

## **Supplementary Material**

### **Nickel catalyzed arylation of acrolein diethyl acetal : A substitute to the 1,4-addition of arylhalides to acrolein**

**S. Condon\*, D. Dupré, J. Y. Nédélec.**

Laboratoire d'Electrochimie, Catalyse et Synthèse Organique, CNRS - Université Paris XII-  
UMR 7582, 2 rue Henri Dunant 94320 Thiais. France.  
sylvie.condon@glvt-cnrs.fr

#### **Supporting Information Available:**

General procedures for the preparation of  $\beta$ -arylated aldehydes and for  
 $\gamma$ -arylated enolethers  
Procedure for the hydrolysis of isolated enolethers into aldehydes  
Characterization of selected compounds.

All solvents and reagents were purchased from commercial sources and used as received. DMF and AN were stored under an argon atmosphere. Acrolein diethyl acetal is the commercial product. GC analysis was carried out using a 25m DB-1 capillary column.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Bruker AC-200 (200MHz) spectrometer. Mass spectra were obtained on a GCQ Thermoquest spectrometer coupled to a chromatograph fitted with a 25m CPSIL5 CB capillary column. IR spectra were recorded using a Perkin-Elmer spectra 283B infra red spectrophotometer. The electrochemical cell has been previously described. (<sup>see</sup> *Synthesis*, **1990**, 369-380)

**General procedure for the preparation of  $\beta$ -arylated aldehydes:** Typically, reaction was conducted in an undivided cell equipped with a nickel grid (area: 30 cm<sup>2</sup>) as the cathode and iron rod as the anode, under argon atmosphere. Tetrabutylammonium bromide (0.15g; 0.46 mmol), tetrabutylammonium iodide (0.11g; 0.30 mmol) and 1,2 dibromoethane (80 $\mu$ l; 1mmol) were dissolved in a mixture of DMF (27 mL)/ pyridine (3 mL). Then, a short electrolysis (0.15A) was conducted at room temperature for 20 minutes. The current was turned off; nickel bromide hydrate (0.18 g; 0.75 mmol), acrolein diethyl acetal (3mL; 19 mmol) were introduced. The reaction mixture was heated at 70°C and organic halide (7.5 mmol; 1 eq.) is added. The electrolysis was run at constant current density (0.3 A dm<sup>-2</sup>). The reaction was monitored by GC and stopped after the organic halide was consumed. Then, at room temperature a 6N solution of aqueous HCl (20 mL) was added and mixture was allowed to stir for 30 min. The reaction mixture was poured into water (100 mL). The aqueous layer was extracted with three 100 mL portions of diethyl ether. The organic extracts were combined, washed twice with 50 mL portion of water, then brine and dried over MgSO<sub>4</sub>. The crude product obtained after evaporation of the solvent was purified by flash chromatography on silica gel (230-400 Mesh). All isolated products are oils.

**4-(3-oxopropyl)benzonitrile:** The product was obtained according to the general product. Yield 24%, 0.286g ; eluent: 10% ethylacetate in pentane to remove side product then, 25% ethylacetate in pentane to get the product.  $^1\text{H}$  NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  9.64 (s, 1H), 7.40 (d, 2H,  $J$  = 8.24 Hz), 7.17 (d, 2H,  $J$  = 8.24 Hz), 2.77 (m, 4H);  $^{13}\text{C}$  NMR (50.321 MHz, CDCl<sub>3</sub>)  $\delta$  200.4, 146.1, 132.1, 129.0, 118.7, 109.8, 44.1, 27.8; IR 2800, 2700, 2200, 1720, 1660, 1600, 1500, 1450, 1170 cm<sup>-1</sup>; MS, 159, 158, 131 (100%), 130, 117, 116, 103.

**3-(4-trifluoromethyl)phenylpropanal:** The product was obtained according to the general procedure. Yield 28%, 0.424g ; eluent: 2.5% ethylacetate in pentane to remove side product then, 10% ethylacetate in pentane to get the product.  $^1\text{H}$  NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  9.78 (s, 1H), 7.52 (d, 2H,  $J$  = 8.06 Hz), 7.30 (d, 2H,  $J$  = 8.06 Hz), 2.97 (m, 2H), 2.80 (m, 2H);  $^{19}\text{F}$  NMR (188 MHz, CDCl<sub>3</sub>)  $\delta$  - 62.26 ; IR 3030, 2800, 2720, 1720, 1600, 1400, 1320 cm<sup>-1</sup>; MS, 203, 202 (100%), 183, 160, 133, 109, 91.

