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The Synthesis of Benzyloxy Substituted DP-PPV and Examination of the Horner-Wadsworth-Emmons Reaction in the Synthesis of DP-PPV

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THE SYNTHESIS OF BENZYLOXY SUBSTITUTED DP-PPV AND EXAMINATION OF THE HORNER-WADSWORTH-EMMONS REACTION IN THE SYNTHESIS OF DP-PPV

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

By

JEREMY M. LEAR
B.S., Wright State University, 2012

2014
Wright State University

WRIGHT STATE UNIVERSITY

GRADUATE SCHOOL

May 28, 2014

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Jeremy M. Lear ENTITLED The Synthesis of Benzyloxy Substituted DP-PPV and Examination of the Horner-Wadsworth-Emmons Reaction in the Synthesis of DP-PPV. BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

Jeremy M. Lear, M.S., Department of Chemistry, Wright State University, 2014. The Synthesis of Benzyloxy Substituted DP-PPV and Examination of the Horner-Wadworth-Emmons Reaction in the Synthesis of DP-PPV.

In the interest of the synthesis of polymers that have the potential to possess inherent light-emitting properties (LEDs) the synthesis of a novel 1,4-bis(chloromethyl)-benzene monomer, 5-benzyloxy-1,4-dichloromethyl-2,3-diphenyl benzene was carried out. The monomer was polymerized via the Gilch polymerization method to yield, poly(5-benzyloxy-2,3-diphenylphenylene vinylene). The polymer was characterized by TGA (5% weight loss at 267°, GPC (weight average molecular weight of 7136 Da, number average molecular weight of 6603 Da), UV-Vis and fluorescence studies (absorbance maximum at 406 nm, emission maximum at 510 nm).

The Horner-Wadsworth-Emmons variant of the Wittig was applied in the synthesis of poly(2,3-diphenyl-1,4-phenylenevinylene) (DP-PPV) from 2,3-diphenylterephthalaldehyde and 1,4-bis(diethoxyphosphorylmethyl)-2,3-diphenyl benzene, which was synthesized via the Michaelis-Arbuzov reaction. Four trials were carried out to determine an optimal method for the order of addition of the monomers and base. The optimum polymer was characterized by TGA (5% weight loss of 319°), UV-Vis and fluorescence studies (absorbance maximum at 430 nm, emission maximum at 496 nm when excited at 416 or 424 nm).

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ACKNOWLEDGMENTS

I would like to give a special thanks to my advisor, Dr. William Feld for giving me the opportunity to work and develop in his group. His guidance, patience and teaching inspired me to work hard and to stay determined. I would not be the chemist, student, or person I am today if it were not for him and for that I am forever grateful.

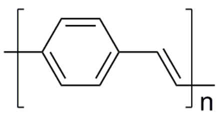
I would also like to acknowledge the faculty, staff, and graduate students of the Wright State Chemistry Department for all I have learned from them and experienced with them as a student over the past two years.

DEDICATION

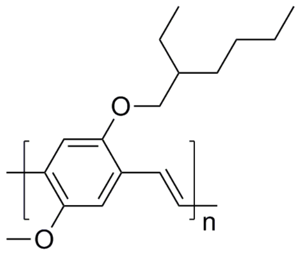
I would like to dedicate this work to my family; my parents, Kevin and Nancy, my brother and his family, Jordan, Star and Jaidyn, my Grandma Jane and my friends. Their friendship, love, and support has given me the strength and drive to achieve my goals. I cannot thank them enough for all they have given me.

INTRODUCTION

Organic conjugated polymer use in light emitting diodes (LEDs) has increased because of the ideal optoelectronic properties of the systems and the potential to reduce processing costs versus inorganic LEDs.[1-3] Of these, poly(phenylene vinylene) (PPV) **1** is promising, but solubility and processability issues exist, so to remedy this and to enhance physical properties, derivatives of **1** with alkoxy and phenyl groups, poly[2-methoxy-5-(2'-ethylhexoxy)-1,4-phenylenevinylene] **2** and poly(2,3-diphenyl-1,4-phenylenevinylene) **3**, respectively, have been synthesized.[4-8]



1



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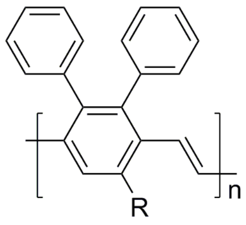


3

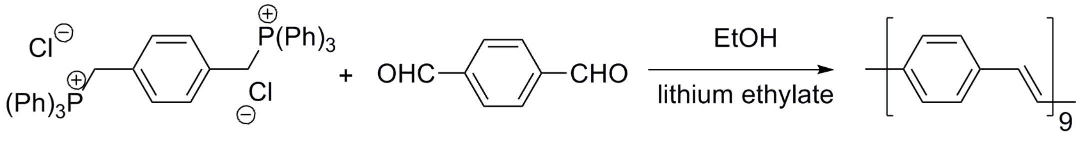
The synthetic steps that lead to **3** (R = H) enable modifications to the pendant phenyl rings and the main chain. The use of a protected phenol (benzyloxy group, R = OBn), would be expected to enhance optoelectronic properties and water solubility. Polymerization methods used in the syntheses of PPVs include sulfonium and chlorine precursor routes and the Wittig and Horner-Wadsworth-Emmons (HWE) reactions.[6, 9-12]

The objectives of this research were to 1) synthesize poly(5-benzyloxy-2,3-diphenylphenylene vinylene) **3** (R = OBn, OH) via a Gilch method, 2) to apply the HWE in the synthesis of **3** and 3) characterize the polymers.

HISTORICAL

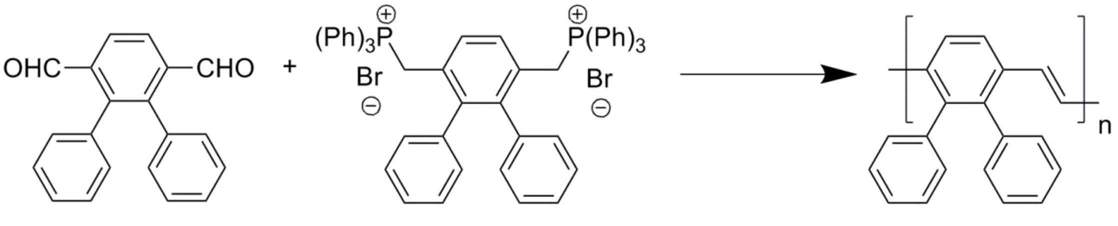
The Wittig and Horner-Wadsworth-Emmons Reactions

The utility of the Wittig reaction in polymerizations to yield fully conjugated systems was first demonstrated in 1960 by McDonald and Campbell in the synthesis of poly(phenylene vinylene) (PPV) **1**, from *p*-xylylene-bis(triphenylphosphonium chloride) **4** and terephthalaldehyde **5**. Polymer **1** was yellow in color, produced in quantitative yield, found to have a melting point above 400°C and had a number average molecular weight (M_n) of 1200 Da.[9]



4 **5** **1**

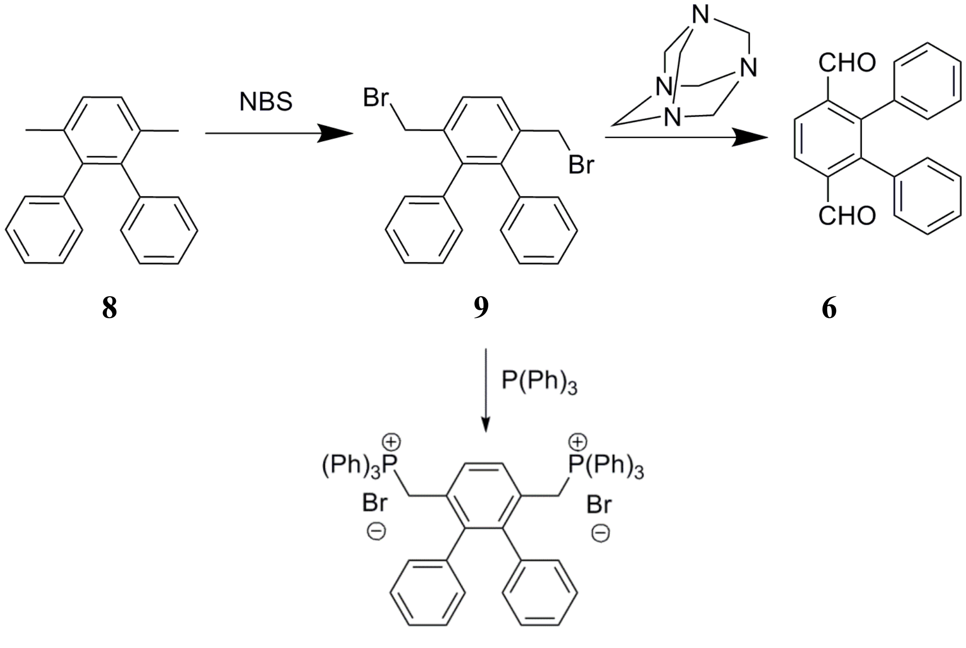
In 1982 Ganesan synthesized poly[(2,3-diphenyl-1,4-phenylene)vinylene] (DP-PPV) **3** via a phase transfer catalyzed Wittig between 2,3-diphenylterephthalaldehyde **6** and 2,3-diphenyl-p-xylene bis(triphenylphosphine bromide) **7**.[7]



6 **7** **3**

Production of **6** and **7** began with the synthesis of 1,4-dimethyl-2,3-diphenylbenzene **8** using a known procedure.[10] The benzylic positions of **8** were brominated using N-bromosuccinimide (NBS) to yield 1,4-bis(bromomethyl)-2,3-

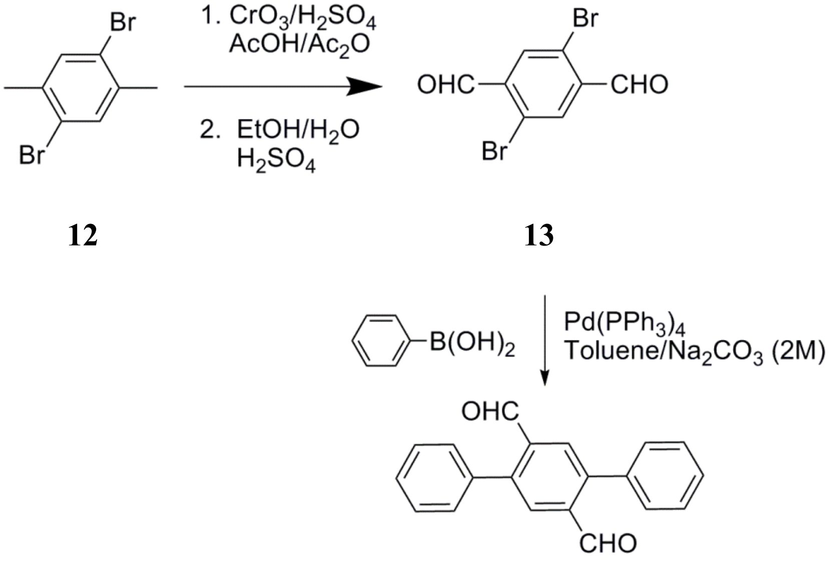
diphenylbenzene **9**, which was converted to **6** via the Sommelet reaction using hexamethylenetetramine and to **7** using triphenylphosphine.[7]



7

Polymerization of **6** and **7** resulted in a pale green fluorescent polymer **3** in 80% yield. Polymer **3** had an M_n of 1470 Da, $T_{d5\%}$ of 100° and an endotherm ranging between 150° and 300° on the DSC trace with decomposition occurring above 300°. It was also found that polymer **3** was soluble in chlorinated solvents, partially soluble in aliphatic ketones and had limited solubility in ethereal and higher alkane solvents.[7]

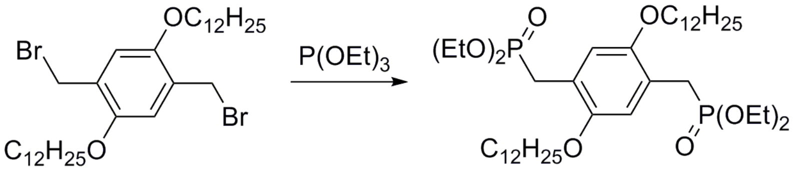
The Horner-Wadsworth-Emmons reaction was used by Wu et al. to produce the poly(2,5-diphenyl-1,4-phenylene-1,2-ethenylene-2,5-didodecyloxy-1,4-phenylene-1,2-ethenylene) (TP-PPV) **10**.[11] Synthesis of the monomer 1,1',4',1'']Terphenyl-2',5'-dicarbaldehyde **11**, began with the oxidation of the benzylic positions of 2,5-dibromo-1,4-xylene **12** to yield 2,5-dibromobenzene-1,4-dicarbaldehyde **13**. The reaction involves a tetraacetate intermediate that can be hydrolyzed. A Suzuki coupling reaction between **13** and phenylboronic acid yielded **11**.



12 **13**

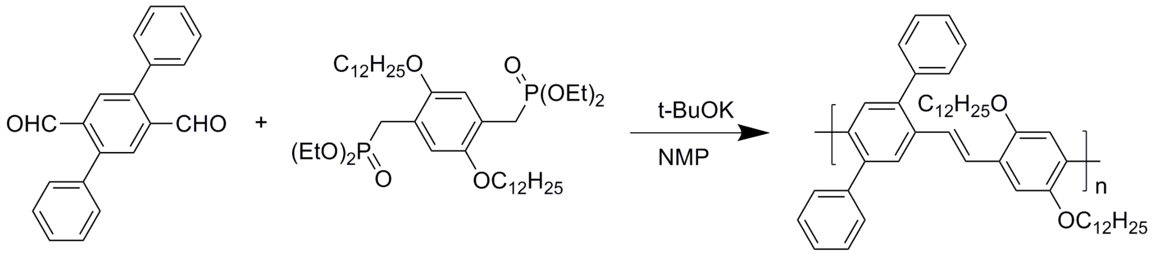
11

The other monomer, 2,5-didodecyloxy-p-xylylene-bis(diethylphosphonate) **14**, was made via the Michaelis-Arbuzov reaction between 1,4-bis(bromomethyl)-2,5-didodecyloxybenzene **15** and triethylphosphite.[12]



15 **14**

Synthesis of polymer **10** was achieved via the Horner-Wadsworth-Emmons polycondensation of **11** and **14**. The polymer was found to be fully soluble in chloroform and THF, had a weight-average molecular weight (M_w) of 16,100 Da, a PDI of 1.41, a $T_{d5\%}$ of 392° and had no transitions in the DSC. Thin films of **10** had a UV-Vis absorbance maximum at 470 nm and a corresponding PL emission at 554 nm (yellow light).[11]

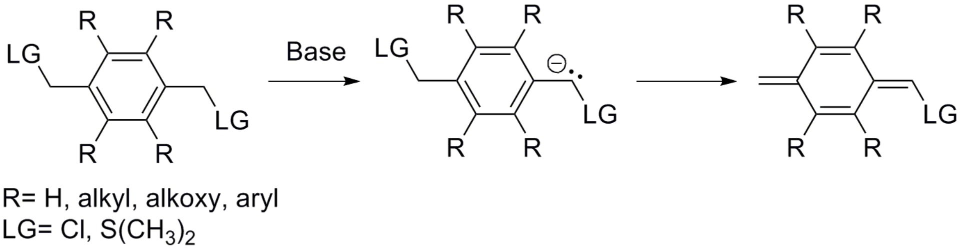


11 **14** **10**

Precursor Methods

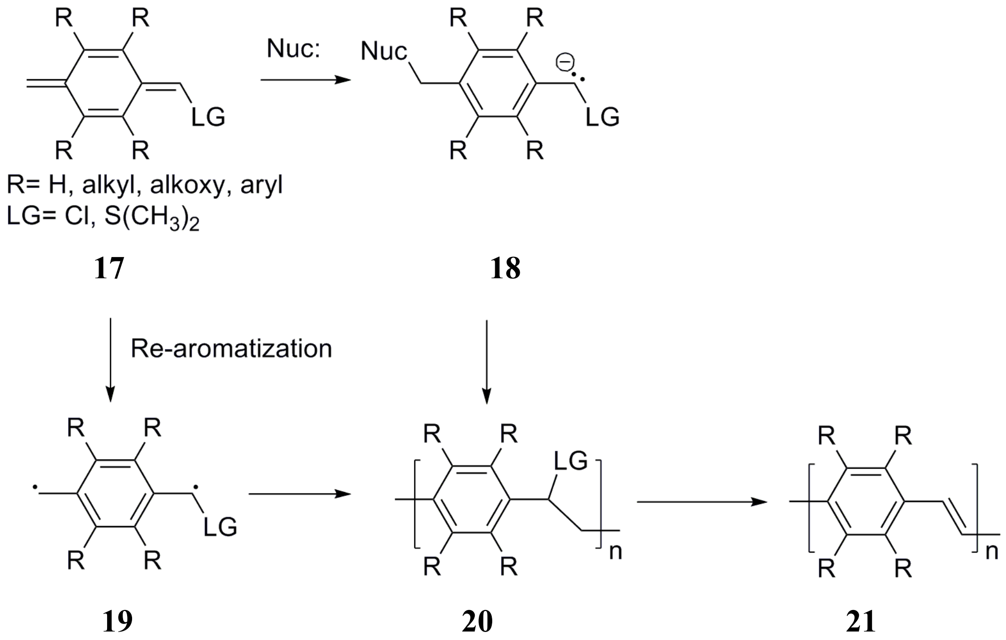
In an attempt to avoid premature precipitation of insoluble oligomers associated with the synthesis of fully conjugated polymers, precursor methods were developed.[13] Fully conjugated films can be produced via water or organic soluble precursor polymers that can be cast into films and chemically or thermally eliminated to varying degrees to yield the desired system.[13-15] The eliminated species can vary and the following are examples of the Sulfonium Salt Precursor (SPR) and the Chlorine Precursor (CPR) methods used to generate derivatives of PPV **1** and DP-PPV **3**.

A unique feature of the precursor methods is that they are mechanistically bimodal and can proceed through either a diradical or an anionic species.[16-18] The bimodal nature is a result of the 1,6 elimination that occurs when the base removes a proton from **16.** The anion charge is resonance stabilized through loss of one of the leaving groups (LG) to form the quinoid intermediate **17**, now a bifunctional monomer.



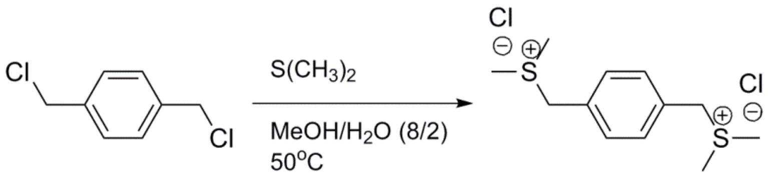
16 **17**

Intermediate **17** can either undergo nucleophilic attack to form the anion **18** or re aromatize to form the diradical **19**. Both mechanisms converge to yield the precursor polymer **20**, which can then be converted to **21** chemically or thermally.[16-18]



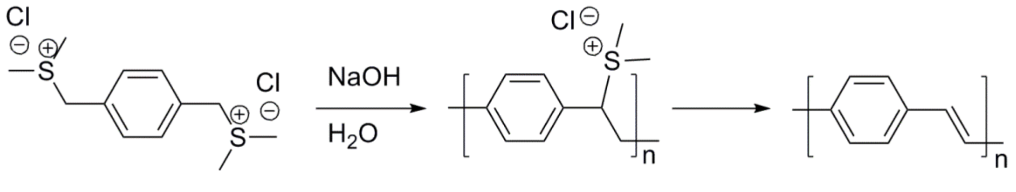
Sulfonium Salt Precursor Method

The Sulfonium Salt Precursor (SPR) method was employed by Gagnon et al. in 1986 to synthesize **1**.[13] The synthesis of the sulfonium salt monomer, *p*-xylylene-bis(dimethylsulfonium chloride) **22** was carried out by reacting α,α'-dichloro-*p*-xylylene **23** with excess dimethyl sulfide in methanol.



