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Studies Toward the Optimization of Energy Migration in Rigid-Rod Surfactant Polymers

by

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ABSTRACT

Rigid-rod *p*-phenyleneethynylene surfactant polymers were synthesized in an attempt to obtain polymer alignment and possibly enhance energy migration in those polymer chains. Two methods were investigated in this thesis to determine if alignment of the polymer chains could be obtained. The first of these methods was through the use of the inherent anisotropy of lyotropic liquid crystalline polymers, and the second method was through the preparation of aligned Langmuir-Blodgett thin films. The two types of surfactant polymers that were synthesized, ionic and non-ionic, did not yield any lyotropic liquid crystal solutions, mainly because of the low solubility of the polymers. However, some of the non-ionic polymers did give alignment in Langmuir-Blodgett thin films, which was measured using polarized UV-Vis spectroscopy. In the course of these studies, a polymer containing a pendant 15-crown-5 was determined to show particular sensitivity to potassium ions. This effect was measured using UV-Vis and fluorescence spectroscopy. The same effect was not seen with lithium or sodium.

Thesis Supervisor: Timothy M. Swager

Title: Professor of Chemistry

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To my family, for their support.

To Beth, for all the support and love.

Chapter 1

Introduction to Conjugated Polymers, Lyotropic Liquid Crystals, and Langmuir-Blodgett Thin Film Preparation

i. Conjugated Polymers

Conjugated organic polymers, which are polymers that have a highly delocalized π system, have become increasingly important in materials research, bringing forth many new discoveries in recent years.[1] The initial discovery that doped *trans*-polyacetylene (Figure 1.1) can exhibit conductivities as high as 1.5 x 10^5 S/cm, that of a conducting metal, led many efforts of research in this area.[2] Initially, most of the effort was directed at trying to overcome the setbacks of polyacetylene, which is insoluble and very sensitive to air oxidation. Both of these attributes make polyacetylene very difficult to process for any useful applications. In an attempt to overcome these problems, other polymers (Figure 1.1) were developed, some of which were also highly conductive when doped.[3] Although some of the polymers shown in Figure 1.1 are also insoluble, addition of alkyl- or alkoxy- chains to the polymer backbone has led to soluble analogs of most of these polymers.

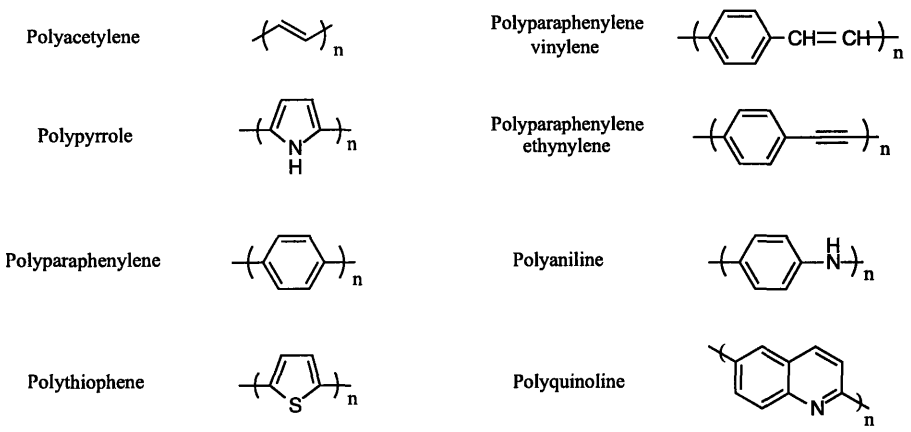


Figure 1.1. Examples of conjugated polymers.

Aside from the developments in conducting polymers, research in conjugated polymers has brought forth a number of other applications. Some of the most notable applications discovered to date are those in electroluminescent devices (for example, LEDs) and chemical sensors.

The first of these areas, LEDs, has recently garnered worldwide interest. The use of

The first of these areas, LEDs, has recently garnered worldwide interest. The use of organic polymers in LEDs would bring many advantages over conventional inorganic semiconductor technology. Some of these advantages are that organic polymers are easily processed to form useful structures, they can be more economically feasible in large display areas, and there are a large number of different colors available. Some of these colors were only recently available in inorganic semiconductors.[4,5]

Another area that has also been gaining widespread interest is the use of conjugated polymers in chemical sensing devices. There are two main methods in which conjugated polymers are used as chemical sensors. In the first method, the sensor is based on conductivity changes in a conjugated polymeric material upon binding of an analyte. In the second method, optical changes in a conjugated polymer (a change in either the absorption or the emission wavelength of light) signal the binding of an analyte to a receptor.

ii. Chemical Sensor Background

The need for chemical sensors, whether monomeric or polymeric, is continually growing. There have been many monomeric chemosensors developed for the detection of ions, aromatic hydrocarbons, and sugar molecules.[6] The ability to measure "real-time" concentrations of analytes such as K^+ in a person's bloodstream during heart surgery is extremely important. This detection can be accomplished using fluorescent receptors such as the coumarin dye shown in Figure 1.2, which can measure intracellular K^+ concentration.[7]

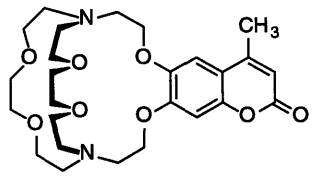


Figure 1.2. Coumarin dye/cryptand-based K^+ sensor.

Most of the chemical sensors used today are monomeric receptors that are based on

decrease, or a wavelength shift in the absorption or emission of light. Some of the most sensitive of these chemosensors use fluorescence as the signal, because fluorescence spectroscopy is a very sensitive technique, and it is even possible to detect the fluorescence of a single molecule. One main setback of this type of sensor is that high sensitivity can be obtained only by having a very large binding constant between the receptor and the analyte. This leads to two possible problems: First, for the detection of certain analytes, it may be impossible to develop receptors with large binding constants, and second, a large binding constant can produce an irreversible sensor that must somehow be "reset" to is its original condition. These problems would require more complicated and expensive devices.

Numerous chemical sensors are commercially available at this point in time. A very common and inexpensive one, phenolphthalein, changes color in visible light at a certain pH, effectively making it a H^+ ion sensor. However, this sensor is very limited in actual applications. Other, more complicated mechanical sensing devices, such as catalytic devices,[8] are used to determine the concentration of compounds by destructive methods. An example of a catalytic device is one that uses a solid-phase catalyst to determine the concentration of flammable gases by reacting them with oxygen:

$$CH_4 + O_2 \xrightarrow[\Delta]{\text{Catalyst}} CO_2 + 2H_2O$$

In this case, the heat of reaction is used to determine the concentration of flammable gas present. This type of device is limited by the necessity of high temperature for the reaction to proceed, and at this temperature, the catalyst is slowly degraded and can easily be poisoned by reaction with compounds such as thiols. Other problems with this type of sensor are that the reaction is irreversible and that the sensor is not specific for a single compound; any one of a number of flammable gases would be detected.

iii. Sensor Amplification

Another way to obtain high sensitivity while circumventing the problem of

irreversibility is to the use a method that can amplify the response of a binding event. This is where the use of conjugated polymers has become increasingly important. In this method, the collective property of the system, either conductivity or energy migration, is used to amplify a binding event. In the case of conductivity, any binding event on a single polymer chain, acting essentially as a defect, can cause dramatic changes in the conductivity of the material as a whole.[9] Some examples of polymeric systems that have been developed based on conductivity changes are shown below (Figure 1.3).[10]

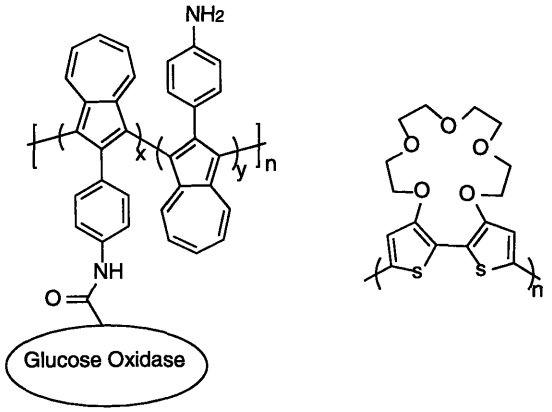
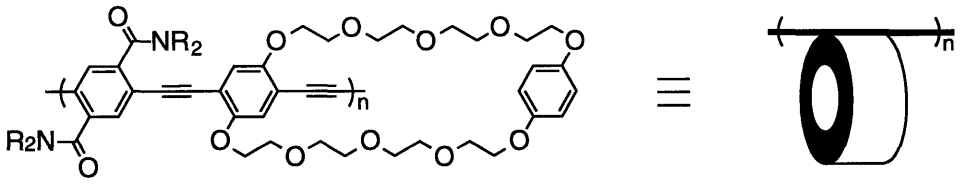


Figure 1.3. Examples of conducting polymer sensors.

The first example that is shown, a polyazulene functionalized with glucose oxidase, is a glucose-sensitive polymer. Reaction of the polymer-bound enzyme with glucose causes an oxidation of the polymer, which in turn causes an increase in the conductivity. The second example shown is a bithiophene-crown polymer that is sensitive to ionic species. Binding of a metal ion by the crown ether causes a twisting of the polymer's backbone, which then causes a decrease in conductivity.

In the case of energy migration amplifying the binding of an analyte, the polymer acts as an antenna that funnels energy to the receptor that has bound an analyte. This will either lead to a quenching of the fluorescence by this site or, if it is a local minima in the band structure, cause a shift in the wavelength of fluorescence. As proof of this concept, Swager has developed a conjugated polymeric system that amplifies the quenching effect upon

binding of a paraquat molecule to a cyclophane receptor built into the polymer backbone.[11] This poly(*p*-phenyleneethynylene), containing a diamidobenzene and a cyclophane receptor, is shown in Figure 1.4. Also shown is an illustration of the cyclophane receptor on the rigid-rod polymer.



R = C_8H_{17}
M_n = 65,000

Figure 1.4. *p*-Phenyleneethynylene polymer with cyclophane receptor that binds paraquat.

An illustration of the amplification of a binding event through energy migration is shown in Figure 1.5. The excitation formed by absorption of ultraviolet light can migrate along the polymer backbone until it encounters the paraquat molecule, which quenches the fluorescence. The use of the polymer gives a 65-fold enhancement of quenching over a single receptor model system. This amplification caused by the energy migration is limited, however, by the lifetime and mobility of the excitations. Beyond a molecular weight of ~65,000, there is no further enhancement in sensitivity to paraquat.

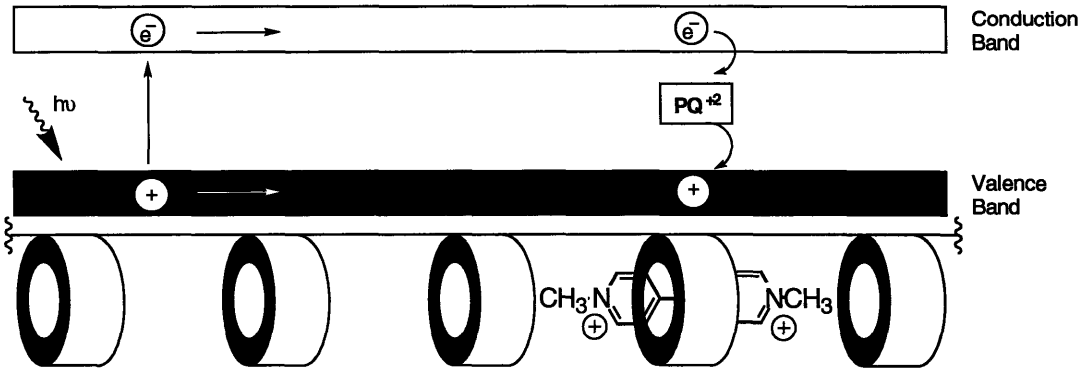


Figure 1.5. Diagram of amplified quenching effect of paraquat on a cyclophane-containing conjugated polymer.[11]

Amplification of a chemical sensor through energy migration in a conjugated polymer may be further enhanced by effectively extending the conjugation of the polymer. Even though the *p*-phenyleneethynylene polymer is expected to have a rigid-rod backbone, acetylene-phenyl bonds do allow for more bending of the bond than would have been expected. This extra bending allows the polymer, which is very long, to coil up on itself and the solvent. This is the reason that even though polymers such as the paraquat sensor developed by Swager can be made with molecular weight higher than 65,000, the effective length of the polymer is limited by its morphology in solution.

iv. Amplification Enhancement

There are two methods investigated in this thesis to determine if the amplification of energy migration in rigid-rod p-phenyleneethynylene polymers could be enhanced by aligning the polymer chains. The first of these methods was through the use of the inherent anisotropy of lyotropic liquid crystalline polymers, and the second method was through the preparation of aligned Langmuir-Blodgett thin films.

The first method of alignment described would make use of the inherent order of the liquid crystalline state, which is a phase of matter between that of crystals and that of liquids. Liquid crystals maintain some of the order found in crystalline solids, while also maintaining the fluid properties of a liquid. Two main categories of liquid crystals are thermotropic and lyotropic, and they can both be either monomeric or polymeric.[12,13] Thermotropic liquid crystals form a liquid crystal phase, or mesophase, throughout a certain temperature range, while lyotropics form a mesophase over a concentration range in one or multiple solvents, which is also affected by temperature.

Lyotropic liquid crystals phases are usually formed by the dissolution of an amphiphilic molecule in a solvent at a particular concentration range. An amphiphilic molecule is one that contains both a polar (hydrophilic) group and a non-polar (hydrophobic)

group. A classic example of an amphiphile is a surfactant such as sodium dodecylsulfate, shown in Figure 1.6 along with a common illustration used to describe surfactants. A round ball is used to signify the polar group of the molecule, and a tail is used to signify the non-polar chain of the surfactant. The surfactant shown here is an example of an anionic surfactant. Other types of surfactants can be cationic, zwitterionic (both charges), or non-ionic.

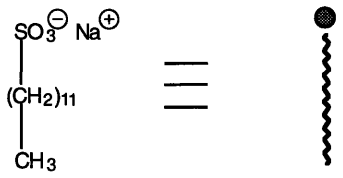


Figure 1.6. A surfactant (sodium dodecylsulfate) and an illustration.

Because of the nature of the molecule, when a surfactant is dissolved in a solvent such as water, the molecules aggregate to form supramolecular structures. One such structure is a micelle, which is a spherical structure that has all the hydrophilic groups pointing outward, while the hydrophilic chains are grouped together and protected from the water on the inside. However, if the surfactant is dissolved in a nonpolar solvent, an inverted micelle forms. As its name implies, this type of micelle is inverted, with the hydrophobic chains pointing outward and the polar groups on the inside of the micelle. By changing the concentration of the surfactant in solution, it is possible to form other supramolecular structures such as the columnar and lamellar phases. Illustrations of the micelle and columnar phases are shown in Figure 1.7.

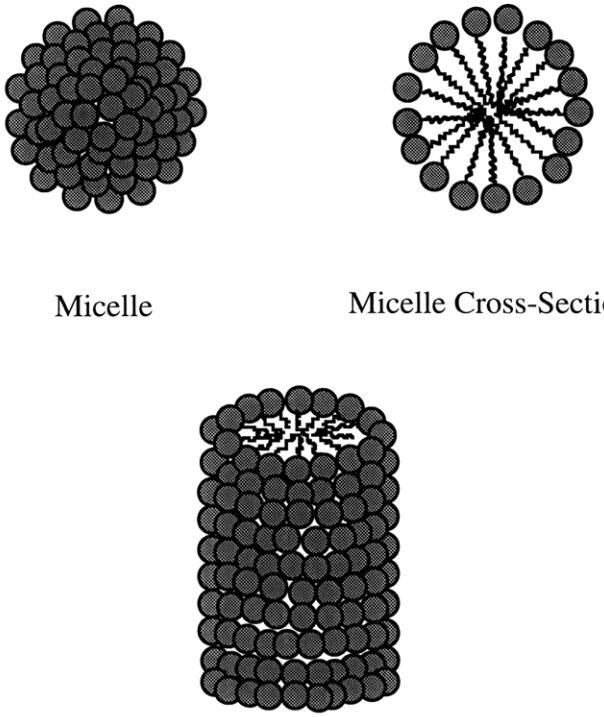


Figure 1.7. Micelle and columnar phases.

The most famous of all lyotropic liquid crystals, Kevlar, forms a liquid crystal phase when dissolved in concentrated sulfuric acid. In this phase, greater orientation is obtained such that when the polymer is extruded, the polymer chains are aligned and there is a much greater strength to the material. So much, in fact, that Kevlar is 30 times stronger than nylon, which is extruded from the liquid phase.[12]

The orientation that is obtained in the liquid crystal phase can also be used for other purposes. It was proposed that enhanced sensitivity in poly(*p*-phenyleneethynylene) sensors could be obtained by the use of the orientation in lyotropic liquid crystals. By synthesizing rigid-rod surfactant polymers that form lyotropic liquid crystalline phases, it was envisioned that an orientation would be obtained that could lead to greater energy migration by an excitation in the polymer backbone. It would also be possible to then dope a lyotropic liquid crystalline polymer solution with a small quantity of receptor-containing polymer. This

would align with the surfactant polymers in the liquid crystal phase and gain enhanced sensitivity.

Another method that could be used to obtain greater energy migration in p-phenyleneethynylene polymers is the preparation of aligned Langmuir-Blodgett (LB) thin films. It would be possible to use the same surfactant polymers that were prepared for lyotropic ordering, to form these LB films. These aligned films would have the added advantage of allowing for the preparation of solid state chemical sensing devices that could be used in actual applications.

In the Langmuir-Blodgett thin film preparation technique[14] (Figure 1.8), a surface active (surfactant) molecule, either monomeric or polymeric, is dissolved in a solvent and dispersed on the surface of the subphase, which is usually water (a). The molecules are compressed by Teflon barriers until they form a compact monolayer (b), and then by dipping a solid substrate through the surface of the subphase, mono- or multilayers can be deposited on the surface of the substrate (c). Depending on the surface of the substrate, either hydrophilic or hydrophobic, the polar group of the molecule will be directly against the substrate or pointing outward from it.

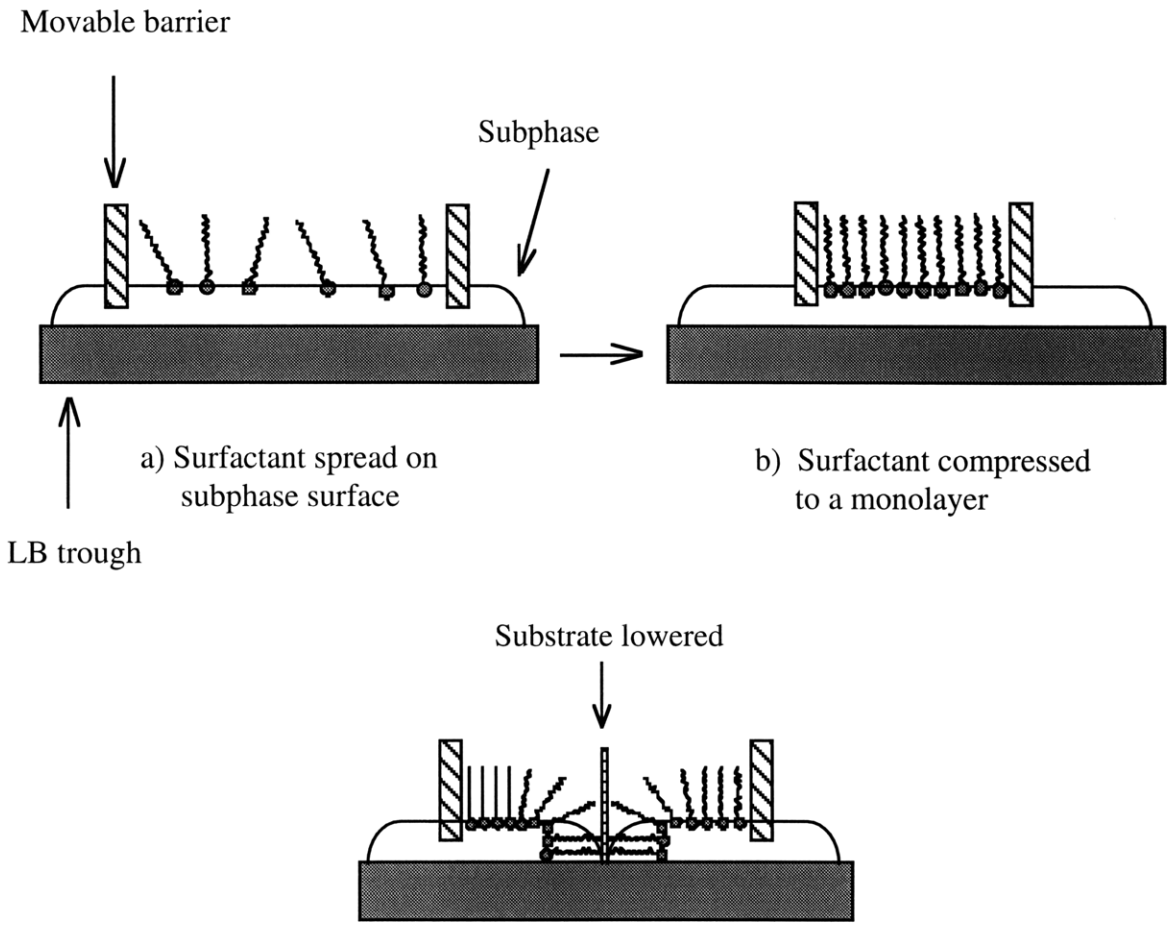


Figure 1.8. Illustration describing the LB thin film preparation technique.

By depositing the surfactant polymers on the surface of the subphase and compressing to a monolayer, and further, by depositing a monolayer on a substrate, alignment of the polymer chains is obtained. The alignment of the polymers deposited on a glass slide can be determined by measuring the order parameter. This is calculated by using the equation below[15] and measuring the UV-Vis absorption of polarized light that is parallel or perpendicular to the direction of dipping the solid substrate.

$$\text{Optical Order Parameter} = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}$$

As this equation shows, a perfectly ordered sample, with all the polymer chains aligned in a single direction, would have an order parameter of one, while a sample with completely disordered polymers would have an order parameter of zero. Order parameters anywhere between 0 and 1 indicate an intermediate degree of polymer order.

Chapter 2

Synthetic Work Toward Surfactant Polymers

i. Introduction

In order to achieve alignment of rigid-rod phenyleneethynylene polymers through either lyotropic liquid crystalline solutions or Langmuir-Blodgett thin films, it was necessary for us to synthesize surfactant polymers. The two types of surfactant polymers we investigated were ionic and non-ionic surfactant polymers. In the case of ionic surfactant polymers, where the polar groups desired were cationic, anionic, or zwitterionic, the polar groups were removed from the polymer backbone by a six-carbon alkyl chain. In the case of non-ionic surfactants, the polar group was attached directly to the polymer backbone. Examples of ionic and non-ionic surfactant polymers targets are shown in Figure 2.1.

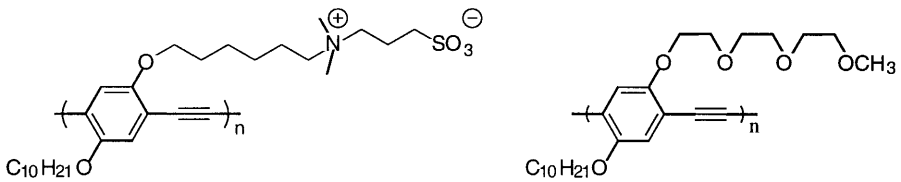
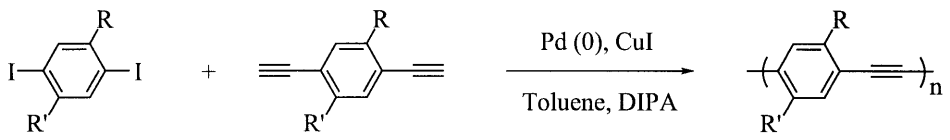


Figure 2.1. Examples of a rigid-rod surfactant polymers.

ii. Palladium Coupling Reaction

An integral part of the synthesis of the surfactant polymers in this research was the Sonogashira-Hagihara[16,17] palladium coupling reaction used to create high molecular weight polymers. This reaction has been previously used by the Swager group[11] to produce polymers with a molecular weight greater than 1 x 10^6. The two components necessary for this reaction are the aryl diiodide and the aryl diacetylene. It is possible to run the palladium coupling reaction with an aryl dibromide; however, higher reaction temperature is required and lower molecular weights are obtained.

A generic example of this reaction is shown below, where R and R' can be either the same or different groups.



The reaction also requires stoichiometric amounts of diisopropylamine and catalytic amounts of Pd(0) and CuI. It is possible to use either $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ as the palladium source, but $PdCl_2(PPh_3)_2$ is avoided for the synthesis of polymers. $PdCl_2(PPh_3)_2$ is reduced to Pd(0) by reaction with diisopropylamine, but it is also possible to reduce the palladium by reductive coupling of two copper acetylide groups (formed during the reaction). This produces a diacetylene, which affects the desired molecular weight of the polymer due to a stoichiometry imbalance.

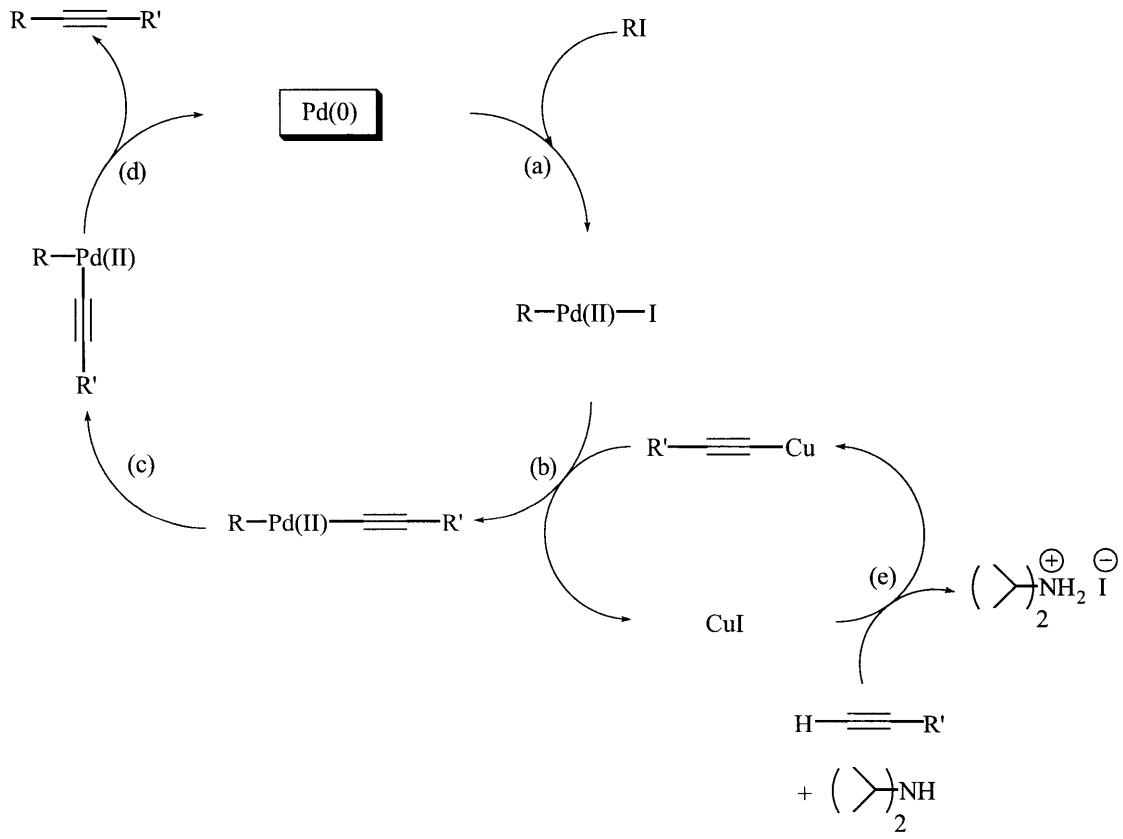


Figure 2.2. Palladium coupling reaction catalytic cycle.

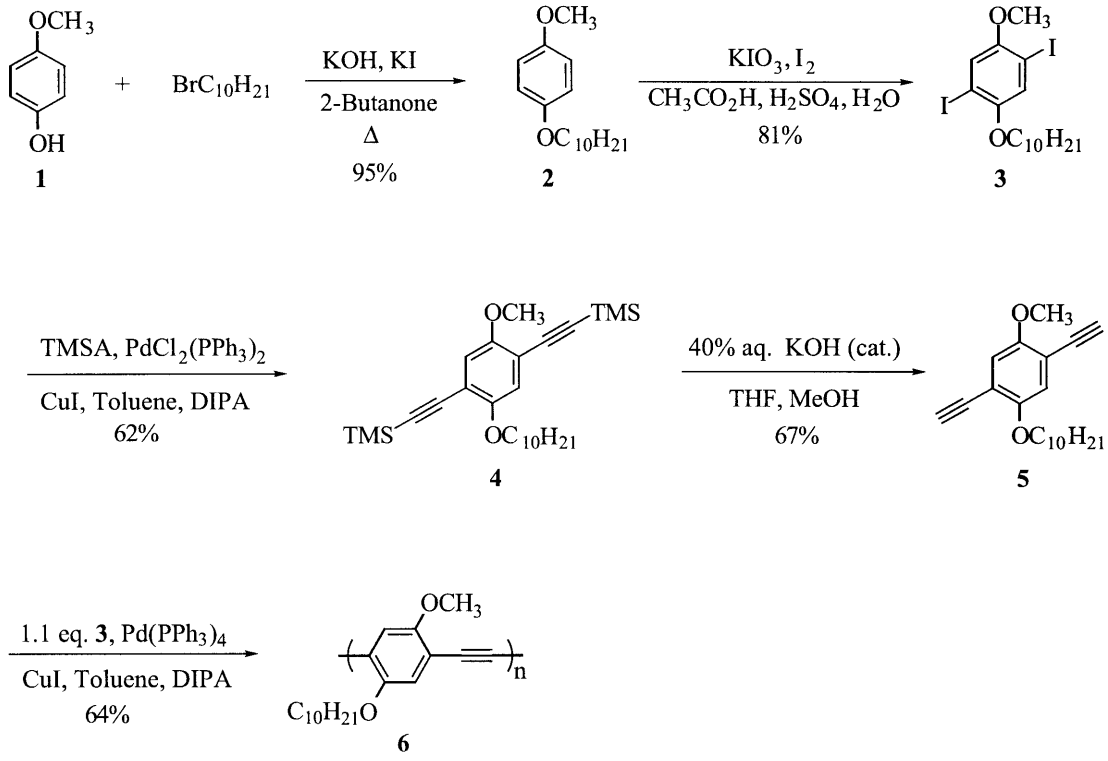
The catalytic cycle of the Sonogashira-Hagihara palladium coupling reaction is shown in Figure 2.2.[18] The catalytic cycle begins with the oxidative insertion of the palladium(0) into the RI bond (a), followed by transmetallation of the copper acetylide with the newly formed Pd(II) species (b). The Pd(II) species now contains two alkyl groups, R and R', which can isomerize to a cis position (c) and then reductively eliminate (d) to form the new alkyl-alkyl bond and Pd(0). The Pd(0) can now complete the catalytic cycle again.

In an another catalytic cycle that is connected with the main palladium cycle, the CuI is catalytically regenerated. In this cycle, the copper acetylide is formed by the reaction of diisopropylamine with the terminal acetylene, and then reaction with the CuI (e). The copper acetylide then participates in the transmetallation described before (b), which regenerates the CuI to participate in the cycle again.

iii. Results

In an attempt to produce soluble rigid-rod p-phenyleneethynylene surfactant polymers that could be used in alignment studies, a series of polymers were synthesized. All of these polymers were synthesized as regular hydrophobic polymers using the palladium catalyzed coupling reaction (*vida supra*) and then, if possible, were subjected to reaction conditions that would convert them to surfactant analogs. In most cases, however, solubility of the polymers was low, and thus did not allow for their conversion to surfactant analogs. In initial studies, a model polymer was synthesized that turned out to be a surfactant polymer itself, capable of producing aligned Langmuir-Blodgett films. The synthesis of this polymer is shown in Scheme 1.

Scheme 1



The synthesis of polymer **6** begins with commercially available p-methoxyphenol in a Williamson ether synthesis with 1-bromodecane to give the aryl ether **2** in 95% yield. Standard iodination procedures[19] were used to iodinate the aromatic ring in the ortho positions to give compound **3** in 81% yield. Coupling of two equivalents of (trimethylsilyl)acetylene to diiodide **3** using palladium catalysis produced **4** (62%), which was then converted to the terminal acetylene **5** (67%) using a catalytic amount of 40% aqueous KOH solution in a tetrahydrofuran and methanol mixture. Coupling of terminal acetylene **5** with diiodide **3** using tetrakis(triphenylphosphine)palladium afforded the rigid-rod polymer **6**. It was necessary to use an offset stoichiometry to obtain polymers of lower molecular weight. Initial reactions using the standard 1 equivalent of diiodide to 1.03 equivalents of diacetylene gave insoluble polymers.

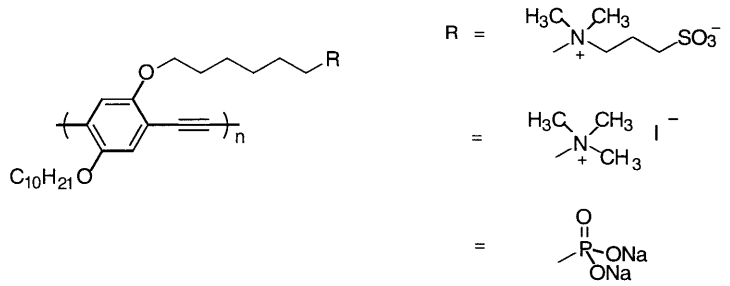
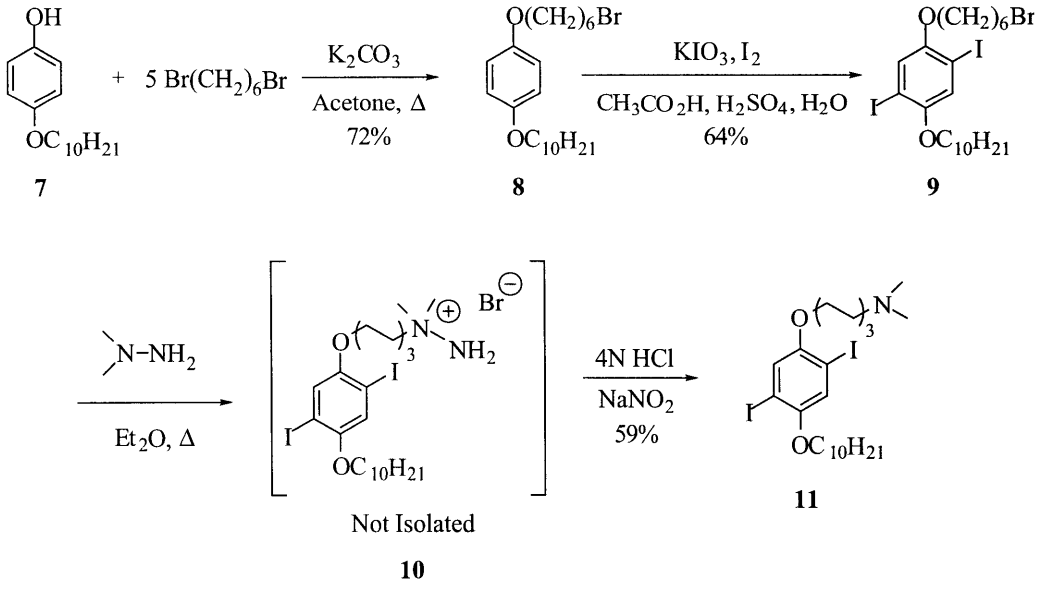


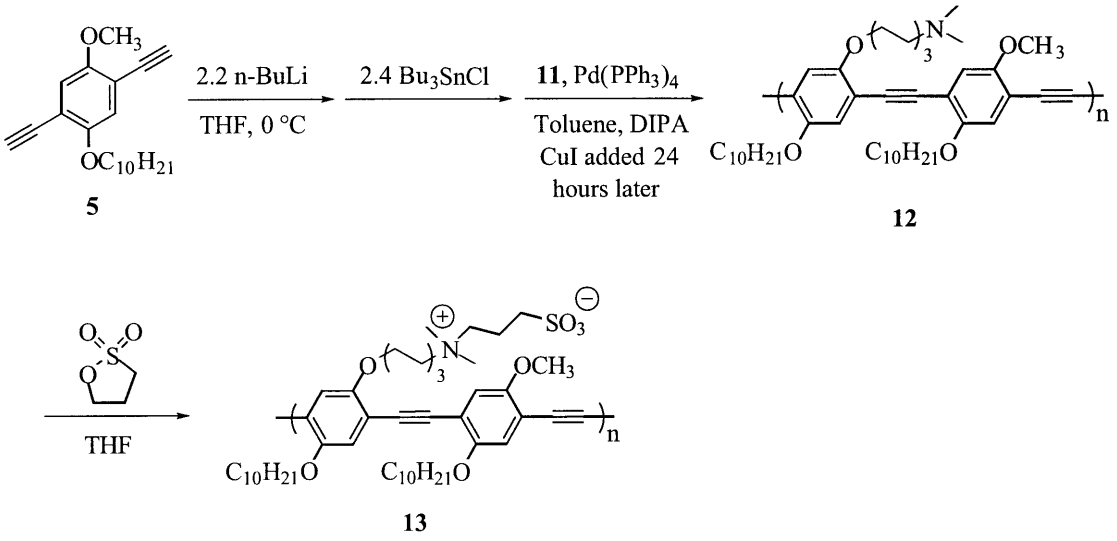
Figure 2.3. Target surfactant polymers.

Some surfactant polymer targets, which are similar to the model polymer synthesized, are shown in Figure 2.3. The desired polar groups for these three molecules are the sulfobetaine, the quaternary ammonium salt, and the phosphonic acid salt. Attempts to synthesize these polymers were made; however, the solubility of either the precursor polymer or the surfactant polymer itself limited the usefulness of these polymers. The synthesis of the first surfactant, sulfobetaine polymer, **12**, is shown below in Scheme 2. The synthesis begins with p-decyloxyphenol, **7**, a compound that was obtained from a research sample of a previous member of the Swager group.[20] Williamson ether synthesis of aryl ether **8** was

Scheme 2



Scheme 2 continued



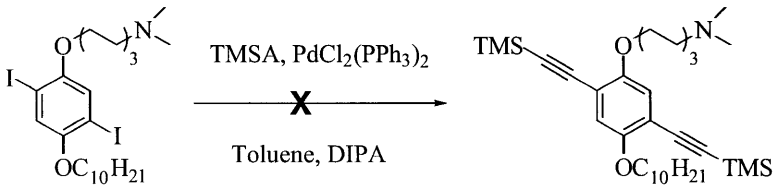
accomplished in 72% yield from the phenol, **7**. Iodination of **8** using a potassium iodate/iodine mixture in acetic acid gave the diiodide **9** in 64% yield. Unfortunately, some of the primary alkyl bromide was converted to the alkyl iodide during the reaction, which cannot be separated from the product. This was somewhat fortunate, though, because this small portion of alkyl iodide reacts faster than the bromide, and the displaced iodide anion acts catalytically in a Finkelstein reaction to speed up S_N2 reactions such as converting **9** to **10**. Preparation of the tertiary amine **11** was accomplished in a one-pot, two-step procedure.[21] In the first step, the alkyl halide **9** was reacted with dimethyl hydrazine to produce the hydrazinium salt, **10**, from which any starting material was removed by rinsing the solid with copious amounts of diethyl ether. In the second step, reaction with sodium nitrite in hydrochloric acid produced the tertiary amine **11** in 59% yield.

Synthesis of polymer **12** by standard palladium coupling procedures gave intractable gels, presumably due to crosslinking by protonic sources. Therefore, an alternative procedure was used, wherein the terminal acetylene **5** was deprotonated by n-butyllithium in tetrahydrofuran, followed by reaction of the di-anion with tributyltin chloride. This intermediate was then reacted in situ with the diiodide **11** as well as catalytic

tetrakis(triphenylphosphine)palladium, to yield the copolymer **12**. Initially, the reaction did not seem to proceed, but upon the addition of a catalytic amount of CuI the reaction progressed rapidly. The mode of action that CuI displays is uncertain. It may associate with the Pd-Ar-I intermediate and thereby activate it toward transmetallation or, alternatively, the CuI may react directly with the stannous acetylide to form a cuprous acetylide, which is also an intermediate in the standard cross-coupling procedures. Polymer **12** was then reacted with 1,3-propanesultone in tetrahydrofuran to yield the sulfobetaine surfactant polymer **13**. This polymer, however, was not soluble enough to investigate or characterize the possible liquid crystalline properties of the material.

Although the surfactant copolymer **13** was not soluble, it was thought that preparing a homopolymer might have better solubility because there would be a larger ratio of hydrophilic groups relative to hydrophobic hydrocarbon sidechains. Attempts at synthesizing a surfactant homopolymer, such as the one shown in Figure 2.1 (*vida supra*), were thwarted by complications in coupling (trimethylsilyl)acetylene to the diiodobenzene monomer **11** (Scheme 3).

Scheme 3

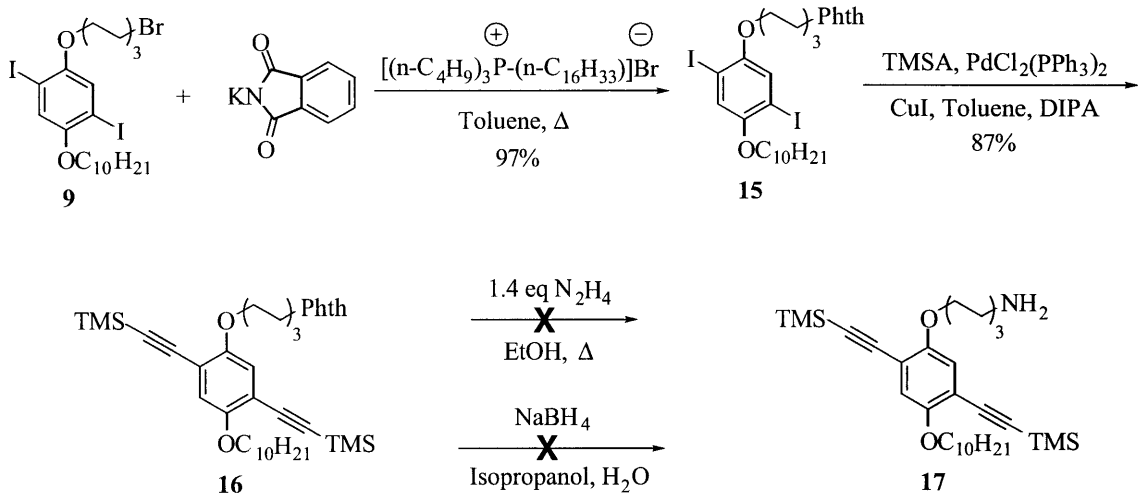


11 **14**

In the reaction shown in Scheme 3, only complex, polymeric mixtures were obtained that could not be separated by column chromatography. The exact reason why this reaction did not work is not understood, but it was thought that attempting another route toward an amine-based surfactant polymer might prove worthwhile. In this case, the primary amine analog

would be synthesized using protecting groups, and then in a final step, the primary amine could be converted to a quaternary ammonium surfactant by exhaustive methylation with methyl iodide. This synthetic Scheme, using a previously synthesized intermediate, **9**, is shown in Scheme 4.

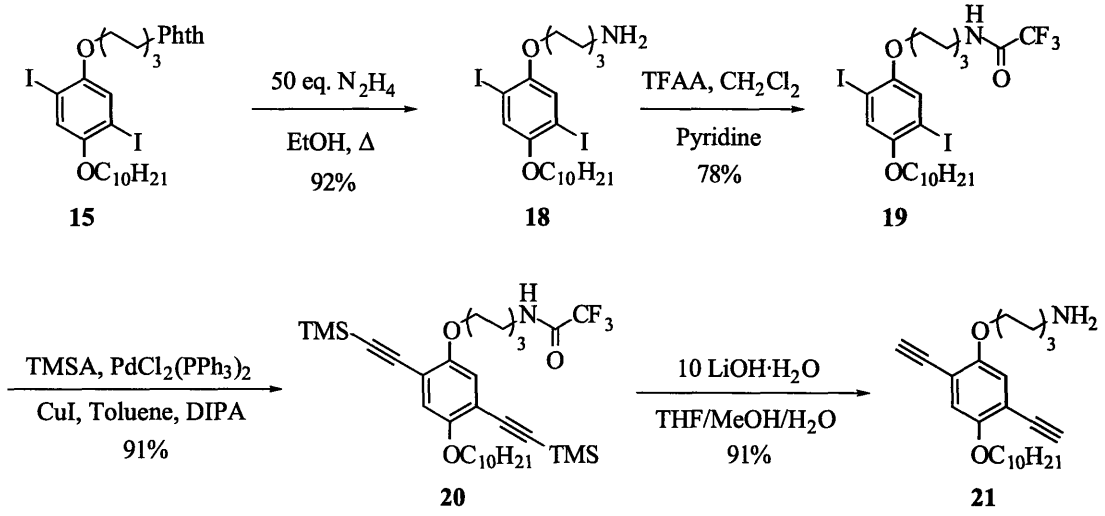
Scheme 4



The primary amine would be prepared by a standard Gabriel synthesis.[22] However, this did not work as simply as would have been expected. Compound **9**, a primary alkyl bromide, was alkylated by potassium phthalimide under phase transfer catalysis conditions[23] to afford the phthalimide derivative, **15**, in 97% yield. Palladium catalyzed coupling of the diiodide **9** and (trimethylsilyl)acetylene was completed before removal of the phthalimide protecting group. By retaining the protecting group, any complications were avoided, and compound **16** was obtained in 87% yield. Difficulties were encountered when trying to remove the phthalimide group in the presence of the acetylene groups. Standard Gabriel reaction conditions using a slight excess of hydrazine monohydrate in refluxing ethanol did not cleanly give the desired product, **17**. Another method using sodium borohydride reduction,[24] followed by heating with acetic acid was attempted; however, this was not

successful in unmasking the primary amine.

