

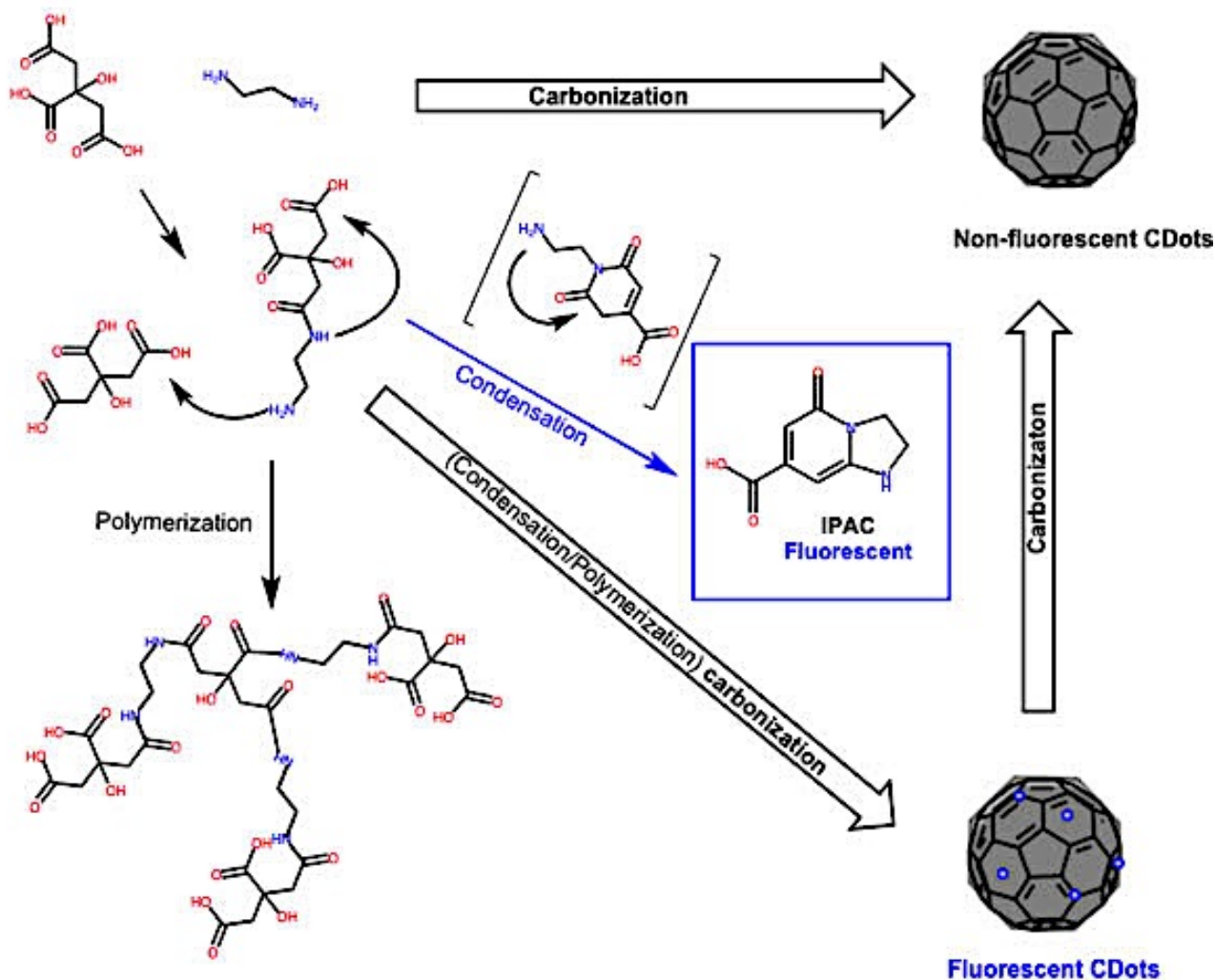
ELECTRONIC SUPPLEMENTARY INFORMATION

**Engineered fluorescent cyclodextrins inspired in carbon dots:  
Competitive supramolecular “off-on” sensors**

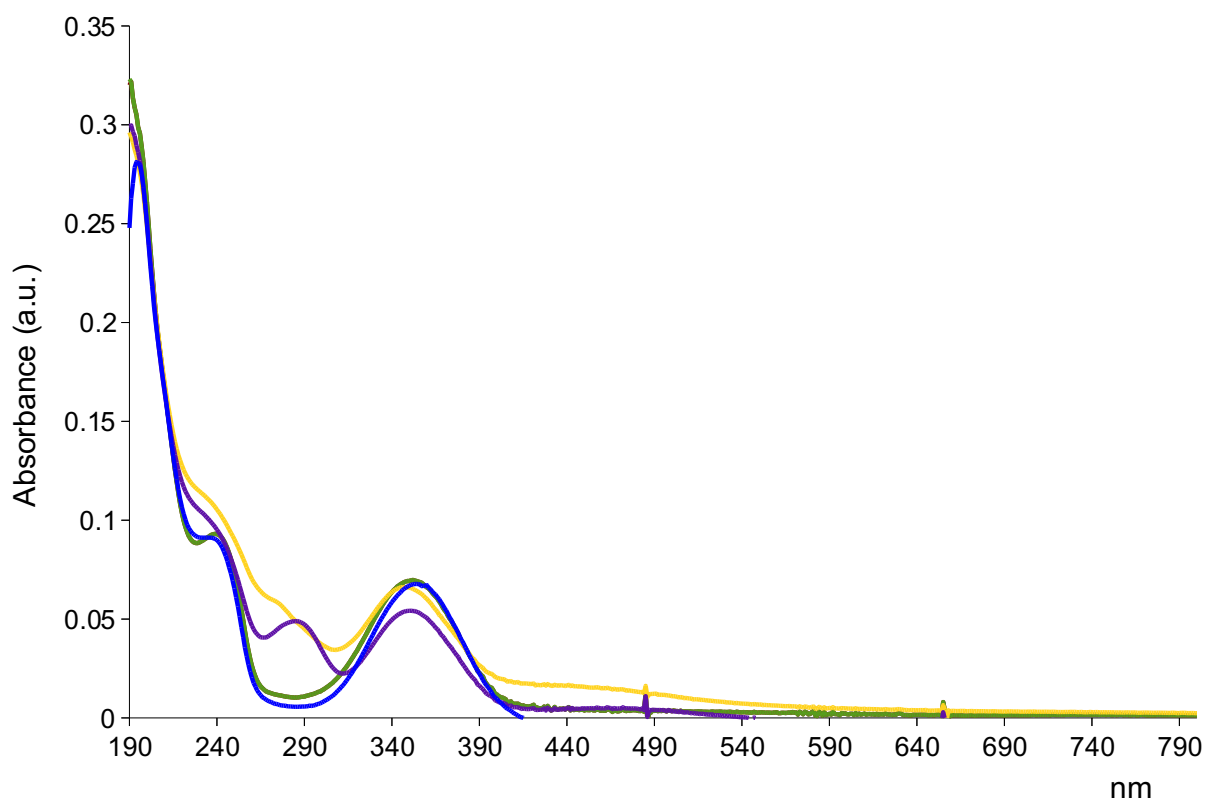
Eduardo De los Reyes-Berbel, Inmaculada Ortiz-Gomez, Mariano Ortega-Muñoz, Alfonso Salinas-Castillo, Luis Fermin Capitan-Vallvey, Fernando Hernandez-Mateo, Francisco Javier Lopez-Jaramillo,\* and Francisco Santoyo-Gonzalez\*

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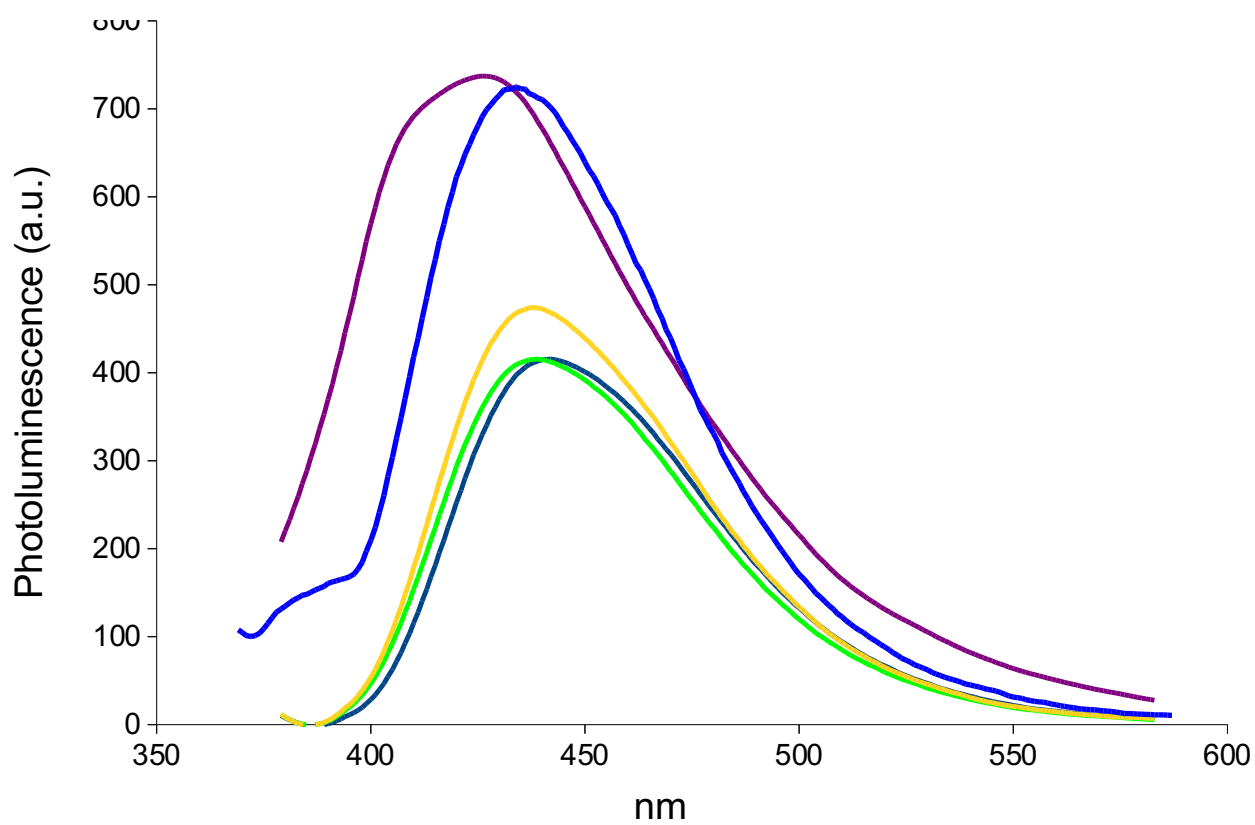
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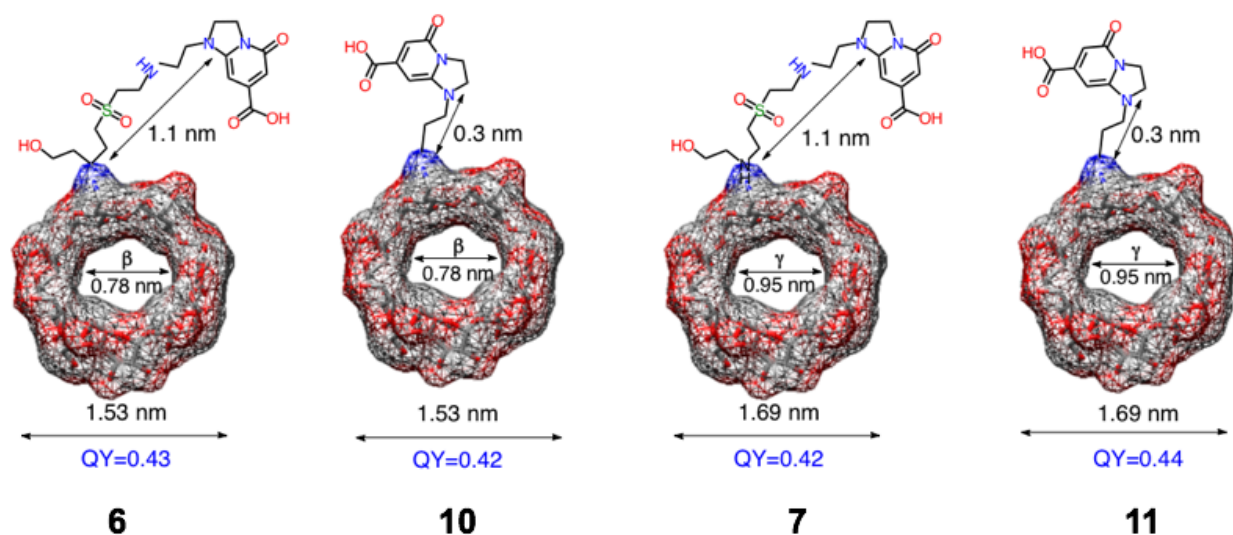
**Scheme S1.** Synthesis of the molecular fluorophore IPAC by reaction of CA with ethylenediamine and relationship between different products. The reaction of CA with ethylenediamine yields fluorescent CNDs via condensation and polymerization. As the pyrolysis proceeds the molecular fluorophore is carbonized to yield non-fluorescent CNDs. The resulting material is intrinsically heterogeneous and the fluorescence depends on both temperature and time of reaction.



