**Synthesis of Trans-9-(2-Phenylethenyl)anthracene via the Wittig Reaction**

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**Introduction:**

Carbon-carbon bonds are the most prevalent in organic molecules that form the basis for a majority of matter on Earth. Therefore, perhaps the most important target for organic synthesis reactions is the formation of carbon-carbon bonds. There are many useful carbon-carbon bond forming reactions, including the use of organometallic reagents, the aldol reaction, the Michael reaction, alkylation reactions, and coupling reactions. Most of these reactions result in the formation of carbon-carbon single bond. It is harder to form carbon-carbon double bonds, especially with stereoselectivity for an alkene product.

The Wittig reaction, discovered by Georg Wittig in 1954, results in the formation of a carbon-carbon double bond, with *trans* alkene stereoselectivity. The reaction utilizes an aldehyde or ketone nucleophile and an phosphorus ylide electrophile to add a substituent of interest.[1]

In this experiment, the Wittig reagent, a phosphorus ylide, benzyltriphenyl-phosphorus ylide, was prepared by deprotonation of the phosphonium salt with sodium hydroxide, benzyltriphenyl-phosphonium chloride. 9-anthracene-carboxaldehyde was used as the aldehyde nucleophile in a reaction with the ylide to form the alkene product, *trans*-9-(2-phenylethenyl)-anthracene (Figure 1). In this reaction, a carbon-carbon double bond

was formed with *trans* stereoselectivity, demonstrating the usefulness of the Wittig reaction.
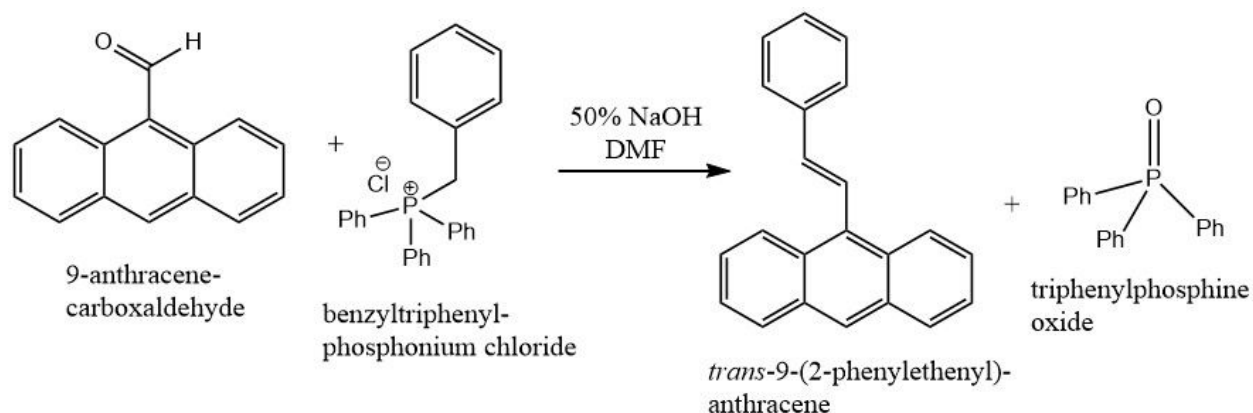


**Figure 1.** Reaction between 9-anthracene-carboxyaldehyde and benzyltriphenyl-phosphonium chloride to form *trans*=9-(2-phenylethenyl)-anthracene and triphenylphosphine oxide.

