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Graphical abstract

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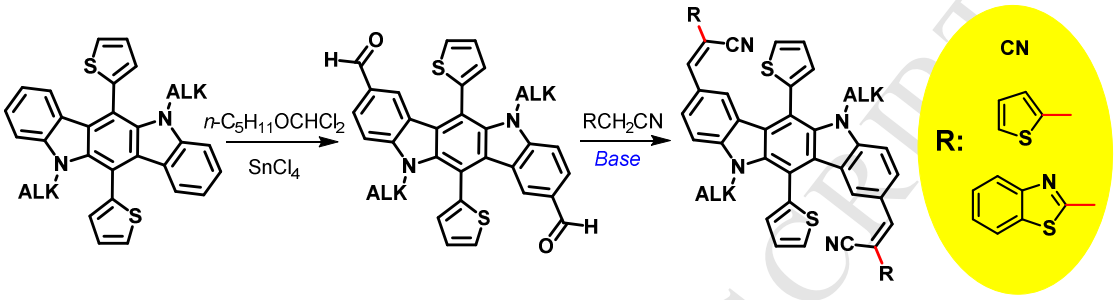

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Synthesis, photophysical and electrochemical properties of novel 6,12-di(thiophen-2-yl) substituted indolo[3,2-*b*]carbazoles

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A B S T R A C T

Novel 5,11-dialkyl-6,12-di(thiophen-2-yl) substituted 5,11-dihydroindolo[3,2-*b*]carbazoles have been obtained and plausible ways for their further modifications via the Friedel-Crafts reaction are presented. The formylation of these indolo[3,2-*b*]carbazoles with dichloromethyl alkyl esters catalysed by Lewis acids leads to the formation of the corresponding 2,8-diformyl derivatives. Applicability of this formylation method for modification of indolo[3,2-*b*]carbazoles bearing electron-rich aromatic substituents at C-6 and C-12 has also been demonstrated. The Knoevenagel condensation of 2,8-dialdehydes with active methylene nitriles has been studied. The measurements of optical and redox properties for a number of new indolo[3,2-*b*]carbazoles have been performed.

Keywords: Indolo[3,2-*b*]carbazole; Indole; Thiophene; Acylation; Luminescence; *N*-Heteroacenes.

1. Introduction

Electro- and photoactive organic compounds containing a fused aromatic sytem with a high π-conjugated structure have received growing attention during the last decade due to their applications as components of advanced materials in electronic devices,[1] such as organic field-effect transistors (OFETs),[2-6] photovoltaic cells (PCs),[7-10] and organic light-emitting diodes (OLEDs).[11-15] Organic compounds are rather attractive for use in these types of electronic devices, due to their low cost and good mechanical properties, and also due to an opportunity to tune their electrical and optical properties through chemical modifications of their structural fragments. The main efforts of chemists are focused today on optimization of charge transport properties and the stability of organic compounds.

Indolo[3,2-*b*]carbazoles represent an important class of ladder-type *N*-heteroacenes, which have various applications in the area of organic electronics and biology.[10] Indeed, derivatives of

indolo[3,2-*b*]carbazoles have been used successfully as hole-transporting layers in OFETs[16-18] (hole mobility 0.03 – 0.22 $cm^2 \cdot V^{-1} \cdot s^{-1}$), and light-emitting layers in OLEDs[19,20] because of their high thermal stability, hole-injecting and transporting properties. Moreover, the indolo[3,2-*b*]carbazole unit has been used as the electron-donating part of the dye for dye-sensitized solar cells (DSSCs),[21] and polymer solar cells (PSCs)[22,23] (Figure 1). Therefore, the development of convenient methods for selective modifications of the family of indolo[3,2-*b*]carbazoles are of great importance for this branch of science and technology.

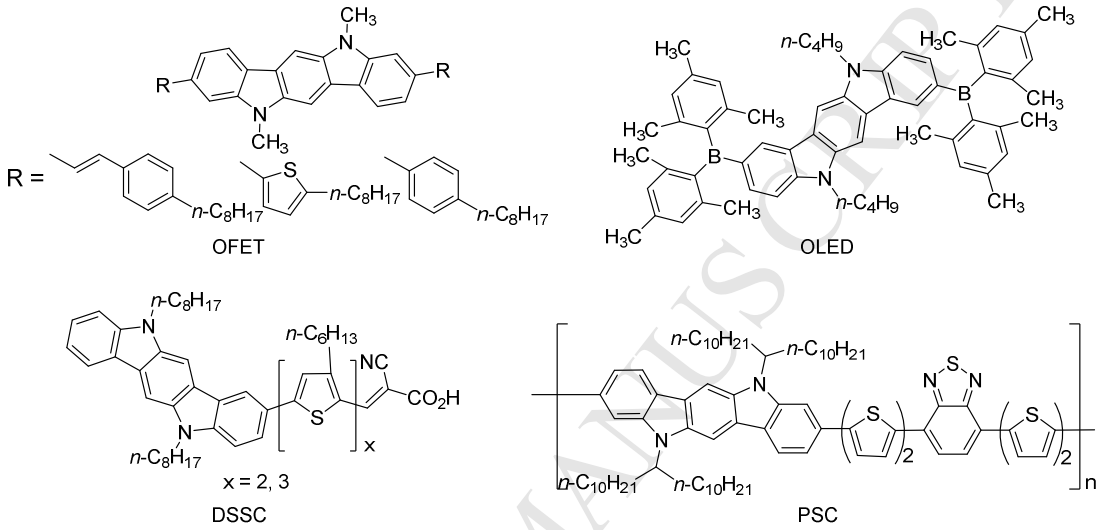
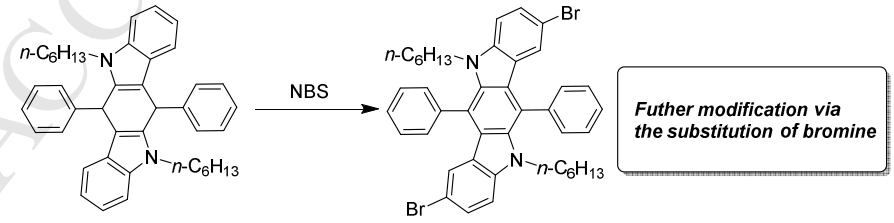


Figure 1. The main pattern structures of indolo[3,2-*b*]carbazoles used for organic electronics

A new approach to the synthesis of 6,12-diaryl substituted 5,6,11,12-tetrahydroindolo[3,2-*b*]carbazoles by reacting benzaldehydes with indole under catalysis by acids has been described in the literature.[24-26] Moreover, a further functionalization has been suggested via the intermediacy of 2,8-dibromo-6,12-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole, which was prepared by oxidative bromination of the corresponding 5,6,11,12-tetrahydroindolo[3,2-*b*]-carbazole with NBS (Scheme 1).[26]



Scheme 1. Bromination and dehydrogenation of indole[3,2-*b*]carbazole derivatives

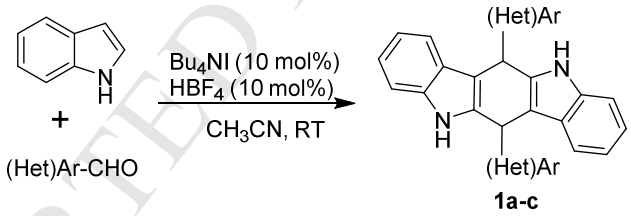
To the best of our knowledge, no data on the modification of indole[3,2-*b*]carbazoles bearing electron-rich aromatic or heteroaromatic rings at C-6 and C-12 (thiophenyl, alkoxyphenyl, etc.) have so far been reported in the literature. Moreover, 5,11-dihydro-6,12-di(thiophen-2-yl)indolo[3,2-*b*]carbazole is of particular interest for the design of electro and

photoactive molecules, since it contains the 1,4-di(thiophen-2-yl)benzene unit, present in the structure of a variety of organic semiconductors.[27]

2. Results and Discussion

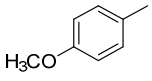
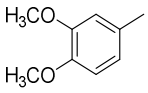
2.1. Synthesis and modification

In this communication we report the synthesis of new 5,11-dialkyl-6,12-di(thiophen-2-yl) substituted 5,11-dihydroindolo[3,2-*b*]carbazoles, and also several ways for their selective modification. It has been found that interaction of thiophene-2-carbaldehyde with indole takes place smoothly under catalysis with hydroiodic acid at room temperature in the dark (the same conditions have been described[26] for benzaldehyde), thus leading to the formation of the corresponding indolo[3,2-*b*]carbazole **1a,** however in low yield. Freshly distilled hydriodic acid (w/w 57%) was used in these experiments, but the highest yield of indolo[3,2-*b*]carbazole **1a** was only 27%, while degradation compounds derived from the starting material were obtained as major products. A solution to this problem was found when a mixture of tetrabutylammonium iodide and HBF_4 (w/w 48%) was used as catalyst, instead of hydroiodic acid. Furthermore, anisaldehyde and veratraldehyde were shown to react with indole successfully under these reaction conditions to give the corresponding indolo[3,2-*b*]carbazoles **1b,c** in nearly quantitative yields (see Scheme 2, Table 1).



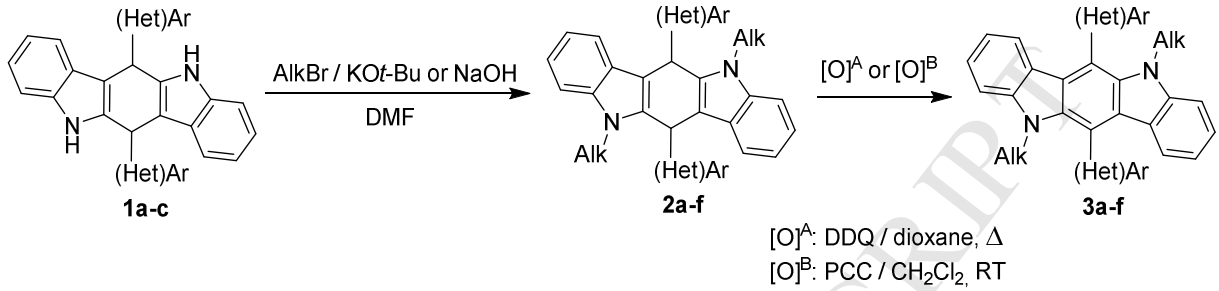
Scheme 2. Synthesis of indolo[3,2-*b*]carbazoles **1**

Table 1. Reaction time and yields of indolo[3,2-*b*]carbazoles **1**

Product **1**	(Het)Ar	Time (h)	Yield (%)
1a		14	73
1b		3	98
1c		4	95

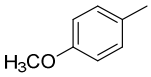
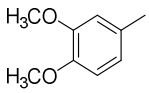
Alkylation of indolo[3,2-*b*]carbazoles **1a-c** has been carried out in DMF solution with an excess of alkyl bromides in the presence of a base to give the bis-alkylated derivatives **2a-f**. For the

base, potassium *tert*-butoxide was used in case of compound **1a**, and sodium hydroxide was used in the case of compounds **1b,c**. 5,11-Dialkyl-5,6,11,12-tetrahydroindolo[3,2-*b*]carbazoles **2a-f** were oxidized with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in refluxing dioxane, or by using pyridinium chlorochromate (PCC) in dichloromethane at room temperature (see Scheme 3, Table 2).



Scheme 3. Two steps synthesis of indolo[3,2-*b*]carbazoles **3**

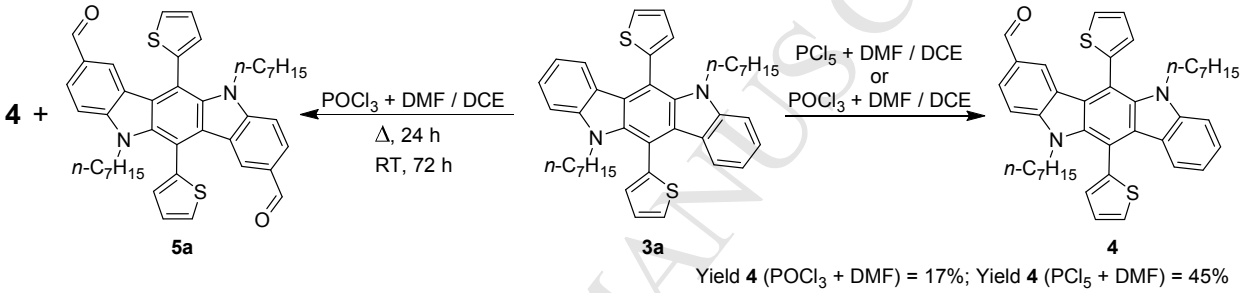
Table 2. Yields of indolo[3,2-*b*]carbazoles **2** and **3** (oxidation with DDQ or PCC)

Indolo[3,2-*b*]carbazoles **2 / 3**	Alk	(Het)Ar	Yield (%) **2** Alkylation	Yield (%) **3** with DDQ	Yield (%) **3** with PCC
2a / **3a**	*n*-C_7H_{15}		83	56	87
2b / **3b**	*n*-C_6H_{13}		75	52	79
2c / **3c**	*n*-C_4H_9		85	55	85
2d / **3d**	*n*-$C_{15}H_{31}$		51	90	95
2e / **3e**	*n*-C_6H_{13}		65	70	89
2f / **3f**	*n*-C_7H_{15}		70	79	93

Aromatization of 5,6,11,12-tetrahydroindolo[3,2-*b*]carbazoles **2a-f** by the action of PCC was carried out at room temperature, and yields of products **3a-f** were higher than those obtained with DDQ. Furthermore, on using PCC as oxidant the isolation procedure for compounds **3a-f** proved to be a more convenient one.

Further modifications of indolo[3,2-*b*]carbazoles **3a-f** have been studied. It should be emphasized that all attempts to cause bromination of compounds **3a-f** or oxidative bromination of compounds **2a-f** under various conditions have failed. Indeed, unidentified mixtures of polybrominated indolo[3,2-*b*]carbazoles were isolated in a number of experiments. It is clear that the previously described method[26] cannot be applied for the modification of indolo[3,2-

b]carbazoles bearing electron-rich (hetero)aromatic substituents at C-6, C-12, because of the low selectivity of bromination. The formylation procedures were applied for functionalization of **3a,** as a model compound, and the Vilsmeier reagent ($POCl_3$-DMF complex) was first examined for this purpose. It has been found that the reaction of indolo[3,2-*b*]carbazole **3a** with an excess of the Vilsmeier reagent (10 eq.) in a refluxing 1,2-dichloroethane (DCE) leads to a mixture of mono- and diformylation products, such as indolo[3,2-*b*]carbazoles **4** and **5a** (2:3, according to the ^{1}H NMR data), respectively. On the other hand, when a similar reaction was carried out at room temperature for 3 days, the monoformylated product **4** was obtained exclusively in 17% yield, while conversion of the starting material **3a** was very poor. The yield of aldehyde **4** could be slightly increased (up to 45%) by using phosphorus(V) chloride to prepare the Vilsmeier reagent, instead of phosphoryl chloride (Scheme 4).



Scheme 4. Formylation of indolo[3,2-*b*]carbazole **3a** with the Vilsmeier reagent

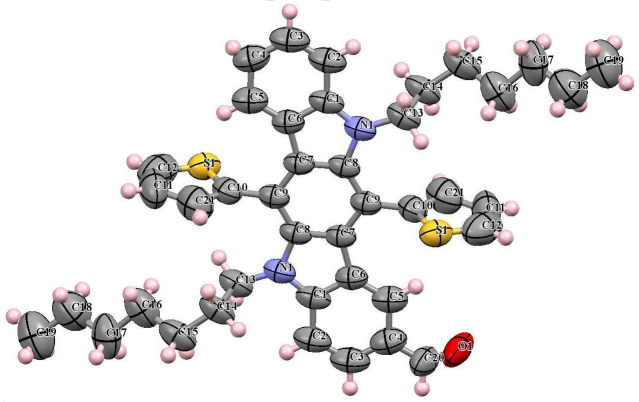
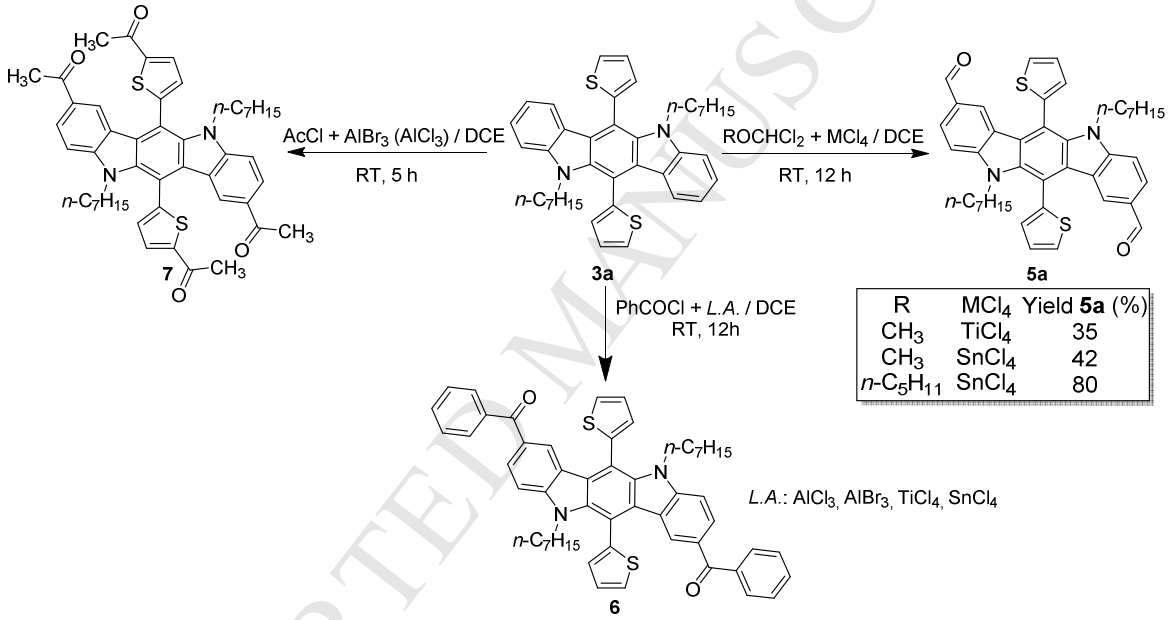


Figure 2. Mercury[28] representation of the X-ray crystal structure of aldehyde **4**. Thermal ellipsoids at 50% probability.

The structure of aldehyde **4** was confirmed unequivocally by X-ray crystallography analysis in addition to elemental analysis, ^{1}H, ^{13}C NMR, and IR spectroscopy (Figure 2). Unfortunately, neither variation of components in the Vilsmeier reagent (*e.g.* PCl_5-DMF, $SOCl_2$-DMF, $COCl_2$-DMF), nor enhanced heating time of the reaction mixture could be successful for the selective synthesis of dialdehyde **5a**.

An attempt to obtain dialdehyde **5a** was undertaken by using the commercially available dichloromethyl methyl ether in the presence of mild Lewis acids, such as titanium(IV) and tin(IV) chlorides (the Rieche formylation[29]), since the synthesis of this derivative was difficult

via the Vilsmeier-Haack reaction. It was found that compound **5a** is formed without any impurities of aldehyde **4** under these formylation conditions, but yields of compound **5a** in the experiments with the commercial dichloromethyl methyl ether proved to be moderate ones (35% with $TiCl_4$, 42% with $SnCl_4$), due to degradation of the starting material **3a**. However, when dichloromethyl pentyl ether[30] was used for formylation of indolo[3,2-*b*]carbazole **3a** in the presence of tin(IV) chloride, dialdehyde **5a** was obtained in 80% yield. The higher yield of dialdehyde **5a** may be a result of the enhanced stability of 1-(het)aryl-1-chloromethyl pentyl ether, which is the key intermediate of the current formylation process.[29] Benzoylation of compound **3a** with benzoyl chloride in the presence of various Lewis acids proceeded similarly to the formylation process, thus leading to the formation of 2,8-di(benzoyl) derivative **6**. The best yield (87%) of product **6** was obtained using tin(IV) chloride (Scheme 5).



Scheme 5. Modification of indolo[3,2-*b*]carbazole **3a** by using the Friedel-Crafts reactions

It is noteworthy that both triformyl and tetraformyl derivatives **5a'** and **5a''** (Figure 3) were not detected in experiments with indolo[3,2-*b*]carbazole **3a** within the reaction times from 1 to 7 days**,** even in the presence of a large excess of dichloromethyl alkyl ethers, and on using stronger Lewis acids (*e.g.* $AlCl_3$, $AlBr_3$). On the other hand, acetylation of indolo[3,2-*b*]carbazole **3a** with an excess of acetyl chloride and aluminium tribromide (trichloride) leads to the formation of tetraacetyl derivative **7** in 45-50% yields (Scheme 5). However, all attempts to cause acetylation of compound **3a** under catalysis with mild Lewis acids, such as tin(IV) or titanium(IV) chlorides have failed; a dark gum was obtained as the only product of the reaction.

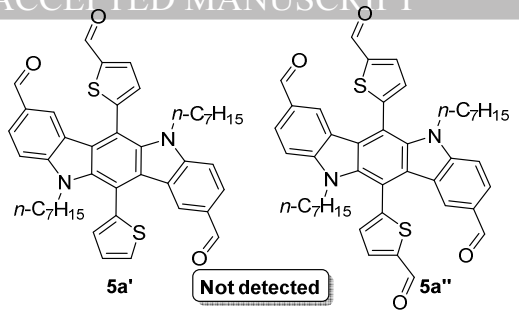
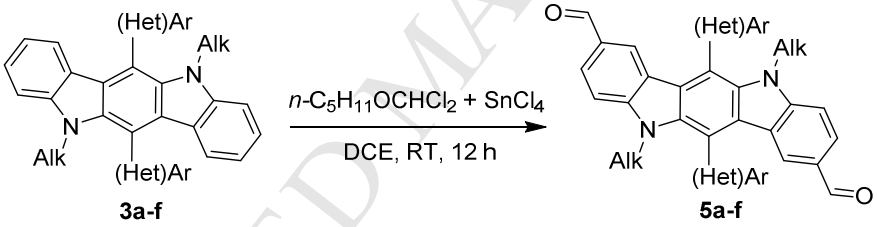


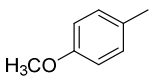
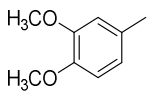
Figure 3. Triformyl and tetraformyl derivatives **5a'** and **5a''**

The optimal conditions found for the Rieche formylation of indolo[3,2-*b*]carbazole **3a** were exploited successfully to formylate other indolo[3,2-*b*]carbazoles **3**. Aldehydes **5a-f** were obtained selectively as the main products, in yields ranging from 43% to 80% (Scheme 6, Table 3). It is noteworthy that this formylation procedure allows one to obtain dialdehydes **5a-f** in analytically pure form after a single crystallization of crude material from an appropriate solvent. The formylation of indolo[3,2-*b*]carbazoles at C-2 and C-8 has been confirmed by 2D NMR experiments, such as ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{1}H-^{15}N HMBC, performed for dialdehyde **5a** (see ESI).



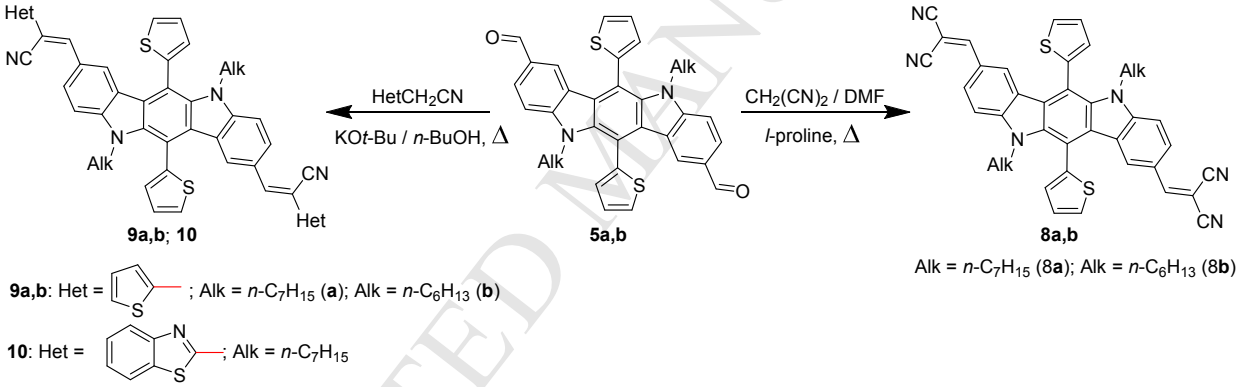
Scheme 6. Preparation of dialdehydes **5** via the Rieche procedure

Table 3. Yields of dialdehydes **5**

Dialdehyde **5**	Alk	(Het)Ar	Yield (%) **5**
5a	*n*-C_7H_{15}		80
5b	*n*-C_6H_{13}		65
5c	*n*-C_4H_9		43
5d	*n*-$C_{15}H_{31}$		74
5e	*n*-C_6H_{13}		68
5f	*n*-C_7H_{15}		56

The ^{1}H NMR spectra of compounds **5a–f** in $CDCl_3$ exhibit a set of resonance signals, corresponding to their symmetrical structures, while protons of the two CHO-groups are observed as a singlet at 9.64 – 9.74 ppm (2H).

Moreover, further transformations of dialdehydes **5** have been studied to investigate their application as building blocks containing the indolo[3,2-*b*]carbazole scaffold. For this purpose, compounds **5a,b** were condensed with a number of C-H active nitriles, such as malononitrile, 2-(thiophen-2-yl)- and 2-(1,3-benzothiazol-2-yl) substituted acetonitriles by exploiting the Knoevenagel reaction. Condensation of aldehydes **5a,b** with a more active malononitrile was carried out under catalysis by *L*-proline (5 mol%) in DMF solution at 100 ˚C for 20 minutes to give 2,8-bis[2,2-di(cyano)vinyl] derivatives **8a,b** in excellent yields. 2-(Thiophen-2-yl)acrylonitrile derivatives **9a,b** were prepared from 2-(thiophen-2-yl)acetonitrile and aldehydes **5a,b** under strongly basic conditions, by using potassium *tert*-butylate in *n*-butanol solution at 80 ˚C. A typical example is illustrated by the reaction of 2-(1,3-benzothiazol-2-yl)acetonitrile with dialdehyde **5a,** leading to the formation of compound **10** (Scheme 7).



Scheme 7. Synthesis of 2,8-di(vinyl)indolo[3,2-*b*]carbazoles **8**, **9**, **10**

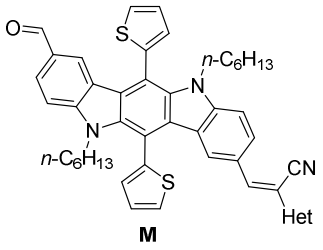


Figure 4. Minor mono-condensation products **M**

It should be noted that minor mono-condensation derivatives **M** were detected by ^{1}H NMR spectroscopy in the crude products, derived from the reaction of aldehyde **5b** with 2-(hetaryl)acetonitriles (Figure 4). Separation of these by-products **M** from the major compounds **9**, **10** proved to be difficult or nearly impossible by means of chromatography and crystallization

methods. However, the formation of mono-condensation by-product could be suppressed in the reaction with 2-(thiophen-2-yl)acetonitrile by using a 10-fold excess of this nitrile.

2.2 Electrochemical and Photophysical Properties

The UV-visible absorption spectra of compounds **3a-f, 8a, 8b, 9a, 9b** and **10** have been recorded at room temperature in a dichloromethane solution, and the results obtained are summarized in Table 4 and Figure 5. All indolo[3,2-*b*]carbazoles exhibited three similar absorption bands: at 270 – 300, 310 – 400 and 370 – 550 nm due to π-π* electronic transitions. The high-energy absorption band (310 – 400 nm) was attributed to the π-π* transition of the indolo[3,2-*b*]carbazole system, and the low-energy (370 – 550 nm) absorption band was attributed to the π-π* transition of the intramolecular charge transfer (ICT) from the indolo[3,2-*b*]carbazole unit to the aromatic terminals. In addition, the absorption bands of the 2,8-substituted indolo[3,2-*b*]carbazole derivatives were broader than those of unsubstituted derivatives. UV-Visible absorption spectra of non- and 2,8-substituted indolo[3,2-*b*]carbazoles are shown in Figure 5.

Table 4. Characteristics of indolo[3,2-*b*]carbazoles **3a-f**, **8a**, **8b**, **9a**, **9b** and **10**.

Compound	λ_{abs}, nm	E_{HOMO}, eV	E_{LUMO}[d], eV	E_g^{opt}, eV	E_m, nm	Φ
3a	292/ 330, 345/ 404, 426	– 4.91	– 2.07	2.84	438, 462	0.213 [a]
3b	290/345/404, 426	– 4.90	– 2.05	2.85	437, 462	0.220 [a]
3c	292/330, 345/404, 426	– 4.89	– 2.04	2.85	437, 462	0.189 [a]
3d	292/330, 345/404, 427	– 4.90	– 2.06	2.84	437, 463	0.181 [a]
3e	258, 290/323, 338/398, 419	– 4.79	– 1.9	2.89	431, 454	0.327 [a]
3f	288/323, 338/400, 419	– 4.75	– 1.86	2.89	432, 454	0.316 [a]
8a	345/458	– 5.05	– 2.51	2.54	562	0.095[b]
8b	344/457	– 5.10	– 2.56	2.54	560	0.003 [b]
9a	358/423	– 5.00	– 2.29	2.71	520	0.005 [b]
9b	357/430	– 5.04	– 2.33	2.71	518	0.009 [b]
10	283/352/470	– 5.12	– 2.65	2.47	570	0.112[c]

E_m - wavelength maximum of the photoluminescent spectrum; Quantum yields were estimated: [a] with 0.05 mol/L H_2SO_4 solution of quinine sulfate as a reference, [b] with 0.1 mol/L KOH solution of fluorescein as a reference, [c] reference was EtOH solution of rhodamine B as a reference;[31] [d] $E_{LUMO} = E_{HOMO} + E_g^{opt}$.

It is known that the UV absorption maximum of a conjugated molecule is associated with conjunction length. Indeed, the absorption maxima in the electronic spectra of **3a-d** were bathochromically shifted compared to **3e,f** (due to the presence of the thiophene unit relative to

phenyl) (Table 4, Figure 5, I) and in **8a**, **8b**, **9a**, **9b** and **10** compared with **3a-f** (resulting from substituents in 2,8–positions instead of a hydrogen atom) (Table 4, Figure 5, II). The highest bathochromic shift was observed in the spectrum of compound **10,** having the most degree of conjugation. The length of the alkyl chain did not have any influence on the position of the absorption maxima (**3f** and **3e**, set **3a-d, 8a** *vs* **8b**, **9a** *vs* **9b**). The optical bandgaps (E_g^{opt}) of **3a-f**, **8a,b**, **9a,b** and **10** have been estimated from the long-wave length absorption edge, and are summarized in Table 4.

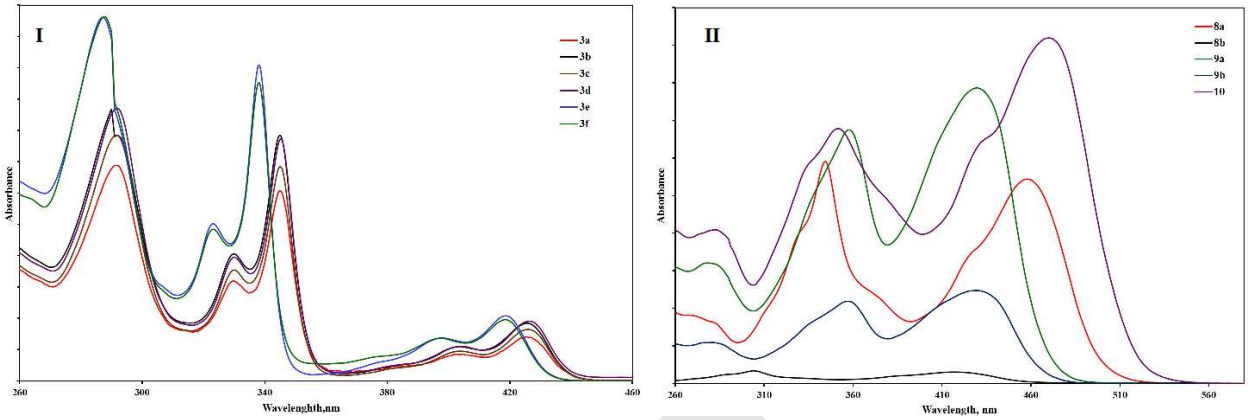


Figure 5. The UV-visible absorption spectra of **3a-f** (**I**) and **8a**, **8b**, **9a**, **9b**, **10** (**II**)

Electrochemical properties of indolo[3,2-*b*]carbazoles were investigated by the cyclic voltammetry method (see ESI). The measurements were performed for 10^{-3} mol/L solutions of the samples in a three electrode cell, using anhydrous dichloromethane and *n*-Bu_4NBF_4 (0.1 M), as a supporting electrolyte under an argon atmosphere at a scan rate of 100 mV/s. The potential of the $Ag/AgNO_3$ reference electrode was calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc+), which has a known oxidation potential of +4.8 eV. The HOMO energy values were estimated from the onset potentials (E_{ox}^{onset}) of the first oxidation event according to the following equations:

$$E_{HOMO}\ (\text{eV}) = -\left[E_{ox}^{onset} - E_{1/2}(\text{Fc/Fc+}) + 4.8\right]$$

where $E_{1/2}$(Fc/Fc+) is the half-wave potential of the Fc/Fc+ couple against the Ag/Ag+ electrode. The LUMO energy levels were determined from optical energy band gaps and E_{HOMO} values (Table 4). It should be noted that the CV curves remained unchanged under multiple successive potential scans. This fact indicates a high stability of these compounds to electrochemical oxidation. Moreover, the high-lying HOMO energy levels for indolo[3,2-*b*]carbazoles **3**,**8**,**9** and **10** suggest that these derivatives have high oxidative stability, and can be regarded as potential hole-transport and injection materials.[32,33]

The photoluminescence spectra of **3a-f, 8a, 8b, 9a, 9b** and **10** have been recorded, and the spectroscopic data are collected in Table 4, and the spectra shown in Figure 6. The PL peak

of **8a**, **8b**, **9a**, **9b**, **10** had a red shift relative to that of **3a-f** which provided further evidence of the extended conjugation resulting from 2,8-substituents. The fluorescence quantum yields (Φ) of **3a-f**, **8a**, **8b**, **9a**, **9b** and **10** in dichloromethane solvent were measured (Table 4).

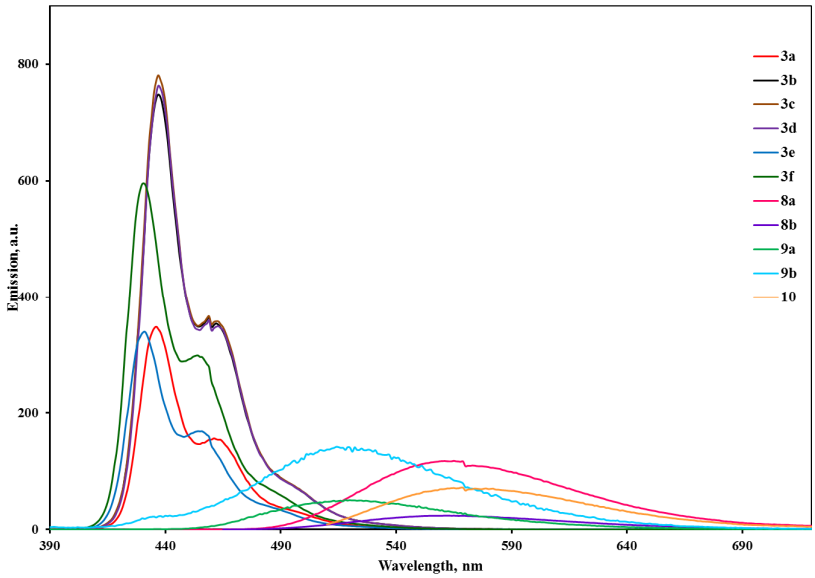


Figure 6. Photoluminescence spectra of **3a-f**; **8a,b**; **9a,b**; **10** in CH_2Cl_2 solution.

These results indicate that introduction of the thiophene moiety (**3a-d**) and 2,8-substituents (**8–10**) decrease the fluorescence quantum yields (relative to compounds **3e,f**), which is not surprising, taking into account the tendency of the thiophene unit to form more planar molecules than the phenyl unit, increasing conjugation with the indolo[3,2-*b*]carbazole core.

3. Conclusion

In summary, we have developed a convenient synthetic procedure for the preparation of 5,11-dialkyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-*b*]carbazoles from simple starting materials, thiophene-2-carbaldehyde and indole. It has been shown that pyridinium chlorochromate is a very effective and convenient reagent for oxidation of alkylated 5,6,11,12-tetrahydroindolo[3,2-*b*]carbazoles into the corresponding 5,11-dihydro derivatives. An efficient method for selective formylation of 6,12-di(thiophen-2-yl)indolo[3,2-*b*]carbazoles with dichloromethyl pentyl ester under catalysis with tin(IV) chloride has been described, providing a route to the corresponding 2,8-formyl derivatives. The Knoevenagel condensation of these 2,8-dialdehydes with C-H active nitriles has been studied. Basic photophysical and electrochemical properties for a number of 2,8-unsubstituted and 2,8-di(vinyl)indolo[3,2-*b*]carbazoles have been determined.

Acknowledgments

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Supplementary Material

Cyclic voltammetry measurements for compounds **3a-f**; **8a,b**; **9a,b**; **10**; ^{1}H, ^{13}C NMR spectra of new compounds. The data of ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{1}H-^{15}N HMBC experiments for compound **5a**.

4. Experimental section

4.1. General information

^{1}H and ^{13}C NMR spectra were obtained on Bruker DRX-400 and AVANCE-500 spectrometers with TMS as the internal standard. ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{1}H-^{15}N HMBC experiments for compound **5a** were performed on a Bruker AVANCE II spectrometer (400 MHz, $CDCl_3$). The ^{13}C NMR spectra of indolo[3,2-*b*]carbazoles **1b**, **1c**, **2c**, **8a** and **10** were not determined due to the poor solubility of these compounds in most deuterated solvents. Elemental analysis was carried on a Eurovector EA 3000 automated analyzer. Melting points were determined on Boetius combined heating stages and were not corrected. IR spectra of samples (solid powders) were recorded on a Spectrum One Fourier transform IR spectrometer (Perkin Elmer) equipped with a diffuse reflectance attachment (DRA). Spectrum processing and band intensity determination were carried out using the special software supplied with the spectrometer. X-ray intensity data were collected with a Xcalibur S diffractometer on standard procedure (Mo-Kα (λ = 0.71069 Å) radiation, T= 295(2) K, ω-scanning with step 1^{o}). Cyclic voltammetry (CV) was performed with a potentiostat/galvanostat Autolab PGSTAT128N at ambient temperature. UV-visible spectra were recorded for a $2\cdot10^{-5}$ M dichloromethane solution with Shimadzu UV-2401PC spectrophotometer. Photoluminescent spectra were recorded for a $1\cdot10^{-6}$ M dichloromethane solution on a Varian Cary Eclipse fluorescence spectrophotometer.

4.2. General procedure for the synthesis of 6,12-di[(het)aryl]-5,6,11,12-tetrahydro-indolo[3,2-*b*]carbazoles (1a-c)

A solution of aqueous 48% (w/w) HBF_4 (5 mmol, 0.92 g) and *n*-Bu_4NI (5 mmol, 1.85 g) in acetonitrile (15 ml) was added to a solution of indole (50 mmol, 5.85 g) and the corresponding (het)arylcarbaldehyde (50 mmol) in acetonitrile (135 ml) on stirring at 15–20 °C (internal cooling!). The resulting dark-red reaction mixture was stirred for the appropriate time (3 – 14 hrs, see Table 1) at ambient temperature. After that, the solid was filtered off, and washed with acetonitrile (40 ml) and methanol (40 ml). The grey colored crude products **1a-c** were purified by crystallization from DMF (50 – 60 ml). Crystallized products were filtered off and washed with hot methanol (50 ml), and dried at 110 °C for 6 hours. Indolo[3,2-*b*]carbazoles **1** decomposed without melting at temperatures above 350 °C.

4.2.1. 6,12-Di(thiophen-2-yl)-5,6,11,12-tetrahydroindolo[3,2-b]carbazole ***(1a)***

White powder; 7.75 g, 73%; Mp > 350 °C. IR (DRA, ν): 3384, 3105, 3084, 1730, 1668, 1576, 1557, 1457, 1438, 1345, 1312, 1275, 1227, 1193, 1175, 1148, 1121, 1040, 1012, 989, 857, 831, 763, 750, 704, 685, 658, 614, 577, 533, 504, 485 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.85 (s, 2H, 2NH), 7.45 (dd, *J* = 3.4, 1.1 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.06 – 6.97 (m, 4H), 6.89 – 6.83 (m, 2H), 6.05 (s, 2H, H-6,12); ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.3, 137.0, 135.8, 126.3, 125.7, 125.7, 125.0, 120.9, 118.6, 118.4, 111.3, 109.2, 34.4.

Anal. Calcd for $C_{26}H_{18}N_2S_2$: C, 73.9; H, 4.29; N, 6.63. Found: C, 73.54; H, 4.40; N, 7.02.

4.2.2. 6,12-Bis(4-methoxyphenyl)-5,6,11,12-tetrahydroindolo[3,2-b]carbazole ***(1b)***

White powder; 11.65 g, 98%; Mp > 350 °C. IR (DRA, ν): 3350, 3052, 3007, 2972, 2839, 1881, 1669, 1609, 1586, 1552, 1509, 1461, 1347, 1317, 1299, 1247, 1201, 1181, 1151, 1134, 1101, 1021, 997, 923, 885, 871, 847, 831, 813, 776, 742, 677, 626, 595, 563, 541, 520 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.62 (s, 2H, 2NH), 7.22 (d, *J* = 8.5 Hz, 6H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.98 – 6.90 (m, 2H), 6.85 – 6.75 (m, 6H), 5.61 (s, 2H, H-6,12), 3.70 (s, 6H, 2CH_3O).

Anal. Calcd for $C_{32}H_{26}N_2O_2 \times 0.1(CH_3)_2NCHO$: C, 81.18; H, 5.63; N, 6.16. Found: C, 81.16; H, 5.64; N, 6.21.

4.2.3. 6,12-Bis(3,4-dimethoxyphenyl)-5,6,11,12-tetrahydroindolo[3,2-b]carbazole ***(1c)***

White powder; 12.75 g, 95%; Mp > 350 °C. IR (DRA, ν): 3359, 2925, 2833, 1677, 1593, 1552, 1509, 1458, 1419, 1343, 1317, 1295, 1257, 1242, 1223, 1183, 1165, 1141, 1026, 1000, 940, 853, 811, 760, 743, 733, 670, 632, 604, 517, 478 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.59 (s, 2H, 2NH), 7.27 – 7.18 (m, 4H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.99 – 6.92 (m, 2H), 6.86 – 6.77 (m, 4H), 6.72 (d, *J* = 8.6 Hz, 2H), 5.62 (s, 2H, H-6,12), 3.71 (s, 6H, 2CH_3O), 3.69 (s, 6H, 2CH_3O).

Anal. Calcd for $C_{34}H_{30}N_2O_4 \times 0.25(CH_3)_2NCHO$: C, 76.04; H, 5.83; N, 5.74. Found: C, 76.00; H, 5.86; N, 5.79.

4.3. General procedure for the synthesis of 5,11-dialkyl-6,12-di(het)aryl-5,6,11,12-tetrahydroindolo[3,2-*b*]carbazole (2a-f) KO*t*-Bu (80 mmol, 9 g; for alkylation of compound **1a**) or a powder of NaOH (80 mmol, 3.2 g; for alkylation of **1b,c**) was added in one portion to a suspension of the corresponding indolo[3,2-*b*]carbazole **1** (20 mmol) in dry DMF (120 ml) and the mixture was stirred at room temperature under an argon atmosphere for 0.5 h. The appropriate alkyl bromide (80 mmol) was added dropwise to the resulting dark-green suspension and the reaction mixture was stirred for 15 hours. After that time the reaction mixture was poured into 50% (v/v) aqueous ethanol (250 ml) and stirred for 1 h. The alkylated products **2** were collected by filtration, washed with ethanol (5×20 ml) and dried at 110 °C. The crude products were quite suitable for the next step of oxidation without further purification. The analytical samples of **2** were obtained by crystallization of crude materials from a mixture (10:1) of ethyl acetate / chloroform.

*4.3.1. 5,11-Diheptyl-6,12-di(thiophen-2-yl)-5,6,11,12-tetrahydroindolo[3,2-b]carbazole **(2a)***

White powder; 10.33 g, 83%; Mp 220 °C. IR (DRA, ν): 3051, 2921, 2852, 1611, 1545, 1468, 1417, 1365, 1272, 1189, 1152, 1116, 1077, 1040, 1019, 919, 884, 854, 835, 736, 702, 684, 602, 557, 492 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.25 – 7.20 (m, 4H), 7.16 – 7.11 (m, 2H), 7.06 (d, *J* = 5.0 Hz, 2H), 7.03 – 6.97 (m, 2H), 6.88 (dd, *J* = 5.1, 3.5 Hz, 2H), 6.10 (s, 2H, H-6,12), 4.24 – 3.80 (m, 4H), 1.89 – 1.51 (m, 2H), 1.39 – 1.12 (m, 16H), 0.96 – 0.91 (m, 2H), 0.88 (t, *J* = 7.0 Hz, 6H, 2C$\underline{H}_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.8, 137.5, 134.9, 125.9, 125.7, 125.3, 124.8, 121.3, 119.3, 118.9, 110.8, 109.4, 44.2, 34.9, 31.8, 29.4, 29.0, 27.1, 22.6, 14.1.

Anal. Calcd for $C_{40}H_{46}N_2S_2 \times 0.15CH_3CO_2C_2H_5$: C, 77.14; H, 7.53; N, 4.43. Found: C, 77.19; H, 7.54; N, 4.45.

*4.3.2. 5,11-Dihexyl-6,12-di(thiophen-2-yl)-5,6,11,12-tetrahydroindolo[3,2-b]carbazole **(2b)***

White powder; 8.92 g, 75%; Mp 255 °C. IR (DRA, ν): 3056, 2955, 2922, 2852, 1611, 1545, 1468, 1434, 1417, 1364, 1272, 1218, 1189, 1153, 1117, 1077, 1040, 1019, 919, 854, 834, 736, 702, 684, 602, 557, 493 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 2H), 7.23 – 7.19 (m, 4H), 7.16 – 7.11 (m, 2H), 7.06 (d, *J* = 5.0 Hz, 2H), 7.03 – 6.98 (m, 2H), 6.87 (dd, *J* = 5.0, 3.6 Hz, 2H), 6.09 (s, 2H, H-6,12), 4.13 – 3.92 (m, 4H), 1.70 – 1.59 (m, 2H), 1.33 – 1.17 (m, 12H), 0.97 – 0.90 (m, 2H), 0.87 (t, *J* = 7.0 Hz, 6H, 2C$\underline{H}_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.8,

137.5, 134.9, 126.0, 125.7, 125.3, 124.8, 121.3, 119.2, 118.9, 110.8, 109.4, 44.2, 35.0, 31.5, 29.3, 26.8, 22.6, 14.0.

