

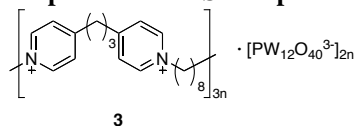
Supporting Information

A Tightly Convolutd Polymeric Phosphotungstate Catalyst: An Oxidative Cyclization of Alkenols and Alkenoic Acids

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Preparation of Solid-phase Tungsten Catalyst **3**



To an aqueous solution (30 mL) of poly[1,8-dibromooctane-co-1,3-di(4-pyridyl)propane] (**1**) (148 mg; 0.63 mmol of a pyridinium unit) was added an aqueous solution (70 mL) of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (**2**) (608 mg; 0.21 mmol) at 25 °C, and the resulting colorless suspension was stirred for 3 days at the same temperature. The precipitates were collected by filtration, washed with water and dried at 5 Pa for 12 h to give **3** (624 mg; 83%) as a colorless powder.

MAS $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz; CDCl_3): δ -16.5 ppm; IR (ATR) ν 3727, 3624, 3062, 2927, 2858, 1638, 1572, 1514, 1469, 1172, 1077, 974, 892, 792, cm^{-1} ; Anal. calcd. for $(\text{C}_{63}\text{H}_{90}\text{N}_6\text{P}_2\text{W}_{24}\text{O}_{80})_n$: C 11.32%, H 1.36%, N 1.26%, found: C 12.45%, H 1.60%, N 1.32%

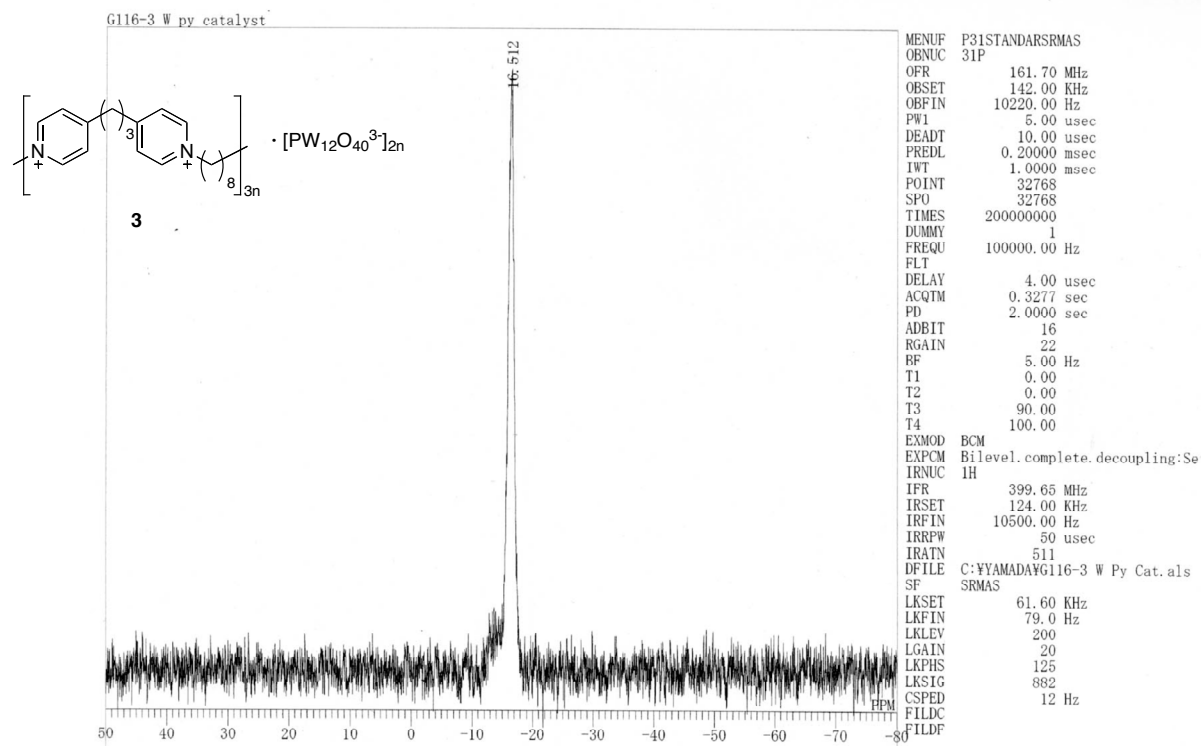
General Procedure for the Oxidative Cyclization of Alkenols **4** or Alkenoic Acids **6**

