Indacenodipyrene Containing Small Molecules and Ladder Polymers

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Dedicated to the memory of Susan A. Odom.

Abstract:

A series of s-indaceno[1,2,3-cd:5,6,7-c'd']dipyrene-containing small molecule and ladder polymers were prepared using a palladium catalyzed arylation reaction. Precursor polymers and their resulting ladder polymers with molecular weights up to 13 kDa were prepared. The rigid, planar materials possessed highest occupied molecular orbital (HOMO) energies of -5.39 to -5.23 eV, lowest unoccupied molecular orbitals (LUMO) energies of -2.42 eV to -2.98 eV, and optical gaps of 1.68 to 2.03 eV. Organic field effect transistors were prepared with derivatives giving hole mobilities up to 2.5 X 10^{-5} $cm^2V^{-1}s^{-1}$.

Introduction

The demand of renewable and sustainable energy has grown exponentially due to industrialization, urbanization, geopolitical changes, and environmental concerns.[1–3] Robust organic semiconducting materials that are thermally and oxidatively stable while possessing high charge carrier mobilities are worthy targets for advancing technologies including organic field effect transistors and solar cells.[4,5] Among the variety of organic materials possible for adaptation to these technologies, conjugated ladder polymer based semiconductors offer opportunities for improved thermal stability and greater interchain pi-stacking interactions owing to the lack of bond rotation along the polymer backbone.[6–22] New synthetic pathways that enable the synthesis of unique carbon backbones in conjugated ladder polymers can provide opportunities to probe the structure-function properties and enable advancement in this field.

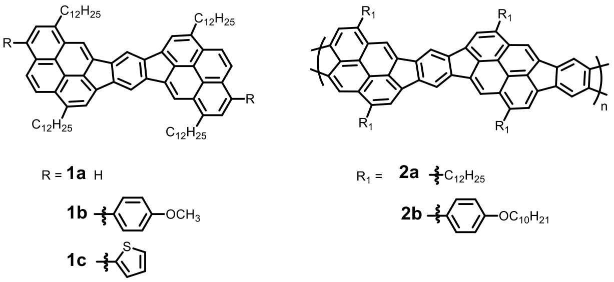
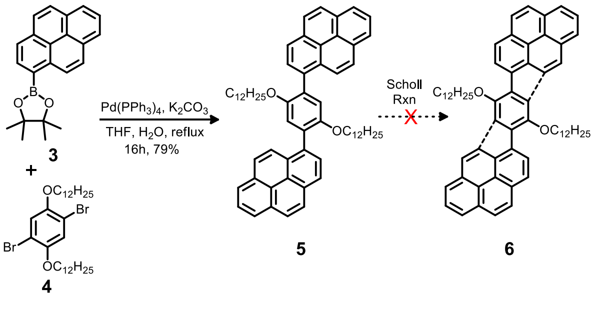


Figure 1: Conjugated small molecule and conjugated ladder polymers based on indacenodipyrene.

Scheme 1: Synthesis of small molecule precursor via Suzuki cross coupling.

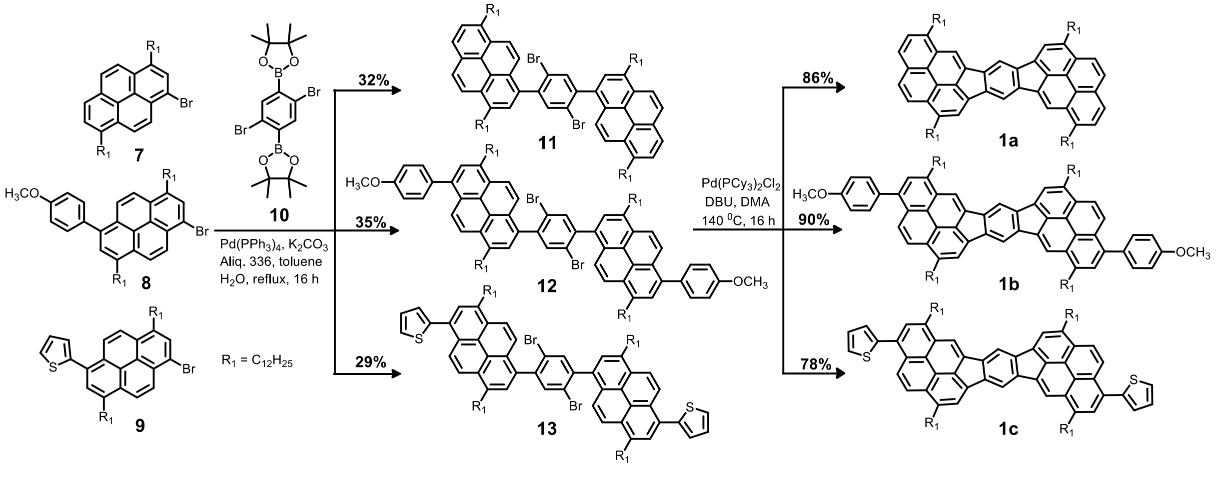


In this contribution, we have synthesized a series of rigid conjugated small molecules and conjugated ladder polymers based on an indacenodipyrene skeleton (Figure 1). The pyrene chromophores provide a large surface area aromatic chromophore that is well-studied in its monomeric form. In addition, this work builds upon a different pyrene-fused s-indacene regioisomer recently reported.[23] A palladium-catalyzed arylation reaction was employed as an efficient rigidification reaction that ultimately forms five-membered rings as the new ladder rungs linking the pyrene chromophores in the small molecules as well as polymeric materials.

Results and Discussion

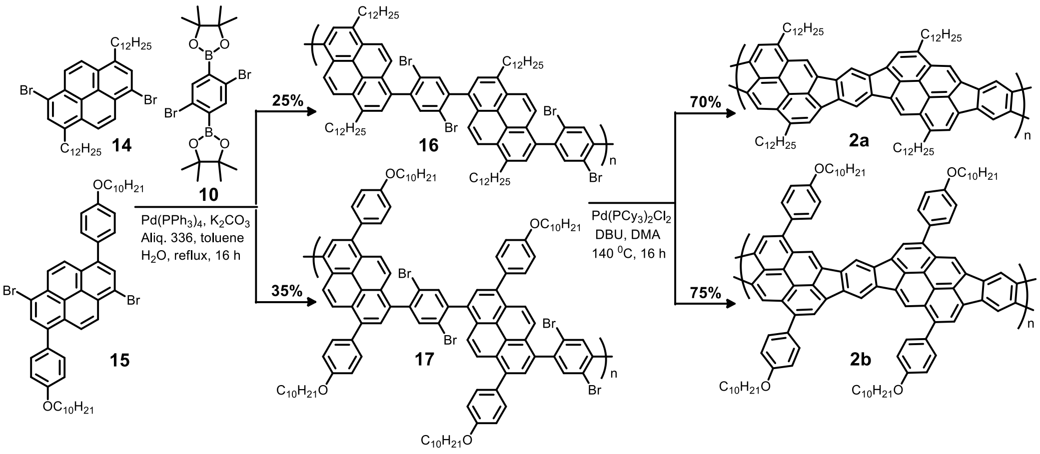
To optimize reaction conditions for the preparation of the conjugated ladder polymers, small molecule derivatives were first prepared. Initial attempts to access the fused indacenodipyrene scaffold followed a Scholl cyclodehydrogenation strategy (Scheme 1).[24,25] Singly borylated pyrene **3** was cross-coupled with 1,4-dibromo-2,5-bis(dodecyloxy)benzene **4** to give precursor **5** in good yields. However, Scholl cyclodehydrogenation reactions utilizing either $FeCl_3$[26] or DDQ[27] with strong organic acids were found to not give the desired product **6**, but instead resulted in retrieval of starting material. As an alternative, we prepared brominated precursors to enable a palladium-catalyzed arylation reaction strategy.[28,29] Mono-brominated pyrene derivatives **7-9** with varying substituents on the pyrene core were prepared (Supporting Information) and reacted with 2,2'-(2,5-dibromo-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **10**[30] to give precursors **11-13** in modest yields of 29-35 %. Here, $[Pd(PCy_3)_2Cl_2]$ as the catalyst and DBU as base was employed to create the five-membered ring bridges to give **1a-c** in isolated yields of 78-90%. It should be noted that a preliminary route to build up a library of diverse substituted structures from a common precursor was investigated. For example, attempts were made to brominate **1a**, which would have provided a scaffold to easily build a library of structures through cross-coupling chemistry (e.g., **1b** and **1c**). However, these attempts were unsuccessful in preparing pure brominated materials for further utilization. This preliminary difficulty led to the less convenient, yet operational method, of stepwise functionalization we report here.

Scheme 2: Synthesis of small molecule derivatives via Suzuki cross coupling and Heck reaction.



With the small molecule derivatives prepared, the reaction chemistry was applied to preparing ladder conjugated polymers. Pyrene precursors were modified from the single bromine containing monomers **7-9** to dibromo-containing monomers **14** and **15**. Polymerization conditions utilized the same Suzuki-Miyaura conditions with monomer **10** to build up the pyrene containing materials. Recycling preparative gel permeation chromatography (GPC) was used to exclude lower molecular weight material and resulted in collected samples of 10 kDa and 13 kDa (based on GPC with polystyrene standards), for **16** and **17**, respectively. The palladium-catalyzed arylation reaction was applied to **16** and **17** to form the laddered polymers **2a** and **2b**. As expected, the solubility of the resulting materials was significantly reduced owing to the extended planarized surfaces. Ladder polymer **2a** was found to be totally insoluble in common organic solvents such as toluene, chloroform, dichloromethane, tetrahydrofuran and dichloroethane at higher temperatures. However, **2b** was found to give some solubility (~0.05 mg/mL) in hot chloroform for limited processing and characterization.

Scheme 3: Synthesis of conjugated ladder polymers via Suzuki cross coupling and arylation reaction.



Solution based UV/Vis absorption spectra of the indacenodipyrene based materials are shown in Figure 2. Overall, the three small molecule derivatives (**1a-c**) were similar, but with small bathochromic shifts with substitutions consisting of the anisole (8 nm) and thiophene (18 nm). The optical band gaps of the pyrene-based materials, as determined by the onset of film-based absorption from the diffuse reflectance absorption spectra (supporting information) were 2.03 eV, 1.98 eV and 1.90 eV for **1a**, **1b** and **1c,** respectively. The precursor polymer **17** onset is significantly hypsochromically shifted in relation to the ring closed compounds **1a-c**. However, upon the arylation reaction, polymer **2b** shows significant bathochromic shift with an onset of 693 nm in solution with the lowest energy transition (470-600 nm) overlapping with the small molecule analogs. The absorption tails to lower energies and suggests expanded delocalization along the polymer backbone in relation to the dimeric pyrene small molecule derivatives.

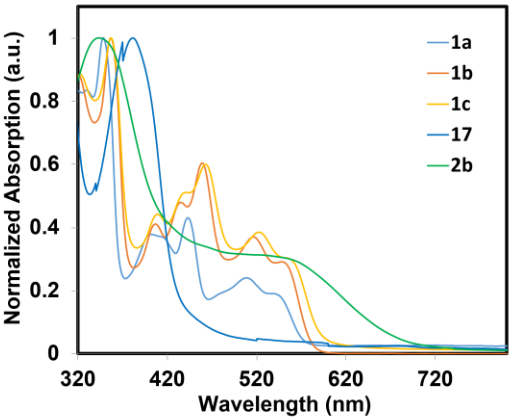


Figure 2: Absorption spectra of small molecules **1a-c** and polymers **17** and **2b** in chloroform.

To further probe the electronic properties of **1a-c**, **16** and **17**, cyclic voltammograms (CV) of the solid films were obtained. Organic films for CV were prepared by drop casting chloroform solutions on a glassy carbon electrode. Analysis of the CV shows the materials have both irreversible oxidation and reduction signals (Figure 3). Utilizing ferrocene as an internal standard, the highest occupied molecular level (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of the materials were evaluated. The HOMO levels ranged from −5.28 eV to −5.39 eV, while the LUMO energies varied between −2.42 to −2.98 eV (Table 1). The optical and electrochemical gaps diverged in absolute value and is presumably owing to the exciton binding energies being considerably different in these systems.[31]

The newly prepared materials were then evaluated in regard to their charge carrier mobilities. Organic field effect transistors with bottom gate and bottom contact arrangements were prepared. Traditional gold contacts deposited on octadecyltrichlorosilane functionalized Si/SiO$_2$ substrates with an active channel of 30 μm were utilized. Films were cast by spin-coating chloroform solutions at 3000 rpm onto the prepared substrates. Typical output and transfer plots of the resulting devices can be found in Figure 4 and Figure 5. The average charge carrier mobilities **1b** and **1c**, as tested in air, were found to be an average of $2.5\text{X}10^{-5}$ and $7.4\text{X}10^{-5}$ $\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$, respectively. No appreciable current was observed for **1a** or polymer **2b**, and were presumed to be owing to inconsistent film formation resulting from poor solubilities. While the charge carrier mobilities in these systems are relatively small, they do demonstrate the materials are active as charge carriers.

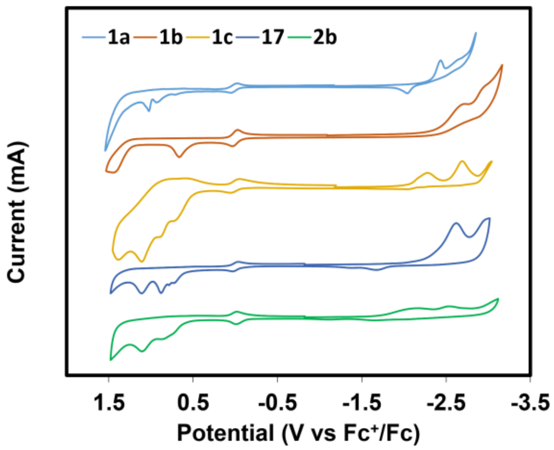


Figure 3: Thin film cyclic voltammetry of **1a-c**, **20** and **2b** in acetonitrile with 0.05 M tetrabutyl ammonium hexafluorophosphate, glassy carbon working electrode, platinum counter electrode, and an Ag/AgCl reference electrode. Scan rate = 100 mV/s. Ferrocene was added as an internal standard and referenced to 0 V.

In conclusion, we have synthesized a series of new indacenodipyrene based small molecule and conjugated ladder polymers by an efficient palladium catalyzed arylation of a dipyrenyl benzene precursor. The small molecule reaction optimization was applied to make conjugated-ladder polymers that possessed bathochromically shifted optical properties and less soluble materials in comparison to the small molecule analogs. The reaction pathway provides a route to new conjugated ladder materials with modest charge carrier mobilities.

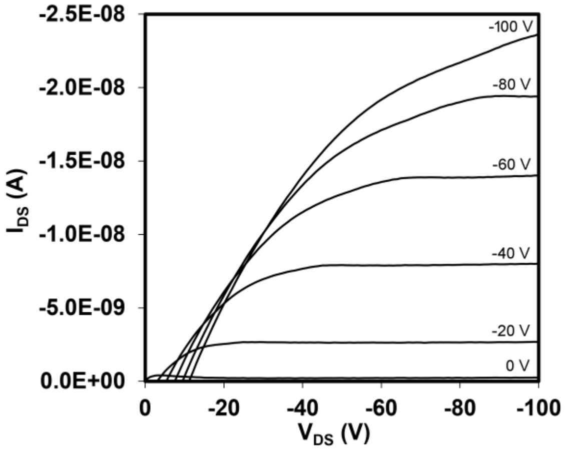


Figure 4: Typical output curves for **1b** showing p-type semiconductor behavior.

Acknowledgments

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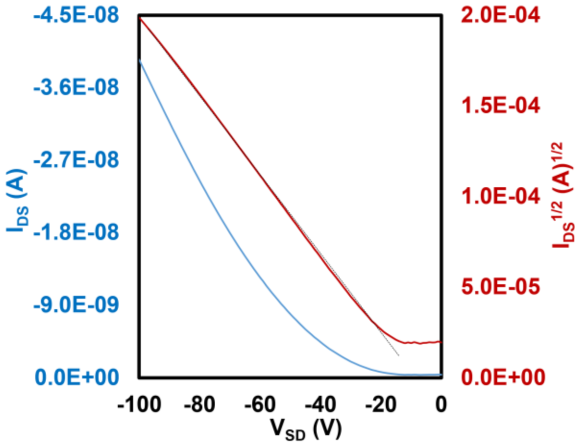

Figure 5: Typical transfer plot for the p-type semiconductor **1b**. V_G = -80V. Average mobility ($h^+ = 2.5 \times 10^{-5}$ cm^2 V^{-1} s^{-1} $\pm 2.1 \times 10^{-6}$).

Table 1. Summary of molecular weight and optoelectronic properties of compounds **1a-c**, **17** and **2b**

Cmpd	$E_{ox/onset}$ (V)	$E_{red/onset}$ (V)	HOMO (eV)	LUMO (eV)	E-chem gap (eV)	λ_{onset} (nm)	Optical gap (eV)
1a	0.59	-2.36	-5.39	-2.44	2.95	610	2.03
1b	0.43	-2.38	-5.23	-2.42	2.81	625	1.98
1c	0.48	-2.01	-5.28	-2.79	2.49	651	1.90
17	0.58	-2.31	-5.38	-2.49	2.89	471	2.63
2b	0.58	-1.82	-5.38	-2.98	2.40	739	1.68

[a] Potentials measured relative to a ferrocenium/ferrocene redox couple used as an internal standard (**Figure 3**). $E_{ox/onset}$ is the onset of oxidation potential, $E_{red/onset}$ is the onset of reduction potential. HOMO and LUMO values calculated on the basis of the oxidation of the ferrocene reference in vacuum (-4.8 eV). Optical gap taken from λ_{onset} of film (SI).

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Supporting Information

Indacenodipyrene Containing Small Molecules and Ladder Polymers

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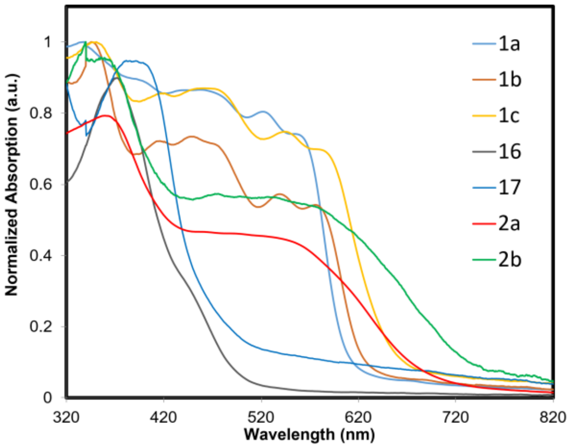
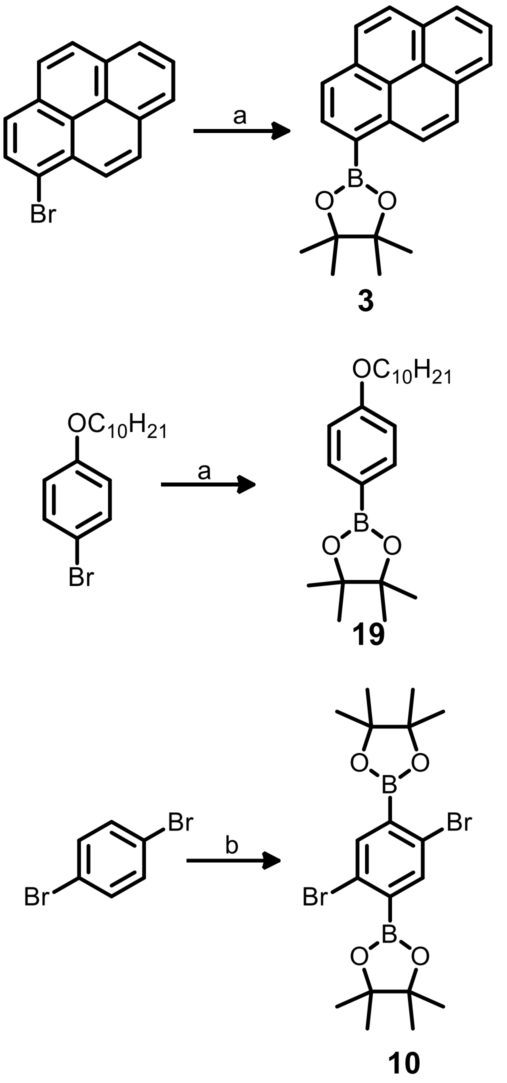


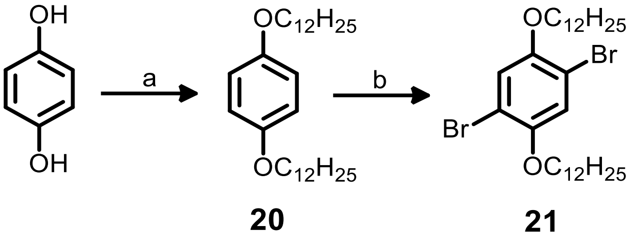
Figure S1. Diffuse reflectance absorption thin film absorption spectra of indacenodipyrene small molecules and polymers.

Scheme S1: Synthesis of Boronic ester derivatives with benzene and pyrene unit



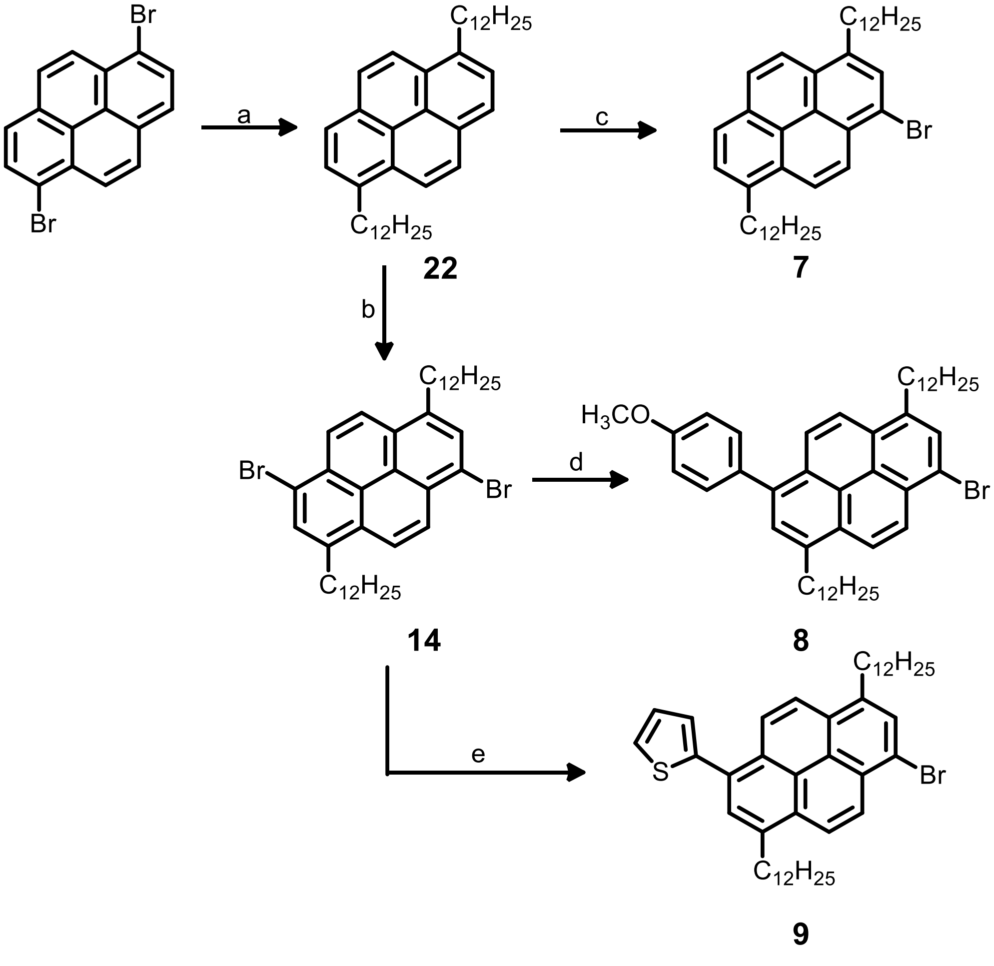
Conditions: a) bis(pinacolato)diborane, Pd(PPh$_3$)$_2$Cl$_2$, KOAc, 1,4-dioxane, 90 ^{0}C, 16 h, 79%; b) bis(pinacolato)diboron, 4,4′-di-*tert*-butyl-2,2′-dipyridyl, (1,5-cyclooctadiene) (methoxy)iridium(I) dimer, cyclohexane, 90 ^{0}C, 16 h, 72%.