23 **22**

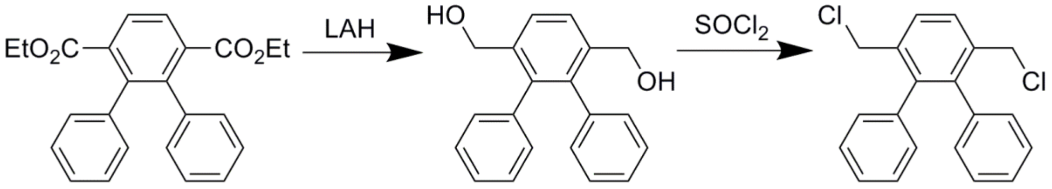
Polymerization of **22** to yield the water soluble, polyelectrolyte precursor, poly(*p*-xylylene-α-dimethylsulfonium chloride) **24**, was achieved by reacting **22** with sodium hydroxide in an aqueous solution. Films of **24** were wet cast and thermally converted to varying degrees to yield different types of **1** that varied in the degree of conjugation.[13]



22 **24** **1**

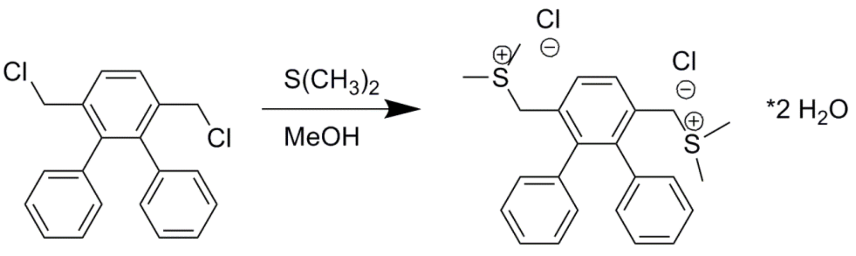
The molecular weights of **1** produced by this method varied between 15 kDa and 2 MDa and the degree of conjugation was tailored through varied thermal conversion. Films of completely conjugated **1** showed broad UV absorbances ranging from 300-500 nm.[13]

In 1989, Paulvannan synthesized films of DP-PPV **3** (R = H) from a water-soluble, sulfonium salt precursor polymer.[19] The multistep pathway began with the preparation of diethyl 2,3-diphenyl-1,4-benzenedicarboxylate **25** using a known method.[20] The ester functions of **25** were reduced using lithium aluminum hydride to form 1,4-bis(hydroxymethyl)-2,3-diphenylbenzene **26**. Reaction of **26** with thionyl chloride yielded 1,4-bis(chloromethyl)-2,3-diphenylbenzene **27**.



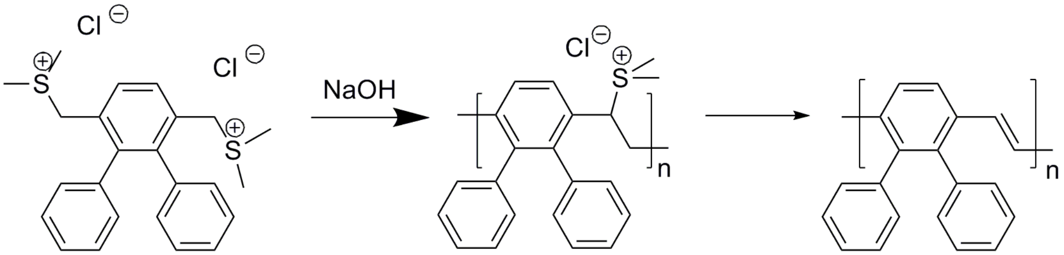
25 **26** **27**

The monomer 2,3-diphenyl-p-xylenebis(dimethylsulfonium chloride) **28** was prepared via the S_N2 reaction between **27** and dimethyl sulfide in methanol.



27 **28**

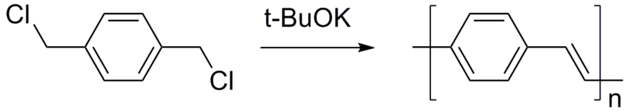
The base-catalyzed polymerization of **28** was carried out using sodium hydroxide in an aqueous media. The precursor polymer, poly(2,3-diphenyl-p-xylenebis(dimethylsulfonium chloride)) **29** was dialyzed (Cutoff of 25 kDa) against water to remove unreacted **28** and low molecular weight **29** to enhance film formation. After dialysis, films of **29** were cast onto Teflon wafers then thermally converted to **3** (R = H).[19]



28 **29** **3**

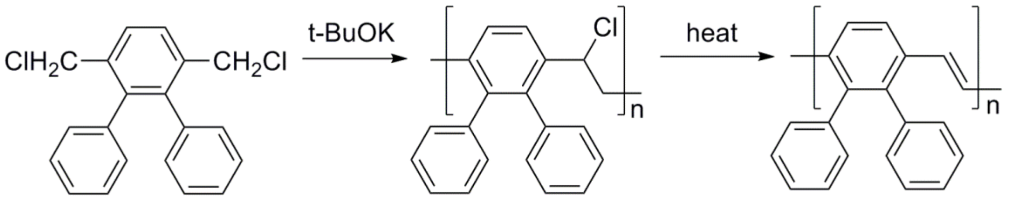
The Chlorine Precursor Method (Gilch and Modified Gilch Reactions)

In 1966, Gilch and Wheelwright first applied dehydrochlorination, removal of HCl, to polymerizations of α,α'-dichloro-*p*-xylene **30** using excess potassium *t*-butoxide. This polymerization became known as the Gilch reaction and is the basis of CPR.[21]



30 **1**

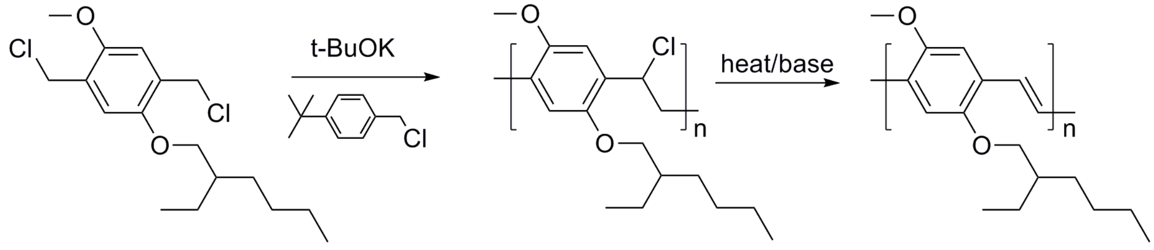
The effectiveness of CPR in the synthesis of **3** (R = H) was demonstrated by Wan et al. in 1997 when it was applied to **27** to form the soluble chlorine precursor, poly[(2,3-diphenyl-*p*-phenylene)(1-chloroethylene)] **31**, which was thermally converted to **3** (R = H) using temperatures between 100-300° for 2 h.[15]



27 **31** **3**

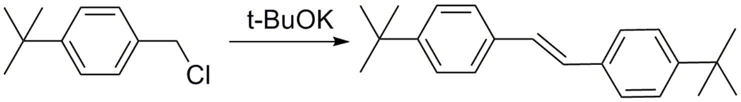
Data from *in situ* photoluminescent (PL) studies established that the conversion to a fully conjugated system was a function of heating temperature and not time of exposure.[15] Films of **31** and films that were converted at 100° to **3** (R = H) had similar absorption spectra and established that limited thermal conversion occurs at this temperature. When conversion took place at 150°, the PL data showed absorption at 390 nm, which signified that thermal conversion was ongoing. A red shift to 405 nm and 410 nm in the absorption spectra of films of **3** (R = H) was seen when conversion temperatures of 200° and 250° were used, however at 300° a blue shift in the spectrum and decreased intensity indicated decomposition of the films.[15]

In 1997, Hsieh et al. introduced a modification to the Gilch method that used the non-polymerizable acidic additive 4-*tert*-butylbenzyl chloride in CPR polymerizations of 1,4-bis(chloromethyl)-2-(2-ethylhexyl)-5-methoxybenzene **32**. As specified previously, the polymerization goes through a precursor polymer **33**, which was converted to **2**, with molecular weight limited by the 4-*tert*-butylbenzyl chloride.



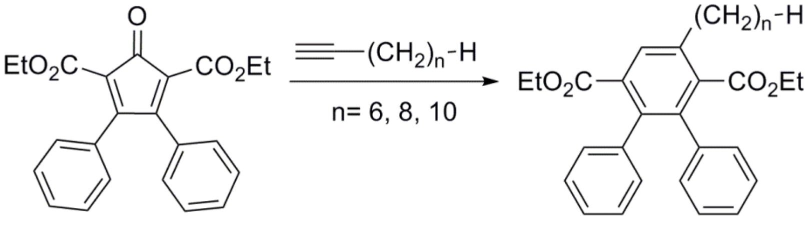
32 **33** **2**

This Modified Gilch reaction was formulated in an attempt to limit the gelation of **2** associated with regular CPR.[18] To examine this, polymerizations of **32** were carried out using increasing concentrations of 4-*tert*-butylbenzyl chloride. The molecular weight data showed that gelation was marginalized and M_w and M_n values decreased in accordance with increasing concentrations of 4-*tert*-butylbenzyl chloride. These results validated the use of the Modified Gilch reaction in CPR. However, one downside is that 4-*tert*-butylbenzyl chloride can react with itself forming 4,4'-di-*tert*-butylstilbene **34**, a low molecular weight by-product that may affect the integrity of the polymer films.[18,21]



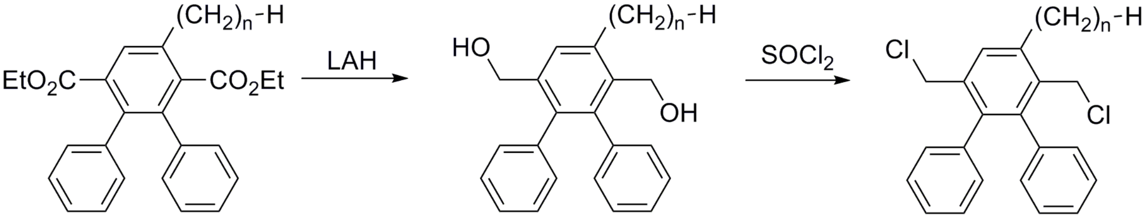
34

The Modified Gilch version of CPR was employed again by Hsieh et al. in 1998 for the synthesis of a family of soluble, main chain alkyl substituted systems of **3** (R = Alkyl).[21] Monomer synthesis began with the Diels-Alder cycloaddition of 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone **35** with either 1-octyne, 1-decyne, or 1-dodecyne to yield diethyl 5-hexyl-2,3-diphenylterephthalate **36a**, diethyl 5-octyl-2,3-diphenylterephthalate **36b**, and diethyl 5-decyl-2,3-diphenylterephthalate **36c**, respectively.



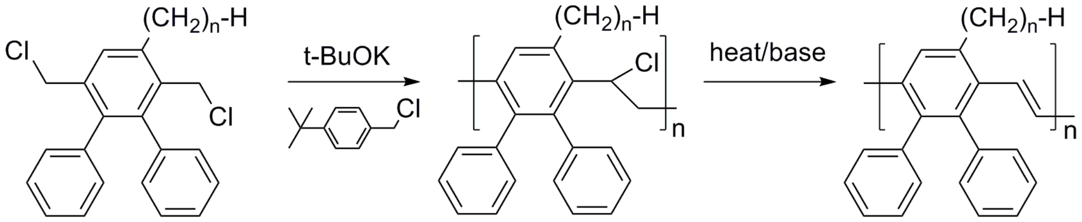
35 **36a-c**

The next step was the reduction of the ethyl ester functions of **36a-c** using LAH to yield 5-hexyl, 5-octyl, 5-decyl 1,4-bis(hydroxymethyl)-2,3-diphenylbenzene **37a-c**. The respective diols were reacted with $SOCl_2$ to yield the monomers 5-hexyl-, 5-octyl-, 5-decyl- 1,4-bis(chloromethyl)-2,3-diphenylbenzene **38a-c**.[21]



36a-c **37a-c** **38a-c**

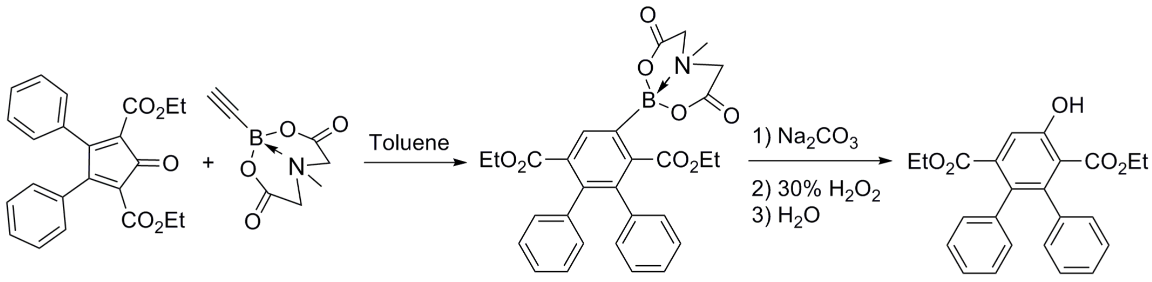
Polymerizations of **38a-c** were carried out using varying amounts of 4-*tert*-butylbenzyl chloride. The polymerization initially yields the respective precursor polymers, **39a-c**, which are converted to poly(5-hexyl-2,3-diphenylphenylene vinylene) poly(5-octyl-2,3-diphenylphenylene vinylene) and poly(5-decyl-2,3-diphenylphenylene vinylene), **40a-c**, respectively.[21]



38a-c **39a-c** **40a-c**

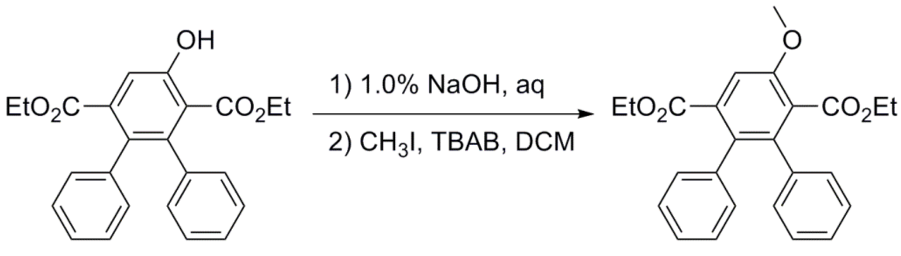
Similar results to those obtained in 1997 were obtained with respect to **40a**. As the concentration of 4-*tert*-butylbenzyl chloride was increased, the M_w and M_n decreased, but films could still be cast, so the utility of the additive was again demonstrated. However, it was found that with an increase in 4-tert-butylbenzyl chloride yields decreased. Thin films of **40a** were found to exhibit blue-green emission at 490 nm, which was blue shifted 10 nm compared to **3** (R = H), presumably by the steric effects generated by the hexyl pendant group. Another important result of the work was the demonstration that derivatives of **3** can be synthesized through variation of the alkyne used in the Diels-Alder reaction.[21]

The synthesis of alkoxy substituted derivatives of **3** (R = OR) was demonstrated in 2011 by Sayers et al. with the synthesis of methoxy substituted **3** using the CPR and the Modified Gilch reactions.[22] The method for introducing the alkoxy group into the monomer began with the Diels-Alder reaction, where **35** was reacted with the alkyne, ethynyl boronic acid MIDA ester **41** to yield diethyl 5-([N-methyliminodiacetato-O,O',N]borane)-2,3-diphenylterephthalate **42**. The C-B bond of **42** was oxidatively cleaved under alkaline conditions to produce the phenol, diethyl 5-hydroxy-2,3-diphenylterephthalate **43**.



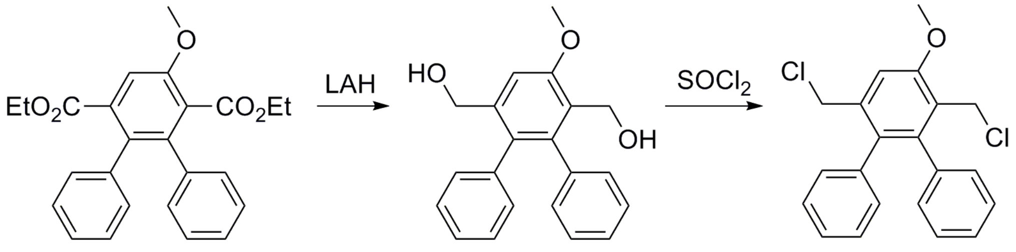
35 **41** **42** **43**

The next step in the synthesis was a phase transfer reaction involving **43** and methyl iodide to yield diethyl 5-methoxy-2,3-diphenylterephthalate **44**.[22]



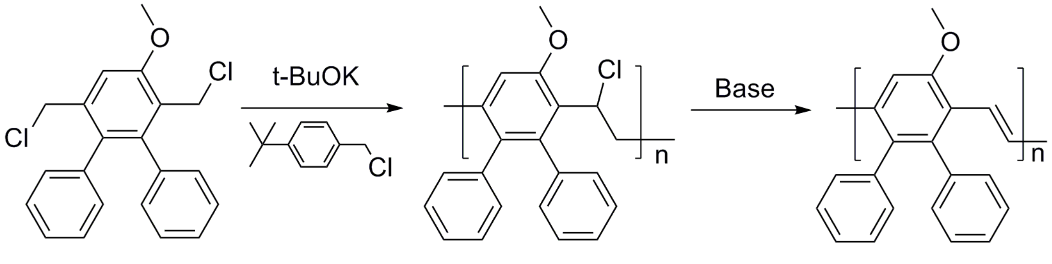
43 **44**

Compound **44** was reduced to 5-methoxy-1,4-bis(hydroxymethyl)-3,4-diphenylbenzene **45** then reacted with thionyl chloride to yield the monomer 5-methoxy-1,4-bis(chloromethyl)-3,4-diphenylbenzene **46**.



44 **45** **46**

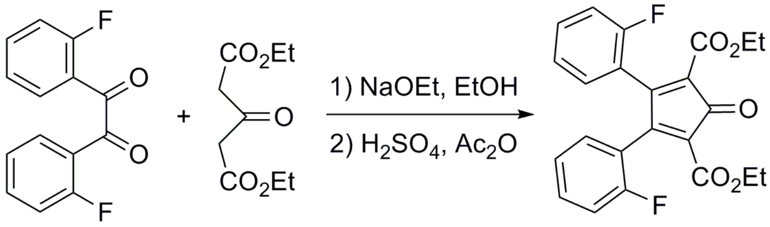
Monomer **46** was polymerized via the Modified Gilch to produce first the chlorine precursor, **47**, which was chemically converted *in situ* to poly(5-methoxy-3,4-diphenylbenzene) **3** (R = OMe). Portions of **3** (R = OMe), which was mostly an insoluble orange gel, were characterized using TGA and DSC, and showed a $T_{d5\%}$ of 381° and a T_g of 126°.[22]



46 **47** **3**

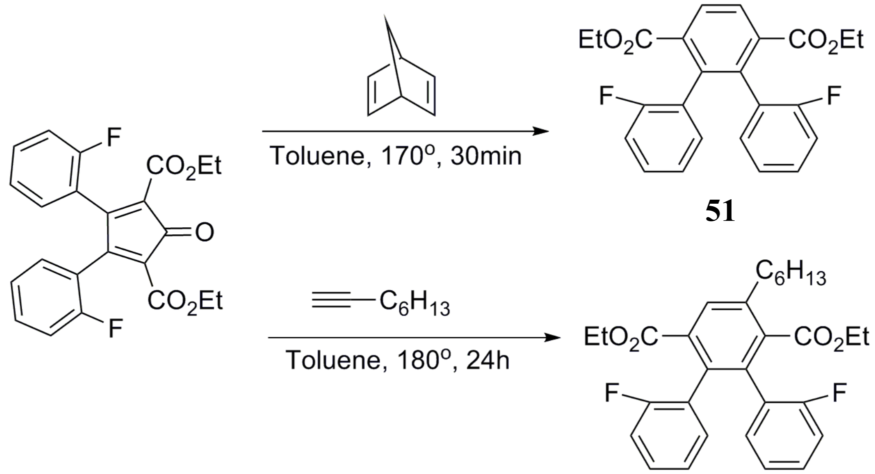
Along with variation of the alkyne used in the Diels-Alder, another method used to produce derivatives of **3** is the modification of the cyclopentadienone. Fogle et al.

demonstrated this in 2011 by the condensation reaction of 2,2'-difluorobenzil **48** and diethyl 1,3-acetonedicarboxylate **49** to yield 2,5-di(ethoxycarbonyl)-3,4-di(2-fluorophenyl)cyclopentadienone **50**.[23]



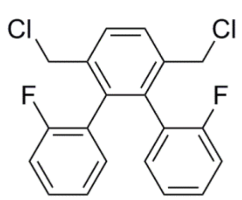
48 **49** **50**

A Diels-Alder cycloaddition was carried out using norbornadiene to convert **50** to diethyl 2,3-di(2-fluorophenyl)terephthalate **51**. The Diels-Alder was also used to generate diethyl 5-hexyl-2,3-di(2-fluorophenyl)terephthalate **52** from **50** and 1-octyne.

