

RECEIVED  
USPC/DOE  
MAY - 1 1991

April 27, 1991  
Department of Chemistry  
Oklahoma State University  
Stillwater, OK 74078

U. S. Department of Energy  
Pittsburgh Energy Technology Center  
Acquisition and Assistance Division  
P. O. Box 10940  
Pittsburgh, P. A.

Attention: Jeffrey C. Bogdan:

Dear Mr. Bogdan:

The third quarterly Technical Progress Report for Task I: Synthesis of 6-Methyl-9-n-propyldibenzothiophene-4-ol (DE-AC22-90PC 90035) is enclosed.

According to Part III, Section J, Attachment B, of the contract, this is to be a draft copy. I have labeled this version of the report accordingly. I assume that you will contact me for changes which are to be included in the final draft.

Sincerely yours,



E. J. Eisenbraun  
Regents Professor  
Principal Investigator  
(405) 744-6673 or 5934

XC: S.J.Firsan, OSU  
Lisa Thompson, OSU (405) 744-5654  
Malvina Farcasiu, U.S. DOE/PETC  
V.U. Rao, U.S. DOE/PETC  
Joanne Wastek, U.S. DOE/PETC

U. S./DOE Patent Clearance is not required prior to publication of this document."

2

April 27, 1991

Quarterly Technical Progress Report No. 3 (draft copy)

Report period: Feb 25, 1991-Apr 25, 1991

CONTRACT TITLE AND NUMBER:

Task I: Synthesis of 6-Methyl-9-n-propyldibenzothiophene-4-ol  
DE-AC22-90PC 90035

CONTRACTOR NAME: Oklahoma State University  
Stillwater, OK 74078

CONTRACT PERIOD: July 25, 1990- July 24, 1992

CONTRACT OBJECTIVE: Synthesis and purification of the title compound.

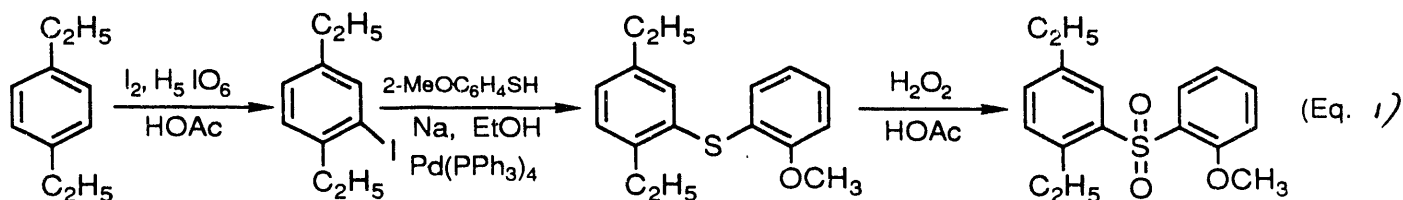
**Technical Summary:** The material covered here has been described to some extent in Status Reports 6, 7 and 8 and can be divided into three parts: (a) The large-scale synthesis of 200+ grams of distilled 1,4-diethyl-2-[(2'-methoxyphenyl)thio]benzene (**5c**), (b) synthesis of the sulfones **8a-c** both as starting materials for chemical cyclization reactions and as solid derivatives for identification purposes, and (c) continued investigation of the cyclization to dibenzothiophenes **6a-c** both by chemical and photochemical means.

*Part A: Synthesis and Characterization of Sulfide 5c.* As requested by DOE/PETC, this material was synthesized, as shown in Eq.1, in a manner similar to the synthesis of the mixture of sulfides **5a+5b** (see Experimental Part). The coupling step was carried out three times in order to accumulate about 223 g of distilled **5c**, bp 181-182 °C/3 mmHg. Of these, 200 g has been shipped to DOE/PETC; the remainder is being used for trial cyclizations. Using **5c** in the cyclization attempts is advantageous over the use of mixtures of **5a+5b** since the compositions of the reaction products are greatly simplified. The identity of sulfide **5c** was established by the

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED 8/8

enclosed data ( $^1\text{H}$  and  $^{13}\text{C}$  NMR; high-resolution mass spectrum). Gas chromatographic analysis showed the purity of the distilled **5c** to be about 97% (triangulation of GC peaks). The closely-related impurities (*ca.* 3%) arose during the coupling reaction step and were not removed by fractional distillation. They are believed to be 2,2'-dimethoxydiphenyl sulfide and  $\text{C}_{10}\text{H}_{13}\text{-S-C}_{10}\text{H}_{13}$ ; but confirmation of that will be provided by GC-MS analysis.



