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# The Synthesis of 2-Indenylphenols: Potential Ligands For Transition Metals

Yoon Jae Kim

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**The Synthesis of 2-Indenylphenols :**

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**Potential Ligands For Transition Metals**

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(TITLE)

BY

**Yoon Jae Kim**

1974-

**THESIS**

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF

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**Master of Science**

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IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY  
CHARLESTON, ILLINOIS

**2001**

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**The Synthesis of 2-Indenylphenol :**  
**Potential Ligands For Transition Metals**

**Yoon Jae Kim**

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**June 8, 2001**

# Table of Contents

Abstract.....	i
Acknowledgements.....	ii
List of Tables.....	iii
List of Figures.....	iv
Chapter 1. Introduction.....	1
Chapter 2. Results and Discussion.....	11
Chapter 3. Conclusions.....	18
Chapter 4. Future Research.....	19
Chapter 5. Experimental Section.....	21
References.....	27
Figures.....	29

## Abstract

The syntheses of 2-(2-indenyl)-phenol and 2-(1-indenyl)-phenol via a three-step sequence have been developed. In the first steps of the sequence, a Grignard reagent formed from 2-iodoanisole or 2-bromoanisole reacted with 1-indanone or 2-indanone in yields that ranged from 11.3% to 67.2%. The second step consisted of acid-catalyzed dehydration of the alcohol formed in step 1 to make a 2-inenyl anisole; yields in the second step were 45.2% to nearly quantitative. Finally, demethylation of the 2-indenyl anisole was achieved with  $\text{AlBr}_3$  in ethanethiol in yields ranging from 52.9% to 0 %. Each product was characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR. The three products in the series leading to 2-(2-indenyl) phenol were also characterized by elemental analysis. Only the 2-(2-hydroxy-2-indenyl) anisole product was pure.

## Acknowledgements

I would like to thank my advisor, Dr. Robert W. Chesnut, for his help and suggestions during this study. I also want to thank Dr. T. Howard Black, Dr. Richard L. Keiter, and Dr. Mark E. McGuire for serving as committee members.

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Finally, I cannot forget to say my thanks to my family and fiancé in my country and my friends here for all of the personal support for me.



# List of Tables

	Page
Table 1. Synthesis of 2-(2-indenyl) anisole in two steps .....	12
Table 2. Synthesis of 2-(2-indenyl) anisole in one step .....	13
Table 3. Demethylation of 2-(2-indanyl) anisole with various reagents.....	13
Table 4. Synthesis of 2-(1-indenyl) anisole in two steps .....	15
Table 5. Synthesis of 2-(1-indenyl) anisole in one step .....	16

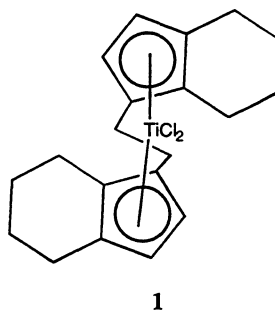
# List of Figures

	Page
Figure 1. $^1\text{H}$ NMR Spectrum of 2-(2-hydroxy-2-indanyl) anisole ( <b>18</b> ).....	29
Figure 2. $^{13}\text{C}$ NMR Spectrum of 2-(2-hydroxy-2-indanyl) anisole ( <b>18</b> ).....	30
Figure 3. $^1\text{H}$ NMR Spectrum of 2-(2-indenyl) anisole ( <b>19</b> ).....	31
Figure 4. $^{13}\text{C}$ NMR Spectrum of 2-(2-indenyl) anisole ( <b>19</b> ).....	32
Figure 5. $^1\text{H}$ NMR Spectrum of 2-(2-indenyl) phenol ( <b>15</b> ).....	33
Figure 6. $^{13}\text{C}$ NMR Spectrum of 2-(2-indenyl) phenol ( <b>15</b> ).....	34
Figure 7. $^1\text{H}$ NMR Spectrum of 2-(1-hydroxy-1-indanyl) anisole ( <b>20</b> ).....	35
Figure 8. $^{13}\text{C}$ NMR Spectrum of 2-(1-hydroxy-1-indanyl) anisole ( <b>20</b> ).....	36
Figure 9. $^1\text{H}$ NMR Spectrum of 2-(1-indenyl) anisole ( <b>21</b> ).....	37
Figure 10. $^{13}\text{C}$ NMR Spectrum of 2-(1-indenyl) anisole ( <b>21</b> ).....	38
Figure 11. $^1\text{H}$ NMR Spectrum of 2-(1-indenyl) phenol ( <b>16</b> ).....	39
Figure 12. $^{13}\text{C}$ NMR Spectrum of 2-(1-indenyl) phenol ( <b>16</b> ).....	40

# Chapter I

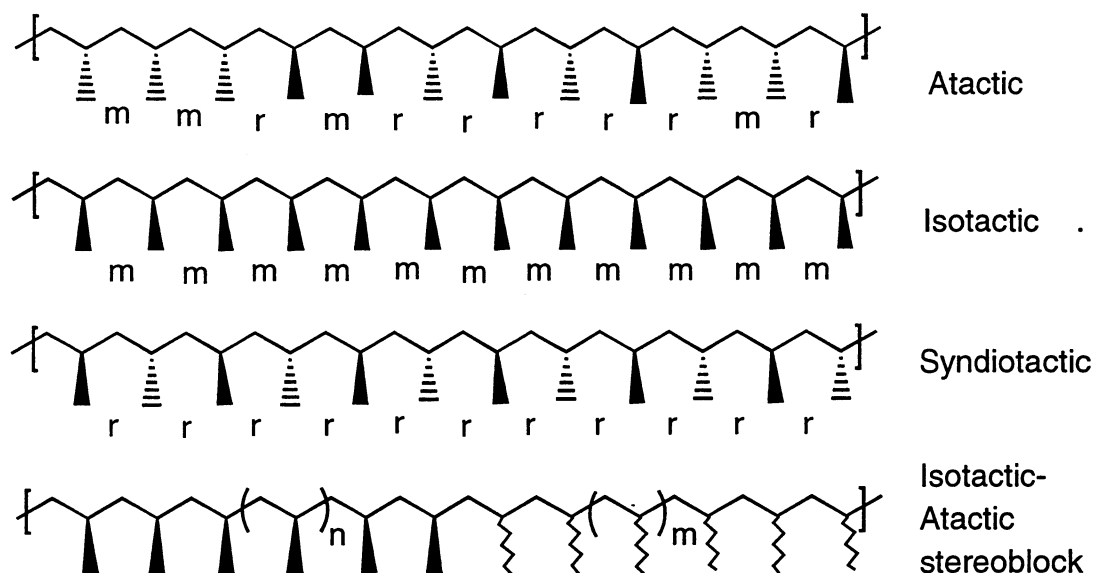
## Introduction

Since Karl Zeigler and Giulio Natta introduced a metal complex catalyst for olefin polymerization and oligomerization in 1955,<sup>1</sup> the development of polymerization catalysts with metallocene ligands has been significant. The first Zeigler-Natta catalyst, a mixture of  $\text{TiCl}_4$  and  $\text{AlEt}_3$ , played a very important role in industrial applications.<sup>1</sup> In 1977, a new type of catalyst was made by Kaminsky and Sinn, who used methylaluminoxane (MAO) with titanocene or zirconocene.<sup>2</sup> This advance initiated the use of metallocenes as single-site catalysts in olefin polymerization. Single-site catalysts have only one type of active site that causes production of polymers with specific microstructures and relatively narrow molecular weight distributions.<sup>1,2</sup> In 1982, *ansa*-titanocene catalysts were synthesized by Brintzinger and co-workers.<sup>3</sup> The *ansa*-titanocene catalysts were significant because their  $\text{C}_2$  symmetry allowed stereospecific polymerization of propylene to provide the isotactic polymer. The *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl) titanium complex **1** is shown in Scheme I-1, and the structures of polypropylene's stereoisomers are shown in Scheme I-2.<sup>4</sup>



*rac*-Ethylenebis(4,5,6,7-tetrahydro-1-indenyl) Titanium Dichloride

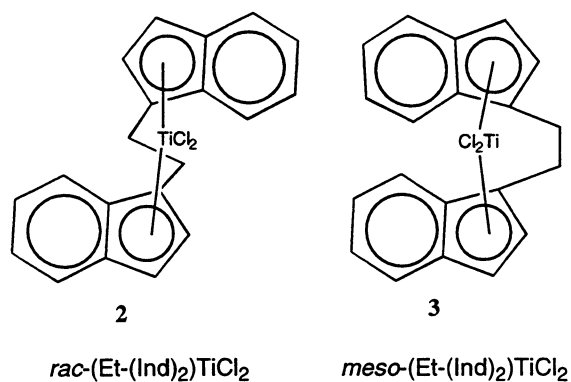
**Scheme I-1**



## Stereoisomers of Polypropylene

### Scheme I-2

Partially stereochemically controlled propylene polymerization was reported by Ewen.<sup>5</sup> A mixture of *rac*- and *meso*-ansa (Et-(Ind)<sub>2</sub>)TiCl<sub>2</sub> and MAO was used to produce isotactic polypropylene. These metallocene stereoisomers are shown in Scheme I-2. The structures of the stereoisomers were confirmed by Zeigler *et al.*<sup>6</sup>

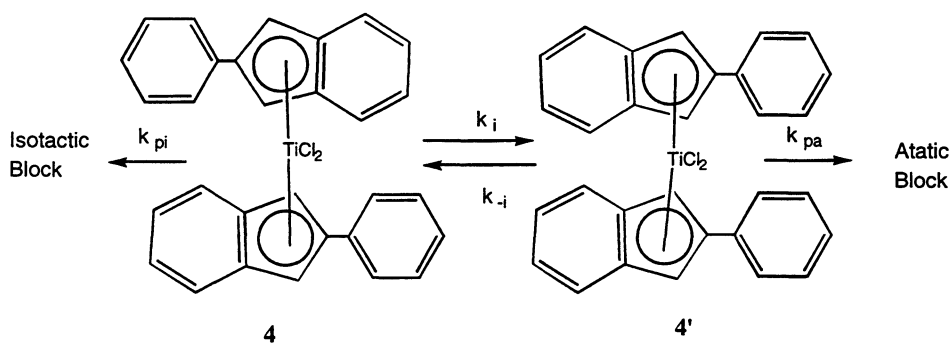


### Scheme I-3

In 1988, Ewen synthesized a different type of catalyst with a  $C_s$  symmetric structure. The zirconocene allowed for the production of syndiotactic polypropylene.<sup>7</sup> In the catalyst, the chirality is centered at the transitional metal and alternation of the polymer chain between two available coordination sites causes the metallocene to produce a syndiotactic structure.<sup>7</sup>

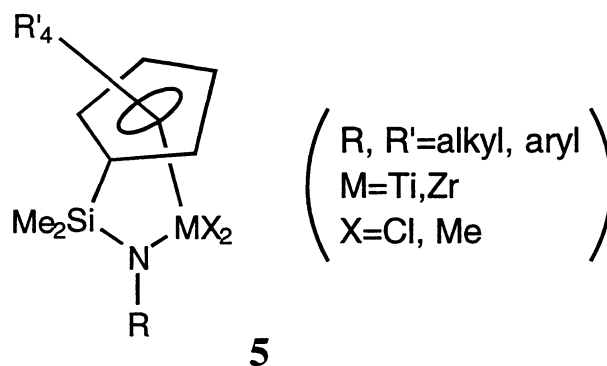
With a chiral zirconocene and MAO, highly stereospecific polyolefins were synthesized by Brintzinger *et al.*<sup>8</sup> In the polymerizations, a chiral *rac*-zirconocene with steric constraint produced only highly isotactic polymers. The stereoisomers of polypropylene are shown in Scheme I-2.<sup>4</sup>

Waymouth demonstrated that when an unbridged metallocene was used as a catalyst, the structure of the complex exchanged between two stereoisomers. Controlling the rate of the rotation of ligands about the metal-ligand bond axis could produce stereoblock polymers. For example, as shown in Scheme I-4, a phenyl group on indene could control the rate of rotation. The rate of the ligand's rotation about the indene-metal axis was slower than the rate of consecutive monomer insertion reactions so that polymerization could still occur. However, rotation was faster than the time for a polymer to reach the termination step. Thus one polymer chain could have both structures.<sup>4, 9-10</sup>



**Scheme I-4**

Because the rate and product structures of olefin polymerization reactions depends on the ligands of the catalyst complexes, the development of new ligands continues to attract interest. One new type of catalyst uses *ansa*-monocyclopentadienyl amido Group IV compounds **5**. The ligand of these complexes was first introduced by Bercaw.<sup>2, 11</sup> The general structure is shown in Scheme I-5.<sup>2</sup>

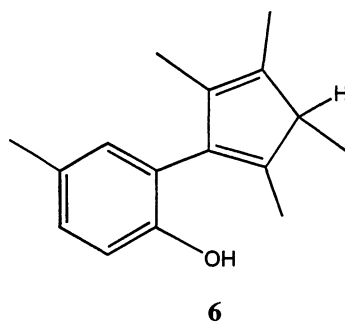


*ansa*-Monocyclopentadienyl Amido Group IV Catalyst.

### Scheme I-5

The main advantage of the cyclopentadienyl amido catalysts is that they allow the co-polymerization of ethylene with other linear  $\alpha$ -olefins. The cyclopentadienyl ring, bridge, and amido groups of ligands can be varied with a predictable effect on catalytic activity. For instance, the steric effect of the ligand in the catalysts could be controlled. The cyclopentadienyl amido catalysts contain nitrogen as an electron donor to stabilize the electrophilic metal center in a complex. The short  $-\text{SiMe}_2$  or  $-\text{CH}_2$  bridge is used in order to constrain the angle occupied by the ligand at the metal center.

