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Cross-Linking Carbon Nanotubes for a Conductive Film

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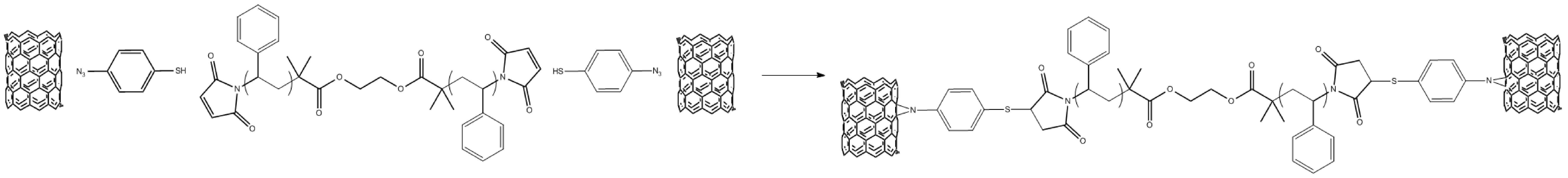
Figure 1: Overall Scheme



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

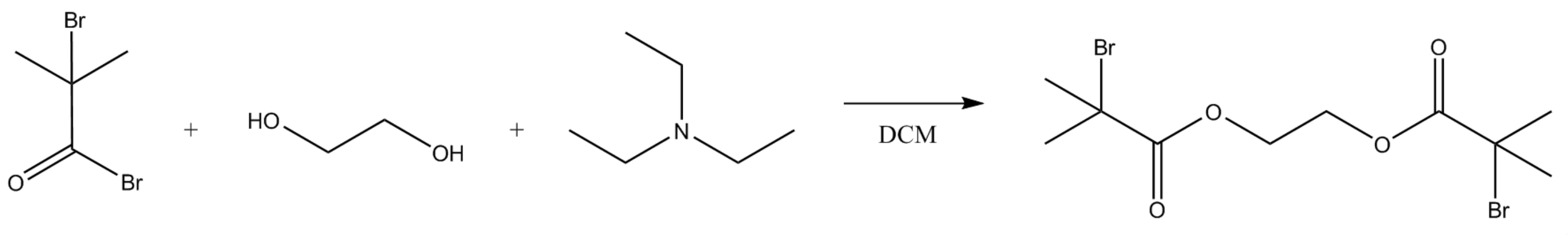


Figure 2: Polystyrene grows on either end of ethylene glycol bis(2-bromoisobutyrate)

