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Development of Synthetic Pathways for Carbon Nanohoops

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Development of Synthetic Pathways for Carbon Nano hoops

Yiwei Huang

**Thesis submitted to the
Eberly College of Arts and Sciences
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Master of Science
in
Chemistry**

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Morgantown, West Virginia
2013**

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ABSTRACT

Development of Synthetic Pathways for Carbon Nanohoops

Yiwei Huang

A synthetic pathway was developed for the preparation of a precursor of a [6]cycloparaphenylene derivative, which represents the shortest repeating carbon nanohoop segment of an armchair (6,6) carbon nanotube. As a key intermediate of the synthetic sequence, *trans,trans*-1,4-di(4-bromophenyl)-1,3-butadiene was synthesized by using the Horner–Wadsworth–Emmons reaction between 4-bromocinnamaldehyde and diethyl 4-bromobenzylphosphonate reported in the literature. The use of $\text{BF}_3 \cdot \text{OEt}_2$ as a Lewis acid for the Lewis acid-catalyzed Diels–Alder reaction between *trans,trans*-1,4-di(4-bromophenyl)-1,3-butadiene and 1,4-benzoquinone was successful in producing *cis*-5,8-di(4-bromophenyl)-5,8-dihydro-1,4-naphthalenediol. The Diels–Alder reaction ensures that the two 4-bromophenyl substituents are *cis* to each other in the six-membered ring, which is of critical importance for the subsequent dimerization reaction. Methylation with dimethyl sulfate in the presence of potassium carbonate afforded the corresponding methylated hydroquinone. The nickel(0)-catalyzed homocoupling reactions produced the corresponding dimers as a mixture of diastereomers with the two 1,4-dimethoxyphenyl groups pointing either in the same direction or in the opposite directions. It is envisioned that aromatization of the dimers could then lead to the [6]cycloparaphenylene derivative.

*Dedicated to
my parents*

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TABLE OF CONTENTS

Title Page.....	i
Abstract.....	ii
Dedication.....	iii
Acknowledgement.....	iv
Table of Contents.....	v
List of Figures.....	vi
List of Schemes.....	vii
List of ^1H and ^{13}C NMR Spectra.....	viii

Part I

Development of Synthetic Pathways for Carbon Nanohoops

1. Introduction.....	1
2. Research Plan.....	7
3. Results and Discussion.....	8
4. Conclusion.....	22

Part II

Experimental Section

Instrumentation, Materials and Manipulation.....	23
References.....	29
Appendix.....	32

LIST OF FIGURES

Figure 1. Structures of single-walled armchair (6,6)-CNT, armchair (8,8)-CNT, zigzag (9,0)-CNT, and zigzag (12,0)-CNT.....	1
Figure 2. Structures of [6]cycloparaphenylene and [12]cyclacene.....	2
Figure 3. MM2-optimized structures of dibromides 18a and 18b	9
Figure 4. (Left) Perspective view of the molecular structure of $C_{22}H_{14}Br_2O_2$ (40) with the atom labeling scheme provided for the non-hydrogen atoms. The thermal ellipsoids are scaled to enclosed 30% probability. (Right) Perspective view of the molecular structure of $C_{22}H_{16}Br_2O_2$ (41) with the atom labeling scheme provided for the non-hydrogen atoms. The thermal ellipsoids are scaled to enclosed 30% probability.....	18
Figure 5. (Left) Structure of a bis-Diels–Alder adduct 43 . (Right) Perspective view of the molecular structure of $C_{38}H_{24}Br_4O_2$ (43) with the atom labeling scheme provided for the non-hydrogen atoms. The thermal ellipsoids are scaled to enclosed 30% probability.....	19
Figure 6. Perspective view of the molecular structure of $C_{24}H_{20}Br_2O_2$ (18b) with the atom labeling scheme provided for the non-hydrogen atoms. The thermal ellipsoids are scaled to enclosed 30% probability.....	21

LIST OF SCHEMES

Scheme 1. Synthesis of [9]-, [12]-, and [18]cycloparaphenylenes.....	3
Scheme 2. Synthesis of [8]cycloparaphenylene.....	4
Scheme 3. Synthesis of [12]cycloparaphenylene.....	6
Scheme 4. A proposed synthetic route for the [6]cycloparaphenylene derivative 20	7
Scheme 5. A proposed synthetic route for dibromide 18	7
Scheme 6. Synthesis of <i>trans,trans</i> -1,4-di(4-bromophenyl)-1,3-butadiene (21).....	10
Scheme 7. Synthesis of diene 21 by ZnCl ₂ - or CuBrSMe ₂ -promoted reductive coupling reaction.....	11
Scheme 8. Synthesis of diene 21 by hydroboration and the Suzuki–Miyaura coupling reaction.....	13
Scheme 9. Formation of benzyne for the Diels–Alder reactions with diene 21	16
Scheme 10. BF ₃ ·OEt ₂ catalyzed Diels–Alder reaction.....	17
Scheme 11. Synthesis of dibromide 18b and the [6]CPP derivative precursor 19b from hydroquinone 42	20

LIST OF ^1H AND ^{13}C NMR SPECTRA

^1H and ^{13}C NMR spectra of compound 23	33–34
^1H and ^{13}C NMR spectra of compound 24	35–36
^1H and ^{13}C NMR spectra of compound 25	37–38
^1H and ^{13}C NMR spectra of compound 27	39–40
^1H and ^{13}C NMR spectra of compound 21	41–42
^1H and ^{13}C NMR spectra of compound 18a	43–44
^1H and ^{13}C NMR spectra of compound 43	45–46
^1H and ^{13}C NMR spectra of compound 40	47–48
^1H and ^{13}C NMR spectra of compound 41	49–50
^1H and ^{13}C NMR spectra of compound 42	51–52
^1H and ^{13}C NMR spectra of compound 18b	53–54
^1H and ^{13}C NMR spectra of compound 19b	55–56

Part I

Development of Synthetic Pathways for Carbon Nanostructures

1. Introduction

Carbon nanotubes (CNTs) are cylindrical nanostructures comprised of carbon atoms. They are allotropes of carbon. Carbon nanotubes were first discovered in 1952 by L. V. Radushkevich and V. M. Lukyanovich.¹ Since the discovery, several methods for the synthesis of carbon nanotubes have been developed, including arc discharge, laser ablation, chemical vapor deposition, flame pyrolysis, and bottom-up organic synthesis approach.²

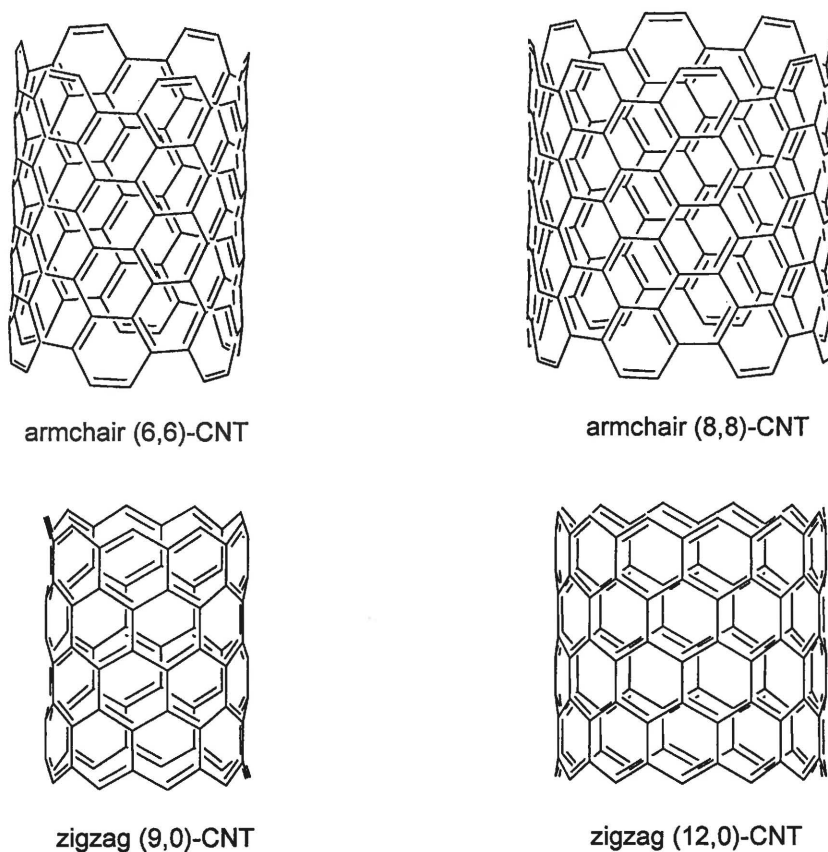


Figure 1. Structures of single-walled armchair (6,6)-CNT, armchair (8,8)-CNT, zigzag (9,0)-CNT, and zigzag (12,0)-CNT.

There are three general types of single-walled carbon nanotubes: armchair, zigzag, and chiral. Typical examples of armchair and zigzag single-walled carbon nanotubes are given in Figure 1.

For armchair carbon nanotubes, [n]cycloparaphenylenes represent the shortest segments of the repeating units. In the cases of zigzag carbon nanotubes, [n]cyclacenes are the shortest repeating units. The structures of [6]cycloparaphenylene and [12]cyclacene, representing the shortest segment of armchair (6,6)-CNT and zigzag (12,0)-CNT, respectively, are depicted in Figure 2. The structure of [6]cycloparaphenylene is constructed by *para* connections of six benzene rings whereas the structure of [12]cyclacene is formed by side-by-side fusing of 12 benzene rings. Several representative [n]cycloparaphenylenes have been synthesized. However, because of the reactive nature of the extended acene derivatives, [n]cyclacenes have not yet been synthesized.

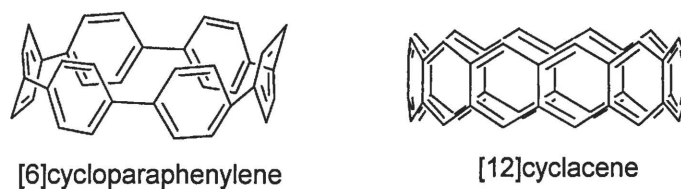
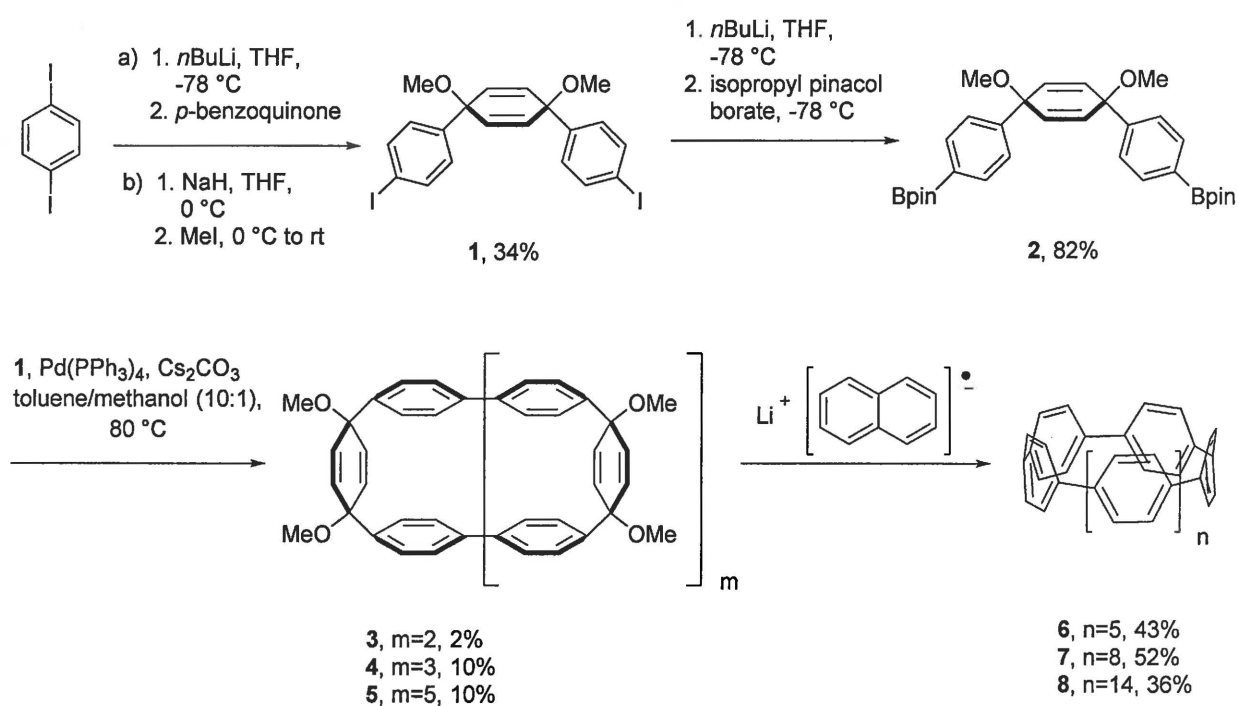


Figure 2. Structures of [6]cycloparaphenylene and [12]cyclacene.

The first synthesis of cycloparaphenylenes was reported by Bertozzi, Jasti and co-workers in 2008 (Scheme 1).³ The first step of the synthetic sequence was monolithiation of 1,4-diiodobenzene with *n*-BuLi at -78 °C, followed by addition of *p*-benzoquinone to generate a *syn*-diol. The diol was alkylated using methyl iodide to form diiodide 1.

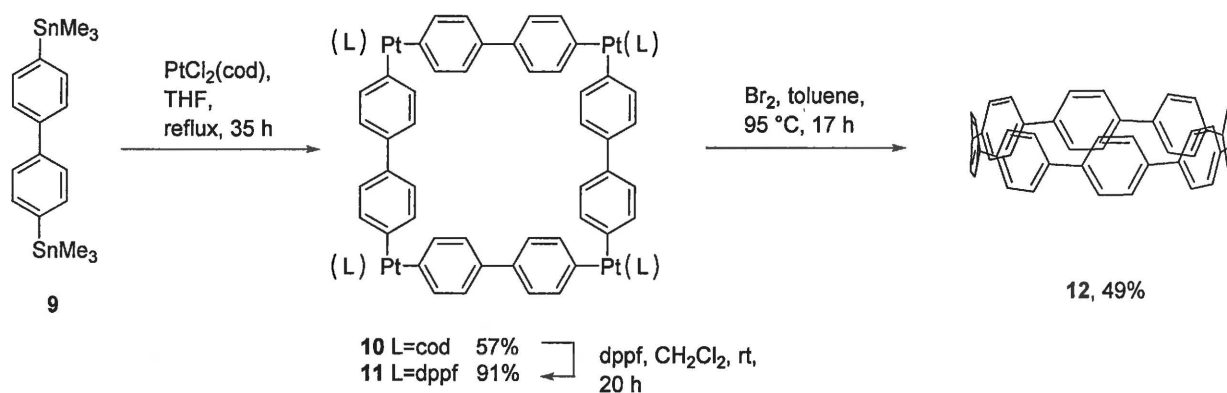
Transformation of diiodide **1** to diboronate **2** followed by the Suzuki–Miyaura coupling reaction with diiodide **1** produced a mixture of macrocycles **3**, **4** and **5**. Each macrocycle was then treated with lithium naphthalenide, leading to the corresponding [9]cycloparaphenylene **6**, [12]cycloparaphenylene **7**, and [18]cycloparaphenylene **8**, respectively. Recently, this general synthetic strategy was extended to the synthesis of [6]cycloparaphenylene.



Scheme 1. Synthesis of [9]-, [12]-, and [18]cycloparaphenylenes.

Yamago and co-workers reported a synthesis of [8]cycloparaphenylene from a square-shaped tetranuclear platinum complex in 2010 (Scheme 2).⁴ 4,4'-Bis(trimethylstannyl)biphenyl (**9**) was used as the starting material in this case. It was treated with one equivalent of PtCl₂(COD) in THF under reflux for 35 hours, affording

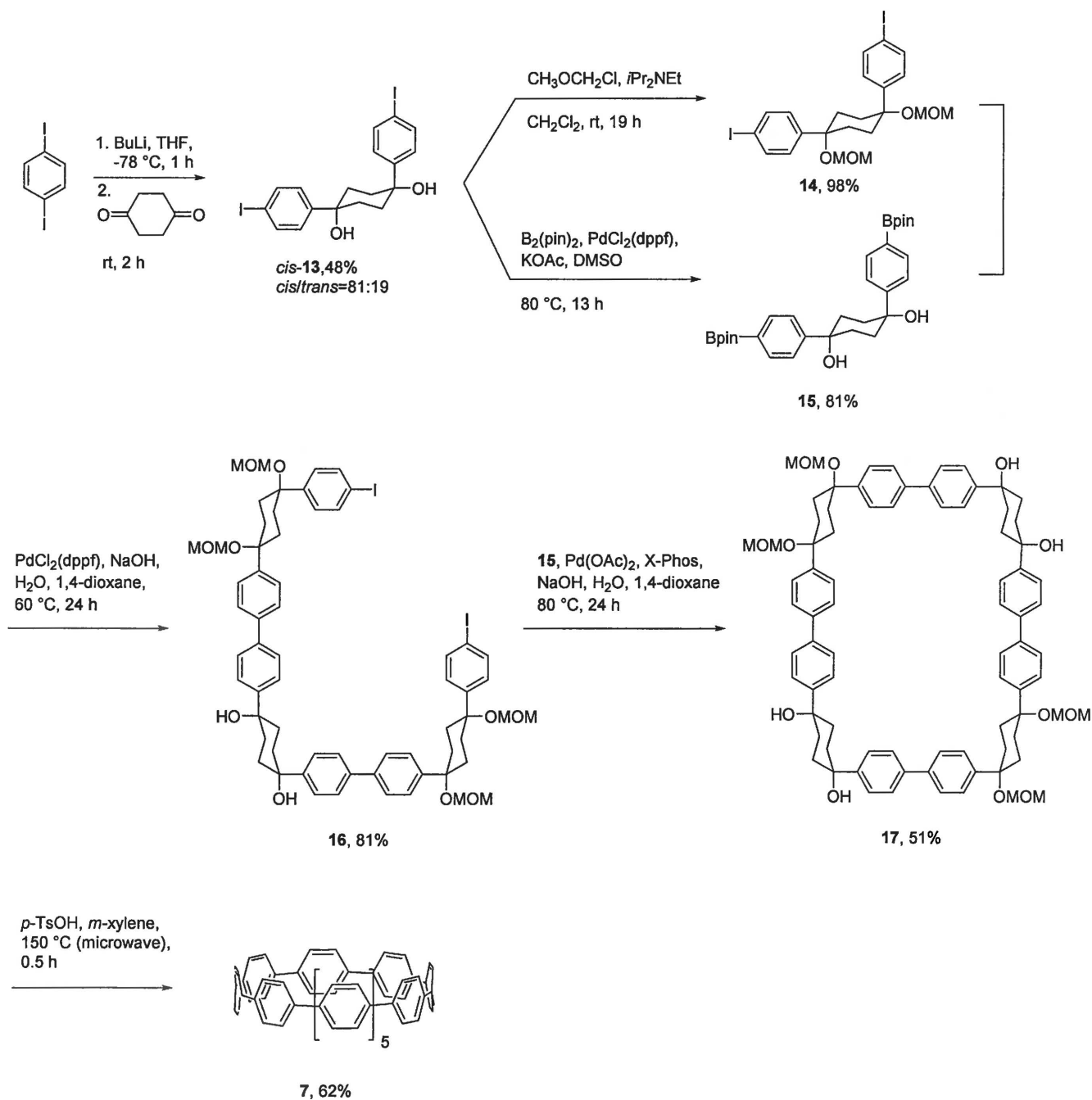
the square-shaped platinum complex **10** in 57% yield. This platinum complex **10** was then treated with four equivalents of 1,1'-bis(diphenylphosphino)ferrocene in dichloromethane at room temperature for 20 hours, producing the square-shaped platinum complex **11** in 91% yield. Reductive elimination reaction was then carried out by treating platinum complex **11** with seven equivalents of bromine in toluene at 95 °C for 17 hours, producing [8]cycloparaphenylene **12** in 49% yield. It was the smallest CPP at that time.



Scheme 2. Synthesis of [8]cycloparaphenylene.

Itami and co-workers reported a selective synthesis of [12]cycloparaphenylene in 2009 (Scheme 3).⁵ In this synthesis route, 1,4-diiodobenzene was first treated with *n*-BuLi at $-78 \text{ }^\circ\text{C}$ for monolithiation to form 4-iodophenyllithium, followed by the addition of 1,4-cyclohexanedione. The *cis*-isomer **13** was produced as the major product (*cis:trans* = 81:19) in 48% yield. The *cis*-diol **13** has an L-shaped structure. The *cis*-diol **13** was

then converted to the methoxymethyl (MOM)-protected diiodide **14** in 98% yield and diboronate **15** in 81% yield. Suzuki–Miyaura coupling between diiodide **14** and diboronate **15** afforded the trimer **16** in 81% yield. Trimer diiodide **16** was then coupled with diboronate **15** again to form the cyclic tetramer **17**. Microwave assisted aromatization reaction occurred when tetramer **17** was treated with *p*-toluenesulfonic acid in *m*-xylene at 150 °C for 30 minutes, producing [12]cycloparaphenylene **7** in 62% yield. Several other cycloparaphenylenes were likewise synthesized.