Scheme S2: Synthesis of 1,4-dibromo-2,5-bis(dodecyloxy)benzene



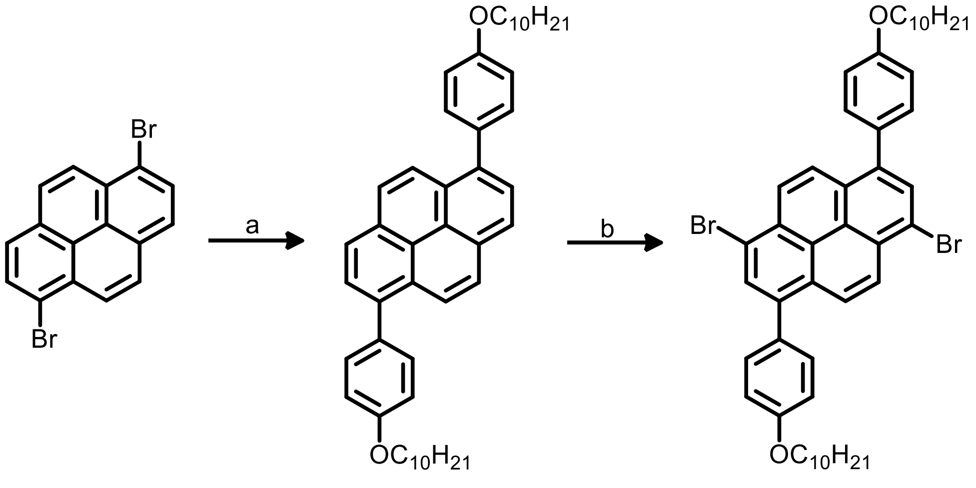
Conditions: a) 1-bromododecane, K_2CO_3, CH_3CN, argon, reflux, 12 h, 85%; b) Br_2, CH_2Cl_2, 0 ^{0}C, rt, overnight, 89%.

Scheme S3: Synthesis of bromide functionalized alkylpyrene derivatives



Conditions: a) 1-bromododecane, Mg turnings, 1,6-dibromopyrene, Ni(dppp)Cl_2, 60 ^{0}C, 36 h, 72%; b) N-bromosuccinimide, DMF, $CHCl_3$, overnight, 84%; c) N-bromosuccinimide, NH_4NO_3, $CHCl_3$, 36 h, 83%; d) 4-methoxyphenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, THF, H_2O, argon, reflux, 16 h, 67%; e) 2-(tributylstannyl)thiophene, $Pd(PPh_3)_4$, toluene, reflux, overnight, 43%.

Scheme S4: Synthesis of 1,6-dibromo-3,8-bis(4-(decyloxy)phenyl)pyrene



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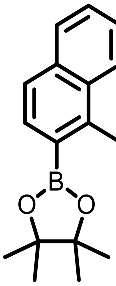
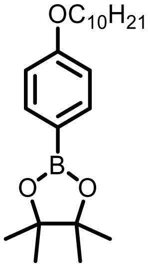
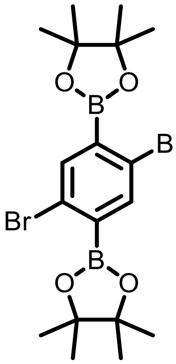
Conditions: a) **3**, Pd(PPh$_3$)$_4$, K$_2$CO$_3$, THF, H$_2$O, reflux, argon, overnight; b) N-bromosuccinimide, DMF, CHCl$_3$, overnight.



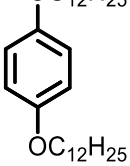
4,4,5,5-tetramethyl-2-(pyren-1-yl)-1,3,2-dioxaborolane (3): In a glove box, 1-bromopyrene (500 mg, 1.80 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (75 mg, 0.11 mmol), bis(pinacolato)diborane (497 mg, 1.96 mmol),KOAc (611 mg, 6.22 mmol) and 20 mL dry 1,4-dioxane were added into a seal tube. The reaction mixture was stirred at 90 ^{0}C for 16 h. After the completion of the reaction, the mixture was poured into water, extracted with CH$_2$Cl$_2$ (30 mL ×3), the resultant organic phase was washed with brine, and dried over anhydrous Na$_2$SO$_4$. After evaporation of the solvent, the residue was purified by flash column chromatography with hexane and 0 to 40% dichloromethane to give 420 mg (72%) of **4** as yellowish solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.09 (d, *J* = 9.2 Hz, 1H), 8.55 (d, *J* = 7.7 Hz, 1H), 8.14 (m, *J* = 35.6, 26.7, 13.4, 7.6 Hz, 7H), 1.51 (s, 12H).



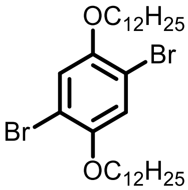
2-(4-(decyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19): In a glove box, 1-bromo-4-decyloxybenzene (500 mg, 1.60 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (67 mg, 0.095 mmol), bis(pinacolato)diborane (446 mg, 1.76 mmol),KOAc (549 mg, 5.59 mmol) and 20 mL dry 1,4-dioxane were added into a seal tube. The reaction mixture was stirred at 90 ^{0}C for 16 h. After the completion of the reaction, the mixture was poured into water, extracted with CH$_2$Cl$_2$ (30 mL ×3), the resultant organic phase was washed with brine, and dried over anhydrous Na$_2$SO$_4$. After evaporation of the solvent, the residue was purified by flash column chromatography with hexane and 0 to 40% dichloromethane to give 456 mg (79%) of **3** as yellowish liquid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 13.1, 6.9 Hz, 2H), 3.99 (t, *J* = 4.5 Hz, 2H), 1.83 – 1.74 (m, 2H), 1.47 (d, *J* = 13.1 Hz, 4H), 1.33 (s, 12H), 1.28 (m, *J* = 3.2 Hz, 10H), 0.89 (t, *J* = 6.9 Hz, 3H).



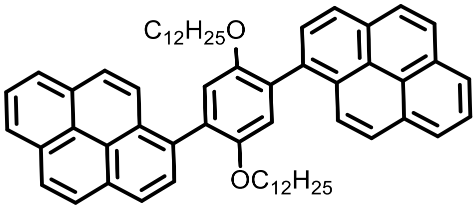
2,2'-(2,5-dibromo-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (10): In a glove box, 1,4-dibromobenzene (1.00 g, 4.24 mmol), (1,5-cyclooctadiene) (methoxy)iridium(I) dimer (28 mg, 0.042 mmol), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (35 mg, 0.13 mmol), bis(pinacolato)diboron (2.70 g, 10.60 mmol) and 25 mL of cyclohexane were added into a seal tube. The reaction mixture was stirred at 90 ^{0}C for 16 h. After cooling to room temperature, the mixture was filtered. The residue was washed with hexane to afford 1.54 g (1.54 g, 73 %) of **5** as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 2H), 1.37 (s, 24H).



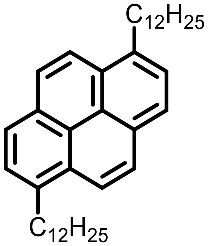
1,4-bis(dodecyloxy)benzene (20): Hydroquinone (1.00 g, 9.08 mmol), 1-bromododecane (4.97 g, 19.98 mmol) and K_2CO_3 (3.77 g, 27.3 mmol) were dissolved in 20 mL acetonitrile under an argon atmosphere. The reaction mixture was stirred at reflux for 36 h. the reaction mixture was cooled to room temperature, filtered, and washed with dichloromethane. The filtrate was concentrated, and the residue was purified by silica gel chromatography with a gradient of 0 to 30% dichloromethane in hexane to give the product as a white solid (85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 4H), 3.89 (t, *J* = 6.6 Hz, 4H), 1.79 – 1.70 (m, 4H), 1.48 – 1.40 (m, 4H), 1.34 – 1.22 (m, 32H), 0.95 – 0.85 (t, 6H).



1,4-dibromo-2,5-bis(dodecyloxy)benzene (21): In an argon environment, to a stirred solution of 1,4-bis(dodecyloxy)benzene (6) (500 mg, 1.20 mmol) in dichloromethane (20 mL) was added dropwise a solution of bromine (0.19 mL, 3.60 mmol) in dichloromethane over 10 minutes min at 0 °C. The reaction was warmed to room temperature and the reaction was stirred at room temperature for overnight. The reaction mixture (an orange suspension) was quenched with sodium thiosulphate. The organic layers were extracted with dichloromethane and dried over $MgSO_4$. After evaporation of the solvent, precipitated into 100 mL methanol to give 610 mg (89%) product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 2H), 3.94 (t, *J* = 6.5 Hz, 4H), 1.84 – 1.75 (m, 4H), 1.46 (m, *J* = 15.3, 7.2 Hz, 4H), 1.35 – 1.22 (m, 30H), 0.88 (t, *J* = 6.9 Hz, 6H).

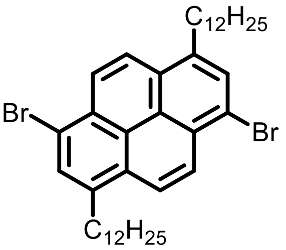


1,1'-(2,5-bis(dodecyloxy)-1,4-phenylene)dipyrene (5): In a glove box, 1,4-dibromo-2,5-bis(dodecyloxy)benzene (7) (100 mg, 0.17 mmol), 4,4,5,5-tetramethyl-2-(1-pyrenyl)-1,3,2-dioxaborolane (135 mg, 0.41 mmol), $Pd(PPh_3)_4$ (11.48 mg, 0.010 mmol) and potassium carbonate (115 mg, 0.83 mmol) were added in dry THF (8 mL) and deionized water (2.0 mL) was added outside the glove box. The resulting mixture was refluxed at 80 ^{0}C for overnight. Upon completion, the reaction was diluted with water, extracted with dichloromethane (10 mL×3), dried on $MgSO_4$. After evaporation of the solvent, the residue was purified by flash column chromatography with hexane and 0 to 30% dichloromethane to give 110 mg (79%) of **8** as yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.26 (dd, 2H), 8.22 (m, *J* = 7.8, 2.9 Hz, 4H), 8.17 (d, *J* = 6.1 Hz, 2H), 8.16 – 8.12 (m, 6H), 8.10 (t, *J* = 1.7 Hz, 1H), 8.04 (m, *J* = 12.1, 8.4, 6.2 Hz, 3H), 7.22 (s, 1H), 7.21 (s, 1H), 3.89 – 3.79 (m, 4H), 1.36 (m, 4H), 1.30 – 1.15 (m, 14H), 1.14 – 0.95 (m, 10H), 0.87 (m, *J* = 7.1 Hz, 18H).^{13}C NMR (101 MHz, $CDCl_3$) δ 150.92, 134.48, 134.46, 131.46, 131.45, 131.12, 131.10, 130.79, 130.77, 130.67, 129.37, 129.34, 128.30, 128.28, 127.49, 127.30, 127.12, 127.05, 126.32, 125.86, 124.99, 124.97, 124.93, 124.92, 124.88, 124.84, 124.43, 118.07, 118.04, 69.82, 69.80, 31.93, 29.55, 29.55, 29.36, 29.35, 29.32, 29.16, 29.06, 25.80, 22.71, 14.16. HRMS (TOF-EI, m/z) calcd. for $C_{62}H_{70}O_2$ [M]+: 846.5376; found: 846.5389.

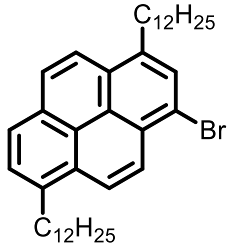


1,6-bis(dodecane)pyrene (22): In a glove box, 1-bromododecane (17) (1.00 g, 4.01 mmol) and magnesium (106 mg, 4.41 mmol), THF (6 mL) and diethyl ether (4 mL) were added into a seal tube. The reaction was stirred at 60 ^{0}C for 36 h. After cooling room temperature, 1,6-dibromopyrene (360 mg, 1.00 mmol) and $Ni(dppp)Cl_2$ (22 mg, 0.041 mmol) was added and the mixture was further stirred 60 ^{0}C for overnight. After cooling to room temperature, the organic layers were extracted with dichloromethane and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified by flash column chromatography with hexane to give 390 mg (72%) of **9** as off white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 9.2 Hz, 2H), 8.08 (d, *J*

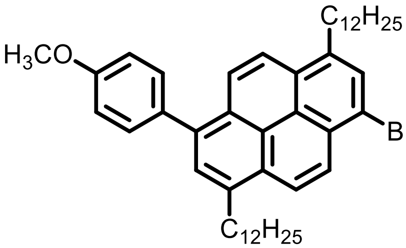
= 5.9 Hz, 2H), 8.04 (d, *J* = 9.3 Hz, 2H), 7.84 (d, *J* = 7.8 Hz, 2H), 3.36 – 3.27 (m, 4H), 1.84 (m, *J* = 15.3, 7.7 Hz, 4H), 1.54 – 1.41 (m, 4H), 1.35 – 1.19 (m, 32H), 0.88 (t, *J* = 8.7, 5.1 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 137.03, 129.48, 128.86, 127.20, 127.15, 125.49, 124.38, 122.54, 33.75, 31.93, 31.91, 29.85, 29.72, 29.69, 29.65, 29.62, 29.38, 29.37, 22.70, 14.13. HRMS (TOF-EI, m/z) calcd. for $C_{40}H_{58}$ [M]+: 538.4539; found: 538.4543.



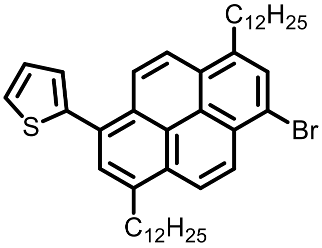
1,6-dibromo-3,8-didodecylpyrene (14): To the solution of 1,6-didodecylpyrene (9) (200 mg, 0.37 mmol) in CHCl$_3$ (10 mL) and DMF (10 mL), NBS (145 mg, 0.81 mmol) was added in oven dried Schlenk flask under argon atmosphere and the resulting reaction mixture was allowed to stir at room temperature for overnight. Then the reaction mixture quenched with methanol (50 mL). The precipitate was filtered and washed with copious amount of acetone to give **10** (216 mg, 84%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.46 (d, *J* = 9.5 Hz, 2H), 8.27 (d, *J* = 9.5 Hz, 2H), 8.14 (s, 2H), 3.33 – 3.27 (t, 4H), 1.86 (m, *J* = 15.3, 7.6 Hz, 4H), 1.51 (m, *J* = 14.8, 6.9 Hz, 4H), 1.28 (m, 32H), 0.89 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.55, 131.69, 128.36, 128.01, 126.19, 126.02, 123.89, 120.31, 33.44, 31.90, 31.71, 29.74, 29.64, 29.61, 29.57, 29.51, 29.33, 22.67, 14.10. HRMS (TOF-EI, m/z) calcd. for $C_{40}H_{56}Br_2$ [M]+: 694.2749; found: 694.2762.



3-bromo-1,6-didodecylpyrene (7): To the solution of 1,6-didodecylpyrene (9) (200 mg, 0.37 mmol) and NH_4NO_3 (9 mg, 0.11 mmol) in CHCl$_3$ (10 mL), NBS (66 mg, 0.37 mmol) was added in oven dried Schlenk flask under argon atmosphere and the resulting reaction mixture was allowed to stir at room temperature for overnight. Then the reaction mixture quenched with water (20 mL) and extracted with DCM (3 x 20 mL). The combined organic layers were dried over MgSO$_4$, filtered and evaporated under reduced pressure to give **11** (190 mg (83%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.42 (d, *J* = 9.5 Hz, 1H), 8.31 (d, *J* = 9.5 Hz, 1H), 8.17 – 8.04 (m, 4H), 7.87 (d, *J* = 7.8 Hz, 1H), 3.36 – 3.24 (tt, 4H), 1.84 (m, *J* = 14.9, 7.5 Hz, 4H), 1.48 (m, *J* = 13.7, 6.6 Hz, 4H), 1.34 – 1.19 (m, 32H), 0.88 (t, *J* = 13.1, 6.9 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 137.92, 137.77, 130.97, 129.56, 128.67, 128.49, 127.85, 127.77, 127.50, 126.77, 125.64, 125.17, 124.87, 124.12, 122.31, 119.42, 33.72, 33.43, 31.95, 31.91, 31.65, 29.80, 29.78, 29.66, 29.63, 29.60, 29.57, 29.54, 29.34, 22.68, 14.11. HRMS (TOF-EI, m/z) calcd. for $C_{40}H_{57}Br$ [M]+: 616.3644; found: 616.3657.

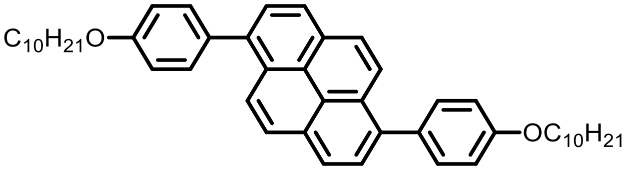


1-bromo-3,8-didodecyl-6-(4-methoxyphenyl)pyrene (8): In a glove box, 1,6-dibromo-3,8-didodecylpyrene (10) (100 mg, 0.14 mmol), 4-methoxyphenylboronic acid (21.8 mg, 0.14 mmol), $Pd(PPh_3)_4$ (9.95 mg, 0.0086 mmol) and potassium carbonate (100 mg, 0.72 mmol) were added in dry THF (5 mL) and deionized water (1 mL) was added outside the glove box. The resulting mixture was refluxed at 80 ^{0}C for overnight. Upon completion, the reaction was diluted with water, extracted 3 times with DCM, dried on $MgSO_4$. After evaporation of the solvent, the residue was purified by flash column chromatography with hexane and 0 to 30% dichloromethane to give 69 mg (67%) of **12** as yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 9.5 Hz, 1H), 8.33 (d, *J* = 9.5 Hz, 1H), 8.18 (d, *J* = 7.5 Hz, 1H), 8.09 (d, *J* = 9.8 Hz, 2H), 7.85 (s, 1H), 7.60 – 7.50 (d, 2H), 7.14 – 7.06 (d, 2H), 3.94 (s, 3H), 3.38 – 3.31 (t, 2H), 3.28 – 3.21 (t, 2H), 1.84 (m, *J* = 15.4, 7.8 Hz, 4H), 1.47 (m, *J* = 22.7, 7.5 Hz, 4H), 1.25 (m, 32H), 0.87 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.99, 137.64, 137.49, 137.25, 133.53, 131.63, 131.13, 129.62, 128.35, 128.17, 127.96, 127.08, 125.52, 125.42, 125.34, 124.10, 122.24, 119.41, 113.80, 55.42, 33.79, 33.44, 31.95, 31.91, 31.65, 29.87, 29.77, 29.66, 29.65, 29.63, 29.62, 29.59, 29.57, 29.53, 29.34, 22.68, 14.12. HRMS (TOF-EI, m/z) calcd. for $C_{47}H_{63}BrO$ [M]+: 722.4062; found: 722.4076.

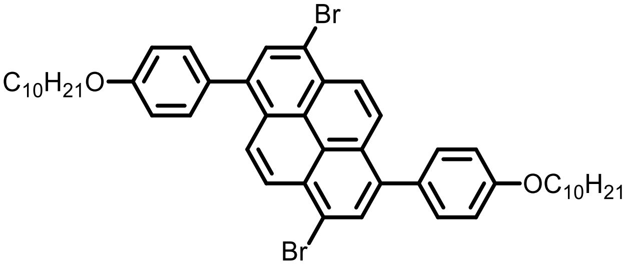


2-(6-bromo-3,8-didodecylpyren-1-yl)thiophene (9): In a glove box, 1,6-dibromo-3,8-didodecylpyrene (10) (100 mg, 0.14 mmol), 2-(tributylstannyl)thiophene (53.5 mg, 0.14 mmol) and $Pd(PPh_3)_4$ (9.95 mg, 0.0086 mmol) were added in dry toluene (5 mL). The resulting mixture was refluxed at 110 ^{0}C for overnight. Upon completion, the reaction was diluted with water, extracted 3 times with DCM, dried on $MgSO_4$. After evaporation of the solvent, the residue was purified by flash column chromatography with hexane and 0 to 10% dichloromethane to give 44 mg (43%) of **13** as yellowish solid. ^{1}H NMR (400 MHz, CDCl3): δ 8.47 (d, *J* = 9.5 Hz, 1H), 8.22 (d, *J* = 10.2 Hz, 2H), 8.08 (dd, *J* = 11.6, 8.5 Hz, 2H), 7.95 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 5.1 Hz, 1H), 7.38 (d, *J* = 3.5 Hz, 1H), 3.32 (q, *J* = 15.2, 7.2 Hz, 4H), 1.85 (m, *J* = 15.0, 7.6

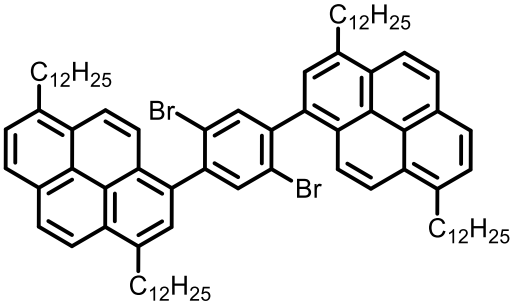
Hz, 4H), 1.57 – 1.43 (m, 4H), 1.26 (m, 32H), 0.88 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.43, 138.02, 137.19, 131.31, 130.31, 129.81, 128.66, 128.30, 128.13, 128.03, 128.02, 127.60, 127.43, 126.89, 126.18, 126.05, 125.36, 125.03, 124.01, 122.81, 119.78, 33.72, 33.45, 31.92, 31.70, 29.66, 29.65, 29.63, 29.59, 29.35, 22.69, 14.13. HRMS (TOF-EI, m/z) calcd. for $C_{44}H_{59}BrS$ [M]+: 698.3521; found: 698.3537.



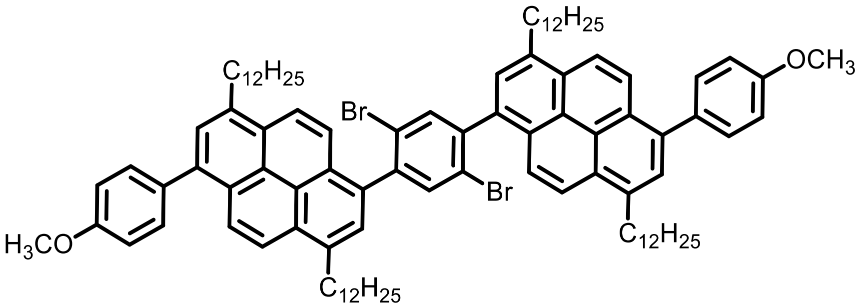
1,6-bis(4-(decyloxy)phenyl)pyrene (23): In a glove box, 1,6-dibromopyrene (100 mg, 0.28 mmol), 2-(4-(decyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3) (220.2 mg, 0.61 mmol), $Pd(PPh_3)_4$ (19.25 mg, 0.017 mmol) and potassium carbonate (193 mg, 1.39 mmol) were added in dry THF (8 mL) and deionized water (1.6 mL) was added outside the glove box. The resulting mixture was refluxed at 80 ^{0}C for overnight. Upon completion, the reaction was diluted with water, extracted 3 times with DCM, dried on $MgSO_4$. After evaporation of the solvent, the residue was purified by flash column chromatography with hexane and 0 to 30% dichloromethane to give 91 mg (49%) of **14** as yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 11.2, 8.6 Hz, 4H), 7.99 (dd, *J* = 24.0, 8.5 Hz, 4H), 7.56 (4, *J* = 8.5 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 4H), 4.09 (t, *J* = 6.6 Hz, 4H), 1.91 – 1.83 (m, *J* = 14.8, 6.9 Hz, 4H), 1.48 – 1.19 (m, 28H), 0.90 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.57, 137.53, 133.43, 131.60, 130.19, 128.95, 127.80, 127.29, 125.30, 125.22, 124.34, 114.40, 68.16, 31.93, 29.63, 29.60, 29.46, 29.38, 29.35, 26.14, 22.70, 14.14. HRMS (TOF-EI, m/z) calcd. for $C_{48}H_{58}O_2$ [M]+: 666.4437; found: 666.4423.



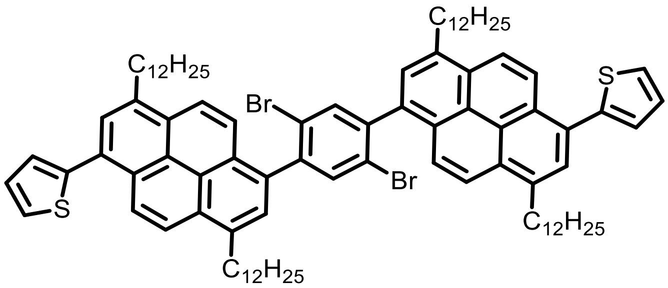
1,6-dibromo-3,8-bis(4-(decyloxy)phenyl)pyrene (15): To the solution of 1,6-bis(4-(decyloxy)phenyl)pyrene (14) 80 mg, 0.12 mmol) in $CHCl_3$ (5 mL)and DMF (5 mL), NBS (53 mg, 0.30 mmol) was added in oven dried Schlenk flask under argon atmosphere and the resulting reaction mixture was allowed to stir at room temperature for overnight. Then the reaction mixture quenched with methanol (50 mL). The precipitate was filtered and washed with copious amount of acetone to give **15** (71 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.39 (d, *J* = 9.5 Hz, 2H), 8.26 (s, 2H), 8.24 – 8.21 (d, 2H), 7.54 – 7.48 (d, 4H), 7.12 – 7.06 (d, 4H), 4.08 (t, *J* = 6.6 Hz, 4H), 1.92 – 1.83 (m, 4H), 1.53 (m, *J* = 15.2, 7.4 Hz, 4H), 1.41 – 1.26 (m, 24H), 0.91 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.98, 138.72, 132.26, 131.65, 131.57, 128.66, 128.40, 126.61, 126.06, 126.01, 120.20, 114.57, 68.20, 31.92, 29.63, 29.60, 29.45, 29.35, 29.33, 26.12, 22.71, 14.14. HRMS (TOF-EI, m/z) calcd. for $C_{48}H_{56}Br_2O_2$ [M]+: 822.2647; found: 822.2667.