*Part B: Synthesis of Sulfones 8a-c:* These crystalline derivatives were synthesized in excellent yield as described in the experimental section by using an excess of hydrogen peroxide in acetic acid. They were characterized by spectroscopic means. Mass spectrometric analysis gave a molecular ion at  $m/e = 304$  verifying that **8a-c** are indeed sulfones and not sulfoxides ( $M^+ = 288$ ).

*Part C/1: Photocyclization reactions:* Even though the photocyclization of **5a+5b** in cyclohexane at  $25\text{ }^\circ\text{C}$  (8 h) produced small amounts of dibenzothiophenes **6a+6b** in the product mixture, our attempts to improve the conversion have been unsuccessful. The details of a number of such photocyclization experiments have been discussed in the second Quarterly Report of February 15, 1991.

*Part C/2: Chemical cyclization reactions:* We stated in the second Quarterly Report that the desired methoxylated dibenzothiophenes **6a** and **6b** would require preparation by a chemical rather than a photochemical route. We also proposed several such alternative routes for exploration. Our initial attempts to cyclize sulfones **8a+8b** using *n*-butyllithium and anhydrous cupric chloride in tetrahydrofuran at  $-78\text{ }^\circ\text{C}$  did not produced the desired cyclic dibenzothiophenes. Instead the product mixture consisted of unreacted sulfones (**8a+8b**, 64%), sulfones

bearing one added butyl group (25%) and three unidentified impurities (11%). In addition, treatment of sulfides **5a+5b** with conc. sulfuric acid-acetic acid at  $-10\text{ }^{\circ}\text{C}$  for 2h resulted in quantitative recovery of unreacted starting material.

### **Current and Future Effort:**

With the above mentioned diethyl sulfide **5c** and diethyl sulfone **8c** on hand, we have begun using them on a small scale in the study of the cyclization to the corresponding dibenzothiophene or dibenzothiophene-5,5-dioxide. Results of these experiments will be reported on in the next status report.

## **Experimental Section**

**1,4-Diethyl-2-[(2'-methoxyphenyl)thio]benzene (5c)** was prepared from **3c** similarly to the preparation of sulfides **5a+5b**<sup>1</sup> starting with 79.1 g of **3c**, 48.3 g of 2-methoxybenzenethiol, 28.8 g of sodium metal, 1.7 g of tetrakis(triphenylphosphine)-palladium(0) and 720 mL of anhydrous ethyl alcohol. After 10 h of reflux under nitrogen, subsequent workup and two fractional distillations using a 12-cm Vigreux column, gave 72 g of purified **5c** as a clear and colorless liquid. Two more such runs afforded a total of 223 g of purified **5c**, bp  $181\text{-}182\text{ }^{\circ}\text{C}/3\text{ mm}$ , the NMR and mass spectra of which are enclosed.

**2-[(2'-Methoxyphenyl)thionyl]-1-methyl-4-n-propylbenzene (8a) and 3-[(2'-methoxyphenyl)thionyl]-1-methyl-4-n-propylbenzene (8b).**<sup>2</sup> A mixture of sulfides **5a+5b** (13.6 g, 0.050 mol) was dissolved in 100 mL of glacial acetic acid and 27 mL (0.26 mol) of 31% aqueous hydrogen peroxide was added over 5 min. The reaction mixture was stirred at room temperature for 23 h and then heated to reflux (35 min) and at reflux (0.5 h). It was then poured onto 500 mL of ice and most of the acetic acid was neutralized by the portionwise addition of 76 g of anhydrous solid sodium carbonate. The resulting solution was extracted with 6 x 50 mL of methylene chloride and the combined

organic extracts were washed with 2 x 50 mL of sat'd sodium carbonate solution, 2 x 50 mL of water, dried (MgSO<sub>4</sub>), filtered, concentrated (rotary evaporator) and pumped (24 h, 2 mm) affording 14.4 g (95 %) of the crude sulfones **8a+8b** as a white, somewhat sticky, crystalline solid. This solid was washed with 5 x 30 mL of low boiling petroleum ether and dried *in vacuo* (48 h) affording 12.7 g (83 %) of a white crystalline free-flowing solid, mp 97-100 °C.

