Synthesis of Repeating Sequence Polyaniline Derivatives

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Submitted to the Graduate Faculty of

Arts and Science in partial fulfillment

of the requirements for the degree of

Masters of Science

University of Pittsburgh

2008

UNIVERSITY OF PITTSBURGH

School of Arts and Science

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SYNTHESIS OF REPEATING SEQUENCE POLYANILINE DERIVATIVES

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In order to increase solubility while maintaining conductivity, polymers incorporating periodic *ortho*-substituted units in the backbone of the classic *para*-polyaniline were prepared. The geometry of the *ortho*-substituted unit was postulated to allow for property enhancing substitution without the disruption π-conjugation. Crucial to this goal was the protection of the *ortho*-diamine unit during synthetic procedures. Of the many motifs that were explored, the urea protection scheme proved to be the most amenable to the coupling reactions required to prepare segmer units with a *para-ortho-para* sequence. Trimeric segmers bearing 0-2 methyl substituents on the *ortho*-substituted unit were prepared. The substituentless and monomethyl segmers were combined with BOC-protected dimers *para*-aniline to yield polymers with modest molecular weights by GPC vs. polystyrene standards (M_n = 4-10 x 10^3, PDI ~1.5). Poor film properties prevented characterization of the conductivity properties.

In an effort to identify a protecting group that would be either practically removable or more compatible with high conductivity, several motifs were explored: sulfonamides, amides, diazaboroles, diazaphosphole oxides and carbamates. All of these motifs proved unreactive to the conditions necessary to prepare the trimeric segmers analogous to those prepared from the urea. Quinoxaline and phenazine derivatives of the basic *ortho*-substituted unit were also prepared. While these derivatives were also difficult to incorporate into trimeric segmers, copolymers were prepared by direct coupling of phenazine units to dimeric *para*-substituted

units. Molecular weights of these copolymers were modest, and the conductivity was found to be within one order of magnitude compared to *para*-polyaniline.

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SYMBOLS AND ABBREVIATIONS

1^o	primary
2^o	secondary
Ac	acetate
anal	analysis
A to Q	ratio of amine to quinone
BINAP	2,2'bis(diphenylphosphino)-1,1'binaphtyl
BOC	tertiary-butoxycarbonyl
br	broad
Bu	butyl
°C	degrees Celsius
cm	centimeter
cm^{-1}	wavenumber
CSA	camphorsulfonic acid
d	doublet (NMR signal
δ	chemical shift
dba	tris(dibenzylideneacetone)dipalladium (0)
dd	doublet of doublets (NMR signal)
DME	dimethoxyethane

DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DP	degree of polymerization
eq.	equivalent
fig.	figure
FTIR	Fourier transform infra-red
EB	emeraldine base
ES	emeraldine salt
EI-MS	electron ionization mass spectrometry
Et	ethyl
g	gram
GC	gas chromatography
GC-MS	gas chromatography mass spectrometry
GPC	gel permeation chromatography
h	hour
I	current
ICP	intrinsically conducting polymer
IR	infra-red
K	degrees Kelvin
LB	leucoemeraldine base
m	meta (aromatic substitution)
m	multiplet (NMR signal)
m	minor product (GC-MS)

M	moles/liter
M	major product (GC-MS)
M^+	parent peak
Me	methyl
MHz	megahertz
min	minutes
mL	milliliter
mmol	millimole
M_n	number average molecular weight
mV	millivolt
M_w	molecular weight
m/z	mass/charge
N/A	not available
NMP	N-methyl pyrrolidinone
o	*ortho* (aromatic substitution)
NMR	nuclear magnetic resonance
p	*para* (aromatic substitution)
PANi	poly(aniline)
PDI	polydispersity index
PVC	poly(vinyl chloride)
ppm	parts per million
q	quartet (NMR signal)
ρ	resistivity

R	resistance
rac	racemic
RT	room temperature
s	singlet (NMR signal)
S	Siemen
σ	conductivity
t	trace (GC-MS)
t	triplet (NMR signal)
$TBABr_3$	Tetrabutylammonium tribromide
^{t}Bu	tertiary butyl
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
tolyl	toluenyl
UV-VIS	ultraviolet/visible
V	volt
vs.	versus
VB	valence band
W	thickness
wt	weight
w/w	percentage by weight

1.0 POLYANILINE: SEGMER DEVELOPMENT AND POLYMER SYNTHESIS

1.1 INTRODUCTION

Ever since Heeger, MacDiarmid, Shirakawa, and co-workers reported their initial findings about polyacetylene's metallic properties,[1,2] the field of conducting polymeric materials has garnered much interest. Conducting polymers offer potential benefits over traditional metallic conductors because conducting polymers combine conductivity with the inherent properties of a polymer. Polyaniline, since being rediscovered in the field of intrinsically conducting materials, has been the lead contender for industrial applications and a great deal of effort has been involved in developing the synthesis and processing methodologies for polyaniline.

1.1.1 Description of Polyaniline

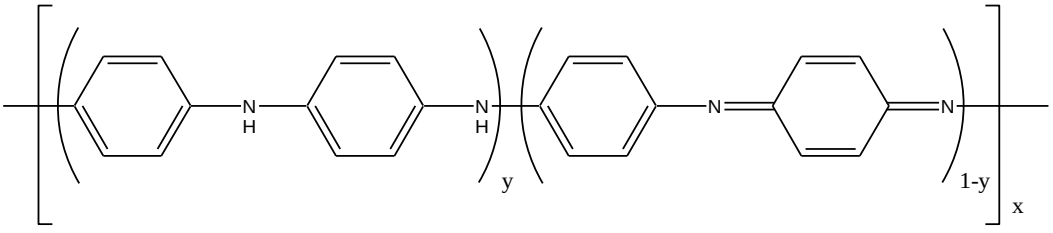


Figure 1. The basic microstructure for *para*-polyaniline.

Poly(*para*-aniline) (*p*-PANi) is general believed to consist of alternating benzenoid and quinoid units as shown in Figure 1. Theoretically, the degree of oxidation can be varied from y = 1 to y = 0.5 to y = 0 giving the completely reduced polymer (leucoemeraldine), the half oxidized polymer (emeraldine), and the completely oxidized polymer (pernigraniline) respectively. To further complicate the matter, PANi can exist in a base form such as emeraldine base or in a protonated salt form such as emeraldine hydrochloride salt [3-5] as shown in Figure 2.

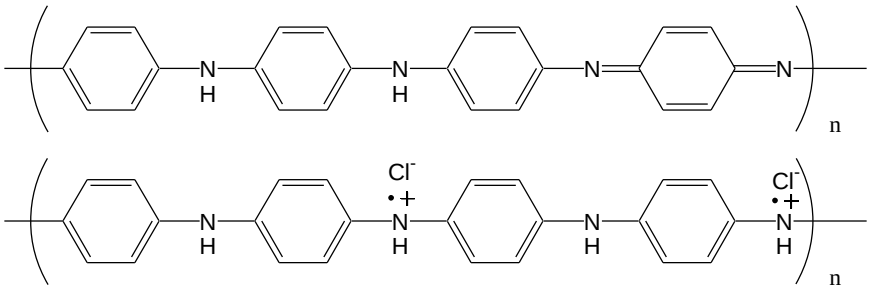


Figure 2. Structure of emeraldine base (top) and emeraldine hydrochloride salt (bottom).

1.1.2 **Methods of Polyaniline Synthesis**

Traditional synthesis of polyaniline can be accomplished in several ways. Polyaniline can by synthesized by either chemical or electrochemical oxidative polymerizations of aniline.[3-5] Recently, metal catalyzed processes have been utilized in the polymerization and will be utilized as the primary method of polymerization in this work.

1.1.2.1 Chemical Synthesis of Polyaniline

Chemical oxidation of aniline is performed in acidic aqueous media using an oxidant such as ammonium peroxydisulfate. A typical chemical oxidation polymerization of aniline would involve polymerization at 0-5 °C with an oxidant in an HCl solution with LiCl.[6] As the

polymerization proceeds, polyaniline precipitates out as the emeraldine hydrochloride salt which can be transformed to the emeraldine base form by treatment with base. The properties of polyaniline produced is dependent upon type of acid used, concentration of acid, oxidant concentration, temperature, reaction time, and presence of neutral salts.[6,7] Molecular weights of polyaniline typically can vary from M_w = 53,000 to M_w = 385,000 for this type of polymerization.

1.1.2.2 Electrochemical Synthesis of Polyaniline

Electrochemical oxidation of aniline is performed via constant current, constant potential, or potential scanning/cycling methods. Generally, electrochemical polymerizations occur at an inert electrode in an electrolytic solution of aniline. The major benefits of using electrochemical polymerizations include control of electrochemical stoichiometry and control of the initiation and termination steps.[7] The resulting PANi polymer is greatly influenced by the conditions used in the polymerization.

1.1.2.3 Metal Catalyzed Synthesis of Polyaniline

Chemical and electrochemical oxidative polymerizations are extremely useful in the synthesis of *para*-PANi. However, the radical couplings utilized in both methods fail on *meta*-substituted or *ortho*-substituted aniline derivatives due to steric and inductance effects.[8] Metal catalyzed C-N bond formation reactions offer an avenue to study both *meta*-substituted and, in our work, *ortho*-substituted PANi derivatives. Two primary metal catalyzed couplings, the Ullmann-Goldberg and palladium couplings, of aryl halides with aryl amines have been utilized in the literature by the Buchwald and Hartwig groups and will function as our primary synthetic methods.

Using the Ullmann-Goldberg copper mediated coupling, *meta*-polyaniline [9-12] and alternating *meta-para*-oligoanilines [13,14] have been prepared for organoferromagnetic purposes. Typical reaction conditions for an Ullmann-Goldberg reaction involve using a copper source such as copper (I) iodide and an inorganic base such as potassium carbonate in an organic solvent at 150 °C for 24-48 h.[15] Recently, Buchwald, Ma, and co-workers have discovered that additives such as amino acids and alkyl diamines promote coupling.[16,17] A drawback to the Ullmann-Goldberg coupling is the allowed radical coupling pathway which produces uncontrollable and largely insoluble materials, possibly due to crosslinking. [11,12,18-20]

The palladium catalyzed coupling of aryl halides and aryl amines is a regiospecific reaction allowing for controlled synthesis of polyaniline derivatives. Both the Hartwig and Buchwald groups have contributed to the advancement of coupling primary and secondary amines with aryl halides.[21-23] The preparation of *meta*-,[24,25] *para*-,[26] and hyperbranched-[24] PANi derivatives as well as oligomers of both *meta*-[27] and *para*-[28] PANi have all been accomplished utilizing the palladium coupling.

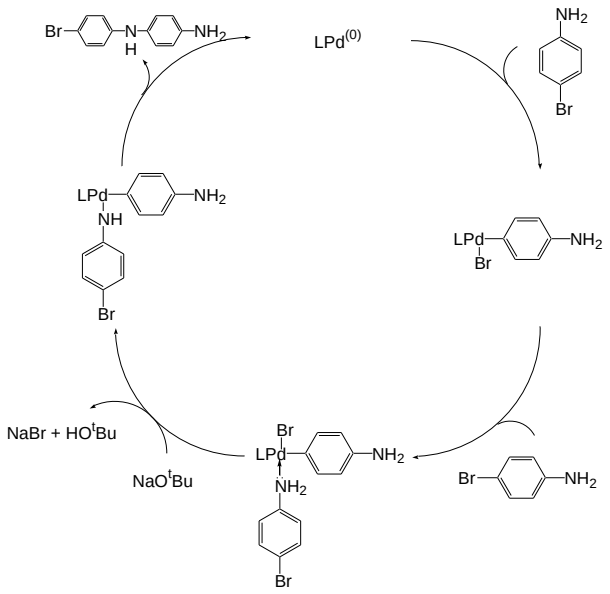


Figure 3. The proposed Pd-catalyzed cycle for *para*-bromoaniline.

Although other pathways have been identified for these systems, the extremely efficient palladium coupling is believed to proceed through the catalytic cycle shown in Figure 3.[29-33] A typical coupling reaction uses a palladium source such as tris(dibenzylideneacetone)dipalladium (Pd_2dba_3) with a bulky phosphine ligand such as 2,2'-bis(diphenylphosphino)-1,1'-binapthyl (BINAP) and sodium *tert*-butoxide (NaO^tBu) as the base in THF at 110 °C for 24 h.[34]

1.1.3 **Synthetic Challenges**

Of the types of polyanilines we have discusses thus far, only *ortho*- and *para*-polyanilines have electrical conducting properties[35] due to the ability of electrons to flow freely along the delocalized π system. The ability of PANi to effectively conduct electrons requires structural rigidity to remain aromatic and leads to low solubility and poor polymer properties.[36]

One approach to increasing the solubility of PANi is to introduce functionality at the *ortho*-position relative to the nitrogen.[37-43] This approach increases the materials solubility but with a distinct decrease in the conductivity[37-43] even under conditions where liquid crystalline substituents are used.[37] One explanation for the decrease in conductivity is that the substituents induce steric strain (Figure 4) and cause chain puckering. Chain puckering reduces π system overlap and effectively localizes the conducting electrons.

We have recently proposed a solution to functionalize PANi without steric strain or chain puckering by preparing an *ortho*-aniline-*para*-aniline copolymer (*p,o*-PANi). A *p,o*-PANi system would allow for functionality on the *ortho*-ring and thus direct the substituent away from the main polymer chain (Figure 4). While the conductivity may be affected by relationships between the new chains, the *p,o*-PANi system should maintain significant conductivity.

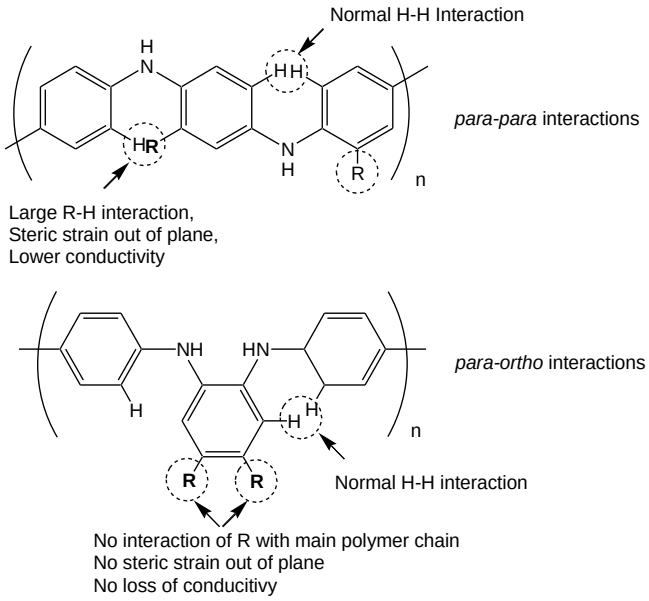


Figure 4. Steric interactions in *p*-PANi and no steric interactions in *p,o*-PANi.

1.1.4 **Synthetic Approach**

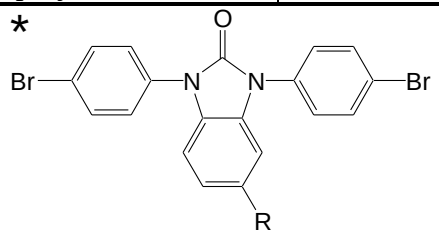
The controlled synthesis of poly(*ortho*-aniline-co-*para*-aniline) is a challenging endeavor. Some *ortho*-aniline units are known to form under chemical oxidative conditions in acidic media.[4445] However, the *para*-position is favored due to less steric hindrance.[7] Direct *o*-polyaniline synthesis are inhibited due to coordination of the *ortho*-diamine to the metal especially palladium. We propose these challenges can be overcome by proper design.

We propose to preassemble *ortho*-ring containing units termed segmers. The recently coined term segmer is distinct from both a monomer and macromonomer (Table 1). The connotation of a monomer is a simple molecule strung together to form a polymer.[46,47] A segmer differs from a monomer in the complexity of the molecule and increased synthetic design. The term macromonomer implies polymerization of an oligomer, long-chain (not necessarily equal length) vinyl monomer, or existing polymer with an available double bond.[46] Often macromonomers are not exact structures with defined limits, e.g. PEG $M_w \approx 1000$. In contrast, a

segmer (Figure 5) is not as large and has a defined chemical structure. Heretofore, we refer to our complex, designed molecules as segmers.

Table 1. Comparison between monomers, segmers, and macromolecules.

Unit	Definition	Examples	Polymer structure
Monomer	Simple molecule used to construct a polymer	Ethylene Acrylonitrile Vinyl acetate	Regular Repeating
Segmer	Designed, complex molecule which has a repeating pattern in a polymer	Segmer A*	Regular Repeating
Macromolecule	Large oligomer, polymer, or long chain vinyl monomer which can be polymerized.	PEG Mw≈ 1000	Repeating, may or may not be regular.



Segmer A

Figure 5. Illustration of targeted Segmer A

Recently, Ward has illustrated the viability of our synthetic reasoning by creating a 5*p,o*-PANi derivative (Figure 6).[48] Using the Ullmann-Goldberg coupling to prepare a segmer followed by a Pd-catalyzed coupling to combine two segmers, Ward has shown that conductivity can be within an order of magnitude as compared to *p*-PANi prepared in a similar manner.[48] While being hampered by small molecular weights, Ward has demonstrated that a *p*-PANi derivative with a regular repeating *ortho*-ring is not detrimental to conductivity of the polymer.[48]

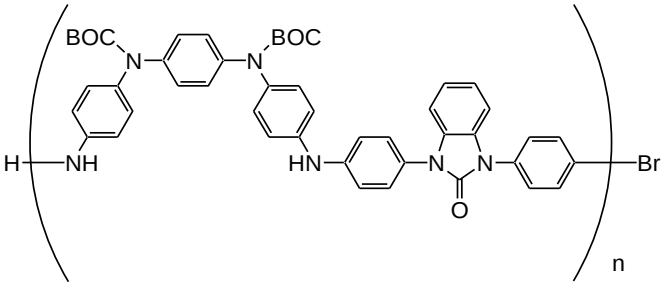


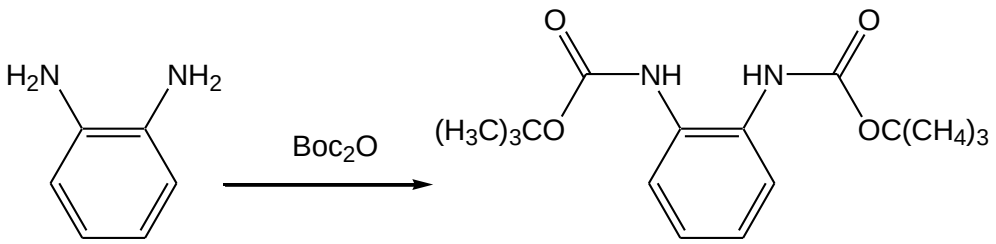
Figure 6. 5 *p,o*-PANi derivative prepared by Ward.

Herein, we report our work to further extend our synthetic abilities to create poly(*ortho*-aniline-co-*para*-aniline) derivatives. We report our attempts to prepare new segmers based upon diamines protected with conventional and unconventional protecting groups. We report our protected diamines reactivity towards both the Ullmann-Goldberg and Pd-catalyzed couplings. We also report our work to extend Ward's research towards creating a substituted 5*p,o*-PANi derivative.

1.2 **RESULTS**

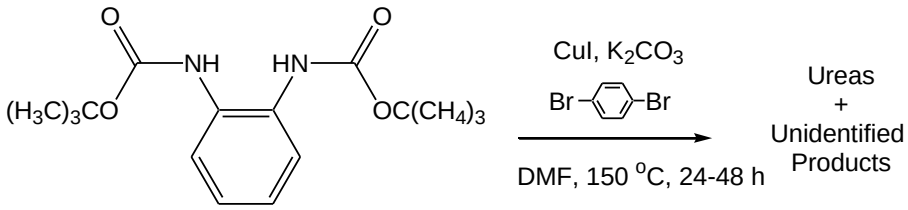
1.2.1 **BOC Protection of *ortho*-Diamine**

In an attempt to prepare a *para-ortho-para* segmer without the uncleavable urea protecting group we attempted an Ullmann-Goldberg coupling on a diBOC-protected *ortho*-diamine. The BOC-protected substrate was prepared by the reaction of *o*-phenylenediamine with two equivalents of BOC_2O in methylene chloride (53% yield) (Scheme 1). The ^1H NMR spectrum of carbamate **1** in $CDCl_3$ exhibited a distinctive broad singlet at δ 7.46 that was consistent with the presence of the secondary N-H moiety. The ^{13}C NMR spectrum showed the expected downfield resonance at δ 154 that is typical for the BOC protecting group. Unfortunately, when subjected to our typical Ullmann-Goldberg conditions in the presence of 1,4-dibromobenzene, urea and unidentified products were observed (Scheme 2).



1

Scheme 1. BOC protection of *o*-phenylenediamine



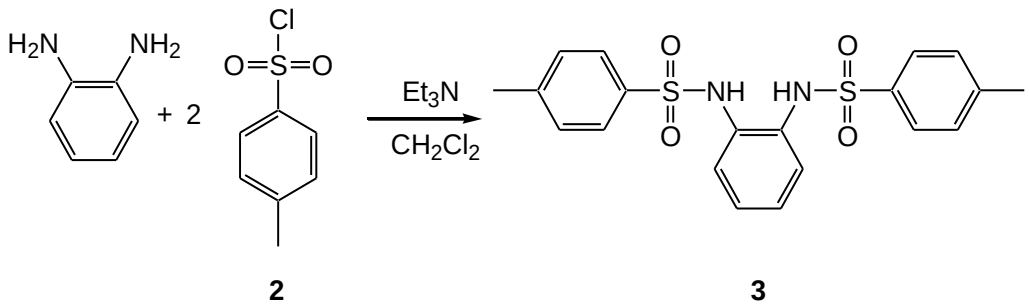
1

Scheme 2. Ullmann-Goldberg reaction of BOC protected *o*-diamine

The complications surrounding performing an Ullmann-Goldberg coupling on a BOC protected *ortho*-diamine led us to consider other protecting groups. In particular we focused on three distinct classes; sulfonamides, amides, and carbamates.

1.2.2 **Synthesis and reactivity of several sulfamides**

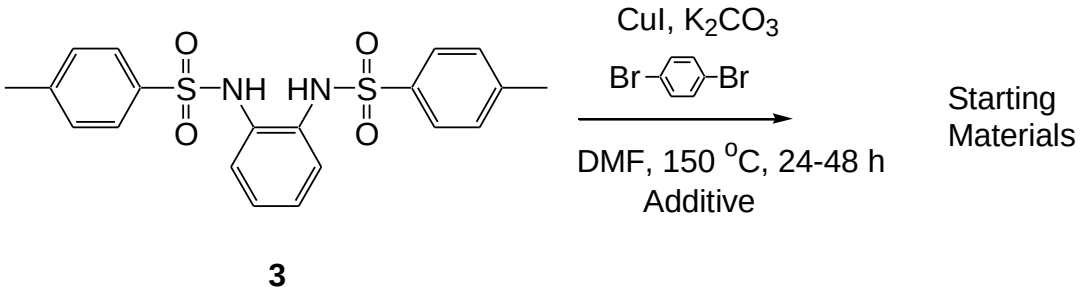
Sulfamide **3** was prepared by the condensation of *o*-phenylenediamine and *p*-toluenesulfonyl chloride **2** in the presence of triethylamine in methylene chloride (71% yield) (Scheme 3). The ^{1}H NMR spectrum of compound **3** in $CDCl_3$ exhibited a singlet at δ 7.57 corresponding to the N-H protons that integrated properly with respect to the methyl protons at δ 2.39. The parent peak (M^{+}) was observable by GC/MS at 416 m/z.



2 **3**

Scheme 3. Preparation of sulfamide 3

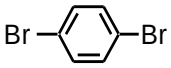
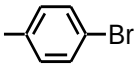
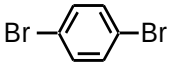
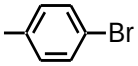
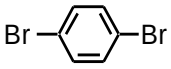
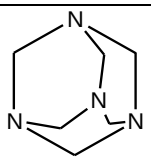
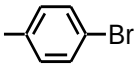
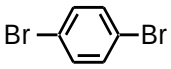
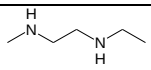
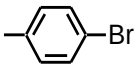
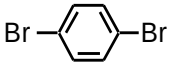
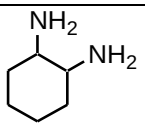
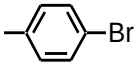
Compound **3** was reacted with 1,4-dibromobenzene under our standard Ullmann-Goldberg coupling conditions in DMF and toluene (Scheme 4). Unfortunately in both solvents the coupling reaction was unsuccessful and yielded only starting materials by GC-MS (Entries 1-2, Table 2). Compound **3** in our standard palladium couplings yielded equally unproductive results as only starting materials were isolated.



3

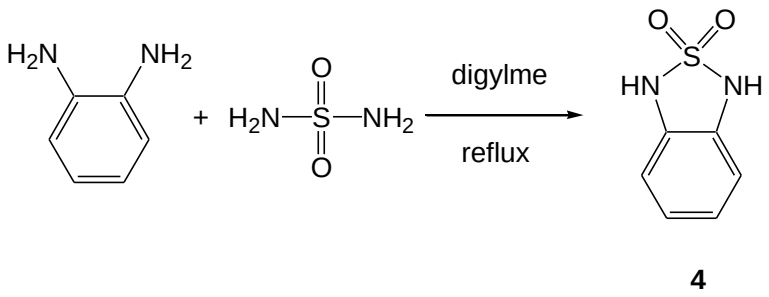
Scheme 4. Ullmann-Goldberg coupling with sulfonamide 3

Table 2. Ullmann-Goldberg coupling of sulfonamides

Entry	Aryl Bromide	Base	Additive	Solvent	Products		
					Time/ min	m/z	Identification (M, m, t)[a]
1		K_2CO_3	None	DMF	3.18	236	 (M)
2		K_2CO_3	None	Toluene	3.19	236	 (M)
3		K_3PO_4		DMF	3.05	236	 (M)
					10.72	247	Unknown (m)
					13.65	337	Unknown (m)
4		K_3PO_4		Toluene	3.07	236	 (M)
					10.85	247	Unknown (m)
					14.84	401	Unknown (m)
5		K_3PO_4		Toluene	3.06	236	 (M)
					10.77	247	Unknown (m)
					15.17	393	Unknown (m)
					15.51	401	Unknown (m)

[a]M = Major product; m= minor product; t= trace product

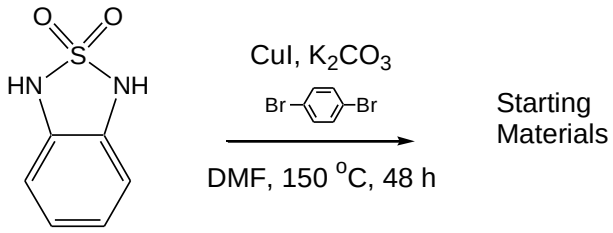
Sulfamide **4** was prepared from *o*-phenylenediamine and sulfonamide in diglyme[49] (23% yield) (Scheme 5). The ^{1}H NMR spectrum indicates the NH signal appears at δ 11.0 and integrates properly with respect to the aryl region at δ 6.84. The ^{13}C NMR spectrum displays the expected single ipso carbon and two distinct aryl CH carbons.



4

Scheme 5. Synthesis of sulfamide 4

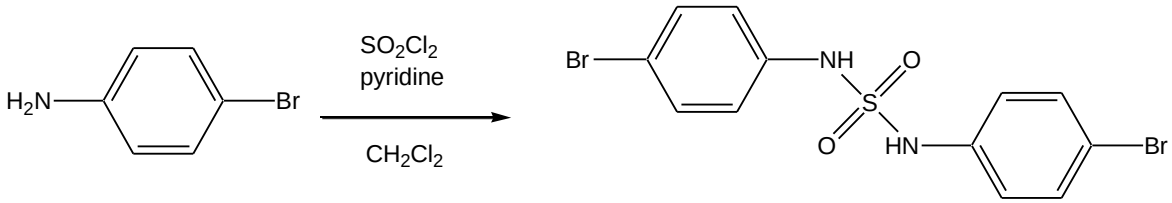
Compound **5** was reacted with 1,4-dibromobenzene under standard Ullmann-Goldberg coupling conditions in DMF (Scheme 6). The reaction yielded only starting materials after work up and analysis by GC-MS. When compound **4** was reacted with 1,4-dibromobenzene under palladium coupling conditions only starting materials were isolated.



4

Scheme 6. Ullmann-Goldberg reaction of sulfamide 4

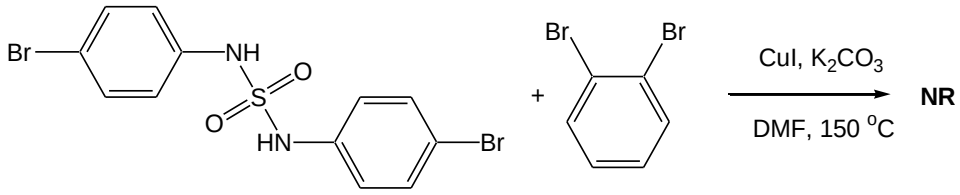
Sulfamide **5** was prepared from *p*-bromoaniline and SO_2Cl_2 in methylene chloride in the presence of pyridine[50] (42% yield) (Scheme 7). The ^{1}H NMR spectrum exhibited a signal at δ 9.30 for the N-H proton which integrated properly with the aryl region at δ 7.38 and δ 7.02. The ^{13}C NMR spectrum indicated two ipso and two aryl CH carbons.



5

Scheme 7. Synthesis of sulfamide 5

Sulfamide **5** was reacted with 1,2-dibromobenzene under standard Ullmann-Goldberg coupling conditions in DMF (Scheme 8). Unfortunately, the reaction yielded only starting materials or unidentifiable minor products by GC-MS. Compound **5** and 1,2-dibromobenzene were also reacted under standard palladium coupling conditions and yielded only starting materials by GC-MS analysis.



5

Scheme 8. Ullmann-Goldberg reaction of sulfamide 5

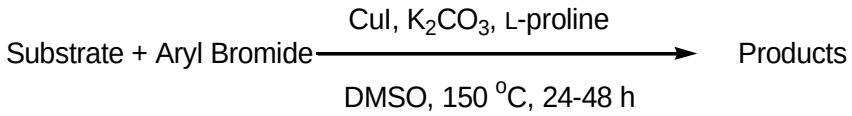
1.2.3 **Optimization of Ullmann-Goldberg Reaction**

In a recent paper reported by Buchwald,[17] the authors reported the utility of certain diamines as additives to the Ullmann-Goldberg reaction. We explored this variation by running a series of reactions utilizing N,N'-dimethyl-ethane-1,2-diamine, 1,2-diaminocyclohexane and hexamethylenetetramine as additives. All of the reactions were run under our typical conditions for an Ullmann-Goldberg coupling. The results (Entries 3-5, Table 2) indicated that none of the additives benefited the reaction.

However, another paper[16] published shortly afterwards which used amino acids as additives to promote the Ullmann-Goldberg coupling. One example in particular involving the coupling of benzylamine with 1,4-dibromobenzene in the presence of L-proline was seemed relevant to our work. We attempted several reactions to study the utility of using L-proline in our system. Based on work done by Ma *et al.*,[16] we decided to add 2 molar equivalents of L-proline

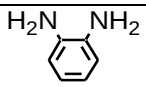
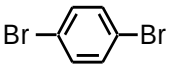
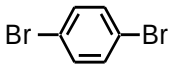
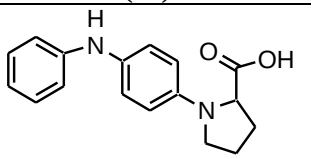
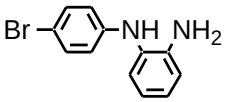
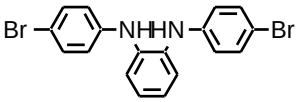
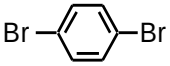
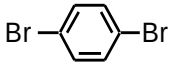
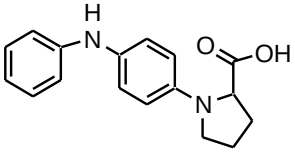
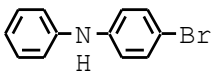
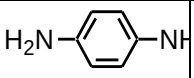
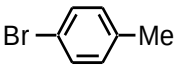
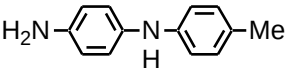
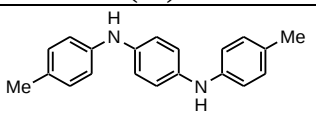
per equivalent of copper catalyst and to fix the reaction time at 24 h. Initial results of the reaction between *o*-phenylenediamine and 1,4-bromobeznene (Entry 1, Table 3) indicated that some of the desired product was being formed, however, low yields were evident in the low abundances in the GC-MS data and the large excess of 1,4-dibromobenzene.

In order to understand the effects of L-proline on the system, we engaged in several small scale experiments to probe different conditional changes (Scheme 9). We reacted aniline with 1,4-dibromobenzene and observed the desired product GC (Entry 2, Table 3). However, when *p*-phenylenediamine is reacted with 4-bromotoluene (Entry 3, Table 3), we observed that the major product was the mono-coupled product while the di-coupled product was formed only in small quantities.



Scheme 9. L-Proline mediated Reaction of Amines with Aryl Bromides

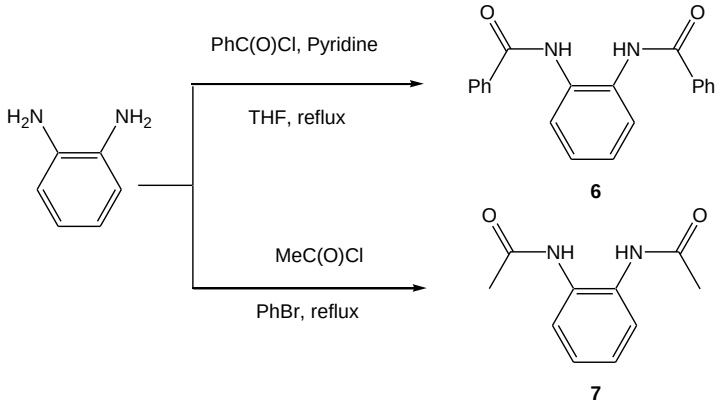
Table 3. L-proline study

Entry	Substrate	Aryl Bromide	Products		
			Time/ min	m/z	Identification[a]
1			3.05	236	 (M)
			4.26	282	 (m)
			10.97	262	 (m)
			15.84	418	 (t)
2			3.15	236	 (M)
			4.27	282	 (m)
			9.53	247	 (m)
3			10.18	198	 (M)
			14.80	288	 (t)

[a]M = Major product; m = minor product; t = trace product

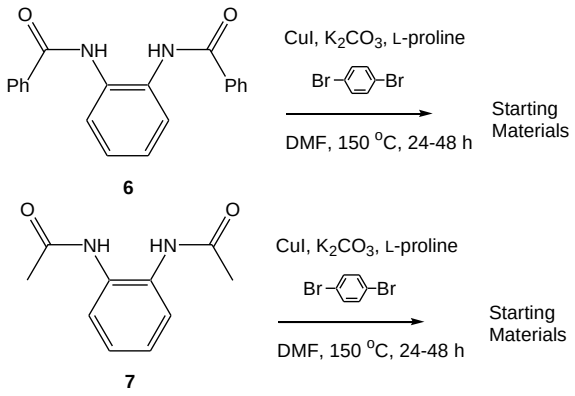
1.2.4 **Amide Synthesis and Reactivity**

We attempted the synthesis of two amides as possible protecting groups for the Ullmann-Goldberg coupling (Scheme 10). Amide **6** was prepared by reaction of *o*-phenylenediamine with benzoyl chloride in THF (56% yield). The characteristic amide signal occurred as a singlet at δ 10.0 in d_6-DMSO. Amide **7** was prepared by reaction of *o*-phenylenediamine with acetyl chloride in bromobenzene (62%). Amide **7** in d_6-DMSO also exhibited a downfield amide resonance at δ 10.4 in the ^{1}H NMR spectrum and the appropriate mass by GC-MS (192 M^+).



Scheme 10. Amide synthesis from *o*-phenylenediamine

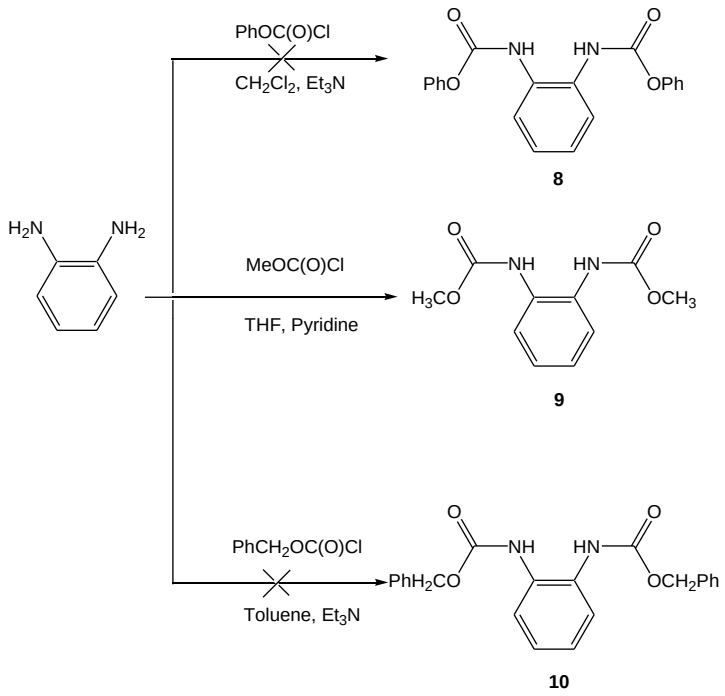
Our attempt at performing the Ullmann-Goldberg reaction with amide **6** and amide **7** using our typical methods was unsuccessful (Scheme 11). When amide **6** was reacted with 1,4-dibromobenzene with L-proline present, a large amount of 1,4-dibromobenzene was observed as unreacted starting material in the GC-MS. When attempts to perform the palladium coupling on amide **6** failed, we were not surprised because of the known problem of palladium coordination. When amide **7** was reacted with 1,4-dibromobeznene with L-proline present, only starting materials were observed in the GC-MS data.



Scheme 11. Ullmann-Goldberg Reaction with Amides 6 and 7

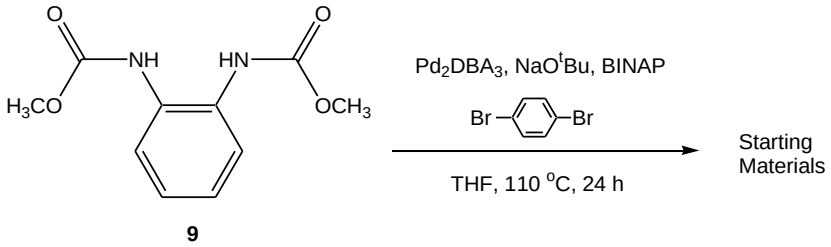
1.2.5 **Carbamate Synthesis and Reactivity**

We attempted to synthesize three different carbamates for use in our typical Ullmann-Goldberg coupling reaction (Scheme 12). After several attempts, carbamates **8** and **10** proved too difficult to synthesize and purify in decent quantities from *o*-phenylenediamine and the corresponding chloroformate. However, carbamate **9** was synthesized from *o*-phenylenediamine and methyl chloroformate (32% yield). The ^{1}H NMR spectrum in d_6-DMSO exhibited a broad singlet at δ 8.78 attributed to the N-H protons and integrated properly to the methyl signal at δ 3.60.



Scheme 12. Carbamate synthesis from *o*-phenylenediamine

Carbamate **9** proved unsuitable as a substrate for palladium coupling (Scheme 13); only starting materials were observed in the reaction mixture by GC/MS. The Ullmann-Goldberg coupling reaction was not performed on carbamate **9**.



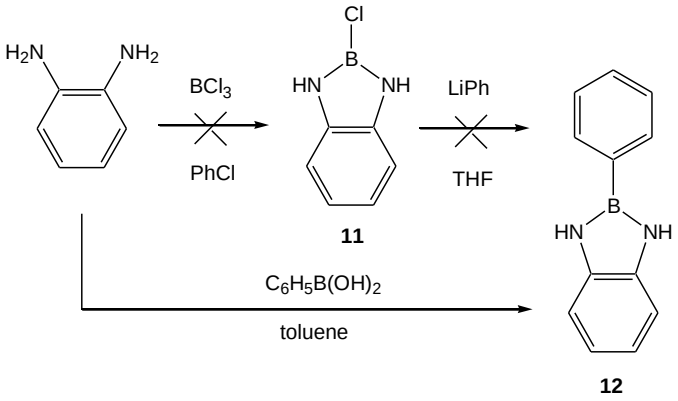
Scheme 13. Pd-Catalyzed Reaction of Carbamate 9

1.2.6 **Synthesis and Reactivity of Bridged Diazaborole**

Since none of our attempts at protecting the diamines with two protecting groups were fruitful, we decided to look at the possibility of utilizing other strategies. One strategy that we found particularly interesting was the idea of creating bridging protecting groups, the strategy

that had proved quite useful in the case of urea. We found that there were several reasonable candidates for these bridging compounds and synthesized several to test their utility in the Ullmann-Goldberg coupling as well as the palladium coupling.

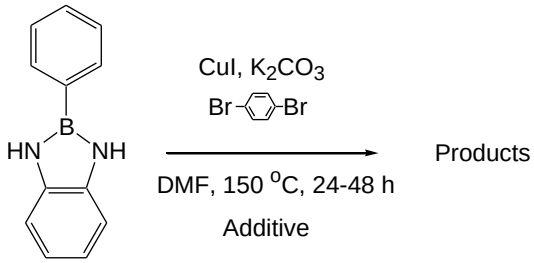
In an attempt to make a bridging *ortho*-diamine compound capable of undergoing the Ullmann-Goldberg coupling or palladium coupling, we synthesized compound **12** (Scheme 14). The literature method by Pellicciotto[51] was attempted but was not successful. An alternate synthesis using *o*-phenylenediamine and phenylboronic acid in toluene was developed and gave compound **12** in good yield (85%). The ^{1}H NMR spectrum in d_4-THF of compound **12** exhibits the distinctive N-H signal at δ8.31 as a broad singlet which integrated properly to the aryl region. The ^{13}C NMR spectrum in d_4-THF was curiously absent one carbon signal which is attributed to either overlap or delay time issues. The compound exhibits a retention time of 9.8 min and an m/z of 194 for the M^+ ion by GC/MS analysis.



Scheme 14. Synthesis of bridged diazaborole 12

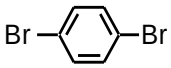
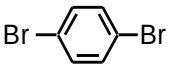
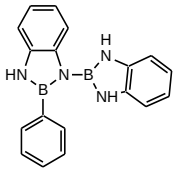
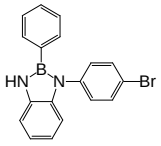
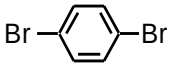
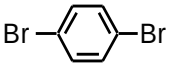
The Ullmann-Goldberg coupling was attempted on compound **12** using a variety of different conditions (Scheme 15). Compound **12** was reacted with both 1,4-dibromobenzene (Entries 1-4, Table 4) and 4-bromotoluene (Entries 5-7, Table 4). Compound **12** was reacted in various solvents (Entries 1-7, Table 4), with L-proline present (Entries 1 & 5, Table 4), and without L-proline (Entries 2-4 & 6-7, Table 4). Unfortunately, in all cases the desired product

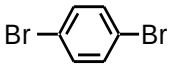
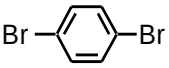
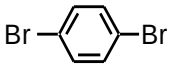
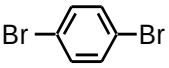
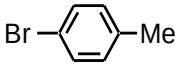
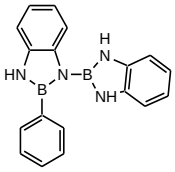
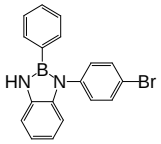
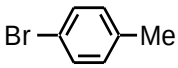
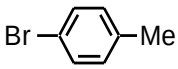
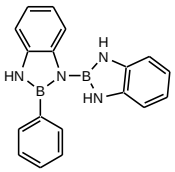
was not observed. The monocoupled product, which exhibited the correct mass and bromide isotope pattern, was observed (Entries 1 & 5, Table 4) when L-proline was used in the reaction. Only starting materials were observed for all of the other entries.



Scheme 15. Ullmann-Goldberg Reaction of Diazaborole

Table 4. Ullmann-Goldberg reactions of diazaboroles

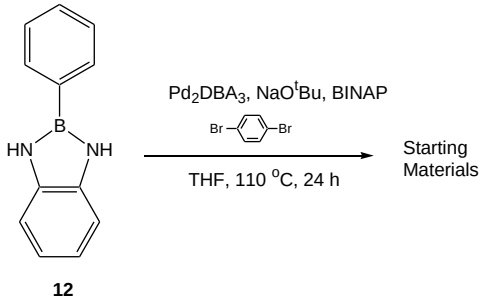
Entry	Aryl Bromide	Base	Additive	Solvent	Products		
					Time/ min	m/z	Identification[a]
1		K_2CO_3	L-proline	DMSO	3.08	236	 (M)
					9.78	194	(**12**) (M)
					12.81	312	 (m)
					14.21	350	 (m)
2		K_2CO_3	None	THF	2.98	236	 (M)
					4.17	284	Unknown (m)
					9.64	194	(**12**) (M)

3		K_2CO_3	None	Toluene	2.96	236	 (M)
					9.64	194	(**12**) (m)
4		NaO^tBu	None	THF	2.96	236	 (M)
5		K_2CO_3	L-proline	DMSO	9.79	194	(**12**) (M)
					12.80	312	 (m)
					13.00	284	 (m)
6		K_2CO_3	None	DMSO	2.61	216	Unknown (m)
					9.84	194	(**12**) (M)
7		K_2CO_3	None	THF	5.99	221	Unknown (m)
					9.70	194	(**12**) (M)
					12.65	312	 (m)

[a]M = Major product; m= minor product; t= trace product

We attempted the palladium coupling on compound **12** hoping to benefit from the strategic placement of the protecting group (Scheme 16). Using our standard conditions with Pd_2DBA_3/ BINAP as our catalyst system, we found that the desired product was present in trace amounts as mostly starting material was observed in the GC-MS. Curiously, a small amount of compound **12** reacted to cleave both boron-nitrogen bonds and couple one equivalent of aryl

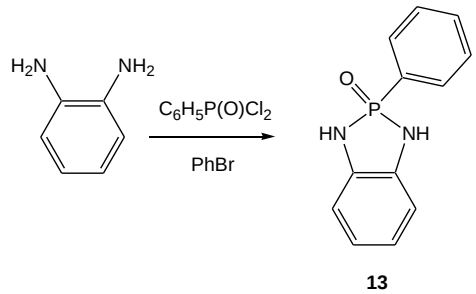
halide. To an even smaller extent, some of compound **12** had been deprotected and coupled with two equivalents of aryl halide to produce the desired product.



Scheme 16. Pd-Catalyzed Reaction of Diazaborole

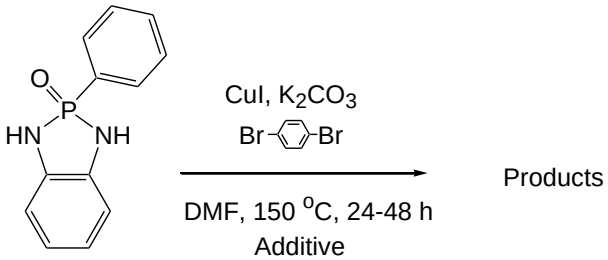
1.2.7 **Synthesis and Reactivity of Bridged Diazaphosphole Oxide**

A diazaphosphole oxide, another *ortho*-diamine bridging compound, was synthesized by methods similar to those used by Wagner *et al.*[52] and Norman *et al.*[53] Compound **13** (Scheme 17) was prepared by reaction of *o*-phenylenediamine with dichlorophosphinoxide in bromobenzene (79% yield). The ^{1}H NMR spectrum in d_6-DMSO exhibited a singlet at δ 8.60 which corresponds to the two N-H protons and integrated properly to the aryl region. The ^{13}C NMR spectrum in d_6-DMSO was complicated because of two different conformations of the molecule and could be completely assigned. The ^{31}P NMR spectrum exhibited only one signal at δ 24.8 relative to phosphoric acid.



Scheme 17. Synthesis of diazaphosphole oxide from *o*-phenylenediamine

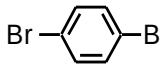
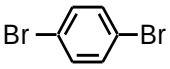
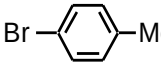
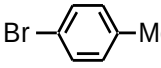
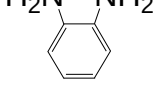
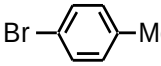
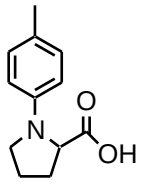
The Ullmann-Goldberg coupling was attempted on compound **13** using a variety of different conditions (Scheme 18). Compound **13** was reacted with both 1,4-dibromobenzene (Entries 1, Table 5) and 4-broomtoulene (Entries 2-4, Table 5). Compound **13** was reacted in various solvents (Entries 1-4, Table 5), with L-proline present (Entries 1-2, Table 5), and without L-proline (Entries 3-4, Table 5). Unfortunately, in all cases the desired product was not observed. Starting materials were either observed or discarded in the work up.



13

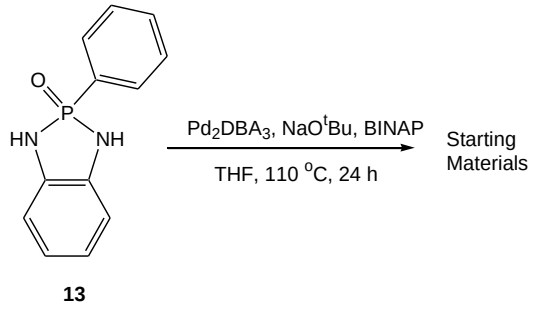
Scheme 18. Ullmann-Goldberg reaction of diazaphosphole oxide

Table 5. Ullmann-Goldberg reactions of diazaphosphole oxides

Entry	Aryl Bromide	Base	Additive	Solvent	Products		
					RT	m/z	Identification[a]
1		K_2CO_3	L-proline	DMSO	3.08	236	 (M)
2		K_2CO_3	L-proline	DMSO	6.43	220	Unknown (M)
3		K_2CO_3	None	DMSO	3.12	108	 (M)
4		K_2CO_3	None	THF	6.00	205	 (M)

[a]M = Major product; m= minor product; t= trace product

We decided to try compound **13** in a palladium coupling to attempt to promote the palladium coupling by occupying the site between the two amino groups (Scheme 19). We attempted the coupling using 4-bromotoluene or 1,4-dibromobenzene and our standard conditions utilizing a Pd_2DBA/BINAP catalyst system in THF. The reaction of **13** with 4-bromotoluene and 1,4-dibromobenzene yielded primarily starting materials by GC-MS analysis. Unexpectedly, the reaction of compound **13** with 1,4-dibromobenzene produced minor amounts of deprotected mono-coupled diamine and trace amounts of deprotected di-coupled diamine as cleavage of both phosphorus-nitrogen bonds was accomplished.

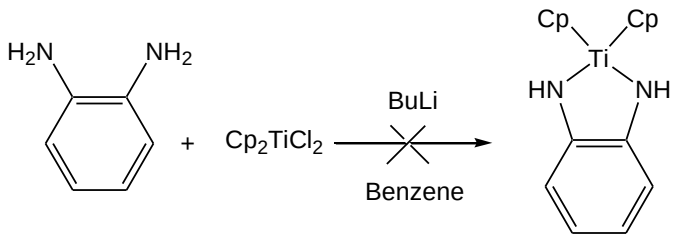


13

Scheme 19. Pd-catalyzed coupling of diazaphosphole oxides

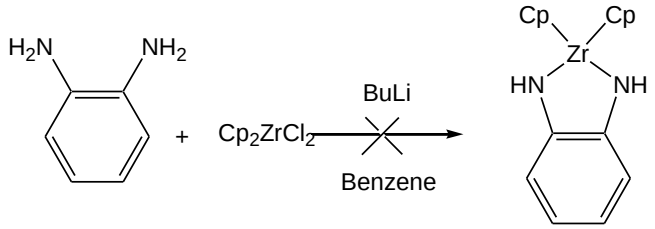
1.2.8 **Metal Complexes as Bridges for Diamines**

We attempted to synthesize *o*-diamine compounds containing a bridged metal complex. From the literature[54] we identified titanium compound **14** (Scheme 20) and zirconium compound **15** (Scheme 21) as possible candidates for use in both coupling methods based upon *o*-phenylenediamine and the corresponding Cp_2MCl_2 (M = Ti, Zr). Unfortunately, we were unable to reproduce the literature synthesis.



14

Scheme 20. Proposed Synthesis of compound 14



15

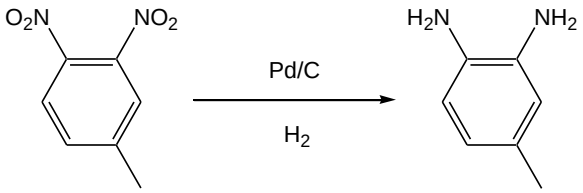
Scheme 21. Proposed Synthesis of compound 15

1.2.9 **Preparation of *ortho*-substituted amines**

After having no success with either protecting the diamine or using bridging protecting groups, we returned to the urea methodology developed by Ward and focused our attention on creating a substituted derivative of the *p,o*-polymer prepared by Ward.[48,55] We attempted to synthesize the appropriately substituted segmer and prepare a polymer which could be compared in terms of properties to the *p,o*-polymer prepared previously by Ward.

Since our intention is to prepare *para,ortho*-copolymers with groups attached to the 4- or 5-positions of the *ortho* rings, we have prepared a trimeric segmer with a methyl substituent. The methyl substituted diamine **17** is not commercially available but can be easily prepared by Pd/C-catalyzed reduction of 3,4-dinitrotoluene **16** under atmospheric hydrogen (Scheme 22).

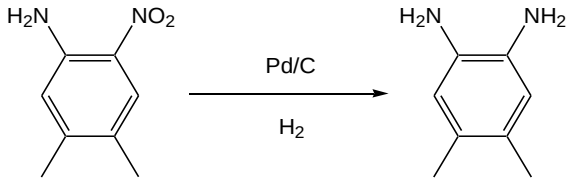
Yields are excellent (> 90%) and the ^{1}H NMR spectrum exhibits the expected resonance for the primary aryl amines at δ 4.01 which integrate properly with respect to the methyl resonance at δ 2.89.



16 **17**

Scheme 22. Hydrogenation of 3,4-dinitrotoluene

Similarly, a dimethyl substituted *ortho*-diamine **19** was prepared by utilizing the commercially available 4,5-dimethyl-2-nitro-aniline **18** in a Pd/C-catalyzed reduction (Scheme 23). Yields were excellent (> 90%) and the ^{1}H NMR spectrum exhibits the expected resonance for the primary aryl amines at δ 3.97 which integrate properly with respect to the methyl resonance at δ 2.84.



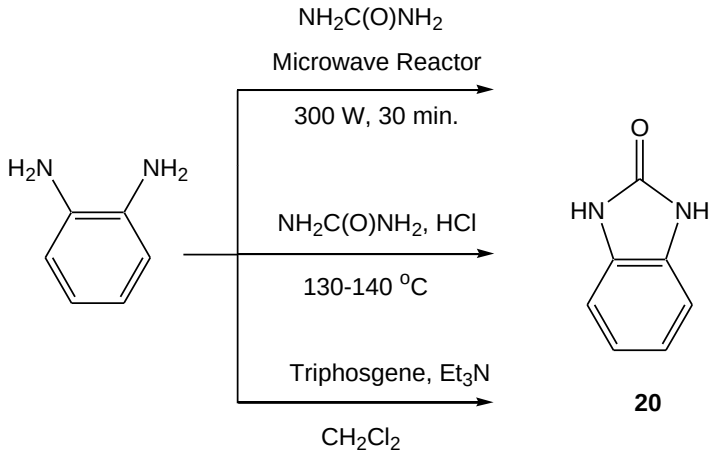
18 **19**

Scheme 23. Hydrogenation of 4,5-dimethyl-2-nitro-aniline

1.2.10 **Urea Synthesis and Characterization**

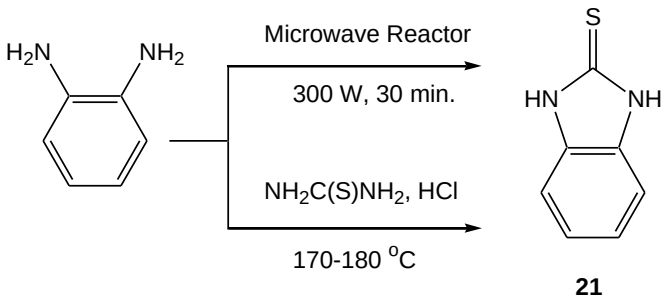
Compound **20** can be synthesized from *o*-phenylenediamine and urea in a variety of ways (Scheme 24). Although the most efficient transformation method was to react the starting materials in a microwave reactor (84% yield), the gas-producing reaction proved difficult to control upon scaling up. Lower and variable yields could be obtained by conventional heating to 130-140 °C of the diamine and urea in the presence of HCl in methanol (32% best yield). In an

attempt to increase yields, we explored an alternative preparation of compound **20**. Based upon a modification of the procedure used by Zhu,[56] treatment of *o*-phenylenediamine with triphosgene in methylene chloride gave **20** in 92% yield. The ^{1}H NMR spectrum in d_6-DMSO of compound **20** has a very distinctive singlet at δ 10.56 corresponding to the amide N-H protons and integrated properly to the aryl region.



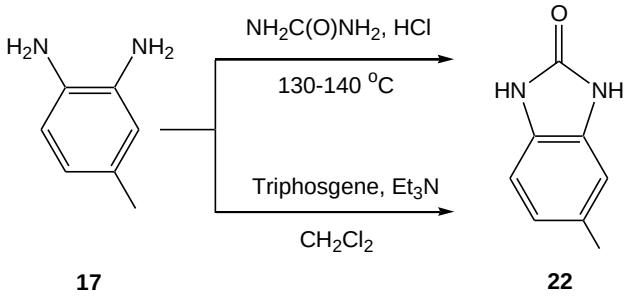
Scheme 24. Synthesis of Urea 20

Compound **21** can be synthesized from *o*-phenylenediamine and thiourea in the same manner as compound **20**. Microwave reaction of the two starting materials affords pure compound **21** (84% yield) but it proved difficult to contain or vent the ammonia gas produced in the microwave reactor system. Reaction of the starting materials with treatment of HCl in methanol requires higher temperatures (170-180 °C) and more time than compound **20** with variable yields (45% best yield). The ^{1}H NMR spectrum in d_6-DMSO exhibits a singlet from the thioamide N-H at δ 12.5 which is typical for these compounds.



Scheme 25. Synthesis of thiourea 21

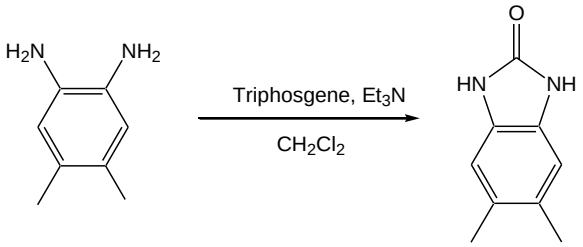
In an attempt to make a 4-methyl-substituted *para-ortho-para*-segmer, we synthesized urea **22** (Scheme 26). Urea **22** was prepared by reaction of 4-methyl-diaminobenzene with urea after treatment with an HCl/methanol solution to give variable yields (49% best yield). Based upon a modification of the procedure by Zhu,[56] a better synthesis of urea **22** was treatment of 4-methyl-diaminobenzene with triphosgene in methylene chloride in the presence of triethylamine (96% yield). The ^{1}H NMR spectrum exhibited the proper amide signal at δ 10.46 which appropriately integrated to the methyl signal at δ 2.18. The ^{13}C NMR spectrum showed three ipso, three aryl, and one alkyl carbon as expected.



Scheme 26. Synthesis of methyl urea 22

Based upon a modification of the procedure by Zhu,[56] a 4,5-dimethyl substituted urea **23** can be prepared by reaction of 4,5-dimethyl-1,2-diaminobenzene with triphosgene in methylene chloride in the presence of triethylamine (Scheme 27) (95.8% yield). The ^{1}H NMR spectrum

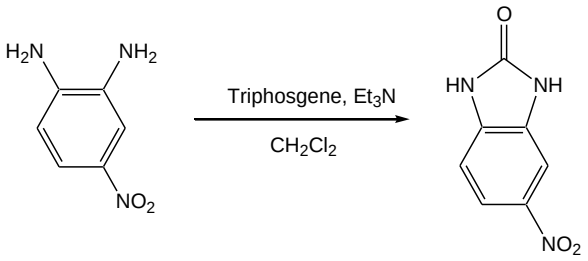
exhibited the proper amide signal at δ 10.13 which appropriately integrated to the methyl signal at δ 2.15. The ^{13}C NMR spectrum showed three ipso, one aryl, and one alkyl carbon as expected.



19 **23**

Scheme 27. Synthesis of dimethyl urea 23

Prepared by a modification of the procedure outlined by Zhu,[56] the nitro substituted urea **24** can be prepared by reaction of 4-nitro-1,2-diaminobenzene with triphosgene in methylene chloride in the presence of triethylamine (Scheme 28) (92% yield). The ^{1}H NMR spectrum exhibited the proper amide signals at δ 11.44 and δ 11.21 and integrated appropriately to the correct pattern of aryl protons at δ 7.91-7.07. The ^{13}C NMR spectrum showed four ipso and three aryl carbons as expected.



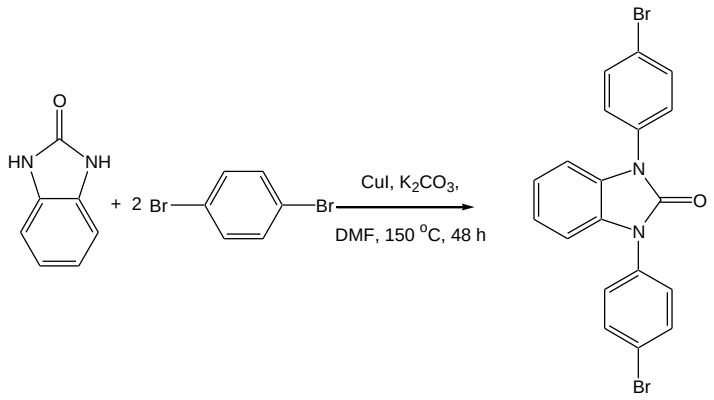
24

Scheme 28. Synthesis of nitro urea 24

1.2.11 **Segmer Synthesis via Ullmann-Goldberg Reaction**

The Ullmann-Goldberg coupling of urea **20** with 1,4-bromobenzene was originally done by Ward in 28% yield with a variety of side products produced.[48,55] Utilizing standard Ullmann-

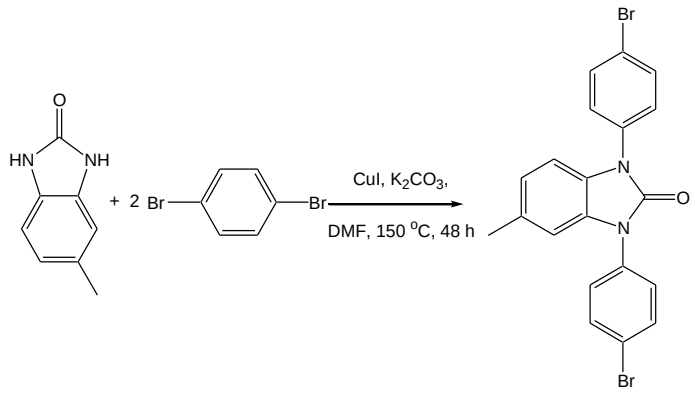
Goldberg conditions under a nitrogen atmosphere, we attempted to couple urea **4** with 1,4-dibromobenzene at 150 °C for 48 h (Scheme 29) and obtained segmer **25** (38% yield crude) after column chromatography (CH_2Cl_2 /Hexanes) (6% yield pure). The ^1H NMR spectrum in $CDCl_3$ shows distinct aryl signals at δ 7.7, 7.5, and 7.1, and comparison to Ward's spectra[48,55] confirms the identification of segmer **25**. The ^{13}C NMR spectrum in $CDCl_3$ exhibits the expected aromatic signals and also compares well to Ward's results.[48,55]



20 **25**

Scheme 29. Synthesis of Segmer 25

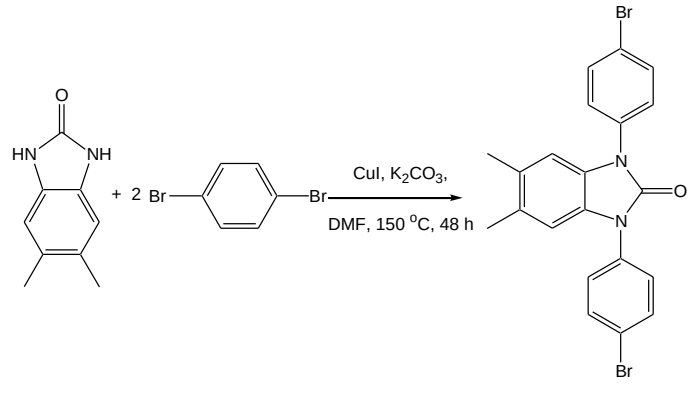
The Ullmann-Goldberg coupling of urea **22** with 1,4-dibromobenzene was expected to proceed in the same fashion as the synthesis of segmer **25**. Segmer **26** was isolated (27% yield crude) by column chromatography (CH_2Cl_2/Hexanes) (6% yield pure) after reaction of urea **22** with 1,4-dibromobenzene at 150 °C for 48 h under standard Ullmann-Goldberg conditions and a nitrogen atmosphere (Scheme 30). The ^1H NMR spectrum in $CDCl_3$ shows aryl signals at δ 7.7, 7.5, and 6.9 and integrates properly to the methyl signal at δ 2.3. The ^{13}C NMR spectrum in $CDCl_3$ exhibits the expected aromatic signals along with one methyl signal.



22 **26**

Scheme 30. Synthesis of Segmer 26

The Ullmann-Goldberg coupling of urea **23** with 1,4-dibromobenzene was expected to proceed in the same fashion as the synthesis of segmers **25**. Segmer **27** was isolated by column chromatography (CH_2Cl_2/ Hexanes) (4.5% yield pure) after reaction of urea **23** with 1,4-dibromobenzene at 150 °C for 48 h under standard Ullmann-Goldberg conditions and a nitrogen atmosphere (Scheme 31). The ^{1}H NMR spectrum in $CDCl_3$ shows aryl signals at δ 7.46 and δ 7.39 which integrated properly to the methyl signal at δ 2.43. The ^{13}C NMR spectrum in $CDCl_3$ exhibits the expected aromatic signals along with one methyl signal.