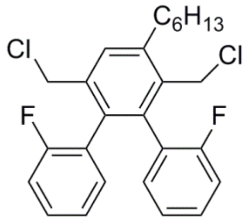


50 **52**

Subsequently,**51** and **52** were reduced and reacted with thionyl chloride to yield the monomers 1,4-di(chloromethyl)-2,3-di(2-fluorophenyl)benzene **53** and 5-hexyl-1,4-di(chloromethyl)-2,3-di(2-fluorophenyl)benzene **54**, respectively.[23]

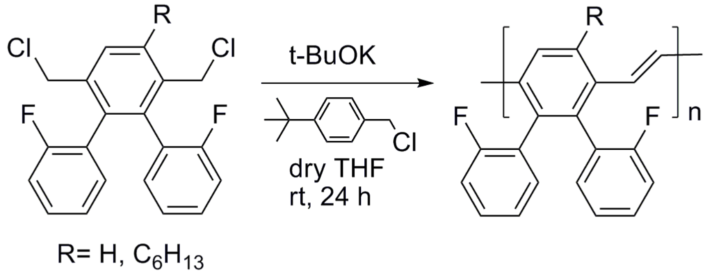


53



54

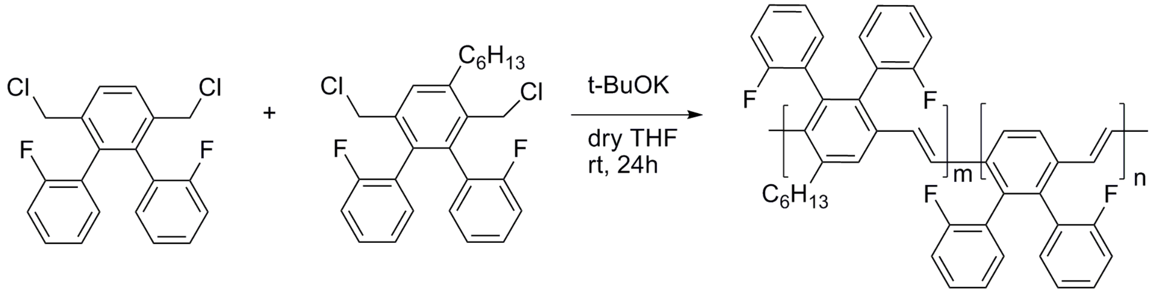
The polymerizations of **53** and **54** utilized the established Modified Gilch procedure to synthesize poly(2,3-bis(2-fluorophenyl)-*p*-phenylene vinylene) **55** and poly(2,3-bis(2-fluorophenyl)-5-hexyl-*p*-phenylene vinylene) **56**.



53, 54 **55, 56**

The analysis of polymers **55** and **56** showed that the additive, 4-*tert*-butylbenzyl chloride, was ineffective at limiting molecular weight. Even at high concentrations, the molecular weights were estimated to be above $3.0*10^5$ Da for **56** and gels resulted for **55**. The ineffectiveness could have resulted from the steric influences introduced by fluoro-substitution of the pendant phenyl rings.[23] Analysis of the TGA data showed that **55** had a $T_{d5\%}$ of 363° and **56** had a $T_{d5\%}$ of 400°. DSC analysis of **55** and **56** showed glass-transition temperatures (T_g) of 252° and 116°, respectively. UV-Vis studies of **56** indicated a blue-shifted spectrum compared to the spectrum of **40a**, which was attributed to the addition of the fluoro groups.[23]

Fogle also copolymerized monomers **53** and **54** using **54:53** feed ratios of 80:20 **57** and 60:40 **58**, which resulted in yields of 85% and 53%, respectively. The copolymerizations were completed without the use of 4-*tert*-butylbenzyl chloride, and resulted in no gelation or precipitation.

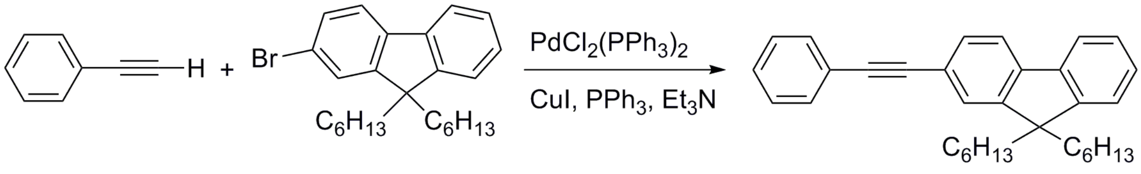


53 **54** **57, 58**

According to the GPC data gathered on **57**, similar molecular weights were obtained for this copolymer and for the polymer **56**, which used 4-*tert*-butylbenzyl chloride. TGA data also showed a $T_{d5\%}$ of 368° for **57** and DSC data established a T_g at 144°. With regards to **58**, the GPC spectrum showed two peaks suggesting that copolymerization may not have occurred at this feed ratio. That withstanding, TGA analysis of **58** resulted in $T_{d5\%}$ of 320° and DSC data resulted in a T_g at 152°.[23]

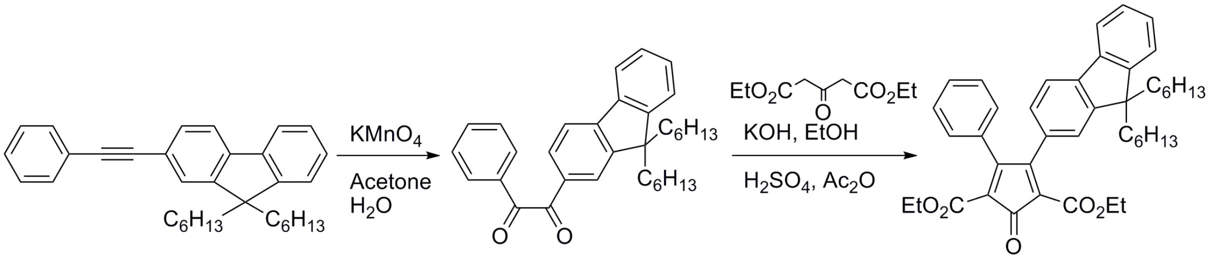
Modifications to the pendant phenyl rings also includes adding alkyl and alkoxy groups as demonstrated by Chen et al. in 2005.[24] The work focused on improving the luminescent properties of **3** by synthesizing derivatives that contained fluorene or 3,7-dimethyloctooxy substitutions on one of the rings, which increases solubility as previously mentioned and increases the steric effects in the systems. Also the CPR used by Chen utilized the Gilch reaction and the radical scavenger 2,6-di *tert* butylphenol, as opposed to 4-*tert*-butylbenzyl chloride.

Synthesis of the fluorene substituted monomer, 1,4-bis(chloromethyl)-2-phenyl-3-(9,9-dihexylfluoren-2-yl)benzene **59** began with the Sonogashira coupling of phenylacetylene **60** and 2-bromo-9,9-dihexylfluorene **61** to yield 9,9dihexyl-2-(2'-phenyl-1-ethynyl)fluorene **62**. Oxidation of the triple bond of **62** using potassium



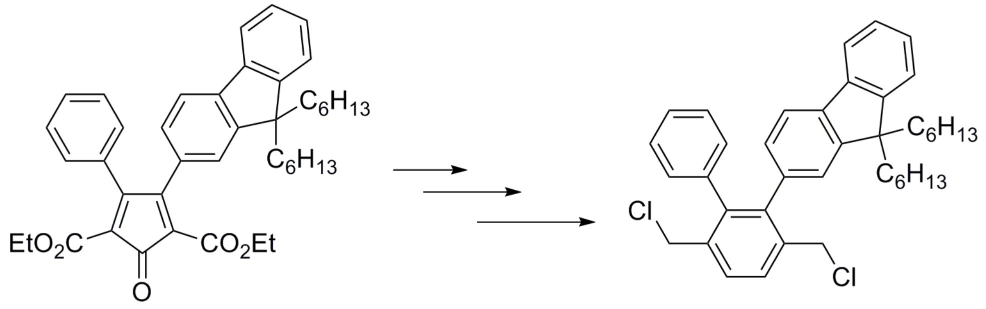
60 **61** **62**

permanganate ($KMnO_4$) was carried out to yield 1-(9,9-dihexyl-2-fluorenyl)-2-phenyl-1,2-ethanedione **63**, which was reacted with ethyl-1,3-acetonedicarboxylate to produce diethyl-4-(9,9-dihexyl-2-fluorenyl)-2-oxo-5-phenyl-3,5-cyclopentadiene-1,3-dicarboxylate **64**.[24]



62 **63** **64**

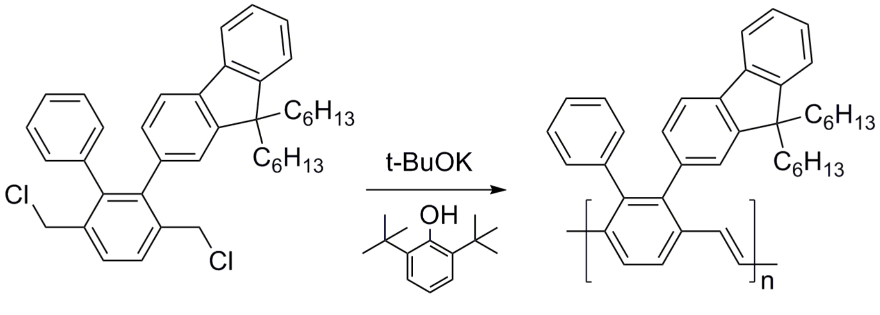
In accordance with the CPR outlined, **64** underwent a Diels-Alder reaction with norbornadiene, was reduced using LAH and reacted with $SOCl_2$ to yield **59**.



64 **59**

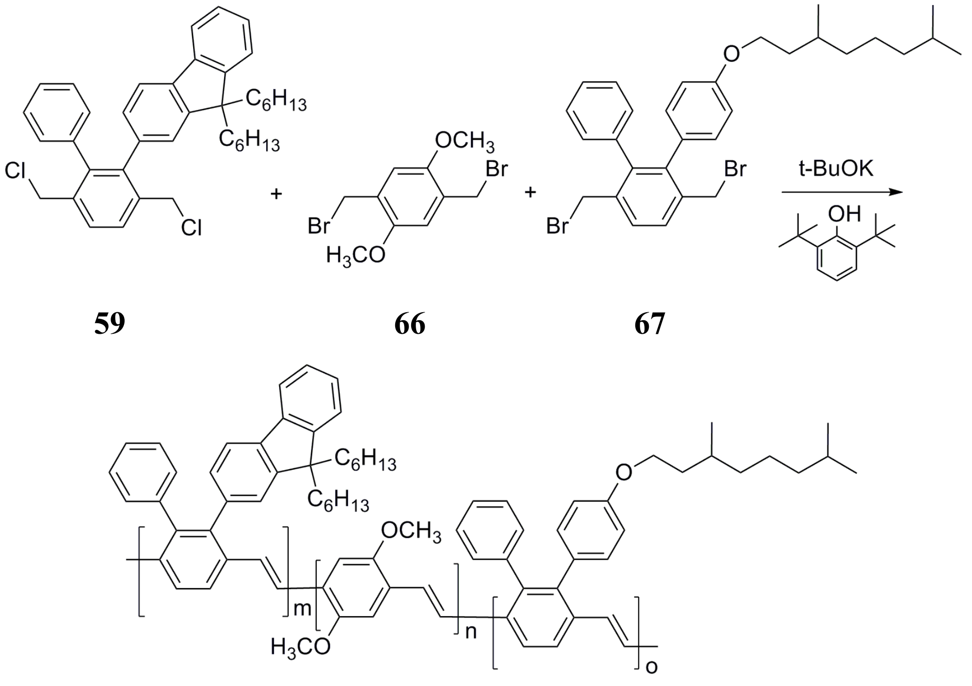
Monomer **59** was homopolymerized to yield poly(2-phenyl-3-(9,9-dihexylfluoren-2-yl)phenylene vinylene) **65**, which had an M_w/M_n ratio of $5.14*10^5$ Da/

3.74×10^5 Da and films exhibited a T_g of 178°, UV-Vis absorption maximum at 444 nm and PL emission at 498 nm.[24]



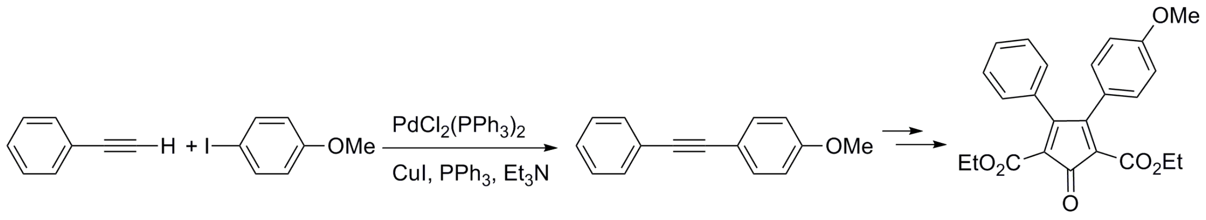
59 **65**

Monomer **59** was copolymerized with variable amounts of 1,4-bis(bromomethyl)-2,5-dimethoxybenzene **66** and 1,4-bis(bromomethyl)-2-[4'-(3,7-dimethyloctoxy)pheny]-3-phenylbenzene **67**, to yield the copolymer **68**. Copolymer **68** made with **59** (80%), **66** (10%),and **67** (10%) was found to have an M_w/M_n ratio of 4.55×10^5 Da/ 3.9×10^5 Da and films exhibited a T_g of 136°, UV-Vis absorption maximum at 450 nm and PL emission at 539 nm.[24]



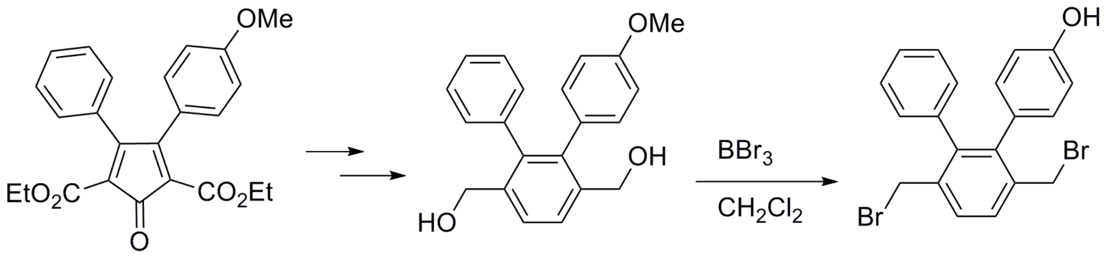
68

Chen also synthesized monomer **67** starting with the Sonogashira reaction between **60** and 4-iodoanisole **69** to yield 1-methoxy-4-(2’-phenyl-1-ethynyl)benzene **70**. Subsequent oxidation and condensation reactions of **70** were carried out to yield 2,5-dicarbethoxy-3-(4’-methoxyphenyl)-4-phenylcyclopentadienone **71**.[24]



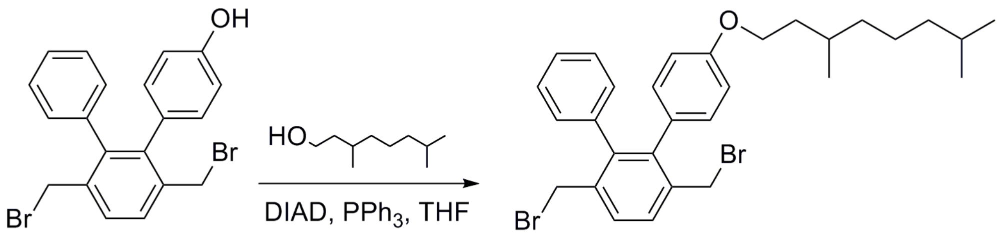
60 **69** **70** **71**

Compound **71**was reacted using the Diels-Alder reaction then reduced with LAH to yield 1,4-bis(hydroxymethyl)-2-(4’-methoxyphenyl)-3-phenylbenzene **72**. The bromination of the hydroxyl groups and demethylation of the methyl-aryl-ether occurred by reacting **72** with boron tribromide (BBr_3) to yield 1,4-bis(bromomethyl)-2-phenoxy-3-phenylbenzene **73**.



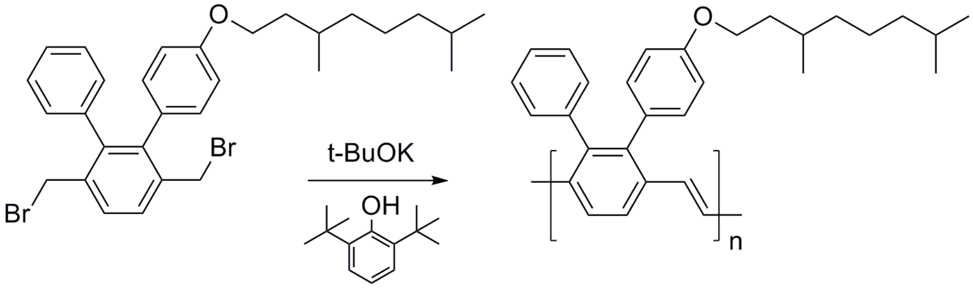
71 **72** **73**

The next step was the Mitsunobu reaction between **73** and 3,7-dimethyloctanol, using triphenylphosphine (PPh_3) and diisopropyl azodicarboxylate (DIAD), to form the alkyl-aryl-ether of monomer **67**.[24]

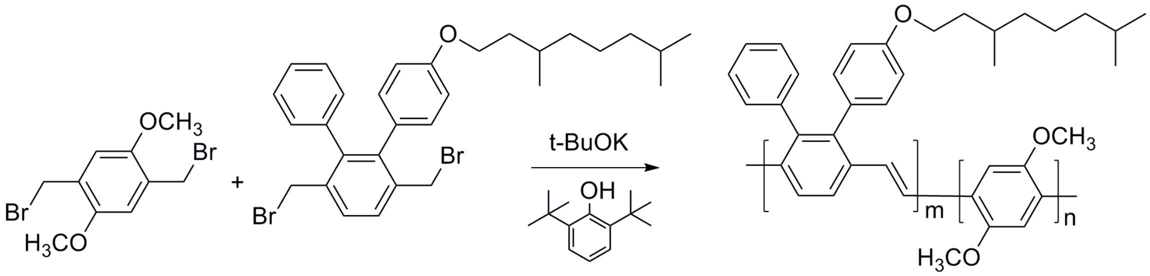


73 **67**

Monomer **67** was homopolymerized to yield poly(2-[4’-(3,7-dimethyloctoxy)pheny]-3-phenylphenylene vinylene) **74**, which had an M_w/M_n ratio of $4.27*10^5$ Da/ $2.78*10^5$ Da and films exhibited a T_g of 145°, UV-Vis absorption maximum at 436 nm and PL emission at 498 nm.



67 **74**



66 **67** **75**

Monomer **67** was also copolymerized with **66** using feed ratios of **67:66** (90:10) to yield the copolymer **75**, which was found to have an M_w/M_n ratio of $3.97*10^5$ Da/ $2.09*10^5$ Da and films exhibited a T_g of 145°, UV-Vis absorption maximum at 441 nm and PL emission at 545 nm.[24]

The purpose of this research was 1) to synthesize main chain substituted benzyloxy (R = OBn) DP-PPV via the Gilch method, 2) to explore the utility of the Horner-Wadsworth-Emmons reaction as a polymerization technique for DP-PPV, and 3) to characterize intermediates and products by melting point, ^1H and ^{13}C NMR, IR, elemental analysis, TGA, DSC, GPC, and UV-VIS/Fluorescence studies.

Experimental

Instrumentation and Chemicals

Melting points were obtained with a DigiMelt MPA-160 or Electrothermal MP Apparatus. Nuclear magnetic resonance (NMR) ^{1}H and ^{13}C spectra were obtained using a Bruker Avance 300 MHz NMR Spectrometer. Solvents for NMR were $CDCl_3$, DMSO-d_6, and Acetone-d_6. Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) spectra were obtained with a TA TGA Q 500 and a TA DSC Q 200 both employing a N_2 atmosphere. Infrared (IR) spectra were recorded as thin films (NaCl) with a Nicolet 6700 FT-IR spectrometer. Elemental analyses were obtained through Midwest Microlab, LLC, Indianapolis, IN. Chemicals were purchased from Aldrich and used as received.

Diethyl 5-([N-methyliminodiacetato-O,O',N]borane)-2,3-diphenylterephthalate 42

Toluene (16 mL), ethynylboronic acid MIDA ester **41** (0.548 g, 3.03 mmol), and 2,5-dicarboethoxy-3,4-diphenylcyclopentadienone **35** (1.14 g, 3.03 mmol) were combined in a Q-tube™ and stirred for 5 min and then heated at 170° for 18-24 h. The Q-tube was cooled to RT and the product was filtered, washed with methanol (3 X 10 mL), dried under vacuum and recrystallized from ethanol to yield **42** as a white solid (1.21 g, 2.29 mmol, 75.6%): mp 280-282° (Lit.[22] 222.8-223.7°); IR (NaCl, cm^{-1}) 1711 (**C=O**), 1774 (**C=O**), 2981 (**Ali CH**), 3030 (**Ar CH**); ^{1}H NMR (300 MHz, acetone-d_6, δ) 0.74 (t, J = 7.17 Hz, 3H, $CO_2CH_2\mathbf{CH_3}$), 0.84 (t, J = 7.13 Hz, 3H, $CO_2CH_2\mathbf{CH_3}$), 3.14 (s, 3H, N-$\mathbf{CH_3}$), 3.81(q, J = 7.16 Hz, 2H, $CO_2\mathbf{CH_2}CH_3$), 3.93 (q, J = 7.12 Hz, 2H, $CO_2\mathbf{CH_2}CH_3$), 4.27 (d, J = 17.19 Hz, 2H, N-**CH_2**), 4.44 (d, J = 17.23 Hz, 2H, N-**CH_2**), 7.00-7.16 (m, 10 H, **Ar CH**), 8.00 (s, 1H, **Ar CH**); ^{13}C NMR (75 MHz, acetone-d_6, ppm) 13.58, 13.86, 50.30, 61.32, 61.83, 64.79, 127.41, 127.60, 127.94, 128.02, 130.66, 131.29, 134.20, 134.59, 139.30, 139.99, 142.15, 142.22, 169.17, 169.38, 172.16. Anal Calcd. for $C_{29}H_{28}BNO_8$: C, 65.80; H, 5.33. Found: C, 65.51; H, 5.29.

