Electronic Supplementary Material (ESI) for Nanoscale.

ELECTRONIC SUPPLEMENTARY INFORMATION

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

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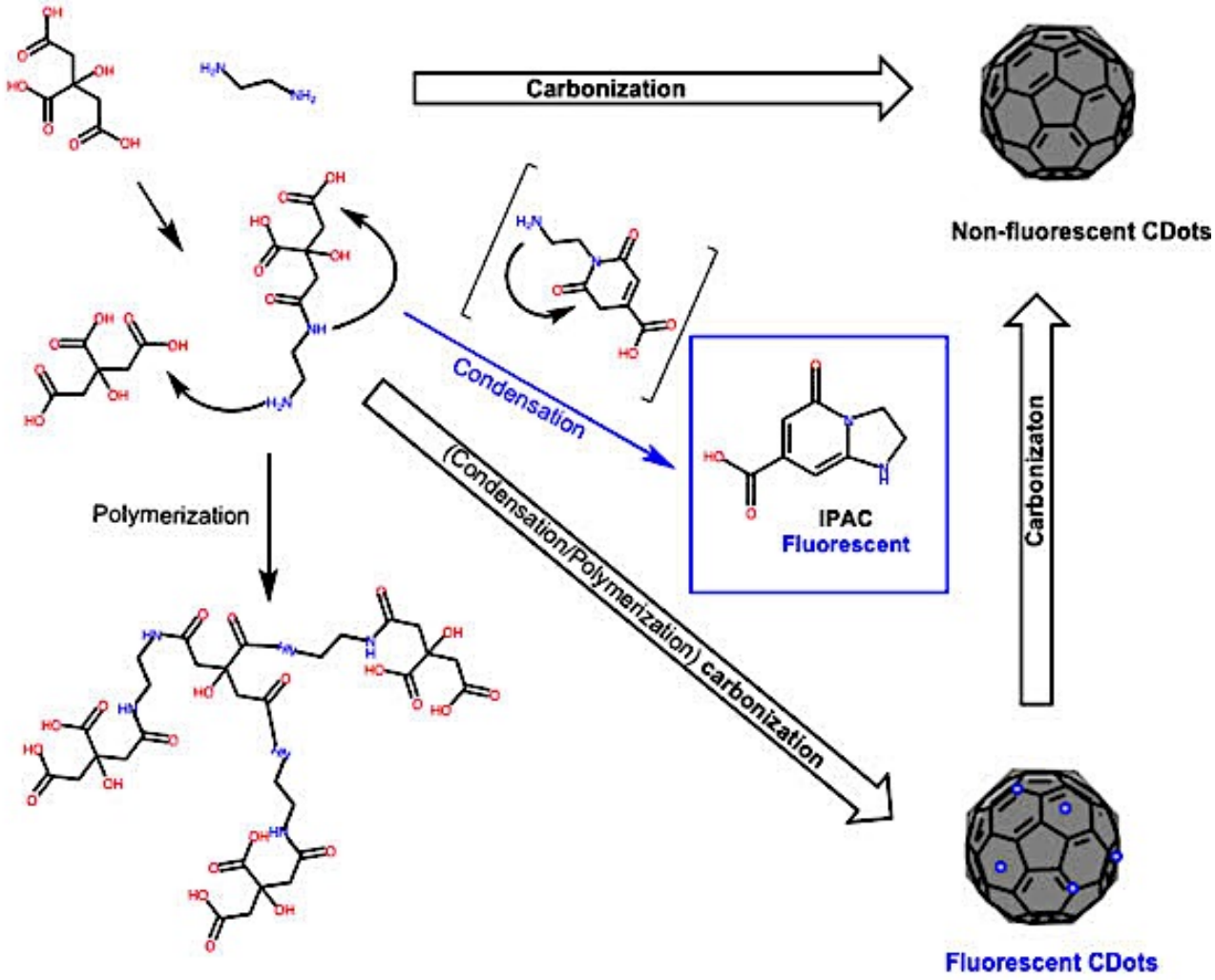


Scheme S1. Synthesis of the molecular fluorophore IPCA by reaction of CA with ethylenediamine and relationship between different products. The reaction of CA with ethylenediamine yields fluorescent CNDs via condensation and polymerization. As the pyrolysis proceeds the molecular fluorophore is carbonized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

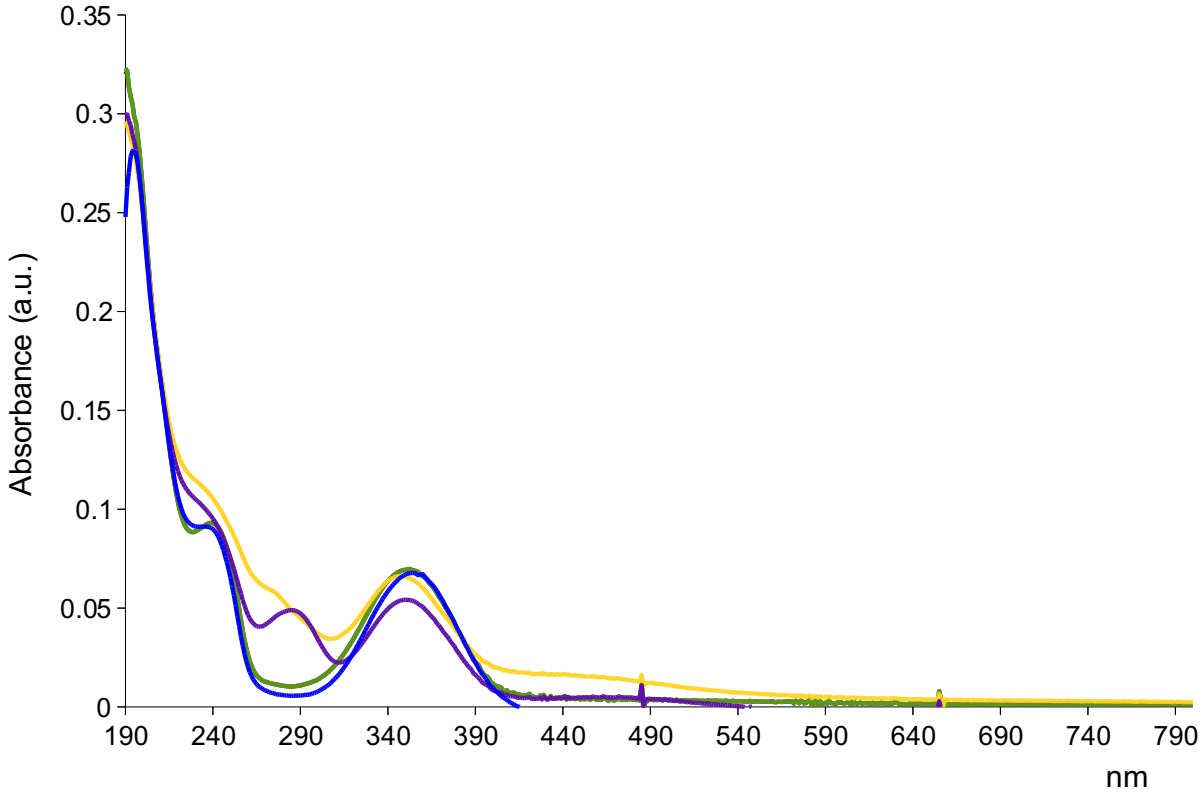


Fig. S1. Uv-vis spectra of **AEIPCA** (**1**) (blue), **AEIPCA-β-CD** (**6**) (magenta), **AEIPCA-γ-CD** (**7**) (yellow), **IPCA-β-CD** (**10)** (green), and **IPCA-γ-CD** (**11**) (red but overlapping with compound **10**)

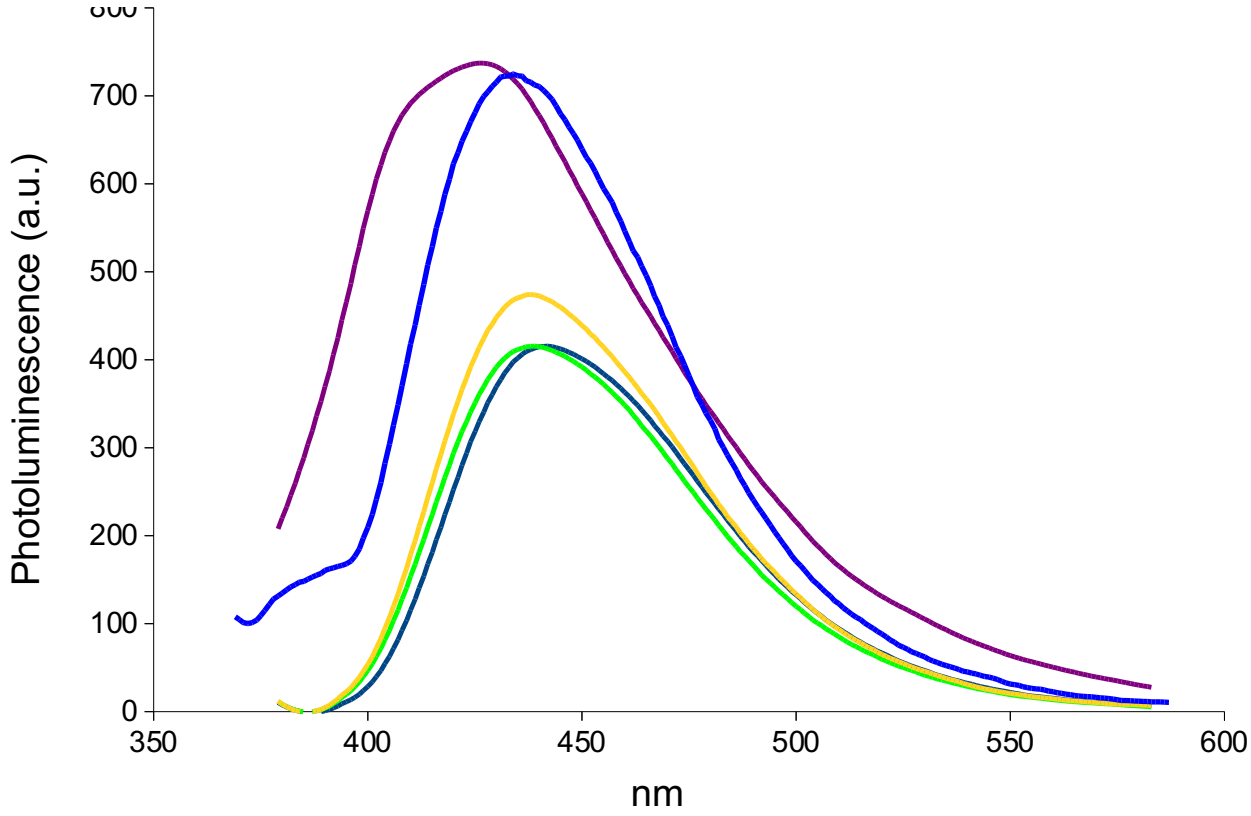


Fig. S2. Photoluminescence spectra of **AEIPCA** (**1**) (blue), **AEIPCA-β-CD** (**6**) (magenta), **AEIPCA-γ-CD** (**7**) (yellow), **IPCA-β-CD** (**10)** (green), and **IPCA-γ-CD** (**11**) (black) resulting from the excitation at 365 nm

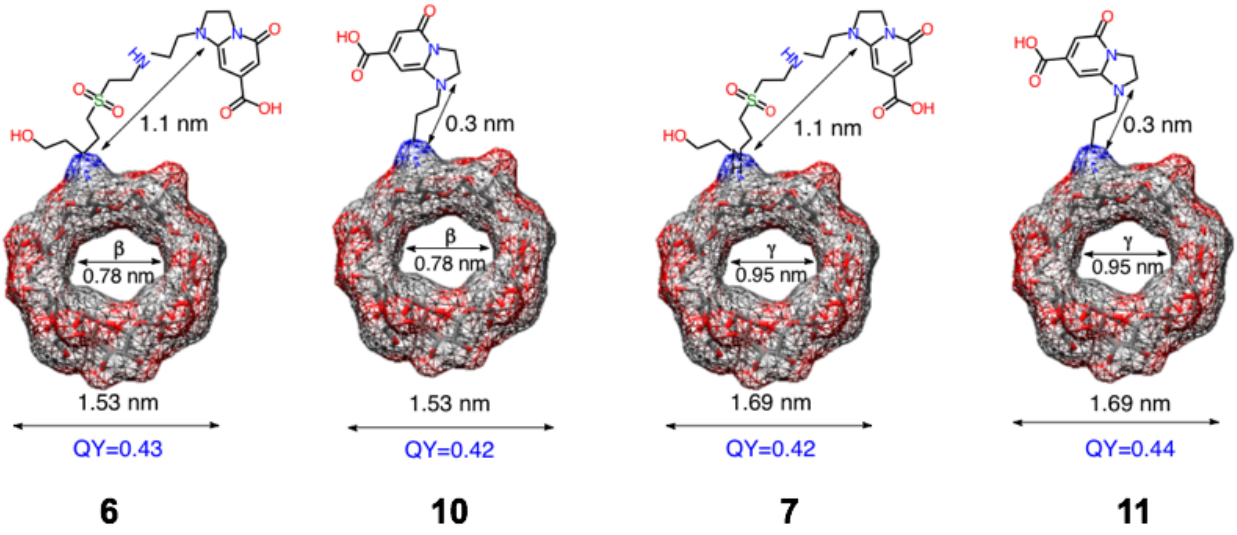


Fig. S3. Main features of **IPCA-CDs: AEIPCA-β-CD** (**6**), **AEIPCA-γ-CD** (**7**), **IPCA-β-CD** (**10)**, and **IPCA-γ-CD** (**11**) The distances between the fluorophore and the CD were estimated from the minimized coordinates. Coordinates were generated using Ghemical 2.956 (T. Hassinen, M. Peräkylä, *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 KJul/mol. The values for CDs are those reported in bibliography from structural studies.