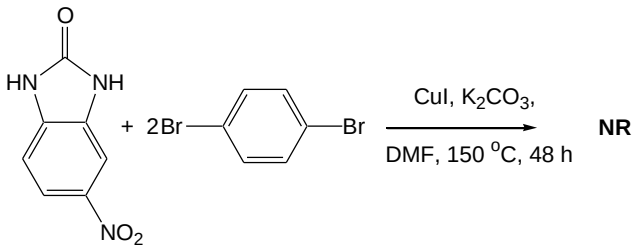


23 **27**

Scheme 31. Synthesis of Segmer 27

The Ullmann-Goldberg coupling of urea **24** with 1,4-dibromobenzene was expected to proceed in the same fashion as established methodology (Scheme 32). However, when urea **24** was reacted with 1,4-dibromobenzene at 150 °C for 48 h under standard Ullmann-Goldberg

conditions and a nitrogen atmosphere, no product was isolated by chromatography (CH_2Cl_2/ Hexanes). Reaction samples analyzed by GC/MS indicated no coupling was occurring even after attempts to modify reaction conditions.

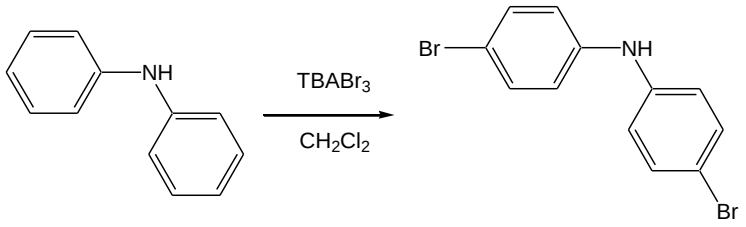


24

Scheme 32. Ullmann-Goldberg reaction of urea 24

1.2.12 **Preparation of BOC-Protected co-monomers**

Compound **28** was prepared by adding $TBABr_3$ to a solution of diphenylamine in dichloromethane (96% yield) (Scheme 33).[57] The pure product displays ^{1}H NMR signals at δ 5.69 for the N-H proton which integrates properly with the aryl region signals at δ 7.38 and 6.94. The ^{13}C NMR spectrum exhibits the expected two ipso carbons and two CH carbons.

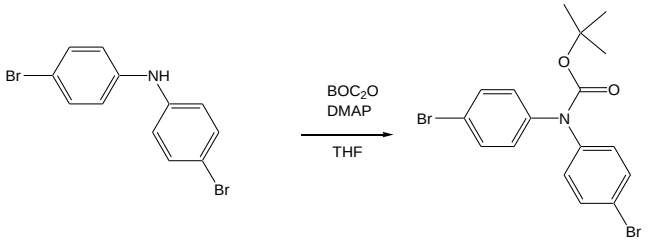


28

Scheme 33. Synthesis of Compound 28

The BOC protected bromo-dimer **29** was prepared according to the methodology outlined by Basel[58] and more recently by Hirao.[59,60] The reaction of compound **28** with DMAP and BOC_2O in dry THF produced the desired dimer **29** in 82% yield (Scheme 34). The ^{1}H NMR spectrum indicates proper integration between the aryl signals at δ 7.41 and δ 7.05 and the *tert*-

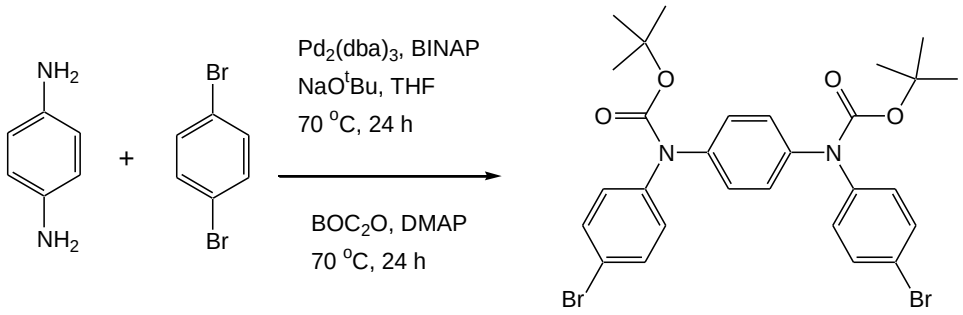
butyl signal at δ 1.44. The ^{13}C NMR spectrum exhibits the expected C=O signal at δ 152.7, three ipso carbons, two aryl carbons, and one alkyl carbon.



28 **29**

Scheme 34. Preparation of Dimer 29

Bromotrimer **30** was prepared by reaction of *p*-diaminobenzene and *p*-dibromobenzene in THF solution under palladium coupling conditions in 52% yield[28] (Scheme 36). The reaction was amiable to performing the coupling and subsequent BOC protection of the amines in a one pot process. The ^{1}H NMR spectrum indicates the proper integration between the aryl signals at δ 7.42, 7.14, and 7.09 and the *tert*-butyl signal at δ 1.45. The ^{13}C NMR spectrum exhibits the expected 5 ipso carbons, 3 aryl carbons, and 1 *tert*-butyl carbon.

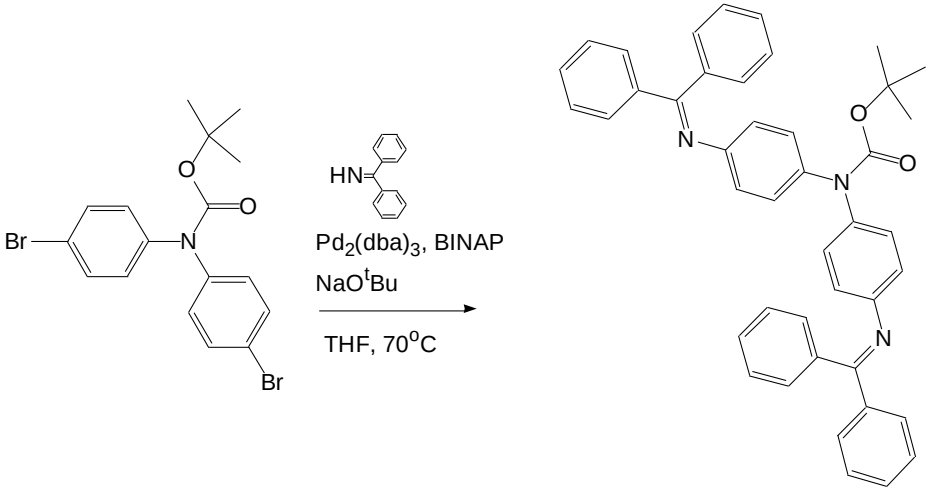


30

Scheme 35. Synthesis of Trimer 30

By modification of the procedure used by Buchwald,[61] diimine **31** can be prepared from compound **29** and benzophenone imine under palladium coupling conditions. The coupling conditions tolerate the BOC protected product and the compound easily crystallizes out of methanol. The ^{1}H NMR spectrum of the product exhibits the expected aryl signals at δ 7.71,

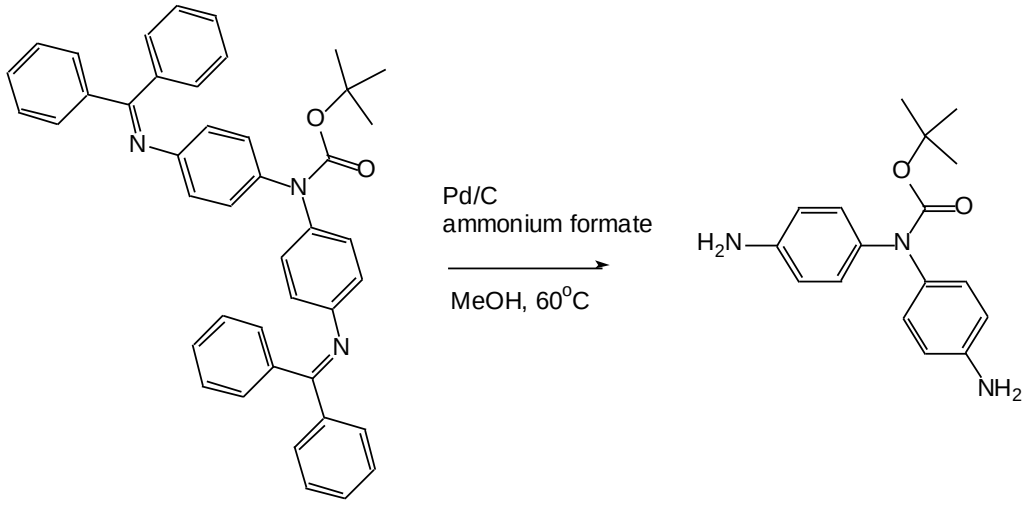
7.40, 7.24, 7.09, 6.90, and 6.62 and the BOC signal at δ 1.35. The ^{13}C NMR spectrum of the product contains the expected C=N and C=O carbons at δ 168.4 and δ 153.7, respectively.



29 **31**

Scheme 36. Preparation of Diimine 31

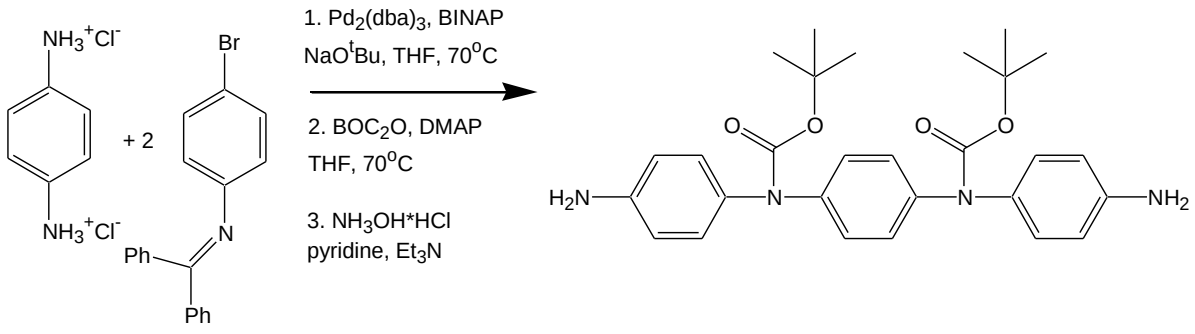
Diimine **31** was reduced to the terminal amine-dimer **32** by reaction with ammonium formate in the presence of palladium catalyst[61] (Scheme 37). Column chromatography of the product gives a white solid. The ^{1}H NMR spectrum confirms the proper integration between the aryl signals at δ 7.00 and δ 6.60 and the NH_2 signal at δ 3.60. The ^{13}C NMR spectrum exhibits the C=O signal at δ 154.5, three ipso carbons, two aryl carbons, and one methyl signal at δ 28.3.



31 **32**

Scheme 37. Synthesis of diamine 32

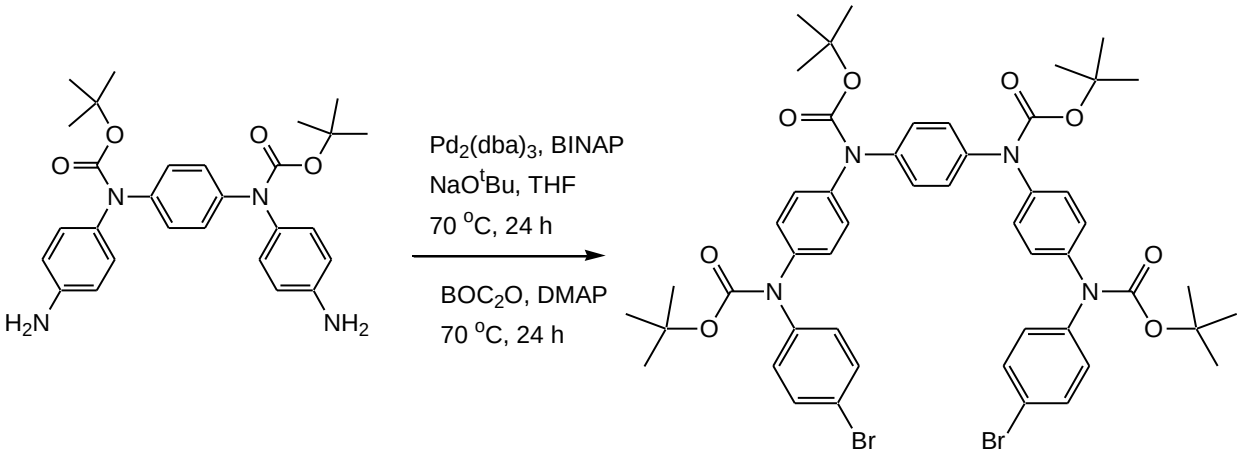
By modification of literature procedures,[28,48] amine-trimer **34** was prepared from 1,4-phenylenediamine hydrochloride and N-(diphenyl-methylene)-4-bromoaniline **33** under palladium coupling conditions in a one-pot coupling and BOC protection process (Scheme 38). Hydroxylamine hydrochloride and pyridine followed by triethylamine was utilized to cleave the diimine without cleaving the BOC groups. The ^{1}H NMR spectrum indicates that the aryl signals at δ 7.06, 6.82, and 6.49 integrate properly to the amine signal at δ 5.08 and the alkyl signal at δ 1.34. The ^{13}C NMR spectrum indicates a C=O carbon at δ 153.5, four ipso carbons, three aryl carbons, and one alkyl carbon.



33 **34**

Scheme 38. Synthesis of amine-trimer 34

Bromo-pentamer **35** was successfully prepared from amine-trimer **34** and *p*-dibromobenzene in THF solution under palladium coupling conditions[28] (Scheme 39). The coupling and subsequent BOC protection was performed in a one-pot process. The ^{1}H NMR spectrum indicates the proper integration between the aryl signals at δ 7.38 and 7.10 and the *tert*-butyl signals at δ 1.41. The ^{13}C NMR spectrum exhibits the expected number of ipso, aryl, and alkyl carbons.



34 **35**

Scheme 39. Preparation of bromo-pentamer 35

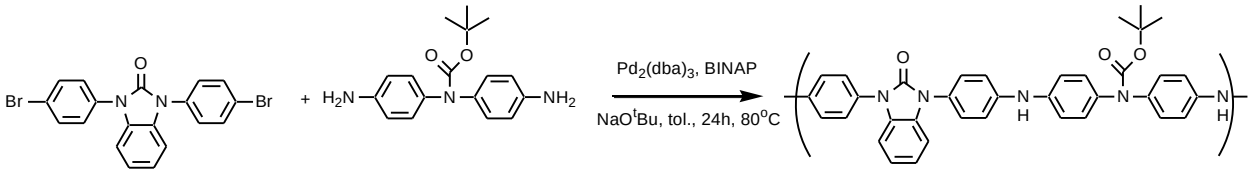
Although never attempted, bromo-pentamer **35** should be easily transformed into the analogous amine-pentamer by utilizing the methodology outlined above.

1.2.13 **4p,o-PANi Polymer**

1.2.13.1 Synthesis

Polymerization of urea segmer **25** with BOC-protected amine-dimer **32** yielded the 4*p,o*-PANi polymer **36** under palladium coupling conditions in 10-40% yield (Scheme 40). The polymer was isolated after reaction by precipitation out of THF solution into methanol.

Insoluble materials were sonicated with THF and precipitated into methanol. The combined precipitated polymer was re-dissolved into THF twice and precipitated twice into methanol to give the final polymer as a pale purple to black solid. The remaining 60-90% of starting material was isolated as insoluble material or short oligomers.



25 **32** **36**

Scheme 40. Synthesis of Polymer 36

The properties of polymer **36** depend on the reactions conditions in a similar manner as described by Ward.[55] Polymerization reaction times longer than 24 h do not give higher molecular weights and give lower yields. The polymerization was performed in both THF and toluene as solvents with neither affording a higher molecular weight. However, several trials in THF indicated a potential side reaction that was not present in the ^{1}H NMR spectrum of polymers prepared from toluene. The polymer was soluble in THF and NMP solvents and insoluble in methylene chloride, chloroform, hexanes, methanol, and acetone. Substitution of BINAP for 2-(di-*t*-butylphosphino)biphenyl was found to have no effect on the molecular weight.

1.2.13.2 NMR Characterization

The ^{1}H NMR spectrum of polymer **36** was acquired in one scan in d_8-THF solvent and exhibits broad features characteristic of a polymeric material. The N-H 1^o and 2^o signals were present at δ 4.43 and δ 6.49 respectively. The broad aryl signal at δ 7.10 indicates overlap of multiple aryl protons. The signal at δ 7.58 corresponds to the end group bromide monomer **25**.

The polymer also exhibited the expected BOC signal at δ 1.39. These results correlate well with the work on 5*p,o*-PANi systems done by Ward.[55]

The complex ^{13}C NMR spectrum was compared to the spectrum of the monomers to confirm incorporation (Figure **7**). The signals at δ 154.4 and δ 153.2 indicated the presence of two unique C=O signals. The expected BOC signals were distinguishable at δ 80.4 (ipso carbon) and δ 28.5 (CH_3).

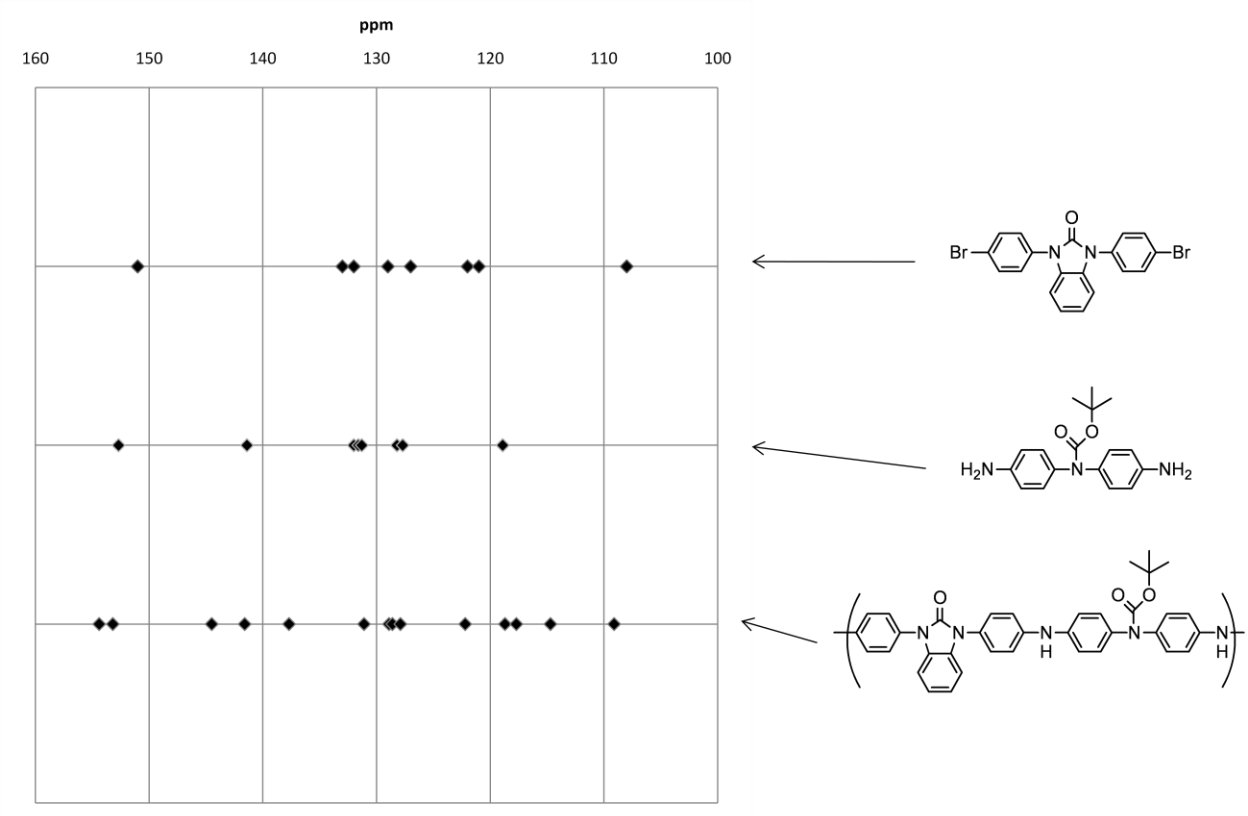


Figure 7. ^{13}C NMR Comparison for polymer 36

1.2.13.3 Molecular Weight Determination

GPC data was collected on a Waters GPC instrument in THF calibrated with polystyrene standards. The molecular weight data for 3 independently prepared samples are summarized in Table 6 below.

Table 6. Molecular weights by GPC for polymer **36**

Sample	Mw (x 10^3)[a]	Mn (x 10^3)	PDI
4*p*,*o*-PANi-1	5.3	7.6	1.4
4*p*,*o*-PANi-2	5.1	6.0	1.2
4*p*,*o*-PANi-3	2.7	3.7	1.4

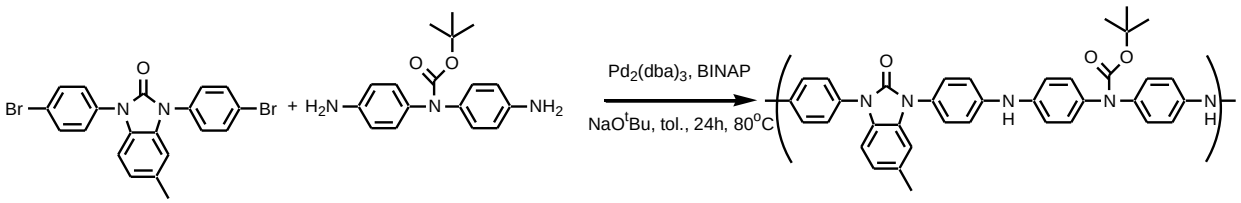
[a]**THF solvent, calibrated to polystyrene standards**

The GPC data indicated small molecular weights around 5.0 x10^3 which corresponds to 8-10 repeat units or 40-50 aryl units. However, GPC data has been found to overestimate the molecular weight of polyaniline polymers.[24] The molecular weight was also determined from the ^{1}H NMR spectrum by end group analysis to be 6-8 repeat units or a molecular weight of 3.6 x10^3- 4.6 x10^3. However, it should be noted that this end group analysis assumes that every change has a different end group on each end. This may not be the case and could lead to significant error in this analysis.

1.2.14 **Methyl Substituted 4p,*o*-PANi**

1.2.14.1 Synthesis

Polymerization of urea segmer 22 with BOC-protected amine dimer **32** yielded the methyl substituted 4p,o-PANi derivative under palladium coupling conditions in 13-48% yield (Scheme 41). The polymer was isolated after reaction by precipitation out of THF solution into methanol. Insoluble materials were sonicated with THF and precipitated into methanol. The combined precipitated polymer was re-dissolved into THF twice and precipitated twice into methanol to give the final polymer as a pale purple to black solid. The remaining 52-87% of starting material was isolated as insoluble material or short oligomers.



Scheme 41. Synthesis of polymer 37

The properties of polymer **37** depend on the reactions conditions in a similar manner as described by Ward.[55] Polymerization reaction times longer than 24 h do not give higher molecular weights and give lower yields. The polymerization was performed in both THF and toluene as solvents with neither affording a higher molecular weight. However, several trials in THF indicated by study of the ^{1}H NMR proton integration a potential side reaction that was not present in the ^{1}H NMR spectra of polymers prepared from toluene. The polymer was soluble in THF and NMP solvents and insoluble in methylene chloride, chloroform, hexanes, methanol, and acetone. Substitution of BINAP for 2-(di-*t*-butylphosphino)biphenyl was found to have no effect on the molecular weight.

1.2.14.2 NMR Characterization

The ^{1}H NMR spectrum of polymer **37** was acquired in one scan in d_8-THF solvent and exhibits broad features characteristic of a polymeric material. The N-H 1^o and 2^o signals were present at δ 4.48 and δ 6.51 respectively. The broad aryl signals at δ 6.95 and δ 7.12 indicated that the methyl substitution shifts multiple aryl protons upfield. The signal at δ 7.58 corresponds to the end group bromide monomer **22**. The polymer also exhibited the expected BOC signal at δ 1.43 and the expected methyl signal at δ 2.31.

The complex ^{13}C NMR spectrum was compared to the spectrum of the monomers to confirm incorporation (Figure 8). The signals at δ 154.4 and δ 153.2 indicated the presence of two unique C=O signals. The expected BOC signals were present at δ 80.4 (ipso carbon) and δ 28.5 (CH_3) while the methyl signal was present at δ 21.6

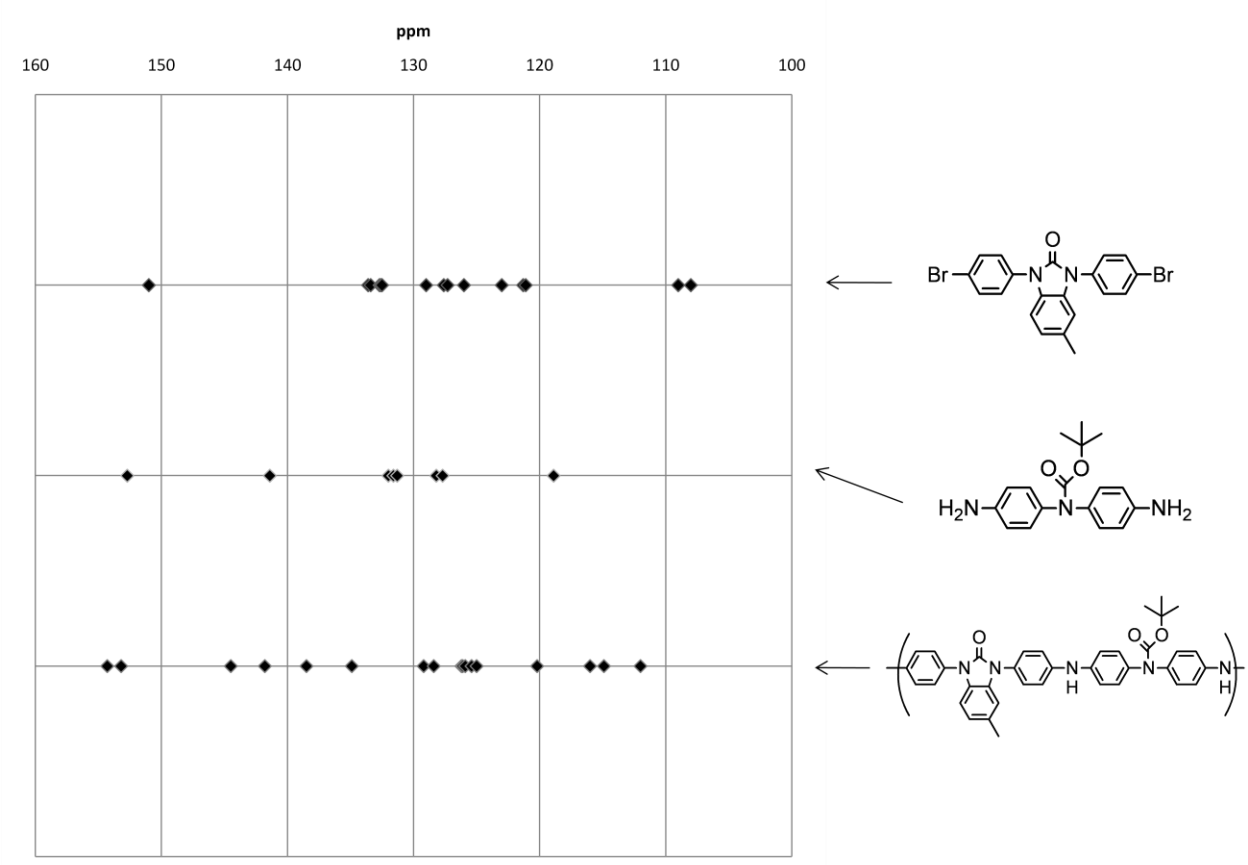


Figure 8. ^{13}C NMR Comparison for polymer 37

1.2.14.3 Molecular Weight Determination

GPC data was collected on a Waters GPC instrument in THF calibrated with polystyrene standards. The molecular weight data for 3 independently prepared samples are summarized in Table 7 below.

Table 7. Molecular Weight by GPC for polymer **37**

Sample	Mw (x 10^3)[a]	Mn (x 10^3)	PDI
Methyl 4*p,o*-PANi-1	6.7	8.2	1.2
Methyl 4*p,o*-PANi-2	8.6	10.	1.2
Methyl 4*p,o*-PANi-3	5.4	7.6	1.4

[a]**THF solvent, calibrated to polystyrene standards**

The GPC data indicated small molecular weights around $5.0x10^3$ - $8.0x10^3$ which corresponds to 8-13 repeat units or 40-65 aryl units. However, GPC data has been found to overestimate the molecular weight of polyaniline polymers.[24] The molecular weight was also determined from the ^{1}H NMR spectrum by end group analysis to be 6-8 repeat units or a molecular weight of $3.6\ x10^3$-$4.8\ x10^3$. However, it should be noted that this end group analysis assumes that every chain has a different end group on each end. This may not be the case and could lead to significant error in this analysis. A 1:1 relative monomer ratio was calculated by comparing the integration per proton of the methyl signal originating from the urea with the integration per proton of the BOC signal originating from the *para*-aniline segment indicating a repeat sequence structure.

1.2.15 **Polymer Film Properties and Doping**

Solutions of both polymers **36** and **37** in THF were cast into films by both spin casting and drop casting. At the concentrations attainable in THF, spin casting gave pale purple films that were too thin to measure the conductivity. Drop casting from pipette gave a thicker film suitable for measuring the conductivity

Films of polymers **36** and **37** were doped by using concentrated HCl in a vapor chamber for 1-2 d. After doping, the films would turn dark green indicating oxidation to the emeraldine

salt form. Upon drying, the films were very brittle and break apart due to the low molecular weights. Exposure of these films to solutions of HCl caused the films to break and crumble.

1.2.16 **Conductivity Measurements**

Conductivity was measured using a four point probe apparatus with a Signatone probe. Polymers **36** and **37**, however, did not show any measurable conductivity. It is unclear if the reason for the high resistance was the relatively low molecular weights if the samples were simply not effectively doped. .

Polymers **36** and **37** were blended with PVC to improve the film characteristics. These films maintained the pale purple color prior to doping and turned green after doping. These films were tested and found to have no conductivity. It is unclear if the major reason was because the blend lowered the conductivity below our measureable level or if the film was ineffectively doped.

1.3 **DISCUSSION**

We have prepared several protected derivatives of *o*-phenylenediamine from three different synthetic classes, sulfonamides, amides, and carbamates. We have shown that sulfonamide **3** is not reactive in either the Ullmann-Goldberg coupling or the palladium coupling under standard conditions. After preparing and characterizing amides **6** and **7**, we have found that neither amide **6** nor amide **7** is reactive in either the Ullmann-Goldberg coupling or the palladium coupling under standard conditions. Carbamate **9** also proved unreactive in the

palladium coupling under standard conditions. The BOC protected carbamate **1** was found to decompose to urea products when subjected to Ullmann-Goldberg standard conditions.

While the inability to perform the Ullmann-Goldberg reaction on sulfonamide, carbamate, and amide derivatives of *o*-phenylenediamine is somewhat unexpected, we speculate that failure in the palladium couplings is due to coordination of palladium to the *ortho*-diamine. Considering the success of the Ullmann-Goldberg coupling with ureas and the similarity of ureas, amides, and carbamates, no coupling of aryl halide to carbamate **9**, amides **6**, or amide **7** is perplexing. Two factors that may contribute to failure of the Ullmann-Goldberg coupling include steric hindrance and chelating of the copper catalyst. While probably not a concern for carbamate **9** or amide **7**, steric influences may prevent reaction for sulfonamide **3** and amide **6**. Chelating of the copper catalyst could occur for both amides and carbamates leading to deactivation of the copper catalyst but probably would not occur for sulfonamide **3**. Additionally, sulfonamide **3** may not activate the N-H bond as well as amides or carbamates precluding the Ullmann-Goldberg coupling. Palladium coordination to *ortho*-diamines is known to occur and may not be deterred by the presence of amides, carbamates, or sulfonamides.

Prompted by work by Buchwald and Ma,[16,17] we have attempted to enhance the Ullmann-Goldberg reaction by addition of amines and amino acids. While utilizing N,N'-dimethyl-ethane-1,2-diamine, 1,2-diaminocyclohexane and hexamethylenetetramine under standard Ullmann-Goldberg conditions for sulfonamide **3** proved futile, we were able to enhance the reaction of *o*-phenylenediamine with 1,4-dibromobenzene utilizing L-proline. The use of L-proline facilitated the first coupling of aryl halide to aryl amine and then failed to couple the second equivalent of aryl halide. We investigated steric factors involving the *ortho*-diamine by reacting *p*-phenylenediamine with 4-bromotoluene and found the primary product to be the

mono-coupled intermediate. When aniline was reacted with 1,4-dibromobenzene, the mono-coupled product was also observed. We speculate that the electronics of the L-proline/Cu system prevent the successful coupling of the second aryl halide.

We have prepared and characterized several bridged, heterocyclic derivatives of *o*-phenylenediamine. Using the previous work by Pellicciotto,[51] we based a synthesis for diazaborole **12**. Diazaborole **12** was unreactive under standard Ullmann-Goldberg conditions; however, did undergo mono-aryl halide coupling when L-proline was present. Under standard palladium coupling conditions, we found it curious that deprotected mono-coupled and deprotected di-coupled diamine was observed since no literature supports N-B bond cleavage.[62,63] We are uncertain whether cleavage of the B-N bond was accomplished via palladium or via base. We prepared diazaphosphole **13** according to literature methods.[52,53] Diazaphosphole **13** was unreactive under standard Ullmann-Goldberg conditions even when L-proline was present. Under standard palladium coupling conditions, we found cleavage of the P-N bond with both mono-coupling and di-coupling diamine products. We are uncertain whether cleavage of the P-N bond was accomplished via palladium or via base; however, there is precedence for P-N bond cleavage by Pd(II) species under certain conditions.[64,65] We were unsuccessful in preparing a titanium **14** and zirconium **15** bridged diamine as described in the literature.[54]

Although bridged *ortho*-diamine compounds are a novel approach, the failure of both the Ullmann-Goldberg and palladium couplings indicates those flaws. Decomposition caused by either the base or catalyst appears to be the main drawback illustrating that any future bridged compound should be stable to both base and catalyst. However, the reactivity of the bridged

compounds is also suspect and remains unclear if any bridging functionality would be as effective as the urea carbonyl.

Considering our previous experience with bridged *ortho*-diamine compounds, we decided to prepare several urea derivatives utilizing different methods. Microwave reaction proved very effective but uncontrollable gas formation was a hindrance. Traditional, acid catalyzed synthesis worked but was too variable probably due to poor mixing and crosslinking. Urea synthesis using triphosgene proved to be the most efficacious due to convenient methodology, isolation, and greatly improved yield allowing for ureas **20**, **22**, **23**, and **24** to be readily prepared from the corresponding diamine.

With urea derivatives in hand, the standard Ullmann-Goldberg coupling was utilized to synthesize segmers **25**, **26**, and **27**. The slightly better than previously reported crude yield[48,55] and decrease in side reactions can be attributed to the purity of urea **20**, **22**, and **23** as prepared by the triphosgene method and the extensive exclusion of oxygen. Although column chromatography of these types of segmers is known to decompose significant amounts of material, stringent purification of segmers **25**, **26**, and **27** made purification by column chromatography a simple process in spite of the low yield. In the end, the low yield of these couplings prevented us from obtaining large quantities of segmers **25**, **26**, and **27**. Curiously, the Ullmann-Goldberg coupling of urea **24** was not accomplished possibly due to the electron withdrawing nature of the nitro group.

Having completed the urea co-monomers, we turned our attention to the preparation of the *para*-aniline based segmer. The methodology for bromination of diphenylamine utilizing $TBABr_3$[57] was surprisingly selective for the *para* position but would be prohibitive on large

scales due to the high cost of the $TBABr_3$ reagent. Incorporation of the BOC protecting group utilizing well established methods[58-60] provided an effective direct route to bromo-dimer **29**.

To investigate the relationship between the number of *ortho* and *para* units, we were interested in extending the length of the *para*-aniline co-monomer. We prepared amine-dimer **32** and amine-trimer **34** using the methodology established by Buchwald in reasonable yields in a one pot synthesis.[28,48] Then we were able to convert the aryl bromide to the aryl amine by a two-step methodology.[61] Bromo-pentamer **35** demonstrated that these methodologies could be combined to build long *para*-aniline units of a known structure.

With both co-monomers in hand, the palladium catalyzed polymerization of **25** and **26** with **32** yielded 4p,*o*-PANi derivatives as a black solid in low to moderate yields. We speculated that the low yields reflect crosslinking of polymer chains[55] creating the appearance of black tar in most cases. We found that the polymer product was dependent on the reaction conditions as described by Ward.[55] However, we found evidence in the ^1H NMR spectrum of potential side reactions occurring in THF that were absent from polymerizations done in toluene. The identity of the phosphine ligand was found to have little influence on the polymer characteristics.

Unfortunately, the low molecular weights observed for 4p,*o*-PANi derivatives were a common problem for our work. We speculate two plausible reasons. First, the occurrence of a small percentage of free amine along the polymer chain creates sites for crosslinking and thus a highly insoluble polymer. Second, we speculate that the polymeric material remains soluble to certain chain lengths. One can envision that after each revolution in the palladium catalyzed cycle, the growing polymer is released from the active catalyst allowing time for precipitation to occur. This would account for the trend of typically low PDI from the expected value of 2.

As a result of the low molecular weights observed in the polymerization of 4p,*o*-PANi derivatives, we were unable to cast good films and hence poor conductivity results. We attempted to blend the polymers with PVC, but were unable to measure any conductivity. Although we believe the conductivity to be similar to Ward's 5p,*o*-PANi systems[48], we have conclusively proven only that the polymers have the designed microstructure.

In conclusion, we have prepared a 4p,*o*-PANi polymer and derivative as a repeating sequence co-polymer which can be used to make interesting conducting polymers as suggested in primary studies.[48,55] We have shown that sulfonamide, carbamate, amide, and bridging derivatives of *o*-phenylenediamine are unreactive in both the Ullmann-Goldberg and palladium couplings. We have prepared various ureas and transformed them the corresponding segmers. We have utilized literature procedures to prepare the *para*-aniline co-monomers and have successfully prepared 4p,*o*-PANi and a methyl-substituted derivative. After careful characterization and study of the polymers, we were unable to measure any conductivity due to poor film quality and low molecular weight. However, we believe the 4p,*o*-PANi system will show equivalent conductivity to *p*-PANi as has been shown for the 5p,*o*-PANi systems.[48,55]

1.4 EXPERIMENTAL SECTION

1.4.1 General

All reactions and manipulations were performed under an atmosphere of nitrogen in either a glove box or using standard Schlenk techniques. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Solvents

were purchased from commercial suppliers and used without further purification unless otherwise noted.

1,4-Dibromobenzene, 4-methyl-benzene-1,2-diamine, 4,5-dimethyl-benzene-1,2-diamine and *o*-phenylenediamine were sublimed before use and stored under a nitrogen atmosphere. Compound **33** was prepared by literature methods.[28]

^{1}H NMR and ^{13}C NMR spectra were acquired on Brucker 300 MHz instruments. Mass spectral data was acquired on a Hewlett Packard Series 5890 GC/5971A MS with a Hewlett Packard Series 1 capillary column. GC data was acquired on a Hewlett Packard Series 6890 GC. GPC data was collected on a Waters GPC system equipped with phenogel columns and a Waters 410 Differential Refractometer calibrated using polystyrene standards. Conductivity measurements were made using a standard four-point probe method.

1.4.2 **(2-*tert*-Butoxycarbonylamino-phenyl)-carbamic acid *tert*-butyl ester (1):**

Compound **1** was prepared by a variation of the method used by Basel and Hassner.[58] To a 100 mL 3-neck round bottom flask equipped with a condenser and gas adapter was added 1,2-diaminobenzene (1.40 g, 12.9 mmol) and BOC_2O (5.52 g, 25.3 mmol) in 30 mL of methylene chloride. The yellow reaction mixture was stirred overnight at room temperature. After 24 hours, the solvent was removed under reduced pressure to give an oil. Recrystallization from absolute ethanol afforded a white solid (2.10 g, 53% yield). ^{1}H NMR: ($CDCl_3$) δ 7.46 (s, 2H, N*H*); 7.11 (m, 2H, aryl); 6.85 (m, 2H, aryl); 1.51 (s, 18H, CH_3). ^{13}C NMR: (DMSO) δ 153 (C=O), 130, 125, 124, 80.8, 28.38.

1.4.3 **N, N'-1,2-phenylenebis[4-methyl-benzenesulfonamide (3):**

The sulfonamide **3** was prepared by a modification to the procedure used by Amundsen.[66] To a 100 mL round bottom flask under nitrogen was added 1,2-diaminobenzene (1.23 g, 11.3 mmol) in 20 mL of methylene chloride. *p*-Toluenesulfonyl chloride 5 (4.34 g, 22.7 mmol) in 20 mL of methylene chloride was added slowly by syringe over 30 min. Triethylamine (6.55 g, 64.7 mmol), which had been previously distilled from calcium hydride, was added by syringe over 30 min. After stirring overnight at room temperature, the mixture was extracted with deionized water (2x20 mL). The organic layer, after being dried over magnesium sulfate, was removed under reduced pressure to give a brown solid (4.12 g, 71%) ^{1}H NMR: ($CDCl_3$) δ 7.57 (d, 4H, aryl); 7.23 (m, 4H, aryl); 7.05 (m, 2H, N*H*); 7.02 (m, 4H, aryl); 2.39 (s, 6H, CH_3). M/z: 416 (M^+).

1.4.4 **1,3-Dihydro-benzo[1,2,5]thiadiazole 2,2-dioxide (4):**

Compound **4** was prepared using a modified procedure by C.W. Rees *et al.*[49] A solution of phenylenediamine (0.60 g, 5.5 mmol) and sulfonamide (check name) (0.91 g, 9.5 mmol) in diglyme (20 mL) was added dropwise to diglyme (80 mL) at reflux over 30 min. After 60 min, the dark red solution was cooled in an ice bath to room temperature. Upon filtering through celite, the filtrate was collected and the diglyme was removed by distillation. The residue was taken up in ether (100 mL) and 2 M HCl (100 mL) was added. The organic layer was separated and washed with brine solution (2x100 mL). After drying over $MgSO_4$, benzyl amine (2.4 g, 22.0 mmol) was added which produced the amide salt which was collected by filtration. The product was then reconstituted by addition to 2 M HCl (100 mL) and extraction into ether (100

mL). After drying over $MgSO_4$, the volatile organics were removed to yield an orange solid (0.22 g, 22.8%). ^{1}H NMR (d_6-DMSO): δ 11.0 (bs, 2H, N-H), 6.84 (m, 4H, aryl). ^{13}C NMR (d_6-DMSO): δ 129.6 (ipso), 121.4 (aryl CH), 110.2 (aryl CH).

1.4.5 **N,N'-bis(4-bromophenyl)-sulfamide (5):**

Compound **5** was prepared according to a variation on the method of Parnell.[50] To a solution of *p*-bromoaniline (2.13 g, 12.4 mmol) and pyridine (1.46 g, 18.4 mmol) in CH_2Cl_2 (dry, 100 mL) was slowly added dropwise SO_2Cl_2 (0.83 g, 6.2 mmol) in CH_2Cl_2 (10 mL). After 2 h, water (100 mL) was added, quenching any remaining SO_2Cl_2. The organic phase was extracted and dried over $MgSO_4$. After removal of volatile organics and drying in the presence of phosphorus pentoxide under reduced pressure, the title compound was isolated as a white solid (0.57 g, 41.8%). ^{1}H NMR (d_8-THF): δ 9.30 (s, 2H, N-H), 7.38 (dd, 4H, aryl CH), 7.02 (d, 4H, aryl CH). ^{13}C NMR (d_8-THF): δ 138.5 (ipso), 132.8 (aryl CH), 122.2 (aryl CH), 117.0 (ipso). M/z: 406 (M+).

1.4.6 **N,N'-1,2-phenylenebisbenzamide (6):**

Under a nitrogen atmosphere in a 100 ml 3-neck round bottom flask was added 1,2-diaminobenzene (1.97 g, 18.2 mmol) and 20 mL of dry THF. Benzyl chloride (2.45 g, 17.4 mmol) was added slowly by syringe to the solution over 15 min followed by pyridine (2.91 g, 36.7 mmol) over an additional 15 min. After refluxing for 30 min, the organic mixture was extracted with deionized water twice (2x20 mL) and dried over magnesium sulfate. The volatile organics, after being dried over magnesium sulfate, were removed under reduced pressure to

leave an orange solid. Recrystallization from absolute ethanol afforded a pink solid (3.27 g, 56%). ^{1}H NMR: (DMSO) δ 10.0 (s, 2H, N*H*), 7.94 (d, 4H, aryl); 7.63 (m, 2H, aryl); 7.55 (m, 6H, aryl); 7.30 (m, 2H, aryl).

1.4.7 **N-(2-Acetylamino-phenyl)-acetamide (7):**

Under a nitrogen atmosphere, acetyl chloride (0.70 g, 8.96 mmol) was added to *o*-phenylenediamine (0.49 g, 4.51 mmol) in bromobenzene (30 mL, distilled). After refluxing overnight, the volatile organics were removed under reduced pressure to leave a white solid. Recrystallization from absolute ethanol afforded a white solid (0.54 g, 62% yield). ^{1}H NMR: (DMSO) δ 10.4 (s, 2H, NH), 8.0 (m, 2H, aryl), 7.6 (m, 2H, aryl), 1.60 (m, 6H, CH_3). M/z: 192 (M+).

1.4.8 **(2-Methoxycarbonylamino-phenyl)-carbamic acid methyl ester (9):**

Under a nitrogen atmosphere in a 100 mL 3-neck round bottom flask was added 1,2-diaminobenzene (0.63 g, 5.84 mmol) and 20 mL of dry THF. Methyl chloroformate (1.22 g, 12.9 mmol) was added slowly by syringe to the solution over 15 min followed by pyridine (1.45 g, 18.3 mmol) over an additional 15 min. After refluxing for 30 min, the organic mixture was extracted with deionized water twice (2x20 mL) and dried over magnesium sulfate. The volatile organics were removed under reduced pressure to leave a solid. Recrystallization from absolute ethanol afforded a white solid (0.42 g, 32%). ^{1}H NMR: (DMSO) δ 8.78 (bs, 2H, N*H*); 7.46 (m, 2H, aryl); 7.10 (m, 2H, aryl); 3.60 (s, 3H, CH_3).

1.4.9 **2-Phenyl-2,3-dihydro-1*H*-benzo[1,3,2]diazaborole (12):**

Method A

Compound **12** was prepared according to a variation on the method of Pellicciotto *et al.*[51] Compound **11** (0.62 g, 4.09 mmol) was cooled to 0 °C in dry THF (20 mL). Phenyl lithium (1.8 M in cyclohexane) (2.5 mL, 4.5 mmol) was added dropwise by syringe to the solution. After stirring overnight, the volatile organics were removed under vacuum, and the remaining solids were extracted with benzene. Upon filtering and removing solvent under reduced pressure, a yellow oil was obtained (0.22 g, 28%).

Method B

A solution of *o*-phenylenediamine (1.68 g, 15.5 mmol) and boronic acid (1.68 g, 15.5 mmol) in toluene (100 mL) equipped with a Dean-Stark trap was refluxed overnight under nitrogen. After the mixture cooled to room temperature, molecular sieves (4Å) were added. After refluxing overnight, the mixture was filtered hot and the volatile organics were removed under reduced pressure. Recrystallization from absolute ethanol afforded a white solid (2.56 g, 85%) ^{1}H NMR; (THF) δ 8.31 (s, 2H, N*H*), 7.83 (m, 2H, aryl), 7.34 (m, 3H, aryl), (7.0) (m, 2H, aryl), 6.81 (m, 2H, aryl). ^{13}C NMR: (THF) δ 138, 133, 129, 128, 118, 111. M/z: 194 (M^{+}).

1.4.10 **2-Phenyl-1,3-dihydro-benzo[1,3,2]diazaphosphole 2-oxide (13):**

The compound was prepared as described by Wagner *et al* and Norman *et al.*[52,53] A mixture of *o*-phenylenediamine (1.41 g, 13.0 mmol) and dichlorophenylphosphinoxide (2.50 g, 12.8 mmol) in bromobenzene (30 mL, distilled) was refluxed overnight under nitrogen. The volatile organics

were removed under reduced pressure to leave a white/blue solid. Recrystallization from absolute ethanol afforded a blue-green solid (2.38 g, 79%). ^{1}H NMR: (DMSO) δ 8.60 (d, 2H, N*H*); 7.55 (m, 5H, aryl), 6.68 (m, 4H, aryl). ^{31}P NMR: δ 24.8. ^{13}C NMR: (THF) δ 136, 134, 133, 132, 128, 119, 110.

1.4.11 **4-Methyl-benzene-1,2-diamine (17):**

Method A

To a 250 mL 3-neck round bottom flask equipped with two gas adapters was added 3,4-dinitrotoluene (4.91 g, 27.0 mmol) and activated Pd(0) on carbon (0.44 g, 9% by mass). After evacuation and back filling with nitrogen (3x), methanol (150 mL), which had previously been distilled, was added to the flask. The system was purged with hydrogen gas (3x) and then left stirring under 1 atm of hydrogen (balloon) for 24 h. The solvent was removed under reduced pressure after 24 hours to give a black solid. In a glove box, the solid was taken up in dry THF and then filtered through celite. Removal of the solvent under reduced pressure gave a black solid (3.01 g) in 91% yield.

Method B

To a 250 mL 3-neck round bottom flask equipped with one gas adapter was added 3,4-dinitrotoluene (8.47 g, 46.5 mmol) and activated Pd(0) on carbon (0.72 g, 9% by mass). After evacuation and back filling with nitrogen (3x), methanol (150 mL), which had been distilled

previously, was added. The system was purged with hydrogen gas (5 min) and then left stirring under 1 atm of hydrogen gas (bubbled) for 48 h. The solvent was removed under reduced pressure to give a black solid. In a glove box, the solid was taken up in dry THF and then filtered through celite. Removal of the solvent under reduced pressure gave a black solid which was sublimed at 70 °C under reduced pressure to afford a white solid (5.20 g, 91% yield). ^{1}H NMR: ($CDCl_3$) δ 7.21 (m, 3H, aryl); 4.01 (s, 4H, N*H*$_2$), 2.89 (s, 3H, C*H*$_3$). ^{13}C NMR: ($CDCl_3$) δ 158 (ipso), 155 (ipso), 153 (ipso), 149 (*C*-H), 140 (*C*-H), 140 (*C*-H), 44.1 (*C*H_3).

1.4.12 **4,5-Dimethyl-benzene-1,2-diamine (19):**

To a 250 mL 3-neck round bottom flask equipped with one gas adapter was added 4,5-dimethyl-2-nitro-phenylamine (5.00 g, 30.1 mmol) and activated Pd(0) on carbon (0.50 g, 10% by mass). After evacuation and back filling with nitrogen (3x), methanol (100 mL, distilled) was added to the flask. The system was purged with hydrogen gas (balloon, 3x) and stirred under 1 atm of hydrogen gas (balloon) for 48 h. The solution was filtered and the solvent removed under reduced pressure to leave the crude product. The crude product was sublimed at 70 °C under reduced pressure to afford a white solid (3.73 g, 91.2%). ^{1}H NMR ($CDCl_3$): δ 7.20 (s, 2H, aryl), 3.97 (s, 4H, -NH_2), 2.84 (s, 6H, -CH_3). ^{13}C NMR ($CDCl_3$): δ 132.2 (ipso aryl), 127.7 (ipso aryl), 118.4 (aryl CH), 18.8 (-CH_3).

1.4.13 **1,3-Dihydro-benzoimidazol-2-one (20):**

Method A

In a sealable, thick walled glass test tube, a mixture of *o*-phenylenediamine (0.22 g, 2.05 mmol) and urea (0.13 g, 2.10 mmol) was irradiated with 300 W for 30 min in a CEM microwave reactor. After dissolving the reaction mixture in hot absolute ethanol (10 mL), a white precipitate was isolated by filtration (0.23 g, 84%).

Method B

To *o*-phenylenediamine (5.22 g, 48.3 mmol) was added 2.4 M HCl in methanol (50 mL). After a pink solid precipitated out of solution, the volatile organics were removed under reduced pressure and dried under vacuum for 2 h. Urea (2.90 g, 48.3 mmol) was added to the solid. Upon heating to 130-140 °C, the mixture liquefied and after 5 h, was allowed to cool to room temperature. The solid mixture was triturated with absolute ethanol and filtered. The filtrate was cooled, and the product precipitated out of solution to afford a brown-white solid (2.10 g, 32%).

Method C

Compound **20** was prepared according to a variation on the method of Zhu.[56] Triphosgene (2.02 g, 6.8 mmol) was added slowly over 1 h to a solution of *o*-phenylenediamine (2.16 g, 19.9 mmol) and triethylamine (5.6 mL, 40.2 mmol) in dry CH_2Cl_2 (100 mL). After stirring overnight and quenching with 10% NaOH/H_2O solution (20 mL), the white crystalline product was isolated by filtration and recrystallization from absolute ethanol (4.00 g, 92% yield). ^{1}H NMR (d_6-DMSO):

δ 10.5 (s, 2H, N*H*), 6.90 (m, 4H, aryl). ^{13}C NMR (d_6-DMSO): δ 167.3 (C=O), 139.6 (ipso), 116.6 (aryl CH), 108.8 (aryl CH). DEPT 135 NMR (d_6-DMSO): δ 116.6 (aryl CH), 108.8 (aryl CH).

1.4.14 **1,3-Dihydro-benzoimidazole-2-thione (21):**

Method A

In a sealable, thick walled glass test tube, a mixture of *o*-phenylenediamine (0.25 g, 2.31 mmol) and thiourea (0.19 g, 2.50 mmol) was irradiated with 300 W for 30 min in a CEM microwave reactor. After dissolving the reaction mixture in hot absolute ethanol (10 mL), a white precipitate was isolated by filtration (0.29 g, 84%).

Method B

To *o*-phenylenediamine (0.52 g, 4.85 mmol) was added 2.4 M HCl in methanol (5 mL, 12 mmol). After a white solid precipitated out of solution, the volatile organics were removed under reduced pressure and dried under vacuum for 2 h. Thiourea was added to the dry solid (0.47 g, 6.1 mmol). Upon heating to 170-180 °C in a sand bath, the mixture liquefied and after 7 h, was allowed to cool to room temperature. The solid mixture was triturated with absolute ethanol and filtered. The filtrate was cooled, and the product precipitated out of solution to afford 0.32 g of a green-blue solid (45%). ^{1}H NMR (DMSO) δ 12.50 (s, 2H, N*H*), 7.10 (m, 4H, aryl).

1.4.15 **5-Methyl-1,3-dihydro-benzoimidazol-2-one (22):**

Method A

To 4-methylbenzene-1,2-diamine (0.44 g, 3.63 mmol) was added 2.4 M HCl in methanol (4 mL, 9.6 mmol). After dissolving, the volatile organics were removed under reduced pressure and dried under vacuum for 2 h. Urea (0.23g, 3.81 mmol) was added to the remaining solid. Upon heating to 130-140 °C, the mixture liquefied and after 5 h, was allowed to cool to room temperature. The solid mixture was triturated with absolute ethanol and filtered. The filtrate was cooled and the product precipitated out of solution to afford 0.26 g of a green-blue solid (49%). ^{1}H NMR: (DMSO) δ 10.46, (d, 2H, N*H*), 6.52 (m, 3H, aryl), 2.18 (s, 3H, CH_3). ^{13}C NMR: (DMSO) δ 155 (C=O), 129 (ipso), 129 (ipso), 127 (ipso), 120 (C-H), 108 (C-H), 108 (C-H), 20.9 (CH_3).

Method B

Compound **22** was prepared according to a variation on the method of Zhu.[56] Triphosgene (2.30 g, 7.7 mmol) was added slowly over 1 h to a solution of 4-methylbenzene-1,2-diamine (2.55 g, 20.8 mmol) and triethylamine (5.8 mL, 41.7 mmol) in dry CH_2Cl_2 (100 mL). After stirring overnight and quenching with 10% NaOH/H_2O solution (20 mL), the white crystalline product was isolated by filtration and recrystallization from absolute ethanol (2.92 g, 96% yield). ^{1}H NMR (d_6-DMSO): δ 10.5 (s, 2H, N*H*), 6.90 (m, 4H, aryl). ^{13}C NMR (d_6-DMSO): δ 164.1 (C=O), 137.3 (ipso), 134.4 (ipso), 126.1 (ipso), 118.2 (aryl CH), 109.6 (aryl CH), 108.2 (aryl CH), 21.5 (CH_3). DEPT 135 NMR (d_6-DMSO): δ 118.2 (aryl CH), 109.6 (aryl CH), 108.2 (aryl CH), 21.5 (CH_3).

1.4.16 **5,6-Dimethyl-1,3-dihydro-benzoimidazol-2-one (23):**

Compound **23** was prepared according to a variation on the method of Zhu.[56] Triphosgene (3.13 g, 10.5 mmol) was added slowly over 1 h to a solution of 4,5-methyl-benzene-1,2-diamine (4.11 g, 30.1 mmol) and triethylamine (9.46 g, 93.5 mmol) in dry CH_2Cl_2 (120 mL). After stirring overnight and quenching with 10% NaOH/H_2O solution (20 mL), the product, in the form of tan needles, was isolated by filtration and recrystallization from absolute ethanol (4.68 g, 96%). ^{1}H NMR (d_6-DMSO): δ 10.13 (bs, 2H, N-H), 6.58 (s, 2H, aryl), 2.15 (s, 6H, alkyl). ^{13}C NMR (d_6-DMSO: δ 155.4 (C=O), 127.7 (CH and ipso), 109.5 (ipso), 19.4 (CH_3). DEPT 135: (d_6-DMSO) δ 109.5 (up, CH), 19.4 (up, CH_3).

1.4.17 **5-Nitro-1,3-dihydro-benzoimidazol-2-one (24):**

Compound **24** was prepared according to a variation on the method of Zhu.[56] A solution of triphosgene (11.3 g, 0.37 mol) in dry dichloromethane (70 mL) was added over 2 h to a solution of 5-nitro-1,2-phenylenediamine (17.4 g, 0.11 mol) and triethylamine (distilled, 7 mL) in dry dichloromethane (150 mL). After stirring overnight and quenching with 10% NaOH/H_2O solution (20 mL), the product, in the form of yellow needles, was isolated by filtration and recrystallization from absolute ethanol (18.7 g, 92% yield). ^{1}H NMR (d_6-DMSO): δ 11.44 (s, 1H, -NH-), 11.21 (s, 1H, -NH-), 7.91 (d, 1H,-C<u>H</u>=CH-C(ipso)=CH-), 7.63 (s, 1H, -CH=CH-C(ipso)=C<u>H</u>-), 7.07 (d, 1H, -CH=C<u>H</u>-C(ipso)=CH-). ^{13}C NMR (d_6-DMSO): δ 155.4 (C=O), 141.2 (*ipso*), 135.7(*ipso*), 129.7(*ipso*), 117.8 (aryl CH), 108.1 (aryl CH), 103.6 (aryl CH).

1.4.18 **1,3-Bis-(4-bromo-phenyl)-1,3-dihydro-benzoimidazol-2-one (25):**

Compound **25** was prepared according to a variation on the method of Ward.[48] In a glove box under nitrogen, urea **20** (1.61 g, 12.0 mmol), copper (I) iodide (0.45 g, 2.3 mmol), potassium carbonate (3.90 g, 28.2 mmol), and 1,4-dibromobenzene (6.36 g, 26.9 mmol) were combined in 150 mL of DMF that had been dried over molecular sieves and de-oxygenated. Outside the glove box the reaction was heated to 150 °C under nitrogen for 48 h. The cooled mixture was diluted with 150 mL of ethyl acetate and 150 mL of NH_4OH/H_2O solution (pH ≈ 10) was added. After washing the aqueous phase (2x100 mL with ethyl acetate) and organic phase (2x100 mL with brine solution) separately, the combined organics were dried over magnesium sulfate, and the volatile organics were removed under reduced pressure to leave a solid. Excess 1,4-dibromobenzene was removed by sublimation at 52 °C and column chromatography of the solid in CH_2Cl_2/ hexanes afforded a white solid (2.02 g, 38% yield crude, 6% yield pure). ^{1}H NMR ($CDCl_3$): δ 7.70 (d, 4H, aryl), 7.50 (d, 4H, aryl), 7.14 (s, 4H, aryl). ^{13}C NMR ($CDCl_3$): δ 151 (C=O), 133 (ipso), 132 (*C*H), 129 (ipso), 127 (*C*H), 122 (*C*H), 121 (ipso), 108 (*C*H). M/z: 444 (M+).

1.4.19 **1,3-Bis-(4-bromo-phenyl)-5-methyl-1,3-dihydro-benzoimidazol-2-one (26):**

Compound **26** was prepared according to a variation on the method of Ward.[48] In a glove box under nitrogen, urea **22** (2.92 g, 20.0 mmol), copper (I) iodide (0.75 g, 3.9 mmol), potassium carbonate (6.10 g, 44.1 mmol), and 1,4-dibromobenzene (10.4 g, 44.2 mmol) were combined in 200 mL of DMF which had been dried over molecular sieves and de-oxygenated. Outside the glove box the reaction was heated to 150 °C under nitrogen for 48 h. The cooled mixture was

diluted with 200 mL of ethyl acetate and 200 mL of NH_4OH/H_2O solution (pH ≈ 10). After washing the aqueous phase (2 x 100 mL with ethyl acetate) and organic phase (2 x 100 mL with brine solution) separately, the combined organics were dried over magnesium sulfate, and the volatile organics were removed under reduced pressure to leave a solid. Excess 1,4-dibromobenzene was removed by sublimation at 52 °C and column chromatography of the solid in CH_2Cl_2/hexanes afforded a white solid (2.44 g, 27% yield crude, 6% yield pure). ^{1}H NMR ($CDCl_3$): δ 7.70 (m, 4H, aryl), 7.50 (m, 4H, aryl), 6.95 (m, 3H, aryl). ^{13}C NMR ($CDCl_3$): δ 151 (C=O), 133.6 (ipso), 133.4 (*C*H), 132.7(*C*H), 132.6(*C*H), 132.5(*C*H), 129 (ipso), 127.6(*C*H), 127.3, 126 (ipso), 123 (*C*H), 121.3 (ipso), 121.1 (ipso), 109 (*C*H), 108 (*C*H). M/z: 458 (M+).

1.4.20 **1,3-Bis-(4-bromo-phenyl)-5,6-dimethyl-1,3-dihydro-benzoimidazol-2-one (27):**

Compound **27** was prepared according to a variation on the method of Ward.[48] In a glove box under nitrogen, urea **23** (1.12 g, 6.9 mmol), copper (I) iodide (0.25 g, 1.3 mmol), potassium carbonate (2.21 g, 16.0 mmol), and 1,4-dibromobenzene (3.44 g, 14.6 mmol) were combined in 100 mL of DMF which had been dried over molecular sieves and de-oxygenated. Outside the glove box the reaction was heated to 150 °C under nitrogen for 48 h. The cooled mixture was diluted with 150 mL of ethyl acetate and 150 mL of NH_4OH/H_2O solution (pH ≈ 10). After washing the aqueous phase (2x100 mL with ethyl acetate) and organic phase (2x100 mL with brine solution) separately, the combined organics were dried over magnesium sulfate, and the volatile organics were removed under reduced pressure to leave a solid residue. Excess 1,4-dibromobenzene was removed by sublimation at 52 °C and column chromatography of the solid in CH_2Cl_2/hexanes afforded a white solid (0.14 g, 4.5%). ^{1}H NMR ($CDCl_3$): δ 7.46 (m, 6H,

aryl), 7.39 (m, 4H, aryl), 2.43 (s, 6H, -CH_3). ^{13}C NMR ($CDCl_3$): δ 155.0 (C=O), 134.9 (ipso aryl), 131.5 (ipso aryl), 129.7 (aryl CH), 128.8 (aryl CH), 128.7 (aryl CH), 127.5 (ipso aryl), 105.4 (ipso aryl), 20.8 (-CH_3). M/z: 472 (M+).

1.4.21 **Bis-(4-bromo-phenyl)-amine (28):**

Compound **28** was synthesized using a modification of the procedure outlined by Berthelot *et al.*[57] To a solution of diphenylamine (12.55 g, 74.1 mmol) in dichloromethane (200 mL) was added $TBABr_3$ (71.50 g, 148.3 mmol). The orange solution quickly turned pale yellow, and was washed with 1M sodium thiosulfate (2 x 200 mL) followed by water (2x200 mL) in a 1 L separatory funnel. After drying over magnesium sulfate and removal of volatile organics, an orange tar was recovered and dissolved in ether (150 mL). After washing with water (100 mL) and drying over magnesium sulfate, removal of volatile organics afforded a white solid (23.4 g, 96%). ^{1}H NMR ($CDCl_3$): δ 7.38 (d, 4H, aryl), 6.94 (d, 4H, aryl), 5.69, (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 141.6 (ipso), 132.2 (CH), 119.4 (CH), 113.3 (ipso). M/z: 327 (M+).

1.4.22 **Bis-(4-bromo-phenyl)-carbamic acid *tert*-butyl ester (29):**

Compound **29** was prepared by modification of the procedure outlined by Basel[58] and more recently by Hirao.[59,60] To a solution of bis-(4-bromo-phenyl)-amine (10.44 g, 31.9 mmol) and DMAP (0.78 g, 6.4 mmol) in dry THF (100 mL) was added a solution of BOC_2O (13.93 g, 63.8 mmol) in dry THF (75 mL). After refluxing for 3 h and removal of volatile organics, column chromatography of the crude product in EtOAc/hexanes gave a white solid (11.21 g, 82%). ^{1}H NMR ($CDCl_3$): δ 7.41 (d, 4H, aryl), 7.05 (d, 4H, aryl), 1.44 (s, 9H, *tert*-butyl). ^{13}C NMR

($CDCl_3$): δ 152.7 (C=O), 141.4 (ipso), 131.6 (aryl CH), 128.2 (aryl CH), 118.9 (ipso), 81.6 (BOC ipso), 27.9 (CH_3). DEPT 135 NMR ($CDCl_3$): δ 131.6 (aryl CH), 128.2 (aryl CH), 27.9 (CH_3). M/z: 427 (M+).