Scheme 5



It was thought that the problem with the phthalimide removal was the protected acetylene functionality. By removing the phthalimide protecting group and then using another more labile protecting group, it could have been possible to obtain the same desired compound. This synthetic attempt is shown in Scheme 5. Removal of the phthalimide using standard Gabriel conditions gave only low yields. Eventually, conditions for the phthalimide removal were found, using 50 equivalents of hydrazine monohydrate.[25] This cleanly produced the desired compound **18** in 92% yield. The primary amine was then protected as a trifluoroacetamide (**19**) in 78% yield. The trifluoroacetamide is a very labile protecting group and should be easily removed under basic conditions.[26] Coupling of (trimethylsilyl)acetylene groups to **19**, using standard palladium catalysis, gave **20** in 91% yield, with no disturbance of the trifluoroacetamide. Removal of both the trifluoroacetamide and the trimethylsilyl protecting groups was accomplished in 91% yield using 10 equivalents of $LiOH{\cdot}H_20$. However, at this point, attention was directed at synthesizing another type of surfactant.

After failing to prepare a nitrogen-based surfactant, it was thought that it might be

possible to obtain lyotropic liquid crystallinity by synthesizing a phosphonic acid surfactant whose properties could be controlled by changing the pH of solution. The target polymer, shown in Figure 2.4, is similar to the previous nitrogen-based polymer in all respects except for the different polar ionic group. In this method of synthesizing a surfactant polymer, the ionic group is effectively protected as a phosphonate ester through the polymer synthesis, and can then be converted to the phosphonic acid using a number of different methods. One important requirement for this deprotection is that it be quantitative, so that all of the esters are converted to the acid. The reaction shown in Figure 2.4, when used on monomeric phosphonate esters, is quantitative,[27,28] so it was thought that this should be suitable for reaction on a polymer.

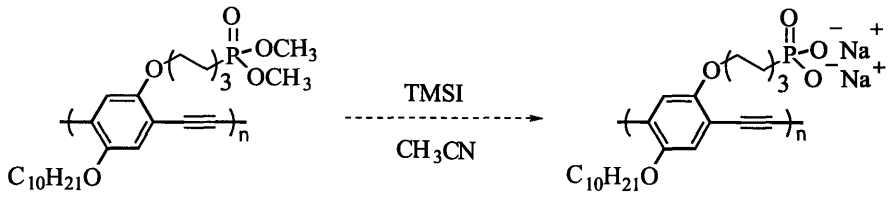
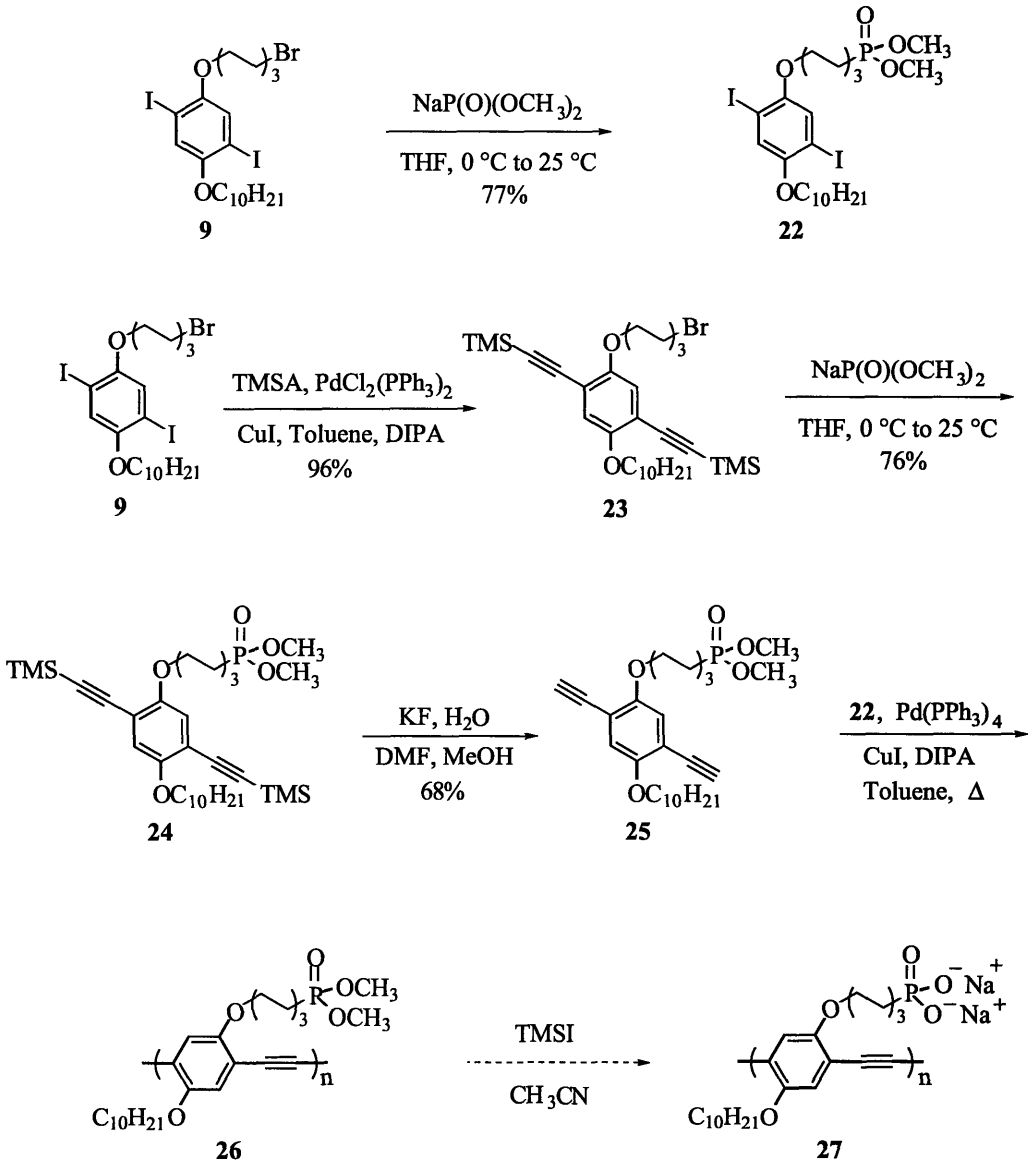


Figure 2.4. Phosphonic acid surfactant polymer target.

The completion of the synthesis of this polymer was not attained, because the solubility of the non-ionic precursor did not allow the last reaction to be completed. The synthesis of this polymer (Scheme 6) begins with compounds that were used in making the previous amine-based surfactant polymer. Compound **22** was prepared under anhydrous Michaelis-Becker reaction conditions[29] by addition of the alkyl halide **9** to the preformed sodium dimethyl phosphite. This afforded phosphonate ester **22** in 77% yield. Compound **9** was used once again, by coupling two equivalents of (trimethylsilyl)acetylene under palladium catalysis to give compound **23** in 96% yield. This reaction proceeded cleanly, with no disruption of the primary alkyl halide. Compound **23** was then subjected to the same Michaelis-Becker conditions as above, which produced phosphonate ester **24** in

Scheme 6



76% yield. The phosphonate ester was obtained with both acetylene protecting groups intact, which were subsequently removed using potassium fluoride in dimethylformamide at room temperature.[30] This method, which afforded the terminal acetylene **25** in 68% yield, was used instead of the standard hydroxide deprotection, so that no hydrolysis of the phosphonate ester would occur. The pendant phosphonate ester containing polymer, **26**, was initially synthesized using standard polymerization conditions between diiode **22** and diacetylene **25**,

but this yielded insoluble polymers after precipitation. By using an offset stoichiometry, only low molecular weight polymers were obtained, which would not precipitate in methanol.

Thus far, attempts at synthesizing an ionic surfactant polymer had not produced any results, so it was thought that it might be advantageous to focus attention on non-ionic surfactants. The polar group that would be used in this type of surfactant was an ethylene glycol group. The two types of interest would be a triethylene glycol monomethyl ether and a crown ether. It was hoped that the polar ethylene glycol portion of the molecule might give added solubility, and also, in the case of the 15-crown-5, that the liquid crystalline phases might be induced by addition of various salts. Additionally, by synthesizing polymers using different monomers, the triethylene glycol and the 15-crown-5, it was possible to develop a library of non-ionic surfactant polymers. The polymers that were synthesized are shown in Figure 2.5.

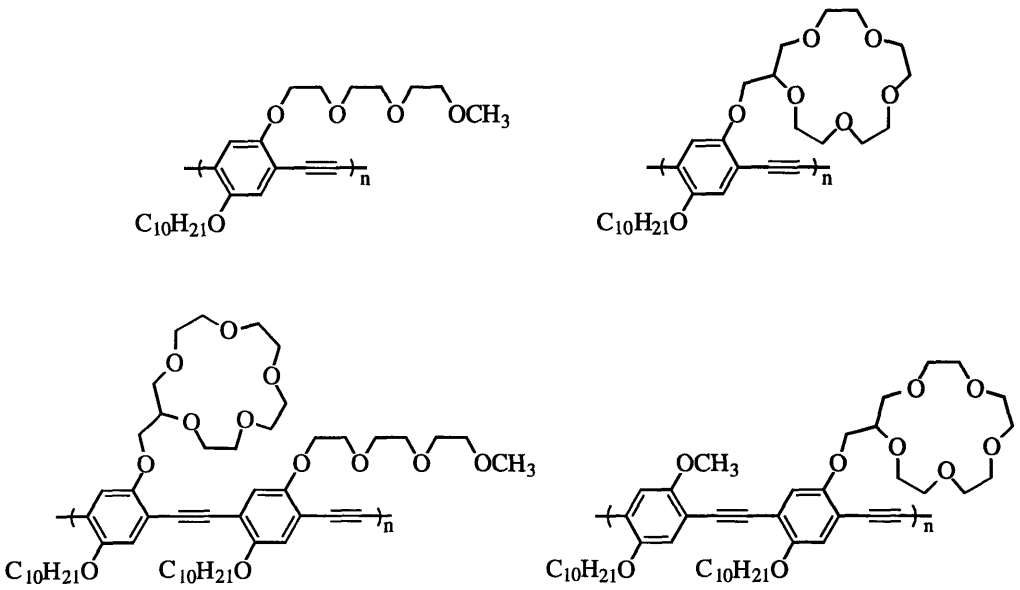
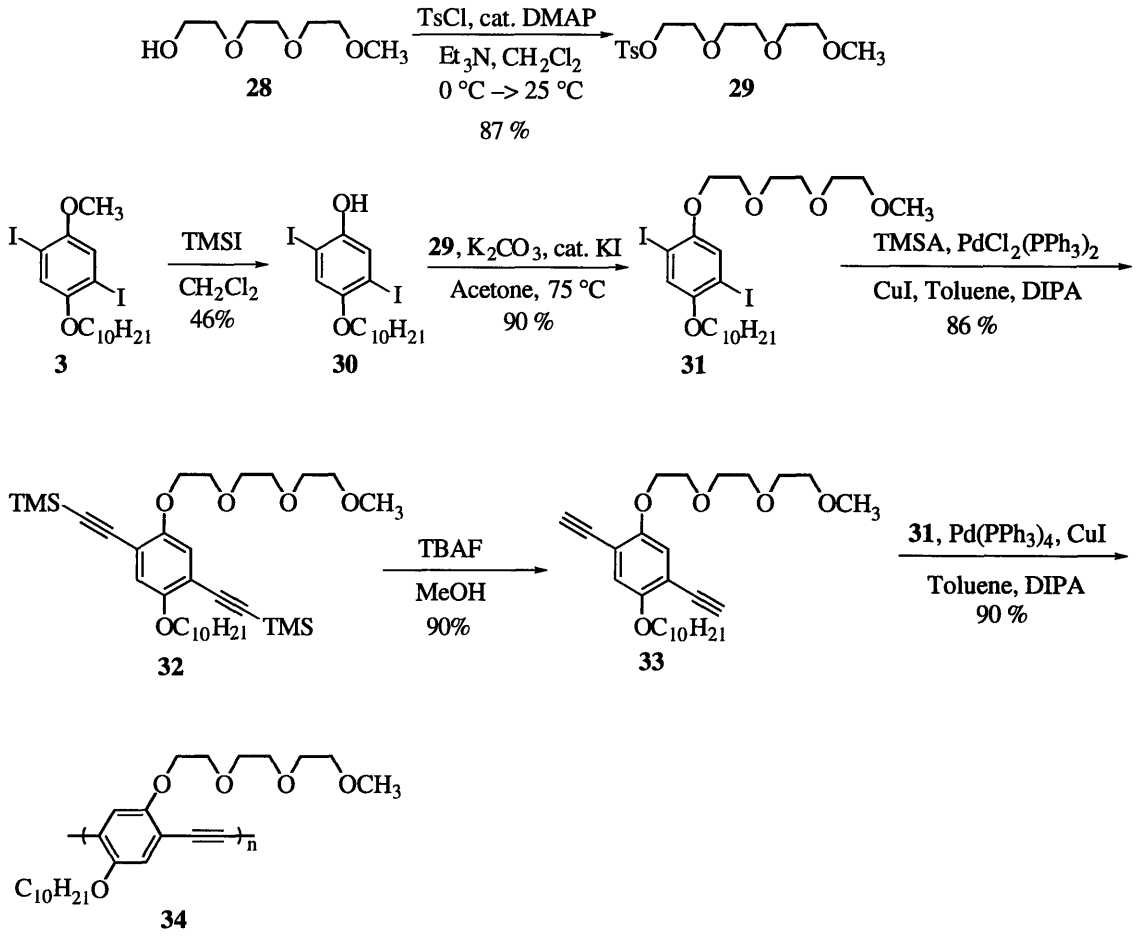


Figure 2.5. Non-ionic surfactant polymer targets.

As in the previous cases with ionic polymers, the solubility of some of these non-ionic polymers was too low to be useful. However, in a few cases, it was possible to adjust the reaction stoichiometry, thereby producing soluble, lower molecular weight polymers.

Studies with these nonionic surfactant polymers did not produce any lyotropic liquid crystalline phases, but during these studies an interesting ionic sensitivity based on changes in fluorescence was discovered. This effect was particular to the 15-crown-5/methoxy copolymer. The syntheses of these polymers are shown in Scheme 7.

Scheme 7

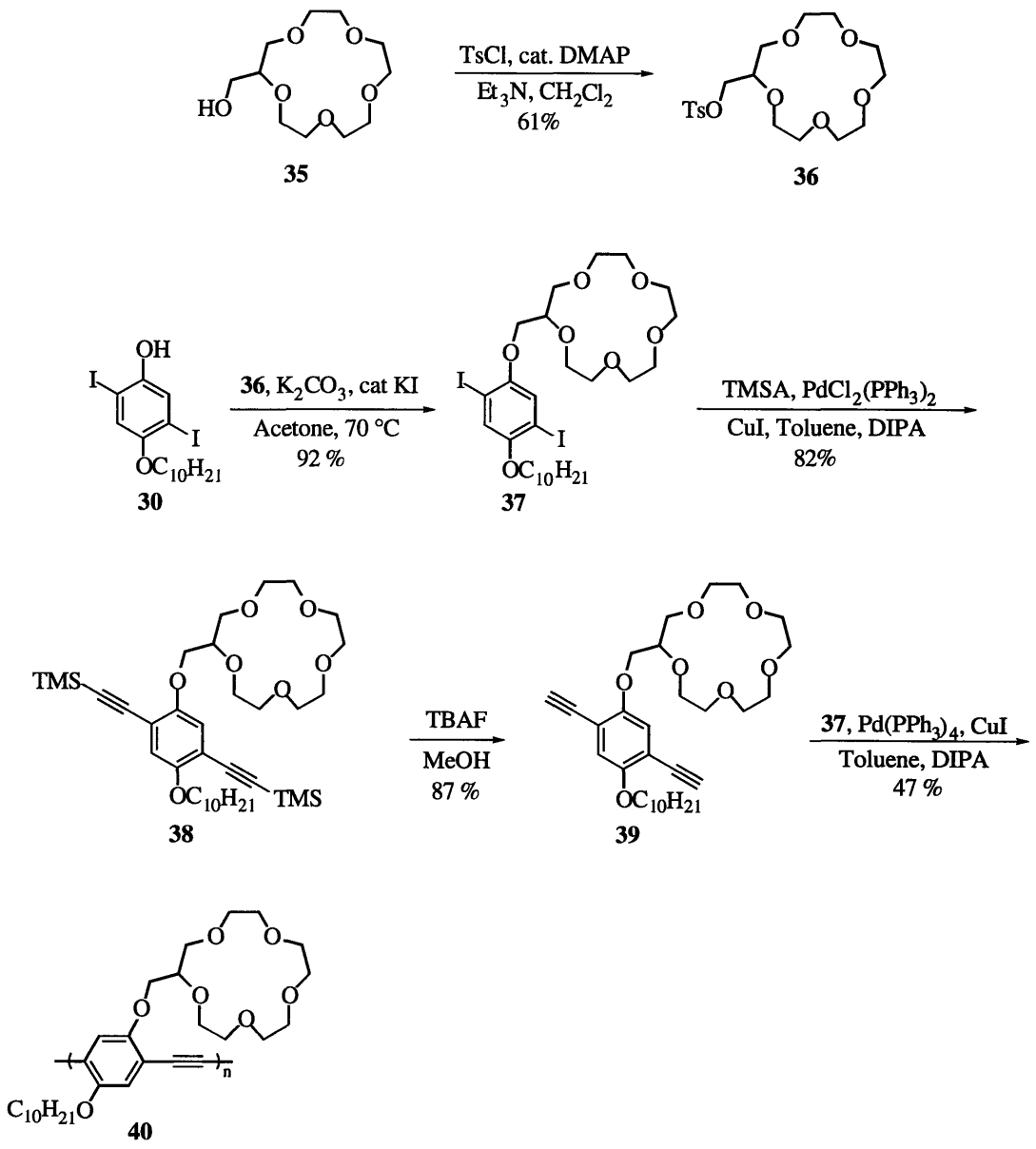


In the first step of the convergent synthesis, commercially available triethylene glycol monomethylether, **28**, was converted to the tosylate derivative **29** in 87% yield using tosyl chloride, triethylamine, and a catalytic amount of 4-dimethylaminopyridine (DMAP). Selective removal of the methyl ether of compound **3** using one equivalent trimethylsilyl iodide produced phenol **30** in 46% yield based on recovered starting material. Reaction of

the phenol, **30**, under standard Williamson ether conditions with tosylate **29** produced the triethylene glycol ether, **31**, in 90% yield. Palladium catalyzed coupling between diiodide **31** and two equivalents of (trimethylsilyl)acetylene gave compound **32** in 86% yield. Deprotection of acetylene **32** to produce terminal acetylene, **33**, was accomplished in 90% yield using tetrabutylammonium fluoride (TBAF) in methanol. Initially, the synthesis of polymer **34** was completed using standard palladium coupling conditions; however, this resulted in only partially soluble polymers. After changing reaction conditions to a different monomer stoichiometry, lower molecular weight polymers were obtained.

Synthesis of the pendant 15-crown-5 homopolymer, **40** (Scheme 8), was accomplished in a synthetic strategy very similar to the one in Scheme 7. The synthesis begins by preparing tosylate **36** from commercially available 2-hydroxymethyl 15-crown-5, **35**, in 61% yield. A lower yield was obtained than that of the corresponding tosylation in Scheme 7 because of difficulty in isolating the product. The 15-crown-5 has a high affinity for the ions found in the silica gel used for column chromatography, which makes separation difficult. Williamson ether synthesis between the tosylate, **36**, and phenol **30** gave compound **37** in 92% yield. Purification of this compound is easier than the crown, **36**, because of the larger ratio of non-polar to polar groups on the molecule. Coupling of the diiodide, **37**, with two equivalents of (trimethylsilyl)acetylene gave **38** in 82% yield. Removal of the trimethylsilyl protecting groups to give the terminal acetylene, **39**, was done in 87% yield using tetrabutylammonium fluoride. This method of deprotection was used rather than KF or KOH, because the alkali metals might get complexed between two crown ether molecules. However, compound **33** was unstable, and after long periods at room temperature (even under vacuum), it decomposed from a clear oil to a red one. It is possible that some metal

Scheme 8

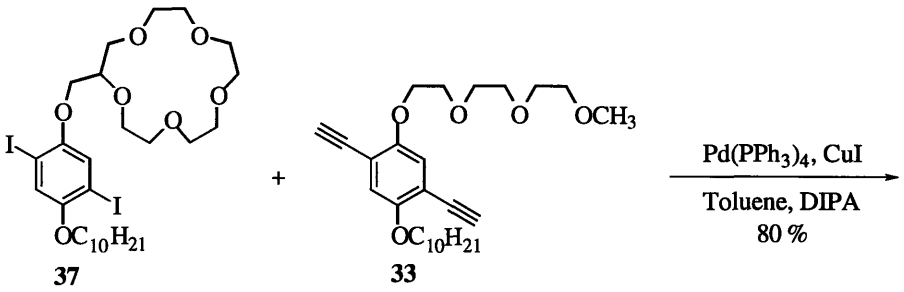


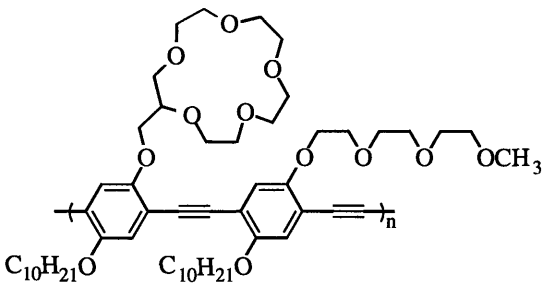
ions from one of the previous reactions were trapped within the crown ethers and caused unwanted reactions to occur. Polymerization of diiodide **37** and diacetylene **39** under palladium catalysis gave polymer **40** in 47% yield. This low yield reflects the fact that the reaction produced only low molecular weight oligomers. This may have been because the diacetylene, **39,** was not used right after purification, and was somewhat decomposed.

The syntheses of two other non-ionic surfactant polymers are shown in Scheme 9 and

Scheme 10. The monomers used to synthesize these polymers are from previous schemes, and they have just been combined to form different polymers. The first of these, polymer **41**, was synthesized by reaction of the pendant crown/diiodo benzene, **31,** with the pendant triethylene glycol/diethynyl benzene **27**. The reaction was done using standard palladium coupling stoichiometries to produce polymer **41** in 80% yield. Once precipitated, however, this polymer was not soluble.

Scheme 9



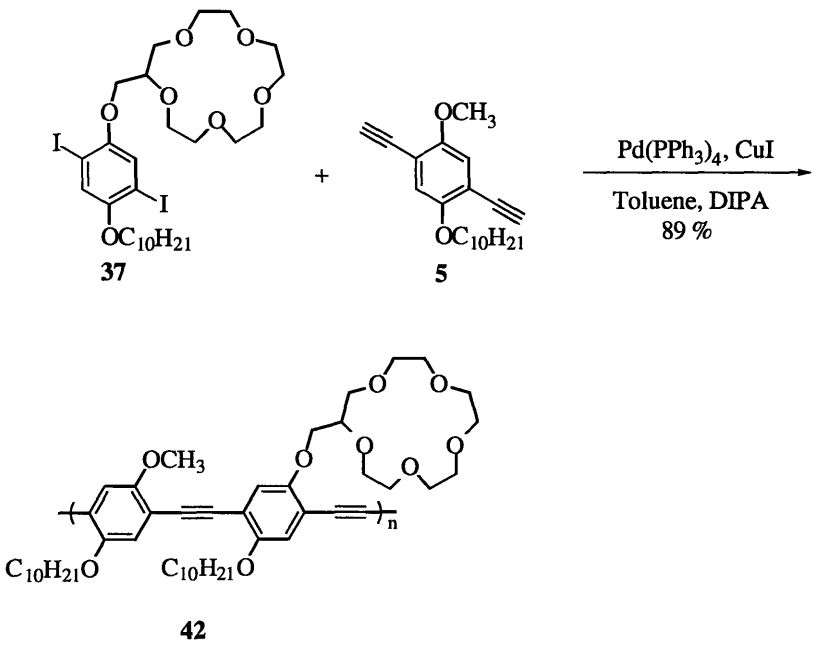


41

As shown in Scheme 10, by combining the pendant crown ether/diiodo benzene monomer, **31**, with the diacetylene, **5**, it was possible to synthesize copolymer **42** in 89% yield. The synthesis of this polymer was accomplished using an offset stoichiometry so that the reaction would yield lower molecular weight polymers that were soluble. After synthesizing polymer **42**, studies to determine if the polymer was a liquid crystal were completed. At this time, it was discovered that **42** had an unusual fluorescence sensitivity to

potassium ions. This was not the case with lithium or sodium ions. Also, this was the only polymer out of the non-ionic surfactant polymers that had any significant sensitivity to alkali metals.

Scheme 10



Chapter 3

Results on Surfactant Polymers

i. LB Alignment of Polymers

Even though some of the polymers prepared were not fully soluble, or perhaps were intended for other purposes, it was possible to use them for the preparation of Langmuir-Blodgett thin films. In the case of a polymer that was not fully soluble, the solution of the polymer was filtered, and the soluble portion was used to make LB films. Although in some cases this did not allow the Area/Repeat Unit of the polymer to be calculated exactly, it did not affect the actual formation of the LB film. These films, made on glass slides, could then be used for characterization. The different polymers that were used for LB film preparation are shown below.

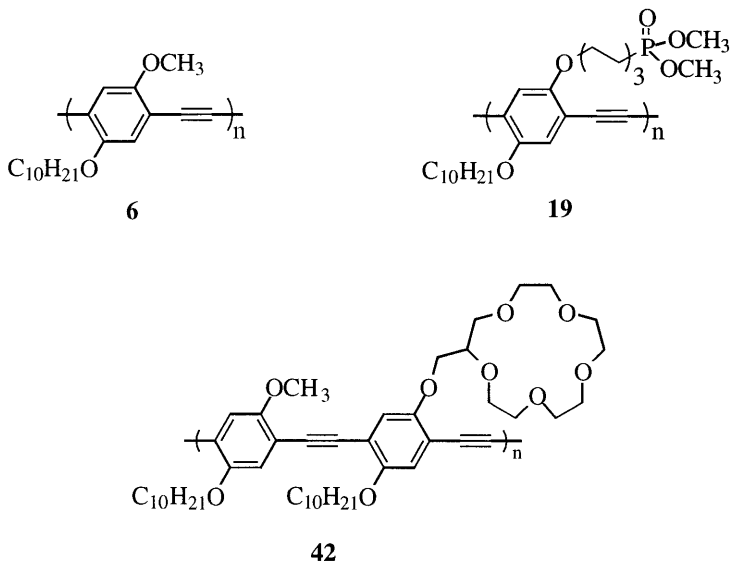


Figure 3.1. Surfactant polymers used for LB films.

LB films of the three polymers shown in Figure 3.1 were made on glass slides so that the Order Parameter, OP, could be measured using UV-Vis spectroscopy.[31] The films were made by depositing a small portion of a 1mg/mL chloroform solution of the polymer on the surface of the subphase (water), compressing the Teflon barriers to form a monolayer of the polymer on the surface, and then dipping a glass slide through the polymer on the surface. For UV-Vis studies, the LB film was deposited in either a monolayer or 10 layers on a

hydrophobic glass slide that had been treated with hexamethyldisilazane. The transfer ratio, which is the percentage of polymer out of 100% possible that was transferred to the solid substrate, was then calculated by the software provided by Nima Technology Ltd.

Examples of the UV-Vis spectra obtained from a 10-layer sample are shown in Figure 3.2. These LB films were prepared from polymer **42** on the LB trough with pure water as the subphase. In these spectra, the anisotropy of the LB film can be seen by the different absorbances of the film, where the dipping direction of the substrate is either parallel or perpendicular to the plane of polarized light used in the UV-Vis spectrum. In this case, as in all the others, the parallel direction has a greater absorbance than the perpendicular direction, which shows that there is a greater ordering of the polymers in the direction parallel to dipping. The order parameter, which depends on the number of layers deposited, is calculated using the absorbance at λ_{max} of these two spectra.

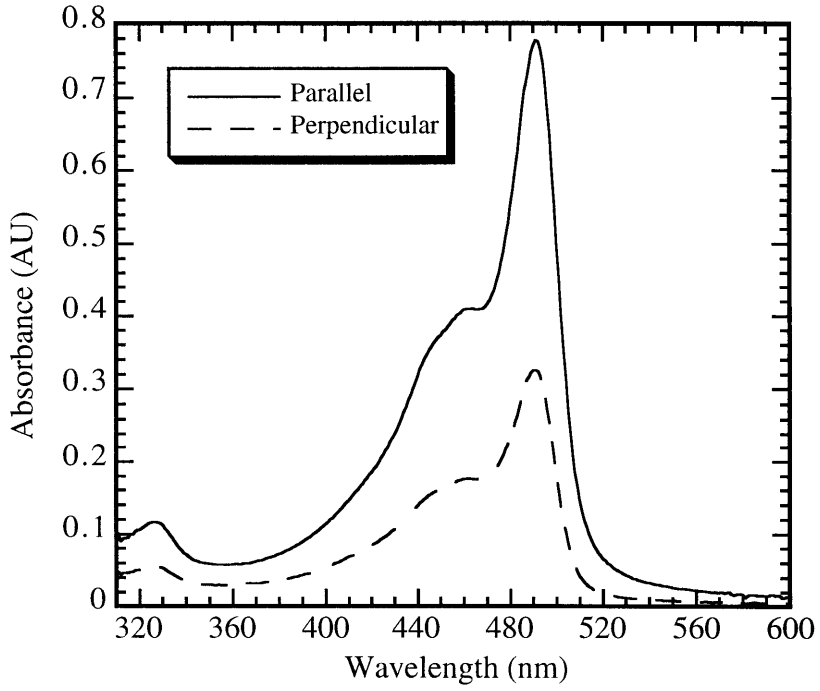


Figure 3.2. UV-Vis spectrum of 10-layer LB film of **42**. The two spectrums show the anisotropy of the polymer film.

A table containing the various polymers and their order parameters is shown below

(Table 3.1). As can be seen in this table, there is a small, but definite, anisotropy in the LB films. In the case of polymer **19**, the order parameter for the ten-layer film is not available, because of problems in making an LB film with more than one layer. When trying to add more than one layer to the LB film, the downward dip of the glass slide would transfer the polymer as usual. However, upon removal from the subphase, the transfer ratio (amount added to LB film) was actually negative, indicating a loss of polymer from the LB film.

Polymer	(OP) 1 Layer	(OP) 10 Layers
6	0.26	0.18
19	0.27	n/a
42	0.25	0.32

Table 3.1. Order parameters of single-layer and 10-layer LB films.

The polymer that shows the greatest ordering is **42**. This polymer is interesting not only because it is a non-ionic surfactant polymer, but because addition of alkali metals to a solution of the polymer can cause the crown ether in the polymer to bind the metal ions, making it an ionic surfactant polymer. Because of this interesting property, an experiment to measure the Area/Repeat Unit of the polymer with varying alkali metals in the water subphase was completed. A plot showing the pressure-area isotherm of **42** with different subphases is shown in Figure 3.3. In this experiment, the subphases used were pure water, 1M KCl, and 1M NaCl.

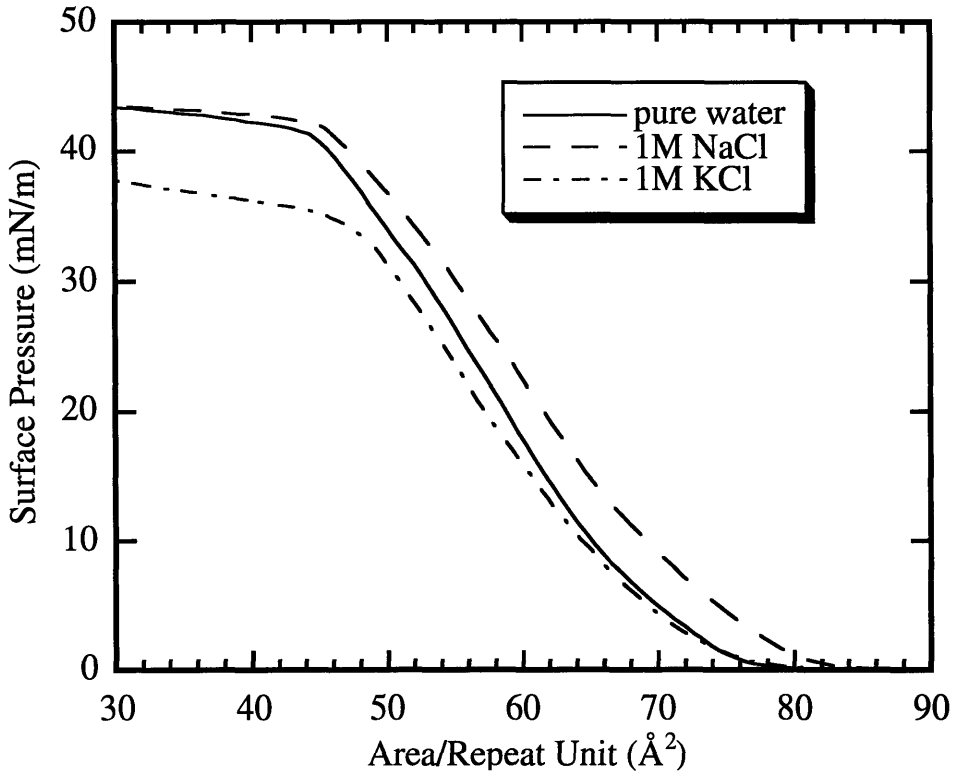


Figure 3.3. Pressure-Area isotherm for **42** with different subphases.

From this plot, it can be seen that there is a slight difference in the Area/Repeat Unit of **42** with the different subphases. The Area/Repeat Unit is determined by extrapolating a line from steepest part of the curve to the baseline, and the number at the baseline should be the Area/Repeat Unit. The largest Area/Repeat unit, 74 Å^2, is found when using 1M NaCl as the subphase. The other two subphases used, pure water and 1M KCl, give similar Area/Repeat units, both of which are smaller than the one found when using 1M NaCl. It was not possible to form LB films with the salt solutions as subphases, because as the substrate was removed from the subphase, a large amount of salt was left on the surface.

ii. Ion Sensitivity

With the same polymer, **42**, another interesting phenomenon was discovered. There is a

significant change in the fluorescence spectrum of **42** upon addition of potassium ions (0.2M KPF_6 in CH_3CN) to the polymer solution. Interestingly, there is no significant change when lithium or sodium ions are added to the solution of **42**. The exact nature of this interaction is unknown as of yet, but it can be inferred that there is some interaction of the pendant 15-crown-5 species with the potassium ions. In another interesting note, the homopolymer of the pendant 15-crown-5, **40**, does *not* show any significant effects upon addition of potassium or sodium ions to the solution.

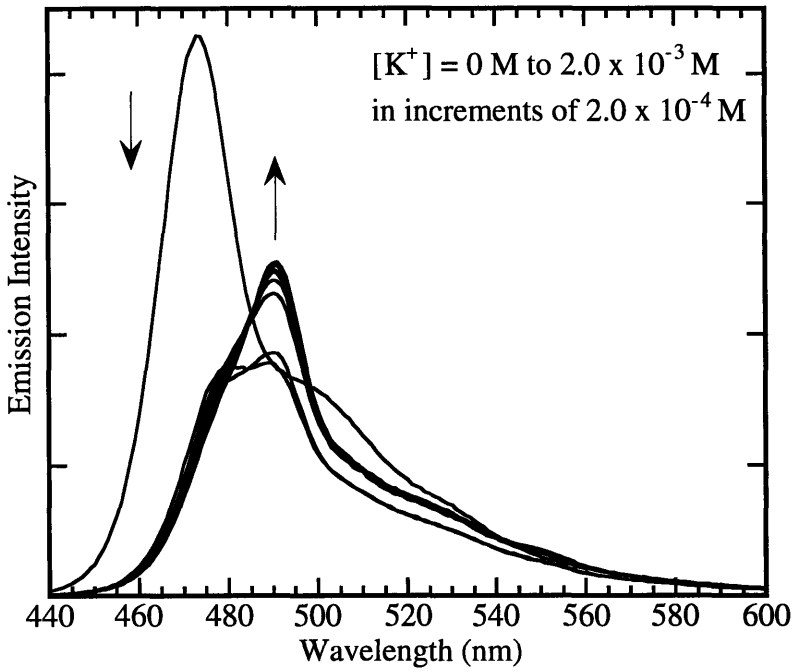


Figure 3.4. Fluorescence spectra of **42** before and after the addition of potassium salts.

The fluorescence spectra of **42**, including the initial pure polymer solution and those after addition of potassium ions, are shown in Figure 3.4. Addition of a 3 μL aliquot of 0.2M KPF_6 in CH_3CN, causes the λ_{max} at 473 nm to decrease and split into two peaks at 480 nm and 490 nm. Further addition of potassium causes the growth of a new maximum at 490 nm. Both of these are shown by the arrows in the figure.

The UV-Vis absorption spectrum of **42** is shown in Figure 3.5. The two spectra shown are the pure polymer solution and that after addition of 30 μL of a 0.2M KPF_6 solution in CH_3CN. The addition of the potassium ions caused a 10 nm red shift in the absorbance.

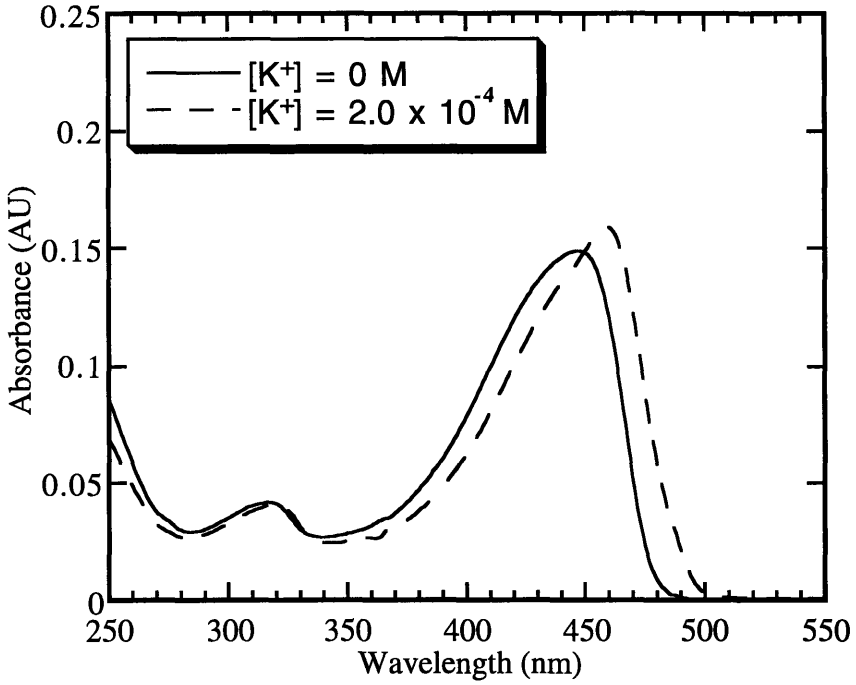


Figure 3.5 UV-Vis absorption spectrum of **42** before and after addition of potassium ions.

In trying to determine the nature of the effect that the potassium ion has on the fluorescence of polymer **42**, it is useful to understand the interaction between crown ethers and alkali metals. In particular, 15-crown-5, which is contained in both polymers **40** and **42**, binds both sodium and potassium. Sodium is the correct size to fit directly inside the 15-crown-5, in a 1:1 ligand to ion ratio. Potassium, which is bigger, must sit in between two 15-crown-5 molecules to be bound. Examples of these effects are shown in the top of Figure 3.5. Another binding mode, which may be applicable to polymer **42**, is that between a lariat crown ether and an alkali metal. This is shown in the bottom of Figure 3.6, where an extra

arm extends above the crown, creating an additional binding site. Potassium, which likes

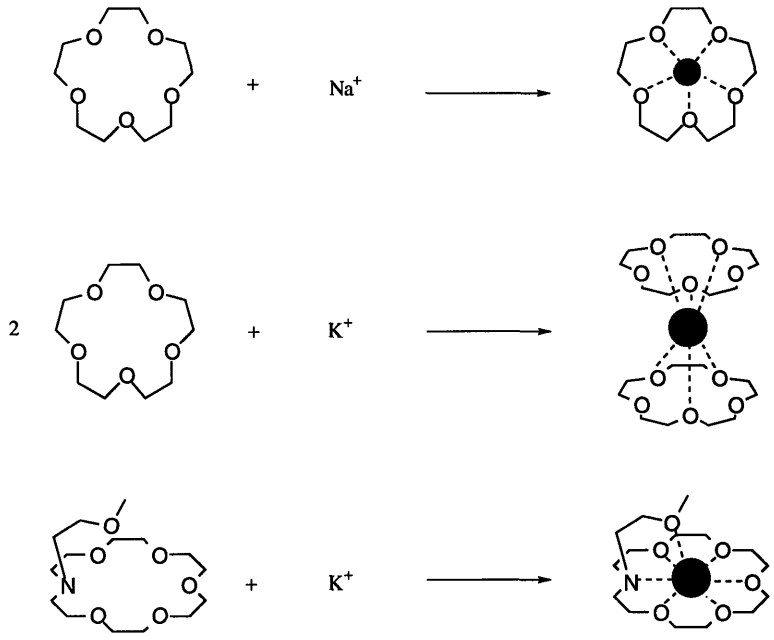


Figure 3.6. Crown ether interactions with alkali metals.

to bind to six or seven oxygens,[32] can make use of the lariat shown in Figure 3.6 or a 15-crown-5 with a lariat arm. Two possibilities of potassium binding to polymer **42** are shown in Figure 3.7. In the first possibility, the potassium ion is bound between the proximate methoxy- and 15-crown-5 in essentially a lariat crown ether. This would most likely affect the twisting of the polymer backbone, which would in turn affect the fluorescence. In the second possibility, the potassium ion is complexed between two crown ethers on different molecules, which would bring the polymer chains closer to each other and allow for cofacial π interactions between two different polymer chains.

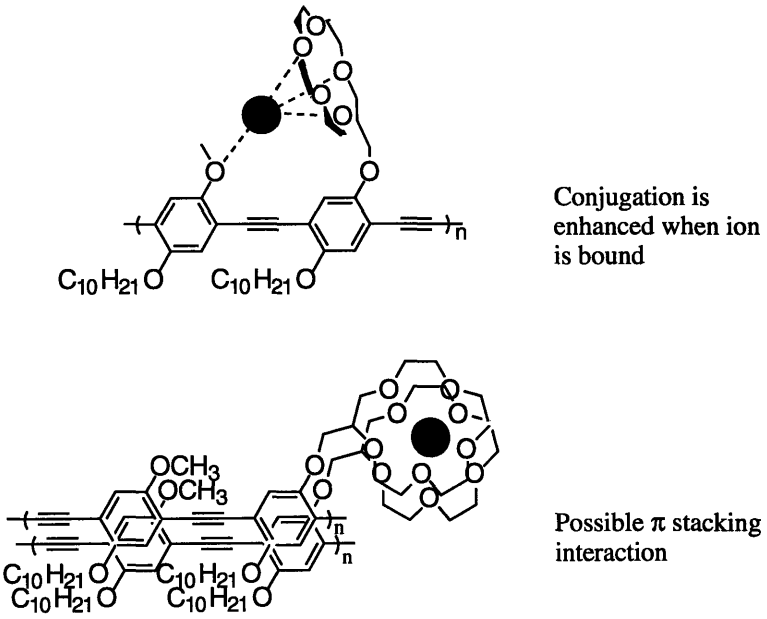


Figure 3.7. Possible interactions of **42** with potassium ions.

iii. Conclusions

The syntheses of both ionic and non-ionic surfactant polymers have been described. Surfactant polymers that form liquid crystalline phases were not obtained, most likely due to solubility problems. Although the research done in this thesis was limited by the solubility of surfactant polymers or their respective precursors, some polymers were still able to be used for alignment in Langmuir-Blodgett thin films. Respectable order parameters were obtained for these polymers, especially for the pendant 15-crown-5 polymer, **42**. This polymer also showed significant changes in its fluorescence spectrum upon the addition of potassium salts. This effect was not seen with lithium or sodium, nor was it seen with the very similar polymer **40**.