  The mechanism for the synthesis of *trans*-9-(2-phenylethenyl)-anthracene begins with the formation of the phosphorus ylide, which involves the deprotonation on the benzyltriphenyl-phosphonium ion, forming the ylide zwitterion. The carbanion is then able to attack the carbonyl on 9-athracene-carboxyaldehyde, forming a large intermediate molecule. The negatively charged oxygen then attacks the positively charged phosphorus, closing the molecule into a key, 4 membered cyclic transition state. This cyclic ring collapses, cleaving the molecule by the carbon-phosphorus bond electrons falling into a π carbon-carbon bond, cleaving the former carbon-oxygen carbonyl bond. The resulting two products are the alkene *trans*-9-(2-phenylethenyl)-anthracene and the byproduct triphenylphosphine oxide.[2] Because of the cyclic transition state, only the *trans* product forms.[3]
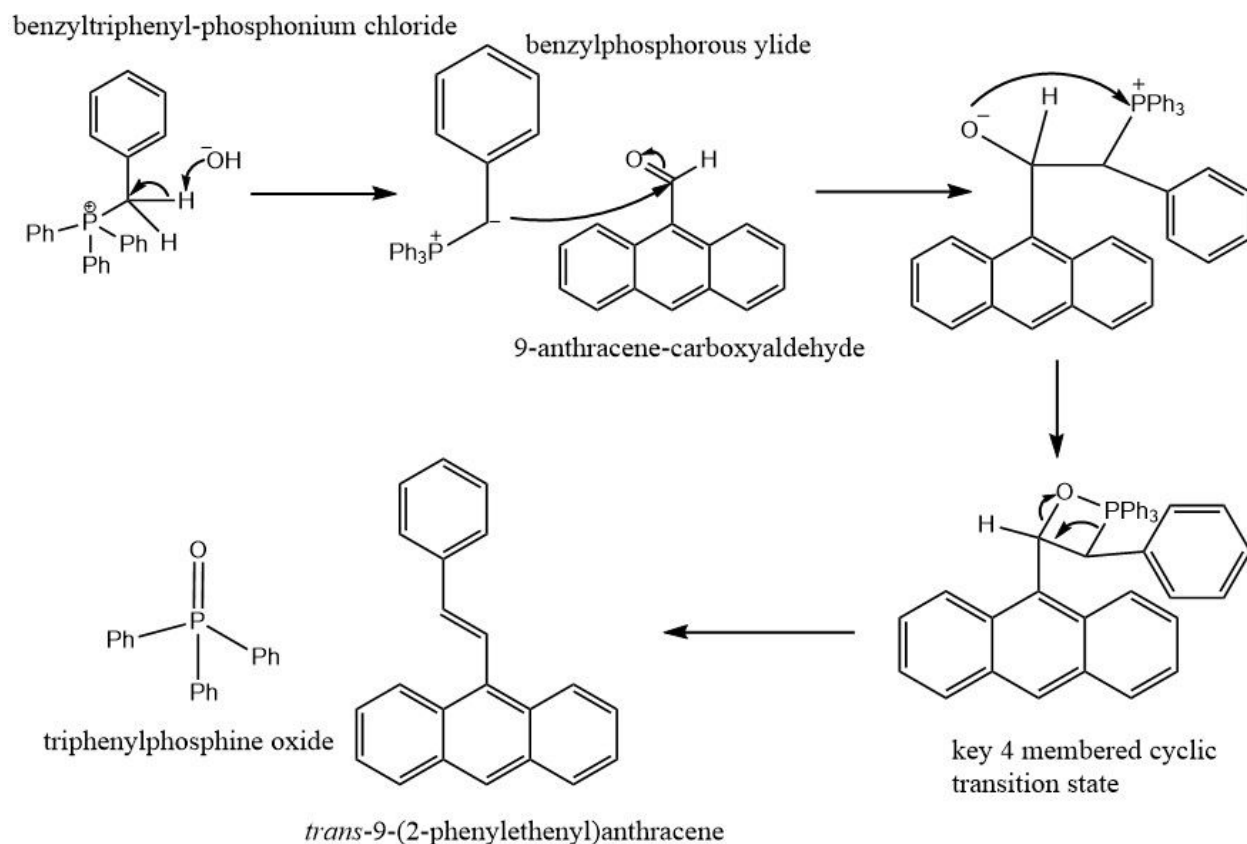
**Figure 2.** Mechanism of Wittig reaction between benzylphosphorous ylide and 9-anthracene-carboxyaldehyde to form trans-9-(2-phenylethenyl)anthracene

*Trans*-9-(2-phenylethenyl)anthracene was synthesized via the Wittig reaction between benzyltriphenyl-phosphonium chloride and 9-anthracenecarboxyaldehyde. The reaction was monitored by TLC and the product was purified by column chromatography. The product mixture was worked up by the addition of a water/1-propanol mixture. The product was then characterized by $^1$H NMR, IR, and melting point analyses.