**ethyl 3-(3-oxopropyl)benzoate:** The product was obtained according to the general procedure. Yield 40%, 0.618g ; eluent: 10% ethylacetate in pentane to remove side product then, 25% ethylacetate in pentane to get the product.  $^1\text{H}$  NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  9.78 (s, 1H), 7.84 (m, 2H), 7.37 (m, 2H), 4.35 (q, 2H,  $J$  = 7.12 Hz), 2.97 (m, 2H), 2.79 (m, 2H), 1.38 (t, 3H,  $J$  = 7.12 Hz);  $^{13}\text{C}$  NMR (50.321 MHz, CDCl<sub>3</sub>)  $\delta$  200.6, 166.1, 140.4, 132.5, 130.4, 128.9, 128.2, 127.1, 60.6, 44.6, 27.4, 13.9 ; IR 2700, 1740, 1720, 1600, 1580, 1440, 1380 cm<sup>-1</sup>; MS, 206, 177, 160 (100%), 149, 136, 131, 119, 105, 91, 77.

**4-(3-oxopropyl)acetophenone:** This product can also be obtained according to the general procedure. Yield 42%, 0.55g ; eluent: 10% ethylacetate in pentane to remove side product then, 25% ethylacetate in pentane to get the product.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  9.81 (s, 1H), 7.87 (d, 2H,  $J = 8.24$  Hz), 7.29 (d, 2H,  $J = 8.24$  Hz), 3.01 (m, 2H), 2.82 (m, 2H), 2.57 (s, 3H);  $^{13}\text{C}$  NMR (50.321 MHz,  $\text{CDCl}_3$ )  $\delta$  200.8, 197.7, 146.2, 135.4, 128.8, 128.6, 44.7, 28.0, 26.6 ; IR 2700, 1720, 1670, 1600, 1400, 1450, 1250  $\text{cm}^{-1}$ ; MS, 176, 161 (100%), 148, 133, 105.

**General procedure for the preparation of  $\gamma$ -arylated enoethers:** Typically, reaction was conducted in an undivided cell equipped with a nickel grid (area: 30  $\text{cm}^2$ ) as the cathode and iron rod as the anode, under argon atmosphere. Tetrabutylammonium bromide (0.15g; 0.46 mmol), tetrabutylammonium iodide (0.11g; 0.30 mmol) and 1,2 dibromoethane (80 $\mu\text{l}$ ; 1mmol) were dissolved in a mixture of DMF (27 mL)/ pyridine (3 mL). Then, a short electrolysis (0.15A) was conducted at room temperature for 20 minutes. The current was turned off; nickel bromide hydrate (0.18 g; 0.75 mmol), acrolein diethyl acetal (3mL; 19 mmol) were introduced. The reaction mixture was heated at 70°C and organic halide (7.5 mmol; 1 eq.) is added. The electrolysis was run at constant current density (0.3 A  $\text{dm}^{-2}$ ). The reaction was monitored by GC and stopped after the organic halide was consumed. Then, the mixture was hydrolyzed with 1N HCl (100 mL) and diluted with diethyl ether (100 mL). The aqueous layer was extracted with diethyl ether (100 mL); the combined organic layers were washed with  $\text{H}_2\text{O}$  (100 mL) and sat. NaCl (100 mL), dried ( $\text{MgSO}_4$ ) and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel (230-400 Mesh). All isolated enoethers are oils.

**Procedure for the hydrolysis of the isolated enoether into aldehyde ( in Table, note g):**

Isolated enol ether (0.75 g ; 3.67 mmol) was solubilized into 20 mL AcOH/ water (3/1; v/v) solution and the reaction mixture was then heated to reflux for 45 minutes. The mixture was then diluted in diethyl ether (100 mL) and water (100 mL) was added. Sodium bicarbonate powder was added until aqueous layer became basic. The organic layer was washed with water (100 mL), brine (50 mL), then dried over  $\text{MgSO}_4$ . After evaporation to dryness, aldehyde (0.352 g; 54.5%) was obtained as pure product (GC 98.5 %).

