Stony Brook University

Macrocyclic Hosts for Polymerization of Diiodobutadiyne

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Ce Chen

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Abstract of the Thesis

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All-carbon materials have been widely investigated because of their potential thermal, electrical and physical properties. Carbyne, which would have all sp hybridized carbons, has received considerable attention. Polydiiododiacetylene (PIDA), which has a carbon backbone and iodine atom substituents, serves as a potential precursor to carbyne. We propose that carbyne could result from complete deiodination of PIDA in the presence of Lewis bases such as triethyl amine, pyridine and pyrrolidine. To avoid aggregation of PIDA or carbyne strands during this process, we aim to prepare PIDA as a polyrotaxane through topochemical polymerization, using a macrocyclic cocrystallizing agent, or "host", containing pyridine segments. In this work, the structure and synthesis of macrocyclic host have been thoroughly investigated. The conformation of the macrocyclic host was optimized through equilibrium conformer using the AM1 semi-empirical modeling and multiple possible conformations were proposed to predict the macrocyclic rings' sizes. A route was chosen to synthesize the target macrocyclic host, which

has four main segments; glycol ether group, pyridyl, alkynyl and oxalyl group. This route includes Sonogashira coupling with 4-pentyn-1-ol, tosylation of hydroxyl, substitution of tosyl group, Staudinger reaction and coupling with ethyl oxalyl chloride. This synthetic route has been pursued and all intermediates were successfully synthesized.

Dedication Page

This thesis is dedicated to my parents:

Yuping Chen and Hua Xiao

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List of Abbreviations

PIDA	Polydiiododiacetylene
PE-a-CTFE	Poly(ethylene-alt-chlorotrifluoroethylene)
Tr	Tris(3,5-di-t-butylphenyl)methyl
DB24C8	Dibenzo-24-crown-8
DP24C8	Dipyrido-24-crown-8
CD	Cyclodextrin
PDA	Polydiacetylene
XB	Halogen bond
C_4I_2	Diiodobutadiyne
TLC	Thin layer chromatography
DMF	Dimethylformamide
dppe	1,2-bis(diphenylphosphino)-ethane
RBF	Round bottom flask
THF	Tetrahydrofuran
pyz	Pyrazine(pyz)
dabco	1, 4-diazabicyclooctane

Acknowledgments

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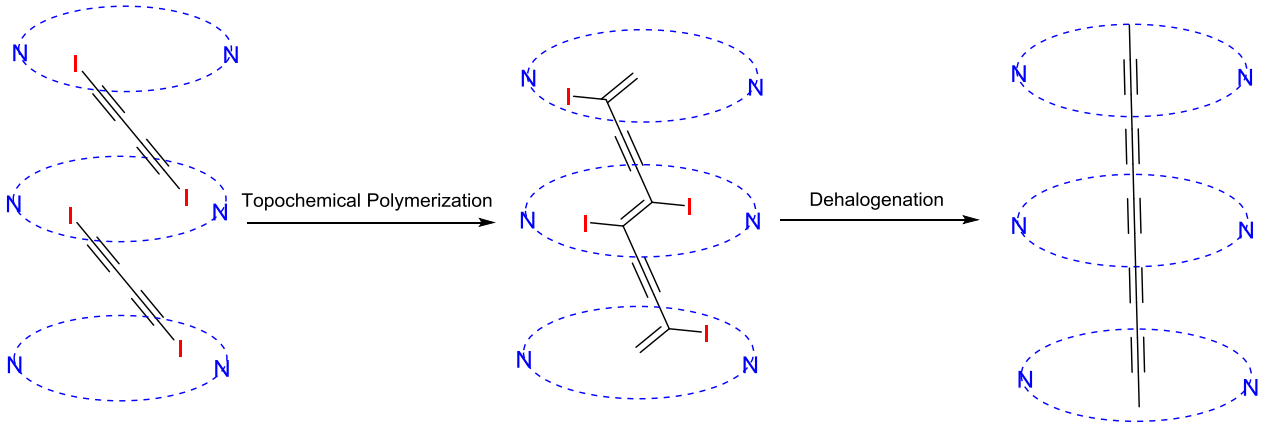
Finally, I would like to show my great gratitude to my friends and parents, for continuous support. Without them, I could not image what the life will be here. I love everyone I had in my life

Chapter 1. Introduction

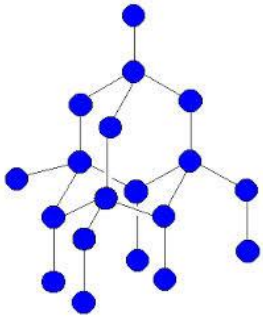
All-carbon materials have received considerable attention in the past. Carbyne, a new allotrope of carbon, is still under controversy on its synthesis and properties. The goal of this project is to prepare the polymer PIDA (polydiiododiacetylene) as a polyrotaxane complex, encapsulated in a column of macrocyclic hosts. The polyrotaxane structure will prevent aggregation of the PIDA strands, allowing for the complete dehalogenation of the polymer to make carbyne. The proposed route is shown in **Scheme 1.1**. PIDA, a precursor of carbyne, can be made from diiodobutadiyne via topochemical polymerization and host-guest strategy with macrocyclic hosts, in which the macrocyclic hosts will self-assemble into a columnar structure and diiodobutadiynes will form halogen bonds with the hosts.



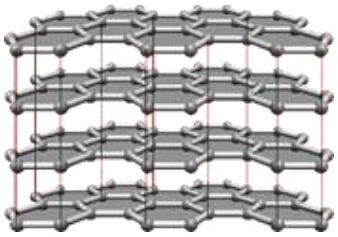
Scheme 1.1 A new route of carbyne

1.1 All-carbon materials

All-carbon materials have been widely investigated because of their potential properties, such as their electrical conductivity, thermal conductivity and hardness. They exist in different forms with various properties, such as diamond, graphite, carbon nanotube, graphene, fullerene and carbyne (**Figure 1.1**).



Diamond



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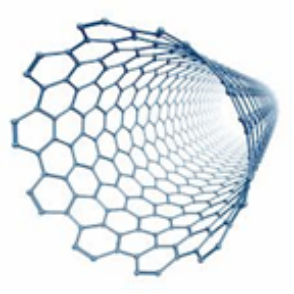
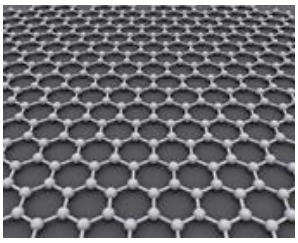
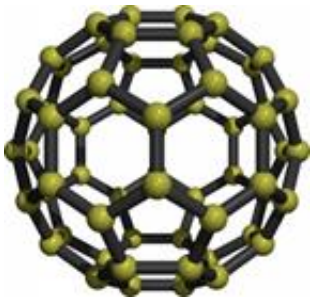


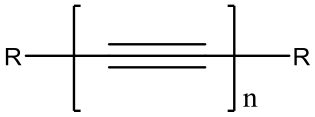
Carbon Nanotube



Graphene



Fullerene



Carbyne

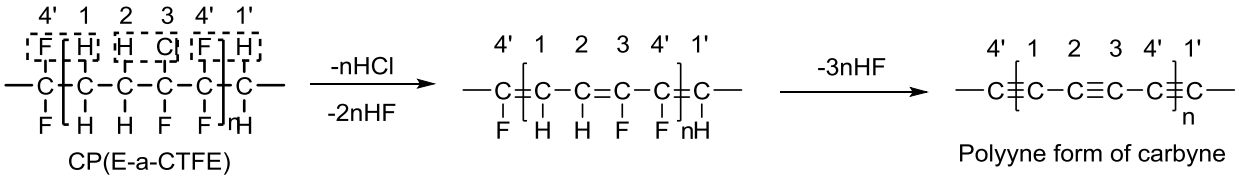
Figure 1.1 Allotropes of carbon

Diamond, consisting of all sp^3 hybridized carbons, has many unusual properties, such as extreme hardness, high optical transmittance and wide band gap etc.[1] Because of these properties, the synthesis of diamond is of great interest. It can be synthesized through chemical vapor deposition.[1b] Graphite is made of sp^2 hybridized carbon. The structure is layered and it behaves as a good conductor.[2] Fullerenes exist in different sizes, such as C_{60}, C_{70} and C_{82}. The C_{60} fullerene was first discovered through laser irradiation of graphite by Kroto and coworkers.[3] It is an all-carbon cage-like molecule with each atom sp^2 hybridized and directly bonded to three neighbors.[3] Graphene can be used in composite material, electric batteries and in hydrogen storage.[4] Carbon nanotubes usually have different sizes, which depends on length and diameter. Because of their special electrical, electrochemical and optical properties, carbon nanotubes have

been widely investigated in electronics, biological and energy applications.[5] Carbyne, having all-sp-hybridized carbon, is highly reactive. It will be discussed in section **1.2**.

1.2 Attempts to make carbyne

Carbyne, an sp hybridized all-carbon chain, is a new allotrope of carbon and has attracted considerable interest. Because of its instability, it is less well known than the other carbon allotropes. The investigation of carbyne or carbyne-like structures is still underway and the results are often unclear. Researchers have tried to synthesize carbyne or carbyne-like materials in several ways, such as chemical dehydrohalogenation and electrochemical synthesis. Evsyukov et al. studied dehydrohalogenation of poly (ethylene-alt-chlorotrifluoroethylene)(PE-a-CTFE)to make carbyne.[6] PE-a-CTFE was treated with potassium tert-butoxide in tetrahydrofuran to form a halogen-substituted polyenyne structure. The theoretical synthesis is showed below.

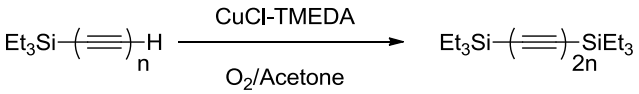


Scheme 1.2 Chemical dehydrohalogenation[6]

However, elimination of hydrogen halides was incomplete, which the authors hypothesized might result from "insufficient strength of the base, sterical hindrances caused by its bulkiness as well as by alternation defects in the original copolymer".[6] Wang and coworkers claimed to form carbyne-like material via electrochemical methods.[7] 1, 1, 2-Trichloroethane was dehydrochlorinated on a Ni cathode in dimethylsulfoxide electrolyte solution under anaerobic conditions.[7] However, this method was not effective because of the electrochemical carbon,

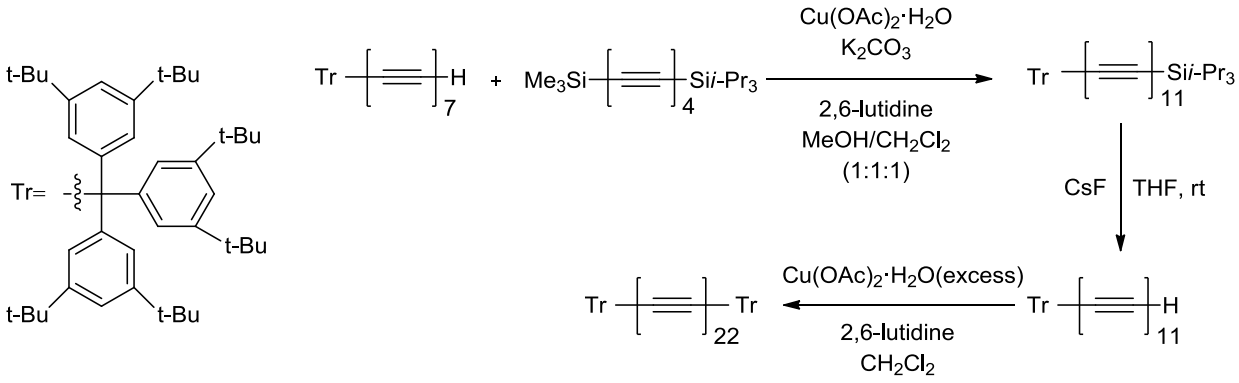
which caused oxidation with O_2 and cross-linking of polyyne-like chains. In the above reports, no evidence of formation of carbyne was observed and the properties of carbyne remain elusive.

Recently, polyynes, analogues of carbyne, have been widely investigated to predict the properties of carbyne. Polyynes are one-dimensional chains with alternating single and triple bonds. Walton and coworkers first reported to synthesize polyyne chains through Hay coupling (**Scheme 1.3**).[8] The length of polyyne chain varied from four to sixteen triple bonds.



Scheme 1.3 Walton's method[8]

Tykwinski and coworkers also synthesized several polyynes with a variety of end groups, in which bulky end groups would increase the stability and solubility of polyynes. In 2010, Tykwinski reported the synthesis of polyynes with as manys as 44 sp-carbons.[9] They used bulky tris(3,5-di-t-butylphenyl)methyl (Tr) as end groups to stabilize the chain. The synthesis method is shown in **Scheme 1.4**.



Scheme 1.4 Tykwinski's method[9]

When the polyynes become larger, the effect on stability by the end groups becomes insufficient. In order to overcome this issue, some researchers have encapsulated polyynes into macrocycles to form rotaxanes or polyrotaxanes.

1.3 Rotaxane and polyrotaxane

A rotaxane consists of a linear molecule with end-groups, which is threaded through a macrocyclic molecule. The macrocyclic molecule should have large enough cavities to thread the linear species, and the end-groups will prevent dethreading.[10] There are four main approaches to obtain rotaxane: clipping, threading, slipping and active-metal templating.[11] Tykwinski and coworkers synthesized polyyne rotaxanes with 4, 6 and 10 triple bonds in length through active copper-templated coupling, which is showed in **Figure 1.2**.[12] This can help to stabilize the polyyne chain.

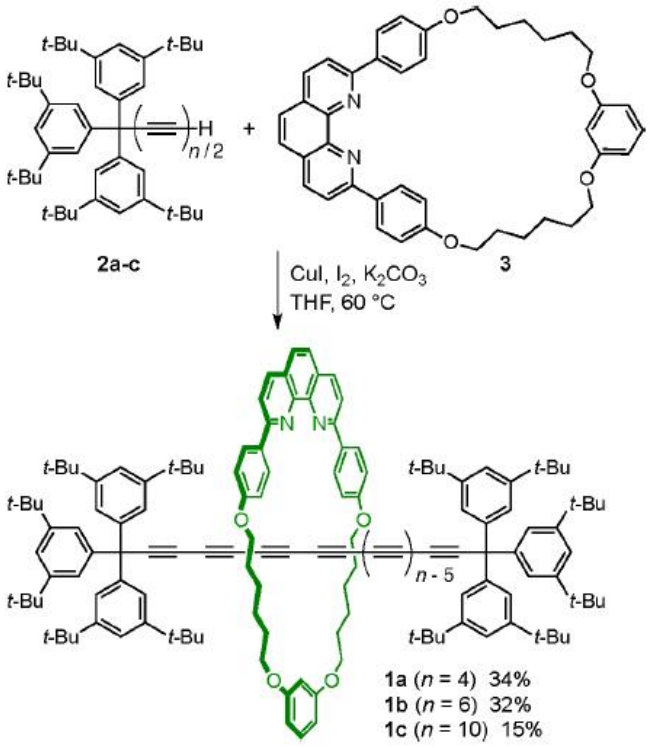


Figure 1.2 Synthsis of rotaxanes via active copper-templated coupling. Reprinted with permission from reference 12. Copyright (2012) American Chemical Society.

Large numbers of rotaxanes are obtained with cyclodextrins through hydrophilic interaction of hydroxyl groups and hydrophobic interaction of the hydrocarbon and ether groups. Hydroxyl groups in cyclodextrin make the molecule hydrophilic outside while the hydrocarbon and ether groups result in a hydrophobic inside. In 1981, Ogino first reported the synthesis of a rotaxane with cyclodextrin in relatively high yield, in which the ring was α- or β- cyclodextrin and the chain was a dimeric cobalt (III) complex.[13] Sugiyama and coworkers also prepared pseudo-rotaxanes and rotaxanes with cyclodextrins to stabilize and to solubilize the polyyne chains.[14] The polyyne chains with α-cyclodextrin demonstrated considerable stabilization effect at ambient temperature in time-course UV/Vis absorption spectra while those without α-cyclodextrin were unstable.[14] Another method to form rotaxanes is hydrogen bonding interactions; Stoddart's group synthesized two different rotaxanes through hydrogen bonding of an ammonium ion with different macrocycles.[15] The two different rotaxanes are showed in **Figure 1.3**. The top rotaxane shows hydrogen bonding result from dibenzo-24-crown-8 (DB24C8) and the ammonium ion. However, the bottom rotaxane shows that a nitrogen atom in the macrocycle can also form a hydrogen bond with hydrogen atoms in the ammonium ion, which makes dipyrido-24-crown-8 (DP24C8) a better receptor.

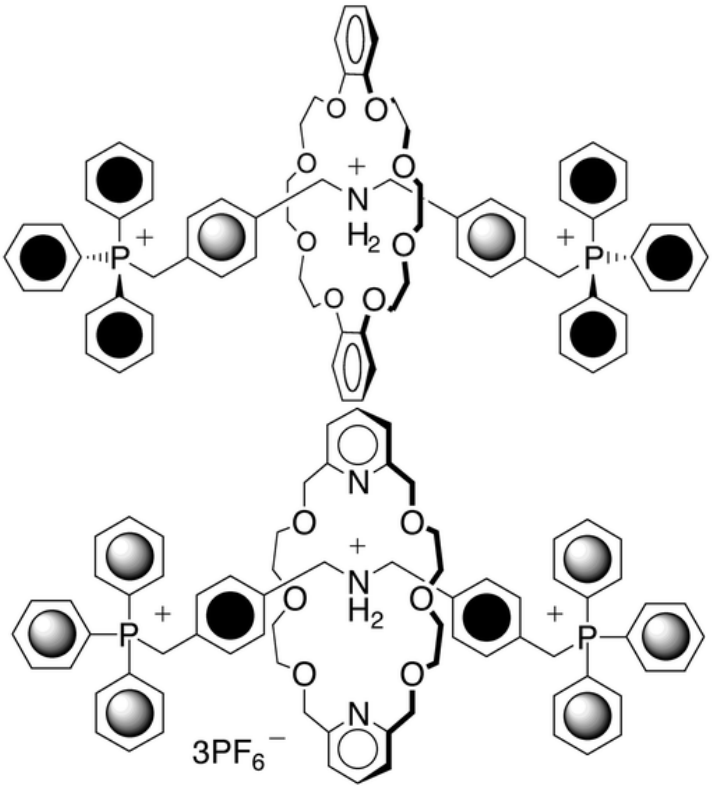


Figure 1.3 Two different rotaxanes. Reprinted with permission from reference 15a. Copyright(1999) American Chemical Society. Reprinted with permission from reference 15b. Copyright (2000) American Chemical Society.

A polyrotaxane, just as its name implies, consists of large numbers of rotaxane segments incorporated in the polymer. In 2003, in order to solubilize poly(azomethine) (compound 1 in **Figure 1.4**) in common organic solvents, the Geckeler group designed fullerene-terminated soluble poly(azomethine) rotaxane.[16] In the polyrotaxane, fullerene was end-capped with an amino group and the macrocycle of β-CD was used to modify the benzene ring.

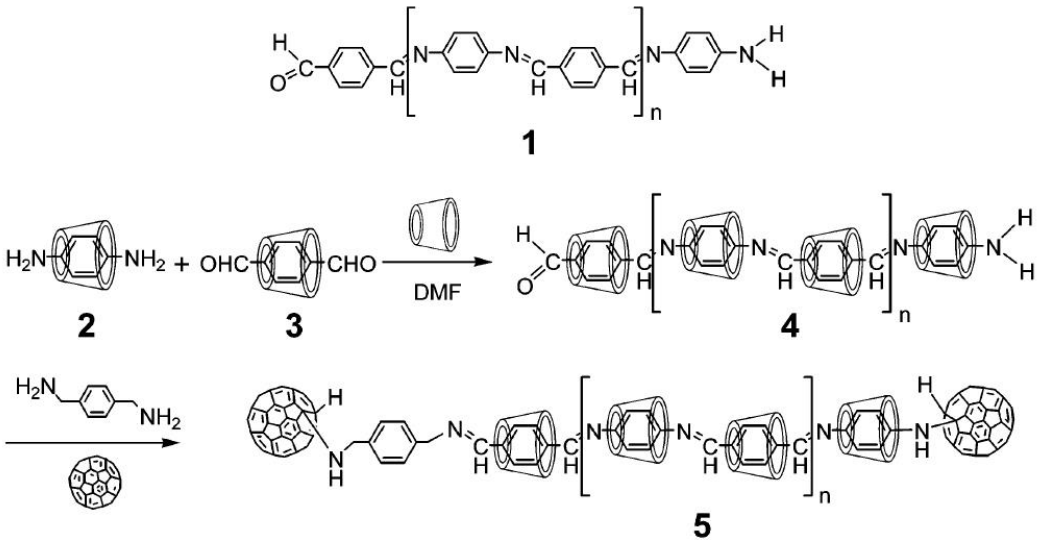


Figure 1.4 Synthesis of the poly(azomethine) rotaxane with fullerene as the end-capping agent. Reprinted with permission from reference 16. Copyright (2003) American Chemical Society.

In my project, the polyrotaxane structure is made from self-assembly of macrocyclic hosts and halogen bond between host and guest diiodobutadiyne. This polyrotaxane structure will prevent aggregation of the PIDA strands, allowing for the complete dehalogenation of the polymer to make carbyne. Also, we think this polyrotaxane structure can help to stabilize the polymer.

1.4 Self-assembly of macrocycles

Supramolecular chemistry is a rapidly growing field, emphasizing assembly of discrete molecules. Traditional chemistry deals with covalent interaction while supramolecular chemistry focuses more on noncovalent interactions, such as hydrogen bonding[17], van der Waals forces[18] and aromatic-aromatic interaction (π-π interactions)[19]. Self-assembly, a main process involved in supramolecular chemistry, will take advantage of these noncovalent interactions to organize discrete molecules into high-order structures. Here I will introduce the self-assembly of macrocycles through hydrogen bonding and π-π interactions.

Aromatic-aromatic interactions, well known as π-π interactions, play important roles in self-assembly of macrocycles. Aromatic rings can be arranged in following conformations; face-to-face, edge-to-face and slipped stack. Hill and coworkers synthesized amphiphilic hexa-peri-hexabenzocoronene, self-assembling via π-π stacking to form a discrete nanotubular object.[20] The object has a uniform and 14-nanometer-wide hollow space. Lauher and coworkers also took advantage of π-π stacking to design a tubular macrocyclic polymer, from which the monomer structure and route to a tubular polymer are shown in **Figure 1.5**.[21] The diacetylene-based macrocycles self-assemble into slipped π-π stack and polymerize via slow annealing. The macrocycle has two different crystalline forms, which are monoclinic and triclinic form, respectively. After slow annealing at 40 °C, the triclinic form appears to undergo single-crystal-to-single-crystal polymerization.[21]

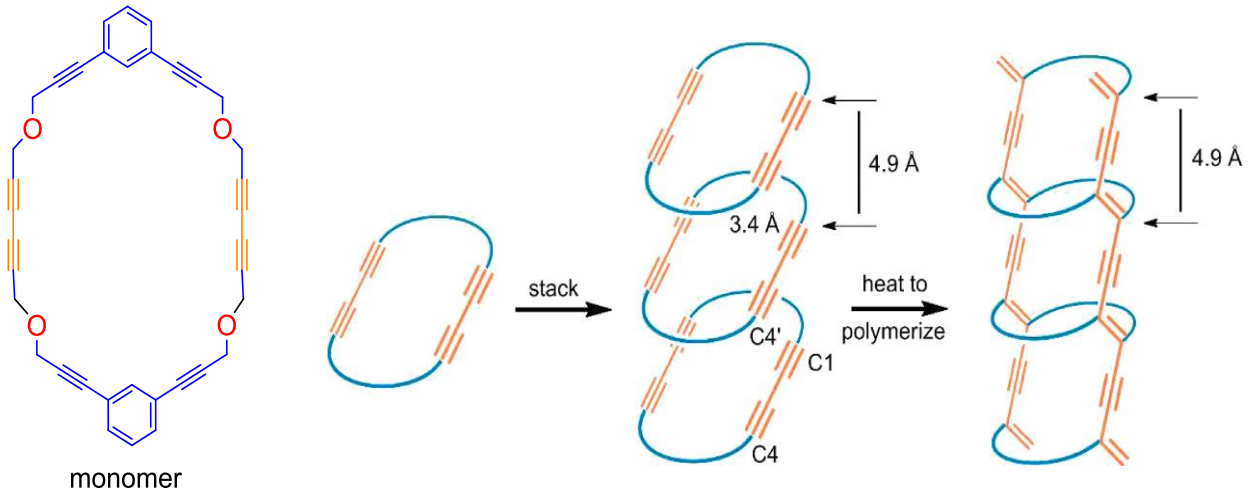


Figure 1.5 Aromatic-aromatic interactions. Reprinted with permission from reference 21. Copyright (2012) American Chemical Society.

Hydrogen bonding is an attractive force that involves a hydrogen and a strong electronegative atom, such as oxygen, nitrogen and fluorine. The electronegative atoms behave as hydrogen bond acceptor and the hydrogen is hydrogen bond donor.[22] Macrocyclic peptides

and ureas can form high order tubular structures via hydrogen bonds. Ghadiri and coworkers used cyclo[-(L-Gln-D-Ala-L-Glu-D-Ala)$_2$-] to self-assemble into hollow tubes via amide hydrogen bonds.[23] Shimizu and coworkers also took advantage of amide hydrogen bond to organize diacetylene macrocycles for topochemical polymerization.[24] In addition, Shimizu and coworkers used macrocyclic bis-ureas to self-assemble into columnar structures through urea hydrogen bonds.[25] In the structure of macrocyclic bis-ureas, two hydrogen atoms in NH group are hydrogen bond donors and the carbonyl groups are hydrogen bond acceptors. The structures of the macrocyclic ureas are shown in **Figure 1.6**. In 2001, they used bis-urea macrocycles with m-xylene to form the self-assembed tubular structures.[25a] The m-xylene keeps the macrocycle rigid. However, this macrocycle forms intramolecular hydrogen bonds. Another bis-urea macrocycle containing m-phenyl ether avoids forming intramolecular hydrogen bonds and organizes into tubular structures with ordered acetic acid dimer filling inside as guest.[25b] The columns are stabilized by hydrogen bonding as well as π-π staking interactions of phenyl ether.