In place of an amido group, a phenolate oxygen atom may serve as the coordinating heteroatom. Marks *et al.* reported a cyclopentadienyl phenolate Group IV metal complex that was shown to have high activity as a polymerization catalyst.<sup>12</sup> Both the ligand and the complex can be synthesized conveniently, and the aryl structure offers the possibility of elaboration with various substituents. Scheme I-6 shows the phenol used by Marks to prepare these new catalysts.

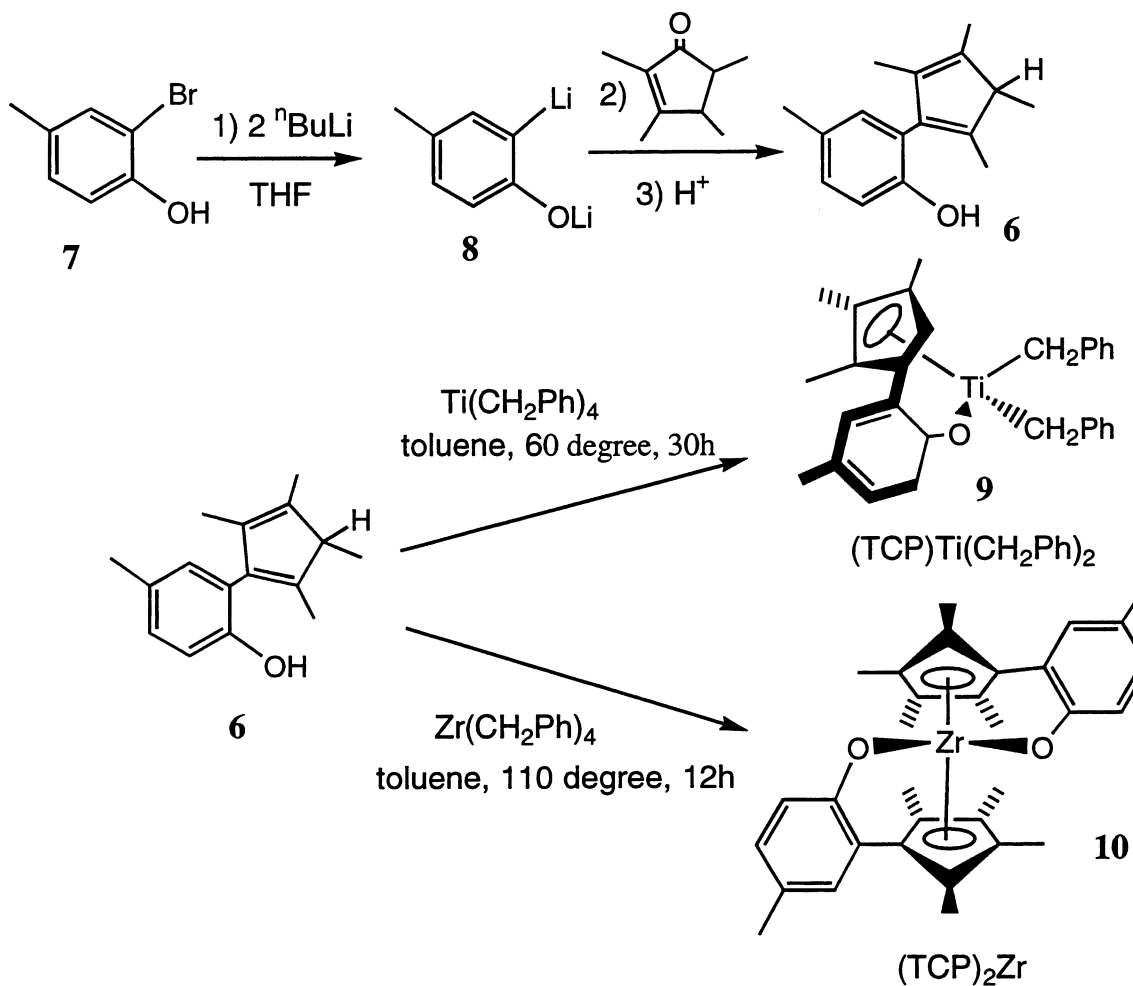


2-(Tetramethylcyclopentadienyl)-4-methylphenol: (TCP)H<sub>2</sub>

### Scheme I-6

To synthesize this compound **6**, 2-bromo-4-methylphenol was treated with *n*-butyllithium and electrophilic 2,3,4,5-tetramethyl-2-cyclopentenone was added. Then the reaction was quenched with concentrated hydrochloric acid. This one-pot procedure afforded the phenol in 46.8% yield. The coordination of 2-(tetramethylcyclopentadienyl)-4-methylphenol with Group IV transition metals was accomplished in a one-step reaction. In the reaction, 2-(tetramethylcyclopentadienyl)-4-methylphenol was heated with

tetrabenzyltitanium in toluene. Scheme I-7 shows the syntheses of the cyclopentadienyl phenolate ligand and its titanium and zirconium complexes.<sup>12</sup>

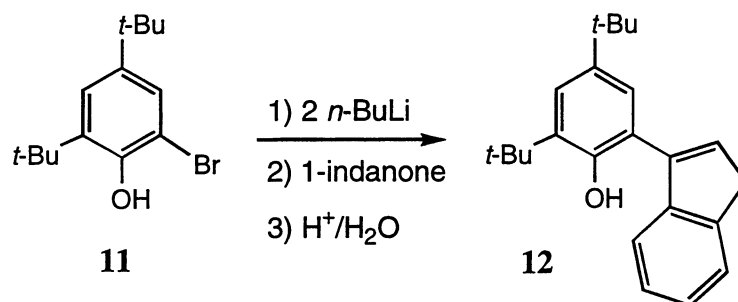


The Syntheses of (TCP)H<sub>2</sub> 6, (TCP)Ti(CH<sub>2</sub>Ph)<sub>2</sub> 9, and (TCP)<sub>2</sub>Zr 10

Scheme I-7<sup>12</sup>



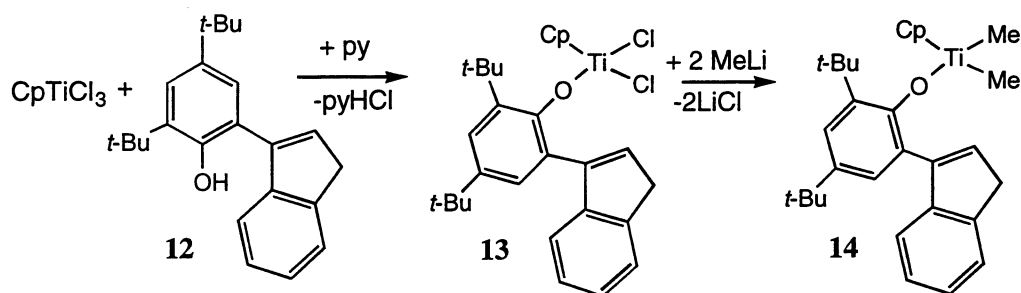
A similar cyclopentadienyl phenolate, made from 2-(indenyl)-4,6-di-*tert*-butyl phenol **12**, has been reported by Rothwell.<sup>13</sup> This ligand can coordinate to the metal via an indenyl group. Rothwell's synthesis was similar to that of Marks and is shown in Scheme I-8.



### Published Synthesis of 2-(Inden-3-yl)-4,6-di-*tert*-butylphenol

#### Scheme I-8

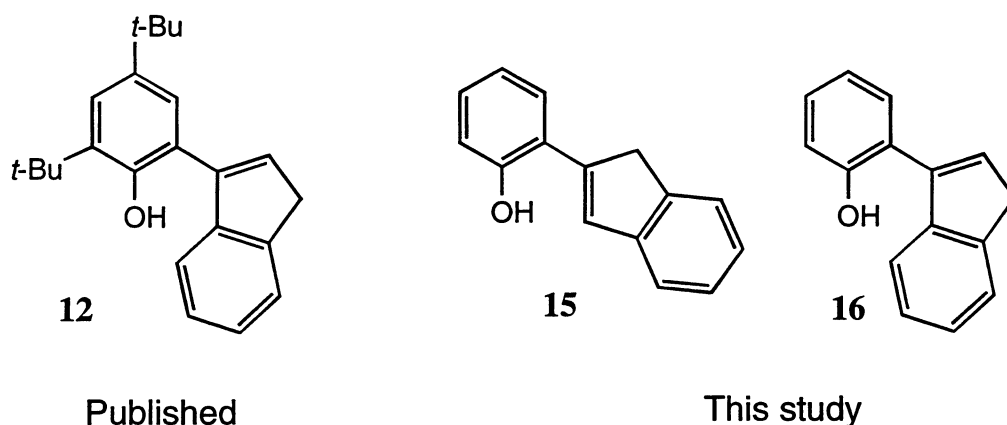
2-(Inden-3-yl)-4,6-di-*tert*-butylphenol **12** was coordinated with titanium, zirconium, and tantalum in the study by Rothwell.<sup>13</sup> In coordination with titanium, the hydroxy oxygen could bind to the metal, but the indenyl ring was not bound in either the dichloro or dimethyl compounds pictured in Scheme I-9.



### Coordination of 2-(Inden-3-yl)-4,6-di-*tert*-butylphenol with Titanium

#### Scheme I-9

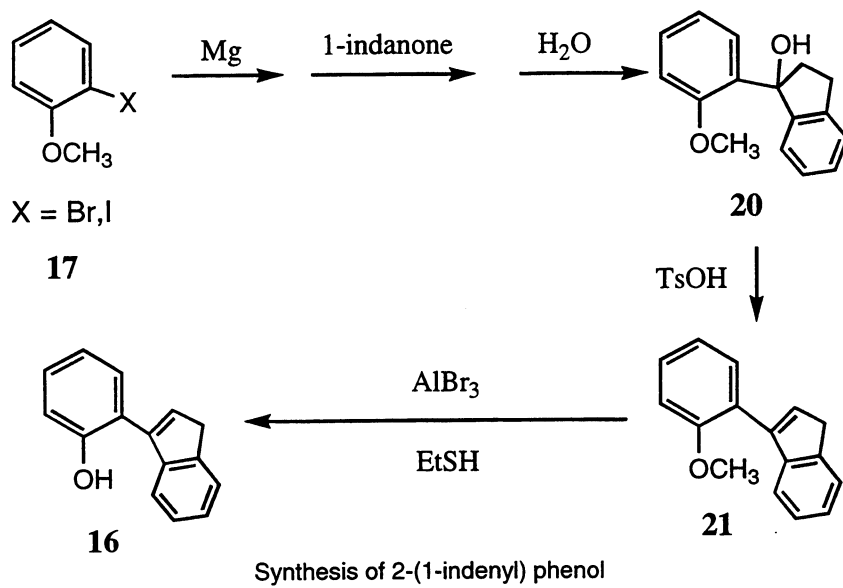
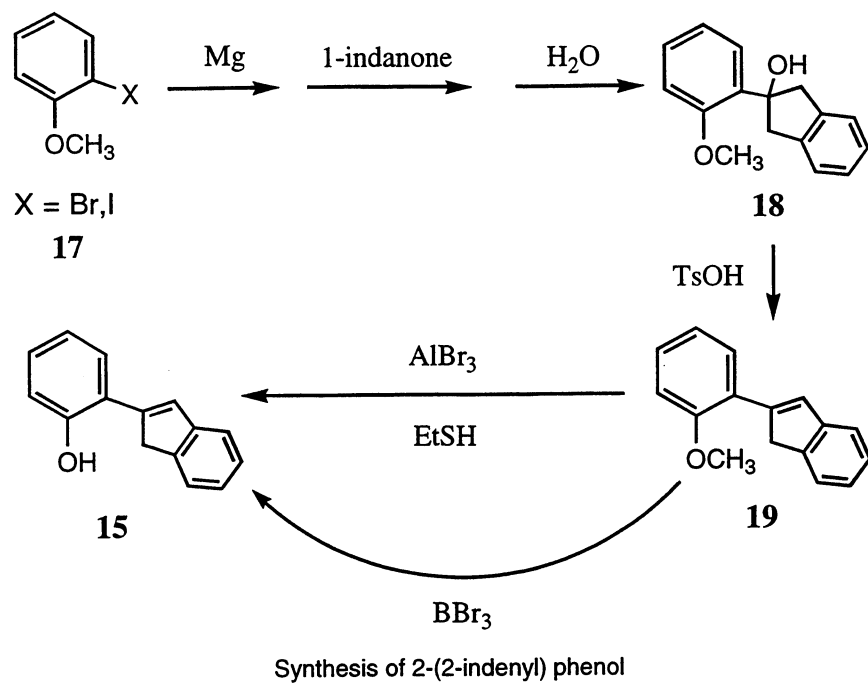
. An indenyl ring can be elaborated for stereocontrol of polymerization unlike a cyclopentadienyl ring. Since an indenyl ring has better structure than a cyclopentadienyl ring, we undertook the synthesis of the indenyl phenols shown in Scheme I-10. The advantage of these compounds possess is that their transition metal complexes should be less soluble in hydrocarbons than those that contain the *tert*-butyl group. Consequently, complexes made from the simpler ligands should be easier to crystallize and to characterize by X-ray crystallography.



