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Cross-Linking Carbon Nanotubes for a Conductive Film

Sajan Patel, College of Chemistry, U.C. Berkeley, B.S. Chemistry, est. 2018
Mentor: Greg O'Bryan, Sandia National Laboratories, Org. 08223, Materials Chemistry Department
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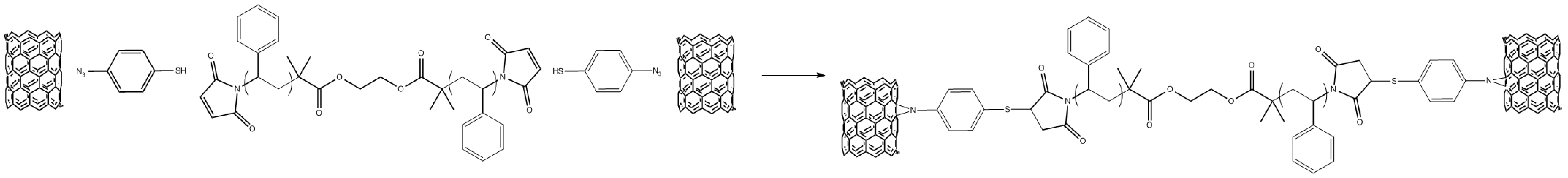
Figure 1: Overall Scheme



Abstract

An azido-thioester was synthesized and used to functionalize carbon nanotubes (CNTs) via a nitrene intermediate. Low molecular weight polystyrene was chain-end functionalized with maleimide groups. The functionalized CNTs are deprotected to reveal free thiols that react with the maleimide-terminated polystyrene via thiol-ene click chemistry to cross-link "buckypaper" films.

Polymerization of Styrene

Figure 2: Synthesis of Difunctionalized Initiator

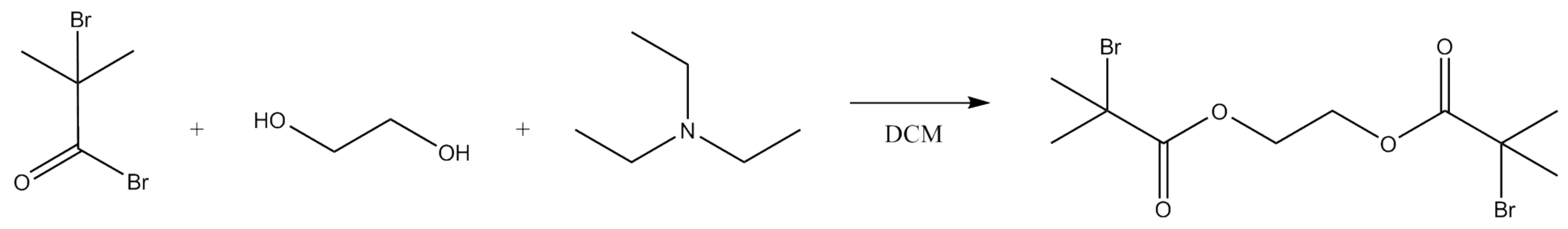


Figure 2: Polystyrene grows on either end of ethylene glycol bis(2-bromoisobutyrate)

