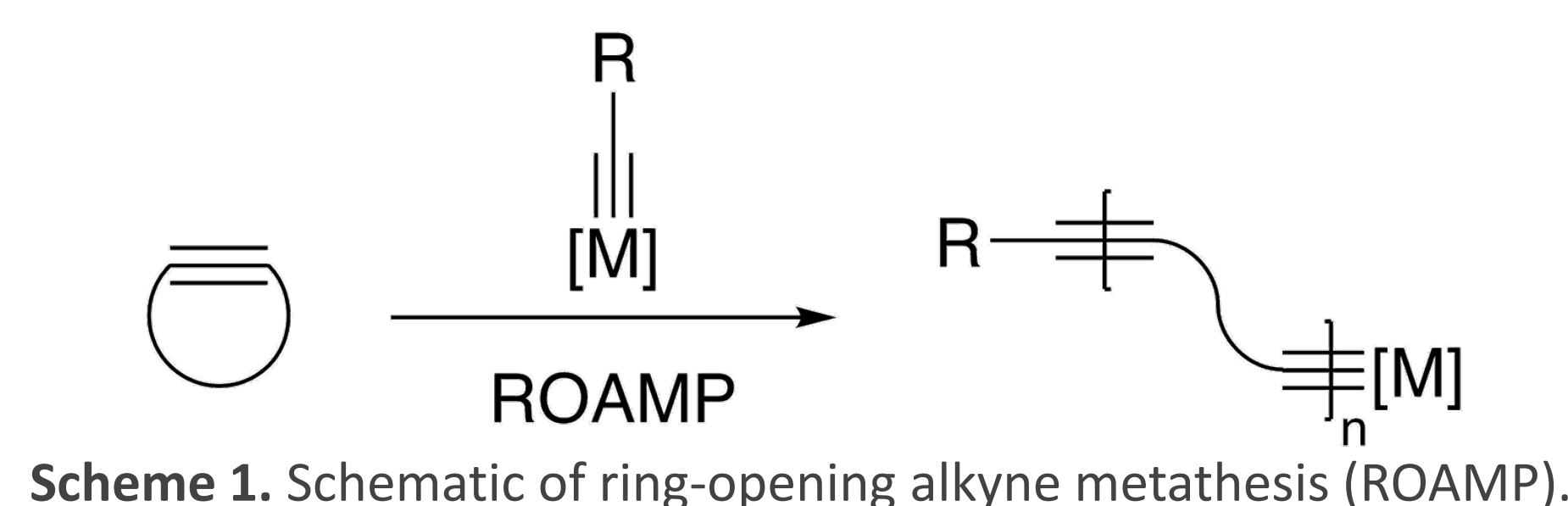


# Bottom-up synthesis of graphene nanoribbons via ring-opening alkyne metathesis polymerization

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## Abstract

Graphene nanoribbons (GNRs), planar strips of carbon atoms which are constrained to nanometer widths in one dimension, are attractive for use in nanoelectronic devices due to their unique electronic and magnetic properties and their unsurpassably low thickness. In this study, chevron-type GNRs were targeted using ring-opening alkyne metathesis polymerization (ROAMP). This would be the first bottom-up GNR synthesis to use a chain-growth, rather than a step-growth, polymerization step, which should allow for unprecedented control over the GNR length. This control, as well as the potential to create GNR heterojunctions from block copolymeric precursors, could facilitate the fabrication of GNR-based devices.



## Introduction

Due to its high charge carrier mobility and unsurpassably low atomic thickness, graphene is a promising material for use in nanoelectronic devices. Because graphene is conducting, a bandgap must be introduced if it is to be used in transistors. This can be done through quantum confinement in graphene nanoribbons (GNRs), strips of graphene constrained to nanometer widths. The bandgap of a GNR is highly sensitive to the edge shape and the width of the GNR. Organic synthetic routes to GNRs are thus desirable, as they offer atomic control over these parameters. GNR syntheses have traditionally been based on step-growth polymerizations. Compared to step-growth polymerizations, chain-growth polymerizations offer greater length control and the ability to produce block copolymers. If incorporated into a GNR synthesis, a chain-growth polymerization would allow for unprecedented control over GNR length and for the production of GNR heterojunctions from block copolymeric precursors. The goal of this proof-of-concept study is the synthesis of GNRs using ring-opening alkyne metathesis polymerization (ROAMP), a chain-growth polymerization.