**1,4-Diethyl-2-[(2'-methoxyphenyl)thionyl]benzene (8c)**, mp 77-78 °C, was prepared similarly to **8a+8b** in 86% yield starting with 5.5 g of sulfide **5c**, 13 mL of 31% aqueous hydrogen peroxide and 50 mL of glacial acetic acid.

**Attempted cyclization of a mixture of 2-methoxy-2'-methyl-5'-*n*-propyldiphenylsulfide (5a) and 2-methoxy-5'-methyl-2'-*n*-propyldiphenylsulfide (5b).**<sup>3</sup> Conc. sulfuric acid (20 mL) was charged into a 100-mL, 2-neck, round-bottom flask equipped with a thermometer, a stopper and a stirr bar. The apparatus was lowered into an ice-salt bath and when the inside temperature reached -12 °C, a solution of 2.74 g (0.0098 mol) of sulfides **5a+5b** in 5 mL of acetic acid was added dropwise over 1h such that the inner temperature remained between -10 °C and -5 °C. After addition was complete, the reaction solution was stirred at -10 °C for another 0.8 h and then poured into 500 mL of ice-water. This was extracted with 4 x 100 mL of dichloromethane and the combined dichloromethane extracts were washed with 50 mL of 2N sodium carbonate solution, 2 x 100 mL of water, 100 mL of saturated brine, dried (MgSO<sub>4</sub>), filtered, concentrated (rotary evaporator), and pumped (4h, 2 mm) affording 2.17 g of an almost colorless liquid that was 100% unreacted starting material **5a+5b** by GC analysis.