1.4.23 **Dibromotrimer (30):**

Compound **30** was prepared via a modified procedure given by Buchwald *et al.*[28] In a 250 mL Schlenk flask under N_2 was combined *p*-phenylenediamine (5.26 g, 48.6 mmol), 1,4-dibromobenzene (24.46 g, 103.7 mmol), $Pd_2(dba)_3$ (0.70 g, 0.76 mmol), BINAP (1.10 g 1.8 mmol), sodium *tert*-butoxide (12.70 g, 132.1 mmol), and dry THF (100 mL). After heating at 70 °C for 24 h, the mixture was cooled to RT. A solution of BOC_2O (22.27 g, 102.0 mmol) and DMAP (1.18 g, 9.7 mmol) in dry THF (60 mL) was added by syringe. After heating to 70 °C for another 24 h, methylene chloride (200 mL) was added to the mixture at RT. After filtration and removal of volatile organics, a crude solid was obtained. Column chromatography (EtOAc/ hexanes) of the crude product afforded a white solid (15.63 g, 52%). ^1H NMR ($CDCl_3$): δ 7.42 (d, 4H, aryl), 7.14 (s, 4H, aryl), 7.09 (d, 4H, aryl), 1.45 (s, 18H, CH_3). ^{13}C NMR ($CDCl_3$): δ 153.3 (C=O), 141.9 (ipso), 140.2 (ipso), 131.9 (CH), 128.5 (CH), 127.2 (CH), 119.1 (ipso), 81.8 (ipso), 28.2 (CH_3). DEPT 135 NMR ($CDCl_3$): δ 131.9 (CH), 128.5 (CH), 127.2 (CH), 28.2 (CH_3). M/z: 618 (M+).

1.4.24 **Bis-[4-(benzhydrylidene-amino)-phenyl]-carbamic acid *tert*-butyl ester (31):**

Compound **31** was prepared by a modification to the procedure used by Buchwald *et al.*[61] In a 150 mL glass bomb under N_2 was combined compound **29** (4.30 g, 10.1 mmol), benzophenone imine (3.84 g, 21.1 mmol), $Pd_2(dba)_3$ (0.10 g, 0.11 mmol), BINAP (0.20 g 0.33 mmol), sodium *tert*-butoxide (3.21 g, 33.4 mmol), and dry THF (60 mL). After heating at 70 °C for 24 h, the mixture was cooled to RT and 100 mL of CH_2Cl_2 was added. After filtration through celite, the mixture was concentrated under reduced pressure and dissolved in 100 mL of methanol. Crystallization out of methanol gave yellow crystals (2.53 g, 40%). ^{1}H NMR ($CDCl_3$): δ 7.71 (m, 4H, aryl), 7.40 (m, 6H, aryl), 7.24 (m, 6H, aryl), 7.09 (m, 4H, aryl), 6.90 (m, 4H, aryl), 6.62 (m, 4H, aryl), 1.35 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$): δ 168.4 (C=N), 153.7 (C=O), 148.5 (ipso), 139.5 (ipso), 138.4 (ipso), 136.0 (ipso), 130.7 (aryl CH), 129.5 (aryl CH), 129.2 (aryl CH), 128.6 (aryl CH), 128.1 (aryl CH), 127.9 (aryl CH), 126.7 (aryl CH), 121.2 (aryl CH), 80.6 (BOC ipso), 28.1 (CH_3). DEPT 135 NMR ($CDCl_3$): δ 130.7 (aryl CH), 129.5 (aryl CH), 129.2 (aryl CH), 128.6 (aryl CH), 128.1 (aryl CH), 127.9 (aryl CH), 126.7 (aryl CH), 121.2 (aryl CH), 28.1 (CH_3). M/z: 628 (M+).

1.4.25 **Bis-(4-amino-phenyl)-carbamic acid *tert*-butyl ester (32):**

Compound **32** was prepared by a modification to the procedure used by Buchwald *et al.*[61] A solution of diimine **31** (4.68 g, 7.4 mmol), ammonium formate (7.05 g, 111.8 mmol), and palladium on carbon (10%) (0.5 g, 10% by weight) were heated for 6 h at 60 °C under nitrogen. After filtration of the cooled solution through celite, volatile organics were removed under reduced pressure. Column chromatography (EtOAc/hexanes) gave a white solid (1.75 g, 78%).

^{1}H NMR ($CDCl_3$): δ 7.00 (d, 4H, aryl), 6.60 (d, 4H, aryl), 3.60 (s, 4H, NH2), 1.43 (s, 9H, CH3). ^{13}C NMR ($CDCl_3$): δ 154.5 (C=O), 144.0 (ipso), 134.6 (ipso), 127.8 (aryl CH), 115.1 (aryl CH), 80.3 (BOC ipso), 28.3 (CH_3). DEPT 135 NMR ($CDCl_3$): δ 127.8 (aryl CH), 115.1 (aryl CH), 28.3 (CH_3). M/z: 299 (M+).

1.4.26 **1,4-Phenylenebis[(4-aminophenyl)-, bis(1,1-dimethylethyl)] carbamic acid ester (34):**

Compound **34** was prepared by a modification of literature procedures.[28,48] In a 150 mL Schlenk flask under N_2 was combined 1,4-phenylenediamine hydrochloride (2.13 g, 11.8 mmol), N-(diphenyl-methylene)-4-bromoaniline (7.99 g, 23.8 mmol), $Pd(OAc)_2$ (0.04 g, 0.18 mmol), BINAP (0.15 g 0.24 mmol), sodium *tert*-butoxide (5.01 g, 52.1 mmol), and dry THF (70 mL). After heating at 70 °C for 24 h, the mixture was cooled to RT. A solution of BOC_2O (9.07 g, 41.5 mmol) and DMAP (0.15 g, 1.2 mmol) in dry THF (30 mL) was added by syringe. After heating to 70 °C for another 24 h, methylene chloride (200 mL) was added to the mixture at RT. After filtration and removal of volatile organics, the residue was dissolved in 150 mL of hot ethanol. Upon cooling, a yellow solid was formed and collected by filtration. This crude material was mixed with hydroxylamine hydrochloride (2.06 g, 29.6 mmol), and pyridine (3.75 g, 47.5 mmol), chloroform (200 mL), THF (50 mL), and ethanol (25 mL). After 3 h of stirring, triethylamine (distilled) (12.0 g, 118.8 mmol) was added and stirring continued for 3 h. After concentration under reduced pressure, the remaining solid was heated in 300 mL of 2-propanol, 60 mL of chloroform, and 30 mL of water for 10 min. After cooling overnight, a white solid was collected and dried under vacuum (3.67 g, 63%). ^{1}H NMR (d_6-DMSO): δ 7.06 (s, 4H, aryl), 6.82 (d, 4H, aryl), 6.49 (d, 4H, aryl), 5.08 (s, 4H, -NH_2), 1.34 (s, 18H, CH_3). ^{13}C NMR (d_6-DMSO): δ

153.5 (C=O), 147.1 (ipso), 140.3 (ipso), 131.1 (ipso), 128.2 (aryl CH), 126.0 (aryl CH), 113.8 (aryl CH), 79.9 (BOC ipso), 28.9 (CH_3). DEPT 135 NMR (d_6-DMSO): δ 128.2 (aryl CH), 126.0 (aryl CH), 113.8 (aryl CH), 28.9 (CH_3).

1.4.27 **Bromopentamer (35):**

Compound **35** was prepared via a modified procedure given by Buchwald *et al.*[28] In a 250 mL Schlenk flask under N_2 was combined amine trimer **34** (4.05 g, 8.2 mmol), 1,4-dibromobenzene (6.00 g, 25.4 mmol), $Pd_2(dba)_3$ (0.16 g, 0.17 mmol), BINAP (0.27 g 0.45 mmol), sodium *tert*-butoxide (2.40 g, 25.0 mmol), and dry THF (80 mL). After heating at 70 °C for 24 h, the mixture was cooled to RT. A solution of BOC_2O (6.30 g, 28.9 mmol) and DMAP (0.20 g, 1.6 mmol) in dry THF (50 mL) was added by syringe. After heating to 70 °C for another 24 h, methylene chloride (150 mL) was added to the mixture at RT. After filtration and removal of volatile organics, a crude solid was obtained. Column chromatography (EtOAc/ hexanes) of the crude product afforded a white solid (3.59 g, 44%). ^{1}H NMR ($CDCl_3$): δ 7.38 (d, 4H, aryl), 7.10 (m, 16H, aryl), 1.41 (s, 36H, *tert*-butyl). ^{13}C NMR ($CDCl_3$): δ 153.5 (C=O), 153.3 (C=O), 141.8 (*ipso*), 140.3 (*ipso*), 140.1 (*ipso*), 139.8 (*ipso*), 131.7 (aryl CH), 128.3 (aryl CH), 127.0 (b, 3 aryl CH), 118.9 (*ipso*), 81.5 (BOC *ipso*), 81.3 (BOC *ipso*), 28.1 (-CH_3), 27.8 (-CH_3)

1.4.28 **Typical Synthesis of 4p,*o*-PANi and derivatives (36 and 37):**

Ortho-para macromonomer **25** (0.12 g, 0.27 mmol), PANi dimer **32** (0.08 g, 0.27 mmol) NaO^tBu (0.10 g, 1.0 mmol), $Pd_2(dba)_3$ (0.004 g, 0.004 mmol) and 2-(di-*tert*-

butylphosphino)biphenyl (0.0032 g, 0.01 mmol) were transferred to a glass bomb equipped with a Teflon value and suspended in dry THF (2 mL). The glass bomb was sealed and heated to 80 °C for 2 d. After cooling to room temperature, the THF solution was pipetted dropwise into 15 mL of methanol to precipitate the polymer. THF (2 mL) was added to the reaction flask and sonication (30 min-overnight) was used to dissolve any remaining solids. After sonication, the THF solution was added dropwise to 15 mL of methanol. After centrifugation and decantation of methanol, the precipitated polymers were dissolved in THF (2 mL) with sonication (30 min-2h). The combined THF solutions (4 mL) were added dropwise into 20 mL of methanol precipitating out the polymer. After centrifugation and decantation, the polymer was again dissolved in THF (2 mL) and precipitated into methanol (20 mL). The product was collected and dried overnight under vacuum to give a pale purple to black solid (10-40% yield).

1.4.28.1 ^{1}H NMR of 4*p,o*-PANi (36):

^{1}H NMR (d_8-THF): δ 7.30 (bm, 4H, aryl), 7.10 (bm, 16H, aryl), 1.39 (bs, 9H, CH_3). ^{13}C NMR (d_8-THF): δ 154.4 (C=O), 153.2 (C=O), 144.5 (ipso), 141.6 (ipso), 137.7 (ipso), 131.1 (aryl), 128.9 (aryl), 128.6 (aryl), 127.9 (aryl), 122.2 (aryl), 118.7 (aryl), 117.7 (aryl), 114.7 (aryl), 109.1 (aryl), 80.4 (BOC ipso), 28.5 (BOC-CH_3).

1.4.28.2 ^{1}H NMR of 4*p,o*-PANi derivative (37):

^{1}H NMR (d_8-THF): δ 7.41 (bm, 6H, aryl), 7.12 (bm, 10H, aryl), 6.95 (bm, 3H, aryl), 2.31 (bs, 3H, aryl CH_3), 1.43 (bs, 9H, BOC-CH_3). ^{13}C NMR (d_8-THF): δ 154.3 (C=O), 153.2 (C=O), 144.5 (ipso), 141.8 (ipso), 138.5 (ipso), 134.9 (ipso), 129.2 (aryl), 128.4 (aryl), 126.2 (aryl),

126.1 (aryl), 125.9 (aryl), 125.4 (aryl), 125.4 (aryl), 125 (aryl), 120.2 (aryl), 116 (aryl), 114.9 (aryl), 112 (aryl), 77.6 (BOC-ipso), 25.7 (BOC-CH_3), 18.7 (aryl CH_3).

2.0 POLYANILINE: PHENAZINE DERIVATIVES

2.1 INTRODUCTION

2.1.1 The Microstructure of *para*-Polyaniline

The structure of *para*-poly(aniline) (*p*-PANi) has been described differently as new discoveries about the polymer were uncovered. In 1910-1912, polyaniline was described as an octamer that existed in four different oxidation states.[8,67] Today, the microstructure of polyaniline is believed to consist of alternating benzenoid and quinoid units[68] as shown in Figure 9.

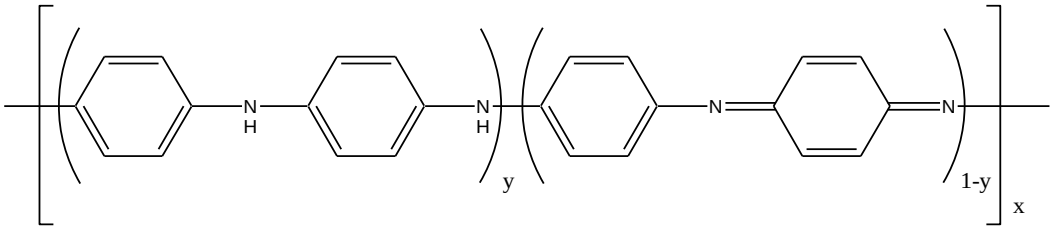


Figure 9. Structure of *p*-PANi

The degree of oxidation can be varied producing the completely reduced leucoemeraldine form, the half oxidized emeraldine form, or the completely oxidized pernigraniline form.[3-5] To further complicate the situation, PANi can exist in a base form such as emeraldine base or in a protonated salt form such as the conducting emeraldine hydrochloride salt[3-5] as shown in Figure 10.

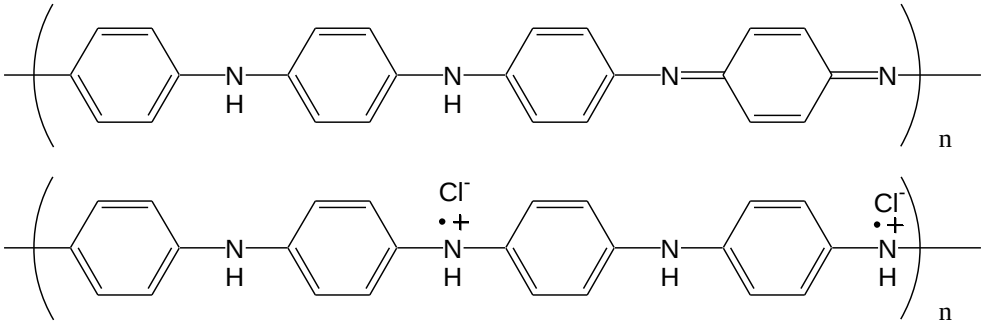


Figure 10. (Top) emeraldine base and (bottom) emeraldine hydrochloride salt form of *p*-PANi

2.1.2 **Effects of Structure on Conductivity and Solubility**

Due to the rigid nature of p-PANi necessary to maintain the electroactive nature of the polymer, p-PANi suffers from low solubility and poor polymer properties.[36] Attempting to increase the solubility of p-PANi, the two existing methodologies either utilize a solubilizing counter-ion dopant such as camphorsulfonate[36,69] or substitute a solubilizing substituent in the polymer backbone at the *ortho*-position relative to the nitrogen.[37-41,43,70] The latter approach induces steric strain in the polymer backbone lowering the conductivity of the polymer[37-41,43,70] as shown in Figure 11.

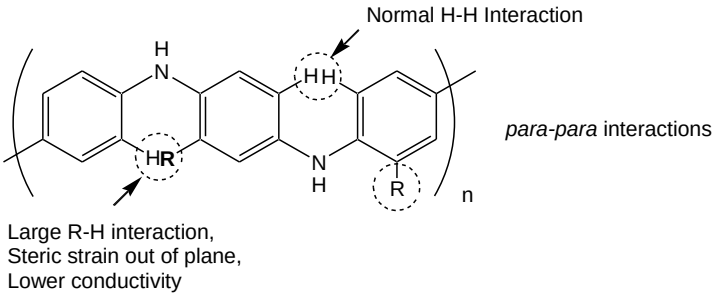


Figure 11. Steric interactions in *p*-PANi

2.1.3 **Synthetic Approach**

Previously we have proposed to incorporate a repeating *ortho*-unit in the polymer backbone[48,55] (Figure 12). Theoretically, a repeating *ortho*-unit would allow for solubilizing substitution along the polymer backbone without inducing steric strain and maintaining the conductivity of a *para*-unit. However, the effect of *ortho*-units on chain-chain relationships is not clear.

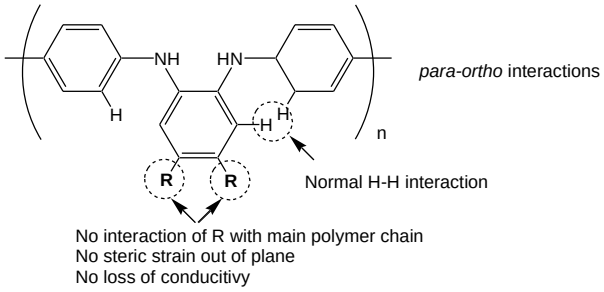


Figure 12. Steric interactions in *p,o*-PANi

2.1.4 **4p,o-PANi and 5p,o-PANi Systems**

Having previously documented the various problems with incorporating an *ortho*-unit into the polymer backbone, Ward successfully completed the synthesis of a 5*p,o*-PANi polymer utilizing a urea moiety to protect the *ortho*-unit[48,55] (Figure 13). While the conductivity of this polymer blended with PVC was found to be similar to the conductivity of *p*-PANi blended with PVC, no 5*p,o*-PANi derivative was prepared with a substitution on the *ortho*-unit.[48,55]

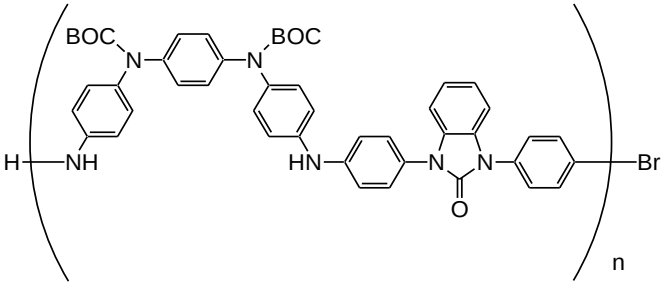


Figure 13. Ward's 5p,o-PANi

We have prepared in this work a 4p,o-PANi polymer system similar to Ward's 5p,o-PANi system with the incorporation of substitution on the *ortho*-unit (Figure 14). Our inability to effectively determine the conductivity of these materials due to poor molecular weights has lead us to consider alternative structures.

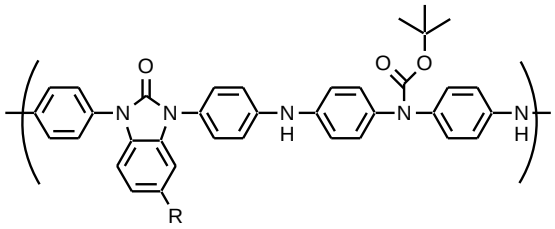


Figure 14. Proposed 4*p,o*-PANi structure

2.1.5 **Problems associated with Ureas in Polyaniline**

Initial computational studies done by Bredas indicate that the conductivity of a polymer system can be estimated. Through computer modeling, Bredas was able to predict accurately the theoretical ionization potential as compared to experimental results and found a correlation between the theoretical bandwidth and the conductivity of the polymer.[71-73]

Building upon the work done by Bredas *et al.*, Burke found that polymer systems containing ether linkages such as poly(phenylene oxide) (PPO) were less conductive than polymers containing only carbon-carbon bonds such as poly(*p*-phenylene) (PPP) (Figure 15).

Polymer systems including carbonyl moieties, such as poly(phenylcarbonyl) (PPC), were found to have BW slightly larger than PPO but drastically lower than PPP.[74]

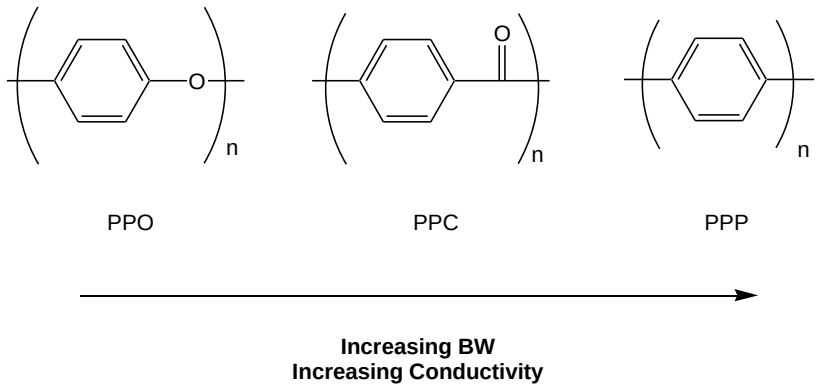


Figure 15. Conductivity relationship between selected phenyl based polymers

While acid doping cleaves the BOC carbonyl, one potentially conductivity reducing carbonyl remains in both the 4p,o-PANi and 5p,o-PANi systems. Burke suggests that conductivity may be retained if a suitable alternative pathway exsists[74] possibly explaining the observed conductivity in 5p,o-PANi systems.[48,55] We desired to explore the viability of removing the carbonyl moiety from our polymer system.

2.1.6 **New Design Architectures: Quinoxalines**

Having attempted other bridging moieties for *ortho*-diamine systems earlier in this work, we considered creation of a simple six member heterocyclic ring. In our retrosynthetic approach, we envisioned these compounds, known generally as hydroquinoxalines, could be prepared from diones and *ortho*-diamine starting materials (Figure 16).

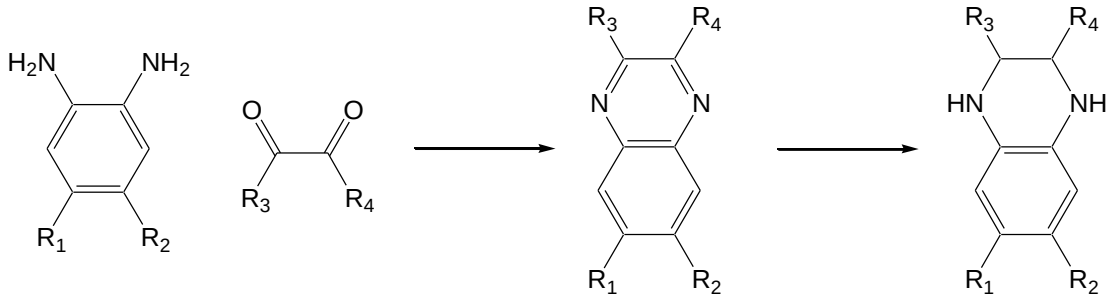


Figure 16. Proposed Route to Quinoxaline Monomers

The preparation of quinoxalines from *ortho*-diamines and diones is well established in the literature. Of the reported methods using sulfamic acid/MeOH,[75] high pressure,[76] microwave,[77] and aqueous conditions,[78] we choose to modify the simple refluxing methodology used by Naskar *et al.*[79] The reduction of quinoxalines to tetrahydroquinoxalines has been accomplished using indium[80,81] or rhodium[82] catalysts, borane,[83] diborane,[84] and lithium aluminum hydride.[85]

2.1.7 **New Design Architectures: Phenazines**

Remarkably, phenazine compounds have long been important organic compounds. In 1856 while attempting to prepare quinine, Sir William Henry Perkin prepared mauveine, an impure mixture of substituted phenazines. Mauveine became the first successful synthetic dye and since then, phenazine has been utilized primarily in the dye industry.[86] Recently, interest in phenazine derivatives has been increasing in pharmaceuticals and electrochromic devices.[87]

In 1886, Merz[88] and Ris[89] were the first to provide a synthesis of phenazine which left no doubt about the ring structure. They reacted pyrocatechols with *ortho*-phenylenediamines at 200 °C to give methylphenazine[88] and phenazine,[89] although Morley[90] later reported drastic modifications were necessary to obtain suitable results.

Since 1886, phenazine has been prepared many ways and sometimes with a significant amount of difficulty. Phenazine has been prepared by condensation of *o*-quinone with *o*-

phenylenediamine,[91] condensation of 1,2-cyclohexadione with *o*-phenylenediamine in the presence of iodine[92] or palladium charcoal,[90,93] reaction of *o*-aminodiphenylamines with lead oxide,[94] reaction of 2-nitrodiphenylamine with iron,[95] reduction of 2,2'-dinitrodiphenylamine followed by cyclization and oxidation,[96,97] and condensation of *o*-bromoaniline.[98]

We envisioned a duel synthetic route that could provide two interesting polymers. Following Clemo and McIlwain's example,[92] we envisioned condensing various substituted *ortho*-phenylenediamines with 1,2-cyclohexadione to give tetrahydrophenazine derivatives (step A) (Figure 17). Following several examples,[90,92,93] an oxidation step (step B) followed by subsequent reduction step (step C) based upon the work of Sugimoto[99] of the tetrahydrophenazine derivatives would afford the desired phenazine derivative (Figure 17). Alternatively, reduction of the tetrahydrophenazine derivatives (step D) based upon the work of Morley[90] would afford the octahydrophenazine derivative, another potentially interesting monomer.

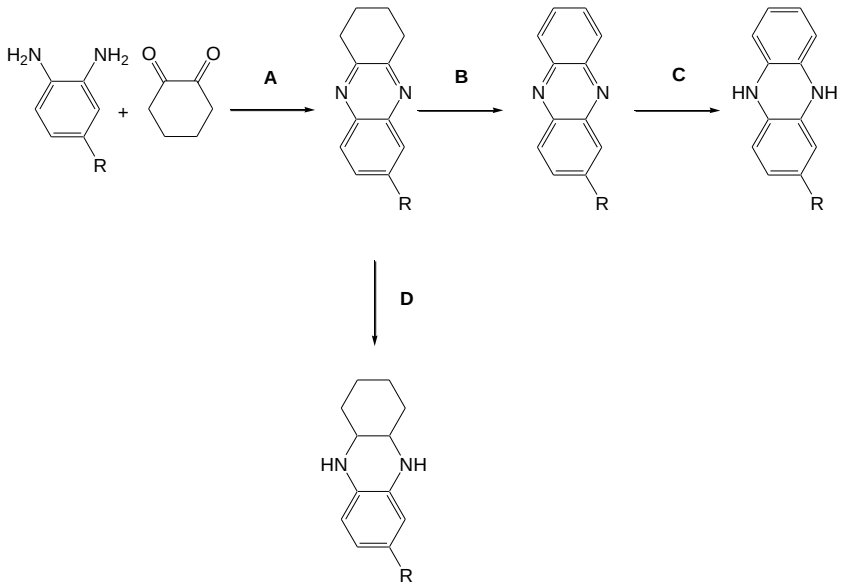


Figure 17. Proposed Route to Phenazine Monomers

2.1.8 **Direct Synthesis of Phenazine Compounds Utilizing Benzoquinones**

While 1,2-cyclohexyldione is commercially available, 4,5-subsituted 1,2-cyclohexyldiones are exceedingly hard to prepare and require multi-step synthesis[100,101] to prepare simple methyl substituted derivatives. We were interested in preparing phenazine derivatives that had substitution at the 2,3,7, and 8 positions. A quick survey of the literature showed that many of the synthetic methods to substituted phenazines required rigorous conditions or several synthetic steps to obtain the desired phenazine product often with low yields.

We reasoned that a large library of phenazine derivatives could be made by the very simple condensation of *ortho*-benzoquinone with *ortho*-diamines (Figure 18). Indeed, the early work of Kehrmann and Mermod[91] confirm the fact that phenazine can be synthesized by reacting o-quinone with o-phenylenediamine in low yields. Others have shown that this type of condensation works for the synthesis of other phenazine derivatives as well.[102,103]

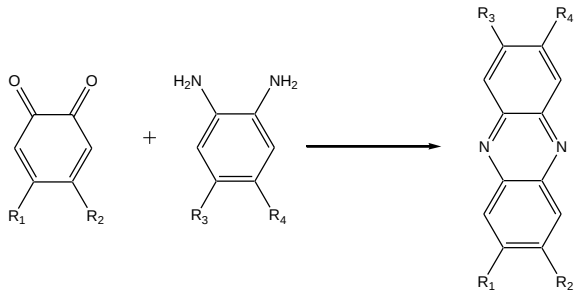


Figure 18. Direct Route to Phenazine Monomers

The preparation of [1,2]benzoquinone has been reported on extensively in the literature. In general, the methods consist of oxidation of phenol or catechol and can be categorized into chemical oxidation methods with transition metals,[104,105] chemical oxidations without transition metals,[106-108] chemical oxidations in the presence of non-oxidative additives such as resins[109] or silica,[110] and biological oxidations.[111-114]

Like [1,2]benzoquinone, the preparation of 4-methyl-[1,2]benzoquinone has been reported extensively in the literature. In general, the methods consist of oxidation of a substituted phenol or substituted catechol and can be categorized into chemical oxidations with transition metals,[115] chemical oxidations without transition metals,[116-122] and biological oxidations.[123-128]

Although to a lesser extent, the preparation of 4,5-dimethyl-[1,2]benzoquinone is reported in the literature. The typical synthetic route involves oxidation of a substituted phenol or catechol by chemical oxidation with a transition metal[129] or without.[106,118,130] We also desired to prepare an ethyl ester substituted derivative of [1,2]benzoquinone and hoped to modify a literature procedure to prepare this derivative.

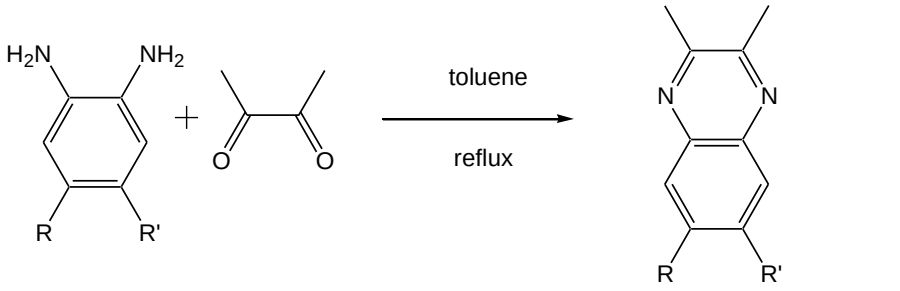
Herein, we report our effects to create polyaniline derivatives without non-removable carbonyl groups. We report our attempts to make polyaniline derivatives from quinoxalines derivatives. We report our attempts to make polyaniline derivatives from phenazine derivatives.

2.2 **RESULTS**

2.2.1 **Synthesis of Quinoxaline Monomers**

In our search for a suitable replacement for the urea protection group, we devised a simple method of protecting the *ortho* amine with a bridging moiety formed from the condensation of a diketone with the diamine. Reduction of the resulting quinoxaline would yield a diamine that could be used in a polymerization. Aware of literature methods,[75-78,131] we

modified the methodology of Naskar[79] for reacting 2,3-butadione with various *ortho* amines (Scheme 42).



1a R = R' = H
1b R = R' = Me
1c R = H; R' = C(O)OMe

2a R = R' = H
2b R = R' = Me
2c R = H; R' = C(O)OMe

Scheme 42. Synthesis of quinoxalines

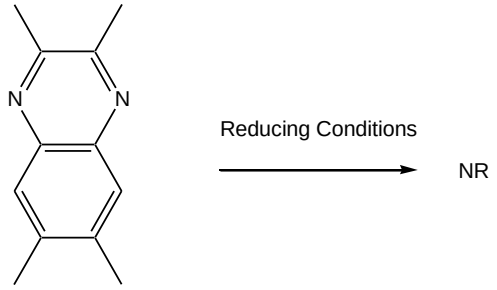
The reaction of 1,2-diaminobenzene with 2,3-butadione yielded the predicted quinoxalines **2a** in 84% (Scheme 42). The ^{1}H NMR spectrum exhibits proper integration of the aryl signals at δ 7.92 and δ 7.61 and the methyl signal at δ 2.68. The ^{13}C NMR spectrum contains the expected C=N signal at δ 153.4, one ipso carbon, two aryl carbons, and one methyl signal.

The reaction of 4,5-dimethyl-*o*-phenylenediamine with 2,3-butadione yielded the expected quinoxalines **2b** in 76% yield (Scheme 42). The ^{1}H NMR spectrum exhibits the proper integration between the aryl signal at δ 7.66 and the two methyl signals at δ 2.64 and δ 2.40. The ^{13}C NMR spectrum shows one C=N signal at δ 152.2, two ipso carbons, one aryl carbon, and two methyl carbons.

The reaction of 3,4-diamino-benzoic acid methyl ester with 2,3-butadione yielded the expected quinoxalines **2c** in 65% yield (Scheme 42). The ^{1}H NMR spectrum exhibits the proper integration between the aryl signals at δ 8.61, δ 8.17, and δ 7.92; the ester methyl signal at δ 3.97; and the methyl signal at δ 2.68. The ^{13}C NMR spectrum exhibits the C=O signal at δ

166.3; two C=N signal at δ 155.6 and δ 154.6; three ipso carbons; three aryl carbons; and two methyl signals.

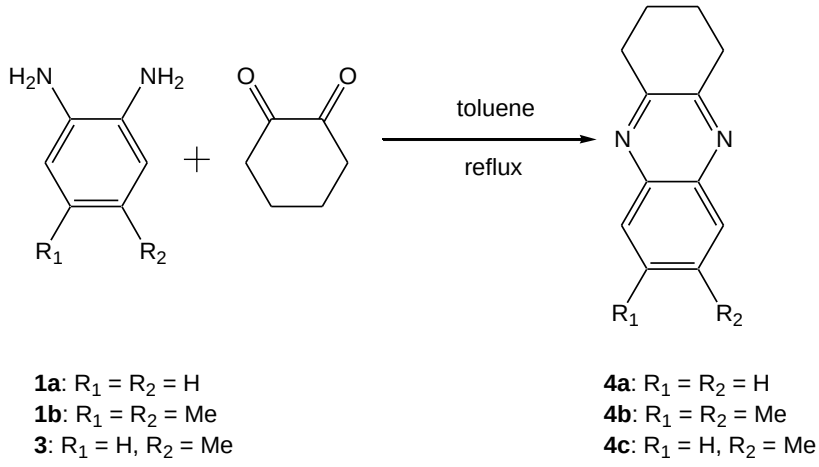
The reduction of quinoxaline **2b** was attempted under various reducing conditions (Scheme 43). The reaction of quinoxaline **2b** and sodium dithionite in refluxing ethanol gave only starting materials upon work-up. Reaction of quinoxalines **2b** with sodium in refluxing ethanol may have reduced the compound as evident by a color change of the solution, but upon isolation only the starting materials were evident by GC-MS and NMR spectrum. After an exhaustive search of the literature, other references to the reduction of quinoxalines were discovered;[80-85] however, none of them were attempted.



Scheme 43. Reduction of quinoxaline 2b

2.2.2 **Synthesis of Tetrahydrophenazines**

After having little success with quinoxalines, we considered similar reactions with 1,2-cyclohexadione instead of 2,3-butadione. We were aware of the preparation of tetrahydrophenazines by Clemo and McIlwain[92] by complicated condensation reactions. Instead, we proposed a simple, straightforward condensation leading directly to the desired tetrahydrophenazine products (Scheme 44).



1a: $R_1 = R_2 = H$
1b: $R_1 = R_2 = Me$
3: $R_1 = H$, $R_2 = Me$

4a: $R_1 = R_2 = H$
4b: $R_1 = R_2 = Me$
4c: $R_1 = H$, $R_2 = Me$

Scheme 44. Synthesis of tetrahydrophenazines

We preferred to synthesize compound **4a** by reaction of *o*-phenylenediamine with 1,2-cyclohexadione in toluene (Scheme 44). Compound **4a** could be isolated after crystallization out of methylene chloride in 76% yield. The ^{1}H NMR spectrum exhibits the proper integration between the aryl signals at δ 7.95 and δ 7.65 and the cyclohexyl protons at δ 3.12 and δ 2.00. The ^{13}C NMR spectrum exhibits one C=N carbon at δ 154.1 and 3 aryl signals along with two cyclohexyl methylene carbons.

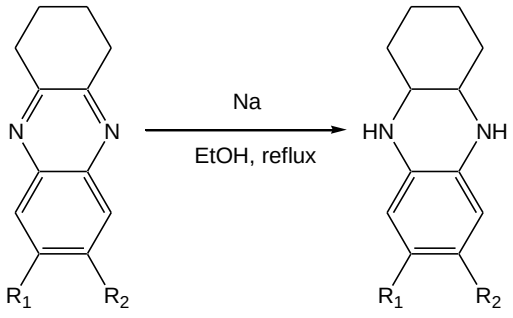
The monomethyl derivative **4c** was prepared by reaction of 4-methyl-*o*-phenylenediamine with 1,2-cyclohexadione in refluxing toluene in 62% yield (Scheme 44). The ^{1}H NMR spectrum shows proper integration between the aryl signals at δ 7.75, δ 7.65, and δ 7.28, and the cyclohexyl methylene protons at δ 3.27 and δ 1.95, and the methyl signal at δ 2.47. The ^{13}C NMR spectrum exhibits the expected two C=N signals at δ 153.8 and δ 152.9, three aryl ipso, three aryl CH, four cyclohexyl methylene carbons, and one alkyl carbon.

The dimethyl derivative **4b** was prepared by reaction of 4,5-dimethyl-*o*-phenylenediamine and 1,2-cylcohexadione in refluxing toluene in 81% yield (Scheme 44). The

^{1}H NMR spectrum exhibits one aryl signal at δ 7.58, two cyclohexyl methylene proton signals at δ 3.07 and δ 1.98, and one alkyl signal at δ 2.39. The ^{13}C NMR spectrum displays the C=N signal at δ 152.8, two ipso carbons, one aryl carbon, two methylene carbons, and one alkyl carbon.

2.2.3 **Preparation of Octahydrophenazines**

We modified the procedure used by Morley to effectively synthesize a series of octahydrophenazines.[90] Octahydrophenazine **5a** was prepared by dissolving tetrahydrophenazine **4a** in absolute ethanol in the presence of sodium metal in 82% yield (Scheme 45). The reaction was complete when the solution turned from yellow to colorless indicating complete reduction of the imine bond. The ^{1}H NMR spectrum exhibited proper integration between the aryl signal at δ 6.52, the N-H signal at δ 3.52, the methine signal at δ 2.91, and the cyclohexyl methylene signals. The ^{13}C NMR spectrum displayed the expected one ipso carbon, two aryl carbons, one hexyl methine carbon, and two hexyl methylene carbons.



4a: $R_1 = R_2 = H$ **5a**: $R_1 = R_2 = H$
4b: $R_1 = R_2 = Me$ **5b**: $R_1 = R_2 = Me$
4c: $R_1 = H$, $R_2 = Me$ **5c**: $R_1 = H$, $R_2 = Me$

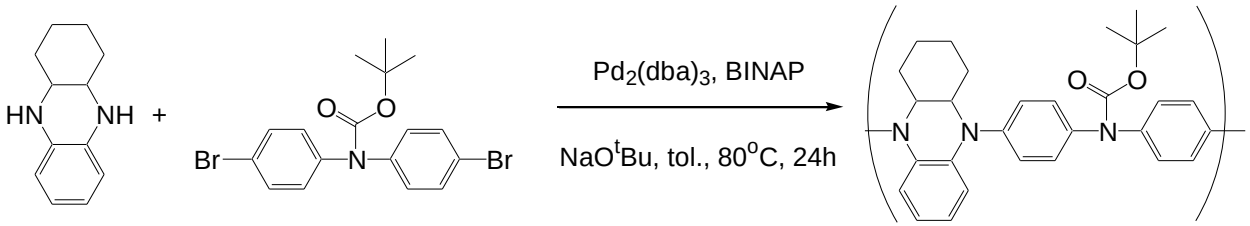
Scheme 45. Preparation of octahydrophenazines

The monomethyl derivative **5c** was prepared by dissolving tetrahydrophenazine **4c** in absolute ethanol in the presence of sodium metal in 84% yield. The ^{1}H NMR spectrum displays proper integration between aryl signals at δ 6.40, the NH signal at δ 3.50, the methine signal at δ 2.89, and the methylene signals. The ^{13}C NMR spectrum exhibits the expected three ipso carbons, three aryl carbons, two methine carbons, four methylene carbons, and one alkyl carbon.

The dimethyl derivative **5b** was prepared by dissolving tetrahydrophenazine **4b** in absolute ethanol in the presence of sodium metal in 82% yield. The ^{1}H NMR spectrum exhibits the proper integration between the aryl signal at δ 6.32, the N-H signal at δ 3.51, the methine signal at δ 2.90, and the cyclohexyl methylene signals. The ^{13}C NMR spectrum exhibits two ipso carbons, one aryl carbon, one methine carbon, two methylene carbons, and one alkyl carbon.

2.2.4 **Poly(octahydrophenazine-*alt*-(aniline)$_2$) Synthesis**

Polymerization of octahydrophenazine **5a** with BOC-protected segmer **6** yielded the octahydrophenazine-*alt*-(aniline)$_2$ polymer **7** under palladium coupling conditions in 9% yield (Scheme 46). The polymer was isolated after reaction by precipitation out of THF solution into methanol. Insoluble materials were sonicated with THF and precipitated into methanol. The combined precipitated polymer was re-dissolved into THF twice and precipitated twice into methanol to give the final polymer as a tan solid. The remaining 91% of the starting material was isolated as insoluble material or short oligomers. The polymer was soluble in THF and methylene chloride, and insoluble in hexanes, methanol, and acetone.



5a **6** **7**

Scheme 46. Synthesis of polymer 7

2.2.4.1 Molecular Weight Determination

GPC data was collected on a Waters GPC instrument in THF calibrated with polystyrene standards. The molecular weight data are summarized in Table 8 below.

Table 8. GPC molecular weight data for polymer **7**

Sample	Mw (x 10^3)[a]	Mn (x 10^3)	PDI
OHP-*alt*-A_2[b]	3.8	5.4	1.4

[a]**THF solvent, calibrated to polystyrene standards**
[b]**octahydrophenazine-alt-(aniline)$_2$**

The GPC data indicated small molecular weights around 3.0 x10^3-4.0 x10^3 which corresponds to 6-9 repeat units or 18-27 aryl units. However, GPC data has been found to overestimate the molecular weight of polyaniline polymers.[24]

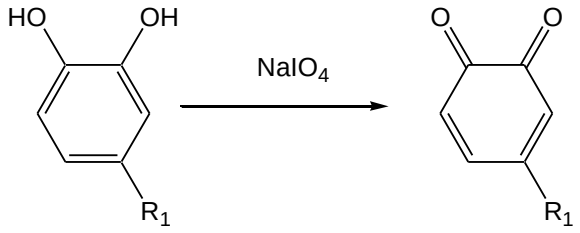
The relatively low molecular weight and low yield discouraged us from attempting more than one polymerization attempt on these octahydrophenazine polymers. The predicted extra complexity of the NMR spectrum encouraged us to first study the phenazine system before fully investigating these polymers. Also, the concern about the cyclohexyl group lowering the conductivity of the resulting polymer lead us to first investigate phenazine polymers which showed more promise as conductive polymers.

2.2.5 **Phenazine Derivatives: *Ortho*-Quinone Synthesis**

We also prepared derivatives of phenazine containing substituents that could either increase the solubility of the resulting polymer or be post-polymerization modifiable. After an extensive literature survey, we decided one route to phenazine derivatives by condensation of *ortho*-quinones with *ortho*-diamines.

The reported methodology of the synthesis of *ortho*-quinones was extensive in the literature. We found methodologies utilizing methods such as AgO,[104] NaOCl/resin,[109] copper cellouse,[111] MnO_2,[105] ammonium persulfate/wet SiO_2,[110] and H_2O_2/I_2.[106] After attempting several of these methodologies, we modified the methodology outlined by Kaiser[107] and Sammes[108] for preparing *ortho*-quinines using sodium periodate with moderate success. In certain circumstances, we utilized Fremy's salt[130,132] in the synthesis of *ortho*-quinines.

Preparation of quinone **9a** was accomplished by reaction of catechol in water with sodium periodate utilized as the oxidant in 34% yield (Scheme 47). The ^{1}H NMR spectrum exhibited proper integration between the aryl signals at δ 7.0 and δ 6.37. The ^{13}C NMR spectrum exhibits the C=O signal at δ 180.2 and two aryl carbon signals.



8a: R_1 = H
8b: R_1 = Me
8c: R_1 = C(O)OEt

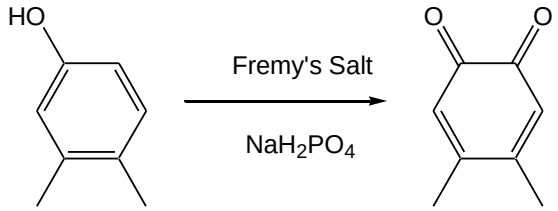
9a: R_1 = H
9b: R_1 = Me
9c: R_1 = C(O)OEt

Scheme 47. Preparation of quinones

The monomethyl derivative **9b** was prepared according to Sammes[108] by reaction of 4-methylcatechol with sodium periodate in 61% yield (Scheme 47). The ^{1}H NMR spectrum shows proper integration between aryl signals at δ 6.86, δ 6.31, and δ 6.20; and the methyl signal at δ 2.13. The ^{13}C NMR spectrum exhibits two C=O signals at δ 179.9 and δ 179.1; one ipso carbon; and three methine carbons.

The ethyl ester derivative **9c** was prepared by reaction of 3,4-dihydroxy-benzoic acid ethyl ester with sodium periodate in THF/water solution in 80% yield (Scheme 47). The ^{1}H NMR spectrum shows the proper integration between the aryl signals at δ 7.58, δ 7.50, and δ 6.86; and the ethyl group signals at δ 4.28 and δ 1.34.

The dimethyl derivative **11** was prepared by reaction of 4,5-dimethyl phenol with Fremy's salt in 55% yield (Scheme 48). The ^{1}H NMR spectrum shows proper integration between the aryl signal at δ 6.19 and the methyl signal at δ 2.13. The ^{13}C NMR spectrum exhibits the expected C=O signal at δ 180.1, one ipso carbon, one aryl carbon, and one methyl carbon.

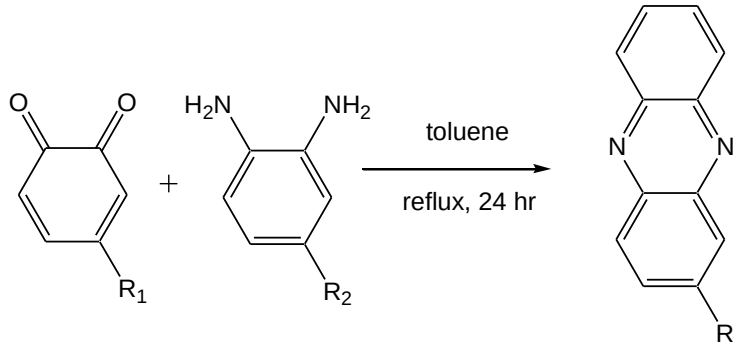


10 **11**

Scheme 48. Synthesis of quinone 11

2.2.6 **Phenazine Derivatives: Reactions of *Ortho*-Quinones and Diamines**

While there are several complicated methods of preparing specific phenazine derivatives, we desired to find a simple methodology that would allow for a wide variety of phenazine derivatives to be prepared. We envisioned condensing *ortho*-quinones with *ortho*-diamines to yield the desired phenazine derivatives allowing us to change functionalization on both the quinone and the diamine (Scheme 49).



9a: R_1 = H **3**: R_2 = Me **12a**: R = Me
9c: R_1 = C(O)OEt **1a**: R_2 = H **12b**: R = C(O)OEt

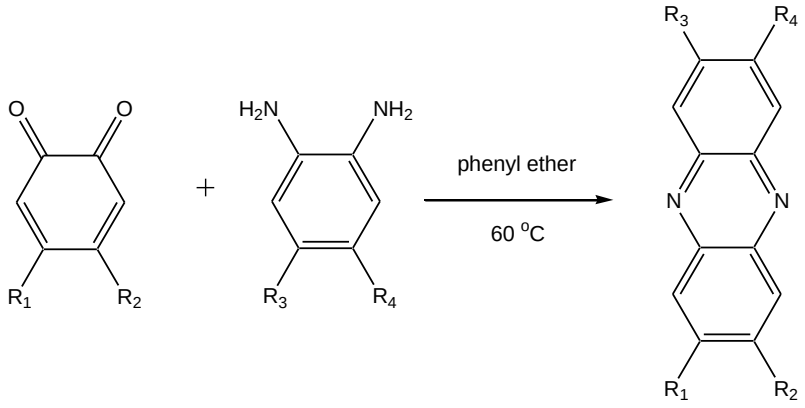
Scheme 49. Reaction of substituted quinones with substituted amines in toluene

Initially we attempted to synthesize 2-methyl-phenazine from 4-methyl-*ortho*-phenylenediamine **3** and [1,2]benzoquinone **9a** in refluxing toluene utilizing a Dean-Stark trap to remove water (Scheme 49). We were able to recover compound **12a** in 22% yield after column chromatography. The ^{1}H NMR spectrum of compound **12a** shows the proper integration between the aryl signals at δ 7.51, δ 7.41, δ 7.27, δ 7.10, and δ 6.96; and the methyl signal at δ 1.94. The ^{13}C NMR spectrum exhibited the expected five ipso carbons, seven aryl carbons, and one alkyl carbon.

The ethyl ester phenazine derivative **12b** was prepared from the quinone **9c** and *ortho*-phenylenediamine **1a** in toluene with a similarly low yield of 27% (Scheme 49). The ^{1}H NMR spectrum of compound **12b** shows the proper integration between the aryl signals at δ 8.97, δ

8.35, δ 8.23, and δ 7.86; and the ethyl quartet and triplet at δ 4.48 and δ 1.47 respectively. The ^{13}C NMR exhibits the expected C=O signal at δ 165.6, five ipso carbons, seven aryl carbons, one methylene carbon, and one methyl carbon.

We hypothesized that if we could lower the temperature of reaction the quinone would be less susceptible to decomposition and would improve the yield of the phenazine product. Our experimental apparatus consisted of a vacuum source connected to a Dean-Stark trap equipped with P_2O_5 in the arm connected to the reaction flask. This set-up allowed us to pull vacuum on the system during the reaction. In this manner, 2,3-dimethyl-phenazine **13b** was synthesized from *ortho*-phenylenediamine **1a** and 4,5-dimethyl-[1,2]benzoquinone **11** in phenyl ether at 60 °C in 59% yield (Scheme 50). The ^{1}H NMR spectrum of compound **13b** shows the proper integration between the aryl signals at δ 8.18, δ 7.95, and δ 7.76; and the methyl signal at δ 2.53. The ^{13}C NMR spectrum exhibits the expected three ipso carbons, three aryl carbons, and one alkyl carbon.



9c: R_1 = H, R_2 = C(O)OEt
11: R_1 = R_2 = Me
11: R_1 = R_2 = Me
11: R_1 = R_2 = Me
11: R_1 = R_2 = Me

1b: R_3 = R_4 = Me
1a: R_3 = R_4 = H
1b: R_3 = R_4 = Me
1c: R_3 = H, R_4 = C(O)OMe
3: R_3 = H, R_4 = Me

13a: R_1 = H, R_2 = C(O)OEt, R_3 = R_4 = Me
13b: R_1 = R_2 = Me, R_3 = R_4 = H
13c: R_1 = R_2 = R_3 = R_4 = Me
13d: R_1 = R_2 = Me, R_3 = H, R_4 = C(O)OMe
13e: R_1 = R_2 = R_4 = Me, R_3 = H

Scheme 50. Reaction of substituted quinones with substituted amines in phenyl ether

The trimethyl phenazine derivative **13e** was prepared from 4,5-dimethyl-[1,2]benzoquinone **11** and 4-methyl-*ortho*-phenylenediamine **3** in phenyl ether at 60 °C in 56% yield (Scheme 50). The ^{1}H NMR spectrum shows the proper integration between the aryl signals at δ 8.05, δ 7.92, and δ 7.59; and the alkyl signals at δ 2.66 and δ 2.52. The ^{13}C NMR spectrum exhibits the expected seven ipso carbons, five aryl carbons, and two alkyl carbons.

The tetramethyl phenazine derivative **13c** was prepared from 4,5-dimethyl-[1,2]benzoquinone **11** and 4,5-dimethyl-*ortho*-phenylenediamine **1b** in phenyl ether at 60 °C in 41% yield (Scheme 50). The ^{1}H NMR spectrum shows the proper integration between the aryl signal at δ 6.54 and the methyl signal at δ 2.00. The ^{13}C NMR spectrum exhibits the C=N signal at δ 142.7, one ipso carbon, one aryl carbon, and one alkyl carbon.

The dimethyl ethyl ester phenazine derivative **13a** was prepared from quinone **9c** and 4,5-dimethyl-*ortho*-phenylenediamine **1b** in phenyl ether at 60 °C in 14% yield (Scheme 50). The ^{1}H NMR spectrum shows the proper integration between the aryl signals at δ 8.91, δ 8.32, δ 8.17, and δ 7.92; the ethyl quartet and triplet signals at δ 4.45 and δ 1.46 respectively; and the methyl signal at δ 2.53. The ^{13}C NMR spectrum exhibits the expected C=O signal at δ 165.9, seven ipso carbons, five aryl carbons, one methylene carbon, and two methyl carbons.

The dimethyl methyl ester phenazine derivative **13d** was prepared from quinone **11** and 3,4-diamino-benzoic acid methyl ester **1c** in phenyl ether at 60 °C in 34% yield (Scheme 50). The ^{1}H NMR spectrum shows the proper integration between the aryl signals at δ 8.80, δ 8.22, δ 8.10, and δ 7.82; the methoxy signal at δ 3.97; and the alkyl signal at δ 2.46. The ^{13}C NMR spectrum exhibits the expected C=O signal at δ 166.3, seven ipso carbons, five aryl carbons, one methoxy carbon, and two alkyl carbons.

As a final adjustment to our synthesis of phenazine derivatives, we hypothesized that we might be able to improve the yields of these phenazine compounds by utilizing sonication. We chose to study the reaction of quinone **11** with 4,5-dimethyl-*ortho*-phenylenediamine **1b** (Scheme 50).

Table 9. Sonication reaction of quinone **11** and diamine **1b**

Trial	Sample	Solvent	Time (hr)	Mol ratio (A to Q)	Theo (mg)	GC (mg)	%	Rxn Notes
A	1	THF	2	1:1	20.79	11.85	56.9	Sonic + 55°C
	2	THF	8	1:1	20.79	10.72	51.5	Sonic + 55°C
B	1	THF	2	1:2	18.12	12.2	67.3	Sonic + 55°C
	2	THF	8	1:2	18.12	10.79	59.5	Sonic + 55°C
C	1	THF	2	2:1	18.46	8.98	48.6	Sonic + 55°C
D	1	THF	8	1:1.5	23.08	14.77	64.0	Sieves RT
E	1	THF	8	1:1.5	24.22	15.91	65.7	Control RT
F	1	THF	8	1:1.5	19.07	2.68	14.0	Na RT
G	1	THF	2	1:1.5	22.12	13.57	61.3	Sieves + sonic + 55 °C
	2	THF	8	1:1.5	22.12	16.86	76.2	Sieves + sonic + 55 °C
H	1	THF	2	1:1.5	20.79	17.07	82.1	Sonic + 55°C
	2	THF	8	1:1.5	20.79	15.59	74.7	Sonic + 55°C
I	1	CH_2Cl_2	2	1:1.5	20.98	20.11	95.8	Sonic + 55°C
	2	CH_2Cl_2	8	1:1.5	20.98	14.83	70.6	Sonic + 55°C
J	1	Tol.	2	1:1.5	28.80	35.06	87	Sonic + 55°C
	2	Tol.	8	1:1.5	28.80	24.34	84.5	Sonic + 55°C
K	1	CH_2Cl_2	2	1:1.5	137.7	99.9	72.5	Isolated via column

Trials A, B, C, and H were used to establish the optimal stoichiometric ratio and reaction time. Because of the inability to obtain high purity in the quinone, the optimal stoichiometric ratio is greater than 1:1 of diamine to quinone (A to Q). We chose an optimal ratio of 1:1.5 in the hopes of maximizing the yield while keeping waste of the valuable quinone to a minimum as indicated in Trial H1. Trials A, B, C, and H indicate that the reaction suffers from increased reaction time. This might be a result of alternative reaction pathways, decomposition, or reversibility of the reaction.

Trials D, E, F, and G demonstrated the effects of specific changes to the reaction conditions. Trial D utilizes the addition of molecular sieves. Comparison of the yield for Trial D shows no improvement over the control (Trial E) and slightly reduced yield as compared to Trial H2. Trial F shows the expected reduced yield due to reaction of the quinone with sodium

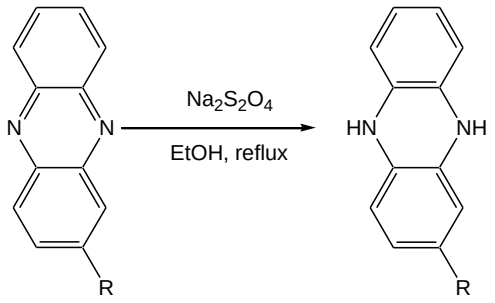
metal. The utilization of sonication, sieves, and heat (Trial G) compares slightly unfavorably to simple sonication and heat (Trial H).

Trials H, I, and J compared the effect of solvent on the reaction. Using methylene chloride as the solvent (Trial I) improves the yield as compared to both THF (Trial H) and toluene (Trial J). This result may be an indication of the solvent's ability to separate the product from water preventing the reversibility of the reaction.

Trial K was isolated by column chromatography and compares favorably to the GC yields in Trial I.

2.2.7 **Reduction of Phenazine and Phenazine Derivatives**

According to the work done by Sugimoto,[99] commercially available phenazine **14** was reduced to 5,10-dihydrophenazine **15b** by addition of sodium dithionite at 78 °C in 65% yield (Scheme 51). Compound **15b** was air sensitive and quickly turns from white to green to blue as oxidation occurs and was kept under a nitrogen atmosphere. The ^{1}H NMR spectrum includes the N-H signal at δ 7.21 and the aryl signals at δ 6.24 and δ 5.99. The ^{13}C NMR spectrum exhibits the expected ipso and two aryl carbons.



13a: R = C(O)OEt
14: R = H

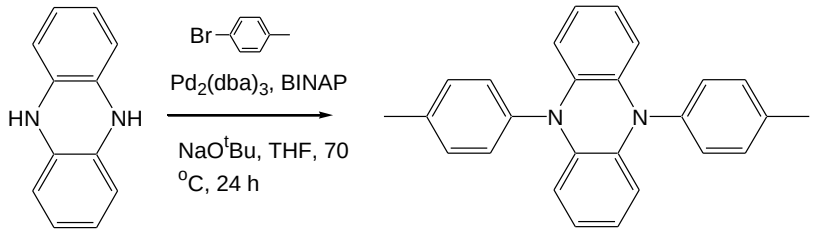
15a: R = C(O)OEt
15b: R = H

Scheme 51. Reduction of phenazines to dihydrophenazines

The ethyl ester dihydrophenazine derivative **15a** can be prepared by reduction of compound **13a** by sodium dithionite in refluxing ethanol in 75% yield (Scheme 51). The ^{1}H NMR spectrum shows the proper integration between the aryl signals at δ 6.91, δ 6.50, δ 6.27, and δ 5.96; the amine signals at δ 7.88 and δ 7.52; and the ethyl group signals at δ 4.13 and δ 1.22 respectively. The ^{13}C NMR spectrum exhibits the expected C=O signal at δ 165.4, twelve aryl carbons, one methylene, and one methyl carbon.

2.2.8 **Reactivity of Dihydrophenazine Derivatives**

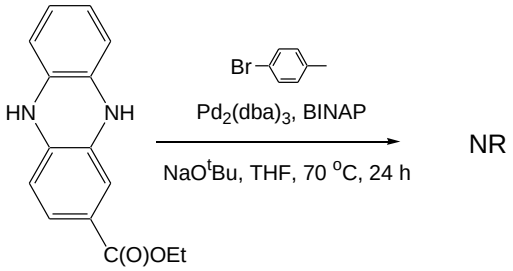
In order to ascertain the reactivity of the phenazine derivatives, 5,10-dihydrophenazine **15b** was reacted with 4-bromotoluene under standard palladium conditions yielding compound **16** in 70% yield. The ^{1}H NMR spectrum shows the proper integration between the aryl signals at δ 7.09, δ 6.91, δ 6.31, and δ 5.88; and the alkyl signal at δ 2.07. The ^{13}C NMR spectrum exhibits the expected three ipso carbons, four aryl carbons, and one alkyl carbon.



15b **16**

Scheme 52. Reactivity of dihydrophenazine 15b under palladium coupling conditions

Curiously, the ethyl ester dihydrophenazine **15a** produced the ethyl ester phenazine **12b** and not the expected product. The ethyl ester dihydrophenazine was equally unreactive under polymerization conditions. We speculated that the presence of the ethyl ester moiety created a favorable pathway for oxidation to the phenazine under standard palladium coupling conditions.

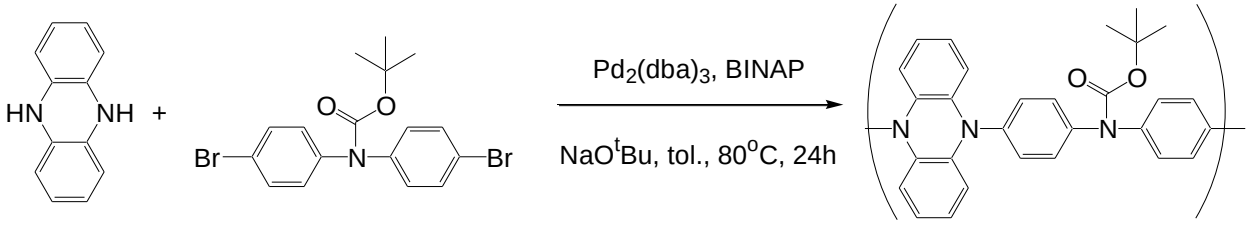


15a

Scheme 53. Reactivity of dihydrophenazine 15a under palladium coupling conditions

2.2.9 **Poly(phenazine-*alt*-(aniline)$_2$) Synthesis**

Polymerization of 5,10-dihydrophenazine **15b** with BOC-protected segmer **6** yielded the phenazine-*alt*-(aniline)$_2$ polymer **17** under palladium coupling conditions in 10-55% yield (Scheme 54). The polymer was isolated after reaction by precipitation out of THF solution into methanol. Insoluble materials were sonicated with THF and precipitated into methanol. The combined precipitated polymer was re-dissolved into THF twice and precipitated twice into methanol to give the final polymer as a tan solid. The remaining 45-90% of the starting material was isolated as insoluble material or short oligomers.



15b **6** **17**

Scheme 54. Preparation of polymer 17

The properties of polymer **17** depend on the reactions conditions in a similar manner as described by Ward.[55] Polymerization reaction times longer than 24 h do not give higher molecular weights and give lower yields. The polymerization was performed in both THF and

toluene as solvents with neither affording a higher molecular weight. However, the ratio of the ^{1}H NMR integration of the aryl protons from monomer **6** and the aryl protons from monomer **15b** indicated in several trials in THF a potential side reaction that was not present in the ^{1}H NMR spectra of polymers prepared from toluene. The polymer was soluble in THF and NMP solvents and insoluble in methylene chloride, chloroform, hexanes, methanol, and acetone. Substitution of BINAP for 2-(di-*t*-butylphosphino)biphenyl was found to have no effect on the molecular weight.

2.2.9.1 NMR Characterization

The ^{1}H NMR spectrum of polymer **17** was acquired in one scan in d_8-THF solvent and exhibits broad features characteristic of a polymeric material. The characteristic signals at δ 6.23 and δ 5.67 were used to verify incorporation of the phenazine moiety into the polymer structure. The doublet at δ 7.61 was assigned to the aryl protons closest to the phenazine moiety. The doublet at δ 7.39 corresponded to the protons on either side of the BOC-protected nitrogen. The polymer also exhibited the expected BOC signal at δ 1.42.

The complex ^{13}C NMR spectrum was compared to the spectrum of the monomers to confirm incorporation (Figure 19). The signal at δ 154.0 indicated the presence of one unique C=O signal. The expected BOC signals were distinguishable at δ 81.5 (ipso carbon) and δ 28.6 (CH_3).

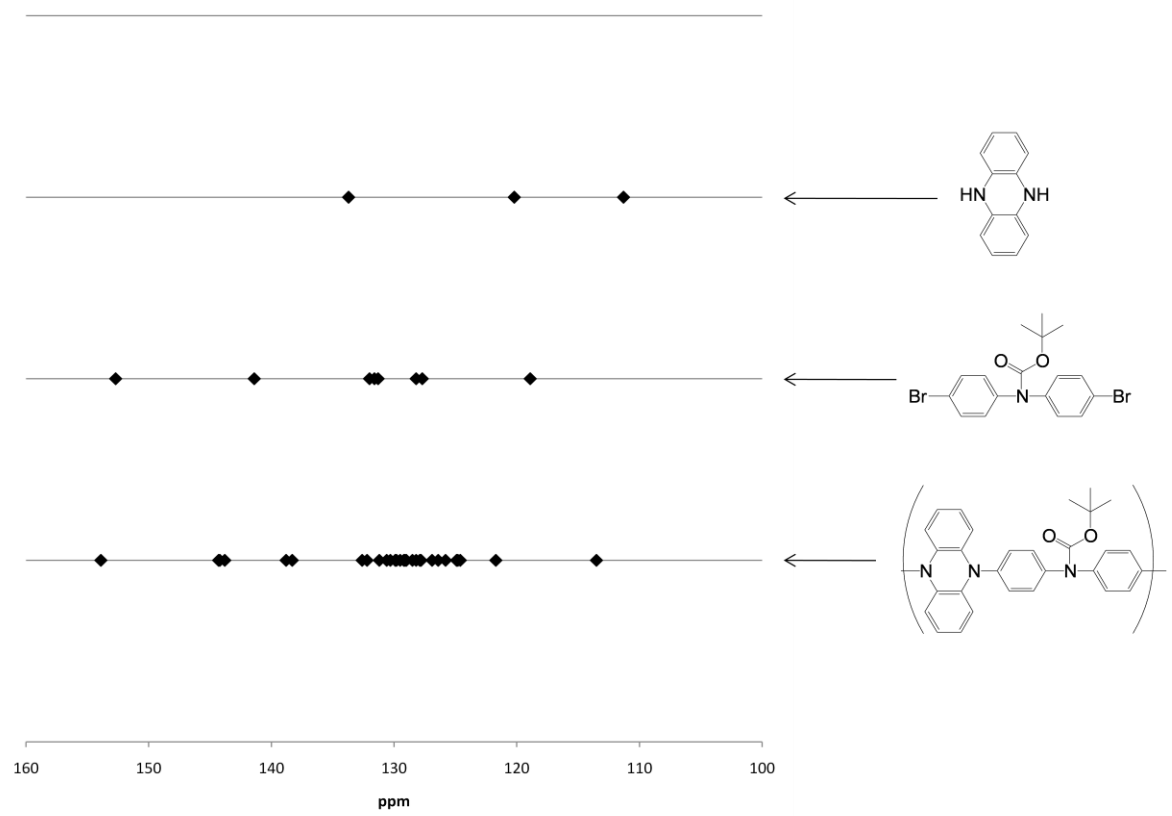


Figure 19. NMR comparison of polymer 17 to respective monomers

2.2.9.2 Molecular Weight Determination

GPC data was collected on a Waters GPC instrument in THF calibrated with polystyrene standards. The molecular weight data for seven independently prepared samples are summarized in Table 10 below.