## Indenyl Phenols

### Scheme I-10

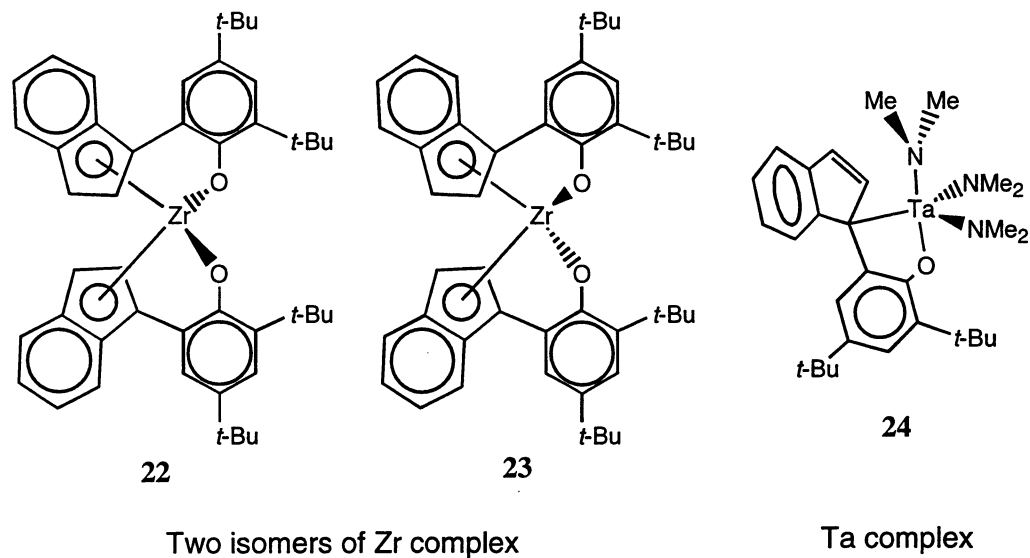
Our synthetic route consisted of a Grignard addition to an indanone followed by dehydration to form the indenyl group. Deprotection of the phenolic oxygen was also necessary. The synthesis of 2-(2-indenyl) phenol **15** and 2-(1-indenyl) phenol **16** are shown in Scheme I-11. Either phenol should be the precursor of an interesting ligand in a transition metal complex.



## Synthesis of 2-Indenyl Phenols

**Scheme I-11**

2-(Inden-3-yl)-4,6-di-*tert*-butylphenol **12** and  $Zr(NMe_2)_4$  reacted to form a complex. NMR spectra proved that the complex has two isomers. The synthesis of tantalum complex was also introduced in the study of Rothwell. Two isomers of the zirconium complex as well as the tantalum complex are shown in Scheme I-12.



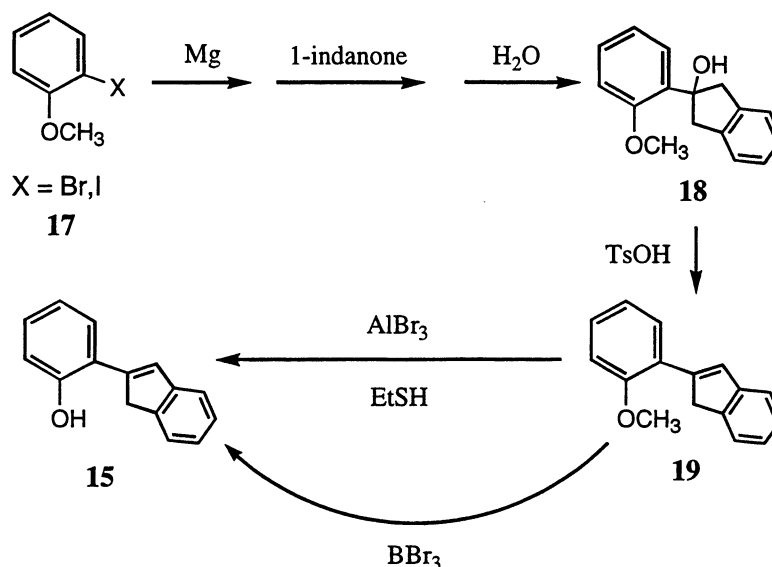
Complexes of 2-(Inden-3-yl)-4,6-di-*tert*-butylphenol with Zr and Ta

Scheme I-11

## Chapter II

### Results and Discussion

#### A. Synthesis of 2-(2-indenyl) Phenol

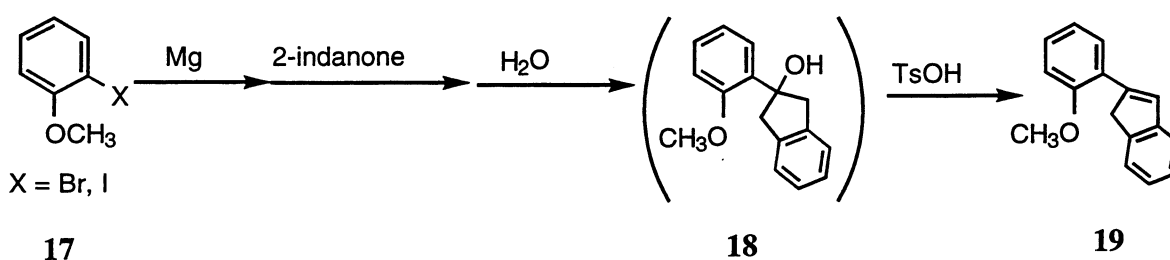


**Scheme II-1**

Scheme II-1 shows the scheme used to synthesize 2-(2-indenyl) phenol **15**. A Grignard reagent prepared from either 2-bromoanisole or 2-iodoanisole **17** was added to 2-indanone. Although aryl iodides form Grignard reagents more rapidly than do aryl bromides, there was no noticeable effect on yield in our experiments. Two methods of purifying 2-(2-hydroxy-2-indanyl) anisole **18** were evaluated. Flash chromatography was carried out on silica gel, or the product was recrystallized from diethyl ether. Evidence from thin-layer chromatography suggested that product purity was the same, regardless of the purification technique.

The dehydration of 2-(2-hydroxy-2-indanyl) anisole **18** followed the Grignard reaction. 2-(2-Hydroxy-2-indanyl) anisole **18** was refluxed in a Dean-Stark apparatus with an acid catalyst, *p*-toluenesulfonic acid monohydrate (*p*-TsOH•H<sub>2</sub>O), for three to five hours. The dehydration reactions produced white solids in nearly quantitative yields.

After the Grignard reaction, dehydration without the isolation of 2-(2-hydroxy-2-indanyl) anisole **18** gave the best yield on a large scale as shown in Scheme II-2. Since the product has a high R<sub>f</sub> (0.83 - 0.85) in flash chromatography in benzene, purification of the product was convenient. The results are summarized in Table 1 and Table 2.



**Scheme II-2. Synthesis of 2-(2-indenyl) anisole.**

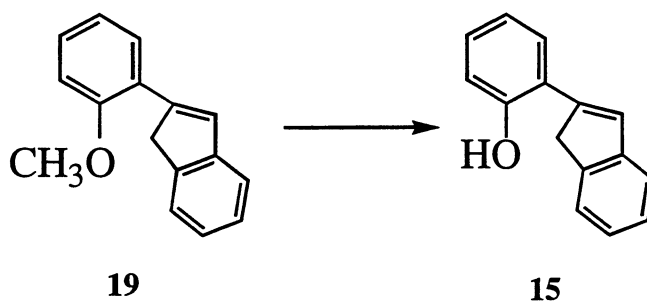
**Table 1. Synthesis of 2-(2-Indenyl) Anisole in two steps.**

Starting Material	Limiting Reagent in Grignard Reaction (2-indanone)	Isolation In Grignard Reaction	Yield In Grignard Reaction	Yield In Dehydration	Total % Yield
2-bromo-anisole	2.53g (19.1 mmol)	Flash Chromatography	2.48g (53.9%)	2.16g (94.2%)	49.9%
	1.50g (11.3 mmol)	Recrystallization	1.00g (36.8%)	0.936g (99.8%)	36.7%
2-iodo-anisole	1.52g (11.5 mmol)	Flash Chromatography	0.970g (36.7%)	0.900g (100%)	36.7%

**Table 2. Synthesis of 2-(2-Indenyl) Anisole 19 in one step.**

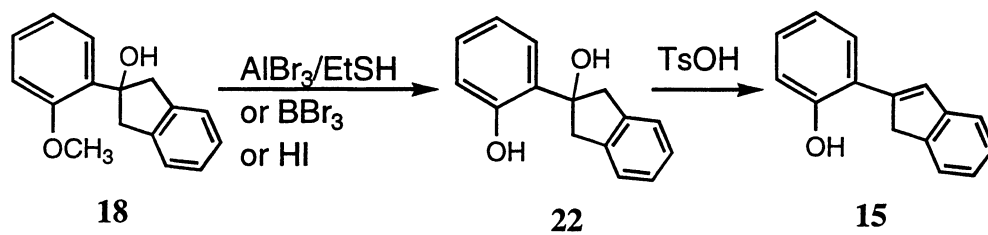
Starting Material	Limiting Reagent in Entire Reaction (2-indanone)	Yield in Grignard Reaction followed by Dehydration	Total % Yield
2-bromo-anisole	4.00g (30.27 mmol)	6.52g (96.9%)	96.9%
2-iodo-anisole	1.50g (11.3 mmol)	1.20g (49.1%)	49.1%

Demethylation to convert the methoxy group in 2-(2-indenyl) anisole **19** to a hydroxy group was attempted in three ways. (1) The reaction with aluminum bromide and ethanethiol gave the best results in terms of both yield and purity of the product.<sup>14</sup> (2) Demethylation with boron tribromide made the intended product with several by-products.<sup>15</sup> The  $R_f$  values of these by-products made more separation from the product very difficult. Moreover, the yield of this reaction was low. (3) The attempt to demethylate 2-(2-indenyl) anisole with concentrated HI produced the target product in amounts that were detectable by TLC, but no product could be isolated by flash chromatography despite evaluation of several solvent systems.

**Table 3. Demethylation of 2-(2-indenyl) anisole with various reagents.**

Reagent for Demethylation	Yield
$\text{AlBr}_3$ / EtSH	52.9%
$\text{BBr}_3$	31.6%
HI	0 %

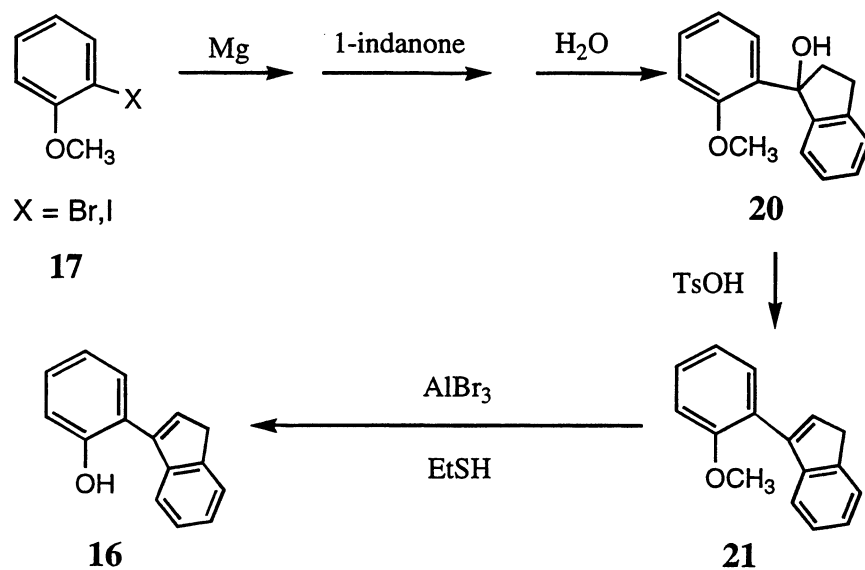
To improve the overall yield of the series of reactions, a change in the procedure was evaluated. Demethylation of 2-(2-hydroxy-2-indanyl) anisole **18** was attempted prior to dehydration. The proposed alternative route is shown in Scheme II-3. However, attempts to react with aluminum bromide/ethanethiol, boron tribromide, or concentrated HI did not yield demethylated product that could be identified by TLC.



Proposed Unsuccessful Alternate Route to 2-(2-Indenyl) Phenol.

**Scheme II-3**

### B. Synthesis of 2-(1-indenyl) Phenol



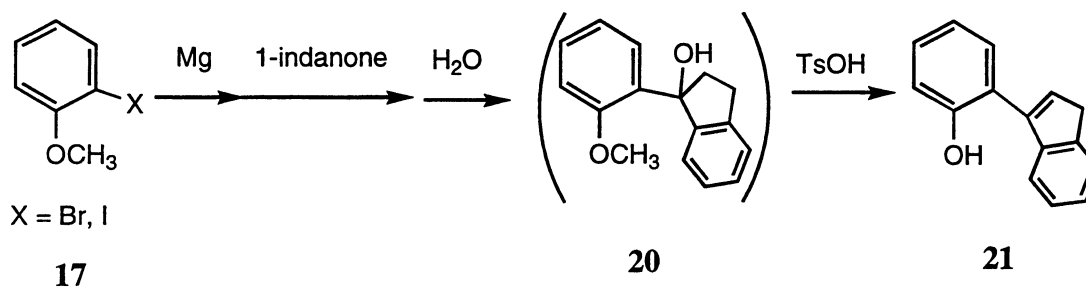
**Scheme II-4**



Procedures for the synthesis were the same as those used to prepare 2-(2-indenyl) phenol **15**. The Grignard reaction employing 2-iodoanisole resulted in a better yield than did the reactions with 2-bromoanisole. The crude 2-(1-hydroxy-1-indanyl) anisole **20** was a yellow oil with high viscosity and a white solid was isolated only by flash chromatography. Recrystallization did not give any pure product, but gave an oily mixture. For large scale reactions, 2-(1-hydroxy-1-indanyl) anisole **20** was not isolated from the yellow oily crude product. The crude product was dehydrated and 2-(1-indenyl) anisole **21** was isolated. The results are summarized in Table 4 and Table 5.

2-(1-Hydroxy-1-indanyl) anisole **20** was dehydrated with *para*-toluenesulfonic acid monohydrate. Unlike 2-(2-indenyl) anisole **19**, 2-(1-indenyl) anisole **21** was not stable in a solution and the yield was lower.