Anal. Calcd for $C_{38}H_{42}N_2S_2$: C, 77.24; H, 7.16; N, 4.74. Found: C, 77.17; H, 7.0; N, 4.46.

4.3.3. 5,11-Dibutyl-6,12-di(thiophen-2-yl)-5,6,11,12-tetrahydroindolo[3,2-b]carbazole ***(2c)***

White powder; 9.11 g, 85%; Mp 230 °C. IR (DRA, ν): 3039, 2968, 2944, 2867, 2845, 1907, 1874, 1781, 1678, 1610, 1579, 1546, 1469, 1456, 1417, 1365, 1346, 1271, 1230, 1194, 1148, 1110, 1086, 1038, 1015, 1000, 921, 880, 852, 826, 787, 763, 744, 736, 715, 701, 685, 598, 584, 554, 530, 491 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.24 – 7.19 (m, 4H), 7.17 – 7.10 (m, 2H), 7.07 (d, *J* = 5.0 Hz, 2H), 7.04 – 6.97 (m, 2H), 6.89 (dd, *J* = 5.0, 3.5 Hz, 2H), 6.10 (s, 2H, H-6,12), 4.14 – 3.93 (m, 4H), 1.71 – 1.58 (m, 2H), 1.35 – 1.20 (m, 4H), 0.96 – 0.89 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 6H, 2C$\underline{H}_3$).

Anal. Calcd for $C_{34}H_{34}N_2S_2$: C, 76.36; H, 6.41; N, 5.24. Found: C, 76.0; H, 6.34; N, 5.27.

4.3.4. 5,11-Dipentadecyl-6,12-di(thiophen-2-yl)-5,6,11,12-tetrahydroindolo[3,2-b]carbazole ***(2d)***

White powder; 8.68 g, 51%; Mp 170 °C. IR (DRA, ν): 3052, 2919, 2850, 1792, 1611, 1546, 1468, 1434, 1418, 1359, 1270, 1190, 1152, 1078, 1043, 1018, 919, 889, 855, 832, 736, 703, 683, 603, 557, 531, 492 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 2H), 7.25 – 7.20 (m, 4H), 7.16 – 7.11 (m, 2H), 7.06 (dd, *J* = 5.1, 0.8 Hz, 2H), 7.03 – 6.97 (m, 2H), 6.88 (dd, *J* = 5.1, 3.5 Hz, 2H), 6.10 (s, 2H, H-6,12), 4.14 – 3.91 (m, 4H), 1.72 – 1.59 (m, 2H), 1.34 – 1.15 (m, 48H), 0.96 – 0.91 (m, 2H), 0.88 (t, *J* = 6.8 Hz, 6H, 2C$\underline{H}_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.8, 137.5, 134.9, 125.9, 125.7, 125.2, 124.8, 121.3, 119.2, 118.9, 110.8, 109.4, 44.2, 34.9, 31.9, 29.7, 29.7, 29.7, 29.6, 29.6, 29.4, 27.2, 22.7, 14.1.

Anal. Calcd for $C_{56}H_{78}N_2S_2 \times 0.2CH_3CO_2C_2H_5$: C, 79.24; H, 9.32; N, 3.25. Found: C, 79.24; H, 9.49; N, 3.54.

4.3.5. 5,11-Dihexyl-6,12-bis(4-methoxyphenyl)-5,6,11,12-tetrahydroindolo[3,2-b]carbazole ***(2e)***

White powder; 8.3 g, 65%; Mp 210–1 °C. IR (DRA, ν): 3031, 3008, 2924, 2845, 1884, 1609, 1583, 1542, 1508, 1464, 1414, 1364, 1322, 1300, 1256, 1221, 1170, 1139, 1102, 1028, 921, 823, 758, 735, 665, 638, 610, 599, 556, 522 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 6.1 Hz, 4H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.10 – 7.05 (m, *J* = 7.2 Hz, 2H), 6.97 – 6.91 (m, *J* = 7.4 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 4H), 5.70 (s, 2H, H-6,12), 4.03 – 3.76 (m, 4H), 3.71 (s, 6H, 2C$\underline{H}_3$O), 1.63 – 1.50 (m, 2H), 1.28 – 1.08 (m, 12H), 0.86 (t, *J* = 7.0 Hz, 6H, 2C$\underline{H}_3$),

0.81 – 0.66 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 137.3, 136.2, 135.9, 129.7, 125.8, 120.9, 119.1, 118.7, 113.9, 111.7, 109.2, 55.1, 44.2, 39.4, 31.5, 29.2, 26.8, 22.6, 14.0.

Anal. Calcd for $C_{44}H_{50}N_2O_2 \times 0.2CH_3CO_2C_2H_5$: C, 82.33; H, 7.91; N, 4.33. Found: C, 82.29; H, 7.61; N, 4.60.

4.3.6. 6,12-Bis(3,4-dimethoxyphenyl)-5,11-diheptyl-5,6,11,12-tetrahydroindolo[3,2-b]carbazole ***(2f)***

White powder; 10,25 g, 70%; Mp 195 °C. IR (DRA, ν): 3361, 2923, 2854, 1674, 1591, 1509, 1462, 1419, 1363, 1259, 1225, 1179, 1143, 1029, 851, 810, 760, 734, 625, 551 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.21 – 7.17 (m, 2H), 7.13 – 7.07 (m, 2H), 7.01 – 6.92 (m, 4H), 6.79 – 6.70 (m, 4H), 5.70 (s, 2H, H-6,12), 4.10 – 3.83 (m, 4H), 3.81 (s, 6H, 2C$\underline{H}_3$O), 3.71 (s, 6H, 2C$\underline{H}_3$O), 1.67 – 1.54 (m, 2H), 1.35 – 1.06 (m, 16H), 0.87 (t, *J* = 7.1 Hz, 6H, 2C$\underline{H}_3$C), 0.84 – 0.75 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 148.0, 137.6, 136.8, 135.9, 126.1, 121.3, 121.2, 118.8, 112.2, 111.8, 56.04, 56.00, 32.0, 31.1, 29.5, 29.2, 27.4, 22.8, 14.2.

Anal. Calcd for $C_{48}H_{58}N_2O_4$: C, 79.30; H, 8.04; N, 3.85. Found: C, 79.60; H, 7.81; N, 3.83.

4.4. General procedures for the synthesis of 5,11-dialkyl-6,12-di(het)aryl-5,11-dihydroindolo[3,2-*b*]carbazole (3a-f)

Method A. The oxidation procedure with DDQ

DDQ (13 mmol, 3 g) was added to the appropriate indolo[3,2-*b*]carbazole **2** (10 mmol) in dioxane (100 ml). The resulting solution was heated under reflux with stirring for 5 h. The solvent was distillated off under vacuum and the residue was dissolved in chloroform (100 ml). The chloroform solution was washed with 10% aqueous solution of K_2CO_3 (5×25 ml) and dried with $MgSO_4$. The solvent was removed in vacuum and the crude compounds **3** was purified by crystallization from ethyl acetate or DMF. The pure products were washed on a filter with methanol (25 ml).

Method B. The oxidation procedure with PCC

PCC (10 mmol, 2.15 g) was added portion wise to the appropriate indolo[3,2-*b*]carbazole **2** (10 mmol) in dichloromethane (100 ml) at 10 °C with stirring. The resulting dark mixture was stirred at room temperature for 2 h. *n*-Hexane (25 ml) was added and the reaction mixture was filtered

through a layer of silica (5 cm × 4 cm). The obtained yellow filtrate was concentrated under vacuum and the crude product was purified by crystallization from DMF.

4.4.1. 5,11-Diheptyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-b]carbazole ***(3a)***

Light-yellow crystals; 3.45 g, 56% (with DDQ); 5.37 g, 87% (with PCC); Mp 185 °C. IR (DRA, ν): 3069, 2925, 2849, 1921, 1885, 1799, 1608, 1577, 1548, 1497, 1455, 1433, 1388, 1357, 1322, 1281, 1229, 1158, 1129, 1092, 1027, 991, 896, 847, 832, 762, 741, 701, 608, 565, 540 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 4.3 Hz, 2H), 7.41 – 7.28 (m, 8H), 6.95 – 6.91 (m, 2H), 6.65 (d, *J* = 7.9 Hz, 2H), 4.07 – 3.81 (m, 4H), 1.70 – 1.58 (m, 4H), 1.34 – 1.17 (m, 12H), 1.15 – 1.00 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 6H, 2C$\underline{H}_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 139.1, 133.7, 128.2, 127.7, 127.2, 125.7, 124.1, 122.5, 122.4, 118.4, 110.4, 108.5, 44.5, 31.8, 29.1, 29.0, 26.9, 22.6, 14.1.

Anal. Calcd for $C_{40}H_{44}N_2S_2$: C, 77.88; H, 7.19; N, 4.54. Found: C, 77.64; H, 7.22; N, 4.49.

4.4.2. 5,11-Dihexyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-b]carbazole ***(3b)***

Light-yellow crystals; 3,06 g, 52% (with DDQ); 4,65 g, 79% (with PCC); Mp 215 °C. IR (DRA, ν): 3067, 2956, 2928, 2853, 1921, 1885, 1799, 1678, 1608, 1577, 1547, 1497, 1478, 1466, 1455, 1432, 1387, 1357, 1322, 1286, 1262, 1229, 1157, 1129, 1091, 1043, 1027, 986, 923, 905, 848, 832, 788, 762, 741, 700, 608, 565, 539 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 5.2, 0.9 Hz, 2H), 7.39 – 7.29 (m, 8H), 6.94 – 6.91 (m, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 4.03 – 3.84 (m, 4H), 1.69 – 1.59 (m, 4H), 1.31 – 1.15 (m, 8H), 1.12 – 1.02 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 6H, 2C$\underline{H}_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 139.1, 133.6, 128.2, 127.7, 127.2, 125.7, 124.1, 122.5, 122.4, 118.4, 110.4, 108.5, 44.5, 31.5, 29.1, 26.6, 22.6, 14.0.

Anal. Calcd for $C_{38}H_{40}N_2S_2$: C, 77.51; H, 6.85; N, 4.76. Found: C, 77.58; H, 7.08; N, 4.67.

4.4.3. 5,11-Dibutyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-b]carbazole ***(3c)***

Light-yellow crystals; 2.93 g, 55% (with DDQ); 4.52 g, 85% (with PCC); Mp 261 °C. IR (DRA, ν): 3067, 2953, 2870, 1914, 1793, 1736, 1608, 1576, 1548, 1498, 1456, 1433, 1388, 1358, 1321, 1304, 1278, 1228, 1159, 1128, 1111, 1089, 1044, 1027, 1005, 987, 948, 896, 833, 803, 762, 735, 701, 692, 601, 565, 538 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 5.2, 1.0 Hz, 2H), 7.40 – 7.30 (m, 8H), 6.96 – 6.91 (m, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 4.06 – 3.76 (m, 4H), 1.70 – 1.58 (m, 4H), 1.17 – 1.06 (m, 4H), 0.84 (t, *J* = 7.4 Hz, 6H, 2C$\underline{H}_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 139.1, 133.6, 128.2, 127.7, 127.2, 125.7, 124.1, 122.5, 122.4, 118.4, 110.4, 108.5, 44.2, 31.2, 20.2, 13.8.

Anal. Calcd for $C_{34}H_{32}N_2S_2 \times 0.15CH_3CO_2C_2H_5$: C, 76.12; H, 6.13; N, 5.13. Found: C, 76.11; H, 6.26; N, 5.28.

4.4.4. 5,11-Dipentadecyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-b]carbazole ***(3d)***

Light-yellow crystals; 7.57 g, 90% (with DDQ); 8.0 g 95% (with PCC); Mp 107−8 °C. IR (DRA, ν): 3099, 3048, 2916, 2849, 1921, 1799, 1608, 1575, 1550, 1497, 1468, 1433, 1389, 1358, 1322, 1286, 1278, 1260, 1231, 1220, 1159, 1139, 1127, 1090, 1044, 1026, 999, 986, 913, 852, 831, 778, 762, 742, 718, 703, 687, 610, 565, 540, 461 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 5.1, 1.0 Hz, 2H), 7.40 – 7.28 (m, 8H), 6.95 – 6.90 (m, 2H), 6.65 (d, *J* = 7.9 Hz, 2H), 4.07 – 3.81 (m, 4H), 1.69 – 1.58 (m, 4H), 1.33 – 1.16 (m, 44H), 1.12 – 1.02 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 6H, 2C$\underline{H}_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 139.1, 133.6, 128.2, 127.7, 127.2, 125.7, 124.1, 122.5, 122.4, 118.4, 110.4, 108.5, 44.5, 31.9, 29.70, 29.66, 29.65, 29.57, 29.56, 29.4, 29.3, 29.1, 26.9, 22.7, 14.1.

Anal. Calcd for $C_{56}H_{76}N_2S_2$: C, 79.94; H, 9.11; N, 3.33. Found: C, 79.79; H, 9.01; N, 3.02.

4.4.5. 5,11-Dihexyl-6,12-bis(4-methoxyphenyl)-5,11-dihydroindolo[3,2-b]carbazole ***(3e)***

Light-yellow crystals; 4.46 g, 70% (with DDQ); 5.67 g, 89% (with PCC); Mp 195 °C. IR (DRA, ν): 3065, 2955, 2925, 2854, 1891, 1606, 1574, 1528, 1499, 1453, 1441, 1385, 1365, 1350, 1321, 1281, 1242, 1183, 1170, 1147, 1103, 1089, 1029, 1008, 940, 924, 829, 795, 740, 676, 646, 601, 561, 531 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 – 6.53 (m, 16H, H_{Ar}), 3.99 (s, 6H, 2C$\underline{H}_3$O), 1.64 – 1.37 (m, 4H), 1.3 – 1.17 (m, 4H), 1.18 – 1.05 (m, 4H), 1.03 – 0.89 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 6H, 2C$\underline{H}_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 142.5, 132.8, 131.6, 131.0, 125.2, 123.2, 123.0, 122.5, 117.8, 117.5, 114.3, 108.2, 55.5, 44.5, 31.5, 28.7, 26.5, 22.6, 14.0. ^1H NMR (400 MHz, DMF-d_7) δ 7.69 – 7.65 (m, 4H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.33 (m, 6H), 6.92 – 6.80 (m, 2H), 6.67 (d, *J* = 7.4 Hz, 2H), 4.06 (s, 6H, 2C$\underline{H}_3$O), 3.99 – 3.93 (m, 4H), 1.59 – 1.49 (m, 4H), 1.32 – 1.11 (m, 8H), 1.05 – 0.94 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 6H, 2C$\underline{H}_3$). ^{13}C NMR (101 MHz, DMF-d_7) δ 160.0, 142.7, 131.7, 130.7, 125.4, 123.1, 122.9, 122.2, 122.12, 122.10, 117.8, 114.6, 108.8, 55.3, 44.2, 31.3, 26.3, 22.5, 13.5.

Anal. Calcd for $C_{44}H_{48}N_2O_2$: C, 82.98; H, 7.60; N, 4.40. Found: C, 82.83; H, 4.42; N, 4.10.

4.4.6. 6,12-bis(3,4-dimethoxyphenyl)-5,11-diheptyl-5,11-dihydroindolo[3,2-b]carbazole ***(3f)***

Light-yellow powder; 5.75 g, 79% (with DDQ); 6.74 g, 93% (with PCC); Mp 190−1 °C. IR (DRA, ν): 3047, 2998, 2928, 2851, 1606, 1582, 1527, 1504, 1465, 1407, 1388, 1350, 1323, 1248, 1229, 1179, 1160, 1137, 1092, 1027, 949, 905, 888, 851, 812, 760, 739, 673, 635, 598, 559, 537 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 – 6.62 (m, 14H, H_{Ar}), 4.08 (s, 6H, 2C$\underline{H}_3$O),

3.86 (s, 3H, C$\underline{H}_3$O), 3.85 (s, 3H, C$\underline{H}_3$O), 1.61 – 1.52 (m, 4H), 1.30 – 1.13 (m, 12H), 1.06 – 0.93 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 6H, 2C$\underline{H}_3$). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.27 – 7.22 (m, 3H), 7.17 – 7.09 (m, 3H), 6.82 (t, *J* = 7.5 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 6H, 2C$\underline{H}_3$O), 3.88 – 3.77 (m, 4H), 3.74 (s, 6H, 2C$\underline{H}_3$O), 1.51 – 1.36 (m, 4H), 1.27 – 1.19 (m, 4H), 1.19 – 1.07 (m, 8H), 0.97 – 0.88 (m, 4H), 0.84 (t, *J* = 7.2 Hz, 6H, 2C$\underline{H}_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 148.9 142.3, 132.5, 131.1, 125.2, 123.0, 122.8, 122.6, 118.0, 117.6, 113.4, 111.5, 108.2, 56.1, 55.91, 55.90, 44.4, 31.8, 29.0, 26.9, 22.5, 14.1.

Anal. Calcd for $C_{48}H_{56}N_2O_4 \times 0.35CH_3CO_2C_2H_5$: C, 78.50; H, 7.84; N, 3.71. Found: C, 78.49; H, 7.77; N, 3.64.

4.5. Procedure for the preparation of 5,11-diheptyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-*b*]carbazole-2-carbaldehyde (4)

PCl_5 (6.5 mmol, 1.35 g) was added portionwise to dry DMF (8.2 mmol, 0.6 g) in dry 1,2-dichloroethane (25 ml) with vigorous stirring at 0 °C for 0.5 h. A solution of compound **3a** (0.65 mmol, 0.4 g) in dry 1,2-dichloroethane (5 ml) was added dropwise to the solution of the Vilsmeier reagent. The resulting dark-yellow solution was stirred at room temperature for 3 days and poured into ice water (100 ml) which contained K_2CO_3 (50 mmol, 6.9 g). The mixture was stirred for 1 h and the organic layer was separated and dried with $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography (*n*-hexane / dichloromethane, 5:2) to afford the desired product **4**.

Yellow crystals (from ethyl acetate); 190 mg, 45%; Mp 155 °C. IR (DRA, ν): 3067, 2925, 2853, 2739, 2318, 1687, 1603, 1548, 1499, 1454, 1433, 1356, 1334, 1310, 1278, 1231, 1175, 1156, 1129, 1086, 1042, 1026, 993, 969, 898, 831, 801, 737, 693, 604, 565, 439 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H, C$\underline{H}$O), 7.96 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.76 (dd, *J* = 5.2, 0.9 Hz, 1H), 7.71 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.45 – 7.31 (m, 7H), 7.01 (s, 1H), 6.96 (m, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 4.12 – 3.79 (m, 4H), 1.74 – 1.59 (m, 4H), 1.32 – 1.18 (m, 12H), 1.13 – 0.94 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 6H, 2C$\underline{H}_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.7, 145.9, 142.6, 138.4, 138.3, 134.2, 133.8, 128.43, 128.40, 128.1, 128.0, 127.8, 127.76, 127.7, 127.5, 126.2, 125.8, 124.9, 124.0, 122.50, 122.49, 122.3, 118.7, 111.4, 110.9, 108.9, 108.7, 68.0, 44.8, 44.5, 31.8, 31.7, 30.9, 29.4, 29.2, 28.92, 28.90, 26.9, 26.8, 25.6, 22.55, 22.53, 14.0.

Anal. Calcd for $C_{41}H_{44}N_2OS_2$: C, 76.36; H, 6.88; N, 4.34. Found: C, 76.26; H, 6.91; N, 4.27.

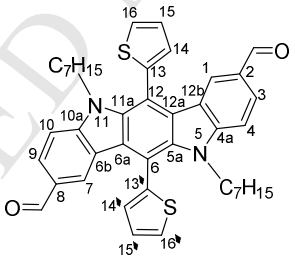
Crystallographic data for compound **4**: Yellow crystals 0.25×0.20×0.15 mm, θ < 26.39°, 8941 reflections were collected, 3524 independent reflections (R_{int} 0.0256), completeness 98.1%. Crystals belong to the triclinic space group P2(1)/n, a= 9.1480(11) Å, b= 12.8407(13) Å, c= 15.0631(19) Å, α= 90.00°, β= 95.411(10)°, γ= 90.00°, μ= 0.186 mm^{-1}. The SHELXTL program[34]

was used for solution and structure refinement. The details of the refinement and the final R indices: R_1= 0.0495 [I>2σ(I)], wR_2= 0.1247 [I>2σ(I)], R_1= 0.1371 (all data), wR_2= 0.1385 (all data), S= 0.995. Deposition number CCDC 979740 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.6. General procedure for the synthesis of 5,11-dialkyl-6,12-di(het)aryl-5,11-dihydroindolo[3,2-*b*]carbazole-2,8-dicarbaldehydes (5a-f)

$SnCl_4$ (8 mmol, 2.1 g) was added dropwise to solution of a appropriate indolo[3,2-*b*]carbazole **3** (1 mmol) and dichloromethyl pentyl ester (8 mmol, 1.37 g) in dry 1,2-dichloroethane (20 ml) with stirring at 0 °C and the resulting solution was stirred at room temperature for 12 h. The reaction mixture was then poured onto ice water (100 ml) with conc. HCl (2 ml) and vigorously stirred for 2 h. The organic layer was separated and dried with $MgSO_4$. The solvent was removed under vacuum and the solid residue was purified by crystallization from ethyl acetate. The pure dialdehydes were filtrated and washed with methanol (5 ml), and dried at 110 °C for 2 h.

4.6.1. 5,11-Diheptyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-b]carbazole-2,8-dicarbaldehyde ***(5a)***



Lemon-yellow crystals; 540 mg, 80%; Mp 197−8 °C. IR (DRA, ν): 3072, 2926, 2854, 2731, 1681, 1601, 1568, 1499, 1463, 1431, 1378, 1356, 1281, 1236, 1197, 1158, 1127, 1080, 1043, 998, 954, 918, 805, 700, 678, 660, 564, 443 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 2H, 2C<u>H</u>O), 7.99 (dd, *J* = 8.6, 1.3 Hz, 2H, H-3,9), 7.79 (dd, *J* = 5.1, 0.8 Hz, 2H, H-16,16′), 7.45 (dd, *J* = 5.1, 3.5 Hz, 2H, H-15,15′), 7.41 (d, *J* = 8.6 Hz, 2H, H-4,10), 7.38 – 7.35 (m, 2H, H-14,14′), 7.00 (s, 2H, H-1,7), 4.15 – 3.95 (m, 4H, 2NC<u>H</u>$_2$), 1.77 – 1.61 (m, 4H), 1.34 – 1.19 (m, 12H), 1.16 – 1.02 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 6H, 2C<u>H</u>$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6 (2<u>C</u>HO), 145.9 (C-4a,10a), 137.5 (C-13,13′), 134.4 (C-5a,11a), 128.6 (C-14,14′), 128.3 (C-6a,12a), 128.2 (C-15,15′), 128.0 (C-16,16′), 127.7 (C-1,7), 126.3 (C-3,9), 124.8 (C-2,8), 122.2 (C-6b,12b), 111.8 (C-5,11), 109.1 (C-4,10), 44.9, 31.7, 29.4, 28.9, 26.8, 22.5, 14.0.

Anal. Calcd for $C_{42}H_{44}N_2O_2S_2$: C, 74.96; H, 6.59; N, 4.16. Found: C, 74.84; H, 6.57; N, 4.04.

4.6.2. 5,11-Dihexyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-b]carbazole-2,8-dicarbaldehyde ***(5b)***

Lemon-yellow crystals; 420 mg, 65%; Mp 240−1 °C. IR (DRA, ν): 3070, 2927, 2855, 2727, 1674, 1603, 1569, 1499, 1462, 1429, 1355, 1313, 1287, 1236, 1197, 1158, 1077, 1045, 998, 950, 890, 844, 813, 700, 679, 659, 598, 564, 505 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 2H, 2CHO), 7.98 (dd, *J* = 8.6, 1.4 Hz, 2H), 7.79 (dd, *J* = 5.1, 0.8 Hz, 2H), 7.48 – 7.34 (m, 6H), 7.00 (s, 2H), 4.18 – 3.89 (m, 4H), 1.75 – 1.62 (m, 4H), 1.34 – 1.17 (m, 8H), 1.15 – 1.03 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 6H, 2CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 145.9, 137.5, 134.4, 128.5, 128.3, 127.7, 126.3, 124.8, 122.2, 111.8, 109.1, 44.9, 31.4, 29.3, 26.5, 22.5, 14.0.

Anal. Calcd for $C_{40}H_{40}N_2O_2S_2$: C, 74.50; H, 6.25; N, 4.34. Found: C, 74.47; H, 6.25; N, 4.48.

4.6.3. 5,11-Dibutyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-b]carbazole-2,8-dicarbaldehyde ***(5c)***

Light-yellow powder; 250 mg, 43%; Mp 271−2 °C. IR (DRA, ν): 3058, 2948, 1716, 1609, 1579, 1496, 1484, 1444, 1394, 1348, 1310, 1266, 1246, 1206, 1174, 1109, 1076, 1050, 1039, 1010, 944, 907, 893, 852, 812, 777, 748, 703, 663, 563, 532, 474, 455 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 2H, 2CHO), 7.99 (dd, *J* = 8.6, 1.4 Hz, 2H), 7.79 (d, *J* = 5.2 Hz, 2H), 7.51 – 7.32 (m, 6H), 7.00 (s, 2H), 4.18 – 3.97 (m, 4H), 1.75 – 1.63 (m, 4H), 1.20 – 1.09 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H, 2CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 146.0, 137.5, 134.4, 128.6, 128.4, 128.1, 128.0, 127.7, 126.3, 124.8, 122.3, 111.9, 109.1, 44.6, 31.4, 20.1, 13.7.

Anal. Calcd for $C_{36}H_{32}N_2O_2S_2$: C, 73.44; H, 5.48; N, 4.76. Found: C, 73.30; H, 5.63; N, 4.87.

4.6.4. 5,11-Dipentadecyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-b]carbazole-2,8-dicarbaldehyde ***(5d)***

Yellow needles; 660 mg, 74%; Mp 115 °C. IR (DRA, ν): 2918, 2851, 2728, 1679, 1606, 1569, 1500, 1459, 1429, 1392, 1378, 1356, 1314, 1285, 1237, 1201, 1151, 1105, 1079, 1044, 999, 957, 910, 891, 836, 806, 752, 716, 655, 598, 566 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.74 (s, 2H, 2CHO), 7.98 (dd, *J* = 8.6, 1.5 Hz, 2H), 7.78 (dd, *J* = 5.2, 1.0 Hz, 2H), 7.44 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.00 (d, *J* = 0.9 Hz, 2H), 4.15 – 3.94 (m, 4H), 1.76 – 1.61 (m, 4H), 1.34 – 1.19 (m, 44H), 1.16 – 1.01 (m, 4H), 0.87 (t, *J* = 6.9 Hz, 6H, 2CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 145.9, 137.5, 134.4, 128.6, 128.4, 128.2, 128.0, 127.7, 126.3, 124.8, 122.3, 111.8, 109.1, 44.9, 31.92, 31.90, 29.7, 29.64, 29.62, 29.53, 29.51, 29.37, 29.36, 29.34, 29.2, 26.8, 22.7, 14.1.

Anal. Calcd for $C_{58}H_{76}N_2O_2S_2$: C, 77.63; H, 8.54; N, 3.12. Found: C, 77.50; H, 8.42; N, 3.27.

*4.6.5. 5,11-Dihexyl-6,12-bis(4-methoxyphenyl)-5,11-dihydroindolo[3,2-b]carbazole-2,8-dicarbaldehyde **(5e)***

Lemon-yellow crystals; 470 mg, 68%; Mp 255−6 °C. IR (DRA, ν): 2933, 2857, 2800, 2727, 1901, 1677, 1603, 1566, 1531, 1503, 1462, 1351, 1286, 1241, 1201, 1137, 1105, 1081, 1057, 1026, 953, 896, 835, 813, 735, 713, 695, 684, 661, 643, 614, 574, 535 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.64 (s, 2H, 2CHO), 7.94 (dd, *J* = 8.6, 1.5 Hz, 2H), 7.60 – 7.53 (m, 4H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.26 – 7.22 (m, 4H), 6.98 (d, *J* = 1.4 Hz, 2H), 4.02 (s, 6H, $2CH_3O$), 3.99 – 3.88 (m, 4H), 1.62 – 1.53 (m, 4H), 1.28 – 1.19 (m, 4H), 1.17 – 1.10 (m, 4H), 1.02 – 0.93 (m, 4H), 0.87 (t, *J* = 7.3 Hz, 6H, $2CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 160.2, 145.9, 133.5, 131.2, 129.5, 128.2, 127.8, 125.5, 123.6, 122.9, 118.8, 114.9, 108.9, 55.68, 55.65, 55.63, 44.8, 31.4, 28.9, 26.4, 22.5, 13.9.

Anal. Calcd for $C_{46}H_{48}N_2O_4$: C, 79.74; H, 6.98; N, 4.04. Found: C, 79.76; H, 7.18; N, 4.12.

*4.6.6. 6,12-Bis(3,4-dimethoxyphenyl)-5,11-diheptyl-5,11-dihydroindolo[3,2-b]carbazole-2,8-dicarbaldehyde **(5f)***

Lemon-yellow crystals; 440 mg, 56%; Mp 188−9 °C. IR (DRA, ν): 2932, 2854, 2799, 2725, 1901, 1673, 1601, 1564, 1528, 1506, 1461, 1409, 1352, 1331, 1237, 1201, 1159, 1138, 1083, 1025, 955, 904, 811, 768, 717, 694, 663, 565 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 2H, 2CHO), 7.98 (dd, *J* = 8.6, 1.4 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.26 – 7.19 (m, 4H), 7.15 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.07 (d, *J* = 1.2 Hz, 2H), 4.10 (s, 6H, $2CH_3O$), 4.04 – 3.89 (m, 4H), 3.88 (s, 3H, CH_3O), 3.87 (s, 3H, $2CH_3O$), 1.66 – 1.54 (m, 4H), 1.31 – 1.10 (m, 12H), 1.07 – 0.95 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 6H, $2CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.5, 150.0, 149.7, 145.9, 133.4, 129.67, 129.65, 128.3, 128.0, 125.5, 123.5, 122.7, 122.3, 122.2, 118.8, 113.3, 113.2, 112.0, 109.0, 56.4, 56.2, 56.1, 44.8, 31.7, 29.3, 29.0, 26.8, 22.5, 14.0.

Anal. Calcd for $C_{50}H_{56}N_2O_6$: C, 76.89; H, 7.23; N, 3.59. Found: C, 76.73; H, 7.60; N, 3.91.

4.7. General procedure for benzoylation and acetylation of indolo[3,2-*b*]carbazole 3a

$SnCl_4$ (5.2 mmol, 1.35 g; in the case of **6**) or $AlBr_3$ (5.2 mmol, 1.4 g; in the case of **7**) was slowly added to a solution of compound **3a** (0.65 mmol, 0.4 g) in dry dichloromethane (20 ml) with vigorous stirring at 0 °C. Benzoyl chloride (5.2 mmol, 0.73 g in the case of **6**) or acetyl chloride (5.2 mmol, 0.41 g; in the case of **7**) was added dropwise to the resulting dark-green solution and the mixture was stirred at room temperature for appropriate time (12 h for compound **6**; 5 h for compound **7**). The reaction mixture was then poured onto ice water (100 ml) and vigorously

stirred for 1 h. The organic layer was separated, washed with a 5% aqueous solution of NaOH (5×20 ml) and dried with $MgSO_4$. The solvent was removed under vacuum and the crude product was purified by crystallization from ethyl acetate / chloroform (20:1) (for compound **6**) or DMF (for compound **7**). The product **6** or **7** was filtered and washed with hot methanol (10 ml), then dried at 110 °C.

4.7.1. (5,11-Diheptyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-b]carbazole-2,8-diyl)bis(phenylmethanone) ***(6)***

Yellow crystals; 500 mg, 87%; Mp 235 °C. IR (DRA, ν): 3074, 2927, 2855, 1644, 1603, 1566, 1499, 1447, 1431, 1464, 1393, 1356, 1342, 1310, 1267, 1143, 1158, 1177,1082, 1044, 999, 963, 934, 898, 827, 793, 850, 766, 728, 698, 645, 600, 565 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.66 – 7.62 (m, 4H), 7.61 – 7.57 (m, 2H), 7.49 – 7.45 (m, 4H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.31 (dd, *J* = 5.2, 1.0 Hz, 2H), 7.23 – 7.19 (m, 2H), 7.04 (d, *J* = 1.0 Hz, 2H), 7.00 (dd, *J* = 5.2, 3.4 Hz, 2H), 4.17 – 3.82 (m, 4H), 1.70 – 1.61 (m, 4H), 1.30 – 1.18 (m, 12H), 1.11 – 1.00 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 6H, 2C$\underline{H}_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 144.9, 139.1, 137.3, 134.3, 131.1, 129.8, 128.3, 128.2, 128.1, 128.0, 127.7, 127.4, 126.9, 124.7, 121.5, 111.6, 108.6, 44.7, 31.7, 29.3, 28.9, 26.8, 22.5, 14.0.

Anal. Calcd for $C_{54}H_{52}N_2O_2S_2$×0.2$CH_3CO_2C_2H_5$: C, 78.10; H, 6.41; N, 3.32. Found: C, 78.13; H, 6.25; N, 3.35.

4.7.2. 1,1'-(6,12-Bis(5-acetylthiophen-2-yl)-5,11-diheptyl-5,11-dihydroindolo[3,2-b]carbazole-2,8-diyl)bis(ethan-1-one) ***(7)***

Yellow powder; 270 mg, 50%; Mp 224−5 °C. IR (DRA, ν): 3087, 2924, 2852, 1660, 1603, 1567, 1507, 1457, 1442, 1394, 1358, 1303, 1273, 1253, 1160, 1100, 1068, 996, 952, 926, 884, 817, 765, 740, 723, 699, 646, 624, 612, 590, 574, 560, 491 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 8.7, 1.6 Hz, 2H), 8.04 (d, *J* = 3.7 Hz, 2H), 7.46 (d, *J* = 3.7 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 1.5 Hz, 2H), 4.25 – 3.87 (m, 4H), 2.75 (s, 6H), 2.40 (s, 6H), 1.81 – 1.60 (m, 4H), 1.36 – 1.15 (m, 12H), 1.19 – 0.98 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, DMF-d_7) δ 196.0, 190.6, 146.8, 145.7, 145.3, 133.9, 131.7, 129.1, 126.5, 124.2, 123.9, 121.1, 111.3, 109.5, 44.8, 31.7, 26.6, 26.3, 25.5, 22.3, 13.5.

Anal. Calcd for $C_{48}H_{52}N_2O_4S_2$×0.5$(CH_3)_2NCHO$: C, 72.36; H, 6.81; N, 4.26. Found: C, 72.33; H, 7.02; N, 4.05.

4.8. General procedure for the Knoevenagel condensation of dialdehydes 5a,b with malononitrile

L-Proline (0.9 – 1 mg, 5 mol%) was added to a solution of the appropriate dialdehyde **5** (0.15 mmol) and malononitrile (1.2 mmol, 80 mg) in DMF with stirring at 100 °C. The mixture was stirred at the same temperature for 0.5 h and the precipitate was filtered, washed with hot methanol and dried at 110 °C to afford the compounds **8a,b** in analytical pure form.

*4.8.1. 2,2'-((5,11-Diheptyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-b]carbazole-2,8-diyl)bis(methanylylidene))dimalononitrile **(8a)***

Orange crystals; 112 mg, 97%; Mp > 350 °C. IR (DRA, ν): 3102, 2929, 2856, 2290, 2219, 1677, 1608, 1555, 1500, 1448, 1429, 1382, 1357, 1309, 1282, 1243, 1216, 1169, 1131, 1082, 1044, 1000, 933, 887, 867, 845, 804, 724, 675, 630, 615 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 8.7, 1.2 Hz, 2H), 7.80 (d, *J* = 5.0 Hz, 2H), 7.50 – 7.40 (m, 6H), 7.38 – 7.34 (m, 2H), 6.65 (s, 2H), 4.13 – 3.92 (m, 4H), 1.75 – 1.59 (m, 4H), 1.35 – 1.21 (m, 10H), 1.14 – 1.05 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 6H, 2C$\underline{H}_3$), 0.86 – 0.80 (m, 2H).

Anal. Calcd for $C_{48}H_{44}N_6S_2$: C, 74.97; H, 5.77; N, 10.93. Found: C, 74.99; H, 5.60; N, 10.82.

*4.8.1. 2,2'-((5,11-Dihexyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-b]carbazole-2,8-diyl)bis(methanylylidene))dimalononitrile **(8b)***

Orange crystals; 103 mg, 92%; Mp > 350 °C. IR (DRA, ν): 2930, 2858, 2293, 2221, 1680, 1609, 1560, 1502, 1449, 1430, 1383, 1357, 1310, 1288, 1244, 1218, 1170, 1147, 1131, 1084, 1045, 1000, 952, 934, 887, 844, 804, 722, 675, 631, 615 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 9.0, 1.4 Hz, 2H), 7.81 (dd, *J* = 5.3, 0.9 Hz, 2H), 7.48 – 7.42 (m, 6H), 7.37 – 7.34 (m, 2H), 6.65 (s, 2H), 4.16 – 3.91 (m, 4H), 1.71 – 1.63 (m, 4H), 1.26 – 1.16 (m, 6H), 1.14 – 1.06 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 6H, 2C$\underline{H}_3$), 0.86 – 0.80 (m, 2H). ^{13}C NMR (101 MHz, DMF-d_7) δ 142.4, 138.1, 133.9, 129.1, 128.3, 128.1, 127.3, 124.5, 124.1, 123.5, 122.5, 114.1, 109.4, 44.4, 31.3, 26.3, 25.1, 22.3, 13.5.

Anal. Calcd for $C_{46}H_{40}N_6S_2$: C, 74.56; H, 5.44; N, 11.34. Found: C, 74.37; H, 5.54; N, 11.37.

4.9. General procedure for the Knoevenagel condensation of dialdehydes 5a,b with 2-(hetaryl)acetonitriles

KO*t*-Bu (1.5 mmol, 120 mg) was added to a solution of the appropriate dialdehyde **5** (0.15 mmol) and 2-(hetaryl)acetonitrile (3 mmol, 370 mg – 2-(thiophen-2-yl)acetonitrile; 520 mg – 2-(benzo[*d*]thiazol-2-yl)acetonitrile) in anhydrous *n*-butanol (10 ml) with stirring at 80 °C. The mixture was stirred at the same temperature for 1 h, then the reaction mixture was neutralized by

addition of excess glacial acetic acid (1 ml). The precipitate was filtered, washed with hot methanol and dried at 110 °C to afford the compounds **9a,b** or **10** in analytical pure form.

4.9.1. (2E,2'E)-3,3'-(5,11-Diheptyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-b]carbazole-2,8-diyl)bis(2-(thiophen-2-yl)acrylonitrile) ***(9a)***

Yellow crystals; 120 mg, 90%; Mp 248−9 °C. IR (DRA, ν): 3092, 3011, 2952, 2923, 2848, 2209, 1874, 1689, 1607, 1587, 1567, 1498, 1467, 1449, 1431, 1356, 1311, 1278, 1247, 1218, 1170, 1158, 1129, 1082, 1044, 998, 957, 908, 843, 822, 804, 758, 728, 690, 642, 629, 605, 580, 505, 488, 469 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 5.1 Hz, 2H), 7.48 – 7.37 (m, 6H), 7.31 (dd, *J* = 3.5, 0.9 Hz, 2H), 7.27 (dd, *J* = 4.1, 0.9 Hz, 2H), 7.22 (s, 2H), 7.07 (dd, *J* = 5.0, 3.7 Hz, 2H), 6.73 (s, 2H), 4.13 – 3.87 (m, 4H), 1.74 – 1.60 (m, 4H), 1.30 – 1.21 (m, 12H), 1.16 – 1.03 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 6H, 2C$\underline{H}_3$). ^{13}C NMR (101 MHz, DMF-d_7) δ 143.9, 141.7, 139.6, 137.4, 134.4, 129.4, 128.6, 128.4, 126.5, 126.2, 125.9, 125.3, 124.6, 122.5, 117.6, 115.3, 112.0, 110.1, 102.5, 31.6, 26.6, 22.3, 13.5.

Anal. Calcd for $C_{54}H_{50}N_4S_4$: C, 73.43; H, 5.71; N, 6.34. Found: C, 73.20; H, 5.61; N, 6.18.

4.9.2. (2E,2'E)-3,3'-(5,11-Dihexyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-b]carbazole-2,8-diyl)bis(2-(thiophen-2-yl)acrylonitrile) ***(9b)***

Yellow crystals; 103 mg, 80%; Mp 255−6 °C. IR (DRA, ν): 2930, 2858, 2293, 2221, 1680, 1609, 1560, 1502, 1449, 1430, 1383, 1357, 1310, 1288, 1244, 1218, 1170, 1147, 1131, 1084, 1045, 1000, 952, 934, 887, 844, 804, 722, 675, 631, 615 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 9.1, 0.9 Hz, 2H), 7.75 (dd, *J* = 5.2, 0.9 Hz, 2H), 7.47 – 7.35 (m, 6H), 7.31 (dd, *J* = 3.6, 1.0 Hz, 2H), 7.27 (d, *J* = 1.0 Hz, 2H), 7.22 (s, 2H), 7.07 (dd, *J* = 5.1, 3.7 Hz, 2H), 6.73 (s, 2H), 4.09 – 3.88 (m, 4H), 1.74 – 1.61 (m, 4H), 1.33 – 1.16 (m, 8H), 1.16 – 1.02 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 6H, 2C$\underline{H}_3$). ^{13}C NMR (101 MHz, DMF-d_7) δ 143.9, 141.7, 139.6, 137.4, 134.3, 129.4, 128.6, 128.4, 126.5, 126.2, 125.9, 125.3, 124.6, 124.4, 122.5, 117.6, 112.0, 110.1, 102.5, 44.6, 31.3, 26.3, 22.4, 13.5.

Anal. Calcd for $C_{52}H_{46}N_4S_4$: C, 73.03; H, 5.42; N, 6.55. Found: C, 73.07; H, 5.29; N, 6.60.

4.9.3. (2E,2'E)-3,3'-(5,11-Diheptyl-6,12-di(thiophen-2-yl)-5,11-dihydroindolo[3,2-b]carbazole-2,8-diyl)bis(2-(benzo[d]thiazol-2-yl)acrylonitrile) ***(10)***

Orange powder; 100 mg, 68%; Mp 290−1 °C. IR (DRA, ν): 3063, 2926, 2854, 2211, 1686, 1607, 1574, 1560, 1500, 1449, 1430, 1384, 1356, 1311, 1281, 1245, 1166, 1129, 1087, 1045, 1004, 948, 847, 802, 756, 725, 700, 645, 614, 576 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 8.8, 1.1 Hz, 2H), 8.09 (d, *J* = 8.2 Hz, 2H), 8.03 (s, 2H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 5.3

Hz, 2H), 7.56 – 7.47 (m, 4H), 7.47 – 7.38 (m, 6H), 6.92 (s, 2H), 4.13 – 3.90 (m, 4H), 1.75 – 1.64 (m, 4H), 1.38 – 1.20 (m, 12H), 1.17 – 1.06 (m, 4H), 0.90 (t, J = 6.9 Hz, 6H, 2C$\underline{H}_3$).

Anal. Calcd for $C_{60}H_{52}N_6S_4$: C, 73.14; H, 5.32; N, 8.53. Found: C, 73.24; H, 5.24; N, 8.37.