Table 10. GPC Molecular weights for polymer **17**

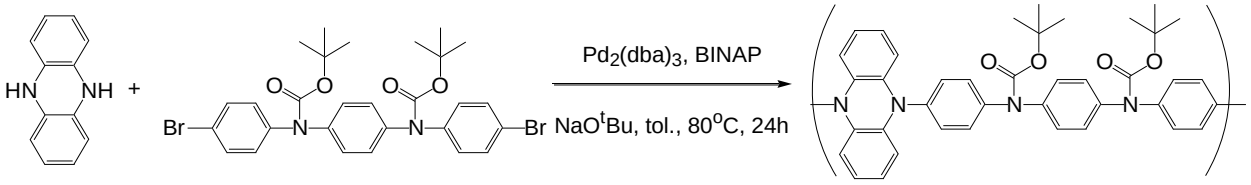
Sample	Mw (x 10^3)[a]	Mn (x 10^3)	PDI
Phenazine-*alt*-(aniline)$_2$-1	13.	17.	1.3
Phenazine-*alt*-(aniline)$_2$-2	15.	22.	1.5
Phenazine-*alt*-(aniline)$_2$-3	6.4	9.9	1.2
Phenazine-*alt*-(aniline)$_2$-4	6.0	8.8	1.5
Phenazine-*alt*-(aniline)$_2$-5	6.0	8.8	1.5
Phenazine-*alt*-(aniline)$_2$-6	5.9	9.0	1.5
Phenazine-*alt*-(aniline)$_2$-7	8.3	14.	1.7

[a]**THF solvent, calibrated to polystyrene standards**

The GPC data indicated small molecular weights around 6.0 $x10^3$ – 1.5 $x10^4$ which corresponds to 13-34 repeat units or 39-102 aryl units. However, GPC data has been found to overestimate the molecular weight of polyaniline polymers.[24] The molecular weight was not determined from the ^{1}H NMR by end group analysis because no end group signal was identifiable. A 1:1 relative monomer ratio was calculated by comparing the integration per proton of the aryl protons originating from the phenazine with the integration per proton of the BOC signal originating from the *para*-aniline segment indicating a repeat sequence structure.

2.2.10 **Poly(phenazine-*alt*-(aniline)$_3$) Synthesis**

Polymerization of 5,10-dihydrophenazine **15b** with BOC-protected segmer **18** yielded the phenazine-*alt*-(aniline)$_3$ polymer **19** under palladium coupling conditions in 8-60% yield (Scheme 55). The polymer was isolated after reaction by precipitation out of THF solution into methanol. Insoluble materials were sonicated with THF and precipitated into methanol. The combined precipitated polymer was re-dissolved into THF twice and precipitated twice into methanol to give the final polymer as a tan solid. The remaining 40-80% of the starting material was isolated as insoluble material or short oligomers.



15b **18** **19**

Scheme 55. Synthesis of polymer 19

The properties of polymer **19** depend on the reactions conditions in a similar manner as described by Ward.[55] Polymerization reaction times longer than 24 h do not give higher

molecular weights and give lower yields. The polymerization was performed in both THF and toluene as solvents with neither affording a higher molecular weight. After careful analysis of the ^{1}H NMR spectra, several trials in THF indicated a potential side reaction that was not present in the ^{1}H NMR spectra of polymers prepared from toluene. The polymer was soluble in THF and NMP solvents and insoluble in methylene chloride, chloroform, hexanes, methanol, and acetone. Substitution of BINAP for 2-(di-*t*-butylphosphino)biphenyl was found to have no effect on the molecular weight.

2.2.10.1 NMR Characterization

The ^{1}H NMR spectrum of polymer **19** was acquired in one scan in d_8-THF solvent and exhibits broad features characteristic of a polymeric material. The characteristic signals at δ 6.35 and δ 5.63 were used to verify incorporation of the phenazine moiety into the polymer structure. The doublet at δ 7.53 was assigned to the aryl protons closest to the phenazine moiety. The singlet at δ 7.33, which overlaps the doublet at δ 7.32, corresponded to the 4 symmetric protons between BOC-protected nitrogens. The doublet at δ 7.32 coupled with the doublet at δ 7.53 and was assigned to the protons on either side of the BOC-protected nitrogens. The polymer also exhibited the expected BOC signal at δ 1.41.

The complex ^{13}C NMR spectrum was compared to the spectrum of the monomers to confirm incorporation (Figure 20). The signal at δ 154.0 indicated the presence of one unique C=O signal. The expected BOC signals were distinguishable at δ 81.5 (ipso carbon) and δ 28.5 (CH_3).

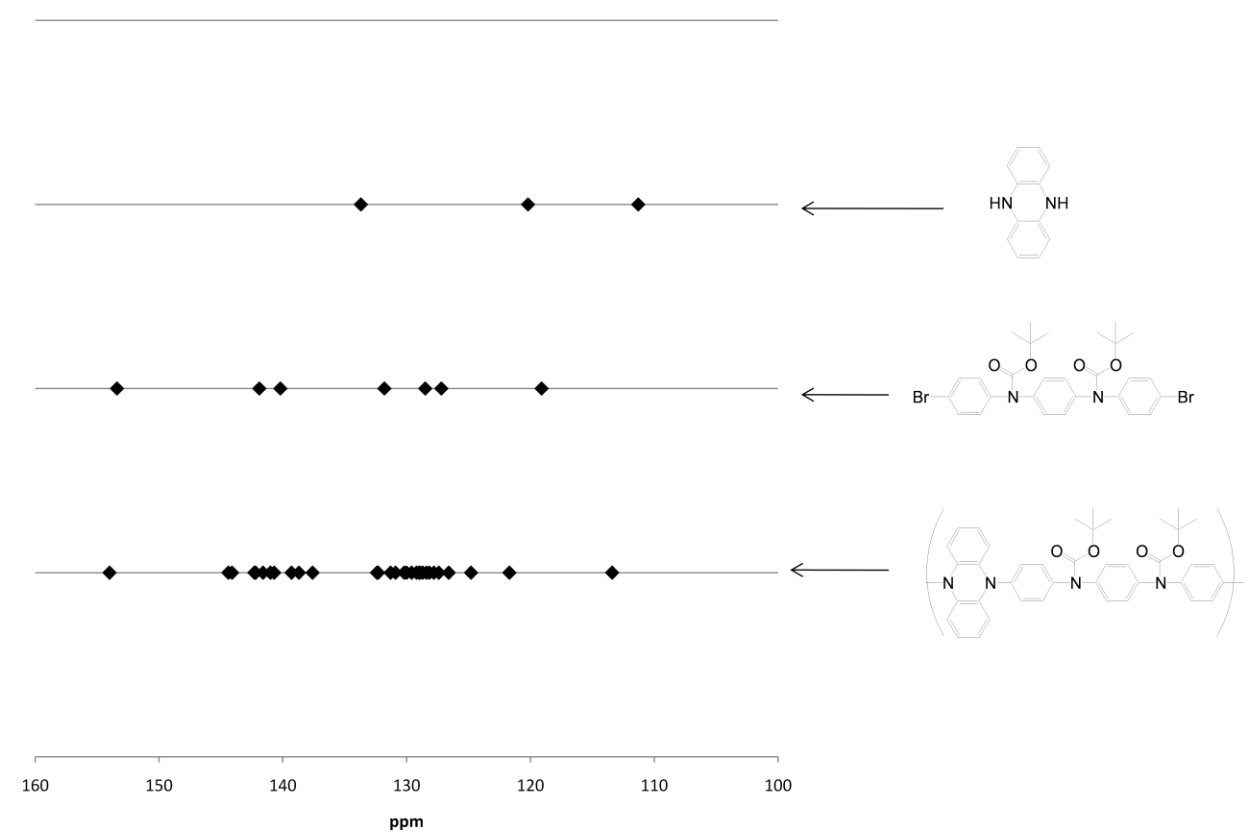


Figure 20. NMR comparison of polymer 19 with respective monomers

2.2.10.2 Molecular Weight Determination

GPC data was collected on a Waters GPC instrument in THF calibrated with polystyrene standards. The molecular weight data for two independently prepared samples are summarized in Table 11 below.

Table 11. GPC Molecular weight data for polymer **19**

Sample	Mw (x 10^3)[a]	Mn (x 10^3)	PDI
Phenazine-*alt*-(aniline)$_3$-1	6.9	8.8	1.3
Phenazine-*alt*-(aniline)$_3$-2	5.8	7.2	1.2

[a]**THF solvent, calibrated to polystyrene standards**

The GPC data indicated small molecular weights around 5.0 $x10^3$ – 7.0 $x10^3$ which corresponds to 7-11 repeat units or 28-44 aryl units. However, GPC data has been found to overestimate the molecular weight of polyaniline polymers.[24] The molecular weight was not determined from the ^{1}H NMR spectrum by end group analysis because no end group signal was identifiable. A 1:1.1 relative monomer ratio (phenazine to aniline) was calculated by comparing the integration per proton of the aryl protons originating from the phenazine with the integration per proton of the BOC signal originating from the *para*-aniline segment indicating a repeat sequence structure. This result may indicate a slight preference for chain ends to be terminated in bromides.

2.2.11 **Polymer Film Properties and Doping**

Solutions of both polymers **17** and **19** in THF were cast into films by both spin casting and drop casting. At the concentrations attainable in THF, spin casting gave pale purple films that were too thin to measure the conductivity. Drop casting from pipette gave a thicker film suitable for measuring the conductivity

Films of polymers **17** and **19** were doped by using concentrated HCl in a vapor chamber for 1-2 d. After doping, the films would turn dark green indicating oxidation to the emeraldine salt form. Upon drying, the films were very brittle due to the low molecular weights. Exposure of these films to solutions of HCl caused the films to break and crumble.

2.2.12 **Conductivity Measurements**

Conductivity was measured using a four point probe apparatus with a Signatone probe. Conductivity measurements on films of polymers **17** and **19** were ineffective due to the quality of the films.

Polymer **17** was blended with PVC to improve the film characteristics. These films maintained the pale purple color prior to doping and turned green after doping. Solutions and the corresponding films were made out of various ratios of PVC to polymer. For comparison, similar ratios of *p*-polyaniline was blended with PVC and cast into films. The results of these measurements are summarized below (Figure 21).

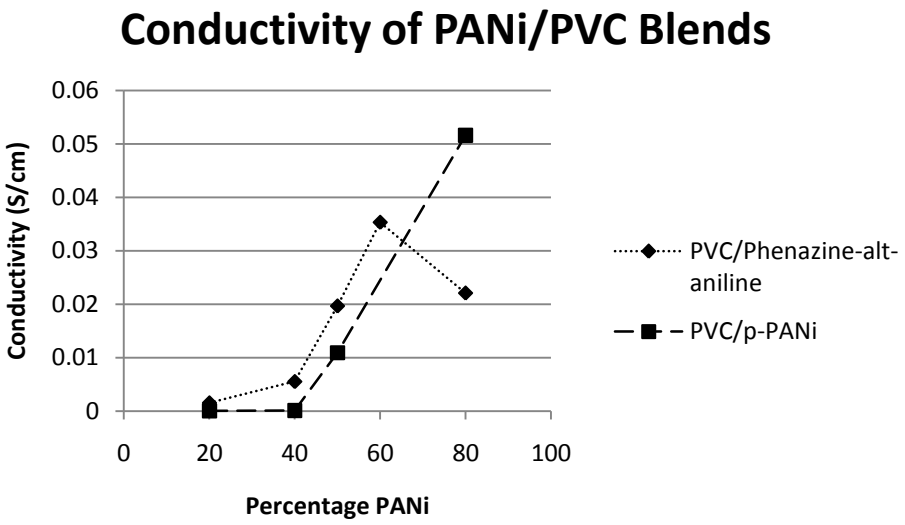


Figure 21. Conductivity of PANi/ PVC Blends

For both *p*-PANi and polymer **17**, the general observed trend was that the conductivity increases as the percentage of conductive polymer increases. For most cases, the conductivity of PVC/polymer **17** was comparable to the conductivity of PVC/*p*-PANi. The lower conductivity

of PVC/polymer **17** at 80% resulted from a sharp decrease in the quality of the film at this percentage of conductive polymer.

We compared our results to the work done by Singh[133] (Figure 22). The conductivity measurement show good agreement with our polymers. We attained a slightly higher conductivity at 60% and 80% conductive polymer while Singh and co-workers were able to detect conductivity at 20% conductive polymer. Curiously, Singh and co-workers report a conductivity at 100% *p*-PANi of only 0.065 S/cm. We measured the conductivity of 100% *p*-PANi to be 1.58 S/cm which is more in line with literature values.[134]

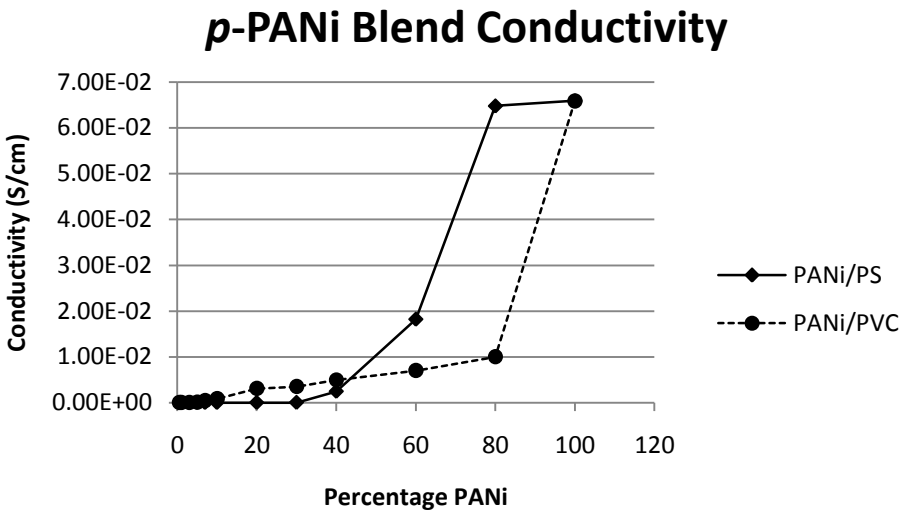


Figure 22. Conductivity of PANi/PVC blends from literature

2.3 **DISCUSSION**

Our original goal was to find a suitable replacement for the bridging urea moiety in the 4p,*o*-PANi studied in this work and 5p,*o*-PANi systems studied by Ward. Considering our previous work with bridged *ortho*-diamines, we attempted to prepare suitable monomers based

upon quinoxaline and phenazine architectures. Based upon these architectures, we prepared several new and interesting polymeric materials.

Our route to quinoxaline architectures utilized the known condensation of amines with ketones. We prepared a series of quinoxaline derivatives **2a-2c** in moderate yields (65% - 85%) as possible monomers. While we attempted to reduce the imine bond to the amine, we were unable to prepare and isolate the dihydroquinoxaline derivatives even in the presence of sodium metal. Unable to prepare the dihydroquinoxaline derivatives, we considered other ketones suitable for reaction with amines.

Using 1,2-cyclohexadione and the same methodology, we successfully prepared a series of tetrahydrophenazine derivatives **4a-4c** in moderate yields (62% - 81%) which improves on the yield of similar compounds done by Clemo and McIlwain.[92] These diimine compounds were remarkable air stable and crystallizable.

In order to prepare suitable monomers, we modified the procedure outlined by Morley[90] to prepare a series of octahydrophenazines **5a-5c** from the tetrahydrophenazines **4a-4c** by reaction with sodium metal in modest yields (82% - 84%). These compounds are extremely oxidant sensitive and readily convert back to the tetrahydrophenazine and require storage under a nitrogen atmosphere.

Our attempt to polymerize the octahydrophenazine **5a** and BOC-protected segmer **6** yielded an octahydrophenazine-*alt*-(aniline)$_2$ polymer **7** in poor yield (9%). While no NMR data was collected, GPC results suggested that the molecular weight of the polymer was extremely small (3.0×10^3 - 4.0×10^3). Amid concerns about the effects of the cyclohexyl group on the conductivity, we decided to first exam the related phenazine system returning to the octahydrophenazine system later.

A simple way to access several different phenazine derivatives was to react *ortho*-diamines with benzoquinone derivatives. After attempting many literature procedures,[104-106,109-111] we were able to prepare several [1,2]benzoquinone derivatives **9a-9c** by modifying the procedure of Kaiser[107] and Sammes[108] in modest yields (34% - 80%). Utilization of Fremy's salt[132] allowed us to prepare the dimethyl quinone derivative **11**. These compounds were difficult to purify and often had a short shelf life.

With our benzoquinone derivatives in hand, we were successful at producing phenazine derivatives **12a** and **12b** in low yields (22% - 27%) by refluxing in toluene. Not satisfied with yield, we were able to improve the yield for derivatives **13a-e** by 10% - 30% using phenyl ether as solvent at a lower temperature (60 °C) under vacuum. We theorize that the better yields were a result of less decomposition of the quinone during reaction.

Our final attempt to maximize the yield of phenazine product utilized sonication and produced some success with reasonable yields (55% - 95%). Due to impurities in the quinone, the optimal stoichiometry between amine and quinone was 1:1.5. Increasing the reaction time from 2 h to 8 h led to a decrease in yield probably though decomposition pathways. Addition of molecular sieves and heating to 55 °C was found to have little effect on the yield of the reaction. Methylene chloride was found to be a superior solvent to other common organic solvents possibly due to better exclusion of water. The GC yields correlated well to the isolated yields obtained through column chromatography. While various literature methodologies range from 10-30% yield for phenazine compounds,[90,92,93,135] we have developed a methodology utilizing sonication to produce phenazine compounds in 75-95% yield. Our new methodology provides quick access to large library of substituted phenazine compounds.

In order to prepare suitable monomers, we modified the procedure outlined by Sugimoto[99] preparing two 5,10-dihydrophenazine derivatives **15a** and **15b** in moderate yields (65% - 75%). While 5,10-dihydrophenazine **15b** was reactive under palladium coupling conditions, the ethyl ester dihydrophenazine derivative **15a** was not reactive yielding only the oxidized ethyl ester phenazine **12b**.

With both monomers in hand, polymerization of 5,10-dihyrophenazine **15b** with BOC-protected segmer **6** or segmer **8** yielded phenazine-*alt*-(aniline)$_2$ **17** and phenazine-*alt*-(aniline)$_3$ **19** polymers respectively in modest yields (10% - 55%, 8% - 60%). The polymer products were unaffected by increases in reaction time over 24 h and substitution of phosphine ligand. While being soluble in THF, the polymer products were insoluble in most common organic solvents. Utilizing toluene as the reaction solvent provided fewer occurrences of side reactions then using THF as the reaction medium. NMR analysis of the polymers was consistent with an alternating co-polymer structure. GPC data estimated the polymer to be of modest molecular weight comparable to the 5p,*o*-PANi polymers studied by Ward.[48]

Unfortunately, films of polymers **17** and **19** drop casted from THF solutions produced brittle, poor-quality films after doping with HCl. After attempting several different doping conditions and methods, we were unable to successfully prepare a doped film with a measureable conductivity.

While unable to make a direct measurement of the conductivity, polymer **17** was blended with PVC successfully to produce films with a measurable conductivity after doping with HCl. We were able to show that the conductivity of our blends increases as the percentage of conductive polymer increases up until the film quality inhibits the conductivity. We were able to show that our phenazine-*alt*-(aniline)$_2$ polymer blended with PVC was as conducting as *p*-PANi

blended with PVC for specific ratios. Our results correlated well with work done on polyaniline/PVC blends reported by Singh.[133]

In conclusion, we have prepared several alternatives to the 4p,*o*-PANi system developed by us and the 5p,*o*-PANi system developed by Ward.[48] While our attempt to utilize a quinoxaline moiety was unsuccessful, our attempts at utilizing the phenazine moiety showed significant promise. While hampered by low molecular weights, we were able to measure the conductivity of a phenazine-*alt*-(aniline)$_2$ polymer by blending with PVC. Comparison of our polymer blend with *p*-PANi showed equivalent conductivity per ratio of conductive polymer and agreement with work done in the literature.[133]

2.4 **EXPERIMENTAL**

2.4.1 **General**

All reactions and manipulations were performed under an atmosphere of nitrogen in either a glove box or using standard Schlenk techniques. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Solvents were purchased from commercial suppliers and used without further purification unless otherwise noted.

After purchasing from commercial sources, 4-methyl-benzene-1,2-diamine, 4,5-dimethyl-benzene-1,2-diamine and *o*-phenylenediamine were sublimed before use and stored under a nitrogen atmosphere. Phenazine, sodium periodate, Fremy's salt, catechol, 3,4-dimethyl-phenol, 4-methyl-benzene-1,2-diol, 3,4-diamino-benzoic acid methyl ester, and 3,4-dihydroxy-benzoic

acid ethyl ester were purchased from commercial sources and used without further purification. The preparation of BOC protected compounds **6** and **18** are described earlier in this work.

^{1}H NMR and ^{13}C NMR spectra were acquired on Brucker 300 MHz instruments. Mass spectral data was acquired on a Hewlett Packard Series 5890 GC/5971A MS with a Hewlett Packard Series 1 capillary column. GC data was acquired on a Hewlett Packard Series 6890 GC. GPC data was collected on a Waters GPC system equipped with phenogel columns and a Waters 410 Differential Refractometer calibrated using polystyrene standards. Conductivity measurements were made using a standard four-point probe method.

2.4.2 **2,3-Dimethyl-quinoxaline (2a):**

Compound **2a** was prepared by modification of the procedure outlined by Naskar *et al.*[79] To 100 mL of toluene in a 3-neck RB equipped with a Dean-Stark trap and condenser was added *o*-phenylenediamine (4.02 g, 37.2 mmol) and butane-2,3-dione (3.3 mL, 37.6 mmol). After refluxing overnight and collection of water, the mixture was filtered through celite. Purification by column chromatography in EtOAc/hexanes yielded the product as a yellow solid (4.92 g, 84%). ^{1}H NMR ($CDCl_3$): δ 7.92 (m, 2H, aryl), 7.61 (m, 2H, aryl), 2.68 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 153.4 (C=N), 141.0 (ipso), 128.7 (aryl CH), 126.3 (aryl CH), 23.1 (CH_3). DEPT 135 NMR ($CDCl_3$): δ 128.7 (aryl CH), 126.3 (aryl CH), 23.1 (CH_3).

2.4.3 **2,3,6,7-Tetramethyl-quinoxaline (2b):**

Compound **2b** was prepared by modification of the procedure outlined by Naskar *et al.*[79] To 100 mL of toluene in a 3-neck RB equipped with a Dean-Stark trap and condenser was added 4,5-

dimethyl-*o*-phenylenediamine (3.77 g, 27.7 mmol) and butane-2,3-dione (2.5 mL, 28.4 mmol). After refluxing overnight and collection of water, the mixture was filtered through celite. Removal of volatile organics and purification by column chromatography in EtOAc/hexanes gave a yellow solid (3.95 g, 76%). ^{1}H NMR ($CDCl_3$): δ 7.66 (s, 2H, aryl), 2.64 (N=C-CH_3), 2.40 (C_{aryl}-CH_3). ^{13}C NMR ($CDCl_3$): δ 152.2 (C=N), 139.9 (ipso), 138.9 (ipso), 127.4 (CH), 23.0 (CH_3), 20.2 (CH_3). DEPT 135 NMR ($CDCl_3$): δ 127.4 (CH), 23.0 (CH_3), 20.2 (CH_3).

2.4.4 **2,3-Dimethyl-quinozaline-6-carboxylic acid methyl ester (2c):**

To 100 mL of toluene in a 3-neck RB equipped with a Dean-Stark trap and condenser was added 3,4-diamino-benzoic acid methyl ester (3.03 g, 18.2 mmol) and butane-2,3-dione (1.6 mL, 18.2 mmol). After refluxing overnight and collection of water, the mixture was filtered through celite. Removal of volatile organics and purification by column chromatography in EtOAc/hexanes yielded a yellow solid (2.54 g, 65%). ^{1}H NMR ($CDCl_3$): δ 8.61 (s, 1H, aryl), 8.17 (m, 1H, aryl), 7.92 (d, 1H, aryl), 3.97 (s, 3H, -OCH_3), 2.68 (s, 6H, N=C-CH_3). ^{13}C NMR ($CDCl_3$): δ 166.3 (C=O), 155.6 (C_{ipso}=N), 154.6 (C_{ipso}=N), 143.1 (ipso), 140.2 (ipso), 131.0 (aryl CH), 130.1 (ipso), 128.5 (aryl CH), 128.4 (aryl CH), 52.4 (-OCH_3), 23.3 (CH_3), 23.2 (CH_3). DEPT 135 ($CDCl_3$): δ 131.0 (aryl CH), 128.5 (aryl CH), 128.4 (aryl CH), 52.4 (-OCH_3), 23.3 (CH_3), 23.2 (CH_3).

2.4.5 **1,2,3,4-Tetrahydro-phenazine (4a):**

To 150 mL of toluene in a 3-neck RB equipped with a Dean-Stark trap and condenser was added *ortho*-phenylenediamine (9.29 g, 85.9 mmol), and 1,2-cyclodione (9.60 g, 85.6 mmol). After

refluxing overnight and collection of water, the mixture was filtered through celite. Removal of volatile organics and crystallization out of CH_2Cl_2/hexanes gave the yellow crystalline product (12.01 g, 76%). ^{1}H NMR ($CDCl_3$): δ 7.95 (m, 2H, aryl), 7.65 (m, 2H, aryl), 3.12 (m, 4H, -CH_2-), 2.00 (m, 2H, alkyl). ^{13}C NMR ($CDCl_3$): δ 154.1 (C=N), 141.3 (-C=N-**C**-), 128.9 (aryl), 128.3 (aryl), 33.2 (-CH_2-), 22.8 (-CH_2-). ^{13}C DEPT 135 ($CDCl_3$) δ 127.4 (CH), 33.0 (CH_2), 22.9 (CH_2), 20.2 (CH_3)

2.4.6 **7,8-Dimethyl-1,2,3,4-tetrahydro-phenazine (4b):**

To 150 mL of toluene in a 3-neck RB equipped with a Dean-Stark trap and condenser was added 4,5-dimethyl-*ortho*-phenylenediamine (7.00 g, 51.4 mmol), and 1,2-cyclohexadione (5.76 g, 51.4 mmol). After refluxing overnight and collection of water, the mixture was filtered through celite. Removal of volatile organics and crystallization out of CH_2Cl_2/hexanes gave the yellow crystalline product (8.79 g, 80%). ^{1}H NMR ($CDCl_3$): δ 7.58 (s, 2H, aryl), 3.07 (s, 4H, alkyl), 2.39 (s, 6H, -CH_3), 1.98 (s, 4H, alkyl). ^{13}C NMR ($CDCl_3$): δ 152.8 (C=N), 140.1 (aryl ipso), 139.1 (aryl ipso), 127.4 (aryl), 33.0 (-CH_2-), 22.9 (-CH_2-), 20.2 (-CH_3). ^{13}C DEPT 135 ($CDCl_3$) δ 127.4 (CH), 33.0 (CH_2), 22.9 (CH_2), 20.2 (CH_3)

2.4.7 **7-Methyl-1,2,3,4-tethrahydro-phenazine (4c):**

To 150 mL of toluene in a 3-neck RB equipped with a Dean-Stark trap and condenser was added 4-methyl-*ortho*-phenylenediamine (10.50 g, 85.9 mmol), and 1,2-cyclodione (9.58 g, 85.4 mmol). After refluxing overnight and collection of water, the mixture was filtered through

celite. Removal of volatile organics and crystallization out of CH_2Cl_2/hexanes gave the yellow crystalline product (10.53 g, 62%). ^{1}H NMR ($CDCl_3$): δ 7.75 (d, 1H, aryl CH), 7.65 (s, 1H, aryl CH), 7.28 (d, 1H, aryl CH), 3.27 (m, 4H, hexyl CH_2), 2.47 (s, 3H, CH_3), 1.95 (m, 4H, hexyl CH_2). ^{13}C NMR ($CDCl_3$): δ 153.8 (C=N), 152.9 (C=N), 141.1 (ipso), 139.5 (ipso), 139.1 (ipso), 131.0 (aryl CH), 127.7 (aryl CH), 127.1 (aryl CH), 33.1 (hexyl CH_2), 33.1 (hexyl CH_2), 22.7 (hexyl CH_2), 22.7 (hexyl CH_2), 21.8 (CH_3). DEPT 135 ($CDCl_3$): δ 131.0 (aryl CH), 127.7 (aryl CH), 127.1 (aryl CH), 33.1 (hexyl CH_2), 33.1 (hexyl CH_2), 22.7 (hexyl CH_2), 22.7 (hexyl CH_2), 21.8 (CH_3).

2.4.8 **1,2,3,4,4a,5,10,10a-Octahydro-phenazine (5a):**

Compound **5a** was prepared by variation on the method outlined by Morley.[90] Excess sodium metal (2.84 g, 123.9 mmol) was added to a solution of diimine **4a** (8.79 g, 41.3 mmol) in 150 mL of absolute ethanol. After refluxing for 6 h, the sodium had been completely consumed and the solution changed from yellow to colorless indicating complete reduction of the imine bond. Upon cooling, the product precipitated out of solution and was collected by filtration. The white product was dried under reduced pressure in the presence of P_2O_5. (7.35 g, 82%). ^{1}H NMR ($CDCl_3$): δ 6.52 (m, 4H, aryl), 3.52 (s, 2H, NH), 2.91 (m, 2H, hexyl CH), 1.85 (m, 4H, hexyl CH_2), 1.37 (m, 4H, hexyl CH_2). ^{13}C NMR ($CDCl_3$): δ 133.7 (ipso), 118.6 (aryl CH), 114.3 (aryl CH), 55.1 (hexyl CH), 31.5 (CH_2), 24.2 (CH_2). DEPT 135 ($CDCl_3$): δ 118.6 (aryl CH), 114.3 (aryl CH), 55.1 (hexyl CH), 31.5 (hexyl CH_2), 24.2 (hexyl CH_2).

2.4.9 **7,8-Dimethyl-1,2,3,4,4a,5,10,10a-octahydro-phenazine (5b):**

Compound **5b** was prepared by variation on the method outlined by Morley[90]. Excess sodium metal (2.90 g, 126.2 mmol) was added to a solution of diimine **4b** (8.79 g, 41.4 mmol) in 100 mL of absolute ethanol. After refluxing for 6 h, the sodium had been completely consumed and the solution changed from yellow to colorless indicating complete reduction of the imine bond. Upon cooling, the product precipitated out of solution and was collected by filtration. The white product was dried under reduced pressure in the presence of P_2O_5 (7.34 g, 82%). ^{1}H NMR ($CDCl_3$): δ 6.32 (s, 2H, aryl), 3.51 (bs, 2H, NH), 2.90 (m, 2H, hexyl CH), 2.12 (s, 6H, CH_3), 1.78 (m, 4H, hexyl CH_2), 1.40 (m, 4H, hexyl CH_2). ^{13}C NMR ($CDCl_3$): δ 131.6 (ipso), 126.3 (ipso), 116.2 (aryl CH), 55.4 (hexyl CH), 31.6 (hexyl CH_2), 24.2 (hexyl CH_2), 18.8 (CH_3).

DEPT 135 ($CDCl_3$): δ 116.2 (aryl CH), 55.4 (hexyl CH), 31.6 (hexyl CH_2), 24.2 (hexyl CH_2), 18.8 (CH_3).

2.4.10 **7-Methyl-1,2,3,4,4a,5,10,10a-octahydro-phenazine (5c):**

Compound **5c** was prepared by variation on the method outlined by Morley.[90] Excess sodium metal (3.66 g, 159.3 mmol) was added to a solution of diimine **4c** (10.53 g, 53.1 mmol) in 150 mL of absolute ethanol. After refluxing for 7 h, the sodium had been completely consumed and the solution changed from yellow to colorless indicating complete reduction of the imine bond. Upon cooling, the product precipitated out of solution and was collected by filtration. The white product was dried under reduced pressure in the presence of P_2O_5 (8.98 g, 84%). ^{1}H NMR ($CDCl_3$): δ 6.40 (m, 3H, aryl), 3.50 (m, 2H, NH), 2.89 (m, 2H, hexyl CH), 2.17 (s, 3H, CH_3), 1.60 (m, 4H, hexyl CH_2), 1.42 (m, 4H, hexyl CH_2). ^{13}C NMR ($CDCl_3$): δ 133.8 (ipso), 131.3

(ipso), 128.2 (ipso), 119.0 (aryl CH), 115.1 (aryl CH), 114.6 (aryl CH), 55.3 (hexyl CH), 55.3 (hexyl CH), 31.5 (hexyl CH_2), 31.5 (hexyl CH_2), 24.3 (hexyl CH_2), 24.3 (hexyl CH_2).

2.4.11 **[1,2]benzoquinone (9a):**

Compound **9a** was synthesized by modification of the procedure outlined by Kaiser *et al.*[107] In a 2 L separatory funnel, sodium periodate (9.07 g, 42.4 mmol) was added to a solution of catechol (4.24 g, 38.5 mmol) in 800 mL of water. After shaking for 5 min, the dark red solution was extracted with methylene chloride (2 x 200 mL), and the combined organic extracts were dried over magnesium sulfate. After filtration through celite and removal of volatile organics, a residual red solid was collected as the title compound (1.42 g, 34%). ^{1}H NMR ($CDCl_3$): δ 7.0 (dd, 2H, cyclohexyl CH), 6.37 (dd, 2H, cyclohexyl CH). ^{13}C NMR ($CDCl_3$): δ 180.2 (C=O), 139.0 (CH), 130.8 (CH).

2.4.12 **4-methyl-[1,2]benzoquinone (9b):**

Compound **9b** was synthesized by modification of the procedure outlined by Sammes *et al.*[108] In a 2 L separatory funnel, sodium periodate (14.5 g, 67.8 mmol) was added to a solution of 4-methylcatechol (7.53 g, 60.7 mmol) in 500 mL of water. After shaking for 5 min, the dark red solution was extracted with methylene chloride (2 x 200 mL), and the combined organic extracts were dried over magnesium sulfate. Upon removal of volatile organics, a residual red solid was collected as the title compound (4.57 g, 61%). ^{1}H NMR: ($CDCl_3$) δ 6.86 (d, 1H,-CH=C<u>H</u>-C(CH_3)=CH-), 6.31 (d, 1H, -C<u>H</u>=CH-C(CH_3)=CH-), 6.20 (s, 1H, -CH=CH-C(CH_3)=C<u>H</u>-), 2.13

(s, 3H, -CH=CH-C(C<u>H</u>$_3$)=CH-). ^{13}C NMR: ($CDCl_3$) δ 179.9 (C=O), 179.1 (C=O), 151.5 (ipso), 143.0 (CH), 129.5 (CH), 127.8 (CH), 22.7 (CH_3).

2.4.13 **3,4-Dioxo-cyclohexa-1,5-dienecarboxylic acid ethyl ester (9c):**

Compound **9c** was prepared by modification of the procedure outlined by Sammes *et al.*[108] In a 2 L separatory funnel, sodium periodate (4.50 g, 21.0 mmol) was added to a solution of 3,4-dihydroxy-benzoic acid ethyl ester (3.49 g, 19.1 mmol) in THF/water (100:500 mL). After shaking for 5 min, the dark red solution was extracted with methylene chloride (2 x 200 mL), and the combined organic extracts were dried over magnesium sulfate. Upon removal of volatile organics, a residual orange solid was collected as the title compound (2.76 g, 80%). ^{1}H NMR: ($CDCl_3$) δ 7.58 (s, 1H, -CH=CH-C$_{ipso}$=C<u>H</u>-), 7.50 (d, 1H, -CH=C<u>H</u>-C$_{ipso}$=CH-), 6.86 (d, 1H, -C<u>H</u>=CH-C$_{ipso}$=CH-), 4.28 (q, 2H, -CH_2-), 1.34 (t, 3H, -CH_3).

2.4.14 **4,5-dimethyl-[1,2]benzoquinone (11):**

Compound **11** was prepared by modification of the procedure outlined by Teuber.[130] In a 5 L RB flask, a solution of 4,5-dimethylphenol (4.14 g, 33.9 mmol) in diethyl ether (100 mL) was added to a solution of Fremy's salt (22.9 g, 85.3 mmol) buffered with sodium dihydrophosphate monohydrate (4.50 g, 32.6 mmol) in 1000 mL of distilled deionized water. After 20 min of vigorous mixing, the light purple solution had turned dark red and was extracted in a 2 L separatory funnel with methylene chloride (2 x 300 mL). The combined extracts were dried over magnesium sulfate, and upon removal of volatile organics, the title compound was isolated as a

red solid (2.52 g, 55% yield). ^{1}H NMR: ($CDCl_3$) δ 6.19 (s, 2H,-C=C<u>H</u>-), 2.13 (s, 6H, -CH_3). ^{13}C NMR: ($CDCl_3$) δ 180.1 (C=O), 152.6 (*ipso*), 127.6 (aryl CH), 20.8 (-CH_3)

2.4.15 **2-Methyl-phenazine (12a):**

To 50 mL of toluene in a 3-neck RB equipped with a Dean-Stark trap and condenser was added 4-methyl-*ortho*-phenylenediamine (0.65 g, 4.7 mmol), and [1,2]benzoquinone (0.51 g, 4.7 mmol). After refluxing overnight and collection of water, the mixture was filtered through celite. Removal of volatile organics and purification by column chromatography (EtOAc/hexanes) gave a yellow solid (0.20 g, 22%). ^{1}H NMR ($CDCl_3$): δ 7.51 (dd, 1H, aryl CH), 7.41 (d, 1H, aryl CH), 7.27 (s, 1H, aryl CH), 7.10 (dd, 1H, aryl CH), 6.96 (d, 1H, aryl CH), 1.94 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 143.6 (ipso), 143.4 (ipso), 143.0 (ipso), 142.3 (ipso), 141.2 (ipso), 133.5 (aryl CH), 130.2 (aryl CH), 129.8 (aryl CH), 129.6 (aryl CH), 129.5 (aryl CH), 129.0 (aryl CH), 127.6 (aryl CH), 22.2 (CH_3). DEPT 135 ($CDCl_3$): δ 133.5 (aryl CH), 130.2 (aryl CH), 129.8 (aryl CH), 129.6 (aryl CH), 129.5 (aryl CH), 129.0 (aryl CH), 127.6 (aryl CH), 22.2 (CH_3).

2.4.16 **Phenazine-2-carboxylic acid ethyl ester (12b):**

To 50 mL of toluene in a 3-neck RB equipped with a Dean-Stark trap and condenser was added quinone **9c** (0.55 g, 3.1 mmol) and *ortho*-phenylenediamine (0.33 g, 3.1 mmol). After refluxing 6 h and collection of water, the mixture was filtered through celite. Removal of volatile organics followed by purification by column chromatography in EtOAc/hexanes yielded a yellow solid (0.21 g, 27%). ^{1}H NMR ($CDCl_3$): δ 8.97 (s, 1H, aryl), 8.35 (d, 1H, aryl), 8.23 (m, 3H, aryl), 7.86

(m, 2H, aryl), 4.48 (q, 2H, -CH_2-), 1.47 (-CH_3). ^{13}C NMR ($CDCl_3$): δ 165.6 (C=O), 144.6 (ipso), 144.3 (ipso), 144.1 (ipso), 142.5 (ipso), 132.8 (aryl CH), 131.9 (ipso), 131.5 (aryl CH), 130.9 (aryl CH), 129.9 (aryl CH), 129.8 (aryl CH), 129.7 (aryl CH), 129.3 (aryl CH), 61.7 (CH_2), 14.3 (CH_3). ^{13}C NMR DEPT 135 ($CDCl_3$): δ 132.8 (aryl CH), 131.5 (aryl CH), 130.9 (aryl CH), 129.9 (aryl CH), 129.8 (aryl CH), 129.7 (aryl CH), 129.3 (aryl CH), 61.7 (CH_2), 14.3 (CH_3).

2.4.17 **7,8-Dimethyl-phenazine-2-carboxylic acid ethyl ester (13a):**

A Dean-Stark trap containing phosphorus pentoxide in the collection arm was attached to a round bottom flask containing 4,5-dimethyl-benzene-1,2-diamine (0.38 g, 2.8 mmol), 3,4-dioxo-cyclohexa-1,5-dienecarboxylic acid ethyl ester (0.50 g, 2.8 mmol), and phenyl ether (2.0 g, 11.6 mmol). After stirring the mixture overnight at 60 °C under vacuum, the material was purified by column chromatography in ethyl acetate/hexanes (10:90) to give a yellow solid (0.11 g, 14%). ^{1}H NMR ($CDCl_3$): δ 8.91 (s, 1H, aryl), 8.32 (d, 1H, aryl), 8.17 (d, 1H, aryl), 7.92 (bs, aryl), 4.45 (q, 2H, -OC$\underline{H}_2$$CH_3$), 2.53 (s, 6H, CH_3), 1.46 (t, 3H, -$OCH_2C\underline{H}_3$). ^{13}C NMR ($CDCl_3$): δ 165.9 (C=O), 144.3 (ipso), 143.7 (ipso), 143.5 (ipso), 143.3 (ipso), 142.4 (ipso), 142.0 (ipso), 132.7 (CH), 131.2 (ipso), 129.6 (CH), 128.6 (CH), 128.1 (CH), 127.9 (CH), 61.6 (-O$\underline{C}H_2CH_3$), 20.8 (CH_3), 20.7 (CH_3), 14.3-$OCH_2\underline{C}H_3$). DEPT 135 ($CDCl_3$): δ 132.7 (CH), 129.6 (CH), 128.6 (CH), 128.1 (CH), 127.9 (CH), 61.6 (-O$\underline{C}H_2CH_3$), 20.8 (CH_3), 20.7 (CH_3), 14.3-$OCH_2\underline{C}H_3$).

2.4.18 **2,3-Dimethyl-phenazine (13b):**

A Dean-Stark trap containing phosphorus pentoxide in the collection arm was attached to a round bottom flask containing 4,5-dimethyl-[1,2]benzoquinone (0.12 g, 0.8 mmol), *ortho*-

phenylenediamine (0.10 g, 0.9 mmol), and phenyl ether (2.0 g, 11.8 mmol). After stirring the mixture overnight at 60 ^{o}C under vacuum, the material was purified by column chromatography in ethyl acetate/hexanes (10:90) to give a yellow solid (0.11 g, 59%). ^{1}H NMR ($CDCl_3$): δ 8.18 (m, 2H, aryl), 7.95 (s, 2H, aryl), 7.76 (m, 2H, aryl), 2.53 (s, 6H, -CH_3). ^{13}C NMR ($CDCl_3$): δ 143.1 (ipso), 143.0 (ipso), 141.9 (ipso), 129.7 (aryl CH), 129.5 (aryl CH), 127.9 (aryl CH), 20.7 (CH_3). ^{13}C NMR DEPT 135 ($CDCl_3$): δ 129.7 (aryl CH), 129.5 (aryl CH), 127.9 (aryl CH), 20.7 (CH_3).

2.4.19 **2,3,7,8-Tetramethyl-phenazine (13c):**

A Dean-Stark trap containing phosphorus pentoxide in the collection arm was attached to a round bottom flask containing 4,5-dimethyl-[1,2]benzoquinone (0.11 g, 0.8 mmol), 4,5-dimethyl-*ortho*-phenylenediamine (0.11 g, 0.8 mmol), and phenyl ether (1.0 g, 5.8 mmol). After stirring the mixture overnight at 60 °C under vacuum, the material was purified by column chromatography in ethyl acetate/hexanes (10:90) to give a yellow solid (0.07 g, 41%). ^{1}H NMR (d_6-DMSO): δ 6.54 (s, 4H, aryl), 2.00 (s, 12H, CH_3). ^{13}C NMR (d_6-DMSO): δ 142.7 (C=N), 125.9 (ipso), 117.1 (CH), 18.6 (CH_3).

2.4.20 **7,8-Dimethyl-phenazine-2-carboxylic acid methyl ester (13d):**

A Dean-Stark trap containing phosphorus pentoxide in the collection arm was attached to a RB flask containing 4,5-dimethyl-[1,2]benzoquinone (0.08 g, 0.6 mmol), 3,4-diamino-benzoic acid methyl ester (0.11 g, 0.7 mmol), and phenyl ether (1.0 g, 5.8 mmol). After stirring the mixture overnight at 60 °C under vacuum, the material was purified by column chromatography in ethyl

acetate/hexanes (10:90) to give a yellow solid (0.050 g, 30%). ^{1}H NMR ($CDCl_3$): δ 8.80 (s, 1H, aryl), 8.22 (dd, 1H, aryl), 8.10 (d, 1H, aryl), 7.82 (bs, 2H, aryl), 3.97 (s, 3H, -OCH_3), 2.46 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 166.3 (C=O), 144.2 (ipso), 143.6 (ipso), 143.4 (ipso), 143.2 (ipso), 142.3 (ipso), 141.8 (ipso), 132.7 (CH), 130.7 (ipso), 129.6 (CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 52.5 (-OCH_3), 20.7 (CH_3), 20.6 (CH_3). DEPT 135 ($CDCl_3$): δ 132.7 (CH), 129.6 (CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 52.5 (-OCH_3), 20.7 (CH_3), 20.6 (CH_3).

2.4.21 **2,3,7-Trimethyl-phenazine (13e):**

A Dean-Stark trap containing phosphorus pentoxide in the collection arm was attached to a RB flask containing 4,5-dimethyl-[1,2]benzoquinone (0.11 g, 0.8 mmol), 4-methyl-*ortho*-phenylenediamine (0.11 g, 0.9 mmol), and phenyl ether (1.0 g, 5.8 mmol). After stirring the mixture overnight at 60 °C under vacuum, the material was purified by column chromatography in ethyl acetate/hexanes (10:90) to give a yellow solid (0.11 g, 56%). ^{1}H NMR ($CDCl_3$): δ 8.05 (d, 1H, aryl), 7.92 (m, 3H, aryl), 7.59 (m, 1H, aryl), 2.66 (s, 3H, CH_3), 2.52 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 143.1 (ipso), 142.8 (ipso), 142.4 (ipso), 141.8 (ipso), 141.7 (ipso), 141.2 (ipso), 140.4 (ipso), 132.8 (aryl CH), 128.9 (aryl CH), 127.9 (aryl CH), 127.8 (aryl CH), 127.5 (aryl CH), 22.2 (CH_3), 20.67 (CH_3), 20.63 (CH_3).

2.4.22 **5,10-Dihydro-phenazine-2-carboxylic acid ethyl ester (15a):**

Compound **15a** was synthesized using a modified procedure outlined by Sugimoto *et al.*[99] Under a nitrogen atmosphere, a mixture of phenazine-2-carboxylic acid ethyl ester (0.20 g, 0.8 mmol) in absolute ethanol (50 mL) was heated to reflux for 5 min to obtain a homogenous yellow

solution. A solution of sodium dithionite (0.24 g, 1.4 mmol) in an equal volume of water (50 mL) was added in one portion. Immediately after addition, a white precipitate formed and heating was discontinued. After cooling to room temperature, the white precipitate was collected via filtration and dried overnight at 52 °C in the presence of phosphorus pentoxide under vacuum (0.15 g, 75%). ^{1}H NMR: (d_6-DMSO) δ 7.88 (s, 1H, NH), 7.52 (s, 1H, NH), 6.91 (m, 1H, aryl), 6.50 (s, 1H, aryl), 6.27 (m, 2H, aryl), 5.96 (m, 3H, aryl), 4.13 (q, 2H, -CH_2-), 1.22 (t, 3H, -CH_3). ^{13}C NMR: (d_6-DMSO) δ 165.4 (C=0), 139.2 (aryl), 133.7 (aryl), 133.5 (aryl), 132.2(aryl), 123.7(aryl), 121.4(aryl), 121.0(aryl), 120.4(aryl), 111.9(aryl), 111.4(aryl), 110.7(aryl), 110.2 (aryl), 59.7 (-CH_2-), 14.3 (-CH_3)

2.4.23 **5,10-Dihydro-phenazine (15b):**

Compound **15b** was synthesized using a modified procedure outlined by Sugimoto *et al.*[99] Under a nitrogen atmosphere, a mixture of phenazine (2.12 g, 11.8 mmol) and absolute ethanol (50 mL) was heated to reflux for 5 min to obtain a homogenous yellow solution. Immediately after heating, a solution of sodium dithionite (21 g, 120 mmol) in water (200 mL) was added. A white precipitate formed immediately. After cooling to room temperature, the precipitate was collected via filtration and dried overnight at 52 °C in the presence of phosphorus pentoxide under vacuum to afford a white/green product (1.39 g, 65%). ^{1}H NMR: (d_6-DMSO) δ 7.21 (bs, 2H, N-H), 6.24 (m, 4H, aryl), 5.99 (m, 4H, aryl). ^{13}C NMR: (d_6-DMSO) δ 133.7 (ipso), 120.2 (aryl CH), 111.3(aryl CH).

2.4.24 **5,10-Di-*p*-tolyl-5,10-dihydro-phenazine (16):**

Under nitrogen and in a glass bomb were combined 5,10-dihydrophenazine **15b** (0.39 g, 2.2 mmol), 4-bromo-*p*-toluene (0.6 mL, 4.9 mmol), $Pd_2(dba)_3$ (0.04 g, 0.04 mmol), BINAP (0.05 g, 0.09 mmol), sodium *tert*-butoxide (0.43 g, 4.5 mmol), and 3 mL of dry THF. After heating at 70 °C in a closed system for 24 hrs, CH_2Cl_2 (20 mL) was added and the mixture was filtered through celite. Purification by column chromatography (EtOAc/hexanes) afforded a yellow solid (0.55 g, 70%). ^{1}H NMR (C_6D_6): δ 7.09 (m, 4H, aryl CH), 6.91 (m, 4H, aryl CH), 6.31 (m, 4H, aryl CH), 5.88 (m, 4H, aryl CH), 2.07 (s, 6H, CH_3). ^{13}C NMR (C_6D_6): δ 138.1(ipso), 137.8 (ipso), 137.4 (ipso), 132.1 (aryl CH), 131.3 (aryl CH), 121.3 (aryl CH), 113.0 (aryl CH), 21.0 (CH_3).

2.4.25 **Poly(phenazine-*alt*-(aniline)$_2$) (17):**

5,10-Dihydrophenazine (0.14 g, 0.77 mmol), PANi dimer **6** (0.33 g, 0.77 mmol), NaO^tBu (0.18 g, 1.9 mmol), $Pd_2(dba)_3$ (0.01 g, 0.01 mmol) and BINAP (0.02 g, 0.04 mmol) were transferred to a glass bomb equipped with a Teflon value and suspended in dry THF (2 mL). The glass bomb was sealed and heated to 80^{o}C for 2 d. After cooling to room temperature, the THF solution was pipetted dropwise into 15 mL of methanol to precipitate the polymer. THF (2 mL) was added to the reaction flask and sonication (30 min-overnight) was used to dissolve any remaining solids. After sonication, the THF solution was added dropwise to 15 mL of methanol. After centrifugation and decantation of methanol, the precipitated polymers were dissolved in THF (2 mL) with sonication (30 min- 2h). The combined THF solutions (4 mL) were added dropwise into 20 mL of methanol precipitating out the polymer. After centrifugation and decantation, the

polymer was again dissolved in THF (2 mL) and precipitated into methanol (20 mL). The product was collected and dried overnight under vacuum to give a tan solid (10 - 55% yield). ^{1}H NMR (d_8-THF): δ 7.61 (d, 4H, aryl), 7.39 (d, 4H, aryl), 6.23 (m, 4H, phenazine aryl), 5.67 (m, 4H, phenazine aryl), 1.42 (bs, 9H, BOC-CH_3). ^{13}C NMR (d_8-THF): δ 153.9 (C=O), 144.3 (ipso), 144.2 (ipso), 143.8 (ipso), 138.8 (ipso), 138.3 (ipso), 132.6 (aryl), 132.2 (aryl), 131.2 (aryl), 130.6 (aryl), 130.3 (aryl), 129.9 (aryl), 129.8 (aryl), 129.5 (aryl), 129.2 (aryl), 129.1 (aryl), 129 (aryl), 128.5 (aryl), 128.2 (aryl), 127.9 (aryl), 127.8 (aryl), 126.9 (aryl), 126.4 (aryl), 125.8 (aryl), 124.9 (aryl), 124.8 (aryl), 124.6 (aryl), 121.7 (aryl), 113.5 (aryl), 81.8 (BOC-ipso), 81.5 (BOC-ipso), 81.3 (BOC-ipso), 28.5 (BOC-CH_3).

2.4.26 **Poly(phenazine-*alt*-(aniline)$_3$) (19):**

5,10-Dihydrophenazine (0.15 g, 0.81 mmol), PANi dimer **18** (0.50 g, 0.81 mmol), NaO^{t}Bu (0.20 g, 2.0 mmol), $Pd_2(dba)_3$ (0.01 g, 0.01 mmol) and BINAP (0.02 g, 0.04 mmol) were transferred to a glass bomb equipped with a Teflon value and suspended in dry THF (2 mL). The glass bomb was sealed and heated to 80 °C for 2 d. After cooling to room temperature, the THF solution was pipetted dropwise into 15 mL of methanol to precipitate the polymer. THF (2 mL) was added to the reaction flask and sonication (30 min-overnight) was used to dissolve any remaining solids. After sonication, the THF solution was added dropwise to 15 mL of methanol. After centrifugation and decantation of methanol, the precipitated polymers were dissolved in THF (2 mL) with sonication (30 min- 2h). The combined THF solutions (4 mL) were added dropwise into 20 mL of methanol precipitating out the polymer. After centrifugation and decantation, the polymer was again dissolved in THF (2 mL) and precipitated into methanol (20 mL). The product was collected and dried overnight under vacuum to give a tan solid (8 - 60% yield). ^{1}H

NMR (d_8-THF): δ 7.53 (d, 4H, aryl), 7.33 (s, 4H, aryl), 7.31 (d, 4H, aryl), 6.35 (m, 4H, phenazine aryl), 5.62 (m, 4H, phenazine aryl), 1.41 (BOC-CH_3). ^{13}C NMR (d_8-THF): δ 154 (C=O), 144.4 (ipso), 144.1 (ipso), 142.2 (ipso), 142.3 (ipso), 141.6 (ipso), 141 (ipso), 140.7 (ipso), 139.3 (ipso),138.7 (ipso), 137.6 (ipso), 132.4 (aryl), 132.3 (aryl), 131.3 (aryl), 130.9 (aryl), 130.2 (aryl), 130 (aryl), 129.6 (aryl), 129.2 (aryl), 129 (aryl), 128.9 (aryl), 128.7 (aryl), 128.4 (aryl), 128.17 (aryl), 127.8 (aryl), 127.4 (aryl), 126.6 (aryl), 124.8 (aryl), 121.7 (aryl), 113.4 (aryl), 81.6 (BOC-ipso), 81.5 (BOC-ipso), 28.5 (BOC-CH_3).

3.0 CYCLIZATION OF DIENES VIA METALLO-ENE MECHANISM

3.1 INTRODUCTION

The petroleum and plastics industry was effectively revolutionized with Karl Ziegler and Guilio Natta's discovery of a remarkable class of catalysts. Essentially, the Ziegler-Natta catalyst, exceptionally good at polymerizing α-olefins and dienes under a wide range of conditions, combined a transition metal with an organometallic compound from Group I, II, or III .[136]

As Ziegler-Natta catalysis was developing, researchers began characterizing the microstructures of the polymers being created. Papers by Gaylord [137-141] and others[142-145] report cyclic units in polymerizations of 1,3-butadiene[137-145] and other dienes[146,147] with titanium catalysts. Gaylord and co-workers proposed a mechanism (Figure 23) for cyclization of 1,3-butadiene by titanium catalysts.[141]

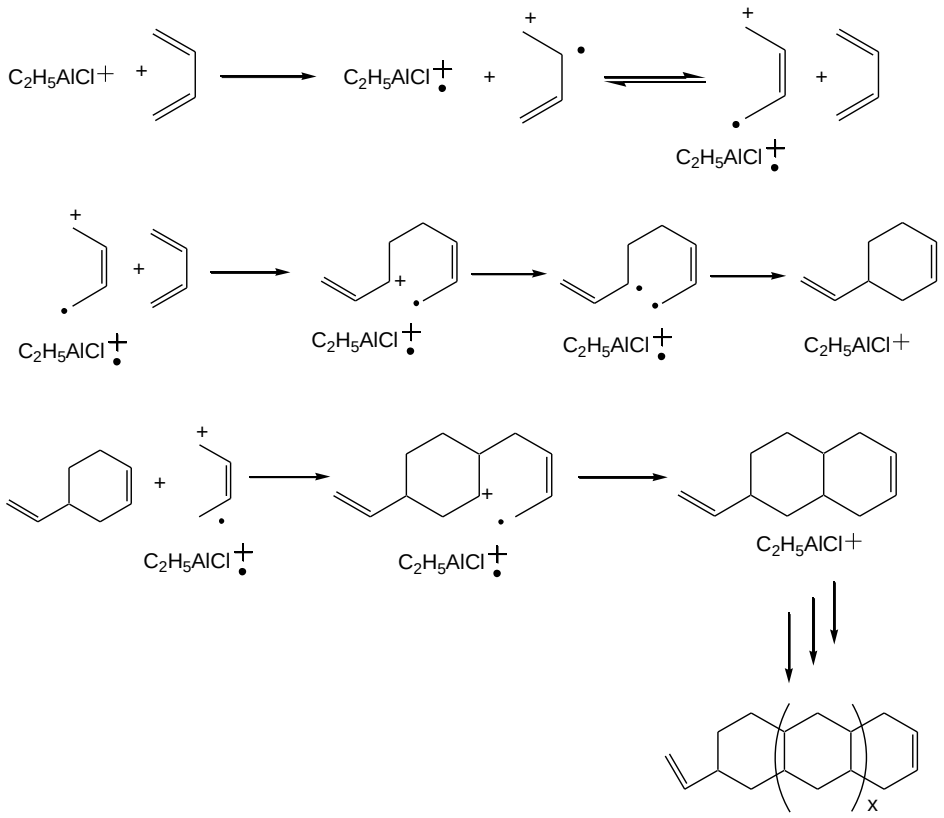


Figure 23. Proposed mechanism for cyclic units by Gaylord for 1,3-butadiene

These results were contrary to some reports by Saltman and co-workers[148] around the same time and are largely ignored without mention in the literature since the work was published by Gaylord and co-workers. In the late 1990's, Gaylord's work became relevant to Cohen who was working on extensions of the lithium-ene[149-151] and magnesium-ene[152] reactions.

Cohen hypothesized that the metallo-ene reaction (Figure 24) could be responsible for Gaylord's observation of cyclic units. While disagreeing with the mechanism developed by Gaylord, Cohen applied the well known metallo-ene reaction[153] toward titanium catalyzed 1,3-butadiene polymerization.

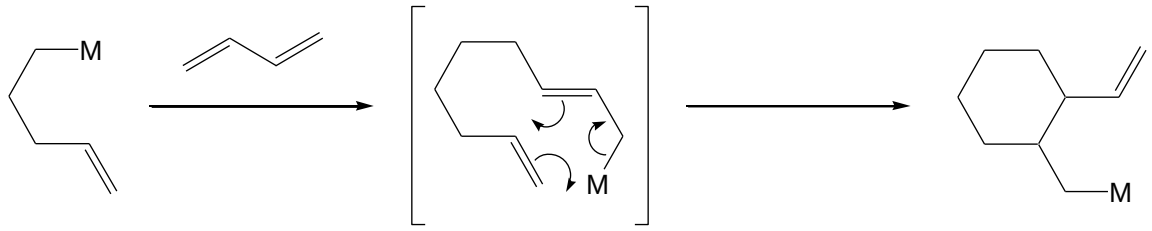


Figure 24. Metallo-ene reaction

Initially, Cohen and co-workers attempted to polymerize conjugated dienes with alkyllithium compounds. When their attempts yielded unexpected results, Cohen and co-workers turned to alkyltitanium compounds. Alkyltitanium compounds with suitable unsaturation have been reported to cyclize to 5-member rings in the presence of a Lewis acid.[154-159] Cohen and co-workers demonstrated that the titanium-ene reaction was possible[160] (Figure 25) and postulated a potential mechanism based upon the metallo-ene reaction for the cyclic polymerization of 1,3-butadiene (Figure 26).[161]

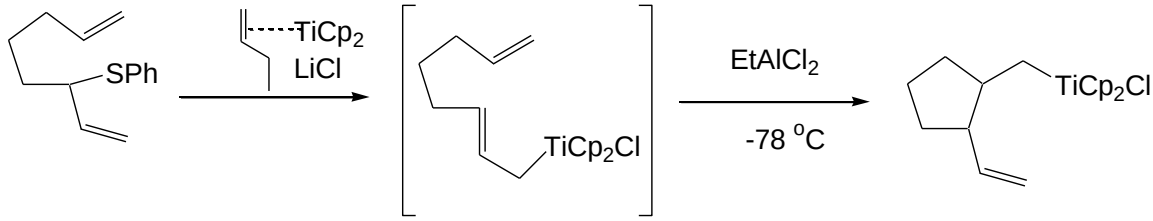


Figure 25. Metallo-ene reaction with titanium under Ziegler-Natta conditions

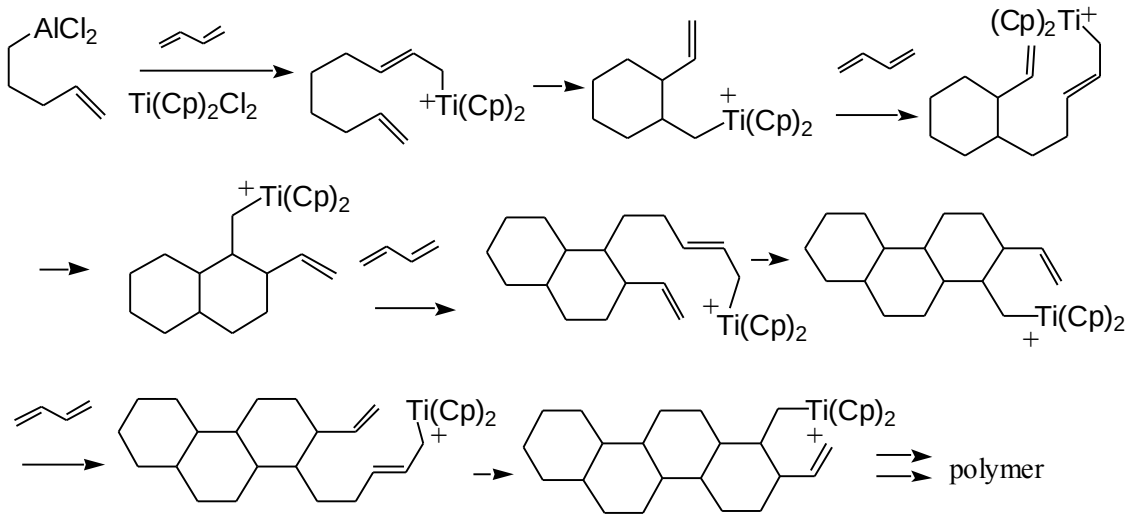


Figure 26. Proposed mechanism for formation of cyclic units in polybutadiene

Cohen suggested that conditions of slow addition and proper catalyst design should help promote cyclization of dienes.[161] Initial attempts at producing cyclic oligomers by post-doctorial student Duc produced spectra in which the vinyl region integrated very poorly to the alkyl region suggesting that cyclization had occurred (Figure 27).[161,162] Duc found the ratio of proton integration for the polymerization of 2-methyl-1,3-butadiene (isoprene) to be around 1:29 (vinyl: alkyl);[162] yet, the theoretical maximum ratio for non-cyclic isoprene polymerization is 1:7 (vinyl: alkyl, for 1,4-polyisoprene) (Figure 28). While improper integration can be explained by many reasons, Duc's observations provided the basis for further research into the possibility of cyclization via the metallo-ene mechanism.