Chapter 4

Experimental Section

General Methods. Air- and moisture-sensitive reactions were carried out in flame-dried glassware using standard Schlenk-line or drybox techniques under an inert atmosphere of dry argon. All chemicals used were of reagent grade and were purchased from Aldrich unless otherwise noted. Anhydrous toluene was used from Aldrich Kilo-lab metal cylinders. CH_2Cl_2 and THF were used directly from Aldrich Sure-seal bottles. Diisopropylamine was distilled over solid KOH pellets and degassed by three freeze-pump-thaw cycles. Tetrakis(triphenylphosphine)palladium (0) and *trans*-dichlorobis(triphenylphosphine)-palladium (II) were purchased from Strem chemicals and used as received. (Trimethylsilyl)acetylene was purchased from Farchan Laboratories and used as received. ^1H NMR spectra were acquired on Bruker AC-250, Varian XL-300, Varian Unity 300, or Varian VXR-500 spectrometers. ^{13}C NMR spectra were obtained on a Varian VXR 500 (125.66 MHz) spectrometer. ^1H and ^{13}C NMR spectra were taken in $CDCl_3$ with ^1H chemical shifts reported relative to internal tetramethylsilane (0.00 ppm) and ^{13}C chemical shifts reported relative to $CDCl_3$ (77.00 ppm). Analytical thin-layer chromatography was performed on Merck 60 F_{254} precoated silica gel plates (250 μm thickness). Flash chromatography was performed using Lagand silica gel 60 as the stationary phase. Polymer molecular weights were determined with a Hewlett-Packard 1100 series HPLC equipped with a PLgel mixed-C column (5 μ) using THF as the mobile phase at a rate of 1 mL/min. Gel permeation chromatography (GPC) measurements were made relative to mondisperse polystyrene standards purchased from Polymer Laboratories. UV-Vis spectra were obtained on a Hewlett-Packard 8453 diode array spectrophotometer. Fluorescence spectra of solutions were measured at room temperature using a Spex Fluorolog spectrofluorometer. The excitation wavelength for all spectra was 420nm. Langmuir-Blodgett (LB) thin films were prepared on a 601M LB trough from NIMA Technology, Ltd., using purified water from a Barnstead Nanopure system.

p-Decyloxyanisole (2). A 1L, three-necked round bottomed flask equipped with a stir bar

and a condenser was charged with *p*-methoxyphenol (**1**) (32.98 g, 0.27 mol, 0.98 eq), 1-bromodecane (56.25 mL, 0.27 mol, 1 eq.), potassium hydroxide (30.79 g, 0.55 mol, 2 eq.), potassium iodide (5.86 g, 40 mmol, 0.13 eq) and 2-butanone (500 mL). The reaction mixture was heated to reflux for 24 hours. After cooling to room temperature, the mixture was partitioned between diethyl ether (750 mL) and water (500 mL). The organic layer was separated, washed sequentially with saturated aqueous NH_4Cl (2 x 500 mL) and water (500 mL), and then dried ($MgSO_4$), and concentrated *in vacuo*. Recrystallization from THF-MeOH afforded **2** as large white plates (68.10 g, 95%). ^1H NMR (300 MHz, $CDCl_3$) δ 6.83 (s, 4H), 3.89 (t, J = 6.6 Hz, 2H), 3.76 (s, 3H), 1.75 (qn, J = 6.6 Hz, 2H), 1.5–1.2 (br m, 14H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.83, 153.50, 115.57, 114.76, 68.81, 55.85, 32.11, 29.81, 29.78, 29.64, 29.61, 29.54, 26.28, 22.89, 14.31.

2,5-Diiodo-4-decyloxyanisole (3). A 3L, three-necked round bottomed flask equipped with a stir bar and a condenser was charged with *p*-decyloxyanisole (**2**) (30.79 g, 0.12 mol, 1 eq.), potassium iodate (10.00 g, 50 mmol, 0.41 eq.), and iodine (32.60 g, 0.13 mol, 1.11 eq.). Glacial acetic acid (1200 mL), conc. sulfuric acid (12 mL), and water (120mL) were added, and the mixture heated to reflux for two days. After cooling to room temperature, the excess iodine was quenched with 10% aqueous $Na_2S_2O_4$ (500 mL). The resulting mixture was further diluted with water (500 mL), filtered, and the solid dissolved in CH_2Cl_2 (750 mL). The organic layer was washed sequentially with 10% aqueous $Na_2S_2O_4$ (100 mL) and saturated aqueous NaCl (100 mL), and then dried ($MgSO_4$), and concentrated *in vacuo* . Recrystallization in CH_2Cl_2-MeOH afforded **3** (48.60 g, 81%) as white needles. ^1H NMR (250 MHz, $CDCl_3$) δ 7.19 (s, 1H), 7.18 (s, 1H), 3.93 (t, J = 6.4 Hz, 2H), 3.82 (s, 3H), 1.80 (qn, J = 8.1 Hz, 2H), 1.55–1.20 (br m, 14H), 0.88 (t, J = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.17, 152.92, 122.88, 121.44, 86.34, 85.41, 70.34, 57.13, 31.86, 29.51, 29.50, 29.28, 29.24, 29.11, 25.99, 22.65, 14.09.

2,5-Bis-((trimethylsilyl)ethynyl)-4-decyloxyanisole (4). A 250 mL Schlenk flask equipped with a stir bar was charged with 2,5-diiodo-4-decyloxyanisole **(3)** (20.00 g, 40 mmol, 1 eq.), *trans*-dichlorobis(triphenylphosphine)palladium (II) (0.82 g, 1.20 mmol, 0.03 eq.), and copper(I)iodide (0.46 g, 2.4 mmol, 0.06 eq.). The flask was placed under argon, and then toluene (250 mL) and diisopropylamine (14.0 mL, 0.10 mol, 2.5 eq.) were successively added by syringe. The deep-red solution was treated with (trimethylsilyl)acetylene (13.0 mL, 90 mmol, 2.2 eq.), and stirred for 48 hours at room temperature. The black mixture was concentrated *in vacuo*, and the residue dissolved in hexanes. The hexanes solution was filtered through a one inch plug of silica gel and eluted with chloroform. The solvent from the filtrate was once again evaporated and the resulting solid recrystallized (methanol) to afford **4** as yellow needles (11.05 g, 62%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.91 (s, 1H), 6.89 (s, 1H), 3.95 (t, J = 6.3 Hz, 2H), 3.83 (s, 3H), 1.79 (qn, J = 8.2 Hz, 2H), 1.50–1.15 (br m, 14H), 0.88 (t, J = 6.9 Hz, 3H), 0.27 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.14, 154.07, 117.83, 113.39, 101.01, 100.90, 100.18, 100.15, 69.49, 56.36, 31.86, 29.61, 29.56, 29.40, 29.35, 29.30, 26.00, 22.65, 14.07, -0.02, -0.07.

2,5-Diethynyl-4-decyloxyanisole (5). A 250 mL round bottomed flask equipped with a stir bar was charged with 2,5-bis((trimethylsilyl)ethynyl)-1-methoxy-4-decyloxybenzene **(4)** (5.14g, 10 mmol), THF (40 mL) and methanol (20 mL). The flask was capped and argon was bubbled through the solution for 30 minutes. The reaction mixture was treated with an oxygen-free 40% aqueous KOH solution (2 mL), stirred for 19 hours, and then poured into hexanes (200 mL). The organic solution was washed with water (3 x 100 mL), and then dried ($MgSO_4$), and concentrated *in vacuo*. The resulting residue dissolved in hexanes-CH_2Cl_2 (1:1) and filtered through a one inch plug of silica gel. The filtrate was once again concentrated *in vacuo*, and the resulting solid recrystallized from hexanes to afford **5** as light yellow needles (2.36 g, 67%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.97 (s, 1H), 6.96 (s, 1H), 3.98 (t, J = 6.7 Hz, 2H), 3.86 (s, 3H), 3.39 (s, 1H), 3.35 (s, 1H), 1.81 (qn, J = 7.9 Hz, 2H), 1.53–

1.12 (br m, 14H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.31, 154.07, 117.95, 115.98, 113.37, 112.55, 82.55, 82.52, 79.70, 69.70, 56.35, 31.88, 29.54, 29.51, 29.30, 29.11, 25.87, 22.65, 14.08.

Polymer (6). A 25 mL Schlenk flask equipped with a stir bar was charged with 2,5-diiodo-4-decyloxyanisole **(3)** (200 mg, 0.39 mmol, 1 eq.), 2,5-diethynyl-4-decyloxyanisole **(5)** (0.107 g, 0.34 mmol, 0.9 eq.), and copper(I)iodide (5.5 mg, 29 μmol, 0.06 eq.). The flask was placed under argon, and tetrakis(triphenylphosphine)palladium (0) (15 mg, 13 μmol, 0.03 eq.) was added under a nitrogen atmosphere. Diisopropylamine (1.25 mL, 8.9 mmol, 23 eq.) and toluene (3.5 mL) were successively added by syringe, and the mixture stirred at room temperature for 30 minutes. The fluorescent yellow mixture was heated to 60 °C, stirred for 14 hours, and then cooled to room temperature. The resulting polymer was precipitated in acetone (100 mL), filtered, and rinsed with hot ethanol and hexanes, to afford **6** as an amorphous yellow solid (141 mg, 63%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.05 (m, 2H), 4.05 (br m, 2H), 3.92 (m, 3H), 1.86 (m, 2H), 1.52 (m, 2H), 1.41–1.08 (br, 12H), 0.87 (t, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (including low intensity peaks corresponding to end groups) 153.92, 153.85, 153.72, 153.55, 117.52, 117.33, 115.5–115.1, 91.8–91.2, 69.78, 69.74, 69.68, 69.64, 56.52, 56.46, 56.39, 31.90, 29.69–29.57, 29.51–29.41, 29.40–29.28, 26.03, 26.01, 25.98, 25.95, 29.67, 14.09; GPC: M_w = 44,818; M_n = 13,940; PDI = 3.22

1-((6-Bromohexyl)oxy)-4-decyloxybenzene (8). A 500 mL three-necked round bottomed flask equipped with a stir bar and condenser was charged with 1,6-dibromohexane (50 mL, 0.33 mol, 5 eq.), potassium carbonate (17.76 g, 0.13 mol, 2 eq.), and acetone (100 mL). The reaction mixture was heated to reflux and a solution of *p*-decyloxyphenol **(7)** (14.92 g, 64 mmol, 1 eq.) in acetone (80 mL) was added dropwise at 10 mL/hr using a syringe-pump. After 48 hours, the flask was cooled to room temperature, and the solution concentrated *in vacuo*. The residue was dissolved in $CHCl_3$ (300 mL), washed sequentially with water (150

mL) and saturated aqueous NH_4Cl (2 x 150 mL), and then dried ($MgSO_4$), and concentrated *in vacuo*. Ethanol was added to the residue to precipitate a white solid, which was filtered and rinsed with more ethanol. After recrystallization ($CHCl_3$-EtOH), 18.55 g (72%) of **8** was obtained as large white plates. ^1H NMR (300 MHz, $CDCl_3$) δ 6.81 (s, 4H), 3.90 (m, 4H), 3.42 (t, J = 6.9 Hz, 2H), 1.89 (m, 2H), 1.75 (m, 4H), 1.55–1.15 (br m, 18H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.19, 153.00, 115.30, 115.28, 68.55, 68.26, 33.75, 32.65, 31.86, 29.55, 29.53, 29.39, 29.36, 29.29, 29.17, 27.90, 26.02, 25.27, 22.65, 14.09.

1-((6-Bromohexyl)oxy)-4-decyloxy-2,5-diiodobenzene (9). A 100 mL round bottomed flask equipped with a stir bar and a condenser was charged with 1-((6-bromohexyl)oxy)-4-decyloxybenzene **(8)** (1.01 g, 2.4 mmol, 1 eq.), potassium iodate (0.22 g, 1.01 mmol, 0.40 eq.), and iodine (0.68 g, 2.68 mmol, 1.1 eq.). Glacial acetic acid (25 mL), conc. sulfuric acid (0.25 mL), and water (2.5 mL) were added, and the mixture heated to reflux for 17 hours. After cooling to room temperature, the excess iodine was quenched with 10% aqueous $Na_2S_2O_4$. The mixture was diluted with $CHCl_3$ (100 mL) and the organic layer washed sequentially with saturated aqueous $NaHCO_3$ (3 x 50 mL) and saturated aqueous NaCl (50 mL), and then dried ($MgSO_4$), and concentrated *in vacuo*. Flash chromatography (10% CH_2Cl_2/90% hexanes, R_f = 0.23) afforded **9** as a white solid (1.03 g, 63%), which contained approximately 23% primary alkyl iodide. ^1H NMR (300 MHz, $CDCl_3$) δ 7.17 (s, 2H), 3.93 (m, 4H), 3.44 (t, J = 6.9 Hz, 2H), 3.22 (t, J = 6.9 Hz, iodide), 1.9–1.7 (br m, 6H), 1.6–1.4 (br m, 6H), 1.4–1.2 (br m, 12H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.72, 152.51, 122.56, 122.52, 86.25, 86.23, 70.14, 69.85, 33.57, 33.23 (iodo), 32.53, 31.76, 29.98 (iodo), 29.42, 29.40 (iodo), 29.18, 29.14, 29.02, 28.82, 27.67, 25.88, 25.14, 24.90, 22.55, 14.06.

1-((6-(Dimethylamino)hexyl)oxy)-4-decyloxy-2,5-diiodobenzene (11). A 100 mL three-

necked round bottomed flask equipped with a stir bar and a condenser was charged with 1-((6-bromohexyl)oxy)-4-decyloxy-2,5-diiodobenzene (**9**) (7.0 g, 10 mmol, 1 eq.), diethyl ether (20 mL), and dimethylhydrazine monohydrate (1.24 mL, 16 mmol, 1.55 eq.). The mixture was heated to reflux, by which time a white solid (**10**) began to form. After cooling to room temperature the solvent was decanted from the solid in the reaction flask, and the remaining white solid rinsed with diethyl ether (4 x 50 mL). A 4N HCl (100 mL) solution was used to rinse the solid into a 250 mL three-necked flask equipped with a stir bar and a condenser. The flask was cooled to 0 °C in an ice bath, and a solution of $NaNO_2$ (2.10 g, 30 mmol, 2.90 eq.) in water (10 mL) was added dropwise to the reaction mixture. After warming to room temperature overnight, the flask was again cooled in ice, and a 50% aqueous NaOH solution was added until the solution was strongly basic. The solution was washed with water (3 x 50 mL) and then dried ($MgSO_4$), and concentrated *in vacuo*. Flash chromatography (90% CH_2Cl_2/10% methanol, $R_f = 0.47$) afforded **11** (3.88 g, 59%) as a white solid. ^1H NMR (250 MHz, $CDCl_3$) δ 7.17 (s, 2H), 3.93 (t, $J = 6.3$ Hz, 4H), 2.28 (m, 8H), 1.80 (m, 4H), 1.53–1.20 (br m, 20H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.76, 152.65, 122.66, 122.60, 86.23, 70.22, 70.07, 59.54, 45.24, 31.83, 29.48, 29.47, 29.51, 29.20, 29.05, 28.99, 27.30, 26.97, 25.94, 25.91, 22.62, 14.08.

Polymer (12). An oven-dried 25 mL Schlenk tube equipped with a stir bar was charged with 2,5-diethynyl-4-decyloxyanisole (**5**) (0.47 g, 151 μmol, 1 eq.) and placed under argon before adding THF (1.5 mL) to dissolve the solid. The flask was cooled to 0 °C in an ice bath and n-butyllithium (0.23 mL, 1.44 M in hexanes, 2.2 eq) was added *via* syringe to the solution, causing it to turn to a blue-green mixture. After stirring for 30 minutes, tributyltin chloride (0.10 mL, 369 μmol, 2.4 eq.) was added to the solution, which caused it to turn a clear orange color. A separate 25 mL Schlenk tube was equipped with a stir bar and charged with 1-((6-(dimethylamino)hexyl)oxy)-4-decyloxy-2,5-diiodobenzene (**11**) (0.089 g, 1.41×10^{-4} mol, 0.95 eq.). The flask was placed under argon and tetrakis(triphenylphosphine)palladium (0) (5

mg, 4.33 μmol, 0.03 eq.) was added under a nitrogen atmosphere. Diisopropylamine (1.50 mL, 11 mmol, 71 eq.) and toluene (1 mL) were successively added by syringe, and then the contents were transferred to the aforementioned flask *via* cannula. After 24 hours, a small quantity of copper(I)iodide was added to the reaction mixture under argon flow. After a few minutes the solution began to fluoresce a green color. The mixture was heated to 75 °C for three hours, and then precipitated in rapidly stirring acetone (50 mL), filtered, and rinsed with hot acetone, ethylenediamine, and finally hot hexanes. After drying under high vacuum, 0.12 g (117%) of **12** was obtained as an orange solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.02 (m, 4H), 4.10–3.85 (br m, 7H), 2.22 (m, 8H), 1.87 (m, 6H), 1.6–1.05 (br m, 36H), 0.87 (br t, J= 6.8 Hz, 6H)

Polymer (13). Polymer **(12)** (11 mg, 15.4 μmol, 1 eq.), 1,3-propanesultone (2.1 mg, 17 μmol, 1.1 eq.), and THF (1.5 mL) were combined in a 3 mL round bottomed flask. After stirring for 4 hours, the solution was concentrated *in vacuo*, to yield polymer **(13)**, which was not soluble.

1-((6-(Dimethylamino)hexyl)oxy)-4-decyloxy-2,5-bis(trimethylsilyl)ethynyl)benzene (14). A 25 mL Schlenk flask equipped with a stir bar and was charged with 1-((6-(dimethylamino)hexyl)oxy)-4-decyloxy-2,5-diiodobenzene **(11)** (0.99 g, 1.57 mmol, 1 eq.), *trans*-dichlorobis(triphenylphosphine)-palladium (II) (34 mg, 48 μmol, 0.03 eq.), and copper(I)iodide (23 mg, 0.12 mmol, 0.06 eq.). The flask was placed under argon and then diisopropylamine (2.0 mL, 0.014 mol, 2.5 eq.) and toluene (10 mL) were added successively by syringe. (Trimethylsilyl)acetylene (0.5 mL, 3.5 mmol, 2.2 eq.) was added by syringe, causing the solution to become a viscous, dark-brown mixture. Toluene (10 mL) was added and the mixture stirred at room temperature for 48 hours. The reaction mixture was filtered through a one inch plug of silica and eluted with CH_2Cl_2-MeOH (1:1). The filtrate was concentrated *in vacuo* and the residue chromatographed (5% methanol/94% CH_2Cl_2/1%

triethylamine) unsuccessfully. No product was obtained.

1-((6-(Phthalimido)hexyl)oxy)-4-decyloxy-2,5-diiodobenzene (15). 1-((6-bromohexyl)oxy)-4-decyloxy-2,5-diiodobenzene (**9**) (0.46 g, 0.69 mmol, 1 eq.), potassium phthalimide (0.18 g, 0.97 mmol, 1.25 eq.), hexadecyltributylphosphonium bromide (50 mg, 95 μmol, 0.1 eq.), and toluene (2.5 mL) were combined in a 15 mL round bottomed flask. The flask was equipped with a stir bar and a condenser, and heated to reflux for 24 hours. After cooling to room temperature, the reaction mixture was filtered and the resulting solid rinsed with diethyl ether. The filtrate was concentrated *in vacuo* to yield a yellow solid. Flash chromatography (25% hexanes/75% CH_2Cl_2, $R_f = 0.29$) afforded **15** (0.49 g, 97%) as a white solid. ^1H NMR (250 MHz, $CDCl_3$) δ 7.84 (m, 2H), 7.69 (m, 2H), 7.15 (s, 2H), 3.92 (t, $J = 6.3$ Hz, 4H), 3.71 (t, $J = 7.3$ Hz, 2H), 1.79 (m, 6H), 1.56–1.20 (m, 18H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.34, 152.74, 152.62, 133.76, 132.04, 123.07, 122.62, 122.57, 86.20, 70.22, 69.98, 37.85, 31.84, 29.49, 29.47, 29.25, 29.21, 29.06, 28.90, 28.48, 26.46, 25.95, 25.65, 22.63, 14.09.

1-((6-(Phthalimido)hexyl)oxy)-4-decyloxy-2,5-((trimethylsilyl)ethynyl)benzene (16). A 25 mL Schlenk flask equipped with a stir bar was charged with 1-((6-(phthalimido)hexyl)oxy)-4-decyloxy-2,5-diiodobenzene (**15**) (0.39 g, 0.53 mmol, 1 eq.), *trans*-dichlorobis(triphenylphosphine)palladium (II) (15 mg, 21.4 μmol, 0.03 eq.), and copper(I)iodide (28 mg, 0.15 mmol, 0.10 eq.). The flask was placed under argon, and then toluene (5 mL) and diisopropylamine (0.30 mL, 2.14 mmol, 3.0 eq.) were successively added by syringe. The deep-red solution was treated with (trimethylsilyl)acetylene (0.20 mL, 1.42 mmol, 2.2 eq.), and stirred at room temperature for 24 hours. The black mixture was concentrated *in vacuo*, and then filtered through a one inch plug of silica gel and eluted with CH_2Cl_2-MeOH (1:1). The solvent from the filtrate was once again evaporated to yield a black solid. Flash chromatography (10% diethyl ether/90% petroleum ether, $R_f = 0.16$)

afforded **16** (0.32 g, 87%) as a light orange solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.84 (m, 2H), 7.71 (m, 2H), 6.87 (s, 2H), 3.93 (m, 4H), 3.70 (t, J = 7.2 Hz, 2H), 1.9–1.65 (br m, 6H), 1.6–1.15 (br m, 18H), 0.88 (t, J = 6.9 Hz, 3H), 0.25 (m, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.35, 153.93, 153.79, 133.78, 132.08, 123.09, 117.04, 117.01, 113.82, 113.78, 100.95, 100.05, 69.32, 69.06, 37.89, 31.84, 29.59, 29.54, 29.38, 29.28, 29.11, 28.54, 26.60, 25.97, 25.56, 22.64, 14.09, -0.09.

1-((6-Aminohexyl)oxy)-4-decyloxy-2,5-diiodobenzene (18). 1-((6-(phthalimido)hexyl)oxy)-4-decyloxy-2,5-diiodobenzene **(15)** (2.10 g, 2.87 mmol, 1 eq.), hydrazine monohydrate (7.0 mL, 0.14 mol, 50 eq.), and 95% ethanol (125 mL) were combined in a 250 mL round bottomed flask equipped with a stir bar and a condenser, and the solution heated to reflux for 24 hours. After cooling to room temperature, the reaction mixture was partitioned between diethyl ether (400 mL) and water (200 mL), and the organic layer was washed with water (4 x 200 mL). The aqueous layers were collected and extracted with diethyl ether (250 mL). The combined organic fractions were combined dried (K_2CO_3) and concentrated *in vacuo*. Flash chromatography (10% methanol/89% CH_2Cl_2/1% triethylamine, R_f = 0.16) afforded **18** (1.59 g, 92%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (s, 2H), 9.30 (m, 4H), 2.71 (t, J = 6.6 Hz, 2H), 1.82 (m, 4H), 1.56–1.21 (br m, 20H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.75, 152.64, 122.61, 122.60, 86.22, 86.21, 70.22, 70.06, 41.98, 33.45, 31.83, 29.48, 29.47, 29.25, 29.20, 29.05, 29.02, 26.46, 25.95, 25.86, 22.62, 14.08.

1-((6-(Trifluoroacetamido)hexyl)oxy)-4-decyloxy-2,5-diiodobenzene (19). A flame-dried 25 mL round bottomed flask equipped with a stir bar was charged with 1-((6-aminohexyl)oxy)-4-decyloxy-2,5-diiodobenzene **(18)** (0.18 g, 0.29 mmol, 1 eq.) and placed under argon before adding CH_2Cl_2 (10 mL) and pyridine (0.15 mL, 1.86 mmol, 6 eq.) to dissolve the solid. The solution was cooled to -15 °C in a ice/NaCl bath, after which

trifluoroacetic anhydride (0.13 mL, 0.92 mmol, 3 eq.) was added *via* syringe, turning the solution a gold color. The reaction mixture was warmed to room temperature over 90 minutes and then concentrated *in vacuo* to yield a golden, gummy residue. Flash chromatography (15% EtOAc/85% hexanes, $R_f = 0.25$) afforded **19** (0.16 g, 78%) as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.17 (s, 2H), 6.25 (br s, 1H), 3.93 (m, 4H), 3.39 (q, J = 6.7 Hz, 2H) 1.80 (m, 4H), 1.72–1.20 (br m, 20H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.15 (J = 36.6 Hz), 152.86, 152.56, 122.66, 122.62, 115.79 (J = 288.0 Hz), 86.27, 86.17, 70.27, 69.90, 39.86, 31.85, 29.51, 29.50, 29.28, 29.23, 29.07, 28.86, 28.83, 26.29, 25.97, 25.67, 22.64, 14.10.

1-((6-(Trifluoroacetamido)hexyl)oxy)-4-decyloxy-2,5-((trimethylsilyl)ethynyl)benzene (20). A 10 mL Schlenk flask equipped with a stir bar was charged with 1-((6-(trifluoroacetamido)hexyl)oxy)-4-decyloxy-2,5-diiodobenzene **(19)** (0.11 g, 0.16 mmol, 1 eq.), *trans*--dichlorobis(triphenylphosphine)palladium (II) (4.1 mg, 5.84 μmol, 0.03 eq.), and copper(I)iodide (2.6 mg, 0.14 mmol, 0.06 eq.). The flask was placed under argon, and then toluene (5 mL) and diisopropylamine (0.20 mL, 2.14 mmol, 3.0 eq.) were successively added *via* syringe. The deep-red solution was treated with (trimethylsilyl)acetylene (0.15 mL, 1.06 mmol, 2.2 eq.), and stirred at room temperature for 18 hours. The resulting black mixture was filtered through a one inch plug of silica gel and eluted with ethyl acetate. The filtrate was concentrated *in vacuo* to yield a black solid. Flash chromatography (10% EtOAc/90% hexanes, $R_f = 0.20$) afforded **20** (90 mg, 91%) as a light brown solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.88 (s, 2H), 6.25 (br s, 1H), 3.94 (m, 4H), 3.39 (q, J = 6.7 Hz, 2H), 1.75 (m, 4H), 1.65–1.15 (br m, 20H), 0.88 (t, J = 6.9 Hz, 3H), 0.25 (m, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.08, 153.71, 117.12, 117.11, 113.93, 113.79, 101.03, 100.91, 100.23, 100.04, 69.38, 68.99, 39.89, 31.88, 29.63, 29.59, 29.42, 29.33, 29.31, 29.04, 28.95, 26.38, 26.01, 25.59, 22.68, 14.12, -0.05, -0.07.

1-((6-Aminohexyl)oxy)-4-decyloxy-2,5-diethynylbenzene (21). A 10 mL round bottomed flask equipped with a stir bar was charged with 1-((6-(trifluoroacetamido)hexyl)oxy)-4-decyloxy-2,5-((trimethylsilyl)ethynyl)benzene **(20)** (25 mg, 3.93 μmol, 1 eq.) and 5 mL THF-methanol-H_2O (2:2:1). The flask was capped and argon was rapidly bubbled through the solution for 10 minutes. Lithium hydroxide monohydrate (16 mg, 0.39 mmol, 10 eq.) was added to the solution and the reaction mixture stirred at room temperature for 24 hours. The solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 (50 mL). The organic solution was then washed sequentially with saturated aqueous NH_4Cl (25 mL), saturated aqueous $NaHCO_3$ (50 mL), and saturated aqueous NaCl (25 mL) and then concentrated *in vacuo*. Flash chromatography (94% CH_2Cl_2/5% methanol/1% triethylamine, $R_f = 0.15$) afforded **21** (14 mg, 91%) as a yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ 6.94 (m, 2H), 4.70 (br s 2H), 3.96 (m, 4H), 3.40(s, 1H), 3.33 (s, 1H), 2.85 (t, J = 7.0 Hz, 2H), 1.80 (m, 4H), 1.66 (m, 2H), 1.55–1.15 (br m, 18H), 0.88 (t, J = 7.0 Hz, 3H)

1-((6-(Dimethylphosphinoyl)hexyl)oxy)-4-decyloxy-2,5-diiodobenzene (22).
A flame-dried 50 mL Schlenk flask equipped with a stir bar was charged with NaH (0.11 g, 4.5 mmol, 3 eq.) and THF (20 mL) and cooled to 0 °C in an ice bath. Dimethyl phosphite (0.50 mL, 5.45 mmol, 3.2 eq.) was added via syringe and the mixture was allowed to warm to room temperature over 60 minutes. The clear solution was treated with 2-(1-bromohexyloxy)-5-decyloxy-1,4-diiodobenzene **(9)** (1.00 g, 1.50 x mmol, 1 eq.) in THF (5 mL), and then stirred at room temperature for 24 hours in the absence of light. The flask was heated to 50 °C for 11 hours, and then filtered through a one inch plug of silica using ethyl acetate as the eluent. The filtrate was concentrated *in vacuo* to yield a white solid. Flash chromatography (EtOAc, $R_f = 0.30$) followed by recrystallization (hexanes) afforded **22** (0.55 g, 77%) as a white fluffy solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.17 (s, 2H), 3.93 (t, J= 6.2 Hz, 4H), 3.74 (d, J = 10.6 Hz, 6H), 1.85–1.20 (br m, 26H), 0.88 (t, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.78, 152.59, 122.60, 122.59, 86.21, 86.16, 70.22, 69.93, 52.20

(d, J = 6.8 Hz), 31.83, 30.11 (d, J = 17.0 Hz), 29.48, 29.47, 29.25, 29.20, 29.05, 28.77, 25.94, 25.54, 24.52 (d, J = 140.5 Hz), 22.62, 22.20 (d, J = 5.03 Hz), 14.08.

1-((6-Bromohexyl)oxy)-4-decyloxy-2,5-((trimethylsilyl)ethynyl)benzene (23). A 25 mL Schlenk flask equipped with a stir bar was charged with 1-((6-bromohexyl)oxy)-4-decyloxy-2,5-diiodobenzene **(9)** (0.5 g, 0.75 mmol, 1 eq.), *trans*-dichlorobis(triphenylphosphine)-palladium (II) (16 mg, 23 μmol, 0.03 eq.), and copper(I)iodide (9 mg, 47 μmol, 0.06 eq.). The flask was placed under argon, and then toluene (10 mL) and diisopropylamine (0.40 mL, 2.8 mmol, 4.0 eq.) were successively added by syringe. The deep-red solution was treated with (trimethylsilyl)acetylene (0.24 mL, 1.7 mmol, 2.2 eq.), and stirred at room temperature for 24 hours. The black mixture was filtered through a one inch plug of silica gel and eluted with CH_2Cl_2. Concentration of the filtrate *in vacuo* yielded a black oil. Flash chromatography (30% CH_2Cl_2/70% hexanes, R_f = 0.25) afforded **23** (0.44 g, 96%) as a light yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.89 (s, 2H), 3.94 (m, 4H), 3.42 (t, J = 6.8 Hz, 2H), 1.83 (m, 6H), 1.60–1.15 (br m, 20H), 0.88 (t, J = 6.8 Hz, 3H), 0.24 (m, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.01, 153.75, 117.08, 113.87, 113.83, 100.97, 100.93, 100.10, 100.02, 69.33, 69.01, 33.70, 33.44 (iodo), 32.71, 31.85, 30.21 (iodo), 29.60, 29.55, 29.39, 29.29, 29.09, 27.89, 25.98, 25.19, 24.96 (iodo), 22.65, 14.10, 6.85 (iodo), -0.05, -0.09.

1-((6-(Dimethylphosphinoyl)hexyl)oxy)-4-decyloxy-2,5-((trimethylsilyl)ethynyl)benzene (24). A flame-dried 50 mL Schlenk flask equipped with a stir bar was charged with NaH (0.111 g, 4.64 mmol, 3 eq.) and THF (20 mL) and cooled to 0 °C in an ice bath. Dimethyl phosphite (0.50 mL, 5.45 mmol, 3.2 eq.) was added via syringe and the mixture allowed to warm to room temperature over 60 minutes. The clear solution was then treated with 1-((6-bromohexyl)oxy)-4-decyloxy-2,5-((trimethylsilyl)ethynyl)benzene **(23)** (1.01g, 1.66 mmol, 1 eq.) in THF (5 mL) and then stirred at room temperature for 24 hours in the absence of light. The flask was heated to 60 °C for 24 hours, and then filtered through a one inch plug of silica

using EtOAc-CH_2Cl_2 (1:1) as the eluent. The filtrate was concentrated *in vacuo* to afford **24** (0.80 g, 76%) as a light yellow solid. This product was used without further purification. ^1H NMR (250 MHz, $CDCl_3$) δ 6.88 (s, 2H), 3.94 (t, J = 6.3 Hz, 4H), 3.73 (d, J = 10.9 Hz, 6H), 1.85–1.20 (br m, 26H), 0.88 (t, J = 6.8 Hz, 3H), 0.25 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.92, 153.70, 116.98, 116.97, 113.79, 113.73, 100.91, 100.86, 100.03, 99.94, 69.25, 68.96, 52.11 (d, J = 6.4 Hz), 31.78, 30.20 (d, J = 17.0 Hz), 29.53, 29.48, 29.32, 29.22, 28.92, 25.91, 25.40, 24.56 (J = 140.5 Hz), 22.58, 22.22 (J = 5.0 Hz), 14.03, -0.15, -0.16.

1-((6-(Dimethylphosphinoyl)hexyl)oxy)-4-decyloxy-2,5-diethynylbenzene (25). A 100 mL three-necked round bottomed flask equipped with a stir bar was charged with 1-((6-(dimethylphosphinoyl)hexyl)oxy)-4-decyloxy-2,5-((trimethylsilyl)ethynyl)benzene **(24)** (0.42 g, 0.66 mmol, 1 eq.), DMF (30 mL), water (0.15 mL) and methanol (0.30 mL). The flask was capped and argon was rapidly bubbled through the solution for 20 minutes. Potassium fluoride (0.123 g, 2.12 mmol, 3 eq.) was then added to the flask, and the solution stirred at room temperature for 24 hours. The DMF was removed under high vacuum, and the resulting pink residue dissolved in $CHCl_3$ and filtered. The solid was recrystallized (CH_2Cl_2-hexanes) and chromatographed (EtOAc) to afford **25** (0.22 g, 67%) as a white solid. ^1H NMR (300 MHz, $CDCl_3$) δ 6.94 (m, 2H), 3.97 (t, J = 6.9 Hz, 4H), 3.74 (d, J = 10.8 Hz, 6H), 3.33 (m, 2H), 1.85–1.20 (br m, 26H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.98, 153.78, 117.62, 117.60, 113.16, 113.17, 82.50, 82.46, 79.70, 79.69, 69.59, 69.30, 52.25 (d, J = 6.4 Hz), 31.89, 30.19 (d, J = 16.9 Hz), 29.55, 29.53, 29.31, 29.08, 28.79, 25.87, 25.42, 24.57 (d, J = 140.7 Hz), 22.67, 22.22 (d, J = 5.0 Hz), 14.12.

Polymer (26). A 10 mL Schlenk flask equipped with a stir bar was charged with 1-((6-(dimethylphosphinoyl)hexyl)oxy)-4-decyloxy-2,5-diiodobenzene **(22)** (80 mg, 0.12 mmol, 1 eq.), 1-((6-(dimethylphosphinoyl)hexyl)oxy)-4-decyloxy-2,5-diethynylbenzene **(25)** (0.58 g, 0.12 mmol, 1.03 eq.), and copper(I)iodide (1.5 mg, 7.88 μmol, 0.07 eq.). The flask was

placed under argon, and tetrakis(triphenylphosphine)palladium (0) (12 mg, 10.4 μmol, 0.09 eq.) was added under a nitrogen atmosphere. Toluene (1.5 mL) and diisopropylamine (0.20 mL, 1.43 mmol, 12 eq.) were successively added by syringe, and the reaction mixture was heated to 60 °C for 14 hours. After cooling to room temperature, CH_2Cl_2-1,2-dichlorobenzene (1:1) was added to dissolve the orange gel. The resulting viscous solution was precipitated in hexanes (400 mL), filtered, and rinsed with hot hexanes to afford **26** as an intractable amorphous solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.55 (br s), 7.01 (br s), 4.04 (br m), 3.75–3.45 (br m), 1.95–1.15 (br m), 0.88 (br t)

Triethylene glycol monomethyl ether *p*-toluenesulfonate (29). A 250 mL three-necked round bottomed flask equipped with a stir bar and an addition funnel was charged with triethylene glycol monomethyl ether (5.01 g, 31 mmol, 1 eq.), 4-dimethylaminopyridine (80 mg, 0.66 mmol, 0.02 eq.), CH_2Cl_2 (100 mL), triethylamine (8.75 mL, 62.8 mmol, 2 eq.), and the cooled to -15 °C in an ice/NaCl bath. *p*-Toluenesulfonyl chloride (9.18 g, 48 mmol, 1.5 eq.) in CH_2Cl_2 (75 mL) was added dropwise from the addition funnel to the reaction mixture over 30 minutes, and then the flask was allowed to warm to room temperature overnight. The brown solution washed sequentially with saturated aqueous $NaHCO_3$ (180 mL), 5% aqueous HCl (200 mL), saturated aqueous $NaHCO_3$ (200 mL), and saturated aqueous NaCl (200 mL) and then dried ($MgSO_4$), and concentrated *in vacuo*. Flash chromatography (15% EtOAc/85% CH_2Cl_2, R_f = 0.36) afforded **29** (8.64 g, 87%) as a light yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.16 (t, *J* = 4.9 Hz, 2H), 3.69 (t, *J* = 5.0 Hz, 2H), 3.95 (m, 6H), 3.53 (m, 2H), 3.37 (m, 3H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.62, 132.68, 129.62, 127.71, 71.62, 70.45, 70.26, 70.25, 69.07, 68.39, 58.75, 21.39.

1,4-Diiodo-3-decyloxyphenol (30). A flame-dried 250 mL Schlenk flask equipped with a stir bar was charged with 2,5-diiodo-4-decyloxyanisole **(3)** (10.08 g, 19.5 mmol, 1 eq.) and

then placed under argon. CH_2Cl_2 (100 mL) and trimethylsilyl iodide (3.0 mL, 21 mmol, 1.05 eq.) were successively added, causing the solution to turn light yellow. The flask was stirred at room temperature for 4 days in the absence of light, and then methanol (10 mL) was added to the quench the excess trimethylsilyl iodide. The reaction mixture was washed sequentially with saturated aqueous NaCl (150 mL), saturated aqueous $NaHCO_3$ (150 mL), and saturated aqueous NaCl (100 mL) and then dried (Na_2SO_4), and concentrated *in vacuo*. Flash chromatography (50% hexanes/50% CH_2Cl_2, $R_f = 0.26$) afforded 2.71 g of **30** in 46% yield based on recovered **3** (4.05 g). ^1H NMR (250 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.02 (s, 1H), 3.91 (t, J = 6.4 Hz, 2H), 1.80 (qn, J = 6.6 Hz, 2H), 1.60–1.20 (br m, 14H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.56, 149.70, 124.75, 120.82, 87.57, 84.39, 70.32, 31.88, 29.52, 29.51, 29.29, 29.25, 29.07, 25.99, 22.66, 14.13; MS $(M + H)^+$ found 501.98663, calc'd for $C_{16}H_{24}I_2O_2$ 501.98658

1-((Triethylene glycol monomethyl ether)oxy)-4-decyloxy-2,5-diiodobenzene (31). A 250 mL three-necked round bottomed flask equipped with a stir bar and a condenser was charged with 1,4-diiodo-3-decyloxyphenol **(30)** (0.97 g, 1.93 mmol, 1 eq.), triethylene glycol monomethyl ether *p*-toluenesulfonate **(29)** (0.69 g, 2.17 mmol, 1.1 eq.), potassium carbonate (0.80 g, 5.80 mmol, 3 eq.), potassium iodide (31 mg, 0.18 mmol, 0.1 eq.), and acetone (100 mL). The mixture was heated at 75 °C for 48 hours, and then cooled to room temperature. The solvent was removed *in vacuo*, and the residue partitioned between CH_2Cl_2 (250 mL) and water (250 mL). The organic layer was separated, washed with saturated aqueous NaCl (100 mL), and then dried ($MgSO_4$), and concentrated *in vacuo*. Flash chromatography (35% EtOAc/ 65% hexanes, $R_f = 0.41$) afforded **31** as a white solid (1.30 g, 90%). ^1H NMR (250 MHz, $CDCl_3$) δ 7.25 (s, 1H), 7.16 (s, 1H), 4.10 (m, 2H), 3.90 (m, 4H), 3.80 (m, 2H), 3.67 (m, 4H), 3.56 (m, 2H), 3.38 (s, 3H), 1.78 (qn, J = 6.5 Hz, 2H), 1.55–1.20 (br m, 14H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.16, 152.67, 123.60, 122.52, 86.45, 86.18, 71.91, 71.09, 70.71, 71.55, 70.30, 70.24, 69.59, 59.01, 31.86, 29.51, 29.49, 29.27, 29.23,

29.07, 25.98, 22.64, 14.09.

1-((Triethylene glycol monomethyl ether)oxy)-4-decyloxy-2,5-((trimethylsilyl)ethynyl)benzene (32). A 100 mL Schlenk flask equipped with a stir bar was charged with 1-((triethylene glycol monomethyl ether)oxy)-4-decyloxy-2,5-diiodobenzene **(31)** (0.60 g, 0.93 mmol, 1 eq.), *trans*-dichlorobis(triphenylphosphine)-palladium (II) (19.2 mg, 27.4 μmol, 0.03 eq.), and copper(I)iodide (14.3 mg, 75.1 μmol, 0.06 eq.). The flask was placed under argon, and then toluene (50 mL) and diisopropylamine (0.60 mL, 4.28 mmol, 4.0 eq.) were successively added. The orange solution was treated with (trimethylsilyl)acetylene (0.30 mL, 2.1 mmol, 2.2 eq.), and stirred at room temperature for 48 hours. The black mixture was filtered through a one inch plug of silica gel and eluted using ethyl acetate. The filtrate was removed *in vacuo* to yield a black oil that was chromatographed (25% EtOAc/75% hexanes, $R_f = 0.31$) to afford **32** as a golden oil (0.47 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (s, 1H), 6.88 (s, 1H), 4.12 (t, J = 5.1 Hz, 2H), 3.94 (t, J = 6.6 Hz, 2H), 3.87 (m, 2H), 3.79 (m, 2H), 3.66 (m, 4H), 3.54 (m, 2H), 3.37 (s, 3H), 1.76 (m, 2H), 1.48 (m, 2H), 1.40–1.20 (br m, 12H), 0.88 (t, J = 6.9 Hz, 3H), 0.26 (m, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.32, 153.55, 117.76, 117.28, 114.16, 114.02, 101.02, 100.85, 100.23, 100.09, 71.92, 71.12, 70.75, 70.51, 69.69, 69.55, 69.41, 58.97, 31.84, 29.59, 29.54, 29.38, 29.30, 29.28, 25.98, 22.63, 14.06, -0.07, -0.10.

1-((Triethylene glycol monomethyl ether)oxy)-4-decyloxy-2,5-diethynylbenzene (33). A 25 mL two-necked round bottomed flask was equipped with a stir bar and charged with 1-((triethylene glycol monomethyl ether)oxy)-4-decyloxy-2,5-((trimethylsilyl)ethynyl)benzene **(32)** (0.40 g, 0.676 mmol, 1 eq.) and methanol (15 mL). The flask was capped and argon bubbled through the solution for 45 minutes. Tetrabutylammonium fluoride hydrate (0.48 g, 1.85 mmol, 2.4 eq.) was then added to the flask under argon and the mixture stirred at room temperature for 2 hours. The red solution was then concentrated *in vacuo* and the residue

partitioned between CH_2Cl_2 (100 mL) and water (50 mL). The organic layer was washed with saturated aqueous NaCl (50 mL), and then dried ($MgSO_4$), and concentrated *in vacuo*. Flash chromatography (35% EtOAc/65% hexanes, $R_f = 0.23$) afforded **33** (0.27 g, 90%) as a red solid. ^1H NMR (250 MHz, $CDCl_3$) δ 7.00 (s, 1H), 6.94 (s, 1H), 4.15 (t, J = 5.2 Hz, 2H), 3.97 (t, J = 6.6 Hz, 2H), 3.87 (m, 2H), 3.77 (m, 2H), 3.67 (m, 4H), 3.56 (m, 2H), 3.38 (s, 3H), 3.33 (s, 2H), 1.78 (qn, J = 7.8 Hz, 2H), 1.55–1.20 (br m, 14H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.25, 153.63, 118.35, 117.50, 113.47, 113.20, 82.59, 82.52, 79.67, 79.55, 71.89, 71.00, 70.66, 70.51, 69.56, 69.54, 69.48, 58.97, 31.85, 29.50, 29.48, 29.27, 29.04, 25.83, 22.63, 14.07.

Polymer (34). A 10 mL Schlenk flask equipped with a stir bar was charged with 1-((triethylene glycol monomethyl ether)oxy)-4-decyloxy-2,5-diiodobenzene **(31)** (73.1 mg, 0.11 mmol, 1 eq.), 1-((triethylene glycol monomethyl ether)oxy)-4-decyloxy-2,5-diethynylbenzene **(33)** (51.6 g, 0.11 mmol, 1.03 eq.), and copper(I)iodide (3.9 mg, 20.5 μmol, 0.07 eq.). The flask was placed under argon, and tetrakis(triphenylphosphine)-palladium (0) (8 mg, 6.92 μmol, 0.18 eq.) was added under a nitrogen atmosphere. Toluene (3.0 mL) and diisopropylamine (1.25 mL, 8.91 mmol, 79 eq.), were successively added by syringe, and the mixture stirred at room temperature for 30 minutes. As the mixture became viscous, toluene (2 mL) was added, after which, the mixture was heated to 60 °C for 24 hours. The polymer solution was then precipitated in methanol, filtered, and rinsed with hot methanol, giving polymer **34** as an amorphous orange solid (85 mg, 90%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (br m), 7.06 (s), 7.01 (s), 4.24 (br m), 4.04 (br m), 3.92 (br m), 3.78 (br m), 3.62 (br m), 3.51 (br m), 3.35 (br s), 1.86 (br, m), 1.64 (br m), 1.50 (br m), 1.40–1.1 (br m), 0.87 (t, J = 6.9 Hz); GPC (soluble portion): M_w = 693,530; M_n = 151,731; PDI = 4.57.