To a suspension of **3** (13 mg) in 30% aq H_2O_2 (5 mmol) was added **4** or **6** (2 mmol) (and mesitylene (an internal standard for the determination of a GC yield)), and the resulting suspension was stirred at 50 °C for 24 h. After the reaction mixture was cooled to 25 °C, *t*-butyl methyl ether was added, and the resultant organic layer was separated by decantation. After the addition and extraction process were carried out for three times, the combined organic layer was subjected to GC-MS analysis for the determination of a GC yield (for **5a**, **5b**, **5c** and **5d**). The organic layer was washed with sat. aqueous $\text{Na}_2\text{S}_2\text{O}_3$, dried over MgSO_4 , dried in vacuo, and purified by silica gel column chromatography to give the cyclized product (for **5e**, **5f**, **5g**, **7a**, **7b** and **7c**). The recovered **3** was dried in vacuo, and subjected to the next series of the reaction under similar reaction conditions.

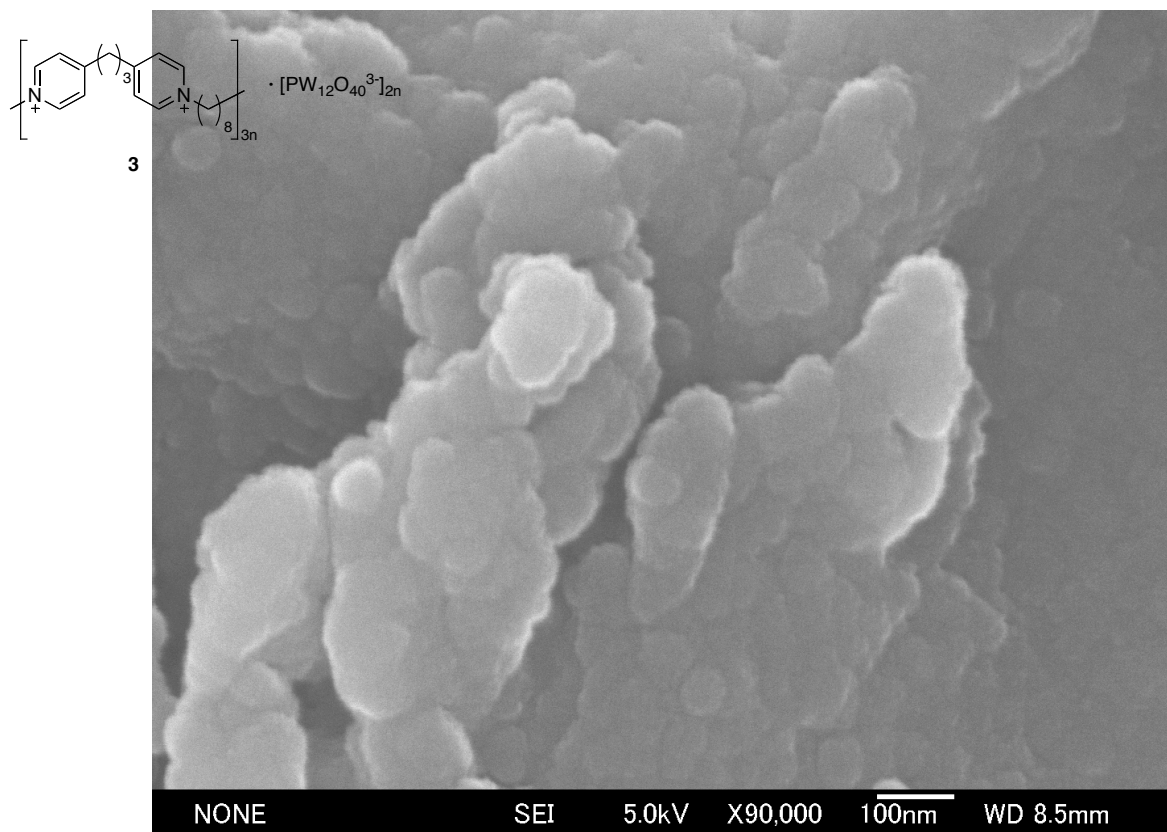
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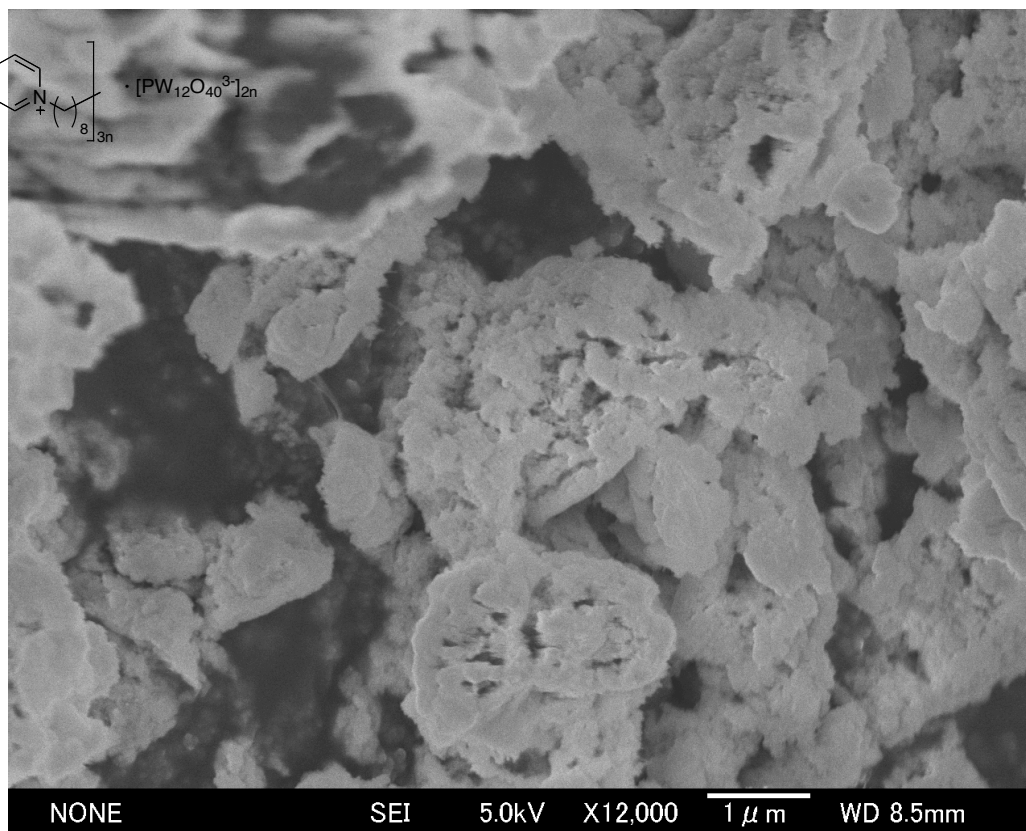
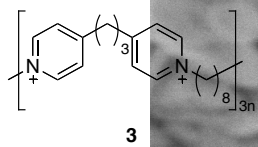
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MAS ^{31}P NMR of 3