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Supplementary Material

Synthesis, photophysical and electrochemical properties of novel 6,12-di(thiophen-2-yl) substituted indolo[3,2-*b*]carbazoles

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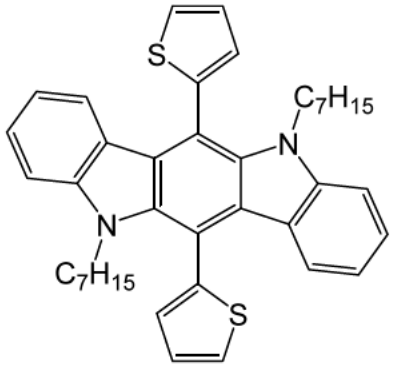
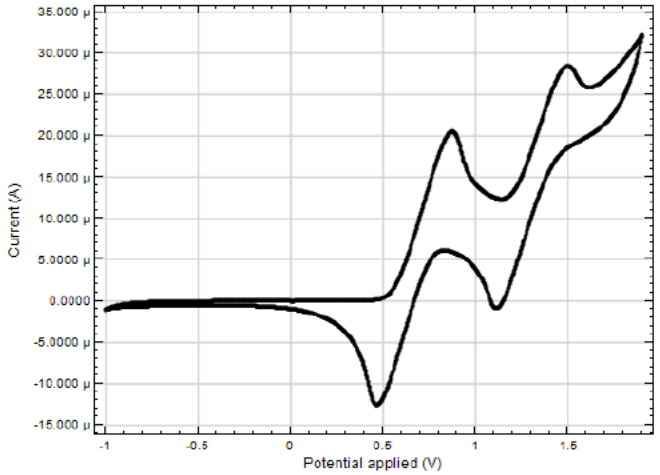
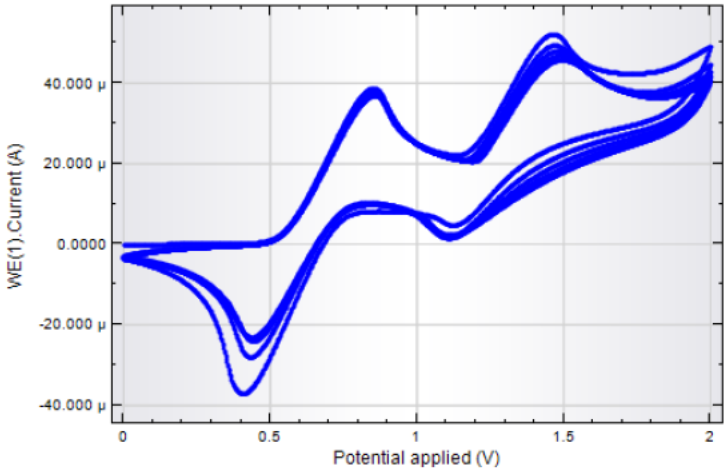
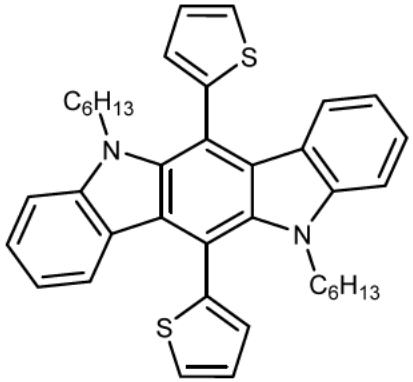
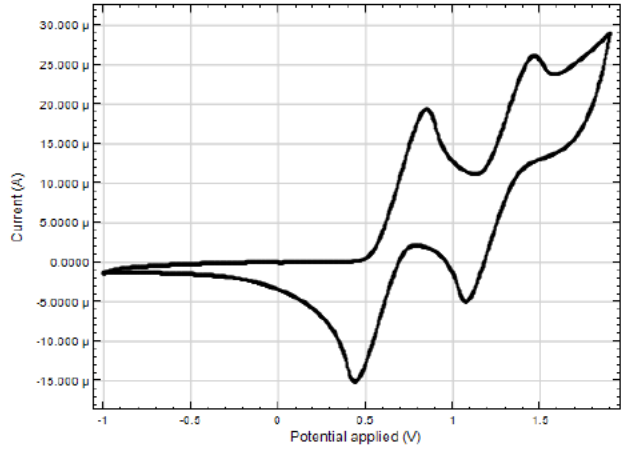
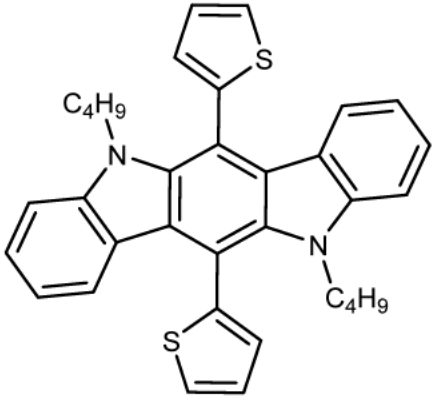
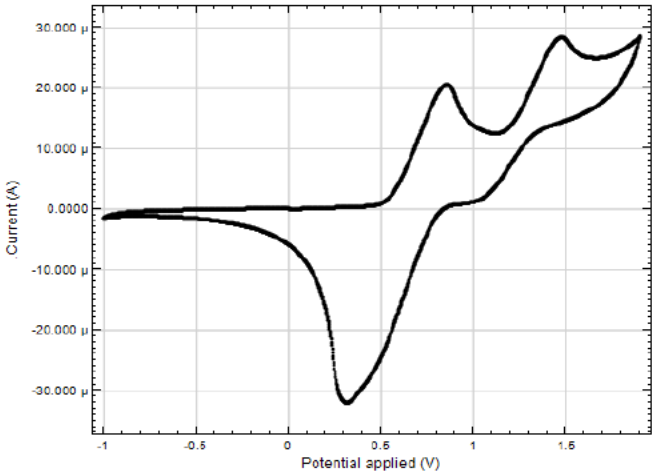
*1. Cyclic voltammetry measurements for **3a-f**; **8a,b**; **9a,b**; **10***

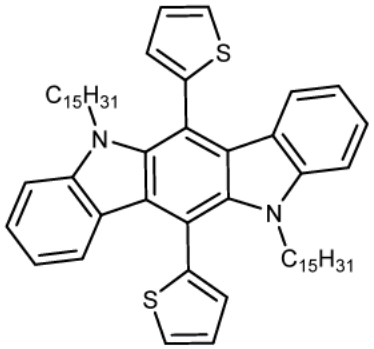
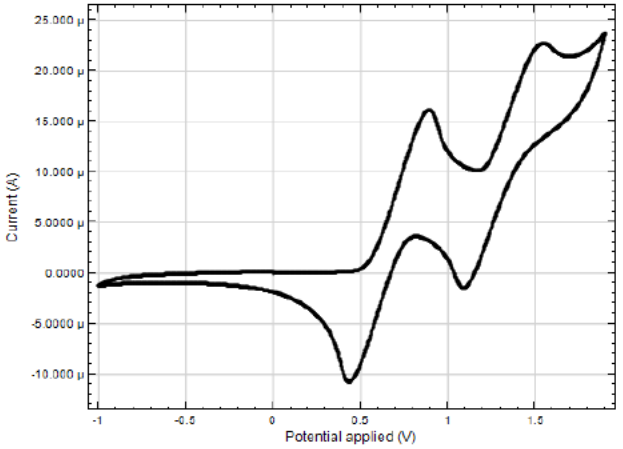
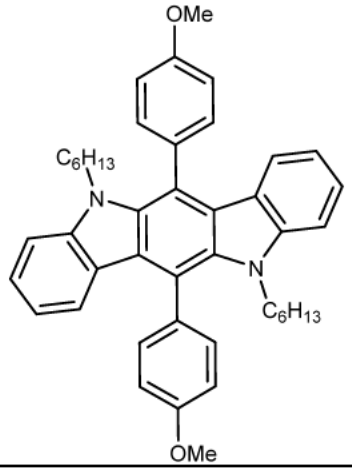
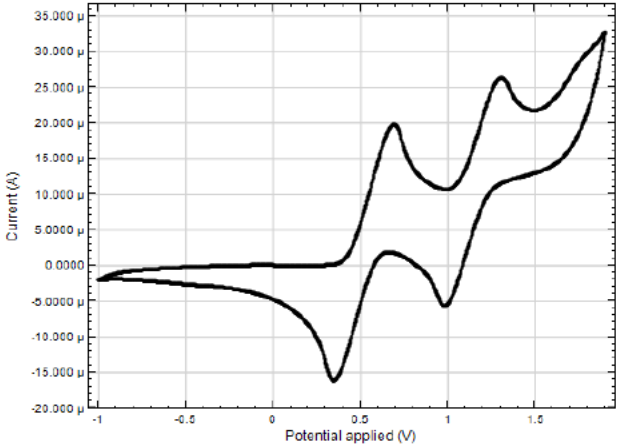
Cyclic voltammetry was carried out on a Metrohm Autolab PGSTAT**128N** potentiostat with a standard three-electrode configuration. Typically, a three electrodes cell equipped with a glass carbon working electrode, a $Ag/AgNO_3$ (0.01M) reference electrode, and a glass carbon rod counter electrode was employed. The measurements were done in anhydrous dichloromethane with tetrabutylammonium tetrafluoroborate (0.1 M) as the supporting electrolyte under an argon atmosphere at a scan rate of 100 mV/s. The potential of $Ag/AgNO_3$ reference electrode was calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc+), which has a known oxidation potential of +4.8 eV. The HOMO energy values were estimated from the onset potentials (E_{ox}^{onset}) of the first oxidation event according to the following equations:

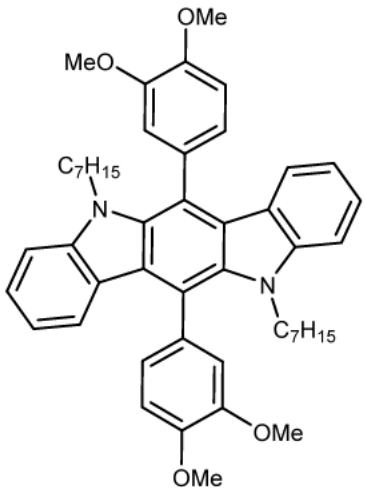
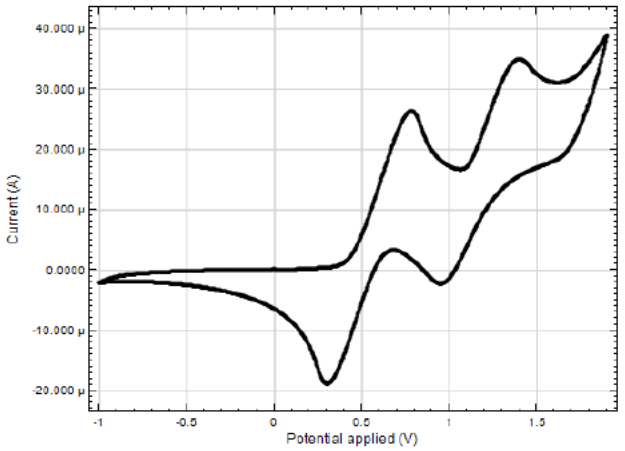
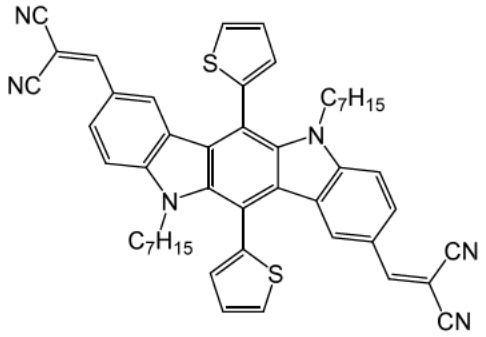
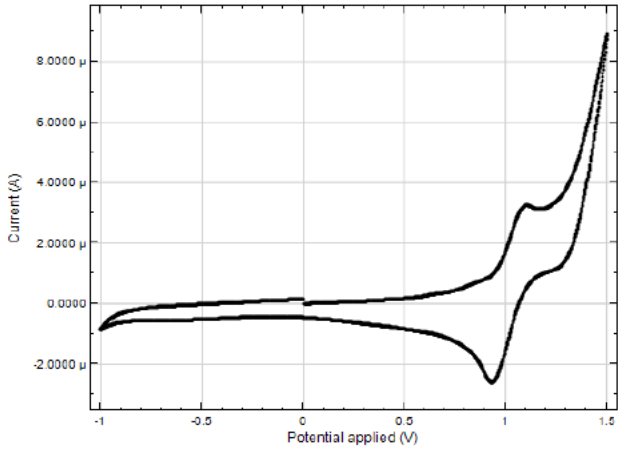
$$E_{HOMO}\ (eV) = -\left[E_{ox}^{onset} - E_{1/2}(Fc/Fc+) + 4.8\right]$$

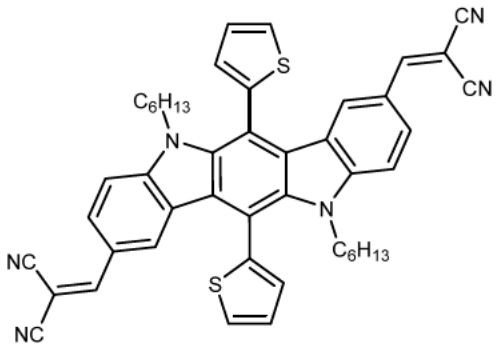
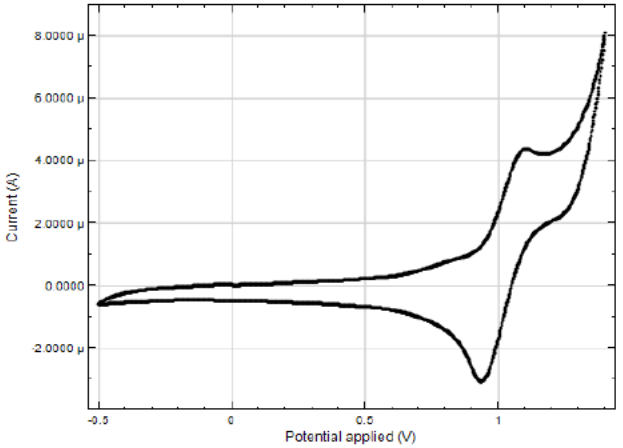
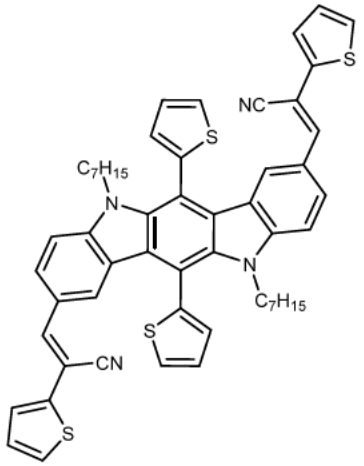
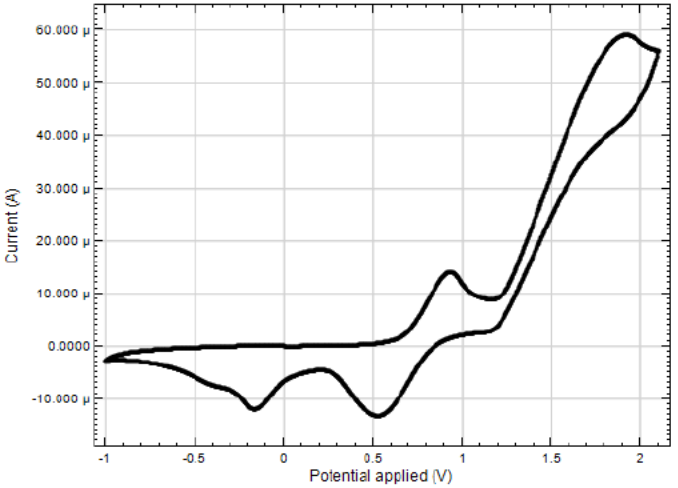
where $E_{1/2}(Fc/Fc+)$ is the half-wave potential of the Fc/Fc+ couple against the Ag/Ag+ electrode.

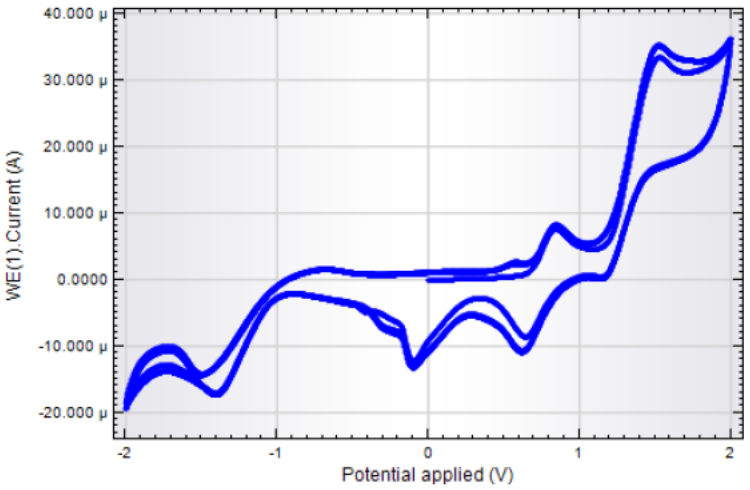
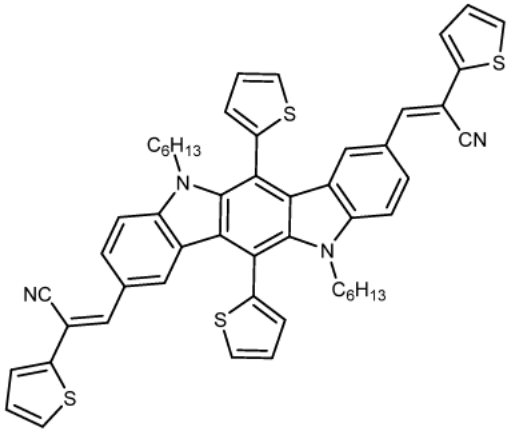
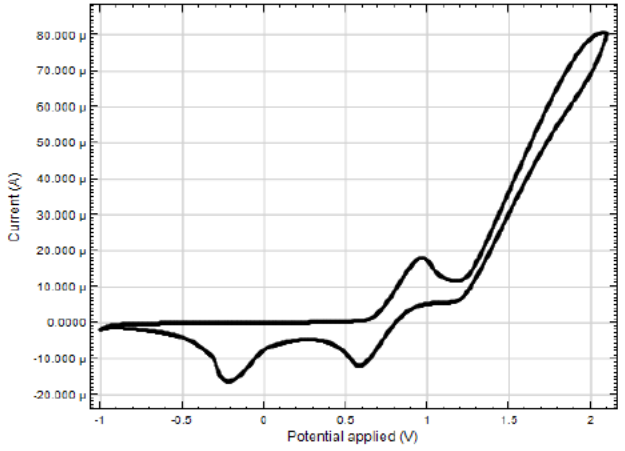
Compound	Structure	CV graphic	Oxidation potential
3a		 ***Multiple scans:*** 	E_{ox}^{onset}=0,51 V E_{HOMO} (eV) = – 4,91

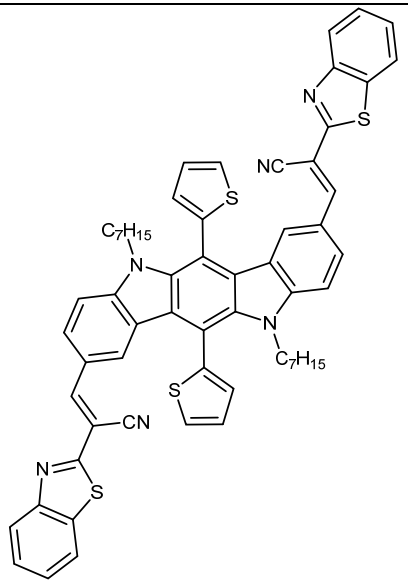
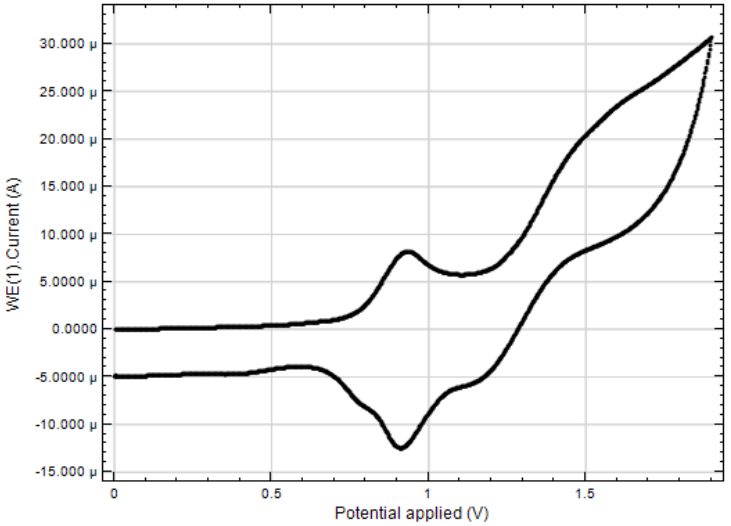
3b			E_{ox}^{onset}=0,50 V E_{HOMO} (eV) = – 4,90
3c			E_{ox}^{onset}=0,49 V E_{HOMO} (eV) = – 4,89

3d			E_{ox}^{onset}=0,50 V E_{HOMO} (eV) = – 4,90
3e			E_{ox}^{onset}=0,39 V E_{HOMO} (eV) = – 4,79

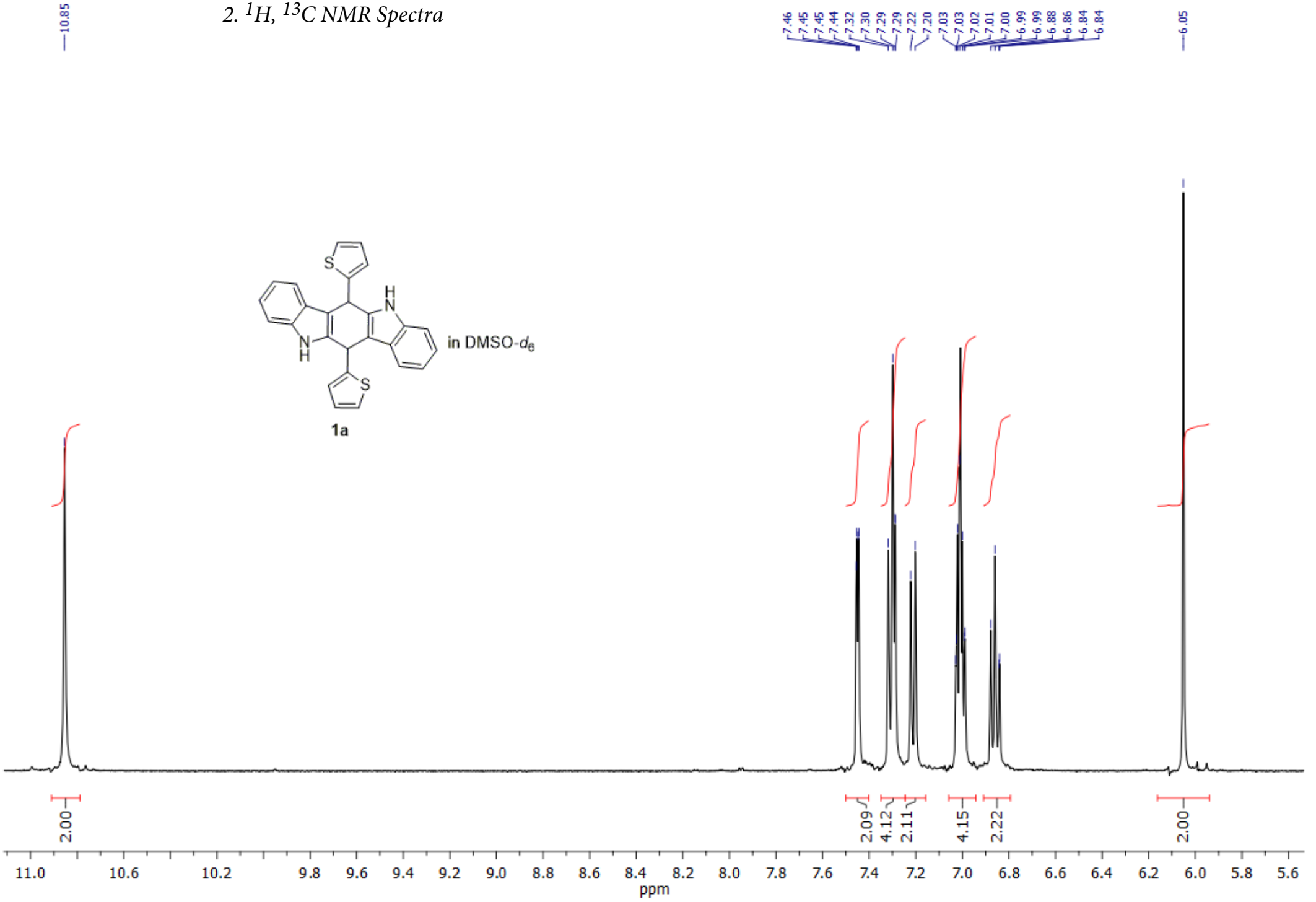
3f			E_{ox}^{onset}=0,35 V E_{HOMO} (eV) = – 4,75
8a			E_{ox}^{onset}=0,65 V E_{HOMO} (eV) = – 5,05

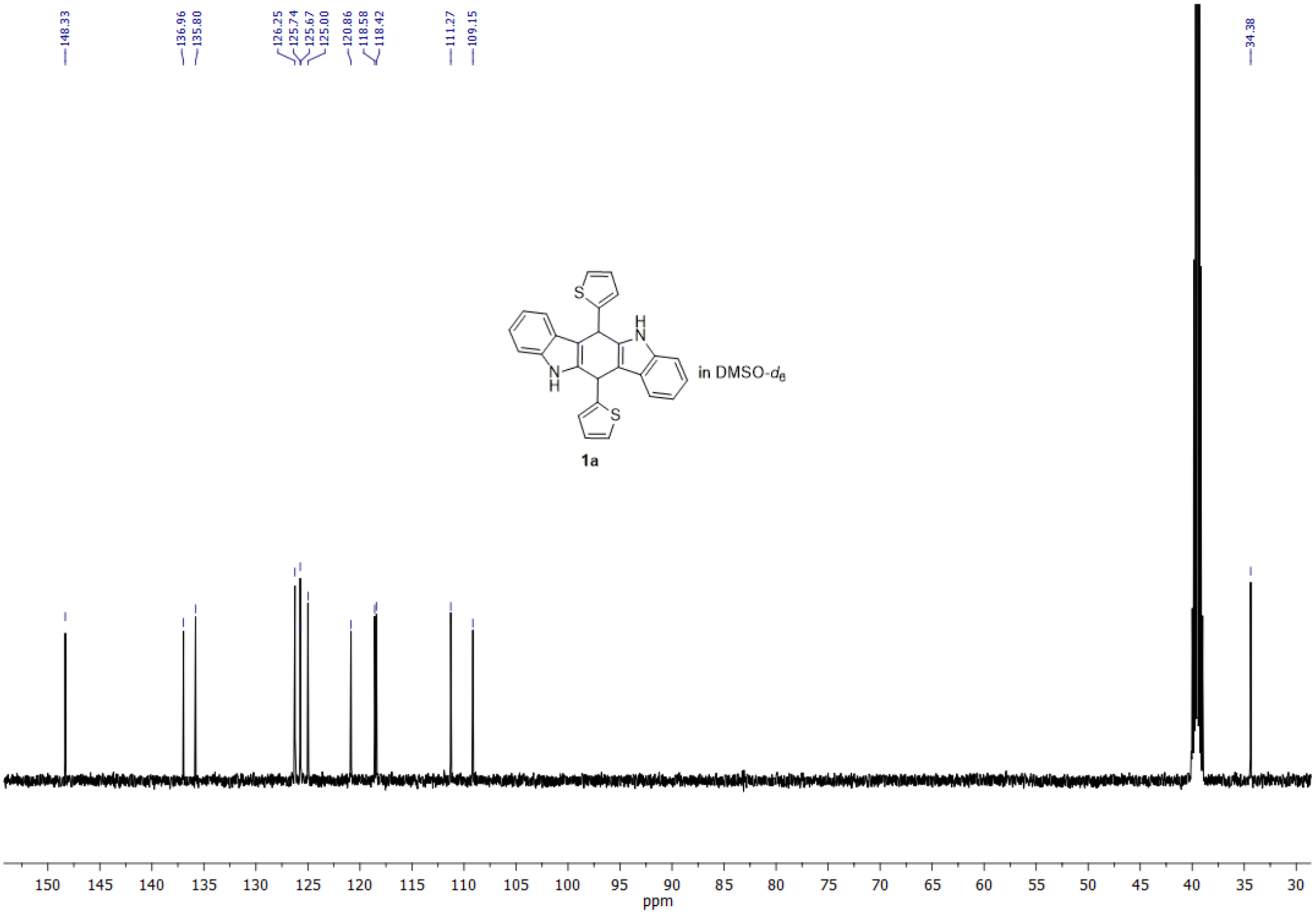
8b			E_{ox}^{onset}=0,70 V E_{HOMO} (eV) = – 5,10
9a			E_{ox}^{onset}=0,60 V E_{HOMO} (eV) = – 5,00

		Multiple scans: 	
9b			E_{ox}^{onset}=0,64 V E_{HOMO} (eV) = – 5,04

10			E_{ox}^{onset}=0,72 V E_{HOMO} (eV) = – 5,12

2. ^{1}H, ^{13}C NMR Spectra

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135.80
126.25
125.74
125.67
125.00
120.86
118.58
118.42
111.27
109.15
34.38
S
H
N
N
H
S
in DMSO-d_6
1a
150
145
140
135
130
125
120
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110
105
100
95
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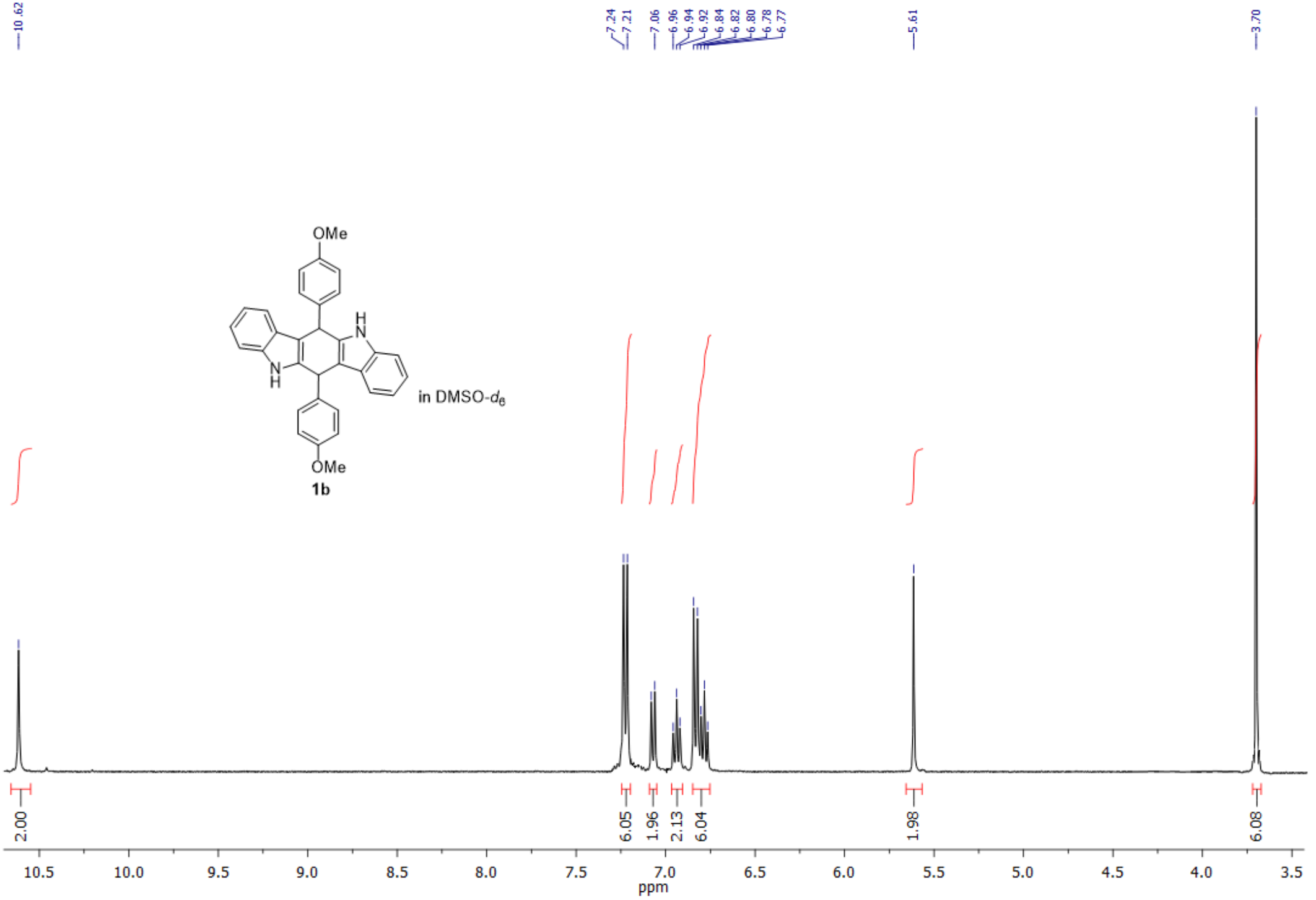
70
65
60
55
50
45
40
35
30
ppm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7.06
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6.92
6.84
6.82
6.80
6.78
6.77
5.61
3.70
OMe
H
N
N
H
OMe
1b
in DMSO-d_6
2.00
6.05
1.96
2.13
6.04
1.98
6.08
10.5
10.0
9.5
9.0
8.5
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7.5
7.0
6.5
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5.0
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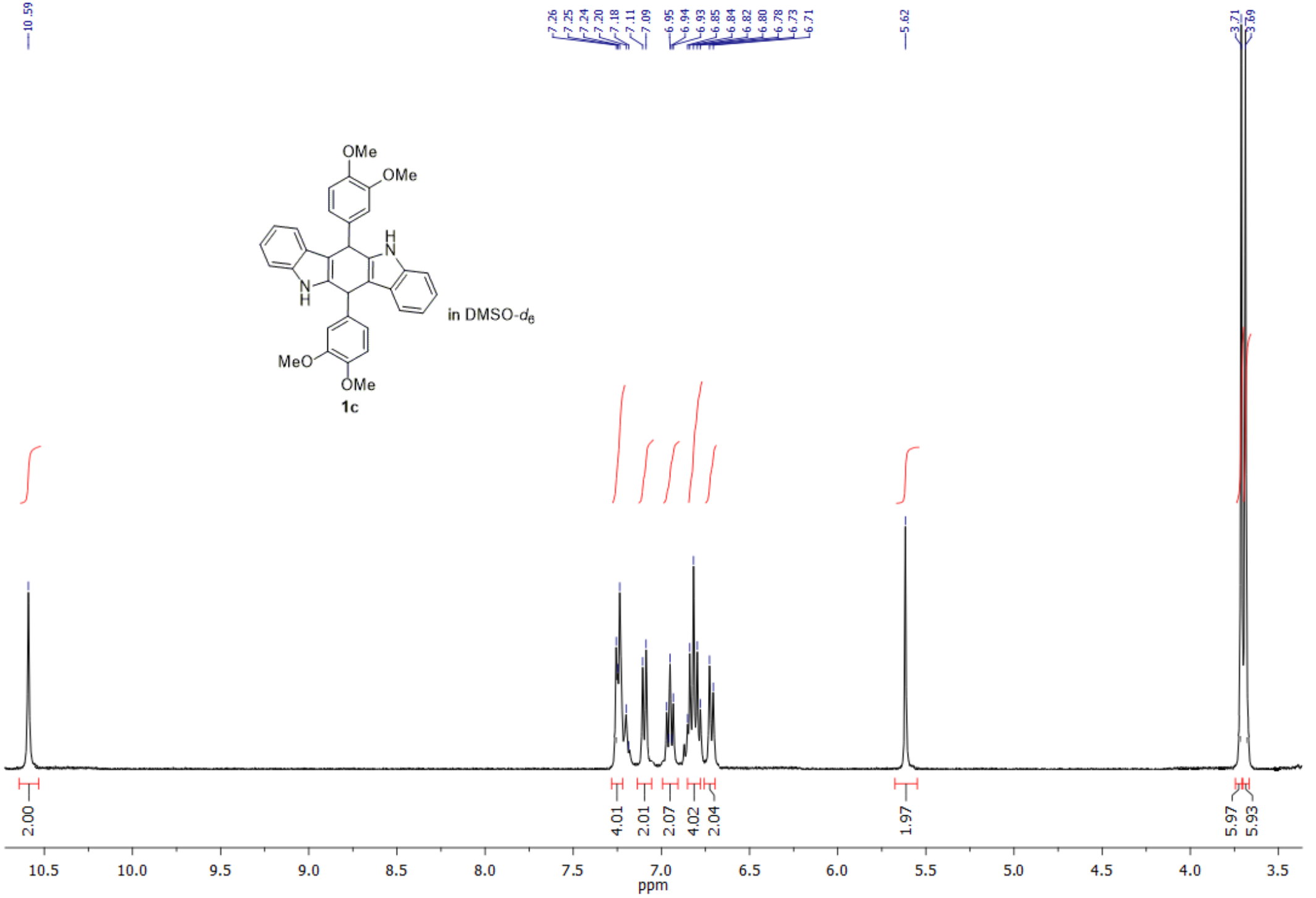
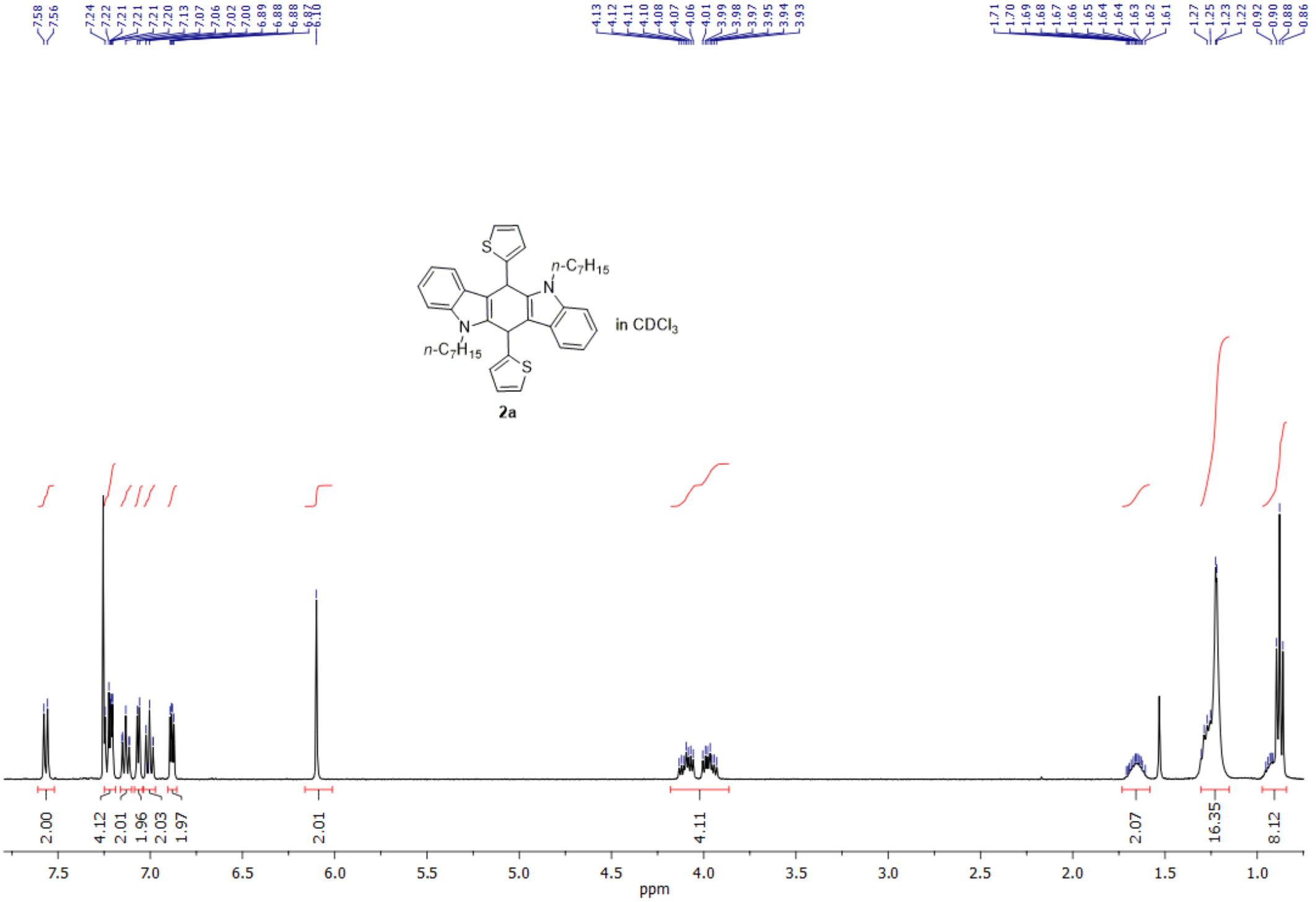
4.0
3.5
ppm

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7.24
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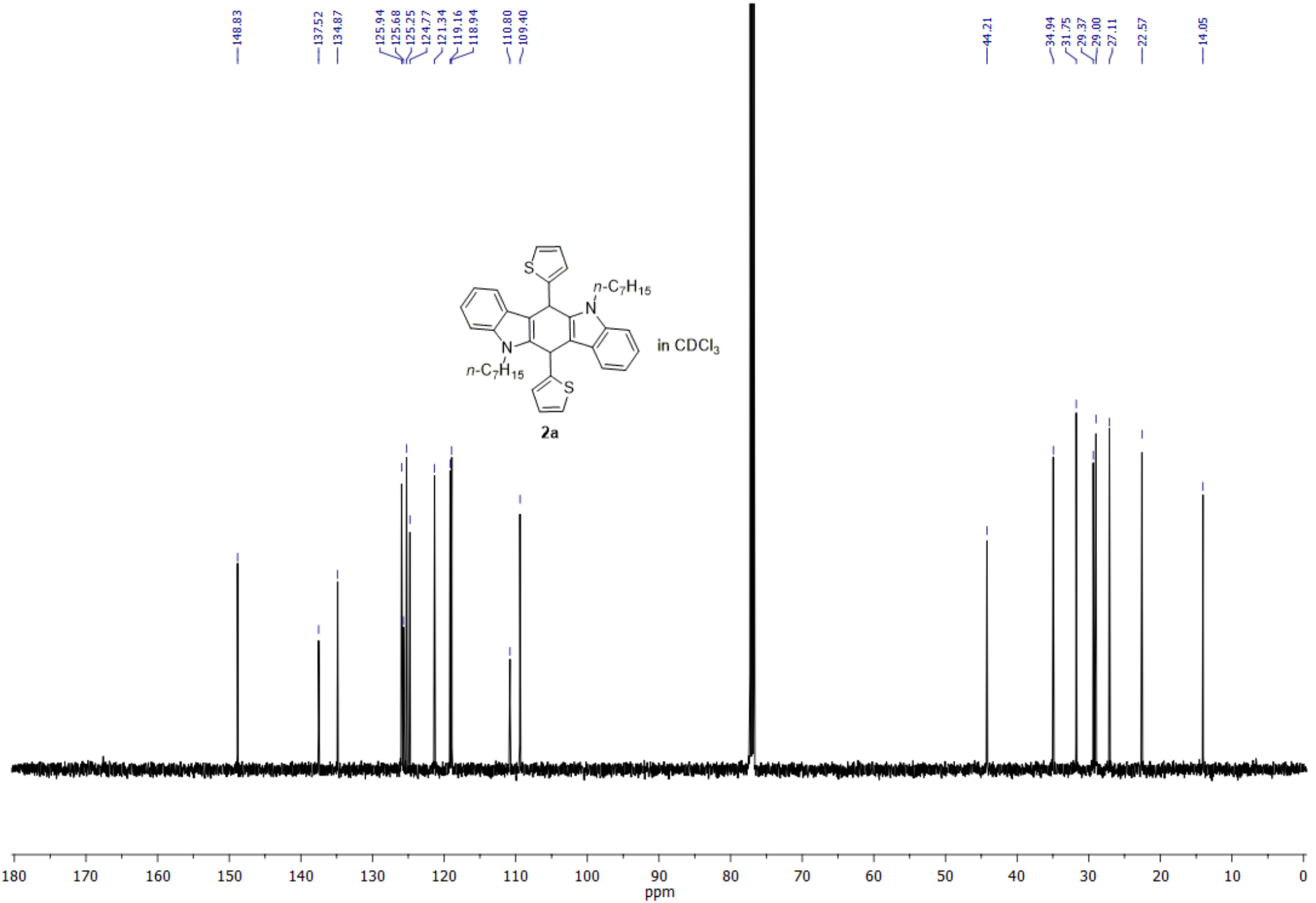
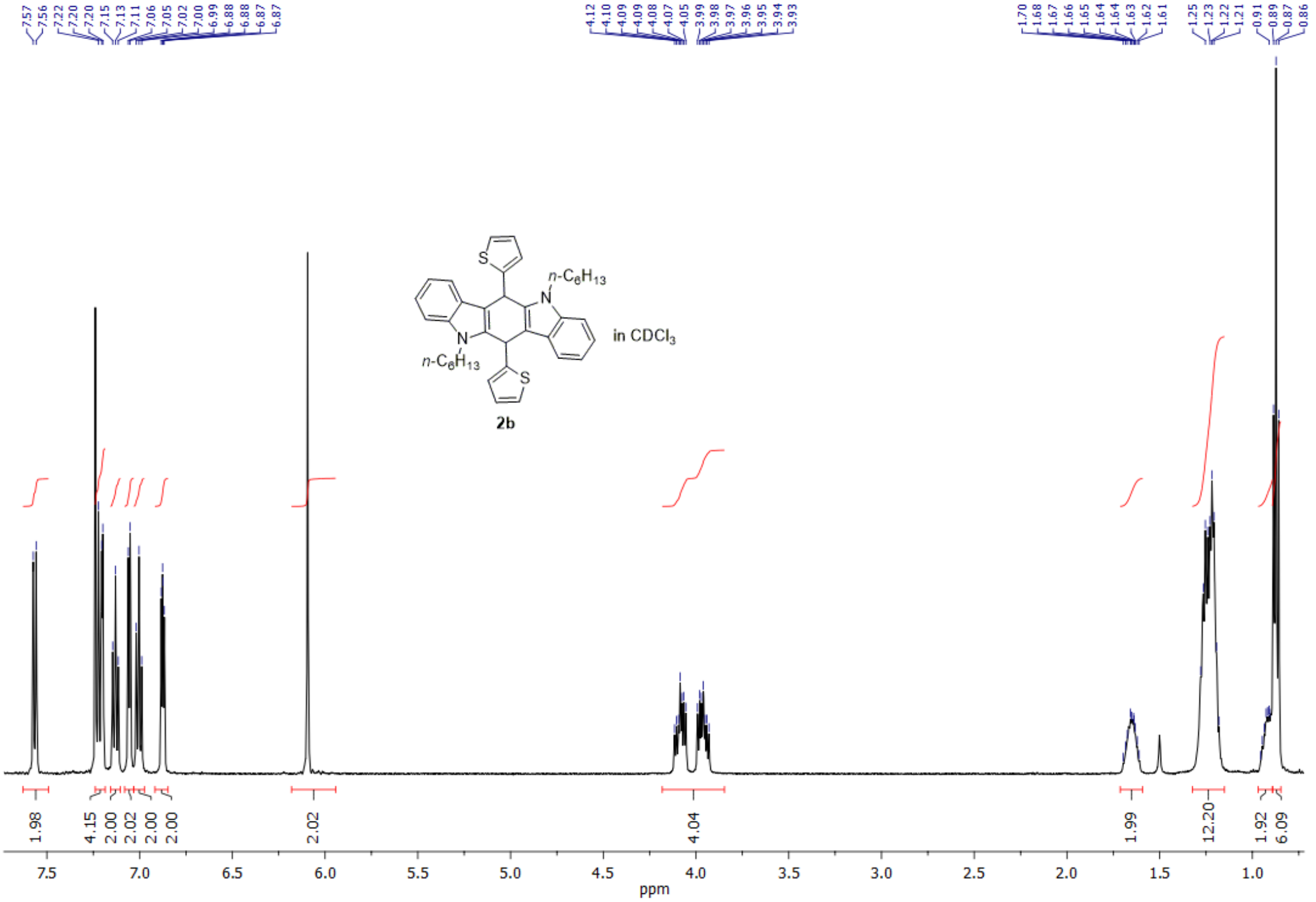
7.21
7.21
7.21
7.20
7.13
7.07
7.06
7.02
7.00
6.89
6.88
6.88
6.87
6.10
4.13
4.12
4.11
4.10
4.08
4.07
4.06
4.01
3.99
3.98
3.97
3.95
3.94
3.93
1.71
1.70
1.69
1.68
1.67
1.66
1.65
1.64
1.64
1.63
1.62
1.61
1.27
1.25
1.23
1.22
0.92
0.90
0.88
0.86
S
N
n-C7H15
n-C7H15
S
in CDCl3
2a
2.00
4.12
2.01
1.96
2.03
1.97
2.01
4.11
2.07
16.35
8.12
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

