Supporting Information

A New Luminescent Ordered Liquid Crystalline Molecules with a 3-cyano-2-pyridone framework

Deepak Devadiga,[a] Ahipa T.N.,[a] VanishreeBhat S,[b] Sandeep Kumar[bc]*

[a] Centre for Nano and Material Sciences, Jain University, Jain Global Campus, Bangalore – 562112, India.

[b] Raman Research Institute, Soft Condensed Matter group, C. V. Raman Avenue, Bangalore 560080, India

[c] Department of Chemistry, Nitte Meenakshi Institute of Technology (NMIT), Yelahanka, Bangalore, 560064, India

* Corresponding Author e-mail address: tn.ahipa@jainuniversity.ac.in

Contents:

1. Experimental:

1.1. Materials and methods

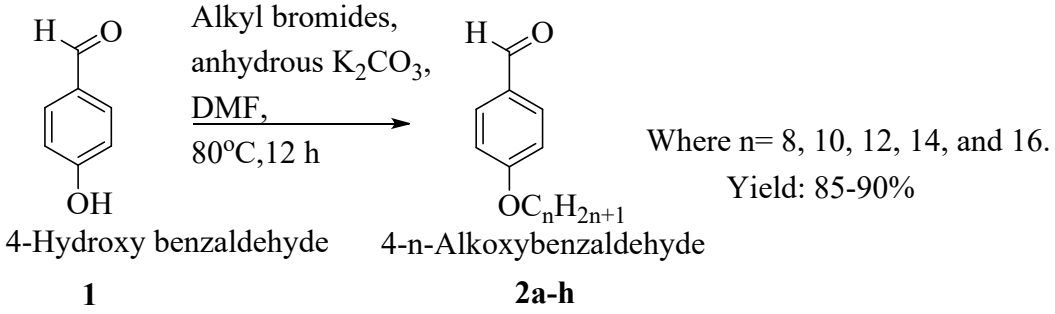
Alkyl bromides (n=8, 10, 12, 14, and 16) were procured from Spectrochem Pvt. Ltd. Mumbai (India). Ammonium acetate, methanol and ethylcyanoacetae were procured from SD-Fine-Chem Ltd, Mumbai (India). Ethylacetate was procured from Avra synthesis Pvt. Ltd. Telangana, India. IR spectra were collected using Bruker ALPHA eco-ATR-IR on ZnSe Crystal. ^{1}H and ^{13}C NMR spectra were obtained using 400 MHz and 100 MHz Bruker spectrometer with $CDCl_3$ as solvent and TMS as internal standard. ESI-MS was obtained from a Water Alliance e2695/HPLC-TQD Mass spectrometer. UV-visible absorption and emission properties were measured using UV-1800 SHIMADZU UV-spectrophotometer and RF-5301 PC, SHIMADZU spectrophotometer equipped with a Xe-lamp as an excitation source, respectively. Emission and excitation slit widths were kept as fixed, while recording emission spectra of all the samples. Mettler Toledo differential scanning calorimeter (DSC) was used to determine the transition temperatures by using 2-4 mg of sample at a scan rate of 5 ºC/min. The mesophase textures were observed using an Olympus BX51 polarizing optical microscope equipped with a Mettler FP82HT heating stage and a Mettler FP90 central processor. X-ray diffraction (XRD) measurements on powder samples were carried out using PAN alytical, Empyrean diffractometer using Cu-Kα (λ = 1.54 Å) beam. The sample was filled in Lindemann capillaries (0.7 mm diameter).

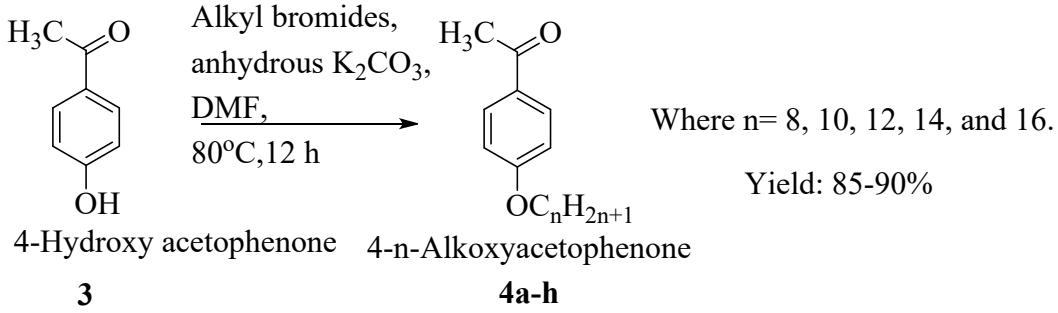
Cyclic voltammetry (CV) data were determined in a N_2-saturated three-electrode system, where, the working, counter and reference electrodes are glassy carbon, platinum and Ag/Ag^+, respectively. The glassy carbon electrode was polished with 1.0μm alumina slurry and then sonicated for 10 min in distilled water. The **Pn**-series compound solution in chloroform was drop casted on to the glassy carbon disk and dried to get a uniform thin film, which was later dipped into acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. Further, the electrochemical measurements were made at a scan rate of 100 mV/s. The Ag/Ag^+ reference electrode was calibrated using a ferrocene/ ferrocenium (Fc/Fc^+) redox couples as an external standard.

1.2. Synthesis

Step 1: Synthesis of 4-n-alkoxy benzaldehyde (**2a-h**) and 4-n-alkoxy acetophenone (**4a-h**)

The 4-n-alkoxy benzaldehyde (**2a-h**) and 4-n-alkoxy acetophenone (**4a-h**) were prepared from 4-hydroxybenzadehyde (**1**) and 4-hydroxyacetophenone (**2**) respectively by reacting with the corresponding alkyl bromide following the standard procedures.[1-2]



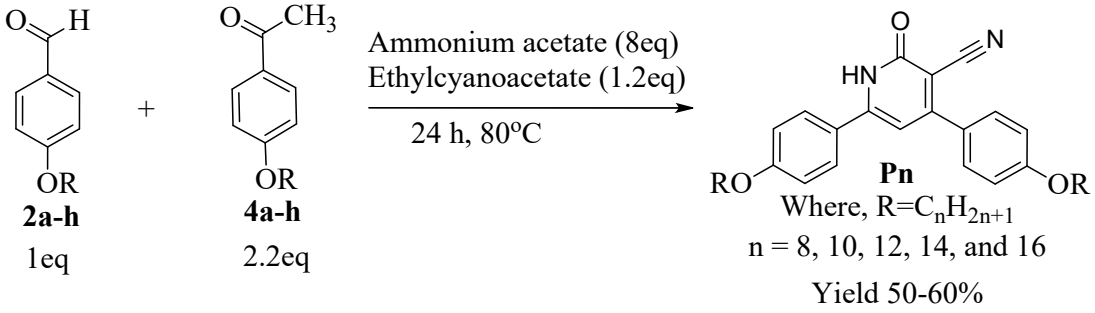


Scheme S1: General synthetic route for **2a-h** and **4a-h**

Step 2: Synthesis of 4,6-bis(4-alkoxyphenyl)-2-oxo-1,2-dihydropyridine-3-carbonitrile (**Pn**)

A mixture of 4-n-alkoxybenzaldehyde (**2a-h,** 1 equivalent), 4-n-alkoxyacetophenone (**4a-h,** 2 equivalent), and ethyl cyanoacetate (**5,** 1.2 equivalent) was taken in 1,4-dioxane and added ammonium acetate (8 equivalent) to it and stirred the reaction mixture at 80 °C for 24 h. After completion of the reaction, reaction mixture was added to the water and obtained precipitate was

filtered. Finally crude product was washed with little amount of methanol and ethyl acetate to obtain the pure expected compounds (**Pn**). Data for the synthesized compounds are given below,



Scheme S2: General synthetic route for **Pn**

Data for 4,6-bis(4-octyloxyphenyl)-2-oxo-1,2-dihydropyridine-3-carbonitrile (**P-8**): Pale greenish yellow solid, yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.77 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.05 (dd, *J* = 17.5, 8.3 Hz, 4H), 6.67 (s, 1H), 4.03 (bs, 4H), 1.81 (bd, *J* = 6.2 Hz, 4H), 1.46 (bs, 4H), 1.30 (bs, 16H), 0.90 (bs, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.20, 162.21, 161.27, 160.42, 150.24, 129.79, 128.83, 128.19, 123.59, 115.43, 114.89, 105.38, 97.70, 68.39, 68.28, 31.83, 29.35, 29.24, 29.16, 26.04, 26.00, 22.67, 14.12. IR (ATR, cm^{-1}): 3084, 2919, 2850, 2208, 1632, 1597, 1511, 1175, 826. ESI-MS (m/z): $(M+H)^+$ = 529.72.

Data for 4,6-bis(4-decyloxyphenyl)-2-oxo-1,2-dihydropyridine-3-carbonitrile (**P-10**): Pale greenish yellow solid, yield 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.06 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.04 (dd, *J* = 16.8, 8.3 Hz, 4H), 6.67 (s, 1H), 4.02 (bs, 4H), 1.81 (bd, *J* = 5.7 Hz, 4H), 1.46 (bs, 4H), 1.28 (bs, 23H), 0.89 (bs, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.31, 162.19, 161.23, 160.35, 150.28, 129.78, 128.88, 128.19, 123.54, 116.46, 115.38, 114.86, 105.38, 97.61, 68.36, 68.25, 31.90, 29.57, 29.39, 29.33, 29.14, 26.02, 25.99, 22.69, 14.13. IR (ATR, cm^{-1}): 3083, 2919, 2851, 2210, 1631, 1597, 1513, 1176, 826. ESI-MS (m/z): $(M+H)^+$ =585.89.

Data for 4,6-bis(4-dodecyloxyphenyl)-2-oxo-1,2-dihydropyridine-3-carbonitrile (**P-12**): Pale greenish yellow solid, yield 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.81 (s, 1H), 7.88 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.05 (dd, *J* = 17.6, 8.6 Hz, 4H), 6.67 (s, 1H), 4.03 (t, *J* = 6.1 Hz, 4H), 1.81 (bd, *J* = 6.6 Hz, 4H), 1.46 (bs, 4H), 1.27 (bs, 32H), 0.88 (bs, 6H). ^{13}C NMR (100

MHz, $CDCl_3$) δ 164.28, 162.20, 161.25, 160.37, 150.28, 129.78, 128.86, 128.20, 123.57, 116.45, 115.40, 114.87, 105.38, 97.64, 68.37, 68.27, 31.93, 29.68, 29.65, 29.60, 29.39, 29.36, 29.14, 26.02, 25.99, 22.70, 14.13. IR (ATR, cm^{-1}): 3083, 2919, 2850, 2211, 1632, 1598, 1512, 1176, 825. ESI-MS (m/z): $(M+H)^+$ = 642.02.