(2-(*p*-Toluenesulfonyl)methyleneoxy)-15-crown-5 (36). A 250 mL three-necked round bottomed flask equipped with a stir bar and an addition funnel was charged with 2-

hydroxymethyl 15-crown-5 (1.11 g, 4.43 mmol, 1 eq.), 4-dimethylaminopyridine (13 mg, 0.11 mol, 0.02 eq.), CH_2Cl_2 (100 mL), triethylamine (1.50 mL, 11 mmol, 2 eq.), and then cooled to -15 °C in an ice/NaCl bath. A solution of *p*-toluenesulfonyl chloride (1.33 g, 6.95 mmol, 1.5 eq.) in CH_2Cl_2 (75 mL) was then added dropwise from the addition funnel to the reaction mixture over a period of 30 minutes. The reaction mixture was allowed to warm to room temperature overnight while stirring, and then washed with 5% aqueous HCl (2 x 100 mL), dried ($MgSO_4$), and concentrated *in vacuo*. Flash chromatography (95% EtOAc/5% ethanol, R_f = 0.42 to 0.09 streak) afforded **36** (1.09 g, 61%) as a clear, viscous oil. ^1H NMR (250 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 4.20–3.95 (br m, 3H), 3.85–3.45 (br m, 18H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.49, 132.68, 129.54, 127.69, 76.75, 70.89, 70.53, 70.35, 70.23, 70.19, 70.14, 70.11, 70.02, 69.64, 65.90, 21.37.

1-(2-methyleneoxy-15-crown-5)-4-decyloxy-2,5-diiodobenzene (37). A 50 mL round bottomed flask equipped with a stir bar and a condenser was charged with 1,4-diiodo-3-decyloxyphenol **(30)** (0.98 g, 1.96 mmol, 1 eq.), (2-*p*-toluenesulfonyl)methyleneoxy)-15-crown-5 **(36)** (0.87 g, 2.15 mmol, 1.1 eq.), potassium carbonate (0.82 g, 5.94 mmol, 3 eq.), potassium iodide (33 mg, 0.201 mmol, 0.1 eq.), and acetone (25 mL). The mixture was heated to reflux for 48 hours and then allowed to cool to room temperature. The reaction mixture was partitioned between ethyl acetate (100 mL) and water (100 mL), and then the organic layer washed with water (100 mL). Evaporation of the organic layer gave a viscous brown oil, which was chromatographed (75% EtOAc/25% CH_2Cl_2, R_f = 0.41 to 0.25, streak) to afford **37** (1.30 g, 91%) as a light yellow, viscous oil that solidified upon standing. ^1H NMR (250 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.16(s, 1H), 4.10–3.80 (br m, 7H), 3.75–3.55 (br m, 16H), 1.80 (qn, *J* = 8.0 Hz, 2H), 1.55–1.20 (br m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.96, 152.60, 122.70, 122.62, 86.22, 85.94, 77.93, 71.22, 70.87, 70.84 (br), 70.80, 70.78, 70.57, 70.52, 70.50, 70.44, 70.27, 31.83, 29.48, 29.47, 29.25, 29.20,

29.06, 25.95, 22.61, 14.07.

1-(2-methyleneoxy-15-crown-5)-4-decyloxy-2,5-bis((trimethylsilyl)ethynyl)benzene (38). A 10 mL Schlenk flask equipped with a stir bar was charged with 1-(2-methyleneoxy-15-crown-5)-4-decyloxy-2,5-diiodobenzene (**37**) (0.30 g, 0.41 mmol, 1 eq.), *trans*-dichlorobis-(triphenylphosphine)palladium (II) (9.1 mg, 13 μmol, 0.03 eq.), and copper(I)iodide (4.8 mg, 25 μmol, 0.06 eq.). The flask was placed under argon, and then toluene (7.50 mL) and diisopropylamine (0.30 mL, 2.14 mmol, 4.0 eq.) were successively added via syringe. The orange solution was treated with (trimethylsilyl)acetylene (0.20 mL, 1.42 mmol, 2.2 eq.), and stirred at room temperature for 24 hours. The resulting black mixture was filtered through a one inch plug of silica gel and eluted with ethyl acetate-ethanol (1:1). Concentration of the filtrate *in vacuo* yielded a brown solid. Flash chromatography (75% CH_2Cl_2/25% EtOAc, R_f = 0.29 to 0.11, streak) afforded **38** (0.22 g, 81%) as a light yellow viscous oil, that solidified upon standing. ^1H NMR (250 MHz, $CDCl_3$) δ 6.91 (s, 1H), 6.89 (s, 1H), 4.05–3.55 (br m, 23H), 1.79 (qn, J = 8.2 Hz, 2H), 1.55–1.15 (br m, 14H), 0.88 (t, J = 6.9 Hz, 3H), 0.27 (m, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.08, 153.58, 117.32, 116.86, 113.96, 113.69, 101.08, 100.87, 100.20, 99.85, 78.05, 73.42, 71.14, 71.12, 70.91, 70.84, 70.82, 70.59, 70.57, 70.52, 70.15, 69.40, 31.85, 29.59, 29.55, 29.39, 29.29, 25.98, 22.64, 14.08, -0.04, -0.09.

1-(2-methyleneoxy-15-crown-5)-4-decyloxy-2,5-diethynylbenzene (39). A 25 mL two-necked round bottomed flask equipped with a stir bar was charged with 1-(2-methyleneoxy-15-crown-5)-4-decyloxy-2,5-bis((trimethylsilyl)ethynyl)benzene (**38**) (0.19 g, 0.28 mmol, 1 eq.) and methanol (15 mL). The flask was capped and argon was bubbled through the solution for 15 minutes. Tetrabutylammonium fluoride hydrate (0.20 g, 0.77 mmol, 2.4 eq.) was added under argon, and the reaction mixture stirred at room temperature for 2 hours. The reaction mixture was concentrated *in vacuo*, to yield a brown oil, which was dissolved in CH_2Cl_2 (125 mL) and washed with water (2 x 125 mL). The organic layer was collected and

once again concentrated *in vacuo*. Flash chromatography (50% CH_2Cl_2/47% EtOAc/3% ethanol, R_f = 0.35 to 0.18, streak) afforded **39** (0.13 g, 87%) as a light red oil. ^1H NMR (300 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6.94 (s, 1H), 4.15–3.55 (br m, 23H), 3.33 (s, 1H), 3.31 (s, 1H), 1.78 (m, 2H), 1.50–1.20 (br m, 14H), 0.88 (t, J = 7.2 Hz, 3H)

Polymer (40). A 10 mL Schlenk flask equipped with a stir bar was charged with 1-(2-methyleneoxy-15-crown-5)-4-decyloxy-2,5-diiodobenzene **(37)** (63 mg, 86.2 μmol, 1 eq.), 1-(2-methyleneoxy-15-crown-5)-4-decyloxy-2,5-diethynylbenzene **(39)** (47 mg, 88.9 μmol, 1.03 eq.), and copper(I)iodide (2 mg, 10.5 μmol, 0.07 eq.). The flask was placed under argon, and tetrakis(triphenylphosphine)palladium (0) (10 mg, 8.65 μmol, 0.10 eq.) was added under a nitrogen atmosphere. Toluene (3.0 mL) and diisopropylamine (1.25 mL, 8.91 mmol, 103 eq.) were successively added by syringe, and the mixture stirred at 60 °C for 48 hours. The resulting polymer solution was precipitated in methanol, and the polymer collected by centrifuge. This afforded **40** as a yellow solid (40.7 mg, 47%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (br m), 7.00 (br m), 4.20-3.45 (br m), 1.84 (br m), 1.66 (br m), 1.55-1.15 (br m), 0.87 (t, J = 6.8 Hz); GPC: M_w = 16,137; M_n = 8,095; PDI = 1.99.

Polymer (41). A 10 mL Schlenk flask equipped with a stir bar was charged with 1-(2-methyleneoxy-15-crown-5)-4-decyloxy-2,5-diiodobenzene **(37)** (71 mg, 96 μmol, 1 eq.), 1-((triethylene glycol monomethyl ether)oxy)-4-decyloxy-2,5-diethynylbenzene **(33)** (44 mg, 99.0 μmol, 1.03 eq.), and copper(I)iodide (3.5 mg, 18.4 μmol, 0.06 eq.). The flask was placed under argon, and tetrakis(triphenylphosphine)palladium (0) (9 mg, 7.8 μmol, 0.10 eq.) was added under a nitrogen atmosphere. Toluene (4.0 mL) and diisopropylamine (1.50 mL, 11 mmol, 111 eq.) were successively added by syringe, and the mixture stirred at 60 °C for 15 hours. The dark-brown polymer was precipitated in acetone (200 mL), filtered, and rinsed with hot acetone and hot hexanes. After drying under high vacuum, polymer **41** was

obtained as a rust-colored solid (only partially soluble), (71 mg, 80%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.00(br m), 4.20-3.45(br m), 3.34 (s), 1.85 (br m), 1.55-1.15 (br m), 0.87 (t)

Polymer (42). A 10 mL Schlenk flask equipped with a stir bar was charged with 1-(2-methyleneoxy-15-crown-5)-4-decyloxy-2,5-diiodobenzene (**37**) (64 mg, 86.5 μmol, 1 eq.), 2,5-diethynyl-4-decyloxyanisole (**5**) (27 mg, 85.8 μmol, 1.03 eq.), and copper(I)iodide (1.6 mg, 8.40 μmol, 0.06 eq.). The flask was placed under argon, and tetrakis-(triphenylphosphine)palladium (0) (10 mg, 8.65 μmol, 0.06 eq.) was added under a nitrogen atmosphere. Toluene (3.0 mL) and diisopropylamine (1.50 mL, 11 mmol, 111 eq.)were successively added by syringe, and the mixture was stirred at 60 °C for 24 hours. The cooled polymer solution was precipitated in methanol, filtered, and rinsed with hot methanol. After drying under high vacuum, polymer **42** was obtained as a bright yellow powder (61 mg, 89%). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.55 (br m), 7.04 (br m), 4.20-3.50 (br m), 1.86 (br m), 1.51 (br m), 1.40-1.15 (br m), 0.87 (t, J = 6.9 Hz); GPC: M_w = 113,791; M_n = 32,905; PDI = 3.46.

Fluorescence Measurements. A fluorescence cuvette was filled with 3.0 mL of 2.7 μM solution of **42** in THF. 3 μL aliquots of a 0.2 M KPF_6 solution in CH_3CN were added to the polymer solution, and the cuvette shaken for 60 seconds. Following equilibration, the final spectra were taken; equilibration was determined when the spectrum remained unchanged with time.

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Appendix

NMR Spectra of Compounds

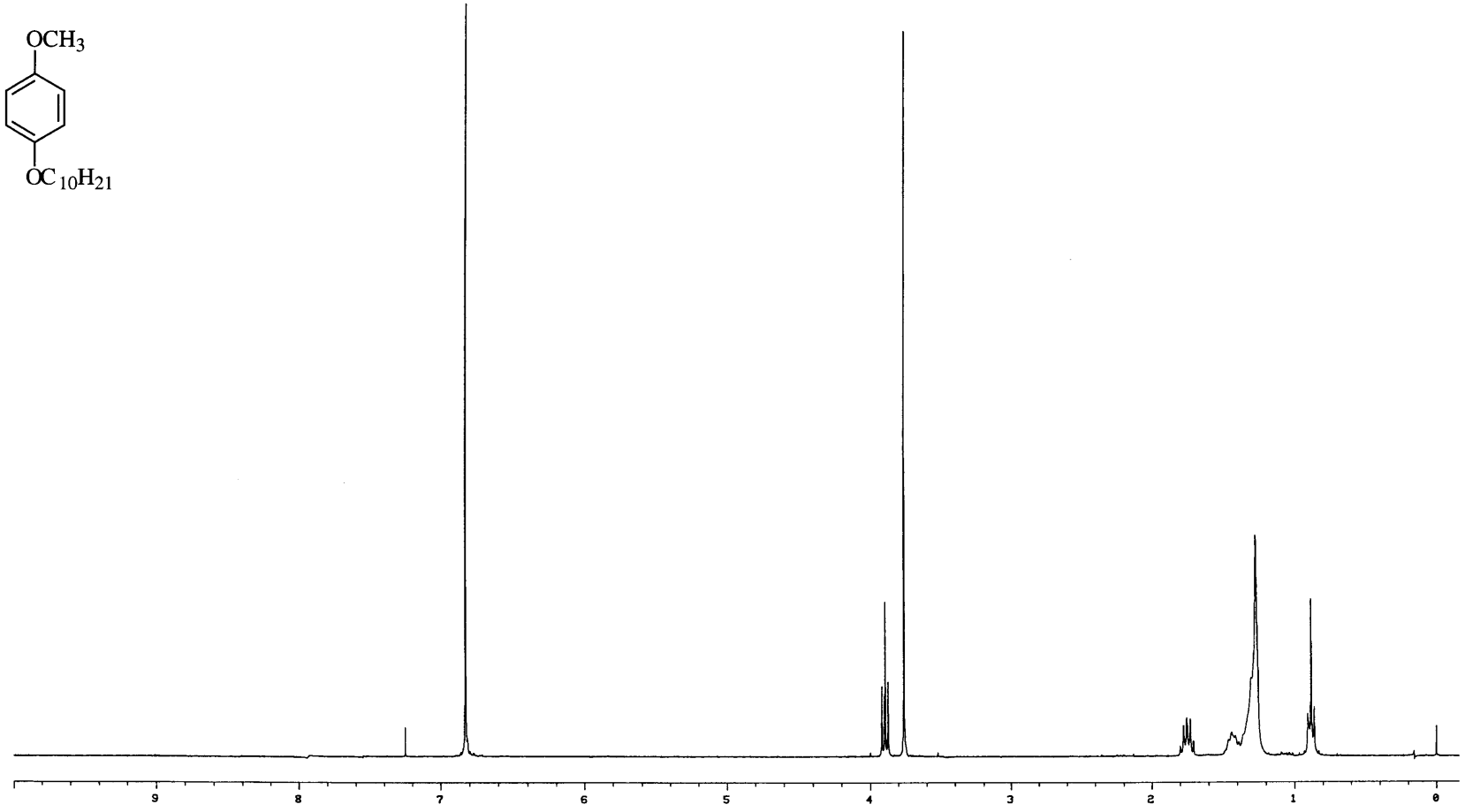

Figure A1.1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **2**

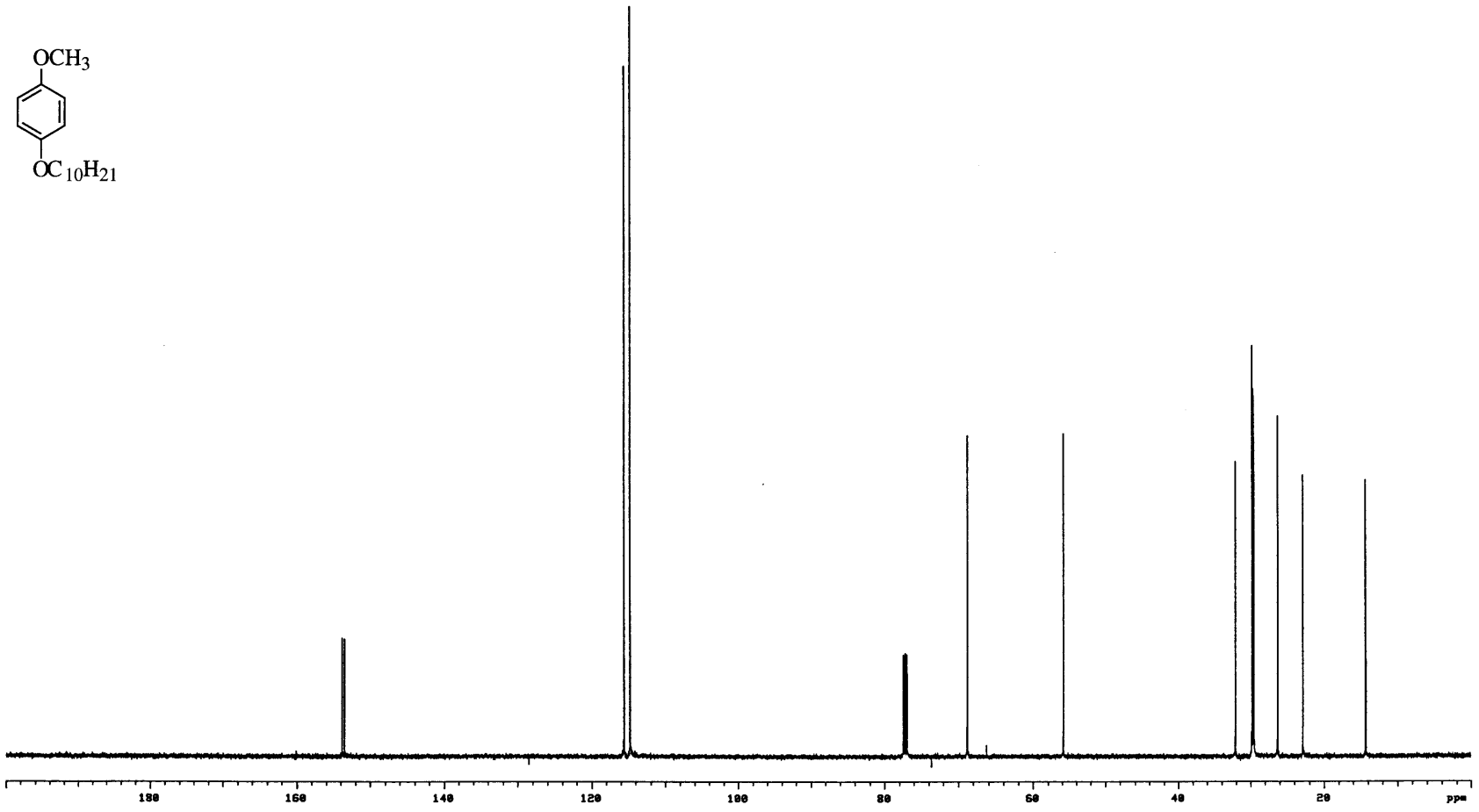

Figure A1.2. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **2.**

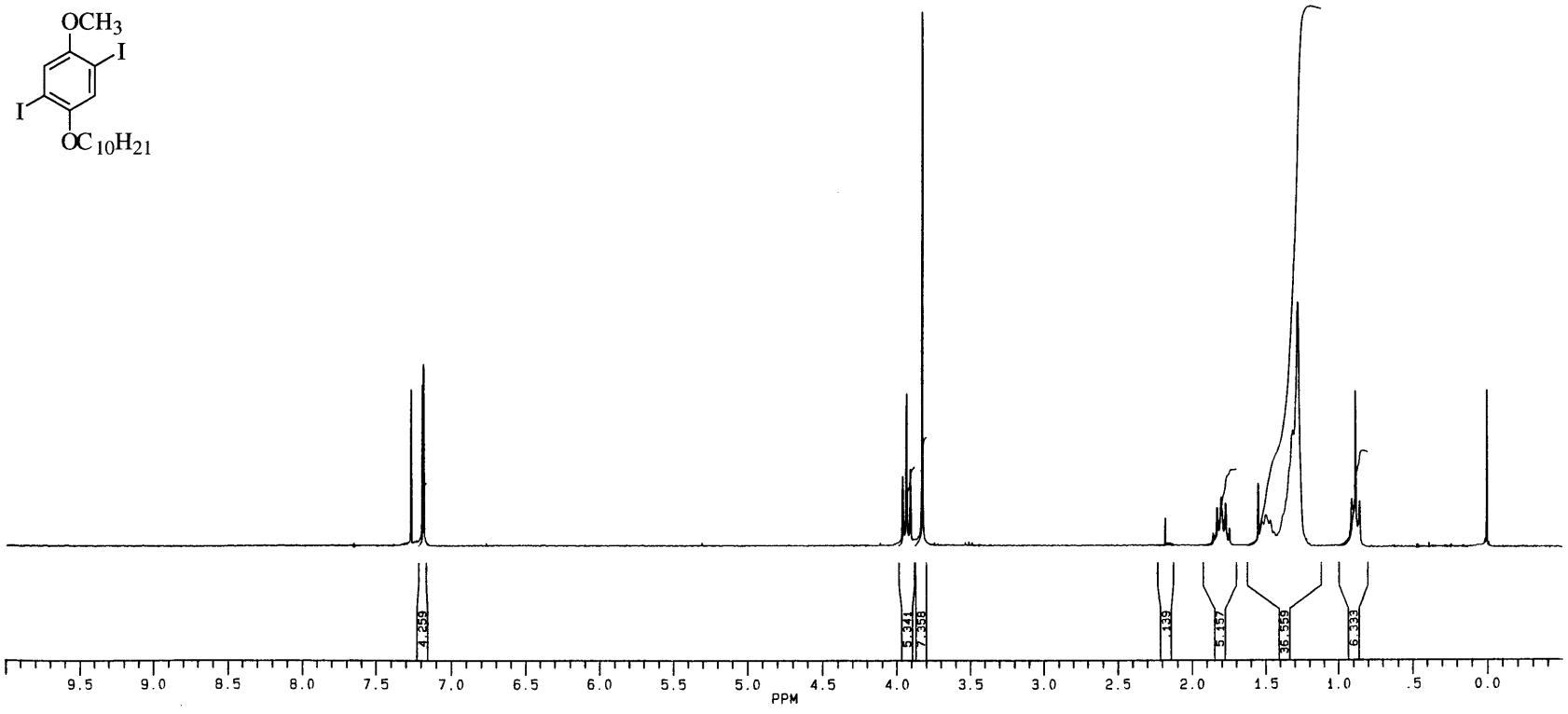

Figure A1.3. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **3**.

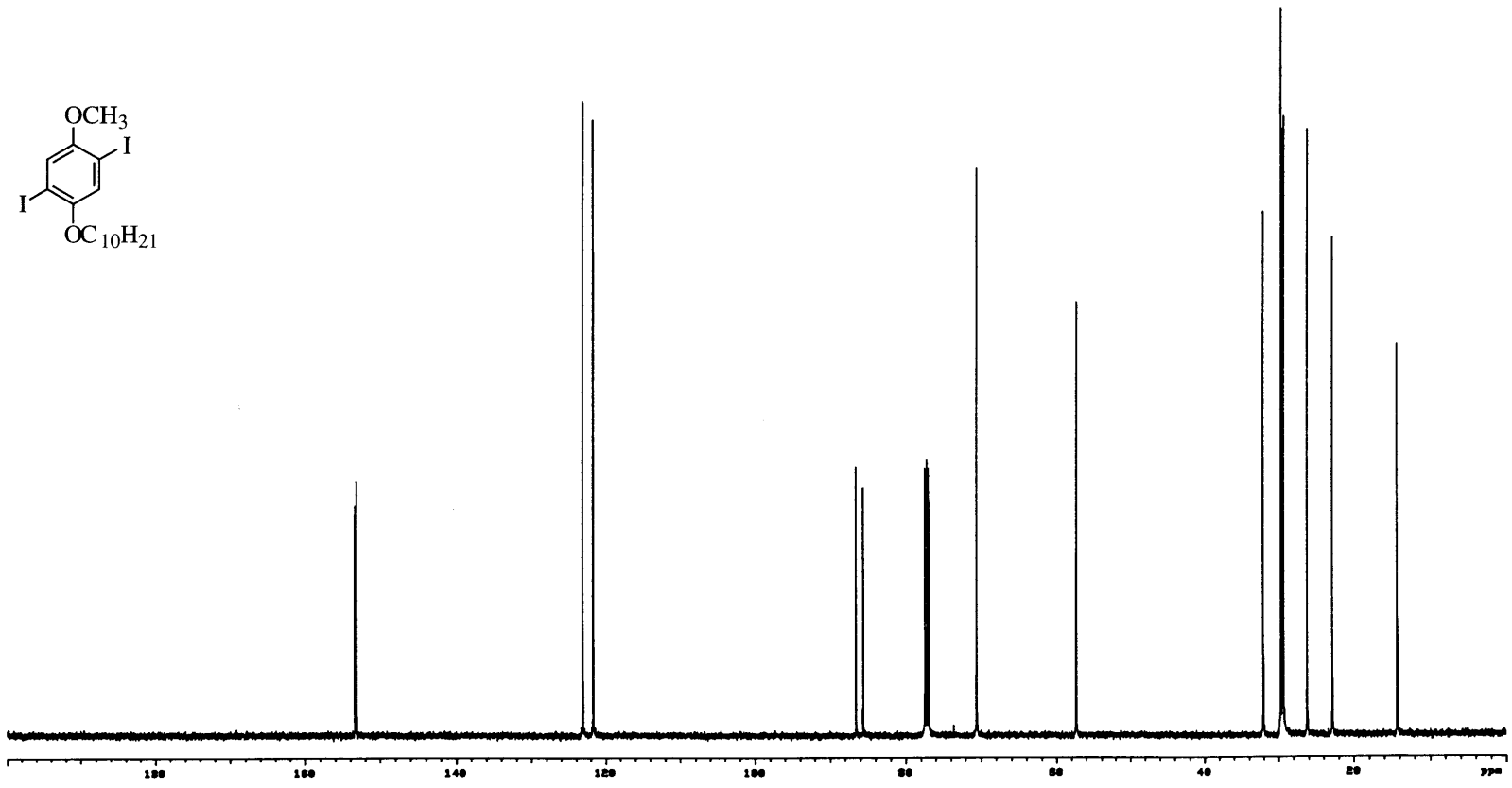

Figure A1.4. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3**.

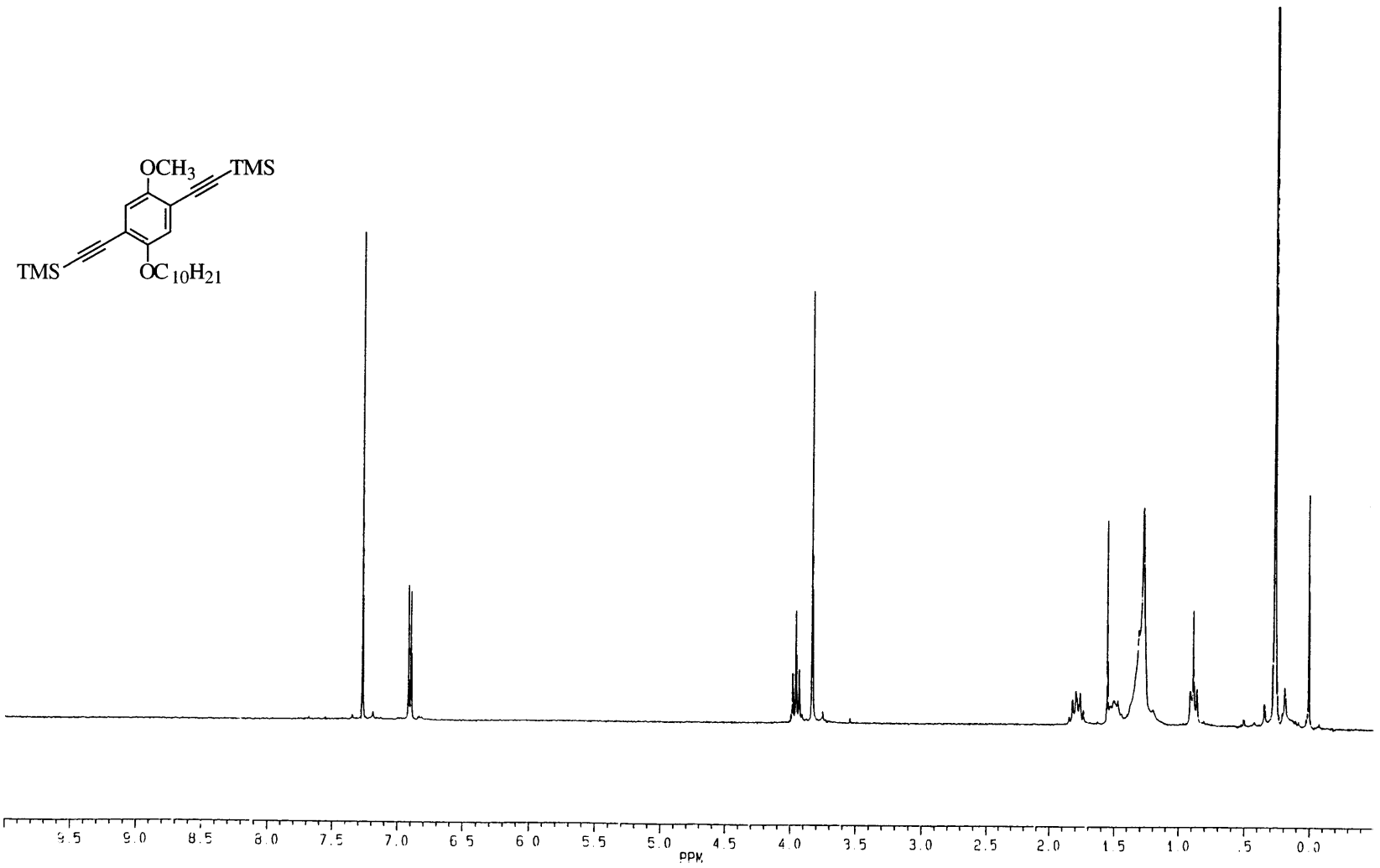

Figure A1.5. ^{13}C NMR spectrum (250 MHz, $CDCl_3$) of compound **4**.

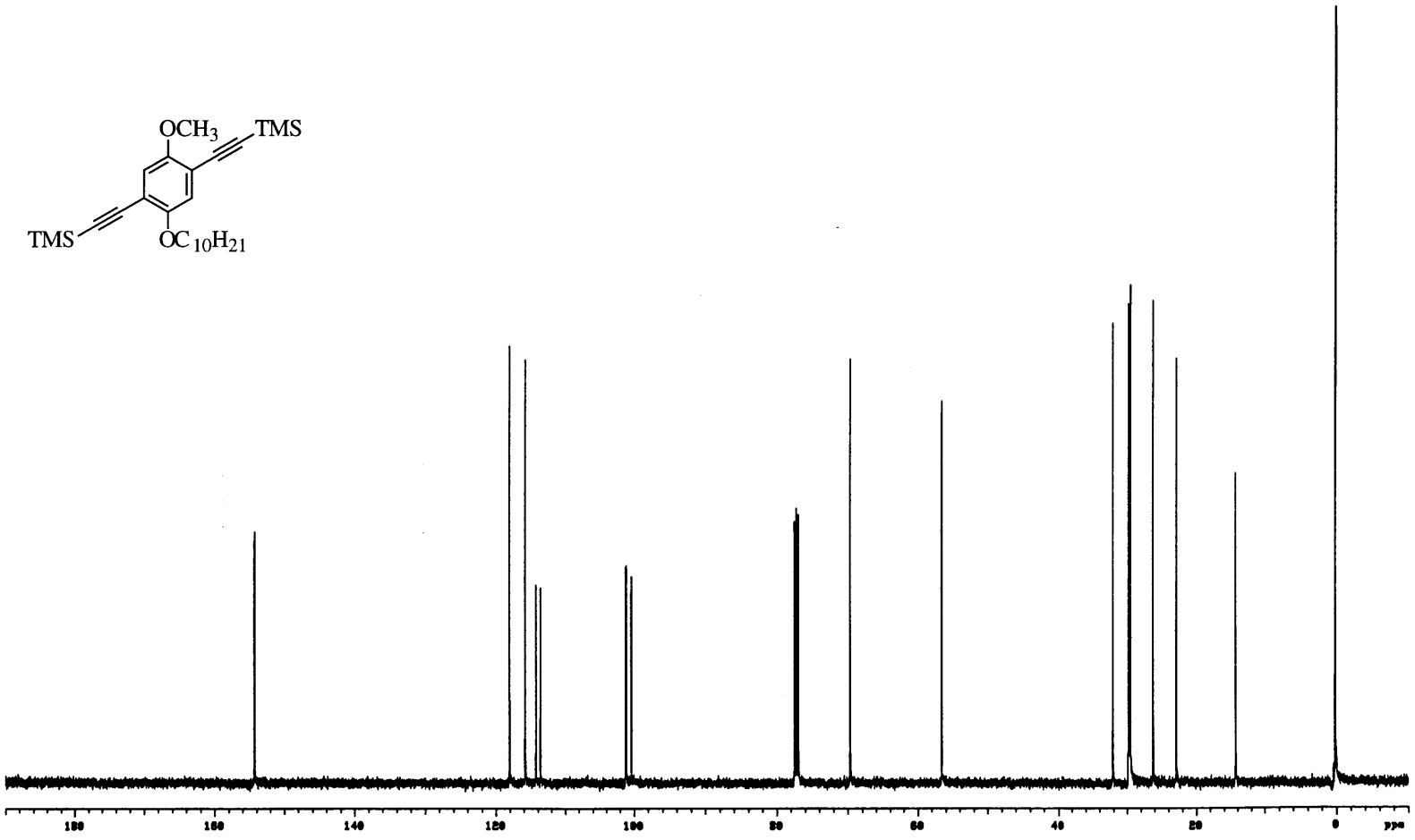

Figure A1.6. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **4**.

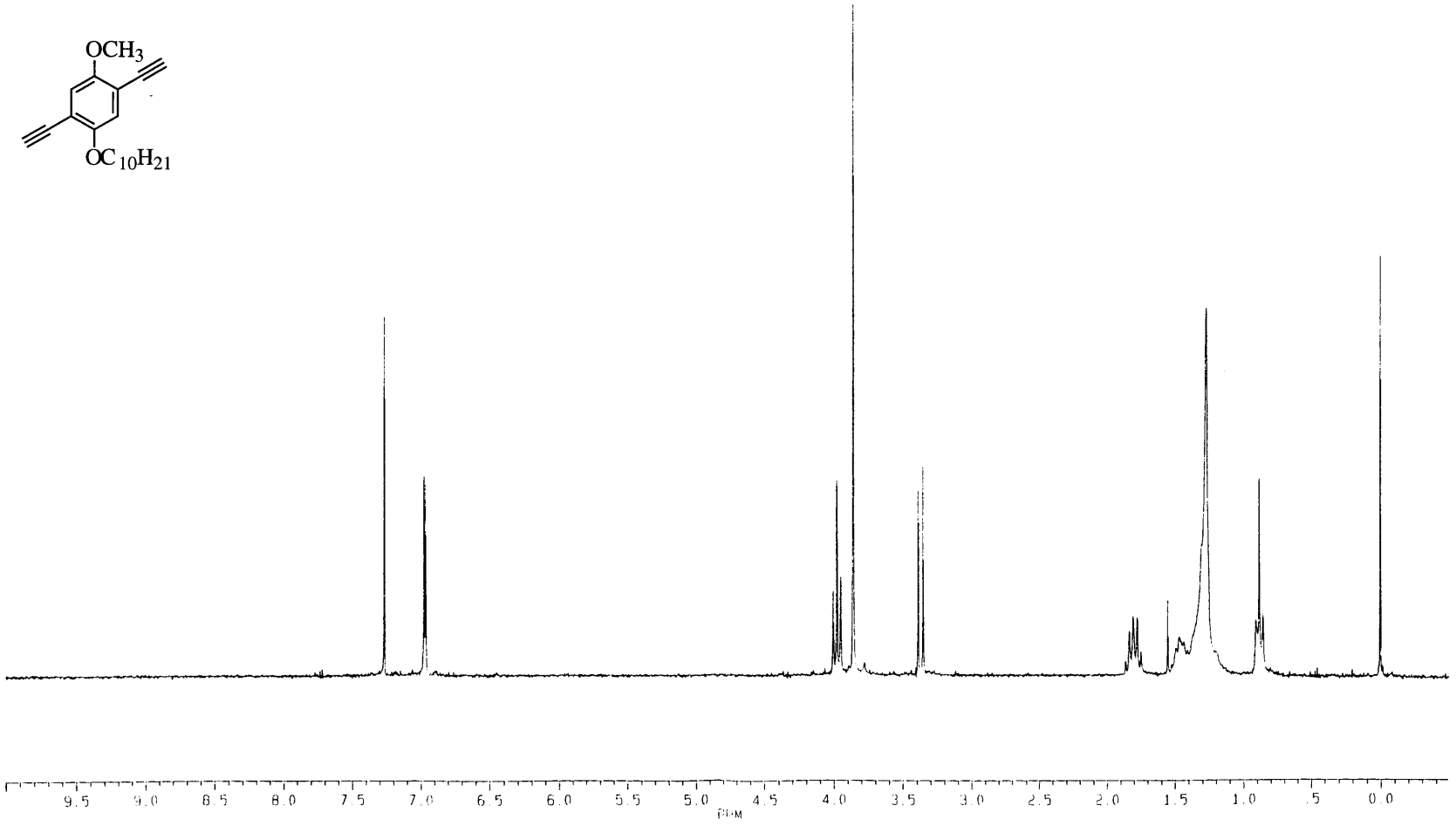

Figure A1.7. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **5**.

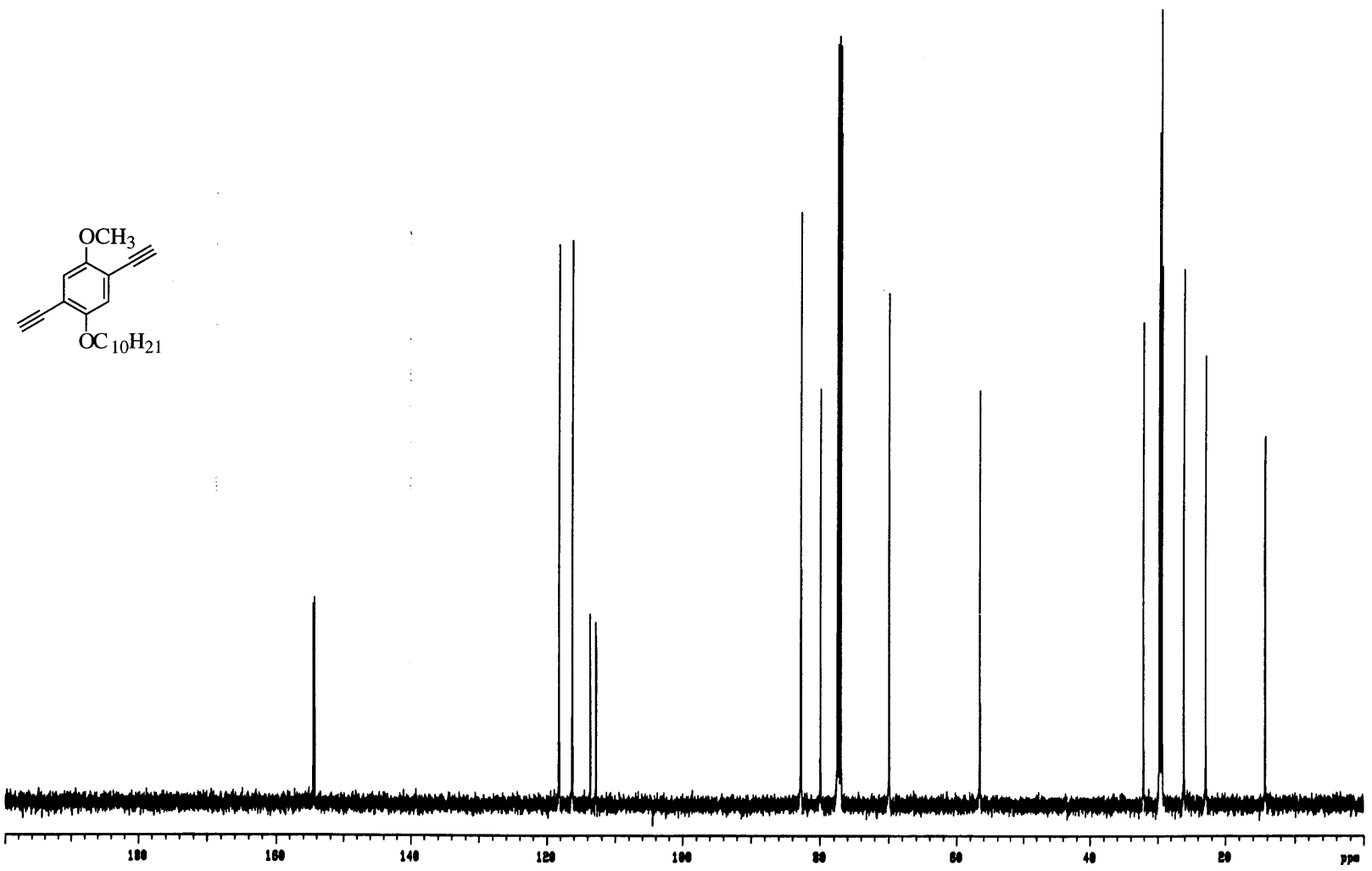

Figure A1.8. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **5**.

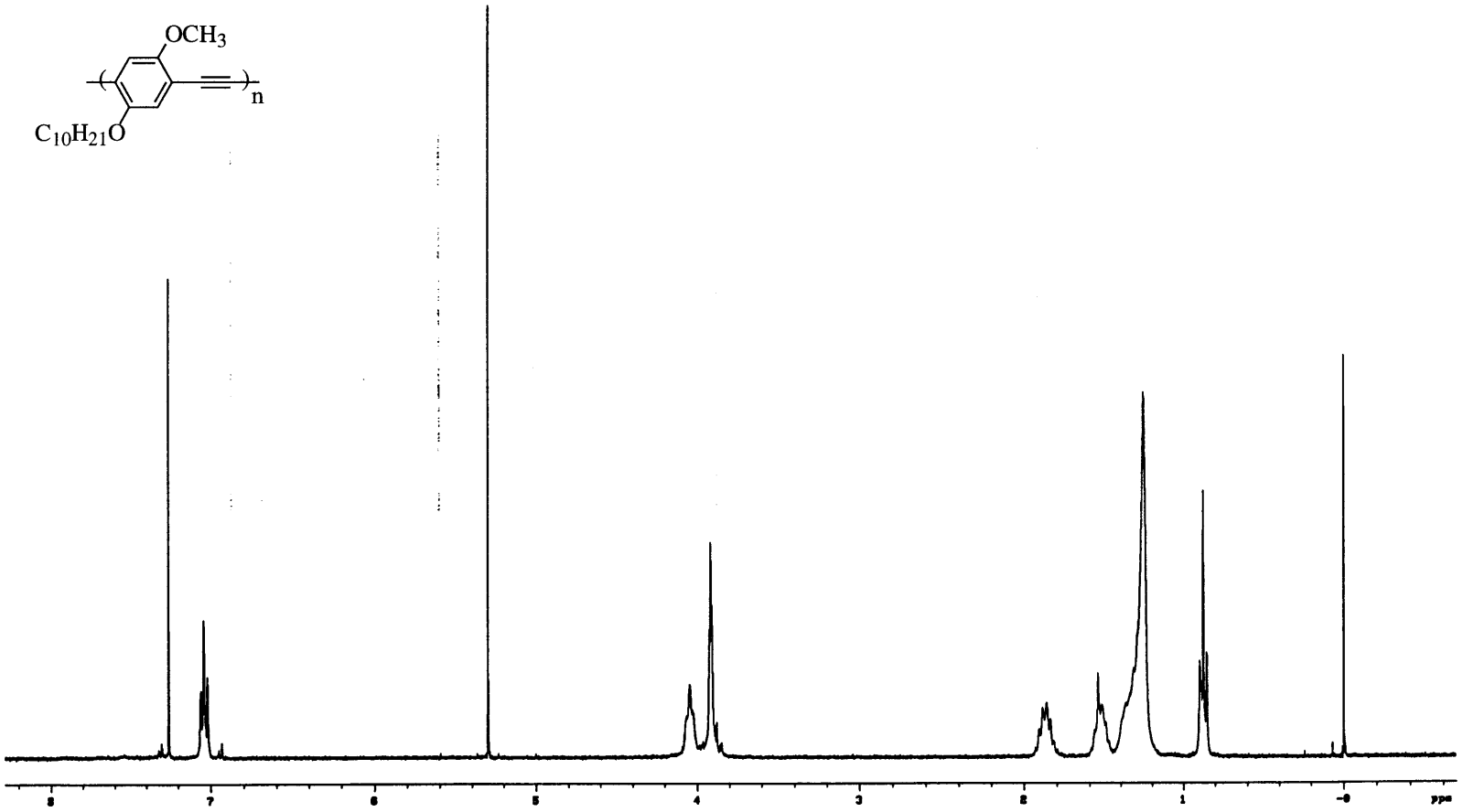

Figure A1.9. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **6**.