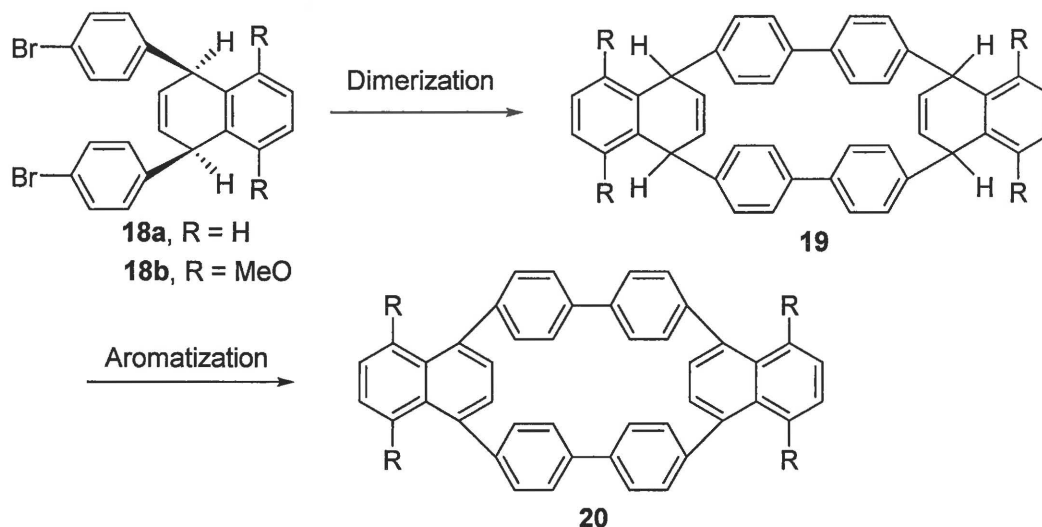


Scheme 3. Synthesis of [12]cycloparaphenylene.

So far, synthesis of [6]-, [7]-, [8]-, [9]-, [10]-, [11]-, [12]-, [13]-, [14]-, [15]-, [16]-, and [18]cycloparaphenylene have been reported.^{3–13} Also, some cycloparaphenylene derivatives have been successfully synthesized.^{14–18}

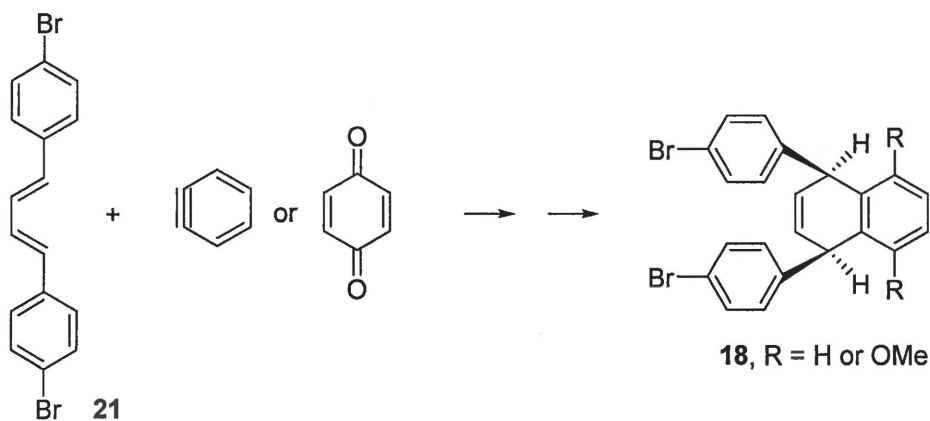
2. Research Plan

Our research goal is to develop a new synthetic pathway to the [6]cycloparaphenylene ([6]CPP) derivative **20**. To achieve this goal, we plan to use the synthetic sequence outlined in Scheme 4 for its preparation.



Scheme 4. A proposed synthetic route for the [6]cycloparaphenylene derivative **20**.

The precursor **18** is to be prepared by the Diels–Alder reaction between *trans*, *trans*-1,4-di(4-bromophenyl)-1,3-butadiene (**21**) and a suitable dienophile, such as benzyne or *p*-benzoquinone (Scheme 5).



Scheme 5. A proposed synthetic route for dibromide **18**.

3. Results and Discussion

Compound **18** is a key intermediate in the design for the synthesis of the [6]cycloparaphenylene derivative **20**. In the structure of dibromide **18**, the two hydrogen atoms on the six-membered ring are *cis* to each other. As a result, the two bromo-substituted phenyl rings are *cis* to each other as well. In addition, the two R groups on the benzene ring could also play a very significant role. With the presence of 1,3-allylic strains, the two bromo-substituted phenyl rings would be close to being parallel to each other, which would be very helpful in directing the following coupling reactions toward the formation of a dimer because of the reduced ring strain in the [6]cycloparaphenylene precursor **19**.

The MM2-optimized structure of **18a** (R = H) depicted in Figure 3 indicates that the two 4-bromophenyl substituents are oriented not parallel to each other. On the other hand, the MM2-optimized structure of **18b** (R = MeO) showed that the two 4-bromophenyl substituents are close to being parallel to each other. The parallel orientation of the two 4-bromophenyl substituents in **18b** minimizes the 1,3-allylic strain arising from the steric interactions between the methoxy group and its neighboring 4-bromophenyl group.

In most of the reported cycloparaphenylene syntheses, the greatest challenge is to overcome the enormous strain energy in the bent aromatic systems, which leads to very low yields of cycloparaphenylenes of small ring sizes, formation of a variety of large size cycloparaphenylenes, and a combination of these two problems. The parallel orientations of the two 4-bromophenyl substituents in **18b** could greatly minimize the ring strains. As a result, the subsequent coupling reaction could favor the formation of the dimer **19**,

leading to the [6]cycloparaphenylene derivative **20** containing only six benzene units in the cyclic system.

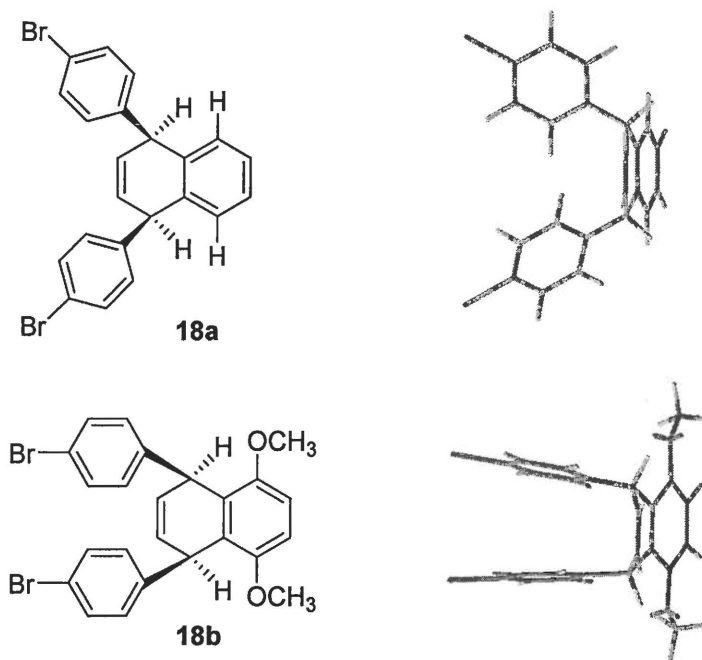
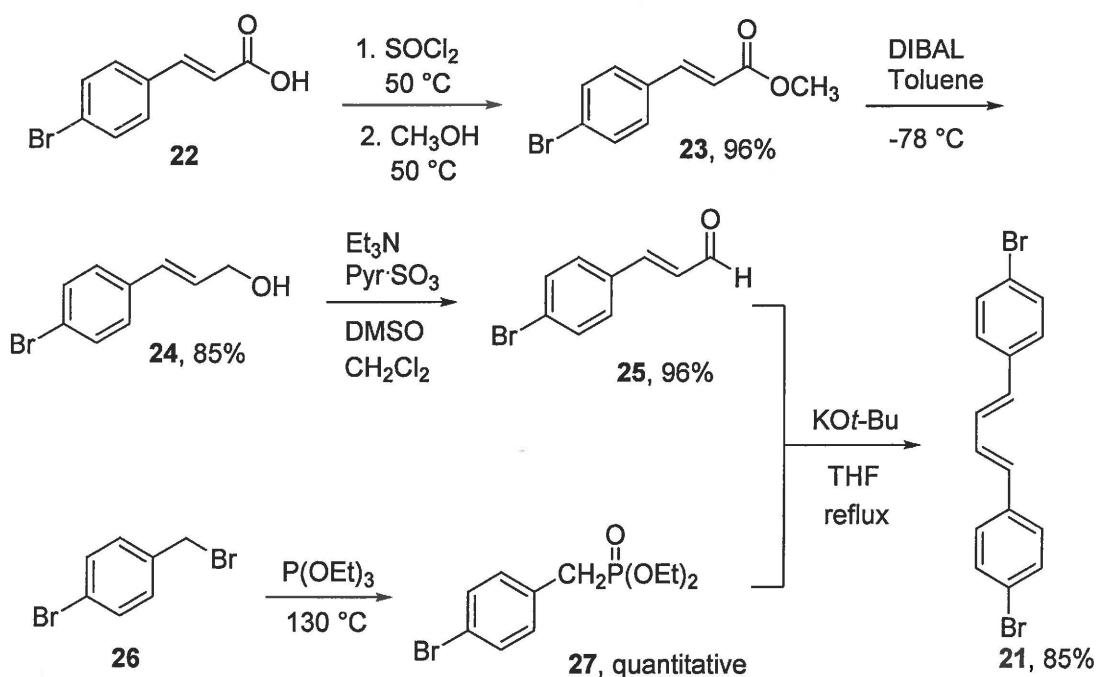


Figure 3. MM2-optimized structures of dibromides **18a** and **18b**.

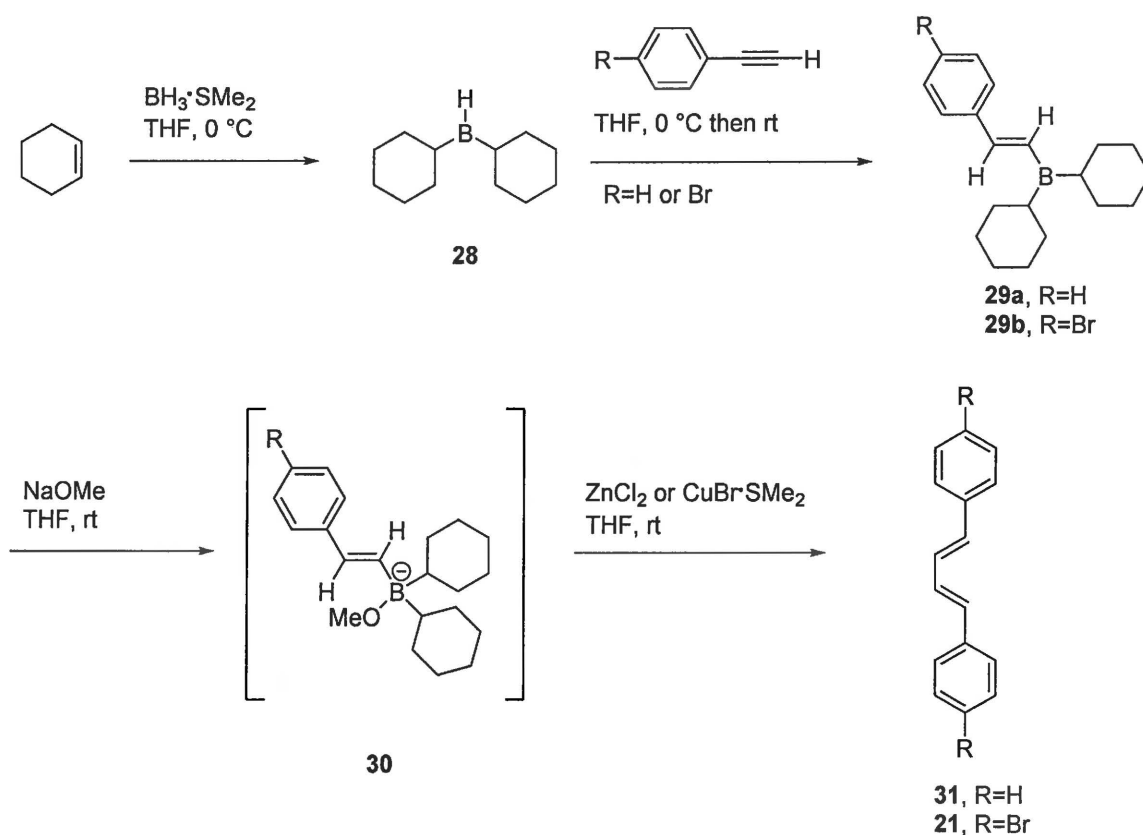
As it was mentioned early, the two 4-bromophenyl substituents in **18b** are *cis* to each other. This *cis* relationship could be achieved by the Diels–Alder reaction between dibromide **21** and *p*-benzoquinone as outlined in Scheme 5. Dibromide **21** was previously synthesized by the Horner–Wadsworth–Emmons reaction between **25** and **27** as outlined in Scheme 6.¹⁹ The synthetic sequence outlined in Scheme 6 was carried out, and several grams of *trans,trans*-1,4-di(4-bromophenyl)-1,3-butadiene(**21**) were obtained.



Scheme 6. Synthesis of *trans,trans*-1,4-di(4-bromophenyl)-1,3-butadiene (**21**).

In addition, two new synthetic methods for the preparation of dienes were explored in order to provide flexibility for introducing other functionalities on the diene. The first method was outlined in Scheme 7, and phenylacetylene was used in the model study. Dicyclohexylborane(**28**) was obtained from hydroboration of cyclohexene using one-half equivalent of borane-dimethyl sulfide complex,²⁰ which then served as a hydroborating reagent for the second hydroboration reaction with phenylacetylene to produce (*E*)-alkenyldicyclohexylborane **29a**.²¹ Borane **29a** was transferred into a suspension of NaOCH_3 in THF at room temperature to form the ate complex **30**, which was then transferred into one-half equivalent of zinc chloride solution in THF²² or a suspension of one equivalent of copper(I) bromide-dimethyl sulfide complex in THF²³, to form the *trans,trans*-1,4-diphenyl-1,3-butadiene **31**. However, the model study using

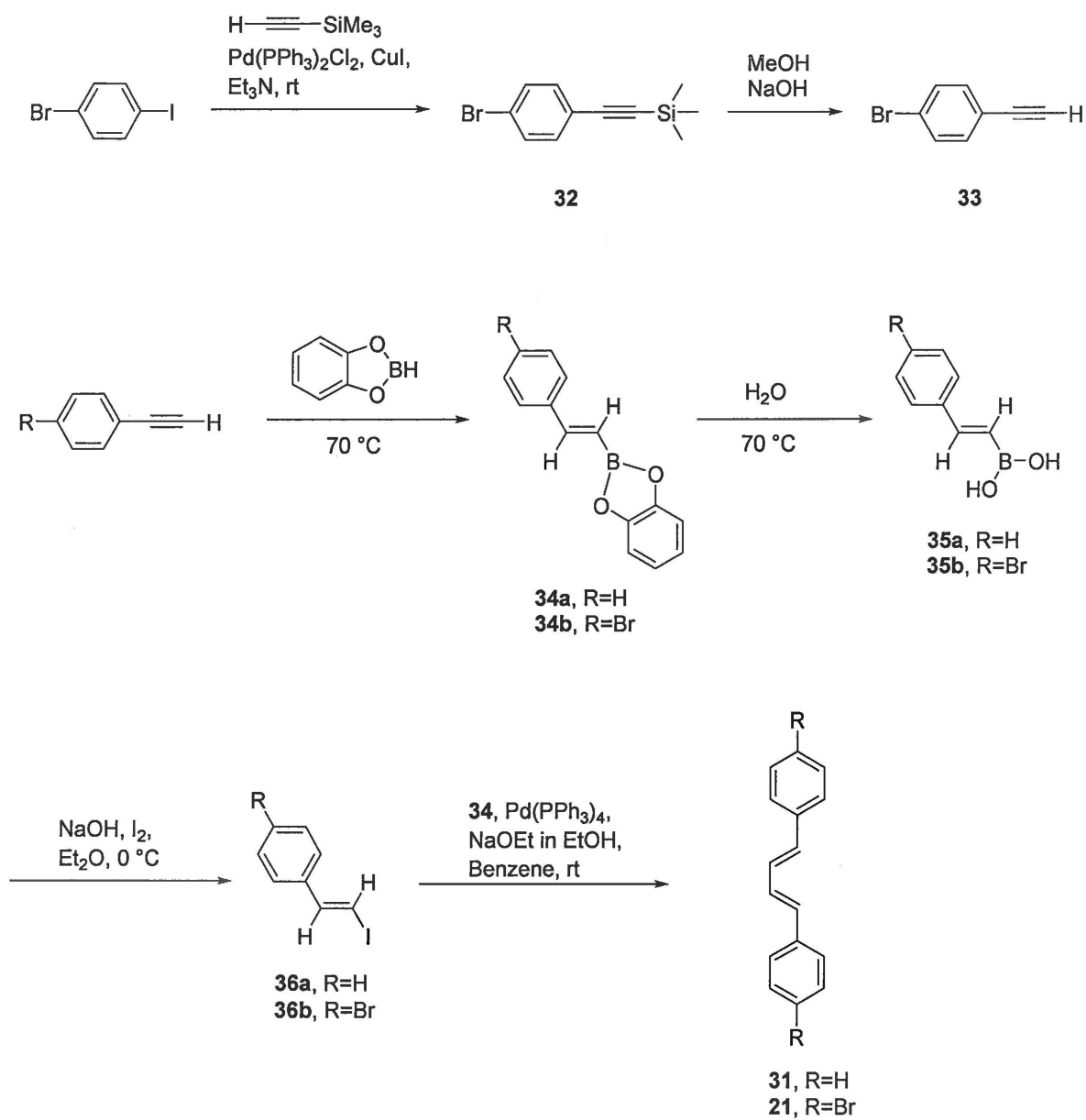
phenylacetylene as the starting material produced only low yields of diene **31** presumably because of small scales of the reaction.



Scheme 7. Synthesis of diene **21** by ZnCl_2 - or $\text{CuBr} \cdot \text{SMe}_2$ -promoted reductive coupling reaction.

The second method which combined the hydroboration reaction and the Suzuki–Miyaura coupling reaction was shown in Scheme 8. The starting material 4-bromophenylacetylene **33** was obtained through the Sonogashira coupling reaction between 1-bromo-4-iodobenzene and (trimethylsilyl)acetylene, which produced (4-bromophenyl)ethynyltrimethylsilane **32**, followed by desilylation with the treatment of aqueous sodium hydroxide solution in a mixture of diethyl ether and methanol. Hydroboration of phenylacetylene and 4-bromophenylacetylene **33** with catecholborane

at 70 °C produced the corresponding 2-(*E*-alkenyl)-1,3,2-benzodioxaboroles **34a** and **34b**, respectively. Hydrolysis of **34a** and **34b** at 70 °C afforded the corresponding alkenylboronic acids **35a** and **35b**, respectively. Treatment of boronic acids **35a** and **35b** with iodine in diethyl ether in the presence of sodium hydroxide afforded alkenyl iodides **36a** and **36b**, respectively.^{20,24} The following Suzuki–Miyaura coupling reaction between **36a** and **34a** produced diene **31**. Similarly, diene **21** could be produced from coupling between **34b** and **36b**.²⁵ However, in the case of 4-bromophenylacetylene **33**, the overall yield of corresponding alkenyl iodide **36b** was very low, so this method was not further used to synthesize diene **21** in this research project. Nevertheless a success of this method could be very useful for the synthesis of other dienes to further enhance the versatility of this research project in the future.



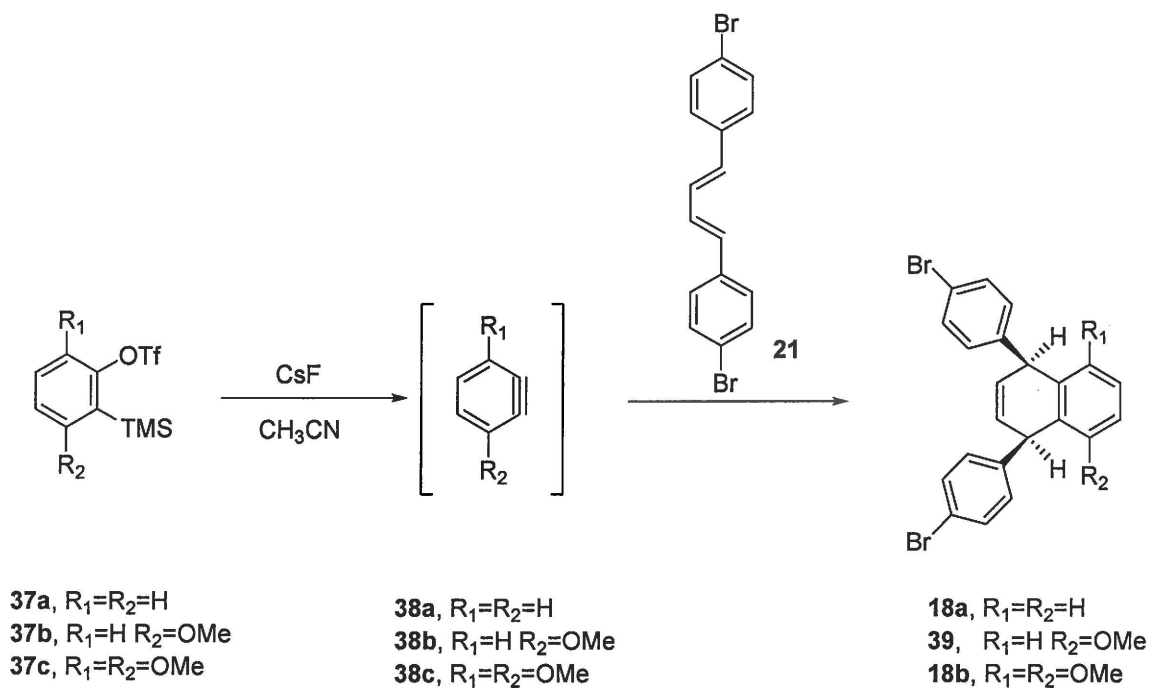
Scheme 8. Synthesis of diene **21** by hydroboration and the Suzuki–Miyaura coupling reaction.

