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A practical general method for the preparation of long acenes

Andrej Jancarik, * Gaspard Levet and André Gourdon *

Abstract: The field of long acenes, the narrowest of the zig-zag graphene nanoribbons, has been an area of significant interest in the past decade due to potential applications in organic electronics, spintronics and plasmonics. However their low solubility and high reactivity has so far hindered their preparation on large scales. We report here a concise strategy for the synthesis of higher acenes through Diels-Alder condensation of arynes with a protected tetraene ketone. After deprotection by cleavage of the ketal, the obtained monoketone precursors cleanly yield the corresponding acenes through quantitative cheletropic thermal decarbonylation in the solid state, at moderate temperatures of 155 to 205 °C. This approach allows the preparation of heptacene, benzo[a]hexacene, cis- and trans-dibenzopentacene and offers a valuable new method for the synthesis of even larger acenes.

Acenes are polyaromatic hydrocarbons consisting of linearly fused benzene units and can be considered as the narrowest zig-zag graphene nanoribbons. This topology, with only one Clar aromatic sextet^[1] spread over the entire molecule, leads to a decrease of the HOMO-LUMO gap and an increase in the chemical reactivity with increasing number of benzene rings. The nature of electronic structure of long acenes is still actively discussed, in particular the partial contribution of the open-shell singlet state to the electronic ground-state configuration beyond decacene.^[2–5] On the other hand, these compounds are predicted to show attractive electronic and magnetic properties.^[6] They have been suggested for use as molecular wires in single molecule electronics, for solar-cells applications,^[7] for spintronics^[8] and plasmonics,^[9] as semi-conducting materials^[10,11] in organic-field effect transistors^[12] and in organic light emitting diodes.^[13]

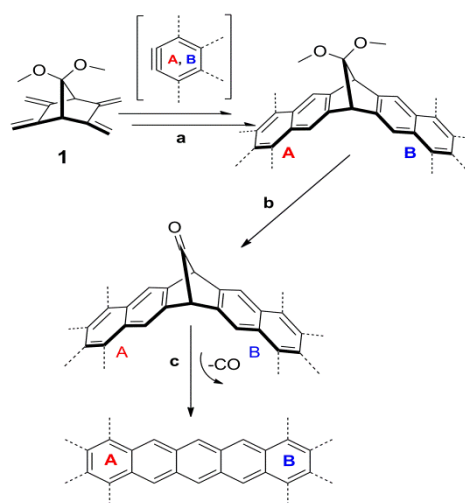
To overcome the inherent fragility of long acenes and to improve their solubility and processability, it is possible to attach electron deficient or bulky substituents^[14–20] or to introduce heteroatoms into the acene framework like sulfur or nitrogen atoms.^[10,14–17,21,22] However, the electronic properties of such materials cannot be compared with their parent acenes.

Since these later are poorly soluble, prone to (photo)oxidation and dimerize in solution, their synthesis remains “a formidable challenge” to quote R. Dorel and A.M. Echavarren.^[16] The only way to study them is to prepare more stable, and if possible soluble, precursors that can be converted

in a final step in the solid state through a unimolecular process to the target acenes. This approach has been employed for the synthesis of acenes^[23] up to undecacene^[24] in low concentration in argon cold matrices, or in PMMA^[25] by photochemical bis-decarbonylation using the Strating-Zwanenburg reaction,^[26] and to explore their photophysical properties.^[15,27,28] More recently, long acenes have been isolated by on-surface synthesis at low-temperature metallic surfaces under ultra-high vacuum, through deoxygenation of epoxides,^[29–31] dehydrogenation of partially saturated precursors^[32,33] and bis-decarbonylation of α -diketones.^[34,35] These strategies allowed the investigation through scanning tunnelling spectroscopy of the electronic properties^[36] of polyacenes up to undecacene and to follow the decrease in energy gap as the number of six-membered rings increases.

In contrast, the preparation in bulk of acenes beyond pentacene has been described only recently. Hexacene has been prepared in 2012 by T.J. Chow et al.^[37] by cheletropic thermal decarbonylation of the carbonyl-bridged precursor and heptacene by H.F. Bettinger et al. in 2017^[38] by thermal cleavage of diheptacene in the solid state, more than 70 years after the first attempted synthesis. Both studies showed that these two long acenes are stable at room temperature, resolving an old controversy and opening new avenues to the preparation of even longer acenes.

We present here a strategy, summarized in the Scheme 1, general enough to prepare a large variety of long acenes beyond pentacene. The starting compound is (1s,4s)-7,7-dimethoxy-2,3,5,6-tetramethylenebicyclo[2.2.1]heptane **1**.^[39] This tetraene can undergo Diels-Alder cycloaddition with arynes, to give, after aromatization, stable, non-planar and not fully aromatized protected acenes, which after cleavage of the ketals yields the CO bridged precursors.



Scheme 1. (a) Diels-Alder reactions of protected tetramethylenebicycloheptanone **1** with ben-zyne in one or two steps. (b) cleavage of the ketal to yield the ketone. (c) heating at ca 190–220 °C in the solid state yields the corresponding planar acene.

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Quantitative formation of the target acene is then carried out by heating in the solid state at ca 200°C^[40] with carbon monoxide as the sole by-product. This has allowed preparation, of heptacene **2**, dibenzopentacene isomers **3** and **4**, and benzo[*a*]hexacene **5** as representative examples of this method (Figure 1).

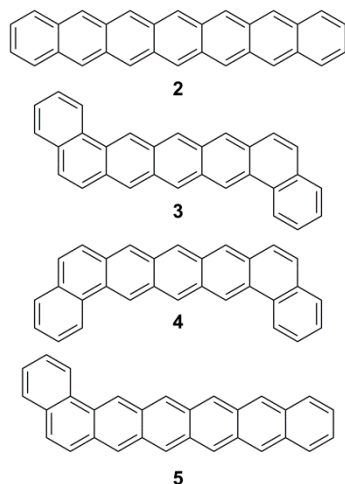
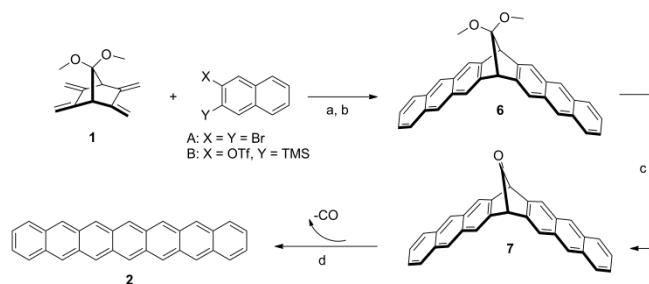


Figure 1 Seven-membered ring acenes: **2**, heptacene; **3**, dibenzo[*a,l*]pentacene; **4**, dibenzo[*a,n*]pentacene; **5**, benzo[*a*]hexacene.

1*s,4s*)-7,7-dimethoxy-2,3,5,6-

tetramethylenebicyclo[2.2.1]heptane 1. Compound **1** can be obtained from dimethyl fulvene in seven steps as described in ref^[39] and we have recently reinvestigated and simplified this synthesis at larger scale, ca tens of grams^[41] to obtain **1** without any need of purification by chromatography.

Heptacene 2. Heptacene has recently been prepared in bulk, by thermal cleavage of diheptacene by H.F. Bettinger et al.,^[38] more than seventy years after the first attempted synthesis by Clar.^[42] Before this breakthrough, heptacene in stabilizing matrix had been observed by D.C. Neckers et al.^[25] through photogeneration from a bridged α -diketone using a polymer matrix, and under UHV by on-surface dehydrogenation of the corresponding hydroacene,^[32] or using surface-assisted decarbonylation of an α -diketone precursor on a Ag(111).^[34] Using our strategy, we have also obtained heptacene in bulk, which remains so far the longest acene made as pure solid. Diels-Alder addition of **1** with two 2,3-naphthyne molecules, prepared in situ by reaction of CsF with 3-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate in acetonitrile (route A) or *n*-butyllithium with 2,3-dibromonaphthalene in toluene (route B), followed by oxidation with DDQ in toluene, gives **6** in ca 60% yields. The moderately soluble colourless carbonyl adduct **7** is then obtained by cleavage of the ketal by trimethylsilyl iodide in DCM in 99% yield.



Scheme 2. Synthesis of heptacene **2**: (a) A, *n*-BuLi, toluene. (b) DDQ, toluene 63%. or (a) B, CsF/acetonitrile. (b) DDQ, toluene 60%. (c) TMSI, DCM, 99%. (d) neat, 220°C, quant

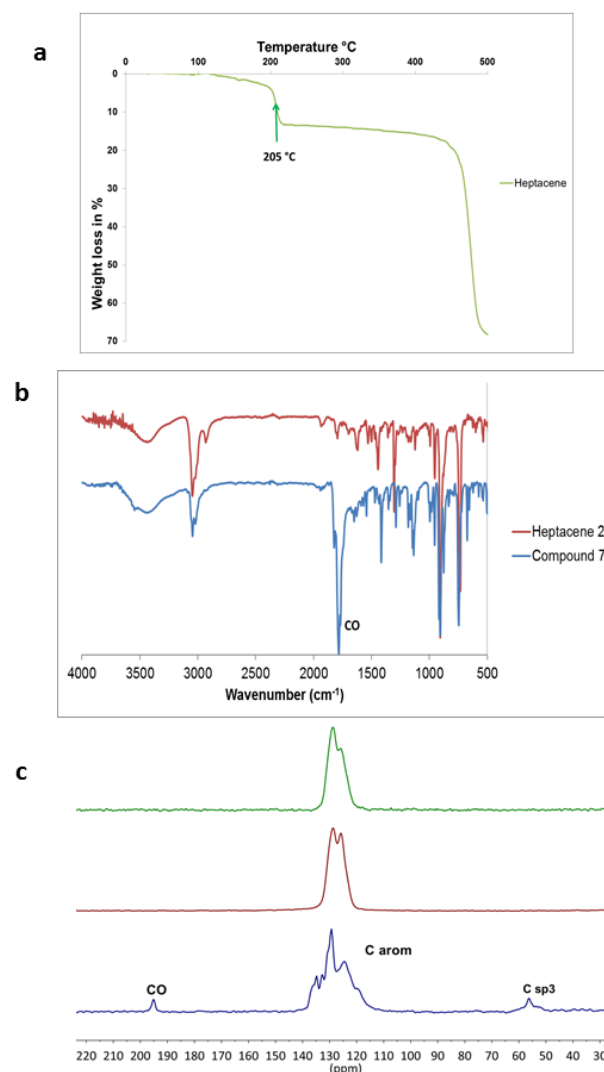


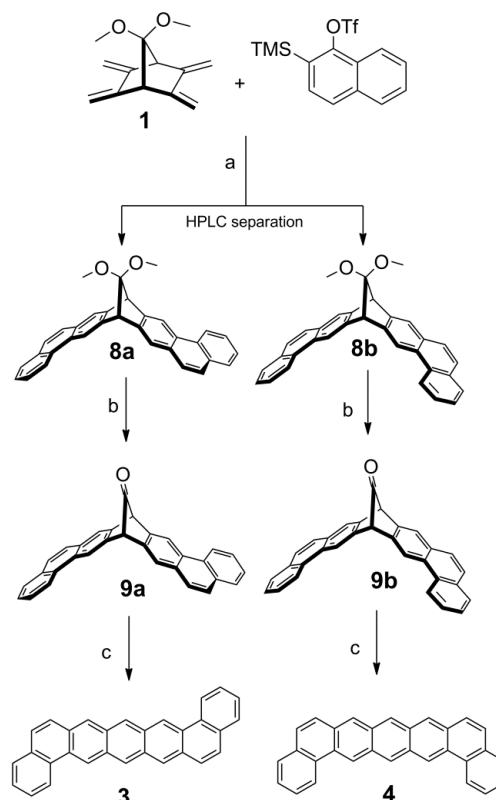
Figure 2. Formation of heptacene **2** by thermal decarbonylation of **7**: (a) Thermal Gravimetric Analysis of **7** showing the decarbonylation at 205 °C to yield **2**. (b) FTIR spectra (KBr pellets) of **2** and **7** showing the disappearance of the CO peak at 1782 cm⁻¹. (c) Carbon CPMAS spectra of **7** (bottom, blue), **2** (middle, red) just after decarbonylation, and **2** after six weeks at room temperature under argon (top, green).

The conversion of **7** to heptacene (Figure 2) was followed by thermal gravimetric analysis (Figure 2a). A weight loss of 7.9% (calcd. 6.9%) accompanied by a colour change from white to dark blue, occurred at 205°C, corresponding to the formation of heptacene by cheletropic CO extrusion. Under these conditions, heptacene is thermally stable up to 420 °C. The CO extrusion can also be followed by FTIR with the disappearance of the carbonyl peak of **7** observed at 1782 cm⁻¹ (Figure 2b). This transformation has been also shown by solid state cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy (Figure 2c). The spectrum of the precursor **7** showed three signals, one at 56.3 ppm (bridgehead sp³ carbons), a broad peak at 119-137 ppm (aromatic carbons) and the carbonyl carbon at 195.1 ppm. After heating for 15 minutes at 220°C in a glove box, the peaks corresponding to bridgehead and carbonyl carbons disappear leaving only a narrower doublet at 125.6 and 129.0 ppm (aromatic carbons). Keeping **2** in a glove-box for six weeks did not lead to any significant change in the spectrum. This is in contrast with results reported for thermally prepared heptacene which progressively dimerized to diheptacene.^[38] It is proposed that the packing of our precursor **7** does not favour the dimerization of heptacene **2** in the solid state.

Dibenzopentacenes 3 and 4. Dibenzopentacenes (DBPen) have been extensively studied both theoretically and experimentally (in the case of trans-DBPen) for their potential uses in organic electronics.^[43] This interest has been renewed by the discovery of superconductivity of trans-DBPen doped with alkali metals with a high critical temperature of 33.1K.^[44] However these results have never been reproduced and are still controversial.^[45,46] One explanation could be that the known synthesis of **3** (**4** has not yet been described) leads to raw products, requiring multiple train-sublimation purifications^[43] so that the exact superconductive phase from raw trans-DBPen remains unknown

Following the route described in Scheme 2 with 1,2-naphthyne in place of 2,3-naphthyne, we have obtained dibenzo[a,i]pentacene **3** (trans-DBPen) and dibenzo[a,n]pentacene **4** (cis-DBPen) as shown in Scheme 3. Diels-Alder addition of **1** with 1,2-naphthyne, prepared in situ by reaction of 1-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate with CsF in acetonitrile, followed by aromatization using DDQ in refluxing toluene gave a 1:1 mixture of isomers **8a** and **8b** in 77 % yield. These two regioisomers can be separated by chiral HPLC giving **8b** and a mixture of the trans-DBPen **8a** diastereoisomers which has not been resolved (see Sup. Mat). The proton NMR of **8a** shows a sp³ singlet at 4.91 ppm, integrating for two hydrogens, whereas that of **8b** shows two singlets at 4.85 and 4.96 ppm each integrating for one hydrogen, further indicating their different aromatic conjugation.

Cleavage of the ketal **8a/8b** by trimethylsilyl iodide in dichloromethane yielded the stable and soluble DBPen precursors **9a/9b** respectively in nearly quantitative yields.



Scheme 3. Preparation of trans **3** and cis-dibenzopentacene **4**: (a) CsF, acetonitrile, 77%. (b) after separation of isomers: TMSI, DCM, 99%. (c) neat, 200°C, quant.

