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## Reagents and solvents:

All the substrates and products were obtained from commercial suppliers such as J&K Scientific and TCI etc. The solvents were supplied by Merck, Fischer Scientific and Sinopharm Chemical Reagent Co., LTD. Benzyl- $\alpha,\alpha$ - $d_2$ -alcohol was supplied by CDN Isotopes, Quebec, Canada. Anatase  $TiO_2$  (ST-01) used in this paper was purchased from Ishihara Sangyo Kaisha, LTD., Japan. All the reagents and solvents were directly used without further purification.

## Procedure for the preparation of eosin Y- $TiO_2$ :

0.075 mmol of eosin Y was put into a 100 mL beaker containing 30 mL of anhydrous ethanol for 10 min of ultrasonication. Then, 3 g of anatase  $TiO_2$  (Ishihara ST-01) was put into the dispersed eosin-Y in anhydrous ethanol for a further 10 min of ultrasonication. After that the mixture was magnetically stirred at 500 rpm for 12 h. Then eosin Y- $TiO_2$  was collected with a rotary evaporator equipped with a vacuum pump and subsequently dried at 100 °C at vacuum drying chamber.

## General procedure for the selective oxidation of alcohol:

In a typical reaction, 54.3 mg of eosin Y- $TiO_2$ , 0.2 mmol of alcohols and 0.004 mmol of TEMPO were added to 5 mL of  $CH_3CN$  in a 10 mL Pyrex vessel. Then the reaction mixture was stirred for 30 min in dark to reach adsorption equilibrium.  $O_2$  was purged into the Pyrex vessel to raise the initial pressure to 0.1 MPa. The reaction mixture was magnetically stirred at 1500 rpm and illuminated with green LEDs in an air-conditioned room to warrant the reaction temperature constantly

at 25 °C. At the end of reaction, the eosin Y-TiO<sub>2</sub> particles were separated from the reaction mixture by centrifugation and the products were quantitatively analysed by gas chromatography (GC) equipped with a flame ionization detector (FID) using chlorobenzene as the internal standard. The structures of products were confirmed by comparison with the retention time with standard samples and further confirmed by gas chromatography–mass spectrometry (GC-MS).

### **General instrumentation and conditions:**

The gas chromatography (GC) quantitative measurements of conversions of substrates and selectivities of products were made on a gas chromatograph (Agilent 7890B) equipped with a flame ionization detector (FID) using high pure N<sub>2</sub> as the carrier gas and an Agilent J&W DB-5 capillary column (30 m×0.32 mm×0.25 µm, 19091J-413) in the case of entries 1-13, Table 7 and entries 1-6, 9 and 10, Table 8.

For some substrates in Table 8 including entries 7 and 8, an Agilent J&W DB-17 capillary column (30 m×0.32 mm×0.25 µm, 123-1732) was used for the quantitative analysis of the products.

Standard GC-FID analysis conditions: injector temperature 250 °C, detector temperature 280 °C, column temperature program: 50 °C (hold 1 min) raised up to 280 °C (hold 2 min) at a rate of 20 °C/min. The results were all obtained using a split mode with a split ratio is 30:1. Gas chromatography–mass spectrometry (GC-MS) analysis was performed on a Shimadzu GC 2010 gas chromatograph equipped with a Shimadzu GCMS-QP2010 Ultra electron ionization mass

spectrometer using a Restek (Rxi®-5Sil MS) capillary column (30 m×0.25 mm×0.25 μm) with high pure He as the carrier gas.

**Light source:**

The reaction was usually irradiated with a green light LEDs. The LEDs were supplied by Shenzhen Qilai Optoelectronics Science and Technology Co., LTD. China. In detail, four LED lamps were fastened in a circle around a magnetic stirrer in which the light irradiation was centered on the 10 mL Pyrex vessel. For green light LEDs, the irradiating wavelength range is  $530\pm 10$  nm with the peak at 530 nm. Thus, the possible heating of the reaction medium the infrared light and possible leaking of UV light is completely excluded. The reaction medium was maintained at room temperature of 25 °C by electronic fan cooling and air-conditioning throughout the experimental process.

Figures S1: GC-FID results for Table 7.