Data for 4,6-bis(4-tetradecyloxyphenyl)-2-oxo-1,2-dihydropyridine-3-carbonitrile (**P-14**): Pale greenish yellow solid, yield 50%. ^1H NMR (400 MHz, $CDCl_3$) δ 12.75 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.05 (dd, *J* = 17.5, 8.4 Hz, 4H), 6.66 (s, 1H), 4.03 (bs, 4H), 1.81 (bd, *J* = 6.0 Hz, 4H), 1.46 (bs, 4H), 1.26 (bs, 40H), 0.88 (bs, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.31, 162.19, 161.23, 160.34, 150.28, 129.78, 128.87, 128.19, 123.54, 116.46, 115.38, 114.86, 105.37, 97.61, 68.36, 68.25, 31.93, 29.68, 29.61, 29.59, 29.57, 29.39, 29.37, 29.16, 26.02, 25.99, 22.70, 14.13. IR (ATR, cm^{-1}): 3084, 2917, 2849, 2224, 1626, 1605, 1515, 820. ESI-MS (m/z): $(M+H)^+$ = 698.10.

Data for 4,6-bis(4-hexadecyloxyphenyl)-2-oxo-1,2-dihydropyridine-3-carbonitrile (**P-16**): Pale greenish yellow solid, yield 60%. ^1H NMR (400 MHz, $CDCl_3$) δ 12.79 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.05 (dd, *J* = 17.5, 8.5 Hz, 4H), 6.67 (s, 1H), 4.03 (bs, 4H), 1.81 (bd, *J* = 6.5 Hz, 4H), 1.46 (bs, 4H), 1.26 (bs, 48H), 0.88 (bs, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.34, 162.21, 161.25, 160.35, 150.31, 129.80, 128.90, 128.21, 123.55, 116.49, 115.39, 114.87, 105.38, 97.62, 68.37, 68.27, 31.95, 29.73, 29.70, 29.64, 29.61, 29.43, 29.40, 29.18, 26.05, 26.01, 22.72, 14.15. IR (ATR, cm^{-1}): 3079, 2917, 2849, 2224, 1626, 1607, 1515, 820. ESI-MS (m/z): $(M+H)^+$ = 754.07.

2. Analytical data

2.1. ATR-IR spectra

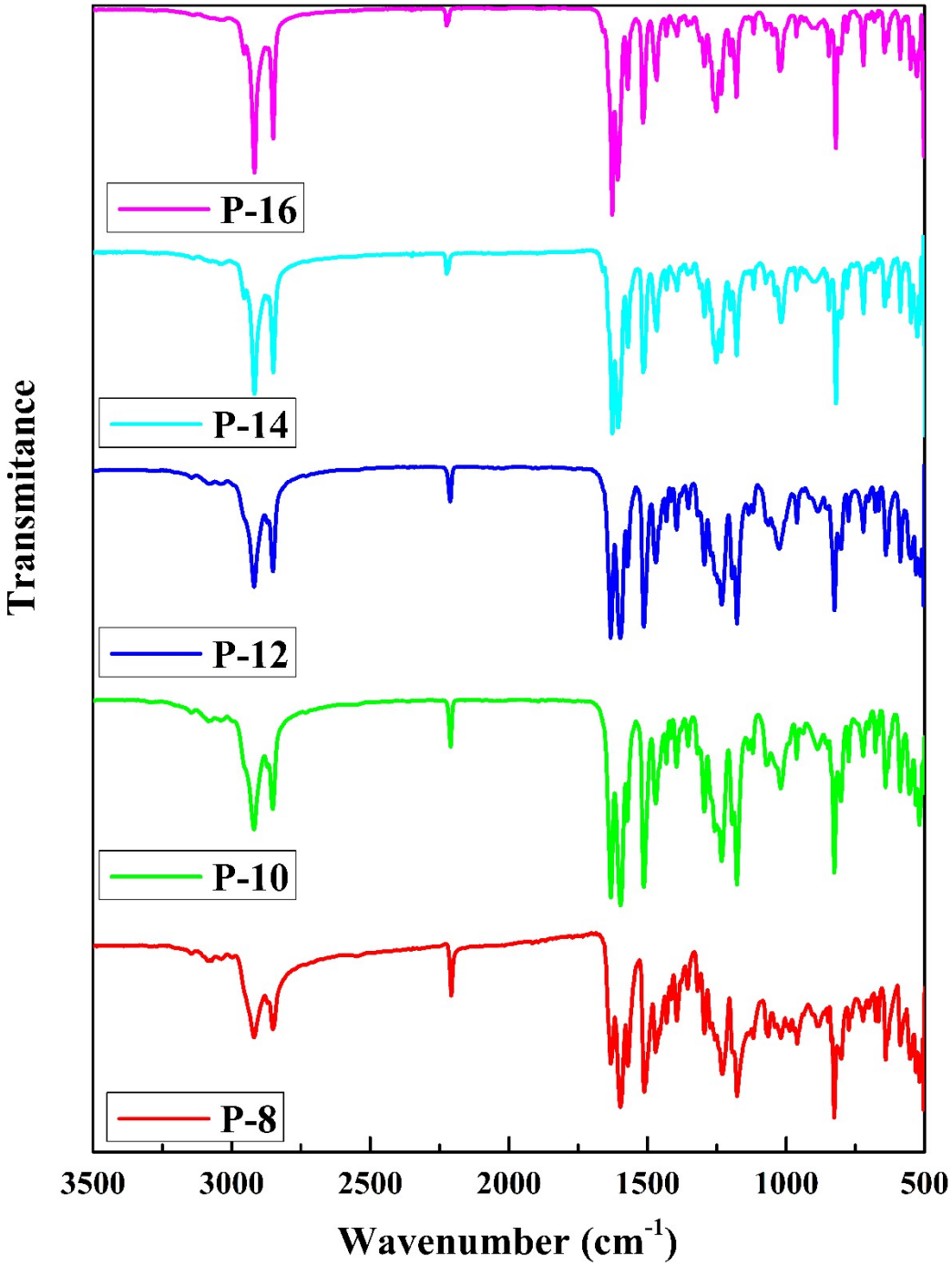


Figure S1: ATR-IR spectra of **Pn** series

2.2. ^{1}H and ^{13}C NMR spectra

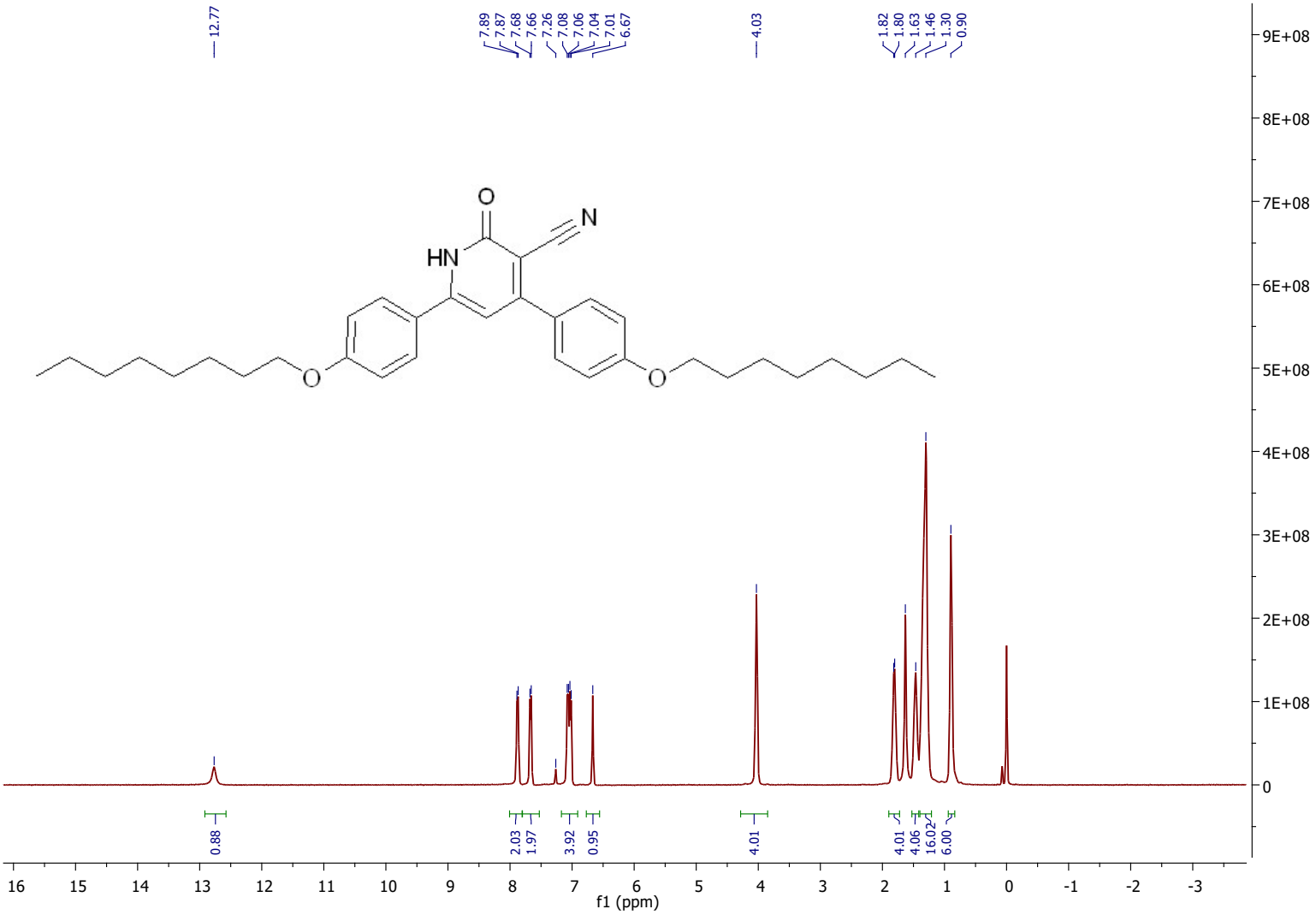


Figure S2: ^{1}H NMR spectrum of **P-8** in $CDCl_3$ (400 MHz).