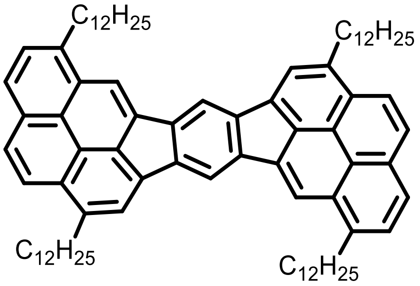
3,3'-(2,5-dibromo-1,4-phenylene)bis(1,6-didodecylpyrene) (11): In a glove box, 3-bromo-1,6-didodecylpyrene (11) (50 mg, 0.081 mmol), 2,2'-(2,5-dibromo-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5) (19.7 mg, 0.040 mmol), $Pd(PPh_3)_4$ (2.80 mg, 0.0024 mmol), potassium carbonate (28.06 mg, 0.20 mmol) and 1 drop of aliquot 336 were added in dry toluene (1.8 mL) and deionized water (0.60 mL) was added outside the glove box. The resulting mixture was refluxed at 110 ^{0}C for overnight. Upon completion, the reaction was diluted with water, extracted 3 times with DCM, dried on $MgSO_4$. After evaporation of the solvent, the residue was purified by flash column chromatography with hexane and 0 to 20% dichloromethane to give 33 mg (32%) of **16** as yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 – 8.26 (m, 4H), 8.18 – 8.11 (m, 4H), 8.01 – 7.86 (m, 8H), 3.50 – 3.28 (m, 8H), 2.00 – 1.83 (m, 8H), 1.58 – 1.47 (m, 8H), 1.36 – 1.19 (m, 64H), 0.94 – 0.82 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.95, 137.55, 137.53, 136.48, 136.47, 135.93, 134.07, 129.71, 129.22, 128.68, 128.66, 128.59, 128.58, 127.76, 127.51, 127.48, 127.15, 127.13, 125.62, 124.99, 124.98, 124.64, 124.61, 123.38, 123.36, 123.28, 123.19, 122.49, 33.84, 33.79, 33.73, 32.02, 31.98, 31.89, 31.79, 31.72, 29.91, 29.87, 29.86, 29.80, 29.66, 29.63, 29.61, 29.60, 29.33, 29.32, 22.66, 14.08. HRMS (TOF-EI, m/z) calcd. for $C_{86}H_{116}Br_2$ [M]+: 1306.7522; found: 1306.7491.



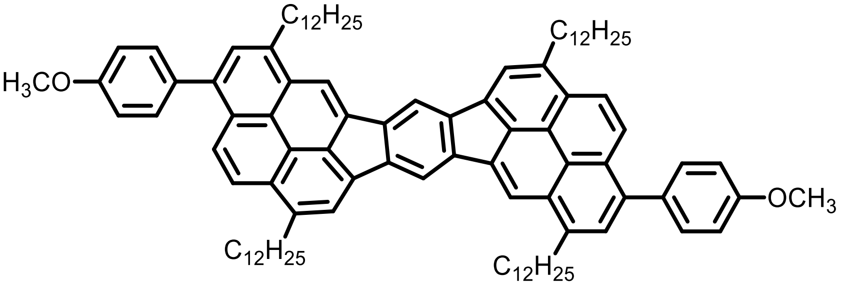
8,8'-(2,5-dibromo-1,4-phenylene)bis(1,6-didodecyl-3-(4-methoxyphenyl)pyrene) (12): In a glove box, 1-bromo-3,8-didodecyl-6-(4-methoxyphenyl)pyrene (12) (50 mg, 0.069 mmol), 2,2'-(2,5-dibromo-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5) (16.8 mg, 0.035 mmol), $Pd(PPh_3)_4$ (2.40 mg, 0.0021 mmol), potassium carbonate (23.9 mg, 0.17 mmol) and 1 drop of aliquot 336 were added in dry toluene (1.8 mL) and deionized water (0.60 mL) was added outside the glove box. The resulting mixture was refluxed at 110 ^{0}C for overnight. Upon completion, the reaction was diluted with water, extracted 3 times with DCM, dried on $MgSO_4$. After evaporation of the solvent, the residue was purified by flash column chromatography with hexane and 0 to 30% dichloromethane to give 36 mg (35%) of **17** as yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 – 8.22 (m, 6H), 8.01 – 7.85 (m, 8H), 7.64 – 7.55 (m, 4H), 7.17 – 7.10 (m, 4H), 4.01 – 3.89 (s, 6H), 3.48 – 3.27 (m, 8H), 1.92 (m, *J* = 17.6, 8.7 Hz, 8H), 1.63 – 1.45 (m, 8H), 1.36 – 1.18 (m, 64H), 0.96 – 0.80 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.96, 143.03, 137.30, 137.27, 137.06, 137.03, 136.23, 136.22, 135.89, 134.10, 133.78, 131.69, 129.36, 129.03, 128.66, 127.95, 127.92, 127.49, 127.46, 127.19, 127.18, 126.02, 126.01, 125.88, 125.66, 123.47, 123.45, 123.24, 123.15, 122.45, 113.81, 55.44, 31.92, 29.69, 29.65, 29.62, 29.36, 22.69, 14.13. HRMS (TOF-EI, m/z) calcd. for $C_{100}H_{128}Br_2O_2$ [M]+: 1518.8281; found: 1518.8276.



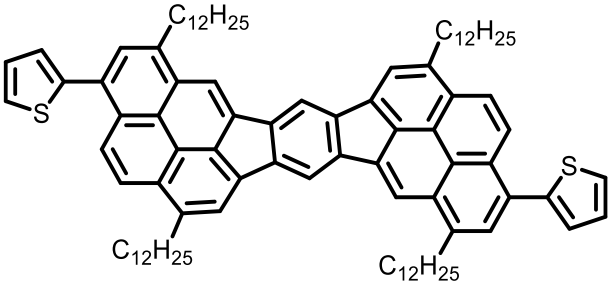
2,2'-((2,5-dibromo-1,4-phenylene)bis(3,8-didodecylpyrene-6,1-diyl))dithiophene (13): In a glove box, 2-(6-bromo-3,8-didodecylpyren-1-yl)thiophene (13) (40 mg, 0.057 mmol), 2,2'-(2,5-dibromo-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5) (13.9 mg, 0.029 mmol), $Pd(PPh_3)_4$ (1.98 mg, 0.0017 mmol), potassium carbonate (19.8 mg, 0.14 mmol) and 1 drop of aliquot 336 were added in dry toluene (1.5 mL) and deionized water (0.50 mL) was added outside the glove box. The resulting mixture was refluxed at 110 ^{0}C for overnight. Upon completion, the reaction was diluted with water, extracted 3 times with DCM, dried on $MgSO_4$. After evaporation of the solvent, the residue was purified by flash column chromatography with hexane and 0 to 20% dichloromethane to give 24 mg (29%) of **18** as yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 – 8.53 (d, 2H), 8.36 – 8.26 (m, 4H), 8.04 – 7.92 (m, 8H), 7.54 (m, *J* = 5.3, 3.2, 1.1 Hz, mH), 7.41 (m, *J* = 3.4, 1.2 Hz, 2H), 7.33 – 7.27 (m, 2H), 3.40 (m, *J* = 19.3, 11.4 Hz, 8H), 2.01 – 1.83 (m, 8H), 1.64 – 1.46 (m, 8H), 1.24 (m, *J* = 19.6 Hz, 64H), 0.96 – 0.78 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.98, 142.72, 136.99, 136.97, 136.63, 135.91, 134.41, 130.05, 130.03, 129.63, 129.60, 129.01, 128.85, 128.67, 128.65, 127.97, 127.75, 127.73, 127.46, 127.42, 126.08, 125.74, 125.28, 125.03, 123.45, 123.43, 123.17, 123.08, 123.00, 33.80, 31.91, 29.68, 29.64, 29.61, 29.35, 22.68, 14.12. HRMS (TOF-EI, m/z) calcd. for $C_{94}H_{120}Br_2S_2$ [M]+: 1470.7193; found: 1470.7173.



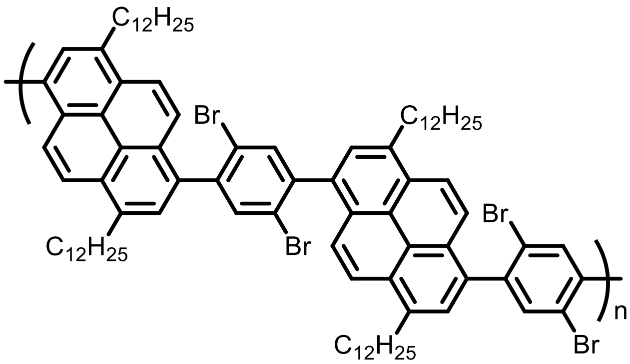
5,9,14,18-tetradodecyl-s-indaceno[1,2,3-cd:5,6,7-c'd']dipyrene (1a): In the glove box, 3,3'-(2,5-dibromo-1,4-phenylene)bis(1,6-didodecylpyrene) (16) (20 mg, 0.015 mmol), Pd(PCy_3)$_2$$Cl_2$ (10.0 mg, 0.014 mmol), DBU (0.10 mL), and DMA (2 mL) were added to a 10 mL seal tube. The seal tube was removed from the glove box and placed into a preheated oil bath where it was heated at 140 °C for overnight. After cooling, the reaction mixture was poured into 100 mL methanol, filtered, washed with copious amount of acetone and dried over high vacuum to give the product 15 mg (86%) as brick red solid. ^{1}H NMR (300MHz, $C_2D_2Cl_4$, 80 ^{0}C): δ 8.28 (s, 2H), 8.13 (s, 2H), 7.77 (s, 2H), 7.63 (d, *J* = 9.5 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 9.1 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 2.93 (t, *J* = 7.4 Hz, 4H), 2.85 (t, *J* = 7.6 Hz, 4H), 1.48 – 1.36 (m, 8H), 1.00 (m, 8H), 0.71 (m, *J* = 25.7 Hz, 64H), 0.25 (t, *J* = 6.2 Hz, 12H). HRMS (TOF-EI, m/z) calcd. for $C_{86}H_{114}$ [M]+: 1146.8999; found: 1146.8976.



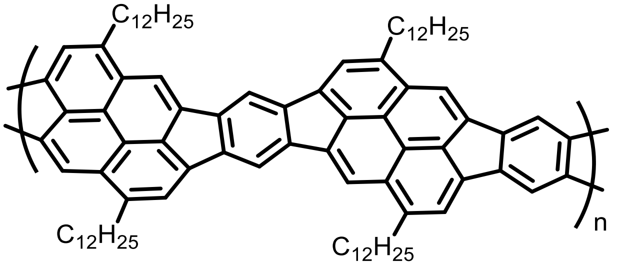
5,9,14,18-tetradodecyl-3,12-bis(4-methoxyphenyl)-s-indaceno[1,2,3-cd:5,6,7-c'd']dipyrene (1b): In the glove box, 8,8'-(2,5-dibromo-1,4-phenylene)bis(1,6-didodecyl-3-(4-methoxyphenyl)pyrene) (17) (20 mg, 0.013 mmol), Pd(PCy_3)$_2$$Cl_2$ (8.70 mg, 0.012 mmol), DBU (0.10 mL), and DMA (2 mL) were added to a 10 mL seal tube. The seal tube was removed from the glove box and placed into a preheated oil bath where it was heated at 140 °C for overnight. After cooling, the reaction mixture was poured into 100 mL methanol, filtered, washed with copious amount of acetone and dried over high vacuum to give the product 16 mg (90%) as red solid. ^{1}H NMR (300MHz, $C_2D_2Cl_4$, 60 ^{0}C) δ 8.33 (s, 2H), 8.18 (s, 2H), 7.80 (s, 2H), 7.57 (q, *J* = 9.3 Hz, 4H), 7.28 (s, 2H), 7.01 (d, *J* = 8.2 Hz, 4H), 6.52 (d, *J* = 8.1 Hz, 4H), 3.40 – 3.28 (s, 6H), 2.96 (t, 4H), 2.83 (t, 4H), 1.42 (m, *J* = 27.4 Hz, 8H), 0.99 (m, 8H), 0.67 (m, 64H), 0.25 (t, *J* = 5.2 Hz, 12H). HRMS (TOF-EI, m/z) calcd. for $C_{100}H_{126}O_2$ [M]+: 1358.9758; found: 1358.9736.



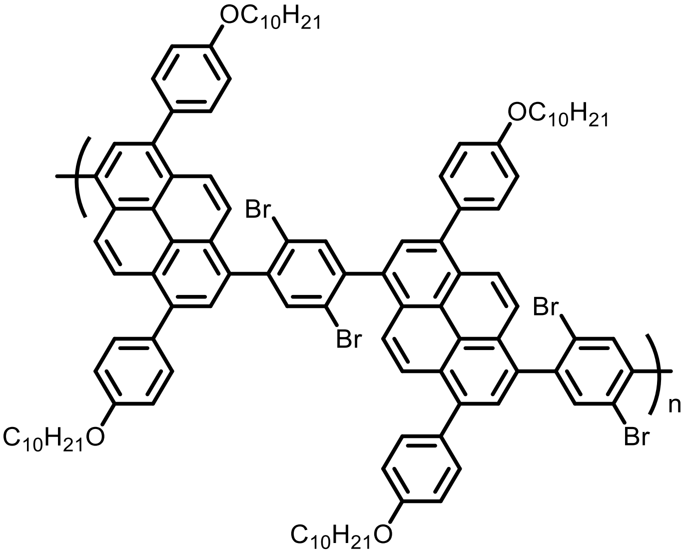
2,2'-(5,9,14,18-tetradodecyl-s-indaceno[1,2,3-cd:5,6,7-c'd']dipyrene-3,12-diyl)dithiophene (1c): In the glove box, 2,2'-((2,5-dibromo-1,4-phenylene)bis(3,8-didodecylpyrene-6,1-diyl))dithiophene (18) (20 mg, 0.014 mmol), Pd(PCy_3)$_2$$Cl_2$ (9 mg, 0.012 mmol), DBU (0.10 mL), and DMA (2 mL) were added to a 10 mL seal tube. The seal tube was removed from the glove box and placed into a preheated oil bath where it was heated at 140 °C for overnight. After cooling, the reaction mixture was poured into 100 mL methanol, filtered, washed with copious amount of acetone and dried over high vacuum to give the product 14 mg (78%) as red solid. ^{1}H NMR (300MHz, $C_2D_2Cl_4$, 60 ^{0}C) δ 8.23 (s, 2H), 8.10 (s, 2H), 7.83 (d, *J* = 9.6 Hz, 2H), 7.75 (s, 2H), 7.62 (d, *J* = 9.7 Hz, 2H), 7.39 (s, 2H), 6.94 (d, *J* = 5.1 Hz, 2H), 6.81 (d, 2H), 6.67 (t, *J* = 4.6 Hz, 2H), 2.89 (d, *J* = 8.0 Hz, 2H), 2.82 (d, *J* = 5.9 Hz, 2H), 1.48 – 1.32 (m, 5H), 1.06 – 0.94 (m, 5H), 0.67 (s, 41H), 0.26 (d, *J* = 5.1 Hz, 6H). HRMS (TOF-EI, m/z) calcd. for $C_{94}H_{118}S_2$ [M]+: 1310.8675; found: 1310.8713.



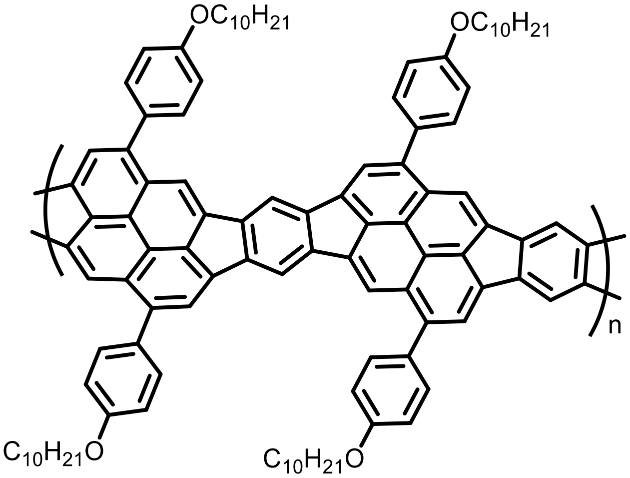
Poly[3-(2,5-dibromophenyl)-1,6-didodecylpyrene] (16): In a glove box, 1,6-dibromo-3,8-didodecylpyrene (10) (50 mg, 0.072 mmol), 2,2'-(2,5-dibromo-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5) (35 mg, 0.072 mmol), Pd(PPh_3)$_4$ (8.32 mg, 0.0072 mmol), potassium carbonate (50.04 mg, 0.36 mmol) and 1 drop of aliquot 336 were added in dry toluene (1.8 mL) and deionized water (0.60 mL) was added outside the glove box. The resulting mixture was refluxed at 110 ^{0}C for 3 days. Upon completion, the reaction was diluted with dichloromethane and water and extracted 3 times with DCM. After evaporation of the solvent, the reaction mixture was precipitated into 100 mL methanol, filtered, washed with copious amount of acetone and dried over high vacuum. Recycling preparative GPC was used to further purify the polymer to 14 mg (25%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 7.59 (m, *J* = 167.6 Hz, 16H), 3.66 – 2.90 (m, 8H), 2.07 – 1.71 (m, 8H), 1.38 – 1.06 (m, 72H), 0.90– 0.76 (m, 12H).



Poly[5,12-didodecylindeno[1,2,3-cd]pyrene] (2a): In the glove box, Poly[3-(2,5-dibromophenyl)-1,6-didodecylpyrene] (19) (14 mg, 0.0089 mmol), $Pd(PCy_3)_2Cl_2$ (6 mg, 0.0080 mmol), DBU (0.10 mL), and DMA (2 mL) were added to a 10 mL seal tube. The seal tube was removed from the glove box and placed into a preheated oil bath where it was heated at 140 °C for overnight. After cooling, the reaction mixture was poured into 100 mL methanol, filtered, washed with copious amount of acetone, dichloromethane and dried over high vacuum to give 8 mg (70%) as purple solid. We are unable to get molecular weight and NMR spectrum due to the insolubility of polymer in common organic solvent like as chloroform, dichloromethane, tetrahydrofuran, 1,1,2,2-dichloroethane.

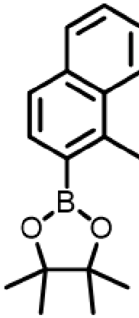


Poly[1,6-bis(4-(decyloxy)phenyl)-3-(2,5-dibromophenyl)pyrene] (17): In a glove box, 1,6-dibromo-3,8-bis(4-(decyloxy)phenyl)pyrene (15) (50 mg, 0.061 mmol), 2,2'-(2,5-dibromo-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5) (29.57 mg, 0.061 mmol), $Pd(PPh_3)_4$ (7.05 mg, 0.0061 mmol), potassium carbonate (42.40 mg, 0.31 mmol) and 1 drop of aliquot 336 were added in dry toluene (1.8 mL) and deionized water (0.60 mL) was added outside the glove box. The resulting mixture was refluxed at 110 ^{0}C for 3 days. Upon completion, the reaction was diluted with dichloromethane and water and extracted 3 times with DCM. After evaporation of the solvent, the reaction mixture was precipitated into 100 mL methanol, filtered, washed with copious amount of acetone and dried over high vacuum. Recycling preparative GPC was used to further purify the polymer to 19 mg (35%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 7.48 (m, *J* = 124.5 Hz, 24H), 7.09 – 6.96 (m, 8H), 4.09 – 3.80 (m, 8H), 1.88 – 1.64 (m, 8H), 1.55 – 1.39 (m, *J* = 28.3 Hz, 8H), 1.31 – 1.12 (m, 48H), 0.86 – 0.74 (m, 12H).



5,12-bis(4-(decyloxy)phenyl)indeno[1,2,3-cd]pyrene (2b): In the glove box, Poly[1,6-bis(4-(decyloxy)phenyl)-3-(2,5-dibromophenyl)pyrene] (20) (15 mg, 0.0084 mmol), $Pd(PCy_3)_2Cl_2$ (6 mg, 0.0075 mmol), DBU (0.10 mL), and DMA (2 mL) were added to a 10 mL seal tube. The seal tube was removed from the glove box and placed into a preheated oil bath where it was heated at 140 °C for overnight. After cooling, the reaction mixture was poured into 100 mL methanol, filtered, washed with copious amount of acetone, dichloromethane and dried over high vacuum to give 9 mg (75%) as purple solid. We are unable to get molecular weight due to the almost insolubility of polymer in tetrahydrofuran. But we have found ^{1}H NMR owing to very tiny solubility of polymer in chloroform. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 7.49 (m, *J* = 71.2 Hz, 20H), 7.15 – 6.84 (m, 8H), 4.46 – 3.81 (m, 8H), 1.38 – 0.65 (m, *J* = 91.9, 64.1, 48.2 Hz, 76H).

Compound 3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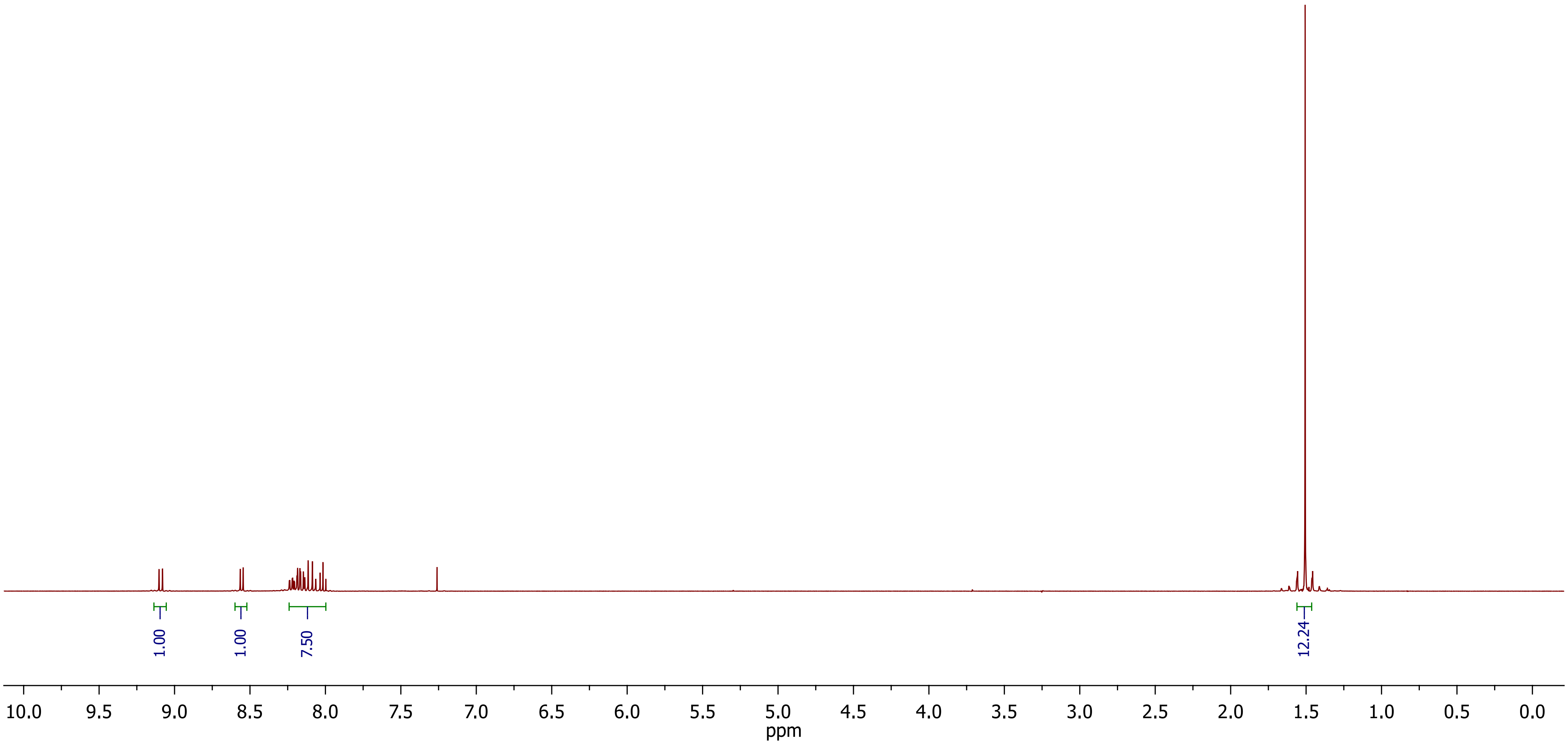
O
O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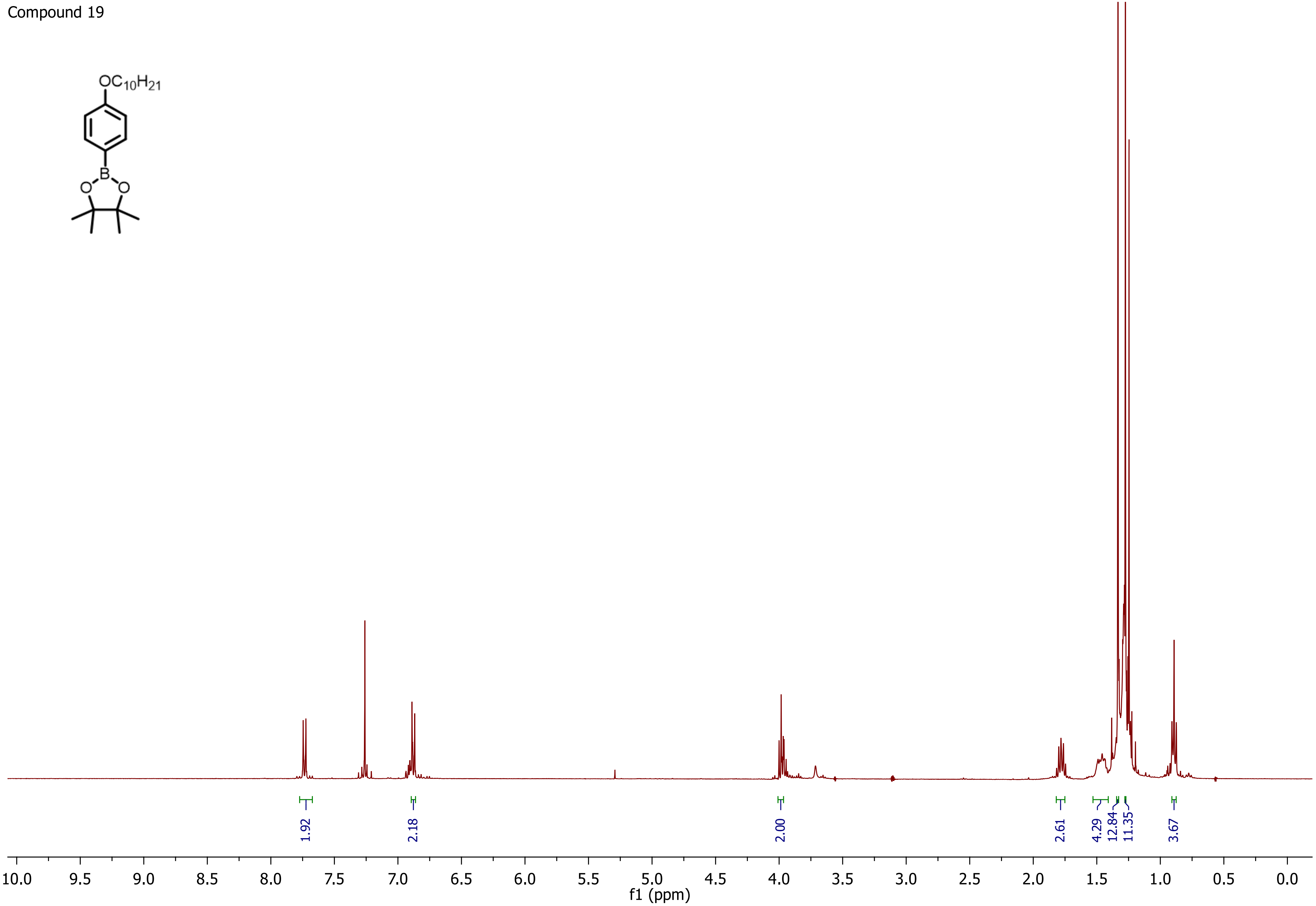
ppm

