

## **Microwave-assisted green synthesis of levulinate esters as biofuel precursors using calix[4]arene as an organocatalyst under solvent-free conditions**

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## GENERAL TECHNIQUES

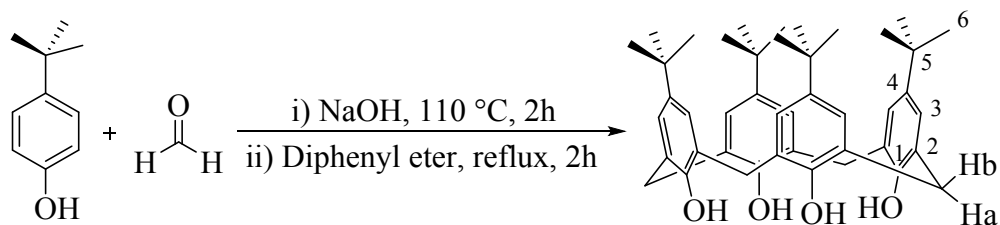
Analytical grade commercial solvents and reagents were purchased from Sigma-Aldrich, and used as received. Infrared spectra were recorded as neat using a FT-IR Varian 660 Fourier transform infrared spectrometer. Values are expressed in wavenumbers ( $\text{cm}^{-1}$ ) and recorded in a range of 4000–400  $\text{cm}^{-1}$ . NMR spectra were recorded at 25 °C in  $\text{CDCl}_3$  and  $\text{D}_2\text{O}$  on a Varian Mercury 300 spectrometer operating at 300 MHz for  $^1\text{H}$  and 75 MHz for  $^{13}\text{C}$ . All chemical shifts are reported in parts per million (ppm) and were measured relative to the solvent in which the sample was analyzed ( $\text{CDCl}_3$   $\delta = 7.26$  for  $^1\text{H}$  NMR and  $\delta = 77.0$  for  $^{13}\text{C}$  NMR;  $\text{D}_2\text{O}$   $\delta = 4.79$  for  $^1\text{H}$  NMR). Coupling constants ( $J$ ) are reported in hertz (Hz). The chromatograms and spectrum mass was determined for gas chromatography coupled to a mass spectrometer using a SHIMADZU GCMS-QP2010C Ultra mass spectrometer and method with the following specifications: column RTx-5 MS, 30 m, DI 0.25 mm; carrier gas helium; injector temperature: 220 °C; oven temperature was: 40 °C (2 min), ramped to 5 °C  $\text{min}^{-1}$  up to 100 °C (held for 5 min), ramped to 30 °C  $\text{min}^{-1}$  up to 200 °C (held for 5 min).

## EXPERIMENTAL PROCEDURES

### Synthesis of calix[ $n$ ]arenes

#### Synthesis of the *p-tert*-butylcalix[4]arene

The synthesis of the *p-tert*-butylcalix[4]arene involving the condensation of the *p-tert*-butylphenol, formaldehyde solution with a basic medium and under heating, as shown in Scheme 1, following the methodology described by Gutsche et al<sup>1</sup>. The product was obtained as a white solid in 77% yield.