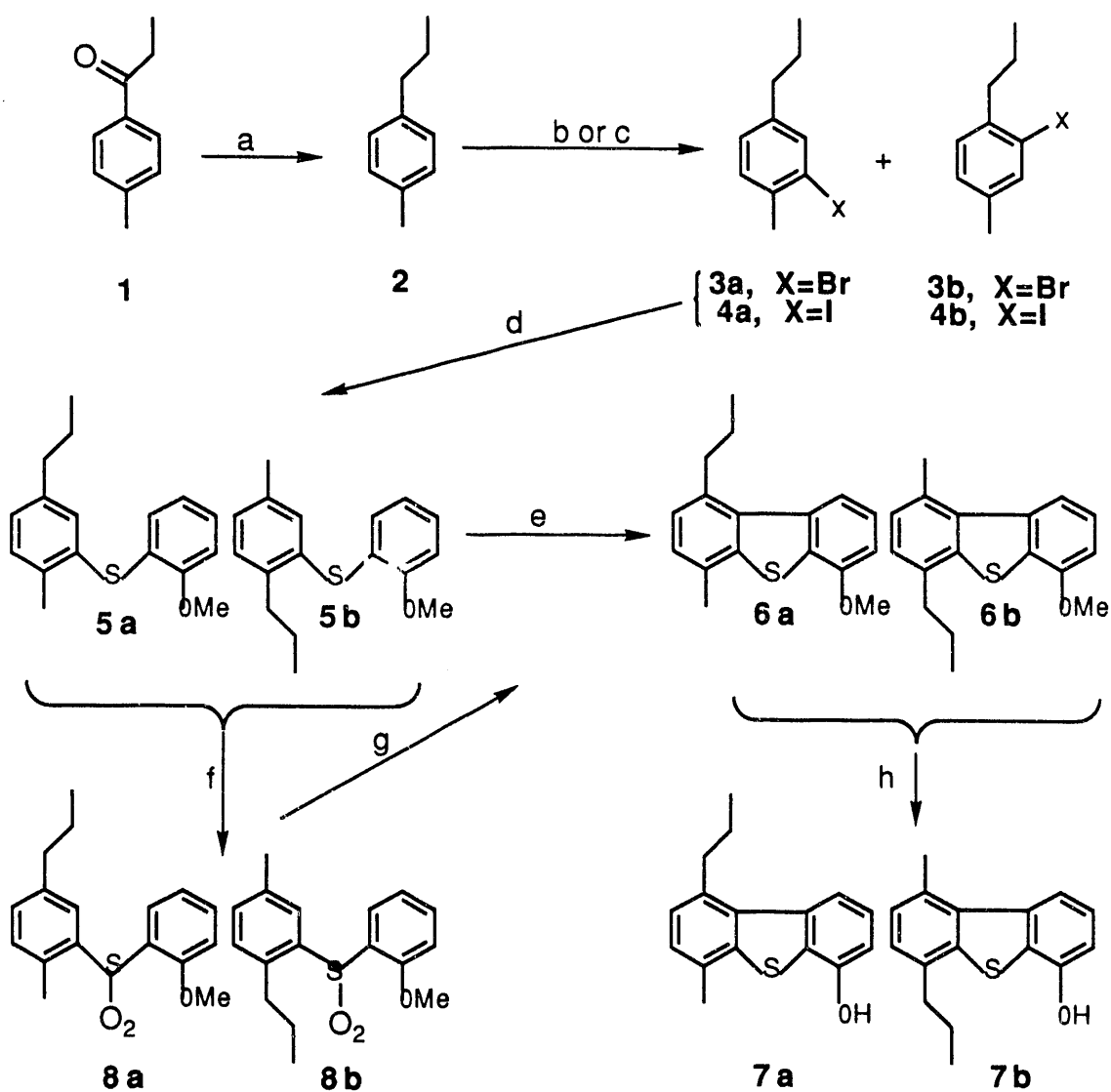
**Attempted cyclization of a mixture of 2-Methoxy-2'-methyl-5'-*n*-propyldiphenyl sulfone (8a) and 2-Methoxy-5'-methyl-2'-*n*-propyldiphenyl sulfone (8b).**<sup>4,5</sup> A dry, 250-mL, 3-neck, round-bottom flask was fitted with a stirr bar, a thermometer and two stoppers. Two syringe needles served as inlet and outlet for argon gas. The apparatus was flushed with argon,

charged with a solution of 3.04 g (0.01 mol) of sulfones in 150 mL of dry tetrahydrofuran and then lowered into a dry ice-acetone bath. When the inside temperature reached  $-78\text{ }^{\circ}\text{C}$ , a solution of 14.0 mL (0.035 mol, 3.5 equiv) of n-butyllithium in hexanes (Aldrich, 2.5 M) was introduced followed by stirring at  $-78\text{ }^{\circ}\text{C}$  for 0.5 h. Anhydrous cupric chloride (2.83 g, 0.021 mol, 2.1 equiv) was then added followed by stirring at  $-78\text{ }^{\circ}\text{C}$  for 1h. The heterogeneous reaction mixture was allowed to reach  $18\text{ }^{\circ}\text{C}$  during 1h and was stirred at  $18\text{ }^{\circ}\text{C}$  for another hour. Water (10 mL) was then added followed by 5% hydrochloric acid (10 mL) and 150 mL of ether. The two layers were separated and the ether layer was washed with water (2 x 100 mL), dried ( $\text{MgSO}_4$ ), filtered, concentrated (rotary evaporator) and pumped affording 3.53 g of the crude product as a viscous, light-brown oil that consisted (by GC) of unreacted sulfones (**8a+8b**, 64%), sulfones bearing one added butyl group (25%) and three unidentified impurities (11%).

