The Synthesis and Polymerization Behavior of Polyynes

A Dissertation Presented

by

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to

The Graduate School

in Partial Fulfillment of the

Requirements

for the Degree of

Doctor of Philosophy

in

Chemistry

Stony Brook University

August 2012

Stony Brook University

The Graduate School

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Abstract of the Dissertation

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Polyynes are 1-dimensional rods composed of sp-hybridized carbon atoms, which have attracted much interest due to their electronic, optical, and physical properties. These carbon oligomers can serve as possible precursors to graphitic ribbons, as subjecting aggregates to heat and/or irradiation can lead to topochemical polymerization. Furthermore, polyynes can serve as models for understanding conjugation, and can be used to predict the properties of carbyne, the linear allotrope of carbon. In this work, the synthesis, characterization, and polymerization behavior of polyynes with various end groups have been thoroughly explored. An iterative synthetic strategy was developed to prepare tetraynes, pentaynes, hexaynes, and heptaynes, via a series of iodination and Stille coupling reactions. The advantage of this route over existing methods is that the required starting materials are simple, easily accessible, and relatively stable. This method is particularly effective for accessing polyynes with an odd number of carbon-carbon triple bonds, and has allowed for the preparation of the novel iodine-capped pentayne, diiododecapentayne. The topochemical polymerization of diiodohexatriyne was also achieved by applying a host-guest strategy that aligns the monomers in the proper orientation for controlled polymerization via halogen bonding interactions. Bis(nitrile) oxalamide hosts form co-crystals with the guest triyne in a stoichiometric ratio of 1:2, as determined by X-ray diffraction. Raman spectroscopy was used to confirm the polymerization of diiodohexatriyne, as the increased disorder in the crystal made it difficult to elucidate the structure using XRD. In addition, the synthesis of diynes containing nitrile end groups was also pursued, to determine the effects of electron withdrawing groups on polymerization behavior. Dicyanodiacetylene was initially targeted, since the 1,4-topochemical polymerization of this diyne would result in a unique, very electron poor polymer. Although efforts towards dicyanodiacetylene were unsuccessful, a synthetic route towards cyanoiodobutadiyne was developed using modified Cadiot-Chodkiewicz coupling conditions. The topochemical polymerization of this novel push-pull diyne monomer was pursued using both symmetric and asymmetric host molecules bearing oxalamide functionalities.

Table of Contents

List of Figures

List of Schemes

List of Tables

Acknowledgments

I would like to thank my dissertation advisor, Dr. Nancy Goroff, for her guidance, support, and encouragement throughout my graduate research career. She has helped me expand my knowledge and mature as a scientist through my research experience both in and out of the lab. In addition, I would also like to acknowledge the chair and third member of my dissertation committee, Dr. Andreas Mayr and Dr. Kathlyn Parker. Their help and encouragement during my first and third meetings, and suggestions during my research seminars are appreciated. I also thank Dr. Dina Merrer of the Chemistry Department at Barnard College, for taking the time to serve as my outside member for my dissertation committee.

I would also like to express my gratitude to the Goroff group members, both past and present. I thank Christopher Wilhelm and Liang Luo for helping me get started in the group. I also thank the current group members David Connors, Allison Black, Daniel Resch, Xiuzhu Ang, Hongjian Jin, Xianzhi Liu, and Matthew Freitag for their helpful suggestions with experiments and continued moral support throughout my time at Stony Brook. I especially thank Allison Black for her insight on polyyne synthesis, and Daniel Resch for his invaluable help with X-ray crystallography. I also thank Matthew Freitag for his assistance with determining the ideal conditions for growing co-crystals as discussed in Chapter 4 of this dissertation.

In addition, I would like to acknowledge all who have contributed to this work through collaborative efforts. I must thank Prof. Gary Halada and Christopher Young for helping me with Raman Spectroscopy, Prof. Clare P. Grey, Prof. Brian Phillips, and Andrew Ilott for helping in MAS NMR experiments, Dr. James Quinn for help with scanning electron microscopy, Prof. Peter Khalifah and Andrew Malingowski for help with obtaining XRD data, and Dr. Charles Iden for help with mass spectrometry. I also thank Professors Joseph Lauher and Frank Fowler for helpful discussions.

I must thank Dr. James Marecek for his patience and assistance with NMR experiments. He has been so flexible with his schedule and always made himself available if I needed help. I also thank Dr. Francis Picart for his help with setting up accounts on the NMR instruments. In addition, I thank Katherine Hughes for her help with administrative matters, the entire Main Office staff of the Chemistry Department, and the NSF and GAANN for funding.

This dissertation is dedicated to my parents, my brother, and my husband. This would not have been possible without your continuous love, support, and encouragement. I am blessed to have you in my life, and I greatly appreciate all that you have done for me.

Publications

DeCicco, R. C.; Black, A.; Li, L.; Goroff, N.S. An iterative method towards the synthesis of symmetric polyynes. *Eur. J. Org. Chem.*, published online July 2012.

Chapter 1: Introduction

1.1 Conjugated Organic Polymers

Conjugated organic polymers have attracted much interest due to their potential applications in electronic and optical devices. The highly delocalized π system that results from overlapping p_z-orbitals of sp^2-hybridized carbon atoms along the polymer chain (Figure 1.1) allows these materials to behave as semiconductors.[1, 2] The π- π* transitions usually correspond to an energy gap ranging from 1.5 to 3 eV, indicating that light absorption or emission takes place in the visible range.[2] This small gap renders conjugated organic polymers useful in the fabrication of organic light-emitting diodes (OLEDs),[3, 4] thin-film transistors (OTFTs),[5, 6] and solar cells.[7, 8] Some common examples of conjugated organic polymers that have been employed for such devices are shown in Figure 1.2 below.[1, 3, 9]

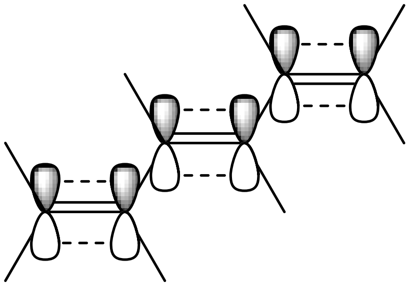
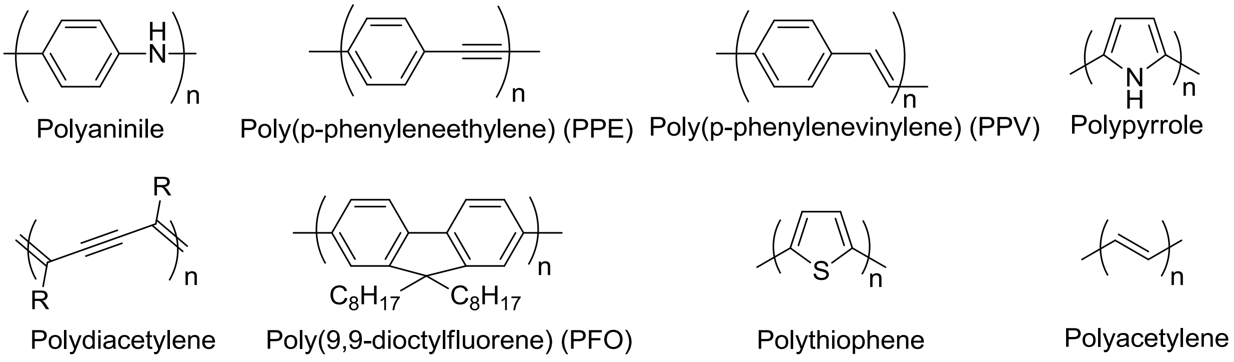


Figure 1.1 Overlapping p_z orbitals from adjacent carbons in polyacetylene[1]



Polyaninile

Poly(p-phenyleneethylene) (PPE)

Poly(p-phenylenevinylene) (PPV)

Polypyrrole

Polydiacetylene

Poly(9,9-dioctylfluorene) (PFO)

Polythiophene

Polyacetylene

Figure 1.2 Examples of conjugated organic polymers[1, 3, 9]

To serve in such applications, these polymers must demonstrate some degree of conductivity (σ), which is determined by the number of charge carriers (n) and their mobility (μ) and are related by the equation:[10]

$$\sigma = n \mu e$$

where e represents the charge of an electron. The number of charge carriers (electrons and/or holes) can be increased through doping, while the increased delocalization of π conjugated polymers improves charge carrier mobility.[10] Doping of organic materials differs from inorganics in that the former can occur unintentionally by contaminants, such as oxygen, that are present during the synthesis or processing procedures.[2] Therefore, the process of controlled doping of organic semiconductors needs to be explored.[2, 11]

Improving the conductivity of conjugated organic polymers through doping was first demonstrated by Shirakawa, MacDiarmid, and Heeger's work with polyacetylene (Figure 1.3).[12] Pure polyacetylene showed low electrical conductivity (σ); however when exposed to chlorine, bromine, iodine, or arsenic pentafluoride (AsF_5), the conductivity improved drastically.[12] This pioneering effort in doping conjugated organic polymers earned Shirakawa, MacDiarmid, and Heeger the Nobel Prize in Chemistry in 2000.

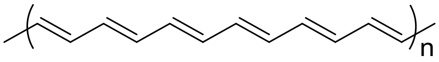


Figure 1.3 Polyacetylene

1.2 Polyynes

Polyynes are 1-dimensional rods composed of sp-hybridized carbon atoms (Figure 1.4). The electronic, optical, and physical properties of these carbon oligomers have made polyynes the subject of much research.[13] Of particular interest are the third-order nonlinear optical properties. Theoretical and experimental studies indicate that sp-hybridized carbon chains have large multiphoton absorption cross-sections, suggesting potential applications in photonics, medical technology, analytical chemistry, and biology.[13-15]

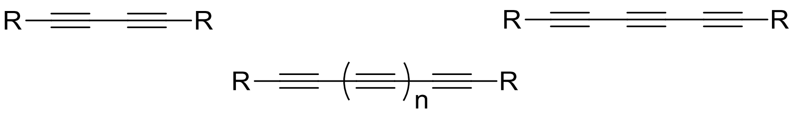


Figure 1.4 Structure of polyynes

While lack of side chains decreases stability and solubility, the simple structure of polyynes makes them useful models for studying conjugation.[16] Since polyynes are cylindrically symmetric, conjugation along the polyyne rod is not disrupted by bond rotation. This characteristic distinguishes polyynes from other conjugated oligomers, suggesting they could serve as molecular wires since electron transport through the backbone is not interrupted.[17] Polyynes can also be used to predict the properties of carbyne, the linear allotrope of carbon (Figure 1.5).[13]

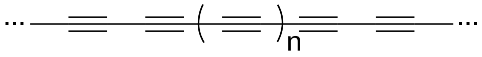


Figure 1.5 Carbyne

Furthermore, these oligomers can serve as possible precursors to polydiacetylenes, nanotubes, fullerenes, graphitic materials, and other carbon-rich compounds.[18-20] Figure 1.6 illustrates the proposed formation of graphitic ribbons from polyynes, which may be achieved by subjecting aggregates to heat and/or irradiation to promote a topochemical polymerization.[21]

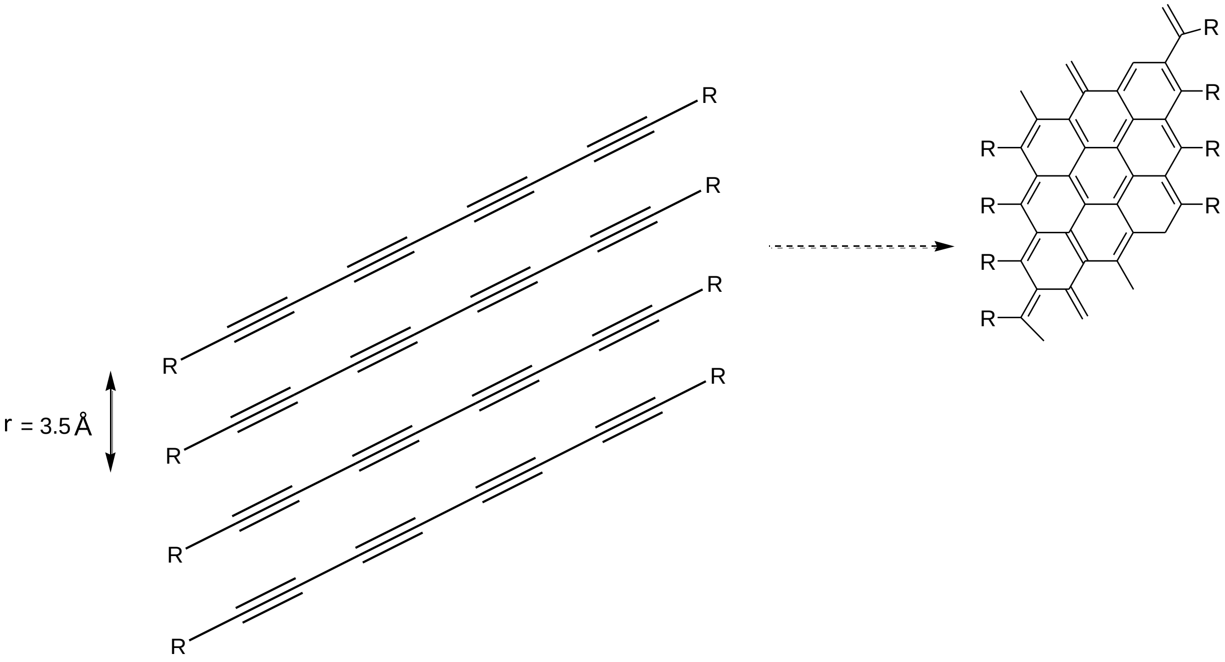


Figure 1.6 Polyynes as precursors to graphitic ribbon

Polyynes are also found in a number of natural products with biological activity, indicating that the applications of these compounds span beyond the scope of materials science.[22-25] Figure 1.7 illustrates polyyne natural products derived from *O. amentacea*, which have demonstrated cytotoxic activity.[24]

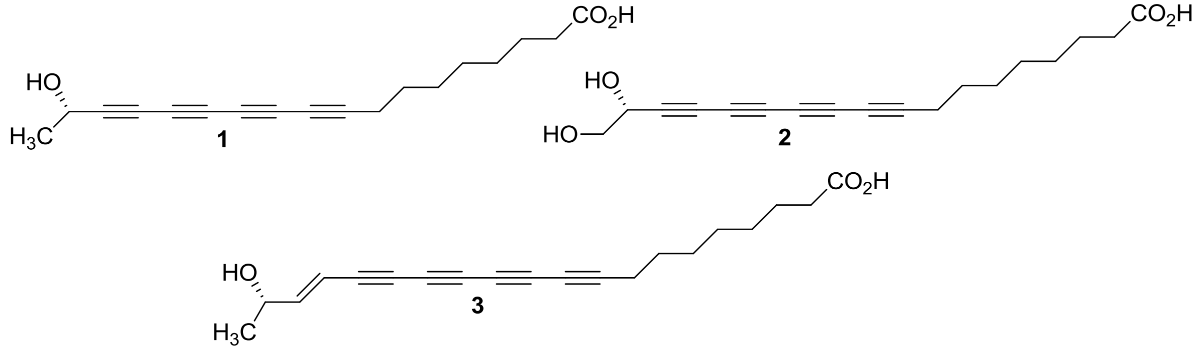
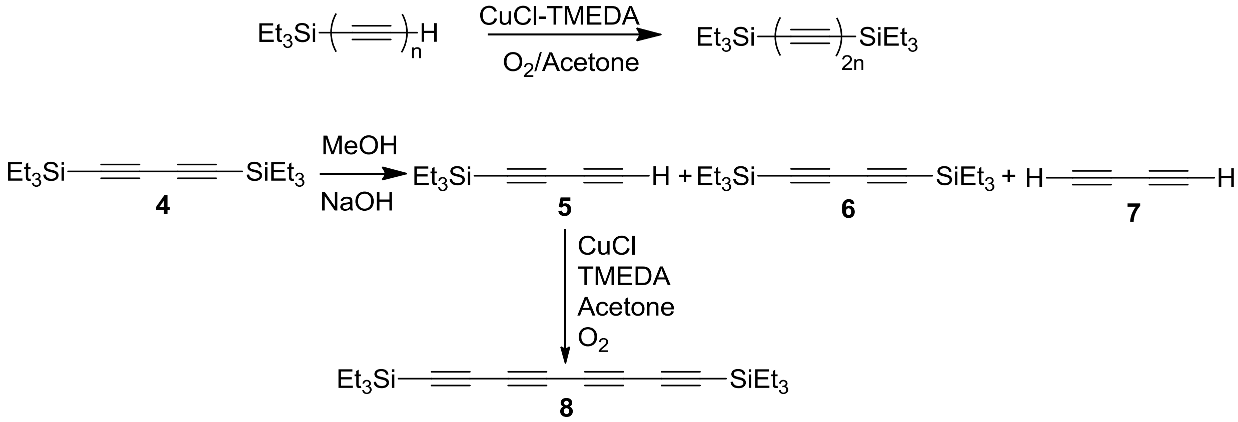


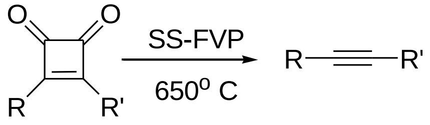
Figure 1.7 Examples of polyyne natural products derived from O. amentacea: (*S*)-Minquatynoic acid (**1**), 18-hydroxyminquartynoic acid (**2**), and *E*-15,16-dihydrominquartynoic acid (**3**)[24]

1.2.1 Synthetic Background

The synthesis of long polyyne chains was first reported by Walton and co-workers, who used Cu-catalyzed oxidative Hay coupling techniques to synthesize triethylsilyl-capped polyynes ranging from 4 to 16 C≡C bonds in length (Scheme 1.1).[26] Nearly twenty years later, Diederich and co-workers reported the synthesis of shorter polyynes from a variety of substituted 3,4-dialkynyl-3-cyclobutene-1,2-diones, using solution-spray flash vacuum pyrolysis techniques (Scheme 1.2).[27]

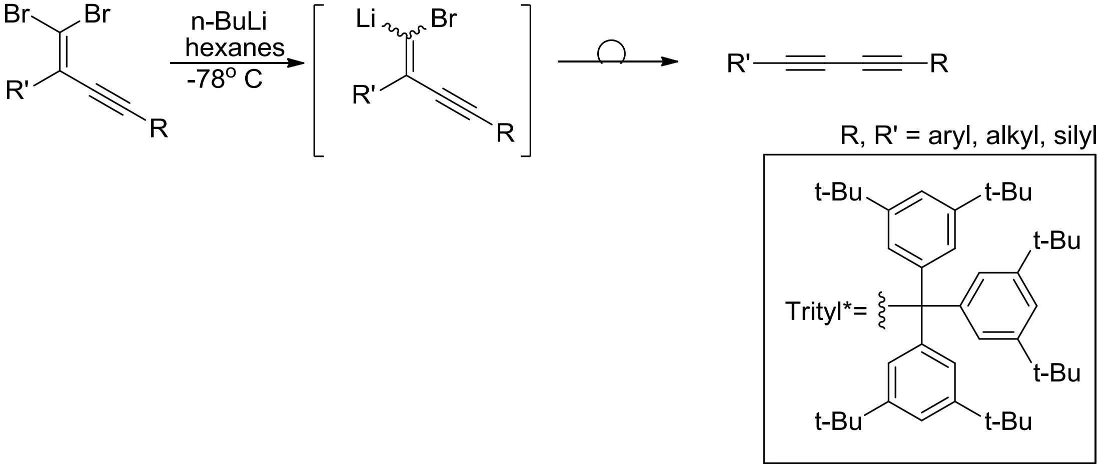


Scheme 1.1 Walton's method[26]



Scheme 1.2 Diederich's method[27]

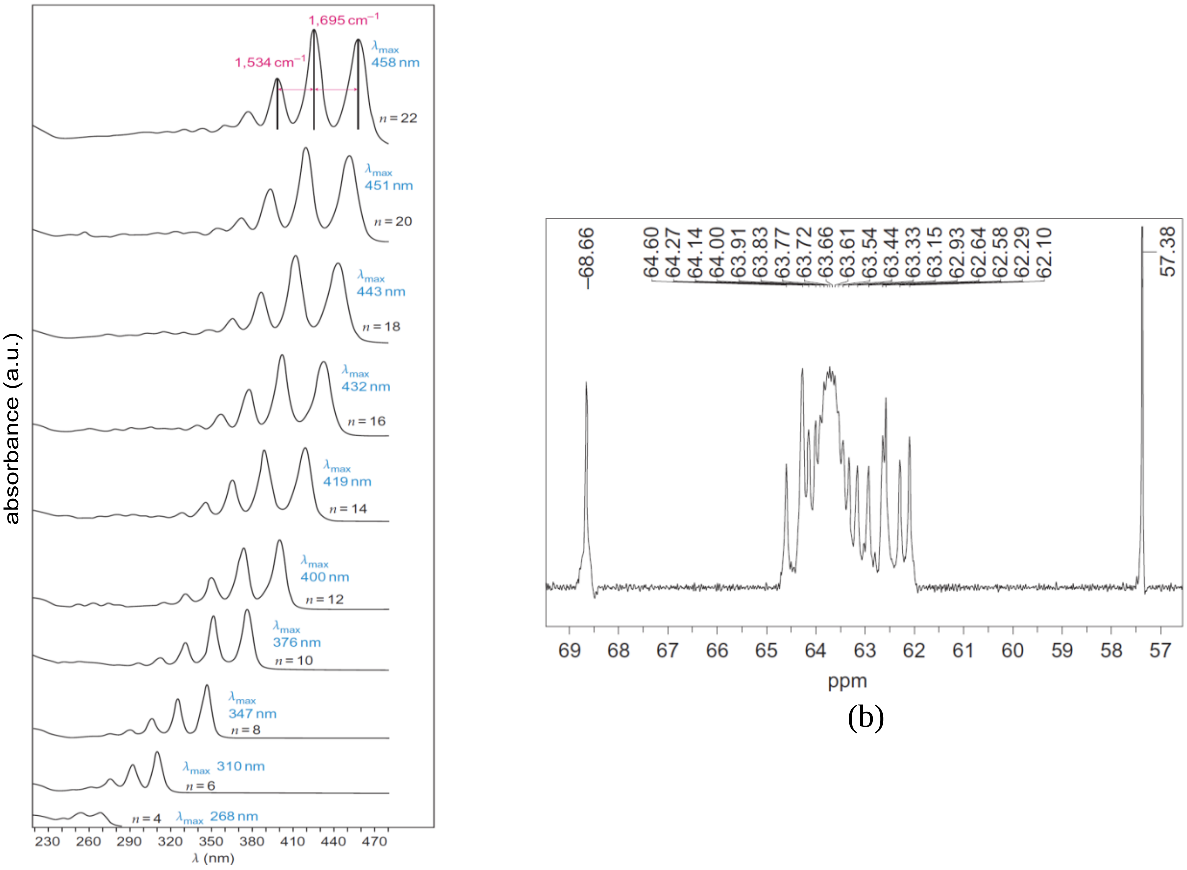
Tykwinski and co-workers synthesized polyynes containing two to ten carbon-carbon triple bonds, with various end groups, using the Fritsch-Buttenburg-Wiechell (FBW) rearrangement (Scheme 1.3).[13] Bulky substituents such as triisopropylsilyl and *tert*-butyl groups were used to increase the stability and solubility of polyynes without compromising the electronic properties of the sp-hybridized carbon atoms within the chain.[13,28] Although this method was effective for chains as long as nine C≡C in length, oxidative coupling reactions were necessary when targeting decaynes and longer polyynes. Recently, Chalifoux and Tykwinski have reported the synthesis of polyynes containing up to 22 C≡C bonds, using oxidative coupling conditions. In this synthesis, bulky tris(3,5-di-*t*-butylphenyl)methyl (“trityl*”) end groups were employed, which provided stabilization to the longer polyynes.[29]



Scheme 1.3 Tykwinski’s method [13]

Since the trityl*-capped polyynes are the longest polyynes that have been reported, the spectroscopic data were carefully examined as a means of predicting the properties of carbyne.[29] UV-vis spectra showed a bathochromic shift in λ_{max} with increasing chain length (Figure 1.8a), as typically observed in polyynes.[13, 29, 30] This shift is consistent with a decreased HOMO-LUMO bandgap energy (E_g) from increased conjugation. The UV-vis spectra also suggests an asymptotic limit around 485 nm, once the chain length reaches 48 carbon-carbon triple bonds, corresponding to the predicted λ_{max} of carbyne.[29, 31, 32] A ^{13}C NMR spectrum was also obtained for the longest polyyne of the series (Figure 1.8b), containing 21 unique peaks between 62.1 and 64.6 ppm, with the median being around 63.7 ppm.[29] Based on this spectrum, the predicted ^{13}C

NMR of carbyne is expected to have a single broad signal around this median value, which is in agreement with previous predictions.[13, 29, 31-33]

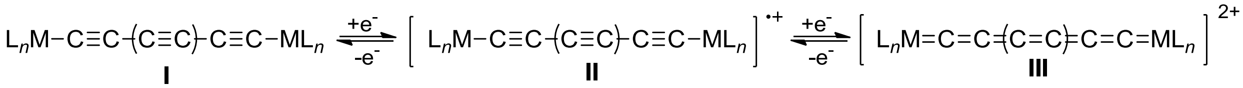


(b)

(a)

Figure 1.8 UV-vis spectra for trityl*-capped polyynes (a) and ^{13}C NMR for longest reported compound (b)[29] Reprinted by permission from Macmillan Publishers Ltd: Nature Chemistry (reference 29), Copyright 2010.

In addition to the organic polyynes that have been discussed, the synthesis of transition metal-capped polyynes has been thoroughly explored. Bulky ligands on the metals increase the stability of these carbon oligomers by shielding the internal carbon-carbon triple bonds, thus providing protection from intermolecular contacts.[25, 32] In addition to increased stability, the redox and charge- or electron-transfer properties of polyynes that contain metal end groups suggests that these compounds can be incorporated in the fabrication of molecular-scale devices.[32, 34] Tobe and Wakabayashi proposed that in the redox cycle of polyynes (Scheme 1.4) containing an even number of carbon-carbon triple bonds with transition metal end caps (**I**), a dicationic species (**III**) can result from two one-electron oxidation processes, via a radical cation intermediate (**II**).[25]



$$\underset{\textbf{I}}{L_nM{-}C{\equiv}C{-}(C{\equiv}C){-}C{\equiv}C{-}ML_n} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \underset{\textbf{II}}{\left[L_nM{-}C{\equiv}C{-}(C{\equiv}C){-}C{\equiv}C{-}ML_n\right]^{\bullet+}} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \underset{\textbf{III}}{\left[L_nM{=}C{=}C{=}(C{=}C){=}C{=}C{=}ML_n\right]^{2+}}$$

Scheme 1.4 Proposed redox cycle of polyynes with transition metal end groups[25]

Several metals have been incorporated into the end groups of polyynes, which were typically synthesized using oxidative homocoupling reactions. Coat and co-workers and Sakurai and co-workers have reported the synthesis of iron-containing polyynes,[35, 36] while Bruce and co-workers prepared polyynes with ruthenium and cobalt end caps.[37, 38] Gold-capped polyynes were synthesized by Lu and co-workers, and the Gladsyz group has prepared polyynes with rhenium and platinum end groups.[39-41] Of these compounds, the platinum-capped polyynes synthesized by Gladysz and co-workers contained the longest chains of carbon-carbon triple bonds.[32] Oxidative Hay coupling conditions resulted in polyynes with terminal bis(phosphine)-pentafluorophenylplatinum groups that were 4 to 12 carbon-carbon triple bonds in length (Figure 1.9).[32] The group later reported the synthesis of platinum-capped polyyne chains containing up to 14 carbon-carbon triple bonds.[33, 42]

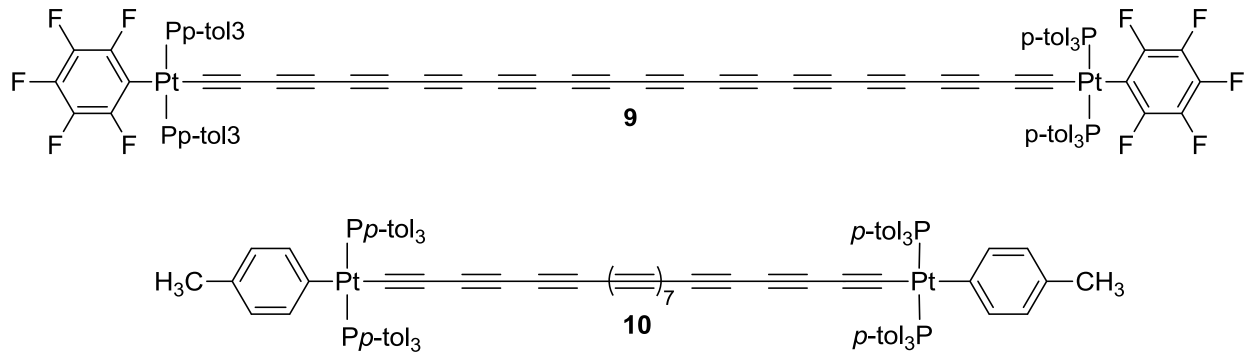
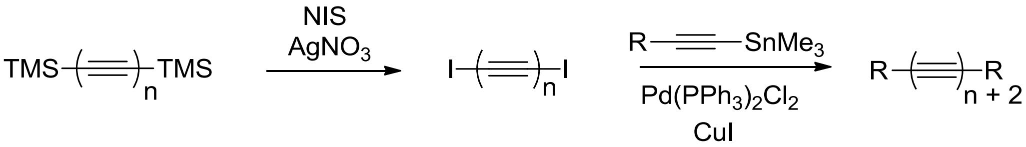


Figure 1.9 Platinum-capped polyynes containing 12 (**9**) and 14 (**10**) carbon-carbon triple bonds, reported by Gladysz and co-workers[32, 33, 42]

The synthetic method for preparing polyynes presented here is based on the strategy developed by Lei Li, which consists of a series of iodination and Stille coupling reactions (Scheme 1.5).[16] Tin acetylides couple to both ends of a diiodopolyyne, resulting in a silyl-protected carbon rod that can be further iodinated and employed in successive coupling reactions. The length of the polyyne is symmetrically increased by two carbon-carbon triple bonds with each iodination/coupling cycle. This synthetic route is particularly appealing because the intermediates are relatively stable and the method does not require the synthesis of complex starting materials.



Scheme 1.5 Iterative synthetic route[16]

1.3 Polydiacetylenes

Polydiacetylenes (PDAs) have been the subject of much research due to their potential electronic, optical, and biological applications.[43-45] With a backbone comprised of alternating double and triple bonds, these π-conjugated polymers can serve as precursors to linear carbon, or carbyne, assuming elimination of the R group side chains is feasible (Figure 1.10).[46]

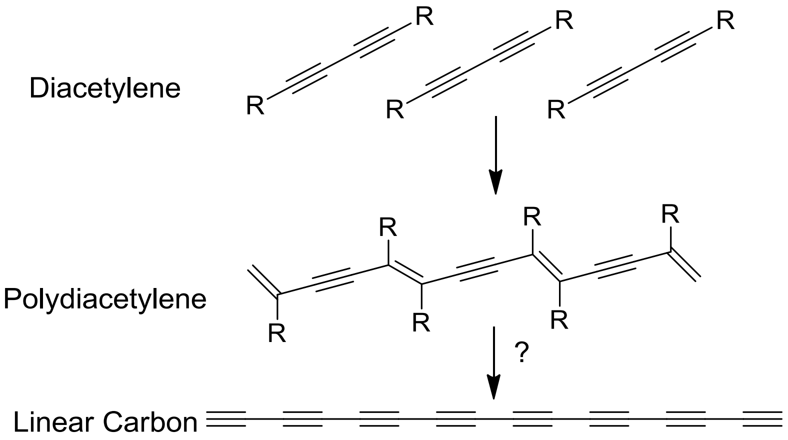
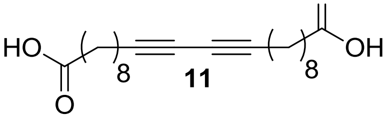


Figure 1.10 Poly(diacetylenes) as precursors to linear carbon[46]

PDAs differ from other organic polymers because they can be obtained as large single crystals in the solid state.[47] These conjugated polymers can be used in thin film crystals, and can serve as biosensors, optical switches, and even be incorporated into drug delivery systems.[43, 45, 48, 49] Eaidkong and co-workers used PDAs to detect volatile organic compounds (VOCs), indicating that they can also be applied to efforts that address environmental and safety concerns.[50] Figure 1.11 shows an example of a diacetylene monomer that was employed by this group, in the fabrication of PDA coated paper which demonstrated the ability to detect various organic solvent vapors.[50]



11

Figure 1.11 Diacetylene monomer (**11**) used to prepare PDA paper[50]

The visible blue-to-red (λ_{max} ~650 nm → λ_{max} ~550) color change that some PDAs undergo when exposed to various external stimuli such as heat, stress, pH or salt changes, or organic solvents, makes them very useful in optical sensing devices.[50-52] This color change results from conformational changes in the polymer backbone, and the reversibility is contingent on the nature of the side chains present.[53] While the blue PDA chains are known to be planar, it is believed that the red PDAs have some degree of twisting in the chain, which can reduce or interrupt conjugation.[54] Despite the differences in chain geometry between blue and red PDAs, it has been reported that the bond lengths for both types are quite similar.[54] This suggests that this difference in geometry likely stems from the chain conformation or the effect of the side groups that are present.[54]

1.3.1 Preparation of Polydiacetylenes via Topochemical Polymerization

The formation of PDAs by topochemical polymerization of diyne monomers was first reported by Wegner in the late 1960s.[55] Expanding upon Wegner's work, Baughman was able to outline the parameters that were required for the 1,4-polymerization of diynes.[56] The ideal distance (*r*) between the monomers was determined to be 4.9Å, while the spacing (*d*) between the reacting carbons (C1 and C4) should be close to the van der Waals contact distance of 3.5Å.[56] The diyne monomers should be tilted at a 45° angle from the translational axis in order to achieve the appropriate *r* and *d* distances. These parameters for 1,4-topochemical polymerization are illustrated in Figure 1.12.

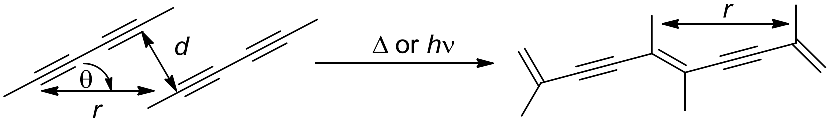


Figure 1.12 Parameters for 1,4-topochemical polymerization, r = ~4.9 Å, θ = 45º, d = 3.5 Å[56, 57]

To align the monomers according to the spacial requirements outlined by Baughman, different end groups were explored. Various PDAs were synthesized using this method;

however the types of diynes that could serve as polymer precursors were limited. Fowler and Lauher's more recent development of a host-guest strategy has expanded the types of diyne monomers that can undergo 1,4-polymerization.[57,58] In this method, the diyne monomers serve as guests, which are held in the proper alignment for polymerization by host molecules. The hosts are carefully designed to self-assemble in a framework with a spacing that correlates to the repeat distance defined by Baughman. Oxalamide and urea functionalities were incorporated into the host molecules, which have been shown to form hydrogen bonding networks with repeat distances of 5.0Å and 4.6Å, respectively (Figure 1.13).[57] These distances translate to the repeat distance between the monomer guests, thus aligning them in the proper orientation for 1,4-topochemical polymerization. Fowler and Lauher's host-guest strategy has been associated with successful single-crystal-to-single-crystal polymerization of diynes, triynes, and trienes.[57]

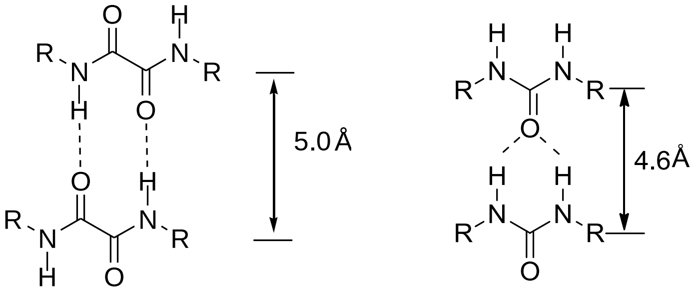


Figure 1.13 Hydrogen bonding networks in oxalamides and ureas[58]

In addition to the hydrogen bonding host-guest interactions that have allowed for 1,4-polymerization of diyne monomers, halogen bonding has also proven capable of aligning monomers in the proper orientation for polymerization to occur. In collaboration with Fowler and Lauher, the Goroff group has demonstrated that halogen bonding between the Lewis acidic iodine atoms in diiodobutadiyne guest monomers and Lewis basic hosts (Figure 1.14a) effectively translates the proper spacing for a 1,4-topochemical polymerization.[57, 59-62] Removal of the host after polymerization results in isolated poly(diiododiacetylene) (Figure 1.14b), a simple PDA composed of only carbon and iodine atoms.[59]

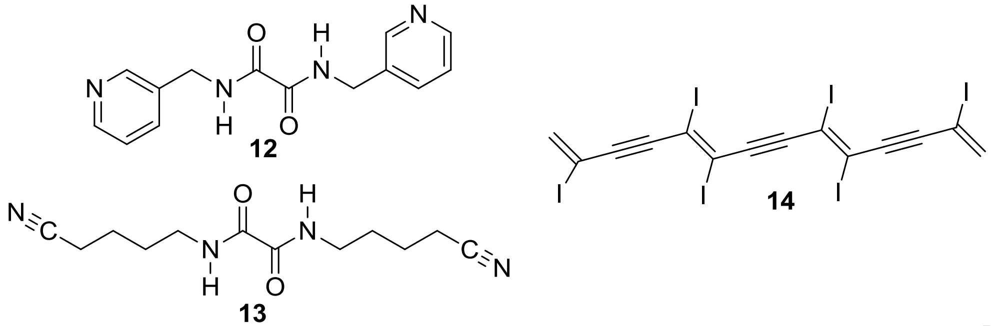


Figure 1.14 (a) Lewis basic oxalamide hosts, (b) Poly(diiododiacetylene)[59]

1.4 Polytriacetylenes

1.4.1 The Topochemical Polymerization of Triynes

The topochemical polymerization of triynes can proceed in either a 1,4- or 1,6 fashion. Hence, achieving ordered polymerization is more complicated compared to diyne monomers. A 1,4-polymerization results in a polymer with a poly(*trans*-ene-yne) backbone, whereas 1,6-polymerization produces a poly(*trans*-ene-diyne) backbone (Figure 1.15).[63]

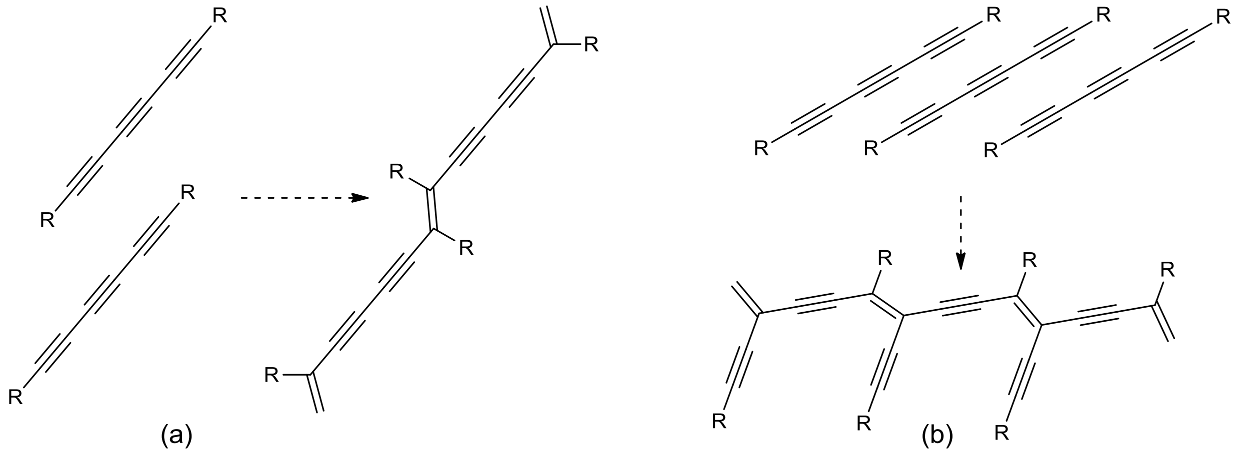


Figure 1.15 (a) 1,6- and (b) 1,4-topochemical polymerization of triyne[63, 64]

The polymerization of triynes can be controlled by the repeat distance (*r*) between the monomer units.[57, 65] According to the parameters that were outlined by Baughman, the repeat distance between the monomers should be ~4.9 Å to achieve 1,4-topochemical polymerization.[56] If 1,6-polymerization is desired, *r* should be approximately 7.4 Å with a tilt angle (θ) of 30º, which would result in an intermolecular C1-C6 distance (*d*) of 3.5 Å—the van der Waals contact distance.[63, 65, 66]

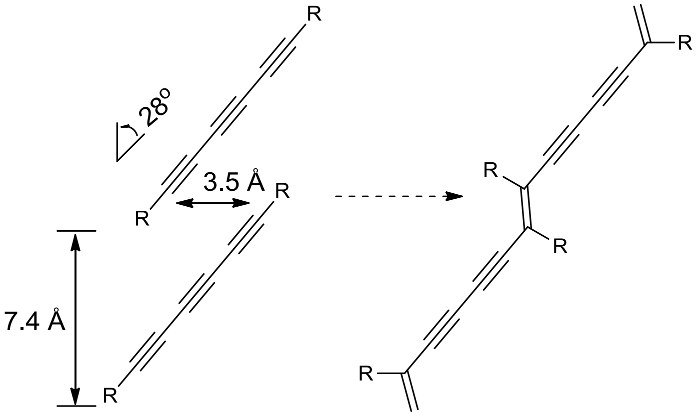


Figure 1.16 Parameters for 1,6-topochemical polymerization of triynes[65]

While the 1,4-topochemical polymerization of triynes is not unique, the 1,6-polymerization of triynes is much less common.[66, 67] Lauher and Fowler were first to report the 1,6-topochemical polymerization of triynes, using vinylogous amide pyridine host **76** and triacetylene diacid **77** (Figure 1.17).[65, 68]

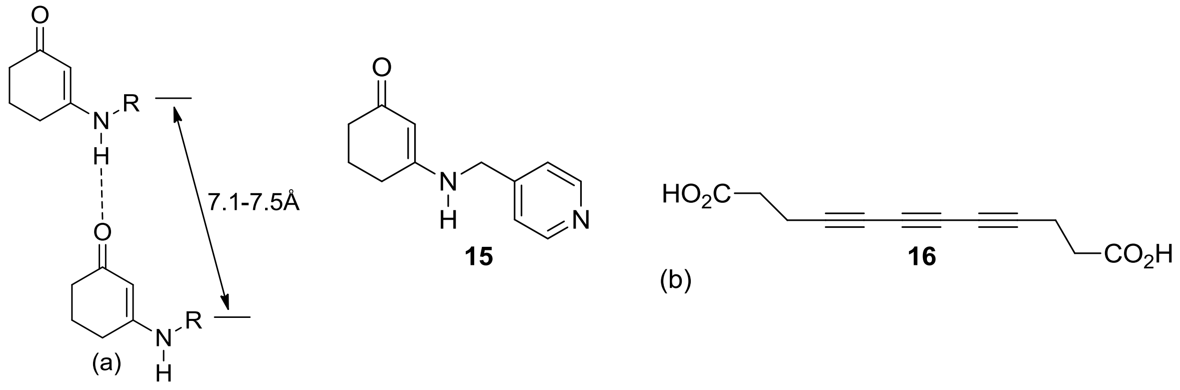


Figure 1.17 (a) The translation distance of aminoquinones (b) Host **15** and guest **16** used to achieve 1,6-topochemical polymerization of triynes [65]

Frauenrath and co-workers attempted to achieve 1,6-polymerization of triynes by exploiting perfluorophenyl-phenyl interactions to control the packing of the monomer units. Previous experiments with diacetylenes indicated that these complementary interactions are capable of aligning the monomers in the proper orientation for 1,4-topochemical polymerization to occur.[69, 70] Of the group of triynes that were employed, compounds **17**, **18**, and **19**, shown in Figure 1.18, underwent topochemical polymerization.[63] Raman and solid state ^{13}C NMR data suggested 1,4-polymerization was the predominant reaction that occurred.[63]

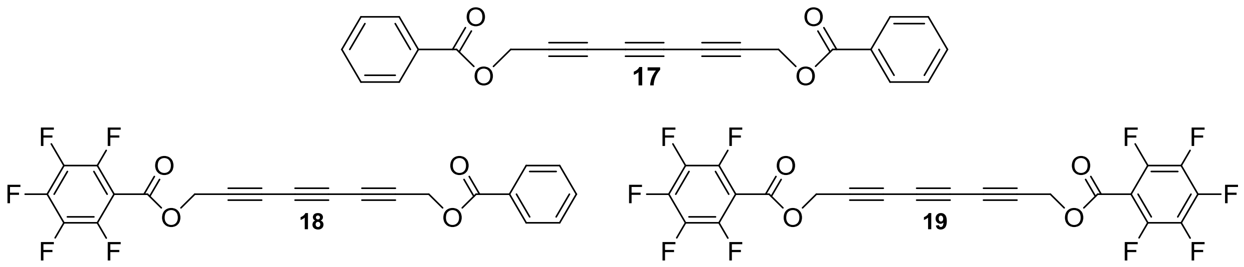
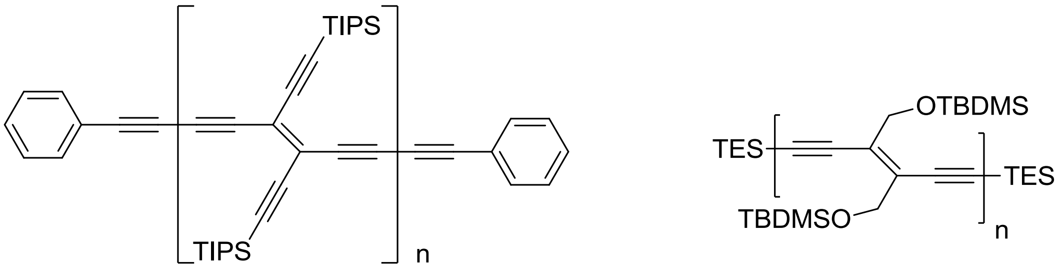


Figure 1.18 Triynes employed by Frauenrath and co-workers[63]

1.4.2 Alternative Approaches towards Polytriacetylenes

Prior to the work described above, Diederich and co-workers reported the synthesis of polytriacetylenes using oxidative Glaser-Hay coupling oligomerization techniques.[71, 72] In these cases, topochemical polymerization was not employed to form the polytriacetylenes.



20a-e n = 1-5

21a-g n = 1,2,4,6,8,12,16

Figure 1.19 Polytriacetylenes synthesized by Diederich and co-workers[71, 72]

1.5 Nitrile-Containing Conjugated Organic Molecules

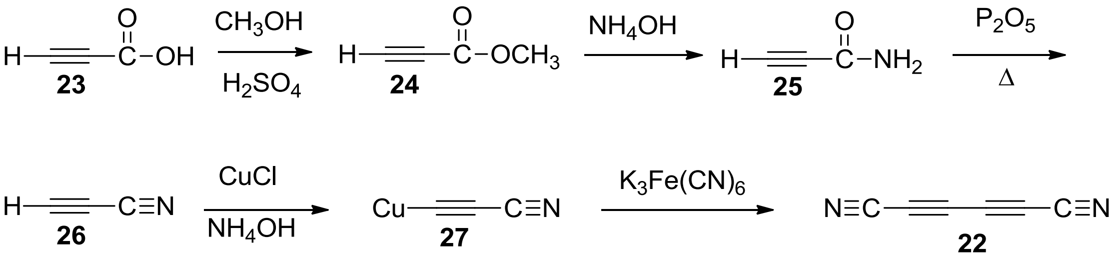
1.5.1 Cyano-capped Polyynes

Mono- and dicyanopolyynes have been identified in interstellar medium, and have thus attracted the attention of chemists, physicists, and astronomers alike.[30, 73, 74] Cyanoacetylene and dicyanoacetylene have been detected in the atmosphere and solid phase of Titan, Saturn's largest moon.[73] Titan has been referred to as a frozen early Earth, and is therefore thought to contain information regarding the composition of our planet in its initial stages.[74] Cyanoacetylene has therefore been viewed as a possible precursor to some of the early building blocks of life on Earth.[75]

The linearity of cyano-capped polyynes suggests that they can serve as model compounds for carbyne.[30] Dicyanopolyynes, in particular, can be used to predict the properties of the linear allotrope of carbon, since they do not contain bulky end groups that provide stability. The absence of large end groups decreases the distance between individual chains, which promotes polymerization in the solid state.[30] In theory, cyano- and dicyanopolyynes could possess synthetic utility, with use in cycloaddition reactions, the synthesis of inorganic compounds, and generation of radical sources; however these compounds are too unstable for such purposes.[76]

1.5.2 Dicyanopolyynes: Synthetic Background

Dicyanodiacetylene (**22**) was first prepared by Moureu and Bongrand in 1920 using potassium ferricyanide (aq.) and cuprous cyanoacetylene.[77] In the 1950s, experimental modifications were made by Brockman, as well as Saggiomo and co-workers, both of whom developed similar methods for the synthesis of **22** (Scheme 1.6).[77, 78] Miller and Lemmon made slight alterations to the reported route in 1967, resulting in modest yield improvements and simpler procedures.[79] Despite the changes that were made, the new methods still had "many pitfalls."[79]



Scheme 1.6 Saggiomo's synthesis of dicyanodiacetylene[78]

Dicyanodiacetylene was described as a white crystalline solid with a melting point of 64.5-65°C, and a characteristic unpleasant odor.[77-79] The compound is also a strong lachrymator.[79] Sublimation techniques were employed to isolate dicyanodiacetylene, which is reported to slowly darken *in vacuo* at room temperature, but is reportedly stable at -75 ºC.[77-79] All procedures involved in the preparation of this diyne were carried out in the absence of oxygen, as the material readily decomposes when exposed to air.[78]

Nearly thirty years after Miller and Lemmon's synthesis of dicyanodiacetylene, Hirsch and co-workers reported the preparation of dicyanopolyynes using graphite vaporization in the presence of cyanogen.[30, 80] Temperatures up to 6000 ºC were required to form a mixture of chains containing 3 to 8 carbon-carbon triple bonds, which was separated from the soot via extraction in 7% overall yield.[30] Preparative HPLC was used to isolate the individual compounds, which were described as colorless crystals that were very soluble in chloroform and toluene and stable at -18 ºC in dilute solutions in the dark.[30] Cyano-capped triynes and tetraynes were the major components of the product mixture, accounting for 55% and 35%, respectively.[30] ^{13}C NMR spectra were obtained for the compounds ranging from 3 to 6 carbon-carbon triple bonds in length, which are shown in Figure 1.20 below. The signal around ~104 ppm corresponds to the cyano group, while the sp carbon adjacent to the nitrile appears ~50 ppm.[30] The internal carbons appear in the 60 – 67 ppm region—a trend that spears to be true for many polyynes, regardless of the end groups. Based on these spectral observations, the ^{13}C NMR spectrum for carbyne is predicted to contain one multiplet of peaks around 63 ppm.[30]

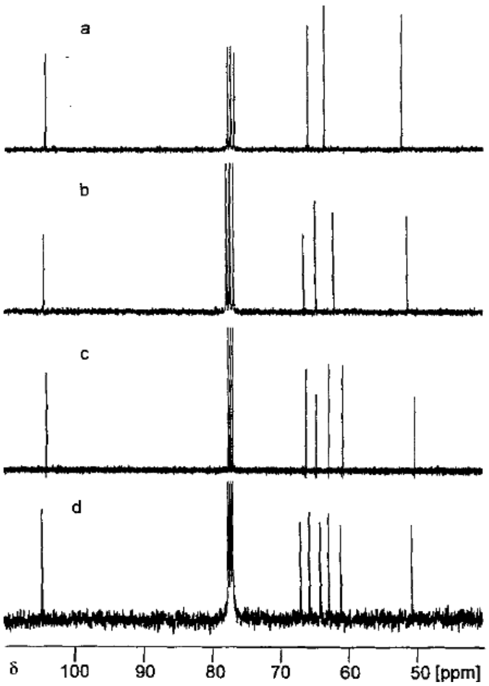


Figure 1.20 ^{13}C NMR (62.9 MHz, 25 ºC, $CDCl_3$) of a) NC-(C≡C)$_3$-CN (**28**), b) NC-(C≡C)$_4$-CN (**29**), c) NC-(C≡C)$_5$-CN (**30**), and d) NC-(C≡C)$_6$-CN (**31**)[30] Reprinted with permission from reference 30, Copyright 1997, John Wiley & Sons, Inc.

Hirsch and co-workers also explored the polarization of the carbon-carbon triple bonds due to the charge distribution that results from the presence of the cyano- groups.[30, 81] Octa-2,4,6-triynedinitrile (**28**) and deca-2,4,6,8-tetraynedinitrile (**29**) were subjected to [4 + 2], [3 + 2], and [2 + 2] cycloaddition reactions, and the observed regioselectivity suggests that the polarization of the carbon-carbon triple bonds adjacent to the nitrile groups are larger than the central triple bonds.[30, 81] Nucleophilic and radical additions to octa-2,4,6-triynedinitrile (**28**) were also explored, and the results once again demonstrated exclusive reaction at the terminal carbon-carbon triple bonds, with C1 being the preferred site of attack over C2.[81] Resonance stabilization of the anionic or radical intermediates that form during these reactions account for the regioselectivity that is observed, shown in Figure 1.21 below.[81] This behavior suggests that a variety of newly functionalized eneynes can be accessed from dicyanopolyynes.[81]

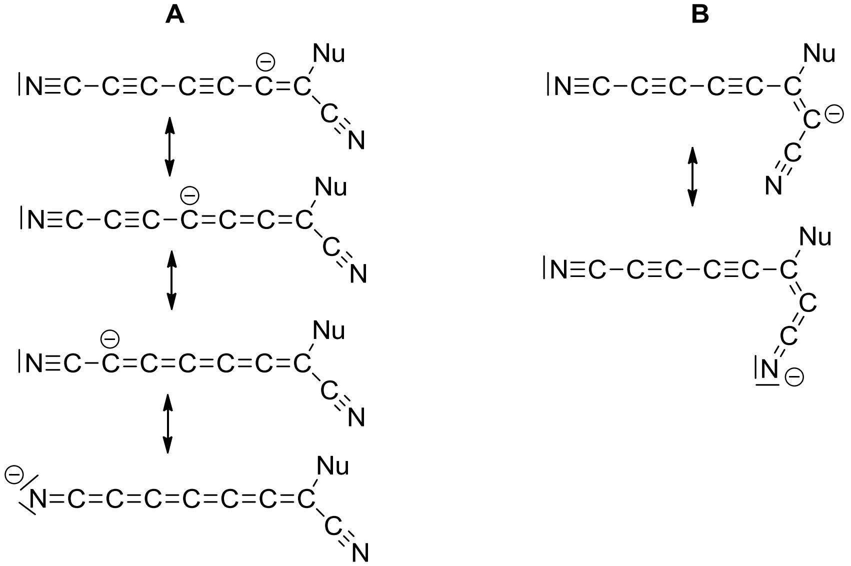


Figure 1.21 Carbanionic intermediates formed by nucleophilic attack on **28** at carbon 1(A) and carbon 2 (B)[81]

Cataldo and co-workers reported the synthesis of dicyanopolyynes using graphite electrodes arced in liquid nitrogen.[82-84] Similar to Hirsch's method, high temperatures (>4000 ºC) were required, which allowed elemental carbon to vaporize from the electrodes and subsequently oligomerize.[82] The oligomers were quenched with liquid nitrogen, resulting in cyano-capped polyynes ranging from 2 to 4 carbon-carbon triple bonds in length, with diycanodiacetylene as the major component of the product mixture.[82] A small amount of terminal polyynes was also produced, which resulted from the presence of moisture in the system.[82] The electronic absorption spectra of the polyynes that were formed using this method are shown in Figure 1.22.[82]

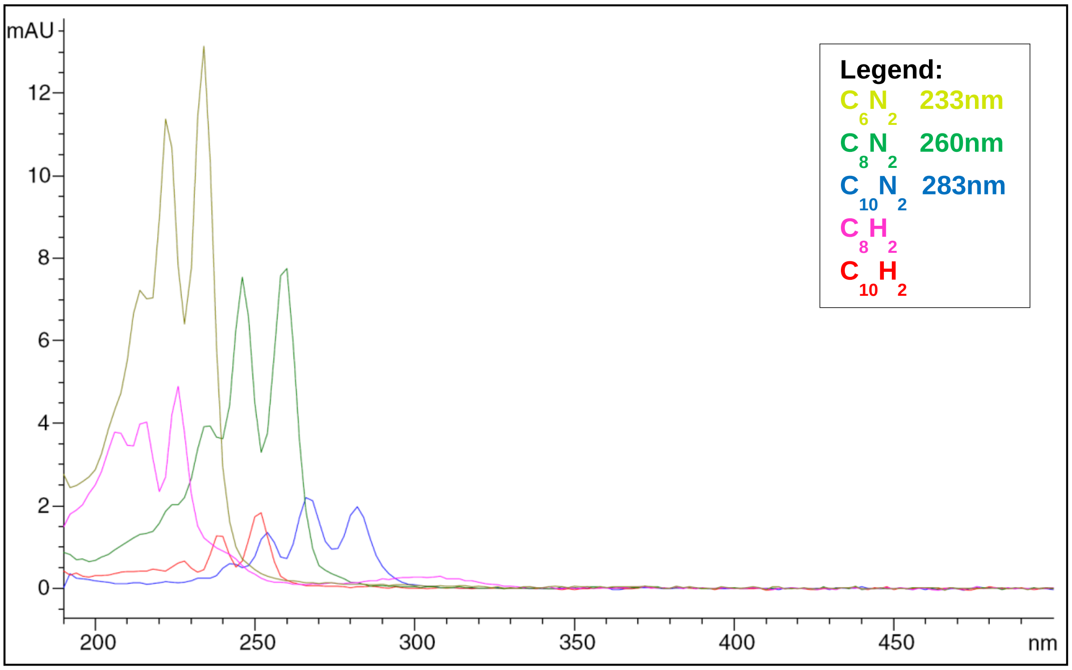
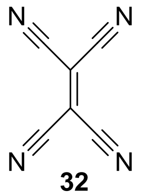


Figure 1.22 Electronic absorption spectra of the polyynes formed from graphite electrodes arched in liquid nitrogen[82] Reprinted from Tetrahedron, 60, Cataldo, F., Polyynes and cyanopolyynes synthesis from the submerged electric arc: About the role played by the electrodes and solvents in polyynes formation, 4265-4274, 2004, with permission from Elsevier.

1.5.3 Tetracyanoethylene and Tetracyanobutadiene

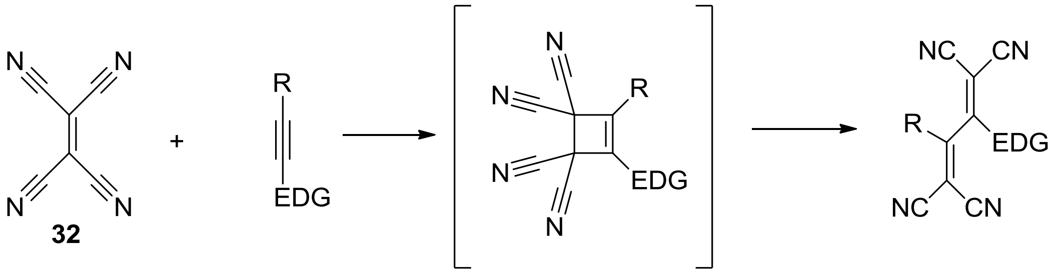
Tetracyanoethylene (TCNE, **32**) was first reported in 1957, from the copper-catalyzed thermolysis of dibromomalononitrile.[85] This compound is very versatile, and can act as a good dienophile due to the electron withdrawing nature of the nitrile groups.[86] Furthermore, TCNE contains good leaving groups, can easily undergo oxidation or reduction, and has many potential coordination modes, thus making it a good ligand.[87] The high electron affinity of TCNE allows it to readily and reversibly accept one or two electrons to form the radical anion or dianion.[87] It is therefore often used to add acceptor functionalities into organic molecules to prepare donor-acceptor compounds with potential applications in optics and electronics.[88] TCNE has been referred to as the "*E. coli*" of electron-transfer chemistry, due to the wide investigation of this compound as an electron acceptor.[89]



32

Figure 1.23 Tetracyanoethylene

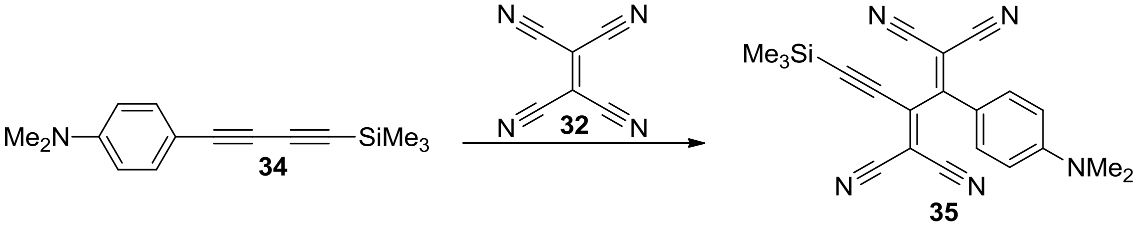
The [2+2] cycloaddition reaction between tetracyanoethylene and electron rich alkynes allows for the preparation of various tetracyanobutadienes (TCBDs) with donor-acceptor properties.[88, 90] This reaction proceeds through a cyclobutene intermediate, as shown in Scheme 1.7 below. Product yields are typically high, but can be influenced by both sterics and the electron density of the alkynes that are employed.[90, 91]



Scheme 1.7 Sythesis of tetracyanobutadienes

Donor-acceptor tetracyanobutadienes have attracted much interest due to their high third-order nonlinear optical properties.[88] One major benefit of using organic chromophores is that their physical properties can be altered via modifications in chemical structure. Donor-acceptor TCBDs have also demonstrated thermal stability, suggesting they can be used in vapor deposition thin film fabrication methods.[91]

Michinobu and co-workers explored the synthesis of donor-substituted TCBDs by incorporating electron-rich (dimethylamino)phenyl alkynes and diynes in the [2+2] cycloaddition reaction with tetracyanoethylene.[88, 91] When diynes were employed, the reaction took place at the more electron-rich carbon-carbon triple bond, which was closer to the substituted aromatic ring (Scheme 1.8).[91] Ferrocene moieties were also show to be effective donors in the synthesis of tetracyanobutadienes; however when poly(arylethynylene)s were used, the reaction did not proceed as readily, possibly due to sterics or slow diffusion of the polymers themselves.[90] Some examples of the TCBDs that have been described are shown in Figure 1.24.[91]



Scheme 1.8 Addition of TCNE to diynes[91]

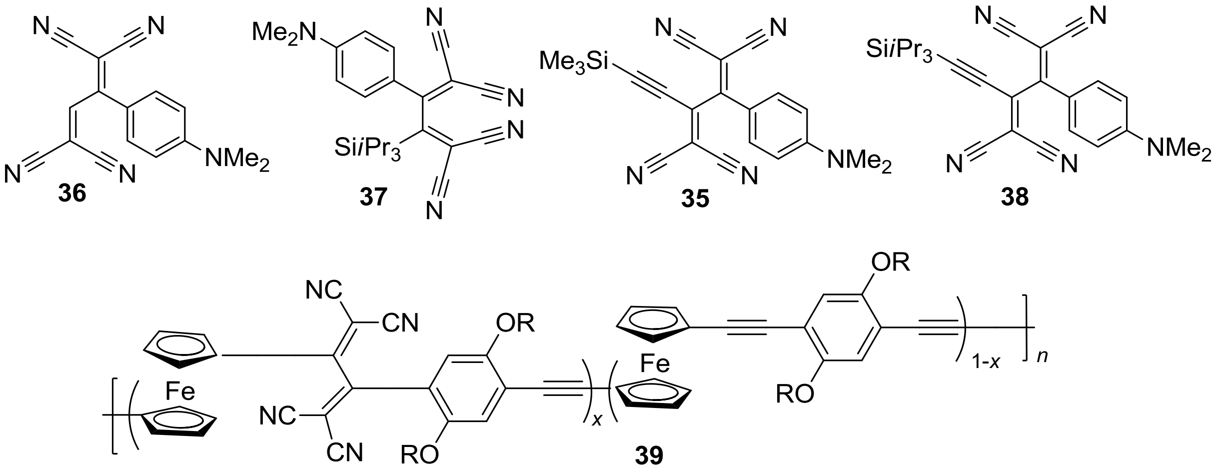


Figure 1.24 Donor-acceptor tetracyanobutadienes synthesized by Michinobu and co-workers[91]

Crystal structures of the tetracyanobutadienes revealed a distorted geometry, which results from rotation about the central single bond.[91] Despite this twisted conformation, the dicyanovinyl groups and the adjacent donor group are almost coplanar. Therefore, intramolecular charge transfer (CT) interactions remain efficient.[88] The quinoid character of these compounds, which is determined by the bond length alternation in the aryl rings, was used to assess charge transfer efficiency.[91] When examining the crystal packing of TCBDs, it was observed that the aryl donor moities stack in an antiparallel fashion, as do the CN moities (Figure 1.25).[91] Although tetracyanoethylene and tetracyanobutadiene have demonstrated interesting properties and potential applications, the synthesis and poylmerization of diynes containing nitrile end groups will be the focus of this work, as a means of preparing novel, electron poor polymers.

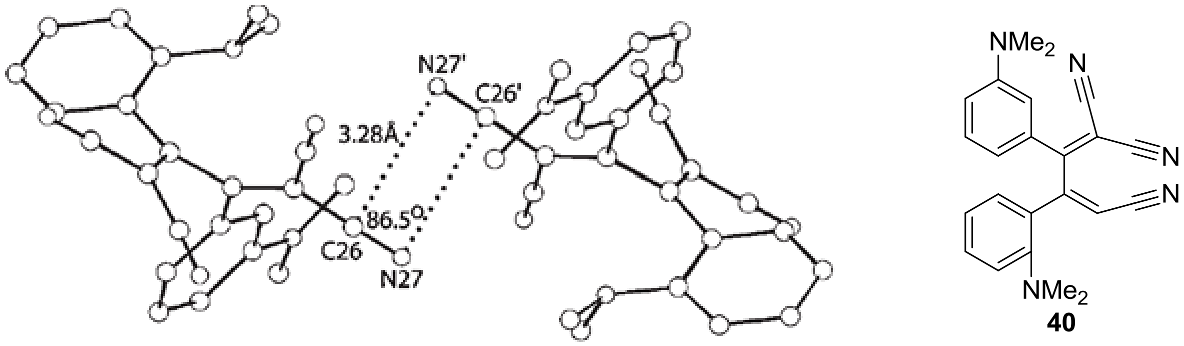


Figure 1.25 Crystal packing of TCBD with aryl donors (**40**), illustrating the antiparallel alignment of the CN moieties[91] Reprinted with permission from reference 91, Copyright 2006, John Wiley & Sons, Inc.

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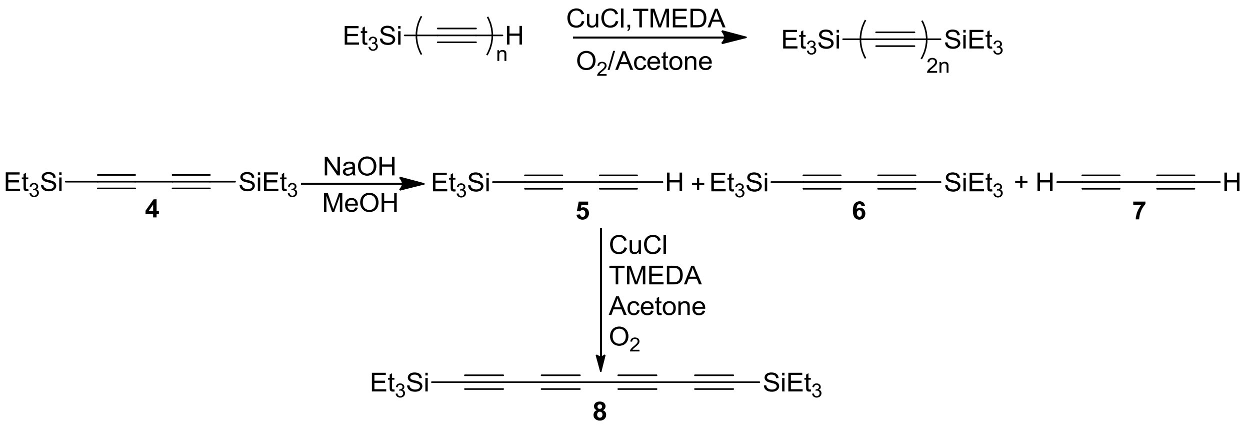
Chapter 2: The Iterative Method for the Synthesis of Polyynes

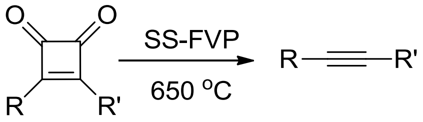
2.1 Previous Synthetic Routes towards Polyynes

The synthesis of long polyyne chains was pioneered by Walton and co-workers in 1972.[1] Copper-catalyzed oxidative Hay coupling techniques were employed, resulting in the synthesis of triethylsilyl-capped polyynes ranging from 4 to 16 C≡C bonds in length (Scheme 2.1).[1] The product of this coupling reaction was treated with sodium hydroxide to deprotect one end of the polyyne and subsequently use the material in another Hay coupling reaction. This technique resulted in a statistical mixture of monodeprotected, protected, and completely deprotected polyyne products which were difficult to separate.[1] The monodeprotected polyyne was used in a coupling reaction to increase the number of triple bonds once again; however the presence of two additional products in the mixture makes this process less than ideal.



Scheme 2.1 Walton's method[1]

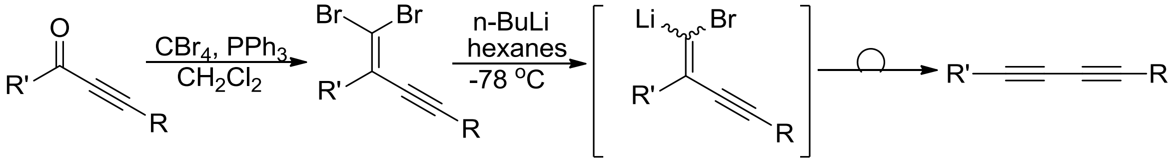
Solution-spray flash vacuum pyrolysis (SS-FVP) was used by Diederich and co-workers to form polyynes with up to 5 carbon-carbon triple bonds from a variety of substituted 3,4-dialkynyl-3-cyclobutene-1,2-diones (Table 2.1).[2] This method was effective in making various polyynes containing phenyl or silyl end groups in relatively good yield; however the synthesis of the required precursors is quite challenging and the experimental setup that is employed is not easily accessible.

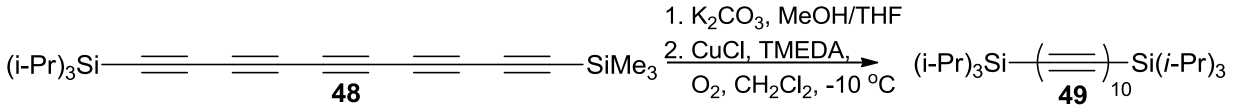


Compound	R	R'	% Yield
41	Ph-	Ph-	98
42	PhC≡C-	PhC≡C-	97
43	PhC≡C-C≡C-	PhC≡C-C≡C-	59
44	*n*-PrC≡C-	*n*-PrC≡C-	78
45	$Me_3SiC{\equiv}C$-	$Me_3SiC{\equiv}C$-	99
46	*i*-$Pr_3SiC{\equiv}C$-C≡C-	*i*-$Pr_3SiC{\equiv}C$-C≡C-	42
47	*i*-$Pr_3SiC{\equiv}C$-	$Me_3SiC{\equiv}C$-	71

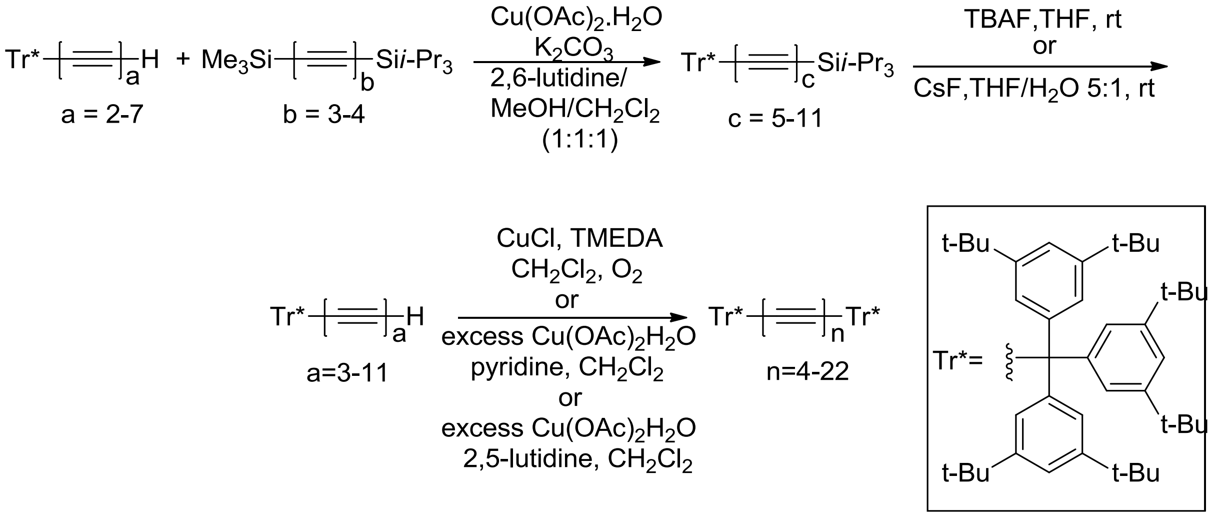
Table 2.1 Diederich's method[2]

Tykwinski's synthesis of polyynes containing 2 to 10 carbon-carbon triple bonds with various end groups centers on the Fritsch-Buttenburg-Wiechell (FBW) rearrangement (Scheme 2.2).[3] Bulky substituents such as triisopropylsilyl and *tert*-butyl groups were used due to their ability to increase the stability and solubility of polyynes without compromising the electronic properties of the sp-hybridized carbon atoms within the chain.[3,4] Although this method was effective for chains as long as nine C≡C in length, oxidative coupling reactions were necessary when targeting decaynes. In 2010, Tykwinski reported the synthesis of polyynes containing up to 22 C≡C bonds using oxidative coupling conditions. Extremely bulky tris(3,5-di-*t*-butylphenyl)methyl (trityl*) groups were employed as end caps for these polyynes—all containing an even number of triple bonds (Scheme 2.3).[5]





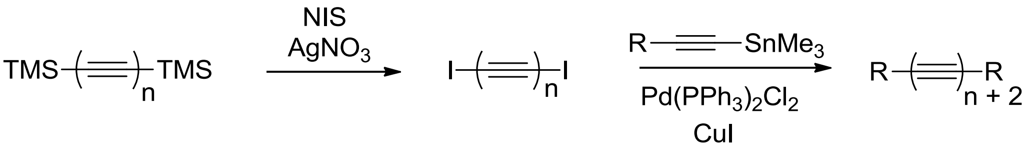
Scheme 2.2 Tykwinski's method[3]



Scheme 2.3 Tykwinski's synthesis of longer polyynes[5]

2.2 Iterative Synthetic Method

The synthetic method towards polyynes that is described here is based on the strategy developed by Lei Li, in which short carbon rods are iodinated and subsequently used in a palladium-catalyzed Stille coupling reaction with silyl-protected tin acetylides.[6] The tin acetylides couple to both ends of the iodinated polyyne, ultimately resulting in a silyl-protected carbon rod. These newly formed rods can be iodinated and used in a Stille coupling reaction once again, where each iodination/coupling cycle symmetrically increases length of polyyne by two C≡C bonds (Scheme 2.4). This synthetic method is particularly appealing because it avoids the synthesis of complex starting materials and incorporates relatively stable intermediates.



Scheme 2.4 Iterative synthetic method

The cross-coupling of diiodopolyynes, which is central to this method, has been rarely reported in the literature. Hirsch and co-workers coupled diiodoacetylene to bridged terminal alkynes that were connected by an alkyl tether, using Cadiot-Chodkiewicz conditions. Product mixtures were obtained, and the reactions proceeded in low yields.[7] Similary, Cataldo and co-workers reported the synthesis of diarylpolyynes from the Cadiot-Chodkiewicz coupling of diiodoacetylene and phenyl- or napthyl-capped copper acetylides.[8, 9] These reactions yielded mixtures of polyynes of different lengths, and the individual components were not isolated.[8, 9] Bruce and co-workers reported the palladium-catalyzed cross-coupling of diiodoalkynes and gold(I) alkynyl complexes.[10-12] Although the literature examples are not in abundance, they do support our method in which diiodopolyynes provide a general synthetic route towards symmetric polyynes. The tetraynes, pentaynes, hexaynes, and heptayne that have been prepared by this method are summarized in Table 2.1.

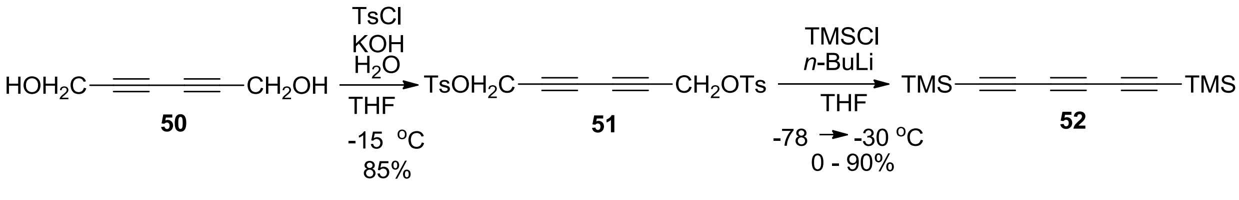
Table 2.2 Polyyne Synthesis via Stille Coupling

Diiodopolyyne	Sn Acetylide	Product	Temperature (° C)	% Yield (isolated)
I—≡—≡—I **70**	TMS—≡—SnMe$_3$ **57**	TMS—≡—(≡)$_2$—≡—TMS **71**	0	59
70	TIPS—≡—SnMe$_3$ **58**	TIPS—≡—(≡)$_2$—≡—TIPS **78**	25	77*
I—≡—≡—≡—I **56**	**57**	TMS—≡—(≡)$_3$—≡—TMS **61**	0	61
56	**58**	TIPS—≡—(≡)$_3$—≡—TIPS **46**	0	40
56	Ph—≡—SnMe$_3$ **59**	Ph—≡—(≡)$_3$—≡—Ph **62**	0	28
I—≡—(≡)$_2$—≡—I **72**	**58**	TIPS—≡—(≡)$_4$—≡—TIPS **123**	0	47*
72	**59**	Ph—≡—(≡)$_4$—≡—Ph **73**	0	16
I—≡—(≡)$_3$—≡—I **66**	**58**	TIPS—≡—(≡)$_5$—≡—TIPS **67**	-15	10

*results obtained by Lei Li

2.2.1 Synthesis of Polyynes with an Odd Number of Carbon-Carbon Triple Bonds

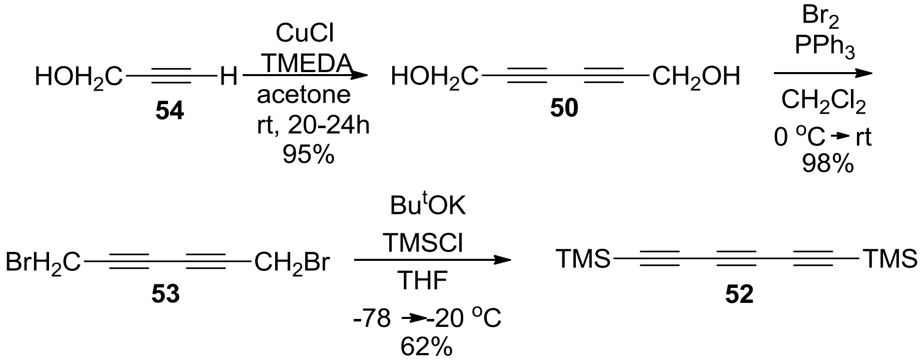
The first step towards polyynes that contain an odd number of C≡C bonds is the synthesis of 1,6-bis(trimethylsilyl)-1,3,5-hexatriyne (C_6TMS_2, **52**). Compound **52** was initially obtained from 2,4-hexadiyn-1,6-bis(p-toluenesulfonate) precursor **51** based on procedures outlined by Rubin and co-workers (Scheme 2.5).[2]



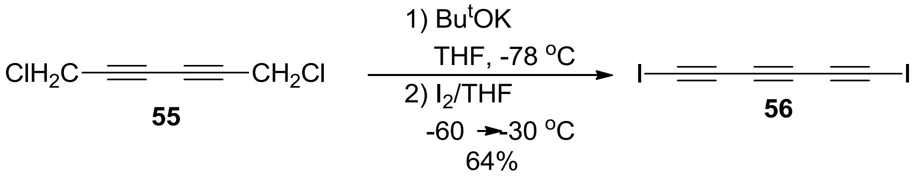
Scheme 2.5 Synthesis of 1,6-bis(trimethylsilyl)-1,3,5-hexatriyne using Rubin's method[2]

The synthesis of 2,4-hexadiyn-1,6-bis(p-toluenesulfonate) from the diol precursor typically proceeded without problems; however difficulty was encountered when allowing the tosylated product to react with *n*-BuLi and TMSCl to obtain triyne **52**. The unstable nature of 2,4-hexadiyn-1,6-bis(p-toluenesulfonate) presented a challenge, as the compound is known to readily polymerize.[13] In addition, this reaction is extremely moisture sensitive, as the presence of water destroys the BuLi and ultimately hinders product formation. Numerous trials of this reaction were performed—varying time, temperature, and amount of *n*-BuLi. Product yields varied greatly, with the highest yield (90%) resulting from a trial in which a new bottle of *n*-BuLi was used. This result supported the hypothesis that lithium hydroxide, which was present in older bottles of BuLi, was replacing the tosylate group and causing dimerized byproducts to form—a suggestion initially made by David Connors.

Due to the difficulty that was encountered when trying to carry out Rubin's synthesis of triyne **52**, an alternative approach was pursued which also incorporated 2,4-hexadiyne-1,6-diol as the starting material (Scheme 2.6). Subjecting propargyl alcohol to Hay coupling conditions afforded diol precursor **50** in high yield, and bromination of this compound using Werner's method was nearly quantitative to form **53**.[14, 15] A procedure described by Hlavatý and co-workers served as the basis for the synthesis of triyne **52** (Scheme 2.7), although the addition of trimethylsilyl chloride (TMSCl) and the workup was based on Rubin's work.[2, 16] One major advantage to using dibromohexadiyne **53** instead of 2,4-hexadiyn-1,6-bis(p-toluenesulfonate) (**51**) is that the former is much more stable than the latter, and can be stored in the freezer for several days. In addition, the use of *n*-BuLi is completely avoided, which eliminates the reagent condition as a variable which hindered reaction success in past attempts.



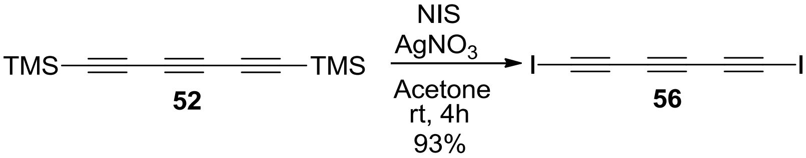
Scheme 2.6 Modified synthesis of 1,6-bis(trimethylsilyl)-1,3,5-hexatriyne (**52**)



Scheme 2.7 Hlavtý's synthesis of **56**[16]

The iodination of 1,6-bis(trimethylsilyl)-1,3,5-hexatriyne (**52**) was achieved with *N*-iodosuccinimide (NIS) and silver nitrate ($AgNO_3$) (Scheme 2.8). Although Nishikawa and co-workers reported that a catalytic amount of $AgNO_3$ and 1.2-1.5 equivalents (per silyl group) of NIS was required for the iodination of trimethylsilylacetylenes,[17] these amounts were found to be inadequate for compounds that contained multiple triple bonds. When 1 equivalent of $AgNO_3$ and 2.5 equivalents of NIS were used, the reaction did not go to completion in the 3 hour reaction time that was reported.[17] The presence of monoiodinated material ($TMSC_6I$) in the product mixture indicated that complete reaction did not occur. After several reaction trials, it was determined that 2.5 equivalents of $AgNO_3$ and 4 equivalents of NIS were necessary to ensure that complete iodination was achieved. It is critical that the reaction proceeds quickly, as the resulting diiodoalkyne (C_6I_2, **56**) is significantly less stable than its silyl-capped precursor. When iodinating longer bis(trimethylsilyl) polyynes, we observed that an even greater excess of

$AgNO_3$ and NIS is required for these compounds to complete the iodination reaction in 3-4 hours. The iodination of longer polyynes may proceed more slowly due to complexation of the silver to the internal carbon-carbon triple bonds.

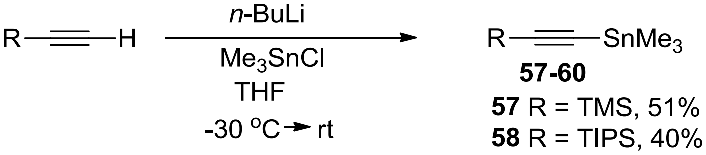


52

56

Scheme 2.8 Iodination of C_6TMS_2

Stille coupling conditions were employed for the reaction of diiodopolyyne **56** and various tin acetylides that were prepared according to literature methods (Scheme 2.9).[18] The tin reagents were purified by extraction and distillation techniques to ensure that the resulting acetylides were completely free of impurities. This rigorous purification process resulted in relatively low isolated yields of TIPS, TMS, and Ph tin acetylides.



57-60
57 R = TMS, 51%
58 R = TIPS, 40%
59 R = Ph, 55%
60 R = TBDMS, 67%

Scheme 2.9 Preparation of tin acetylides [6, 18]

The typical experimental setup for the Stille coupling reaction is illustrated in Figure 2.1 below. The diiodoalkyne and tin acetylide are dissolved in dry THF and placed in a heart-shaped flask that is wrapped with foil, and the catalyst mixture in dry THF is kept in a separate flask which is also wrapped with foil. Both mixtures are placed in separate ice (or dry ice/acetone) baths, and the diiodoalkyne/tin acetylide solution is added to the catalyst mixture via cannula.

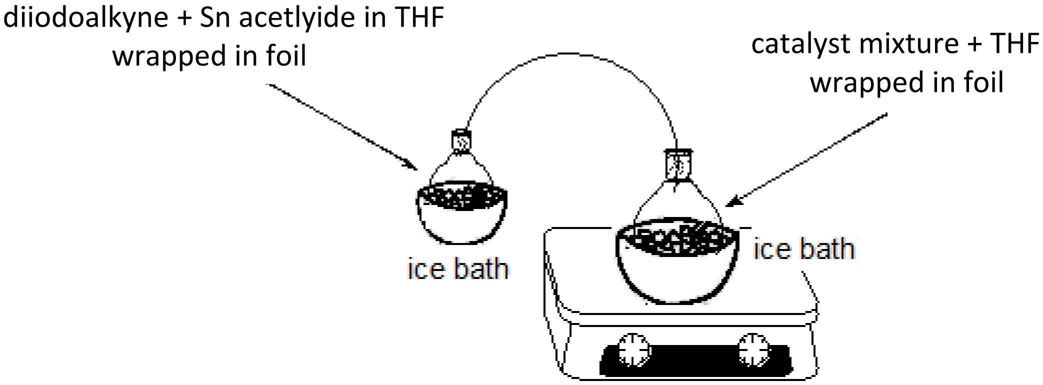
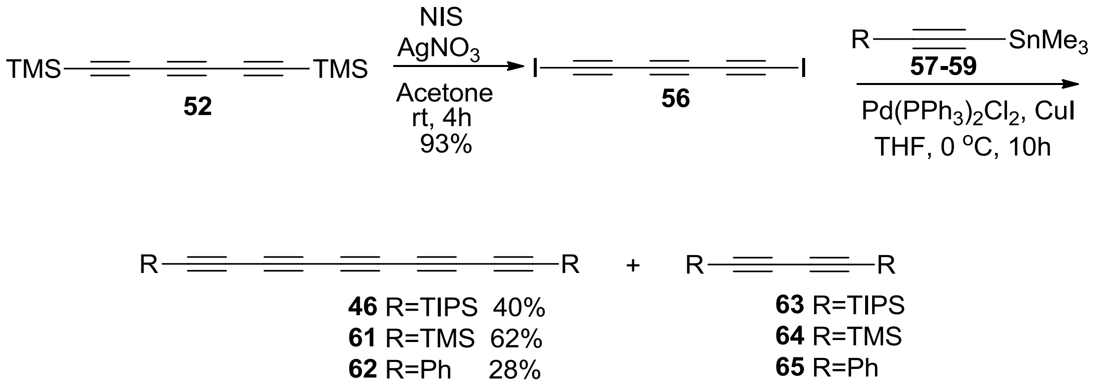


Figure 2.1 Experimental setup for Stille coupling reaction

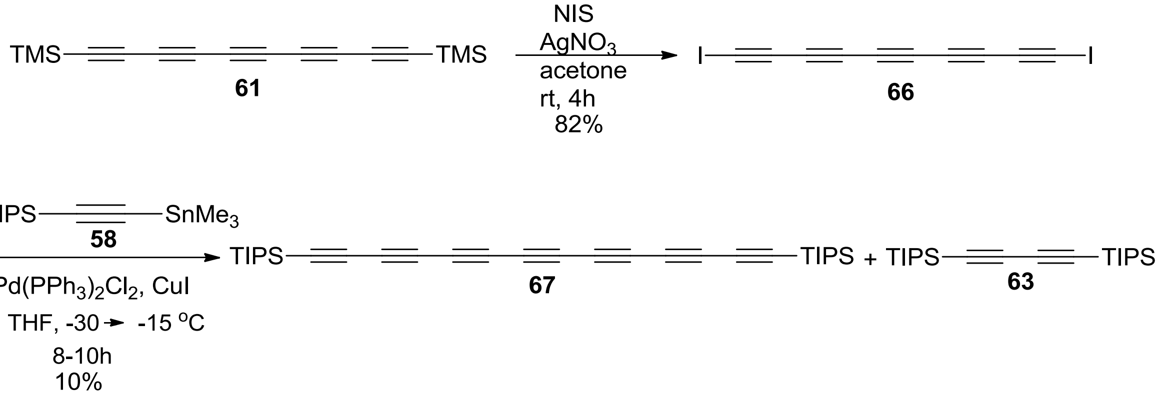
The synthesis of pentaynes from diiodohexatriyne (C_6I_2) **56** was thoroughly explored as a means of optimizing the catalyst ratio, reaction temperature, and purification methods used in the Stille coupling reaction. The synthetic route and isolated pentayne yields are outlined in Scheme 2.10. After numerous reaction trials, it was determined that the amounts of CuI and $Pd(PPh_3)_2Cl_2$ required to obtain the desired cross coupling product as the major component in the crude mixture were 23 mol% (11.5 mol% per I) and 12 mol% (6 mol% per I), respectively. Keeping the C_6I_2/tin acetylide solution in an ice bath (0 °C) for the entire reaction minimized decomposition of the diiodotriyne starting material. The reaction flask was also placed in an ice bath to decrease decomposition. When C_6I_2 reacted with trimethylsilyl tin acetylide **57**, an overall yield of 62% isolated $C_{10}TMS_2$ (**61**) was achieved, with minimal amount of homocoupled diyne present in the crude product mixture. The use of silica for chromatography also proved crucial, as trials with alumina correlated to significantly lower yields. The C_4TMS_2 that resulted from homocoupling of the organostannane was easily separated from the product by vacuum sublimation. The ability to recover the diyne and use it in future iodination reactions adds to the overall atom efficiency of this method.



Scheme 2.10 Synthesis of pentaynes

The yields for triisopropylsilyl- and phenyl-capped pentaynes ($C_{10}TIPS_2$ **46** and $C_{10}Ph_2$ **62**, respectively) were lower than that obtained for $C_{10}TMS_2$. This was mainly due to the methods required for isolation of $C_{10}TIPS_2$ and $C_{10}Ph_2$. Chromatography was used to separate $C_{10}Ph_2$ from the homocoupled diyne byproduct. Separation was difficult since the two compounds have very similar polarities and therefore move close together on silica. Many of the fractions that were collected from the column contained both products, thus decreasing the yield of pure pentayne that was isolated. To isolate $C_{10}TIPS_2$, a recrystallization method described by Li was employed, which incoporated a 1:10 mixture of chloroform/warm methanol followed by the dropwise addition of 3N hydrochloric acid.[6] This procedure was effective when Li separated C_8TIPS_2 from C_4TIPS_2, but only worked once when $C_{10}TIPS_2$ was subjected to these conditions.

The iodination of $C_{10}TMS_2$ using NIS and $AgNO_3$ resulted in the novel compound 1,10-diiodo-1,3,5,7,9-decapentayne (**66**, Scheme 2.11). This polyyne demonstrated less stability than its shorter analogs, exploding at 55-56 °C. When working with the diiodopentayne, it was crucial to keep it in solution at temperatures below 0 °C, as black insoluble material formed in solution relatively quickly at temperatures above 0 °C. When compound **66** reacted with triisopropyl tin acetylide **58**, the flask containing the diiodoalkyne was kept in a dry ice/acetone bath (between -30 and -15 ºC). $C_{14}TIPS_2$ (**67**) was successfully synthesized; however product isolation was difficult. Chromatography was required and some of the diiodopentayne decomposed over the course of the reaction, therefore only 10 % of the pure heptayne **67** was recovered.

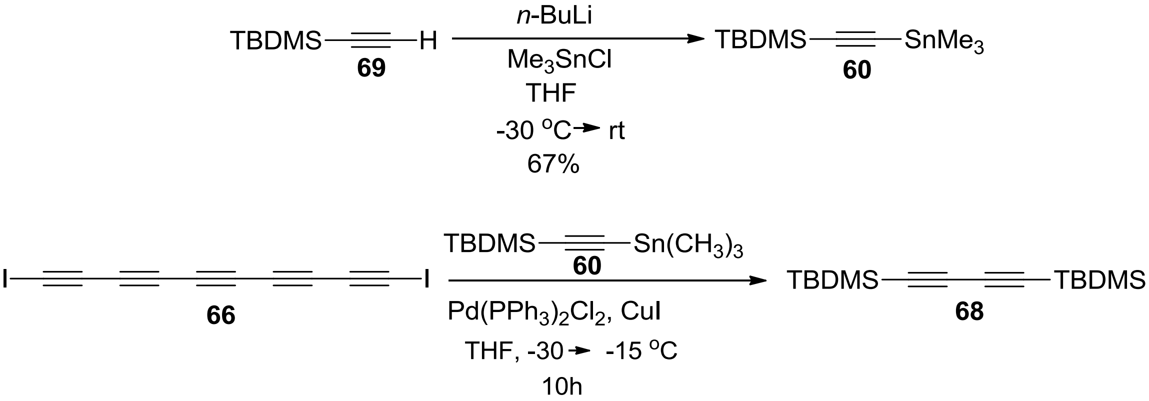


Scheme 2.11 Synthesis of $C_{14}TIPS_2$

The synthesis of $C_{14}TIPS_2$ was repeated several times, in an attempt to improve the yield of the reaction. In addition to the difficulty in separating the product chromatographically and decomposition of the starting diiodoalkyne, it was also observed that the silyl-capped polyynes have a high affinity for grease that came from the hexanes which was used for chromatography and extractions. This affinity was particularly prominent for heptaynes, as more iterations of the coupling/iodination resulted in a higher grease concentration. Since these polyynes are nonpolar, separating them from the grease was not feasible. To alleviate this issue, pentanes or HPLC grade hexanes should be used.

To further explore the effect of bulky end groups on polyyne stability, heptaynes with *tert*-butyldimethylsilyl (TBDMS) end groups were also targeted. A slight excess of *n*-BuLi was used in the synthesis of the tin acetylide (Scheme 2.12), since the boiling point of any remaining starting acetylene is too high to remove from the product mixture via vacuum distillation.

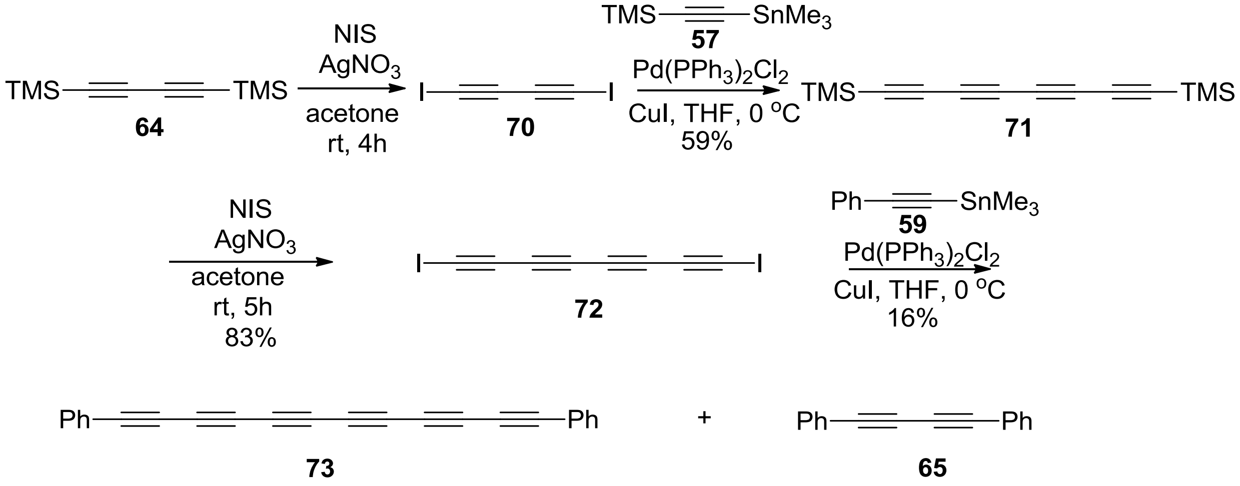
Diiodopentayne **66** was treated with *tert*-butyldimethylsilyl(trimethylstannyl)ethyne (**60**); however only homocoupled product **68** was observed. This result once again illustrates the instability of $C_{10}I_2$ and suggests that heptaynes may be the limit of this method, although there are very few alternatives for heptayne synthesis.



Scheme 2.12 Synthesis of TBDMS tin acetylide (top) and attempted synthesis of TBDMS-capped heptaynes (bottom)

2.2.2 Synthesis of Polyynes with Even Number of Carbon-Carbon Triple Bonds

Polyynes with an even number of carbon-carbon triple bonds are prepared from diiodobutadiyne (**70**), which is obtained from the iodination of commercially available bis(trimethylsilyl)butadiyne **64**. The synthesis of TMS-capped tetraynes and Ph-capped hexaynes is shown in Scheme 2.13 below. For both Stille coupling steps, 12 mol % $Pd(PPh_3)Cl_2$ and 23 mol% CuI (per mol C_nI_2) was used. The diiodoalkyne was kept in an ice bath (~0 °C) and shielded from light to prevent decomposition. In earlier syntheses of tetraynes via Lei Li's method, C_4I_2 was not kept below room temperature; however low yields that were achieved in when repeating these experiments suggested the need to limit decomposition of the diiodoalkyne by lowering the temperature. By maintaining a temperature of 0 °C, 59% of C_8TMS_2 (**71**) was isolated. This yield was a significant improvement compared to reactions that were run at room temperature. As with other TMS-capped polyynes a silica plug followed by vacuum sublimation was used for product isolation. Separating $C_{12}Ph_2$ from diyne byproduct required chromatography; thus the yield of the phenyl-capped hexayne was rather low.



Scheme 2.13 Synthesis of tetraynes and hexaynes

Optimization of the experimental conditions for the Stille coupling of diiodopolyynes and tin acetylides involved careful examination of method of addition, temperature, and catalyst ratio. In the process of developing this route, Lei Li observed that the method and rate of reagent addition were crucial to the success of the reaction.[6] She determined that adding a solution of the diiodoalkyne and tin acetylide to the catalyst mixture increased the effective catalyst concentration relative to the alkyne reactants, and as a result, the amount of cross-coupling product was also increased. When all starting materials were mixed at once, a black insoluble material formed during the reaction, suggesting the diiodoalkyne had undergone random polymerization.[6] Trials in which a solution of the diiodoalkyne, diiodobutadiyne (**70**), was slowly added to the catalyst mixture provided better results. Adding the iodoalkyne to the catalyst mixture over a period of 10-11 h proved optimal, while shorter addition times resulted in homocoupling of both the diiodoalkyne and the tin acetylide, as well as the unwanted formation of longer polyynes, as suggested by ^{13}C NMR.

The catalyst ratios were thoroughly explored when synthesizing silyl-capped pentaynes, as discussed in Section 2.2.1. In addition, model studies were conducted by Allison Black, who explored the coupling between iodophenylacetylene and trimethylsilyl tin acetylide **57**. In this model system, all three possible products—the cross-coupled diyne and both homocoupled diynes—could be identified and quantified, unlike the polymeric material that results from homocoupling of diiodopolyynes. These experiments indicated that the concentration of copper iodide is particularly important to promote cross-coupling in this reaction. The Stille coupling is a palladium-catalyzed reaction; however it has been suggested that a copper cocatalyst transmetalates with the organnostannane to form a copper acetylide, which in turn may transmetalate with palladium more quickly than the stannane alone.[19, 20] Therefore, the stannane can react faster with the diiodoalkyne, thus minimizing homocoupling of the diiodoalkyne. The results that were obtained in the model studies coincided with the experimental results for the synthesis of pentaynes, suggesting that the ideal catalyst ratios of palladium and copper are 12 mol% (6 mol% per iodine) and 23 mol% (11.5 mol% per iodine), respectively.

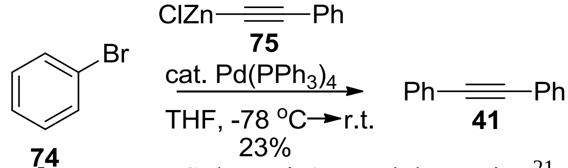
The length of the diiodopolyynes that were used in the Stille coupling determined the temperature that was required to limit decomposition. For shorter diiodopolyynes, such as diiodobutadiyne and diiodohexatriyne, a temperature of 0 ºC was sufficient. When diiodopentayne **66** was employed, however, a temperature of -15 to -25 ºC was necessary, as this compound readily decomposes at 0 ºC in solution. In addition to maintaining low temperatures, it is also important to keep the diiodoalkyne/tin acetylide solution and the reaction mixture in the dark, as the decomposition of diiodopolyynes is enhanced by light.

2.3 Alternative Coupling Methods

2.3.1. The Synthesis of Polyynes Using Negishi Coupling Conditions

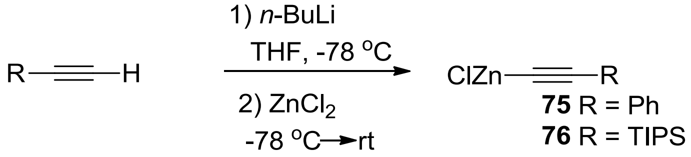
The synthesis of tetraynes has been explored by Negishi coupling conditions that were described by former group member Lei Li.[6] Unlike the Stille coupling, this method does not incorporate toxic tin reagents, thus making the Negishi coupling particularly appealing. While Li was able to synthesize TMS and TIPS-capped tetraynes using Negishi conditions, the product yields were lower than those that were obtained when using Stille coupling conditions. The only trial in which the Negishi reaction proved superior to the Stille coupling correlated to the synthesis of phenyl-capped hexayne $C_{12}Ph_2$ (**73**) which Li was able to isolate in 86% yield.[6]

Before delving into the synthesis of tetraynes from C_4I_2 (**70**), the Negishi coupling was briefly explored with a model reaction that was previously reported by Audra Selvaggio.[21] In this experiment, bromobenzene was coupled to phenylzinc acetylide, resulting in diphenylacetylene (**41**). The model reaction is shown in Scheme 2.14.[21]



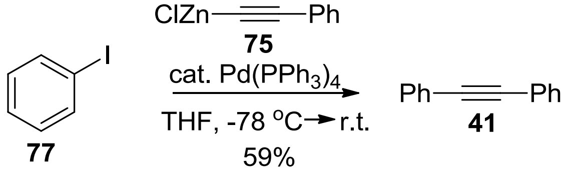
Scheme 2.14 Selvaggio's model reaction[21]

Some difficulty was encountered when trying to repeat this model reaction, due to the lack of reactivity of bromobenzene. In the first few experimental attempts, the crude product mixture was composed of bromobenzene, phenylacetylene, and diphenylbutadiyne (**65**), without any product (**41**) present. Since iodobenzene is known to be more reactive than the bromine analog, the model reaction was altered to incorporate iodobenzene. In addition to this challenge, significant difficulty was encountered when trying to form the zinc acetylides (Scheme 2.15), particularly due to zinc chloride's innate sensitivity to moisture. Any excess moisture would inhibit reaction between the lithiated acetylene and the zinc by destroying the lithiated species, therefore the $ZnCl_2$ was flame dried for about 20 minutes using a heating mantle, and kept under vacuum for about 45 minutes before being used. The white, round $ZnCl_2$ pellets would melt and re-solidify during this process, which affected the solubility of the resulting residue. To counteract any $ZnCl_2$ loss due to decomposition during heating, a slight excess of the reagent (~1.2 eq. relative to iodobenzene) was used.