### Scheme II-5. Synthesis of 2-(1-Indenyl) Anisole.



**Table 4. Synthesis of 2-(1-Indenyl) Anisole in two steps.**

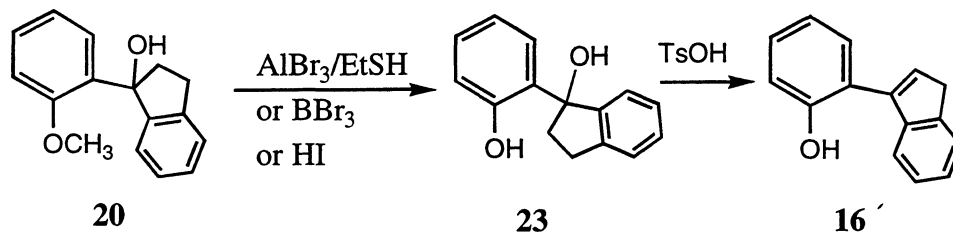
Starting Material	Limiting Reagent in Grignard Reaction (1-indanone)	Isolation In Grignard Reaction	Yield In Grignard Reaction	Yield In Dehydration	Total % Yield
2-bromo-anisole	1.50g (11.3 mmol)	Flash Chromatography	1.28g (48.9%)	1.16g (97.6%)	47.7%
2-iodo-anisole	1.52g (11.5 mmol)	Flash Chromatography	0.970g (36.7%)	0.900g (100%)	36.7%

**Table 5. Synthesis of 2-(1-Indenyl) Anisole in one step.**

Starting Material	Limiting Reagent in Entire Reaction (1-indanone)	Yield in Grignard Reaction followed by Dehydration	Total % Yield
2-bromo-anisole	4.00g (30.27 mmol)	2.51g (37.3%)	37.3%

Demethylation of 2-(1-indenyl) anisole **21** with aluminum bromide and ethanethiol produced 2-(1-indenyl) phenol **16**.<sup>14</sup> The isolation of 2-(1-indenyl) phenol **16** was attempted by flash chromatography in benzene. However, the product was not separated from the impurities. Finally, on a small scale, the crude product was separated by thin layer chromatography in benzene : hexane = 6 : 1 and a yellow solid was collected. Although one clear spot appeared under UV and iodine detection in TLC, <sup>1</sup>H and <sup>13</sup>C NMR proved that the product was not completely pure. The attempt to demethylate 2-(1-indenyl) anisole with concentrated HI did not result in product that could be isolated.

An alternative procedure was evaluated. Demethylation was attempted prior to dehydration. All three reagents for the demethylation reaction (aluminum bromide/ethanethiol, boron tribromide, and concentrated hydroiodic acid) were used. TLC showed three compounds, including one new product. By R<sub>f</sub> values, two compounds were identified as 2-(1-hydroxy-1-indanyl) anisole **20** and 2-(1-indenyl) anisole **21**. 2-(1-Indenyl) phenol **16** may have been the third product. The proposed reactions are shown in Scheme II-6.



Proposed Unsuccessful Alternative Route to 2-(1-Indenyl) Phenol

**Scheme II-6**

## Chapter III

### Conclusions

We have developed the synthesis of 2-(2-indenyl)-phenol **15** and 2-(1-indenyl)-phenol **16** in a three-step sequence. An indanone was added to a Grignard reagent formed from 2-bromoanisole **17**. The product was dehydrated with an acid catalyst, *p*-toluenesulfonic acid monohydrate (*p*-TsOH•H<sub>2</sub>O). Finally, the methyl group in anisole was removed with various reagents.

All of the steps yielded the expected products. Most of steps except the demethylation of 2-(1-indenyl) anisole **21** gave 50 % or higher yield, and the total synthesis of 2-(2-indenyl) phenol **15** was accomplished in 32.6% isolated yield. Moreover, all the steps have been studied by varying the reactions to improve procedures. Grignard reactions without isolation of the intermediate product followed by dehydration gave the best yield on a large scale. Demethylation reactions gave the best results with aluminum bromide and ethanethiol; the reactions with boron tribromide and with concentrated HI had lower yields.

Each compound was characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra that were consistent with the proposed structure. The three compounds in the synthetic route to 2-(2-indenyl) phenol **15** were also analyzed by elemental analysis. Only 2-(2-hydroxy-2-indanyl) anisole **18** was pure to elemental analysis.

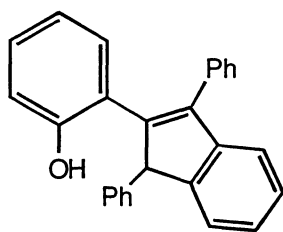
The synthesis of 2-indenyl phenols could prove useful as a route to ligands of olefin polymerization catalysts. The reactions with other indanones could extend the applications of this study. Coordination of the ligands with transition metals represents a future direction for this project.

## Chapter IV

### Future Research

Although this study has been partially successful, it needs further development.

1. 2-(2-Indenyl) phenol **15** has been synthesized, and the product has been characterized by TLC, elemental analysis, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR. However, as the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for 2-(2-indenyl) phenol **15** showed, the product needs purification. In fact, elemental analysis data showed that all products except 2-(2-hydroxy-2-indanyl) anisole **18** were not completely pure.
2. 2-(1-Indenyl) phenol **16** has been synthesized and characterized by the same techniques used to synthesize 2-(2-indenyl) phenol **15**, but the final product is not pure. This product should be purified in the future.
3. Procedures for the chemistry shown in Scheme II-1 and Scheme II-4 need to be refined further.
4. Employing different indanone derivatives such as 1,3-diphenyl-2-indanone **24** could provide useful results. Since 1,3-diphenyl-2-indanone **24** has two bulky phenyl groups, the ligand made from it would have greater steric demands than the unsubstituted ligand when coordinated to transition metal. As a result, the ligand might find an application in polymerization catalyst, since it might inhibit coordination of anion to the metal.

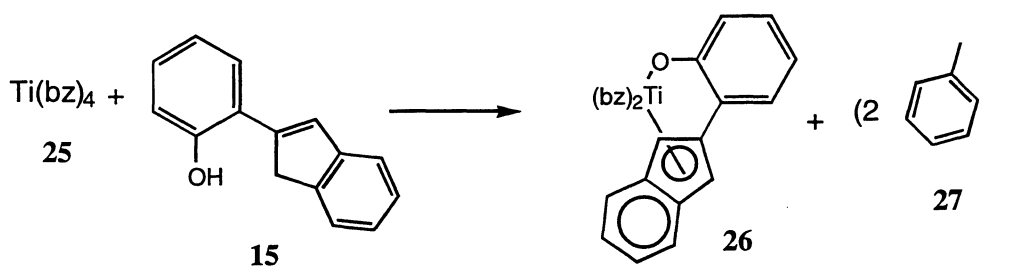


24

1,3-diphenyl-2-indanone

**Scheme IV-1**

5. Indenyl phenol ligands should be coordinated to Group IV transition metals such as Ti and Zr. Many Ti or Zr - indenyl complexes have been applied as homogeneous catalysts in stereospecific olefin polymerization. A proposed reaction for coordination of an indenyl phenol ligand to Ti is shown in Scheme IV-2.



**Scheme IV-2**

# Chapter V

## Experimental Section

### Reagents

Aluminum bromide ( $\text{AlBr}_3$ , 98+%), boron tribromide ( $\text{BBr}_3$ , 99+%), *n*-butyllithium (*n*-BuLi, 2.5M in hexane), copper (I) bromide ( $\text{CuBr}$ , 98%), ethanethiol ( $\text{EtSH}$ , 97%), hydriodic acid ( $\text{HI}$ , 55%), 2-iodoanisole (98%), 1-indanone (99+%), sodium nitrite ( $\text{NaNO}_2$ , 99.99%), and *p*-toluenesulfonic acid monohydrate ( $p\text{-TsOH}\cdot\text{H}_2\text{O}$ , 98.5%) were purchased from Aldrich Chemical Co. and used as received. 2-Bromoanisole (97%) was synthesized<sup>16</sup> or obtained from Aldrich Chemical Co. 2-Indanone (98%) was purchased from Aldrich Chemical Co. or was synthesized by Anthony M. Kantowicz and Dr. Robert W. Chesnut. Since 2-indanone is very unstable at room temperature, it was purified by steam distillation and stored in a cold room. Anhydrous diethyl ether and tetrahydrofuran (THF) were obtained from Fisher Scientific Chemical Co. and Mallinckrodt Chemical Co., respectively, and freshly distilled from sodium and benzophenone under nitrogen. Benzene from Fisher Scientific Chemical Co. and hexane from Mallinckrodt Chemical Co. were used without further purification. All water used was deionized. All flash chromatography was carried out on 200-400 mesh silica.

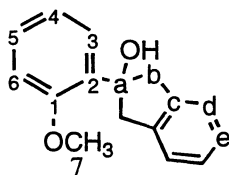
### Physical and Analytical Measurements.

All  $^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra were recorded on a GE QE-300 MHz FT-NMR spectrometer. The chemical shifts for  $^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra were referenced to internal solvent resonances using deuteriochloroform ( $\text{CDCl}_3$ ) from Aldrich Chemical Co. and are reported relative to tetramethylsilane (TMS) as an internal standard in parts per million (ppm) (for  $^1\text{H}$  NMR, s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and b, broad). Melting

points were obtained in capillary tubes with a Thomas-Hoover capillary melting point apparatus, and are uncorrected. Thin-layer Chromatography (TLC) was performed on Analtech silica gel GF chromatography plates using benzene as the eluent. Elemental analysis was performed in the University of Illinois Microanalysis Laboratory.

### **The Synthesis of 2-(2-Hydroxy-2-indanyl) anisole (18)**

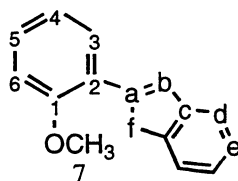
A solution of 5.40 g (28.9 mmol) of 2-bromoanisole in 10.0 mL of Et<sub>2</sub>O was added to 0.700 g (28.7 mmol) of Mg. Crushed Mg turnings, heated under Ar atmosphere, were used to activate the Grignard reaction. The solution was refluxed for five hours until most of the Mg disappeared. After the heat was removed, a solution of 2.53 g (19.1 mmol) of 2-indanone in 10 mL of Et<sub>2</sub>O was added dropwise to the brown Grignard reagent. The color of the solution changed to yellow. In 20 minutes, 5 mL of water was added to quench the reaction. The Addition of 10 mL of EtOAc produced two layers. The organic layer was washed with 10 mL each of water, NaHCO<sub>3</sub>(aq), water again, and brine, and dried over MgSO<sub>4</sub>. The white solid product was isolated by flash chromatography in benzene. Yield = 2.48g; 53.9%. TLC: R<sub>f</sub> = 0.21 in benzene. <sup>1</sup>H NMR: (CDCl<sub>3</sub>) δ 7.39 – 6.94 (m, 8H, two aromatics), 3.91 (s, 3 H, methoxy(7)), 3.59 - 3.32 (d, 4H, indanyl(b)). (Figure 1); <sup>13</sup>C NMR: (CDCl<sub>3</sub>) δ 157.05 (anisole aromatic(1)), 141.39, 132.99, 128.54, 126.44, 124.63, 120.77, 111.07, 82.88 (indanyl hydroxy(a)), 55.27 (anisole methoxy (7)), 46.56 (indanyl (b)). (Figure 2); Anal. Calcd for C<sub>16</sub>H<sub>16</sub>O<sub>2</sub>: C, 79.97; H, 6.71. Found C, 79.78; H, 6.83





### The synthesis of 2-(2-indenyl) anisole (19)

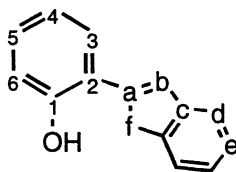
To 1.11 g (4.62 mmol) of 2-(2-hydroxy-2-indanyl) anisole **18** dissolved in 50 mL of benzene was added 0.291 g (1.53 mmol) *p*-TsOH•H<sub>2</sub>O. The solution was refluxed in a Dean-Stark apparatus for three hours. Solvent was evaporated by air purging and the crude product was purified by flash chromatography in benzene. Yield of white solid product = 1.04 g; 100%. TLC: R<sub>f</sub> = 0.88 in benzene. <sup>1</sup>H NMR: (CDCl<sub>3</sub>) δ 7.56 – 7.14 (m, 7H, two aromatics), 7.02 – 6.94 (m, 2H, mixture of one aromatic and one indenyl), 3.94 (s, 3H, methoxy(7)), 3.86 (s, 2H, indenyl(f)). (Figure 3); <sup>13</sup>C NMR: (CDCl<sub>3</sub>) δ 157.52 (anisole aromatic(1)), 145.92, 143.12, 142.86, 130.59, 128.61, 126.38, 125.17, 124.49, 123.28, 120.97, 120.64, 111.19, 104.91, 55.29 (anisole methoxy (7)), 40.90 (indenyl). (Figure 4); Anal. Calcd for C<sub>16</sub>H<sub>14</sub>O: C, 86.46;H 7.26. Found C, 86.19; H, 6.30.



### The Synthesis of 2-(2-Indenyl) phenol (15)

A 3.0 g (13.5 mmol) sample of 2-(2-indenyl) anisole **19** was dissolved in 4 mL of newly distilled methylene chloride. In a glove bag, 14.4 g (54.0 mmol) of AlBr<sub>3</sub> was placed in a 50 mL round bottom flask with a stirring bar. In a hood, the solution was cooled in an ice bath, and then 10 mL of EtSH was added. 2-(2-Indenyl) anisole solution was added dropwise to the cooled solution and the entire solution was stirred for 1.5 hour at 0 °C. In two minutes, the dark red color turned to milky brown. In 1.5 hour, 10 mL of water was added dropwise to quench the reaction.