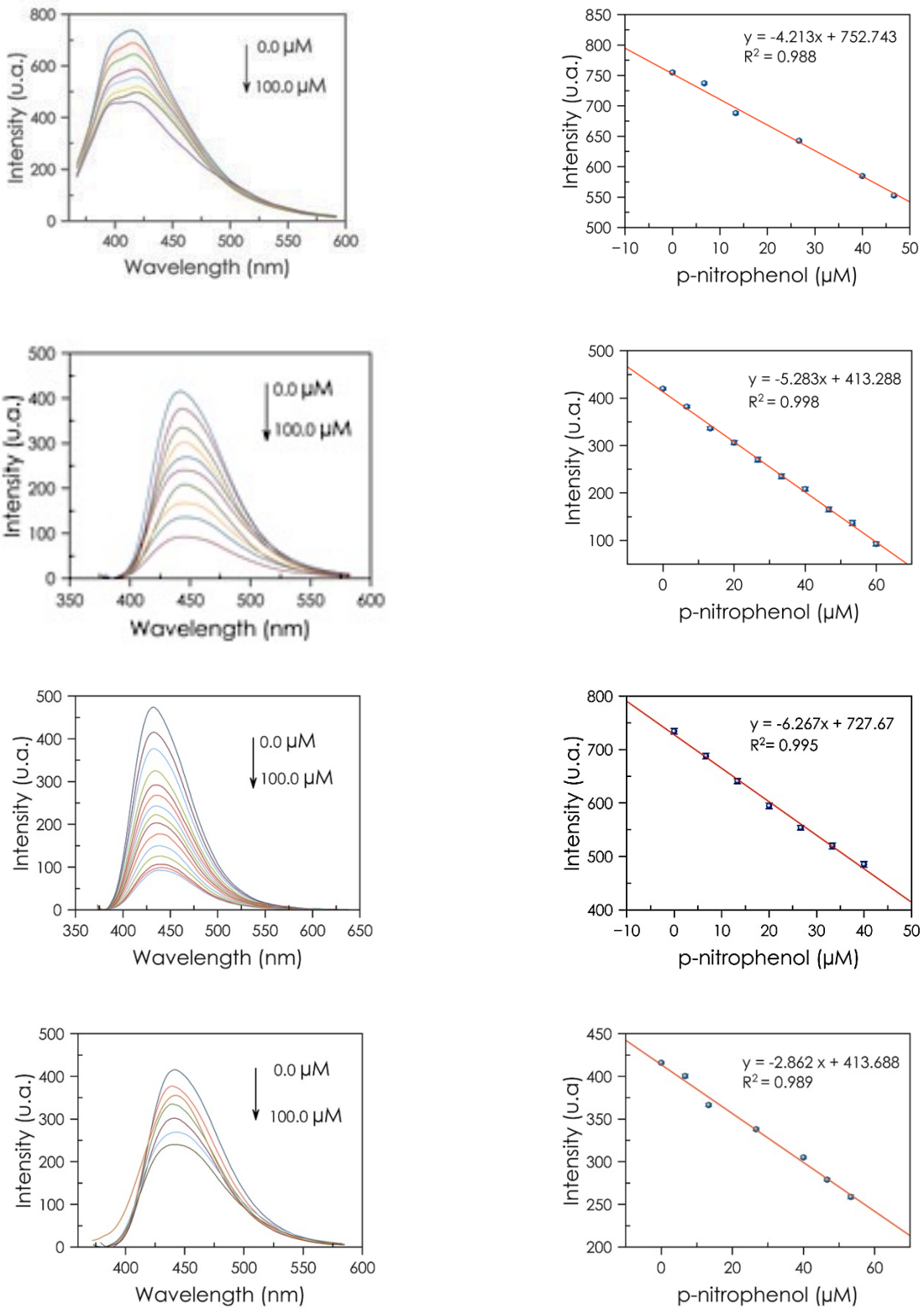


Fig. S4. Fluorescence spectra (left) and plot of fluorescence versus the concentration of *p*NP (right) for **IPCA-CDs.** From top to bottom **AEIPCA-β-CD** (**6**), **AEIPCA-γ-CD** (**7**), **IPCA-β-CD** (**10)**, and **IPCA-γ-CD** (**11**).

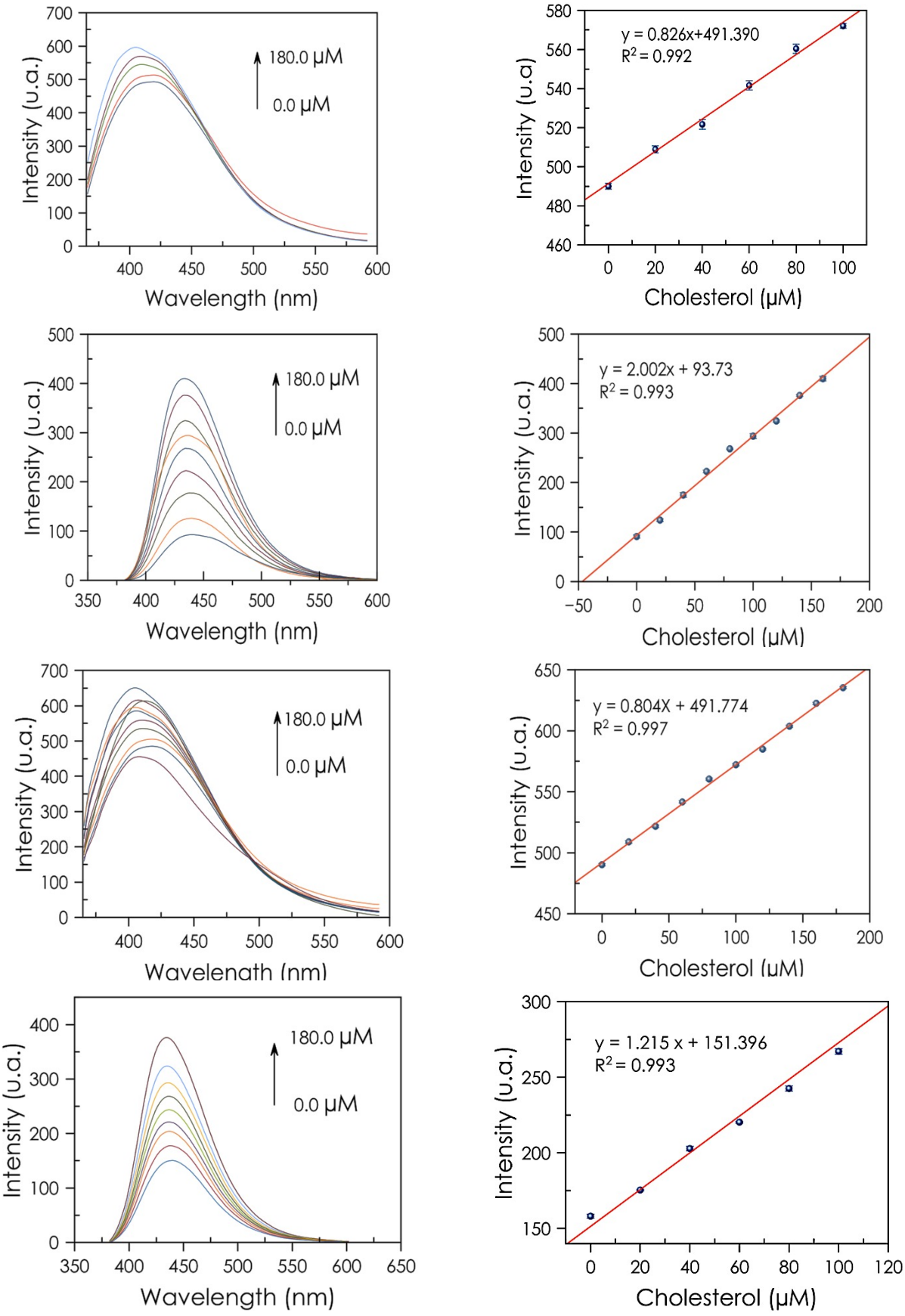


Fig. S5. Fluorescence spectra (left) and plot of fluorescence versus the concentration of Chol (right) for the **IPCA-CDs** quenched with 40 μM *p*NP. From top to bottom **AEIPCA-β-CD** (**6**), **AEIPCA-γ-CD** (**7**), **IPCA-β-CD** (**10**), and **IPCA-γ-CD** (**11**),

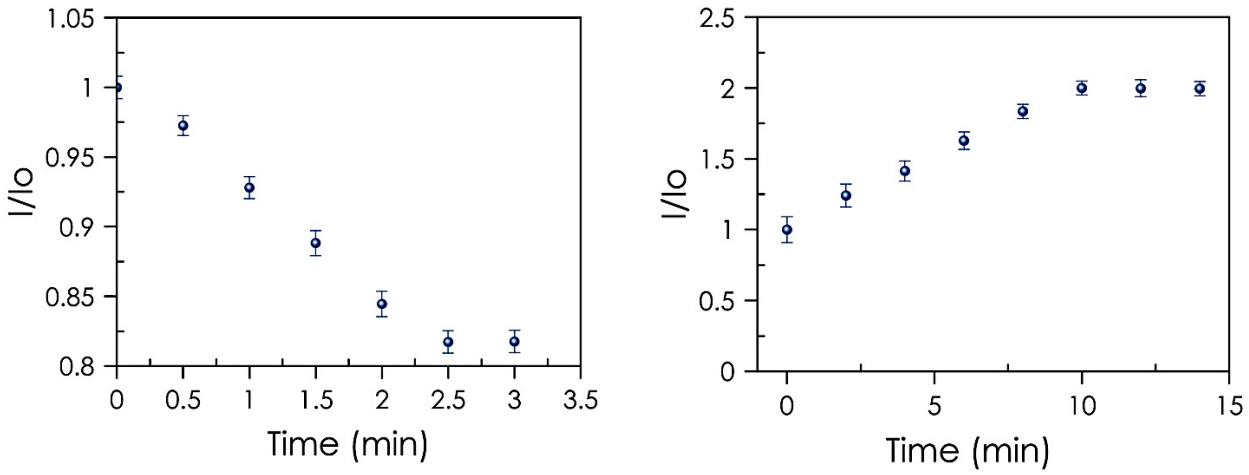
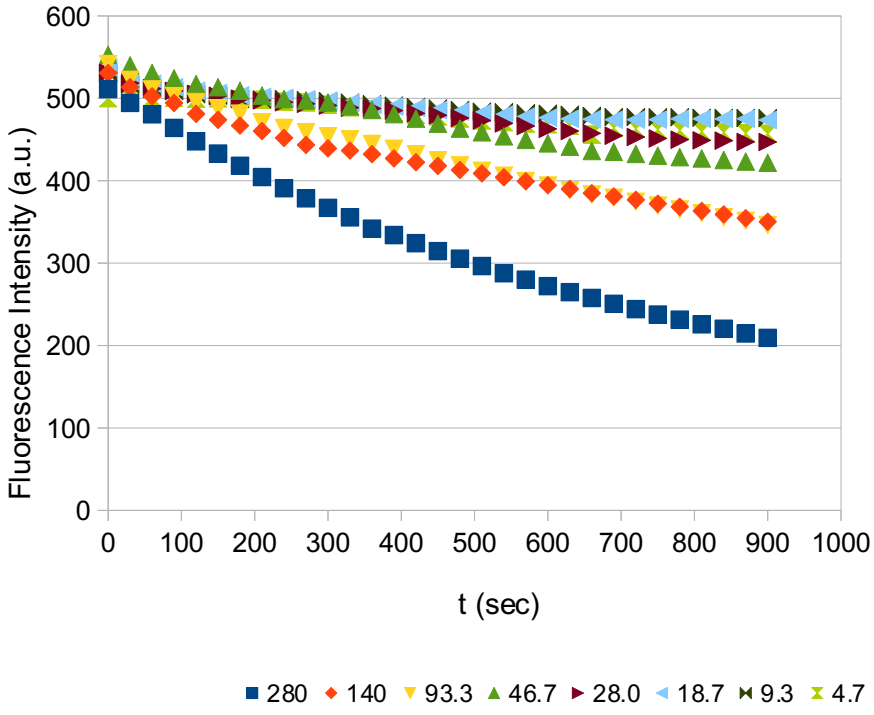


Fig. S6. Evolution of the fluorescence as a function of time upon addition of *p*NP (quenching) and Chol (recovery). I_0 is the fluorescence intensity initial and I is the fluorescence intensity final.