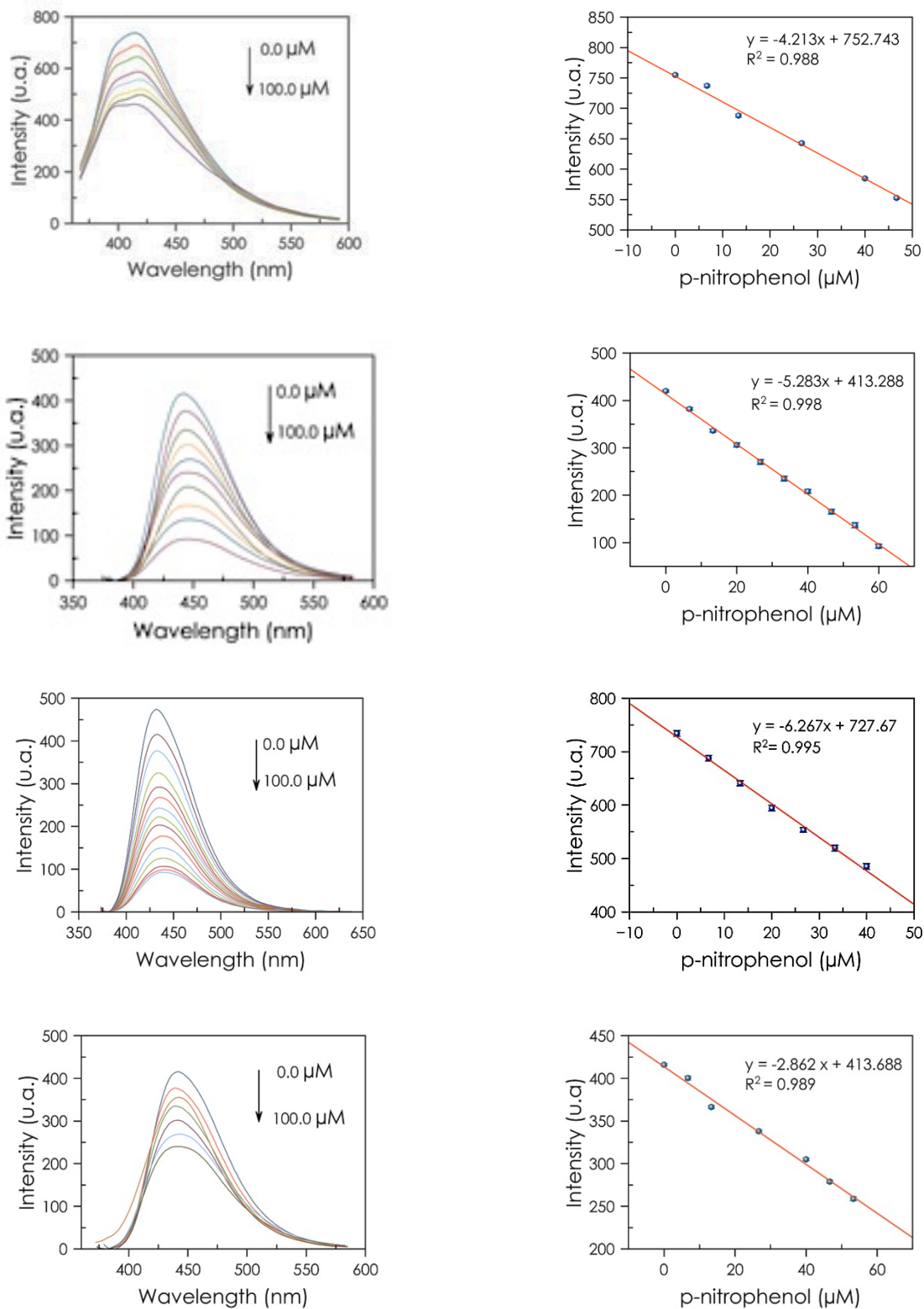
**Fig. S1.** Uv-vis spectra of **AEIPCA** (1) (blue), **AEIPCA-β-CD** (6) (magenta), **AEIPCA-γ-CD** (7) (yellow), **IPCA-β-CD** (10) (green), and **IPCA-γ-CD** (11) (red but overlapping with compound 10)



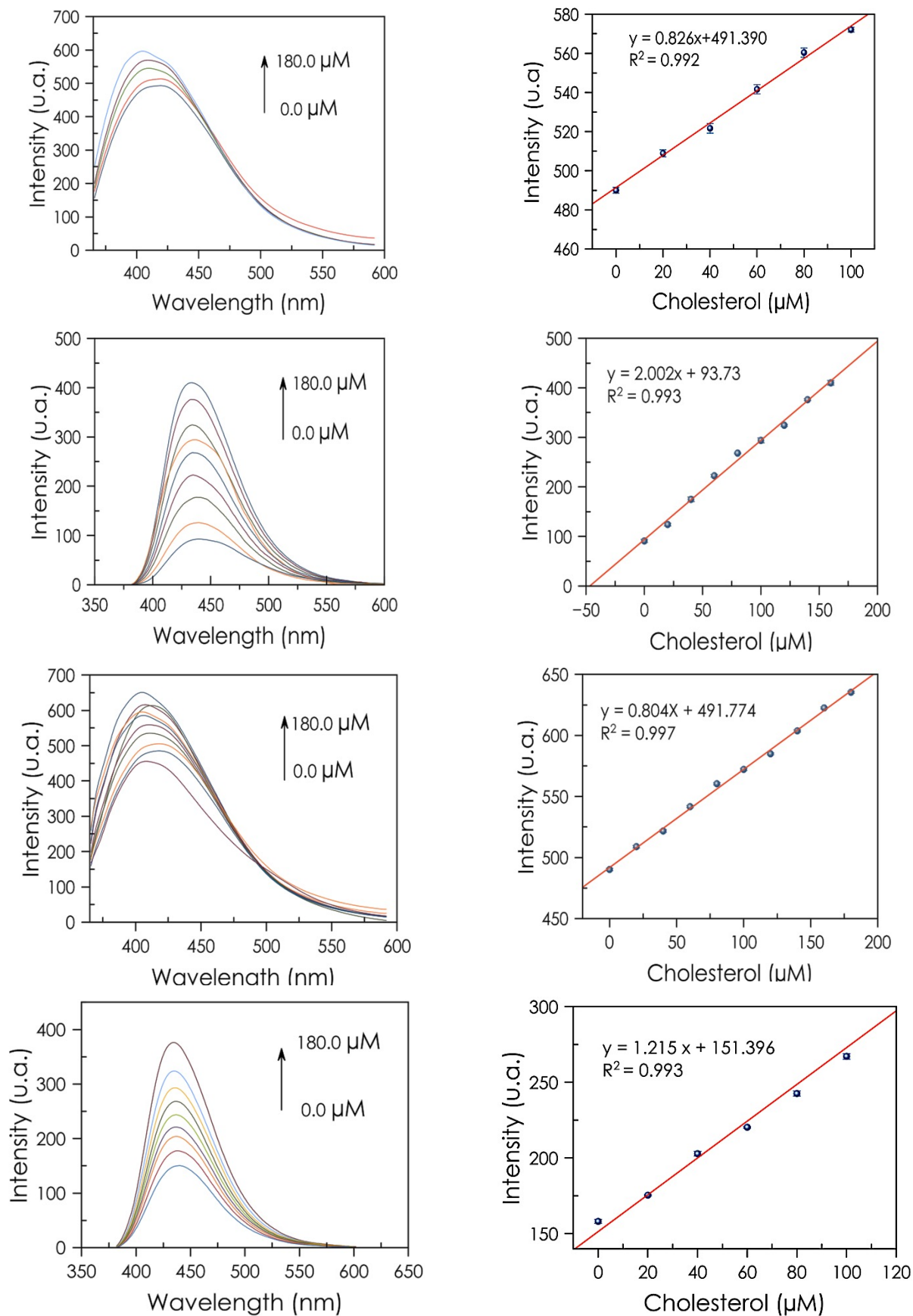
**Fig. S2.** Photoluminescence spectra of **AEIPCA (1)** (blue), **AEIPCA-β-CD (6)** (magenta), **AEIPCA-γ-CD (7)** (yellow), **IPCA-β-CD (10)** (green), and **IPCA-γ-CD (11)** (black) resulting from the excitation at 365 nm



**Fig. S3.** Main features of **IPCA-CDs**: **AEIPCA- $\beta$ -CD (6)**, **AEIPCA- $\gamma$ -CD (7)**, **IPCA- $\beta$ -CD (10)**, and **IPCA- $\gamma$ -CD (11)** The distances between the fluorophore and the CD were estimated from the minimized coordinates. Coordinates were generated using Ghemical 2.956 (T. Hassinen, M. Peräkylä, *J. Comput. Chem.* **2001**, 22, 1229-1242) and minimized by molecular mechanics with the tripos 5.2 forcefield until the gradient energy was lower than 0.001 KJ/mol. The values for CDs are those reported in bibliography from structural studies.

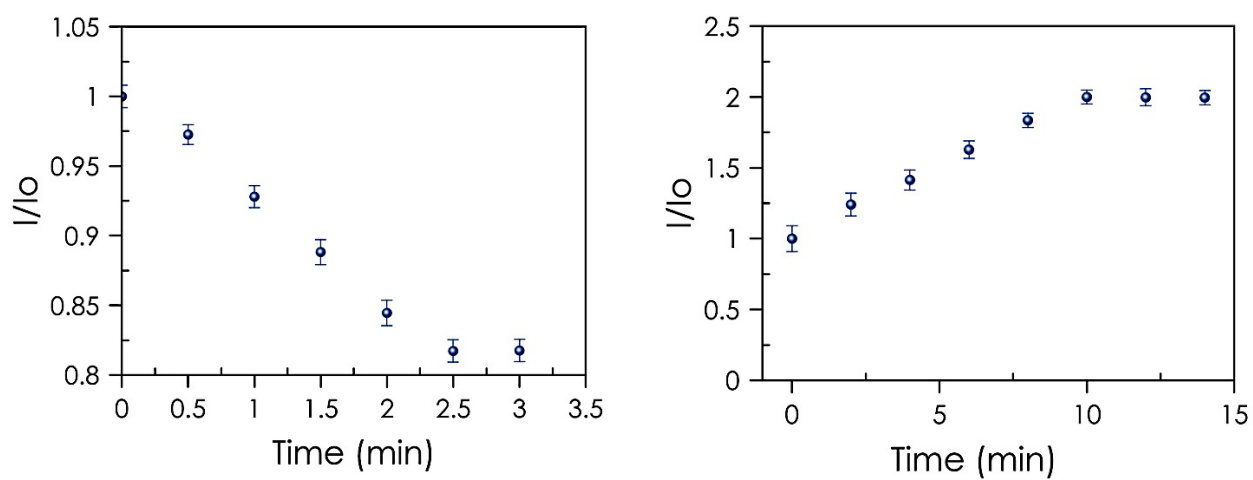


**Fig. S4.** Fluorescence spectra (left) and plot of fluorescence versus the concentration of pNP (right) for IPCA-CDs. From top to bottom **AEIPCA-β-CD (6)**, **AEIPCA-γ-CD (7)**, **IPCA-β-CD (10)**, and **IPCA-γ-CD (11)**.

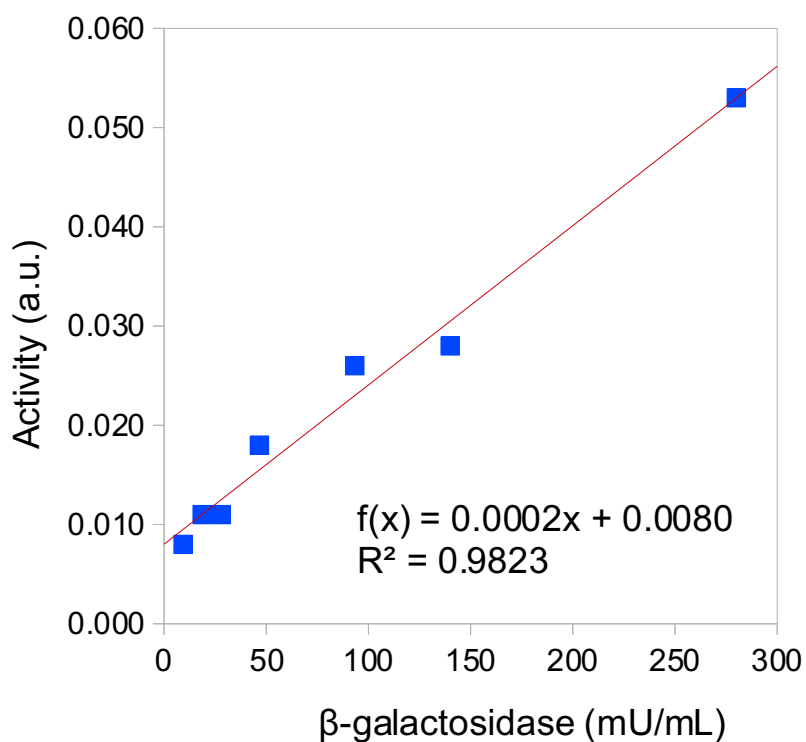
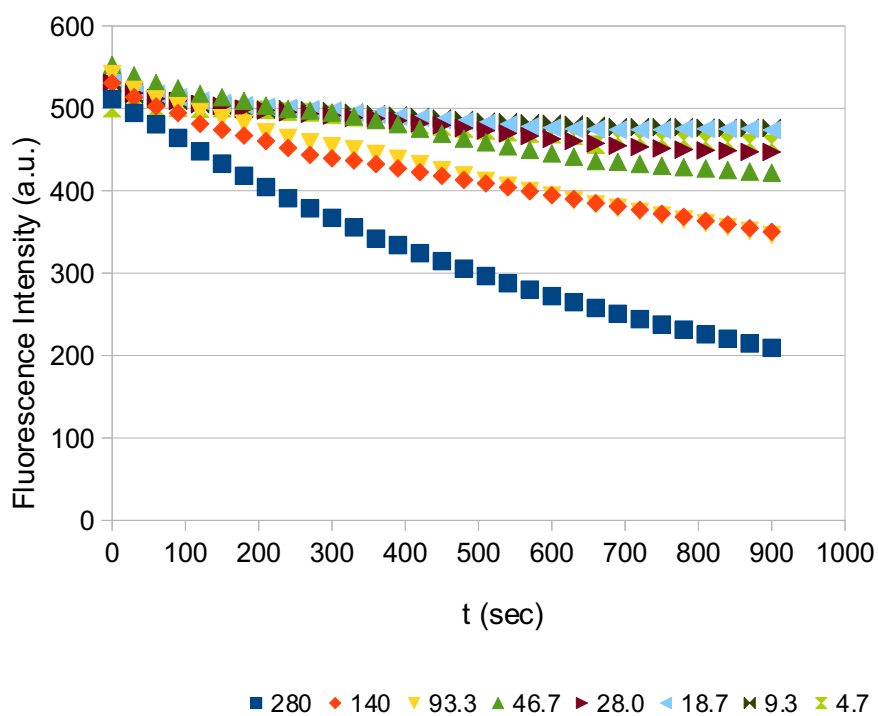


**Fig. S5.** Fluorescence spectra (left) and plot of fluorescence versus the concentration of Chol (right) for the **IPCA-CDs** quenched with 40 μM pNP. From top to bottom **AEIPCA-β-CD (6)**, **AEIPCA-γ-CD (7)**, **IPCA-β-CD (10)**, and **IPCA-γ-CD (11)**,





**Fig. S6.** Evolution of the fluorescence as a function of time upon addition of *p*NP (quenching) and Chol (recovery).  $I_0$  is the fluorescence intensity initial and  $I$  is the fluorescence intensity final.

