

Supplementary Material

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

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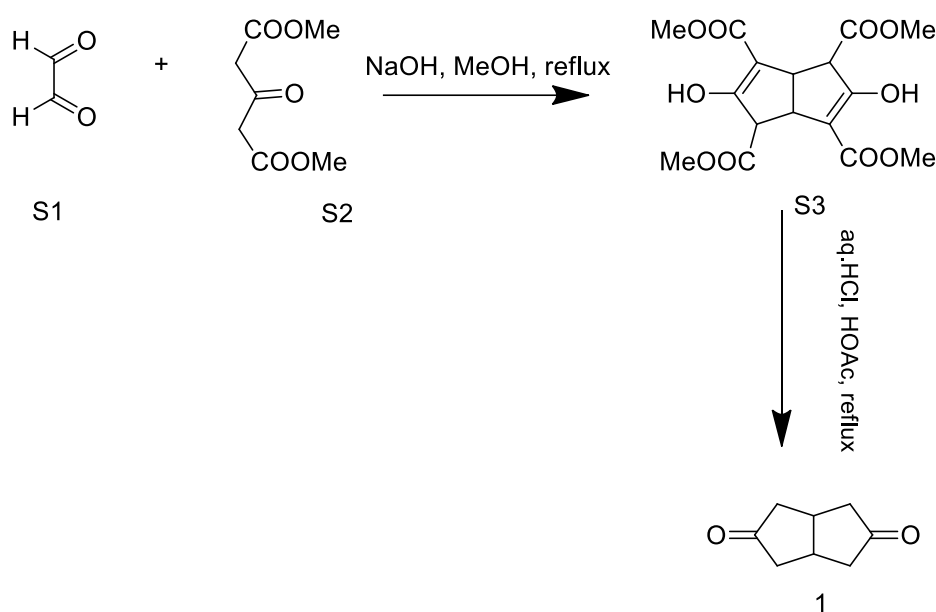
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1. General experimental information

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.

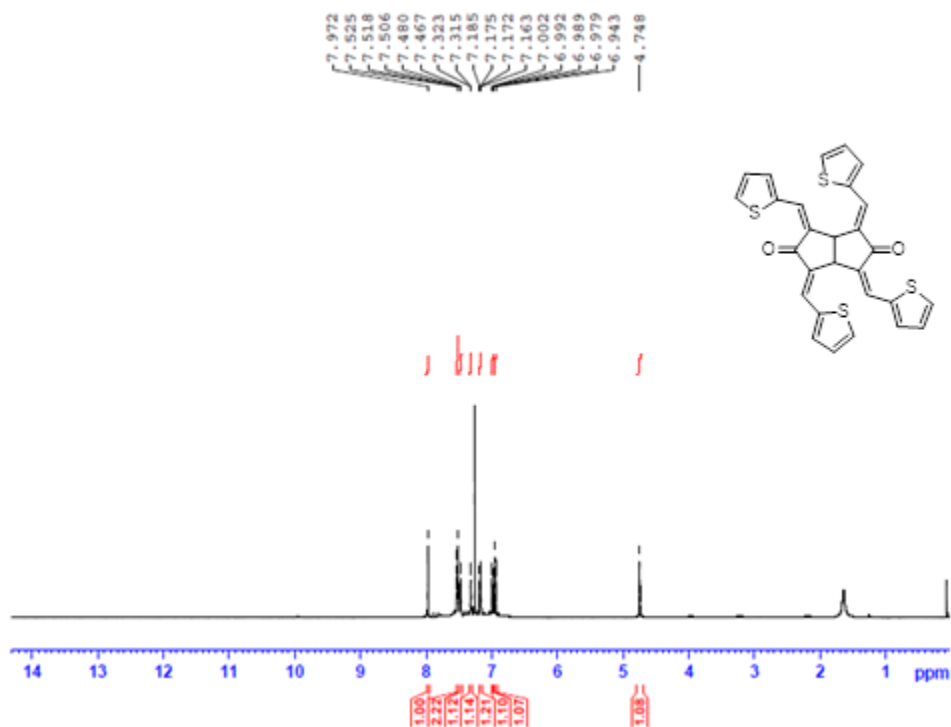
In a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar, 10 mL of chloroform and a solution of the disodium salt in 50 mL of water was taken. The two-phase mixture was stirred rapidly as 10 mL of cold 1 M hydrochloric acid was added. The layers were separated and the aqueous phase was extracted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