With **21** in hand, the Diels–Alder reaction between **21** and *p*-benzoquinone was investigated. Several conditions were used, including (a) heating at 75 °C in benzene, (b) heating at 95 °C in benzene, (c) heating at 138 °C in *p*-xylene, (d) heating at 55 °C in

glacial acetic acid, (e) room temperature in glacial acetic acid, (f) room temperature in a mixture of solvent of glacial acetic acid and ethanol in the presence of hydroquinone, and (g) heating at 65 °C in a mixture of solvent of glacial acetic acid and ethanol in the presence of hydroquinone.²⁶⁻³⁰ However, none of these conditions worked.

So we decided to investigate the Diels–Alder reaction of diene **21** with a more reactive dienophile, benzyne. The method of using a fluoride to induce the 1,2-elimination of TMS and OTf groups to generate benzyne for the Diels–Alder reaction with diene **21** was investigated, as shown in Scheme 9. Three triflates, 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**37a**), 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**37b**) and 3,6-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**37c**) were used. The Diels–Alder reaction between diene **21** and triflate **37a** was carried out first. In the initial experiment, 3 equivalents of triflate **37a** was added in one portion to a mixture of diene **21** and cesium fluoride (6 equiv) in acetonitrile, and the reaction mixture was stirred under a nitrogen atmosphere at room temperature for 18 hours. After 18 hours, all of the diene were consumed, and the desired DA adduct **18a** was formed. The structure of **18a** was elucidated by ¹H NMR with the appearance of two distinct peaks from the benzylic protons at δ 4.69 and the alkenyl protons at δ 5.91. However, in addition to the desired DA adduct **18a**, a substantial amount of byproducts was formed. In order to avoid the formation of byproducts, the amount of triflate **37a** was decreased to 1.5 equivalents and 3 equivalents of cesium fluoride were used, with all the other conditions remained the same. However, this time a lot of diene **21** remained unreacted after 18 hours. After careful consideration of the potential source of the problem, we thought that this problem

could come from the low solubility of diene **21**. Since **21** was not very soluble, once the very reactive benzyne **38a** was generated *in situ*, there would not have enough diene **21** to react with it, and the highly reactive benzyne **38a** could then lead to some other reactions such as polymerization, which led to a lot of byproducts. In order to solve this problem, two modifications were made. The first one was using a mixed solvent of dichloromethane and acetonitrile to increase the solubility of diene, and the second one was adding the triflate dropwise over a period of 12 hours, which was achieved by utilizing a pressure equalizing funnel. In this way, the small amount of triflate which was dripped into the reaction mixture would react with the small amount of cesium fluoride that dissolved in acetonitrile to generate a small amount of benzyne, which would then immediately react with the diene that dissolved in the mixed solvent to form the desired DA adduct. And the experiment result proved that our hypothesis was correct, with much less byproducts formed. Also, by monitoring the reaction, it was found that all the diene was consumed after the addition of 2 equivalents of triflate. Unfortunately, when the same method was applied to 3-methoxybenzyne **38b** and 3,6-dimethoxybenzyne **38c**, which were generated from 3-methoxy-2-(trimethylsilyl)phenyl triflate (**37b**) and 3,6-dimethoxy-2-(trimethylsilyl)phenyl triflate (**37c**), respectively, the yields were extremely low with most of the diene remained unreacted. Even by increasing the amount of triflates **38b** and **38c**, the yields did not improve too much.



Scheme 9. Formation of benzyne for the Diels–Alder reactions with diene **21**

Then the Diels–Alder reaction between diene **21** and *p*-benzoquinone was re-investigated in the presence of a Lewis acid. Boron trifluoride-diethyl etherate, aluminum chloride and titanium tetrachloride were used to investigate the Lewis-acid catalyzed Diels–Alder reaction.^{31, 32} The experiment was not successful in the case of $TiCl_4$ -catalyzed DA reaction, but the $BF_3 \cdot OEt_2$ -catalyzed DA reaction was very successful, and three products **40**, **41** and **42** were obtained after purification by flash column chromatography (Scheme 10). The X-ray crystal structures of **40** and **41** are shown in Figure 4. In a 1-g-scale diene Diels–Alder reaction that was catalyzed by $BF_3 \cdot OEt_2$, 110 mg of the benzoquinone adduct **40** (9% yield), 62 mg of the desired DA adduct **41** (5% yield) and 940 mg of a mixture of **41** and the hydroquinone adduct **42** were isolated (73% yield total). The combined yield of **41** and **42** was 78%. We expected adduct **41** could be converted to **42** upon purification by silica gel column chromatography. However since it

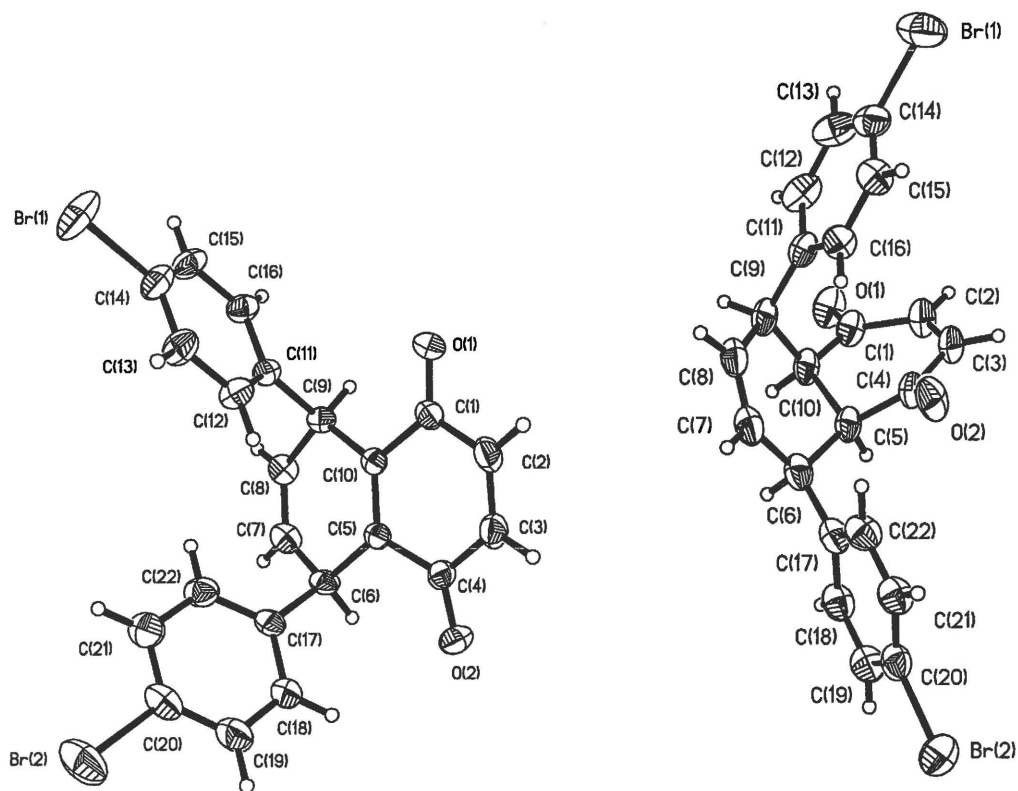


Figure 4. (Left) Perspective view of the molecular structure of $C_{22}H_{14}Br_2O_2$ (**40**) with the atom labeling scheme provided for the non-hydrogen atoms. The thermal ellipsoids are scaled to enclosed 30% probability. (Right) Perspective view of the molecular structure of $C_{22}H_{16}Br_2O_2$ (**41**) with the atom labeling scheme provided for the non-hydrogen atoms. The thermal ellipsoids are scaled to enclosed 30% probability.

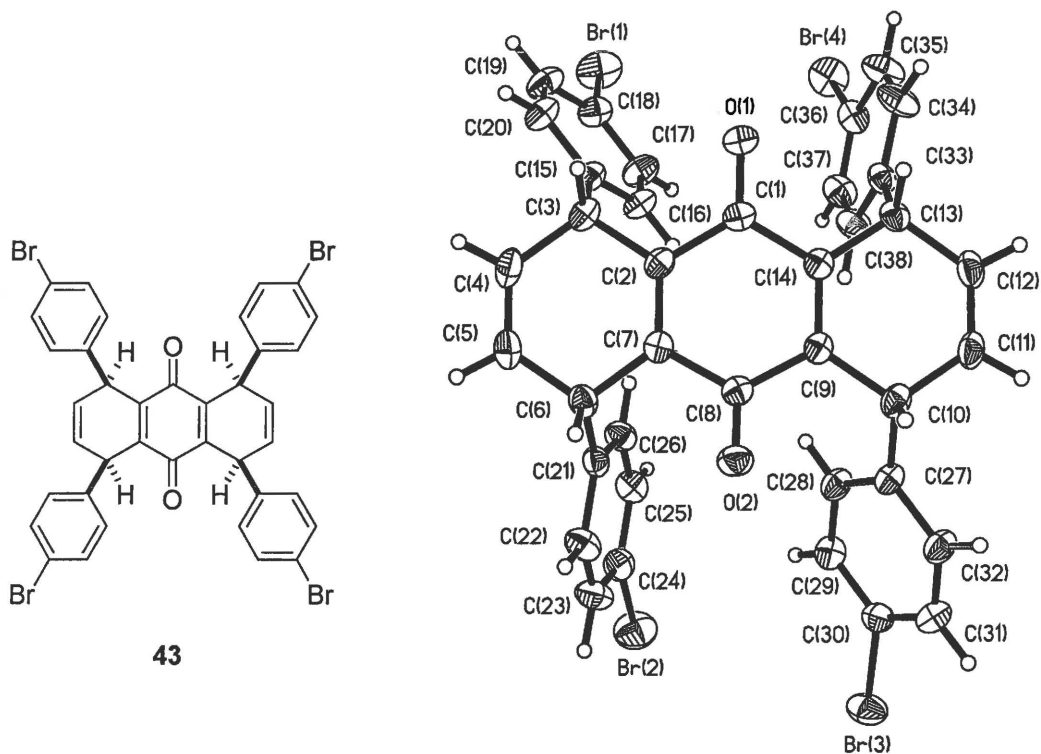
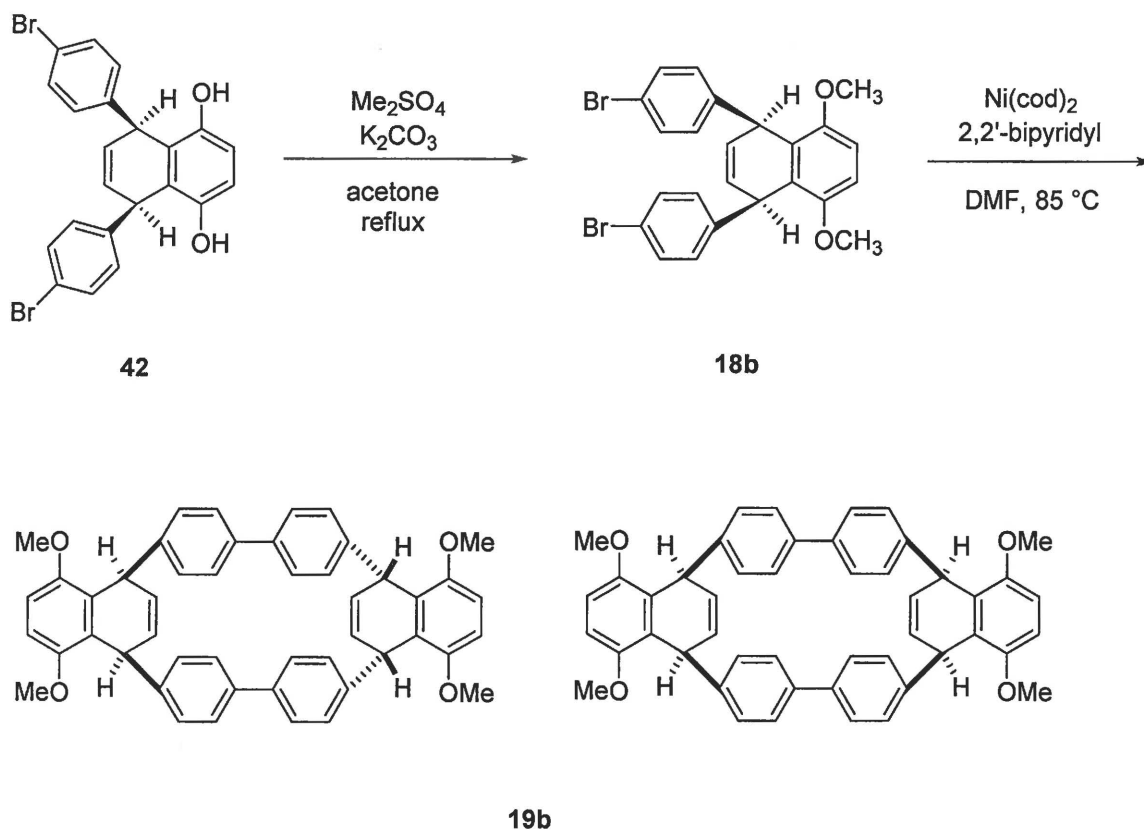


Figure 5. (Left) Structure of a bis-Diels–Alder adduct **43**. (Right) Perspective view of the molecular structure of $C_{38}H_{24}Br_4O_2$ (**43**) with the atom labeling scheme provided for the non-hydrogen atoms. The thermal ellipsoids are scaled to enclosed 30% probability.

The methylation reaction of hydroquinone **42** was then carried out by treating **42** with a strong methylating reagent, dimethyl sulfate, in the presence of potassium carbonate in anhydrous acetone under reflux for 18 hours to afford dibromide **18b** in 79% yield (Scheme 11).^{33, 34} After a literature review³³, it is apparent that instead of converting **41** to **42** first, compound **41** could be used directly to conduct the methylation reaction using the same condition, so the conversion from **41** to **42** which was mentioned early

was probably not necessary. It could save a step of the synthetic sequence with one less silica gel column chromatography, which could further improve the overall yield of the synthetic scheme. The structure of **18b** was established by X-ray structure analysis (Figure 6). In the crystal structure of dibromide **18b**, the two 4-bromophenyl groups are not parallel to each other, which is different from our previous MM2-optimized structures. It is possible that the preferred conformation of the dibromide **18b** in solution may be different from the one in crystal lattice.



Scheme 11. Synthesis of dibromide **18b** and the [6]CPP derivative precursor **19b** from hydroquinone **42**.

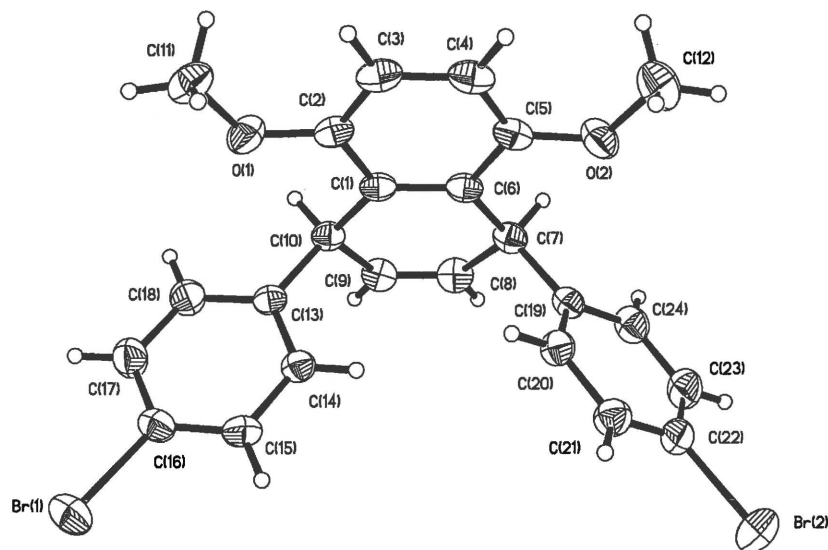


Figure 6. Perspective view of the molecular structure of $C_{24}H_{20}Br_2O_2$ (**18b**) with the atom labeling scheme provided for the non-hydrogen atoms. The thermal ellipsoids are scaled to enclosed 30% probability.

The [6]CPP derivative precursor **19b** was obtained by the nickel(0)-catalyzed homocoupling reaction (Scheme 11). Dibromide **18b**, 2.5 equivalents of bis(1,5-cyclooctadiene)nickel(0) and 2.5 equivalents of 2,2'-bipyridyl were loaded in a glove box. Since the second step of the coupling reactions to form the dimer was an intramolecular reaction, a low concentration of monomer would increase the yield for the dimer. DMF was added to make the concentration of dibromide **18b** at 5.56 mM. The crude 1H NMR spectrum indicated the existence of a ratio of 3:2 of the two diastereomers of the dimer **19b** (Scheme 11), one with the methoxy signal at 3.84 ppm (major), and the other at 3.86 ppm (minor). However, upon purification by flash column chromatography, only the

major diastereomer of the dimer was successfully isolated in 21% yield. The ^1H and ^{13}C NMR spectra are consistent with the structure of **19b**. It is interesting to note that the signals from the aromatic hydrogens of the two biphenyl groups are shifted upfield significantly to δ 6.67 (doublet) and δ 6.60 (doublet). The upfield shifts of those proton signals can be attributed to the close proximity of the two biphenyl units, placing their aromatic hydrogens in the shielding regions of the aromatic ring current. In addition, the HRMS data further confirmed the formation of the dimer **19b**. Furthermore, we believe that the more upfield methoxy signals (3.5–3.7 ppm) and more downfield aromatic proton signals (7.2–7.6 ppm) of the crude ^1H NMR spectrum were from trimers, tetramers, and perhaps cyclic products of larger ring sizes.

4. Conclusion

A synthetic pathway has been successfully developed for the concise synthesis of **19b**, which could serve as the precursor of the [6]cycloparaphenylene derivative **20b**. The Lewis acid-catalyzed Diels–Alder reaction and the Ni(0)-catalyzed homocoupling reaction are the two key steps of the synthetic sequence. It is envisioned that upon aromatization, compound **19b** could be converted to the [6]cycloparaphenylene derivative **20b** as a carbon nanohoop of an armchair (6,6) carbon nanotube.

Part II

Experimental Section

Glassware used for all reactions were dried in an oven (100 °C) for at least 12 hours. All reactions were conducted under a nitrogen atmosphere unless otherwise indicated. Tetrahydrofuran ($\geq 99.9\%$, anhydrous, inhibitor-free), borane dimethyl sulfide complex, zinc chloride solution (0.5 M in THF), copper(I) iodide (98%), catecholborane (98%), benzene (99.8%, anhydrous), thionyl chloride (99.5%, low iron), sulfur trioxide pyridine complex (98%), diethyl ether ($\geq 99.7\%$, anhydrous, contains 1 ppm BHT as inhibitor), boron trifluoride diethyl etherate, 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (97%) (**37a**), dimethyl sulfate ($\geq 99.8\%$), 2,2'-bipyridyl ($\geq 99\%$) were purchased from Aldrich. Cyclohexene (99%), phenylacetylene (98%), sodium methoxide (anhydrous powder), triethylamine (99.7%), iodine (99.5%, resublimed), sodium ethoxide (21% in ethanol), methanol (99.8%, extra dry), diisobutylaluminium hydride (1M solution in hexane), toluene (99.8%, extra dry), dichloromethane (99.9%, extra dry, stabilized), dimethyl sulfoxide (99.7%, extra dry, over molecular sieve), triethyl phosphite (98%), potassium *tert*-butoxide (98+%), *p*-benzoquinone (99%), *p*-xylene (99%), hydroquinone (99.5%), cesium fluoride (99%), acetonitrile (99.9%, extra dry), aluminium chloride (98.5%, anhydrous, powder), titanium(IV) chloride (1 M solution in dichloromethane), acetone (99.8%, extra dry), *N,N*-dimethylformamide (99.8%, extra dry) were purchased from Acros. Copper(I) bromide-dimethyl sulfide complex was purchased from Alfa Aesar. 1-bromo-4-iodobenzene (99%), (trimethylsilyl)acetylene (99%), 4-bromocinnamic acid (98%), 4-bromobenzyl bromide (99%) were purchased from Oakwood. Trans-

dichlorobis(triphenylphosphine)palladium(II) (99%), tetrakis(triphenylphosphine) palladium(0) (99%), bis(1,5-cyclooctadiene)nickel(0) (98+%) were purchased from Strem. 3-Methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (>95.0%) (**37b**) was purchased from TCI. Absolute ethanol was purchased from AAPER Alcohol and Chemical CO. Sodium hydroxide ($\geq 97.0\%$, pellets), potassium carbonate (anhydrous, $\geq 99.0\%$, granular powder), glacial acetic acid (≥ 99.7 w/w %) were purchased from Fisher Chemical. All chemicals were used as received. Silica gel for flash column chromatography was purchased from Dynamic Adsorbents Inc. ^1H NMR (600 MHz), ^{13}C NMR (150 MHz) and ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) spectra were recorded in CDCl_3 using CHCl_3 (^1H δ 7.26) and CDCl_3 (^{13}C δ 77.0) as internal standards.

Compounds **21**, **23**, **24**, **25**, and **27** were prepared according to the reported procedure.¹⁹ 3,6-Dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (**37c**) was prepared according to the reported procedure.^{35,36}

Compound 18a. To a mixture of 100 mg of diene **21** (0.275 mmol) and 125 mg of cesium fluoride (99%, 0.815 mmol) in 20 mL of anhydrous acetonitrile and 10 mL of anhydrous dichloromethane was added dropwise a solution of 2-(trimethylsilyl)phenyl triflate (97%, 0.553 mmol) in 25 mL of anhydrous acetonitrile from a pressure equalizing funnel under a nitrogen atmosphere. The addition was finished in 12 hours. After an additional 6 hours of stirring, distilled water was added and the reaction mixture was extracted with dichloromethane. The combined organic layers were dried over sodium sulfate and concentrated. The residue was purified by flash column chromatography

(silica gel, ethyl acetate:hexanes = 1:10) to produce 98 mg of **18a** (0.223 mmol, 81% yield) as a yellow solid (initially a viscous oil which under vacuum became a foam-like solid): ^1H NMR (CDCl_3 , 400 MHz) δ 7.45 (4 H, d, $J = 8.4$ Hz), 7.09–7.12 (6 H, m), 6.99–7.01 (2 H, m), 5.91 (2 H, d, $J = 1.6$ Hz), 4.69 (2 H, d, $J = 1.2$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 144.47, 136.06, 131.75, 130.38, 129.55, 127.86, 126.69, 120.42, 44.80. HRMS calcd for $\text{C}_{22}\text{H}_{16}\text{Br}_2\text{Na}$ (MNa^+) 462.9491, found 462.9485.