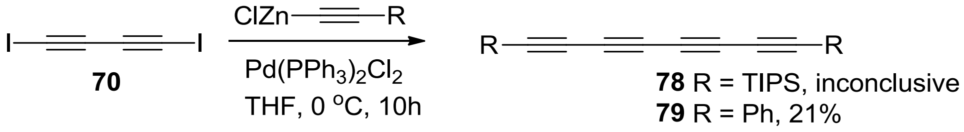
Scheme 2.15 Preparation of zinc acetylides[6]

After several repetitions of the model reaction with iodobenzene, diphenylacetylene **41** was obtained in 59%, based on NMR data (Scheme 2.16). The crude product mixture was composed of C_2Ph_2, C_4Ph_2, phenylacetylene, and iodobenzene in a ratio of 1.0 : 0.01 : 0.06 : 0.18, accounting for the two phenyl groups that are present in diphenylacetylene and diphenylbutadiyne.



Scheme 2.16 Synthesis of diphenylacetylene

Once the model reaction was successful, the focus was shifted towards the synthesis of Ph- and TIPS-capped tetraynes, using diiodobutadiyne and the respective zinc acetylides (Scheme 2.17).[6] The experimental set up for this reaction is rather complex, as the need to independently add the diiodoalkyne and zinc acetylide to the catalyst solution requires the use of two cannulas. Since Li noted the importance of adding the reagents at a specific rate, it is imperative to closely monitor the dripping to ensure the addition is occurring at a relatively consistent rate throughout the entire duration of the reaction.[6] Although Li only kept the reaction flask cold, both the diiodoalkyne and the reaction mixture were kept at 0 ºC to prevent the C_4I_2 from decomposing prior to reacting. A schematic representation of the typical experimental setup for this reaction is illustrated in Figure 2.2.



Scheme 2.17 Synthesis of tetraynes using Negishi coupling conditions

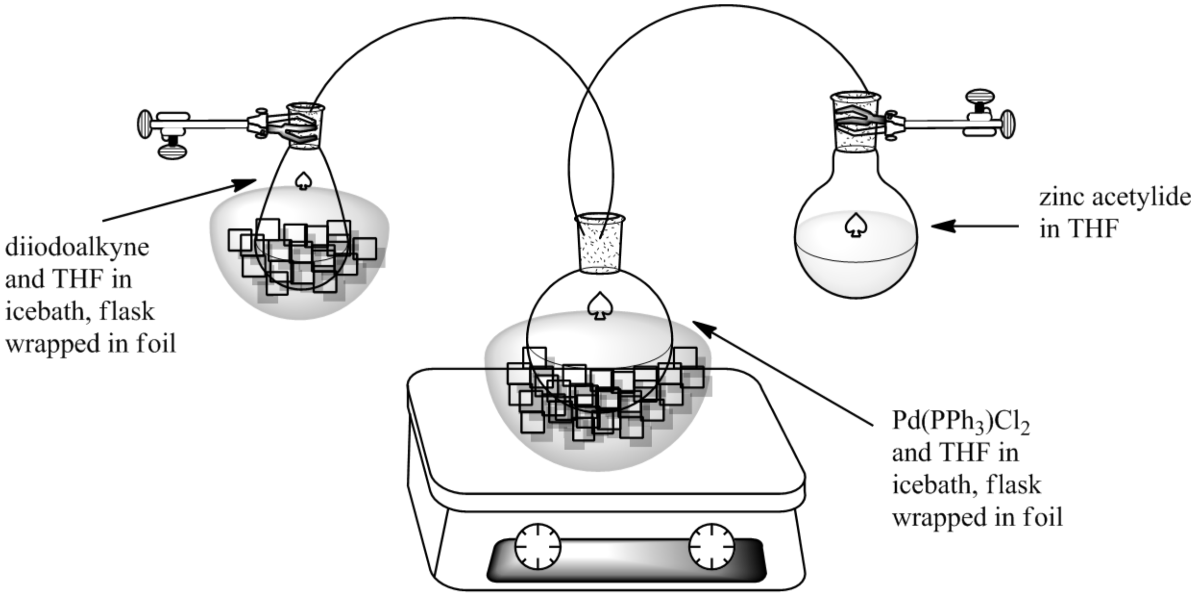
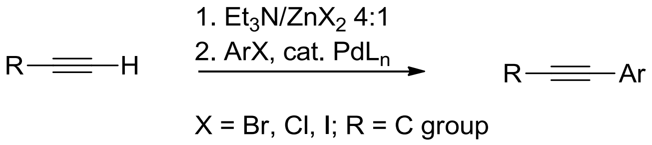


Figure 2.2 Experimental setup for Negishi coupling reaction

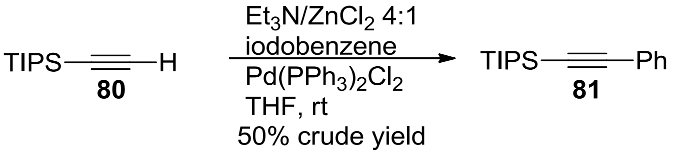
The most favorable results were obtained when phenylacetylene was coupled to diiodobutadiyne (**70**). The crude product was a mixture of the desired tetrayne, homocoupled diyne, Ph-capped hexayne, and remaining terminal acetylene, which is difficult to separate. Instead of resorting to column chromatography, the yield of C_8Ph_2 (**79**) was calculated based on the molar ratio that was determined by comparing the integration values of a phenyl carbon that was in an analogous position for all four products. The yield of C_8Ph_2 was 21%, which was comparable to Li's yields of 21% for C_8TIPS_2 and 30% for C_8TMS_2 (both determined by NMR).[6] Only one of the four trials that incorporated TIPS acetylene produced the desired tetrayne, with C_4TIPS_2 and TIPS acetylene also present in the crude mixture. Contrary to the phenyl-capped alkynes which have distinguishable ^{13}C NMR peaks, the signals in the proton and carbon NMR that correlate to the isopropyl groups for TIPS-capped alkynes are often superimposed on one another. This makes integration very difficult, and thus inhibits the calculation of a yield based on NMR spectra. In the remaining cases, TIPS acetylene was the main component of the product mixture, suggesting that the zinc acetylide did not successfully form. This result was consistently obtained, even when a new bottle of *n*-BuLi was used. These findings ultimately suggest that the formation of zinc acetylides needed to be investigated further, to ensure that the appropriate amount of reagent is available to couple to the diiodoalkyne.

The literature was explored in order to determine the feasibility of characterizing zinc acetylides before subjecting them to Negishi coupling conditions. Although not much information was obtained regarding characterization of zinc acetylides, an alternative procedure was found in which *n*-BuLi was replaced with triethylamine (Scheme 2.18).[22] This procedure was particularly appealing, because it claimed to eliminate the need for any flame drying or other rigorous moisture removing preparation steps.



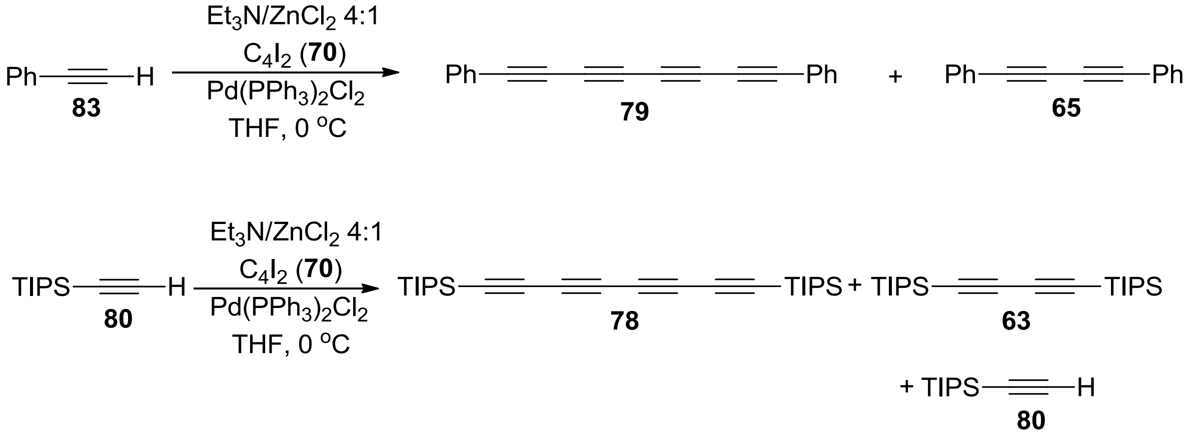
Scheme 2.18 Alternative Negishi coupling[22]

Before applying these reaction conditions to the synthesis of tetraynes from C_4I_2 (**70**), model reactions were performed with iodobenzene. Replacing C_4I_2 with iodobenzene allowed for any unreacted starting material to be visible in the crude product mixture, as the latter does not decompose into material that cannot be characterized. Both zinc bromide and zinc chloride were employed in several reaction trials; however better results were obtained with zinc chloride (Scheme 2.19).

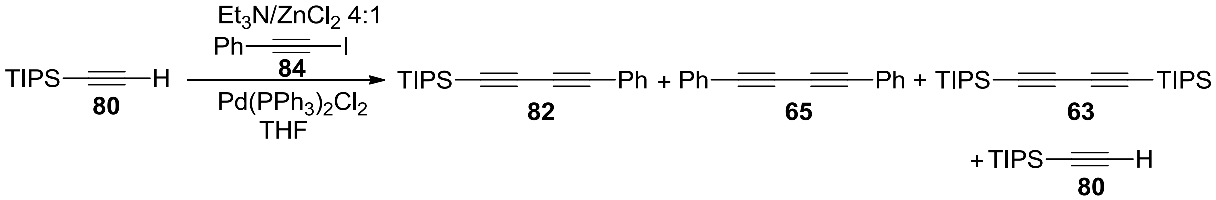


Scheme 2.19 Model alternative Negishi coupling

Once success was achieved with the model reaction, the modified Negishi conditions were applied to the synthesis of tetraynes (Scheme 2.20). When phenylacetylene was employed in this reaction, the crude material was a mixture of the desired tetrayne **79** and bis(diphenyl)butadiyne (**65**). The ratio of C_8Ph_2 to C_4Ph_2 was 1.00 to 0.76, based on the ^{13}C NMR spectrum that was obtained for the crude mixture. Several trials were also conducted using triisopropylsilyl acetylene, however the ratio of products in the crude mixture was difficult to determine due to overlapping peaks in both the ^{1}H and ^{13}C NMR spectra. It was also interesting to note that in some cases, iodotriisopropylsilyl acetylene was present in the crude product mixture—a result that was not anticipated and suggested possible decomposition of C_4I_2. In an attempt to gain some insight into this result, the reaction was repeated with iodophenylacetylene instead of C_4I_2. The crude product mixture contained the desired phenyltriisopropylsilylbutadiyne (**82**), as well as bis(diphenyl)butadiyne (**65**), bis(triisopropylsilyl)butadiyne (**63**), and triisopropylsilyl acetylene (**80**) (Scheme 2.21).



Scheme 2.20 Synthesis of tetraynes using modified Negishi coupling conditions

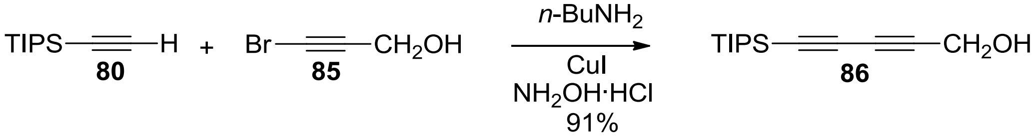


Scheme 2.21 Further exploration of Negishi coupling

The results that were obtained for the synthesis of tetraynes by Negishi coupling conditions suggested the reaction was not as efficient as the Stille coupling, which reaffirmed the results that were obtained by Li.[6] While this method avoids the use of tin reagents, the crude product mixtures that resulted from Negishi reactions contained more byproducts and starting material than the Stille coupling. Product isolation was very difficult, and therefore, this method will not be pursued any further.

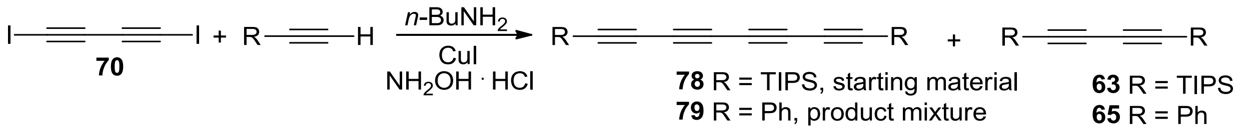
2.3.2 The Synthesis of Polyynes Using Cadiot-Chodkiewicz Coupling Conditions

The Cadiot-Chodkiewicz reaction was attempted with C_4I_2 (**70**) and different terminal acetylenes, in hopes of determining an alternate means of coupling alkynes that does not involve tin. A procedure outlined by Marino and Nguyen was used as a reference in the first set of experiments, as they reported the coupling of silyl protected acetylenes with various bromoalkynes in high yield (Scheme 2.22).[23]



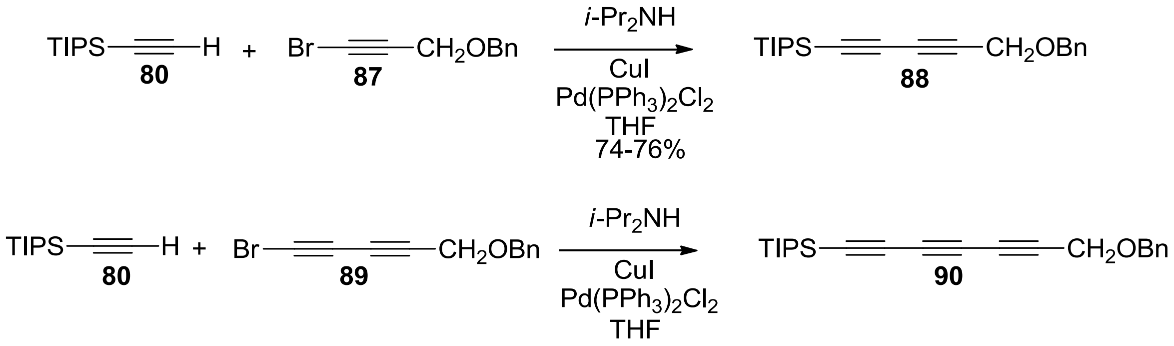
Scheme 2.22 Cadiot-Chodkiewicz coupling reported by Marino and Nguyen[23]

Cadiot-Chodkiewicz conditions were applied to the synthesis of symmetric polyynes. Diiodobutadiyne (**70**) reacted with phenylacetylene in the presence of *n*-$BuNH_2$, CuI, and hydroxylamine hydrochloride (Scheme 2.23). A mixture of C_4Ph_2 and C_8Ph_2 was obtained, and it was difficult to determine the product ratio, as peaks in the aromatic region overlapped. This reaction was also attempted with TIPS acetylene, as the literature reported better results compared to phenylacetylene.[23] Unfortunately, only unreacted starting material was visible in the NMR spectra for both trials that were performed. This result implied that the reaction time suggested by the literature was too short for the alkynes that were incorporated.



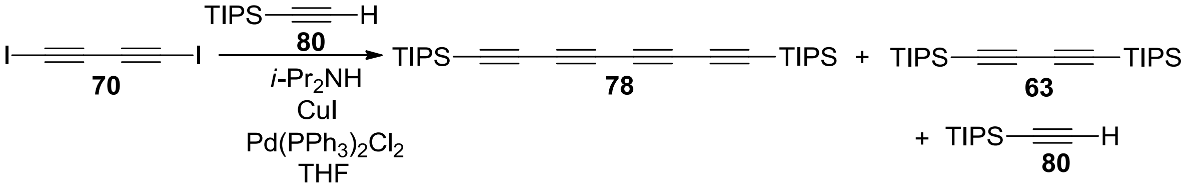
Scheme 2.23 Cadiot-Chodkiewicz coupling attempt with C_4I_2

To further explore the possibility of using the Cadiot-Chodkiewicz reaction, a modified version was attempted, based on a procedure described by Hwang and co-workers.[24] In this method, diisopropylamine was used instead of *n*-$BuNH_2$ and $Pd(PPh_3)_2Cl_2$ was incorporated in addition to CuI (Scheme 2.24).[24] While the reported yield for the diyne product was rather high, there was a significant decrease in the yield when a triyne was targeted.[24] These results suggest that polyyne stability and chain length are inversely related—a concept that is supported by the yields that were obtained for the polyynes synthesized via Stille coupling conditions.



Scheme 2.24 Cadiot-Chodkiewicz coupling reported by Hwang and co-workers[24]

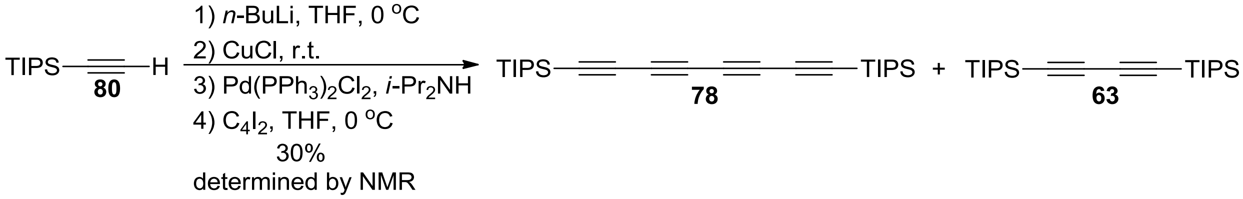
When subjecting C_4I_2 and triisopropylsilyl acetylene to the Cadiot-Chodkiewicz conditions reported by Kim and co-workers, mixed results were obtained (Scheme 2.25). NMR spectra of the crude product contained only peaks for C_4TIPS_2 in the first 2 trials, and a mixture of C_4TIPS_2, C_8TIPS_2, and TIPS acetylene for the third trial (which involved dropwise addition of C_4I_2 and the terminal acetylene to the catalyst mixture). The results that were obtained suggested that both sets of Cadiot-Chodkiewicz conditions that were explored were not effective when trying to couple to C_4I_2.



Scheme 2.25 Attempted synthesis of C_8TIPS_2 using Hwang's method

In addition to the work that was previously described, the Cadiot-Chodkiewicz coupling reaction was thoroughly explored by Allison Black. Before applying the coupling conditions to diiodobutadiyne, model studies were conducted with iodophenyl acetylene and terminal silyl acetylenes, thus allowing all homocoupled byproducts to be observed and quantified. Various bases, catalysts, temperatures, solvents, and reaction times were explored, until conditions for almost complete selectivity of the cross-coupled product were determined. The results of the model reaction indicated that adding sodium thiosulfate to reduce any I_2 that is generated *in situ*, minimized the amount of homocoupled byproducts that are observed. In addition, the use of piperidine as the amine base and hydroxylamine hydrochloride to ensure that the copper remains in the +1 state promoted heterocoupling of iodophenyl acetylene and TIPS acetylene. These experimental conditions were applied to the coupling of diiodobutadiyne; however no clear trend was observed and statistical mixtures of cross-coupled diyne, and homocoupled byproducts were consistently obtained. Instead, the conditions outlined by Kim and co-workers were most favorable for promoting the cross-coupling of diiodobutadiyne and TIPS acetylene.

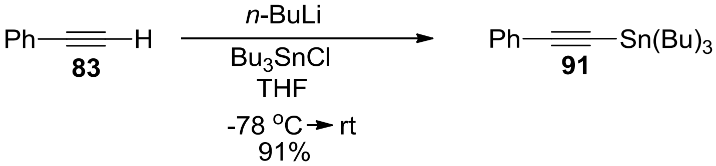
Black further examined variations of Cadiot-Chodkiewicz coupling reactions in which copper acetylides were formed in *situ*, and subsequently coupled to iodoalkynes. The copper acetylides were prepared from triisopropylsilyl acetylene by the methods described by Cataldo[9] and Hirsch.[25] While the conditions reported by Hirsch (Scheme 2.26) yielded more promising results, the amount of cross-coupling that was observed remained inferior compared to the Stille coupling. Upon very thorough examination of the Cadiot-Chodkiewicz coupling reaction, it was decided that the Stille coupling is the most effective method for the symmetric double coupling to diiodopolyynes.



Scheme 2.26 Synthesis of **78** by Hirsch's method[25]

2.4 Expanding the Scope of the Stille Coupling Reaction

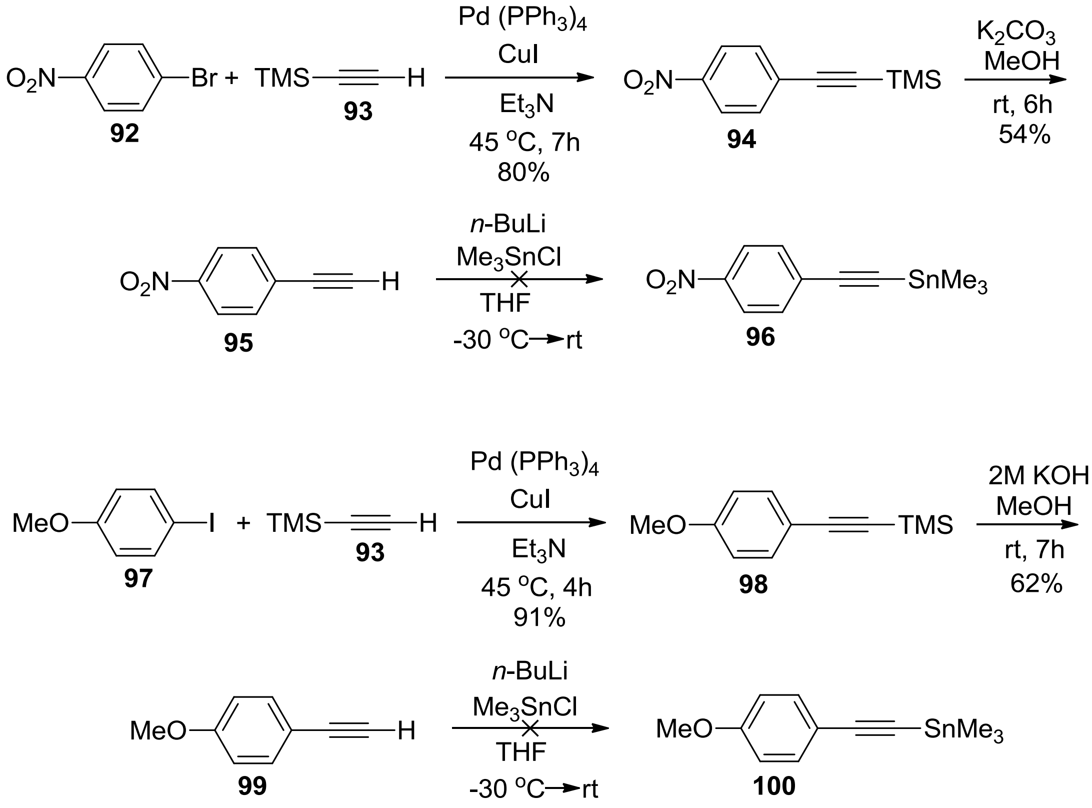
The Stille coupling reaction was further explored to determine the scope of polyynes that could be obtained using this method. In initial modifications, the Stille coupling reaction was performed using tributyltin acetylides, which were prepared from tributyl tin chloride (Bu_3SnCl), in place of Me_3SnCl that was used in previous reactions. The stability and low volatility of tributyl tin chloride compared to its trimethyl counterpart makes the compound more desirable to work with, particularly due to the adverse health effects associated with tin reagents in general. The synthesis of phenyl(tributylstannyl)ethyne (**91**) was similar to the procedure used with trimethyltin chloride, shown in Scheme 2.27.[26]



Scheme 2.27 Preparation of phenyl(tributylstannyl)ethyne (**91**)[26]

One of the difficulties encountered when using tributyl(phenyl)tin acetylide **91** in the Stille coupling reaction with C_4I_2 was trying to remove tin byproducts from the resulting C_8Ph_2/C_4Ph_2 mixture. The literature suggested the use of cesium fluoride (CsF) when working with tributyl tin compounds as a means of eliminating unwanted tin compounds from the product mixture. Various amounts of CsF were added to the catalyst mixture in several experimental trials.[27] Unfortunately, even when nearly 10 equivalents of CsF (relative to the amount of tin) were used, the product mixture contained excess material derived from the tin acetylide, as demonstrated by NMR spectra which had peaks corresponding to butyl groups. Additional attempts involved adding excess CsF to the reaction mixture after the addition of the diiodoalkyne/tin acetylide solution was complete and stirring overnight; however the undesired material was still present in the product mixture. While tributyl tin compounds may be better to work with in regards to health and safety, the difficulty in removing excess material derived from these compounds suggests that they will not replace the trimethyltin acetylides that have been typically used in the Stille couplings performed thus far.

To further explore the versatility of the Stille coupling reaction, the synthesis of phenyltin acetylides containing electron withdrawing and electron donating groups was pursued. Nitrophenyl- and methoxyphenyl acetylene were synthesized based on procedures described by Lei Li, which were then subjected to the same conditions used for preparing the other tin acetylides that have been used thus far (Scheme 2.28).[6]

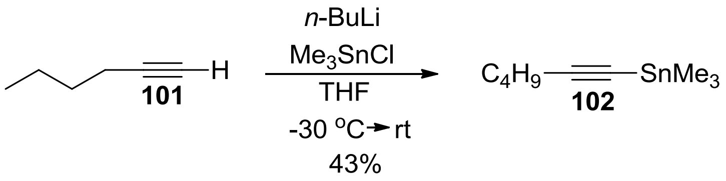


Scheme 2.28 Synthesis of substituted phenyltin acetylides[6,18,28, 29]

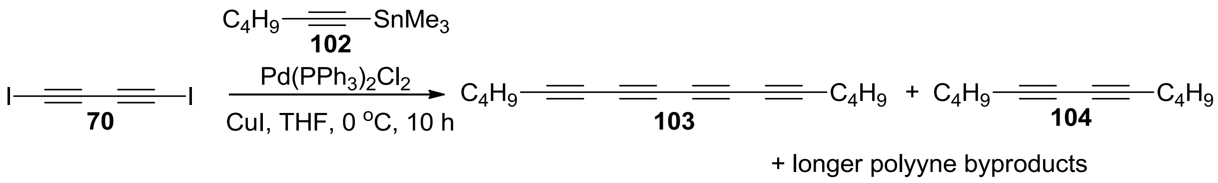
Despite the numerous attempts to make compounds **96** and **100**, NMR data for all reaction trials suggested the presence of the unreacted terminal acetylenes **95** and **99**, even when excess *n*-BuLi or *t*-BuLi was used. Fresh *n*-BuLi provided the same results that were obtained in other trials. It was particularly surprising to find that the electron-poor nitro-substituted acetylene was not easily deprotonated, although difficulty that was encountered with the methoxy compound was also unexpected since the exact procedure was reported in the literature.[18] While the synthesis of the desired acetylenes proceeded rather smoothly the reaction of the substituted acetylenes with trimethyltin chloride did not go to completion, despite many variations in conditions and reaction times. Due to the toxicity of the tin reagents used in these reactions, additional time was not allotted to preparing these electron rich and electron poor tin acetylides.

Tetraynes with long alkyl and polyethylene glycol (PEG) end caps were also targeted, via the coupling of diiodobutadiyne and the appropriate tin acetylides. These end groups were initially chosen as a means of studying the effect that they would have on the aggregation behavior of polyynes. Both trimethyl- and tributyltin chloride were employed in the synthesis of the tin acetylides, however much difficulty was encountered when attempting to remove tributyltin byproducts from the crude product mixture, which was consistent with previous experimental results.

The synthesis of tetraynes with alkyl end groups was attempted by the Stille coupling of diiodobutadiyne with alkyl-substituted tin acetylides (Scheme 2.30). In the initial experimental trials, 1,8-dibutyl-1,3,5,7-octatetrayne (**103**) was targeted, as the synthesis of this compound had been previously reported with the copper catalyzed dimerization of 1-butyl-1,3-butadiyne.[30, 31] To prepare the tin acetylide **102** required for our method, 1-hexyne reacted with *n*-BuLi and $SnMe_3Cl$, as shown in Scheme 2.29 below. The resulting tin acetylide reacted with diiodobutadiyne under the Stille coupling conditions that have been previously optimized.

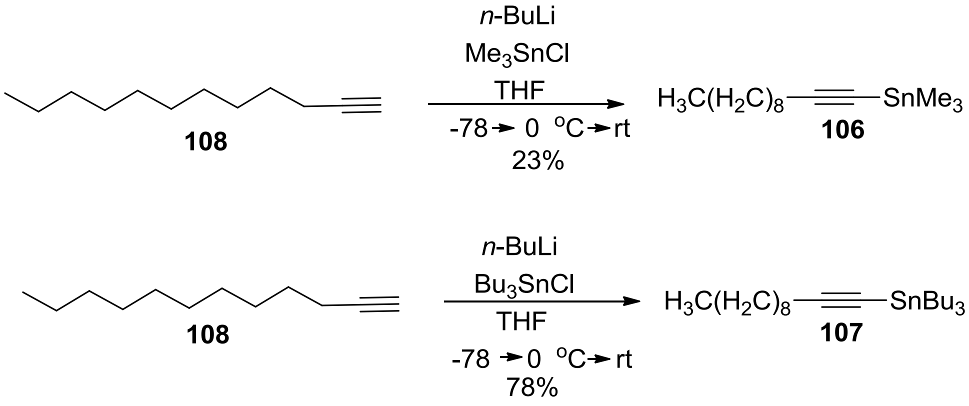


Scheme 2.29 Synthesis of 1-(trimethylstannyl)-1-hexyne[32]



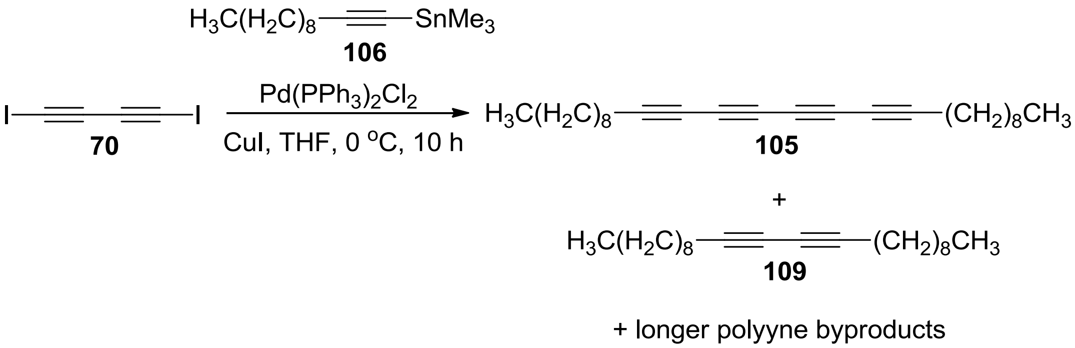
Scheme 2.30 Synthesis of 1,8-dibutyl-1,3,5,7-octatetrayne **103**

Rather than pursue the synthesis of model compound **103**, a tetrayne with longer alkyl end groups (**105**) was targeted. As with the butyl-capped analog, the first step in this synthetic route involved making the required tin acetylide. Both trimethyl- and tributyltin chloride were used to synthesize the corresponding tin acetylides (**106** and **107**, respectively). The synthesis of **106** and **107** is shown in Scheme 2.31. Despite the increased reaction time, excess terminal acetylene, (1-undecyne **108**) was always present in the product mixture. A larger amount of terminal acetylene remained when trimethyltin chloride was used, so vacuum distillation was used to remove 1-undecyne. The high boiling point of the tin acetylide allowed the product to remain in the flask, which was rinsed with hexanes and concentrated *in vacuo* to isolate the product. During this process, some of the tin acetylide often mixed in with the terminal acetylene, resulting in relatively low product yields for compound **106.**



Scheme 2.31 Synthesis of alkyl tin acetylides **106** and **107**[26, 32]

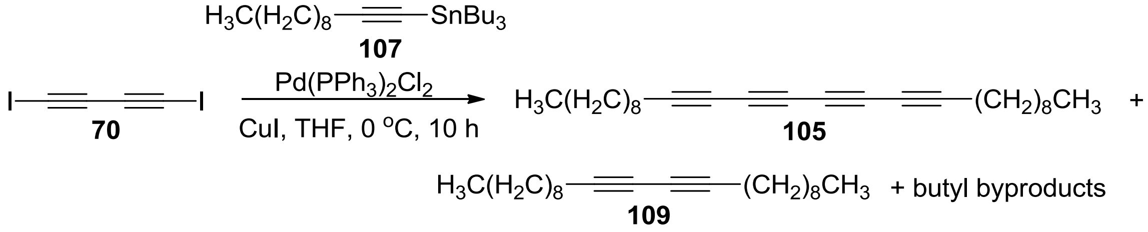
Tin acetylides **106** and **107** were employed in Stille coupling reactions with diiodobutadiyne, using the optimum palladium and copper catalyst ratios that were determined during when exploring the synthesis of silyl-capped polyynes. The synthesis of tetrayne **105** from **106** is shown in Scheme 2.32. In addition to the desired tetrayne and diyne byproduct that typically results from these coupling reactions, additional peaks in the alkynyl region (60-65 ppm) were visible in the ^{13}C NMR spectrum, suggesting the formation of longer polyynes (particularly hexaynes). We saw this phenomenon before when synthesizing bis(trimethylsilyl)octatetrayne (**71**) from diiodobutadiyne (**70**) and trimethyl((trimethylstannyl)-ethynyl)silane (**57**), thus suggesting that addition of the diiodoalkyne/tin solution to the catalyst mixture was too fast.



Scheme 2.32 Synthesis of **105** with trimethyltin acetylide **106**

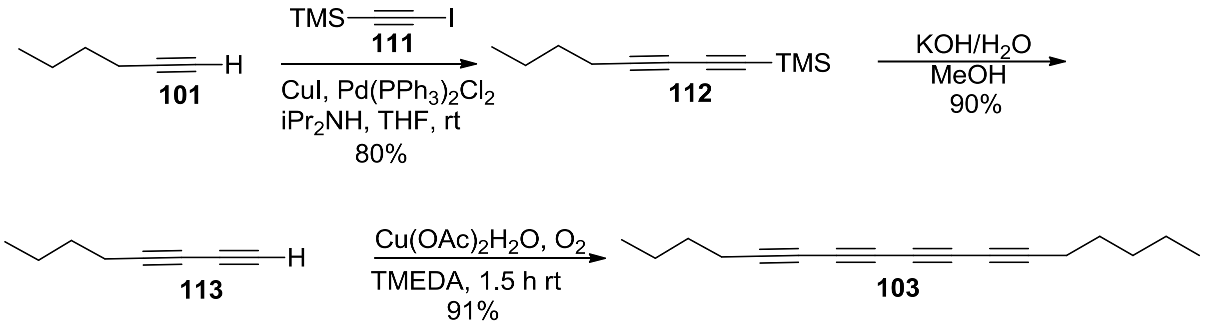
Additional trials were performed, trying to monitor the addition as closely as possible; however the crude product mixture always appeared to contain a larger amount of the homocoupled diyne byproduct **109** compared to the desired tetrayne. In several trials that were performed, the crude yields based on the total recovered mass were less than 40%. Since the diiodobutadiyne/tin reagent solution was kept in an ice bath, decomposition of the starting material should have been minimal. This implies that the long alkyl chain on the tin acetylide may have caused aggregation resulting in decomposition, which may account for some of the mass lost.

The synthesis of tetrayne **105** was also attempted using tributyltin acetylide **107** (Scheme 2.33). Although this tin acetylide was produced in significantly higher yield than **106**, much difficulty was encountered when trying to remove the butyl byproducts from the crude product mixture. Numerous techniques were applied, based on procedures for removal of tributyltin byproducts that were outlined by the Department of Chemistry at the University of Rochester.[33] The addition of cesium or potassium fluoride was not successful, and stirring the reaction with aqueous sodium hydroxide to increase the polarity of the tin byproducts was also ineffective. A plug that used triethylamine as the eluent was also attempted; however all of these methods failed to remove the tin byproducts, as extra peaks corresponding to butyl groups were visible in the ^{13}C NMR spectrum of the crude product mixture. Since both the desired product and butyltin byproducts are nonpolar, separation was not achieved.

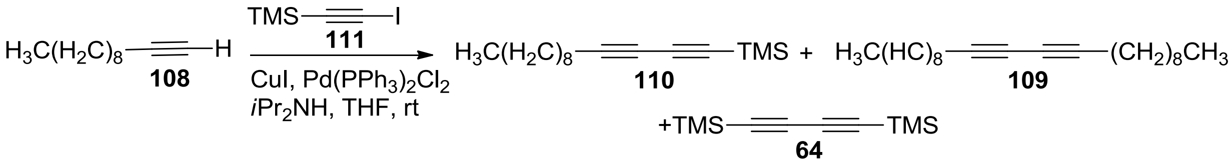


Scheme 2.33 Synthesis of **105** with tributyltin acetylide **107**

Since the Stille coupling reaction gave a mixture of products, an alternative route towards **105** was explored, based on procedures outlined by Olesik and co-workers for the synthesis of tetrayne **103** (Scheme 2.34).[31] When coupling 1-undecyne and iodo trimethylsilyl acetylene by the conditions previously described, a mixture of the desired cross coupled product (**110**), along with the diynes that resulted from homocoupling of both the terminal acetylene and iodotrimethylsilyl acetylene (**109** and **64**, respectively) was produced (Scheme 2.35). While these coupling conditions have proven effective when coupling propargyl amines to brominated silyl acetylenes, that system contained a terminal alkyne and halo alkyne with different electronics and polarities. The results obtained in this lab have suggested that the selectivity of this particular coupling reaction is determined by the electronics of the alkynes, and that cross coupling is favored when these characteristics differ between the starting alkynes. Since a mixture of products was obtained, and the desired cross coupled product was not the major component of the crude mixture, this method was not pursued any further for the synthesis of tetrayne **105**.

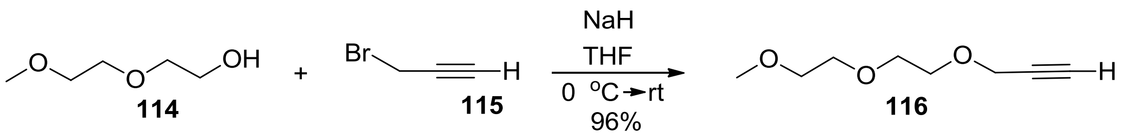


Scheme 2.34 Synthesis of tetraynes reported by Olesik[31]

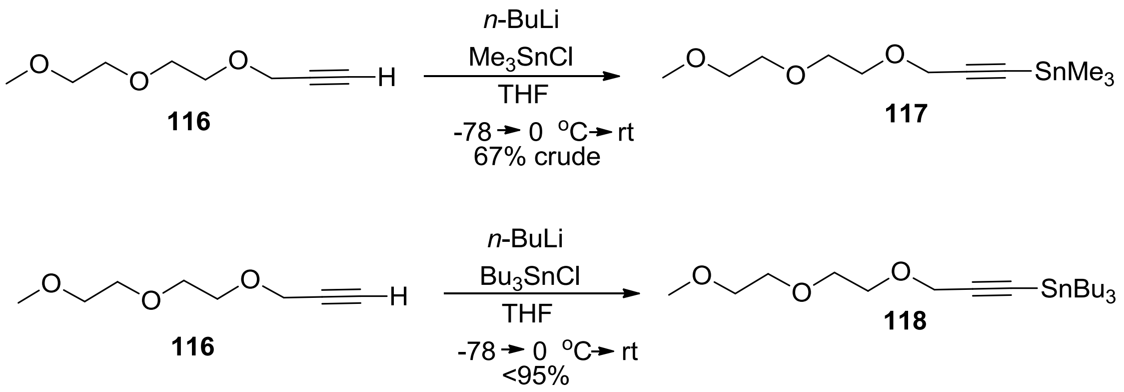


Scheme 2.35 Synthesis of **110**

PEGylated tetraynes were also pursued, as the electron donating nature of these groups would make the aggregation behavior of these compounds interesting to study. The first step towards preparing the appropriate tin acetylides (**117** and **118**) involved reacting diethyleneglycol monomethyl ether with sodium hydride and propargyl bromide, resulting in 3-[2-(2-methoxy-ethoxy)-ethoxy]-propyne **116** (Scheme 2.36).[24] Alkyne **116** then reacted with trimethyl- and tributyltin chloride, and the tributyltin acetylide was produced in higher yield with only a minimal amount of terminal acetylene remaining in the crude product mixture (Scheme 2.37).

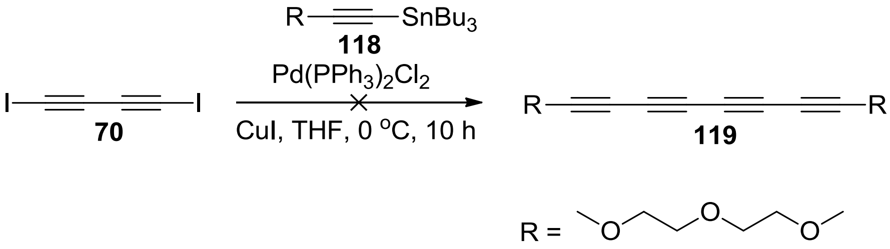


Scheme 2.36 Synthesis of **116**[24]



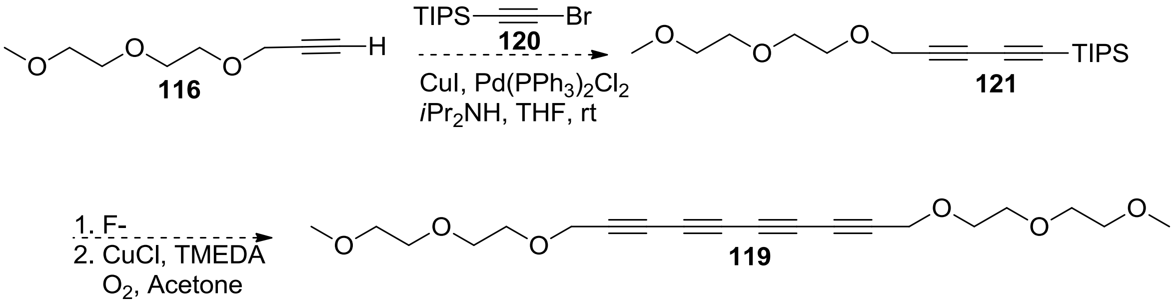
Scheme 2.37 Synthesis of diethyleneglycol monomethyl ether tin acetylides **117** and **118**[26]

Tributyltin acetylide **118** was easier to prepare and presumably less toxic than **117**, therefore it was employed in the Stille coupling reaction in an attempt to form tetrayne **119** (Scheme 2.38). The difference in polarity between the target tetrayne and any tributyltin byproducts in the crude product allowed for facile elimination of the unwanted butyl byproducts chomatrographically; however the ^{13}C NMR spectra that resulted after numerous reaction trials did not confirm the presence of tetrayne in the crude product. The peaks corresponding to the ethylene groups in the diethylene glycol chain were visible, as well as the terminal methyl group, but there was no indication of alkynyl carbons (60-80 ppm).



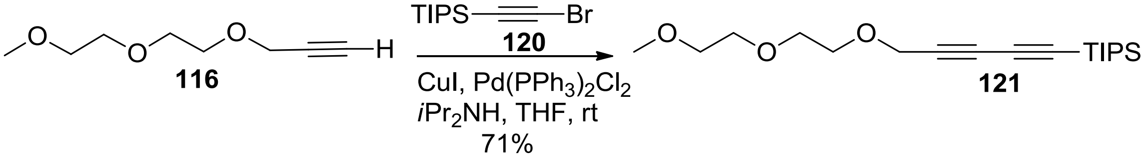
Scheme 2.38 Attempted synthesis of tetrayne **119**

An alternative route was explored, which featured cross-coupling conditions based on work by Hwang and co-workers,[24] followed by a Hay coupling reaction (Scheme 2.39). Both of these reactions have been successful in our hands, hence they were chosen as an alternative means to form **119**.



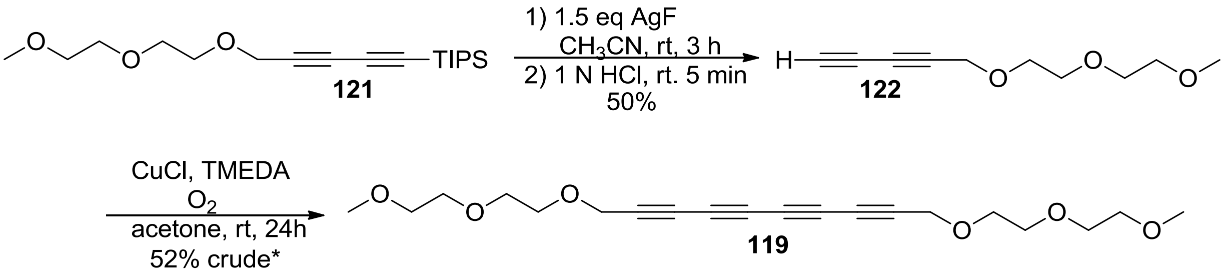
Scheme 2.39 Alternative route towards **119**

The coupling between alkyne **116** and bromotriisopropylsilyl acetylene **120** proceeded smoothly, in moderate yield (Scheme 2.40). A small amount of bis(triisopropylsilyl)butadiyne (**63**) formed from homocoupling of **120**; however this was easily removed with a short plug (SiO_2/hexanes).



Scheme 2.40 Synthesis of **121**[24]

The next step in this route was removal of the TIPS group to form the terminal diyne that will be used in the Hay coupling reaction (Scheme 2.41). To form terminal diyne **122**, silver fluoride was used, based on a procedure outlined by Kim and co-workers.[34] The final step towards tetrayne **119** involved the Hay coupling of terminal diyne **122**, which proceeded in moderate yield; however black insoluble material in the crude product mixture suggested some decomposition of the terminal diyne had occurred.



Scheme 2.41 Synthesis of PEGylated tetrayne **119**

2.5 Spectroscopic Studies of Polyyne Aggregation

Studying the effect of aggregation can provide information regarding the properties of bulk material. Previous group members obtained UV-Vis spectra for poly(diiododiacetlyene) (PIDA), which demonstrated absorbance at longer wavelength (above 600 nm).[35] Aggregation of the polymer chains was considered a possible cause of these longer wavelength absorption peaks. UV-Vis studies of tetraynes and pentaynes were pursued to gain information regarding polyyne aggregation behavior. UV-Vis spectra of polyynes have demonstrated an increase in λ_{max} in accordance with the number of carbon-carbon triple bonds, a trend which indicates the HOMO-LUMO bandgap energy decreases with increasing conjugation.[3, 5] These observations suggested that the λ_{max} for C_8TMS_2 (**71**) and $C_{10}TIPS_2$ (**46**) should be above 250nm.[4]

The first set of UV-Vis experiments that were performed encompassed solutions of C_8TMS_2 in hexanes with varying concentrations. Spectra for solutions 1-20 that were prepared in decreasing concentrations are shown below. Plots of absorbance as a function of concentration for the peaks at 228, 280, and 392 nm showed linear trends, in accordance with Beer's Law (Figure 2.4).

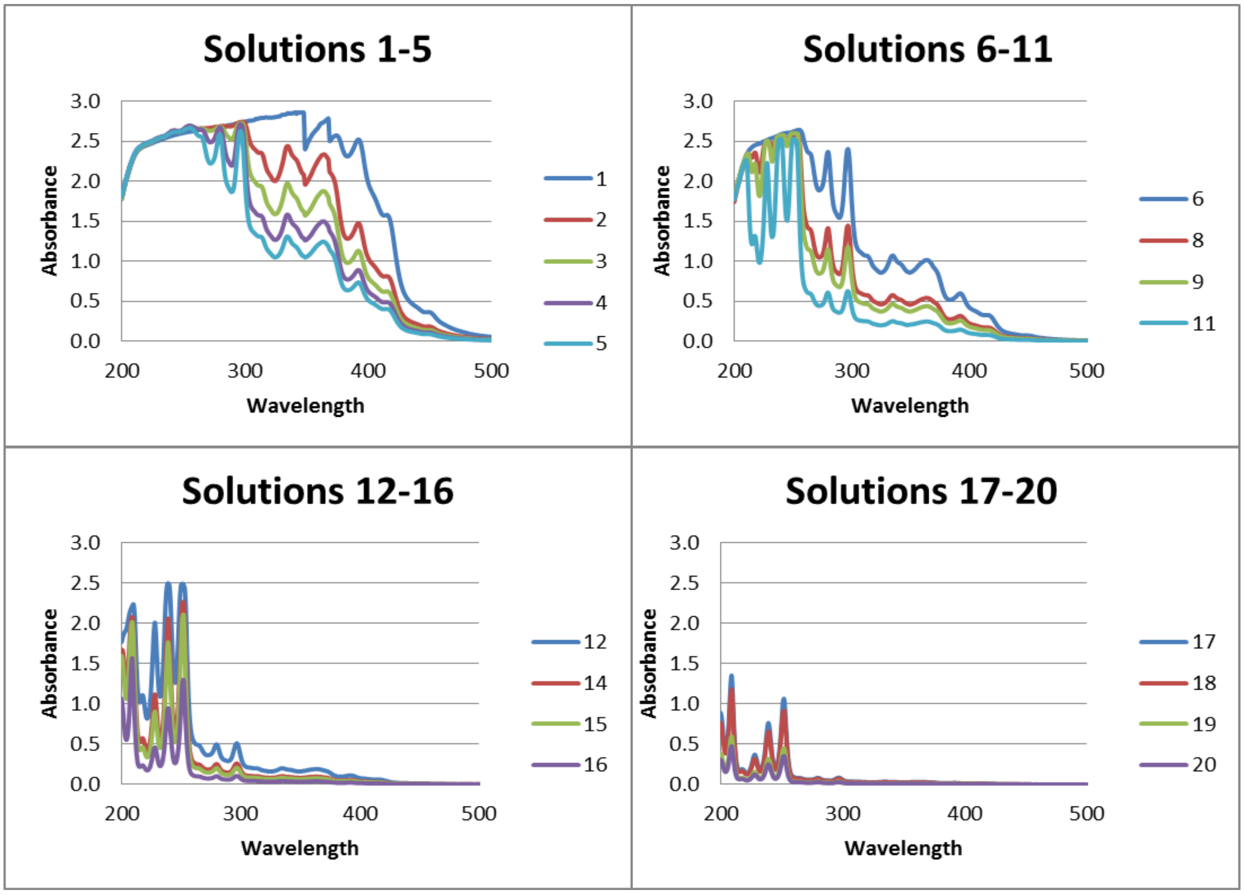


Figure 2.3 UV-Vis absorption spectra for solutions of C_8TMS_2 in hexanes

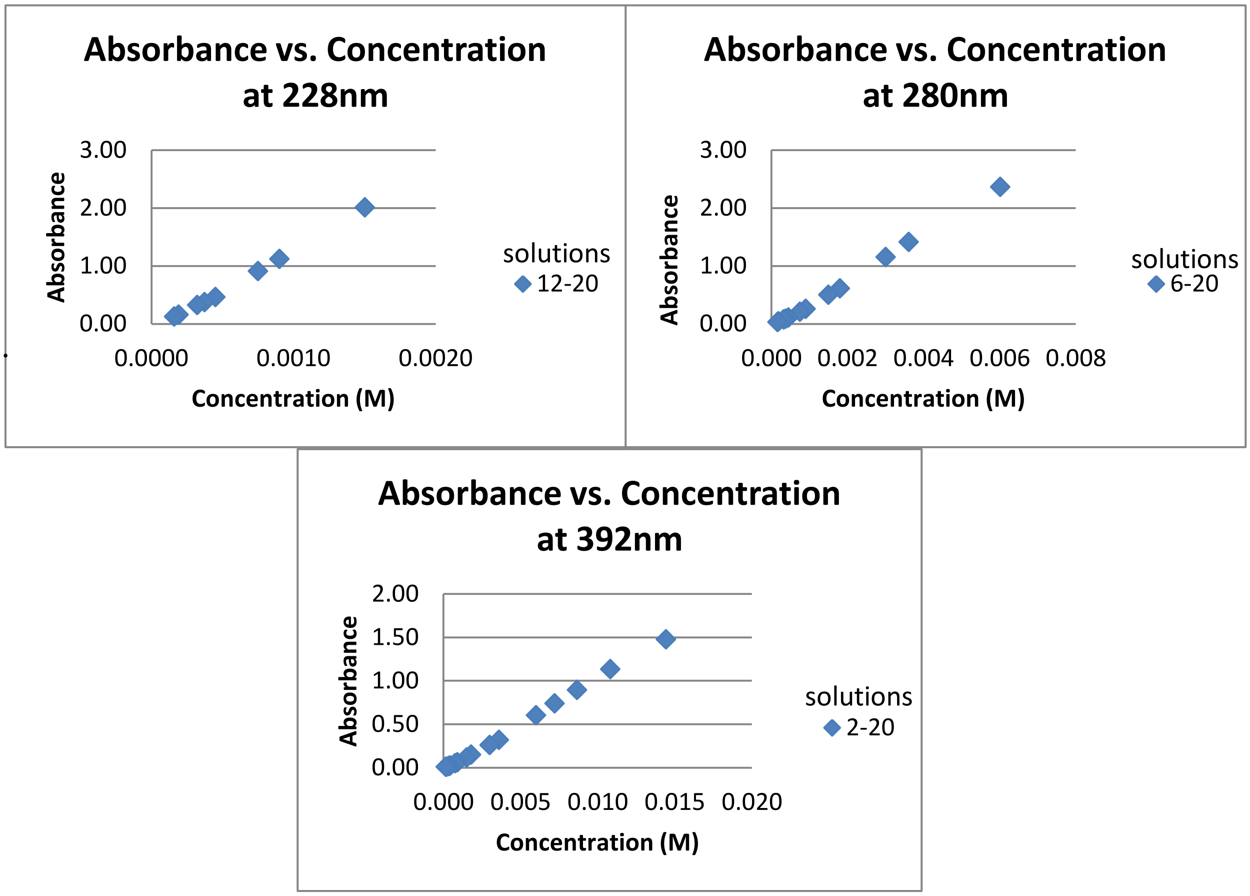


Figure 2.4 Absorbance vs. concentration for 228, 280, and 392 nm

The ratio between the absorbance values at these wavelengths for solutions of different concentrations were explored to gain some insight regarding aggregation behavior. Since peaks at longer wavelengths were thought to be attributed to aggregation, a simultaneous decrease in absorbance at 228 nm and increase at 280 or 392 nm as the concentration increased may provide some evidence that the peaks at longer wavelengths are a product of aggregation. When looking at the graphical representations of these ratios, the ratio between A_{280} and A_{228} increases with concentration, thus indicating that the absorbance at 280 nm is increasing as concentration increases (Figure 2.5). Comparison between A_{392} and A_{280} did not show much change as the solutions became more concentrated, while the ratio between the absorbance at 392 nm and 228 nm seems to be proportional to concentration. This observation may support the idea that the peak at 392 nm is becoming relatively larger while the one at 228 nm is decreasing due to an increase in aggregation that would be found in a more concentrated solution; however more data is needed before any conclusions can be drawn.

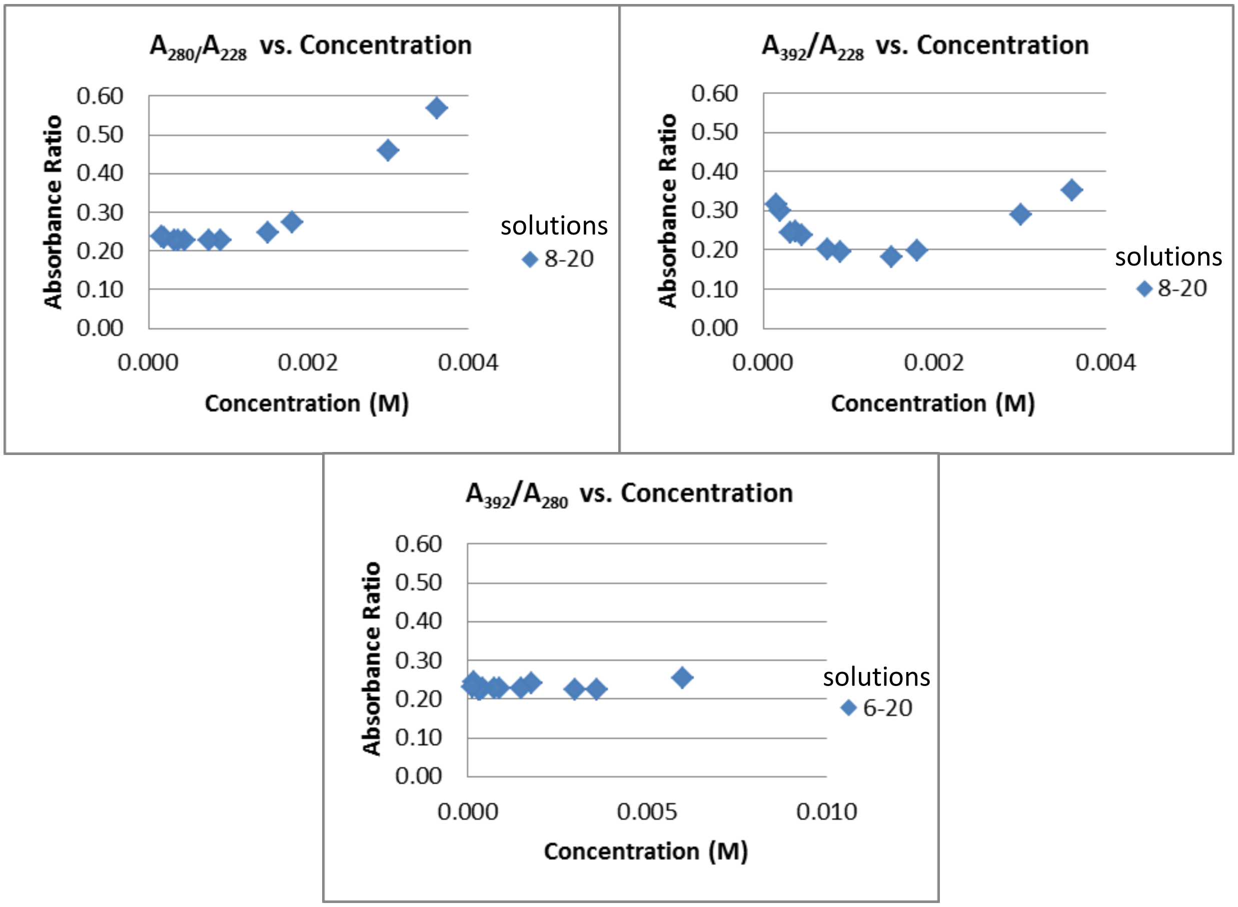


Figure 2.5 Absorbance ratios vs. concentration for 228, 280, and 392 nm

To further explore the relationship between concentration and aggregate formation, additional studies were conducted in the same manner using $C_{10}TIPS_2$ (**46**). Plots of absorbance as a function of concentration for the peaks at 231, 394, and 441 nm (Figure 2.6) once again depicted linearity, as observed with C_8TMS_2 (**71**).

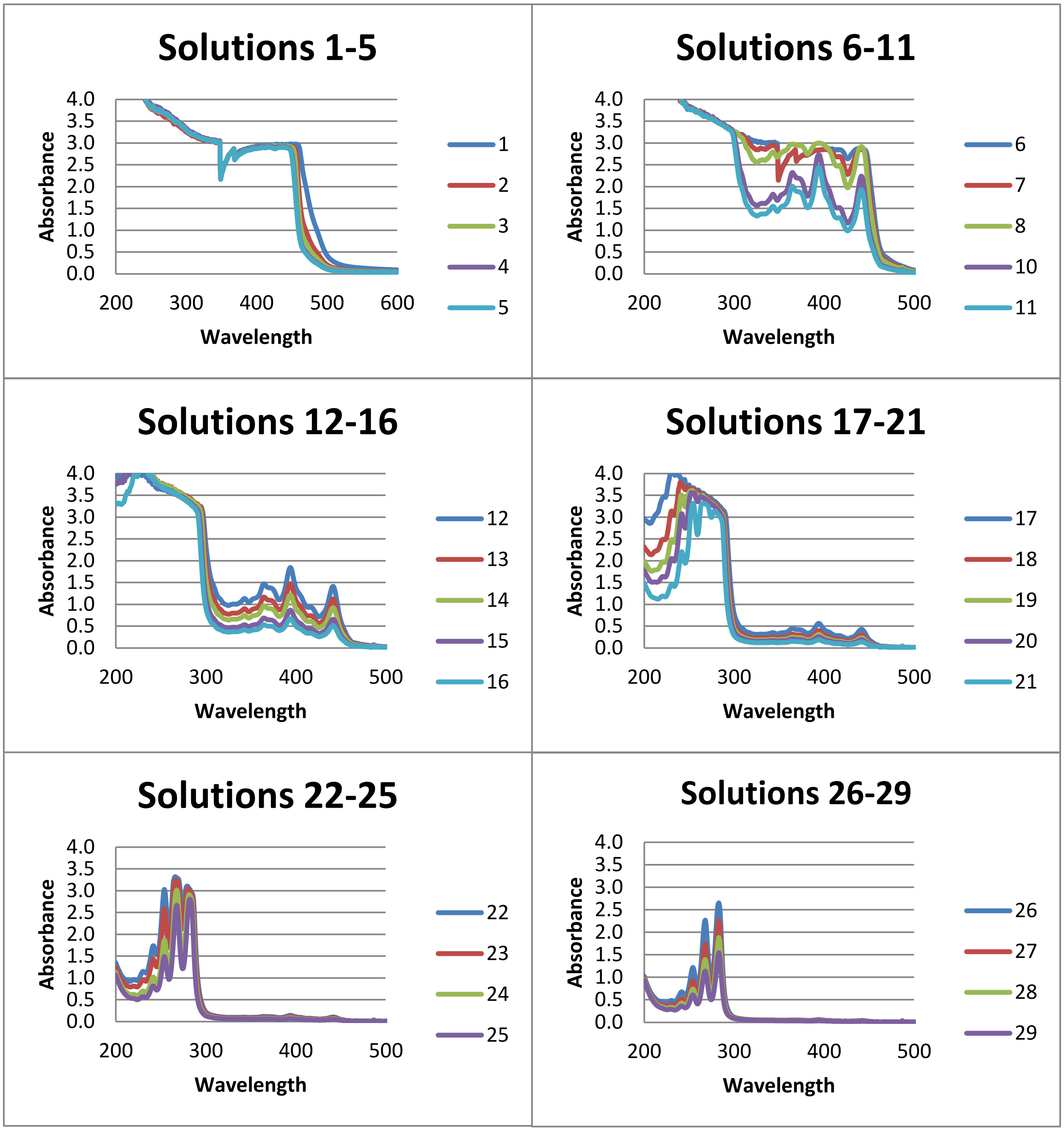


Figure 2.6 UV-Vis absorption spectra for solutions of $C_{10}TIPS_2$ in hexanes

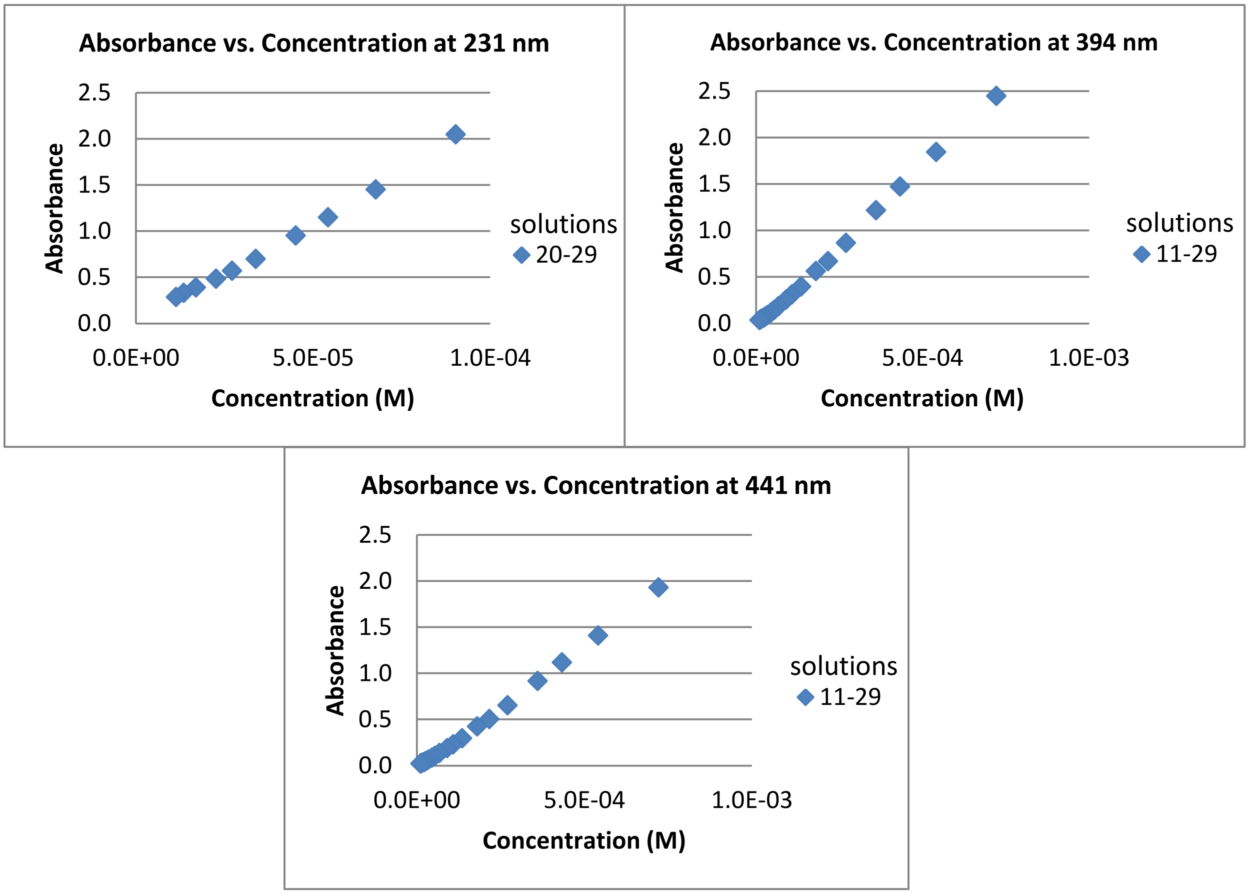


Figure 2.7 Absorbance vs. concentration for 231, 394, and 441 nm

The ratio between the absorbance values at these wavelengths for solutions of different concentrations were explored in an analogous manner to the analysis of spectra obtained for C_8TMS_2, in an attempt to gain additional information regarding aggregation behavior (Figure 2.8). A simultaneous decrease in absorbance at 231 nm and increase at 394 or 441 nm as the concentration increased is consistent with the idea that the peaks at longer wavelengths are a product of aggregation. The graphical representations of these ratios indicate that the ratio between A_{441} and A_{394} increases with concentration initially, but quickly levels out. A similar trend was found when comparing A_{441} to A_{231}, however the ratio appeared to fluctuate a bit more than A_{441}/A_{394}. Comparison between A_{393} and A_{231} did not provide much information, since the ratio did not clearly increase or decrease as the concentration increased. The UV-Vis data that was obtained did not allow for any concrete conclusions to be drawn; therefore, additional studies with other polyynes were put aside.

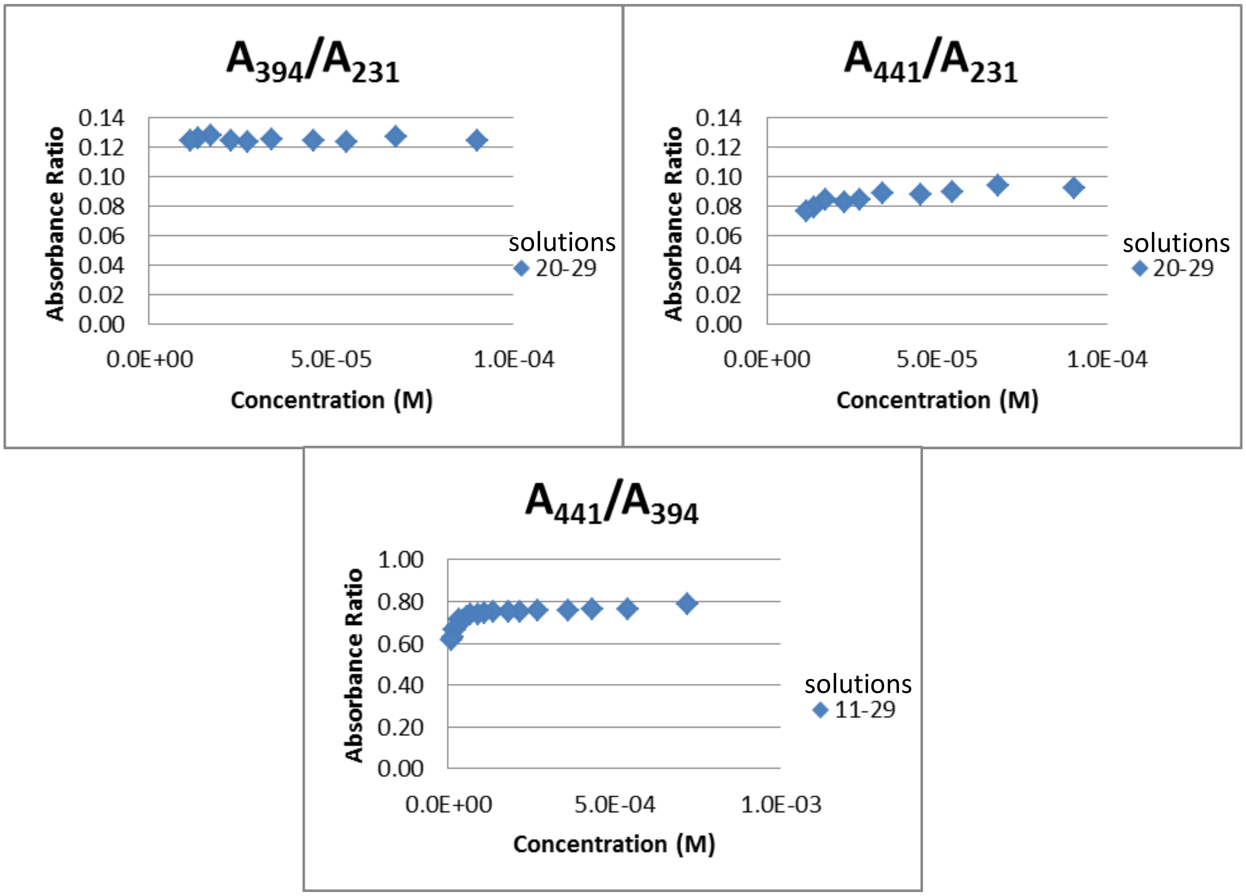


Figure 2.8 Absorbance ratios vs. concentration for 231, 394, and 441 nm

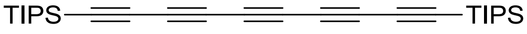
2.6 Summary

The iterative method for the synthesis of symmetric polyynes that was developed by Lei Li was thoroughly explored in this work. Experimental conditions including catalyst ratios, temperature, and reaction time were optimized through the synthesis of pentaynes as well as model studies, resulting in a reliable method for the preparation of shorter polyynes with silyl or phenyl end groups. A novel diiodopentayne, $C_{10}I_2$ (**66**) was synthesized by this method, and was employed in a Stille coupling reaction to prepare 1,14-bis(triisopropylsilyl)-1,3,5,7,9,11,13-

tetradecaheptayne ($C_{14}TIPS_2$, **67**), which has not been reported until now. The synthesis of polyynes with electron withdrawing and donating groups was also attempted; however difficulties were encountered when trying to form the appropriate tin acetylides. Similarly, the Stille coupling did not appear to be the most favorable reaction when targeting tetraynes with alkyl or polyethylyne glycol end groups, due to problems in purifying the tin acetylides and in the coupling reaction, respectively. Despite these results, the Stille coupling proved to be more effective for the symmetric double coupling to diiodopolyynes than the Negishi and Cadiot-Chodzkiewicz coupling reactions.

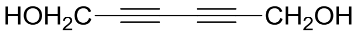
2.7 Experimental

General Methods: Reagents were purchased reagent grade from Aldrich, Fischer Scientific/Acros Organics, VWR, Strem, or GFS Chemicals, and were used without further purification, except where stated. Tetrahydrofuran was distilled under argon from sodium/benzophenone. Copper iodide was purified by recrystallization. High purity hexanes should be used when preparing silyl-capped polyynes, to avoid possible grease contamination caused by the low polarity of these compounds. All reactions were performed under an inert argon atmosphere, unless stated otherwise. Iodination and coupling reactions of polyynes were carried out in aluminum-foil wrapped flasks in an unlighted hood. All diiodopolyynes were washed with aqueous $Na_2S_2O_3$ immediately prior to use. Column chromatography: Alumina (50-200 mesh) from Acros Organics. Silica gel-60 (230-400 mesh) from Sorbent Technologies. Thin Layer Chromatography (TLC): plastic sheets covered with silica gel purchased from Acros. Melting points were measured on a Thomas Hoover Capillary melting point apparatus. ^1H and ^{13}C NMR spectra were obtained using Varian Gemini-300 MHz, Inova-400 MHz, or Inova-500 MHz instruments, and were taken in deuterated chloroform unless noted otherwise. EI-Mass spectra and high resolution EI-mass spectra were obtained from the University of Illinois SCS Mass Spectrometry Laboratory.



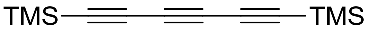
46

1,10-Bis(triisopropylsilyl)-1,3,5,7,9-decapentayne (46). In a heart-shaped flask wrapped in aluminum foil, diiodohexatriyne (**56**, 0.123 g, 0.377 mmol) and triisopropylsilyl(trimethylstannyl)ethyne (**58**, 0.253 g, 0.734 mmol) were dissolved in 20 mL dry THF. CuI (0.016 g, 0.084 mmol, 22 mol %) and $Pd(PPh_3)_2Cl_2$ (0.035 g, 0.050 mmol, 13 mol %) were combined in a round-bottom flask wrapped with foil and the system was degassed and backfilled with Ar. 5 mL THF was added to this flask, and both flasks were kept in ice baths (0 °C). The solution of **56** and **58** was added to the catalyst mixture via cannula, over a period of 9 h. After stirring for an additional 2 h at room temperature, solvent was removed *in vacuo*, and excess catalyst was removed using a short plug (SiO_2/hexanes). A 10:1 mixture of warm MeOH/$CHCl_3$ was used for recrystallization. The mixture was placed in a 45 °C water bath, and 3N HCl was added dropwise until a visible yellow suspension formed. The liquid was cooled to room temperature and placed in the freezer. Vacuum filtration was used to isolate **46** as a yellow solid (0.065 g, 40% yield). ^{1}H NMR (400 MHz, C_6D_6, 25 ºC): δ 0.99 (br); ^{13}C NMR (100 MHz, C_6D_6, 25 ºC): δ 90.65, 87.18, 63.42, 63.41, 62.49, 18.95, 11.87.[2]



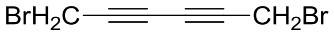
50

2,4-Hexadiyne-1,6-diol (50).[14] CuCl (0.657 g, 6.64 mmol) was dissolved in 20 mL acetone and TMEDA (0.1.24 mL, 8.22 mmol) was added. Oxygen was bubbled through the solution for 5-7h, and the reaction was allowed to stir under O_2 overnight. The dark green catalyst mixture was filtered, and propargyl alcohol (0.6 mL, 10.3 mmol) was added dropwise at 40° C. The reaction mixture was stirred at this temperature for 24h. Solvent was removed *in vacuo*, and 35 mL ethyl acetate was added. The organic liquid was washed with 30 mL sat. aq. NH_4Cl, and extracted with 5 30 mL portions of ethyl acetate. The combined organic extract was washed with 40 mL brine and dried over Na_2SO_4. Filtration and removal of solvent *in vacuo* resulted in 0.618 g crude material, which was purified via chromatography (SiO_2/hexanes, EtOAc) to afford 0.592 g (~100 %) of light orange solid. ^{1}H NMR (400 MHz, acetone-d_6, 25 ºC): δ 4.36 (t, 2 H, *J* = 4 MHz), 4.27 (d, 4 H, *J* = 4 MHz) ; ^{13}C NMR (100 MHz, acetone-d_6, 25 ºC): δ 50.9, 69.0, 79.6.[14]



52

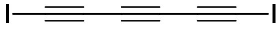
1,6-Bis(trimethylsilyl)-1,3,5-hexatriyne (52). Potassium t-butoxide (0.551 g, 4.91 mmol) was dissolved in 20 mL THF and the solution was cooled to -78 °C using a dry ice/acetone bath. A solution of 1,6-dibromo-2,4-hexadiyne (**53**, 0.290 g, 1.23 mmol) in 20 mL THF was added to the reaction mixture via cannula. After stirring for 2 h, the mixture reached -60 °C, and trimethylsilyl chloride (0.63 mL, 4.9 mmol) was added. The reaction was allowed to stir for 3.5 h, without further cooling. 30 mL sat. aq. NH_4Cl was added and the mixture was extracted with 3 x 30 mL of hexanes. Removal of solvent resulted in **52** as mixture of brown oil and short needle-like crystals (0.17 g, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 0.20 (br); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 87.9, 87.4, 61.9, -0.6.[2]



53

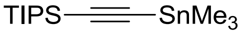
1,6-Dibromo-2,4-hexadiyne (53).[15] Triphenylphosphine (2.55 g, 9.72 mmol) was dissolved in 50 mL of dry dichloromethane,and the solution was cooled to 0°C. After adding bromine (0.50 g, 9.73 mmol) dropwise, the solution stirred at 0°C for an additional 30 min. 2,4-hexadiyne-1,6-diol (**50**, 0.42 g, 3.83 mmol) was added and the mixture was stirred for 1 h at 0°C followed by 1 h at room temperature. A short plug (SiO_2/hexanes) was used for purification, resulting in 0.897

g (98%) of colorless oil that solidified in the freezer. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 3.97 (s); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 13.8, 70.2, 75.2.[15]

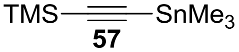

56

1,6-Diiodo-1,3,5-hexatriyne (56).[36] 1,6-Bis(trimethylsilyl)-1,3,5-hexatriyne (**52**, 0.1327 g, 0.608 mmol) was dissolved in 200 mL acetone in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.263 g, 1.55 mmol) and NIS (0.858 g, 3.81 mmol) were added and the reaction mixture was allowed to stir in the dark at room temperature for 6 h. Ice water (200 mL) and hexane (200 mL) were added, and the organic layer was extracted with 3 x 100 mL portions of hexane. The resulting yellow solution was washed with sat. aq. Na_2SO_3 and dried over $MgSO_4$. Filtration and removal of solvent resulted in 0.186 g (93%) of pale yellow solid. ^{13}C NMR (125MHz, $CDCl_3$, 25 ºC): δ 0.02, 59.7, 78.4.[36]

General Procedure for the Preparation of Tin Acetylides:[18]


58

Triisopropylsilyl(trimethylstannyl)ethyne (58): Triisopropylsilyl acetylene (4.50 g, 25.0 mmol) was dissolved in 50 mL THF, and the solution was cooled to -30 °C using a dry ice/acetone bath. *n*-BuLi (1.6M/hexanes, 15.0 mL, 25.0 mmol) was added dropwise over 15 min. After stirring for 15 min at -30 °C, $SnMe_3Cl$ (1M/THF, 25.0 mL, 25.0 mmol) was added, and the mixture was stirred for an additional 30 min before warming to room temperature and stirring for 1 h. Hexanes (100 mL) was added to the reaction mixture, resulting in the formation of a white precipitate. The mixture was washed with 25 mL H_2O, and the organic layer was dried over $MgSO_4$. The solution was filtered and solvent was removed *in vacuo*, leaving a cloudy yellow liquid. Vacuum distillation (~90 °C) was used to isolate **1c** as a colorless liquid (5.50 g, 64 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ1.07(br, 21H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 115.1, 113.5, 18.6, 11.2, -7.6.[37]


57

Trimethylsilyl(trimethylstannyl)ethyne (57): colorless liquid; (79% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 0.27 (s, 9H), 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 117.4, 113.1, 0.2, -7.7.[38]


59

Phenyl(trimethylstannyl)ethyne (59): yellow liquid; (55 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.45-7.44 (m, 2H), 7.26-7.25 (m, 3H), 0.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 131.8, 128.1, 128.0, 123.5, 108.9, 93.2, -7.7.[39]

$\mathrm{TBDMS{-}C{\equiv}C{-}SnMe_3}$

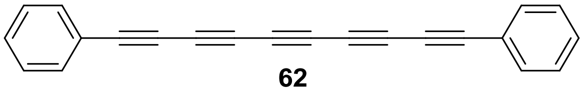
60

***tert*-Butyltrimethylsilyl(trimethylstannyl)ethyne (60)**: colorless liquid; (67% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): 0.92 (s, 9H), 0.27 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 115.7, 113.8, 26.0, 16.4, -4.4, -7.7.[40]

$\mathrm{TMS{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}TMS}$

61

1,10-Bis(trimethylsilyl)-1,3,5,7,9-decapentayne (61). In a heart-shaped flask wrapped in aluminum foil, diiodohexatriyne (**56**, 0.113 g, 0.347 mmol) and trimethylsilyl((trimethylstannyl)ethynyl)ethyne (**57**, 0.179 g, 0.686 mmol) were dissolved in 20 mL dry THF. CuI (0.015 g, 0.079 mmol, 23 mol %) and $Pd(PPh_3)_2Cl_2$ (0.028 g, 0.041 mmol, 12 mol %) were combined in a round-bottom flask wrapped with foil and the system was degassed and backfilled with Ar. 5 mL THF was added to the flask, and both flasks were kept in ice baths (0 °C). The solution of **56** and **57** was added to the catalyst mixture via cannula, over a period of 10 h. After stirring for an additional 2 h at room temperature, solvent was removed *in vacuo* and excess catalyst was removed using a short plug (SiO_2/hexanes). Vacuum sublimation was used to isolate **61** as a brown solid (0.060 g, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 0.21 (br); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 88.63, 87.71, 62.62, 62.23, 62.17, -0.65.[41]



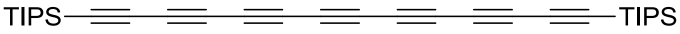
62

1,10-Bis(phenyl)-1,3,5,7,9-decapentayne (62). In a heart-shaped flask wrapped in aluminum foil, diiodohexatriyne (**56**, 0.198 g, 0.608 mmol) and phenyl(trimethylstannyl)ethyne (**59**, 0.321 g, 1.21 mmol) were dissolved in 20 mL dry THF. CuI (0.026 g, 0.14 mmol, 22 mol %) and $Pd(PPh_3)_2Cl_2$ (0.051 g, 0.073 mmol, 12 mol %) were combined in a round-bottom flask wrapped with foil and the system was degassed and backfilled with Ar. 5 mL THF was added to the flask, and both flasks were kept in ice baths (0 °C). The solution of **56** and **59** was added to the catalyst mixture via cannula, over a period of 9 h. After stirring for an additional 2 h at room temperature, solvent was removed *in vacuo* and excess catalyst was removed using a short plug (SiO_2/hexanes). Column chromatography (SiO_2/hexanes) was used to isolate **62** as a light yellow solid (0.47 g, 28% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.56-7.54 (m, 4H), 7.44-7.40 (m, 2H), 7.36-7.32, (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 133.3, 130.2, 128.6, 120.3, 77.5, 74.4, 67.3, 64.5, 62.8.[2]

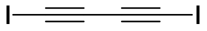
$\mathrm{I{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}I}$

66

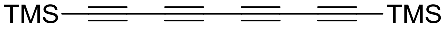
1,10-Diiodo-1,3,5,7,9-decapentayne (66). 1,10-Bis(trimethylsilyl)-1,3,5,7,9-decapentayne (**61**, 0.096 g, 0.36 mmol) was dissolved in 200 mL acetone in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.186 g, 1.09 mmol) and *N*-iodosuccinimide (0.488 g, 2.17 mmol) were added and the reaction mixture was allowed to stir at room temperature for 4 h. Ice water (200 mL) and hexanes (200 mL) were added, and the aqueous layer was extracted with 3 x 100 mL of hexanes. The combined organic layers were washed with 15% aq. $Na_2S_2O_3$. The resulting yellow solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in **66** as a yellow solid that decomposed at 55-56 °C (0.11 g, 82% yield). ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 79.0, 62.6, 61.4, 59.3, 2.3. MS (EI): m/z (%): 373 (100) [M^+], 246 (18) [M^+ - I], 128 (60) [I^+], 119 (42) [M^+ - 2I]. HRMS (EI) *m/z* calcd for $C_{10}I_2$ 373.80900, found 373.80923.


67

1,14-Bis(triisopropylsilyl)-1,3,5,7,9,11,13-tetradecaheptayne (67). In a heart-shaped flask wrapped in aluminum foil, diiodododecapentayne (**66**, 0.056 g, 0.150 mmol) and triisopropylsilyl(trimethylstannyl)ethyne (**58**, 0.100 g, 0.291 mmol) were dissolved in 20 mL dry THF. CuI (0.007 g, 0.037 mmol, 24 mol %) and $Pd(PPh_3)_2Cl_2$ (0.013 g, 0.018 mmol, 12 mol %) were combined in a round-bottom flask wrapped with foil and the system was degassed and backfilled with Ar. 5 mL THF was added to the flask, and both flasks were kept in ice baths (the diiodopentayne and tin solution was kept between -15 and -30ºC, and the catalyst mixture was kept at 0 ºC). The solution of **66** and **58** was added to the catalyst mixture via cannula, over a period of 10 h. After stirring for an additional 2 h at room temperature, solvent was removed *in vacuo*, and excess catalyst was removed using a short plug (SiO_2/hexanes). Column chromatography (SiO_2/hexanes) was used to isolate **67** as dark yellow oil (0.007 g, 10% yield). ^1H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 1.09 (br); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ 89.34, 87.39, 62.97, 62.93, 62.62, 62.26, 61.20, 18.49, 11.27. HRMS (EI) *m/z* calcd for $C_{32}H_{42}Si_2$ 482.28251, found 482.28314.

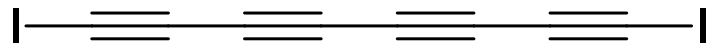

70

1,4-Diiodobutadiyne (70).[6] Bis(trimethylsilyl)butadiyne (**64**, 0.321 g, 1.65 mmol) was dissolved in 200 mL acetone in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.729 g, 4.29 mmol) and NIS (1.13 g, 5.01 mmol) were added and the reaction mixture was allowed to stir in the dark at room temperature for 4 h. Ice water (200 mL) and hexane (200 mL) were added, and the organic layer was extracted with 3 x 100 mL portions of hexane and washed with sat. aq. $Na_2S_2O_3$. The resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in 0.448 g (90%) of pale yellow solid. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 1.4, 58.9, 62.1, 78.9.[6]


71

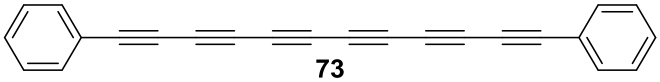
1,8-Bis(trimethylsilyl)-1,3,5,7-octatetrayne (71). Diiodobutadiyne (**70**, 0.239 g, 0.792 mmol) and trimethylsilyl(trimethylstannyl)ethyne (**57**, 0.414 g, 1.58 mmol) were dissolved in 20 mL dry THF in a heart-shaped flask wrapped in aluminum foil. The flask was placed in an ice bath (0 °C). CuI (0.036 g, 0.19 mmol, 24 mol %) and $Pd(PPh_3)_2Cl_2$ (0.065 g, 0.093 mmol, 12 mol %) were combined in a round-bottom flask wrapped with foil and the system was degassed and backfilled with Ar. 5 mL THF was added to the flask, and the solution of **70** and **57** was added to the catalyst mixture via cannula over a period of 10 h. The mixture was stirred for 2 h after the addition, solvent was removed *in vacuo*, and excess catalyst was removed using a short plug

(SiO_2/hexanes). Vacuum sublimation was used to isolate **71** as brown oil that contained solid needles (0.11 g, 59 % yield). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.21 (br); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 88.01, 87.83, 62.16, 62.14, -0.57.[36]



72

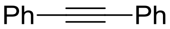
1,8-Diiodo-1,3,5,7-tetrayne (72).[36] 1,8-Bis(trimethylsilyl)1,3,5,7-tetrayne (**71**, 0.111 g, 0.457 mmol) was dissolved in 200 mL acetone in a round-bottom flask wrapped with aluminum foil. $AgNO_3$ (0.199 g, 1.17 mmol) and NIS (0.515g, 2.29 mmol) were added and the reaction mixture was allowed to stir in the dark at room temperature for 5 h. Ice water (200 mL) and hexane (200 mL) were added, and the organic layer was extracted with 3 100 mL portions of hexane and washed with sat. aq. $Na_2S_2O_3$. The resulting solution was dried over $MgSO_4$. Filtration and removal of solvent resulted in 0.132 g (83%) of pale yellow solid. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 1.4, 58.9, 62.1, 78.9.[36]



73

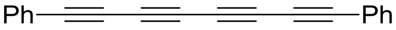
1,12-Bis(diphenyl)-1,3,5,7,9,11-dodecahexayne (73). In a heart-shaped flask wrapped in aluminum foil, diiodooctatetrayne (**72**, 0.132 g, 0.377 mmol) and phenyl(trimetylstannyl)ethyne (**59**, 0.194 g, 0.732 mmol) were dissolved in 20 mL dry THF. CuI (0.018 g, 0.095 mmol, 25 mol %) and $Pd(PPh_3)_2Cl_2$ (0.032 g, 0.046 mmol, 12 mol %) were combined in a round-bottom flask wrapped with foil and the system was degassed and backfilled with Ar. 5 mL THF was added to the flask, and both flasks were kept in ice baths (0 °C). The solution of **72** and **59** was added to the catalyst mixture via cannula, over a period of 11 h. After addition, the mixture was stirred for 2 h at room temperature and solvent was removed *in vacuo*. Excess catalyst was removed using a short plug (SiO_2/hexanes). Column chromatography (SiO_2/hexanes) was used to isolate **73** as a light orange solid (0.018 g, 16 % yield). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.56-7.54 (m, 4H), 7.42-7.41 (m, 2H), 7.36-7.33 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 133.5, 130.4, 128.5, 120.1, 77.5, 74.3, 67.2, 64.6, 63.6, 62.5.[42]

General Procedure for Negishi reaction:[6]



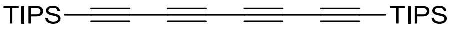
41

Diphenylacetylene (41).[21] Zinc chloride (0.277 g, 2.03 mmol) was flame dried under vacuum for 20 minutes using a heating mantle. After removing from heat, the zinc was allowed to remain under vacuum for an additional 45 minutes. Phenylacetylene (0.180 mL, 1.64 mmol) was dissolved in 3 mL anhydrous THF, and the solution was cooled to -78°C using a dry ice/acetone bath. *n*-BuLi (1.25 mL, 2.00 mmol) was added dropwise, and the solution was stirred for 30 minutes. The ZnCl was dissolved in 5 mL THF, and was added to the reaction mixture via cannula. After stirring for 15 minutes, the reaction was warmed to room temperature over a period of 45 minutes. The solution was added dropwise to a mixture of iodobenzene (0.153 mL, 1.36 mmol) and $Pd(PPh_3)_4$ (0.041 g, 0.035 mmol, 3 mol %) in 5 mL THF at 0°C. After warming to room temperature overnight, the reaction was quenched with 50 mL sat. aq. NH_4Cl and extracted with 2 50 mL portions of EtOAc. The organic phase was washed with sat. aq. NaCl and dried over $MgSO_4$. Filtration and removal of solvent *in vacuo* afforded 0.182 g yellow oily solid (59% yield determined by NMR spectra). ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.35-7.41 (m, 8H), 7.53-7.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 89.3, 121.7, 128.2, 128.3, 131.6.[21]


79

1,8-Bis(phenyl)1,3,5,7-octatetrayne (79). Zinc chloride (0.397 g, 2.9 mmol) was flame dried under vacuum for 20 minutes using a heating mantle. After removing from heat, the zinc was allowed to remain under vacuum for an additional 45 minutes. Phenylacetylene (0.26 mL, 2.36 mmol) was dissolved in 7 mL anhydrous THF, and the solution was cooled to -78°C using a dry ice/acetone bath. *n*-BuLi (1.80 mL, 1.22 mmol) was added dropwise and the solution was stirred for 30 minutes. ZnCl (in 7 mL THF) was added dropwise, and the solution was stirred for 20 minutes at -78°C and 30 minutes at rt. This solution and a solution of C_4I_2 (0.292 g, 0.968 mmol, in 15 mL THF) were simultaneously added to $Pd(PPh_3)_2Cl_2$ (0.068 g, 0.097 mmol) in 8 mL THF at 0°C using two double ended needle over a period of 10 h. Solvent was removed *in vacuo*, and a short plug was run (SiO_2/hexanes) to remove any residual catalyst. Column chromatography did not afford complete isolation of product, so a 21% yield was calculated using ^{13}C NMR. Product peaks: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 7.33-7.39 (m, 3H), 7.51-7.55 (m, 2H) ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 63.6, 67.2, 74.4, 77.7, 120.5, 128.5, 130.0, 133.2.[43]

Alternative Negishi coupling:[22]


78

1,8-Bis(triisopropylsilyl)-1,3,5,7-tetrayne (78). Zinc chloride (0.113 g, 0.829 mmol) was flame dried under vacuum for 20 minutes using a heating mantle. After removing from heat, the zinc was allowed to remain under vacuum for an additional 40 minutes before adding 3 mL dry THF. Triethylamine (0.46 mL, 3.31 mmol) was added, and the solution was stirred for 10 minutes at room temperature. Triisopropylsilyl acetylene (0.16 mL, 1.72 mmol) was added and the reaction was stirred for 1 hour before adding $Pd(PPh_3)_2Cl_2$ (0.021g, 0.03 mmol). A solution of C_4I_2 (0.110 g, 0.364 mmol) in 9 mL dry THF was kept in a heart shaped flask wrapped in foil and placed in an ice bath (0°C) The iodoalkyne was added dropwise via cannula over a period of 4 h, and the reaction was allowed to stir for an additional 12h. A short plug was run (SiO_2/hexanes) and removal of solvent *in vacuo* afforded 0.097 g brown oil (65% crude yield). NMR spectra revealed a mixture of C_8TIPS_2 (**78**), C_4TIPS_2 (**63**), and triisopropylsilyl acetylene. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 1.07, 1.09, 1.10; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 11.05, 11.31, 11.34, 18.45, 18.50, 18.56, 61.39, 62.24, 81.58, 85.62, 86.21, 89.66, 90.24, 94.70.[3]

$\mathrm{Ph{-}{\equiv}{-}TIPS}$

81

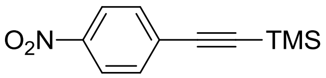
Phenyl(triisopropylsilyl)acetylene (81). Zinc chloride (0.281 g, 2.06 mmol) was flame dried under vacuum for 20 minutes using a heating mantle. After removing from heat, the zinc was allowed to remain under vacuum for an additional 40 minutes before adding 4.2 mL dry THF. Triethylamine (1.16 mL, 8.25 mmol) was added, and the solution was stirred for 10 minutes at room temperature. Triisopropylsilyl acetylene (0.38 mL, 1.72 mmol) was added and the reaction was stirred for 1 hour before adding $Pd(PPh_3)_2Cl_2$ (0.056 g, 0.079 mmol). A solution of iodobenzene (0.095 mL, 0.847 mmol) in 5 mL dry THF was added dropwise via cannula over a period of 3 h, and the reaction was allowed to stir for an additional 12h. EtOAc (20 mL) was added, and the mixture was washed with 10 mL sat. aq. NH_4Cl and 10 mL $NaHCO_3$. The organic extract was dried over $MgSO_4$. Filtration and removal of solvent *in vacuo* afforded 0.109 g orange oily solid (50% crude yield). ^1H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 1.11 (s, 21H), 7.26-7.27 (m, 3H), 7.44-7.45(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 11.3, 18.6, 90.4, 107.1, 123.5, 128.1, 128.2, 132.0.[44]

Cadiot-Chodkiewicz Procedure A.[23] CuI (0.003 g, 0.014 mmol) was added to a 5 mL solution of *n*-$BuNH_2$ (30%). A few crystals of hydroxylamine hydrochloride were added to remove the blue color from the solution. Phenylacetylene (0.09 mL, 0.819 mmol) was added and the solution was immediately cooled in an ice-water bath. C_4I_2 (0.100 g, 0.332 mmol) was added, the mixture was warmed to room temperature, and the flask was wrapped with foil. The reaction was stirred for 1h, and the product was extracted with 3 30 mL portions of hexane and dried over $MgSO_4$. Filtration and removal of solvent *in vacuo* resulted in 0.029 g of orange oil. ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 63.6, 67.2, 73.9, 74.4, 77.7, 81.5, 120.5, 121.8, 126.1, 128.2, 128.4, 128.5, 129.2, 129.9, 132.5, 133.2.

Cadiot-Chodkiewicz Procedure B.[24] C_4I_2 (0.089 g, 0.297 mmol) was dissolved in 7 mL THF and triisopropylacetylene (0.16 mL, 0.713 mmol) was added to the flask that was wrapped with foil. CuI (0.004 g, 0.022 mmol) and $Pd(PPh_3)Cl_2$ (0.013g, 0.018 mmol) were combined in a round bottom flask, which was then degassed. THF (5 mL) and *i*-Pr_2NH (0.17 mL, 1.209 mmol) were added to the catalyst mixture, and the C_4I_2/acetylene mixture was added via cannula at a rate of 1 drop/10 s. After stirring overnight, the reaction mixture was absorbed onto SiO_2 and a plug was run using hexanes as an eluent. The resulting solution was washed with sodium thiosulfate and dried over $MgSO_4$. Filtration and removal of solvent *in vacuo* resulted in 0.081 g orange oil. A yield was not calculated since the material was a mixture of products in a ratio that was hard to determine. ^1H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 1.08-1.09; ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 11.03, 11.28, 11.33, 18.45, 18.49, 18.55, 29.72, 61.37, 62.21, 81.55, 85.19, 89.64, 90.22, 94.72.

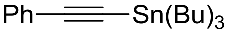
CuCl Purification.[45] Copper chloride (5.35 g, 54.0 mmol) was dissolved in 60 mL 0.1M HCl and stirred for 10 min. Deionized water was added to the blue/green suspension, causing a white precipitate to form which was isolated using vacuum filtration. The solid was washed with 20 mL portions of methanol, ethanol, acetone, and diethyl ether, and dried in the vacuum oven.

CuI Purification. Potassium iodide (18.2 g, 109 mmol) was dissolved in 32 mL H_2O and 1.25 g CuI (6.54 mmol) was added. After stirring under argon for 1 h, 1.27g (106 mmol) charcoal was added and the mixture was stirred with moderate heat for 30 min. The mixture was cooled to room temperature and filtered under argon. 30 mL H_2O was added and the white precipitate that formed was isolated after 45 min using vacuum filtration (under Ar). The solid was washed with water, ethanol, and ether (10 mL portions) and dried overnight in the vacuum oven (~100°C). The purified compound was stored in a Schlenk flask that had been degassed and filled with Ar, and was placed in a desiccator.



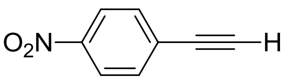
94

1-(4-Nitrophenyl)-2-trimethylsilyl-ethyne (94).[28] 4-Bromo nitrobenzene (0.500 g, 2.47 mmol), $Pd(PPh_3)_4$ (0.049 g, 0.042 mmol), CuI (0.025 g, 0.134 mmol), and trimethylsilylacetylene (0.42 mL, 0.292 g, 2.97 mmol) were added to 25 mL of Et_3N. The reaction mixture was heated to 40°C and stirred for 6.5 h at this temperature. TLC revealed starting material was still present, so an additional 0.38 mL (2.47 mmol) trimethylsilylacetylene was added. After stirring an additional 1.5 h, the reaction was stopped, solvent was removed *in vacuo*, and a short plug (Al_2O_3/hex:EtOAc 10:1) was used to remove excess catalyst. Solvent was removed, resulting in 0.727 g light brown solid (>100%, NMR showed presence of C_4TMS_2). ^1H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 0.27, (s, 9H), 7.53-7.60 (d, 2H, J = 8.8 Hz), 8.16-8.17 (d, 2H, J = 9.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC): δ -0.3, 100.6, 102.7, 123.4, 129.9, 132.7, 147.2.[28]



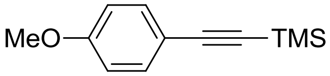
91

Phenyl(tributylstannyl)ethyne (91).[26] Phenylacetylene (1.13 mL, 1.02 g, 10.3 mmol) was dissolved in 30 mL THF and the solution was cooled to -78°C using a dry ice/acetone bath. *n*-BuLi (1.6M/hexanes, 8.00 mL, 12.8 mmol) was added dropwise over 15 min. After stirring for an additional 10 min at -78°C, Bu_3SnCl (4.18 mL, 5.02 g, 12.8 mmol) was added dropwise over a period of 35 min. The reaction was warmed to room temperature and stirred for 45 min. Solvent was removed *in vacuo* and the resulting liquid was extracted with 2 30 mL portions of hexane. The combined organic layers were washed with water, and removal of solvent afforded 3.69 g (91%) light yellow liquid. ^1H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 0.93-0.94 (m, 9H), 1.06-1.08 (m, 6H), 1.37-1.40 (m, 6H), 1.61-1.65 (m, 6H), 7.24-7.26 (m, 3H), 7.43-7.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 11.1, 13.6, 26.9, 28.8, 93.0, 110.0, 124.0, 127.7, 128.0, 131.8.[26]



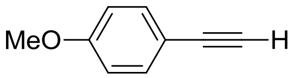
95

4-Nitrophenylacetylene (95).[28] A mixture of 1-(4-nitrophenyl)-2-trimethylsilyl-ethyne (**94**, 0.213 g, 0.971 mmol) and bis(trimethylsilyl)butadiyne (0.106 g, 0.260 mmol) was dissolved in 40 mL MeOH. Potassium carbonate (0.426 g, 3.08 mmol) was added, and the reaction mixture was stirred at room temperature for 6 h. Saturated aq. NH_4Cl (100 mL) was added, and the mixture was extracted with 3 50 mL portions of ethyl acetate. The combined organic layer was dried over $MgSO_4$. Column chromatography (SiO_2/hex:EtOAc 10:1) afforded 0.079 g (54%) of pale yellow solid. ^1H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 3.35, (s, 1H), 7.63-7.65 (d, 2H, *J* = 8.8 Hz), 8.18-8.20 (d, 2H, *J* = 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 81.6, 82.3, 123.5, 128.9, 132.9, 147.5.[28]



98

1-(4-Methoxyphenyl)-2-trimethylsilyl-ethyne (98).[46] See procedure for 1-(4-nitrophenyl)-2-trimethylsilyl-ethyne; however the reaction time was only 4h. A light yellow oil was obtained in 91% yield. ^1H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 0.27, (s, 9H), 3.76, (s, 3H), 6.74-6.76 (d, 2H, *J* = 8.8 Hz), 7.32-7.34 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ -0.6, 55.0, 92.2, 105.2, 113.7, 115.2, 133.4, 159.7.[46]



99

4-Methoxyphenylacetylene (99).[29] 1-(4-Methoxyphenyl)-2-trimethylsilyl-ethyne (0.225 g, 1.20 mmol) was dissolved in 10 mL MeOH and 2M KOH (4 mL) was added. After stirring for 7h at room temperature, the reaction mixture was filtered and the filtrate was diluted with 10 mL water. The product was extracted with 3 20 mL portions of ether and dried over $MgSO_4$. Filtration and removal of solvent *in vacuo* resulted in 0.078 g (54%) light brown oil. ^1H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 3.02, (s, 1H), 3.80 (s, 3H), 6.84-6.86 (d, 2H, *J* = 8.8 Hz), 7.45-7.47 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 55.2, 75.8, 83.6, 113.9, 133.5, 159.9.[29]

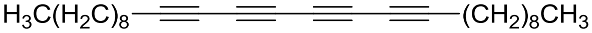
$C_4H_9{-}{\equiv}{-}Sn(CH_3)_3$

102

1-(Trimethylstannyl)-1-hexyne (102).[32] 1-Hexyne (1.00 mL, 8.64 mmol) was dissolved in 30 mL dry THF and the solution was cooled to -30°C using a dry ice/acetone bath. *n*-BuLi (1.6M/hexanes, 5.40 mL, 8.64 mmol) was added dropwise over 10 min. After stirring for 1 h at -30°C, trimethyltin chloride (1M/THF, 8.60 mL, 8.40 mmol) was added and the mixture was stirred for 30 minutes at -30°C and 1 h at room temperature. Hexanes (60 mL) was added to the reaction mixture, resulting in the formation of a white precipitate. The mixture was extracted with 30 mL hexanes and 30 mL H_2O, and the organic layer was washed with 4 30 mL portions of H_2O and dried over $MgSO_4$. Removal of solvent *in vacuo* resulted in 0.910 g (43%) light yellow oil. ^1H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 0.21 (s, 9H), 0.87 (t, 3H, *J* = 6.9 Hz), 1.35-1.47 (m, 4H), 2.19 (t, 2H, *J* = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ -7.9, 13.5, 19.7, 21.9, 31.1, 81.7, 110.9.[32]

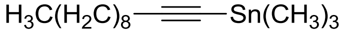
103

1,8-Dibutyl-1,3,5,7-octatetrayne (103). Diiodobutadiyne (**70**, 0.143 g, 0.473 mmol) and 1-(trimethylstannyl)-1-hexyne (**102**, 0.224 g, 0.997 mmol) were dissolved in 20 mL dry THF in a heart shaped flask. CuI (0.021 g, 0.110 mmol, 23 mol %) and $Pd(PPh_3)_2Cl_2$ (0.040 g, 0.056 mmol, 12 mol %) were combined in a round bottom flask and the system was degassed six times before adding 5 mL dry THF. Both flasks were wrapped in foil and placed in ice baths (~0°C). The diiodoalkyne/tin solution was added to the catalyst mixture dropwise via cannula over a period of 10 h. Solvent was removed *in vacuo* and excess catalyst was removed using a short plug (SiO_2/hexanes). Removal of solvent afforded 0.035 g (35% crude yield) of yellow oil. The ^{1}H NMR ($CDCl_3$) spectrum contained many peaks in the region between 0.80 and 2.32 ppm, suggesting the presence of several types of butyl groups. The presence of multiple products was confirmed by ^{13}C NMR (400 MHz, $CDCl_3$, 25 ºC), which contained numerous peaks in the alkynyl region (60-65 ppm) and alkyl region (13-30 ppm), along with the expected product peaks: δ 13.5, 19.2, 22.6, 30.4, 61.0, 61.5, 65.7, 80.4.[31]



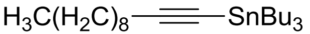
105

Hexacosa-10,12,14,16-tetrayne (**105**). Diiodobutadiyne (**70**, 0.174 g, 0.579 mmol) and trimethyl-undec-1-ynyl-stannane (**106**, 0.344 g, 1.09 mmol) were dissolved in 18 mL dry THF in a heart shaped flask wrapped with aluminum foil. CuI (0.025 g, 0.130 mmol, 22 mol %) and $Pd(PPh_3)_2Cl_2$ (0.049 g, 0.070 mmol, 12 mol %) were combined in a round bottom flask and the system was degassed six times before adding 5 mL dry THF. Both flasks were wrapped in foil and placed in ice baths (~0°C). The diiodoalkyne/tin solution was added to the catalyst mixture dropwise via cannula over a period of 10 h. Solvent was removed *in vacuo* and excess catalyst was removed using a short plug (SiO_2/hexanes). Removal of solvent afforded 0.057 g (28% crude yield) of yellow oil. The ^{1}H NMR ($CDCl_3$) spectrum contained many peaks in the between 0.80 and 2.32 ppm, suggesting the presence of several types of alkyl. The presence of multiple products was confirmed by ^{13}C NMR ($CDCl_3$), which contained peaks for both the desired tetrayne (**105**) as well as the homocoupled diyne byproduct (**109**). The ratio of **105** to **109** was 1.00 to 3.82, which was determined by the integration of analogous sp-carbon peaks in the ^{13}C NMR (the alkyl peaks for the two products were indistinguishable). Column chromatography (SiO_2/hexanes) was attempted; however further examination of the resulting fractions by ^{13}C NMR revealed the presence of longer polyynes, suggested by the presence of additional peaks in the 60 ppm region.