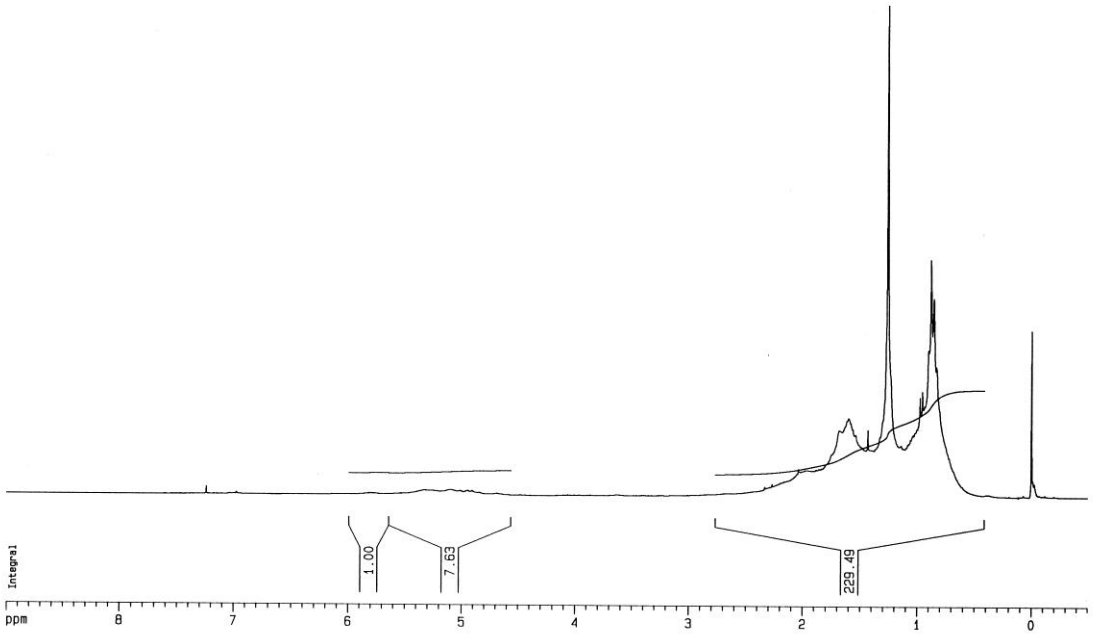


Figure 27. Polymerization of isoprene by Duc

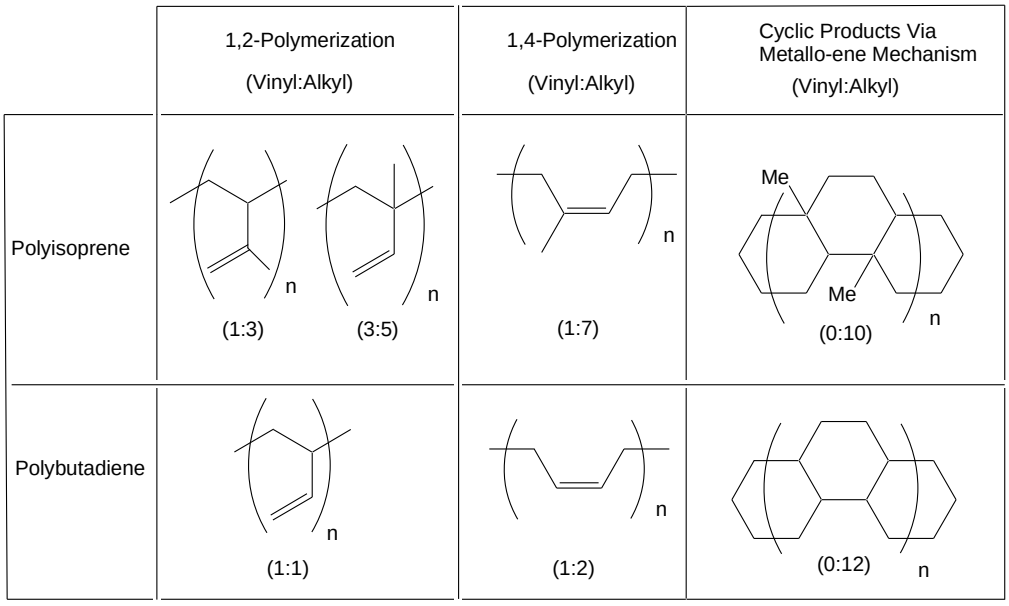


Figure 28. Theoretical integration ratios for polybutadiene and polyisoprene

Herein, we report our attempts to isolate and identify cyclic oligomer or polymer units in the polymerization of 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), and 2,3-dimethyl-1,3-butadiene. We report the characterizations of the oligomers/polymers made under conditions suggested by Cohen to facilitate the metallo-ene reaction.

3.2 **RESULTS AND DISCUSSION**

We initially began our research by obtaining samples of 1,2-polybutadiene and low molecular weight, predominately *cis*-1,4-polybutadiene from Aldrich (Figure 29). The ^{1}H NMR spectrum in $CDCl_3$ of 1,2-polybutadiene exhibited two vinyl signals (δ 5.38 and 4.96) and two alkyl (δ 2.06 and 1.20) signals with proper integration (1:1). The ^{13}C NMR spectrum in $CDCl_3$ showed two sp^2 carbons and two alkyl carbons. The ^{1}H NMR spectrum in $CDCl_3$ of *cis*-1,4-polybutadiene exhibited the expected vinyl (δ 5.38) and alkyl (δ 2.04) signals with proper integration (1:2). The ^{13}C NMR spectrum in $CDCl_3$ of *cis*-1,4-polybutadiene showed one sp^2 carbon and two alkyl carbons attributed to the *cis* (δ 27.6) as well as minor amounts of the *trans* (δ 32.8) isomer.

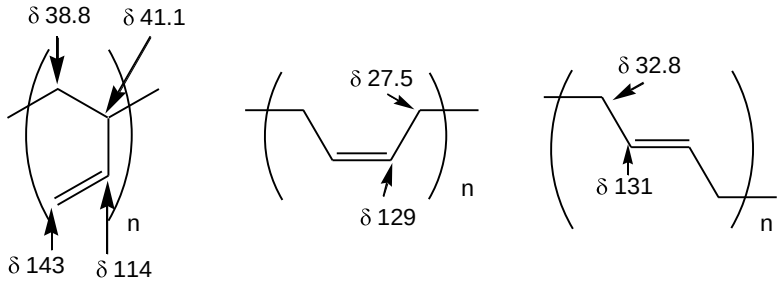
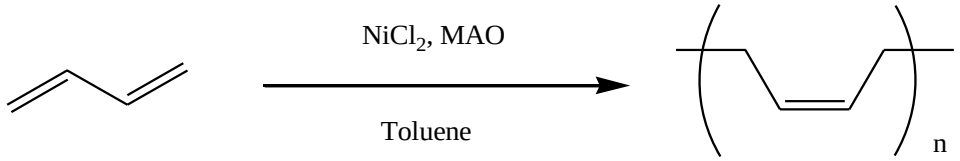


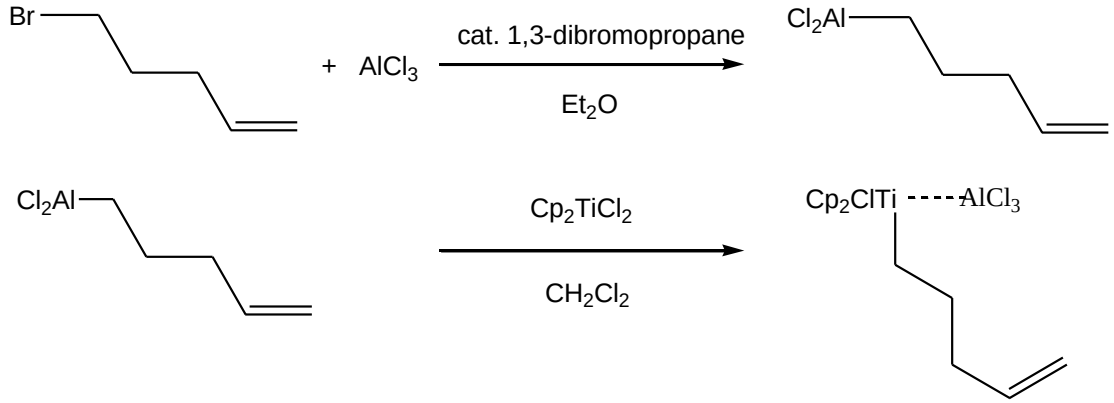
Figure 29. ^{13}C NMR shifts for cis/trans-1,4- and 1,2-polybutadiene from Aldrich

In an attempt to make some 1,4-polybutadiene under experimental conditions, we repeated a synthesis described by Endo and Yamanaka[163] (Scheme 56). We found the polymer produced to be primarily *cis*-1,4-polybutadiene. The ^{1}H NMR spectrum in $CDCl_3$ exhibited a vinyl signal at δ 5.36 and an alkyl signal at δ 2.06 which is consistent with *cis*-1,4-polybutadiene. The ^{13}C NMR spectrum in $CDCl_3$ confirmed identification of the polymer with signals at δ 129 and 27.6 as *cis*-1,4-polybutadiene.



Scheme 56. Polymerization of butadiene by NiCl2/MAO catalyst

We then attempted reactions involving 3 different dienes; 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), and 2,3-dimethyl-1,3-butadiene. We used our titanium catalyst system[161,162] generated *in situ* from 5-bromo-1-pentene, aluminum trichloride, and titanocene dichloride (Scheme 57) as our catalytic system for the entire set of experiments.

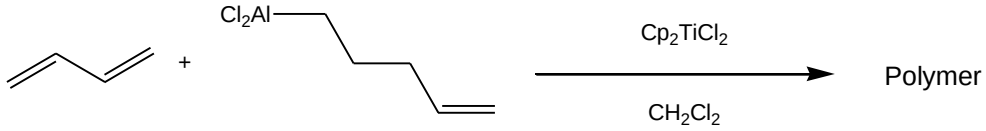


Scheme 57. Generation of titanium catalyst system

3.2.1 **Diene Polymerizations**

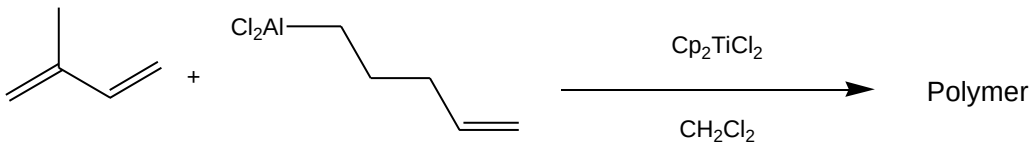
In an attempt to isolate cyclic oligomers, we synthesized the titanium catalyst *in situ* and polymerized a small amount (1 mL) of 1,3-butadiene (24% yield) (Scheme 58). The ^{1}H NMR spectrum in $CDCl_3$ indicated *cis*-1,4-polybutadiene with signals at δ 5.38 and 2.07. The proton integration ratio of 1:5 (expected 1:2 for *cis*-1,4-polybutadiene) and appearance of other broad alkyl signals suggested that the product might be a mixture of 1,4-polybutadiene and cyclic structures. GC-MS analysis, however, did not show signals consistent with the presence of low

molecular weight cyclics. The ^{13}C NMR spectrum in $CDCl_3$ was complicated; however, signals at δ 130, 32.9, and 27.3 indicated *cis*/*trans*-1,4-polybutadiene was present. We identified using DEPT 135 ^{13}C NMR spectroscopy two signals (δ 17.8 and 14.3) that, although probably methyl signals, may have been methine signals which are required for cyclic oligomers or 1,2-polymerization.



Scheme 58. Polymerization of butadiene under Cohen conditions

At the same time, we attempted polymerizations of isoprene (1 mL) using similar conditions to the 1,3-butadiene polymerizations with the *in situ* catalyst (Scheme 59). Since we did not have authentic samples, we assigned the spectra based on literature[164] and chemical shifts predicted by Chem Draw Ultra™ software (Cambridge Soft, Version 6.0) (Figure 30). Although the polymer isolated (88% yield) exhibited an integration ratio of 1:17, the ^{1}H NMR spectrum in $CDCl_3$ showed primarily *cis*/*trans*-1,4-polyisoprene (Figure 30: III or IV) with a vinyl signal at δ 5.0 and some 1,2-polyisoprene (Figure 30: II) with a signal at δ 5.3 and 5.0. The ^{13}C NMR spectrum exhibited signals (δ 138, 124, 39.9, 26.9, 16.2) assignable to *cis*/*trans*-1,4-polyisoprene (Figure 30: III or IV) and signals (δ 115, 23.6, 15.5) assignable to 1,2-polyisoprene (Figure 30: II).



Scheme 59. Polymerization of isoprene under Cohen conditions

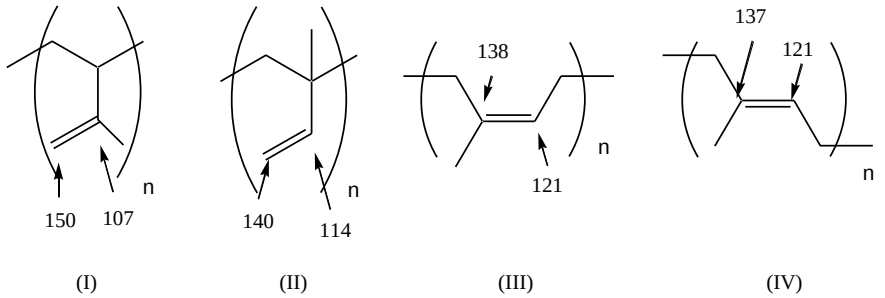
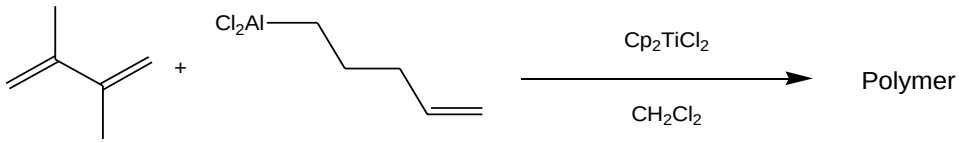


Figure 30. Predicted ^{13}C NMR signals for polyisoprene

In another attempt to isolate cyclic oligomers, we polymerized 2,3-dimethyl-1,3-butadiene using our *in situ* titanium catalyst system (Scheme 60). After generating the *in situ* catalyst, 2,3-dimethyl-1,3-butadiene (1 mL) was polymerized overnight. The polymer isolated (82% yield) exhibited no vinyl signals and broad alkyl signals in the ^{1}H NMR spectrum in $CDCl_3$ as expected. The ^{13}C NMR spectrum in $CDCl_3$ shows two signals at δ 132 and 128 corresponding to *trans*-1,4-polymerization and *cis*-1,4-polymerization, respectively, based upon isoprene and butadiene assignments.

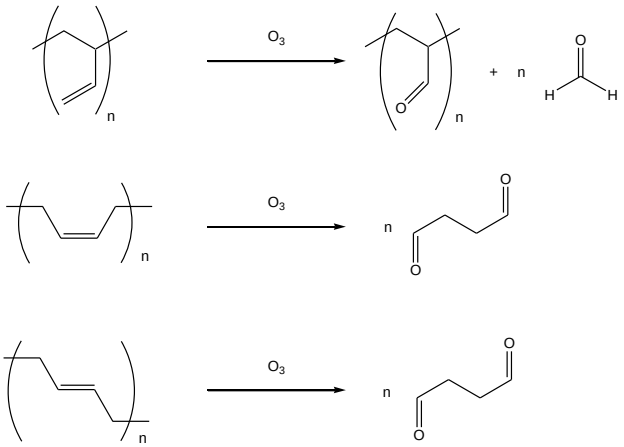


Scheme 60. Polymerization of 2,3-dimethyl-1,3-butadiene under Cohen conditions

3.2.2 **Changes in Reaction Condition and Ozonolysis:**

In an attempt to promote cyclic oligomer formation, we varied the conditions of polymerization. Changing the temperature of polymerization (0 °C or RT) and rate of addition (all at once or slow by syringe) afforded us the same results as detailed above. However, as the possibility that cyclic material was present in small quantities, we were interested in trying to

separate any cyclic material from the oligomer. Since ozonolysis cleaves double bonds effectively to produce aldehydes and ketones, we decided that ozonolysis would allow us to liberate any cyclic structures from the oligomeric material (Scheme 61). While presumably leaving cyclic structures and 1,2-polymerized segments behind, we removed the low molecular weight products from the ozonolyzed *cis*/*trans*-1,4-polymer under high vacuum. Unfortunately, no cyclic oligomers were observed by GC/MS in the ozonolysis of samples made from 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene. We also found high mass loss which is consistent with the composition of each sample being primarily *cis*/*trans*-1,4-polymer.



Scheme 61. Ozonolysis of 1,2-polybutadiene and cis/trans-1,4-polybutadiene

In conclusion, we have attempted to show the presence of cyclic oligomers by polymerizing 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene under conditions proposed by Cohen.[161] We have found no evidence for the production of cyclic oligomers by our *in situ* titanium catalyst systems in NMR spectra or GC-MS data other than the initially observed improper integration ratios.[162] We do not conclude that the Cohen mechanism is not possible or does not occur in titanium catalyzed Ziegler-Natta systems or our system. However, we do conclude that we found no evidence for such a mechanism in our study.

3.3 **EXPERIMENTAL**

3.3.1 **General**

All reactions and manipulations were performed under an atmosphere of argon using standard Schlenk techniques. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Solvents were purchased from commercial suppliers and used without further purification unless otherwise noted.

1,3-Butadiene and isoprene were distilled under vacuum from calcium hydride and stored as a liquid at 0° C. Aluminum trichloride (Aldrich), 5-bromo-1-pentene (Aldrich), Li dispersion (Aldrich), 1,3-dibromopropane (Aldrich), and titanocene dichloride (Strem) were used without further purification. Nickel (II) chloride was dried from nickel (II) chloride hexahydrate at 110° C for 5 h. MAO was used as prepared by Decker[165].

^{1}H NMR and ^{13}C NMR spectra were acquired on Brucker 300 MHz instruments. Mass spectral data was acquired on a Hewlett Packard Series 5890 GC/5971A MS with a Hewlett Packard Series 1 capillary column.

3.3.2 **Standard 1,2-Polybutadiene and 1,4-Polybutadiene**

A sample of 1,2-polybutadiene was obtained from Aldrich. ^{1}H NMR: ($CDCl_3$) δ 5.35 (m, 1H, vinyl *H*), 4.96 (m, 1H, vinyl *H*), 2.14 (m, 1H, C*H*), 1.20 (m, 2H, CH_2). ^{13}C NMR: ($CDCl_3$) δ 143 (H_2C=CH), 114 (H_2C=*C*H), 41.1 (*C*H), 38.8 (*C*H_2).

A sample of low molecular weight predominately *cis*-1,4-polybutadiene was obtained from Aldrich. ^{1}H NMR: ($CDCl_3$) δ 5.40 (bs, 2H, vinyl *H*), 2.04 (bs, 4H, C*H*$_2$). ^{13}C NMR: ($CDCl_3$) δ 131 (C=C, *trans*), 129 (C=C, *cis*), 32.8 (*trans* CH_2), 27.5 (*cis* CH_2).

3.3.3 **Standard 1,3-Butadiene Polymerization using $NiCl_2$**

A sample of *cis*/*trans*-polybutadiene was prepared according to the method used by Endo and Yamanaka.[163] Under a nitrogen atmosphere, MAO (0.45 g, 7.8 mmol) was added to a solution of $NiCl_2$ (0.023 g, 0.17 mmol) in 20 mL of toluene in a Fisher-Porter tube equipped with a gas inlet valve and cooled to -78 °C. 1,3-Butadiene (ca. 3 mL) was transferred into the Fisher-Porter tube and sealed. After warming to room temperature over 2 h, the pressure was observed to have dropped from 25 PSI to 5 PSI. Upon addition of the mixture to a solution of 1% HCl in methanol and filtration, a white polymer was collected (1.32 g). ^{1}H NMR: ($CDCl_3$) δ 5.40 (bs, 2H, vinyl *H*), 2.04 (bs, 4H, C*H*$_2$). ^{13}C NMR: ($CDCl_3$) δ 129 (C=C), 32.8 (*trans* CH_2), 27.5 (*cis* CH_2).

3.3.4 **1,3-Butadiene Polymerizations**

Under an argon atmosphere, dry diethyl either (3 mL) was added to lithium dispersion (30% by weight) (0.22 g, 9.7 mmol) along with 1-2 drops of dibromopropane. After cooling to 0° C, 5-bromo-1-pentene (0.5 mL, 4.2 mmol) was added dropwise over 1 h and allowed to react at 0° C for 1 h. Upon warming to room temperature and cannula transferring to a solution of aluminum

trichloride (0.46 g, 3.4 mmol) in dry ether (10 mL) under an argon atmosphere, the mixture was allowed to stir at -78° C for ½ h and then warmed to room temperature over 2 h. The removal of volatile organics under reduced pressure was followed by addition of 20 mL of dry dichloromethane and dropwise addition of titanocene dichloride (0.88 g, 3.5 mmol) in 20 mL of dry dichloromethane over 1 h. After 2 h at -78° C, 1,3-butadiene (1 mL, 0.61 g, 11.0 mmol) was added either all at once or slowly by syringe (both gave similar results), and the mixture was allowed to warm to room temperature overnight. The organic layer was separated after addition of a 5% solution of Na_2CO_3/ H_2O (20 mL), and was washed twice with 5% sodium carbonate solution (2x 10 mL). Upon drying over magnesium sulfate and removal of volatile organics under reduced pressure, an oil was obtained. (0.15 g, 24% yield) ^{1}H NMR: ($CDCl_3$) δ 5.40 (bs, 2H, vinyl *H*), 2.04 (bs, 4H, C*H*$_2$). ^{13}C NMR: ($CDCl_3$) δ 130 (C=C), 32.8 (*trans* CH_2), 27.5 (*cis* CH_2).

3.3.5 **2-Methyl-1,3-Butadiene (Isoprene) Polymerizations**

Under an argon atmosphere, dry diethyl either (3 mL) was added to lithium dispersion (30% by weight) (0.22 g, 9.7 mmol) along with 1-2 drops of dibromopropane. After cooling to 0° C, 5-bromo-1-pentene (0.5 mL, 4.2 mmol) was added dropwise over 1 h and allowed to react at 0° C for 1 h. Upon warming to room temperature and cannula transferring to a solution of aluminum trichloride (0.46 g, 3.4 mmol) in dry ether (10 mL) under an argon atmosphere, the mixture was allowed to stir at -78° C for ½ h and then warm to room temperature over 2 h. The removal of volatile organics under reduced pressure was followed by addition of 20 mL of dry

dichloromethane and dropwise addition of titanocene dichloride (0.82 g, 3.4 mmol) in 20 mL of dry dichloromethane over 1 h. After 2 h at -78° C, isoprene (1 mL, 0.68 g, 10.0 mmol) was added either all at once or slowly by syringe (both gave similar results), and the mixture was allowed to warm to room temperature overnight. The organic layer was separated after addition of a 5% solution of Na_2CO_3/ H_2O (20 mL), and was washed twice with 5% sodium carbonate solution (2x 10 mL). Upon drying over magnesium sulfate and removal of volatile organics under reduced pressure, an oil was obtained (0.60 g, 88% yield). ^{1}H NMR: ($CDCl_3$) d 5.30 (s, 1H, vinyl *H*), 5.0 (bs, 1H, vinyl *H*), 1.61 (s, 3H, C*H*$_3$). ^{13}C NMR: ($CDCl_3$) δ 138 (1,4-Me*C*=C), 124 (1,4-MeC=*C*), 115 (1,2-C=*C*), 39.9 (1,4-*C*H_2), 26.9 (1,4-*C*H_2), 25.9 (1,2-*C*H_2), 16.2 (1,4-*C*H_3), 15.5 (1,2-*C*H_3).

3.3.6 **2,3-Dimethyl-1,3-Butadiene Polymerizations**

Under an argon atmosphere, dry diethyl either (3 mL) was added to lithium dispersion (30% by weight) (0.25 g, 10.8 mmol) along with 1-2 drops of 1,3-dibromopropane. After cooling to 0° C, 5-bromo-1-pentene (0.5 mL, 4.2 mmol) was added dropwise over 1 h and allowed to react at 0° C for 1 h. Upon warming to room temperature and cannula transferring to a solution of aluminum trichloride (0.87 g, 6.5 mmol) in dry ether (10 mL) under an argon atmosphere, the mixture was allowed to stir at -78° C for ½ h and then warmed to room temperature over 2 h. The removal of volatile organics under reduced pressure was followed by addition of 20 mL of dry dichloromethane and dropwise addition of titanocene dichloride (0.86 g, 3.4 mmol) in 20 mL of dry dichloromethane over 1 h. After 2 h at -78° C, 2,3-dimethyl-1,3-butadiene (1 mL, 0.78 g,

9.5 mmol) was added either all at once or slowly by syringe (both gave similar results), and the mixture was allowed to warm to room temperature overnight. The organic layer was separated after addition of a 5% solution of Na_2CO_3/ H_2O (20 mL), and was washed twice with 5% sodium carbonate solution (2x 10 mL). Upon drying over magnesium sulfate and removal of volatile organics under reduced pressure, an oil was obtained (0.64 g, 82% yield). ^{1}H NMR: ($CDCl_3$) δ 1.69 (s, 4H, C*H*$_2$), 0.88 (s, 6H, C*H*$_3$). ^{13}C NMR: ($CDCl_3$) δ 132 (*C*=*C trans*), 128 (*C*=*C cis*), 29 (*C*H_2), 18 (*C*H_3).

3.3.7 **Ozonolysis Treatment**

A sample (typically between 100-200 mg) was dissolved in dichloromethane and cooled to -78° C. Ozone was bubbled through the solution until a pale blue color was observed. Dimethyl sulfide (1 mL) was added, and after 15 min removal of the volatile organics left a yellow oil (5-10 mg, 2 - 10% yield.)

APPENDIX A: CHAPTER 1

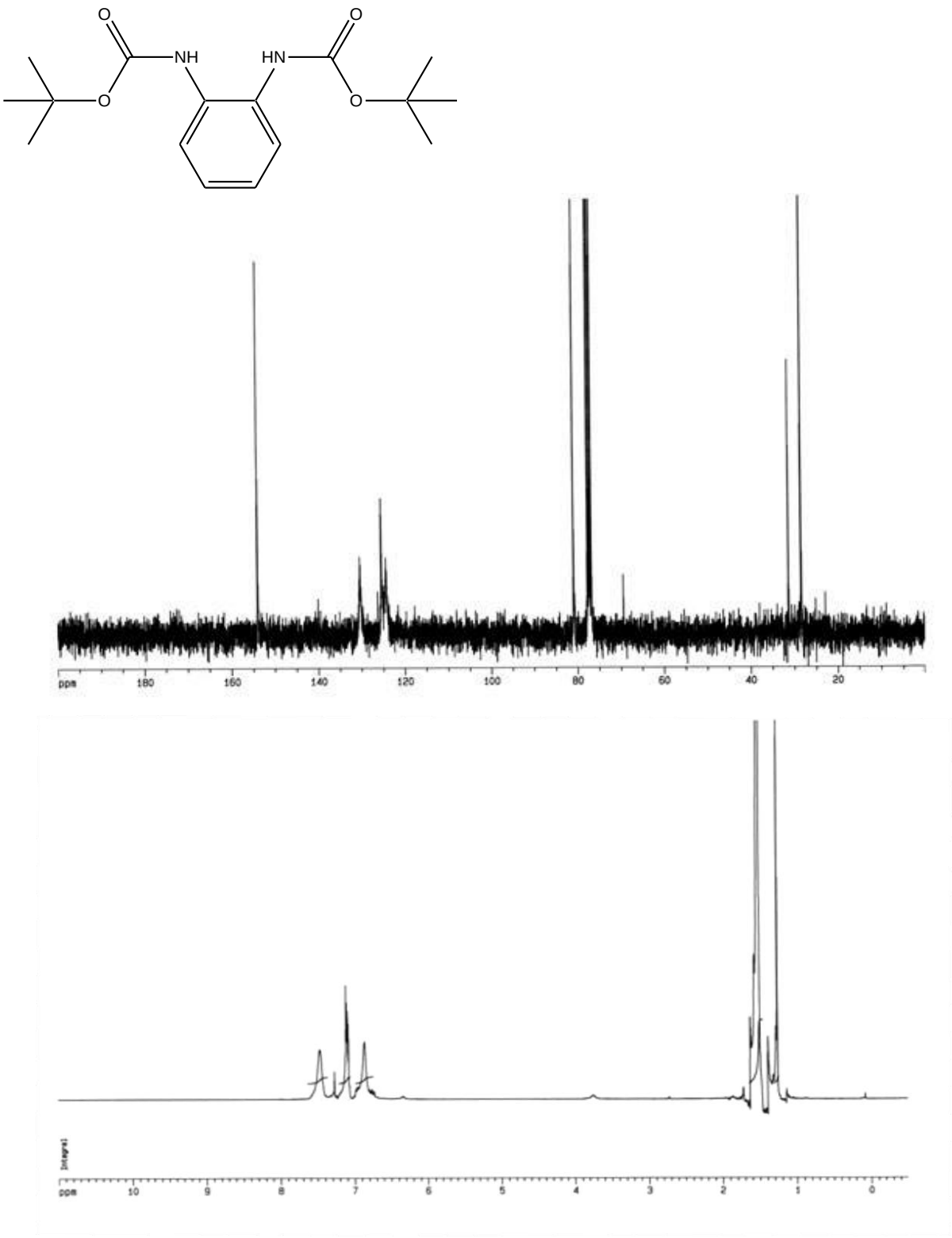


Figure A.1. (Top) ^{13}C NMR of di-BOC protected diamine **1** in $CDCl_3$. ^{1}H NMR of di-BOC protected diamine **1** in $CDCl_3$.

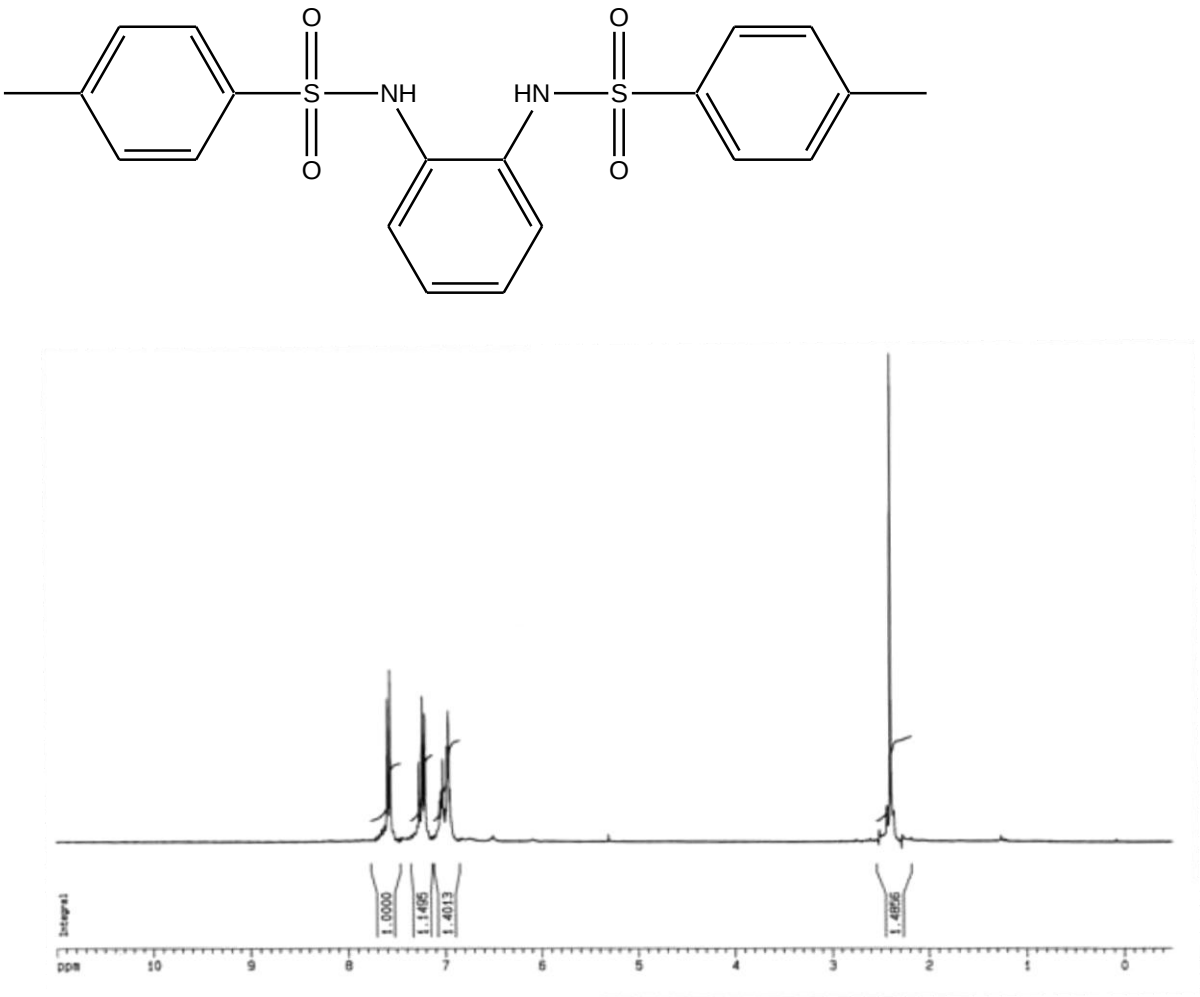


Figure A.2. ^{1}H NMR of sulfonamide **3** in $CDCl_3$.

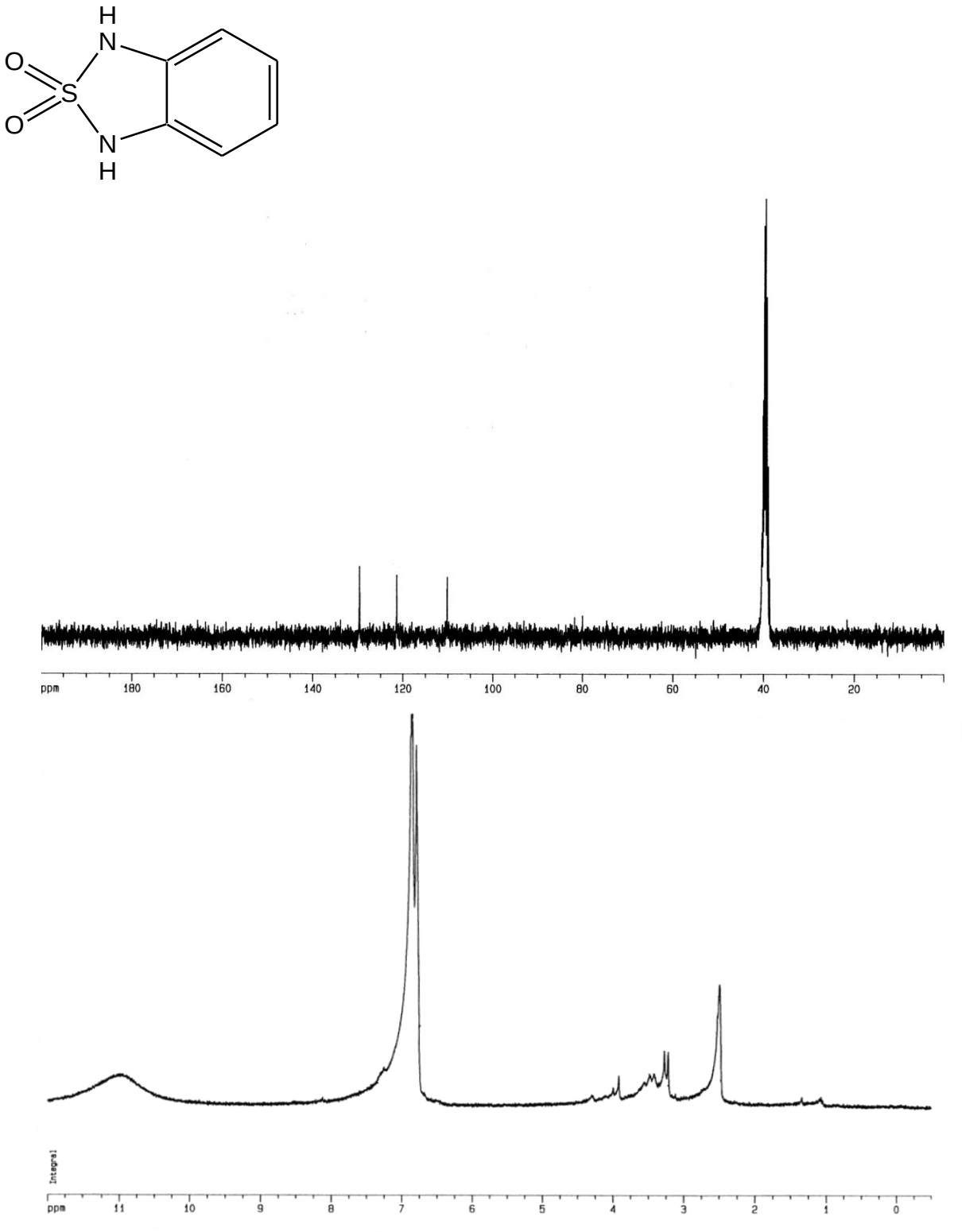


Figure A.3. (Top) ^{13}C NMR of sulfamide **4** in DMSO-d_6. (Bottom) ^{1}H NMR of sulfamide **4** in DMSO-d_6.

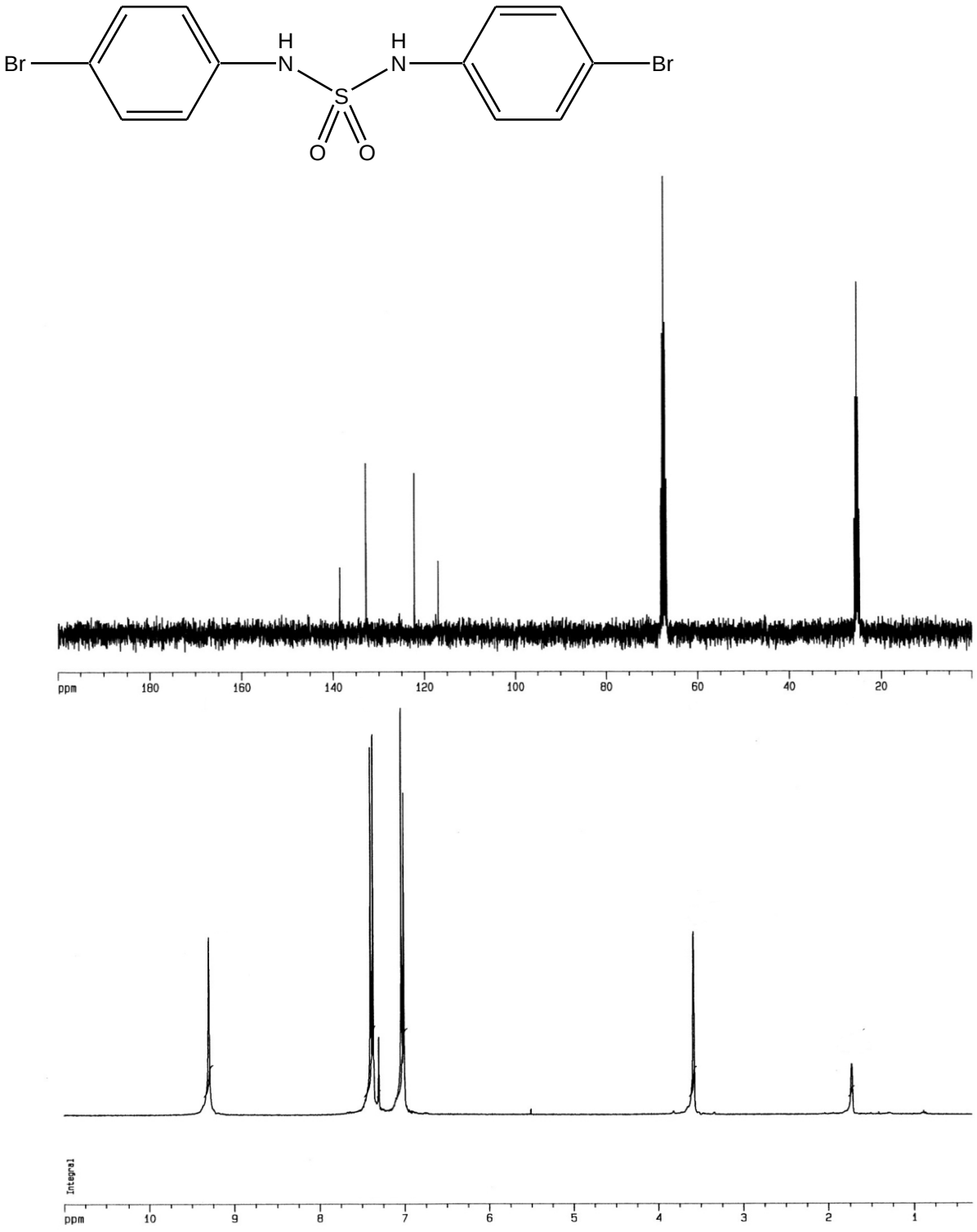
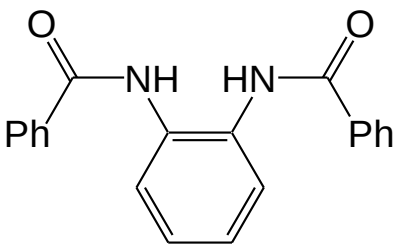


Figure A.4. (Top) ^{13}C NMR of sulfamide **5** in THF-d_8. (Bottom) ^{1}H NMR of sulfamdie **5** in THF-d_8.



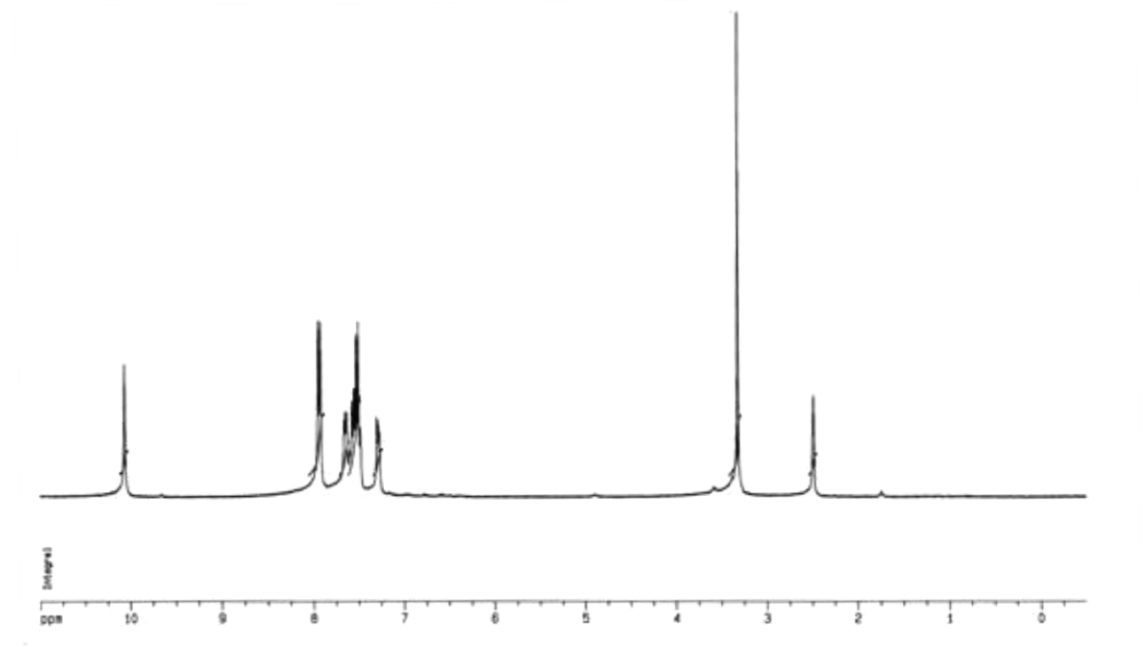


Figure A.5. (Bottom) ^{1}H NMR of amide **8** in DMSO-d_6.

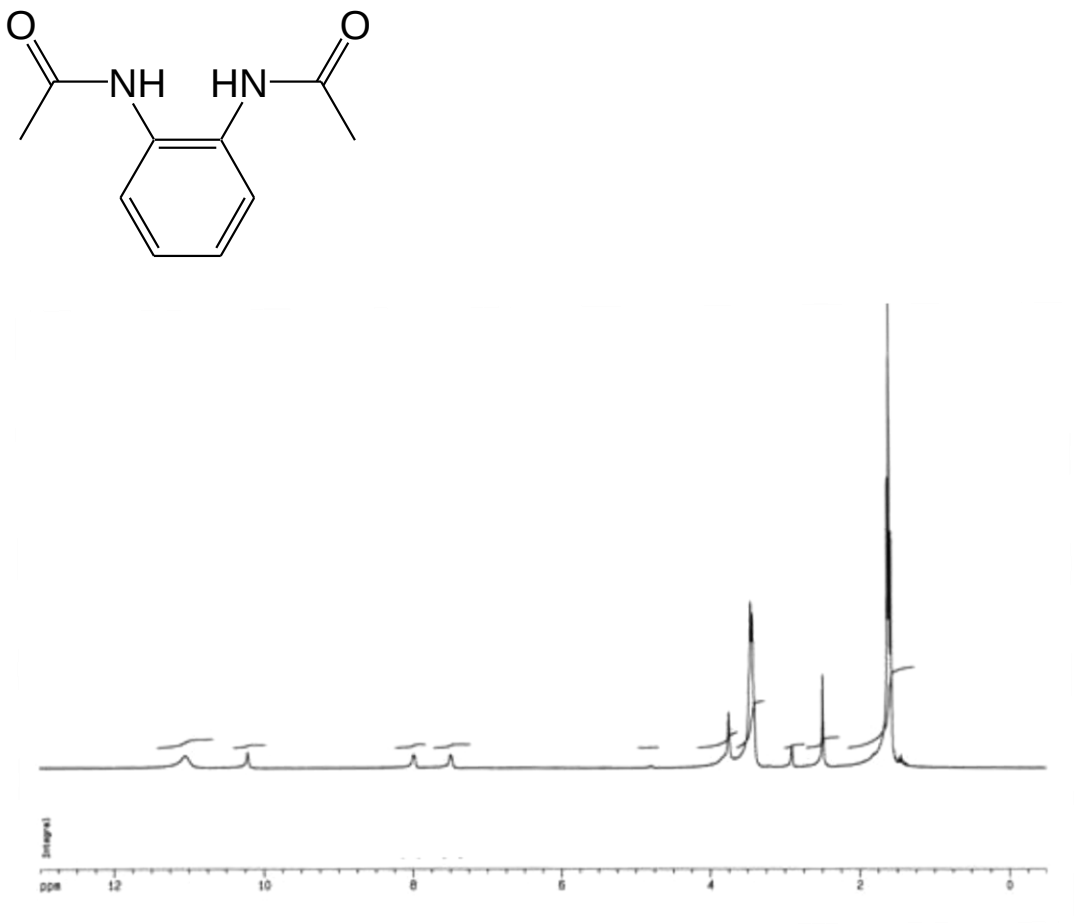


Figure A.6. (Bottom) ^{1}H NMR of amide **7** in DMSO-d_6.

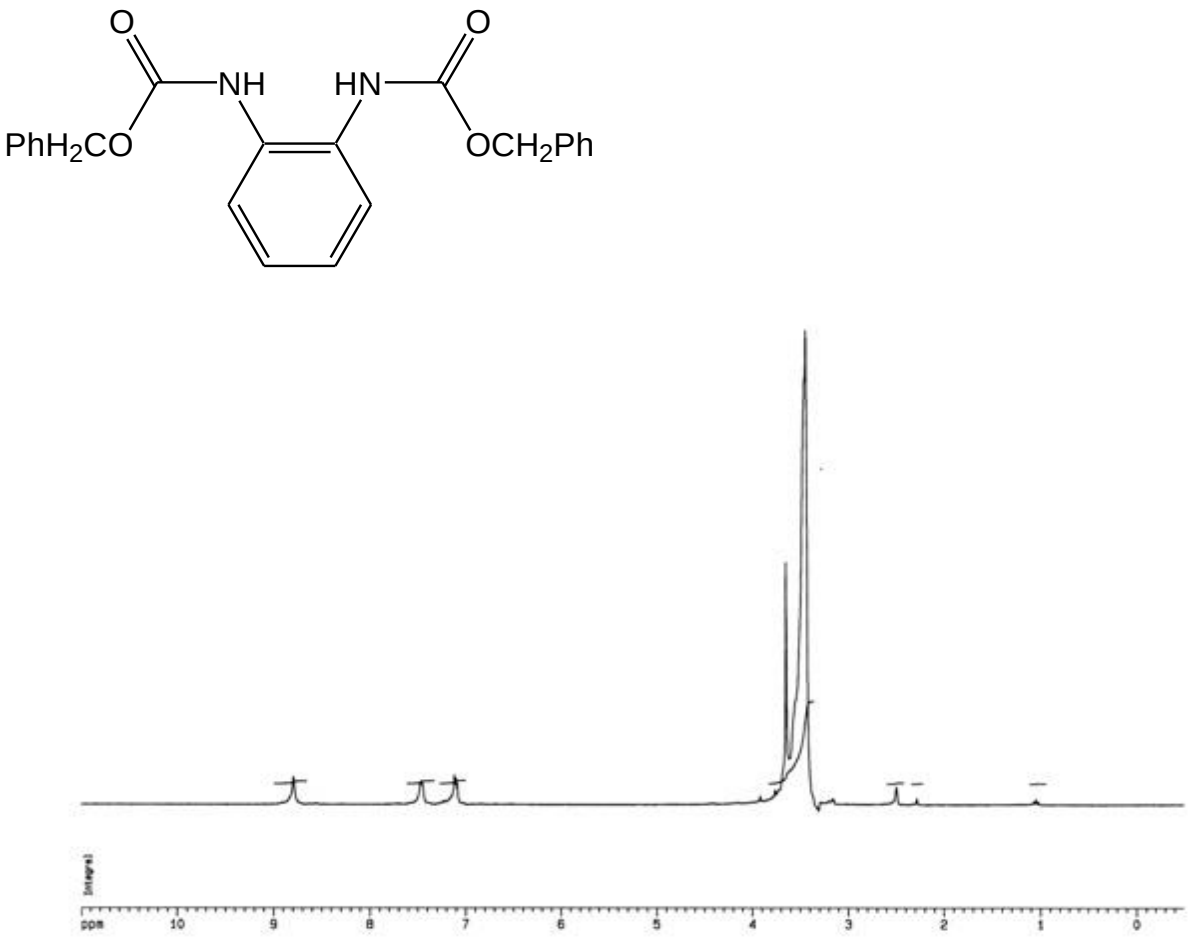


Figure A.7. ^{1}H NMR of carbamate **10** in DMSO-d_6.

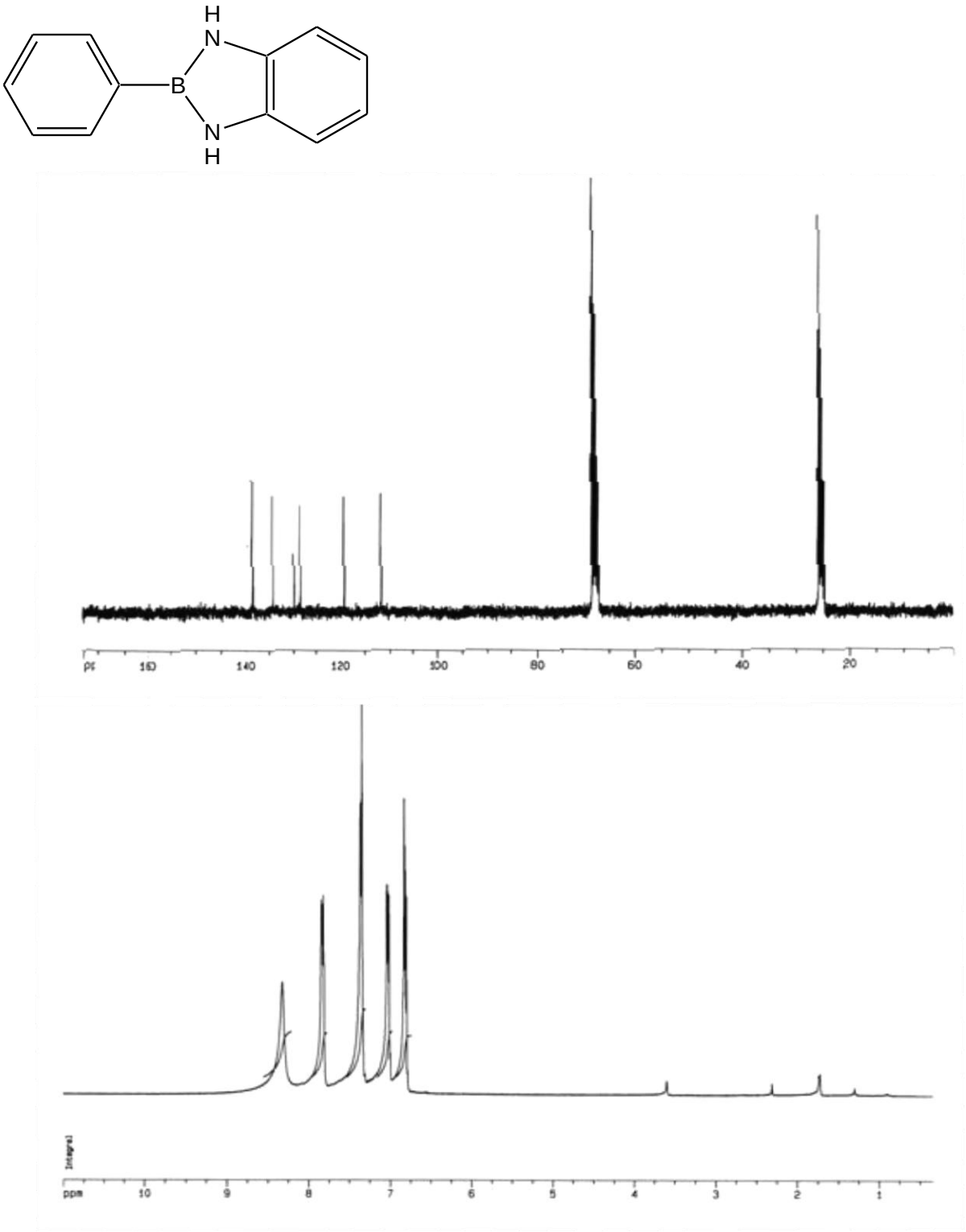


Figure A.8. (Top) ^{13}C NMR of diazaborole **12** in THF-d_8. (Bottom) ^{1}H NMR of diazaborole **12** in THF-d_8.

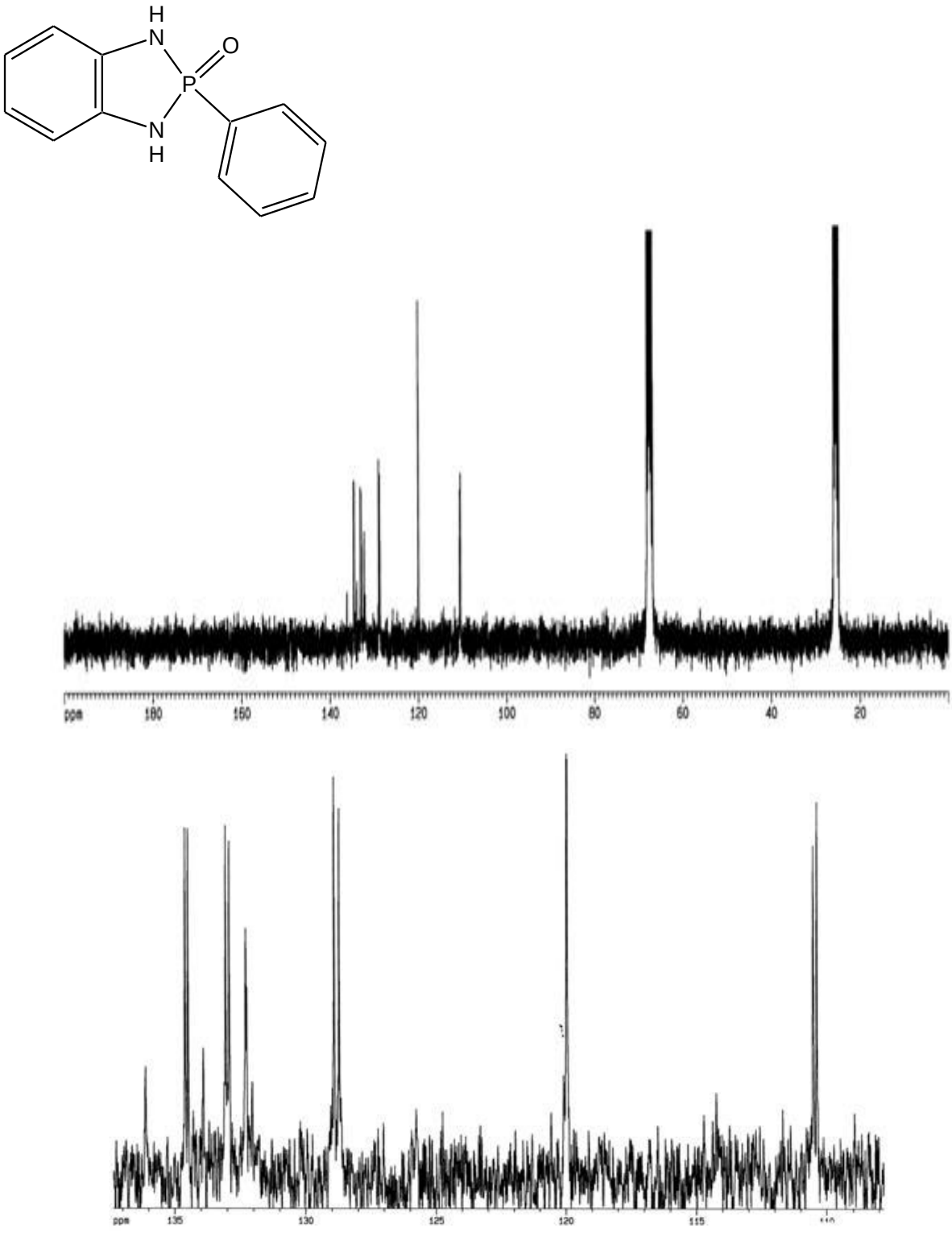


Figure A.9. (Top) ^{13}C NMR of diazaphosphole **13** in THF-d_8. (Bottom) ^{13}C NMR expansion of diazaphosphole **13** in THF-d_8.

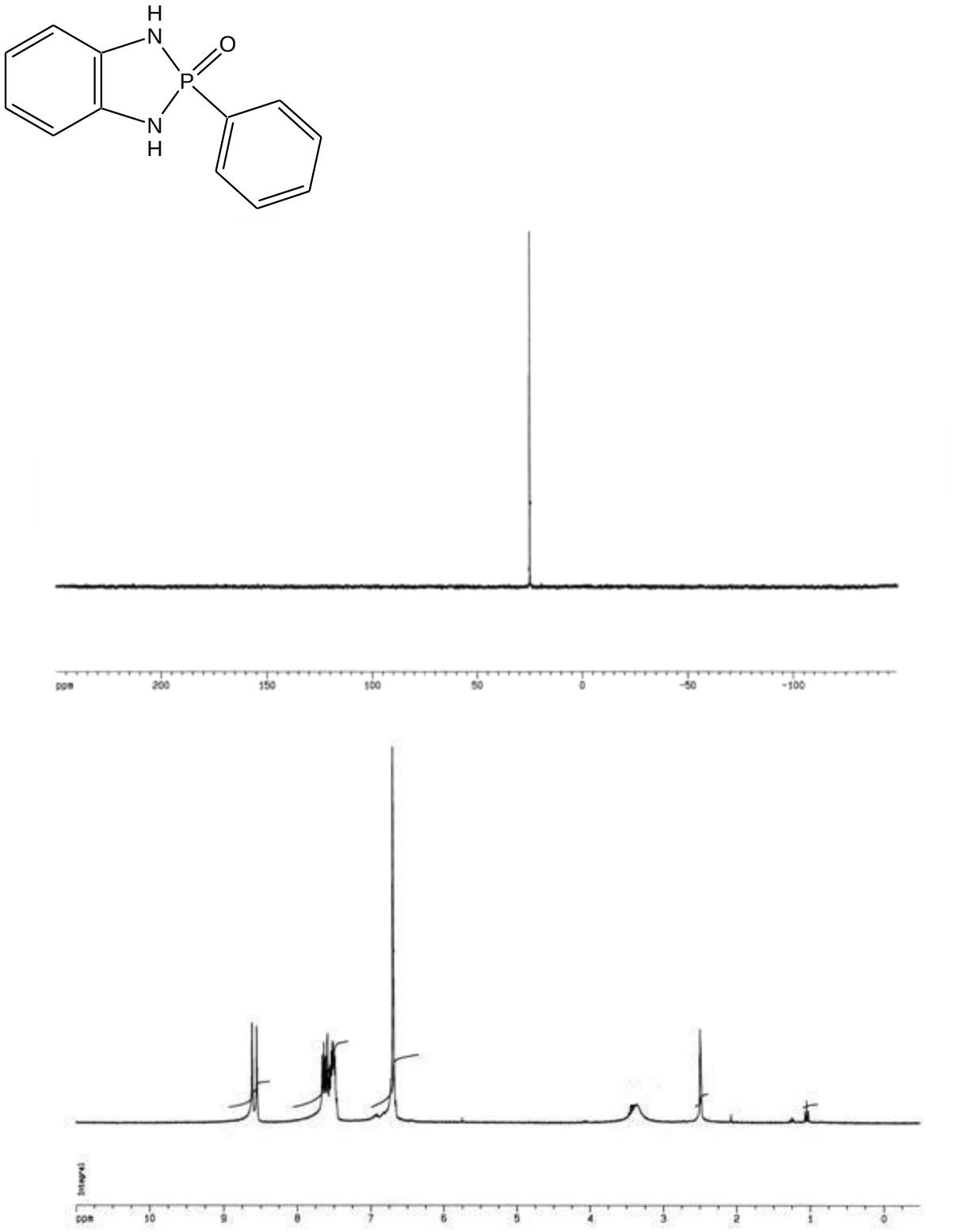


Figure A.10. (Top) ^{31}P NMR of diazaphosphole **13** in DMSO (standard reference H_3PO_4). (Bottom) ^{1}H NMR of diazaphosphole **13** in DMSO-d_6.

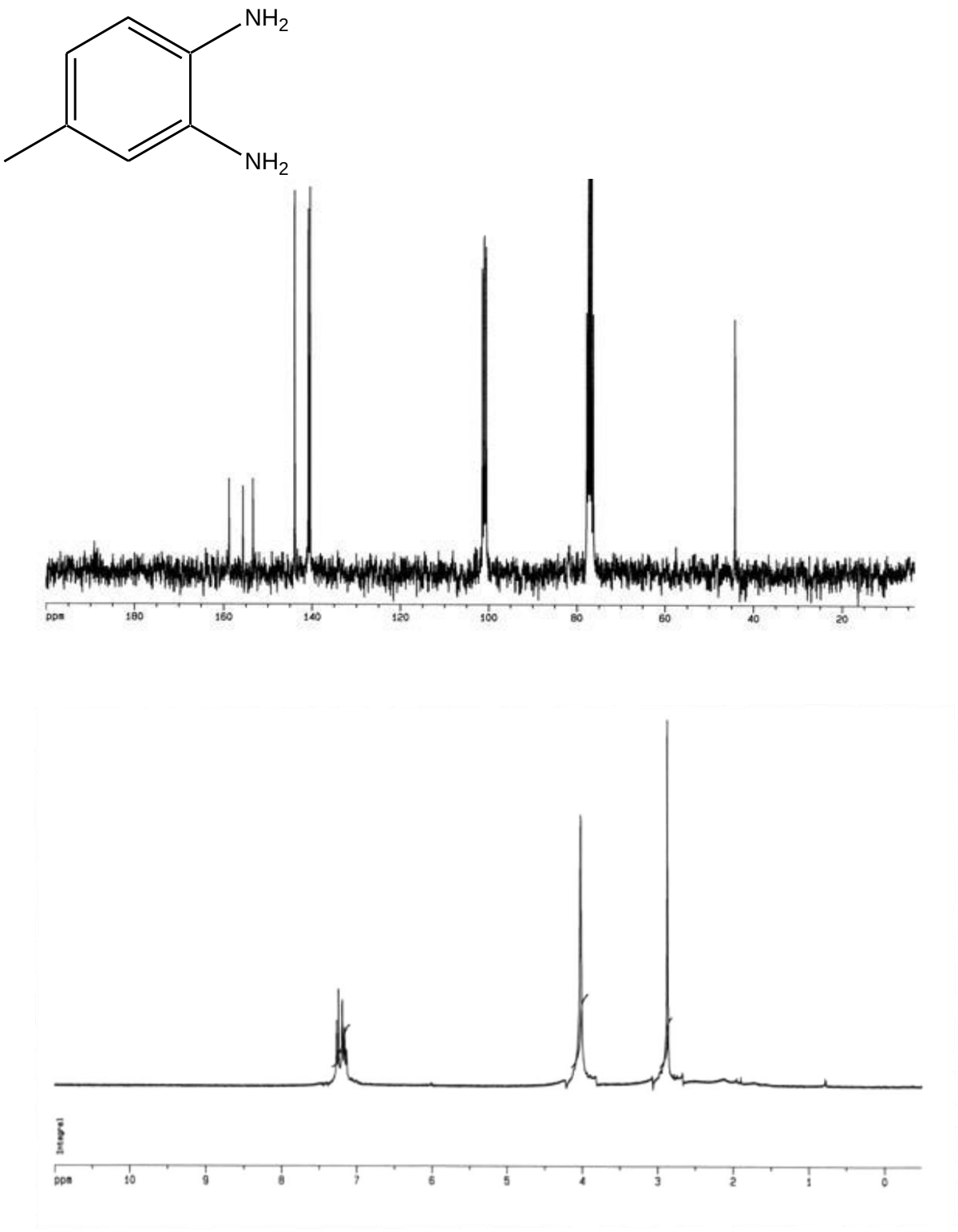


Figure A.11. (Top) ^{13}C NMR of diamine **17** in $CDCl_3$. (Bottom) ^{1}H NMR of diamine **17** in $CDCl_3$.

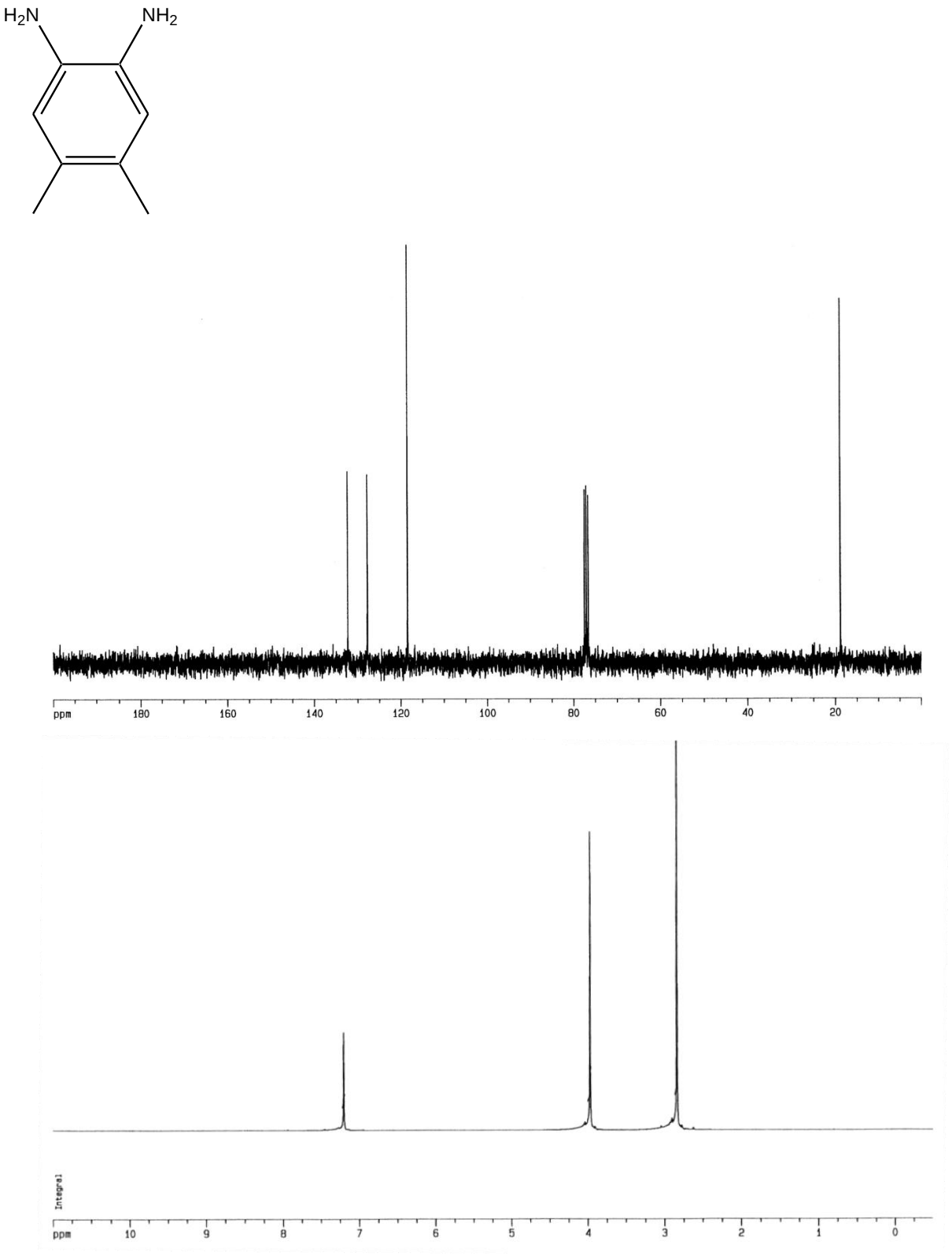


Figure A.12. (Top) ^{13}C NMR of diamine **19** in $CDCl_3$. (Bottom) ^{1}H NMr of diamine **19** in $CDCl_3$.