Compound 19



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7.5
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5.0
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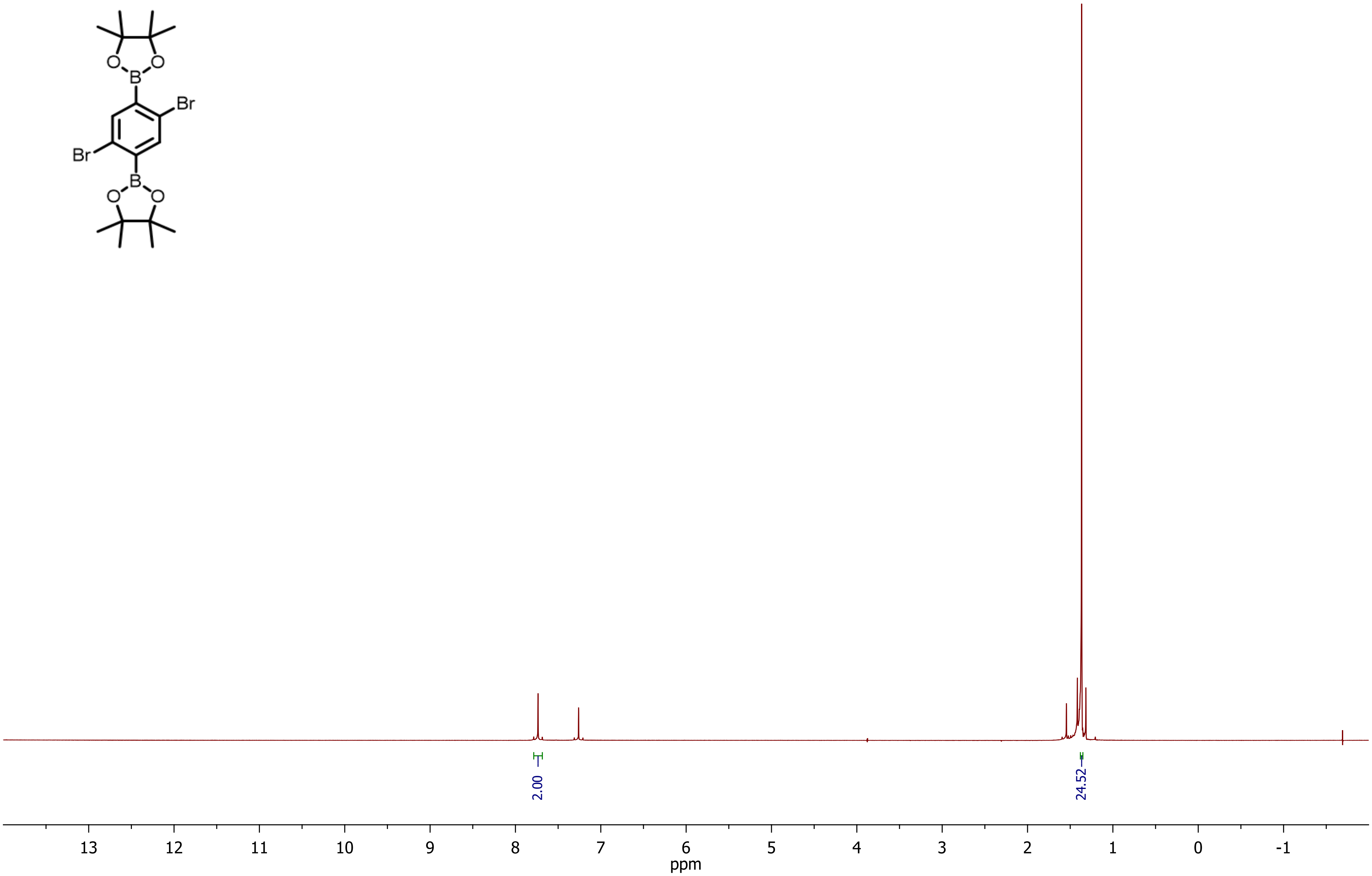
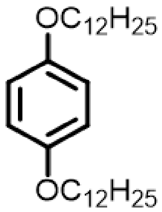
f1 (ppm)

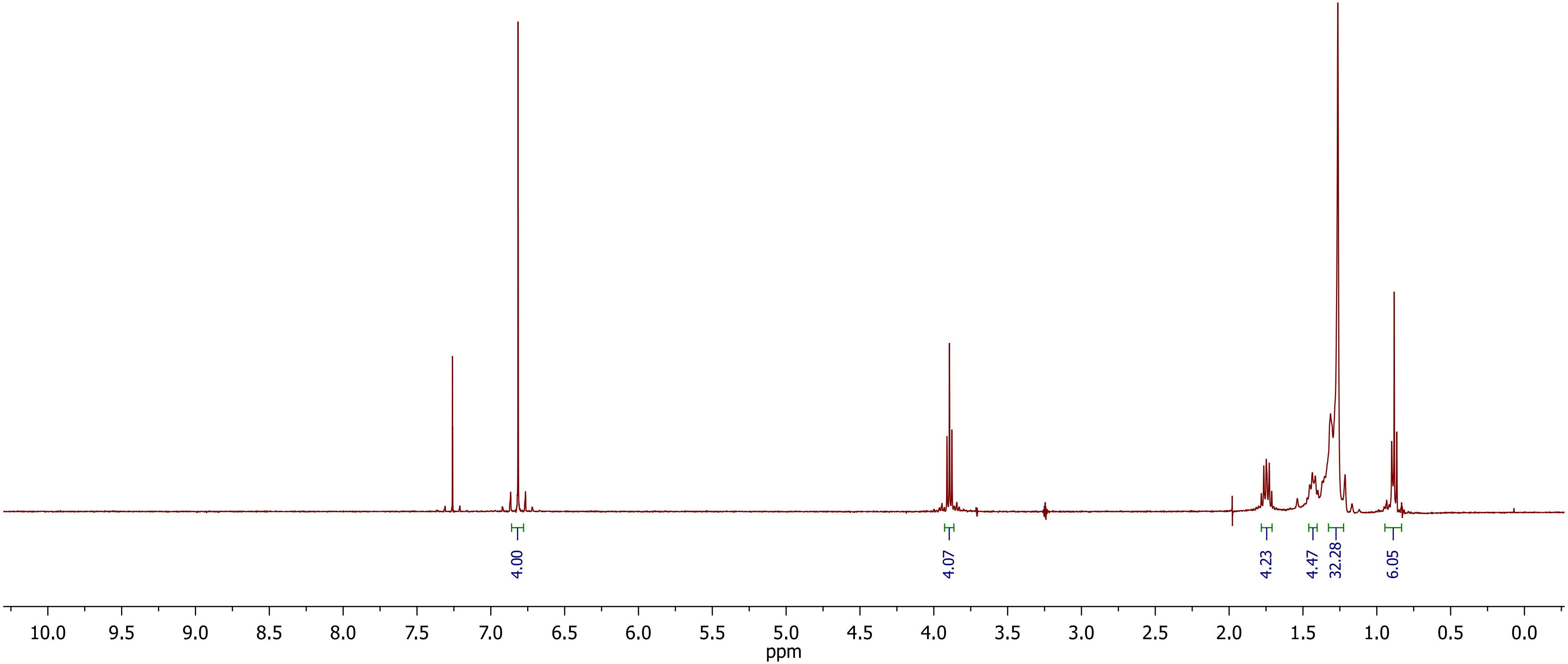
Compound 10



Compound 20



OC12H25
OC12H25



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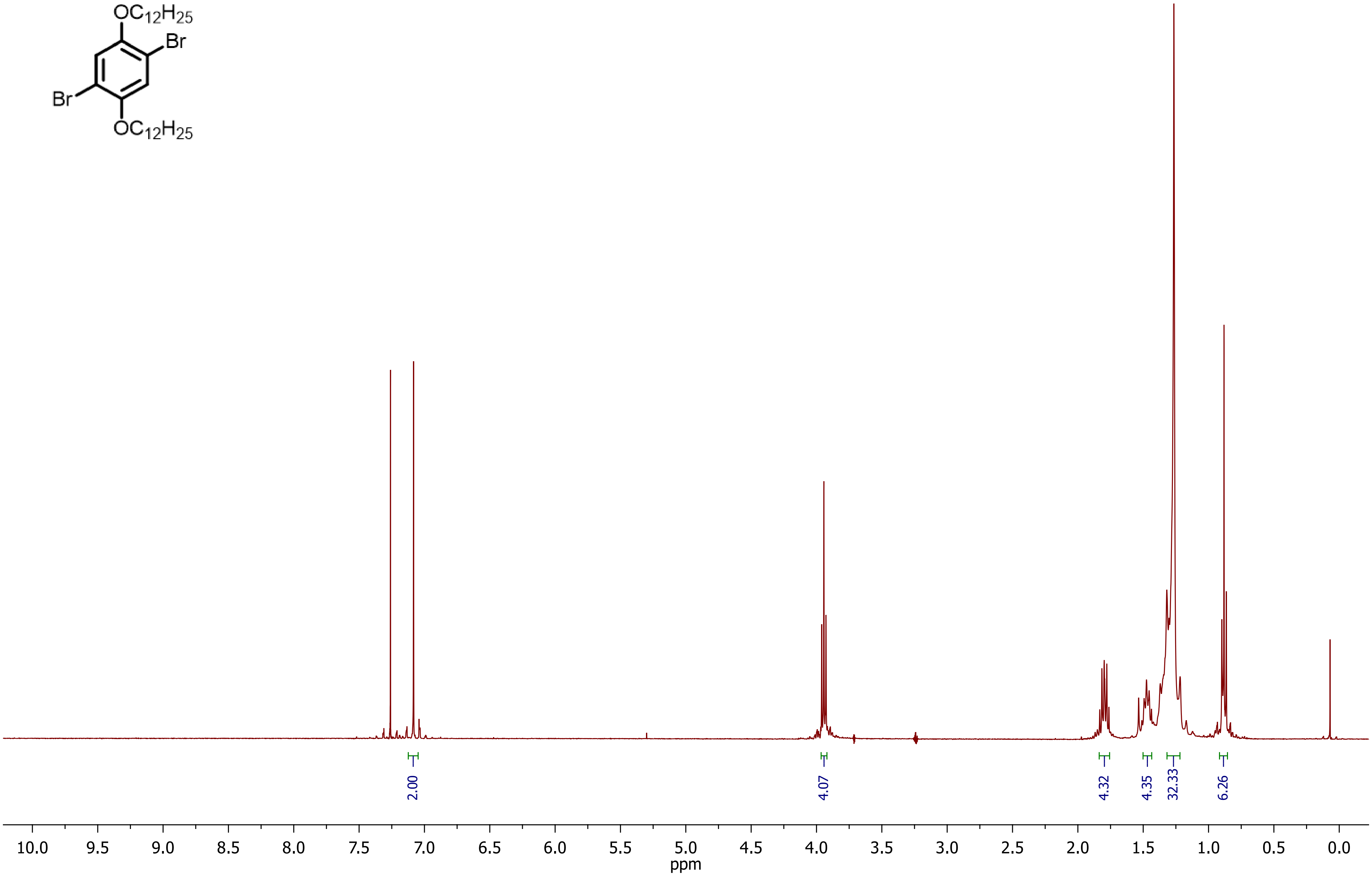
ppm

Compound 21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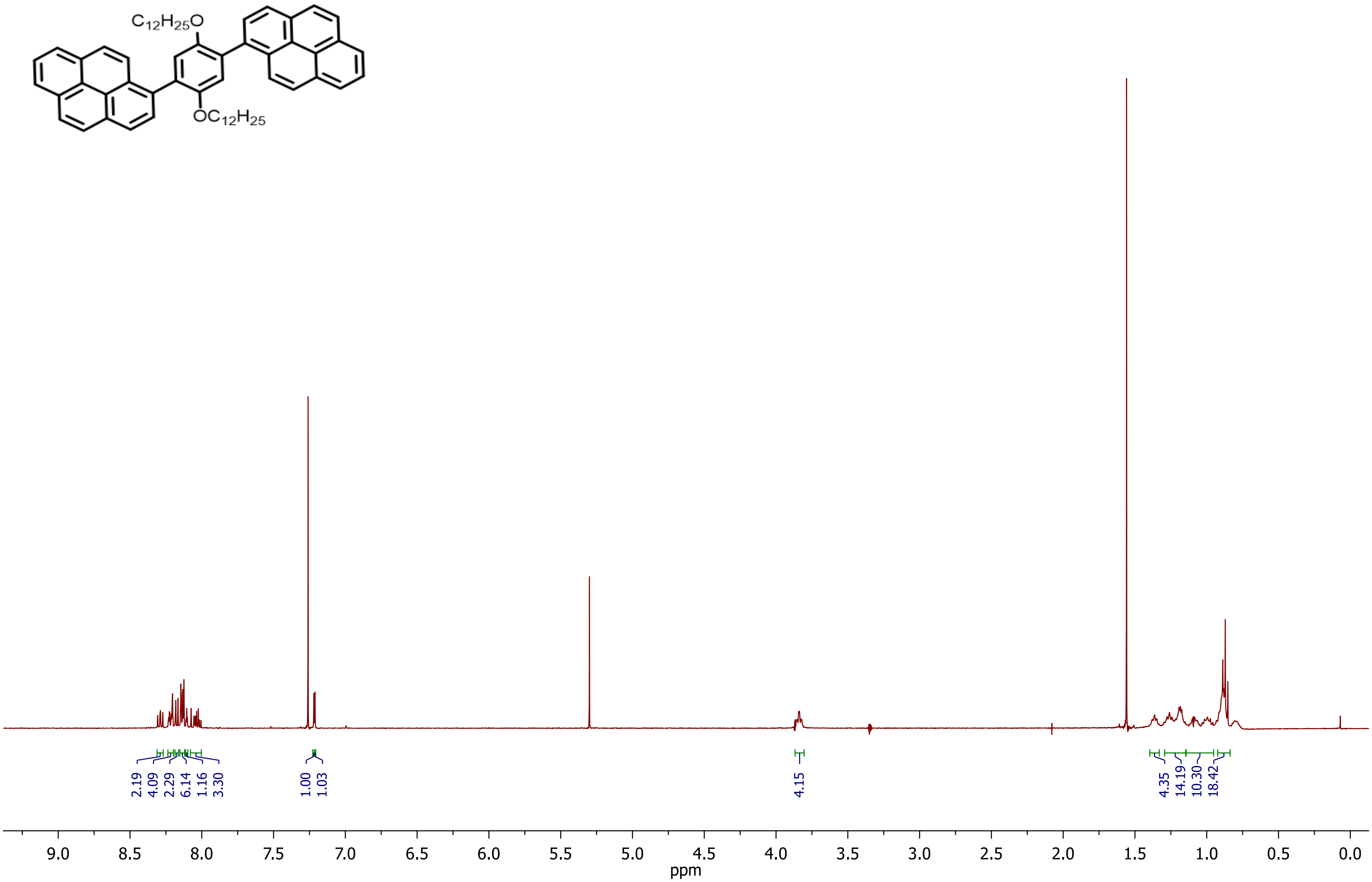
ppm

Compound 5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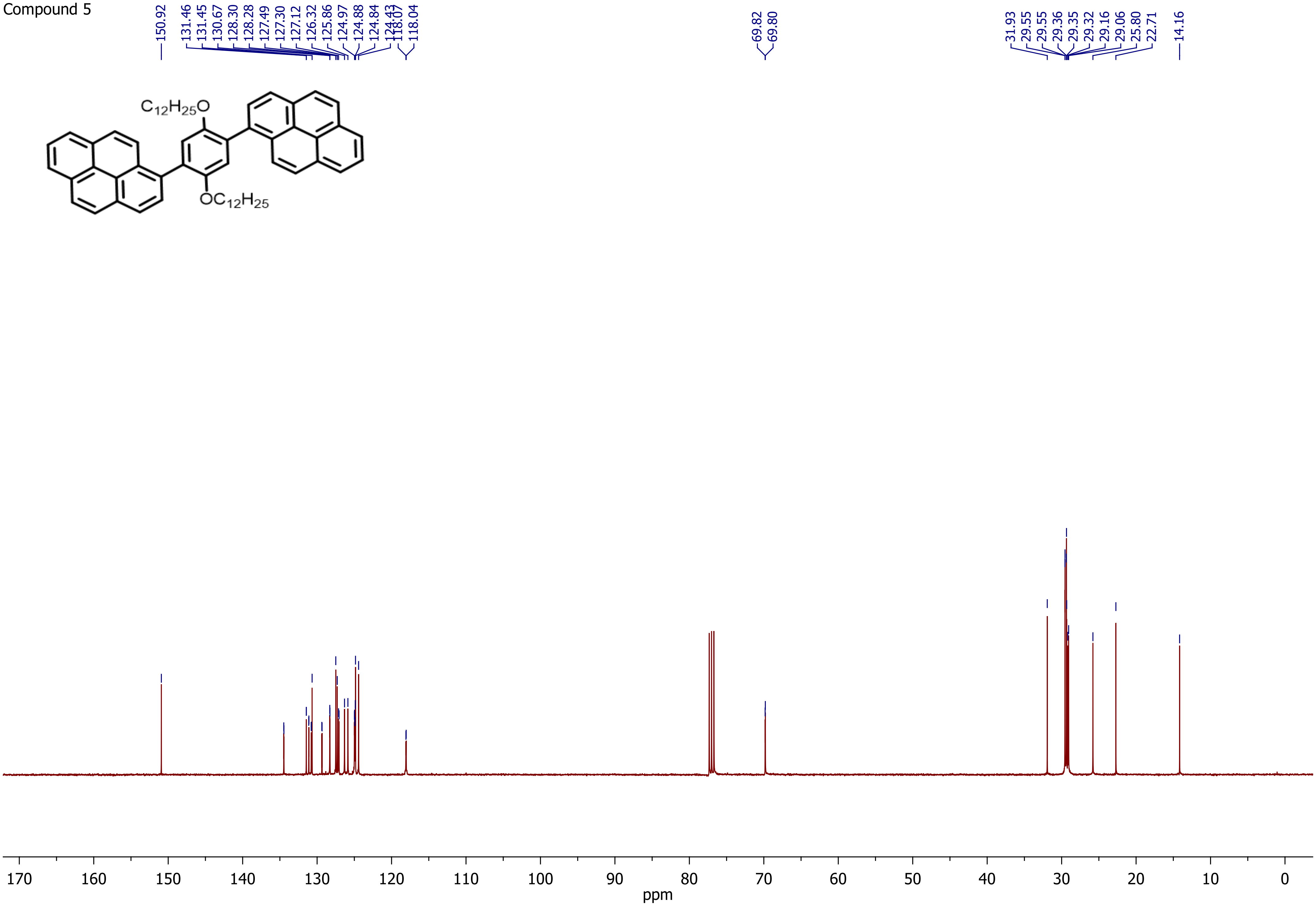
Compound 5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OC12H25
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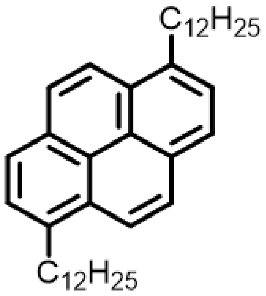
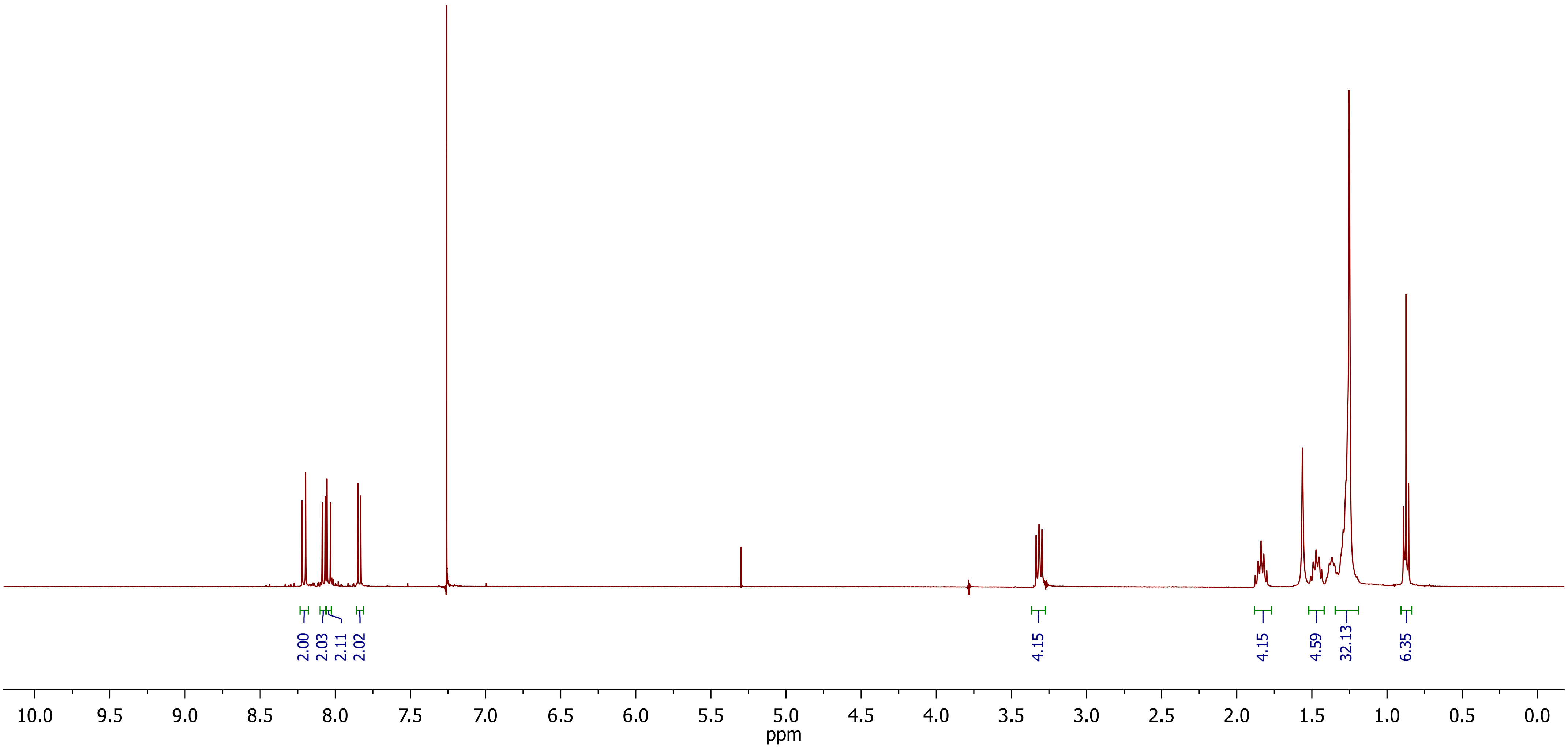
0
ppm