Table: entry 9

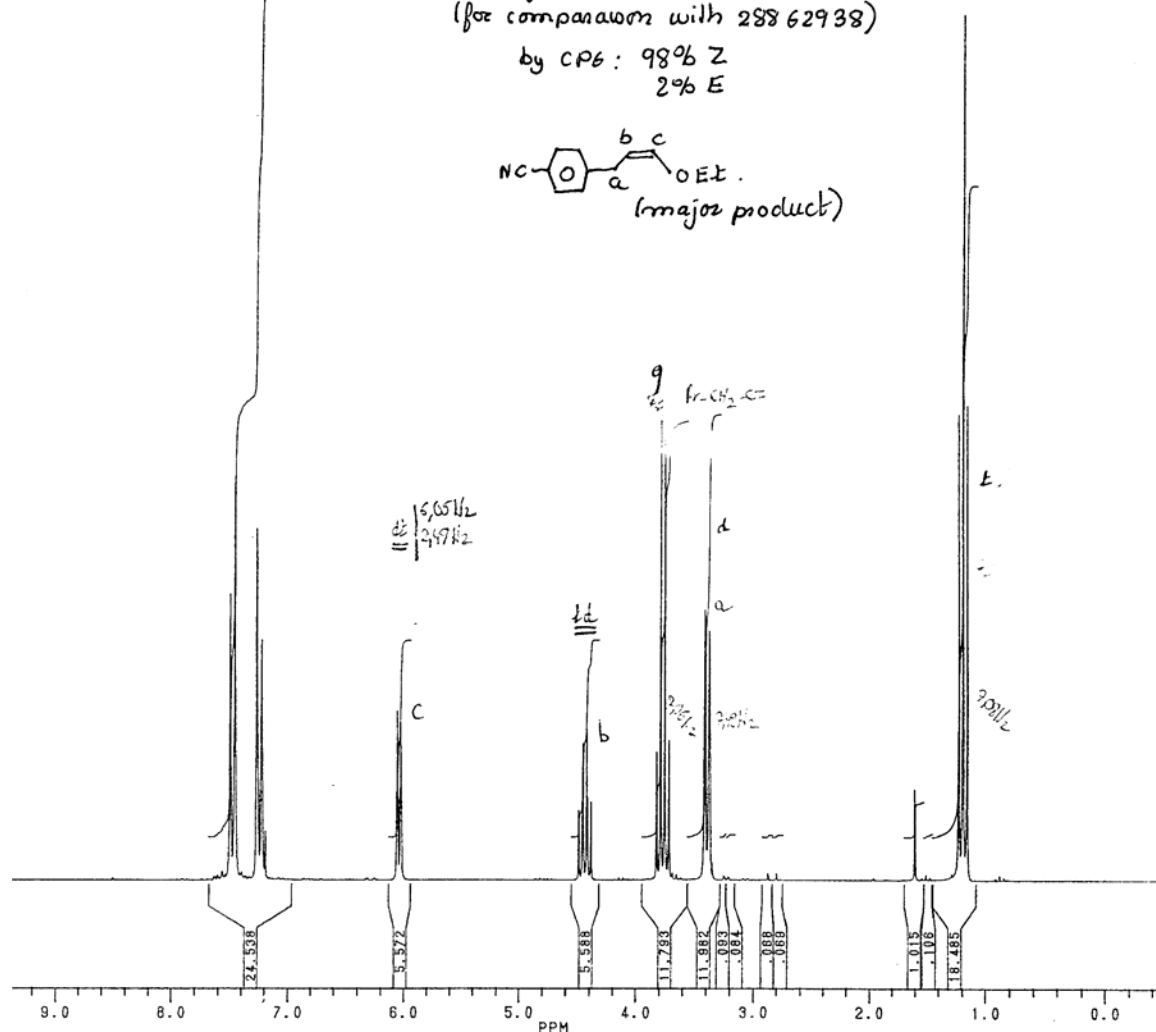
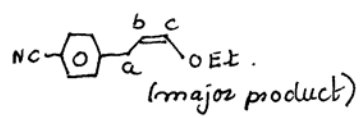
288G2528 30 MG IN CDCL3 12/07/01