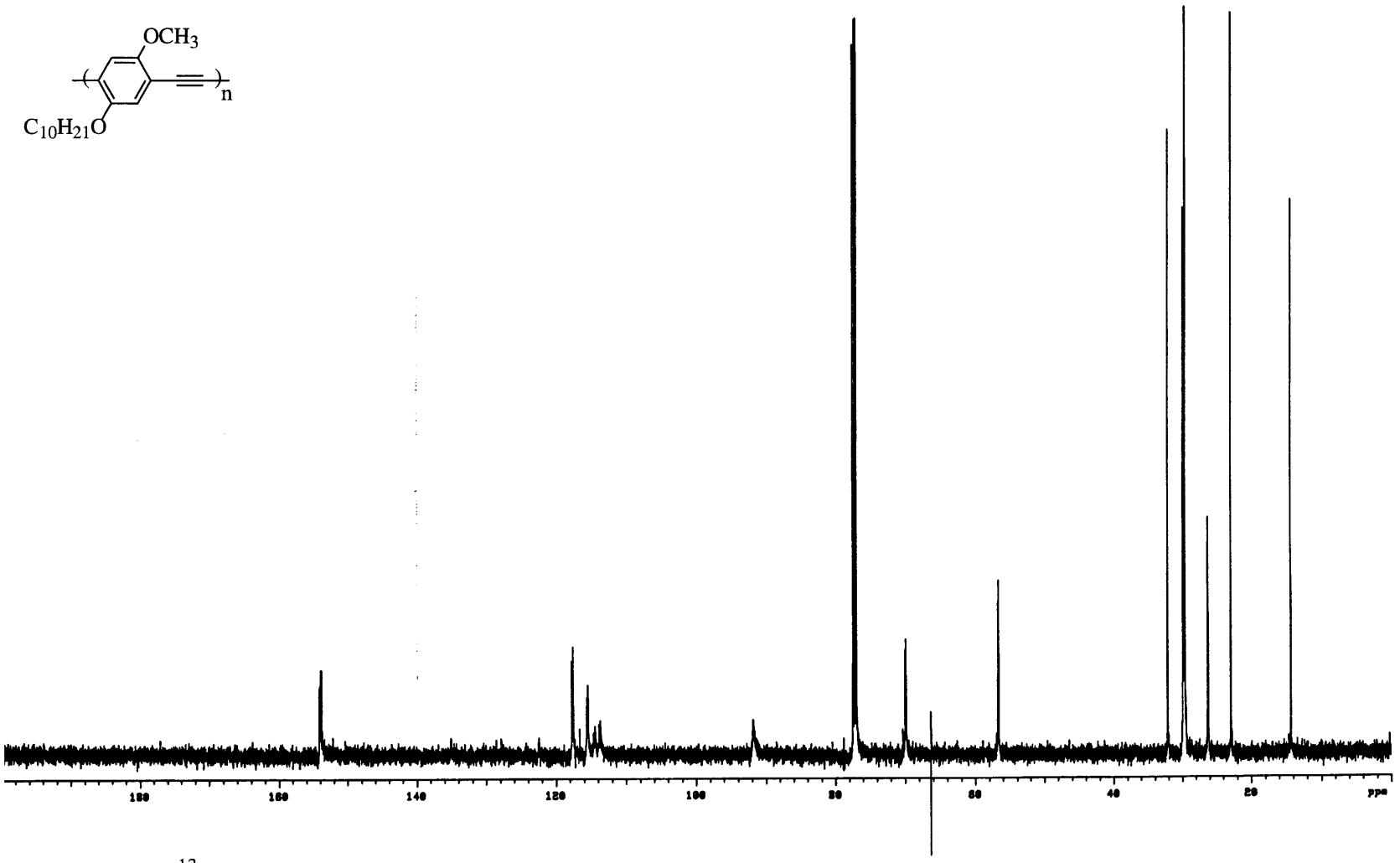

Figure A1.10. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **6.**

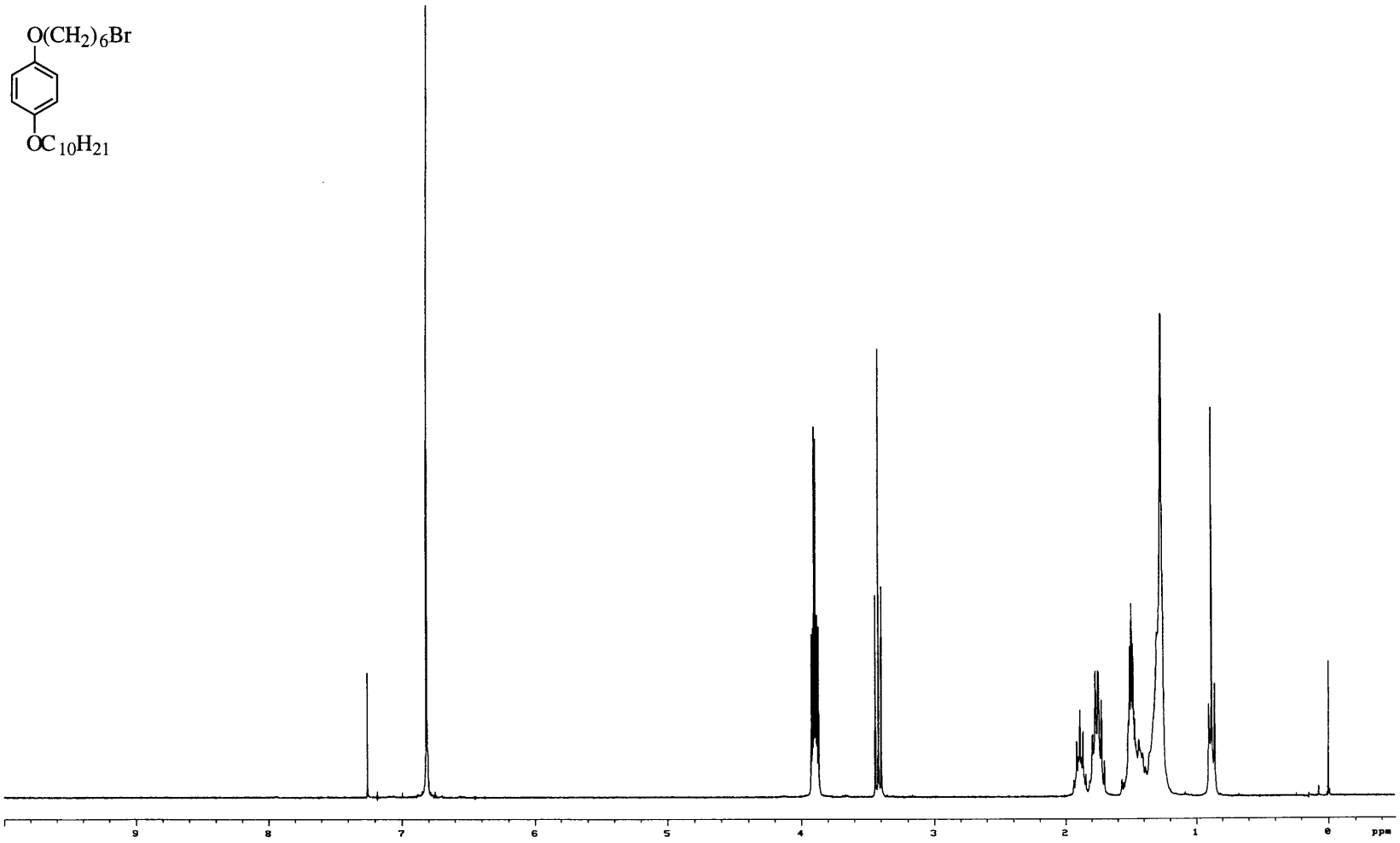

Figure A1.11. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **8**.

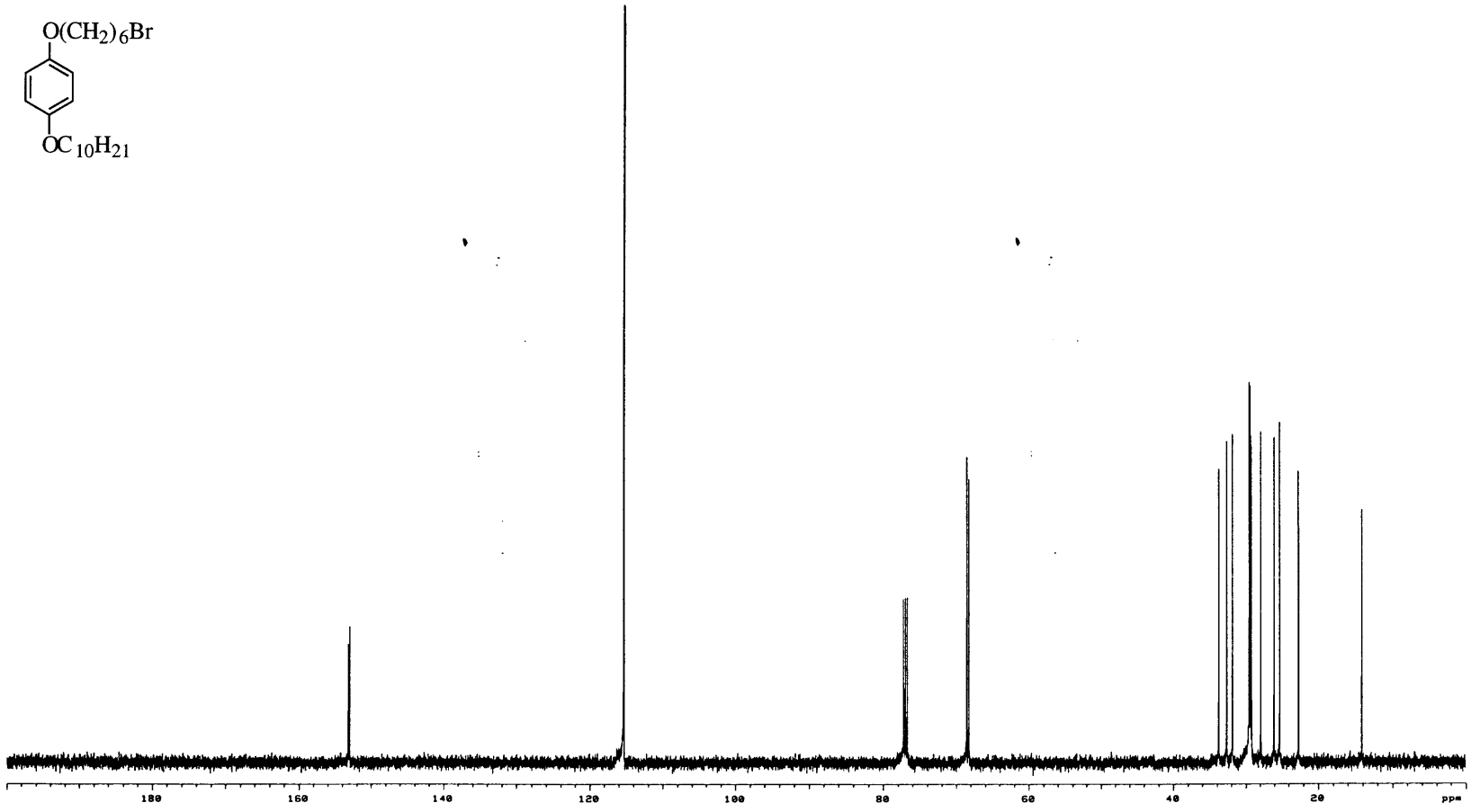

Figure A1.12. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **8.**

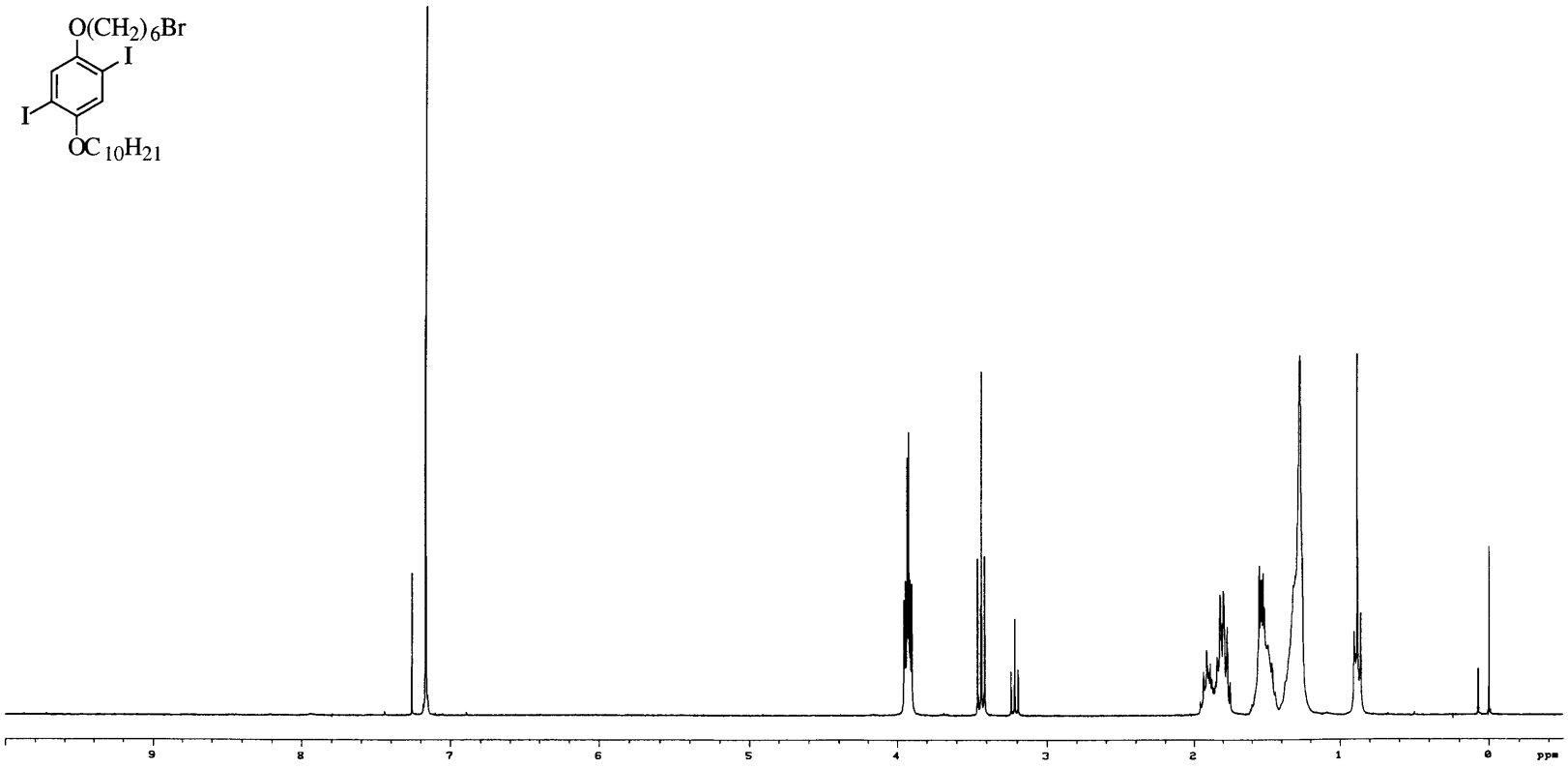

Figure A1.13. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **9**.

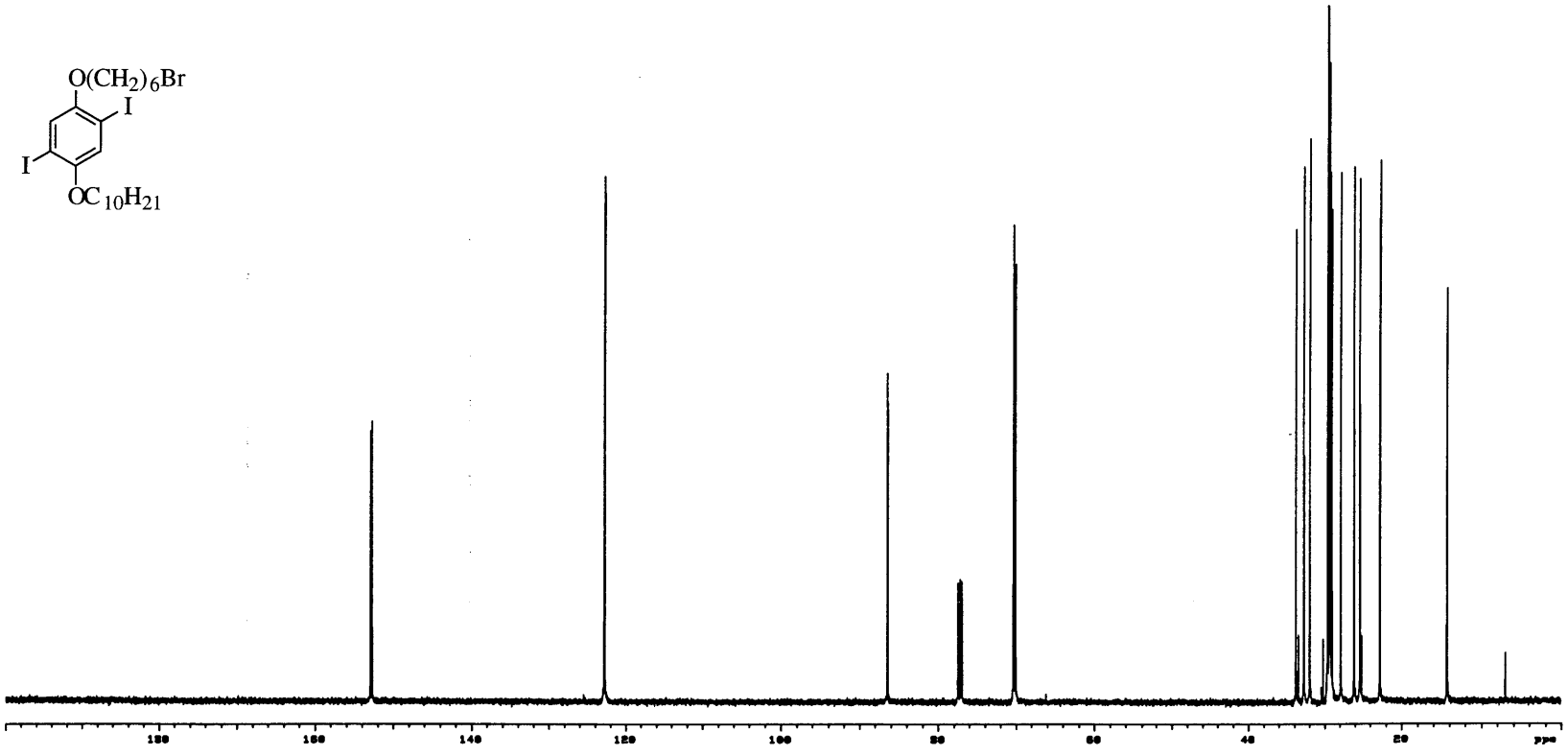

Figure A1.14. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **9.**

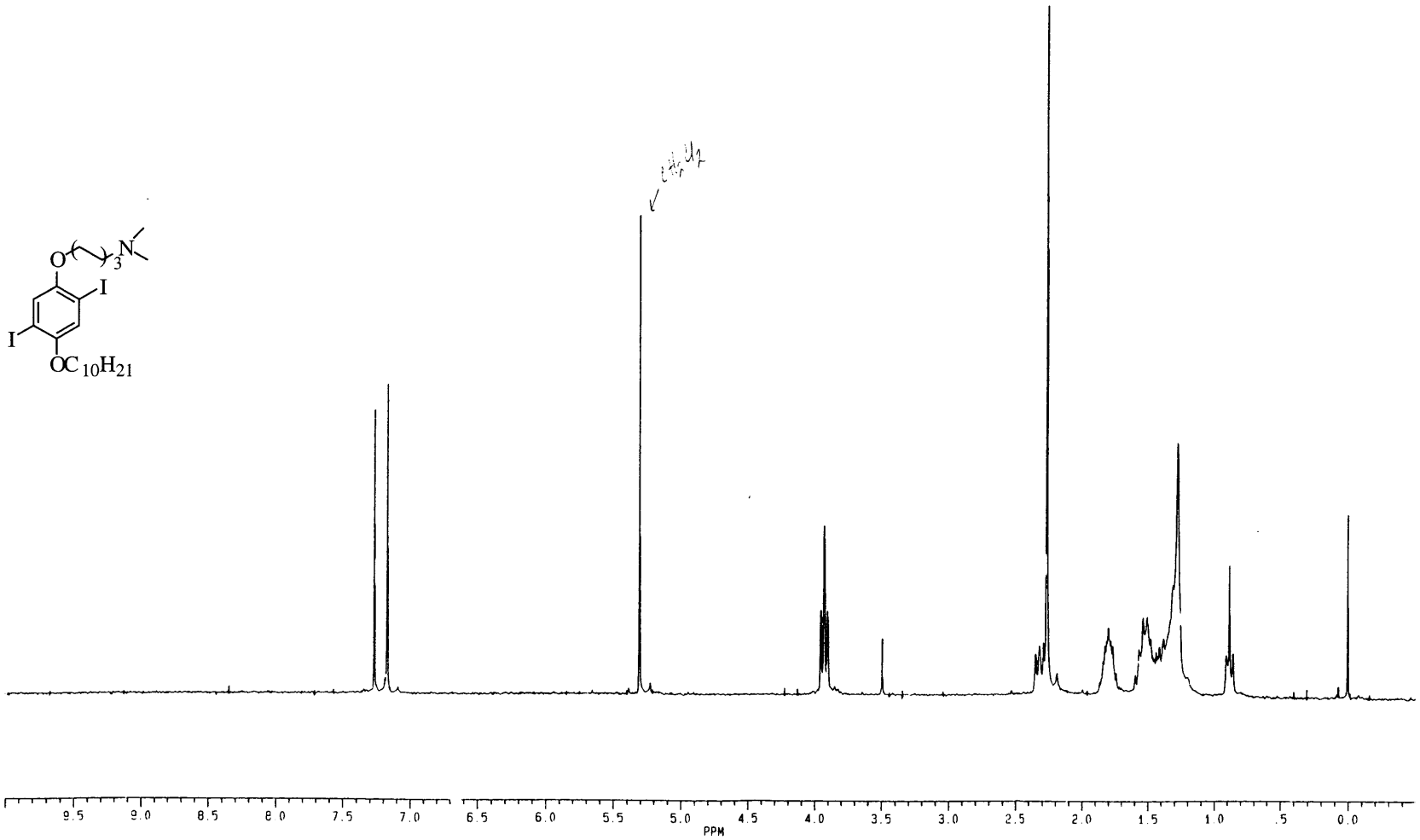

Figure A1.15. ^{13}C NMR spectrum (250 MHz, $CDCl_3$) of compound **11**.

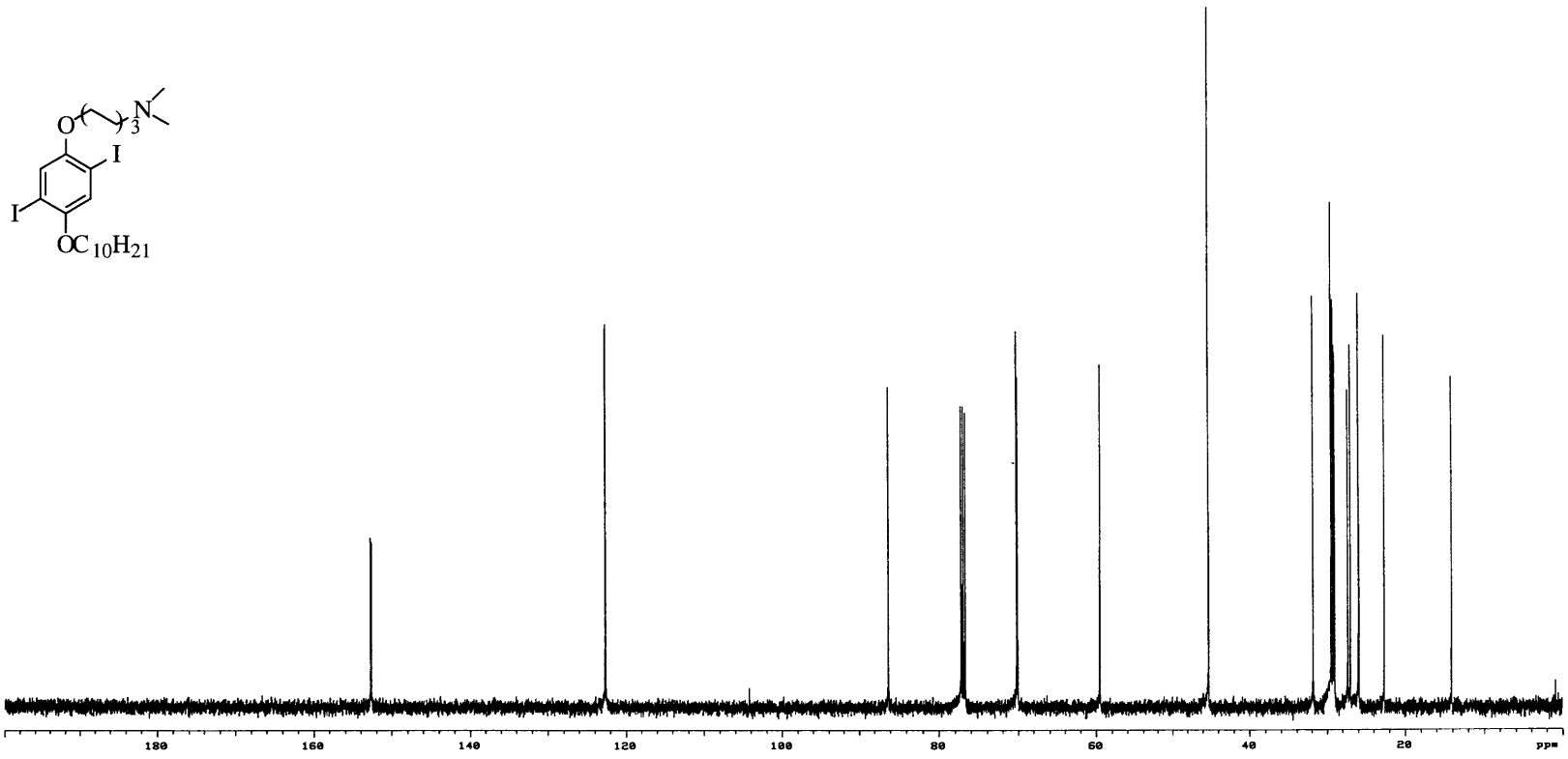

Figure A1.16. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **11**.

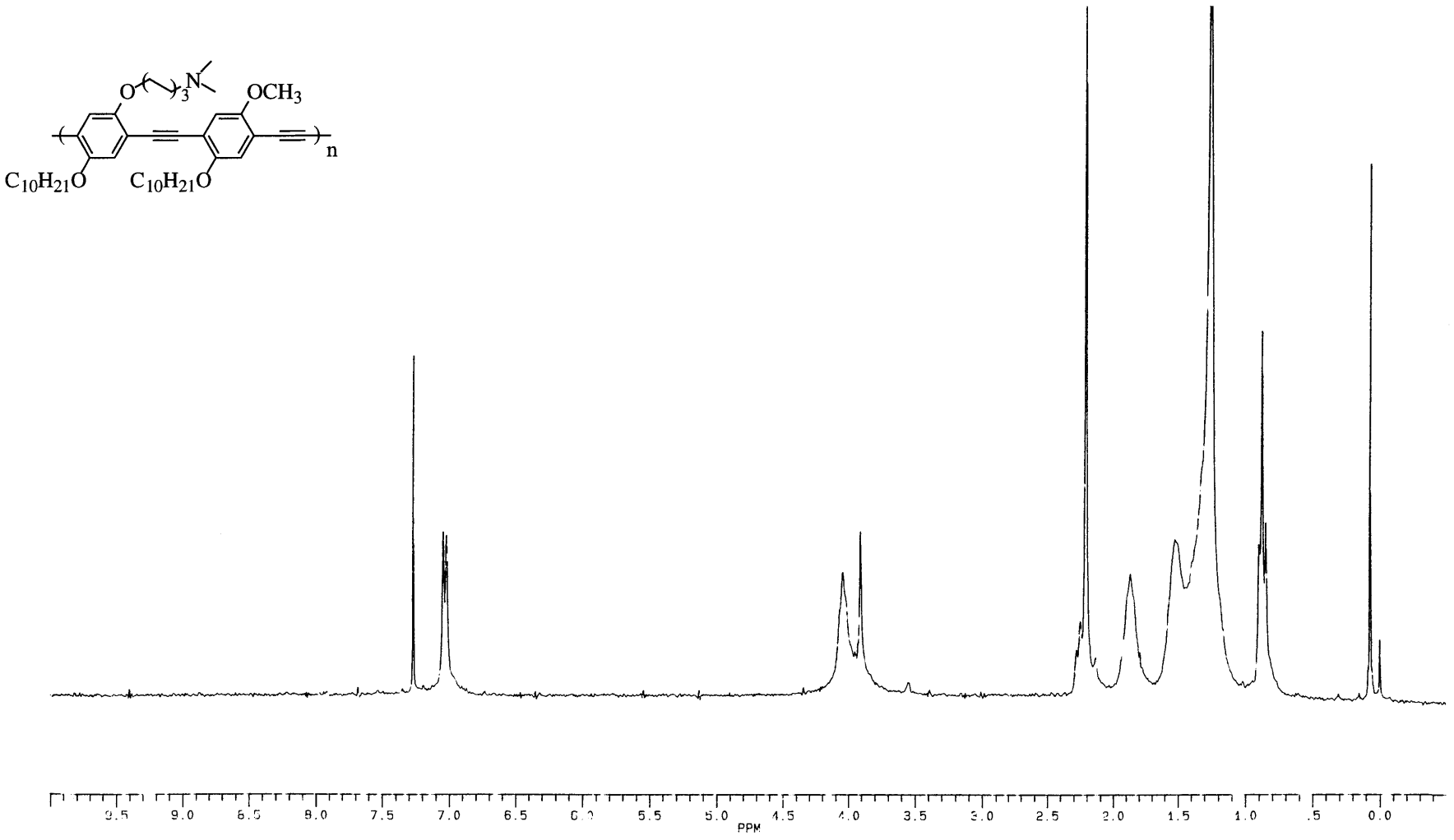

Figure A1.17. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **12.**

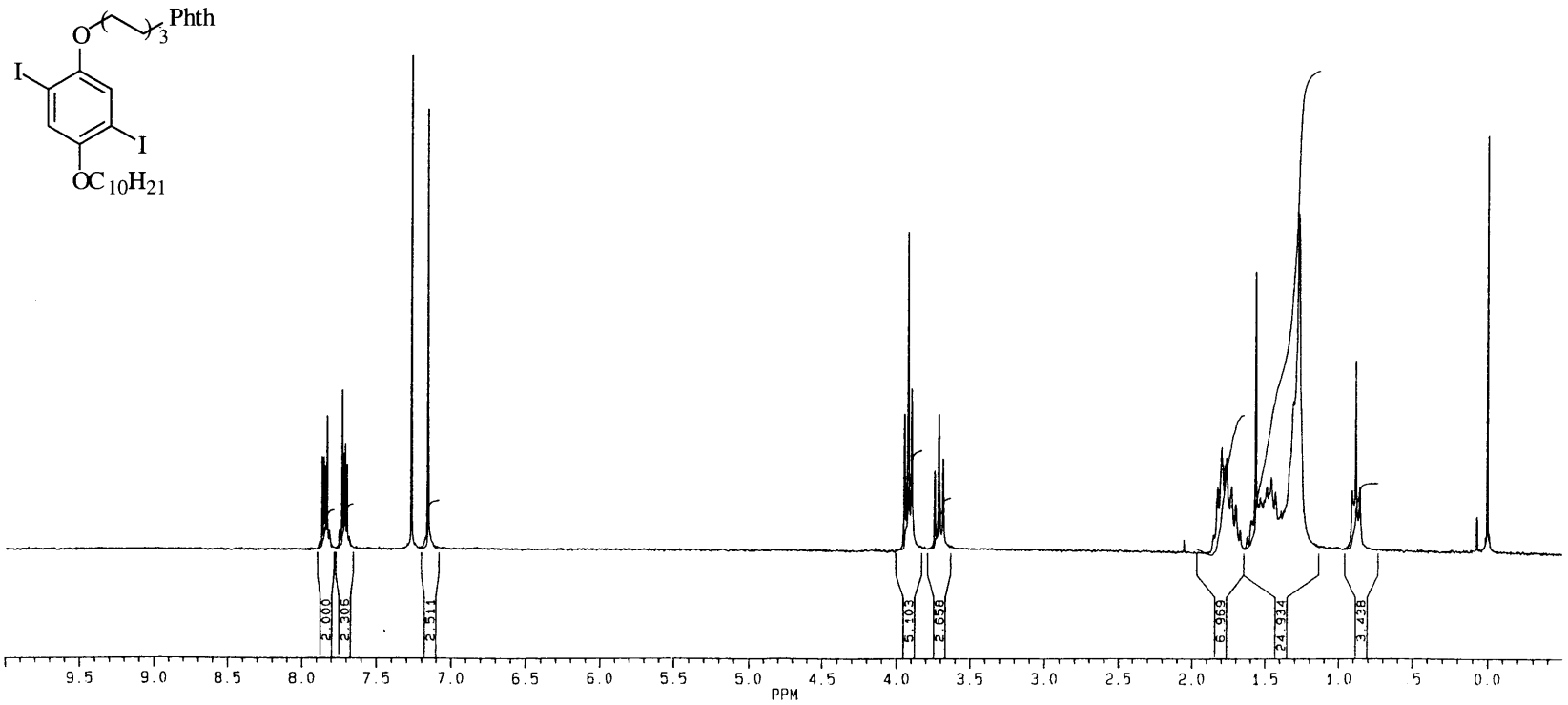

Figure A1.18. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **15**.

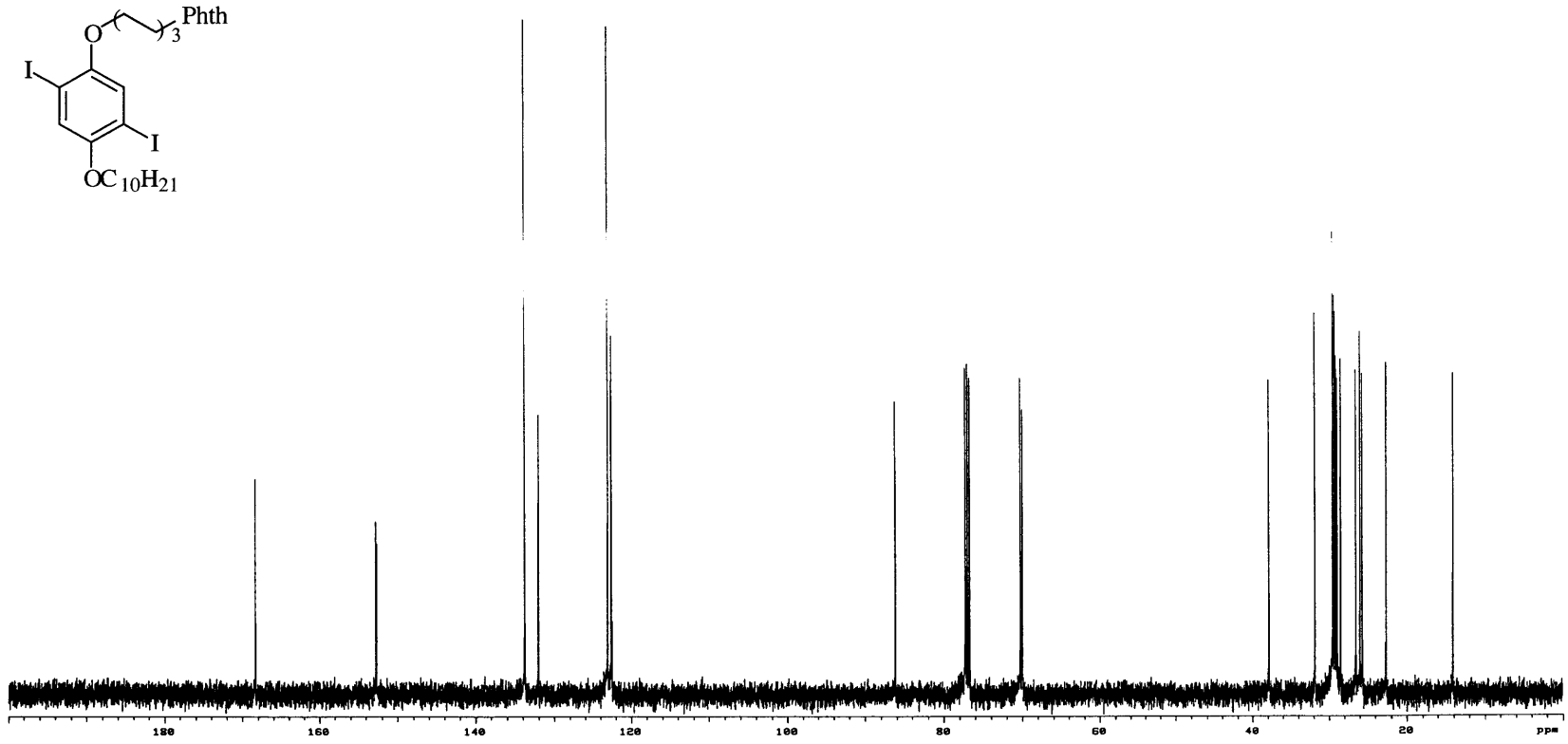

Figure A1.19. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **15**.

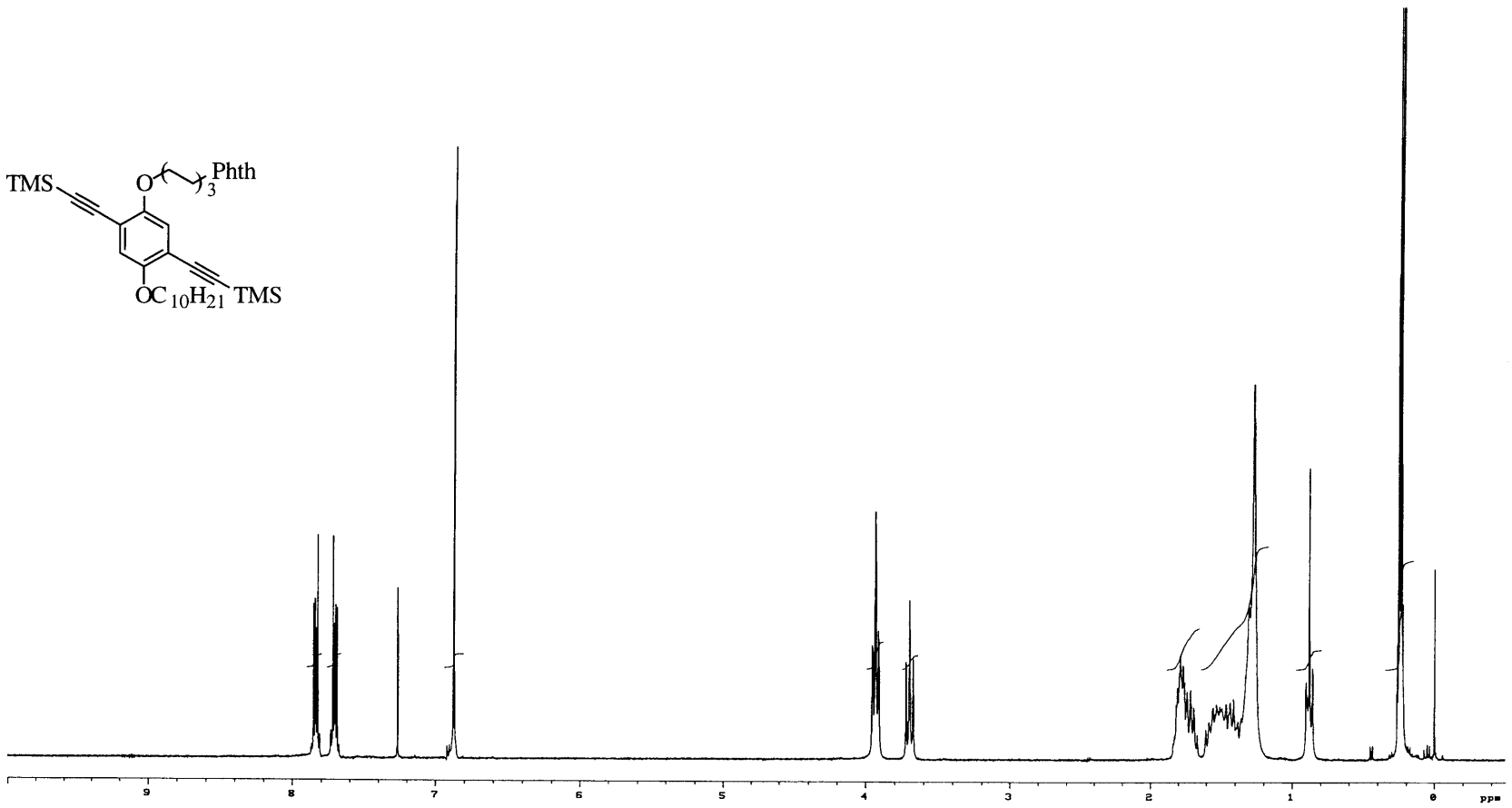

Figure A1.20. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **16.**

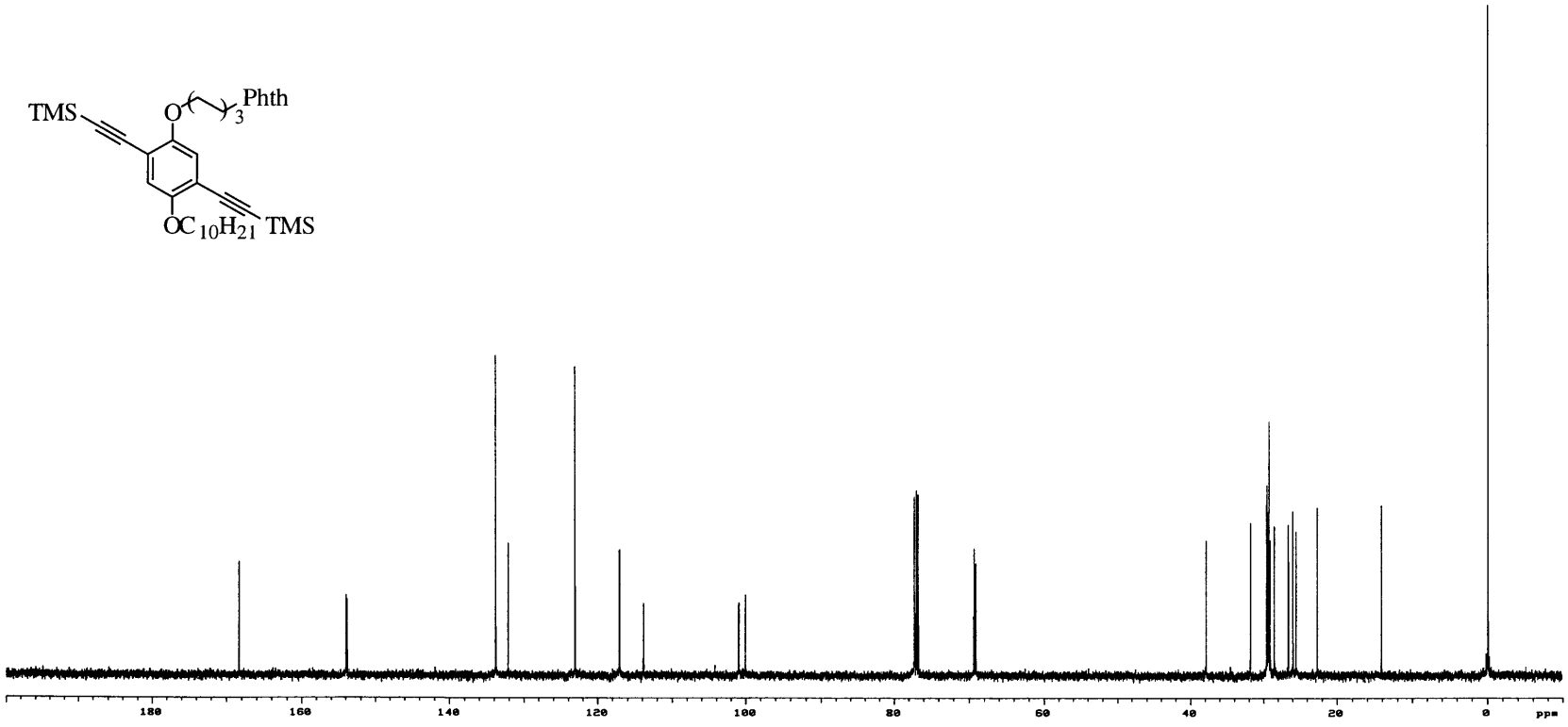

Figure A1.21. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **16**.

