

Supplementary Material

Dichotomous stereocontrol in Claisen-Schmidt condensations: synthesis of a propeller shaped rigid system

C. Nithya, C. S. Aswathi, and T. S. Saumya *

Department of Applied Chemistry, Cochin University of Science & Technology, Kochi-682022, Kerala, India

Email: saumyatsoman@gmail.com

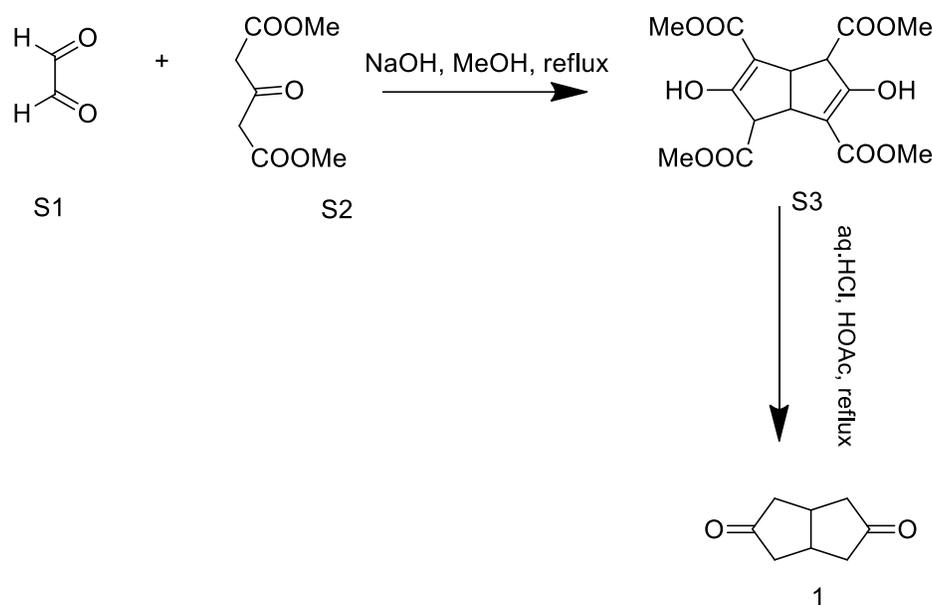
Table of Contents

I. General experimental information	S2
2. Synthesis of Tetrahydropentalene-2,5(1H,3H)-dione	S2
3. ¹ H and ¹³ C NMR spectra of 6	S3
4. ¹ H and ¹³ C NMR spectra of 3	S4
5. ¹ H NMR spectra of 5	S5

1. General experimental information

All reactions were carried out in oven dried glassware. All starting materials were purchased from *Sigma-Aldrich* or from *spectrochem* and were used without further purification. Progress of reactions was monitored by thin layer chromatography using dried and activated silica gel TLC plates (aluminum sheets coated with silica gel, E. Merck). Visualization of TLC plates was done by exposure to iodine vapors or UV lamp. The products were further purified by recrystallization from appropriate solvent systems. ^1H NMR spectra were measured on Bruker Avance 400/500 MHz instruments in CDCl_3 . The data were recorded as follows: chemical shift in ppm downfield of tetramethylsilane taken as internal standard on the δ scale, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet), coupling constant (Hz) and integration. Mass spectral data were obtained by direct injection to Waters 3100 mass detector with an electrospray ionization unit.