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7.56
7.22
7.20
7.20
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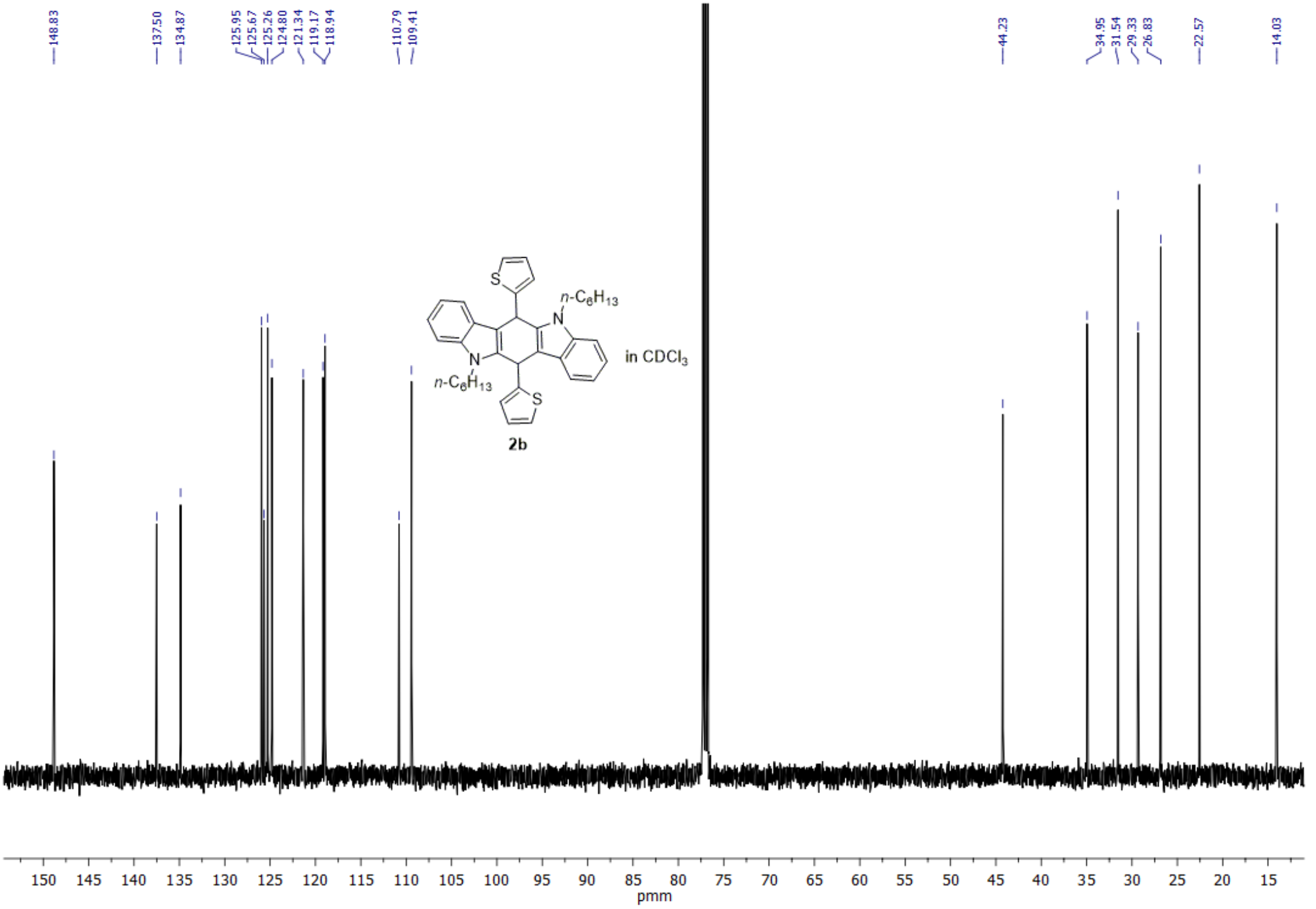
7.11
7.06
7.05
7.02
7.00
6.99
6.88
6.88
6.87
6.87
4.12
4.10
4.09
4.09
4.08
4.07
4.05
3.99
3.98
3.97
3.96
3.95
3.94
3.93
1.70
1.68
1.67
1.66
1.65
1.64
1.64
1.63
1.62
1.61
1.25
1.23
1.22
1.21
0.91
0.89
0.87
0.86
S
N
n-C6H13
n-C6H13
S
in CDCl3
2b
1.98
4.15
2.00
2.02
2.00
2.00
2.02
4.04
1.99
12.20
1.92
6.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm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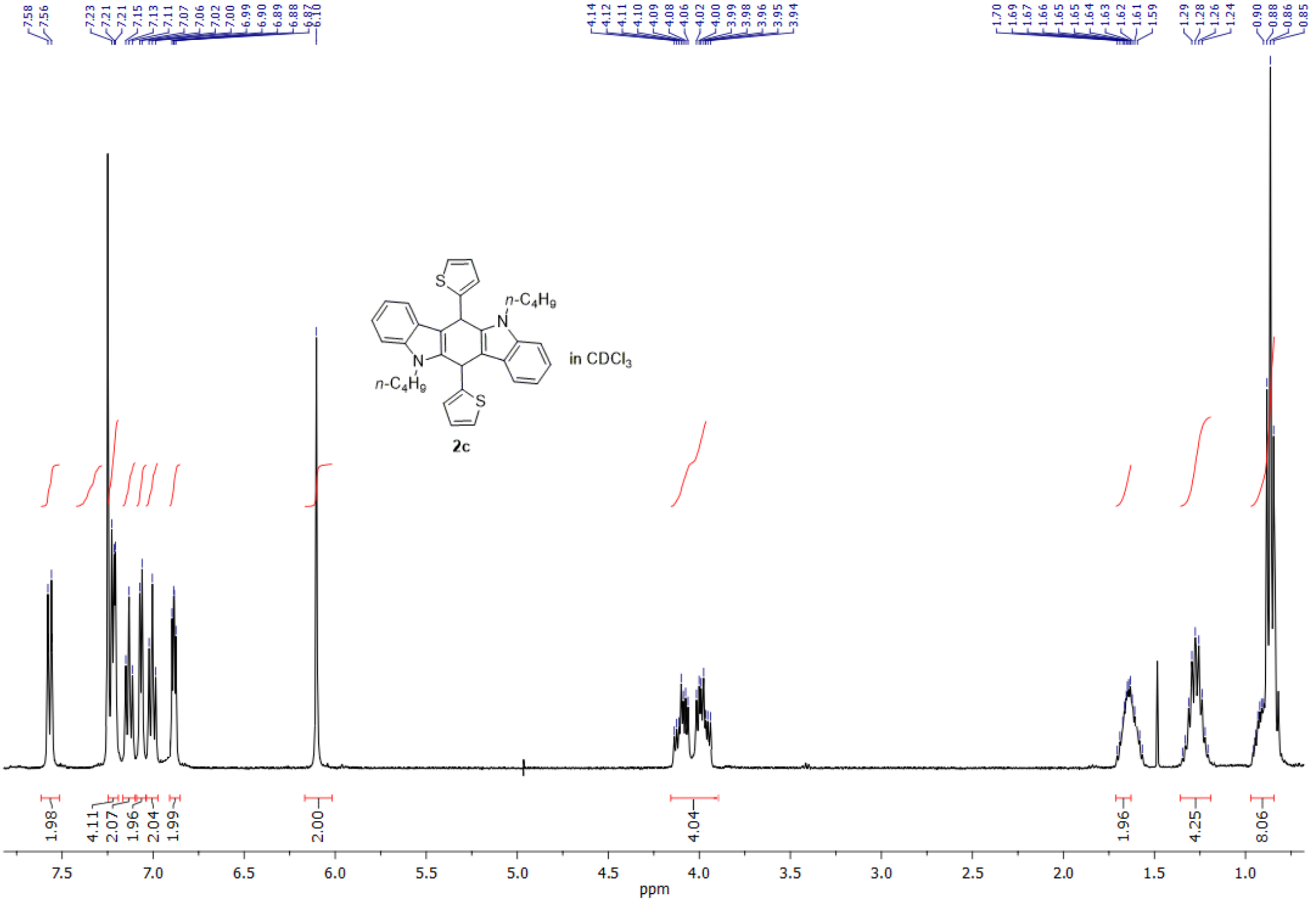
34.95
31.54
29.33
26.83
22.57
14.03
S
N
n-C6H13
n-C6H13
S
in CDCl3
2b
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
pmm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7.56
7.23
7.21
7.21
7.15
7.13
7.11
7.07
7.06
7.02
7.00
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6.90
6.89
6.88
6.87
6.10
4.14
4.12
4.11
4.10
4.09
4.08
4.06
4.02
4.00
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3.96
3.95
3.94
1.70
1.69
1.67
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1.65
1.65
1.64
1.63
1.62
1.61
1.59
1.29
1.28
1.26
1.24
0.90
0.88
0.86
0.85
S
n-C4H9
N
N
n-C4H9
S
in CDCl3
2c
1.98
4.11
2.07
1.96
2.04
1.99
2.00
4.04
1.96
4.25
8.06
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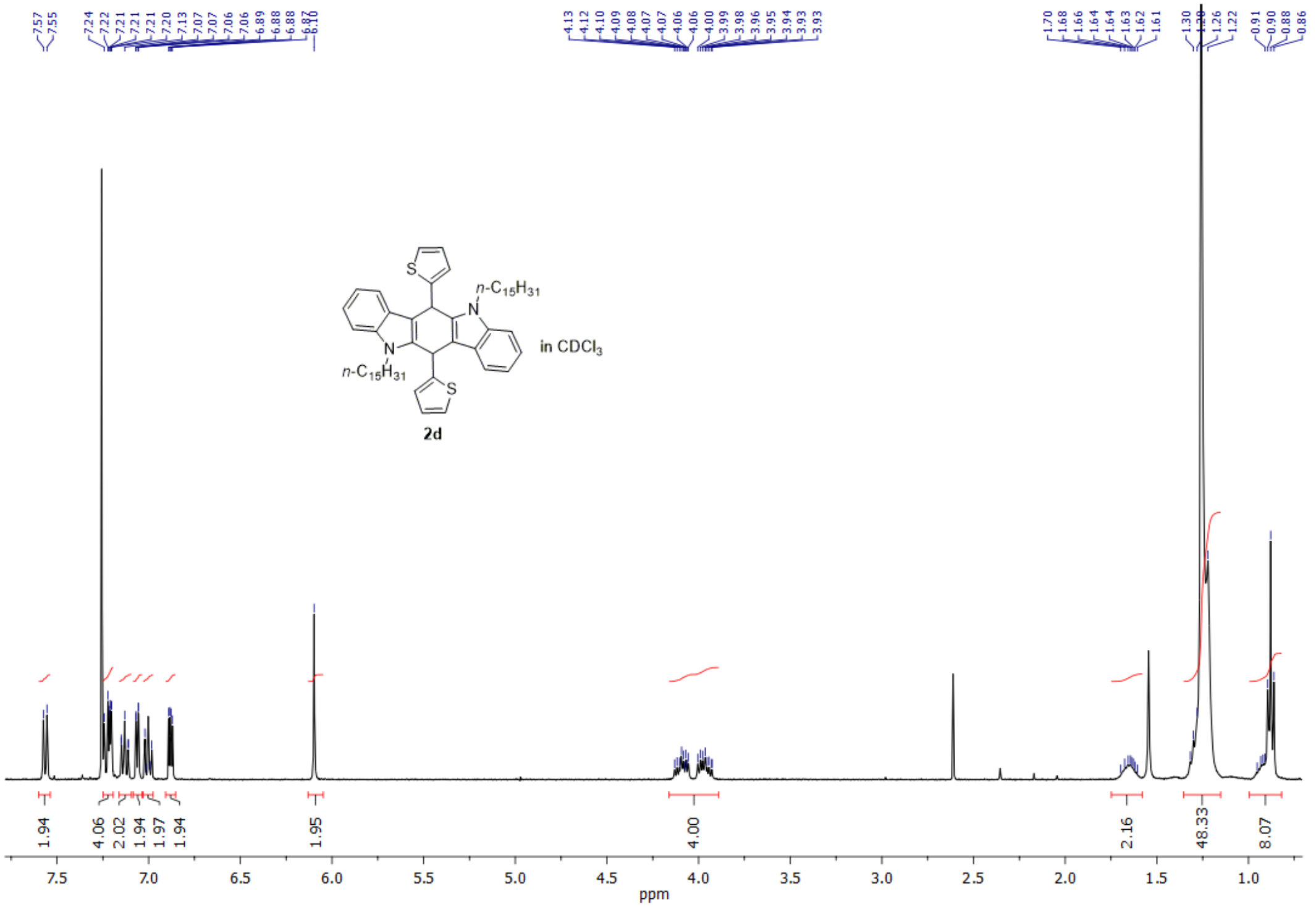
1.5
1.0
ppm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7.24
7.22
7.21
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7.13
7.07
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1.70
1.68
1.66
1.64
1.64
1.63
1.62
1.61
1.30
1.26
1.22
0.91
0.90
0.88
0.86
S
N
n-C15H31
n-C15H31
S
in CDCl3
2d
1.94
4.06
2.02
1.94
1.97
1.94
1.95
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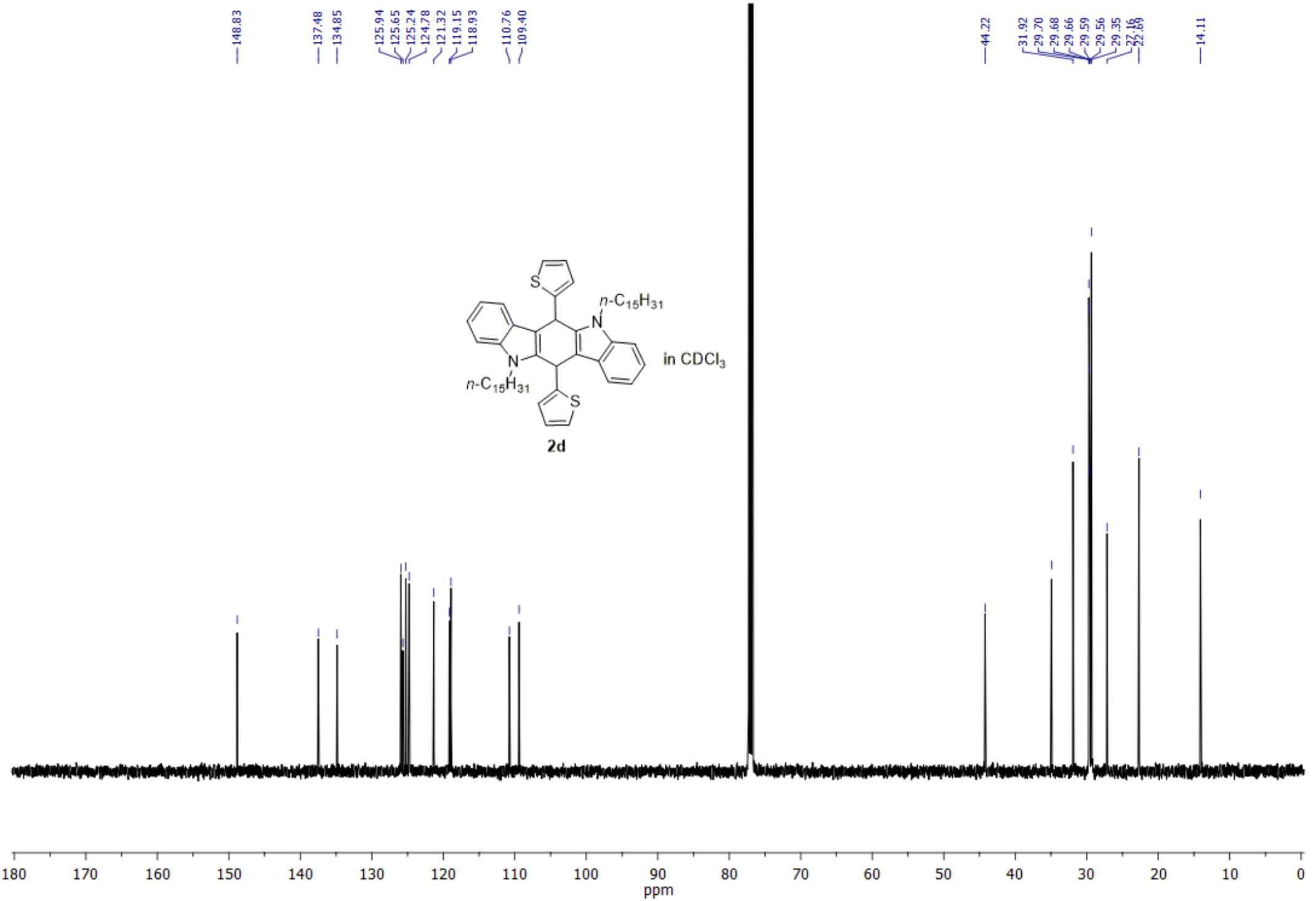
ppm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134.85
125.94
125.65
125.24
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121.32
119.15
118.93
110.76
109.40
44.22
31.92
29.70
29.68
29.66
29.59
29.56
29.35
14.11
S
N
n-C15H31
n-C15H31
S
in CDCl3
2d
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140
130
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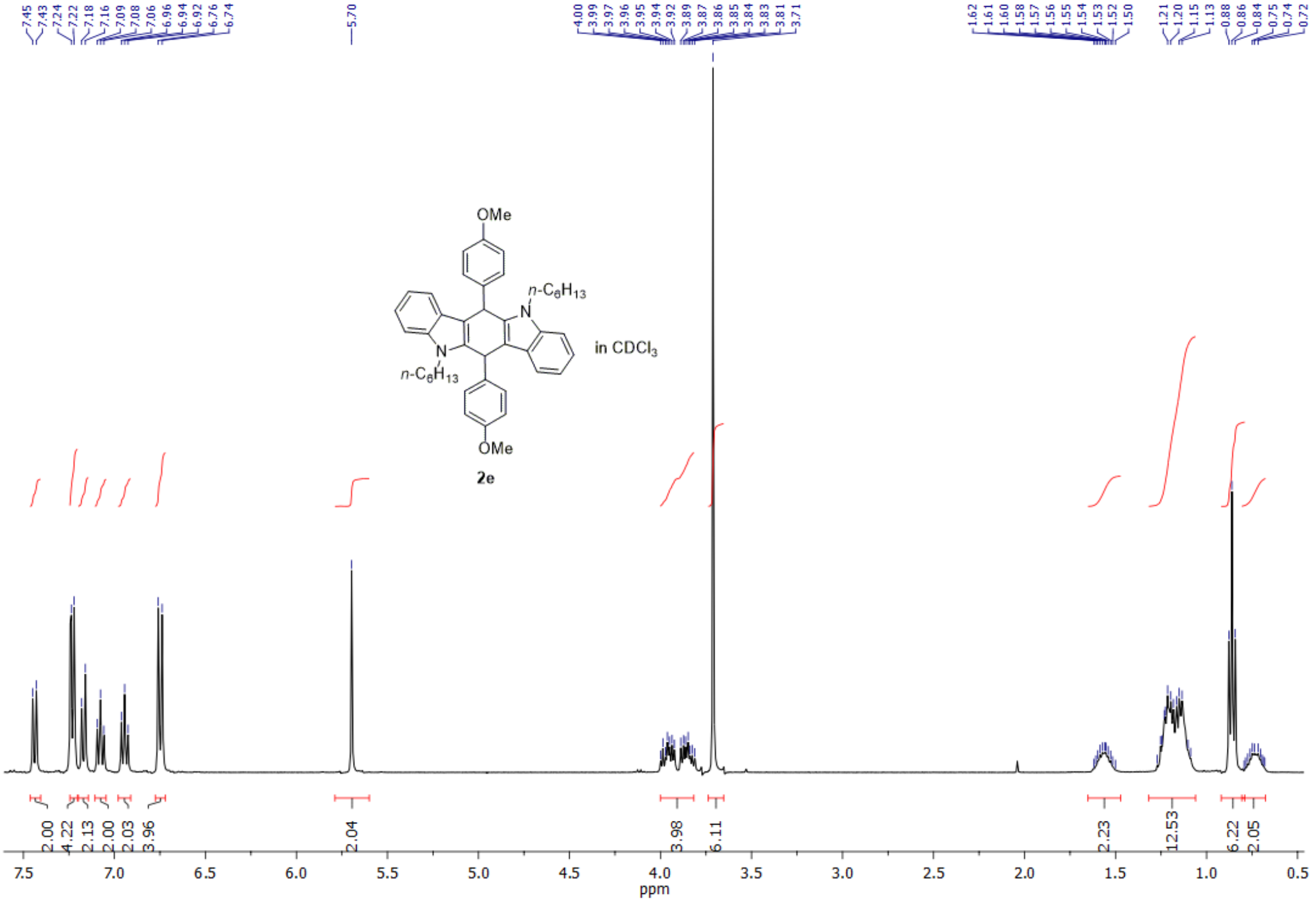
20
10
0
ppm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1.58
1.57
1.56
1.55
1.54
1.53
1.52
1.50
1.21
1.20
1.15
1.13
0.88
0.86
0.84
0.75
0.74
0.72
OMe
n-C8H13
N
N
n-C8H13
OMe
in CDCl3
2e
2.00
4.22
2.13
2.00
2.03
3.96
2.04
3.98
6.11
2.23
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6.5
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4.5
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3.5
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2.0
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1.0
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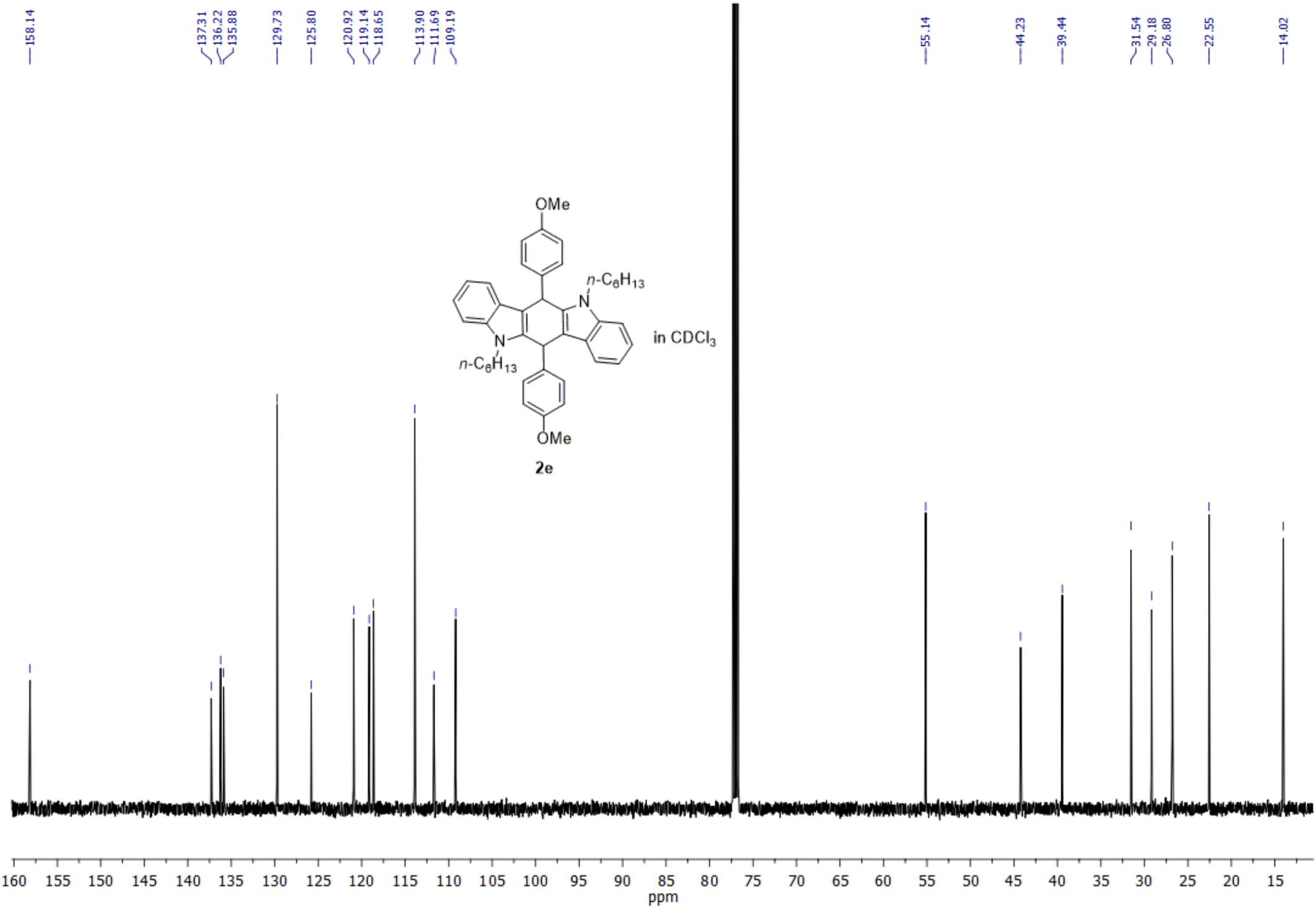
ppm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55.14
44.23
39.44
31.54
29.18
26.80
22.55
14.02
OMe
n-C6H13
N
N
n-C6H13
OMe
2e
in CDCl3
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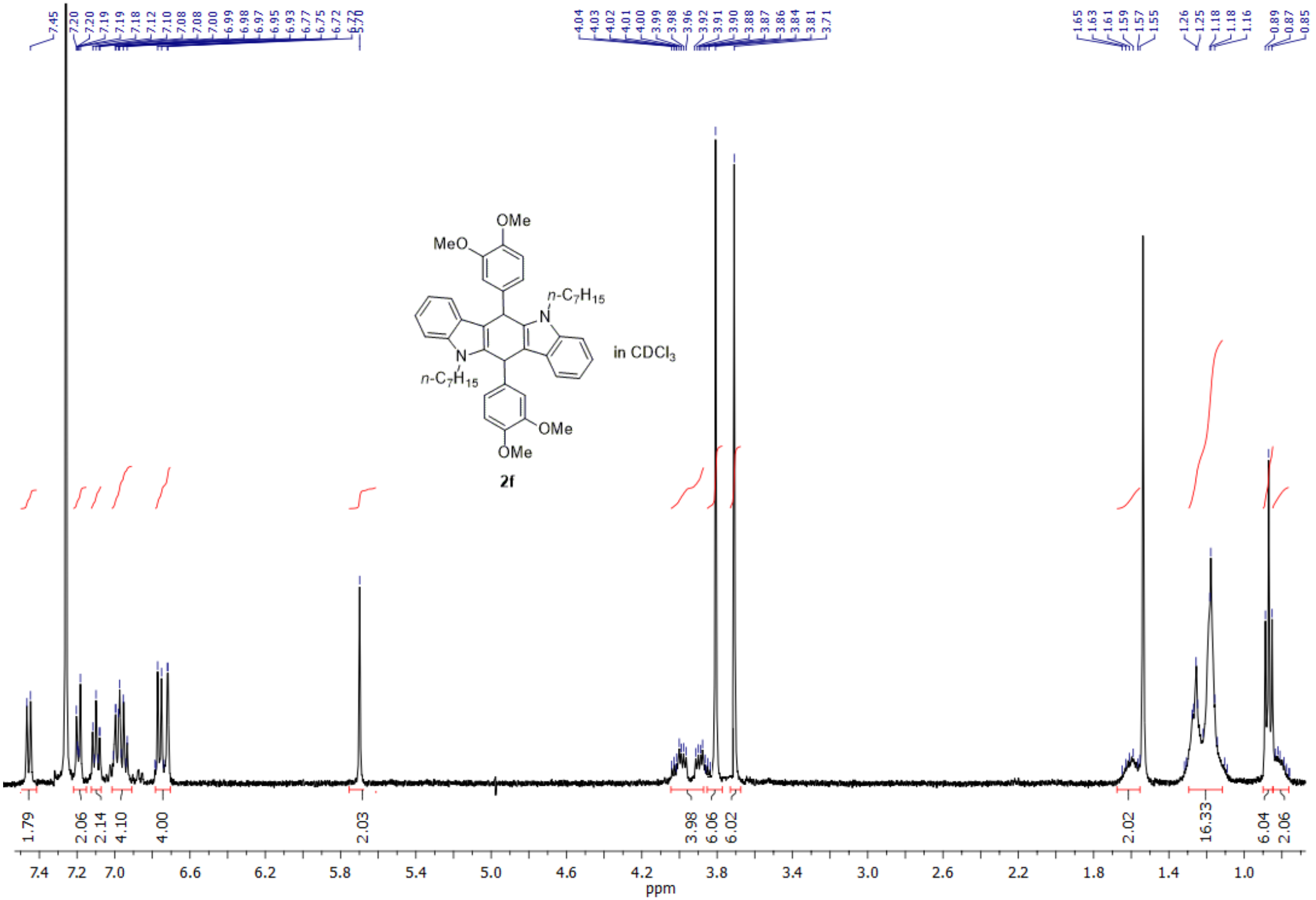
ppm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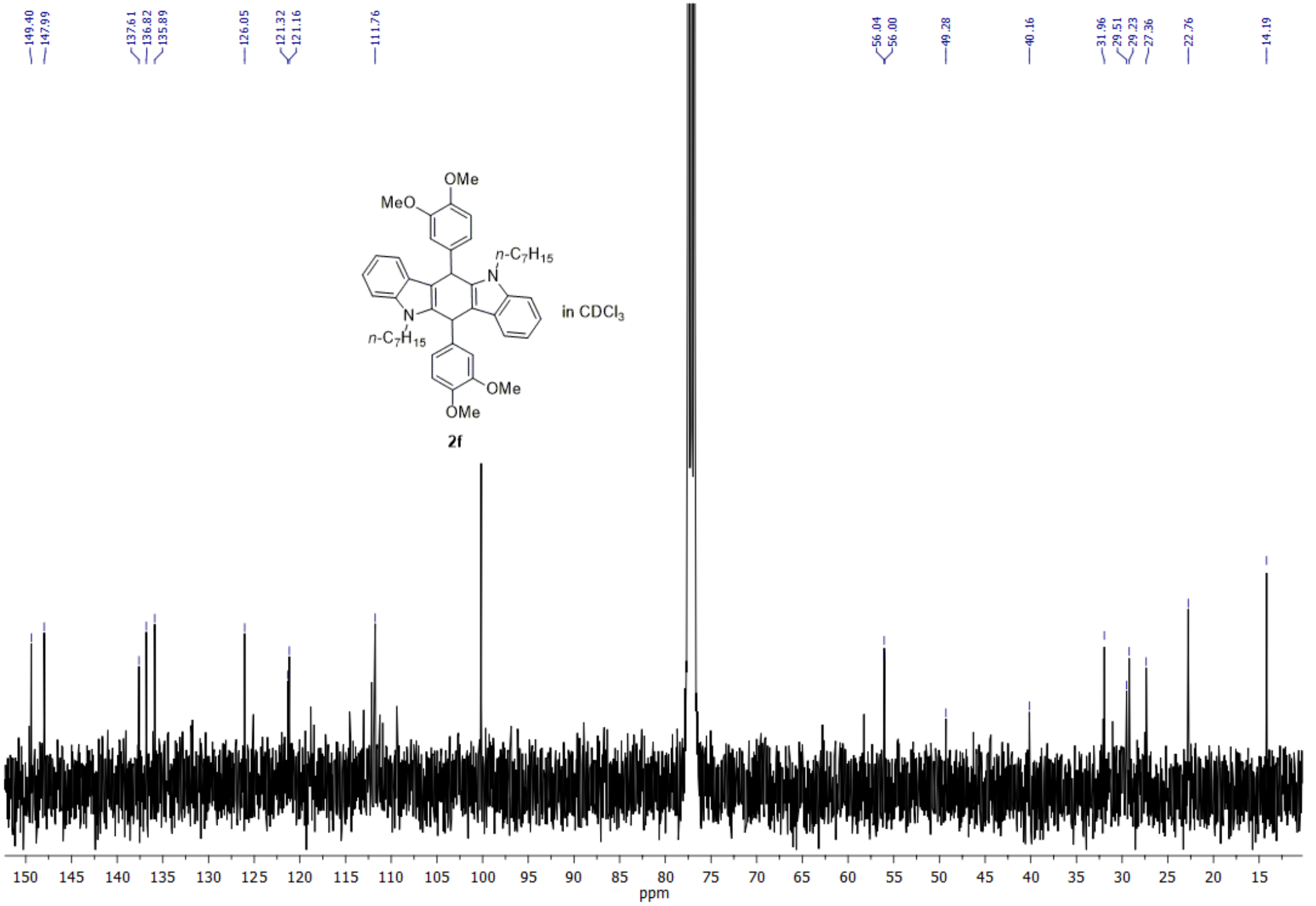
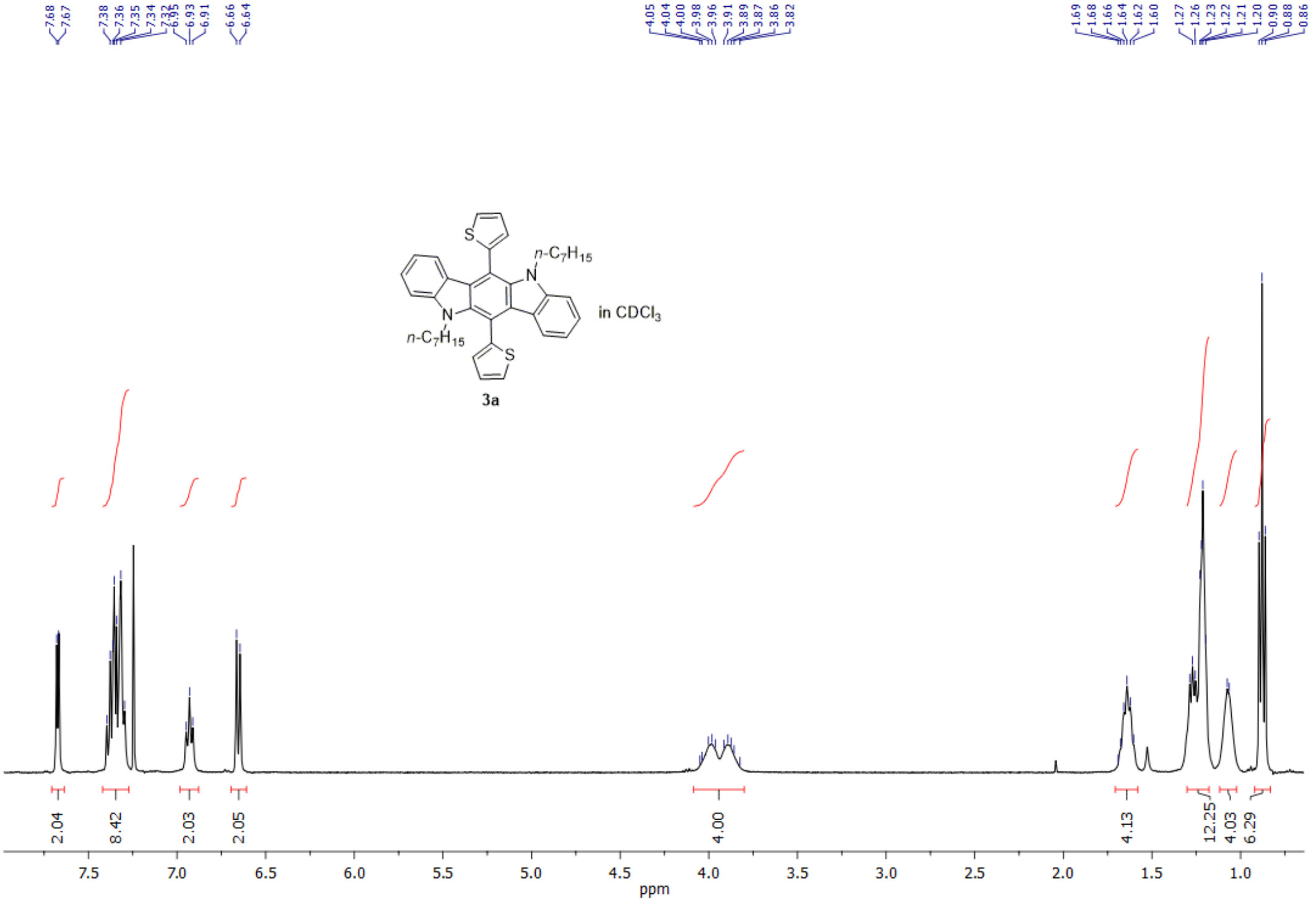
OMe
OMe
2f
in CDCl3
ppm