The TGA profiles of these precursors (Sup. Mat) exhibit CO expulsion at 185°C for **9a** and 155°C for **9b**, with corresponding weight losses of 6.4 % and 7.6 % (calcd. 6.9 %) together with a colour change from white to deep red. Differential thermal analysis (DTA) showed a phase transition at 465 °C for **3** and at 350 °C for **4**. Vaporization started for both compounds at ca 320-350 °C. As in the case of heptacene, the CO extrusion has been followed by carbon CP-MAS NMR and FTIR in the solid state (see Sup. Mat.). Similarly, the spectra of cis-DBPen **9b** showed a C sp³ peak at 55.0 ppm, a multiplet between 110 and 140 ppm (C arom.) and a very weak singlet at 191.1 ppm for the CO carbon. For the trans-DBPen isomer **9a**, peaks are seen at 55.7 ppm (C sp³) and 110-140 ppm (C arom.) with the peak for the carbonyl not apparent. Heating the solid samples for 15 min in a glove-box at 170 °C for **9a** or 200 °C for **9b** gave the corresponding acenes **3** and **4**. After CO extrusion, the solid state ¹³C NMR spectra shows only one peak at 125.5 ppm for **3** and 125.9 ppm for **4** attributed to the aromatic carbon atoms. Comparison of the infra-red spectra of the carbonyl precursors **9a** and **9b**, before and after decarbonylation shows the loss of carbonyl bands at 1785 cm⁻¹ (**9a**) and 1787 cm⁻¹ (**9b**) respectively. As DBPen isomers are less prone to dimerization in solution at room temperature, it is possible to carry out this decarbonylation in a high boiling point solvent like 1,1,2,2-tetrachloroethane under moderate pressure. The UV-Vis spectra of DBPen isomers were obtained by dissolving the precursors **9a/9b** and heating at 190°C for 15 min to obtain the compounds

3 and **4**. The spectra were measured at room temperature (Figure 3 and Sup Mat).

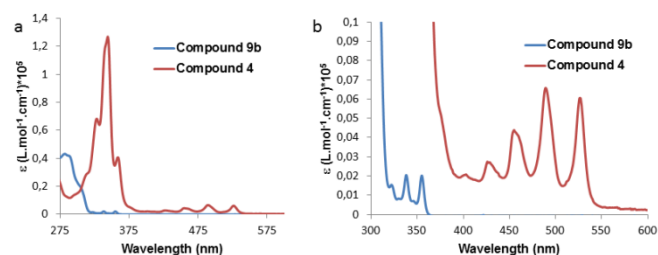
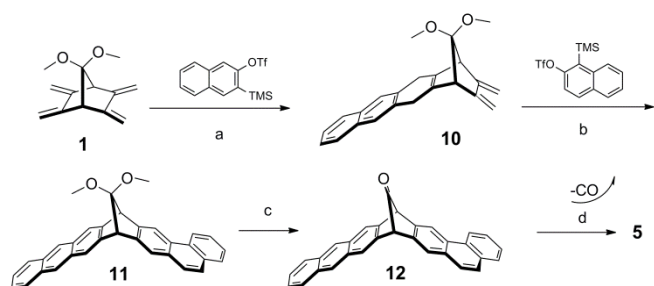


Figure 3. Optical absorption spectra of **9b** and **4** in 1,1,2,2-tetrachloroethane: (a) Full spectra of the carbonylated precursor **9b** (blue) and after thermal decarbonylation, **4** (red). (b) zoom of the p band region. Spectra of **9a** and **3** are very similar and reported in Sup. Mat.

The p band regions of **3** and **4** shows a pattern very similar to that of pentacene with four bands at 427, 459, 490 and 527 nm for **3** (426, 455, 489, 526 nm for **4**), with an hypsochromic shift of 45-65 nm with respect to pentacene in solution due to the addition of a second aromatic sextet.^[47]

Benzo[a]hexacene 5. In order to extend the potential of this approach, we have focused on the preparation of asymmetric acenes through reaction of only one diene of the tetraene **1** (Scheme 4).



Scheme 4. (a) 3-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate, CsF, acetonitrile, 46%. (b) 1-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate, CsF, acetonitrile; DDQ, toluene, 80%. (c) TMSI, DCM, 96% (d) neat, 200°C, quant.

Diels-Alder addition of **1** with 1.3 equivalents of 2,3-naphthyne, prepared in situ by reaction of CsF with 3-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate in acetonitrile, gave the cis-diene **10** in 46%. This can then be used in other Diels-Alder reactions with arynes, as, for instance, 1,2-naphthyne, obtained in situ from 1-(trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate. After oxidation by DDQ in toluene, **11** was obtained in 80% yield as a mixture of two stereoisomers. Cleavage of the later ketal in conditions similar to those used in the preparation of **6** and **8** provided **12** in 96% yield as a white solid. The TGA profiles of **12** showed a CO extrusion at 175 °C corresponding to a weight loss of 7.2 % (calcd.: 6.9 %) to give blue benzo[a]hexacene **5**. As with previous compounds, the formation of **5** in the solid state from its precursor **12** was followed by ¹³C CPMAS NMR. At room temperature, the

spectrum of **12** shows a peak at 55.7 ppm, corresponding to the sp³ carbon, a broad multiplet at 118-136 ppm for the aromatic carbons, and one at 191.7 ppm for the bridging carbonyl group. Decarbonylation at 190 °C under an argon atmosphere for fifteen minutes gave **5**, which shows only one single broad CPMAS peak at 125.0 ppm. Similarly to the previous acenes, decarbonylation is also demonstrated by disappearance of the CO band at 1785 cm⁻¹ in the IR spectrum of **12**, after heating to yield benzo[a]hexacene **5**.

Absorption spectra of thin films. Solid state absorption spectra of thin films of compounds **9a**, **9b** and **12** were obtained by spin-casting on a quartz plate (transparency > 93% at a wavelength 380 nm) from a solution of these compounds in DCM and drying in air. They were then converted to the corresponding acenes **2-4** by heating at 200°C under an argon atmosphere for one minute and the spectra recorded under argon. Due to the low solubility of **7** it was not possible to spincoat thin layers of this compound. However, optical absorption spectra of thin films of heptacene **2** were obtained recently by H.F. Bettinger by sublimation on sapphire at low temperature (16 K).^[38] It was shown that annealing the films to higher temperatures resulted in a decrease of the poorly resolved p bands. Figure 4 shows the optical absorption spectra of benzo[a]hexacene **5** and its carbonylated precursor **12**.

The spectrum of **12** shows three main bands at 401, 379 and 351 nm attributed to the anthracene parts present in the structure. These features disappear after decarbonylation, with the spectrum of **5** comprising four bands at 609, 665, 717, 770 nm with a pattern similar to those of DBPen **3** and **4** with a bathochromic shift of ca 190 nm (see Sup. Mat). The thin layer

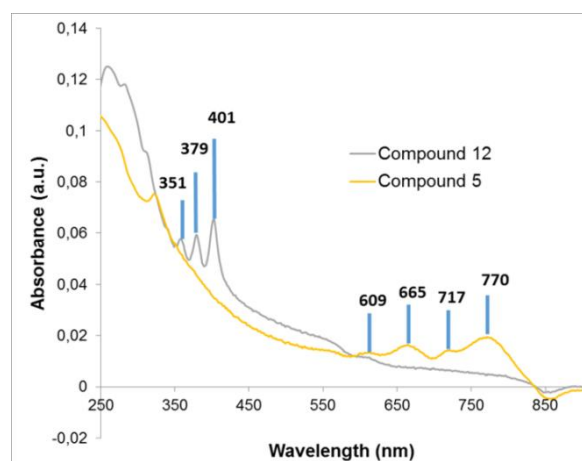


Figure 4 Absorption spectra of thin films: benzo[a]hexacene **5** (yellow) and its carbonylated precursor **12** (grey)

spectra of the DBPen isomers **3** and **4** also show a four bands pattern similar to those observed in solution with a bathochromic shift of 55-60 nm as expected for thin films versus solution spectra.

To sum up, we describe here a general method allowing for the preparation of pure oligoacenes larger than pentacene,

despite their chemical and photochemical fragility. The purity and good thermal stability of these compounds will permit the studies of their semiconducting properties for applications including field-effect transistors. Our current work focuses on the semi-preparative scale synthesis of significantly longer linear or branched acenes above heptacene, by successive Diels-Alder reactions from **1** or **10** with bis-arynes, of donor-acceptor oligoacenes by asymmetric reactions following the strategy developed for the preparation of **5**

Experimental Section

General experimental details, synthesis and characterization for all compounds, solution ¹H and ¹³C NMR, ¹³C CPMA, FTIR, and UV-Vis spectra can be found in the Supplementary Information.

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Keywords • Acenes • Heptacene • Dibenzopentacene • Benzohexacene • Alternant hydrocarbons

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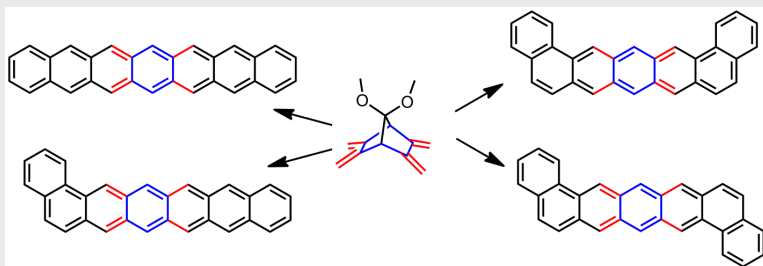
Conflicts of interest

The authors declare no conflict of interest

Andrej Jancarik,* Gaspard Levet and
André Gourdon*

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**A practical general method for the
preparation of long acenes**



Symmetrical and non-symmetrical chemically fragile and poorly soluble acenes beyond pentacene can be obtained from a protected bicyclic tetraene. The method involves Diels-Alder addition with arynes, oxidation and cleavage of the ketal to give a soluble and stable polyaromatic ketone. Solid state cheletropic decarbonylation gives the targeted oligoacene in quantitative yield.

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S1 Experimental Procedures

General information

Starting compounds, catalysts and solvents were purchased from Sigma-Aldrich and TCI. Flash column chromatography was performed by using silica gel (60 Å pore size, 40-63 µm Merck). The reactions were monitored by thin layer chromatography (TLC) on silica gel-coated plates (Merck 60 F₂₅₄). The NMR spectroscopic data in solution were recorded with Bruker Avance 300 MHz and 500 MHz instruments and were calibrated by using the residual undeuterated solvent as an internal reference (CD_2Cl_2 at $\delta\text{H} = 5.33$ ppm, $\delta\text{C} = 53.84$ ppm; CDCl_3 at $\delta\text{H} = 7.26$ ppm, $\delta\text{C} = 77.16$ ppm; tetrachloroethane- d_2 at $\delta\text{H} = 6.00$ ppm, $\delta\text{C} = 73.78$ ppm). Chemical shifts are reported in parts per million (ppm) on the δ scale and coupling constants (J) are in Hertz (Hz). The abbreviations used to describe the multiplicities are s = singlet, dd = doublet of doublets ddd = doublet of doublet of doublet. Mass spectra were recorded at the Service Commun de Spectrometrie de Masse of University Paul Sabatier (Toulouse 3), Toulouse (France) and CP MAS NMR were recorded at the Laboratoire de Chimie de Coordination on a Bruker Avance IIIHD 400 spectrometer equipped with a 2.5 mm probe. Samples were spun at 14 kHz at the magic angle using ZrO_2 rotors. ^{13}C -CP/MAS were recorded with a recycle delay of 1.5 s and a contact time of 3 ms. All chemical shifts for ^{13}C are relative to TMS. Thermal analyses (TG/DSC) were carried out on a Setaram Labsys instrument under flowing helium (45 mL min⁻¹) with the heating rate of 10 °C min⁻¹ from 30 °C to 550 °C. The samples (5 mg) were contained in 100 µL aluminum crucibles. IR spectra were measured on a PerkinElmer Spectrum 100 FT-IR spectrometer with samples as KBr pellets. UV - Vis spectra were recorded on a Varian Cary 5000 spectrophotometer.

Absorption spectra of thin films and in solution

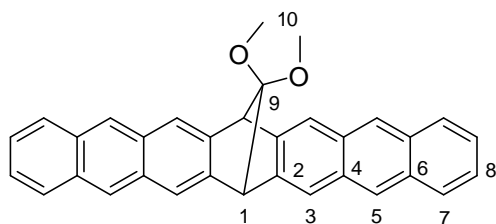
Solid state absorption spectra of compounds **9a/9b**, **12** were obtained by spin-coating on a quartz plate (1 mm thickness, transparency > 93 % at a wavelength 380 nm). A solution with maximum concentration (1 mg/mL for **9a**, 0.25 mg/mL for **9b**, 0.6 mg/mL for **12**) of each compound in dichloromethane was spincasted at 500 rpm for 30 s. The glass plates were installed diagonally inside a 1x1 cm quartz cuvette. All these compounds were converted to the corresponding acenes **3-5** by heating at 200 °C for 1 min under an argon atmosphere and recorded under argon by keeping the glass plate inside a 1x1 cm quartz cuvette. The UV – Vis spectra for **7** and **2** were not measured due to high insolubility. The absorption spectra in solution were made by dissolving compound **9a** (1.63 mg) and **9b** (1.14 mg) in 1,1,2,2-tetrachloroethane (200 mL) and measured in 1x1 cm quartz cuvette. These solutions of **9a** and **9b** were precisely degassed in an Young tube and then heated at 190 °C for 15 min to produce **3** and **4**. The formed solutions of **3** and **4** were cooled to room temperature and in a glovebox transferred to a 1x1 cm quartz cuvettes.

Thermal Gravimetric Analysis

Ca 3-5 mg of samples were precisely weighed in a 100 µl alumina crucible and placed into a Setaram Labsys device. Before analysis, sample and analysis chamber were purged first in vacuo and then by flowing helium (45 ml/min) during 8 hours. The absence of oxygen was checked with a lambda analyzer (Setnag JC15V) coupled with the Labsys device. Dual thermogravimetry (TG) and differential thermal analysis (DTA) of samples were made simultaneously using a ramp rate of 10 °C/min, from 30 °C to 550 °C and with a helium flow of 45 ml/min.

S2 Peak attribution in NMR spectra

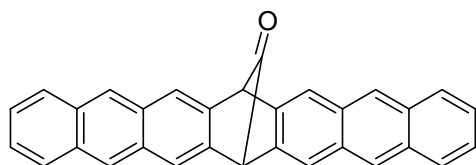
19,19-dimethoxy-7,16-dihydro-7,16-methanoheptacene (6)



¹H NMR (300 MHz, CDCl₃): 3.30 (6H, s, *H*10), 4.47 (2H, s, *H*1), 7.39 - 7.42 (4H, m, *H*8), 7.87 (4H, s, *H*3), 7.91 - 7.94 (4H, m, *H*7), 8.27 (4H, s, *H*5).

¹³C NMR (126 MHz, CDCl₃): 51.44 (*C*10), 54.74 (*C*1), 120.28 (*C*3), 123.39 (*C*9), 125.17 (*C*8), 126.07 (*C*5), 128.08 (*C*7), 131.37 (*C*4), 131.67 (*C*6), 142.19 (*C*2).

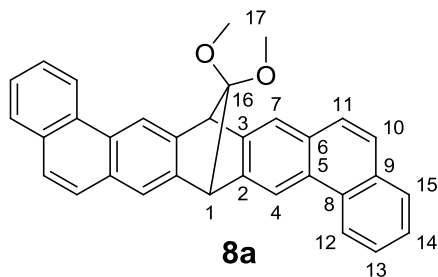
7,16-dihydro-7,16-methanoheptacen-19-one (7)



¹H NMR (500 MHz, tetrachloroethane-*d*₂, 80°C): 5.01 (2H, s), 7.49 (4H, dd, *J* = 6.5, 3.1), 8.01 (4H, dd, *J* = 6.5, 3.3), 8.10 (4H, s), 8.42 (4H, s).

¹³C NMR (126 MHz, tetrachloroethane-*d*₂): Not recorded due to the low solubility.