Table 7, Entry 1

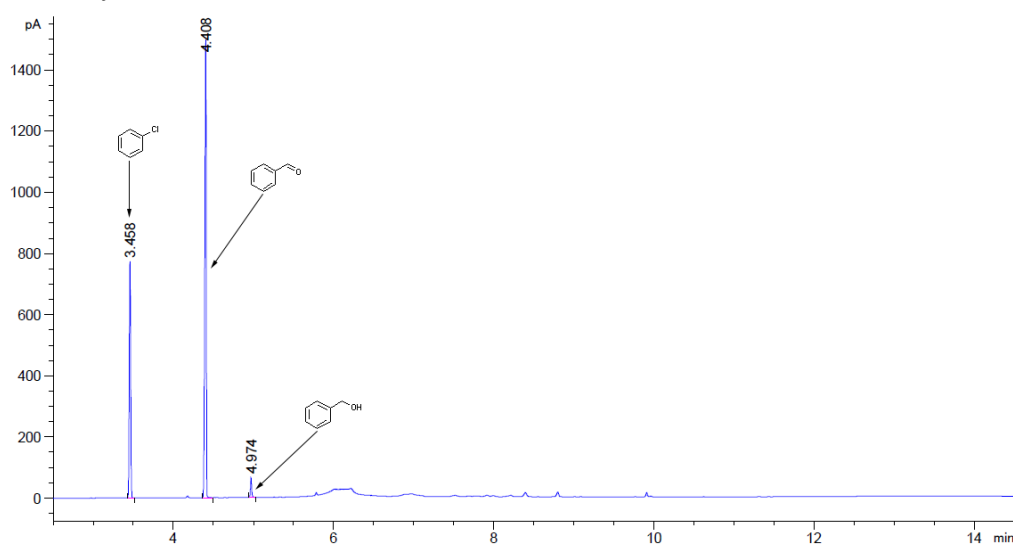


Table 7, Entry 2

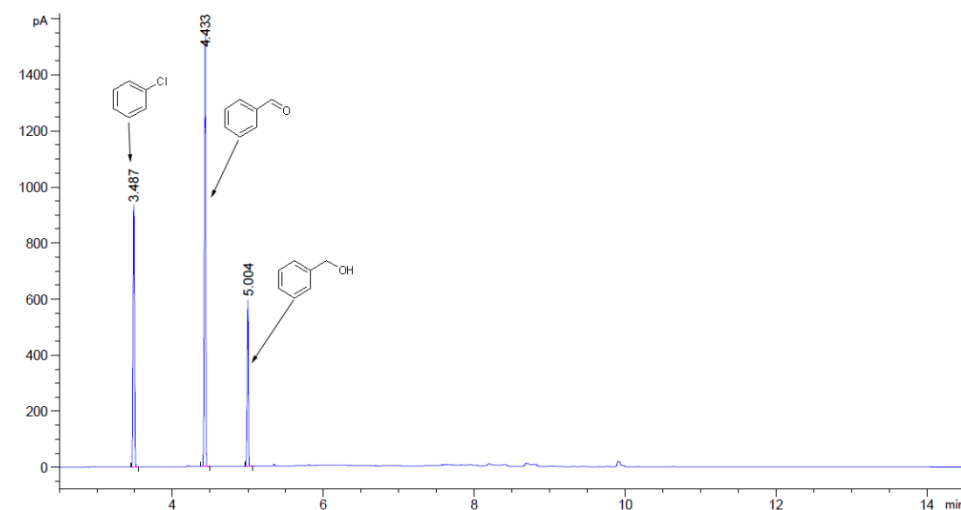


Table 7, Entry 3

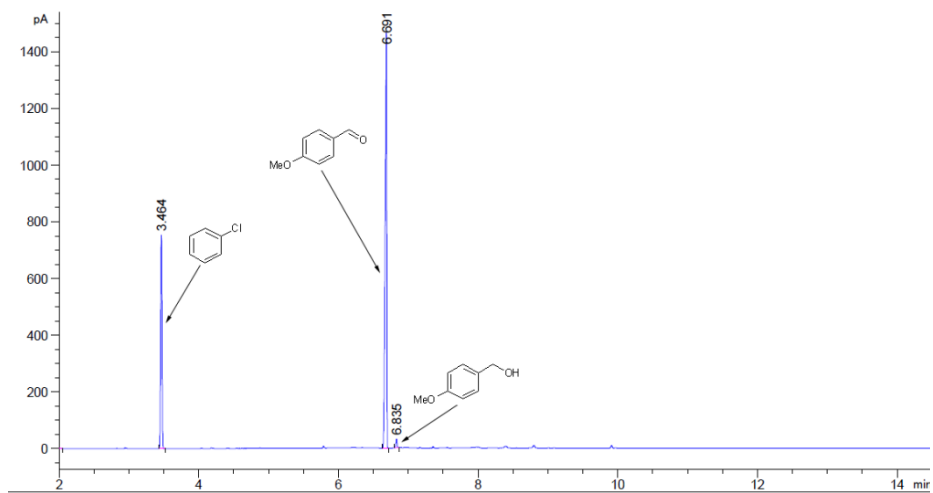