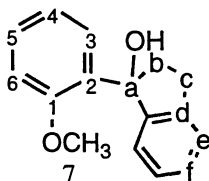
Then, the flask was purged with air for three days to remove the EtSH. Addition of 10 mL of EtOAc produced two layers. The organic layer was washed with 10 mL of NaHCO<sub>3</sub>(aq), water, and brine, and dried over MgSO<sub>4</sub>. The product, a white solid, was purified by flash chromatography in benzene. Yield = 1.40 g : 49.8%. TLC: R<sub>f</sub> = 0.51 in benzene. <sup>1</sup>H NMR: (CDCl<sub>3</sub>) δ 7.50 – 7.14 (m, 7H, two aromatics), 7.02 – 6.88 (m, 2H, mixture of one aromatic and one indenyl), 5.40 (s, 1H, hydroxy), 3.83 (s, 2H, indenyl(f)). (Figure 5); <sup>13</sup>C NMR: (CDCl<sub>3</sub>) δ. 153.23 (phenol aromatic(1)), 145.30, 143.04, 142.76, 129.95, 128.74, 126.62, 124.90, 123.51, 121.15, 120.88, 116.18, 104.93, 41.30(indenyl). (Figure 6); Anal. Calcd for C<sub>15</sub>H<sub>12</sub>O: C, 86.51;H 5.81. Found C, 85.90; H, 5.79.



### **The Synthesis of 2-(1-Hydroxy-1-indanyl) anisole (20)**

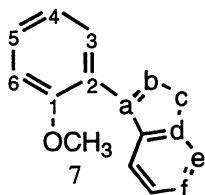
A solution of 4.00g (17.0 mmol) of 2-iodoanisole in 10.0 mL Et<sub>2</sub>O was added to 0.413g (17.0 mmol) of Mg. Crushed Mg turnings, heated under an argon atmosphere, were used to activate the Grignard reaction. The solution was refluxed for 3.5 hours. After heat was removed, 1.50g (11.3 mmol) of 1-indanone, dissolved in 10.0 mL Et<sub>2</sub>O, was added dropwise to the brown Grignard reagent. Water (3.0 mL) was added to the solution to quench the reaction. Addition of 10 mL of EtOAc produced two layers. The organic layer was washed with 10mL of NaHCO<sub>3</sub>(aq), water, and brine, and dried over MgSO<sub>4</sub>. The product, a white solid, was isolated by flash chromatography in benzene. Yield = 1.83 g; 67.2%. TLC: R<sub>f</sub> = 0.23 in benzene. <sup>1</sup>H NMR: (CDCl<sub>3</sub>) δ 7.36 – 6.60 (m, 8H, two aromatics), 4.63 (s, 1H, hydroxy),

3.93 (s, 3 H, methoxy), 3.05 – 2.46 (m, 4H, indanyl). (Figure 7);  $^{13}\text{C}$  NMR: ( $\text{CDCl}_3$ )  $\delta$  156.78 (anisole aromatic(1)), 146.17, 143.75, 133.90, 128.43, 127.48, 126.71, 124.83, 124.61, 120.54, 111.17, 111.10, 104.92, 85.54, 55.40 (anisole methoxy(7)), 43.16 (indanyl), 29.94. (Figure 8)



### **The Synthesis of 2-(1-Indenyl) anisole (21)**

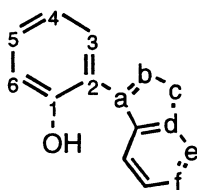
To 2.20 g (9.16mmol) of 2-(1-hydroxy)-indanyl anisole **20** dissolved in 50 mL of benzene was added 0.348 g (1.83 mmol) of *p*-TsOH•H<sub>2</sub>O. The solution was refluxed in a Dean-Stark apparatus for 4.5 hours; 1.0 mL of water condensed. The product, a pale yellowish solid, was separated by flash chromatography in benzene. Yield = 1.99 g; 97.6%. TLC: R<sub>f</sub> = 0.88 in benzene.  $^1\text{H}$  NMR: ( $\text{CDCl}_3$ )  $\delta$  7.51 – 6.98 (m, 8H, two aromatics), 6.57 (t, 1H, indenyl(b)), 3.78 (s, 3H, methoxy(7)), 3.58 (d, 2H, indenyl(c)). (Figure 9);  $^{13}\text{C}$  NMR: ( $\text{CDCl}_3$ )  $\delta$  157.11 (anisole aromatic(1)), 144.77, 143.87, 142.34, 132.34, 130.61, 128.86, 125.85, 125.20, 124.44, 123.71, 121.01, 110.93, 104.89, 55.37 (anisole methoxy(7)), 38.42(indenyl). (Figure 10)



### **The Synthesis of 2-(1-Indenyl) phenol (16)**

A 925 mg (4.16 mmol) sample

of 2-(1-indenyl) anisole **21** was dissolved in 2 mL of newly distilled methylene chloride. In a glove bag, 4.72 g (17.7 mmol) of  $\text{AlBr}_3$  was placed in a 50 mL round bottom flask with a stirring bar. In a hood, the solution was cooled in an ice bath, and then 10 mL of EtSH was added. 2-(1-Indenyl) anisole solution was added dropwise to the cooled solution and the entire solution was stirred for 2 hours at 0 °C. In two minutes, the dark red color turned to milky brown. A 10 mL portion of water was added dropwise to quench the reaction. Then, the flask was purged with air for three days to remove the EtSH. Addition of 10 mL of EtOAc produced two layers. The organic layer was washed with 10 mL each of water,  $\text{NaHCO}_3(\text{aq})$ , water, and brine, and dried over  $\text{MgSO}_4$ . The product was purified by flash chromatography in benzene and 72 mg of yellow solid was separated on TLC plate. The product was not completely pure.  $^1\text{H}$  NMR spectra and  $^{13}\text{C}$  NMR spectra are consistent with the proposed structure. TLC:  $R_f = 0.49$  in benzene.  $^1\text{H}$  NMR: ( $\text{CDCl}_3$ )  $\delta$  7.49 – 6.97 (m, 8H, two aromatics), 6.66 (t, 1H, indenyl(b)), 5.27 (s, 1H, hydroxy), 3.60 (d, 2H, indenyl(c)). (Figure 11);  $^{13}\text{C}$  NMR: ( $\text{CDCl}_3$ )  $\delta$ . 152.24 (anisole aromatic(1)), 145.09, 137.03, 130.18, 129.03, 127.84, 125.82, 120.84, 104.79, 38.69(indenyl), 35.96, 30.00. (Figure 12).



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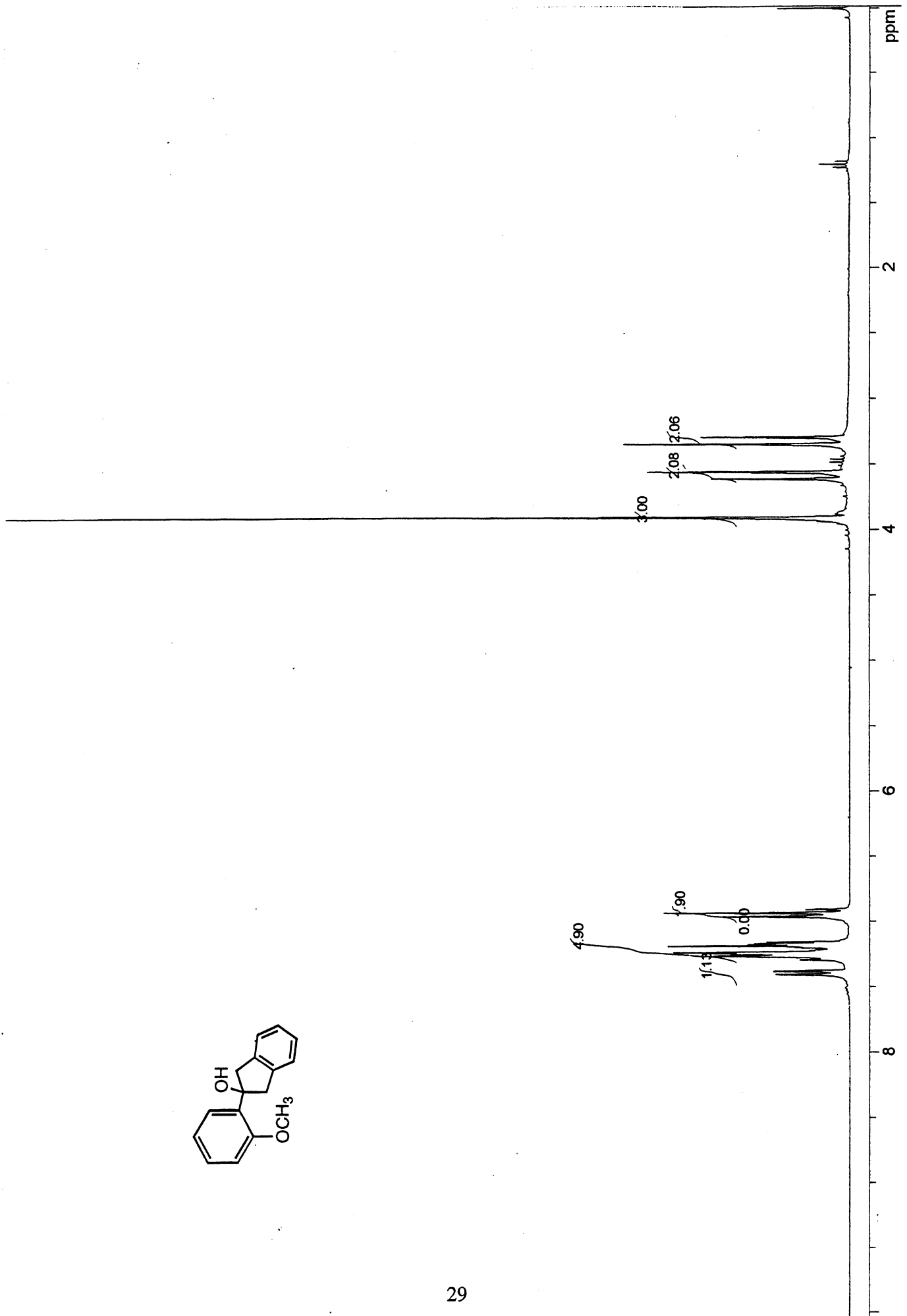
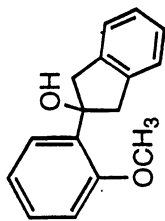


Figure 1. <sup>1</sup>H NMR Spectrum of 2-(2-hydroxy-2-indanyl) anisole (18)

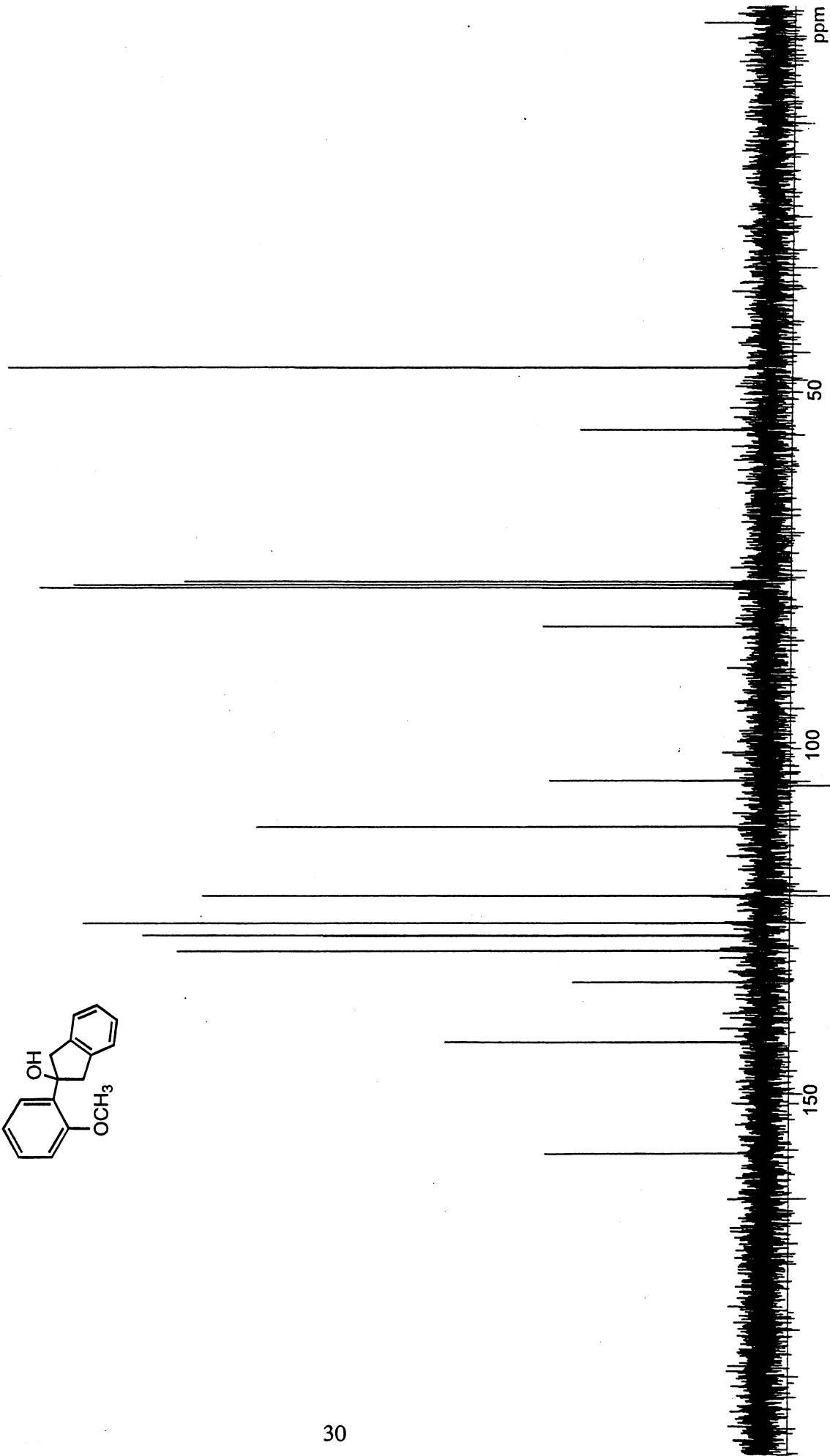
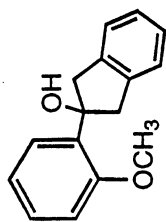