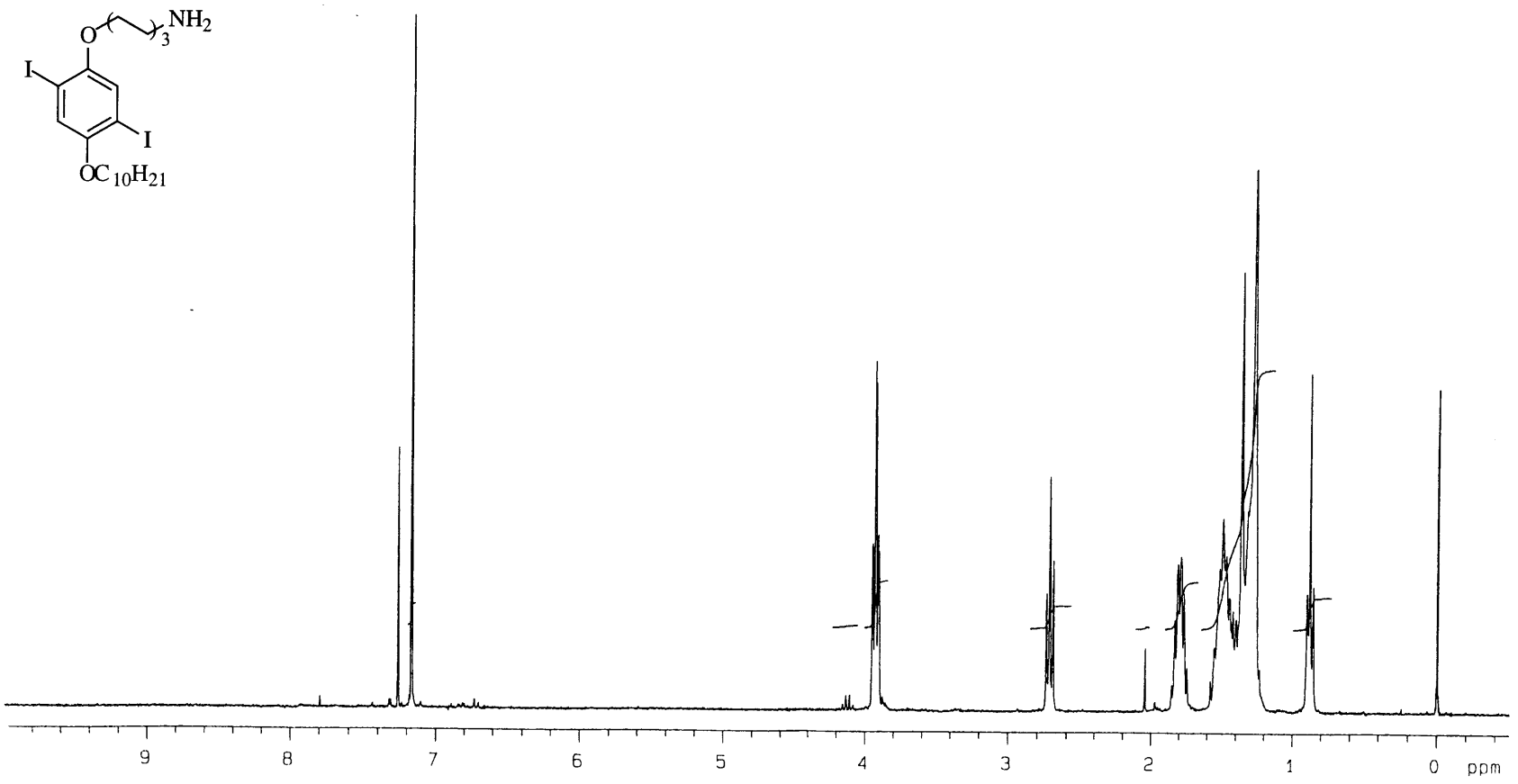

Figure A1.22. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **18**.

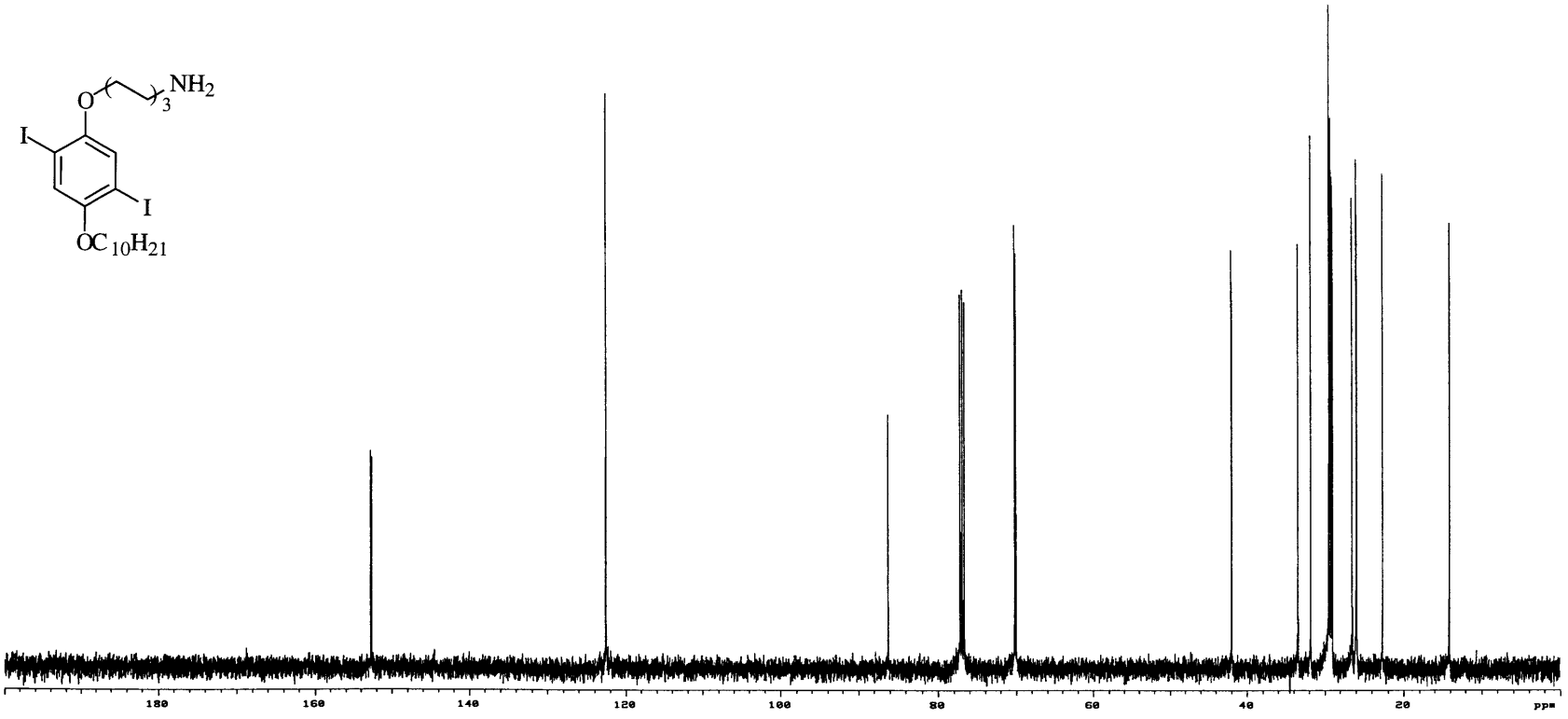

Figure A1.23. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **18**.

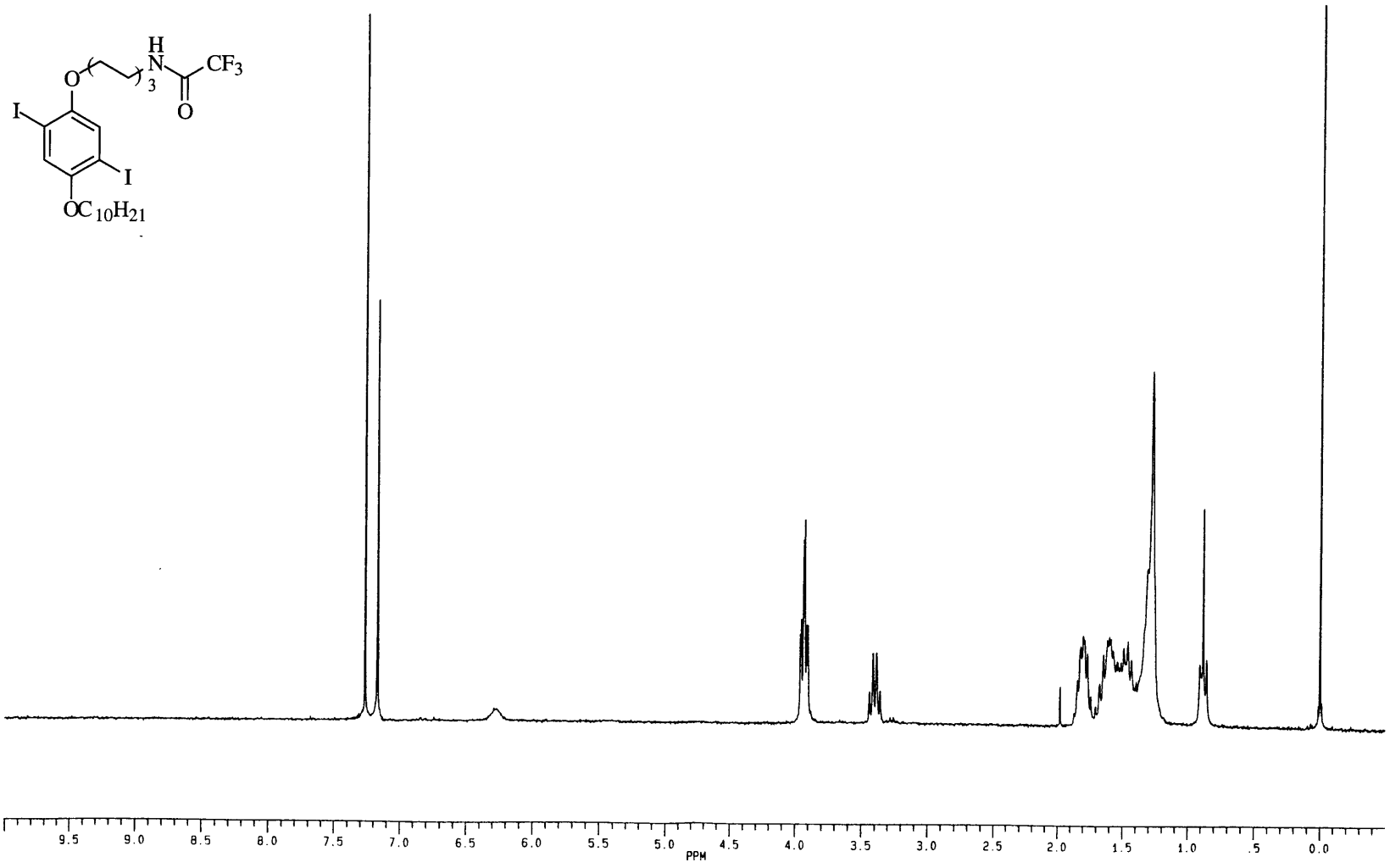

Figure A1.24. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **19**.

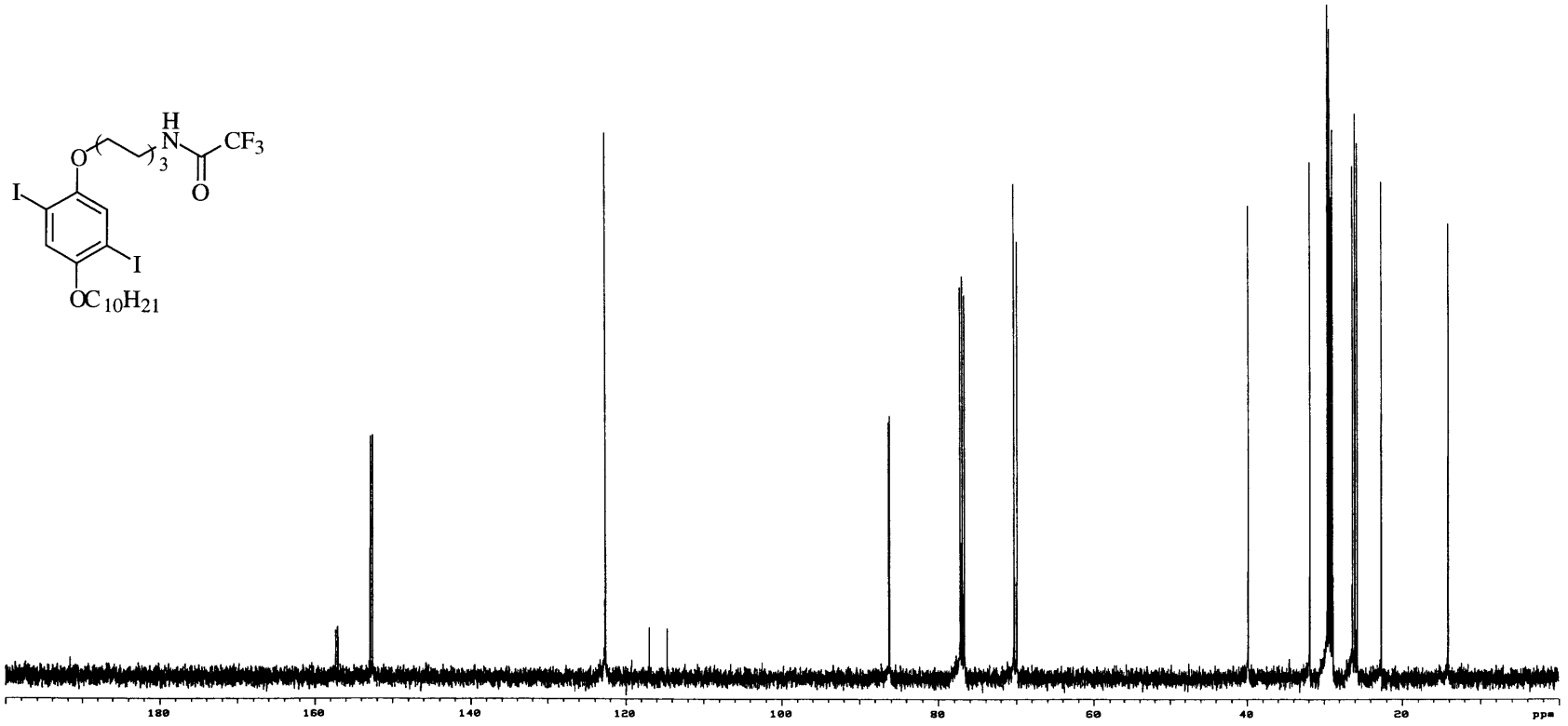

Figure A1.25. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **19**.

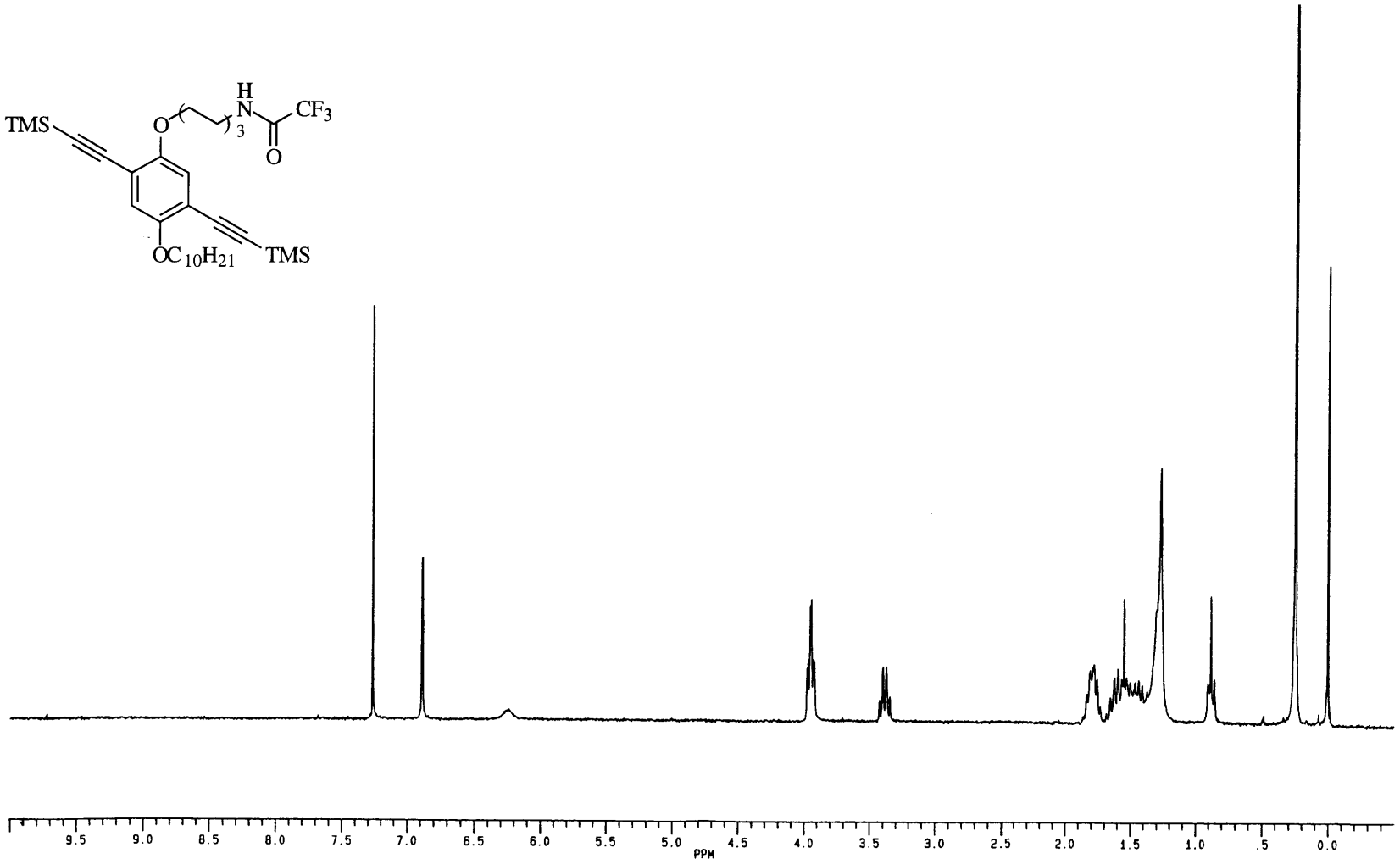

Figure A1.26. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **20**.

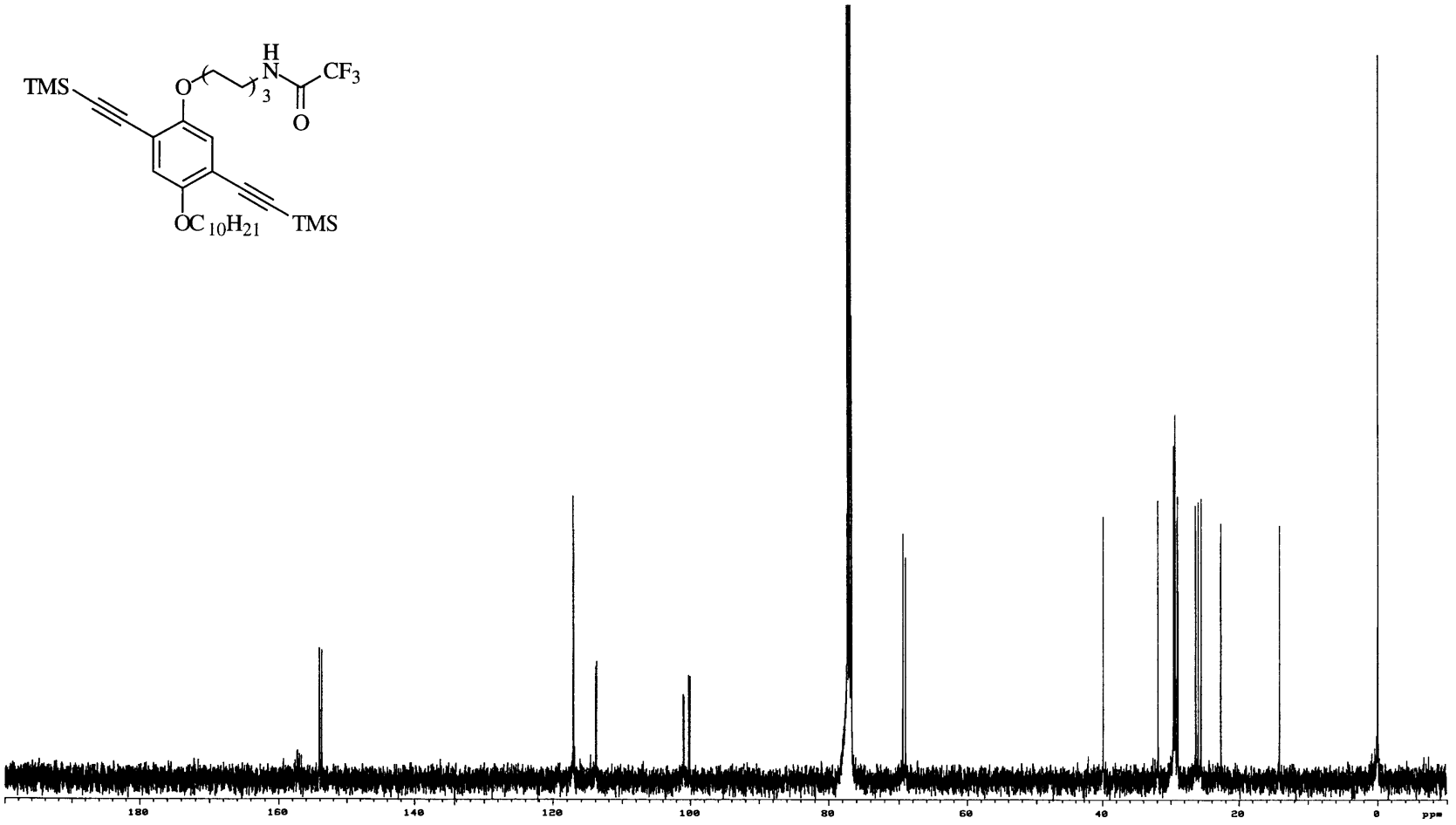

Figure A1.27. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **20**.

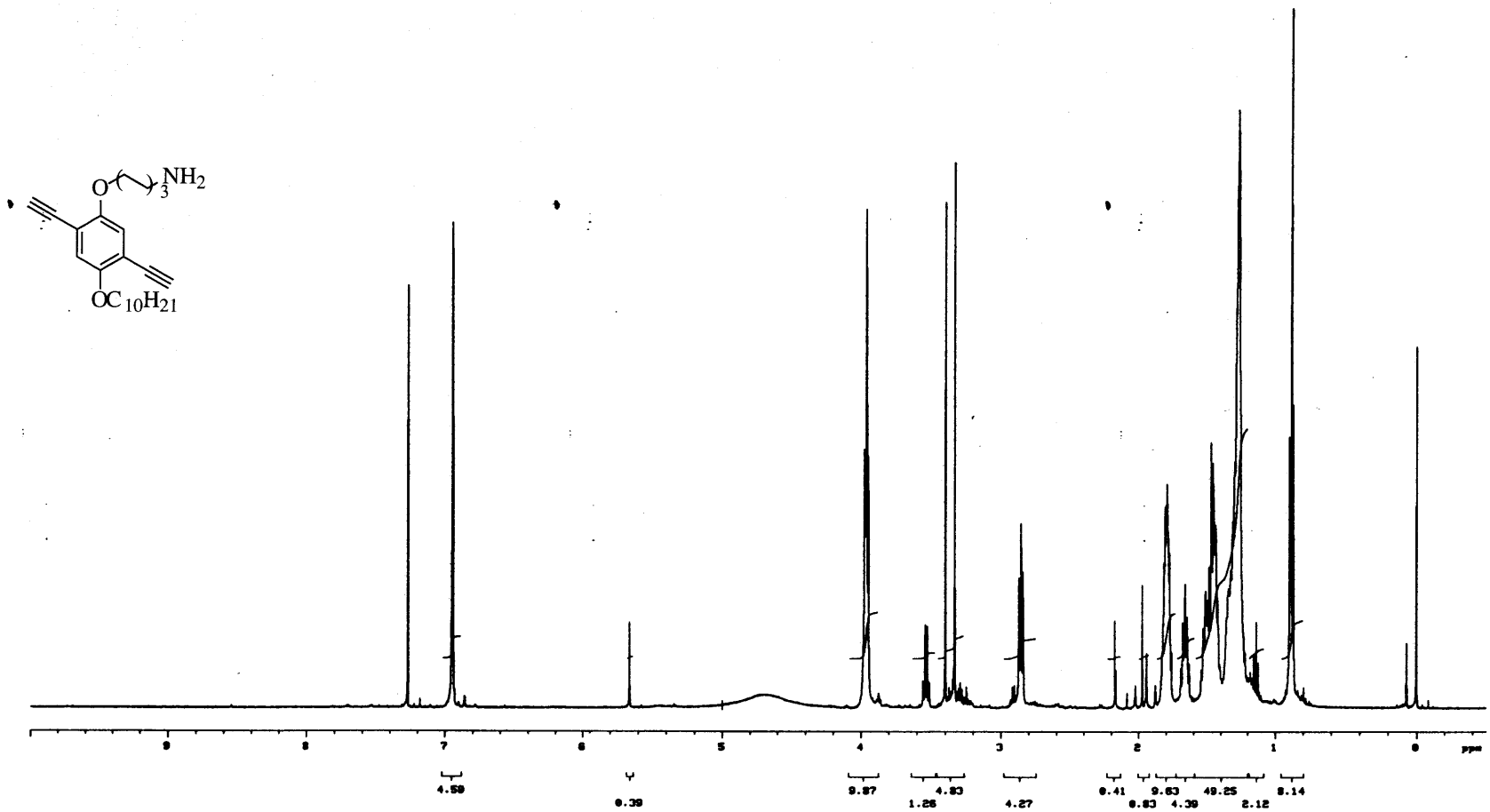

Figure A1.28. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **21.**

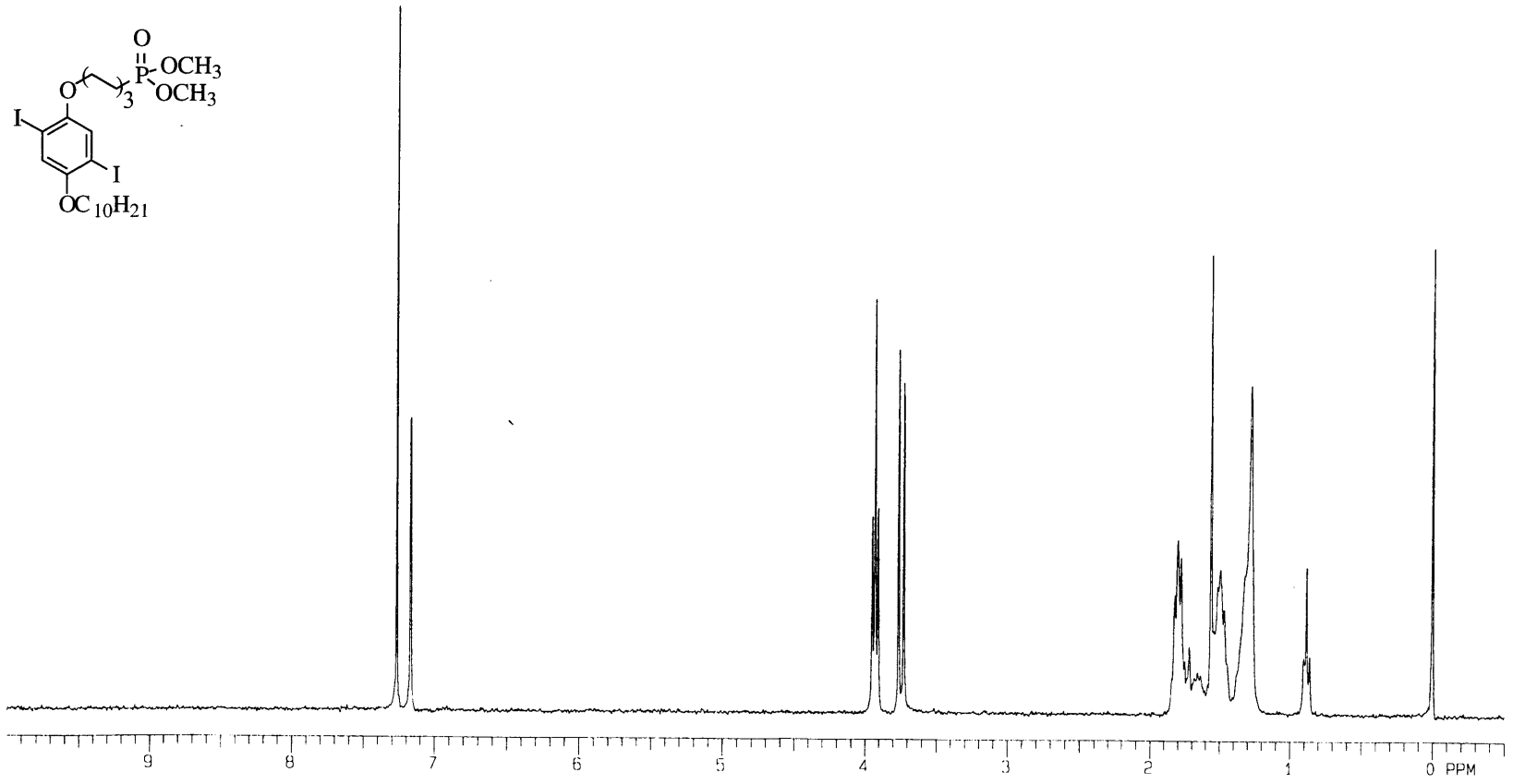

Figure A1.29. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **22**.

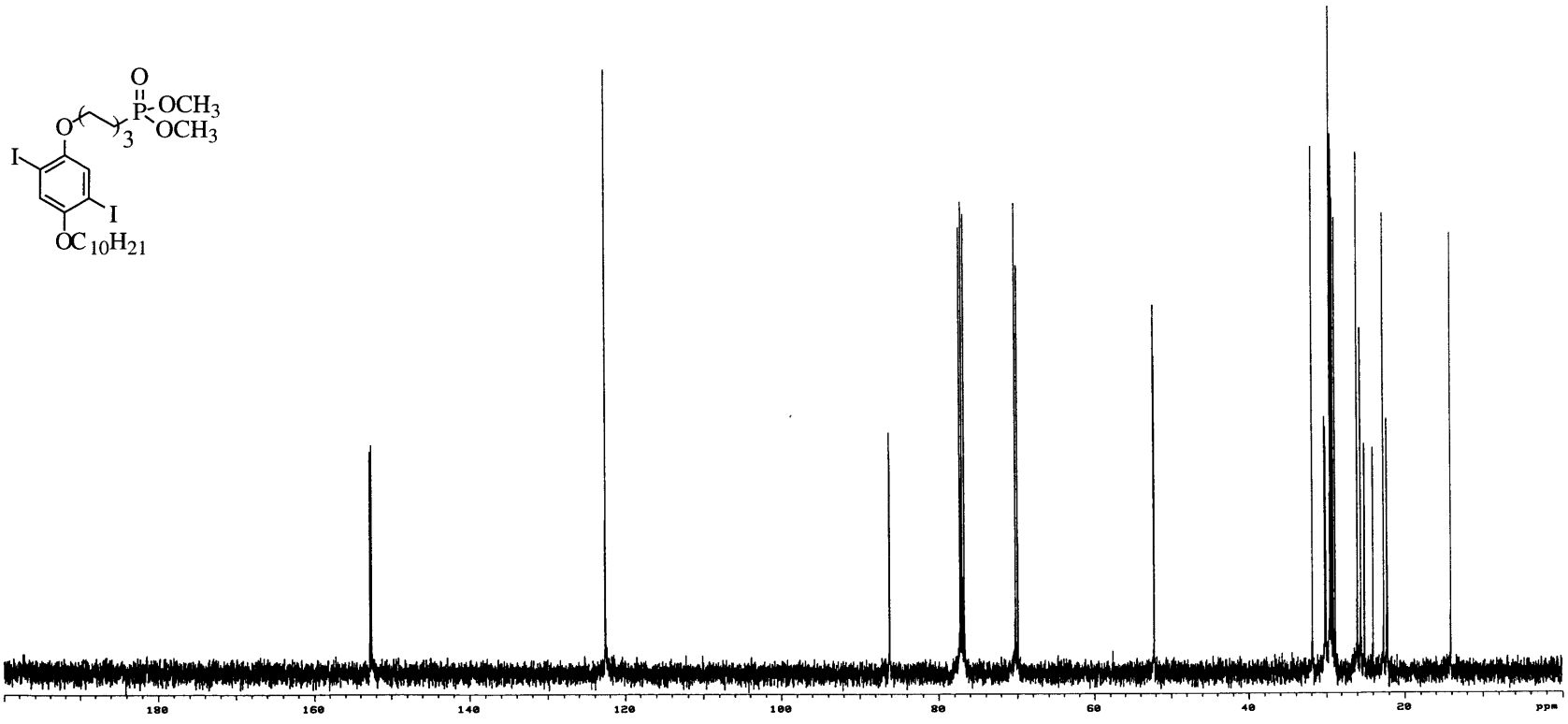

Figure A1.30. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **22**.

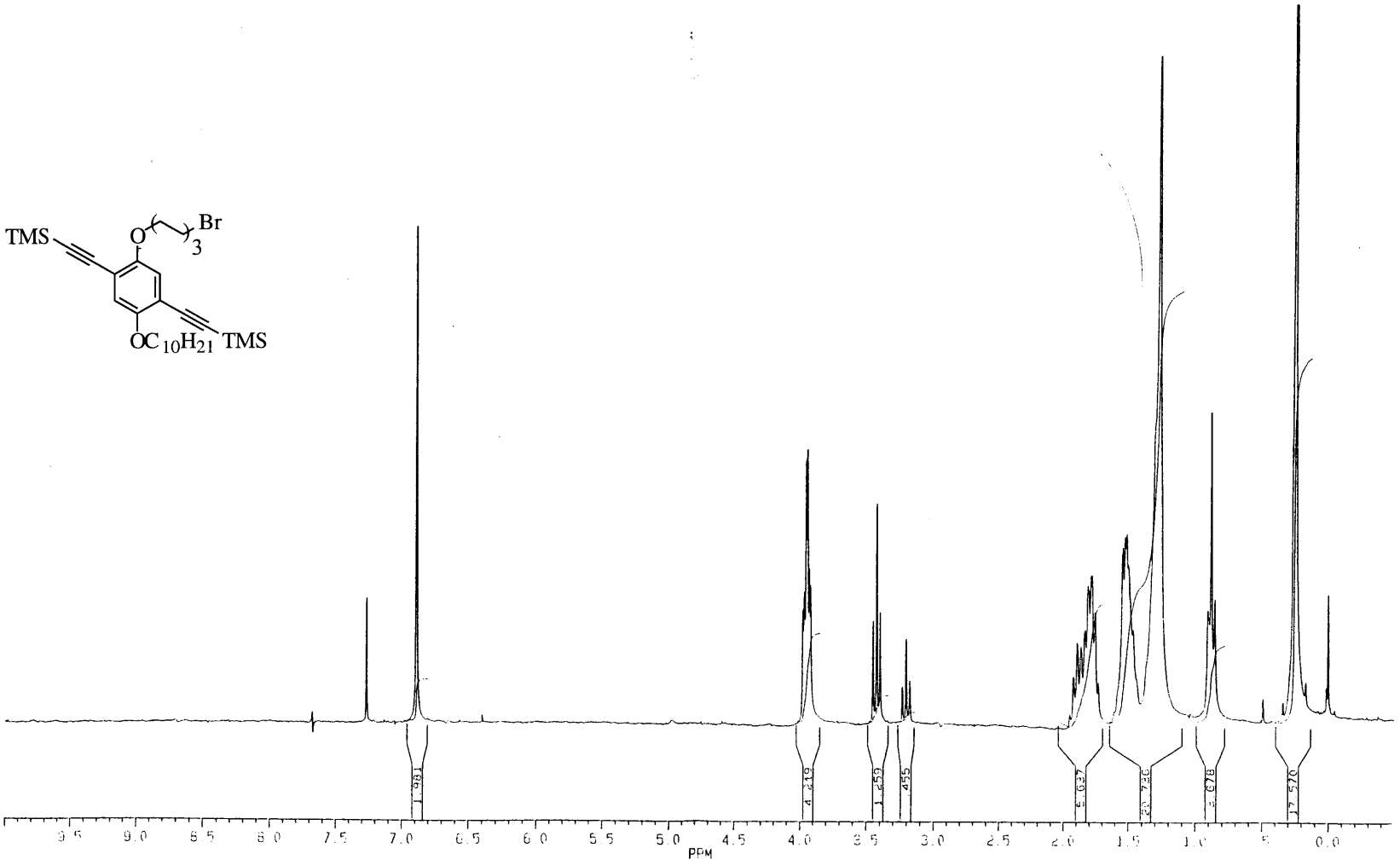

Figure A1.31. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **23**.

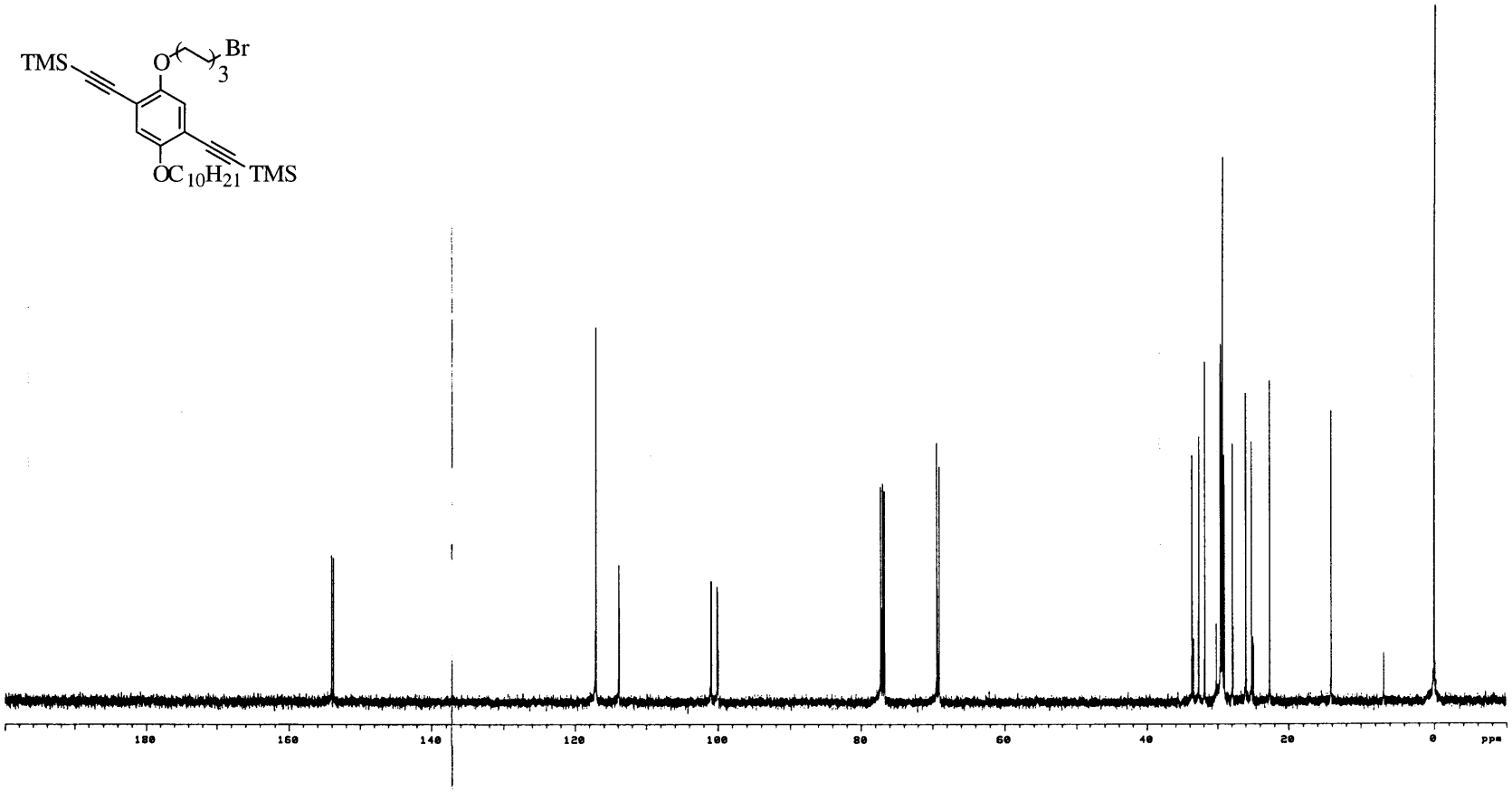

Figure A1.32. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **23**.

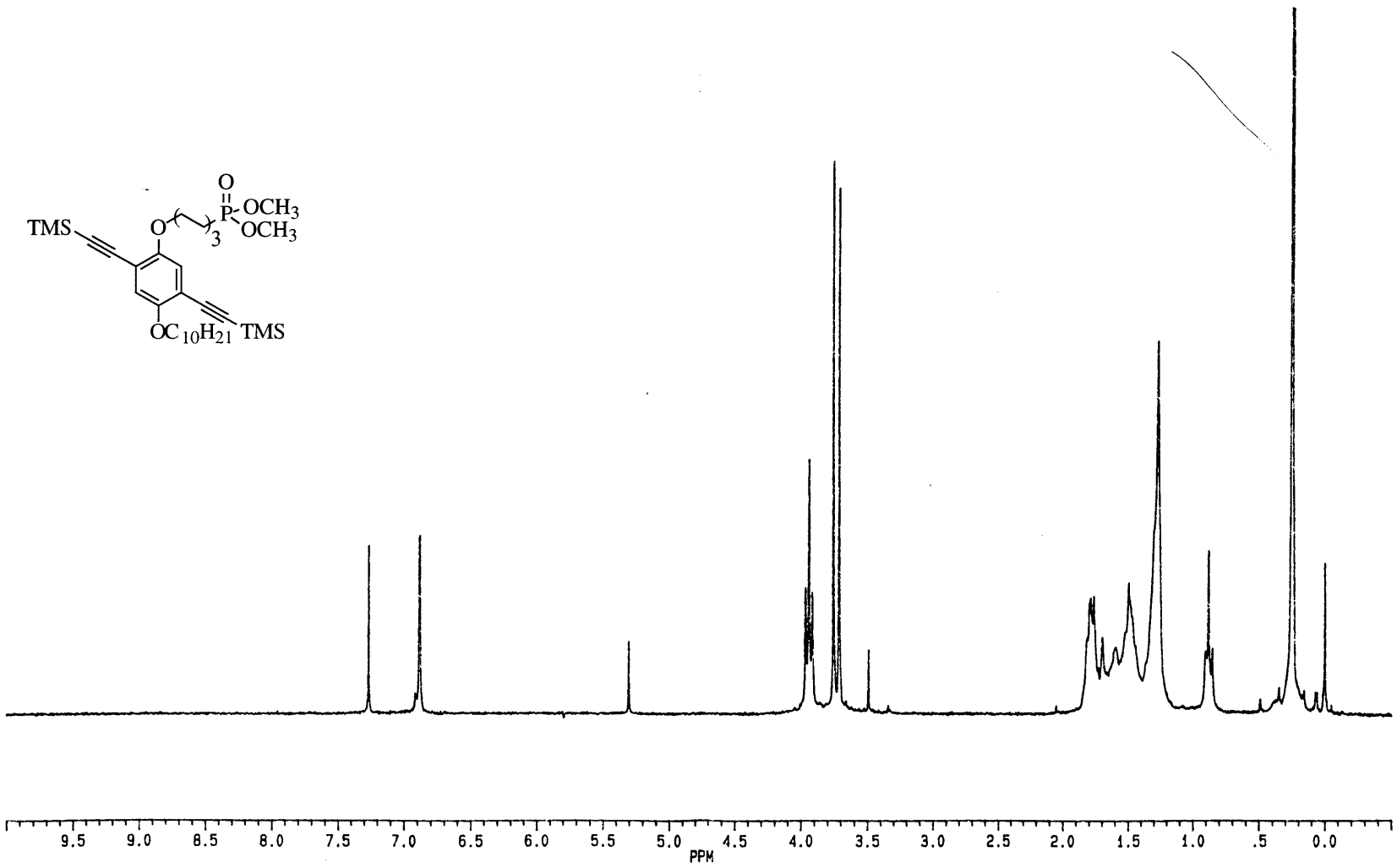

Figure A1.33. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **24**.

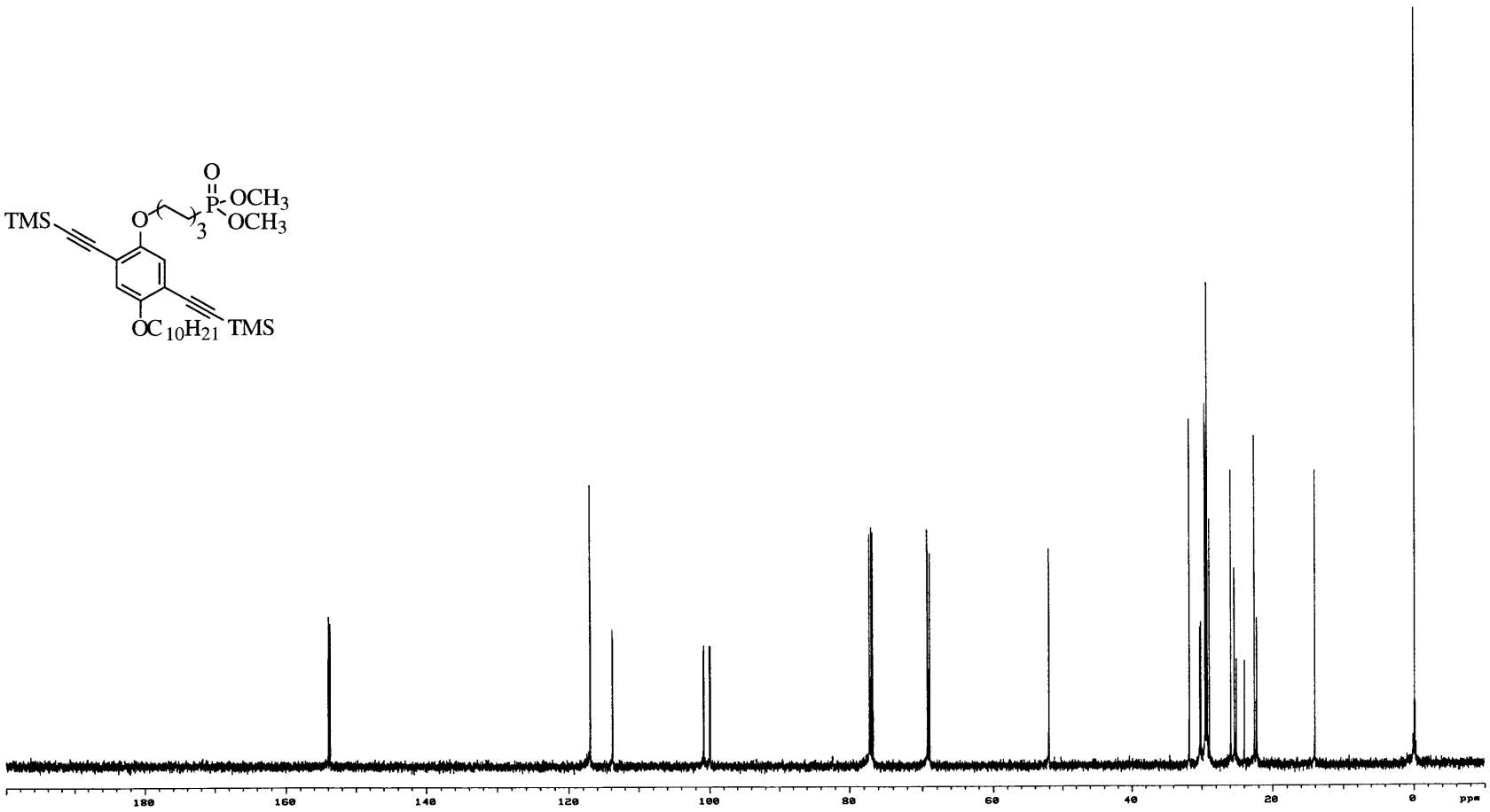

Figure A1.34. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **24**.