Table 7, Entry 4

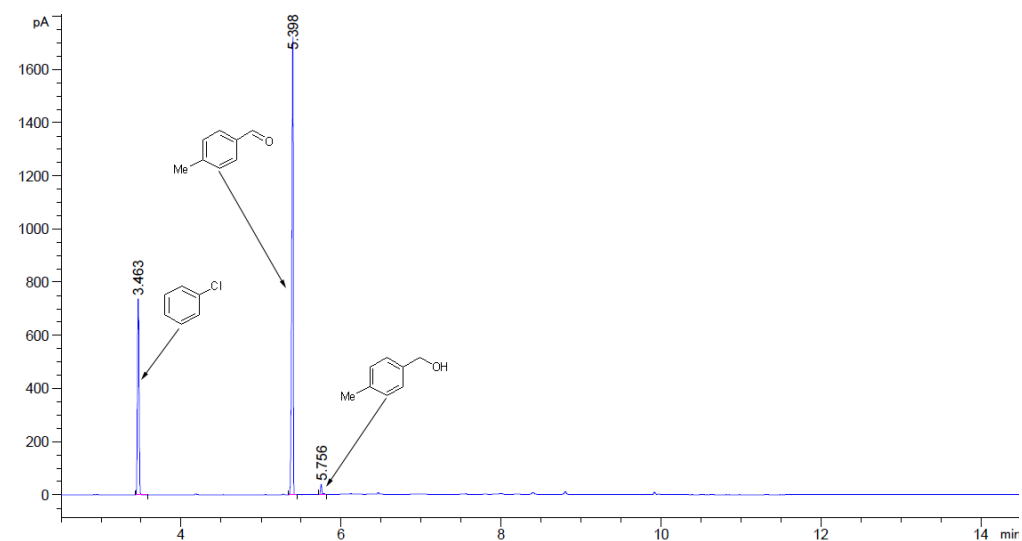


Table 7, Entry 5

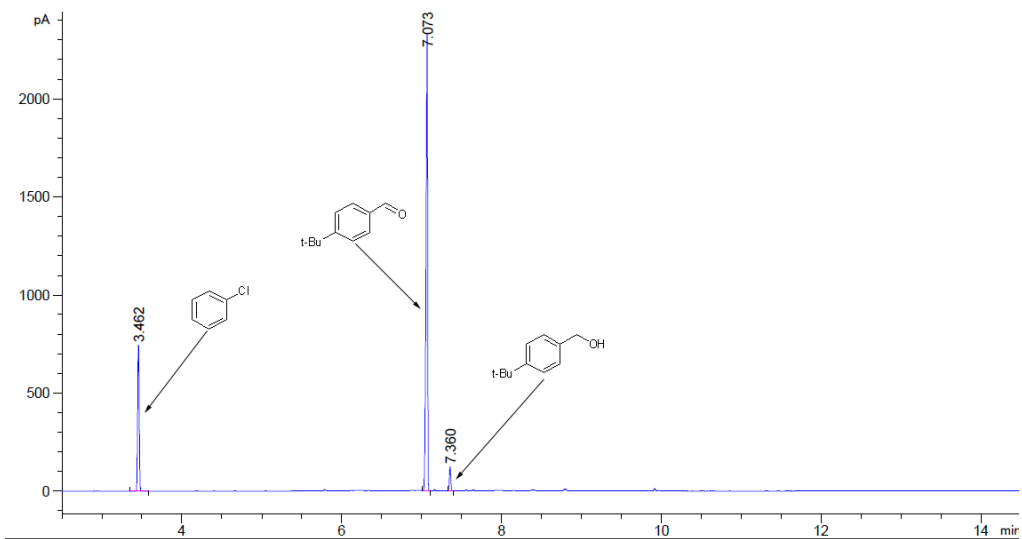


Table 7, Entry 6

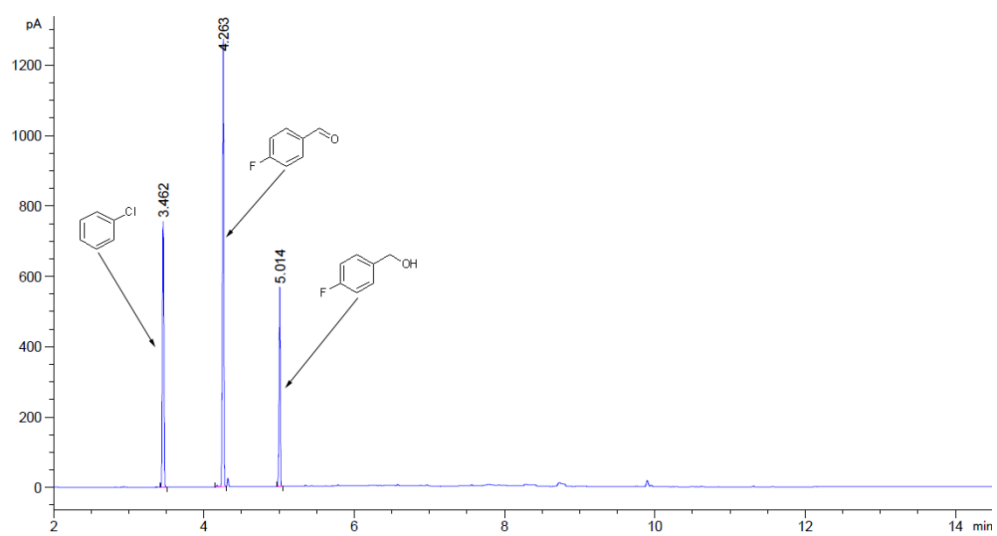