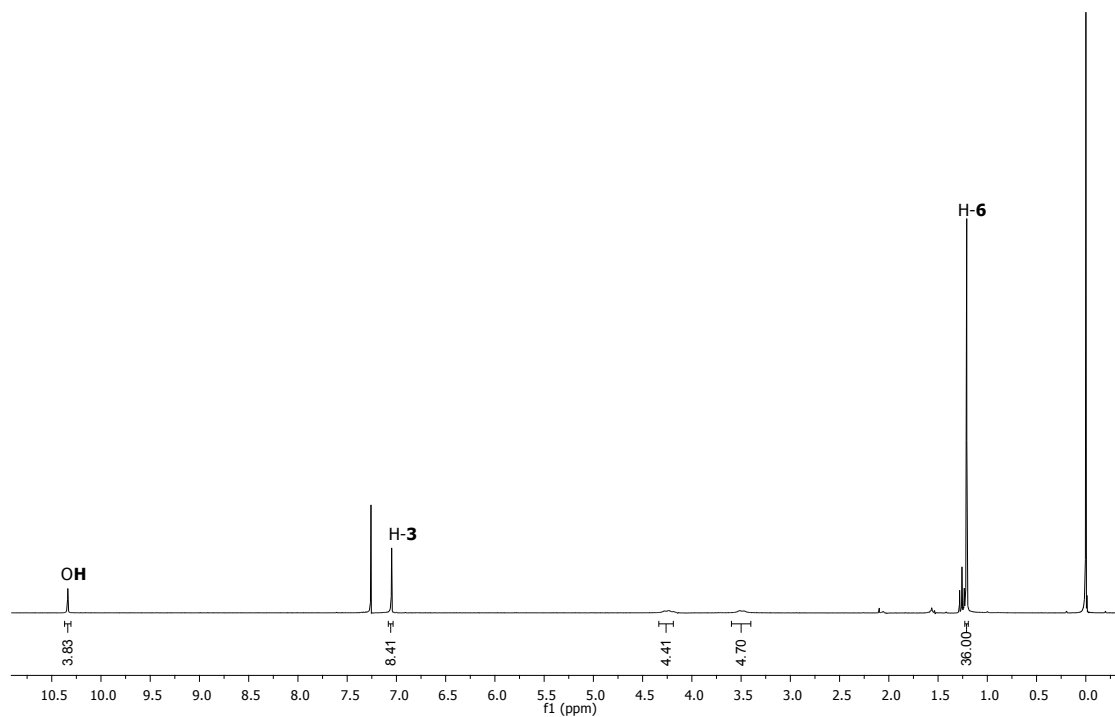


**Scheme 1** - Reaction for obtaining the *p-tert*-butylcalix[4]arene.

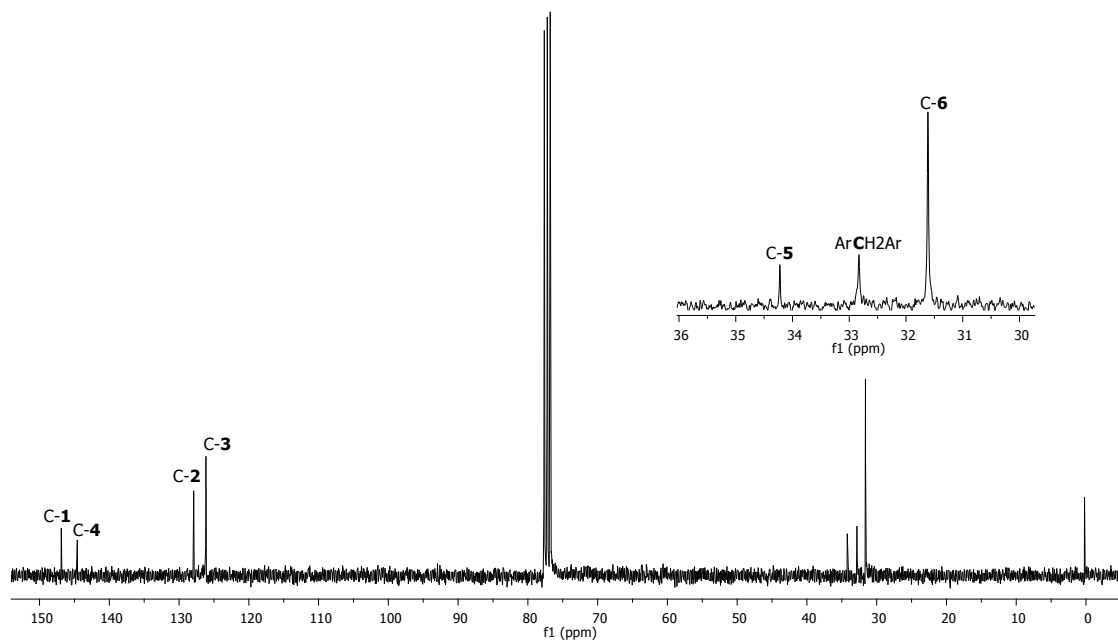
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 1.21 (s, 36H, H-6), 3.48 (d, 4H,  $J$  12.4,  $\text{CH}_2\text{-Ha}$ ), 4.28 (d, 4H,  $J$  12.4,  $\text{CH}_2\text{-Hb}$ ), 7.05 (s, 8H, H-3), 10.34 (s, 4H, OH).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 31.4 (C-6), 32.7 ( $\text{CH}_2$ ), 34.0 (C-5), 125.9 (C-3), 127.6 (C-2), 144.3 (C-4), 146.7 (C-1).

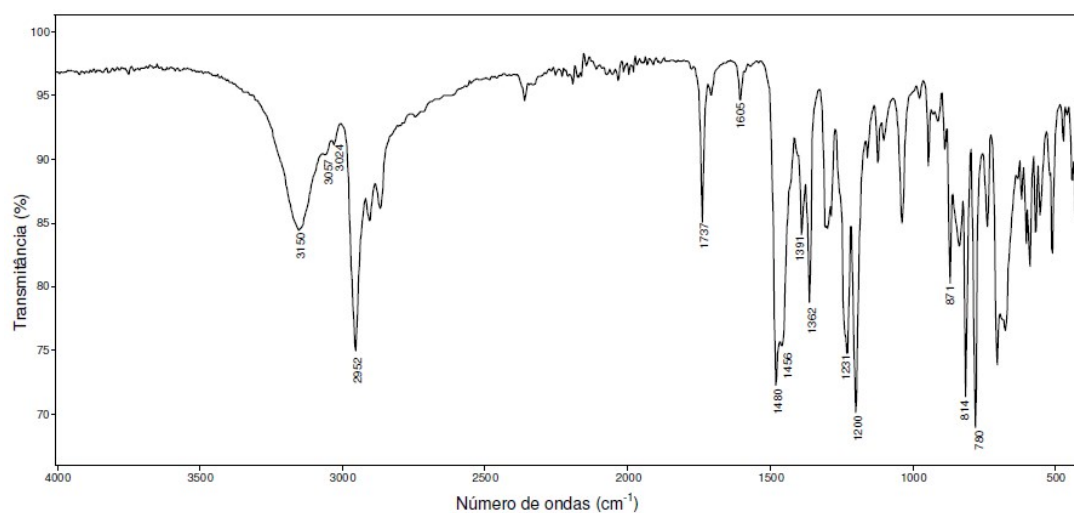
IR (ATR,  $\text{cm}^{-1}$ ): 3150, 3057, 3024, 2952, 1737, 1605, 1480, 1456, 1391, 1362, 1231, 1200, 871, 814, 780.



**Fig. S1.**  $^1\text{H}$  NMR spectrum (300 MHz;  $\text{CDCl}_3$ ) of the *p-tert*-butylcalix[4]arene.



**Fig. S2.**  $^{13}\text{C}$  NMR spectrum (75 MHz;  $\text{CDCl}_3$ ) of the *p*-*tert*-butylcalix[4]arene.

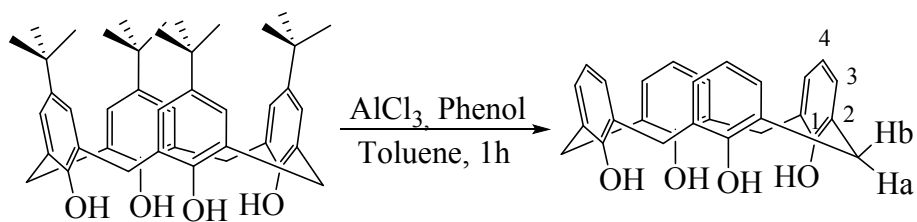


**Fig. S3.** FT Spectrum of the *p*-*tert*-butylcalix[4]arene.

### Synthesis of the calix[4]arene

The synthesis of calix[4]arene was carried out using *p*-*tert*-butylcalix[4]arene, phenol and aluminum chloride anhydrous in toluene following the methodology described by Gutsche et al<sup>2</sup>. The system was kept under stirring and nitrogen atmosphere at room temperature for one hour

(Scheme 2). The desired product, a white solid, was obtained in 81% yield after recrystallization in methanol-chloroform.