Diethyl 5-hydroxy-2,3-diphenylterephthalate 43

A solution of **42** (0.964 g, 1.82 mmol) in ethanol (250 mL) was placed in a 500 mL, round-bottomed flask equipped with a condenser and heated/stirred at 78° for 20 min. The mixture was cooled to RT and Na_2CO_3 (0.207 g, 1.95 mmol) and a 30% H_2O_2 solution (35 mL, 350 mmol) were added and the mixture was stirred for 3 h at RT. The crude product was extracted using ethyl acetate and recrystallized from ethanol. The product was dried under vacuum to yield **43** as a white solid (0.608 g,1.56 mmol, 85.6%): mp 107.2-108.9° (Lit.[22] 108.1-108.7°); IR (NaCl, cm^{-1}) 1135 (**C-O**), 1670 (**C=O**), 1719 (**C=O**), 2917 (**Ali CH**); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 0.68 (t, J = 7.16 Hz, 3H, CO_2CH_2**CH_3**), 0.92 (t, J = 7.13 Hz, 3H, CO_2CH_2**CH_3**), 3.93 (q, J = 7.16 Hz, 2H, CO_2**CH_2**CH_3), 3.99 (q, J = 7.13 Hz, 2H, CO_2**CH_2**CH_3), 6.88-7.11 (m, 10H, **Ar CH**), 7.38 (s, 1H, **Ar CH**), 10.70 (s, 1H, Ar-**OH**); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 12.83, 13.53, 61.23, 61.34, 115.22, 116.87, 126.23, 126.32, 126.90, 127.02, 129.51, 130.33, 132.57, 138.29, 138.61, 140.36, 144.08, 159.85, 167.84, 170.53. Anal Calcd. for $C_{24}H_{22}O_5$: C, 73.83; H, 5.68. Found: C, 72.58; H 5.83.

Diethyl 5-benzyloxy-2,3-diphenylterephthalate 76

A solution of **43** (1.003 g, 2.57 mmol), KI (0.056 g, 0.34 mmol) and K_2CO_3 (0.759 g, 5.49 mmol) in DMF (10 mL) was placed in a 50 mL, round-bottomed flask and heated to 80°. Benzyl chloride (0.5 mL, 4.35 mmol) was added, the solution was heated for 3 h at 80°, cooled to RT, precipitated in deionized water and stirred for 18 h. The crude product was extracted using ethyl acetate, recrystallized from ethanol and dried under vacuum to yield **76** as a white solid (0.831 g, 1.73 mmol, 67.4 %): mp 113.2-114.1° (Lit.[22] 111.9-113.7°); IR (NaCl, cm^{-1}) 1127 (**C-O**), 1732 (**C=O**), 2982 (**Ali CH**), 3059 (**Ar CH**); ^1H NMR (300 MHz, $CDCl_3$, δ) 0.86 (t, J = 7.14 Hz, 3H, $CO_2CH_2\mathbf{CH_3}$), 0.93 (t, J = 7.14 Hz, 3H, $CO_2CH_2\mathbf{CH_3}$), 3.97 (q, J = 7.13 Hz, 2H, $CO_2\mathbf{CH_2}CH_3$), 4.02 (q, J = 7.12 Hz, 2H, $CO_2\mathbf{CH_2}CH_3$), 5.23 (s, 2H, Ph**CH₂**OR), 6.93-7.49 (m, 16H, **Ar CH**); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 13.44, 13.67, 61.13, 70.78, 112.31, 126.43, 127.02, 127.14, 127.20, 127.28, 127.84, 128.00, 128.56, 130.01, 130.07, 134.16, 134.38, 136.31, 137.53, 138.82, 141.09, 153.94, 166.72, 168.29. Anal Calcd. for $C_{31}H_{28}O_5$: C, 77.48; H, 5.87. Found: C, 77.57; H 5.79.

5-benzyloxy-1,4-bis(hydroxymethyl)-2,3-diphenylbenzene 77

A slurry of LAH (0.409 g, 10.8 mmol) in THF (25 mL) was prepared in a 100 mL, three-necked, round-bottomed flask equipped with a condenser and cooled to 0°. A solution of **76** (1.00 g, 2.08 mmol) in THF (25 mL) was added dropwise. The mixture was warmed to RT and stirred for 1 h, heated at 70° for 12 h then cooled to RT. Water (0.5 mL) was added dropwise and the mixture was stirred for 0.5 h. A 15% (w/v) NaOH solution (0.450 g NaOH in 3.0 mL H_2O) and an additional aliquot of H_2O (2 mL) were added, the mixture stirred for 0.5 h, and the THF was evaporated. The crude product was stirred with a 10% (v/v) H_2SO_4 solution (60 mL) for 1 h, filtered and air-dried. The product was recrystallized from ethanol to yield **77** as a white solid (0.619 g, 1.56 mmol, 74.8%): mp 165.4-167.6° (Lit.[22] 170.2-171.0°); IR (NaCl, cm^{-1}) 1124 (**C-O**), 1590 (**Ar**

C=C), 2980 (**Ali CH**), 3426 (broad, strong, -**OH**); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 4.46 (2H, **CH$_2$**OH), 4.52 (2H, **CH$_2$**OH), 5.29 (s, 2H, Ph**CH$_2$**OR), 6.95-7.53 (m, 16H, **Ar CH**); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 58.97, 63.60, 70.54, 109.87, 126.46, 126.50, 127.41, 127.53, 127.64, 128.25, 128.80, 130.21, 130.34, 133.28, 136.64, 138.68, 138.76, 139.58, 142.86, 156.84. Anal Calcd. for $C_{27}H_{24}O_3$: C, 81.79; H, 6.10. Found: C, 81.65; H 6.39.

General Procedure for the Reaction of 1,4-bis(hydroxymethyl)-2,3-diphenylbenzene Derivatives with Thionyl Chloride

In a 10 mL, round-bottomed flask equipped with a drying tube, $SOCl_2$ (1.3 mL, 17.9 mmol) was added dropwise to the appropriate diol (0.4892 g, 1.23 mmol). The mixture was stirred at RT for 16-24 h. The reaction mixture was precipitated in H_2O (25 mL), stirred for 2 h and the crude tan product was filtered and dried under vacuum. The product was purified by column chromatography (silica) using chloroform to yield a brown oil which was dried under vacuum to yield a tan solid.

1,4-bis(chloromethyl)-2,3-diphenyl benzene 27

The compound was obtained as a tan solid (2.0273 g, 6.2 mmol, 88.6%): mp 96.4-98.2° (Lit.[2] 97-99°); IR (NaCl, cm^{-1}) 701 (**sym C-Cl**), 760 (**asym C-Cl**), 2959 (**Ali CH**), 3017 (**Ar CH)**; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 4.40(s, 2H, **CH$_2$**Cl), 7.05-7.2 (m, 10 H, **Ar CH**), 7.65 (s, 1H, **Ar CH**); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 44.55, 126.91, 127.57, 129.47, 130.06, 136.06, 137.98, 141.94. Anal Calcd. for $C_{20}H_{16}Cl_2$: C, 73.40; H, 4.93. Found: C, 73.57; H 5.05.

5-benzyloxy-1,4-bis(chloromethyl)-2,3-diphenylbenzene 78

The compound was obtained as a tan solid (0.446 g, 1.03 mmol, 83.6%): mp 104.8-108.2° (Lit.[22] 110.6-111.7°); IR (NaCl, cm^{-1}) 759 (**sym C-Cl**), 851 (**asym C-Cl**), 1591 (**Ar C=C**), 2925 (**Ali CH**), 3058 (**Ar CH)**; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 4.37 (s, 2H, **CH$_2$**Cl), 4.48 (s, 2H, **CH$_2$**Cl), 5.30 (s, 2H, Ph**CH$_2$**OR), 6.99-7.58 (m, 16 H, **Ar CH**); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 39.55, 44.88, 70.49, 112.20, 125.20, 126.71, 126.88, 127.30, 127.43, 127.55 128.05, 128.66, 130.01, 130.51, 134.51, 136.67, 137.14, 138.05, 143.99, 156.39. Anal Calcd. for $C_{27}H_{22}Cl_2O$: C, 74.83; H, 5.12. Found: C, 75.11; H 5.23.

1,4-bis(diethoxyphosphorylmethyl)-2,3-diphenylbenzene 79

A mixture of **27** (3.738 g, 11.42 mmol) and triethyl phosphite (6 mL, 35 mmol) was placed in a 50 mL, round-bottomed flask equipped with a condenser and heated to 175° in a sand bath, Ethyl chloride was evolved. The mixture was refluxed at 175° for 6.5 h then cooled to RT. Excess triethyl phosphite was removed under vacuum to yield a tan oily powder. The crude product was stirred in hexanes/ethyl acetate overnight, filtered, washed (2 x 5 mL hexanes), and dried under vacuum to yield a tan solid (5.576 g, 10.51 mmol, 92 %): mp 89.2-90.9°; IR (NaCl, cm^{-1}) 961 (**P-O**), 1027 (**P-O**), 1052 (**P-O**), 1250 (**P=O**), 2906 (**Ali CH**), 2981 (**Ar CH**); ^{1}H NMR (300 MHz, CDCl$_3$, δ) 1.24 (t, 6 H, J = 7.05 Hz, P(=O)-OCH$_2$**CH$_3$**), 3.00 (d, 2 H, J = 20.8 Hz, Ph-**CH$_2$**-P(=O)), 3.97 (q, 4 H, J = 7.2 Hz, P(=O)-O**CH$_2$**CH$_3$), 6.97-7.14 (m, 5 H, **Ar CH**), 7.57 (s, 1 H, **Ar CH**); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 16.28 and 16.36 (d, J = 5.6 Hz), 29.87 and 31.71 (d, J = 138.5 Hz), 61.80 and 61.88 (d, J = 6.3 Hz), 126.33, 127.33, 128.67, 129.06, 130.51, 139.53, 142.45. Anal Calcd. for $C_{28}H_{36}O_6P_2$: C, 63.39; H, 6.84. Found: C, 63.54; H 6.84.

Poly(5-benzyloxy-2,3-diphenyl phenylene vinylene) 80

Into a 25 mL, three-necked, round-bottomed flask was placed a solution of **78** (0.200 g, 0.461 mmol) and anhydrous THF (10 mL) that was cooled to 0° under N$_2$. A solution of KO^{t}But (3 mL of 1.0 M in THF, 3 mmol) was added rapidly to the solution that began to turn yellow. The solution was stirred at RT for 24 h to produce a yellow solution with an orange gel precipitate. The polymer was precipitated into methanol (200 mL) and stirred for 2 h, filtered and dried. The polymer was redissolved in chloroform and the insoluble portions (orange) were filtered and the filtrate was evaporated in vacuo to yield **81** as a yellow solid (0.1224 g, 0.340 mmol, 73.8%): $T_d(5\%)$ 266°; IR (NaCl, cm^{-1}) 974 (**out-of-plane C-H**), 1576 (**Ar C=C**), 2926 (**Ali CH**), 3026 (***trans*-vinylene CH**), 3055 (**Ar CH**); UV-Vis Abs. Max. (406 nm); Fluorescence Emission Max (510 nm).

General Procedures for the HWE Synthesis of Poly(2,3-diphenylphenylene vinylene)

In a 100 ml, three-necked, round-bottomed flask, **79** (0.265 g, 0.500 mmol) t-BuOK (1.1 mL of 1.0 M in THF, 1.1 mmol) and THF (20 mL) were dispensed and stirred at RT for 10 min under N_2 (Brown/red solution). In an addition funnel, **6** (0.1430 g, 0.499 mmol) and THF (20 mL) were combined then dispensed rapidly (**Trial 1**) or dropwise over 20 min (**Trial 2)** into the round-bottomed flask (Neon green solution that turned dark green). The reaction mixture was stirred at RT for 24 h under N_2, then quenched with DI H_2O (15 mL) (Green solution turned orange). The majority of the solvent was stripped off and the solid orange residues were filtered and washed with H_2O (2X 15 mL) and the filtrate (Neon green) was extracted with DCM. An emulsion built up during extraction and brine solution (10% w/v) was added to limit extent of the emulsion. The organic layer was collected, the solvent was removed under reduced pressure, and the residues were combined with the filtered solids and dried under vacuum. The polymers were dissolved in chloroform, insoluble portions removed, and precipitated into methanol to yield **3a** and **3b**.

Trial 1

Polymer **3a** was obtained as a yellow powder (0.089 g, 0.314 mmol, 70.2%), T_d5% 236.67°; IR (NaCl, cm^{-1}) 756 (**=C-H**), 1684 (**C=C**), 3030 (**Ar CH**); UV-Vis Abs. Max. (412 nm); Fluorescence Emission Max (416 nm excitation, 496 nm emission).

Trial 2

Polymer **3b** was obtained as a yellow powder (0.084 g, 0.295 mmol, 66.4%), Td5% 251.44° IR (NaCl, cm^{-1}) 756 (**=C-H**), 1684 (**C=C**), 3030 (**Ar CH**); UV-Vis Abs. Max. (412 nm); Fluorescence Emission Max (416 nm excitation, 494 nm emission).

General Procedures for the HWE Synthesis of Poly(2,3-diphenylphenylene vinylene)

In a 100 mL, three-necked, round-bottomed flask, **6** (0.143 g, 0.500 mmol), **79** (0.265g, 0.500 mmol), and THF (40 mL) were combined and stirred at RT for 10 min under N_2. Next, t-BuOK (1.1 mL of 1.0 M in THF, 1.1 mmol) was delivered dropwise over 5 min (**Trial 3**) or rapidly (**Trial 4**) via syringe to the mixture (Initial yellow solution turned dark green). The reaction mixture stirred at RT for 24 h under N_2 (Brown solution) then was quenched with ethanol (20 mL) (Orange mixture). The volatile organics in the mixture were stripped off and the residues were dried under vacuum for 36 h, then H_2O (15 mL) was added to the dried product and the mixture was allowed to sit for 48 h, after which, polymers **3c** and **3d** were filtered, washed with H_2O (2X 15 mL), and dried under vacuum. The polymers were dissolved in chloroform, insoluble portions removed, and precipitated into methanol to yield **3c** and **3d**.

Trial 3

Polymer **3c** was obtained as yellow solid flecks (0.105 g, 0.370 mmol, 83.1%), T_d5% 312.17°, IR (NaCl, cm^{-1}) 756 (**=C-H**), 1684 (**C=C**), 3030 (**Ar CH**); UV-Vis Abs.

Max. (424 nm); Fluorescence Emission Max (416 nm and 424 nm excitations, 494 nm emission).

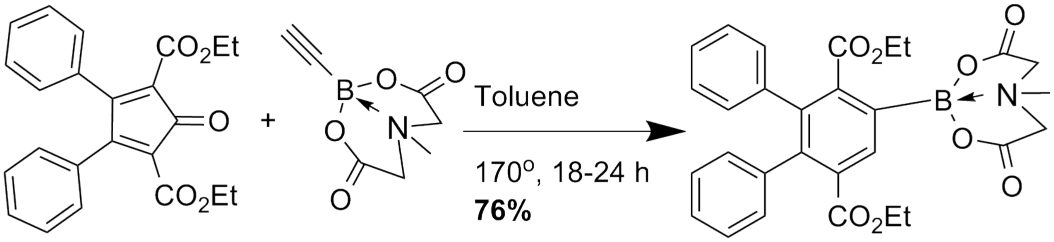
Trial 4

Polymer **3d** was obtained as a fluffy, yellow solid (0.111 g, 0.390 mmol, 87.9%), $T_d5\%$ 318.86° IR (NaCl, cm^{-1}) 756 (**=C-H**), 1684 (**C=C**), 3030 (**Ar CH**); UV-Vis Abs. Max. (430 nm); Fluorescence Emission Max (416 and 424 nm excitations, 496 nm emission).

RESULTS AND DISCUSSION

5-Benzyloxy-1,4-bis(chloromethyl)-2,3-diphenyl benzene 78

The synthesis of diethyl 5-([N-methyliminodiacetato-O,O',N]borane)-2,3-diphenylterephthalate **42** was achieved by a Diels-Alder reaction between 2,5-dicarboethoxy-3,4-diphenylcyclopentadienone **35** and ethynylboronic acid MIDA ester **41** as established by Sayers.[22] A bridged intermediate that initially forms is thermally converted to **42** by the loss of carbon monoxide with the formation of an aromatic ring. Diester **42** was characterized by melting point, IR, ^{1}H NMR, and ^{13}C NMR (**Table 1**).



35 **41** **42**

The melting point of **42** was found to be much higher (>250°) than the previously reported value (222°).[22] Triplicates of sample **42** were carried out and established a melting point range of 280-282°. The IR spectrum (**Figure 4**) of **42** showed two ester carbonyl absorptions at 1711 cm^{-1} (ester) and 1774 cm^{-1} (boronate) and an aromatic C-H absorbance at 3030 cm^{-1}.[25]

The ^{1}H NMR spectrum of **42** (**Figures 1, 2** and **5**) shows typical ethyl ester absorptions. In this case, asymmetry leads to two triplets at 0.74 and 0.84 δ and two quartets at 3.83 and 3.91 δ. The methylene protons of the boronate ring in **42** show

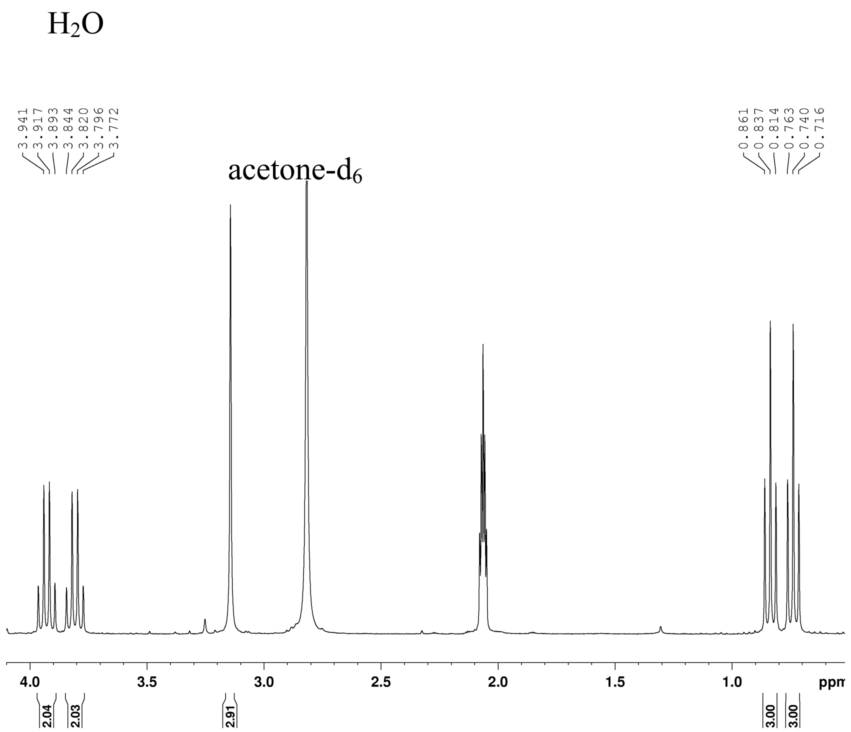


Figure 1. Expanded ^{1}H NMR of the ethyl absorptions in **42**.

a geminal coupling pattern. Doublet absorptions appear (**Figure 2)** at 4.27 and 4.44 δ (J = 17.2 Hz) due to the difference in methylene proton environments. This is most likely due to the rigid conformation of the MIDA ester ring.[26] Absorptions associated with the aromatic protons on the pendent phenyl rings of **43** appear as a multiplet at 7.08 δ. The one hydrogen singlet at 8.00 δ corresponds to the presence of the lone hydrogen on the central benzene ring that was formed in the Diels-Alder reaction. The appearance of this absorption in the ^{1}H NMR spectrum is characteristic of products of cyclopentadienone/terminal alkyne Diels-Alder cycloadditions.

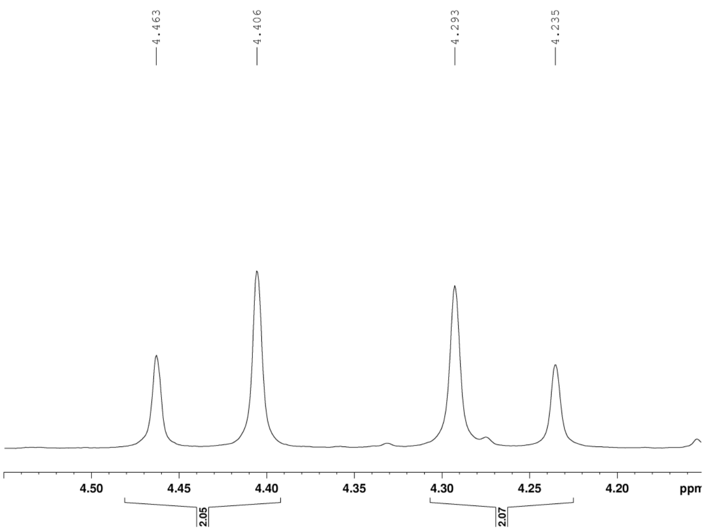
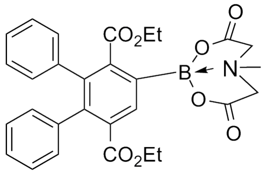


Figure 2. Expanded ^{1}H NMR of the boronate ring methylene absorptions in **42**.