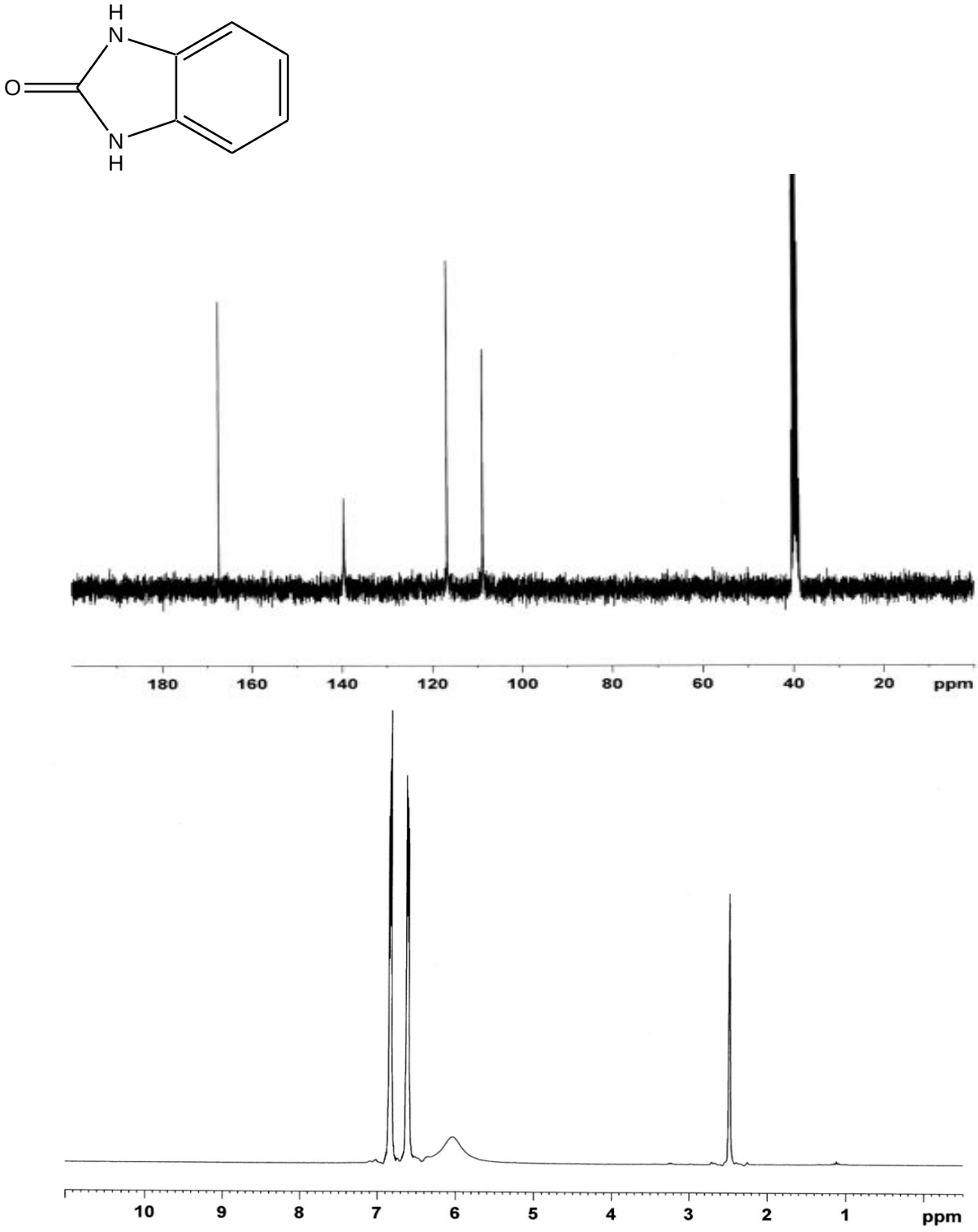


Figure A.13. (Top) ^{13}C NMR of urea **20** in DMSO-d_6. (Bottom) ^{1}H NMR of urea **20** in DMSO-d_6.

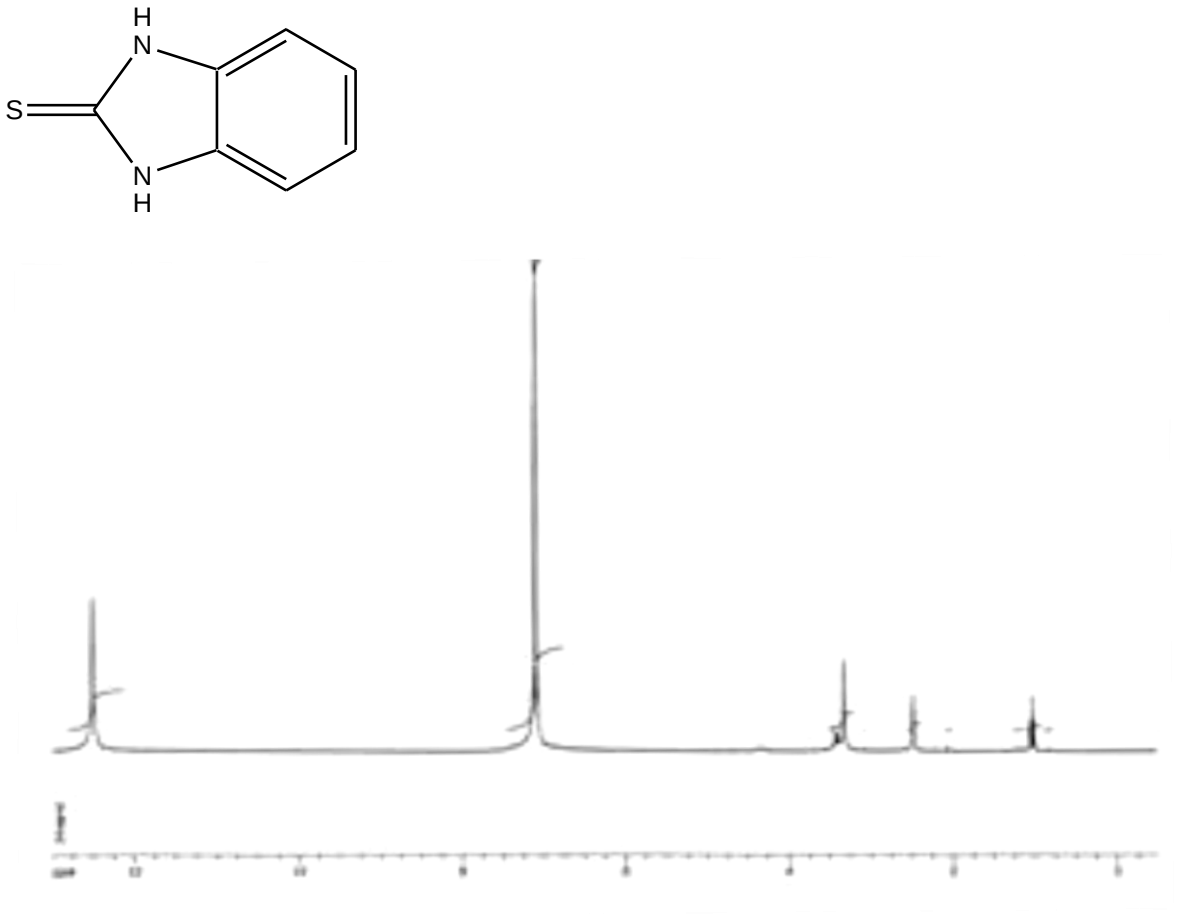


Figure A.14. ^{1}H NMR of thiourea **21** in DMSO-d_6.

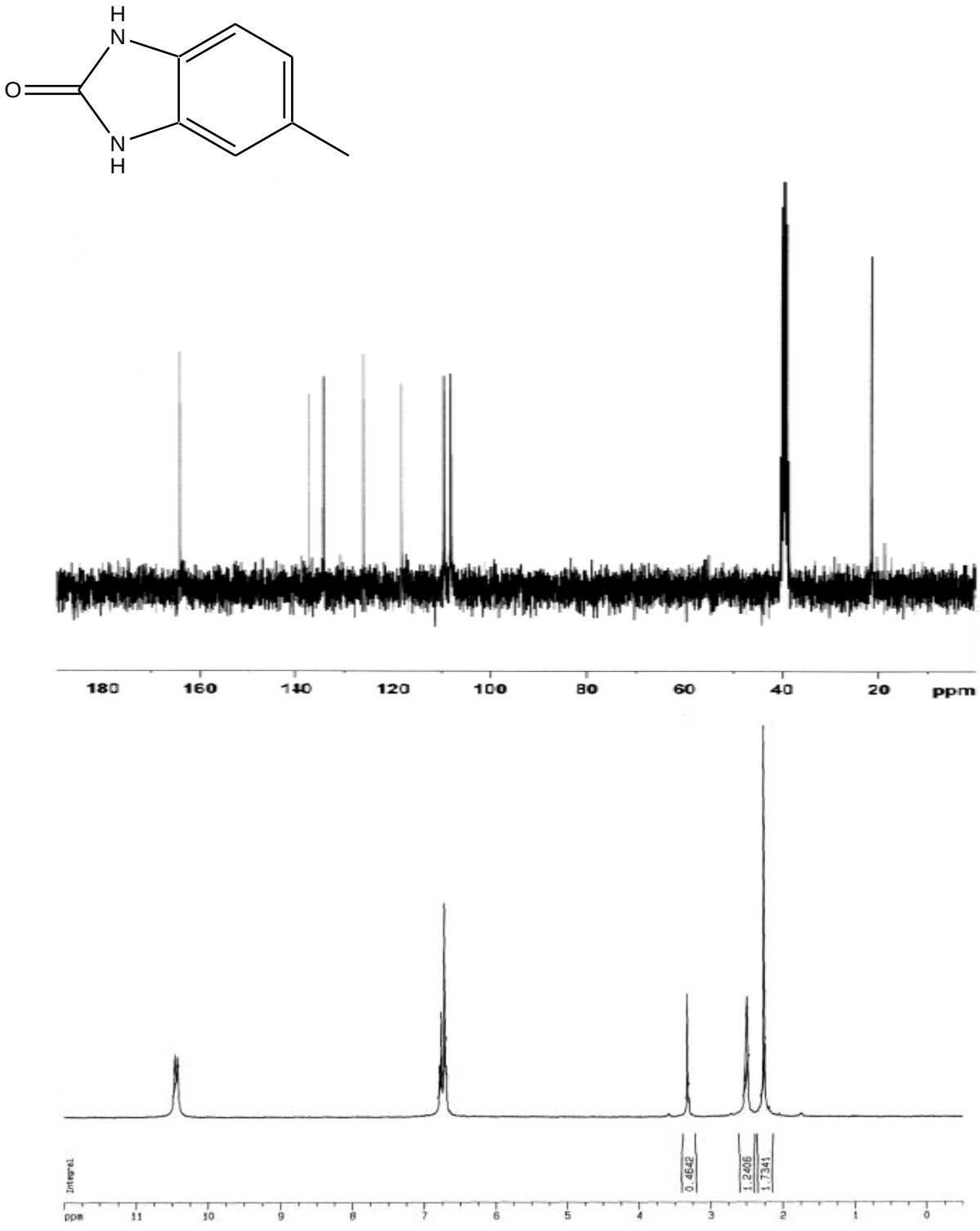


Figure A.15. (Top) ^{13}C NMR of urea **22** in DMSO-d_6. (Bottom) ^{1}H NMR of urea **22** in DMSO-d_6.

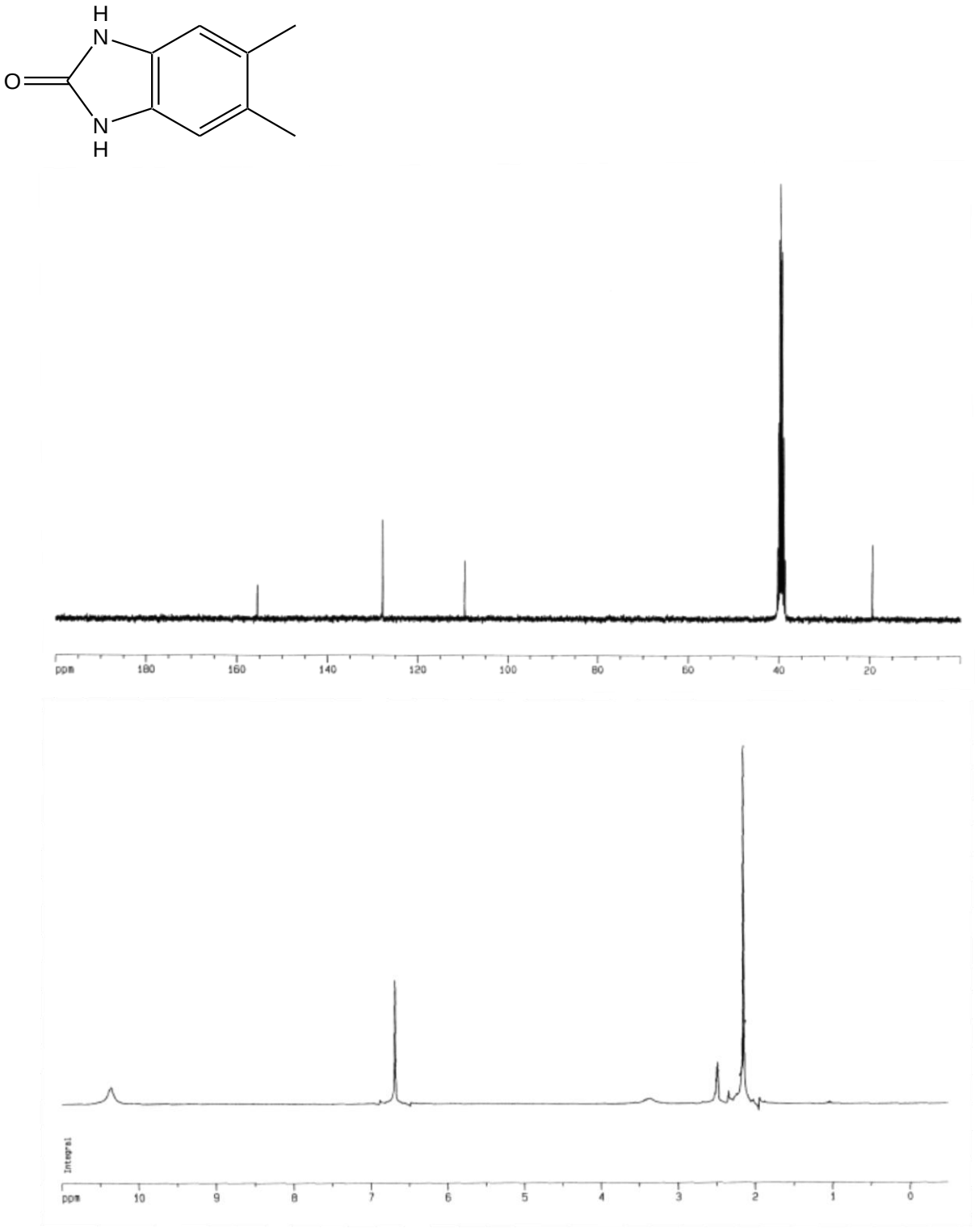


Figure A.16. (Top) ^{13}C NMR of urea **23** in DMSO-d_6. (Bottom) ^{1}H NMR of urea **23** in DMSO-d_6.

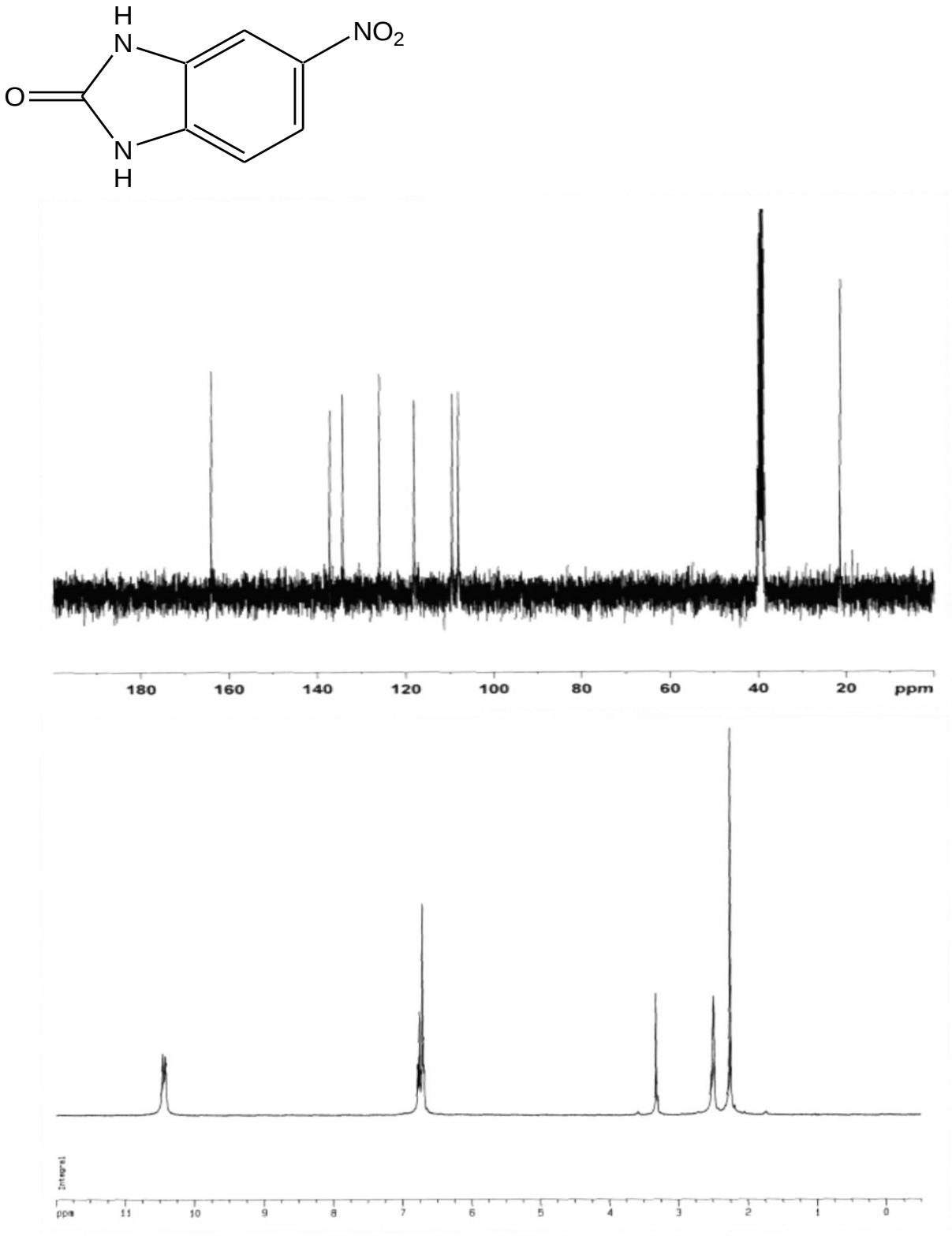


Figure A.17. (Top) ^{13}C NMR of urea **24** in DMSO-d_6. (Bottom) ^{1}H NMr of urea **24** in DMSO-d_6.

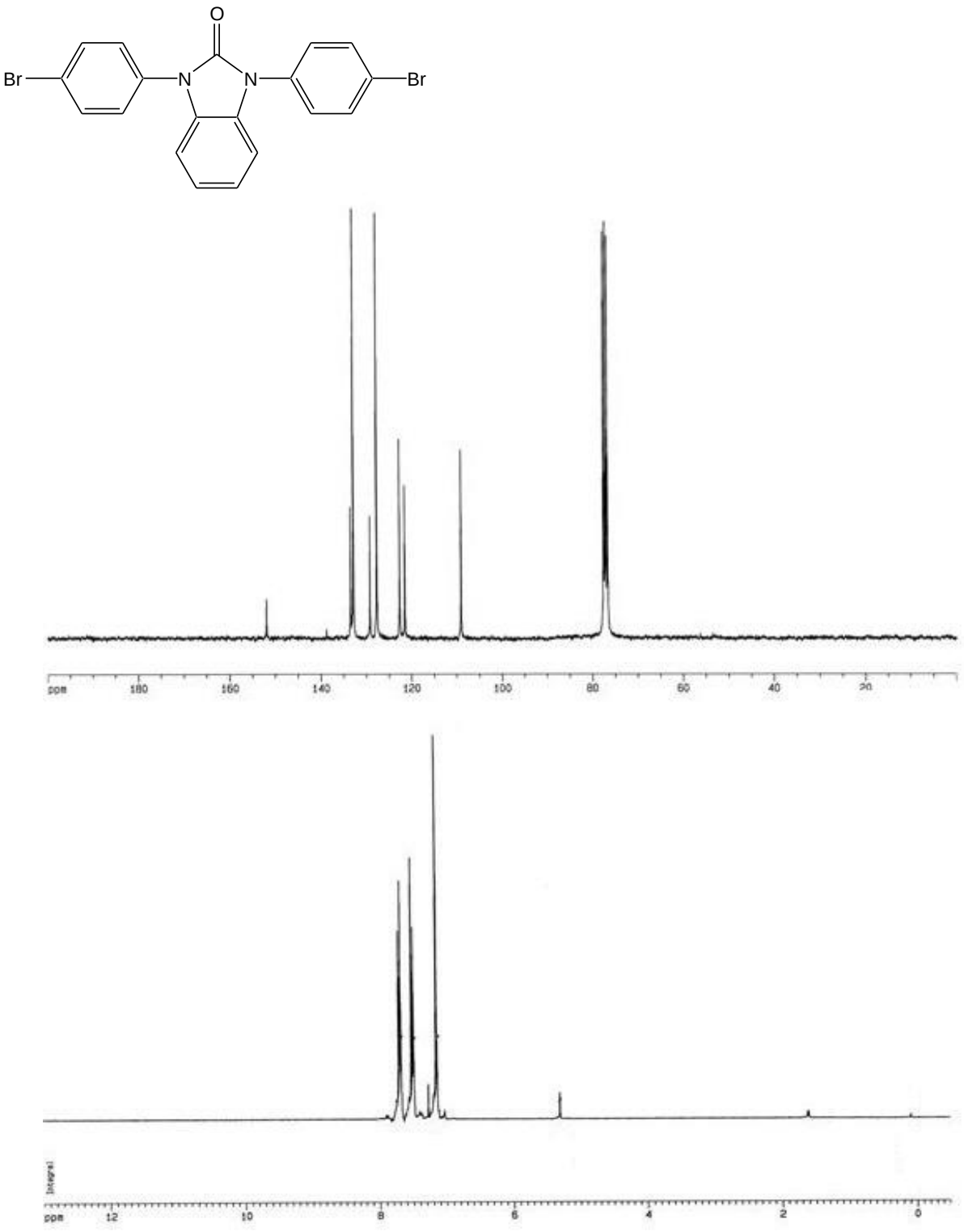


Figure A.18. (Top) ^{13}C NMR of segmer **25** after column chromatography in $CDCl_3$. (Bottom) ^{1}H NMR of segmer **25** after column chromatography in $CDCl_3$.

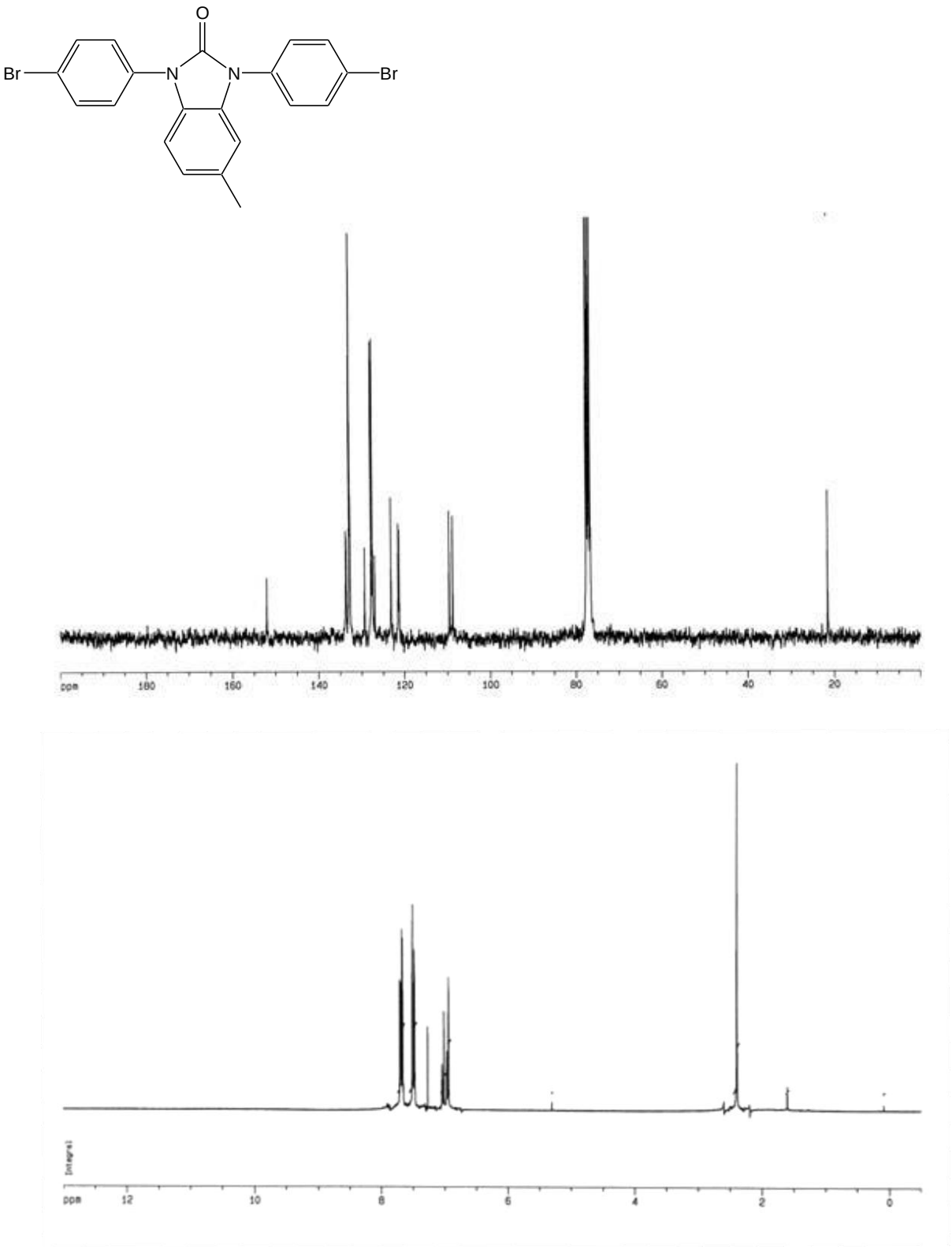


Figure A.19. (Top) ^{13}C NMR of segmer **26** after column chromatography in $CDCl_3$. (Bottom) ^{1}H NMR of segmer **26** after column chromatography in $CDCl_3$.

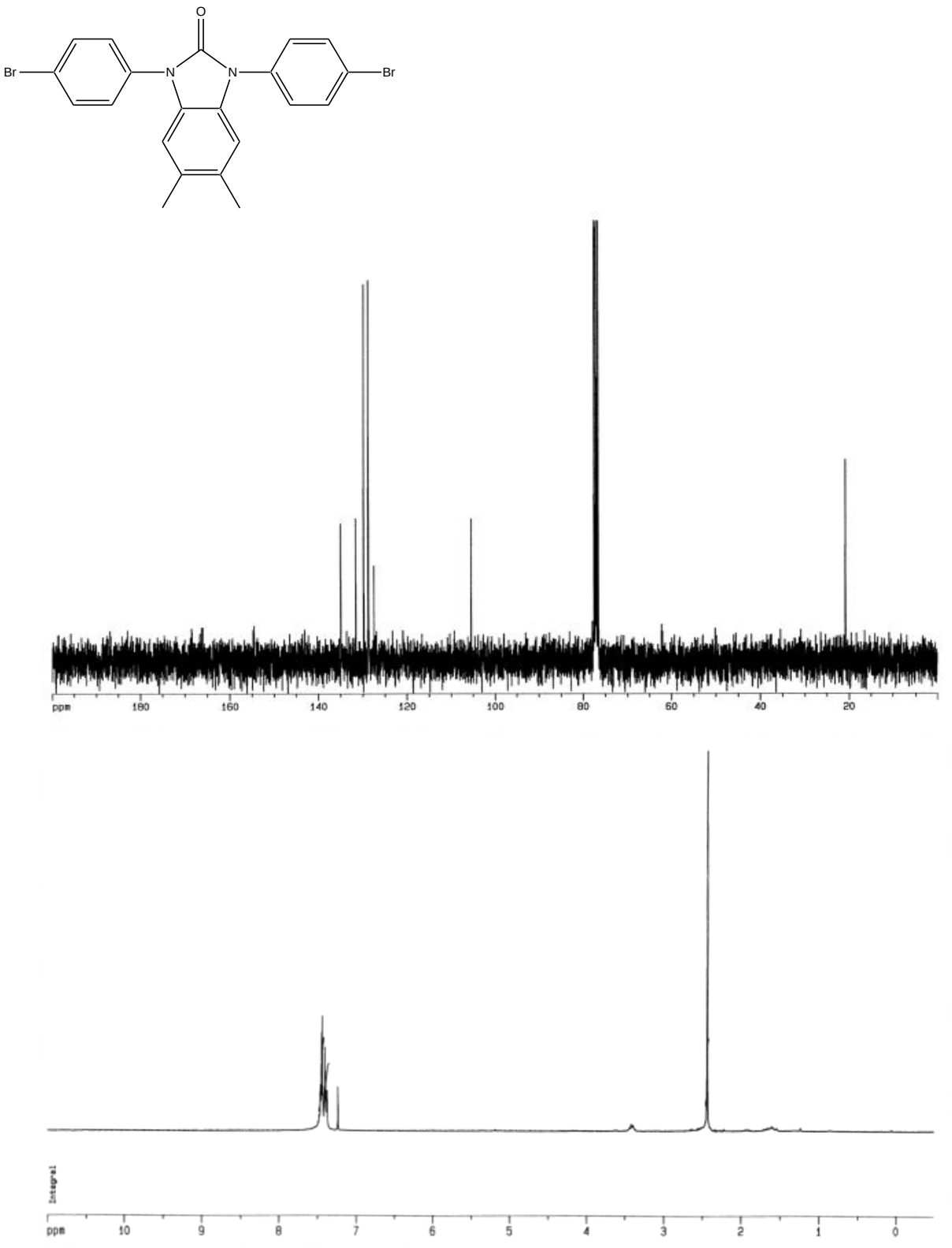


Figure A.20. (Top) ^{13}C NMR of urea segmer **27** in $CDCl_3$. (Bottom) ^{1}H NMR of urea segmer **27** in $CDCl_3$.

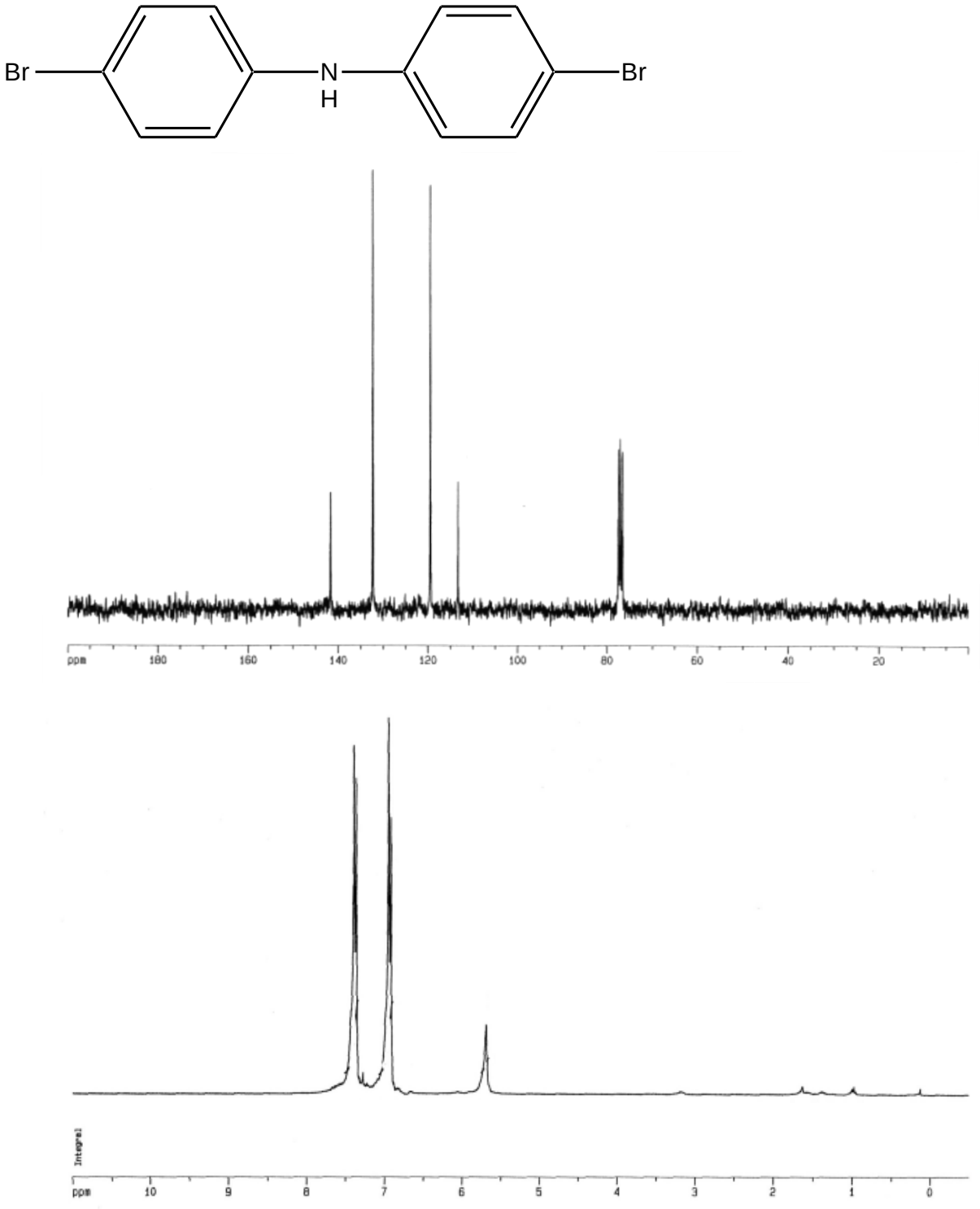


Figure A.21. (Top) ^{13}C NMR of dibromoamine **28** in $CDCl_3$. (Bottom) ^{1}H NMR of dibromoamine **28** in $CDCl_3$.

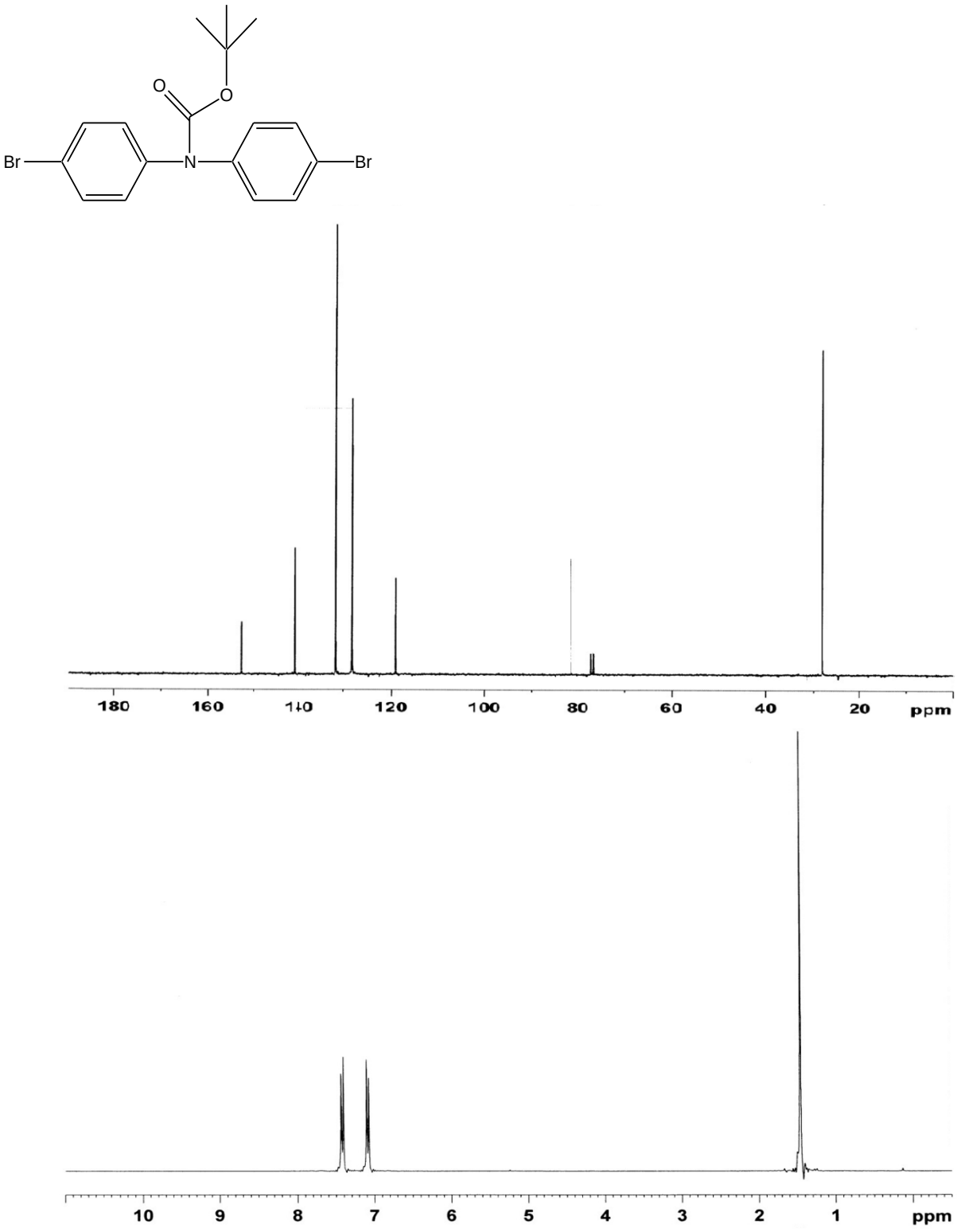


Figure A.22. (Top) ^{13}C NMR of bromodimer **29** in $CDCl_3$. (Bottom) ^{1}H NMR of bromodimer **29** in $CDCl_3$.

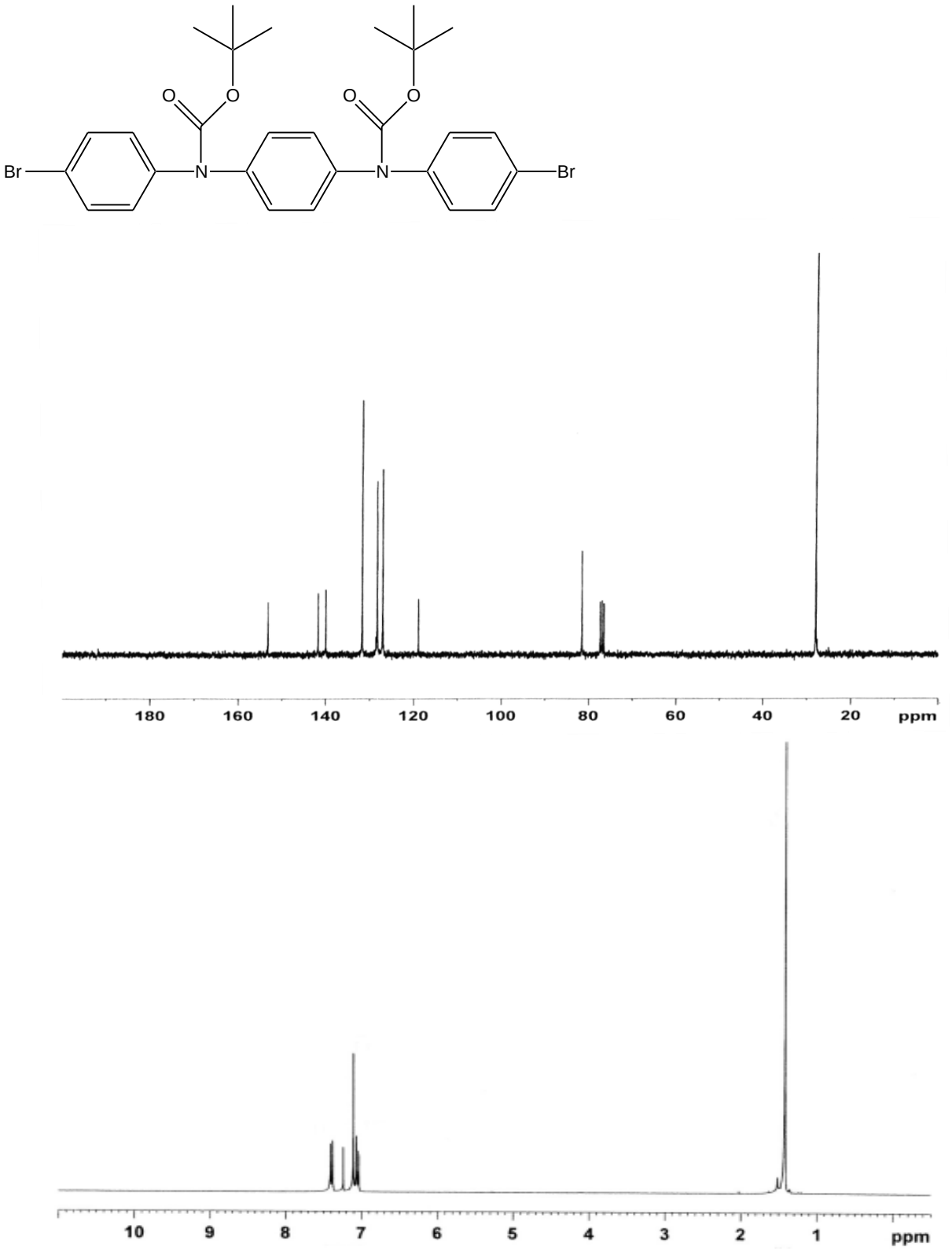


Figure A.23. (Top) ^{13}C NMR of bromotrimer **30** in $CDCl_3$. (Bottom) ^{1}H NMR of bromotrimer **30** in $CDCl_3$.

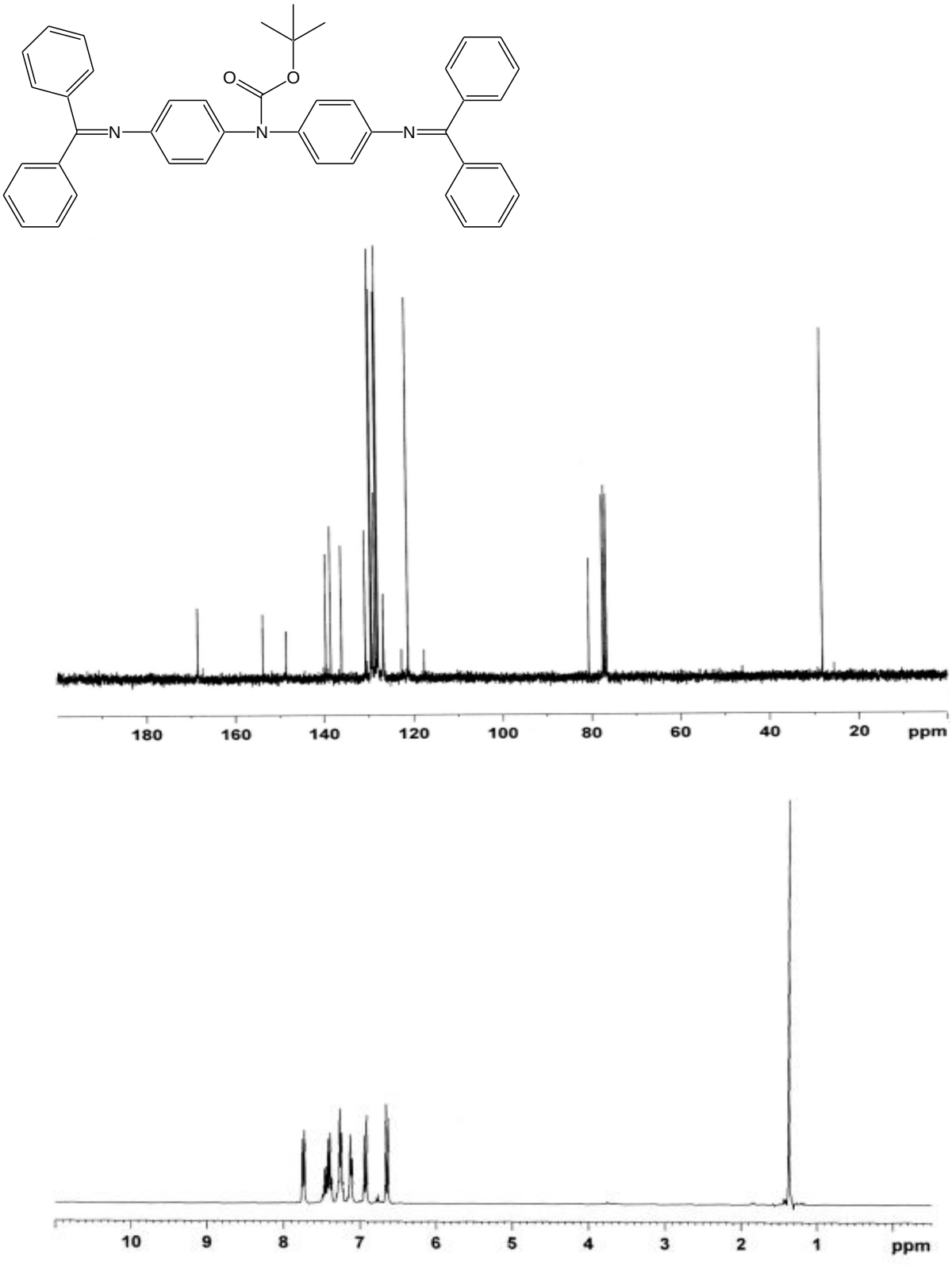


Figure A.24. (Top) ^{13}C NMR of diamine **31** in $CDCl_3$. (Bottom) ^{1}H NMR of diamine **31** in $CDCl_3$.

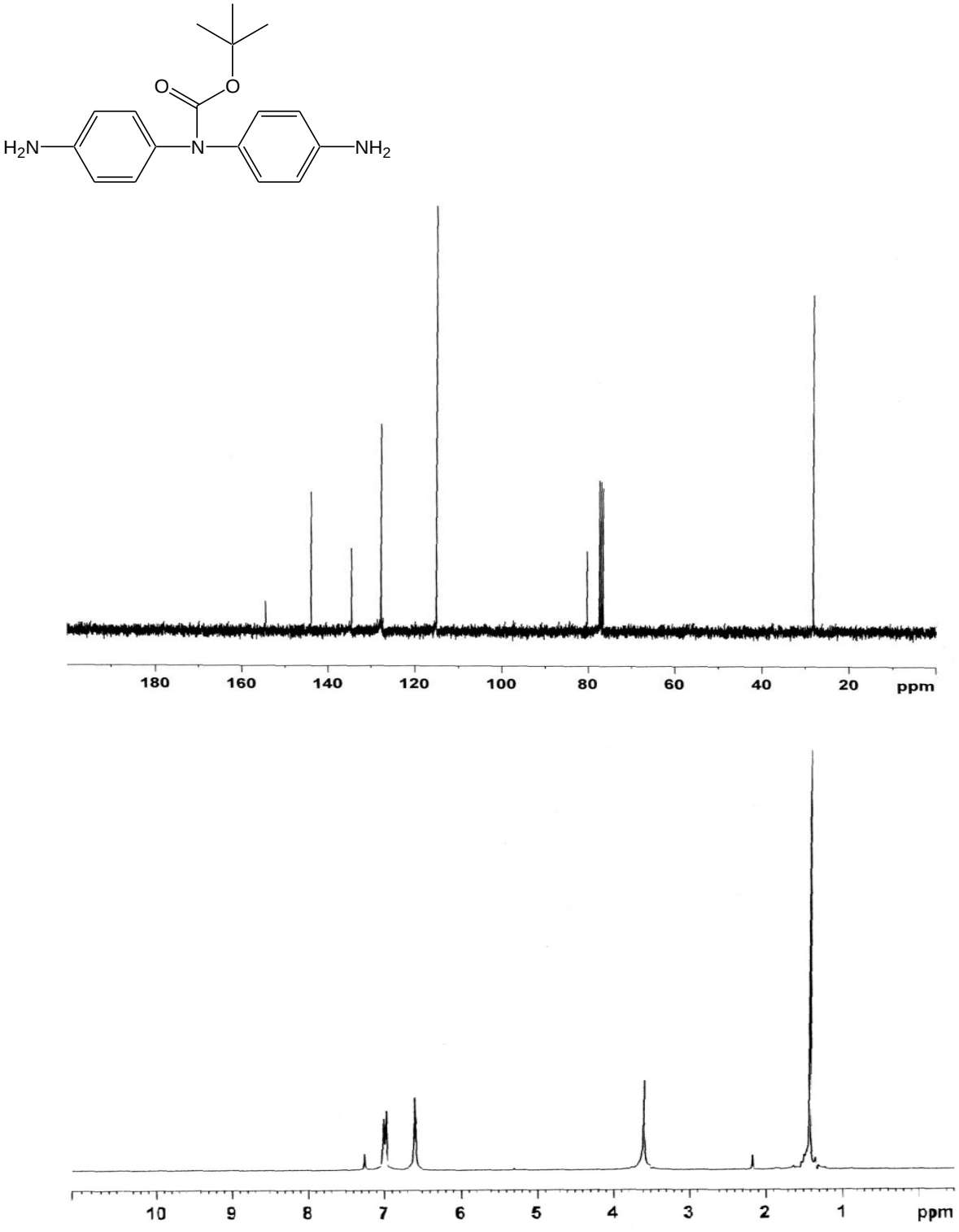


Figure A.25. (Top) ^{13}C NMR of dimeramine **32** in $CDCl_3$. (Bottom) ^{1}H NMR of dimeramine **32** in $CDCl_3$.

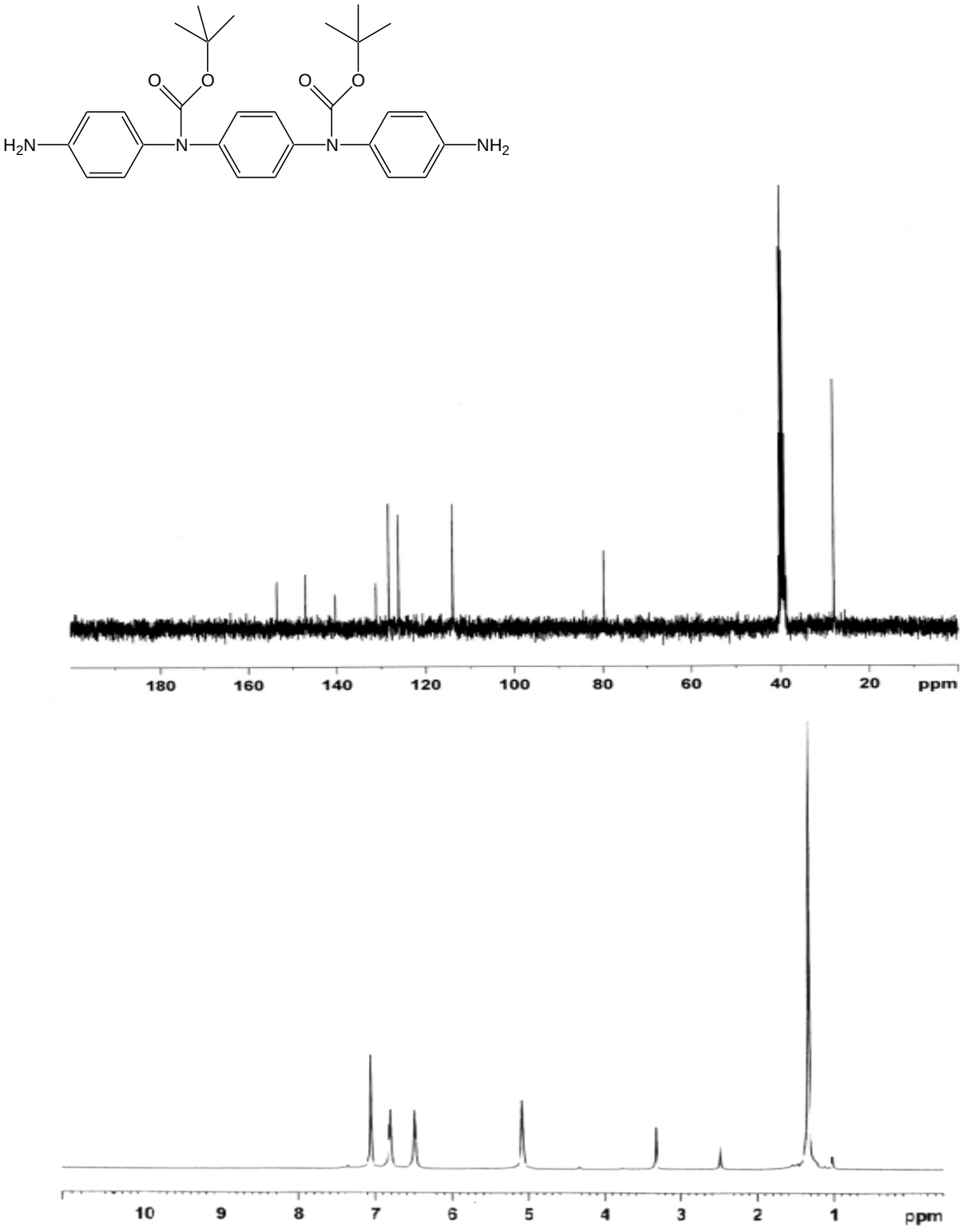


Figure A.26. (Top) ^{13}C NMR of trimeramine **34** in DMSO-d_6. (Bottom) ^{1}H NMR of trimeramine **34** in DMSO-d_6.

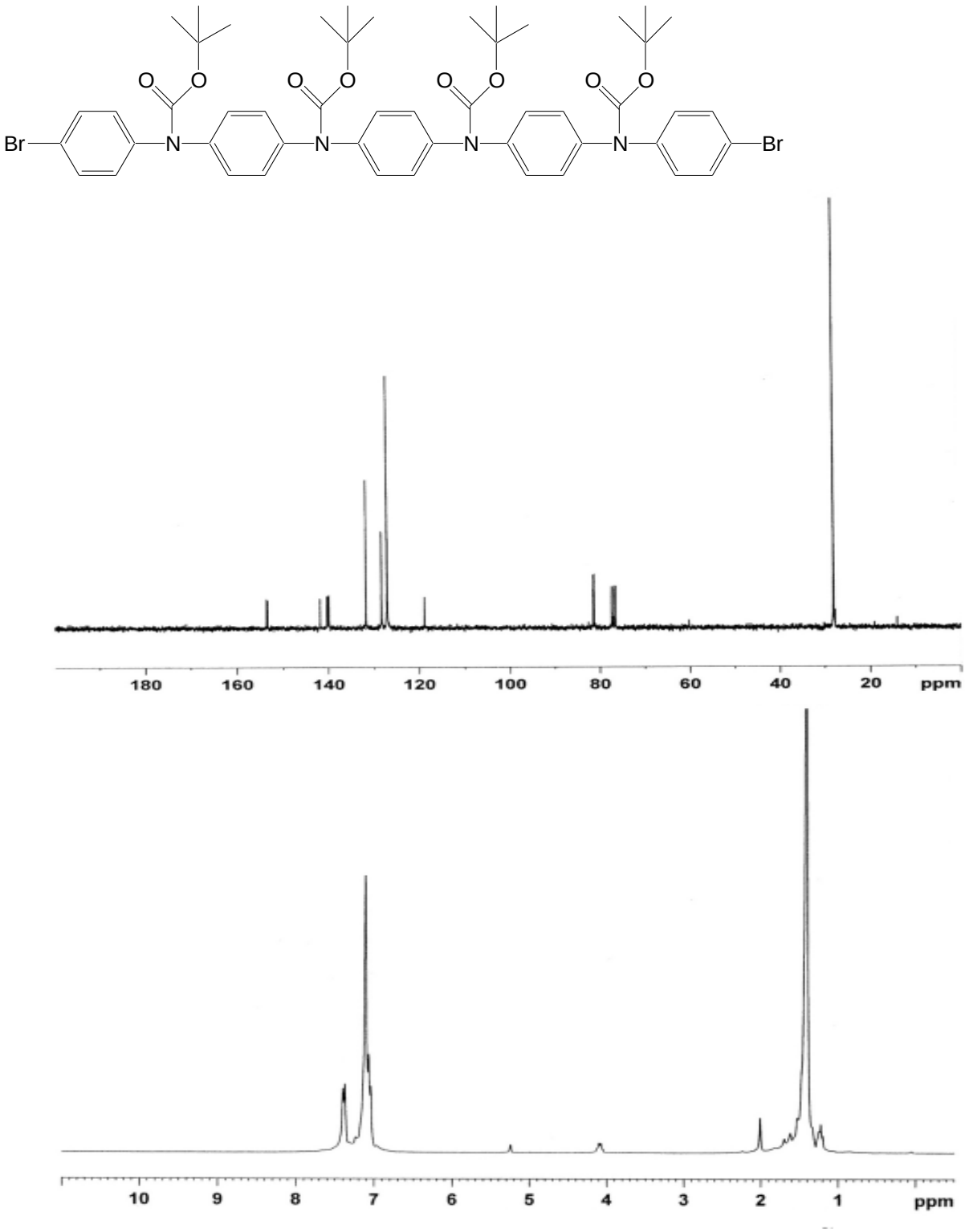


Figure A.27. (Top) ^{13}C NMR of bromopentamer **35** in $CDCl_3$. (Bottom) ^{1}H NMR of bromopentamer **35** in $CDCl_3$.

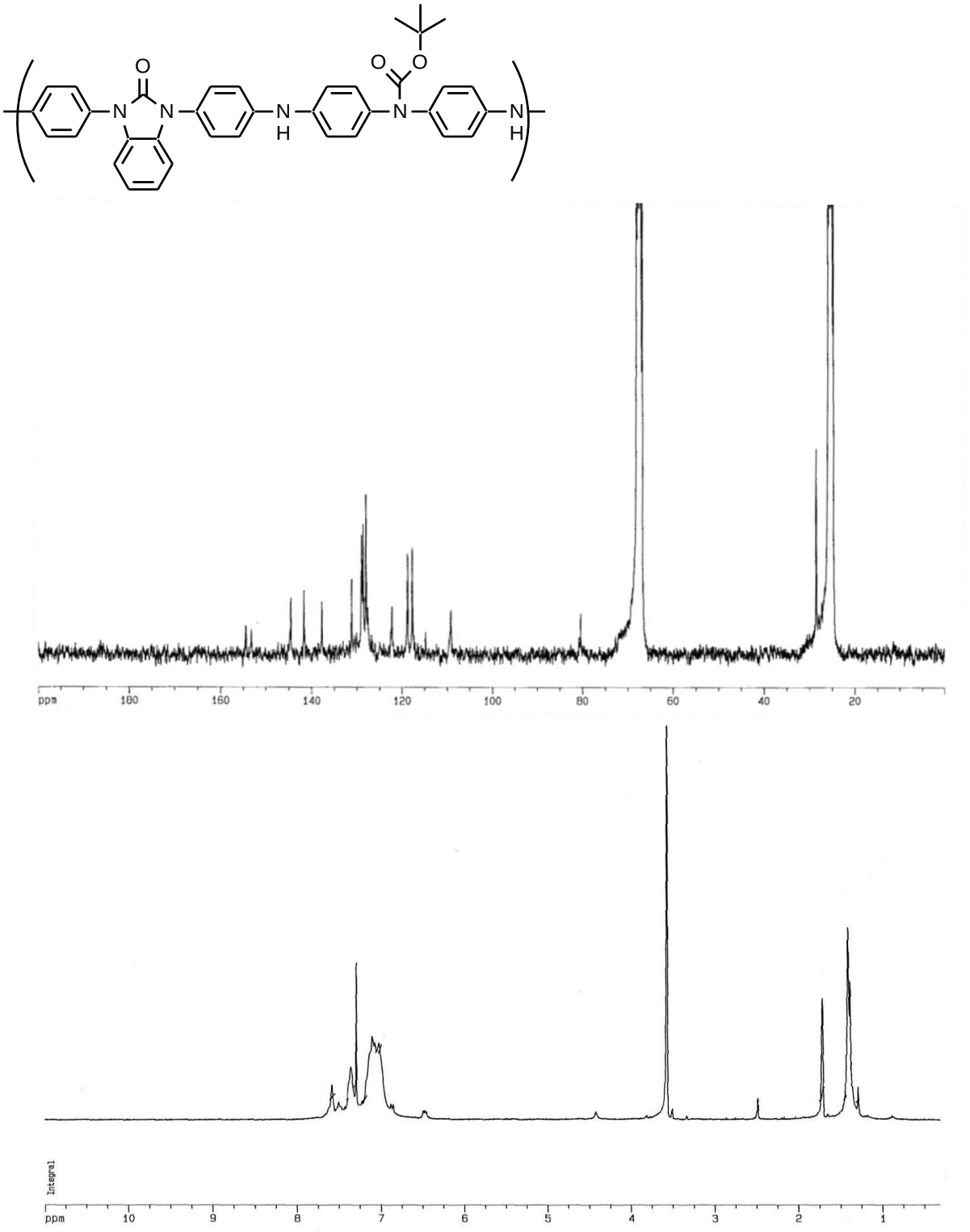


Figure A.28. (Top) ^{13}C NMR of polymer **36** in THF-d_8. (Bottom) ^{1}H NMR of polymer **36** in THF-d_8.

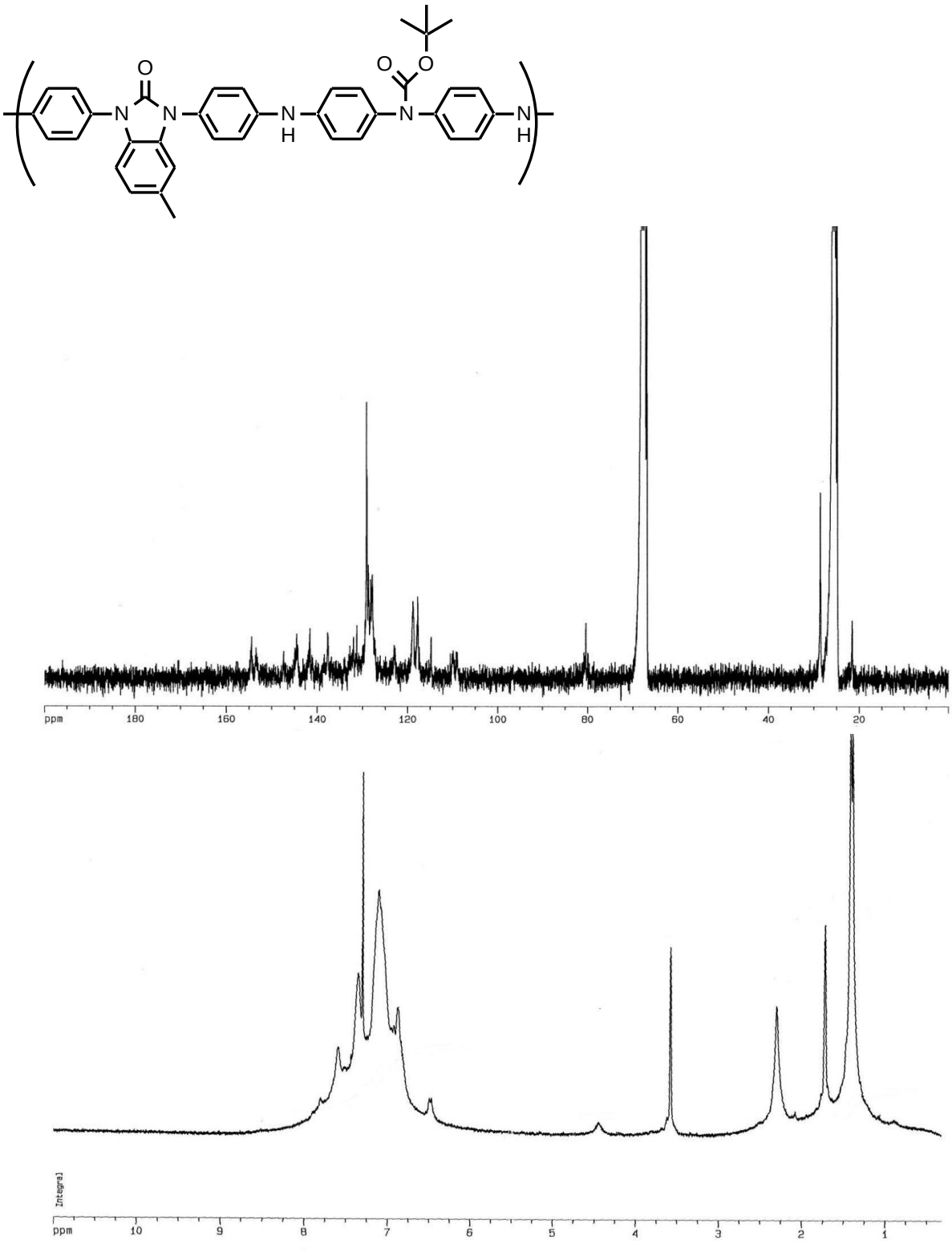


Figure A.29. (Top) ^{13}C NMR of polymer **37** in THF-d_8. (Bottom) ^{1}H NMR of polymer **37** in THF-d_8.