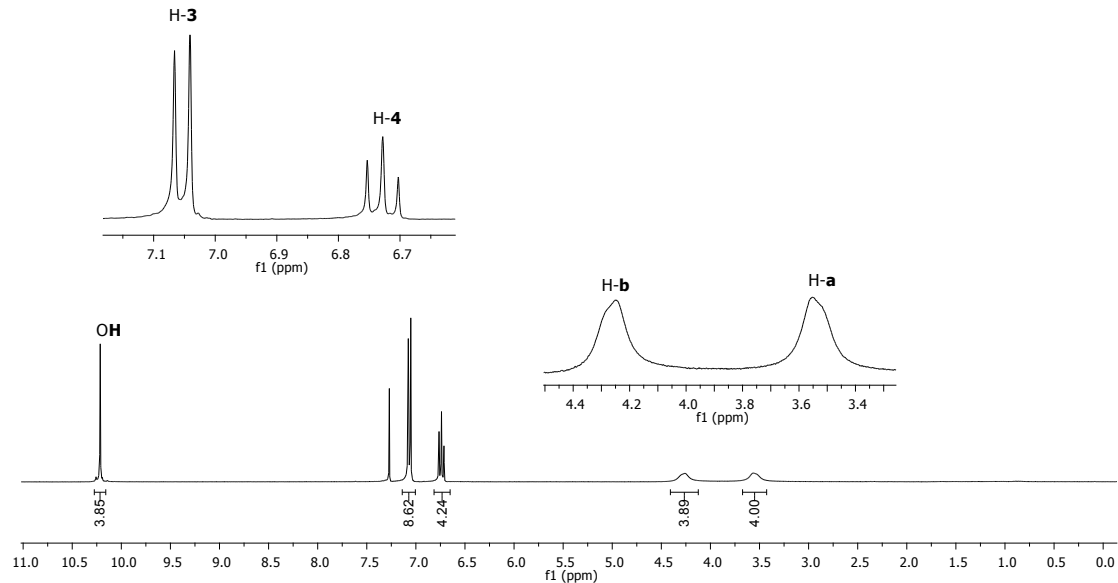


**Scheme 2** - Reaction for obtaining the calix[4]arene.

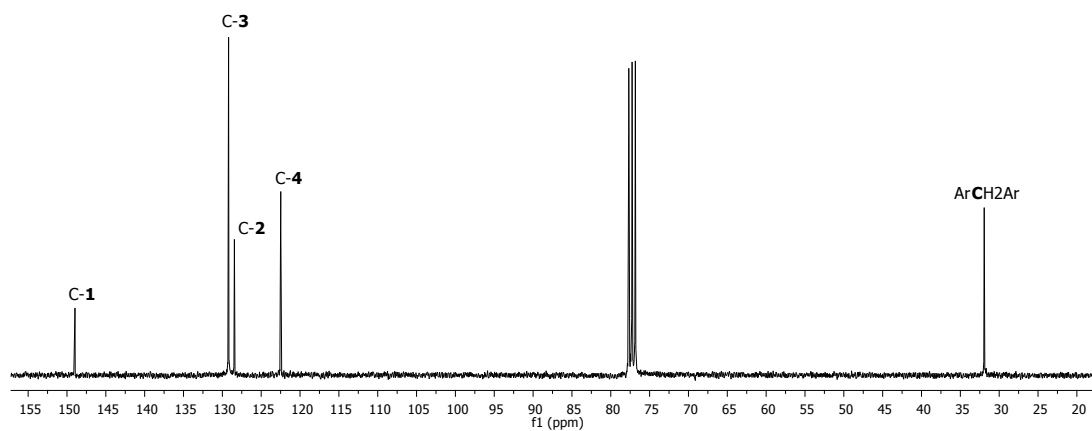
$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 3.56 (d, 4H,  $J$  12.6, H-a), 4.27 (d, 4H,  $J$  12.6, H-b), 6.79 (t, 4H,  $J$  7.5, H-4), 7.08 (d, 8H,  $J$  7.5 Hz, H-3), 10.23 (s, 4H, OH).

$^{13}\text{C NMR}$  (75 MHz;  $\text{CDCl}_3$ ): 31.9 ( $\text{CH}_2$ ), 122.5 (C-4), 128.5 (C-2), 129.2 (C-3), 149.0 (C-1).

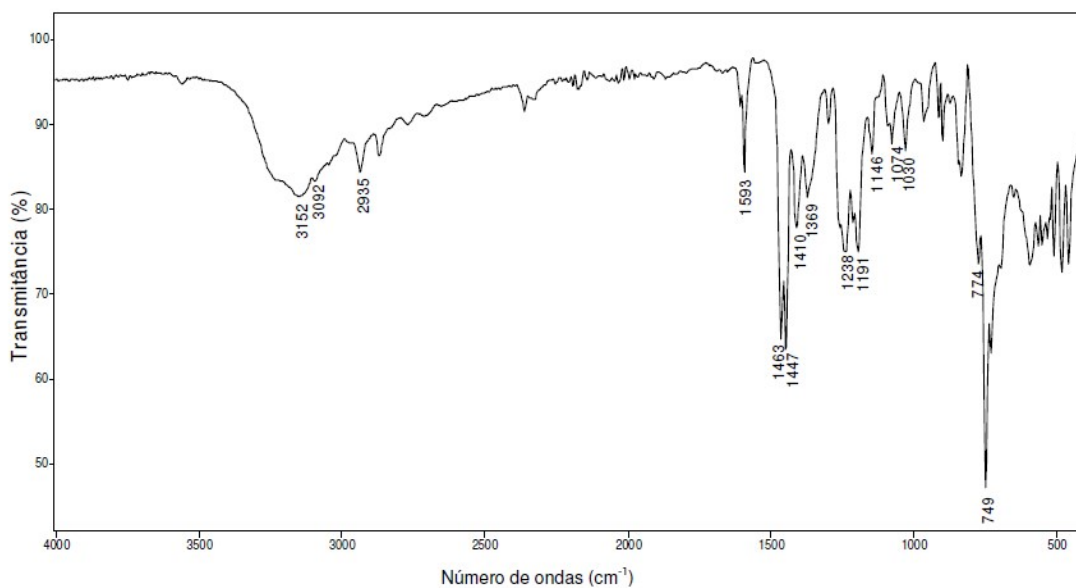
**IR** (ATR,  $\text{cm}^{-1}$ ): 3152, 3092, 2935, 1593, 1466, 1447, 1410, 1369, 1238, 774, 749.



**Fig. S4.**  $^1\text{H NMR}$  spectrum (300 MHz;  $\text{CDCl}_3$ ) of the calix[4]arene.



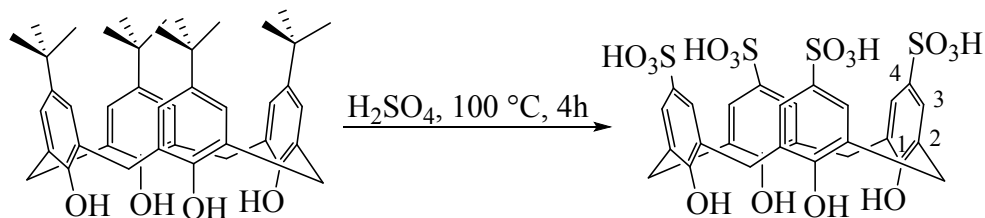
**Fig. S5.**  $^{13}\text{C}$  NMR spectrum (75 MHz;  $\text{CDCl}_3$ ) of the calix[4]arene.