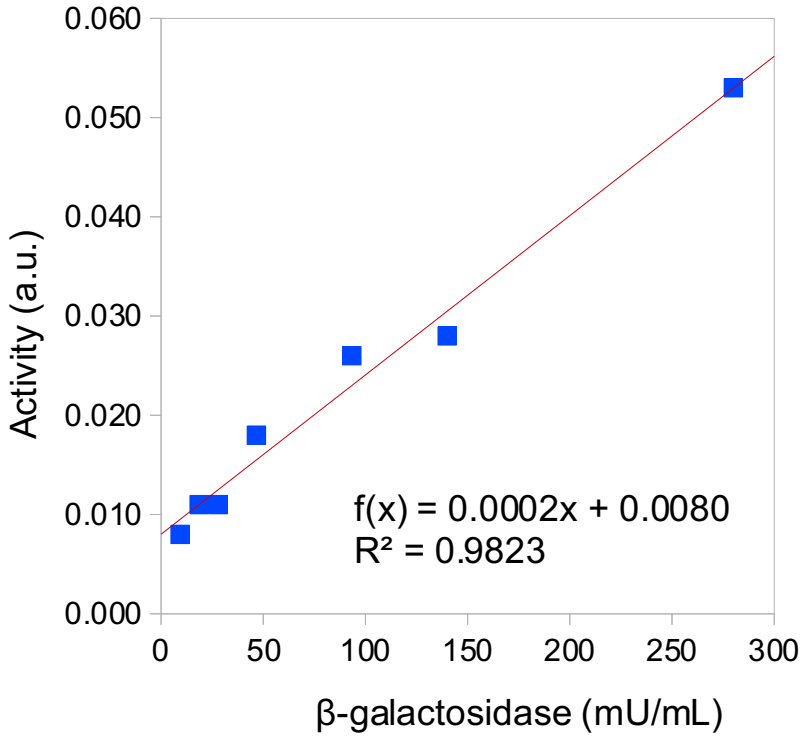
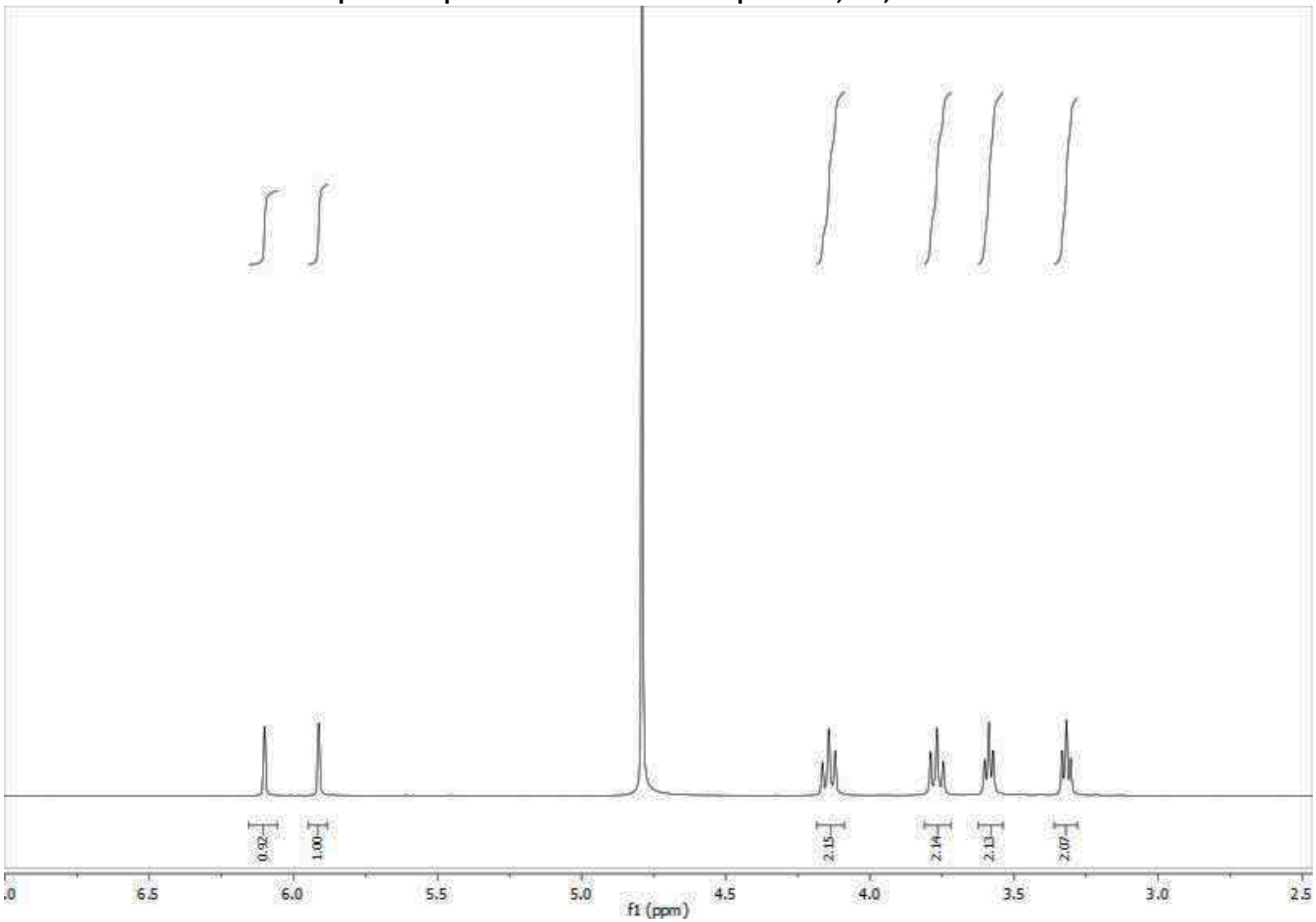


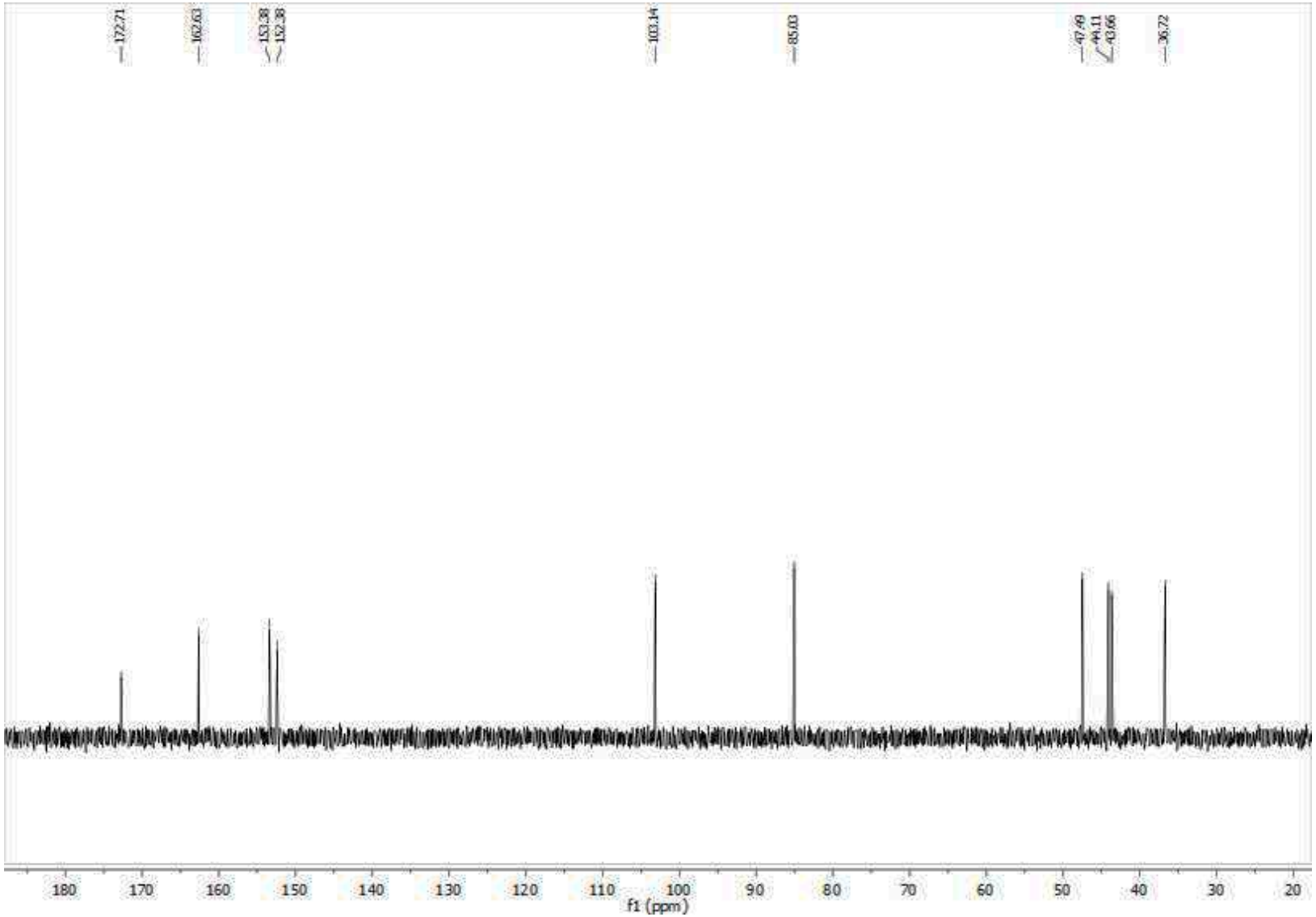
Fig. S7. Fluorescence intensity of **AEIPCA-β-CD** (**6**) as a function of time for different concentrations (mU/mL) of β-galactosidase (up) and linear dependency of the enzymatic activity with the concentration of enzyme (down)

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

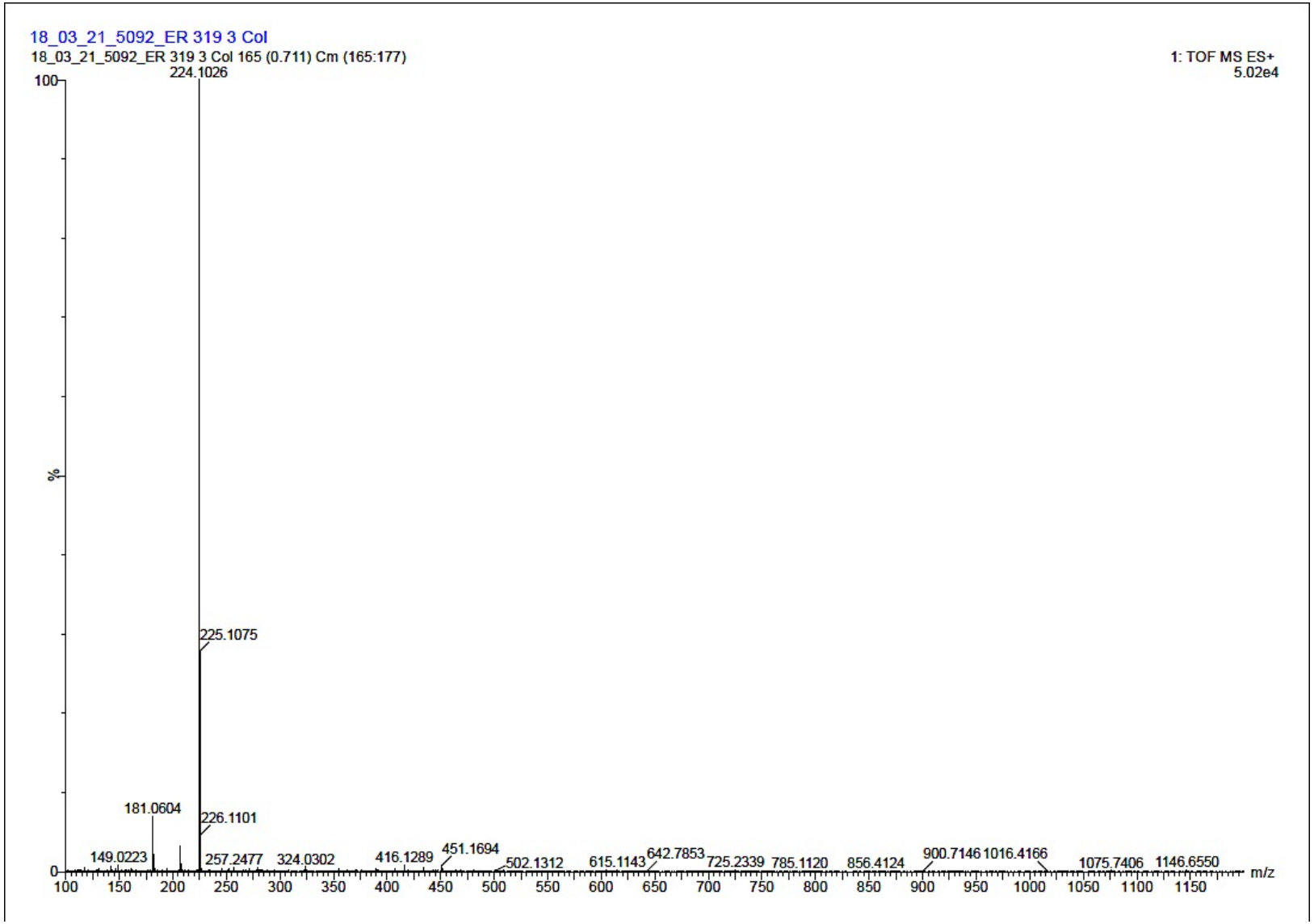
Compound	QY
1	0.47
6	0.43
7	0.42
10	0.42
11	0.44