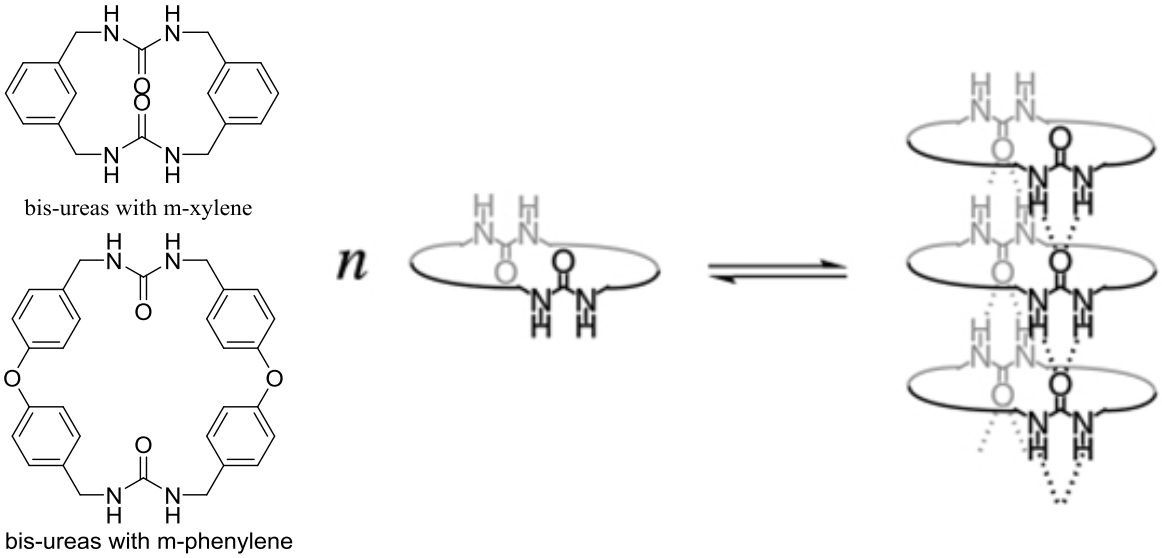


Figure 1.6 Hydrogen bonding networks.[25] Right: Reproduced from reference 25a with permission of Royal Society of Chemistry. Copyright (2001).

Like ureas, oxalamides are also used to form hydrogen bonding networks (**Figure 1.7**). The repeat distances are 4.6 Å and 5.0 Å, respectively.[26] Inspired by the above work, we design a macrocycle with pyridine, alkyne and oxalamide segments. Pyridine and alkyne segments provide beneficial rigidity, helping the macrocycles cocrystalize with diiodobutadiyne through halogen bonds. oxalamide segments are used for forming hydrogen bonding networks.

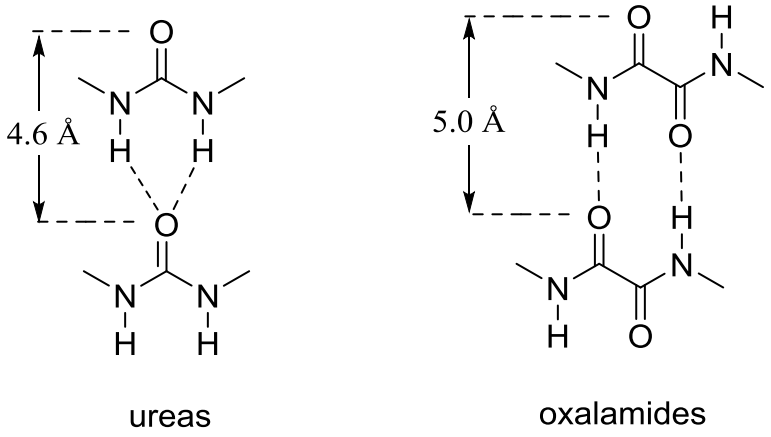
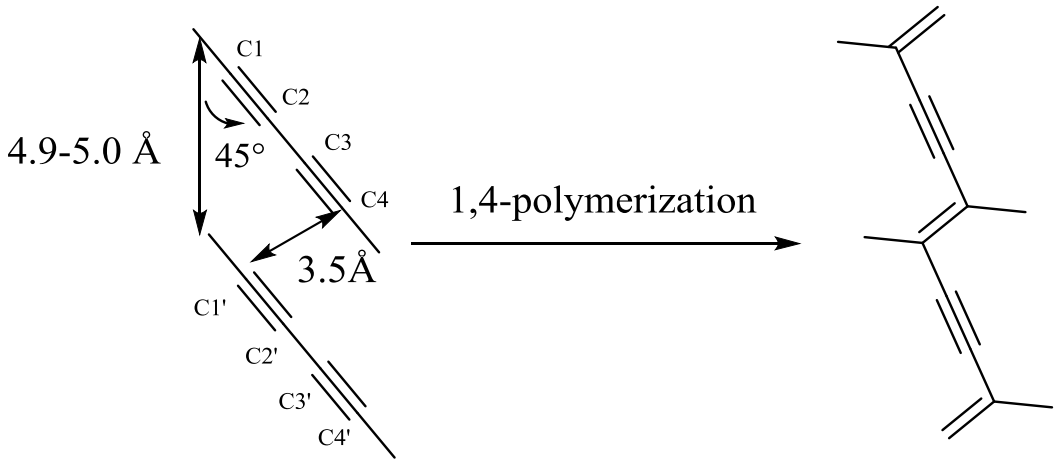


Figure 1.7 Repeat distances of hydrogen bonding networks[26]

1.5 Topochemical polymerization and host-guest strategy

Polydiacetylenes (PDAs), conjugated polymers with alternating double and triple bonds in the backbone, are prepared via topochemical polymerization of aligned diynes. In 1969, the synthesis of PDA was first described by Wegner, introducing the 1, 4-polymization of monomers.[27] In addition, Baughman demonstrated how 1, 4-polymerization of diynes works and reported necessary parameters for the 1, 4-polymerization.[28] The monomers are held in alignment. The distance between adjacent monomers is near 5 Å. The intermolecular distance of reacting carbons (C4 and C1') is close to 3.5 Å, which is close to the van der Waals radius of carbon. The tilt angle between monomer diyne and the vertical translation axis should be 45°.[29] Ideal 1, 4-polymerization of diynes is showed below.



Scheme 1.5 Ideal 1, 4-polymerization of diynes.[29]

In order for topochemical polymerization to occur, the monomers should be aligned to meet the geometric requirements. However, some monomers cannot form the appropriate geometry to polymerize. The host-guest strategy is applied to align the monomers to meet the requirements reported by Baughman. Hydrogen bonding and halogen bonding play important role in host-guest strategy for topochemical polymerization. Recently, Fowler and Lauher developed different kinds of diyne monomers to undergo 1, 4-polymerization using the host-guest strategy.[30] In this way, the diyne monomers play the role of guests, which then form hydrogen bonds with host molecules. The host molecules possessing oxalamides and ureas self-assemble via hydrogen bonding. Because of hydrogen bonding interactions, the diyne monomers are aligned in proper geometry for 1, 4-polymerization. The following is an example of the host-gust strategy for one diyne. In the cocrystals, the oxalamide host molecule is organized through hydrogen bonding with a repeat distance of 4.97 Å and the nicotinyl ester groups of the diyne guest monomers form strong pyridine-carboxylic acid hydrogen bonds to the host molecules.[30]

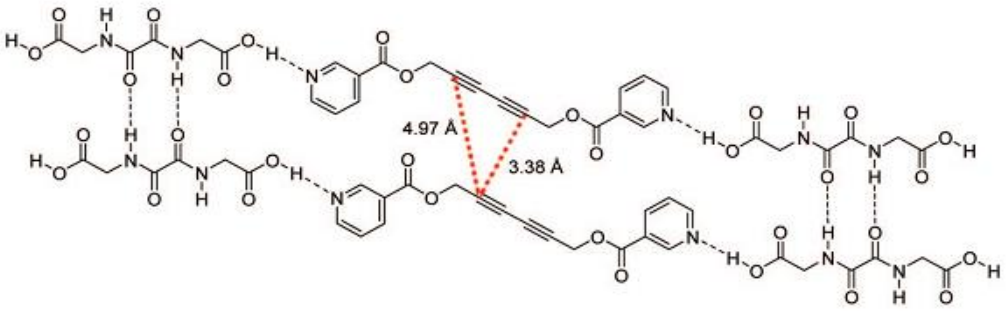


Figure 1.8 Host-gust strategy for diyne. Reprinted with permission from reference 30. Copyright (2008) American Chemical Society.

In addition to Fowler and Lauher's work, the Goroff group also showed that halogen bonding interaction could be applied for 1, 4-polymerization with the host-guest strategy.[31] Both sp^2 and sp hybridized carbons are more electronegative than iodine. Iodoalkynes behave as Lewis acids and form halogen bonds with Lewis bases, such as pyridine and nitriles. The following is an example of the host-gust strategy for diiodobutadiyne (**Figure 1.9**).[29] In this case, diiodobutadiyne plays the role of guest. The hosts with the oxalamide groups are also organized through hydrogen bonds and designed to align diiodobutadiyne in the appropriate geometry for 1, 4-topochemcal polymerization. The repeat distance of diyne monomers is 5.11 Å. The tilt angle is 51°.[29]

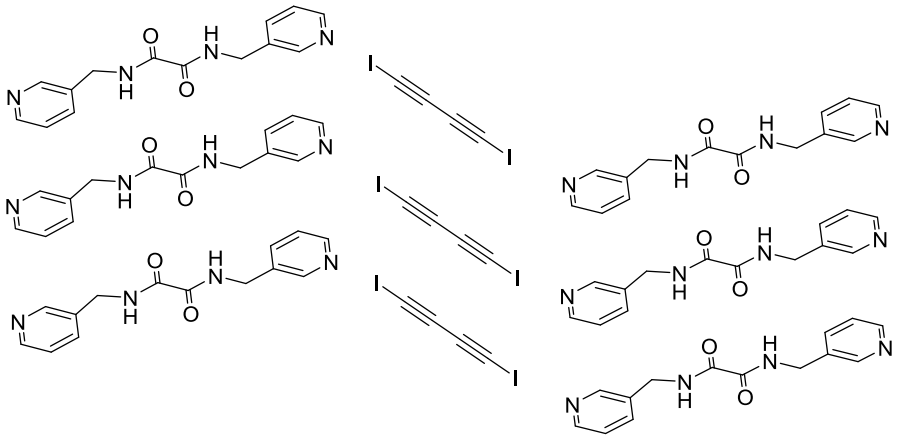
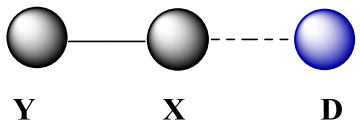


Figure 1.9 Host-gust strategy for diiodobutadiyne[29]

1.6 Halogen bonding interaction and iodoalkynes

The halogen bond (XB) is a non-covalent interaction between a halogen atom and other neutral atom or anions. The general structure of halogen bonds is shown in **Figure 1.10**.[32] In this structure, X is a halogen atom, which accepts electron density. It can be Lewis acid and halogen bond donor. D atom can donate electron density, behaving as a Lewis base and halogen bond acceptor. Y is a carbon, nitrogen, or halogen atom.



D= N, O, S, Br^-, Cl^-
X= halogen atom
Y= C, N, halogen, etc.

Figure 1.10 Formation of halogen bond[32]

The investigation of XB has been continuing for near 200 years. In 1863, the first report on the ability of halogen atoms to form well-defined adducts with electron donor species was described by Frederick Guthrie.[33] In his experiment, I_2 was added to saturated ammonium salt (nitrate or carbonate) and a diiodine/ ammonia system $NH_3 \cdot I_2$ formed. After exposed to air, it decomposes spontaneously into ammonia and iodine.[34] After that, halogen bonds became widely investigated. H. A. Benesi and J. H. Hildebrand identified the iodine-benzene complexe through UV-vis spectra in 1948.[34] In 1954, Hassel's group used X-ray to show the structure of bromine 1, 4-dioxanate.[35] The experiment showed there was a short intermolecular interaction between the oxygen atoms of dioxane and bromine atoms. The interaction was halogen bonding. The distance of O−Br bond was just 2.71 Å, which indicated a strong interaction between the bromine and oxygen atoms.[35]

Pierangleo Metrangolo and Guiseppe Resnati, whose research focuses on halogen bonds, have summarized the characteristics of halogen bonds and their interaction.[32, 36] Polarizability increases when moving down the periodic table from fluorine atom to the iodine atom. Among the four halogen atoms, the order for forming strong halogen bonding is I >Br > Cl >F.[36a] When the halogen atom is attached to an electron withdrawing atom, the more electron withdrawing an atom is, the stronger the halogen bonds. As to halocarbons, the strength order for halogen bonding is C-X (sp)>C-X (sp^2)> C-X (sp^3).[36b] In addition, investigation of halogen bonds examples in the Cambridge Structure Database is also shown in **Figure 1.11**, which showing the angles of D · · X — Y was near 180°.[36a] Goroff and coworkers used diiodobutadiyne and bis(pyridyl)oxalamides to make cocrystals, which were based on halogen bonds between nitrogen atom and iodine.[37] Polymerization of cocrystal was induced under 3.5 GPa pressure. Although the N····I—C angle changed after polymerization, both angles were still near 180°. They were 169.7° and 161.4°. [37]

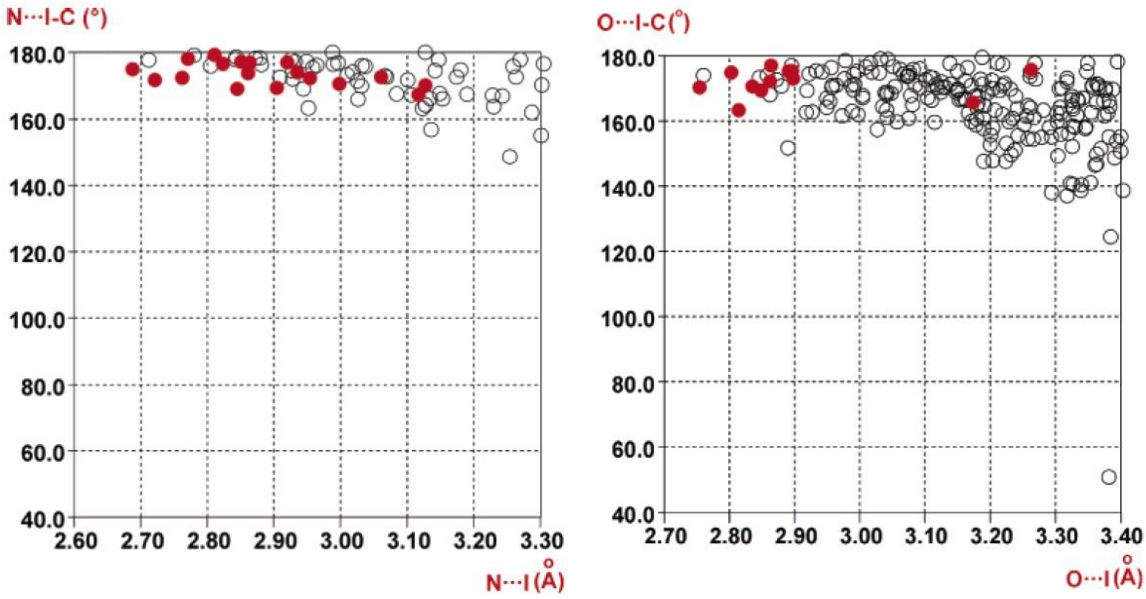


Figure 1.11 Scatterplots derived from the CSD (298,097 crystal structures; only error-free and nonpolymeric structures containing single-bonded iodine atoms and showing no disorder with R < 0.06 are considered) reporting N•••I-C angle (deg) vs N•••I distance (Å) (top) and O•••I-C angle (deg) vs O•••I distance (Å) (bottom) data for crystal structures containing intermolecular N•••I and O•••I contacts, respectively. Red circles correspond to crystals of iodofluorocarbons. Reprinted with permission from reference 36a. Copyright (2005) American Chemical Society.

Iodoalkynes, in which the C is sp hybridized, behave as Lewis acids and can form halogen bonds with some Lewis bases.[38] Diiodoacetylene, one of the families of iodoalkynes, has been extensively investigated to form halogen bonds with various Lewis bases and halide anions. It was used by Yamamoto and coworkers to form halogen bonds with halide anions, which impacted donor's packing geometry.[39] Goroff and coworkers also explored experimental studies of the ^{13}C NMR of 1-iodo-1-hexyne and diiodoetyne in Lewis-basic solvents.[40] They demonstrated acid-base interaction played important role in the α-carbon shift other than solvent polarity. Recently, Brammer and coworkers reported a new route to synthesize diiodoacetylene and its adducts with dimethylformamide(DMF), pyrazine(pyz) and 1, 4-diazabicyclooctane(dabco), in which all halogen-bond chains were connected via N····I—C and O····I—C halogen bonding interaction(**Figure 1.12**).[41] They also concluded that N····I—C

halogen bonds were shorted than those with other halogen bond acceptor group after normalized by van der Waals radii.

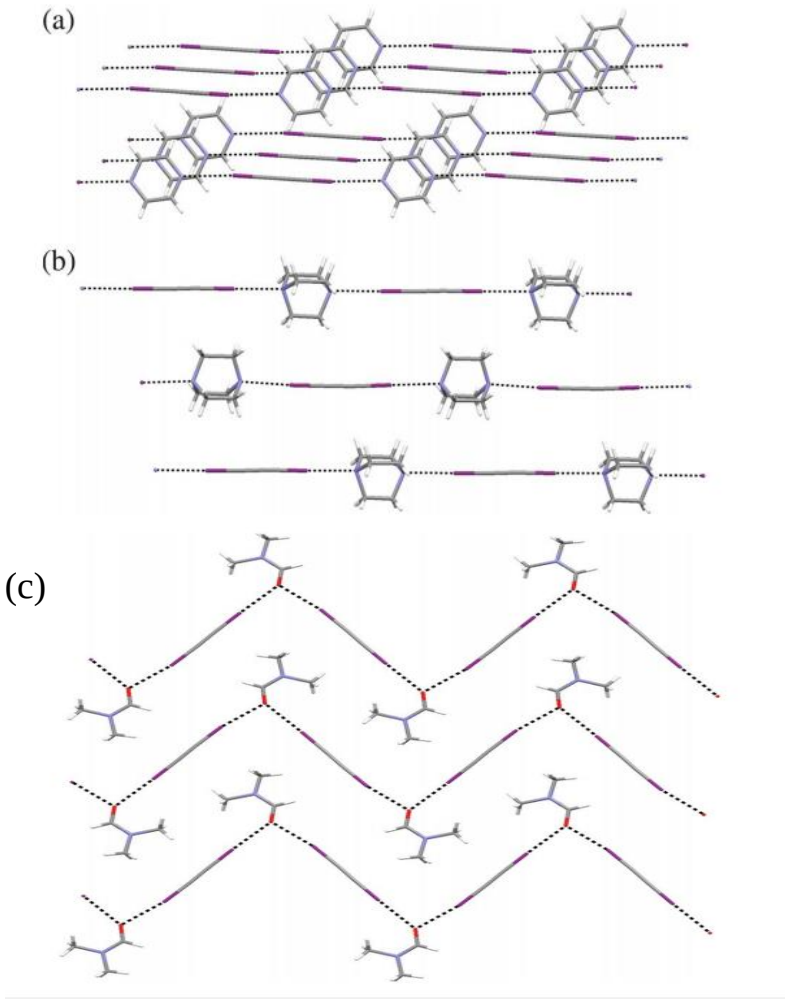


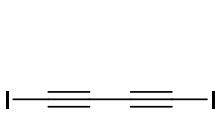
Figure 1.12 Halogen-bonded assemblies: (a) C_2I_2 with pyz. (b) C_2I_2 with dabco. (c) C_2I_2 with DMF. (2). N···I—C and O···I—C halogen bonds are shown as dashed lines**.** Reproduced from reference 41 with permission of Royal Society of Chemistry. Copyright (2012).

Diiodobutadiyne, an analogue of diiodoacetylene, is also a good Lewis acid. The Goroff group used diiodobutadiyne as a guest to cocrystallize with bis(pyridyl)oxalamides and bis(nitrile)oxalamides. They formed strong halogen bonds between the alkynyl iodine and pyridine (nitrile) nitrogen. In those cocrystals, the oxalamide hosts self-assembled into hydrogen-bonded networks, which aligned the diiodobutadiyne for topochemical polymerization.

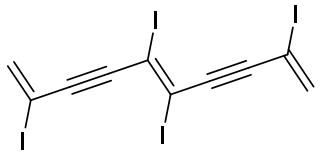
Chapter 2 Previous work from the Goroff group

2.1 Preparation and characterization of PIDA

PIDA, which has a carbon backbone and iodine atom substituents, has been broadly investigated by the Goroff group. PIDA is made from diiodobutadiyne (C_4I_2) through topochemical polymerization. Bis(nitrile)oxalamides and bis(pyridyl)oxalamides are used as hosts to form cocrystals with the guest monomer diiodobutadiyne. The structures of hosts, guest and PIDA are shown in **Figure 2.1**. The cocrystals are characterized by X-ray diffraction (XRD), UV spectroscopy, solid-state NMR and Raman spectroscopy.

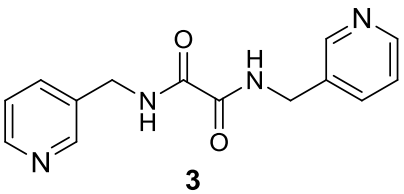


Diiodobutadiyne
Guest
1

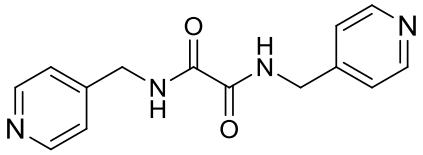


Poly(diiododiacetylene)
PIDA
2

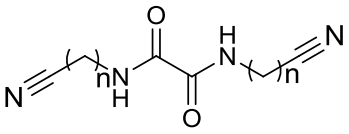
Host



3



4



5 n=3
6 n=4
7 n=5
8 n=6

Figure 2.1 Structures of hosts and guest

In 2006, Sun and coworkers first reported the synthesis of PIDA via host-guest strategy, in which guest **1** and host **5** were used for forming cocrystals and the cocrystals underwent spontaneous topochemical polymerization.[42] The hosts are organized through hydrogen bonds between oxalamide groups, while the guest forms halogen bonds between nitriles and C_4I_2. Attempts to synthesize PIDA with hosts **3** and **4** turned out to be unsuccessful because of steric hindrance around the iodine. Host **5** could form cocrystals with C_4I_2, but the cocrystals do not undergo single-crystal-to-single-crystal polymerization. The XRD analysis of cocrystal of **2** and **6** is shown below. The result demonstrated that oxygen atoms in oxalamide groups are in close contact to iodine atoms.[42]

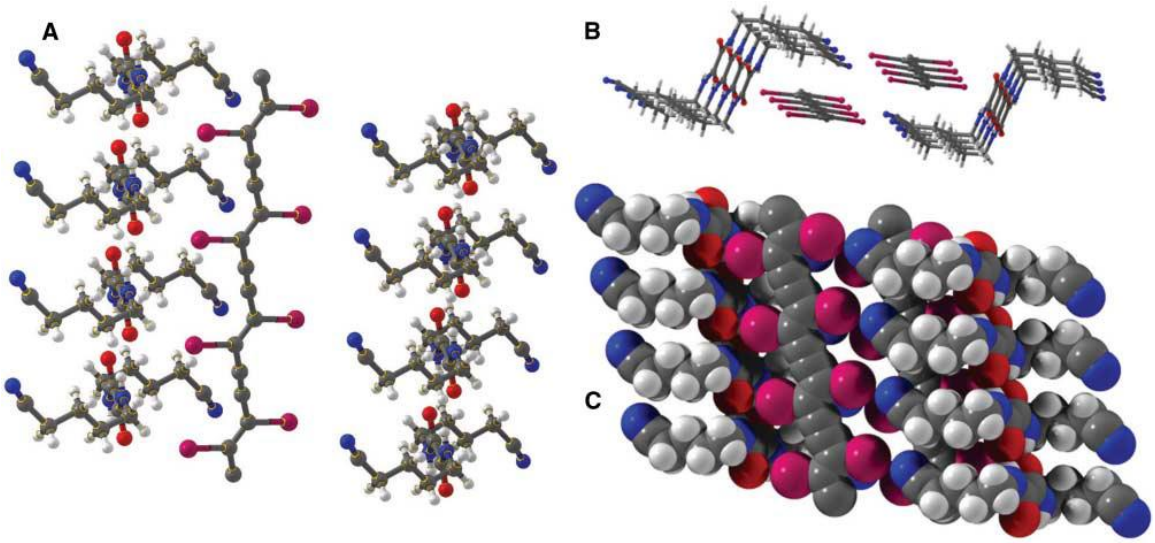


Figure 2.2 Co-crystal of PIDA **2** and host **6**. A: a single polymer chain and hosts. B: the top view in ball-and-stick representation. C: the side view in space filling representation. Reprinted with permission from reference 42. Copyright (2006) the American Association for the Advancement of Science.

In 2008, Wilhelm and coworkers used hosts **3** and **4** to form cocrystals with C_4I_2, which then underwent partial polymerization under external pressure.[29] However, the mosaicity increases when the pressure is high, limiting the further studies on PIDA. In order to certify the

formation of PIDA, XRD analysis and solid state ^{13}C NMR and Raman spectroscopy were conducted. All showed clear signs of polymer. XRD analysis showed the alignment of cocrystals and monomer still existed. Raman spectroscopy showed the formation of PIDA with three high intensity peaks, which are carbon-carbon single bond, double bond and triple bond, respectively. Solid state ^{13}C NMR showed the crystals with host **3** and **4** had near 90% and 55% polymer after pressing, respectively.[29] The solid-state ^{13}C NMR for host **3** and **4** are shown in **Figure 2.3**.