Figure 3: ARGET Atom-transfer Radical Polymerization

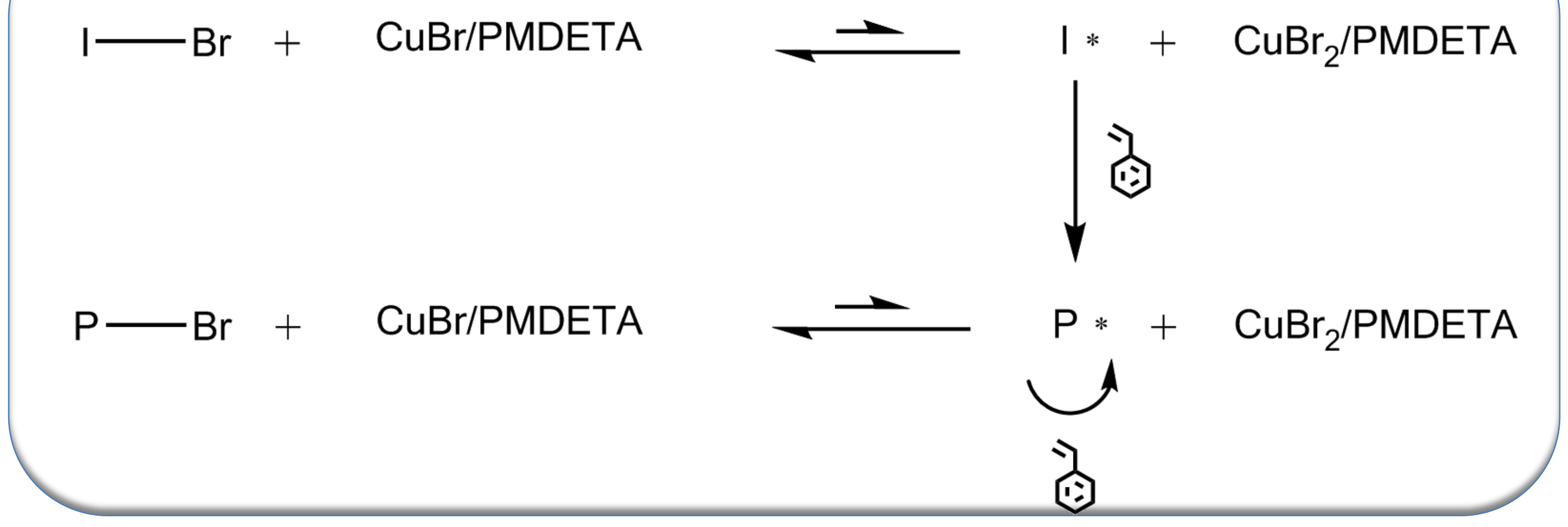
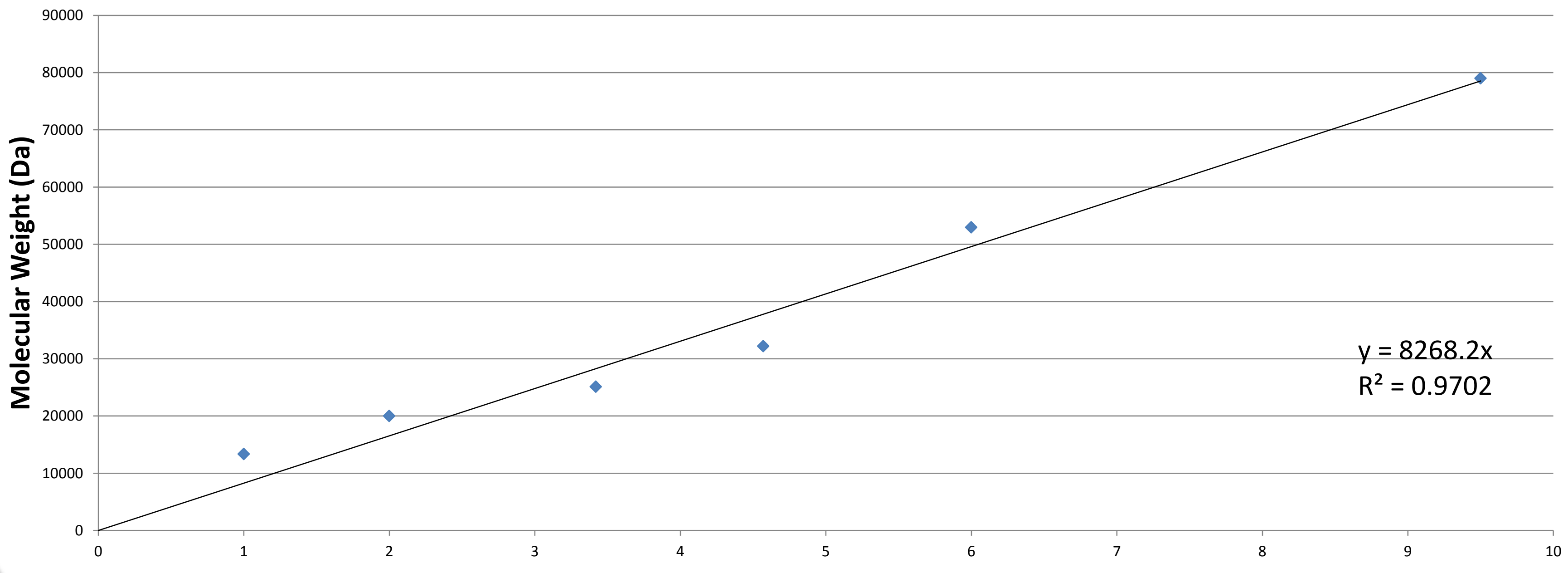