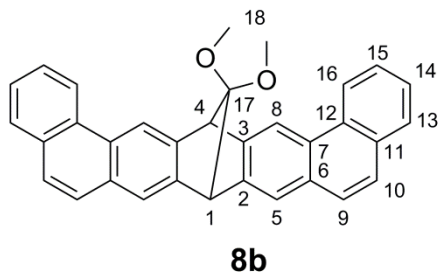
19,19-dimethoxy-8,17-dihydro-8,17-methanodibenzo[*a,l*]pentacene (8a)



¹H NMR (500 MHz, CD₂Cl₂): 3.28 (6H, s, *H*17), 4.91 (2H, s, *H*1), 7.56 (2H, ddd, *J* = 8.0, 6.9, 1.2, *H*14), 7.64 (2H, ddd, *J* = 8.4, 6.9, 1.4, *H*13), 7.67 - 7.72 (4H, ABq, *J*_{AB} = 9.4, *H*10, *H*11), 7.86 (2H, dd, *J* = 7.8, 1.4, *H*15), 7.86 (2H, s, *H*7), 8.66 (2H, d, *J* = 8.0, *H*12), 8.67 (2H, s, *H*4).

¹³C NMR (126 MHz, CD₂Cl₂): 51.67 (*C*17), 56.03 (*C*1), 116.53 (*C*4), 122.21 (*C*7), 123.09 (*C*12), 126.64 (*C*14), 126.87 (*C*11), 126.88 (*C*16), 126.89 (*C*13), 127.44 (*C*10), 129.00 (*C*15), 129.24 (*C*5), 130.86 (*C*8), 131.23 (*C*6), 132.59 (*C*9), 145.10 (*C*3), 145.24 (*C*2).

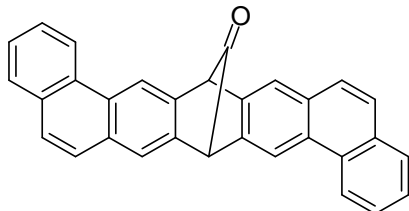
19,19-dimethoxy-8,17-dihydro-8,17-methanodibenzo[*a,n*]pentacene (8b)



¹H NMR (500 MHz, CD₂Cl₂): 3.27 (6H, s, *H*18), 4.85 (1H, d, *J* = 1.5, *H*1), 4.96 (1H, d, *J* = 1.5, *H*4), 7.55 (2H, ddd, *J* = 8.1, 7.0, 1.2, *H*14), 7.64 (2H, ddd, *J* = 8.4, 6.9, 1.4, *H*15), 7.69 (2H, d, *J* = 8.95, *H*9), 7.71 (2H, d, *J* = 8.95, *H*10), 7.84 (2H, s, *H*5), 7.86 (2H, dd, *J* = 7.9, 1.4, *H*13), 8.67 (2H, dd, *J* = 8.5, 1.1, *H*16), 8.68 (2H, s, *H*8).

¹³C NMR (126 MHz, CD₂Cl₂): 51.67 (*C*18), 55.59 (*C*1), 56.47 (*C*4), 116.55 (*C*8), 122.19 (*C*5), 123.08 (*C*16), 126.64 (*C*14), 126.86 (*C*10), 126.87 (*C*17), 126.89 (*C*15), 127.43 (*C*9), 128.99 (*C*13), 129.25 (*C*7), 130.85 (*C*12), 131.22 (*C*6), 132.59 (*C*11), 145.01 (*C*2), 145.33 (*C*3).

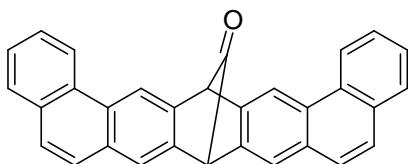
8,17-dihydro-8,17-methanodibenzo[*a,l*]pentacen-19-one (9a)



¹H NMR (500 MHz, tetrachloroethane-*d*₂): 5.27 (2H, s), 7.62 (2H, ddd, *J* = 7.9, 6.9, 1.1), 7.69 (2H, ddd, *J* = 8.4, 7.0, 1.4), 7.74 (2H, d, *J* = 9.0), 7.76 (2H, d, *J* = 9.0), 7.89 (2H, dd, *J* = 7.8, 1.3), 8.07 (2H, s), 8.70 (2H, dd, *J* = 8.5, 1.1), 8.85 (2H, s).

¹³C NMR (126 MHz, tetrachloroethane-*d*₂): 57.47, 116.07, 121.76, 122.56, 126.67 (3C), 127.15, 128.53, 129.28, 129.86, 131.08, 131.82, 138.01, 138.11, 191.01.

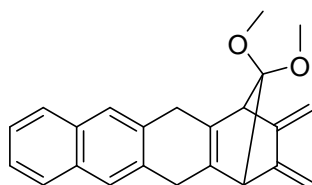
8,17-dihydro-8,17-methanodibenzo[*a,n*]pentacen-19-one(9b)



¹H NMR (500 MHz, tetrachloroethane-*d*₂): 5.16 (1H, s), 5.27 (1H, s), 7.62 (2H, ddd, *J* = 8.0, 7.0, 1.1), 7.69 (2H, ddd, *J* = 8.3, 7.0, 1.4), 7.74 (2H, d, *J* = 9.0), 7.76 (2H, d, *J* = 9.0), 7.89 (2H, dd, *J* = 7.9, 1.4), 8.05 (2H, s), 8.71 (2H, d, *J* = 8.2), 8.87 (2H, s).

¹³C NMR (126 MHz, tetrachloroethane-*d*₂): 57.05, 57.90, 116.09, 121.75, 122.56, 126.67 (3C), 127.15, 128.54, 129.30, 129.88, 131.07, 131.82, 137.92, 138.21, 191.00.

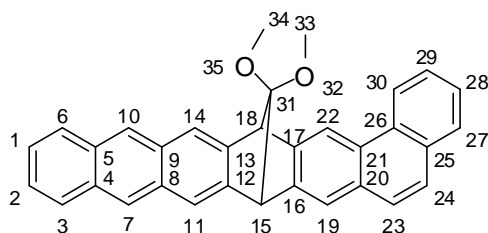
(1*S*)-13,13-dimethoxy-2,3-dimethylene-1,2,3,4,5,12-hexahydro-1,4-methanotetracene (10)



¹H NMR (300 MHz, CD₂Cl₂): 3.21 (3H, s), 3.22 (3H, s), 3.39 (2H, s), 3.52-3.64 (2H, m), 3.67-3.79 (2H, m), 4.98 (2H, s), 5.19 (2H, s), 7.36-7.41 (2H, m), 7.65 (2H, s), 7.71-7.77 (2H, m).

¹³C NMR (75 MHz, CDCl₃): 29.12, 50.56, 52.10, 58.16, 101.79, 118.25, 125.80, 127.56, 127.78, 132.76, 133.16, 136.24, 147.53.

(8*R*)-19,19-dimethoxy-8,17-dihydro-8,17-methanobenzo[*a*]hexacene (11)

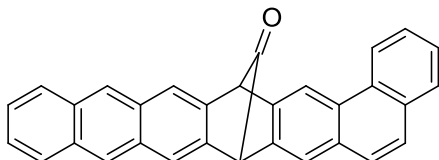


¹H NMR (500 MHz, CD₂Cl₂): 3.27 (3H, s, *H*34), 3.29 (3H, s, *H*33), 4.82 (1H, d, *J* = 1.6, *H*15), 4.87 (1H, d, *J* = 1.5, *H*18), 7.43 (2H, dd, *J* = 6.6, 3.1, *H*1, *H*2), 7.56 (1H, ddd, *J* = 8.0, 7.0, 1.2, *H*28), 7.65 (1H, ddd, *J* = 8.4, 7.0, 1.4, *H*29), 7.68-7.72 (2H, ABq, *J*_{AB} = 9.2,

*H*_{23,24}), 7.85 (1H, s, *H*₁₉), 7.86 (1H, dd, *J* = 8.7, 0.9, *H*₂₇), 7.87 (1H, s, *H*₁₁), 7.89 (1H, s, *H*₁₄), 7.94 – 7.97 (2H, m, *H*₃,*H*₆), 8.29 (2H, s, *H*₇,*H*₁₀), 8.67 (1H, d, *J* = 8.0, *H*₃₀), 8.67 (1H, s, *H*₂₂).

¹³C NMR (126 MHz, CD₂Cl₂): 50.94 (*C*₃₄), 51.13 (*C*₃₃), 54.71 (*C*₁₅), 55.15 (*C*₁₈), 115.91 (*C*₂₂), 119.99 (*C*₁₁), 120.01 (*C*₁₄), 121.56 (*C*₁₉), 122.49 (*C*₃₀), 124.73 (*C*₃₁), 125.04 (*C*₁,*C*₂), 125.73 (*C*₇,*C*₁₀), 126.08 (*C*₂₈), 126.28 (*C*₂₉), 126.30 (*C*₂₄), 126.83 (*C*₂₃), 127.81 (*C*₃,*C*₆), 128.40 (*C*₂₇), 128.84 (*C*₂₁), 130.25 (*C*₂₆), 130.80 (*C*₂₀), 131.01 (*C*₁₂,*C*₁₃), 131.51 (*C*₄,*C*₅), 131.96 (*C*₂₅), 142.69 (*C*₁₂), 142.77 (*C*₁₃), 143.84 (*C*₁₆), 144.06 (*C*₈).

(8*R*)-8,17-dihydro-8,17-methanobenzo[*a*]hexacen-19-one (12)



¹H NMR (500 MHz, tetrachloroethane-*d*₂): 5.08 (1H, s), 5.14 (1H, s), 7.48 (2H, dd, *J* = 6.7, 3.2), 7.62 (1H, ddd, *J* = 7.9, 6.7, 0.9), 7.69 (1H, ddd, *J* = 8.2, 6.9, 1.0), 7.74 (1H, d, *J* = 9.3), 7.77 (1H, d, *J* = 9.3), 7.89 (1H, d, *J* = 7.8), 8.00 (2H, dd, *J* = 6.6, 3.3), 8.04 (1H, s), 8.10 (1H, s), 8.12 (1H, s), 8.40 (2H, s), 8.71 (1H, d, *J* = 8.5), 8.85 (1H, s).

¹³C NMR (126 MHz, tetrachloroethane-*d*₂): 56.86, 57.29, 116.03, 120.54, 120.55, 121.71, 122.56, 125.49 (2C), 126.21 (2C), 126.66, 126.70 (2C), 127.18, 127.91 (2C), 128.55 (2C), 129.40, 129.86, 130.74 (2C), 131.16, 131.49 (2C), 131.81, 136.40, 136.49, 137.79, 137.97, 193.08 (C=O).

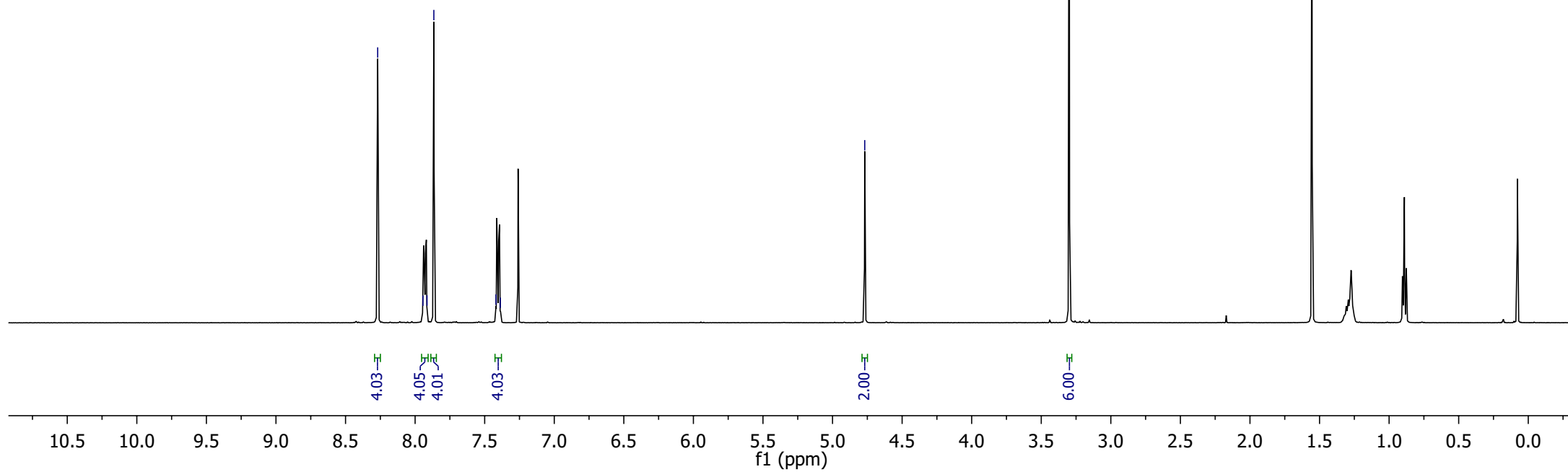
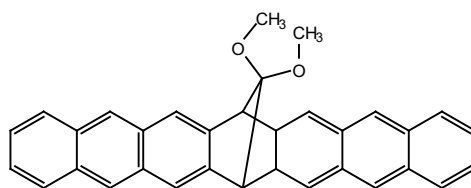
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7.39