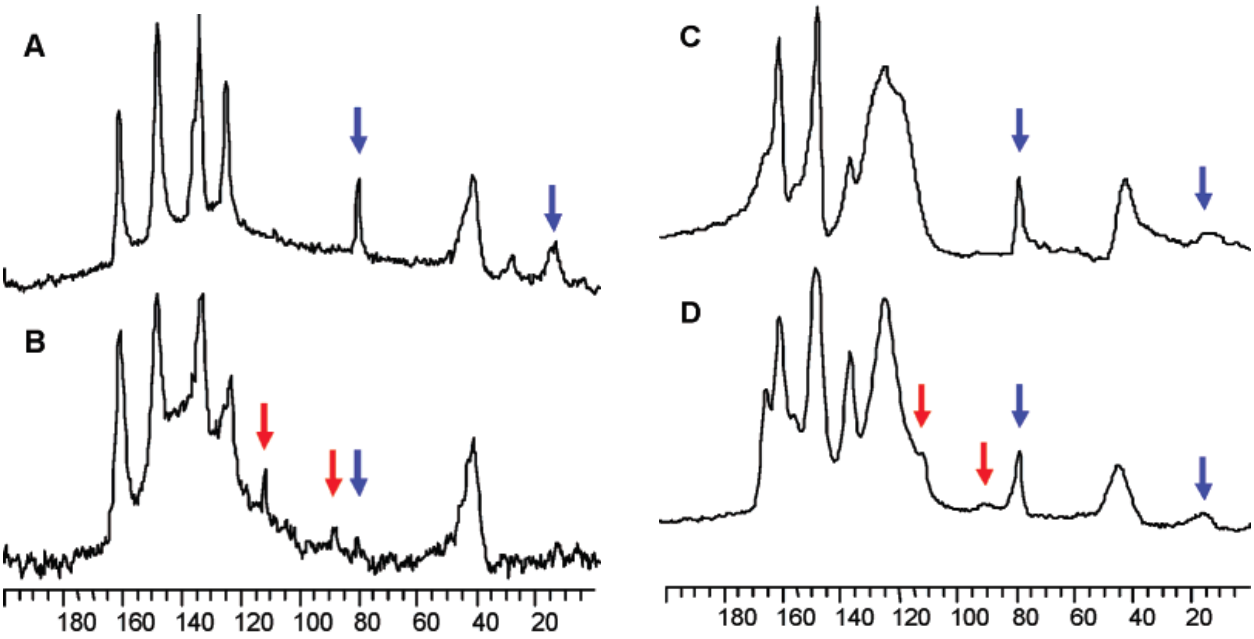


Figure 2.3 ^{13}C MAS NMR spectra of the co-crystals: (A) 3•1 before pressing; (B) 3•1 after pressing to >6 GPa; (C) 4•1 before pressing; (D) 4•1 after pressing to >6 GPa. Blue arrows indicate peaks corresponding to 1; red arrows indicate peaks corresponding to PIDA. Reprinted with permission from reference 29. Copyright (2008) American Chemical Society.

Luo and coworkers also made PIDA with host **6** and **8**, while polymerization with host **7** was disfavored.[43] Full characterization of the polymer was conducted through XRD analysis and solid state ^{13}C NMR, Raman and electron absorption spectroscopy. Raman showed the gradual change of topochemical polymerization of cocrystals of **6** and **1**.

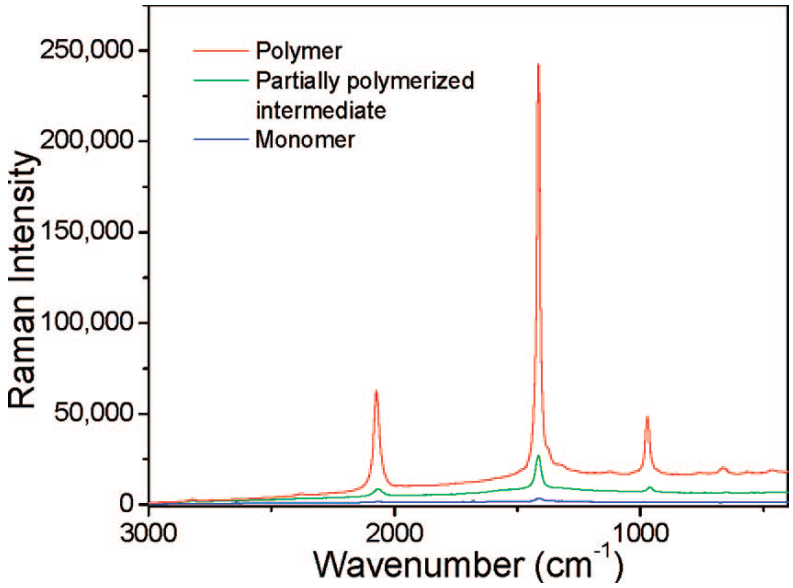
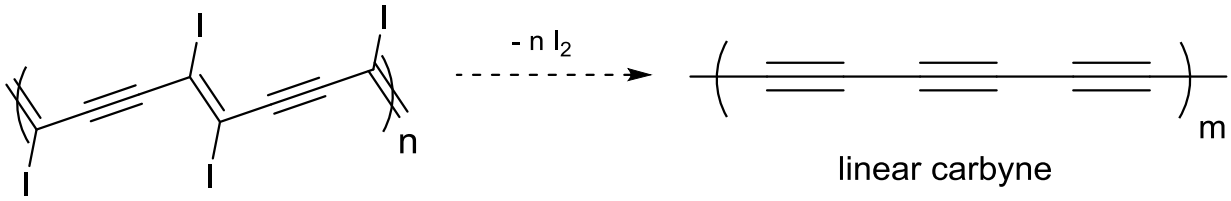


Figure 2.4 Raman spectra of monomer (blue), partially polymerized (green), and polymer (red) cocrystals made by host 5. Reprinted with permission from reference 43. Copyright (2008) American Chemical Society.

2.2 Dehalogenation of PIDA

PIDA, which has a carbon backbone and iodine atom substituents, behaves as a potential precursor to carbyne. This all-carbon material could result from complete deiodination of PIDA, as shown in **Scheme 2.1**.[44]



Scheme 2.1 Deiodination of PIDA

Luo and coworkers showed that the elimination of iodine can be induced with Lewis-base triethylamine as well as pyridine or pyrrolidine under mild conditions.[45] In the experiment, PIDA

aggregates were isolated from cocrystal via sonication and the blue color changed to yellowish-brown after treated with triethylamine. UV spectroscopy was used to characterize the change, shown in **Figure 2.5**. After the base is added in the blue solution, the absorption shoulder at 750 nm starts to decrease. The major absorption peak remains longer, but λ_{max} shifts to shorter wavelength. Although the elimination occurred, the elimination of iodine was incomplete, with 60% iodine eliminated.[45] The isolated PIDA strands aggregate after sonication, leading to cross-linking product. In addition, the internal PIDA strands could not react with Lewis base.

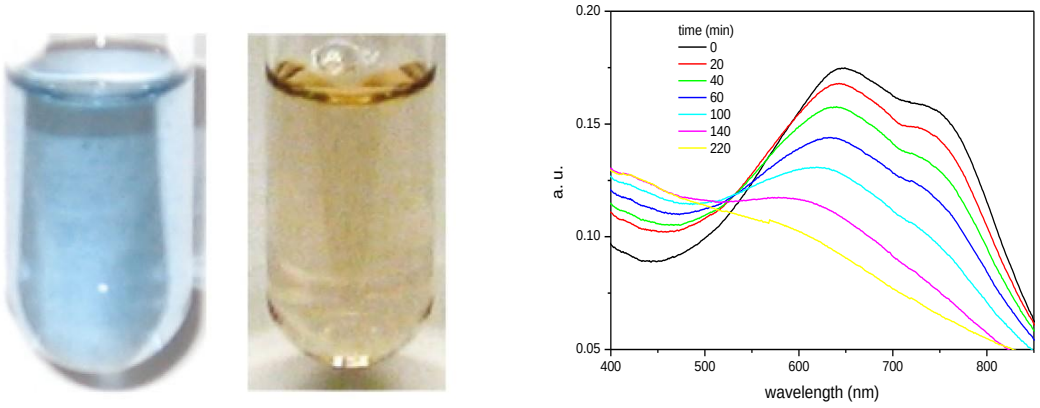
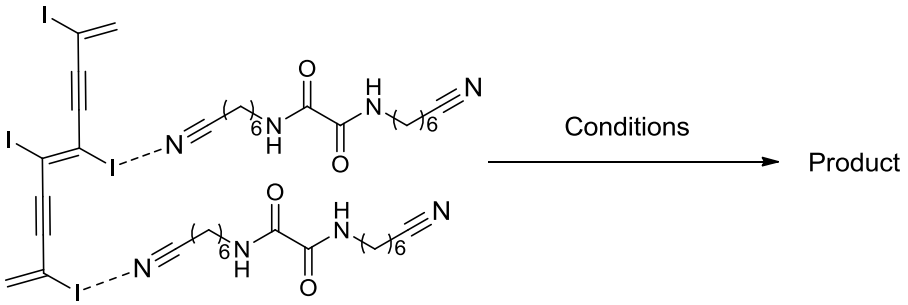


Figure 2.5 Left: Isolated PIDA suspension in methanol turns dark yellow from blue after addition of triethylamine. Right: UV-vis spectroscopy as the color changed from blue to dark yellow. Adapted with permission from reference 45. Copyright (2011) American Chemical Society.

In order to overcome incomplete elimination caused by isolated PIDA aggregates, PIDA cocrystals, which were obtained from diiodobutadiyne and host **8**, were used by Resch to investigate elimination of iodine with different conditions, as shown in **Scheme 2.2.**[46]



Condition:

A: 5000eq pyrrolidine, ((((, H_2O, 24h
B: 663eq pyrrolidine, MeCN, 48h
C: 500eq TBAI, $MeNO_2$
D: 500eq TBAI, EtOH-H_2O=1:1
E: 500eq TBABr, 500eq $Na_2S_2O_3$, MeOH-H_2O=1:1
F: 500eq KI, ((((, MeCN, 24h
G: 250eq PPh_3, MeCN-H_2O=10:1, ((((, 24h
H: 250eq thiourea, MeCN, ((((, 48h

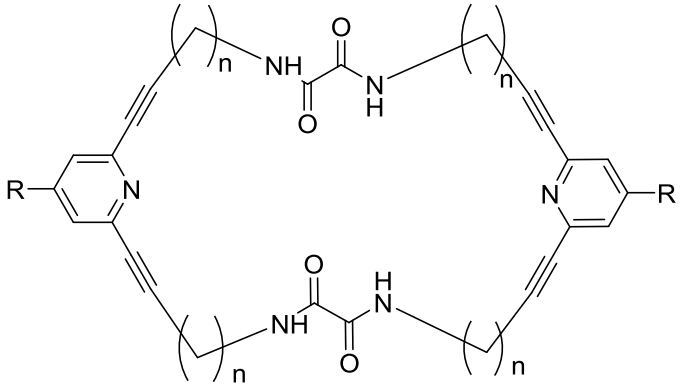
Scheme 2.2 Reactions of PIDA cocrystals with different reagents[46]

Although multiple sets of conditions were tried, no promising results indicated complete deiodination. Under conditions **A**, the product of the pyrrolidine-induced deiodination was characterized by Raman spectroscopy, UV-vis spectroscopy and SEM/EDS. Raman and SEM/EDS only showed the product was a heterogeneous mixture and still contained iodine. UV spectroscopy did not show any identifiable peaks. Using polar aprotic solvent (conditions **B**) did not work either. In addition, iodide and bromide anions were chosen to react with PIDA cocrystals (conditions **C**-**F**). No matter which conditions were used, each reaction showed similar result. If reaction has sulfur reducing agent, the product would contain sulfur element. If without reducing agent, reaction would result in product with iodine. Some other reagents were also used to study deiodination of PIDA (conditions **G** and **H**). Both methods showed the product was amorphous graphite-like carbon and contained other elements from the reagents.

Obviously, deiodination of PIDA is still exploratory, and future efforts need focus on the complete deiodination of PIDA as well as avoiding formation of cross-linking product.

Chapter 3 Result and discussion

3.1 Host design



n=3,4

R=H, $O(CH_2CH_2O)_2CH_3$

Figure 3.1 Designed host

The host macrocycles are designed to interact with diioiobutadiyne to form cocrystals. The macrocycles can be divided into four main segments: R group, pyridyl, alkynyl and oxalyl group. The purpose of adding R group is to increase the macrocyclic ring's solubility in solvents. Gulur Srinivas and coworkers had used glycol ethers to improve organic compounds' solubility in solvent.[47] The pyridyl and alkynyl groups are designed to provide beneficial rigidity, forcing the macrocyclic ring to meet geometric requirement to cocrystallize with diiodobutadiyne. In addition, halogen bonds are formed between nitrogen atoms in the pyridyl groups and the iodine atoms. An oxalyl group is incorporated into the macrocyclic hosts, due to its ability to form hydrogen bonding networks. The macrocyclic hosts will stack through hydrogen bonding with appropriate repeat distances.

A chemical compound's conformation can be predicted by computational modeling. Since the guest has to fit in the macrocyclic host, the conformation of macrocyclic host needs to

be optimized before synthesis. Xianzhi Liu, a previous group member, had focusd on obtaining conformations of only the macrocyclic hosts, which neglected the halogen bonding interactions between host and guest.[48] First, the macrocycles, having different methylene segments and R groups, were optimized through MMFF molecular mechanics model, from which N-N distances were calculated. Since macrocycles without carbon-carbon triple bonds were more flattened than those with triple bonds, Hartree-Fock model with basis set 3-21G was used to further optimize macrocycles with triple bonds, from which different N-N distances were also calculated. However, comformers from both computational methods were flattened, which made parameters of N-N distances meaningless to predict macrocyclic rings' sizes. Halogen bonding interactions of macrocyclic host and guest will affact macrocyclic ring's packing geometry. The computational method should optimize the conformation of macrocyclic hosts with the guest diiodobutadiyne.

In my research, the conformation of the macrocyclic host and guest is calculated through the program Spartan. First, the molecular mechanics model was used for optimizing the conformation of two pyridines and diiodobutadiyne. Later, semi-empirical model was also applied to optimize the conformation. Two pyridines with diiodobutadiyne were optimized via equilibrium geometry using MMFF molecular mechanics model and AM1 semi-empirical model, respectively. The optimized conformations were shown in **Figure 3.2**. After optimization via MMFF molecular mechanics model, the pyridines did not align appropriately near diiodobutadiyne; nitrogen atoms were not in close contact to iodine atoms. However, they did locate at diiodobutadiyne's both sides after optimization via AM1 semi-empirical model, which showed the halogen bonding interaction between macrocyclic hosts and diiodobutadiyne. The

distance of N-I atoms was 3.256 Å, which was shorter than the sum of van der waal radius of nitrogen and iodine atoms (3.53 Å).

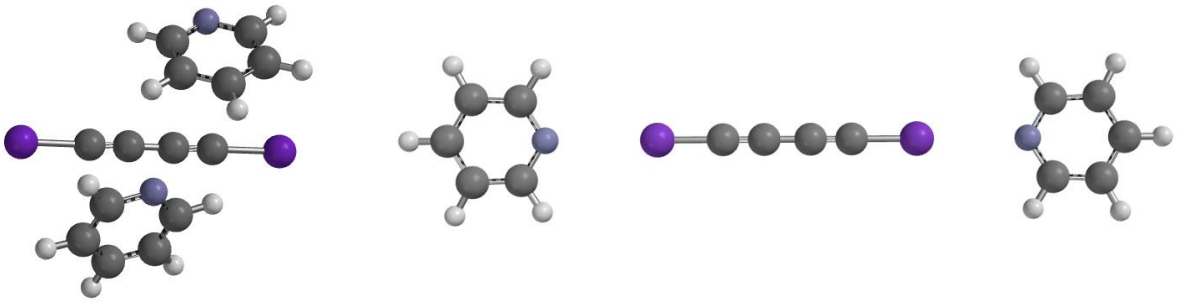


Figure 3.2 Conformation of two pyridines with diiodobutadiyne. Left: conformation was optimized via MMFF molecular mechanics model. Right: conformation was optimized via AM1 semi-empirical model.

Since AM1 semi-empirical model could identify halogen bonding interaction, it was applied to obtain following model structures through equilibrium geometry (**Figure 3.3**). They represent locally optimized geometries. From the following structures, we can see the macrocyclic hosts can form columnar structures through hydrogen bonds and form halogen bonds with iodine atoms.

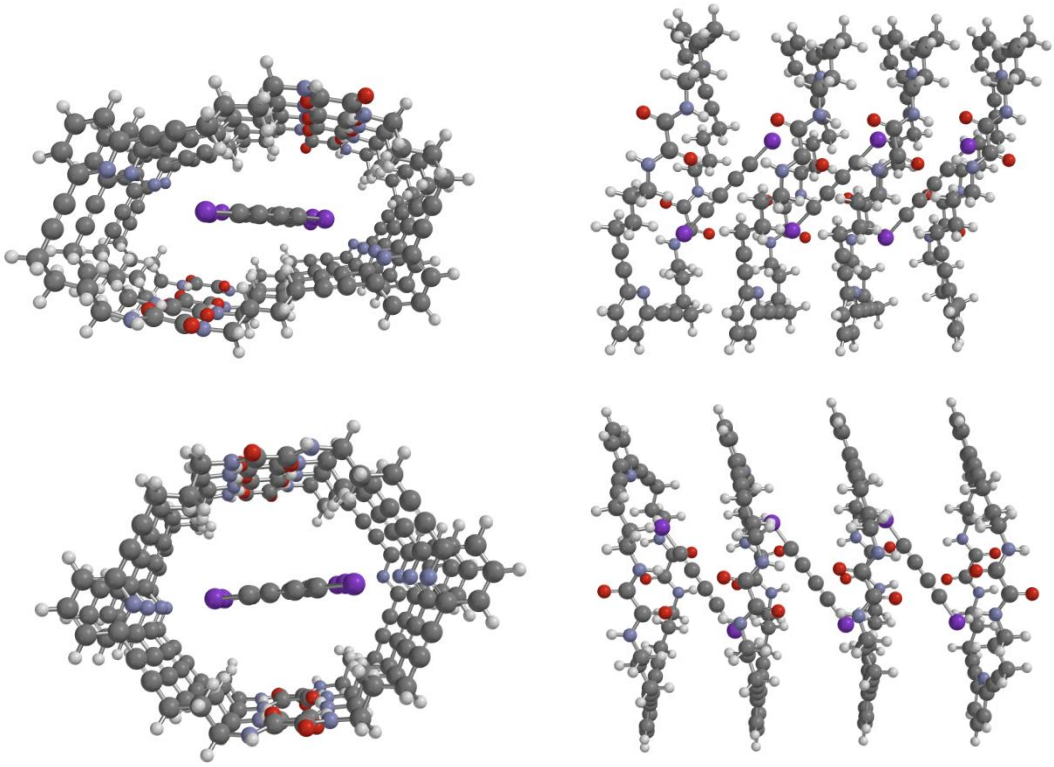
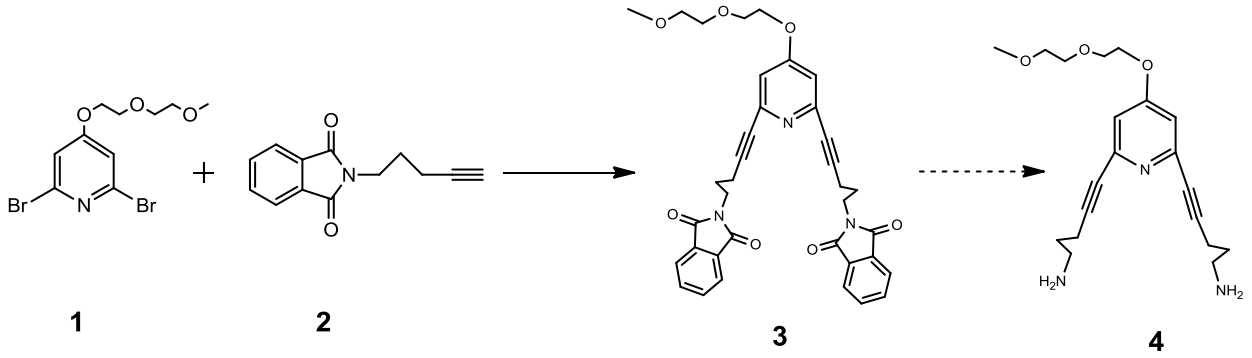


Figure 3.3 Conformation of macrocycles. Top left: top view for macrocycle with n=4 and R= H; Top right: side view for macrocycle with n=4 and R= H; Bottom left: top view for macrocycle with n= 3 and R= H; Bottom right: side view for macrocycle with n=3 and R= H.

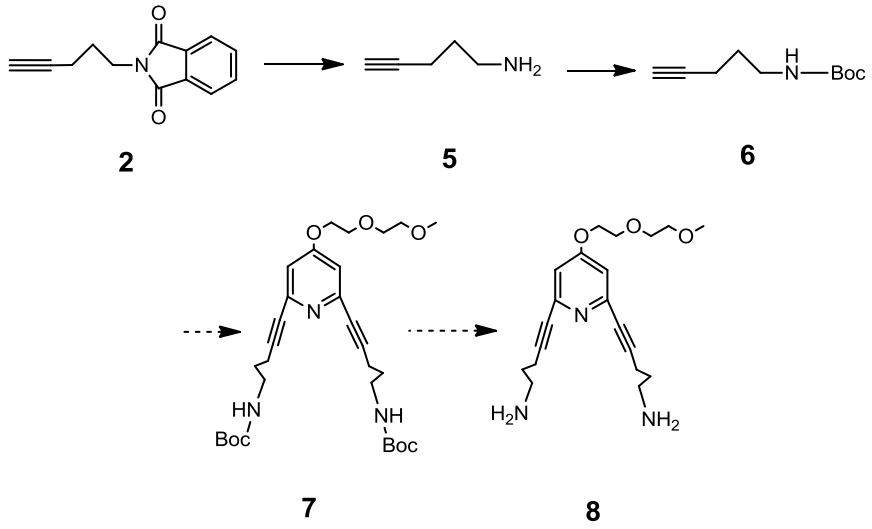
3.2 Host synthesis

Xianzhi Liu attempted to synthesize the target macrocyclic host with glycol ether group.[48] Some main steps are shown in **Scheme 3.1**. In first route, he tried to reduce phthalimide group to amino group through Gabriel synthesis, while it was not successful. Proton and ^{13}C NMR only showed glycol ether group and some peaks belonging to aromatic ring, but didn't show existence of desired product. Liu also attempted to couple tert-butyl pent-4-ynyl carbamate on modified 2, 6-dibromopyridine ring. In this method, the amino group was protected by Boc group and attached to pyridine all at once. According to Liu's description, the desired compound was not demonstrated by TLC and silica gel purification. Compound **6** is volatile and harmful for membrane tissue and respiratory tract.[48] Meanwhile, both routes had difficulties in purification of compounds with amino groups due to their high polarity and instability.

First route



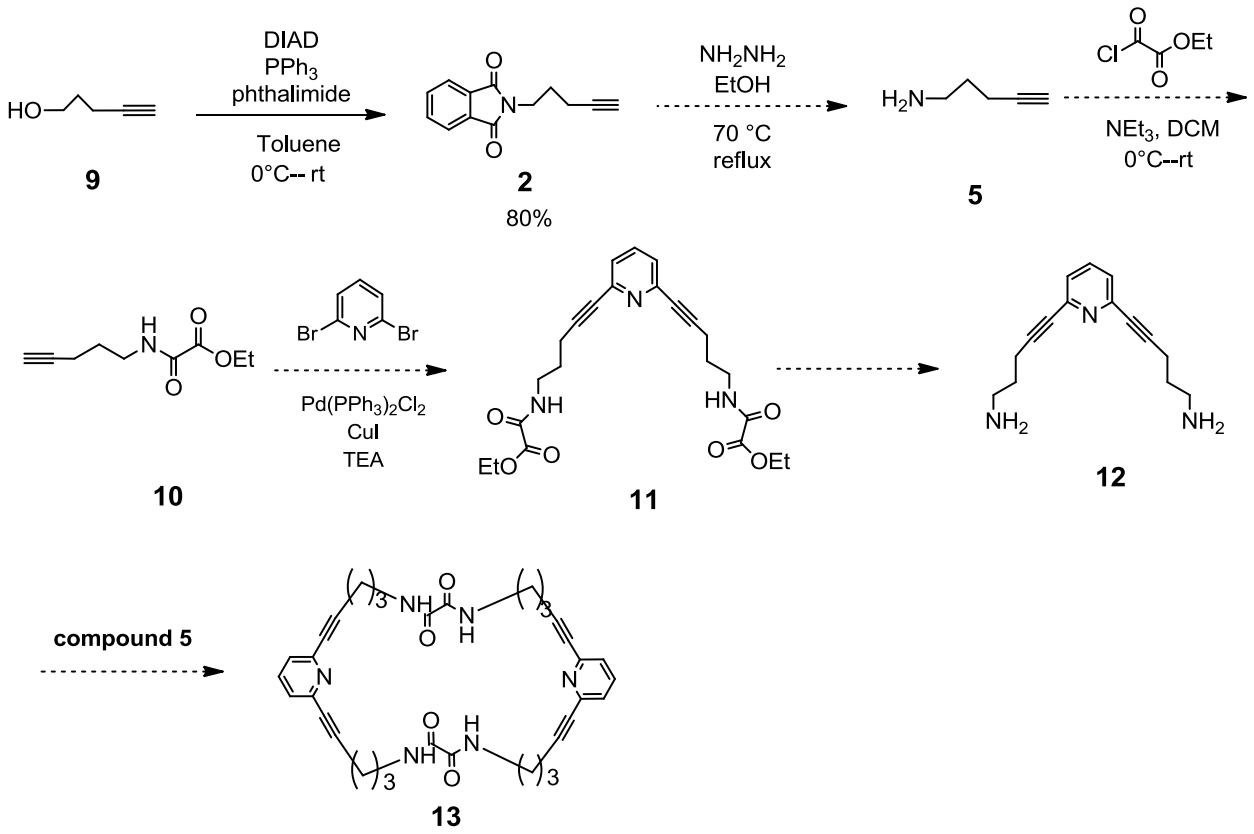
Second Route



Scheme 3.1 Two main routes involved in synthesis of target host[48]

Based on the above results, a new synthetic route was developed which involves coupling ethyl oxalyl moiety on amino group. It is showed in **Scheme 3.2.** In order to save reagents and time, I did not modify 2, 6-dibromopyridine with ethyl glycol ether moiety at the beginning. In this route, Gabriel synthesis was used to make an amino group. Ethyl oxalyl chloride was chosen to react with the amine. The resulting segment could prevent forming polymer when compound **11** reacted with compound **12**. Unfortunately, compound **5** was not verified to be synthesized. According to Guan's work, hydrazine monohydrate was added in RBF to react with 1-

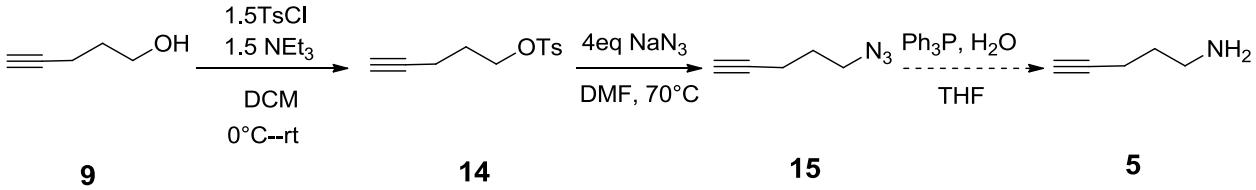
phthalimide-4-pentyne in ethanol, followed by acidification and basification after a white precipitate formed.[49] Since compound **5** is soluble in water and byproduct is hard to remove completely, the isolation of pure product is difficult. The NMRs of crude product are not consistent and some peaks could not be assigned. I also tried to use the crude product to react with ethyl oxalyl chloride. The result showed the reaction was not successful.