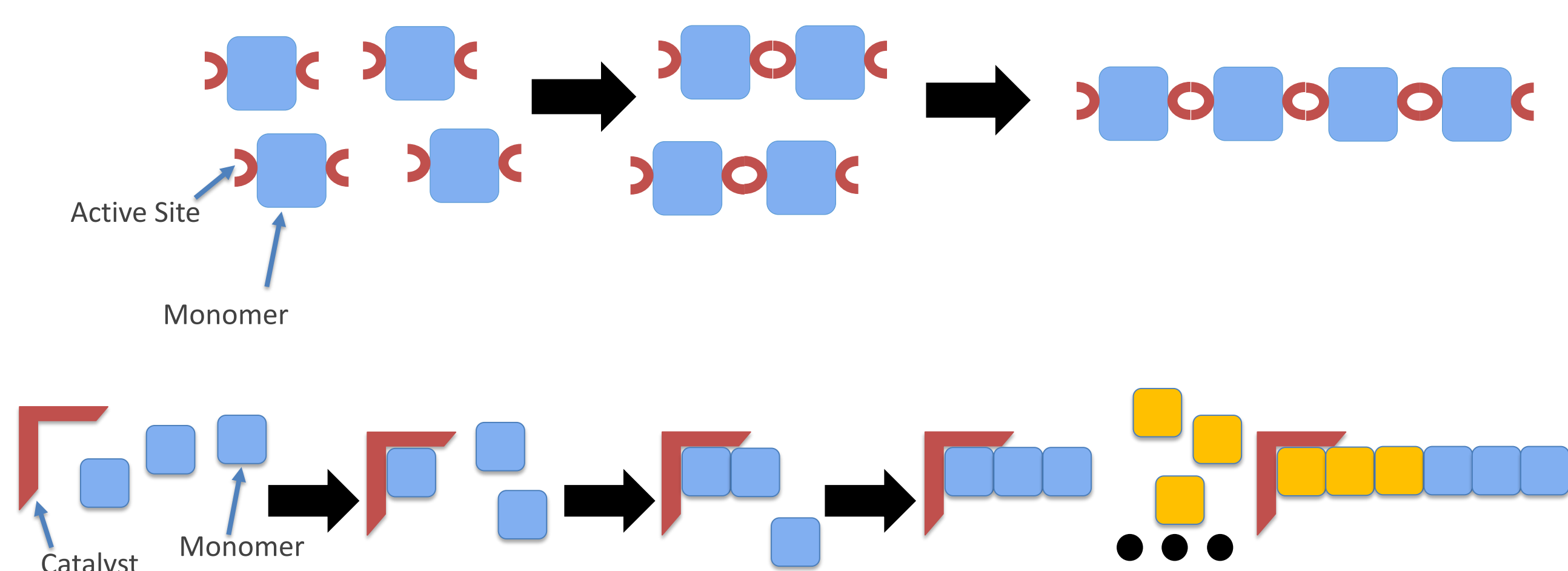