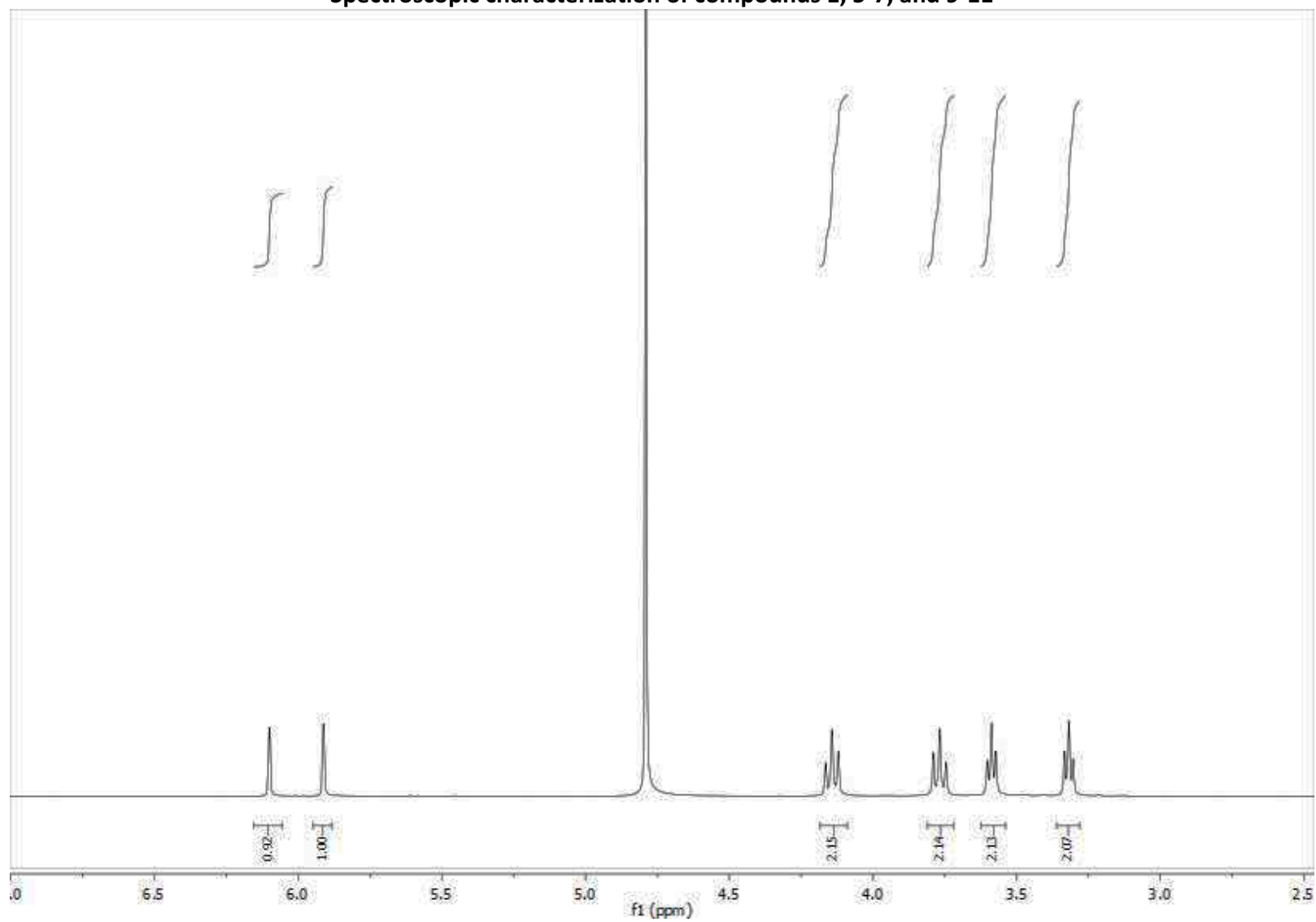


**Fig. S7.** Fluorescence intensity of **AEIPCA- $\beta$ -CD (6)** as a function of time for different concentrations (mU/mL) of  $\beta$ -galactosidase (up) and linear dependency of the enzymatic activity with the concentration of enzyme (down)

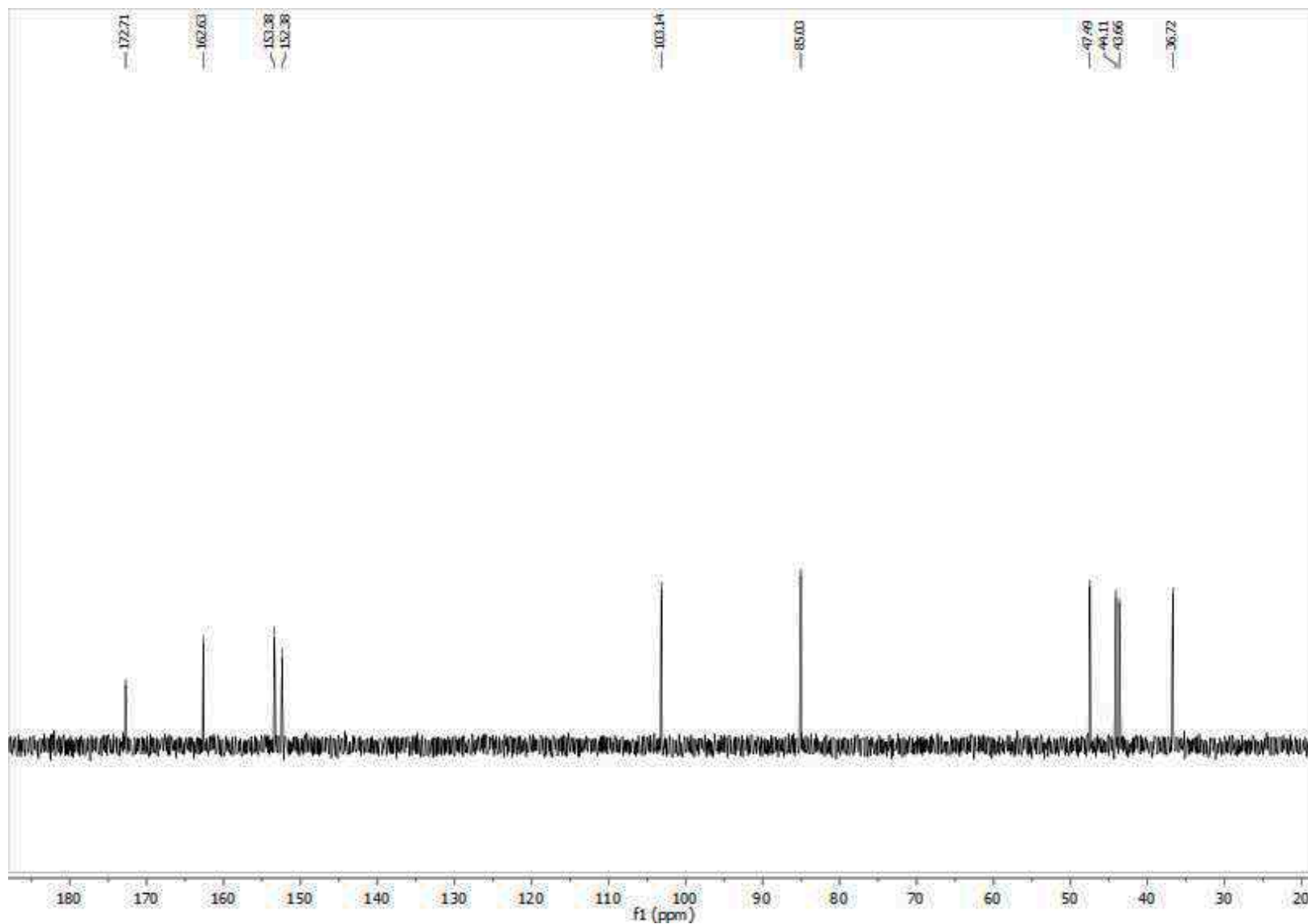
**Table S1.** Fluorescence quantum yield (QY) of compounds **AEIPCA (1)**, **AEIPCA- $\beta$ -CD (6)**, **AEIPCA- $\gamma$ -CD (7)**, **IPCA- $\beta$ -CD (10)**, and **IPCA- $\gamma$ -CD (11)** using quinine sulfate as standard (QY=0.55)

| <b>Compound</b> | <b>QY</b> |
|-----------------|-----------|
| <b>1</b>        | 0.47      |
| <b>6</b>        | 0.43      |
| <b>7</b>        | 0.42      |
| <b>10</b>       | 0.42      |
| <b>11</b>       | 0.44      |

Spectroscopic characterization of compounds 1, 5-7, and 9-11



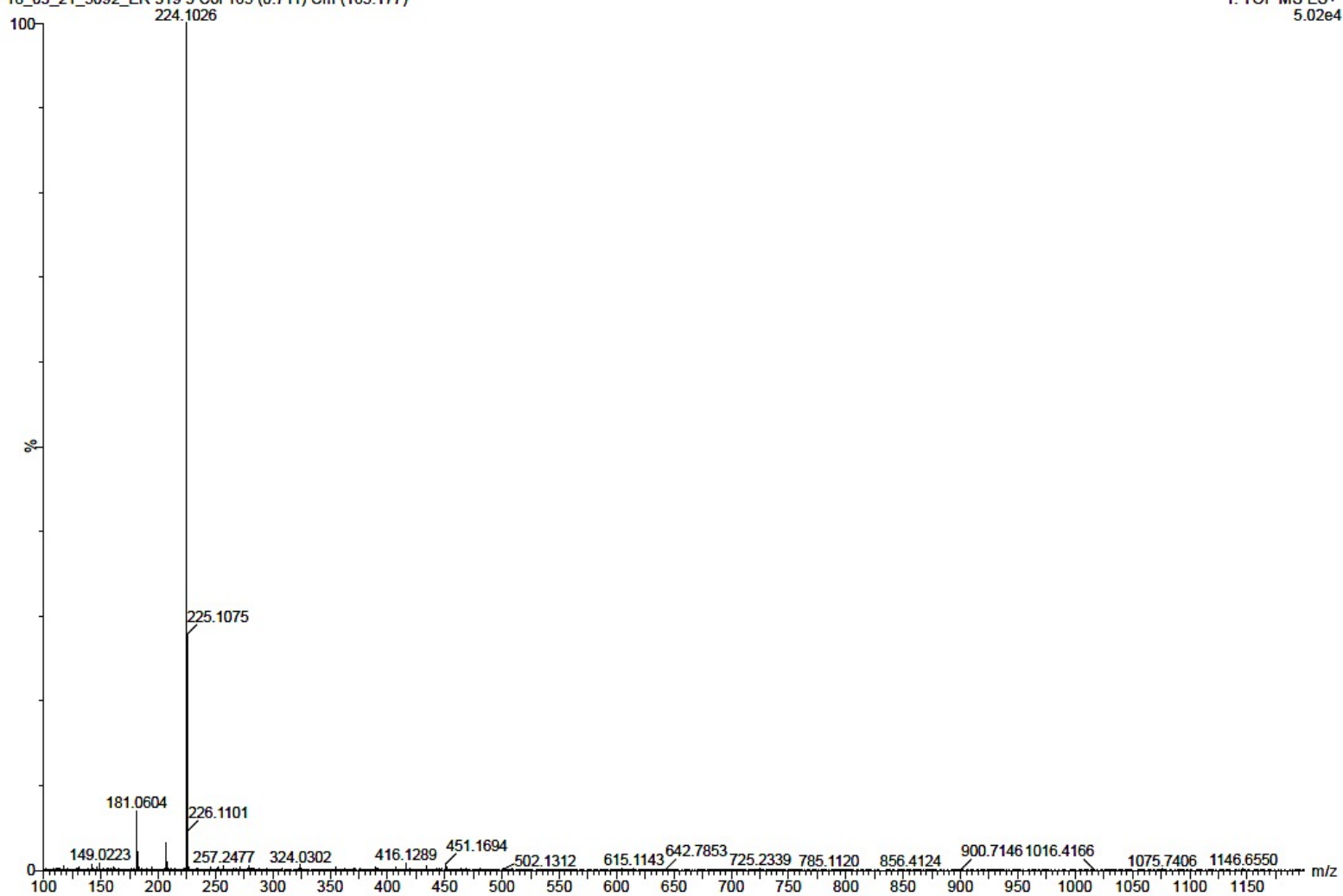
<sup>1</sup>H-NMR spectrum for compound **AEIPCA (1)**