Scheme 3.2 Planned synthetic route of designed host with R= H

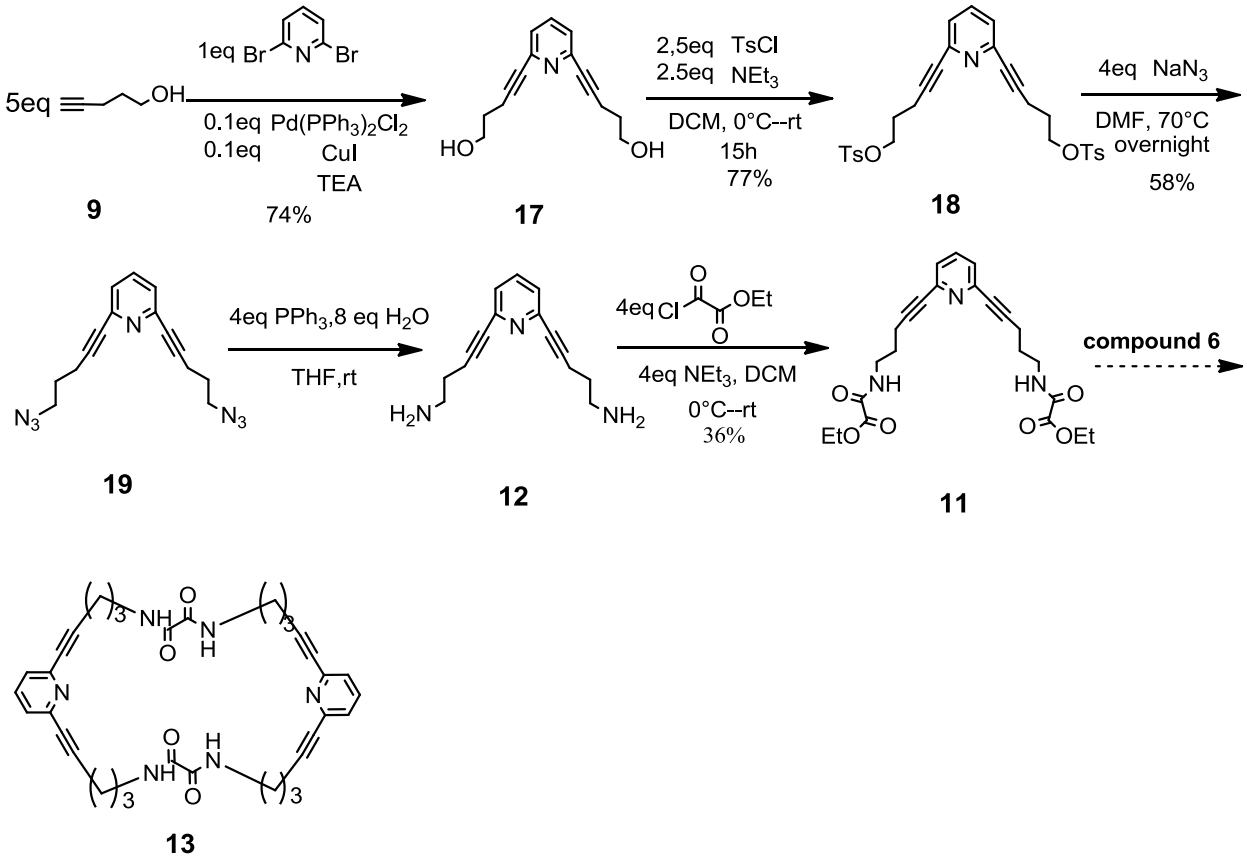
Since Gabriel synthesis from a phthalimido group to an amino group did not work well, a new route (**Scheme 3.3**) is proposed to make compound **5**, in which hydroxyl is substituted with –OTs group. It will further be converted to an azide and reduced to an amino group through Staudinger reaction. A difficulty was experienced during synthesizing the product compound **15**. As described by Saito et. al,[50] sodium azide was added in DMF to react with compound **14** at 70

°C, followed by extraction with diethyl ether. Later I found compound **15** had a low boiling point, which was not described by any resource. The yield was just 35% percent. DMF has a high boiling point and usually is removed by extraction, which leads to loss of product. On the other hand, we found that the desired product **15** had a low boiling point after I observed crude product was pumped out by oil pump. In consideration of these two disadvantages, compound **9** is used to couple with 2, 6-dibromopyridine first.



Scheme 3.3 Alternate synthetic route of 1-amino-4-pentyne

The following route (**Scheme 3.4**) includes Sonogashira coupling with 4-pentyn-1-ol, tosylation of hydroxyl, substitution of tosyl group, Staudinger reaction and coupling with ethyl oxalyl chloride. This synthetic route has been pursued and all intermediates were successfully synthesized.



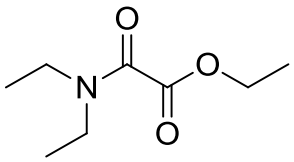
Scheme 3.4 Alternate synthetic route of designed host with R= H

One of the complicated steps in **Scheme 3.4** was coupling compound **9** with 2, 6-dibromopyridine through traditional Sonogashira coupling condition. The reaction was monitored via TLC and stopped after fifteen hours. Comparing with starting material and triethyl amine, there were four clear spots. They were compound **9**, homocoupling product of compound **9**, product **17** and triethyl amine which located at base line. Column chromatography was used to purify the crude product after vacuum filtration. The purification of crude product was a difficulty. 80% ethyl acetate with 20% hexane was used to get rid of byproduct and 100% ethyl acetate was used for obtaining pure product. However, the product came out very slowly after multiple solvents were used. This perhaps was because pyridine ring was protonated and the length of column was too long. In order to overcome this, the length of silicon column could be

reduced and triethyl amine or ammonium hydroxide could be applied to basify the silicon gel. Later I found, 5% methanol with 95% ethyl acetate could purify the product, which saved time and solvent.

Another complicated step in **Scheme 3.4** was the reduction of compound **19**. In order to produce compound **12** quickly, four equivalents of triphenylphosphine were used to push compound **19** to be reduced. TLC showed compound **19** was totally reduced and triphenylphosphine oxide formed. However, compound **12** is very polar and partially soluble in water, which made acidification and basification unsuccessful to obtain pure product. Compound **12** also could not be purified by column chromatography, because it could be stuck in silicon gel. Since starting material was totally reacted and the byproduct was triphenylphosphine, the crude compound **12** was characterized by NMR and MS without further purification.

After Staudinger reaction, the crude compound **12** reacted with ethyl oxalyl chloride in DCM at 0°C and was allowed to warm to room temperature. Surprisingly, the mixture turned to dark purple after ten minutes. After nineteen hours, TLC showed triphenylphosphine was gone and four clear spots formed with other fuzzy spots. An unexpected byproduct formed during the reaction, whose structure (**Figure 3.4**) was confirmed by NMR and MS. In addition, the eluent of 67% hexane with 23% ethyl acetate was chosen to purify compound **11**. However, the desired product could not come out with the appropriate eluent, even with ethyl acetate. Pure methanol was used to collect the remaining compound, which turned out to be compound **11**. It might be because the pyridine ring was protonated and desired product was kept in the column.

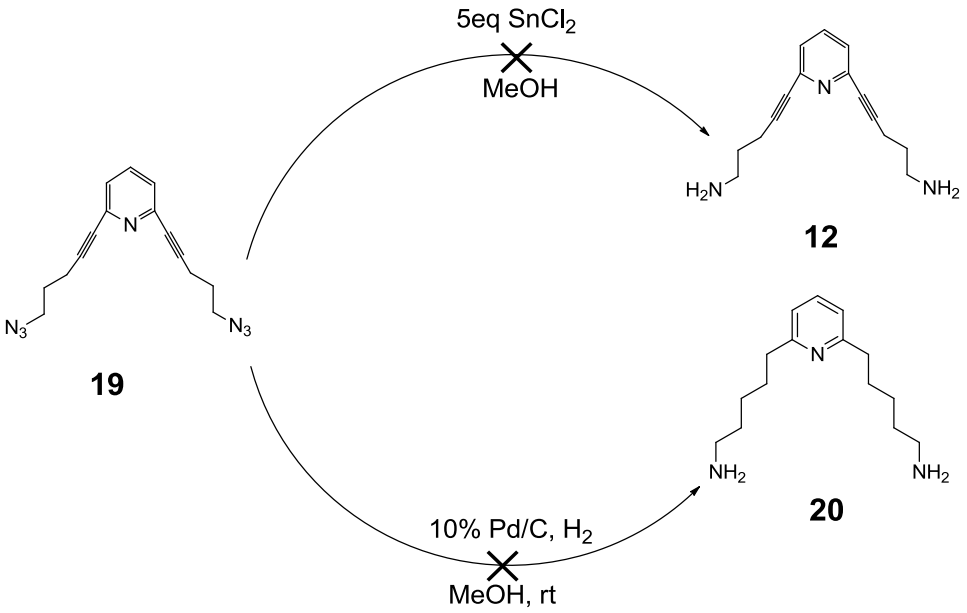


16

Figure 3.4 Unexpected byproduct

The last step in **Scheme 3.4** was the cyclization of compound **11** with compound **12**. Compound **11** reacted with one equivalent of crude compound **12** in 100 mL THF. After concentrating, the resulting mixtures were a little yellow liquid and white solid. The white solid was partially soluble in DCM and methanol while soluble in DMSO. In order to check the possibility of forming the designed macrocycle, the resulting mixtures were characterized by proton and ^{13}C NMR in deuteriumed DMSO. The messy spectrum could not verify the designed macrocycle. This step was only explored once and it needs further investigation. In the future, the yellow liquid and white solid should be collected respectively and characterized. Concentration of starting material may also affect the reaction, which needs further investigated.

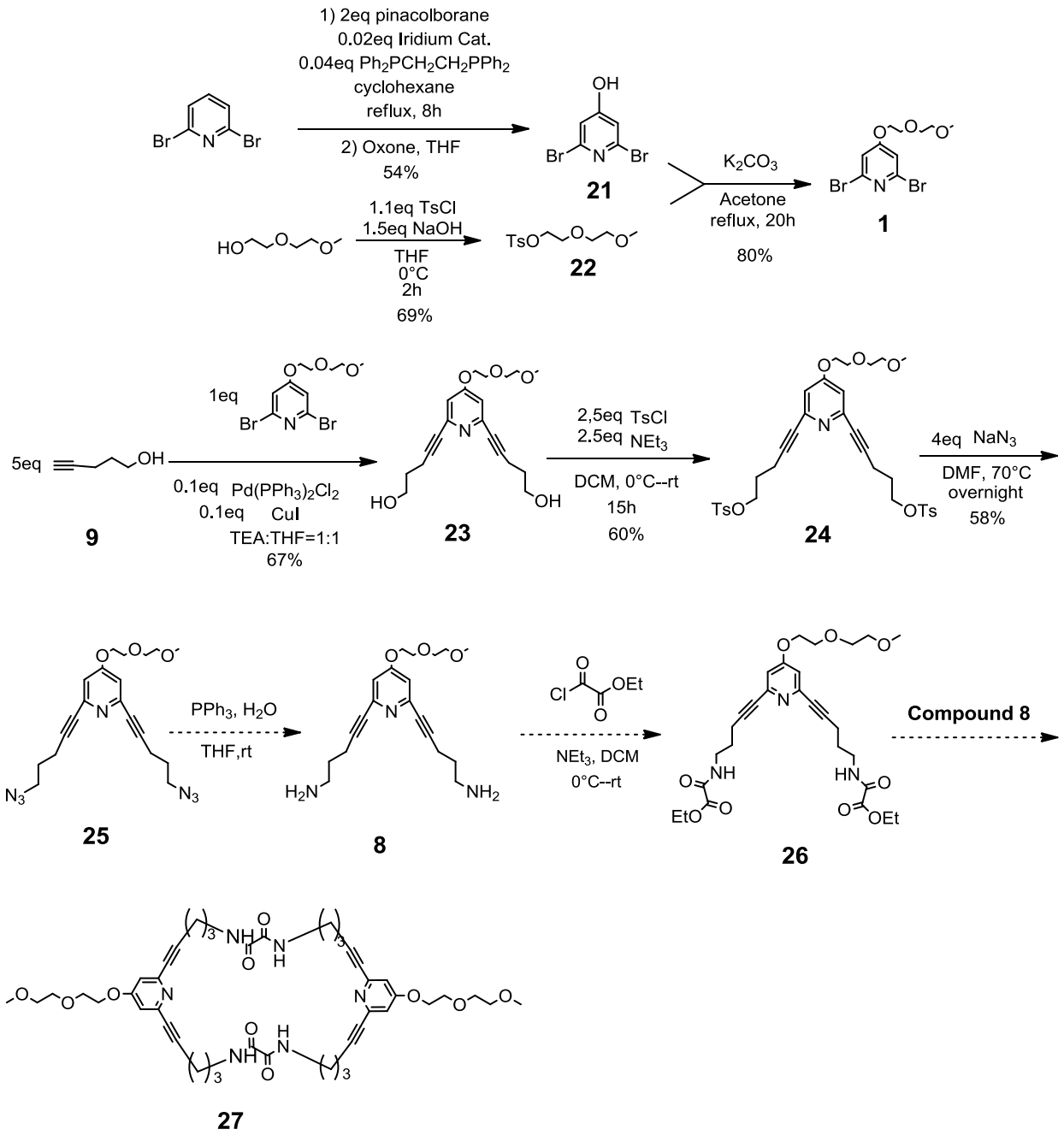
In addition, another two reactions were performed to reduce azide (**Scheme 3.5**). According to Morin's work, azide could be reduced to an amino group via tin (II) chloride in methanol.[51] The advantage of this method was that crude product could be purified via extraction with diethyl ether. However, tin(II) chloride is very poisonous. Hydrogenation was also a good way to reduce azide and alkyne, in which Pd/C can be easily removed via filtration. Neither reactions used too many reagents or byproducts. However, both NMRs were messy and certain peaks were unidentifiable. Both crude products were hard to purify due to the amino group's large polarity and instability.



Scheme 3.5 Two unsuccessful reactions

The glycol ether group is employed to modify pyridyl, which is on the 4 position of pyridyl. There is little literature describing the functionalization on the 4 position of 2, 6-halogen substituted pyridyl. However, Smith et al reported a hydroxyl can be attached to the 4 position on the aromatic ring through borylation and oxidation.[52] To synthesize 4-hydroxyl-2, 6-halogen substituted pyridyl, efficient iridium catalyst, 1, 2-bis (diphenylphosphino)-ethane (dppe) and special solvent cyclohexane were used. Under basic conditions, OTs is a good leaving group. The glycol ether group and hydroxyl on the pyridyl can be connected after the tosylation of diethylene glycol monomethyl ether. Based on Masahiko Inouye's work, the 2, 6-dibromopyridine-4-ol was first obtained by direct iridium-catalyzed borylation of 2, 6-dibromopyridin and oxidation with oxone.[53] However, the yield was only 15% so I doubled the amount of catalyst and expanded the reaction time. Most starting material did not react, which was confirmed through thin layer chromatography and proton NMR. According to the Smith group's work,[52] cyclohexane was used as solvent and the reaction temperature was adjusted to 100 °C. When I adjusted the reaction to these conditions, the yield increased to 51%, which is

consistent with the literature. Compound **1** could not dissolve in triethylamine, which might lead to incomplete reaction. In order to overcome this, THF was added to dissolve compound **1**. In this route (**Scheme 3.6**), the conditions were similar to those in **Scheme 3.4**.

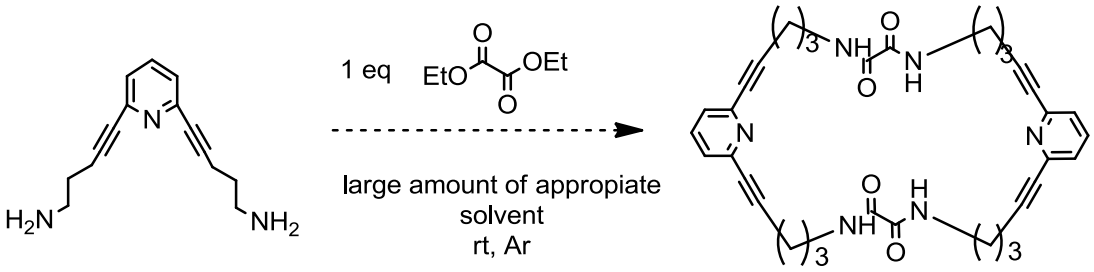


Scheme 3.6 Synthetic route of designed host with R= $O(CH_2CH_2O)_2CH_3$

Chapter 4 Future work

In order to induce topochemical polymerization, monomers should be aligned to meet the geometric requirements. Appropriate host and guest are critical to control the geometric arrangement. Based on simple semi-empirical calculation, compound **13** and **27** were chosen as the target macrocyclic hosts. Single crystals of compound **13** and **27** will be developed, from which packing geometry of hosts will be determined and the sizes of macrocyclic hosts will be accurately predicted.

Since the reaction routes in **Schemes 3.4** and **3.6** are straightforward, future work will focus on synthesizing the designed macrocyclic hosts and preparing cocrystals from the hosts and diiodobutadiyne and characterize the product. The last step of **Scheme 3.4** needs further investigation. According to Liu's work,[54] concentration of solution affected the self-cyclization. When the solution was too concentrated or too diluted, more side products were generated. In the future, appropriate concentration and solvents will be explored. A pure compound **6** can help to reduce complexity of self-cyclization. On the other hand, an alternate route for self-cyclization is worth trying (**Scheme 4.1**).



Scheme 4.1 Alternate route for self-cyclization

. To achieve full dehalogenation, the strategy proposed in Section **2.2** should be tried to prevent cross-linking of PIDA strands.

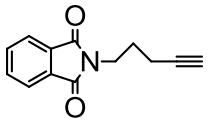
Chapter 5 Experimental section

5.1 Computation

All structures have been optimized in Spartan program via the molecular mechanics model and the semi-empirical model. In both models, equilibrium geometry was selected to calculate the local conformation at the ground state. MMFF force field was used in molecular mechanics model and AM1 method was used in semi-empirical model.

5.2 Synthesis

General methods: All reagents and solvents were purchased from GFS chemicals, Strem chemical, Aldrich, Fisher, Oakwood chemical, VWR or BDH. They were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded with Bruker-300, Bruker-400, and Bruker-500 instruments. In the NMR data, chemical shifts were recorded as ppm. Coupling constants were recorded in hertz (Hz).[singlet (s), doublet (d), doublet of doublet (dd), triplet (t), quartet (q), quintet (qt) or multiplet (m)]. IR spectra were obtained by Thermo Nicolet iS-10 FT-IR.

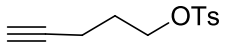


2

N-(4-Pentynyl)phthalimide (2)

4-Pentyn-1-ol (1.05 g, 12.5 mmol), PPh_3 (3.93 g, 15.0 mmol), phthalimide (2.0 g, 13.5 mmol) were added to a RBF with 15 mL toluene. The mixture was cooled to 0 °C and the solution of DIAD (3.16 g, 15.6 mmol) with 3mL was dropwise added into the mixture. When the addition was finished, the reaction was warmed up to room temperature and stirred for 5 hours. And then

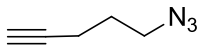
16 mL MeOH was added, the reaction was stirred for another 3 hours. The solution was concentrated to give a crude product, which was purified by silica-gel column chromatography (EA/hexane= 1/5) to give compound **2** as white solid (1.71 g, 80%, m.p. 87-88 °C)**.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (m, 2H), 7.67 (m, 2H), 3.75 (t, *J* = 7.1 Hz, 2H), 2.22 (t, *J* = 2.6 Hz, 2H), 1.90 (m, 3H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) 168.4, 134.0, 132.2, 123.3, 83.1, 69.1, 37.2, 27.3, 16.3.[48]



14

Pent-4-yne-1-tosylate (14)

To a solution of 4-pentyn-1-ol (759 mg, 9 mmol) in dichloromethane (DCM), triethylamine (1.98 mL, 14 mmol) was added. The reaction was kept at 0°C. A solution of tosyl chloride (2.65 g, 14.2 mmol) in DCM was added dropwise into the mixture. After the addition was finished, the reaction was warmed to room temperature and stirred for one day. The reaction mixture was extracted with water. The organic layer was separated and dried over Mg_2SO_4, concentrated to give a crude product, which was purified by column chromatography (Hexane/ EA=10/1 then 3/1) to give a colorless oil (1.64 g, 70%). ESI MS m/z 239.1 $[M+H]^+$, 261.1 $[M+Na]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (m, 2H), 7.31 (m, 2H), 4.11 (t, *J* = 1.4 Hz, 2H), 2.42 (s, 3H), 2.22 (m, 3H), 1.86(s, 1H), 1.83(m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) 144.9, 132.9,129.9, 128.0, 82.2, 69.5, 68.8, 60.4, 27.7, 21.7, 14.7.[55]



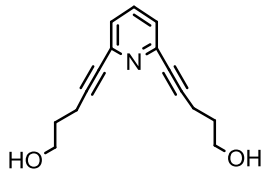
15

Pent-4-yne-1-azide (15)

Pent-4-yne-1-tosylate (500 mg, 2.1 mmol) was added into a solution of sodium azide (34 mg, 5.2 mmol) and dry DMF(20 mL),. The reaction was stirred overnight at 70°C under argon. The reaction mixture was poured into water (20 mL) and extracted with diethyl ether (20 mL) three times. The combined organic layers were washed with water(15 mL) seven times and dried over Mg_2SO_4, concentrated in vacuu to give a pale yellow liquid (80.21 mg, 35%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.43 (t, *J* = 6.7 Hz, 2H), 2.28 (m, 2H), 1.97 (t, *J*= 2.7 Hz, 1H), 1.78 (m, 2H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 82.7, 69.4, 50.1, 27.7, 15.8.[50]

CuI purification[56]

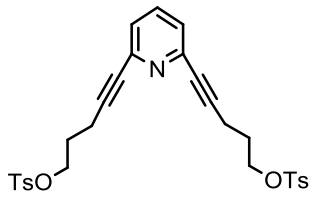
To a solution of potassium iodide (9.1 g, 0.055 mol) in 20 mL H_2O, CuI (0.625 g, 0.033 mol) was added. Under argon for 1 h, charcoal (0.635 g, 0.053 mol) was added and the reaction was stirred at 35 °C for 30 min. The mixture was cooled to room temperature and filtered immediately. H_2O (15 mL) was added and the solution was put in ice bath for 45 min with the flask sealed. The white precipitate that formed was isolated via vacuum filtration. The white solid was dried overnight in the vacuum oven (~50°C).



17

5, 5'-(pyridine-2, 6-diyl)bis(pent-4-yn-1-ol) (17)

To a stirred solution of 2, 6-dibromopyridine (1.42 g, 6 mmol) in 35 mL triethylamine (TEA), $(Ph_3P)_2PdCl_2$ (0.42 g, 0.6 mmol), CuI (0.11 g, 0.6 mmol) and 4-pentyn-1-ol (3.5 mL, 30 mmol) were added. This mixture was stirred at room temperature for 15 h and isolated by vacuum filtration. TEA was removed in *vacuo*. The crude product was purified by column chromatography (EA/ MeOH= 19/1, 1% TEA) to give yellow oil (1.08 g, 74%). ESI MS: m/z 244.2 $[M+H]^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.45 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 4.06 (s, 2H), 3.73 (t, *J* = 6.1 Hz, 4H), 2.49 (t, *J* = 9.3 Hz, 4H), 1.79 (m, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 143.4, 136.5, 125.4, 91.1, 79.9, 60.6, 30.7, 15.7.

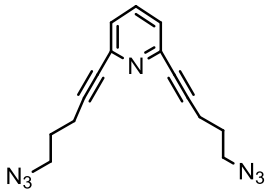


18

Pyridine-2, 6-diylbis(pent-4-yne-5,1-diyl) bis(4-methylbenzenesulfonate) (18)

To a solution of 5, 5'-(pyridine-2, 6-diyl)bis(pent-4-yn-1-ol) (1.08 g, 4.45 mmol) in DCM (15 mL), triethylamine (1.55 mL, 11.12 mmol) was added. The reaction was kept at 0°C. A solution of tosyl chloride (2.08 g, 11.12 mmol) in DCM (15 mL) was added dropwise into the mixture. After the addition was completed, the reaction was warmed to room temperature and stirred for one day. The reaction mixture was concentrated and purified by column chromatography

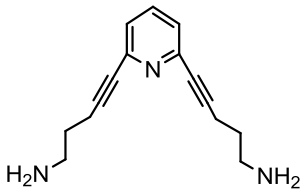
(Hexane/EA= 1/1 then 1/3) to give yellow oil (1.89 g, 77%). ESI MS m/z 552.3 $[M+H]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.68 (d, *J* = 8.0 Hz, 4H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 4H), 7.10 (d, *J* = 7.8 Hz, 2H), 4.08 (t, *J* = 5.9 Hz, 4H), 2.40 (t, *J* = 6.8 Hz, 4H), 2.27(s, 6H), 1.84(m, 4H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) 144.6, 143.1, 136.0, 132.4, 129.6, 127.5, 125.4, 88.3, 80.6, 68.6, 27.2, 21.2, 15.2.