**Results, Discussion, and Conclusion:**

The alkene product *trans*-9-(2-phenylethenyl)anthracene was synthesized via the Wittig reaction between the ylide precursor benzyltriphenyl-phosphonium chloride and the carbonyl

nucleophile 9-anthracenecarboxyaldehyde. The reaction was monitored by TLC, the product mixture was purified by column chromatography, and the presence of pure product was proven by [1]h NMR, IR, and melting point analyses.

The two reactants were specifically chosen for this experiment for various reasons. First, only the *trans* product forms, resulting in easier characterization of the product. Second, the UV active *trans*-9-(2-phenylethenyl)anthracene is able to be visualized on a TLC plate. Third, the product readily crystallizes, allowing for easy separation and collection.

The reaction was monitored by TLC, exploiting the differing polarities of the reactants and products. The ionic phosphonium salt was by far the most polar, and its spot could be visualized at the base of the TLC plate, essentially not moving at all (Rf = 0). Subtle differences in polarities could be seen between the alkene product and the aldehyde reactant. Due to the hydrogen bonding ability of the aldehyde, the aldehyde is slightly more polar, resulting in a smaller Rf value (Rf =0.539) compared to the product (Rf = 0.608). Additionally, the product could be visualized as a strong brilliant blue spot under UV light. After 75 minutes, the aldehyde reactant spot was no longer visible, indicating that the reaction had gone to completion.

In order to precipitate the product, a mixture of 1-propanol and water was added to the reaction mixture. This mixture increased the polarity of the product mixture, allowing the dissolved product to precipitate as a glossy, orange solid. The crude percent yield for the reaction was 70.0%, which is higher than reported percent yields of 40-60%.[4] This indicated the presence of impurities in the crude product, so column chromatography was used to purify the product. 20 fractions were collected from the column. The product eluted within the second fraction of the column eluent, which was visualized with TLC by observing the brilliant blue spot under UV

light. However, the first two fractions containing product also contained an impurity spot, indicating the presence of starting material. Due to the presence of impurities in these fraction, they were not combined with the other pure fractions. The last fraction containing product was fraction 17. Therefore, fractions 4 through 17 were combined to obtain the pure product. The percent recovery for the column chromatography purification was 74.0%. This moderate percent recovery indicates the separation of impurities from the crude product. The purified percent yield for the reaction was 51.8%, which fits within the reported percent yields of 40-60%. It is lower than the higher limit because of the non-inclusion of the first two eluent fractions containing product in the purified product.

The purified product was characterized by $^1$H NMR analysis (Figure 1, Supplementary Materials). 14 aromatic protons peaks were visible, corresponding to the 14 aromatic protons present in *trans*-9-(2-phenylethenyl)anthracene. The key identifiers in the $^1$H NMR spectrum, however, are the alkene proton shifts present at a chemical shift of 6.929 ppm and 7.898 ppm. These protons are shifted further downfield than normal alkene protons because of the electron withdrawing effects of the aromatic rings in *trans*-9-(2-phenylethenyl)anthracene, which deshield these protons. The coupling constants for these protons were 19.2 Hz for the one closer to the anthracene group and 16 Hz for the one closer to the benzyl group. This proves the formation of the *trans* isomer since the coupling constant is greater than 14 Hz.[5] In addition, the absence of an aldehyde proton indicates the successful purification of the product from any remaining starting materials. Two small impurity peaks are visible between 1 and 1.5 ppm. These are probably due to residual water

The purified product was also characterized by IR spectral analysis (Figure 2, Supplementary Materials). The IR spectrum provided conflicting evidence as to the successful formation and purification of *trans*-9-(2-phenylethenyl)anthracene. A strong peak at 3025.24 cm$^{-1}$ corresponds to the alkene and aromatic carbon-hydrogen bonds of the product and carbon-carbon aromatic peaks are visible at 1487.78 cm$^{-1}$ and 1445.22 cm$^{-1}$. However, a carbonyl peak is present at 1725.78 cm$^{-1}$, indicating the presence of residual starting material. The key identifier should have been a carbon-carbon alkene peak at 1675 cm$^{-1}$. However, this peak is absent or extremely weak. The IR data, therefore, does not support the successful formation and purification of *trans*-9-(2-phenylethenyl)anthracene. The discrepancy between the IR and $^1$H NMR data is confusing. The only explanation is contamination of the IR sample, perhaps by the spatula used to crush up the solid. If residual starting material or another carbonyl containing compound was on the spatula, the sample could have been contaminated, explaining the impure IR spectrum.