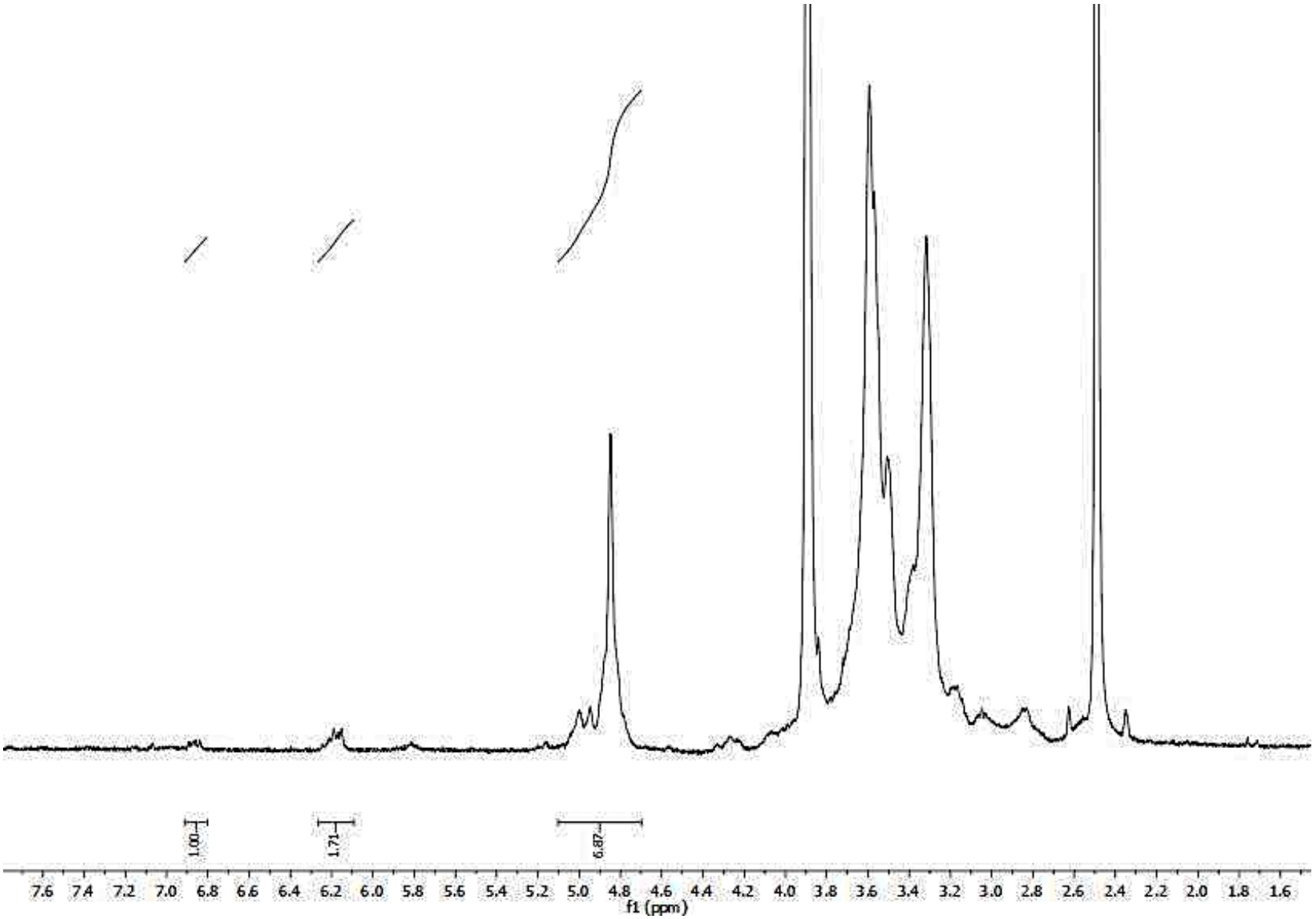
^{1}H-NMR spectrum for compound **AEIPCA (1)**



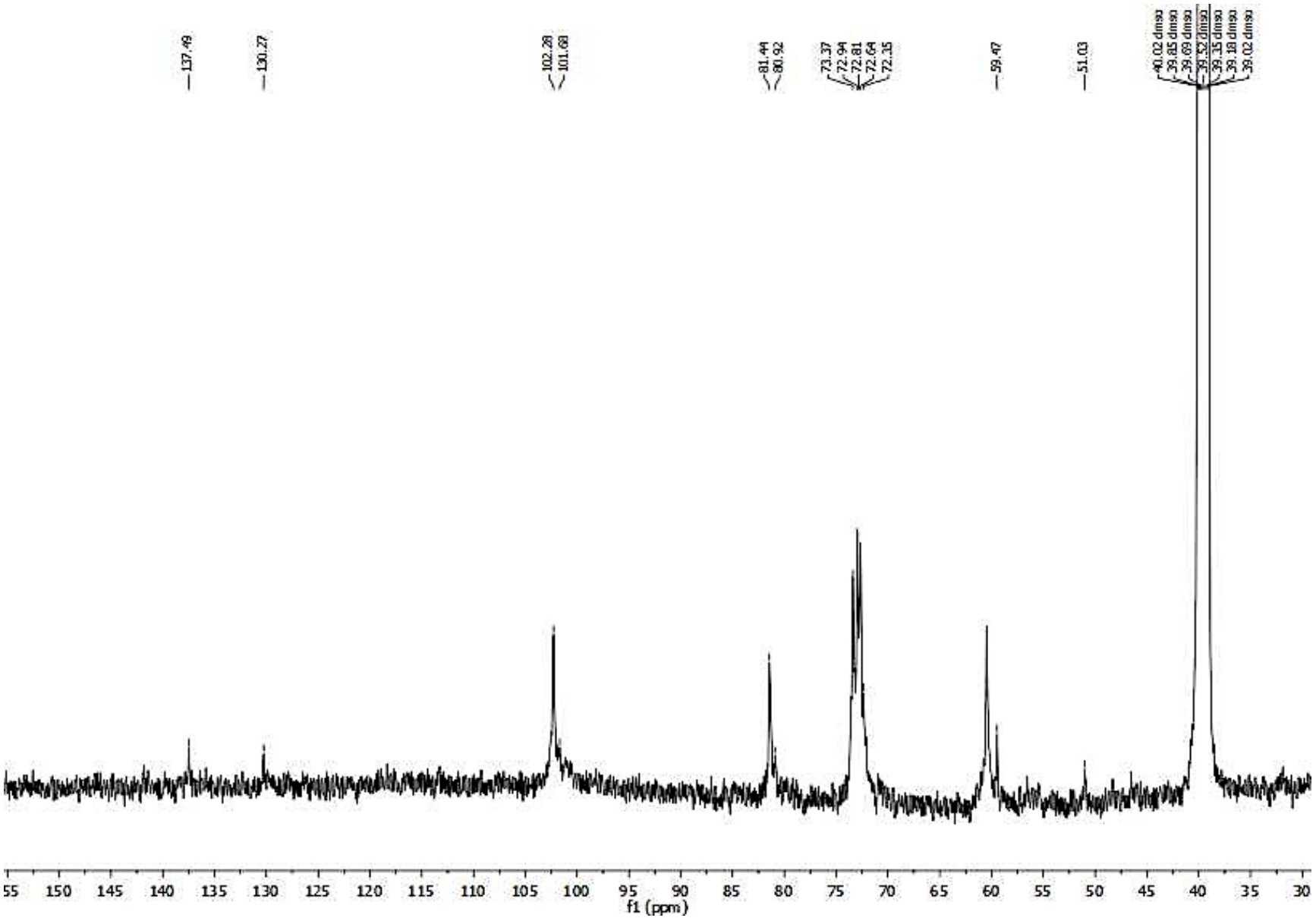
^{13}C-NMR spectrum for compound **AEIPCA (1)**



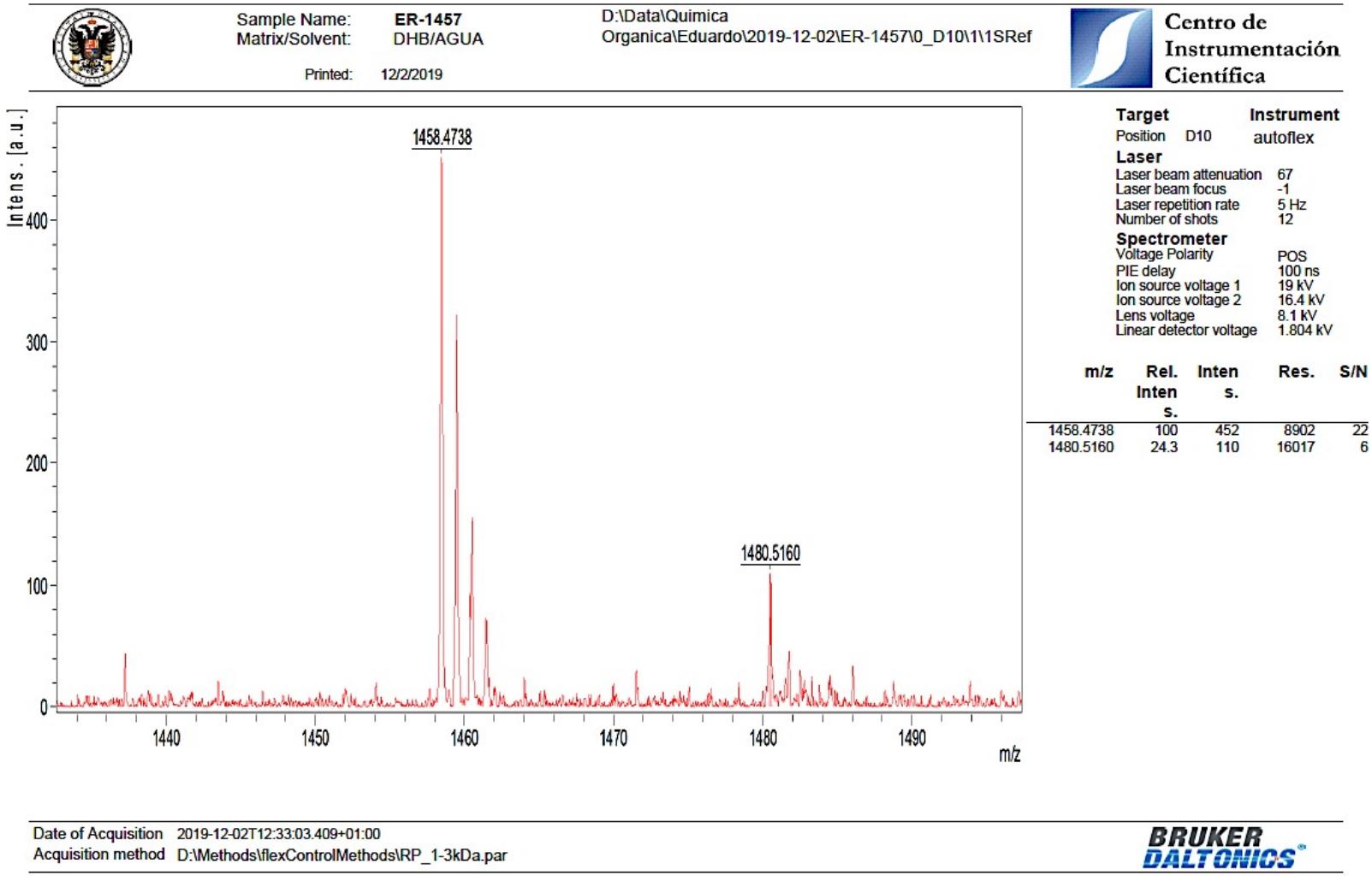
HR-MS (ESI+) spectrum for compound **AEIPCA (1)**



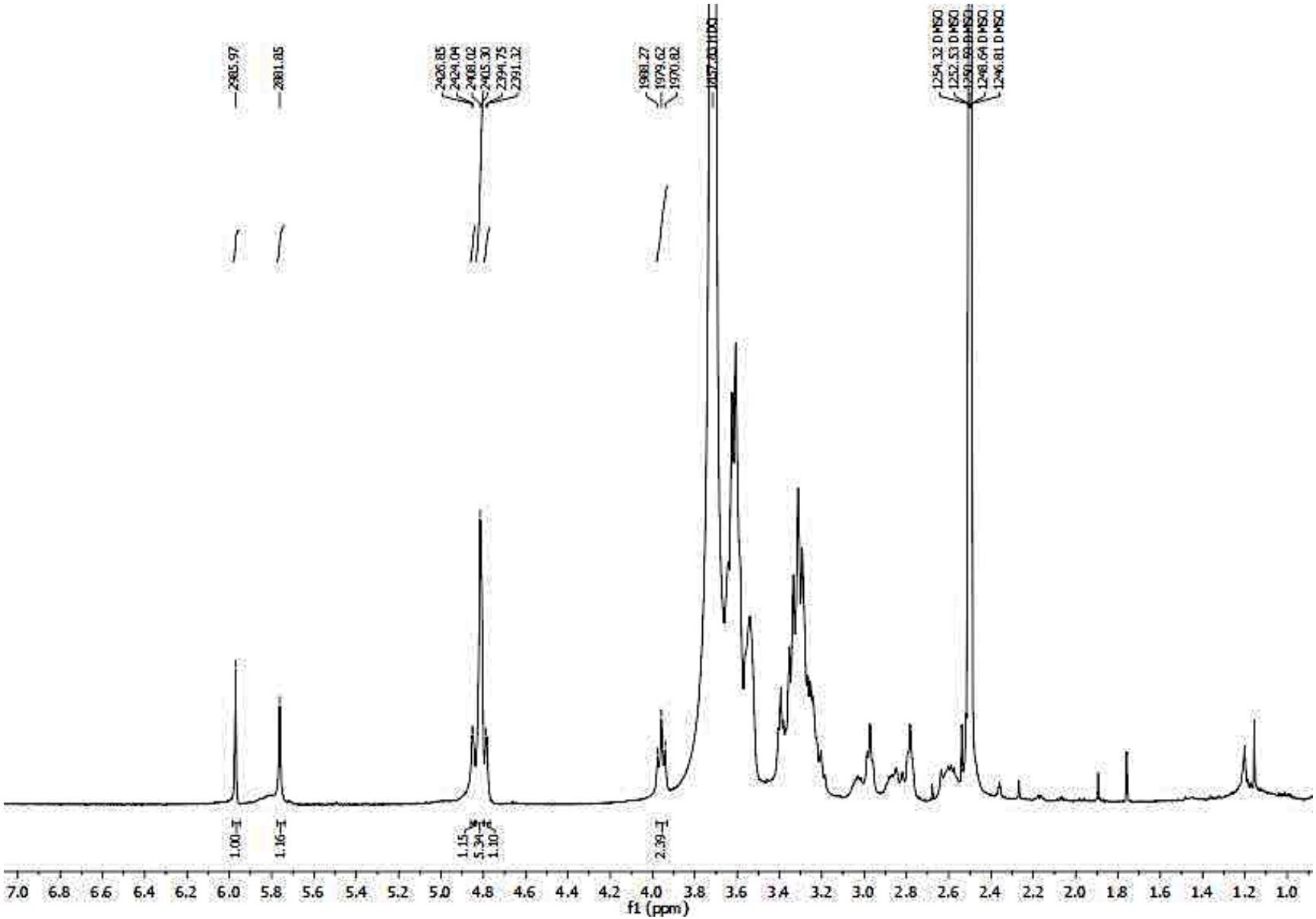
^{1}H-NMR spectrum for compound **VS–γ–CD (5)**