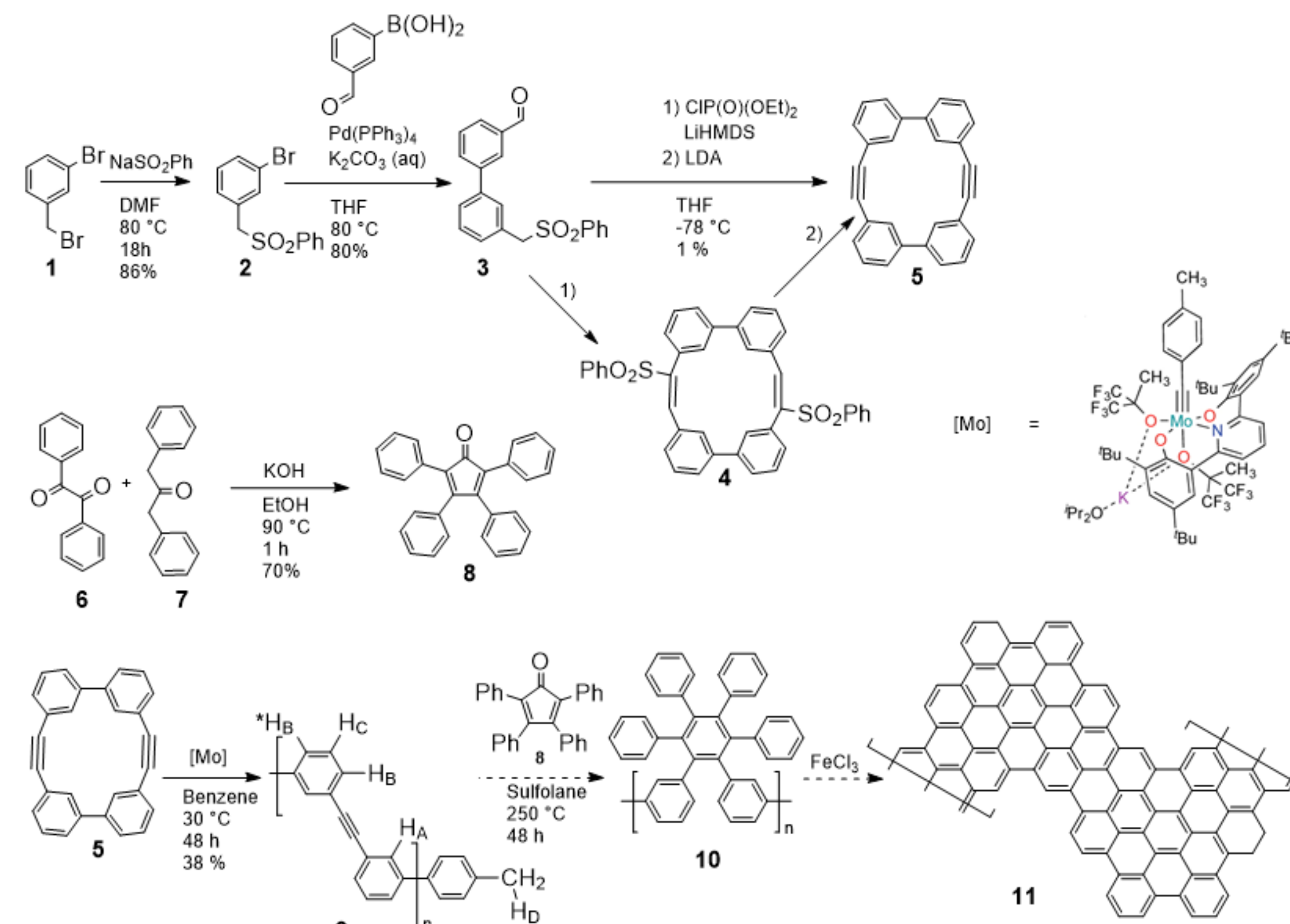