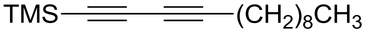
106

Trimethyl-undec-1-ynyl-stannane (106).[32] 1-Undecyne (1.5 mL, 7.6 mmol) was dissolved in 10 mL dry THF and cooled to -78 °C (dry ice/acetone). *n*-BuLi (1.6M/hexanes, 5.0 mL, 8.0 mmol) was added dropwise over 10 min. After stirring for 30 min at -78 °C and 30 min at 0 ºC, the reaction was cooled to -78 °C and trimethyltin chloride (1M/THF, 7.6 mL, 7.6 mmol) was added. The reaction was allowed to warm to room temperature and stirred overnight before extracting with H_2O (20 mL) and hexanes (30 mL). The organic extract was dried over $MgSO_4$. Removal of solvent *in vacuo* resulted in 0.924 g (39%) light yellow oil. Vacuum distillation was used to isolate the tin acetylide (0.535 g, 23% yield) from excess terminal acetylene, although a small amount of terminal acetylene remained, as a very small peak corresponding to the terminal proton was visible in the ^{1}H NMR. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.24 (s, 9H), 0.87 (t, 3H, *J* = 7 Hz) 1.26 (br, 12H) 1.50 (m, 2H), 2.21 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ -7.8, 14.1, 20.1, 22.6, 28.8, 29.0, 29.1, 29.2, 29.4, 31.9, 81.8, 111.1.



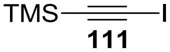
107

Tributyl-undec-1-ynyl-stannane (107):[26] 1-Undecyne (0.44 mL, 2.2 mmol) was dissolved in 10 mL dry THF and the solution was cooled to -78 ºC (dry ice/acetone). *n*-BuLi (1.6M/hexanes, 1.7 mL, 2.7 mmol) was added dropwise, and the mixture was stirred for 30 min. Bu_3SnCl (0.9 mL, 3.3 mmol) was added dropwise over 10 min, and the reaction was allowed to warm to room temperature overnight. Solvent was removed *in vacuo*, and the resulting white cloudy liquid was extracted with 2 x 30 mL hexanes and 30 mL H_2O The combined organic extracts were dried over $MgSO_4$ and filtered under Ar atmosphere. Removal of solvent afforded 0.77 g (78% yield) of colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (m), 1.25-1.33 (m), 1.52 (m), 2.22 (t, 2H, *J* = 4Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.9, 13.6, 16.3, 20.1, 26.9, 27.2, 27.8, 28.2, 28.7, 28.8, 29.1, 29.2, 29.5, 81.2, 111.9.



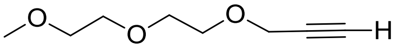
110

Trimethyl-trideca-1,3-diynyl-silane (110).[31] Copper iodide (0.003 g, 0.02 mmol) and $Pd(PPh_3)_2Cl_2$ (0.008 g, 0.01 mmol) were combined in a round-bottom flask, and the system was degassed and backfilled with Ar. Diisopropylamine (2.2 mL, 15 mmol) was added and the solution was stirred for 5 min. 1-Undecyne (0.09 mL, 0.5 mmol) and iodotrimethylsilyl acetylene (0.10 g, 0.45 mmol) were combined in a heart-shaped flask and diisopropylamine (1.1 mL, 7.8 mmol) was added. The alkyne solution was added to the catalyst mixture via cannula, and the reaction was stirred for 3 h at room temperature. The mixture was filtered, and solvent was removed *in vacuo* to afford 0.055 g (49% crude yield) of orange/brown oil. ^{13}H NMR and ^{13}C NMR spectra revealed the presence of **110**, in addition to the diynes that resulted from homocoupling of both starting materials.



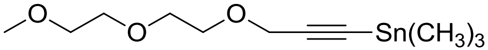
111

1-Iodo-2-trimethylsilylacetylene (111).[47] Trimethylsilylacetylene (0.7 mL, 4.9 mmol) was dissolved in 7 mL dry THF and the solution was cooled to -78 ºC (dry ice/acetone). *n*-BuLi (1.6 M/hexanes, 3.1 mL, 4.9 mmol) was added, and the reaction was stirred for 10 min at -78 ºC, followed by 10 min at 0 ºC. The reaction was cooled down to -78 ºC, and I_2 (1.26 g, 2.96 mmol) was added. The flask was covered in foil and warmed to room temperature. After stirring for 4 h, the reaction was diluted with 50 mL hexanes and washed with sat. aq. Na_2SO_3 (2 x 20 mL) and water (2 x 30 mL), and dried over $MgSO_4$. Filtration and removal of solvent *in vacuo* afforded **111** as a colorless liquid (0.36 g, 33% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -0.1, 20.3, 104.2.[47]



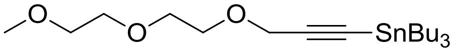
116

3-[2-(2-Methoxy-ethoxy)-ethoxy]-propyne (**116**).[48] Sodium hydride (60% in mineral oil, 0.337 g, 8.42 mmol) and THF (20 mL) were combined in a round-bottom flask, and the suspension was placed in an ice bath (0 °C). Diethyleneglycol monomethyl ether (0.85 mL, 7.0 mmol, in 10 mL THF) was added to the suspension dropwise. After stirring for 15 min, propargyl bromide (0.86 mL, 7.7 mmol) was added and the reaction was allowed to warm to room temperature and stirred overnight. The reaction was slowly quenched with H_2O (10 mL), and an extraction was performed with 30 mL EtOAc and 30 mL H_2O. The aqueous layer was extracted with an additional 30 mL EtOAc, and the combined organic extracts were dried over $MgSO_4$. Removal of solvent *in vacuo* afforded **116** as an orange liquid (0.96 g, 87% yield).). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 1H), 3.31 (s, 3H), 3.57 (m, 2H), 3.61 (m, 2H), 3.63 (m, 4H), 4.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 58.2, 58.8, 68.9, 70.2, 70.3, 71.7, 74.4, 79.5.[48]



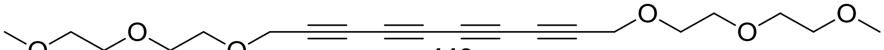
117

{3-[2-(2-Methoxy-ethoxy)-ethoxy]-prop-1-ynyl}-trimethyl-stannane (117).[26] 3-[2-(2-Methoxy-ethoxy)-ethoxy]-propyne (**116**, 0.303 g, 1.91 mmol) was dissolved in 11 mL THF and the solution was cooled to -78 °C (dry ice/acetone). *n*-BuLi (1.6M/hexanes, 1.6 mL, 2.5 mmol) was added dropwise, and the mixture was stirred for 30 min. Trimethyltin chloride (1M/THF, 2.9 mL, 2.9 mmol) was added dropwise over 10 min, and the reaction was allowed to warm to room temperature and stirred overnight. Solvent was removed *in vacuo*, and the resulting cloudy liquid was extracted with EtOAc/H_2O. The organic extract was dried over $MgSO_4$, filtered, and concentrated to afford 0.410 g (67% crude yield) of light yellow oil. NMR spectra revealed the presence of excess terminal acetylene, in addition to the tin acetylide. Further purification was not attempted; rather the tributyltin analog was prepared.



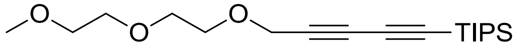
118

{3-[2-(2-Methoxy-ethoxy)-ethoxy]-prop-1-ynyl}-tributyl-stannane (118).[26] 3-[2-(2-Methoxy-ethoxy)-ethoxy]-propyne (**116**, 0.292 g 1.85 mmol) was dissolved in 10 mL THF and the solution was cooled to -78 °C (dry ice/acetone). *n*-BuLi (1.6M/hexanes, 1.5 mL, 2.4 mmol) was added dropwise, and the mixture was stirred for 30 min. Tributyltin chloride (0.75 mL, 2.8 mmol) was added dropwise over 10 min, and the reaction was allowed to warm to room temperature and stirred overnight. Solvent was removed *in vacuo*, and the resulting cloudy liquid was extracted with 3 x 30 mL EtOAc and 30 mL H_2O. The organic extract was dried over $MgSO_4$, filtered, and concentrated to afford 0.79 g (95% crude yield) of colorless oil. A very minimal amount of terminal acetylene was visible in the NMR spectra of the crude material; however further purification was not attempted and the spectrum could not be integrated accurately. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (m), 0.92-0.96 (m), 1.25-1.31 (m), 1.48-1.52 (m), 3.32, 3.49-3.50 (m), 3.59-3.65 9(m), 4.15 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.9, 13.5, 26.8, 27.7, 28.7, 58.8, 59.2, 68.5, 68.9, 70.4, 71.8, 89.6, 105.6.



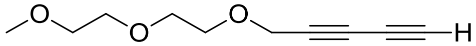
119

1,10-Bis-[2-(2-methoxy-ethoxy)-ethoxy]-deca-2,4,6,8-tetrayne (119). Diiodobutadiyne (**70**, 0.121 g, 0.401 mmol) and **{**3-[2-(2-methoxy-ethoxy)-ethoxy]-prop-1-ynyl}-tributyl-stannane (**118**, 0.357 g, 0.799 mmol) were dissolved in 21 mL dry THF in a heart shaped flask wrapped with aluminum foil. CuI (0.017g, 0.091 mmol, 22 mol %) and $Pd(PPh_3)_2Cl_2$ (0.034 g, 0.048 mmol, 12 mol %) were combined in a round bottom flask and the system was degassed six times before adding 5 mL dry THF. Both flasks were wrapped in foil and placed in ice baths (~0°C). The diiodoalkyne/tin solution was added to the catalyst mixture dropwise via cannula over a period of 10 h. Solvent was removed *in vacuo* and excess catalyst was removed using a short plug (SiO_2/hexanes, then EtOAc, then MeOH). Removal of solvent from the EtOAc fraction resulted in 0.267 g brown oil, while the MeOH fraction afforded 0.106 g brown oil. ^{13}C NMR spectra of both of these fractions contained the peaks for the ethylene groups in the end caps; however there were not enough peaks present between 60-80 ppm to confirm the presence of any alkynes. This result was obtained for several trials.



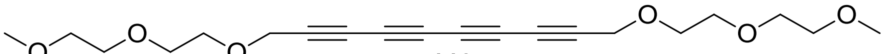
121

Triisopropyl-{5-[2-(2-methoxy-ethoxy)-ethoxy]-penta-1,3-diynyl}-silane (121).[24] (Bromoethynyl)triisopropylsilane (0.213 g, 0.821 mmol) was dissolved in 10 mL THF and 3-[2-(2-methoxy-ethoxy)-ethoxy]-propyne (**116**, 0.16 g, 1.01 mmol, in 5 mL THF) was added. CuI (0.008 g, 0.04 mmol) and $Pd(PPh_3)_2Cl_2$ (0.017 g, 0.024 mmol) were added in one portion. Diisopropylamine (0.23 mL, 1.6 mmol) was added dropwise, and the reaction was stirred at room temperature overnight. The reaction was quenched with 30 mL sat. aq. NH_4Cl, and extracted with 3 x 30 mL EtOAc. The combined organic extracts were dried over $MgSO_4$. Removal of solvent *in vacuo* resulted in 0.298 g (87% crude yield) orange oil. A short plug was run (SiO_2/hexanes, followed by 5:1 hexanes:EtOAc) to remove bis(triisopropylsilyl butadiyne) (**63**) and isolate **121** (0.153 g, 55% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 18H), 3.33 (s, 3H), 3.51 (m, 2H), 3.60 (m, 4H), 3.65 (m, 2H), 4.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 58.8, 58.9, 69.3, 70.3, 70.4, 71.5, 71.8, 72.8, 84.1, 88.8.



122

5-[2-(2-Methoxy-ethoxy)-ethoxy]-penta-1,3-diyne (122).[49] Triisopropyl-{5-[2-(2-methoxy-ethoxy)-ethoxy]-penta-1,3-diynyl}-silane (**121**, 0.094 g, 0.28 mmol) was dissolved in 2.8 mL MeCN and AgF (0.054 g, 0.42 mmol) was added. The reaction was stirred at room temperature for 1.5 h in the dark, and 1M HCl (0.56 mL) was added. After stirring for 10 min, the reaction was diluted with 10 mL Et_2O, washed with 5 mL H_2O, and dried over $MgSO_4$. The solution was passed through a pad of Celite, and solvent was removed *in vacuo* to afford **122** as orange oil (0.017 g, 34% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 2.16 (s, 1H), 3.37(s, 3H), 3.56 (m, 2H), 3.62(m, 2H), 3.67 (m, 4H), 4.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 58.7, 59.0, 67.4, 67.8, 68.0, 69.4, 70.4, 70.5, 71.8, 72.7.



119

1,10-Bis-[2-(2-methoxy-ethoxy)-ethoxy]-deca-2,4,6,8-tetrayne (119). Hay Coupling Method.[14] CuCl (0.012 g, 0.12 mmol) was dissolved in 3 mL acetone and TMEDA (0.02 mL, 0.13 mmol) was added. Oxygen was bubbled through the solution for 6 h, and the reaction was allowed to stir under O_2 overnight. The dark green catalyst mixture was filtered, and 5-[2-(2-methoxy-ethoxy)-ethoxy]-penta-1,3-diyne (**122**, 0.017 g, 0.094 mmol) was added. The reaction mixture was stirred at room temperature for 24h under O_2. Solvent was removed *in vacuo*, and 30 mL ethyl acetate was added. The organic liquid was washed with 20 mL sat. aq. NH_4Cl, and extracted with 3 x 30 mL portions of ethyl acetate. The combined organic extract was washed with 20 mL brine and dried over $MgSO_4$. Filtration and removal of solvent *in vacuo* resulted in 0.009 g (52% crude yield) of brown oil. Some black insoluble material was also present. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.38 (s, 6H), 3.55 (m, 4H), 3.67 (m, 12 H), 4.29 (s, 4H); ^{13}C NMR (125MHz, $CDCl_3$): δ 59.01, 59.03, 61.7, 63.4, 69.6, 70.4, 70.6, 71.2, 71.9, 75.2.

2.8 References

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Chapter 3: Attempts towards the Synthesis and Polymerization of Diynes with Nitrile End Groups

3.1 Dicyanodiacetylene

Dicyanodiacetylene is a short polyyne composed solely of carbon and nitrogen atoms. The synthesis of dicyanodiacetylene (**22**) was pursued due to the electronic properties and potential applications of this compound, particularly in regards to polymerization. The electron-withdrawing nature of the nitrile functionalities makes the carbon-carbon triple bonds very electron poor, and therefore, the polymerization behavior of dicyanodiacetylene would be very interesting to study. The resulting polydiacetylene would be electron deficient, and could have potential applications in optics and electronics (Figure 3.1). Contrary to the behavior that has been observed for the iodine substituents on poly(diiododiacetylene),[1] the nitrile substituents should not eliminate, thus allowing the polydiacetylene to undergo subsequent reactions. The polymerization of dicyanodiacetylene might also result in a more stable species than the diyne monomer, which has been described as very unstable.[2, 3]

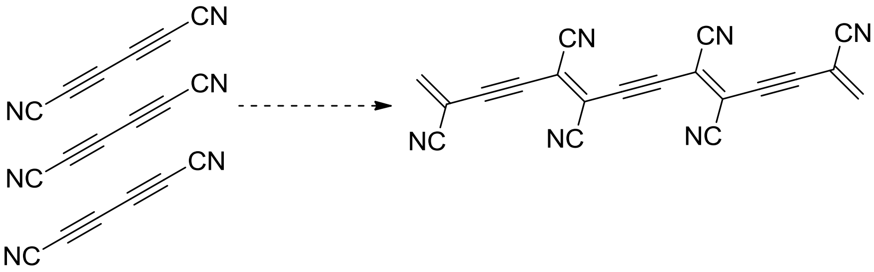
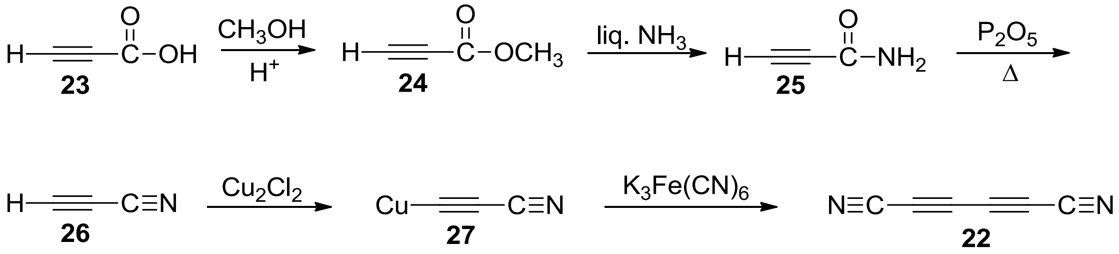


Figure 3.1 1,4-topochemical polymerization of dicyanodiacetylene

3.1.1 Synthetic Background

Dicyanodiacetylene was first prepared by Moureu and Bongrand in 1920 through the coupling of cuprous cyanoacetylene.[2] In the 1950s, experimental modifications were made by

Brockman, as well as Saggiomo and co-workers, both of whom developed similar methods for the synthesis of diyne **22**.[2, 4] Miller and Lemmon made slight alterations to the reported route in 1967, due to difficulties that were encountered when trying to repeat the synthesis, which resulted in modest yield improvements and simpler procedures.[3] The synthesis of dicyanodiacetylene that was reported by Miller and Lemmon is shown in Scheme 3.1.



Scheme 3.1 Miller and Lemmon's synthesis of dicyanodiacetylene[3]

Dicyanodiacetylene was described as a white crystalline solid that melts at 64.5-65°C.[2-4] It has a characteristic unpleasant odor, and is a strong lachrymator.[2-4] Careful handling of this compound is required, as the diyne slowly darkens *in vacuo* at room temperature, but is stable at -75 ºC.[2-4] All procedures involved in the preparation of dicyanodiacetylene were carried out in the absence of oxygen, and sublimation techniques under reduced pressure and low temperature were used for isolation.[4]

Hirsch and co-workers reported the synthesis of dicyanopolyynes with varying lengths by vaporizing graphite in the presence of cyanogen (Figure 3.2).[5, 6] This method required temperatures up to 6000 ºC, and resulted in a mixture of dicyanopolyynes that were 3 to 8 carbon-carbon triple bonds in length.[6] The mixture was extracted from the resulting carbon soot in 7% yield.[6] Preparative HPLC was used to isolate the individual compounds, which were described as colorless crystals that were very soluble in chloroform and toluene and stable at -18 ºC in dilute solutions in the dark.[6] Cyano-capped triynes and tetraynes were the major components of the product mixture, accounting for 55% and 35% of the overall 7% yield, respectively.[6] Although dicyanodiacetylene was not synthesized using this method, it allowed for the preparation of slightly longer dicyanopolyynes.

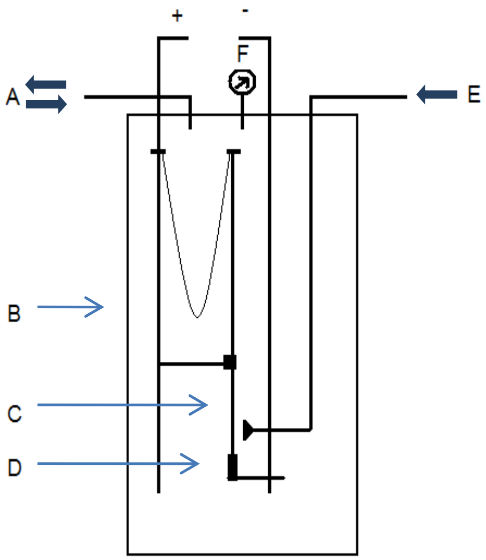
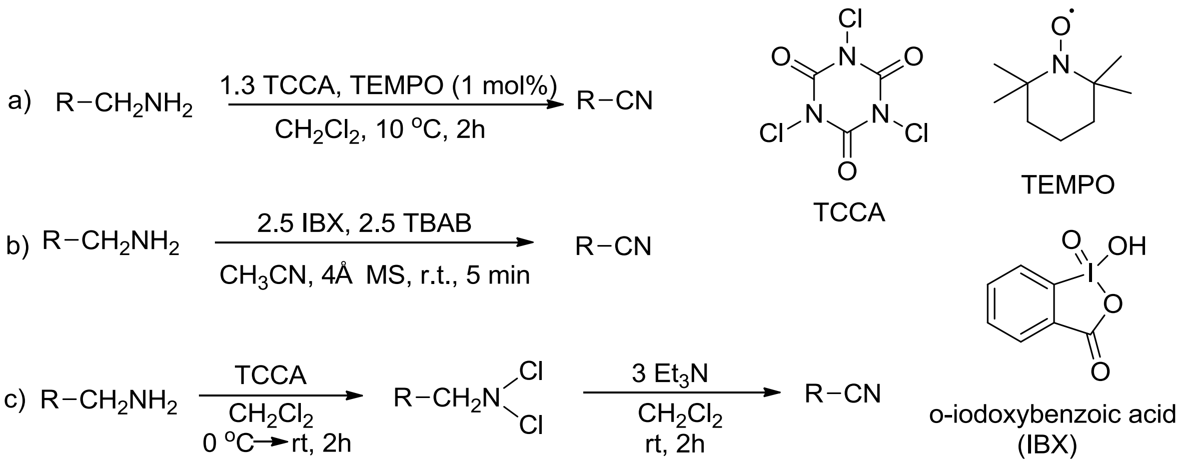


Figure 3.2 Schematic of reactor used for graphite vaporization: Helium supply and connection to vacuum system (A), Pyrex bell jar (B), graphite rod 3mm (C) graphite block 10mm (D) gas inlet tube for cyanogen (E) manometer (F)[5, 6]

Cataldo and co-workers also reported the synthesis of mixtures of dicyanopolyynes using graphite electrodes arced in liquid nitrogen.[7-9] This method also required high temperatures, which resulted in carbon vaporization and oligomerization.[7] Liquid nitrogen was used to quench the reaction, resulting in cyano-capped polyynes ranging from 2 to 4 carbon-carbon triple bonds in length, with dicyanodiacetylene as the major component of the product mixture.[7] In addition to the cyano-capped polyynes, moisture in the system led to the formation of a small amount of terminal polyynes.[7] Although this method allowed for the preparation of dicyanodiacetylene, the experimental conditions that are required are not practical for the purposes of this work.

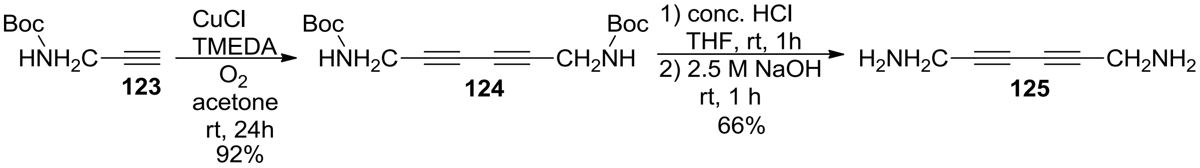
3.1.2 Synthetic Efforts towards Dicyanodiacetylene

The methods of Brockman, Saggiomo, and Miller, which date back more than forty years, had some significant drawbacks. Their synthetic routes went through cyanoacetylene, an intermediate that causes severe burns and blistering if not handled properly. In addition, the overall yield for the diyne was very low, despite conducting the final homocoupling reaction of cuprous cyanoacetylene in a cold room to minimize decomposition. More recent literature was investigated in an effort to determine an alternative route towards dicyanodiacetylene. The oxidation of primary amines to nitriles with mild conditions has been reported. Therefore, it was thought that dicyanodiacetylene could be prepared from the diamine precursor (**125**). Chen and co-workers used trichloroisocyanuric acid (TCCA) and 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO) as oxidizing agents (Scheme 3.2a), while Drouet and co-workers employed *o*-iodoxybenzoic acid (IBX) and tetrabutylammonium bromide (TBAB) (Scheme 3.2b).[10, 11] De Luca and Giacomelli reported the oxidation of amines to nitriles using TCCA and triethylamine, which proceeded through the formation of a dichloroamine intermediate (Scheme 3.2c).[12]



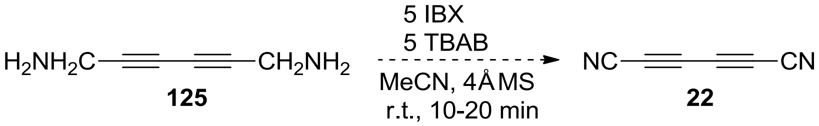
Scheme 3.2 Oxidation of primary amines to nitriles[10-12]

The previously described methods suggested that the synthesis of dicyanodiacetylene from the amine precursor was plausible. Therefore, a route towards 2,4-hexadiynylene-1,6-diamine (**125**) was developed. As shown in Scheme 3.3, Boc-protected propargyl amine was subjected to Hay coupling conditions to obtain *N,N'*-di-*tert*-butoxycarbony-2,4-hexadiynylene-1,6-diamine (**124**) in good yield. Deprotection of diyne **124** afforded 2,4-hexadiynylene-1,6-diamine **125**.



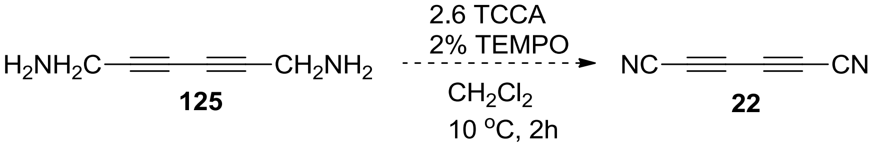
Scheme 3.3 Synthesis of 2,4-hexadiynylene-1,6-diamine (**125**)[13]

Oxidation of diamine **125** to the corresponding nitrile **22** was challenging. Several attempts were made using the IBX/TBAB system (Scheme 3.4); however the results were difficult to interpret since the NMR spectra were very complex. Mass spectrometry and IR did not provide any additional information, except to suggest that the desired product had not formed due to the absence of a defined stretch in the nitrile region in the IR spectrum. This system was not pursued any further, because it was believed that the hypervalent iodine of the IBX might oxidize the bromine in TBAB. If free bromine or bromine radicals formed, there could be side reactions with the triple bonds in the starting material alkyne in the starting material, which would hinder product formation. There was also no literature precedent for the application of this reaction to allyl or propargyl amines. Therefore, there was no conclusive evidence that this method was suitable for our system.[11]



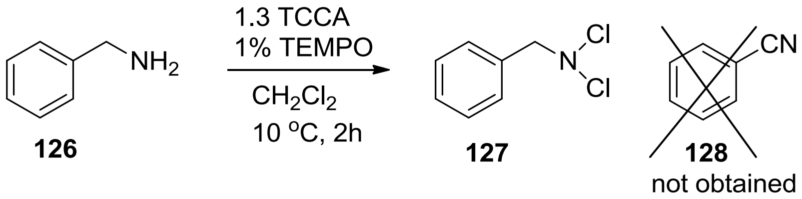
Scheme 3.4 Attempted synthesis of **22** using Drouet's method[11]

The methods described by Chen and co-workers were explored as an alternative way to oxidize **125** to the corresponding nitrile (Scheme 3.5).[10] Diyne **125** was subjected to these reaction conditions several times, and the results were inconclusive. A yellow/orange oily solid was obtained in each case, which differed from the literature description of dicyanodiacetylene **22** as a white solid with a needle-like texture.[2, 4] Attempts to purify the solid using recrystallization or chromatography were not pursued, as the NMR spectra did not indicate product formation. The ^{1}H and ^{13}C NMR spectra were complex, and the ^{13}C NMR did not contain any peaks that would be expected for dicyanodiacetylene.



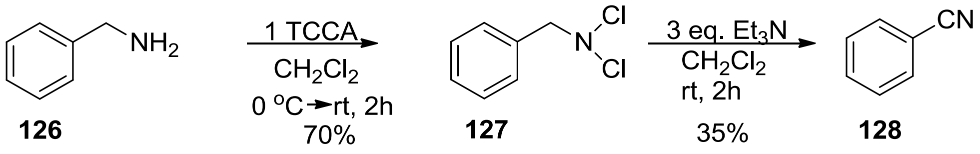
Scheme 3.5 Attempted synthesis of **22** using Chen's method[10]

To further explore the oxidation of amines using TCCA and TEMPO, a model reaction was performed using benzylamine (**126**), which reportedly gave the corresponding nitrile in 90% yield.[10] The exact literature procedure was repeated; however the NMR spectra for the product did not correlate with the known spectral data that have been reported for benzonitrile (**128**), but did indicate the presence of a monosubstituted benzene ring (Scheme 3.6).



Scheme 3.6 Model oxidation reaction[10]

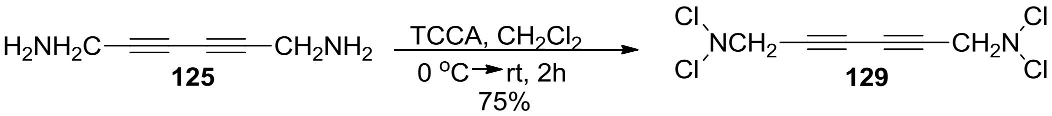
Much insight into the reaction between amines and TCCA was gained from the work of De Luca and Giacomelli, who reported the formation of dichloroamines in the presence of TCCA.[12] They discovered that further reaction with triethylamine was necessary to obtain the desired nitrile. To explore this reaction, the literature procedure was repeated using benzyl amine as shown in Scheme 3.7. Conversion of the amine to dichloroamine **127** was achieved in 70% yield, and the NMR spectra matched the results that were obtained when trying to use Chen's method in previous experiments (Scheme 3.6). This suggested that the TEMPO catalyst was no longer effective. The subsequent elimination reaction with triethylamine yielded benzonitrile, confirming the literature report.



Scheme 3.7 Model synthesis of benzonitrile[12]

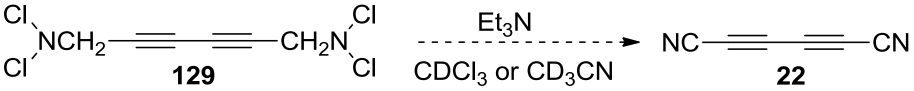
Since the conversion of benzylamine to benzonitrile with TCCA and triethylamine proceeds through an isolable dichloroamine intermediate, bis(dichloroamine)butadiyne **129** was targeted (Scheme 3.8). Diyne **129** was successfully synthesized and isolated using methods described by De Luca and Giacomelli.[12] This compound was stable, and easy to handle, which made it a desirable intermediate towards dicyanodiacetylene (**22**).

The next step towards dicyanodiacetylene was reacting bis(dichloroamine)butadiyne **129** reacted with triethylamine. Due to the instability of dicyanodiacetylene (**22**), this reaction was conducted in deuterated solvent in an NMR tube, so that the product could be detected without isolation of the compound. The ^{1}H NMR spectrum for amine **129** contains a peak at 4.3 ppm, corresponding to the CH_2 group. This signal is expected to disappear once the nitrile is formed, and was therefore used to monitor product formation. The experiments suggest that the elimination reaction proceeds very rapidly, indicated by the instantaneous disappearance of the peak at δ 4.3. Immediately after the triethylamine is added, the reaction mixture changes color from light orange to dark brown/black, which is accompanied by the formation of insoluble black material. The ^{13}C NMR spectra only contained solvent peaks and peaks corresponding to triethylamine hydrochloride salt, and consequently, product formation could not be confirmed.



Scheme 3.8 Synthesis of **129**[12]

Experimental modifications were made to decrease possible product decomposition and gain more information regarding the rate of the reaction and the intermediate(s) that were formed. When the amount of triethylamine was decreased, the mixture underwent the same color change, and CH_2 peak became smaller but did not disappear. Kinetic experiments were attempted to monitor the progress of this reaction; however the size of the CH_2 peak remained constant over a period of 2 hours, once again suggesting this reaction happens immediately upon addition of triethylamine. The reaction temperature was also lowered to 0 °C, which did not prevent decomposition as the mixture turned dark and black solid formed immediately upon the addition of triethylamine. Temperatures below 0 ºC did not change the observed results. Diisopropylethylamine was also used, as a bulkier base might slow down the elimination; however the results that were obtained were identical to what was observed with triethylamine. Removing oxygen from the system also did not improve the results, as the reaction mixture proceeded to turn black upon addition of base. ^{13}C NMR of the reactions that were conducted in deuterated chloroform or acetonitrile contained only solvent peaks, and peaks corresponding to the hydrochloride salt of triethylamine (Scheme 3.9).



Scheme 3.9 Attempts towards **22**

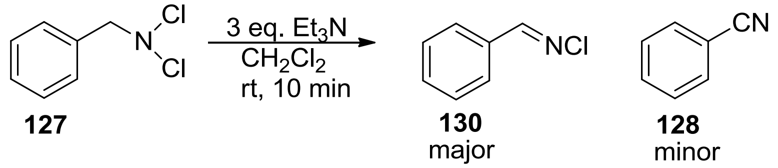
In addition to the NMR experiments, the reaction of diyne **129** with triethylamine was also attempted in the lab. The first few trials were conducted at room temperature in dichloromethane, in accordance with literature procedures.[12] A color change from light orange to black was observed, similar to the experiments that were conducted in the NMR tubes. ^{13}C NMR did not provide any information, as only the chloroform peaks were visible. This reaction was repeated at -50 °C in $CDCl_3$ and carefully degassing all reagents; however the mixture turned black once again and product formation was not suggested by NMR. Similar results were obtained when acetonitrile, dichloromethane, and carbon tetrachloride were used at temperatures ranging from -50 to -20 °C, based on the melting point of the solvent. The results for the elimination reaction with diyne **129** are summarized in Table 3.1.

Table 3.1 Attempted synthesis of dicyanodiacetylene from bis(dichloro)amine diyne **129**

Trial	Equivalents of Et_3N	Solvent	Temperature	Appearance after addition of base	NMR observations
1	6	CD_3CN	25 °C	dark brown/black	CH_2 gone, $Et_3N \cdot HCl$
2	6	$CDCl_3$	25 °C	dark brown/black	CH_2 gone, $Et_3N \cdot HCl$
3*	6	CH_2Cl_2	25 °C	dark brown/black solid isolated after	CH_2 gone, only solvent visible
4	3.9	$CDCl_3$	25 °C	dark brown/black	CH_2 gone, $Et_3N \cdot HCl$
5	4**	$CDCl_3$	25 °C	dark brown/black	CH_2 gone, $i\mathrm{Pr}_2\mathrm{EtN} \cdot HCl$
6	4	$CDCl_3$	0 °C	dark brown/black	CH_2 gone, $Et_3N \cdot HCl$
7	4	$CDCl_3$	-3 °C	light brown	CH_2 gone, $Et_3N \cdot HCl$
8*	6	$CDCl_3$	-50 °C	dark brown/black	CH_2 gone, $Et_3N \cdot HCl$
9*	6	CH_2Cl_2	-65 °C	dark brown/black	CH_2 gone, only solvent visible
10*	6	CCl_4	-20 °C	dark brown/black	CH_2 gone, only solvent visible
11*	6	CH_3CN	-40 °C	dark brown/black	CH_2 gone, only solvent visible

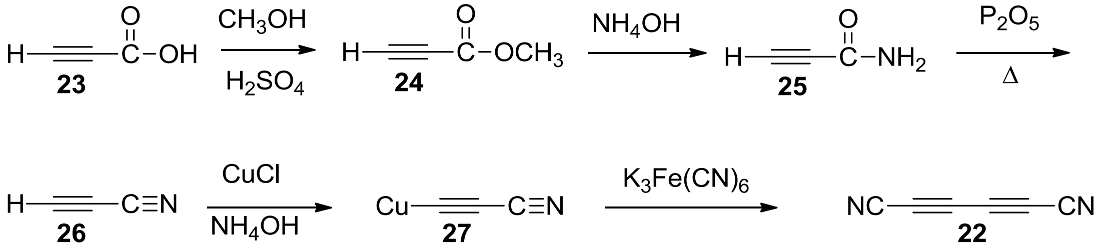
* Reaction was performed in the lab, all others conducted in NMR tube
**Diisopropylethylamine was used in this trial

The model reaction of dichlorobenzylamine **127** with triethylamine was revisited, to determine how quickly the chlorine elimination proceeds. After treatment of amine **127** with 3 equivalents of triethylamine for 10 minutes, the resulting ^{1}H and ^{13}C NMR spectra for the product indicated that chloroimine derivative **130** was the major component of the mixture, with a small amount of benzonitrile present (Scheme 3.10). This provided information regarding the rate of elimination, and suggests that the first chlorine is removed very rapidly, while loss of the second chlorine proceeds more slowly. From this result, it could be inferred that all four chlorine atoms were not removed instantaneously from diyne **129**, and that the reaction may proceed through an unstable bis(chloroimine) intermediate that readily decomposes.



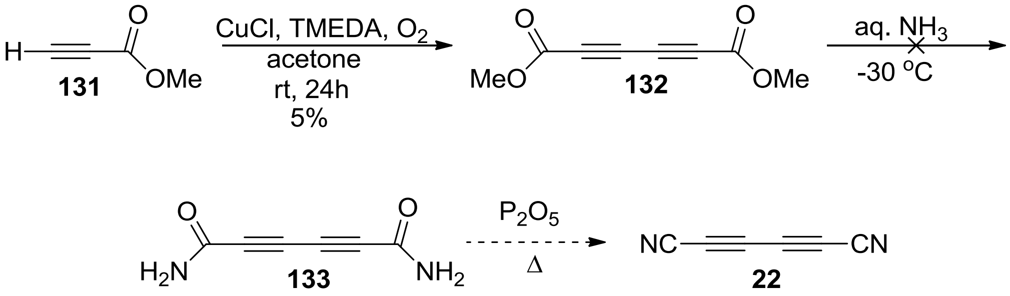
Scheme 3.10 Chloroimine formation

The synthesis of dicyanodiacetylene was also explored using an approach that was similar to the original methods reported by Saggiomo[4] (Scheme 3.11) and Miller.[3] These methods go through cyanoacetylene—a compound that has been noted to "penetrate gloves with ease and cause painful burns and blistering" and is a "powerful lachrymator."[14, 15] In an effort to avoid handling this compound, 2,4-hexadiynediamide **133** was targeted as the precursor to dicyanodiacetylene. Subjecting diyne **133** to dehydration conditions using P_2O_5 should provide access to dicyanodiacetylene, although there were no literature precedents for compound **133**.



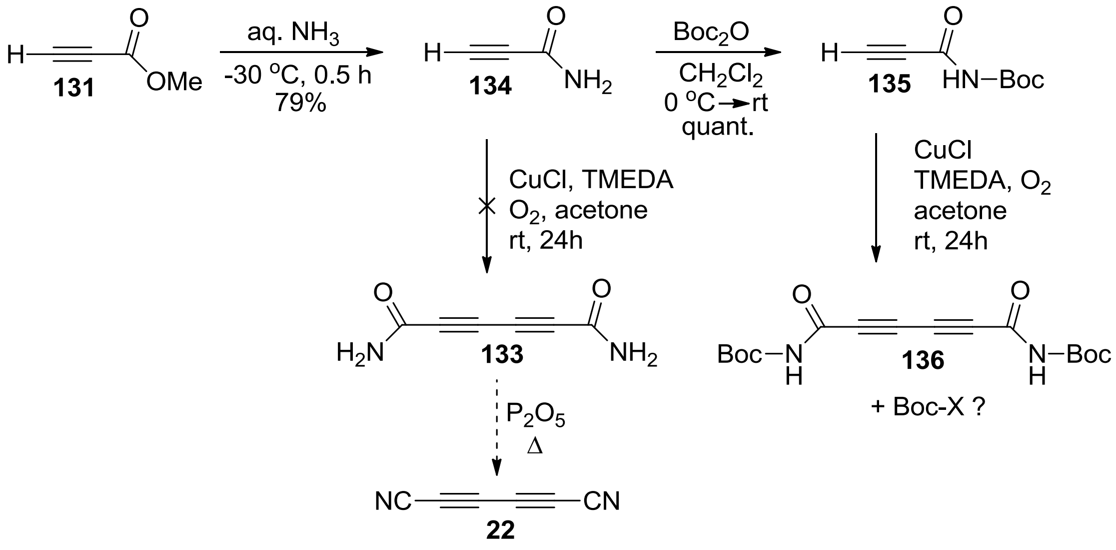
Scheme 3.11 Saggiomo's synthesis of dicyanodiacetylene[4]

One of the proposed routes towards dicyanodiacetylene is shown in Scheme 3.12. Hay Coupling of methylpropiolate (**131**) [16] afforded product; albeit in low yield. This is probably due to the instability of diyne **132**, as a significant amount of black insoluble material formed during the reaction. Subsequent reaction of **132** with concentrated aqueous ammonia did not appear to produce diyne **133**, as ^{1}H and ^{13}C NMR spectra were complicated and did not contain the expected peaks.



Scheme 3.12 Initial route towards **22**

Since difficulties were encountered when trying to convert ester **132** to amide **133**, a similar amidation reaction was performed with methyl propiolate, in accordance with the literature (Scheme 3.13).[14, 15] Propiolamide (**134**) was subjected to Hay Coupling conditions; however a significant amount of black solid formed during the reaction. Both the ^{1}H and ^{13}C NMR spectrum of the crude product resembled starting amide **134**. To prevent any unwanted reaction of the amines, Boc protection of propiolamide (**134**) was performed, using conditions that were reported for the protection of propargyl amine.[17] The NMR spectra that were obtained looked clean and the peaks were in the appropriate regions; however the peak heights in the ^{13}C NMR suggested excess Boc was present relative to propiolamide.[18, 19] Attempts to remove any residual Boc alcohol or other byproducts did not change the spectral data; therefore the material was used directly in the following Hay Coupling step. Alternative protecting conditions using 4-dimethylaminopyridine (DMAP) were employed, but peaks corresponding to compound **135** were not visible in the NMR spectra of the crude material.



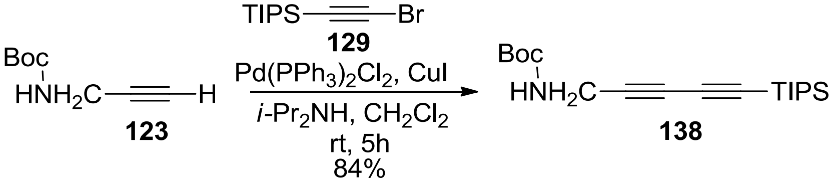
Scheme 3.13 Alternative route towards **22**

3.2 5-Iodo-penta-2,4-diynenitrile

5-Iodo-penta-2,4-diynenitrile (**137**) is an asymmetric diyne that contains both electron donating and withdrawing end groups, giving this compound a push-pull dynamic. Theoretical studies by Jain and Chandrasekhar have indicated that push-pull polyynes typically have lower hyperpolarizibilities compared to polyene analogs, due to mixing of in-plane and out-of-plane π-π* excited configurations in the former.[20] However, incorporating donor and acceptor groups such as I (or Br) and CN, respectively, increases the hyperpolarizabilities of the polyynes because these groups are able to interact with both sets of orthogonal π molecular orbitals.[20] The push-pull nature of 5-iodo-penta-2,4-diynenitrile would make properties of this diyne, and the resulting polymeric material interesting to study. The presence of both donor and acceptor groups could facilitate charge transport throughout the polydiacetylene, and the third-order nonlinear optical properties of push-pull diynes suggests the resulting polymer could have potential applications in electronic or optical devices.[21]

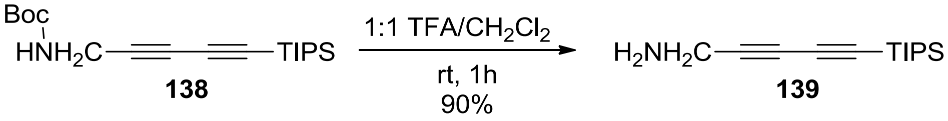
3.2.1 Synthesis of 5-Iodo-penta-2,4-diynenitrile

This synthesis of 5-iodo-penta-2,4-diynenitrile (**137**) was achieved by incorporating some of the reactions that were utilized when targeting dicyanodiacetylene, as there are no previous reports for the preparation of this diyne in the literature. The first step consists of a Cadiot-Chodkiewicz coupling between *tert*-butyl prop-2-ynylcarbamate (**123**) and (bromoethynyl)triisopropylsilane (**120**), based on a procedure described by Hwang and co-workers (Scheme 3.14).[22] Interestingly, the halogenated alkyne has an effect on this reaction, as the cross-coupling of the brominated or iodinated propargyl amine with triisopropylsilyl acetylene yielded poorer results compared to reactions where the silyl acetylene was halogenated. It was also observed that bromoacetylene **120** resulted in higher yield of cross-coupled diyne **138** compared to the iodo analog.



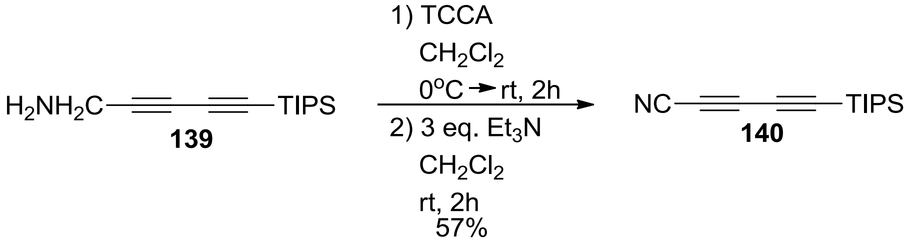
Scheme 3.14 Synthesis of **138**

The next step in the synthetic sequence was cleavage of the Boc protecting group on the amine. Valverde and co-workers reported a series of deprotection conditions that were applied to compounds that contained various silyl groups and determined which conditions were capable of removing Boc groups without also cleaving the silyl group.[23] Based on these results, a 1:1 mixture of trifluroacetic acid (TFA) and dichloromethane was employed for the deprotection, which produced amine **139** in high yield.



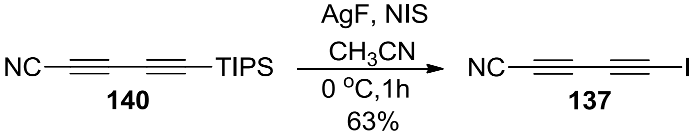
Scheme 3.15 Boc deprotection[23]

The resulting amine was oxidized to the corresponding nitrile with TCCA and triethylamine, based on the procedures that were reported by De Luca and Giacomelli.[12] The nitrile was formed in 57 % over two steps, as shown in Scheme 3.16 below.



Scheme 3.16 Synthesis of **140**[12]

The final step in the synthetic pathway towards 5-iodo-penta-2,4-diynenitrile **137**consists of iodination of the triisopropylsilyl group using silver fluoride (AgF) and *N*-iodosuccinimide (NIS).[24] Conditions that were reported for the bromination of TIPS groups by Kim and co-workers were employed, replacing *N*-bromosuccinimide with *N*-iodosuccinimide. While the iodination of trimethylsilyl groups with silver nitrate and NIS is typically conducted in acetone, the reaction with AgF must be run in acetonitrile, as this is the only organic solvent in which the silver salt is moderately soluble.[24] Three equivalents of each reagent were used and the reaction was conducted at 0 °C, in order to increase the rate of reaction and minimize possible product decomposition. A light yellow solid was isolated in 63 % yield, and a melting point of the product was obtained to assess the stability of the diyne. Compound **137** decomposes and turns black at 100ºC, suggesting its stability is comparable to diiodobutadiyne (**70**, C_4I_2), which decomposes at 90ºC.



Scheme 3.17 Synthesis of **137**

3.2.2 Co-crystallization Experiments with 5-Iodo-penta-2,4-diynenitrile and Symmetric Oxalamide Hosts

To explore the co-crystallization of 5-iodo-penta-2,4-diynenitrile as a means of forming the resulting push-pull polymer, Fowler and Lauher's host-guest strategy was implemented. This method has been associated with successful single-crystal-to-single-crystal polymerization of diacetylenes, triacetylenes, and trienes.[25] As discussed in Chapter 1, the ideal parameters that were determined by Baughman for 1,4-polymerization of diacetylenes include a repeat distance (r) of 4.9-5.0 Å between the monomer units, and a C1-C4 distance (d) of 3.5 Å. This orientation results in a 45º tilt angle (θ), shown in Figure 3.3.[26]

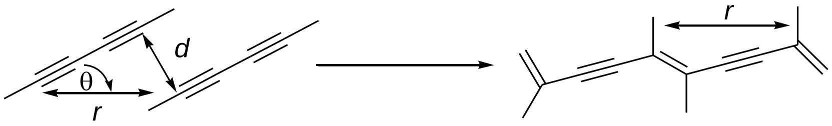


Figure 3.3 Parameters for 1,4-polymerization,[26, 27] r= 4.9 – 5.0 Å, θ = 45º, d = 3.5Å

The hydrogen bonding networks for the urea and oxalamide functionalities of the host compounds correspond to repeat distances of 4.6 and 5.0 Å, respectively (Figure 3.4). Therefore, the host molecules that are employed when targeting the 1,4-polymerization of diacetylenes often contain these moieties. In the Goroff group, oxalamide hosts have been effective in the polymerization of diiodobutaidyne (**70**),[28-30] thus similar hosts were used for the polymerization of 5-iodo-penta-2,4-diynenitrile (**137**).

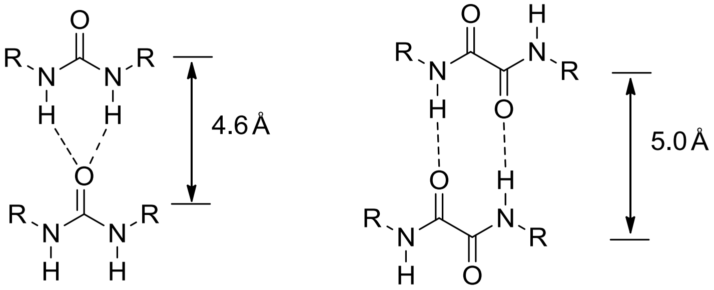
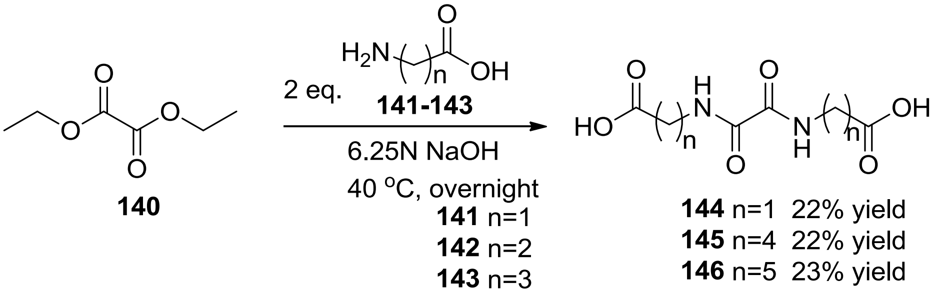


Figure 3.4 Hydrogen bonding networks for the urea (left) and oxalamide (right) groups[31]

The first class of oxalamide hosts that were employed in the co-crystallization experiments with guest **137** contained carboxylic acid end groups. Hydrogen bond interactions between the carboxylic acid groups of the host and the nitrile functionality in 5-iodo-penta-2,4-diynenitrile (**137**) could align the guest monomers in the proper orientation for topochemical polymerization to occur.[25] Oxalyldigylcine **144** was the smallest of the series of carboxylic acid hosts that were synthesized. Additional hosts 5,5′-(oxalyldiimino)dipentanoic acid (**145**) and 6,6′-(oxalyldiimino)dihexanoic acid (**146**) were prepared according to literature procedures.[32] The general synthesis for the carboxylic acid hosts is shown in Scheme 3.18 below.[32, 33]



Scheme 3.18 Synthesis of carboxylic acid hosts[33]

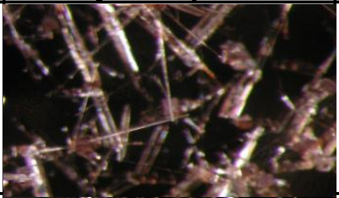
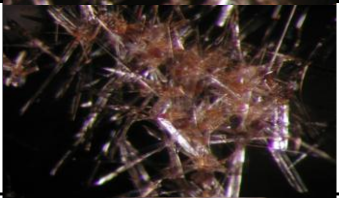
The co-crystals were prepared in an analogous fashion to the procedure that was developed for growing co-crystals of diiodobutadiyne and bis(nitrile) or bis(pyridly) oxalamide hosts.[28, 29] The host and guest were dissolved in solvent, and the mixture was sonicated to ensure that both components dissolved and to break up any aggregation of the solid. Centrifugation was used to collect any excess host that did not go into solution, and the liquid was decanted into crystallization dishes. The dishes were covered with foil that contained small holes which allowed for slow evaporation of the solvent.

The low solubility of the carboxylic acid hosts limited the solvent options for co-crystal preparation. Methanol was the only organic solvent that dissolved the hosts, which became less soluble as the length of the methylene chain increased. Different ratios of methanol/water mixtures were used in some trials to improve the host solubility; however this decreased the solubility of the guest diyne. The solubility of the carboxylic acid hosts improved when warm methanol was used, but the material that resulted from solvent evaporation did not appear to be different than what was obtained in previous trials. In addition to the changing the solvent, the host to guest ratio and type of crystallization dishes that were used were also varied. The majority of evaporation experiments were performed using 50 mL glass crystallizing dishes that were 35 x 50 millimeters. The solid that formed upon solvent evaporation was often difficult to isolate from the glass dishes, therefore, Teflon dishes with the same dimensions were employed in several experimental trials. While the crystals were often easier to remove from the Teflon dishes, characterization of the resulting solid suggested the host and guest were crystallizing independently of one another.

The results of the co-crystallization experiments using 5-iodo-penta-2,4-diynenitrile (**137**) and carboxylic acid oxalamide hosts **144**, **145**, and **146** are summarized in Table 3.2

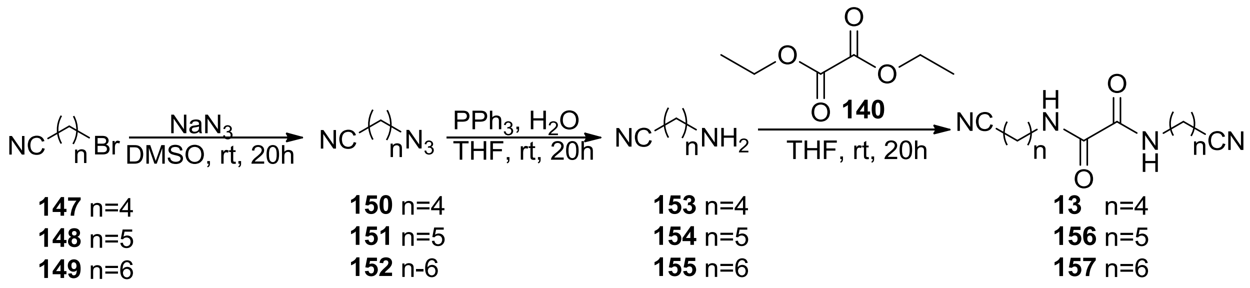
below. There was no conclusive evidence that co-crystals had formed in any of the trials that were performed, as the melting point, crystal structure, and IR spectrum was often characteristic of isolated host. The poor solubility of the carboxylic acid hosts, particularly **145** and **146**, limited the variety of conditions that were explored.

Table 3.2 Co-crystallization experiments with carboxylic acid oxalamide hosts

Host (H)	Ratio H:G	Solvent	Appearance	m.p.	XRD	Other Analysis
144	1:1	MeOH	light brown branched needles and colorless square crystals	130ºC turned black	mounted square crystals, too small	
145	1:1	MeOH*		120°C turned black		*poor solubility
145	1:2	5:1 MeOH: H_2O				
145	1:2	7:2 MeOH: H_2O			mounted colorless crystals, host	
146	1:2	Warm MeOH		130°C turned black	mounted colorless crystals, host	
146	1:3	Warm MeOH		120°C turned black	crystals did not diffract well	IR spectrum suggested CN present

Since carboxylic acid oxalamide hosts did not appear to be ideal for the polymerization of 5-iodo-penta-2,4-diynenitrile , nitrile oxalamide hosts were explored. In this case, the nitrile functionality of the host should interact with the iodine atom of the guest monomer via halogen bonding, in an analogous fashion to the 1,4-topochemical polymerization of diiodobutadiyne (**70**).[28, 29]

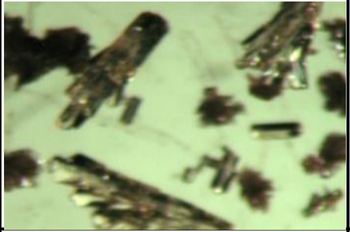
Similar to the experiments that were conducted with the carboxylic acid hosts, nitrile hosts with a varying number of methylene units were explored. *N,N'*-(Bispentanenitrile)-oxalamide (**13**), *N,N'*-(bishexanenitrile)oxalamide (**156**) and *N,N'*-(bisheptanenitrile)oxalamide (**157**) were prepared according to the route illustrated in Scheme 3.19 below. Compounds **156** and **157** were prepared by group member Daniel Resch.



Scheme 3.19 General synthesis of nitrile oxalamide hosts[28]

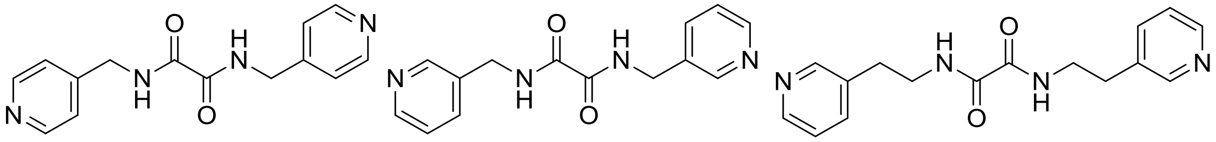
A 1:2 ratio of host to guest was used in all the experiments, to account for any guest that may decompose over the course of solvent evaporation. Teflon crystallization dishes were used in certain trials to facilitate removal of the solid that resulted after solvent evaporation. Acetonitrile was also employed in one set of experiments, based on the optimized conditions determined by Dan Resch when exploring the polymerization of diiodobutadiyne **70**. Despite several attempts with nitrile hosts **13**, **156**, and **157**, there was no evidence that the desired co-crystals had formed (Table 3.3).

Table 3.3 Co-crystallization experiments with nitrile oxalamide hosts

Host (H)	Ratio H:G	Solvent	Appearance	m.p.	XRD	Other Analysis
13	1:2	MeOH		117ºC melted	mounted colorless crystals, host	
156	1:2	MeOH		122-127ºC turned black	mounted crystals, too small to obtain data	
156	1:2	MeOH*		117-122°C turned black	mounted crystals, did not diffract well	IR obtained was identical to host spectrum
157	1:2	MeOH*	Colorless needle-like crystals with some black particles on surface	96-97°C melted, same as host	mounted colorless crystals, host	
157	1:2	MeOH		100°C melted		Raman attempted, no information provided
157	1:1	MeCN		102 ºC melted		

*Teflon dishes used in these experiments

Pyridyl oxalamide hosts were also employed in an attempt to co-crystallize 5-iodo-penta-2,4-diynenitrile (**137**), as diiodobutadiyne has been shown to successfully form co-crystals with these hosts.[34] Based on Lewis basicity, the halogen bonding interaction between the pyridyl nitrogen in the host and the iodine in the guest diyne should be stronger than the nitrile-iodine interaction, which may be conducive to co-crystal formation. Christopher Wilhelm previously prepared co-crystals of diiodobutadiyne and *N,N’*-bis(pyridine-4-ylmethyl)oxalamide (**158**), *N,N’*-bis(pyridine-3-ylmethyl)oxalamide (**12**), and *N,N’*-bis(pyridine-3-ylethyl)oxalamide (**159**) (Figure 3.5), and was able to form the resulting polymer in all cases.[30, 34] When using host **159** spontaneous polymerization was observed, but the respective co-crystals of hosts **159** and **12** and diiodobutadiyne (**70**) required pressure to induce polymerization.[30, 34] The two pyridyl hosts that were used in the experiments with 5-iodo-penta-2,4-diynenitrile were oxalamides **12** and **159**.

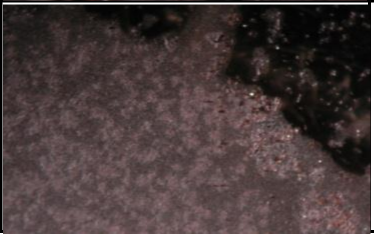


158 **12** **159**

Figure 3.5 Pyridyl oxalamide hosts[30, 34, 35]

The experiments that were performed with the pyridyl hosts did not yield crystalline material. Instead, a dark brown, opaque film formed on the surface of the crystallization dishes, and therefore, only minimal analysis could be performed. The results of the co-crystallization attempts using the pyridyl hosts are summarized in Table 3.4.

Table 3.4 Co-crystallization experiments with pyridyl oxalamide hosts

Host (H)	Ratio H:G	Solvent	Color Appearance	m.p.	XRD	Other Analysis
12	1:1	MeOH		157°C turned black	mounted colorless fibers, too narrow	
12	1:2	MeOH	black/brown solid film		material not crystalline	
159	1:2	MeOH			material not crystalline	IR obtained was identical to host spectrum
159	1:4	MeOH			material not crystalline	

3.2.3 Co-crystallization Experiments with 5-iodo-penta-2,4-diynenitrile and Asymmetric Oxalamide Hosts

The asymmetry of 5-iodo-penta-2,4-diynenitrile (**137**) is a complicating factor when trying to achieve ordered polymerization using symmetric oxalamide hosts containing carboxylic acid, nitrile, or pyridyl end groups. Experimental results suggested that forming hydrogen or halogen bond interactions at only one end of the diyne guest may not be enough to properly align the monomer for ordered polymerization. Therefore, asymmetric oxalamide hosts were targeted.

The presence of a Lewis acid and Lewis base functionality on the same host molecule could allow both the nitrile and iodine ends of 5-iodo-penta-2,4-diynenitrile to be held via hydrogen and halogen bonding interactions, respectively. With the diyne monomer oriented in a fixed position, 1,4-topochemical polymerization may be more likely to occur (Figure 3.6).

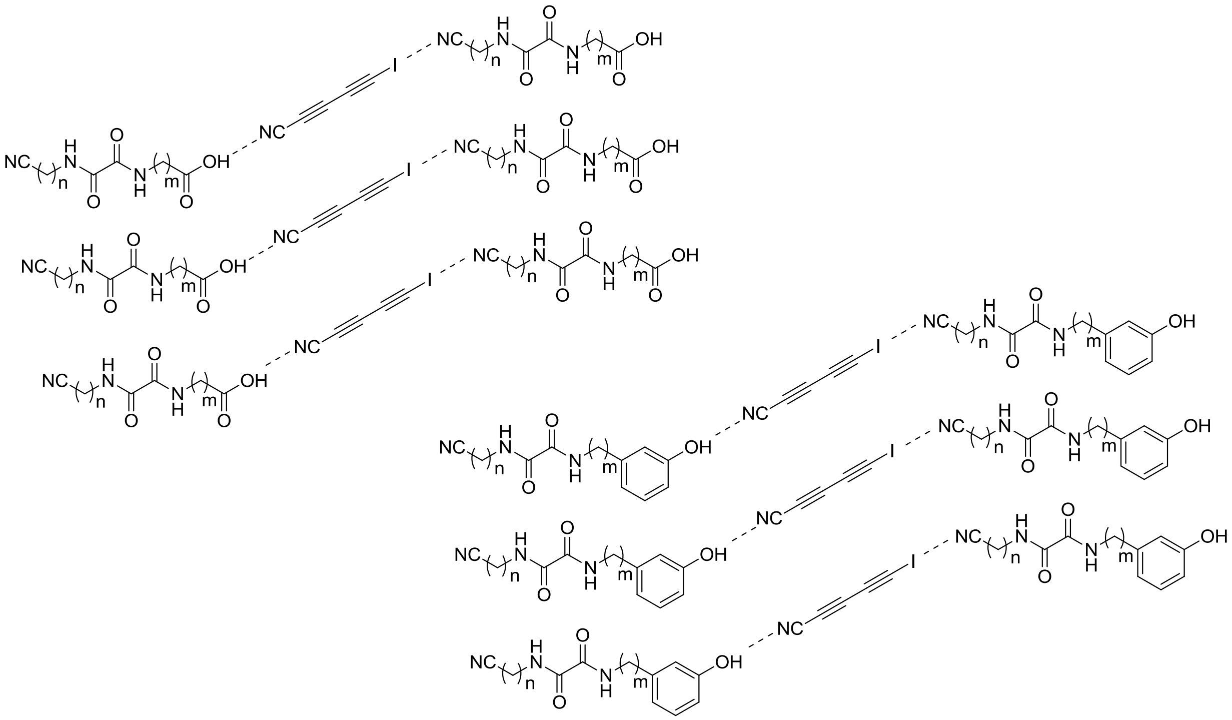
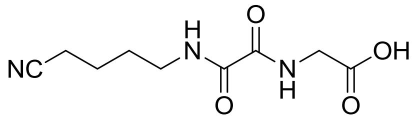


Figure 3.6 Possible host-guest interactions between asymmetric hosts and 5-iodo-penta-2,4-diynenitrile

Initial synthetic efforts were focused on oxalamide hosts that contain both nitrile and carboxylic acid end groups (Figure 3.7). While numerous symmetric nitrile and carboxylic acid hosts have been made in this lab, hosts containing both functionalities have not been previously prepared. The different solubilities of the nitrile amine and the amino acid subunits that are required made it difficult to determine the appropriate reaction conditions for synthesizing the target asymmetric hosts. While the bis(nitrile) oxalamide hosts are prepared in THF, the carboxylic acid hosts require the use of a H_2O/NaOH mixture, because these acids are not soluble in organic solvents. This can be problematic since nitriles can be hydrolyzed under basic conditions, although heat is usually required for this to occur.



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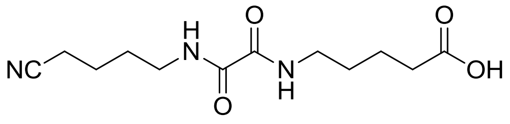

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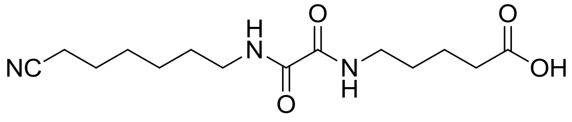
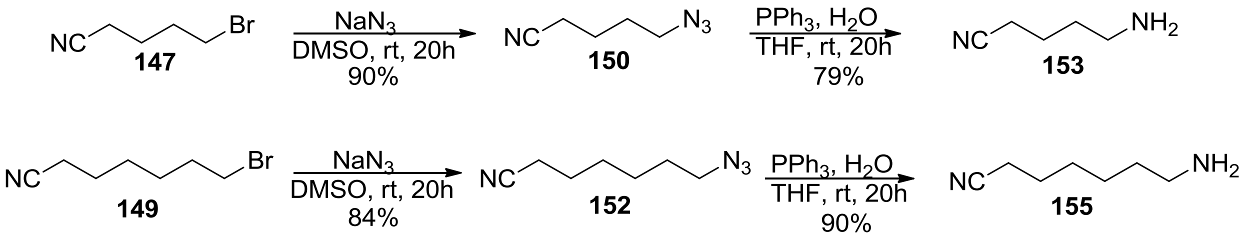


162

Figure 3.7 Initial asymmetric host targets

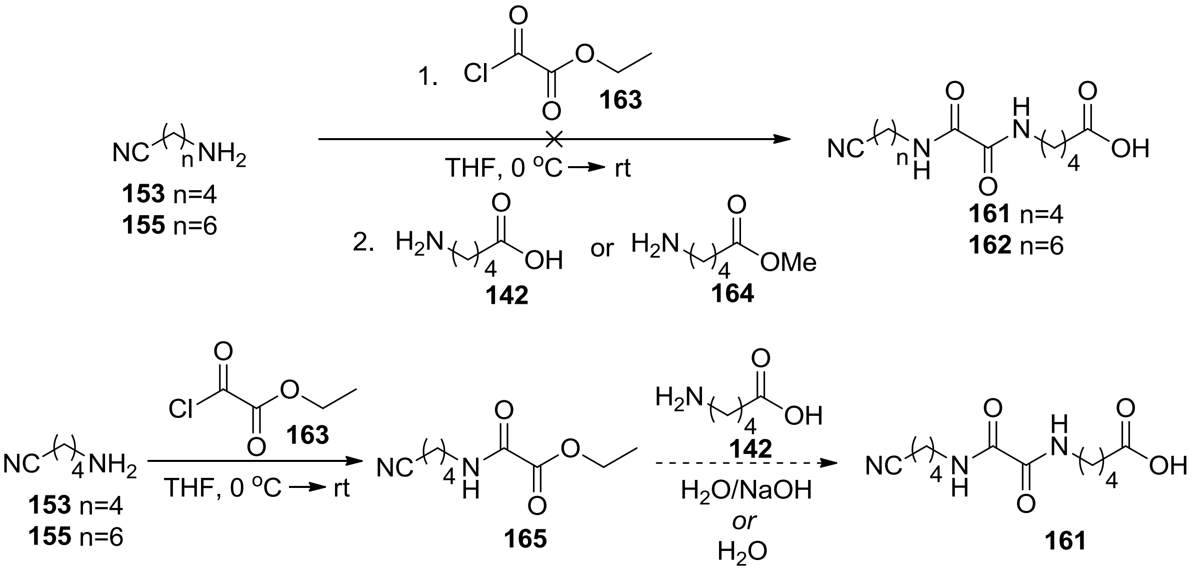
When preparing the hosts shown in Figure 3.7, the nitrile end was constructed before adding the carboxylic acid group. The first step in the synthesis of these asymmetric oxalamide hosts is to prepare the appropriate amino nitrile from the corresponding bromo nitrile via an azide intermediate, using the same procedure for preparing bis(nitrile) oxalamide hosts.[28] The synthesis of 5-aminopentanenitrile (**153**) and 7-aminoheptanenitrile (**155**) is shown in Scheme 3.20.



Scheme 3.20 Synthesis of **153** and **155**[28]

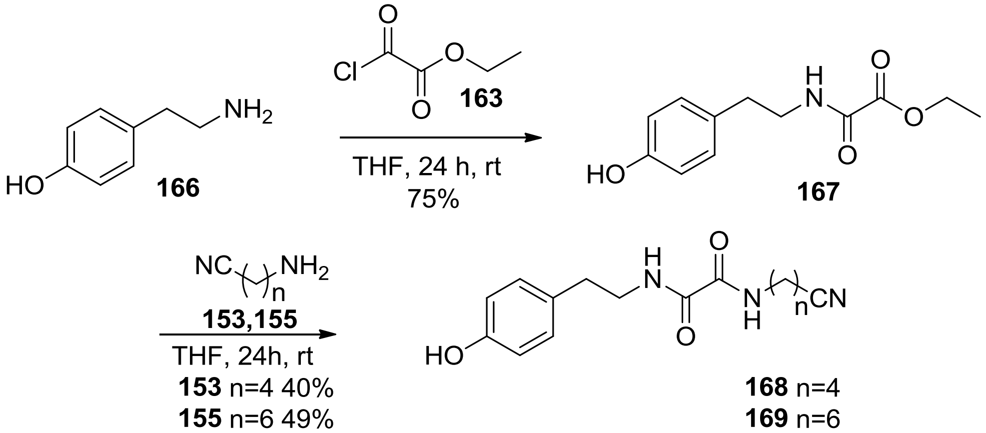
Amines **153** and **155** immediately reacted with one equivalent of ethyl oxalyl chloride (**163**). This reagent is used instead of diethyl oxalate to synthesize asymmetric hosts, since the acid chloride reacts much more readily than the ester thus favoring mono addition of the amine. While the use of ethyl oxalyl chloride has proven successful in the synthesis of asymmetric hosts, the target molecules contained two carboxylic acid end groups and only differed in the length of the methylene chain tether.[32] Former group member Aiwu Sun also synthesized asymmetric oxalamide hosts; however they contained pyridyl and nitrile groups which both serve as amine bases.[36]

The reactions of amines **153** and **155** with ethyl oxalyl chloride were conducted in THF, which is standard for synthesizing bis(nitrile) oxalamide hosts. Performing this reaction in one pot was unsuccessful, as incompatible solubilities impeded any reaction from occurring (Scheme 3.21). Methyl protection of the carboxylic acid was used to increase solubility; however the results were not improved upon this change. Changing the reaction solvent from THF to dimethoxyethane yielded the same results. Hence, in later experiments, the monosubstituted product was isolated prior to reacting with 5-aminovaleric acid (**142**). The NMR spectra for intermediate **165** contained ethyl and carbonyl peaks in addition to peaks that corresponded to the starting amino nitrile, indicating that product formed. This material was subsequently added to a solution of water and 6.25N NaOH, and 5-aminovaleric acid was added. Unfortunately, the NMR spectra that were obtained suggested the presence of the amino acid unit; however peaks corresponding to the nitrile were not visible. Although high temperature and concentrated acid/base is often required for the hydrolysis of nitriles, the NMR data suggest the possibility that the nitrile was hydrolyzed to the corresponding carboxylic acid during the reaction. Additional trials were conducted using water as the reaction solvent; however the solubility difference between the two subunits was too great for reaction to occur.[32]



Scheme 3.21 Attempted synthesis of nitrile acid hosts

Since solubility differences between the nitrile and carboxylic acid groups impeded the successful synthesis of the initial targeted asymmetric hosts, the carboxylic acid moieties were replaced with phenol groups. Amines with para-substituted phenol groups were used to determine the experimental conditions that were suitable for synthesizing the phenol nitrile hosts for cost reasons. Meta-substituted hosts would ultimately be targeted since the alcohol in this position might provide more flexibility when forming hydrogen bond interactions between the phenol and nitrile moieties in the host and guest, respectively. In the first step of the synthetic sequence, 4-(2-aminoethyl)phenol (**166**) reacted with ethyl oxalyl chloride to form intermediate **167**, which subsequently reacted with either 5-aminopentanenitrile (**153**) or 7-aminoheptanenitrile (**155**) to produce hosts **168** and **169** (Scheme 3.22). Using excess THF allowed the phenol component **166** to dissolve, which was not achieved when carboxylic acid groups were incorporated.



Scheme 3.22 Synthesis of *p*-phenol-nitrile hosts

Hosts **168** and **169** were recrystallized from warm MeOH, which is the only organic solvent that these compounds are soluble in. Host **168** formed a colorless crystalline solid, whereas **169** was a white powder. A crystal structure of host **168** is shown in Figure 2 below. This structure was obtained with the aid of Daniel Resch. Unfortunately, the packing of this host is not ordered, which may inhibit alignment of the 5-iodo-penta-2,4-diynenitrile (**137**) guest monomers. It appears that in addition to the hydrogen bond interactions between the oxalamide functionalities, the nitrile and phenol groups can also form hydrogen bonds with the oxalamide moieties.

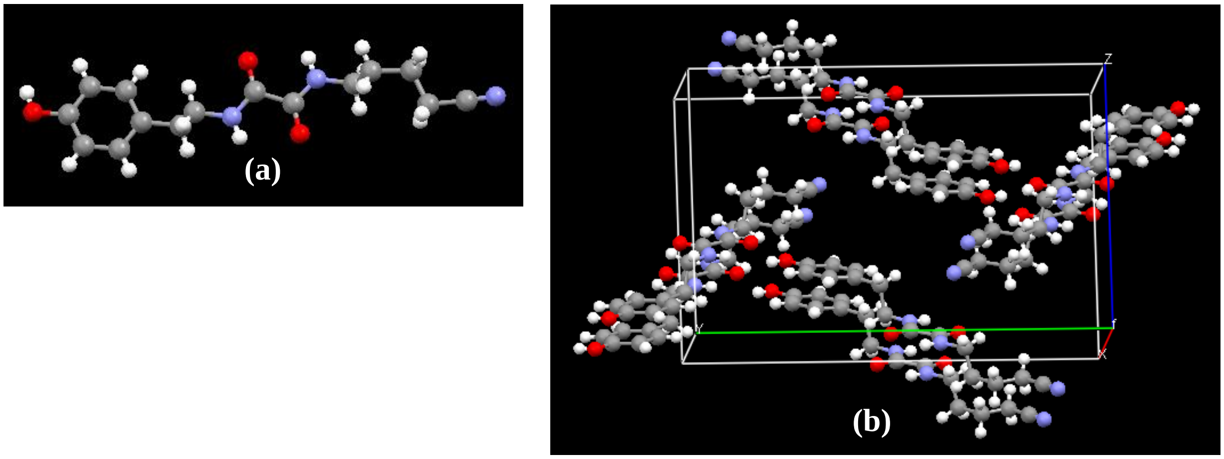
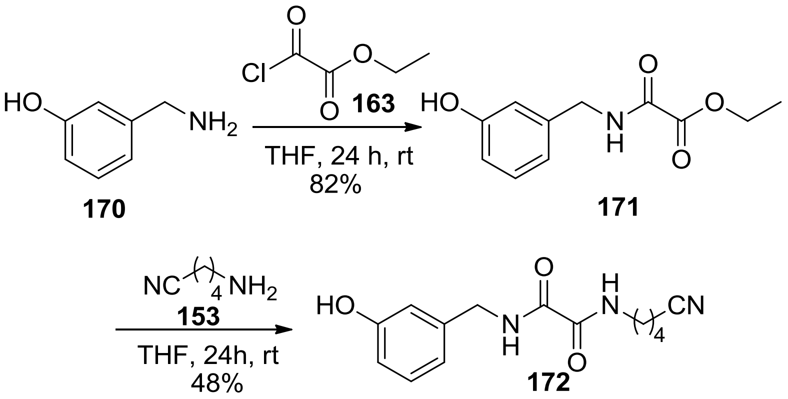


Figure 3.7 Crystal structure (a) and packing (b) of host **168.** Unit cell parameters ($P2_1/n$ spacegroup): a = 5.7200(3) Å, b = 20.7920(10) Å, c = 13.2080(8) Å; α = 90º, β = 96.813(5)º, γ = 90º, V =1559.74

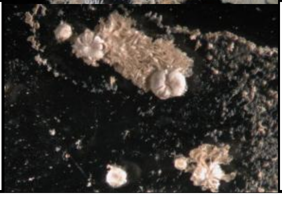
After optimizing the synthesis for the *p*-phenol-nitrile oxalamide hosts, asymmetric hosts containing meta-substituted phenol moieties were targeted. 3-(Aminomethyl)phenol (**170**) reacted with ethyl oxalyl chloride to form intermediate **171**, which was then added to 5-aminopentanenitrile (**153**) to form host **172** (Scheme 3.23). Amine **153** was chosen since bis(nitrile) hosts that contained chains with 4 methylene units have been shown to form higher quality crystals than those with 5 or 6 methylene groups.[37]

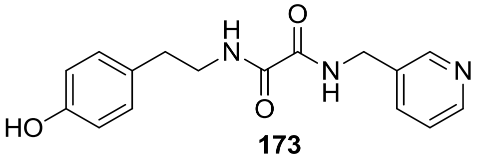


Scheme 3.23 Synthesis of *m*-phenol-nitrile hosts

Compound **172** was considerably less soluble than the *p*-phenol analogs, which seemed counterintuitive since the meta- substituent was expected to add conformational flexibility to the host. When dissolving **172** in methanol to prepare co-crystals, the solution had to be heated rather rigorously with a heat gun, and some of the solid precipitated out of solution upon cooling to room temperature. Despite these solubility problems, host **172** was employed in several co-crystallization experiments with 5-iodo-penta-2,4-diynenitrile (**137**), but there was no evidence of co-crystal formation in any of the trials that were conducted. It appears that the host and guest precipitate out of solution independent of one another, as suggested by melting points that were obtained as well as the morphology of the solid that results from solvent evaporation. Upon close examination, there were usually small amounts of black solid dispersed throughout the surface of the white solid, which suggests that the guest may be decomposing on the surface of the host, rather than forming co-crystals. Asymmetric oxalamide hosts with phenol and pyridyl end groups were also prepared (Figure 3.8); however these hosts were only soluble in DMSO, and were therefore difficult to employ in crystallization experiments. The results of the experiments that incorporated the new asymmetric hosts and 5-iodo-penta-2,4-diynenitrile are summarized in Table 3.5.

Table 3.5 Co-crystallization attempts with asymmetric hosts

Host (H)	Ratio H:G	Solvent	Appearance	m.p.
168	1:1	MeOH		155-160 ºC turned black
168	2:1	MeOH		172-175 ºC melted
168	1:2	MeOH	colorless crystals	145-150 ºC turned black
169	1:1	MeOH		120 ºC turned dark and melted
169	2:1	MeOH		120 ºC turned dark and melted
172	1:2	MeOH		130 ºC turned black and melted
172	1:1	MeOH:CH_2Cl_2 1 : 0.25		140-145 ºC turned black and melted



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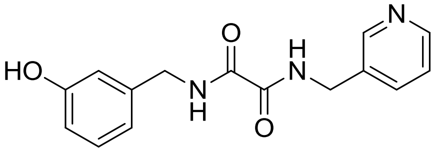


174

Figure 3.8 Phenol-pyridyl oxalamide hosts

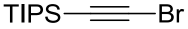
3.3 Summary

The synthesis of dicyanodiacetylene (**22**) was attempted via several different strategies. Oxidation of bis(amine)diyne precursor **125** to the corresponding nitrile was not achieved by adapting the literature methods for oxidizing amines to nitriles. Alternatively, forming dicyanodiacetylene from bis(dichloroamine)diyne **129** was also very challenging, as subjecting the diyne to various elimination conditions resulted in immediate formation of black insoluble material that could not be characterized. Further investigation of the elimination reaction on dichlorobenzyl amine model compound **127** indicated that a chloroimine derivative forms very quickly upon addition of triethylamine. This result suggests that when targeting dicyanodiacetylene, it is unlikely that the decomposed material is the desired product because complete chlorine elimination does not appear to happen instantaneously. It is possible that this reaction proceeds through a bis(chloroimine)diyne intermediate, which is too unstable to survive subsequent chlorine elimination. The additional routes that were pursued also encompassed unstable diyne intermediates, which prevented the synthesis of dicyanodiacetylene.

Exploring the oxidation of amines to nitriles allowed for the development of a route towards 5-iodo-penta-2,4-diynenitrile (**137**). This novel push-pull diyne was employed in co-crystallization experiments with both symmetric and asymmetric oxalamide hosts in an attempt to achieve ordered 1,4-topochemical polymerization. Symmetric carboxylic acid, nitrile, and pyridyl oxalamide hosts were employed, but there was no evidence of co-crystal formation in these experiments. Asymmetric hosts were also designed to address this issue; however the low solubility of these hosts limited the number of solvents that were used for co-crystallization experiments. The results that were obtained suggested that the host and guest monomers were coming out of solution independently of one another. While the ideal co-crystallization conditions have not been determined thus far, additional experiments will be conducted by Xiuzhu Ang in hopes of achieving the ordered polymerization of 5-iodo-penta-2,4-diynenitrile.

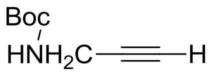
3.4 Experimental Procedures

General Methods: Reagents were purchased reagent grade from Aldrich, Fischer Scientific/Acros Organics, VWR, Strem, or GFS Chemicals, and were used without further purification, except where stated. Tetrahydrofuran was distilled under argon from sodium/benzophenone. Copper iodide was purified by recrystallization. All reactions were performed under an inert argon atmosphere, unless stated otherwise. Iodination reactions were carried out in aluminum-foil wrapped flasks in an unlighted hood. Column chromatography: Alumina (50-200 mesh) from Acros Organics. Silica gel-60 (230-400 mesh) from Sorbent Technologies. Thin Layer Chromatography (TLC): plastic sheets covered with silica gel purchased from Acros. Melting points were measured on a Thomas Hoover Capillary melting point apparatus. ^{1}H and ^{13}C NMR spectra were obtained using Varian Gemini-300 MHz, Inova-400 MHz, or Inova-500 MHz instruments, and were taken in deuterated chloroform unless noted otherwise. High resolution EI-mass spectra were obtained from the University of Illinois SCS Mass Spectrometry Laboratory. High resolution ESI-mass spectra were obtained by Bela Ruzsicska of the ICB&DD at Stony Brook.



120

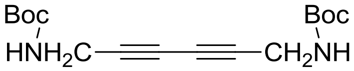
(Bromoethynyl)triisopropylsilane (**120**).[38] Triisopropylsilyl acetylene (0.5 mL, 2.23 mmol), NBS (0.797 g, 4.48 mmol), and $AgNO_3$ (0.191 g, 1.12 mmol) were combined in 25 mL acetone. The solution was allowed to stir in the dark for 2 h at room temperature. Ice water (30 mL) was added, and the reaction mixture was extracted with 3 x 30 mL hexanes. The combined organic layers were washed with water and dried over $MgSO_4$. Removal of solvent *in vacuo* afforded 0.519 g (90%) of colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 18.5, 61.7, 83.4.[38]



$\overset{\text{Boc}}{\text{HN}}\text{H}_2\text{C}-\equiv-\text{H}$

123

***Tert*-Butyl Prop-2-ynylcarbamate** (**123**).[17] Propargyl amine (0.94 mL, 14.7 mmol) was dissolved in 15 mL CH_2Cl_2 and cooled to 0 ºC. A solution di-*tert*-butyl dicarbonate (3.36 g, 15.4 mmol) in 20 mL CH_2Cl_2 was added to the amine solution dropwise over 30 minutes via cannula. The reaction was allowed to warm to room temperature and stirred overnight. Solvent was removed *in vacuo* to afford 2.09 g (92%) of light orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (s, 9H), 2.20 (m, 1H), 3.92 (br s, 2H), 4.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 80.0, 71.2, 28.3.[17]



$\overset{\text{Boc}}{\text{HN}}\text{H}_2\text{C}-\equiv-\equiv-\text{CH}_2\overset{\text{Boc}}{\text{NH}}$

124

***N,N'*-Di-*tert*-butoxycarbony-2,4-hexadiynylene-1,6-diamine (124).**[13] CuCl (0.341 g, 3.44 mmol) was dissolved in 25 mL acetone and TMEDA (0.52 mL, 3.45 mmol) was added. Oxygen was bubbled through the solution for 6 h, and the reaction was allowed to stir under O_2 overnight. The dark green catalyst mixture was filtered and *tert*-butyl prop-2-ynylcarbamate (**123**, 1.66 g, 10.7 mmol). The reaction mixture was stirred at room temperature for 24h. Solvent was removed *in vacuo,* and 30 mL ethyl acetate was added. The organic liquid was washed with 20 mL sat. aq. NH_4Cl, and extracted with 3 x 30 mL EtOAc. The combined organic extract was washed with 20 mL brine and dried over $MgSO_4$. Filtration and removal of solvent *in vacuo* resulted in 1.52 g (92 % crude yield) of light green solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.73 (br, 2H), 3.99 (s, 4H), 1.44 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 80.2, 74.7, 67.3, 31.0, 28.3.[13]

$H_2NH_2C-\equiv-\equiv-CH_2NH_2$

125

2,4-Hexadiynylene-1,6-diamine (125).[13] To a solution of *N,N'*-di-*tert*-butoxycarbony-2,4-hexadiynylene-1,6-diamine (**124**, 1.17 g, 3.79 mmol) in THF (35 mL) was added 8.8 mL concentrated HCl. The reaction mixture was stirred for 1 h, resulting in a white precipitate that was filtered and rinsed with 10 mL additional THF. The solid was dissolved in 10 mL 2.5M NaOH, stirred for 1 h, and extracted with 2 x 30 mL $CHCl_3$. Removal of solvent *in vacuo* resulted in 0.270 g (66%) of light orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.48 (s, 4H), 1.32 (br, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 79.3, 66.9, 32.0.[13]

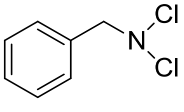
$NC-\equiv-\equiv-CN$

22

Hexa-2,4-diynedinitrile (22).

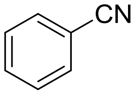
Procedure A.[10] 2,4-Hexadiynylene-1,6-diamine (**125**, 0.093 g, 0.858 mmol) was dissolved in 5 mL CH_2Cl_2 and trichloroisocyanuric acid (0.519 g, 2.23 mmol) was added slowly. TEMPO (0.003 g, 0.019 mmol) was then added and the reaction was stirred for 2 h at 10°C. The reaction was quenched with 4 mL H_2O, and the aqueous layer was extracted with 3 x 1 mL CH_2Cl_2. The combined organic layers were washed with 0.5 N $NaHSO_3$ (2 x 10 mL), 1 N HCl (2 x 5 mL), and H_2O (3 x 10 mL) and dried over Na_2SO_4. Removal of solvent *in vacuo* afforded 0.032 g orange solid contained in a brown oil (literature reports white solid, m.p. 64.5-65.5°C).[6] ^1H NMR and ^{13}C NMR spectra were obtained; however they were very complex and did not suggest product was formed.

Procedure B.[11] To a stirred solution of IBX (0.556 g, 1.98 mmol) in 4 mL acetonitrile was added tetrabutylammonium bromide (0.642 g, 1.99 mmol) and the mixture was stirred for 10 minutes. 2,4-Hexadiynylene-1,6-diamine (**125**, 0.043 g, 0.398 mmol) and 4Å mol sieves were added, and the mixture was stirred for an additional 10 minutes. The reaction was quenched with 10% aq. $NaHSO_3$ and extracted with 3 x 15 mL EtOAc. The organic phase was washed with 2 x 15 mL sat. aq. $NaHCO_3$, 15 mL H_2O, and 15 mL brine and dried over Na_2SO_4. Removal of solvent *in vacuo* resulted in 0.063 g dark brown oil. ^1H NMR and ^{13}C NMR spectra were complex. Mass spec and IR data were used to confirm that the product was not present in the oil.



127

***N,N*- dichlorobenzylamine** (**127**).[12] Benzylamine (0.300 mL, 2.75 mmol) was dissolved in 6 mL CH_2Cl_2 at 0°C and trichloroisocyanuric acid (0.830 g, 3.57 mmol) was added slowly. The reaction was warmed to room temperature and stirred for 2h. The reaction mixture was quenched with 5 mL H_2O and the aqueous layer was extracted with 3 x 10 mL of CH_2Cl_2. The combined organic extracts were washed with 0.5 N aq. $NaHSO_3$ (2 x 5 mL), 1 N aq. HCl (2 x 5 mL), and H_2O (3 x 10 mL) and dried over Na_2SO_4. Removal of solvent *in vacuo* afforded 0.319 g (70%) of colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 4.71 (s, 2H), 7.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 78.8, 128.5, 129.2, 130.0, 134.9.[12]



128

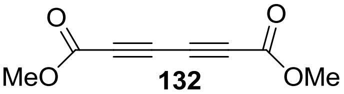
Benzonitrile (**128**).[12] *N,N*-dichlorobenzylamine (**127**, 0.122 g, 0.727 mmol) was dissolved in 3 mL CH_2Cl_2 and triethylamine (0.31 mL, 2.21 mmol) was added. After stirring for 2 h at room temperature, the reaction mixture was washed with 10 mL H_2O, 5 mL 0.1M HCl, and dried over $MgSO_4$. Filtration and removal of solvent *in vacuo* afforded 0.026 g (34%) of colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42-7.51 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 112.4, 118.8, 129.1, 132.1, 132.7.[12]

$Cl_2NH_2C{-}{\equiv}{-}{\equiv}{-}CH_2NCl_2$

129

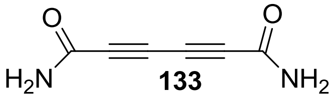
2,4-Hexadiynylene-1,6-dichlorodiamine (129). 2,4-Hexadiynylene-1,6-diamine (**125**, 0.036 g, 0.33 mmol) was dissolved in 5 mL CH_2Cl_2 and the solution was cooled to 0 ºC. TCCA (0.155g, 0.668 mmol) was added and the reaction was stirred at 0 ºC for 15 min and warmed to room temperature. After stirring for 2 h, the reaction was diluted with 5 mL CH_2Cl_2 and filtered.

Solvent was removed *in vacuo* to afford 0.074 g (90%) of orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.38 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 64.1, 72.2, 73.1.



132

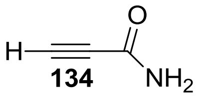
Dimethyl 2,4-hexadiyndioate (132).[16] CuCl (0.118 g, 1.19 mmol) was dissolved in 4 mL acetone and TMEDA (0.06 mL, 0.39 mmol) was added. Oxygen was bubbled through the solution for 2 hours. A solution of methyl propiolate (1.07 mL, 11.9 mmol) in 7 mL acetone was added, and O_2 was bubbled through the solution for 6 h. The reaction was stirred under O_2 overnight, solvent was removed *in vacuo*, and the residue was dissolved in 25 mL Et_2O. Note: a significant amount of black solid was present, which did not go into solution. The Et_2O was washed with 2 x 25 mL 5% aq. HCl, and dried over $MgSO_4$. Filtration and removal of solvent *in vacuo* afforded dark brown oil (0.013 g, 0.08 mmol, 3% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_{3):}$ δ 152.1, 72.3, 68.1, 53.4.[16]



133

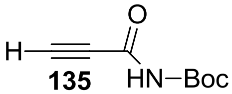
2,4-Hexadiynediamide (133). Dimethyl 2,4-hexadiyndioate (**132**, 0.012 g, 0.07 mmol) was cooled to -30 °C and concentrated aq. NH_3 (0.3 mL) was added slowly. The reaction was stirred for 15 minutes, and was extracted with 3 x 7 mL EtOAc. The combined organic layers were dried over $MgSO_4$, filtered, and solvent was removed *in vacuo* to afford 0.010 g of dark brown/black oil. ^{1}H and ^{13}C NMR spectra of the crude material were difficult to interpret because they were very messy and did not contain the expected product peaks.

Alternative method:[16] CuCl (0.031 g, 0.314 mmol) was dissolved in 3 mL acetone and TMEDA (0.02 mL, 0.13 mmol) was added. Oxygen was bubbled through the solution for 3 h. A solution of propiolamide (**134**, 0.183 g, 2.64 mmol) in 2 mL acetone was added, and O_2 was bubbled through the reaction mixture for 3 h. Note: A significant amount of black solid had formed during this time. The reaction was stirred under O_2 at room temperature overnight, and was concentrated *in vacuo* and the black residue was extracted with 25 mL Et_2O and 15 mL H_2O. The aqueous layer was extracted with an additional 25 mL Et_2O, and the combined organic extract was dried over $MgSO_4$, filtered, and concentrated to afford 0.012 g of pale yellow solid. ^{1}H and ^{13}C NMR revealed that only starting material was present.

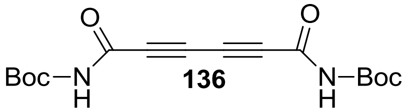


134

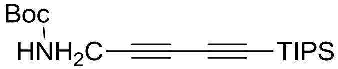
Propiolamide (134).[15] Concentrated aqueous ammonia (3.25 mL) was cooled to -30 °C and methyl propiolate was added dropwise. After stirring for 15 minutes, the reaction was extracted with 3 x 7 mL EtOAc and dried over $MgSO_4$. Filtration and removal of solvent *in vacuo* afforded a light yellow solid (0.611 g, 8.84 mmol, 79% yield). ^{1}H NMR (400 MHz, acetone-d_6): δ 7.38 (br s, 1H), 6.95 (br s, 1H), 2.85 (s, 1H); ^{13}C NMR (100 MHz, acetone-$d_{6):}$ δ 154.1, 78.8, 74.3.[15]


135

N-Propynoyl-1,1-dimethylethyl carbamate (135).[17] Propiolamide (**134**, 0.085 g, 1.23 mmol) was dissolved in 4 mL CH_2Cl_2 and the solution was cooled to 0 ºC. Boc anhydride (0.291 g, 1.33 mmol) was dissolved in 2 mL CH_2Cl_2 and the solution was added to the amide dropwise via cannula. The reaction was stirred at 0 ºC for 30 minutes and room temperature overnight. Solvent was removed *in vacuo* to afford a light yellow oily solid (0.335 g, 1.96 mmol, >100% crude yield). The peaks corresponding to the Boc group were significantly larger than propiolamide peaks; however attempts to remove excess Boc byproducts did not appear to change the relative peak heights. ^1H NMR (400 MHz, CD_3OD): δ 3.85 (s, 1H), 1.92 (s, 18H, should be 9H); ^{13}C NMR (100 MHz, CD_3OD): δ 156.5, 148.3, 86.5, 78.1, 76.2, 27.8. Literature peaks: ^1H NMR (200 MHz, $CDCl_3$): δ 6.35 (br, 1H), 3.29 (s, 1H), 1.52 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.0, 149.0, 83.8, 80.8, 75.6, 28.1.[19]


136

***N,N'*-Di-*tert*-butoxycarbony-2,4-hexadiynediamide (136)**. CuCl (0.020 g, 0.198 mmol) was dissolved in acetone and TMEDA (0.01 mL, 0.06 mmol) was added. Oxygen was bubbled through the solution for 3 h, and a solution of *N*-propynoyl-1,1-dimethylethyl carbamate (**135**, 0.294 g, 1.74 mmol) in 2 mL acetone was added. Oxygen was bubbled through the solution for an addition 4 h, and the reaction was stirred under O_2 overnight. Solvent was removed *in vacuo*, and 30 mL EtOAc was added to the dark green residue. The organic extract was washed with 25 mL sat. aq. NH_4Cl, and the aqueous layer was extracted with 3 x 20 mL EtOAc. The combined organic extract was washed with 25 mL sat. aq. NaCl and dried over $MgSO_4$. Filtration and removal of solvent resulted in 0.203 g (70%) of light orange solid. The peaks corresponding to the Boc group were significantly larger than propiolamide peaks; however attempts to remove excess Boc byproducts did not appear to change the relative peak heights. ^1H NMR (400 MHz, CD_3OD): δ 1.56 (s); ^{13}C NMR (100 MHz, CD_3OD): δ 154.9, 148.5, 86.5, 75.8, 67.9, 27.7.


$\overset{\text{Boc}}{\text{HN}}H_2C{-}{\equiv}{-}{\equiv}{-}\text{TIPS}$

138

(5-Triisopropylsilanyl-penta-2,4-diynyl)-carbamic acid tert-butyl ester (138).[22] (Bromoethynyl)triisopropylsilane (**120**, 0.397 g, 1.53 mmol) was dissolved in 18 mL THF and *tert*-butyl prop-2-ynylcarbamate (**123**, 0.287 g, 1.85 mmol) was added. CuI (0.015 g, 0.081 mmol) and $Pd(PPh_3)Cl_2$ (0.033 g, 0.047 mmol) were added in one portion, and *i*-Pr_2NH (0.43 mL, 3.06 mmol) was added to the reaction mixture dropwise. After stirring for 5 h at room temperature, sat. aq. NH_4Cl (10 mL) was added and the reaction was extracted with 2 x 20 mL Et_2O. Solvent was removed *in vacuo*, and a short plug (SiO_2/hex:EtOAc 6:1) was used to isolate 0.421 g (82 %) product as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 1.04 (s, 21H), 1.42 (s, 9H), 3.98 (s, 2H), 4.84 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.4, 28.2, 30.9, 68.3, 73.2, 80.1, 83.2, 89.1, 155.1. HRMS (ESI) *m/z* calcd for $C_{19}H_{34}NO_2Si$ 336.2359, found 336.2362 $(M+H)^+$

$H_2NH_2C-\equiv-\equiv-\mathrm{TIPS}$

139

5-Triisopropylsilanyl-penta-2,4-diynylamine (**139**).[23] (5-Triisopropylsilanyl-penta-2,4-diynyl)-carbamic acid tert-butyl ester (**138**, 0.804 g, 2.39 mmol) was dissolved in 12.3 mL CH_2Cl_2 and 12.3 mL trifluoroacetic acid was added. After stirring for 1 h at room temperature, the reaction mixture was diluted with 20 mL EtOAc and quenched with sat. aq. $NaHCO_3$. 2M KOH was added until a basic pH ~14 was reached for the aqueous layer, which was extracted with 3 x 20 mL potions of EtOAc. The combined organic extract was dried over $MgSO_4$, filtered, and concentrated to afford 0.507 g (90%) of brown oil. ^1H NMR (400 MHz, $CDCl_3$): δ 1.06 (s, 21 H), 3.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.3, 30.2, 66.3, 72.7, 86.5, 87.7. HRMS (EI) *m/z* calcd for $C_{14}H_{25}NSi$ 235.17563, found 235.17609.

$NC-\equiv-\equiv-\mathrm{TIPS}$

140

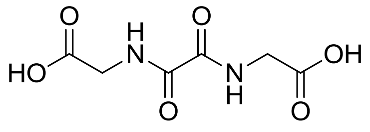
5-Triisopropylsilanyl-penta-2,4-diynenitrile (**140**).[12] 5-Triisopropylsilanyl-penta-2,4-diynylamine (**139**, 0.296 g, 1.26 mmol) was dissolved in 9.0 mL CH_2Cl_2. The reaction was cooled to 0°C, and trichloroisocyanuric acid (TCCA, 0.293 g, 1.26 mmol) was added. After warming to room temperature and stirring for 2 h, the reaction was diluted with 10 mL CH_2Cl_2, filtered, and concentrated, resulting in 0.334 g (1.10 mmol, 87%) of the dichloroamine derivative as an orange solid. The material was dissolved in 9.5 mL CH_2Cl_2, and treated with 0.46 mL (3.27 mmol) triethylamine. After stirring for 2 h at room temperature, the reaction was diluted with 10 mL CH_2Cl_2, quenched with 15 mL H_2O, and extracted with 2 x 20 mL Et_2O. The organic layer was washed with 10 mL H_2O and 10 mL 0.3 N aq. HCl. After drying over $MgSO_4$, the solution was filtered and solvent was removed *in vacuo* to afford 0.166 g (0.72 mmol, 65 %,) of brown oily solid. ^1H NMR (400 MHz, $CDCl_3$): δ 1.10 (m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 18.4, 48.8, 67.5, 86.9, 92.1, 105.3. HRMS (EI) *m/z* calcd for $C_{14}H_{21}NSi$ 231.14433, found 231.14384.

$NC-\equiv-\equiv-I$

137

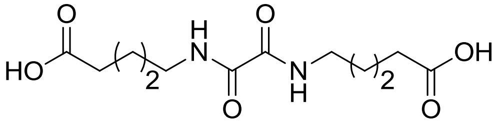
5-Iodo-penta-2,4-diynenitrile (**137**).[24] 5-Triisopropylsilanyl-penta-2,4-diynenitrile (**140**, 0.062 g, 0.268 mmol) was dissolved in 25 mL CH_3CN. AgF (0.113 g, 0.890 mmol) and NIS (0.188 g, 0.837 mmol) were added, and the reaction was allowed to stir at 0ºC in the dark for 1h. The reaction was quenched with 20 mL ice water and extracted with 3 x 20 mL hexanes. The combined organic extract was washed with 10 mL sat. aq. Na_2SO_4 and dried over $MgSO_4$. Solvent was removed *in vacuo*, resulting in 0.034 g (63%) of light yellow solid. ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.9, 46.9, 67.7, 77.2, 104.7. HRMS (EI) *m/z* calcd for C_5HNI 200.90757, found 200.90737.

General Procedure for Synthesis of Dicarboxylic Acid Oxalamide Hosts:[32, 33] A solution of 17 mL 6.25 N NaOH in 75 mL H_2O was heated to 40°C using a water bath. The amino acid (110 mmol) and diethyl oxalate (55 mmol) were added, and the reaction mixture was stirred overnight. After cooling to room temperature, conc. HCl was added until a pH of 2 was reached. The mixture was placed in an ice water bath and the white precipitate was collected using vacuum filtration and washed with a small amount of cold H_2O.