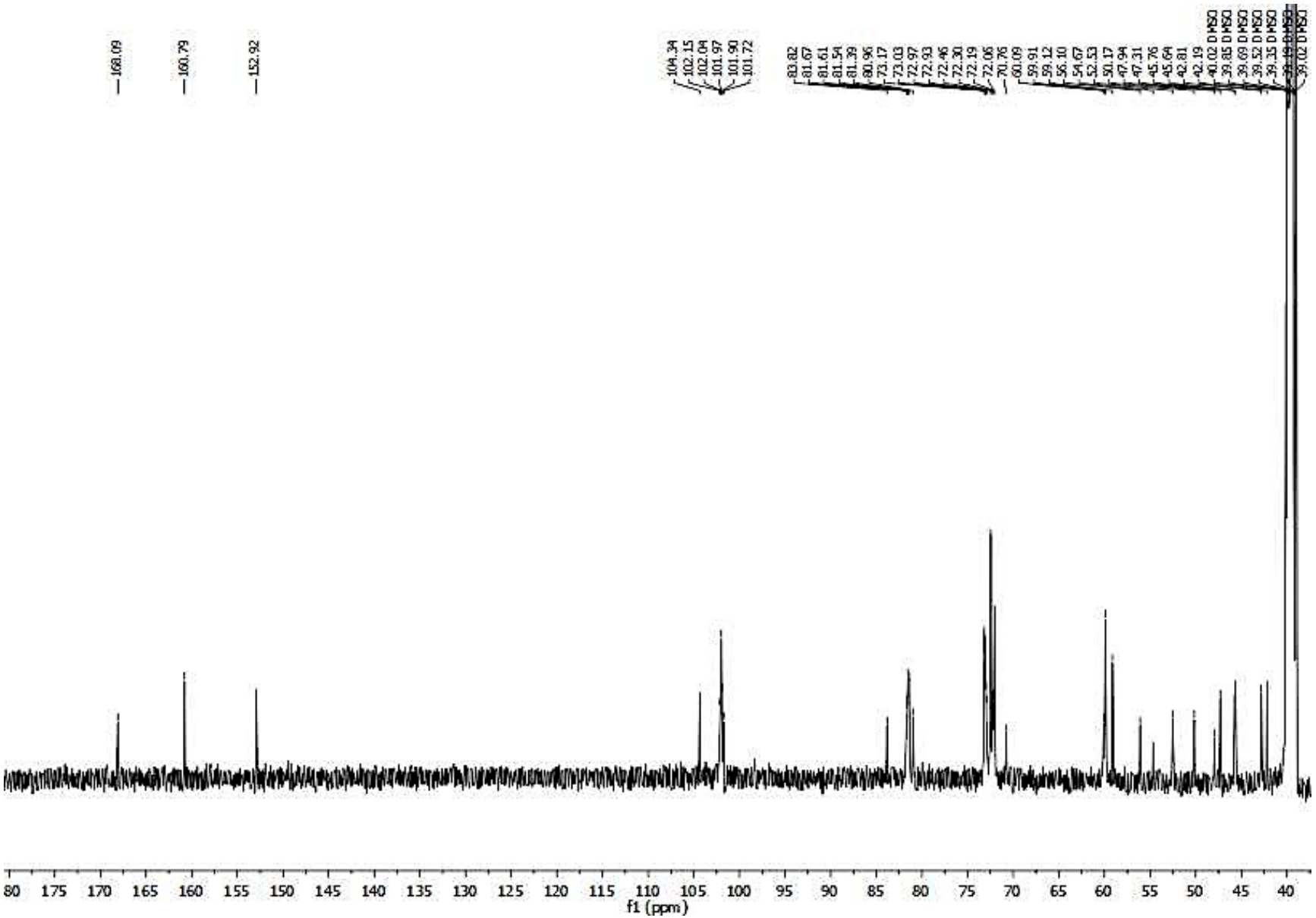
^{13}C-NMR spectrum for compound **VS–γ–CD (5)**



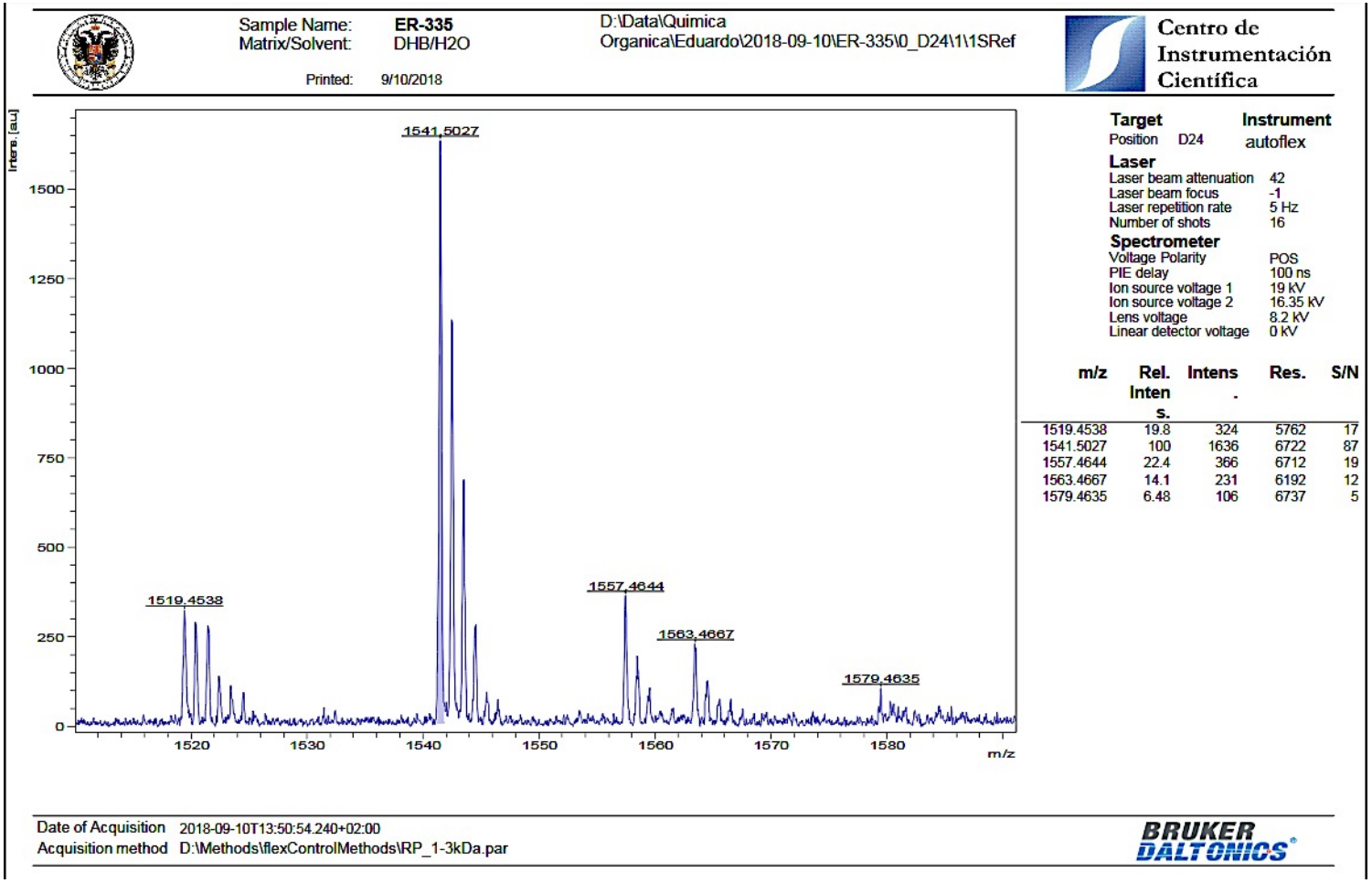
HR-MS (MALDI-TOF) spectrum for compound **VS–γ–CD (5)**



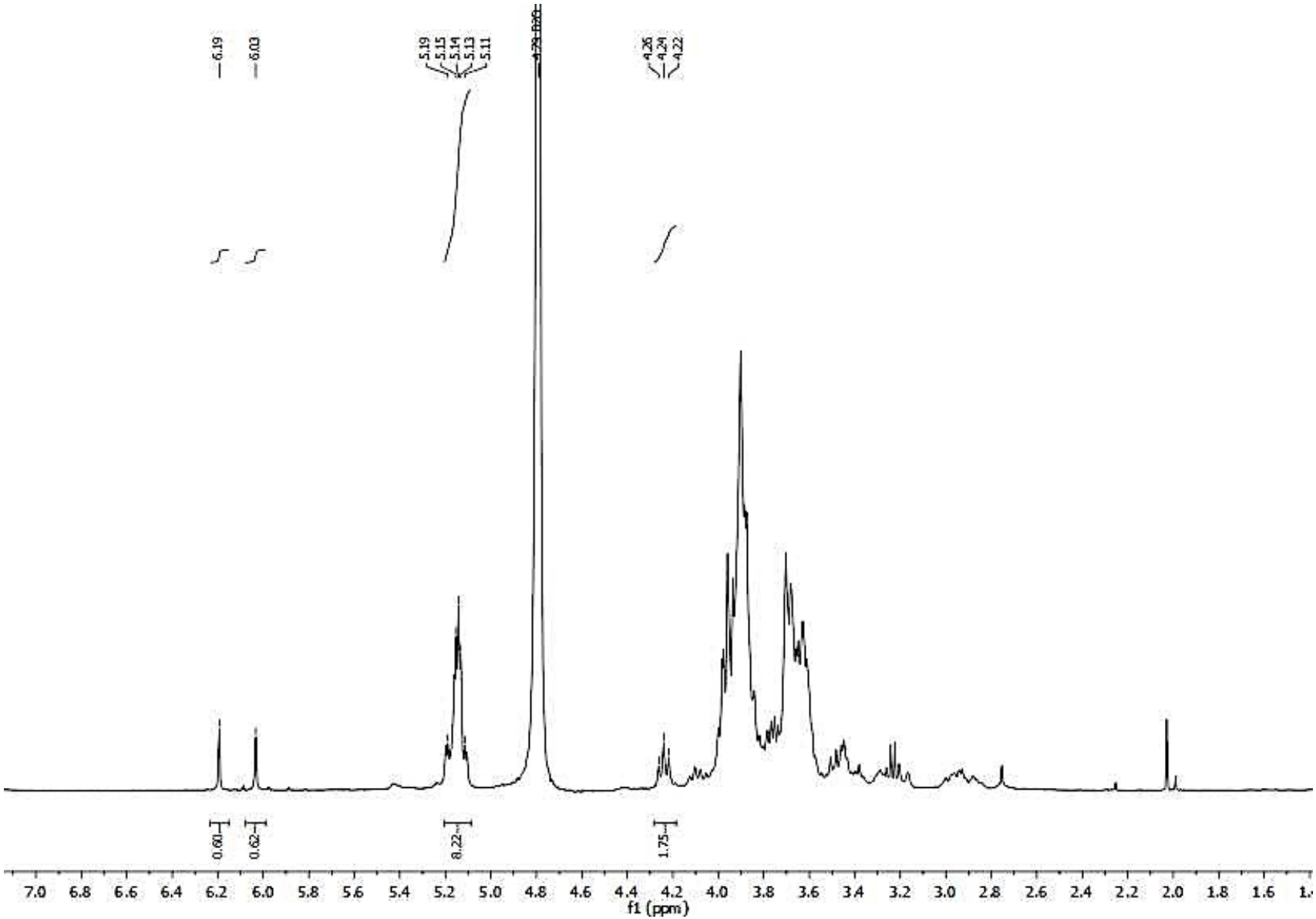
^{1}H-NMR spectrum for compound **AEIPCA–β–CD (6)**