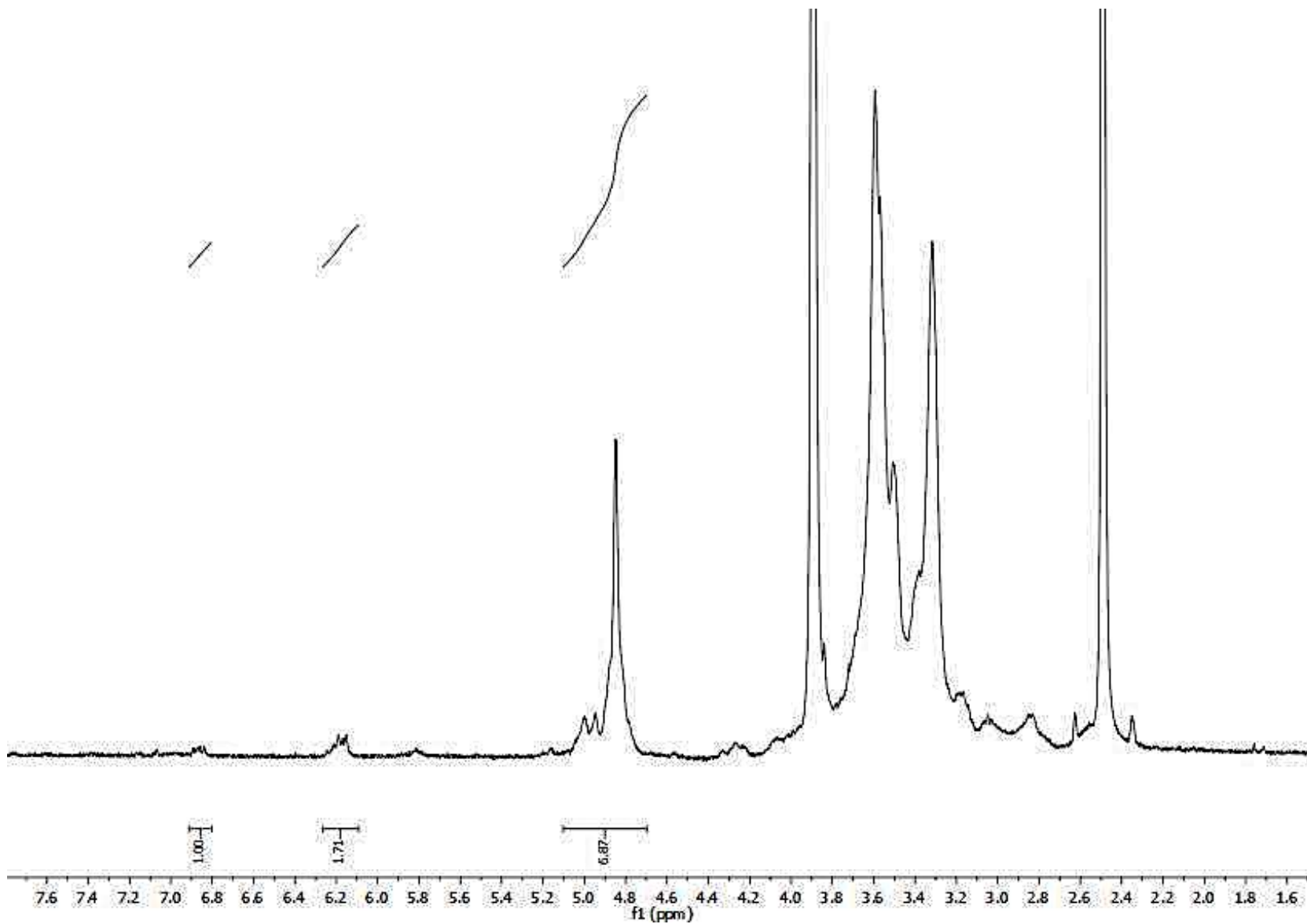
$^{13}\text{C}$ -NMR spectrum for compound **AEIPCA (1)**

18\_03\_21\_5092\_ER 319 3 Col  
18\_03\_21\_5092\_ER 319 3 Col 165 (0.711) Cm (165:177)

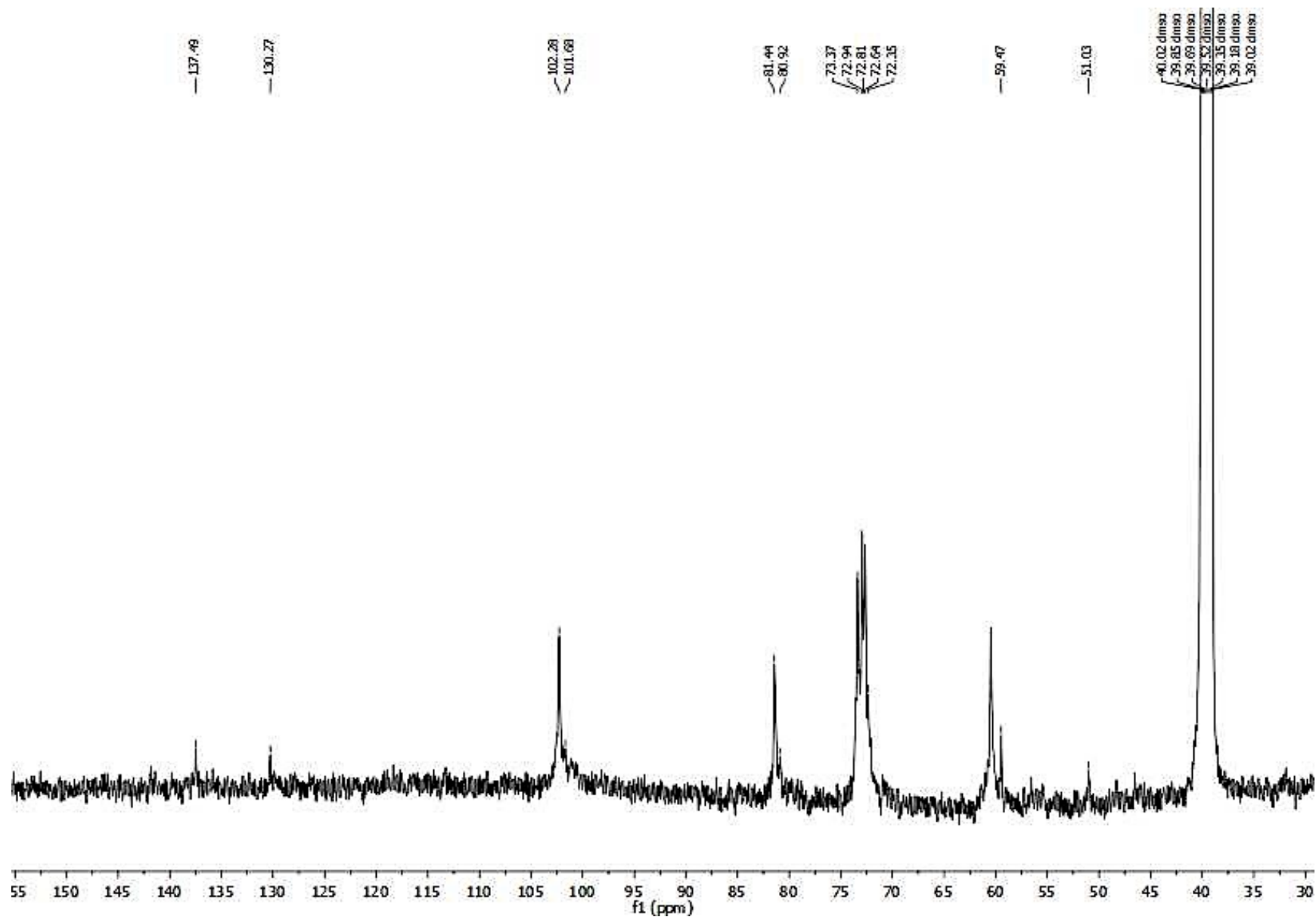
1: TOF MS ES+  
5.02e4



HR-MS (ESI+) spectrum for compound **AEIPCA (1)**



$^1\text{H-NMR}$  spectrum for compound VS- $\gamma$ -CD (5)



$^{13}\text{C}$ -NMR spectrum for compound VS- $\gamma$ -CD (5)





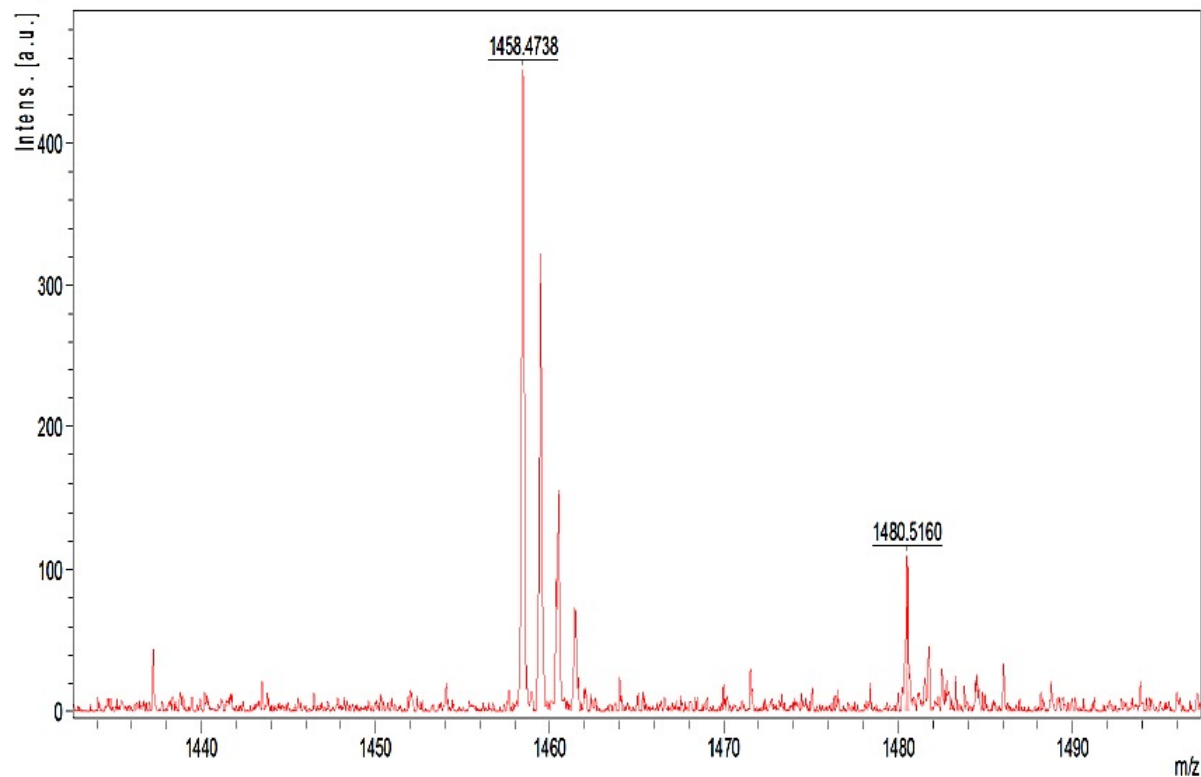
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Matrix/Solvent: DHB/AGUA

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Organica\Eduardo\2019-12-02\ER-1457\0\_D10\1\1SRef



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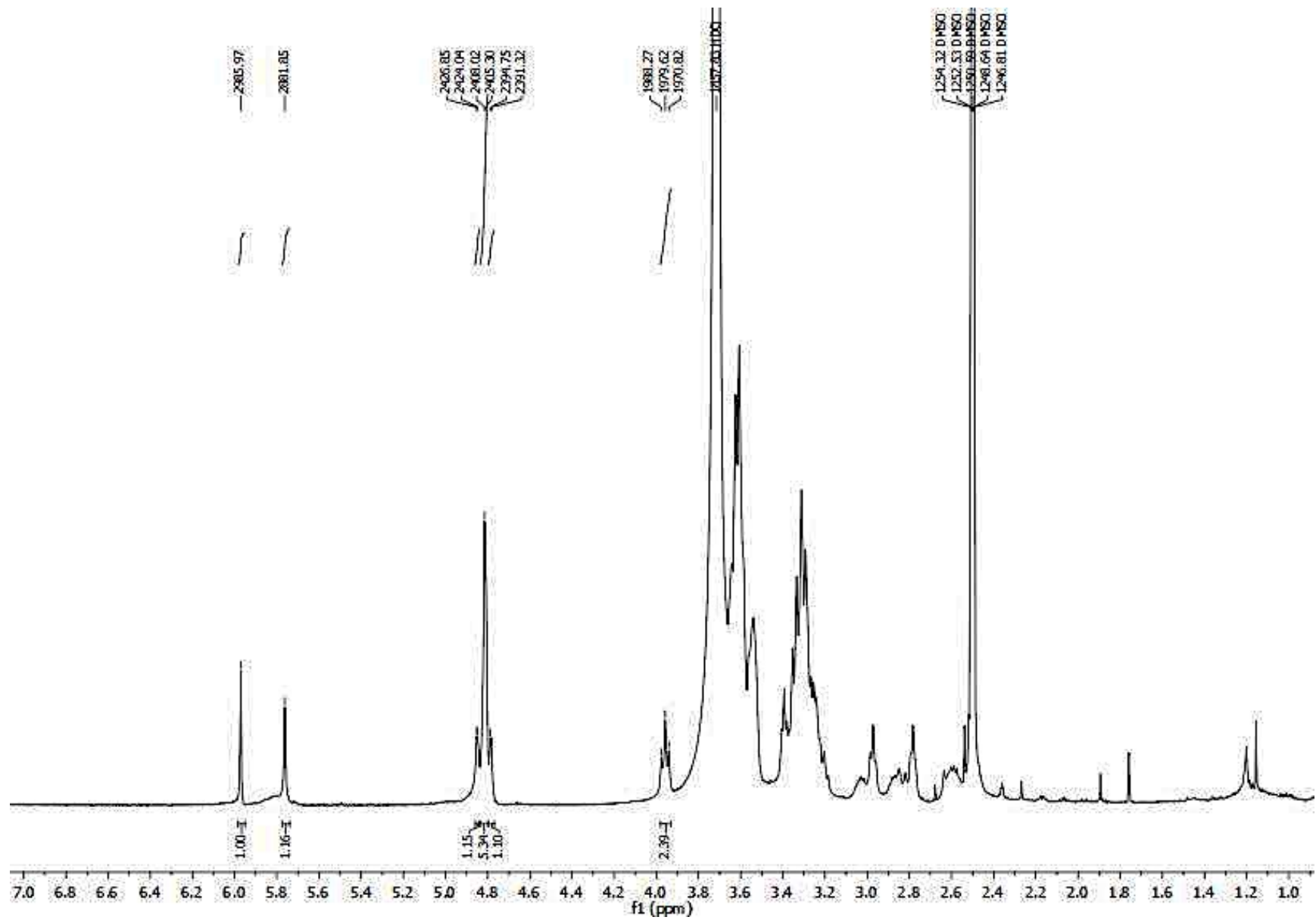
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Number of shots 12  
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Voltage Polarity POS  
PIE delay 100 ns  
Ion source voltage 1 19 kV  
Ion source voltage 2 16.4 kV  
Lens voltage 8.1 kV  
Linear detector voltage 1.804 kV

| m/z       | Rel. Inten. s. | Inten. s. | Res.  | S/N |
|-----------|----------------|-----------|-------|-----|
| 1458.4738 | 100            | 452       | 8902  | 22  |
| 1480.5160 | 24.3           | 110       | 16017 | 6   |