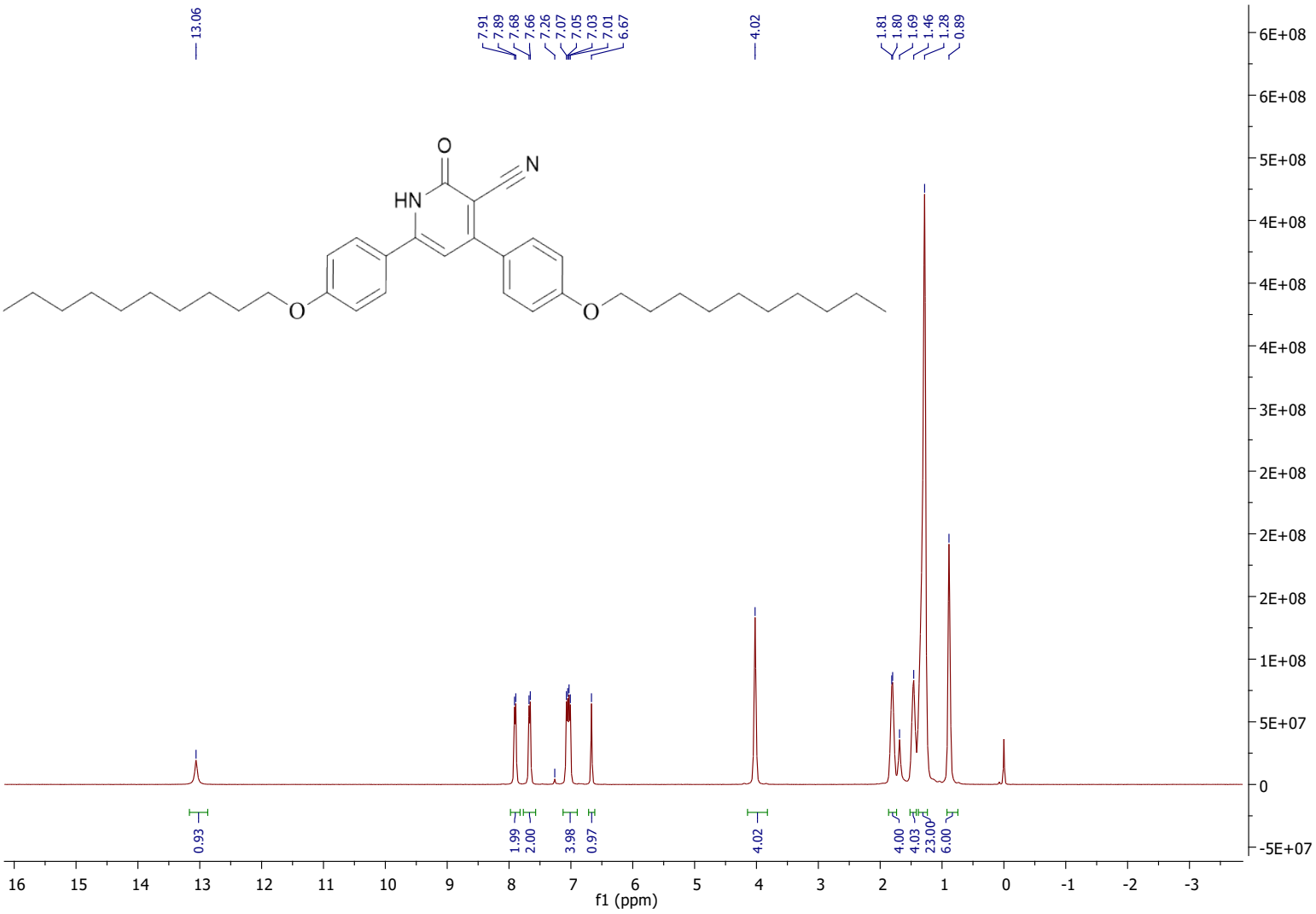


Figure S3: ^{1}H NMR spectrum of **P-10** in $CDCl_3$ (400 MHz).

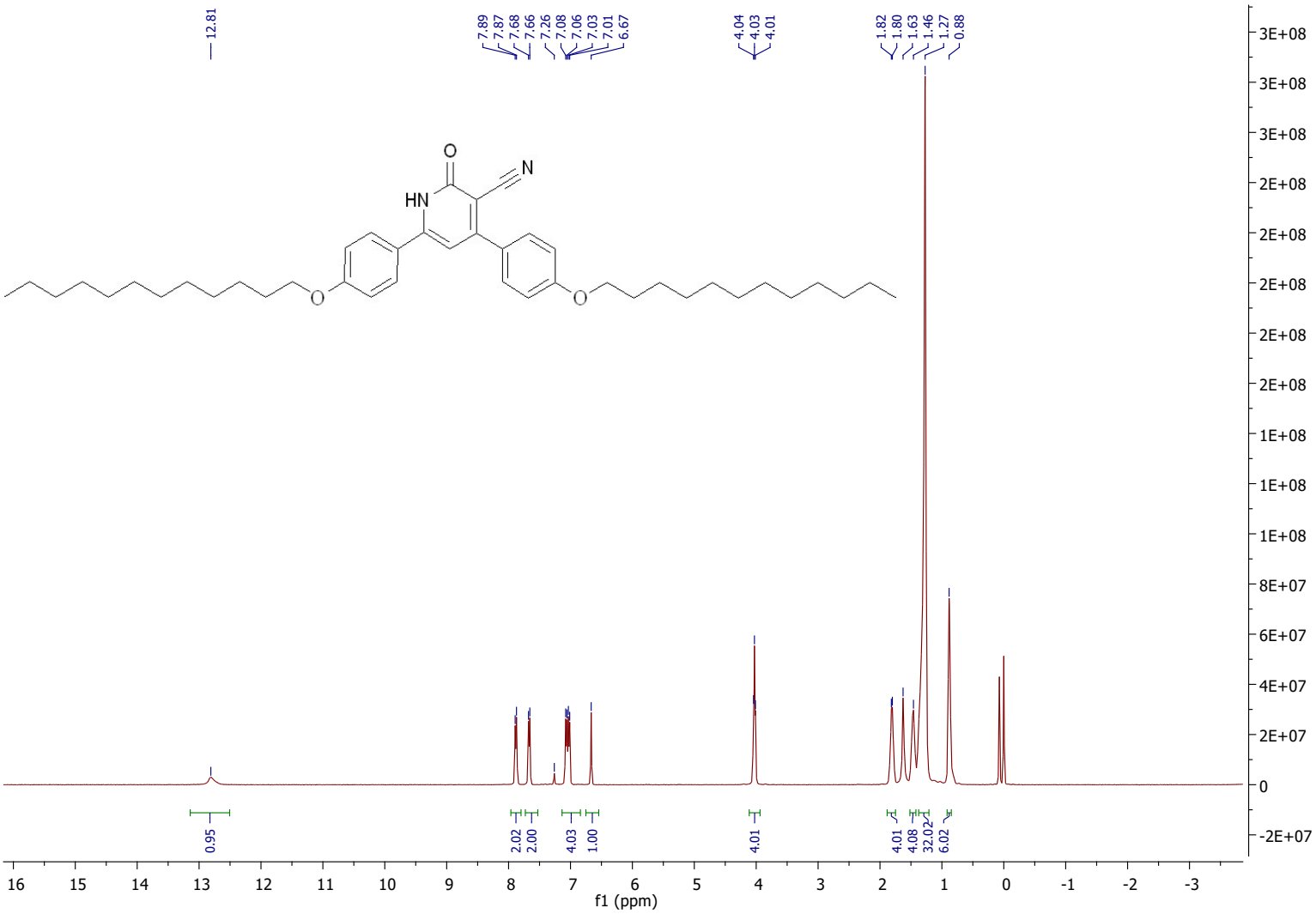


Figure S4: ^{1}H NMR spectrum of **P-12** in $CDCl_3$ (400MHz).