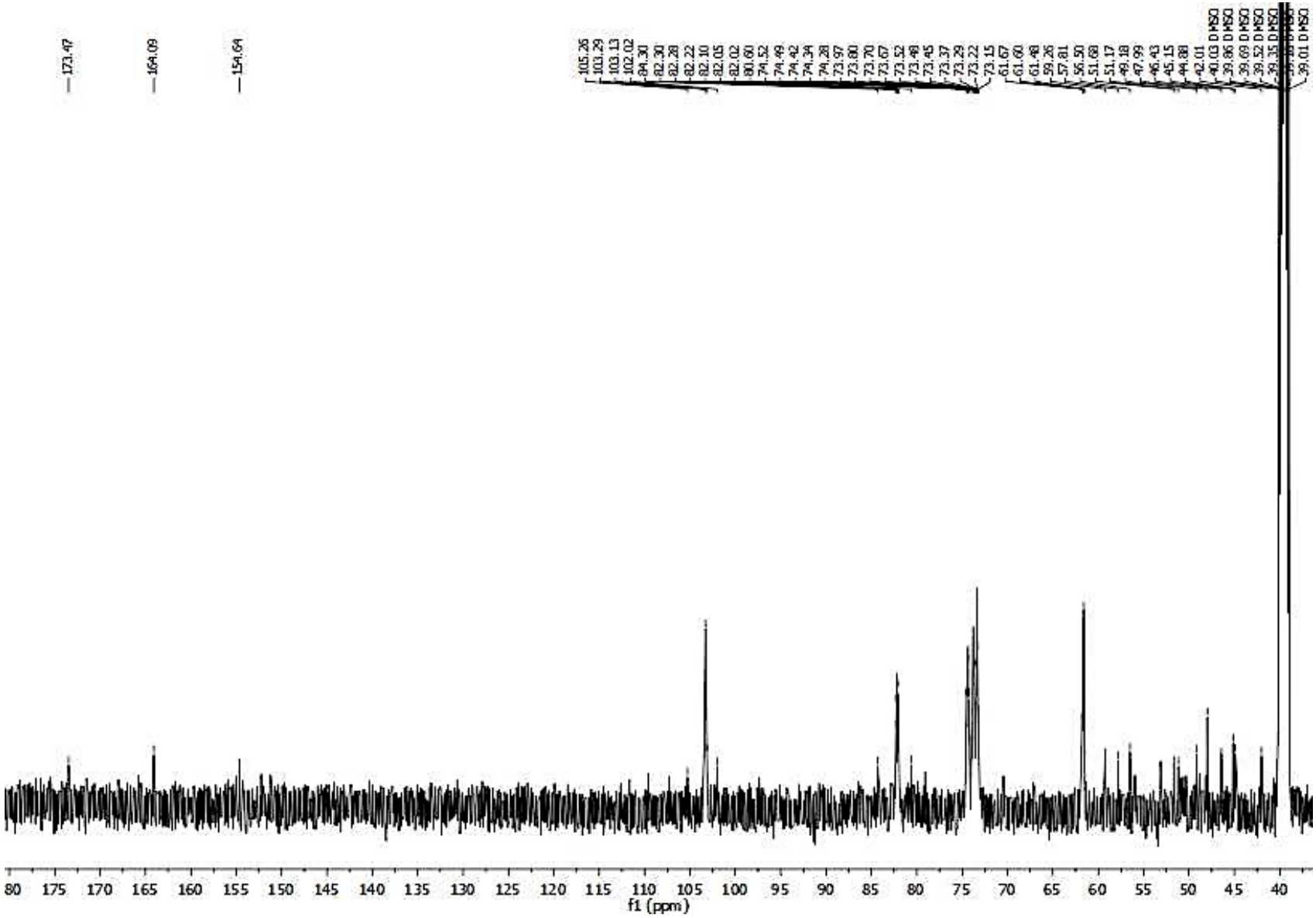
^{13}C-NMR spectrum for compound **AEIPCA**–β–**CD (6)**



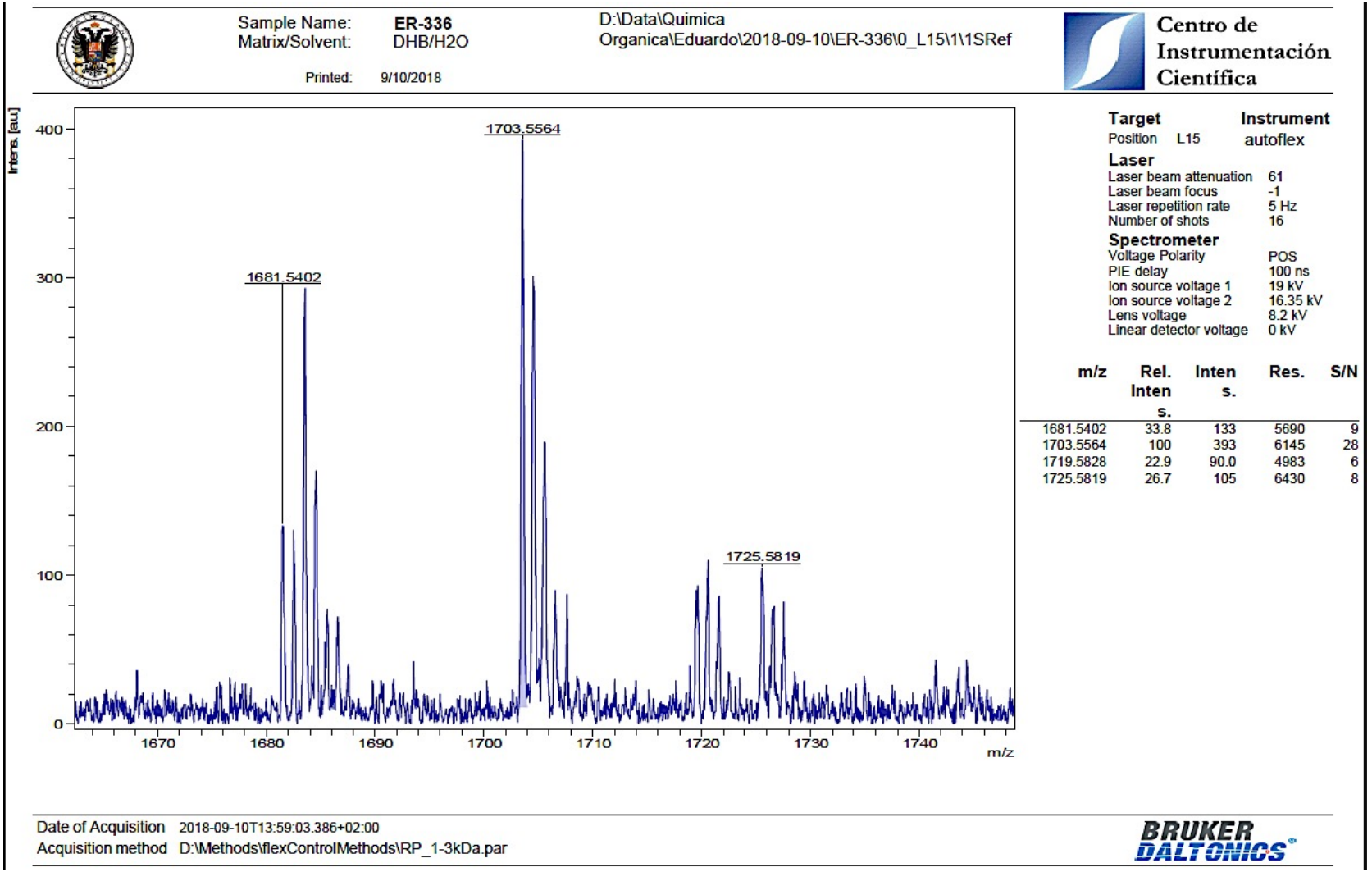
HR-MS (MALDI-TOF) spectrum for compound **AEIPCA–β–CD (6)**



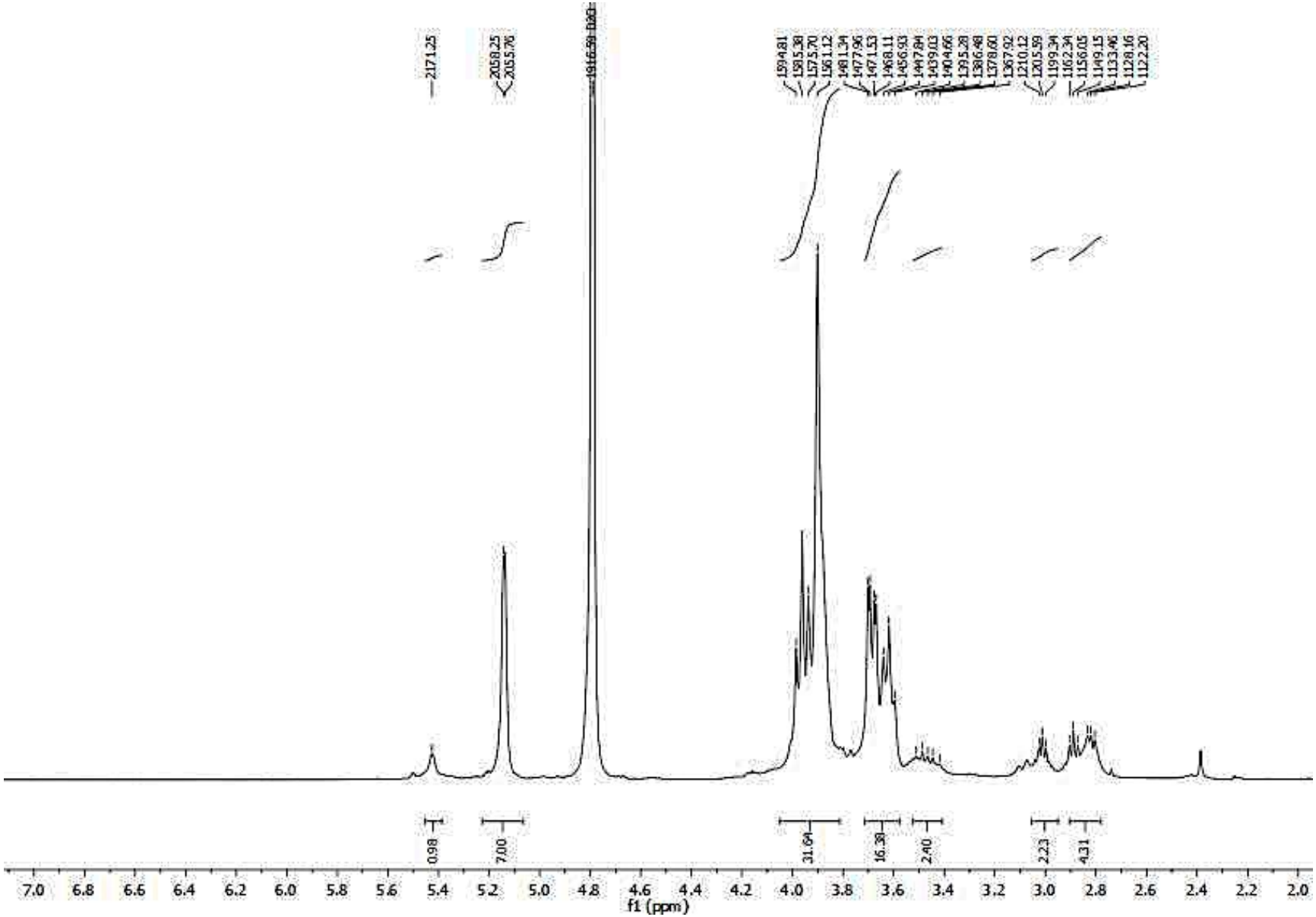
^{1}H-NMR spectrum for compound **AEIPCA–γ–CD (7)**



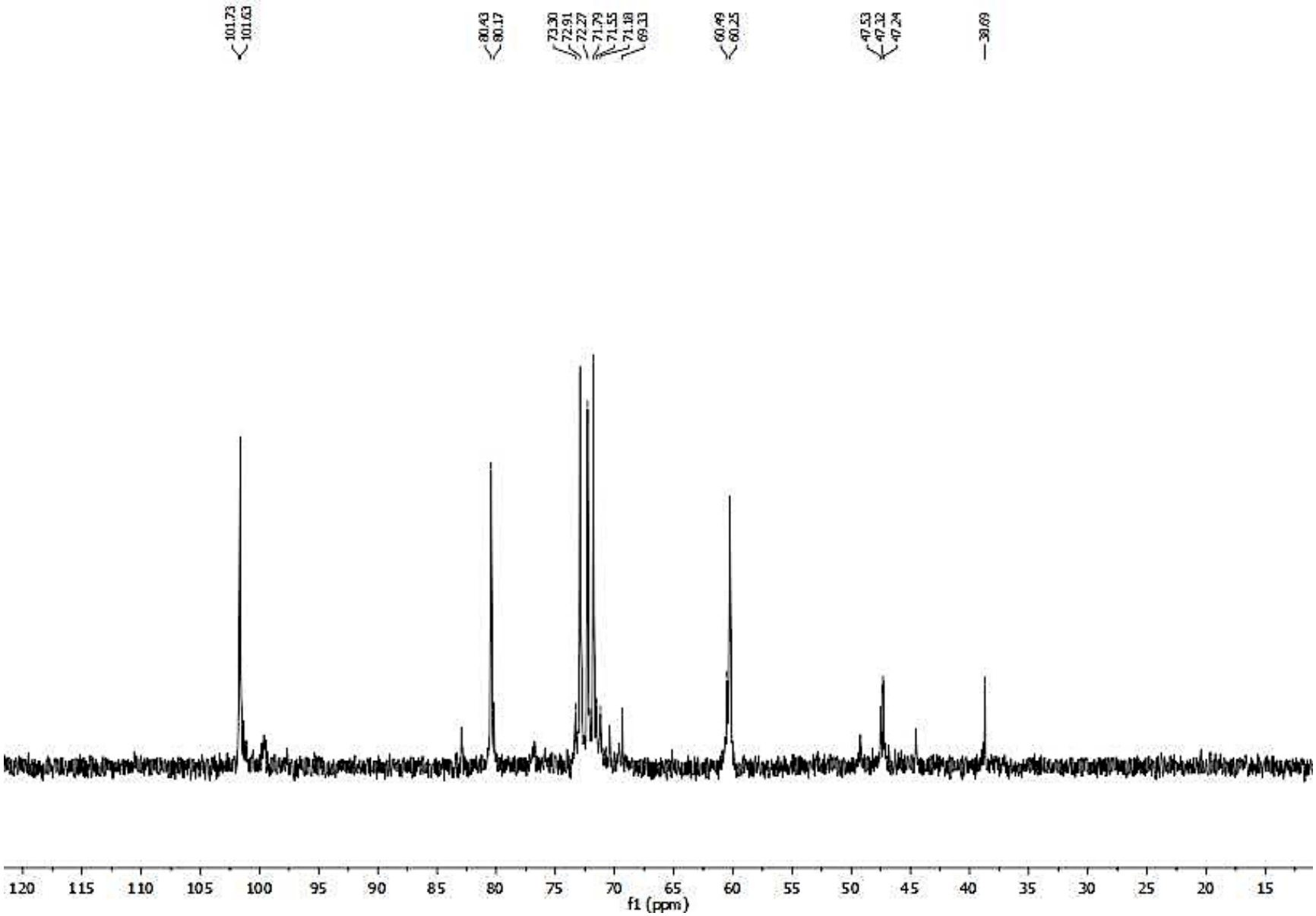
^{13}C-NMR spectrum for compound **AEIPCA–γ–CD (7)**



