



Towards the Synthesis of Benzo[c]phenanthrene

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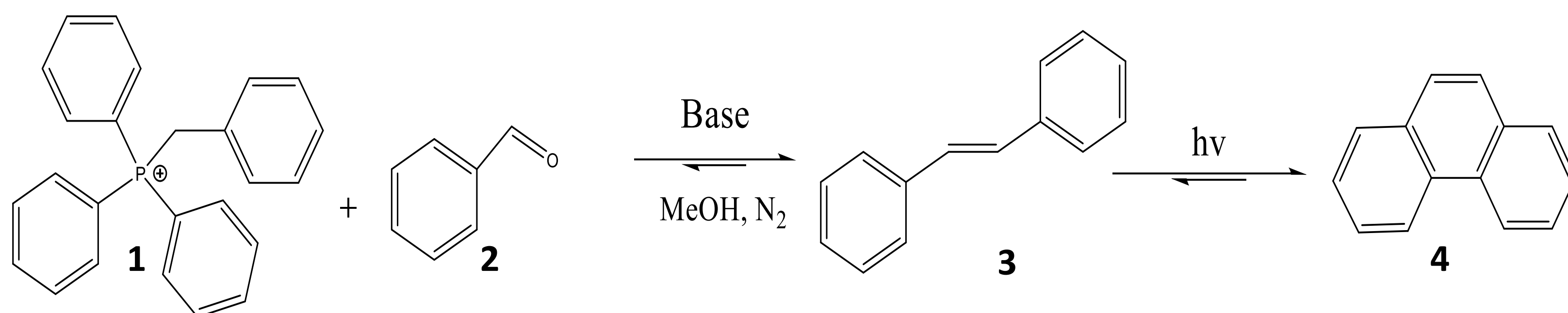
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Background

The oxidative photocyclizations of stilbenes:

The oxidative photocyclizations of stilbenes, discovered earlier during studies of the photochemical isomerization of stilbenes, did not become feasible as a synthetic tool because it contained lots of side reactions. After Mallory discovered in 1964 that iodine could catalyze the reaction, the reaction can be more concentrated solutions and fewer side reactions. The reaction was thoroughly reviewed by Mallory in a large chapter in Organic Reactions in 1984. The scheme of the the oxidative photocyclizations of stilbenes was shown below.

In order to do photocyclization reaction, Stilbene 3 was synthesis by reaction with the Wittig salt 1 and aldehyde 2 in standard conditions. Pure stilbene 3 was convert to 4 by photodehydrocyclization reaction. This method is applied to synthesis Benzo[c]phenanthrene.

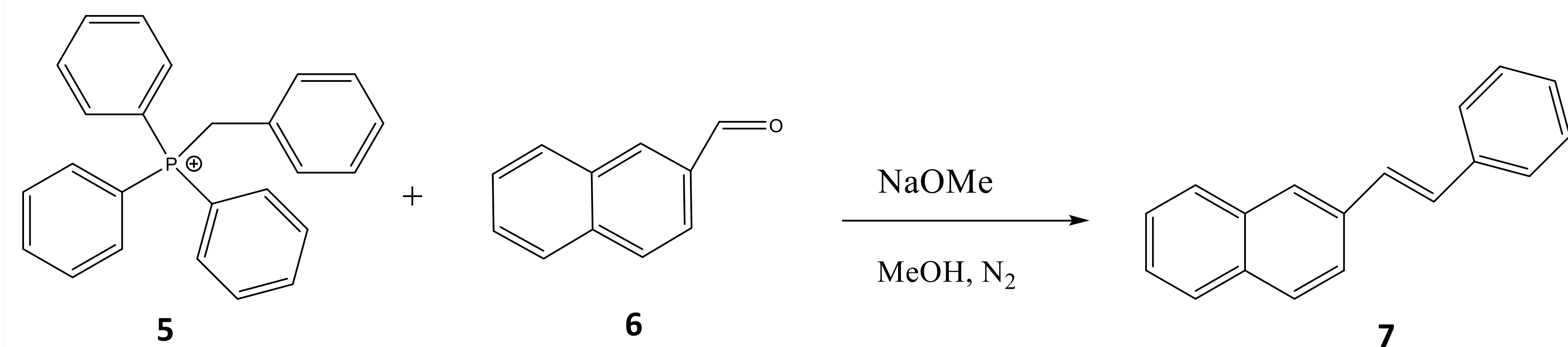


Scheme 1. The synthesis of the oxidative photocyclizations of stilbene

Experimental

The synthesis of 1-(2-naphthyl)-2-phenylethylene (Wittig reaction):