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3.89
3.87
3.86
3.82
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1.68
1.66
1.64
1.62
1.60
1.27
1.26
1.23
1.22
1.21
1.20
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0.88
0.86
S
N
n-C7H15
n-C7H15
S
in CDCl3
3a
2.04
8.42
2.03
2.05
4.00
4.13
12.25
4.03
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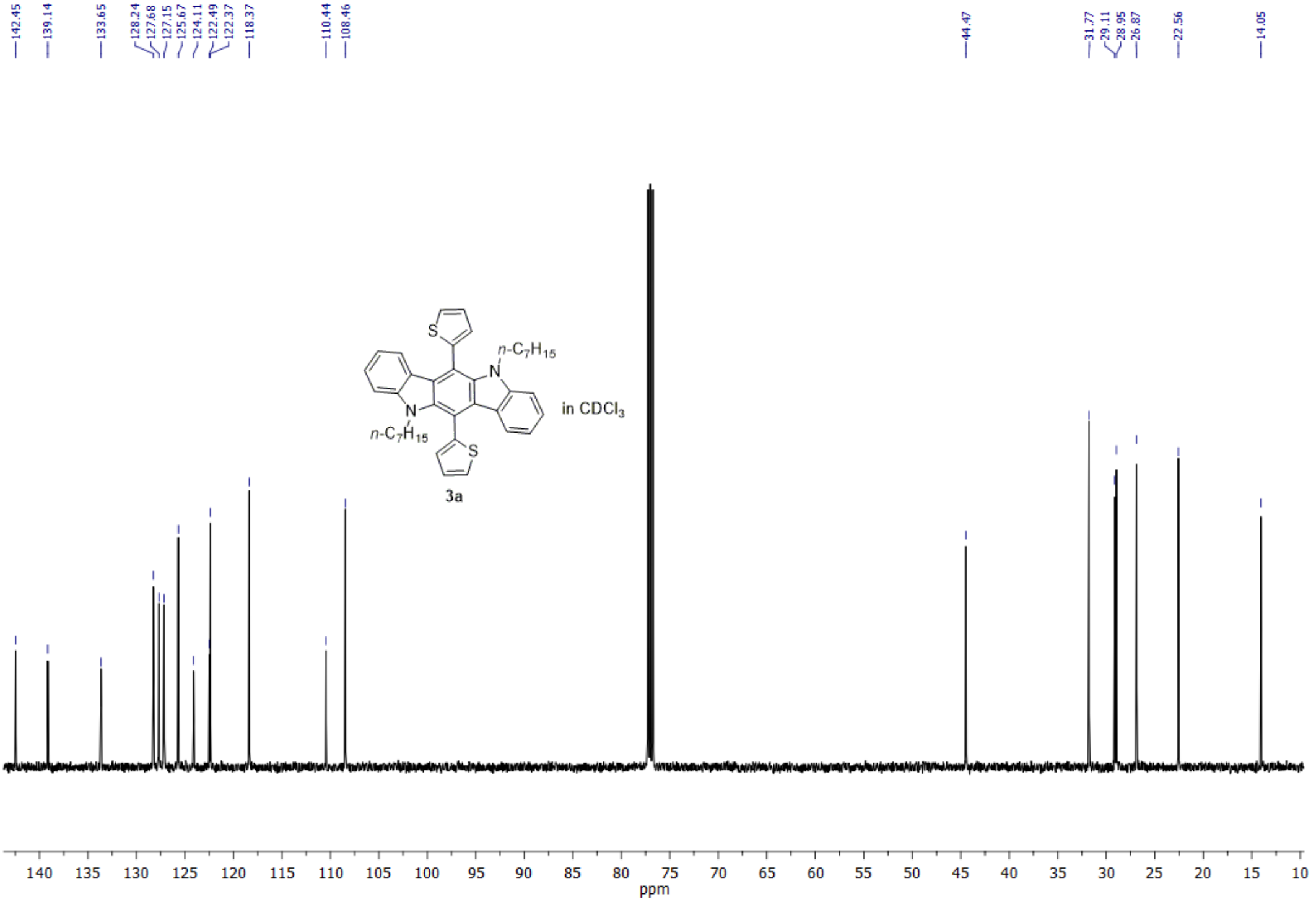
ppm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29.11
28.95
26.87
22.56
14.05
S
N
n-C7H15
n-C7H15
S
in CDCl3
3a
140
135
130
125
120
115
110
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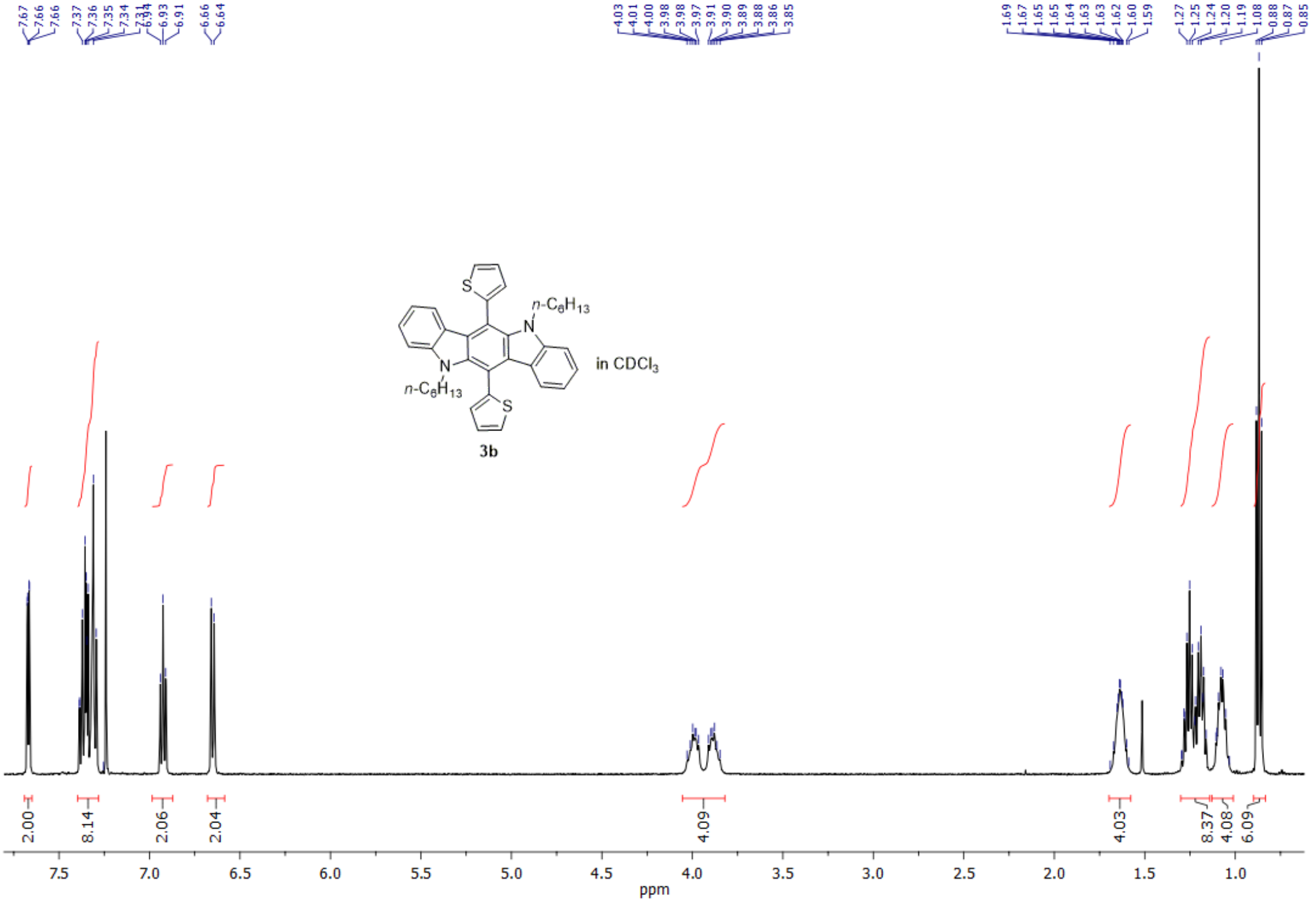
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4.00
3.98
3.98
3.97
3.91
3.90
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3.88
3.86
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1.63
1.62
1.60
1.59
1.27
1.25
1.24
1.20
1.19
1.08
0.88
0.87
0.85
S
N
n-C6H13
n-C6H13
S
in CDCl3
3b
2.00
8.14
2.06
2.04
4.09
4.03
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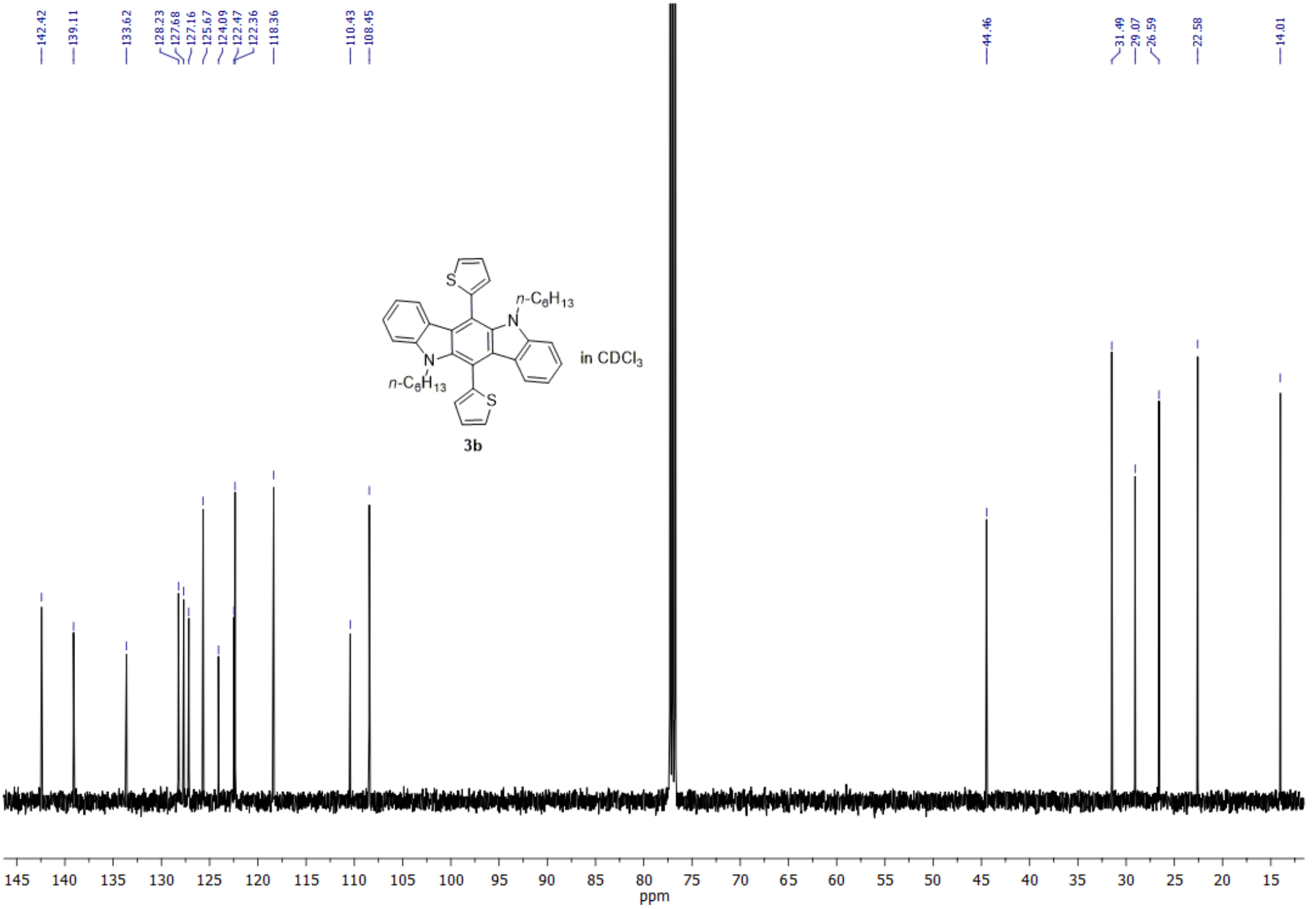
ppm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44.46
31.49
29.07
26.59
22.58
14.01
S
N
n-C6H13
n-C6H13
S
in CDCl3
3b
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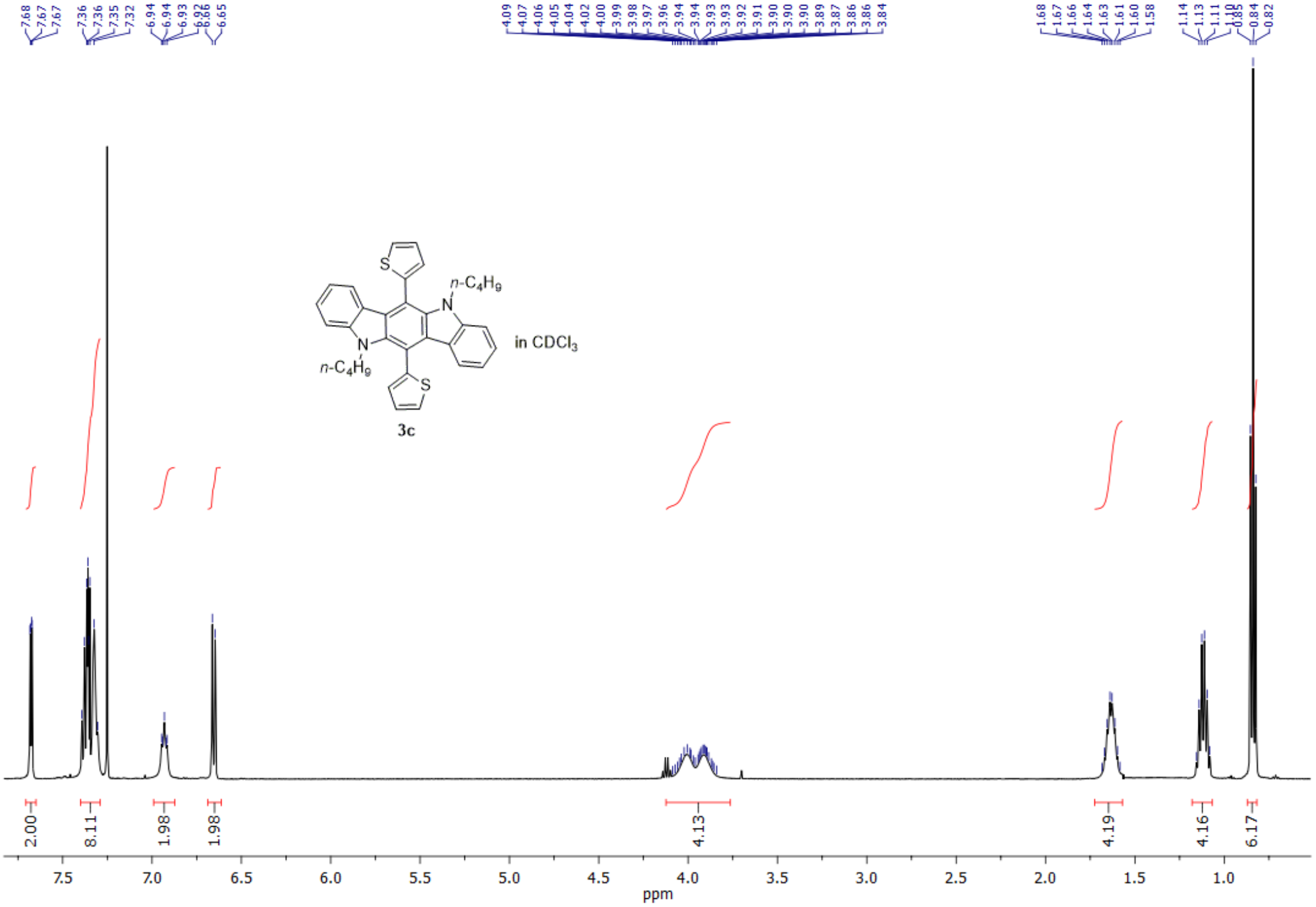
ppm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4.06
4.05
4.04
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4.00
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3.84
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1.64
1.63
1.61
1.60
1.58
1.14
1.13
1.11
0.85
0.84
0.82
S
n-C4H9
N
N
n-C4H9
S
in CDCl3
3c
2.00
8.11
1.98
1.98
4.13
4.19
4.16
6.17
7.5
7.0
6.5
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5.0
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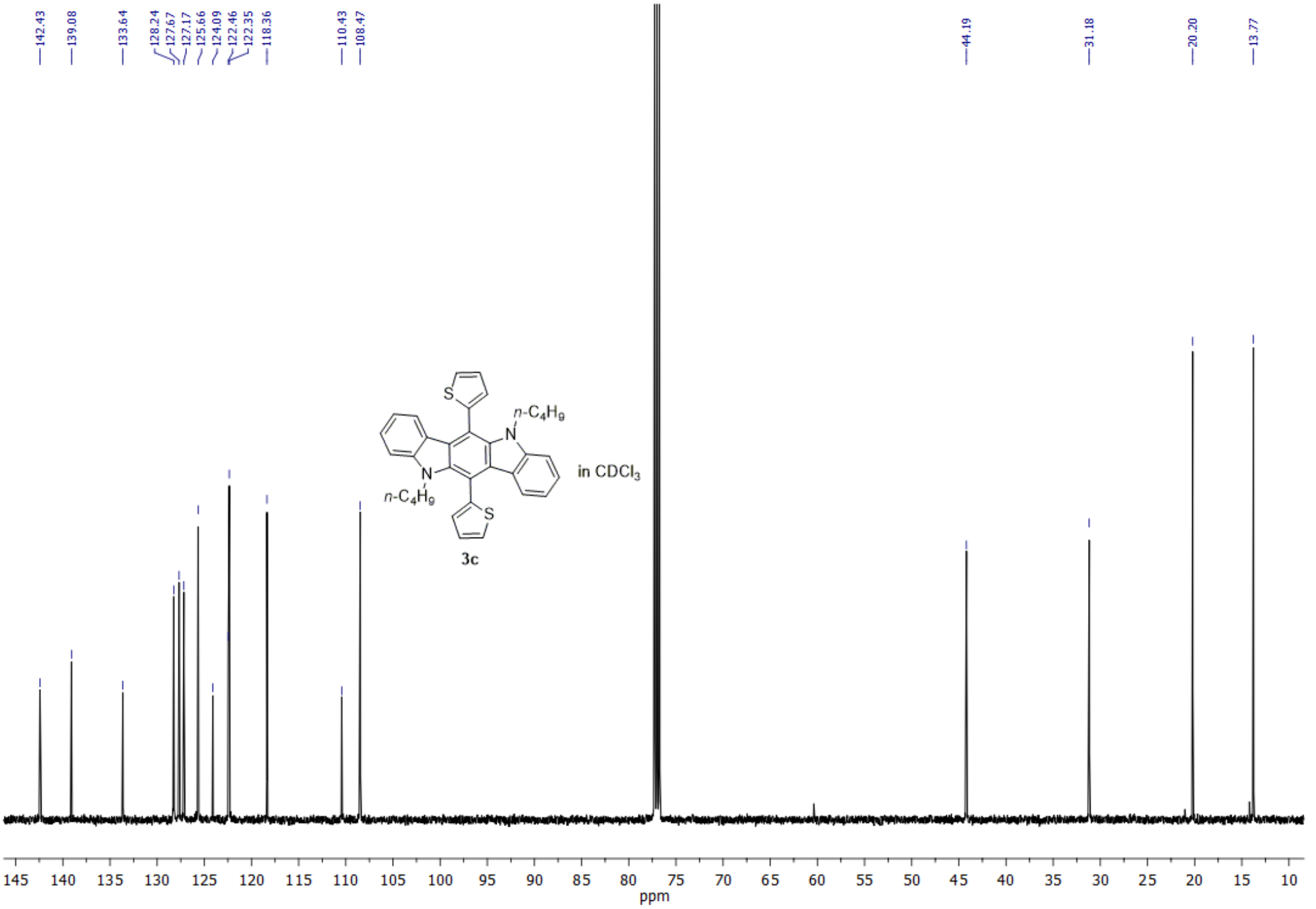
ppm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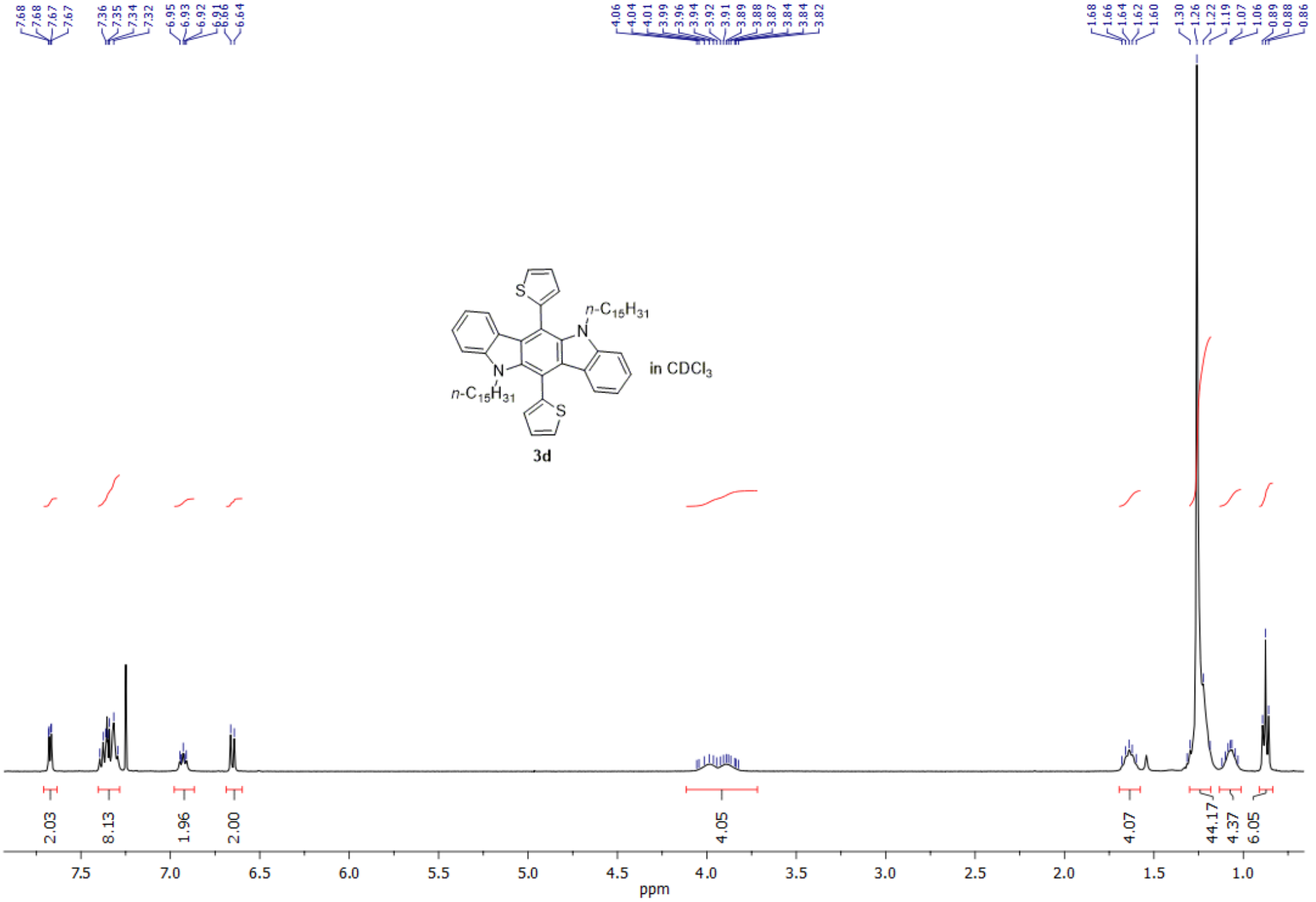
122.35
118.36
110.43
108.47
44.19
31.18
20.20
13.77
S
N
n-C4H9
n-C4H9
S
3c
in CDCl3
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
ppm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3.82
1.68
1.66
1.64
1.62
1.60
1.30
1.26
1.22
1.19
1.07
1.06
0.89
0.88
0.86
S
N
n-C15H31
n-C15H31
S
in CDCl3
3d
2.03
8.13
1.96
2.00
4.05
4.07
44.17
4.37
6.05
7.5
7.0
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5.0
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4.0
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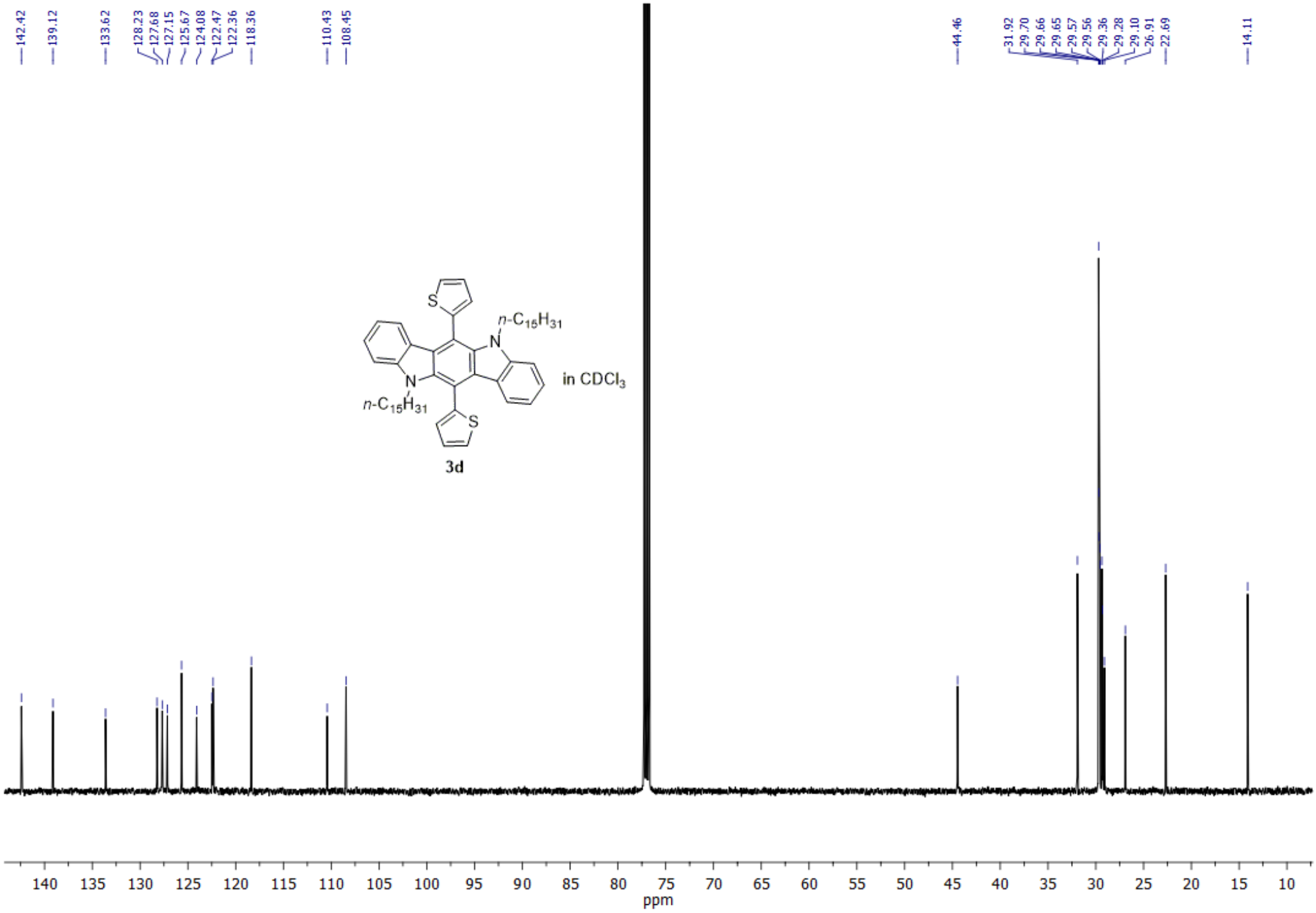
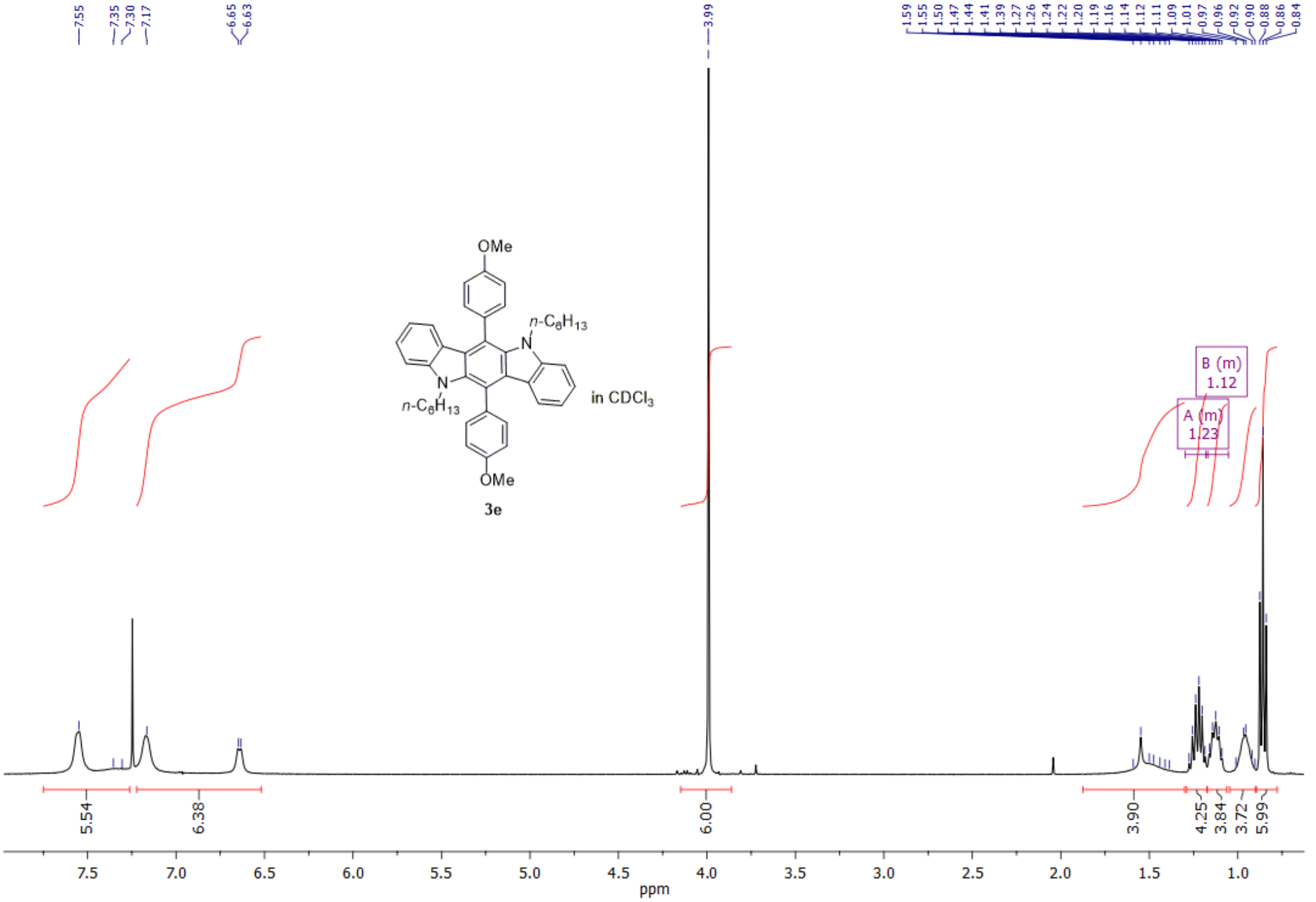
2.0
1.5
1.0
ppm

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1.39
1.27
1.26
1.24
1.22
1.20
1.19
1.16
1.14
1.12
1.11
1.09
1.01
0.97
0.96
0.92
0.90
0.88
0.86
0.84
OMe
n-C6H13
N
N
n-C6H13
OMe
in CDCl3
3e
B (m)
1.12
A (m)
1.23
5.54
6.38
6.00
3.90
4.25
3.84
3.72
5.99
7.5
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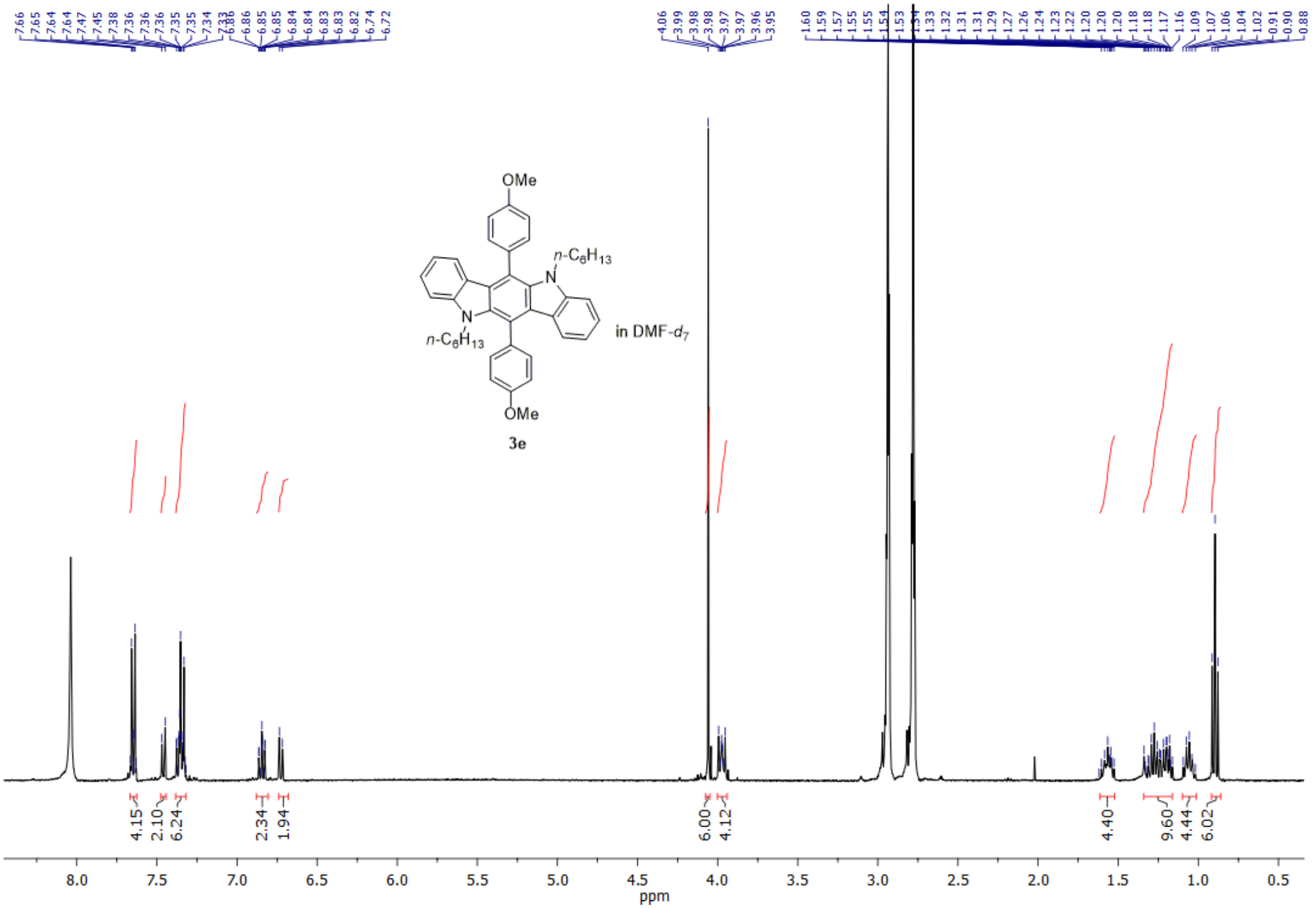
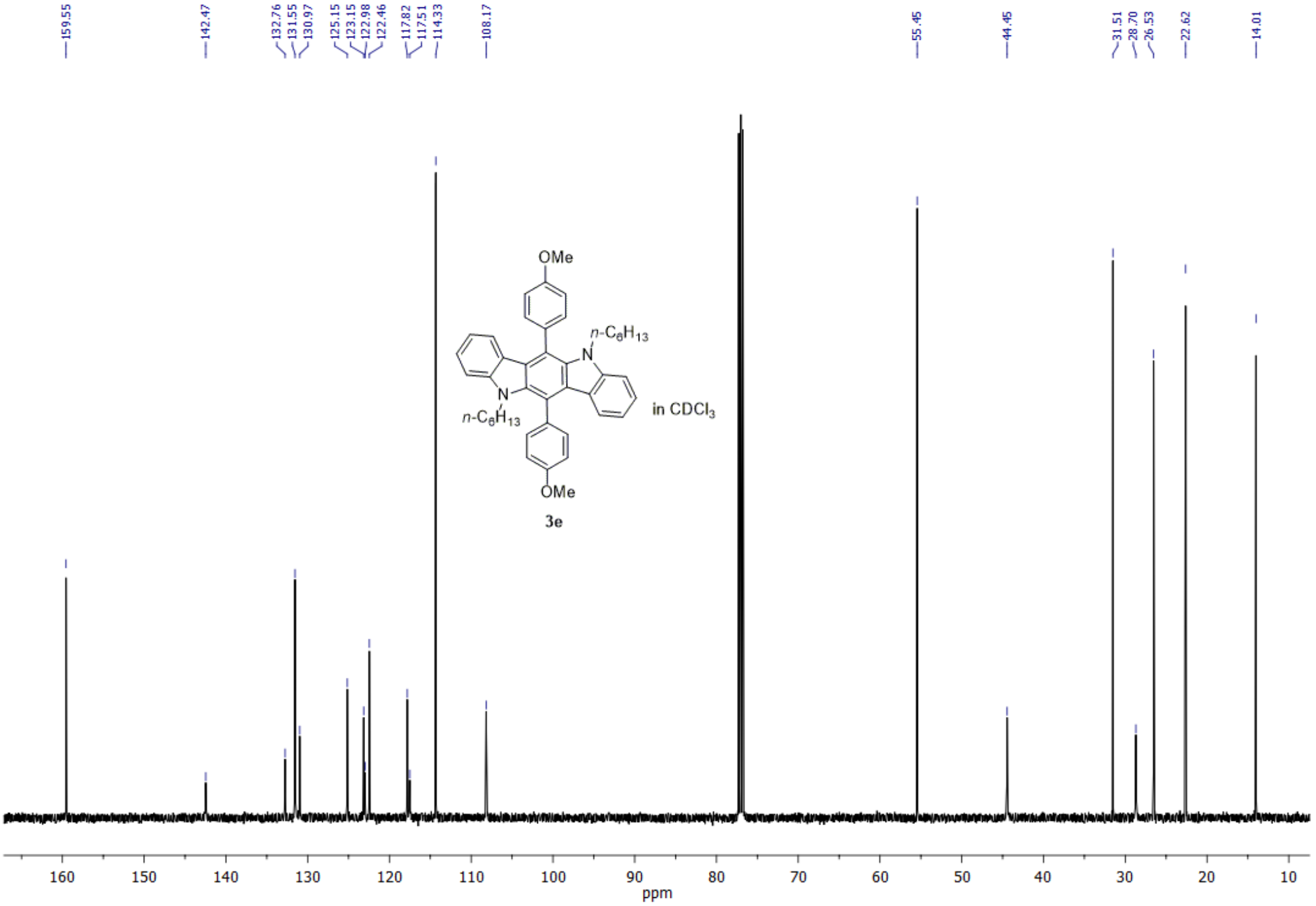
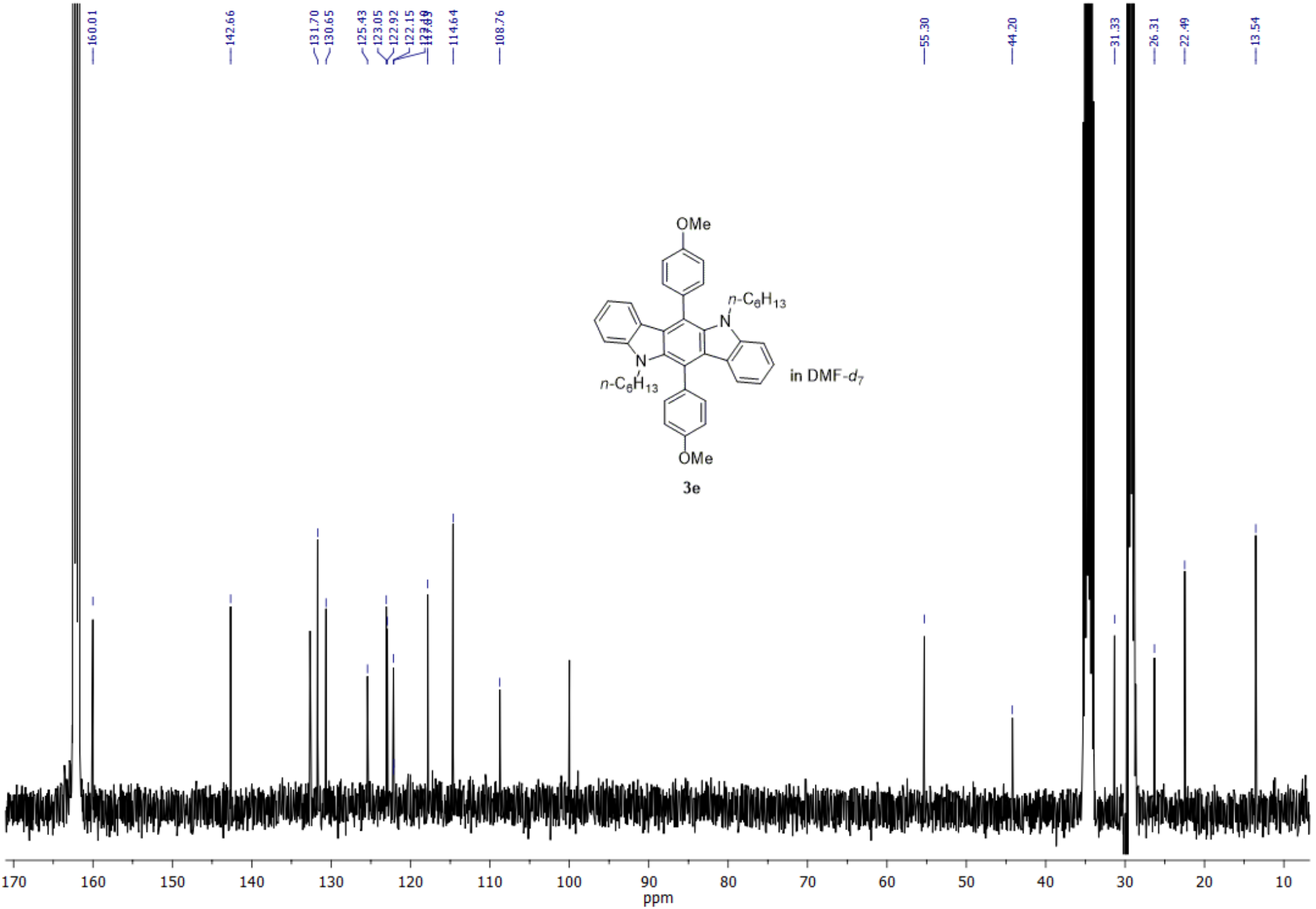
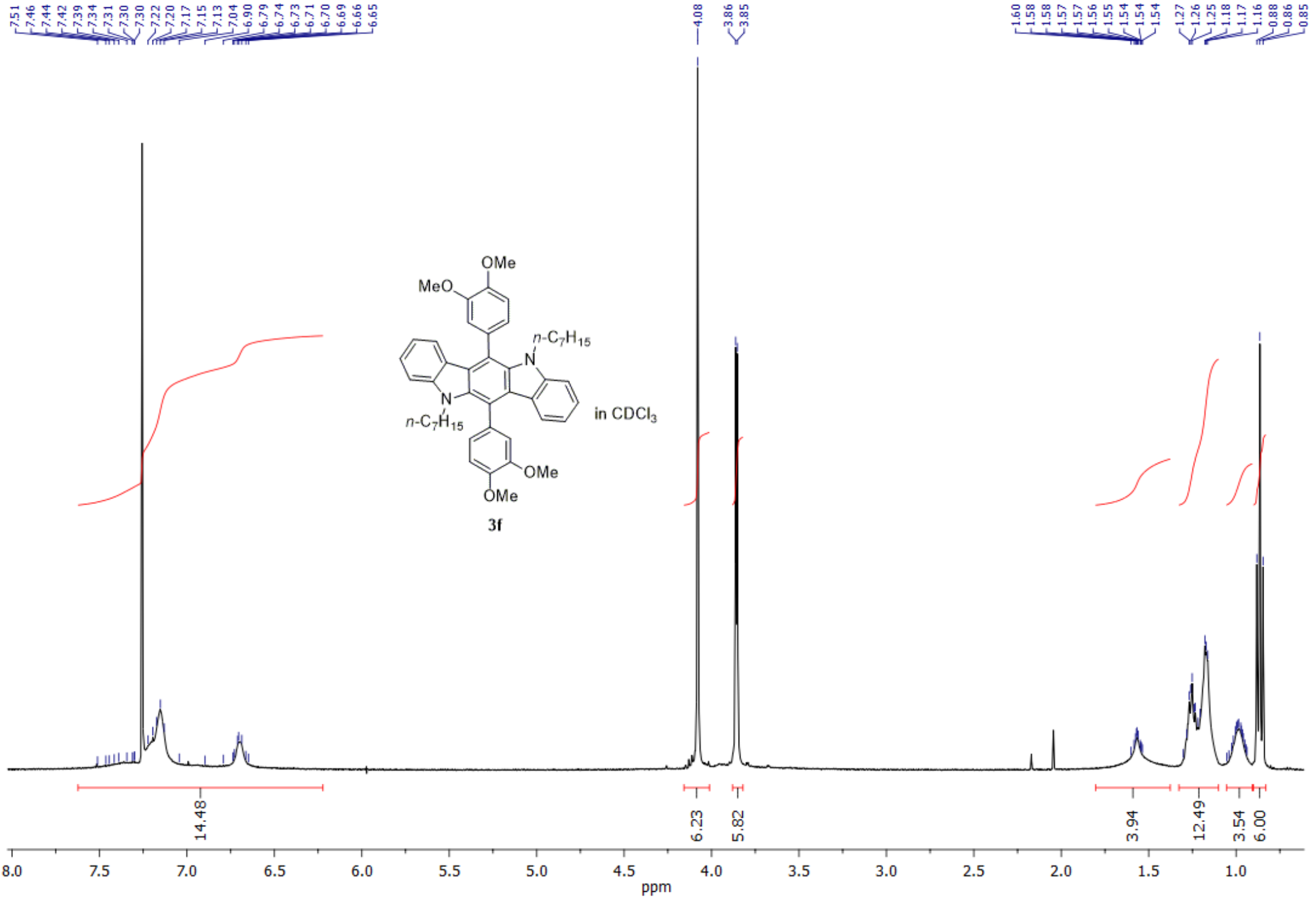
ppm





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7.04
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6.71
6.70
6.69
6.66
6.65
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1.55
1.54
1.54
1.54
1.27
1.26
1.25
1.18
1.17
1.16
0.88
0.86
0.85
OMe
MeO
n-C7H15
N
N
n-C7H15
OMe
OMe
in CDCl3
3f
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12.49
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7.0
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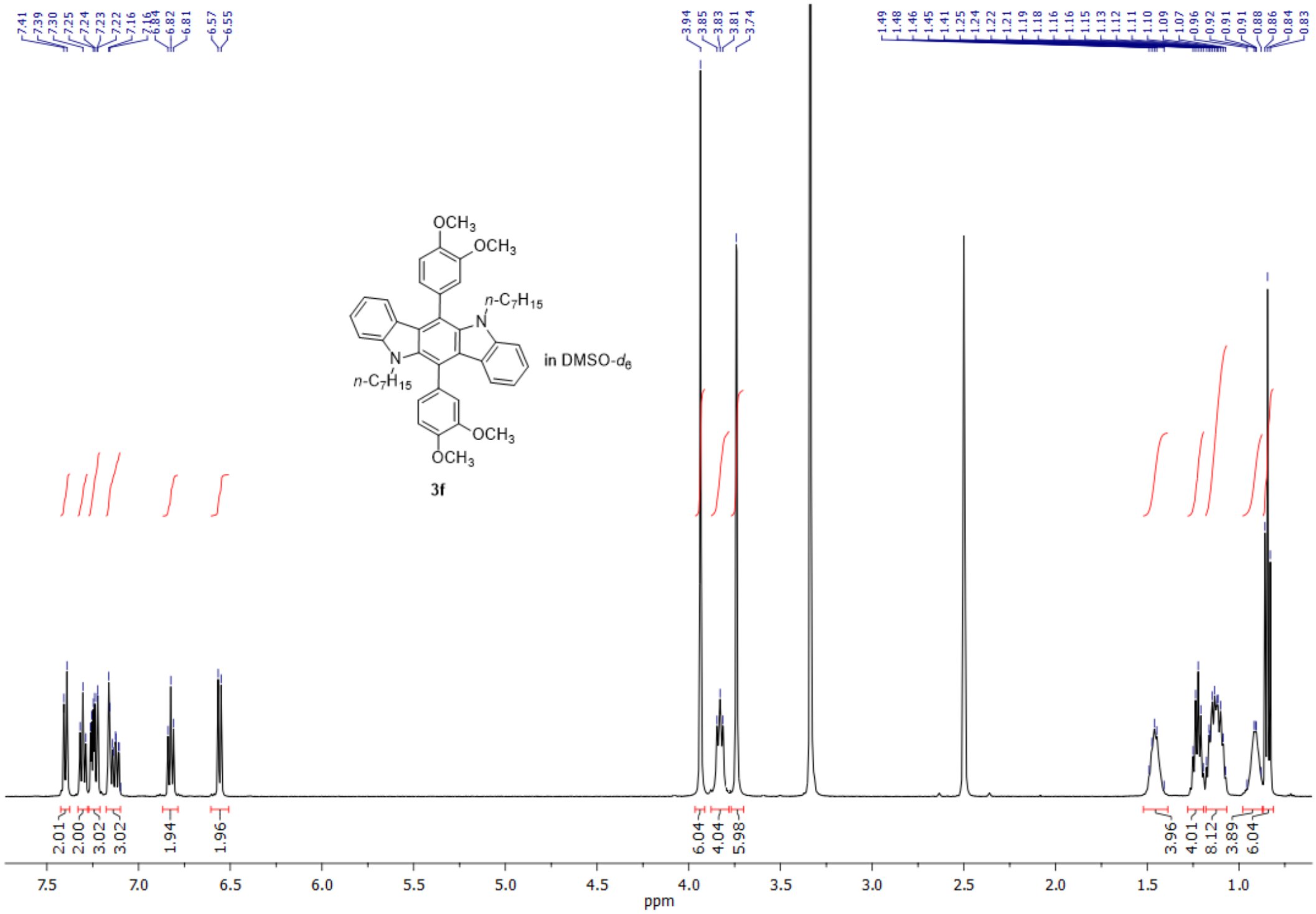
1.0
ppm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1.21
1.19
1.18
1.16
1.16
1.15
1.13
1.12
1.11
1.10
1.09
1.07
0.96
0.92
0.91
0.91
0.88
0.86
0.84
0.83
OCH3
OCH3
n-C7H15
N
N
n-C7H15
OCH3
OCH3
in DMSO-d6
3f
2.01
2.00
3.02
3.02
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6.04
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4.01
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1.0
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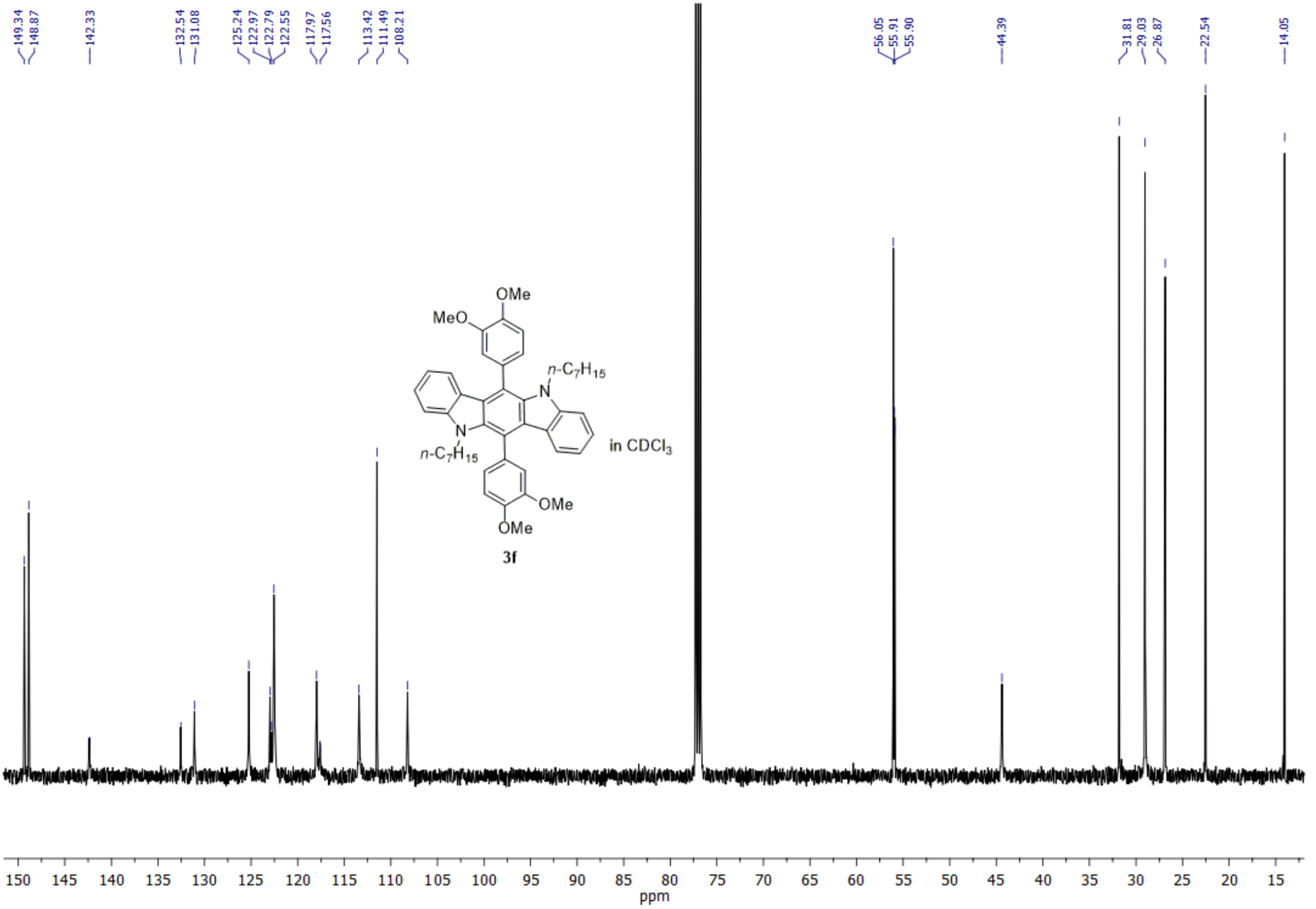