Figure 1. Schematics of step-growth (top) and chain-growth (bottom) polymerizations.

## Methods



Scheme 2. Synthesis of chevron-type GNRs using ROAMP to access **9**.

Scheme 2 shows the proposed synthetic route to chevron-type GNRs. Polymer **9** produced using a 50:1 monomer:catalyst loading was characterized via <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy at 500 Mz in CDCl<sub>3</sub>. The molecular weight distribution of **9** produced using a 5:1 monomer:catalyst loading was found using gel permeation chromatography (GPC). **9** was further characterized using UV-vis absorbance spectroscopy and fluorescence emission and excitation spectroscopy in CHCl<sub>3</sub>. Partially annulated **9** was observed using fluorescence emission spectroscopy in CHCl<sub>3</sub>.

## Results

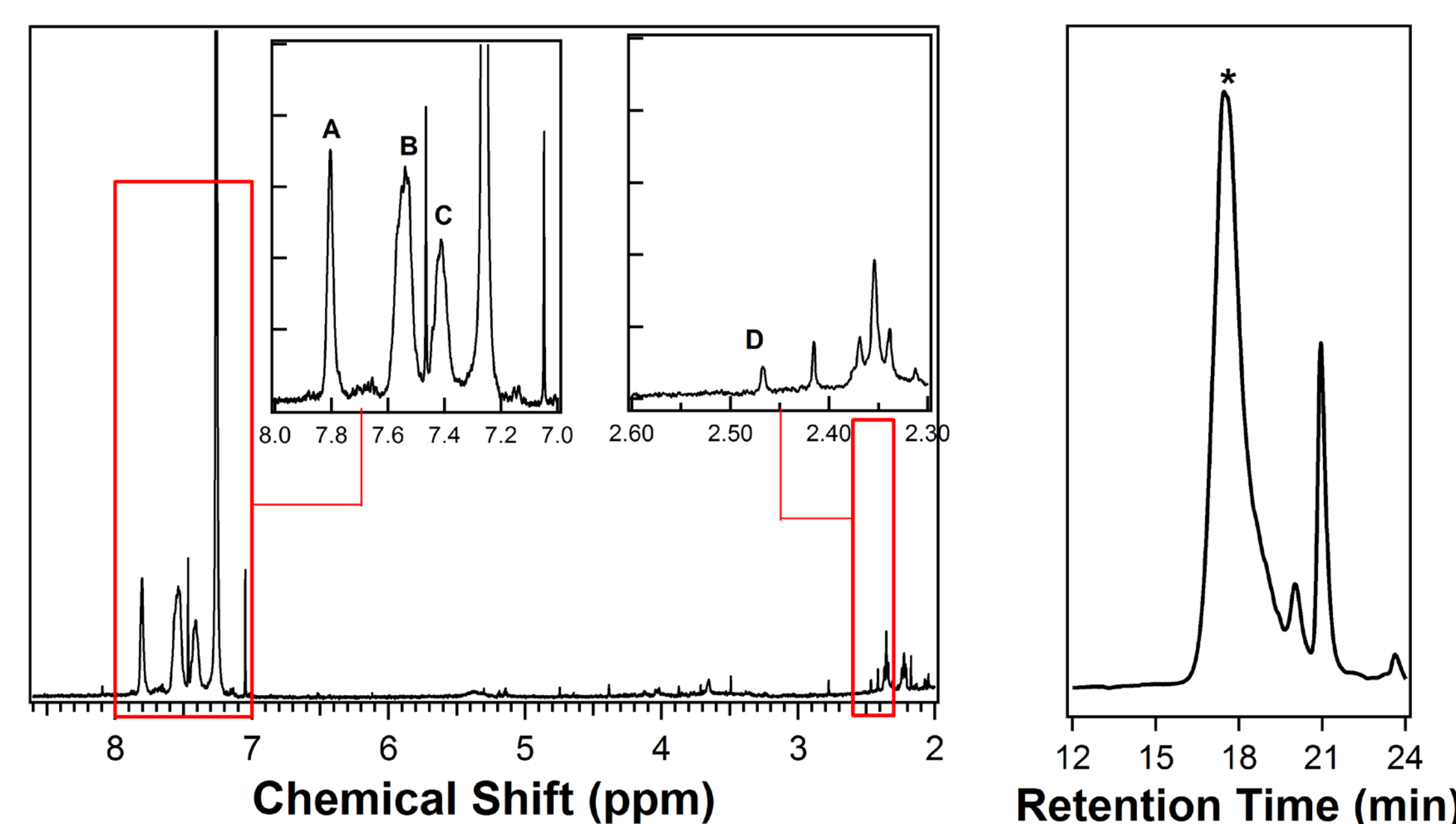


Figure 2. (Left) <sup>1</sup>H NMR spectrum of **9** with peaks labeled according to their assignment in scheme 2. (Right) GPC of **9** with the polymeric peak marked.