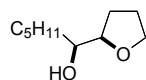
SEM images of 3



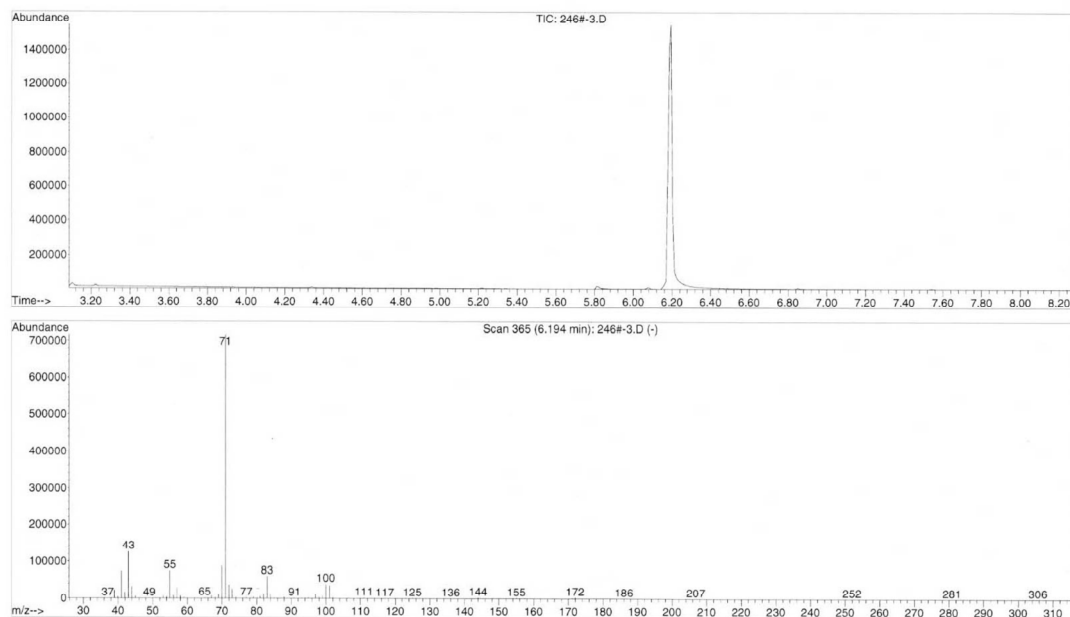


GC-MS charts of the isolated products (5e, 5f, 5g, 7a, 7b and 7c)

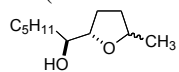
5e



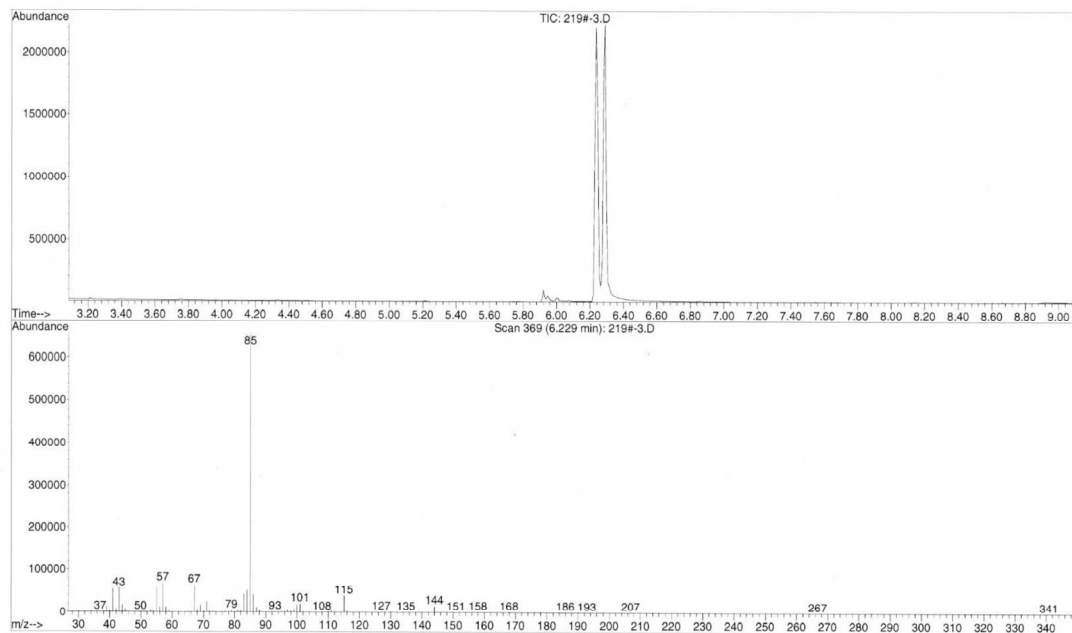
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 Vial Number: 1