Compound 43. A mixture of 36 mg of 1,4-benzoquinone (0.330 mmol) and 66 mg of aluminium chloride (0.488 mmol) in 30 mL of anhydrous dichloromethane was stirred under a nitrogen atmosphere at room temperature for 5 minutes. Then a solution of 100 mg of diene **21** (0.275 mmol) in 40 mL of anhydrous dichloromethane was added via cannula. The reaction mixture was stirred at room temperature for 45 hours. Distilled water was slowly added, and the reaction mixture was extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate and concentrated. The residue was purified by flash column chromatography (silica gel, ethyl acetate:hexanes = 1:10 and then 1:5) to produce 18 mg of **43** (0.022 mmol, 16% yield) as a yellow solid: ^1H NMR (CDCl_3 , 400 MHz) δ 7.26 (8 H, d, $J = 8.8$ Hz), 6.80 (8 H, d, $J = 8.8$ Hz), 5.84 (4 H, d, $J = 2.8$ Hz), 4.67 (4 H, d, $J = 2.4$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 185.43, 141.31, 139.82, 131.77, 129.61, 126.28, 120.90, 39.29. Recrystallization of **43** from dichloromethane/hexanes produced a single crystal suitable for X-ray structure analysis.

Compounds 40, 41, and 42. To a mixture of 1.00 g of diene **21** (2.75 mmol) and 0.360 g of 1,4-benzoquinone (3.30 mmol) in 200 mL of anhydrous dichloromethane under a nitrogen atmosphere was added by using a syringe 0.61 mL of boron trifluoride-diethyl etherate (4.94 mmol). The reaction mixture was stirred at room temperature for 20 hours. Distilled water was slowly added and the reaction mixture was extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate and concentrated. The residue was purified by flash column chromatography (silica gel, ethyl acetate:hexanes = 1:10 and then 1:5) to produce 110 mg of **40** (0.234 mmol, 9% yield) as a yellow solid, 62 mg of **41** (0.131 mmol, 5% yield) as a yellow solid and 940 mg of a mixture of **41** and **42** as a yellow solid. To the 940 mg mixture of **41** and **42** in methanol was added a 2 M hydrochloric acid and the reaction mixture was heated at 60 °C for 1 hour under a nitrogen atmosphere. Water was added and the reaction mixture was extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate and concentrated. Purification by flash column chromatography (silica gel, ethyl acetate:hexanes = 1:5) produced 720 mg of **42** (1.52 mmol, 56% yield) as a white solid.

Compound **40**: $^1\text{H NMR}$ (CDCl_3 , 600 MHz) δ 7.43 (4 H, d, $J = 9.0$ Hz), 7.15 (4 H, d, $J = 7.8$ Hz), 6.69 (2 H, s), 5.91 (2 H, d, $J = 2.4$ Hz), 4.72 (2 H, d, $J = 3.0$ Hz); $^{13}\text{C NMR}$ (CDCl_3 , 150 MHz) δ 185.97, 141.55, 140.17, 136.41, 131.78, 130.14, 126.51, 120.96, 39.95. Compound **41**: $^1\text{H NMR}$ (CDCl_3 , 600 MHz) δ 7.39 (4 H, d, $J = 9.0$ Hz), 7.08 (4 H, d, $J = 8.4$ Hz), 6.20 (2 H, s), 5.99 (2 H, s), 3.84 (2 H, d, $J = 6.6$ Hz), 3.71 (2 H, d, $J = 6.6$ Hz); $^{13}\text{C NMR}$ (CDCl_3 , 150 MHz) δ 198.69, 139.98, 138.49, 131.18, 131.11, 128.63, 121.03, 51.49, 41.14. Compound **42**: $^1\text{H NMR}$ (CDCl_3 , 600 MHz) δ 7.42 (4 H, d, $J = 8.4$ Hz), 7.14 (4 H, d, $J = 9.0$ Hz), 6.63 (2 H, s), 5.90 (2 H, d, $J = 2.4$ Hz), 4.78 (2 H, d, $J =$

3.0 Hz), 4.29 (2 H, br); ^{13}C NMR (CDCl_3 , 150 MHz) δ 147.37, 142.35, 131.88, 129.72, 127.27, 124.78, 120.59, 115.07, 40.83. Recrystallization of **40** and **41** from dichloromethane/hexanes produced single crystals suitable for X-ray structure analyses.

Compound 18b. To a mixture of 0.693 g of **42** (1.48 mmol) and 2.840 g of potassium carbonate (20.5 mmol) in 100 mL of anhydrous acetone under a nitrogen atmosphere was added 1.4 mL of dimethyl sulfate (14.8 mmol) via a syringe, and the reaction mixture was then heated under reflux for 18 hours. Water was added and the reaction mixture was extracted with ethyl acetate and then dichloromethane. The combined organic layers were dried over sodium sulfate and concentrated. The crude solid residue was purified by flash column chromatography (silica gel, ethyl acetate:hexanes = 1:5) to produce 0.580 g of **18b** (1.16 mmol, 79% yield) as a white solid: ^1H NMR (CDCl_3 , 600 MHz) δ 7.33 (4 H, d, $J = 8.4$ Hz), 7.05 (4 H, d, $J = 9.0$ Hz), 6.73 (2 H, s), 5.95 (2 H, d, $J = 3.0$ Hz), 4.83 (2 H, d, $J = 3.0$ Hz), 3.61 (6 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 151.23, 143.67, 131.04, 129.85, 127.74, 127.01, 119.52, 109.21, 55.64, 40.57. HRMS calcd for $\text{C}_{24}\text{H}_{21}\text{Br}_2\text{O}_2$ (MH^+) 498.9903, found 498.9910; calcd for $\text{C}_{24}\text{H}_{20}\text{Br}_2\text{O}_2\text{Na}$ (MNa^+) 520.9722, 522.9702, 524.9681, found 520.9736, 522.9708, 524.9689, respectively. Recrystallization of **18b** from chloroform/hexanes produced a single crystal suitable for X-ray structure analysis.

Compound 19b. In a glove box, a 250-mL flask was charged with 0.500 g of **18b** (1.00 mmol), 0.702 g of bis(cyclooctadiene)nickel(0) (2.50 mmol) and 0.394 g of 2,2'-bipyridyl (2.50 mmol) and then fitted with a water condenser followed by the addition of

180 mL of *N,N*-dimethylformamide. The reaction mixture was heated at 85 °C for 44 hours under a nitrogen atmosphere. After the mixture was allowed to cool to room temperature, brine was added, and the reaction mixture was extracted with ethyl acetate and dichloromethane. The combined organic layers were dried over sodium sulfate and concentrated. The residue was purified by flash column chromatography (silica gel, ethyl acetate:hexanes = 1:20 then 1:10) to produce 72 mg of **19b** (0.106 mmol, 21% yield) as a white solid: ¹H NMR (CDCl₃, 400 MHz) δ 6.90 (4 H, s), 6.78–6.79 (4 H, m), 6.67 (8 H, d, *J* = 8.4 Hz), 6.60 (8 H, d, *J* = 8.0 Hz), 5.17–5.18 (4 H, m), 3.84 (12 H, s); ¹³C NMR (CDCl₃, 100 MHz) δ 150.93, 140.24, 138.35, 133.24, 131.41, 127.35, 125.90, 108.51, 55.91, 37.33. HRMS calcd for C₄₈H₄₀O₄ (M⁺) 680.2921, found 680.2923; calcd for C₄₈H₄₁O₄ (MH⁺) 681.2999, found 681.3009.

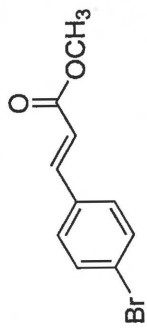
REFERENCES

- [1] Radushkevich, L. V.; Lukyanovich, V. M. *Zh. Fiz. Khim.* **1952**, *26*, 88–95.
- [2] Prasek, J.; Drbohlavova, J.; Chomoucka, J.; Hubalek, J.; Jasek, O.; Adam, V.; Kizek, R. *J. Mater. Chem.* **2011**, *21*, 15872–15884.
- [3] Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 17646–17647.
- [4] Yamago, S.; Watanabe, Y.; Iwamoto, T. *Angew. Chem. Int. Ed.* **2010**, *49*, 757–759.
- [5] Takaba, H.; Omachi, H.; Yamamoto, Y.; Bouffard, J.; Itami, K. *Angew. Chem. Int. Ed.* **2009**, *48*, 6112–6116.
- [6] Xia, J.; Jasti, R. *Angew. Chem. Int. Ed.* **2012**, *51*, 2474–2476.
- [7] Sisto, T. J.; Golder, M. R.; Hirst, E. S.; Jasti, R. *J. Am. Chem. Soc.* **2011**, *133*, 15800–15802.
- [8] Darzi, E. R.; Sisto, T. J.; Jasti, R. *J. Org. Chem.* **2012**, *77*, 6624–6628.
- [9] Iwamoto, T.; Watanabe, Y.; Sakamoto, Y.; Suzuki, T.; Yamago, S. *J. Am. Chem. Soc.* **2011**, *133*, 8354–8361.
- [10] Segawa, Y.; Šenel, P.; Matsuura, S.; Omachi, H.; Itami, K. *Chem. Lett.* **2011**, *40*, 423–425.
- [11] Kayahara, E.; Sakamoto, Y.; Suzuki, T.; Yamago, S. *Org. Lett.* **2012**, *14*, 3284–3287.

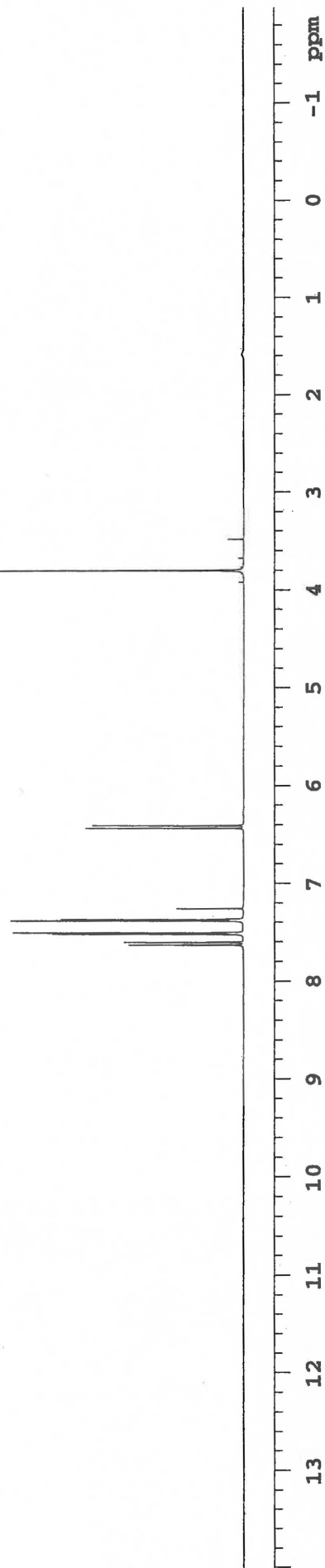
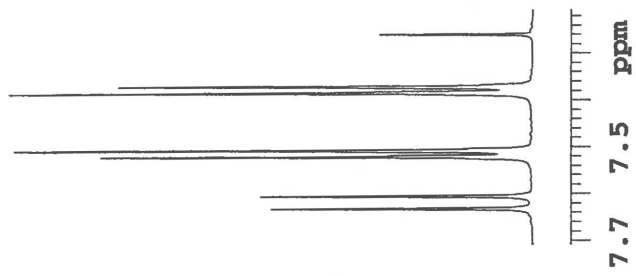
- [12] Segawa, Y.; Miyamoto, S.; Omachi, H.; Matsuura, S.; Šenel, P.; Sasamori, T.; Tokitoh, N.; Itami, K. *Angew. Chem. Int. Ed.* **2011**, *50*, 3244–3248.
- [13] Omachi, H.; Matsuura, S.; Segawa, Y.; Itami, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 10202–10205.
- [14] Omachi, Haruka.; Segawa, Y.; Itami, K. *Org. Lett.* **2011**, *13*, 2480–2483.
- [15] Yagi, A.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2012**, *134*, 2962–2965.
- [16] Xia, J.; Golder, M. R.; Foster, M. E.; Wong, B. M.; Jasti, R. *J. Am. Chem. Soc.* **2012**, *134*, 19709–19715.
- [17] Sisto, T. J.; Tian, X.; Jasti, R. *J. Org. Chem.* **2012**, *77*, 5857–5860.
- [18] Matsui, K.; Segawa, Y.; Itami, K. *Org. Lett.* **2012**, *14*, 1888–1891.
- [19] Davis, M. C.; Groshens, T. J. *Synth. Commun.* **2011**, *41*, 206–218.
- [20] Brown, H. C. *Organic Syntheses via Boranes*; Wiley-Interscience: New York, **1975**.
- [21] Zweifel, G.; Clark, G. M.; Polston, N. L. *J. Am. Chem. Soc.* **1971**, *93*, 3395–3399.
- [22] Molander, G. A.; Zinke, P. W. *Organometallics*, **1986**, *5*, 2161–2162.
- [23] Campbell, J. B.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 549–550.
- [24] Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 5786–5788.
- [25] Miyaura, N.; Yamada, K.; Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 972–980.

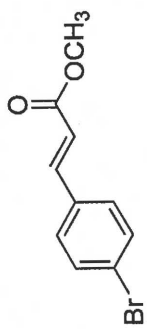
- [26] Braude, E. A.; Jones, E. R. H.; Stern, E. S. *J. Chem. Soc.* **1947**, 1087–1096.
- [27] Ballistreri, F. P.; Maccarone, E.; Perrini, G.; Tomaselli, G. A.; Torre, M. *J. Chem. Soc., Perkin Trans. 2* **1982**, 3, 273–277.
- [28] Frimer, A. A.; Gilinsky-Sharon, P.; Gottlieb, H. E.; Meador, M. A. B.; Johnston, J. C. *Macromolecules* **2005**, 38, 1504–1507.
- [29] Lepage, Y. *Bulletin de la Société Chimique de France* **1963**, 10, 2019–2022.
- [30] Braude, E. A.; Fawcett, J. S.; Webb, A. A. *J. Chem. Soc.* **1954**, 1049–1059.
- [31] Bhargava, G.; Mahajan, M. P.; Saito, T.; Otani, T.; Kurashima, M.; Sakai, K. *Eur. J. Org. Chem.* **2005**, 2005, 2397–2405.
- [32] Castro, M. A.; Miguel del Corral, J. M.; Gordaliza, M.; García, P. A.; Gamito, A. M.; Gualberto, S. A.; Batista, R.; San Feliciano, A. *Synthesis* **2005**, 19, 3202–3208.
- [33] Carreño, M. C.; García-Cerrada, S.; Urbano, A. *Chem. Eur. J.* **2003**, 9, 4118–4131.
- [34] Lou, K.; Prior, A. M.; Wiredu, B.; Desper, J.; Hua, D. H. *J. Am. Chem. Soc.* **2010**, 132, 17635–17641.
- [35] Yoshida, H.; Sugiura, S.; Kunai, A. *Org. Lett.* **2002**, 4, 2767–2769.
- [36] Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, 121, 5827–5828.

APPENDIX

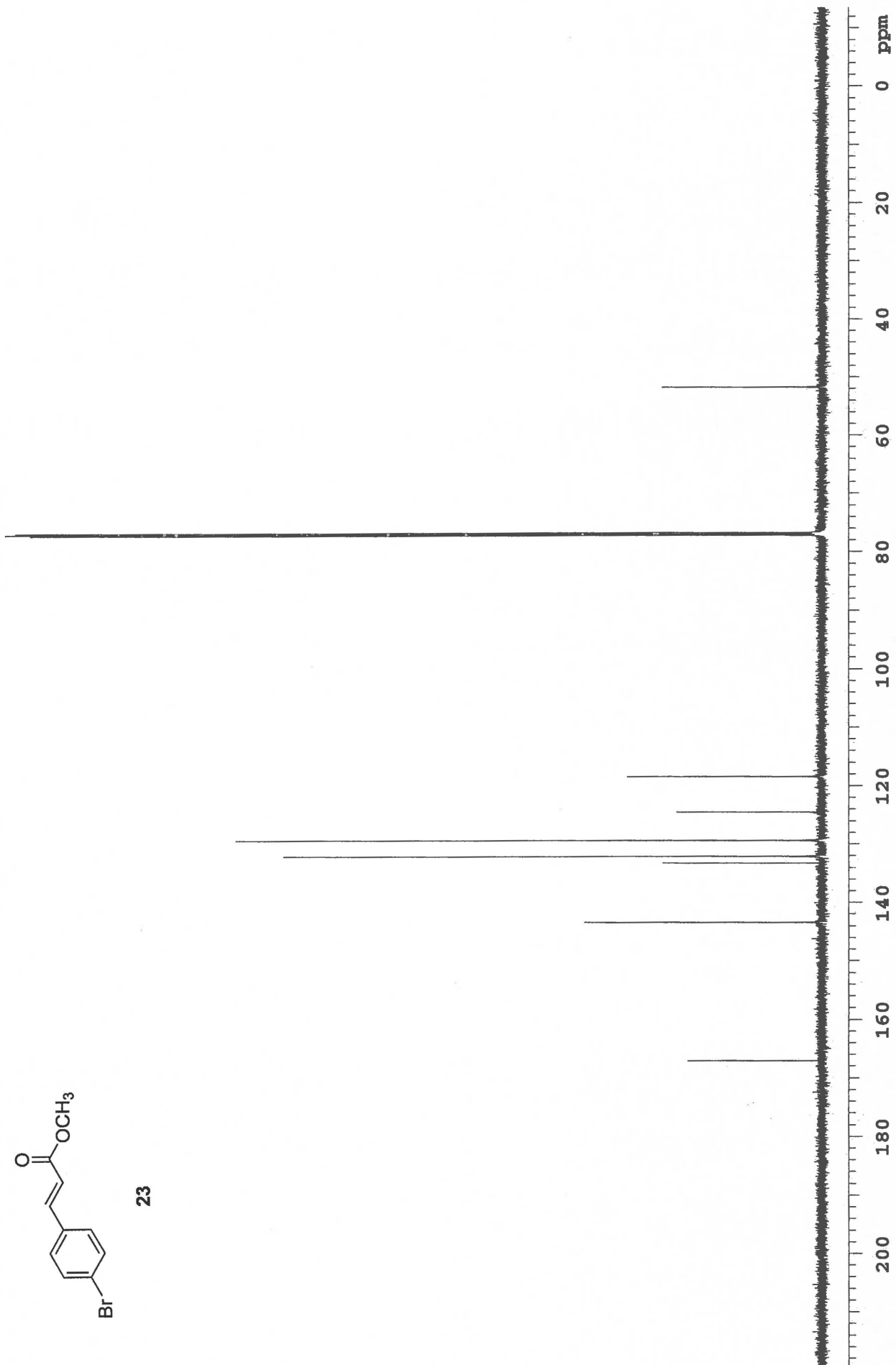


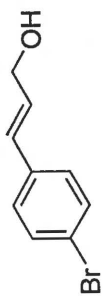
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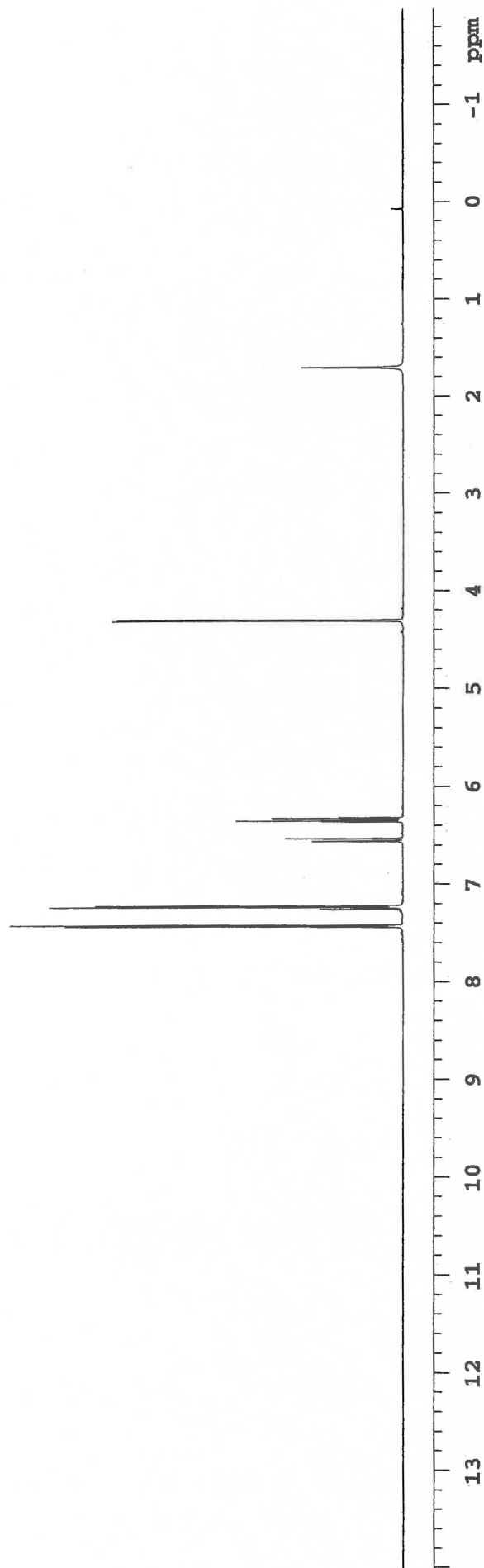
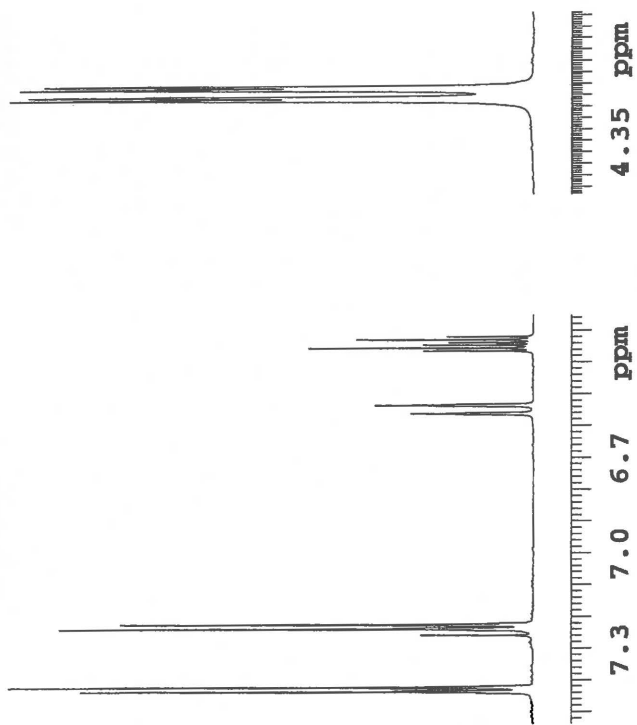