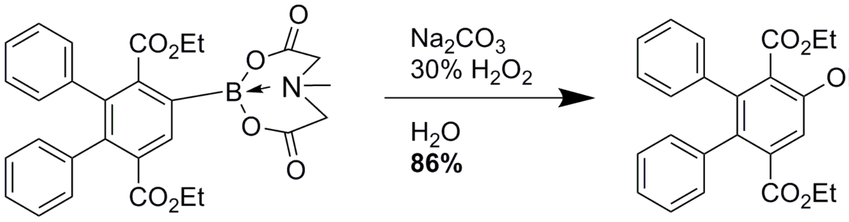
The appearance of two ethyl absorptions (2 quartets/2 triplets) in the ^{1}H NMR spectrum of **42** is reflected in the ^{13}C NMR spectrum (**Figure 6**) by the appearance of carbon signals at 61.32 and 61.83 ppm (methylene) and 13.58 and 13.86 ppm (methyl). The methyl and methylene groups in the boronate ring are easily identified as the absorptions at 50.30 and

Table 1. Spectral Data Summary for **42**.

Compound	IR (cm^{-1}, NaCl plates)	^{1}H NMR (Acetone-d_6, δ)	^{13}C NMR (Acetone-d_6, ppm)
 **42**	1711 (C=O, ester), 1774 (C=O, boronate), 2981 (Ali CH), 3030 (Ar CH)	0.74 (t, 3H, CH_3), 0.84 (t, 3H, CH_3), 3.14 (s, 3H, NCH_3), 3.81 (q, 2H, CH_2), 3.93 (q, 2H, CH_2), 4.27 (d, 1H, NCH_2), 4.44 (d, 1H, NCH_2), 7.00-7.16 (m, 10H, Ar CH), 8.00 (s, 1H, Ar CH)	13.58, 13.86, 50.30, 61.32, 61.83, 64.79, 127.41, 127.60, 127.94, 128.02, 130.66, 131.29, 134.20, 134.59, 139.30, 139.99, 142.15, 142.22, 169.17, 169.38, 172.16

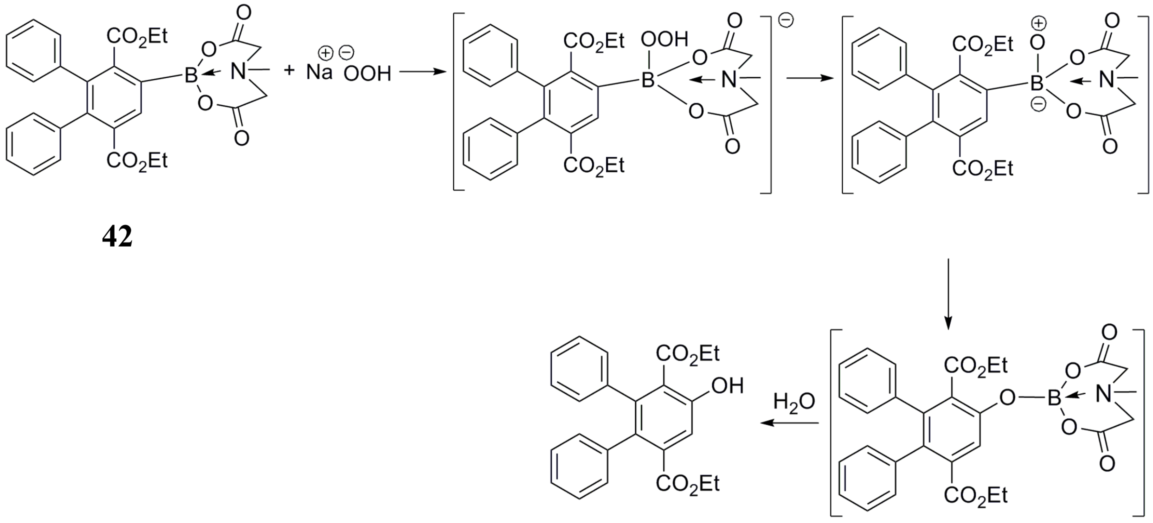
64.79 ppm, respectively. There are twelve aromatic signals in the aromatic region (**Figure 6**), less than the expected fourteen. Fortuitous overlap is the probable cause. Finally, absorptions at 169.17 and 169.38 ppm can be associated with the carbonyl carbons of the ester functionalities in **42**, and the peak at 172.16 ppm can be associated with the carbonyl carbons of the boronate ring.[26]

The synthesis of diethyl 5-hydroxy-2,3-diphenylterephthalate **43** was accomplished via alkaline, oxidative cleavage of the C-B bond in **42** using 30% H_2O_2 and Na_2CO_3 as demonstrated by Sayers.[22]



42 **43**

The reaction mechanism (**Scheme 1**) involves the deprotonation of H_2O_2 by carbonate to provide hydroperoxide anion ($^{-}$OOH) that coordinates with the electrophilic



42

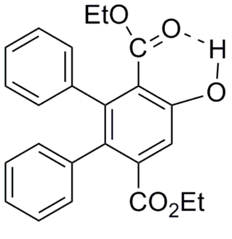
43

Scheme 1. Mechanism for Carbon-Boron Bond Oxidation of **43**.

boron to provide an intermediate from which a hydroxyl group is eliminated. The zwitterion intermediate undergoes a rearrangement in which the positively charged oxygen inserts into the C-B bond, followed by hydrolysis.[27] The product was characterized by melting point, IR, ^{1}H NMR, and ^{13}C NMR.

The IR spectrum of **43** (**Figure 7**) shows an absorbance at 1135 cm^{-1} attributed to the C-O bond and a broad absorption at 3423 cm^{-1} associated with the newly formed phenol functionality.

As before, the asymmetry of **43** leads to two distinct ethyl absorption patterns in the ^{1}H NMR spectrum; two triplets (3H) associated with the methyl groups of the esters at 0.68 and 0.92 δ and overlapping quartets (2H) centered at 3.93 and 3.99 δ (**Figure 8).** The aromatic hydrogen absorptions of **43** appear as 1) a multiplet (10H) at 7.00 δ and 2) a singlet (1H) at 7.38 δ. The singlet position represents an upfield shift compared to the same proton shift in **42** (8.00 δ). The electron-donating nature of the hydroxyl group and the location of the lone proton, which is ortho to the O-H group, account for the shift. The one proton singlet at 10.7 δ (**Figure 8**) reflects the presence of an intramolecular hydrogen bond between the hydroxyl group and the carbonyl of the adjacent ester that causes the proton signal to be sharp and well-defined.

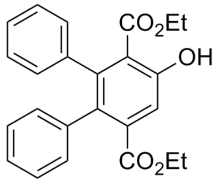


43

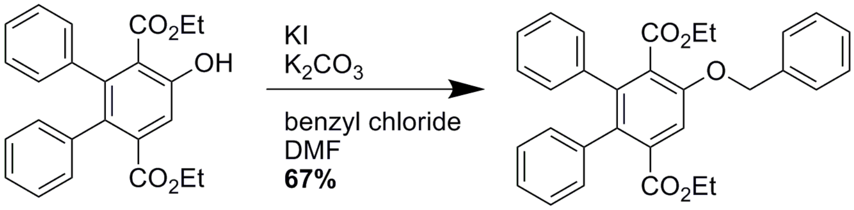
As seen for **42**, the ^{13}C NMR spectrum (**Figure 9**) of **43** mirrors the ^{1}H NMR ethyl asymmetry with the appearance of two methyl carbon absorptions at 12.83 and

13.53 ppm and the methylene carbon absorptions at 61.23 and 61.34 ppm. The expected fourteen aromatic absorptions occur between 115.22 and 159.85 ppm. The aromatic signal at 159.85 ppm corresponds to the aryl carbon bearing the newly formed hydroxyl group. There are two ester carbonyl carbon absorptions at 167.84 and 170.53 ppm, as opposed to the three present in **42**, a result of removing the boronate ring. Spectral data related to **43** is presented in **Table 2**.

Table 2. Spectral Data Summary for **43**.

Compound	**IR (cm^{-1}, NaCl plates)**	**^{1}H NMR (CDCl$_3$, δ)**	**^{13}C NMR (CDCl$_3$, ppm)**
 **43**	1135 (C-O), 1670 (C=O), 1719 (C=O), 2917 (Ali CH), 3423 (OH)	0.68 (t, 3H, CH_3), 0.92 (t, 3H, CH_3), 3.93 (q, 2H, CH_2), 3.99 (q, 2H, CH_2), 6.88-7.11 (m, 10H, Ar CH), 7.38 (s, 1H, Ar CH), 10.70 (s, 1H, Ar OH)	12.83, 13.53, 61.23, 61.34, 115.22, 116.87, 126.23, 126.32, 126.90, 127.02, 129.51, 130.33, 132.57, 138.29, 138.61, 140.36, 144.08, 159.85, 167.84, 170.53

The synthesis of diethyl 5-benzyloxy-2,3-diphenylterephthalate **76** was achieved via the Williamson ether reaction between **43** and benzyl chloride. The reaction involves the generation of a nucleophilic phenoxide derivative that reacts with benzyl chloride via an S_N2 mechanism to yield **76**. Compound **76** was characterized by melting point, IR, ^{1}H NMR and ^{13}C NMR (**Table 3**).

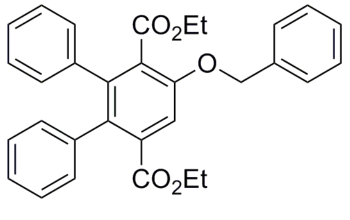


43 **76**

The IR spectrum of **76** (**Figure 10**) showed an absorption at 1127 cm^{-1} (C-O), a carbonyl absorption at 1732 cm^{-1} and an aromatic C-H absorption at 3059 cm^{-}1. The ^{1}H NMR spectrum of **76** (**Figure 11**) shows the two distinct ethyl absorptions as two triplets (3H each) centered at 0.86 and 0.93 δ and two overlapping quartets (2H each) at 3.97 and 4.02 δ. A new singlet absorption (2H) appears at 5.23 δ, which corresponds to the benzylic protons of the benzyloxy group. Also the sharp singlet absorption associated with the hydroxyl group of **43** (**Figure 8**) no longer appears in **Figure 11**.

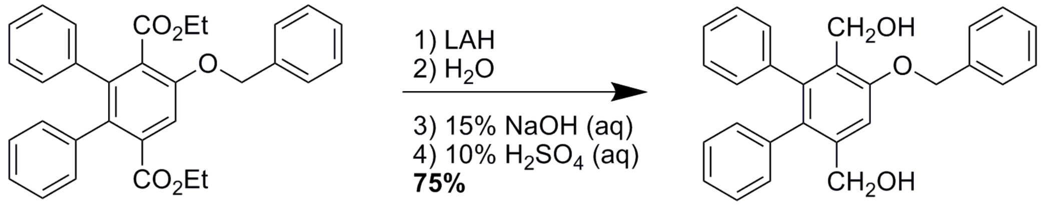
The asymmetry of **76** is reflected in the ^{13}C NMR spectrum of **76** (**Figure 12**), which has methyl carbon absorptions at 13.44 and 13.67 ppm and methylene carbon absorptions appearing as an overlapped signal at 61.13 ppm. A signal at 70.78 ppm corresponds to the benzylic carbon of the benzyloxy group. This peak was identified as a methylene carbon using DEPT 135 (**Figure 13**). Also in **Figure 12** are the expected aromatic carbon absorptions (18C) appearing from 112.31-153.94 ppm.

Table 3. Spectral Data Summary for **76**.

Compound	**IR cm^{-1} (NaCl plates)**	**^{1}H NMR ($CDCl_3$, δ)**	**^{13}C NMR ($CDCl_3$, ppm)**
 **76**	1127 (C-O), 1732 (C=O), 2982 (Ali CH), 3059 (Ar CH)	0.86 (t, 3H, CH_3), 0.93 (t, 3H, CH_3), 3.97 (q, 2H, CH_2), 4.02 (q, 2H, CH_2), 5.23 (s, 2H, CH_2) 6.93-7.49 (m, 16H, Ar CH)	13.44, 13.67, 61.13, 70.78, 112.31, 126.43, 127.02, 127.14, 127.20, 127.28, 127.84, 128.00, 128.56, 130.01, 130.07, 134.16, 134.38, 136.31, 137.53, 138.82, 141.09, 153.94, 166.72, 168.29

The carbonyl carbons have absorptions at 166.72 and 168.29 ppm. All spectral data are summarized in **Table 3**.

The ethyl ester functions of **76** were reduced using LAH to yield 5-benzyloxy-1,4-bis(hydroxymethyl)-2,3-diphenylbenzene **77**. Product **77** was characterized by melting point, IR, ^{1}H NMR and ^{13}C NMR (**Table 4**).



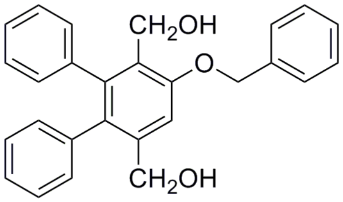
76 **77**

The IR spectrum of **77** (**Figure 14**) shows a broad absorption at 3426 cm^{-1} that is associated with the newly formed hydroxymethyl groups of **77**. Comparison of the IR spectra of **76** and **77** (**Figures 10** and **14),** respectively, indicates that the carbonyl absorptions related to **76** are not present in the IR spectrum of **77** proving that the ester groups have been converted to hydroxymethyl groups.

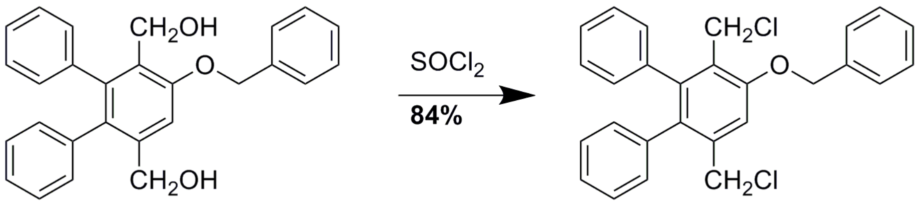
In the ^{1}H NMR spectrum of **77** (**Figure 15**), the ester absorption patterns are no longer present, and a pair of singlet absorptions (2H each) appear at 4.43 and 4.50 δ. These two peaks are associated with the methylene groups of the newly formed hydroxymethyl functions of **77**. The benzylic proton absorption for **77** appears as a singlet (2H) at 5.29 δ and the aromatic proton absorptions appear as a multiplet (16H) from 6.95-7.53 δ.

The ^{13}C NMR of **77** (**Figure 16**) indicates that the ethyl carbons of **76** are no longer present and two new absorptions at 58.97 and 63.60 ppm appear. These peaks are representative of the carbons of the two hydroxylmethyl groups of **77,** and were verified as methylene carbon absorptions using DEPT 135 (**Figure 17**). The benzylic carbon of **77** appears as an absorption at 70.54 ppm and due to signal overlap seventeen aromatic carbons absorptions appear ranging from 109.87 to 156.84 ppm in **Figure 16**.

Table 4. Spectral Data Summary for **77**.

Compound	**IR cm^{-1} (NaCl plates)**	**^{1}H NMR ($CDCl_3$, δ)**	**^{13}C NMR ($CDCl_3$, ppm)**
 **77**	1124 (C-O), 1590 (Ar C=C), 2980 (Ali CH), 3426 (broad, strong, OH)	4.43 (s, 2H, CH_2), 4.50 (s, 2H, CH_2), 5.29 (s, 2H, CH_2) 6.95-7.53 (m, 16H, Ar CH)	58.97, 63.60, 70.54, 109.87, 126.46, 126.50, 127.41, 127.53, 127.64, 128.25, 128.80, 130.21, 130.34, 133.28, 136.64, 138.68, 138.76, 139.58, 142.86, 156.84

Compound **77** was converted to the target monomer, 5-benzyloxy-1,4-bis(chloromethyl)-2,3-diphenylbenzene **78**, using thionyl chloride. The product, **78**, was characterized by melting point, IR, ^{1}H and ^{13}C NMR.



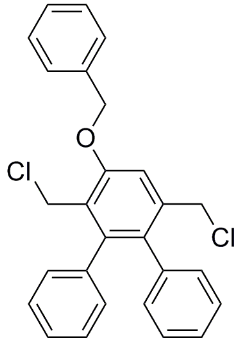
77 **78**

The IR spectrum of **78** (**Figure 18**) has absorptions at 759 and 851 cm^{-1} representing the symmetric and asymmetric stretching modes of the C-Cl bond. Also the broad absorption associated with the hydroxyl groups of **77** is no longer present in **Figure 18**.

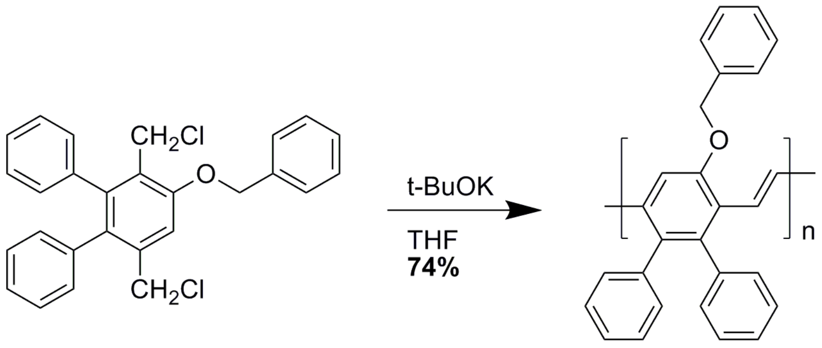
The ^{1}H NMR spectrum of **78** (**Figure 19**) shows two singlet absorptions (2H) at 4.37 and 4.48 δ, representative of the carbons of the two newly formed chloromethyl groups of **78**. The benzylic protons of **78** appear as a singlet absorption (2H) at 5.30 δ and the aromatic proton absorptions are displayed as a multiplet (16H) ranging from 6.99-7.58 δ.

The ^{13}C NMR spectrum of **78** (**Figure 20**) provides more evidence that conversion of **77** occurred. The methylene chloromethyl group carbons have absorptions at 39.55 and 44.88 ppm, as verified by DEPT 135 (**Figure 21**). Also the benzylic carbon of the benzyloxy group has an absorption at 70.49 ppm and, as seen previously, seventeen aromatic carbons appear as absorptions throughout 112.20-156.39 ppm. All spectral data for **78** are presented in **Table 5**.

Table 5. Spectral Data Summary for **78**.

Compound	**IR (cm^{-1}, NaCl plates)**	**^{1}H NMR (CDCl$_3$, δ)**	**^{13}C NMR (CDCl$_3$, ppm)**
 **78**	759 (sym C-Cl), 851 (asym C-Cl), 1591 (Ar C=C), 2925 (Ali CH), 3058 (Ar CH)	4.37 (s, 2H, CH$_2$), 4.48 (s, 2H, CH$_2$), 5.30 (s, 2H, CH$_2$) 6.99-7.58 (m, 16H, Ar CH)	39.55, 44.88, 70.49, 112.20, 125.20, 126.71, 126.88, 127.30, 127.43, 127.55 128.05, 128.66, 130.01, 130.51, 134.51, 136.67, 137.14, 138.05, 143.99, 156.39

Polymerization of monomer **78** was carried out using the Gilch/CPR method discussed previously to yield poly(5-benzyloxy-2,3-diphenyl phenylene vinylene) **80**. Polymerization parameters are displayed in **Table 6**.



78 **80**

Table 6. Parameters for the Polymerization of **78**.

Reaction Time (Temp)	24 h (RT)
Molar Ratio of t-BuOK : **78**	6.5 : 1
Volume of THF	10 mL

After the addition of t-BuOK, the solution turned brown with a blue brim and after an hour there was a noticeable clear residue building up on the surface of the round bottomed flask. Throughout the remainder of the reaction more residue built up and it changed in color from transparent to orange, while the reaction solution was yellow. After precipitation into methanol and collection of the precipitate, compound **80** was isolated as an orange and yellow solid, of which the orange material was found to be mostly insoluble, a result of suspected crosslinking of polymer chains. Polymer **80** was stirred in chloroform to isolate portions that were soluble from the orange gel, and this soluble form of **80** was characterized using IR, TGA, DSC, GPC, UV-Vis and Fluorescence studies.

The IR spectrum of **80** (**Figure 22**) contained absorptions at 974 cm^{-1} (Out-of-Plane C-H), 1576 cm^{-1} (Ar C=C), 2926 cm^{-1} (Ali CH), 3026 cm^{-1} (*trans*-vinylene CH) and 3055 cm^{-1} (Ar CH). TGA analysis of **80** (**Figure 23**) established the T$_d$5% of this polymer to be 266.17°. Additionally, GPC analysis (**Figure 24**) found that the soluble portion of **80** had an M_n = 6603 Da and an M_w = 7136 Da, and as expected films of **80** could not be cast.