Table 7, Entry 7

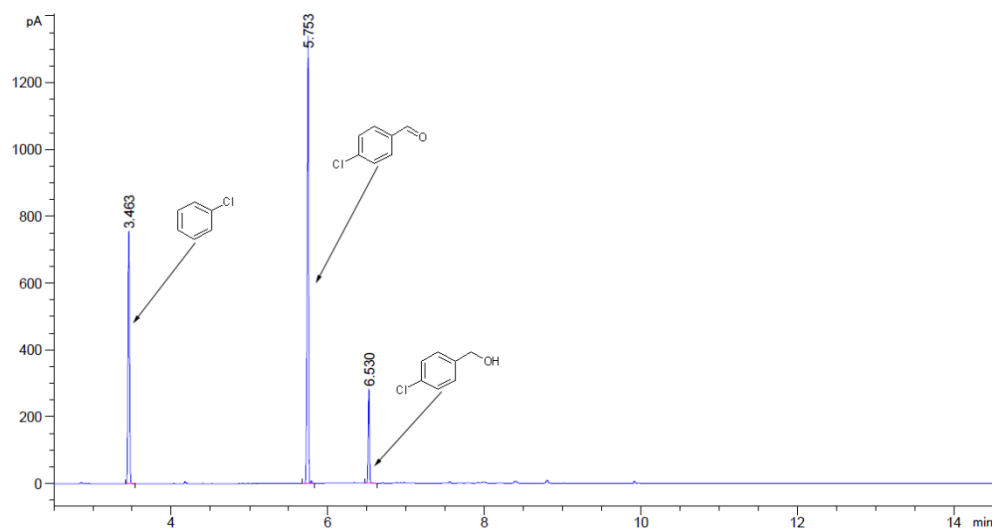


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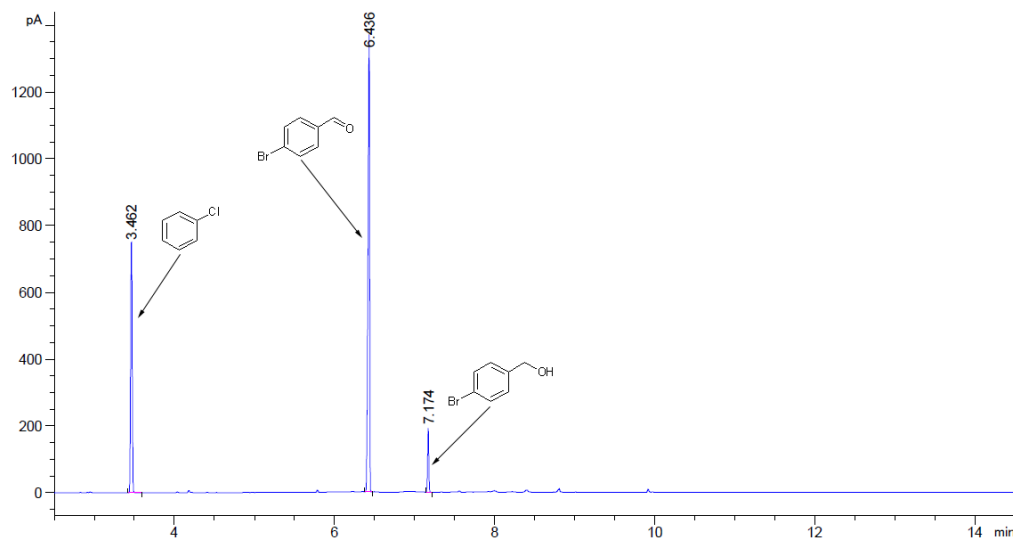