19

2, 6-bis(5-azidopent-1-yn-1-yl)pyridine (19)

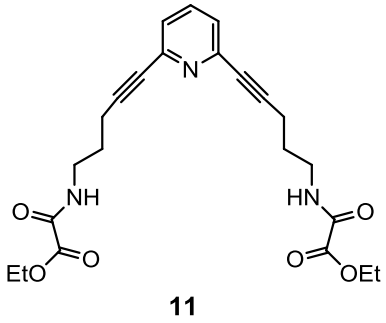
To a solution of sodium azide (0.89 g, 3.4 mmol) in 20 mL dry DMF, pyridine-2, 6-diylbis(pent-4-yne-5,1-diyl) bis(4-methylbenzenesulfonate) (1.89 g, 13.6 mmol) was added. The reaction was stirred overnight at 70°C under argon. The reaction mixture was poured into water (20 mL) and extracted with diethyl ether (40 mL) three times. The combined organic layers were washed with water(20 mL) seven times and dried over Mg_2SO_4, concentrated in vacuu to give pale yellow liquid(0.58 g, 58%). ESI MS m/z 294.2 $[M+H]^+$. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.49 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 3.39 (t, *J* = 6.6 Hz, 4H), 2.46 (t, *J* = 6.9 Hz, 4H), 1.80 (m, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 143.4, 136.2, 125.5, 89.0, 80.7, 50.0, 27.3, 16.4.



12

5, 5'-(pyridine-2, 6-diyl)bis(pent-4-yn-1-amine) (12)

To a solution of 2, 6-bis(5-azidopent-1-yn-1-yl)pyridine (0.293 g, 1 mmol) in 15 mL of THF was added triphenylphosphine (1.05 g, 4 mmol) and water (0.14 mL, 8 mmol). The reaction was stirred under argon for twenty four hours with a vent needle plugged in rubber septum. The crude mixture was dried over $MgSO_4$ and concentrated by rotary evaporation. Without further purification, the crude mixture was used for next step to make compound **12**. ESI MS m/z 121.6 [$(M+2H^+)/2$], 242.1 [$M+H^+$], 263.0[$M+Na^+$], 279.0 [$M+K^+$].

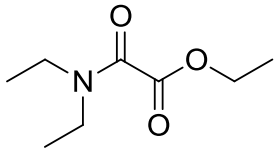


11

Diethyl-2, 2'-((pyridine-2, 6-diylbis(pent-4-yne-5, 1-diyl))bis(azanediyl))bis(2-oxoacetate) (11)

To the solution of crude mixture of 5, 5'-(pyridine-2, 6-diyl)bis(pent-4-yn-1-amine) in DCM (10 mL), triethylamine (0.55 mL, 4 mmol) was added. The reaction was kept at 0 °C. Ethyl oxalyl chloride (0.45 mL, 4 mmol) was dropwise added in the mixture. After the addition was completed, the reaction was warmed to room temperature and stirred for nineteen hours. The

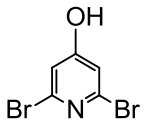
reaction mixture was extracted with saturated sodium bicarbonate solution and saturated sodium chloride solution. The organic layer was dried over Mg_2SO_4, concentrated to give a crude product, which was purified by column chromatography (EA: Hexane= 2:1, EA then MeOH) to give yellow oil (0.16 g, 36%). ESI MS m/z 442.3 $[M+H]^+$, 464.3 $[M+Na]^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 4H), 3.52 (m, 4H), 2.50 (t, *J* = 7.1 Hz, 4H), 1.89 (m, 4H), 1.36 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 160.6, 156.8, 143.5, 136.4, 125.7, 89.3, 81.00, 63.2, 39.0, 27.4, 16.9, 13.9.



16

Ethyl-2-(diethylamino)-2-oxoacetate(16)

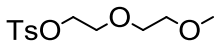
Ethyl-2-(diethylamino)-2-oxoacetate was obtained from the procedure of making diethyl-2, 2'-((pyridine-2, 6-diylbis(pent-4-yne-5, 1-diyl))bis(azanediyl))bis(2-oxoacetate). After the crude product was purified by column chromatography (EA: Hexane= 2:1), ethyl-2-(diethylamino)-2-oxoacetate was obtained as yellow oil (0.023 g). ESI MS m/z 174.1 $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 4.29 (q, *J* = 7.2 Hz, 2H), 3.38 (q, *J* = 7.2 Hz, 2H), 3.25 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) 163.2, 161.4, 61.8, 42.4, 38.9, 14.1, 13.9, 12.4.[57]



21

2, 6-Dibromopyridine-4-ol (21)

2, 6-Dibromopyridine (710.67 mg, 3 mmol), 1, 2-bis (diphenylphosphino) ethane (47.8 mg, 0.12mmol) and $(IrCl(cod))_2$ (cod=1, 5-cyclooctadiene) (40 mg, 0.06 mmol) were dissolved in 10 mL cyclohexane in a RBF, and pinacolborane (1.74 mL, 12 mmol) was added. The reaction was stirred under Ar and refluxed for 8 hours. The resulting mixture was cooled to room temperature, concentrated in vacuum, diluted with 5 mL THF, slowly added into aqueous oxone solution (2.03 g in 10 mL H_2O). The mixture was stirred for 10 min at room temperature, followed by quenching with aqueous $NaHSO_3$ and extracted with diethyl ether (15 mL) three times. The combined organic layers were washed with water and saturated sodium chloride, dried over MgSO4, concentrated, purified by silica-gel column chromatography (EA/Hexane = 1/5) to give white solid(386 mg, 54%, 217-218 °C). ^{1}H NMR (500 MHz, acetone-D_6): δ 7.04 (s, 2H). ^{13}C NMR (500 MHz, acetone-D_6): δ (ppm) 167.6, 141.4, 115.8.[48]



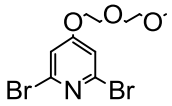
22

2-(2-Methoxy-ethoxy)-ethyl-p-toluene sulfonate (22)

To a solution of glycol ether (1.68g, 10 mmol) in 10 mL THF was added aqueous solution of NaOH (0.8 g, 20 mmol in 2 mL H_2O). An ice bath was used to cool the mixture to 0 C. A solution of TsCl (2.44 g, 13mmol) in 4 mL THF was dropwisely added into the mixture. The mixture was stirred for 2 hours at 0 °C. When the reaction completed, the mixture was poured into cold water (10 mL) and extracted with DCM. The combined organic layers was washed with

water and saturated sodium chloride, dried over $MgSO_4$, filtered, concentrated to give colorless oil (1.60 g, 69%). ESI MS m/z 275.2 $[M+H]^+$, 297.1 $[M+Na]^+$.

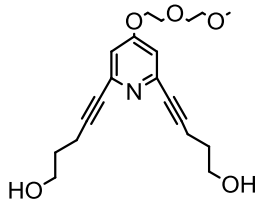
^1H NMR (500 MHz, $CDCl_3$): δ 7.75 (m, 2H), 7.31 (m, 2H), 4.13 (m, 2H), 3.65 (m, 2H), 3.53 (m, 2H), 3.44 (m, 2H), 3.30 (t, *J* = 3.1 Hz, 3H), 2.40 (t, *J* = 2.8 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) 144.9, 132.9, 129.9, 128.0, 71.8, 70.7, 69.3, 68.7, 59.1, 21.7.[48]



1

2, 6-Dibromo-4-[2-(2-hydroxyethyloxy)ethyloxy]pyridine (1)

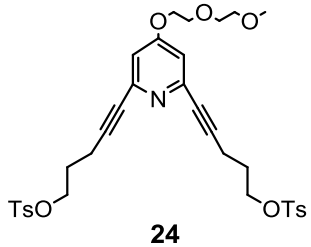
2, 6-Dibromopyridine-4-ol **(**689.5 mg, 2.73 mmol) and 2-(2-methoxy-ethoxy)-ethyl-p-toluene sulfonate (774.6 mg, 2.73 mmol), K_2CO_3 (752.8 mg, 5.45 mmol) were added to a RBF, the mixture was refluxed in acetone for 24 hours at 90 °C. After cooling to room temperature, the resulting mixture was filtered through Celite, concentrated in *vacuo*, purified by column chromatography (EA/Hexane = 1/2) to give white solid(0.78 g, 80%, m.p. 63-63 °C). ESI MS m/z 356.0 $[M+H]^+$, 378.0 $[M+Na]^+$. ^1H NMR (500 MHz, $CDCl_3$): δ 6.98 (s, 2H), 4.16 (m, 2H), 3.82 (m, 2H), 3.66 (m, 2H), 3.53 (m, 2H), 3.36 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) 166.9, 141.1, 114.0, 71.9, 70.9, 69.1, 68.5, 59.2.[48]



23

5, 5'-(4-(2-(2-Methoxyethoxy)ethoxy)pyridine-2,6-diyl)bis(pent-4-yn-1-ol) (23)

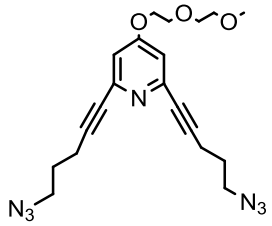
To the stirred solution of 2, 6-dibromo-4-[2-(2-hydroxyethyloxy)ethyloxy]pyridine (354.8 mg, 1 mmol) in 10 mL solvent (TEA: THF=1:1), $(Ph_3P)_2PdCl_2$ (70.18 mg, 0.1 mmol), CuI (18.75 mg, 0.1 mmol) and 4-pentyn-1-ol (0.558 mL, 6 mmol) was added under argon. This mixture was stirred at room temperature for 15 h and isolated by vacuum filtration. TEA and THF were removed in *vacuo*. The crude product was purified by column chromatography (EA/ MeOH= 19:1, 1% TEA) to give a yellow oil (0.24g, 67%). ESI MS m/z 362.3 $[M+H]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.72 (s, 2H), 4.05 (t, *J* = 4.7 Hz, 2H), 3.74 (t, *J* = 4.6 Hz, 2H), 3.68 (t, *J* = 6.1 Hz, 4H), 3.59 (m, 2H), 3.46 (m, 2H), 3.28 (s, 3H), 2.44 (t, *J* = 7.0 Hz, 4H), 1.74 (m, 4H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) 165.0, 144.3, 112.2, 90.6, 79.8, 71.6, 70.5, 68.9, 67.4, 60.4, 58.8, 30.6, 15.5.



24

(4-(2-(2-Methoxyethoxy)ethoxy)pyridine-2,6-diyl)bis(pent-4-yne-5,1-diyl) bis(4-methylbenzenesulfonate) (24)

To the solution of 5, 5'-(4-(2-(2-methoxyethoxy)ethoxy)pyridine-2,6-diyl)bis(pent-4-yn-1-ol) (242.4 mg, 0.673 mmol) in DCM (10 mL), triethylamine (0.234 mL, 1.68 mmol) was added. The reaction was kept at 0°C. A solution of tosyl chloride (314.5 mg, 1.68 mmol) in DCM (10 mL) was added dropwise into the mixture. After the addition was completed, the reaction was warmed to room temperature and stirred for one day. The reaction mixture was concentrated and purified by column chromatography (Hexane/EA= 1/2 then 1/3) to give a yellow oil (270.2 mg, 60%). ESI MS m/z 670.3 $[M+H]^+$, 692.3 $[M+Na]^+$. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.76 (d, *J* = 8.3 Hz, 4H), 7.29 (d, *J* = 8.0 Hz, 4H), 6.76 (s, 2H), 4.14 (m, 6H), 3.82 (t, *J* = 4.6 Hz, 2H), 3.67 (m, 2H), 3.53 (m, 2H), 3.35 (s, 3H), 2.45 (t, *J* = 6.9 Hz, 4H), 2.36 (s, 6H), 1.90 (m, 4H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) 164.7, 144.7, 144.2, 132.5, 129.7, 127.7, 112.5, 87.9, 80.8, 71.7, 70.6, 69.0, 68.7, 67.5, 58.9, 27.3, 21.4, 15.4.



25

2,6-Bis (5-azidopent-1-yn-1-yl)-4-(2-(2-methoxyethoxy)ethoxy)pyridine (25)

To the solution of sodium azide (104.9 mg, 1.6 mmol) in 7 mL dry DMF, (4-(2-(2-methoxyethoxy)ethoxy)pyridine-2,6-diyl)bis(pent-4-yne-5,1-diyl) bis(4-methylbenzenesulfonate) (270.2 mg, 0.4 mmol) was added. The reaction was stirred at 70°C under argon for overnight. The reaction mixture was poured into water (10 mL) and extracted with diethyl ether (20 mL) three times. The combined organic layers were washed by water(10 mL) seven times and dried over Mg_2SO_4, evaporated to give a pale yellow liquid(96.6 mg, 58%). ESI MS m/z 412.3 $[M+H]^+$, 434.3 $[M+Na]^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.81 (s, 2H), 4.12 (t, *J* = 7.7 Hz, 2H), 3.80 (t, *J* = 7.7 Hz, 2H), 3.65 (m, 2H), 3.52 (m, 2H), 3.41 (t, *J* = 6.6 Hz, 4H), 3.34 (s, 3H), 2.48 (t, *J* = 6.9 Hz, 4H), 1.82 (m, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) 164.8, 144.5, 112.6, 88.5, 80.8, 71.7, 70.7, 69.0, 67.5, 58.9, 50.1, 27.3, 16.4.

Reference

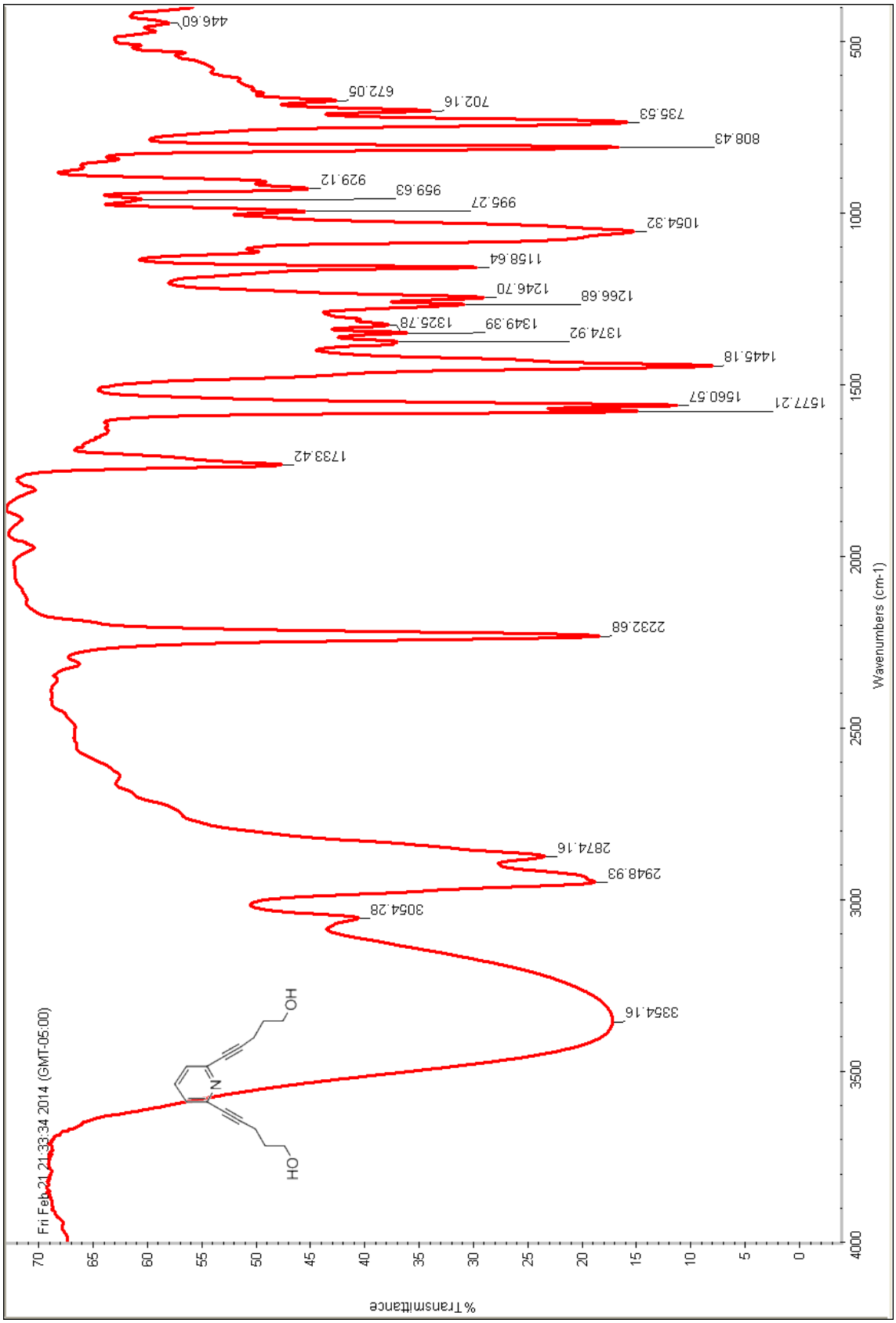
1. (a) Angus, J. C.; Hayman, C. C., Low-pressure, metastable growth of diamond and diamondlike phases. *Science* **1988,** *241* (4868), 913-921; (b) Yarbrough, W. A.; Messier, R., Current issues and problems in the chemical vapor-deposition of diamond. *Science* **1990,** *247* (4943), 688-696.
2. Charlier, J. C.; Gonze, X.; Michenaud, J. P., Graphite interplanar bonding - electronic delocalization and van-der-Waals interaction. *Europhys Lett* **1994,** *28* (6), 403-408.
3. Kroto, H. W.; Heath, J. R.; Obrien, S. C.; Curl, R. F.; Smalley, R. E., C-60 - buckminsterfullerene. *Nature* **1985,** *318* (6042), 162-163.
4. (a) Geim, A. K.; Novoselov, K. S., The rise of graphene. *Nat Mater* **2007,** *6* (3), 183-191; (b) Du, A. J.; Zhu, Z. H.; Smith, S. C., Multifunctional porous graphene for nanoelectronics and hydrogen storage: new properties revealed by first principle calculations. *J Am Chem Soc* **2010,** *132* (9), 2876-2877.
5. (a) Leroux, F.; Metenier, K.; Gautier, S.; Frackowiak, E.; Bonnamy, S.; Beguin, F., Electrochemical insertion of lithium in catalytic multi-walled carbon nanotubes. *J Power Sources* **1999,** *81*, 317-322; (b) Dekker, C., Carbon nanotubes as molecular quantum wires. *Phys Today* **1999,** *52* (5), 22-28; (c) Cherukuri, P.; Bachilo, S. M.; Litovsky, S. H.; Weisman, R. B., Near-infrared fluorescence microscopy of single-walled carbon nanotubes in phagocytic cells. *J Am Chem Soc* **2004,** *126* (48), 15638-15639.
6. Evsyukov, S. E.; Thomas, B.; Heimann, R. B., Chemical dehydrohalogenation of poly (ethylene-alt-chlorotrifluoroethylene). *Mater Chem Phys* **2000,** *66* (1), 34-40.
7. Wang, X. F.; Shi, G. Q.; Liang, Y. Q., Synthesis of carbyne-like nano-particles by electrocatalytic dehydrochlorination of 1,1,2-trichloroethane. *J Electroanal Chem* **1999,** *470* (1), 95-97.
8. Eastmond, R.; Walton, D. R. M.; Johnson, T. R., Silylation as a protective method for terminal alkynes in oxidative couplings - general synthesis of parent polyynes - H(C=C)Nh (N=4-10, 12). *Tetrahedron* **1972,** *28* (17), 4601-4616.
9. Chalifoux, W. A.; Tykwinski, R. R., Synthesis of polyynes to model the sp-carbon allotrope carbyne. *Nat Chem* **2010,** *2* (11), 967-971.
10. Yerin, A.; Wilks, E. S.; Moss, G. P.; Harada, A., Nomenclature for rotaxanes and pseudorotaxanes - (IUPAC recommendations 2008). *Pure Appl Chem* **2008,** *80* (9), 2041-2068.
11. Arico, F.; Badjic, J. D.; Cantrill, S. J.; Flood, A. H.; Leung, K. C. F.; Liu, Y.; Stoddart, J. F., Templated synthesis of interlocked molecules. *Top Curr Chem* **2005,** *249*, 203-259.
12. Movsisyan, L. D.; Kondratuk, D. V.; Franz, M.; Thompson, A. L.; Tykwinski, R. R.; Anderson, H. L., Synthesis of polyyne rotaxanes. *Org Lett* **2012,** *14* (13), 3424-3426.
13. Ogino, H., Relatively high-yield syntheses of rotaxanes - syntheses and properties of compounds consisting of cyclodextrins threaded by alpha,omega-diaminoalkanes coordinated to cobalt(III) Complexes. *J Am Chem Soc* **1981,** *103* (5), 1303-1304.
14. Sugiyama, J.; Tomita, I., Novel approach to stabilize unstable molecular wires by simultaneous rotaxane formation - Synthesis of inclusion complexes of oligocarbynes with cyclic host molecules. *Eur J Org Chem* **2007,** (28), 4651-4653.
15. (a) Rowan, S. J.; Cantrill, S. J.; Stoddart, J. F., Triphenylphosphonium stoppered [2]rotaxanes. *Org Lett* **1999,** *1* (1), 129-132; (b) Chang, T.; Heiss, A. M.; Cantrill, S. J.; Fyfe, M. C. T.; Pease, A. R.; Rowan, S. J.; Stoddart, J. F.; White, A. J. P.; Williams, D. J., Ammonium ion binding with pyridine-containing crown ethers. *Org Lett* **2000,** *2* (19), 2947-2950.

16. Nepal, D.; Samal, S.; Geckeler, K. E., The first fullerene-terminated soluble poly(azomethine) rotaxane. *Macromolecules* **2003,** *36* (11), 3800-3802.
17. Fan, E. K.; Yang, J.; Geib, S. J.; Stoner, T. C.; Hopkins, M. D.; Hamilton, A. D., Hydrogen-bonding control of molecular aggregation - self-complementary subunits lead to rod-shaped structures in the solid-state. *J Chem Soc Chem Comm* **1995,** (12), 1251-1252.
18. Tahara, K.; Lei, S. B.; Adisoejoso, J.; De Feyter, S.; Tobe, Y., Supramolecular surface-confined architectures created by self-assembly of triangular phenylene-ethynylene macrocycles via van der Waals interaction. *Chem Commun* **2010,** *46* (45), 8507-8525.
19. Hunter, C. A.; Sanders, J. K. M., The nature of pi-pi Interactions. *J Am Chem Soc* **1990,** *112* (14), 5525-5534.
20. Hill, J. P., Self-assembled hexa-peri-hexabenzocoronene graphitic nanotube (vol 304, pg 1481, 2004). *Science* **2004,** *306* (5695), 411-411.
21. Hsu, T. J.; Fowler, F. W.; Lauher, J. W., Preparation and structure of a tubular addition polymer: a true synthetic nanotube. *J Am Chem Soc* **2012,** *134* (1), 142-145.
22. Arunan, E.; Desiraju, G. R.; Klein, R. A.; Sadlej, J.; Scheiner, S.; Alkorta, I.; Clary, D. C.; Crabtree, R. H.; Dannenberg, J. J.; Hobza, P.; Kjaergaard, H. G.; Legon, A. C.; Mennucci, B.; Nesbitt, D. J., Defining the hydrogen bond: an account (IUPAC Technical Report). *Pure Appl Chem* **2011,** *83* (8), 1619-1636.
23. Ghadiri, M. R.; Granja, J. R.; Milligan, R. A.; Mcree, D. E.; Khazanovich, N., Self-Assembling Organic Nanotubes Based on a Cyclic Peptide Architecture. *Nature* **1993,** *366* (6453), 324-327.
24. Xu, Y. W.; Smith, M. D.; Geer, M. F.; Pellechia, P. J.; Brown, J. C.; Wibowo, A. C.; Shimizu, L. S., Thermal reaction of a columnar assembled diacetylene macrocycle. *J Am Chem Soc* **2010,** *132* (15), 5334-5335.
25. (a) Shimizu, L. S.; Smith, M. D.; Hughes, A. D.; Shimizu, K. D., Self-assembly of a bis-urea macrocycle into a columnar nanotube. *Chem Commun* **2001,** *17*, 1592-1593; (b) Shimizu, L. S.; Hughes, A. D.; Smith, M. D.; Davis, M. J.; Zhang, B. P.; zur Loye, H. C.; Shimizu, K. D., Self-assembled nanotubes that reversibly bind acetic acid guests. *J Am Chem Soc* **2003,** *125* (49), 14972-14973.
26. Fowler, F. W.; Lauher, J. W., A rational design of molecular materials. *J Phys Org Chem* **2000,** *13* (12), 850-857.
27. Wegner, G., Topochemical reactions of monomers with conjugated triple bonds .I. Polymerization of 2.4-hexadiyn-1.6-diols deivatives in crystalline state. *Z Naturforsch Pt B* **1969,** *B 24* (7), 824.
28. (a) Baughman, R. H., Solid-state synthesis of large polymer single-crystals. *J Polym Sci Pol Phys* **1974,** *12* (8), 1511-1535; (b) Baughman, R. H.; Yee, K. C., Solid-state polymerization of linear and cyclic acetylenes. *Macromol Rev* **1978,** *13*, 219-239.
29. Wilhelm, C.; Boyd, S. A.; Chawda, S.; Fowler, F. W.; Goroff, N. S.; Halada, G. P.; Grey, C. P.; Lauher, J. W.; Luo, L.; Martin, C. D.; Parise, J. B.; Tarabrella, C.; Webb, J. A., Pressure-induced polymerization of diiodobutadiyne in assembled cocrystals. *J Am Chem Soc* **2008,** *130* (13), 4415-4420.
30. Lauher, J. W.; Fowler, F. W.; Goroff, N. S., Single-crystal-to-single-crystal topochemical polymerizations by design. *Accounts Chem Res* **2008,** *41* (9), 1215-1229.
31. 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* (10), 1891-1893.