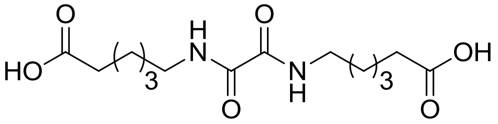
144

***N,N'*-Oxalyldiglycine (144).** White solid, 22% yield. ^{1}H NMR (500 MHz, CD_3OD): δ 4.03 (s); mp. 249-250 °C.[33]



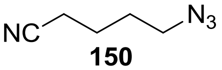
145

5,5′-(Oxalyldiimino)dipentanoic Acid (145). White solid, 22% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ12.0 (bs, 2H), 8.72 (t, 2H, *J* = 6.0 Hz), 3.12 (d, 4H, *J* = 6.4 Hz), 2.20 (t, 4H, *J* = 8 Hz), 1.45 (m, 8H); mp. 210-211 °C.[32]



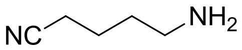
146

6,6′-(Oxalyldiimino)dihexanoic Acid (146). White solid, 23% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ12.0 (bs, 2H), 8.69 (t, 2H, *J* = 8.0), 3.09 (qt, 4H, *J* = 5.0 Hz), 2.17 (q, 4H, *J* = 7.2 Hz), 1.48 (m, 8H), 1.25 (m, 4H); ^{13}C NMR (DMSO-*d*$_6$): 24.1, 25.8, 28.4, 33.5, 159.9, 174.3; mp. 178-180 °C.[32]



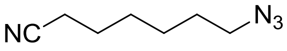
150

5-Azidopentanenitrile 150.[28] Sodium azide (0.668 g, 10.3 mmol) was added to a solution of 5-bromobutanenitrile (0.80 mL, 6.8 mmol) in 17 mL DMSO. After stirring for 20 h at room temperature, 30 mL H_2O was added, and the solution was extracted with 3 x 40 mL Et_2O. The combined organic layers were washed with 2 x 40 mL H_2O and dried over $MgSO_4$. Solvent was removed *in vacuo* to afford colorless oil (0.758 g, 6.15 mmol, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.28 (t, 2H, *J* = 6.0 Hz) 2.33 (t, 2H, *J* = 6.8 Hz), 1.68 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.9, 50.1, 27.4, 22.3, 16.4.[28]



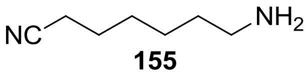
153

5-Aminopentanenitrile 153.[28] 5-Azidopentanenitrile (**150**, 0.462 g, 3.75 mmol) was dissolved in 8.5 mL THF and triphenylphosphine (1.18 g, 4.50 mmol) and water (0.14 mL, 7.78 mmol) were added. The reaction was stirred under Ar for 15 minutes, after which a vent needle was placed in the rubber septum. After stirring at room temperature overnight, a 1:1 mixture of cold hexanes:Et_2O was added (~100 mL), until the solution became cloudy. The mixture was placed in the freezer until triphenylphosphine oxide precipitated out in the form of white solid needles. The solution was filtered and the needles were washed with a small amount of 2M HCl, while the filtrate was concentrated *in vacuo*. The resulting white solid was washed with 2M HCl and the combined HCl layers were basified with 2M KOH, until a pH of 14 was reached. The mixture was then extracted with 4 x 40 mL CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated to afford yellow oil (0.245 g, 2.49 mmol, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.65 (t, 2H, J = 6.8 Hz), 2.29 (t, 2H, J = 7.2 Hz), 1.63 (m, 2H), 1.51 (m, 2H), 1.17 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.4, 40.9, 32.2, 22.5, 16.7.[28]



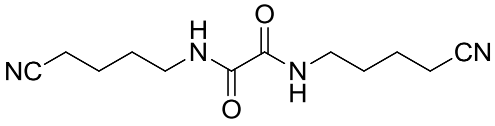
152

7-Azidoheptanenitrile 152.[37] Sodium azide (0.518 g, 7.96 mmol) was added to a solution of 7-bromoheptanenitrile (0.80 mL, 5.30 mmol) in 13 mL DMSO. After stirring for 20 h at room temperature, 30 mL H_2O was added, and the solution was extracted with 3 x 40 mL Et_2O. The combined organic layers were washed with 2 x 40 mL H_2O and dried over $MgSO_4$. Solvent was removed *in vacuo* to afford colorless oil (0.680 g, 4.47 mmol, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.19 (t, 2H, J = 6.8 Hz) 2.26 (t, 2H, J = 7.2 Hz), 1.50-1.59 (m, 4H), 1.30-1.39 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.3, 50.7, 28.0, 27.7, 25.4, 24.7, 16.5.[37]



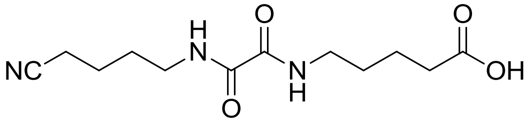
155

7-Aminoheptanenitrile 155.[28] 7-Azidoheptanenitrile (**152**, 0.670 g, 4.41 mmol) was dissolved in 10 mL THF and triphenylphosphine (1.38 g, 5.28 mmol) and water (0.16 mL, 8.89 mmol) were added. The reaction was stirred under Ar for 15 minutes, after which a vent needle was placed in the rubber septum. After stirring at room temperature overnight, a 1:1 mixture of cold hexanes:Et_2O was added (~100 mL), until the solution became cloudy. The mixture was placed in the freezer until triphenylphosphine oxide precipitated out in the form of white solid needles. The solution was filtered and the needles were washed with a small amount of 2M HCl, while the filtrate was concentrated *in vacuo*. The resulting white solid was washed with 2M HCl and the combined HCl layers were basified with 2M KOH, until a pH of 14 was reached. The mixture was then extracted with 4 x 40 mL CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated to afford yellow oil (0.496 g, 3.93 mmol, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.55 (bt, 2H), 2.23 (t, 2H, J = 7.2 Hz), 1.54 (bt, 2H), 1.36-1.33 (m, 4H), 1.24-1.27 (m, 2H), 1.07 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.5, 41.7, 33.0, 28.1, 25.7, 24.9, 16.7[37]



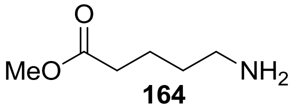
13

***N,N'*-Bis-(4-cyano-butyl)-oxalamide** (**13**).[28] 5-Aminopentanenitrile (**153**, 0.244g, 2.48 mmol) was dissolved in THF and diethyloxalate (0.170 mL, 1.23 mmol) was added. The reaction was stirred at room temperature overnight. Solvent was removed *in vacuo*, and the crude product was recrystallized from MeOH to afford 0.120 g (40% yield) of white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (br, 2 H), 3.39 (m, 4H), 2.41 (m, 4H), 1.76 (m, 8 H).[28]



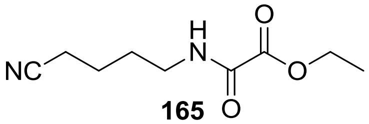
161

5-(2-(4-cyanobutylamino)-2-oxoacetamido)pentanoic acid (161).[32] Ethyl 2-(4-cyanobutylamino)-2-oxoacetate (**165**, 0.183 g, 0.697 mmol) was dissolved in a mixture of 5 mL H_2O and 0.5 mL 6.25N NaOH. 5-Aminovaleric acid (0.082 g, 0.70 mmol) was added, and the reaction was stirred at rt for 2 days. The solution was acidified to pH 2 using concentrated HCl, and was placed in the freezer to allow the host to precipitate out. Since no solid had formed, the solution was extracted with 3 x 30 mL EtOAc, and the combined organic extract was dried over $MgSO_4$, filtered, and concentrated to afford light yellow solid. NMR spectra contained peaks that were similar to amino acid starting material, and did not suggest product formation.



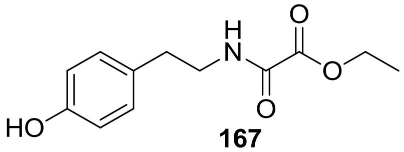
164

5-Amino-n-valeric acid methyl ester (164).[39] Methanol (12 mL) was cooled to 0 °C using an ice bath, and thionyl chloride (0.74 mL, 10.2 mmol) was added slowly. The reaction was stirred at 0 °C for 40 min, and 5-aminovaleric acid (0.299 g, 2.55 mmol) was added. The reaction was warmed to room temperature and stirred overnight. Solvent was removed *in vacuo*, affording a green solid that was rinsed with CH_2Cl_2 and isolated via vacuum filtration (0.098 g, 0.749 mmol, 30% yield). ^{1}H NMR (400 MHz, CD_3OD): δ 3.68 (s, 3H), 2.94 (t, 2H, J = 5.2), 2.41 (t, 2H, J = 6.8), 1.70 (t, 4H, J = 6.8).[40]



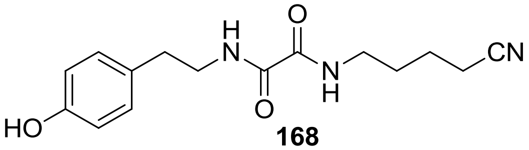
165

Ethyl 2-(4-cyanobutylamino)-2-oxoacetate (165). 5-Aminopentanenitrile (**153**, 0.091 g, 0.93 mmol) was dissolved in 5 mL THF and the solution was cooled to 0 °C. Ethyloxalyl chloride (0.11 mL, 0.98 mmol) was added dropwise, and the reaction was stirred at 0 °C for 30 min, and room temperature for 45 min. Solvent was removed *in vacuo* to afford light yellow oil (0.183 g, 0.697 mmol, 75% crude yield). The ^{1}H NMR spectrum was messy but contained peaks corresponding to the starting aminonitrile as well as additional ethyl peaks consistent with diethyl oxalate, therefore the compound was used without further purification in the next step.



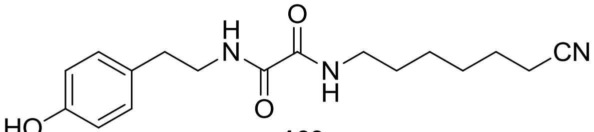
167

***N*-[2-(4-Hydroxy-phenyl)-ethyl]-oxalamic acid ethyl ester** (**167**). 4-(2-Aminoethyl)phenol (0.305 g, 2.22 mmol) was dissolved in 35 mL THF and ethyl oxalyl chloride (0.25 mL, 2.23 mmol) was added. The reaction mixture immediately turned white and cloudy. The reaction was stirred overnight at room temperature. Solvent was removed *in vacuo* to afford a beige solid, which was extracted with 30 mL EtOAc and 30 mL sat. aq. $NaHCO_3$. The organic extract was dried over $MgSO_4$, and removal of solvent afforded yellow oil (0.392 g, 75% yield). ^1H NMR (400 MHz, CD_3OD): δ 7.01 (d, 2H, *J* = 8 Hz), 6.71 (d, 2H, *J* = 8.4), 4.25 (q, 2H, *J* = 7.2 Hz), 3.43 (t, 2H, *J* = 7.6 Hz), 2.73 (t, 2H, *J* = 7.2 Hz), 1.29 (t, 3H, *J* = 7.2 Hz).



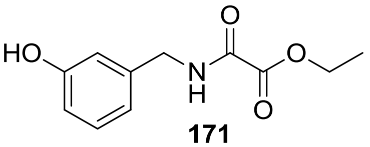
168

***N*-(4-Cyano-butyl)-*N*'-[2-(4-hydroxy-phenyl)-ethyl]-oxalamide (168)**. 38.4 mL 0.147M solution of *N*-[2-(4-hydroxy-phenyl)-ethyl]-oxalamic acid ethyl ester in THF (**167**, 0.126 g, 0.534 mmol) added to a round bottom flask. 5-Aminovaleronitrile (**153**, 0.052 g, 0.534 mmol) was added and the reaction was stirred at room temperature overnight. Solvent was removed *in vacuo* to afford a beige solid which was recrystallized from warm MeOH to afford white solid (0.061 g, 40% yield). m.p. 172-174 ºC, ^1H NMR (400 MHz, CD_3OD): δ 7.05 (d, 2H, *J* = 8.0 Hz), 6.72 (d, 2H, *J* = 8.0), 3.45 (t, 2H, *J* = 8.0 Hz), 3.29 (2H, in CD_3OD peak), 2.74 (t, 2H, *J* = 8.0 Hz), 2.48 (t, 2H, *J* = 8.0 Hz), 1.68-1.66 (m, 4H). HRMS *m/z* calcd for $C_{15}H_{19}N_3O_3$ 289.14263, found 288.13535 $(M-H)^-$.



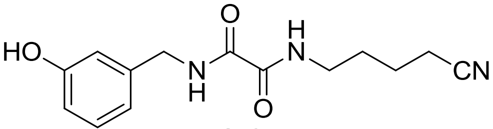
169

***N*-(6-Cyano-hexyl)-N'-[2-(4-hydroxy-phenyl)-ethyl]-oxalamide (169)**. 50 mL 0.147M solution of *N*-[2-(4-hydroxy-phenyl)-ethyl]-oxalamic acid ethyl ester in THF (**167**, 0.165 g, 0.697 mmol) added to a round bottom flask. A solution of 7-aminoheptanenitrile (**155**, 0.088 g, 0.697 mmol) in 4.76 mL THF was added and the reaction was stirred at room temperature overnight. Solvent was removed *in vacuo* to afford a beige solid which was recrystallized from warm MeOH to afford white solid (0.108 g, 49% yield). m.p. 133-135 ºC, ^1H NMR (400 MHz, CD_3OD): δ 7.03 (d, 2H, *J* = 8.4 Hz), 6.71 (d, 2H, *J* = 8.4), 3.43 (t, 2H, *J* = 8.0 Hz), 3.25 (t, 2H, *J* = 7.2 Hz), 2.74 (t, 2H, *J* = 7.6 Hz), 2.43 (t, 2H, *J* = 7.2 Hz), 1.62 (m, 4H), 1.46 (m, 4H). HRMS *m/z* calcd for $C_{17}H_{23}N_3O_3$ 317.17398, found 316.16669 $(M-H)^-$.



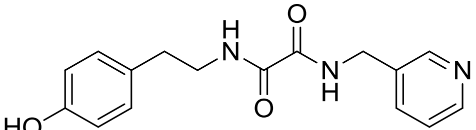
171

***N*-(3-Hydroxy-benzyl)-oxalamic acid ethyl ester (171)**. 3-(Aminomethyl)phenol (0.294 g, 2.38 mmol) was dissolved in 50 mL THF, and the mixture was heated slightly until the amine was completely dissolved. After cooling to room temperature, ethyl oxalyl chloride (0.26 mL, 2.36 mmol) was added. The reaction was stirred at room temperature overnight. Solvent was removed *in vacuo* to afford yellow oil which was extracted with 30 mL EtOAc and 30 mL sat. aq. $NaHCO_3$. The organic extract was dried over $MgSO_4$, filtered, and concentrated to afford light yellow oil (0.442 g, 82 % yield). ^{1}H NMR (400 MHz, CD_3OD): δ 7.10 (t, 1H, *J* = 7.6 Hz), 6.74 (m, 3H), 4.37 (s, 2H), 4.25 (q, 2H, *J* = 7.2 Hz), 1.27 (t, 3H, *J* = 6.8 Hz).



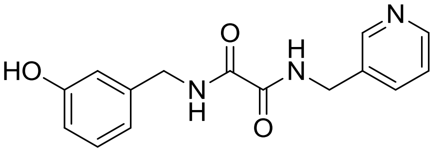
172

***N*-(4-Cyano-butyl)-N'-(3-hydroxy-benzyl)-oxalamide (172)**. 47.16 mL 0.0175 M solution of *N*-(3-hydroxy-benzyl)-oxalamic acid ethyl ester in THF (**171**, 0.188 g, 0.825 mmol) added to a round bottom flask. 5-Aminovaleronitrile (0.081 g, 0.825 mmol) was added and the reaction was stirred at room temperature overnight. Solvent was removed *in vacuo* to afford beige solid which was recrystallized from warm MeOH to afford a white solid (0.108 g, 48% yield). m.p. 148-150 ºC, ^{1}H NMR (400 MHz, CD_3OD): δ 7.14 (t, 1H, *J* = 8.0 Hz), 6.78-6.68 (m, 3H), 4.37 (s, 2H), 3.29 (2H, in CD_3OD peak), 2.50 (t, 2H, *J* = 8.0 Hz), 1.69-1.66 (m, 4H). HRMS *m/z* calcd for $C_{14}H_{17}N_3O_3$ 275.12691, found 274.11976 $(M-H)^-$.



173

***N*-[2-(4-Hydroxy-phenyl)-ethyl]-N'-pyridin-3-ylmethyl-oxalamide (173).**[41] *N*-[2-(4-Hydroxy-phenyl)-ethyl]-oxalamic acid ethyl ester (**167**, 0.091 g, 0.38 mmol) was dissolved in anhydrous 1,4-dioxane and 3-aminomethyl pyridine (0.040 mL, 0.39 mmol) was added. The reaction was stirred at 80 ºC for 3 h and room temperature overnight. Solvent was removed *in vacuo*, and the residue was dissolved in 30 mL EtOAc and washed with 20 mL H_2O. The organic extract was dried over $MgSO_4$, filtered, and concentrated to afford 0.116 g (~100 % crude yield) of light yellow solid. The crude material was recrystallized in hot MeOH, resulting in 0.031 g (0.104 mmol, 27% yield) white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.35 (t, 1H, *J* = 6.4 Hz), 8.73 (t, 1H, *J* = 6 Hz), 8.45 (m, 2H), 7.65 (d, 1H, *J* = 7.6 Hz), 7.35 (m, 1H), 6.98 (d, 2H, *J* = 8.4 Hz), 6.67 (d, 2H, *J* = 8.0 Hz), 4.33 (d, 2H, *J* = 8.0 Hz), 3.17 (d, 2H, *J* = 4.0 Hz), 2.65 (t, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, DMSO-d_6, 25 ºC): δ 160.3, 159.7, 155.7, 148.9, 148.3, 135.3, 134.3, 129.5, 129.1, 123.5, 115.2, 40.3, 33.8, additional CH_2 peak under solvent residual peak. HRMS *m/z* calcd for $C_{16}H_{17}N_3O_3$ 299.12716, found 298.11989 $(M-H)^-$.



174

***N*([3-Hydroxy-benzyl)--*N*'-pyridin-3-ylmethyl-oxalamide (174)**. See procedure for *N*-[2-(4-hydroxy-phenyl)-ethyl]-*N*'-pyridin-3-ylmethyl-oxalamide (**173**).^{1}H NMR (400 MHz, DMSO-d_6, 25 ºC): δ 9.41 (t, 1H, *J* = 6.4 Hz), 9.37 (br, 1H), 9.25 (t, 1H, *J* = 6.5 Hz), 8.50 (d, 1H, *J* = 1.9 Hz), 8.45 (dd, 1H, *J* = 4.8, 1.6 Hz), 7.68-7.66 (m, 1H), 7.36-7.34 (m, 1H), 7.08 (t, 1H, *J* = 7.7 Hz), 6.68-6.62 (m, 3H), 4.35 (d, 2H, *J* = 6.4 Hz), 4.23 (d, 2H, *J* = 6.5 Hz).

General Procedure for Preparing Co-Crystals:[37] A 1:1 (varied) ratio of host to guest (**137**) was dissolved in 12 mL methanol. The mixture was subjected to sonication for 1 minute, and the resulting solution was divided into four test tubes. The solution was centrifuged for 10 minutes, and the liquid was decanted into four 50 mL crystallization dishes. The dishes were covered with aluminum foil, which was punctured 12-15 times using a needle. The dishes were left on the benchtop undisturbed, until solvent evaporation was complete.

3.5 References

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Chapter 4: The Topochemical Polymerization of Diiodohexatriyne

The topochemical polymerization of diiodohexatriyne (**56**, C_6I_2) was explored, using the host-guest strategy that was employed for the preparation of poly(diiododiacetylene) (PIDA).[1, 2] Bis(nitrile) oxalamide hosts were used to prepare co-crystals with C_6I_2. Both Sun and Luo demonstrated that this class of hosts cocrystallizes with diiodobutadiyne (C_4I_2), and the monomer undergoes spontaneous polymerization to form PIDA.[1-3] The crystal structure obtained for the PIDA co-crystal indicates that half the iodine atoms interact with the nitrile end groups via halogen bonding interactions, while the other half are pointed towards the oxalamide oxygen atoms (Figure 4.1 a, b).[1] This 1:2 host to guest stoichiometry was only observed for the nitrile hosts that contained an even number of methylene units between the oxalamide and nitrile functionality.[3] Hosts with an odd number of methylene chains formed co-crystals with diiodobutadiyne in a 1:1 ratio. The PIDA co-crystals undergo a color change from dark blue to gold upon polymerization (Figure 4.1 c).[3]

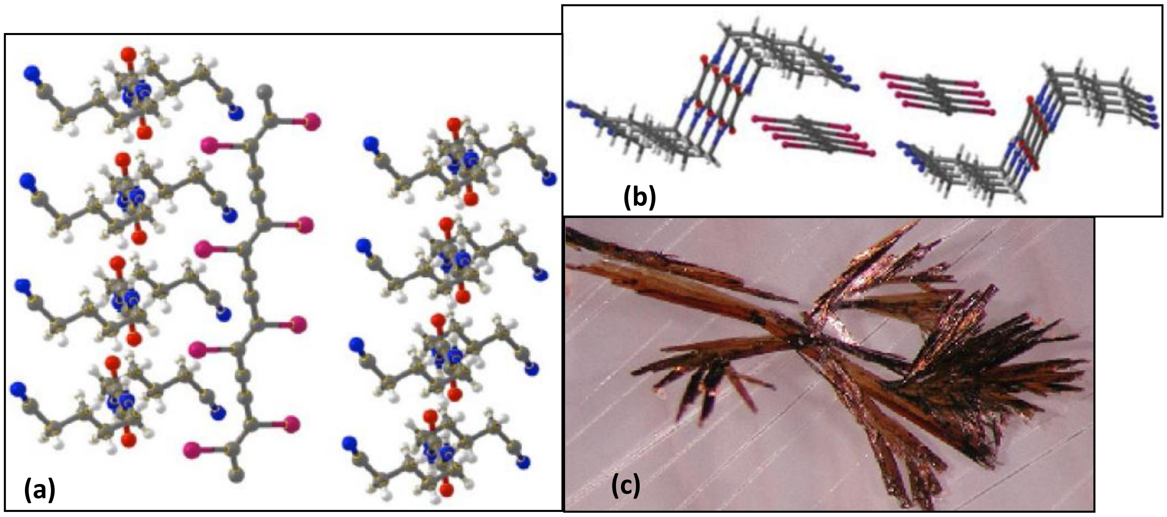


Figure 4.1 PIDA co-crystals formed from diiodobutadiyne (**70**) and bis(nitrile) oxalamide host **13**: (a) polymer strand, (b) top view, (c) golden crystals that result from polymerization[1, 3] From Sun, A.; Lauher, J. W.; Goroff, N. S. Preparation of poly(diiododiacetylene), an ordered conjugated polymer of carbon and iodine. *Science* **2006,** *312,* 1030-1034. Reprinted with permission from AAAS.

4.1 Polytriacetylenes

Achieving ordered polymerization of triynes is more complicated than diyne polymerization, since triynes can undergo 1,4- and 1,6-topochemical polymerizations. As discussed in Chapter 1, this difficulty can be addressed by controlling the repeat distance (*r*) between the monomer units.[4, 5] A repeat distance of ~4.9 Å between the monomers favors 1,4-polymerization, which in the case of diiodohexatriyne would result in a poly(diacetylene) with iodoalkynes and single iodine atoms as the two respective side chains along the backbone. If the repeat distance is approximately 7.4 Å, the monomer would be aligned in the proper orientation for 1,6-polymerization, corresponding to a polytriacetylene with single iodine atom side units.[5-8] The 1,6- and 1,4-topochemical polymerizations of diiodohexatriyne are shown in Figure 4.2 below.

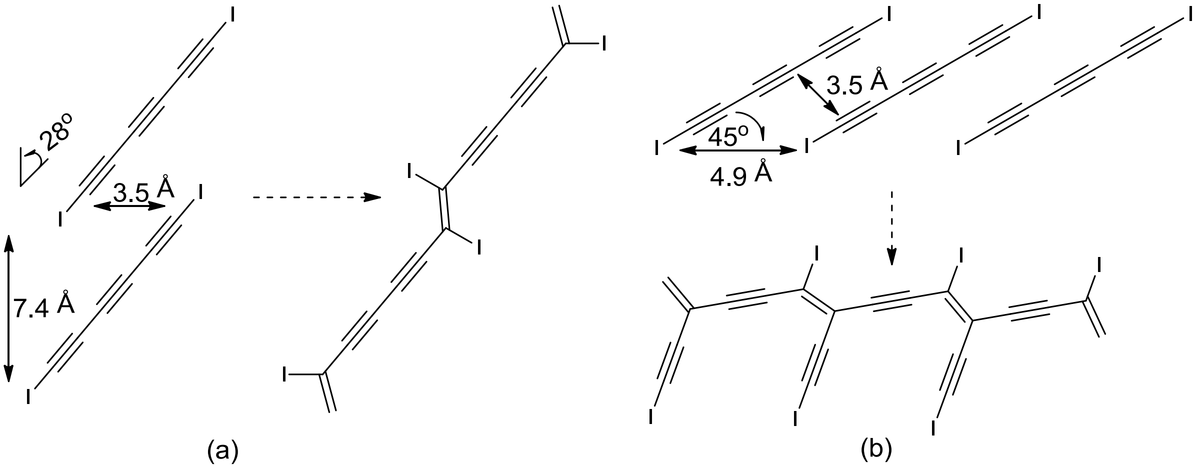


Figure 4.2 (a) 1,6- and (b) 1,4-topochcemical polymerization of diiodohexatriyne (**56**)[5, 9]

The 1,4-topochemical polymerization of triacetylenes has been known for some time.[6, 10] However the 1,6-polymerization was not reported until the work of Lauher and Fowler.[5, 11] Diacid triyne **16** forms co-crystals with vinylogous amide pyridine host **15** (Figure 4.2), which undergo polymerization when subjected to thermal annealing.[4] The single-crystal to single-crystal polymerization is shown in Figure 4.3.[4]

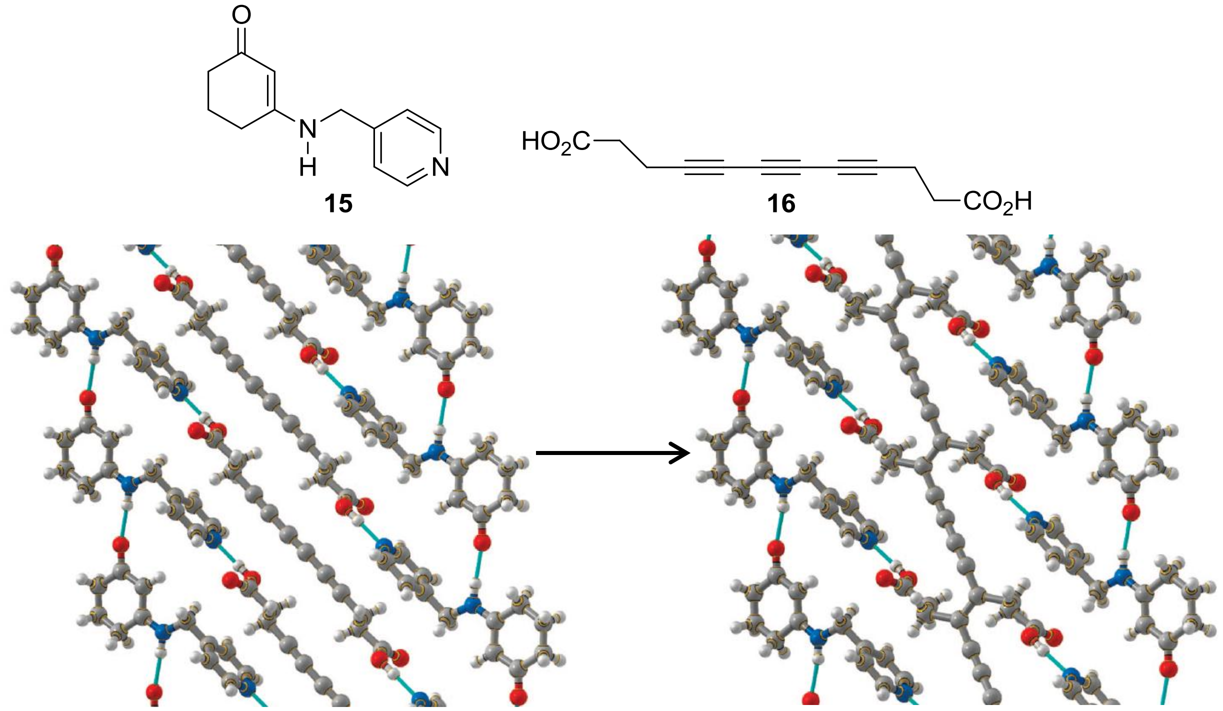


Figure 4.3 1,6-topochemical polymerization of **15·16** co-crystal upon thermal annealing[4, 5, 11] Reprinted with permission from Lauher, J. W.; Fowler, F. W.; Goroff, N. S. Single-crystal-to-single-crystal topochemical polymerizations by design. *Acc.Chem. Res.* **2008,** *41*, 1215-1229. Copyright 2008 American Chemical Society.

4.2 Previous Efforts Using Bis(pyridyl) Oxalamide Hosts and Diiodohexatriyne

In previous work, bispyridyl oxalamide hosts **12** and **158** were employed to form co-crystals with diiodohexatriyne (Figure 4.4).[9] Co-crystals of diiodohexatriyne and **12** have a repeat distance of 5.28 and θ = 44º, which results in a C1-C4 distance, *d* = 3.67 Å. This C1-C4 contact distance was smaller than the 3.9 Å that is required for 1,4-topochemical polymerization. The co-crystals undergo a color change from pale yellow to shiny gray over time or when subjected to heat, UV, or γ radiation; however X-ray crystallography showed no indication of polymer.[9] It is possible that a long repeat distance may have prevented complete polymerization from spreading throughout the chain. In the co-crystal of diiodohexatriyne and **158**, the repeat distance of 4.97 Å was very close to the ideal 4.9 Å; however a large tilt angle of 63º caused by steric repulsion between the host molecules produces a C1-C4 distance (*d*) of 4.67 Å.[9] This distance is larger than the van der Waals contact distance for carbon. Therefore, the C1-C2 contact distance is 4.53 Å, which is shorter than the C1-C4 distance. Since the parameters of the co-crystals did not correlate with the ideal values that were outlined by Baughman, ordered single-crystal-to-single-crystal topochemical polymerization was not achieved.[8, 9]

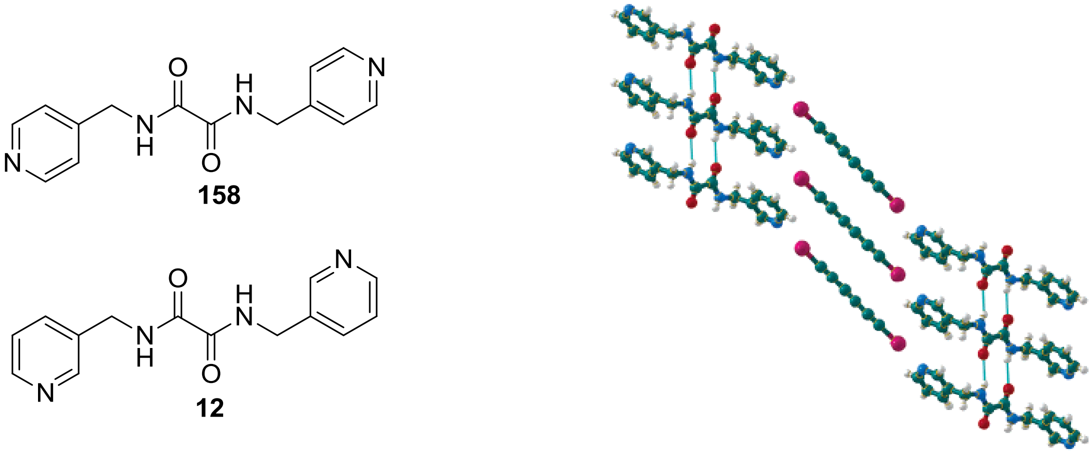
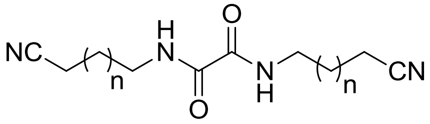


Figure 4.4 Bispyridyl oxalamide hosts **158** and **12**, and crystal structure of **12·56** co-crystal[9] Reprinted with permission from Goroff, N. S.; Curtis, S. M.; Webb, J. A.; Fowler, F. W.; Lauher, J. W. Designed cocrystals based on the pyridine-iodoalkyne halogen bond. *Org. Lett.* 2005, *7*, 1891-1893. Copyright 2005 American Chemical Society.

4.3 Co-Crystallization Experiments and Results

The co-crystallization experiments conducted in this work incorporate nitrile oxalamide hosts containing 4, 5, or 6 methylene units between the oxalamide group and the nitrile group (**13**, **156**, **157**, Figure 4.5). Nitrile hosts had not been used for the preparation of co-crystals with diiodohexatriyne prior to these experiments. The translational distance that results from the self-complementary hydrogen bond network formed by the oxalamide functionalities is 5.0 Å. Therefore, a 1,4-polymerization is expected for this system.



13 n=2

156 n=3

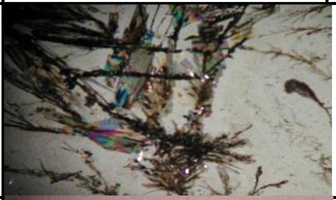
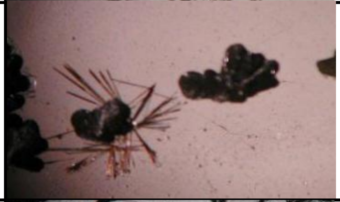
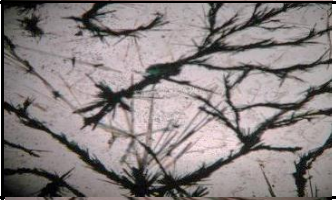
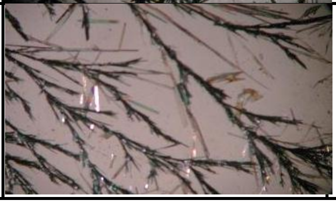
157 n=4

Figure 4.5 Bis(nitrile) oxalamide hosts

In the initial co-crystallization experiments with C_6I_2 and the nitrile oxalamide hosts, acetonitrile was used as the solvent. This solvent was chosen based on experiments conducted by fellow group members Daniel Resch and Siew Yoong Tan, when optimizing the conditions for preparing co-crystals of diiodobutadiyne (**70**) and the bis(nitrile) oxalamide hosts. The diiodohexatriyne co-crystals were prepared in an fashion to the methods that were described in Chapter 3; however, the dishes were placed in an ice bath (0 ºC) to prevent decomposition of the monomer. C_6I_2 is notably less stable than diiodobutadiyne, thus greater care is taken when preparing co-crystals with this guest.

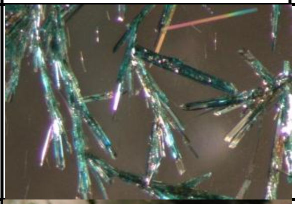
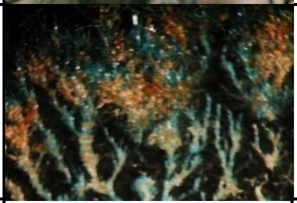
The crystals that formed upon solvent evaporation indicate that host **157** yields the most crystalline material, compared to the shorter analogs. Co-crystals of C_6I_2 and bis(nitrile) oxalamide **157** were green and needle-like, whereas hosts **13** and **156** yielded grey/brown solid and round, amorphous material, respectively. A 1:2 host to guest ratio was more favorable than a 1:1 ratio, with the latter resulting in residual host after solvent evaporation. Raman spectra were obtained for the **157·56** co-crystals to gain some preliminary information regarding polymerization. Three defined peaks were visible, which were indicative of the single, double, and triple bond stretches of a poly(diacetylene). These data will be discussed in more detail later in this chapter. The results of these initial experiments, used to determine which host was most promising for forming co-crystals, are summarized in Table 4.1.

Table 4.1 Initial co-crystal experiments with diiodohexatriyne

Host	Ratio Host:Guest	Solvent (temp)	Appearance	m.p.	Other Analysis
13	1:2	MeCN (0 ºC to rt)			significant amount of excess host present, a mixture of colorless and brown/gray solid present
156	1:2	MeCN (0 ºC to rt)			material not very crystalline
157	1:2	MeCN (0 ºC to rt)		125 ºC turned black	turned dark purple, Raman spectrum peaks around 1100, 1400, 2100 cm^{-1}, XRD attempted, could not be solved
157	1:1	MeCN (0 ºC to rt)		125 ºC turned black	turned dark purple over time, Raman spectrum contained peaks around 1100, 1400, 2100 cm^{-1}

To further explore the co-crystallization of diiodohexatriyne and host **157** and to obtain crystals that were suitable for X-ray diffraction, various experimental changes were made. In combined efforts with Matthew Freitag, solvent, temperature, and host-to-guest ratio were modified, to determine the optimal conditions for co-crystal formation. Of the solvents examined, dichloromethane is the best for producing crystalline material in this system, while the use of methanol and tetrahydrofuran resulted in very fine, powdery solid. Reducing the amount of dichloromethane used to make the solution of diiodohexatriyne and host **157** also did not improve the morphology of the resulting solid. Therefore solutions of higher concentration were not pursued. Two azeotropes of dichloromethane and methanol (1:1 and 10:1 ratios of dichloromethane to methanol) resulted in material that was not as crystalline compared to the co-crystals that were grown in pure dichloromethane. This solvent mixture was explored because it has been effective in the co-crystallization experiments performed by Hongjian Jin, which incorporated dibromobutadiyne and bis(pyridyl) oxalamide hosts. Since the co-crystals grown in methylene chloride yielded the best quality crystals, this solvent system was used in additional trials. The results of these co-crystallization experiments are summarized in Table 4.2.

Table 4.2 Results of diiodohexatriyne co-crystallization experiments with nitrile oxalamide hosts

Host	Host:Guest ratio	Solvent (temp)	Appearance	m.p.	Other Analysis
157	1:2	CH_2Cl_2 (0 ºC to rt)		130 ºC turned black	turned dark purple, Raman spectrum peaks ~1100, 1400, 2100 cm^{-1}, structure of monomer
157	1:2	CH_2Cl_2: MeOH 1:1		130 ºC turned black	crystal quality not as good as those grown in CH_2Cl_2
157	1:2	CH_2Cl_2 concentrated (rt)		130 ºC turned black	using less solvent did not produce better quality crystals
157	1:2	THF (rt)	material not crystalline		no further analysis performed
157	1:2	MeOH (rt)	powdery solid obtained		no further analysis performed

The **157·56** co-crystals that were grown in methylene chloride initially were light green, but darkened to blue and eventually turned shiny purple over a time period of about 2 weeks. This color change, which may be indicative of polymerization, is shown in Figure 4.6. In addition, the material turned black around 125 ºC and did not melt. This provided evidence of co-crystal formation, as the host melts around 99 °C and the guest turns black/explodes around 90 °C.

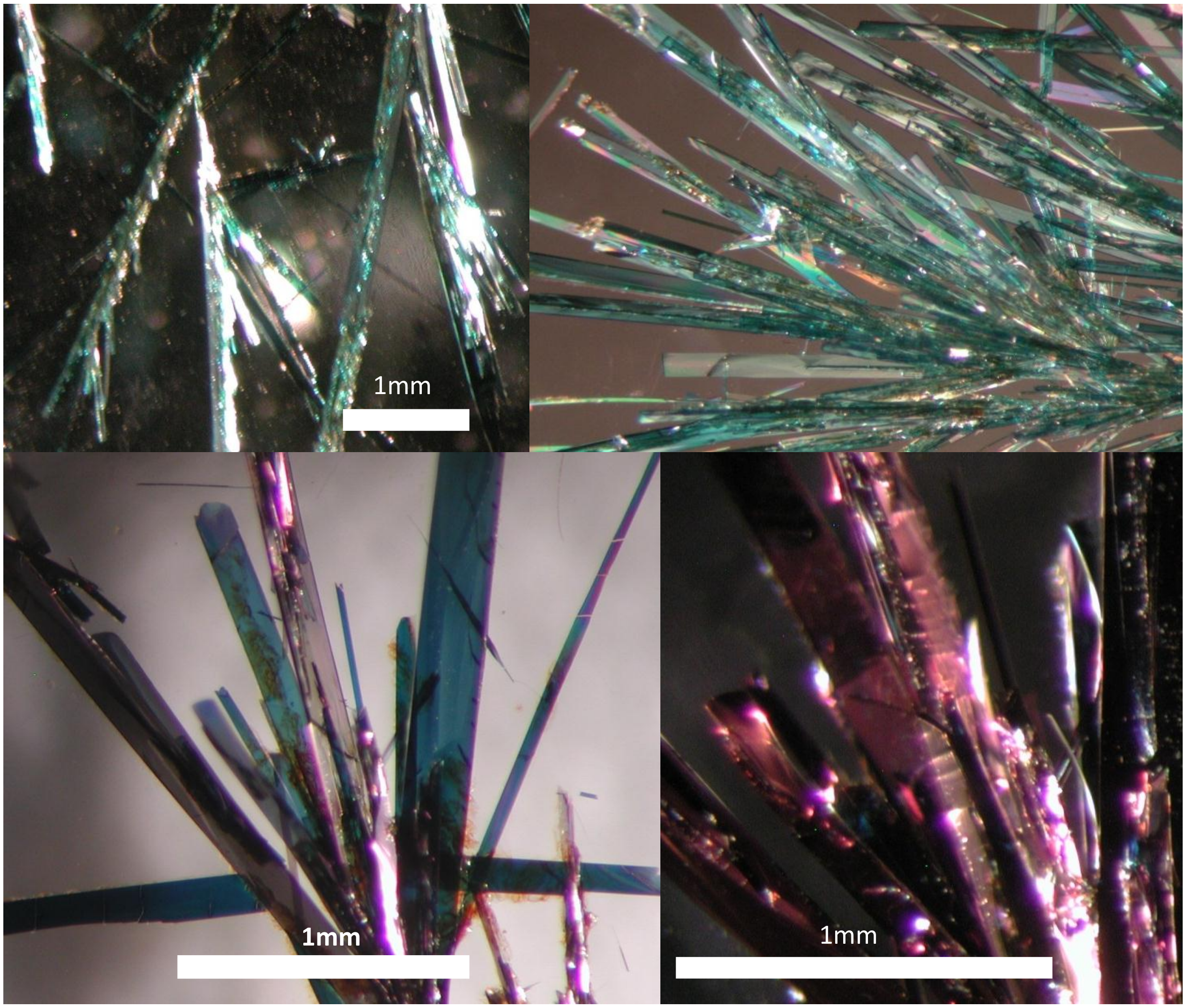
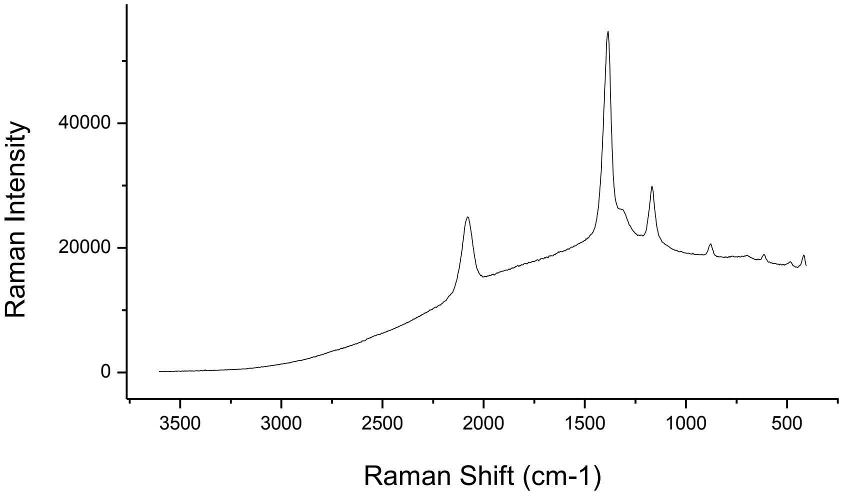


Figure 4.6 Color change in co-crystals of diiodohexatriyne and bis(nitrile) oxalamide host **157**

4.4 Characterization methods

Raman spectroscopy was the first method of characterization that was used to determine if polymeric material was present in the **157·56** co-crystals. This analytical method is an important tool which can be used to identify the presence of carbon-carbon multiple bonds along poly(diacetylene) and poly(triacetylene) backbones.[12] The intensity of Raman scattering depends on a molecule's polarizability, and it can therefore detect small amounts of poly(diacetylenes) or poly(triacetylenes) due to their highly polarizable backbones. Although the relative intensity of the Raman scattering can correlate to the amount of polymerization, the exact percentage of polymer present in the co-crystals cannot be accurately quantified by this method.[7]

The Raman spectrum that was obtained for the purple **157·56** crystals contained three distinct peaks that suggest the presence of polymer (Figure 4.7). The peaks do not have the same frequency as those for poly(diiododiacetylene); however the two peaks around 1400 cm^{-1} and 2100 cm^{-1} are very close to the values reported for the carbon-carbon double bond and carbon-carbon triple bond stretches, respectively for polytriacetylenes.[5, 7] Lauher and Fowler reported the 1,6-topochemical polymerization of triynes, with Raman peaks at 1552 and 2148 cm^{-1} corresponding to the carbon-carbon double and triple bond stretches of the polymer, respectively.[5] Frauenrath and co-workers attempted the 1,6-topochemical polymerization of various phenyl-capped triynes; however the ^{13}C MAS (magic angle spinning) NMR spectra for the polymeric material indicated that 1,4-polymerization occurred.[7] The Raman spectra for these poly(diacetylenes) with ethynyl side chains contained peaks at 1451-1489 and 2110-2129 cm^{-1}.[7] These data indicate that the shifts for the carbon-carbon multiple bonds in both poly(diacetylenes) and poly(triacetylenes) similar, and can vary depending on the conjugation length of the chain.[5, 7, 13] The relative peak intensities in the Raman spectrum of the **157·56** co-crystals were rather low, compared to the spectra that were obtained for fully polymerized poly(diiododiacetylene).[3] This suggests that the co-crystals did not undergo complete polymerization. Therefore, the material was allowed to sit at room temperature for an additional week before taking an additional Raman spectrum. A small amount of the purple co-crystals was heated at 40 °C for 7 days in an attempt to accelerate the polymerization process. The Raman spectra that were obtained for both of these samples were very similar to the initial spectra that were obtained, with no visible increase in relative peak intensity. It is therefore unclear if the amount of polymerization increased, as it is very difficult to deduce any quantitative information from Raman spectroscopy. In all of the experiments that were performed, a 785-nm laser beam was used, at 10% power. When full power was used, the spectrum that was obtained looked very similar to the spectrum of commercial graphite, suggesting that the polymer undergoes a transformation to graphitic material under the Raman laser. This transformation is consistent with what Liang Luo observed when Raman spectra were obtained for isolated poly(diiododiacetylene) under different wavelengths.[3] When a 785-nm laser beam was used, the spectrum contained small peaks correlating to a poly(diacetylene) backbone; however, when switching to a 532-nm laser, the Raman spectrum was consistent with that of commercial graphite.[3]



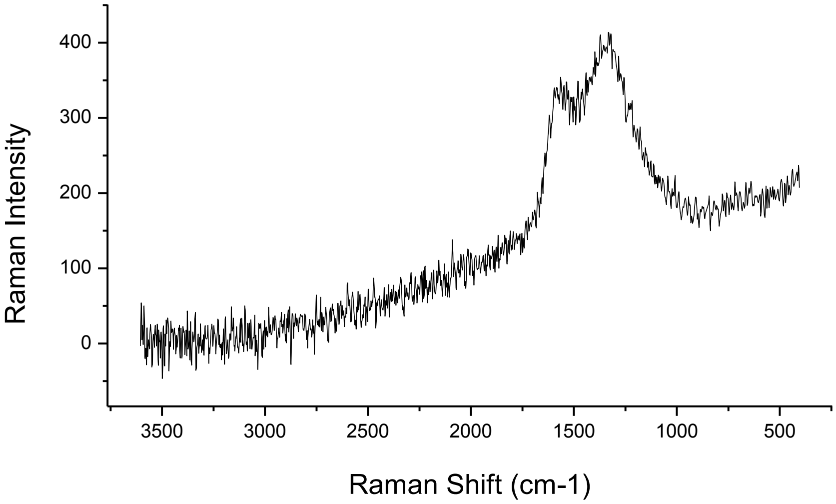


Figure 4.7 Raman spectra for **157·56** co-crystal. Top: 785 nm, 10% power, Bottom: 785 nm, full power

X-ray crystallography was used to determine the structure of the **157·56** co-crystal prior to polymerization. A freshly prepared sample was used in the experiments, immediately after solvent evaporation. A structure was obtained for the green crystal, solved with the help of Daniel Resch. The crystal structure reveals that host **157** forms co-crystals with diiodohexatriyne in a stoichiometry of 1:2, with half of the iodine atoms pointed towards the nitrile nitrogens and the other half interacting with the oxalmide oxygen atoms, via halogen bonding (Figure 4.8). This phenomenon was also observed in the co-crystals of diiodobutadiyne and nitrile host **13**.[1, 3] This structure is the first co-crystal of host **157** to be solved completely. Previous attempts to elucidate the co-crystal structure of this host with diiodobutadiyne (**70**) were unsuccessful, due to disorder within the crystal. Although the structure was not completely solved, the unit cell of the **157·70** co-crystals was determined by Liang Luo.[3] The unit cell parameters were consistent with the data obtained for the **13·70** co-crystals, thus suggesting a 1:2 host to guest ratio. It was therefore not surprising that the **157·56** co-crystals also have a 1:2 host to guest stoichiometry.

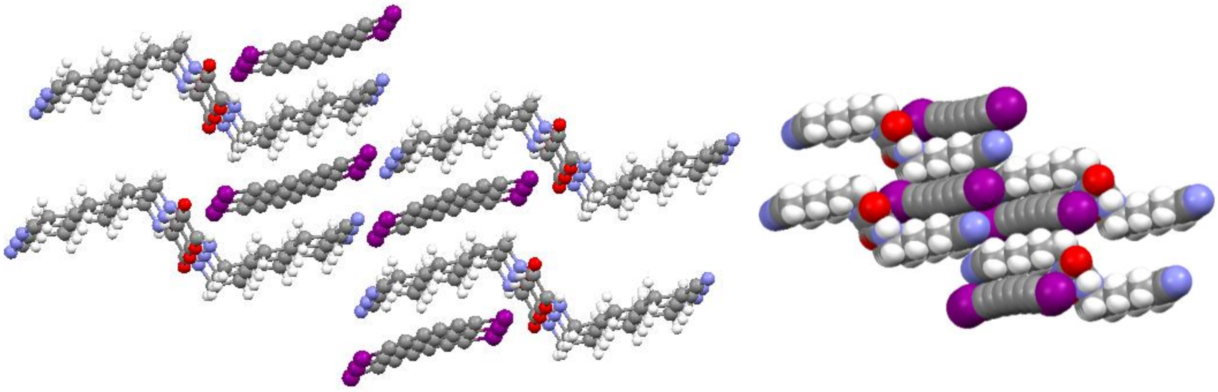


Figure 4.8 Crystal structure of **157·56** co-crystals immediately after solvent evaporation. Unit cell parameters: Space group: P-1; Unit cell dimensions: a = 5.115(5) Å, b = 7.985(5) Å, c = 19.707(5) Å; α = 89.977(5)°, β = 85.015(5)°, γ = 85.045(5)°, Volume = 798.837 $Å^3$

The polymerization of the **157·56** co-crystals was monitored by X-ray diffraction, with the color change that the crystals undergo at room temperature as a guide. After sitting at room temperature for three days, the initial light green crystals become dark blue. The crystal structure obtained at this stage indicated the material was still monomer, and the unit cell parameters were very similar to the values for the green crystal. Another XRD experiment was performed after the crystal was kept at room temperature for eight days. By this time, the material was shiny dark purple and expected to be polymer. Surprisingly, the crystal structure of the purple crystal still correlated to unpolymerized co-crystal, despite the color change. X-ray diffraction depends on average electron density, used to generate a molecular structure. Therefore, the degree of polymerization may have been too small to be detected by this method at this point. The unit cell dimensions that were obtained for these experiments are summarized in Table 4.3. There is a larger difference between the parameters of the green and purple crystals compared to the green and blue crystals; however the cell parameters are still very similar. When examining the packing parameters, the repeat distance (*r*) changes more than the C1-C4 contact distance (*d*), during the color change, and this value becomes closer to the ideal repeat distance (5.0Å) required for 1,4-polymerization (Table 4.4).[8] The thermal ellipsoids for the purple crystal were spherical (Figure 4.9), hence there were no major signs of disorder. This observation indicates that the crystal contains primarily monomer.

Table 4.3 Unit cell dimensions for **157·56** co-crystal in green, blue, and purple phases

Crystal	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)	R1%
0 days rt(green)	5.11(5)	7.98(5)	19.71(5)	89.98(5)	85.01(5)	85.04(5)	798.84	4.99
3days rt (blue)	5.12(18)	7.99(7)	19.70(15)	89.97(7)	85.02(5)	85.05(5)	798.99	5.60
8days rt (purple)	5.08(6)	8.01 (10)	20.01(3)	88.50(2)	80.07(2)	84.97(2)	798.57	4.47

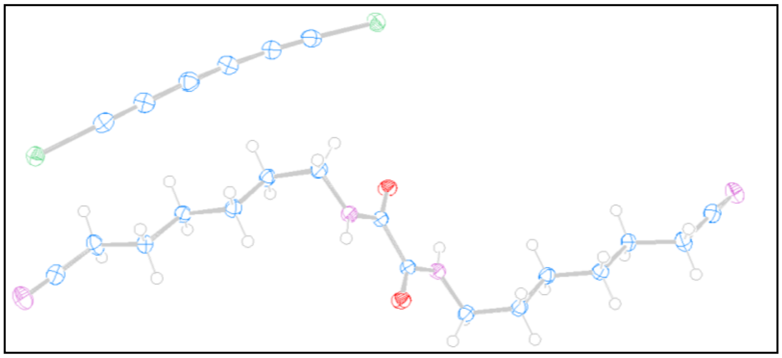


Figure 4.9 ORTEP drawing of thermal ellipsoids in **157·56** purple co-crystal after 8 days at room temperature

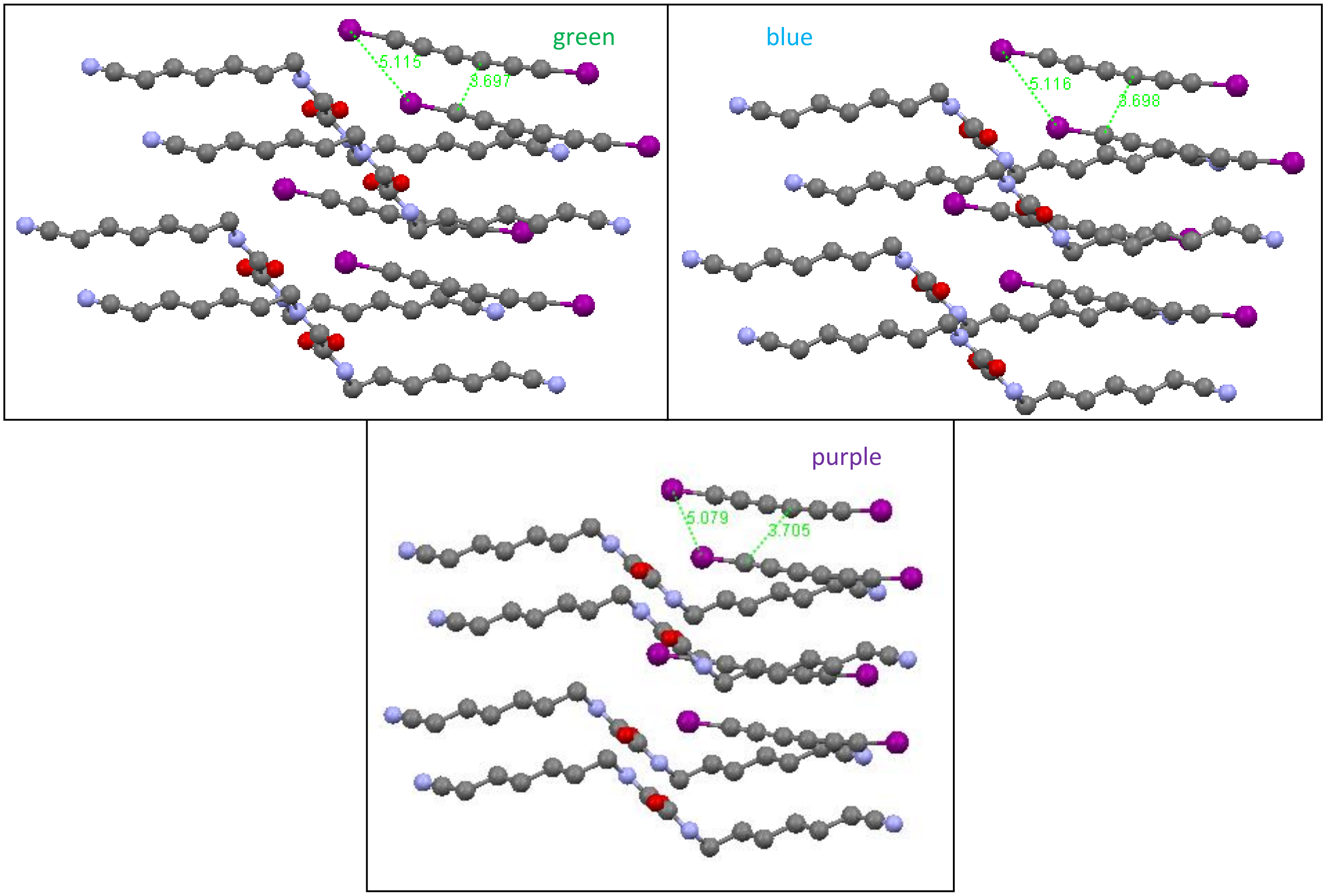


Figure 4.10 Changes in packing observed during color transformation, *r* and *d* indicated in crystal structure, values shown in Table 4.4

Table 4.4 Changes in packing observed during color transformation

Crystal	*r* (Å)	*d* (Å)	θ (°)
Green (0 days rt)	5.115(5)	3.697(1)	52.12(2)
Blue (3 days rt)	5.116(7)	3.698(1)	52.20(2)
Purple (8 days rt)	5.079(8)	3.705(1)	52.88(2)

Since polymerization of the **157·56** co-crystals was difficult to detect using X-ray diffraction, solid state ^{13}C MAS NMR was used as an alternative method for determining the presence of polymer. These experiments were performed by Andrew Ilott, a postdoctoral fellow working in Clare Grey and Brian Phillips's group. A ramped cross-polarization pulse sequence was used, which enhances the signals for dilute spins, such as ^{13}C, by transferring magnetization from the abundant ^{1}H spins in the sample.[14, 15] The ramped cross polarization pulse used in this sequence ensures an equal efficiency in the rate of magnetization transfer to protonated and quaternary ^{13}C positions. This method allows quantitative information to be obtained from the spectra.[15]

Spectra were obtained for isolated bis(nitrile) oxalamide host **157**, and freshly prepared **157·56** green co-crystals. Comparing the spectra facilitated assignment of the peaks corresponding to the host and diiodohexatriyne. These spectra are shown in Figure 4.11 below. Splitting was observed for the diiodohexatriyne peaks, which is not observed in the solution state ^{13}C NMR. This may result from the different environments that the carbon atoms are experiencing, due to the asymmetric structure of the co-crystal. The two sides of the monomer are no longer equivalent, which is indicated by the observed splitting.

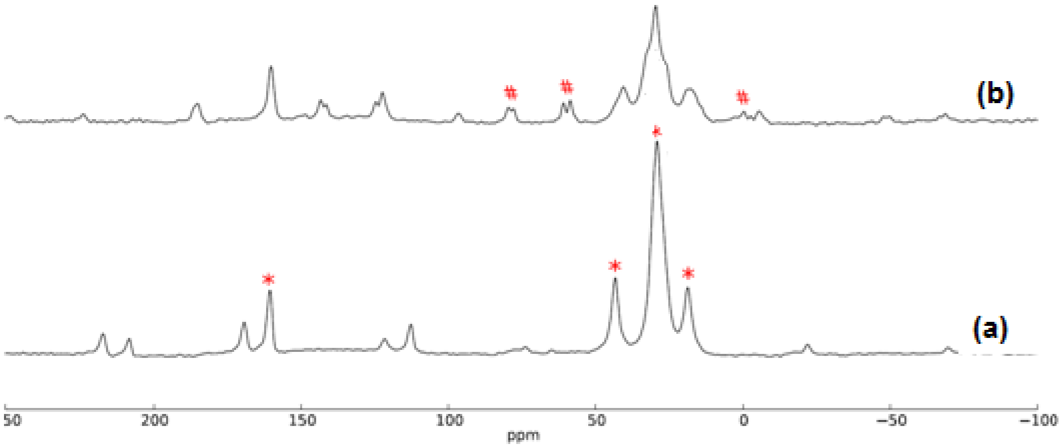


Figure 4.11 ^{13}C MAS NMR spectra for bis(nitrile) oxalamide host **157** (a), and unpolymerized **157·56** co-crystals (b) after 2 days; * corresponds to host, # represents guest centerbands

The co-crystals were allowed to turn purple at room temperature, and additional spectra were obtained at time intervals that were 5 and 21 days after the initial preparation (Figure 4.12). The spectrum that was taken three weeks (21 days) after initial sample preparation contains new peaks around 33, 103, and 108 ppm (marked by red arrows in Figure 4.12). Any additional new peaks that appeared were not well resolved, because the signals were either masked by sidebands, or were very broad. The emergence of these new peaks confirms that polymerization occurs over time. The amount of monomer that underwent polymerization was approximated by comparing the integrated intensities of the monomer and polymer peaks at day 5 and day 21. Integration of the peaks shows a loss of approximately 40% in the monomer peaks and a corresponding increase in intensity in the polymer peaks. Therefore, these values allow for a rough estimate of about 40% conversion from monomer to polymer. Additional experiments will be necessary to obtain more quantitative data. It is interesting to note that the shiny purple co-crystals turned dark black after these experiments were performed, which may have resulted from the sample being stored in the rotor during the entire 3-week duration of the experiment.

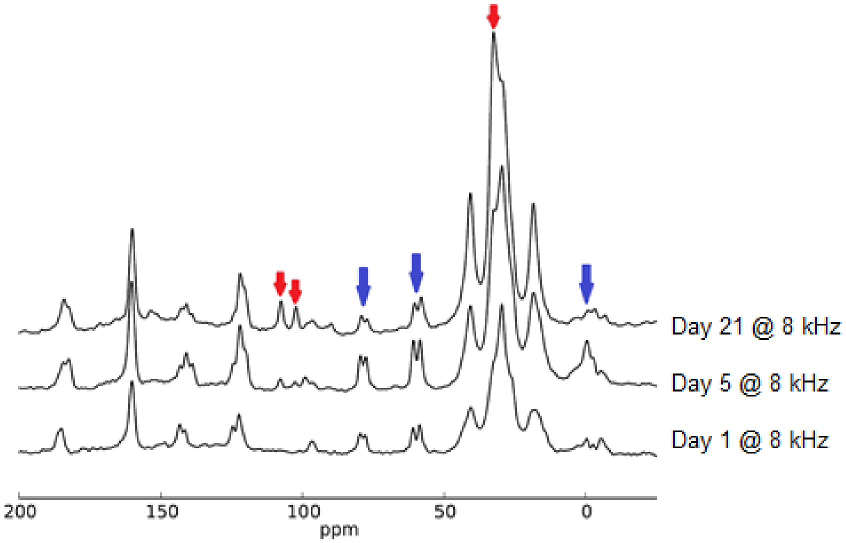


Figure 4.12 Solid-state NMR spectra for partially polymerized co-crystals (left), with blue arrows corresponding to diiodohexatriyne monomer and red arrows indicating new polymer peaks; sample after spectra were obtained (right)

Scanning electron microscopy (SEM) is a technique that can be used to gain information about the surface of a solid. High energy electrons from the microscope interact with the surface atoms of the solid to produce an image that reveals information about the morphology of the sample.[16] The SEM images that were obtained for the purple **157·56** co-crystals indicate that the material is very flat and crystalline. Gold sputtering of the co-crystals was not necessary to see the strands under the microscope, which suggests that the material is conductive. The accelerating voltage used for the experiment was 20 kV. Energy-dispersive X-ray spectroscopy (EDS) was also used as a method for analyzing the chemical composition of the co-crystals. The EDS spectrum indicated that the sample was primarily composed of carbon and iodine, as expected. The signal corresponding to the oxygen in the host is hidden behind one of the iodine signals, while the nitrogen peak for the host is masked by the large carbon peak. The co-crystals that were used for the SEM experiments, as well as the images and EDS spectrum, are shown in Figure 4.13. These data were obtained by James Quinn, of the Material Sciences Department at Stony Brook University.

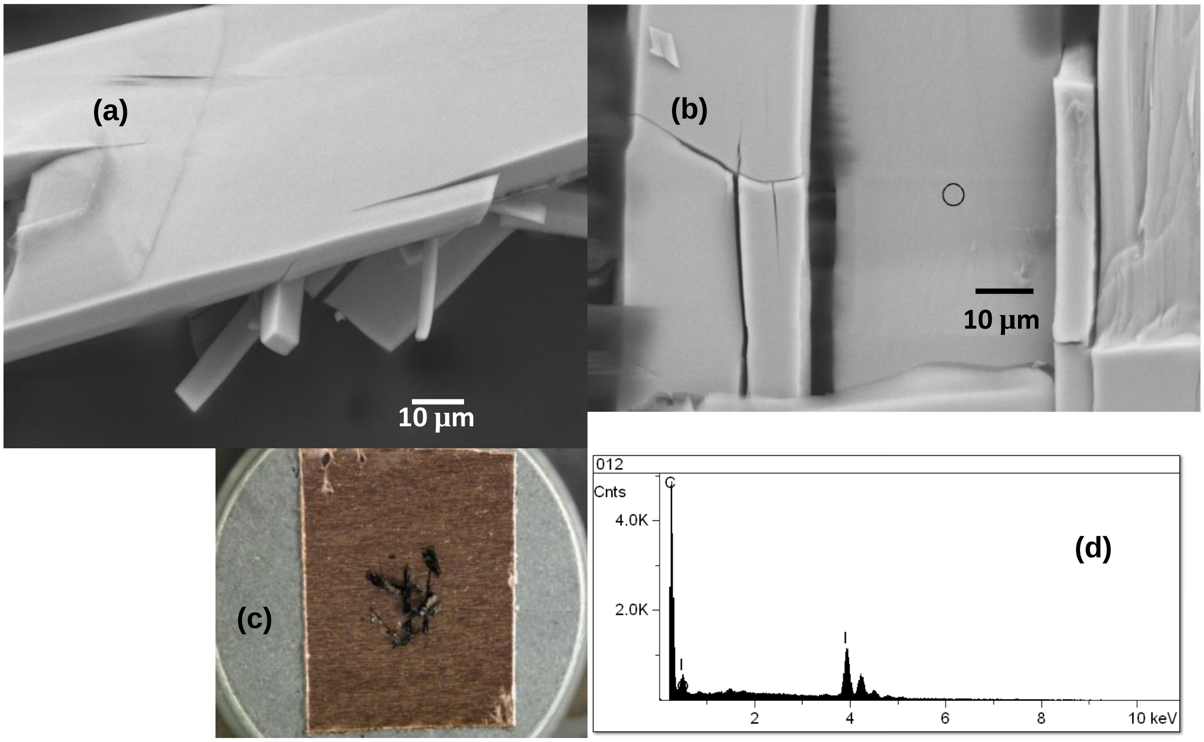


Figure 4.13 (a) SEM images of purple co-crystal, (b) circle indicating where EDS spectrum was measured, (c) **157·56** co-crystals on plate before placing under microscope, (d) EDS spectrum

Infrared (IR) spectroscopy was used to further characterize the **157·56** purple co-crystals. The spectrum contained C=O, C≡N, and N-H stretches around 1630, 2250, and 3300 cm^{-1}, corresponding to the amide, nitrile, and amine groups within the host molecules, respectively. In addition, the presence of the C≡C bonds in diiodohexatriyne was indicated by the peak at 2163 cm^{-1}. The IR spectra of bis(nitrile) oxalamide host **157** and the **157·56** purple co-crystals are shown in Figure 4.14.

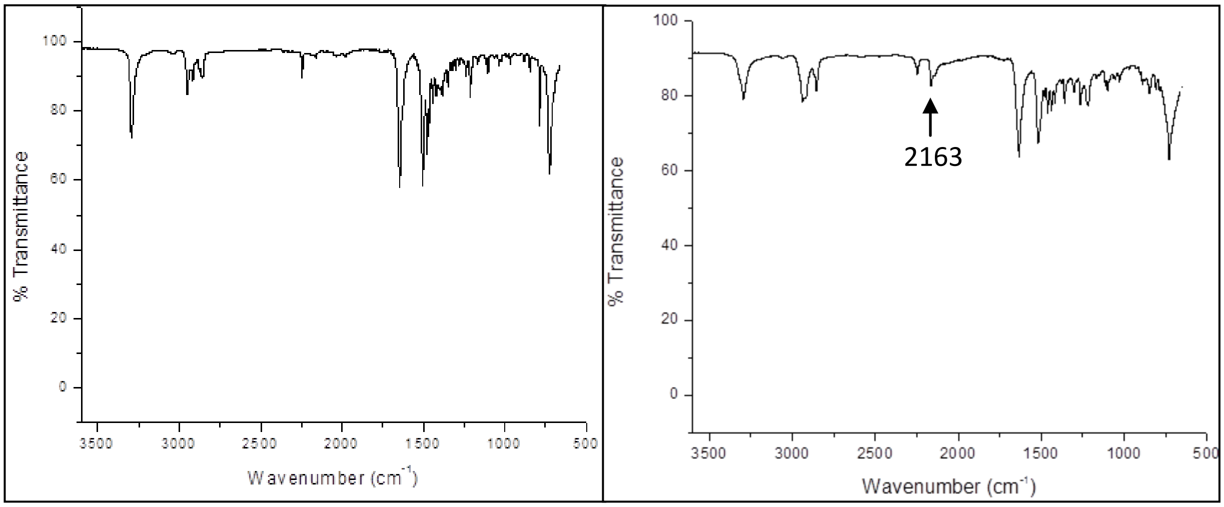


Figure 4.14 FT-IR spectrum of host **157** (left) and **157·56** purple co-crystal (right)

To gain additional insight into the color change that the **157·56** co-crystals undergo, UV-Vis spectroscopy was used. Liang Luo demonstrated that both the unpolymerized and polymerized co-crystals of diiodobutadiyne and bis(nitrile) oxalamide host **13** can form suspensions in water when subjected to sonication.[3] In a similar fashion, a suspension of the green/blue **157·56** co-crystals was prepared, and UV-Vis spectra were obtained for varying dilutions of the suspension. The blue suspension and the corresponding UV-Vis spectrum are shown in Figure 4.15. The spectrum contained peaks at shorter wavelengths (~280-300 nm) corresponding to the monomer, as well as two broad shoulders around 650 and 700 nm, which is similar to the UV-Vis spectra obtained by Liang Luo for **157·70** suspensions.[3] The peaks are much broader and less defined compared to Luo's spectra, a phenomenon that is partially due to the lower concentration of the **157·56** co-crystal suspension. After sitting at room temperature for three days, the suspension was dark gray (Figure 4.15 b). A UV-Vis spectrum was also obtained for the suspension, which contained a similar broad shoulder around 700 nm. Since the gray suspension was more dilute than the original blue suspension, the absorbance had decreased. When preparing the suspensions, some of the solid floated at the top of the water and collected along the sides of the test tube. The same behavior was also observed when trying to form a suspension of the purple co-crystals in water, except in that case the solid remained at the top of the water and a suspension never formed, despite extended periods of sonication. This suggests that once some polymerization has occurred, it is very difficult to break the crystals apart to form a suspension.

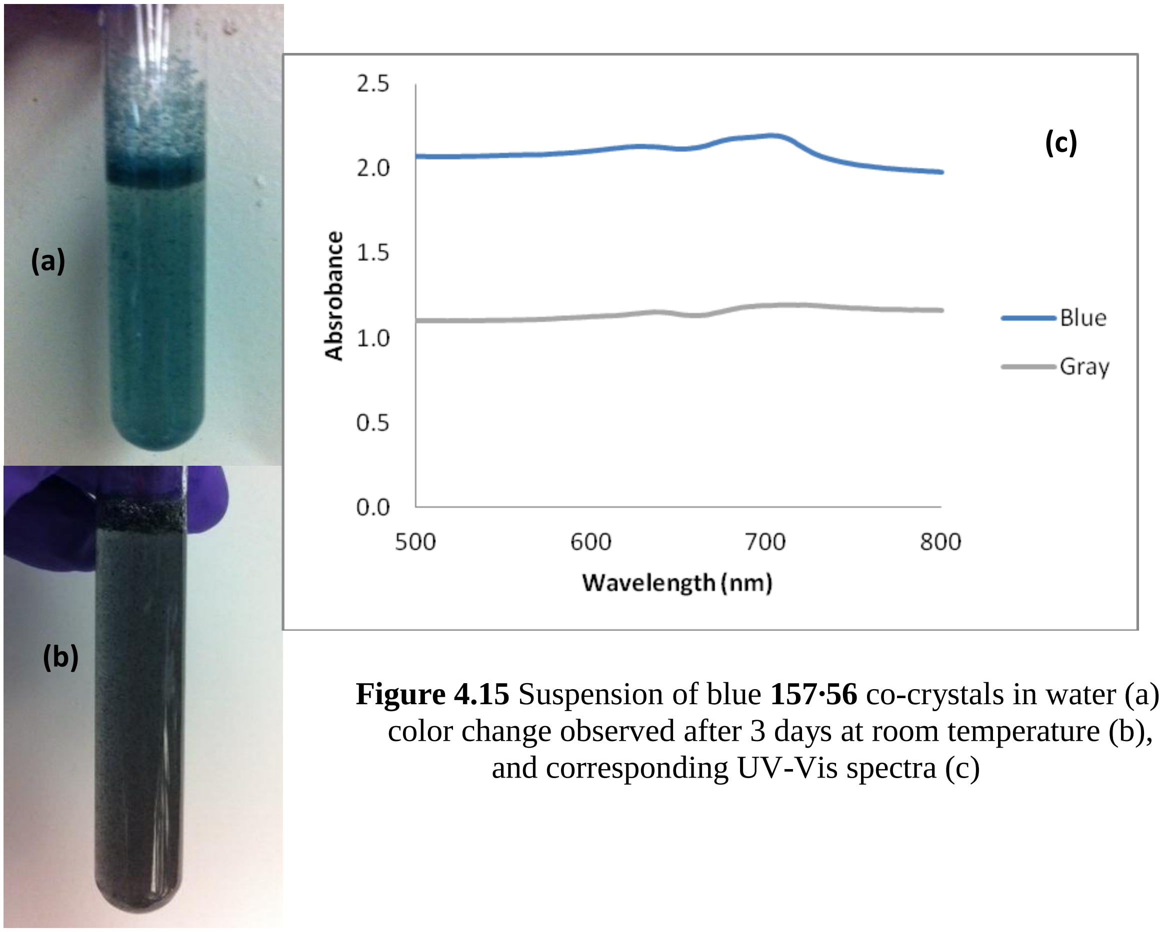


Figure 4.15 Suspension of blue **157·56** co-crystals in water (a), color change observed after 3 days at room temperature (b), and corresponding UV-Vis spectra (c)

Isolation of what was assumed to be polymeric material from the host was performed, by extensively rinsing the purple co-crystals with chloroform. A brown suspension of the co-crystals in chloroform was prepared. The suspension was subjected to sonication overnight and then subjected to centrifugation. Finally, the liquid was decanted, leaving behind black solid. Additional chloroform was added to the solid, and the previously described steps were repeated three additional times. The chloroform washes became lighter in color after each iteration, with the fourth wash being virtually colorless. ^{13}C NMR of the first chloroform wash was obtained, which revealed the presence of host and diiodohexatriyne. There was also a significant amount of black solid that did not dissolve, which is consistent with the behavior of isolated PIDA. This correlated with the expectation that isolation of the polymer from the host would result in an insoluble solid.

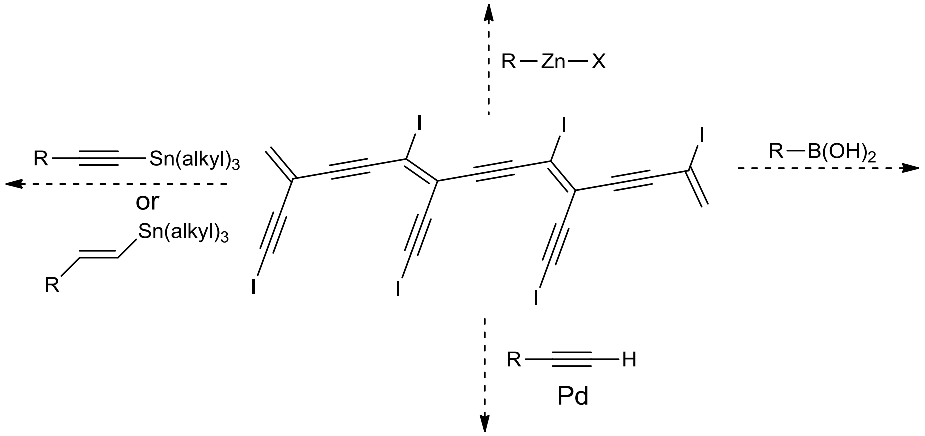
The black solid that resulted from host depletion was further analyzed to gain some additional information regarding the structural characteristics and physical properties of what was assumed to be the isolated polymer. The IR spectrum of this material does not include the characteristic C≡N and C=O stretches of the host that were visible in the spectrum of the co-crystals; this result is consistent with removal of the host by repetitive chloroform rinsing. A Raman spectrum was also obtained, but it did not contain any visible peaks. In previous experiments with poly(diiododiacetlyene), the Raman spectrum for isolated PIDA contained the three characteristic peaks for the polymer; however the intensity was significantly lower compared to the spectrum for the PIDA co-crystals.[3]

To determine if the isolated diiodohexatriyne polymer was a contact explosive, the material was subjected to a hammer test. A small amount of the black solid was placed between two sheets of weighing paper, and was struck with a hammer. Contrary to the results that were obtained by Chris Wilhelm when performing a hammer test on isolated PIDA,[17] this isolated material showed no indication of explosion. The results of these experiments are preliminary, and further characterization must be performed before any concrete conclusions can be made regarding the structure and behavior of the polymer.

4.5 Summary

The co-crystallization of diiodohexatriyne (**56**) and bis(nitrile) host **157** was achieved for the first time. A crystal structure was obtained for the unpolymerized co-crystals, which indicates a 1:2 host-to-guest stoichiometry, analogous to what was observed in the co-crystals of diiodobutadiyne and bis(nitrile) host **13**. The structure of host **157** has never been obtained before, either in isolated form or in the diiodobutadiyne co-crystal. While Raman spectra of the purple material contained defined signals that correlate to the expected peaks for the carbon-carbon single, double, and triple bonds in poly(diacetylenes) and poly(triacetylenes), the low relative intensity of the signals suggest only a minimal amount of polymer was present. This observation was reaffirmed by crystal structures that were obtained by XRD, which indicated that after an eight-day period at room temperature, the majority of the crystal was still unpolymerized monomer, despite the apparent color change. It appears that more time may be required for the monomer to undergo polymerization at room temperature, or that additional stimuli such as mild heating or UV light may be needed to facilitate the process.

Once the 1,4-polymerization of diiodohexatriyne is achieved, the polymer can be fully characterized using the methods that were previously described. Furthermore, additional reactions will be pursued in an attempt to further functionalize the polymer. Transition metal cross-coupling reactions such as Suzuki, Negishi, Sonagashira, or Stille couplings may be attempted (Scheme 4.1) which could replace the iodine atoms with various R groups. The main challenge will be determining the appropriate reaction conditions in which the isolated polymer is somewhat soluble, as attempts to dissolve the material in a variety of organic solvents including dichloromethane, tetrahydrofuran, methanol, pyridine, and hexafluoroisopropanol have been difficult thus far. This work will continue, as the ordered topochemical polymerization of diiodohexatriyne has never been achieved before. The resulting material can serve as a precursor to other carbon-rich materials that may possess interesting optical and electronic properties.



Scheme 4.1 Possible methods for polymer functionalization

4.6 Experimental Procedures and Instrumental Methods

General Methods: Reagents were purchased reagent grade from Aldrich, Fischer Scientific/Acros Organics, VWR, Strem, or GFS Chemicals, and were used without further purification, except where stated. All reactions were performed under an inert argon atmosphere, unless stated otherwise. Iodination of polyynes were carried out in aluminum-foil wrapped flasks in an unlighted hood. All diiodopolyynes were washed with aqueous $Na_2S_2O_3$ immediately prior to use. Column chromatography: Alumina (50-200 mesh) from Acros Organics. Silica gel-60 (230-400 mesh) from Sorbent Technologies. Thin Layer Chromatography (TLC): plastic sheets covered with silica gel purchased from Acros. Melting points were measured on a Thomas Hoover Capillary melting point apparatus. ^1H and ^{13}C NMR spectra were obtained using Varian Gemini-300 MHz, Inova-400 MHz, or Inova-500 MHz instruments, and were taken in deuterated chloroform unless noted otherwise.

General Method for Preparing Co-Crystals. Fresh diiodohexatriyne was synthesized according to the procedure described in Chapter 2. To a 0.025 M solution of guest in CH_2Cl_2 (12 mL) was added 0.5 equivalents of host, (2:1 guest to host ratio), and the solution was sonicated for one minute. The resulting solution was divided into four test tubes and subjected to centrifugation for 10 min. The liquid was decanted into four 50 mL crystallization dishes, which were covered with aluminum foil and placed in an ice bath. The foil was punctured 12-15 times using a needle, and solvent was allowed to evaporate slowly to afford light green/blue crystals. Yields typically ranged from 60 – 70%. Co-crystals were stored in the freezer to slow down polymerization (prevent color change), or at room temperature if purple crystals were desired.

Raman Spectroscopy. Raman spectroscopy was performed by Christopher Young of the Halada group in the Material Sciences Department at Stony Brook University. A Thermo Nicolet Almega dispersive Raman spectrometer coupled with an infinity-corrected, confocal design microscope was used. A 785-nm class I laser was used, and the data were collected in the reflection mode of the microscope at a slit width of 25 μm. The data were analyzed using the Origin Pro 8 SRO Software (OriginLab Corporation, USA).

UV-Vis Spectroscopy. The electronic absorption spectra of the co-crystal suspensions were collected using a Cary-100 UV/Visible Scan Spectrophotometer, scanning from 800 nm to 200 nm with a resolution of 1 nm. Suspensions of fresh **157·56** co-crystals were prepared by placing 0.022 g in 3.5 mL H_2O and subjecting the mixture to sonication for 1 hour. About 1mL of the suspension was used to obtain UV-Vis spectra, and the concentration of the suspension was decreased by one-half for three consecutive spectrum collections. A total of 1.5mL H_2O was added to the original suspension, which was stored at room temperature for 3 days. The suspension turned dark gray, and additional UV-Vis spectra were obtained.

Scanning electron microscopy (SEM): SEM images were taken by James Quinn in the Material Sciences Department at Stony Brook University. A field emission scanning electron microscope (SEM, Leo 1550) was used, which operated at accelerating voltages of 20 kV and was equipped with Energy Dispersive X-ray Analysis (EDAX) capabilities.

Single crystal X-ray diffraction (XRD). Crystals were selected and mounted on glass fibers using epoxy adhesive. Each crystal was centered, and the X-ray intensity data were measured on an Oxford Gemini A Enhance diffractometer by using graphite-monochromated Mo radiation. The experiments were conducted at low temperature, using a CryojetHT. The data was collected using the Crysalis Pro 171.34.44 software.[18] WinGX 1.80.0511,[19] SIR97,[20] and SHELXL 97[21, 22] were used to process the data. The X-ray intensity data for the purple co-crystal were measured on a Bruker AXS SMART APEXII Single Crystal Diffractometer by Dr. Chunhua Hu at the Department of Chemistry of New York University.

Microscopy. Optical microscope images were taken under polarized light with a Nikon SMZ800 optical microscope (Nikon Instruments, Incorporated, Melville, New York).

Solid-State ^{13}C Magic-Angle-Spinning NMR (MAS-NMR): MAS-NMR spectra were measured by Andy Ilott of the Grey/Phillips in the Chemistry Department at Stony Brook University. All of the NMR spectra were taken at room temperature using a Varian Infinity Plus 500 NMR spectrometer, operating at 125.68 MHz and 499.79 MHz for ^{13}C and ^{1}H respectively. The experiments were performed using a 4 mm double resonance probe with a spinning rate of 8 kHz. ^{13}C spectra were collected using a CP RAMP pulse sequence[23] with a contact time of 10 ms and a pulse delay of 2 s. A stepped ramp was applied on the ^{13}C channel, corresponding to a total ramp in power of approximately 10 kHz. Continuous wave ^{1}H decoupling with a power of 50 kHz was applied during the signal acquisition. Isotropic peaks were identified by comparing spectra at multiple spinning speeds.

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Chapter 1

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Chapter 4

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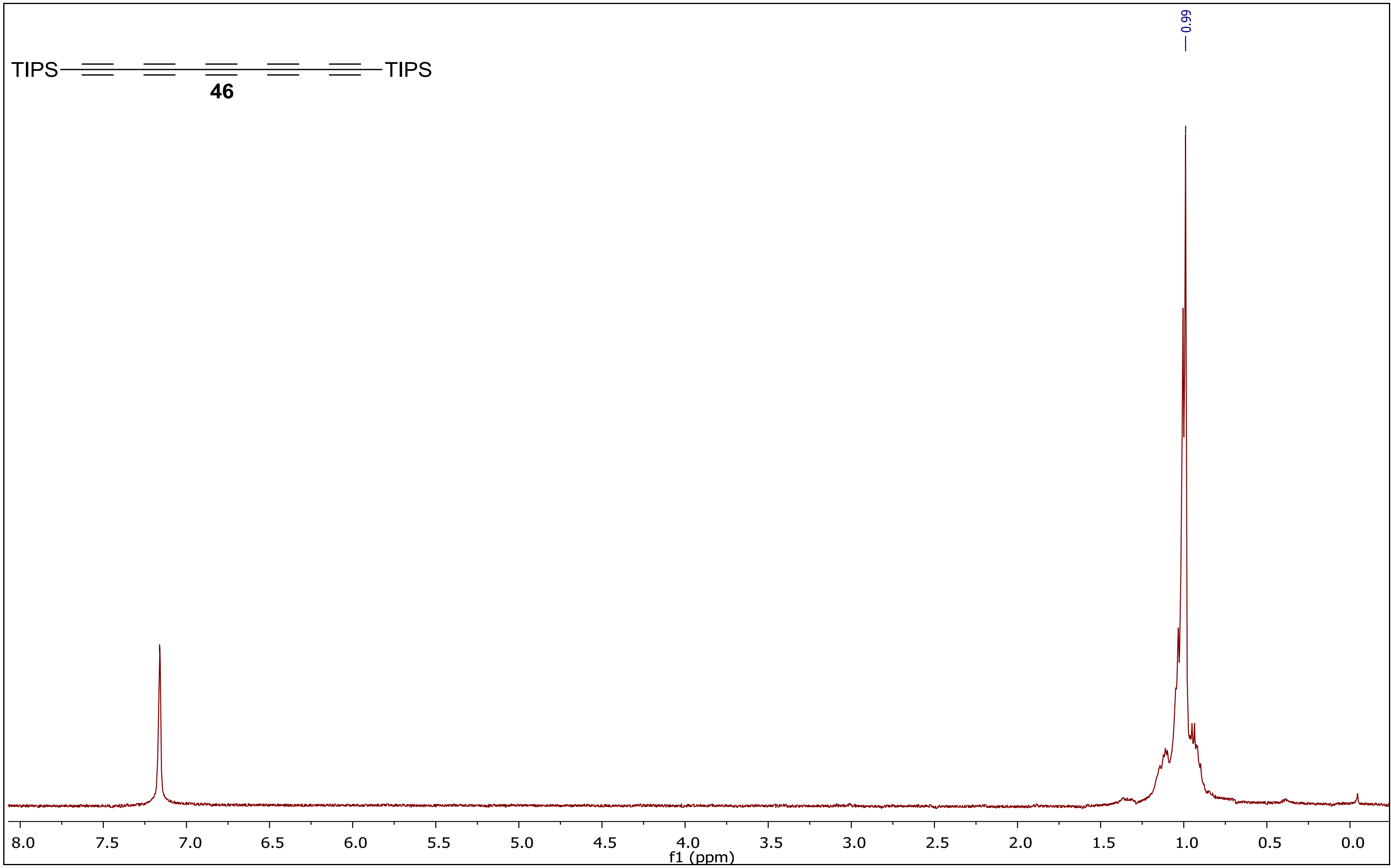
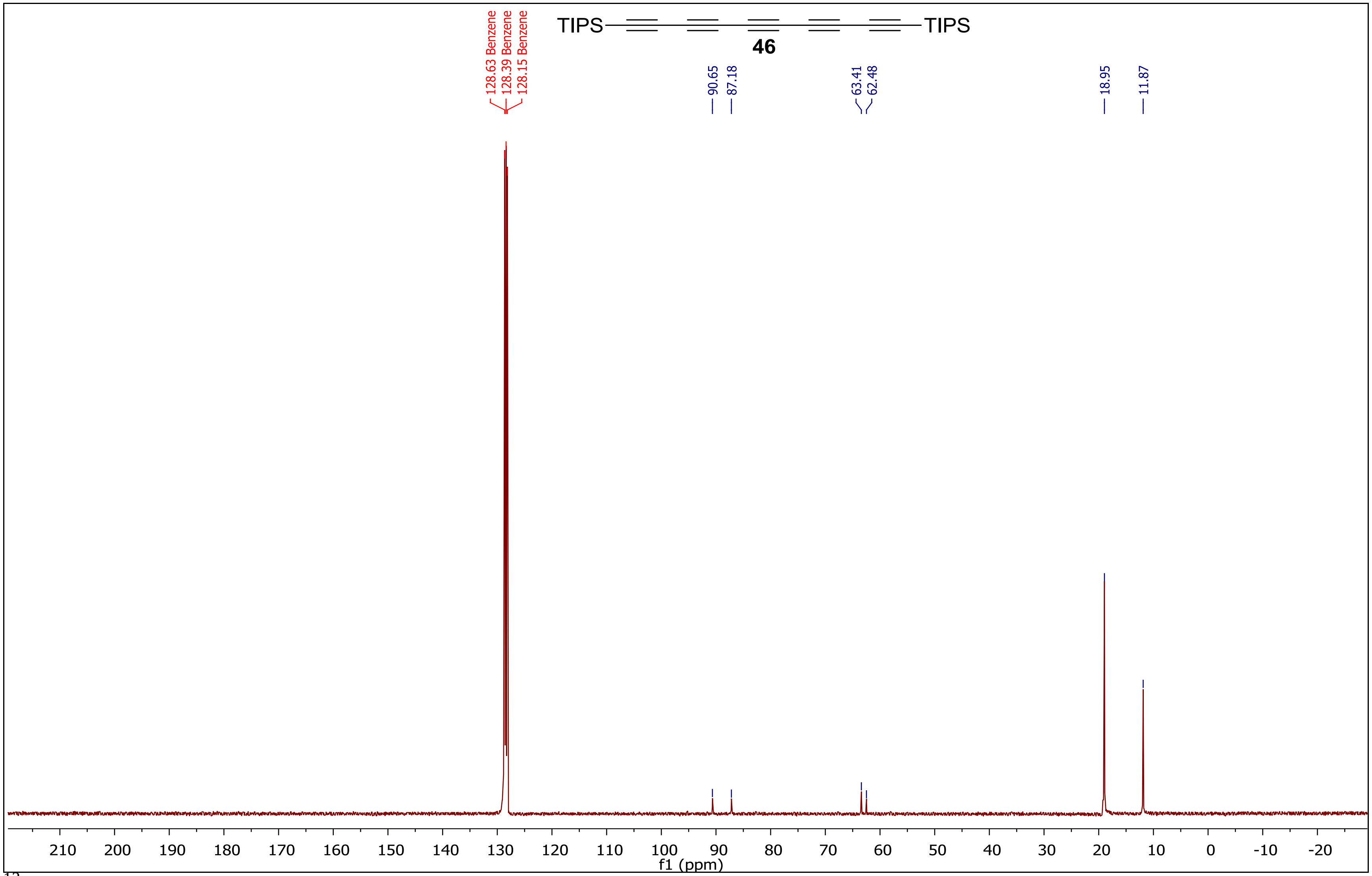
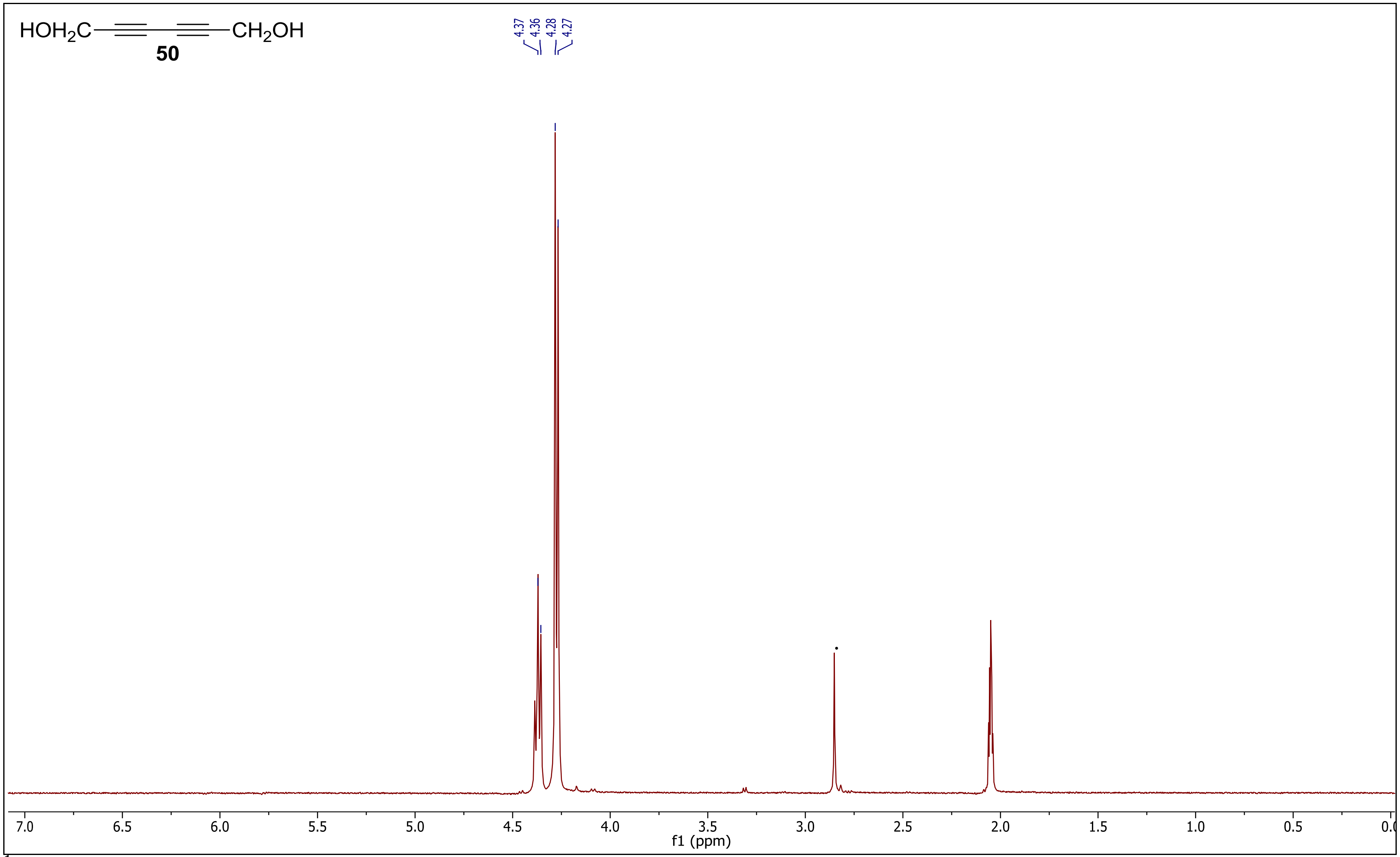


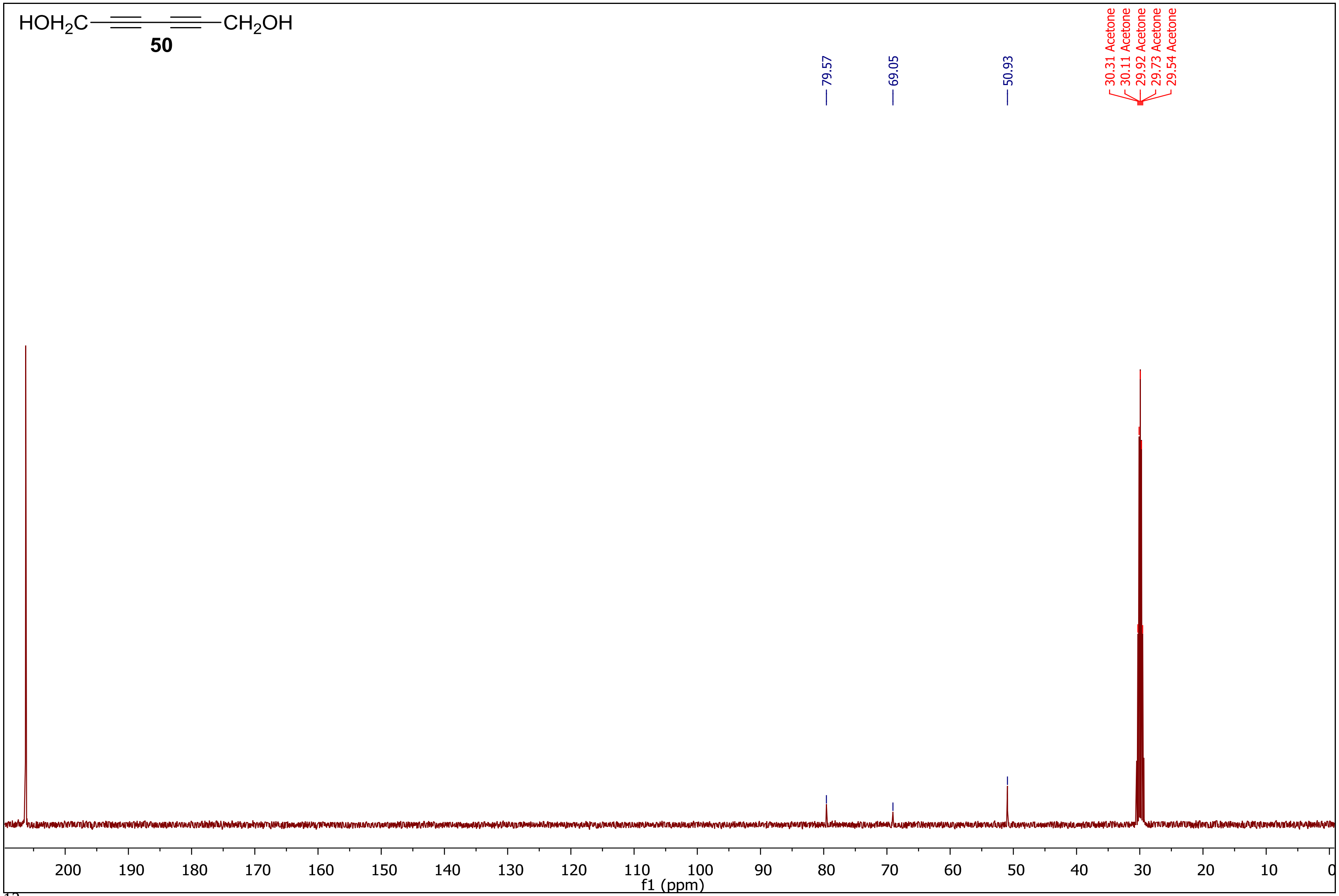
^{1}H NMR spectrum (400 MHz, benzene-d_6) of compound **46.**



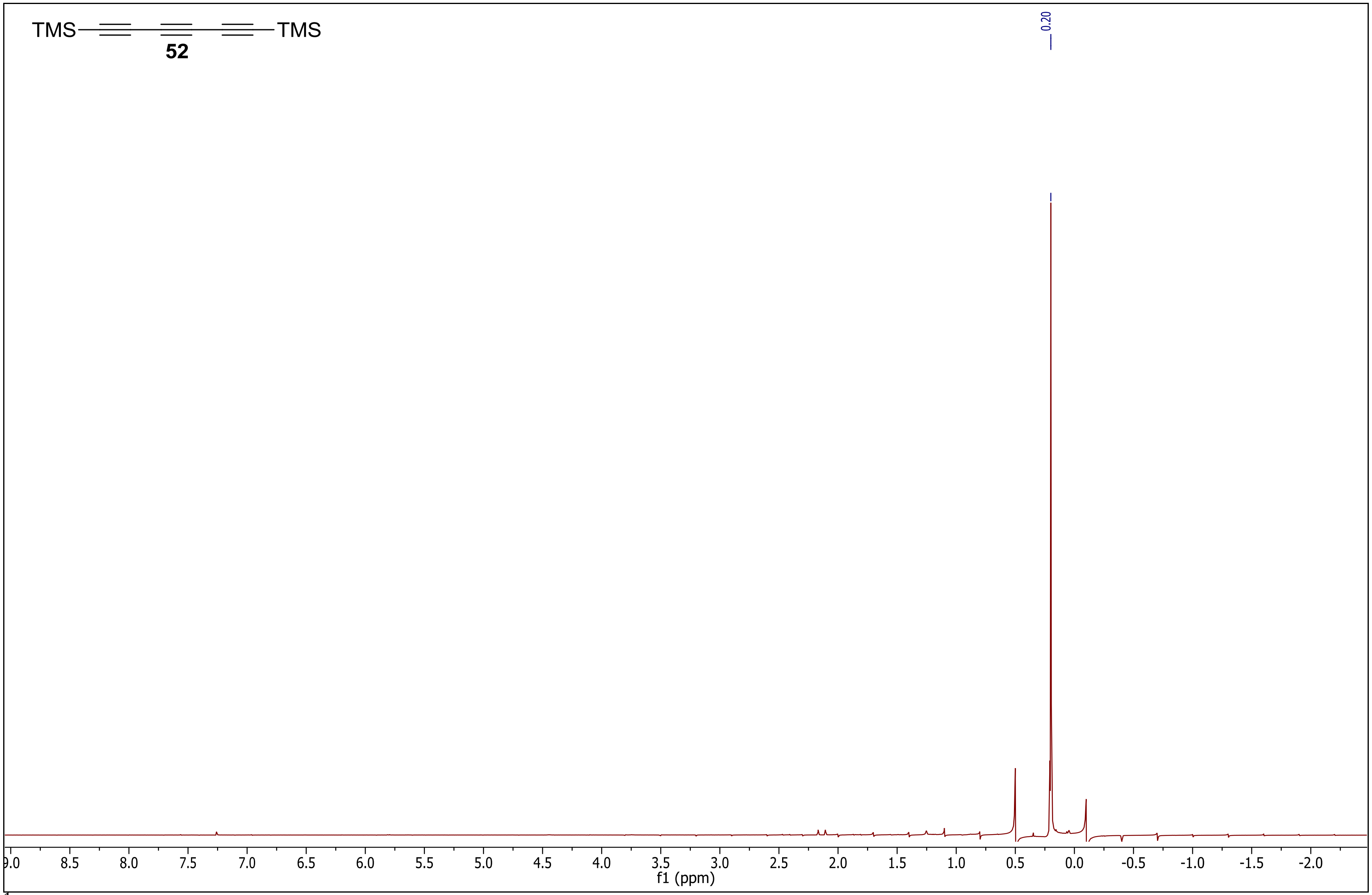
^{13}C NMR spectrum (100 MHz, benzene-d_6) of compound **46.**



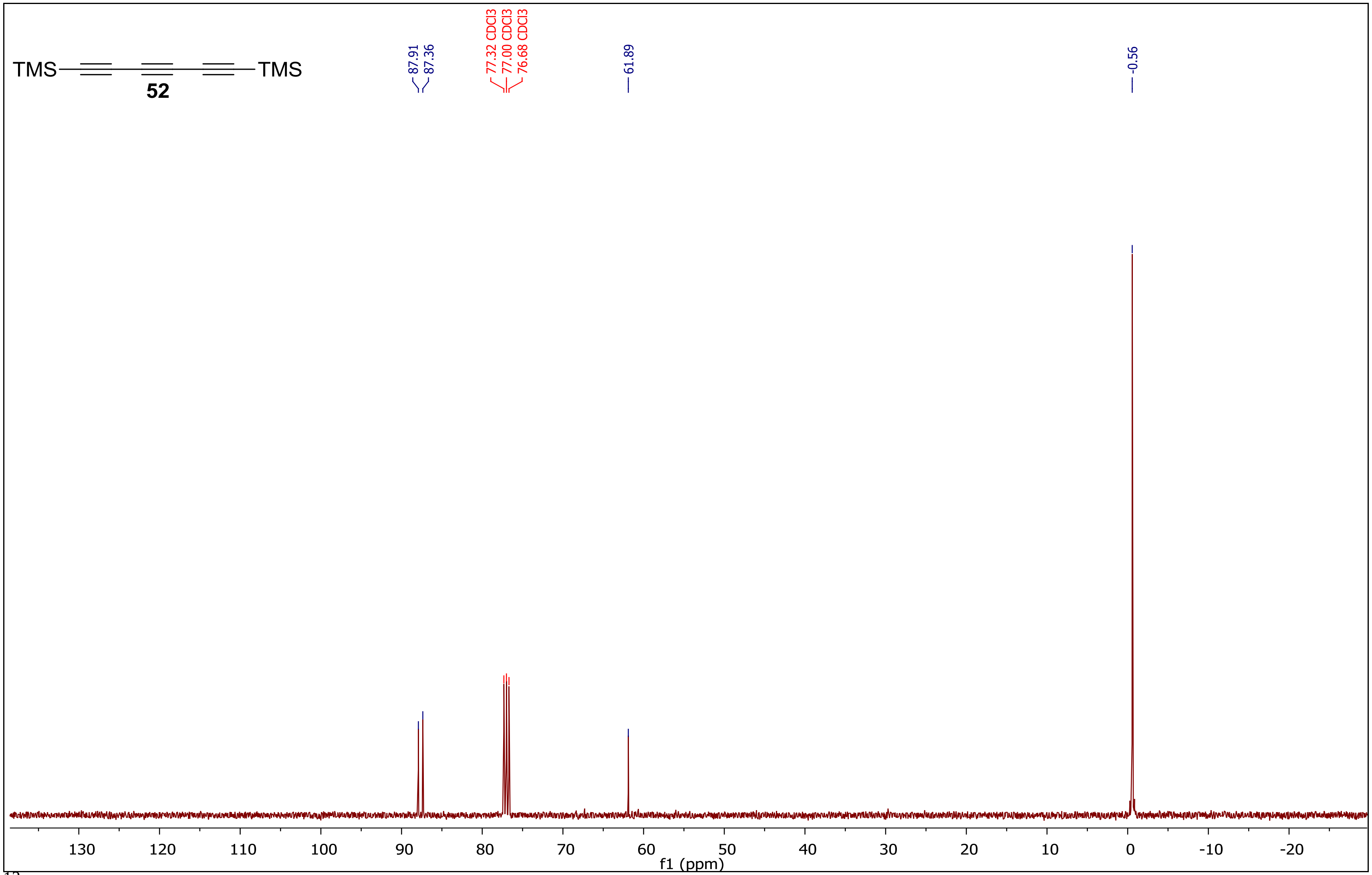
^{1}H NMR spectrum (400 MHz, acetone-d_6) of compound **50.** H_2O (·) denoted.