Table 7, Entry 9



Table 7, Entry 10

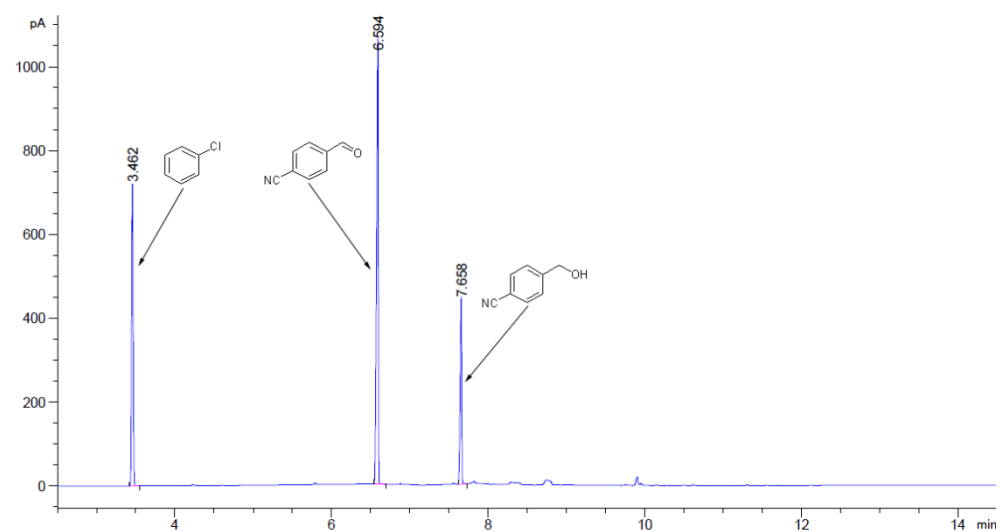


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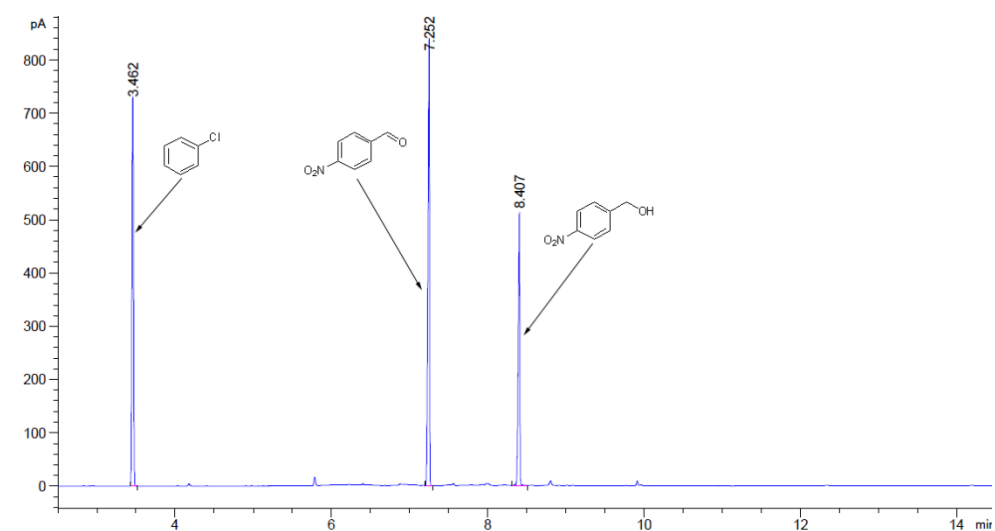


Table 7, Entry 12

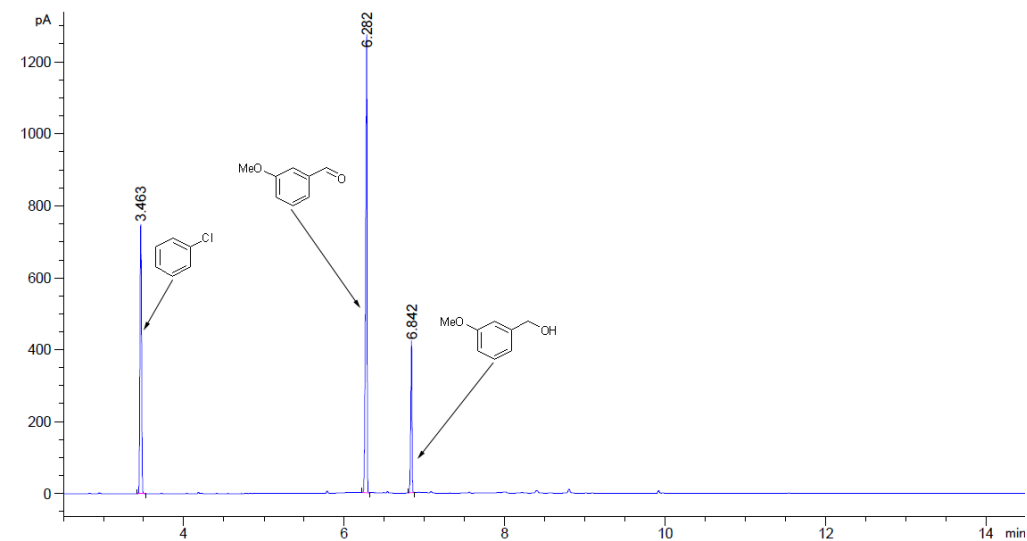
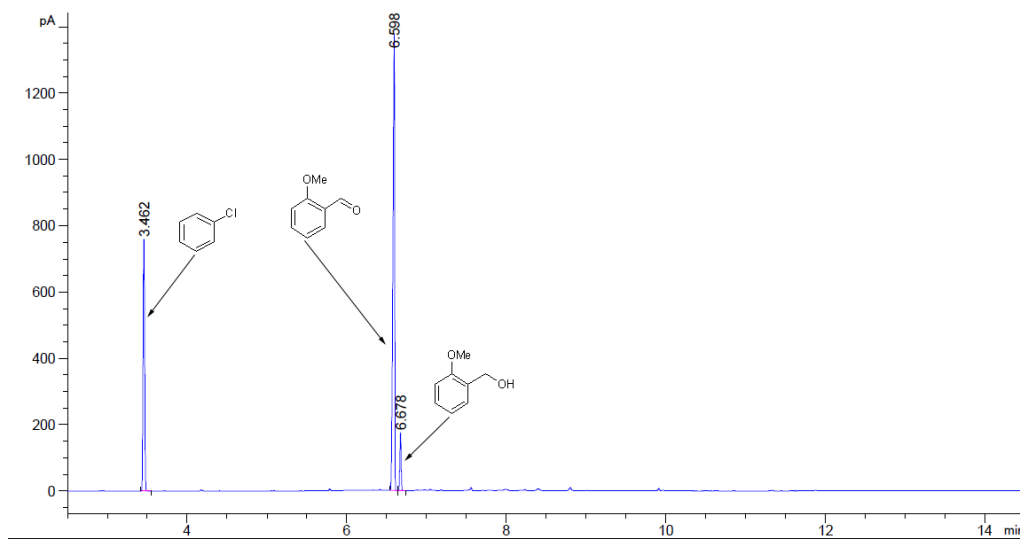




Table 7, Entry 13



Figures S2: GC-FID results for Table 8.