4.77

3.30

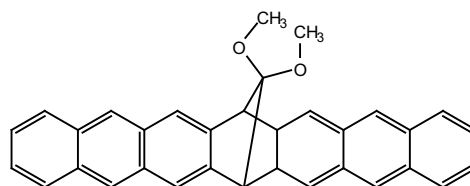
6



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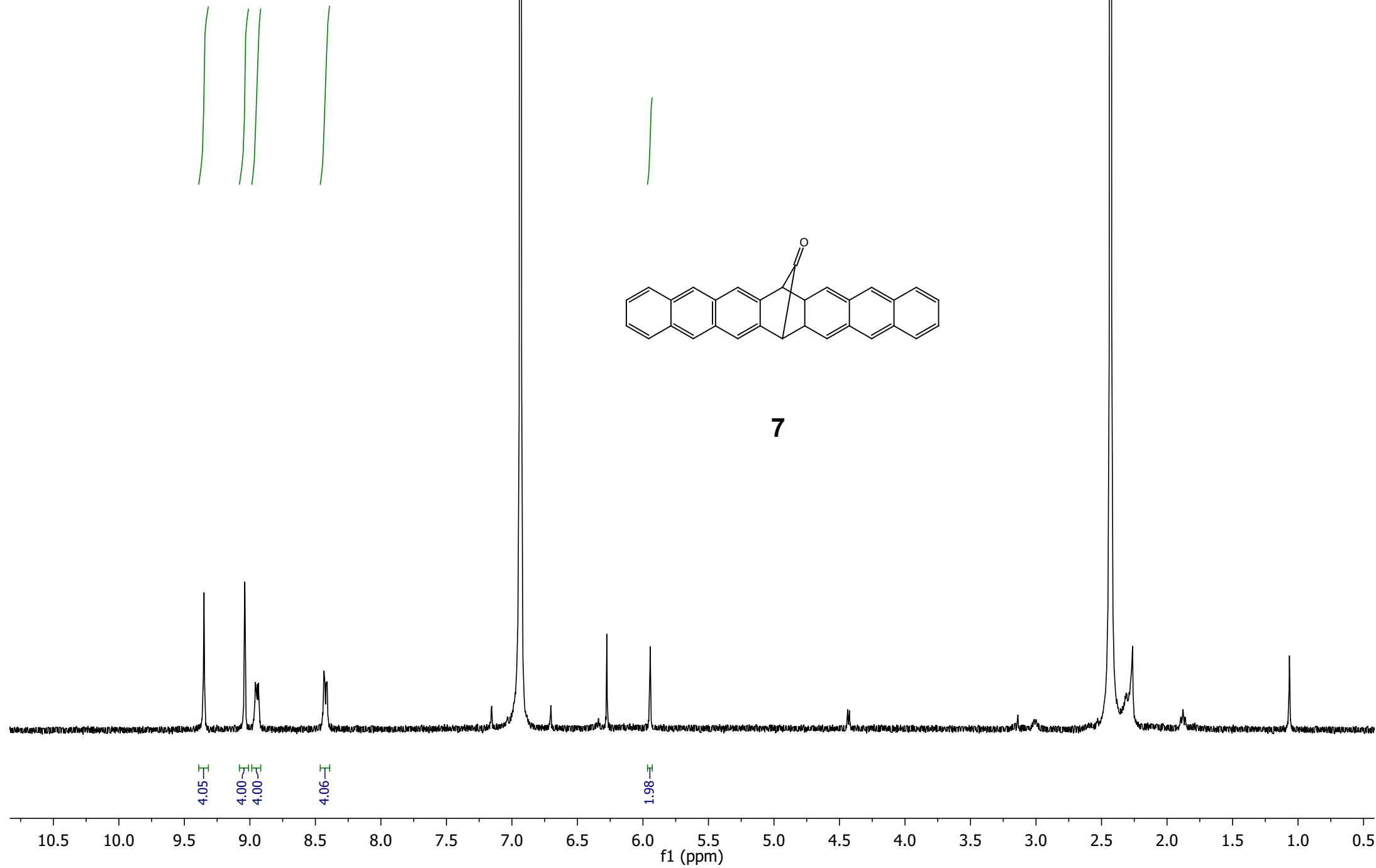
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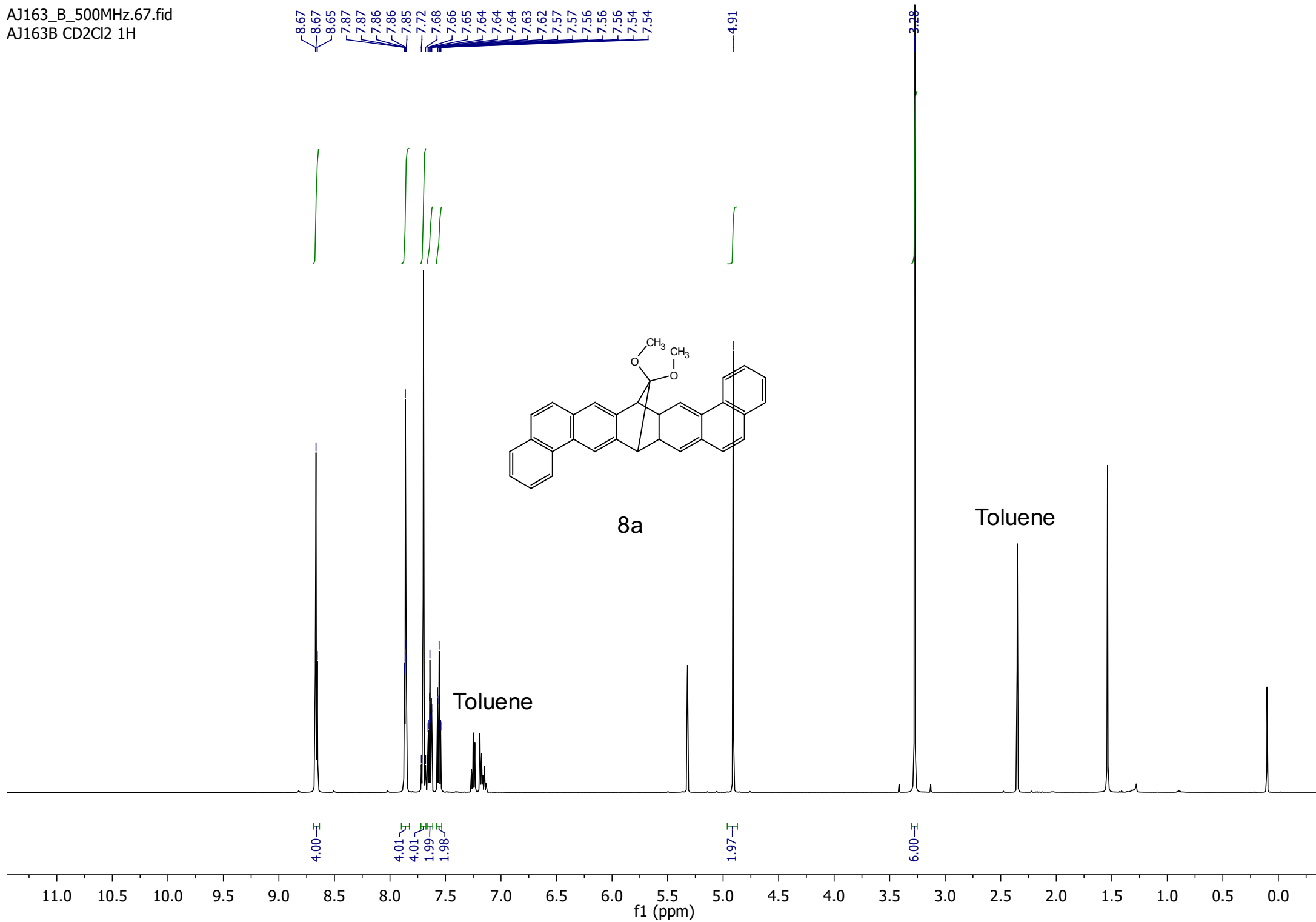


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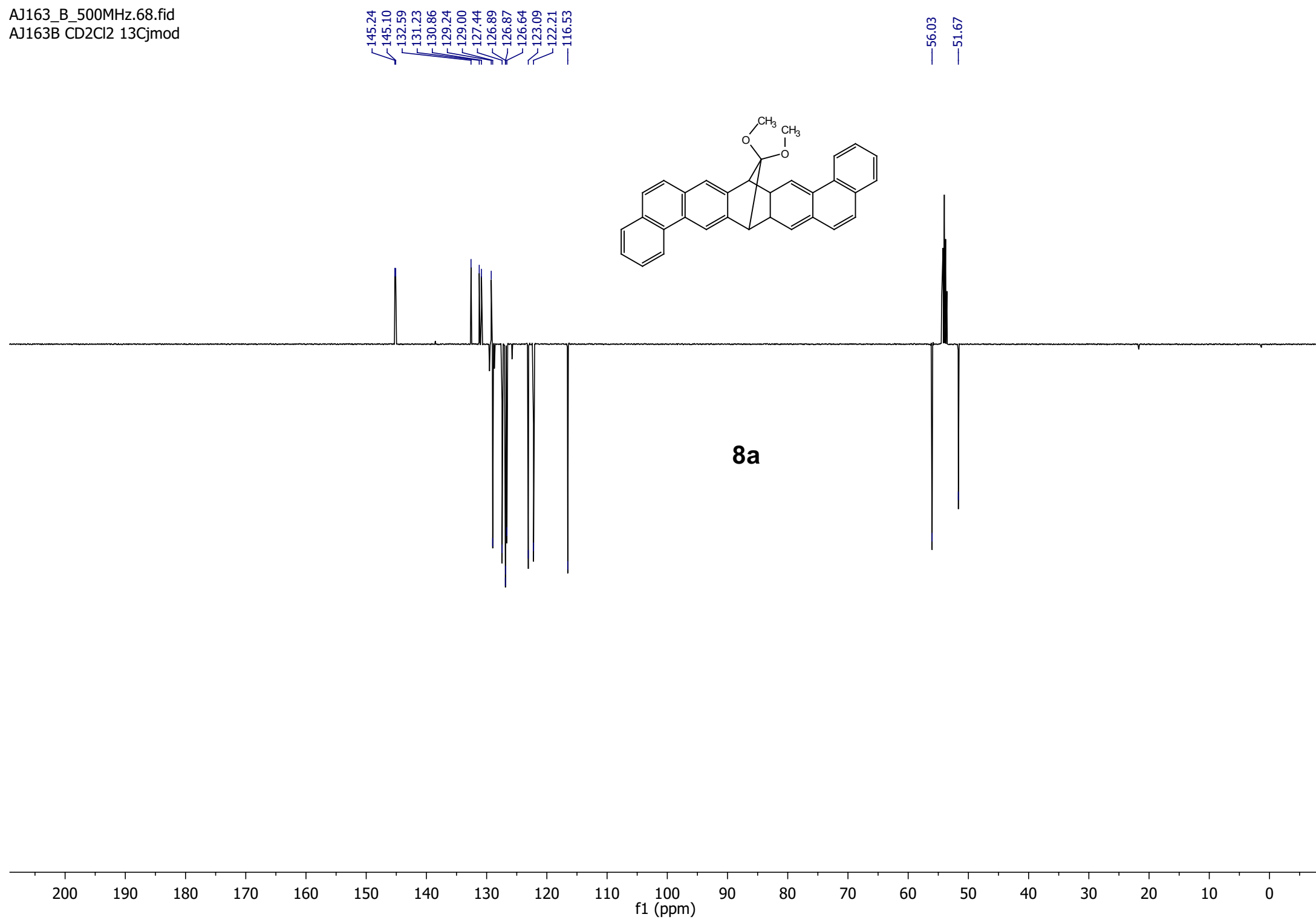
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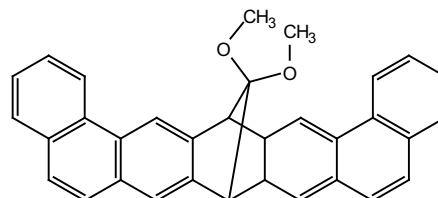


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8.68 8.67 8.66 8.66 7.87 7.87 7.85 7.85 7.84 7.72 7.70 7.70 7.68 7.65 7.65 7.64 7.64 7.63 7.62 7.62 7.57 7.57 7.56 7.55 7.54 7.54 4.97 4.96 4.85 4.85 3.27 3.27



8b

2.02 2.02

2.06 1.99

2.01 2.02

1.00 1.00

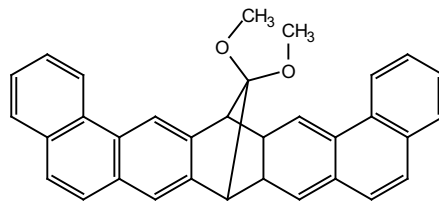
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f1 (ppm)

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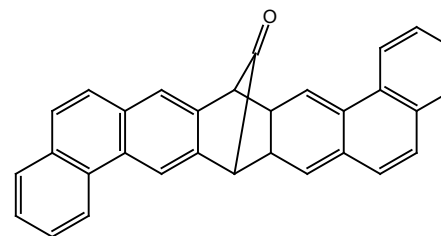
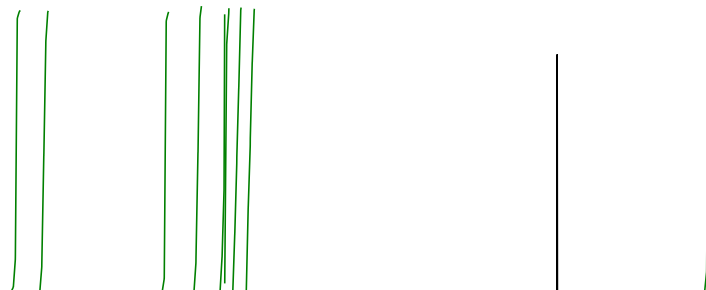


8b

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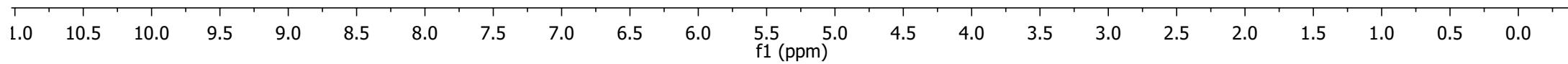
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8.71
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8.69
8.07
7.90
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7.77
7.75
7.75
7.73
7.70
7.70
7.69
7.69
7.68
7.67
7.67
7.63
7.63
7.62
7.62
7.61
7.60
7.60
5.21



9a

2.03
2.03
2.02
2.06
2.00
2.05
2.05
2.04
2.00



—191.01

138.11

138.01

131.82

131.08

129.86

129.28

128.53

127.15

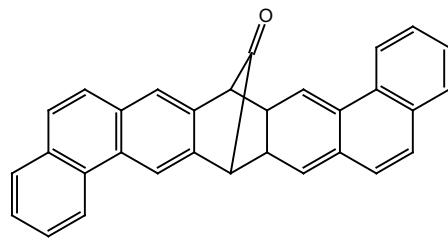
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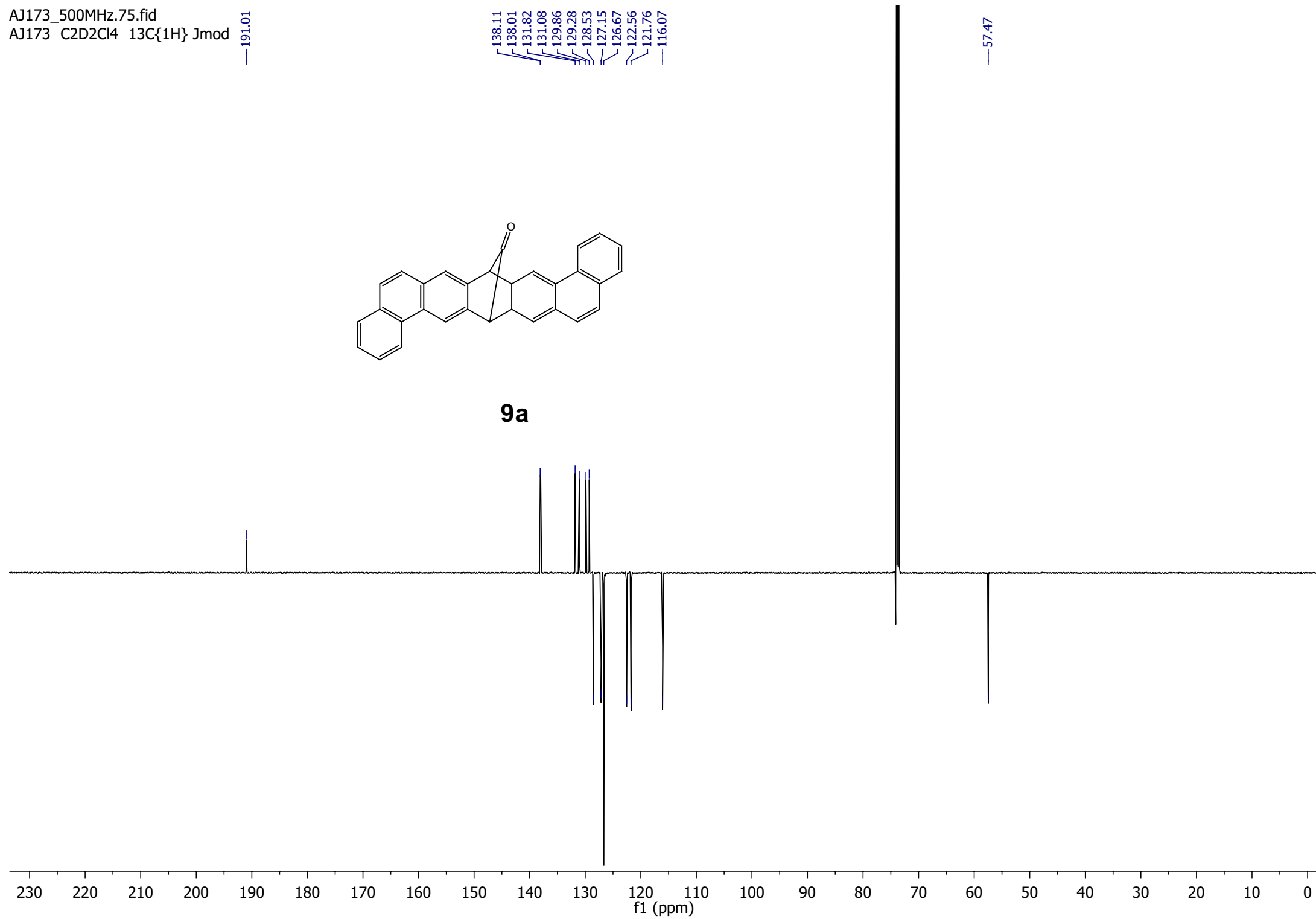
121.76