## Results (cont.)

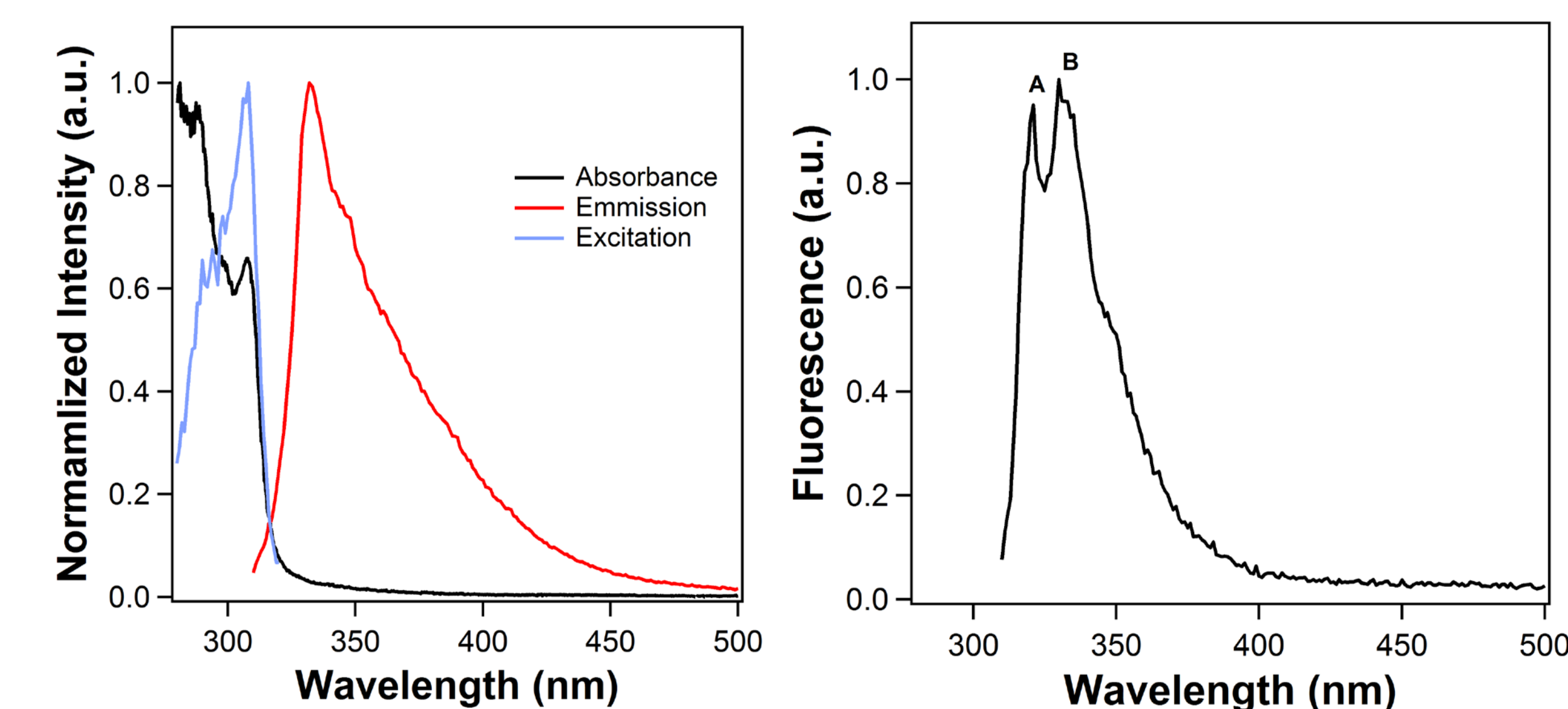


Figure 3. (Left) Absorbance, fluorescence emission, and fluorescence excitation spectra of **9**. (Right) Fluorescence emission spectra of partially annulated **9**. Peak A is assigned to **10** and B to **9**.

## Discussion

<sup>1</sup>H NMR of **9** (Figure 2, left) is consistent with the structure in Scheme 2 and end group analysis reveals a repeat length of 53 monomers, consistent with the 50:1 monomer:catalyst loading used. GPC of **9** (Figure 2, right) shows a polydispersity index (PDI) of 1.27, which is lower than the PDI of 1.5 reported by Narita et al. in their step-growth polymerization-based GNR synthesis. GNR **11** should show an unprecedentedly narrow length distribution. The absorbance and excitation spectra of **9** (Figure 3, left) reveal a bandgap of 4.0 eV. Compared to the emission spectrum of **9**, that of partially annulated **9** (Figure 3, right) shows a new peak at 320 nm, which could be used to monitor the progress of the annulation.

## Future Work

The proposed synthesis would be completed by total annulation of **9** to **10**, characterization of **10**, oxidation of **10**, and characterization of GNR **11**. The tunable length offered by the ROAMP step would be demonstrated by varying the monomer:catalyst loading. The synthesis could be extended to further GNR shapes, width, and functionalities by the invention and synthesis of new ROAMP monomers or functionalization of **8**. If new ROAMP monomers are made, they could be used to produce block copolymers which could then be converted to GNR heterojunctions.

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