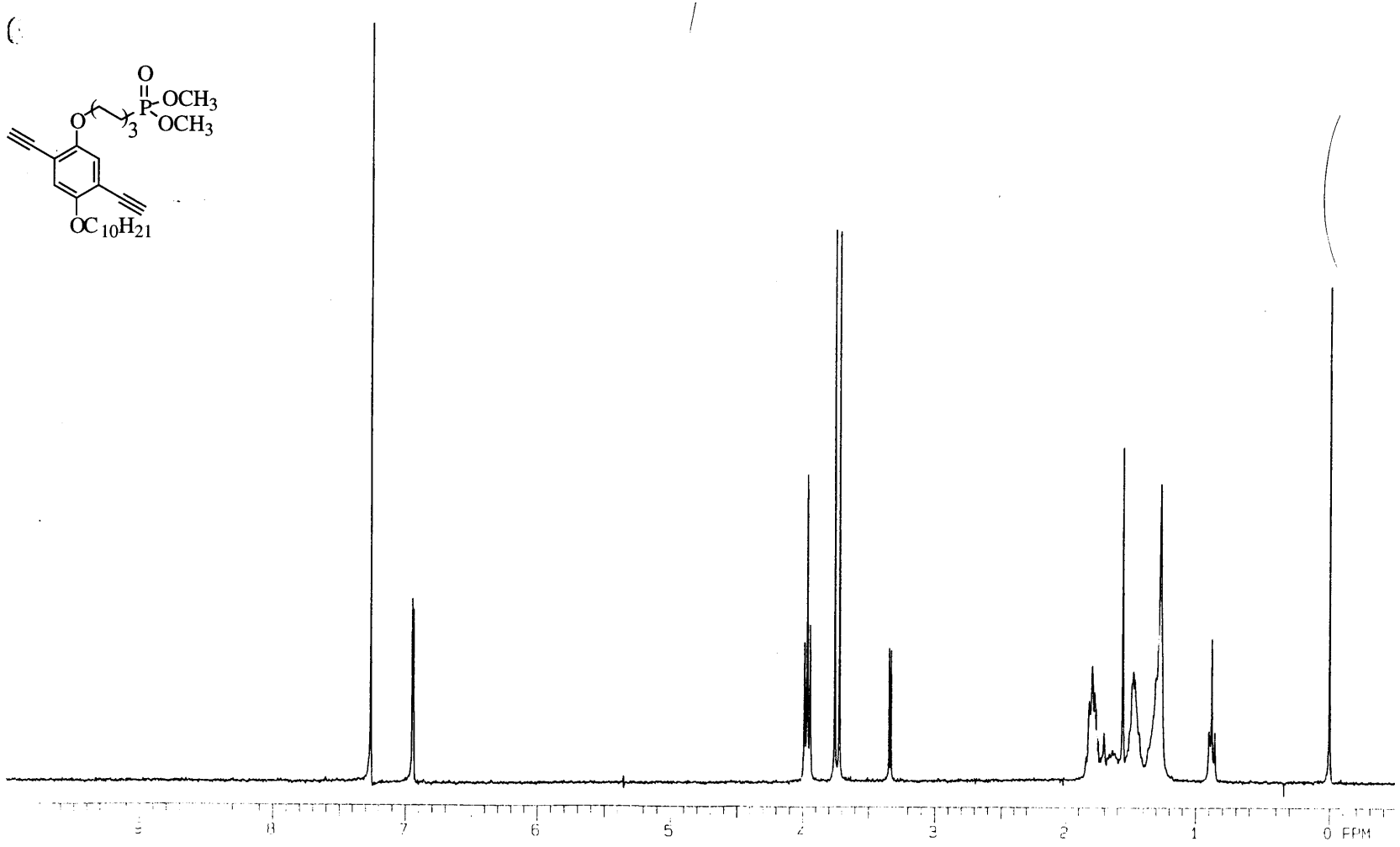

Figure A1.35. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **25**.

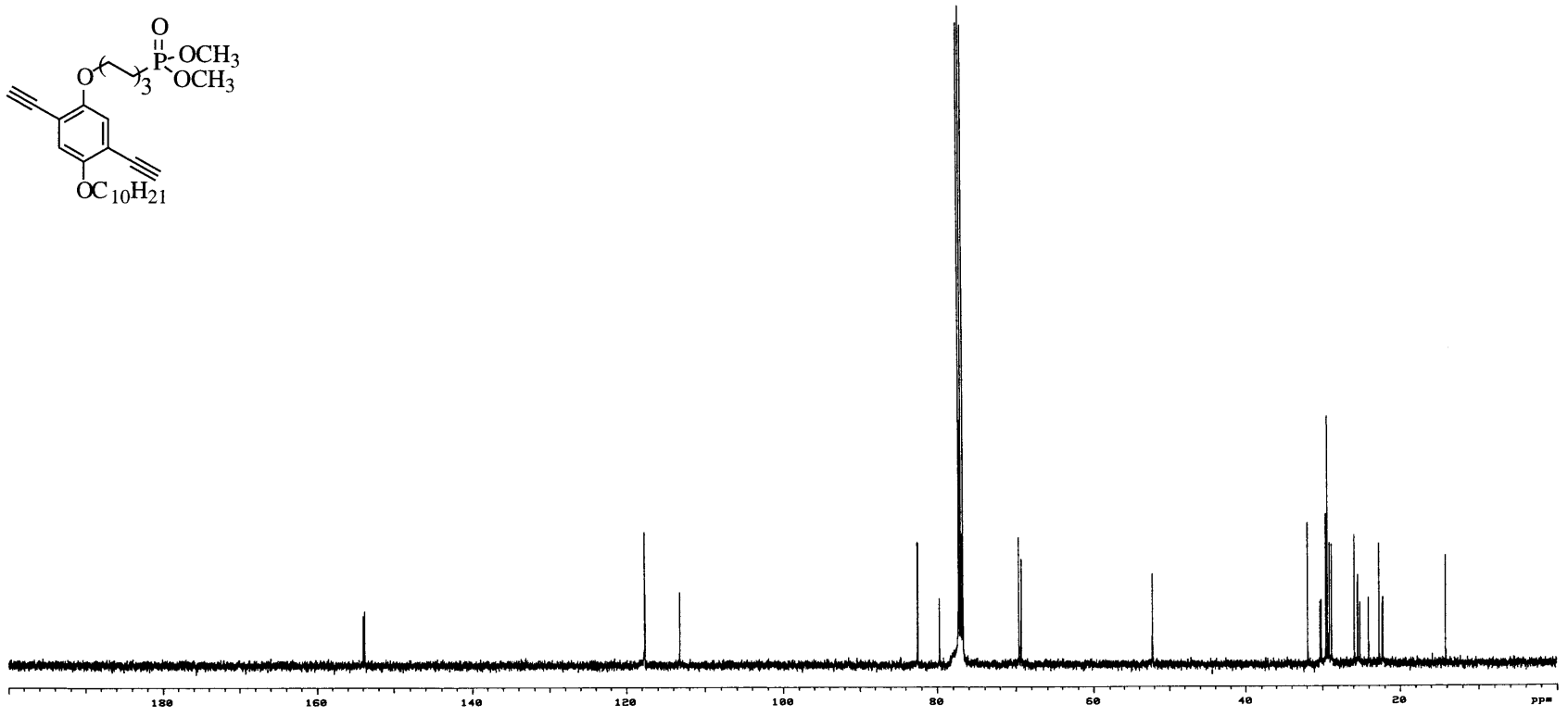

Figure A1.36. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **25**.

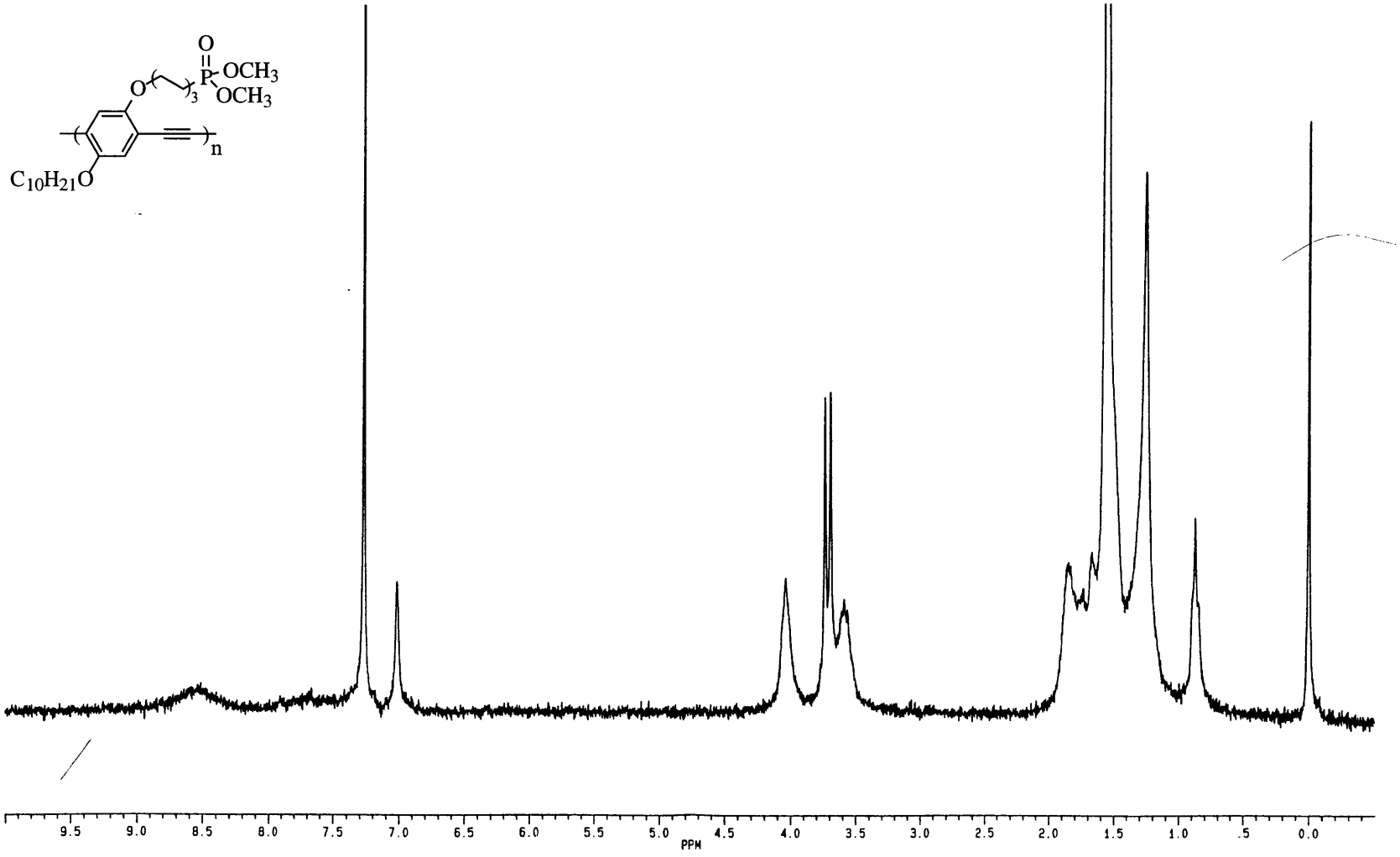

Figure A1.37. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **26**.

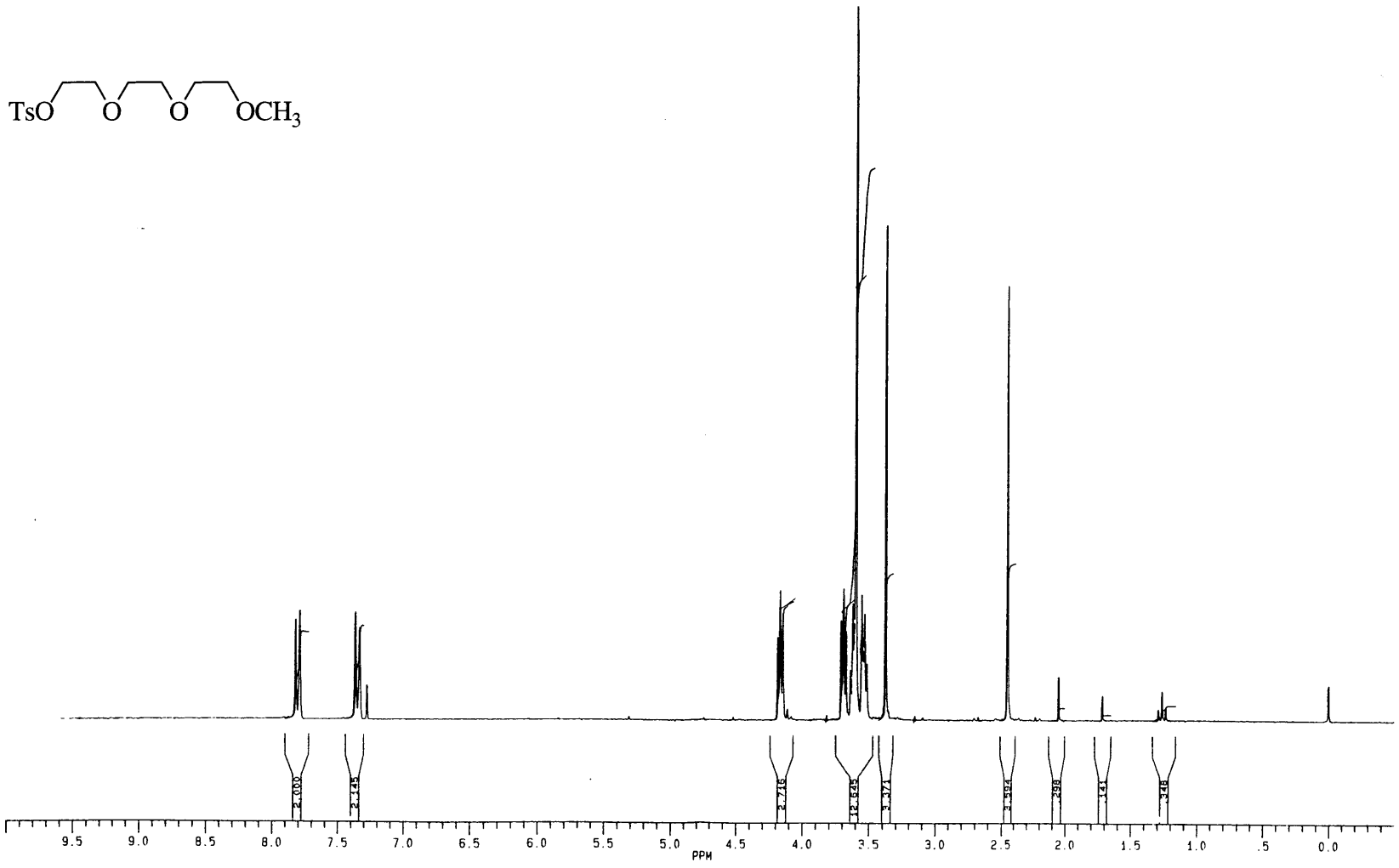

Figure A1.38. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **29**.

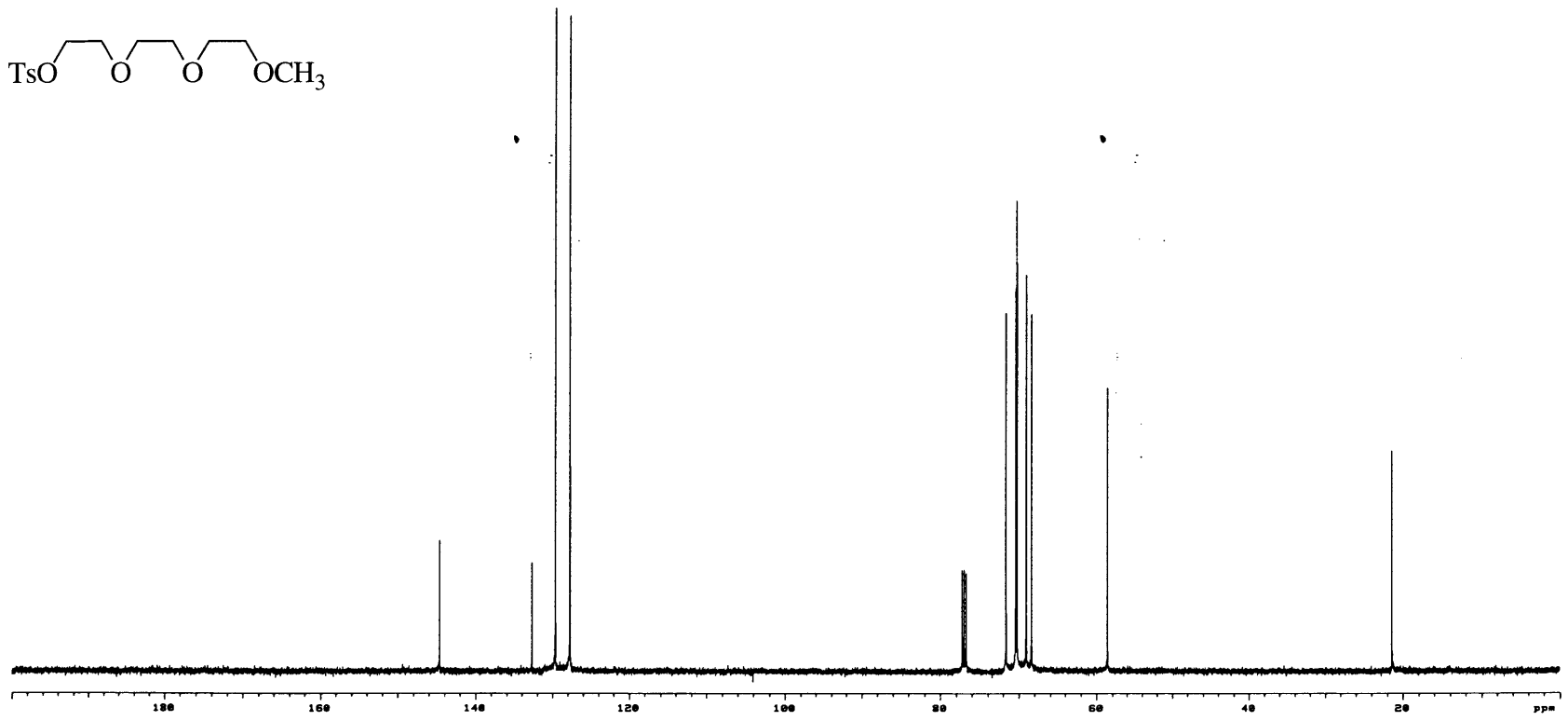

Figure A1.39. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **29**.

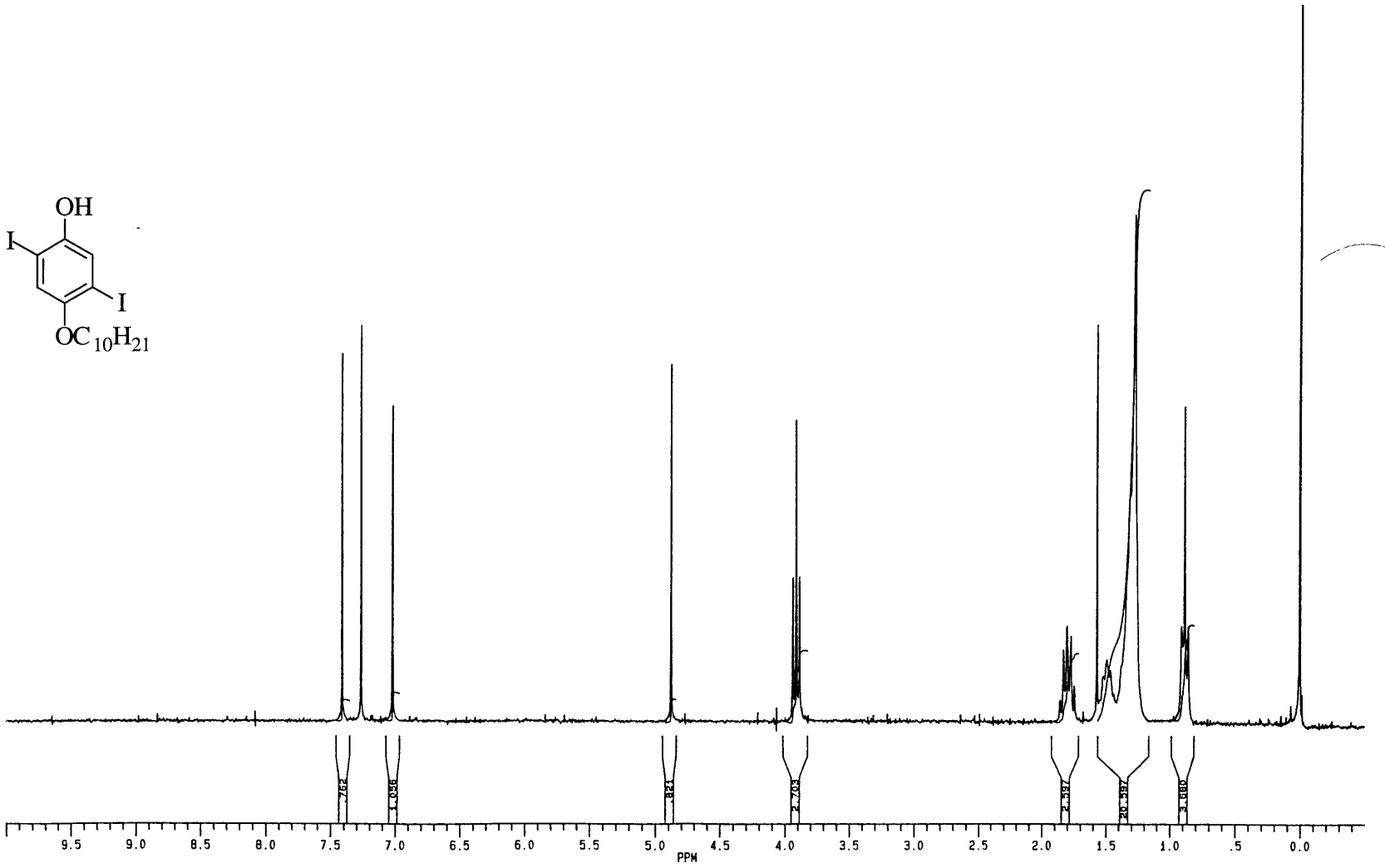

Figure A1.40. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **30**.

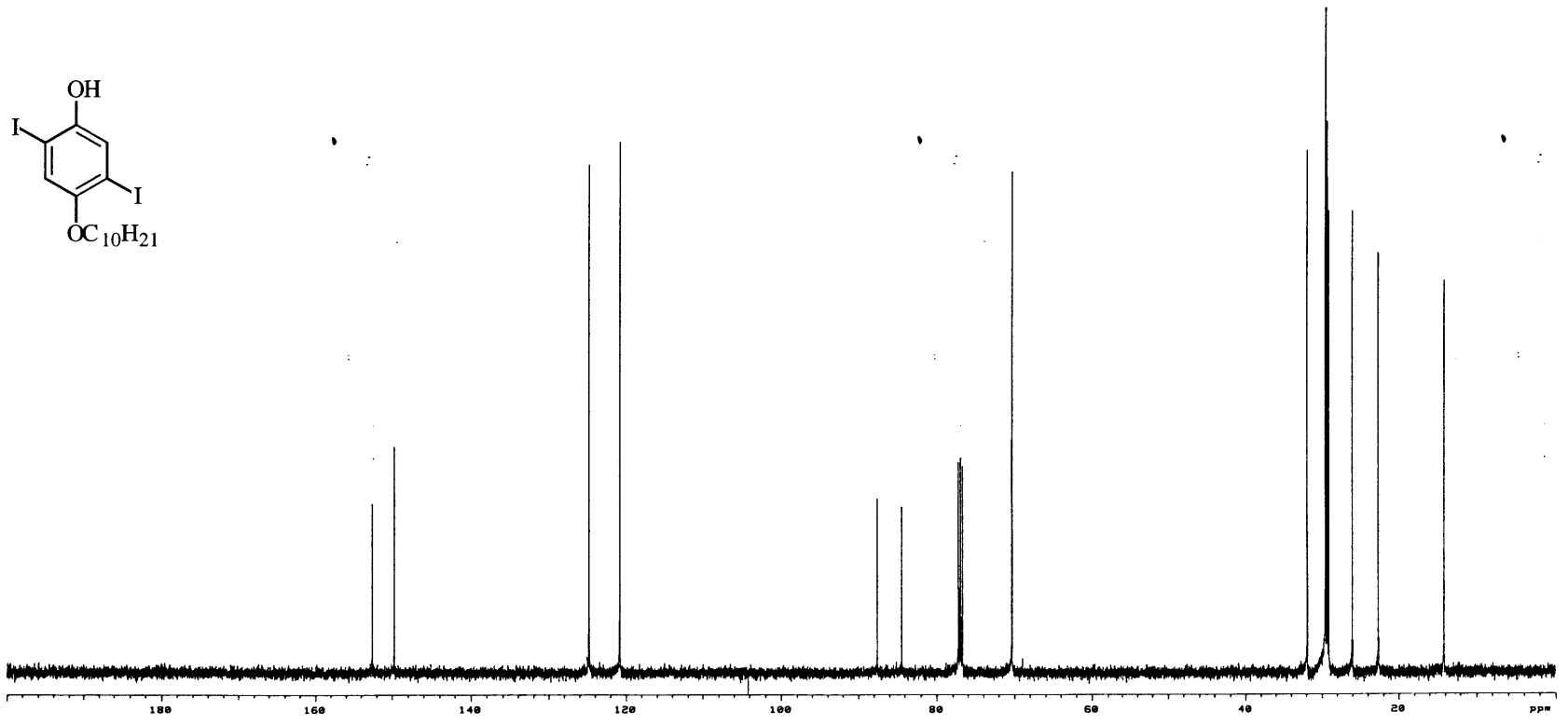

Figure A1.41. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **30**.

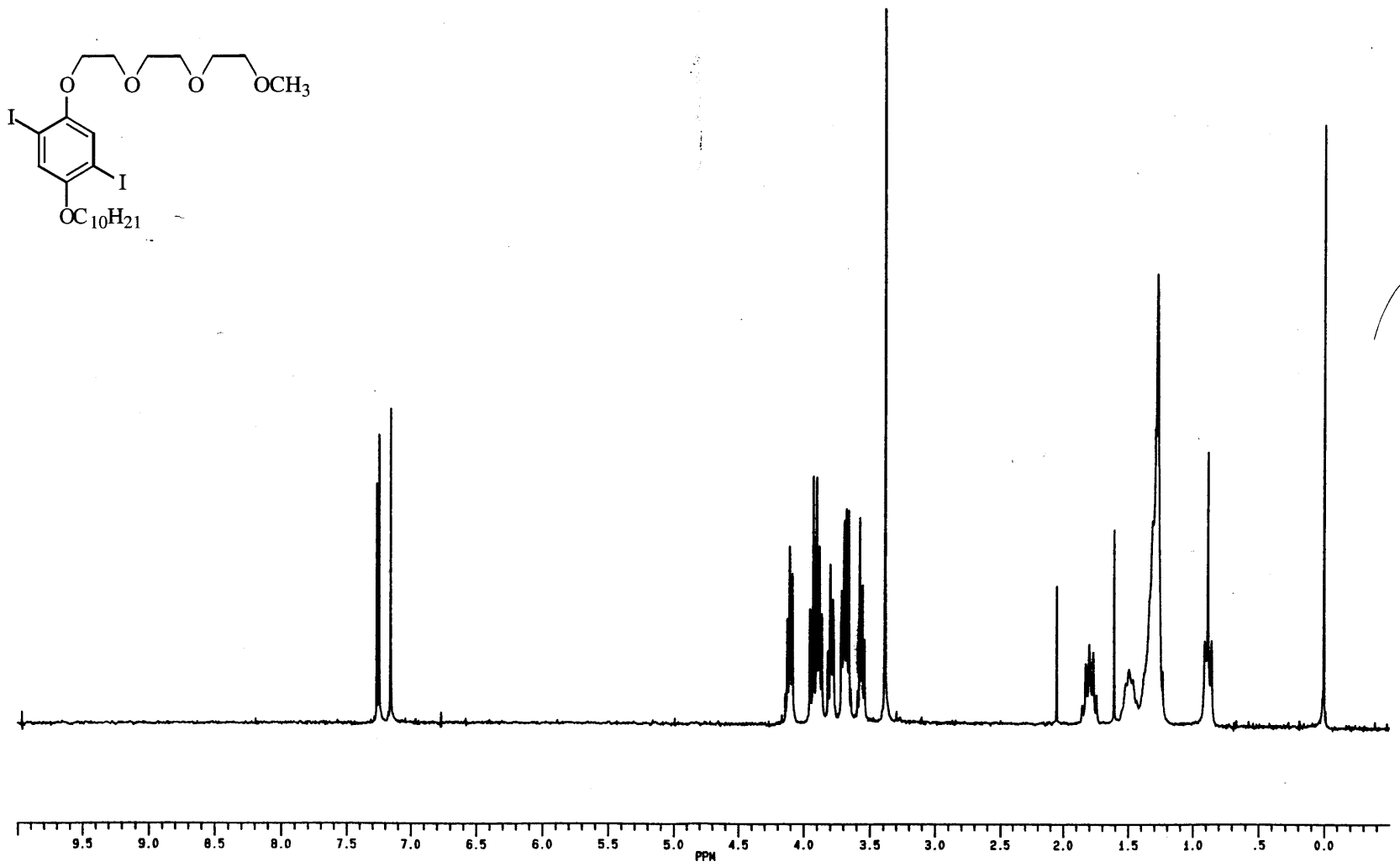

Figure A1.42. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **31**.

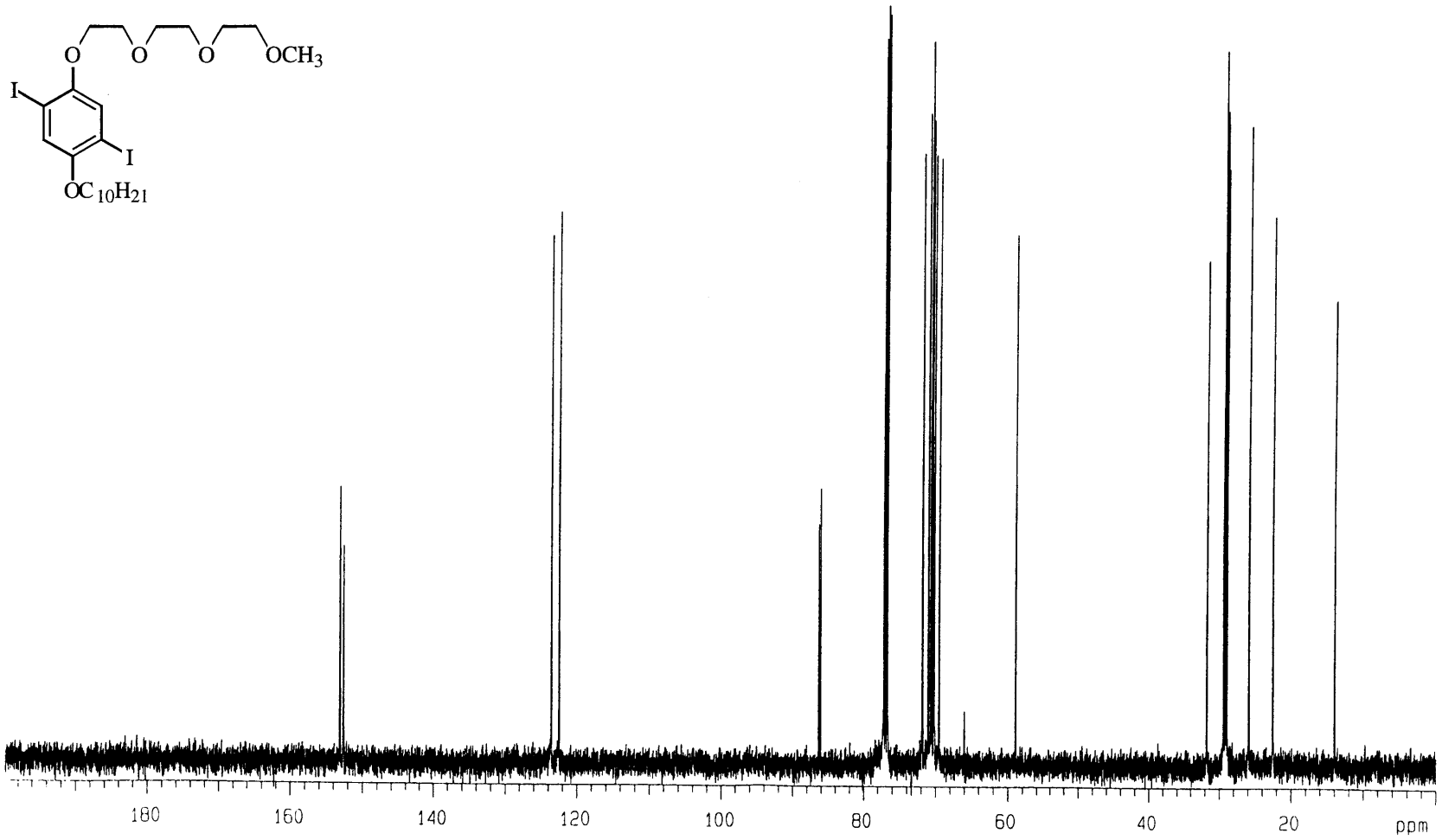

Figure A1.43. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **31**.

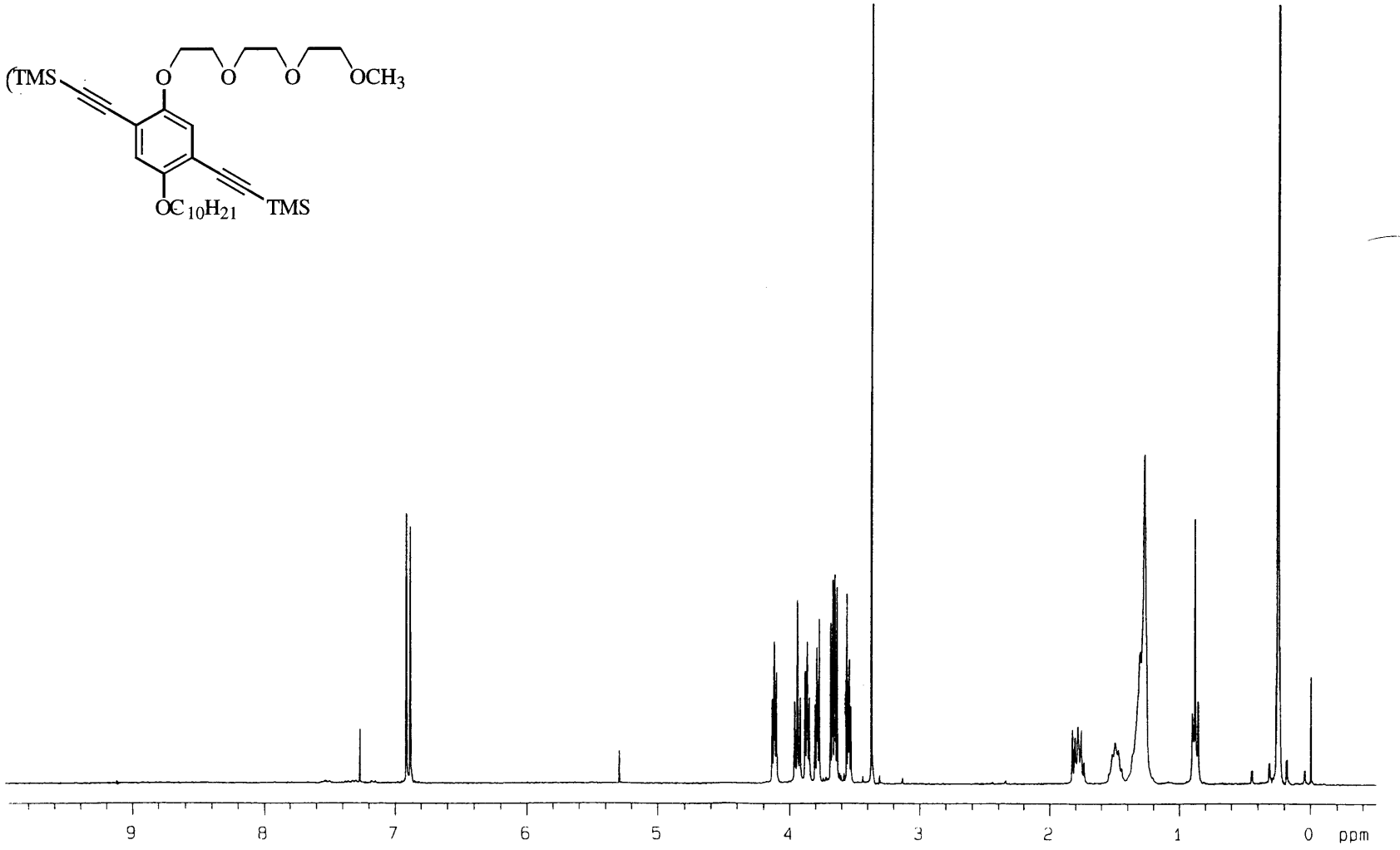

Figure A1.44. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **32**.

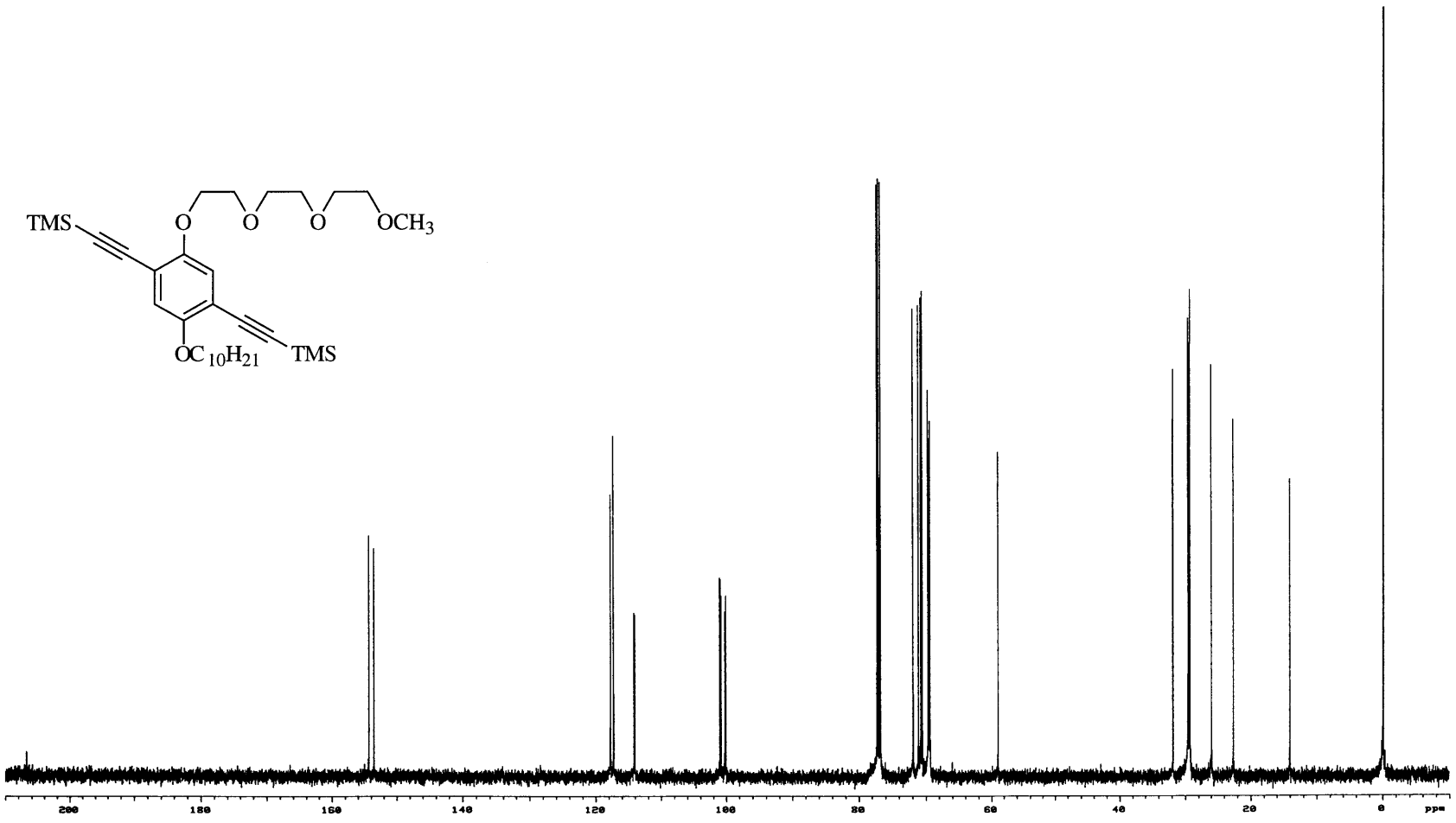

Figure A1.45. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **32**.

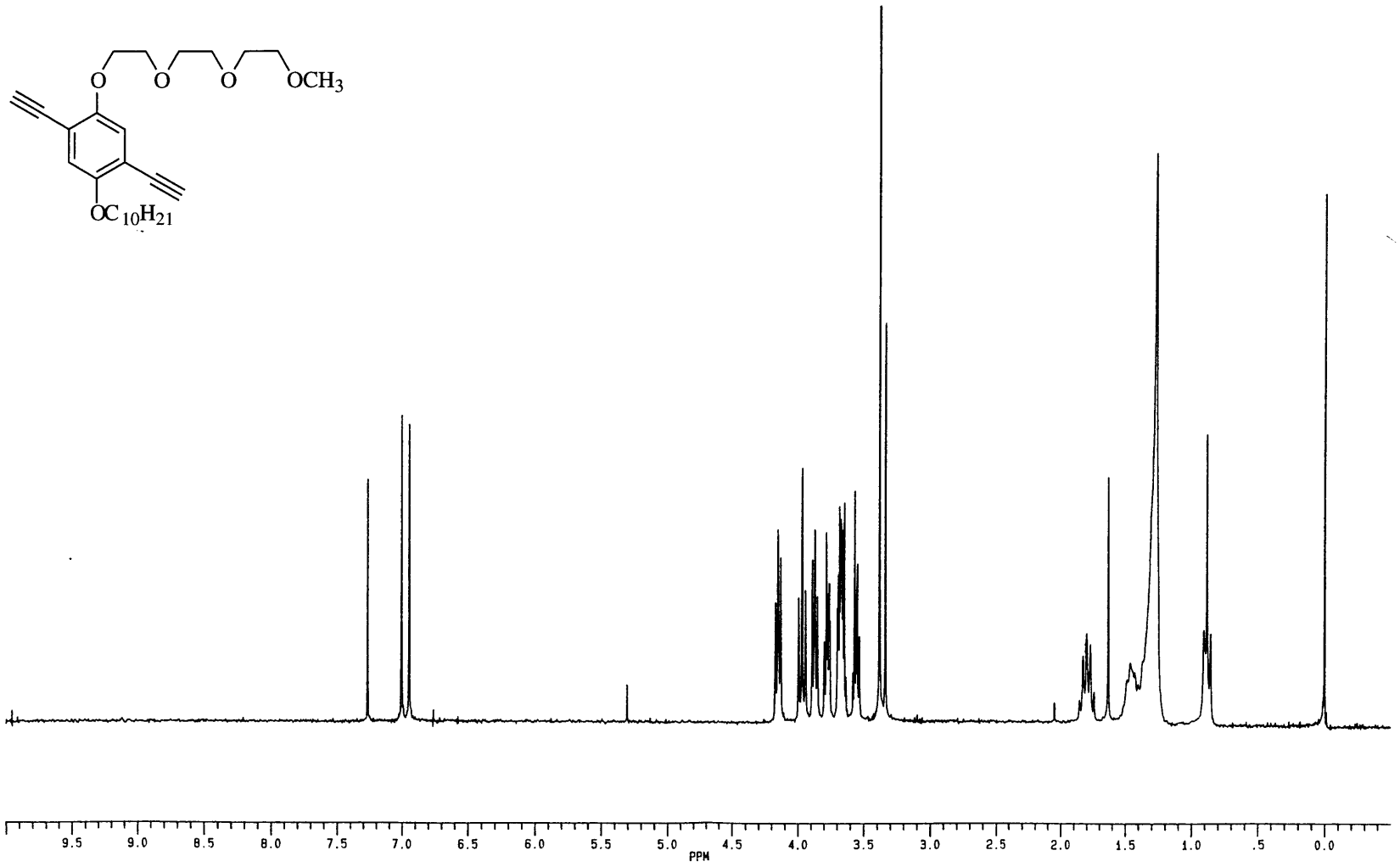

Figure A1.46. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **33**.