116.07

—57.47

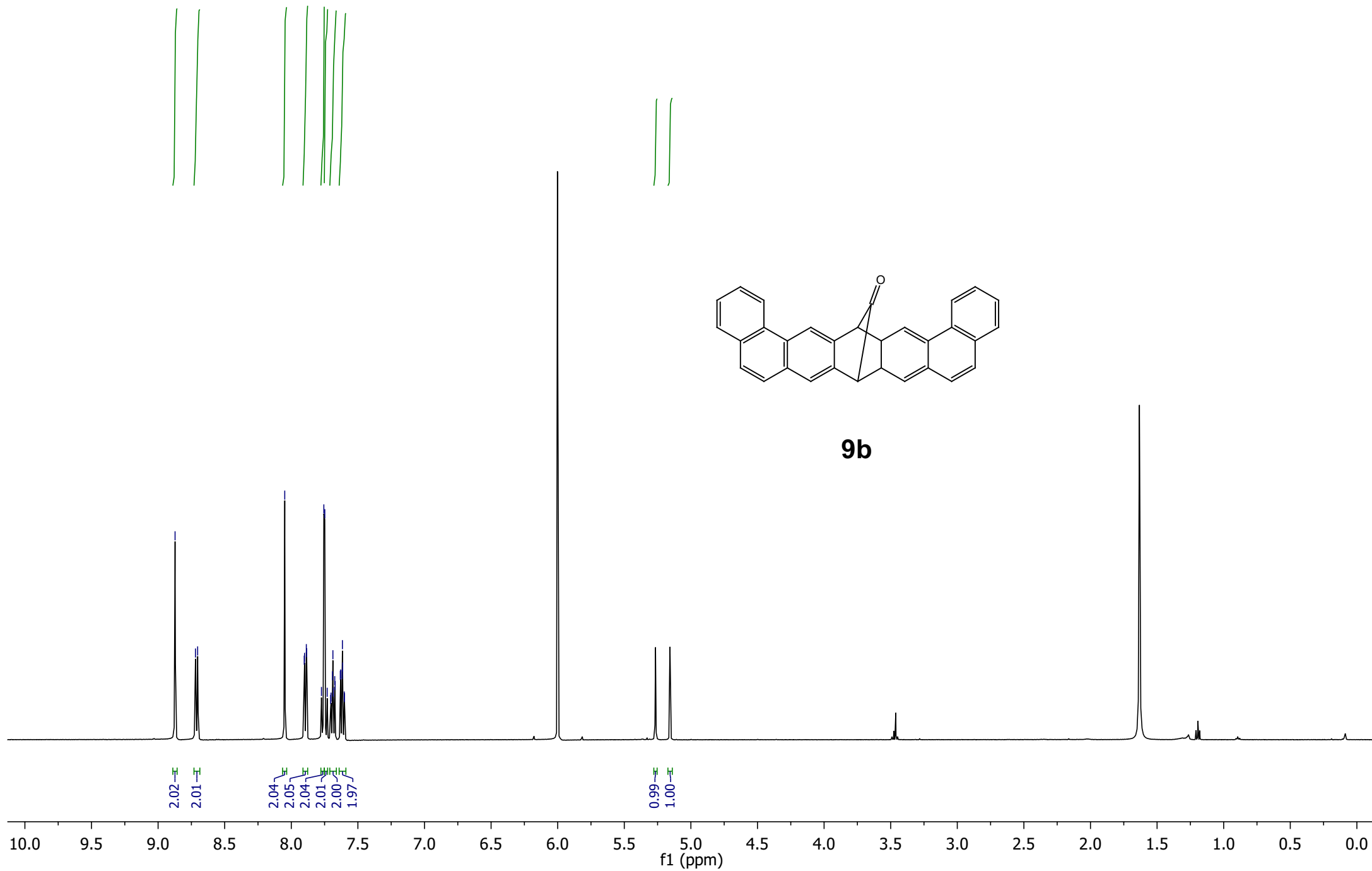


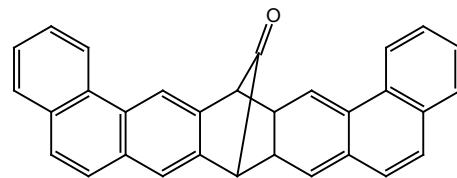
9a



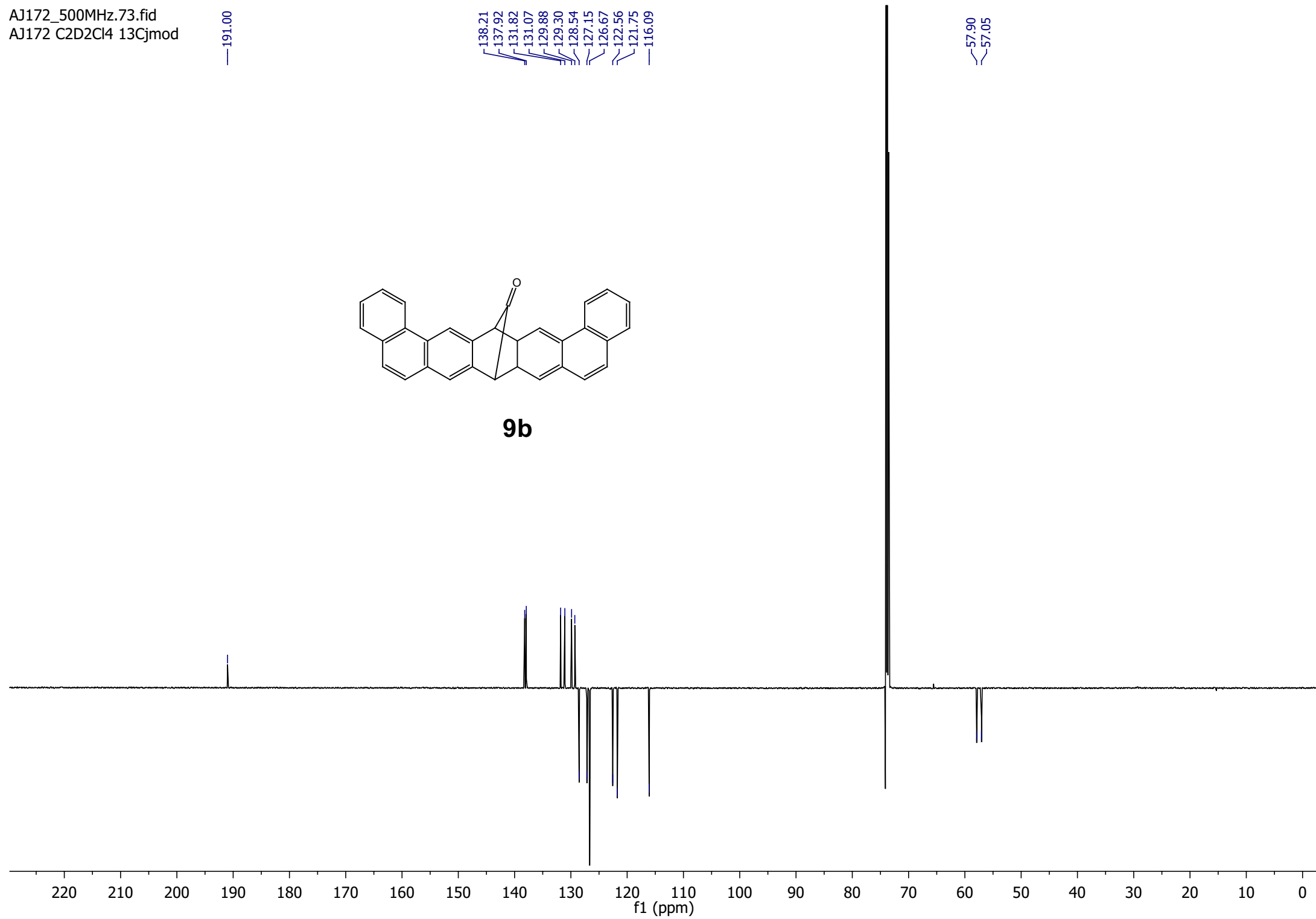
AJ172_500MHz.72.fid
AJ172 C2D2Cl4 1H

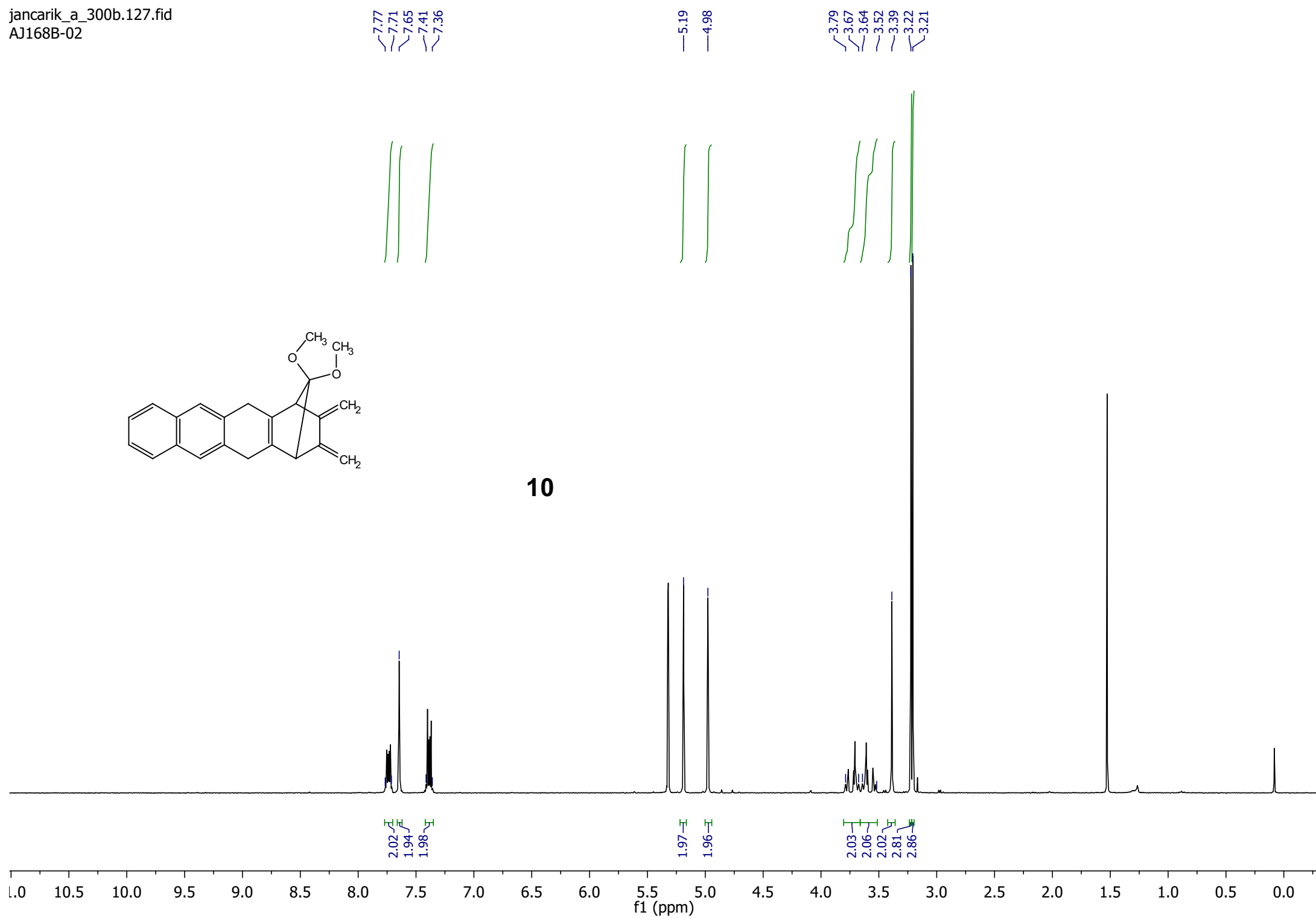
8.87
8.72
8.70
8.05
7.90
7.90
7.89
7.88
7.77
7.76
7.75
7.73
7.70
7.69
7.69
7.68
7.67
7.67
7.63
7.63
7.62
7.62
7.61
7.60
7.60



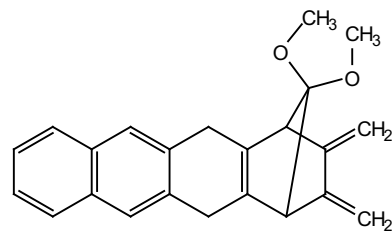


138.21
137.92
131.82
131.07
129.88
129.30
128.54
127.15
126.67
122.56
121.75
116.09