Table 8, Entry 1

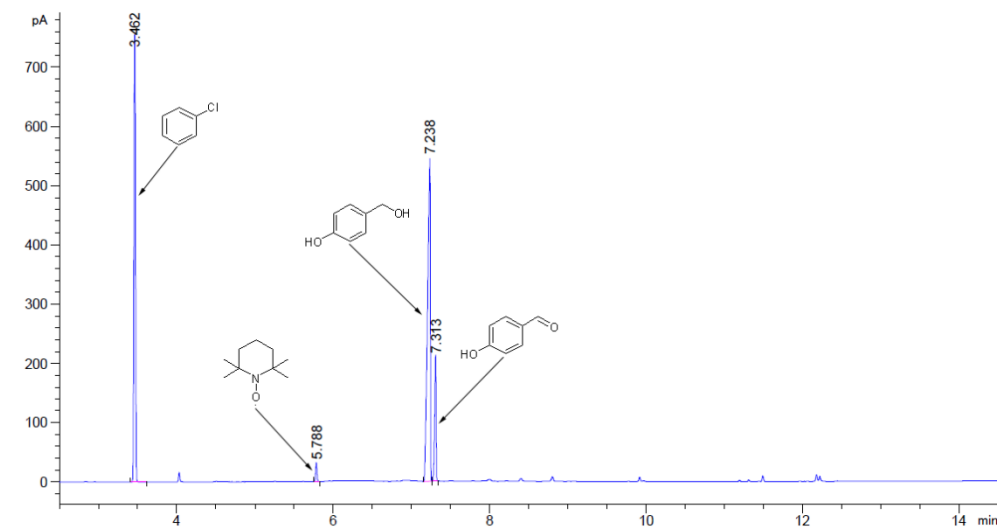


Table 8, Entry 2

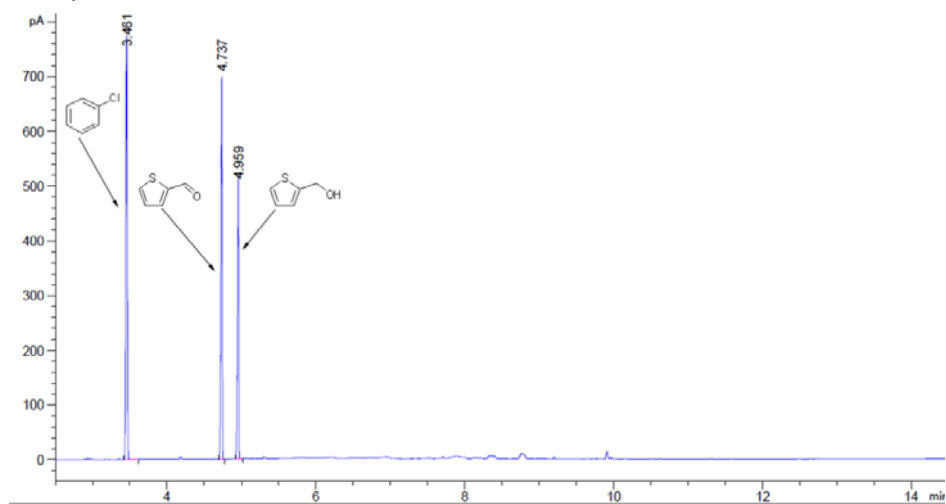


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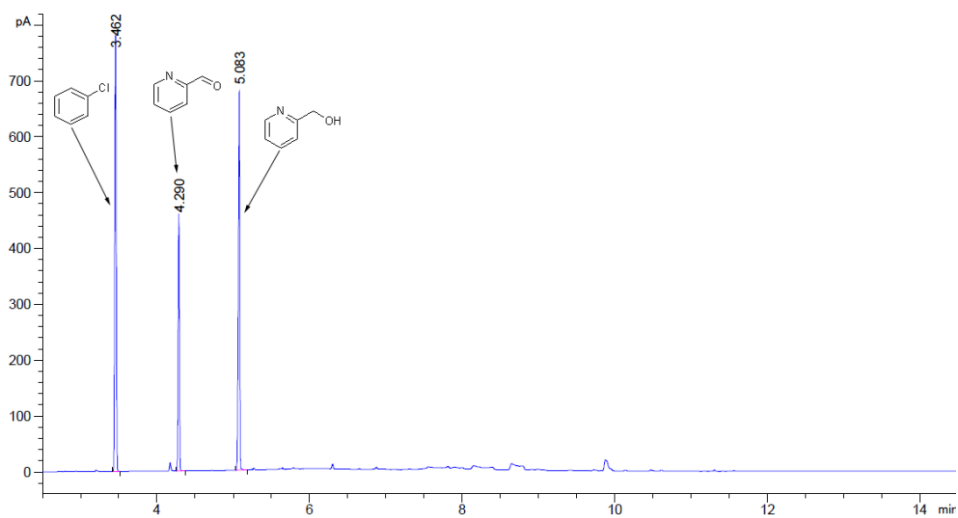