Compound 22


C12H25
C12H25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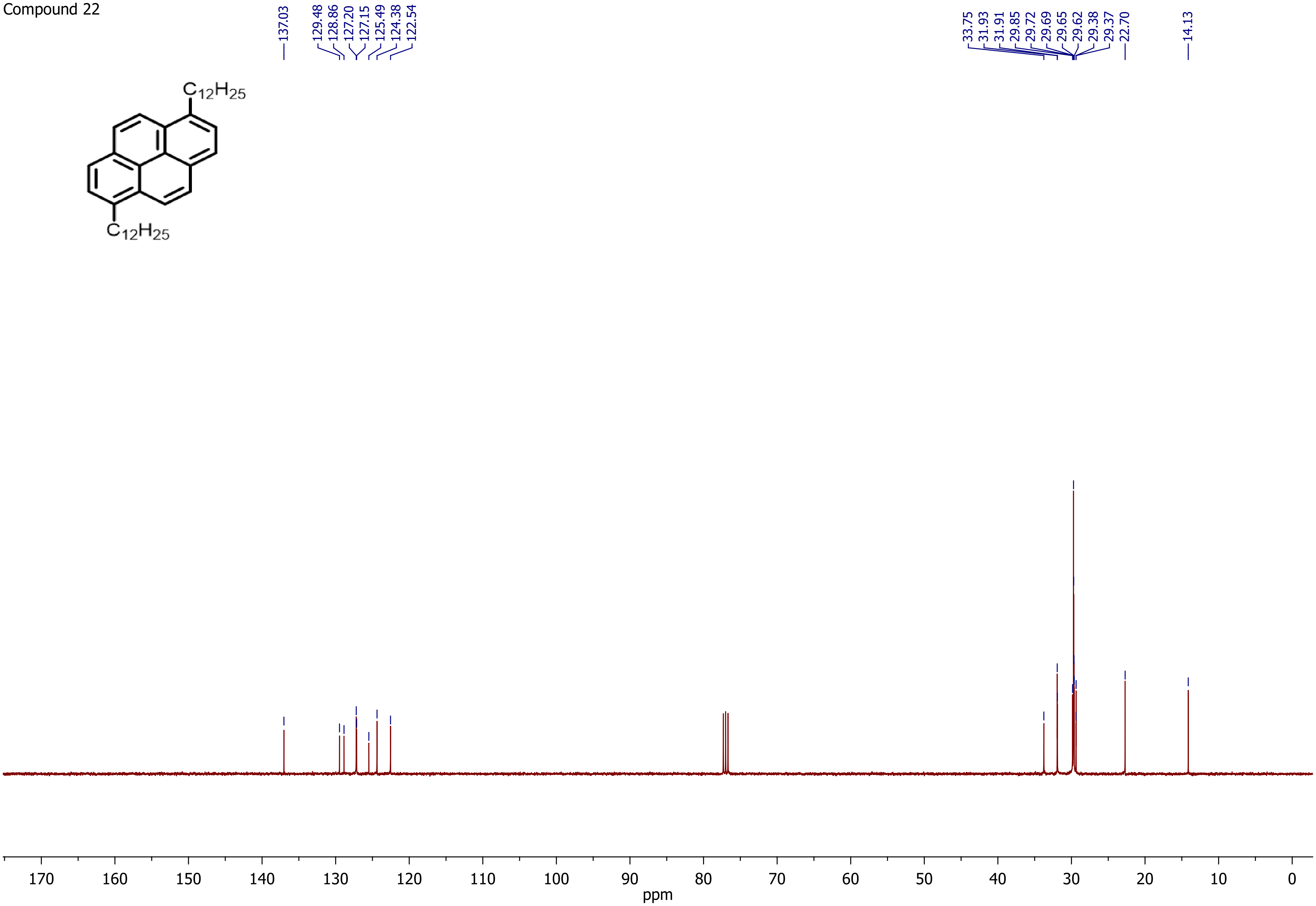
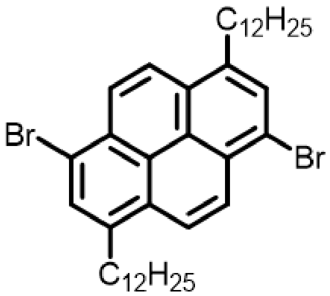
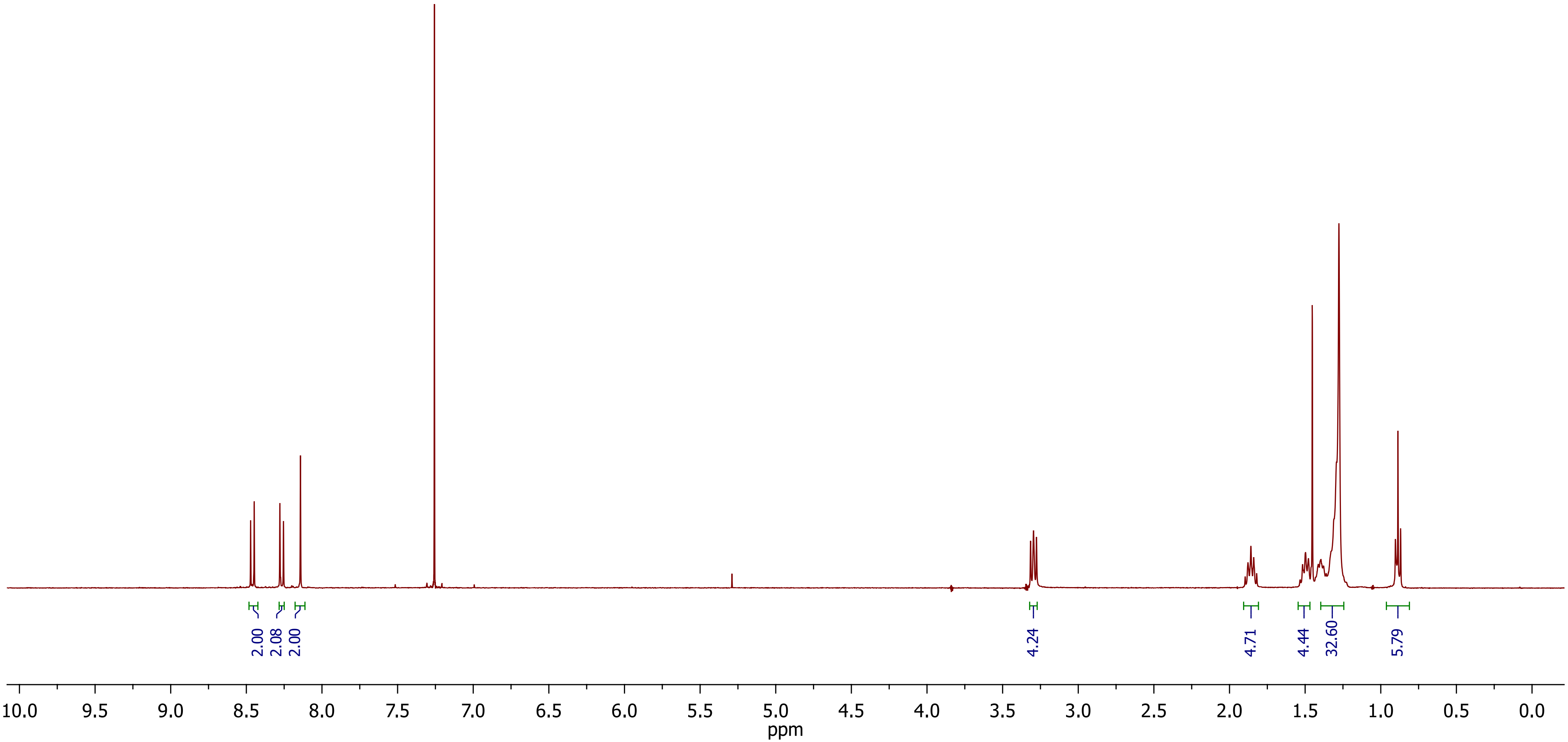
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Compound 22

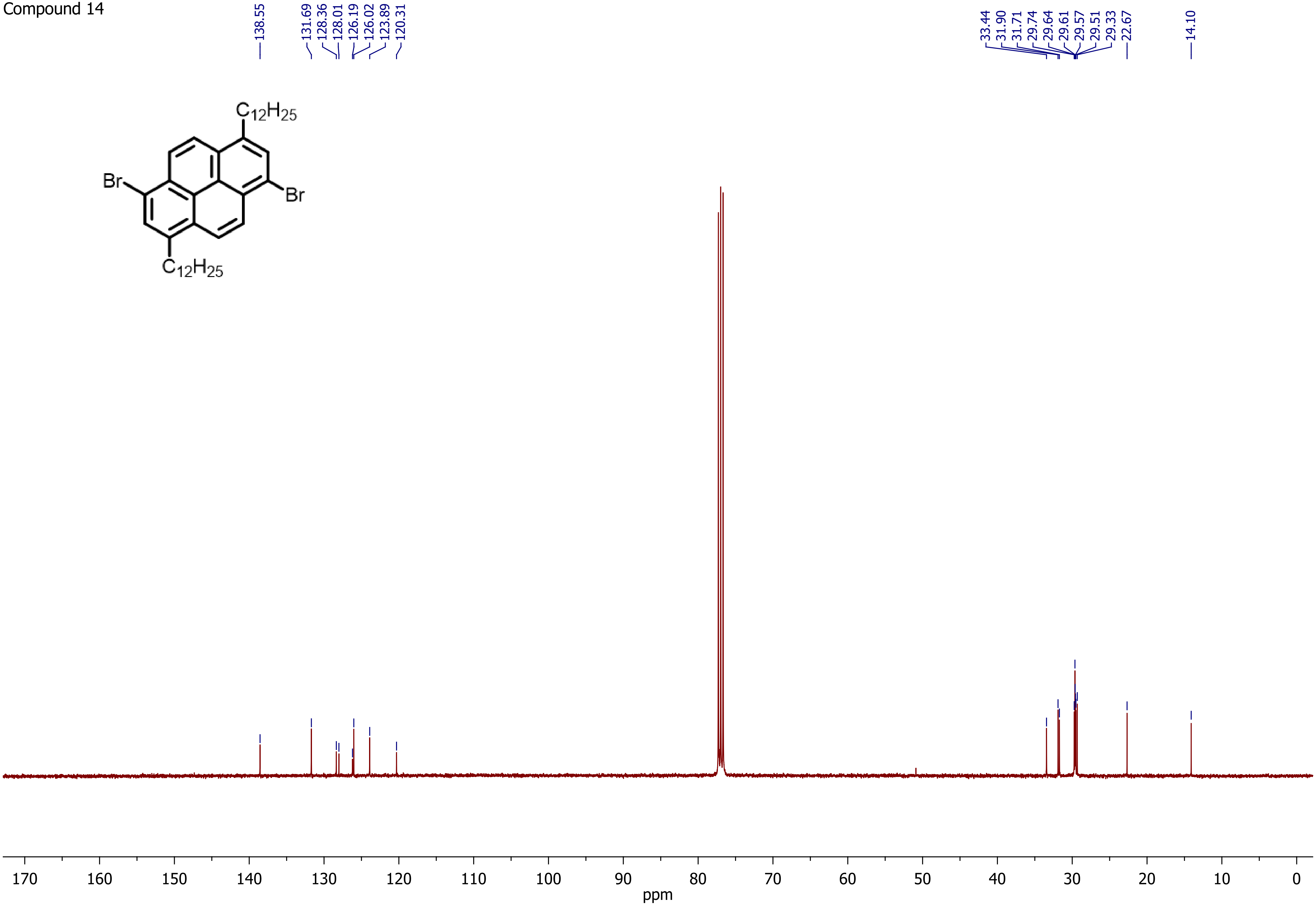

137.03
129.48
128.86
127.20
127.15
125.49
124.38
122.54
33.75
31.93
31.91
29.85
29.72
29.69
29.65
29.62
29.38
29.37
22.70
14.13
$C_{12}H_{25}$
$C_{12}H_{25}$
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 14

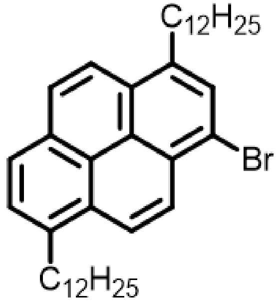

C12H25
Br
Br
C12H25

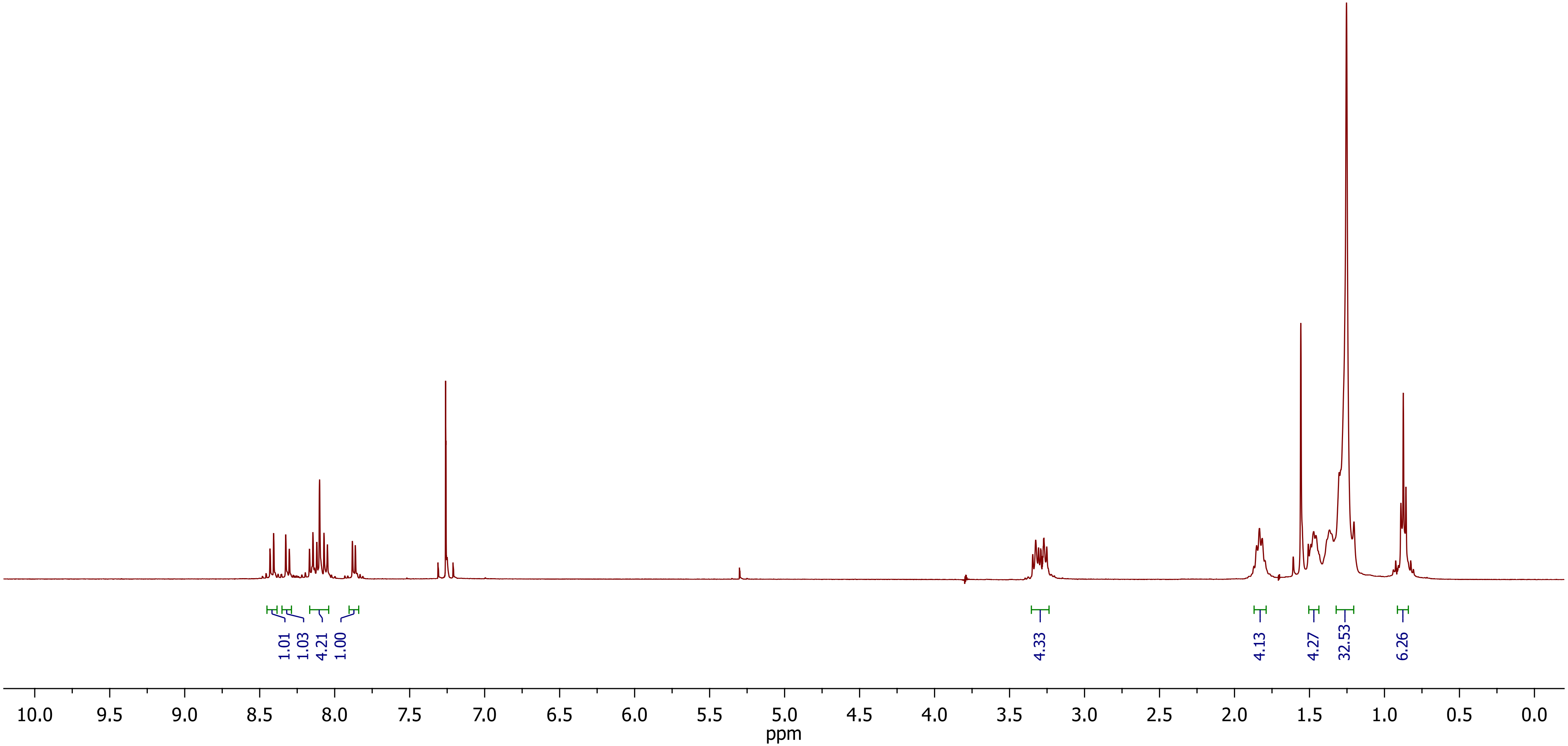

2.00
2.08
2.00
4.24
4.71
4.44
32.60
5.79
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Compound 14

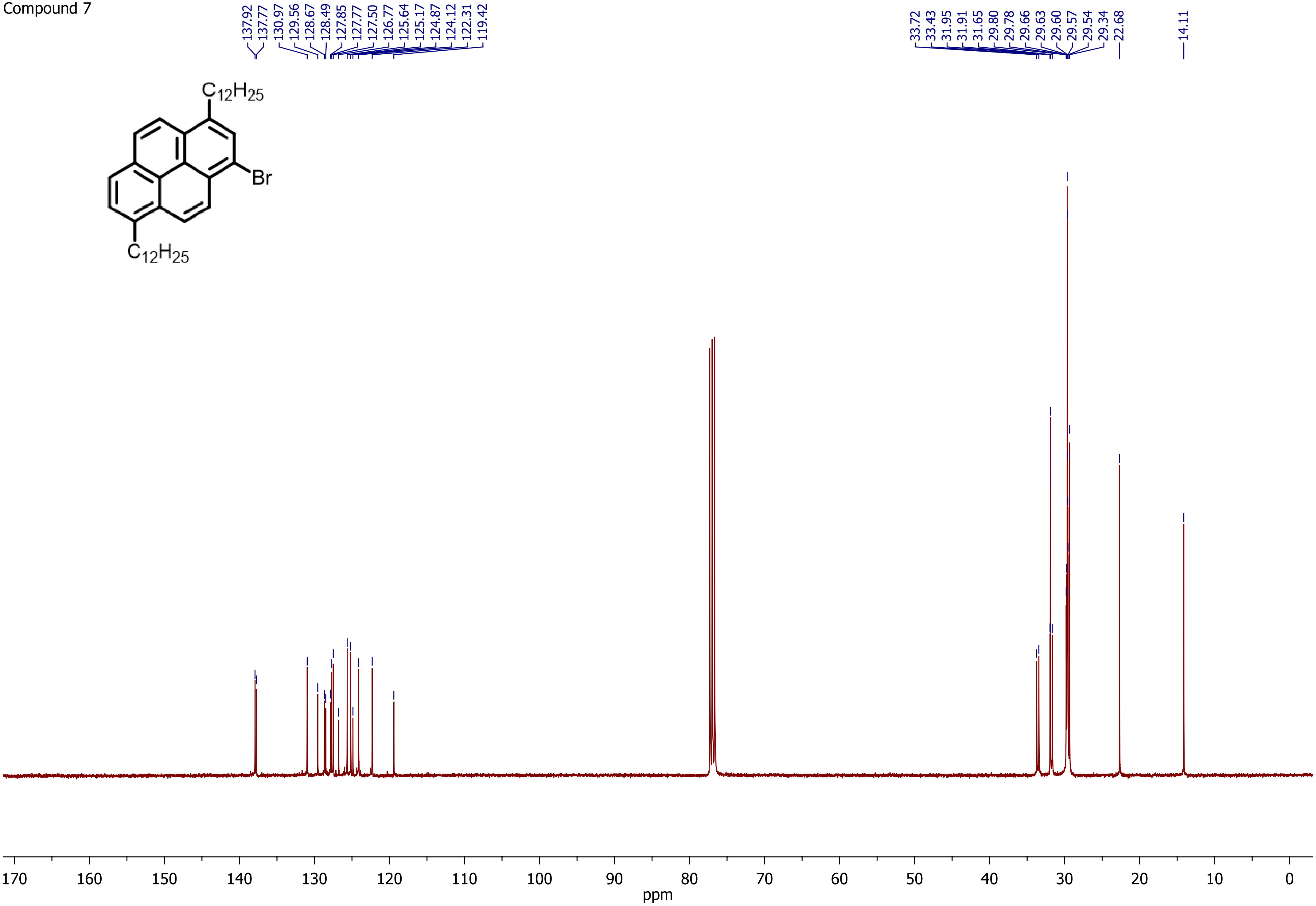

138.55
131.69
128.36
128.01
126.19
126.02
123.89
120.31
33.44
31.90
31.71
29.74
29.64
29.61
29.57
29.51
29.33
22.67
14.10
$C_{12}H_{25}$
Br
Br
$C_{12}H_{25}$
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 7

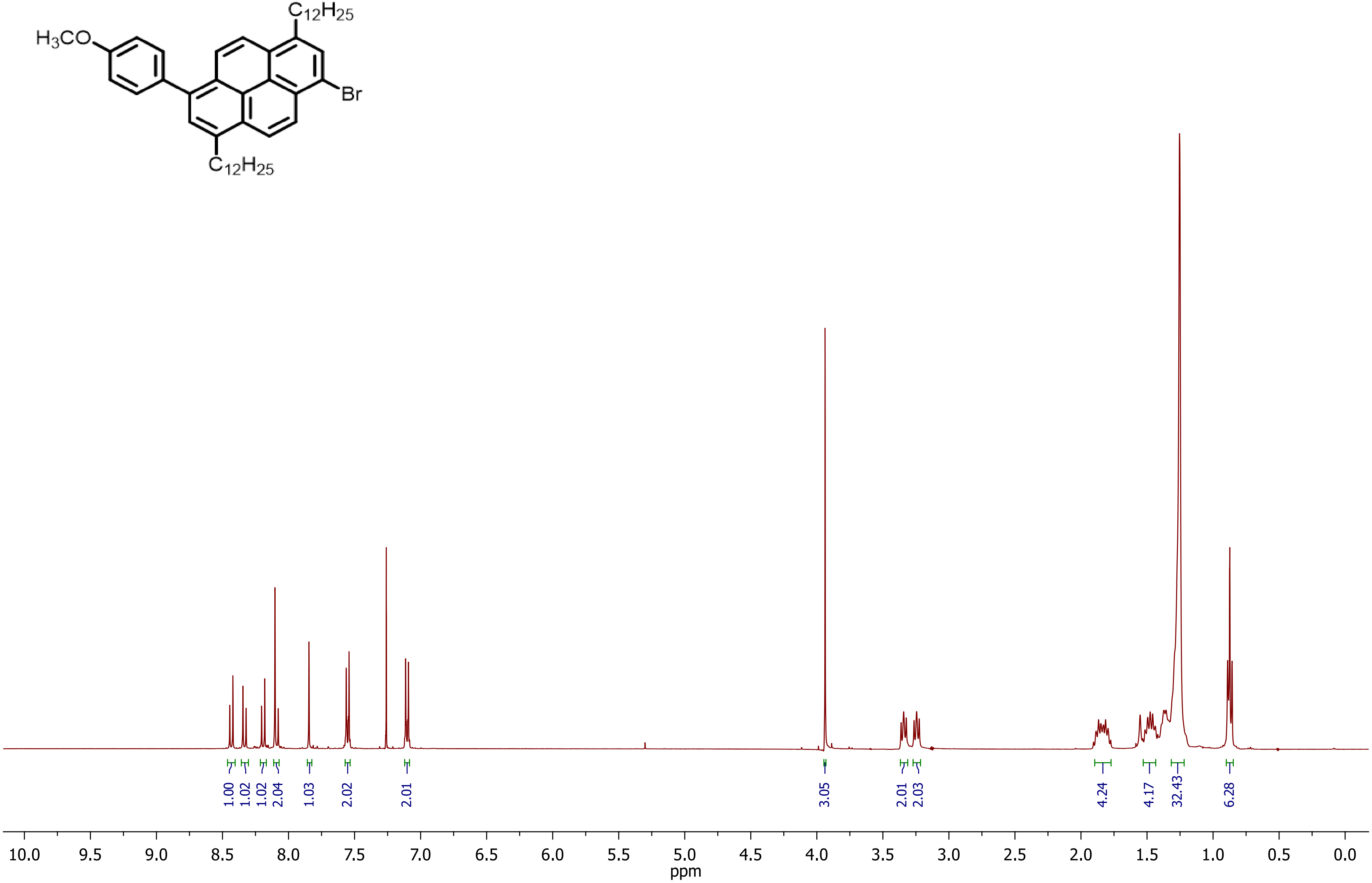

C12H25
Br
C12H25


1.01
1.03
4.21
1.00
4.33
4.13
4.27
32.53
6.26
10.0
9.5
9.0
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
0.5
0.0
ppm