### References and Notes

1. Migita, T.; Shimizu, T.; Asami, Y.; Shiobara, J.-i.; Kato, Y.; Kosugi, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1385-1389.
2. The general procedure for the oxidation of sulfides to sulfones described on p 453 of Pasto, D. J.; Johnson, C. R. *Organic Structure Determination*, Prentice-Hall, Inc.: Englewood Cliffs, NJ (1969) was adapted to the compounds at hand.
3. Wieland, H.; Mueller, C. *Chem. Ber.* **1913**, *46*, 3304-3314.
4. (a) Gogte, V.N.; Palkar, V.S.; Tilak, B.D. *Tetrahedron Lett.* **1960**, (6), 30-34. (b) Pandya, L.J.; Rao, D.S.; Tilak, B.D. *J. Sci. Industr. Res. India* **1959**, *18B*, 516.
5. (a) Gilman, H.; Esmay, D.L. *J. Am. Chem. Soc.* **1953**, *75*, 278. (b) Oita, K.; Gilman, H. *J. Org. Chem.* **1957**, *22*, 336.

## Scheme I-Revised Synthesis Plan for 7a



<sup>a</sup>NH<sub>2</sub>NH<sub>2</sub>, OH<sup>-</sup>, DEG, heat. <sup>b</sup>Br<sub>2</sub>, Fe, I<sub>2</sub> catalyst. <sup>c</sup>I<sub>2</sub>, H<sub>5</sub>I<sub>0</sub><sub>6</sub>, H<sup>+</sup>, HOAc, heat.

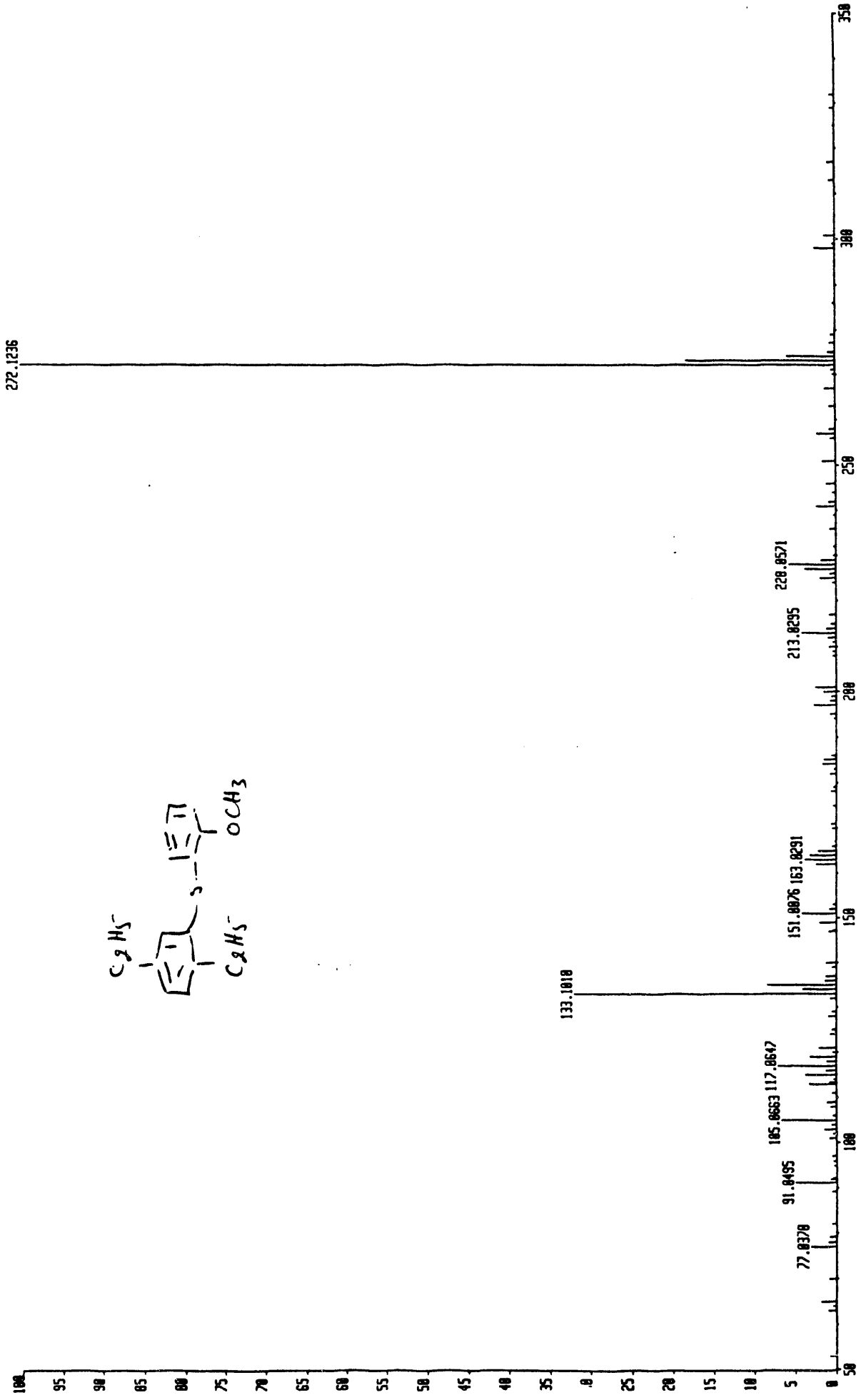
<sup>d</sup>Na, EtOH, 2-Methoxybenzenethiol, Tetrakis(triphenylphosphene)