**Fig. S6.** FT Spectrum of the calix[4]arene.

### Synthesis of the *p*-sulfonic acid calix[4]arene ( $\text{CX}_4\text{SO}_3\text{H}$ )

Catalyst *p*-sulfonic acid calix[4]arene was conducted from calix[4]arene in the presence of concentrated sulfuric acid and heated for four hours as described by Gutsche et al<sup>3</sup> (Scheme 3). The product was obtained in 75% yield as a solid white.

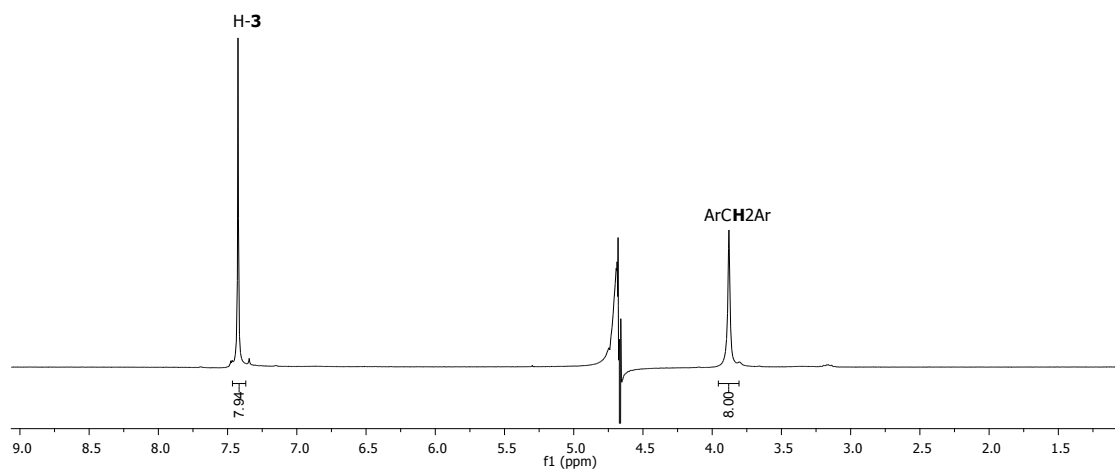


**Scheme 3** - Reaction for obtaining of the *p*-sulfonic acid calix[4]arene (CX4SO<sub>3</sub>H).

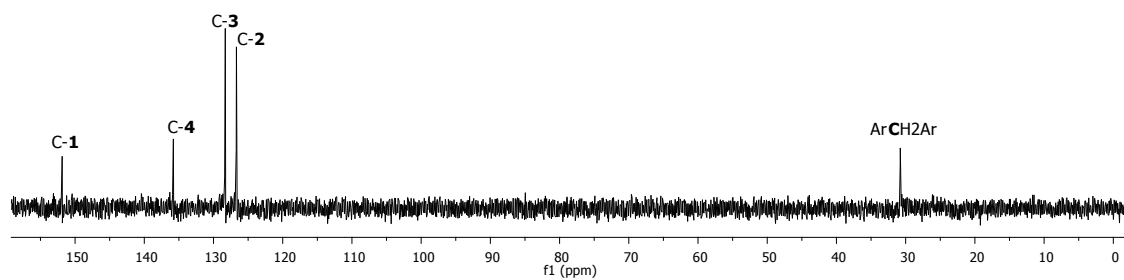
<sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): 3.84 (s, 8H, CH<sub>2</sub>), 7.39 (s, 8H, H-3).

<sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): 30.7 (CH<sub>2</sub>), 126.6 (C-3), 128.2 (C-2), 135.8 (C-4), 151.9 (C-1).

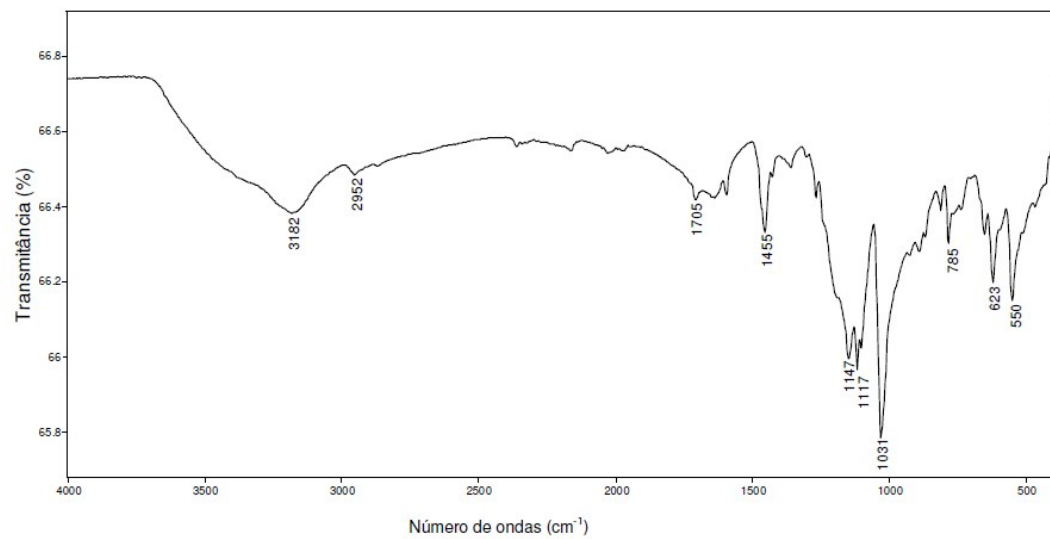
IR (ATR, cm<sup>-1</sup>): 3182, 1705, 1636, 1599, 1455, 1147, 1117, 623.



**Fig. S7.** <sup>1</sup>H NMR spectrum (300 MHz; D<sub>2</sub>O) of the *p*-sulfonic acid calix[4]arene (CX4SO<sub>3</sub>H).