isolated fraction

(for comparison with 28862938)

by CP6: 98% Z

2% E

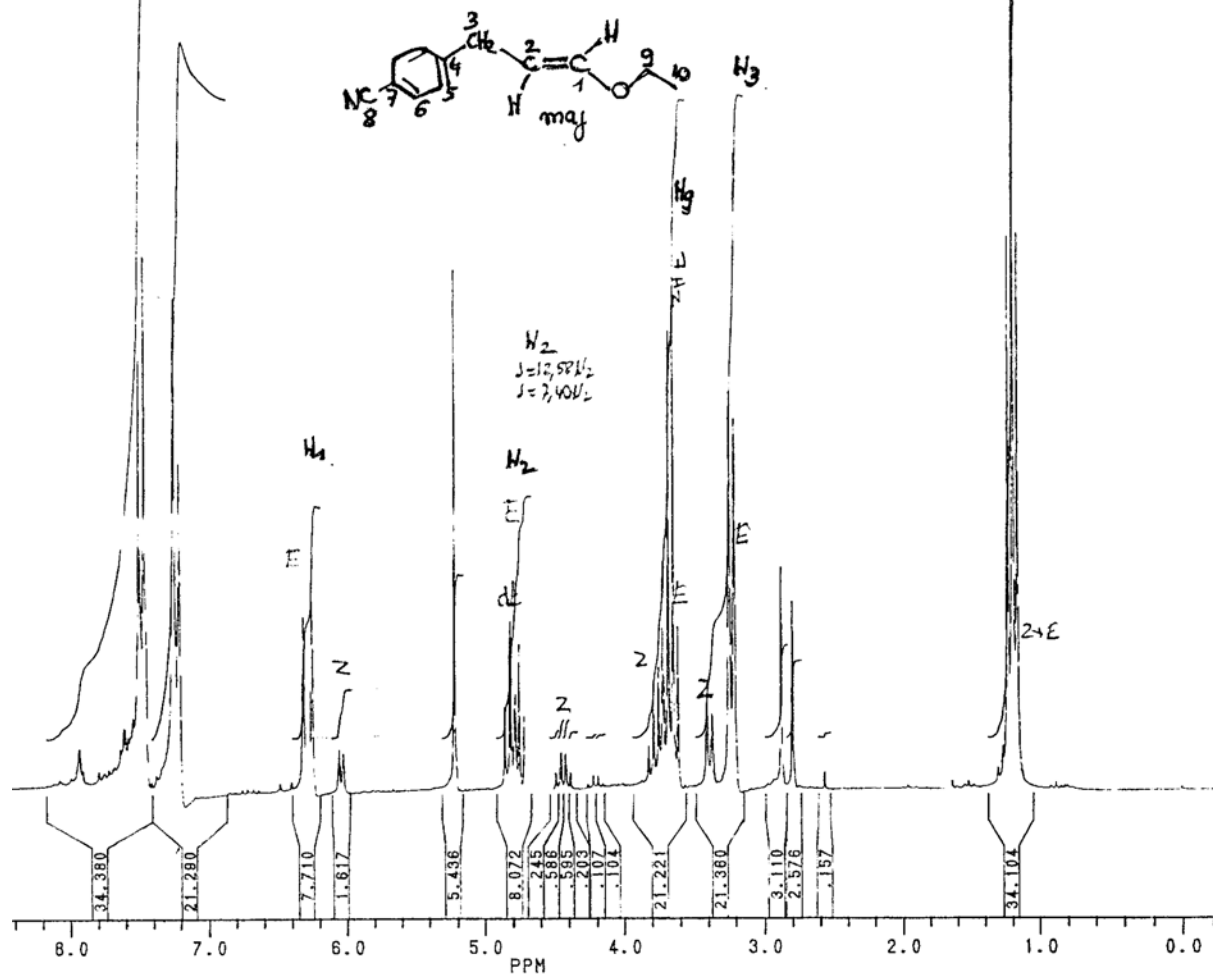


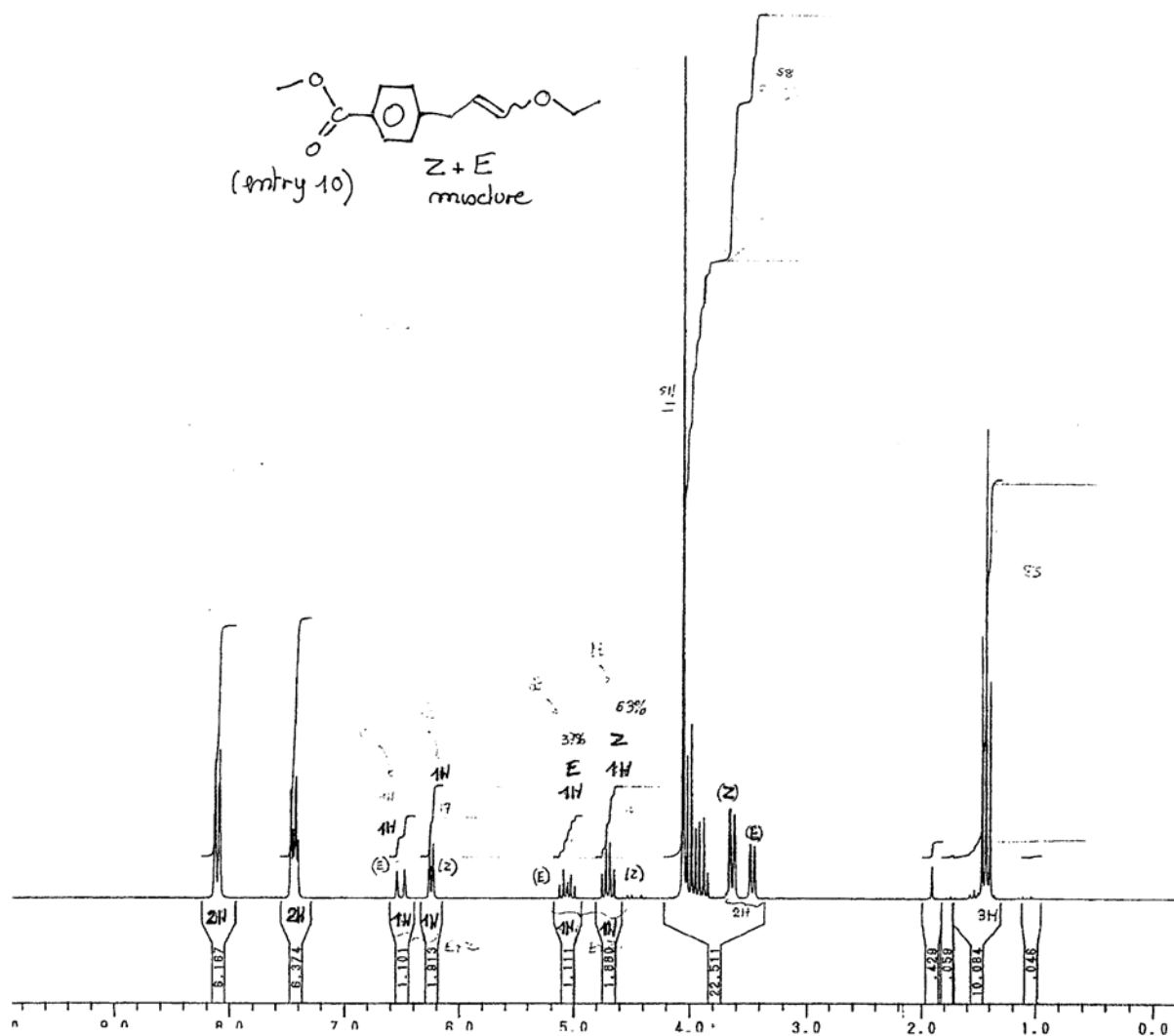
Purification by flash chromatography (silica gel 230-400 Mesh)  
eluent: 2.5% AcOEt in pentane

Table : entry 9

288G2938 39 MG IN CDCL3 23/07/01  
isolated fractions.  
(to be for comparison with 288G2523)

(E) isomer is the major product.  
~83% (E) ~17% (Z)