Figure 3: ARGET Atom-transfer Radical Polymerization

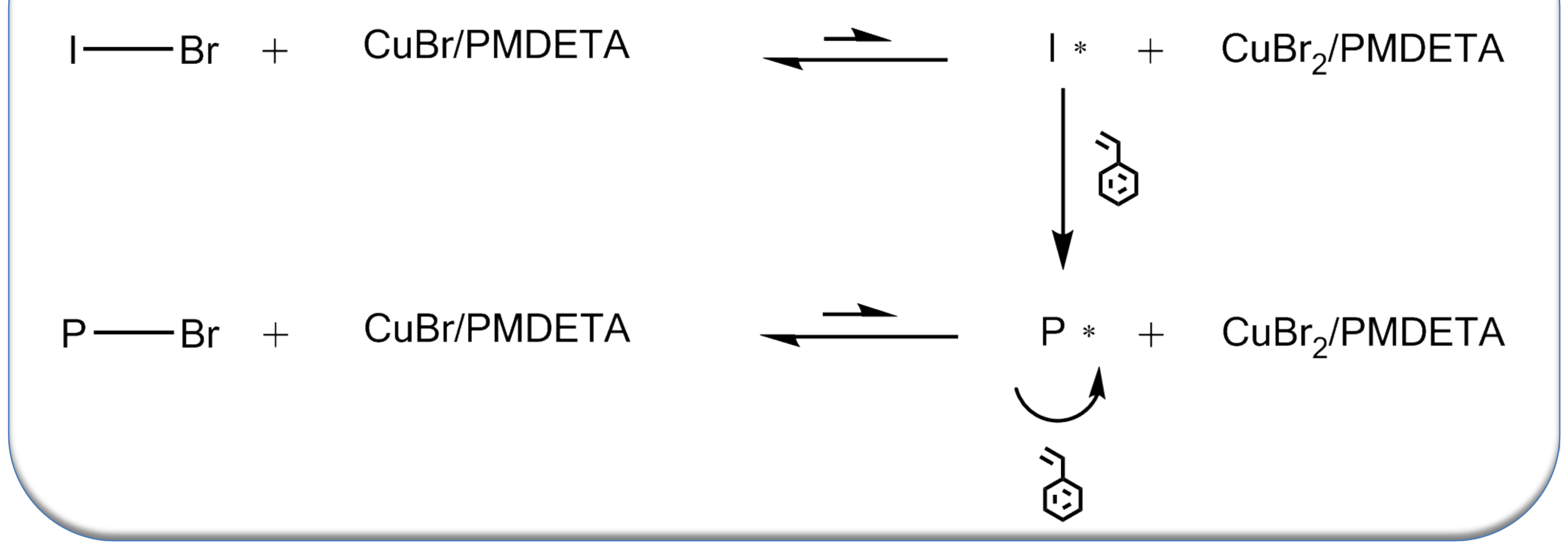
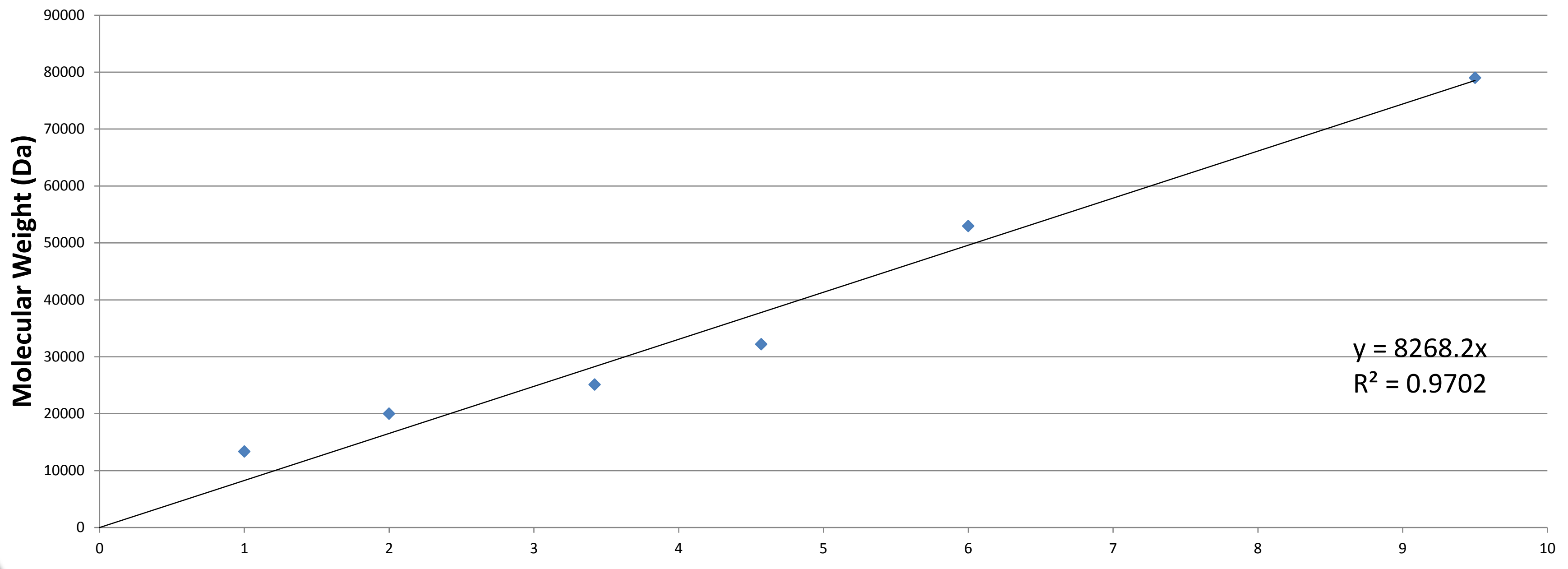


Figure 3: Transfer of bromine atoms limits the rate of the polymerization, making it possible to grow chains of a specified chain length. Stannous octoate was used to reduce the Cu(II) back to Cu(I). Originally, no polymer was produced because the styrene had been filtered using an inadequate amount of aluminum oxide, and some radical inhibitor was still present.