Figure 3: Transfer of bromine atoms limits the rate of the polymerization, making it possible to grow chains of a specified chain length. Stannous octoate was used to reduce the Cu(II) back to Cu(I). Originally, no polymer was produced because the styrene had been filtered using an inadequate amount 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. With conductivity similar to that of silicon and the ability to disperse heat rapidly, CNTs 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

Figure 5: Intended Reaction

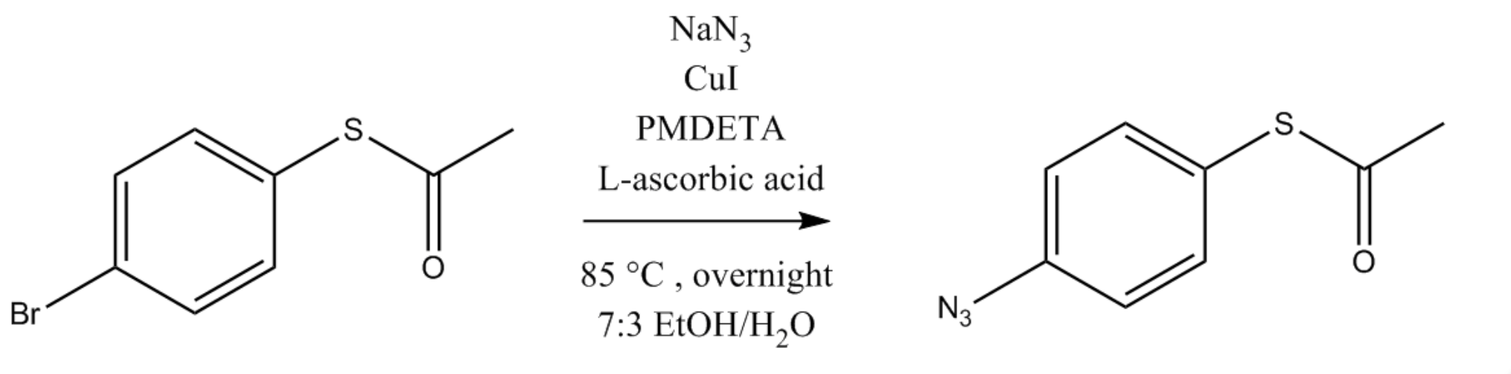
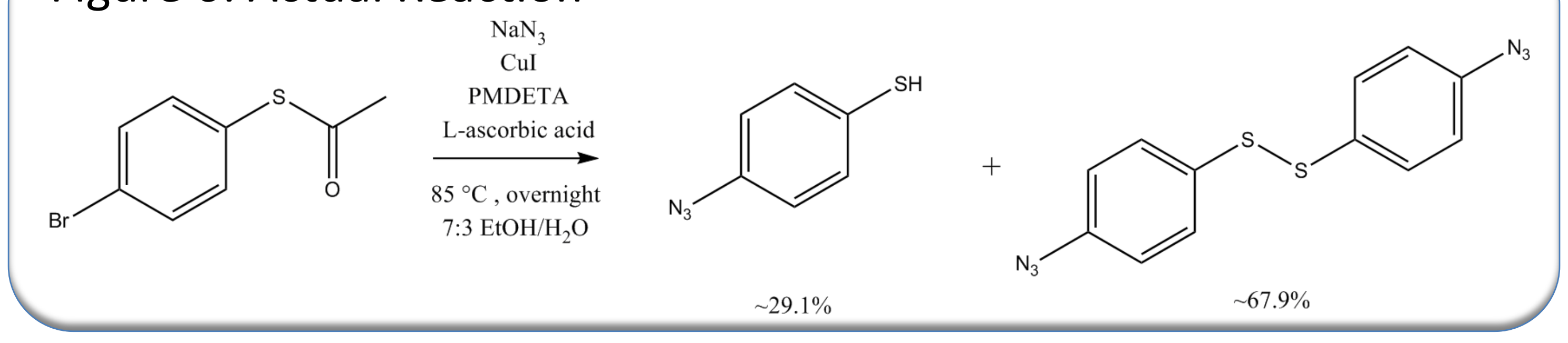
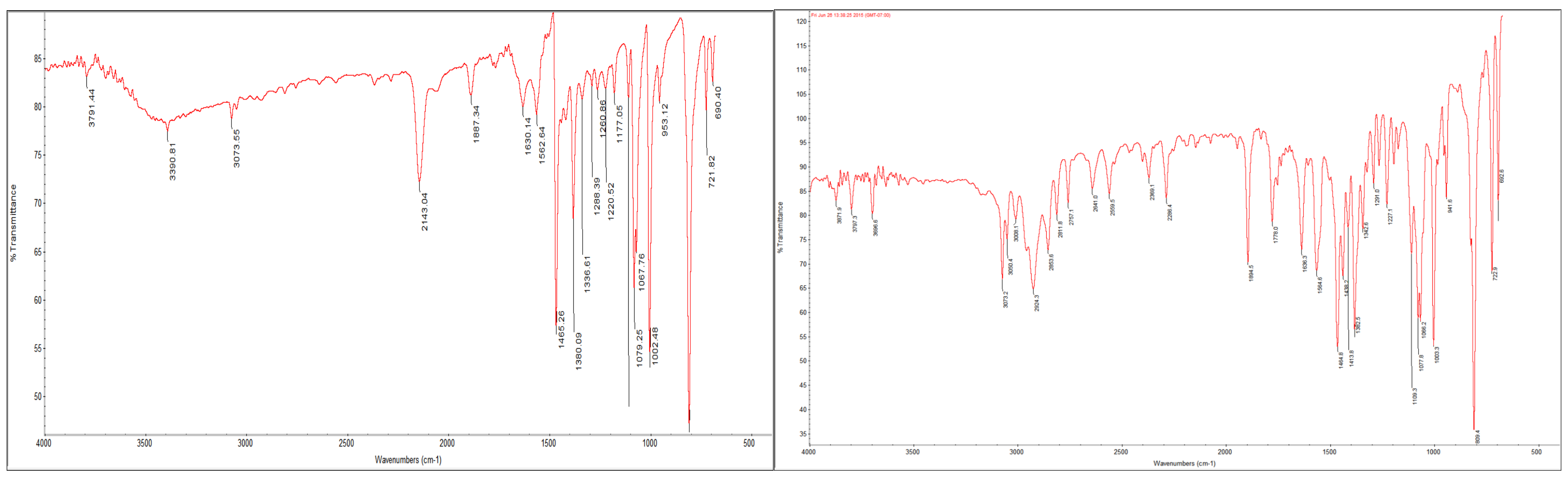


Figure 6: Actual Reaction



Ethanol-water, DMF, and toluene were used as solvents, all resulting in deprotection of the thioester. Therefore, the solvent is not responsible. It is possible that L-ascorbic acid causes deprotection. In that case, excess CuI must be used in the absence of a reducing agent.

Figure 7: (Left) IR spectrum of disulfide shows successful azidonation (Right) IR spectrum of thiol shows successful azidonation



In toluene, the reaction did not go to completion. NMR showed that 4-bromophenylthioacetate was still present. Some of the reactant had been azide-functionalized, confirmed by the presence of shifted aryl hydrogen peaks. However, no methyl peak corresponded to those peaks. Thus, 4-bromophenylthioacetate was not deprotected, while the azide-functionalized molecule was. This means that the electron-withdrawing azide group increases the thioester’s susceptibility to deprotection. The cause of deprotection is currently unknown and should be examined in future work.

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