Melting point analysis was also performed on the purified solid. The melting point range was experimentally determined to be 129.4 - 131.6 ℃, which matches the actual melting point of *trans*-9-(2-phenylethenyl)anthracene of 131 ℃.[4] The accuracy of the experimental melting point and the small range indicates successful formation and purification of *trans*-9-(2-phenylethenyl)anthracene.

In conclusion, *trans*-9-(2-phenylethenyl)anthracene was synthesized via the Wittig reaction between 9-anthracenecarboxyaldehyde and benzyltriphenyl-phosphonium chloride. The product mixture was worked up using the addition of a 1-propanol and water mixture and purified using column chromatography. $^1$H NMR and melting point analysis supported the

successful formation and purification of *trans*-9-(2-phenylethenyl)anthracene, but IR analysis contradicted the conclusions of ^{1}H NMR and melting point analysis. Future experiments could seek to form the same product by reacting an alkane with the Lindlar catalyst. Other experiments could seek to increase the yield of the reaction by testing more reactive nucleophiles. Purification could have been facilitated by experimenting with different solvents, as the first two product fractions contained overlap with impurity spots in this experiment.

**Experimental:**

Benzyltriphenyl-phosphonium chloride (2.0 mmol, 778 mg) and 9-anthracenecarboxyaldehyde (1.0 mmol, 206 mg) were added to dimethylformamide (10 mL). 50% NaOH solution (1 mL) was added dropwise while stirring. The reaction was heated under reflux at 50 ℃ and monitored using TLC (40:60 EtOAc:Hexanes. The reaction was worked up by the addition of 1:1 1-propanol:water solution (10 mL) to precipitate the crude product with a percent yield of 70.0% (0.196 mg), which was isolated by vacuum filtration to yield a glossy orange solid. The product was purified by column chromatography (50:1 Hexanes:Dichloromethane to 20:1 Hexanes:Dichloromethane) with a percent recovery of 74.0% and a purified yield of 51.8% (0.145 mg) to yield a yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 6.929 (d, 1H), 7.243 (t, 1H), 7.357 (m, 6H), 7.676 (d, 2H), 7.898 (d, 1H), 8.021 (d, 2H), 8.352, (d, 2H), 8.403 (s, 1H).  IR (ATR) ν$_{max}$ (cm$^{-1}$) 3025.24, 2926.98, 1725.78, 1487.78, 1445.22. Melting point 129.4 - 131.6 ℃.

# References

(1) Breton, G.The Wittig Reaction: Generation, Observation and Reactivity of a Phosphorus Ylide Intermediate.*J. Chem. Educ.*, **1997**, *74*(1), 114.

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(3) Pike, R. M.; Mayo, D. W.; Butcher, D. W.; Butcher, S. S.; Hinkle, R. J. Microscale organic laboratory: IV: A simple and rapid procedure for carrying out Wittig reactions. *J. Chem. Educ.* **1986**, 63, 917.

(4) Dykstra, S. Experiment 63: Wittig Reaction.

(5) Lampman, G. M.; Koops, R. W.; Olden, C. C. Solvent-Free Wittig Reaction: A Green Organic Chemistry Laboratory *J. Chem. Educ.* **1985**, *62*, 267–268.