Figure 4: Molecular Weight of Polystyrene vs. Time



Introduction

CNTs exhibit high thermal and electrical conductivity and possess great utility in nanoelectronics. Currently, "buckypaper" is prepared by filtering a solution of CNTs suspended in solvent. Once a majority of the solvent has been removed, a thin sheet of aggregated CNTs remains. However, this method produces a brittle film and is not a practical way of depositing CNTs. Thus, a procedure to deposit a robust film of CNTs was designed.

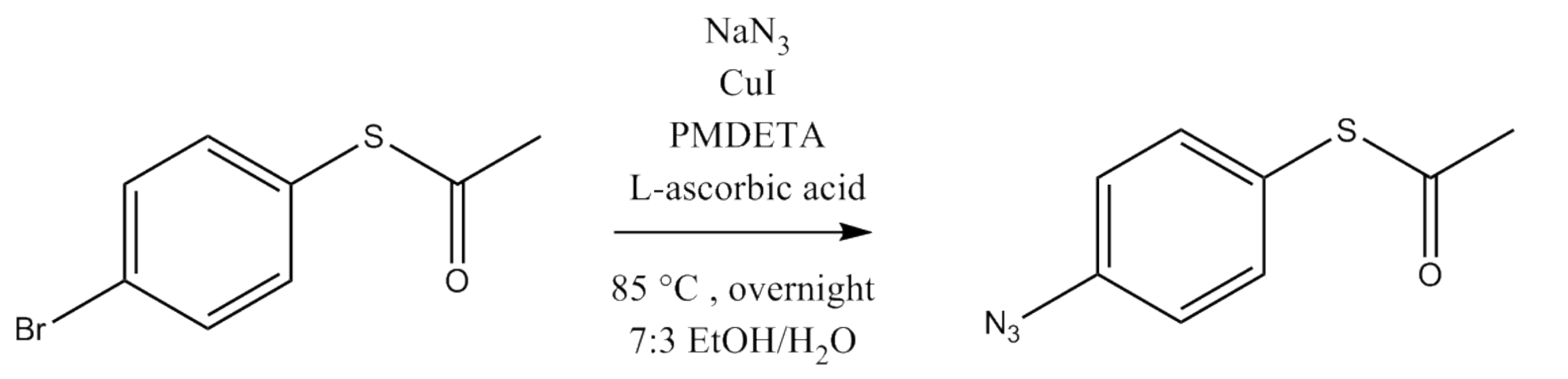
Synthesis of Azido-Thioester

During the process to make the azido coupling agent, 4-bromophenylthioacetate was deprotected, forming unwanted products: 4-azidothiophenol and 4-azidophenyl disulfide.

The cause of this deprotection was tested by adjusting reaction parameters of solvent, reagents, heating mode (traditional vs. microwave), and temperature. However, no conditions were found to provide the desired product or the reason for the deprotection. Finally, the reagent was heated in an ethanol-water system with (a) NaN_3 and (b) CuI. Both conditions caused deprotection.

It was determined that this methodology was not a viable scheme due to the inability to, in a single step, functionalize this reagent with an azide while maintaining the thiol-protecting group. We instead will focus on the commercially available 3-azidopropylthioacetate as a possible substitute for carbon nanotube functionalization. Analytical techniques included GPC, and NMR and IR spectroscopy.

