A Colorful Grignard Reaction

Premise:
Your group is working in the fine chemicals division of a small chemical company. Your assignment is to make the triarylmethane dye crystal violet by using a Grignard synthesis.

The Grignard reagent (1) prepared from 4-bromo-N,N-dimethylaniline (equation 1) is combined with diethyl carbonate, then followed by acid hydrolysis, which leads to crystal violet (2) (equation 2).

\[
\begin{align*}
\text{CH}_3\text{NCH}_3 & \xrightarrow{\text{Mg, THF reflux}} \text{CH}_3\text{NCH}_3 \text{MgBr} \\
\text{CH}_3\text{NCH}_3 \text{MgBr} & \xrightarrow{\text{EtO}_2COEt, \text{THF}} \text{CH}_3\text{NCH}_3^+\text{CH}_3\text{Cl}^-
\end{align*}
\]

Crystal Violet

You will need to pay particular attention to the purity and yield of your product compound since you cannot sell chemicals that are impure, and you certainly want to maximize your profit by obtaining good yields of compounds.

Safety
Tetrahydrofuran (THF) is highly flammable. THF may ignite if it is close to a warm heater stirrer - be careful. Know in advance where the fire extinguisher for your lab is located. If the THF does ignite, call your lab instructor. The flames can be smothered using a fire extinguisher, wet cloth, or they can be allowed to burn out.

Bromobenzenes are irritants. Wear gloves and avoid contact.
Caution: These dyes stain readily. Be careful to avoid contact with skin or clothing. Wear gloves while handling the dye preparation. Crystal Violet is somewhat toxic. Further, the byproducts from the preparation are of unknown toxicity. The dye preparation reported here are not to be used either on clothing or on other articles that will be handled repeatedly.
Preparation of Crystal Violet

Note: All glassware and reactants must be dry. (Why?) This means do not wash your apparatus with water or even rinse it with acetone because that will also react with the Grignard reagent. If the apparatus you receive from the stockroom is not clean and dry, return the wet and/or dirty pieces and get replacements.

The apparatus you set up must include:

1. The ability to heat the reaction without losing all the solvent
2. The ability to keep the reaction relatively dry.
3. The ability to stir the reaction.

A picture of the apparatus is shown in Figure 1 (below, at end of experiment).

The dye preparation is carried out in a 250-mL round-bottomed flask equipped with a magnetic stir bar, reflux condenser, and drying tube. The flask is charged with 0.80 g magnesium turnings, THF (45 mL), 4-bromo-\(N,N\)-dimethylaniline (5.0 g), and a small crystal of iodine. The mixture is warmed gently to reflux (set the hot plate to 200 °C) and maintained there for 30 min, during which time the original dark reddish-brown color changes to the typical “dirty dishwater” shade of the Grignard reagent. Check with your TA to ensure this has indeed happened.

The flask is cooled to room temperature (ice-water bath). Be sure to keep the solution dry. After 15 min. diethyl carbonate (0.49 g) in 5 mL of THF is added in one portion. The mixture is warmed to reflux for an additional 5 min, and then cooled again to room temperature (ice-water bath). Aqueous hydrochloric acid (15 mL of a 10% solution) is added slowly while stirring (the reaction with the remaining unreacted magnesium is vigorous). Keep stirring the mixture for 15 min. The result is a purple solution with some unreacted magnesium in the bottom. Fill one labeled vial from the side shelf with your solution. This is about 20 mL.

Quantitation Measurement

Using an Eppendorf pipet, transfer a 1.0 mL aliquot of the solution in your vial from last period into a clean 100-mL volumetric flask and dilute with water to 100 mL. Mix well. Pour a small volume (~ 10 mL) of this newly diluted liquid into another clean 50-mL beaker. Use the Eppendorf pipet (with a new pipet tip) to transfer 6.0 mL of this solution into another clean, dry 100-mL volumetric flask and dilute with water to 100 mL. Mix well. Pour ~ 40 mL of this solution into a clean, dry beaker.

For Crystal Violet: The absorbance of this solution is measured at 590 nm using a Spectronic-20 “Spec-20” spectrophotometer. An absorbance of 1.85 indicates a yield of 100% (based on the limiting reagent, diethyl carbonate) of crystal violet chloride.

Crystal violet (CV) solutions obey Beer's law. The relationship between absorbance and the CV concentration is given by:

\[ A = \varepsilon l c \quad (3) \]

\(A\) is the reaction solution’s absorbance value, which you will measure; 
\(\varepsilon\) is the molar absorptivity value and for crystal violet, \(\varepsilon = 5.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}\); 
\(l\) is the cell path length (1.00 cm); 
\(c\) is the CV molar concentration, [CV].

Beer's law can be used to calculate [CV] from an absorbance reading.

1. Set the spectrophotometer wavelength to 590 nm.
2. Before beginning the measurements, a 0% and 100% transmittance calibration needs to be
performed according to the instructions on the Spec 20 [0%T with no cuvet (left knob) and 100% T with distilled water blank (right knob)]. Remember to wipe off any fingerprints on the outside of the cuvet with a Kimwipe©. When completed, empty the distilled water cuvet.

3. Rinse the cuvet three times with your solution made in the final dilution.
4. Set the colorimeter to read absorbance.
5. Wipe the outside of the cuvet with a Kimwipe©.
6. Place the cuvet in the spectrometer and read the absorbance value.

**Waste Disposal**
All excess dye solutions should be poured into the acid waste container.