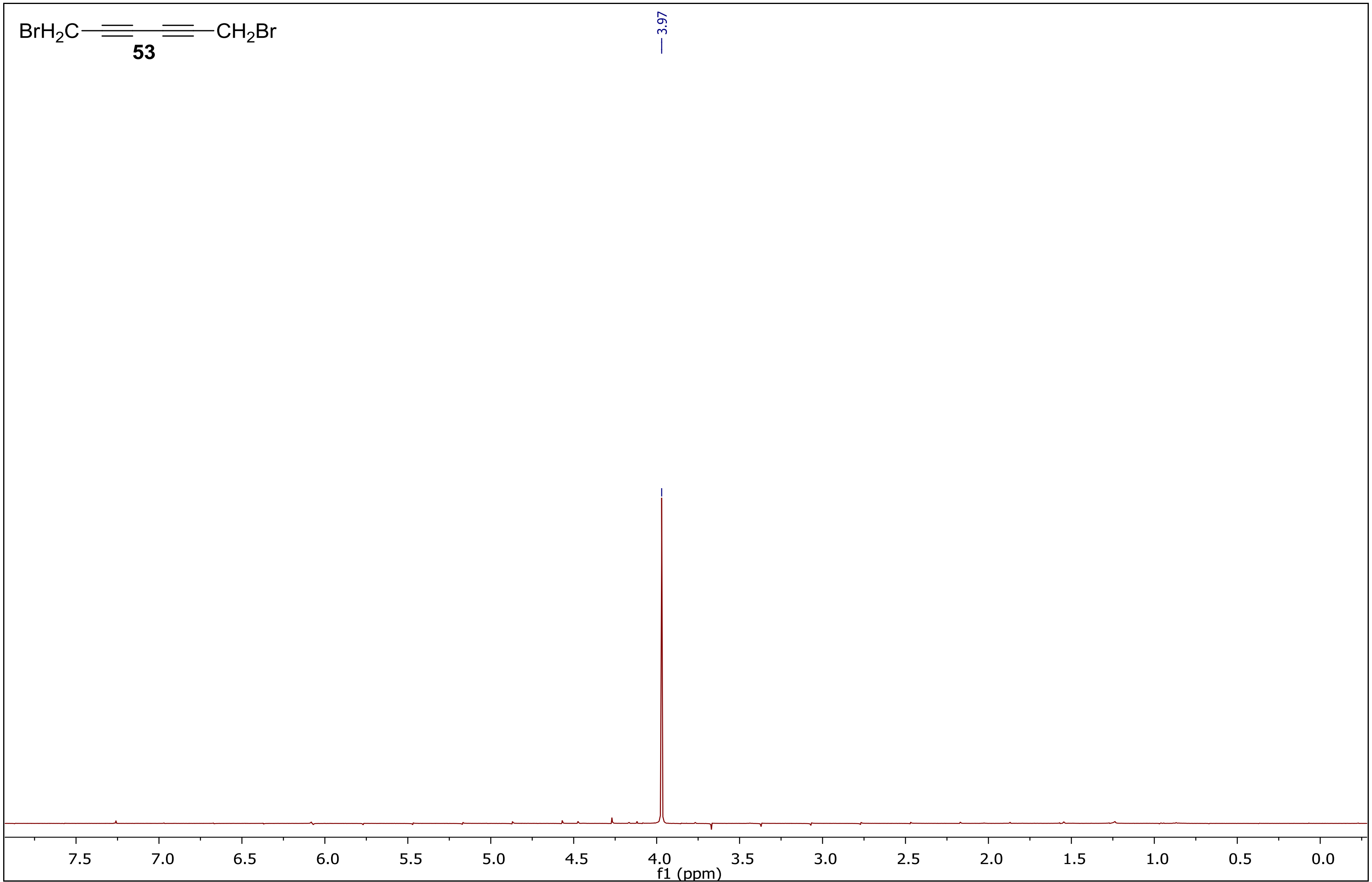
^{13}C NMR spectrum (100 MHz, acetone-d_6) of compound **50.**



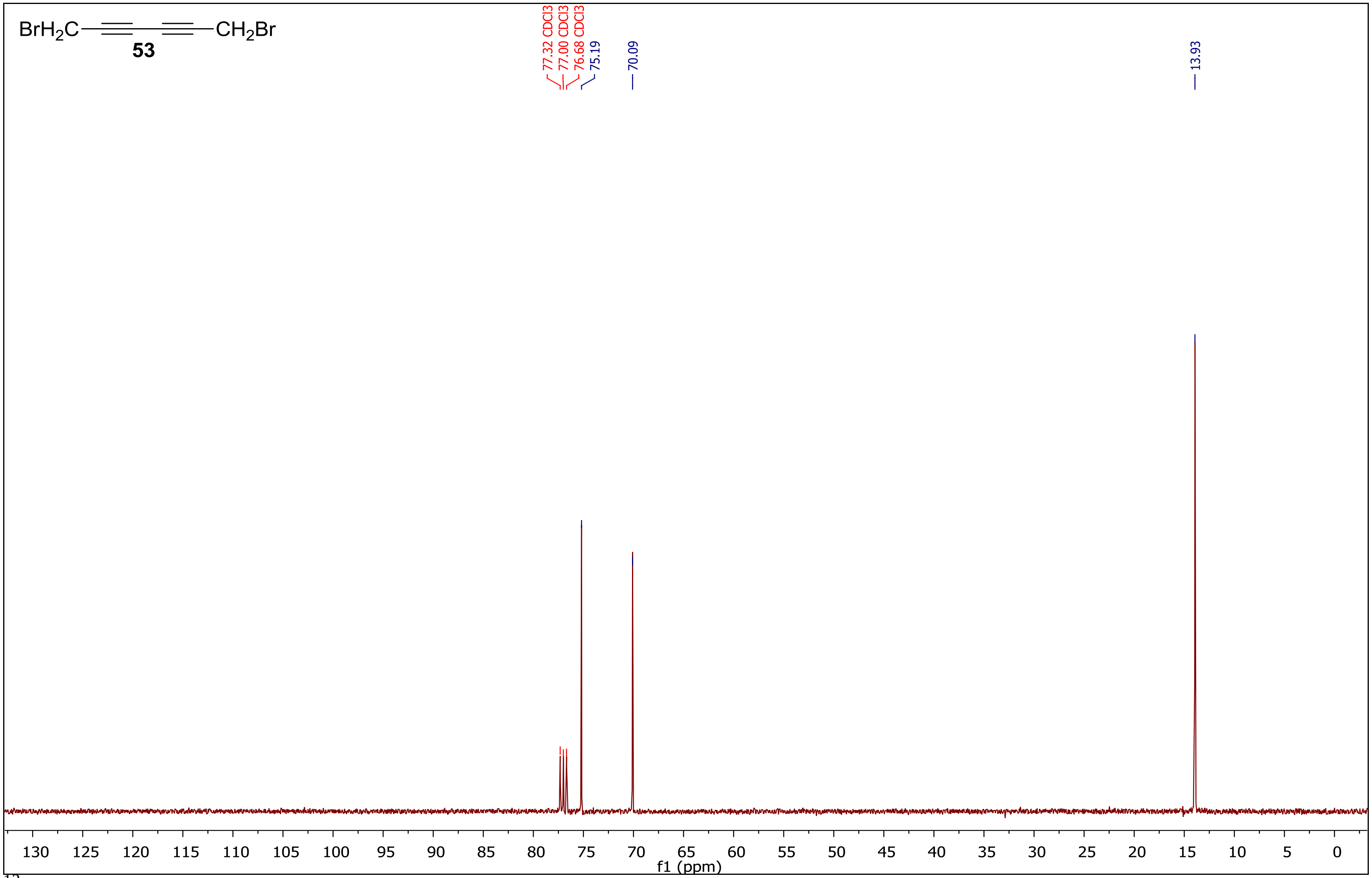
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **52.**



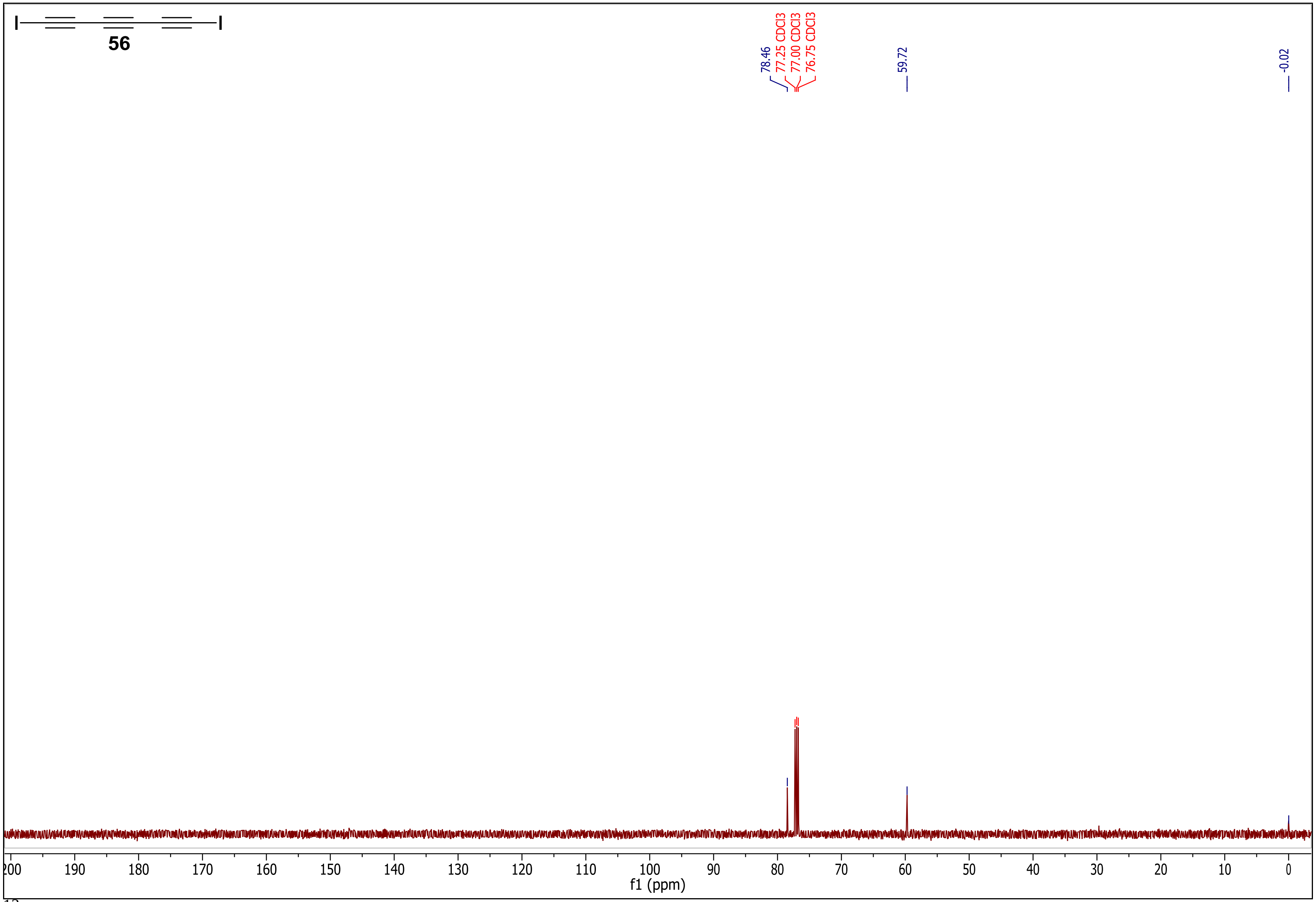
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **52.**



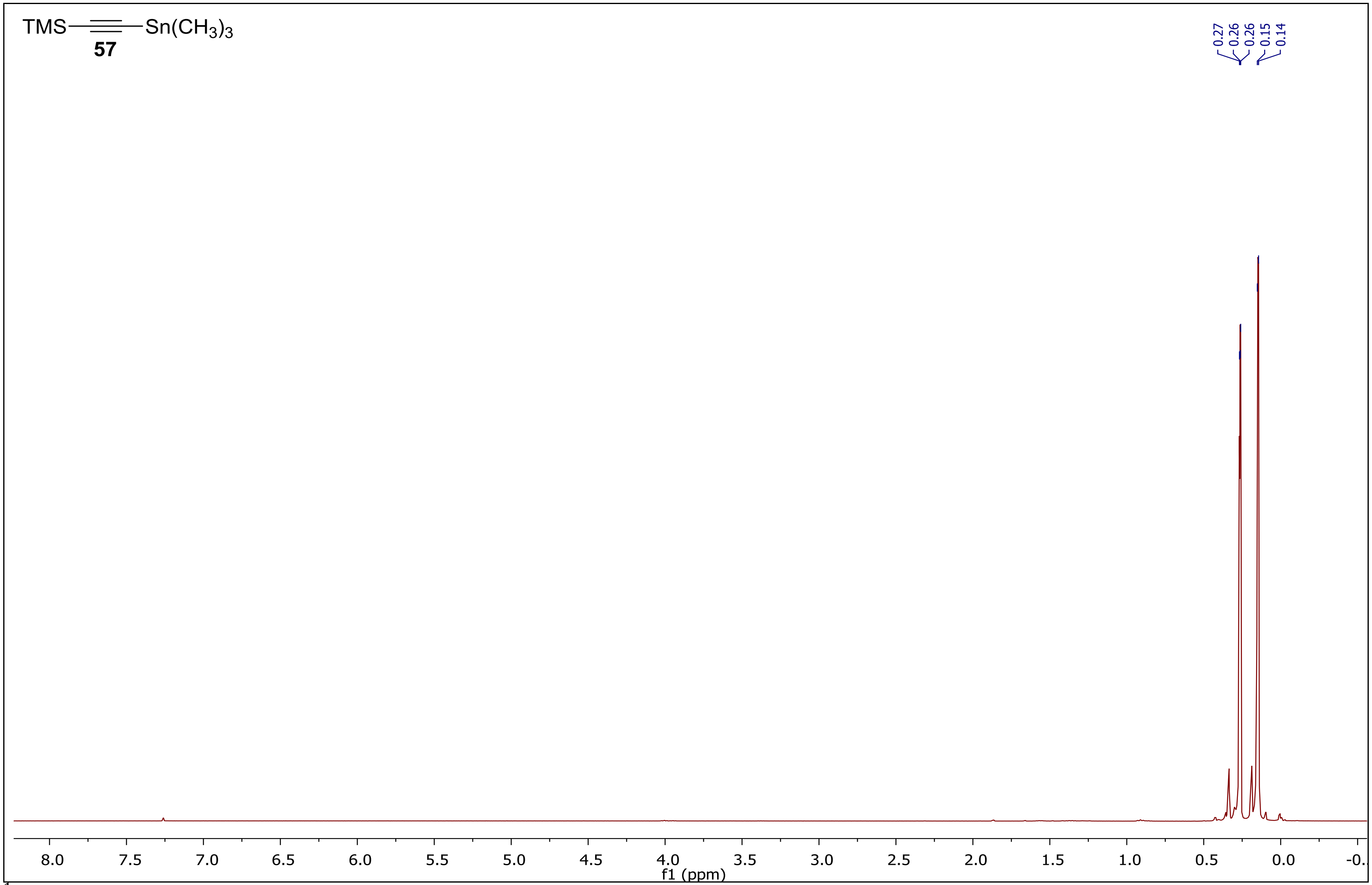
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **53.**



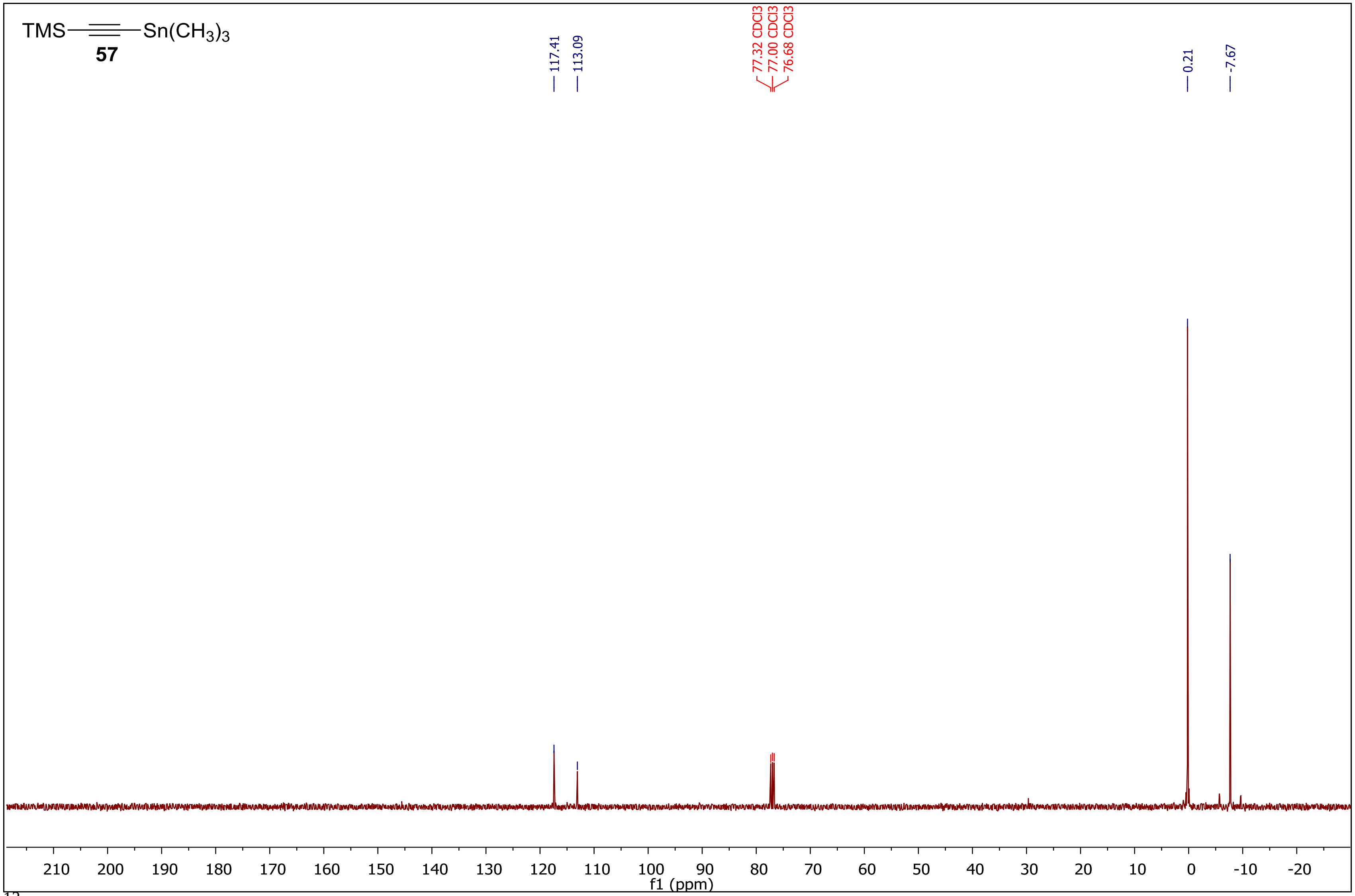
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **53.**



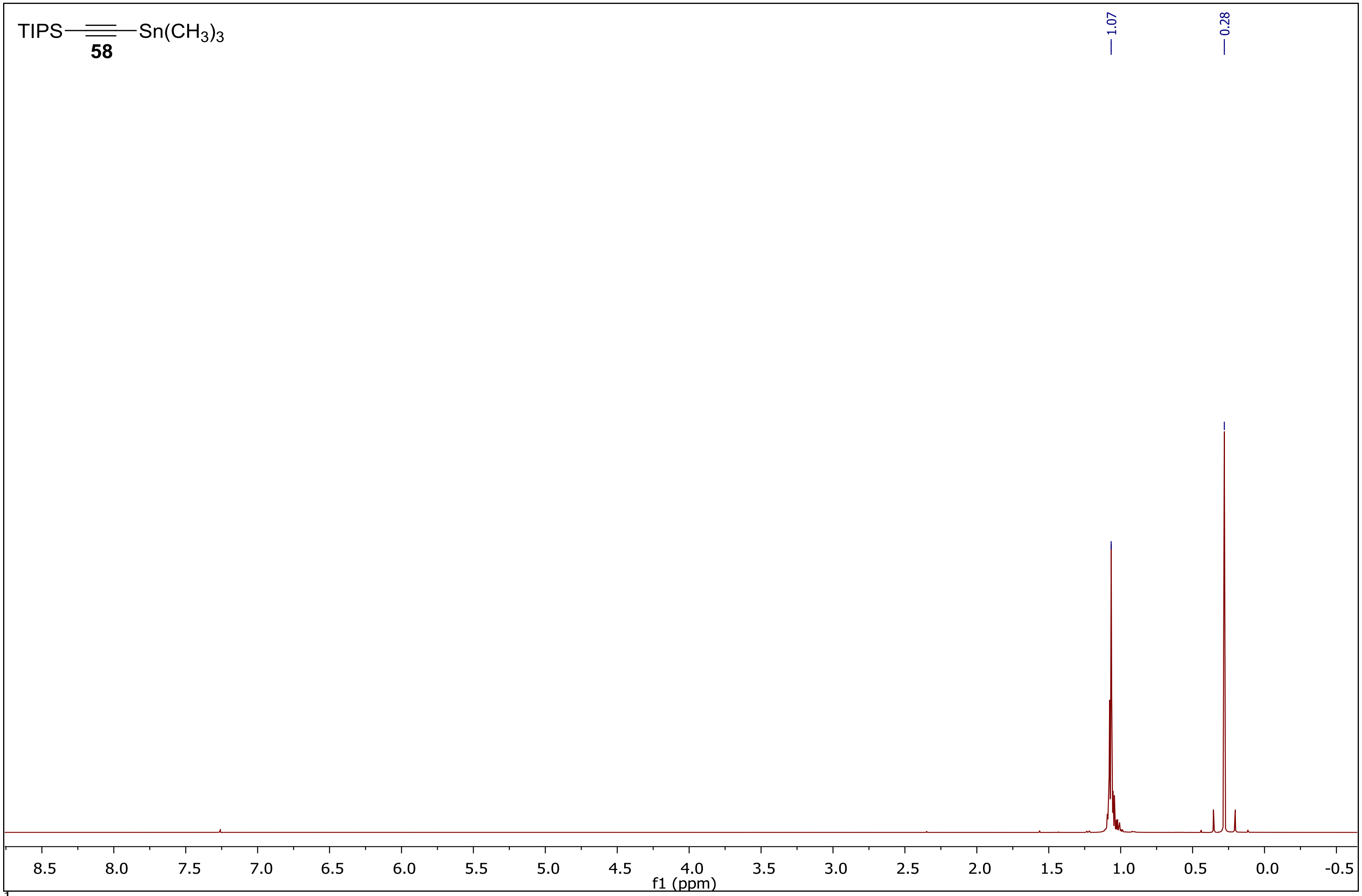
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **56.**



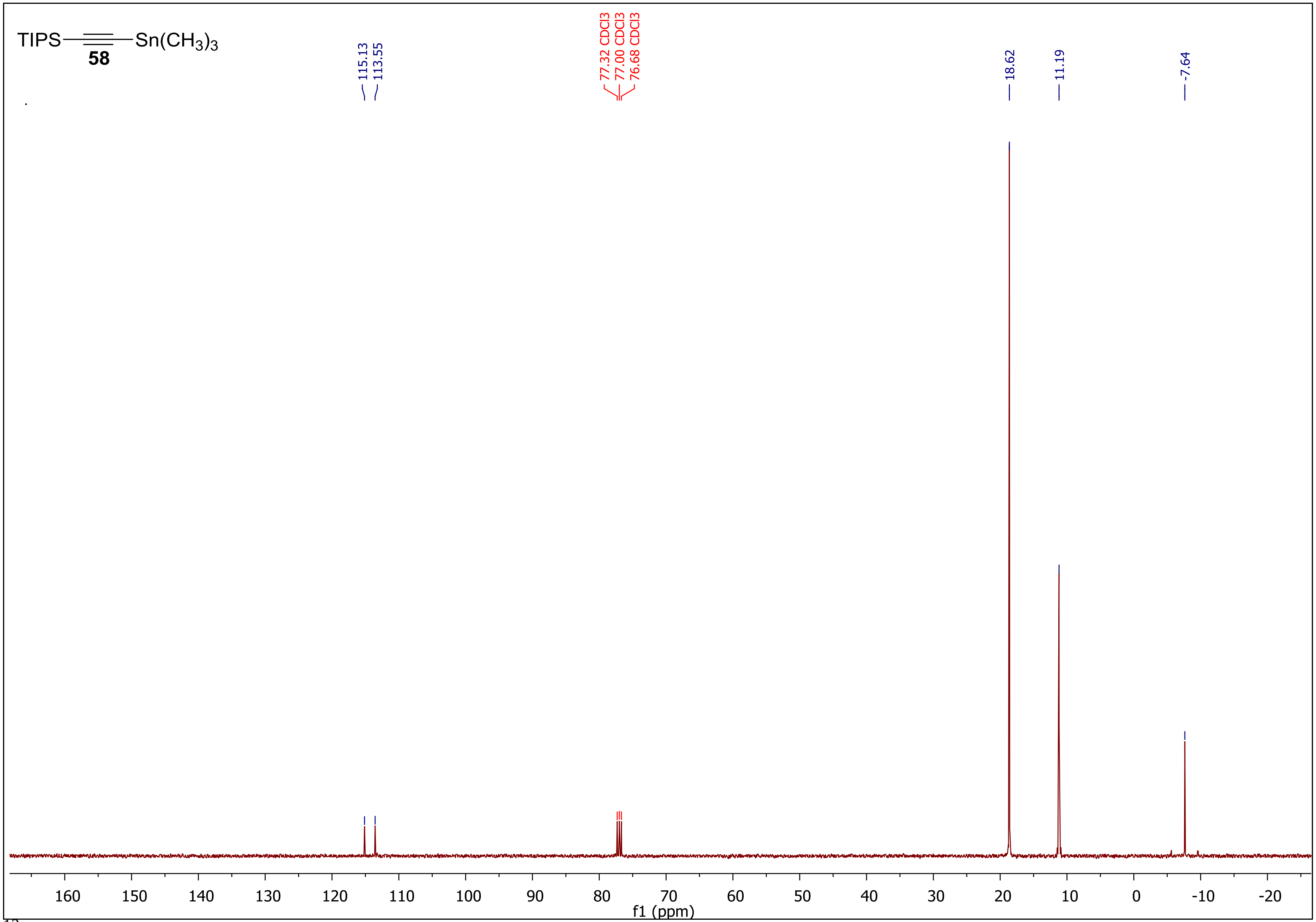
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **57.**



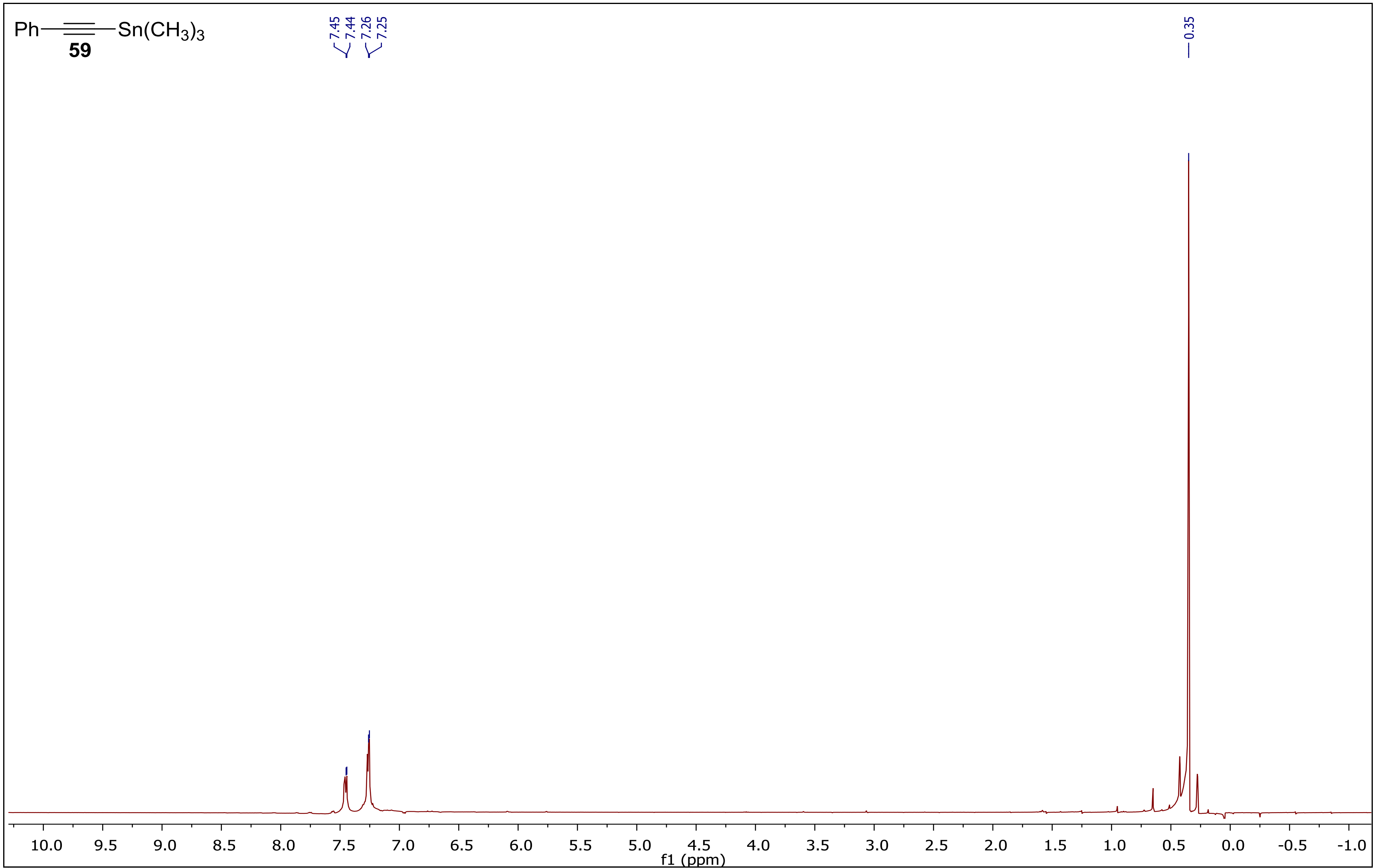
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **57.**



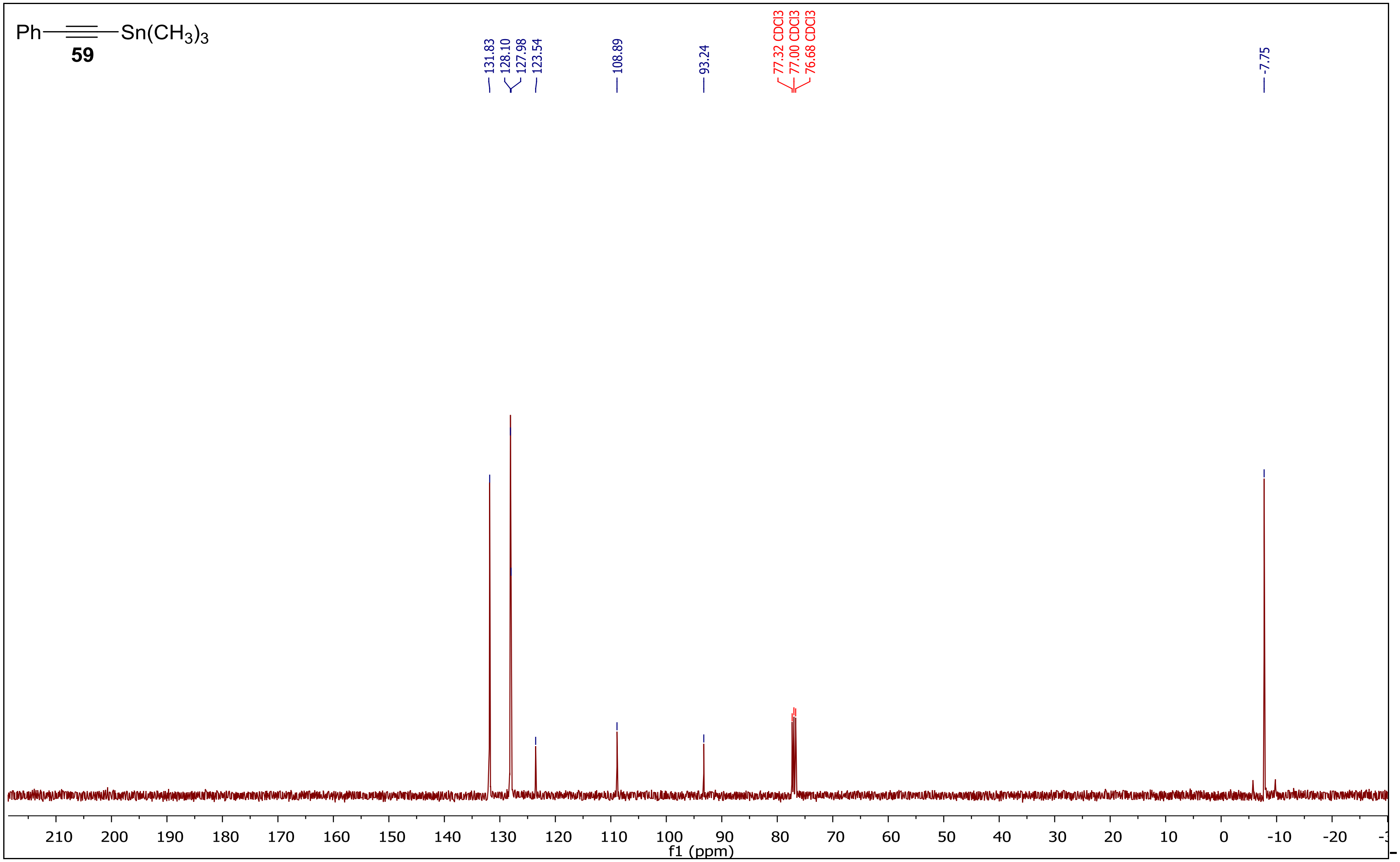
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **58.**



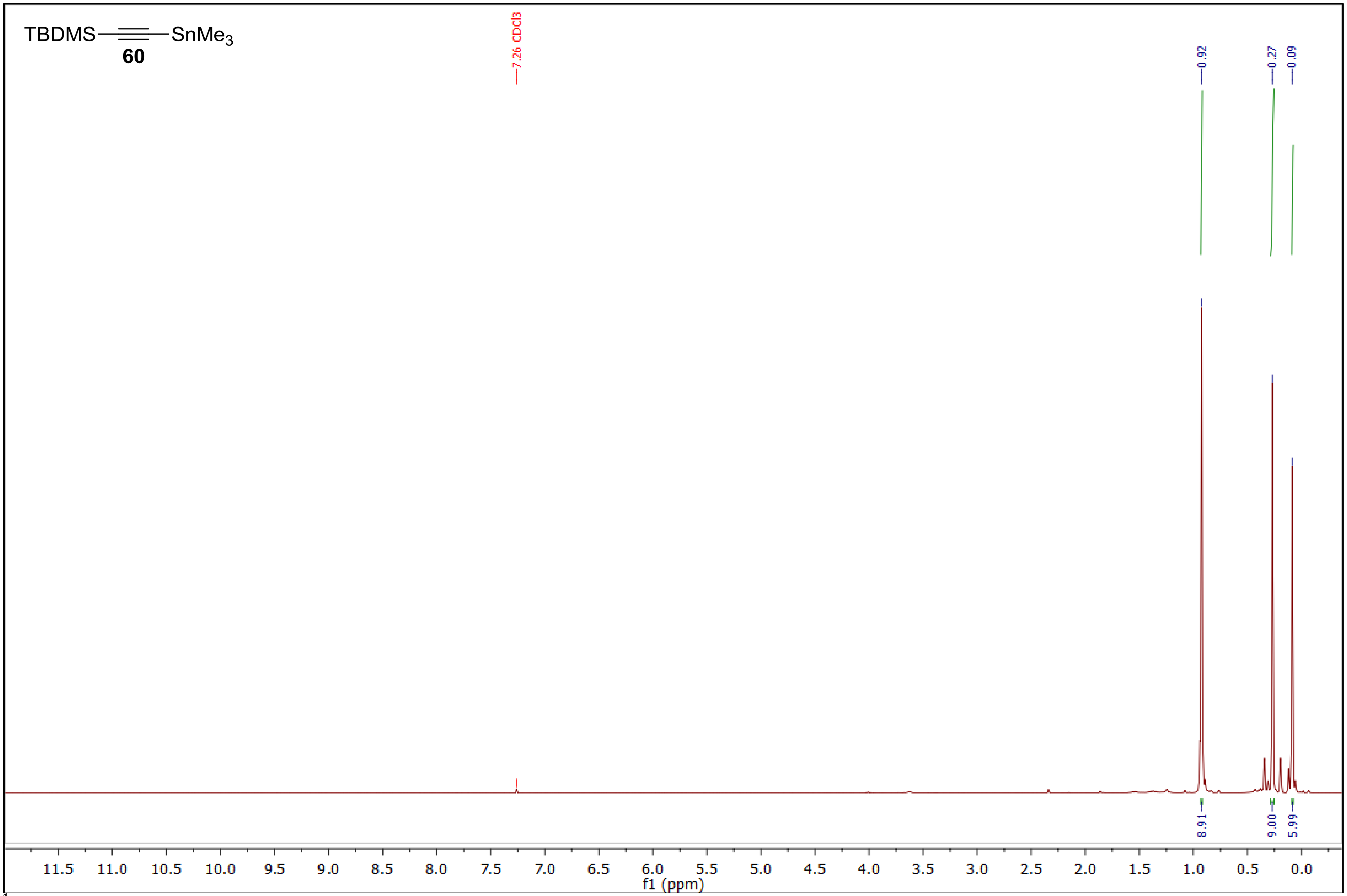
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **58.**



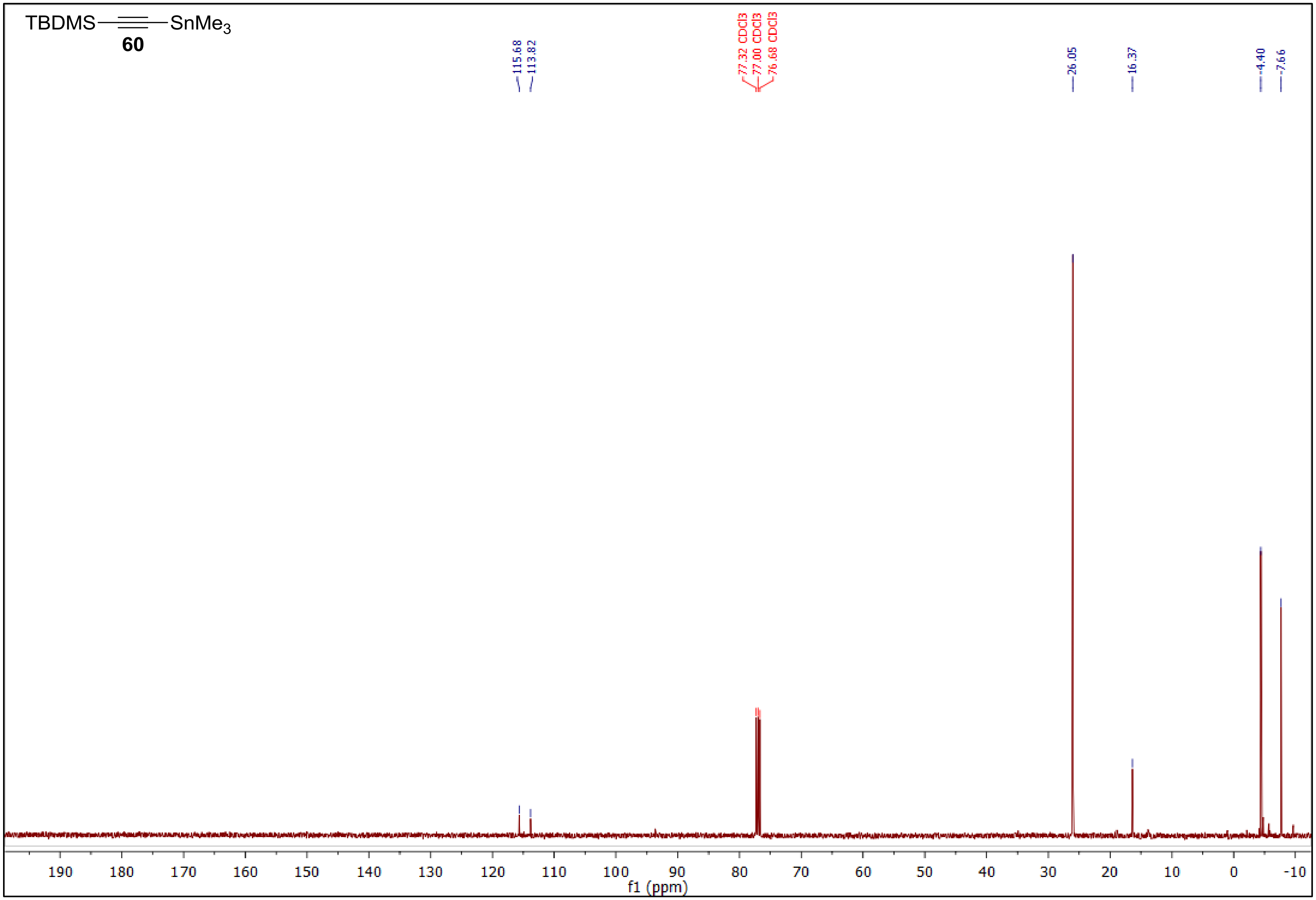
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **59.**



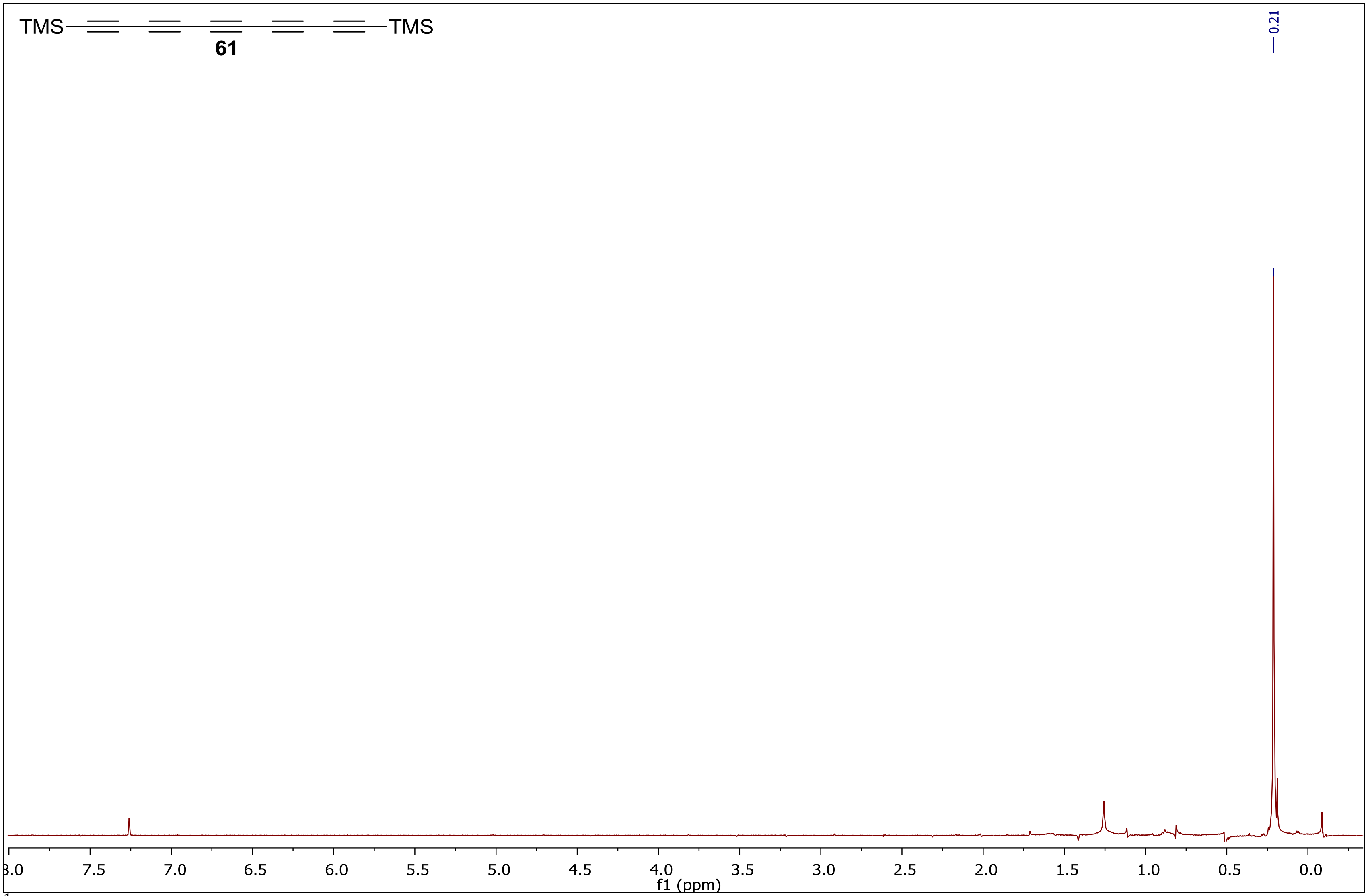
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **59.**



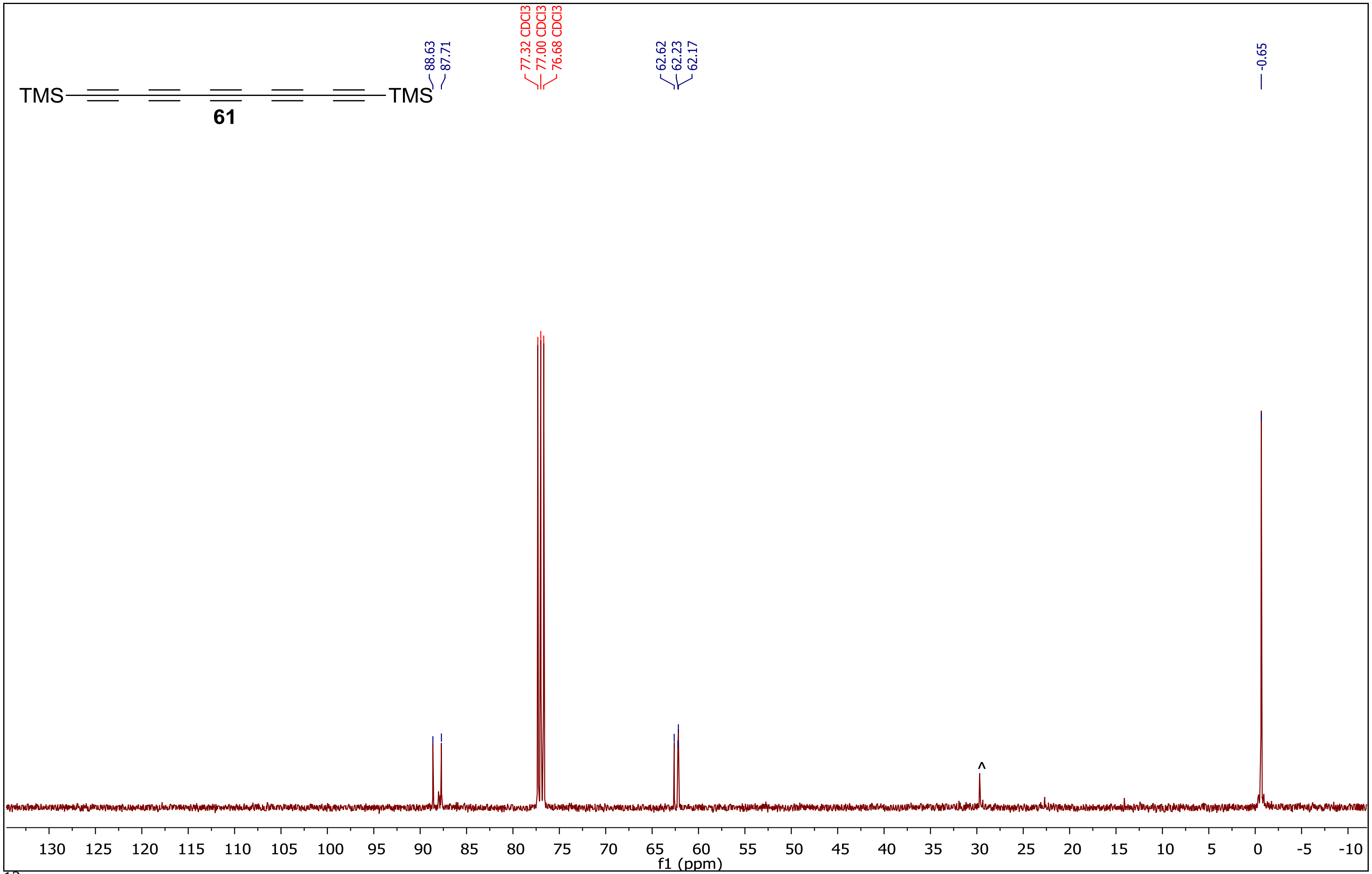
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **60**.



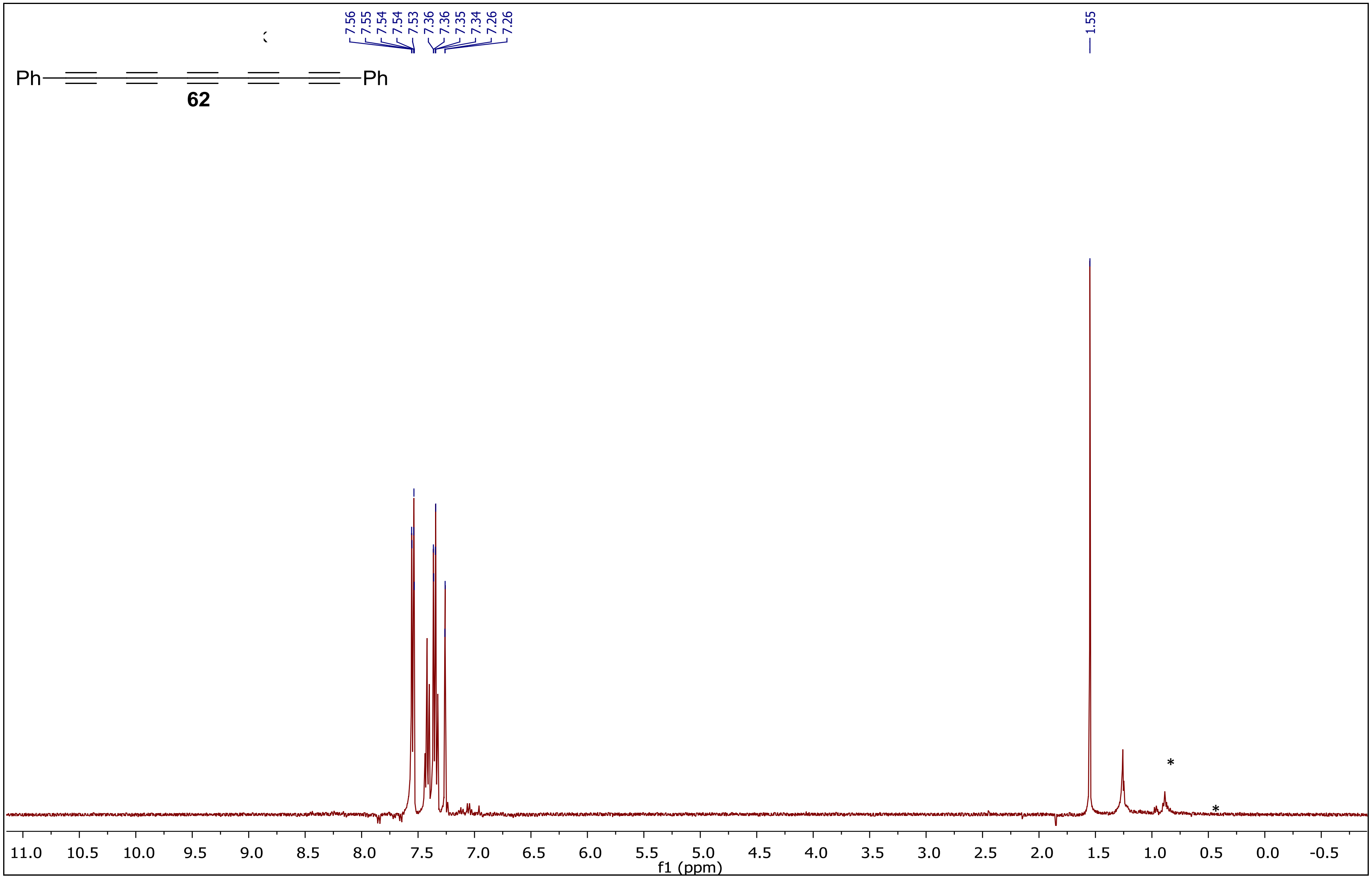
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **60**.



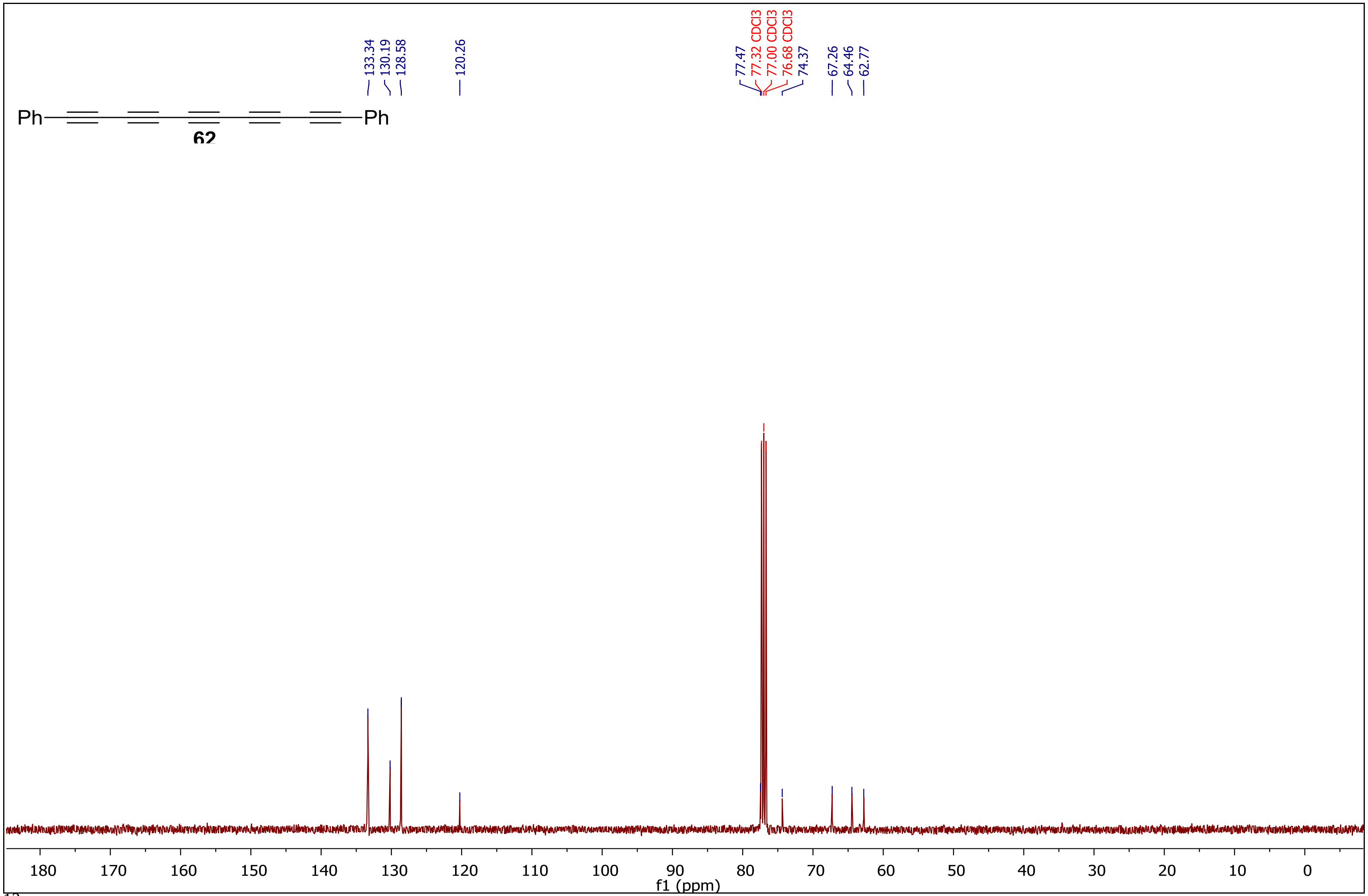
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **61.**



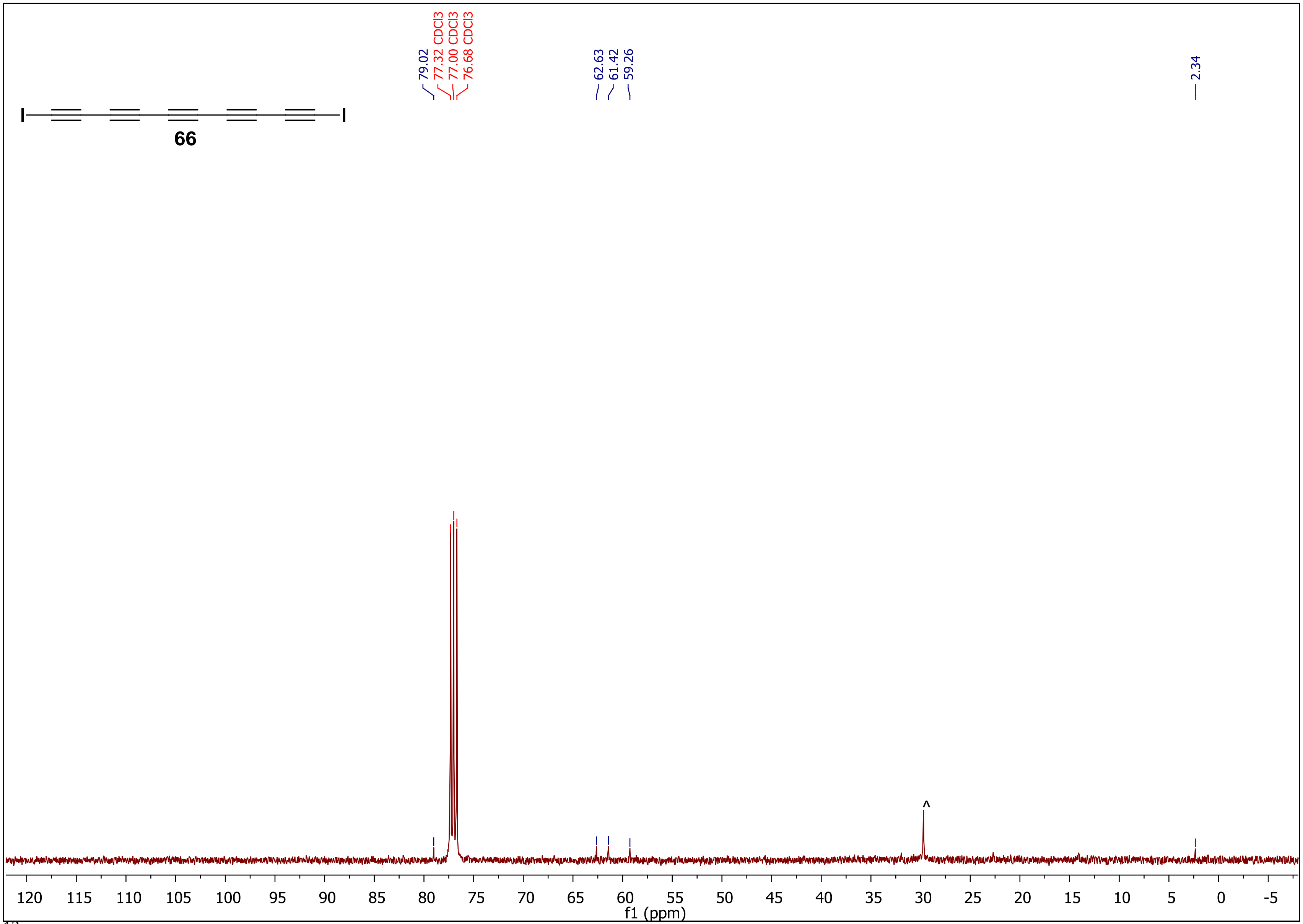
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **61.** Grease (^) denoted.



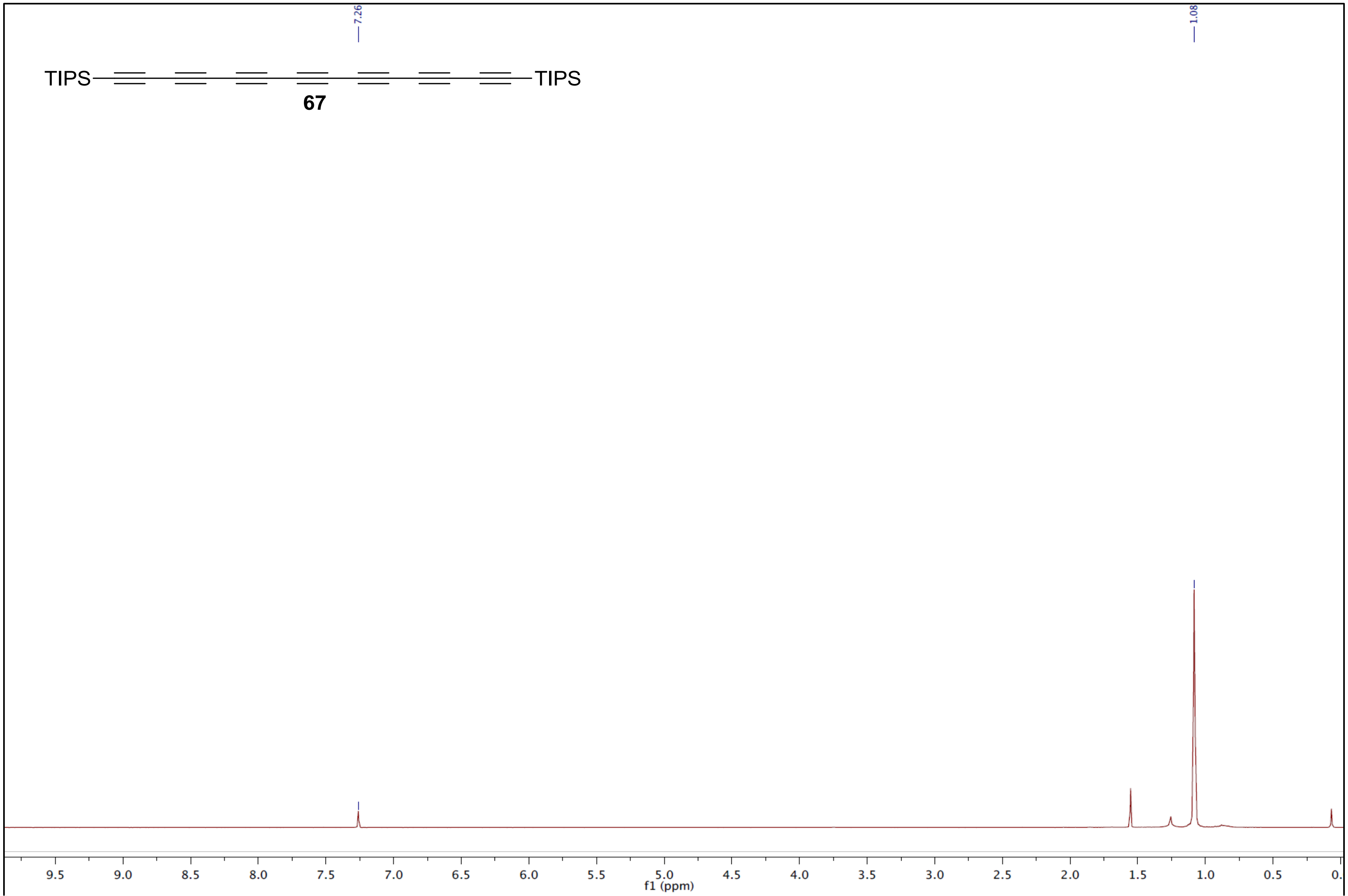
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **62.** Hexanes (*) denoted.



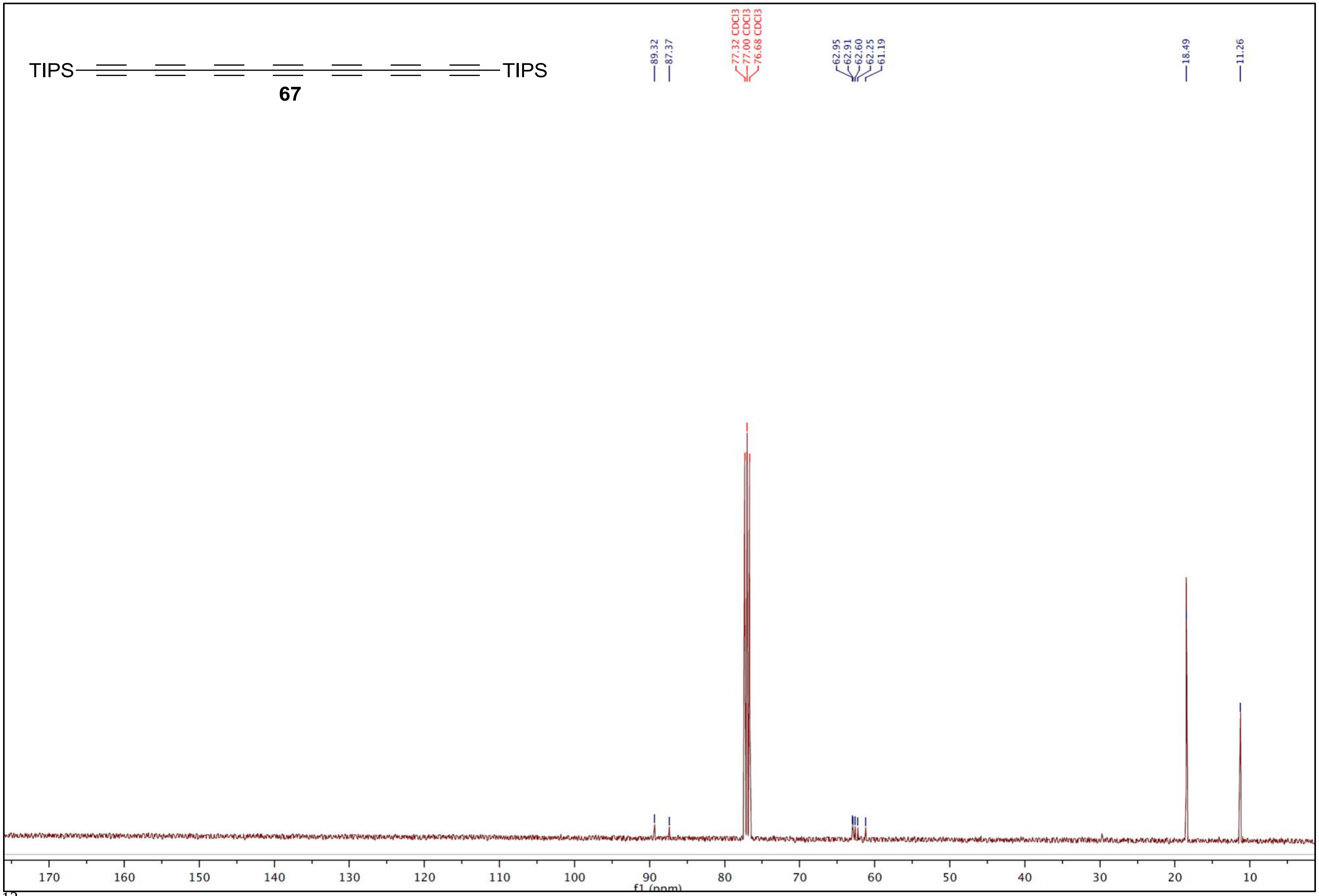
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **62.**



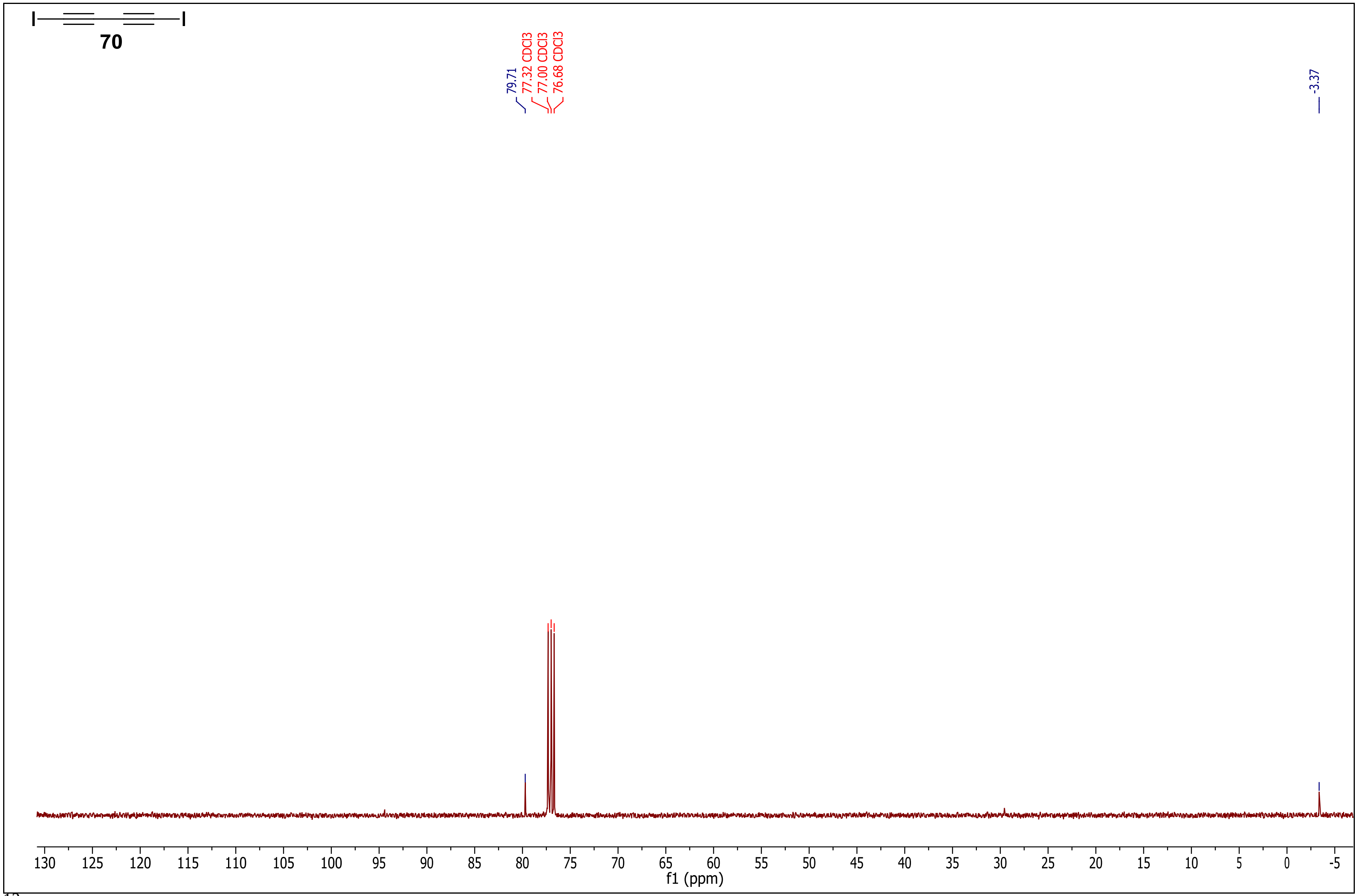
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **66.** Grease (^) denoted.



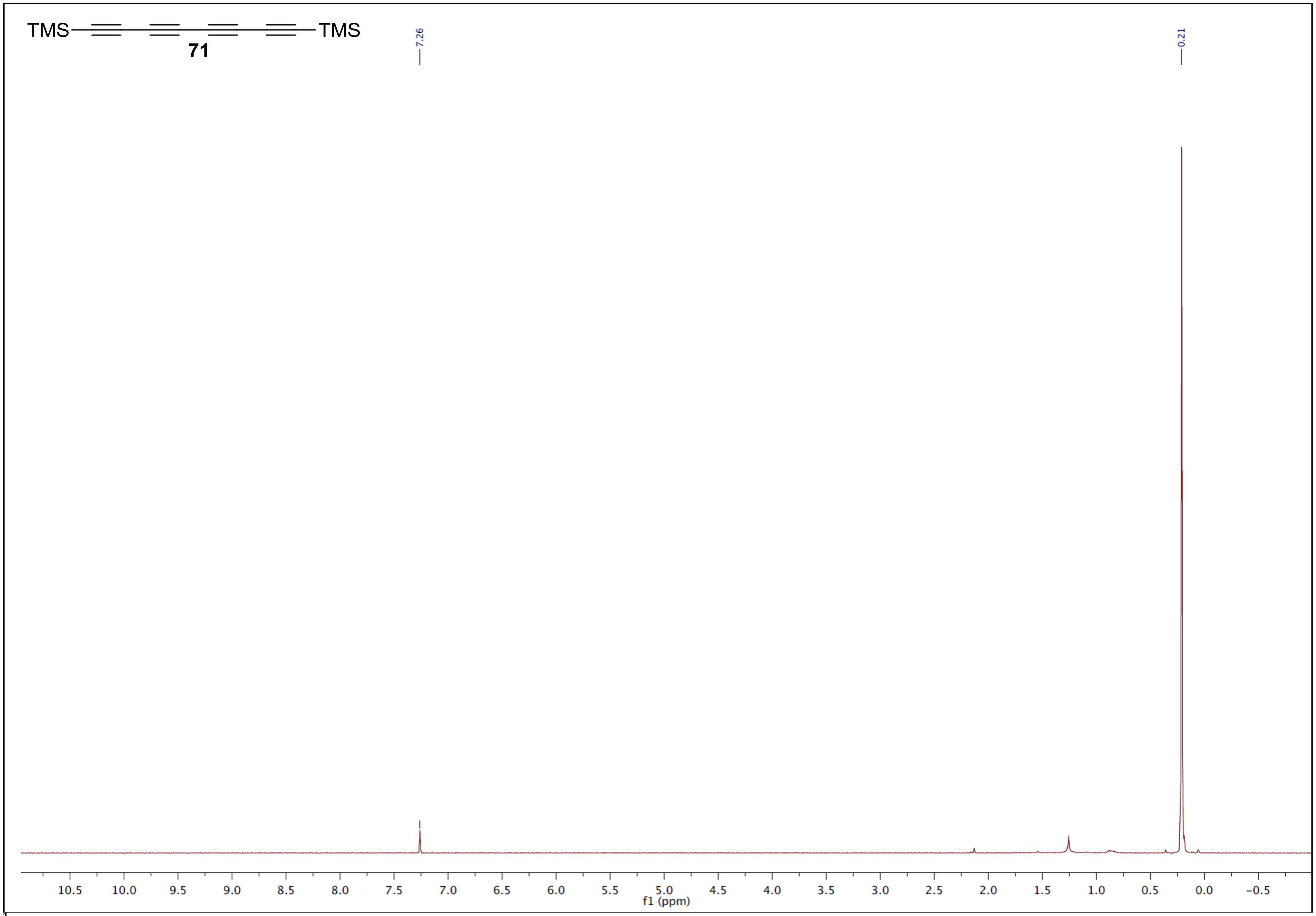
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **67**.



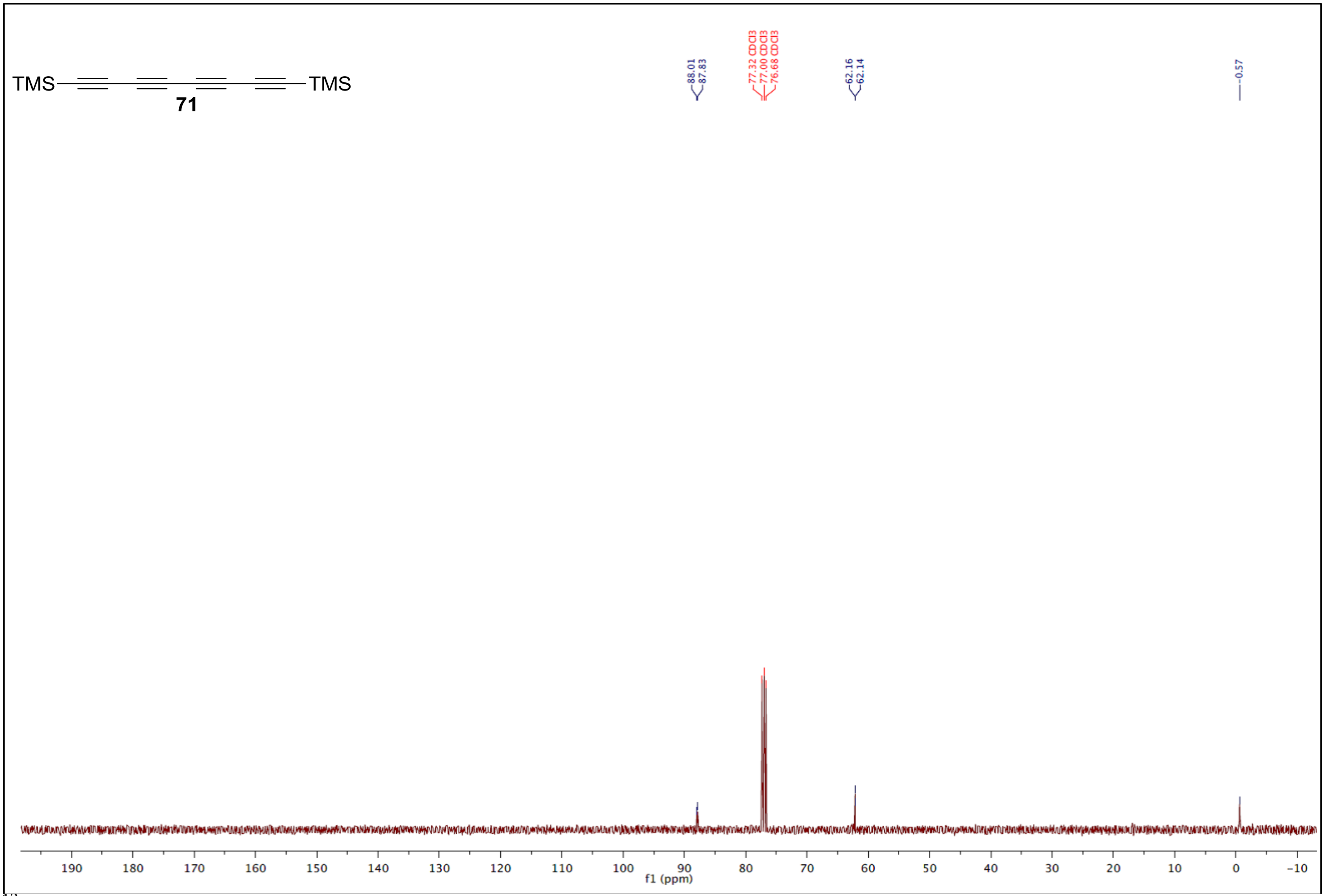
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **67.**



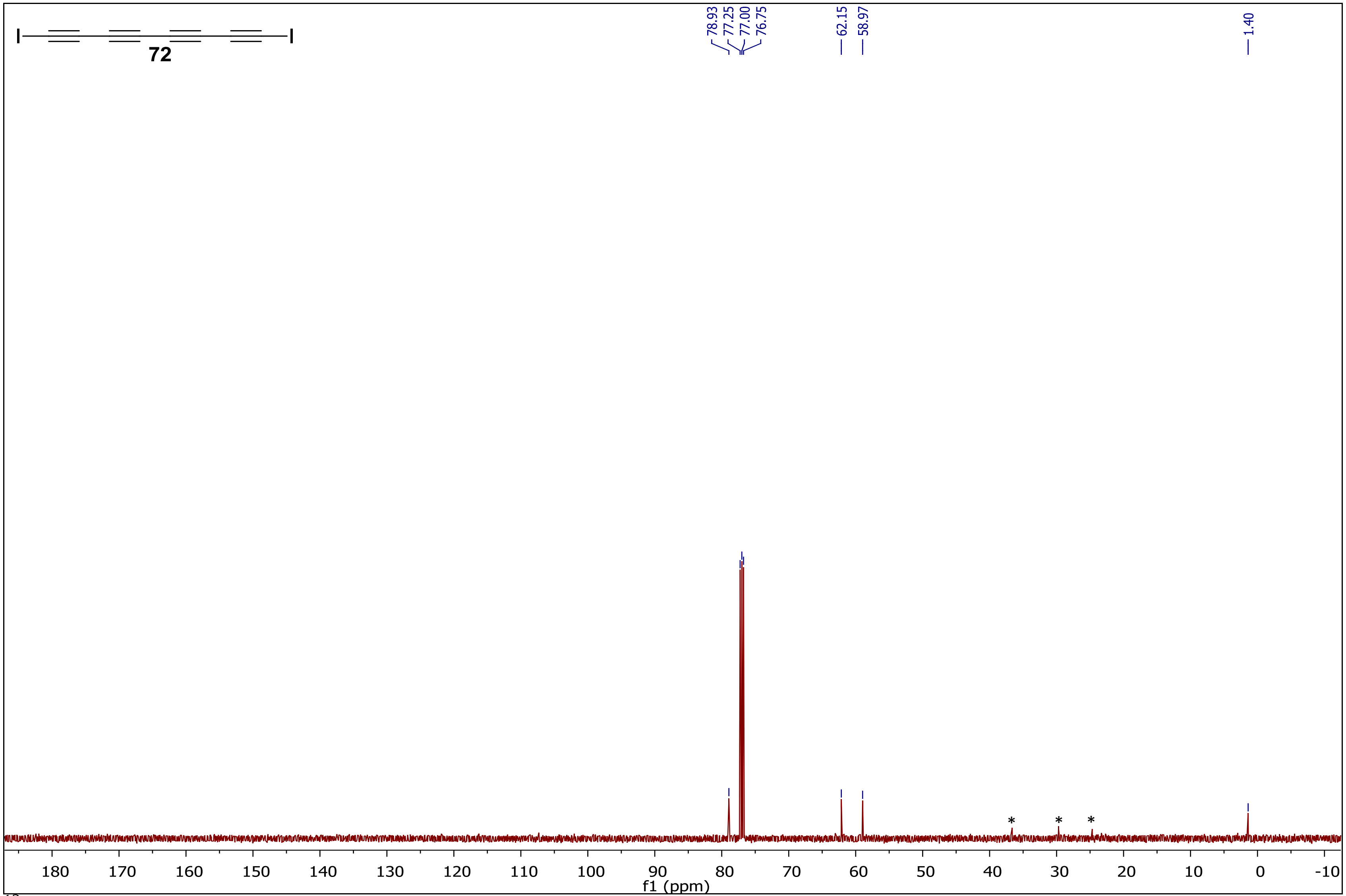
^{13}C NMR spectrum (100 MHz, CDCl3) of compound **70.**



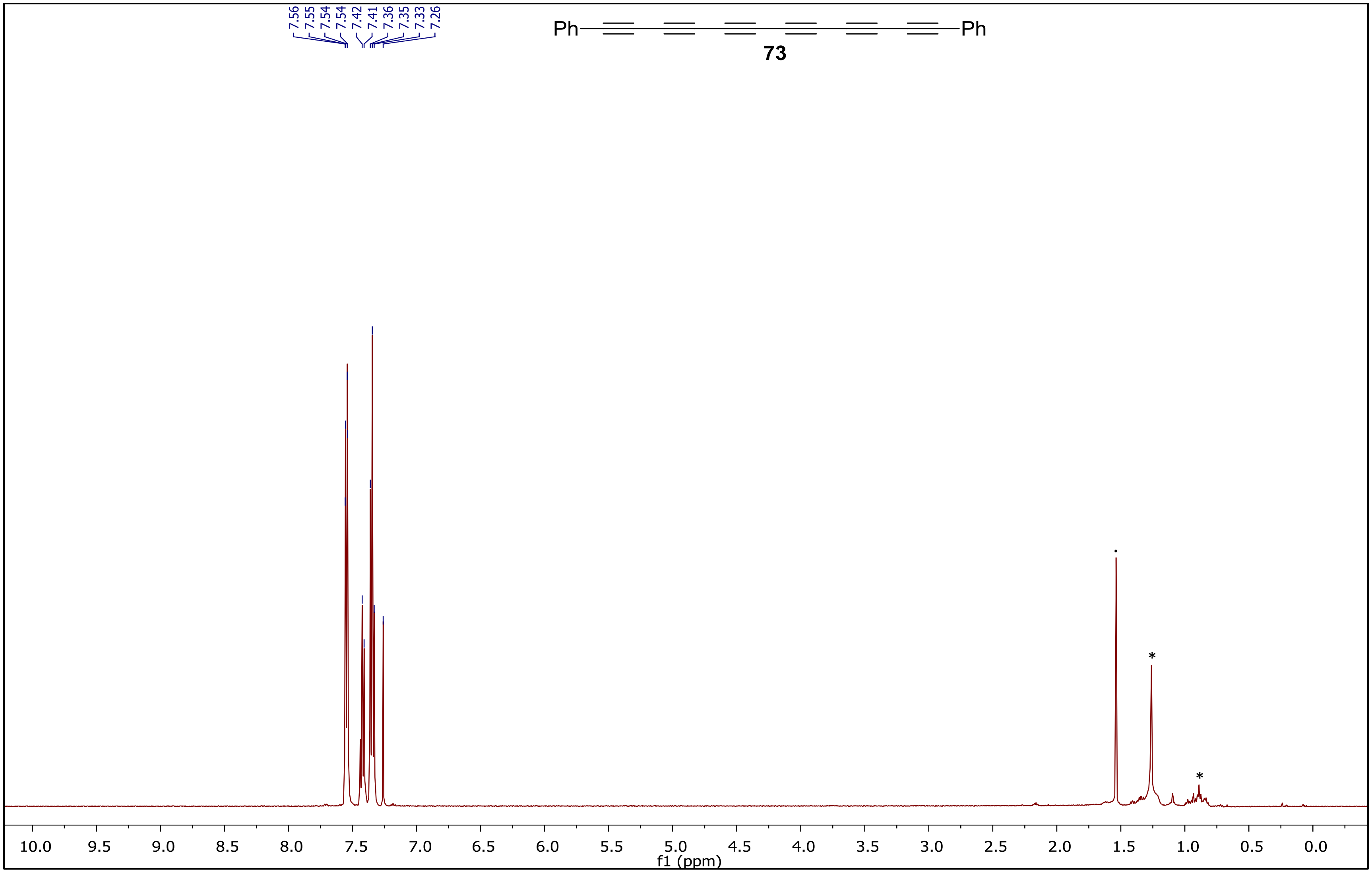
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **71.**



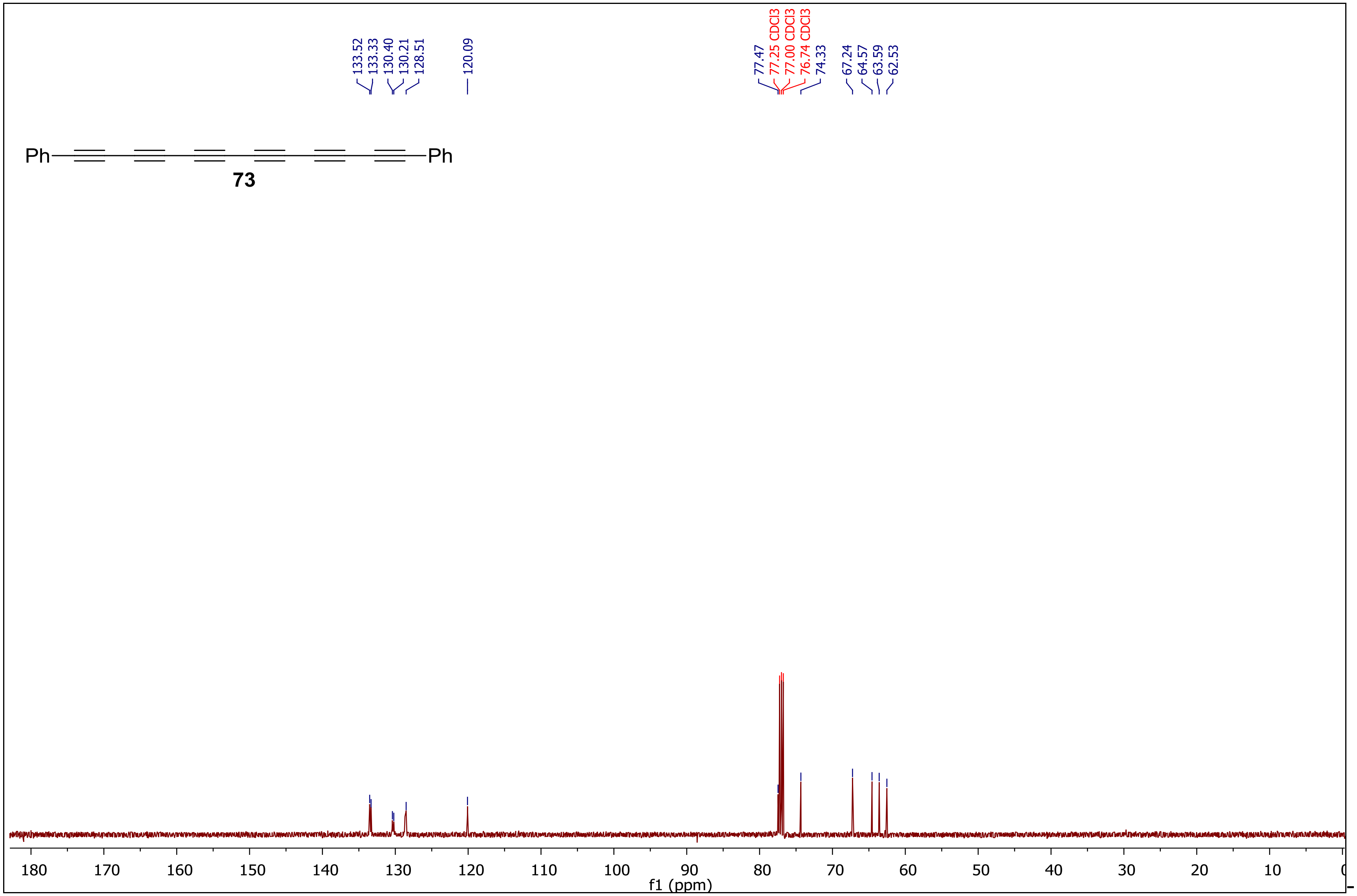
^{13}C NMR spectrum (125 MHz, CDCl$_3$) of compound **71.**



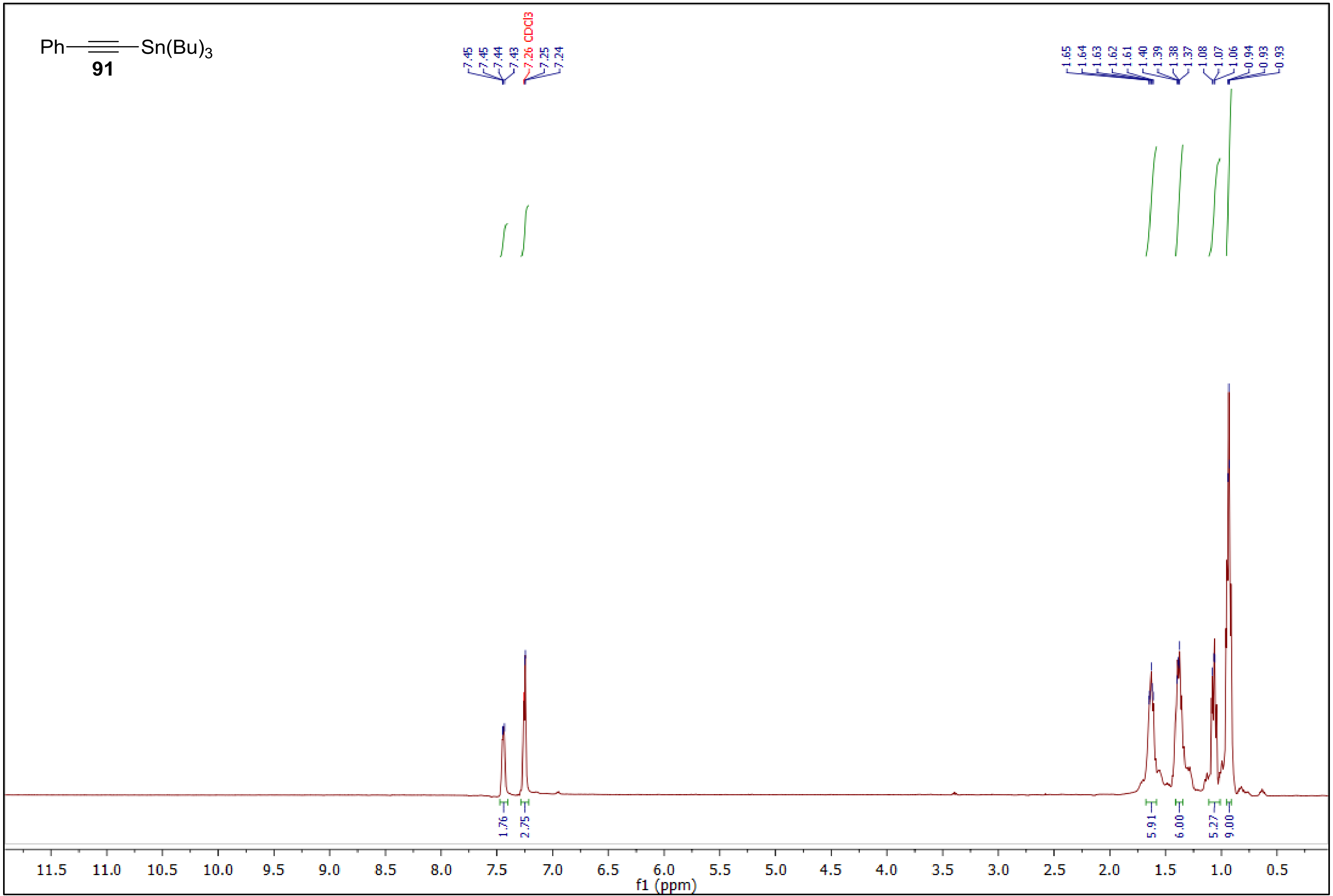
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **72.** Hexanes (*) denoted.



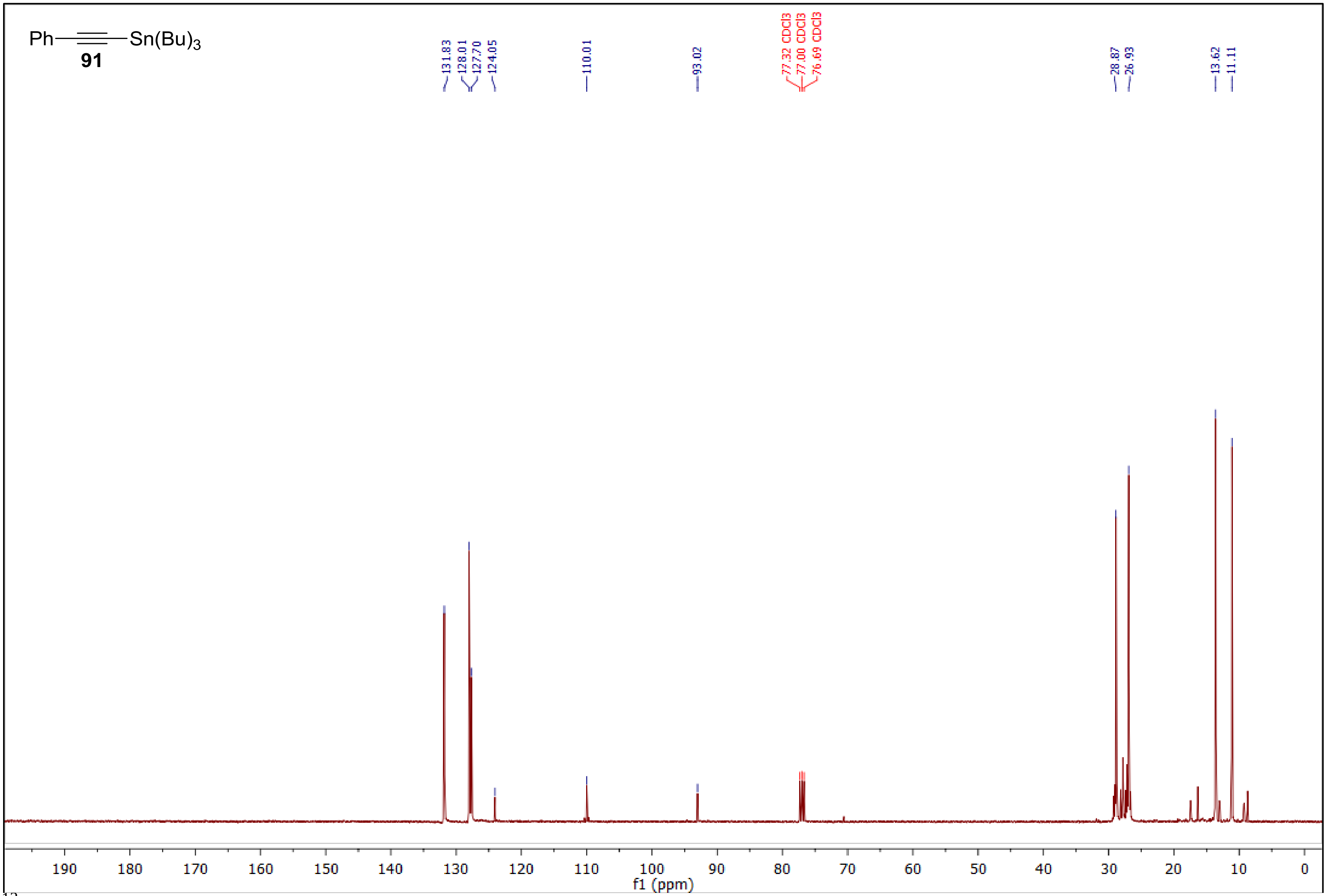
^{1}H NMR spectrum (500 MHz, CDCl$_3$) of compound **73.** Hexanes (*) and H$_2$O (·) denoted.



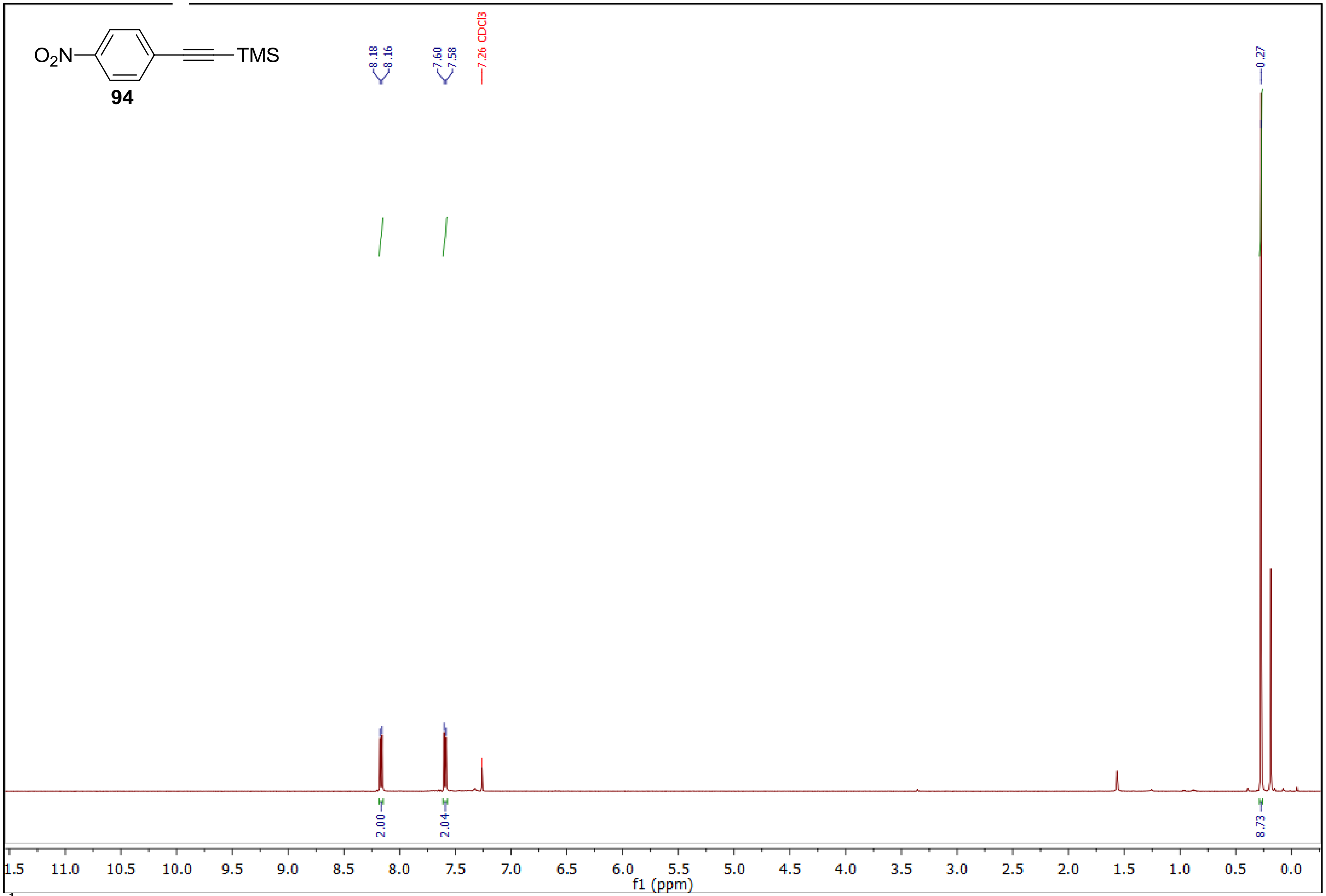
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **73.**



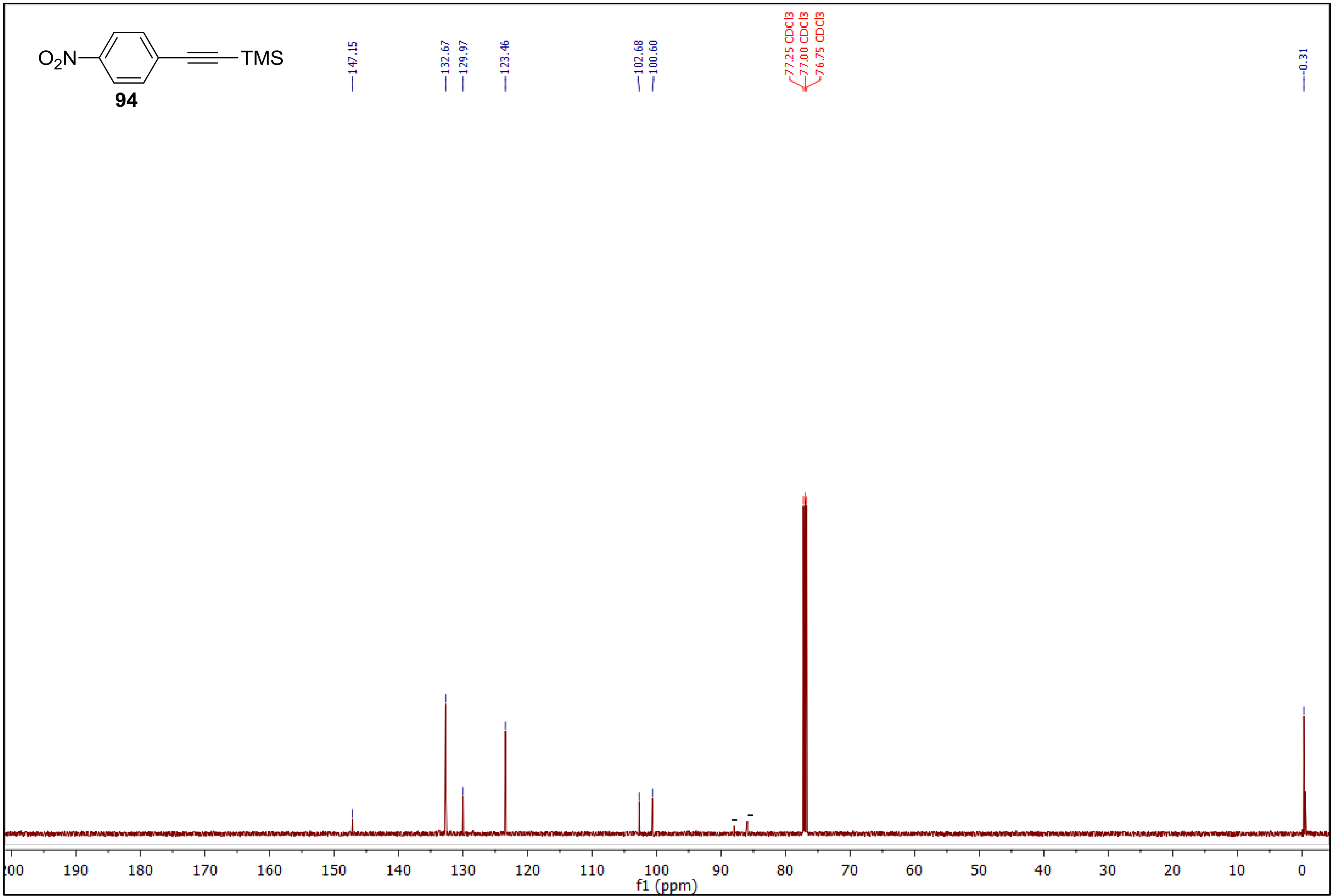
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **91**.