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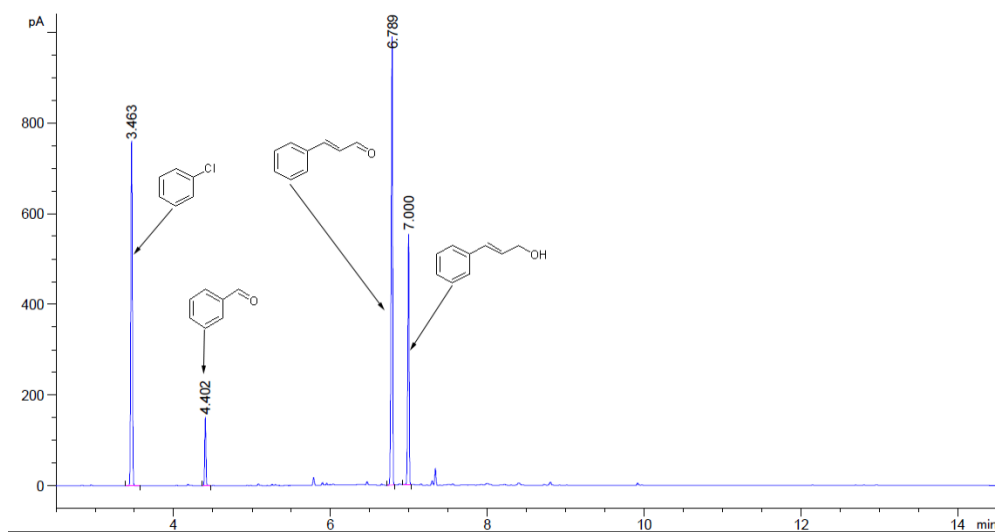


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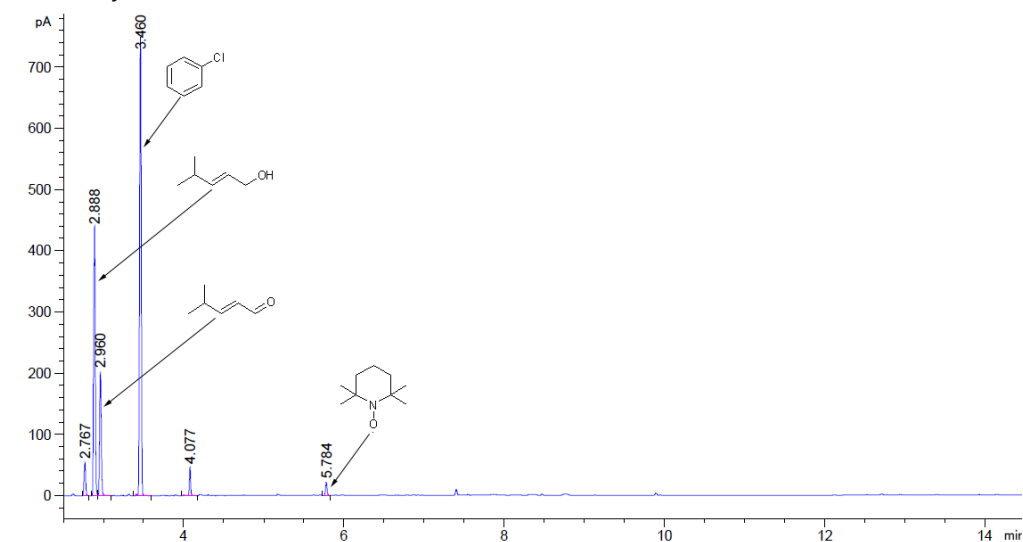


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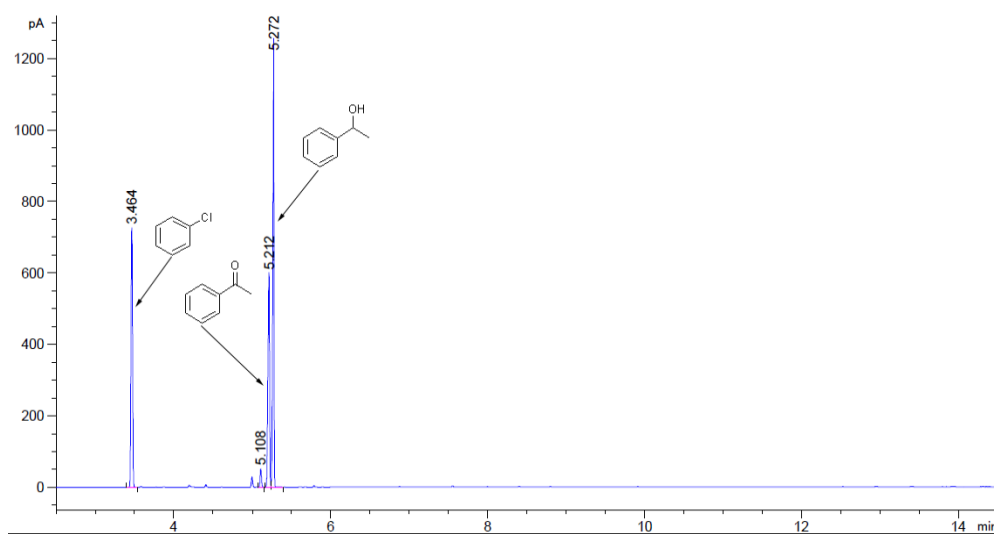