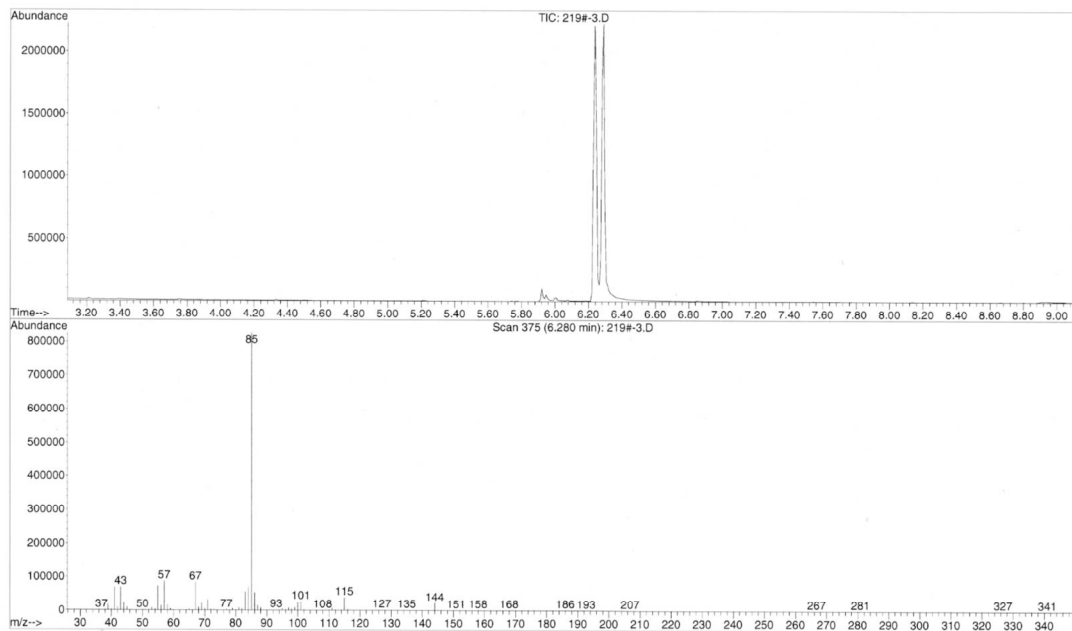
5f (*cis* and *trans* isomers)