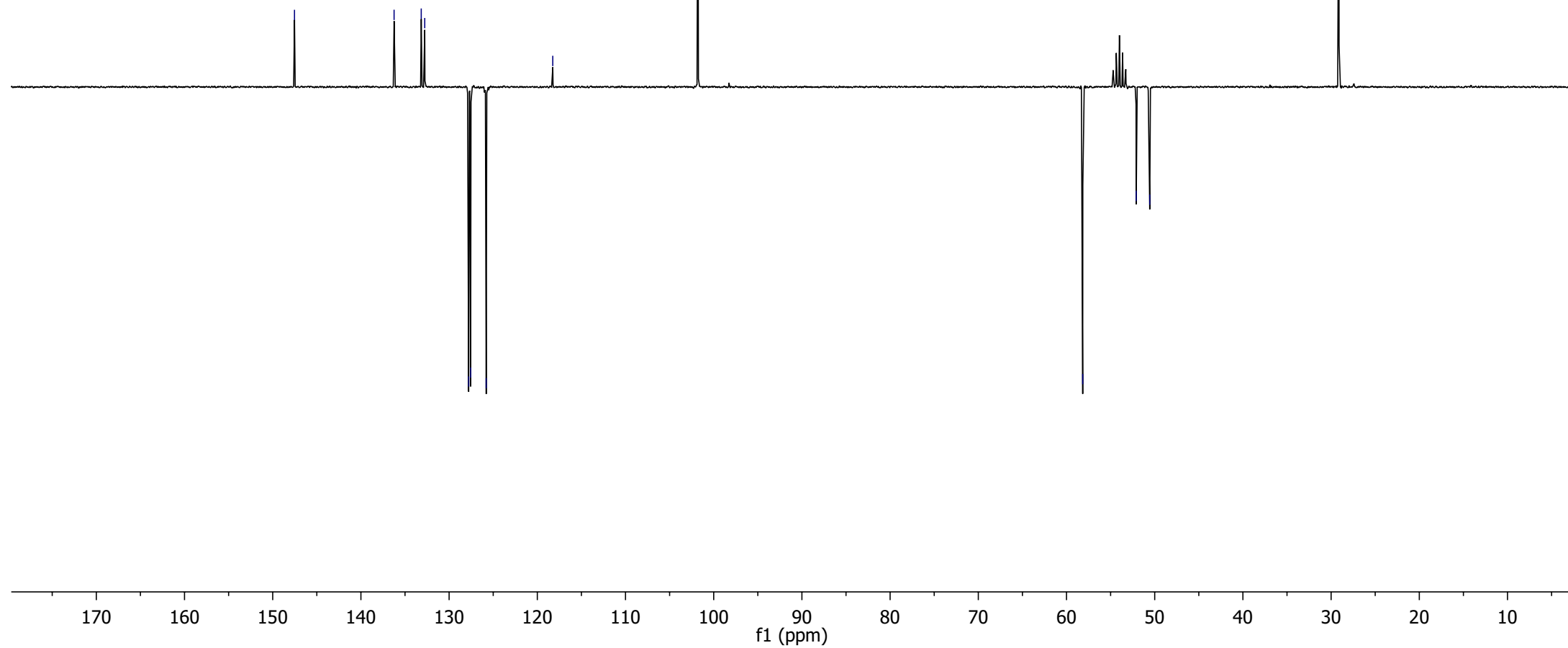




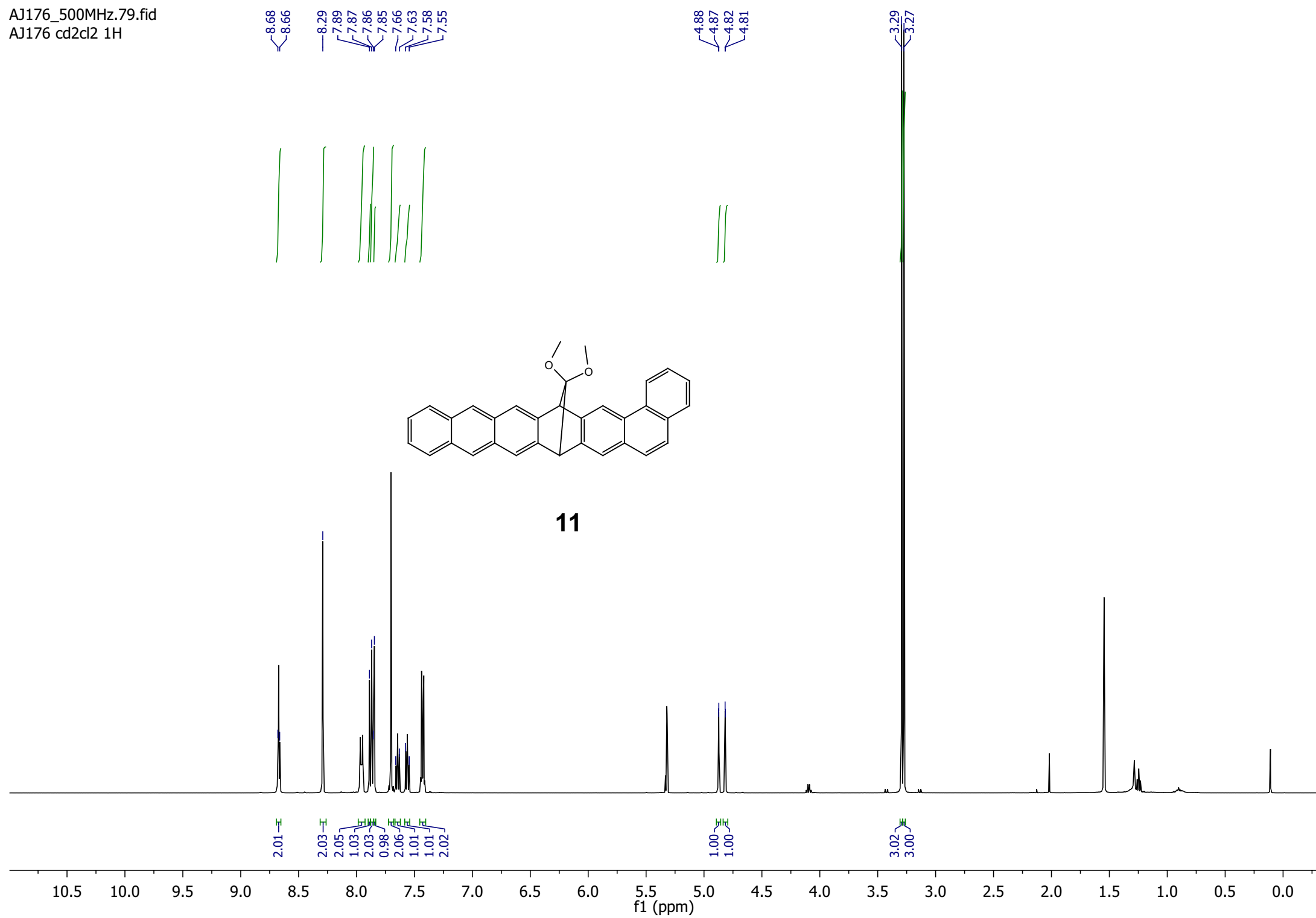
—147.53 —136.24 —133.16 —132.76 —127.78 —127.56 —125.80 —118.25 —101.79 —58.16 —52.10 —50.56 —29.12



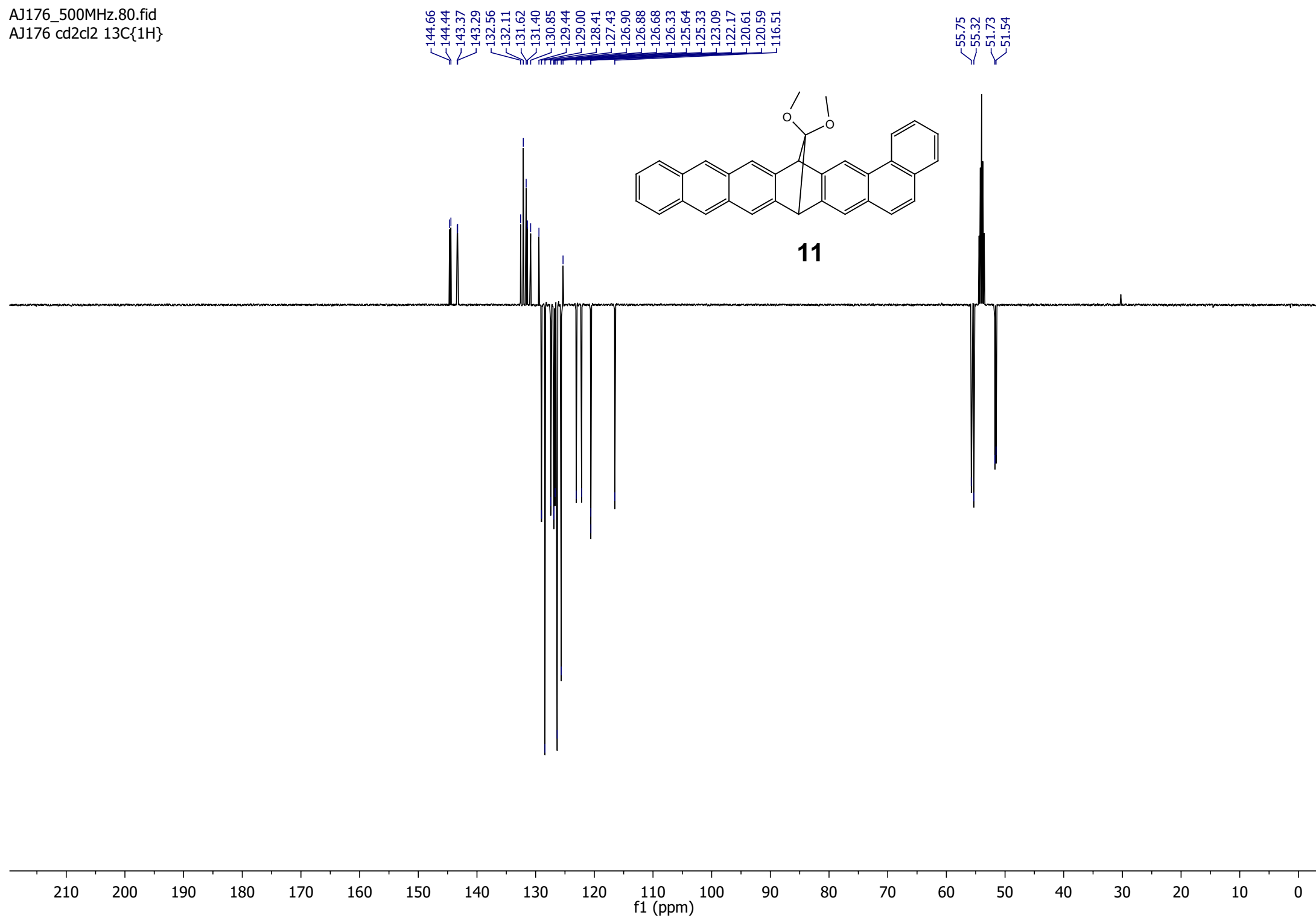
10



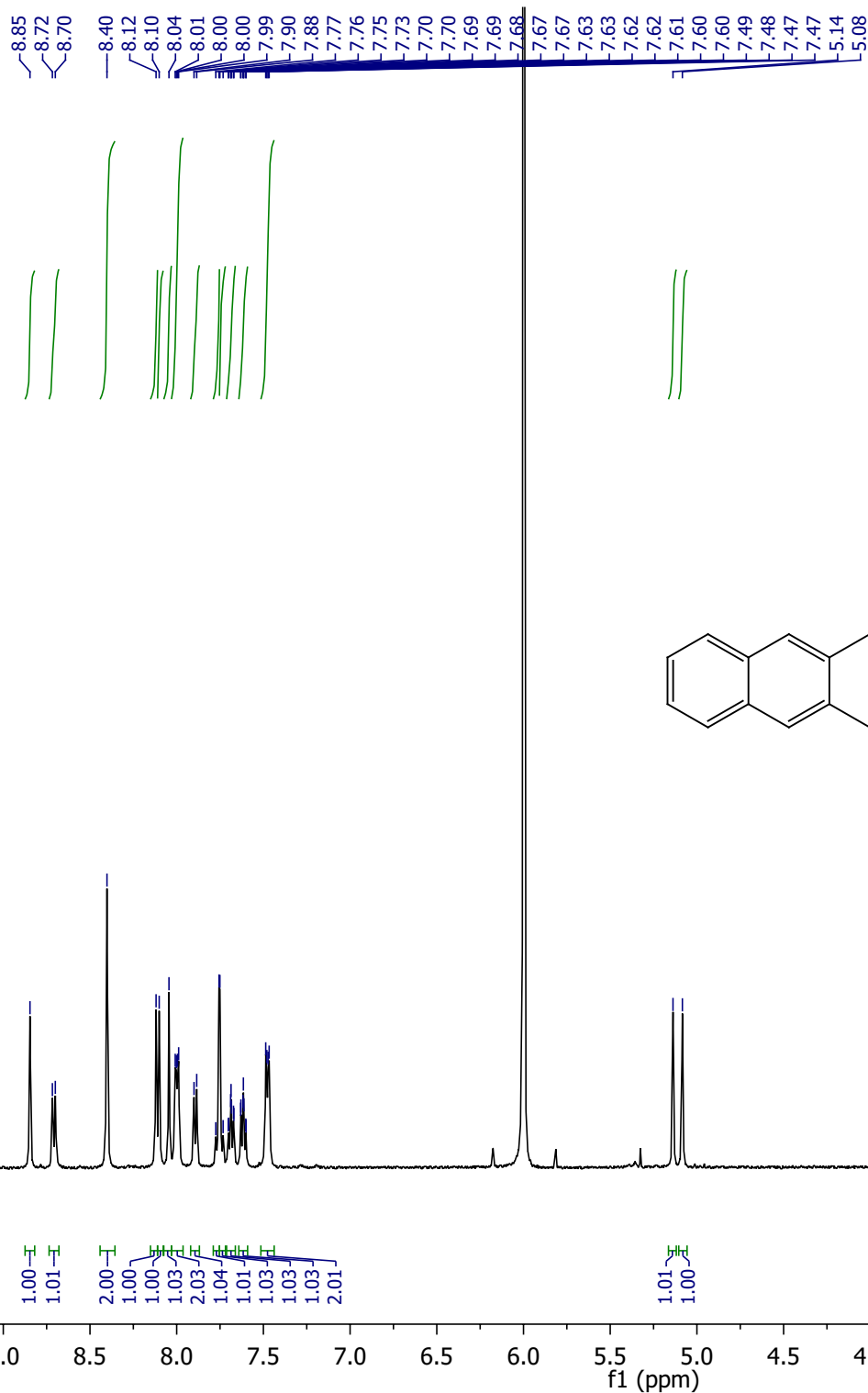
AJ176_500MHz.79.fid
AJ176 cd2cl2 1H



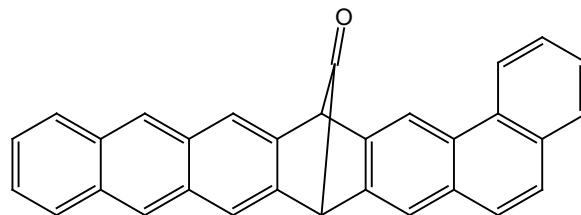
AJ176_500MHz.80.fid
AJ176 cd2cl2 13C{1H}