32. Metrangolo, P.; Meyer, F.; Pilati, T.; Resnati, G.; Terraneo, G., Halogen bonding in supramolecular chemistry. *Angew Chem Int Edit* **2008,** *47* (33), 6114-6127.
33. Gutherie, F., On the iodide of iodammonium, *J. Chem. Soc.*, **1863**,*16*, 239-244
34. Benesi, H. A.; Hildebrand, J. H., Ultraviolet absorption bands of iodine in aromatic hydrocarbons. *J Am Chem Soc* **1948,** *70* (8), 2832-2833.
35. Hassel, O.; Hvoslef, J., The structure of bromine 1,4-dioxanate. *Acta Chem Scand* **1954,** *8* (5), 873-873.
36. (a) Metrangolo, P.; Neukirch, H.; Pilati, T.; Resnati, G., Halogen bonding based recognition processes: a world parallel to hydrogen bonding. *Accounts Chem Res* **2005,** *38* (5), 386-395; (b) Metrangolo, P.; Resnati, G., Halogen bonding: a paradigm in supramolecular chemistry. *Chem-Eur J* **2001,** *7* (12), 2511-2519.
37. Jin, H. J.; Plonka, A. M.; Parise, J. B.; Goroff, N. S., Pressure induced topochemical polymerization of diiodobutadiyne: a single-crystal-to-single-crystal transformation. *Crystengcomm* **2013,** *15* (16), 3106-3110.
38. (a) Holmesla.O; Romming, C., Crystal structure of (1-1) addition compounds of diiodoacetylene with 1,4-dithiane and 1,4-dieselenane respectively. *Acta Chem Scand* **1966,** *20* (9), 2601-2610; (b) Laurence, C.; Queigneccabanetos, M.; Dziembowska, T.; Queignec, R.; Wojtkowiak, B., 1-iodoacetylenes .1. Spectroscopic evidence of their complexes with Lewis-bases - a spectroscopic scale of soft basicity. *J Am Chem Soc* **1981,** *103* (10), 2567-2573.
39. Yamamoto, H. M.; Yamaura, J. I.; Kato, R., Structural and electrical properties of (BEDT-TTF)(2)X(diiodoacetylene) (X=Cl, Br): the novel self-assembly of neutral Lewis acidic molecules and halide anions in a molecular metal. *J Mater Chem* **1998,** *8* (1), 15-16.
40. Webb, J. A.; Klijn, J. E.; Hill, P. A.; Bennett, J. L.; Goroff, N. S., Experimental studies of the C-13 NMR of iodoalkynes in Lewis-basic solvents. *J Org Chem* **2004,** *69* (3), 660-664.
41. Perkins, C.; Libri, S.; Adams, H.; Brammer, L., Diiodoacetylene: compact, strong ditopic halogen bond donor. *Crystengcomm* **2012,** *14* (9), 3033-3038.
42. Sun, A. W.; Lauher, J. W.; Goroff, N. S., Preparation of poly(diiododiacetylene), an ordered conjugated polymer of carbon and iodine. *Science* **2006,** *312* (5776), 1030-1034.
43. Luo, L.; Wilhelm, C.; Sun, A. W.; Grey, C. P.; Lauher, J. W.; Goroff, N. S., Poly(diiododiacetylene): preparation, isolation, and full characterization of a very simple poly(diacetylene). *J Am Chem Soc* **2008,** *130* (24), 7702-7709.
44. Luo, L. Preparation and comprehensive characterization of poly(diiododiacetylene) and spectroscopic studies of its reactions with Lewis bases. Ph.D. Thesis, The State University of New York, Stony Brook, NY, **2009**.
45. Luo, L.; Resch, D.; Wilhelm, C.; Young, C. N.; Halada, G. P.; Gambino, R. J.; Grey, C. P.; Goroff, N. S., Room-temperature carbonization of poly(diiododiacetylene) by reaction with Lewis bases. *J Am Chem Soc* **2011,** *133* (48), 19274-19277.
46. Resch, D. L. Poly(diiododiacetylene): a potential precursor for new all-carbon materials. Ph. D. Thesis, The State University of New York, Stony Brook, NY, **2013**.
47. Srinivas, A. R. G.; Kerr-Phillips, T. E.; Peng, H.; Barker, D.; Travas-Sejdic, J., Water-soluble anionic poly(p-phenylene vinylenes) with high luminescence. *Polym Chem-Uk* **2013,** *4* (8), 2506-2514.
48. Liu, X. Z.Macrocyclic host-guest framework for polymerization of diiodobutadiyne. M. S. Thesis, The State University of New York, Stony Brook, NY, **2013**.

49. Yu, T. B.; Bai, J. Z.; Guan, Z. B., Cycloaddition-promoted self-assembly of a polymer into well-defined beta sheets and hierarchical nanofibrils. *Angew Chem Int Edit* **2009,** *48* (6), 1097-1101.
50. Saito, Y.; Matsumoto, K.; Bag, S. S.; Ogasawara, S.; Fujimoto, K.; Hanawa, K.; Saito, I., C8-alkynyl- and alkylamino substituted 2 '-deoxyguanosines: a universal linker for nucleic acids modification. *Tetrahedron* **2008,** *64* (16), 3578-3588.
51. Rondeau-Gagne, S.; Neabo, J. R.; Desroches, M.; Larouche, J.; Brisson, J.; Morin, J. F., Topochemical polymerization of phenylacetylene macrocycles: a new strategy for the preparation of organic nanorods. *J Am Chem Soc* **2013,** *135* (1), 110-113.
52. Maleczka, R. E.; Shi, F.; Holmes, D.; Smith, M. R., C-H activation/borylation/oxidation: a one-pot unified route to meta-substituted phenois bearing ortho-/para-directing groups. *J Am Chem Soc* **2003,** *125* (26), 7792-7793.
53. Waki, M.; Abe, H.; Inouye, M., Helix formation in synthetic polymers by hydrogen bonding with native saccharides in protic media. *Chem-Eur J* **2006,** *12* (30), 7839-7847.
54. Liu, Bo. Design and preparation of polydiacetylenes using supramolecular chemistry. Ph. D. Thesis, The State University of New York, Stony Brook, NY, **2013.**
55. Ajay, A.; Sharma, S.; Gupt, M. P.; Bajpai, V.; Hamidullah; Kumar, B.; Kaushik, M. P.; Konwar, R.; Ampapathi, R. S.; Tripathi, R. P., Diversity oriented synthesis of pyran based polyfunctional stereogenic macrocyles and their conformational studies. *Org Lett* **2012,** *14* (17), 4306-4309.
56. DeCicco, R. C. The synthesis and polymerization behavior of polyynes. Ph. D. Thesis, The State University of New York, Stony Brook, NY, **2012**.
57. Gadge, S. T.; Bhanage, B. M., Pd/C-catalyzed synthesis of oxamates by oxidative cross double carbonylation of amines and alcohols under co-catalyst, base, dehydrating agent, and ligand-free conditions. *J Org Chem* **2013,** *78* (13), 6793-6797.

Appendix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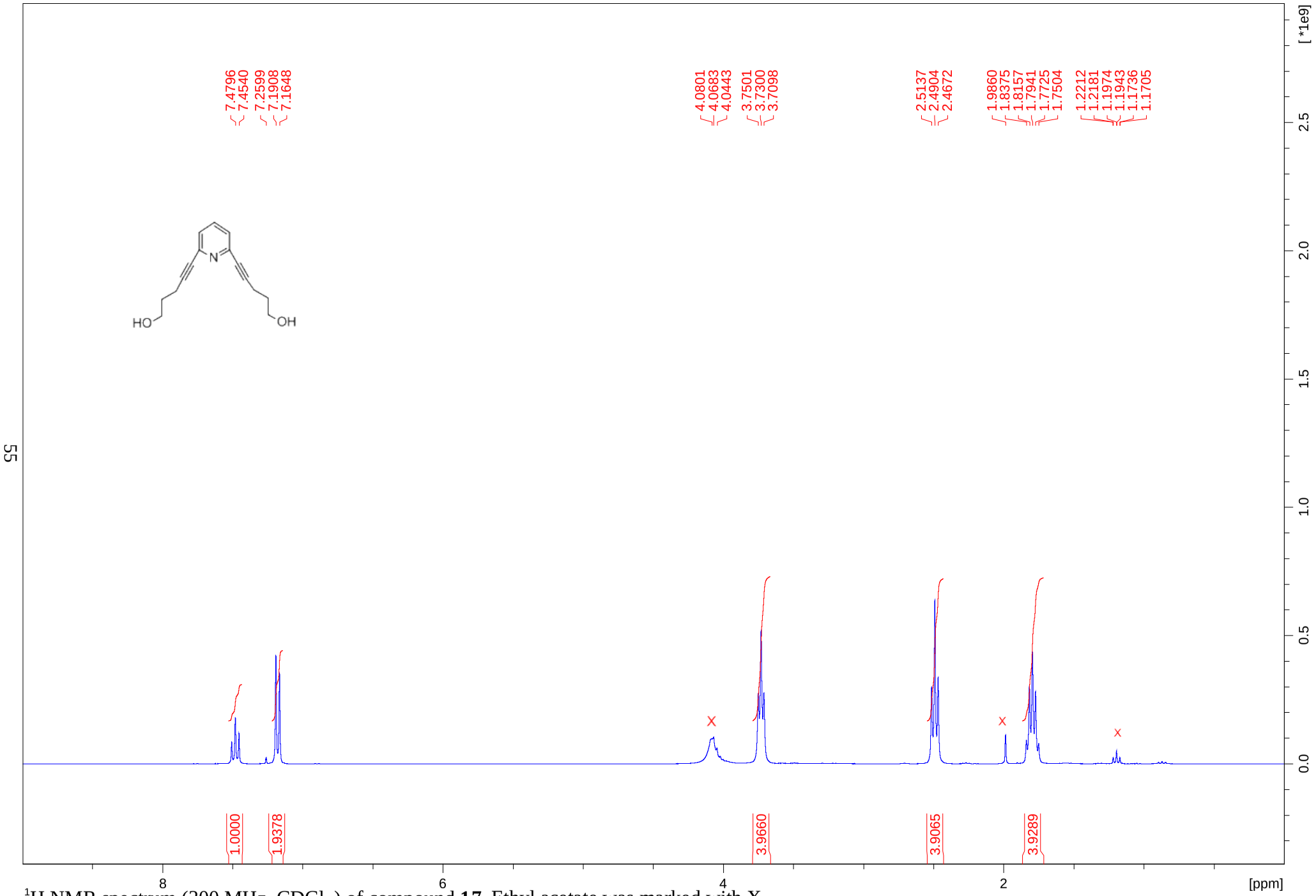
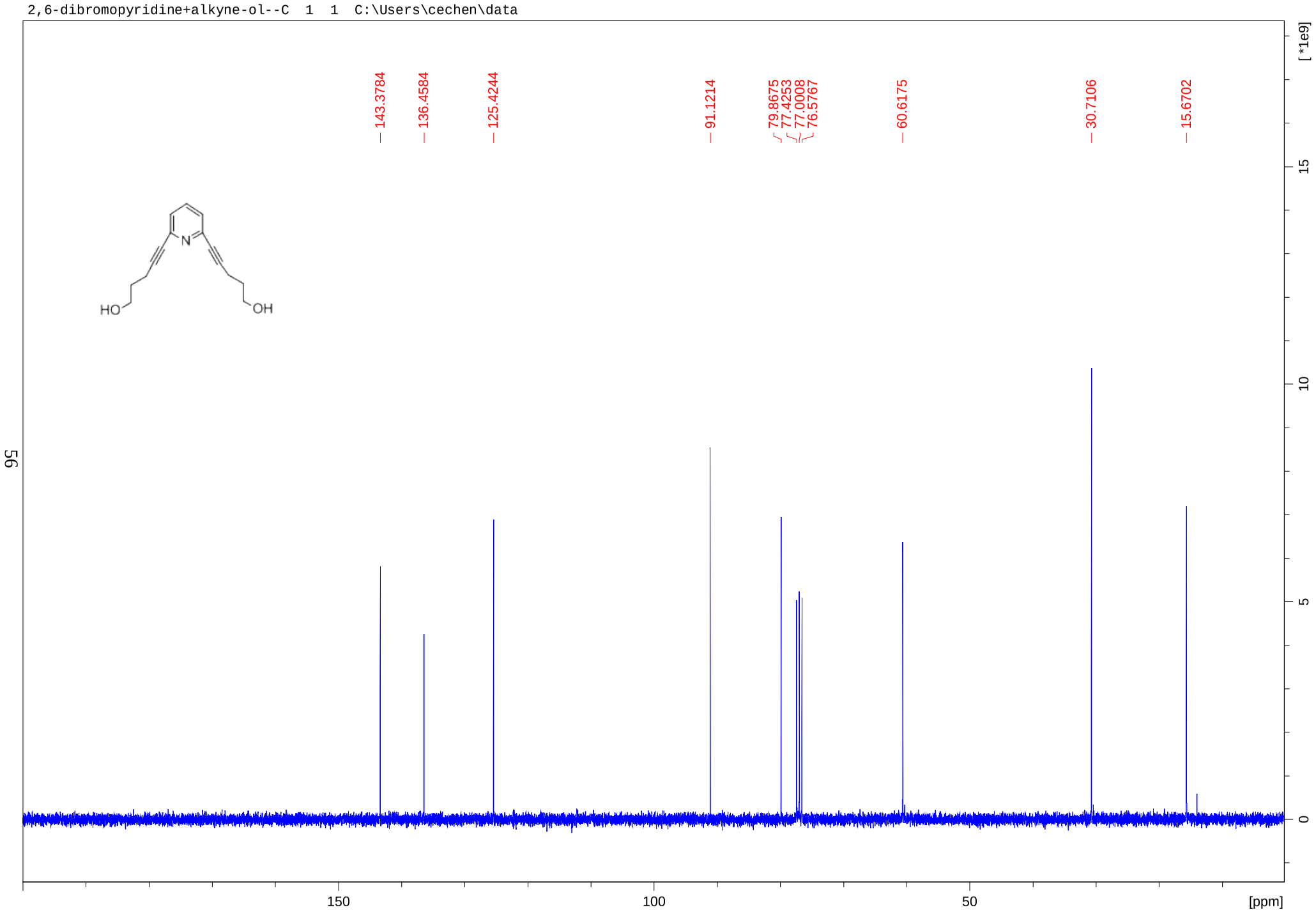
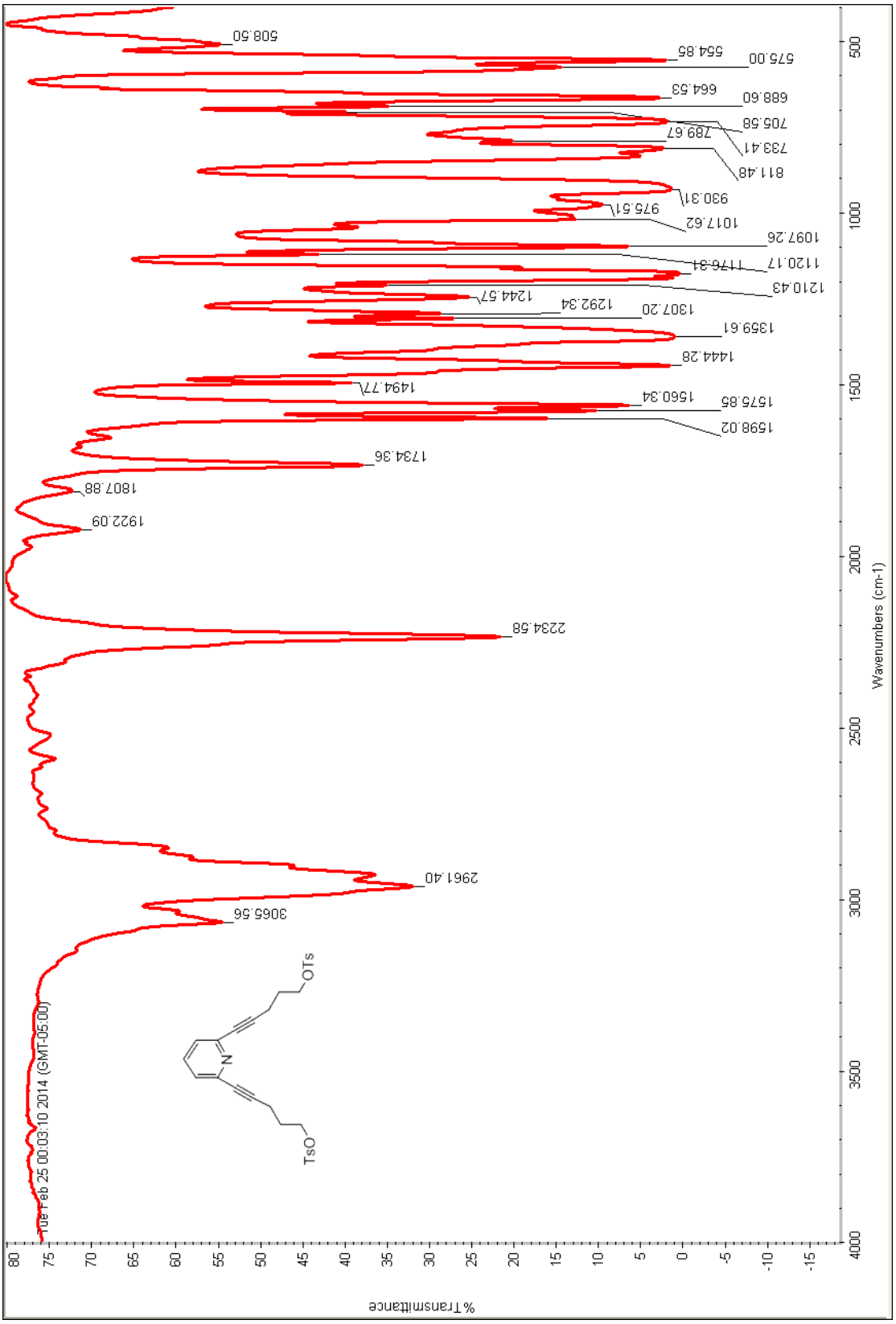


^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **17**. Ethyl acetate was marked with X.



^{13}C NMR spectrum (300 MHz, $CDCl_3$) of compound **17**.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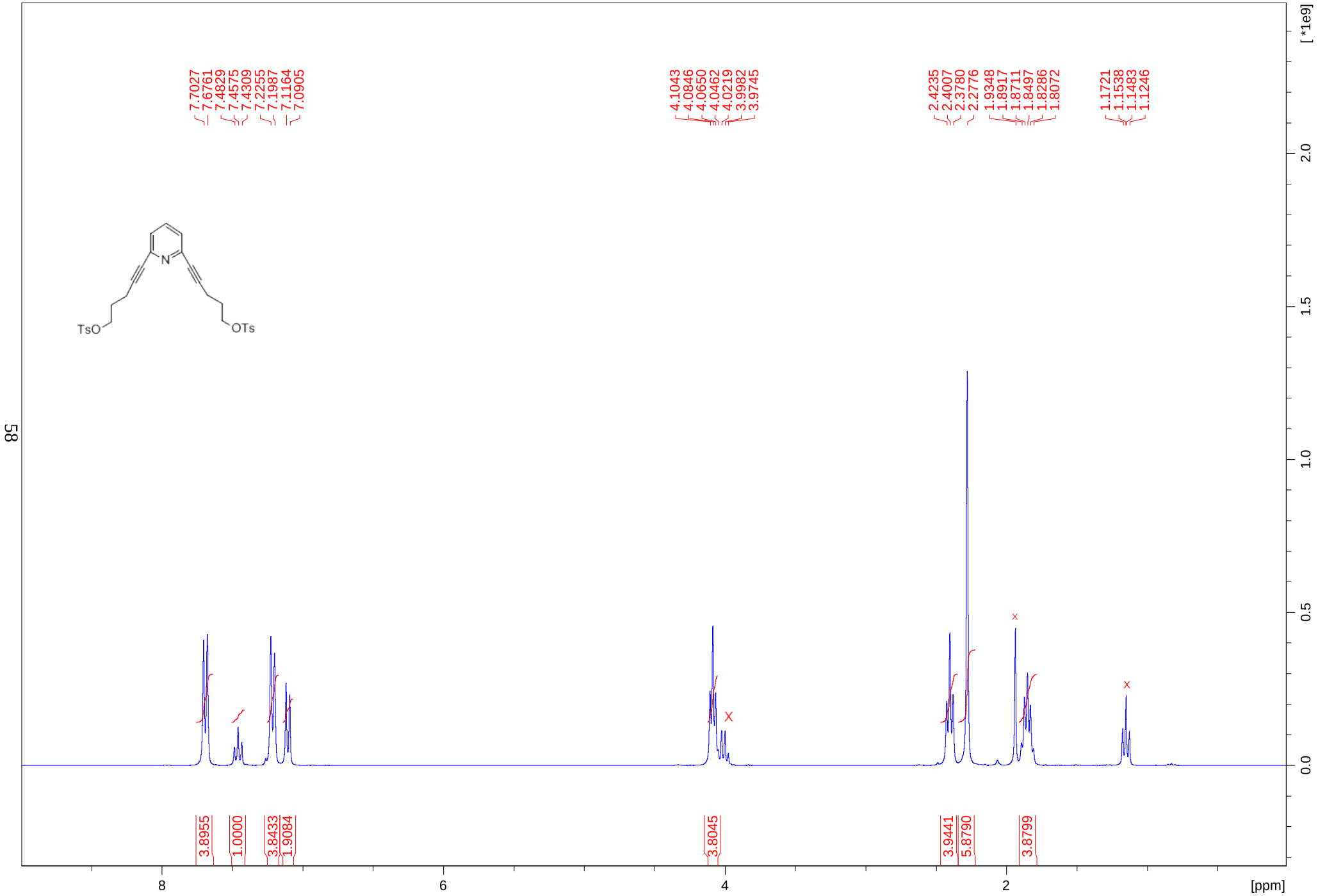
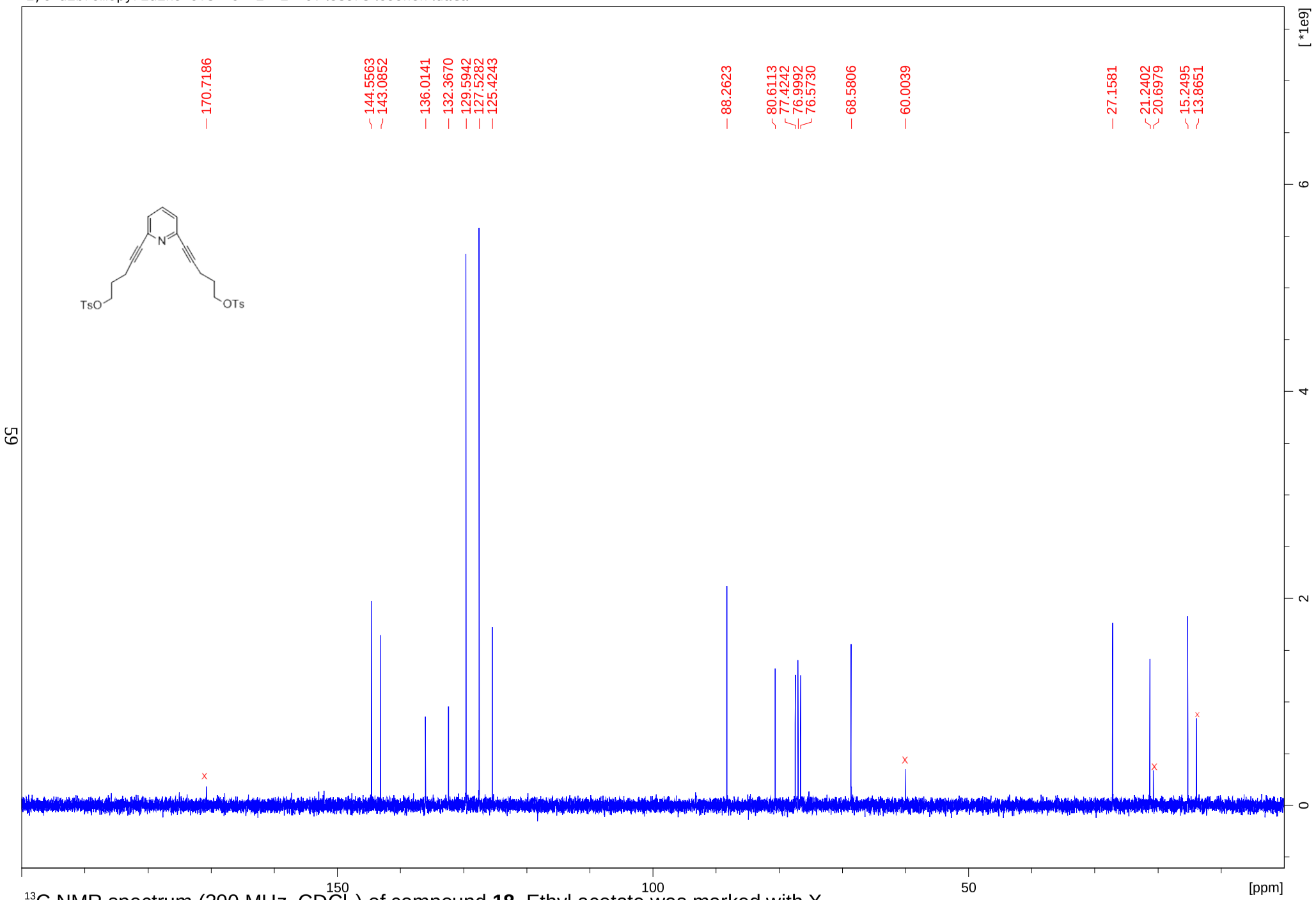
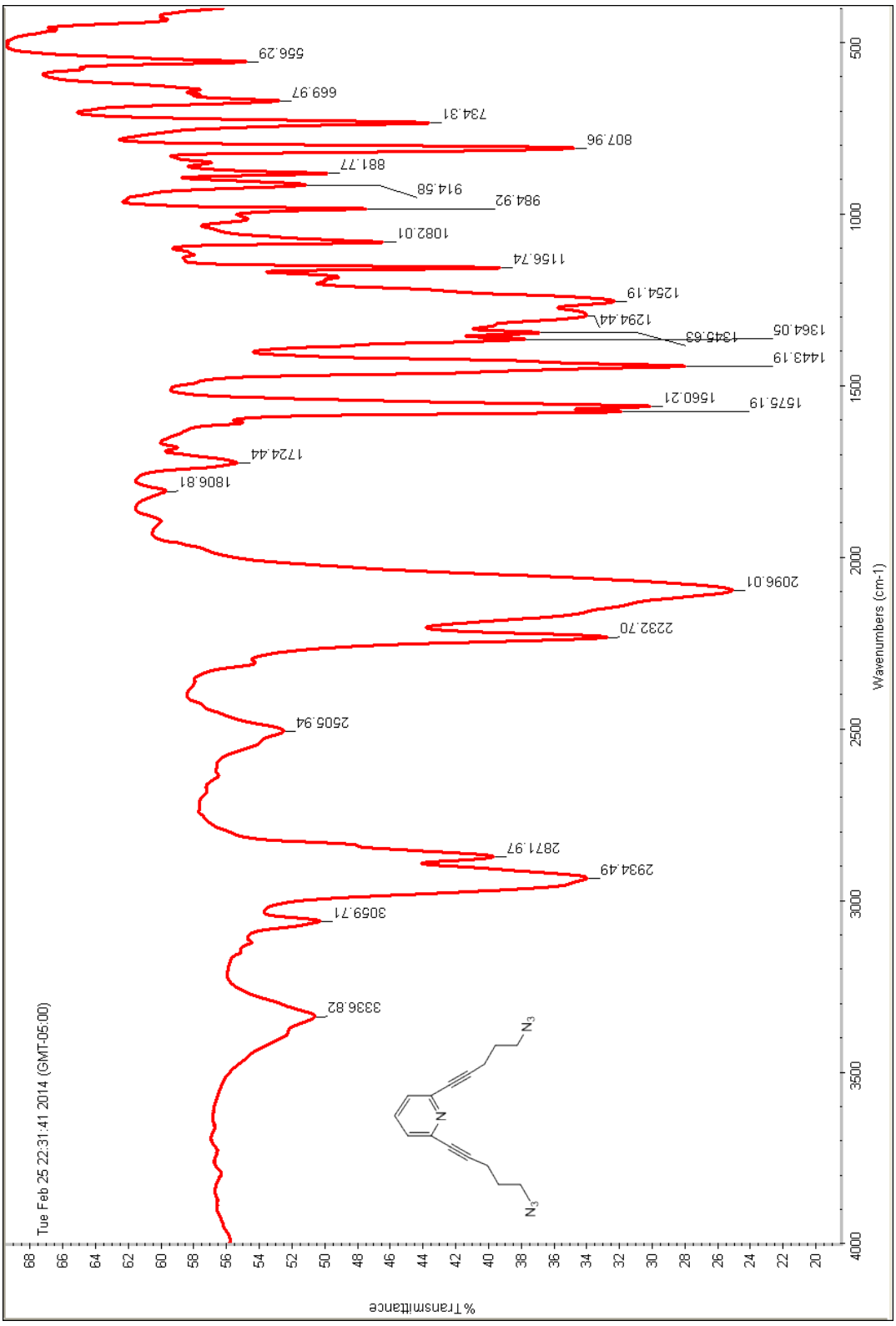
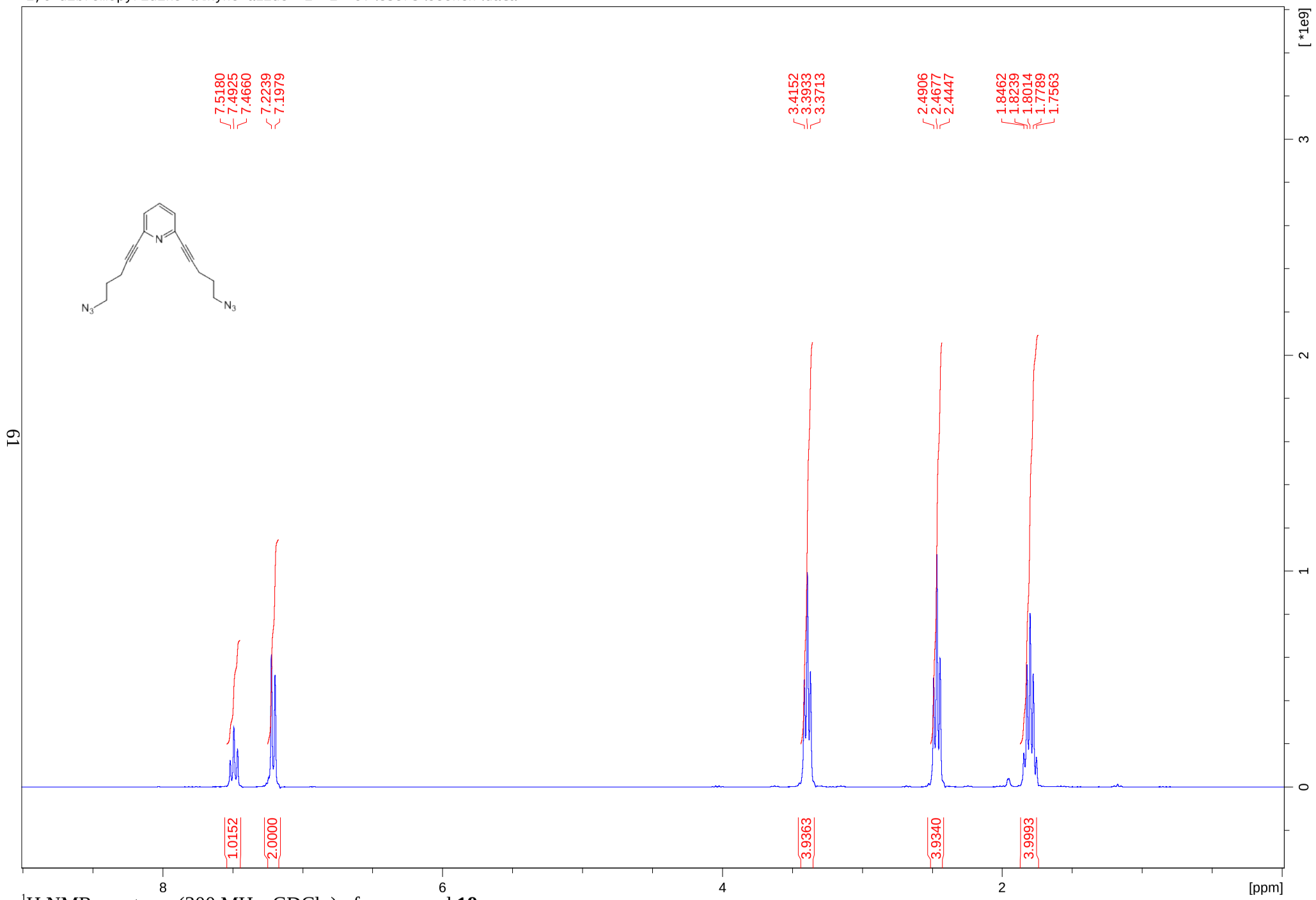