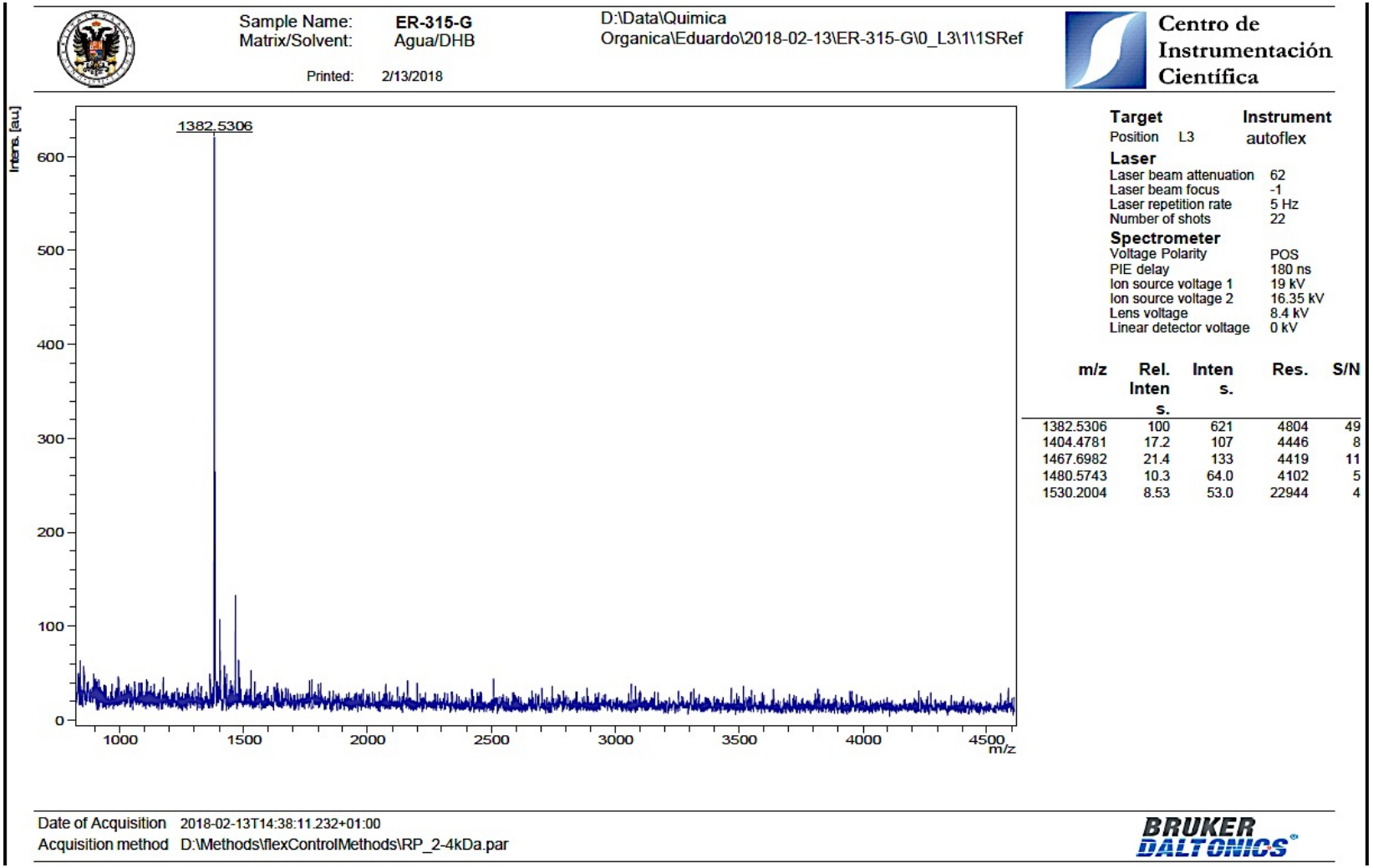
HR-MS (MALDI-TOF) spectrum for compound **AEIPCA–γ–CD (7)**



^{1}H-NMR spectrum for compound **DETA–γ–CD (9)**

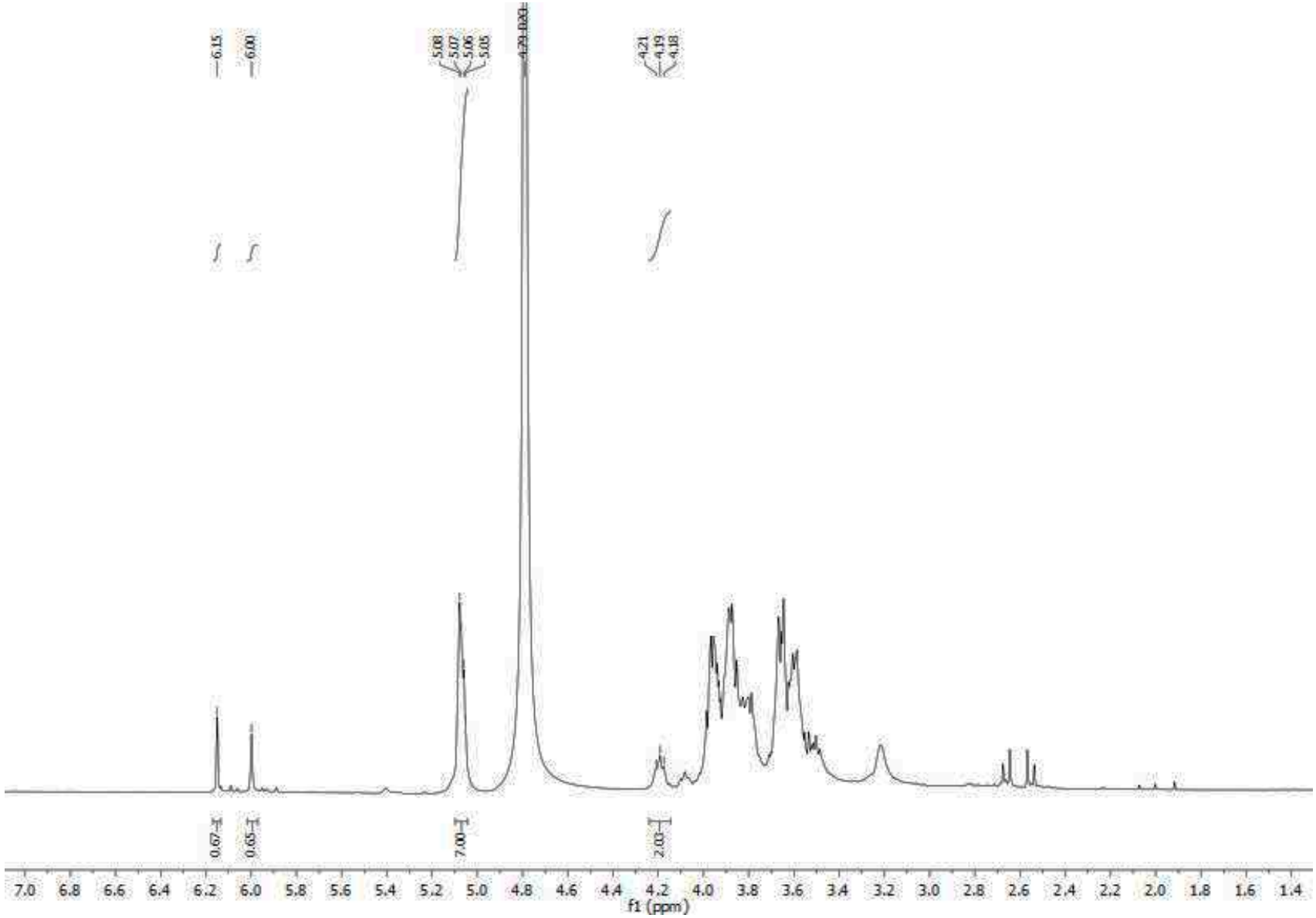


^{13}C-NMR spectrum for compound **DETA–γ–CD (9)**

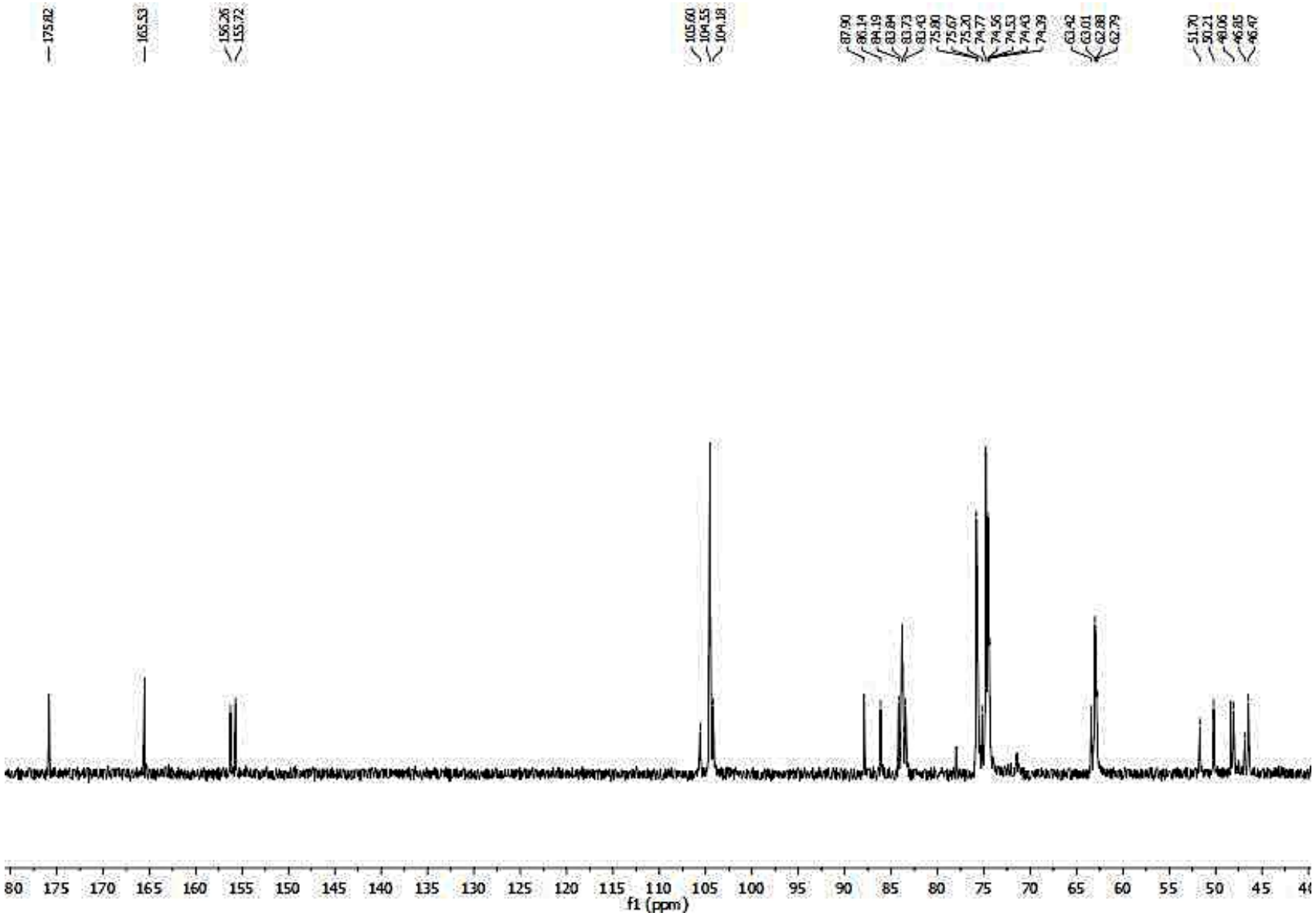


m/z	Rel. Intens.	Intens.	Res.	S/N
1382.5306	100	621	4804	49
1404.4781	17.2	107	4446	8
1467.6982	21.4	133	4419	11
1480.5743	10.3	64.0	4102	5
1530.2004	8.53	53.0	22944	4

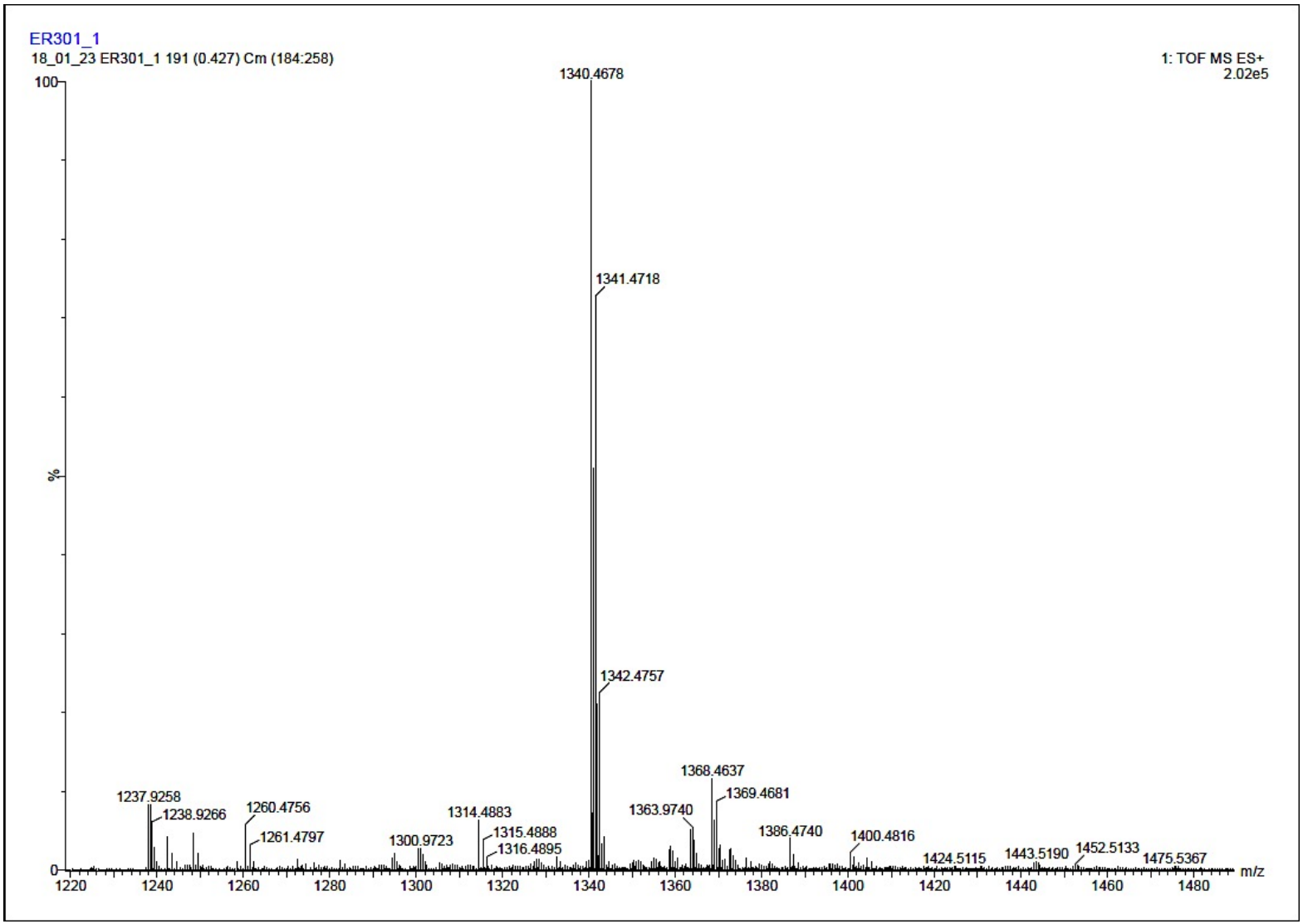
HR-MS (ES^+-TOF) spectrum for compound **DETA–γ–CD (9)**