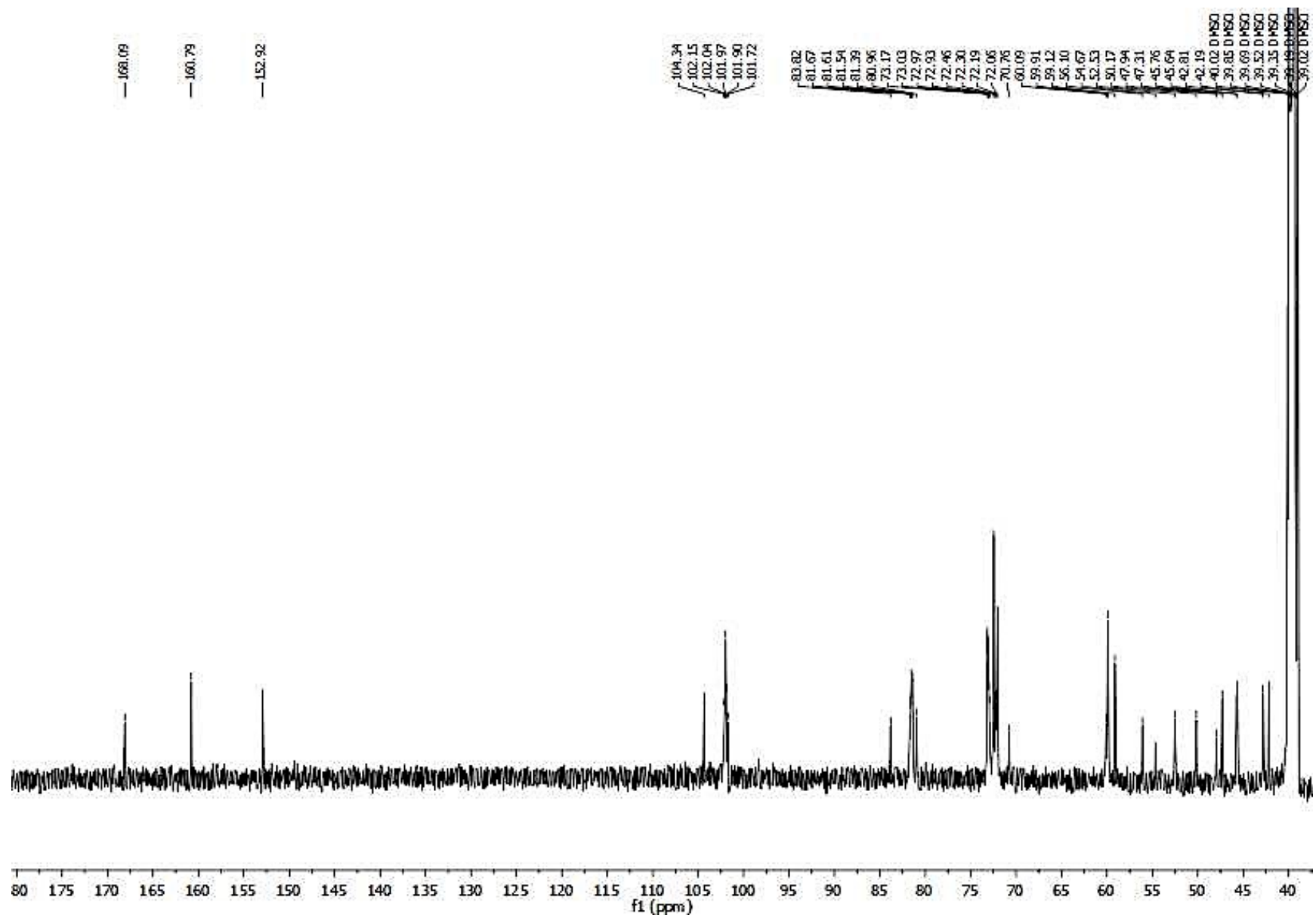
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HR-MS (MALDI-TOF) spectrum for compound **VS- $\gamma$ -CD (5)**



<sup>1</sup>H-NMR spectrum for compound AEIPCA-β-CD (6)



$^{13}\text{C}$ -NMR spectrum for compound **AEIPCA- $\beta$ -CD (6)**



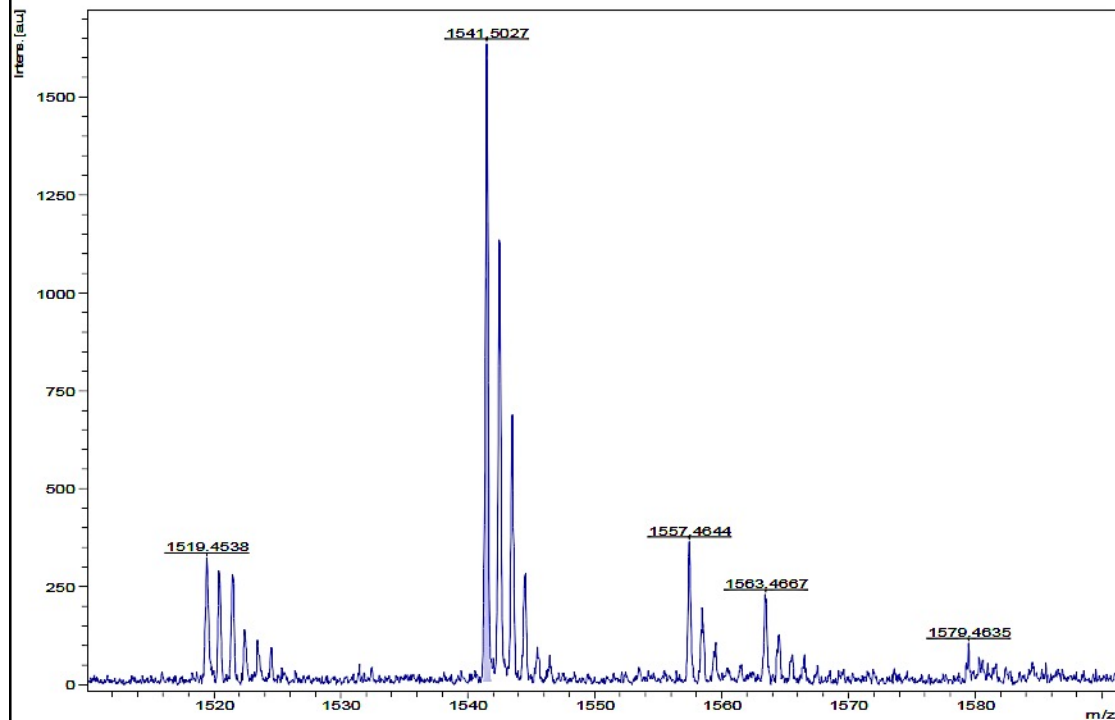
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Matrix/Solvent: DHB/H<sub>2</sub>O

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**Target** Position D24  
**Instrument** autoflex

**Laser**  
Laser beam attenuation 42  
Laser beam focus -1  
Laser repetition rate 5 Hz  
Number of shots 16

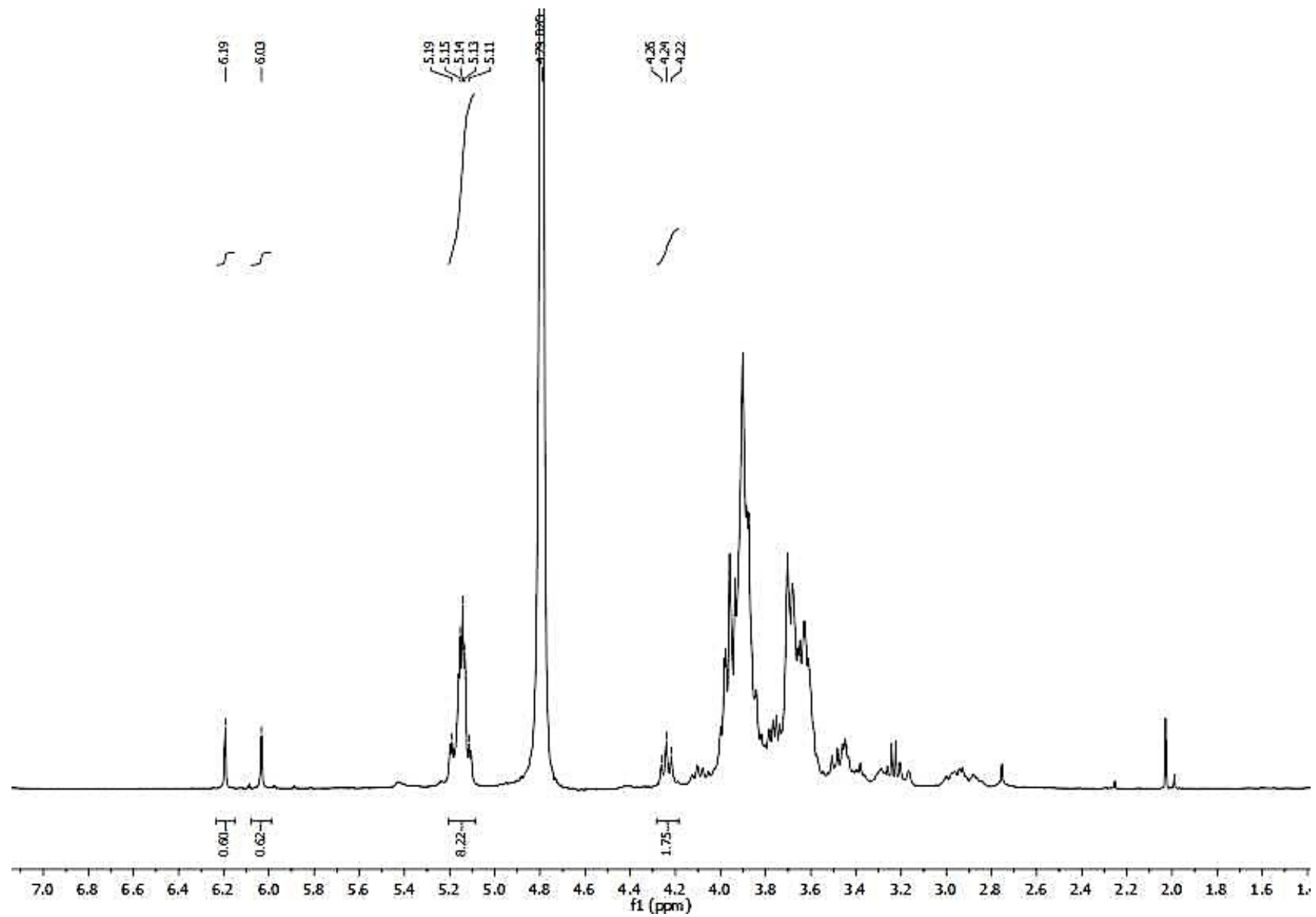
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Voltage Polarity POS  
PIE delay 100 ns  
Ion source voltage 1 19 kV  
Ion source voltage 2 16.35 kV  
Lens voltage 8.2 kV  
Linear detector voltage 0 kV

| m/z       | Rel. Inten. | Intens. | Res. | S/N |
|-----------|-------------|---------|------|-----|
| 1519.4538 | 19.8        | 324     | 5762 | 17  |
| 1541.5027 | 100         | 1636    | 6722 | 87  |
| 1557.4644 | 22.4        | 366     | 6712 | 19  |
| 1563.4667 | 14.1        | 231     | 6192 | 12  |
| 1579.4635 | 6.48        | 106     | 6737 | 5   |