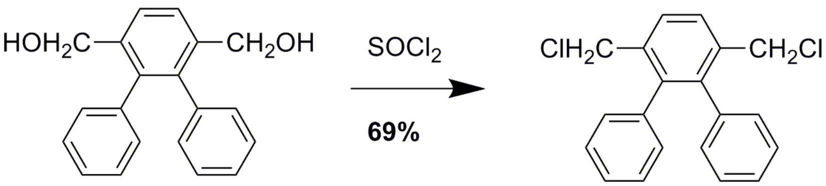
UV-Vis and Fluorescence studies were also carried out to characterize **80**. The UV-Vis spectral data (**Figure 25**) of a 10 ppm solution of **80** in chloroform exhibited a maximum absorption at 406 nm and Fluorescence data (**Figure 26**), gathered using 406 nm as the excitation wavelength, established a maximum emission at 510 nm. A summary of the characterizations of **80** is presented in **Table 7**.

Table 7. Summary of Polymerization and Characterizations of **80**.

Ratio Insoluble **80** : Soluble **80**	3:1
T_d5%	266.17°
M_w / M_n	7136 Da / 6603 Da
Max. Absorbance	406 nm
Max. Emission	510 nm

Poly(2,3-diphenylphenylene vinylene) 3a-3d

Synthesis of the phosphonate monomer, 1,4-bis(diethoxyphosphorylmethyl)-2,3-diphenylbenzene **79** was achieved by first chlorinating 1,4-bis(hydroxymethyl)-2,3-diphenyl benzene **26** to yield 1,4-bis(chloromethyl)-2,3-diphenyl benzene **27**, which was characterized by melting point, IR, ^{1}H and ^{13}C NMR.



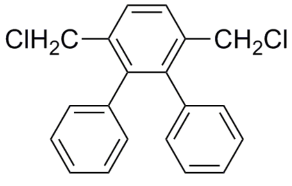
26 **27**

The IR spectrum of **27** (**Figure 27**) exhibits absorptions at 701 and 760 cm^{-1} related to the symmetric and asymmetric sretching modes of the C-Cl bond. Also absorptions at 2959 cm^{-1} (Ali CH) and 3017 cm^{-1} (Ar CH) were observed.

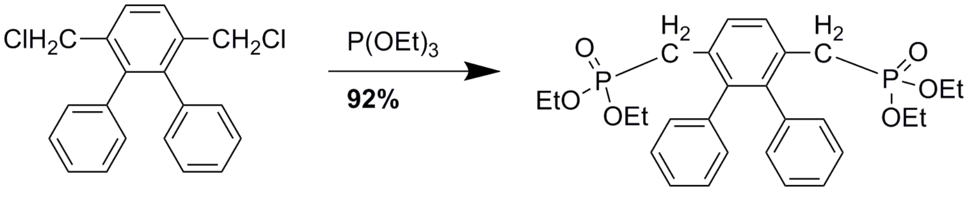
The ^{1}H NMR spectrum of **27** (**Figure 28**) has one singlet absorbance (4H) at 4.40 δ representing the protons of the chloromethyl groups. The aromatic proton absorptions appear as 1) a multiplet (10H) from 7.05-7.2 δ and 2) a singlet (2H) at 7.65 δ related to the pair of hydrogens on the central benzene ring. The symmetrical nature of **27** reduces the number of unique proton absorptions as seen in **Figure 28**.

In the ^{13}C NMR spectrum of **27** (**Figure 29**) the methylene carbons of **27**, as verified by DEPT 135 (**Figure 30**), appear as a single absorption at 44.55 ppm, a result of the symmetry of **27**. The seven unique aromatic carbons of **27** appear as absorptions ranging from 126.91 to 141.94 ppm. All spectral data for **27** are presented in **Table 8**.

Table 8. Spectral Data Summary for **27**.

Compound	**IR cm^{-1} (NaCl plates)**	**^{1}H NMR (CDCl$_3$, δ)**	**^{13}C NMR (CDCl$_3$, ppm)**
 **27**	701 (sym C-Cl), 760 (asym C-Cl), 2959 (Ali CH), 3017 (Ar CH)	4.40 (s, 4H, CH$_2$), 7.05-7.2 (m, 10H, Ar CH), 7.65 (s, 2H, Ar CH)	44.55, 126.91, 127.57, 129.47, 130.06, 136.06, 137.98, 141.94

Compound **27** was converted to 1,4-bis(diethoxyphosphorylmethyl)-2,3-diphenylbenzene **79** via the Michaelis-Arbuzov reaction using triethylphosphite in a neat reaction mixture and was characterized by melting point, IR, ^{1}H and ^{13}C NMR (**Table 9**).



27 **79**

The IR spectrum of **79** (**Figure 31**) has absorptions at 1027 and 1250 cm^{-1} related to the P-O and P=O bonds of **79**. In the ^{1}H NMR spectrum of **79** (**Figures 3** and **32**), the methyl portions of the ethyl phosphoester have a proton absorption that appears as a triplet (6H, J= 7.05 Hz) at 1.24 δ and the methylene portion, which is additionally coupled to ^{31}P, an NMR active nucleus, appears as a quintet (4H, J=7.2 Hz) absorption at 3.97 δ.[28] The benzylic protons of **79** are also coupled to ^{31}P and have an absorption that appears as a doublet (4H, J= 20.8 Hz) at 3.00 δ (**Figure 3**).[28] The coupling to ^{31}P appears in both the ^{1}H and ^{13}C NMR spectra. The aromatic proton absorptions appear as 1) a multiplet (10H) between 6.97-7.14 δ and 2) a singlet (2H) at 7.57 δ.

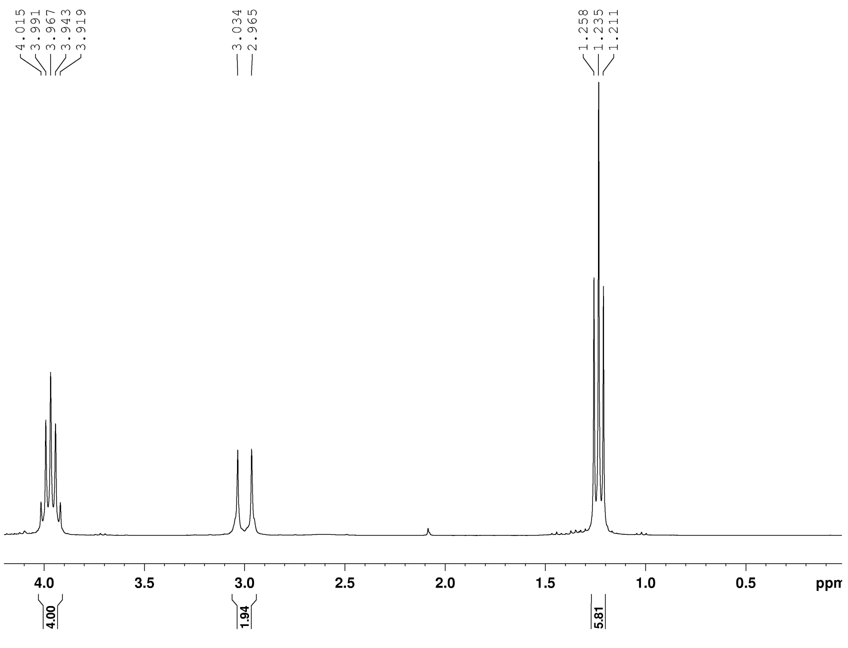
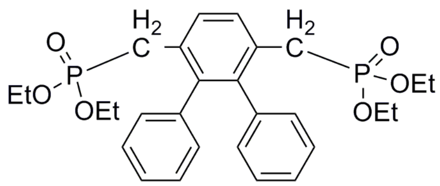


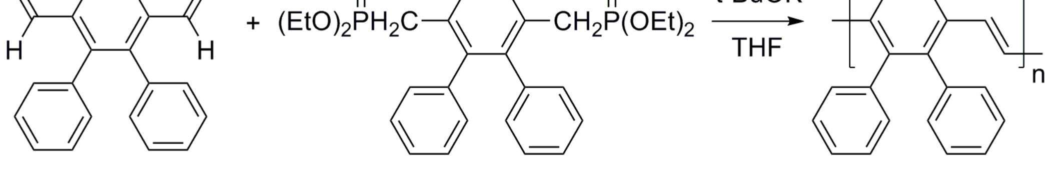
Figure 3. Expanded ^{1}H NMR of the ethyl and benzylic absorptions of **79**.

The ^{13}C NMR spectrum of **79** (**Figure 33**) reflects the symmetrical nature of the compound and also exhibits the ^{31}P coupling discussed previously. The methyl carbons of the ethyl groups of **79** have an absorption that appears as a doublet centered at 16.31 ppm (J= 5.6 Hz) and the methylene carbon absorption appears as a doublet centered at 61.84 ppm (J= 6.3 Hz).[29] The benzylic carbon absorptions of **79** appear as a doublet centered at 30.79 ppm (J= 138.5 Hz).[29] The methylene carbons were confirmed via DEPT 135 (**Figure 34**). The seven unique aromatic carbons of **79** have absorptions ranging from 126.33 to 142.45 ppm. All spectral data for **79** are presented in **Table 9**.

Table 9. Spectral Data Summary for **79**.

Compound	**IR cm^{-1} (NaCl plates)**	**^{1}H NMR (CDCl$_3$, δ)**	**^{13}C NMR (CDCl$_3$, ppm)**
 **79**	961 (P-O), 1027 (P-O), 1052 (P-O), 1250 (P=O), 2906 (Ali CH), 2981 (Ar CH)	1.24 (t, 12H, CH$_3$), 3.00 (d, 4H, CH$_2$), 3.97 (q, 8H, CH$_2$), 6.97-7.14 (m, 10H, Ar CH), 7.57 (s, 2H, Ar CH)	16.28, 16.36, 29.87, 31.71, 61.80, 61.88, 126.33, 127.33, 128.67, 129.06, 130.51, 139.53, 142.45

Polymerization of monomers **6** and **79** was achieved using the HWE reaction to yield poly(2,3-diphenylphenylene vinylene) **3**. Polymerization parameters are displayed in **Table 10**.



6 **79** **3**

Table 10. Parameters for the Polymerization of **6** and **79**.

Reaction Time (Temp)	24 h (RT)
Molar Ratio of t-BuOK : **6** : **79**	2.2 : 1 : 1
Total Volume of THF	40 mL

Trial polymerizations **1-4** were carried out to determine if there was an optimal method for the addition of the monomers and base. Trials **1** (**3a)** and **2** (**3b**) had initial reaction mixtures that turned dark brown/red upon addition of base to **79**. Both reaction mixtures turned dark green with a neon green brim after the addition of **6**. In comparison, Trials **3** (**3c**) and **4** (**3d**) turned dark green with a neon brim immediately upon addition of base to **6** and **79**, with Trial **3** initially appearing as a yellow solution. Also post-reaction workup of the polymers was modified throughout the experiments when emulsion formation during extraction became a problem for **3a** and **3b**. It was reasoned that since the two trials were quenched with H_2O, complete removal of the solvent was not possible and residual THF led to the emulsion. This was remedied by addition of brine solution to the emulsion (**M1**). Trials **3** and **4** were carried out using the modifications of 1) quenching the reaction with ethanol, which is less difficult to remove, 2) drying the crude product longer and 3) allowing the crude product to sit in H_2O for 48h, which eliminated the need for an extraction (**M2**) and provided higher yields (**Table 11**). It should be noted there were marginal amounts of insoluble material for all HWE polymerizations.

Polymers **3a-3d** were characterized using IR, TGA, UV-Vis and Fluorescence studies (**Figure 35-39**) and data are presented in **Table 11**.

Table 11. Summary of Polymerizations and Characterizations of **3a-3d**.

Compound	**Post-Reaction Modification (% Yield)**	**T_d5%**	**UV-VIS** (Max Abs, nm)	**Fluorescence** (Max Emission, nm)
3a	M1 (70.2%)	236.67°	412	496
3b	M1 (66.4%)	251.44°	412	494
3c	M2 (83.1%)	312.17°	424	494
3d	M2 (87.9%)	318.86°	430	496

The combined IR spectra of **3a-3d** (**Figure 35**) show that the polymers have alkene absorptions at 1684 cm^{-1} and aromatic absorptions around 3030 cm^{-1}. Analysis of TGA data shows that **3a** and **3b** were found to be thermally inferior to **3c** and **3d** (**Table 11**). In a comparison of **3a-3d** to the Polymer **3** made by Ganesan via the Wittig reaction, the HWE produced polymers with superior thermal properties, with each trial exceeding the $T_{d5\%}$ of 100° that was determined for **3** made via the Wittig.[7]

UV-VIS data showed **3a** and **3b** exhibited the same absorption maxima, while **3c** and **3d** had different red-shifted absorption spectra relative to **3a** and **3b** (**Table 11**). Fluorescence data established that **3a-3d** had similar emission maxima ranging between 494 and 496 nm. Polymers **3a-3d** could not be cast into films and it was presumed that oligomers were produced.

Summary and Conclusions

- 5-benzyloxy-1,4-bis(chloromethyl)-2,3-diphenylbenzene **78** was successfully polymerized using the Gilch method and CPR to yield poly(5-benzyloxy-2,3-diphenyl phenylene vinylene) **80**.
- The ratio of insoluble to soluble polymer was found to be 3:1, and the isolated soluble portions of **80** were found to be highly fluorescent oligomers.
- HWE trials were successfully employed to synthesize poly(2,3-diphenyl phenylene vinylene) **3a-3d** from 2,3-diphenylterephthalaldehyde **6** and1,4-bis(diethoxyphosphorylmethyl)-2,3-diphenylbenzene **79**.
- Trial 4 (**3d**) yielded the best results with regards to the characterizations carried out.
- Polymers **3a**-**3d** were highly fluorescent, however since films could not be cast, it is expected oligmers were formed.

Future Work

- Determine optimal polymerization technique for alkoxy di(chloromethyl) benzene monomers.
- Investigate other parameters that may affect HWE in synthesis of PPV and DP-PPV systems.
- Synthesize copolymers with PPV and DP-PPV subunits and characterize systems.

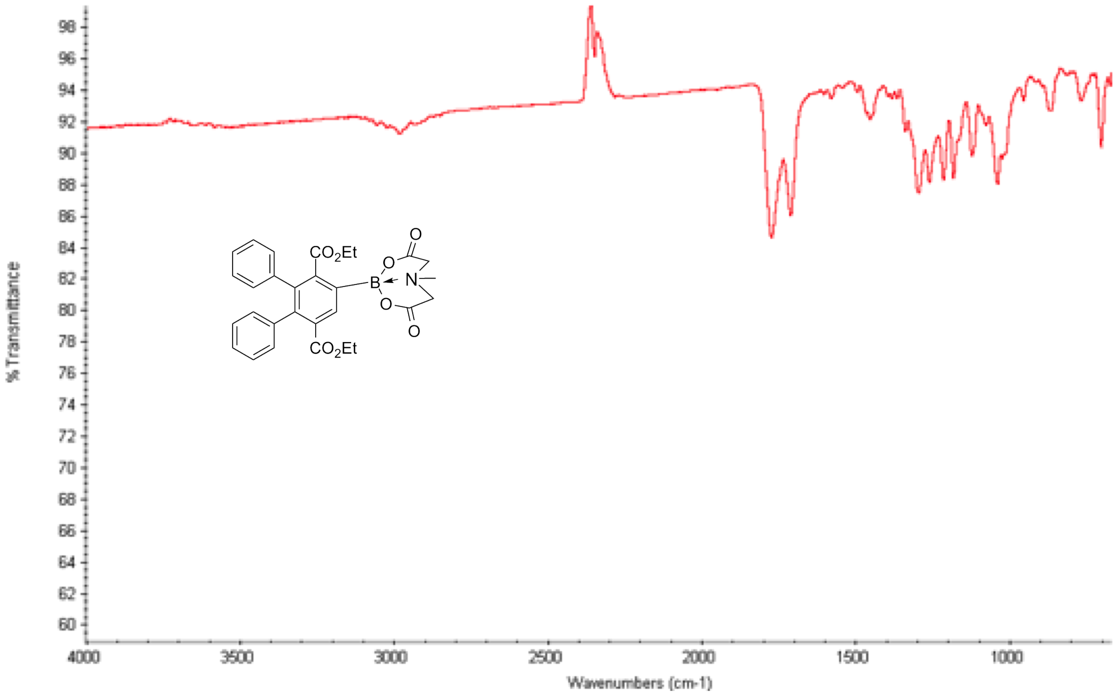


Figure 4. IR Spectrum (NaCl) of **42**.

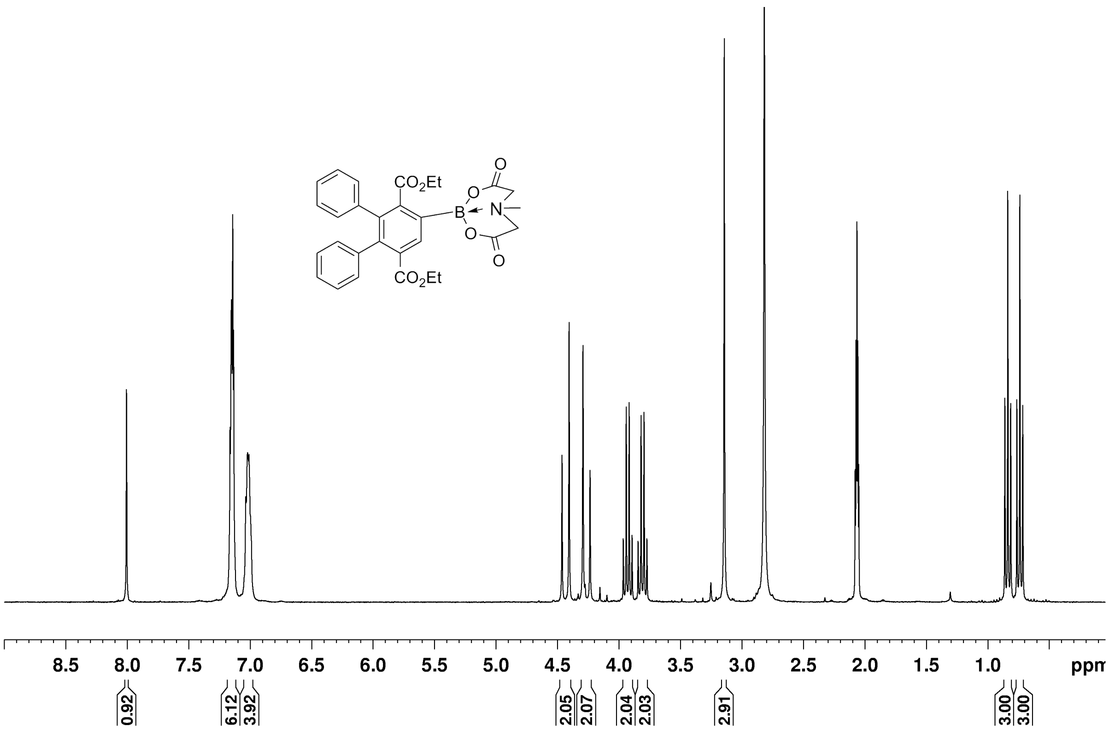


Figure 5. 300 MHz ^{1}H NMR Spectrum (acetone-d$_6$) of **42**.

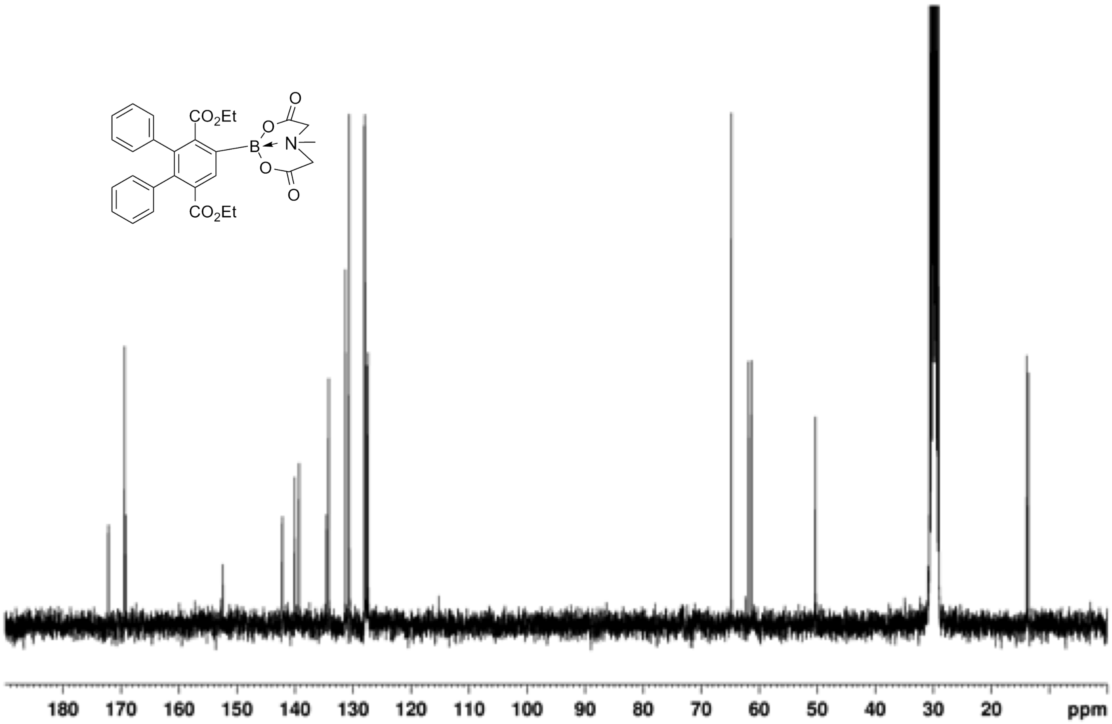


Figure 6. 75 MHz ^{13}C NMR Spectrum (acetone-d_6) of **42**.