Figure 5: Intended Reaction



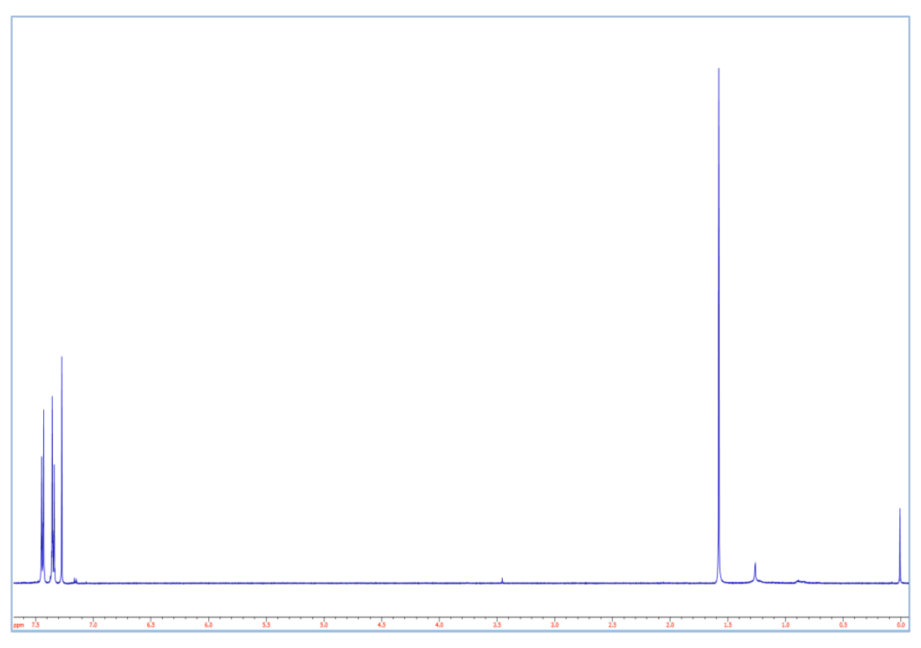


Figure 6: Actual Reaction

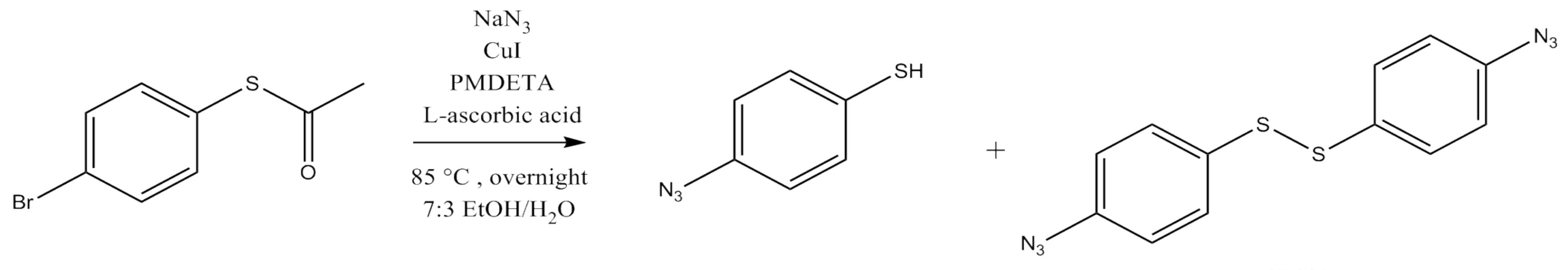
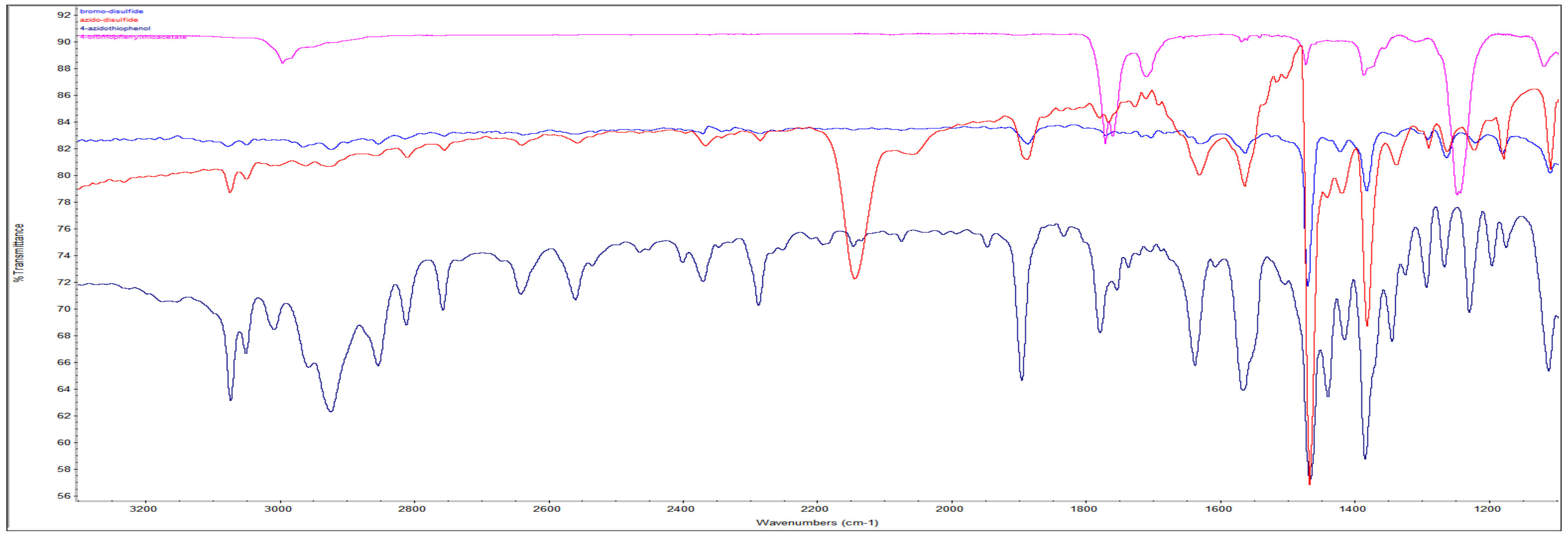


Figure 7: IR Spectra of Products



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