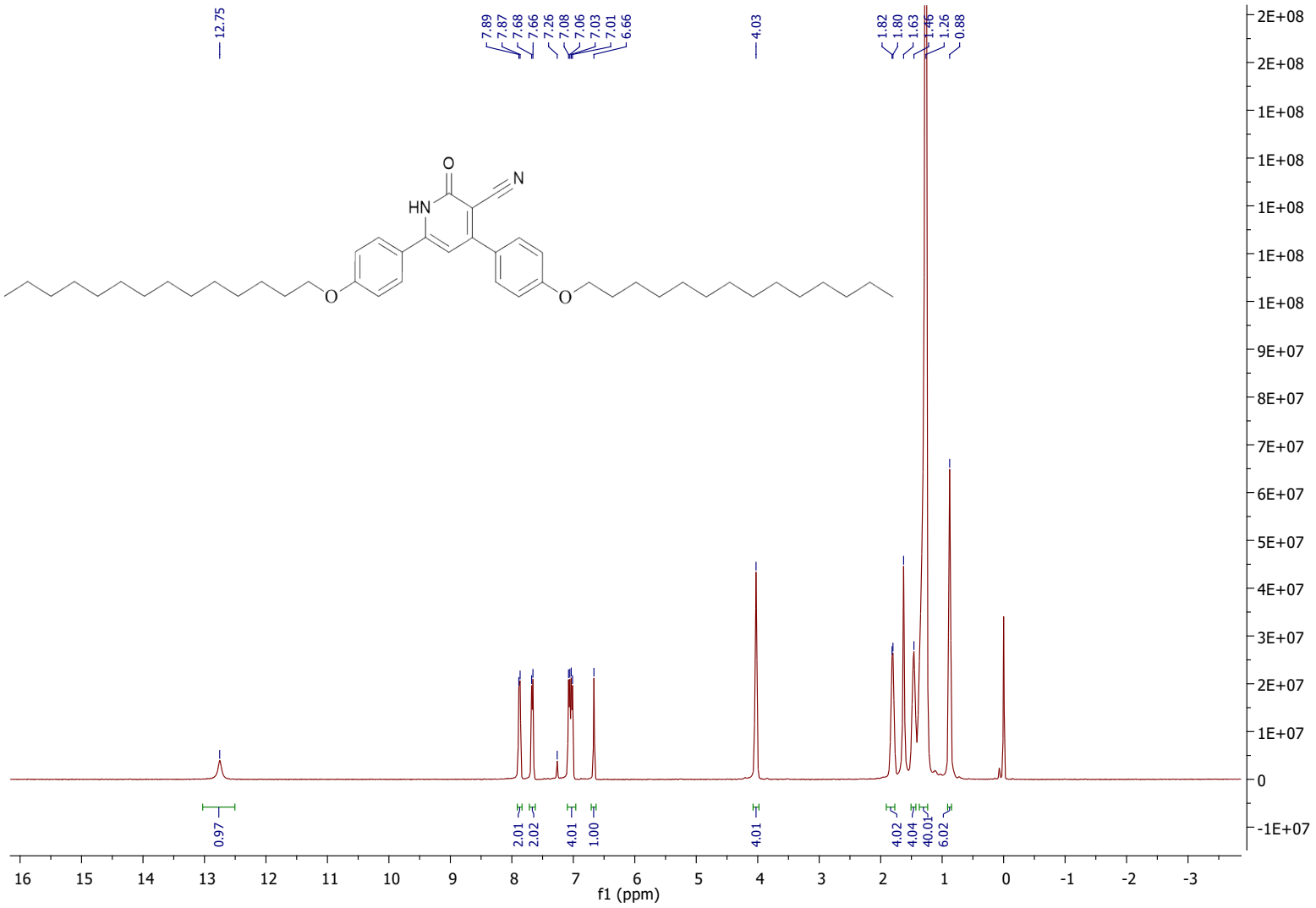


Figure S5: ^{1}H NMR spectrum of **P-14** in $CDCl_3$ (400 MHz).

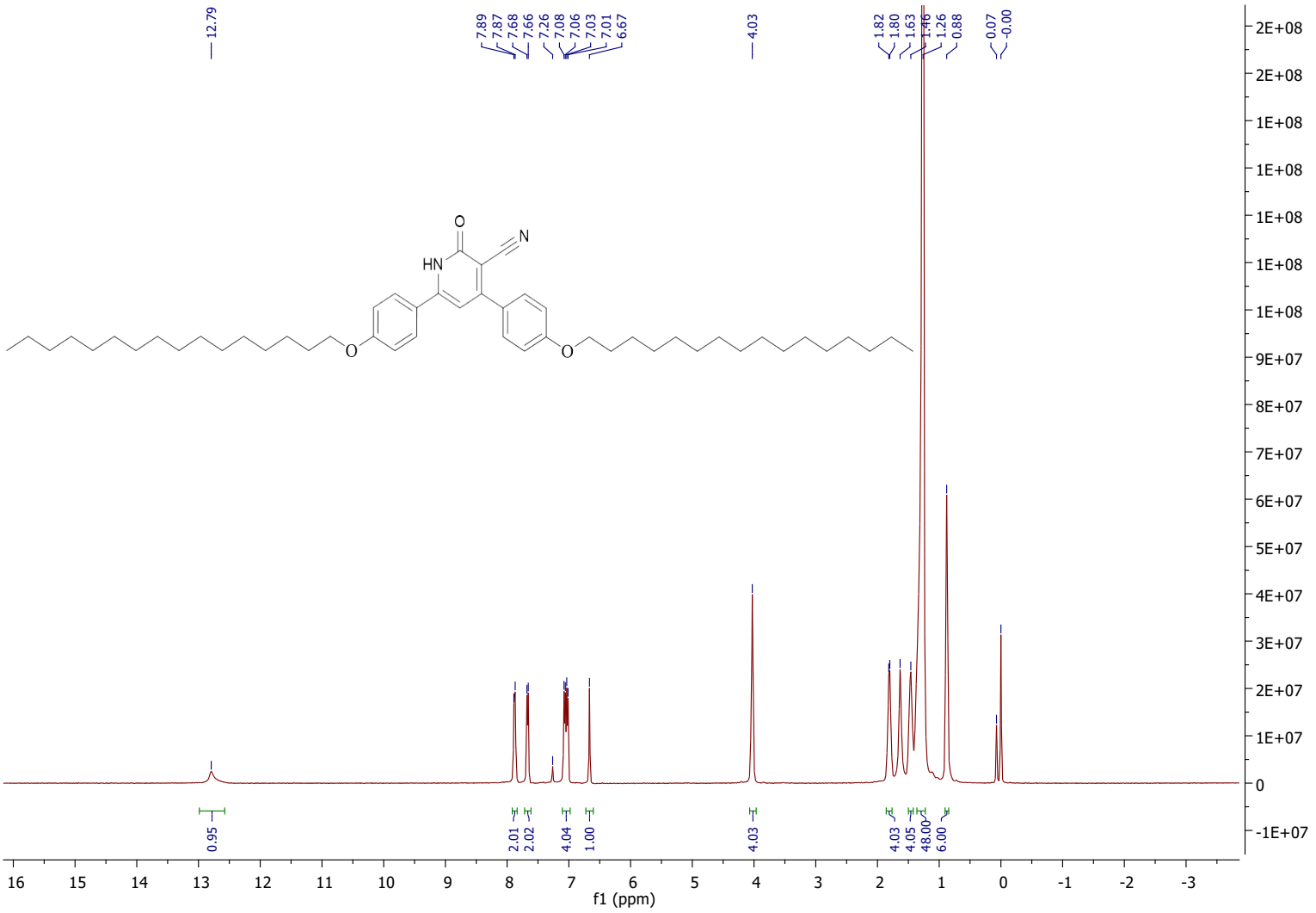


Figure S6: ^{1}H NMR spectrum of **P-16** in $CDCl_3$ (400 MHz).

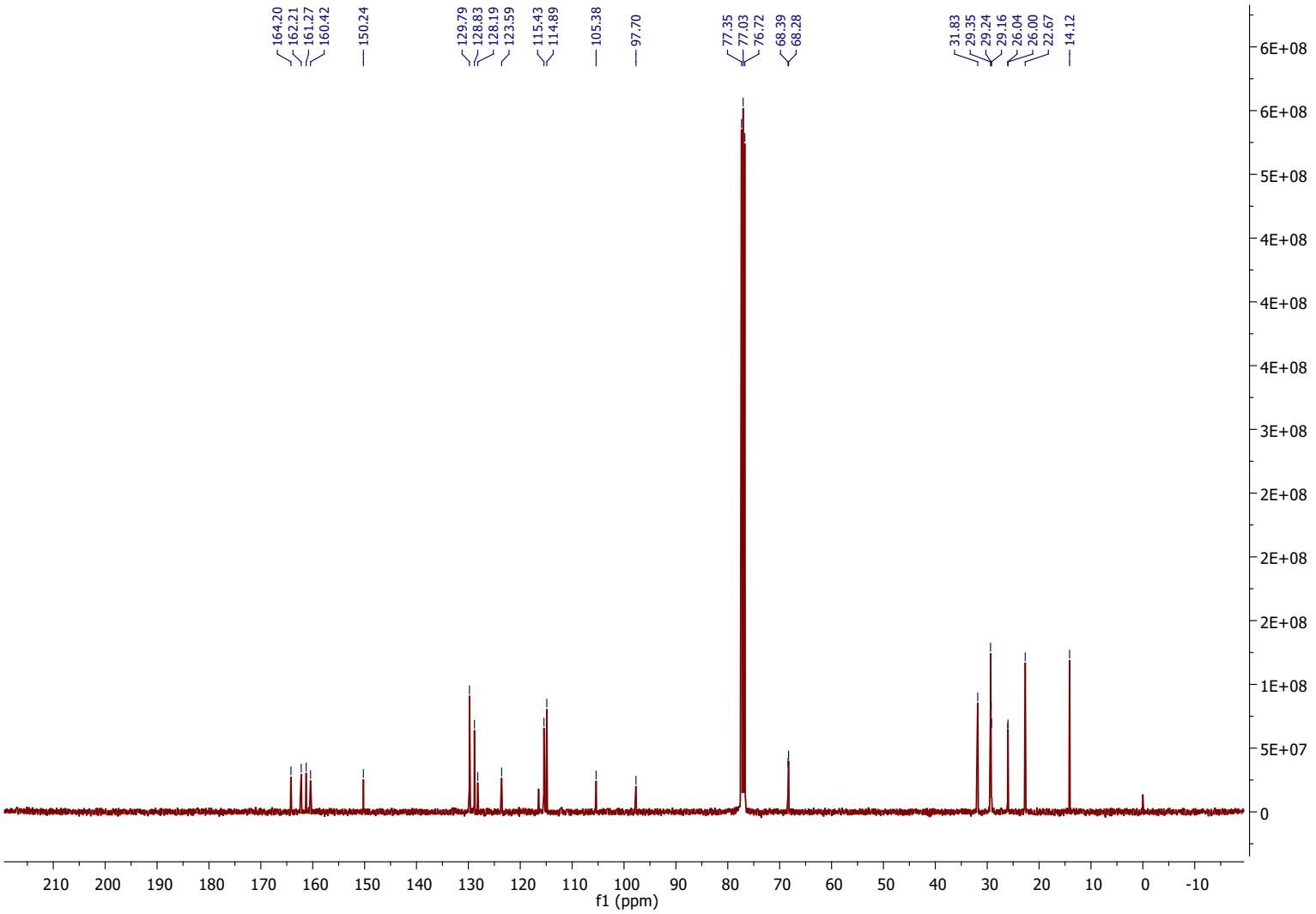


Figure S7: ^{13}C NMR spectrum of **P-8** in $CDCl_3$ (100 MHz).