Compound 7

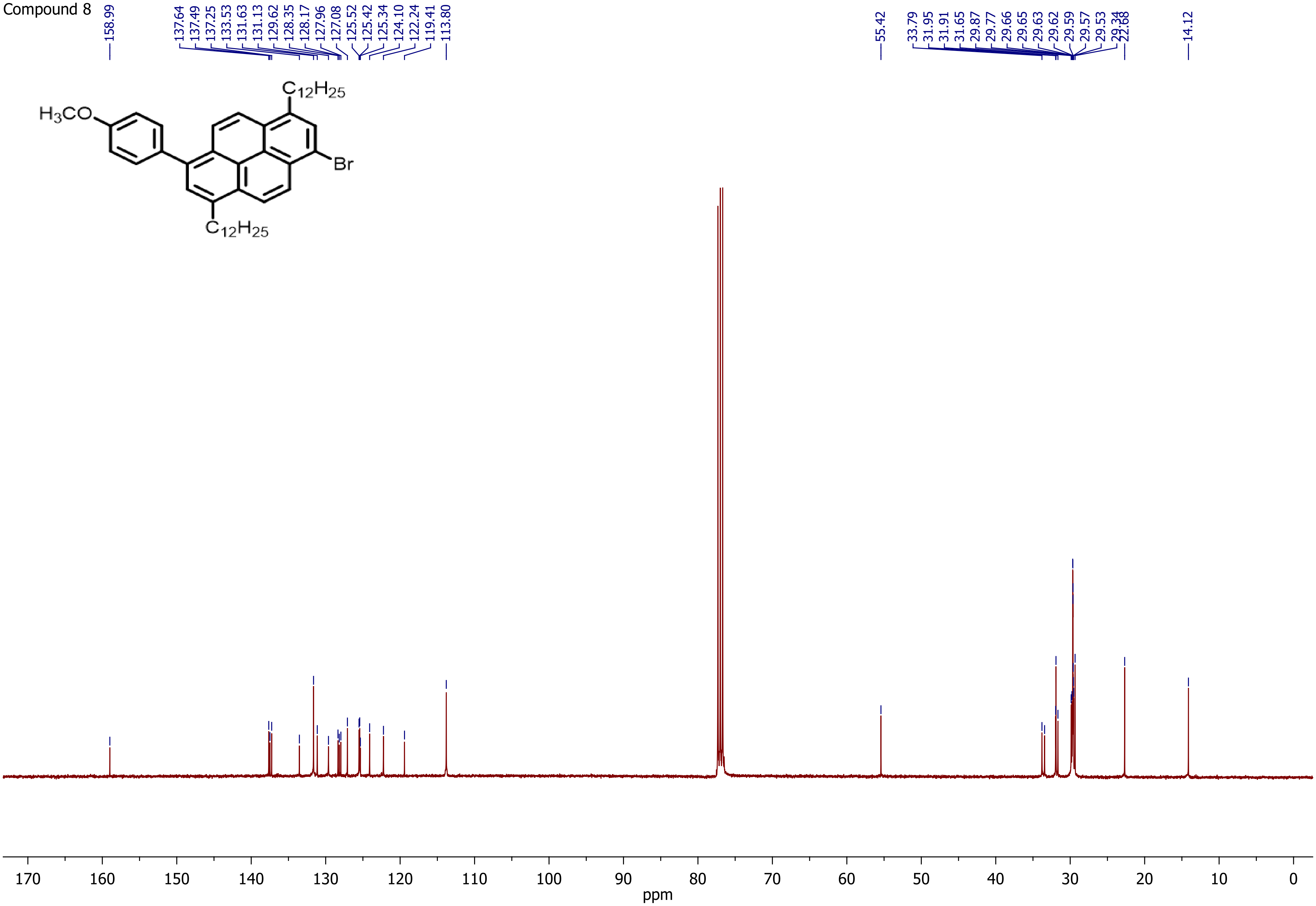

137.92
137.77
130.97
129.56
128.67
128.49
127.85
127.77
127.50
126.77
125.64
125.17
124.87
124.12
122.31
119.42
33.72
33.43
31.95
31.91
31.65
29.80
29.78
29.66
29.63
29.60
29.57
29.54
29.34
22.68
14.11
$C_{12}H_{25}$
Br
$C_{12}H_{25}$
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 8

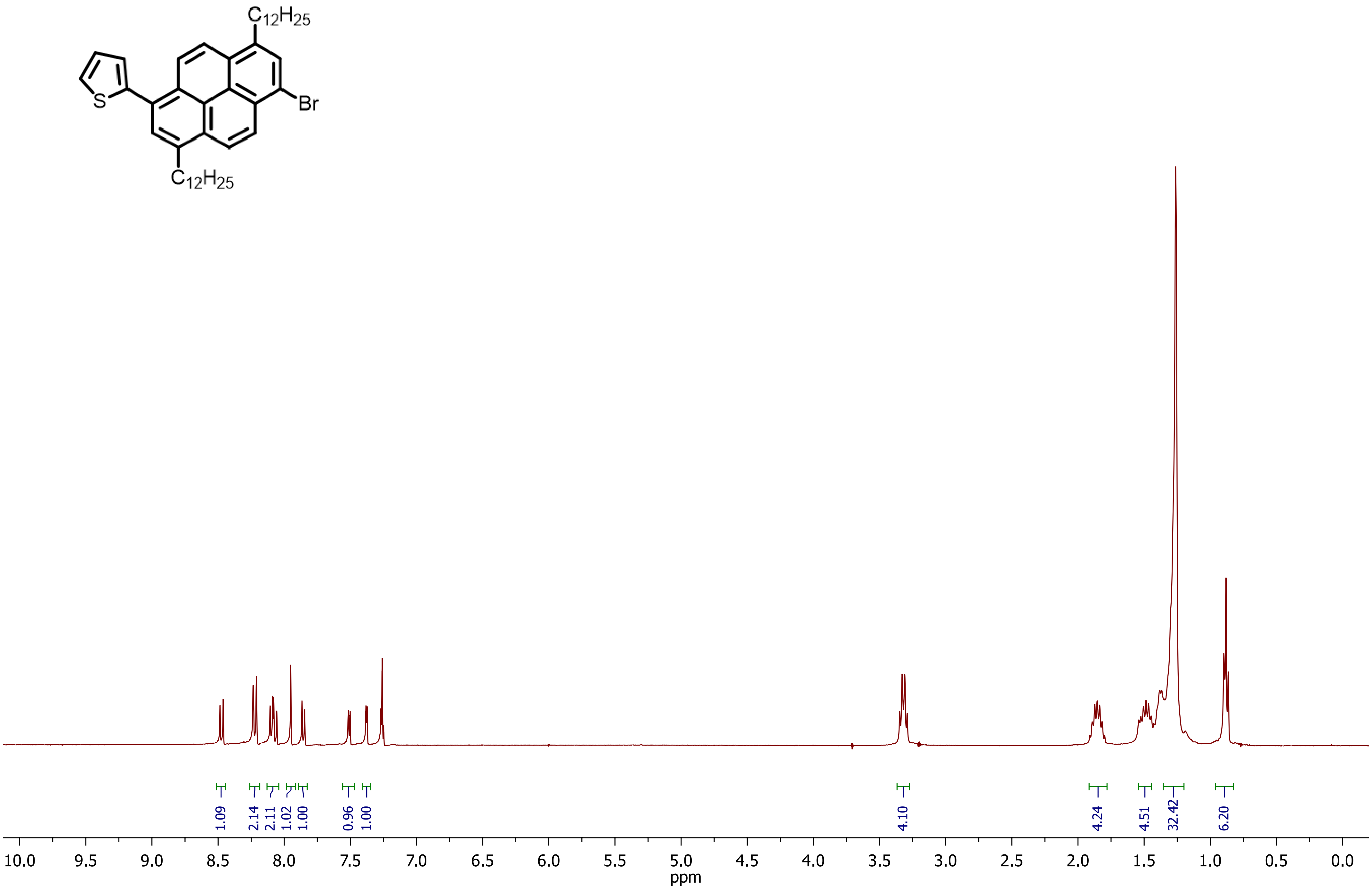


H3CO
C12H25
Br
C12H25
1.00
1.02
1.02
2.04
1.03
2.02
2.01
3.05
2.01
2.03
4.24
4.17
32.43
6.28
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

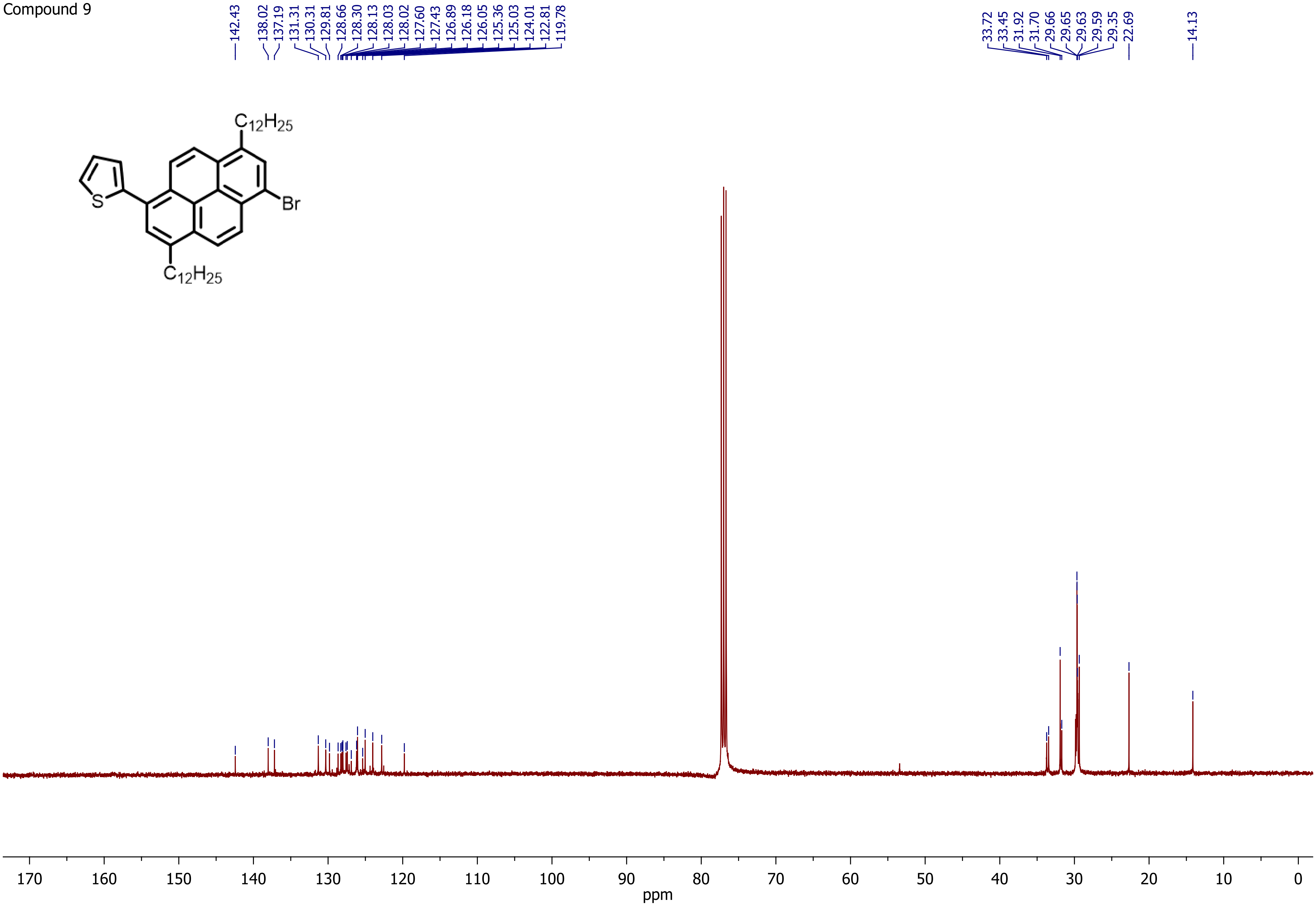
Compound 8


158.99
137.64
137.49
137.25
133.53
131.63
131.13
129.62
128.35
128.17
127.96
127.08
125.52
125.42
125.34
124.10
122.24
119.41
113.80
55.42
33.79
31.95
31.91
31.65
29.87
29.77
29.66
29.65
29.63
29.62
29.59
29.57
29.53
29.34
22.68
14.12
H3CO
C12H25
Br
C12H25
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

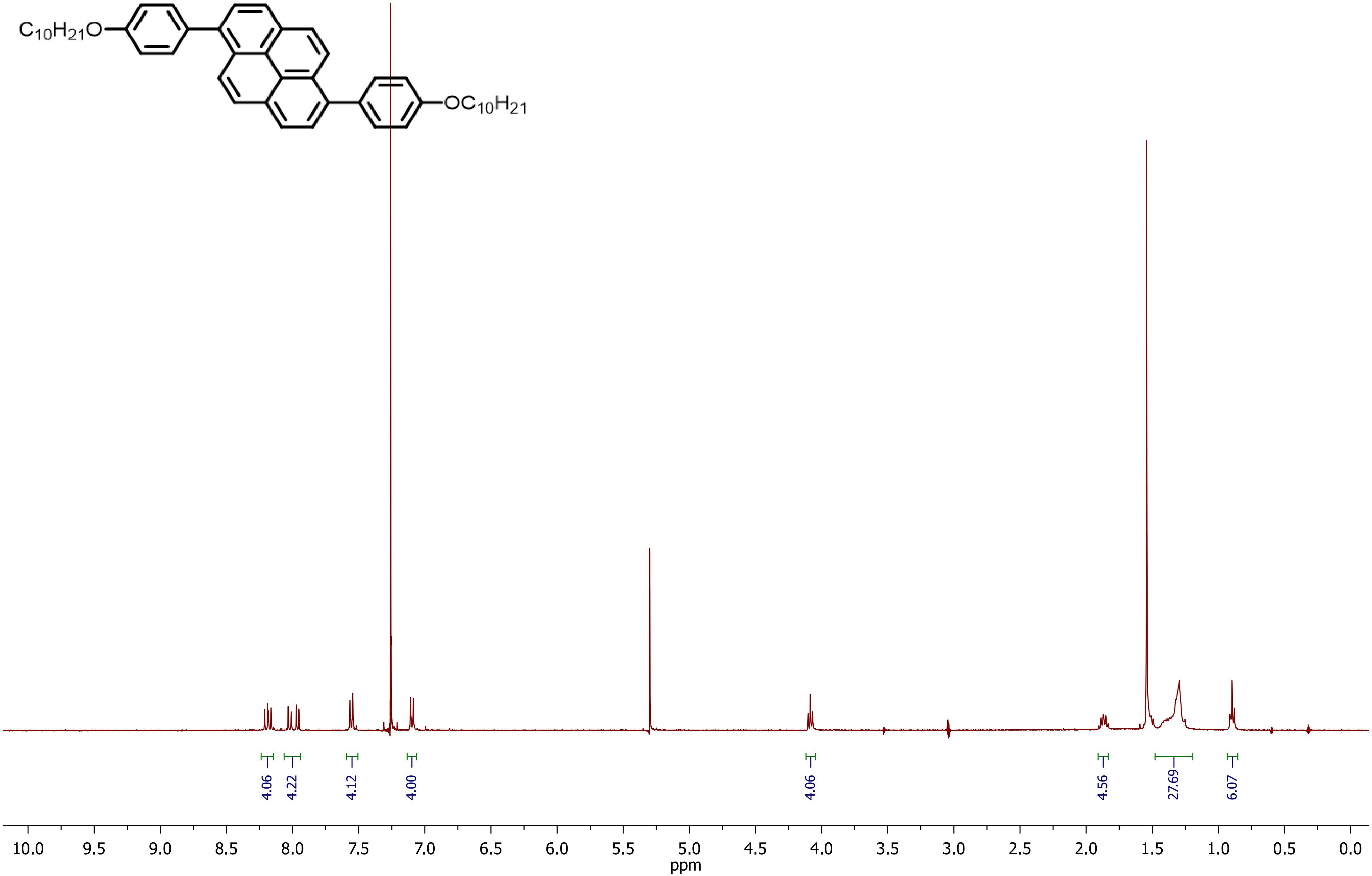
Compound 9


C12H25
S
Br
C12H25
1.09
2.14
2.11
1.02
1.00
0.96
1.00
4.10
4.24
4.51
32.42
6.20
10.0
9.5
9.0
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
0.5
0.0
ppm

Compound 9

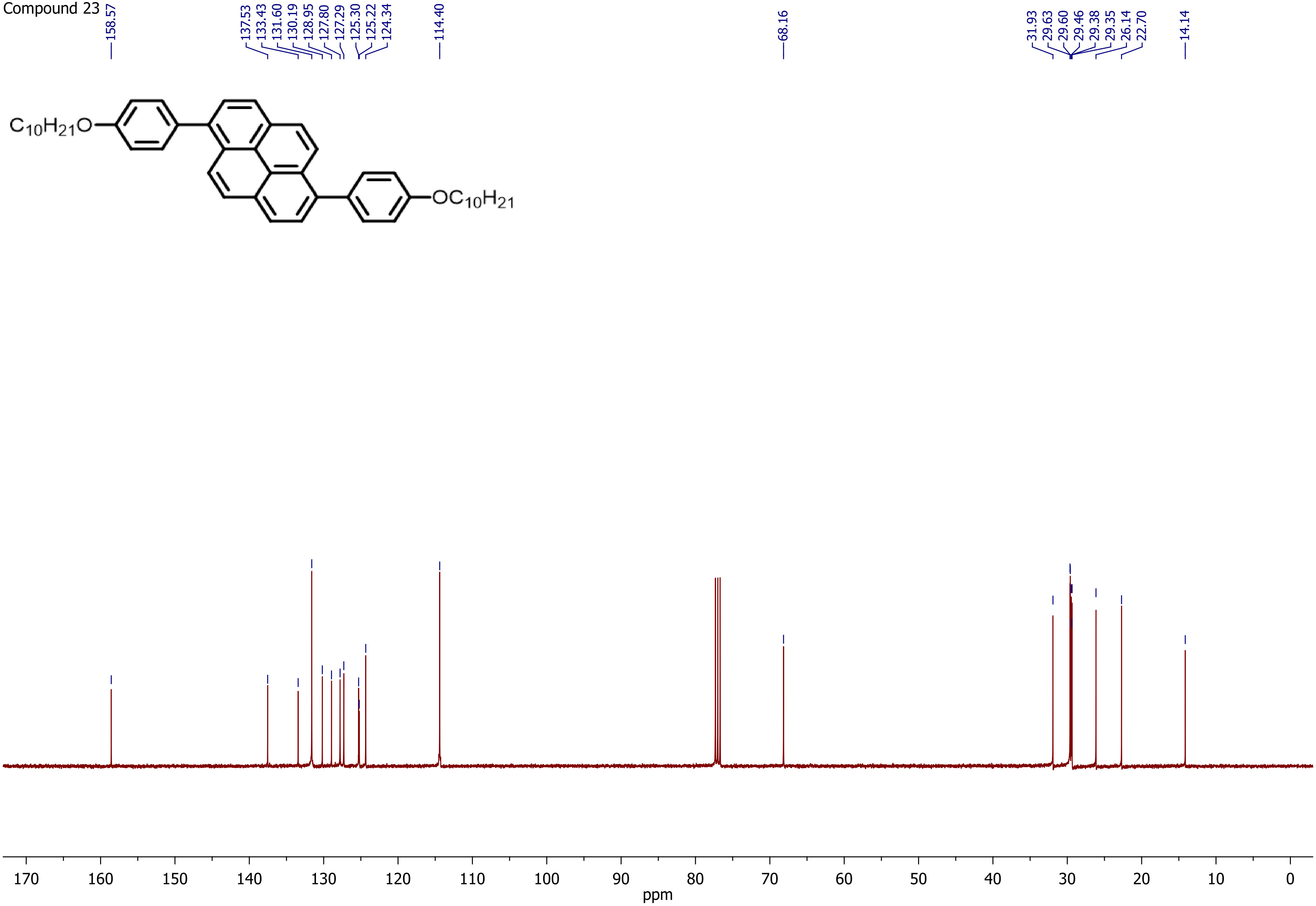

142.43
138.02
137.19
131.31
130.31
129.81
128.66
128.30
128.13
128.03
128.02
127.60
127.43
126.89
126.18
126.05
125.36
125.03
124.01
122.81
119.78
33.72
33.45
31.92
31.70
29.66
29.65
29.63
29.59
29.35
22.69
14.13
$C_{12}H_{25}$
Br
S
$C_{12}H_{25}$
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 23

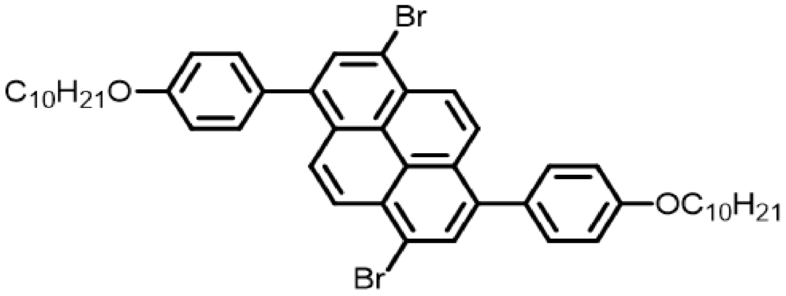


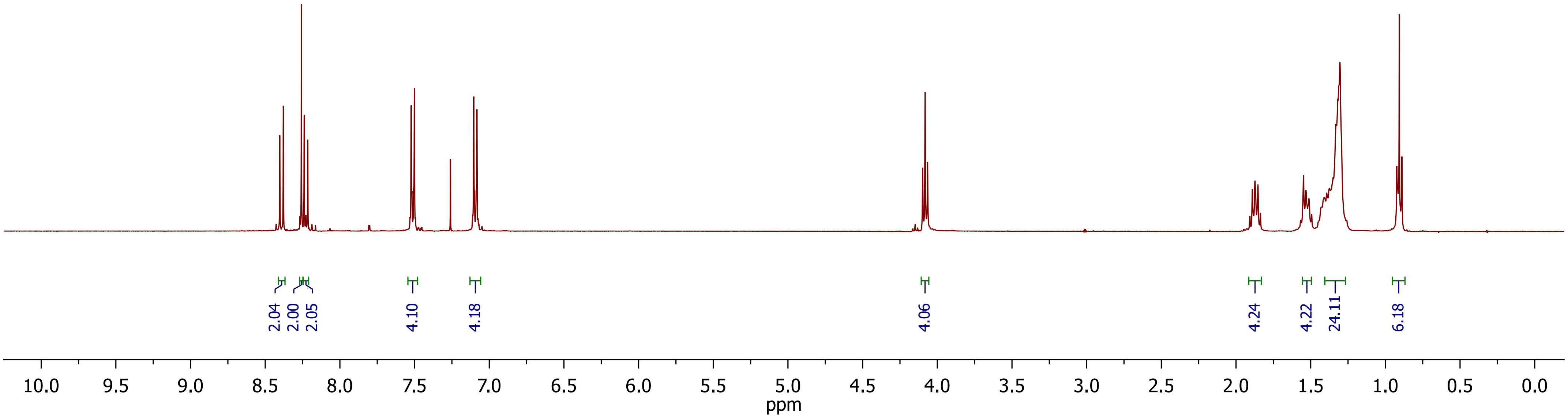
C10H21O
OC10H21
4.06
4.22
4.12
4.00
4.06
4.56
27.69
6.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Compound 23

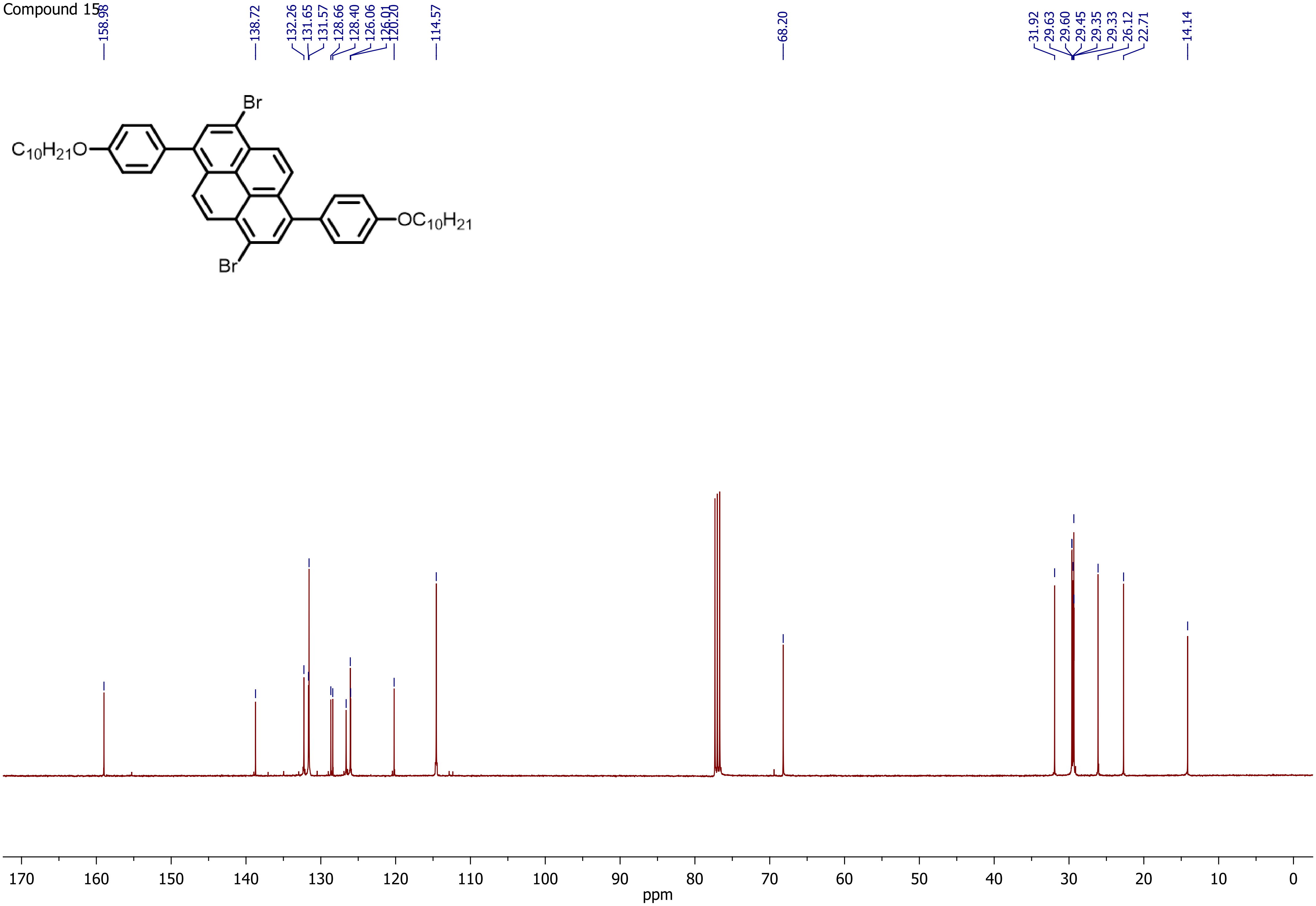

158.57
137.53
133.43
131.60
130.19
128.95
127.80
127.29
125.30
125.22
124.34
114.40
68.16
31.93
29.63
29.60
29.46
29.38
29.35
26.14
22.70
14.14
C10H21O
OC10H21
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 15