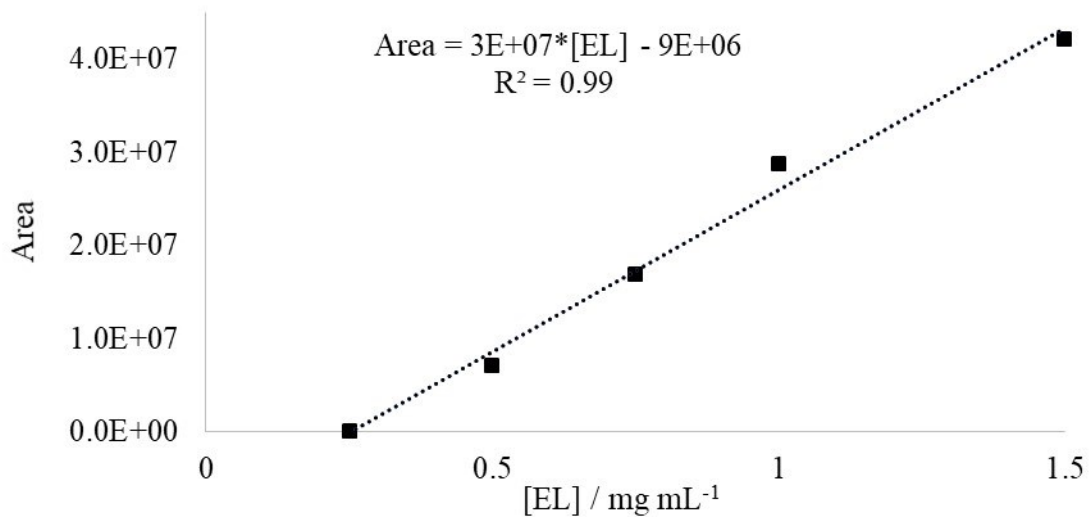


**Fig. S8.**  $^{13}\text{C}$  NMR spectrum (75 MHz;  $\text{D}_2\text{O}$ ) of the *p*-sulfonic acid calix[4]arene ( $\text{CX}_4\text{SO}_3\text{H}$ ).



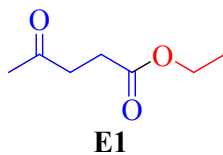
**Fig. S9.** FT Spectrum of the *p*-sulfonic acid calix[4]arene ( $\text{CX}_4\text{SO}_3\text{H}$ ).





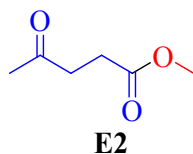
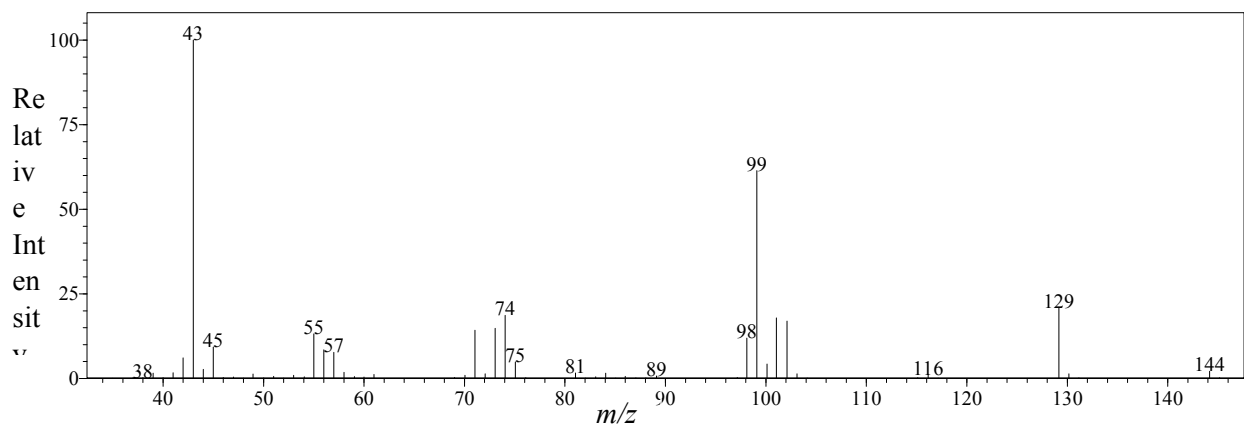
**Fig. S10.** Ethyl Levulinate calibration curve. [EL] = Ethyl Levulinate concentration.

### Spectrum mass of the all compounds



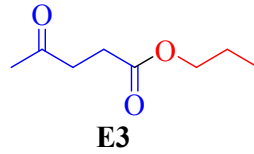
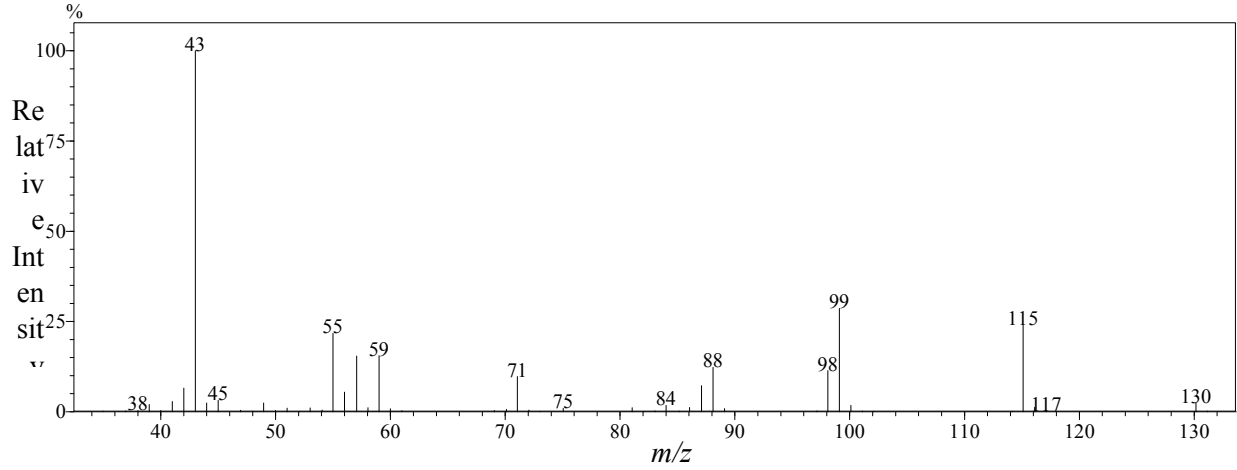
### Ethyl 4-oxopentanone