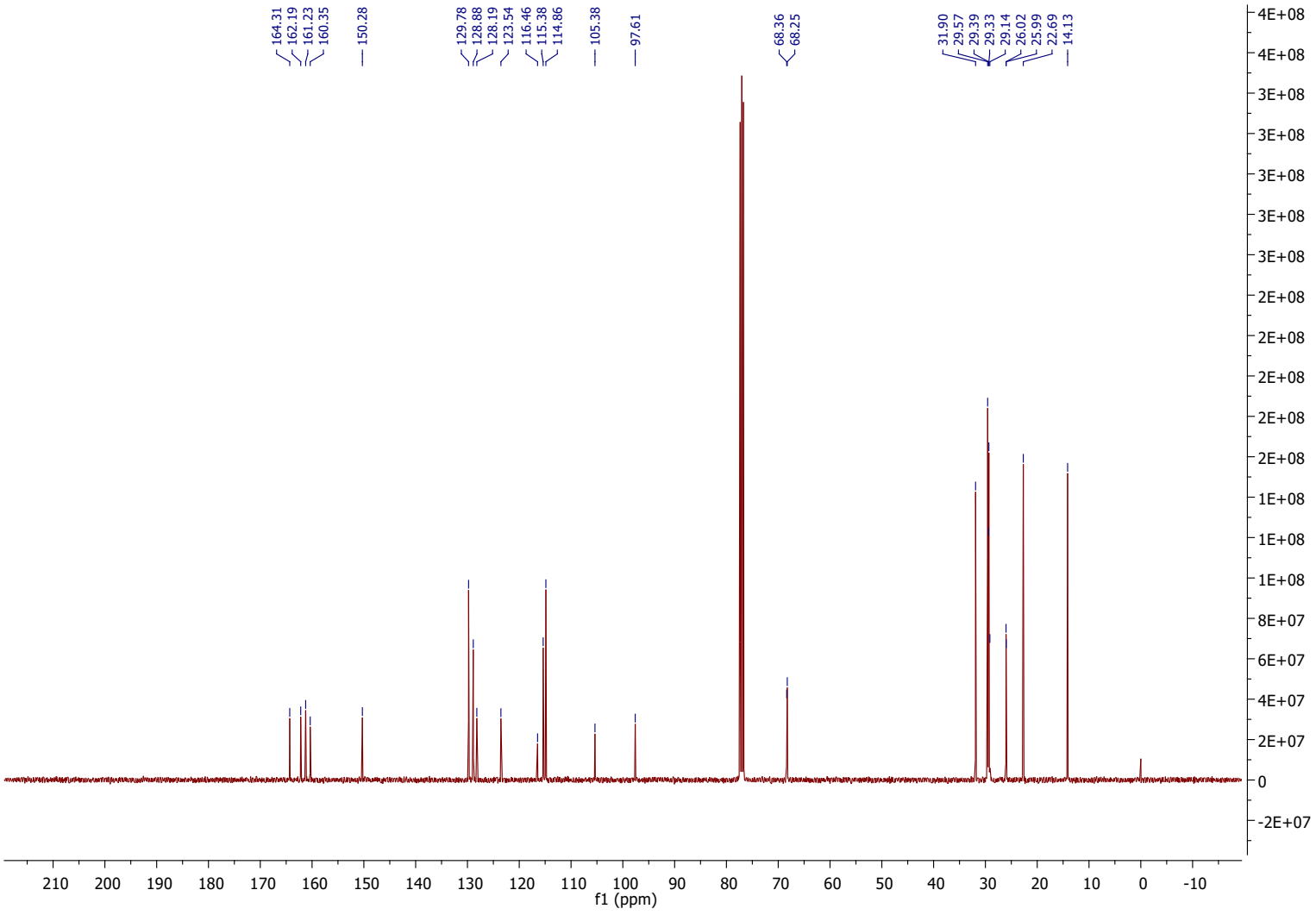


Figure S8: ^{13}C NMR spectrum of **P-10** in $CDCl_3$ (100 MHz).

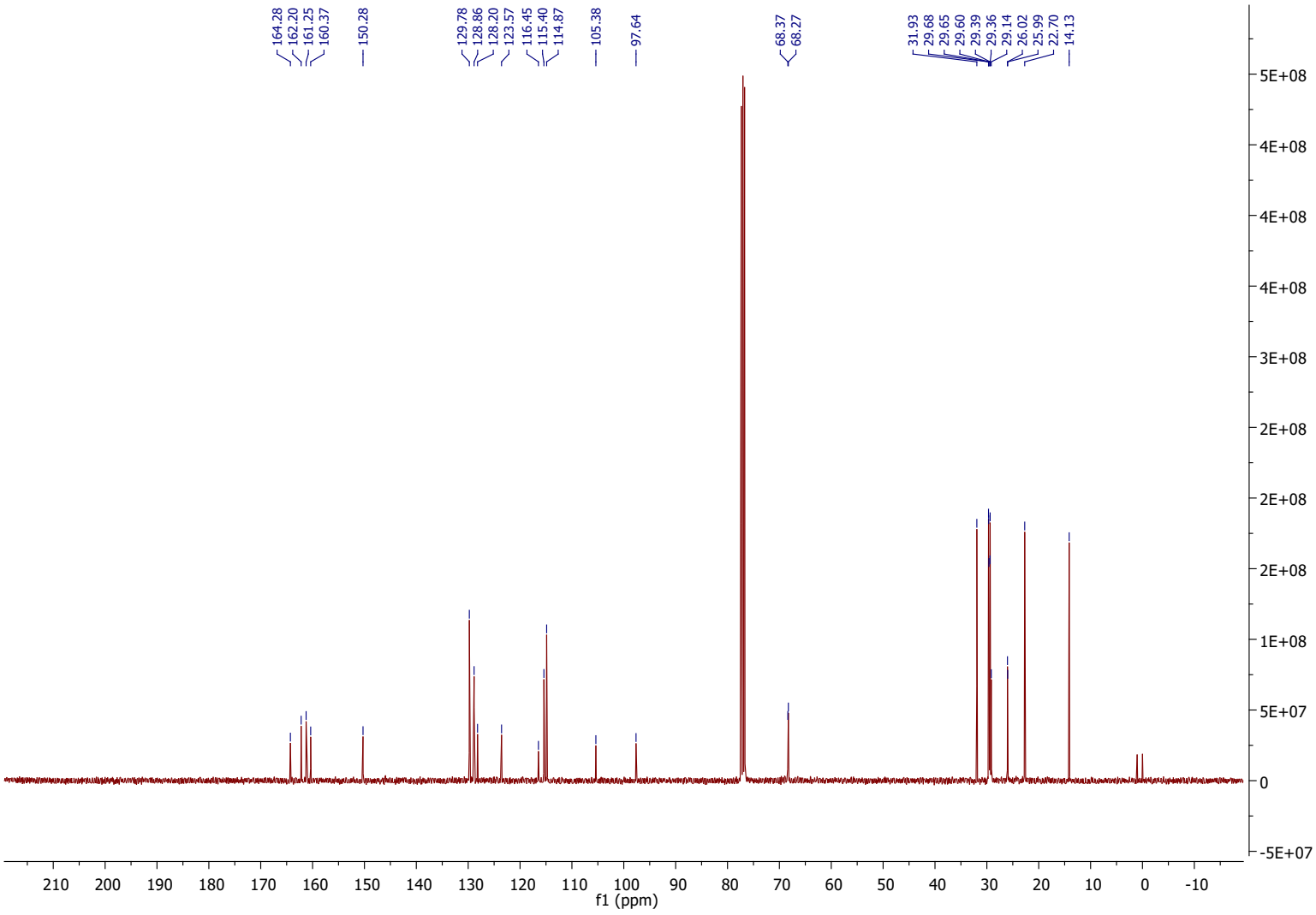


Figure S9: ^{13}C NMR spectrum of **P-12** in $CDCl_3$ (100 MHz).

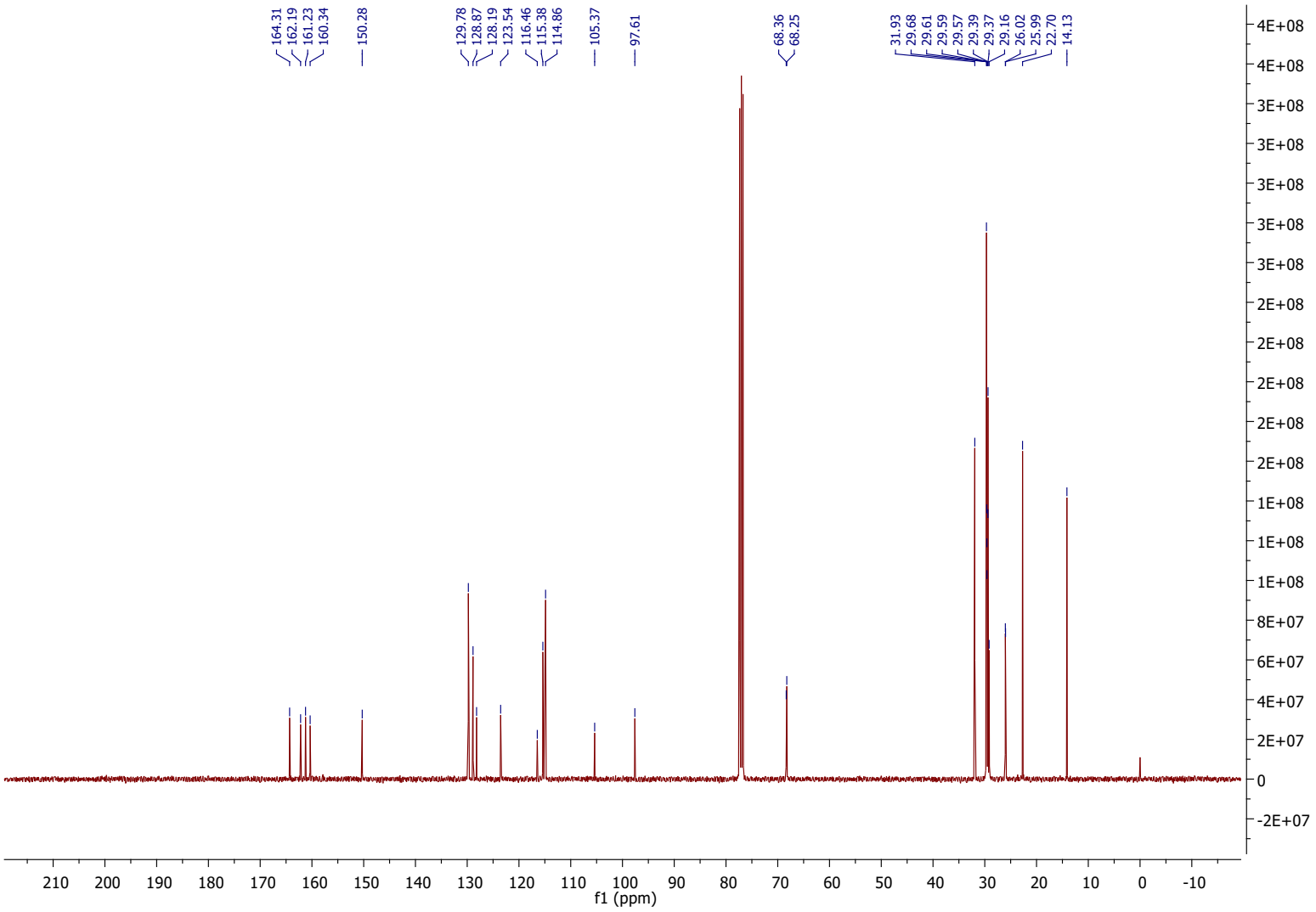


Figure S10: ^{13}C NMR spectrum of **P-14** in $CDCl_3$ (100 MHz).