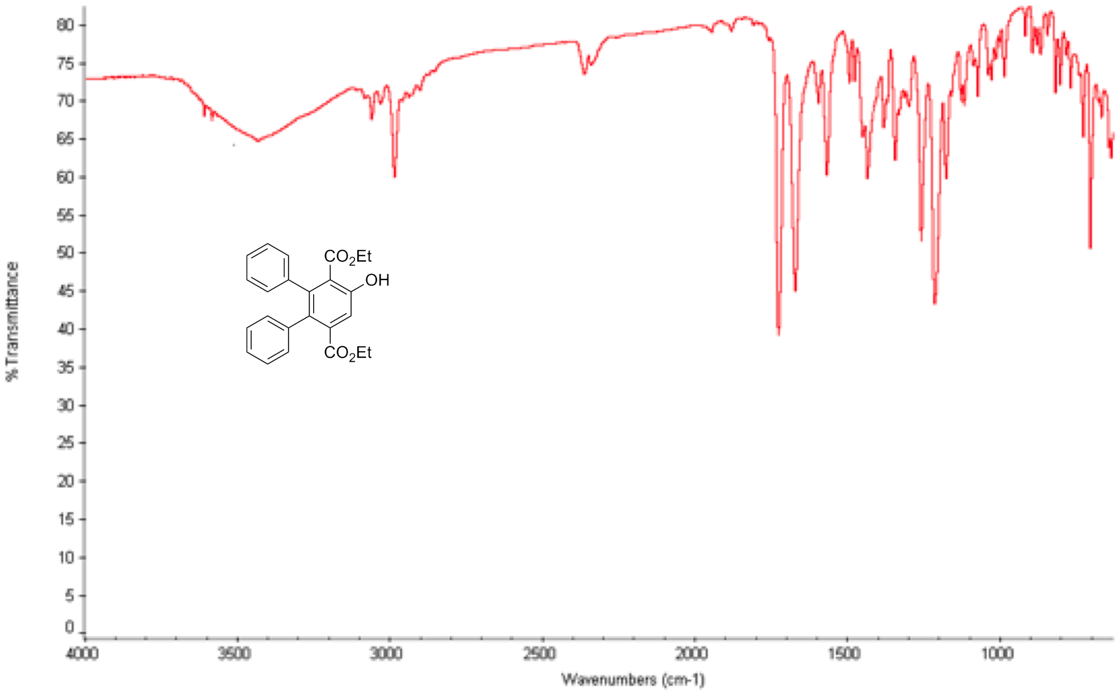


Figure 7. IR Spectrum (NaCl) of **43**.

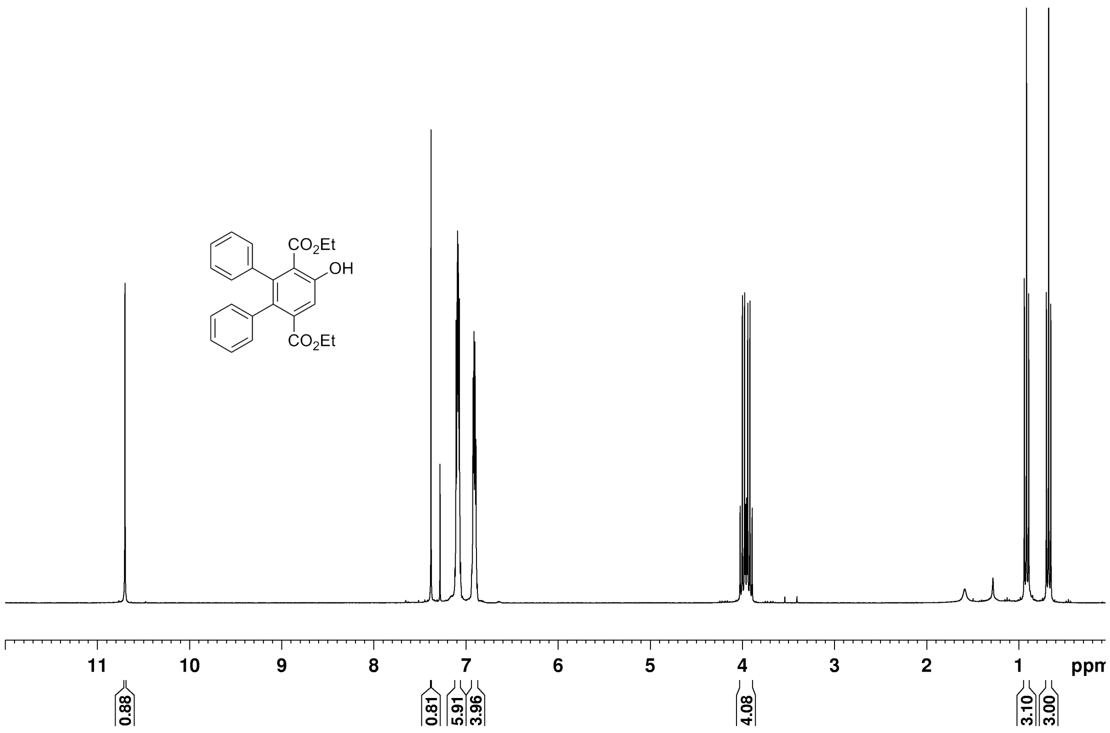


Figure 8. 300 MHz ^{1}H NMR Spectrum (CDCl$_3$) of **43**.

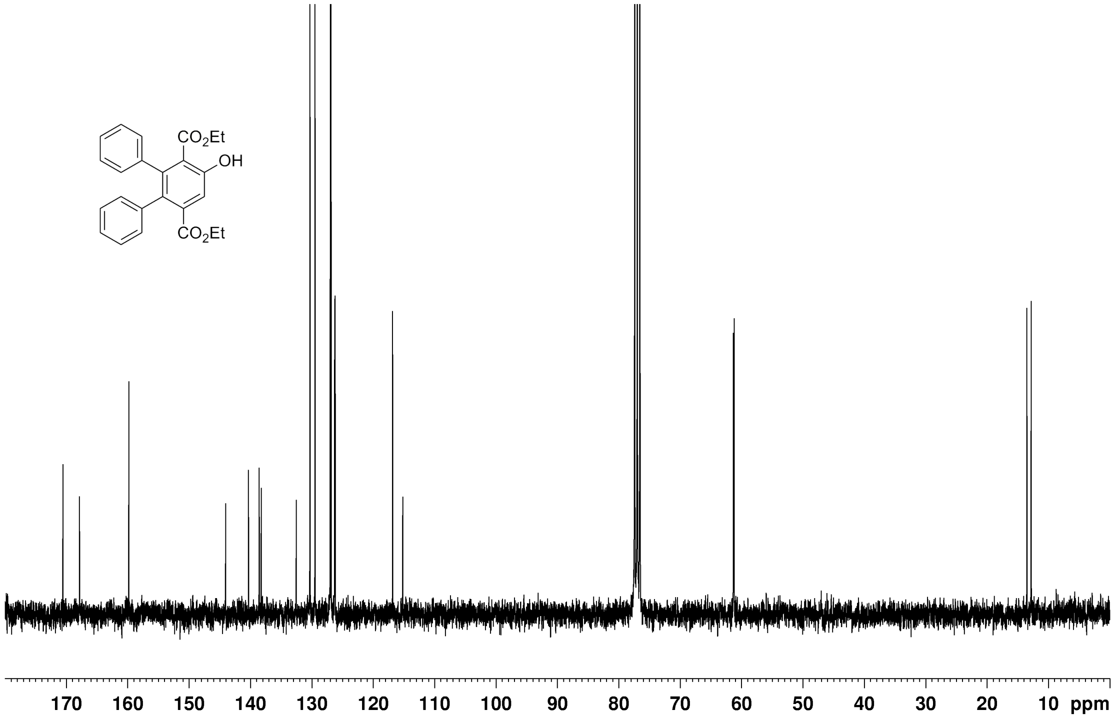


Figure 9. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) of **43**.

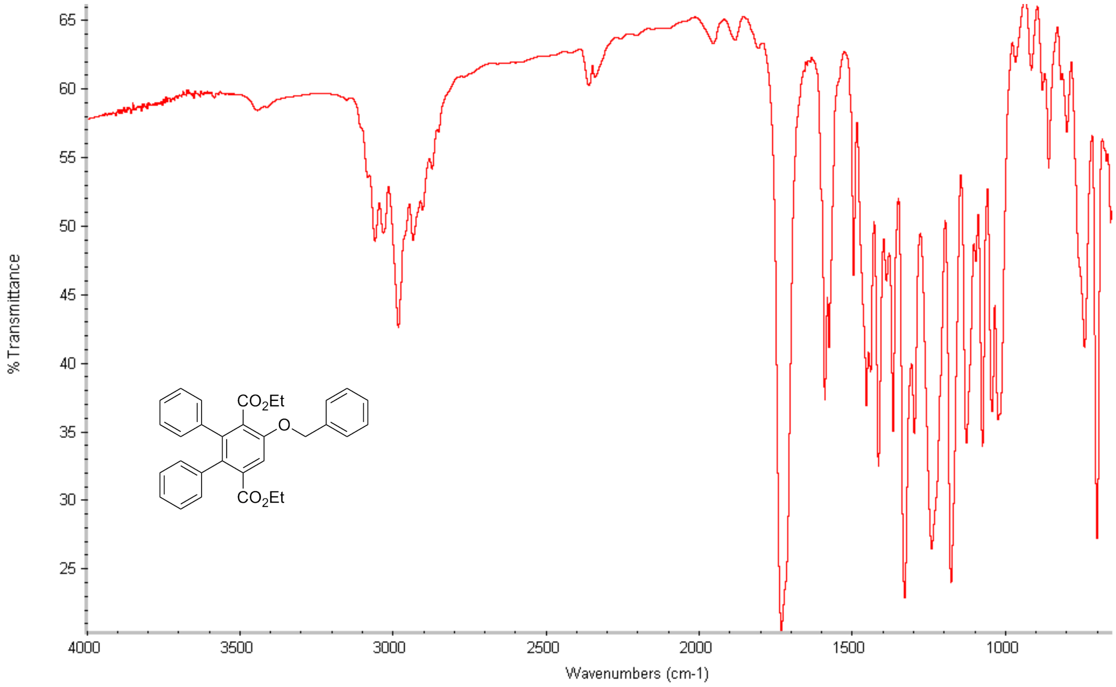


Figure 10. IR Spectrum (NaCl) of **76**.

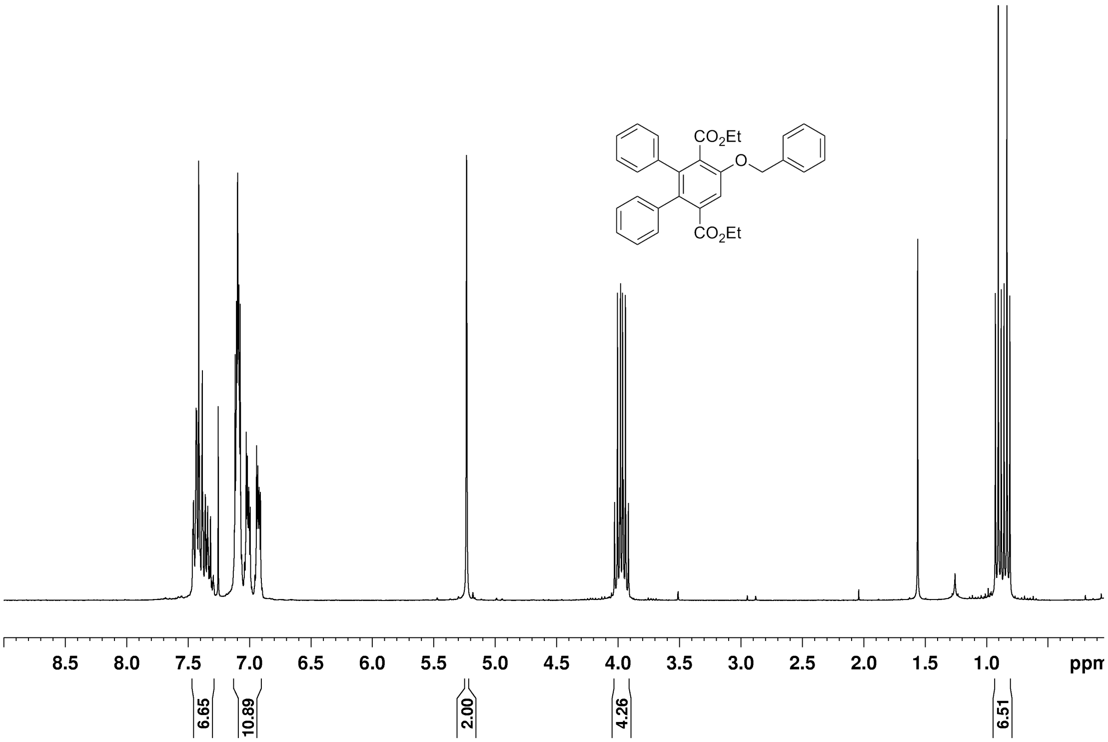


Figure 11. 300 MHz ^{1}H NMR Spectrum (CDCl$_3$) of **76**.

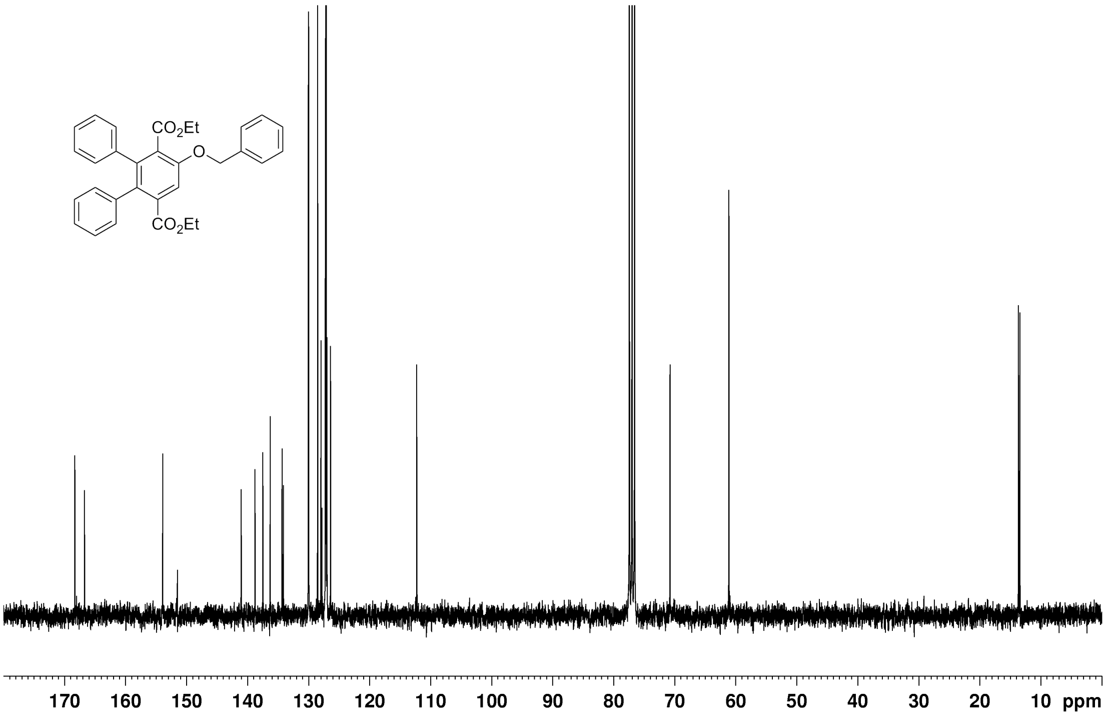


Figure 12. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) of **76**.

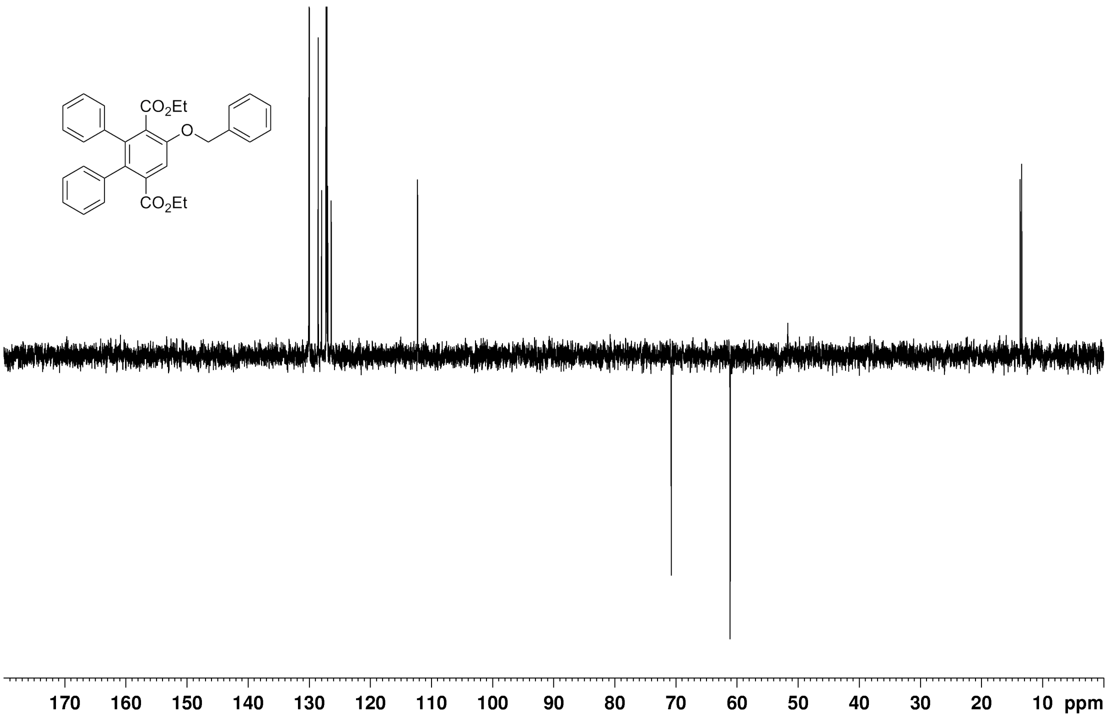


Figure 13. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) DEPT 135 of **76**.

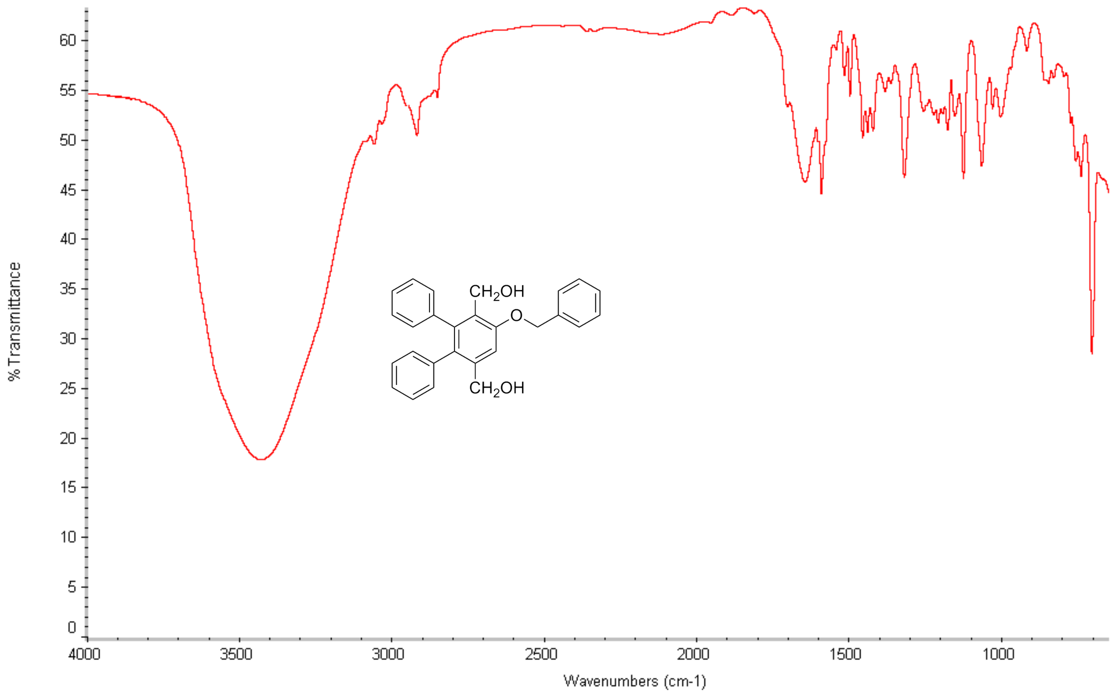


Figure 14. IR Spectrum (NaCl) of **77**.