^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **18**. Ethyl acetate was marked with X.

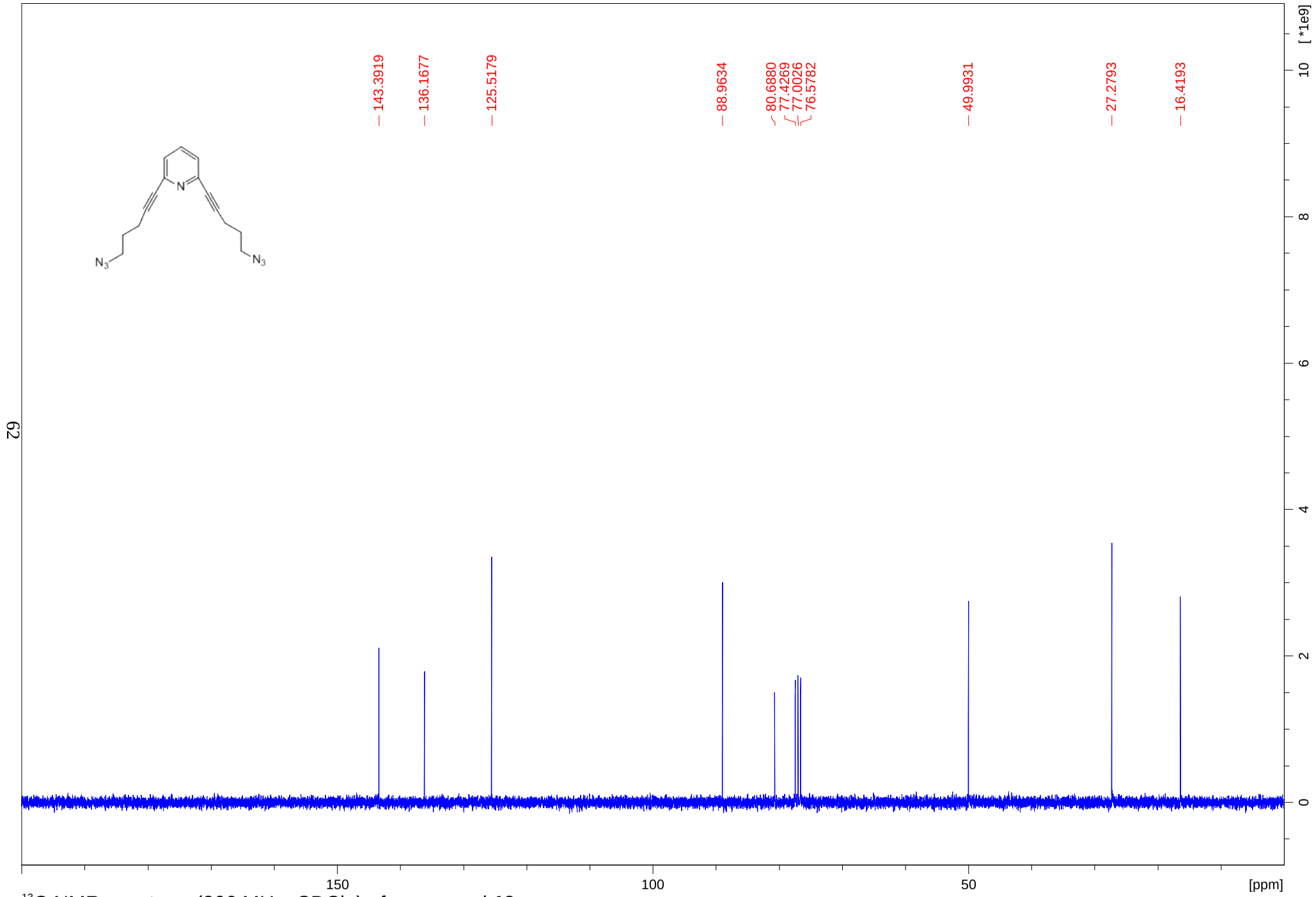


^{13}C NMR spectrum (300 MHz, $CDCl_3$) of compound **18**. Ethyl acetate was marked with X.

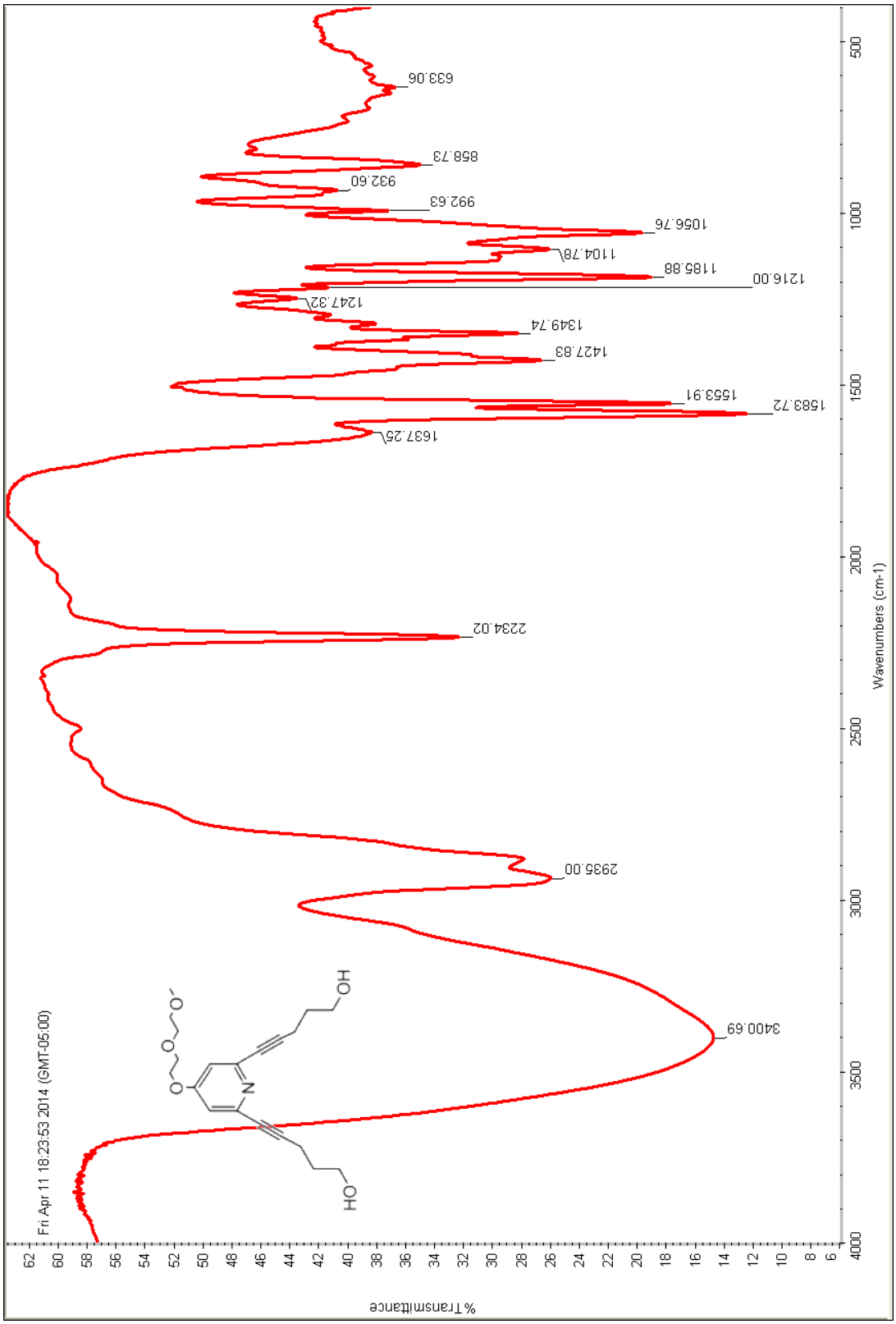

556.29
669.97
734.31
807.96
881.77
914.58
984.92
1082.01
1156.74
1254.19
1294.44
1345.63
1364.05
1443.19
1560.21
1575.19
1724.44
1806.81
2096.01
2232.70
2505.94
2871.97
2934.49
3059.71
3336.82
Tue Feb 25 22:31:41 2014 (GMT-05:00)
%Transmittance
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1500
1000
500
N3
N
N3

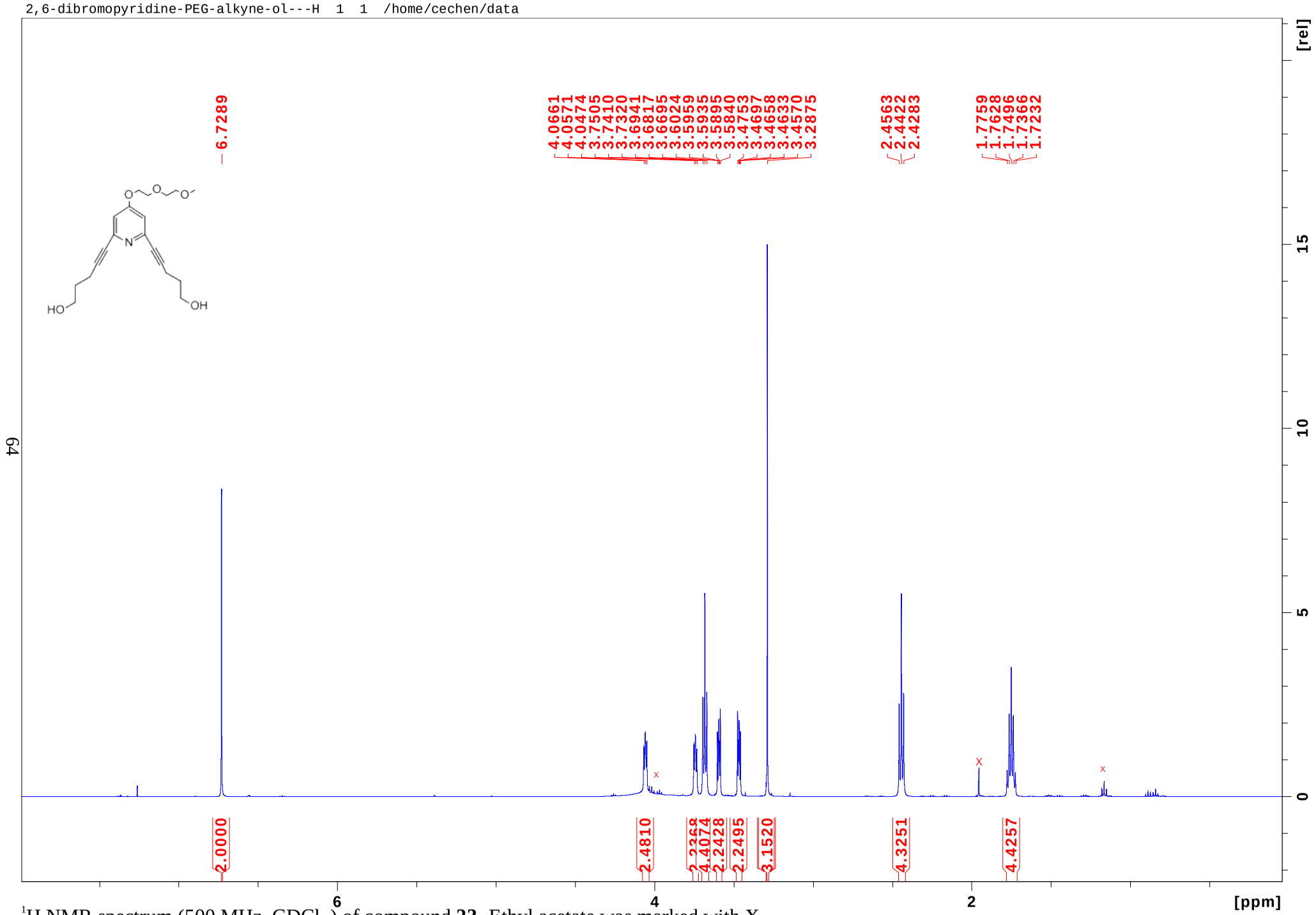


^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **19**.

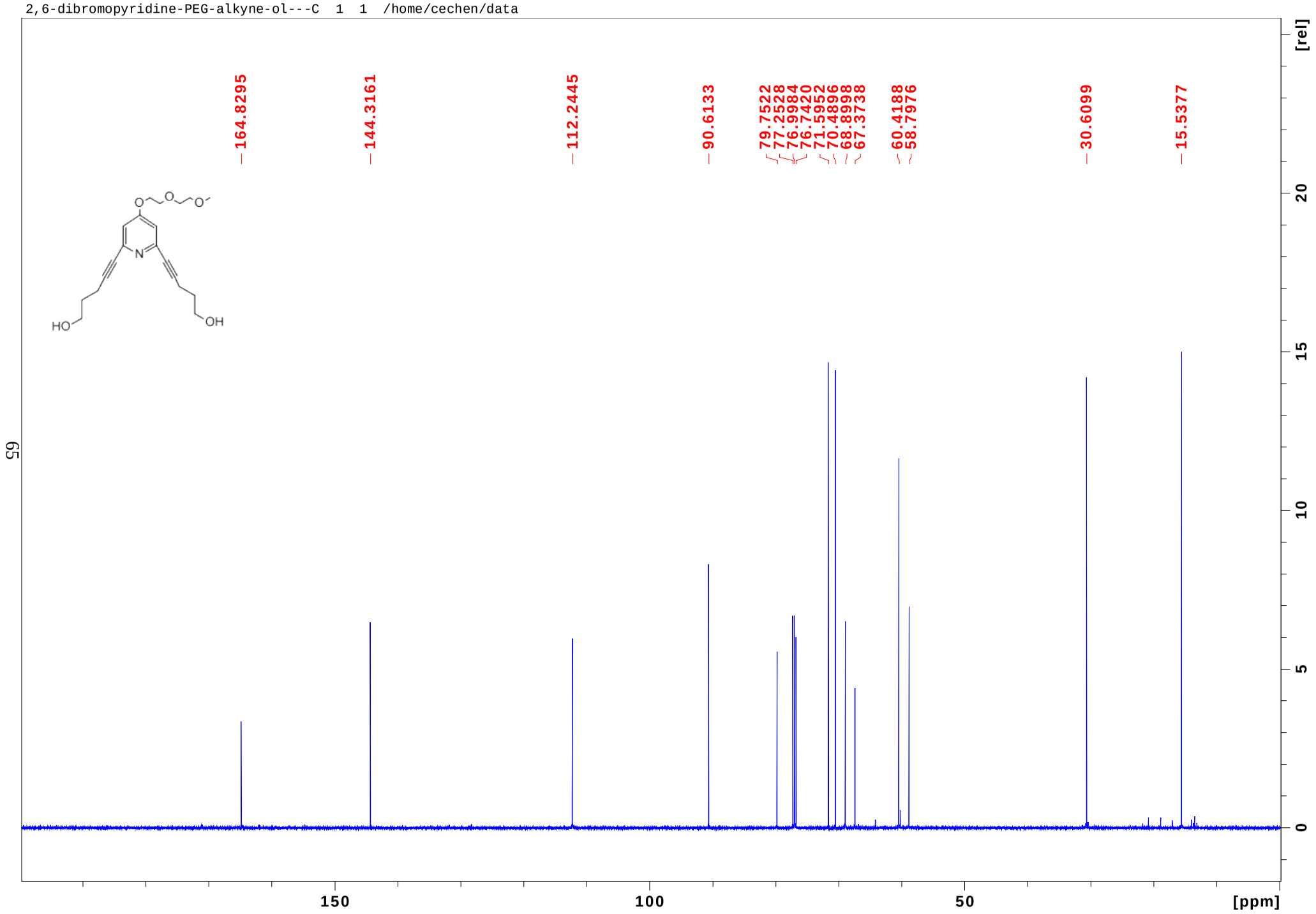


^{13}C NMR spectrum (300 MHz, $CDCl_3$) of compound **19**.

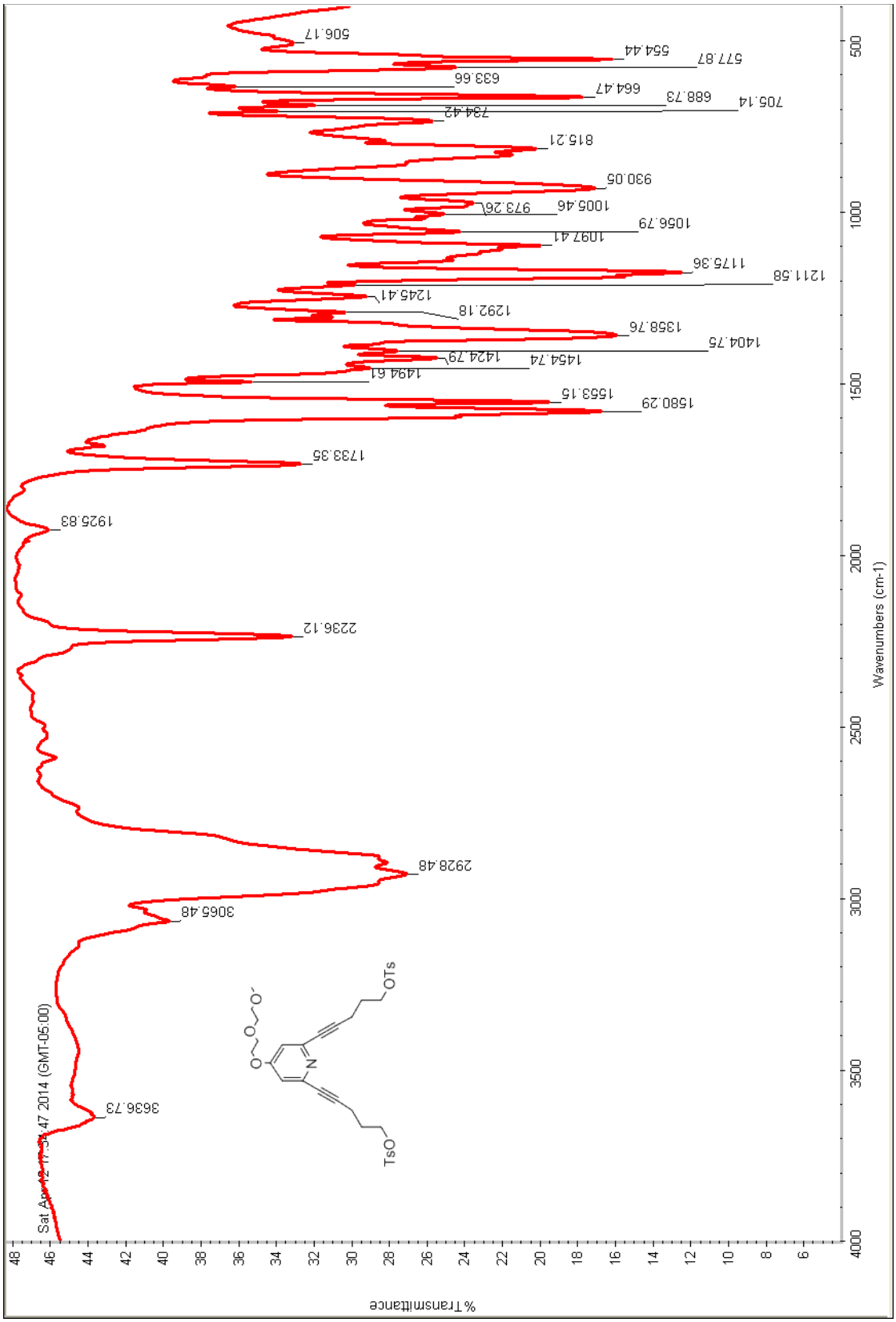

Fri Apr 11 18:23:53 2014 (GMT-05:00)
%Transmittance
Wavenumbers (cm-1)
633.06
858.73
932.60
992.63
1056.76
1104.78
1185.88
1216.00
1247.32
1349.74
1427.83
1553.91
1583.72
1637.25
2234.02
2935.00
3400.69
HO
N
O
OH

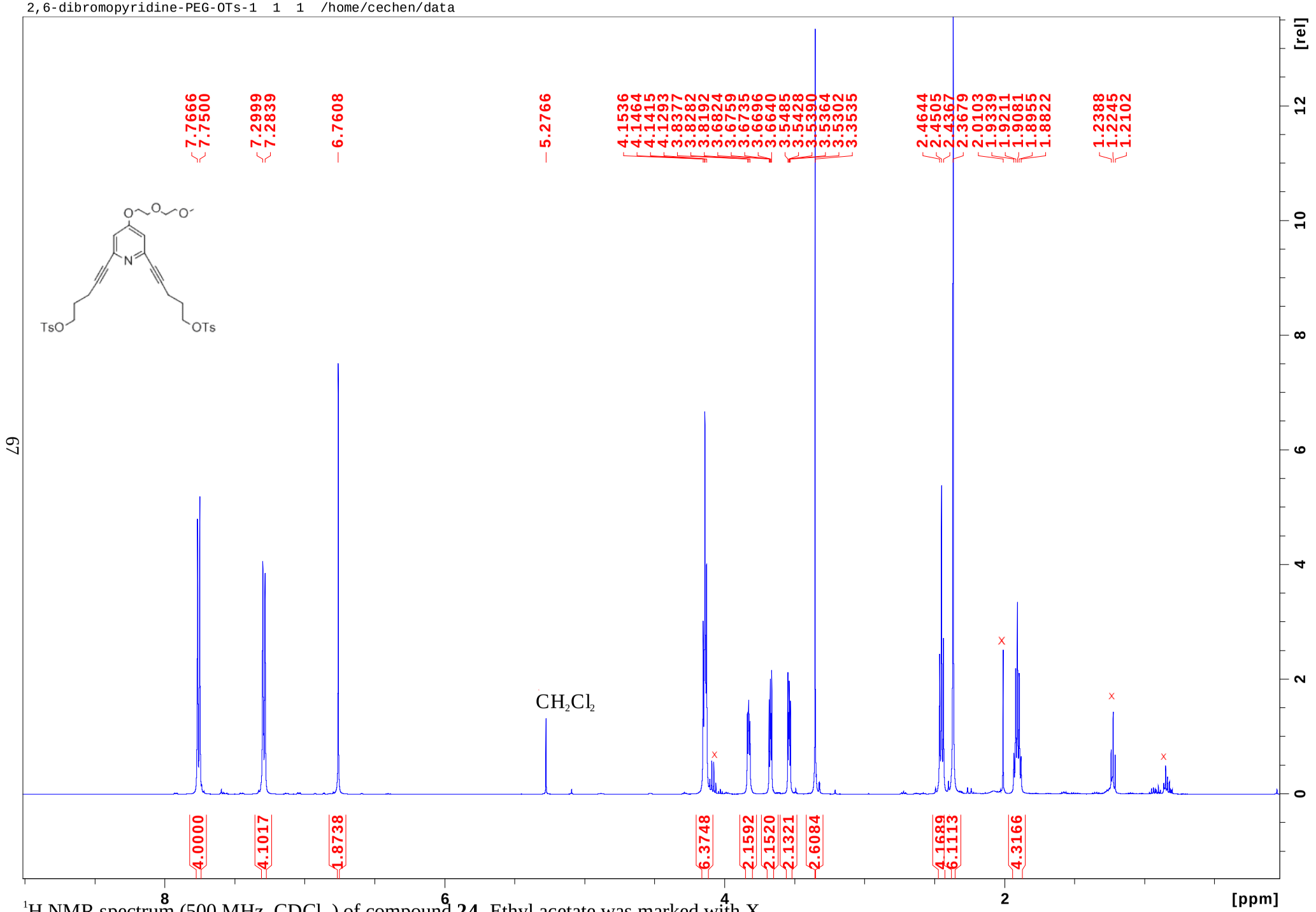


^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **23**. Ethyl acetate was marked with X.