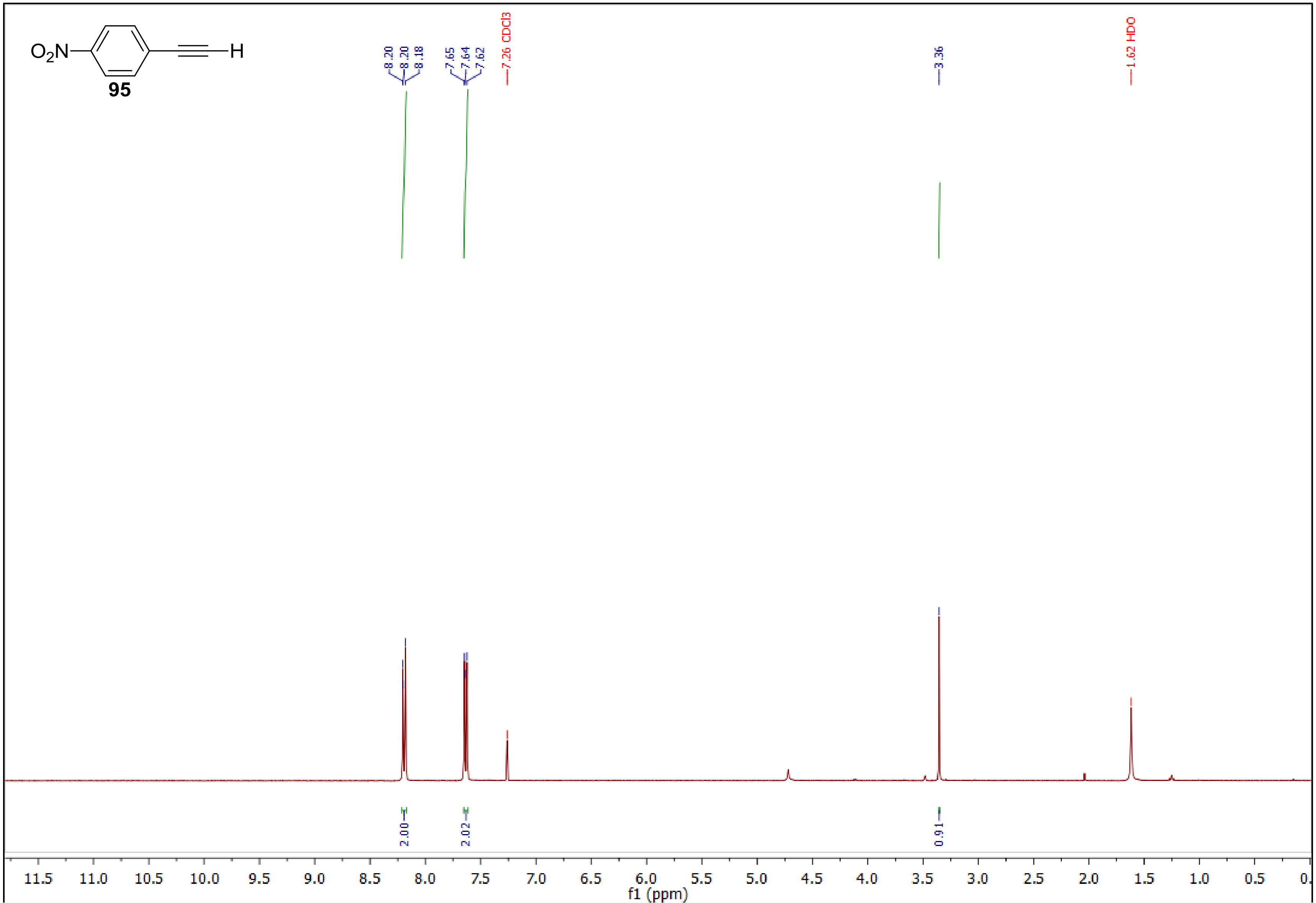
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **91**.



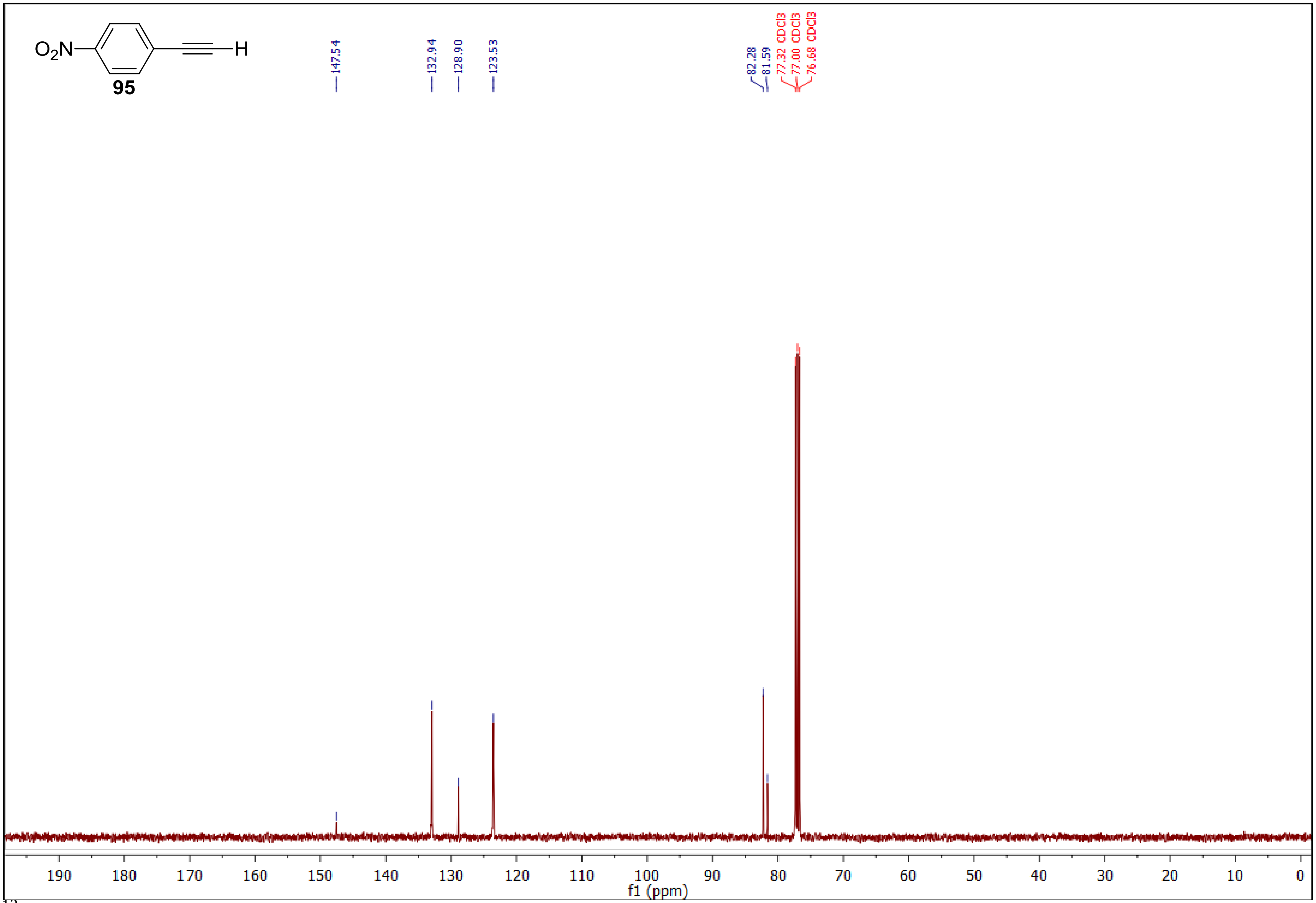
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **94**.



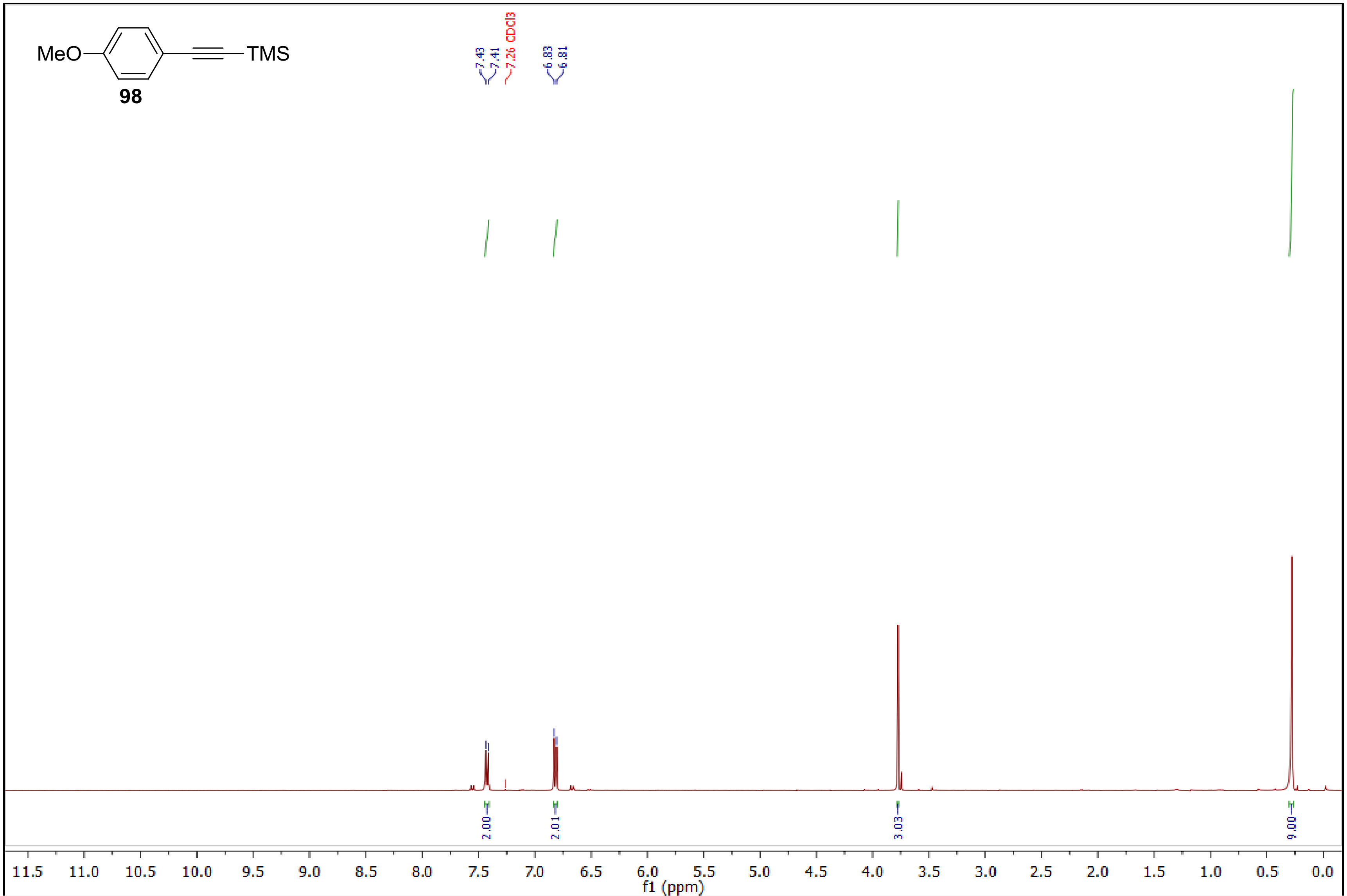
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **94**. Trimethylsilylacetylene (-) denoted.



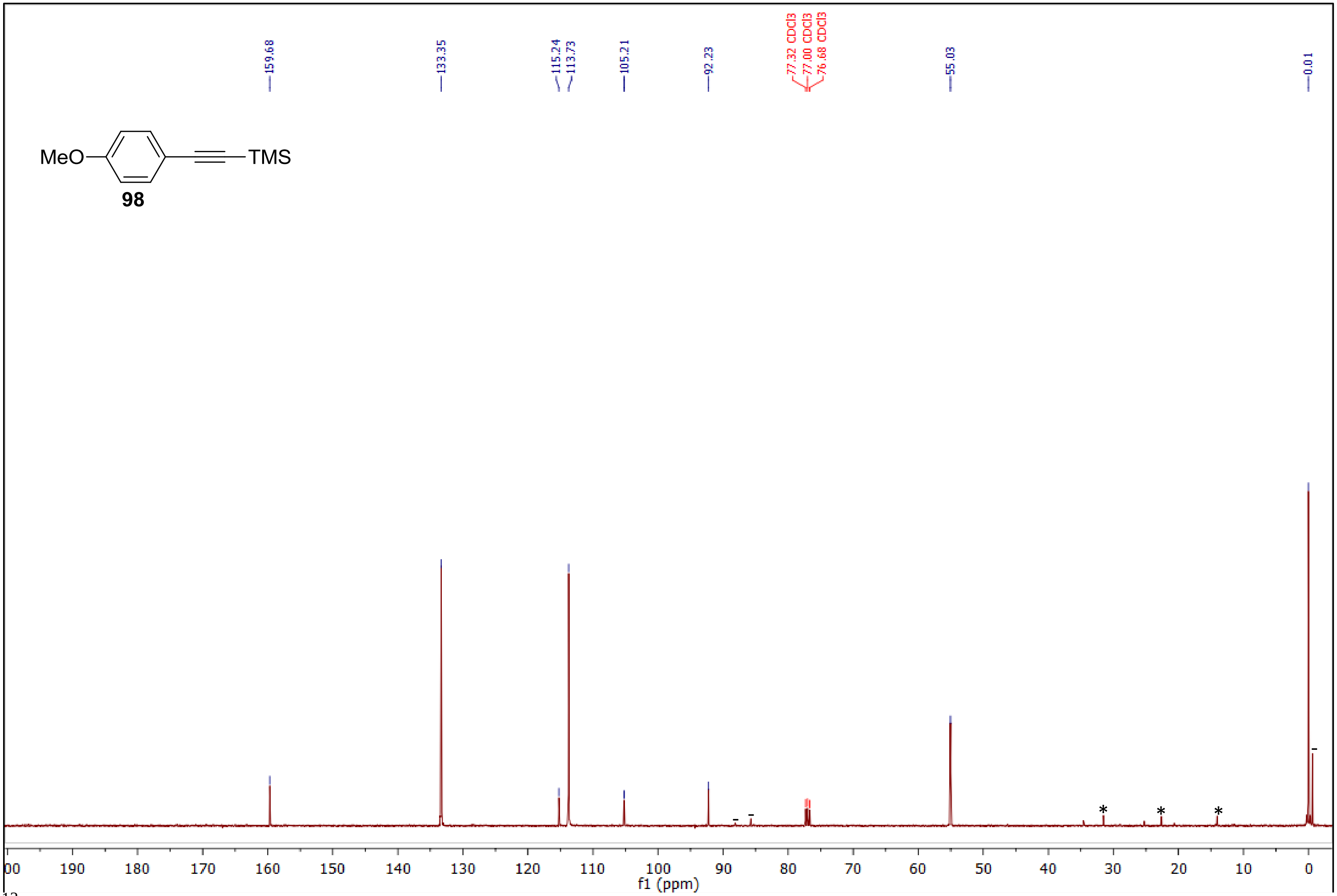
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **95**.



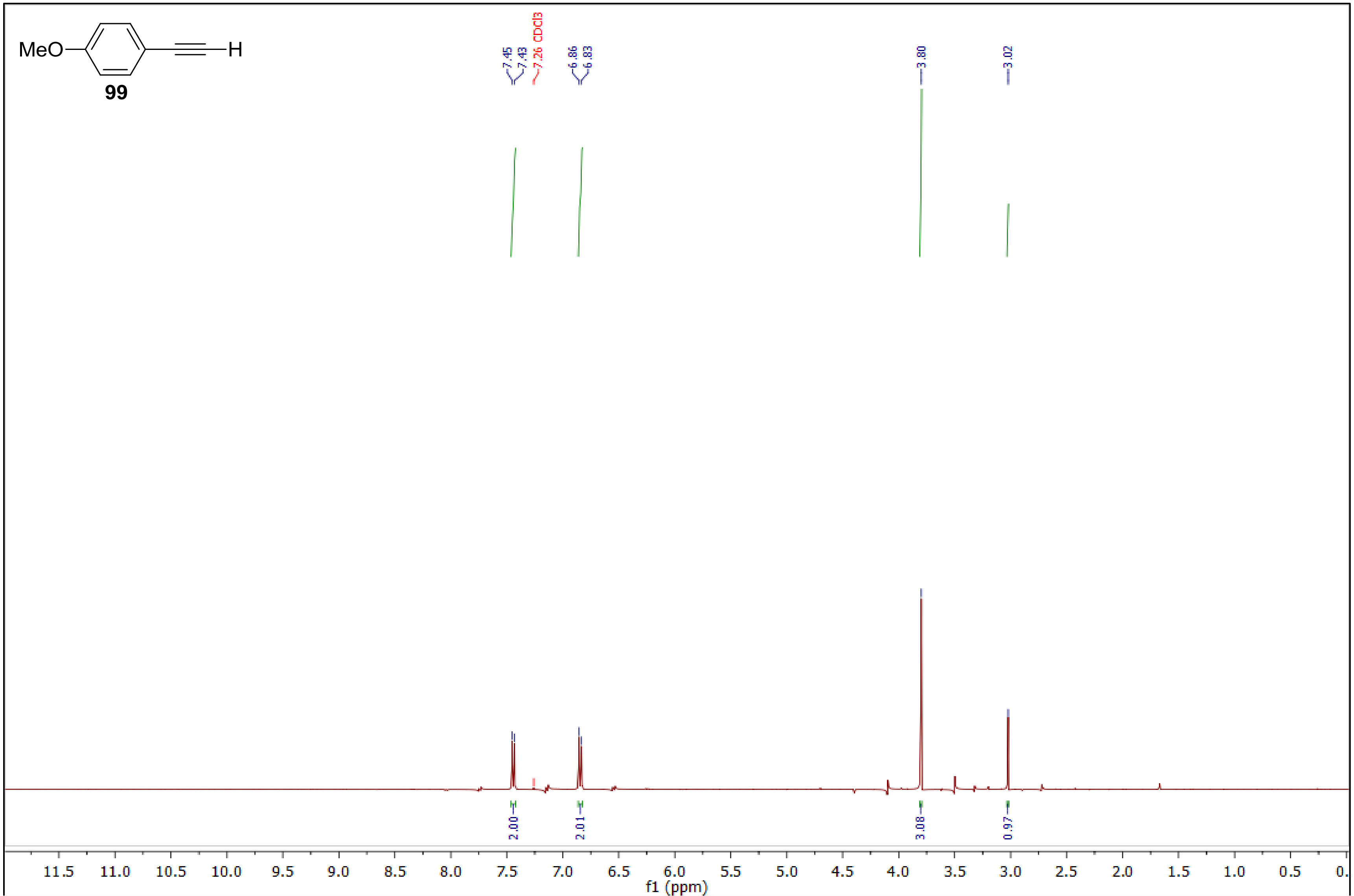
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **95**.



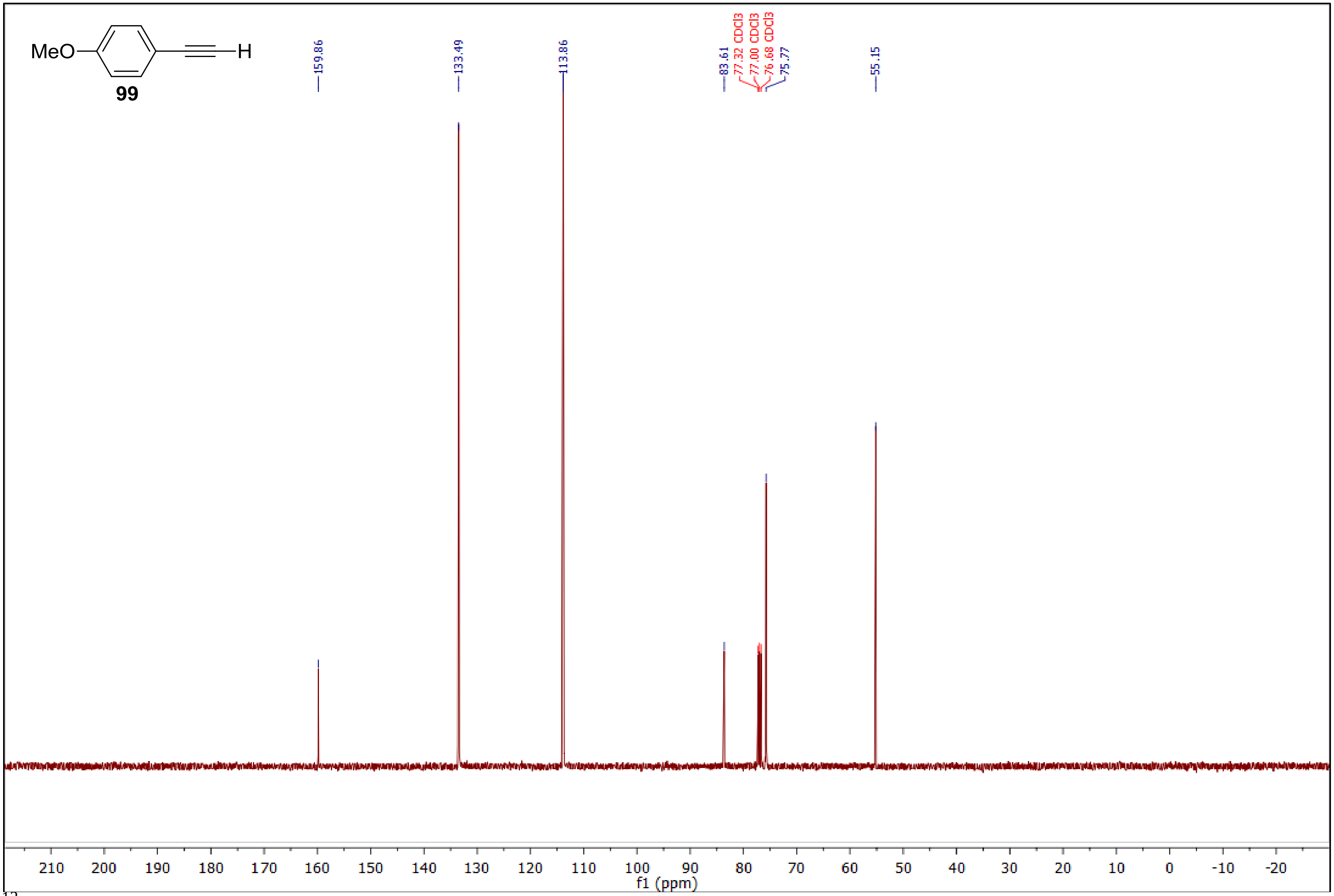
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **98**.



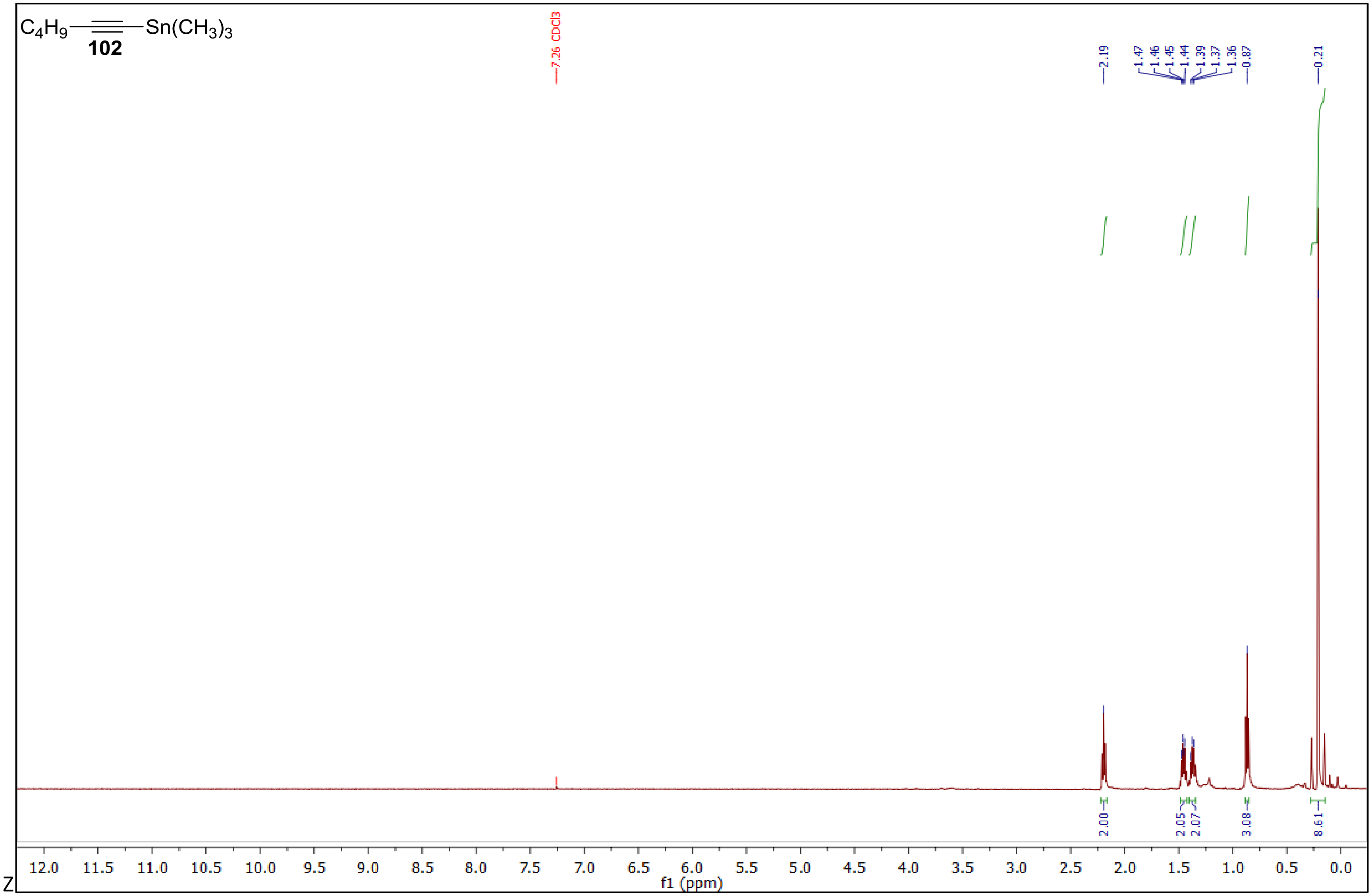
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **98**. Hexanes (*) and trimethylsilylacetylene (-) denoted.



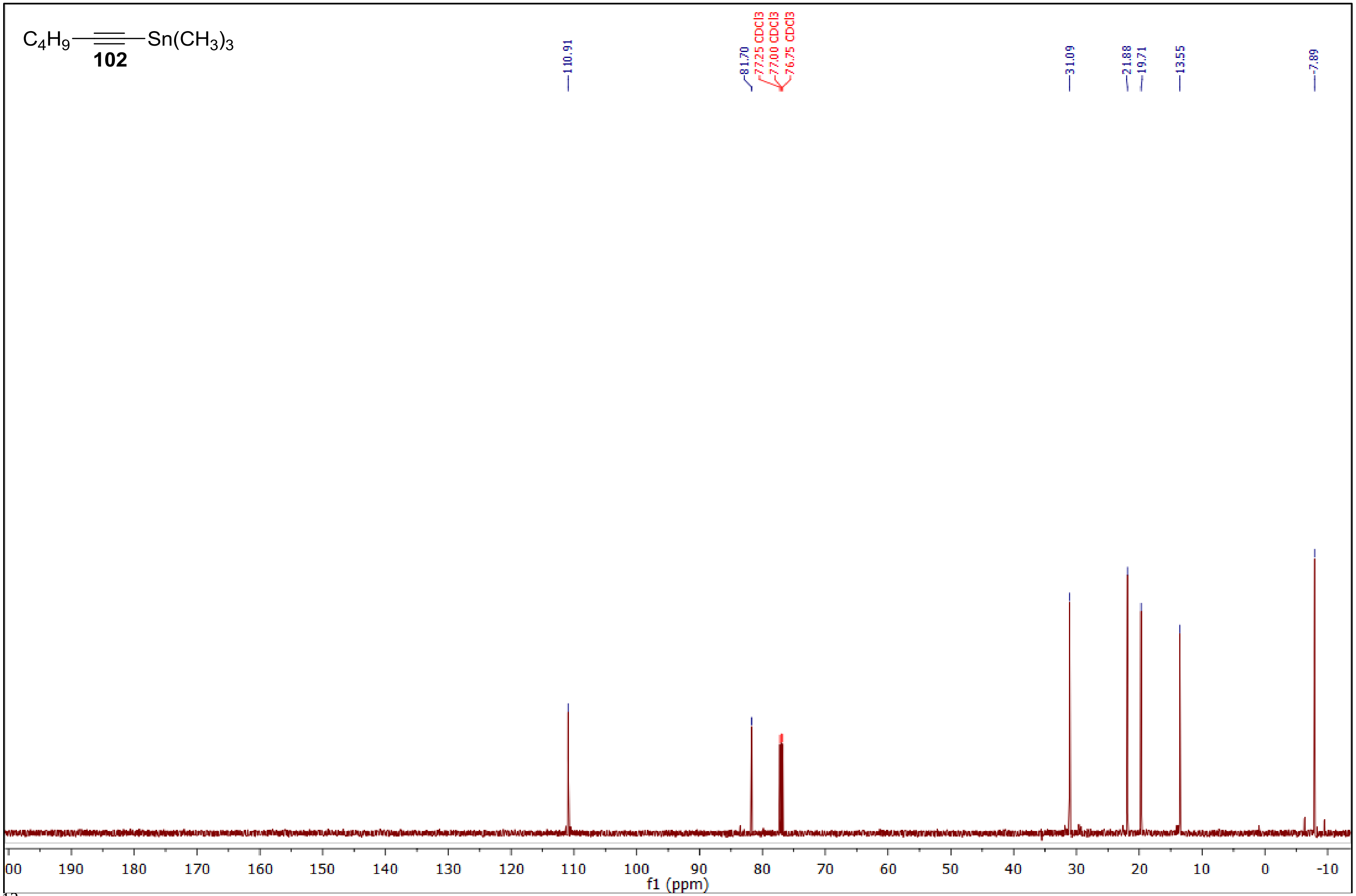
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **99**.



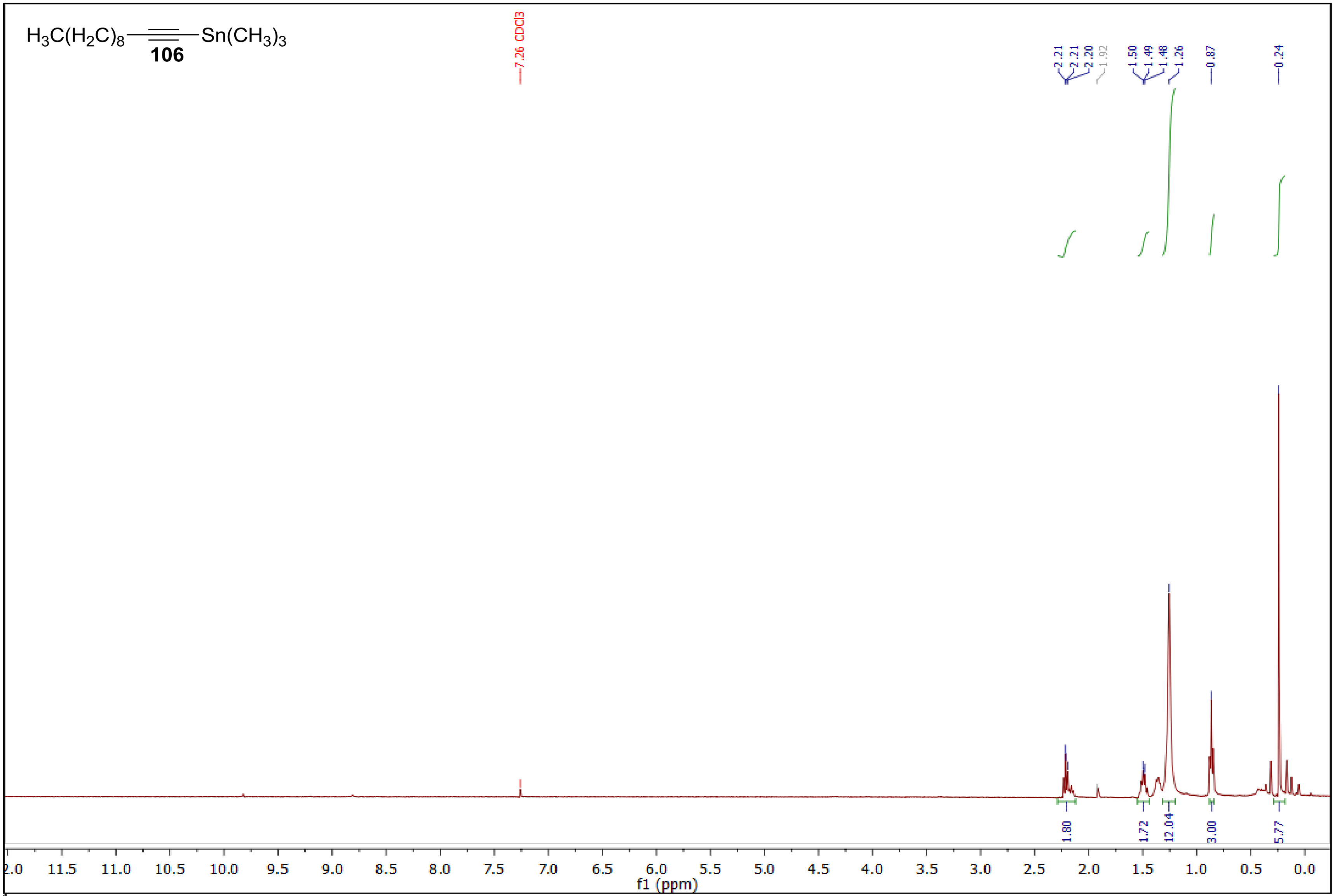
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **99**.



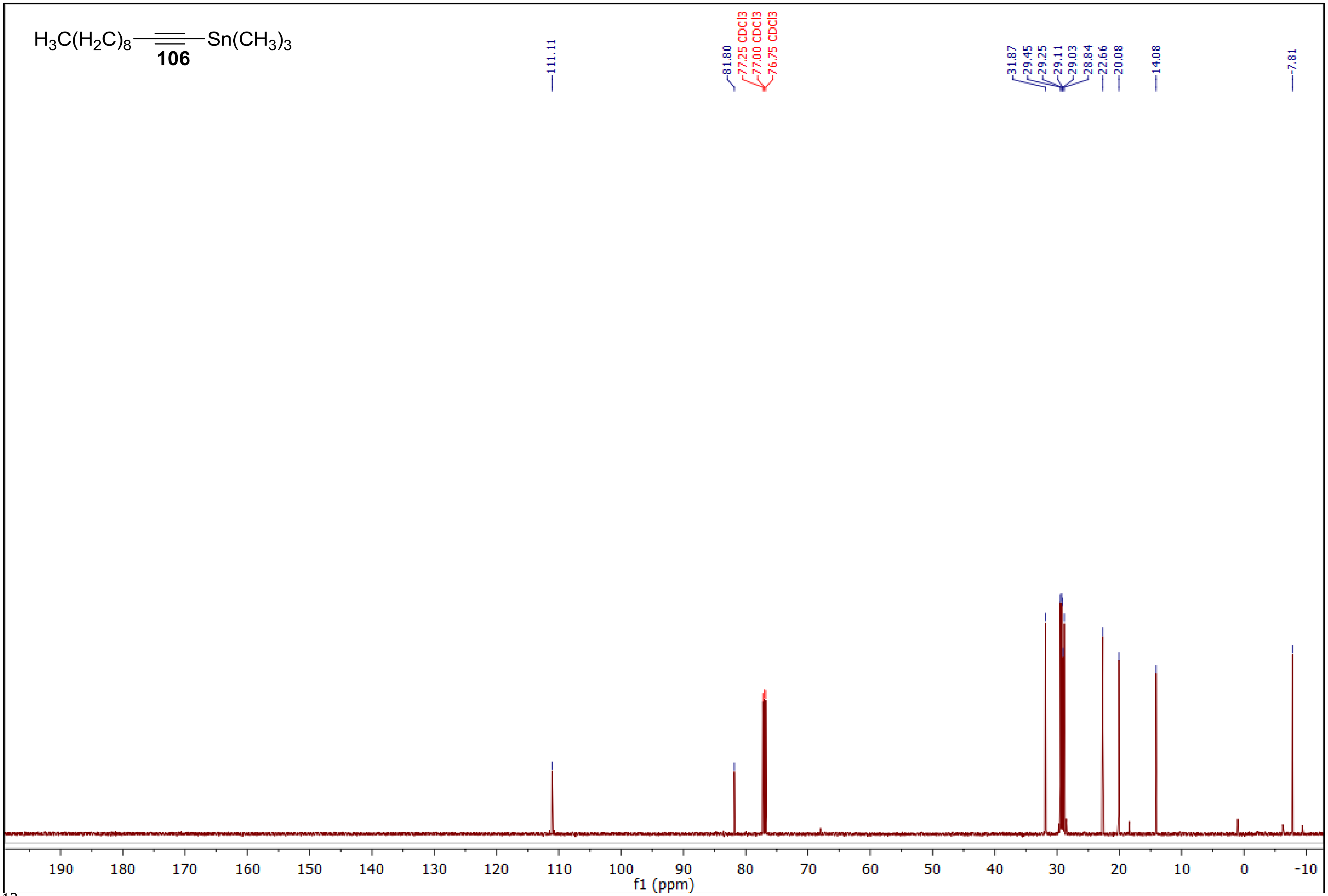
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **102**.



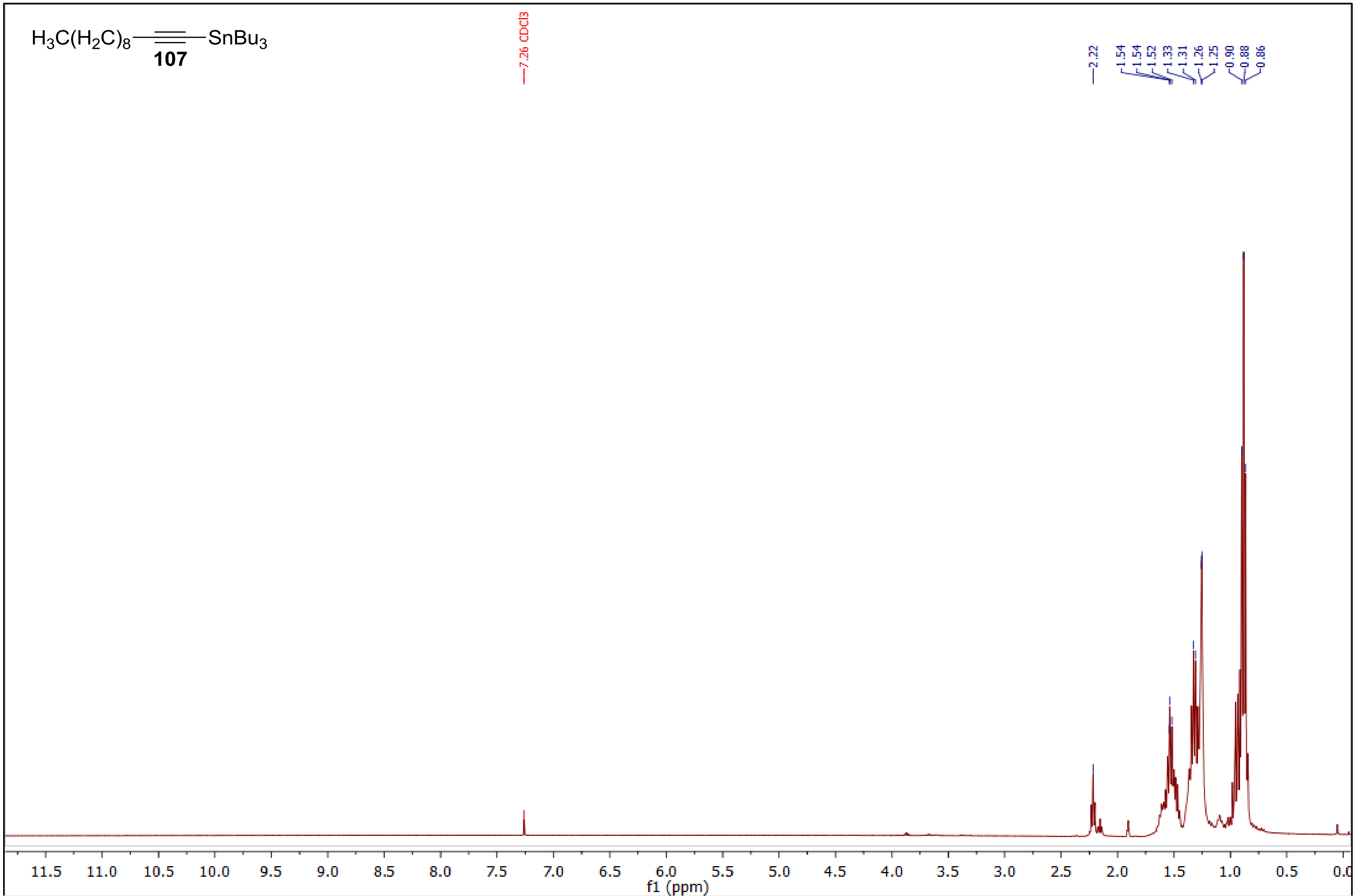
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **102**.



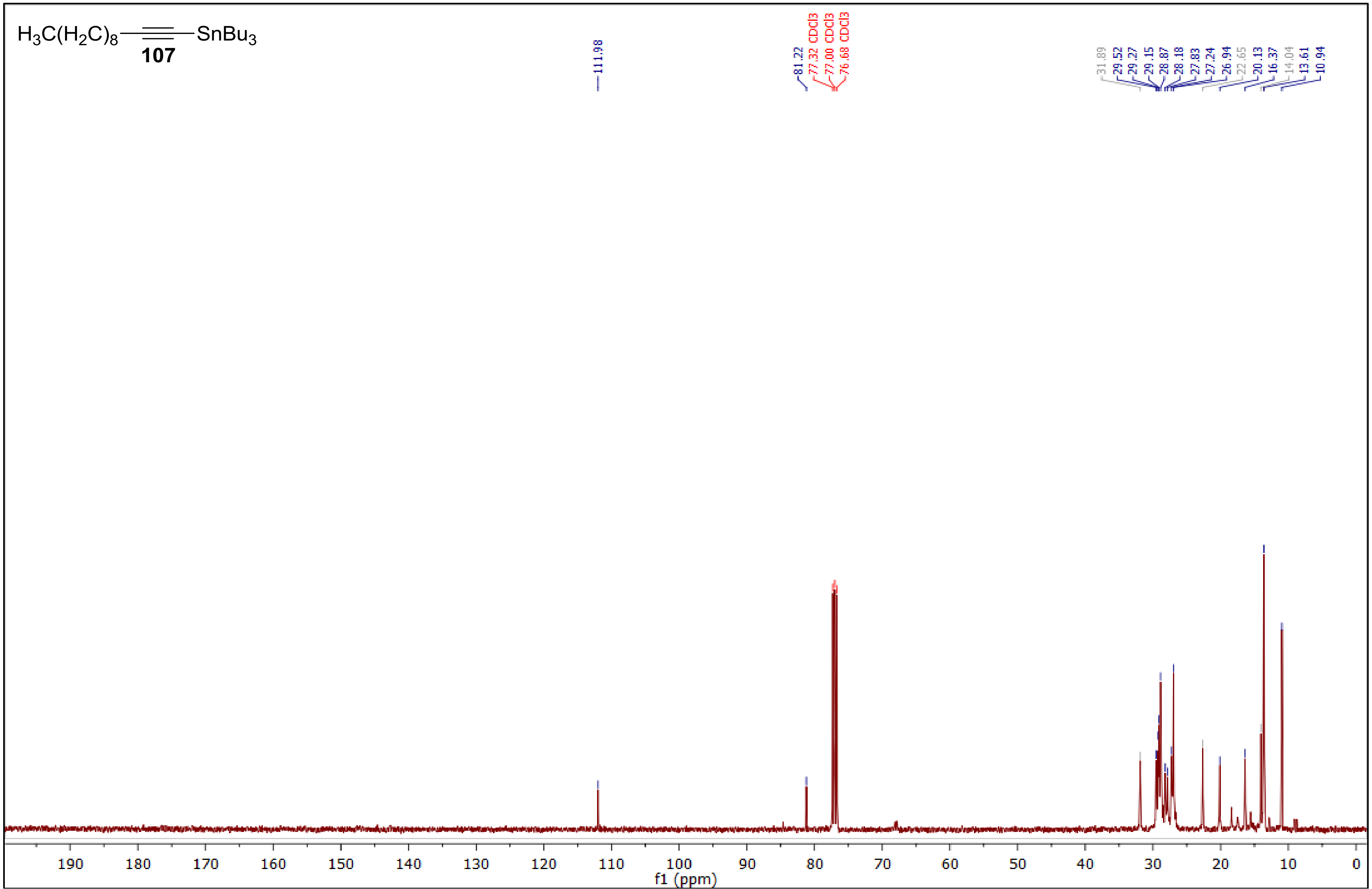
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **106**.



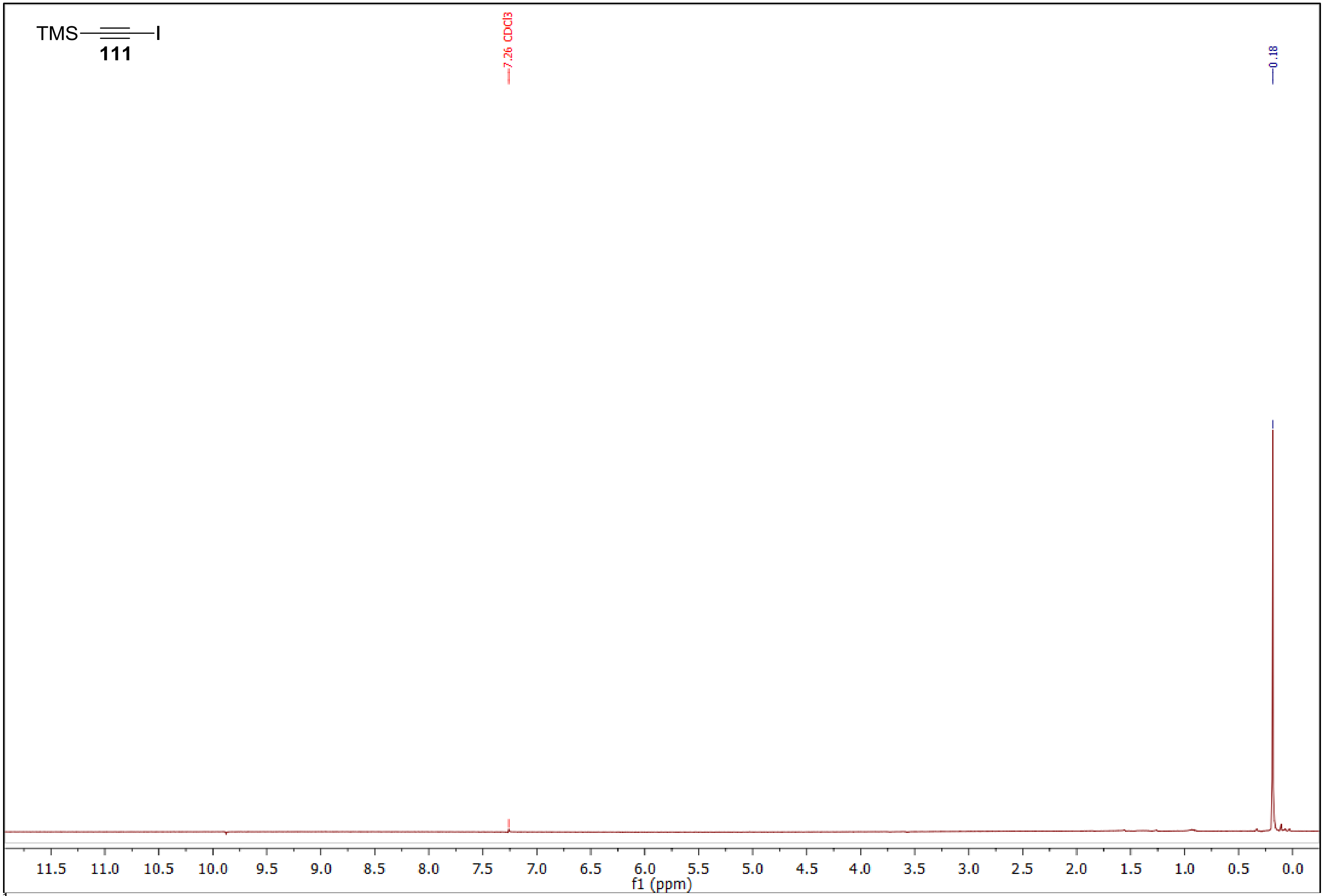
^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **106.**



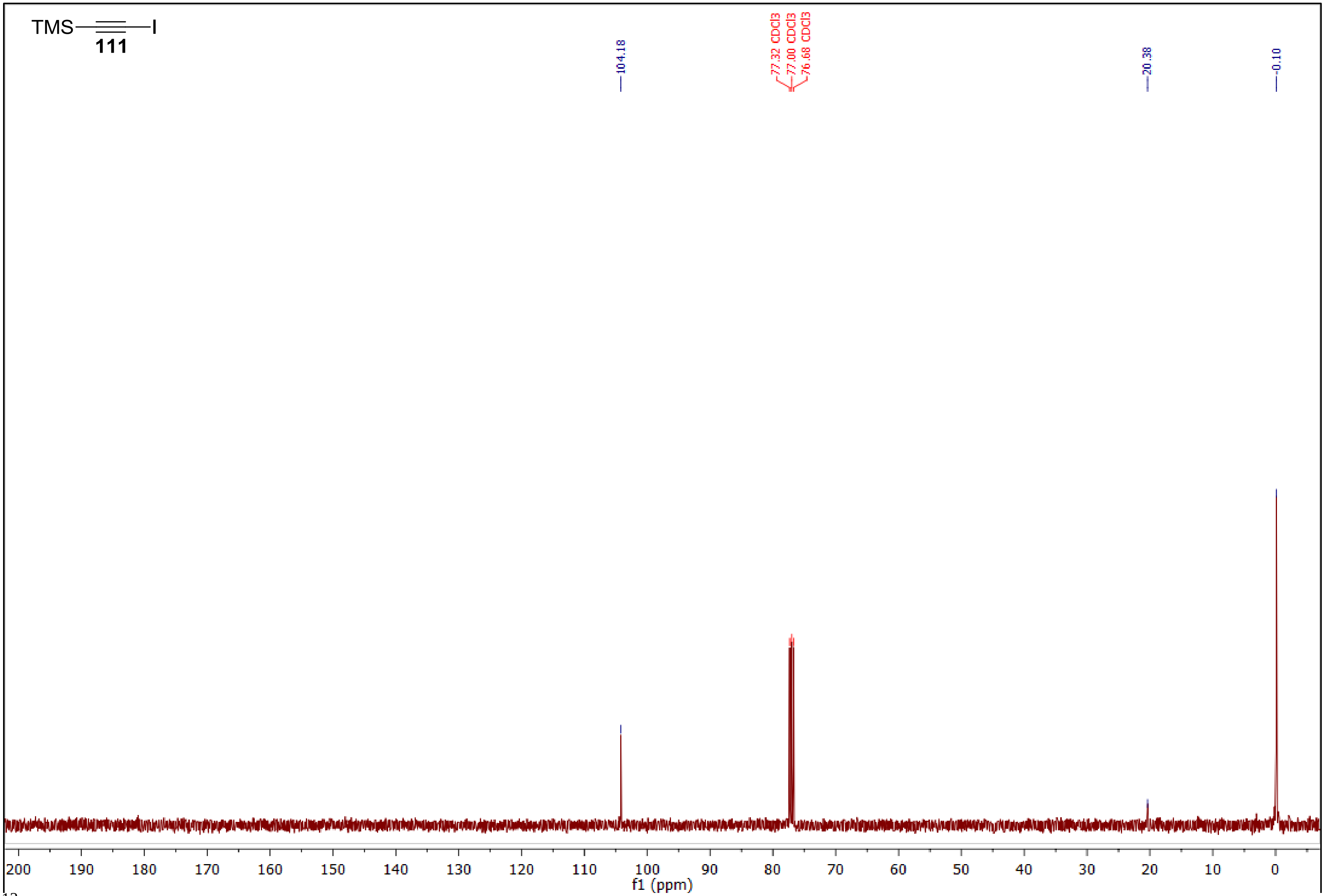
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **107**.



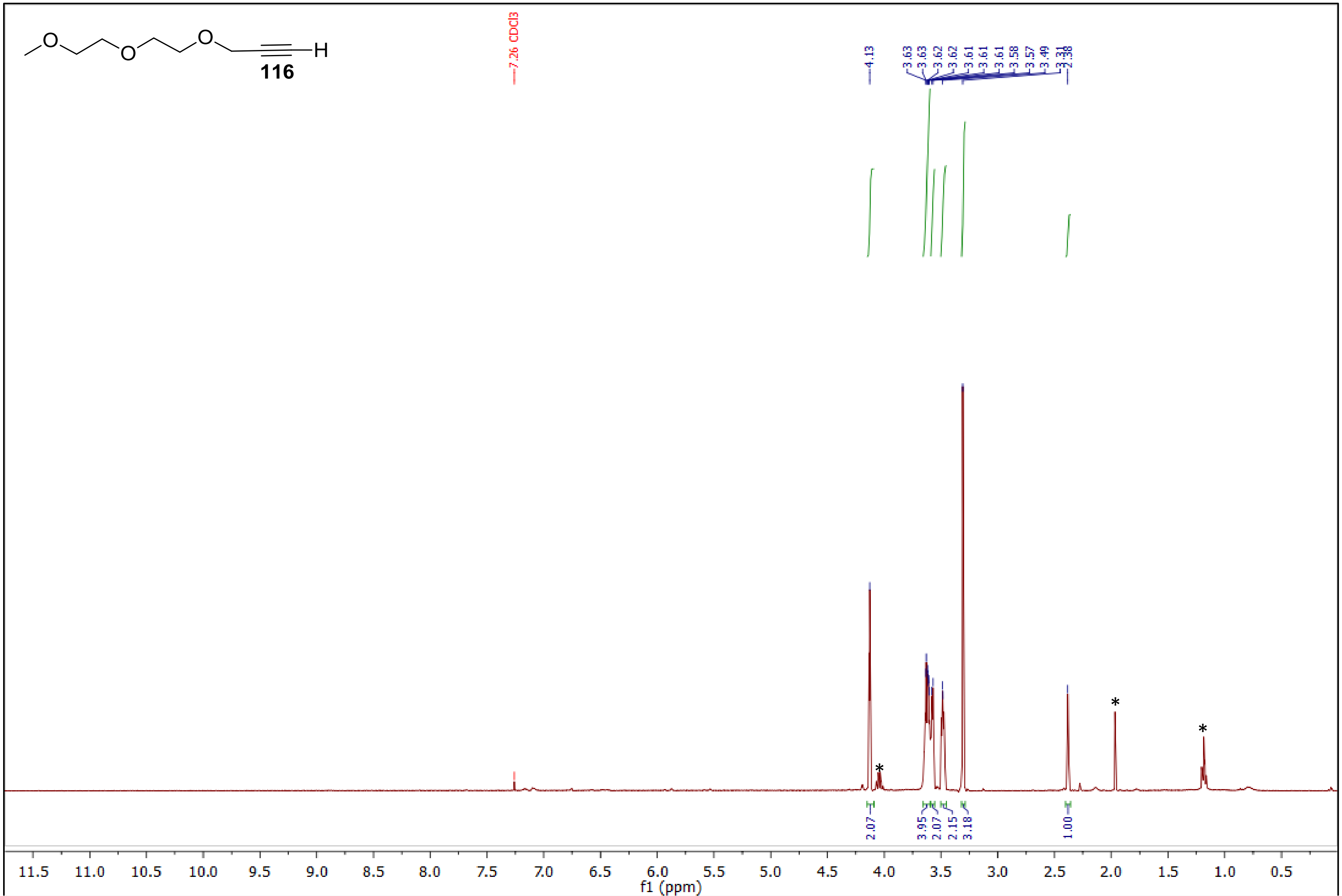
^{1}H NMR spectrum (100 MHz, $CDCl_3$) of compound **107**.



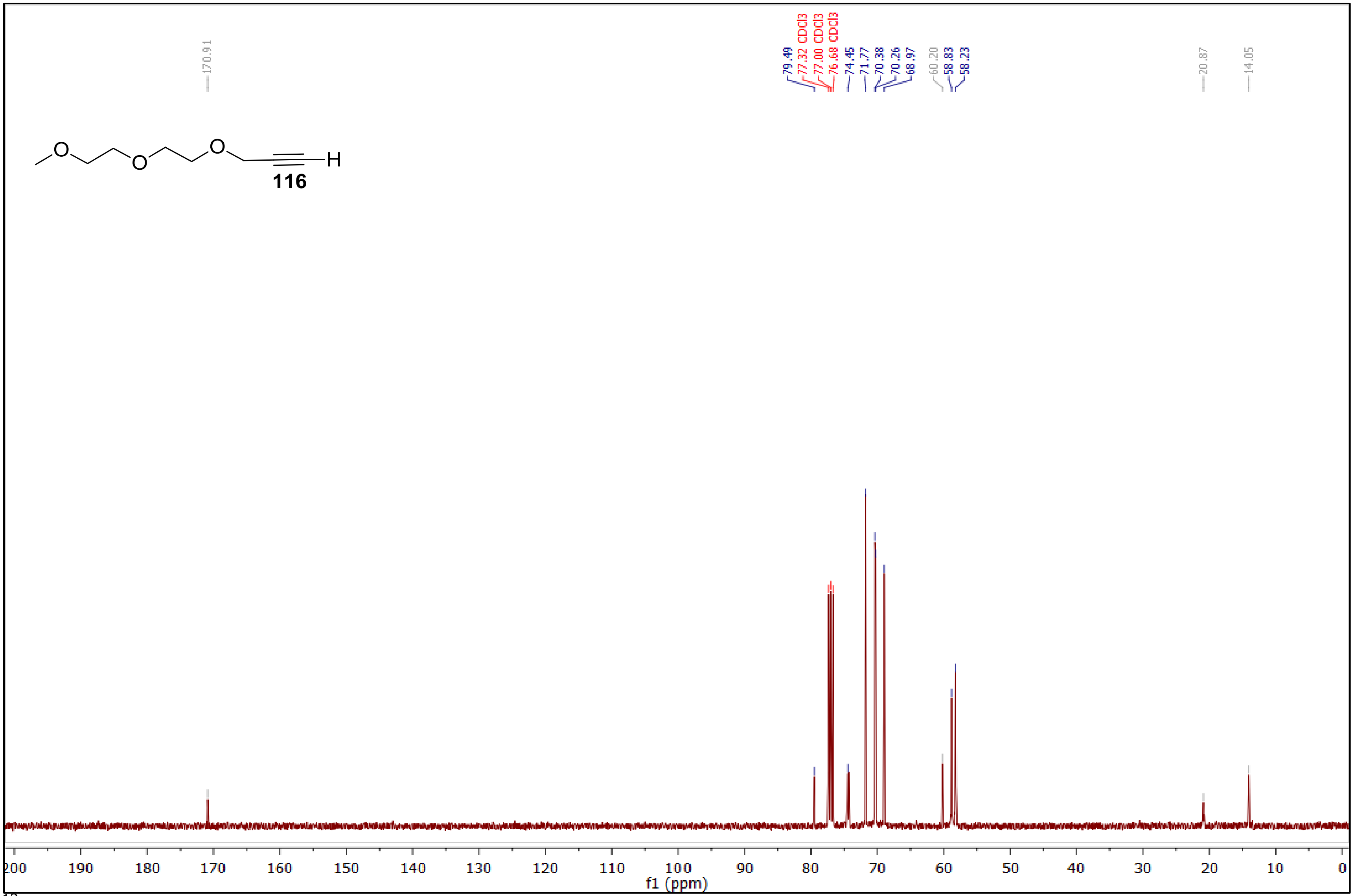
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **111**.



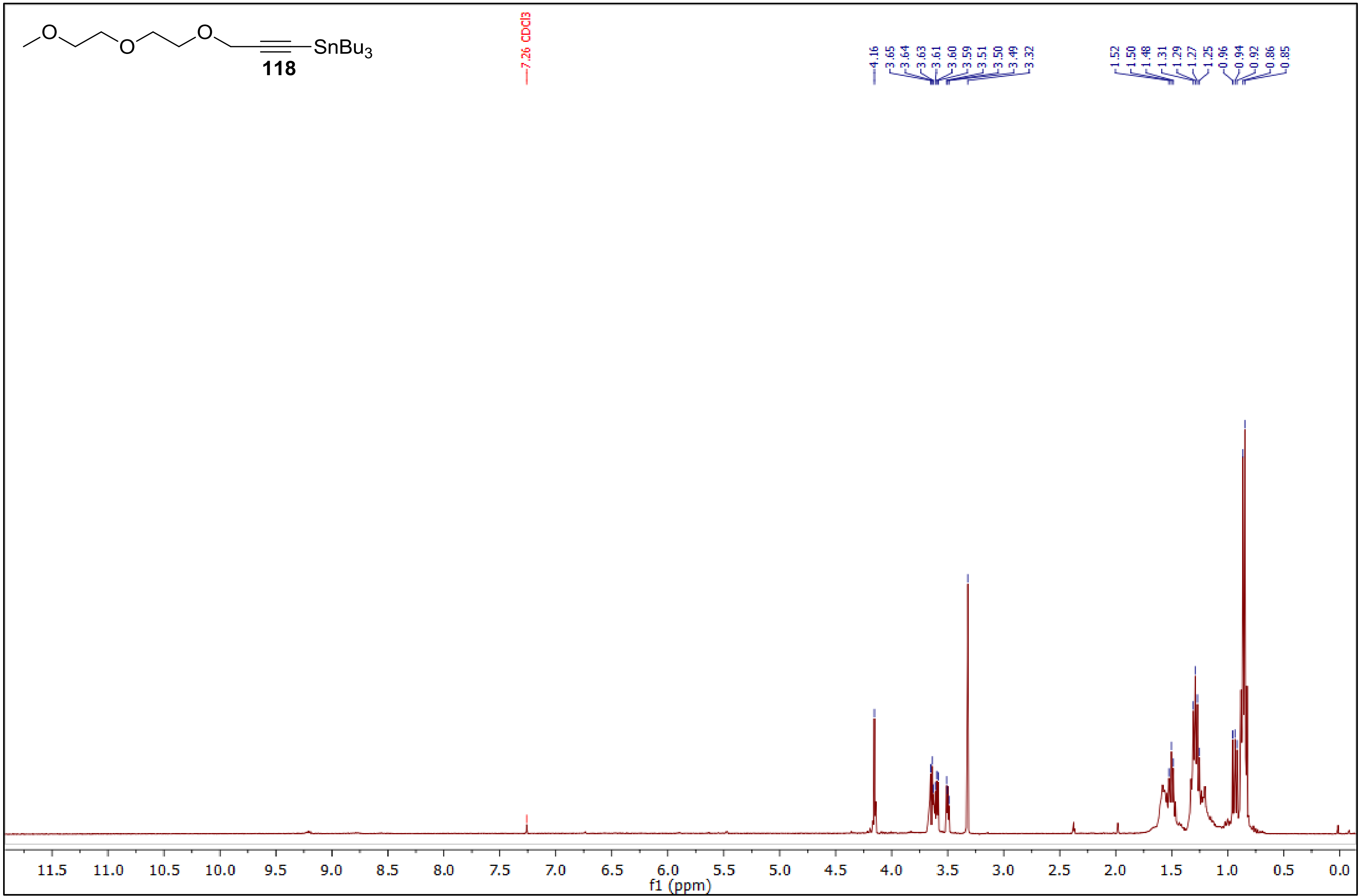
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **111**.



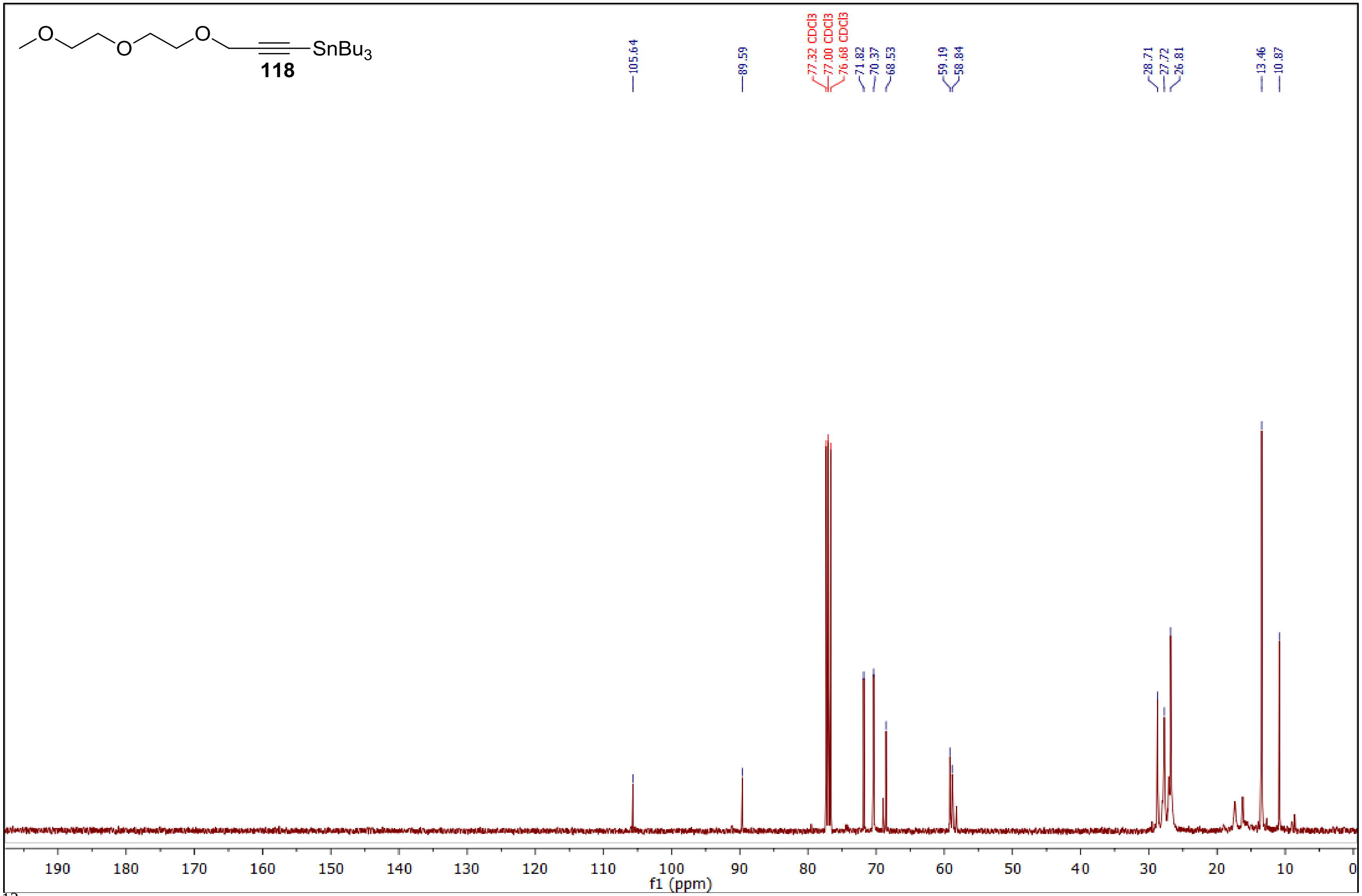
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **116**. Ethyl acetate (*) denoted.



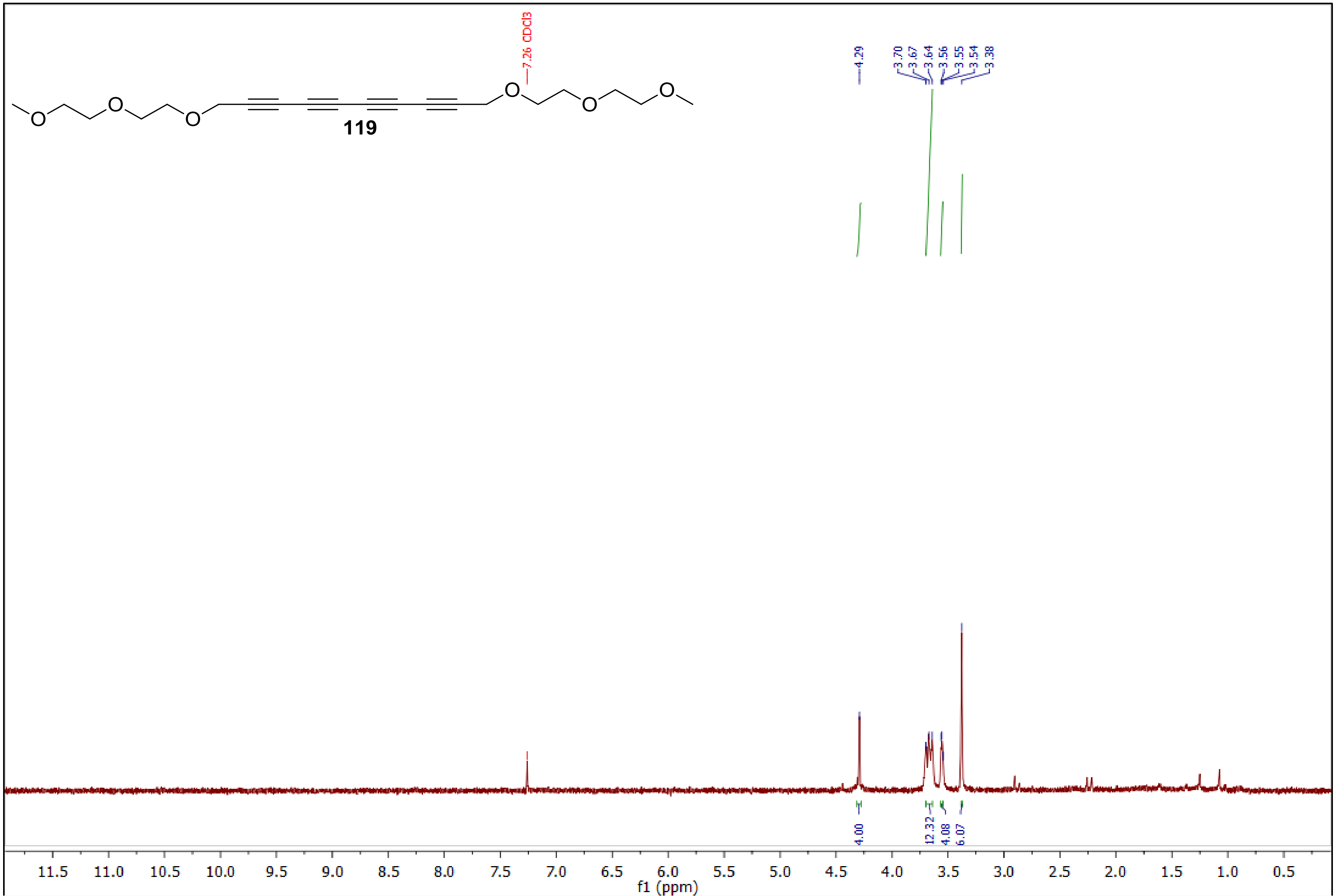
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **116**. Ethyl acetate in gray.



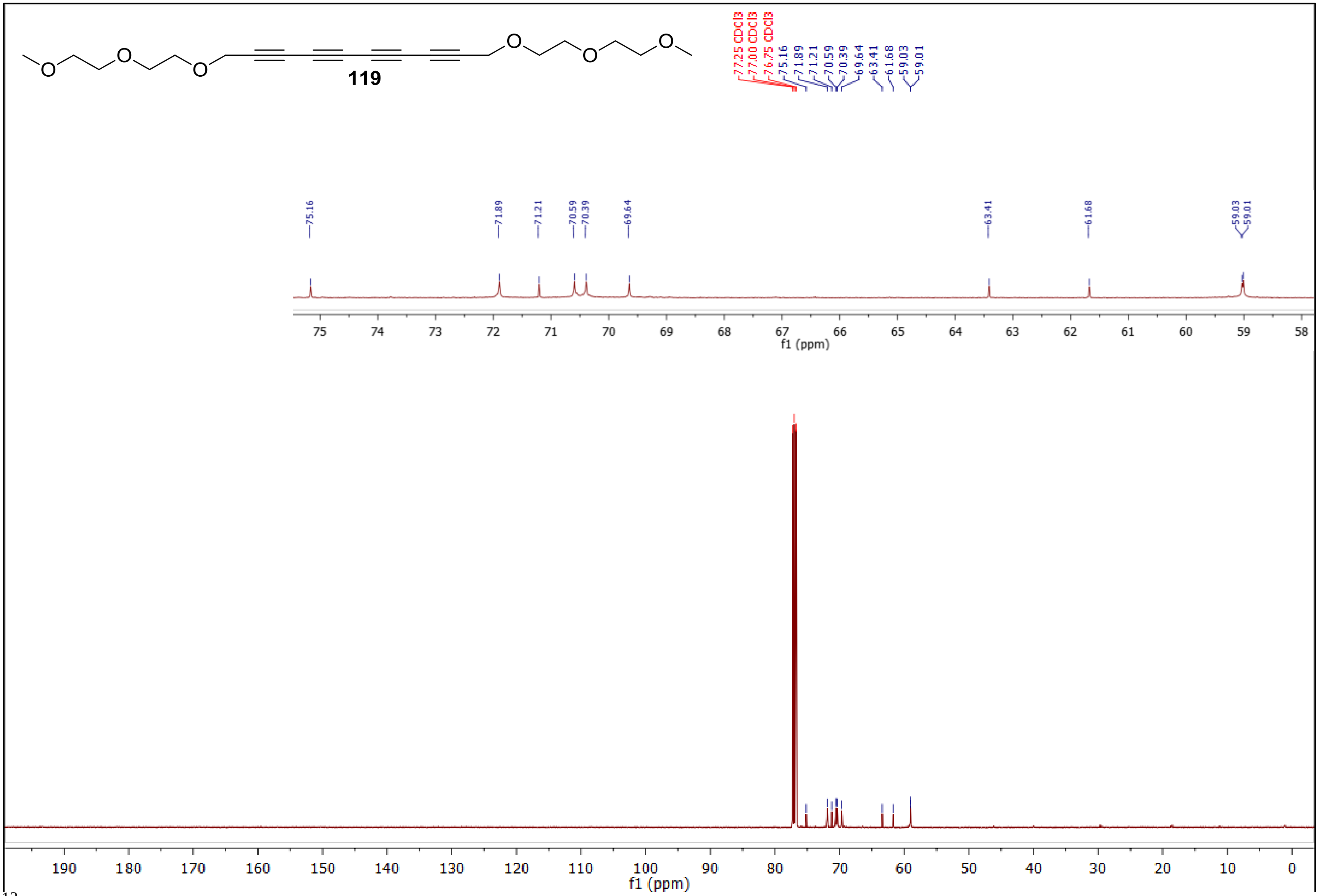
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **118**.


118

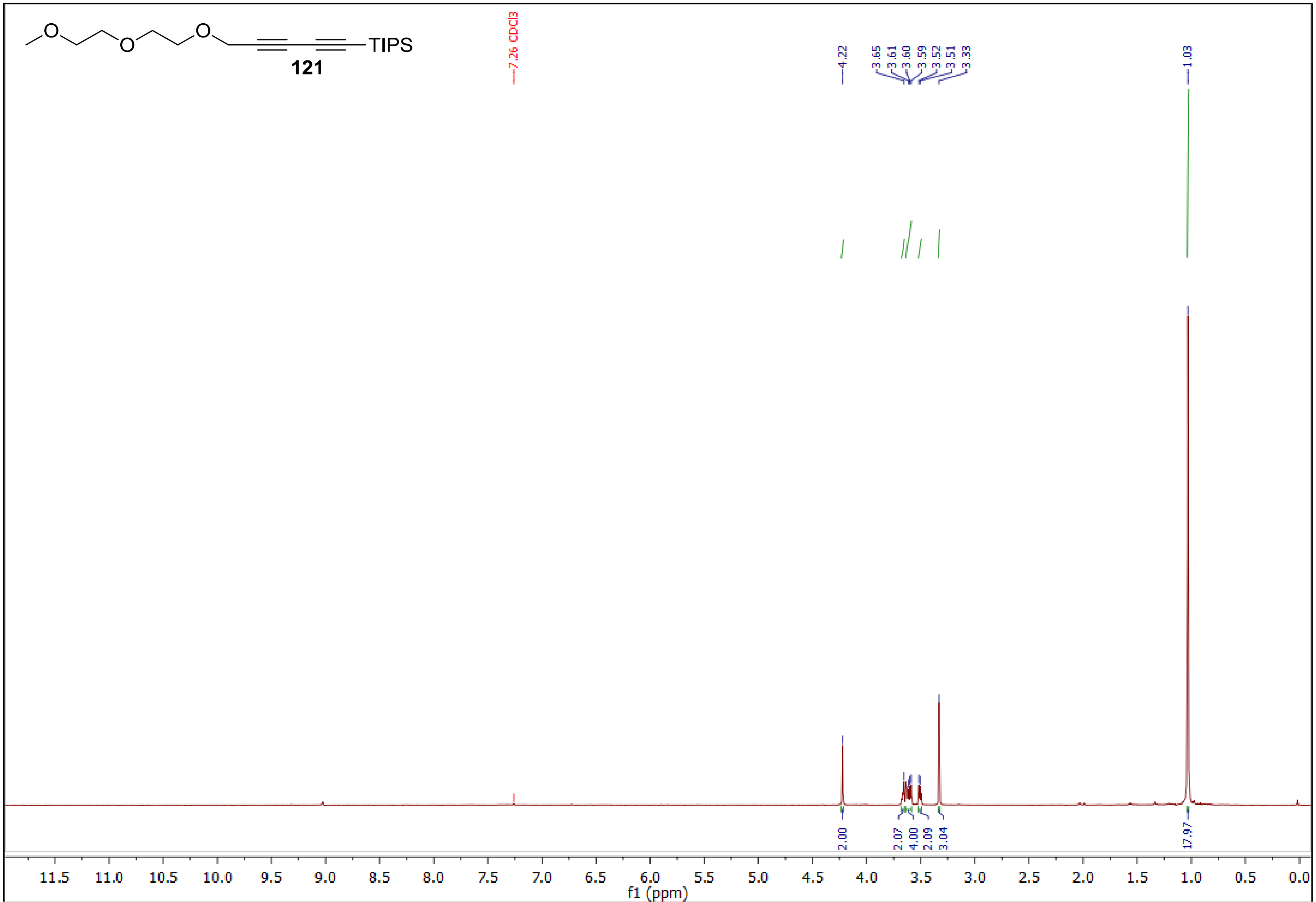
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **118.**



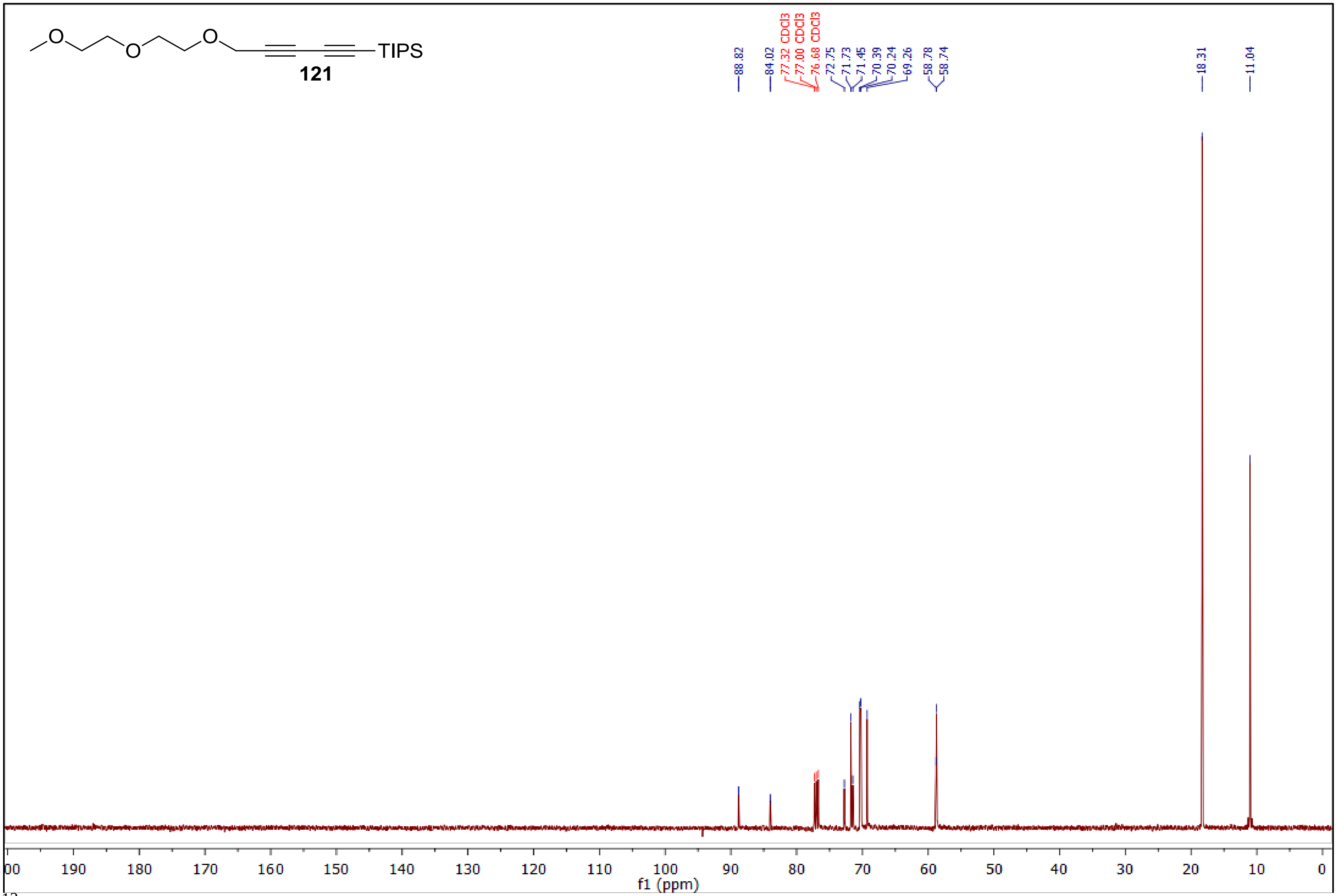
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **119**.



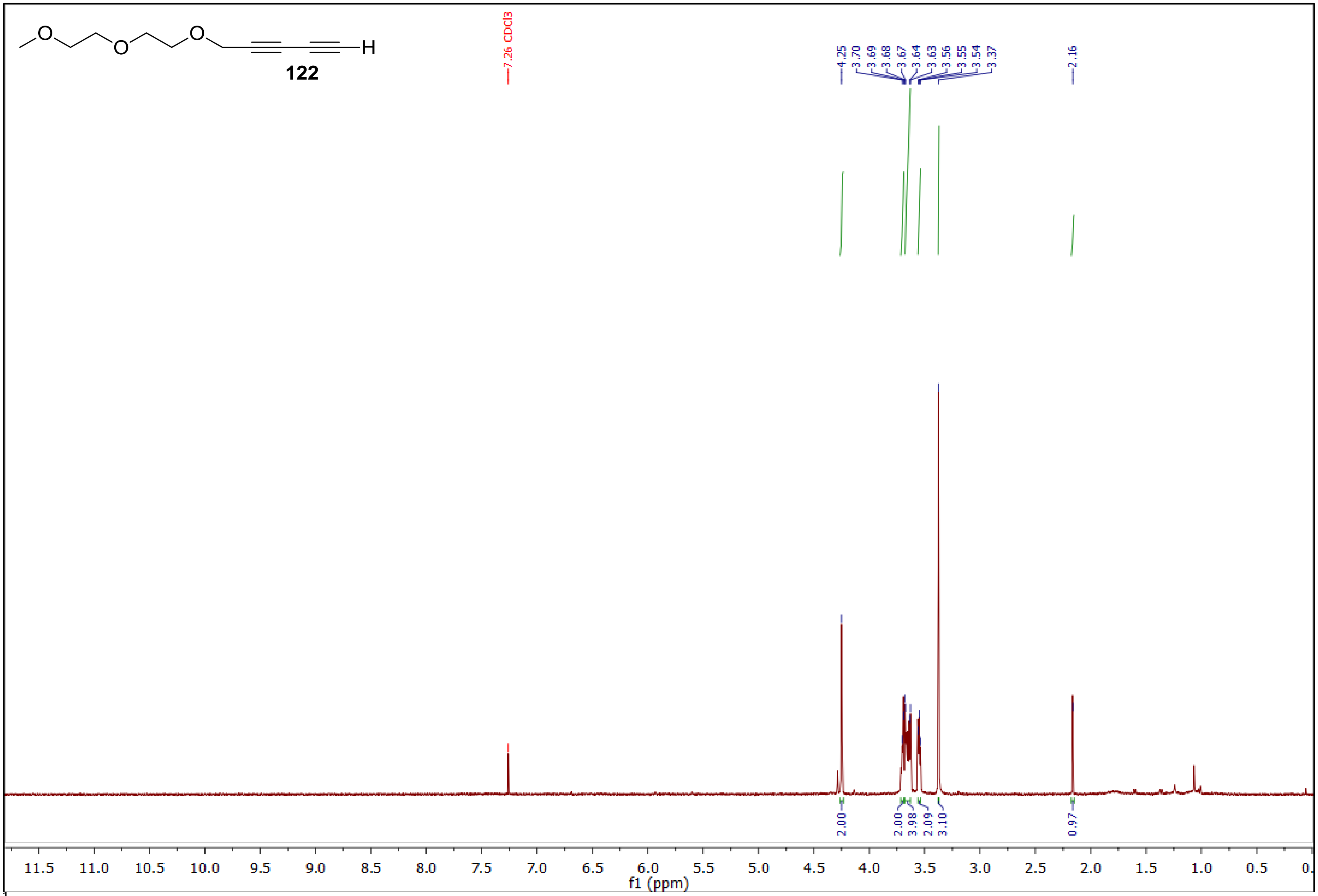
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **119.**



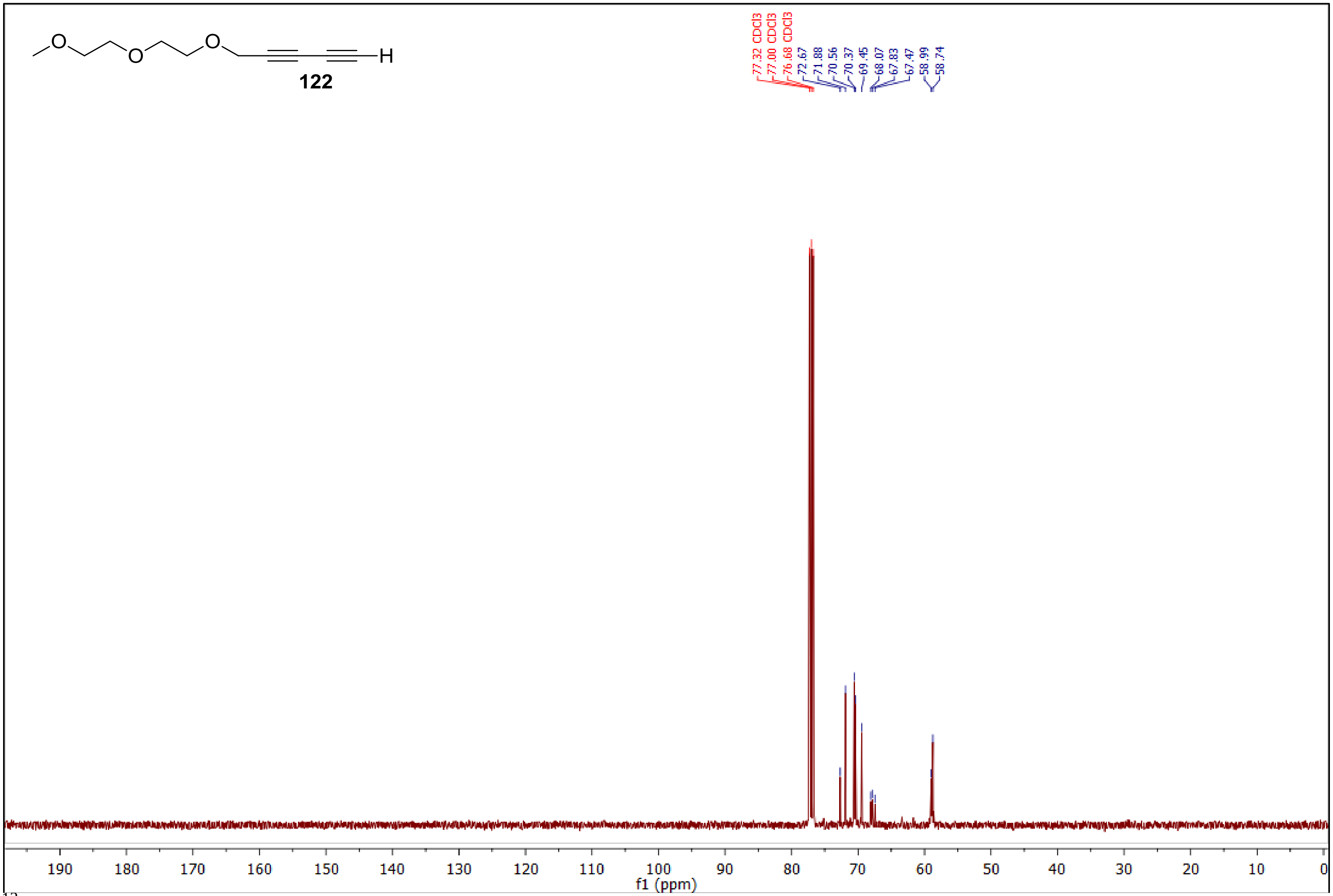
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **121.**



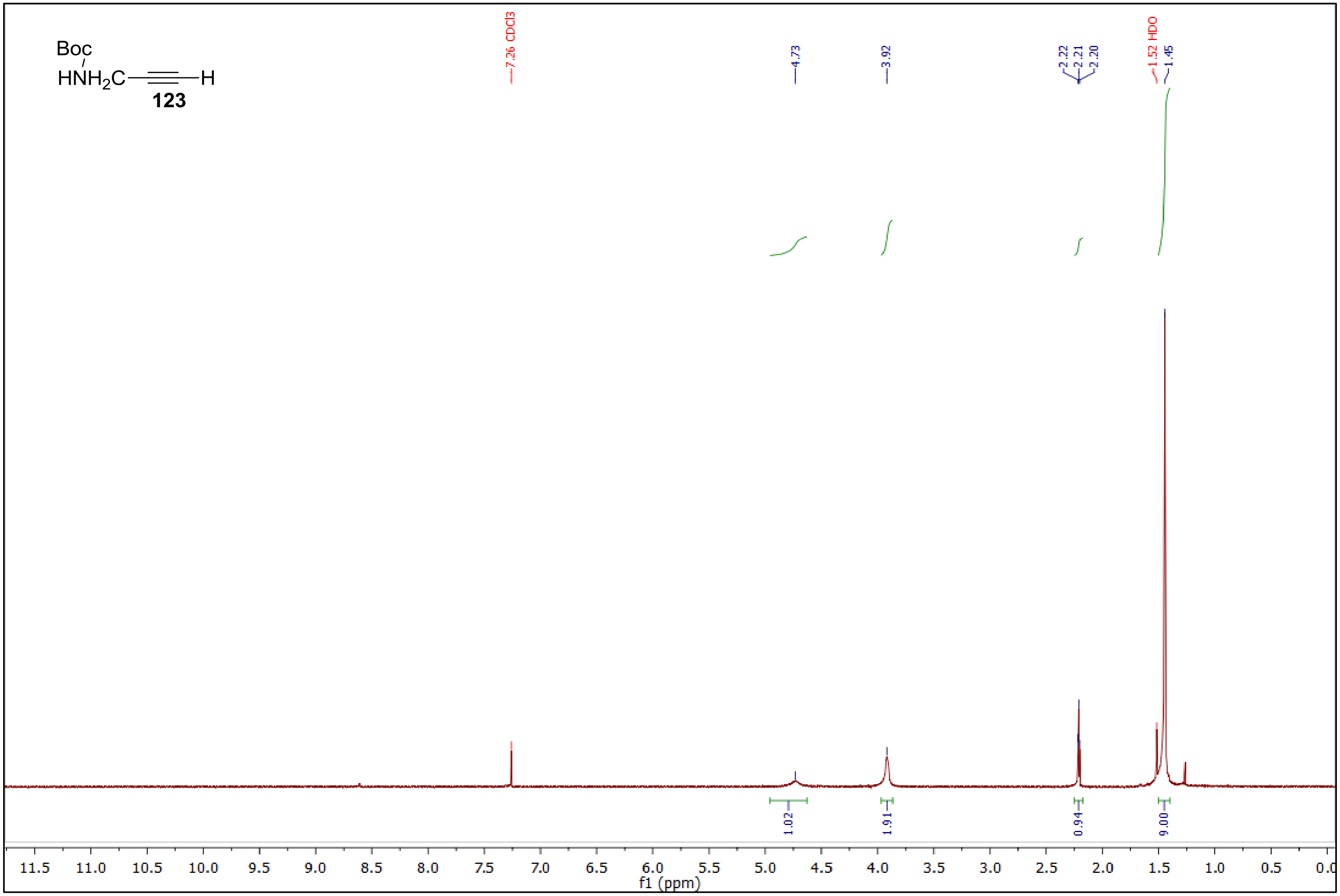
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **121**.



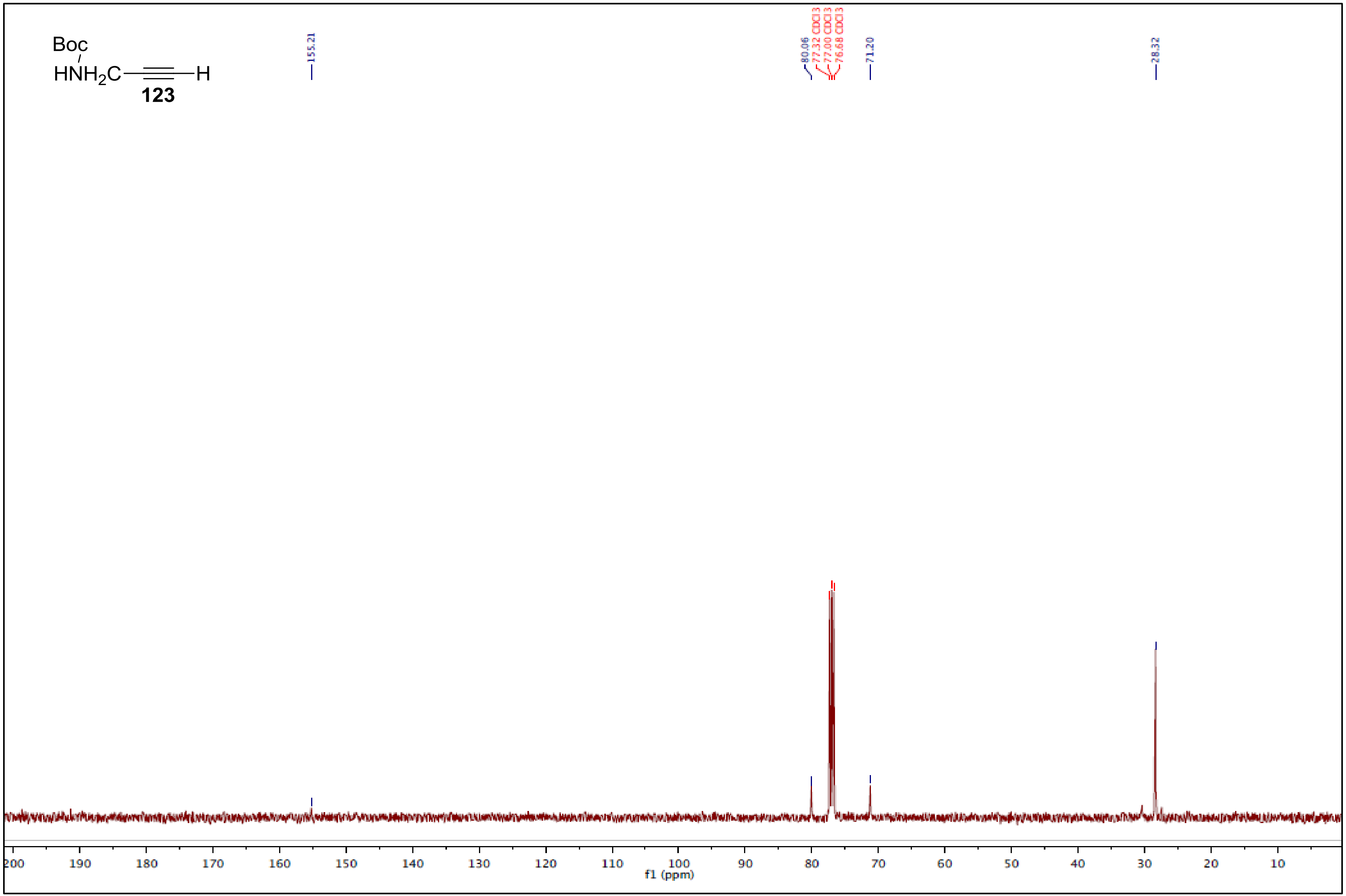
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **122**.



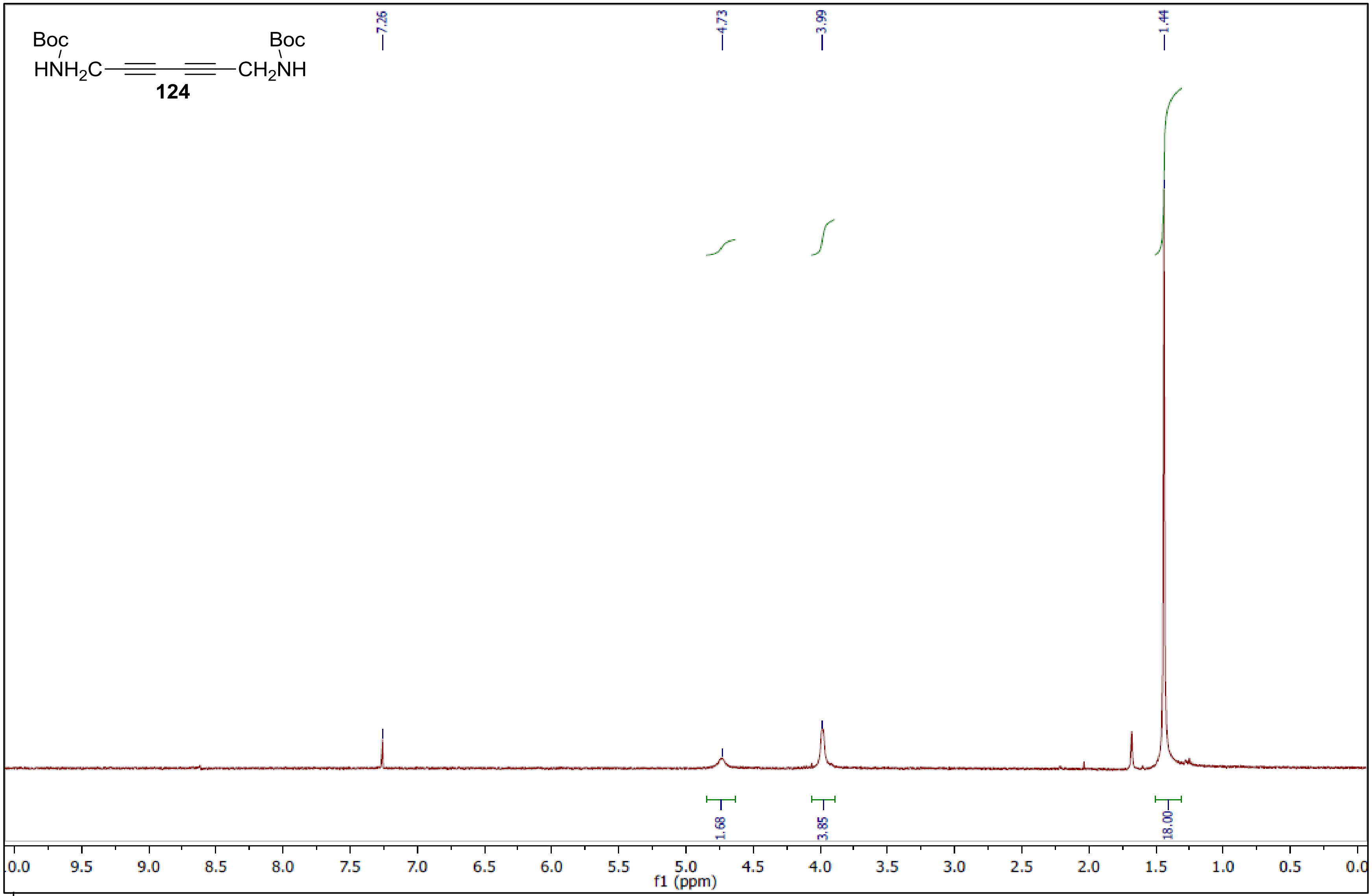
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **122**.