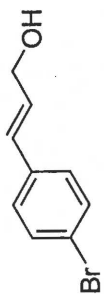
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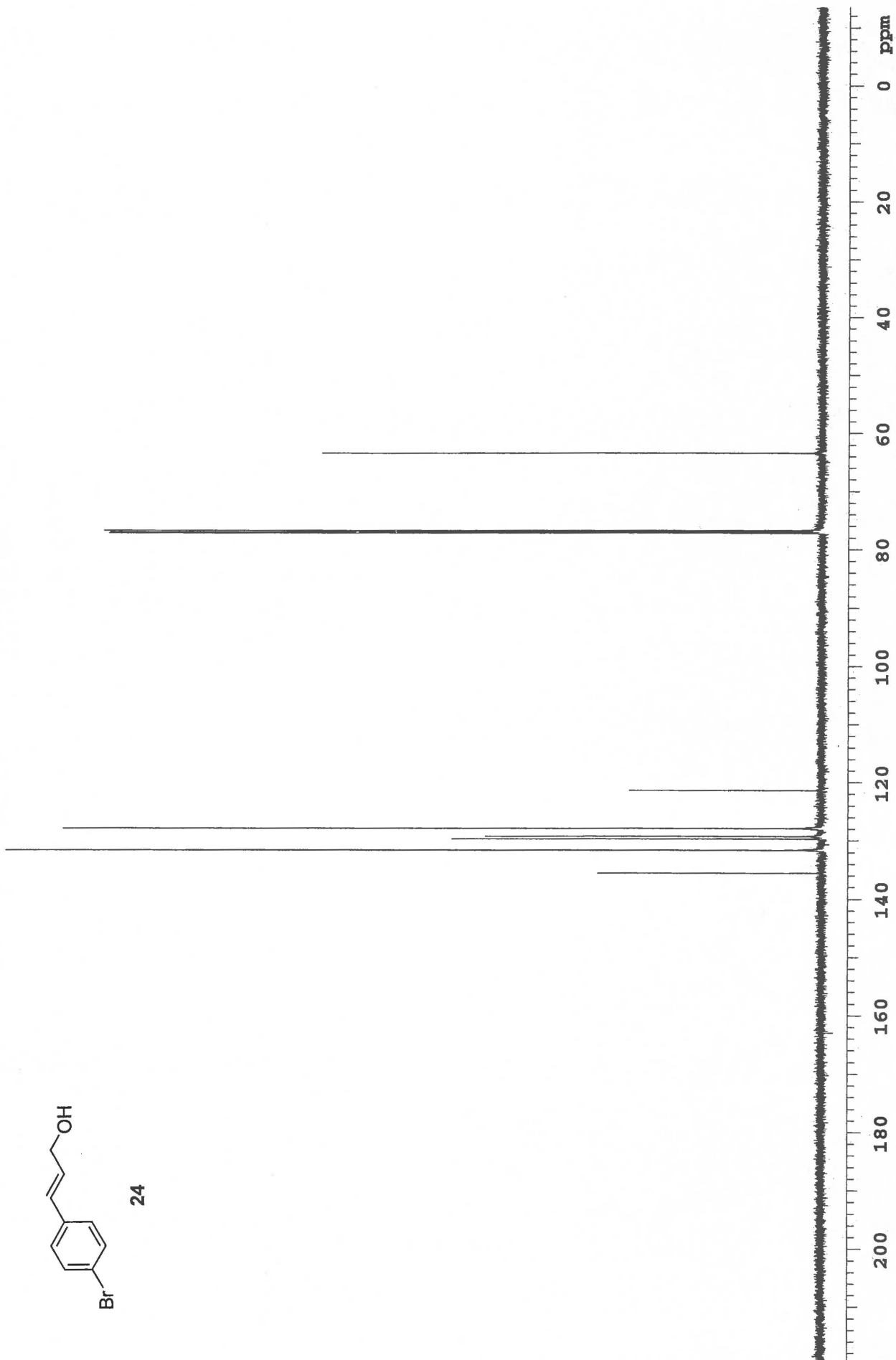


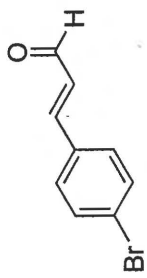
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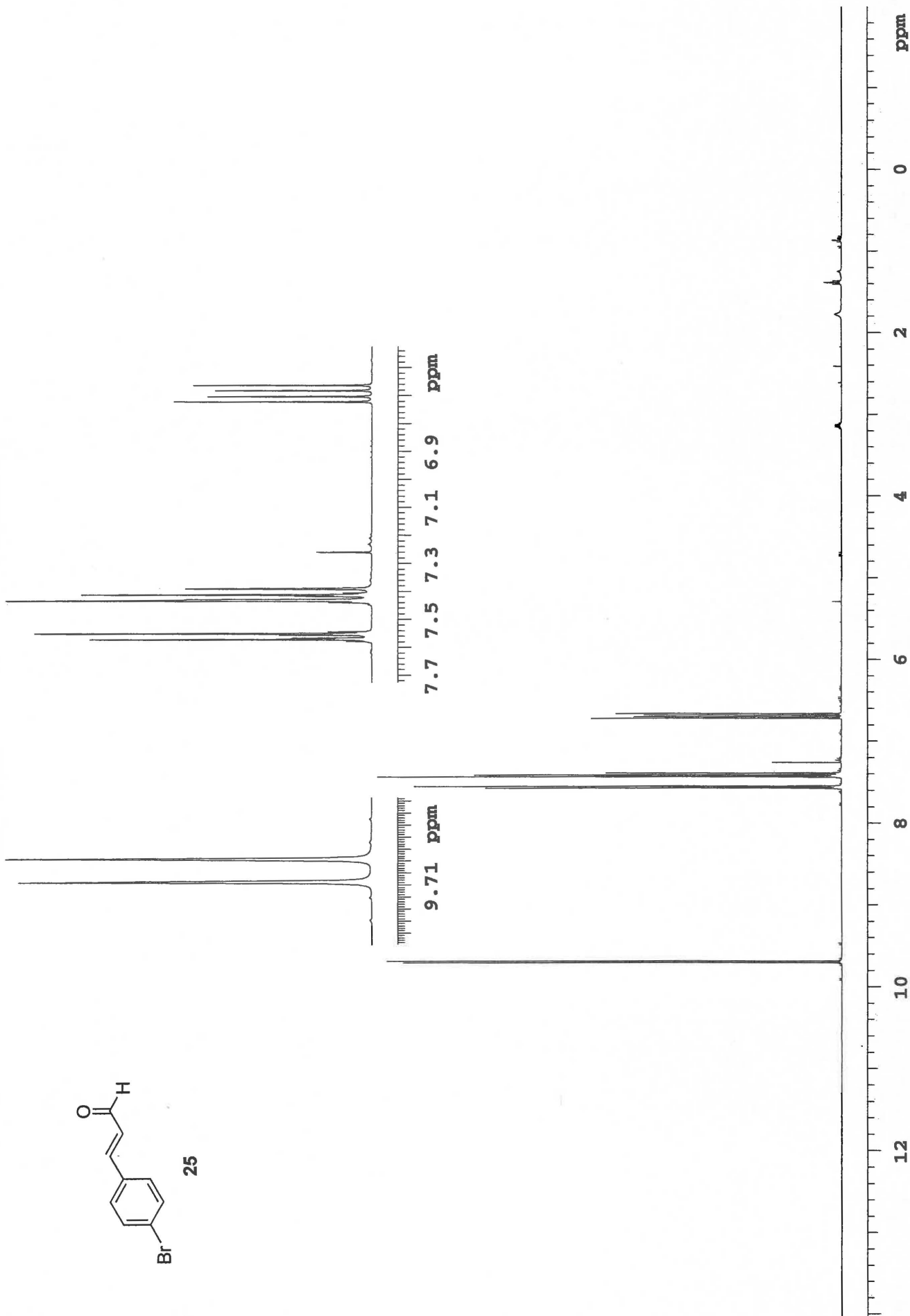


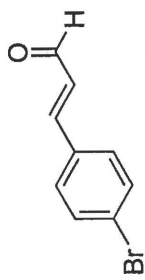
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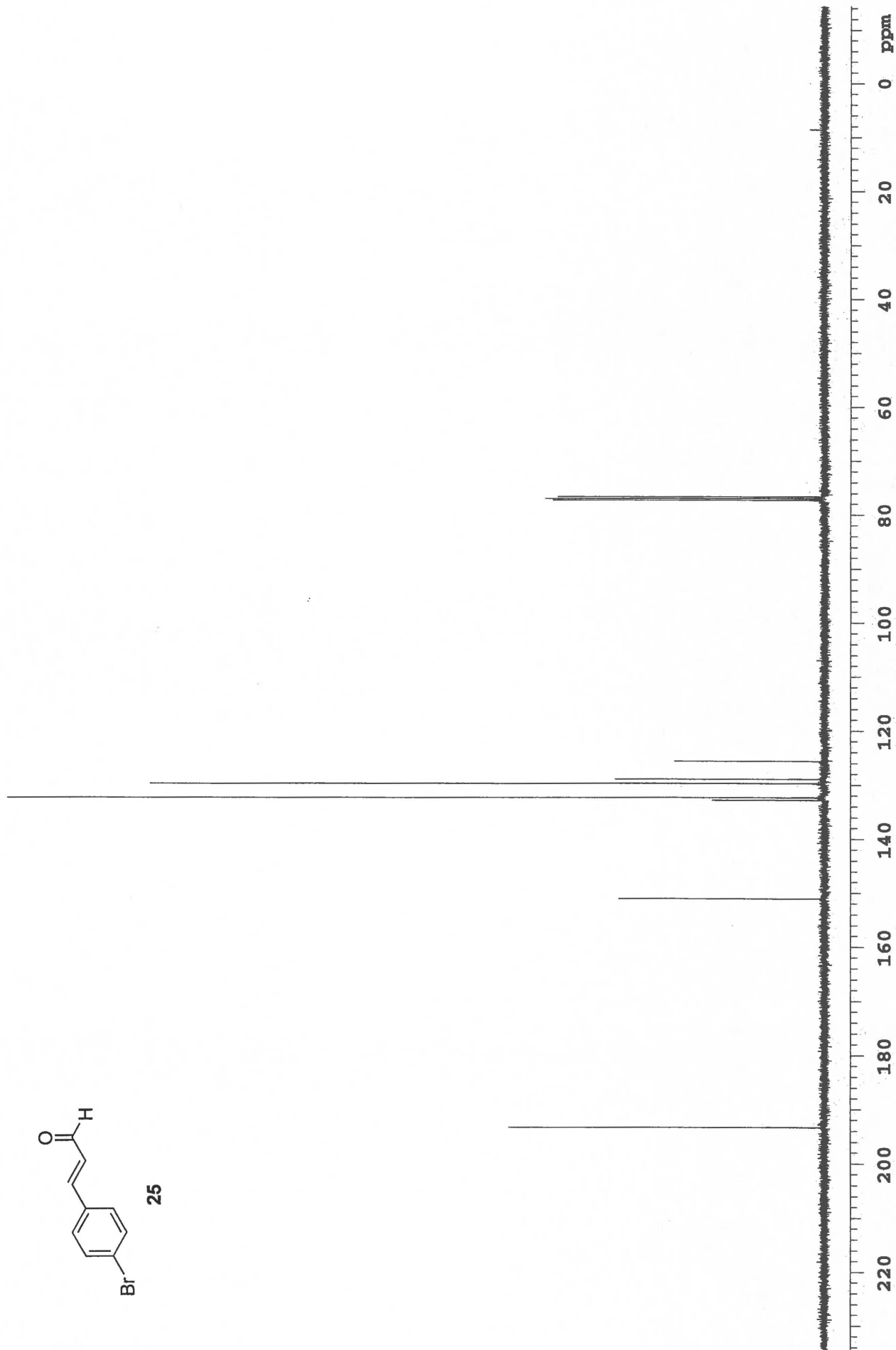


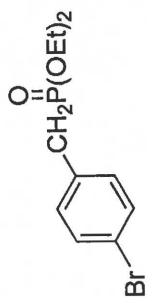
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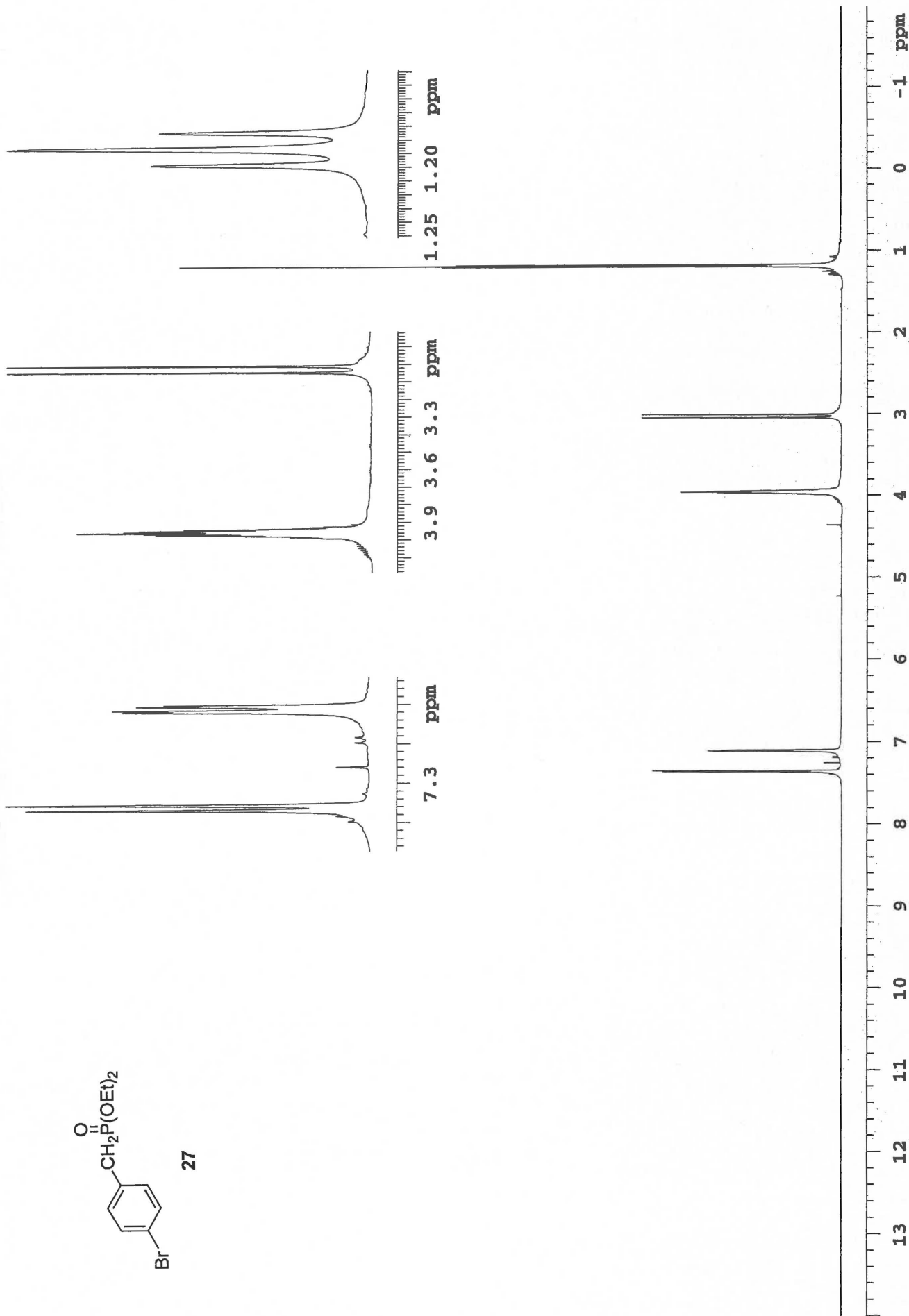


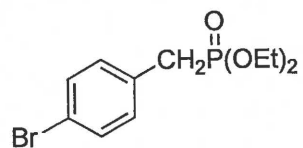
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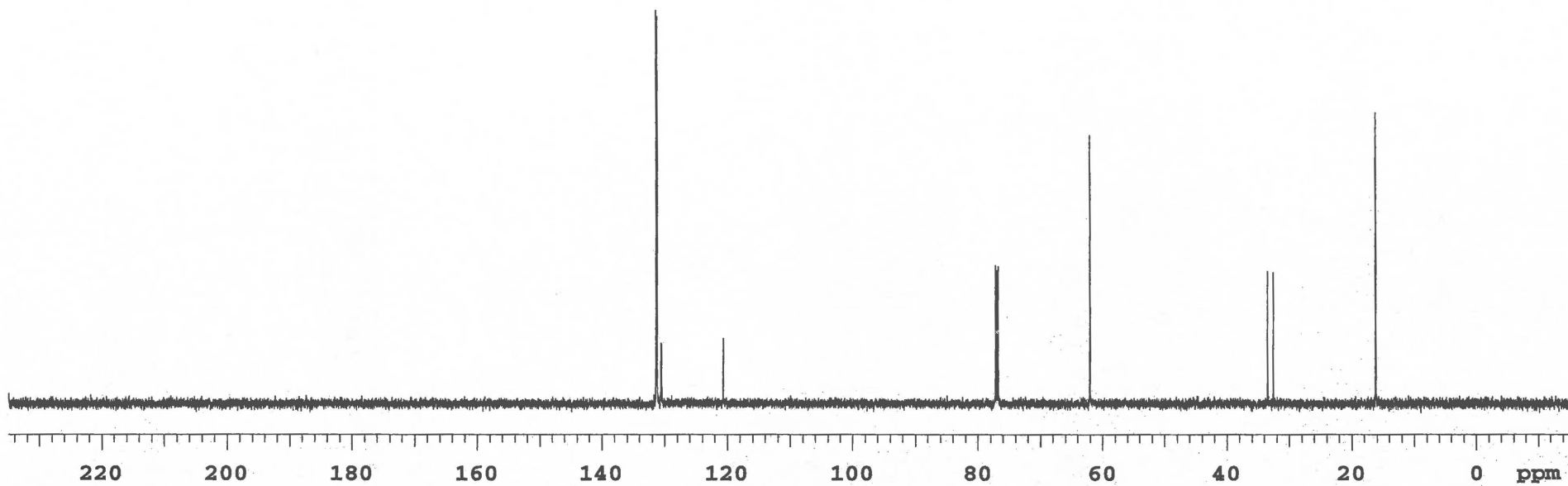
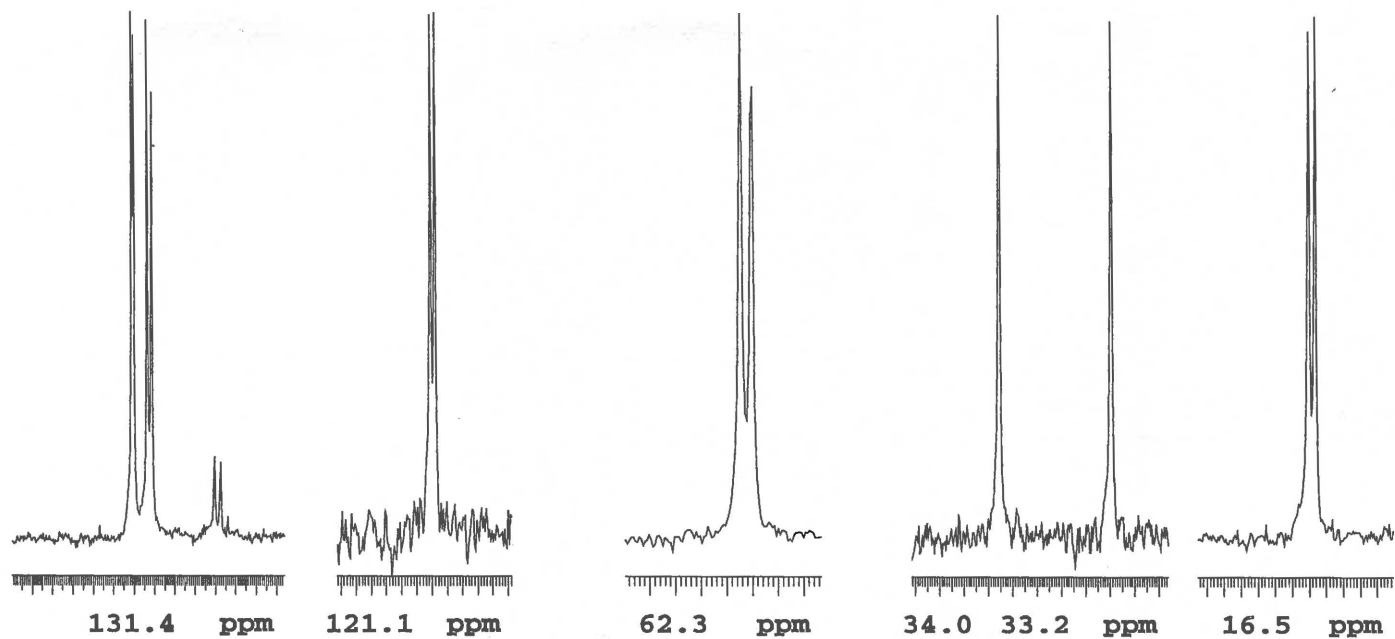