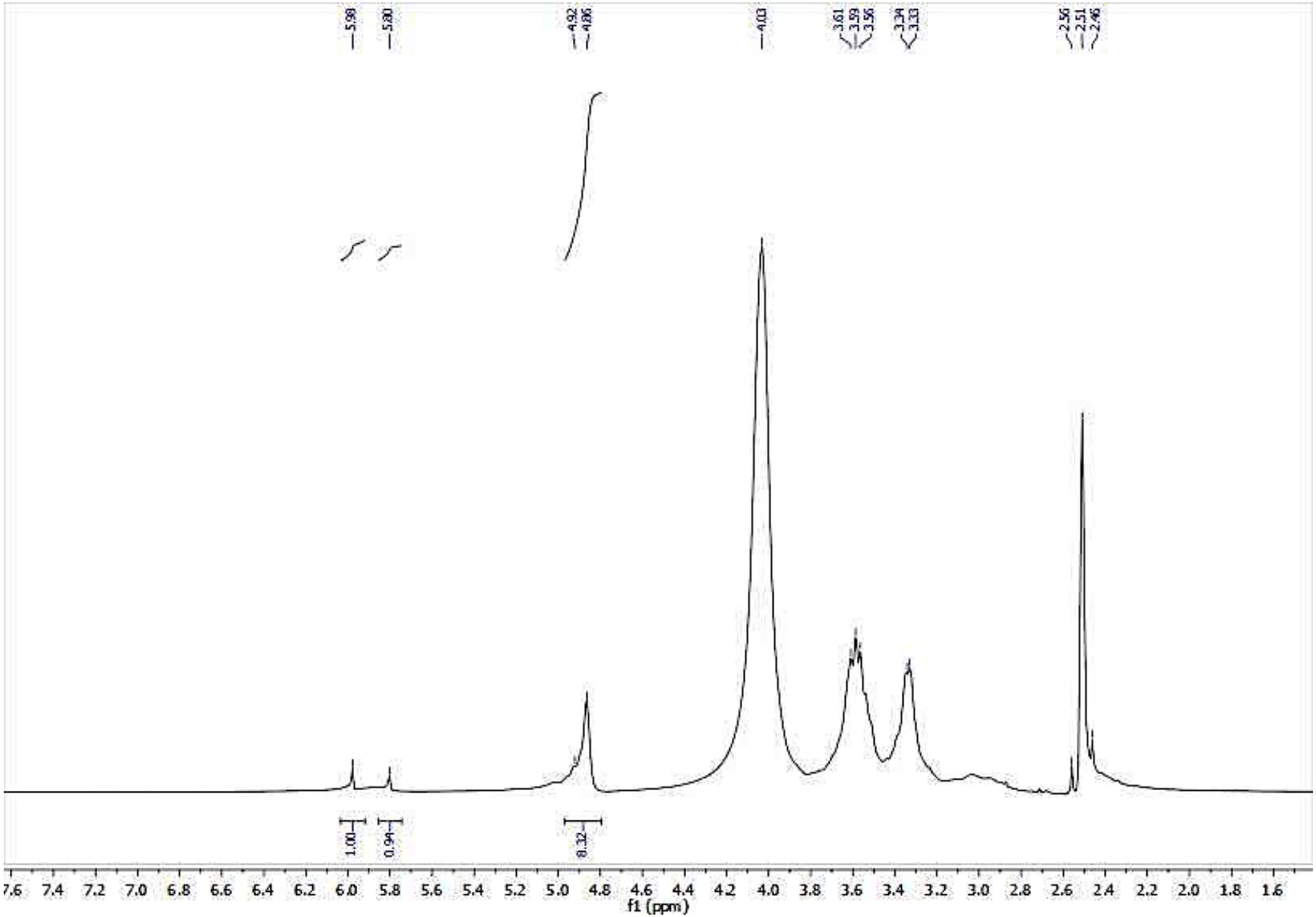
^{1}H-NMR spectrum for compound **IPCA–β–CD (10)**



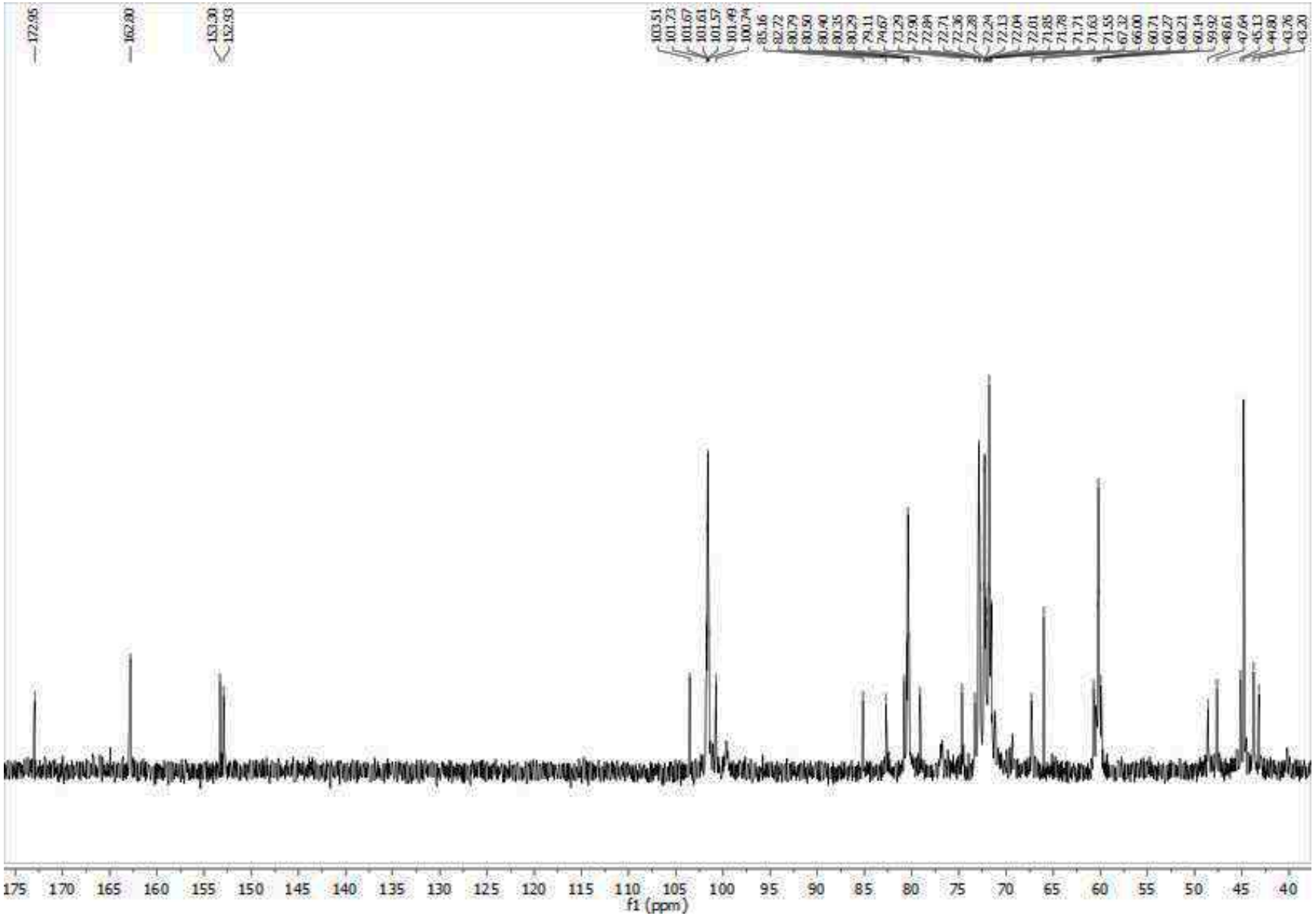
^{13}C-NMR spectrum for compound **IPCA**–β–**CD (10)**



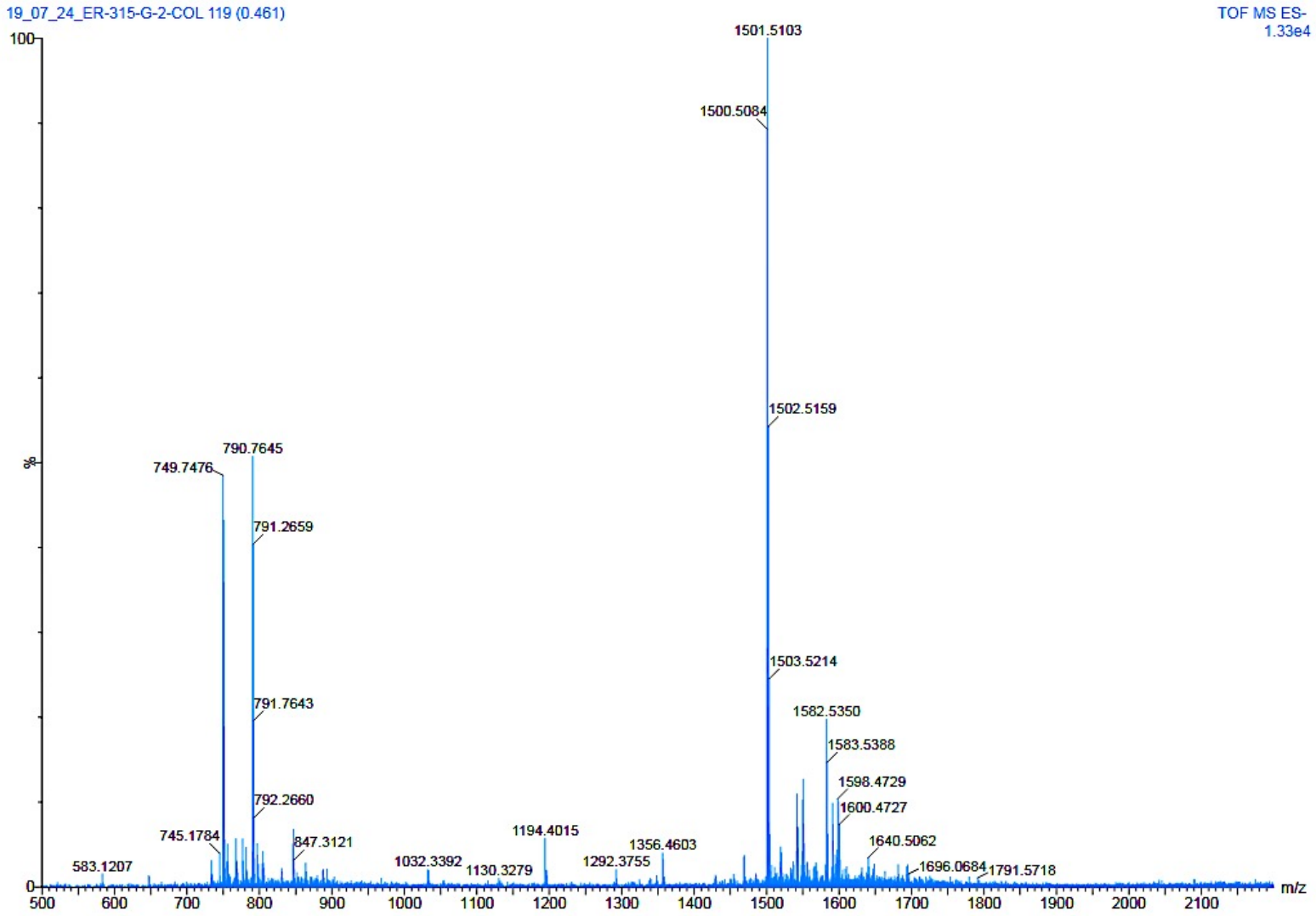
HR-MS (ES^+-TOF) spectrum for compound **IPCA–β–CD (10)**



^{1}H-NMR spectrum for compound **IPCA–γ–CD (11)**



^{13}C-NMR spectrum for compound **IPCA–γ–CD (11)**



HR-MS (ESI^-) spectrum for compound **IPCA–γ–CD (11)**