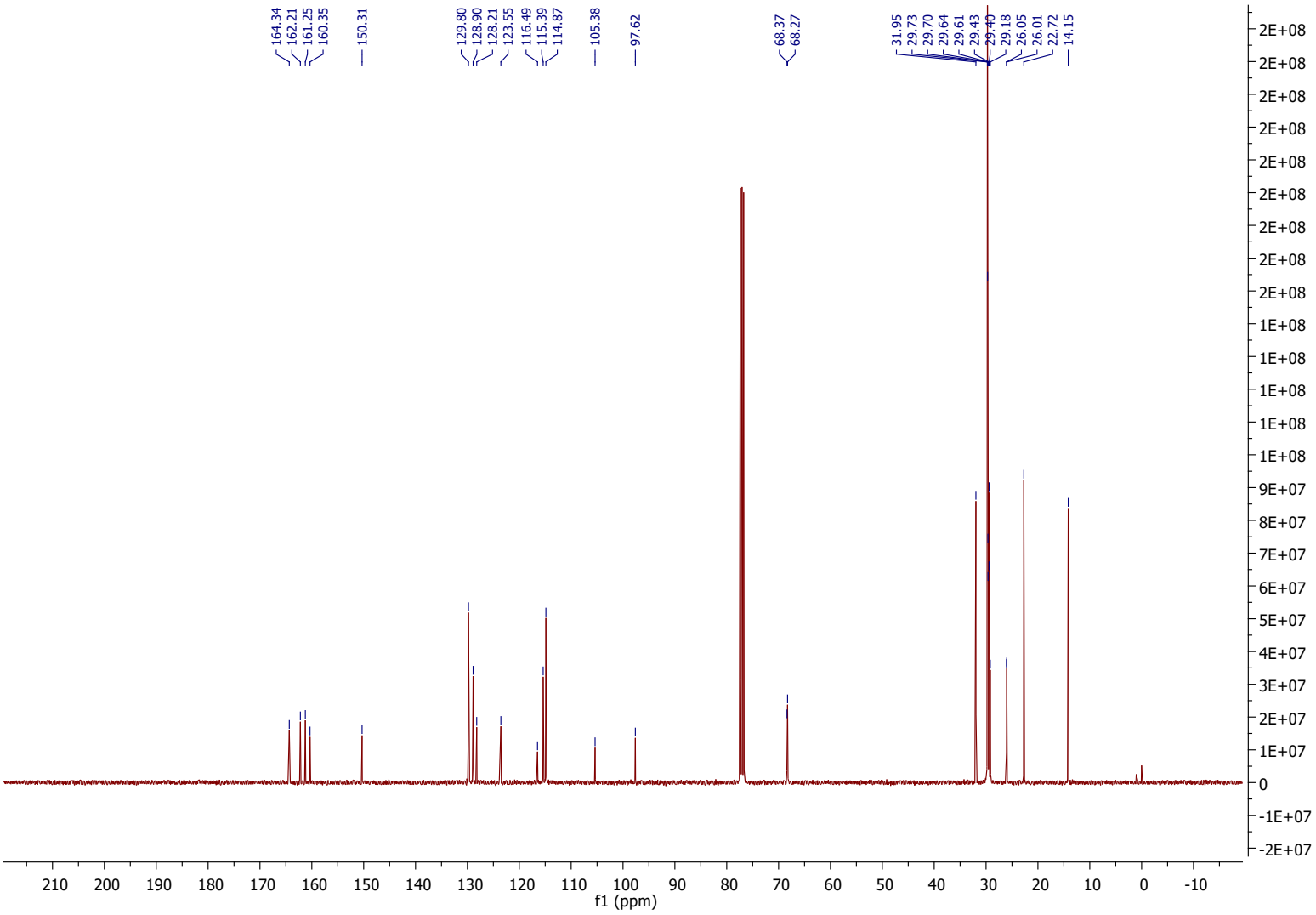


Figure S11: ^{13}C NMR spectrum of **P-16** in $CDCl_3$ (100 MHz).

2.3. ESI-MS spectra

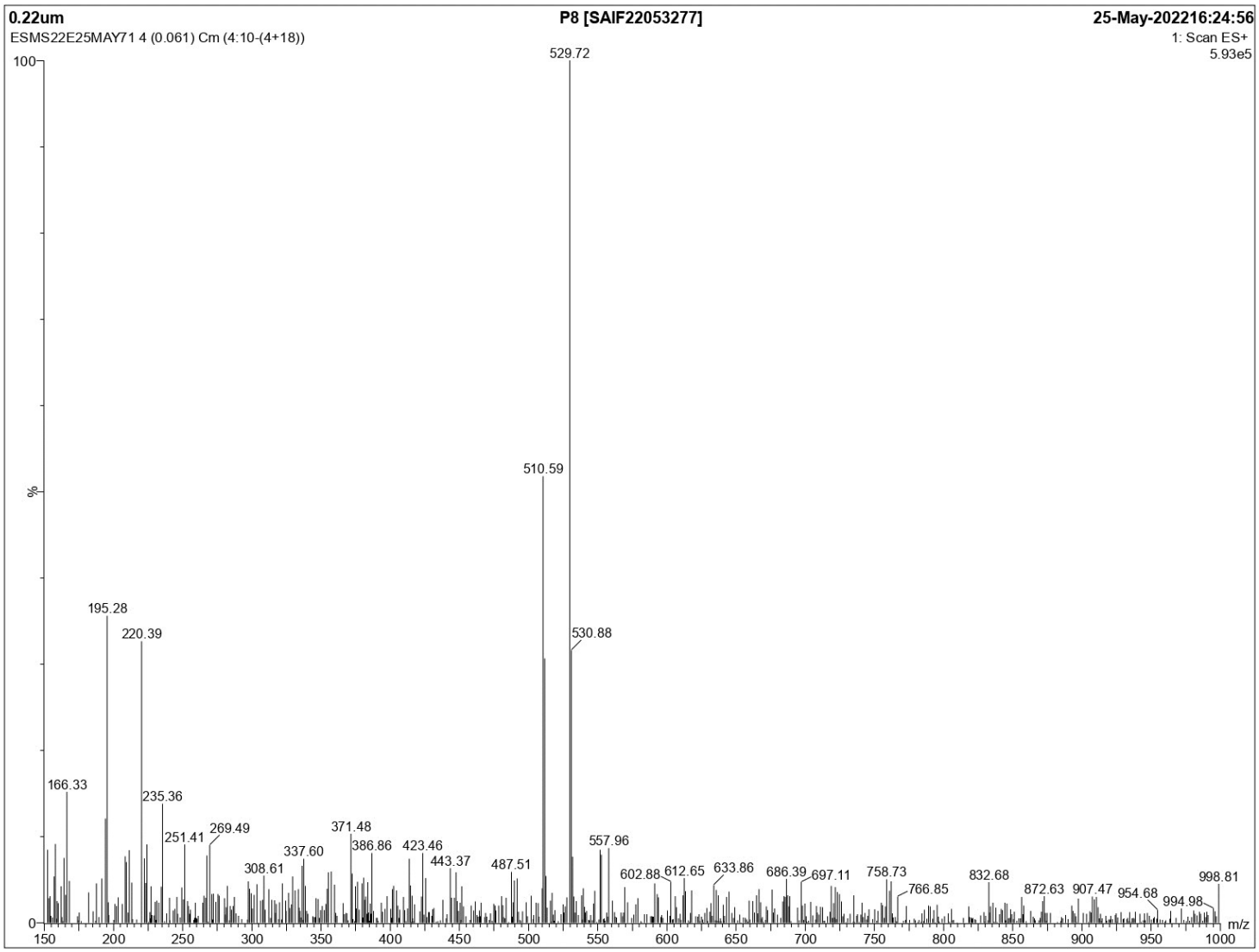


Figure S12: ESI-MS spectrum of **P-8**.