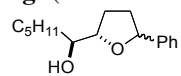
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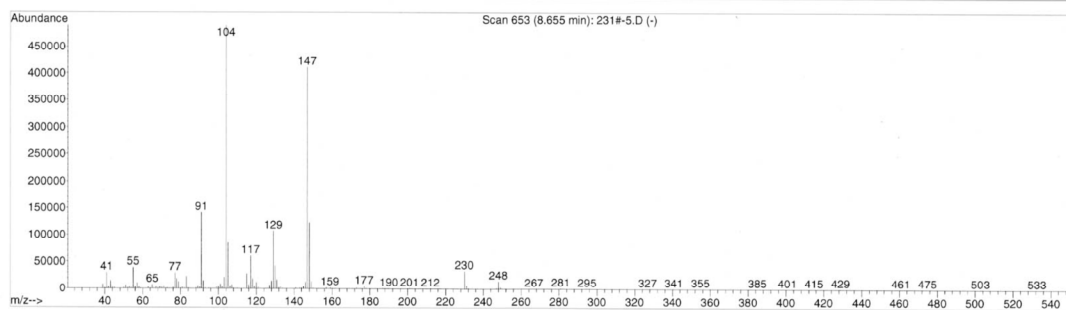
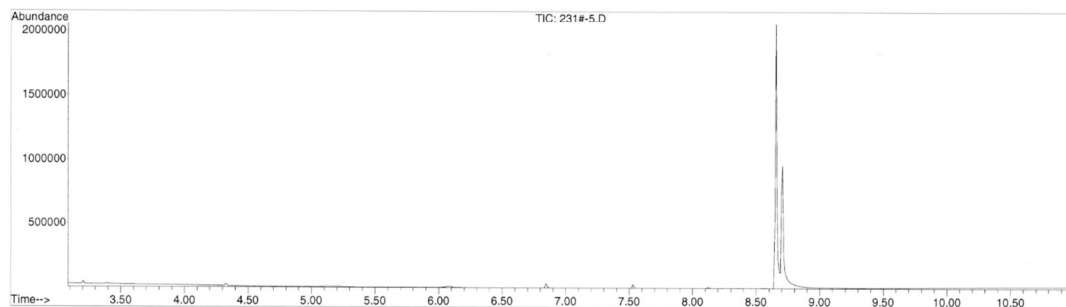
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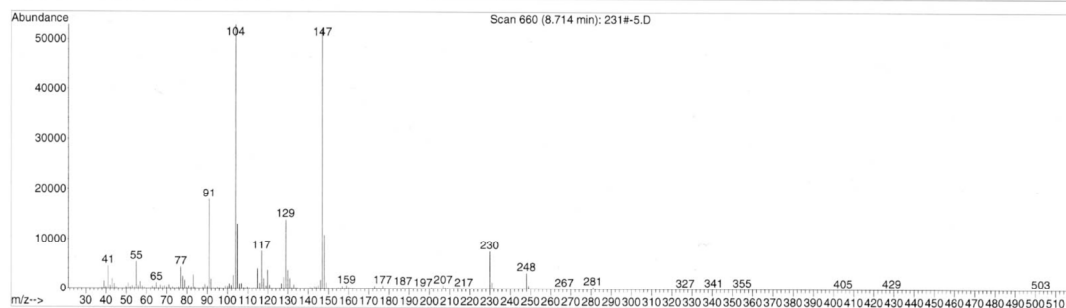
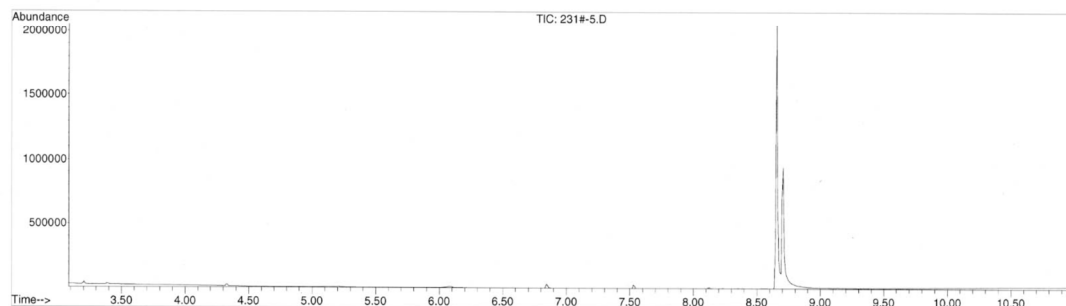
5g (*cis* and *trans* isomers)