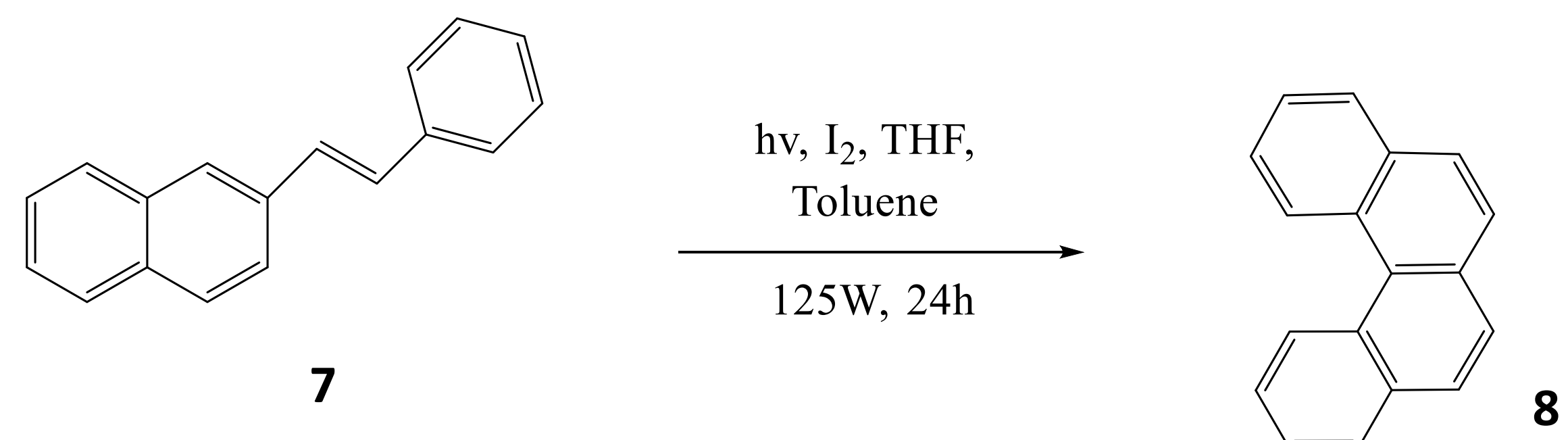
2-naphthaldehyde 6 was converted into 1-(2-naphthyl)-2-phenylethylene 7 by reaction with the Witting salt benzyltriphenylphosphine 5 under a standard condition. The pure product was isolated by recrystallization using ethanol and water.



Scheme 2. The synthesis of 1-(2-naphthyl)-2-phenylethylene

The synthesis of Benzo[c]phenanthrene (The oxidative photocyclizations of stilbenes):

The photodehydrocyclization of 7 in toluene with iodine and THF produce Benzo[c]phenanthrene 8, and 8 was purified by recrystallization using ethyl acetate.