**Figure 1.** 400 MHz $^1$H NMR of *trans*-9-(2-phenylethenyl)anthracene

**Figure 2.** IR Spectrum of *trans*-9-(2-phenylethenyl)anthracene
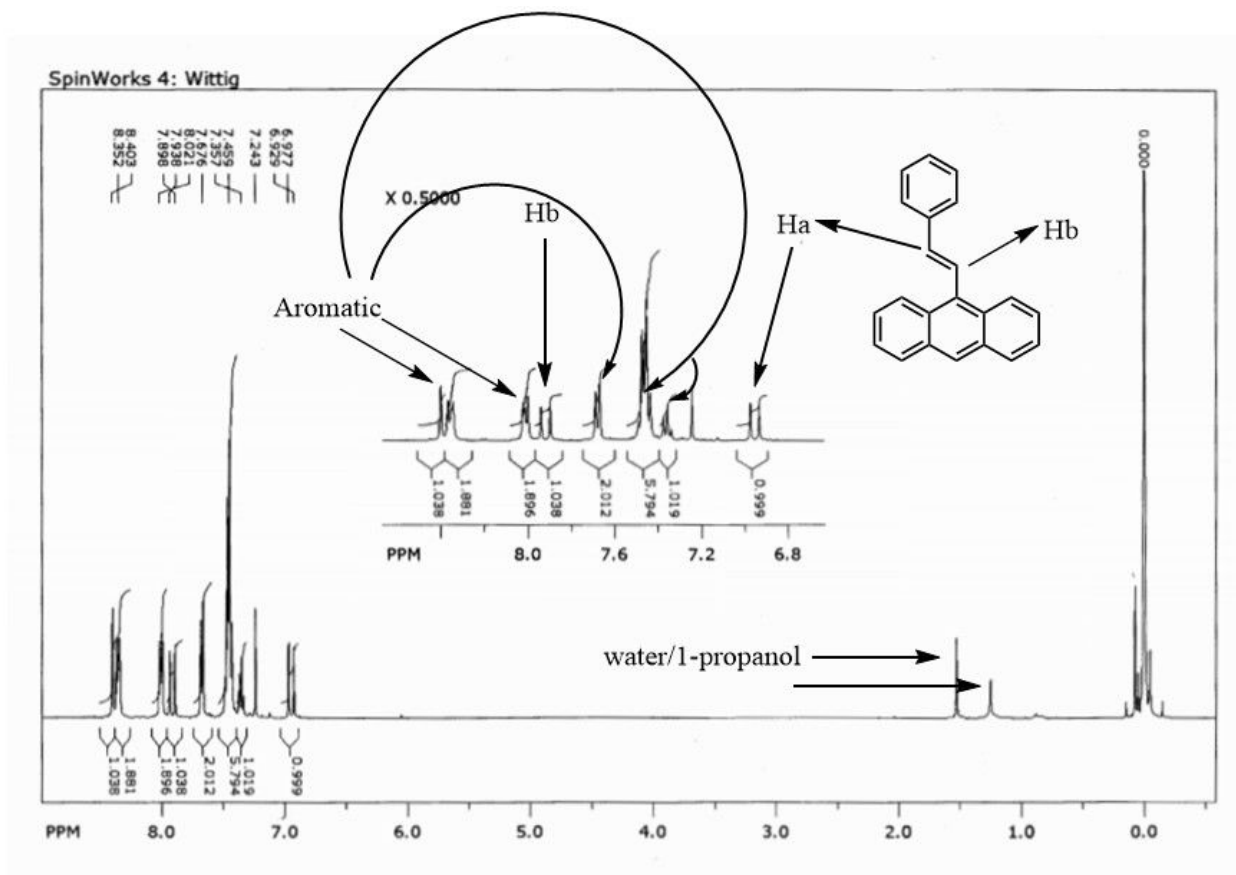