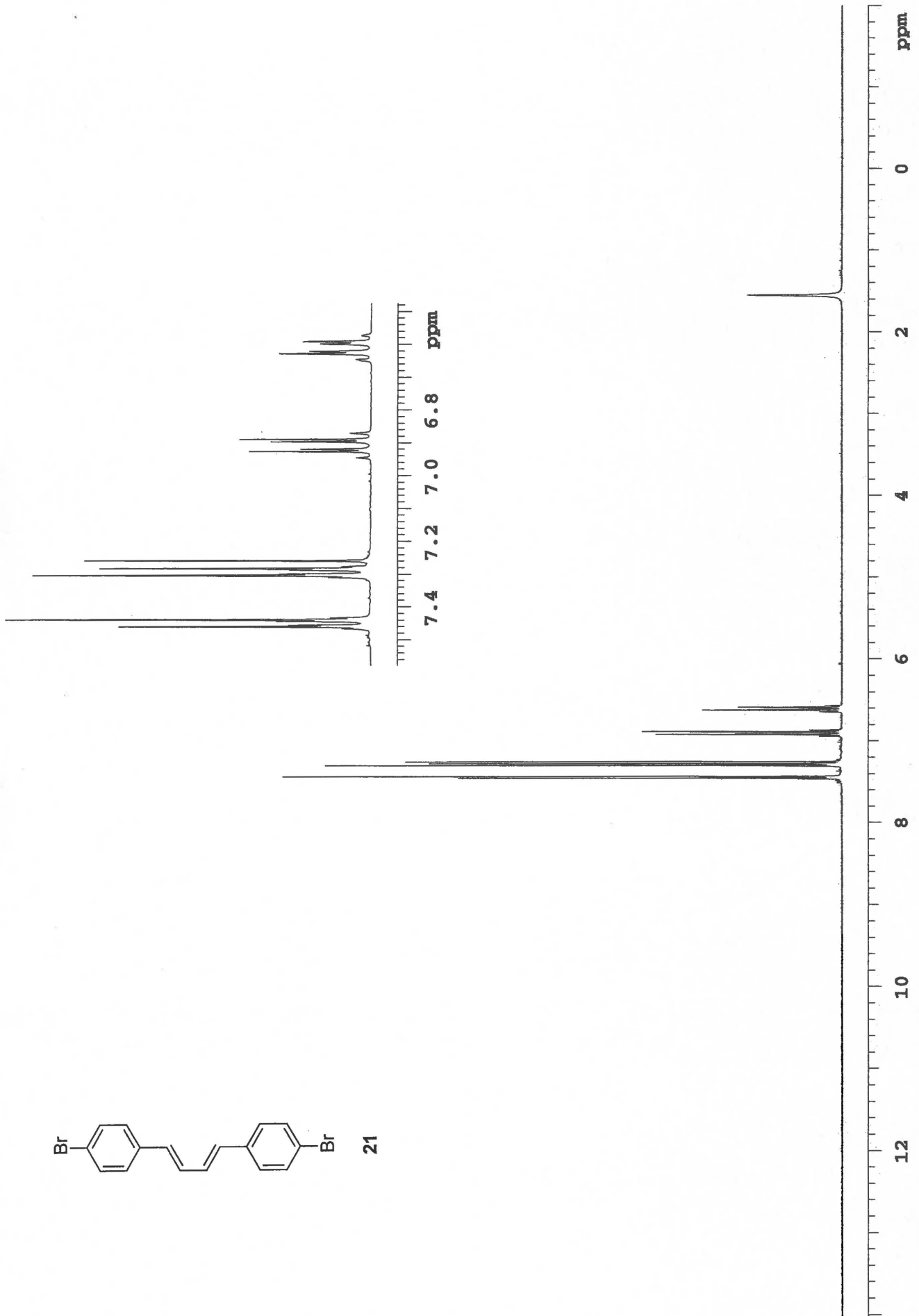
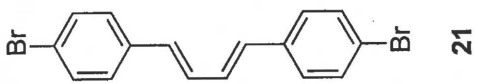
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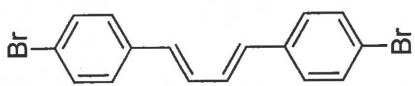




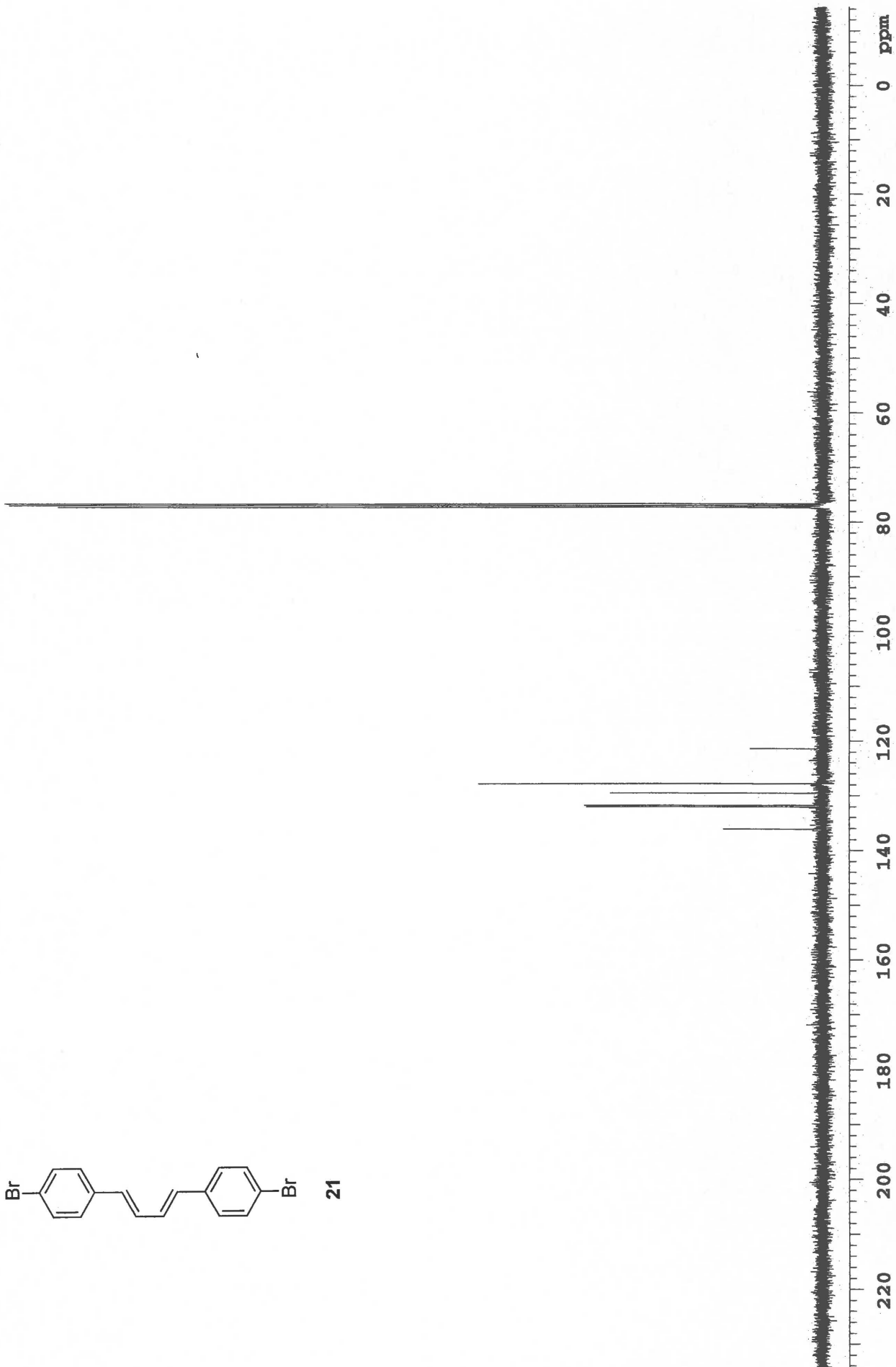
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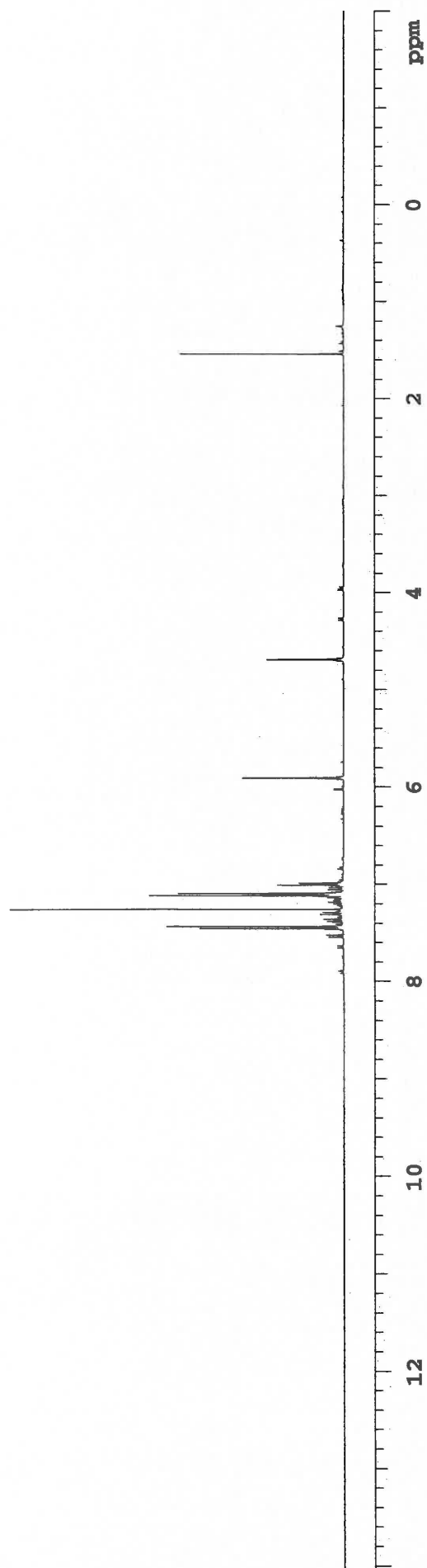
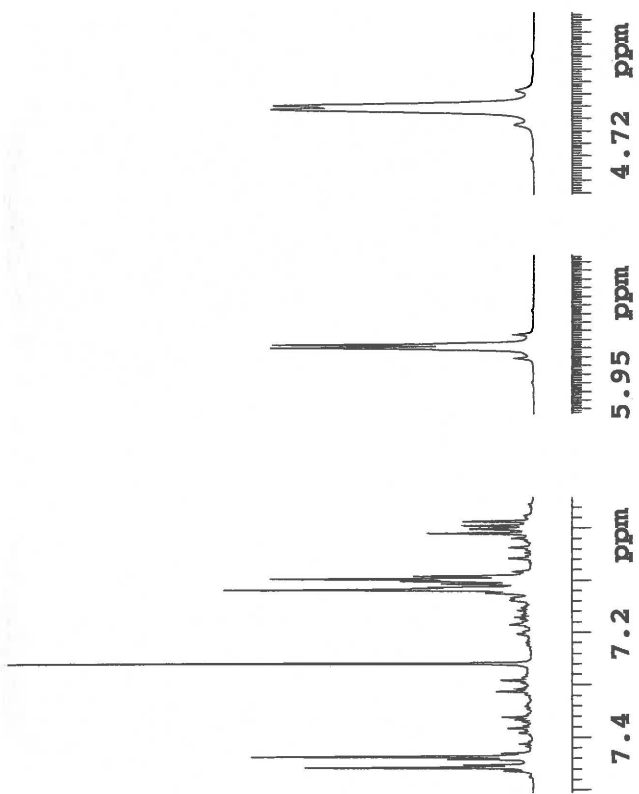
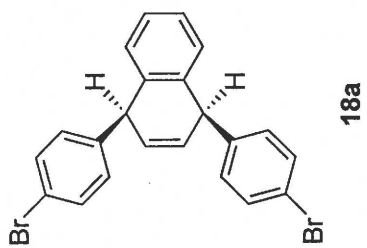


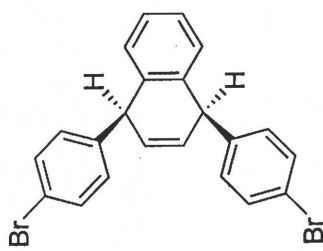




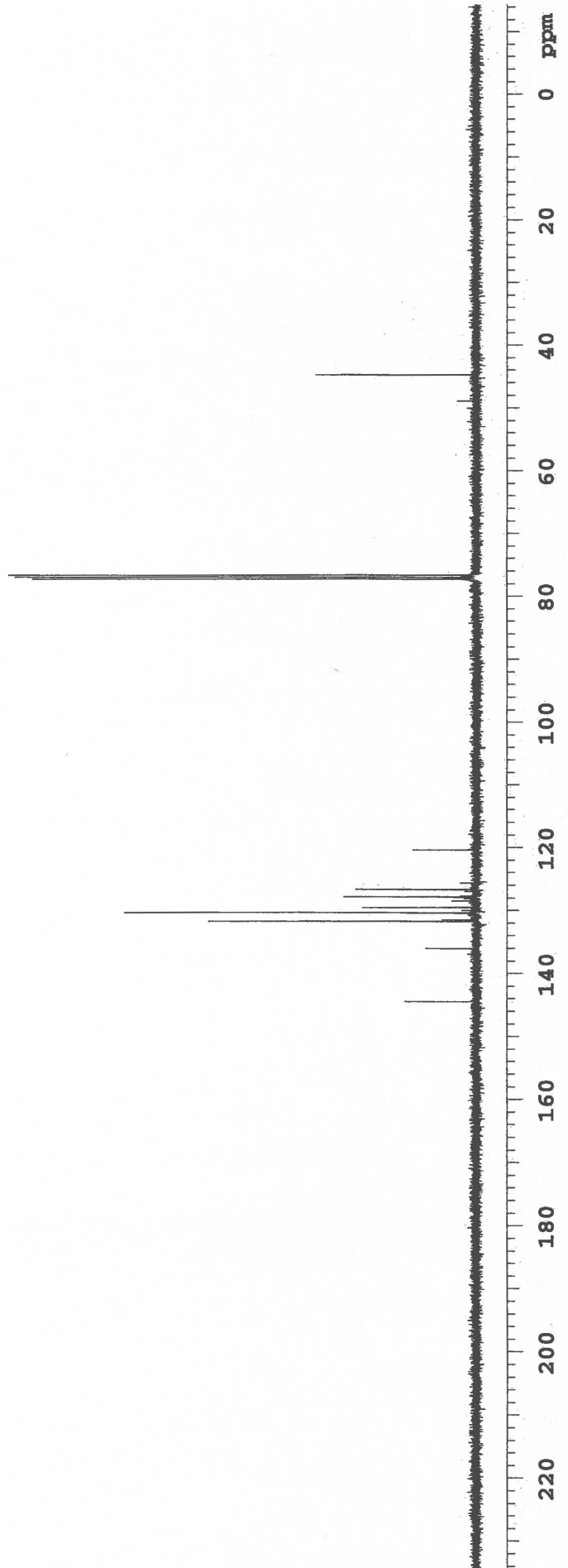
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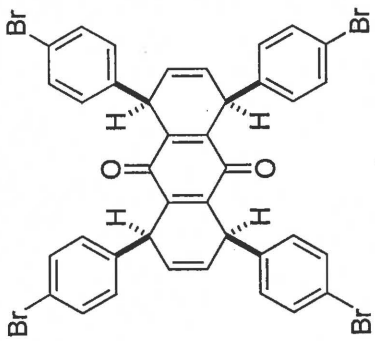




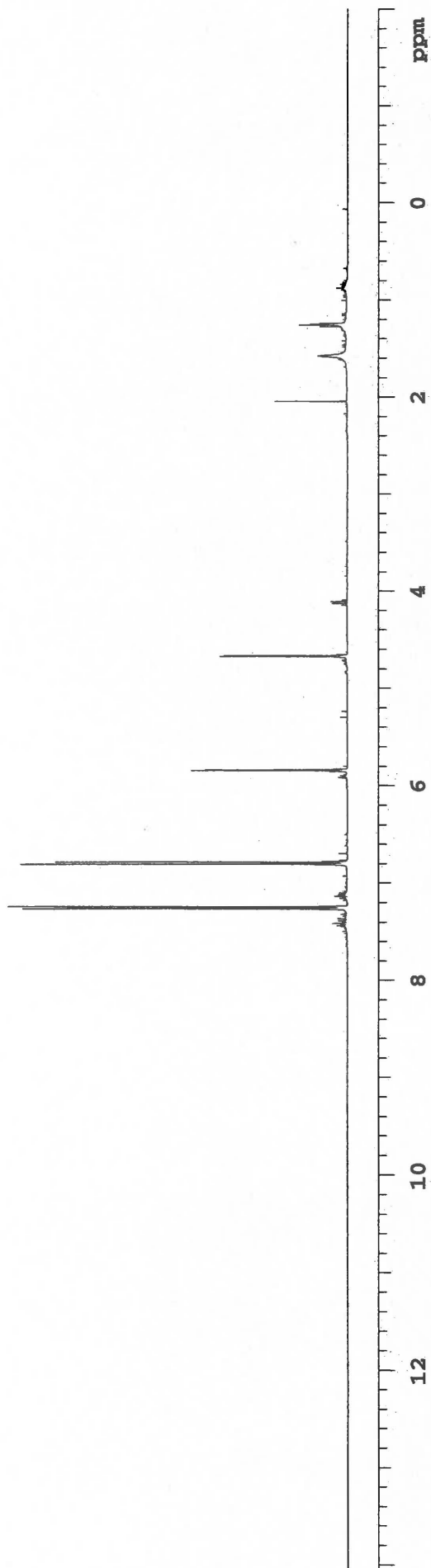
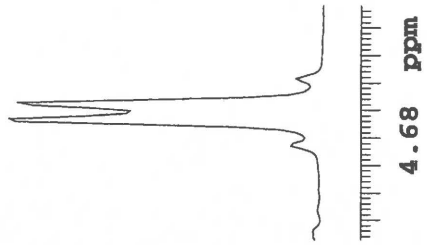
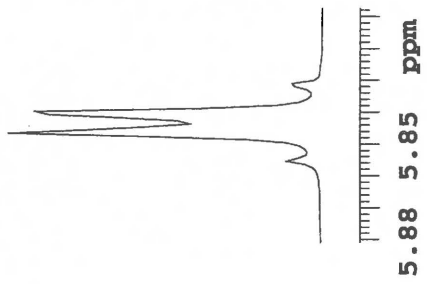
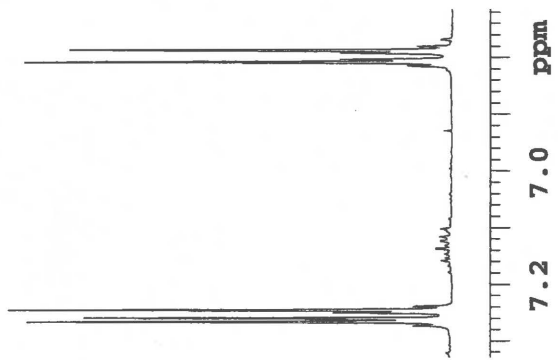