Scheme 3. The synthesis of Benzo[c]phenanthrene

Results and Discussion

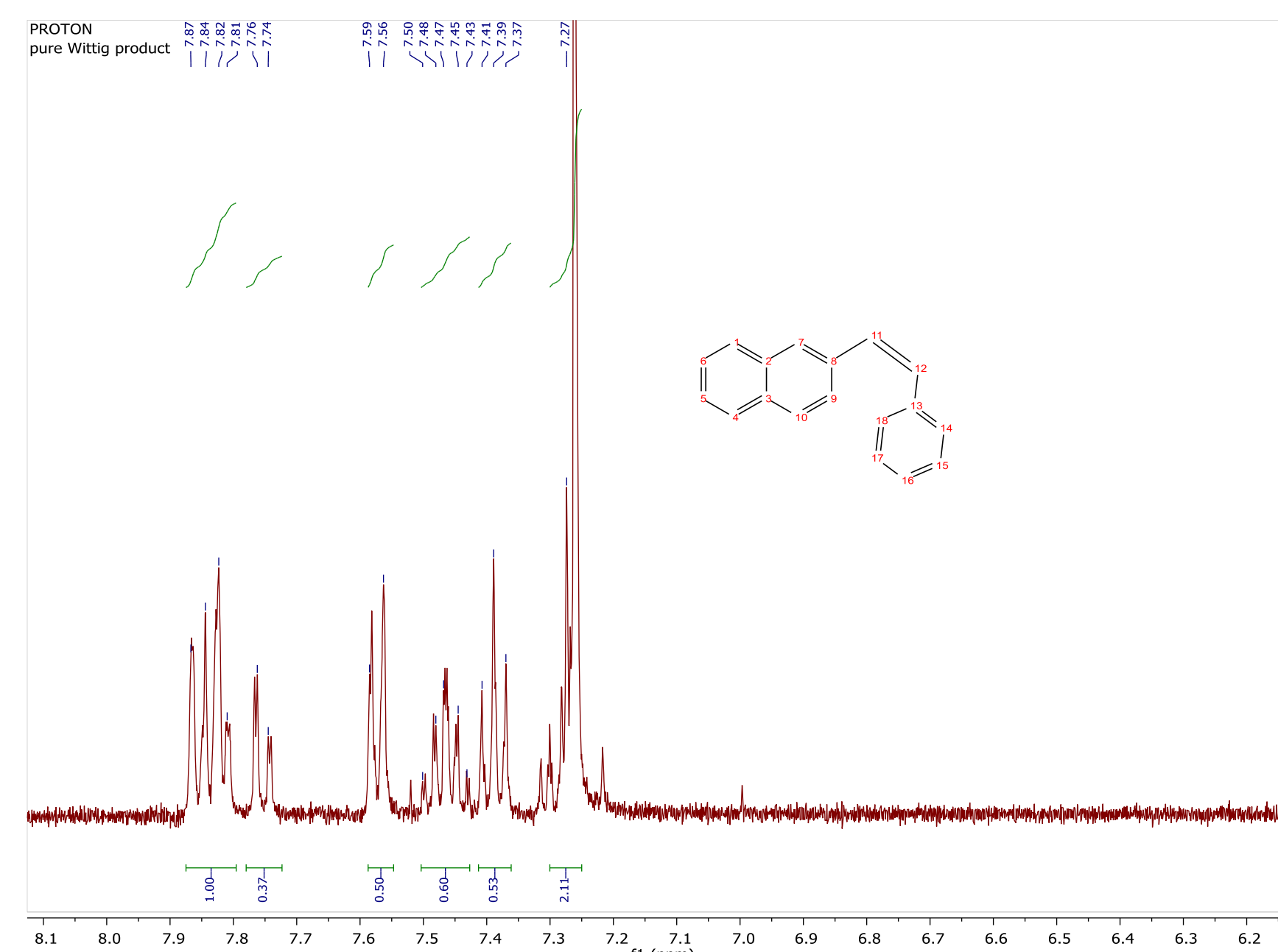


Figure 1. NMR of Pure 1-(2-naphthyl)-2-phenylethylene

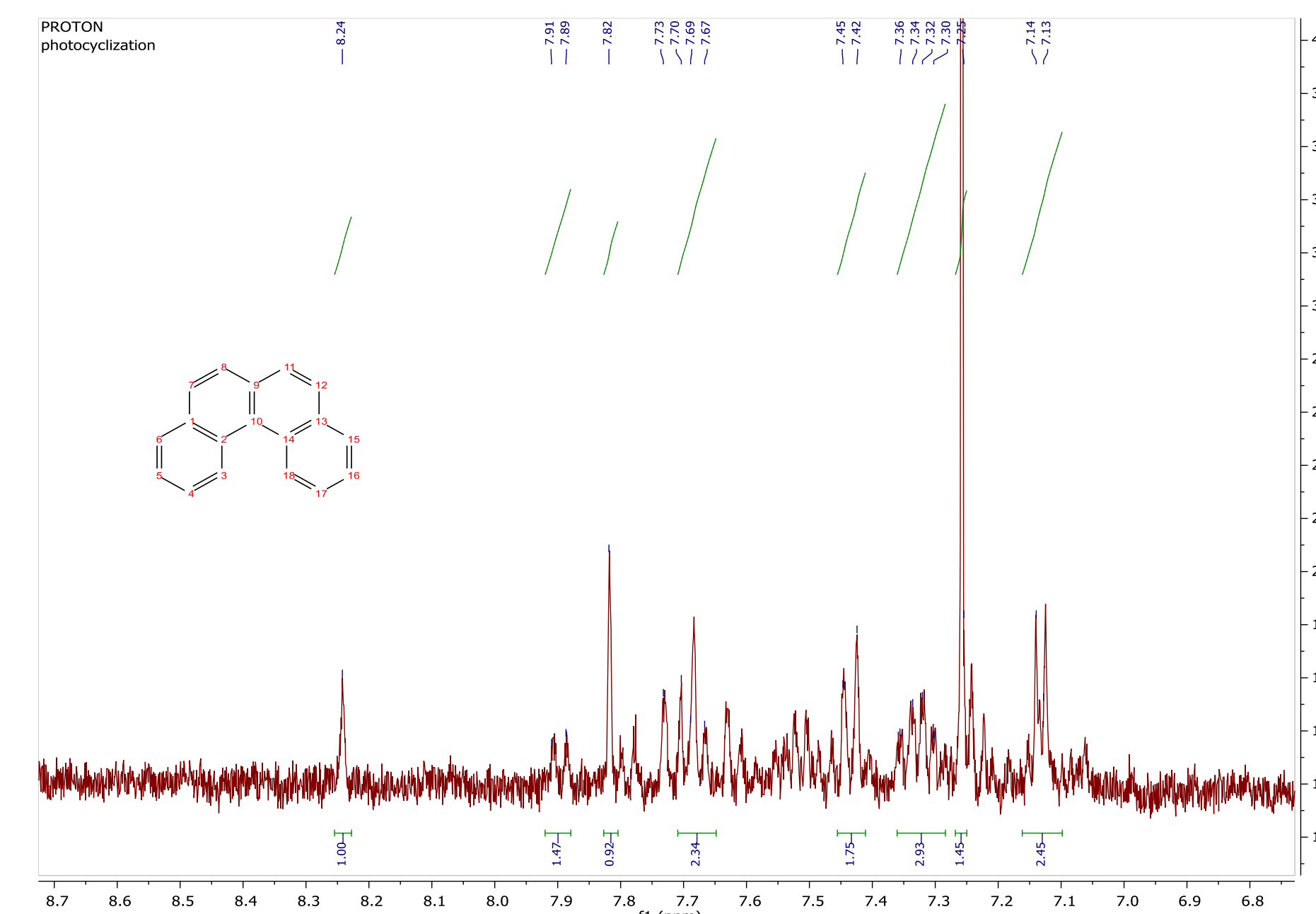


Figure 2. NMR of photocyclodehydrogenation

According to the literature NMR data of 7, it indicated that the pure 7 from the Witting reaction was 1-(2-naphthyl)-2-phenylethylene. However, the Witting reaction's yield was 12.7%, and it was lower than expect. So, the reaction was redone in higher yield 68.9%. Comparing the literature NMR data of 8 with the experimental result, it shows that the product of photodehydrocyclization reaction was not 8. The NMR of final product indicates that it is an aromatic compound. Somehow, it shows that there was lots of acetone after recrystallization. 8 might be lost during the recrystallization or extraction.

Conclusions and future work

Overall, The NMR of Wittig reaction indicates that the 1-(2-naphthyl)-2-phenylethylene was successful made with a lower yield than expect; the final product was not made. So, the reaction was not quite successful. In order to improve the reaction yield, experimenter should keep the nitrogen connecting until the reaction done because the use of strong base require a moisture-free condition to keep base at a high concentration, and a high concentration base can do deprotonation easily. Also, they can use NaOH to replace sodium methoxide to increase deprotonate capability. The NMR of the oxidative photocyclizations of stilbenes indicates that there is no final product. The final product might be lost during the extraction. In order to improve purification, experimenters can do column chromatograph using petroleum ether as eluent.

References and Acknowledgments

1. Photochemistry of Stilbenes. III. Some Aspects of the Mechanism of Photocyclization to Phenanthrenes Frank B. Mallory, Clelia S. Wood, and Janice T. Gordon *Journal of the American Chemical Society* 1964 86 (15), 3094-3102 DOI: 10.1021/ja01069a025

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