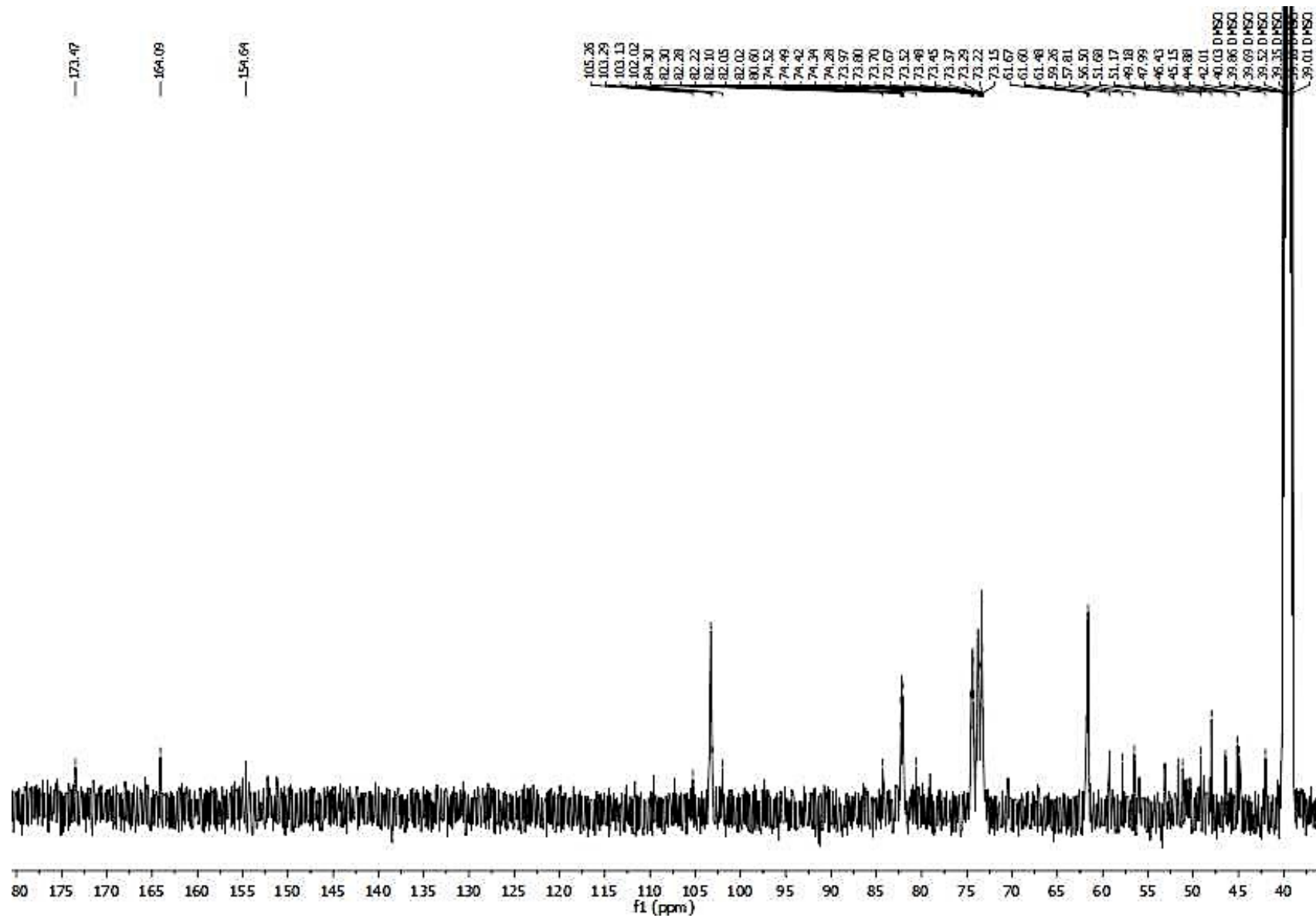
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**DALTONICS**

HR-MS (MALDI-TOF) spectrum for compound **AEIPCA- $\beta$ -CD (6)**



$^1\text{H-NMR}$  spectrum for compound **AEIPCA- $\gamma$ -CD (7)**



$^{13}\text{C}$ -NMR spectrum for compound **AEIPCA- $\gamma$ -CD (7)**



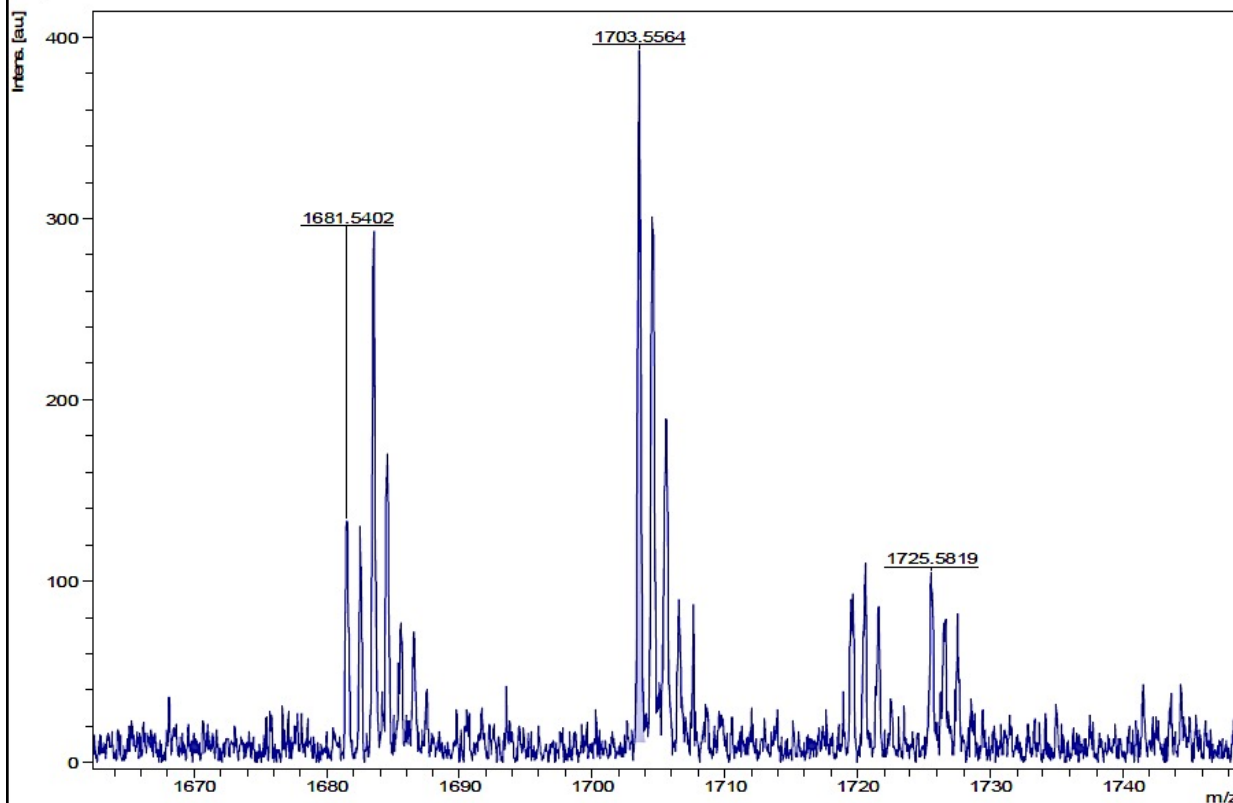
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Matrix/Solvent: **DHB/H<sub>2</sub>O**

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**Target Instrument**

Position L15 autoflex

**Laser**

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Laser repetition rate 5 Hz  
Number of shots 16

**Spectrometer**

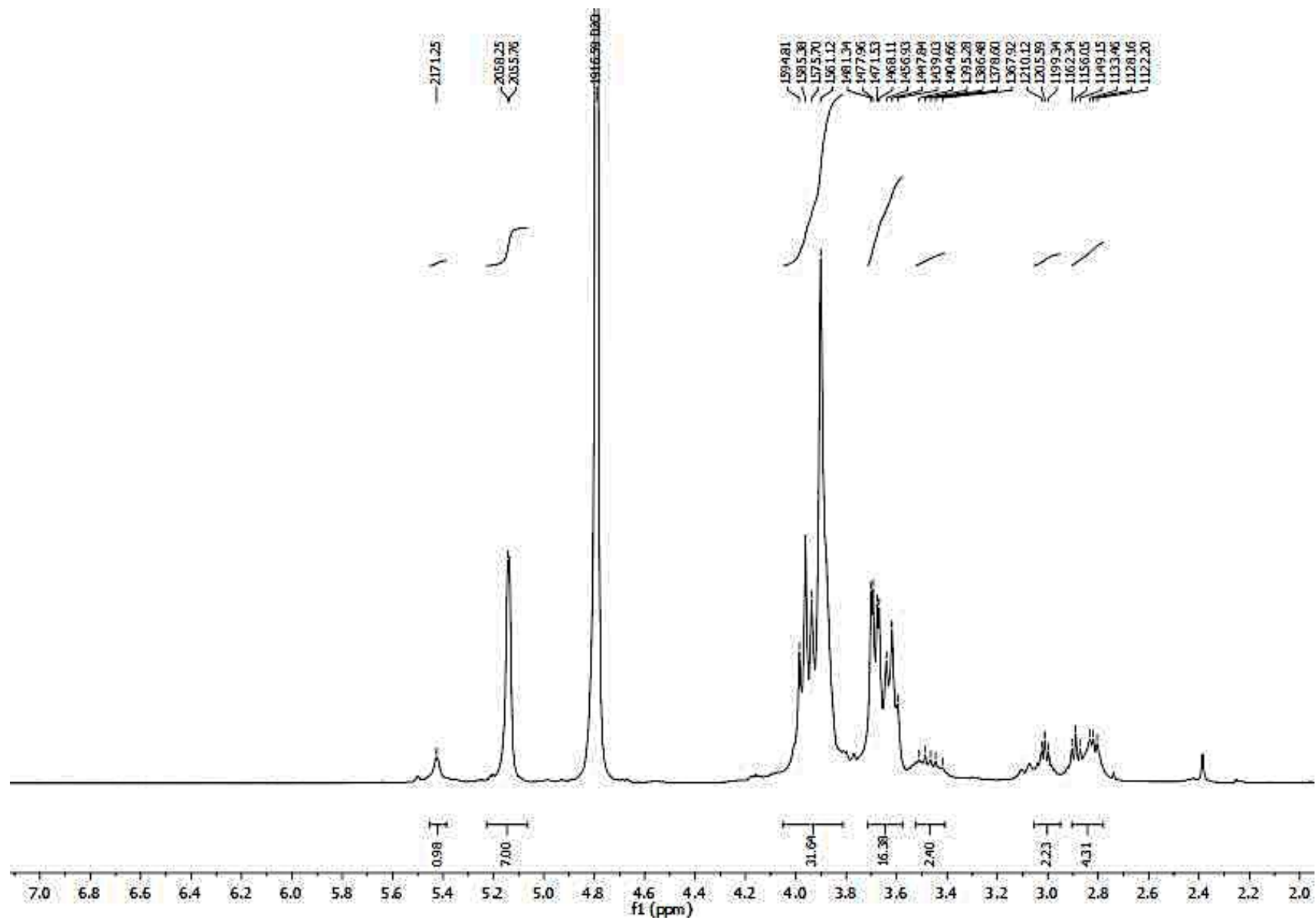
Voltage Polarity POS  
PIE delay 100 ns  
Ion source voltage 1 19 kV  
Ion source voltage 2 16.35 kV  
Lens voltage 8.2 kV  
Linear detector voltage 0 kV

| m/z       | Rel. Inten | Inten s. | Res. | S/N |
|-----------|------------|----------|------|-----|
| 1681.5402 | 33.8       | 133      | 5690 | 9   |
| 1703.5564 | 100        | 393      | 6145 | 28  |
| 1719.5828 | 22.9       | 90.0     | 4983 | 6   |
| 1725.5819 | 26.7       | 105      | 6430 | 8   |

Date of Acquisition 2018-09-10T13:59:03.386+02:00  
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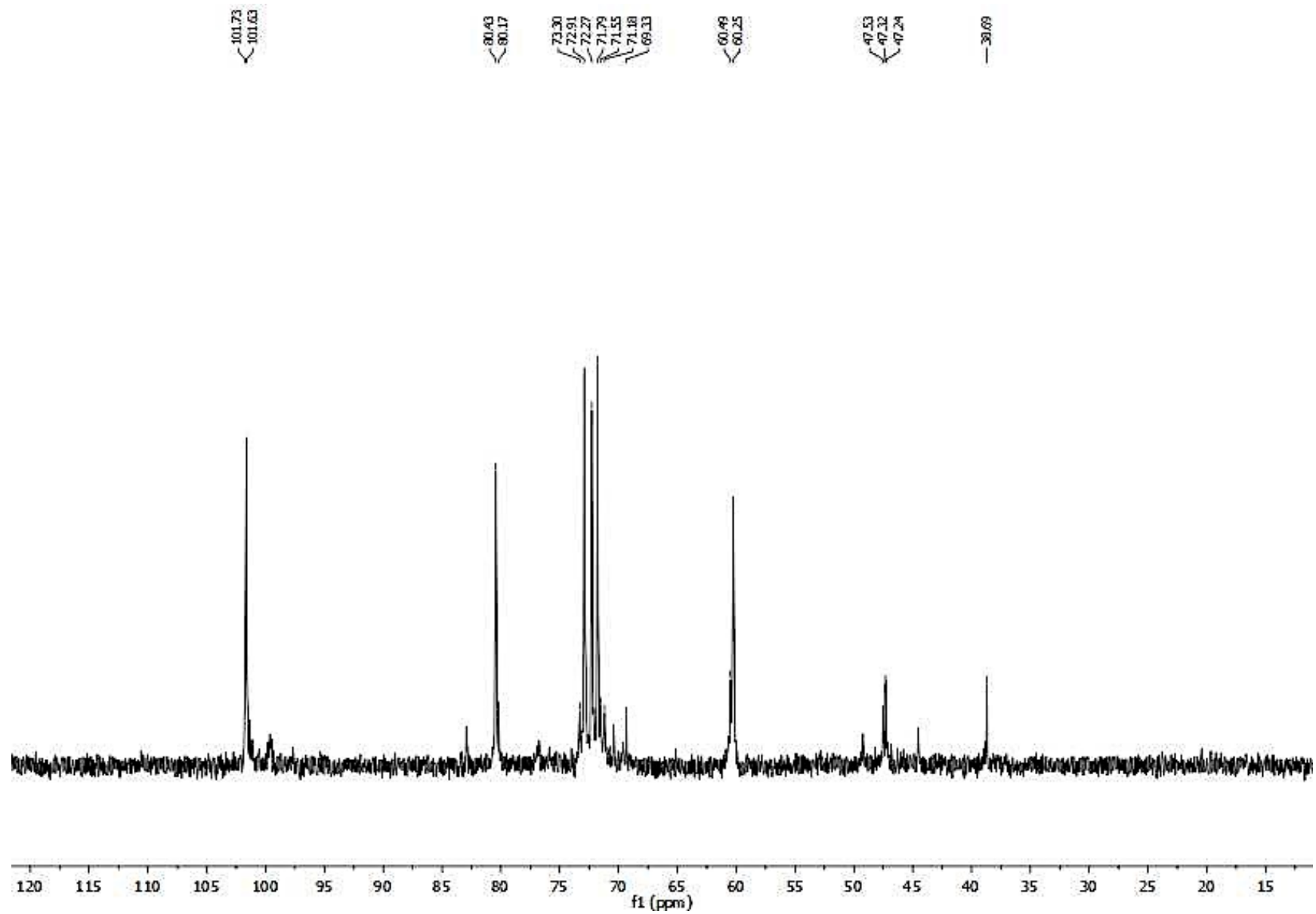
**BRUKER  
DALTONICS**