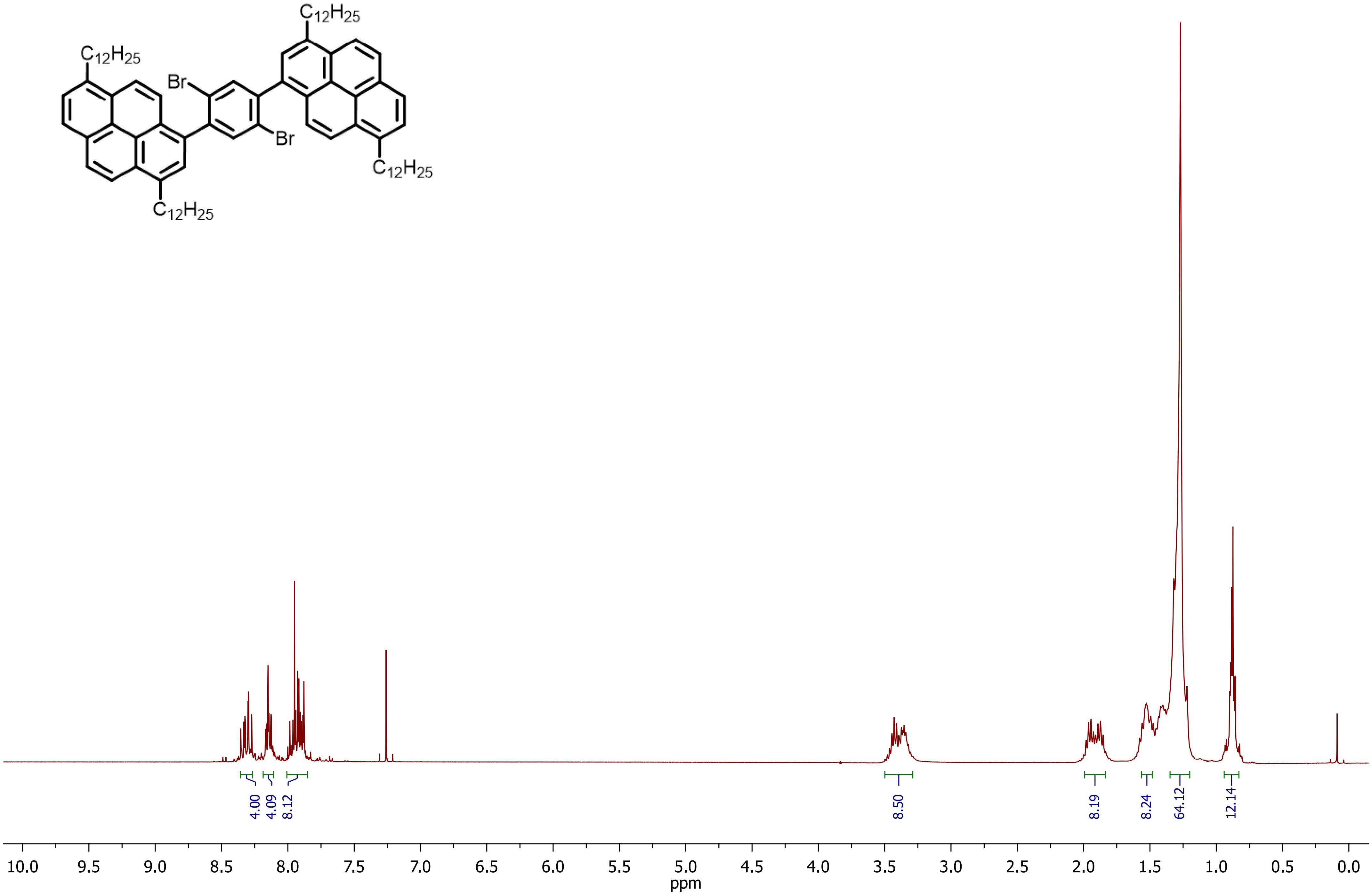

Br
C10H21O
OC10H21
Br


2.04
2.00
2.05
4.10
4.18
4.06
4.24
4.22
24.11
6.18
10.0
9.5
9.0
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
0.5
0.0
ppm

Compound 15

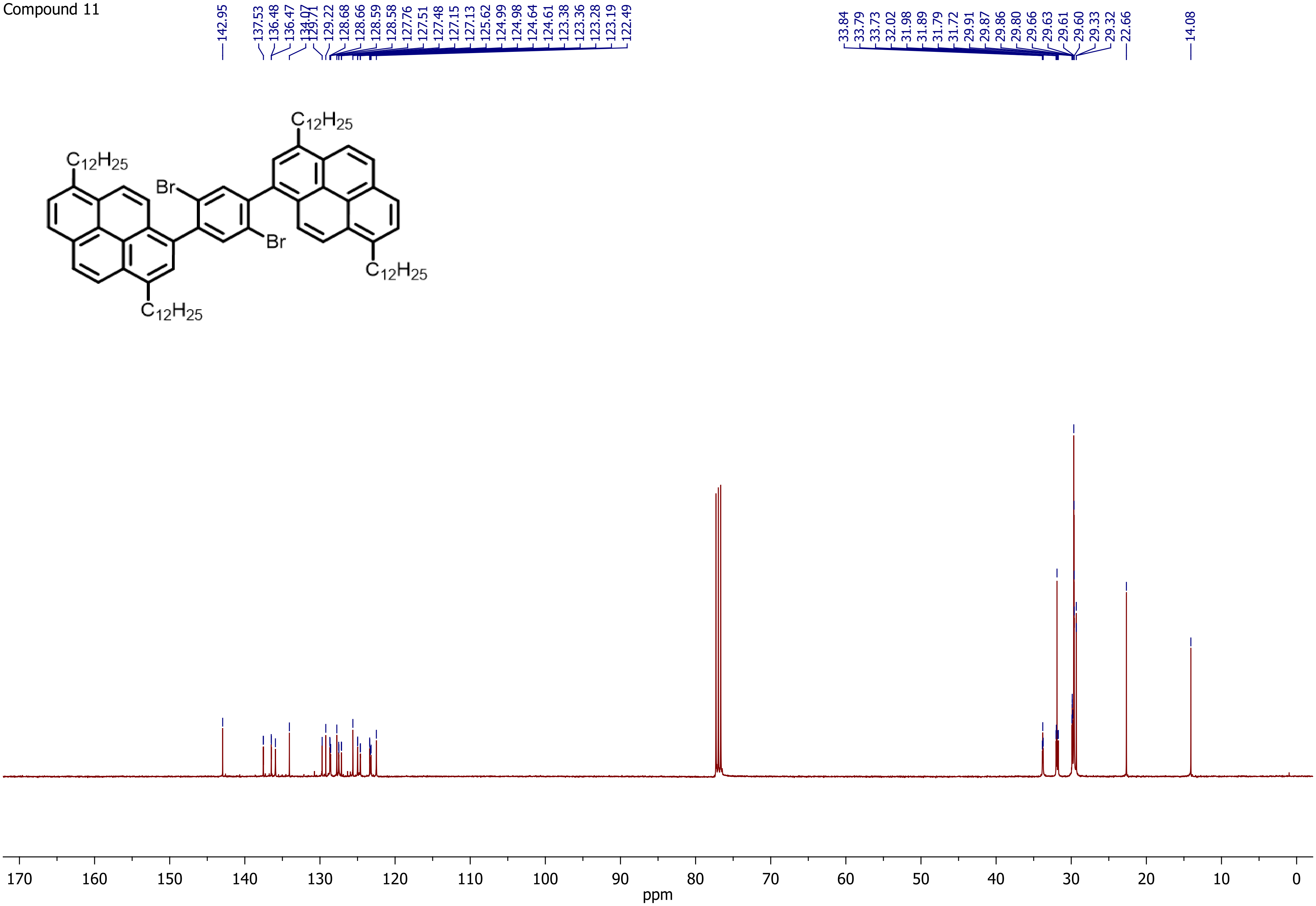

158.98
138.72
132.26
131.65
131.57
128.66
128.40
126.06
126.01
120.20
114.57
68.20
31.92
29.63
29.60
29.45
29.35
29.33
26.12
22.71
14.14
Br
Br
$C_{10}H_{21}O$
$OC_{10}H_{21}$
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 11

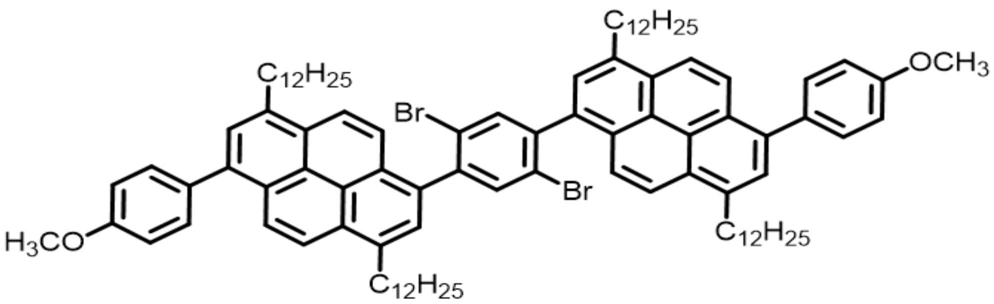

C12H25
C12H25
Br
Br
C12H25
C12H25
4.00
4.09
8.12
8.50
8.19
8.24
64.12
12.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

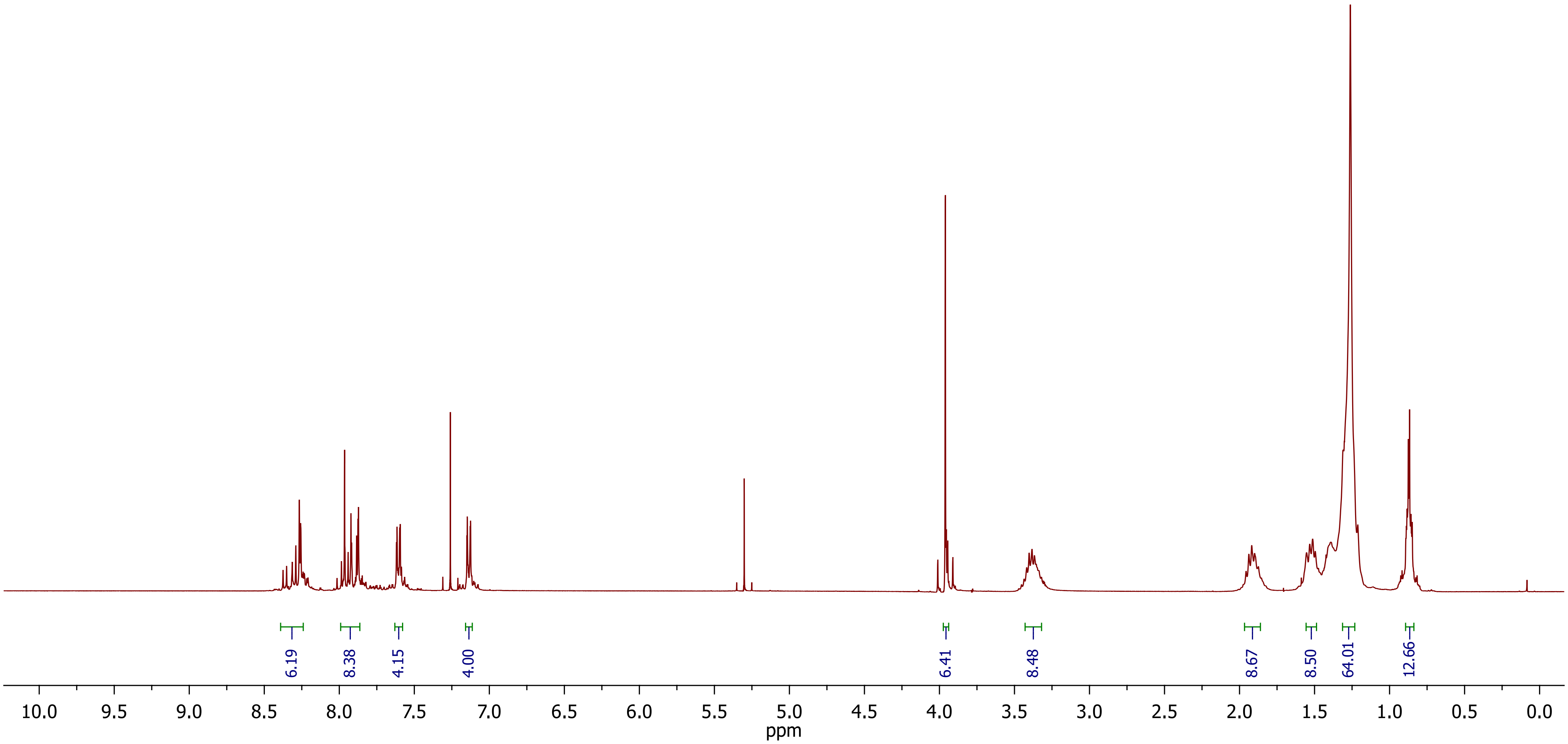
Compound 11

C12H25
C12H25
Br
Br
C12H25
C12H25

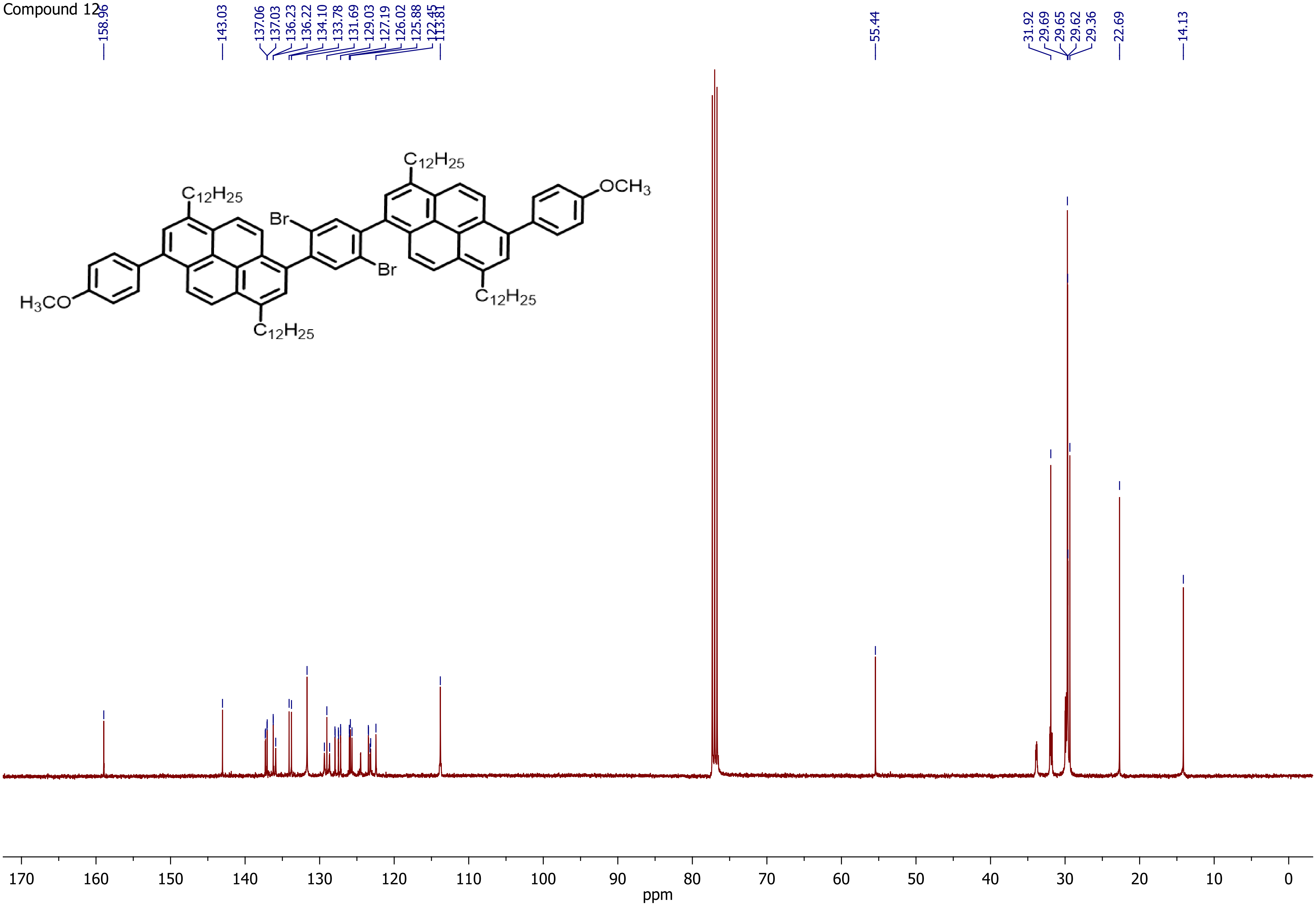

142.95
137.53
136.48
136.47
134.07
129.71
129.22
128.68
128.66
128.59
128.58
127.76
127.51
127.48
127.15
127.13
125.62
124.99
124.98
124.64
124.61
123.38
123.36
123.28
123.19
122.49
33.84
33.79
33.73
32.02
31.98
31.89
31.79
31.72
29.91
29.87
29.86
29.80
29.66
29.63
29.61
29.60
29.33
29.32
22.66
14.08
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 12


C12H25
C12H25
Br
Br
OCH3
H3CO
C12H25
C12H25

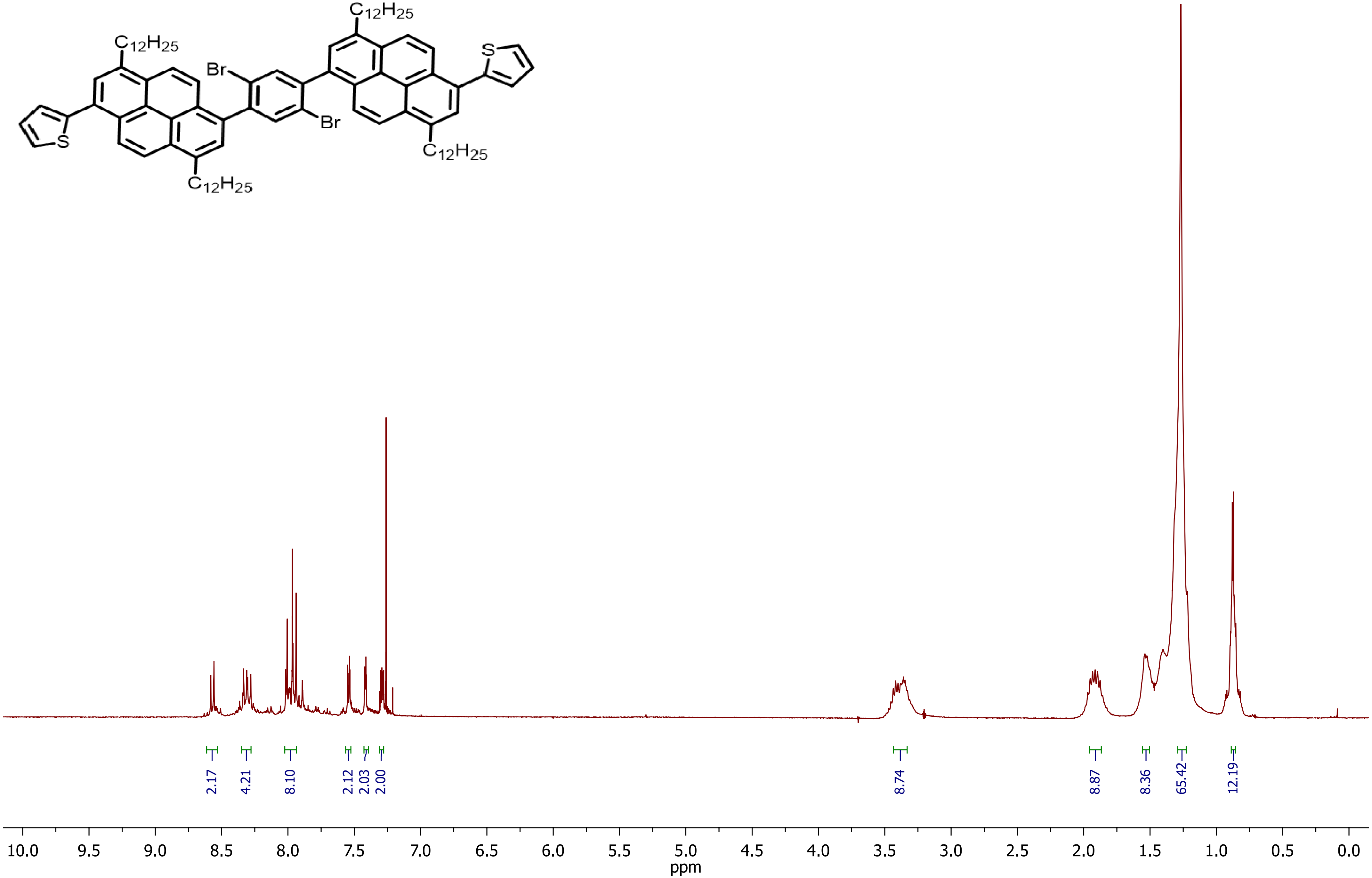

6.19
8.38
4.15
4.00
6.41
8.48
8.67
8.50
64.01
12.66
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Compound 12

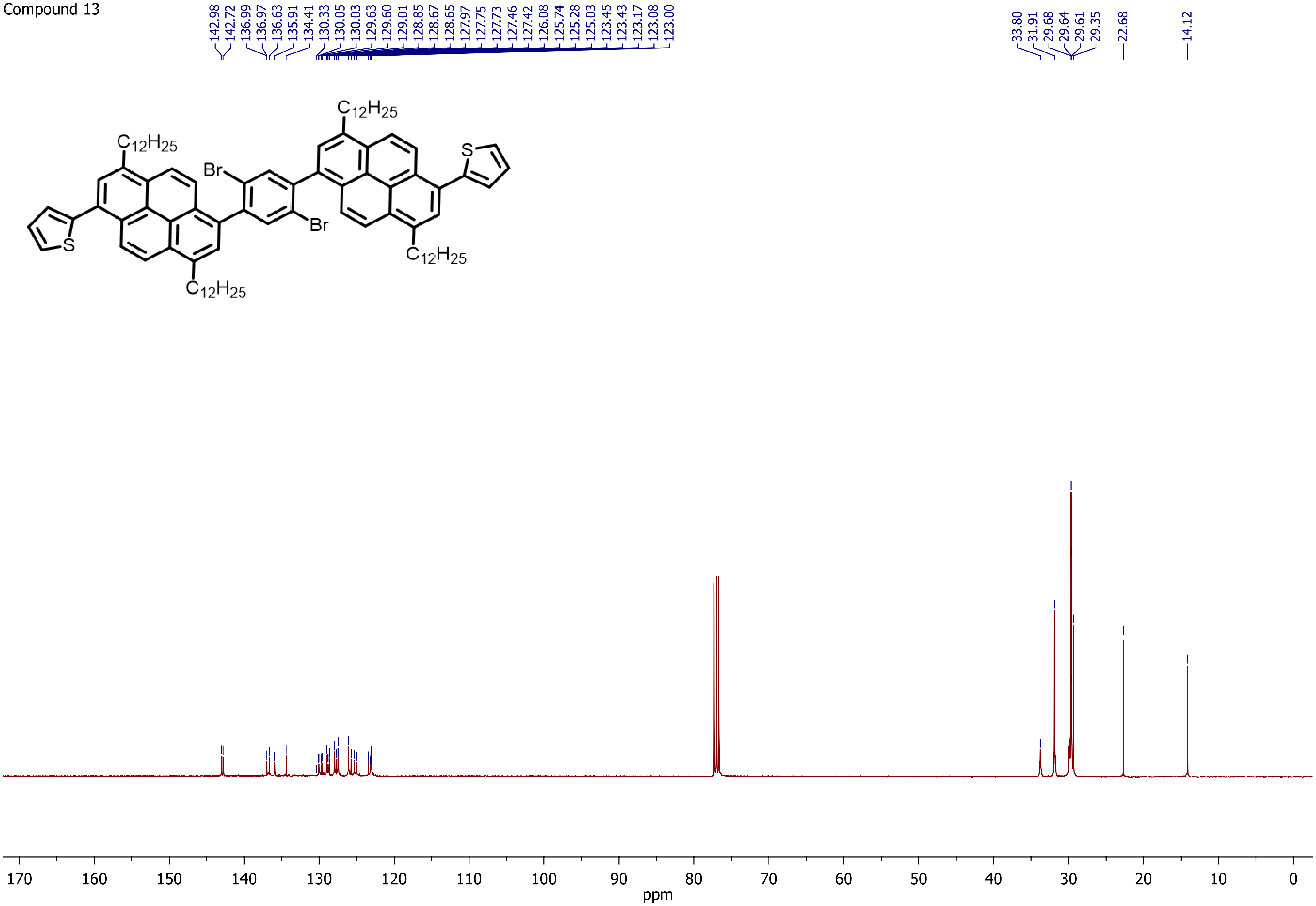


158.96
143.03
137.06
137.03
136.23
136.22
134.10
133.78
131.69
129.03
127.19
126.02
125.88
122.45
113.81
55.44
31.92
29.69
29.65
29.62
29.36
22.69
14.13
$C_{12}H_{25}$
$C_{12}H_{25}$
$C_{12}H_{25}$
$C_{12}H_{25}$
Br
Br
OCH_3
H_3CO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