Table 8, Entry 7

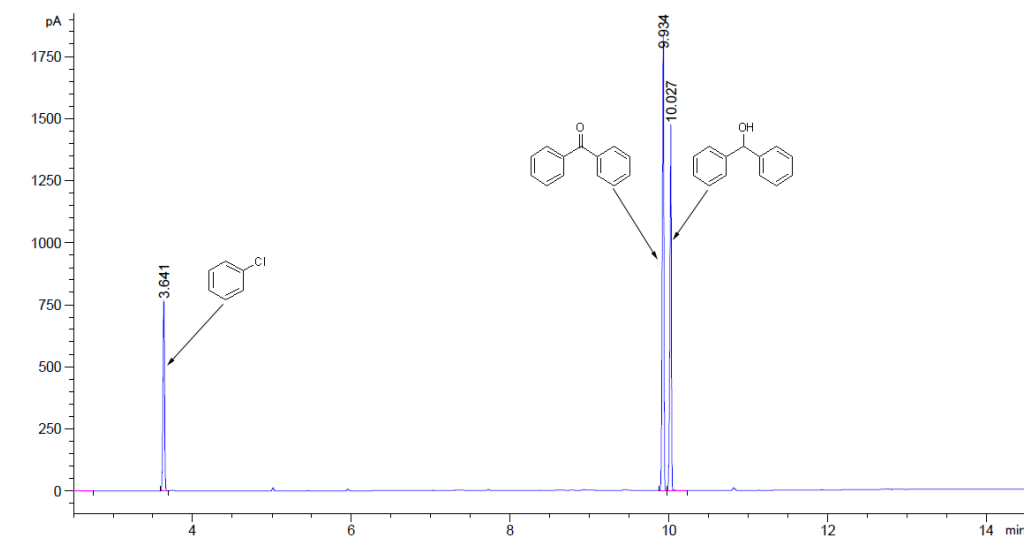


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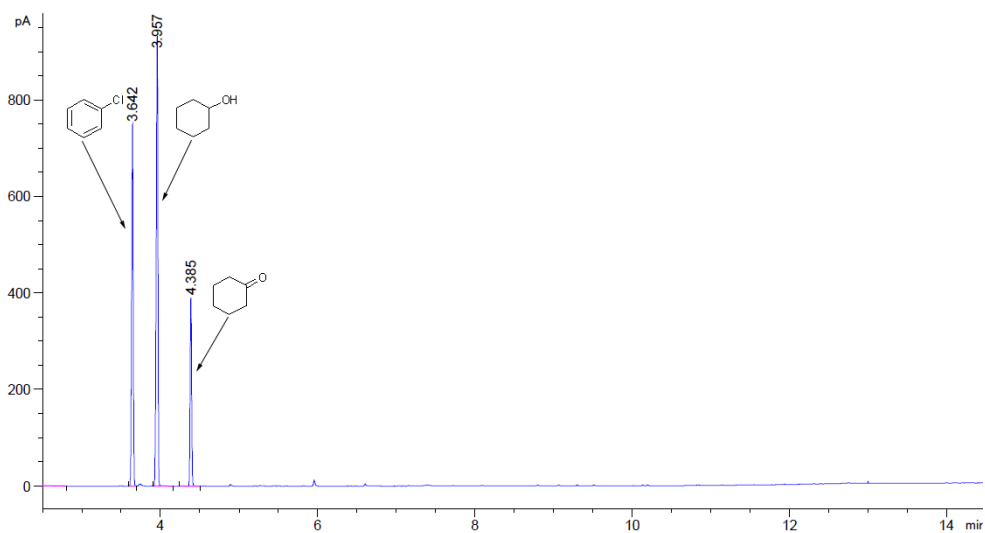


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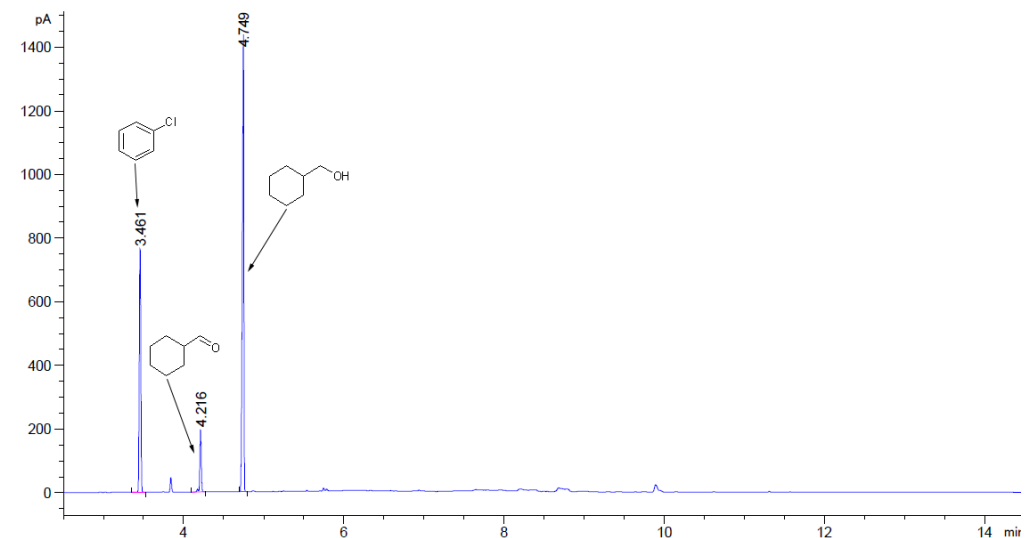


Table 8, Entry 10