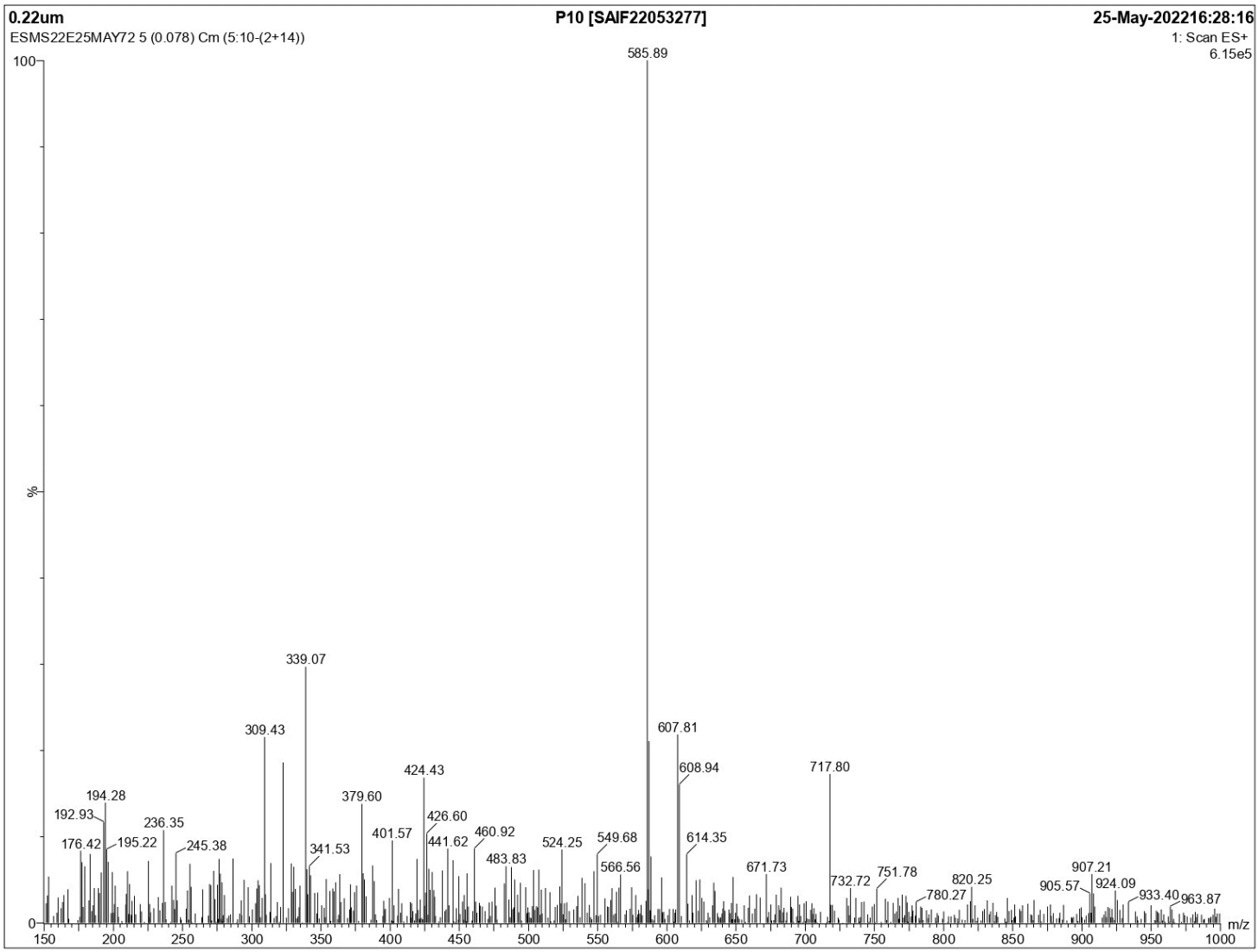


Figure S13: ESI-MS spectrum of **P-10.**

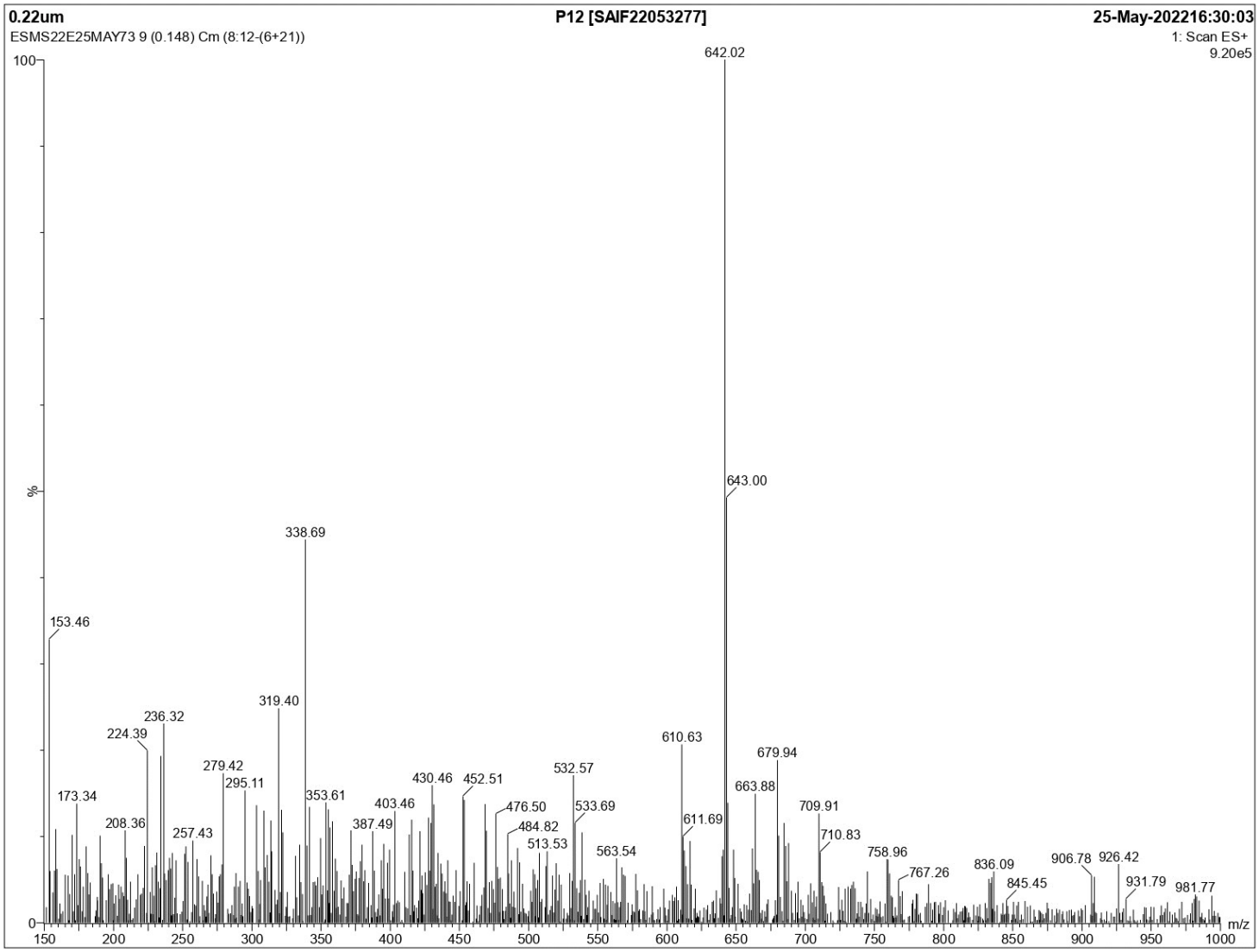


Figure S14: ESI-MS spectrum of **P-12.**

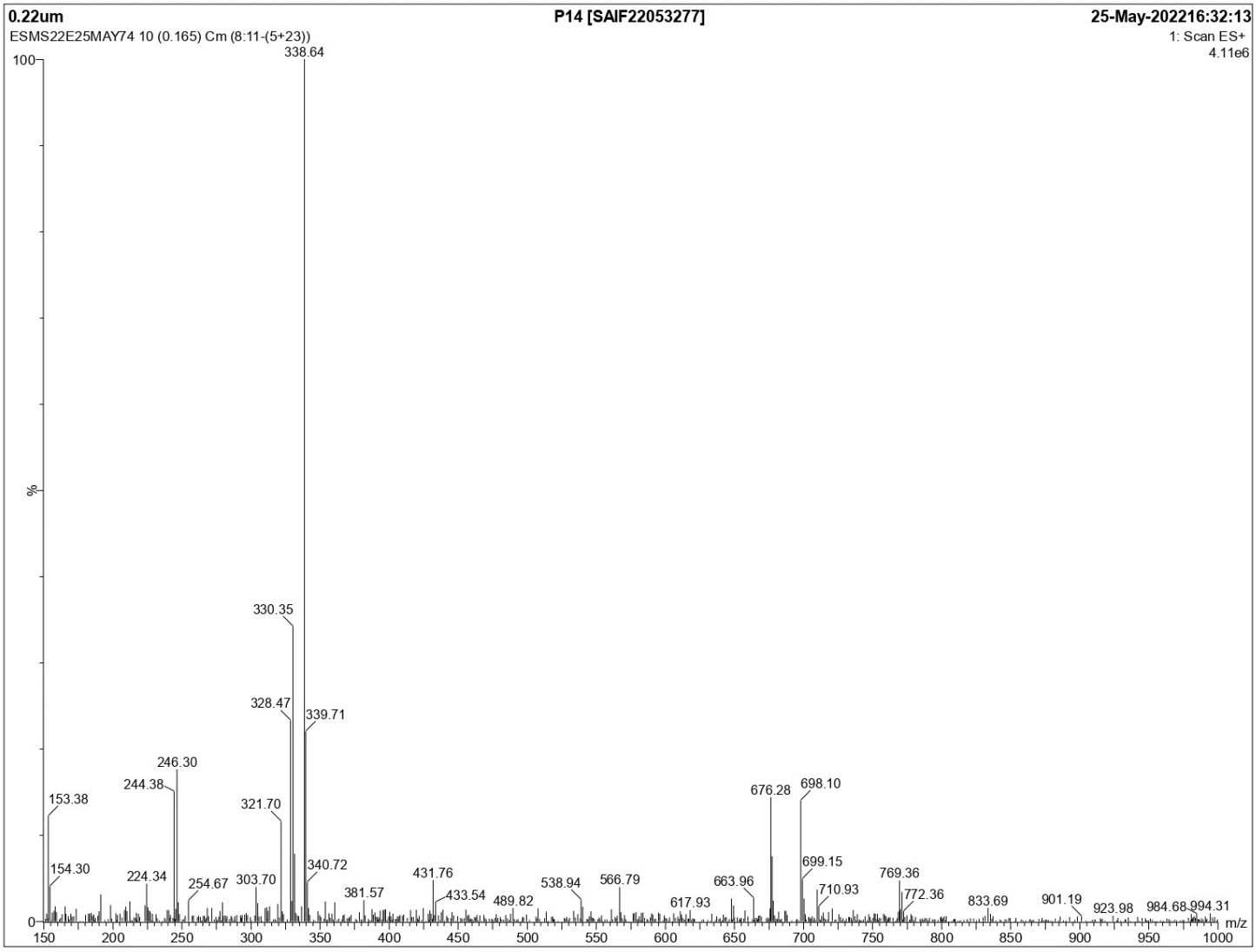


Figure S15: ESI-MS spectrum of **P-14.**

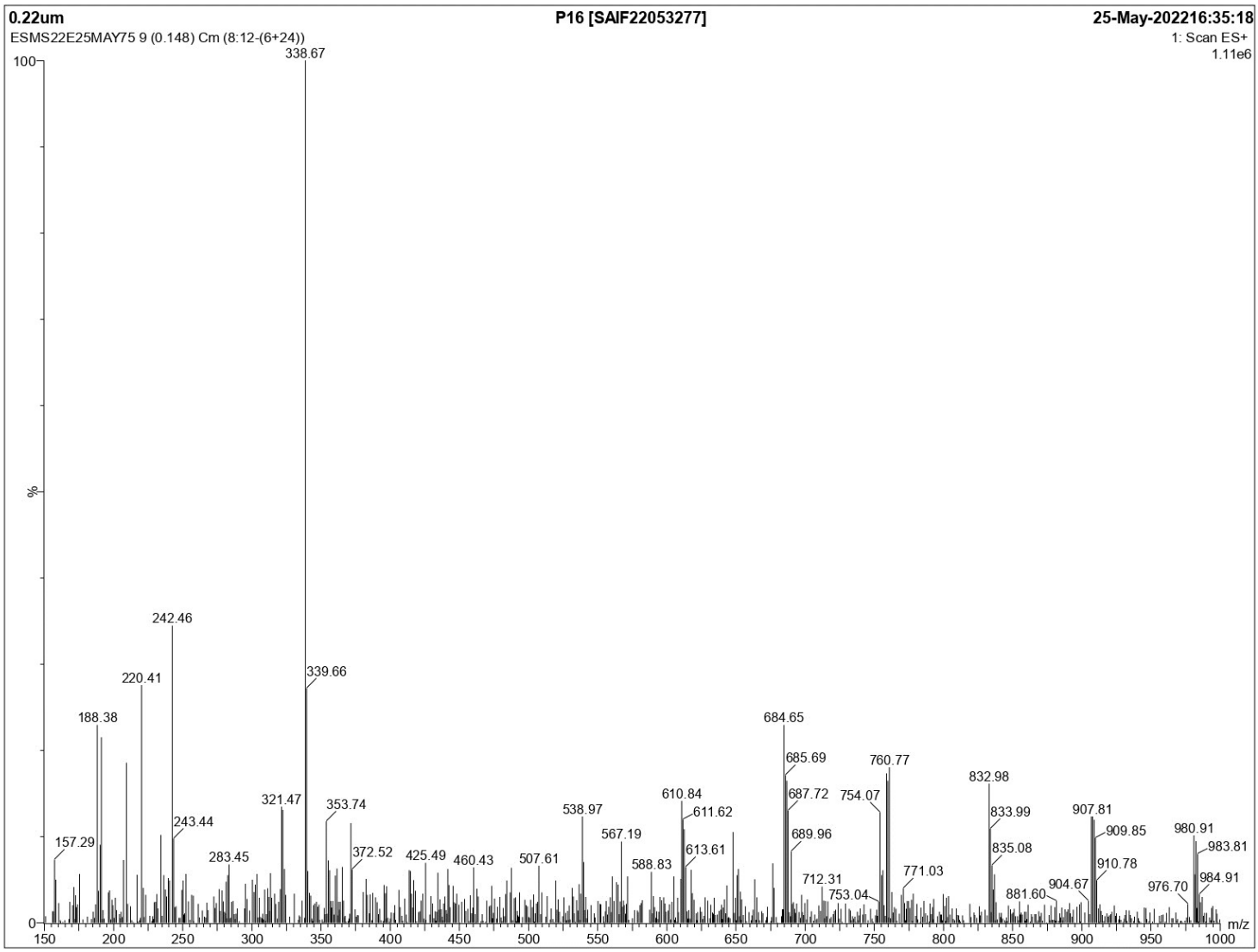


Figure S16: ESI-MS spectrum of **P-16.**

2.4. CIE-Coordinate diagrams

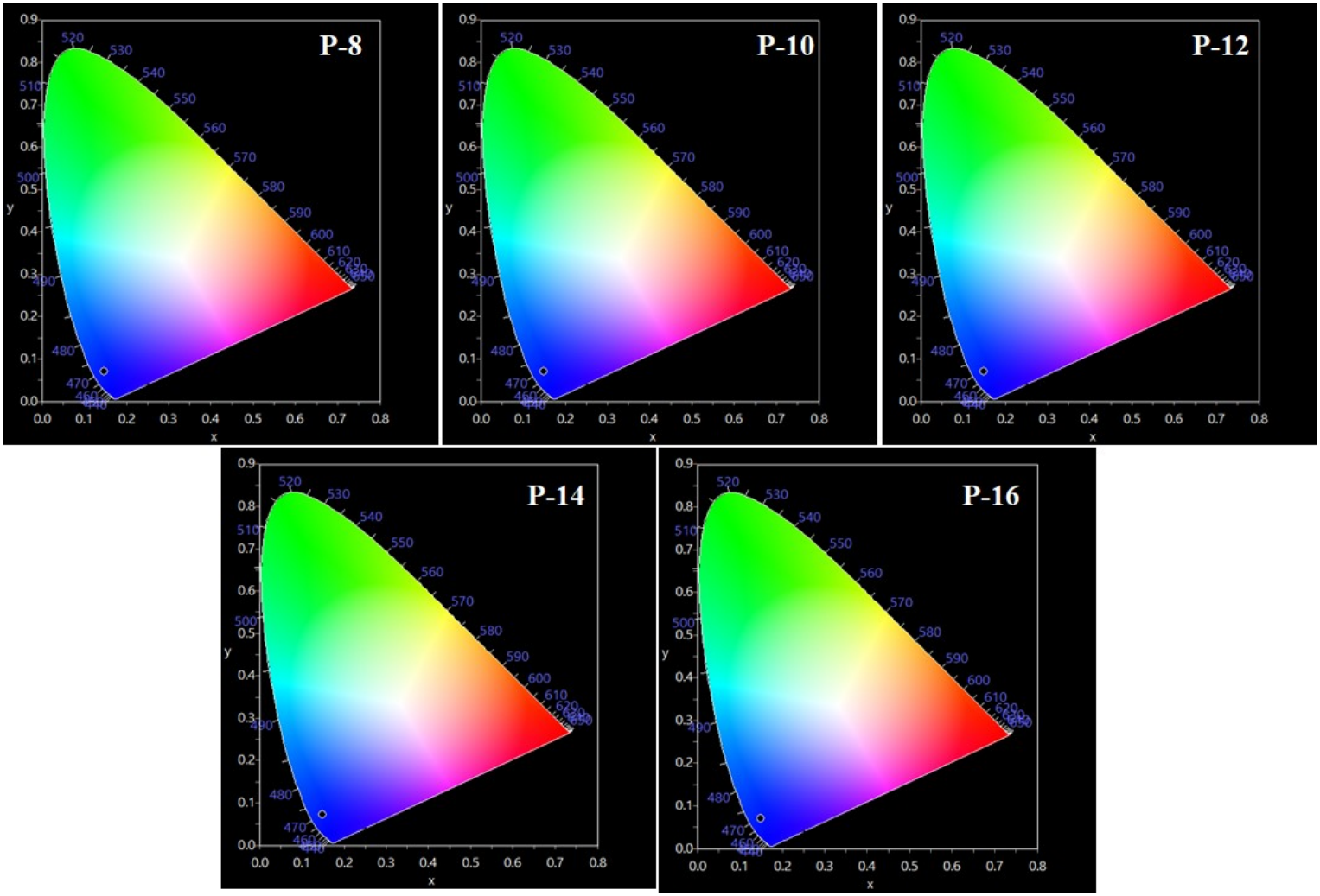


Figure S17: CIE co-ordination images for **Pn**-series.

2.5. Polarized optical microscopy images