1. Synthesis of Tetrahydropentalene-2,5(1H,3H)-dione (1)

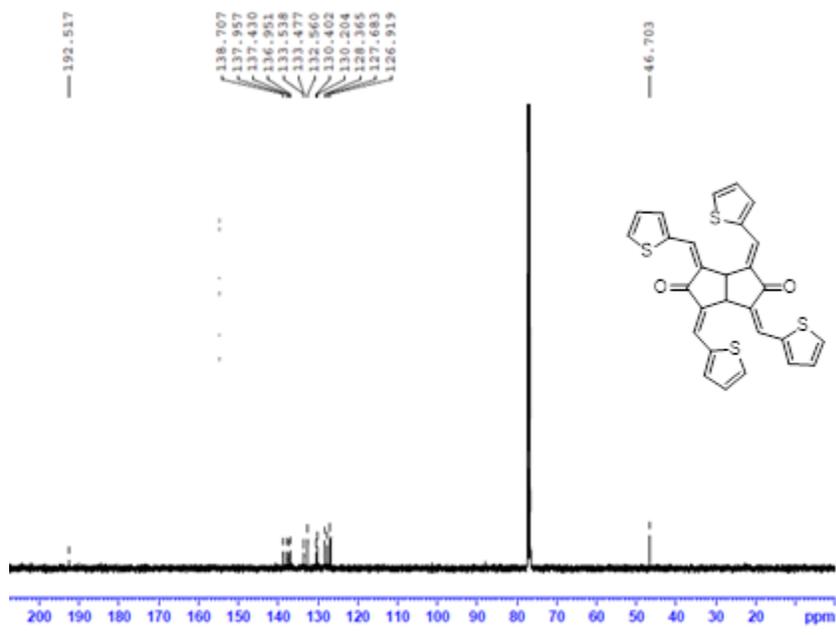


Scheme S1

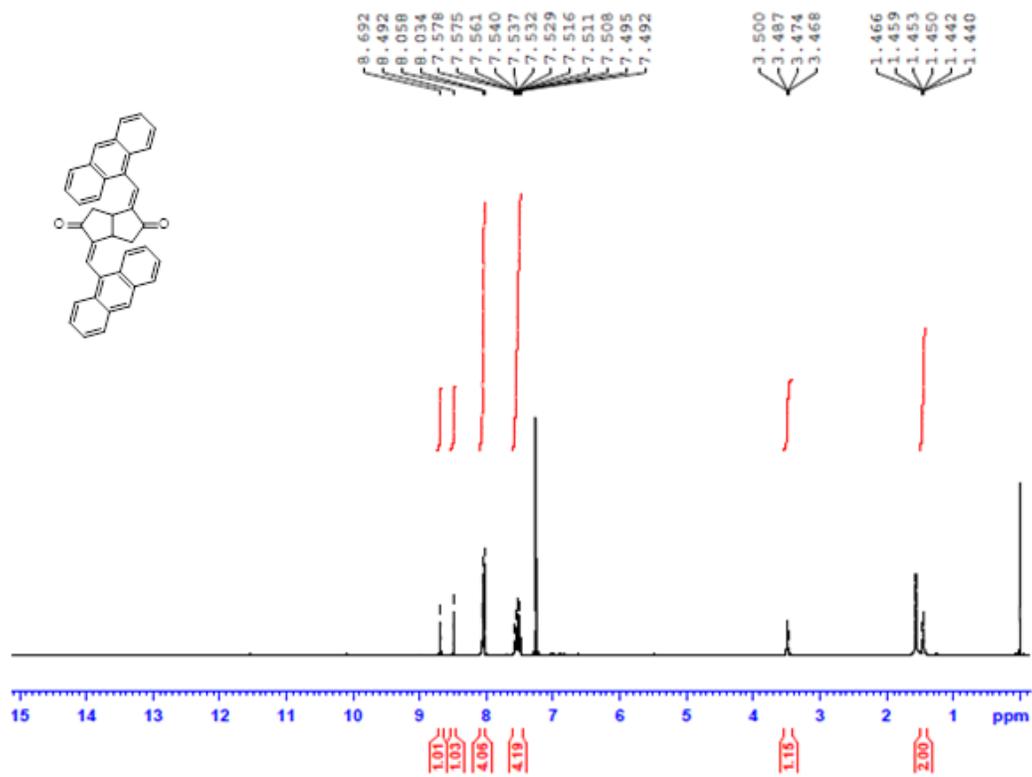
Step 1- Synthesis of Tetramethyl 3,7-dihydroxybicyclo[3.3.0]octa-2,6-diene-2,4,6,8-tetracarboxylate S3

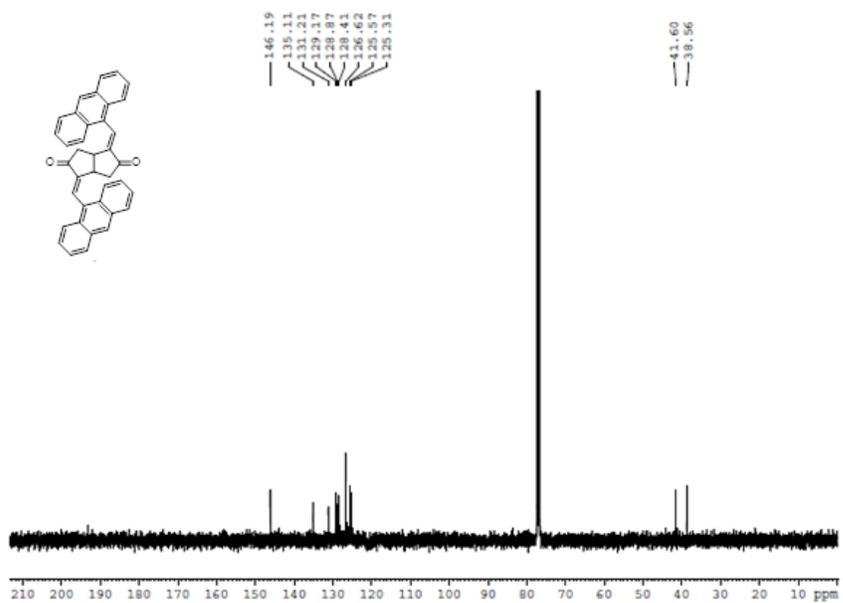
A three-necked, round-bottomed flask was equipped with a thermometer, mechanical stirrer, pressure-equalizing dropping funnel, reflux condenser and a heating mantle. A solution of 6.8 g (0.17 mol) of sodium hydroxide in 25 mL of methanol was prepared in the flask, cooled in an ice bath, and stirred as 30 g (0.17 mol) of dimethyl 1,3-acetonedicarboxylate is added dropwise. The resulting slurry was stirred and heated to reflux, at which point the white salt dissolves. The heating mantle was removed, and the solution was stirred rapidly while aqueous 40% glyoxal (5 g, 0.086 mol) was added at a rate sufficient to maintain the internal temperature at 65 °C. After the addition was completed (40-60 min), the mixture was allowed to cool to room temperature and stirred overnight. The precipitate was collected by suction filtration, washed with 50 mL of methanol and dried under reduced pressure to yield the white to light yellow disodium salt.

In a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar, 10 mL of chloroform and a solution of the disodium salt in 50 mL of water was taken. The two-phase mixture was stirred rapidly as 10 mL of cold 1 M hydrochloric acid was added. The layers were separated and the aqueous phase was extracted with three 50-mL portions of chloroform. The combined organic layer were washed once with saturated sodium chloride, dried



3. ^1H and ^{13}C NMR spectra of 3





4. ¹H NMR spectrum of 5