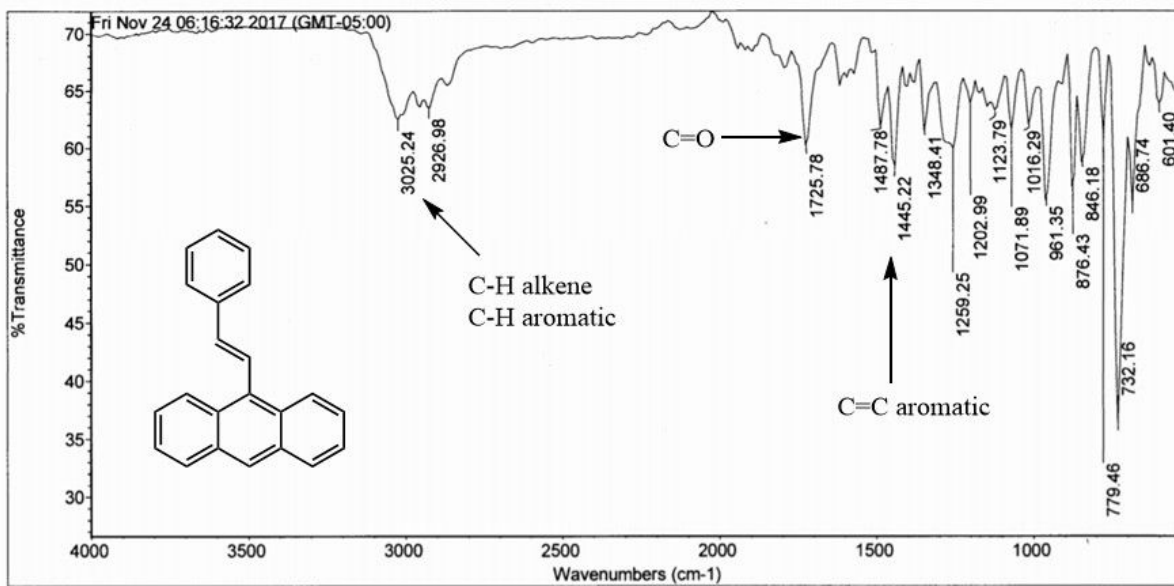**Figure 3.** 60 MHz $^1$H NMR of *trans*-9-(2-phenylethenyl)anthracene
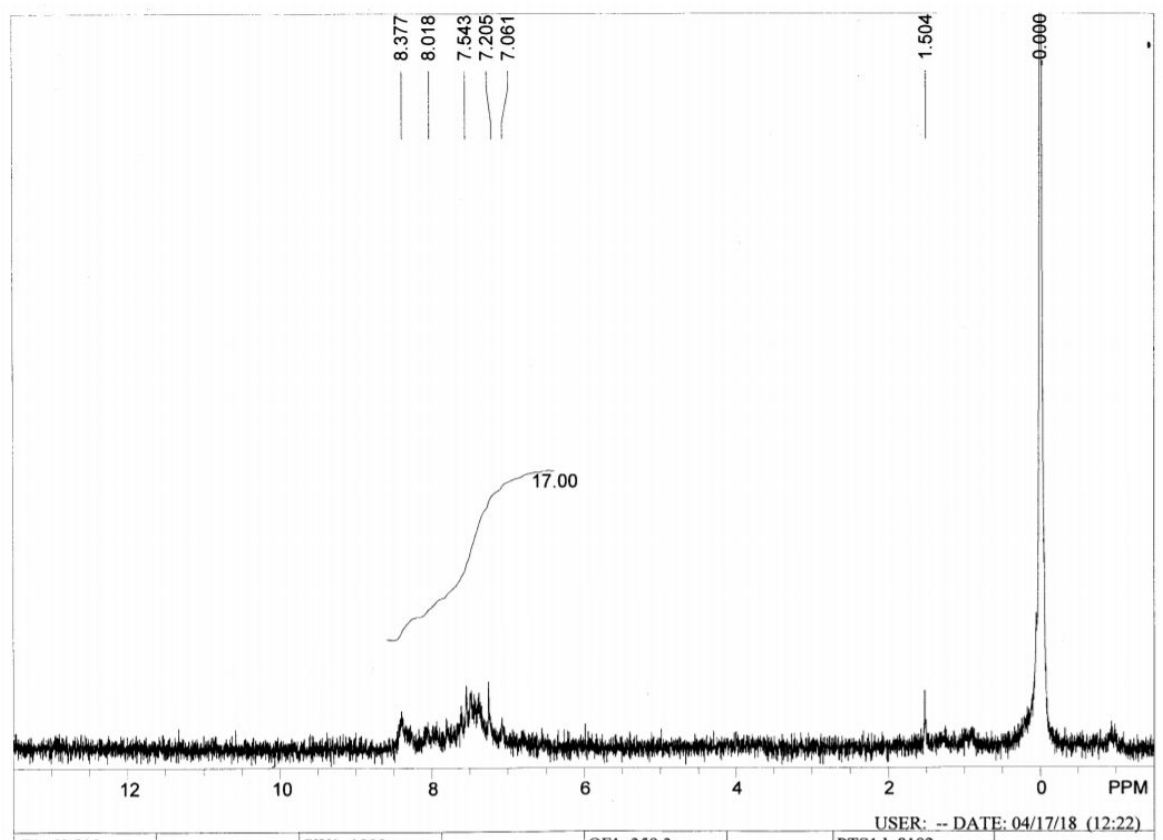


Figure 1

Figure 2



Figure 3