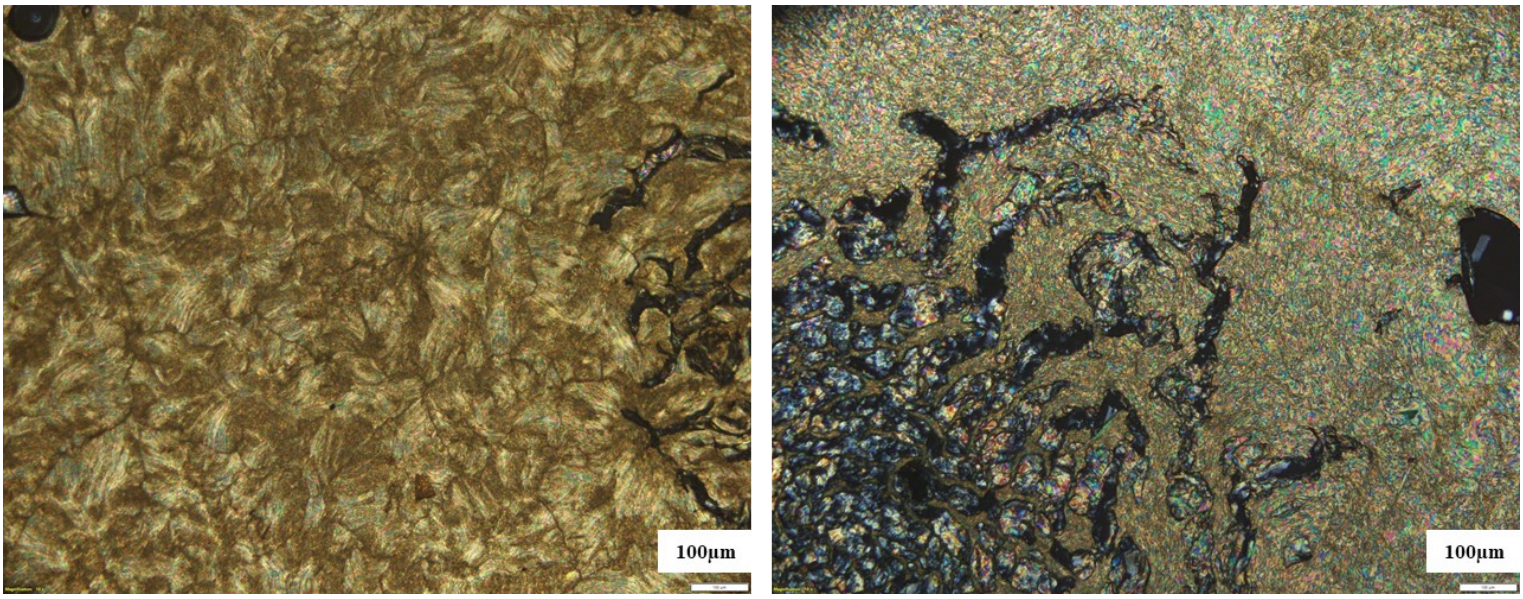


Figure S18: Smearing of the samples **P-12** and **P-14** at 135 °C and 151°C, respectively.

References:

(1) Tantrawong, S.; Styring, P.; Goodby, J.W. Discotic Mesomorphism in Oxovanadium (IV) Complexes Possessing Four Alkyl Substituents. J. Mater. Chem. 1993, 3, 1209-1216.

(2) Kozhevnikov, V. N.; Cowling, S. J.; Karadakov, P. B.; Bruce, D. W. Mesomorphic 1,2,4-triazine-4-oxides in the synthesis of new heterocyclic liquid crystals. J. Mater. Chem. 2008, 18, 1703-1710.