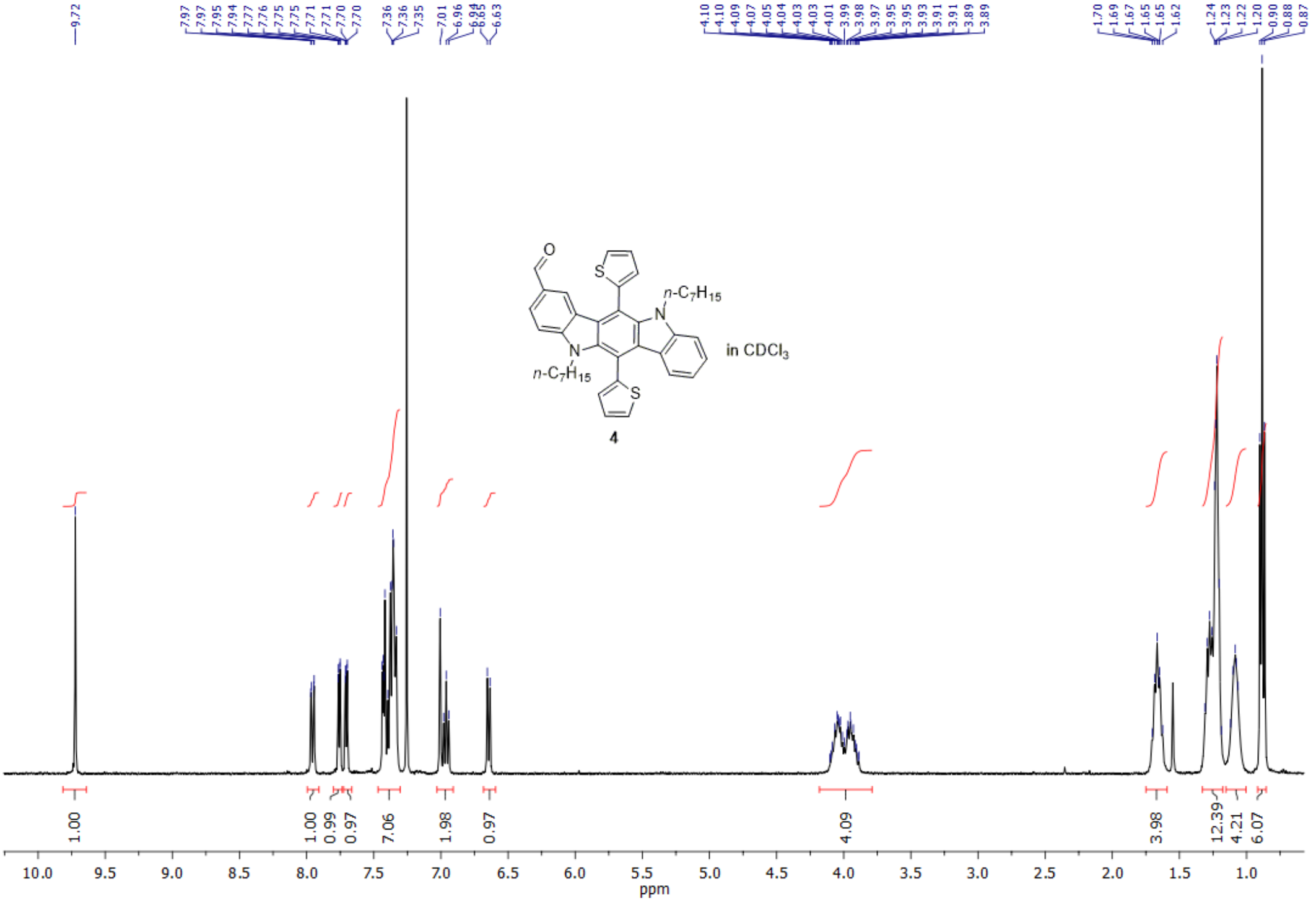
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6.94
6.85
6.63
4.10
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4.09
4.07
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4.04
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1.62
1.24
1.23
1.22
1.20
0.90
0.88
0.87
O
S
n-C7H15
N
N
n-C7H15
S
in CDCl3
4
1.00
1.00
0.99
0.97
7.06
1.98
0.97
4.09
3.98
12.39
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9.5
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7.0
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1.5
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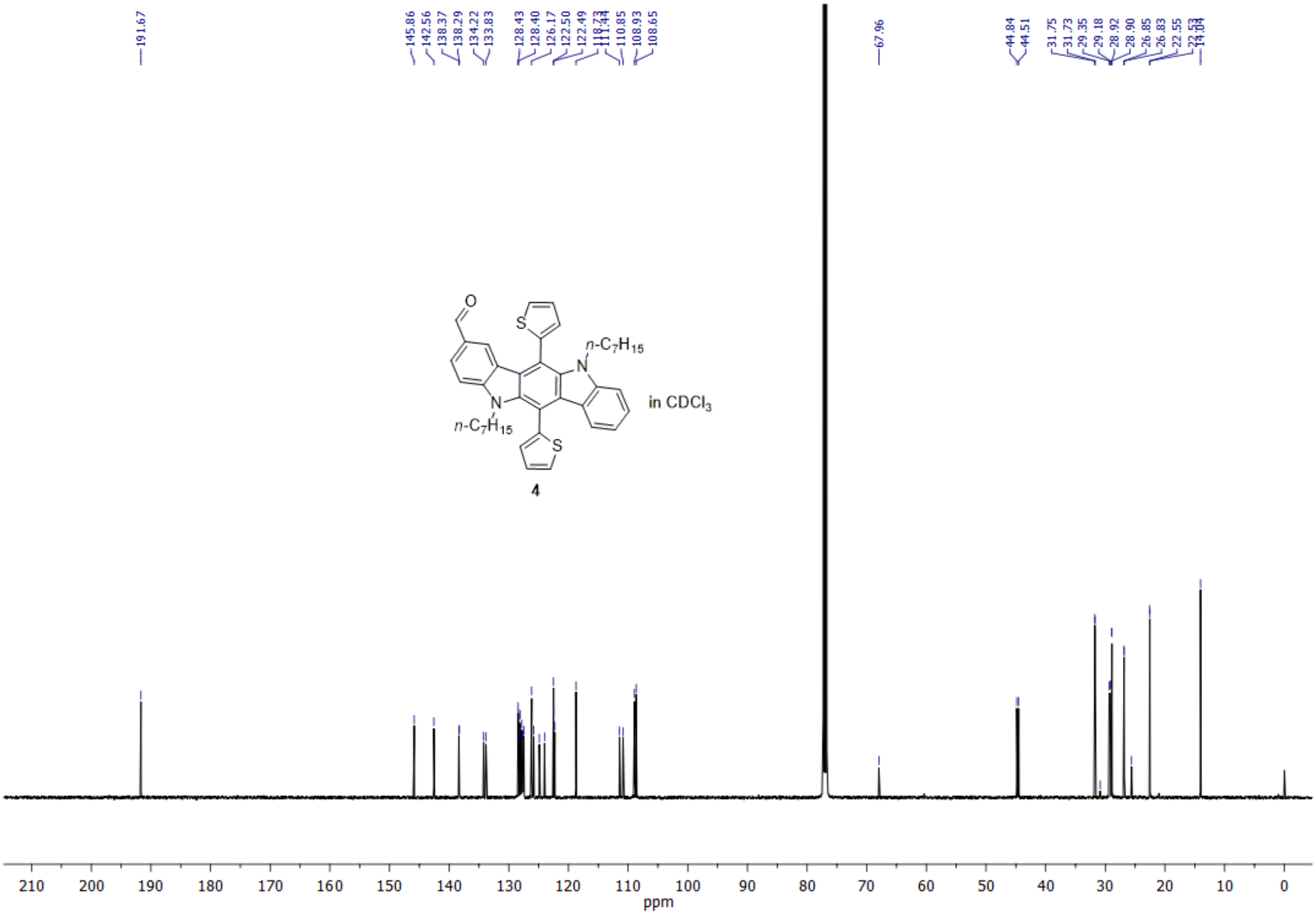
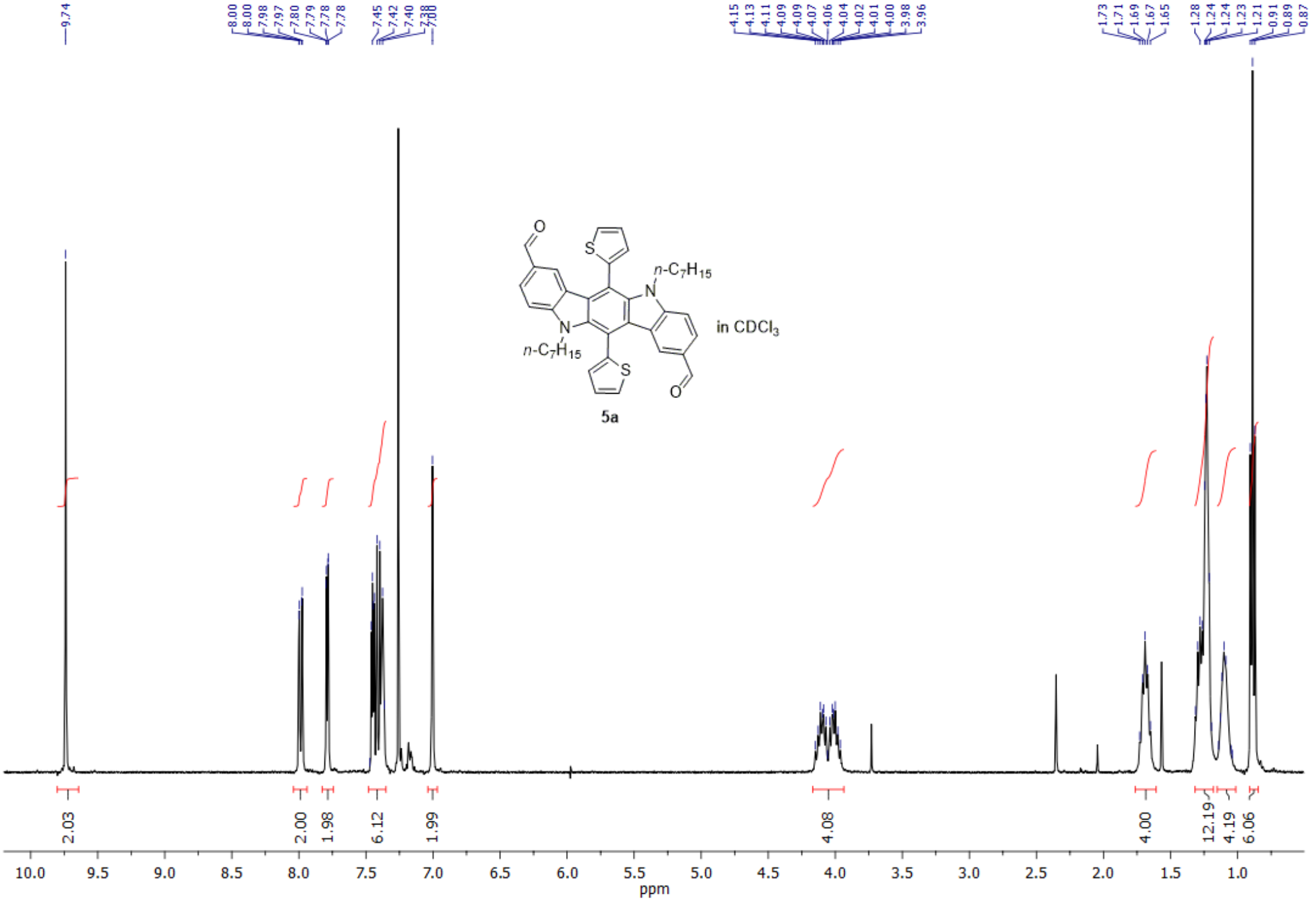
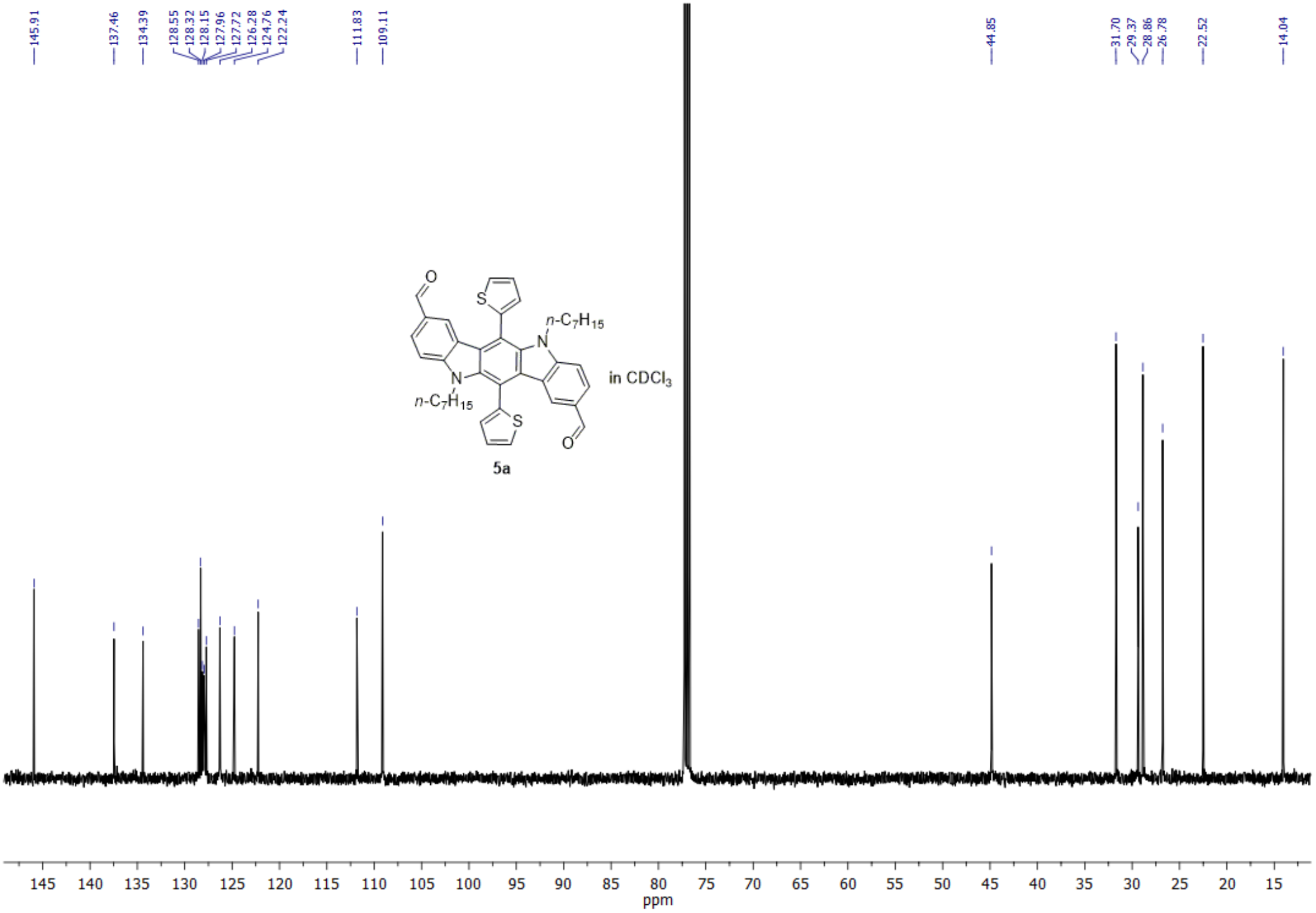
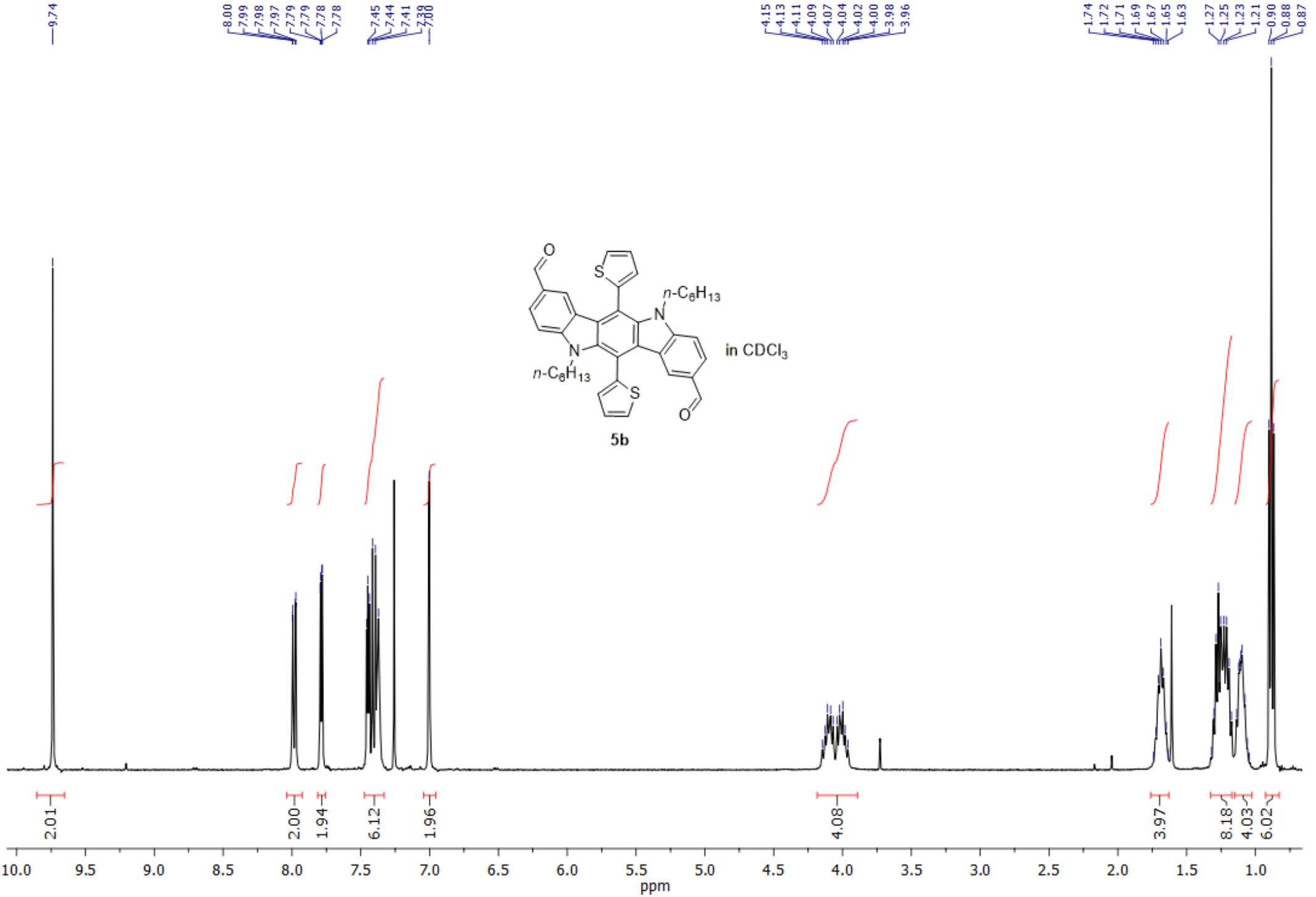
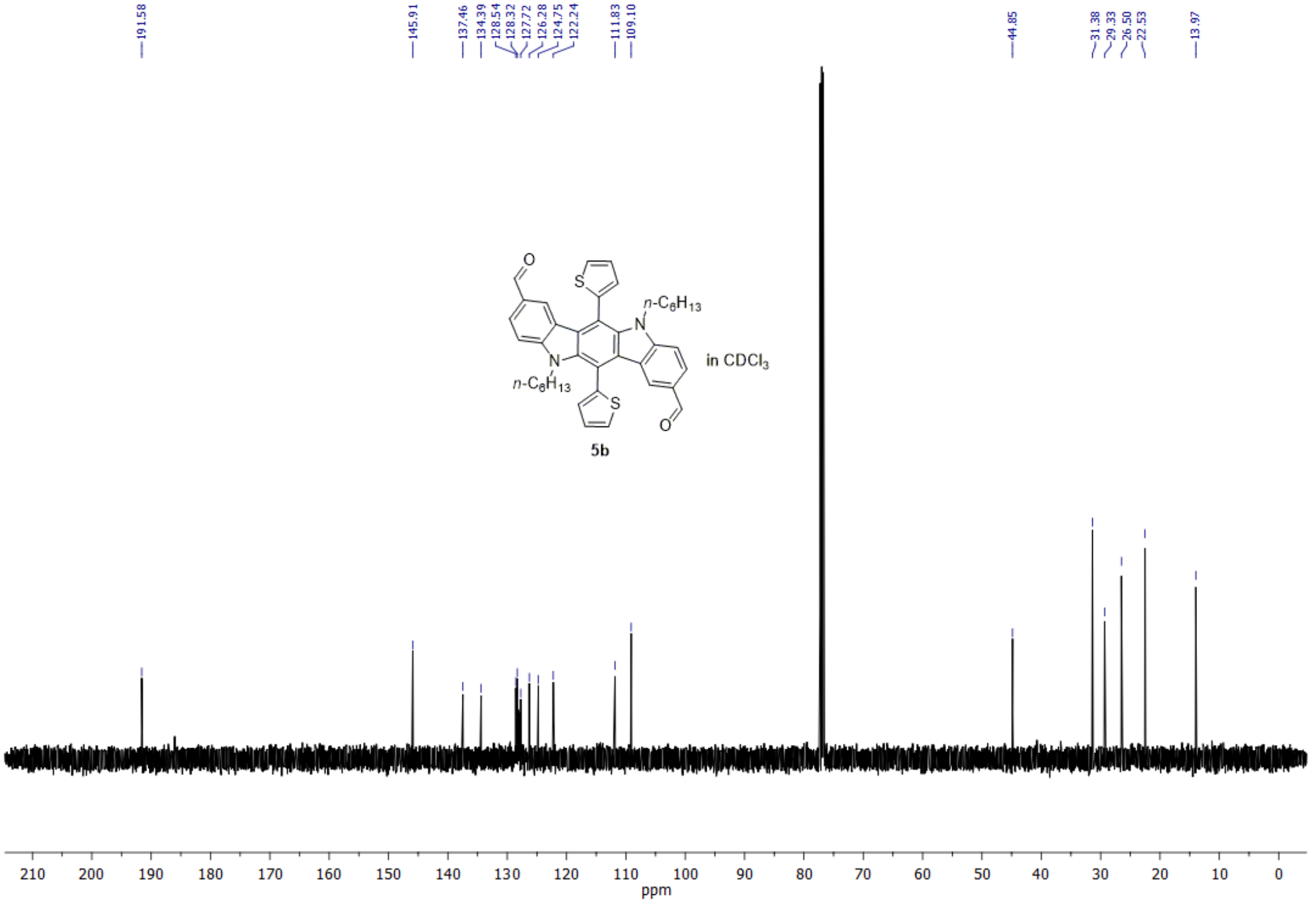
ppm

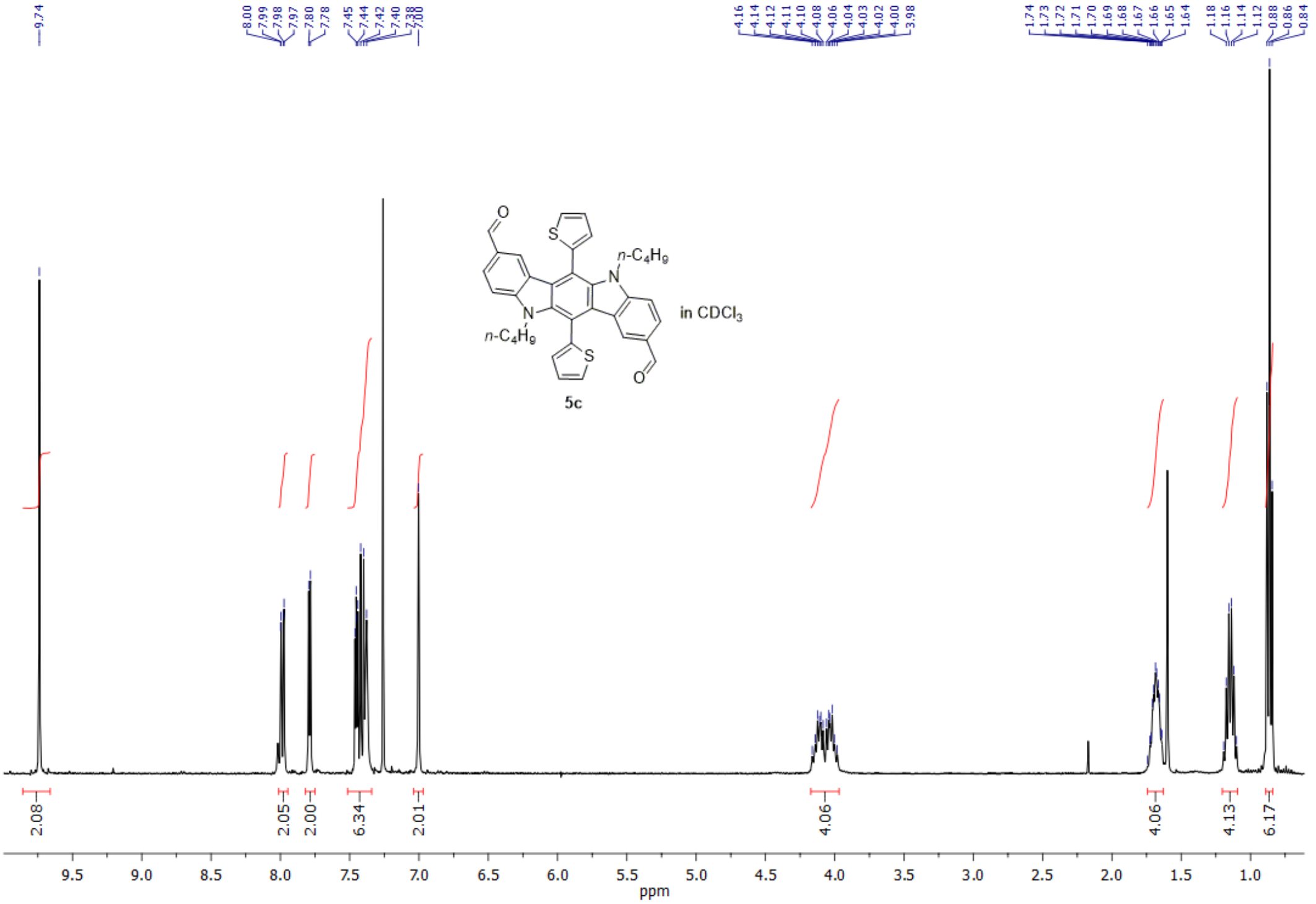








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4.12
4.11
4.10
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4.06
4.04
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4.02
4.00
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1.65
1.64
1.18
1.16
1.14
1.12
0.88
0.86
0.84
O
S
n-C4H9
N
N
n-C4H9
S
O
in CDCl3
5c
2.08
2.05
2.00
6.34
2.01
4.06
4.06
4.13
6.17
9.5
9.0
8.5
8.0
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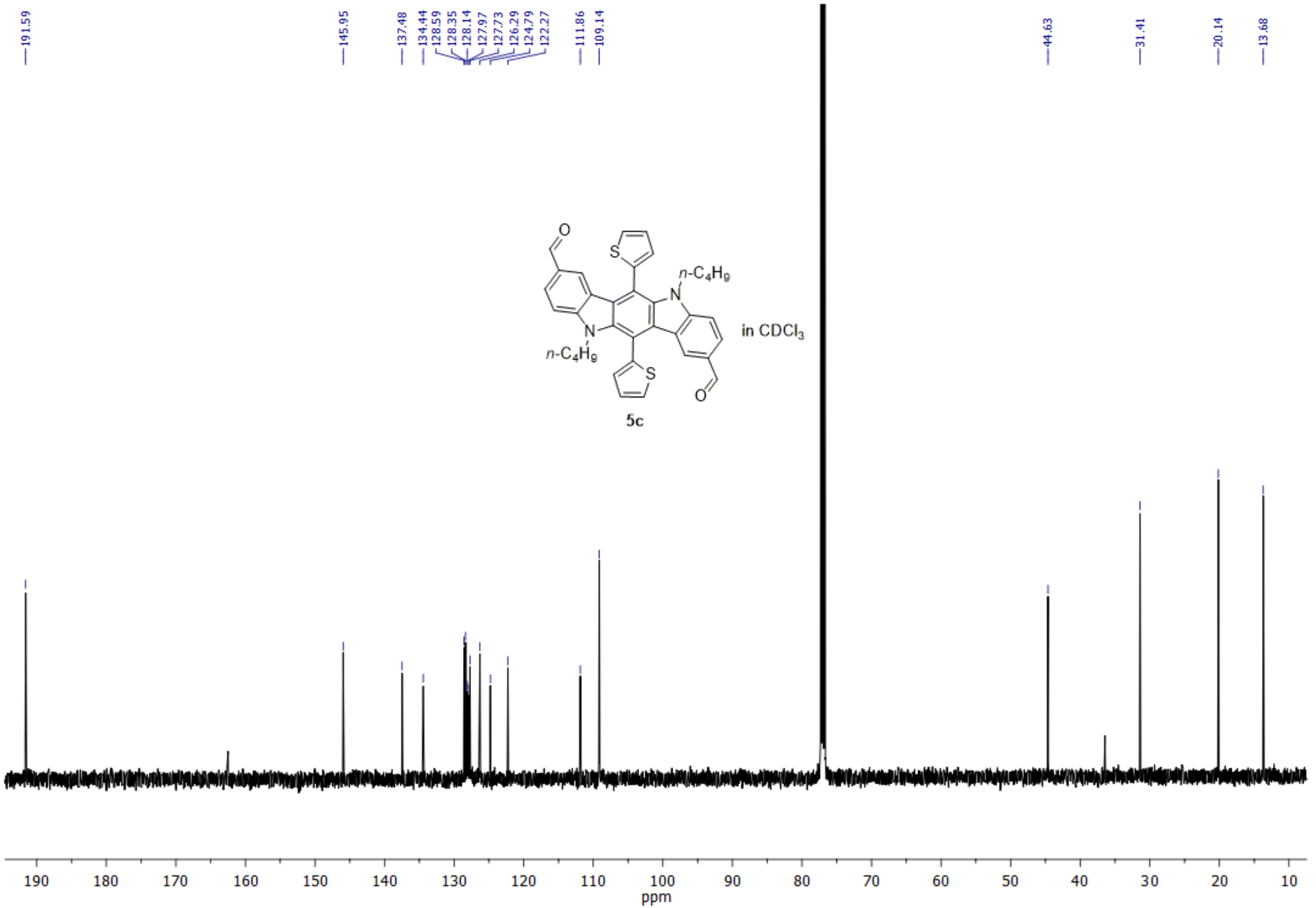
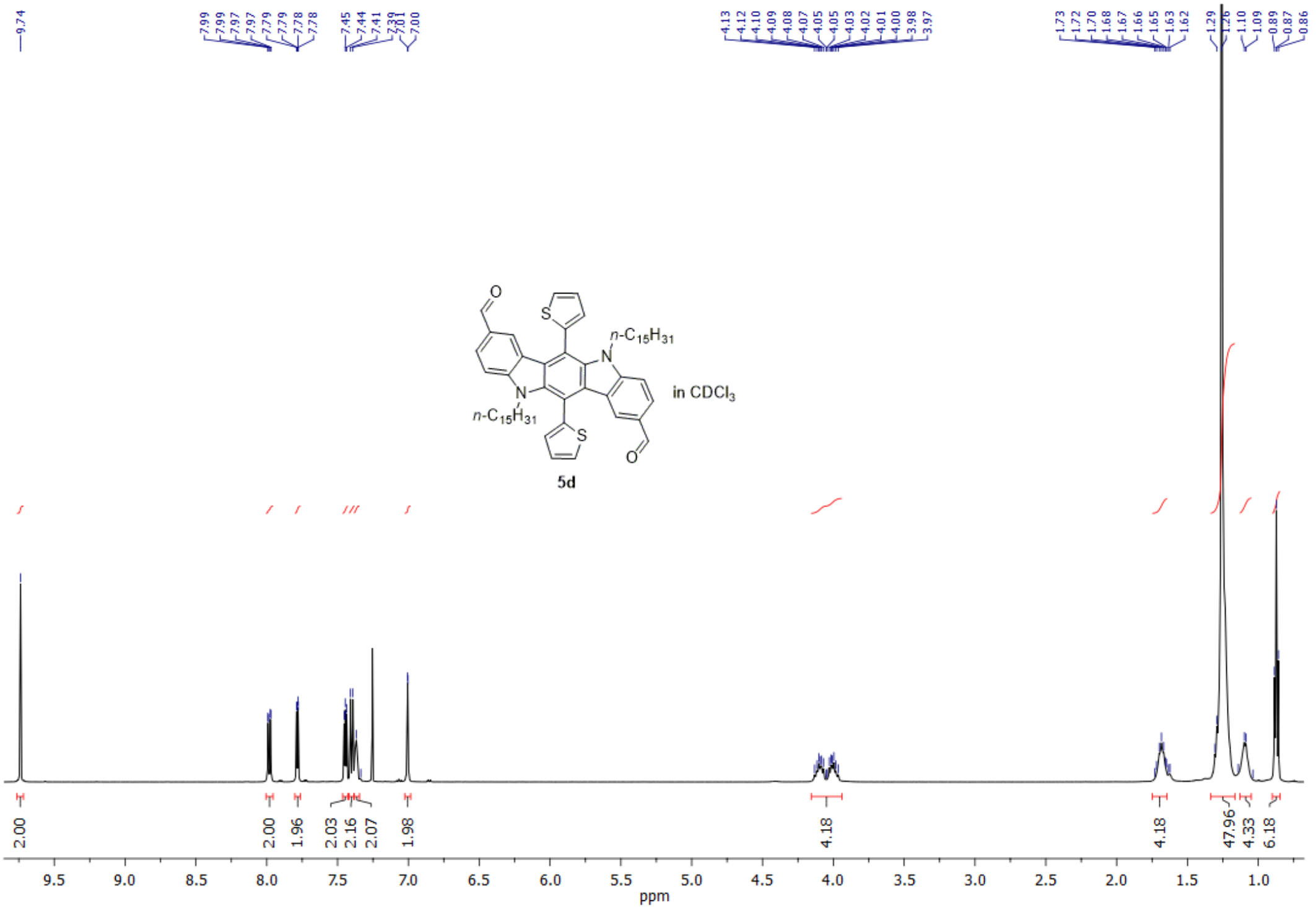
ppm

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7.44
7.41
7.39
7.01
7.00
4.13
4.12
4.10
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4.08
4.07
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4.05
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4.02
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1.70
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1.67
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1.63
1.62
1.29
1.26
1.10
1.09
0.89
0.87
0.86
O
S
n-C15H31
N
N
n-C15H31
S
O
in CDCl3
5d
2.00
2.00
1.96
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2.07
1.98
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4.18
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4.33
6.18
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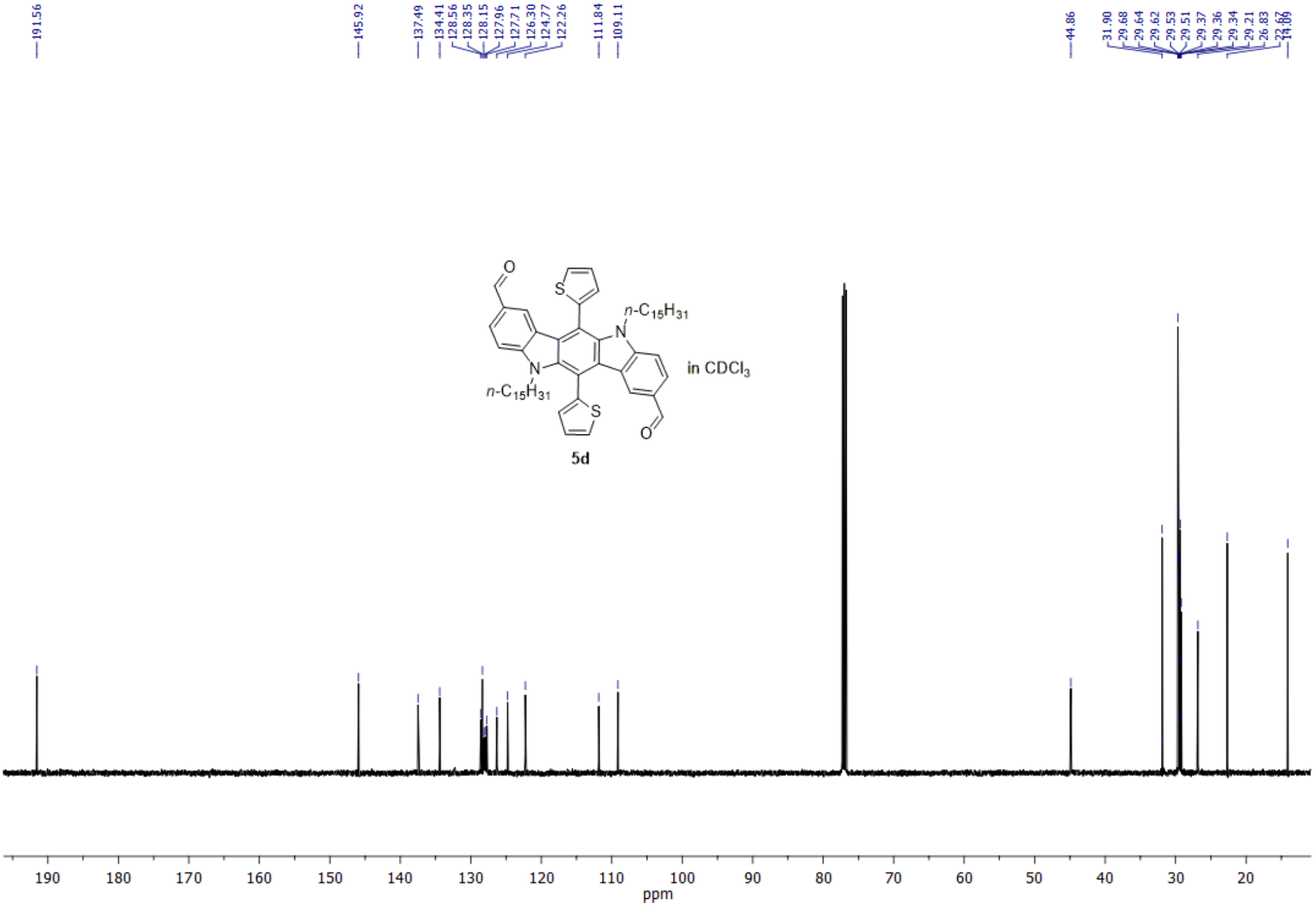
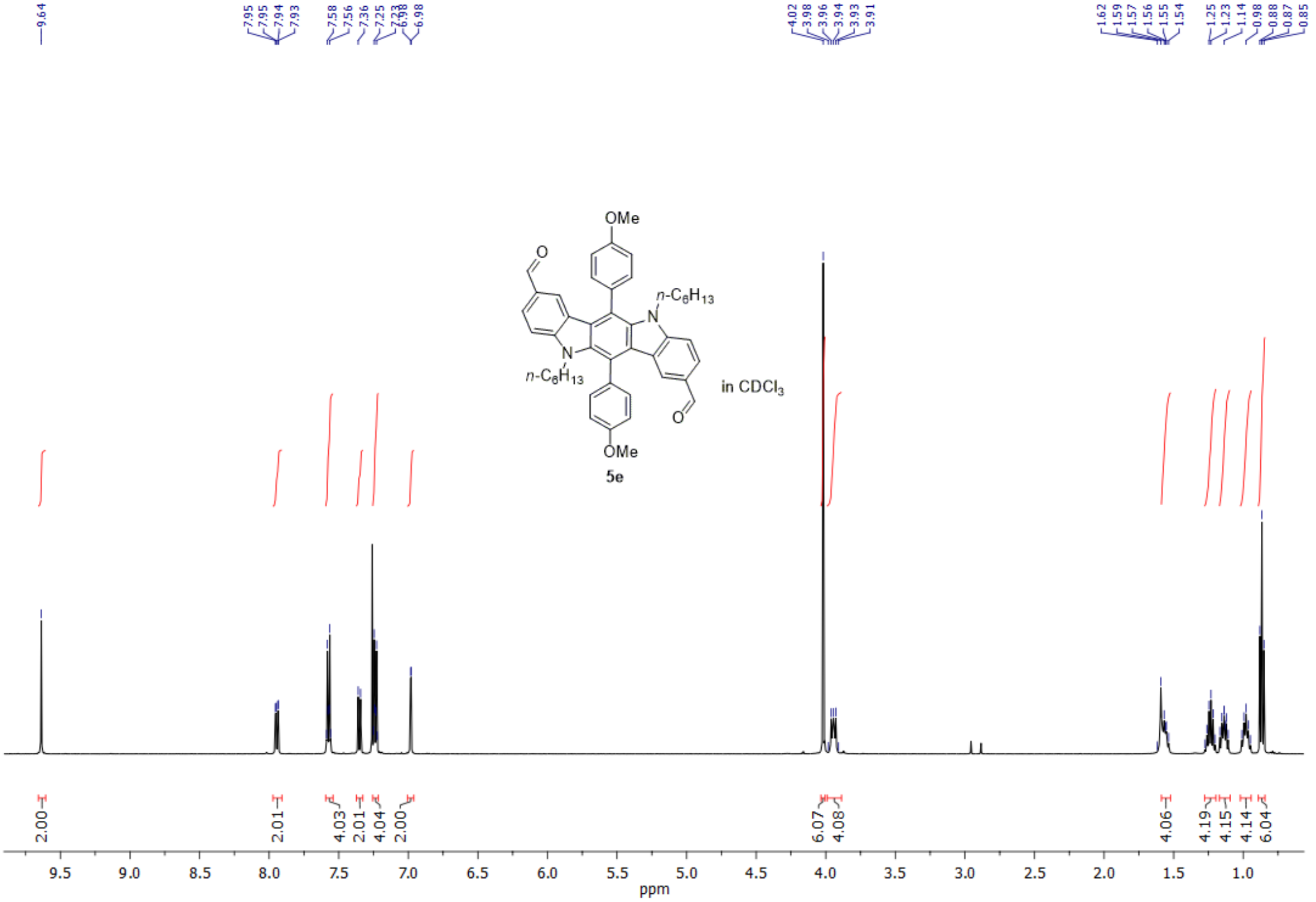
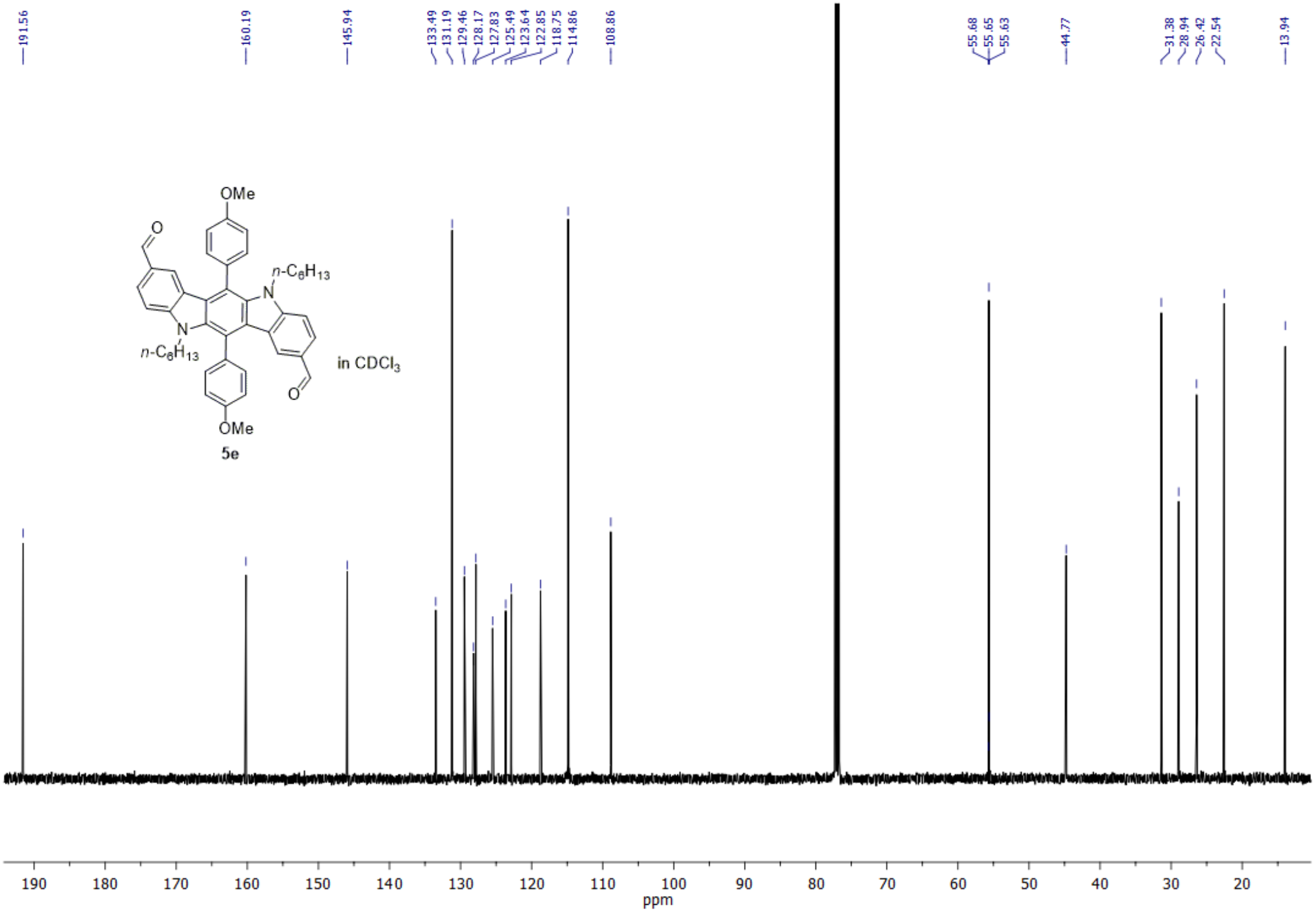
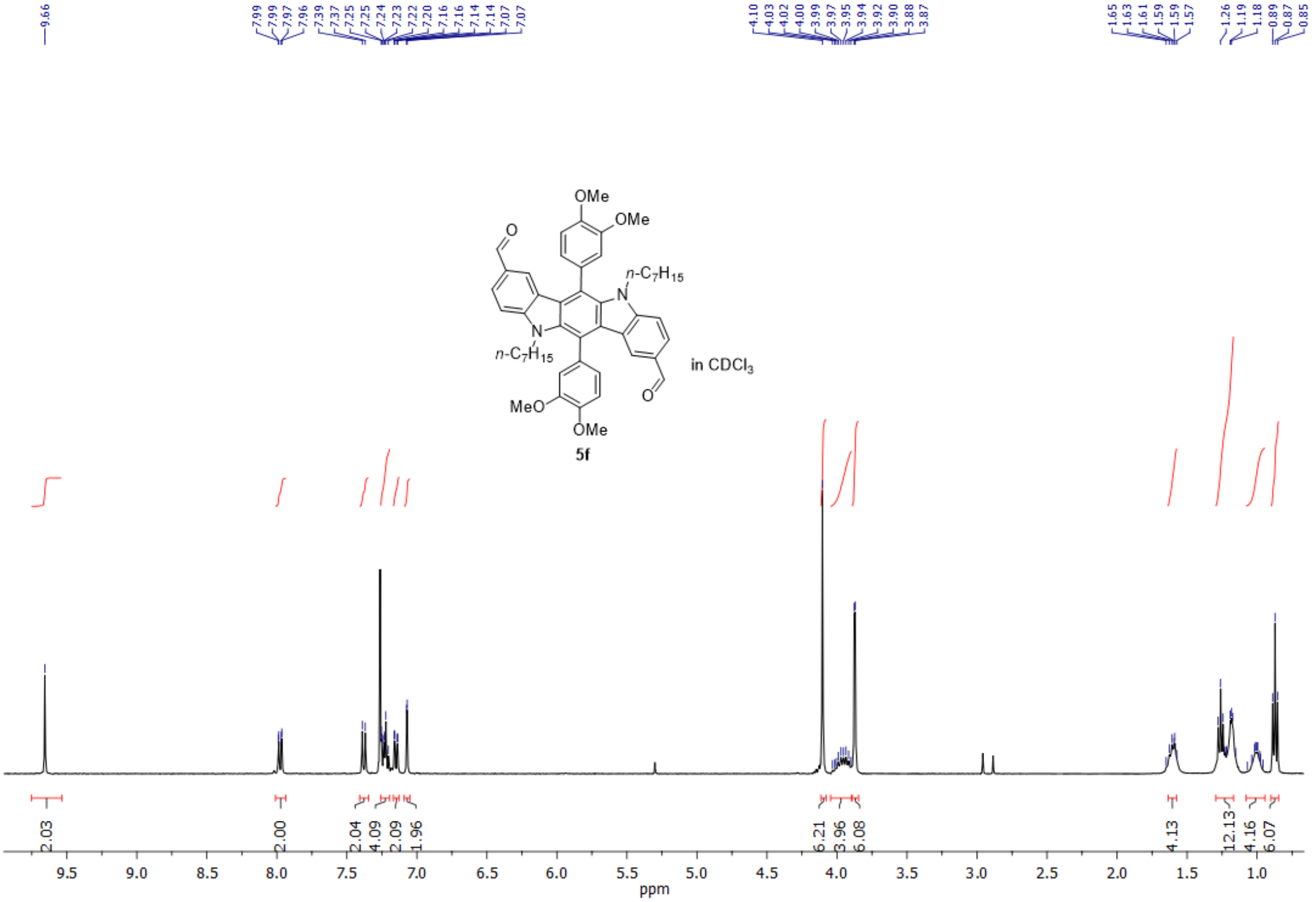
ppm