**GC/MS**  $m/z$  (abundancy %): 144 (4, M<sup>+</sup>), 129 (21), 99 (71), 43 (100).



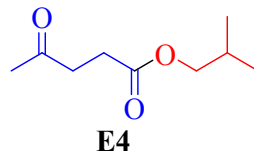
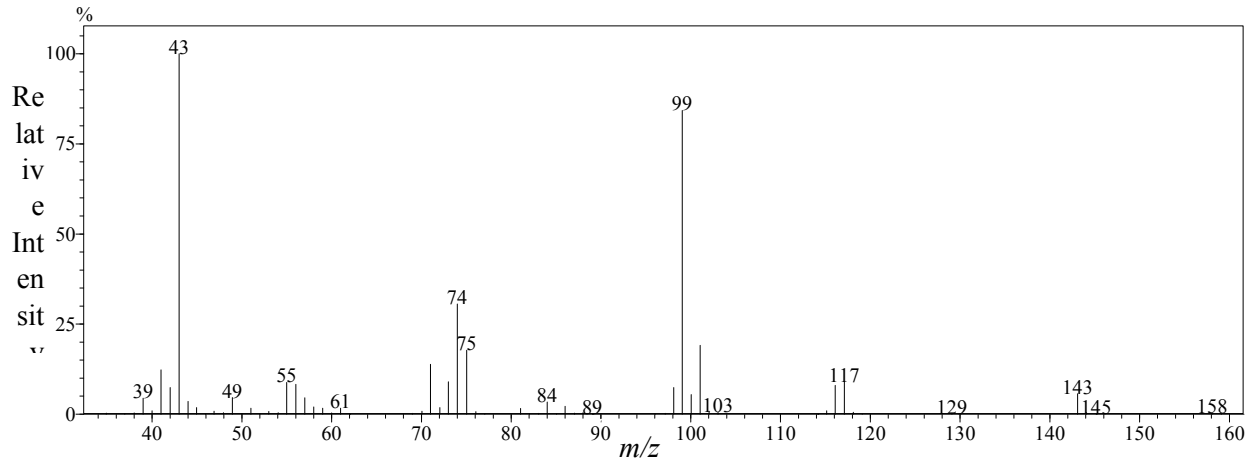
### Methyl 4-oxopentanone

GC/MS  $m/z$  (abundance %): 130 (5, M+), 115 (21), 99 (30), 55 (25), 43 (100).



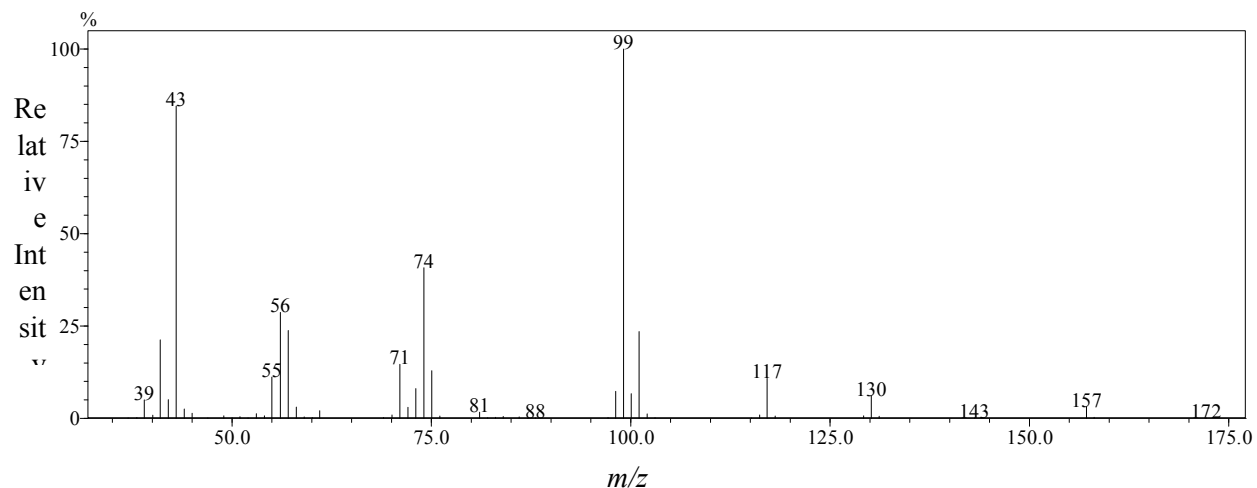
### Propyl 4-oxopentanone

GC/MS  $m/z$  (abundance %): 158 (4, M+), 143 (8), 117 (10), 99 (83), 74 (30), 43 (100).



### Isobutyl 4-oxopentanone

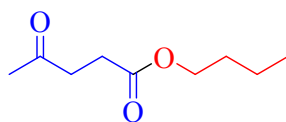
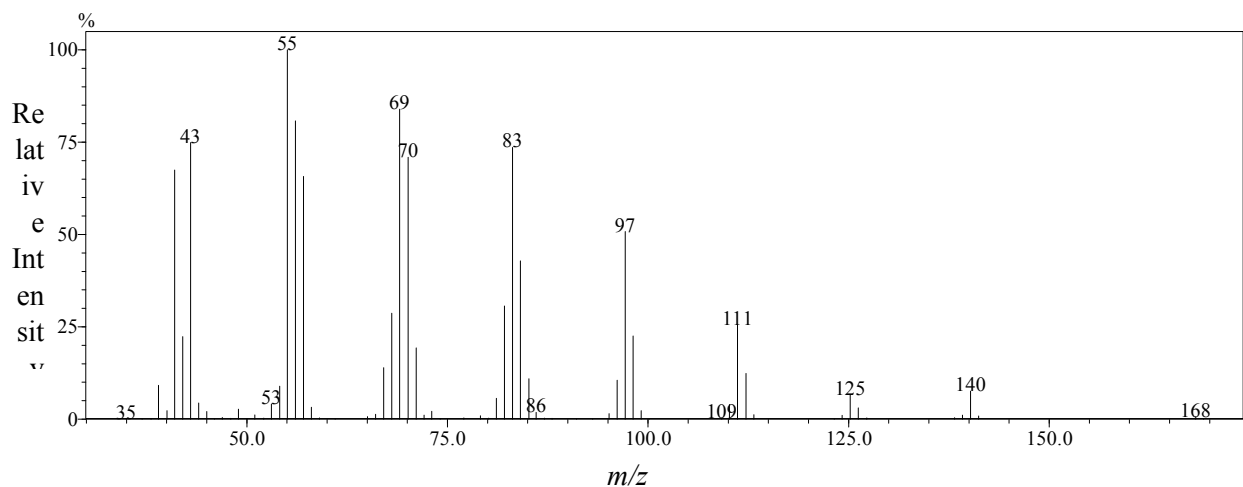
GC/MS  $m/z$  (abundance %): 172 (1, M+), 157 (5), 117 (15), 99 (100), 74 (43), 43 (87).