HR-MS (MALDI-TOF) spectrum for compound **AEIPCA- $\gamma$ -CD (7)**



$^1\text{H-NMR}$  spectrum for compound **DETA- $\gamma$ -CD (9)**





$^{13}\text{C}$ -NMR spectrum for compound **DETA- $\gamma$ -CD (9)**



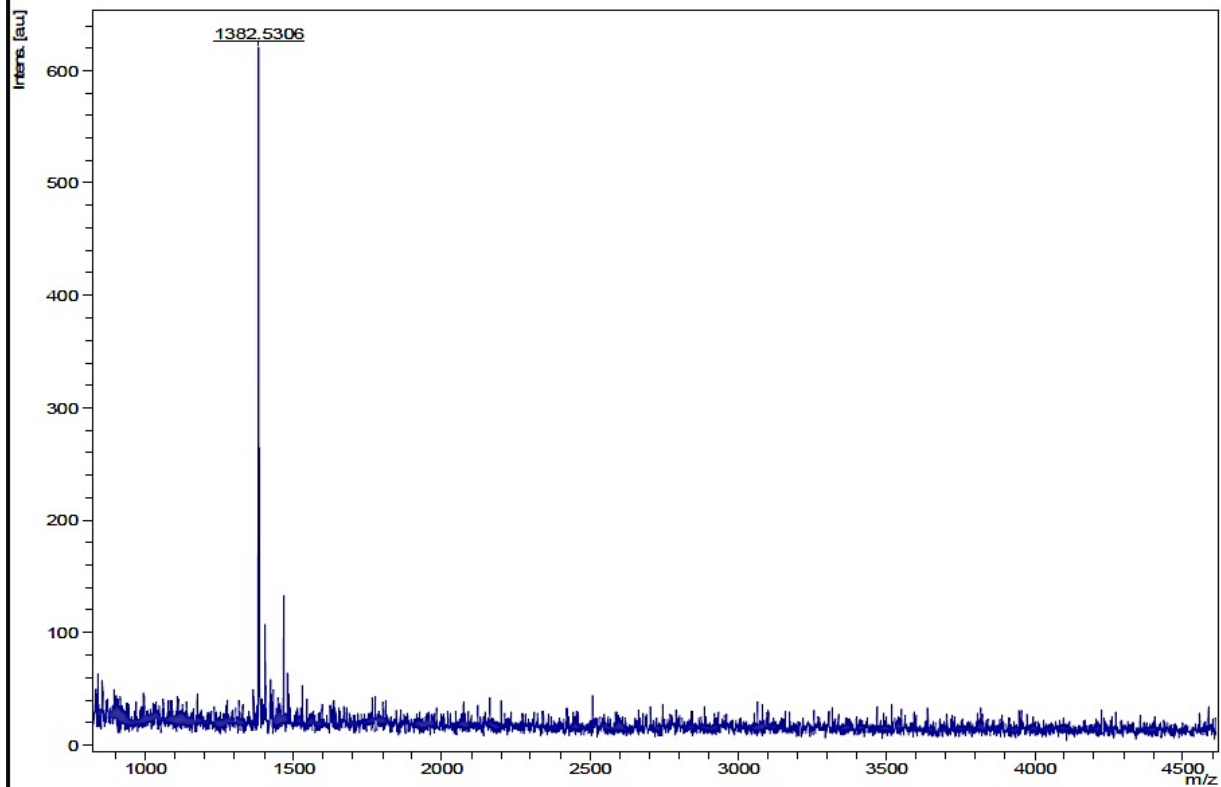
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Matrix/Solvent: **Agua/DHB**

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**Target** Instrument  
Position L3 autoflex

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Laser beam focus -1  
Laser repetition rate 5 Hz  
Number of shots 22

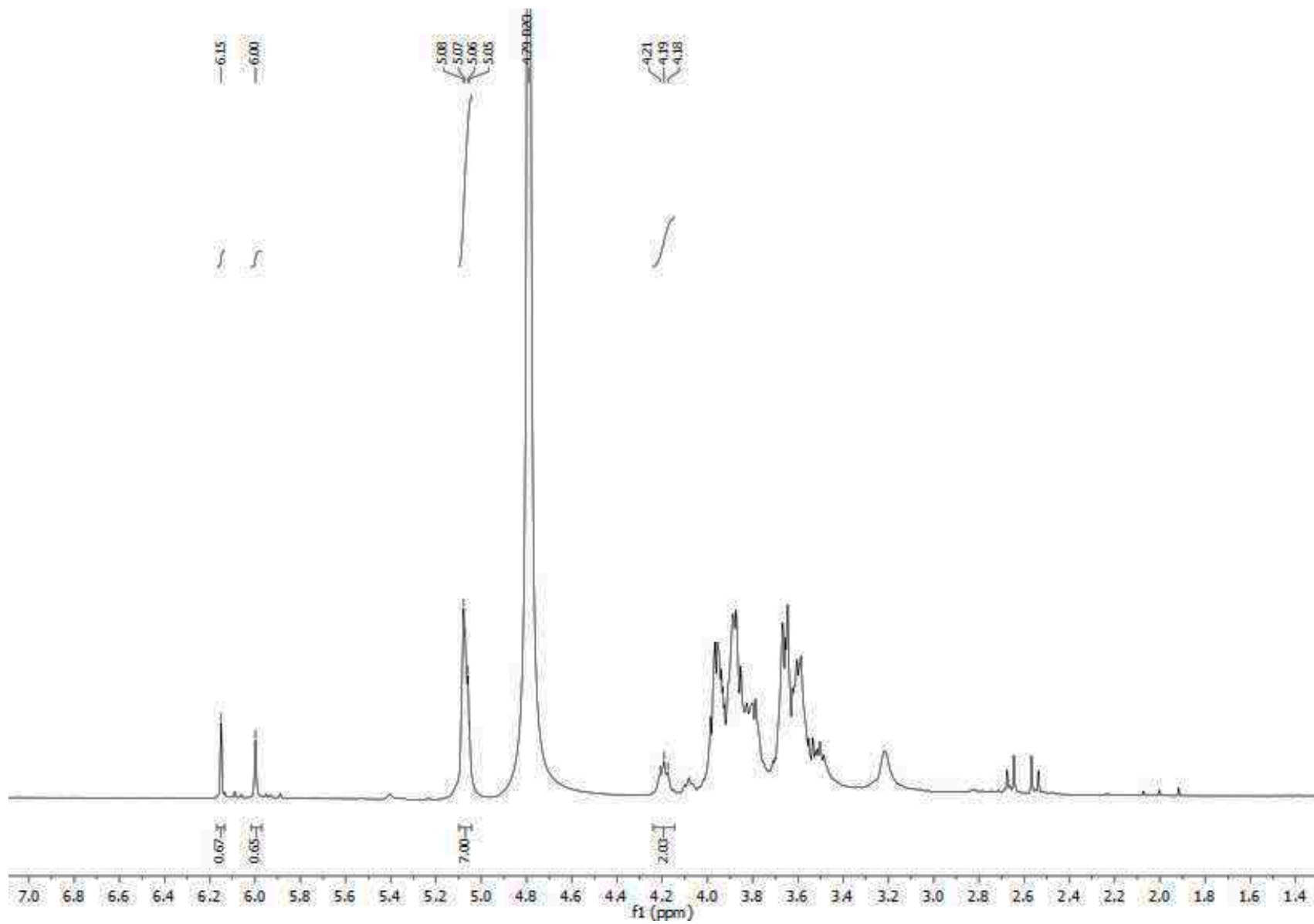
**Spectrometer**  
Voltage Polarity POS  
PIE delay 180 ns  
Ion source voltage 1 19 kV  
Ion source voltage 2 16.35 kV  
Lens voltage 8.4 kV  
Linear detector voltage 0 kV

| m/z       | Rel. Inten. s. | Inten. s. | Res.  | S/N |
|-----------|----------------|-----------|-------|-----|
| 1382.5306 | 100            | 621       | 4804  | 49  |
| 1404.4781 | 17.2           | 107       | 4446  | 8   |
| 1467.6982 | 21.4           | 133       | 4419  | 11  |
| 1480.5743 | 10.3           | 64.0      | 4102  | 5   |
| 1530.2004 | 8.53           | 53.0      | 22944 | 4   |

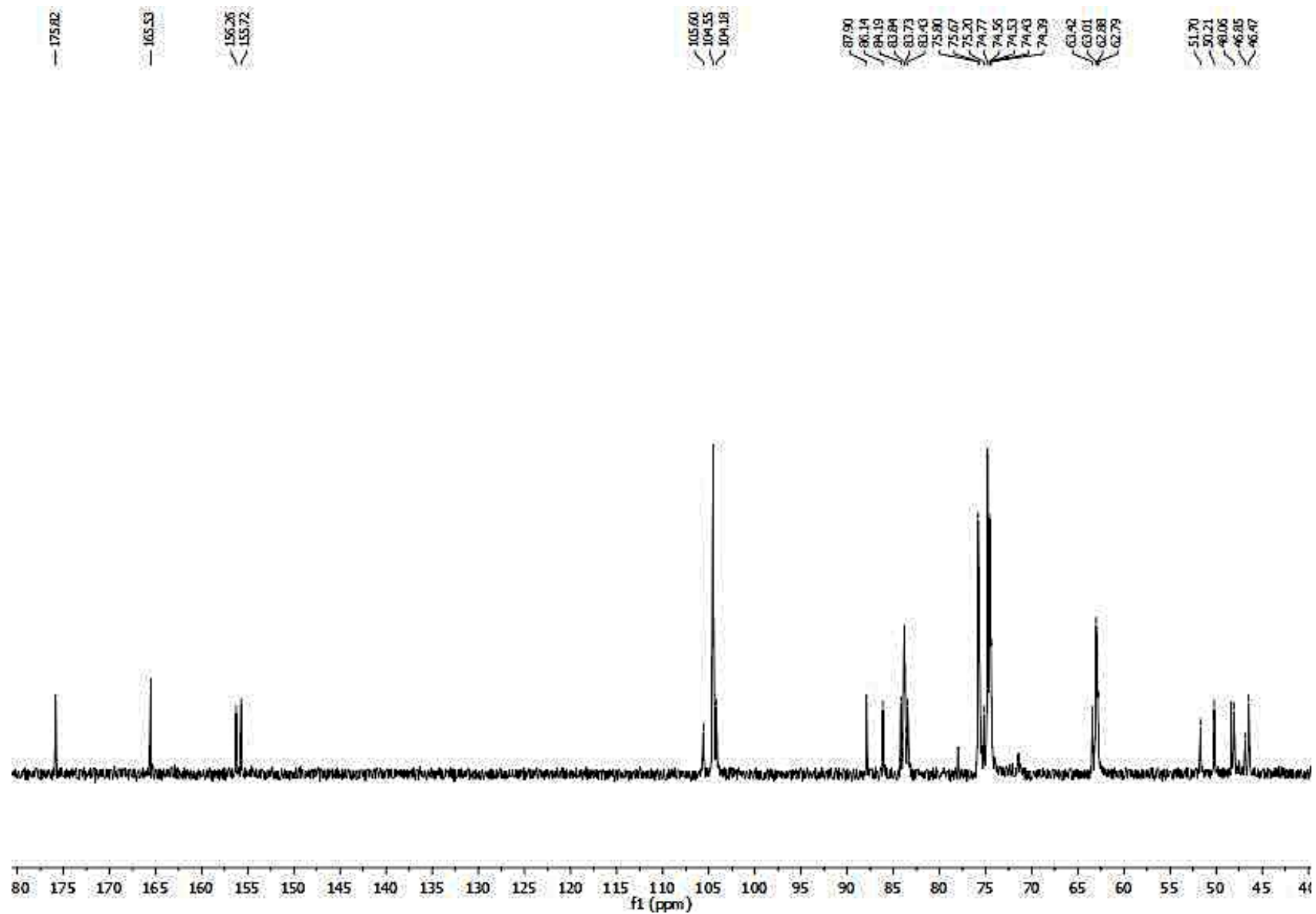
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**DALTONICS**