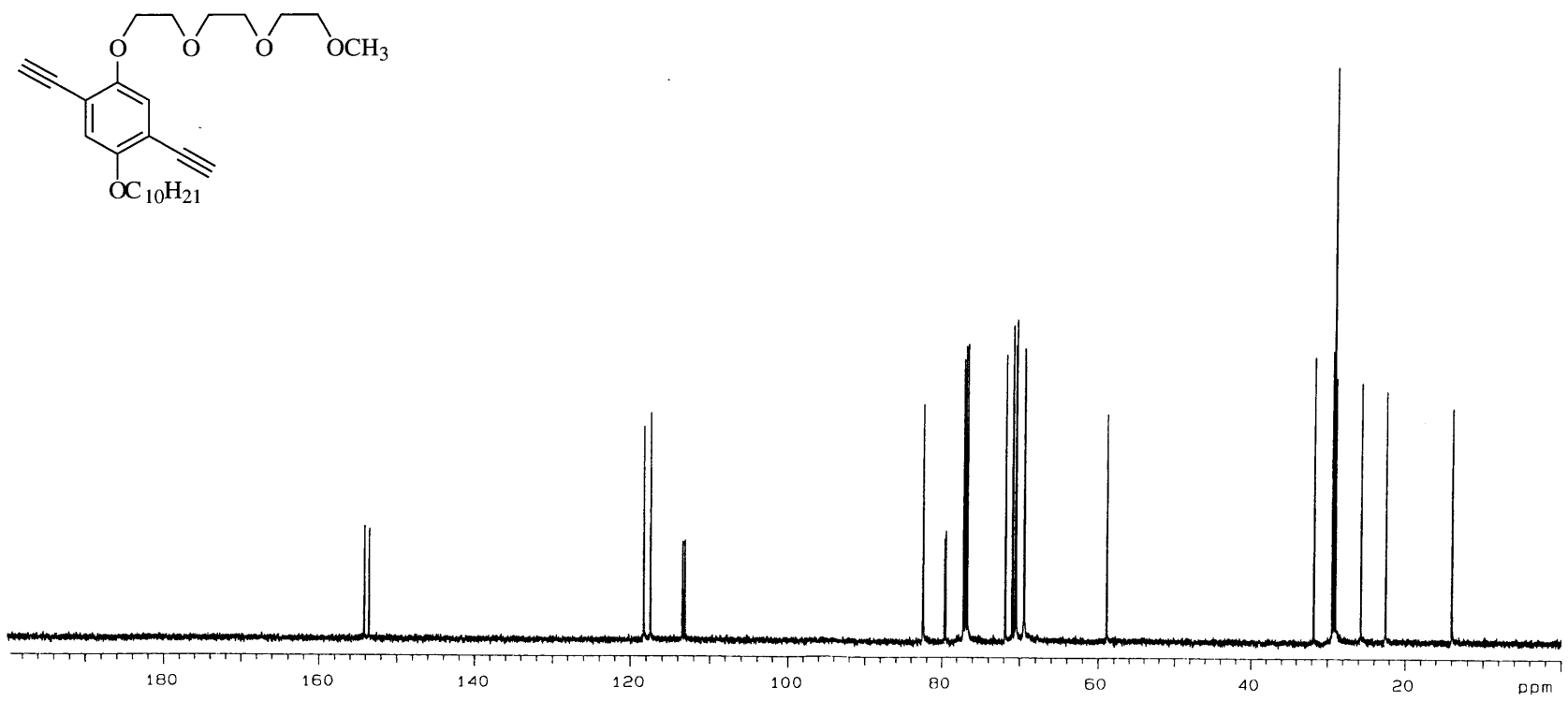

Figure A1.47. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **33**.

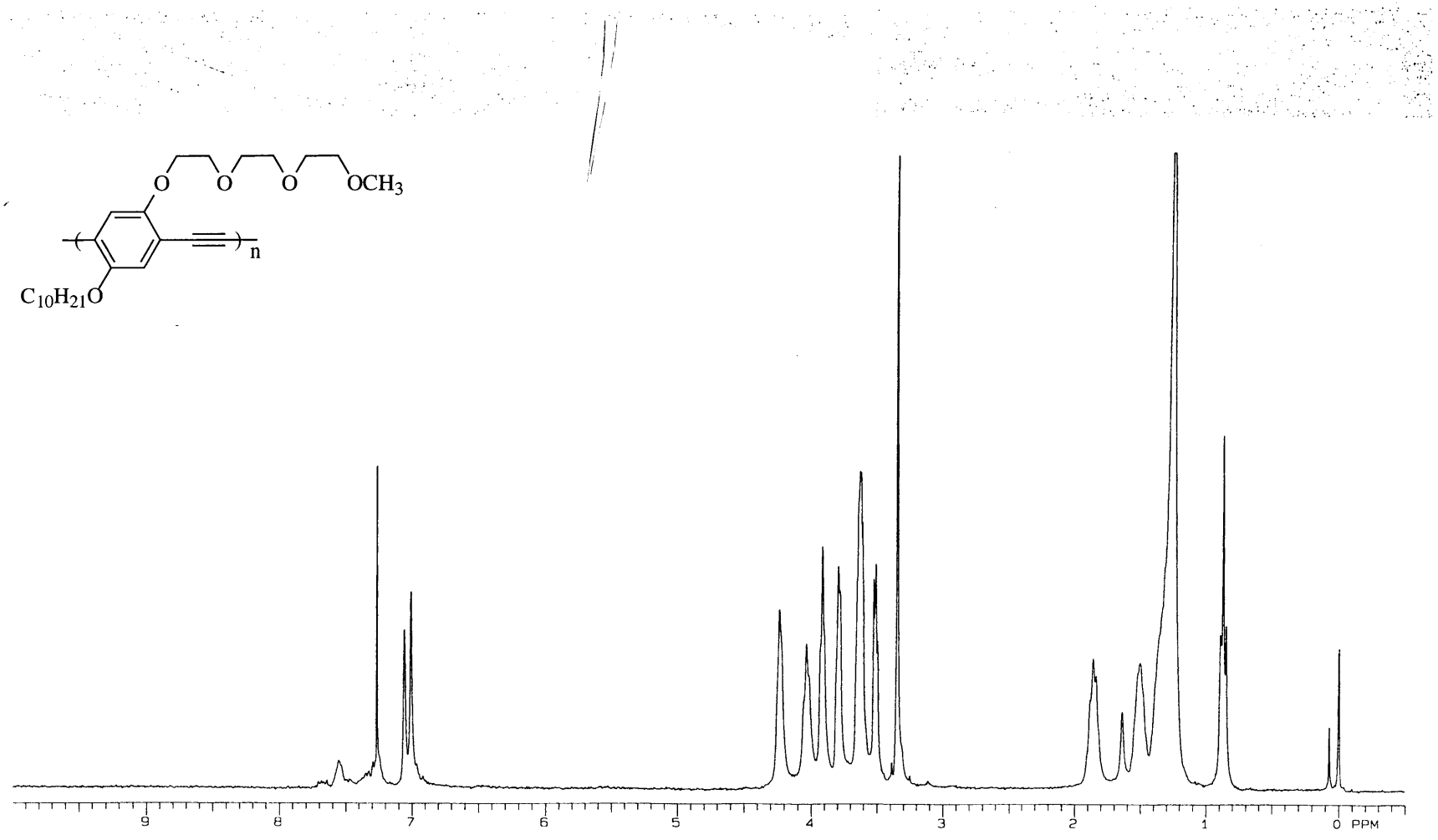

Figure A1.48. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **34**.

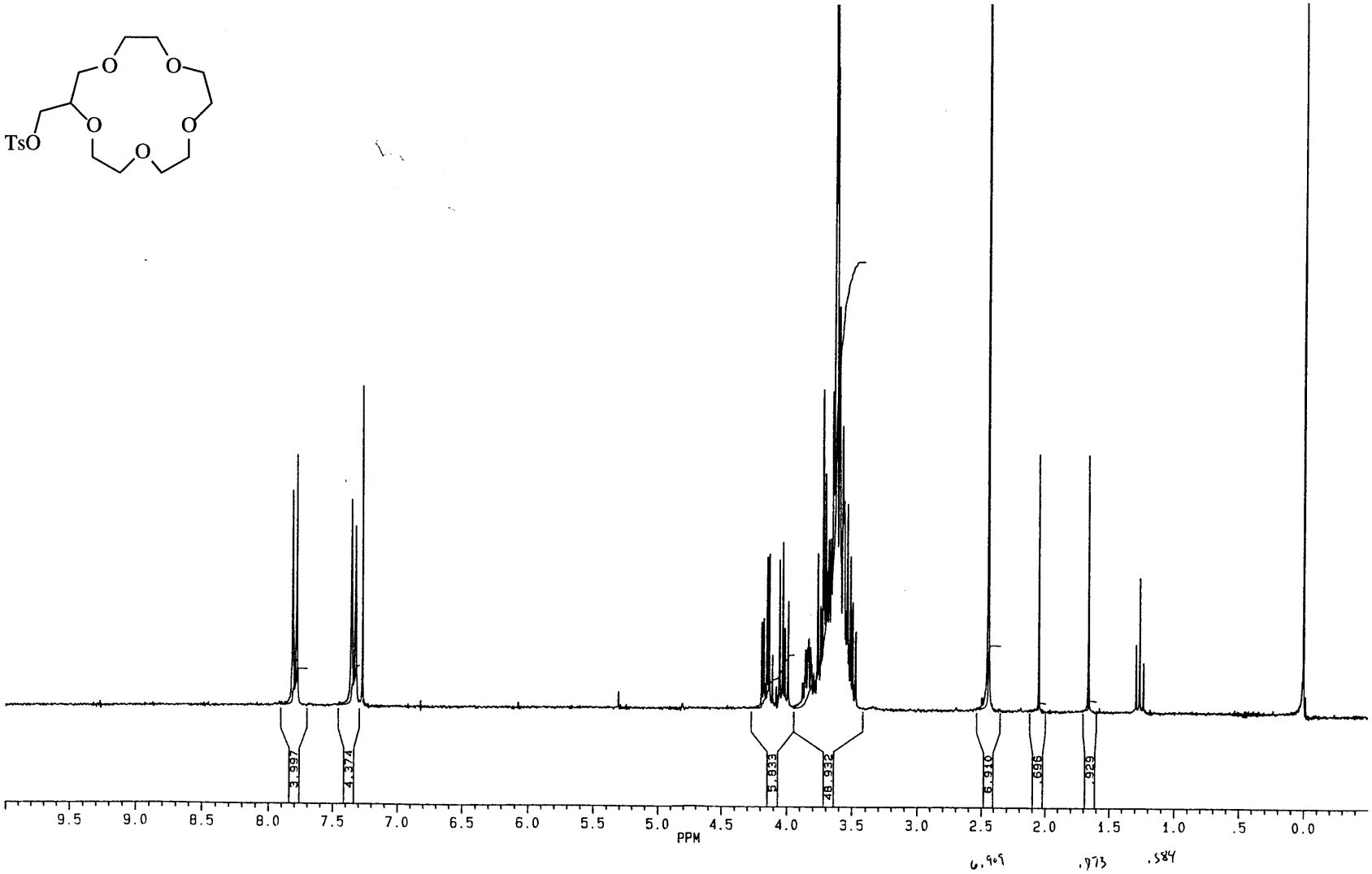

Figure A1.49. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **36**.

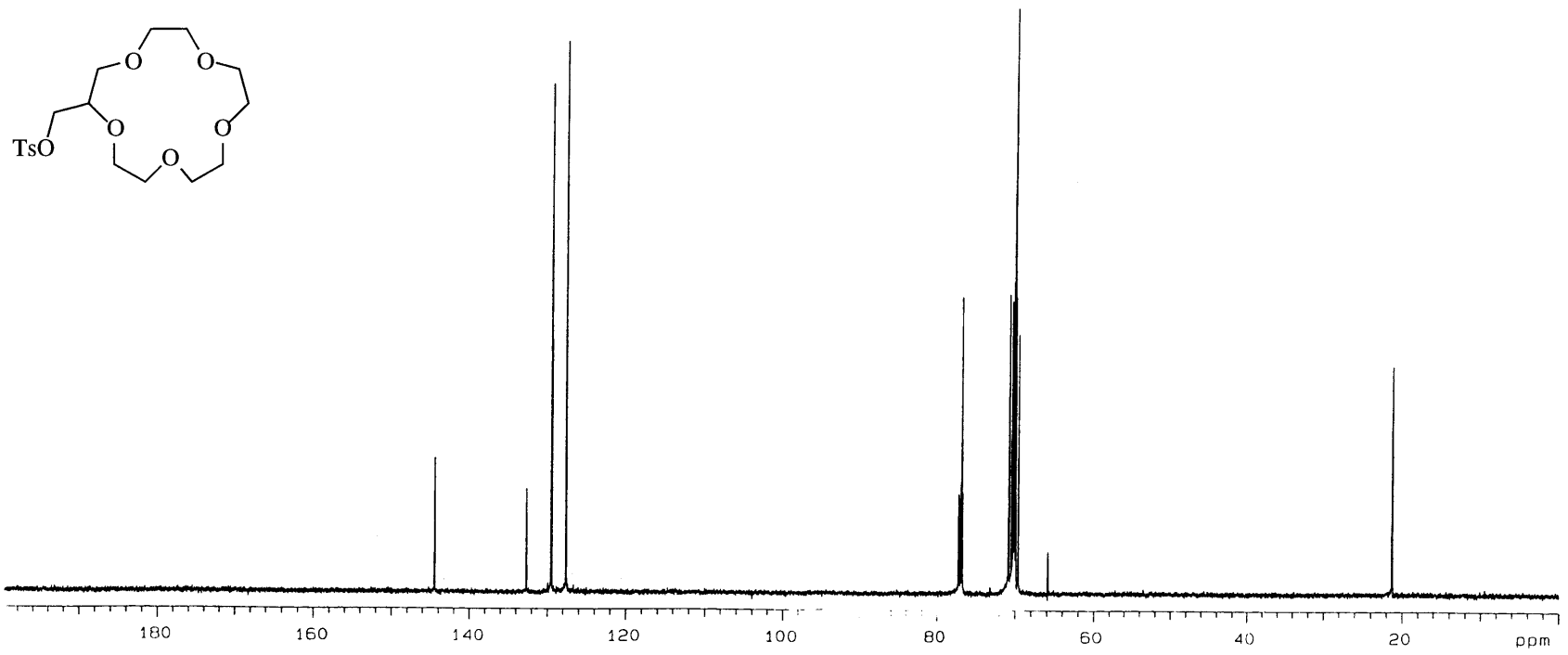

Figure A1.50. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **36**.

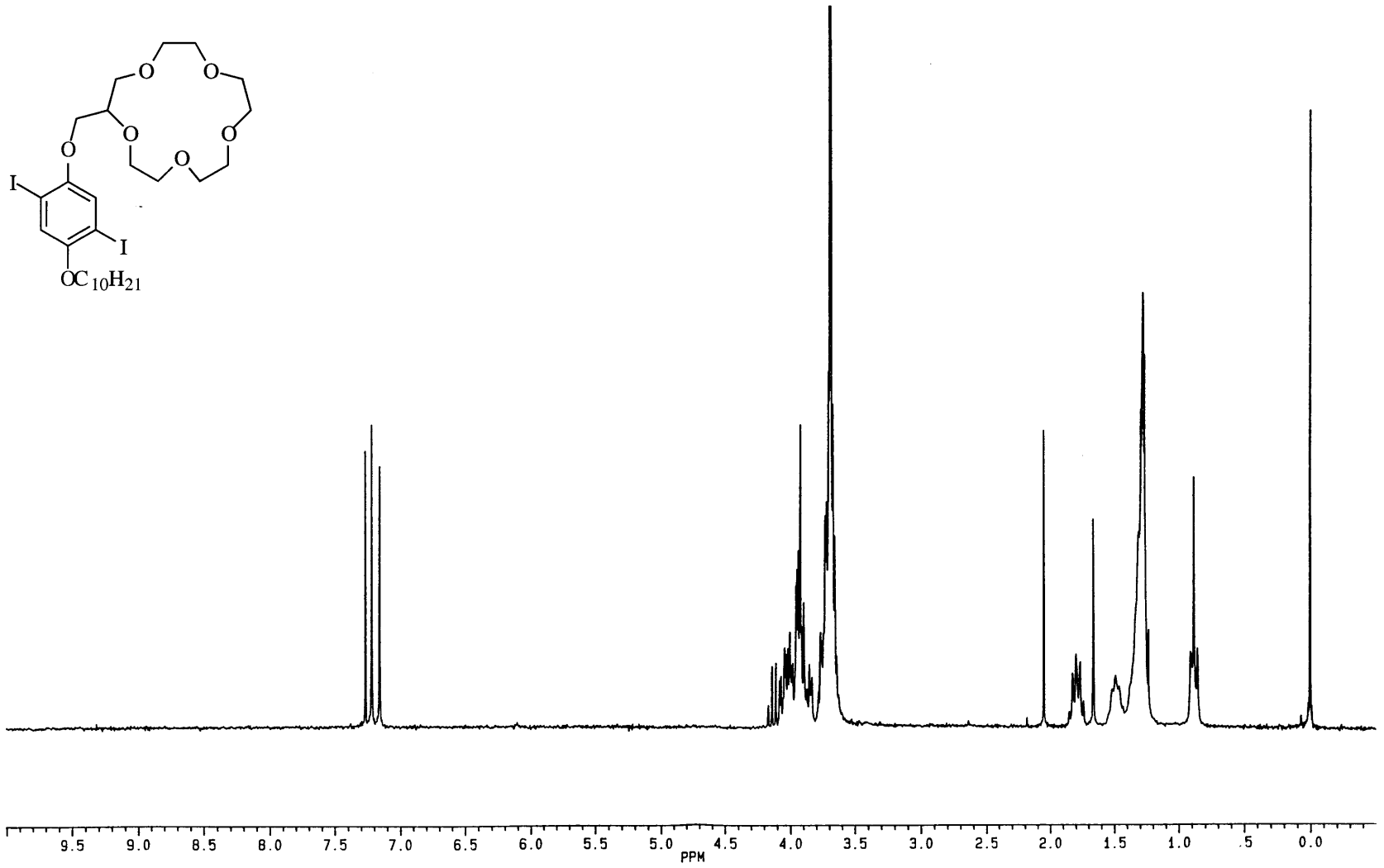

Figure A1.51. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **37**.

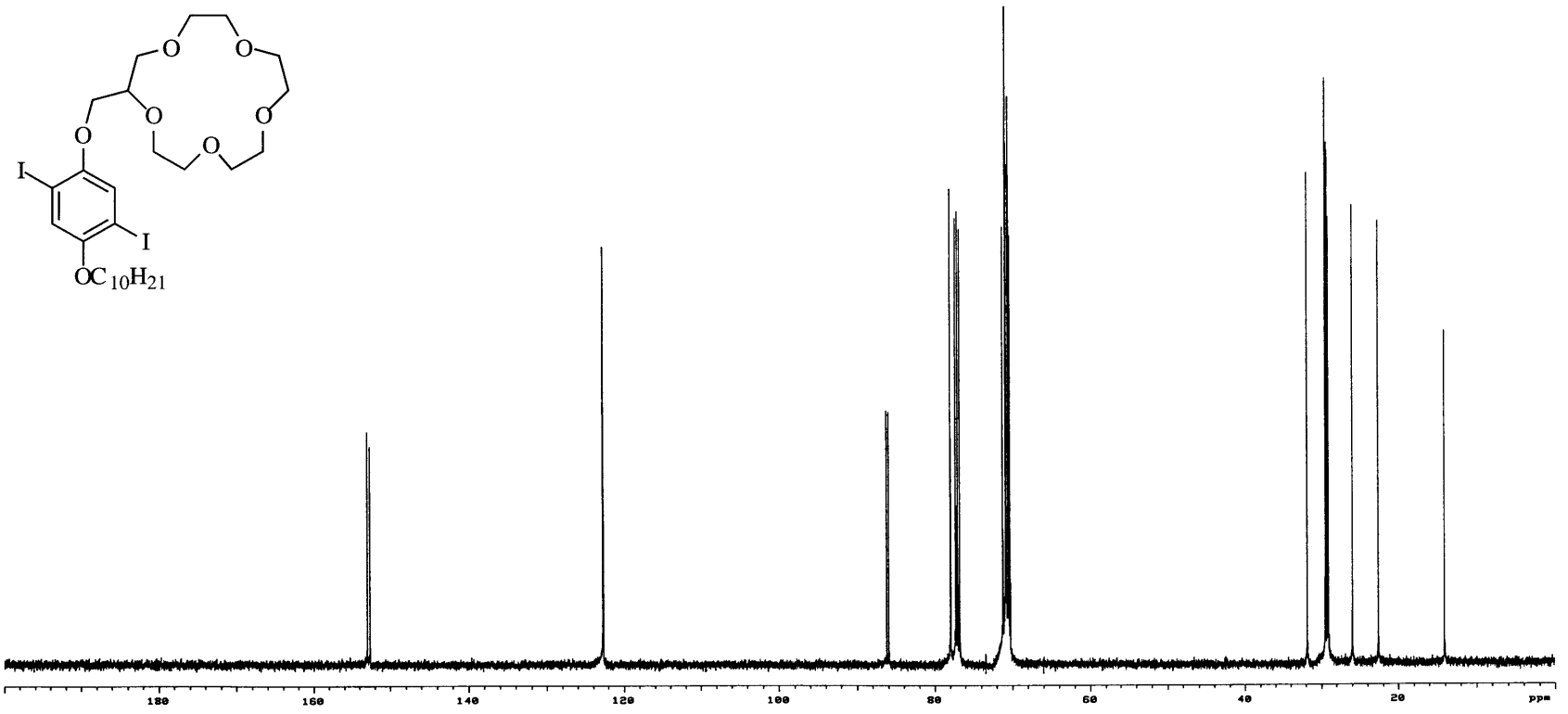

Figure A1.52. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **37**.

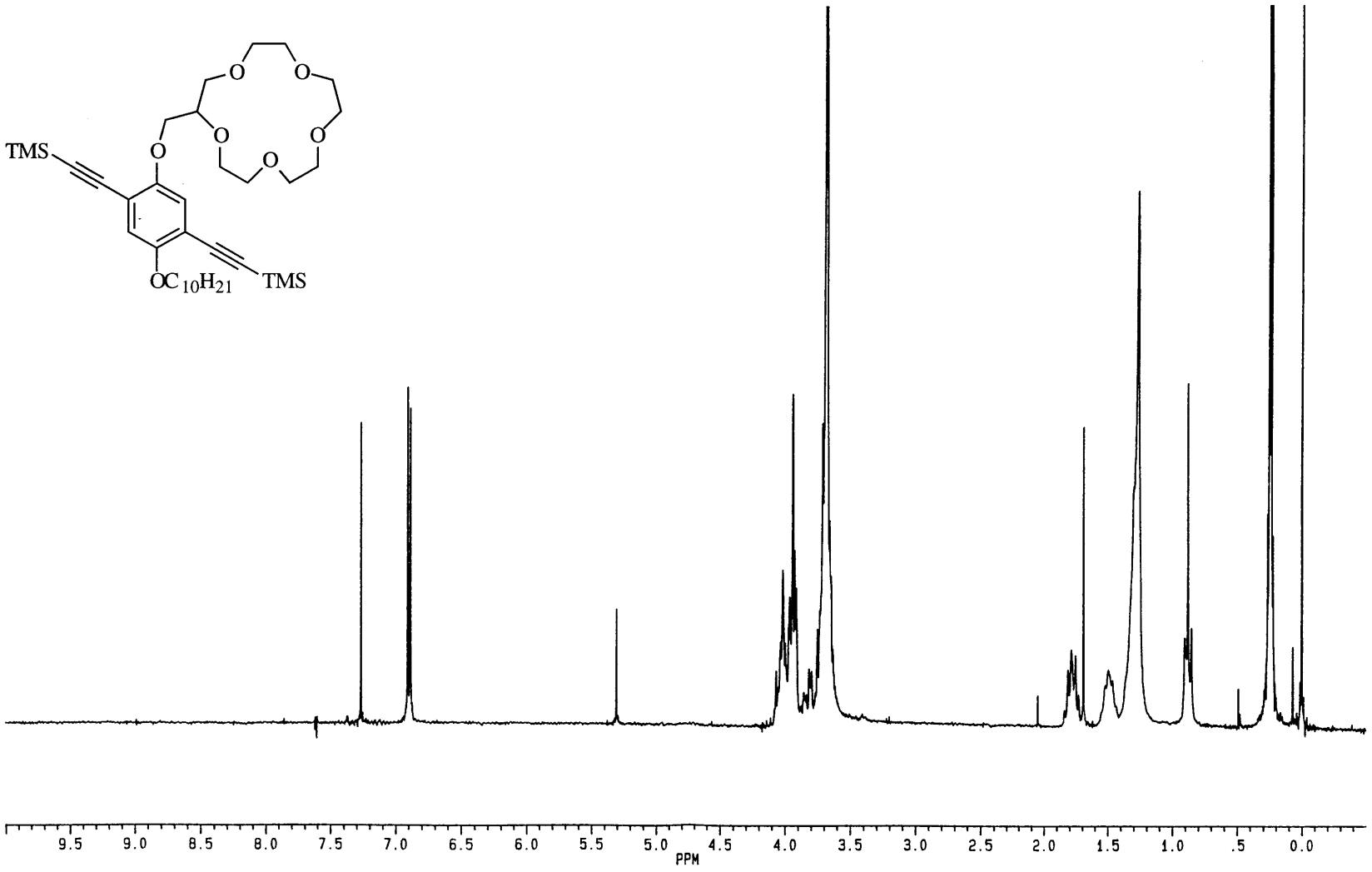

Figure A1.53. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **38**.

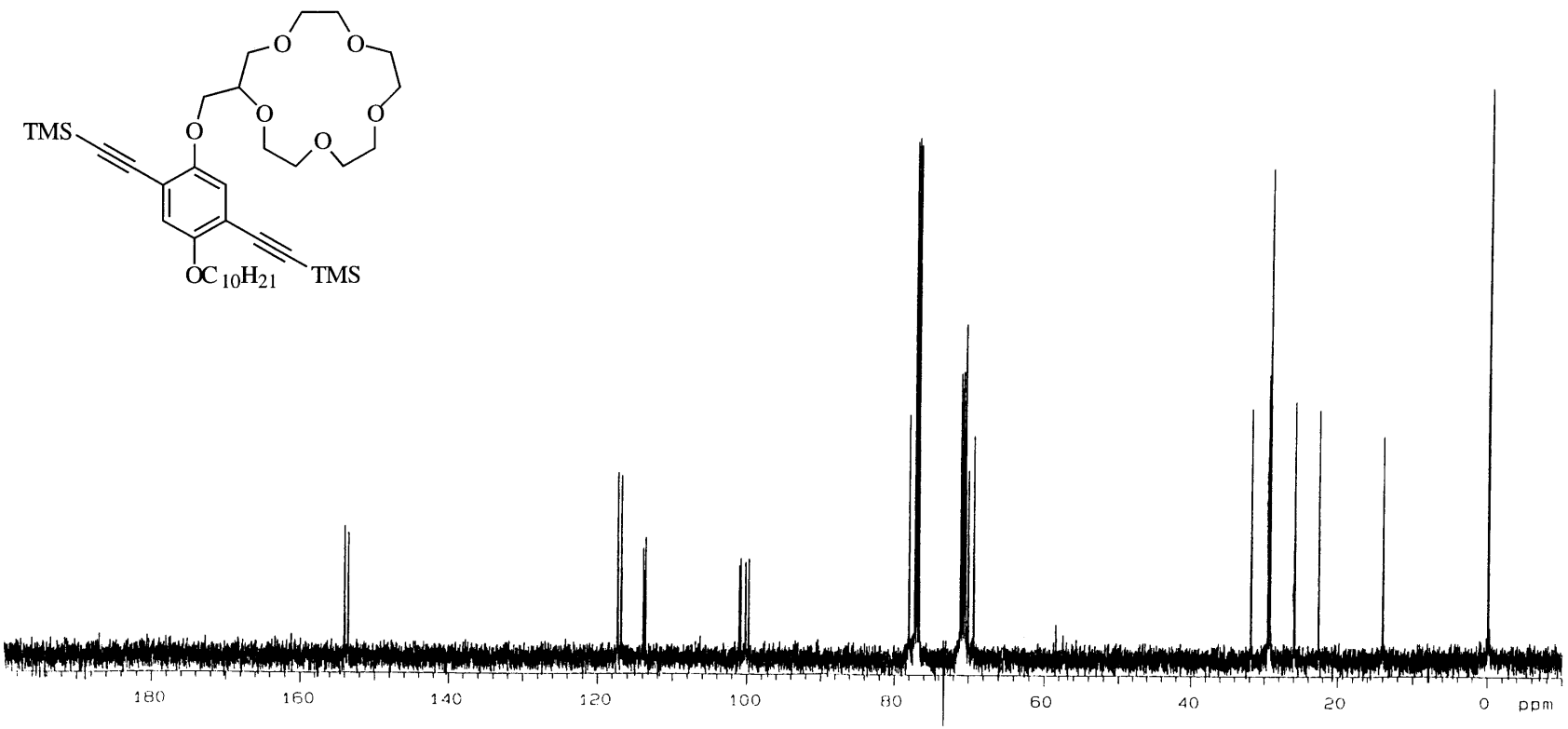

Figure A1.54. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **38**.

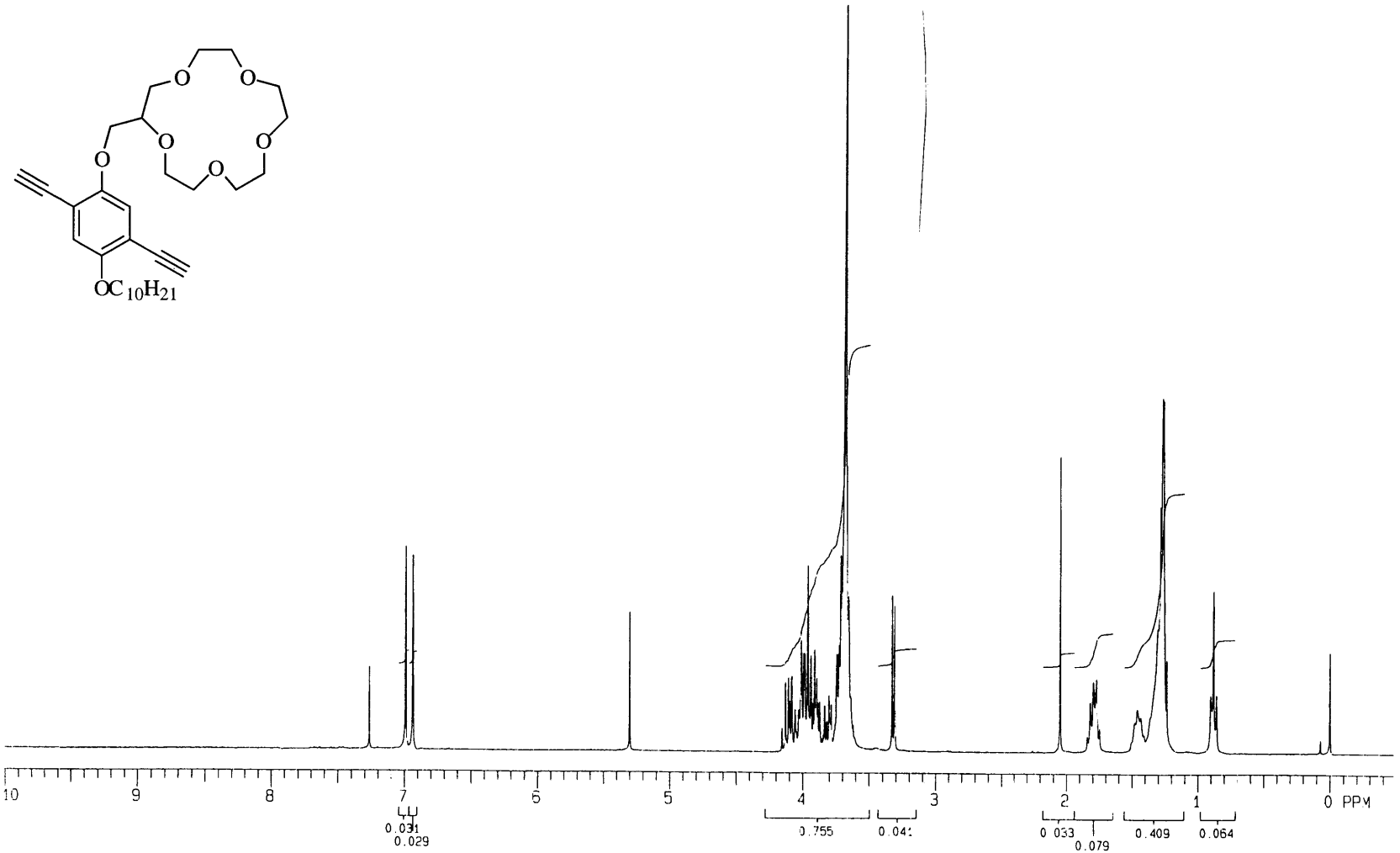

Figure A1.55. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **39**.

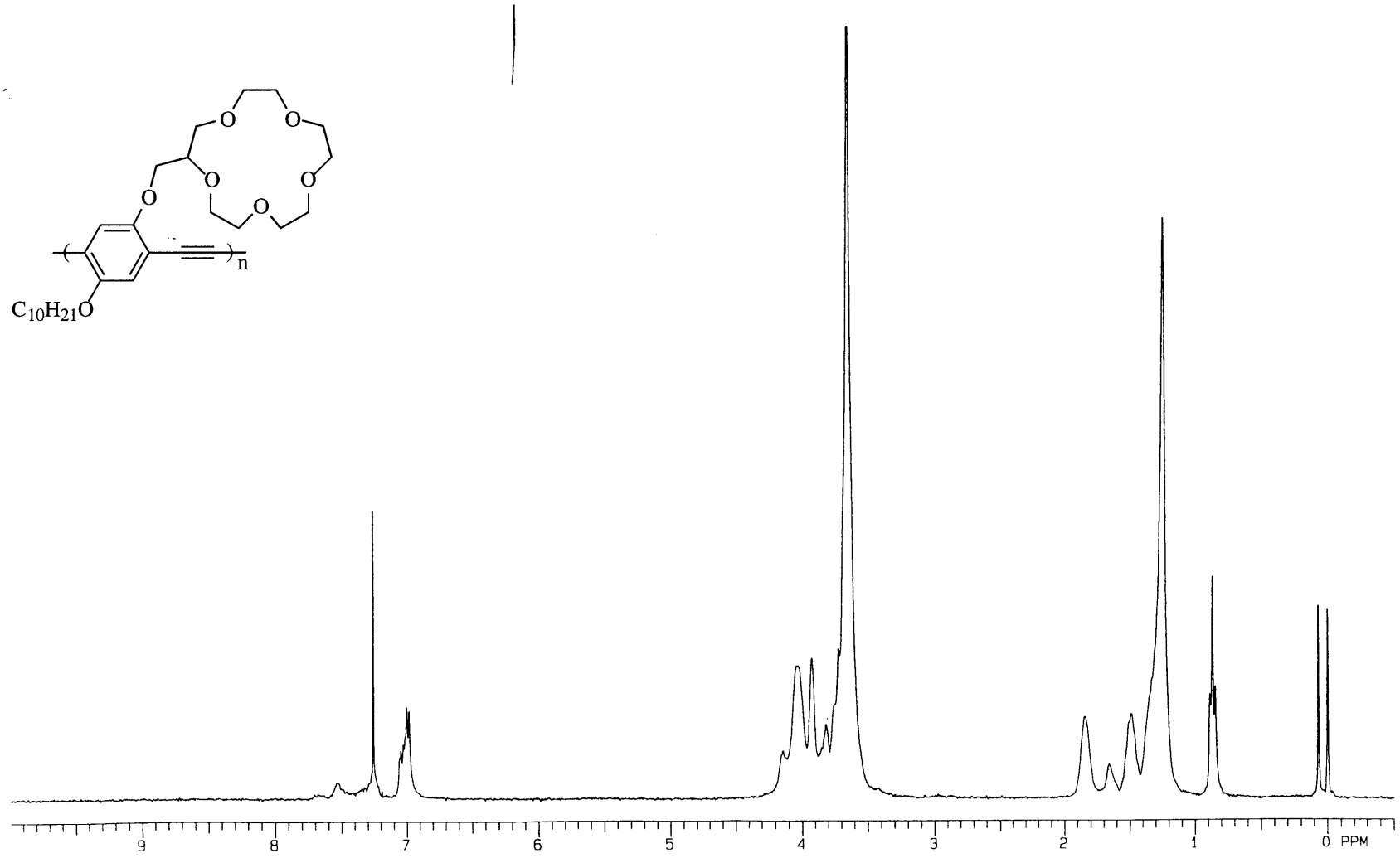

Figure A1.56. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **40**.

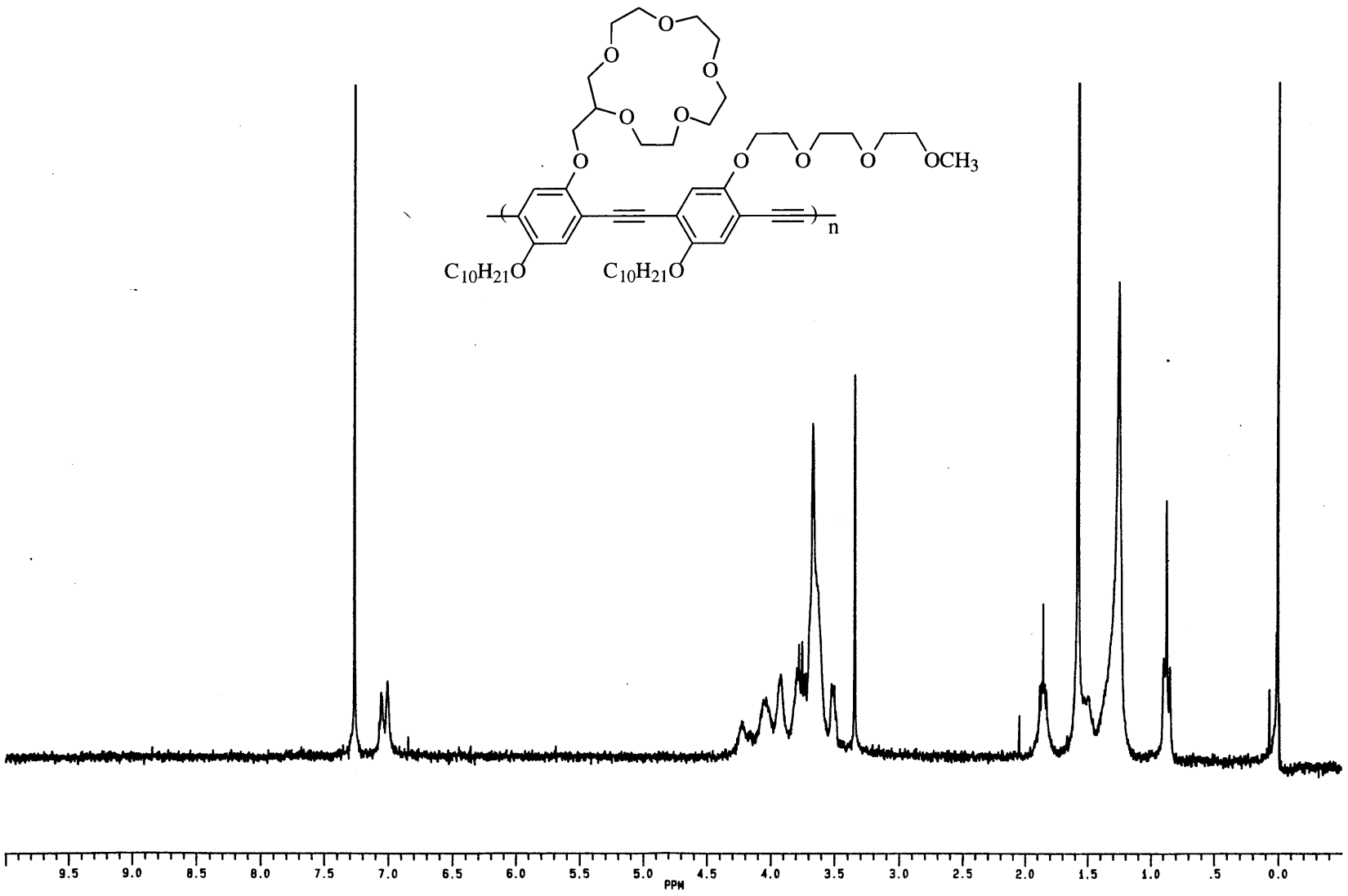

Figure A1.57. ^{1}H NMR spectrum (250 MHz, $CDCl_3$) of compound **41**.

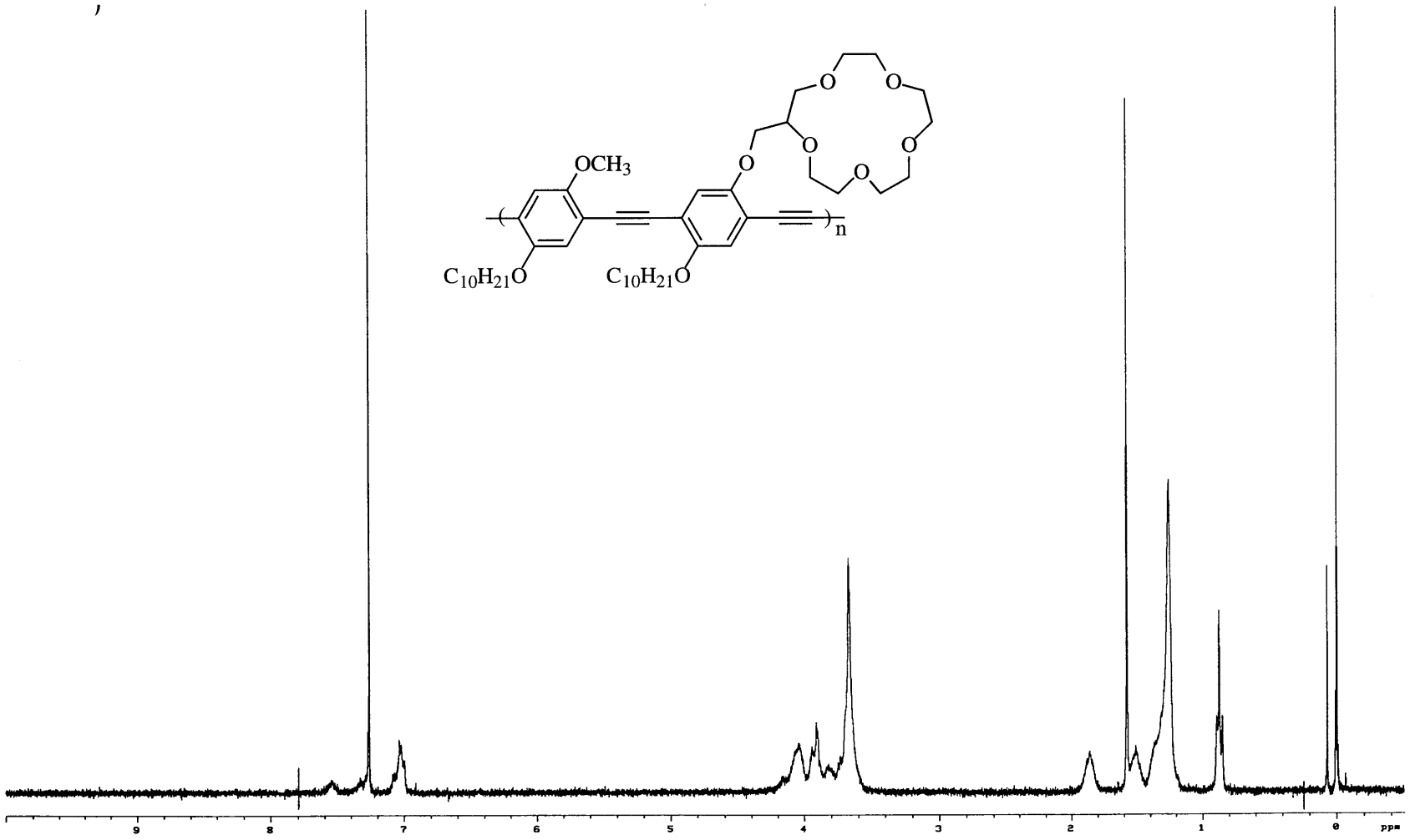

Figure A1.58. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **42**.