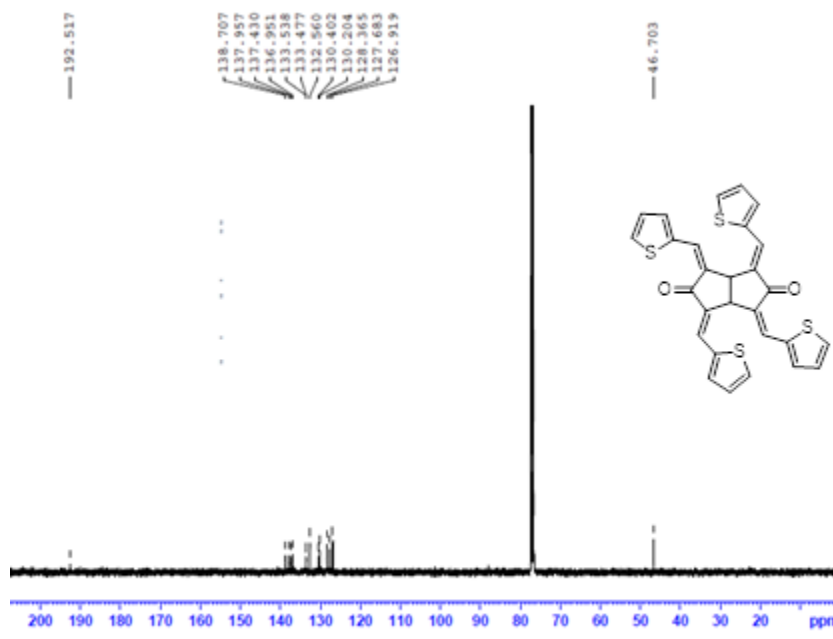
over anhydrous sodium sulfate, and concentrated under reduced pressure by rotary evaporation, keeping the water bath temperature at or below 40 °C. Crystallization of the remaining waxy solid from 2 : 1 hexane-ethyl acetate afforded (54-59% based on dimethyl 1,3-acetonedicarboxylate) of the tetraester, mp 97-100 °C.

Step 2: Synthesis of Tetrahydropentalene-2,5(1*H*,3*H*)-dione

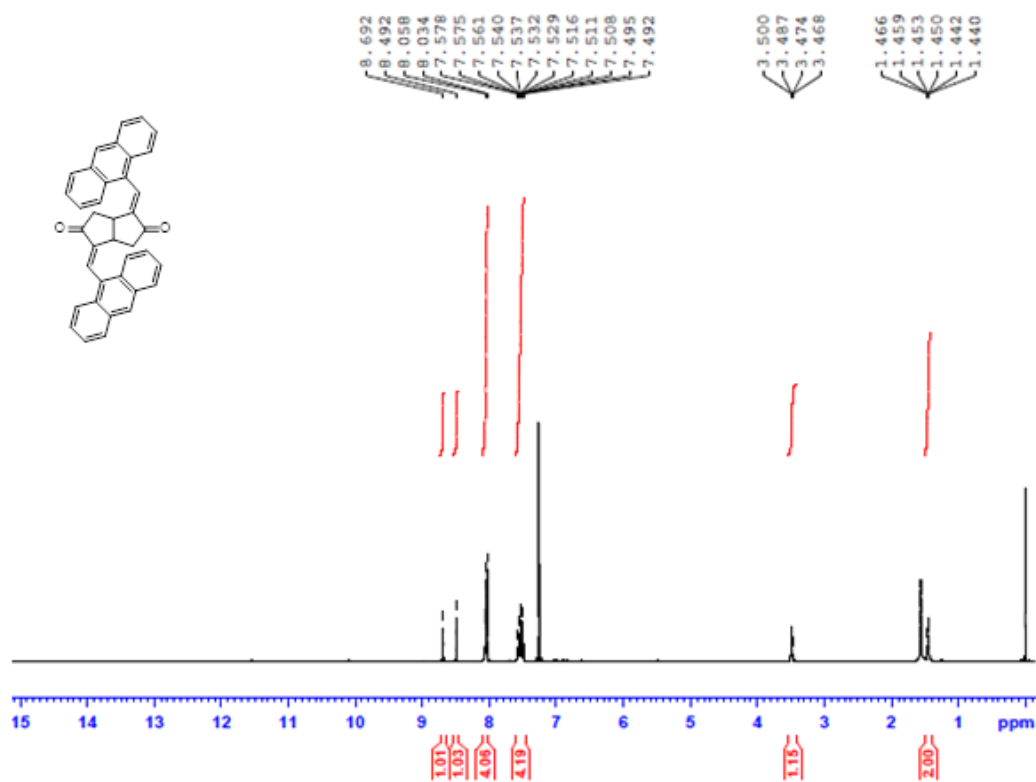
A three-necked round-bottomed flask equipped with two reflux condensers, and a magnetic stirrer was charged with 1.35 g (0.036 mol) of the tetraester, 20 mL of glacial acetic acid, and 50 mL of 1 *M* hydrochloric acid . The mixture was stirred vigorously and heated at reflux for 2.5 h. The solution was cooled in an ice bath and the product was extracted with five 50-mL portions of chloroform. The chloroform extracts were combined, and the solution was concentrated by rotary evaporation (bath temperature at or below 40 °C) until most of the acetic acid is removed. The residue was dissolved in 30 mL of fresh chloroform. The solution was washed with 10-mL portions of saturated sodium bicarbonate until the aqueous layer remains basic to litmus paper, dried with anhydrous sodium sulfate, and evaporated cautiously under reduced pressure. The yield is about 88-90 % of white to light yellow solid with mp 84-85°C . The product was purified by recrystallization from methanol or ethanol or by sublimation at 70 °C.

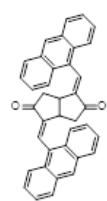
2. ¹H and ¹³C NMR spectra of 6





3. ¹H and ¹³C NMR spectra of 3





4. ^1H NMR spectrum of 5