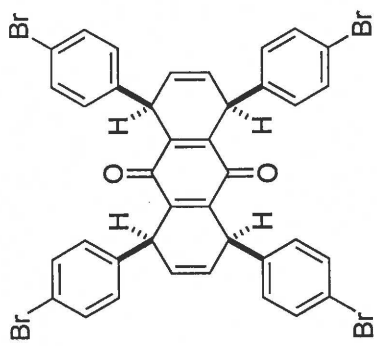
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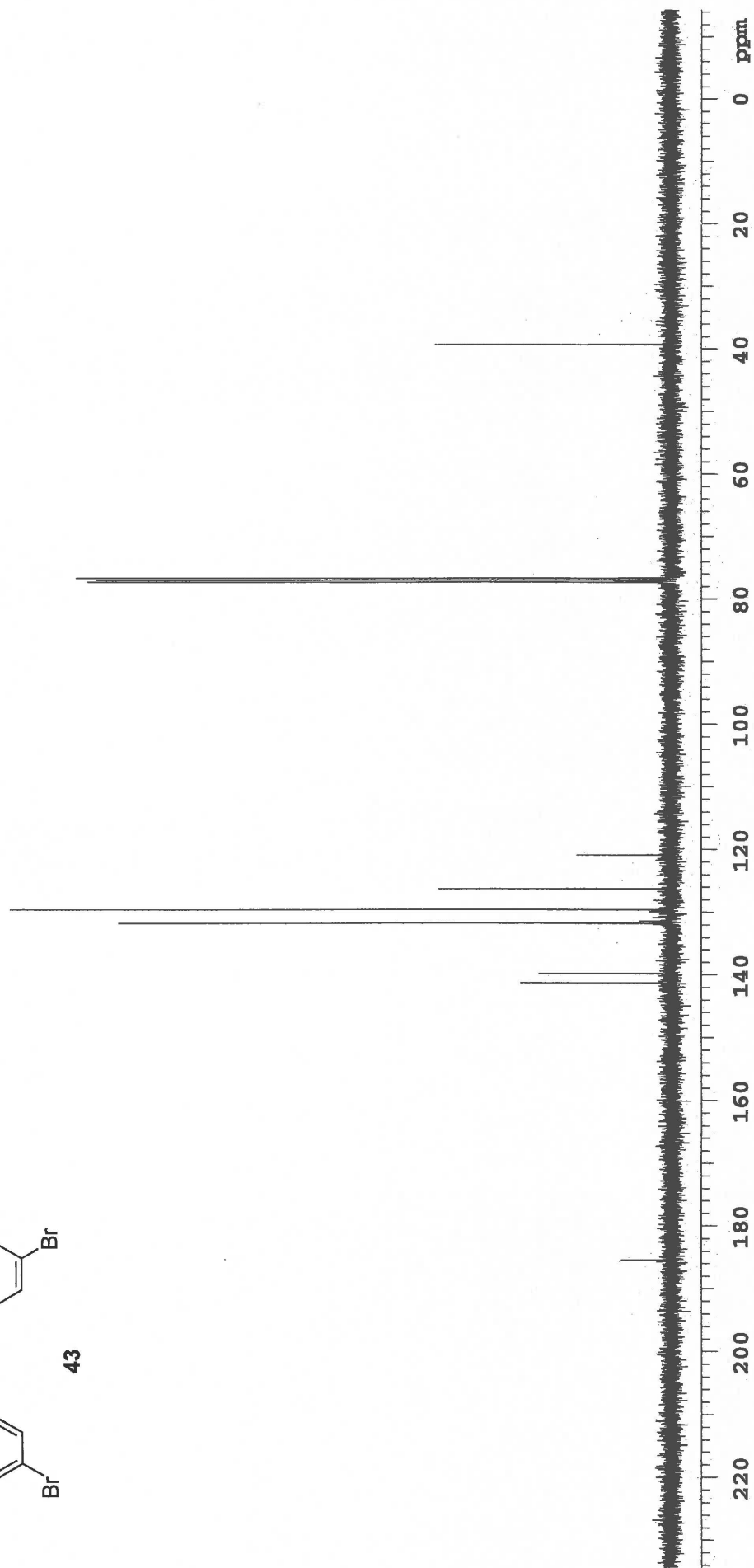


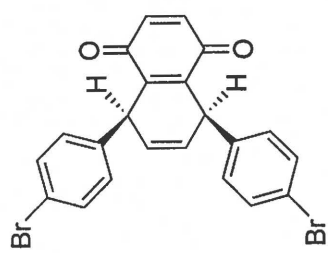
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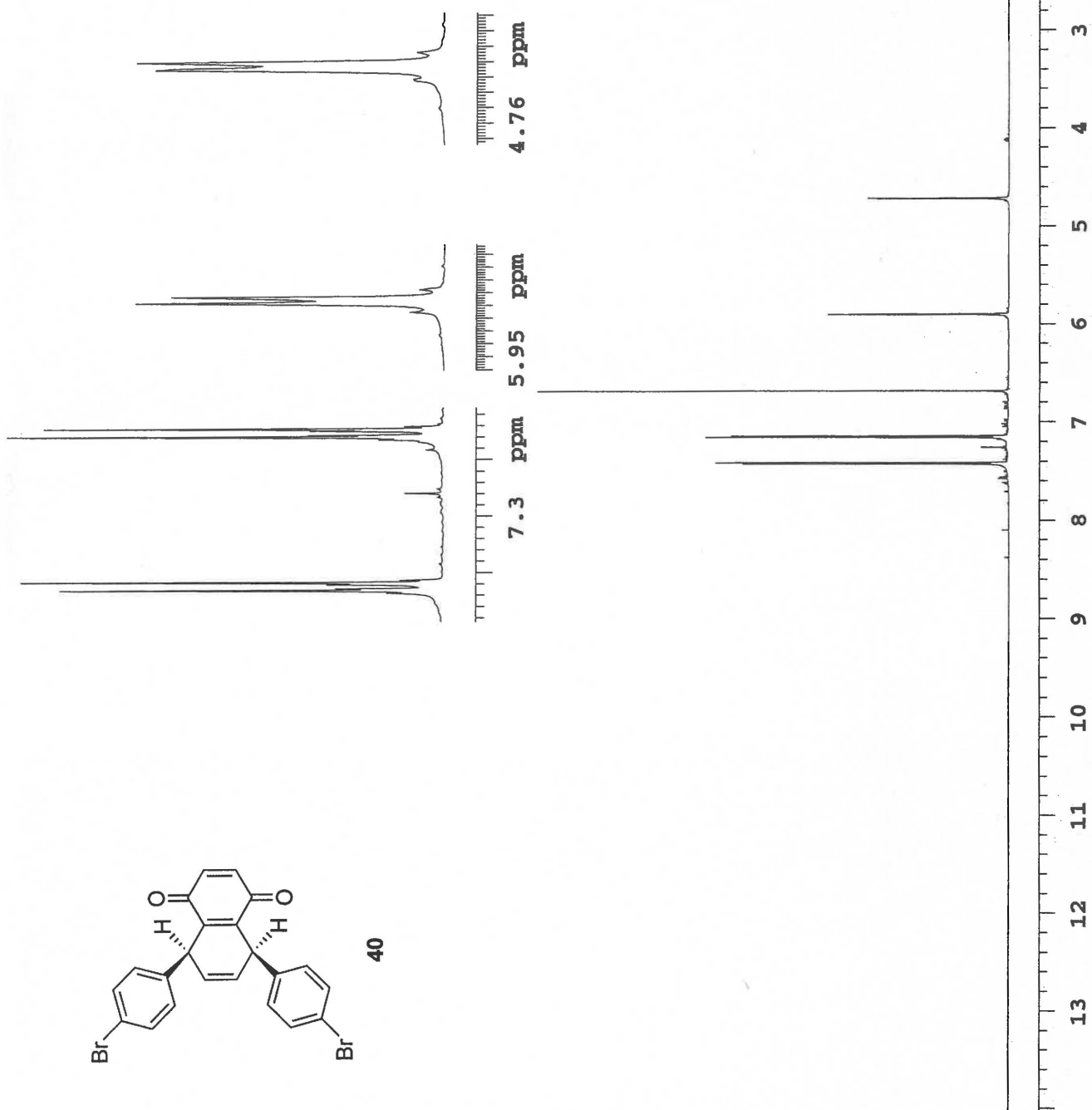


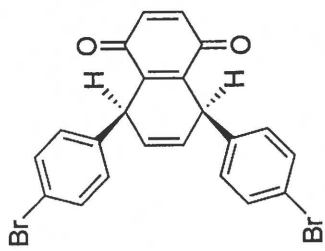
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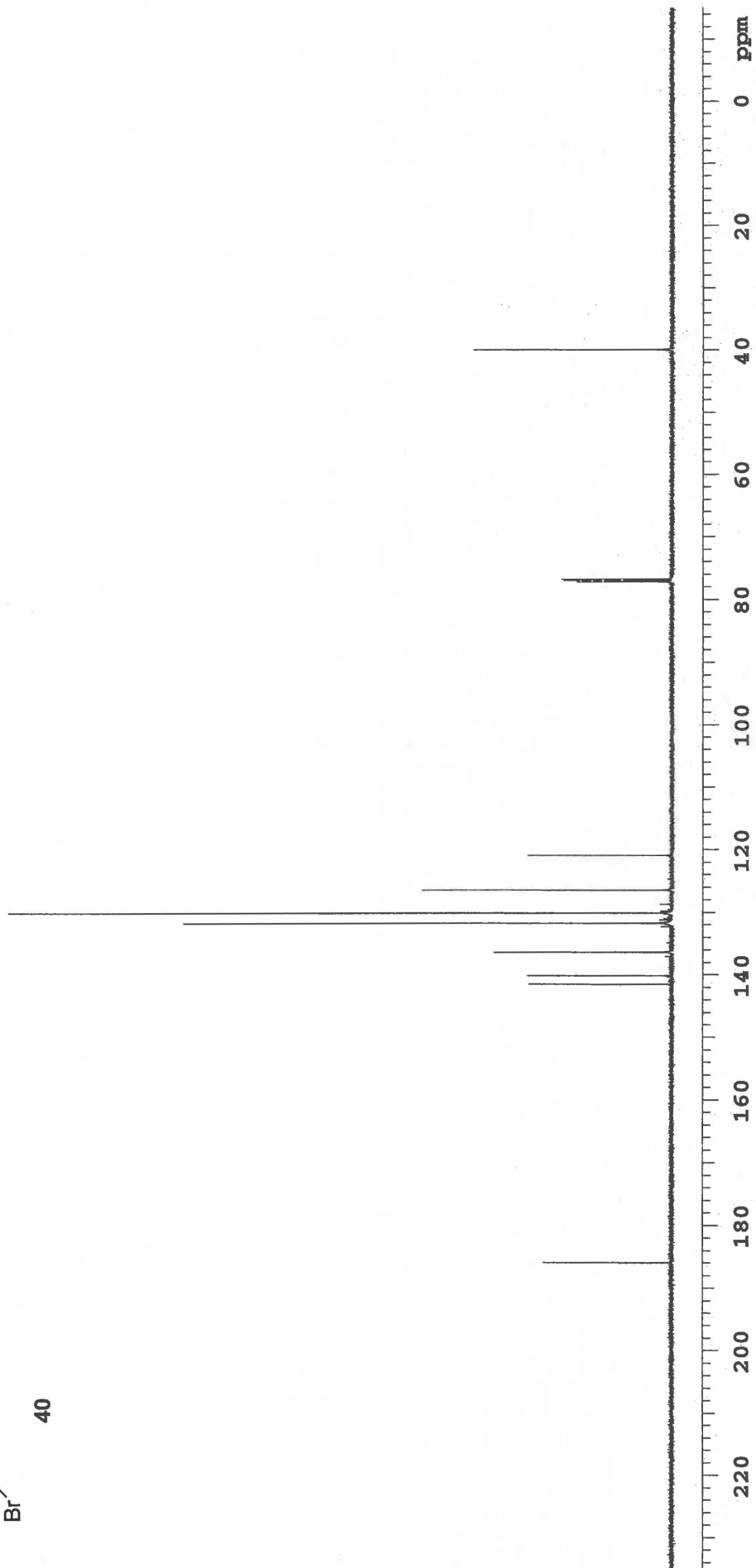


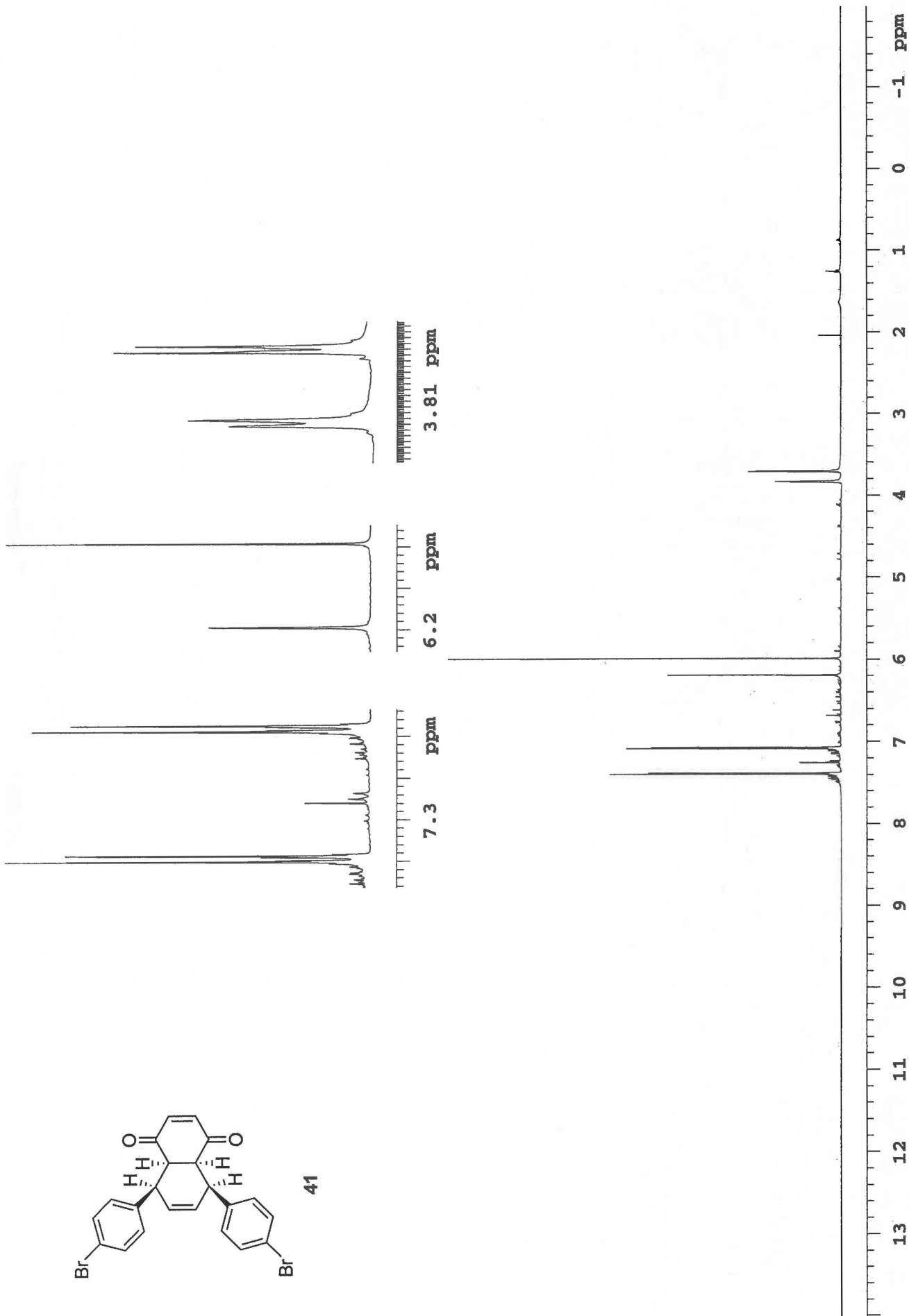
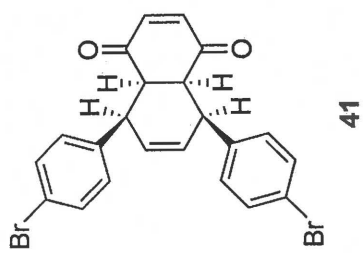
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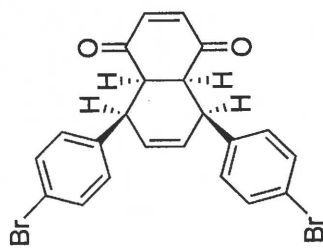




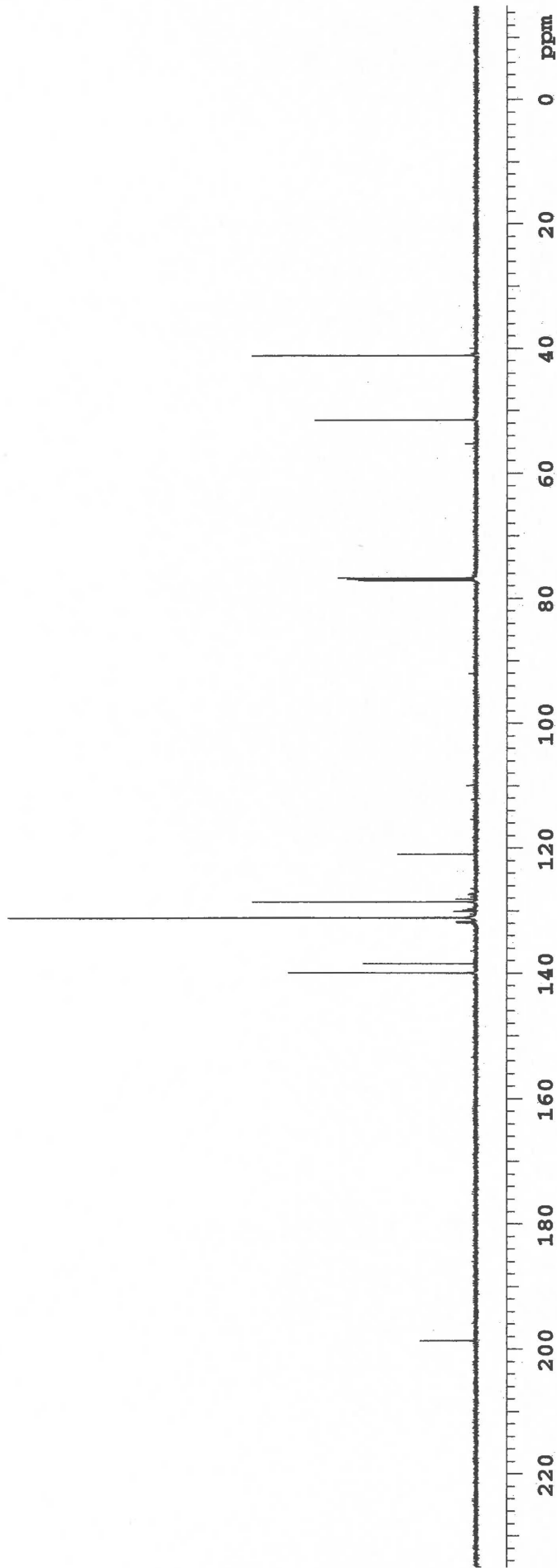
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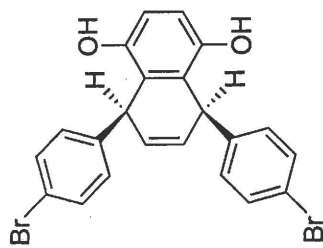




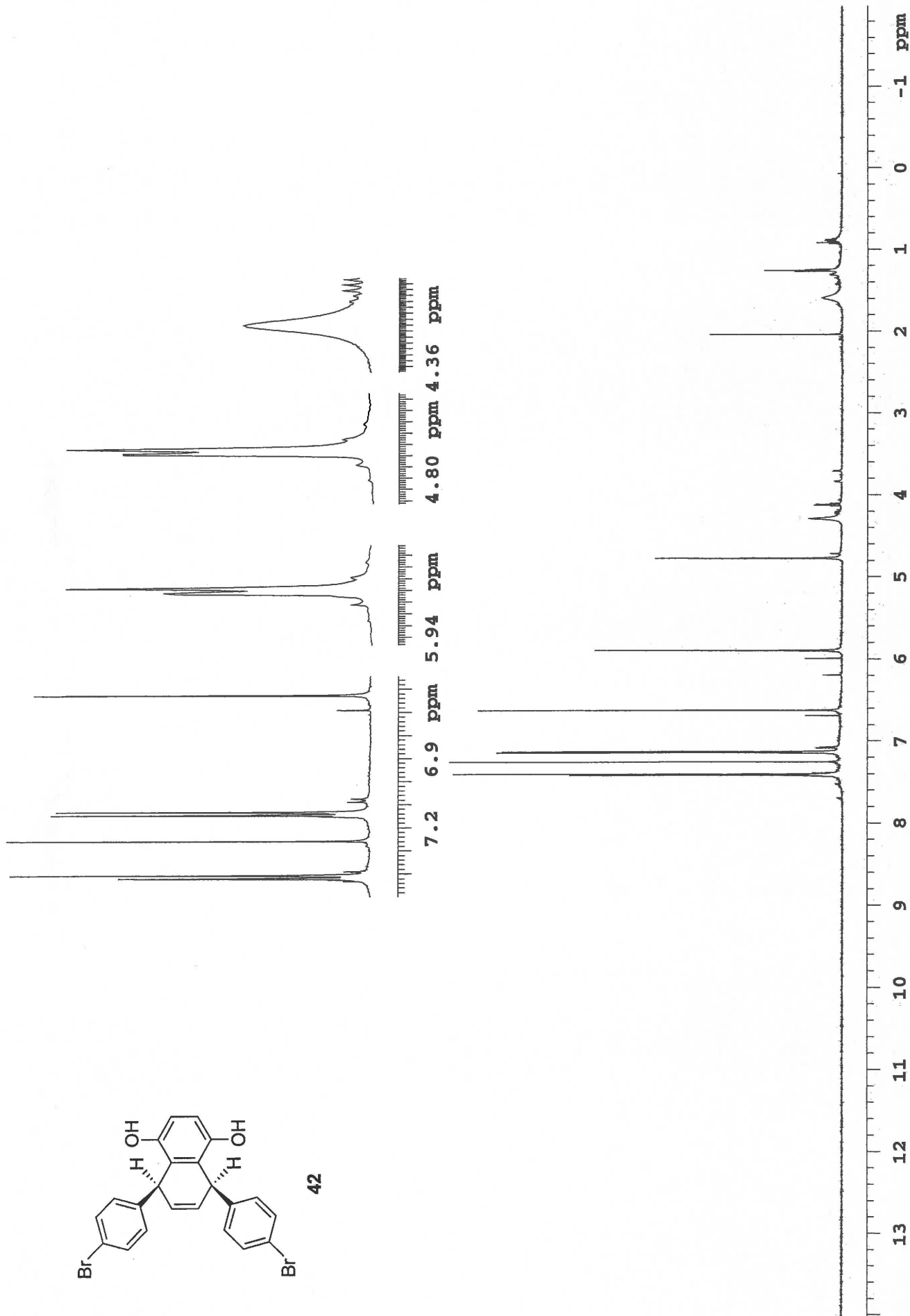


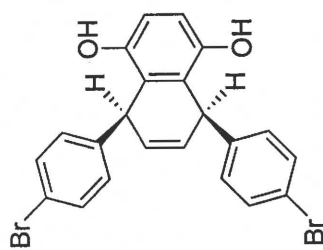
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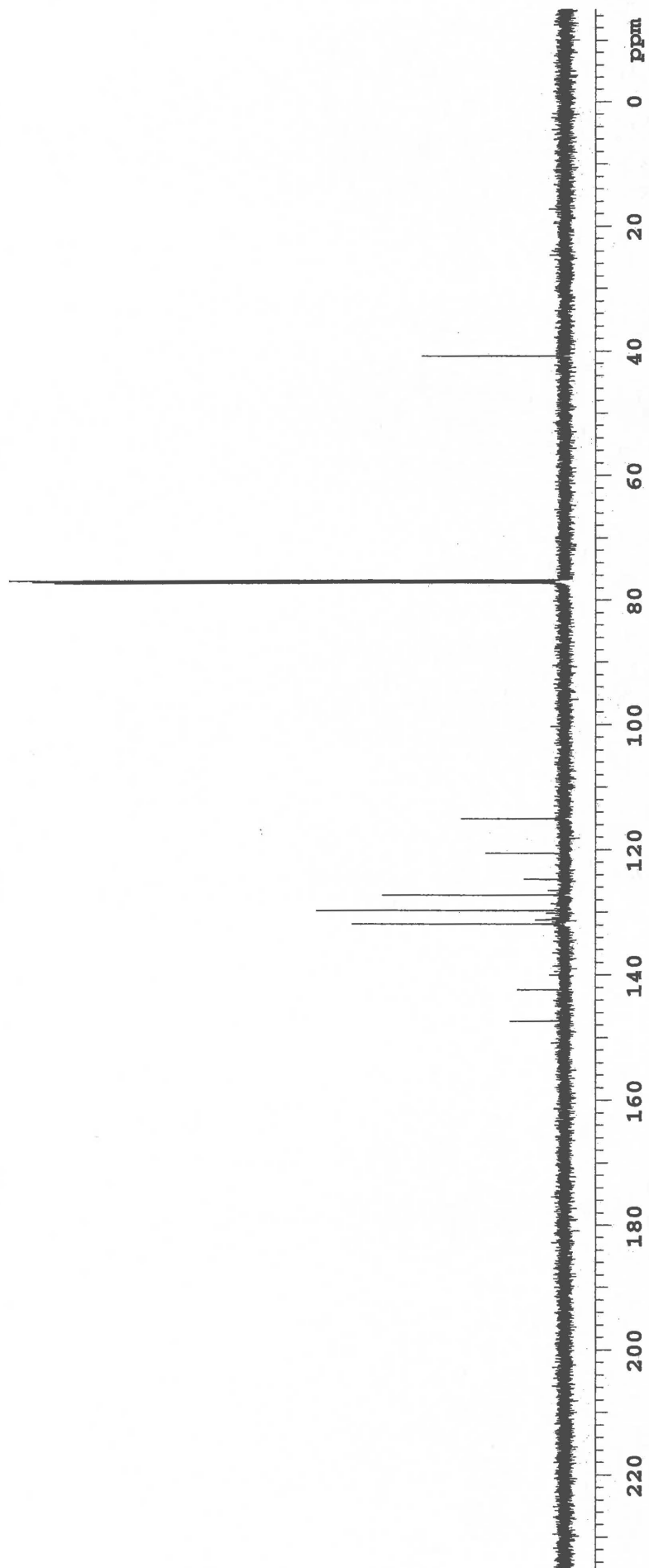


