Our target diacid contains all trans or E- double bonds and we are still trying to prove that the stereochemistry at the 2,3-alkene is what we wanted. Further chemical synthesis is needed to synthesize our goal molecule and research is continuing at creating this molecule.

Synthesizing this molecule supports our aim of developing new methodology for a sustainable and scalable synthesis of a new class of functionalized polymers, initially Nylons, but also potentially polyesters based upon an explored skeleton. An example of our anticipated polymer is shown below. The creation of a new monomer can lead to positive impact in the polymer industry as well as a complete turn around in the unfavorable current state that only a negligible fraction of commercial fibers is bio-derived.



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