palladium (0), heat. <sup>e</sup>UV light, I<sub>2</sub>, solvent. <sup>f</sup>H<sub>2</sub>O<sub>2</sub> (30%), HOAc.

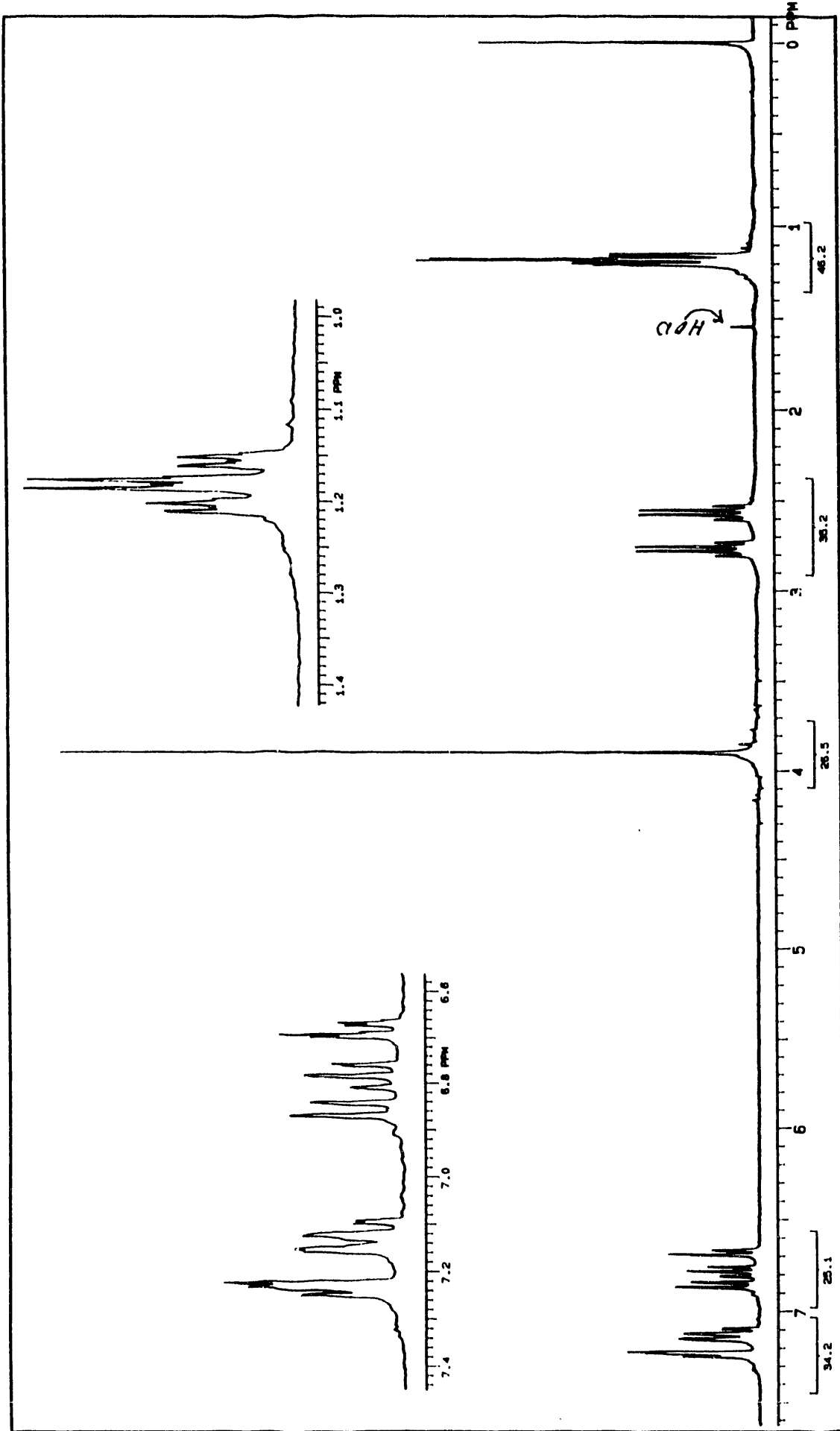
<sup>g</sup>See proposed routes in Scheme II. <sup>h</sup>BBr<sub>3</sub>-Me<sub>2</sub>S complex.