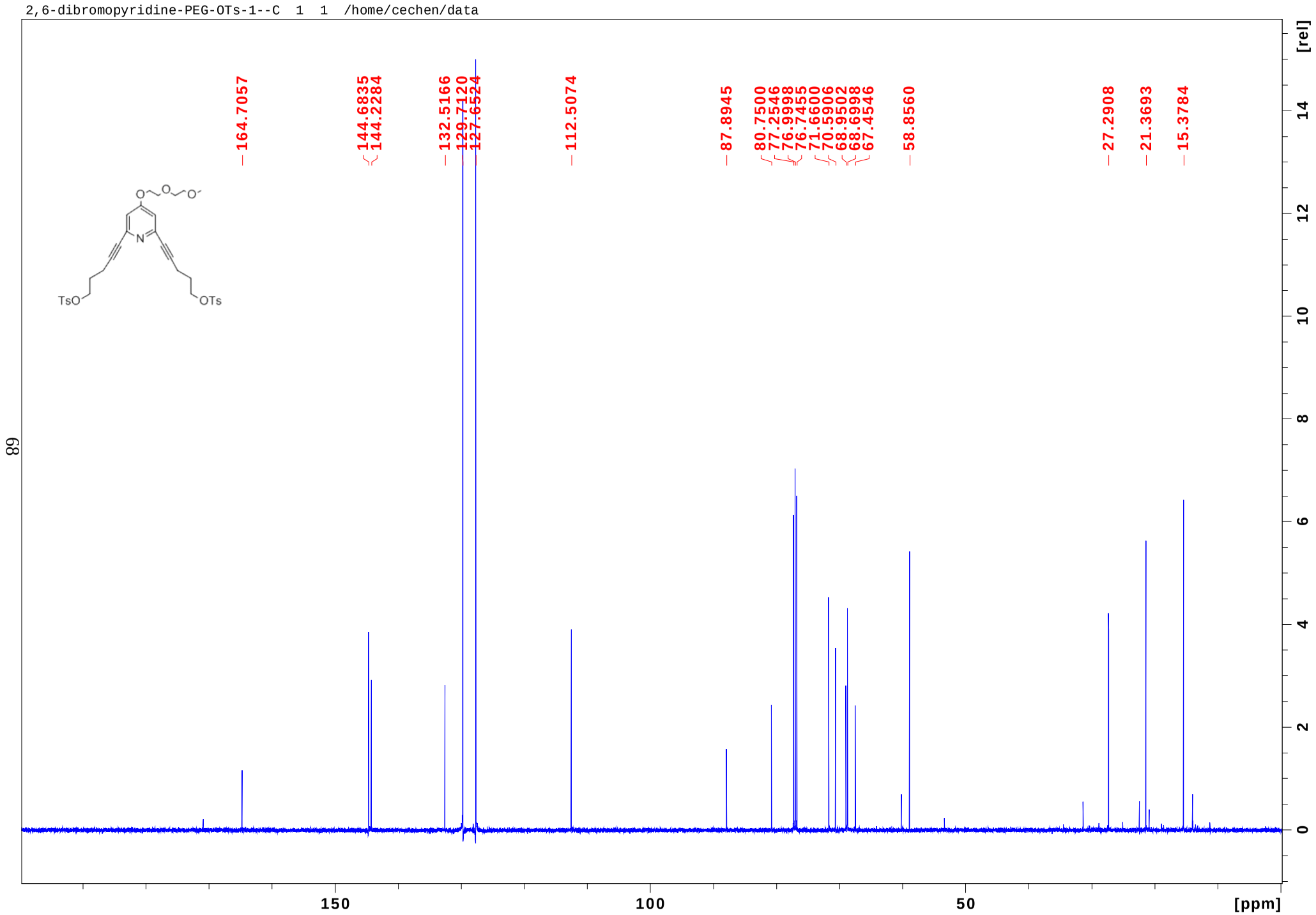


^{13}C NMR spectrum (500 MHz, $CDCl_3$) of compound **23**.

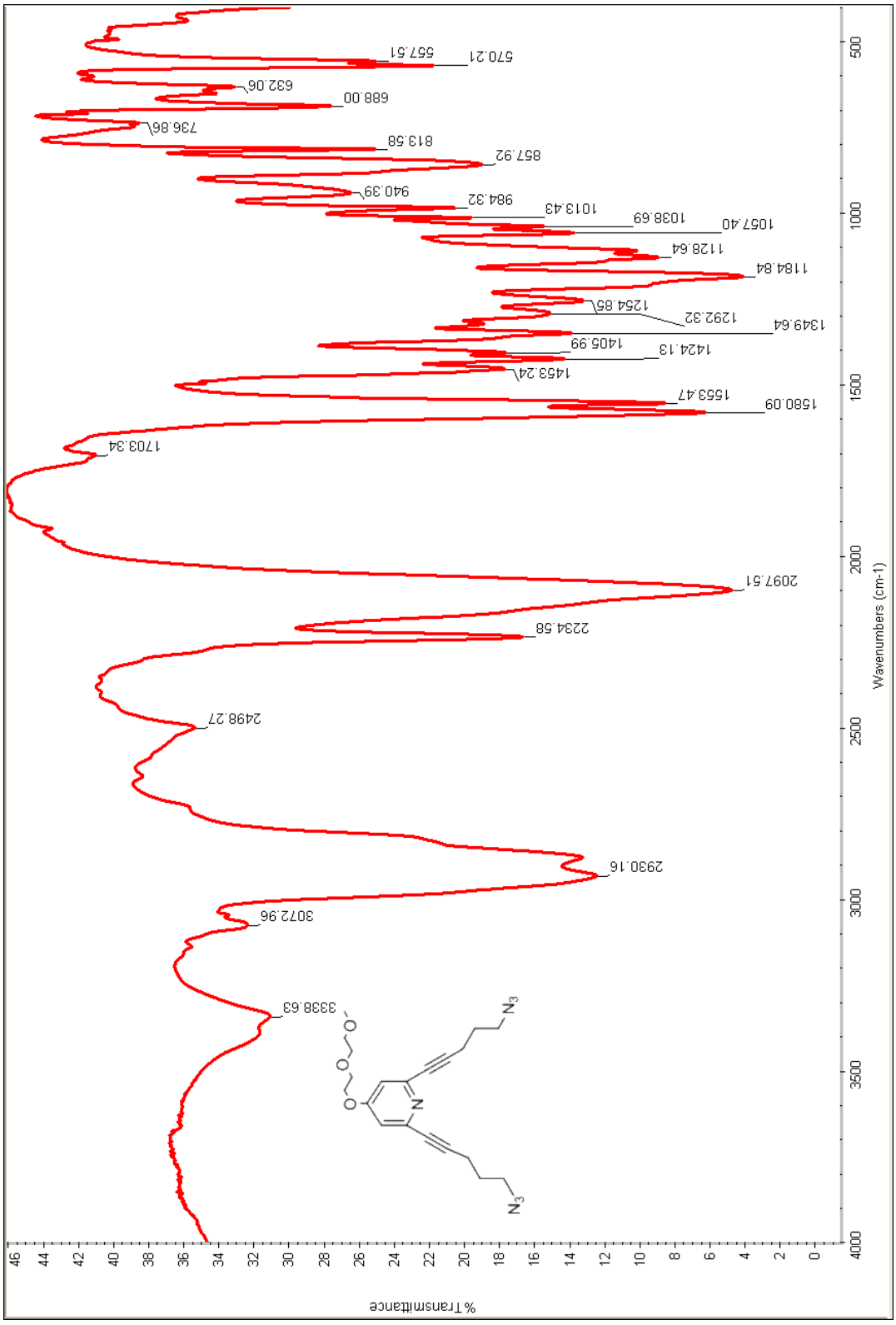

% Transmittance
Wavenumbers (cm-1)
Sat Aug 02 17:35:47 2014 (GMT-05:00)
3636.73
3065.48
2928.48
2236.12
1925.83
1733.35
1580.29
1553.15
1494.61
1454.74
1424.79
1404.75
1358.76
1292.18
1245.41
1211.58
1175.36
1097.41
1056.79
1005.46
973.26
930.05
815.21
784.42
705.14
688.73
664.47
633.66
577.87
554.44
506.17
OTs
TsO
N
O
O
O

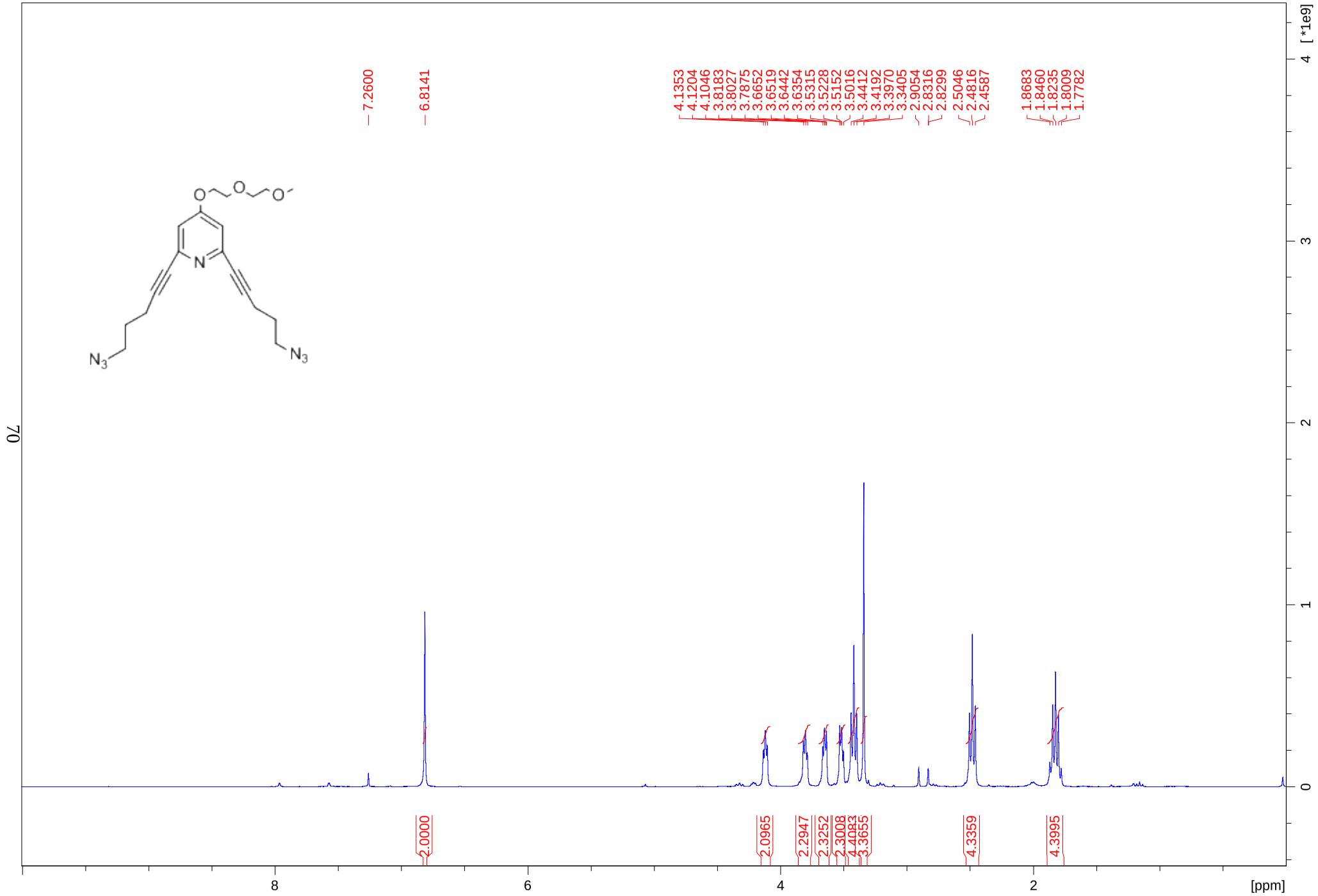


^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **24**. Ethyl acetate was marked with X.

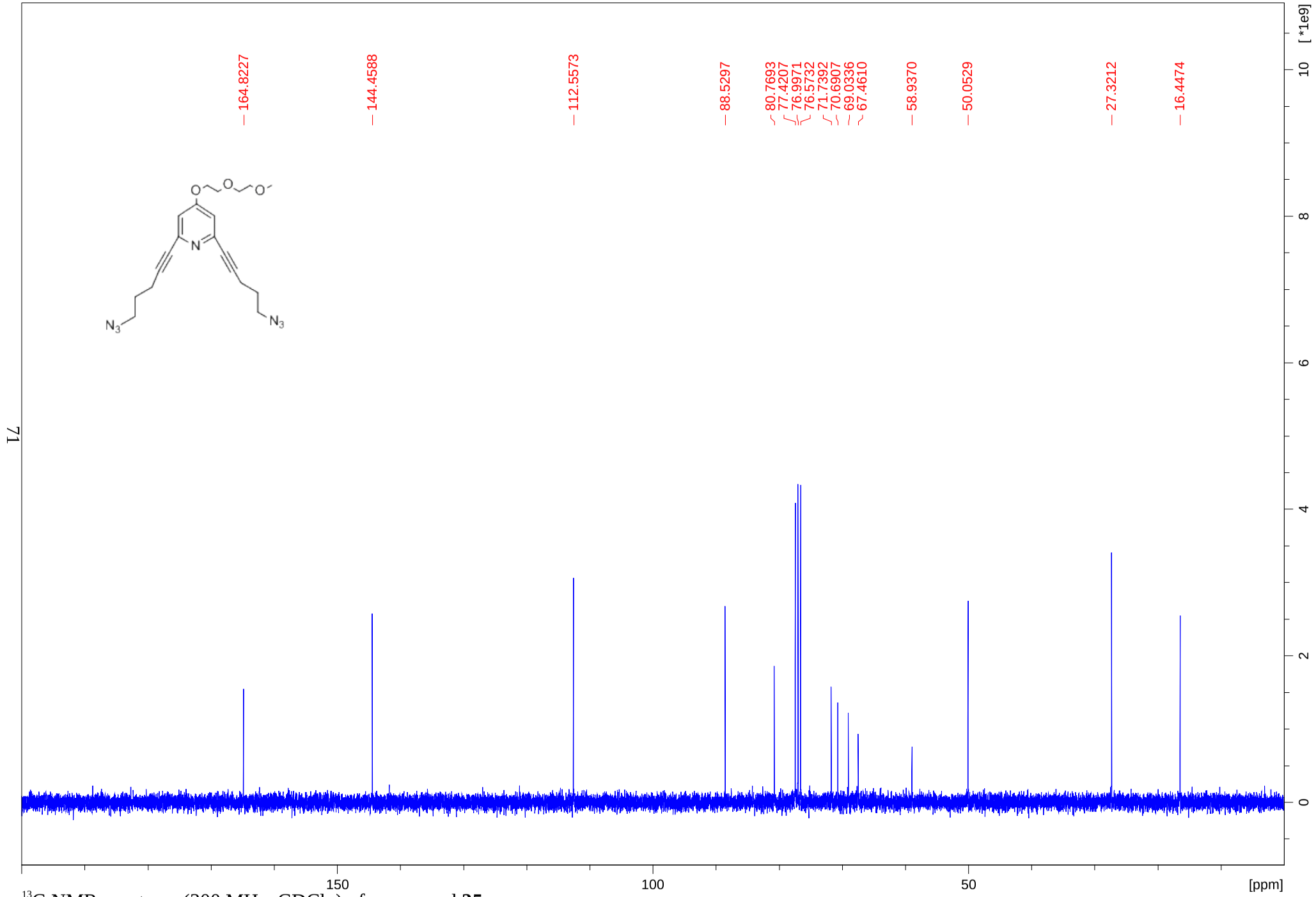


^{13}C NMR spectrum (500 MHz, CDCl3) of compound **24**.

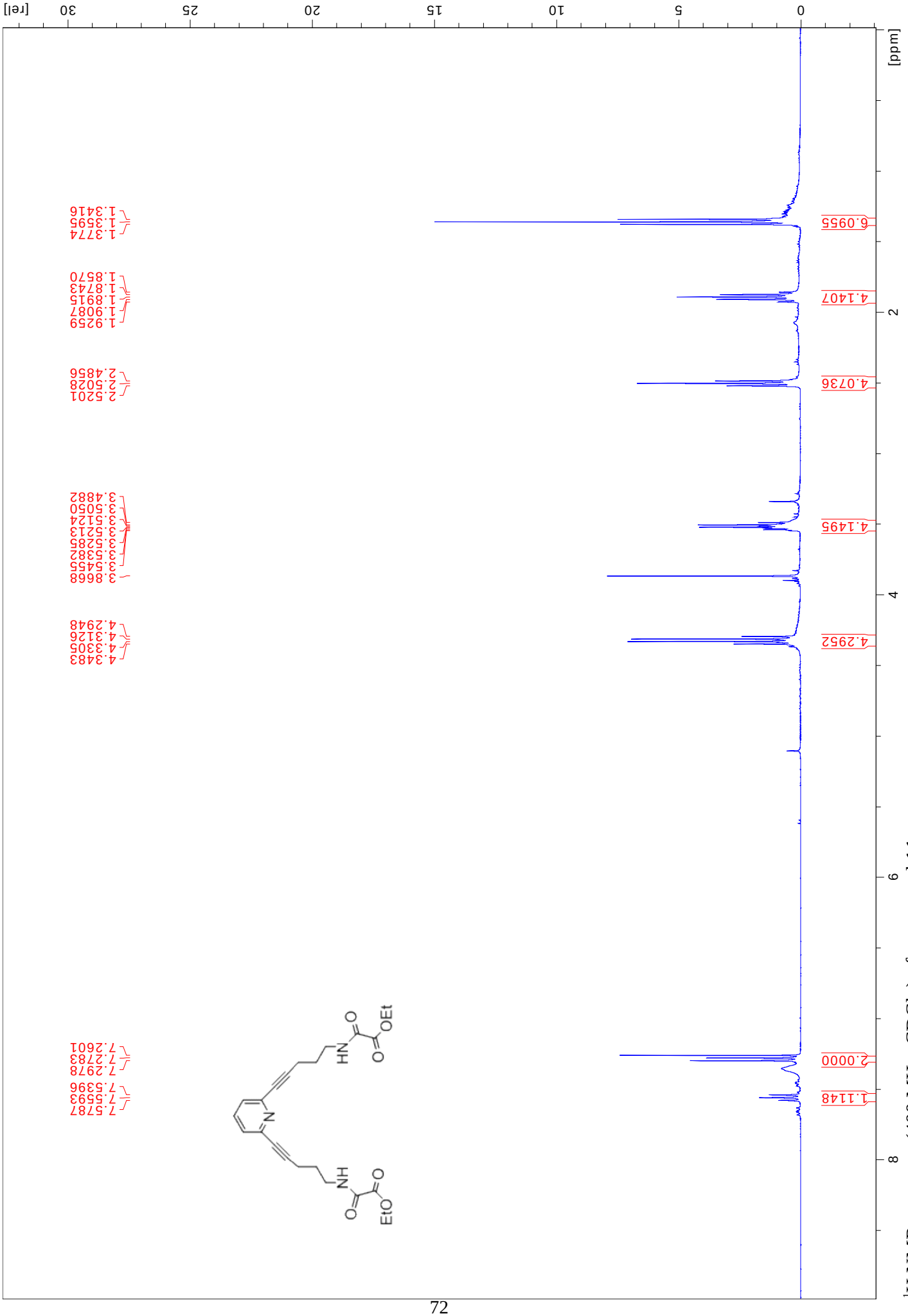

%Transmittance
Wavenumbers (cm-1)
3338.63
3072.96
2930.16
2498.27
2234.58
2097.51
1703.34
1580.09
1553.47
1453.24
1424.13
1405.99
1349.64
1292.32
1254.85
1184.84
1128.64
1057.40
1038.69
1013.43
984.32
940.39
857.92
813.58
736.86
688.00
632.06
570.21
557.51
N3
N3
O
O
O
O
N



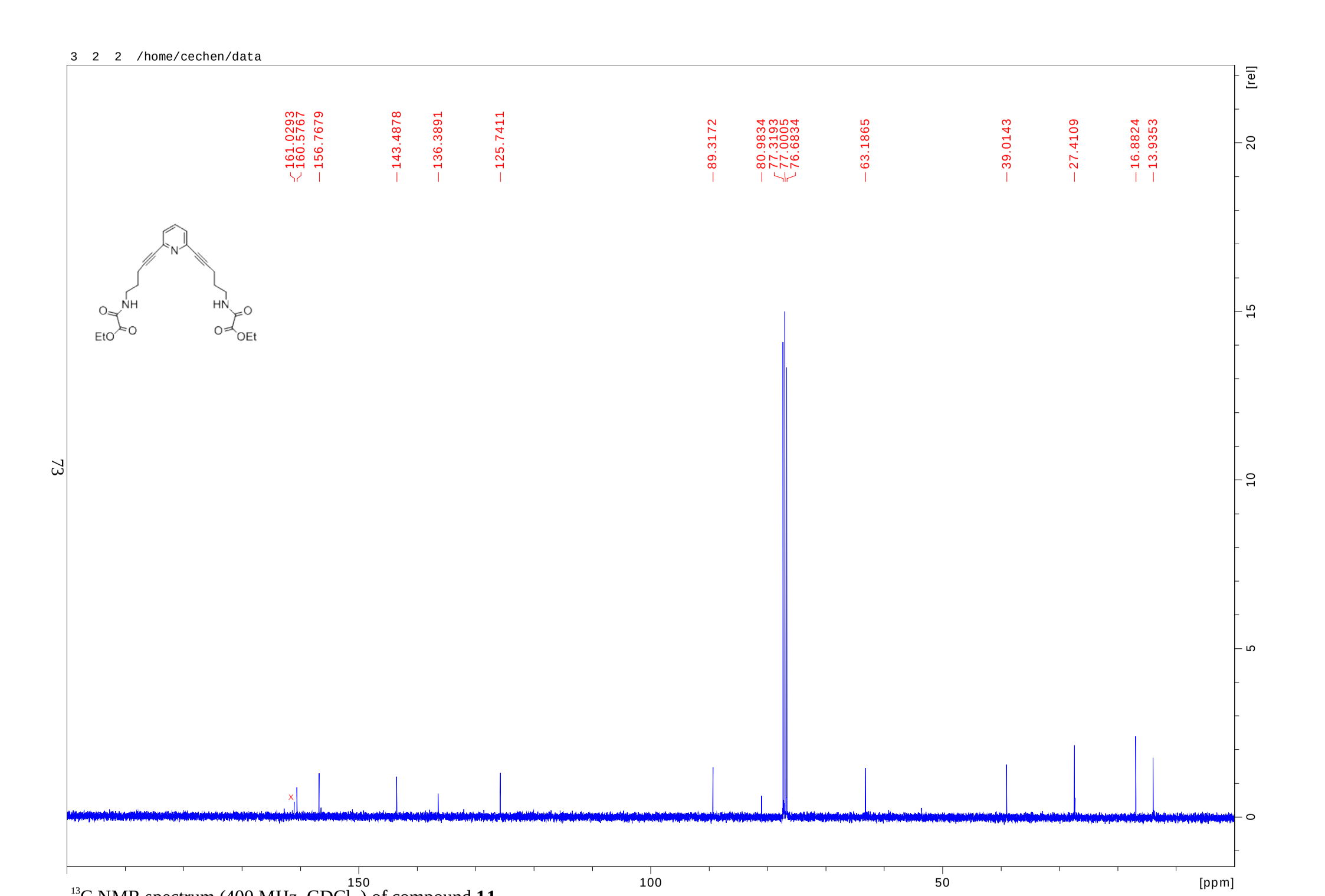
[1]H NMR spectrum (300 MHz, CDCl3) of compound **25**.



^{13}C NMR spectrum (300 MHz, $CDCl_3$) of compound **25**.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **11**.



^{13}C NMR spectrum (400 MHz, $CDCl_3$) of compound **11**.