APPENDIX B: CHAPTER 2

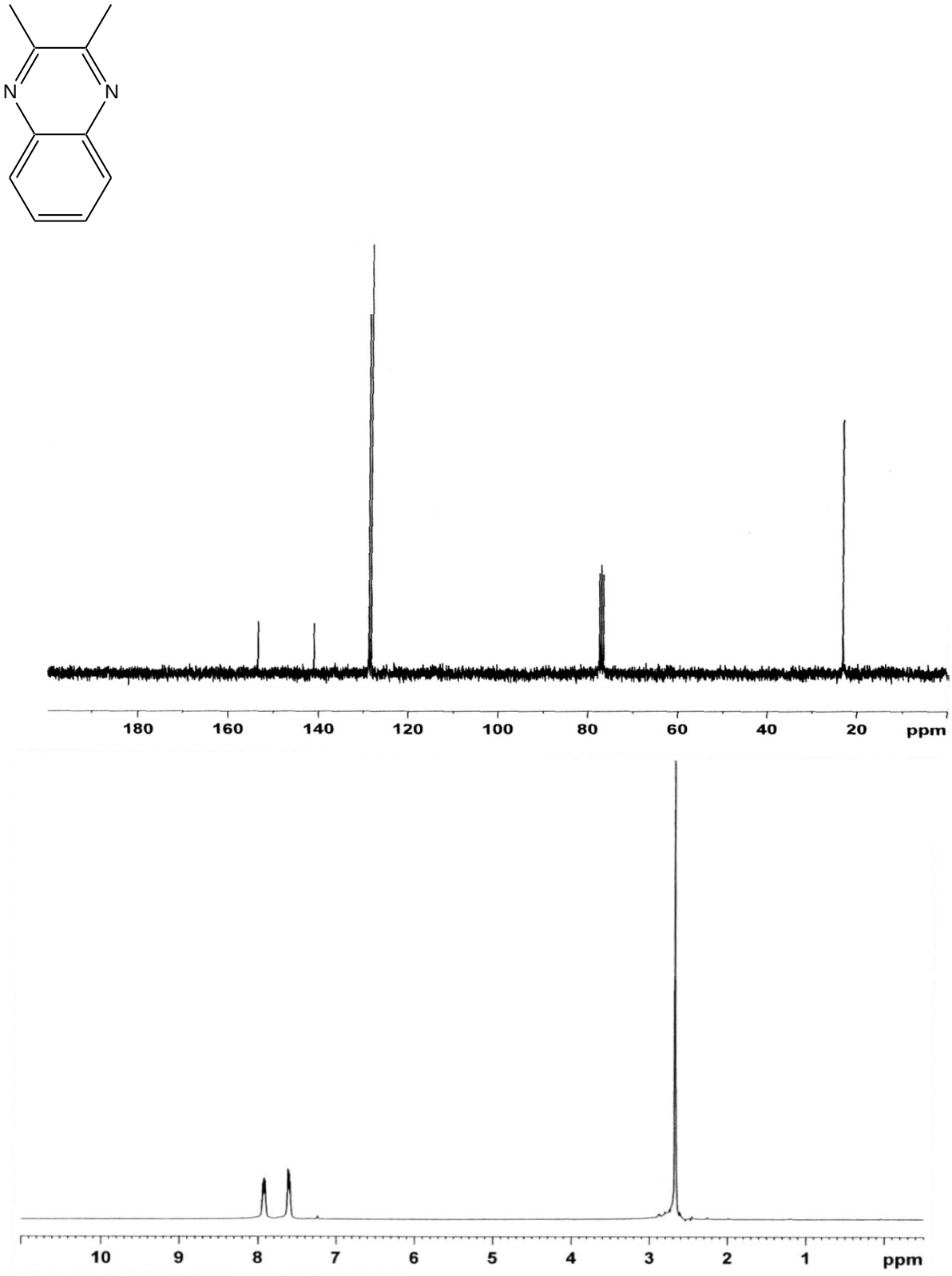


Figure B.1. (Top) ^{13}C NMR of quinoxaline **2a** in $CDCl_3$. (Bottom) ^{1}H NMR of quinoxaline **2a** in $CDCl_3$.

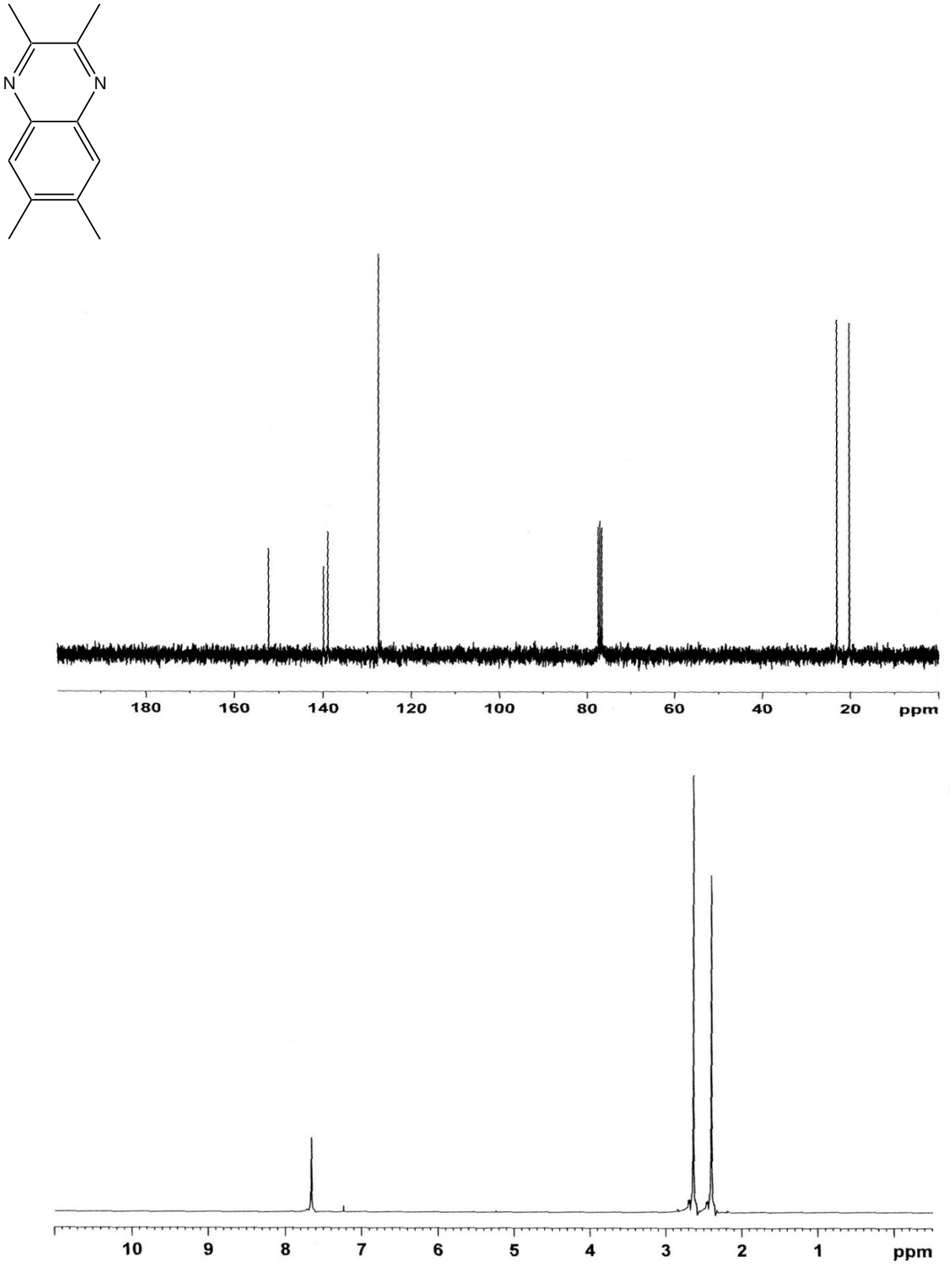


Figure B.2. (Top) ^{13}C NMR of quinoxaline **2b** in $CDCl_3$. (Bottom) ^{1}H NMR of quinoxaline **2b** in $CDCl_3$.

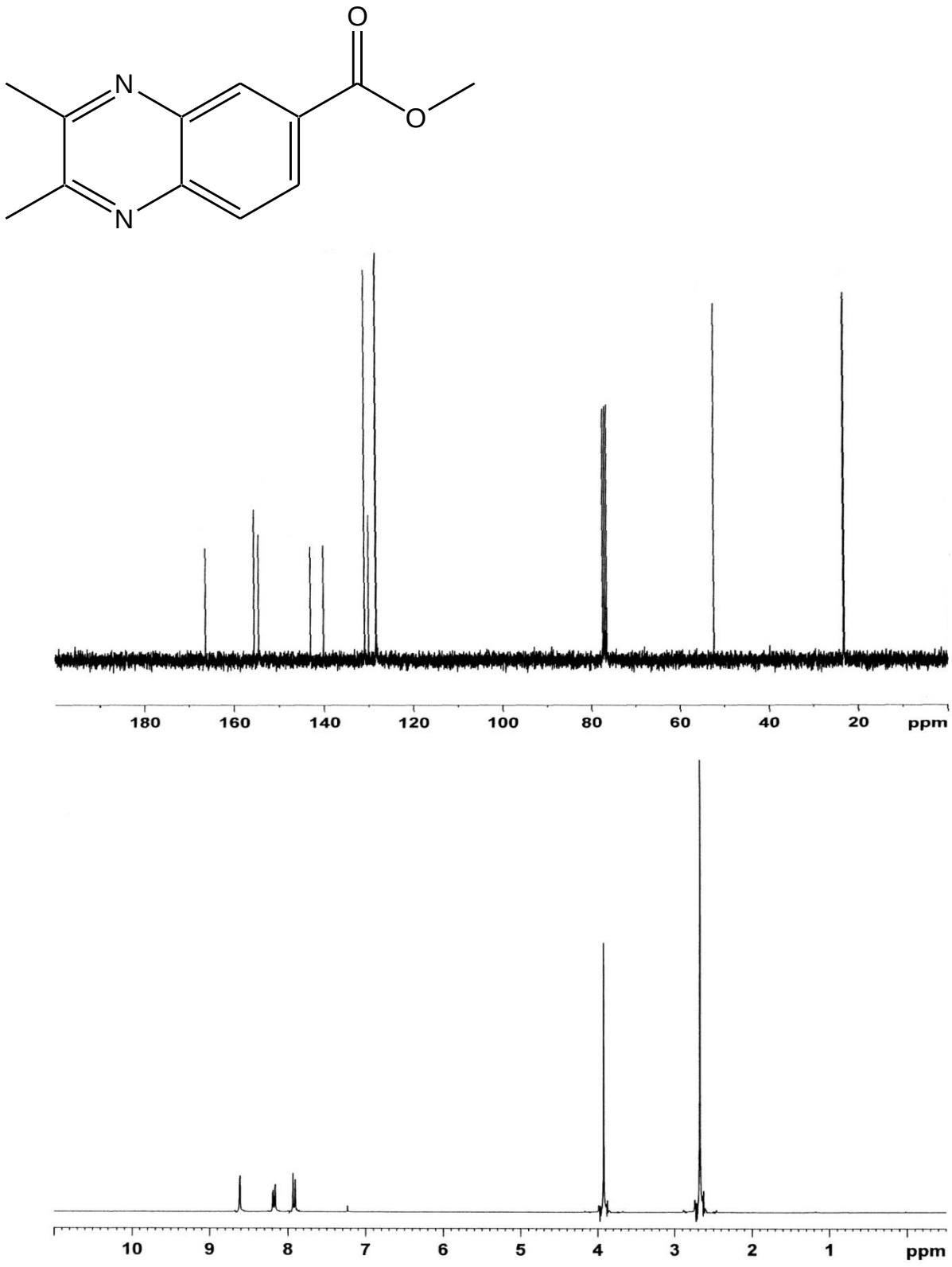


Figure B.3. (Top) ^{13}C NMR of quinoxaline **2c** in $CDCl_3$. (Bottom) ^{1}H NMR of quinoxaline **2c** in $CDCl_3$.

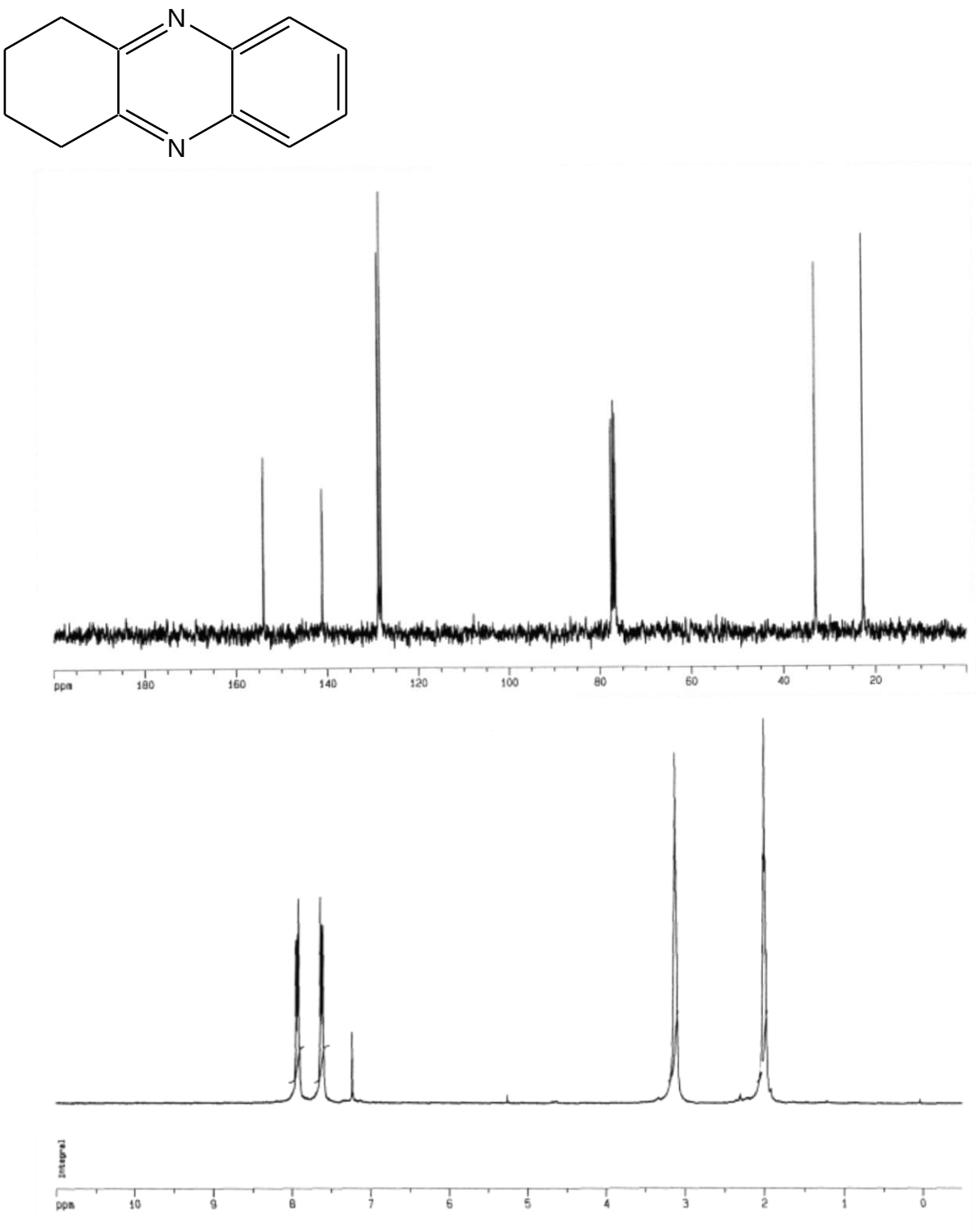


Figure B.4. (Top) ^{13}C NMR of tetrahydrophenazine **4a** in $CDCl_3$. (Bottom) ^{1}H NMR of tetrahydrophenazine **4a** in $CDCl_3$.

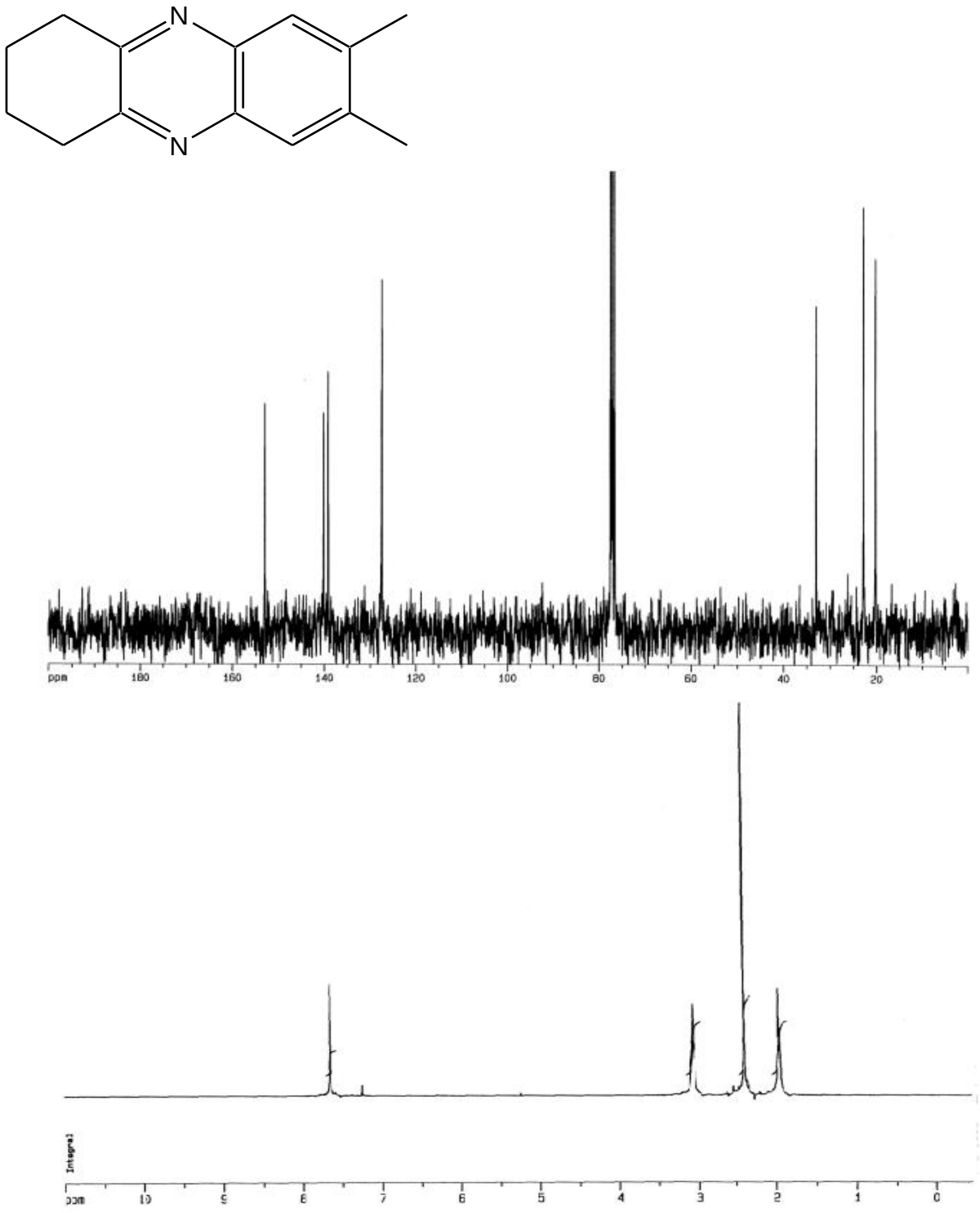


Figure B.5. (Top) ^{13}C NMR of tetrahydrophenazine **4b** in $CDCl_3$. (Bottom) ^{1}H NMR of tetrahydrophenazine **4b** in $CDCl_3$.

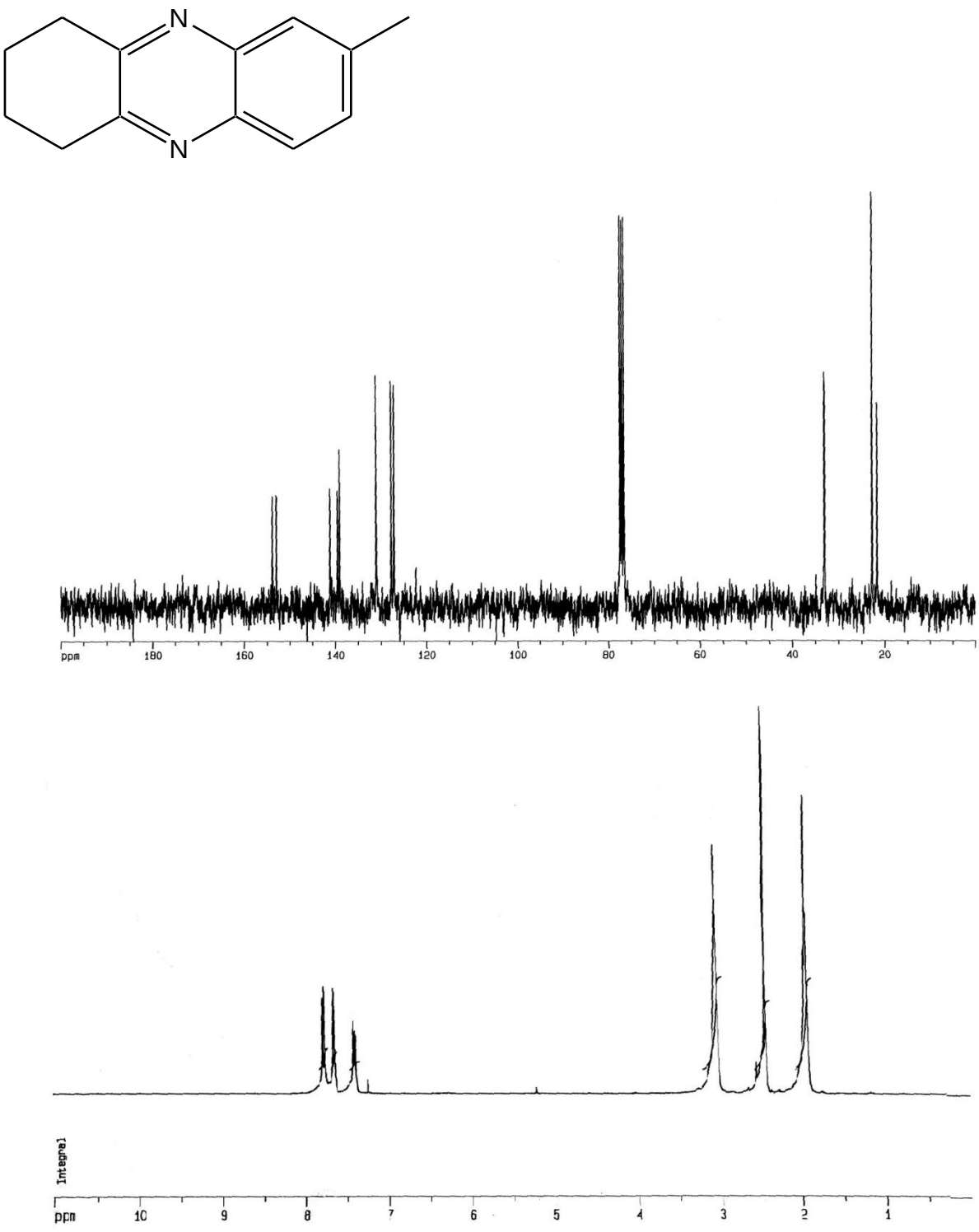


Figure B.6. (Top) ^{13}C NMR of tetrahydrophenazine **4c** in $CDCl_3$. (Bottom) ^{1}H NMR of tetrahydrophenazine **4c** in $CDCl_3$.

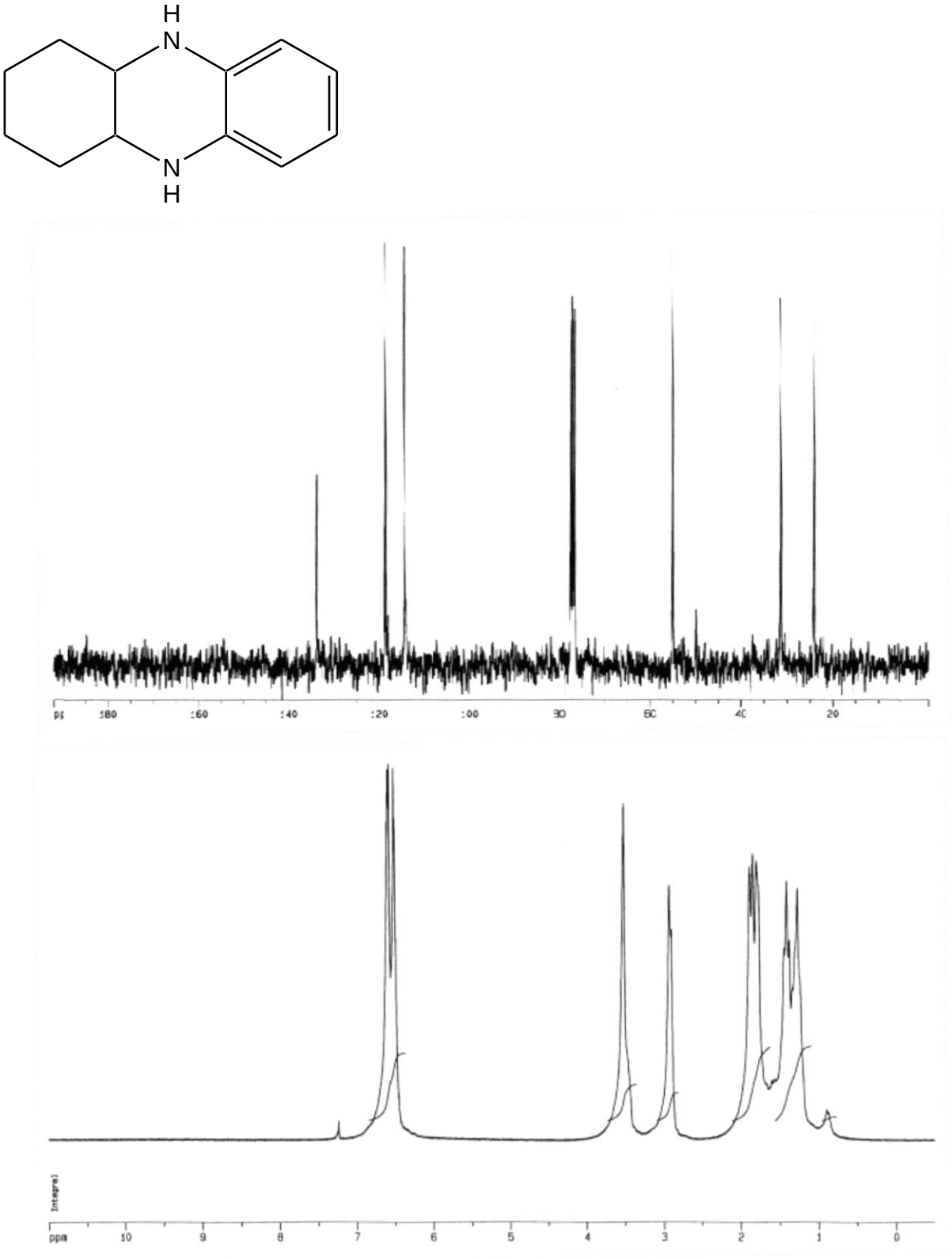


Figure B.7. (Top) ^{13}C NMR of octahydrophenazine **5a** in $CDCl_3$. (Bottom) ^{1}H NMR of octahydrophenazine **5a** in $CDCl_3$.

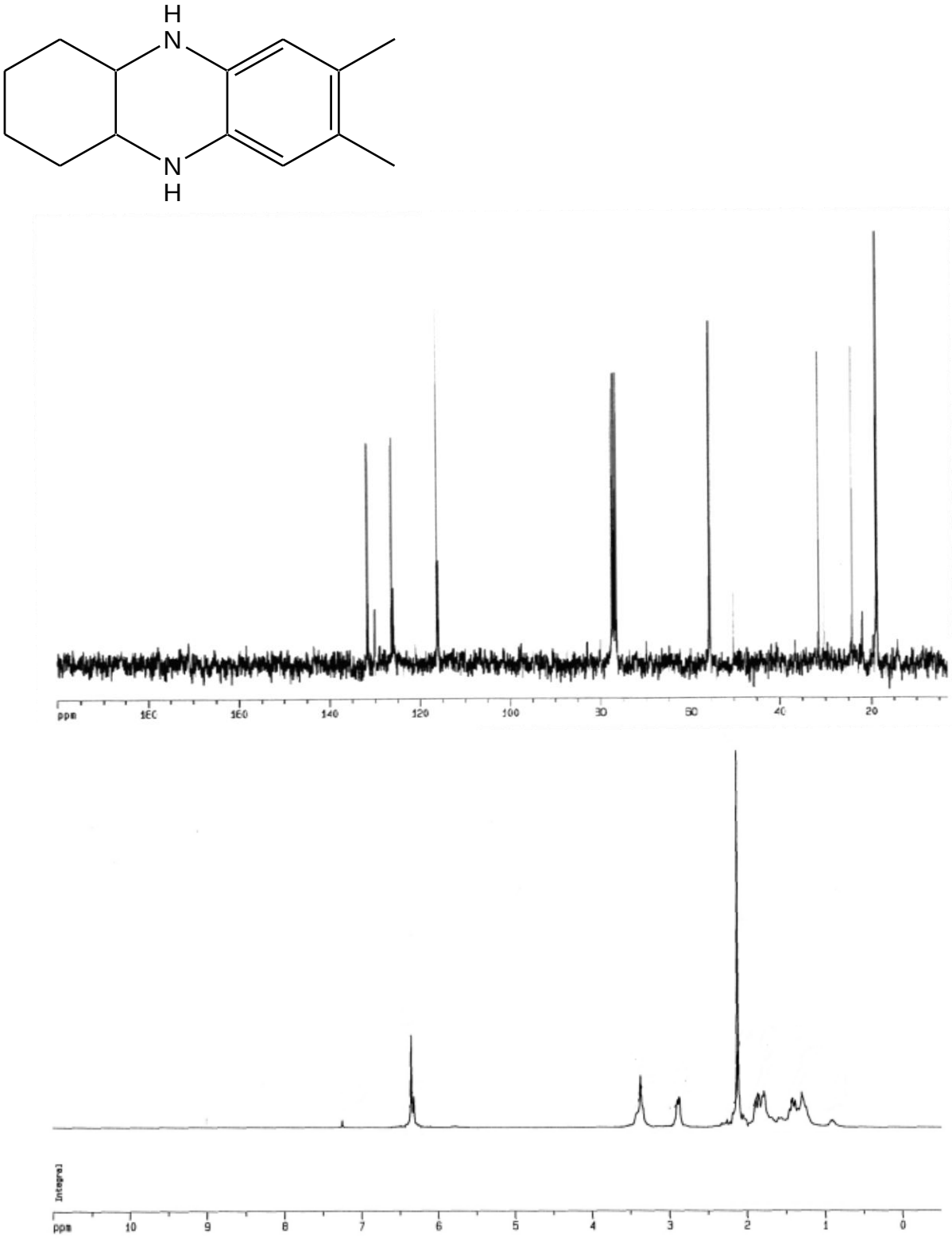


Figure B.8. (Top) ^{13}C NMR of octahydrophenazine **5b** in $CDCl_3$. (Bottom) ^{1}H NMR of octahydrophenazine **5b** in $CDCl_3$.

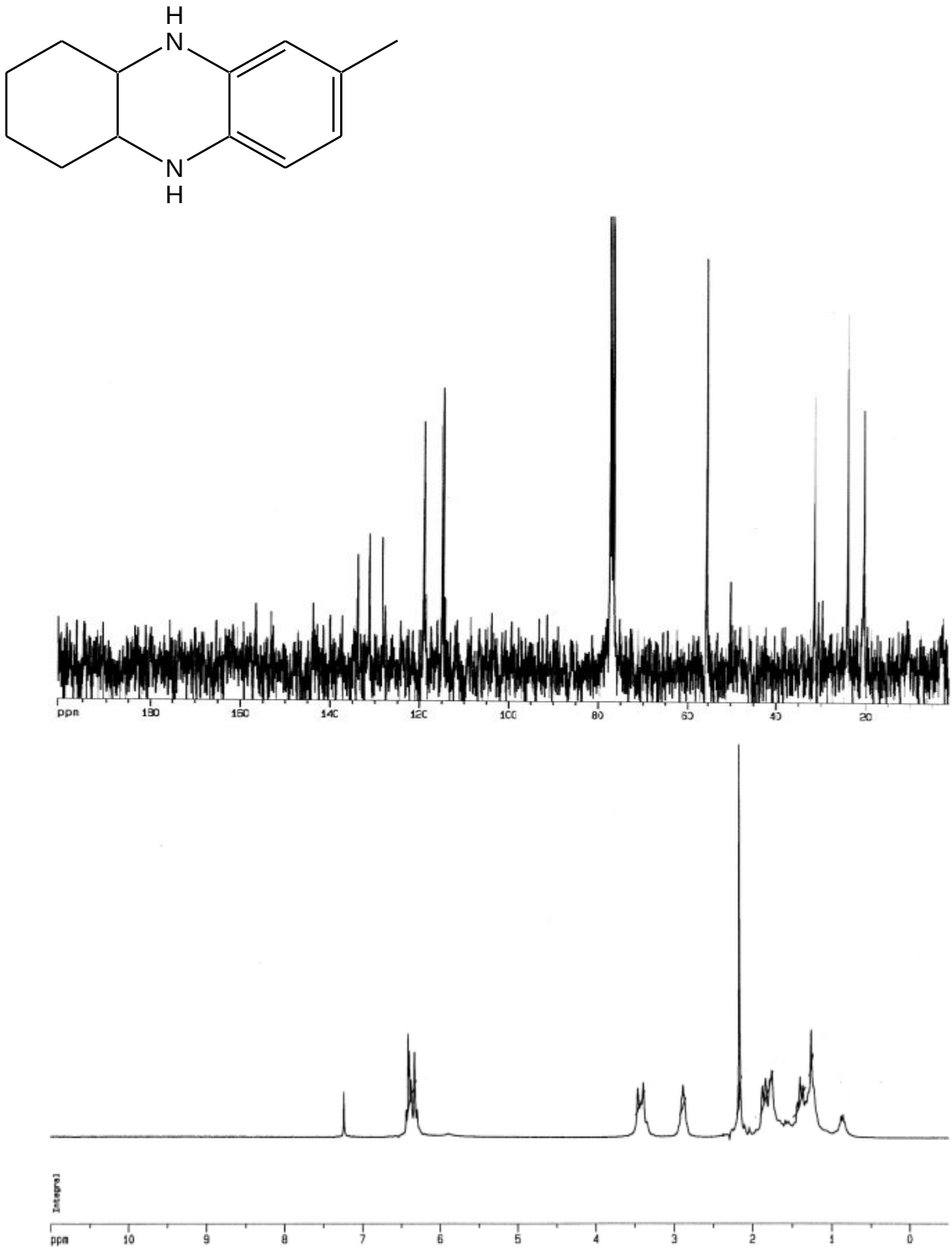


Figure B.9. (Top) ^{13}C NMR of octahydrophenazine **5c** in $CDCl_3$. (Bottom) ^{1}H NMR of octahydrophenazine **5c** in $CDCl_3$.

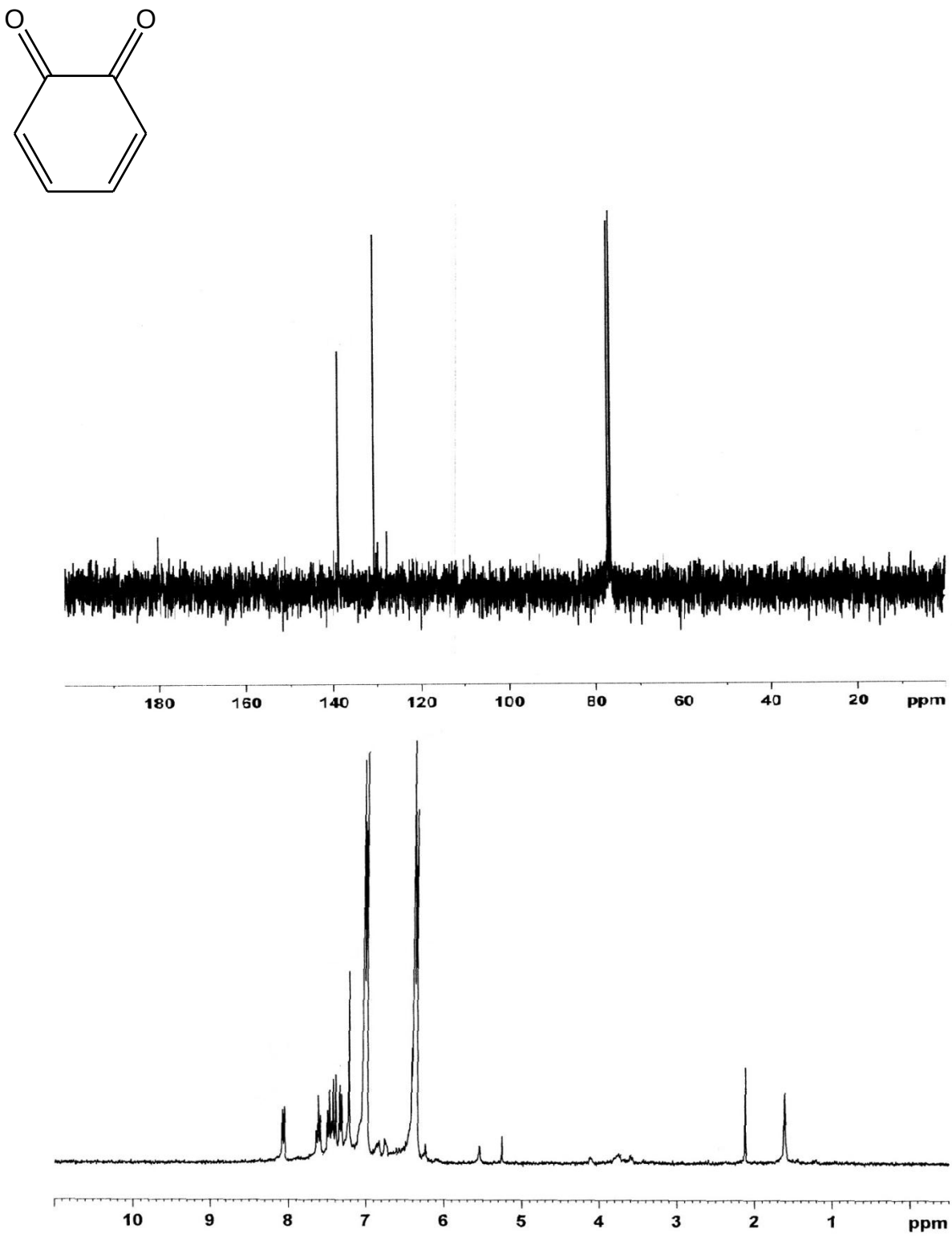


Figure B.10. (Top) ^{13}C NMR of quinone **9a** in in $CDCl_3$. (Bottom) ^{1}H NMR of quinone **9a** in $CDCl_3$.

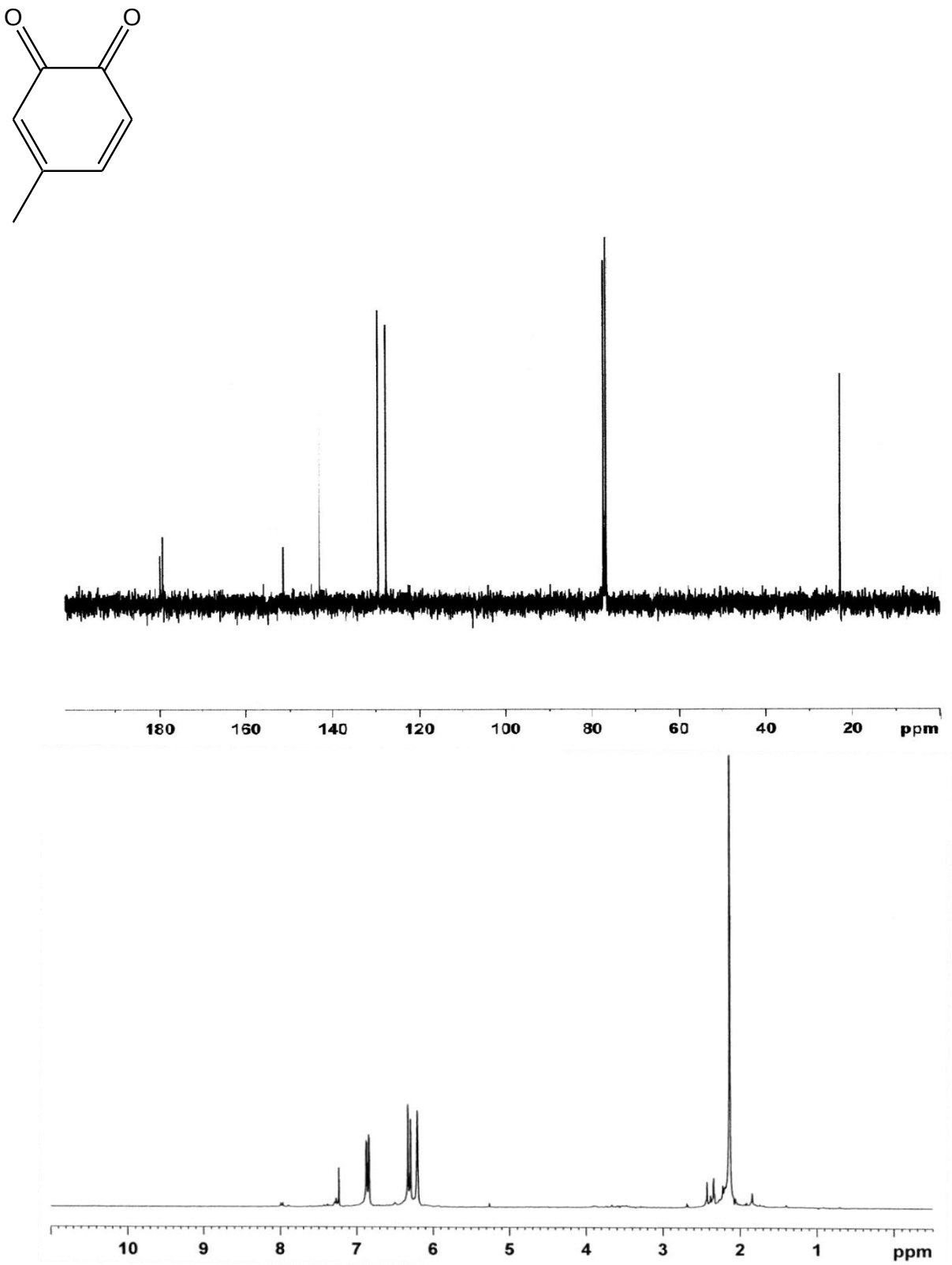


Figure B.11. (Top) ^{13}C NMR of quinone **9b** in $CDCl_3$. Bottom) ^{1}H NMR of quinone **9b** in $CDCl_3$.

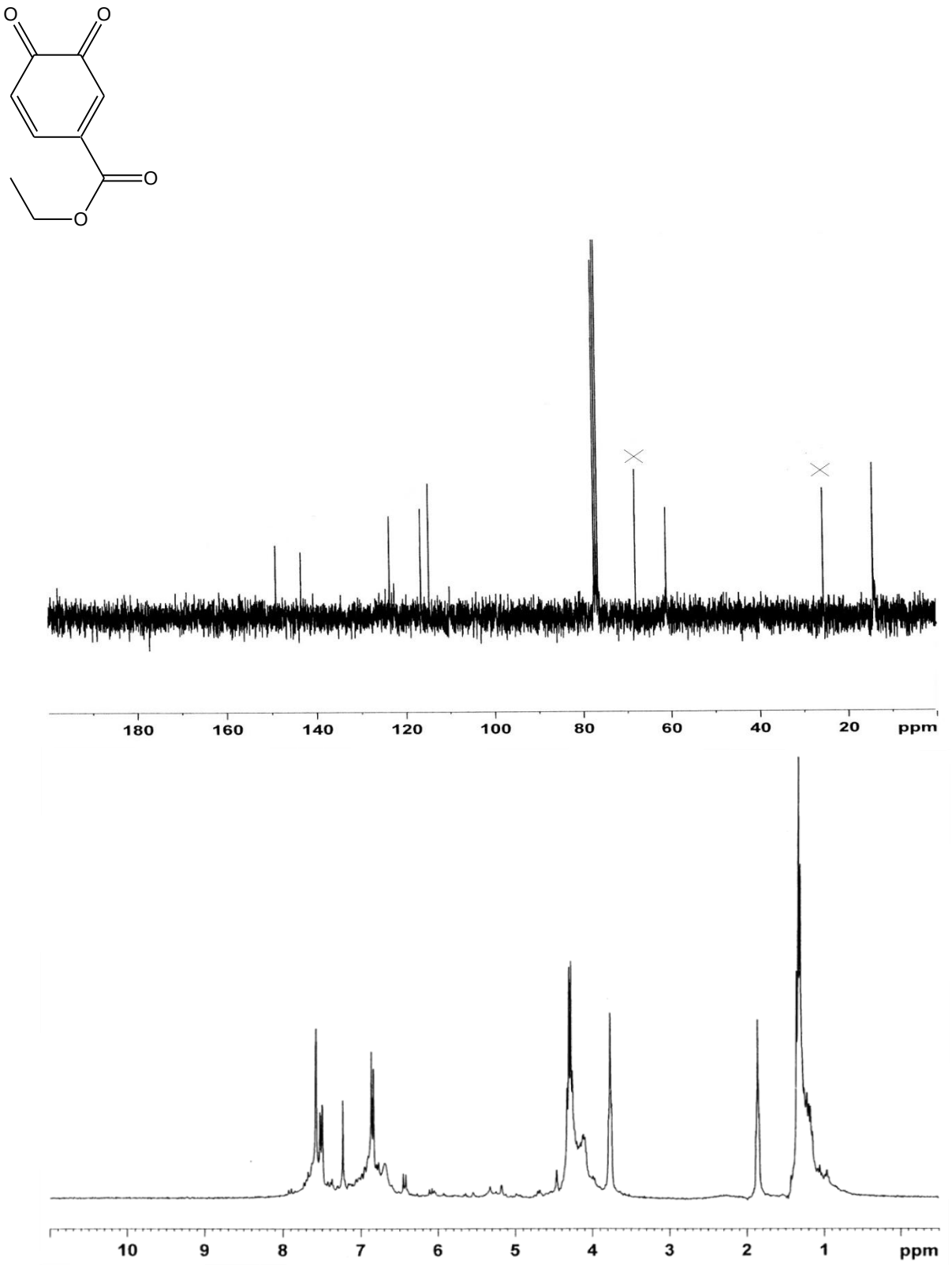


Figure B.12. (Top) ^{13}C NMR of quinone **9c** in $CDCl_3$. (Bottom) ^{1}H NMR of quinone **9c** in $CDCl_3$.

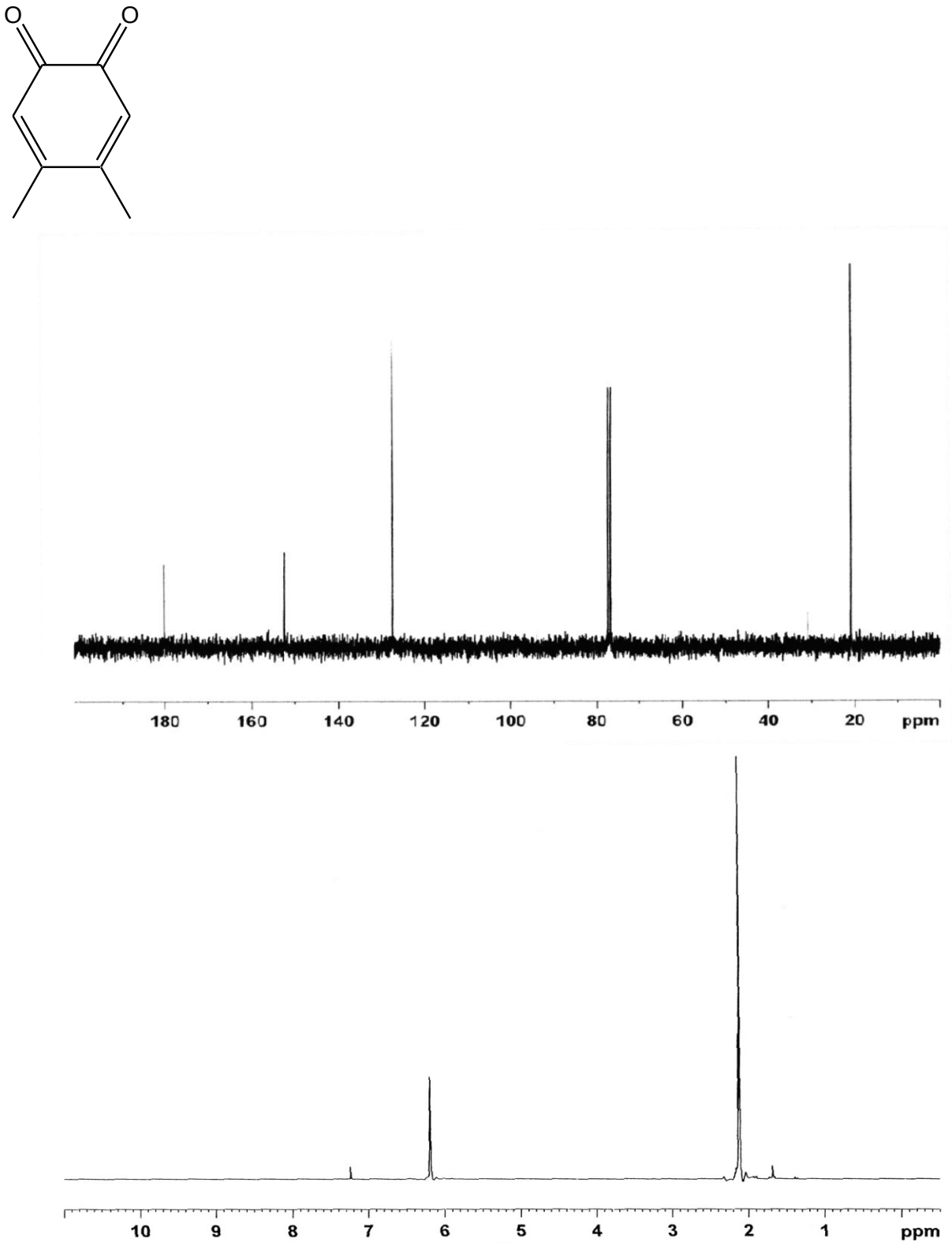


Figure B.13. (Top) ^{13}C NMR of quinone **11** in $CDCl_3$. (Bottom) ^{1}H NMR of quinone **11** in $CDCl_3$.

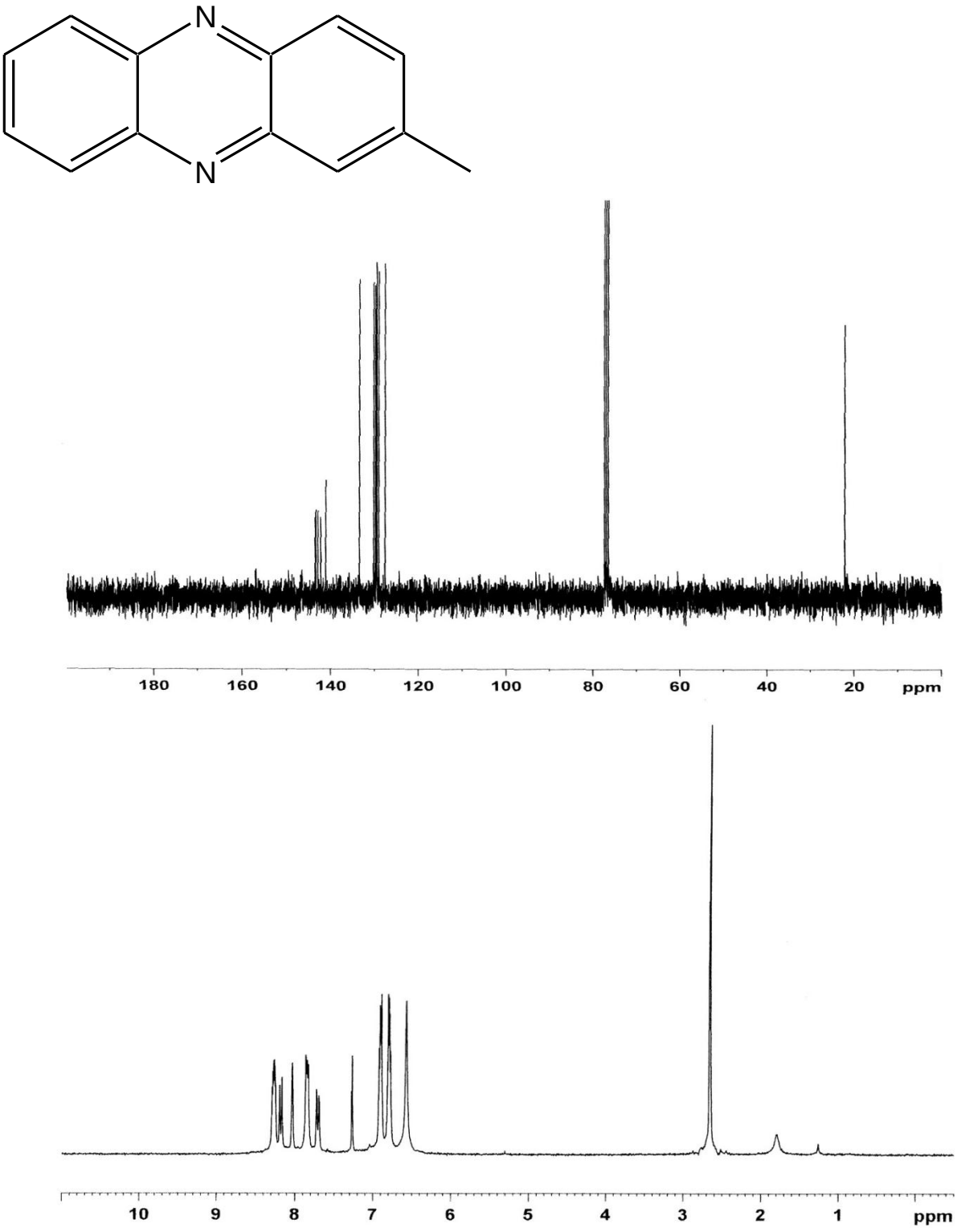


Figure B.14. (Top) ^{13}C NMR of phenazine **12a** in $CDCl_3$. (Bottom) ^{1}H NMR of phenazine **12a** in $CDCl_3$.

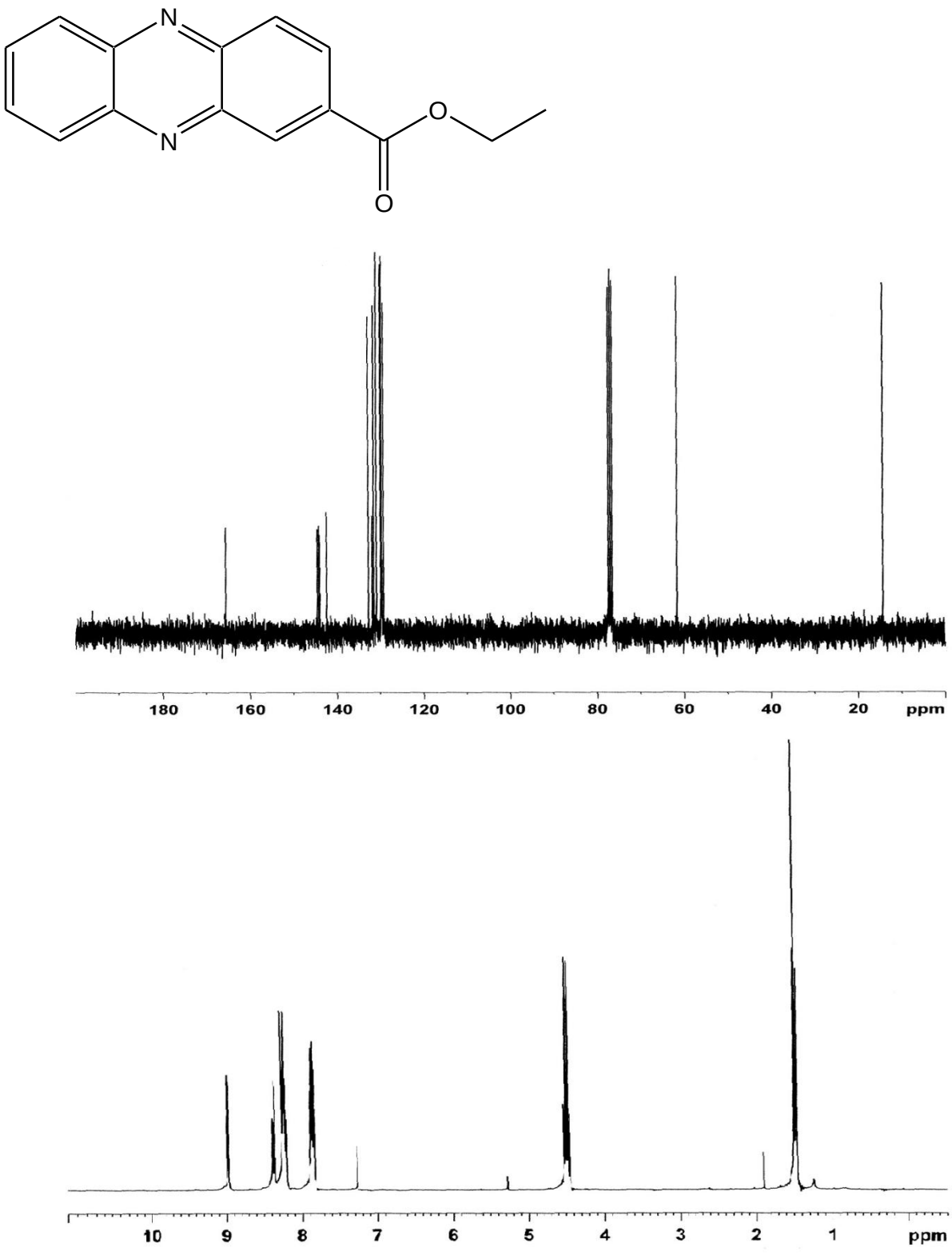


Figure B.15. (Top) ^{13}C NMR of phenazine **12b** in $CDCl_3$. (Bottom) ^{1}H NMR of phenazine **12b** in $CDCl_3$.

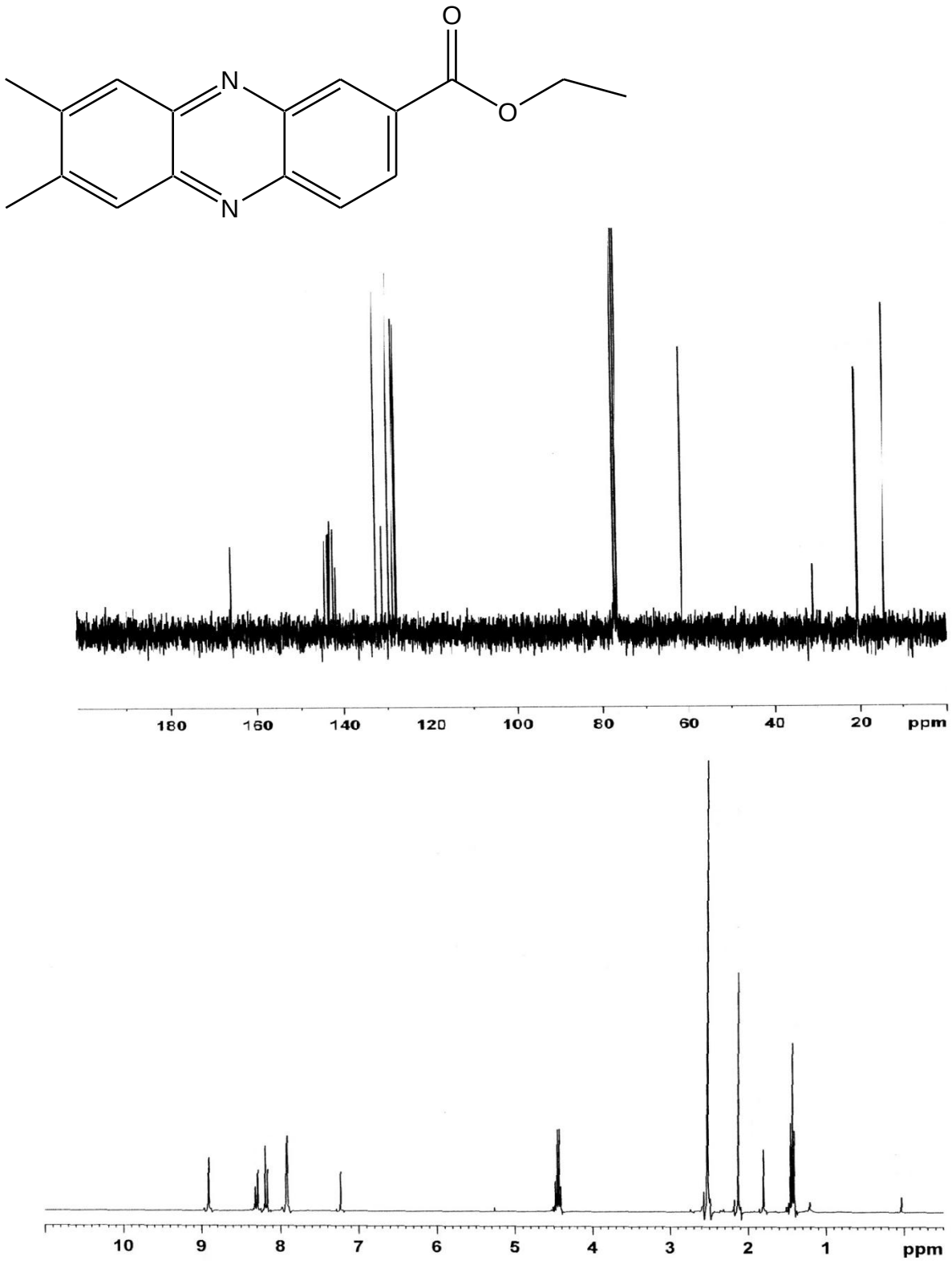


Figure B.16. (Top) ^{13}C NMR of phenazine **13a** in $CDCl_3$. (Bottom) ^{1}H NMR of phenazine **13a** in $CDCl_3$.

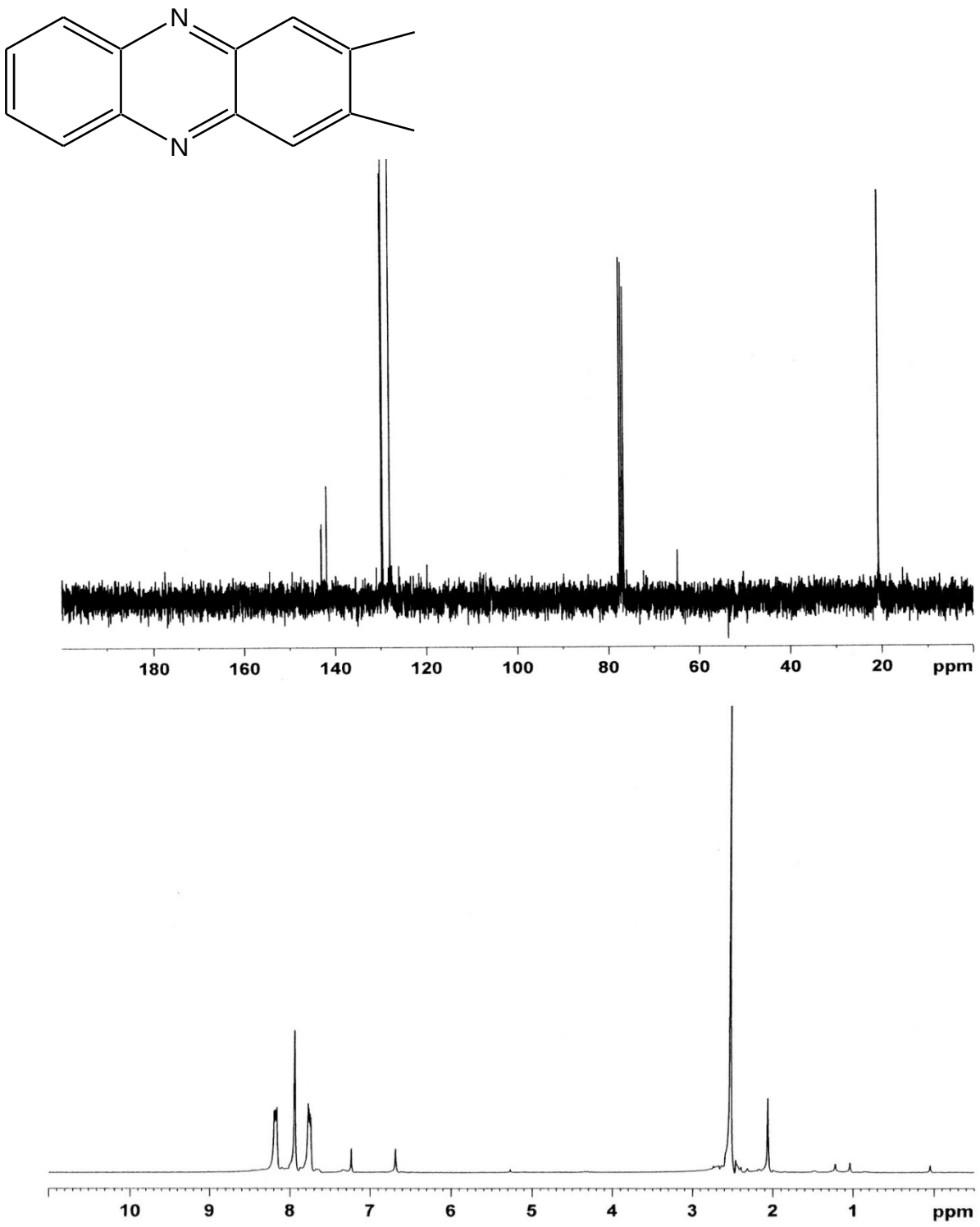


Figure B.17. (Top) ^{13}C NMR of phenazine **13b** in $CDCl_3$. (Bottom) ^{1}H NMR of phenazine **13b** in $CDCl_3$.