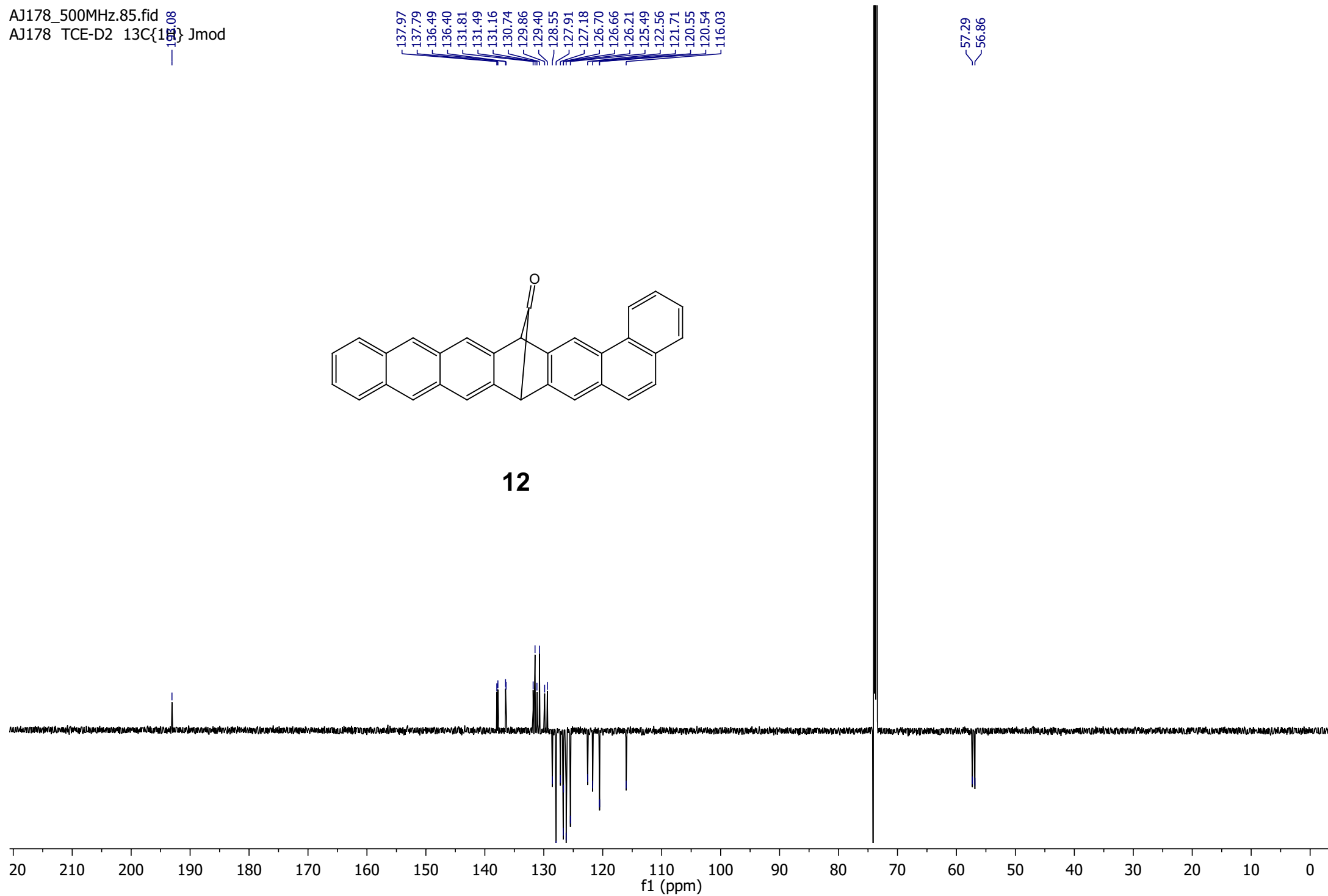
AJ178_500MHz.84.fid
AJ178 TCE-D2 1H



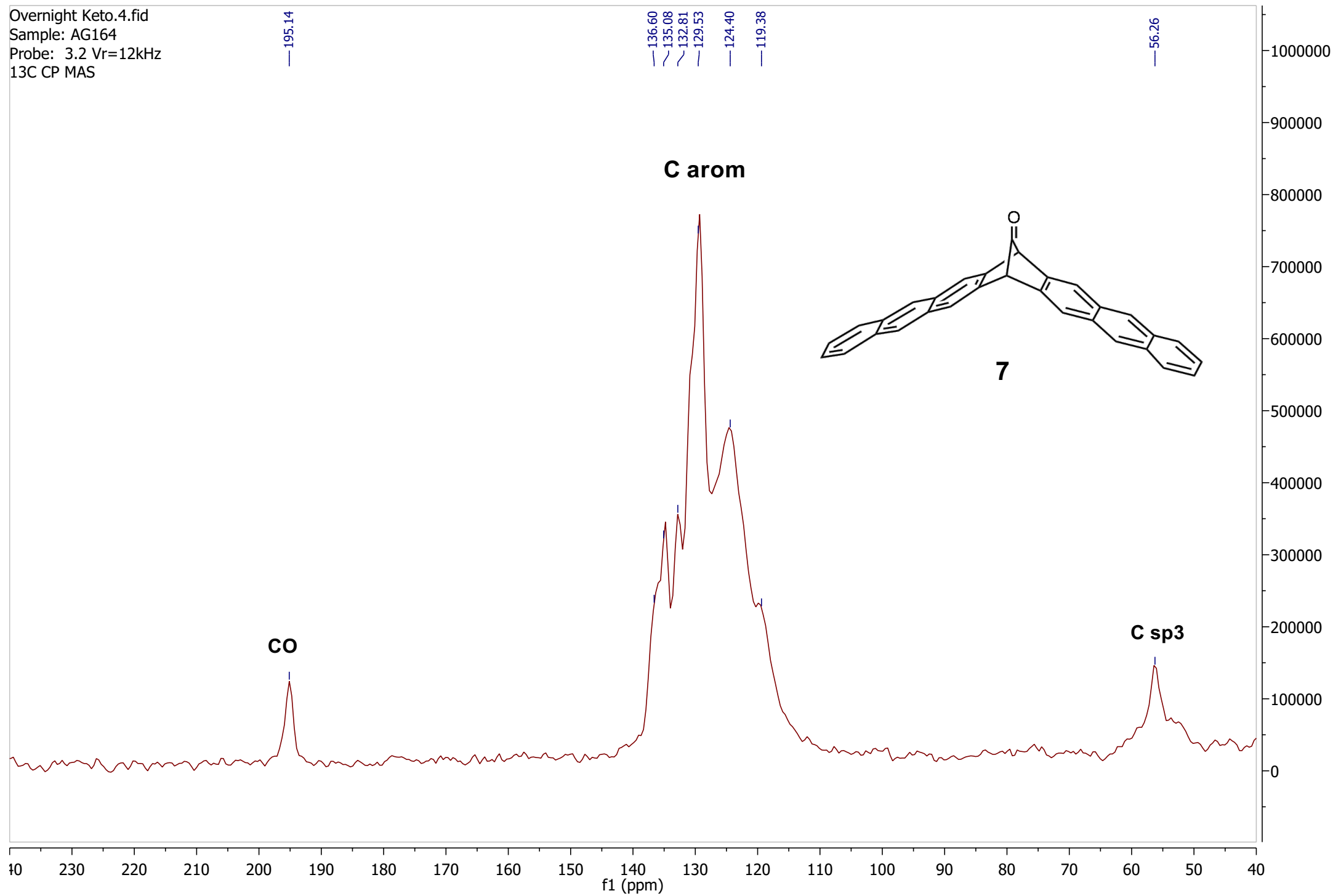
AJ178_500MHz.85.fid
AJ178 TCE-D2 13C{1H} Jmod



12

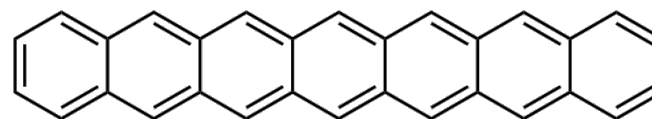


Overnight Keto.4.fid
Sample: AG164
Probe: 3.2 Vr=12kHz
13C CP MAS

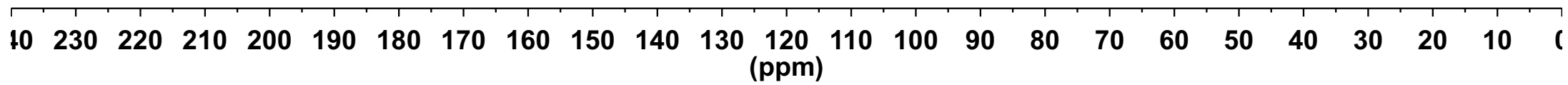


Sample: AG164-200C
Probe: 3.2 Vr=15kHz
13C CP MAS

—129.05
—125.60



2

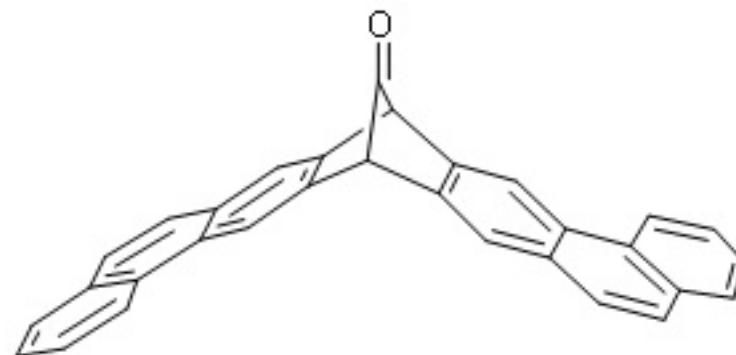


Sample: AJ173
Probe: 2.5 Vr=14kHz
13C CP MAS

137.33
134.53
127.05
122.99

—113.08

—55.66

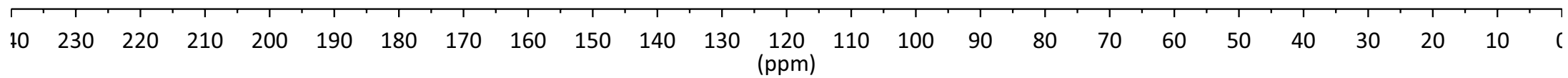


9a

C arom

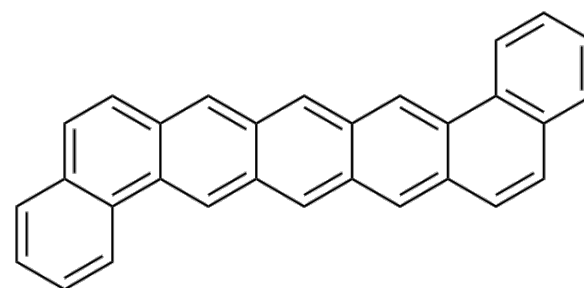
C sp3

CO ?

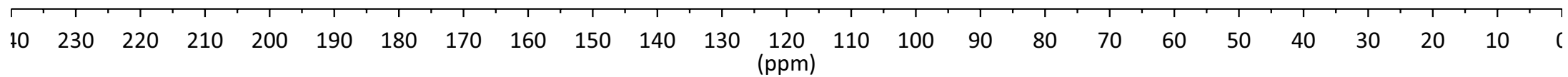


Sample: AJ173 - heated
Probe: 2.5 Vr=14kHz
13C CP MAS

—125.53



3

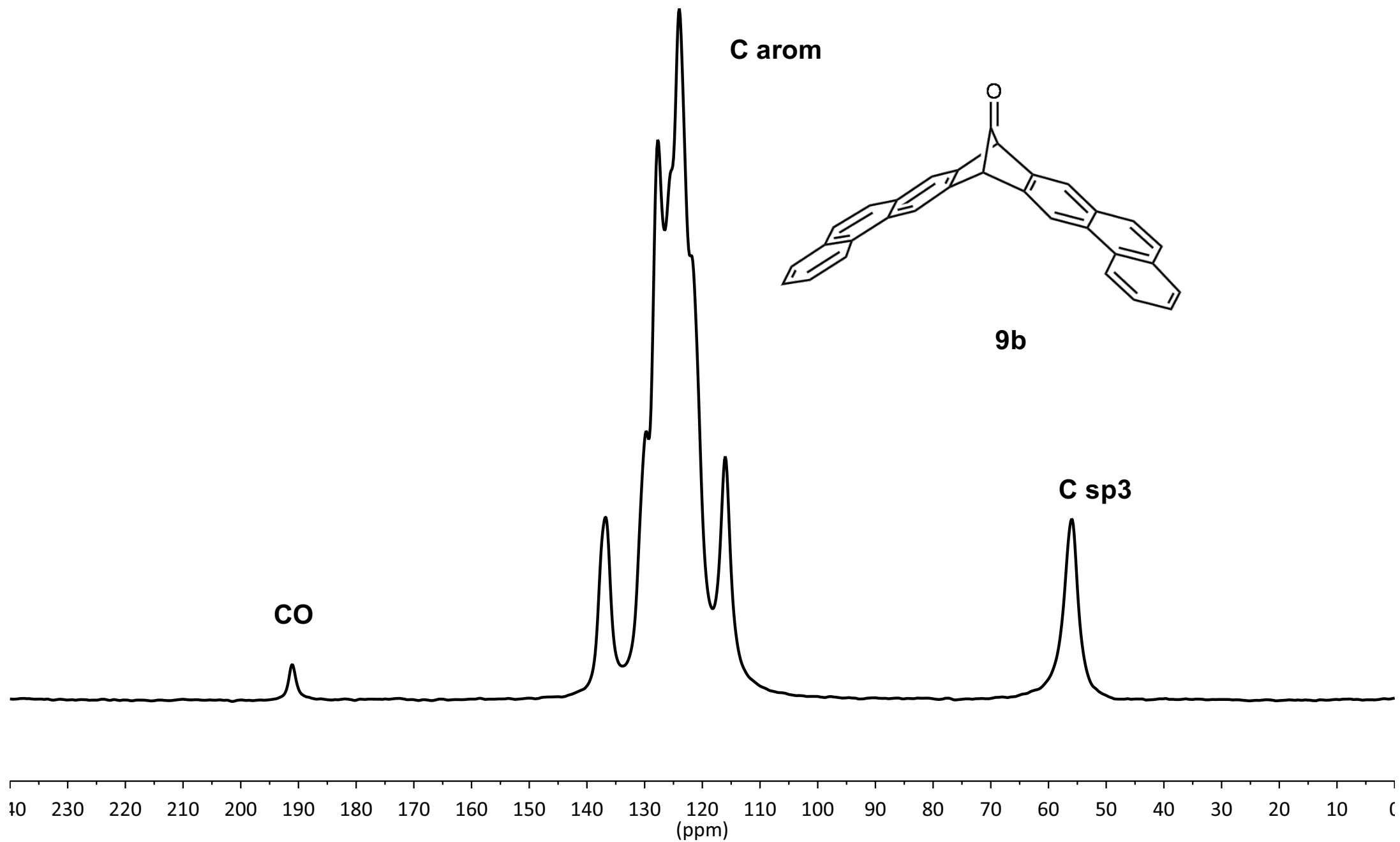


Sample: AJ172
Probe: 2.5 Vr=14kHz
13C CP MAS

—191.08

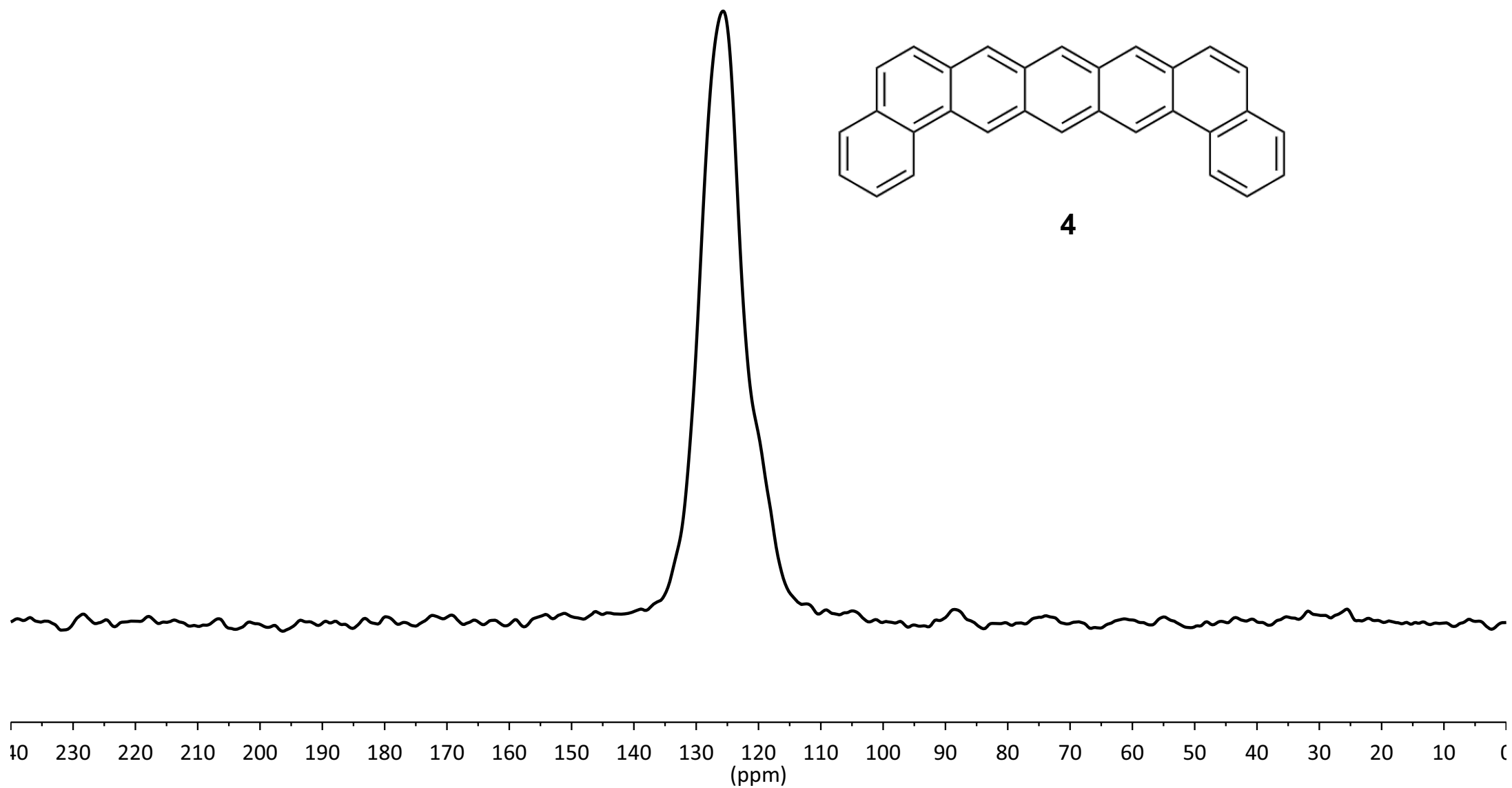
~136.84
/130.16
~127.83
~125.92
~123.95
~121.46
~116.03