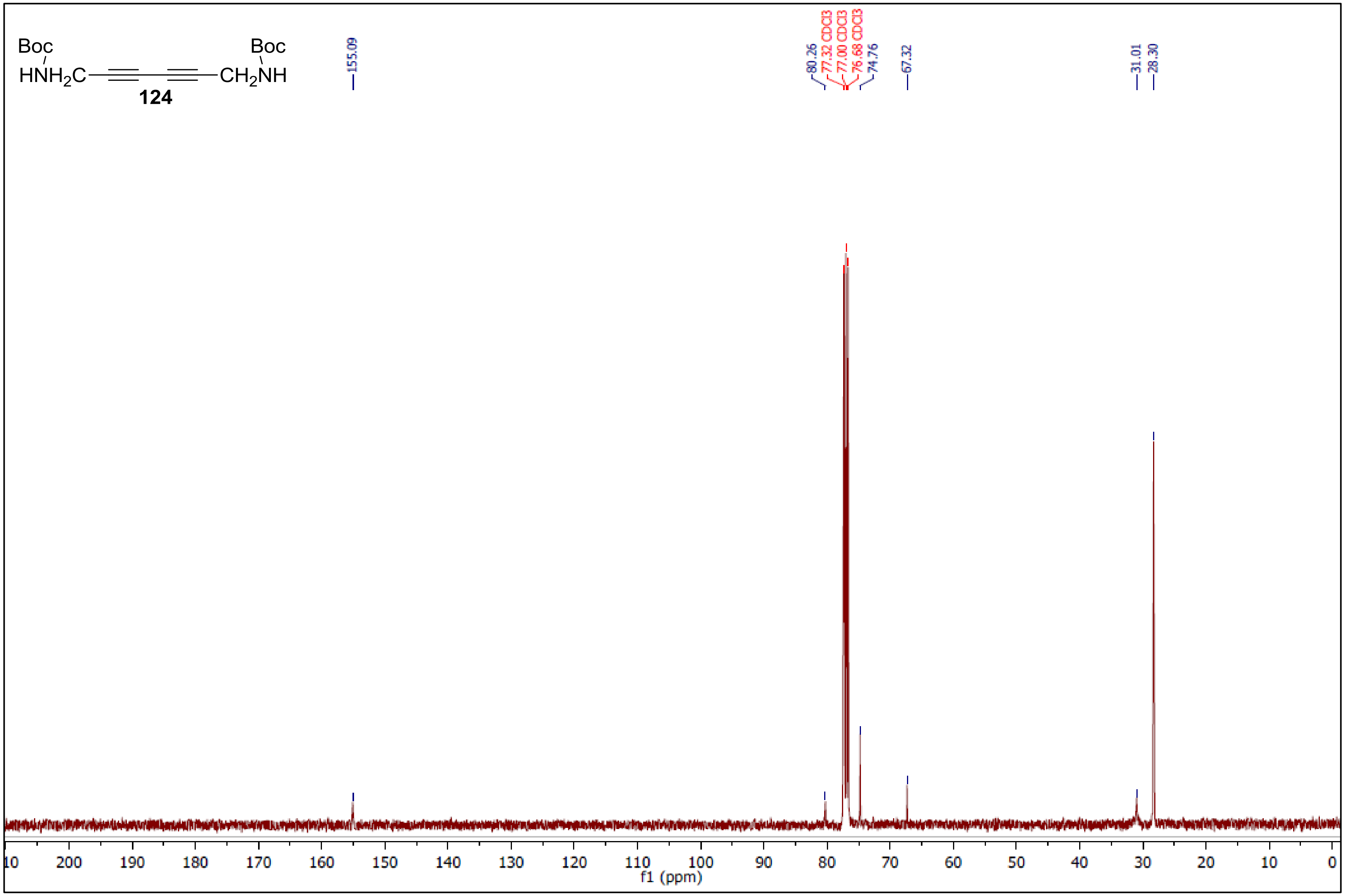
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **123.**



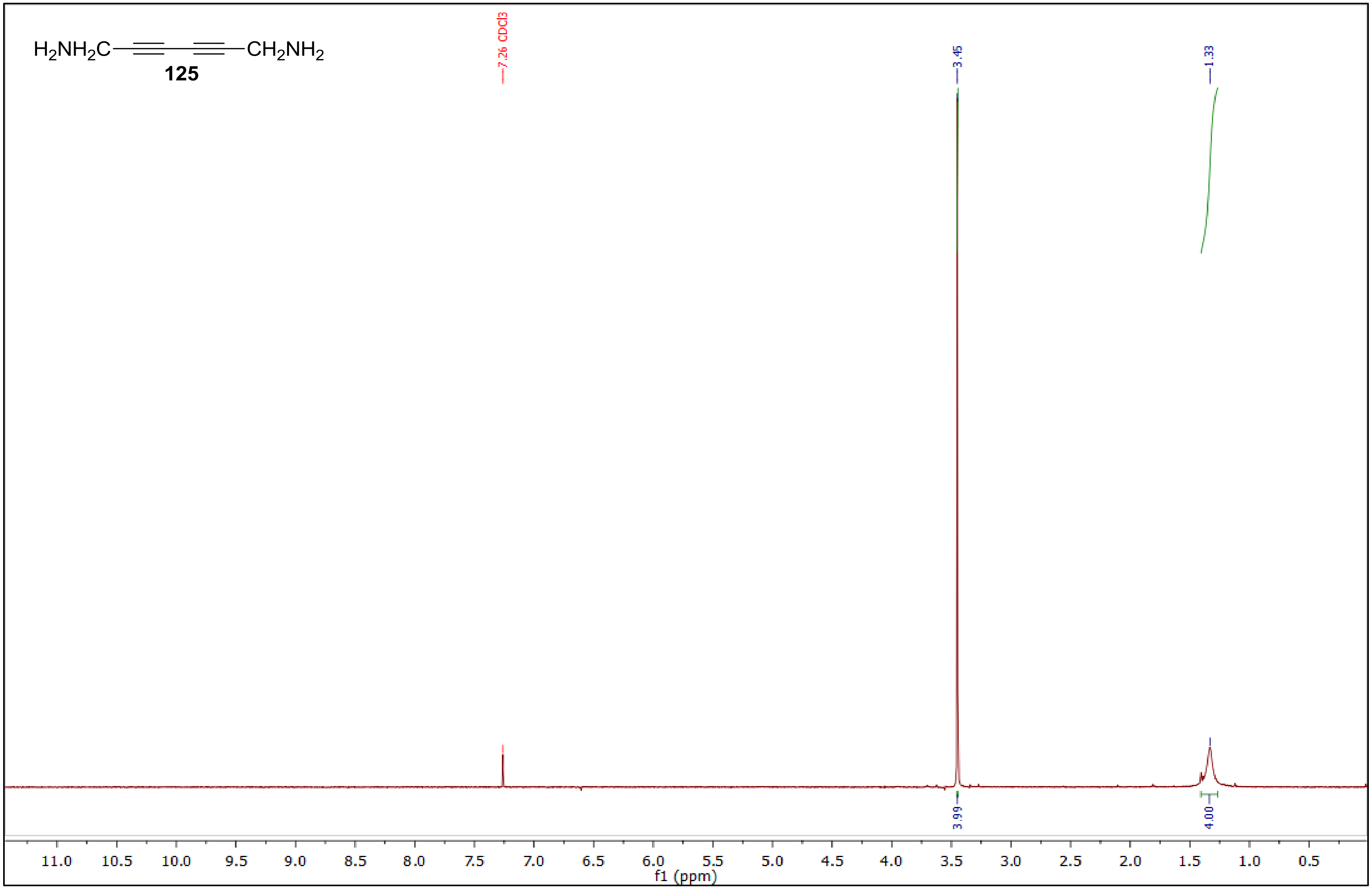
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **123**.



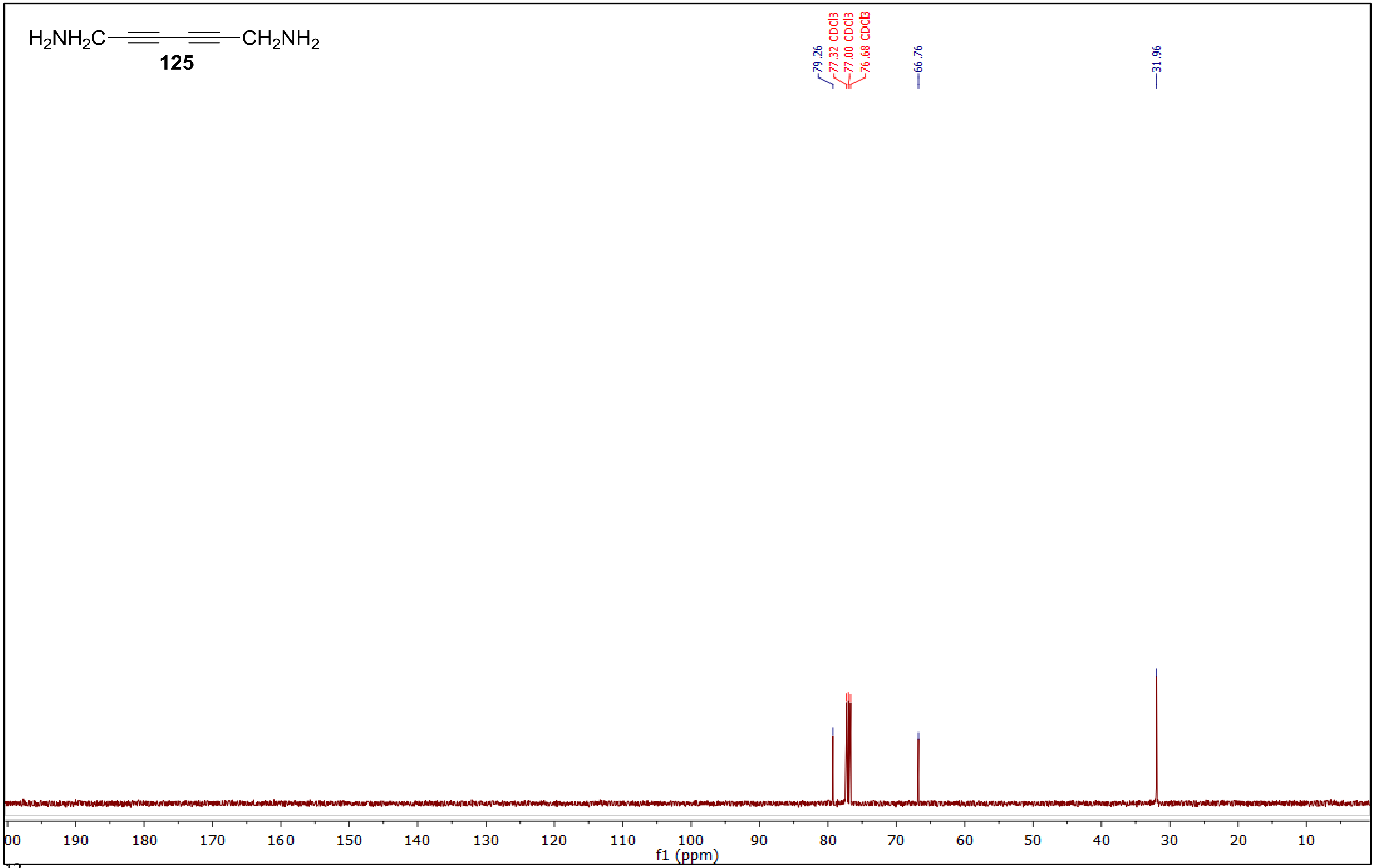
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **124.**



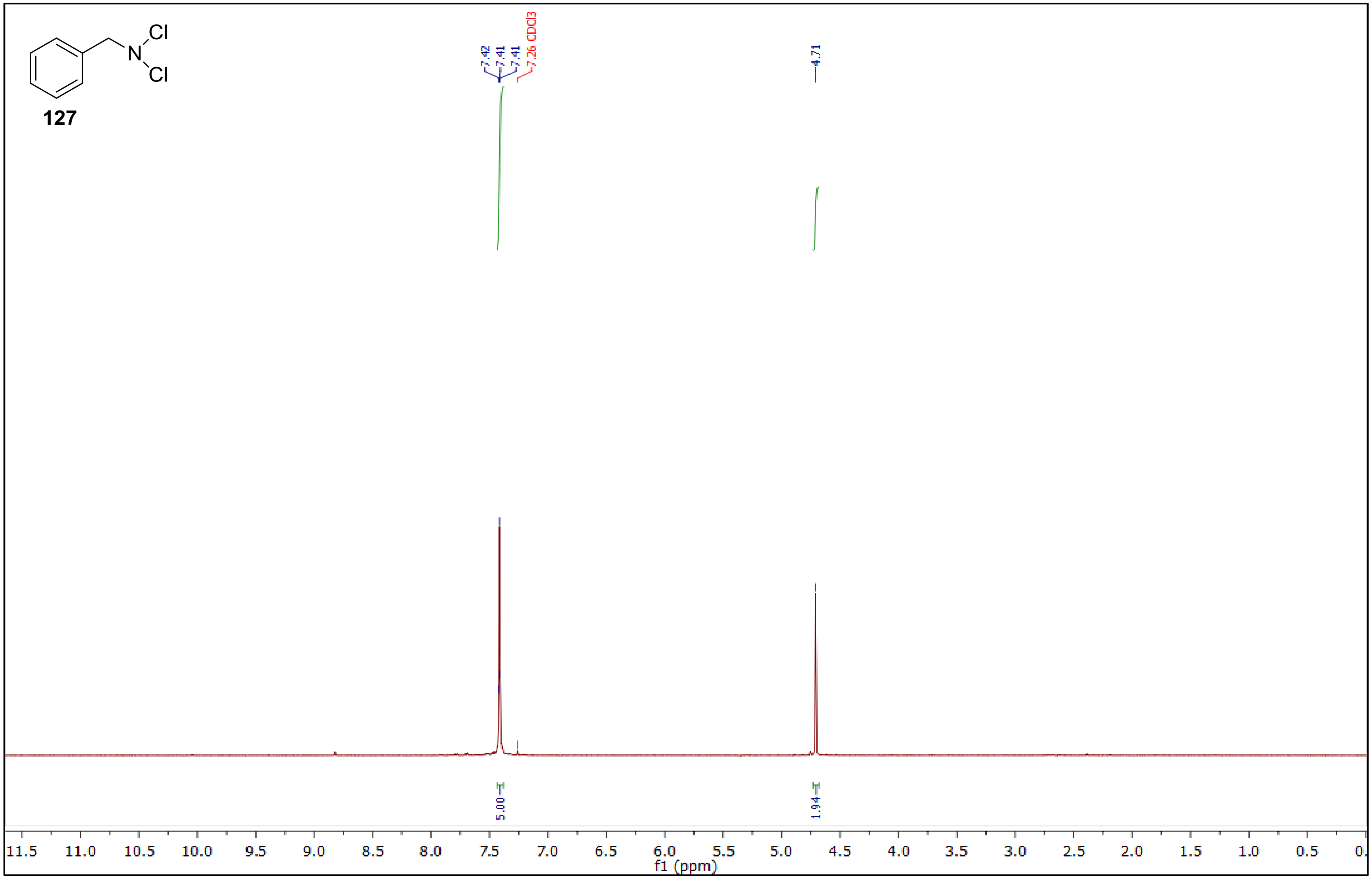
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **124**.



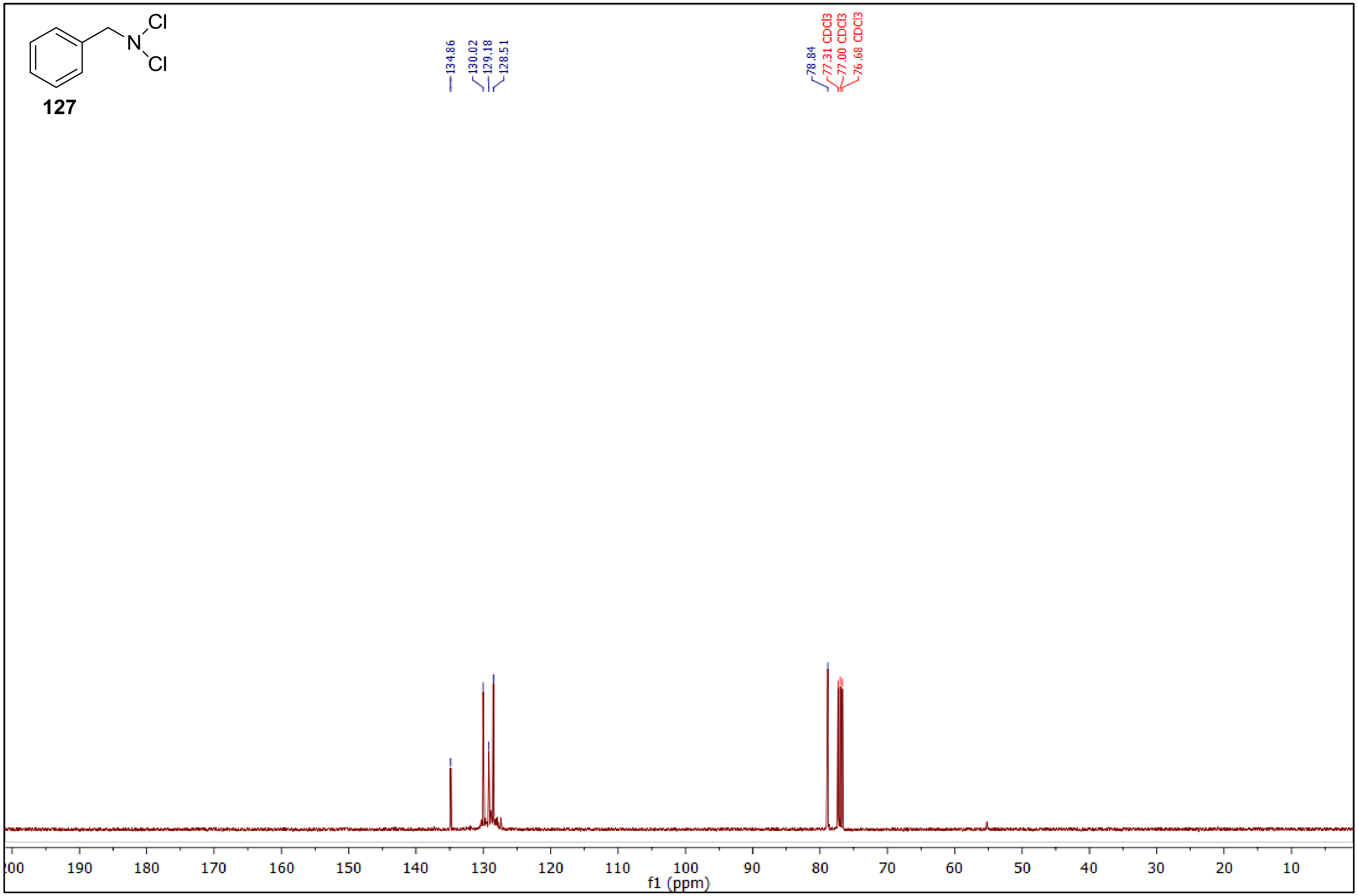
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **125.**



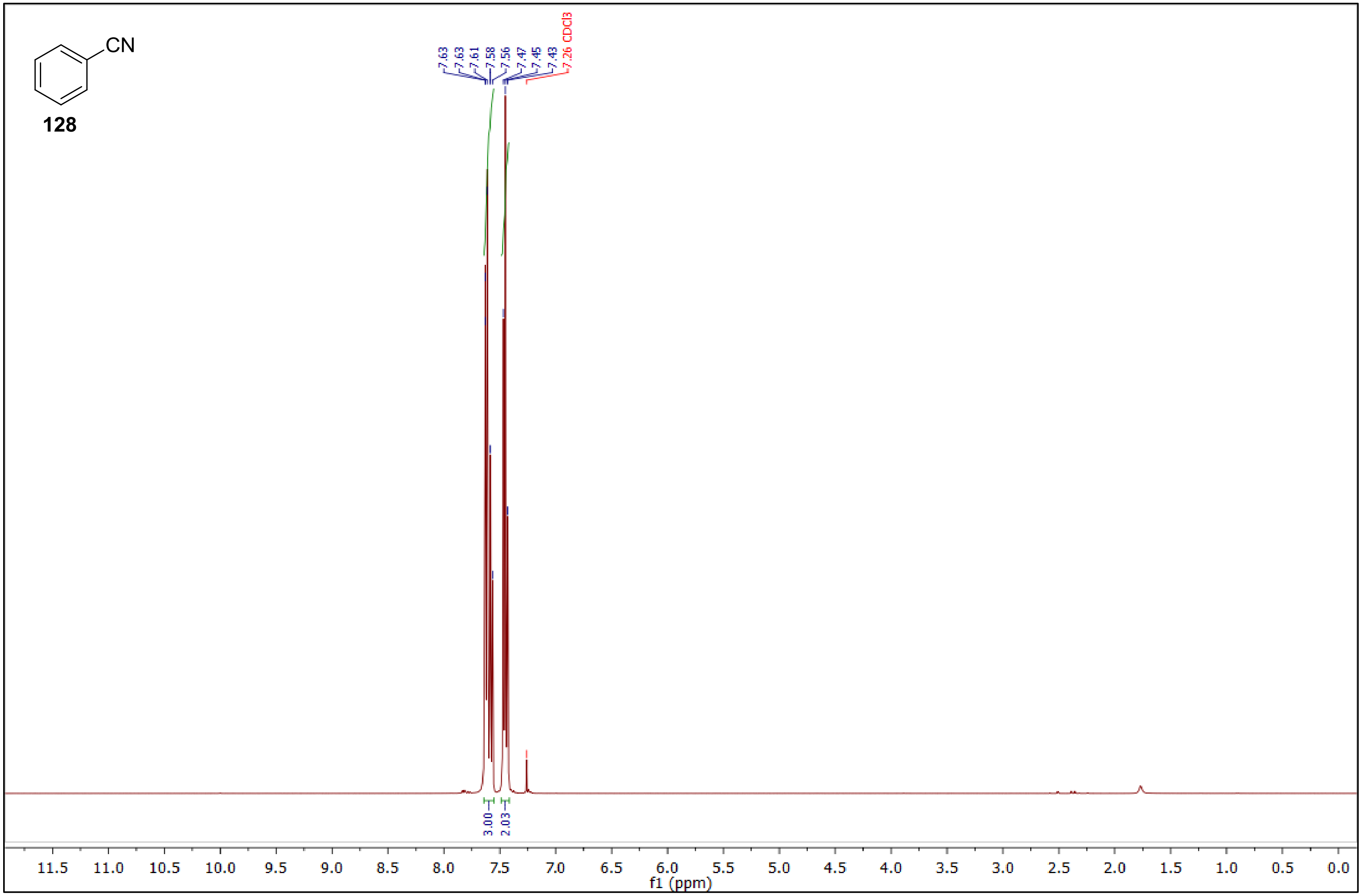
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **125**.



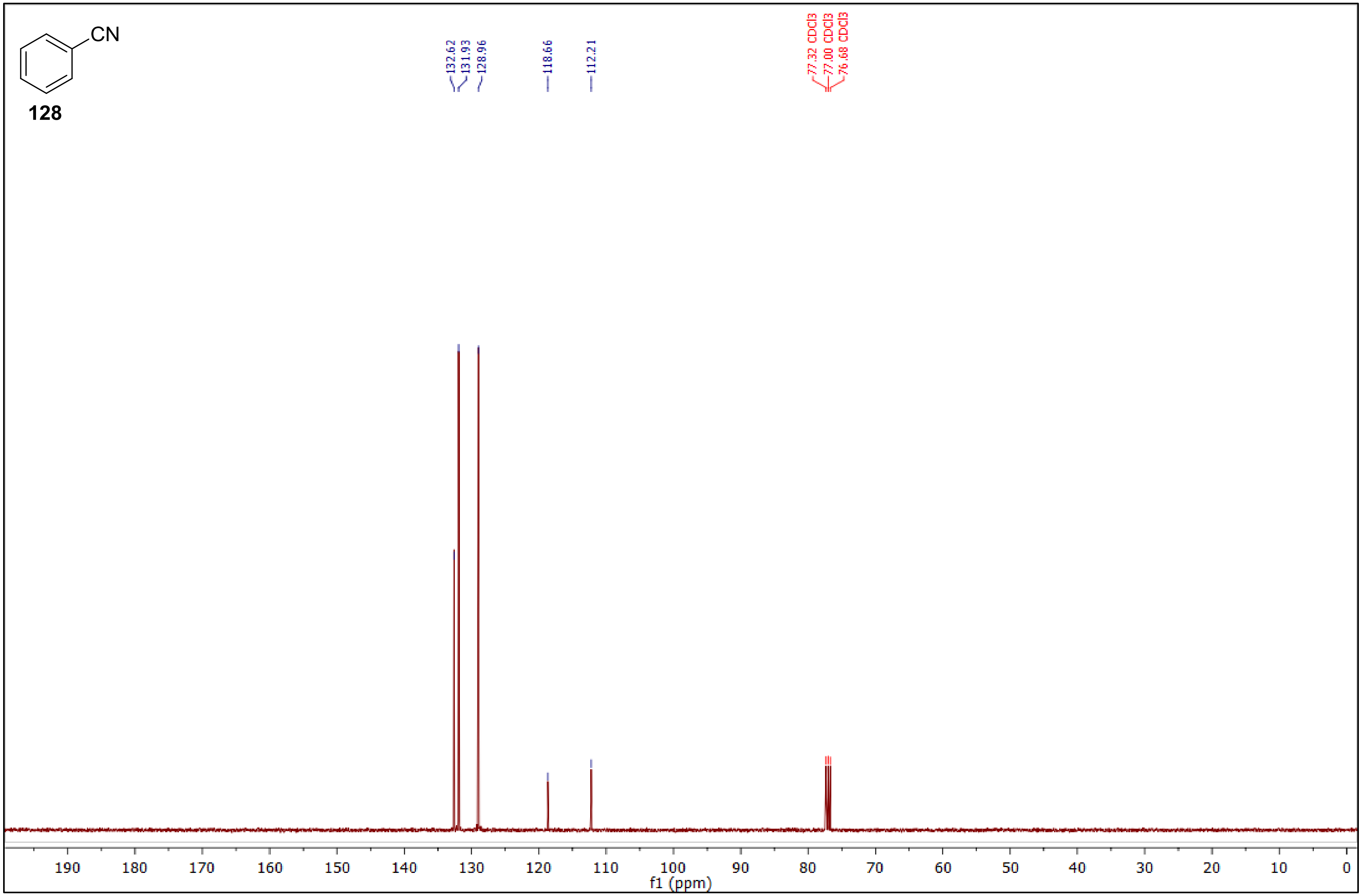
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **127.**



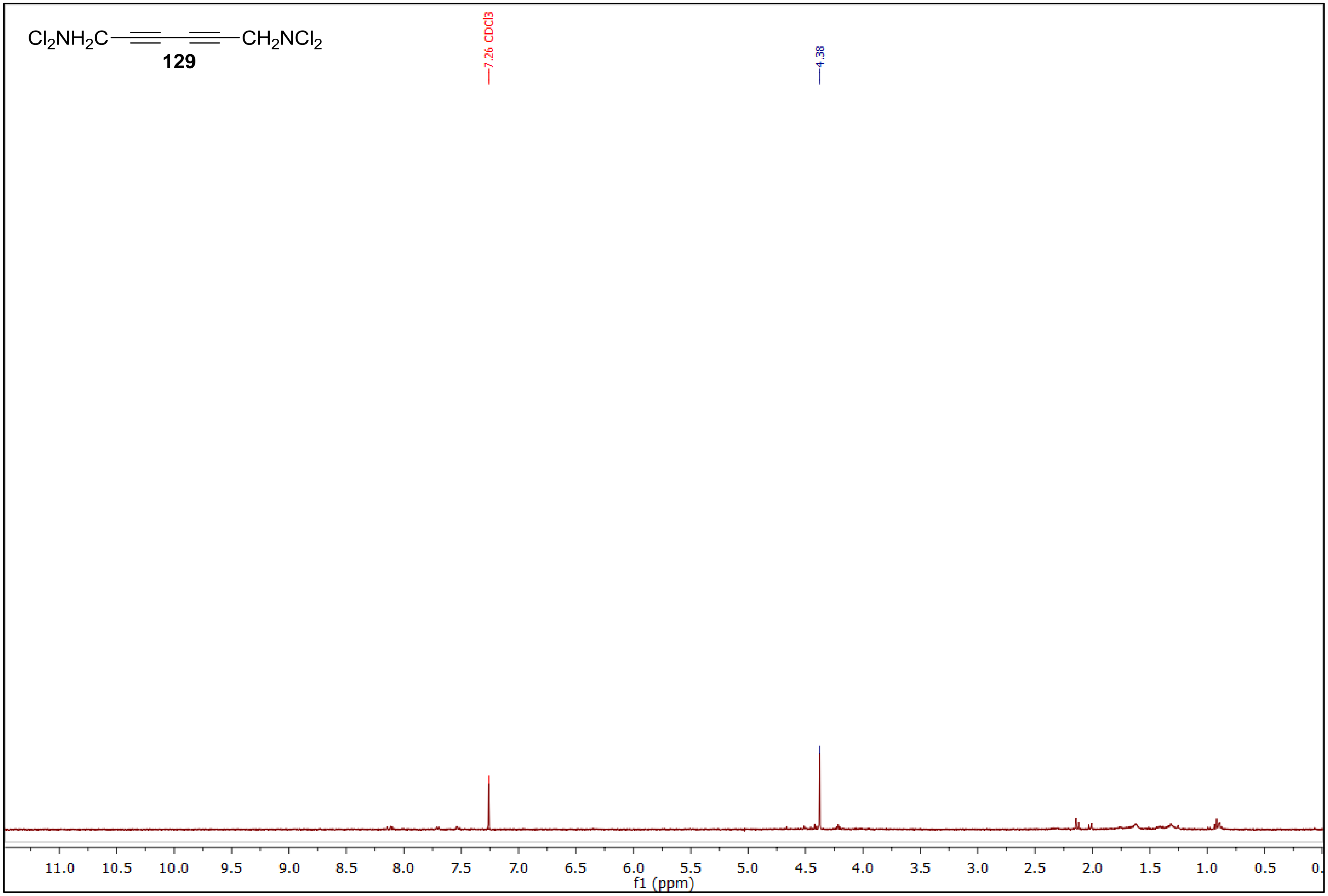
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **127**



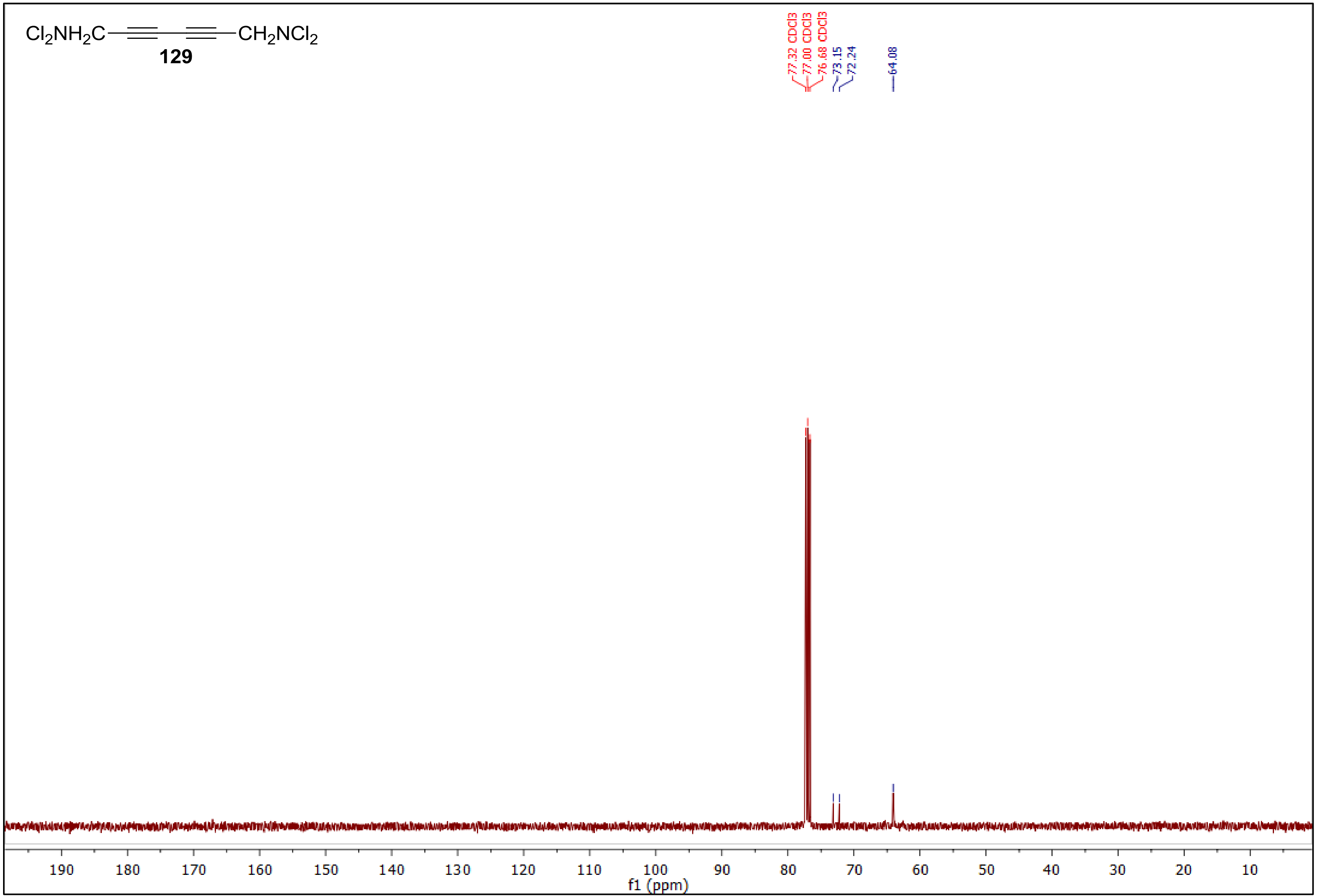
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **128**.



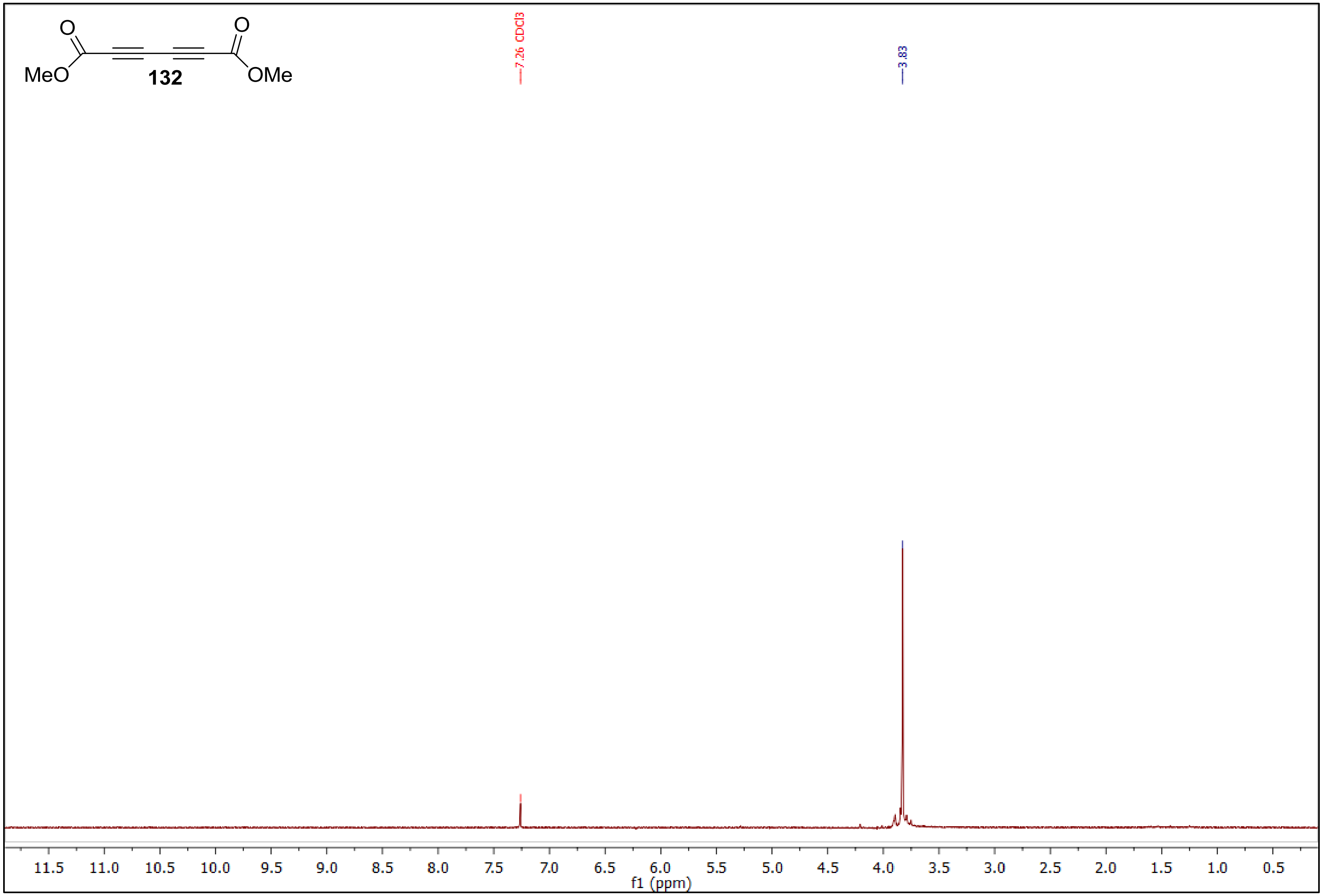
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **128**.



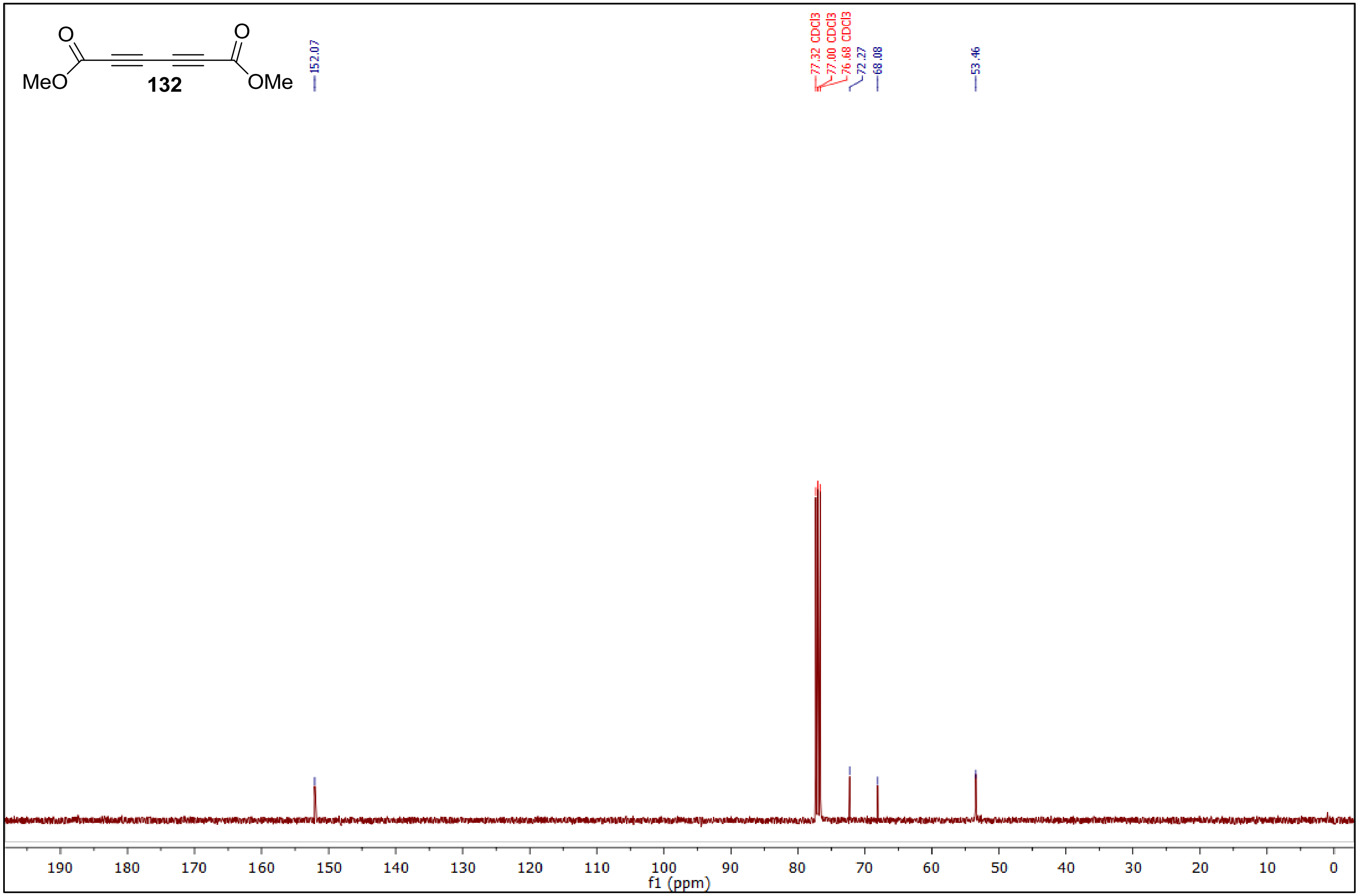
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **129**.



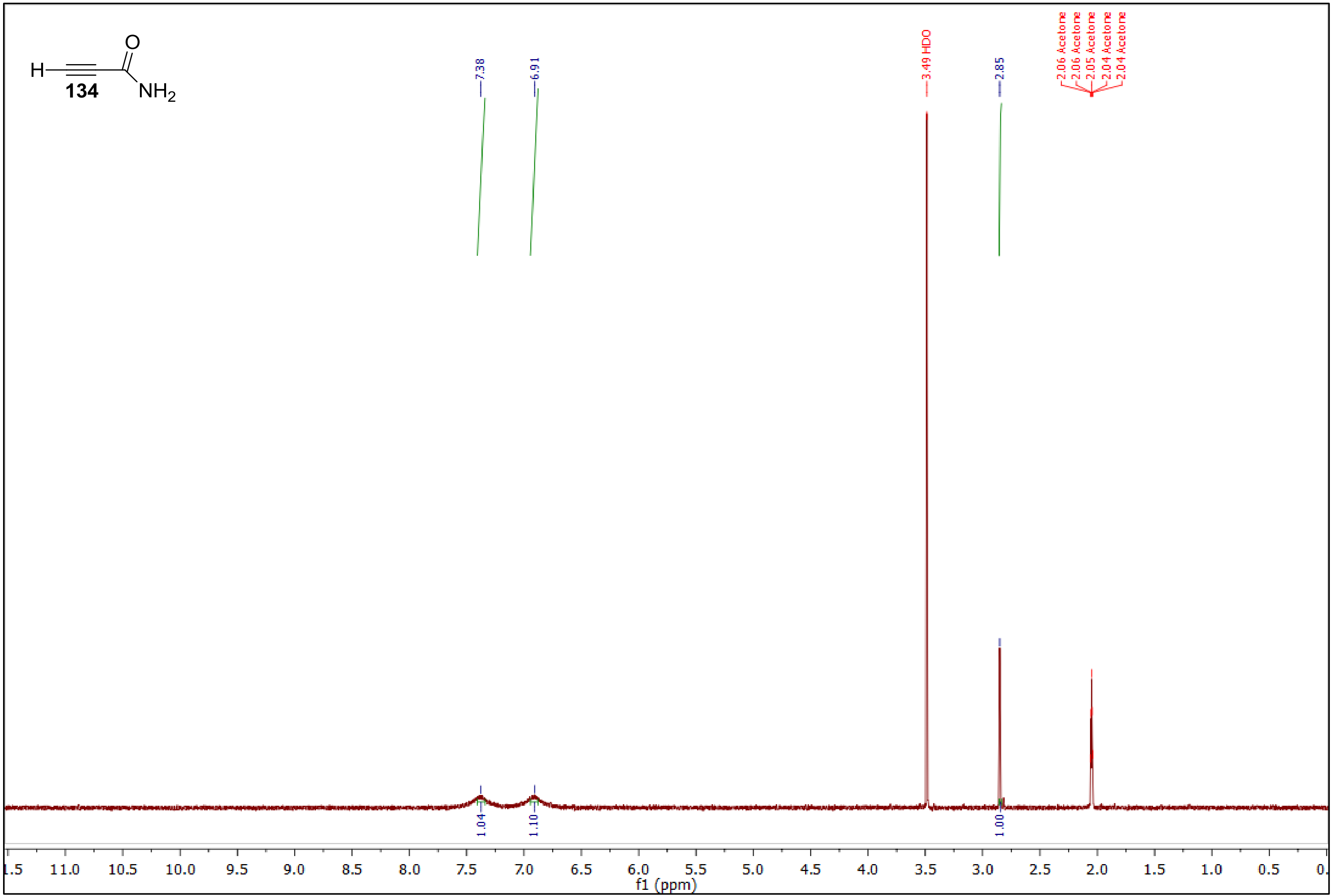
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **129**.



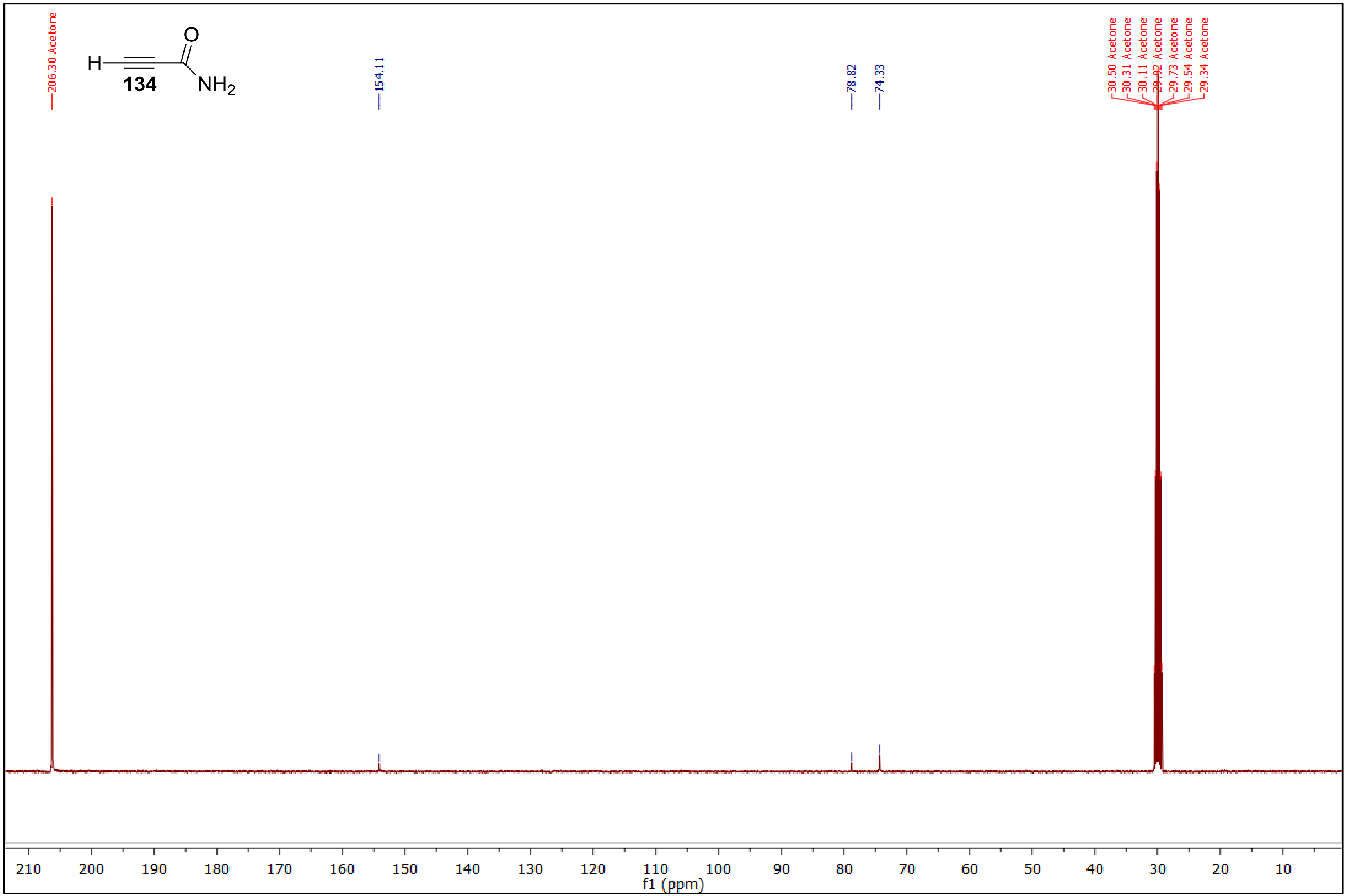
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **132.**



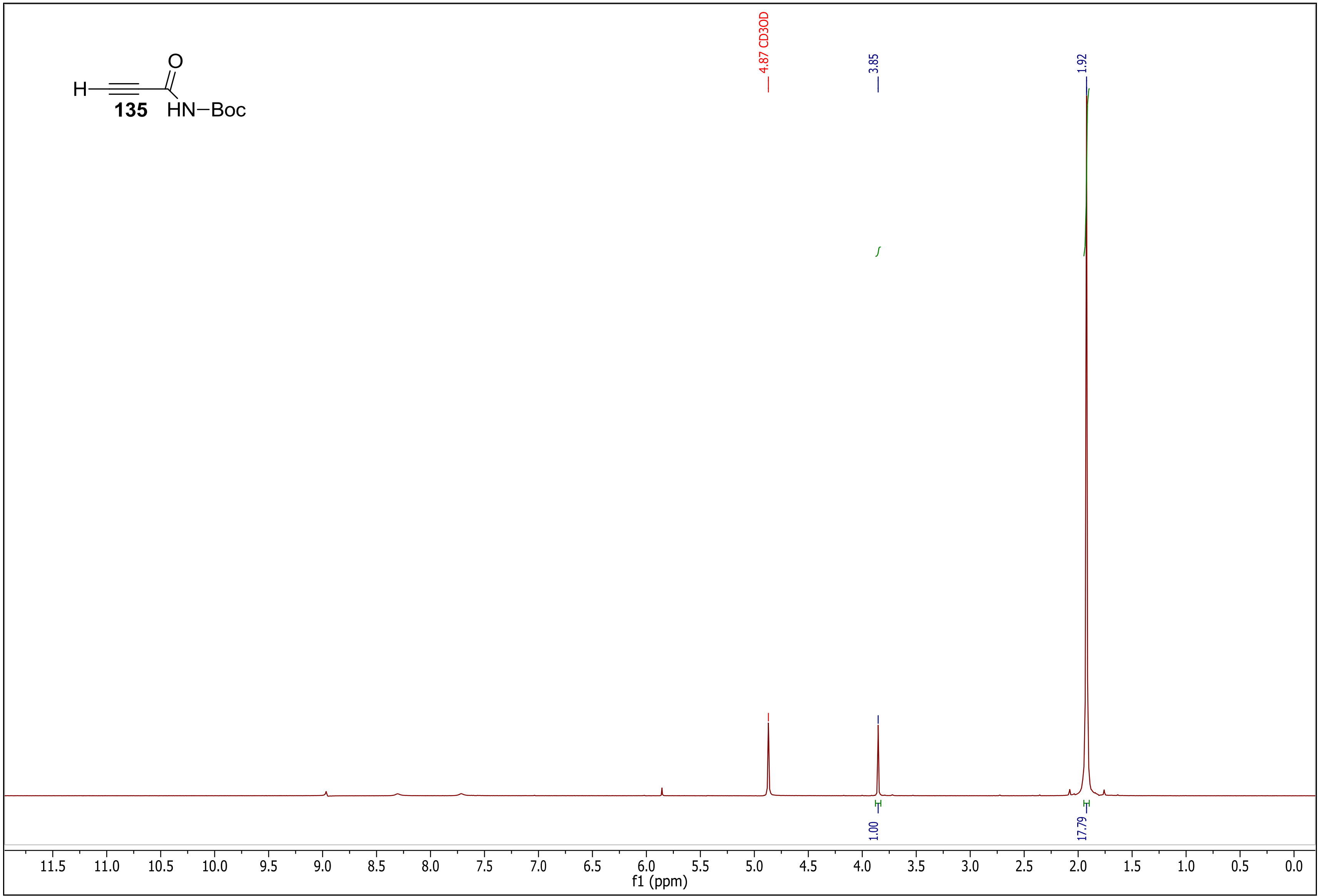
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **132**.



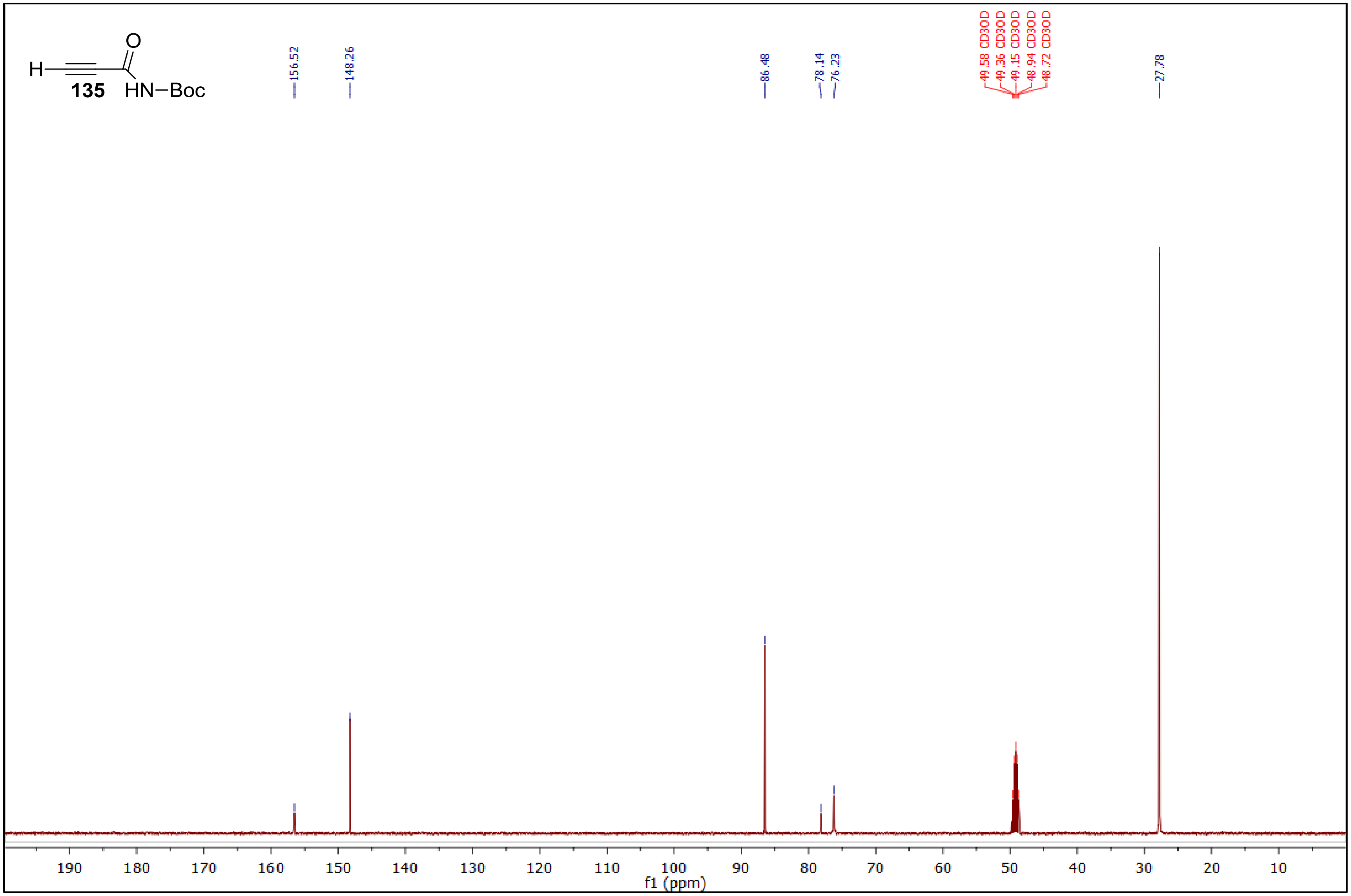
^{1}H NMR spectrum (400 MHz, acetone-d_6) of compound **134**.



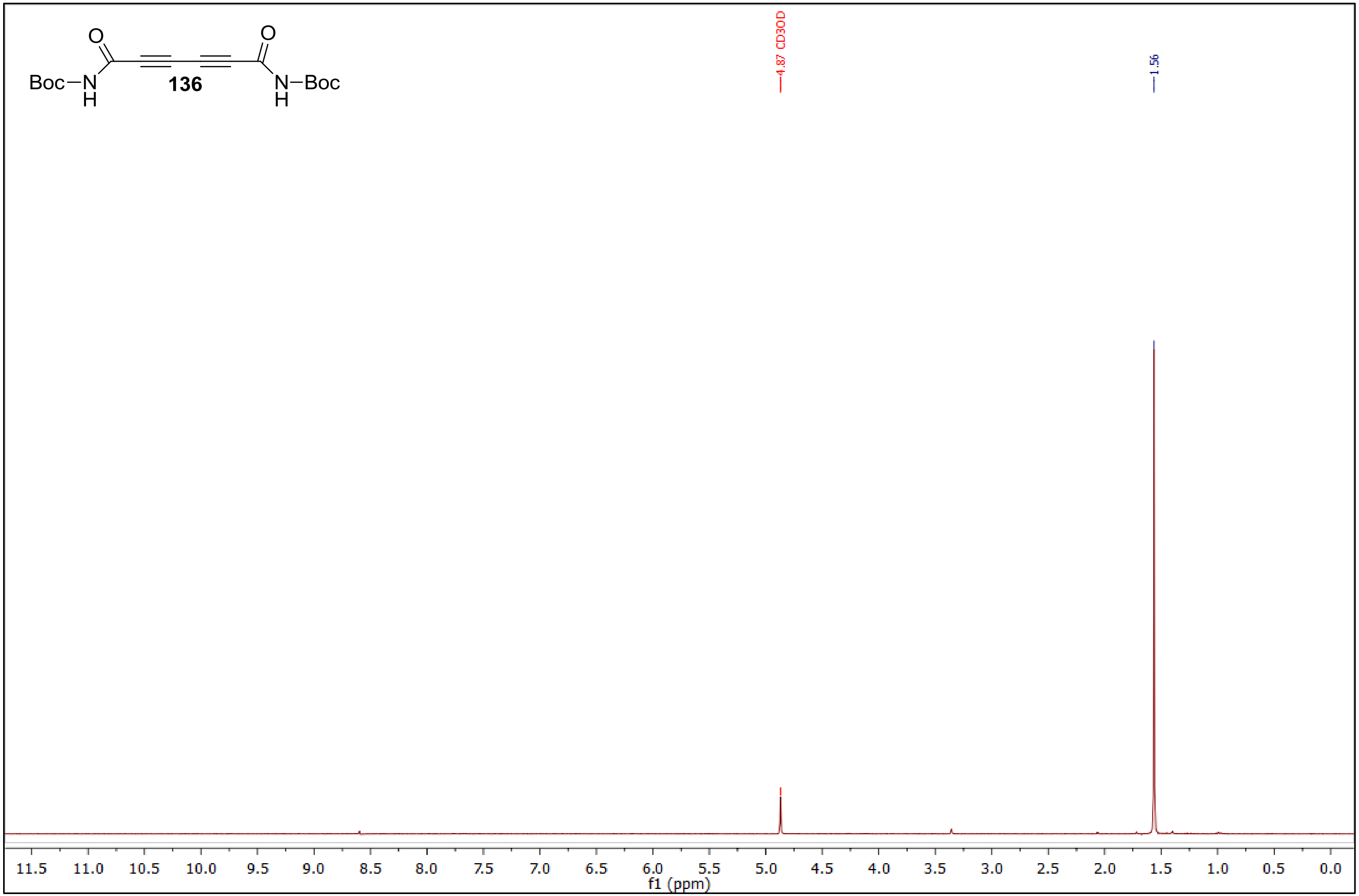
^{13}C NMR spectrum (100 MHz, acetone-d_6) of compound **134**.



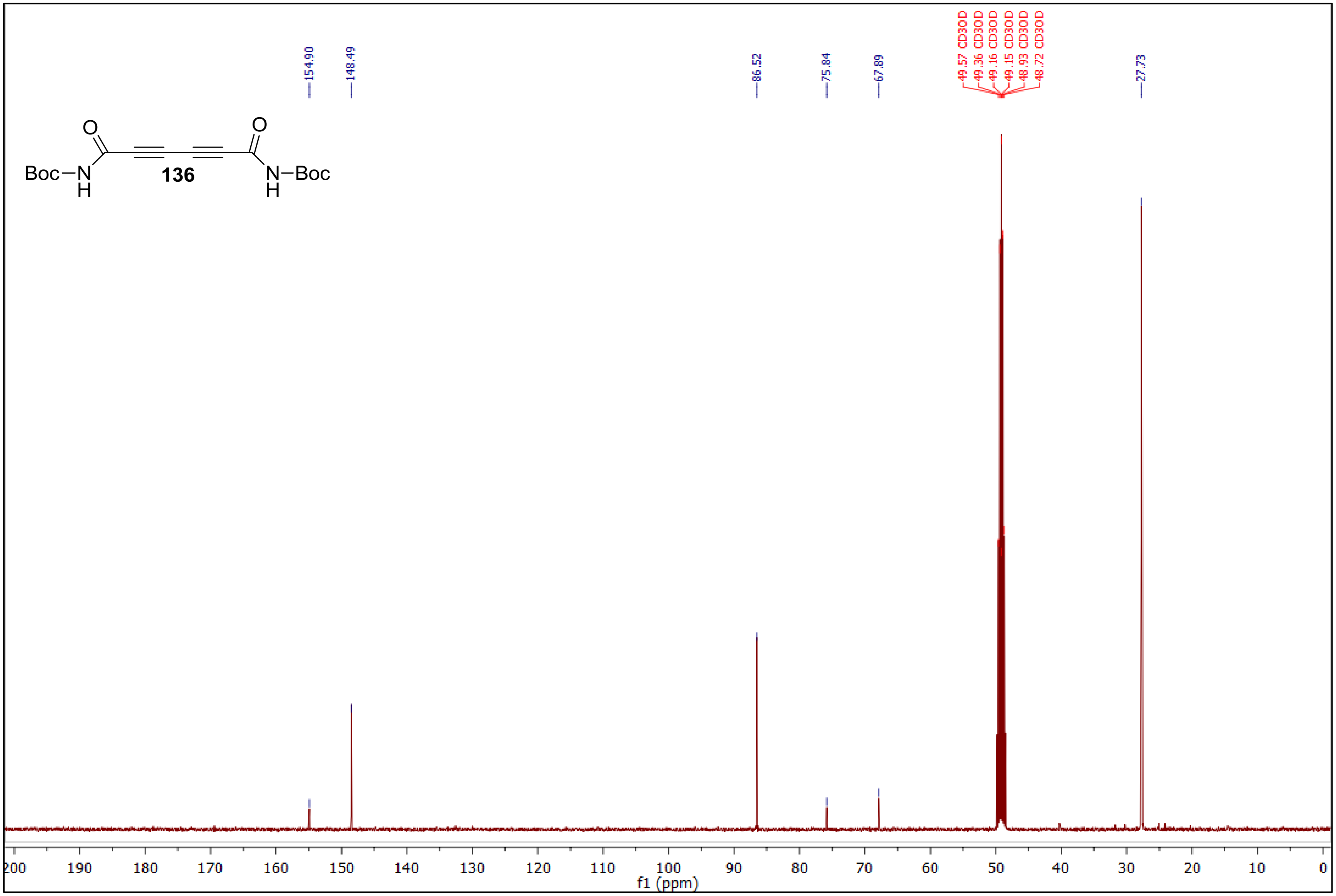
^{1}H NMR spectrum (400 MHz, CD_3OD) of compound **135**.



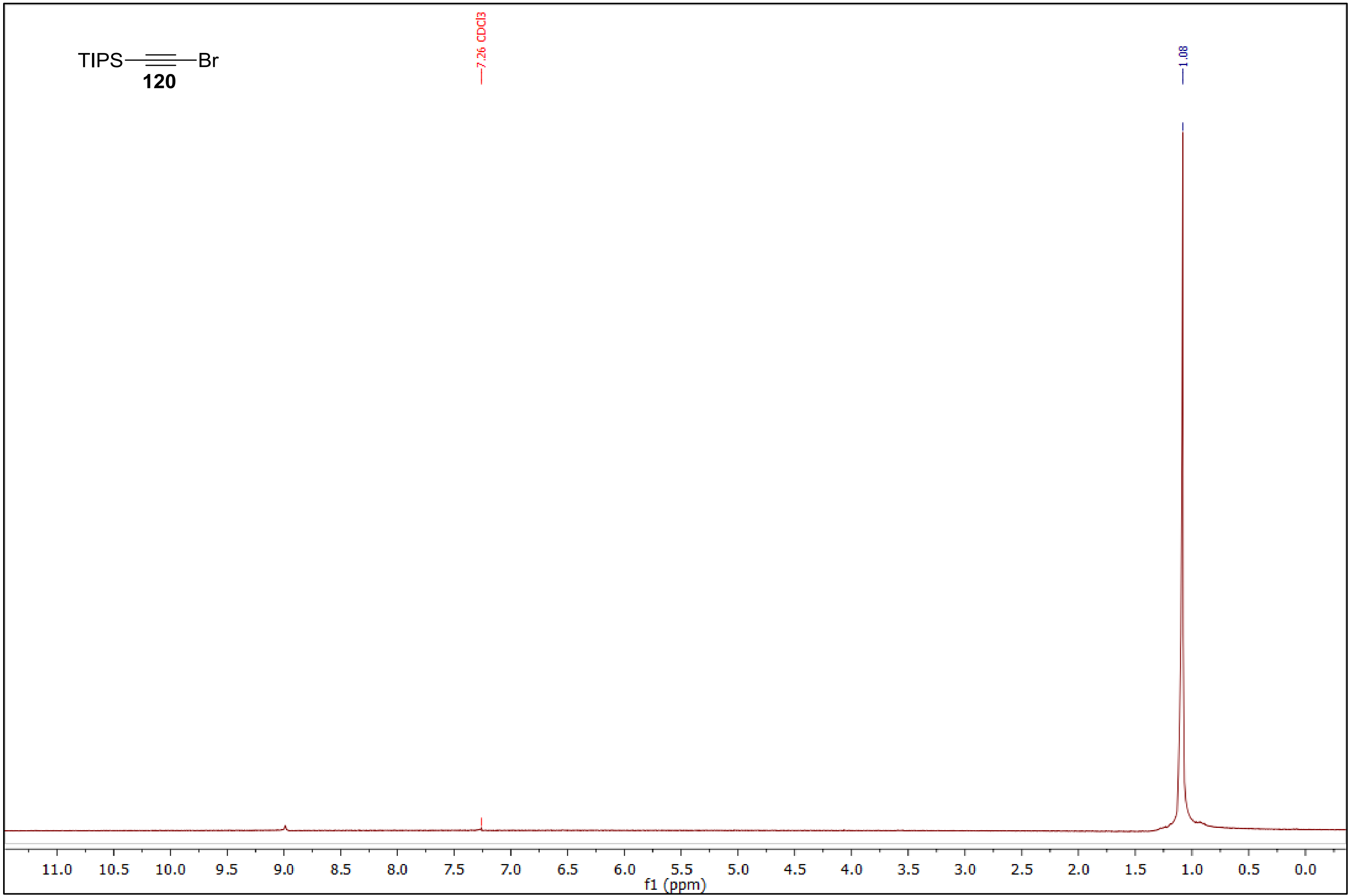
^{13}C NMR spectrum (100 MHz, CD$_3$OD) of compound **135**.



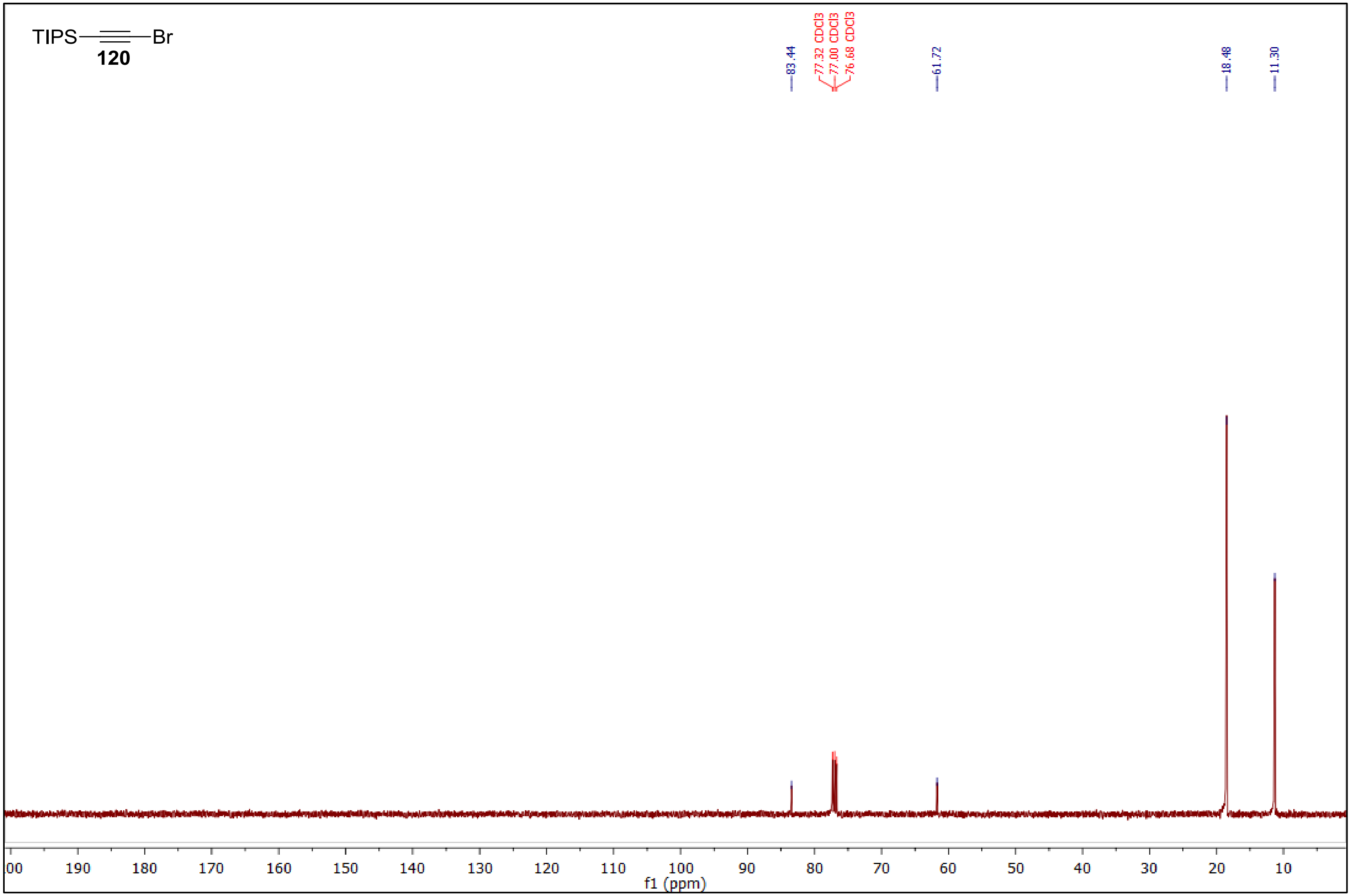
^{1}H NMR spectrum (400 MHz, CD_3OD) of compound **136**



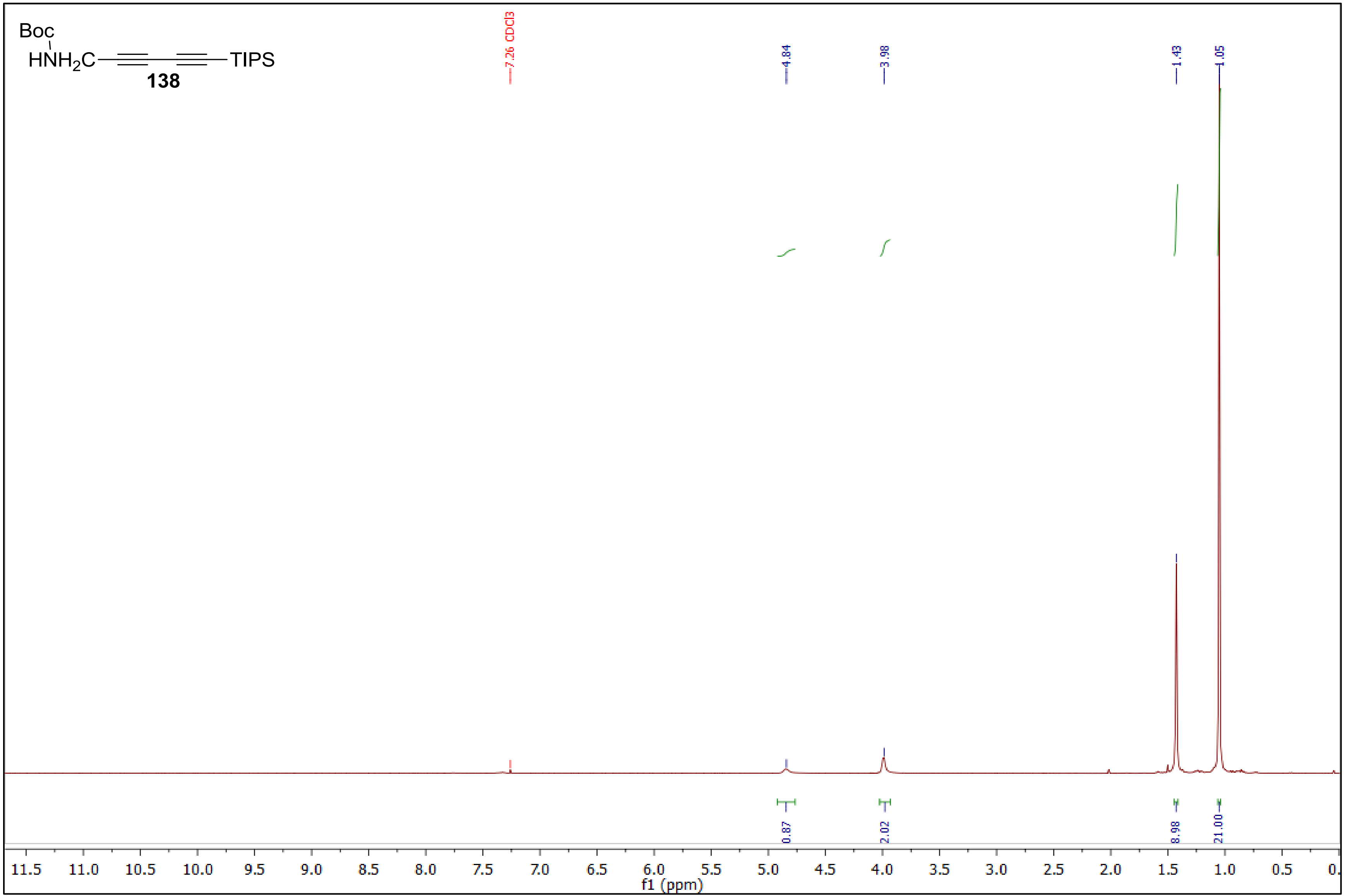
^{13}C NMR spectrum (100 MHz, CD_3OD) of compound **136**.



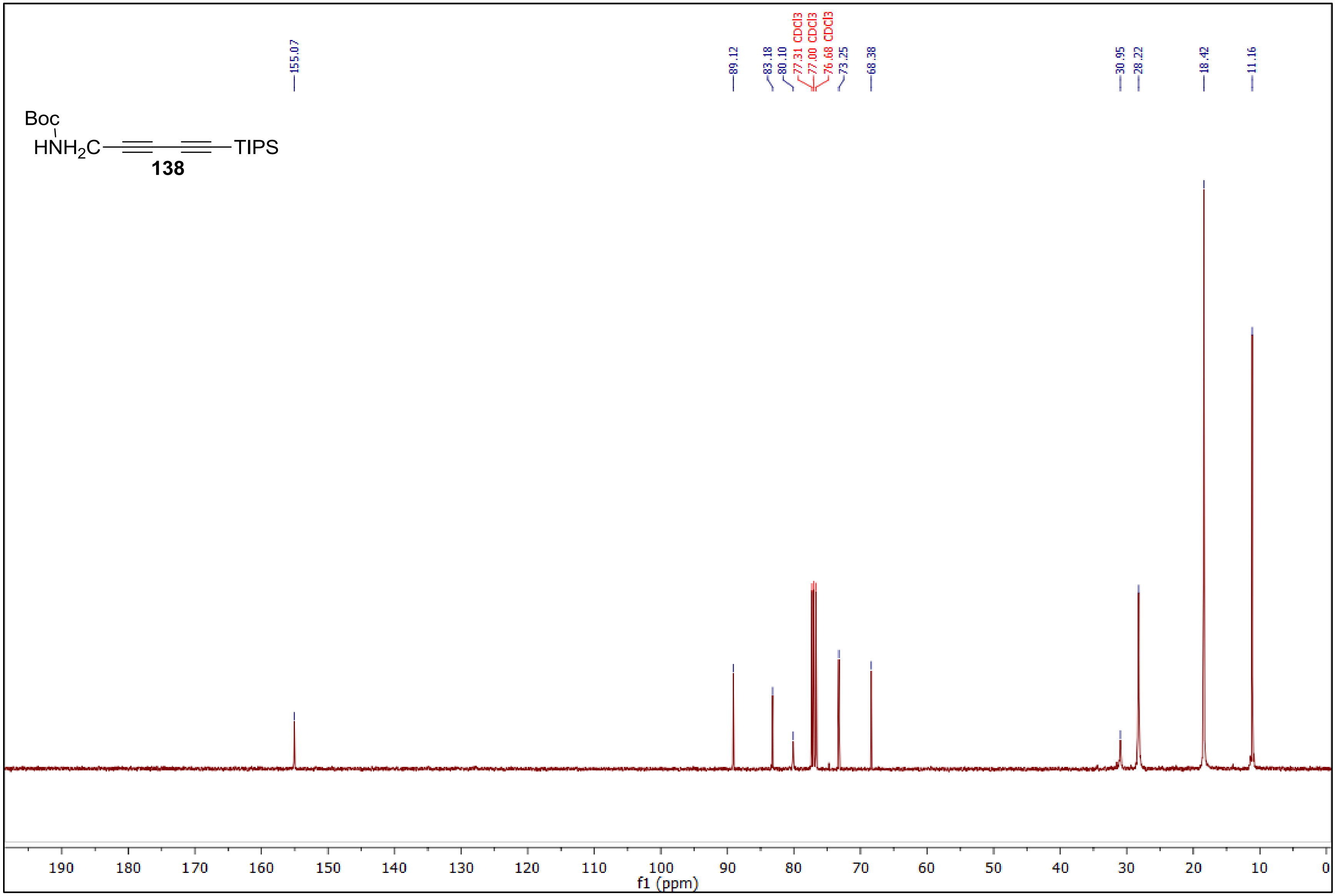
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **120**.



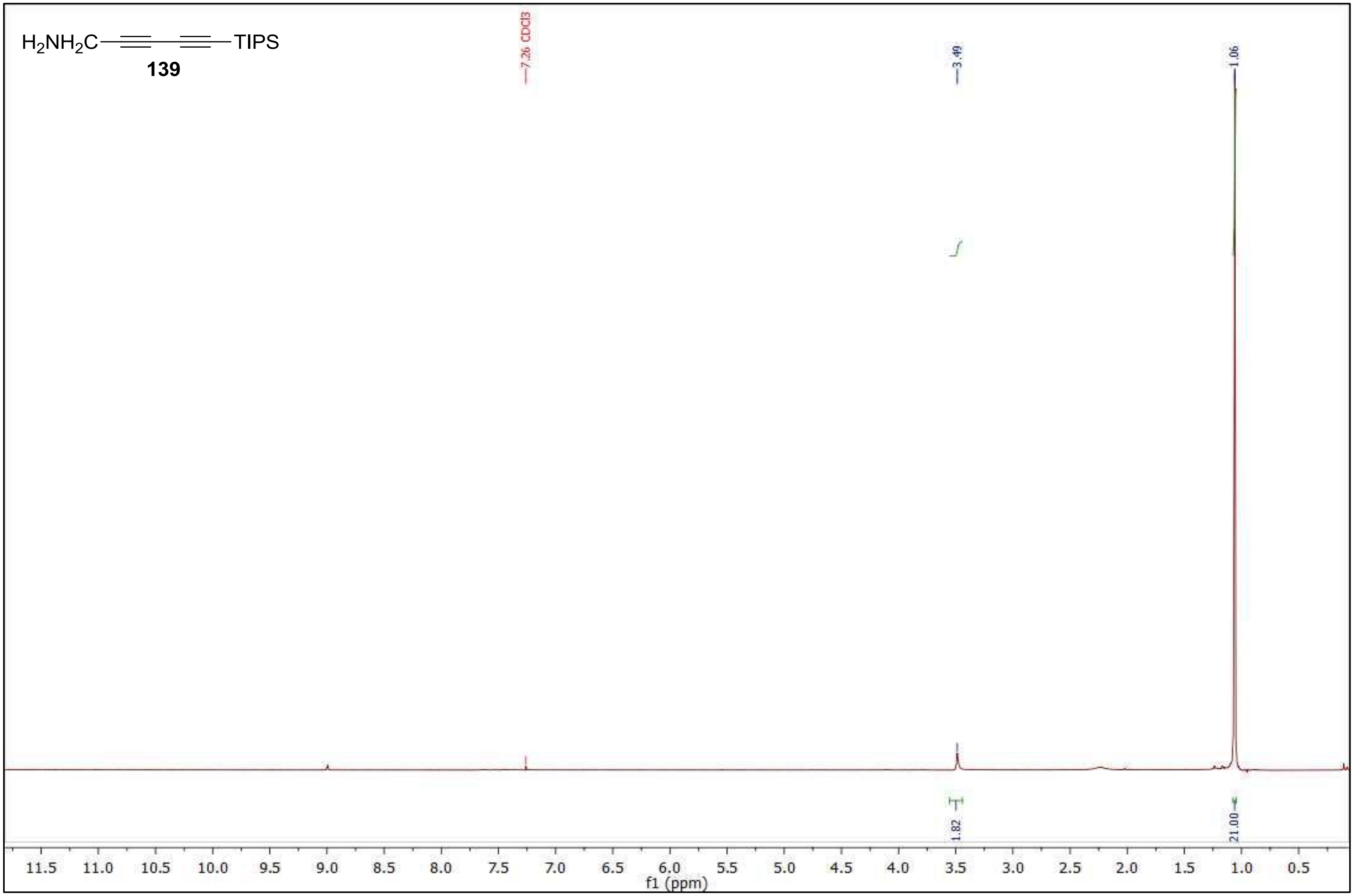
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **120**.



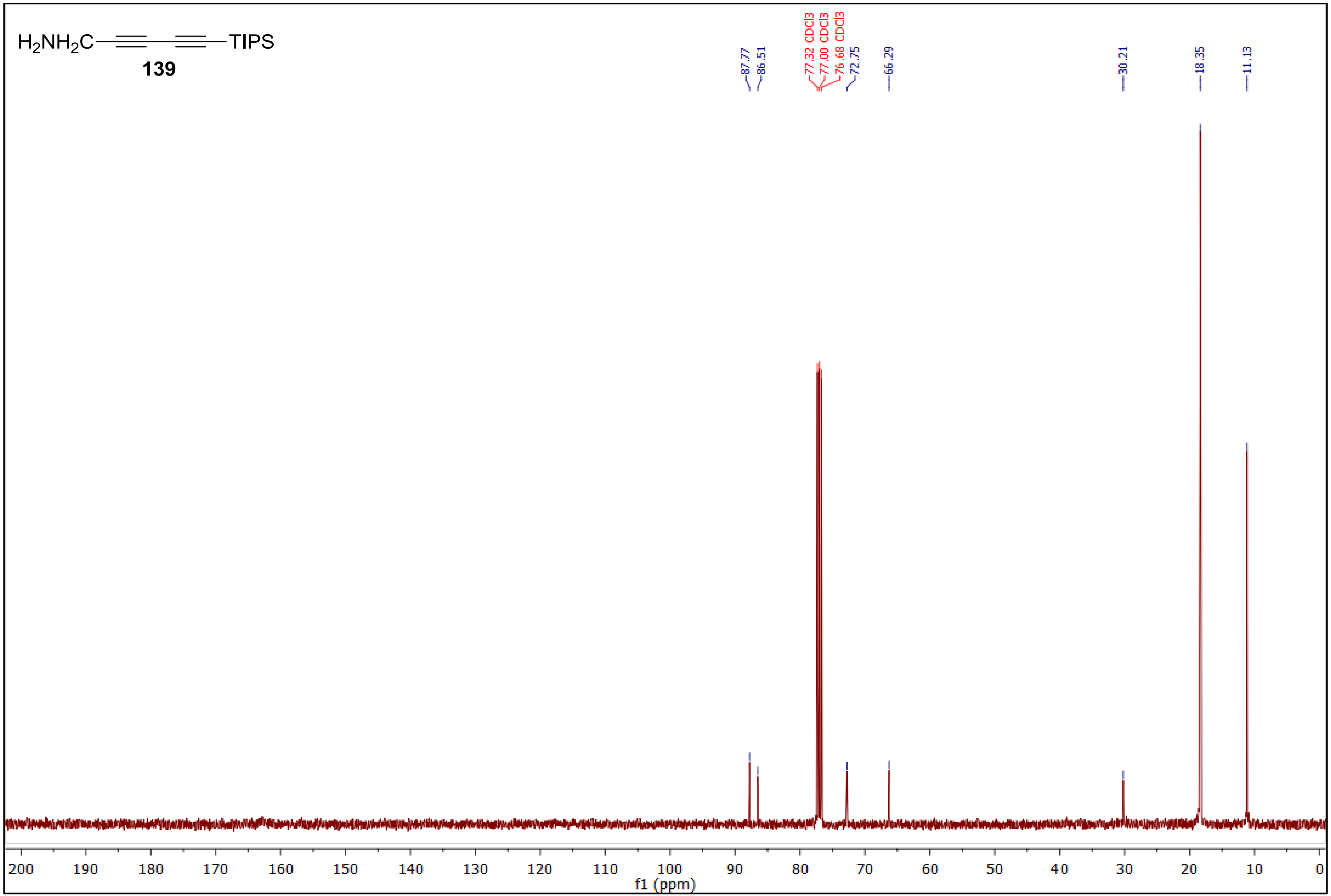
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **138.**



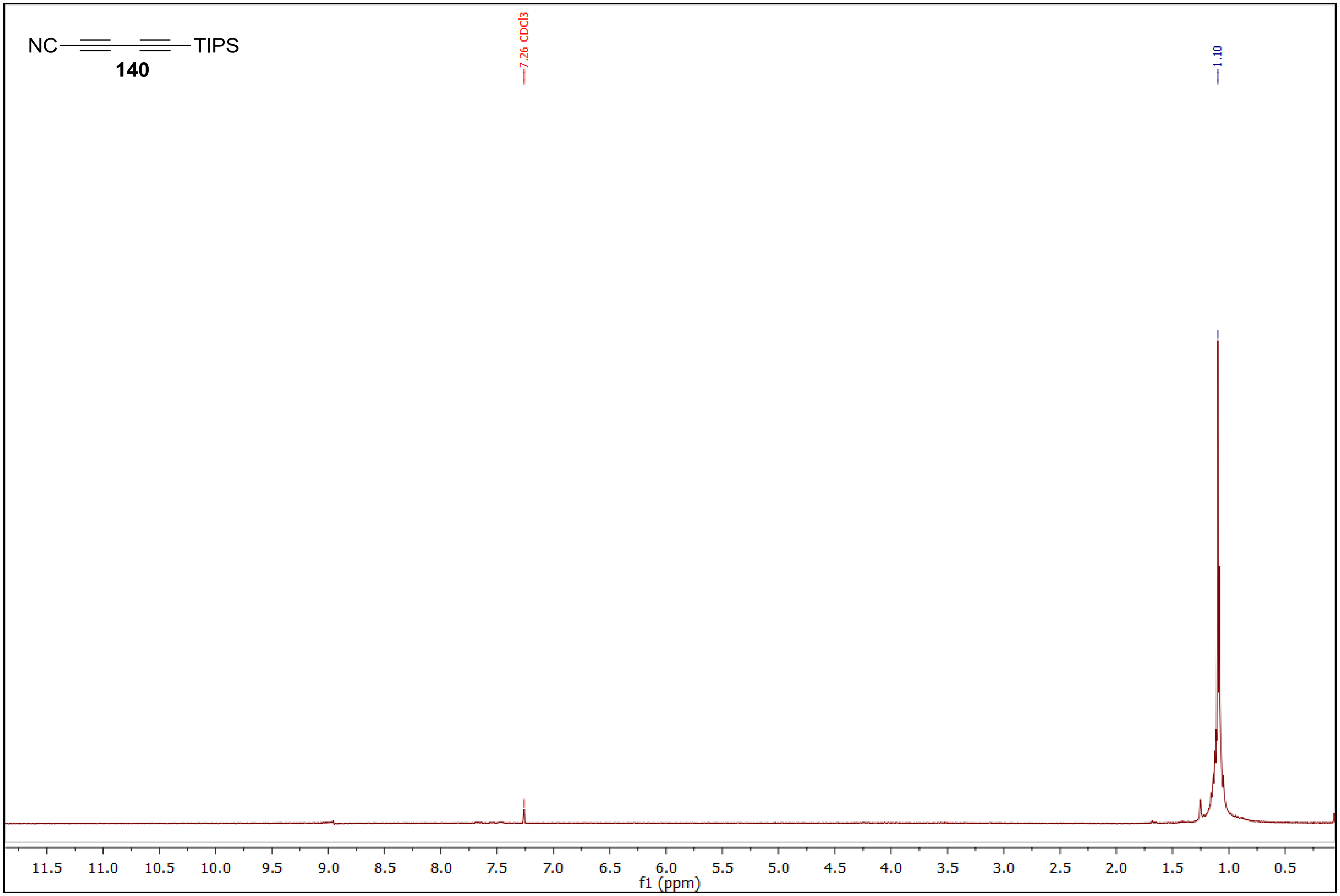
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **138**.



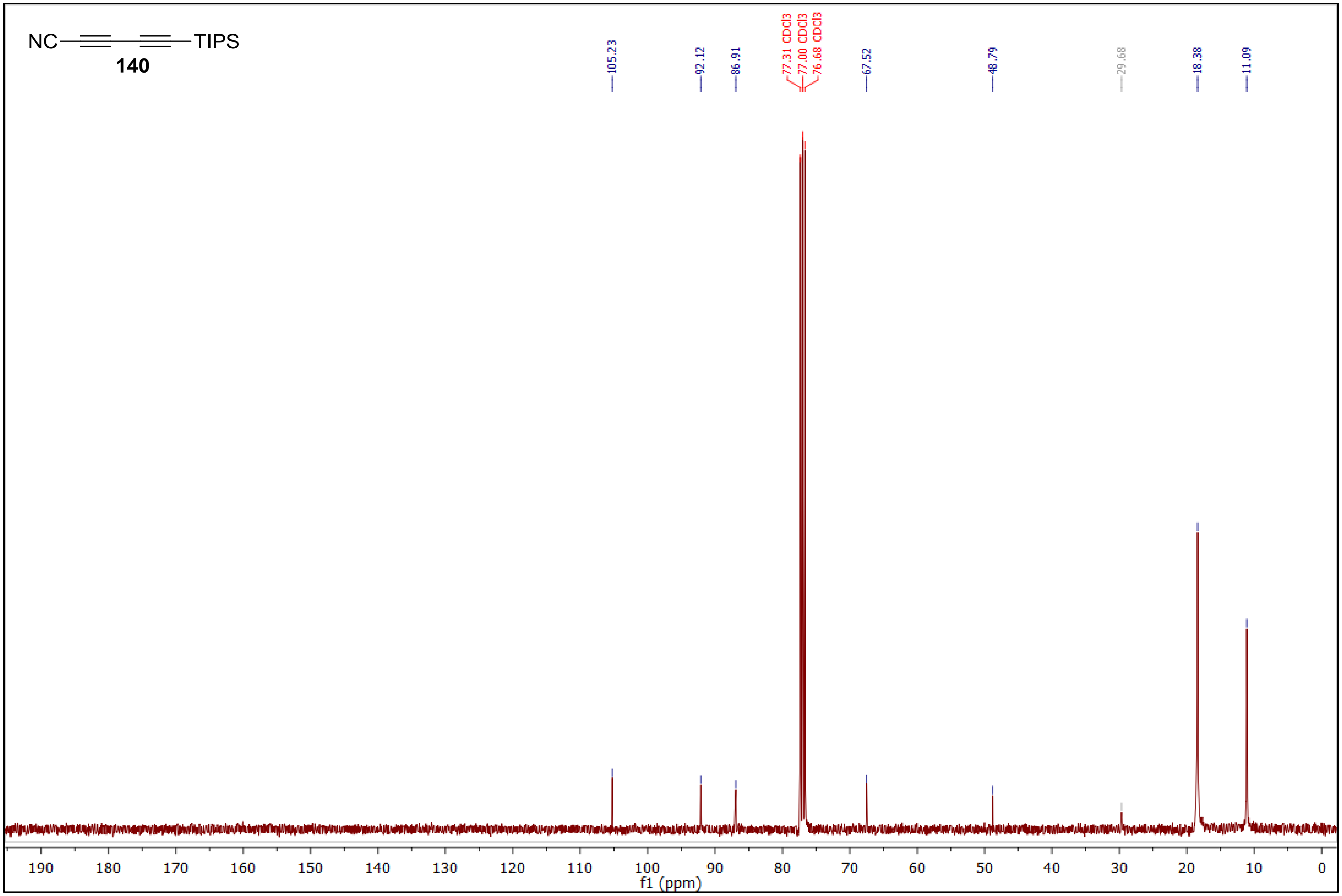
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **139**.



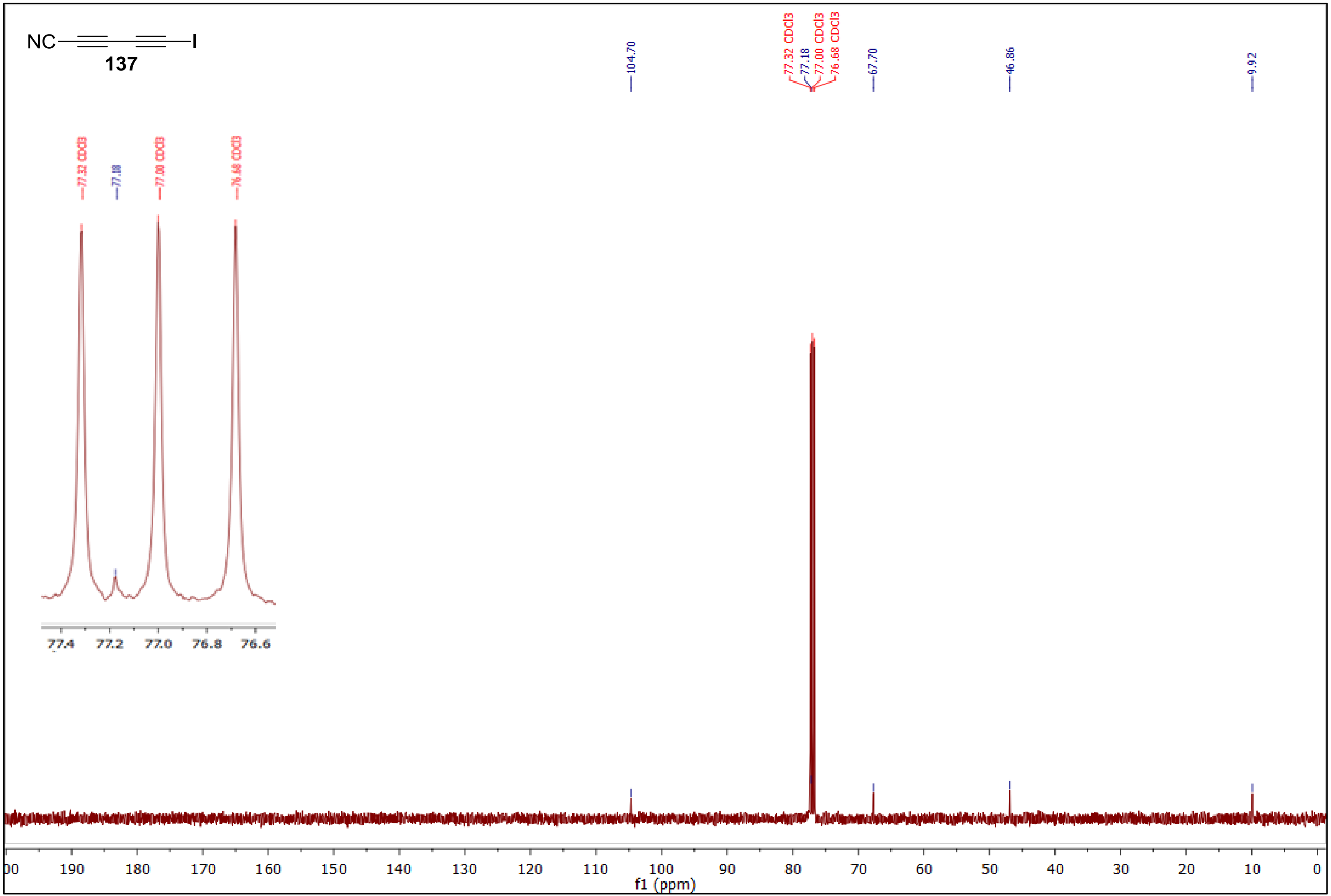
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **139**.



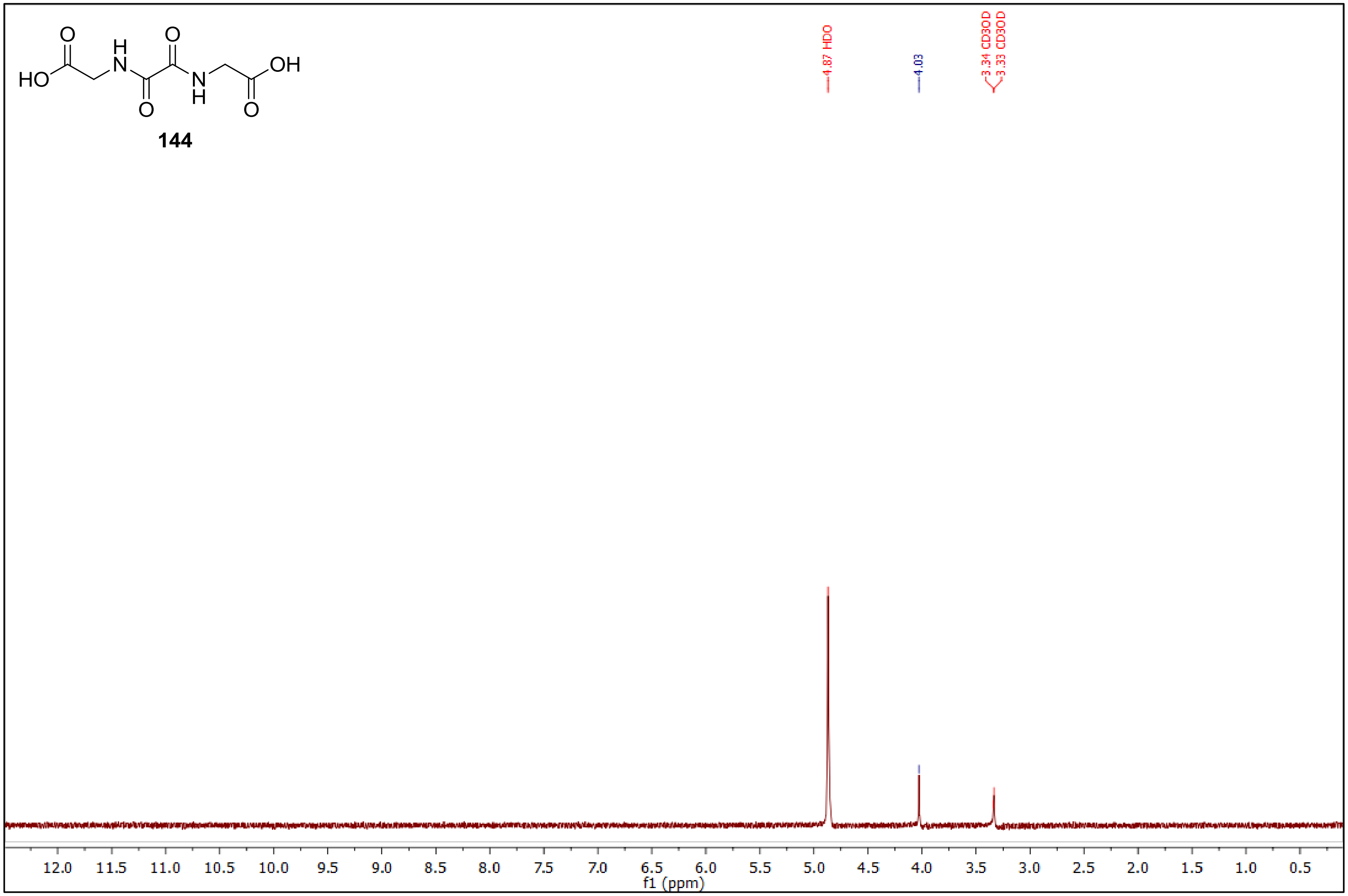
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **140**.



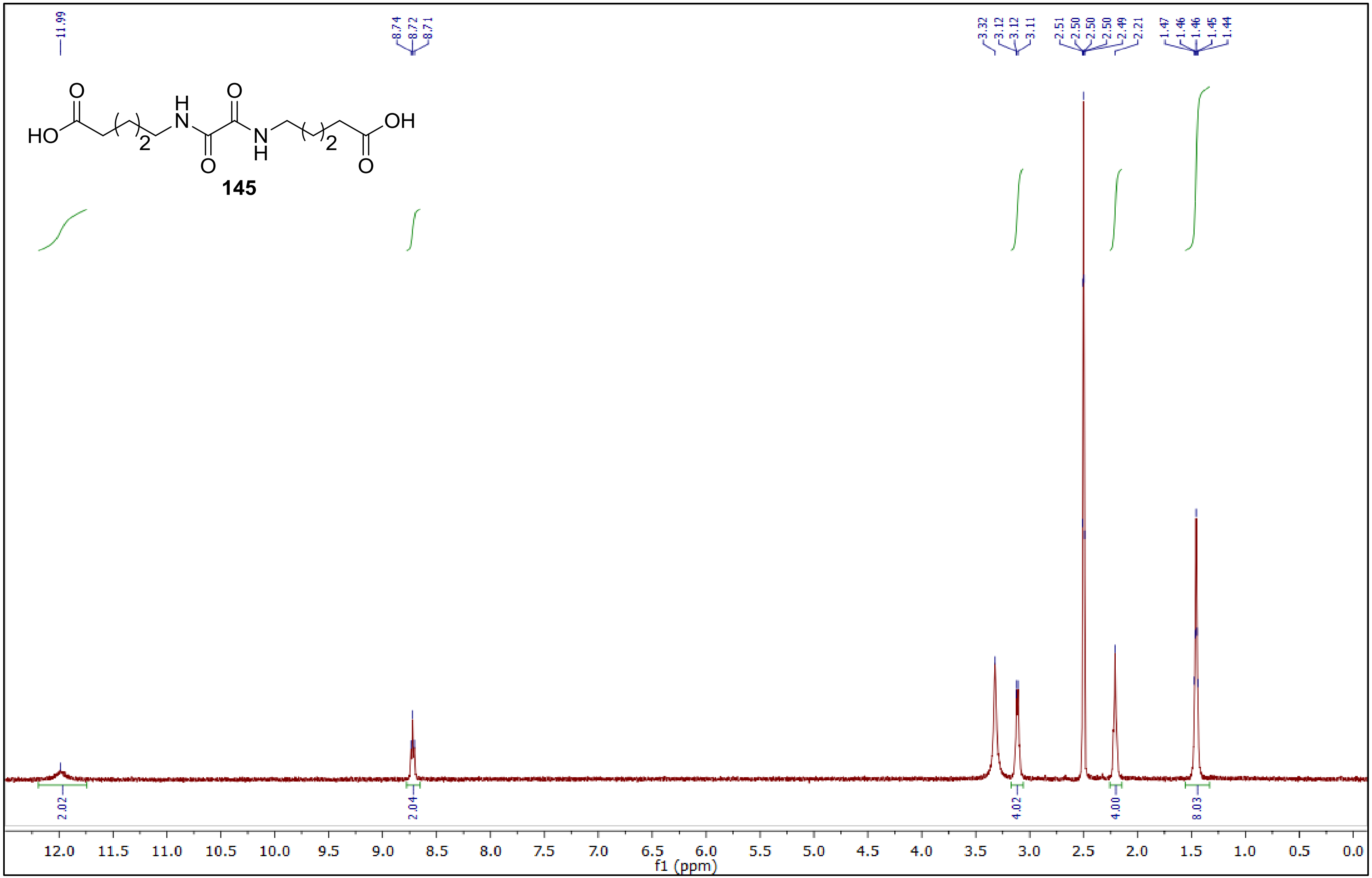
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **140**.



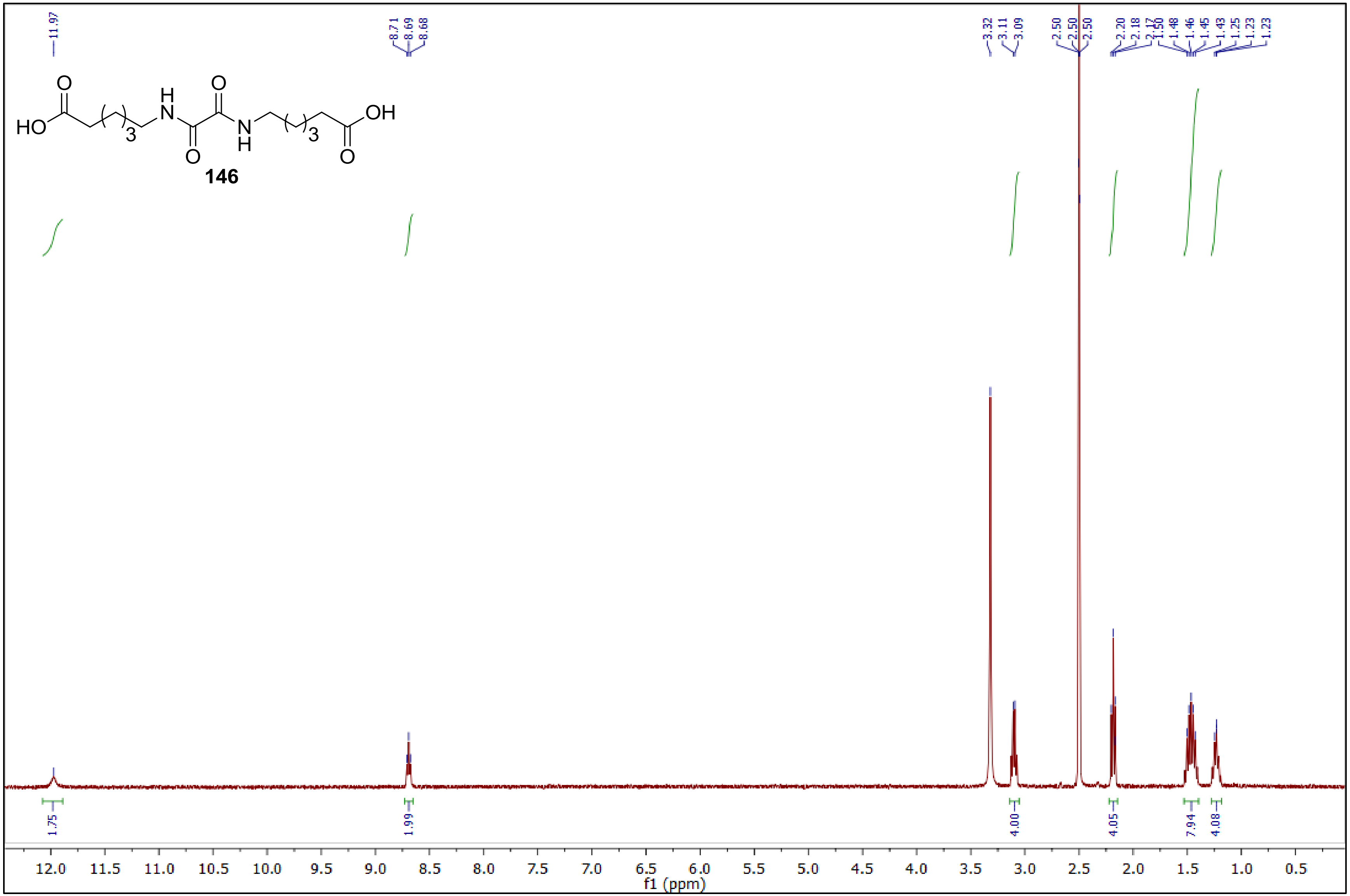
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **137**.