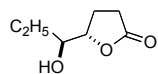


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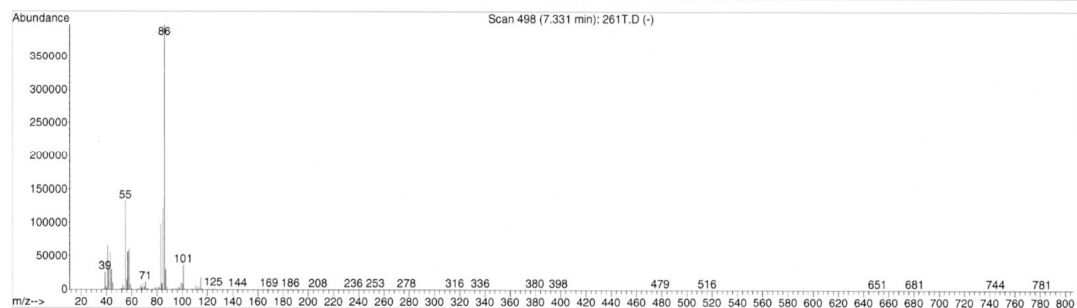
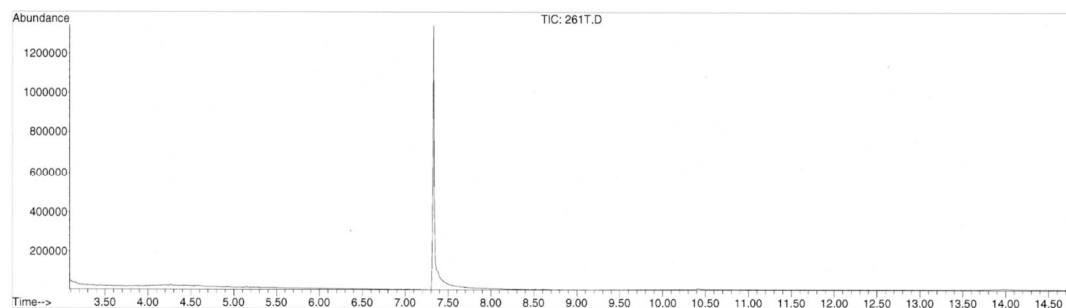
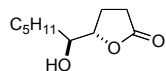


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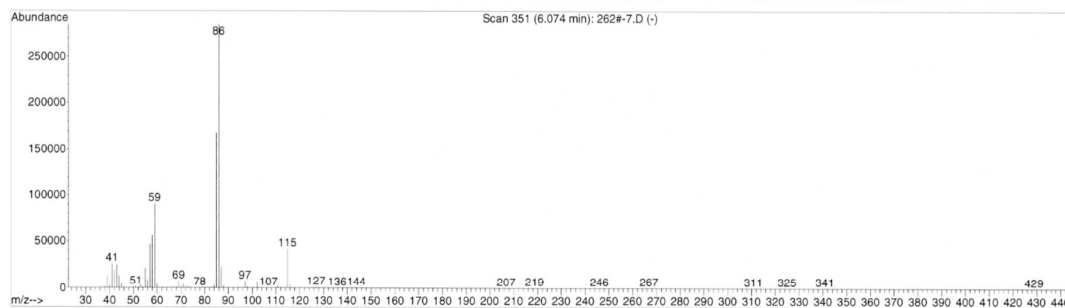
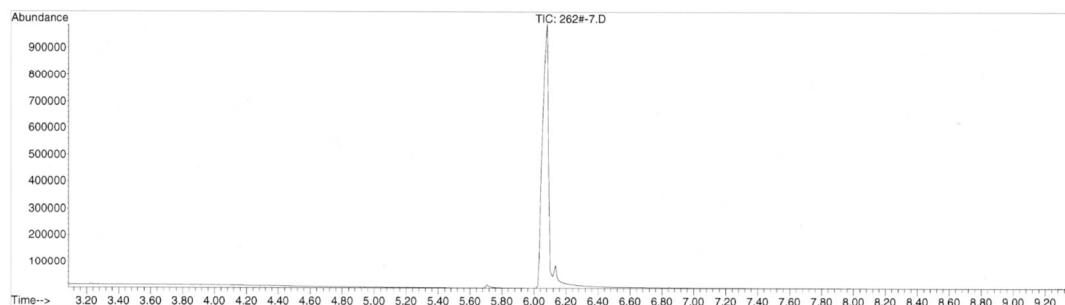


7a

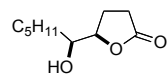
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 Vial Number: 1

**7b**

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 Vial Number: 1



7c



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Operator : Guo
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Sample Name: 250#-5
Misc Info : C.C., 1stube
Vial Number: 1