—56.04



Sample: AJ172 - heated
Probe: 2.5 Vr=14kHz
¹³C CP MAS

—125.95



Sample: AJ174 ?
Probe: 2.5 Vr=14kHz
13C CP MAS

—191.74

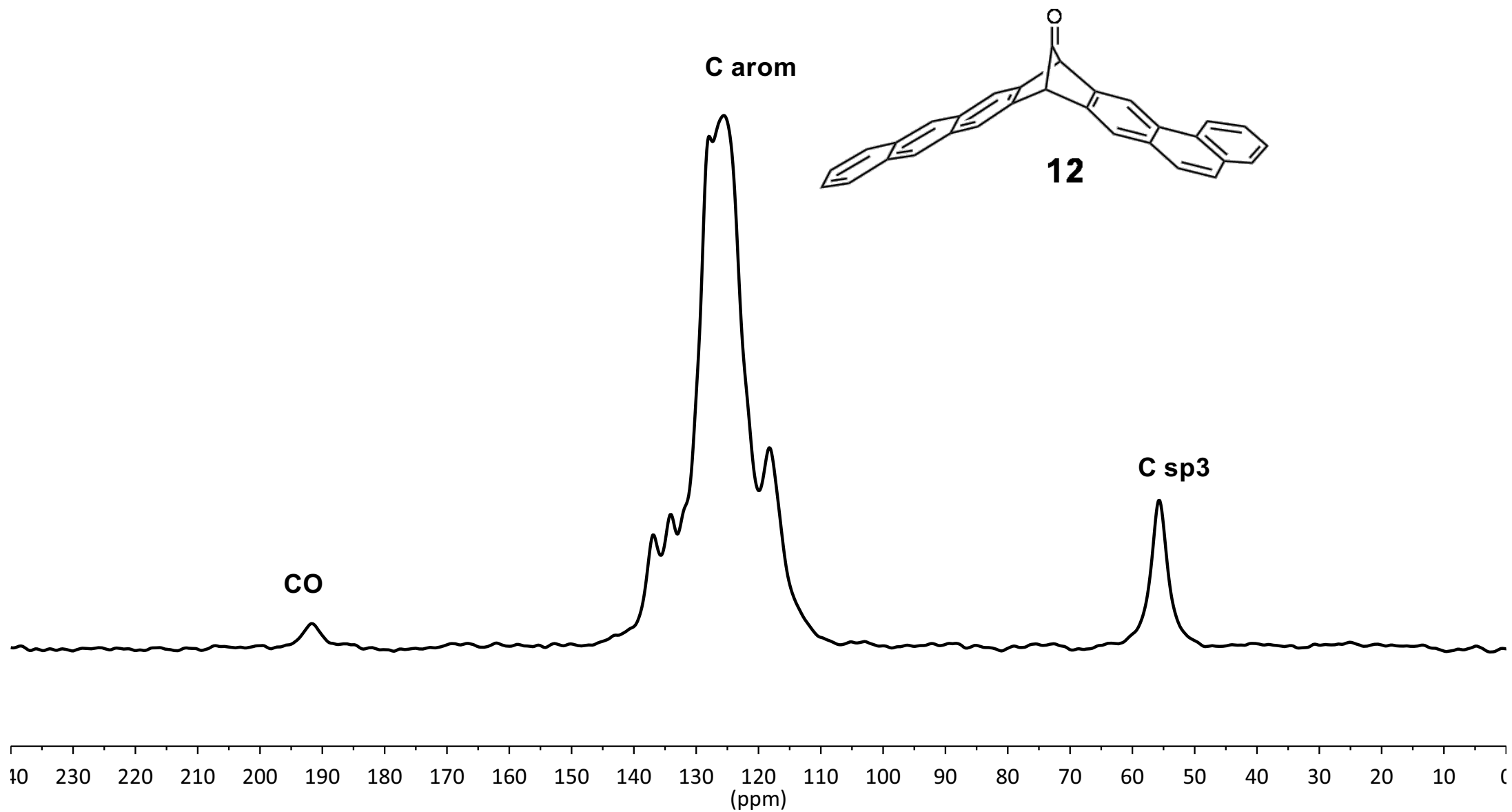
—136.88
~

—134.09
~

—125.56

—118.24

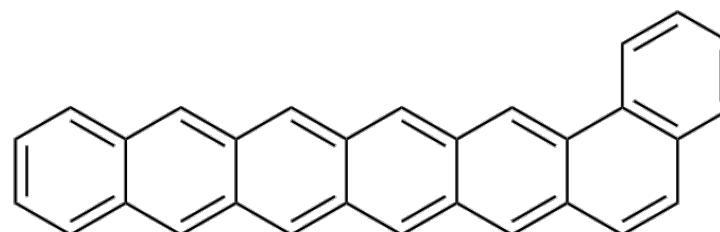
—55.71



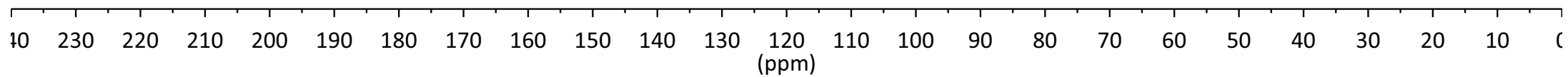
Sample: AJ174 ? - heated
Probe: 2.5 Vr=14kHz
¹³C CP MAS

—124.99

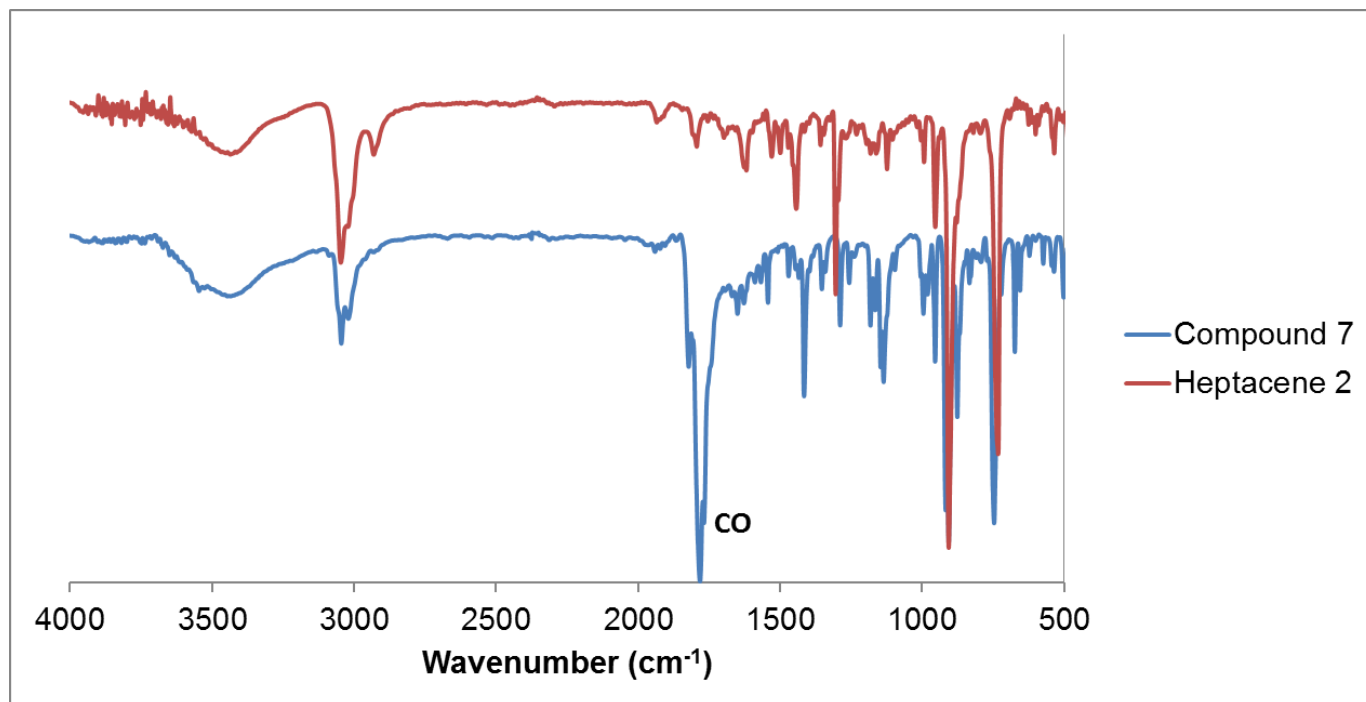
C arom



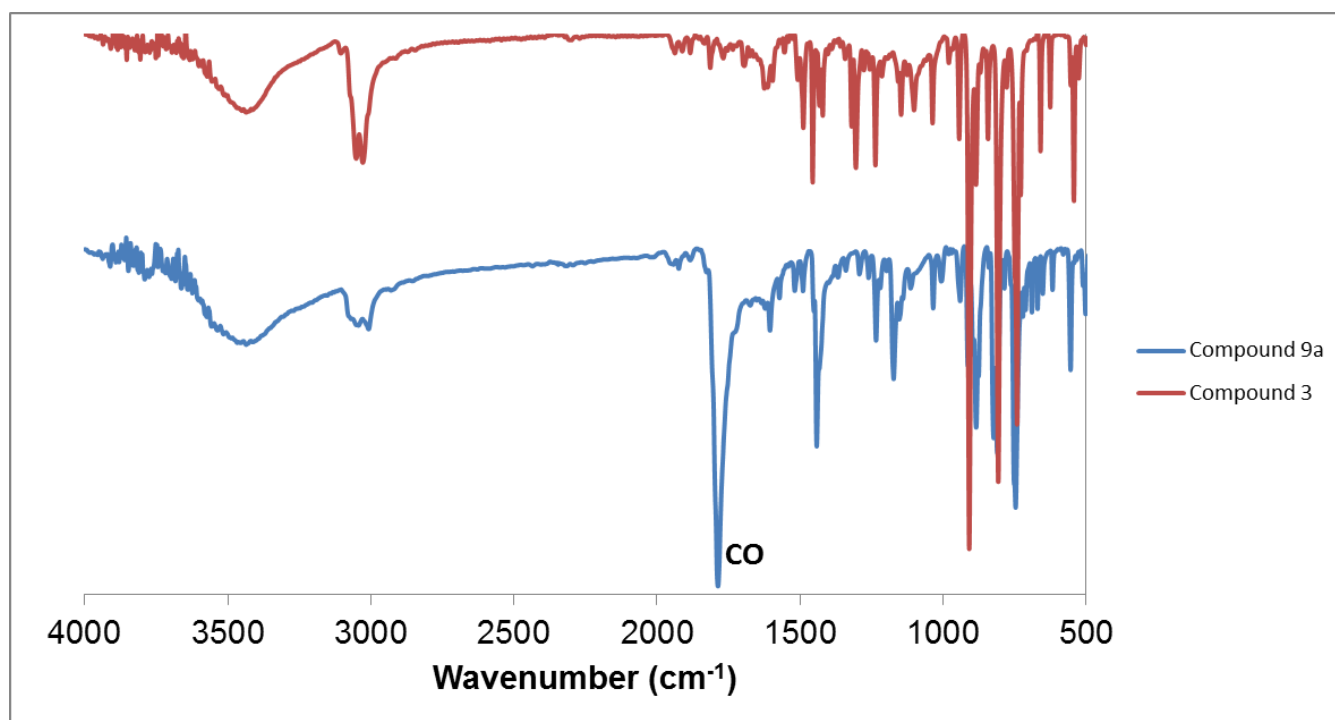
5



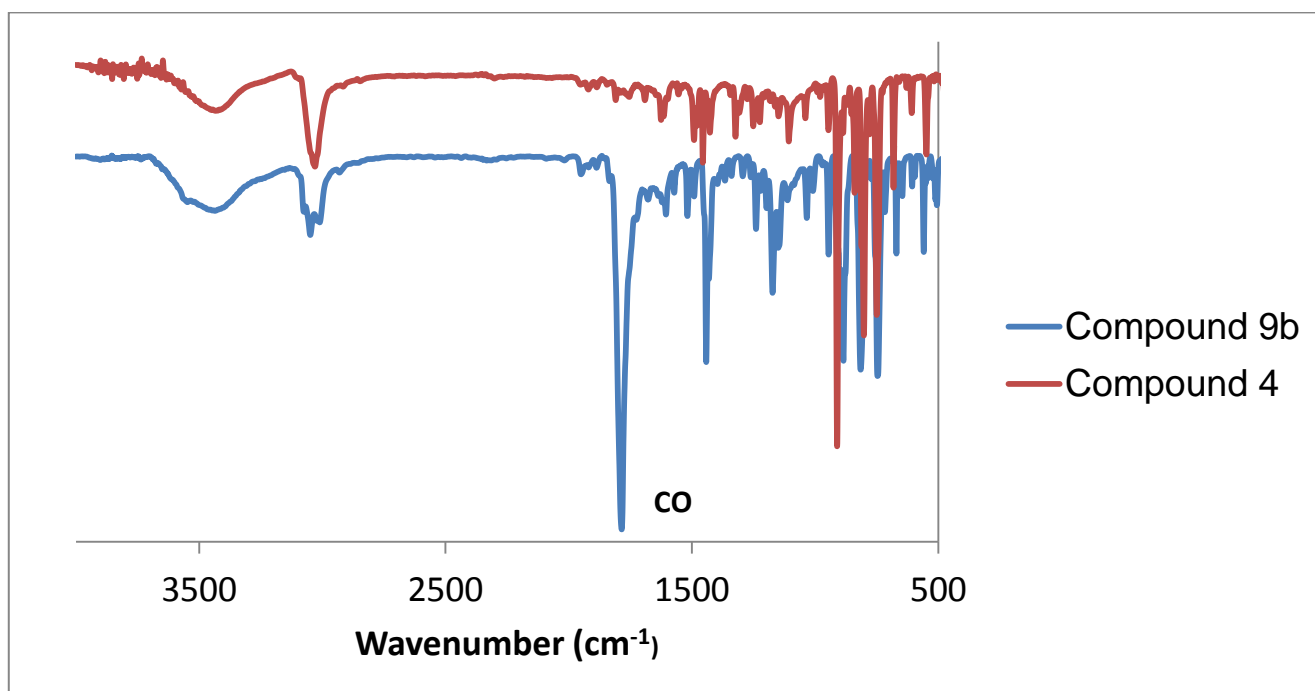
Infrared spectra of acenes and precursors (KBr pellets)



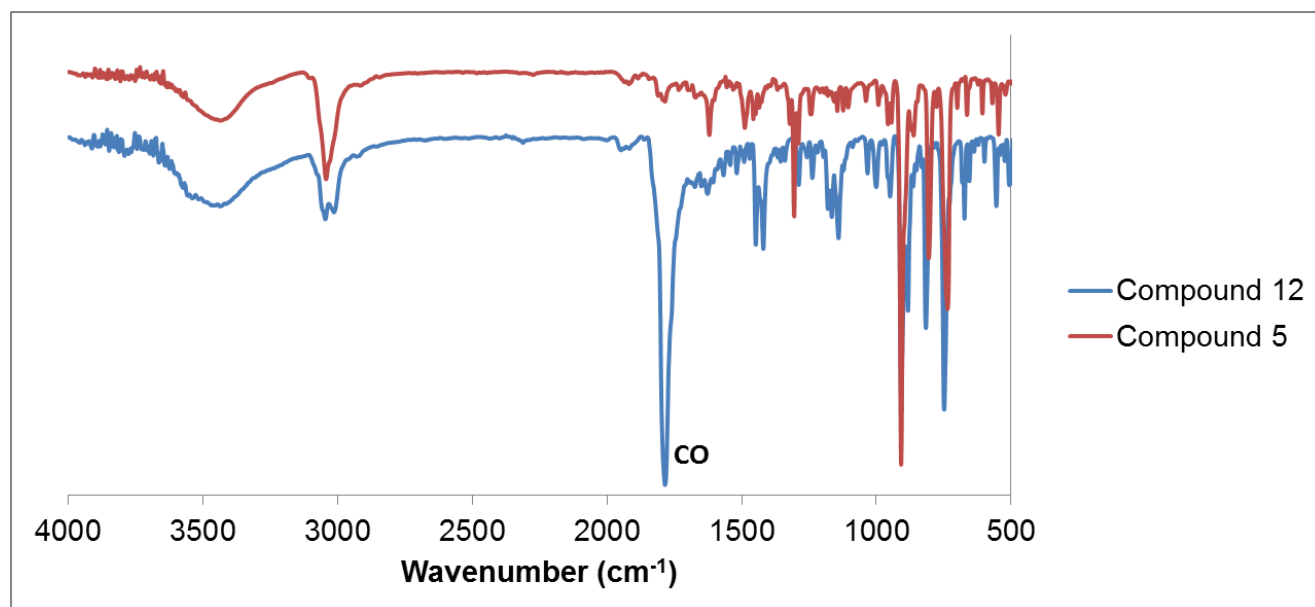
Infrared spectra of heptacene 2 and its precursor 7.



Infrared spectra of *trans*-DBPen 3 and its precursor 9a.



Infrared spectra of *cis*-DBPen 4 and its precursor 9b.



Infrared spectra of benzohehexacene 5 and its precursor 12.

Thermal Gravimetric Analysis of compounds 9b/3, 9a/4, and 12/5 showing the decarbonylation temperatures.