**E5**

**Dodecyl 4-oxopentanone**

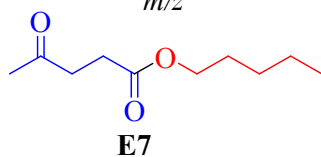
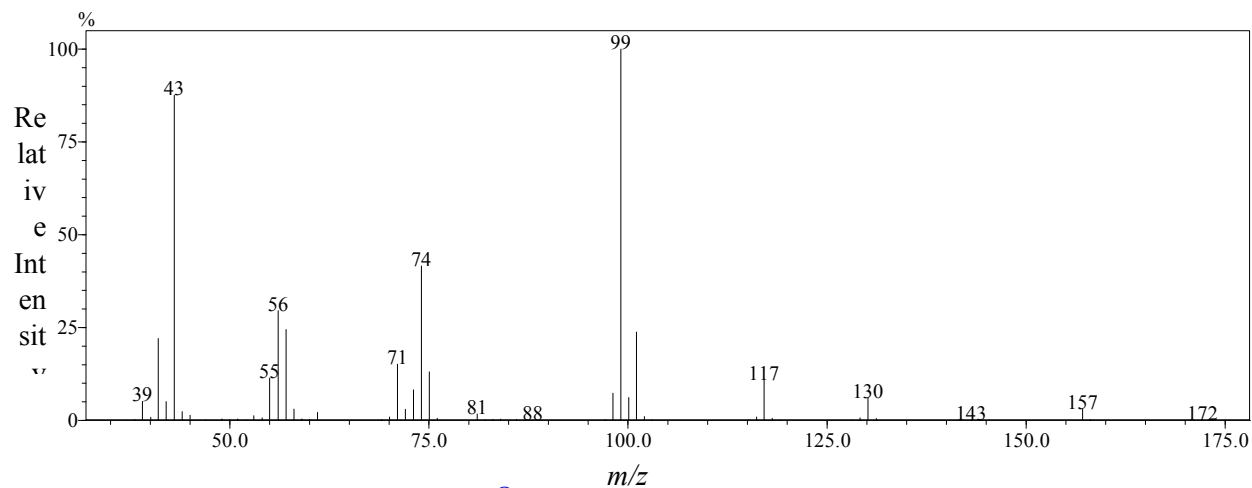
**GC/MS** *m/z* (abundance %): 168 (1, M<sup>+</sup>), 140 (5), 111 (25), 97 (55), 83 (75), 69 (86), 55 (100), 43 (75).



**E6**

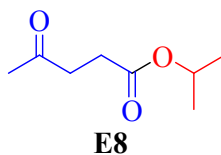
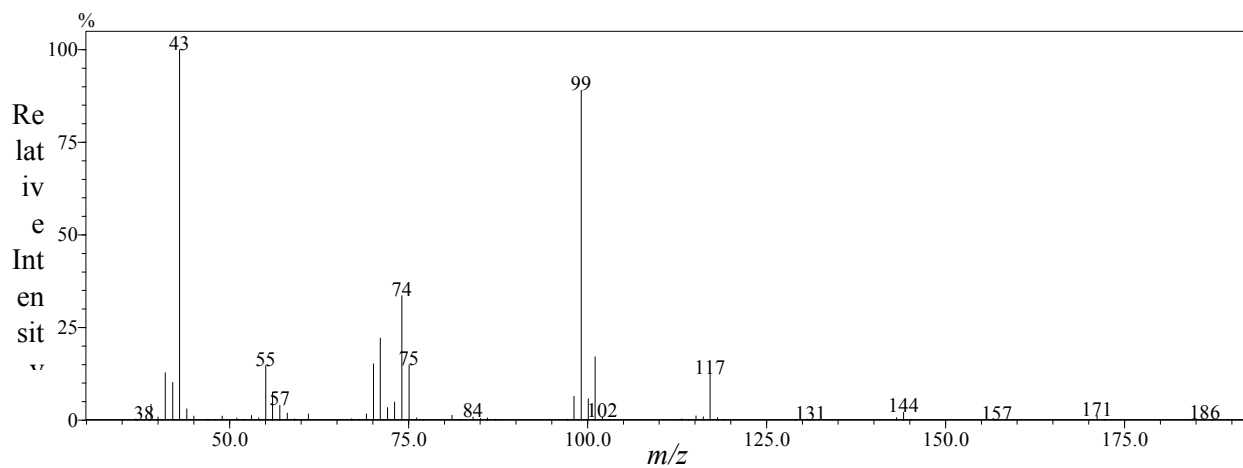
**Butyl 4-oxopentanone**

**GC/MS** *m/z* (abundance %): 172 (1, M<sup>+</sup>), 157 (5), 117 (13), 99 (100), 74 (42), 43 (90).



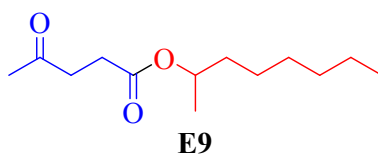
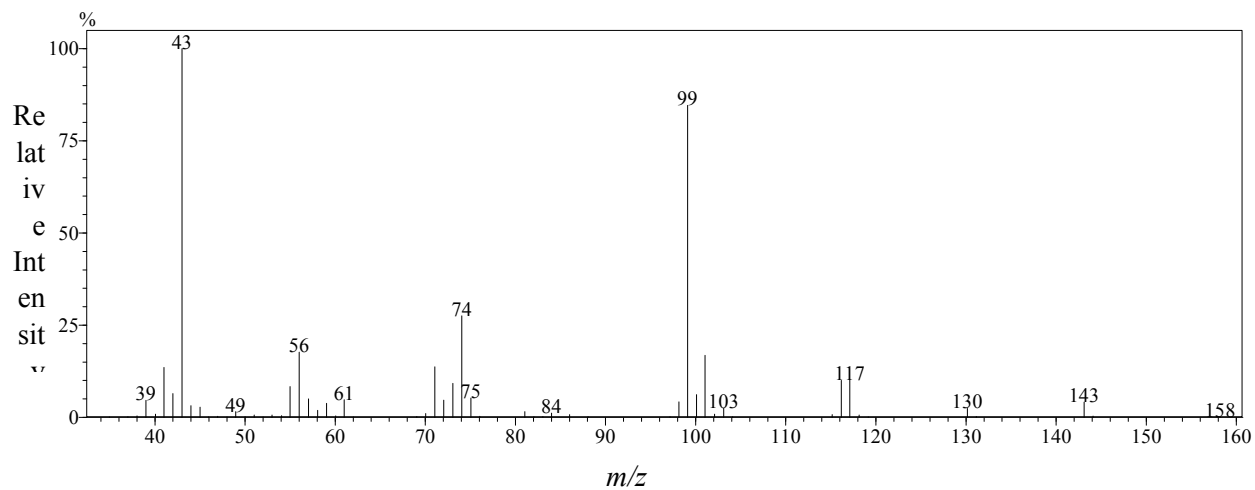
**Pentyl 4-oxopentanone**