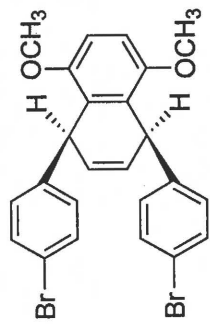
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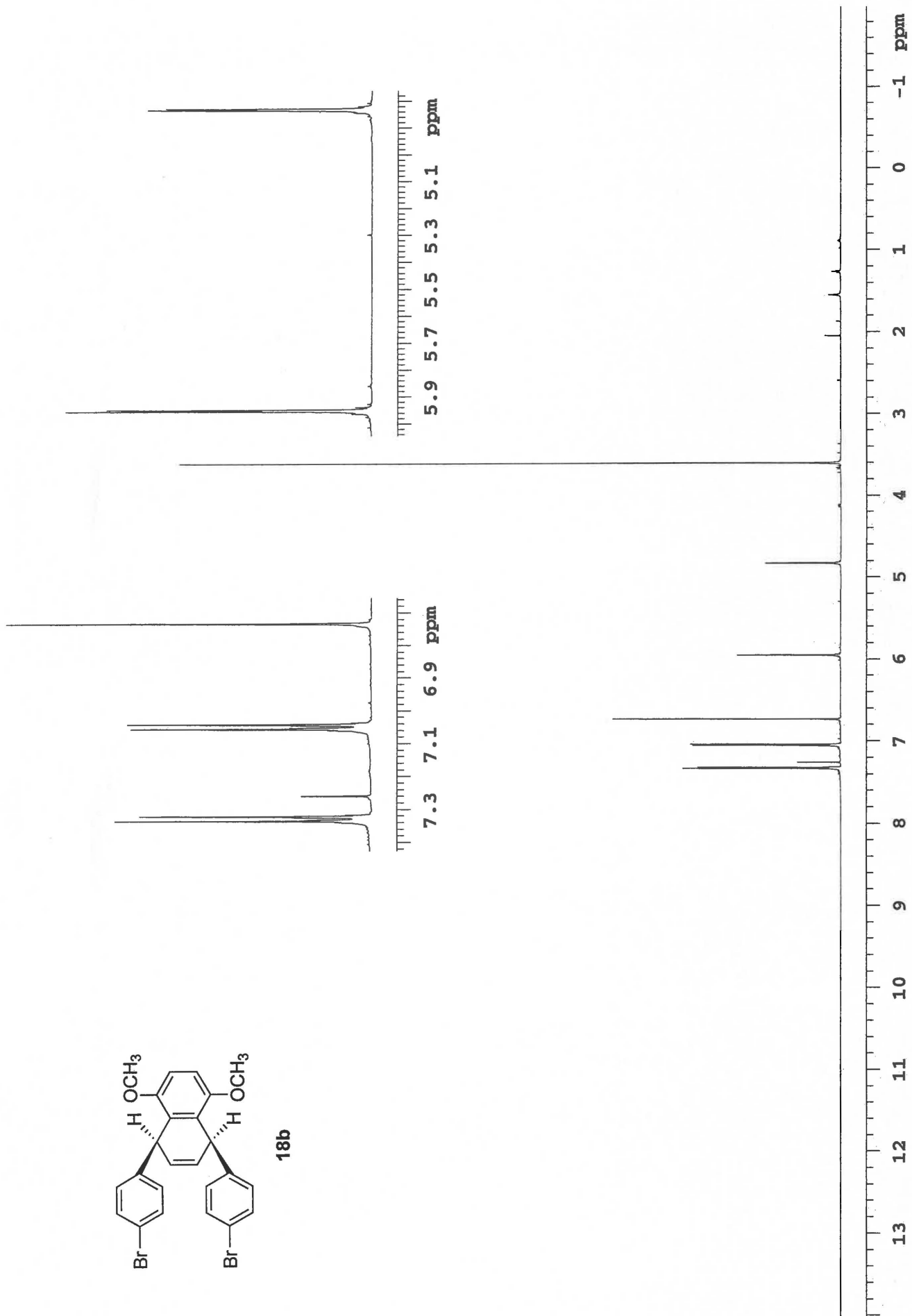


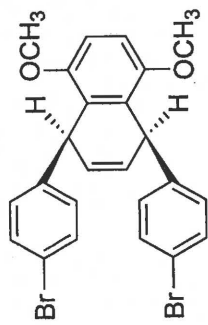
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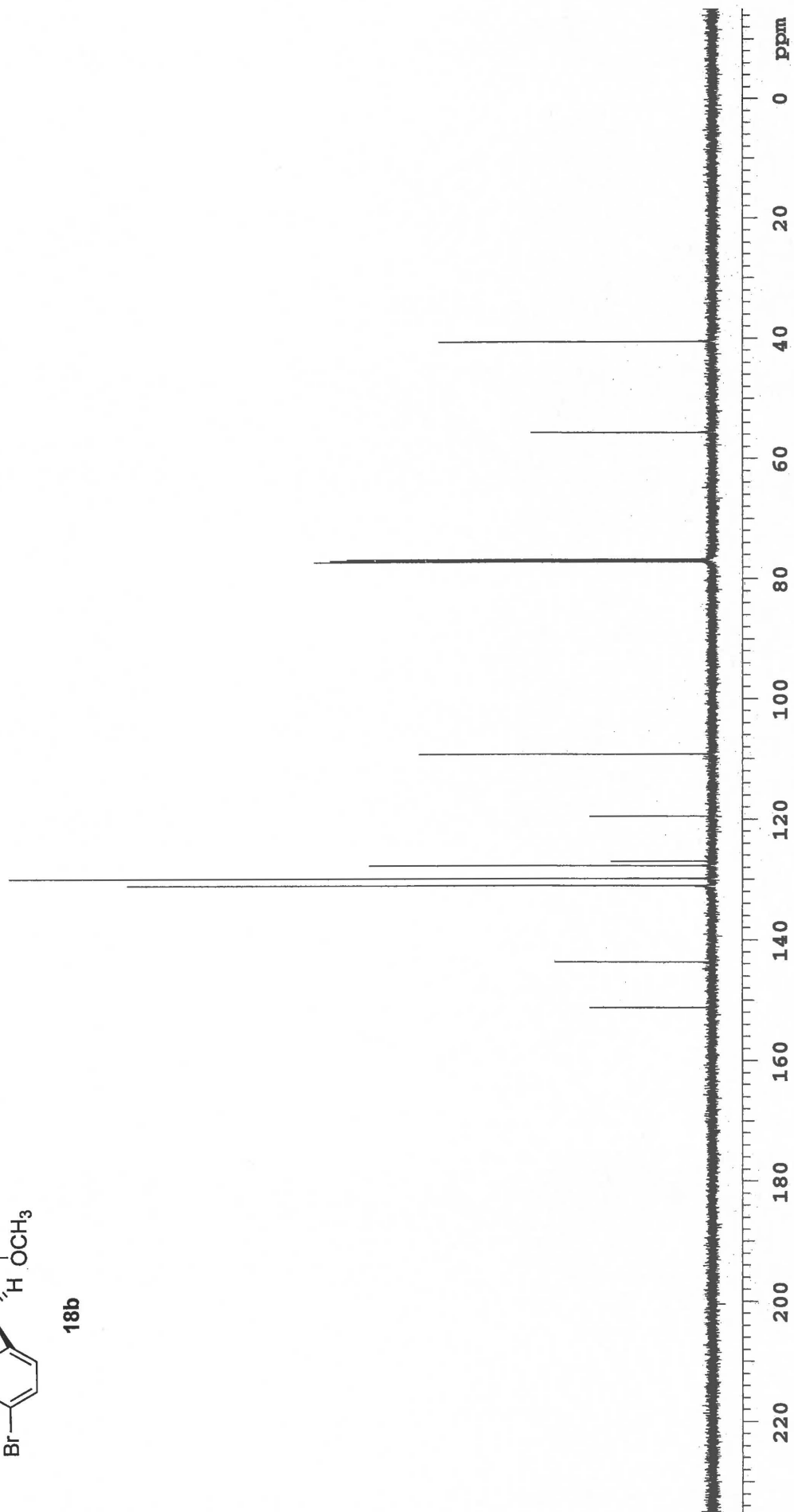


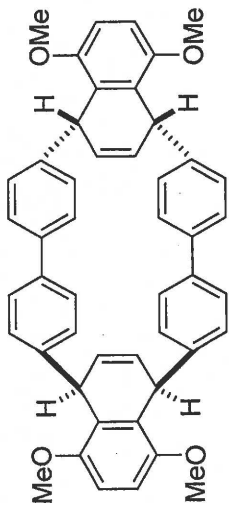
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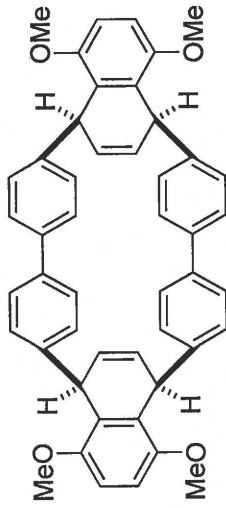


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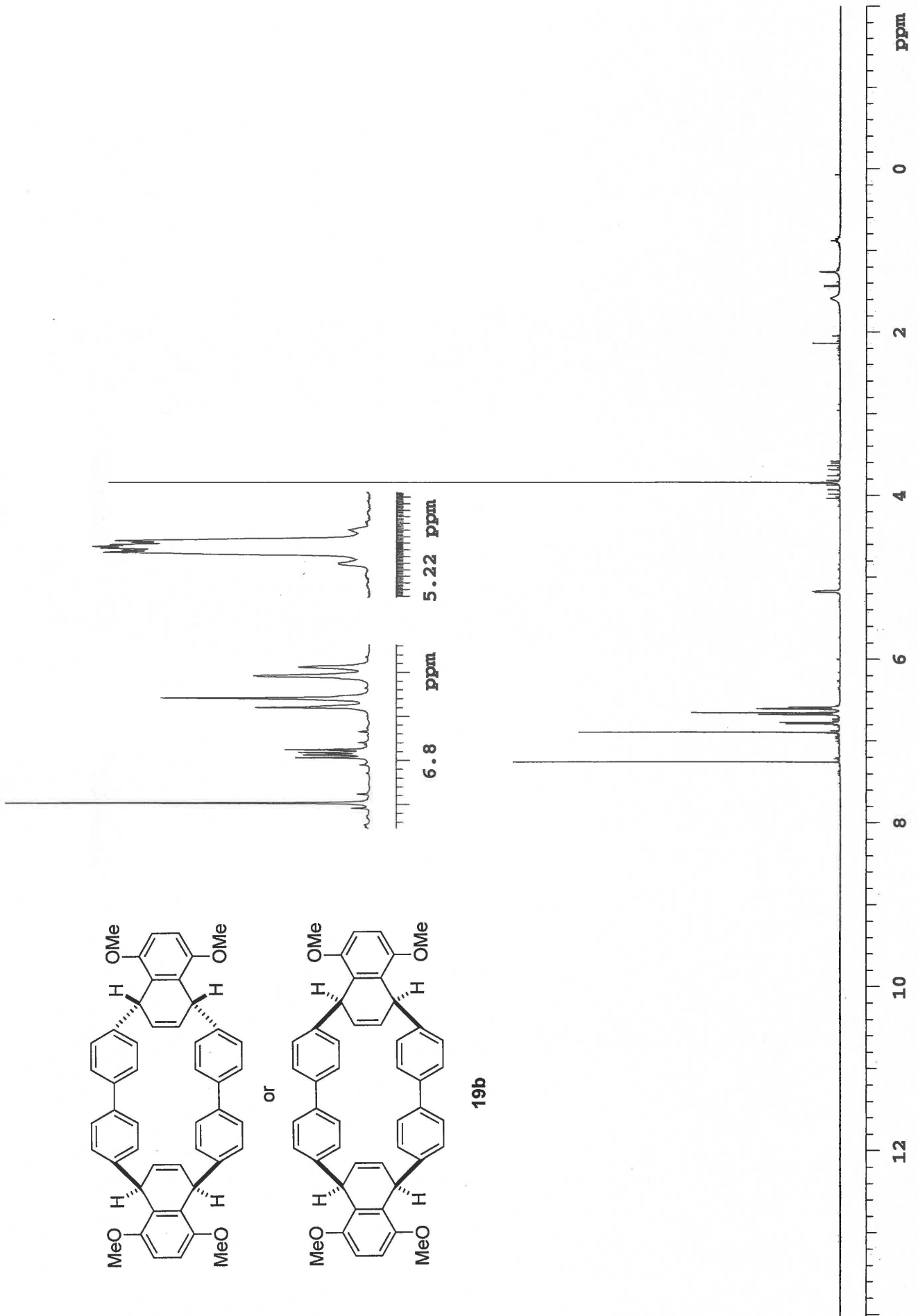


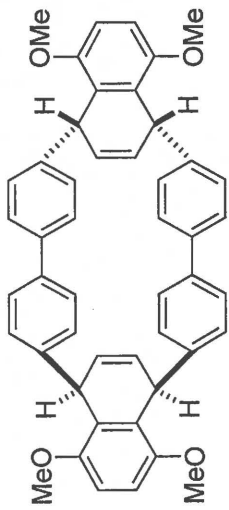


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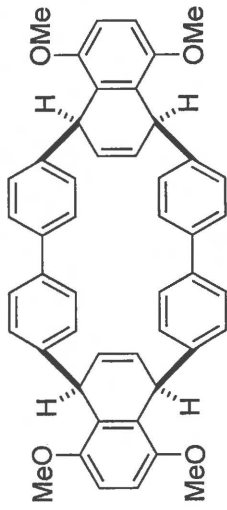


19b

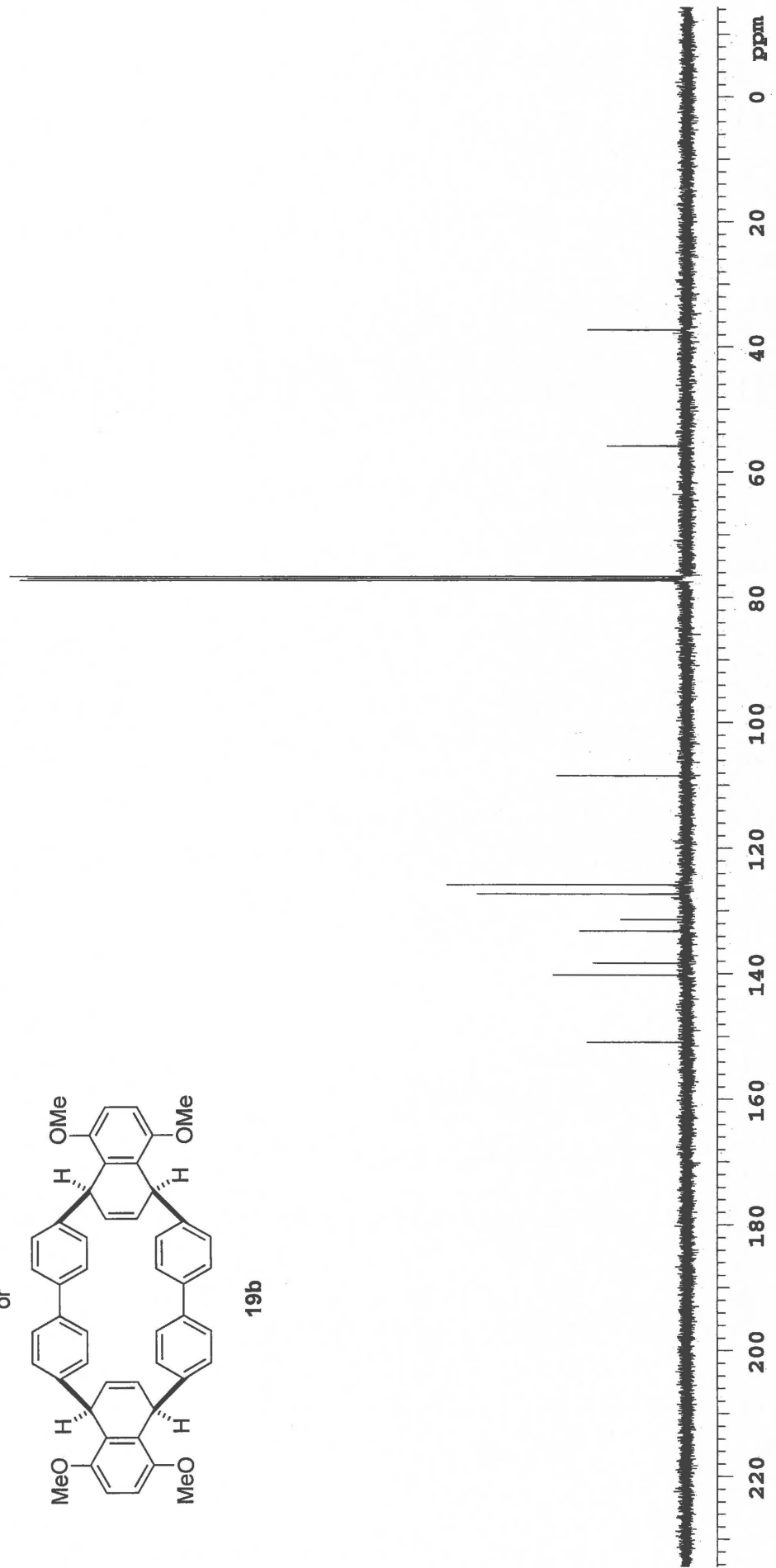




or



19b



Development of Synthetic Pathways for Carbon Nanohoops

Yiwei Huang

Thesis submitted to the
Eberly College of Arts and Sciences
at West Virginia University
in partial fulfillment of the requirements
for the degree of

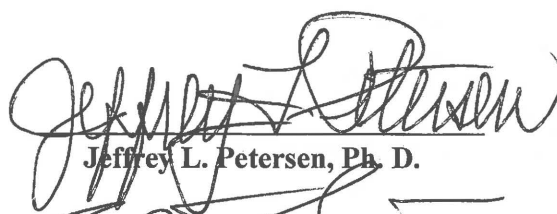
Master of Science

in

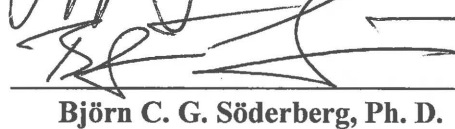
Chemistry

C. Eugene Bennett Department of Chemistry

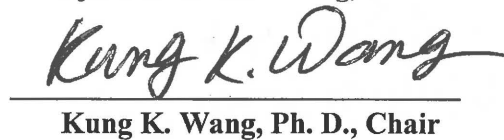
APPROVAL OF THE EXAMINING COMMITTEE



Jeffrey L. Petersen, Ph. D.



Björn C. G. Söderberg, Ph. D.



Kung K. Wang, Ph. D., Chair

7/10/2013

Date