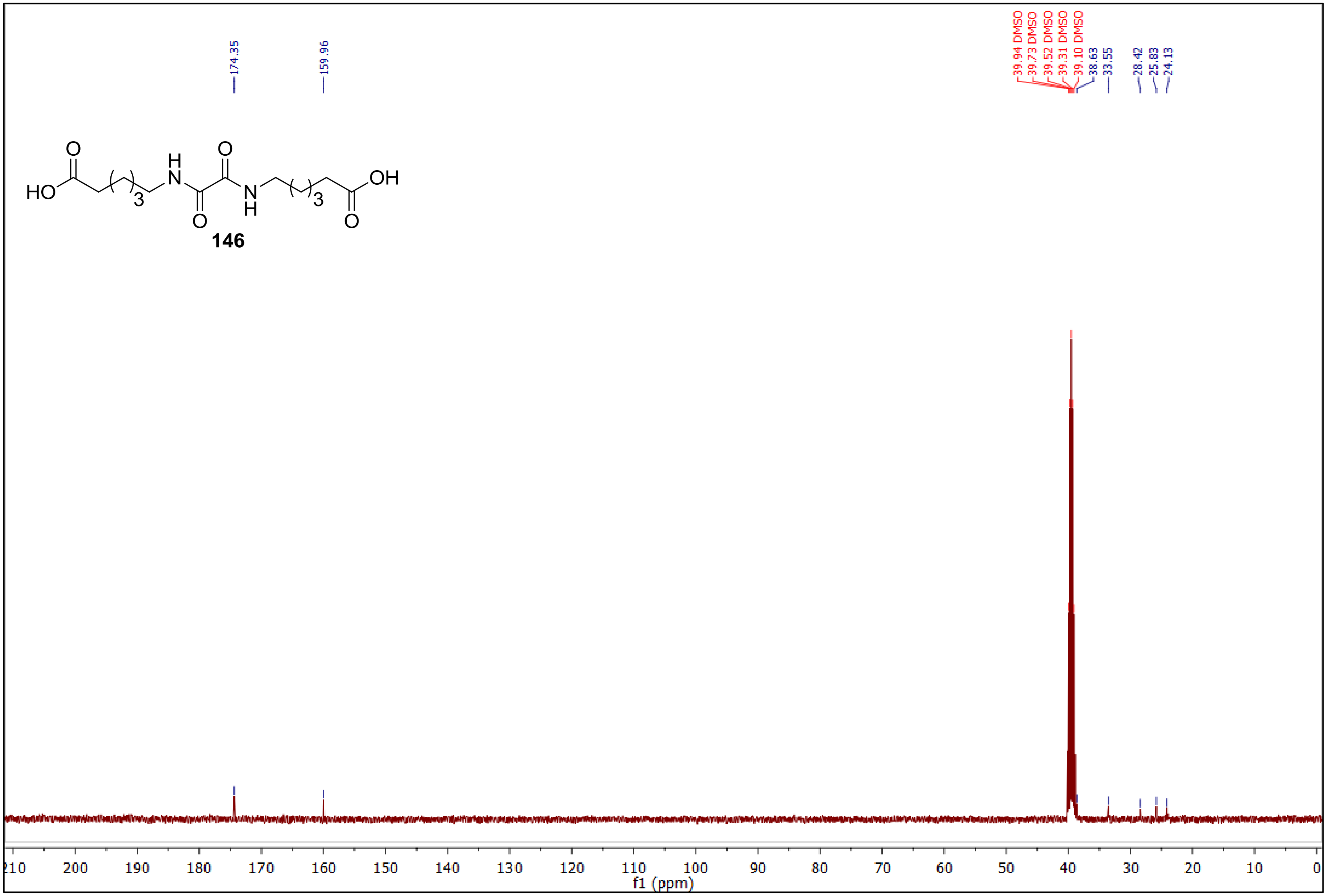
^{1}H NMR spectrum (500 MHz, CD_3OD) of compound **144**.



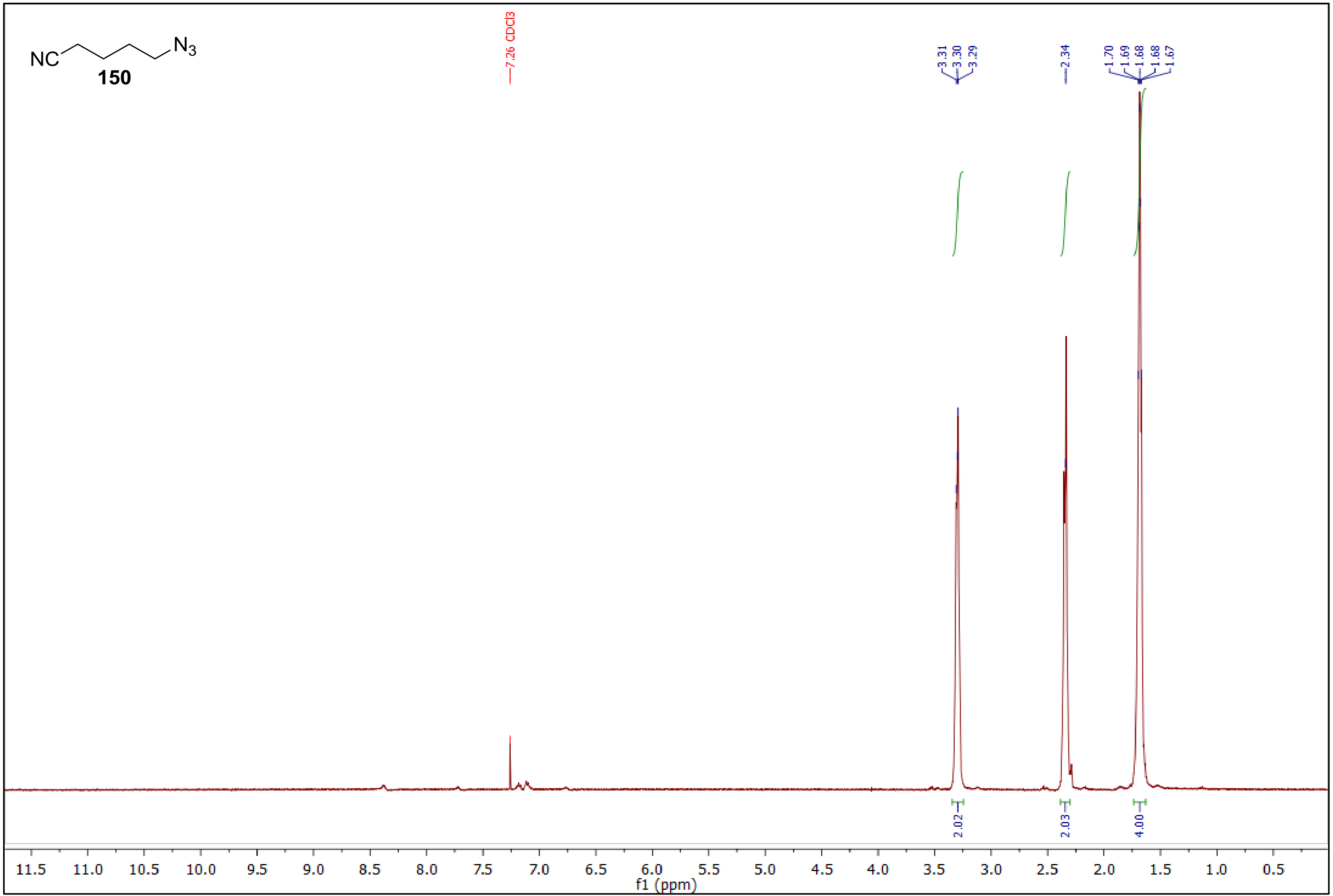
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **145.**



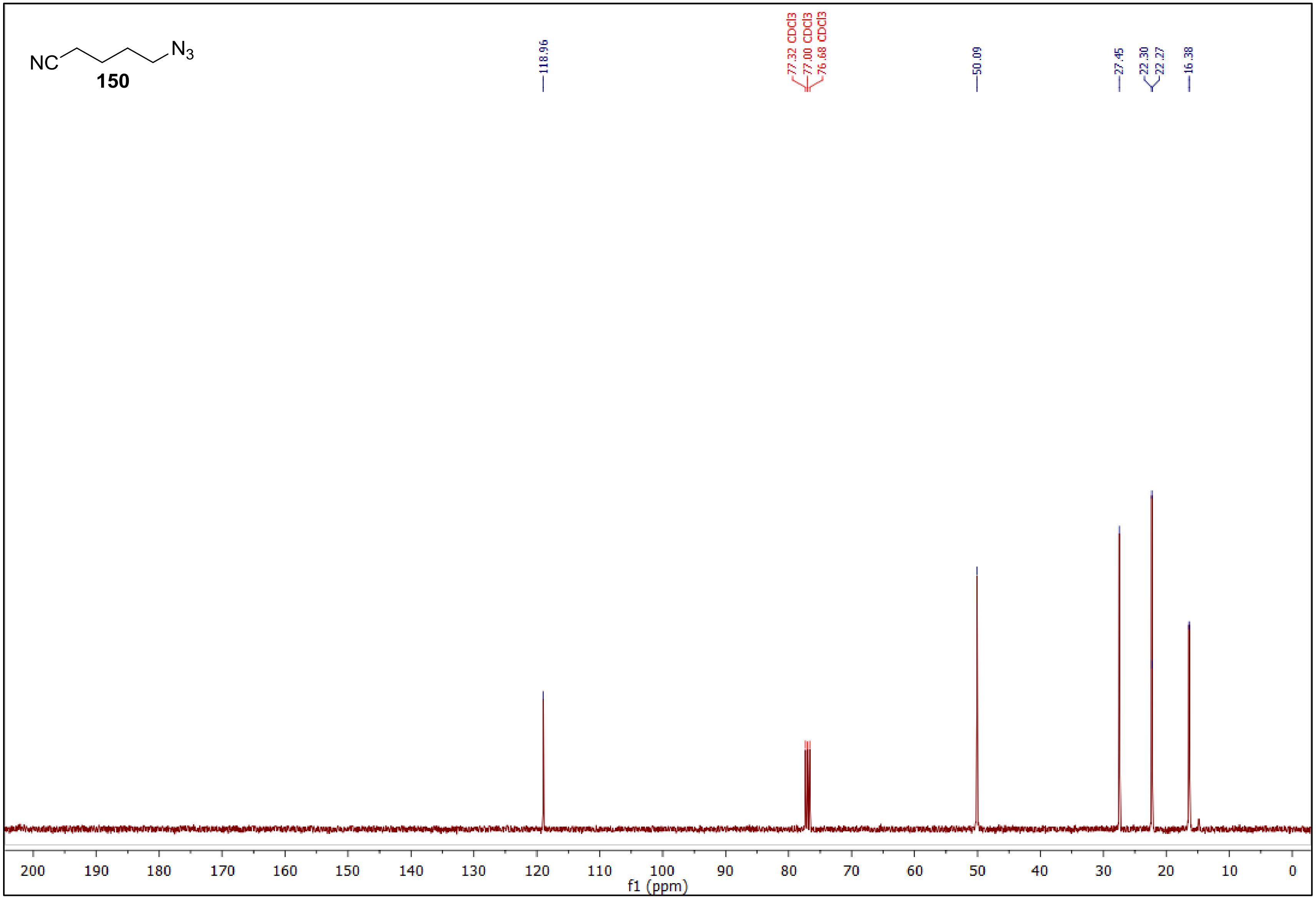
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **146.**



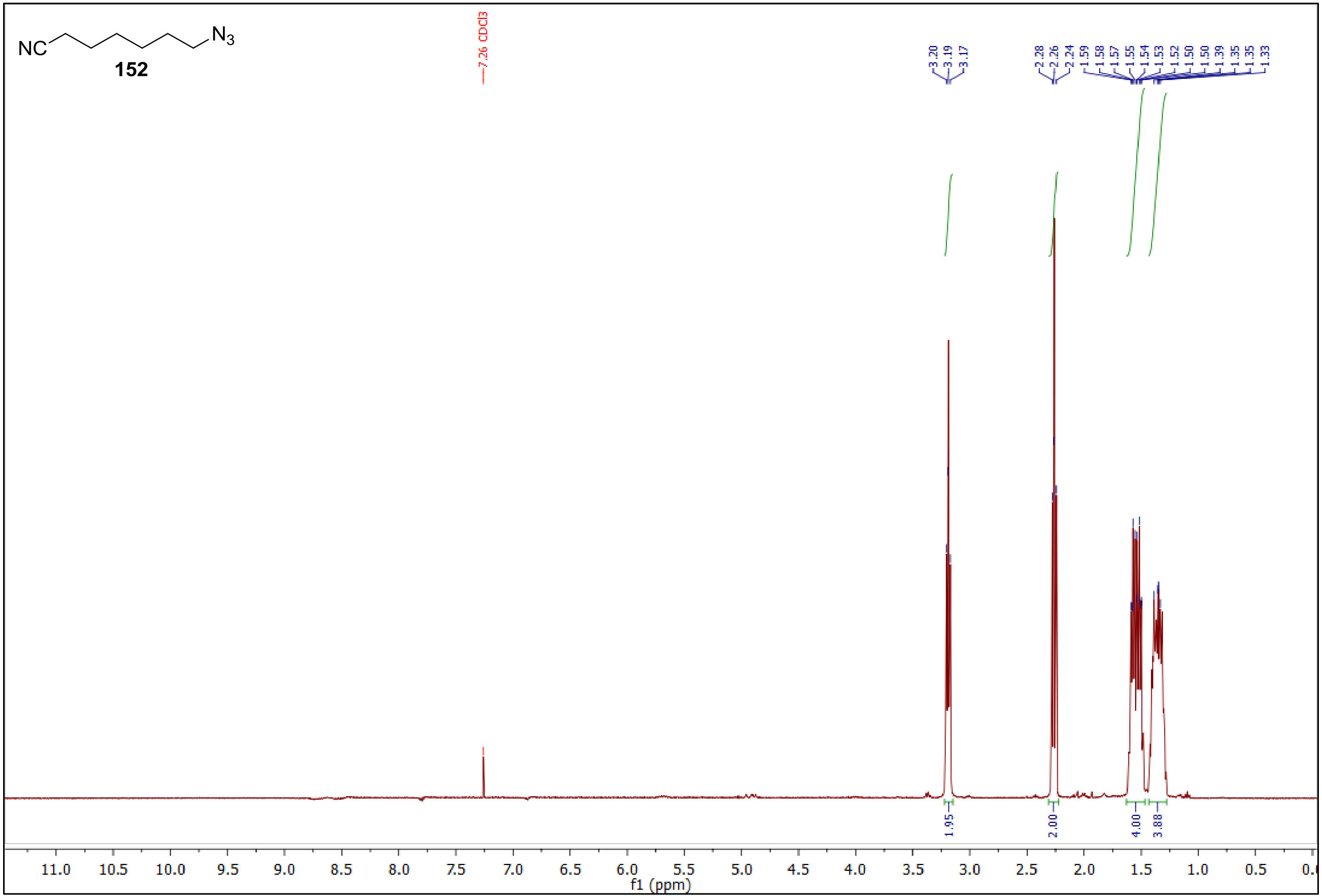
^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **146.**



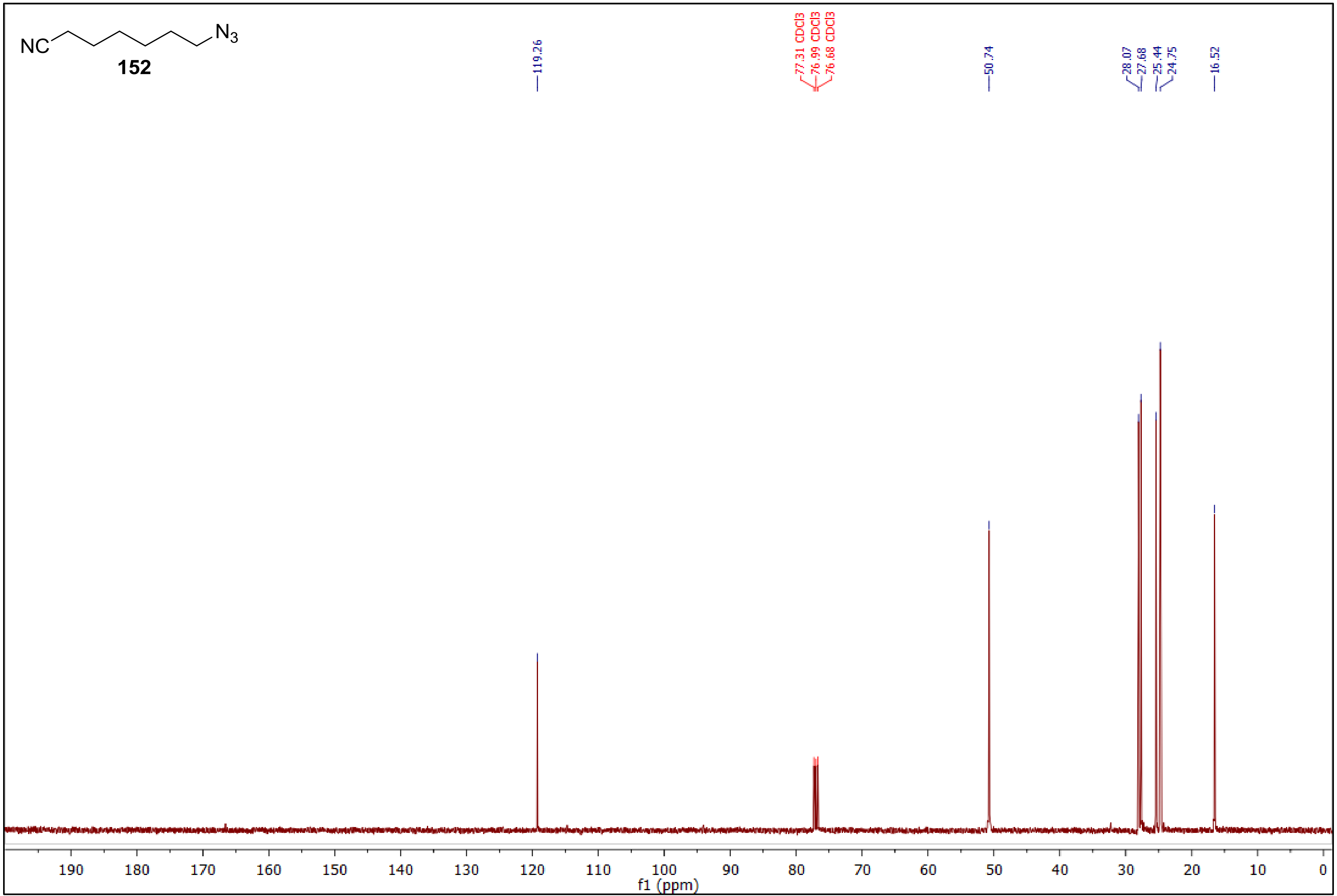
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **150.**



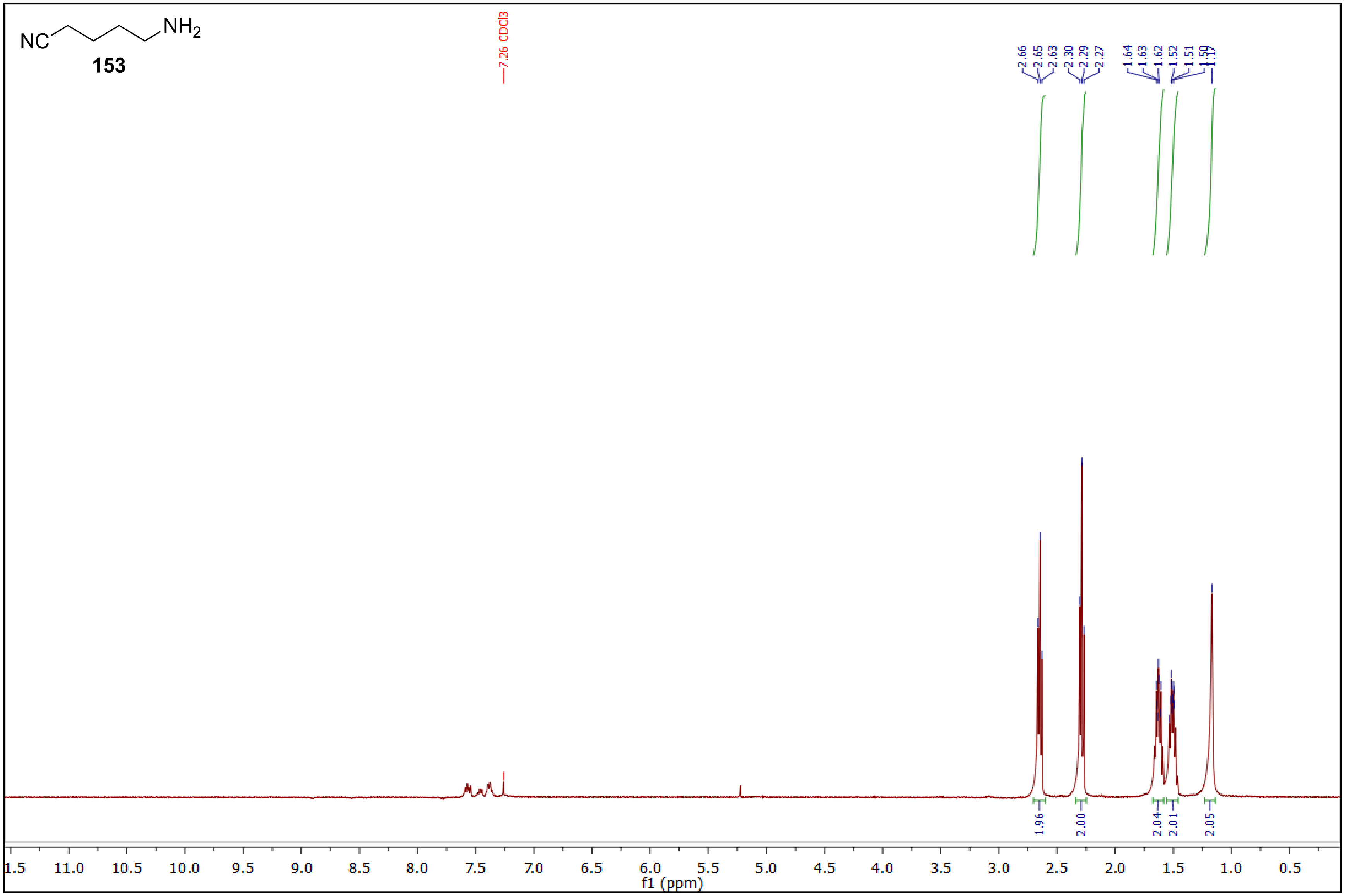
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **150**.



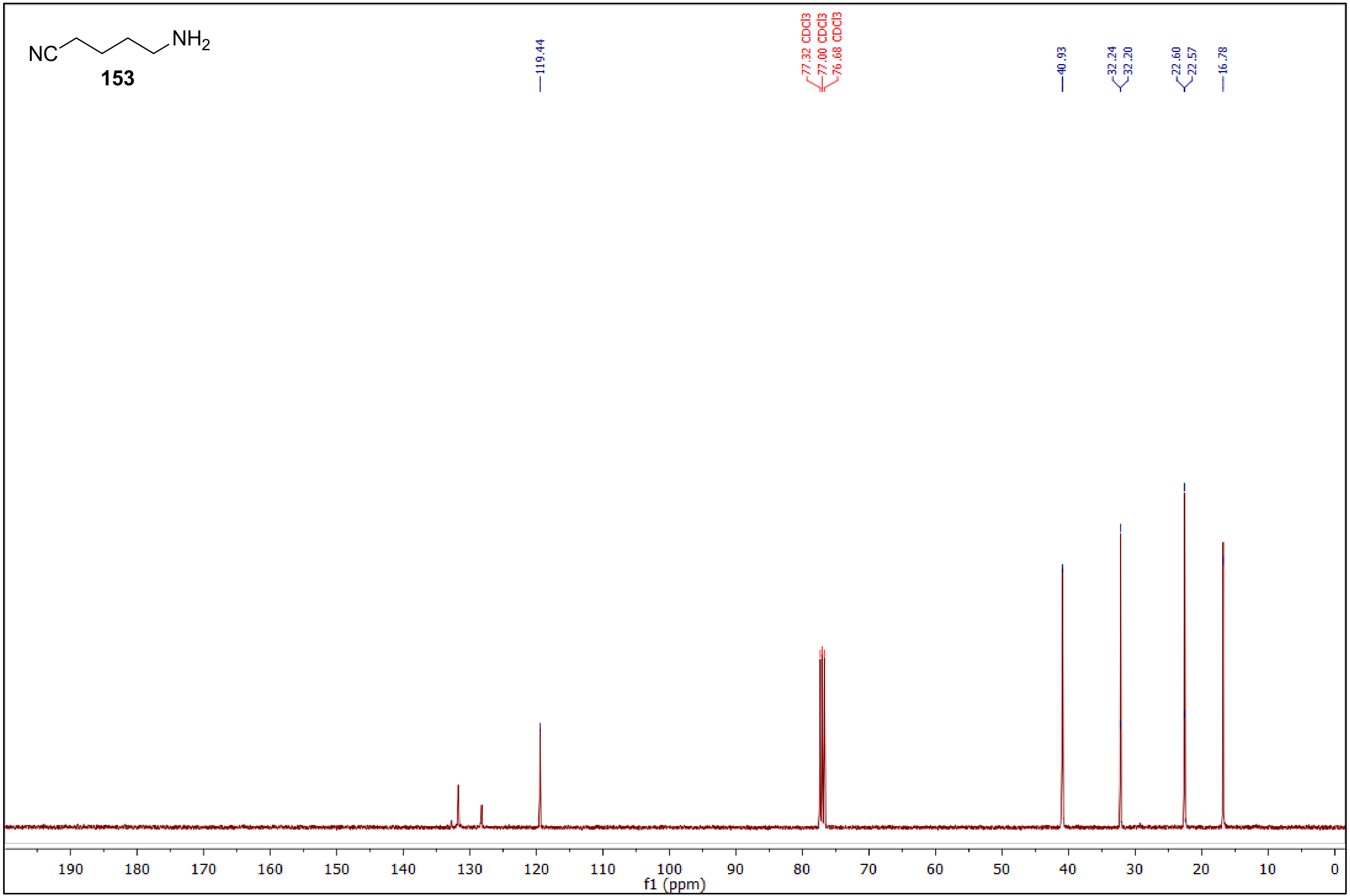
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **152**.



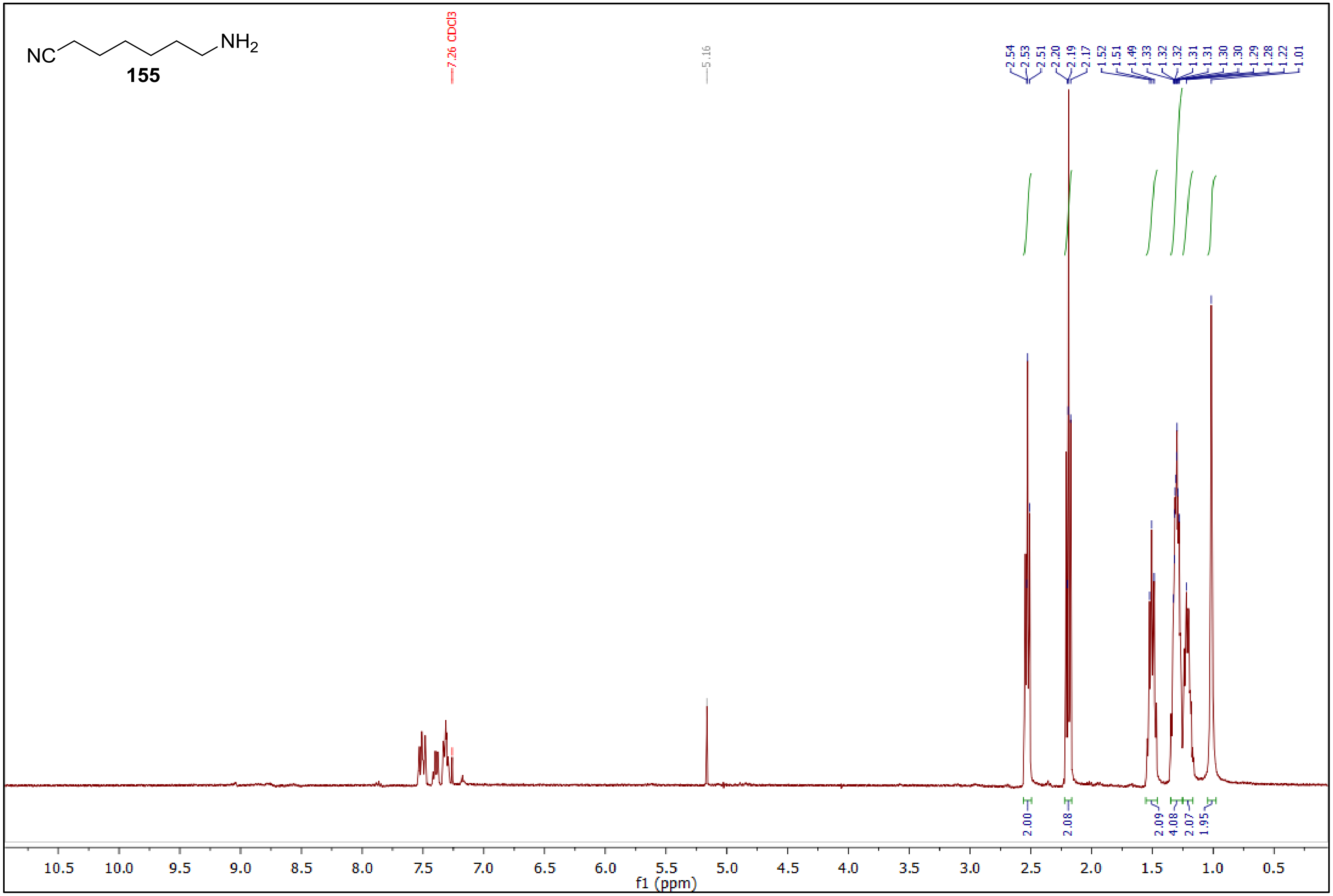
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **152**.



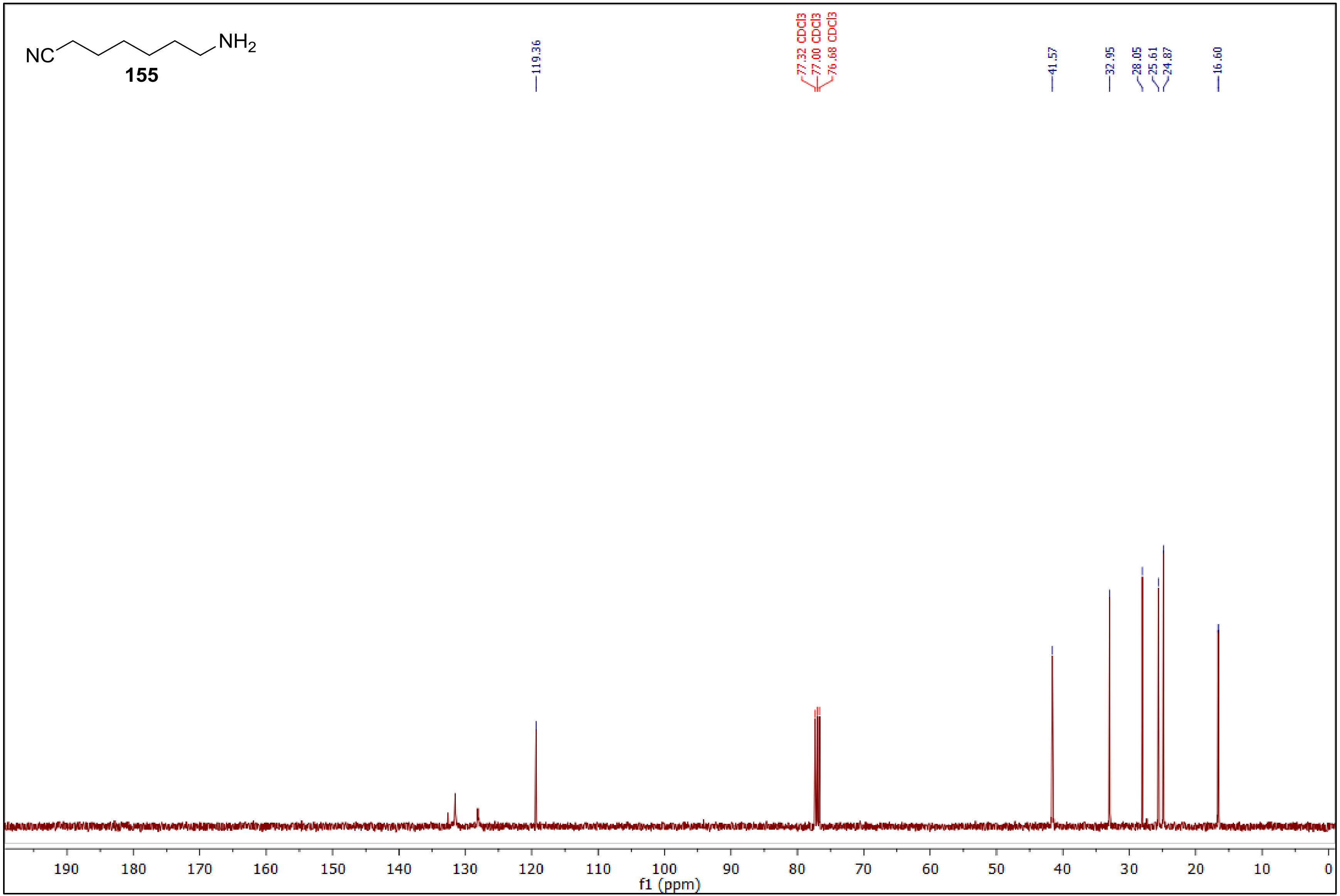
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **153**.



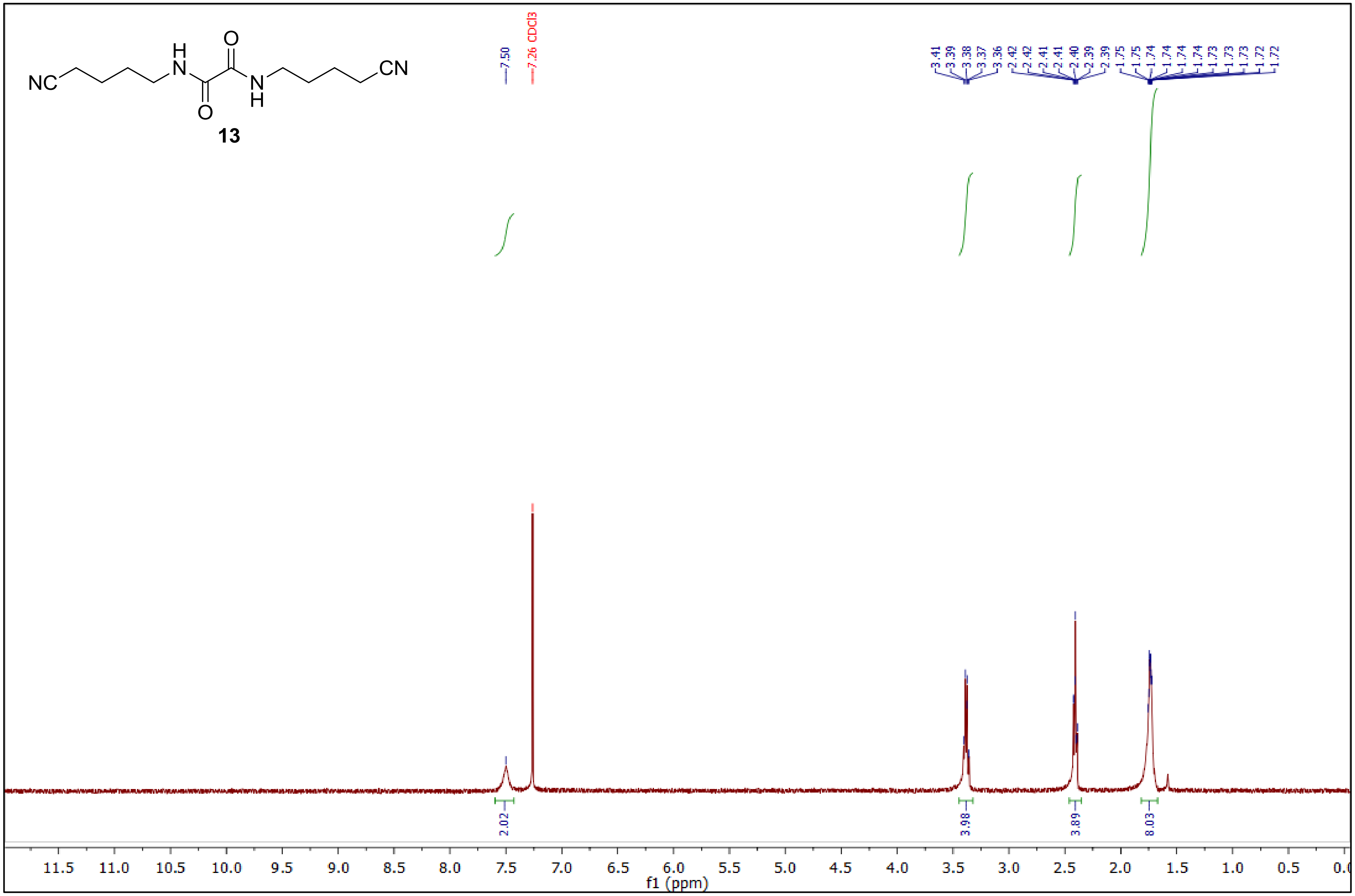
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **153**.



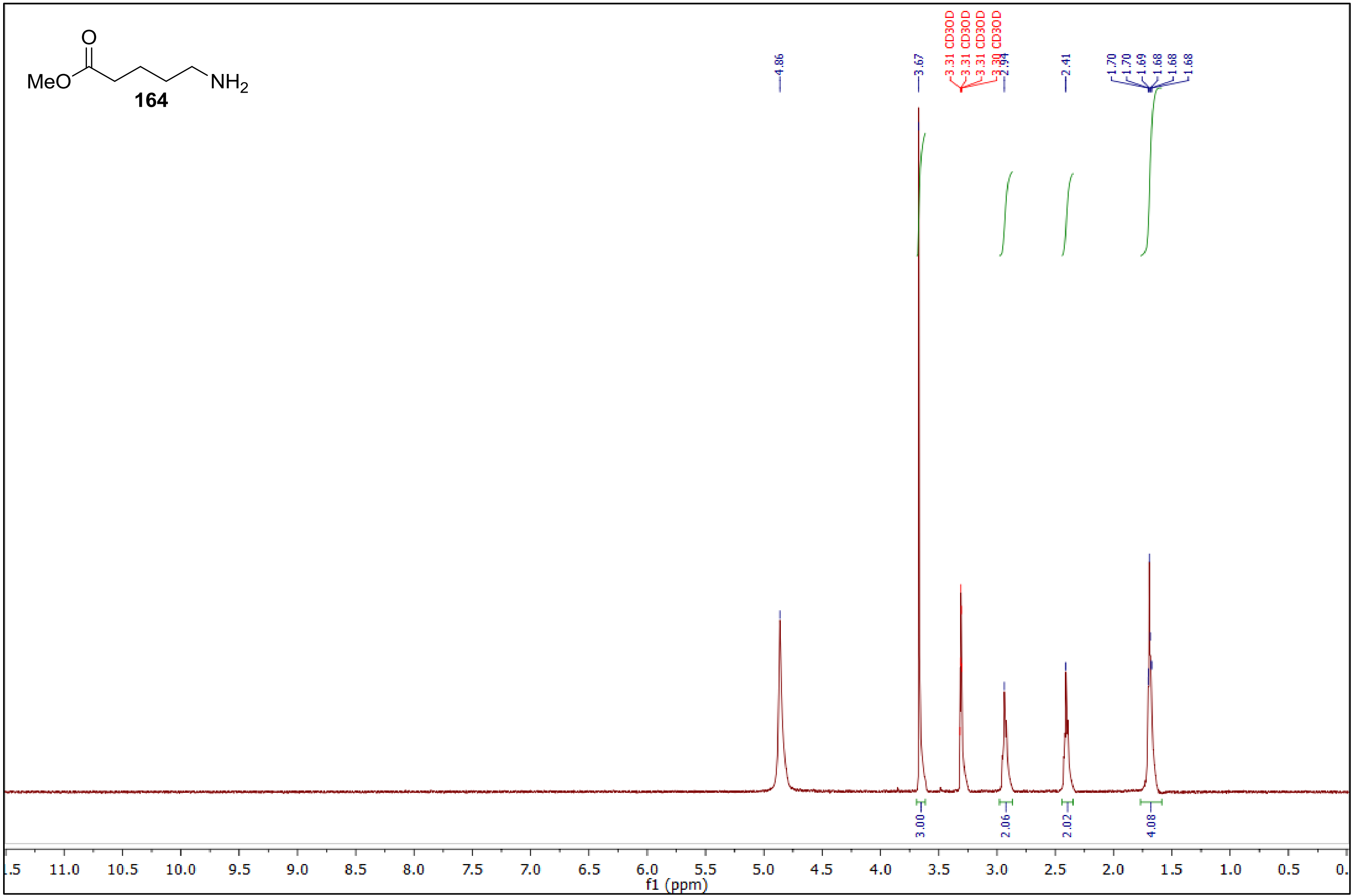
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **155.**



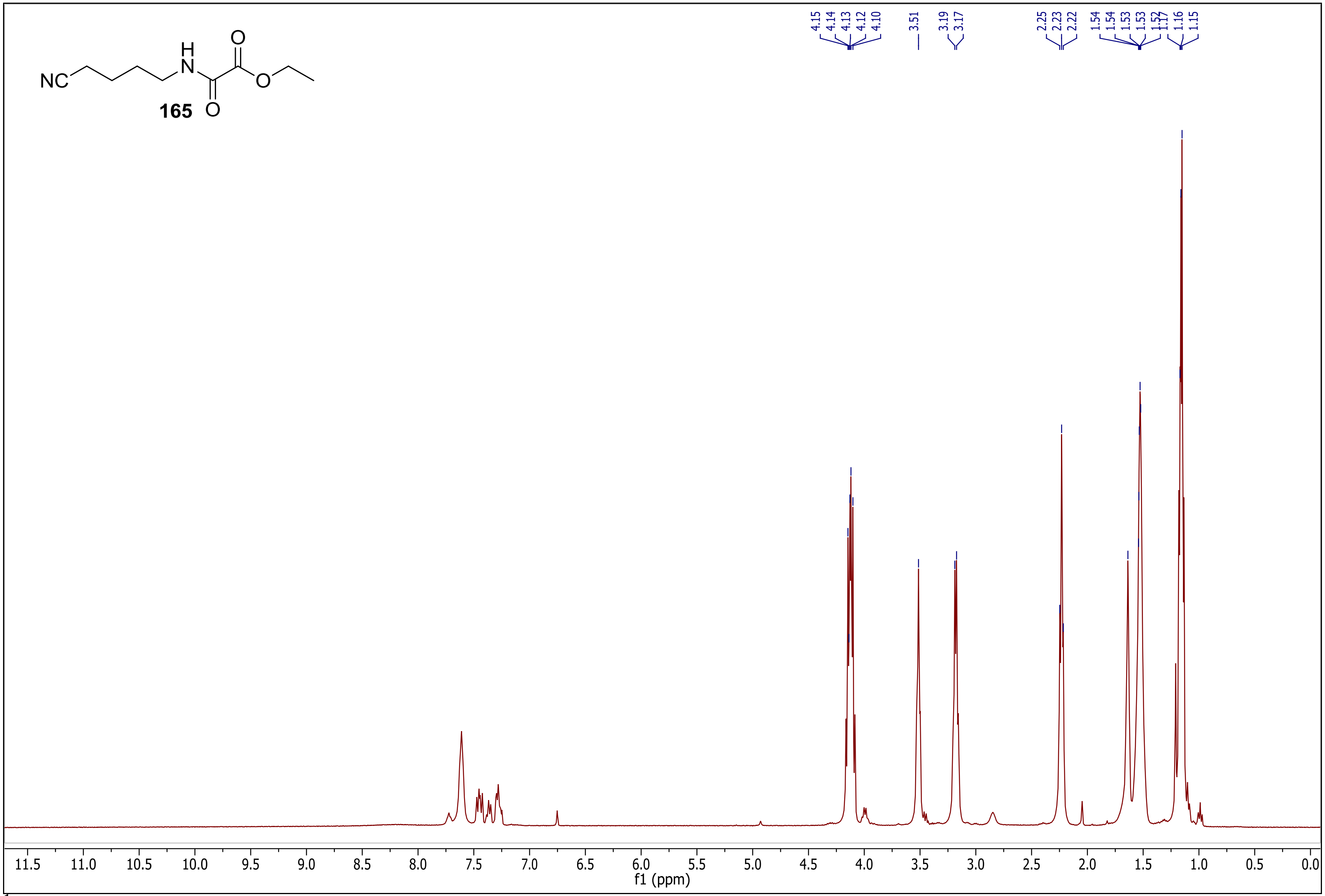
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **155**.



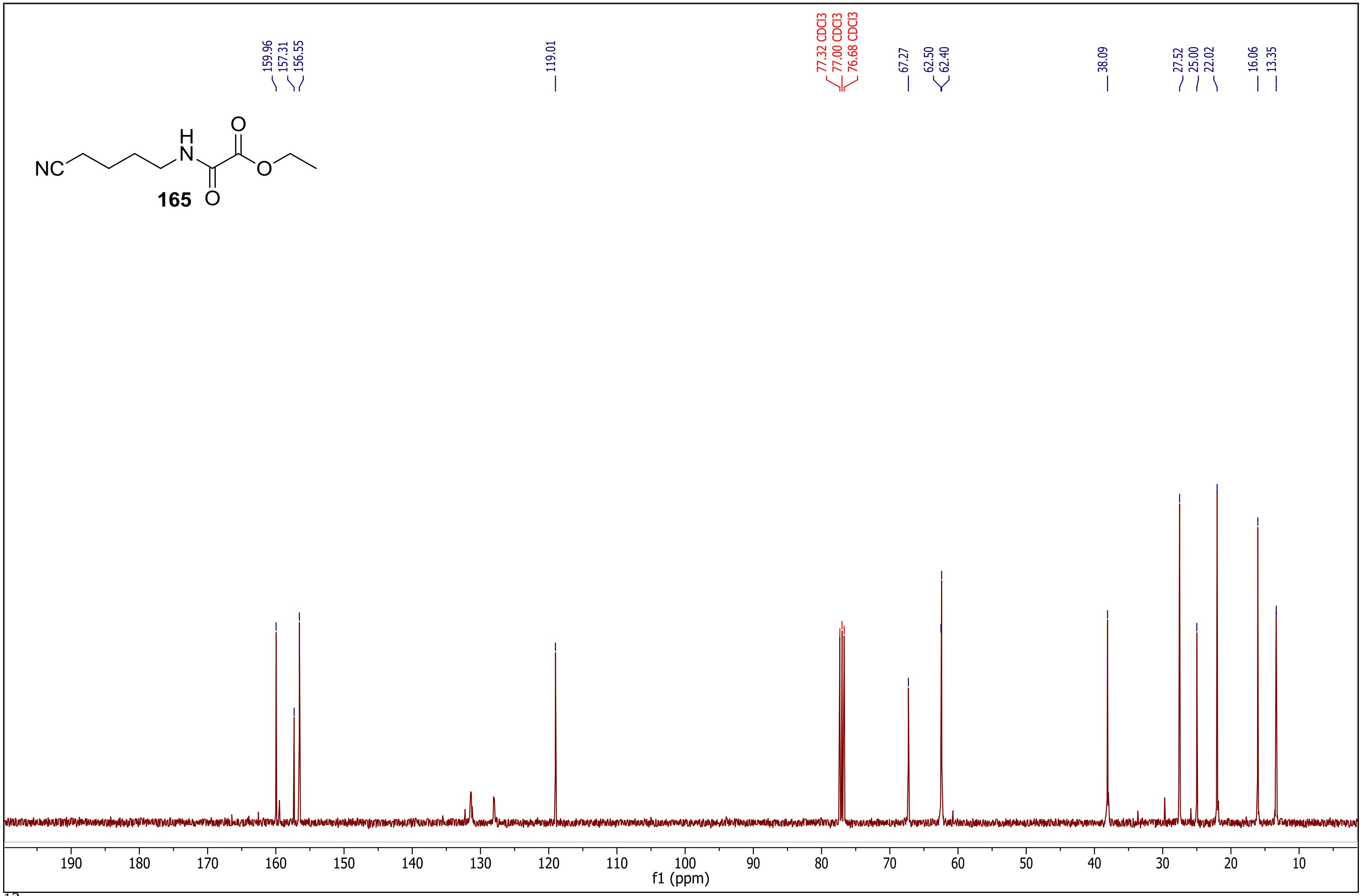
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **13**.



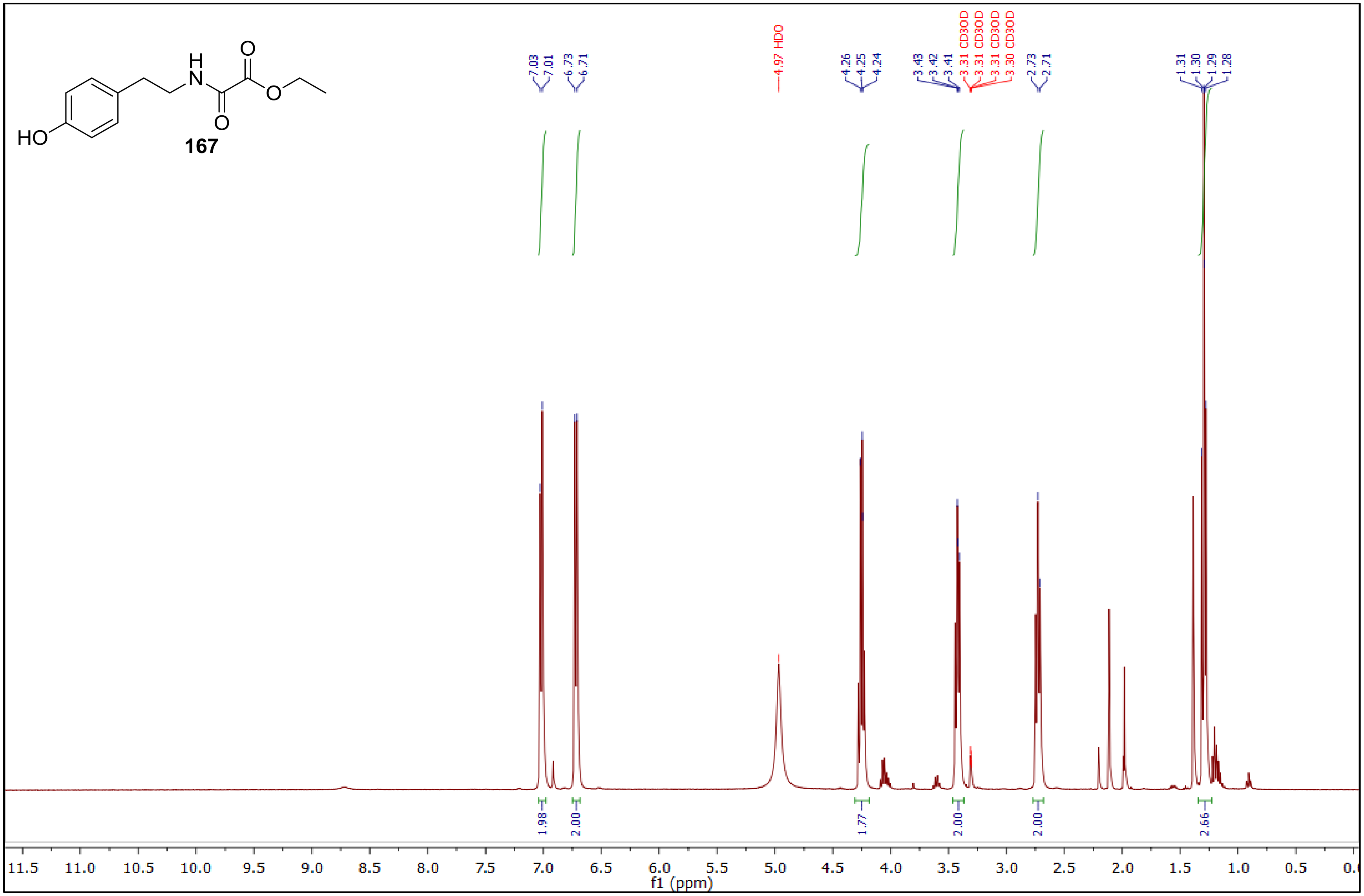
^{1}H NMR spectrum (400 MHz, CD$_3$OD) of compound **164**.



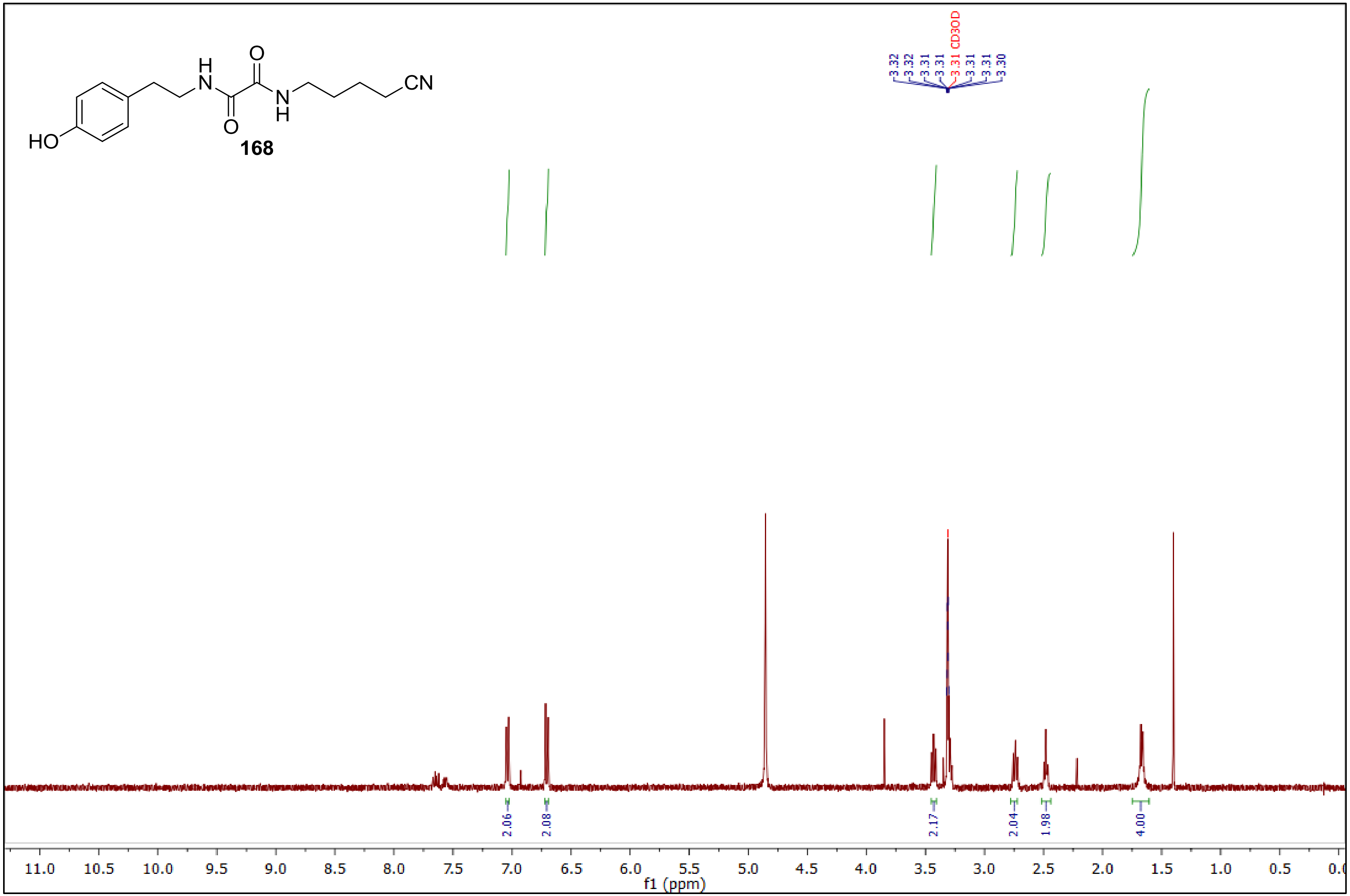
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of compound **165**.



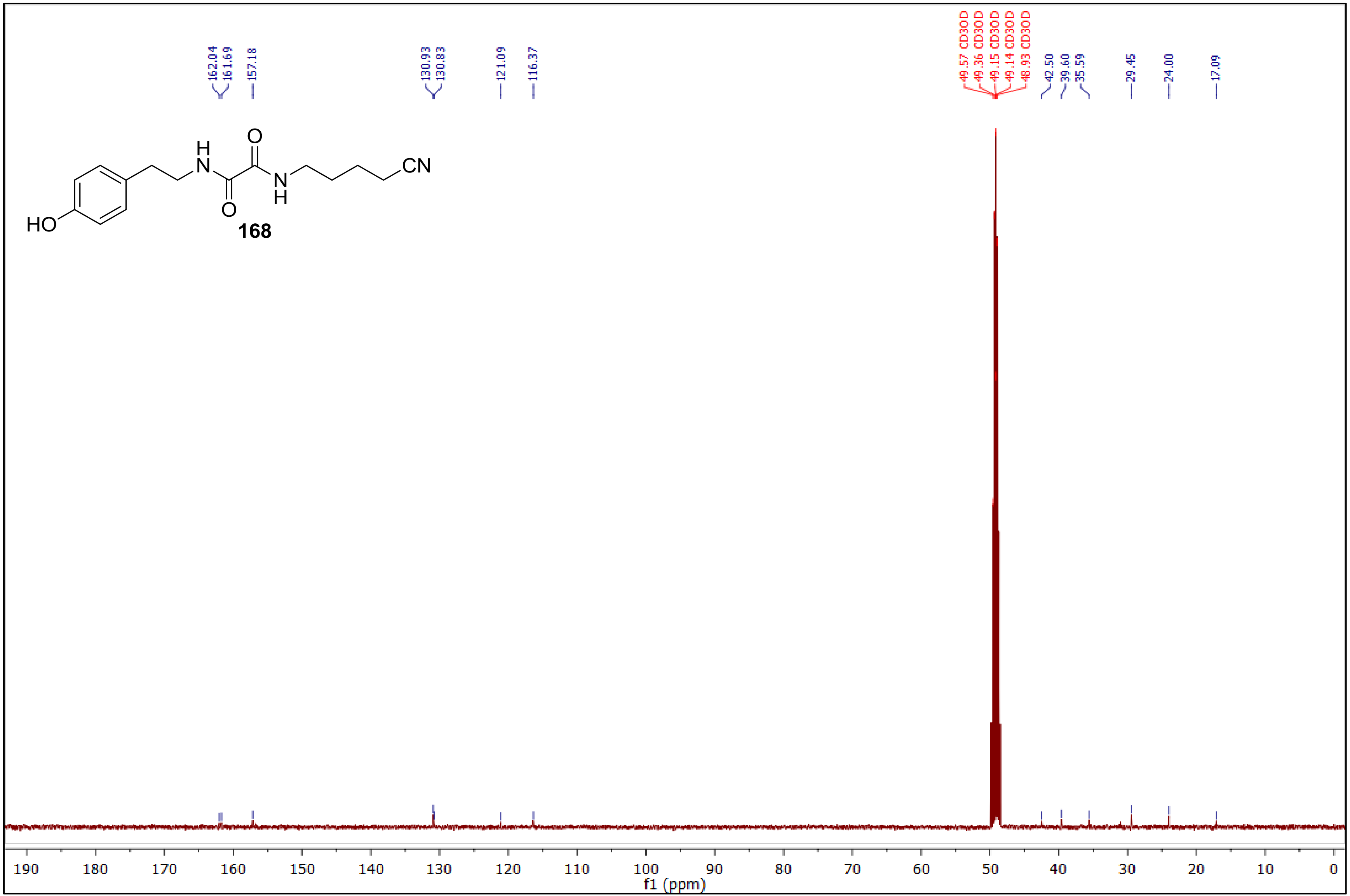
^{13}C NMR spectrum (100 MHz, CDCl$_3$) of compound **165**.



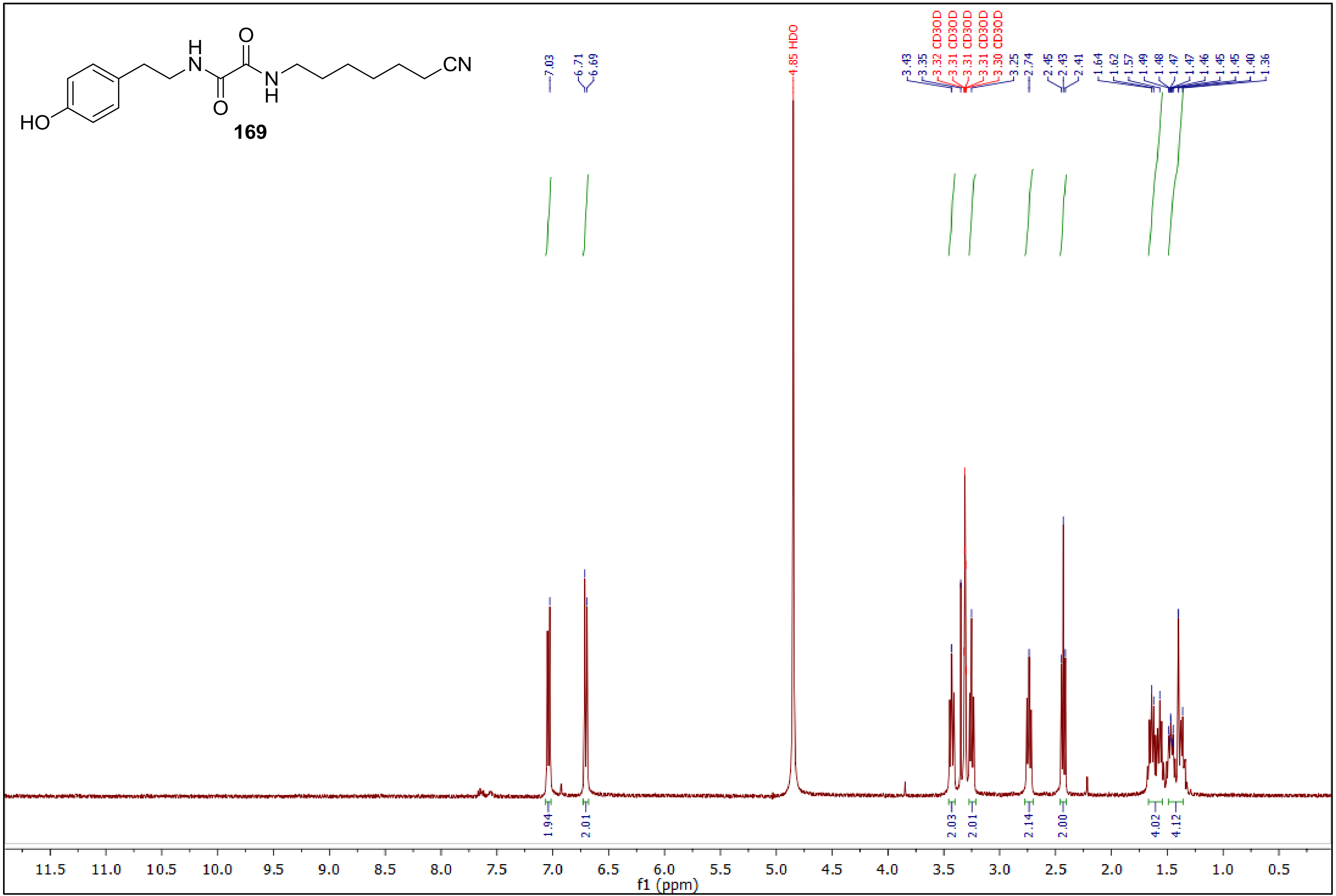
^{1}H NMR spectrum (400 MHz, CD$_3$OD) of compound **167**.



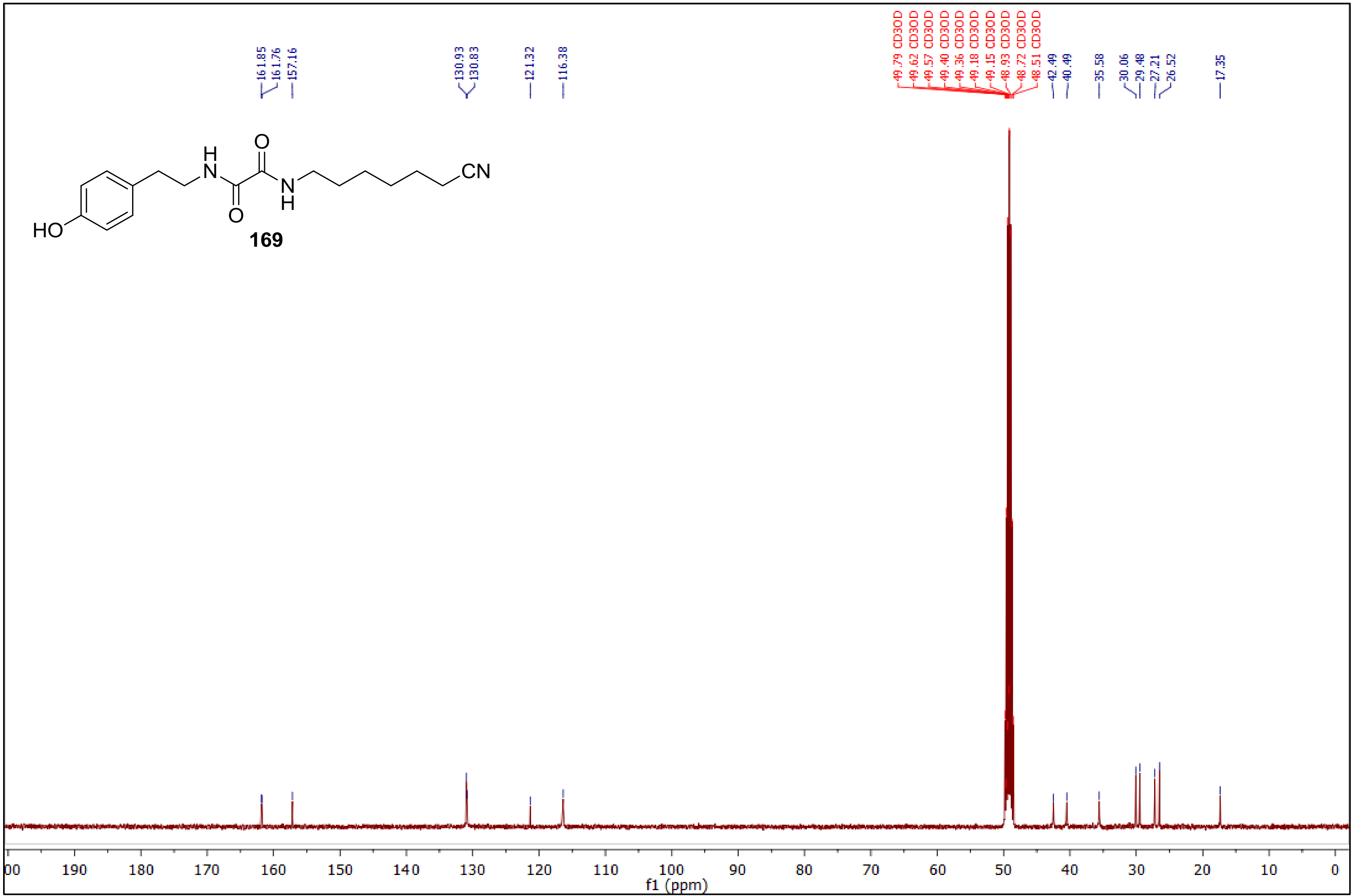
^{1}H NMR spectrum (400 MHz, CD$_3$OD) of compound **168**.



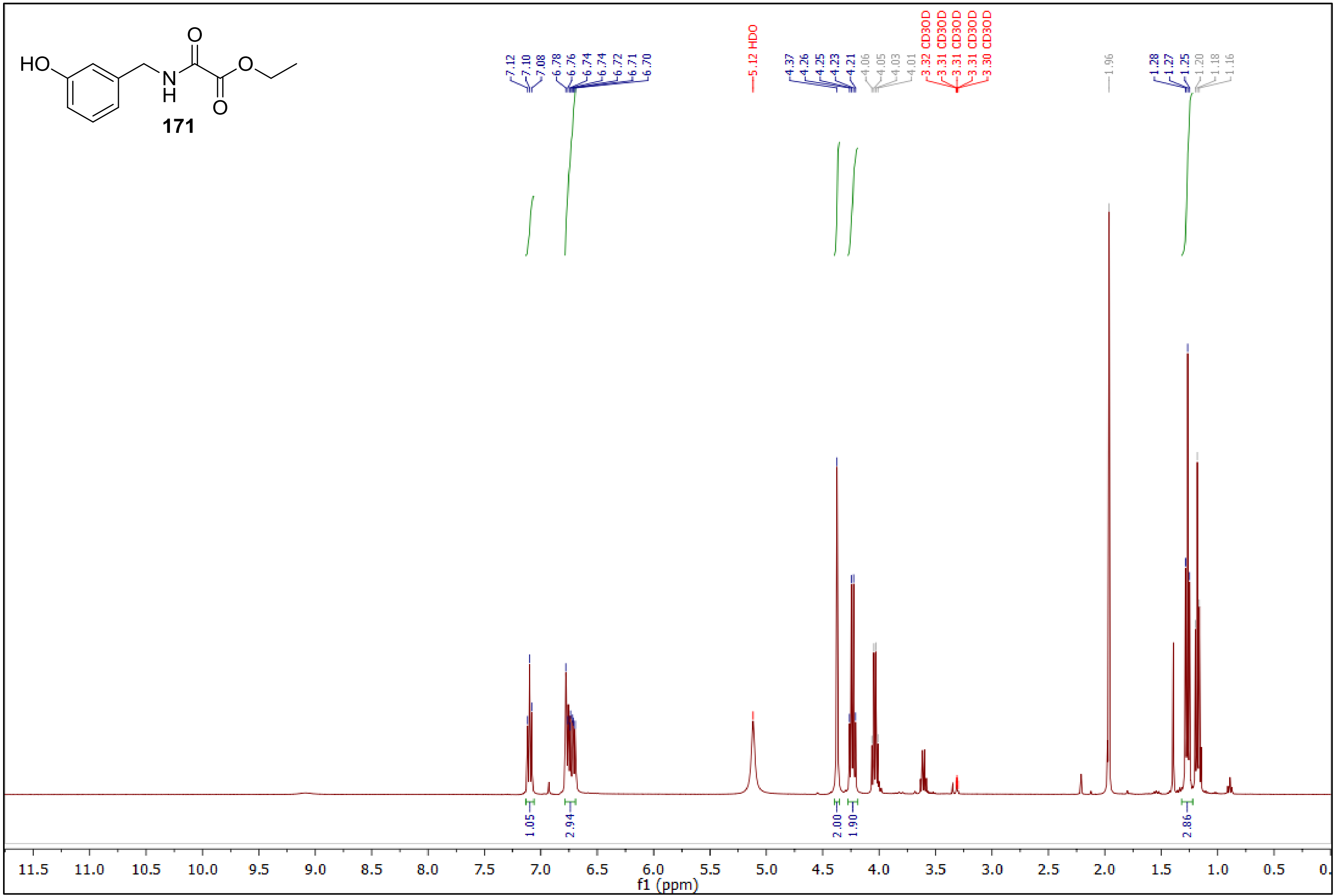
^{13}C NMR spectrum (100 MHz, CD_3OD) of compound **168**.



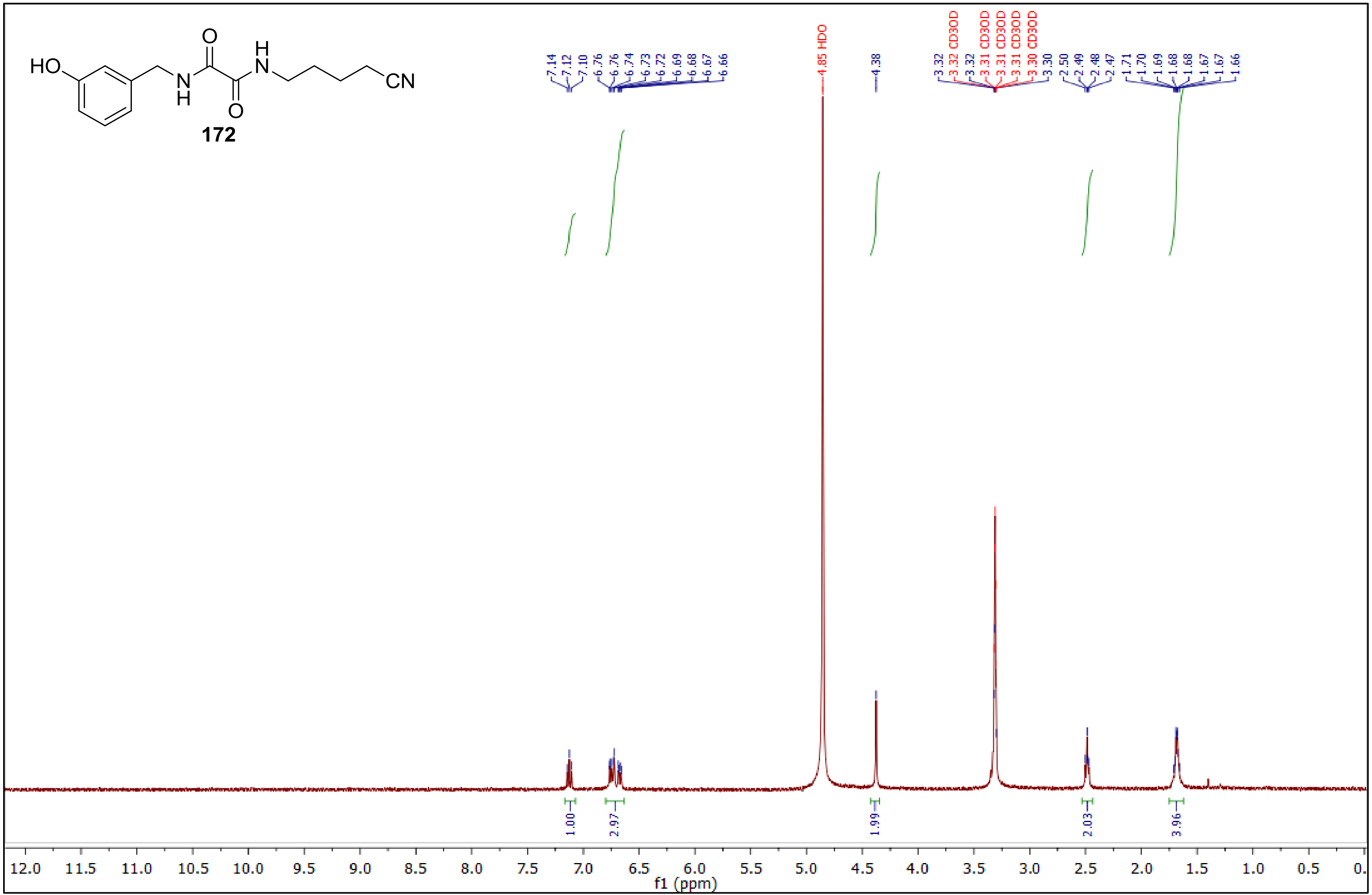
^{1}H NMR spectrum (400 MHz, CD$_3$OD) of compound **169.**



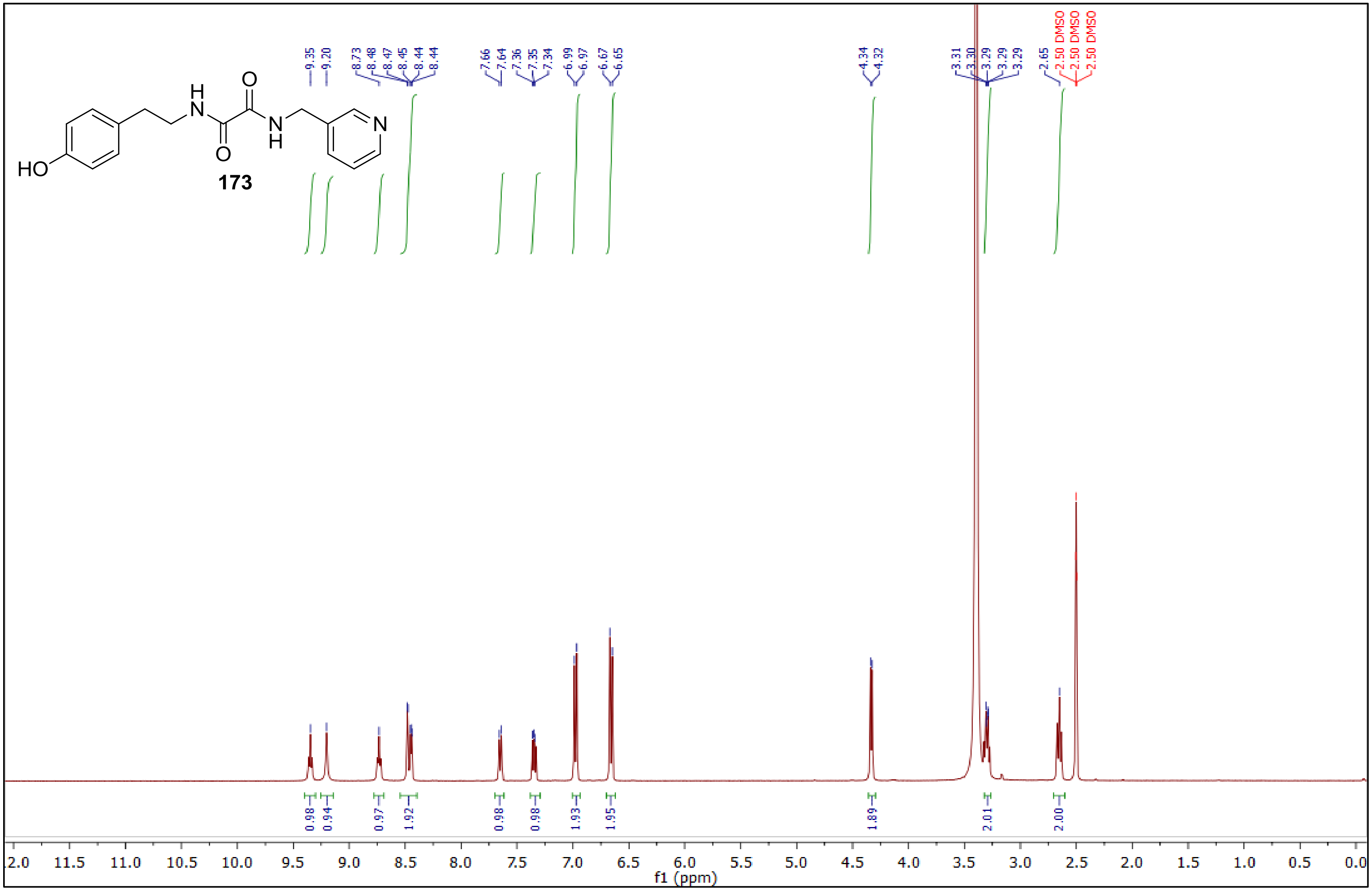
^{13}C NMR spectrum (100 MHz, CD$_3$OD) of compound **169**.



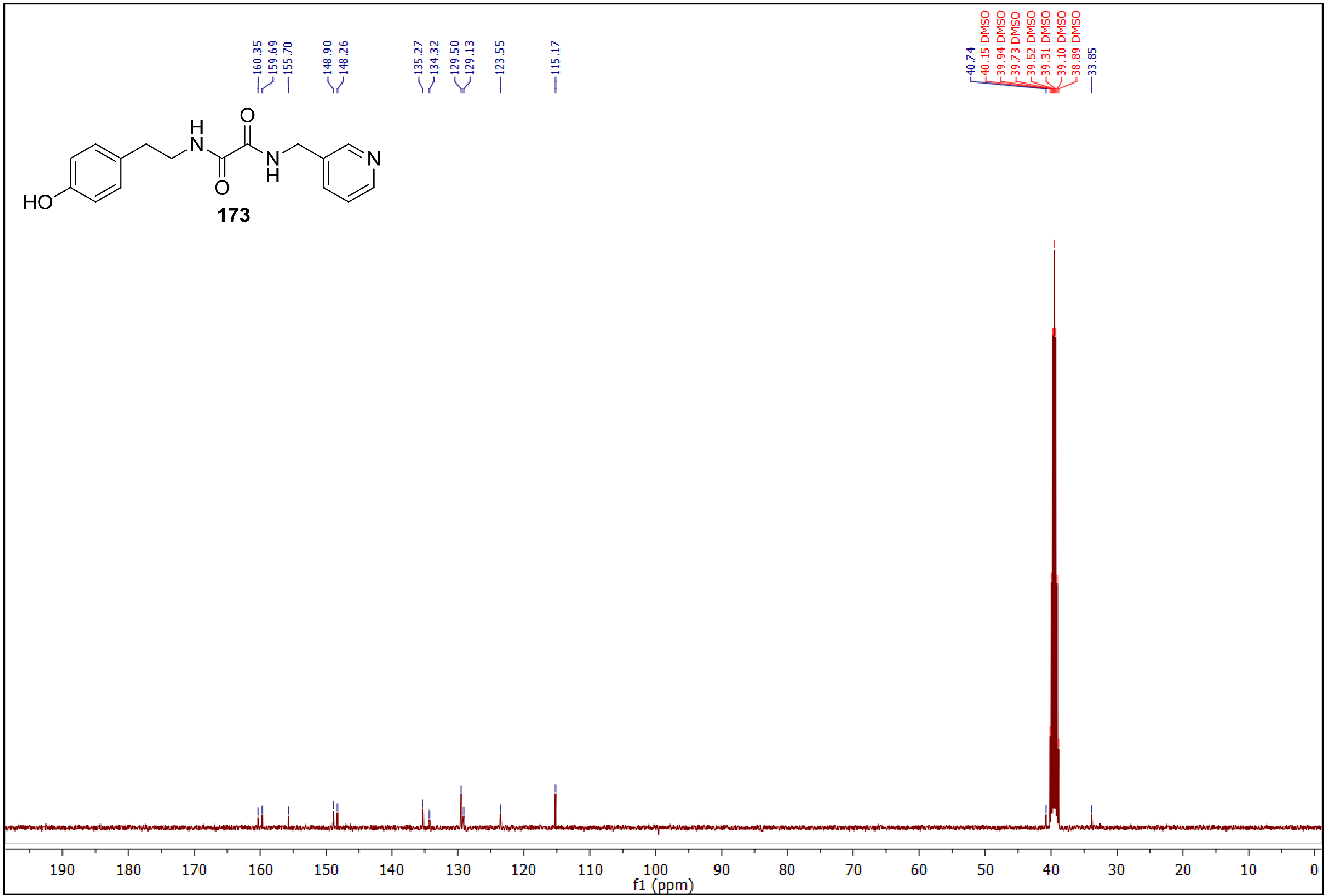
^{1}H NMR spectrum (400 MHz, CD_3OD) of compound **171**.



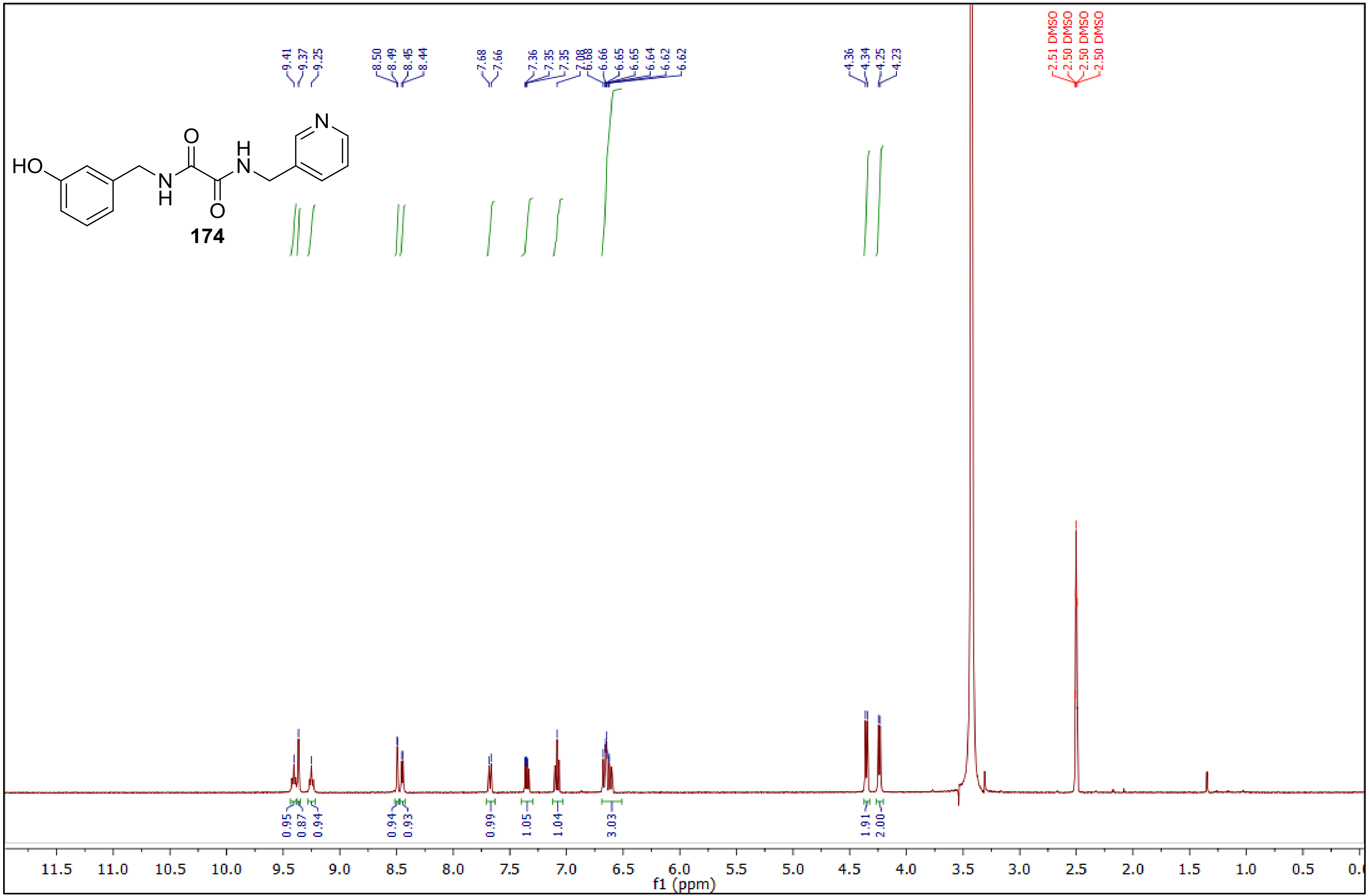
^{1}H NMR spectrum (400 MHz, CD$_3$OD) of compound **172.**



^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **173**.



^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **173**.



^{13}C NMR spectrum (100 MHz, DMSO-d_6) of compound **174.**

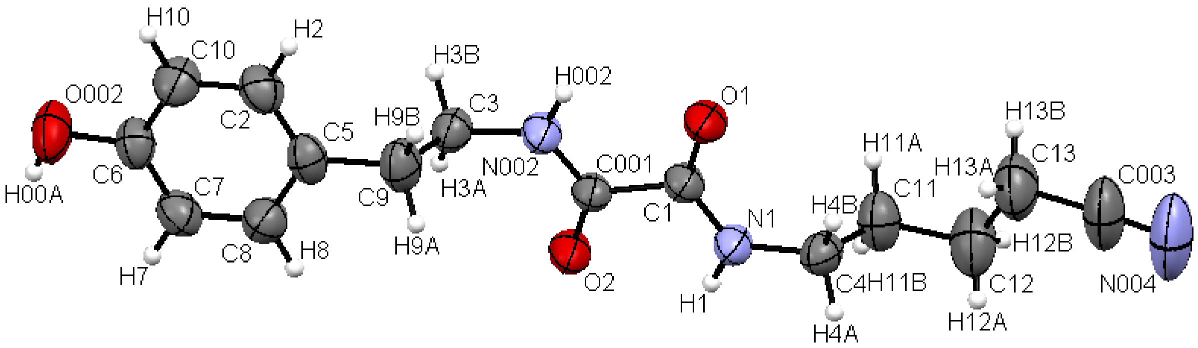


Figure: Crystal Structure of *N*-(4-Cyano-butyl)-*N*'-[2-(4-hydroxy-phenyl)-ethyl]-oxalamide (**168**).

Table 1. Crystal data and structure refinement for **168**

Identification code	phenolnitrilehost
Empirical formula	$C_{15}H_{19}N_3O_3$
Formula weight	289.33
Temperature/K	566(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.7200(3)
b/Å	20.7920(10)
c/Å	13.2080(8)
α/°	90
β/°	96.813(5)
γ/°	90
Volume/Å^3	1559.74(15)
Z	4
ρ_{calc}mg/mm^3	1.232
m/mm^{-1}	0.087
F(000)	616.0
Crystal size/mm^3	0 × 0 × 0
2Θ range for data collection	6.52 to 59.14°
Index ranges	$-7 \le h \le 7$, $-27 \le k \le 28$, $-18 \le l \le 17$
Reflections collected	18661
Independent reflections	3948[R(int) = 0.0518]
Data/restraints/parameters	3948/0/190
Goodness-of-fit on F^2	0.959

Final R indexes [I>=2σ (I)] $R_1 = 0.0788$, $wR_2 = 0.2340$

Final R indexes [all data] $R_1 = 0.1580$, $wR_2 = 0.3091$

Largest diff. peak/hole / e Å^{-3} 0.37/-0.20

Table 2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **168**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	6431(4)	-1606.2(8)	4124.4(17)	61.5(6)
O2	7355(4)	55.0(9)	4244.4(17)	60.7(6)
C1	7495(5)	-1098.7(12)	4349(2)	46.9(7)
N1	9589(4)	-1044.4(10)	4858.2(18)	51.2(6)
N002	4310(4)	-510.9(10)	3442.2(18)	51.5(6)
C001	6356(4)	-453.5(12)	4003.2(19)	44.5(6)
O002	-2559(5)	2173.5(10)	284.4(19)	83.0(8)
C2	-456(6)	578.8(13)	955(2)	58.6(8)
C3	2949(5)	30.9(13)	3010(2)	52.8(7)
C4	11089(5)	-1579.2(13)	5224(2)	55.2(8)
C5	1776(6)	683.8(13)	1449(2)	55.2(8)
C6	-1079(6)	1700.1(13)	671(2)	55.8(8)
C7	1136(6)	1821.0(14)	1164(2)	60.5(8)
C8	2546(6)	1314.5(14)	1547(2)	60.5(8)
C9	3278(6)	139.0(15)	1909(2)	64.7(9)
C10	-1862(6)	1074.0(14)	567(2)	62.6(8)
C11	10930(7)	-1732.5(17)	6315(3)	75.9(10)
C12	12789(8)	-2223.8(18)	6772(3)	92.3(13)
C13	12217(8)	-2892.7(19)	6523(3)	95.4(13)
N004	15617(9)	-3615(2)	7345(3)	127.8(17)
C003	14113(9)	-3314(2)	6984(3)	100.1(14)

Table 3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **168**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
O1	53.7(12)	33.7(10)	92.8(15)	-1.0(9)	-9(1)	-6.7(8)
O2	58.1(13)	35.3(10)	83.2(14)	1.0(9)	-15.4(10)	-7.8(8)
C1	47.8(16)	36.1(13)	55.5(15)	-1.3(11)	1.1(12)	-3.0(11)
N1	47.9(14)	32.6(11)	69.8(15)	0.2(10)	-6.7(11)	-1.6(9)
N002	50.9(13)	34.8(11)	65.3(14)	-0.5(10)	-8.2(11)	-2.7(10)
C001	43.9(15)	36.7(13)	51.0(14)	-0.7(11)	-2.2(11)	-4.4(11)
O002	92.3(17)	47.2(13)	99.8(18)	1.5(12)	-29.1(14)	15.1(12)
C2	70(2)	38.9(15)	66.8(18)	-3.3(13)	7.1(15)	0.2(14)
C3	48.4(16)	46.3(15)	61.2(17)	-1.8(12)	-3.9(13)	4.8(12)
C4	46.9(16)	43.2(15)	73.8(19)	-3.9(13)	-0.4(14)	3.0(12)
C5	67.6(19)	45.7(15)	53.7(16)	3.6(12)	13.1(14)	11.5(13)
C6	68(2)	42.7(15)	55.4(16)	-0.1(12)	-0.2(14)	8.1(13)
C7	69(2)	42.3(15)	69.6(19)	1.5(13)	6.5(15)	-4.4(14)
C8	55.1(18)	56.5(18)	69.0(18)	0.6(14)	3.2(14)	0.9(14)
C9	68(2)	55.2(18)	72(2)	6.6(14)	11.3(16)	17.9(15)
C10	63.7(19)	49.6(17)	71.0(19)	-12.4(14)	-6.6(15)	1.1(14)
C11	85(3)	63(2)	78(2)	9.3(16)	5.2(18)	21.7(18)
C12	112(3)	73(3)	87(3)	8(2)	-12(2)	22(2)
C13	106(3)	69(2)	107(3)	16(2)	-8(2)	21(2)
N004	147(4)	129(3)	107(3)	35(2)	13(3)	82(3)
C003	116(3)	88(3)	95(3)	25(2)	8(3)	49(3)

Table 4. Bond Lengths for **168**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
O1	C1	1.237(3)	C4	C11	1.490(5)
O2	C001	1.226(3)	C5	C8	1.384(4)
C1	N1	1.307(3)	C5	C9	1.505(4)
C1	C001	1.537(4)	C6	C7	1.377(5)
N1	C4	1.452(3)	C6	C10	1.378(4)
N002	C001	1.314(3)	C7	C8	1.385(4)
N002	C3	1.448(3)	C11	C12	1.545(5)
O002	C6	1.358(3)	C12	C13	1.457(5)
C2	C5	1.380(5)	C13	C003	1.469(5)
C2	C10	1.368(4)	N004	C003	1.123(5)

C3	C9	1.505(4)

Table 5. Bond Angles for **168**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	N1	126.3(2)	C8	C5	C9	121.0(3)
O1	C1	C001	119.6(2)	O002	C6	C7	122.9(3)
N1	C1	C001	114.1(2)	O002	C6	C10	117.8(3)
C1	N1	C4	125.1(2)	C7	C6	C10	119.3(3)
C001	N002	C3	123.6(2)	C6	C7	C8	119.8(3)
O2	C001	C1	120.5(2)	C7	C8	C5	121.4(3)
O2	C001	N002	125.5(2)	C5	C9	C3	111.8(2)
N002	C001	C1	114.0(2)	C2	C10	C6	120.3(3)
C10	C2	C5	121.8(3)	C4	C11	C12	113.7(3)
N002	C3	C9	112.0(2)	C13	C12	C11	114.6(4)
N1	C4	C11	112.6(2)	C12	C13	C003	109.9(4)
C2	C5	C8	117.4(3)	N004	C003	C13	177.2(6)
C2	C5	C9	121.6(3)				

Table 6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **168.**

Atom	*x*	*y*	*z*	U(eq)
H1	10119	-662	4987	61
H002	3749	-891	3326	62
H00A	-1921	2524	393	124
H2	-1021	160	885	70
H3A	3420	415	3398	63
H3B	1294	-45	3063	63
H4A	12708	-1476	5140	66
H4B	10644	-1956	4813	66
H7	1684	2241	1239	73
H8	4042	1400	1877	73
H9A	4921	234	1859	78
H9B	2874	-251	1525	78
H10	-3352	988	232	75
H11A	9374	-1902	6378	91

H11B	11116	-1338	6709	91
H12A	14283	-2121	6533	111
H12B	12988	-2177	7508	111
H13A	12017	-2948	5789	115
H13B	10749	-3007	6777	115

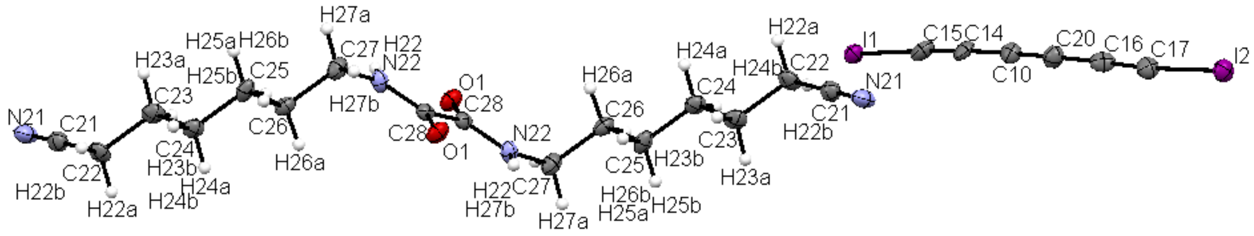


Figure: Crystal structure for **157·56** co-crystals in blue phase.

Table 1. Crystal data and structure refinement for **157·56** co-crystals.

Identification code	c6i2blue2
Empirical formula	$C_{28}H_{26}I_4N_4O_2$
Formula weight	958.16
Temperature/K	117.9
Crystal system	triclinic
Space group	P-1
a/Å	5.11570(18)
b/Å	7.9865(7)
c/Å	19.7042(15)
α/°	89.975(7)
β/°	85.017(5)
γ/°	85.048(5)
Volume/Å^3	798.99(10)
Z	1
ρ_{calc}mg/mm^3	1.9912
m/mm^{-1}	3.930
F(000)	448.5
Crystal size/mm^3	N/A × N/A × N/A
2Θ range for data collection	6.56 to 59.26°
Index ranges	$-6 \leq h \leq 7$, $-10 \leq k \leq 10$, $-26 \leq l \leq 25$
Reflections collected	22519
Independent reflections	4147[R(int) = 0.0834]
Data/restraints/parameters	4147/0/177
Goodness-of-fit on F^2	0.963
Final R indexes [I>=2σ (I)]	$R_1 = 0.0560$, wR_2 = N/A
Final R indexes [all data]	$R_1 = 0.0978$, $wR_2 = 0.1630$
Largest diff. peak/hole / e Å^{-3}	2.49/-1.87

Table 2. Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for **157·56** co-crystals. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
I1	-3074.8(9)	11643.6(6)	5513.9(2)	23.80(17)
I2	9609.4(9)	7994.1(6)	9125.7(2)	27.88(18)
O1	2108(10)	6251(7)	288(3)	26.1(12)
C21	11726(15)	3624(10)	4256(4)	26.1(17)
N22	6252(12)	6204(8)	633(3)	22.2(13)
C10	2595(15)	9617(9)	7046(4)	24.0(16)
C23	10010(14)	4838(10)	3171(4)	26.0(17)
C26	5292(14)	6764(9)	1872(4)	22.9(15)
C28	4452(13)	5696(9)	254(4)	18.9(15)
C14	823(15)	10162(9)	6594(4)	23.4(16)
C15	-711(14)	10721(10)	6194(4)	26.0(17)
C16	5917(15)	8783(10)	7925(4)	27.2(17)
C17	7424(15)	8516(10)	8359(4)	27.4(17)
C22	9387(14)	4255(11)	3923(4)	26.9(17)
C25	7883(14)	6138(10)	2157(4)	24.6(16)
C20	4168(15)	9191(10)	7450(4)	27.7(17)
N21	13492(13)	3125(9)	4521(4)	31.0(16)
C27	5621(15)	7493(10)	1157(4)	25.5(16)
C24	7447(14)	5474(10)	2876(4)	24.1(16)

Table 3. Anisotropic Displacement Parameters ($Å^2\times10^3$) for c6i2blue2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{12}}$	$\mathbf{U_{13}}$	$\mathbf{U_{23}}$
I1	18.2(3)	28.8(3)	25.1(3)	-3.3(2)	-4.66(19)	1.3(2)
I2	24.1(3)	31.8(3)	28.1(3)	0.2(2)	-7.0(2)	3.6(2)
O1	19(3)	27(3)	34(3)	0(2)	-8(2)	-2(2)
C21	23(4)	30(4)	25(4)	-3(3)	-2(3)	3(3)
N22	18(3)	30(3)	18(3)	3(3)	-3(2)	0(3)
C10	25(4)	20(4)	27(4)	1(3)	-5(3)	-1(3)
C23	15(4)	31(4)	31(4)	-1(3)	2(3)	1(3)

C26	18(4)	21(4)	30(4)	-2(3)	-6(3)	-2(3)
C28	17(3)	19(4)	22(4)	-1(3)	-6(3)	7(3)
C14	24(4)	16(4)	33(4)	-5(3)	-10(3)	-3(3)
C15	19(4)	24(4)	37(5)	-4(3)	-7(3)	-5(3)
C16	23(4)	18(4)	39(5)	2(3)	-1(3)	3(3)
C17	27(4)	23(4)	32(4)	1(3)	-5(3)	3(3)
C22	17(4)	37(5)	25(4)	-1(3)	3(3)	7(3)
C25	15(3)	31(4)	28(4)	1(3)	-7(3)	-5(3)
C20	24(4)	32(4)	28(4)	-2(3)	-4(3)	-1(3)
N21	23(3)	35(4)	36(4)	-8(3)	-5(3)	16(3)
C27	25(4)	21(4)	32(4)	1(3)	-12(3)	0(3)
C24	15(3)	28(4)	29(4)	-2(3)	-3(3)	4(3)

Table 4. Bond Lengths for **157·56** co-crystals.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	C15	1.981(8)	C23	C22	1.567(10)
I2	C17	1.979(8)	C23	C24	1.526(10)
O1	C28	1.238(8)	C26	C25	1.529(10)
C21	C22	1.466(11)	C26	C27	1.524(11)
C21	N21	1.125(10)	C28	C28[1]	1.532(14)
N22	C28	1.324(9)	C14	C15	1.218(11)
N22	C27	1.456(10)	C16	C17	1.207(11)
C10	C14	1.370(10)	C16	C20	1.370(11)
C10	C20	1.209(11)	C25	C24	1.518(11)

[1] 1-X,1-Y,-Z

Table 5. Bond Angles for **157·56** co-crystals.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N21	C21	C22	178.7(8)	C14	C15	I1	177.5(7)
C27	N22	C28	122.1(6)	C20	C16	C17	176.3(9)
C20	C10	C14	177.8(8)	C16	C17	I2	174.4(7)
C24	C23	C22	109.3(6)	C23	C22	C21	113.8(6)
C27	C26	C25	114.2(6)	C24	C25	C26	111.9(6)
N22	C28	O1	125.6(7)	C16	C20	C10	177.1(9)

C28[1]	C28	O1	121.4(8)	C26	C27	N22	112.7(6)
C28[1]	C28	N22	113.0(7)	C25	C24	C23	112.8(6)
C15	C14	C10	176.9(8)				

[1] 1-X,1-Y,-Z

Table 6. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) **157·56** co-crystals.

Atom	*x*	*y*	*z*	U(eq)
H22	7845(12)	5757(8)	566(3)	26.6(16)
H23a	11290(70)	5670(50)	3137(17)	31(2)
H23b	11000(80)	3960(40)	2890(6)	31(2)
H26a	4290(80)	5790(30)	1839(18)	27.5(19)
H26b	4500(80)	7670(40)	2169(7)	27.5(19)
H22a	8160(80)	3390(40)	3929(17)	32(2)
H22b	8470(90)	5180(40)	4187(6)	32(2)
H25a	8760(90)	5250(40)	1865(7)	29.5(19)
H25b	9000(80)	7060(40)	2160(18)	29.5(19)
H27a	6950(80)	8290(50)	1132(7)	31(2)
H27b	4050(60)	8200(60)	1063(5)	31(2)
H24a	6260(70)	4590(40)	2888(18)	28.9(19)
H24b	6500(80)	6340(40)	3172(6)	28.9(19)