Figure 2. <sup>13</sup>C NMR Spectrum of 2-(2-hydroxy-2-indanyl) anisole (18)



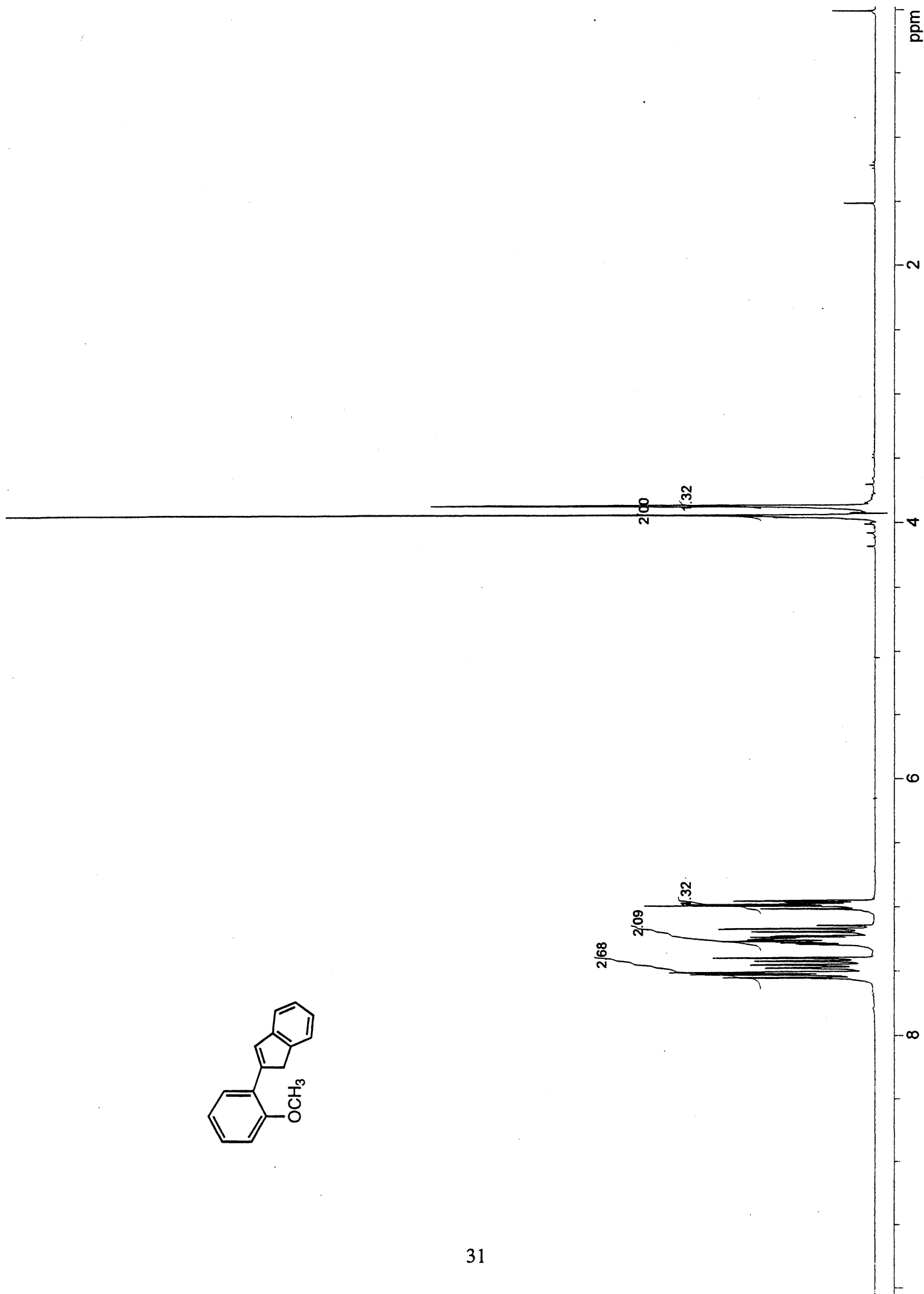
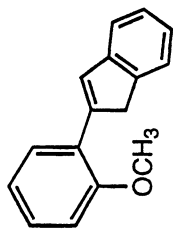


Figure 3. <sup>1</sup>H NMR Spectrum of 2-(2-indenyl) anisole (19)

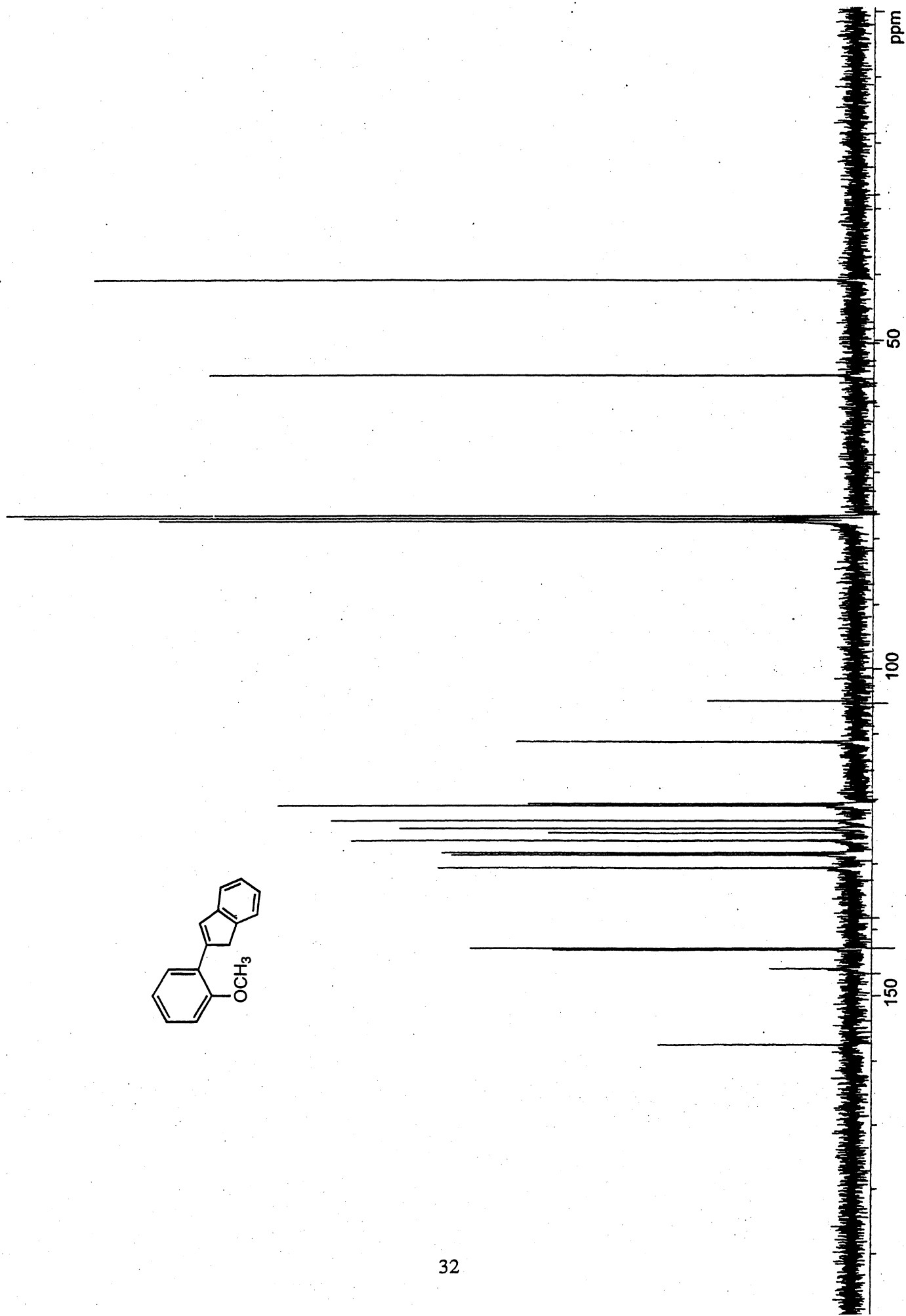
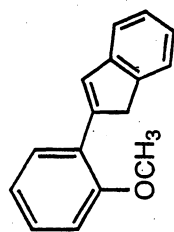


Figure 4. <sup>13</sup>C NMR Spectrum of 2-(2-indenyl) anisole (19)

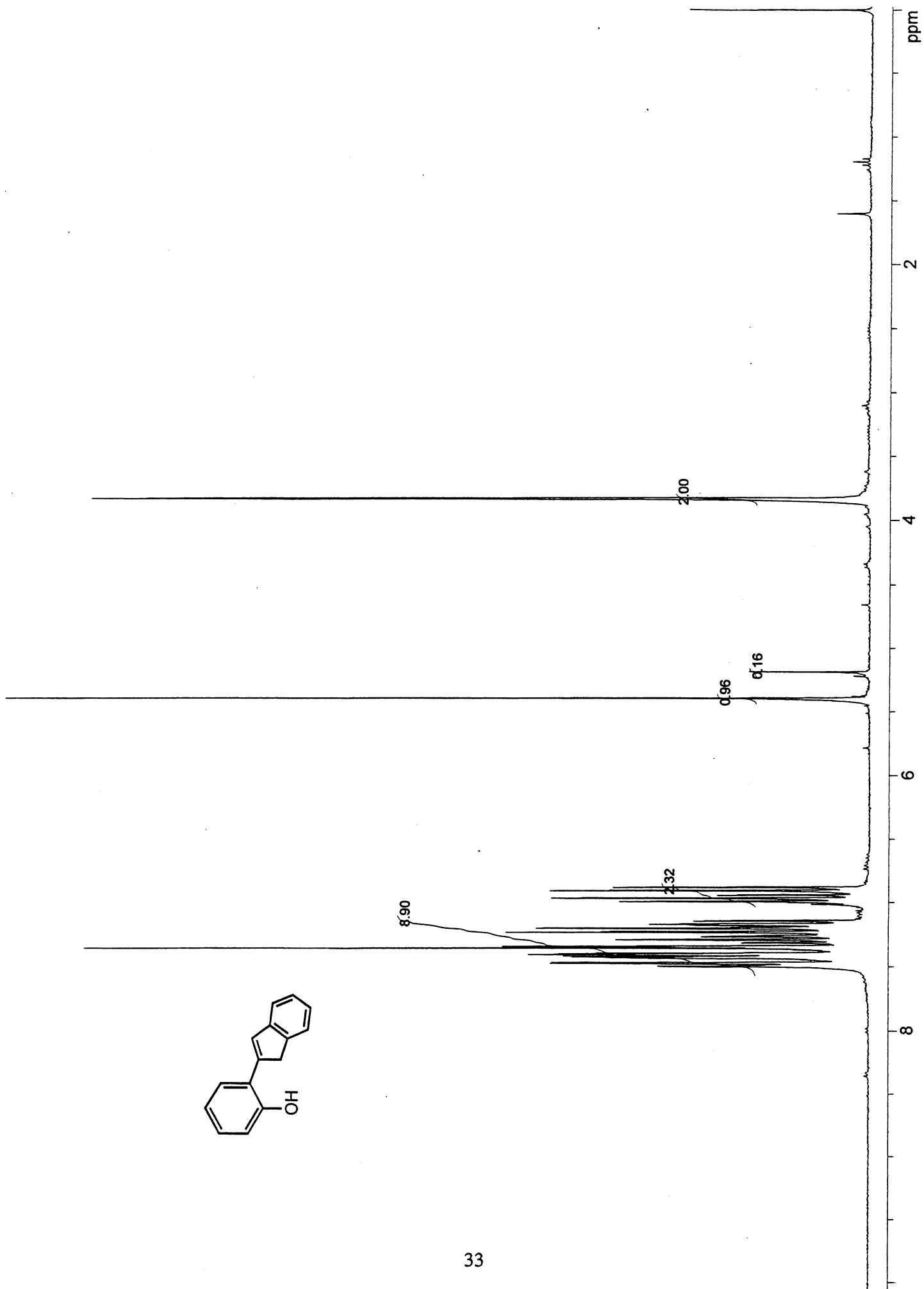
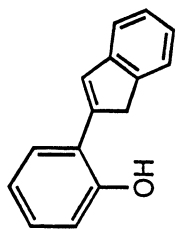


Figure 5. <sup>1</sup>H NMR Spectrum of 2-(2-indenyl) phenol (15)