297F1927 32 MG IN CDCL3 10/10/01

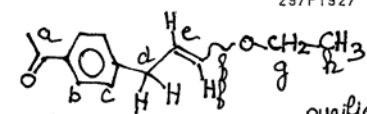
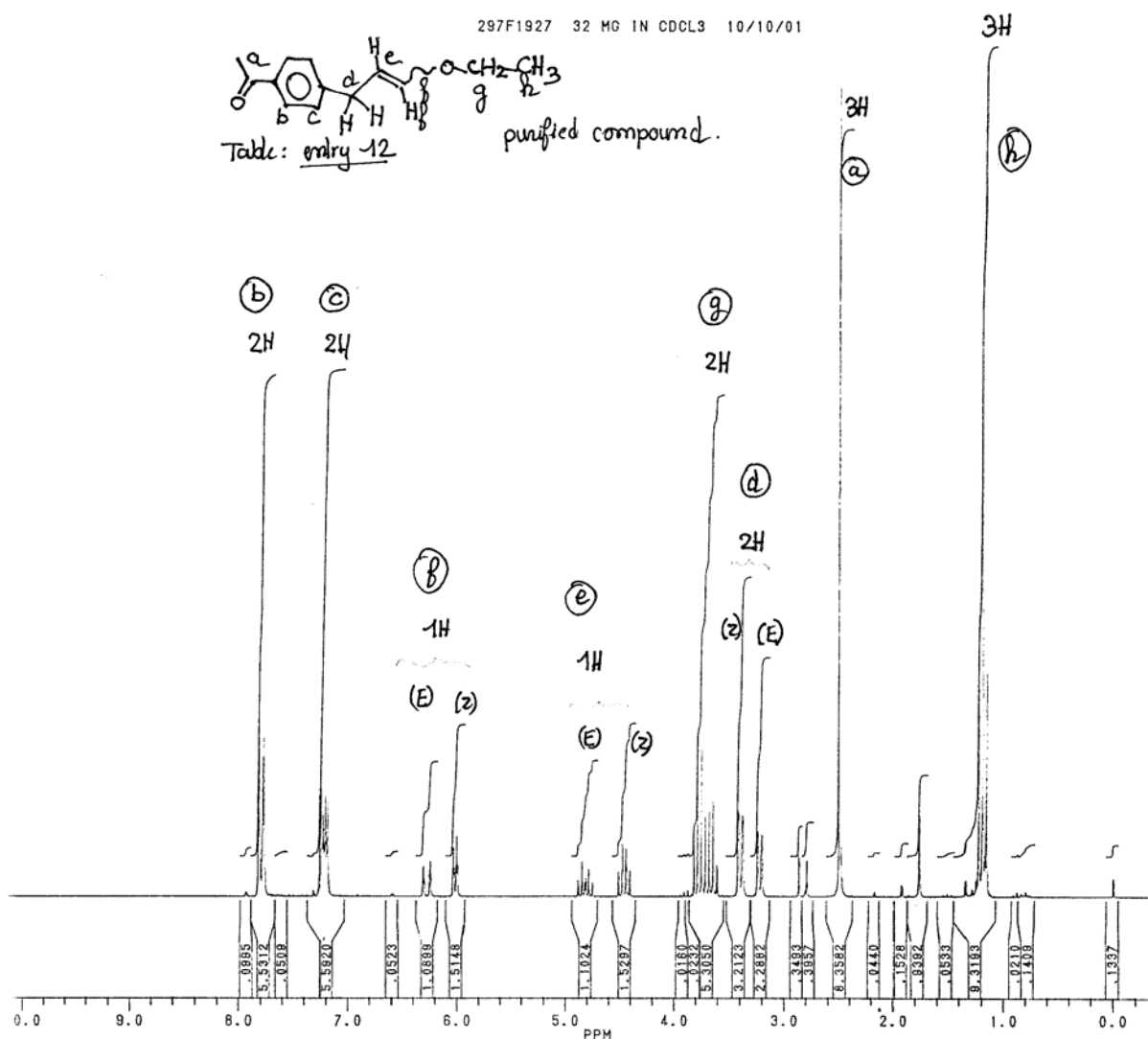


Table: entry 12

purified compound.



• calcd for  $C_{13}H_{16}O_2$  %C : 76.44 ; %H : 7.89  
 found %C : 76.23 ; %H : 7.98

• Purification : flash chromatography (silica gel 230-400 mesh)  
 eluent : 35% RCOEt in pentane to remove side product  
 then 75% RCOEt in pentane.