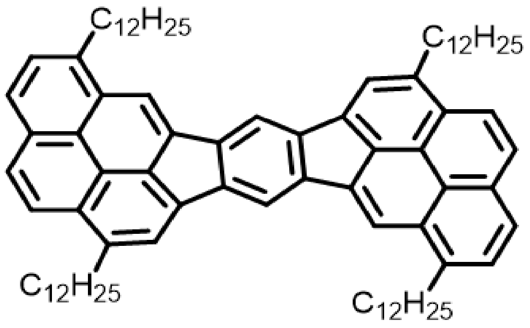
Compound 13

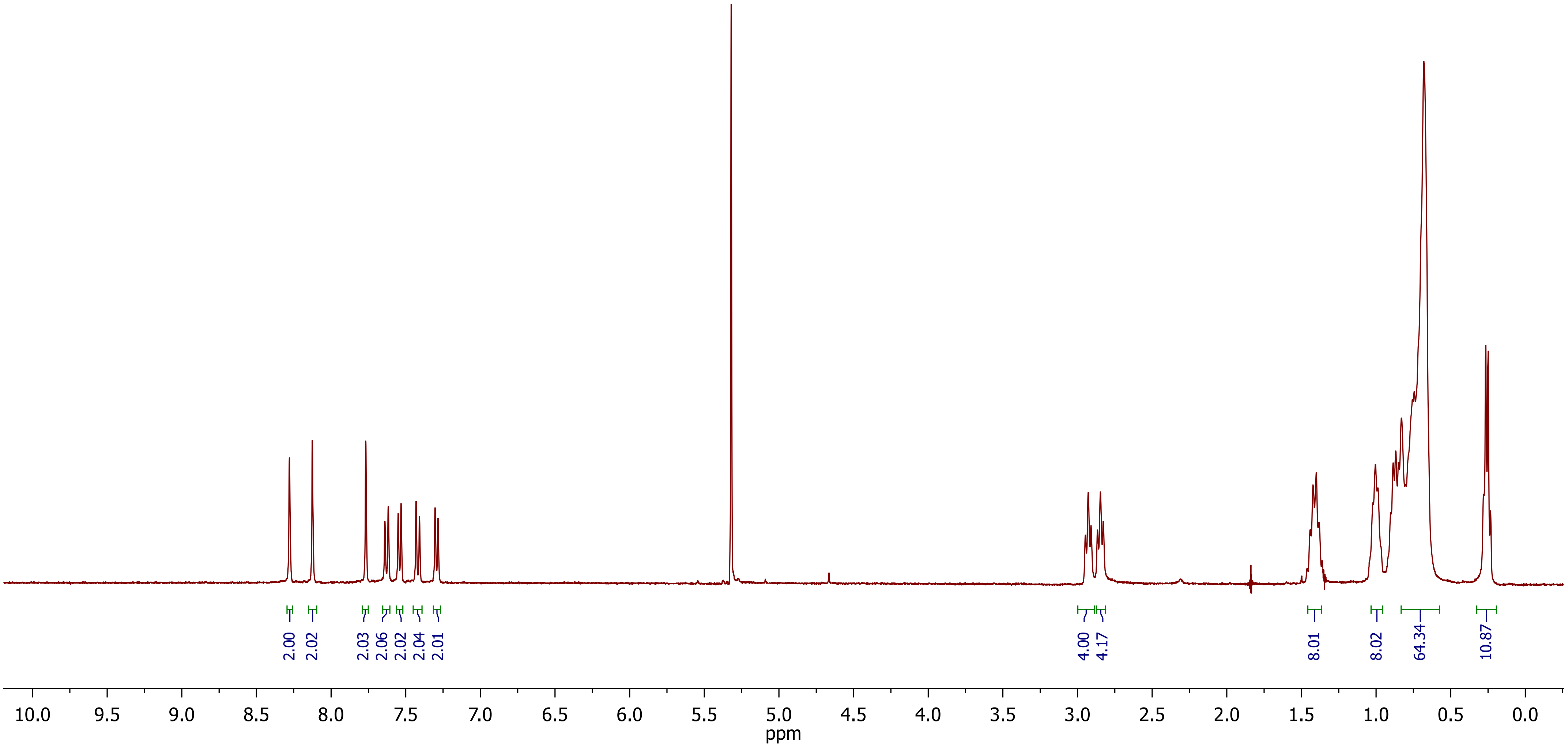

C12H25
C12H25
Br
Br
S
S
C12H25
C12H25
2.17
4.21
8.10
2.12
2.03
2.00
8.74
8.87
8.36
65.42
12.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Compound 13

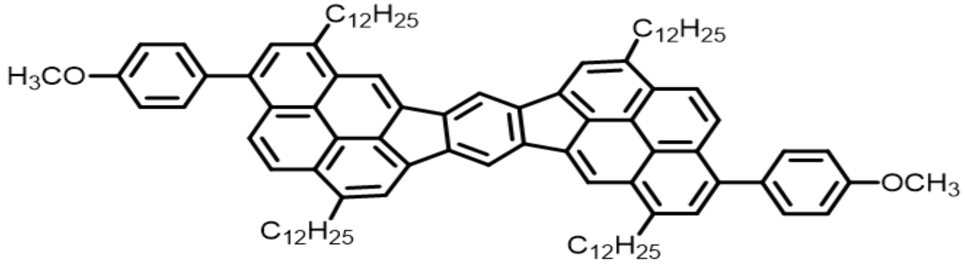

142.98
142.72
136.99
136.97
136.63
135.91
134.41
130.33
130.05
130.03
129.63
129.60
129.01
128.85
128.67
128.65
127.97
127.75
127.73
127.46
127.42
126.08
125.74
125.28
125.03
123.45
123.43
123.17
123.08
123.00
33.80
31.91
29.68
29.64
29.61
29.35
22.68
14.12
C12H25
C12H25
C12H25
C12H25
Br
Br
S
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

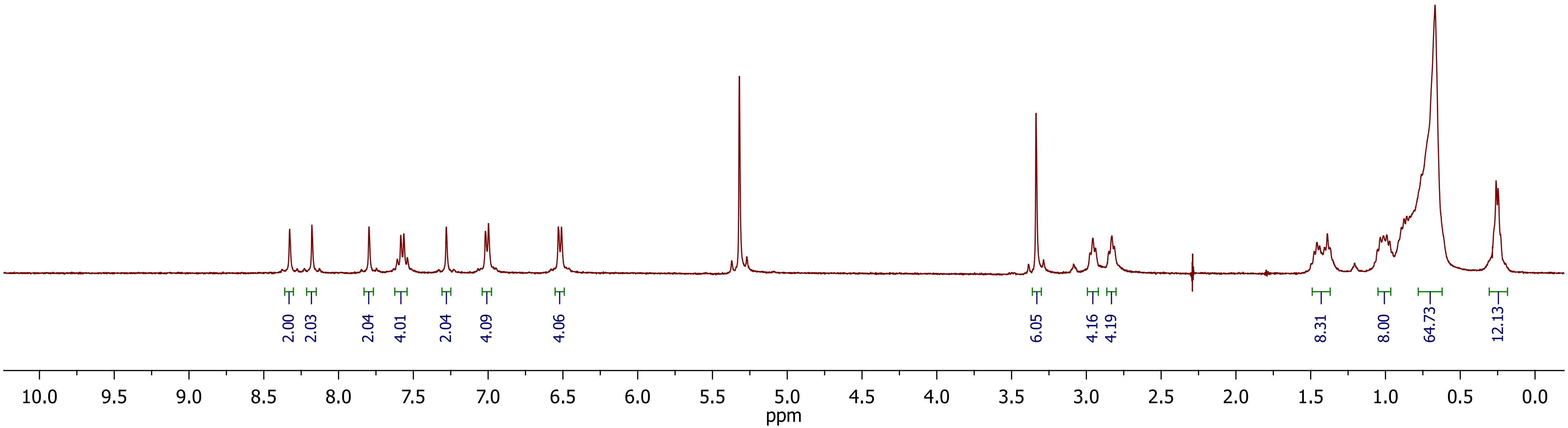
Compound 1a


C12H25
C12H25
C12H25
C12H25

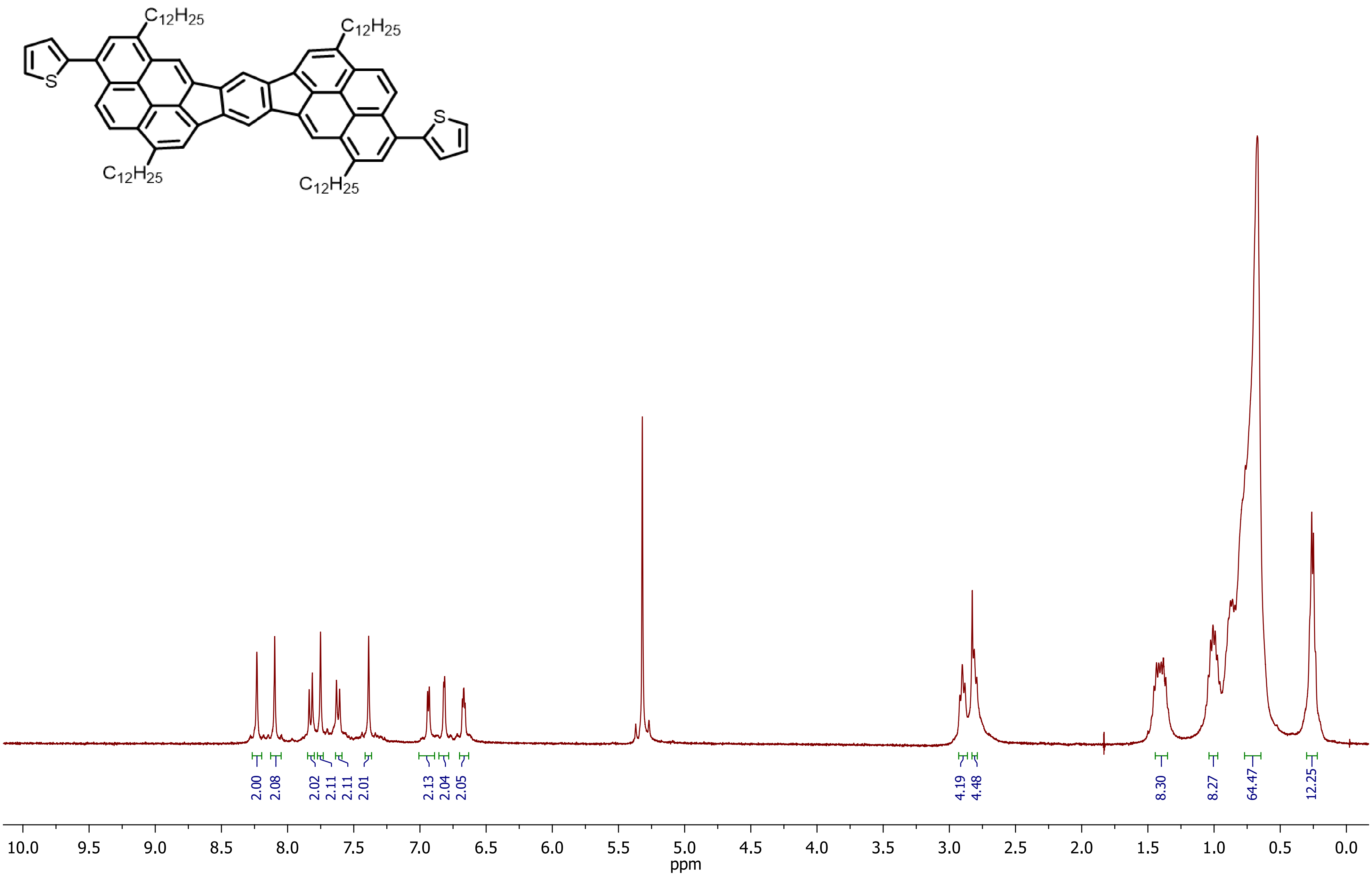

2.00
2.02
2.03
2.06
2.02
2.04
2.01
4.00
4.17
8.01
8.02
64.34
10.87
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Compound 1b

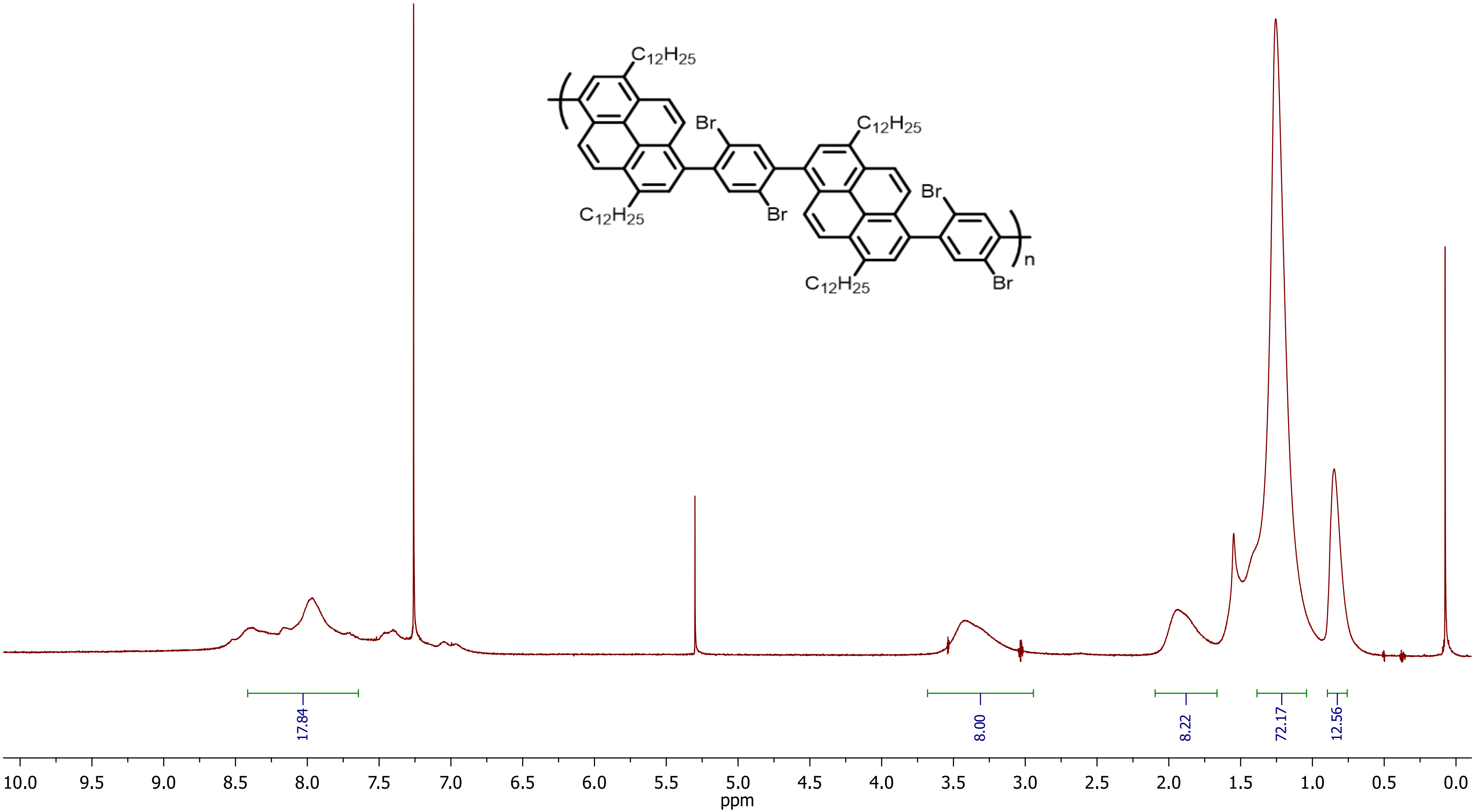

C12H25
C12H25
H3CO
OCH3
C12H25
C12H25


2.00
2.03
2.04
4.01
2.04
4.09
4.06
6.05
4.16
4.19
8.31
8.00
64.73
12.13
10.0
9.5
9.0
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
0.5
0.0
ppm

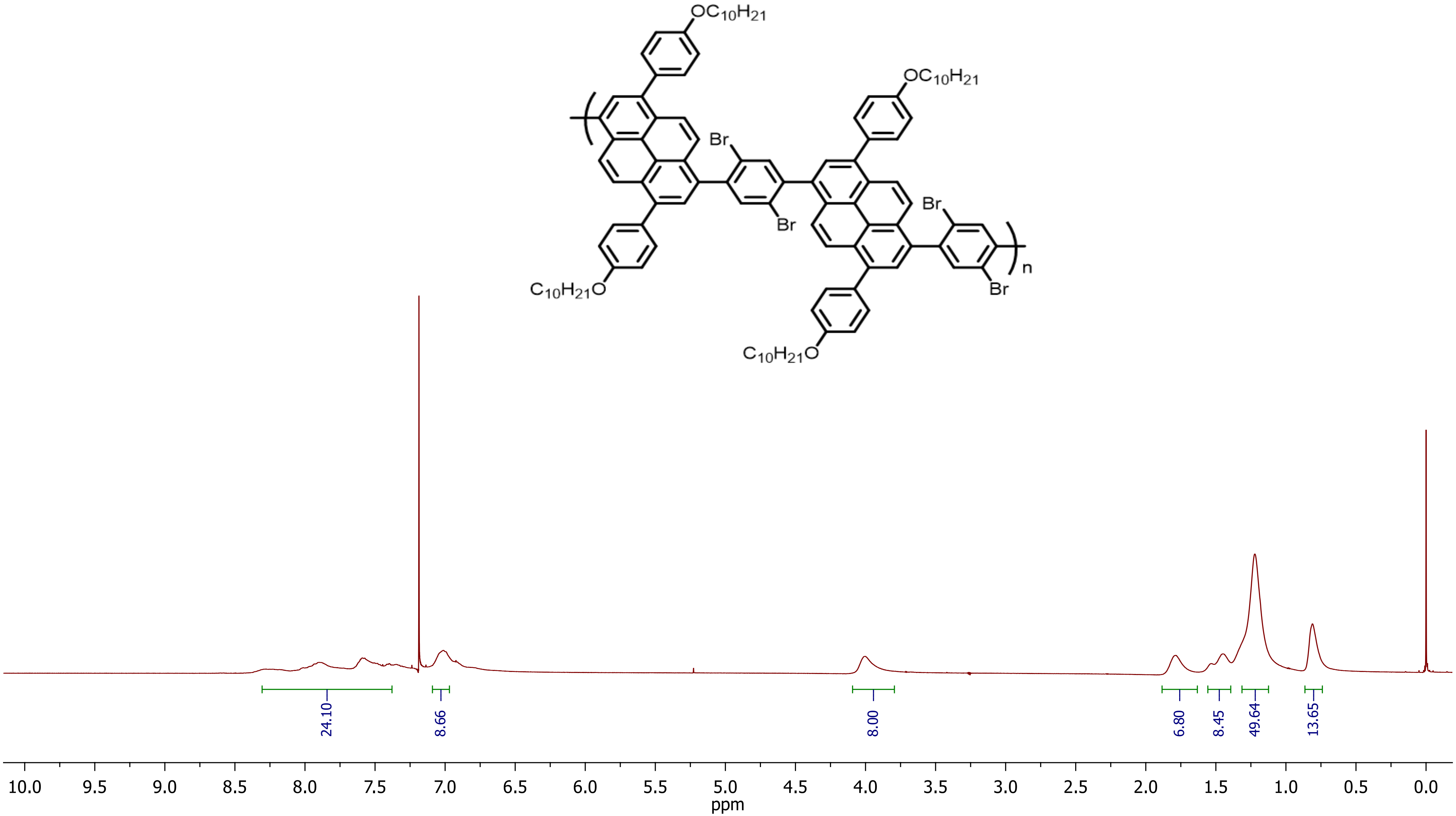
Compound 1c


C12H25
C12H25
C12H25
C12H25
S
S
2.00
2.08
2.02
2.11
2.11
2.01
2.13
2.04
2.05
4.19
4.48
8.30
8.27
64.47
12.25
10.0
9.5
9.0
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
0.5
0.0
ppm

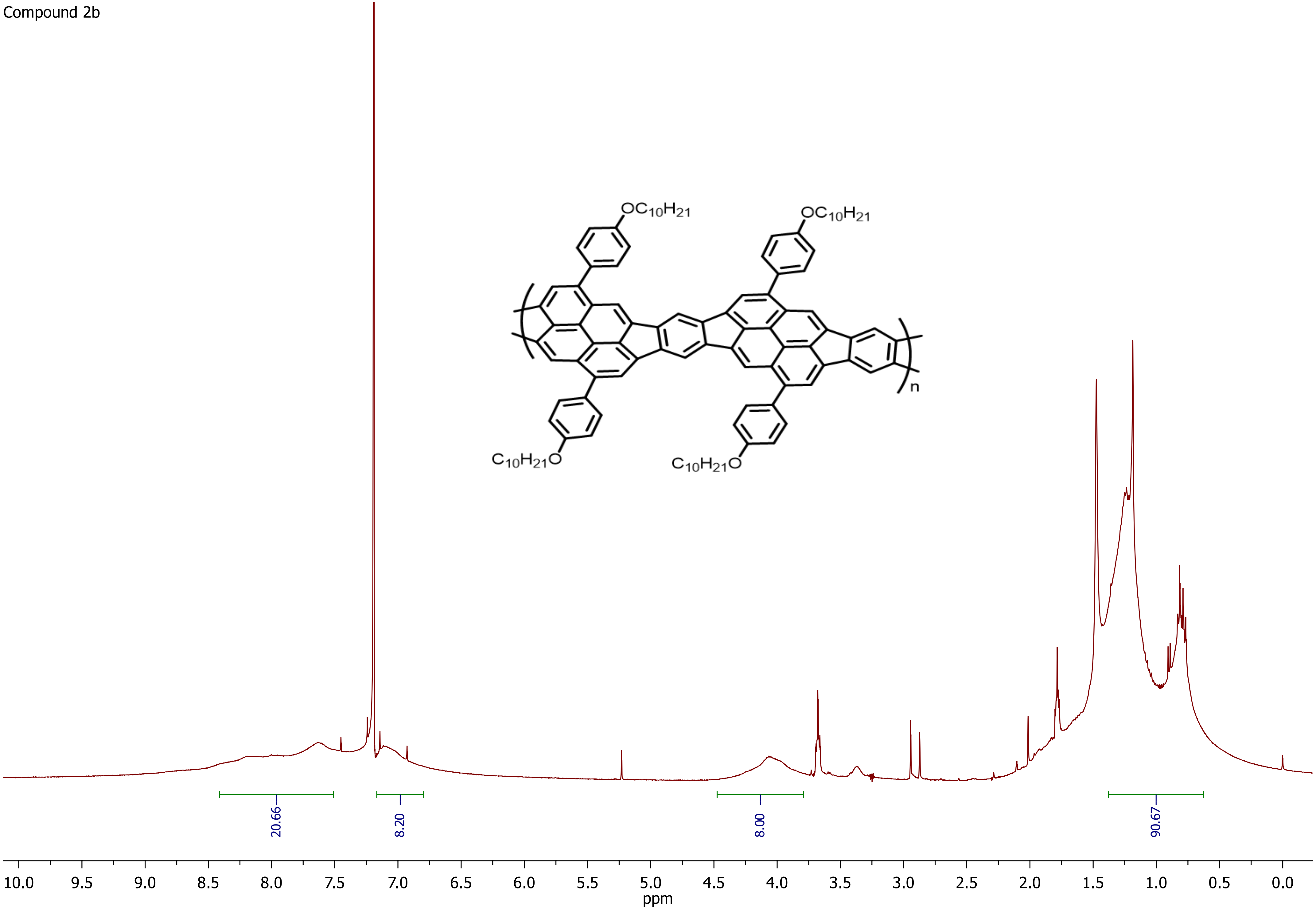
Compound 16


C12H25
Br
C12H25
C12H25
Br
Br
C12H25
Br
n
17.84
8.00
8.22
72.17
12.56
10.0
9.5
9.0
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
0.5
0.0
ppm

Compound 17


OC$_{10}$H$_{21}$
OC$_{10}$H$_{21}$
Br
Br
Br
Br
C$_{10}$H$_{21}$O
C$_{10}$H$_{21}$O
n
24.10
8.66
8.00
6.80
8.45
49.64
13.65
10.0
9.5
9.0
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
0.5
0.0
ppm

Compound 2b



$OC_{10}H_{21}$
$OC_{10}H_{21}$
$C_{10}H_{21}O$
$C_{10}H_{21}O$
n
20.66
8.20
8.00
90.67
10.0
9.5
9.0
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
0.5
0.0
ppm