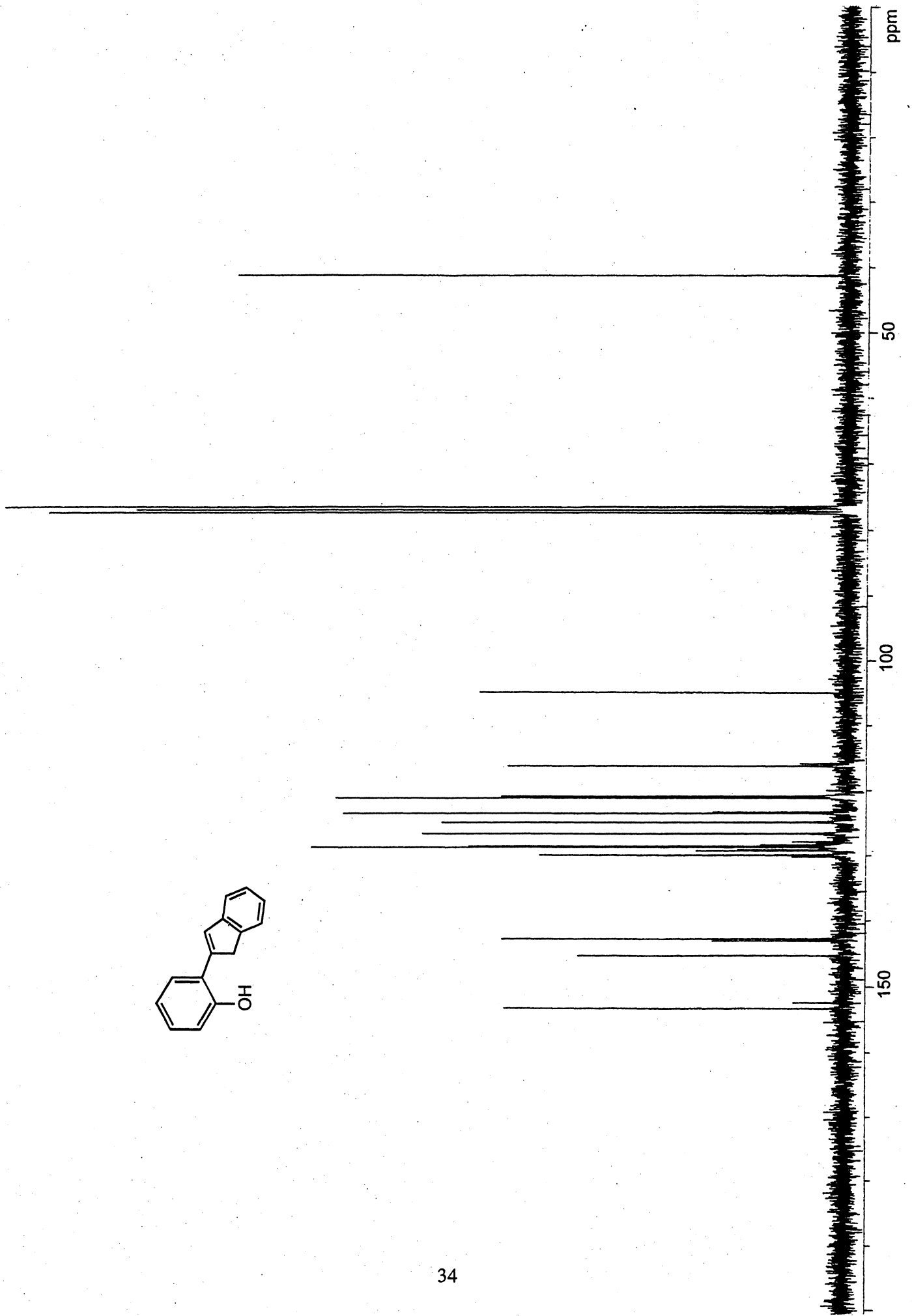
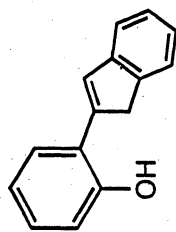
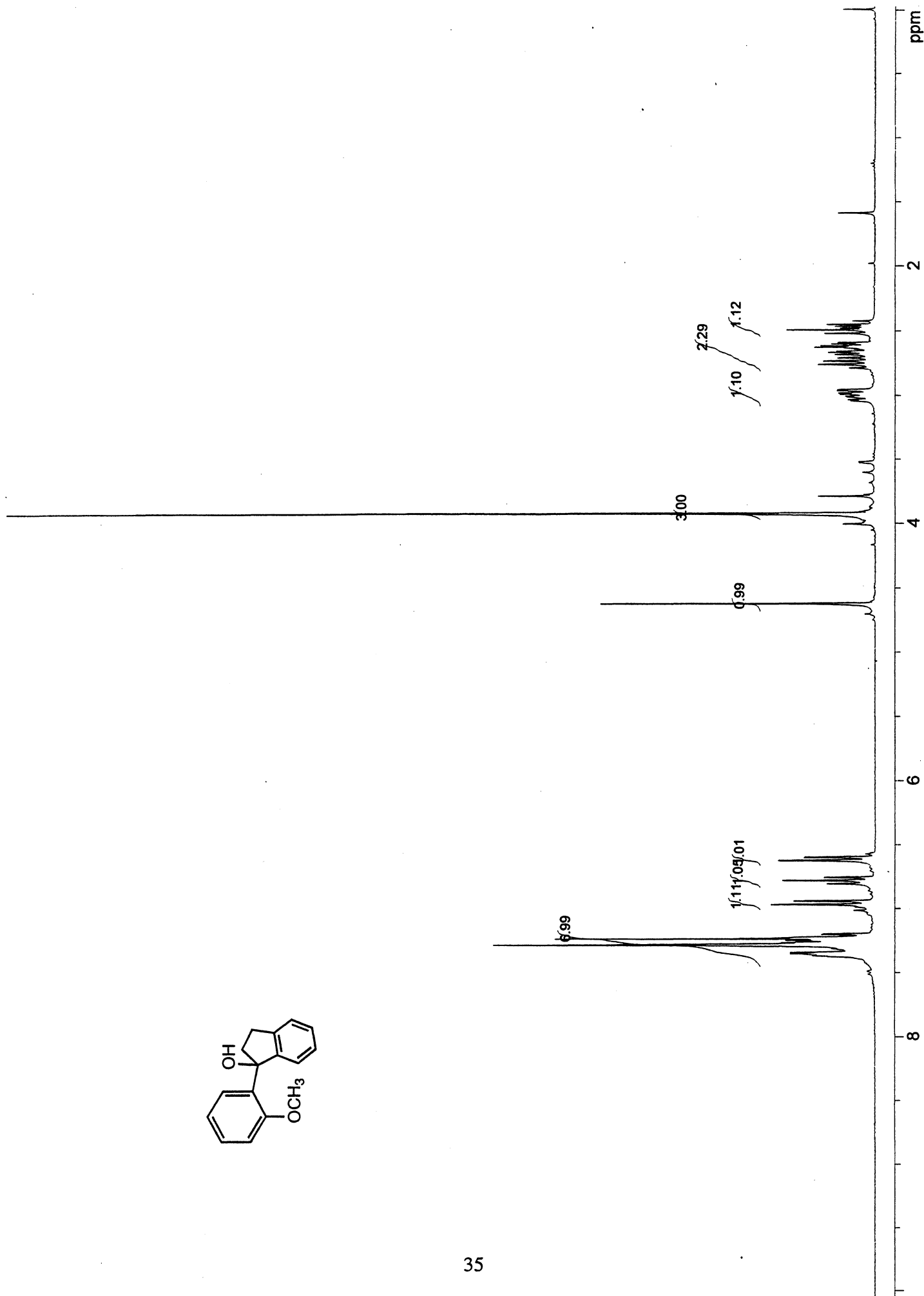
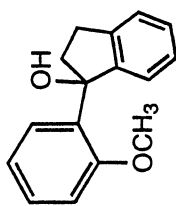


Figure 6.  $^{13}\text{C}$  NMR Spectrum of 2-(2-indenyl) phenol (15)



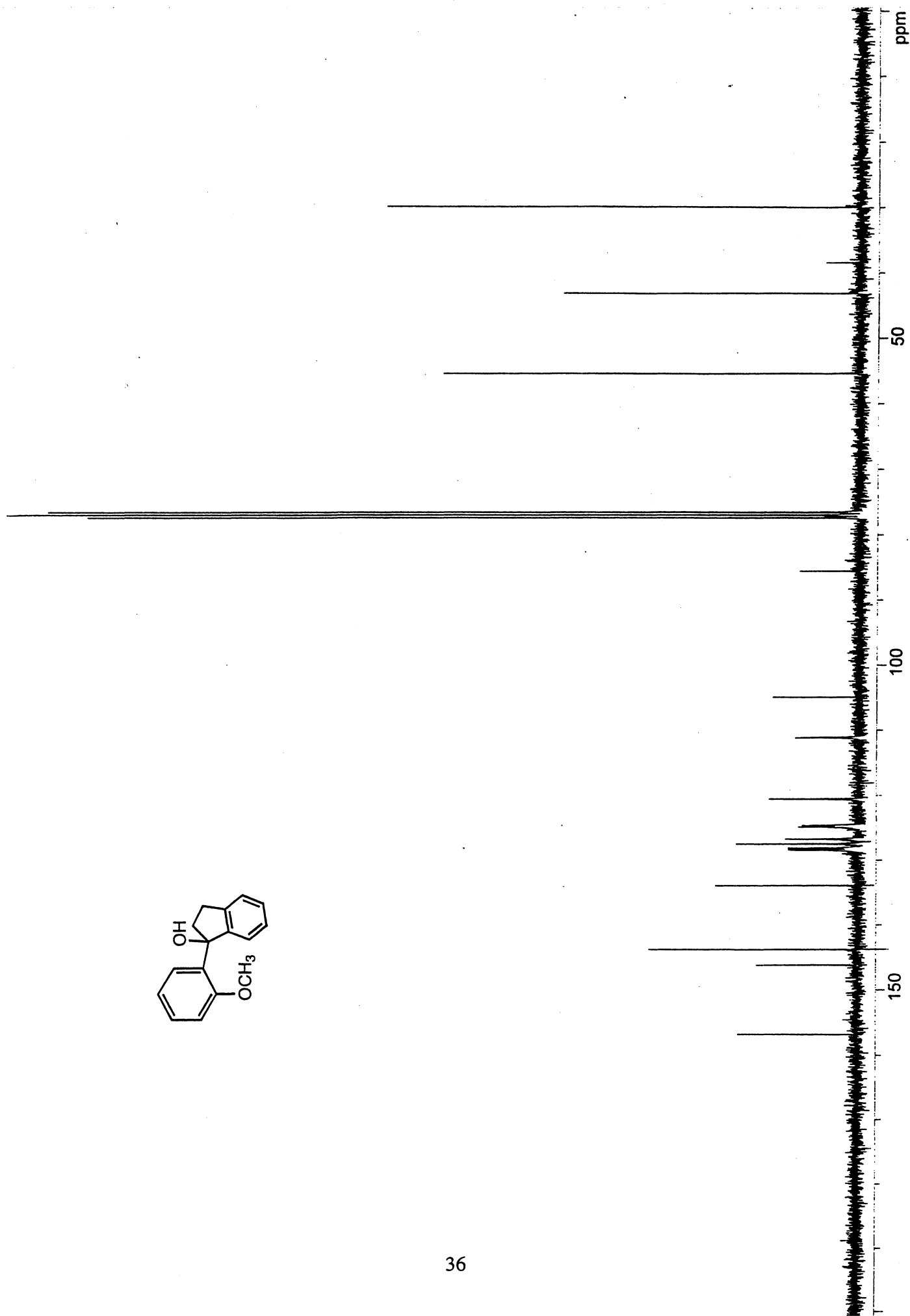
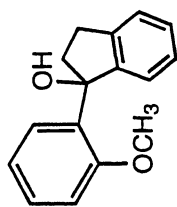


Figure 8. <sup>13</sup>C NMR Spectrum of 2-(1-hydroxy-1-indanyl) anisole (20)

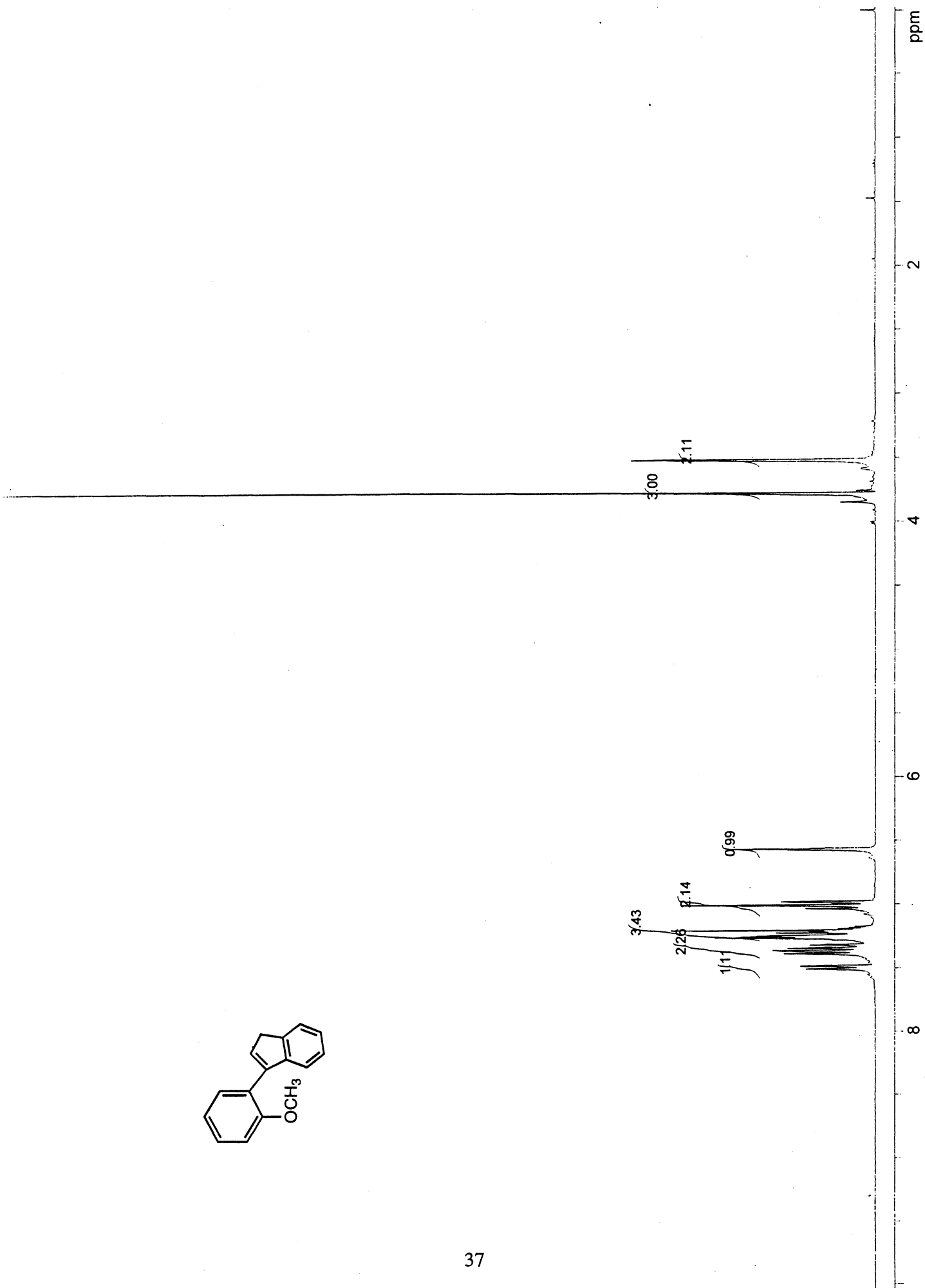
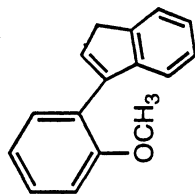