9.66
7.99
7.99
7.97
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7.39
7.37
7.25
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7.24
7.23
7.22
7.20
7.16
7.16
7.14
7.14
7.07
7.07
4.10
4.03
4.02
4.00
3.99
3.97
3.95
3.94
3.92
3.90
3.88
3.87
1.65
1.63
1.61
1.59
1.59
1.57
1.26
1.19
1.18
0.89
0.87
0.85
OMe
OMe
O
n-C7H15
N
N
n-C7H15
MeO
OMe
O
5f
in CDCl3
2.03
2.00
2.04
4.09
2.09
1.96
6.21
3.96
6.08
4.13
12.13
4.16
6.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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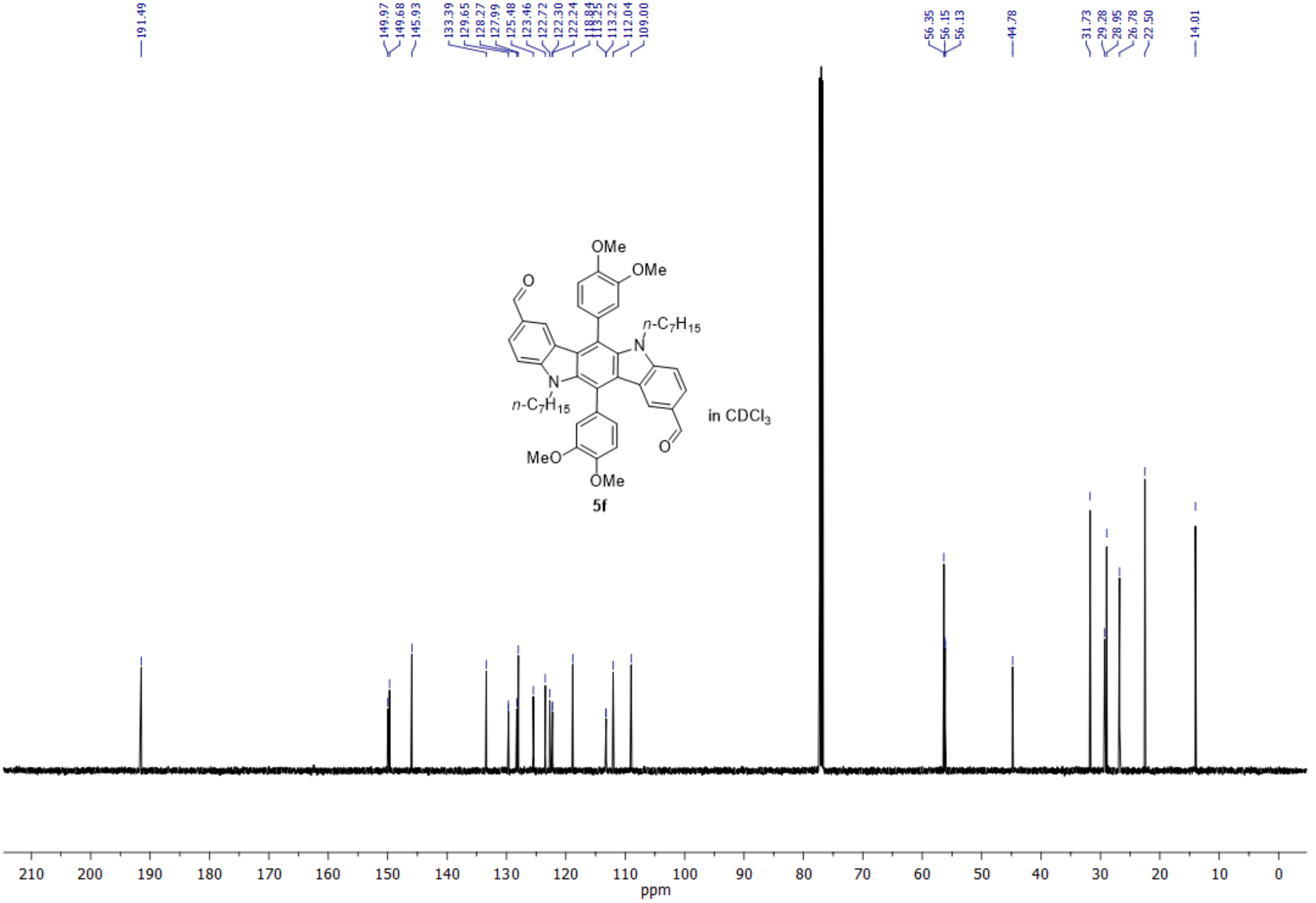
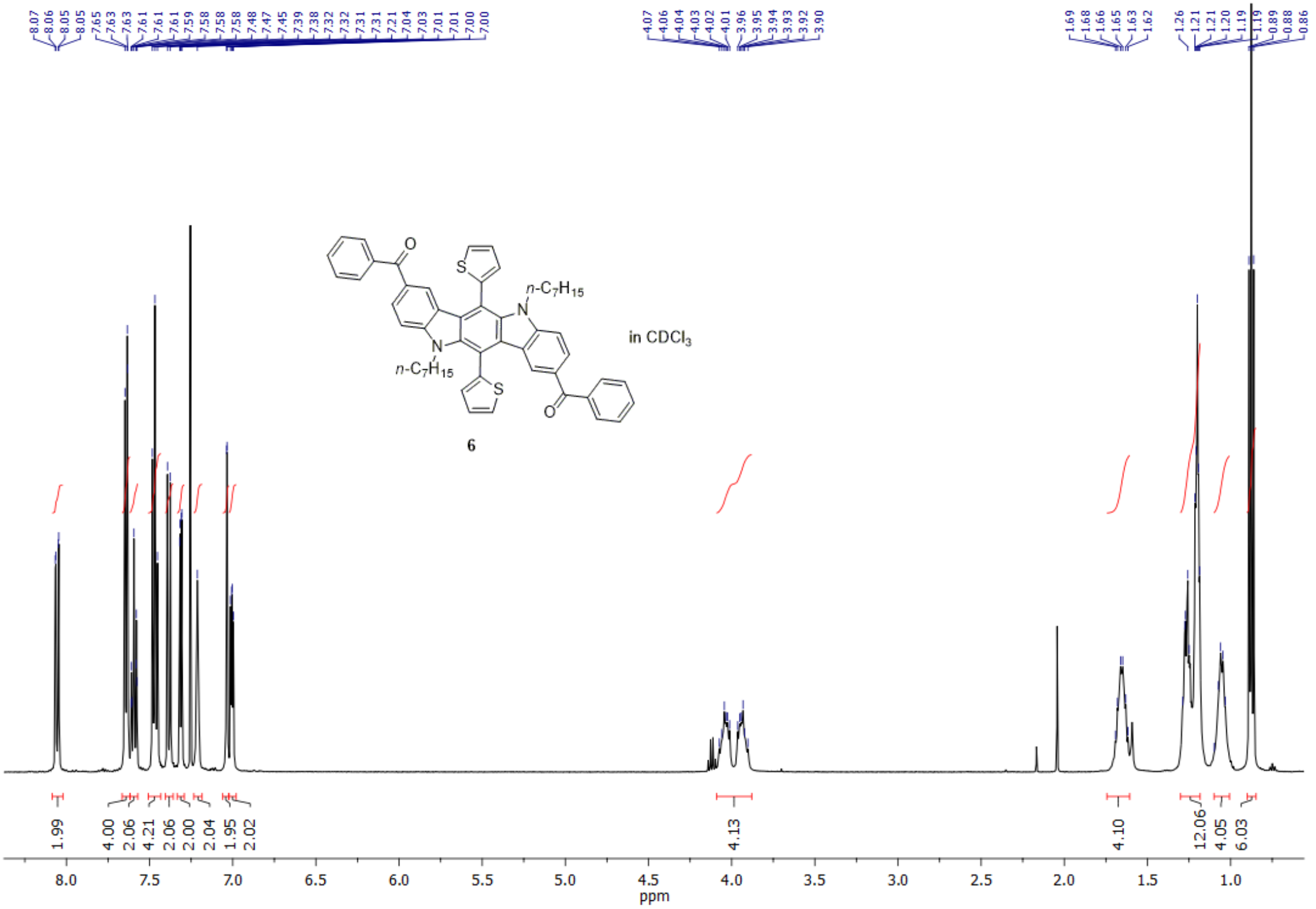
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

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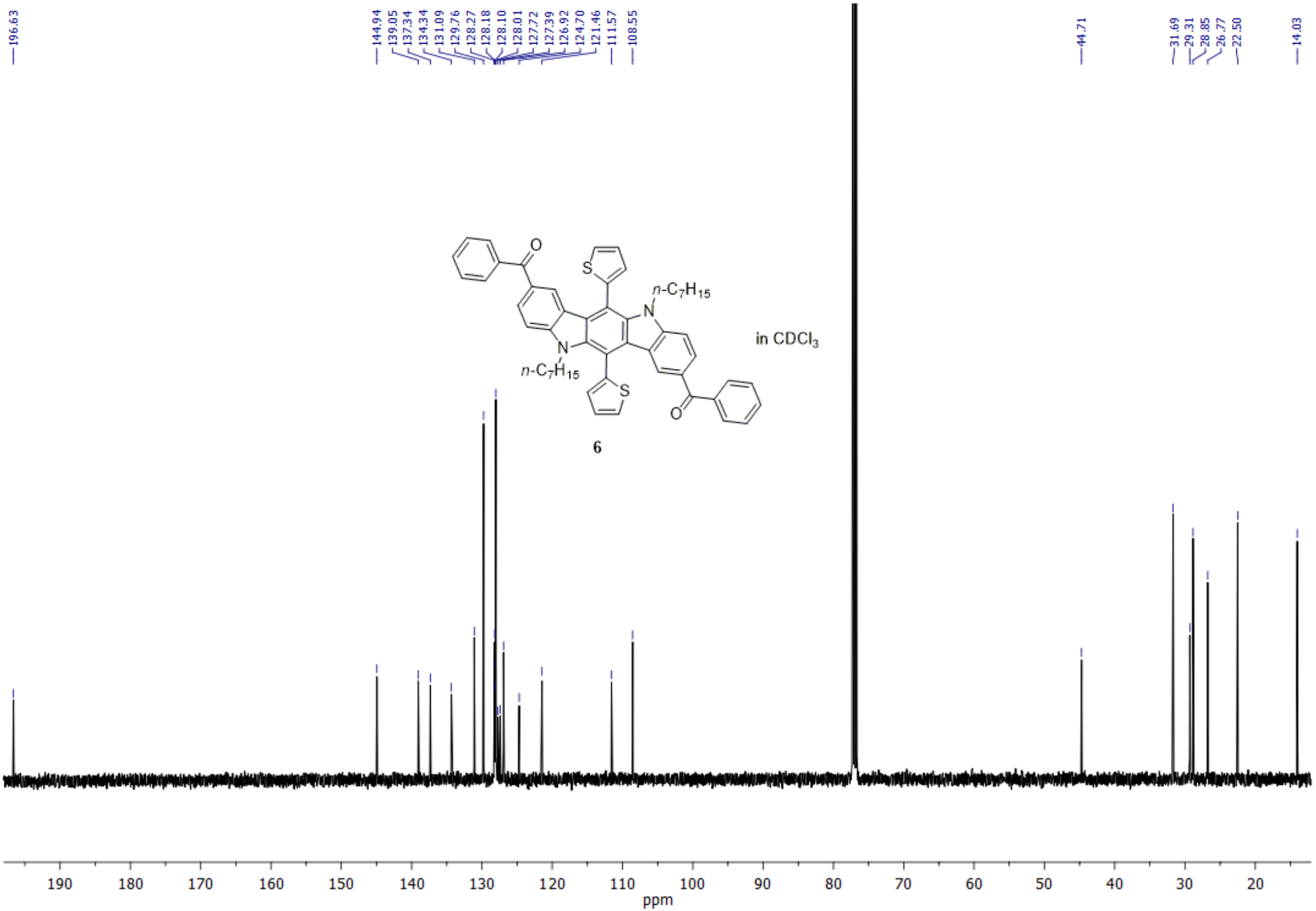
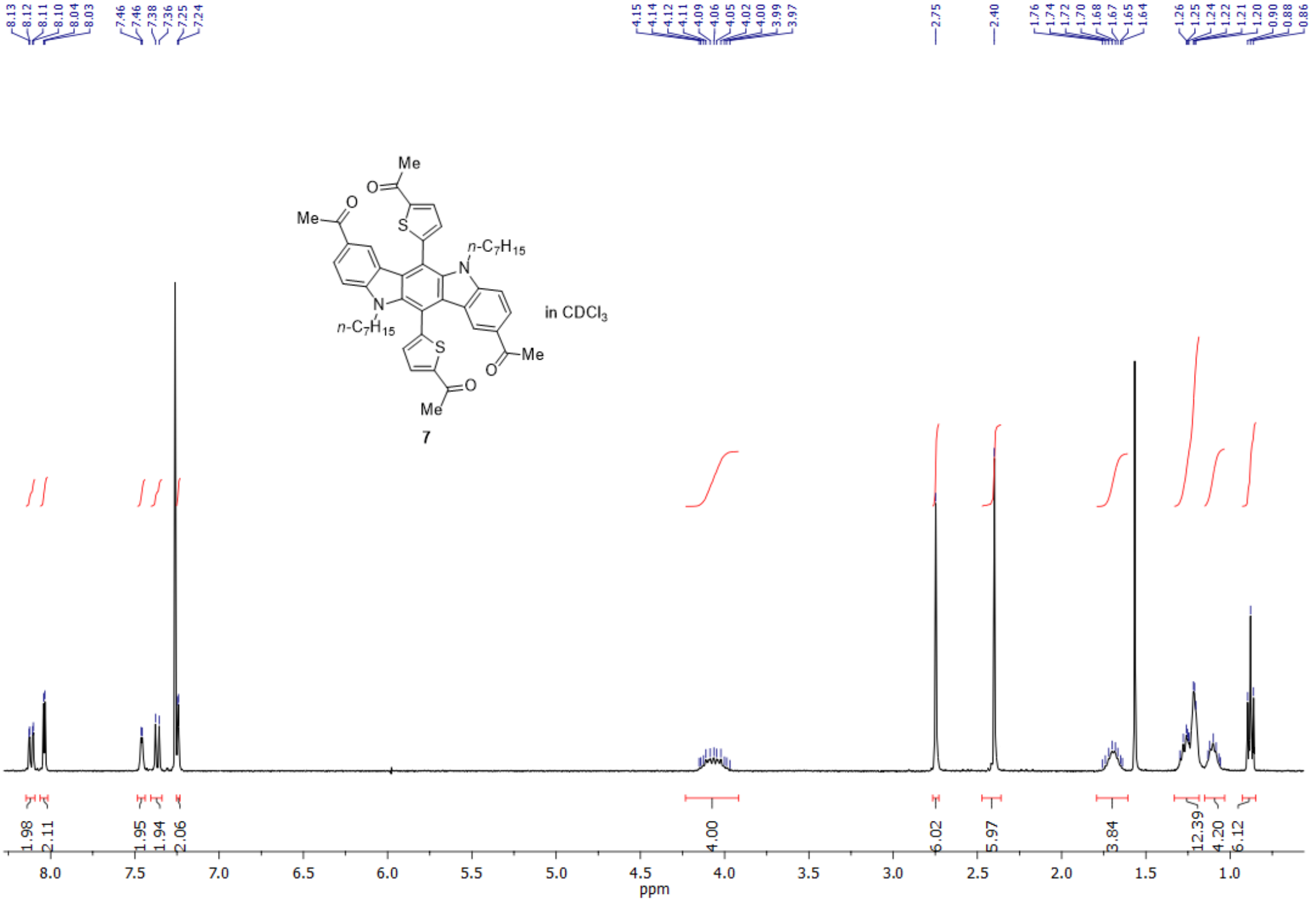
4.07 4.06 4.04 4.03 4.02 4.01 3.96 3.95 3.94 3.93 3.92 3.90
1.69 1.68 1.66 1.65 1.63 1.62
1.26 1.21 1.21 1.20 1.19 1.19 0.89 0.88 0.86
O
S
n-C7H15
N
N
n-C7H15
S
O
in CDCl3
6
1.99 4.00 2.06 4.21 2.06 2.00 2.04 1.95 2.02
4.13
4.10
12.06 4.05 6.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm

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8.12
8.11
8.10
8.04
8.03
7.46
7.46
7.38
7.36
7.25
7.24
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4.14
4.12
4.11
4.09
4.06
4.05
4.02
4.00
3.99
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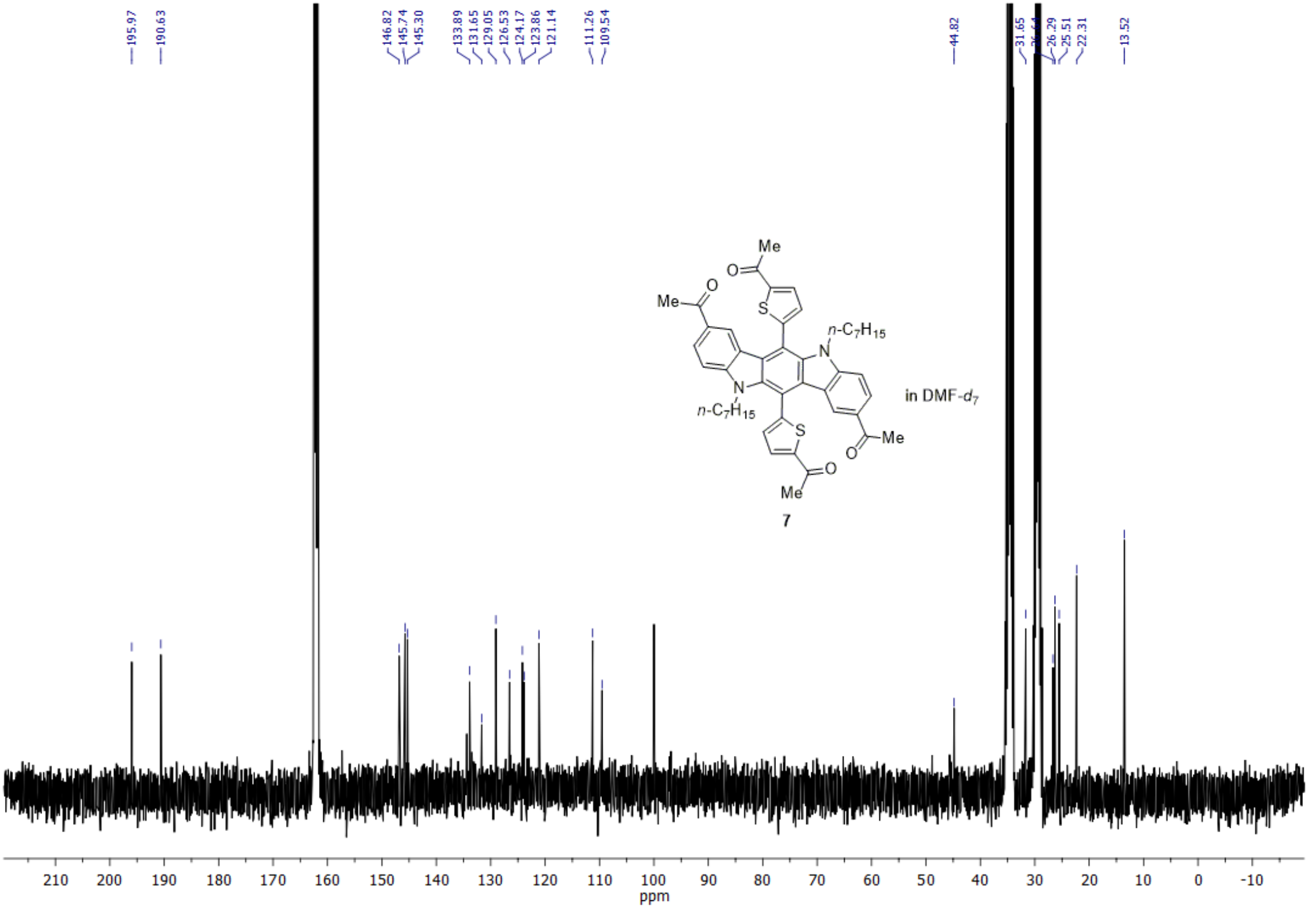
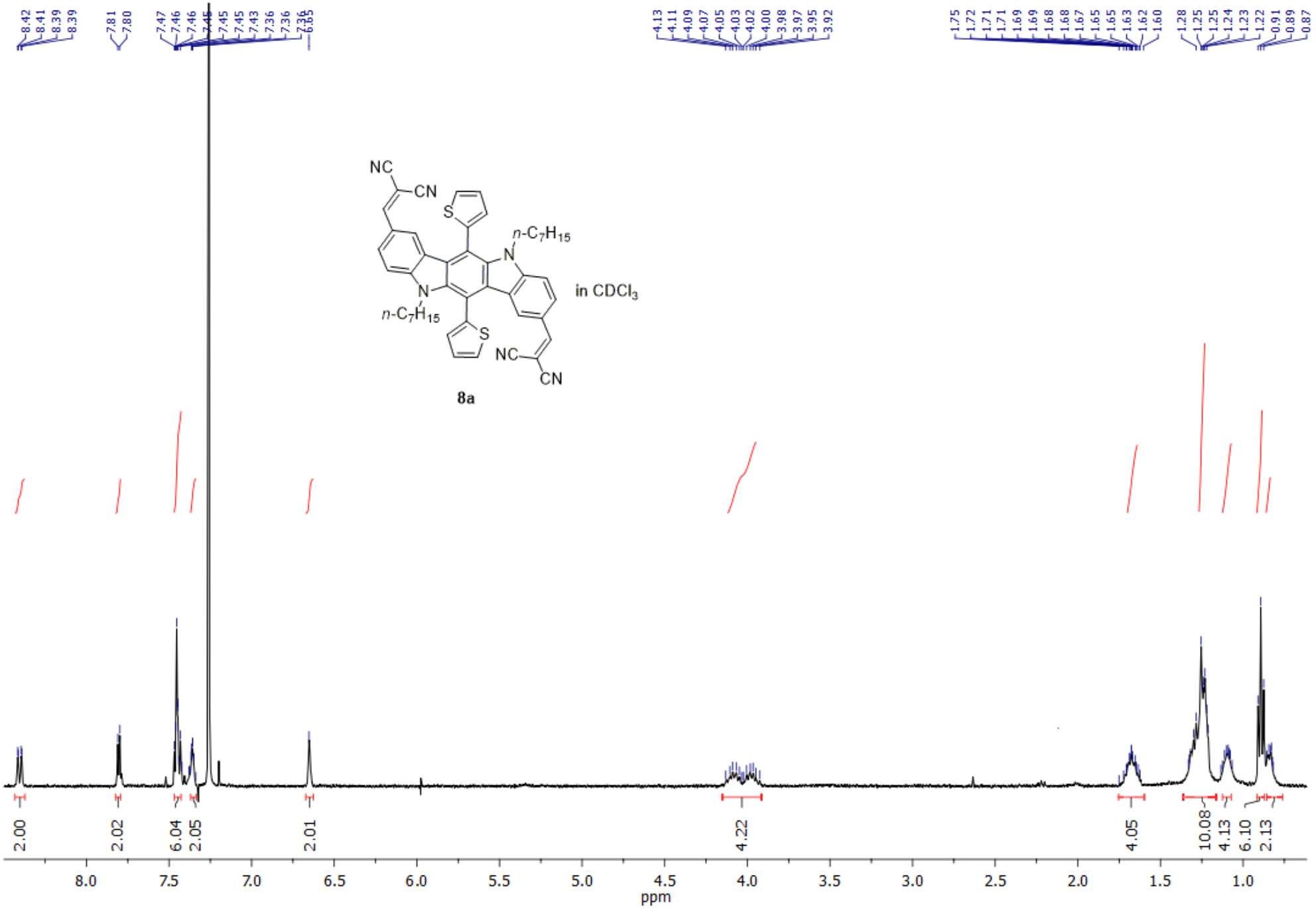
2.40
1.76
1.74
1.72
1.70
1.68
1.67
1.65
1.64
1.26
1.25
1.24
1.22
1.21
1.20
0.90
0.88
0.86
Me
O
Me
O
S
n-C7H15
N
N
n-C7H15
S
O
Me
O
Me
in CDCl3
7
1.98
2.11
1.95
1.94
2.06
4.00
6.02
5.97
3.84
12.39
4.20
6.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

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8.39
8.39
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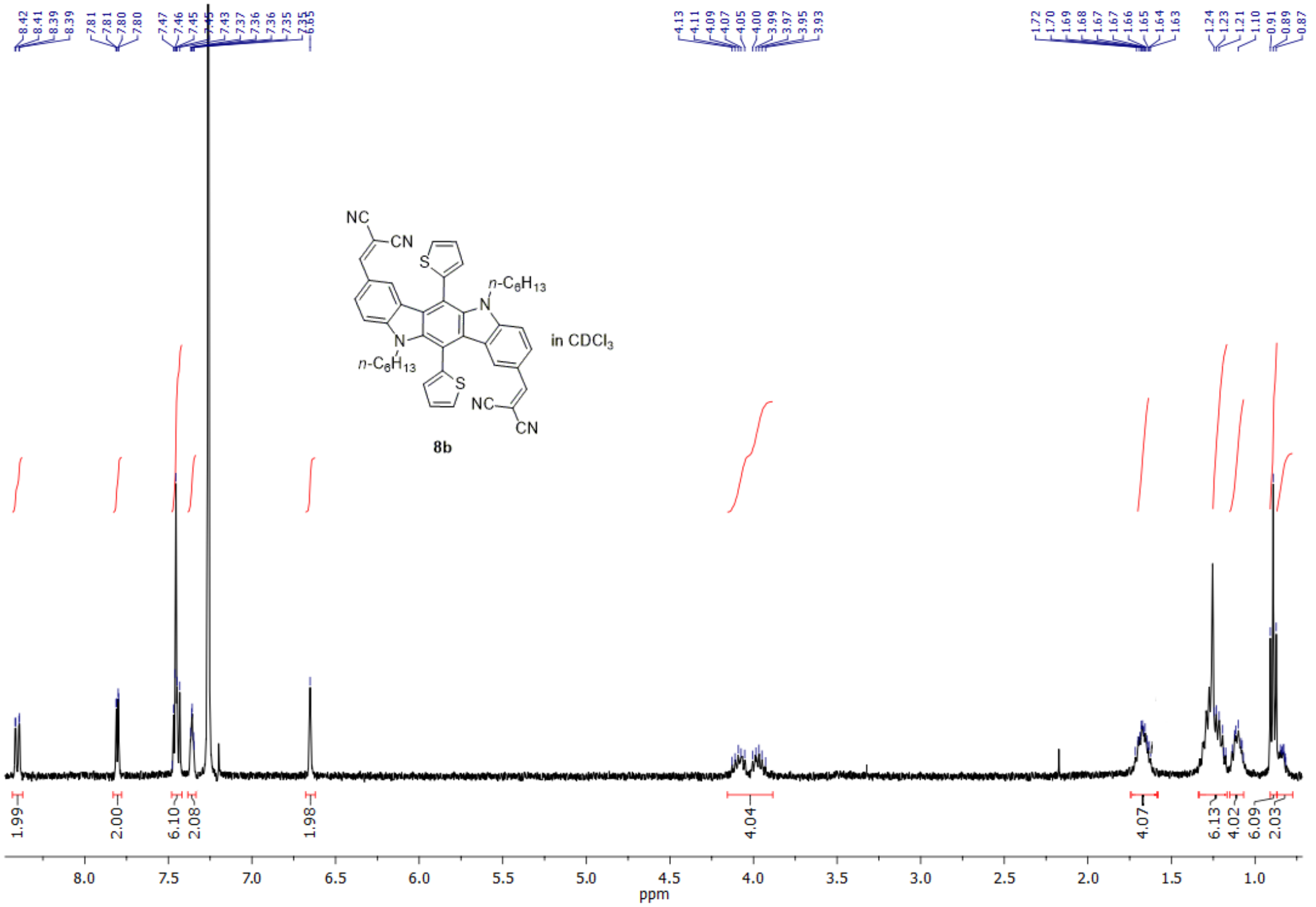
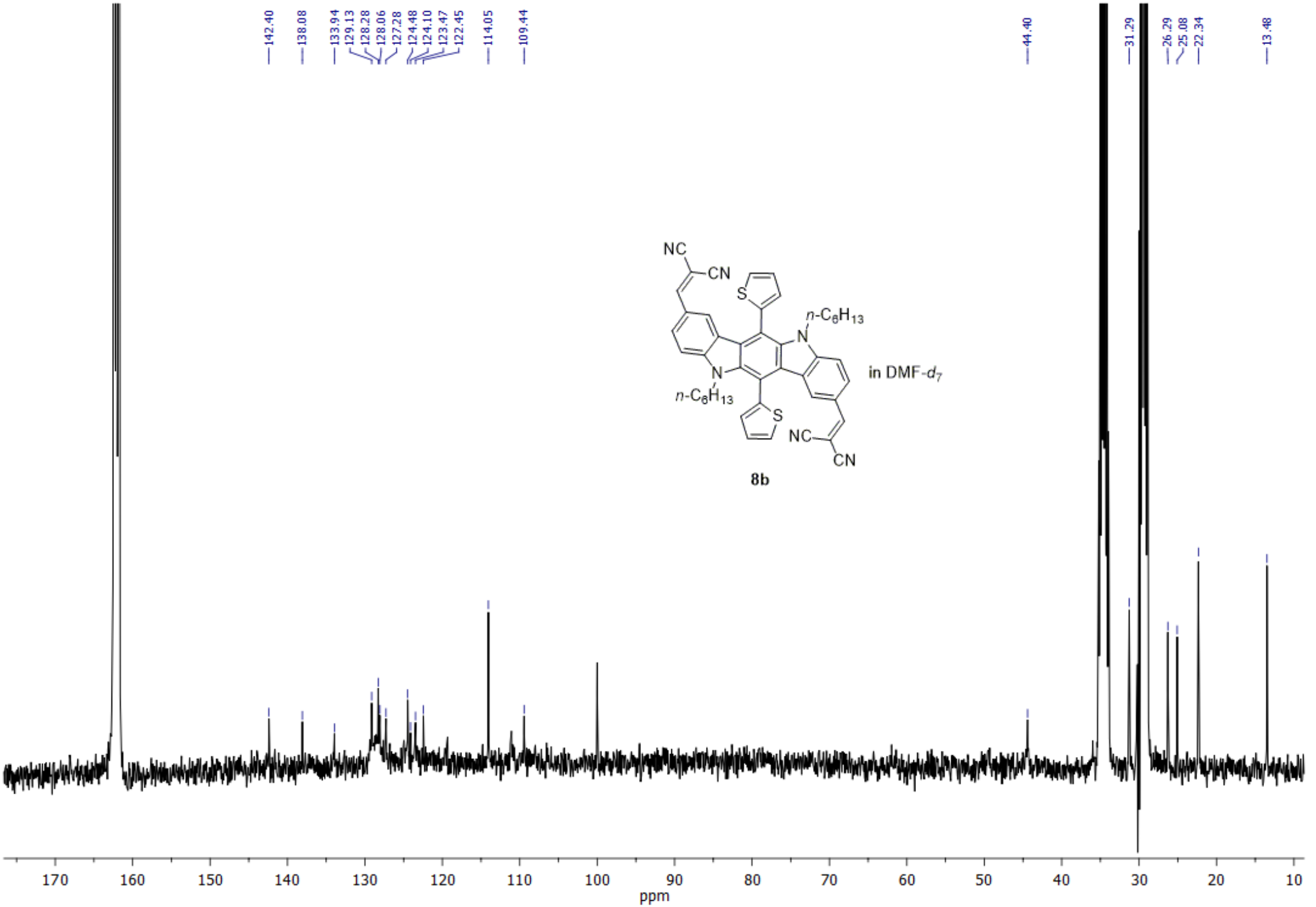
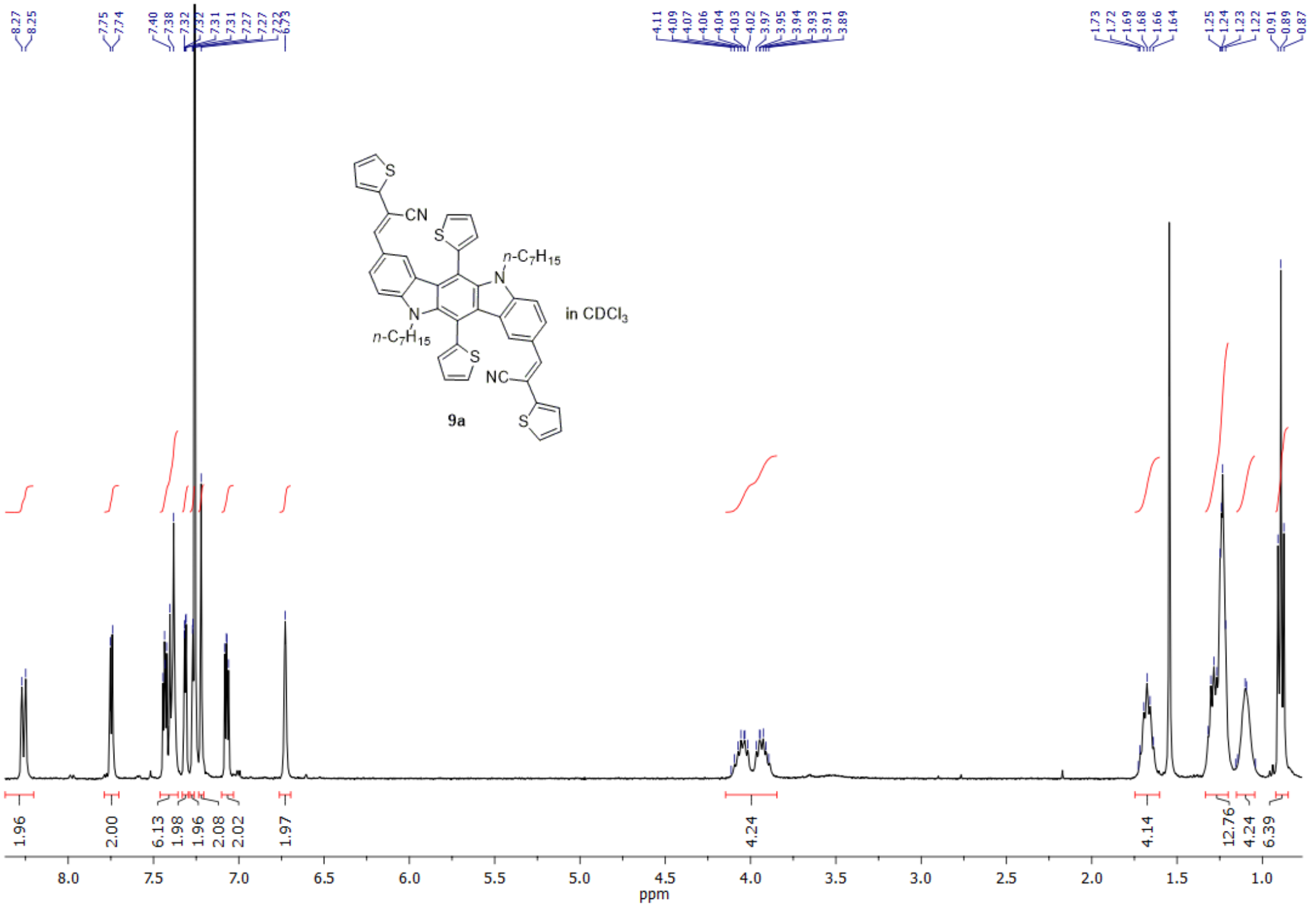
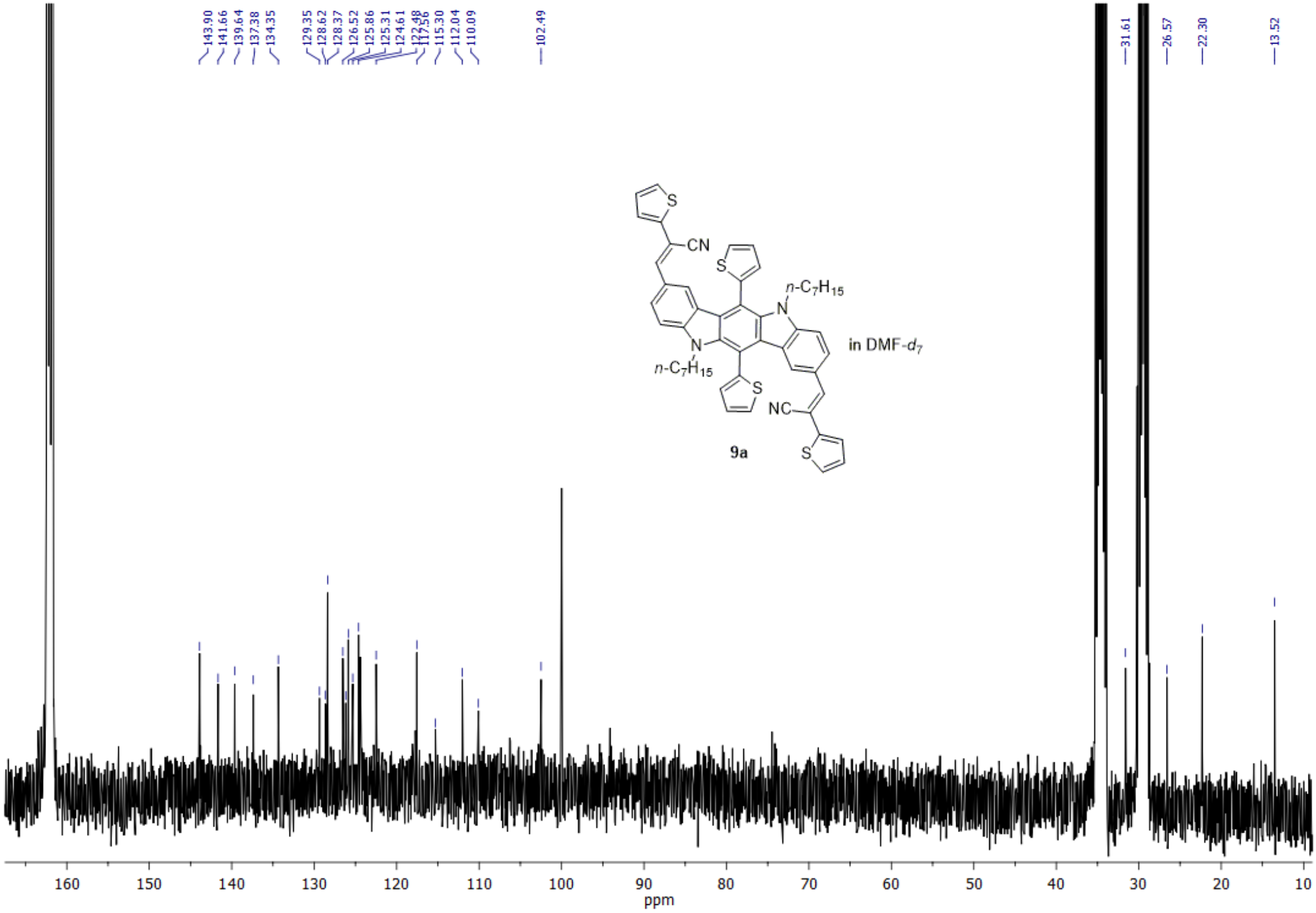
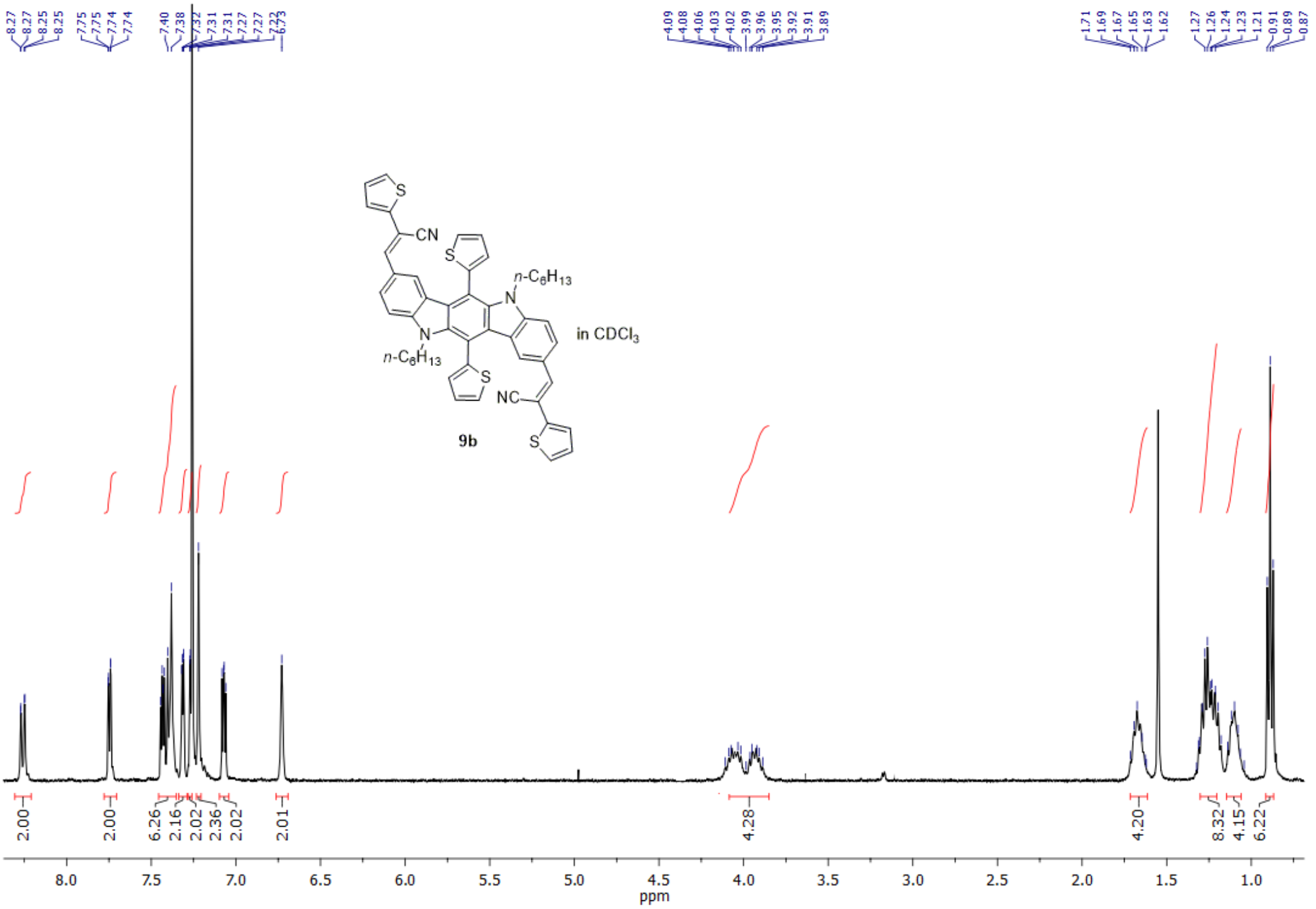
7.47
7.46
7.46
7.45
7.45
7.45
7.43
7.36
7.36
7.36
6.65
4.13
4.11
4.09
4.07
4.05
4.03
4.02
4.00
3.98
3.97
3.95
3.92
1.75
1.72
1.71
1.71
1.69
1.69
1.68
1.68
1.67
1.65
1.65
1.63
1.62
1.60
1.28
1.25
1.25
1.24
1.23
1.22
0.91
0.89
0.87
NC
CN
S
n-C7H15
N
N
n-C7H15
S
NC
CN
in CDCl3
8a
2.00
2.02
6.04
2.05
2.01
4.22
4.05
10.08
4.13
6.10
2.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


8.42
8.41
8.39
8.39
7.81
7.81
7.80
7.80
7.47
7.46
7.45
7.45
7.43
7.37
7.36
7.36
7.35
7.35
6.65
4.13
4.11
4.09
4.07
4.05
4.00
3.99
3.97
3.95
3.93
1.72
1.70
1.69
1.68
1.67
1.67
1.66
1.65
1.64
1.63
1.24
1.23
1.21
1.10
0.91
0.89
0.87
NC
CN
S
n-C6H13
N
N
n-C6H13
S
NC
CN
in CDCl3
8b
1.99
2.00
6.10
2.08
1.98
4.04
4.07
6.13
4.02
6.09
2.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm





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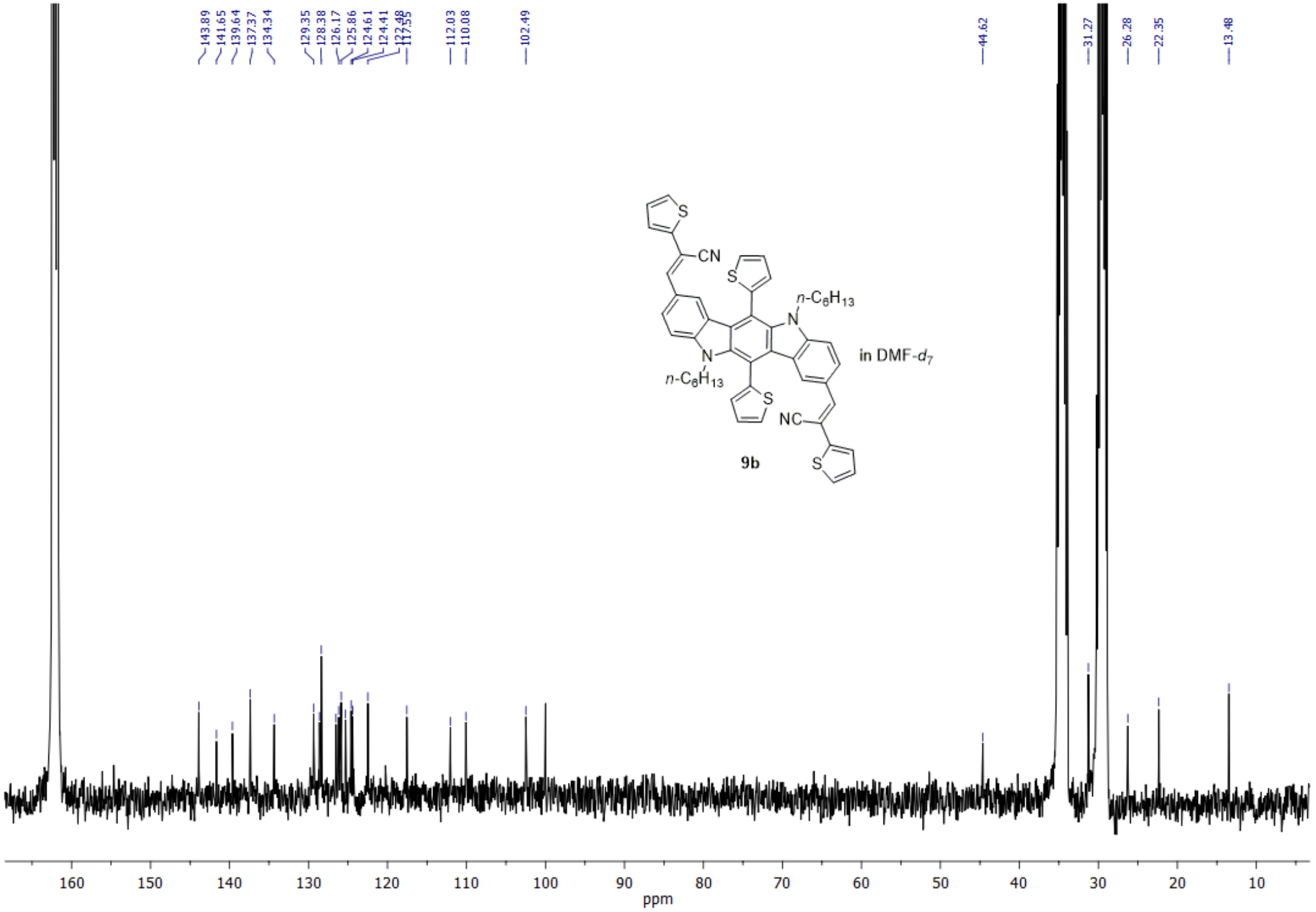
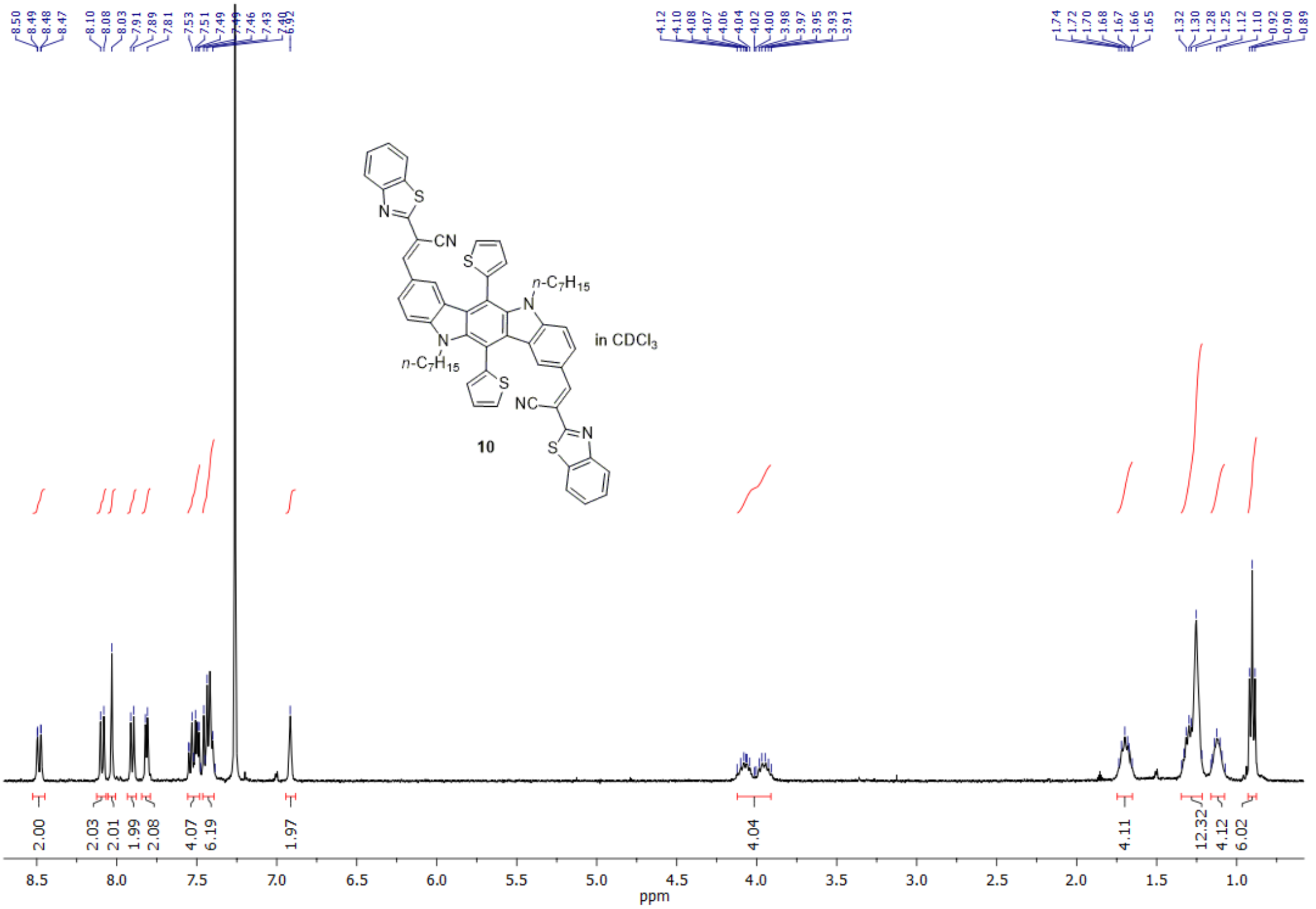
8.25
8.25
7.75
7.75
7.74
7.74
7.40
7.38
7.32
7.31
7.31
7.27
7.27
7.22
6.73
4.09
4.08
4.06
4.03
4.02
3.99
3.96
3.95
3.92
3.91
3.89
1.71
1.69
1.67
1.65
1.63
1.62
1.27
1.26
1.24
1.23
1.21
0.91
0.89
0.87
S
CN
S
n-C6H13
N
N
n-C6H13
S
NC
S
9b
in CDCl3
2.00
2.00
6.26
2.16
2.02
2.36
2.02
2.01
4.28
4.20
8.32
4.15
6.22
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm




8.50
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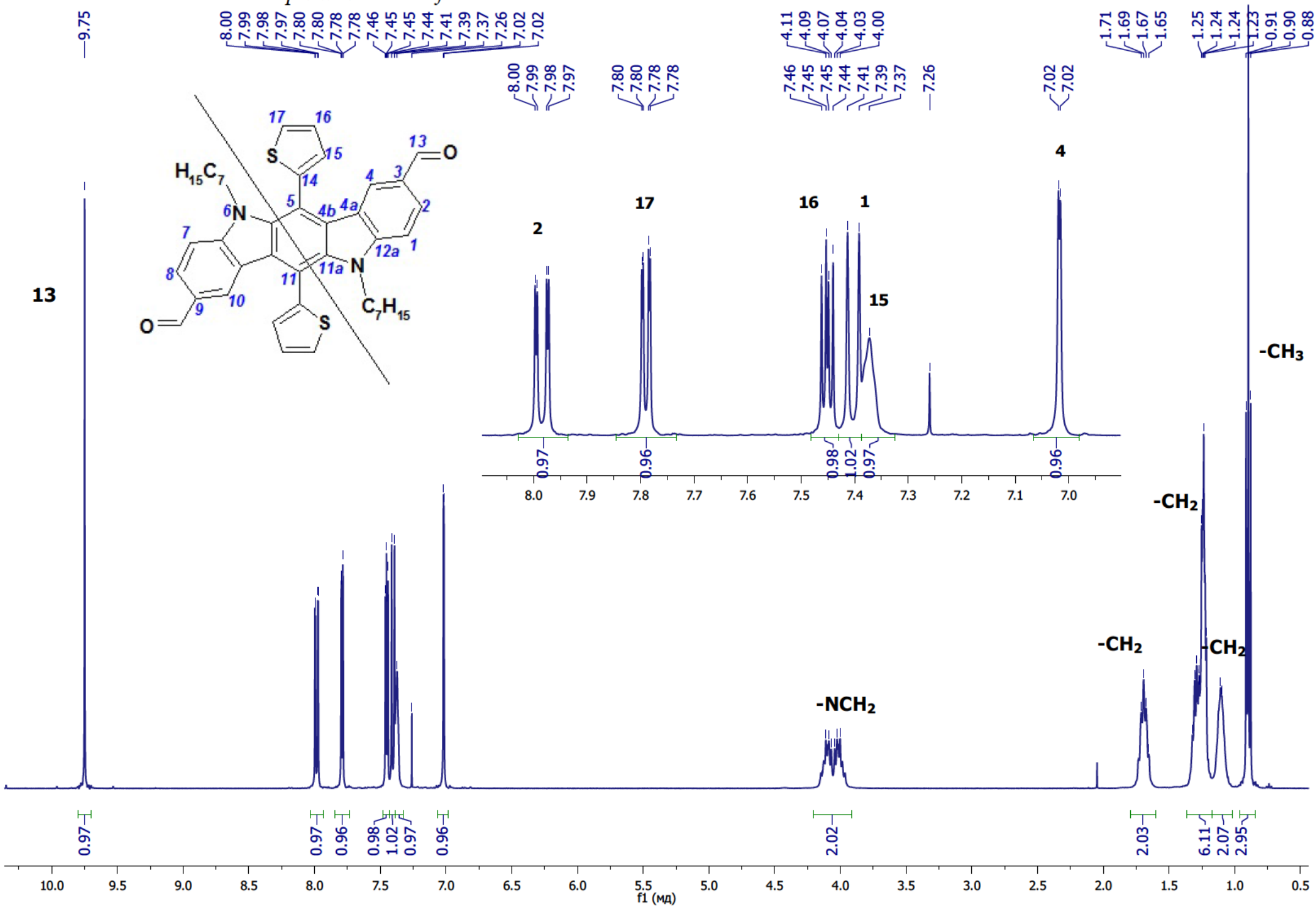
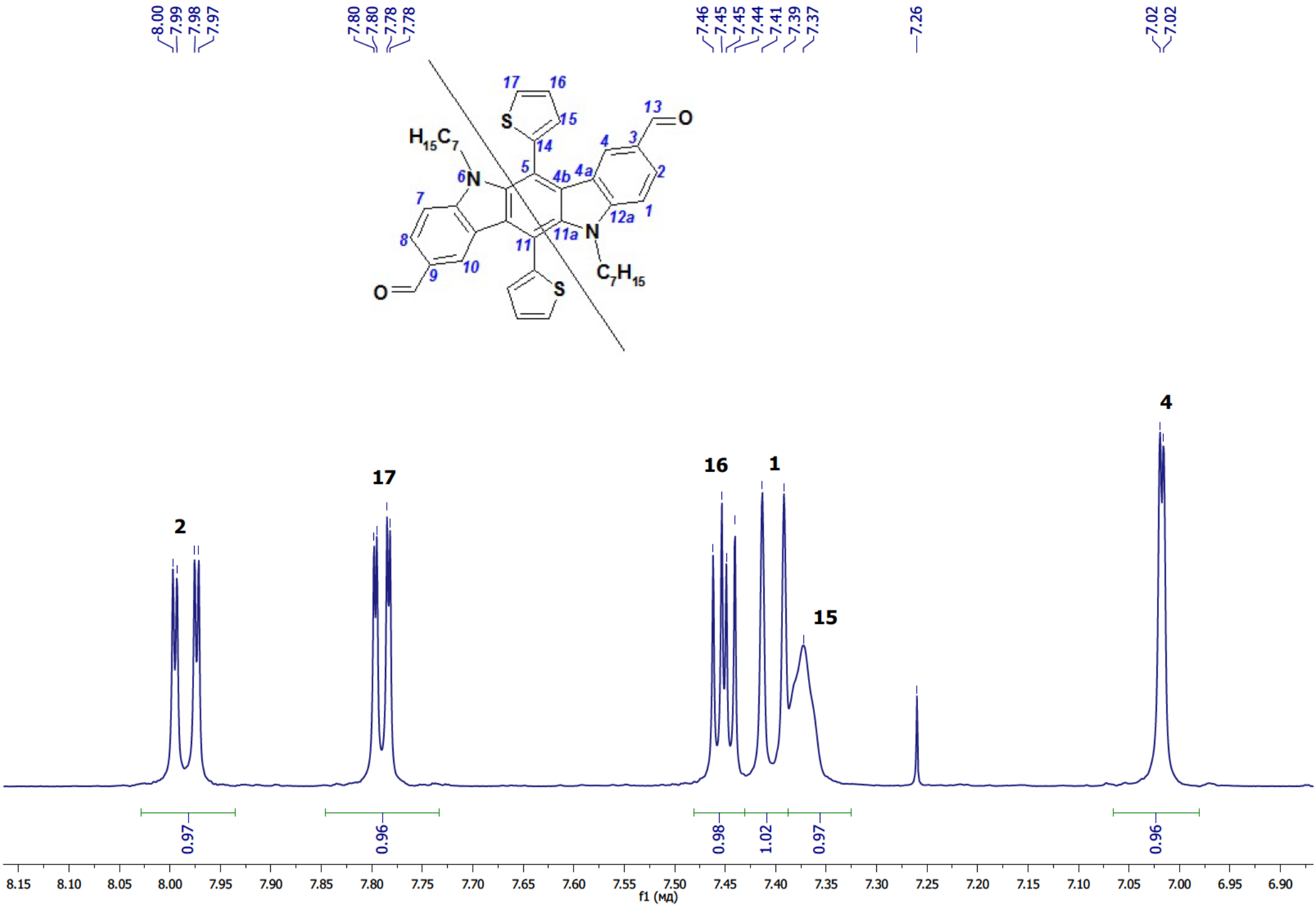
8.48
8.47
8.10
8.08
8.03
7.91
7.89
7.81
7.53
7.51
7.49
7.46
7.43
7.40
6.92
4.12
4.10
4.08
4.07
4.06
4.04
4.02
4.00
3.98
3.97
3.95
3.93
3.91
1.74
1.72
1.70
1.68
1.67
1.66
1.65
1.32
1.30
1.28
1.25
1.12
1.10
0.92
0.90
0.89
S
N
CN
S
n-C7H15
N
N
n-C7H15
S
NC
N
S
in CDCl3
10
2.00
2.03
2.01
1.99
2.08
4.07
6.19
1.97
4.04
4.11
12.32
4.12
6.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

3. 2D NMR experiments data of ***5a***




8.00
7.99
7.98
7.97
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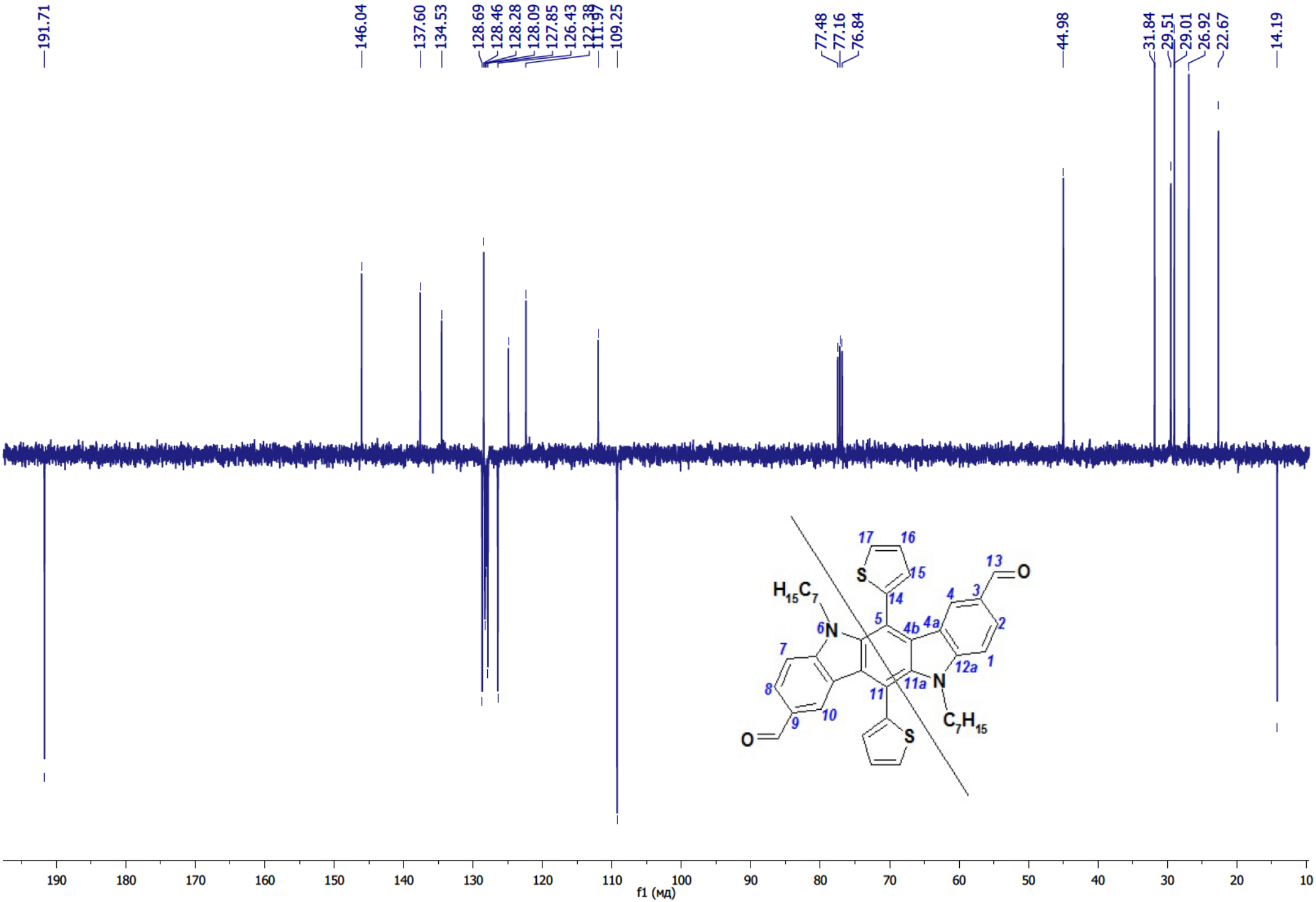
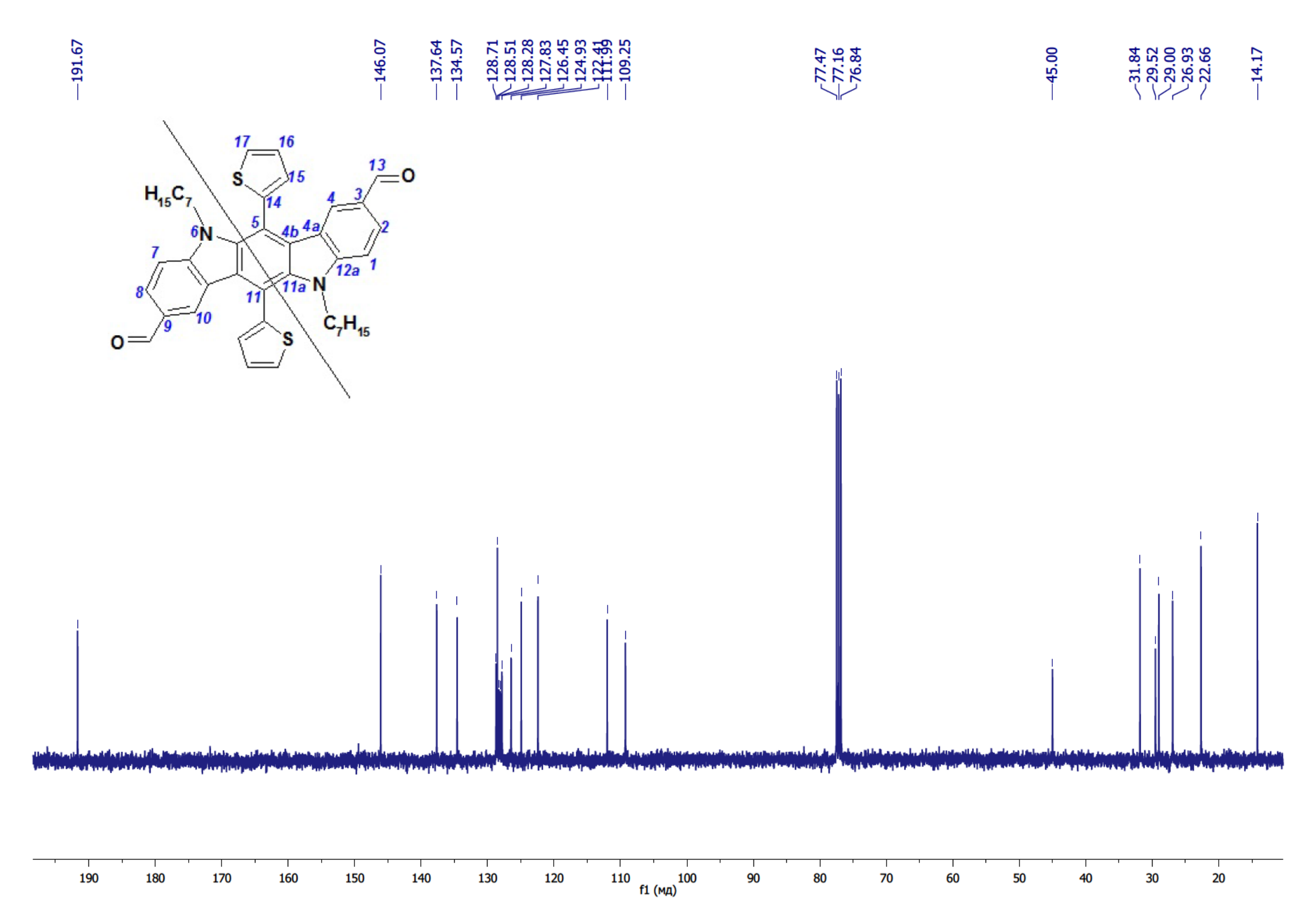
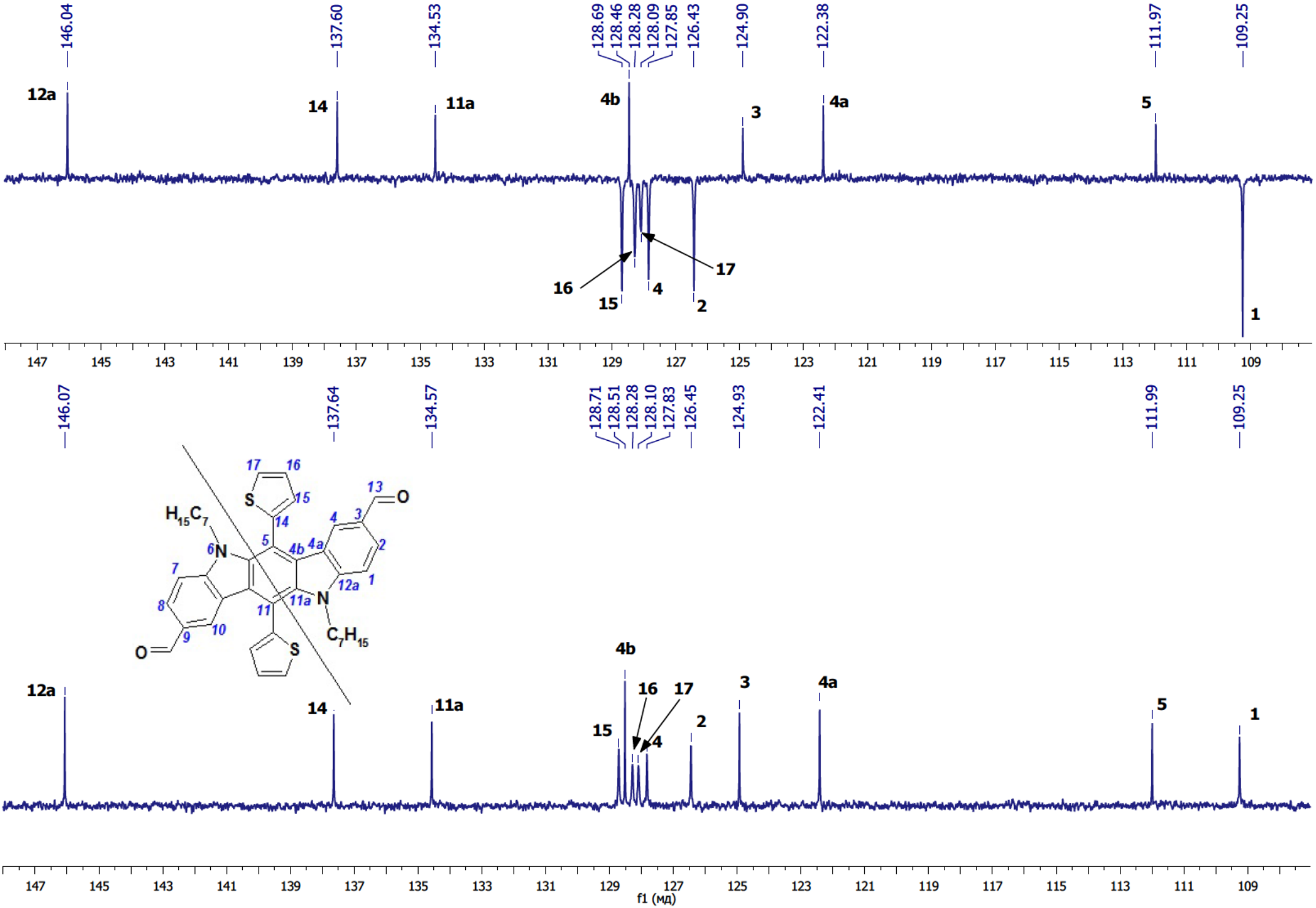
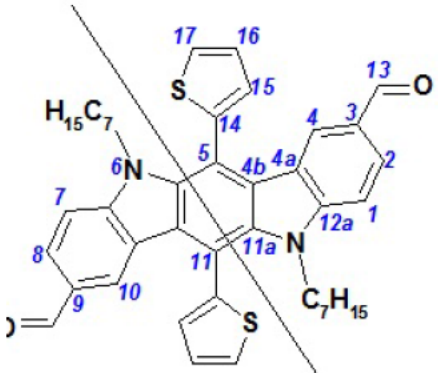
7.80
7.78
7.78
7.46
7.45
7.45
7.44
7.41
7.39
7.37
7.26
7.02
7.02
17
16
S
15
14
13
O
H15C7
6N
5
4b
4a
4
3
2
1
12a
7
8
11a
N
11
C7H15
9
10
O
S
2
17
16
1
15
4
0.97
0.96
0.98
1.02
0.97
0.96
8.15
8.10
8.05
8.00
7.95
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
6.90
f1 (мд)

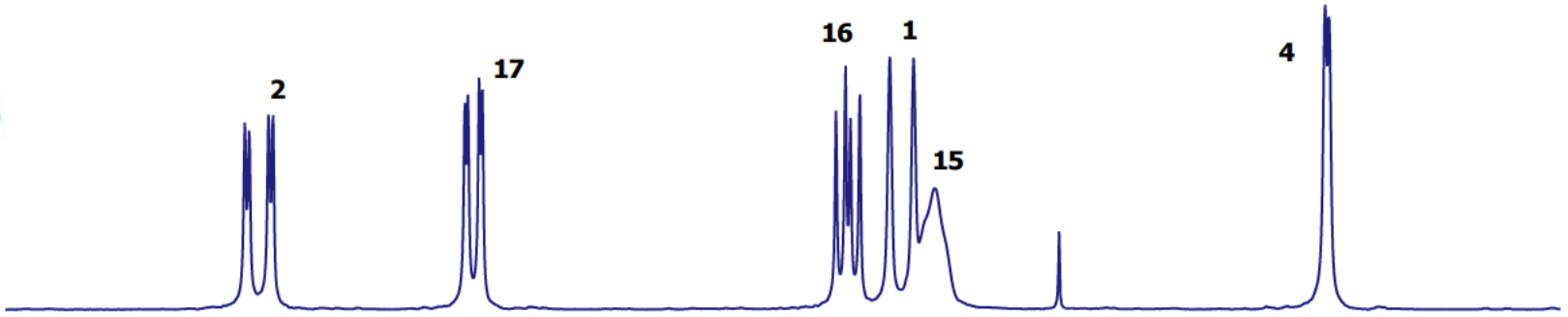

191.71
146.04
137.60
134.53
128.69
128.46
128.28
128.09
127.85
126.43
122.38
111.97
109.25
77.48
77.16
76.84
44.98
31.84
29.51
29.01
26.92
22.67
14.19
H15C7
N
S
O
C7H15
1
2
3
4
4a
4b
5
6
7
8
9
10
11
11a
12a
13
14
15
16
17
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (мд)

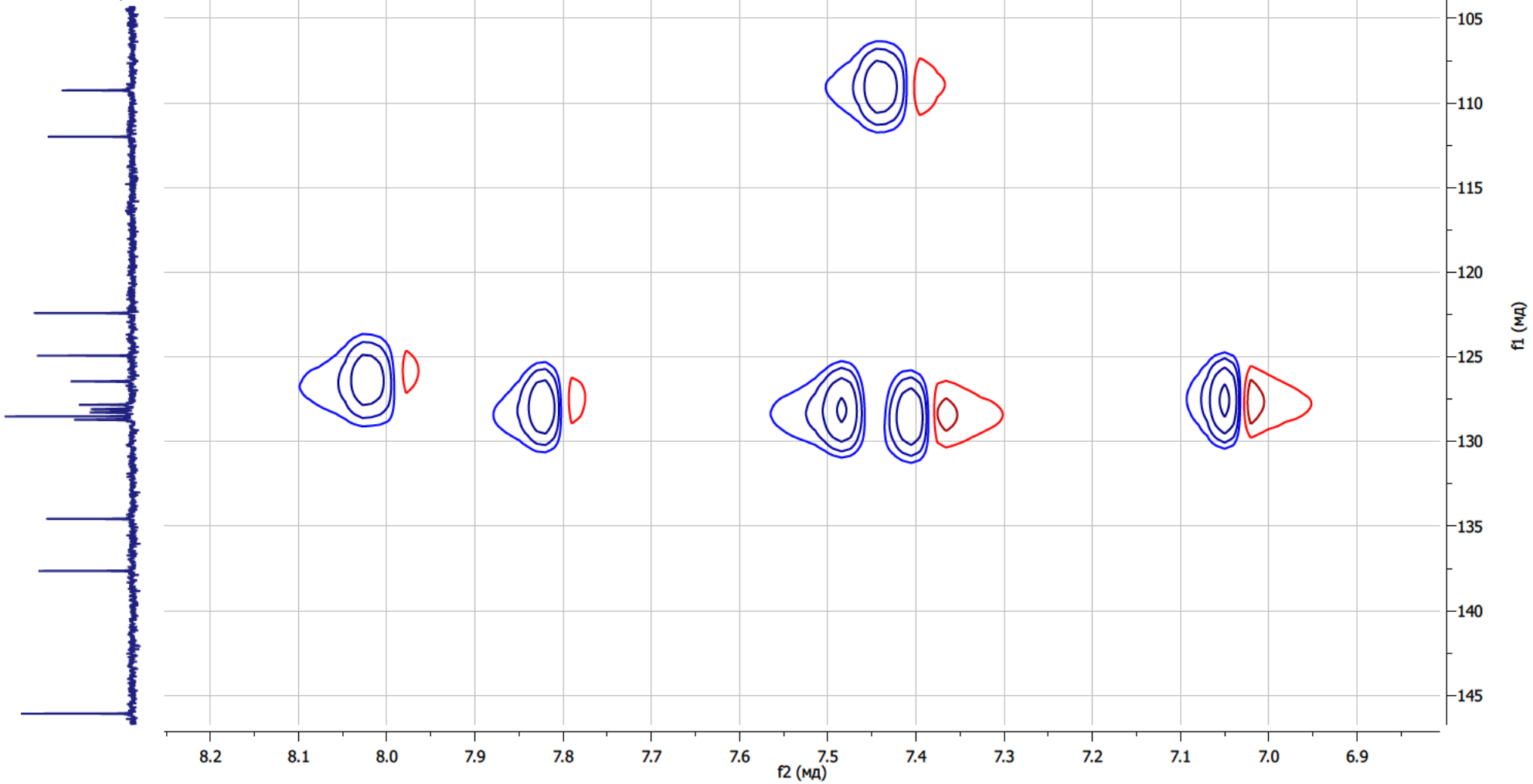

191.67
146.07
137.64
134.57
128.71
128.51
128.28
127.83
126.45
124.93
122.41
111.99
109.25
77.47
77.16
76.84
45.00
31.84
29.52
29.00
26.93
22.66
14.17
H15C7
N
S
O
C7H15
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (мд)

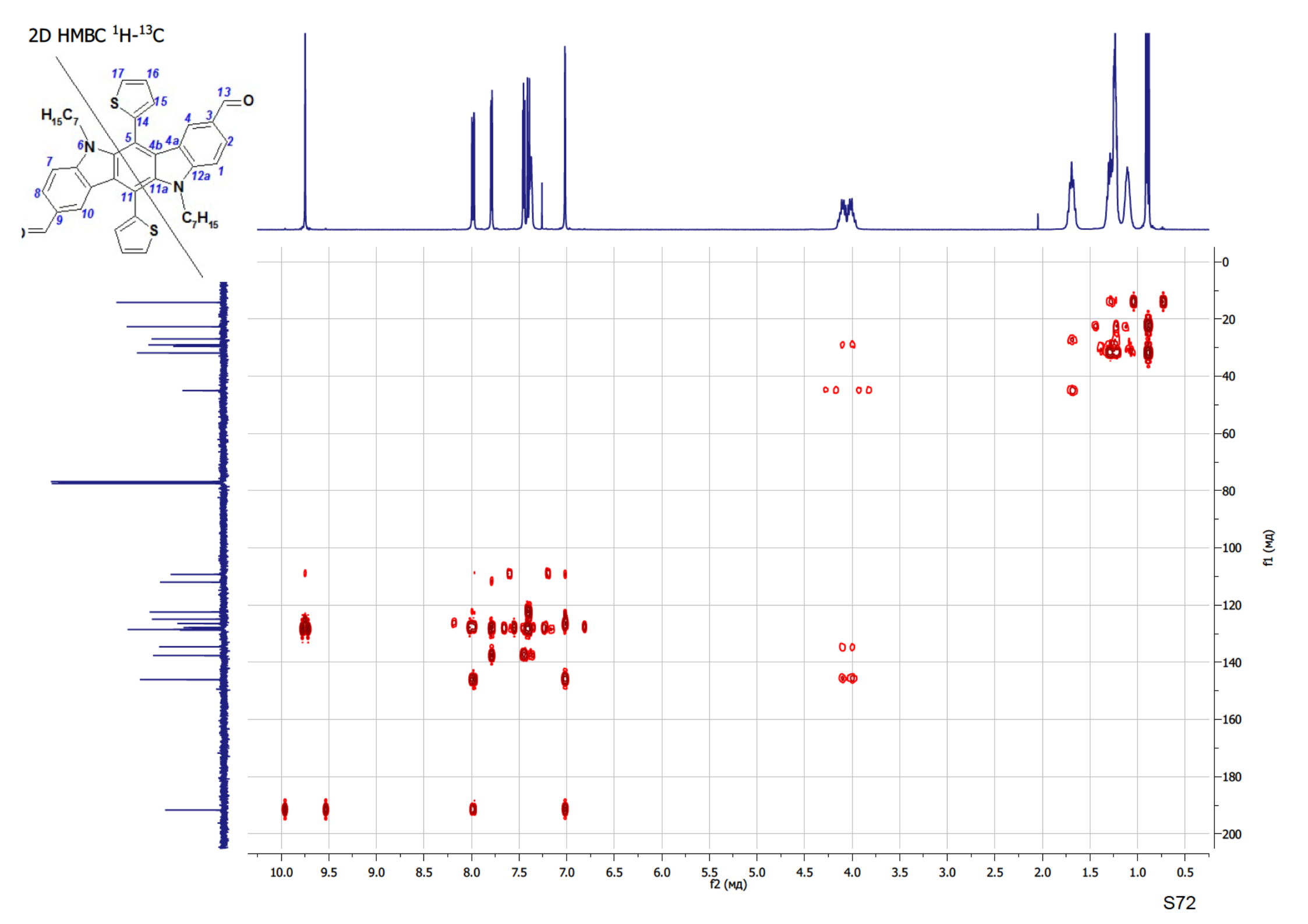

146.04
137.60
134.53
128.69
128.46
128.28
128.09
127.85
126.43
124.90
122.38
111.97
109.25
12a
14
11a
4b
3
4a
5
16
15
4
17
2
1
147
145
143
141
139
137
135
133
131
129
127
125
123
121
119
117
115
113
111
109
146.07
137.64
134.57
128.71
128.51
128.28
128.10
127.83
126.45
124.93
122.41
111.99
109.25
H15C7
N
S
O
C7H15
12a
14
11a
4b
16
17
15
4
2
3
4a
5
1
f1 (мд)

2D HSQC ^{1}H-^{13}C

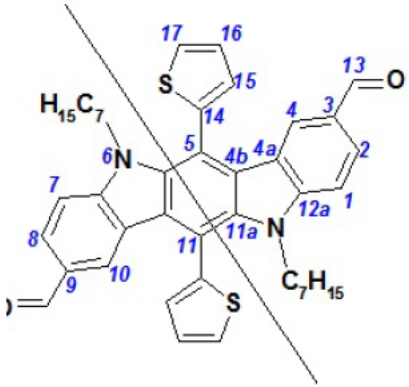


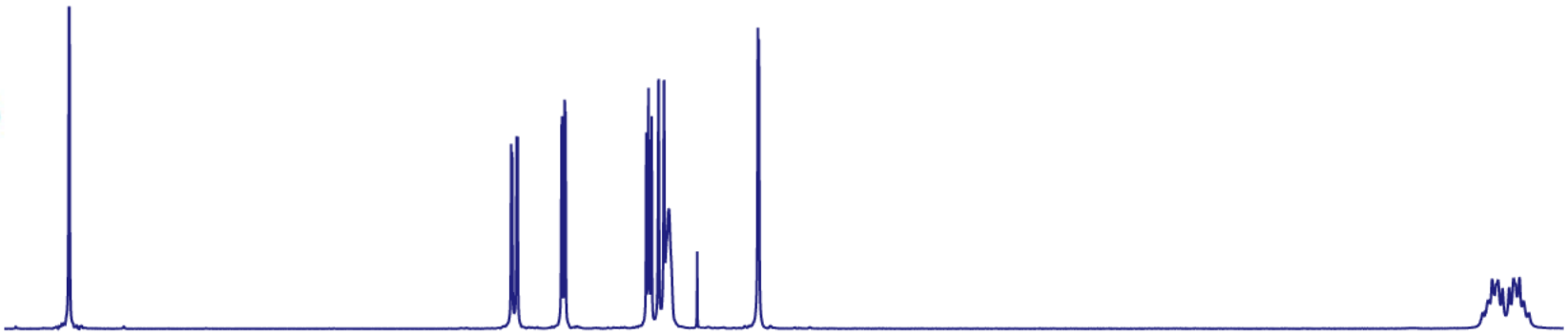


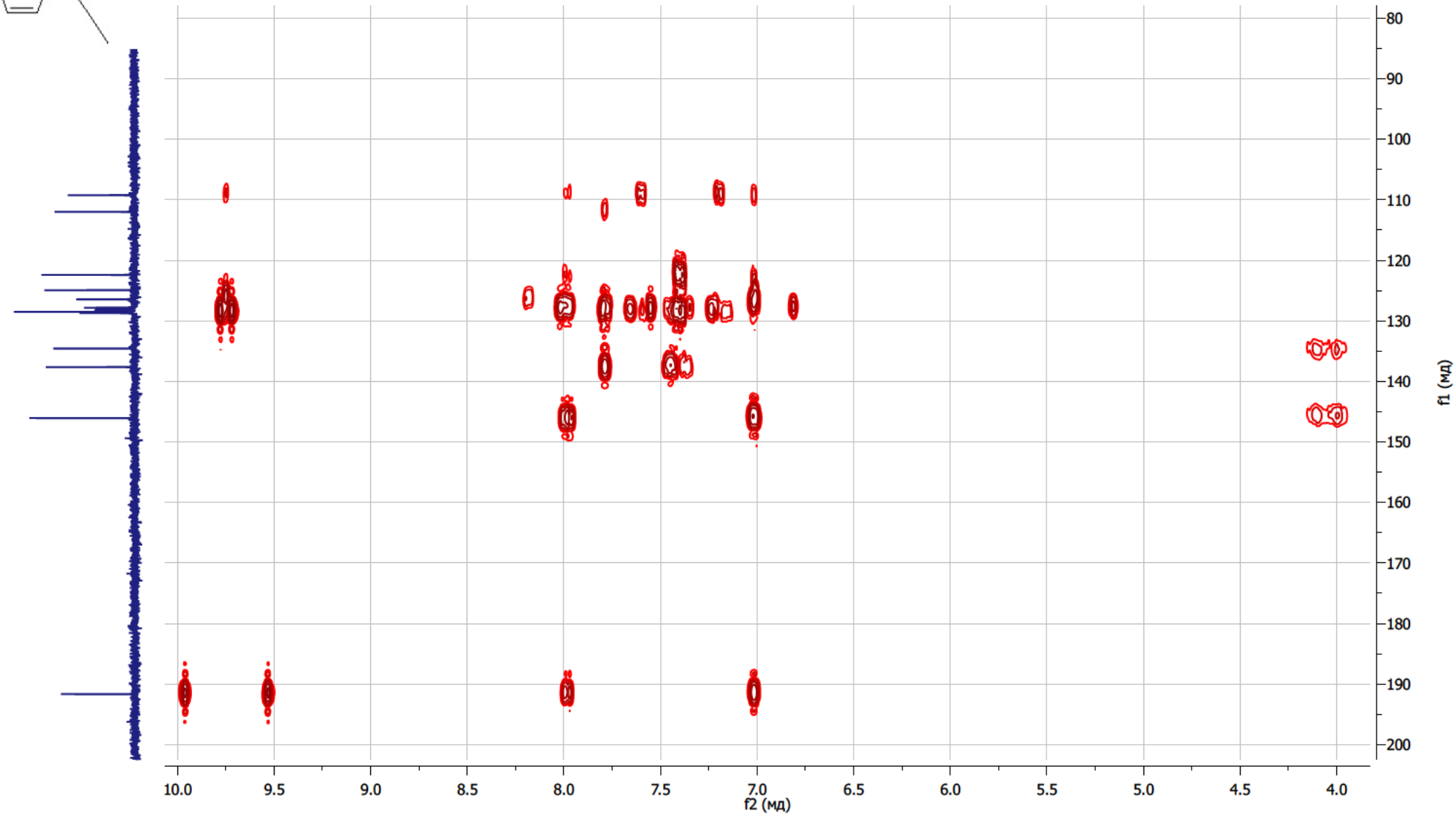


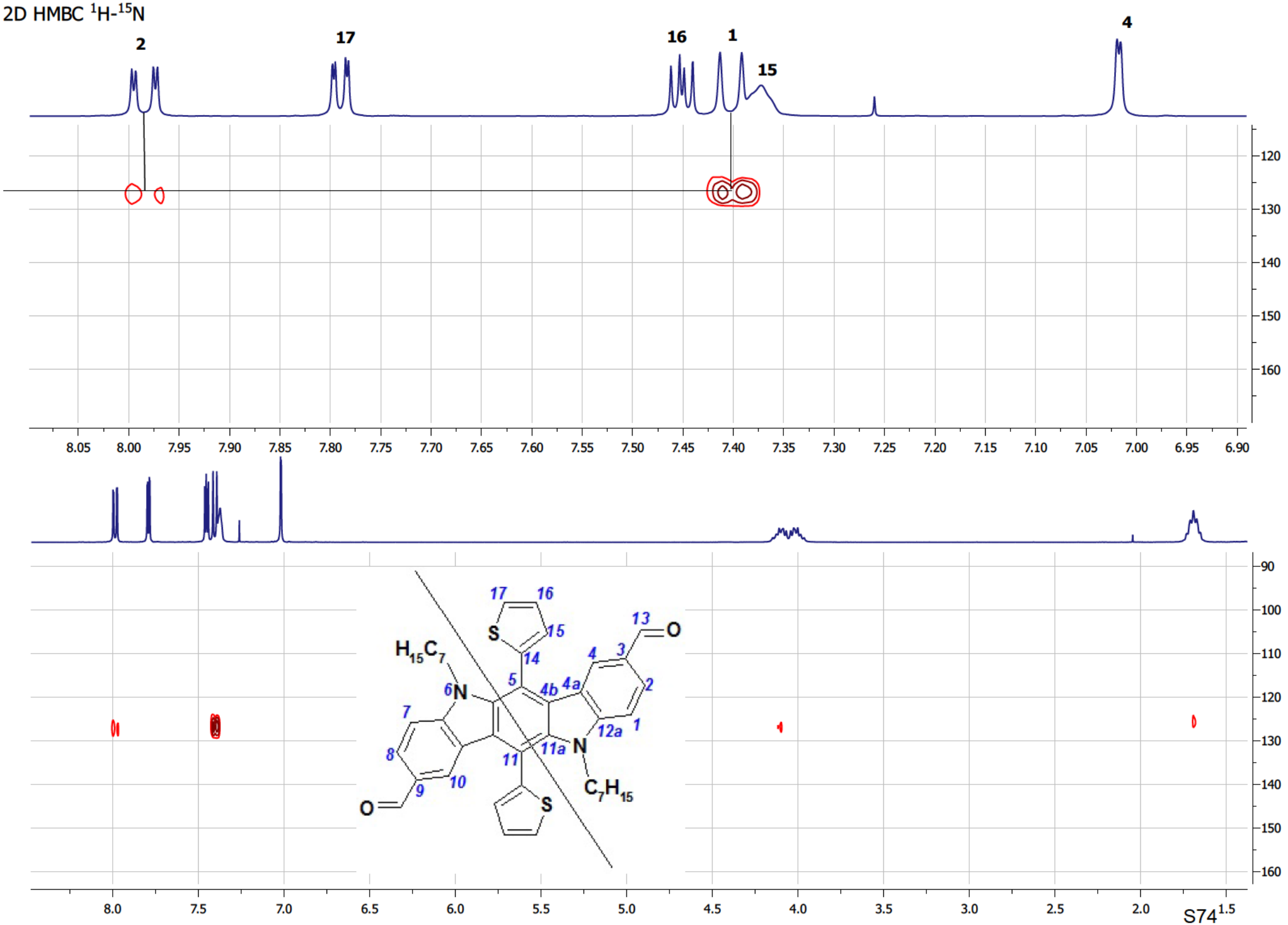

2D HMBC ^{1}H-^{13}C
$H_{15}C_7$
C_7H_{15}
f2 (мд)
f1 (мд)

2D HMBC ^{1}H-^{13}C








2D HMBC ^{1}H-^{15}N
2
17
16
1
15
4
120
130
140
150
160
8.05
8.00
7.95
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
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8.0
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