\* Status report 7

NMR: 16121088  
ARSS: 272.1236







NUMBER: \_\_\_\_\_  
 FILE: \_\_\_\_\_  
 DATE: \_\_\_\_\_  
 XL: XLAA 390

SAMPLE: 9.8-VII-81-E IN CDCL3  
 1,4-DITHIOL-2-(2-METHOXYPHENYLTHIO)  
 BENZENE  
 DOUBLY-DISTILLED  
 BP 181-2 OC AT 3.0 MMHG

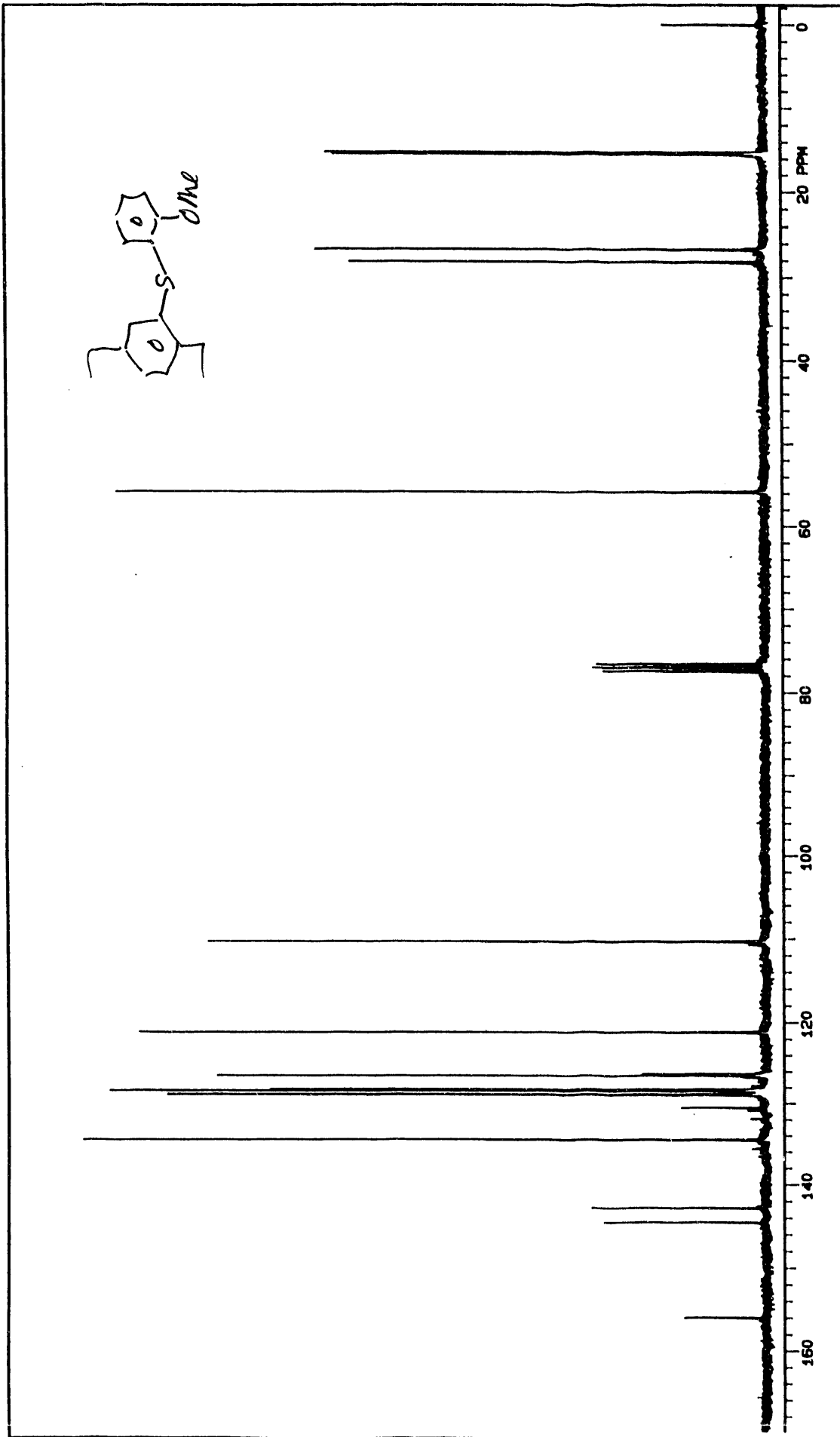
PULP SEQUENCE: STD31  
 TUBE NO.: \_\_\_\_\_  
 TEMP: \_\_\_\_\_ °C  
 SOLVENT: CDCL3