**GC/MS** *m/z* (abundance %): 186 (1, M<sup>+</sup>), 172 (1), 157 (1), 117 (15), 99 (90), 74 (42), 43 (100).



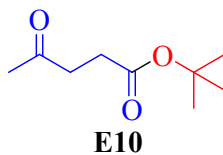
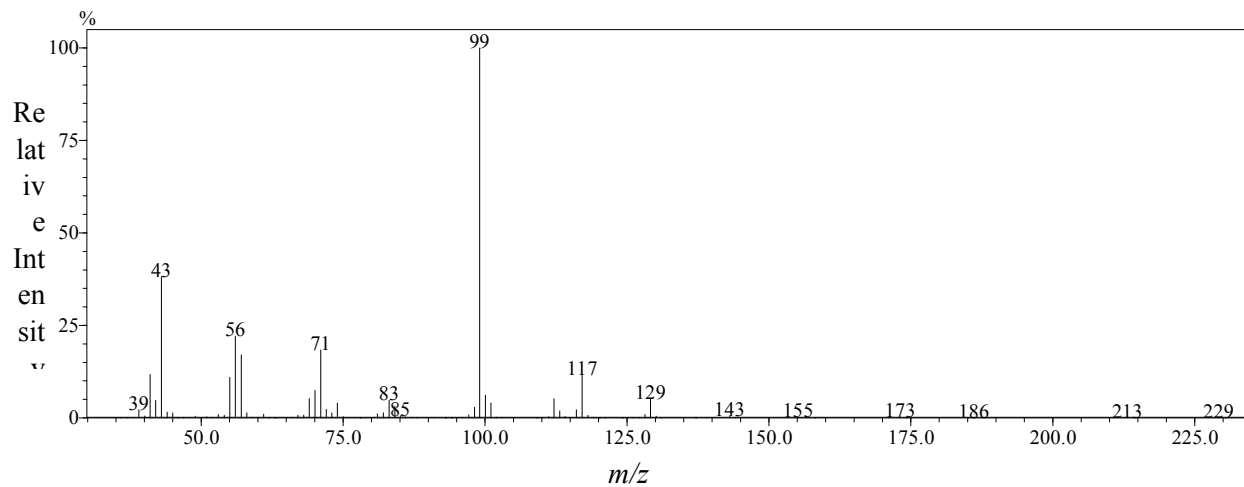
**Isopropyl 4-oxopentanone**

**GC/MS** *m/z* (abundance %): 158 (1, M<sup>+</sup>), 143 (5), 117 (10), 99 (86), 74 (30), 43 (100).



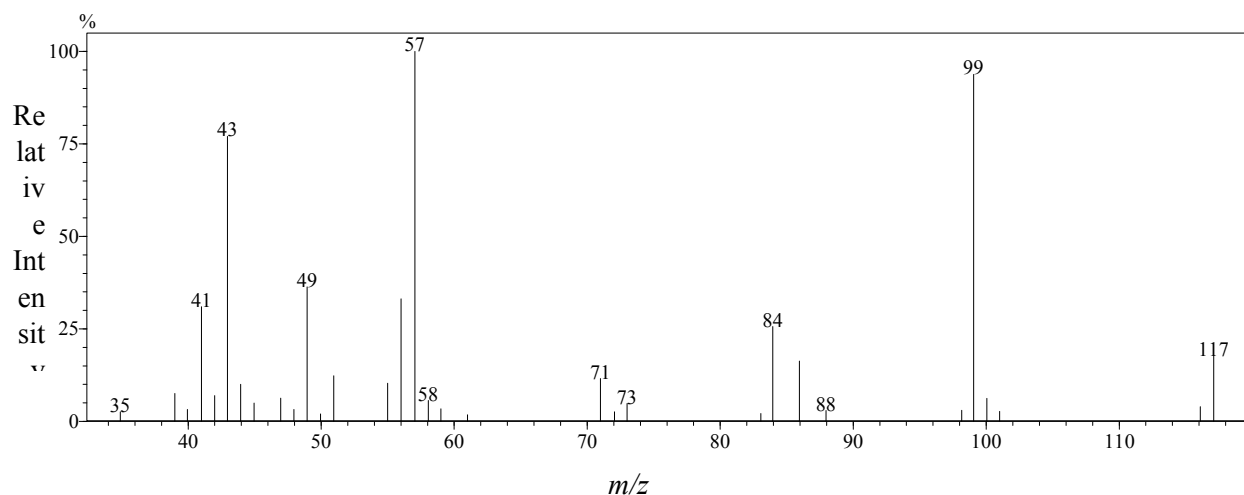
**Octan-2-yl 4-oxopentanone**

**GC/MS** *m/z* (abundance %): 229 (1, M<sup>+</sup>), 129 (7), 117 (15), 99 (100), 71 (20), 56 (25), 43 (40).



**Tert-butyl 4-oxopentanone**

**GC/MS** *m/z* (abundance %): 117 (23), 99 (92), 57 (100), 43 (80).



The characterization of esters E1, E2, E3 and E6 can be found in the work of Vinculano *et al*<sup>4</sup>, that of the ester E4 in latos *et al*<sup>5</sup>, that of the ester E7, E8 e E10 in the work of Yang *et al*<sup>6</sup>, and that of the ester E9 ester in Melchiorre *et al*<sup>7</sup>.

## Referências

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