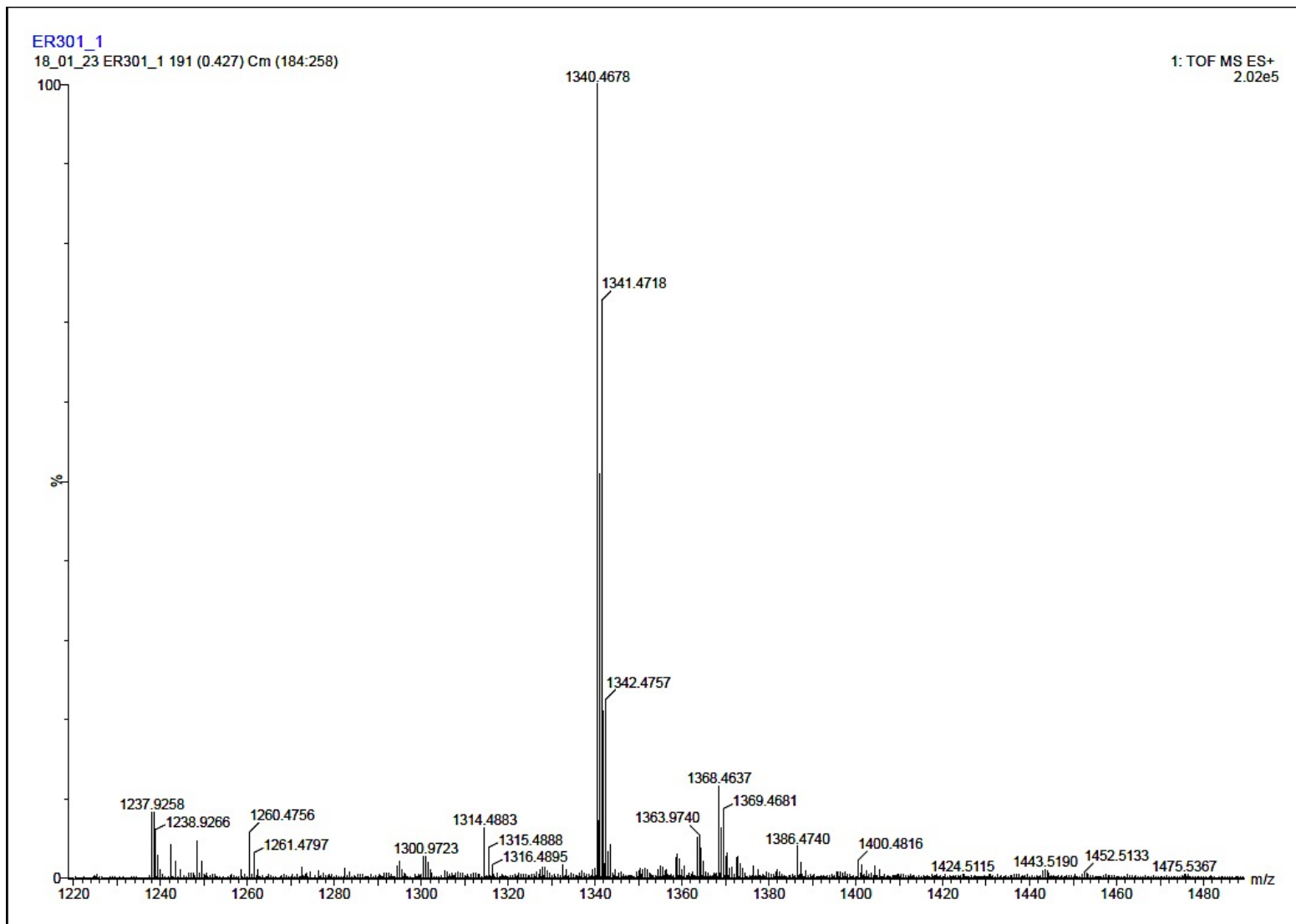
HR-MS (ES<sup>+</sup>-TOF) spectrum for compound **DETA- $\gamma$ -CD (9)**



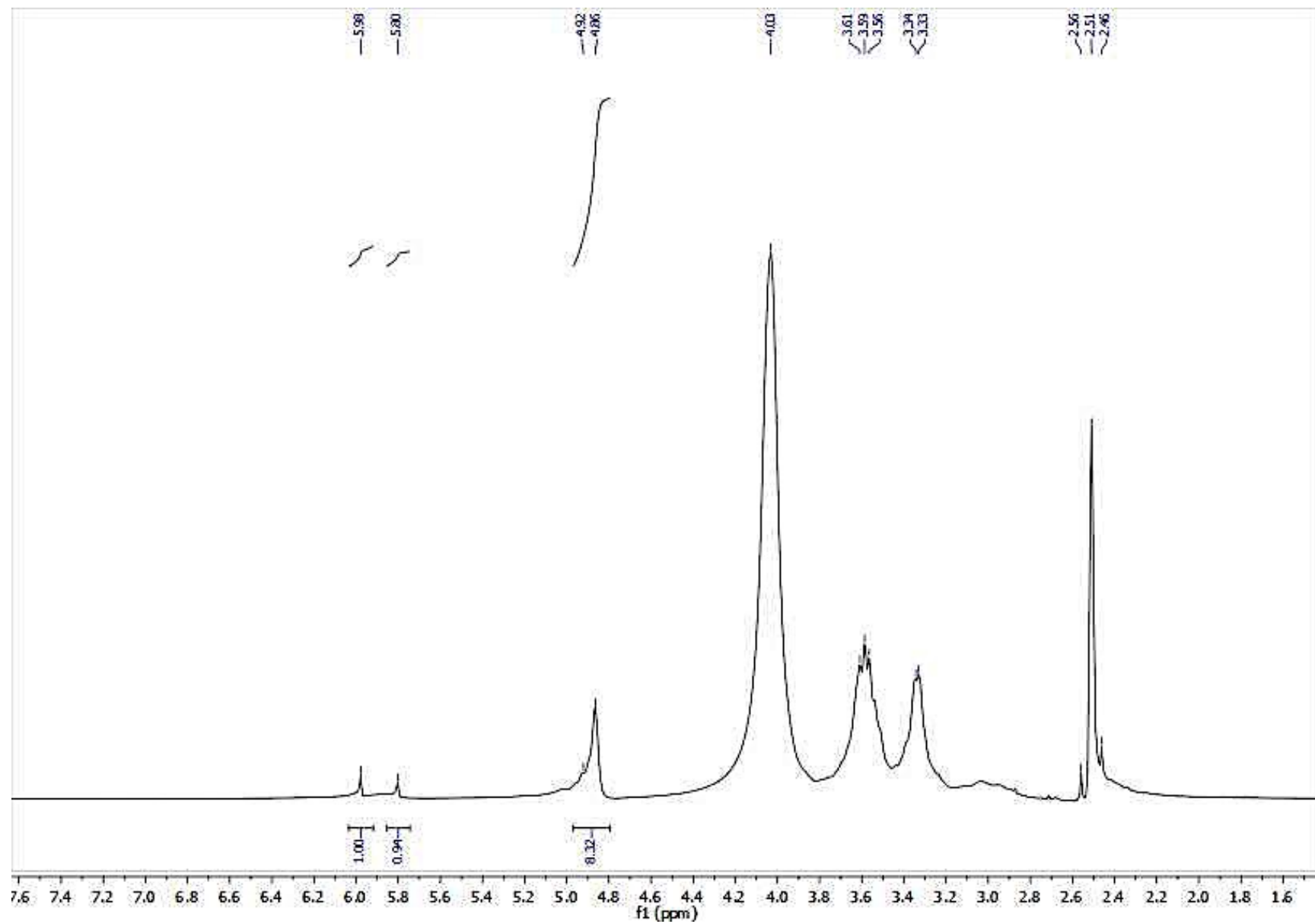
$^1\text{H-NMR}$  spectrum for compound **IPCA- $\beta$ -CD (10)**



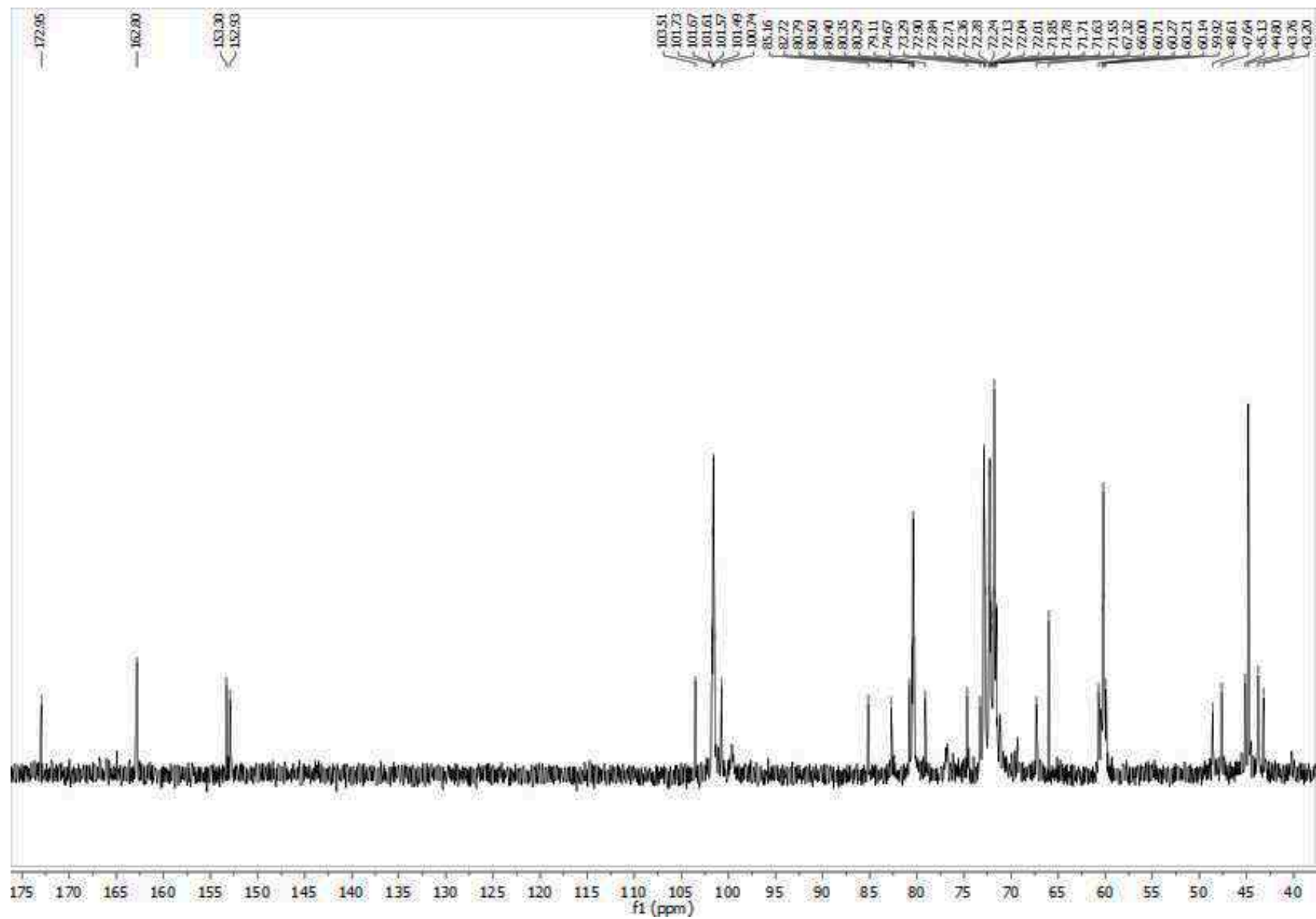
$^{13}\text{C}$ -NMR spectrum for compound IPCA- $\beta$ -CD (10)



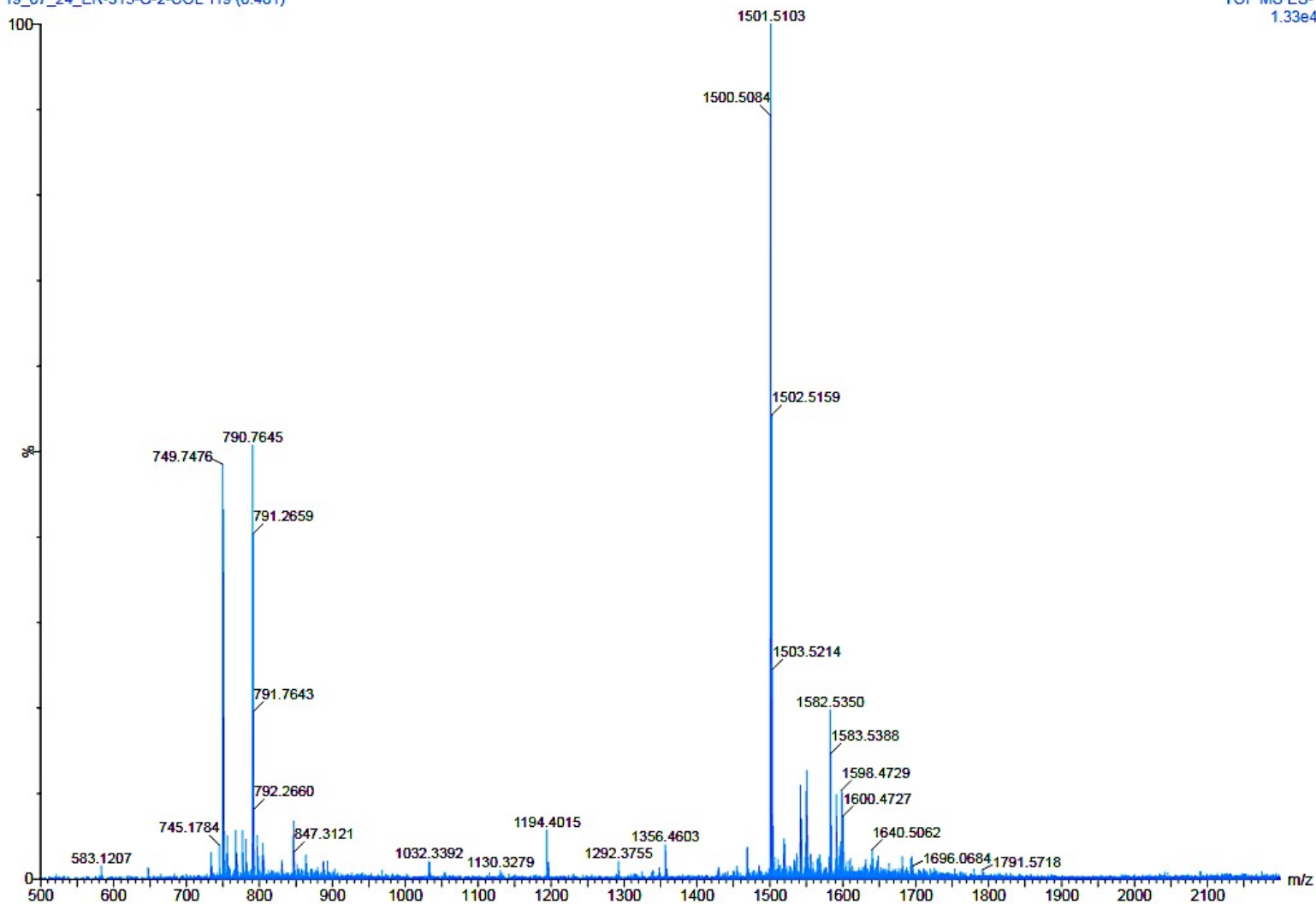
HR-MS (ES<sup>+</sup>-TOF) spectrum for compound **IPCA- $\beta$ -CD (10)**



$^1\text{H-NMR}$  spectrum for compound **IPCA- $\gamma$ -CD (11)**



$^{13}\text{C}$ -NMR spectrum for compound **IPCA- $\gamma$ -CD (11)**



HR-MS (ESI<sup>-</sup>) spectrum for compound **IPCA- $\gamma$ -CD (11)**