EXPERIMENT: \_\_\_\_\_  
 P1: 18 K Hz \_\_\_\_\_ sec CD: \_\_\_\_\_ sec  
 L1: \_\_\_\_\_ Hz AF: \_\_\_\_\_ sec CD: \_\_\_\_\_ sec  
 WAVE: 2000 Hz/gain Start: -49.0 Hz/gain  
 Reference: \_\_\_\_\_

PLOT/PROCESSING: \_\_\_\_\_  
 NUMBER: 1.750 Other: 350.3 Hz  
 MODE: NMR Power: 20 dB  
 Modulation Mode: C Freq: 200 Hz  
 Pulse Width: \_\_\_\_\_ sec Power Ratio: \_\_\_\_\_

11480338  
 NUMBER: 1.750 Freq: 300 MHz  
 Scan Width: 4000.0 Hz Other: 700 Hz  
 Acq. Time: 2.000 sec Delay: 0.0 sec  
 Pulse Width: 8.0 sec Transmits: 4

CONVENT



Number \_\_\_\_\_  
 File \_\_\_\_\_  
 Date \_\_\_\_\_  
 No. SLAA 390

**SAMPLE**  
S.F.-VII-31-E IN CDCl3  
2-(2'-(METHOXYPHENYL)THIO)-  
1,4-DIMETHYLBENZENE  
DOUBLE-DISTILLED  
BP 181-2 OC AT 3.0 MMHG

**Pulse Sequence** SID13C  
 Test Q.D. \_\_\_\_\_ ppm  
 Temp. \_\_\_\_\_ °C  
 Solvent CDCl3

**ANIMIN34X3**  
 Plot Processing 4/18/74

F1 54.1 F2 \_\_\_\_\_ F3 \_\_\_\_\_  
 L1 1.392 L2 \_\_\_\_\_ L3 \_\_\_\_\_  
 Width 12884.8 Height 181.7

Name 13.750 Other 350.3 H<sub>2</sub> 0.0  
 Mass 100 Percent 0.0  
 Molecular Mass 3 Freq. 7890 Hz  
 Pulse Width 17.5 sec Power 100

Name 13.750 Freq. 78.90 Hz  
 Sinc Width 12884.8 Hz Other 1.000 Hz  
 Acc Time 1.112 sec Duty 3.000 sec  
 Pulse Width 17.5 sec Transm. 518

31480330

**END**

**DATE  
FILMED**

7 / 21 / 93