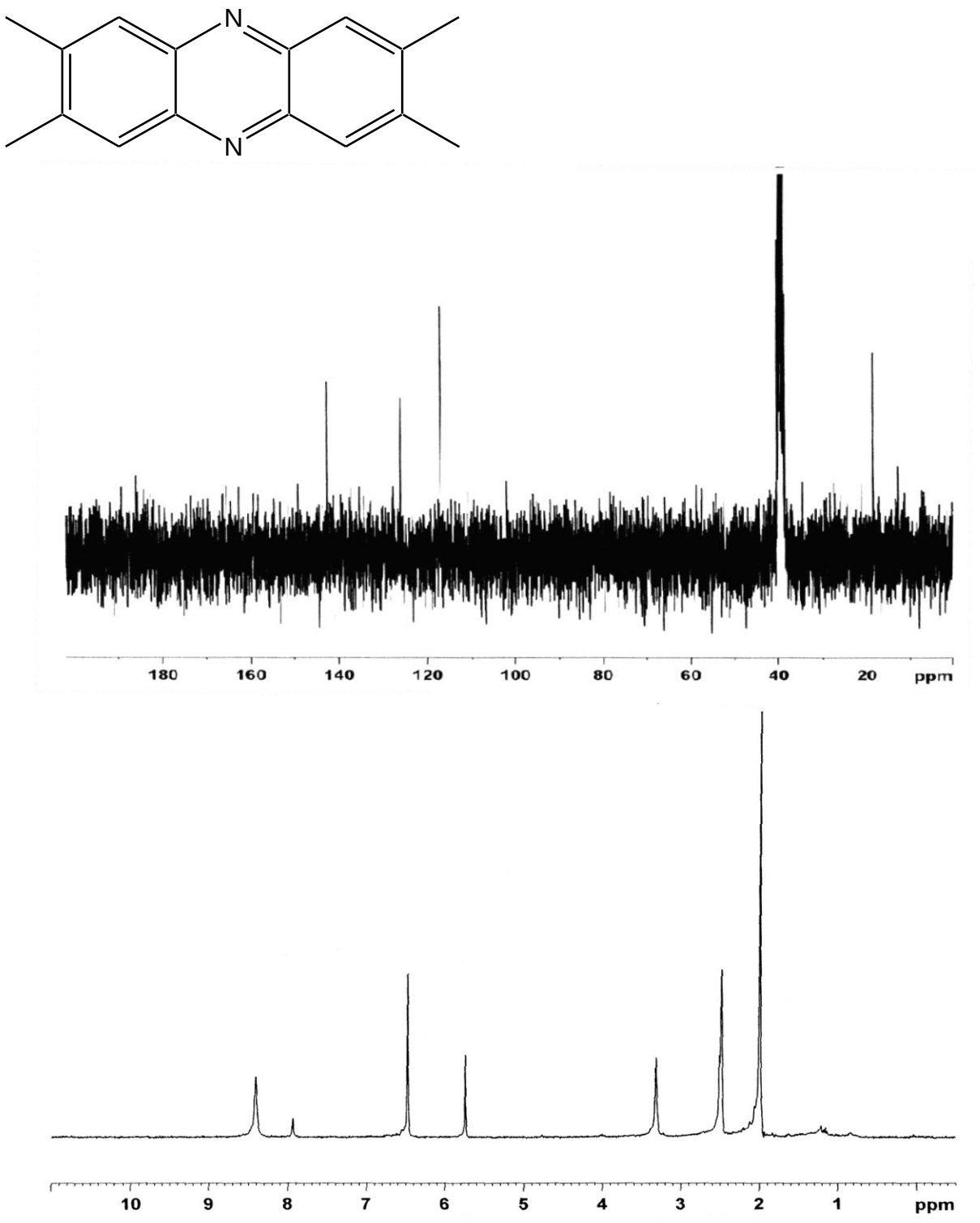


Figure B.18. (Top) ^{13}C NMR of phenazine **13c** in DMSO-d_6. (Bottom) ^{1}H NMR of phenazine **13c** in DMSO-d_6.

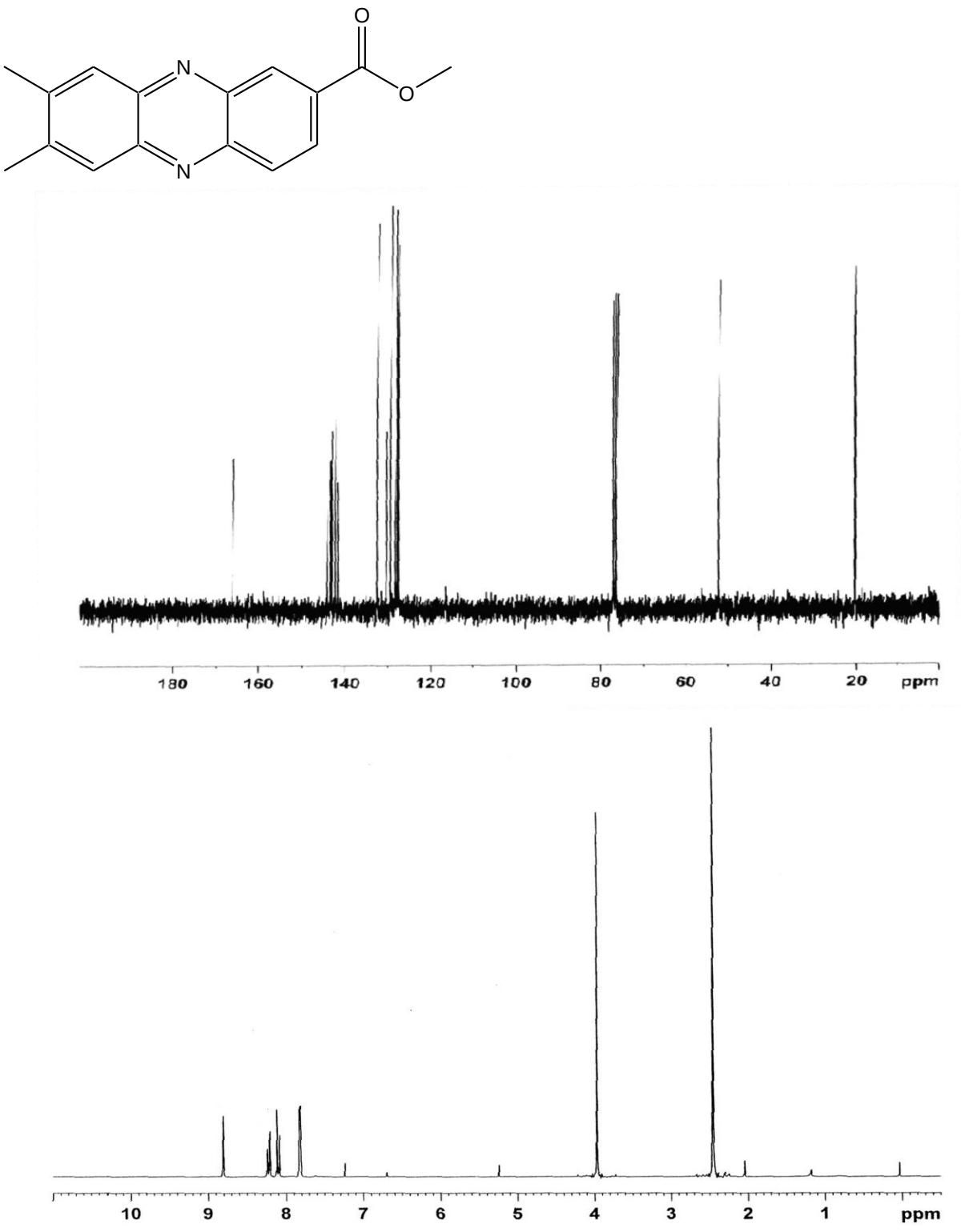


Figure B.19. (Top) ^{13}C NMR of phenazine **13d** in $CDCl_3$. (Bottom) ^{1}H NMR of phenazine **13d** in $CDCl_3$.

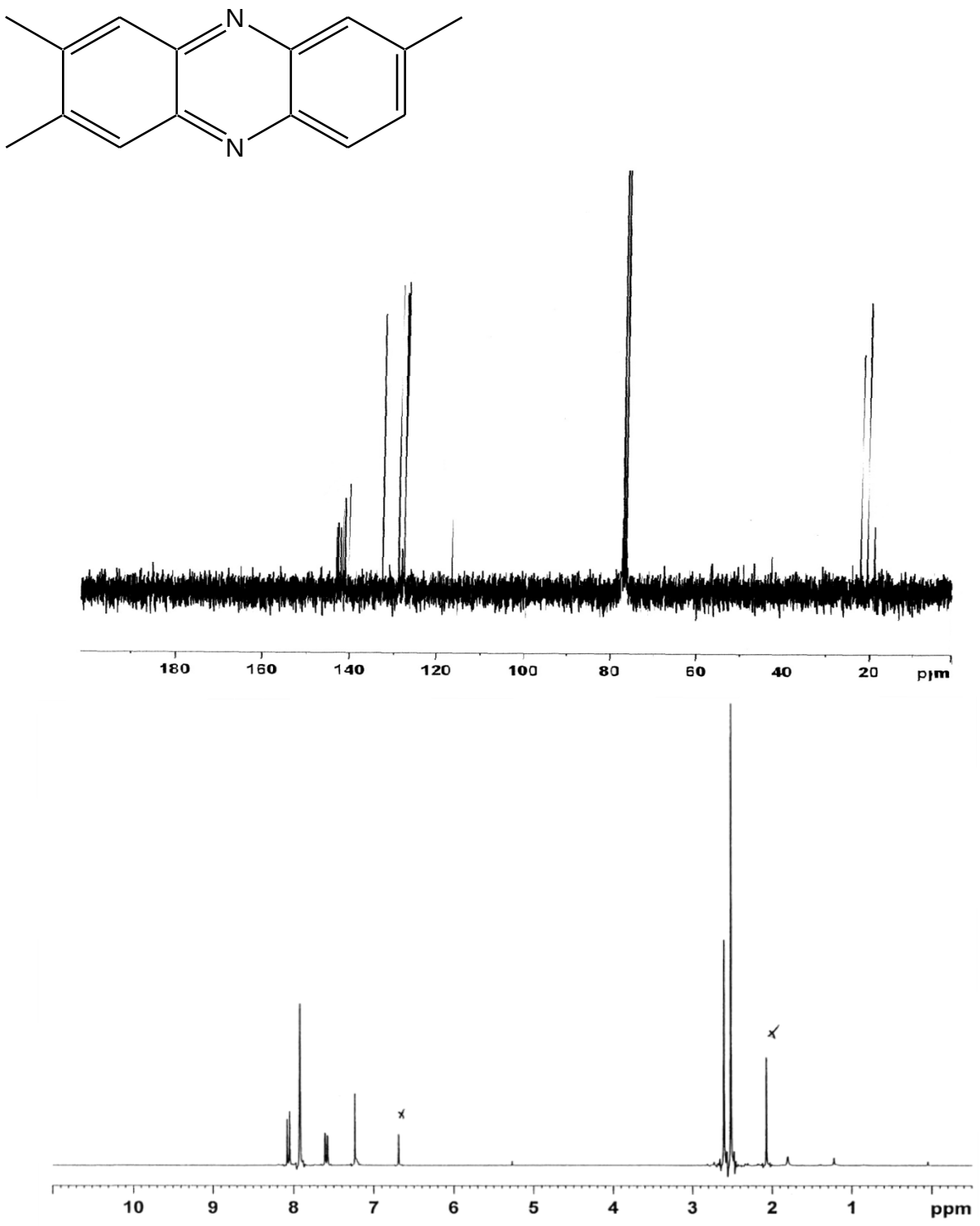


Figure B.20. (Top) ^{13}C NMR of phenazine **13e** in $CDCl_3$. (Bottom) ^{1}H NMR of phenazine **13e** in $CDCl_3$.

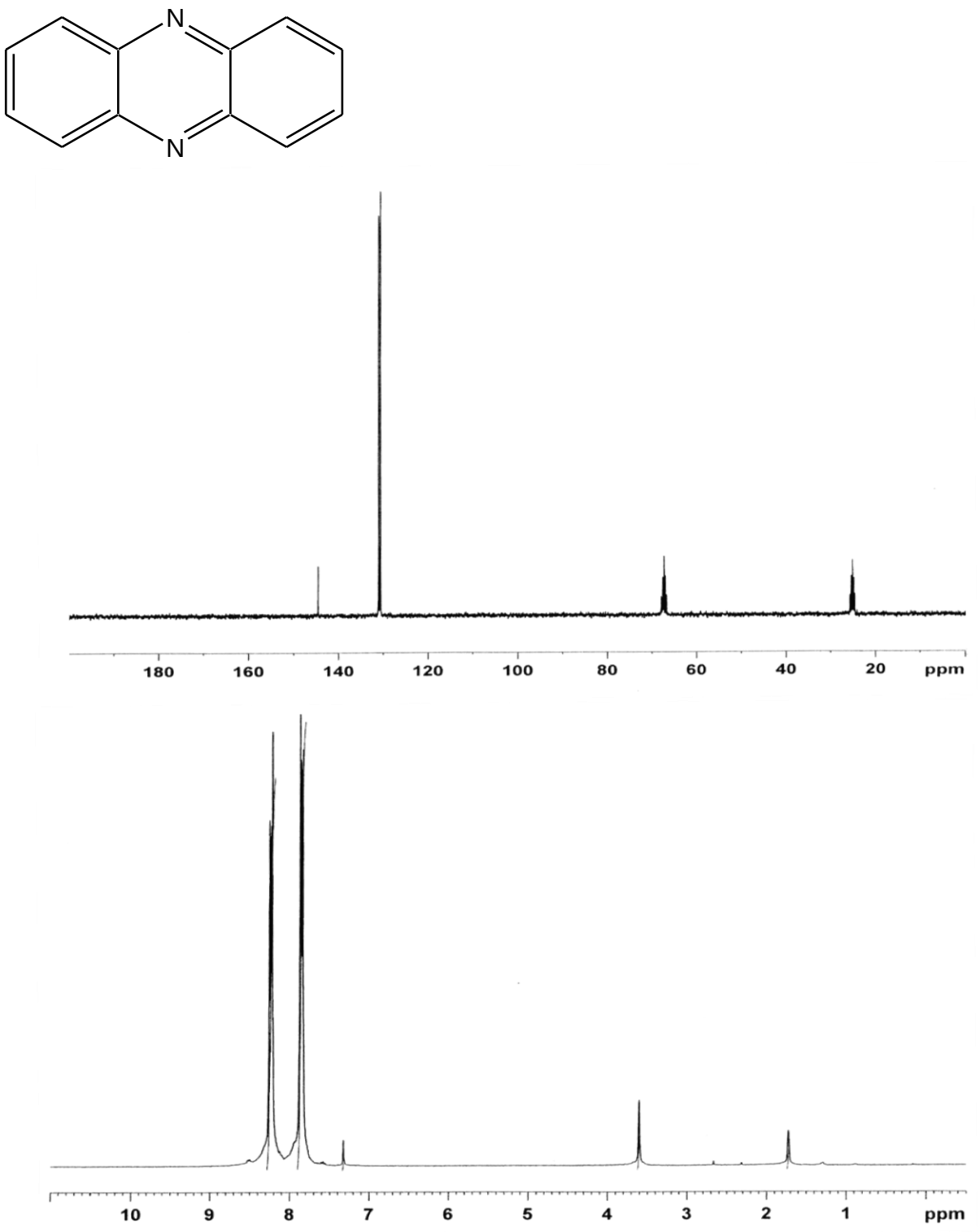


Figure B.21. (Top) ^{13}C NMR of phenazine **14** in THF-d_8. (Bottom) ^{1}H NMR of phenazine **14** in THF-d_8.

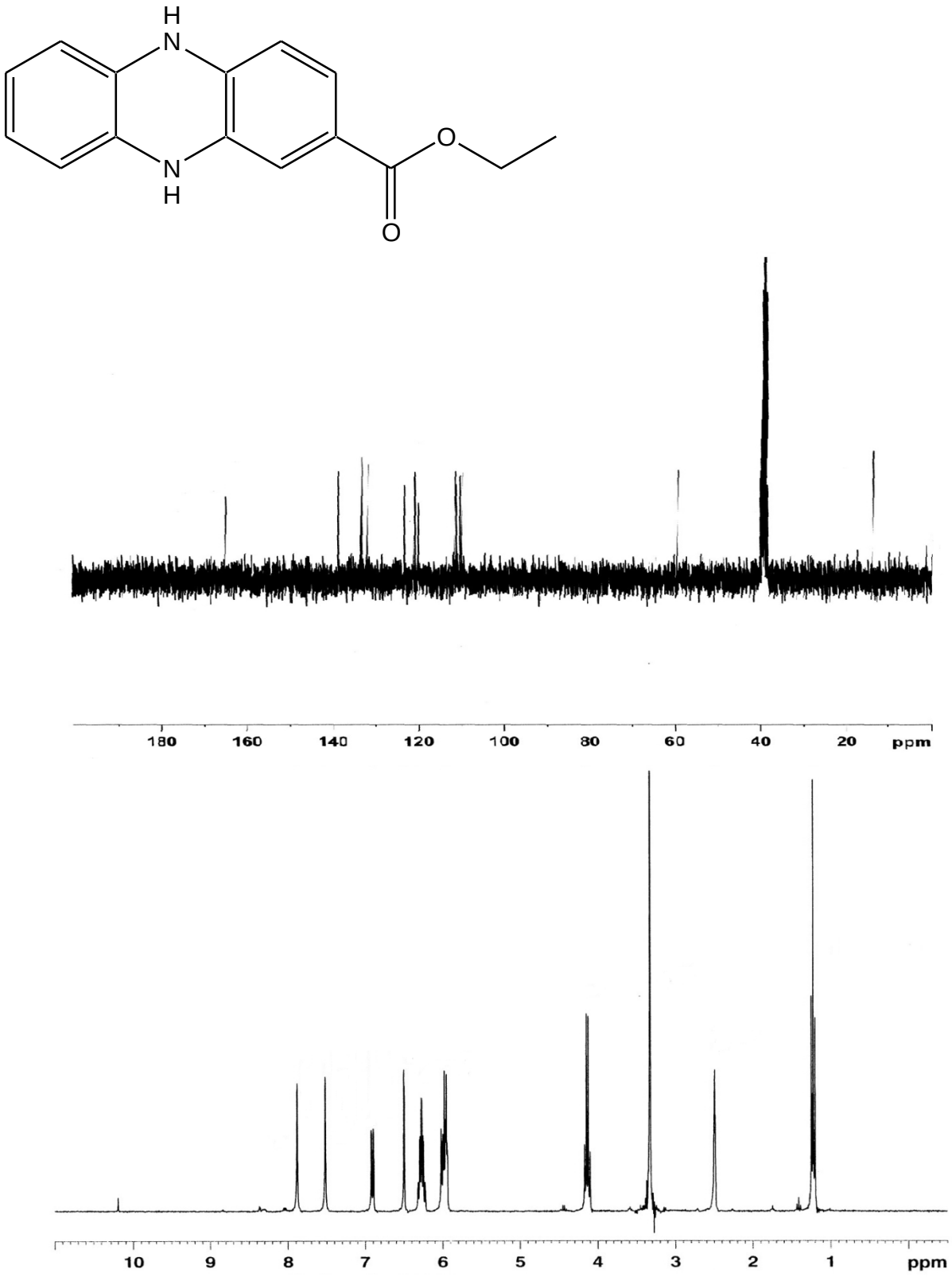


Figure B.22. (Top) ^{13}C NMR of dihydrophenazine **15a** in DMSO-d_6. (Bottom) ^{1}H NMR of dihydrophenazine **15a** in DMSO-d_6.

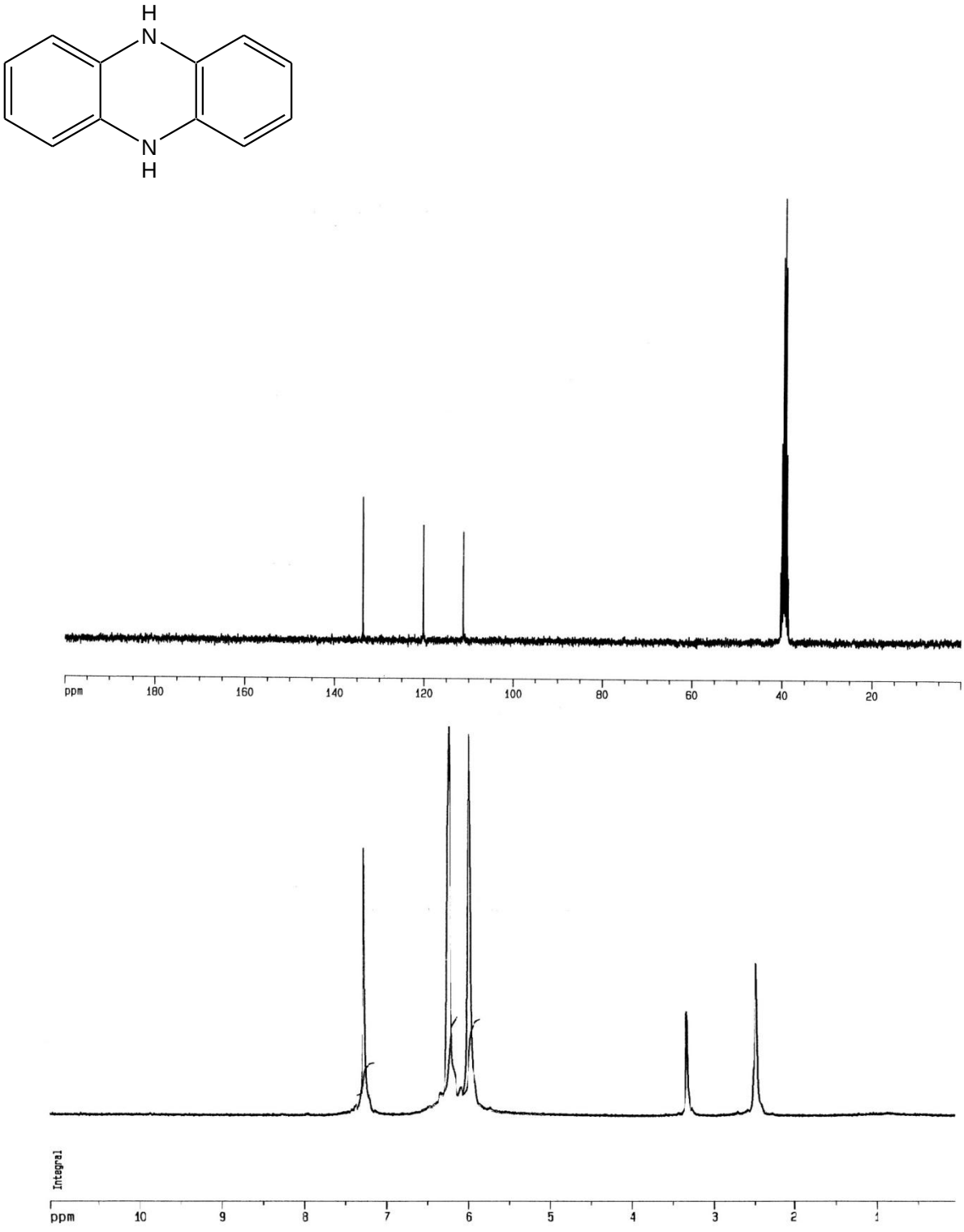


Figure B.23. (Top) ^{13}C NMR of dihydrophenazine **15b** in DMSO-d_6. (Bottom) ^{1}H NMR of dihydrophenazine **15a** in DMSO-d_6.

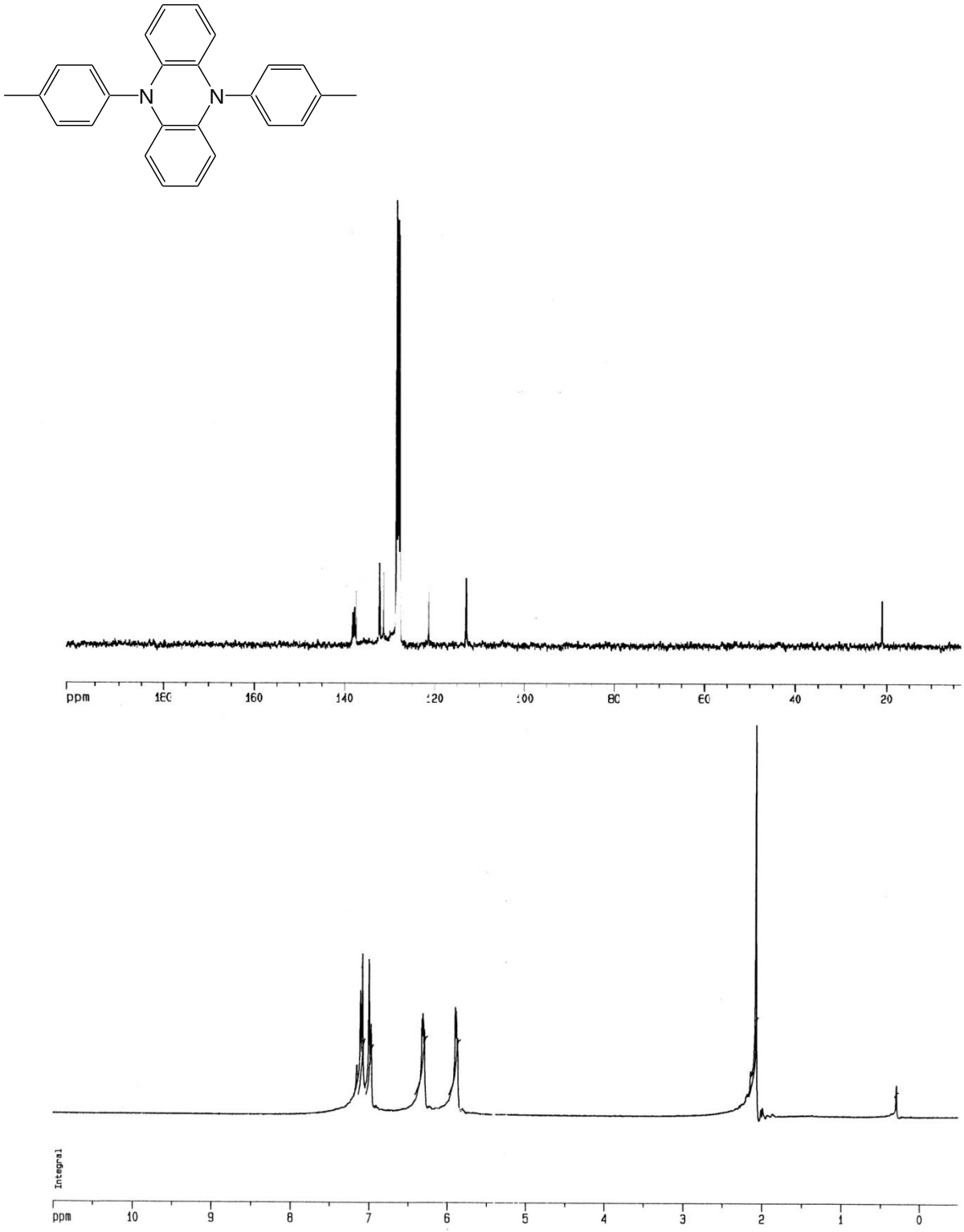


Figure B.24. (Top) ^{13}C NMR of phenazine **16** in C_6D_6. (Bottom) ^{1}H NMR of phenazine **16** in C_6D_6.

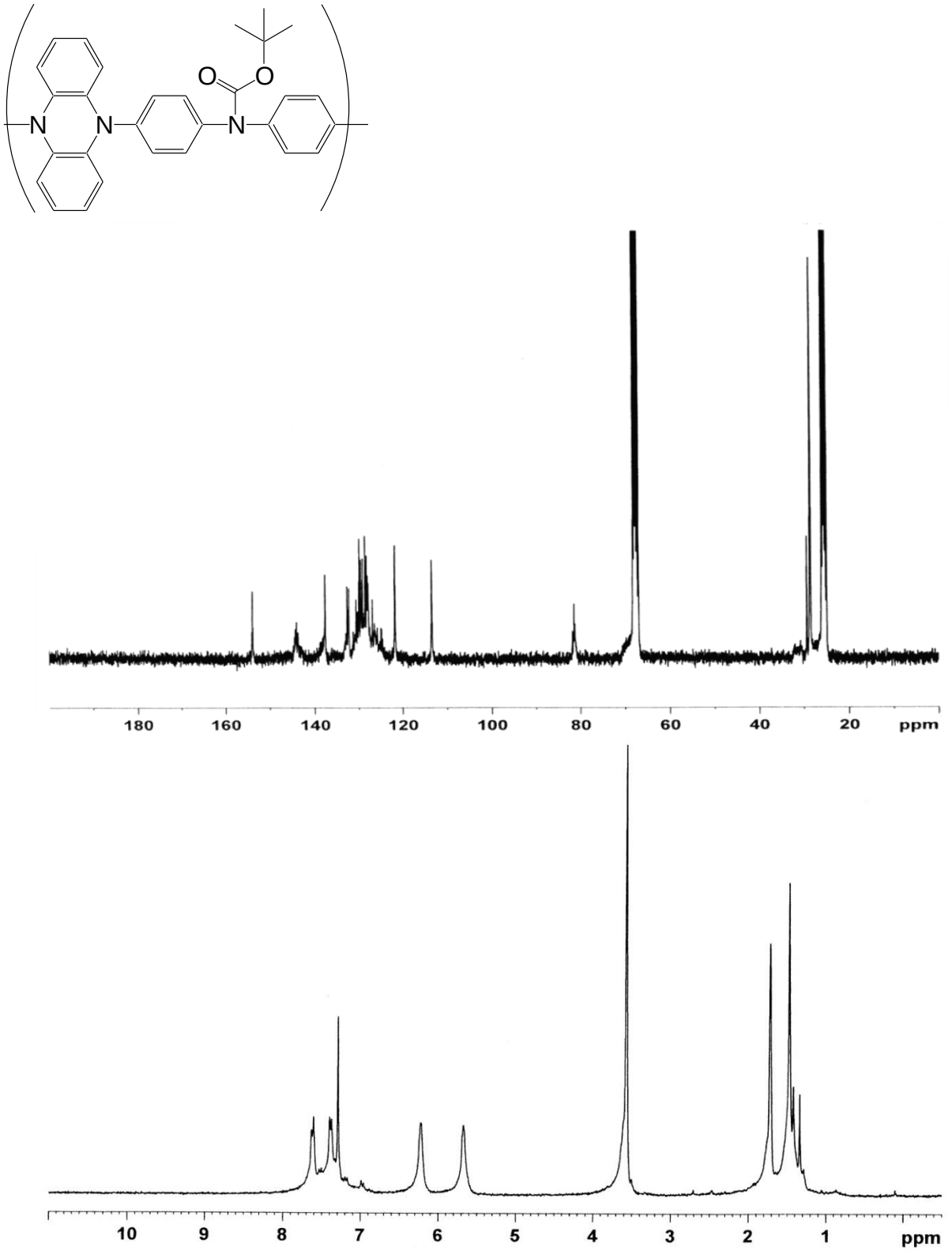


Figure B.25. (Top) ^{13}C NMR of polymer **17** in THF-d_8. (Bottom) ^{1}H NMR of polymer **17** in THF-d_8.

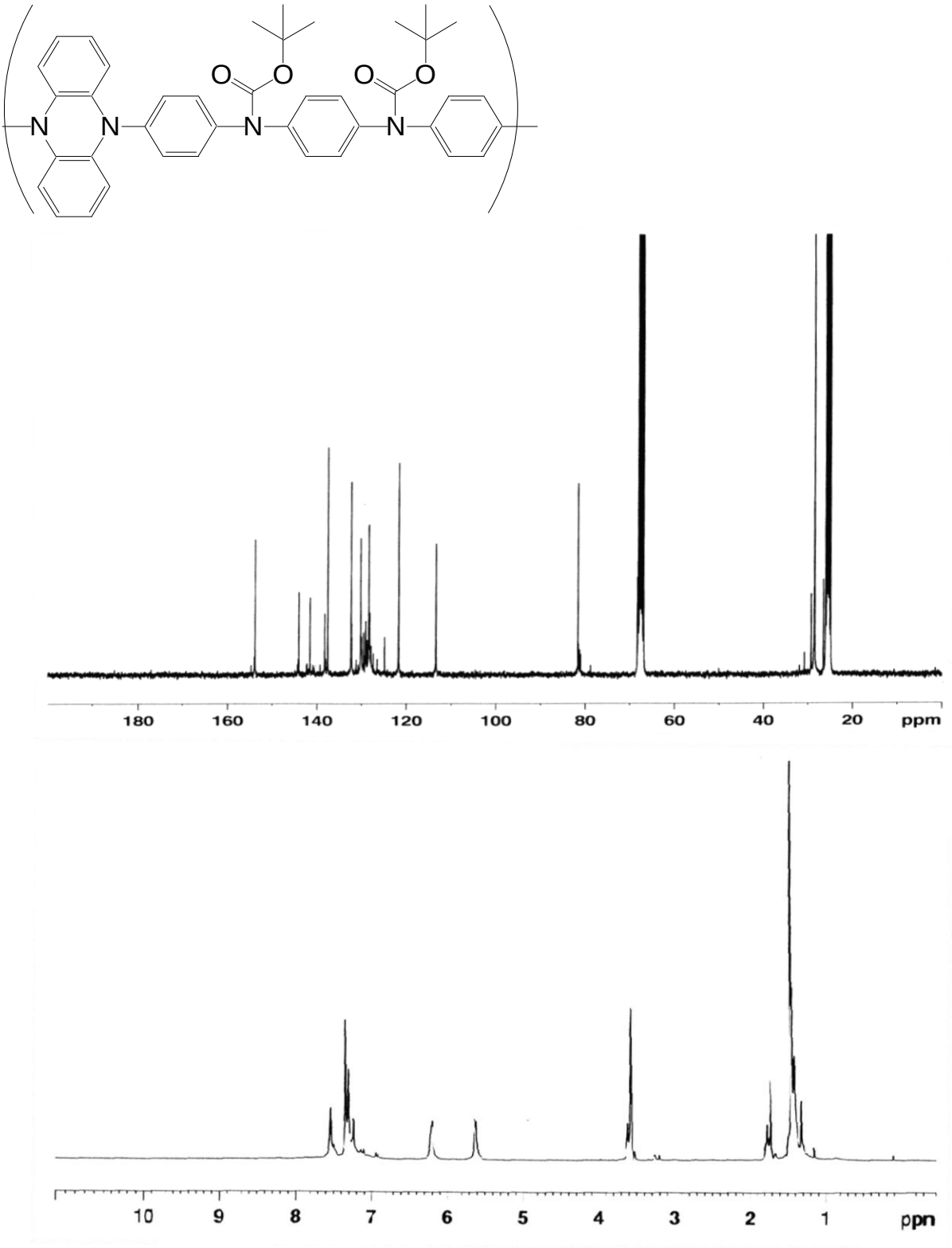


Figure B.26. (Top) ^{13}C NMR of polymer **19** in in THF-d_8. (Bottom) ^{1}H NMR of polymer **17** in THF-d_8.

APPENDIX C: CHAPTER 3

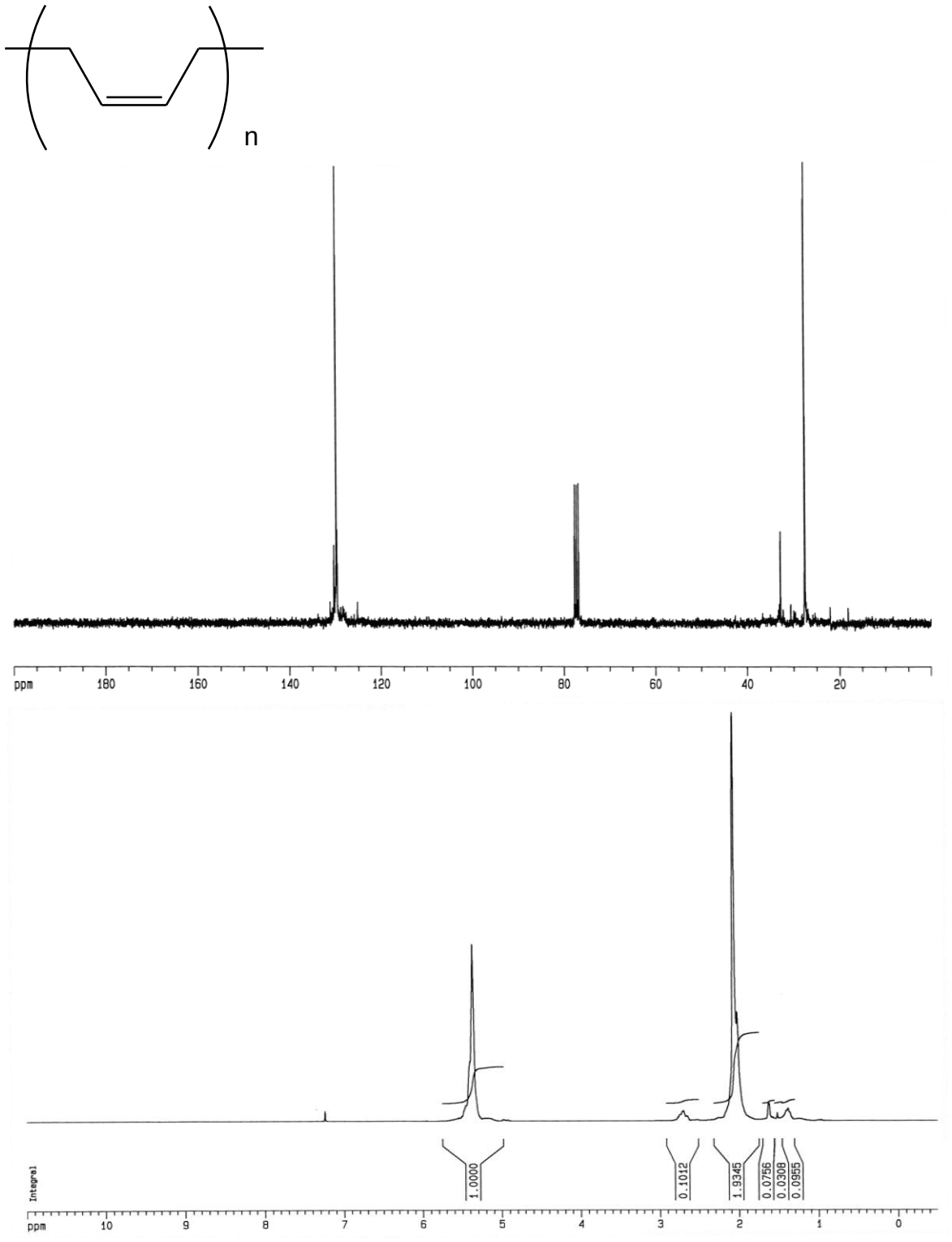


Figure C.1. (Top) ^{13}C NMR of *cis*-1,4-polybutadiene purchased from Aldrich in $CDCl_3$. (Bottom) ^{1}H NMR of 1,4-polybutadiene purchased from Aldrich in $CDCl_3$.

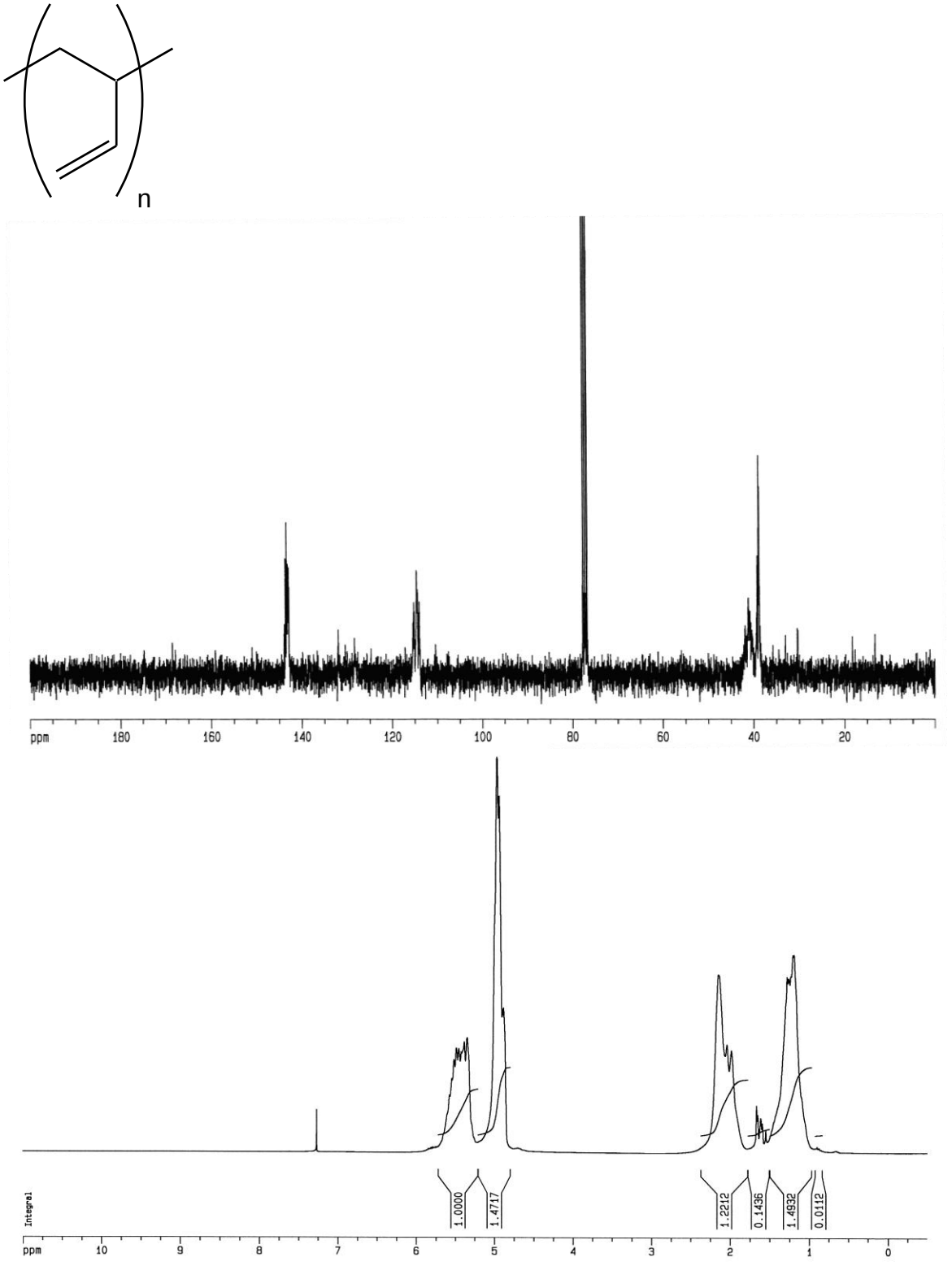


Figure C.2. (Top) ^{13}C NMR of 1,2-polybutadiene purchased from Aldrich in $CDCl_3$. (Bottom) ^{1}H NMR of 1,2-polybutadiene purchased from Aldrich in $CDCl_3$.

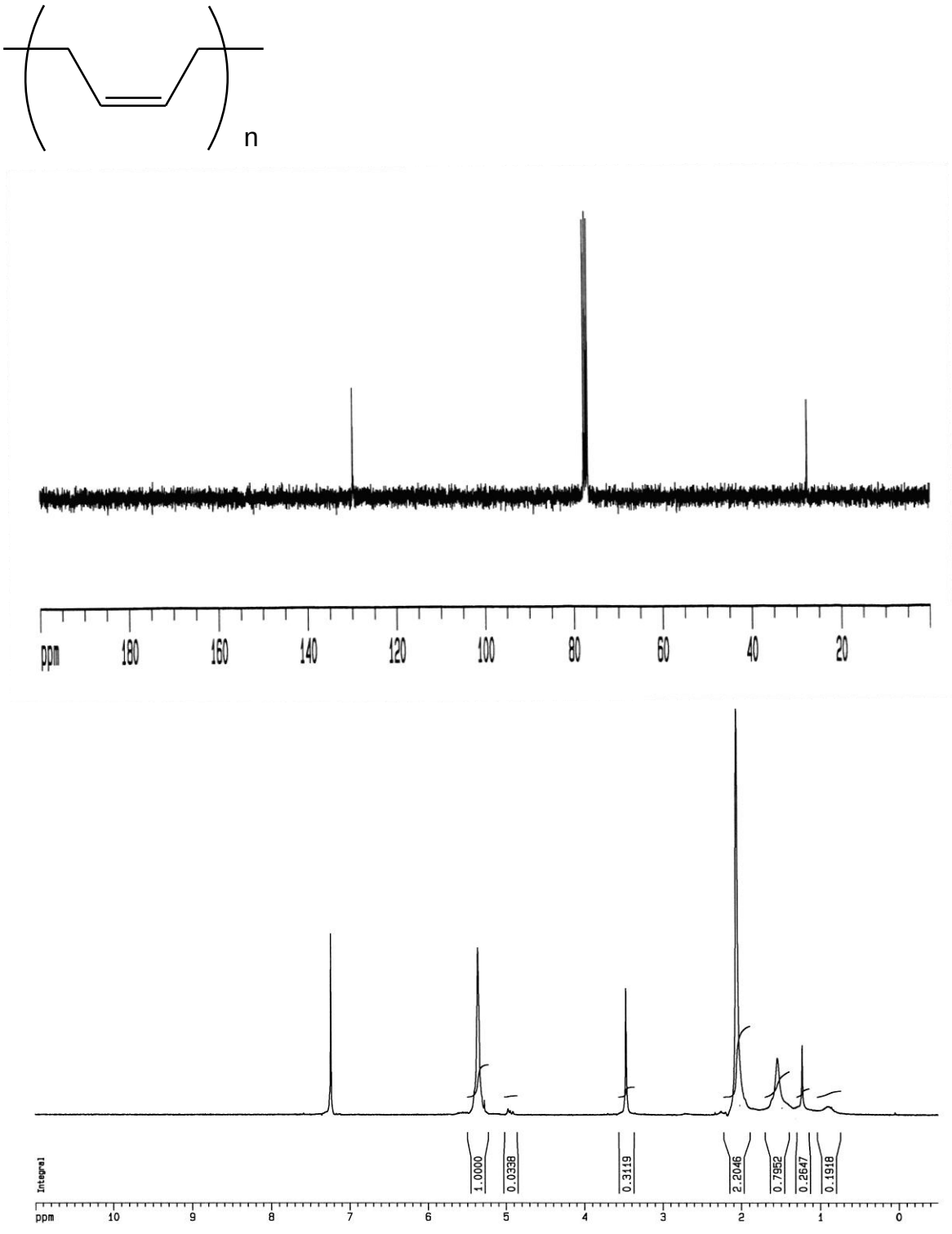


Figure C.3. (Top) ^{13}C NMR of *cis*-1,4-polybutadiene produced from $NiCl_2$ catalyst in $CDCl_3$. (Bottom) ^{1}H NMR of 1,4-polybutadiene produced form $NiCl_2$ catalyst in $CDCl_3$.

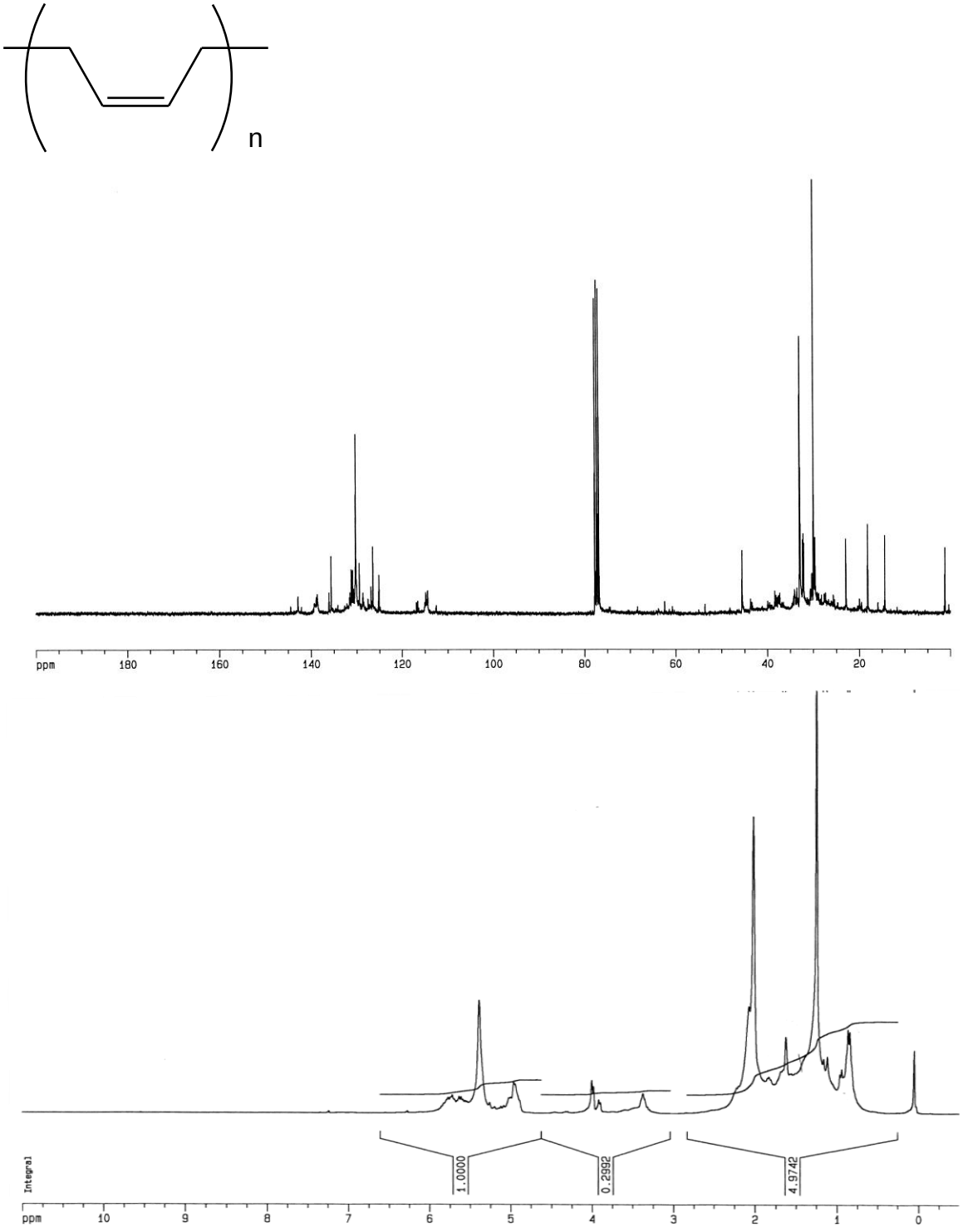


Figure C.4. (Top) ^{13}C NMR of polybutadiene produced by polymerization under Cohen conditions in $CDCl_3$. (Bottom) ^{1}H NMR of polybutadiene produced by polymerization under Cohen conditions in $CDCl_3$.

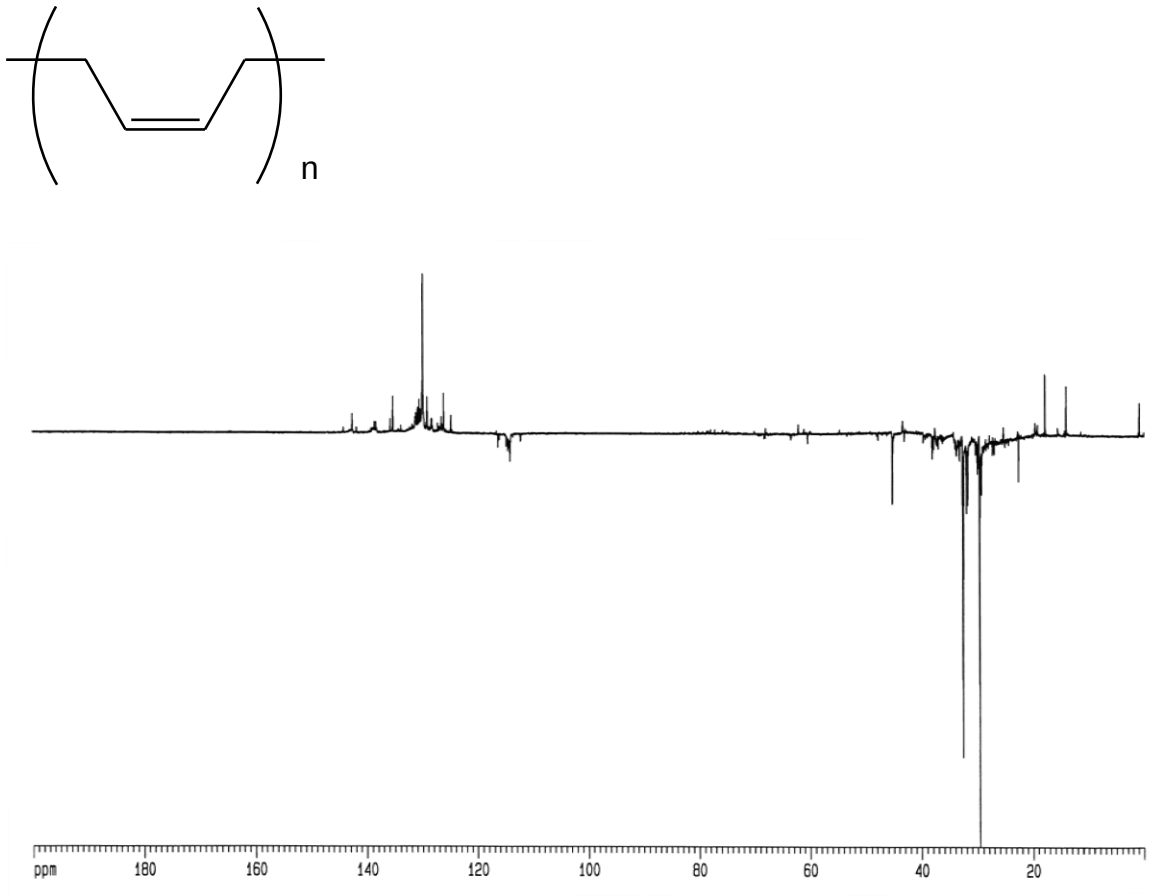


Figure C.5. DEPT 135 ^{13}C NMR of polybutadiene produced by polymerization under Cohen conditions in $CDCl_3$.

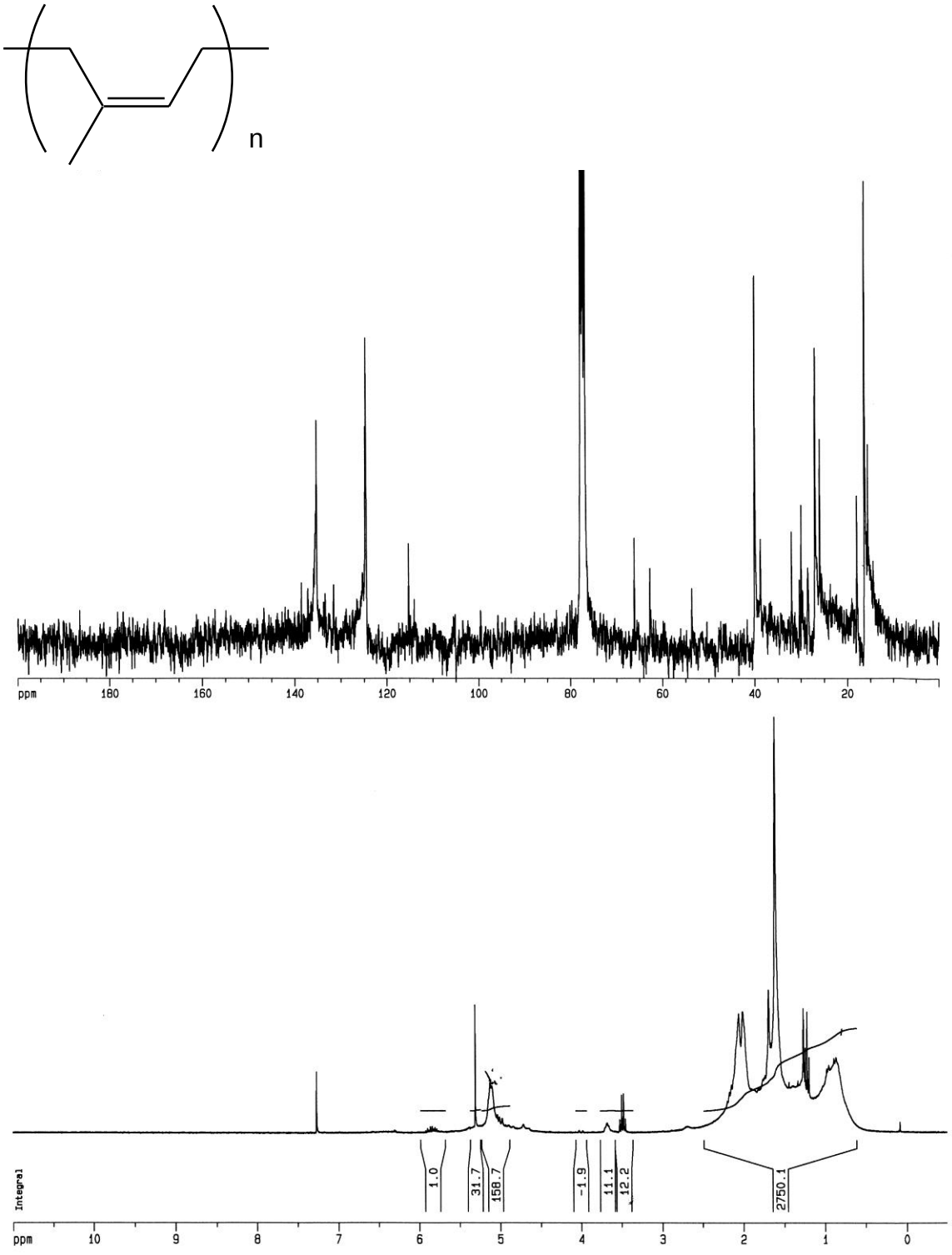


Figure C.6. (Top) ^{13}C NMR of polyisoprene produced by polymerization under Cohen conditions in $CDCl_3$. (Bottom) ^{1}H NMR of polyisoprene produced by polymerization under Cohen conditions in $CDCl_3$.

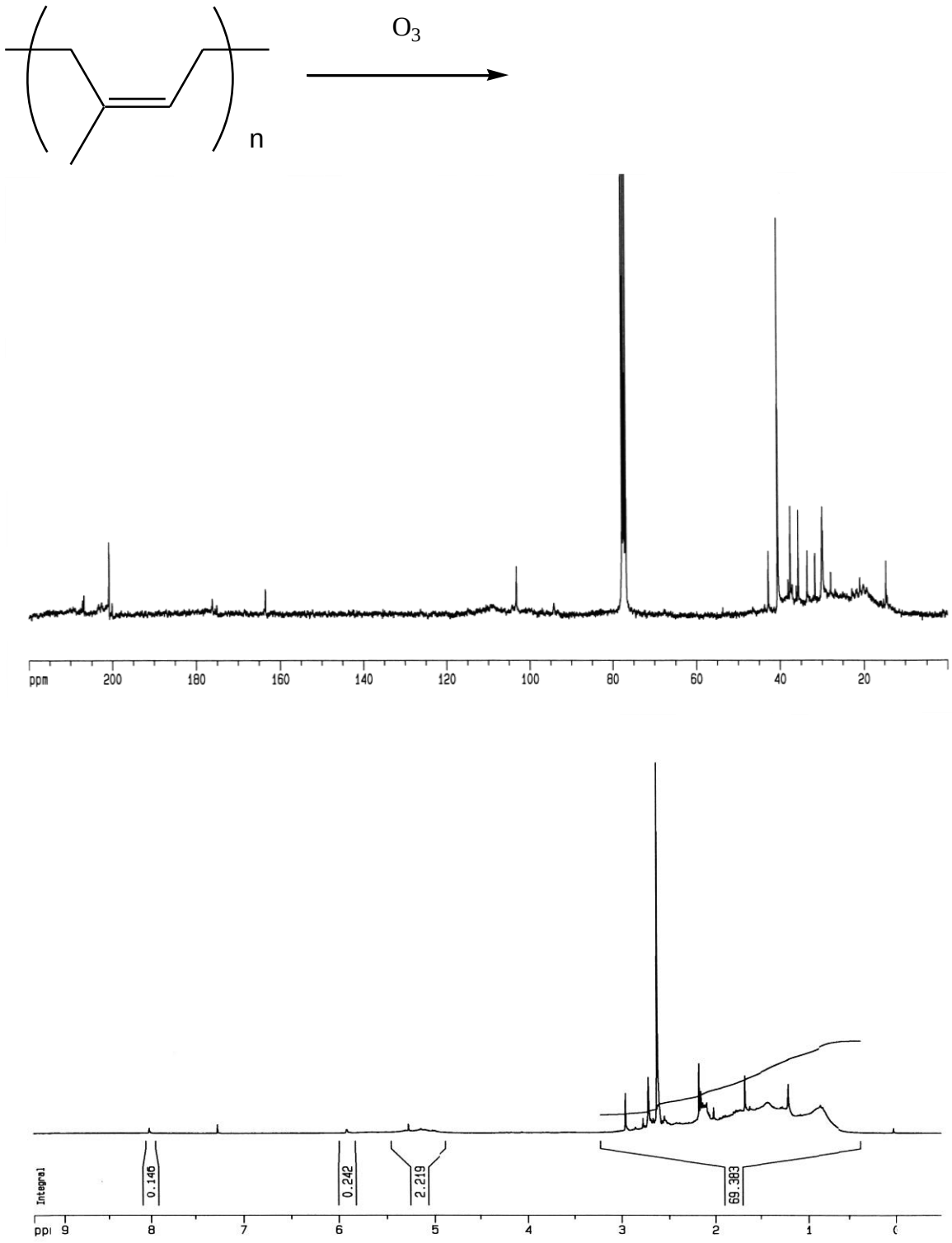


Figure C.7. (Top) ^{13}C NMR of polyisoprene produced by polymerization under Cohen conditions after ozonolysis in $CDCl_3$. (Bottom) ^{1}H NMR of polyisoprene produced by polymerization under Cohen conditions after ozonolysis in $CDCl_3$.

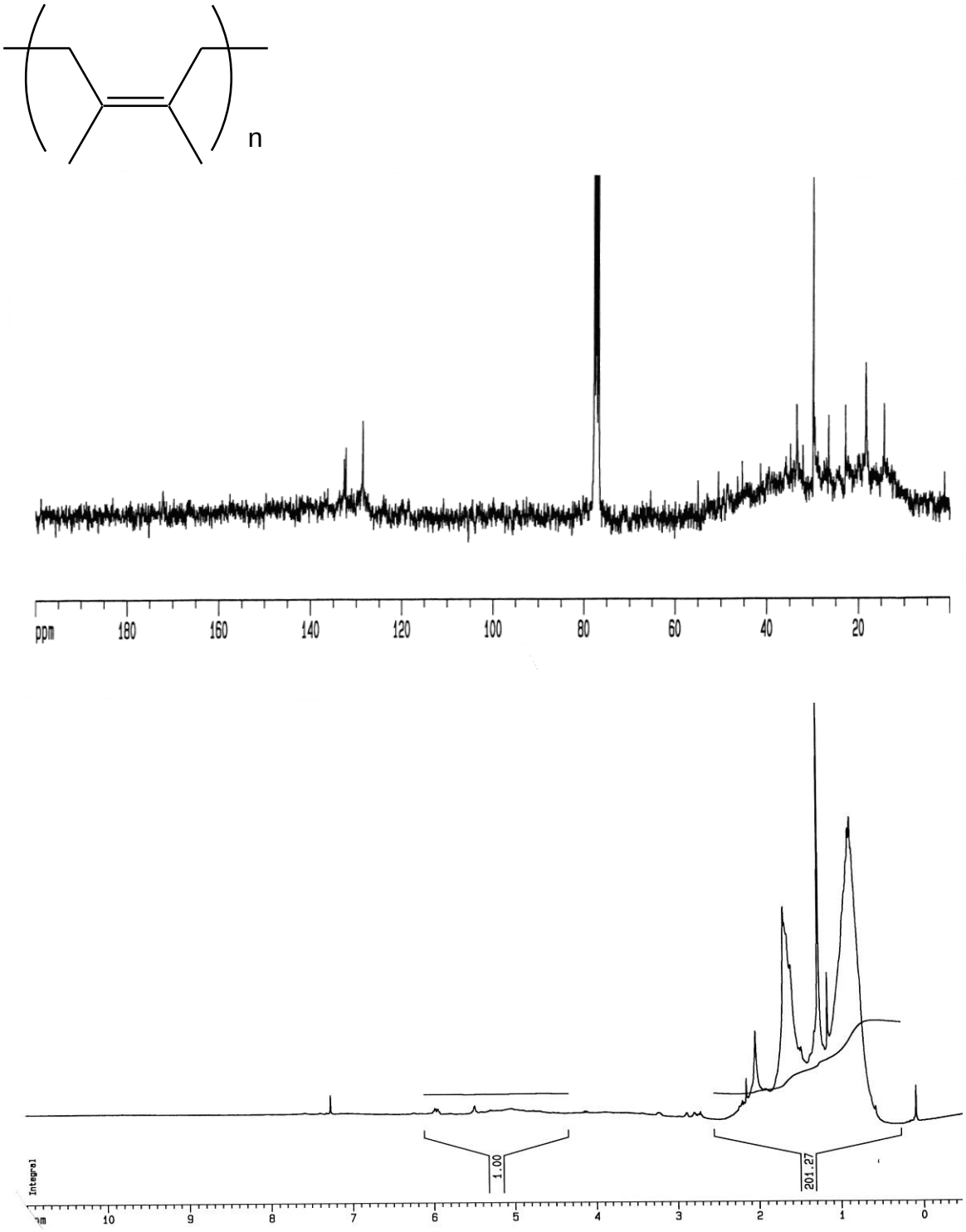


Figure C.8. (Top) ^{13}C NMR of poly(2,3-dimethylbutadiene) produced by polymerization under Cohen conditions in $CDCl_3$. (Bottom) ^{1}H NMR of poly(2,3-dimethyl-butadiene) produced by polymerization under Cohen conditions in $CDCl_3$.

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