Figure 9. <sup>1</sup>H NMR Spectrum of 2-(1-indenyl) anisole (21)

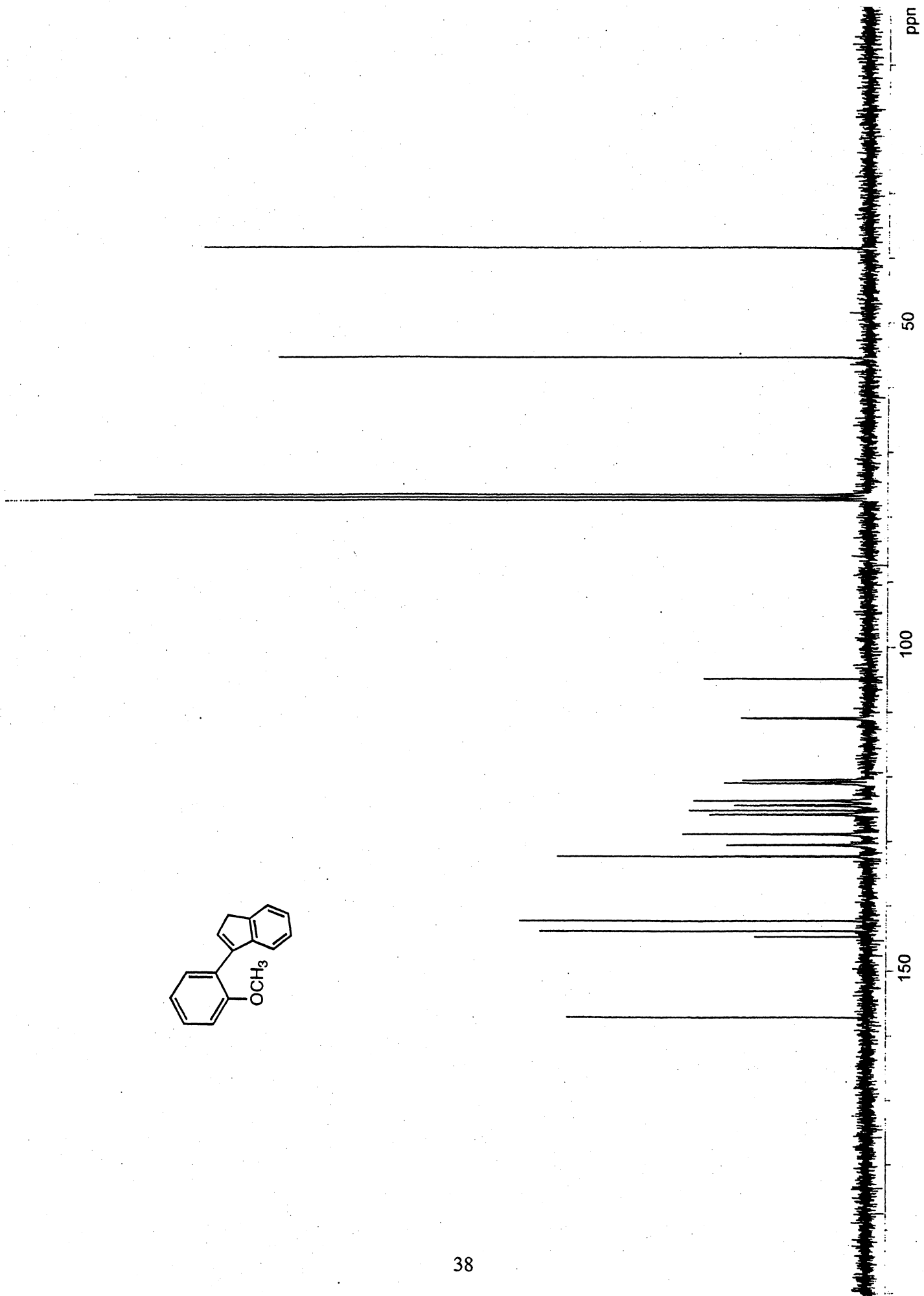
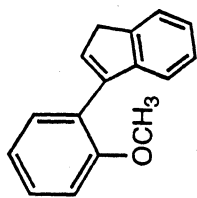


Figure 10. <sup>13</sup>C NMR Spectrum of 2-(1-indenyl) anisole (21)



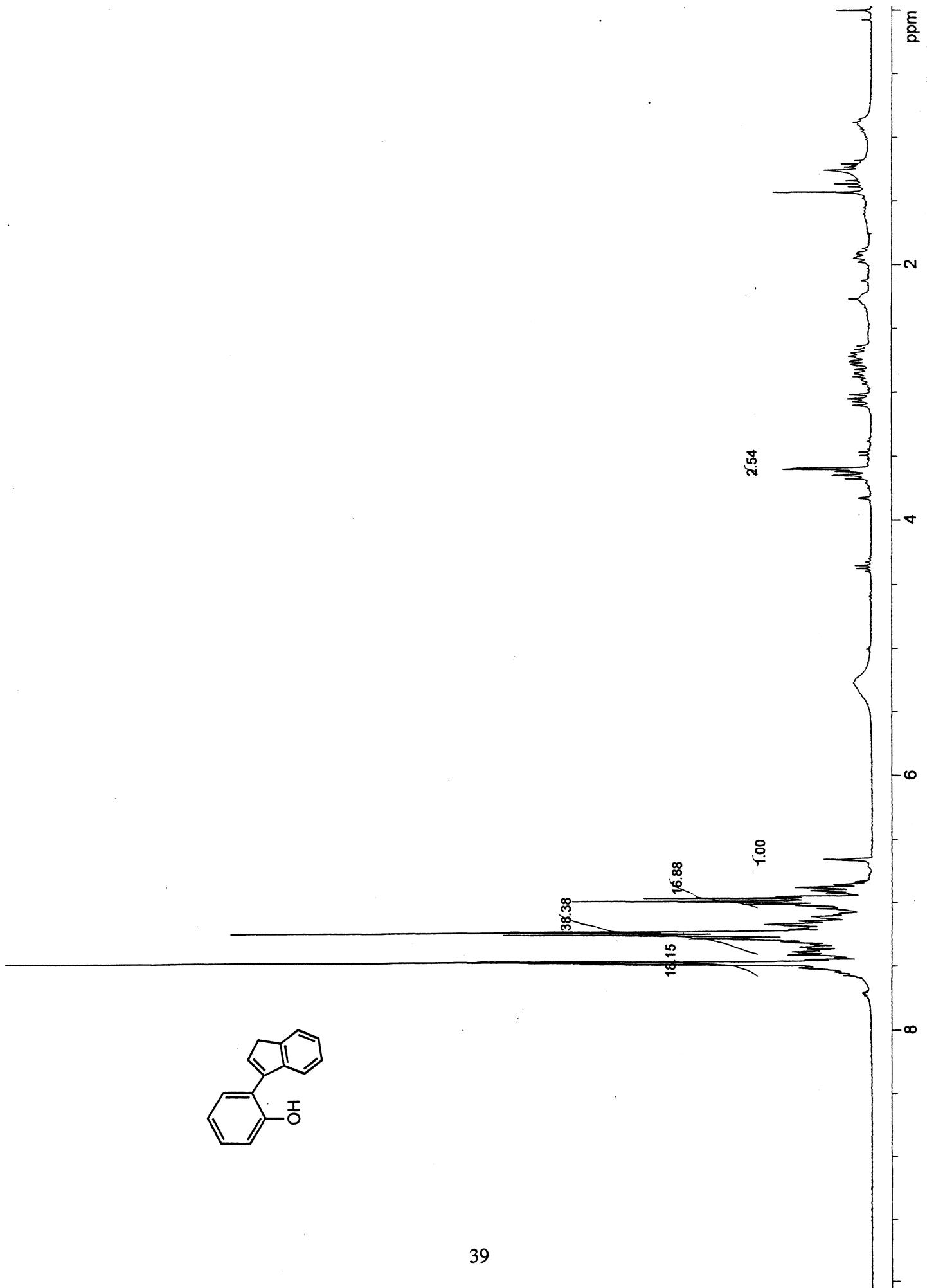
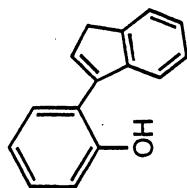


Figure 11. <sup>1</sup>H NMR Spectrum of 2-(1-indenyl) phenol (16)

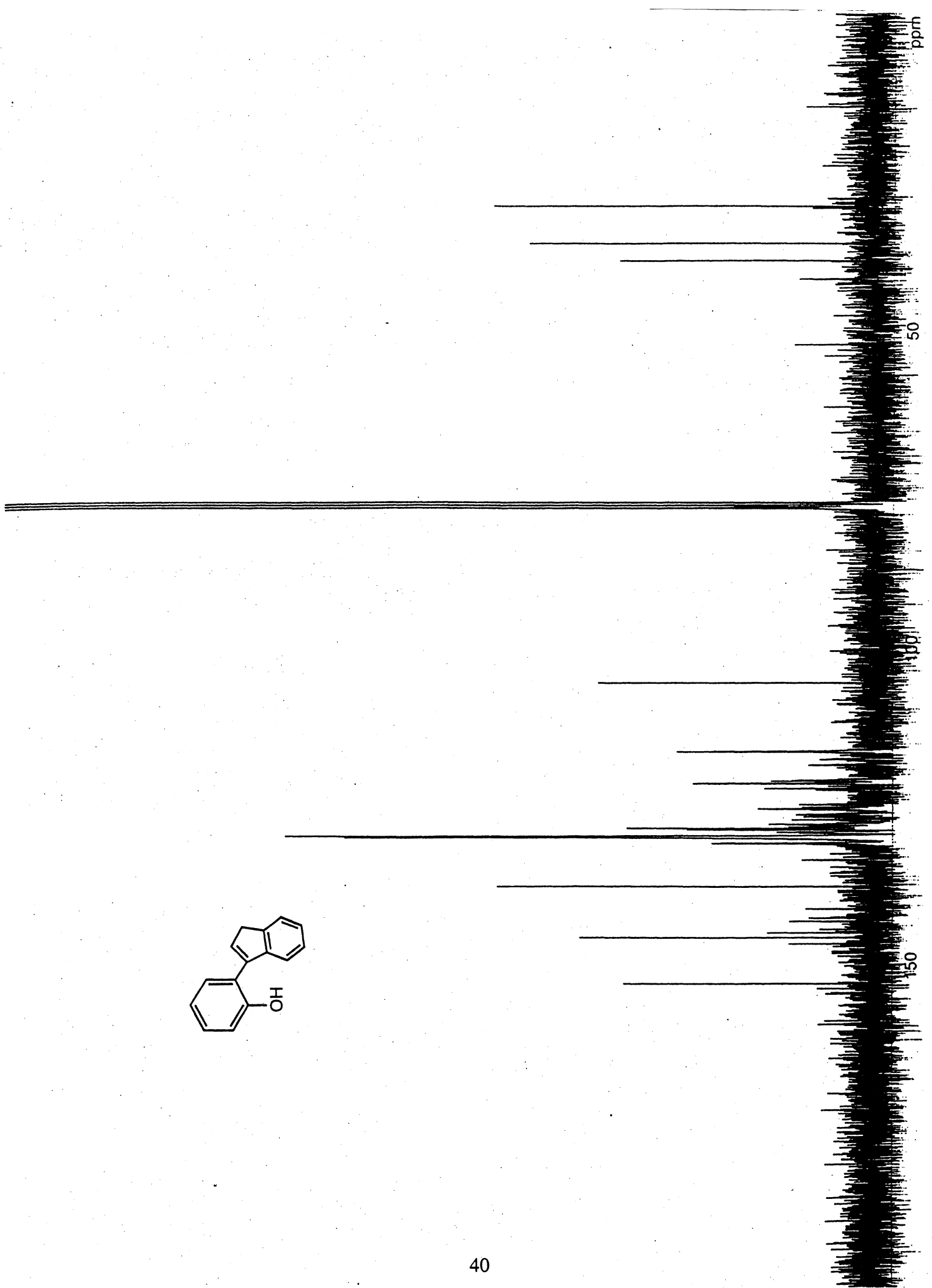
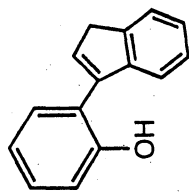


Figure 12.  $^{13}\text{C}$  NMR Spectrum of 2-(1-indenyl) phenol (16)