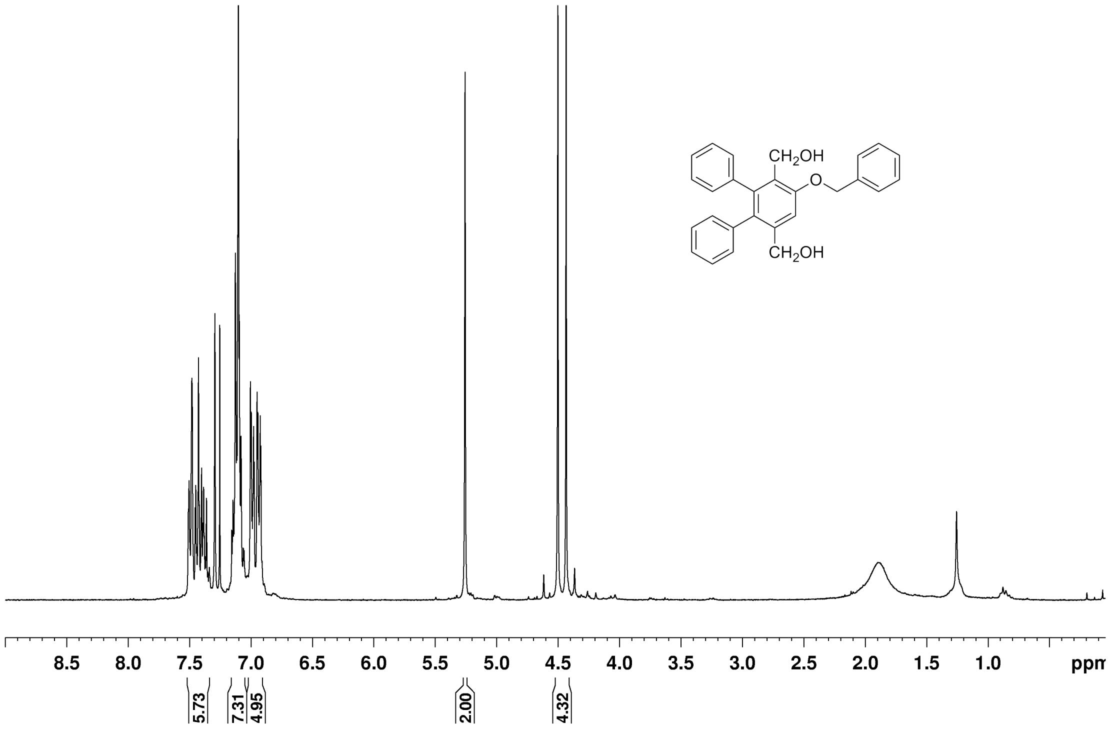


Figure 15. 300 MHz ^{1}H NMR Spectrum (CDCl$_3$) of **77**.

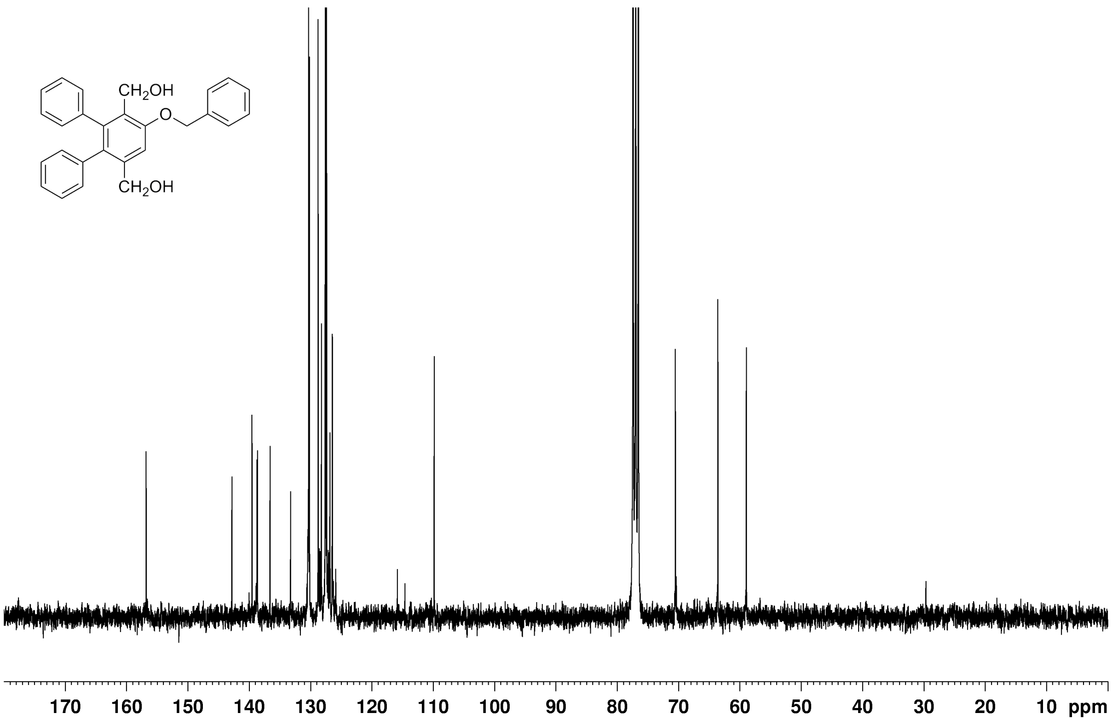


Figure 16. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) of **77**.

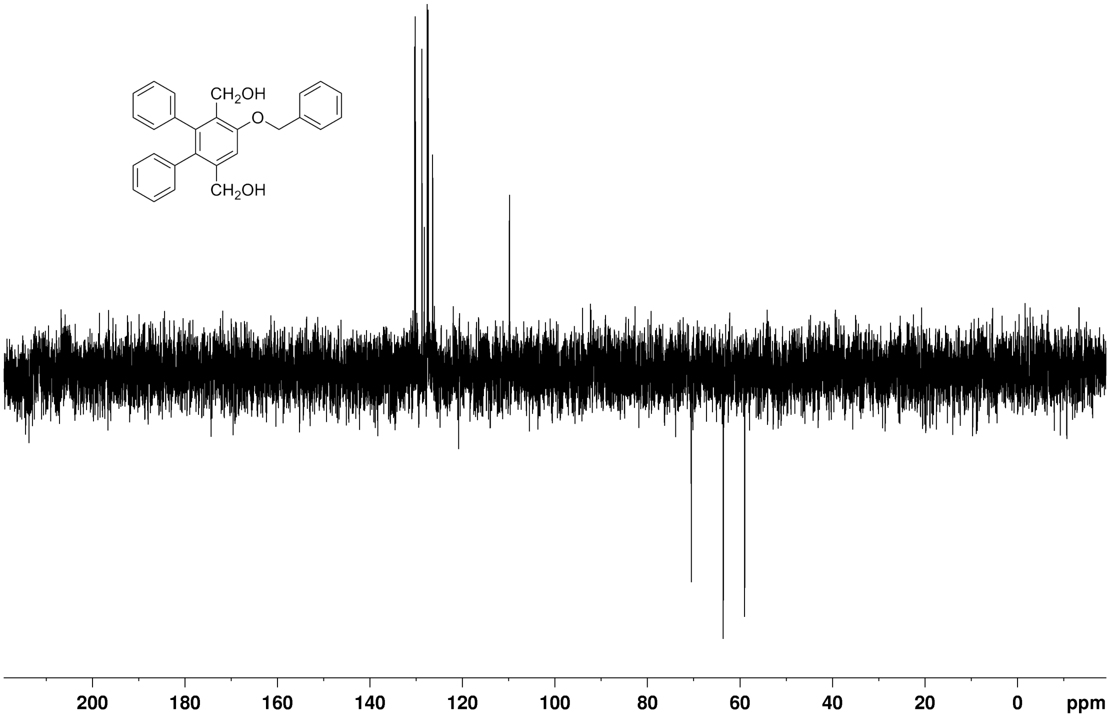


Figure 17. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) DEPT 135 of **77**.

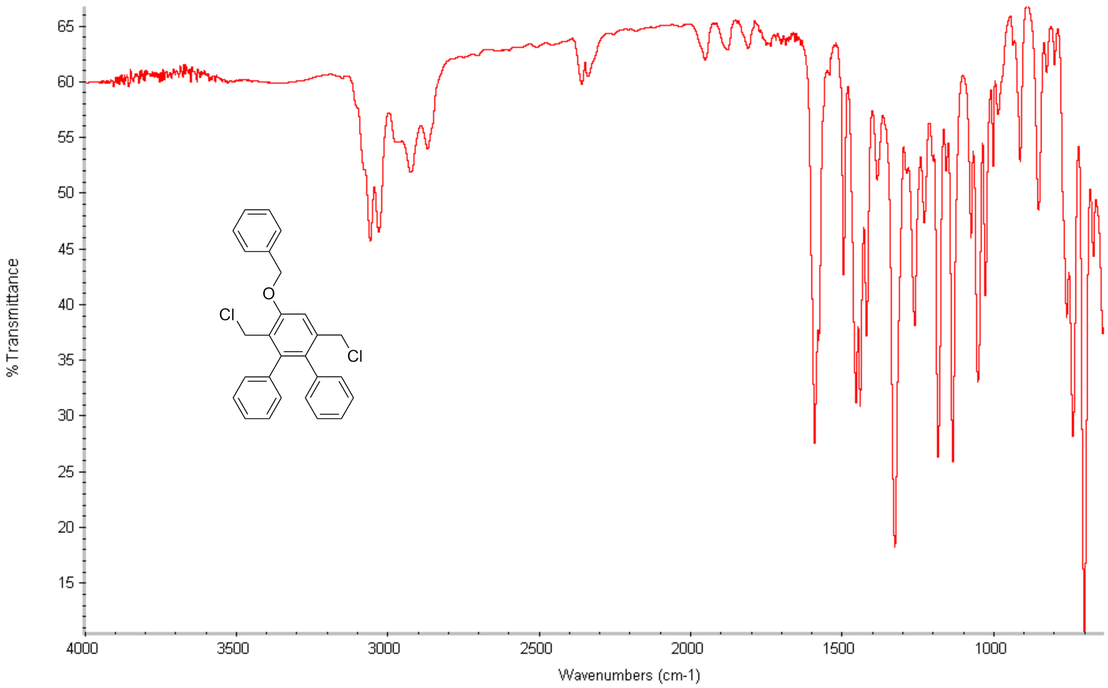


Figure 18. IR Spectrum (NaCl) of **78**.

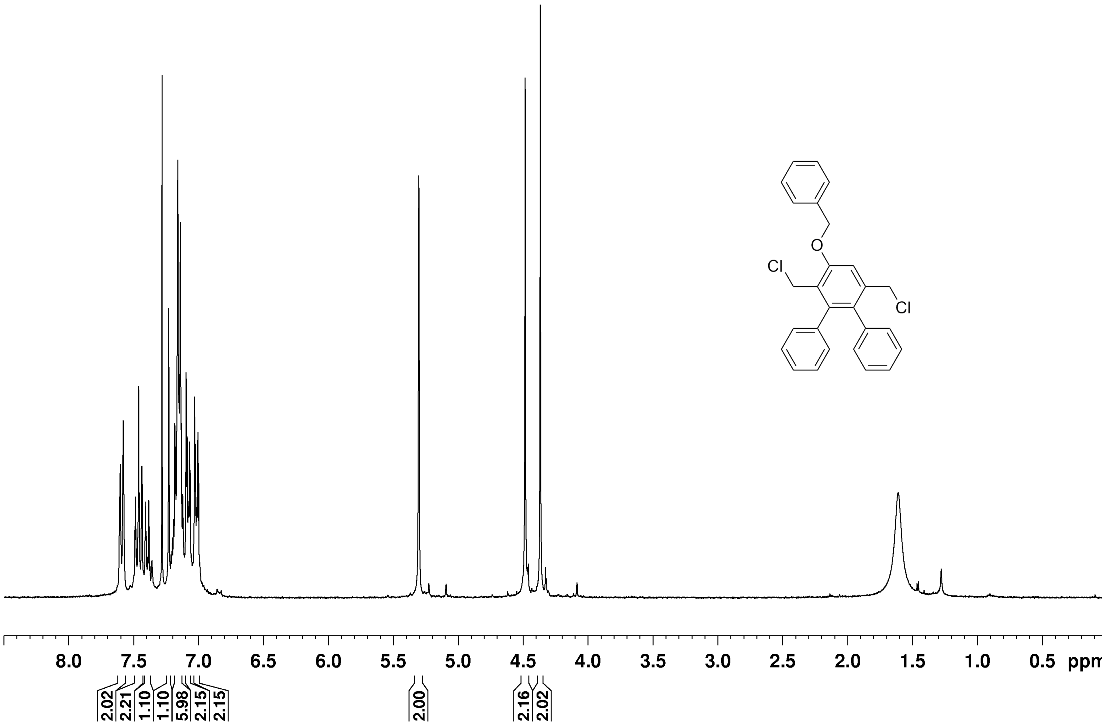


Figure 19. 300 MHz ^{1}H NMR Spectrum (CDCl$_3$) of **78**.

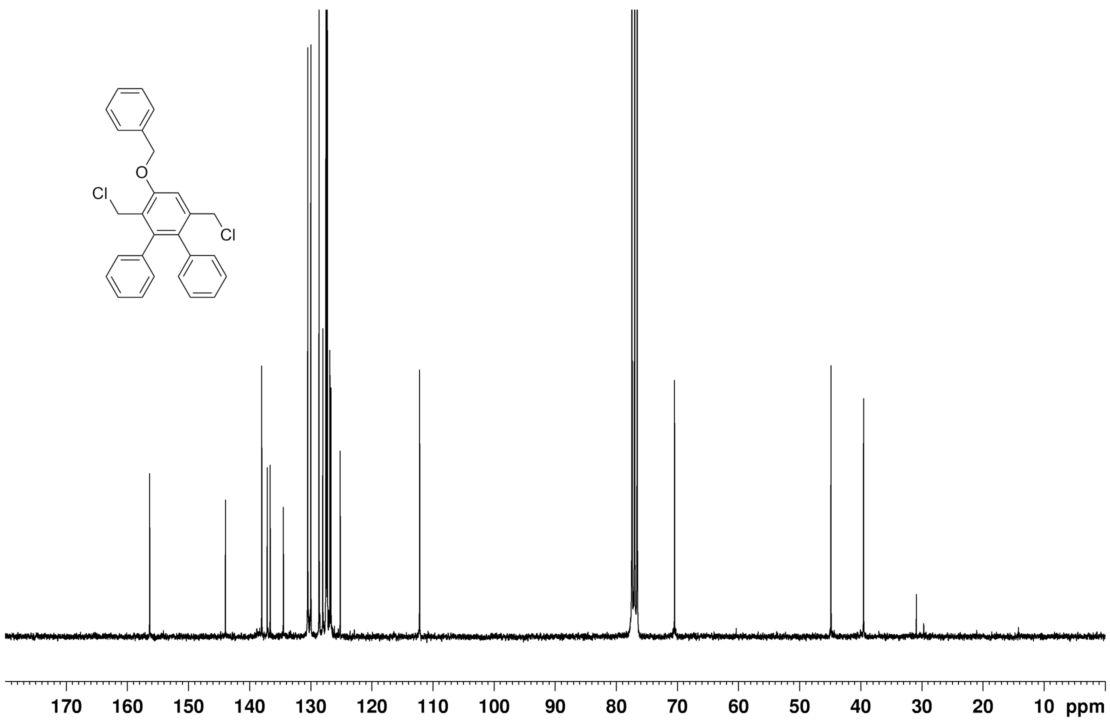


Figure 20. 75 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **78**.

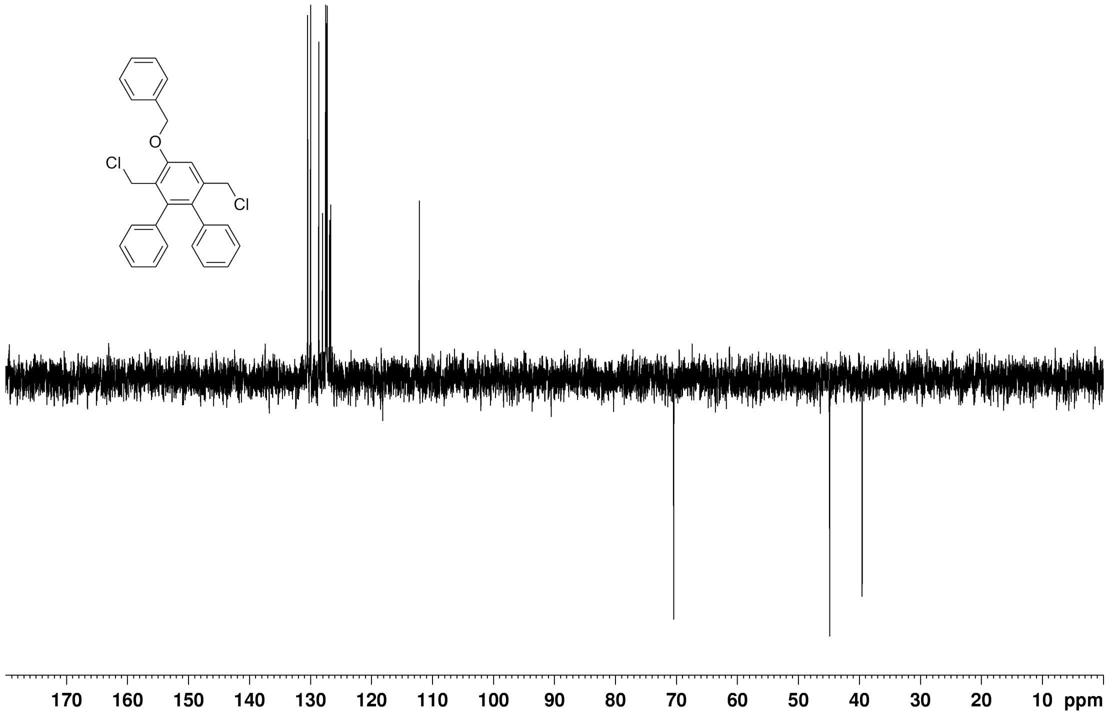


Figure 21. 75 MHz ^{13}C NMR Spectrum ($CDCl_3$) DEPT 135 of **78**.

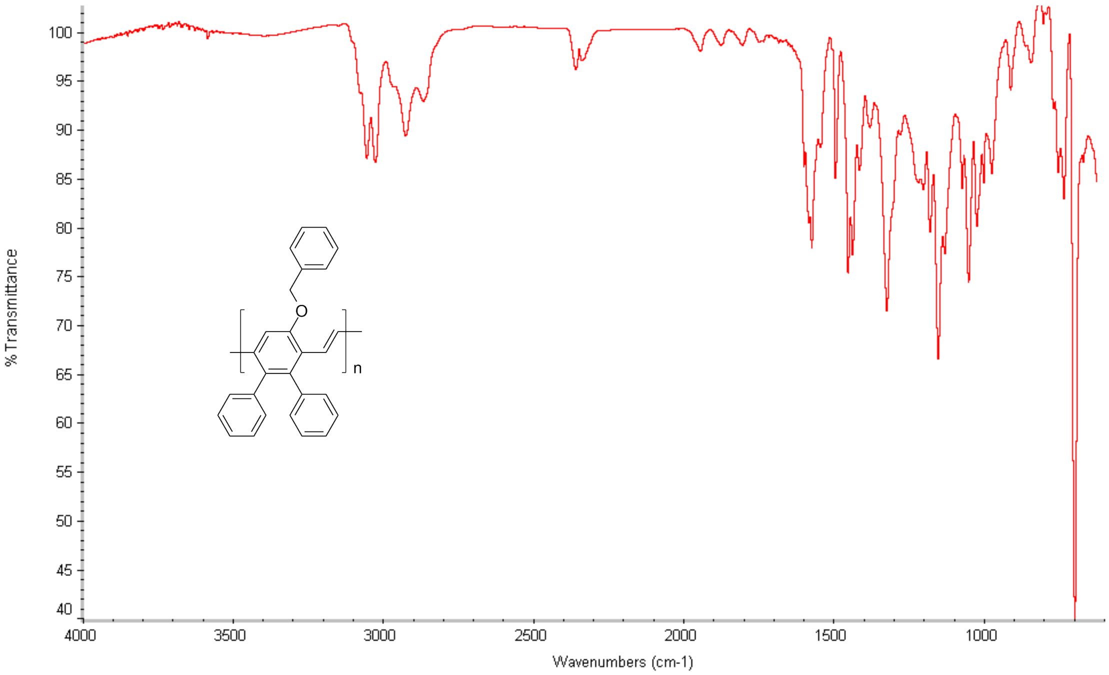


Figure 22. IR Spectrum (NaCl) of **80**.

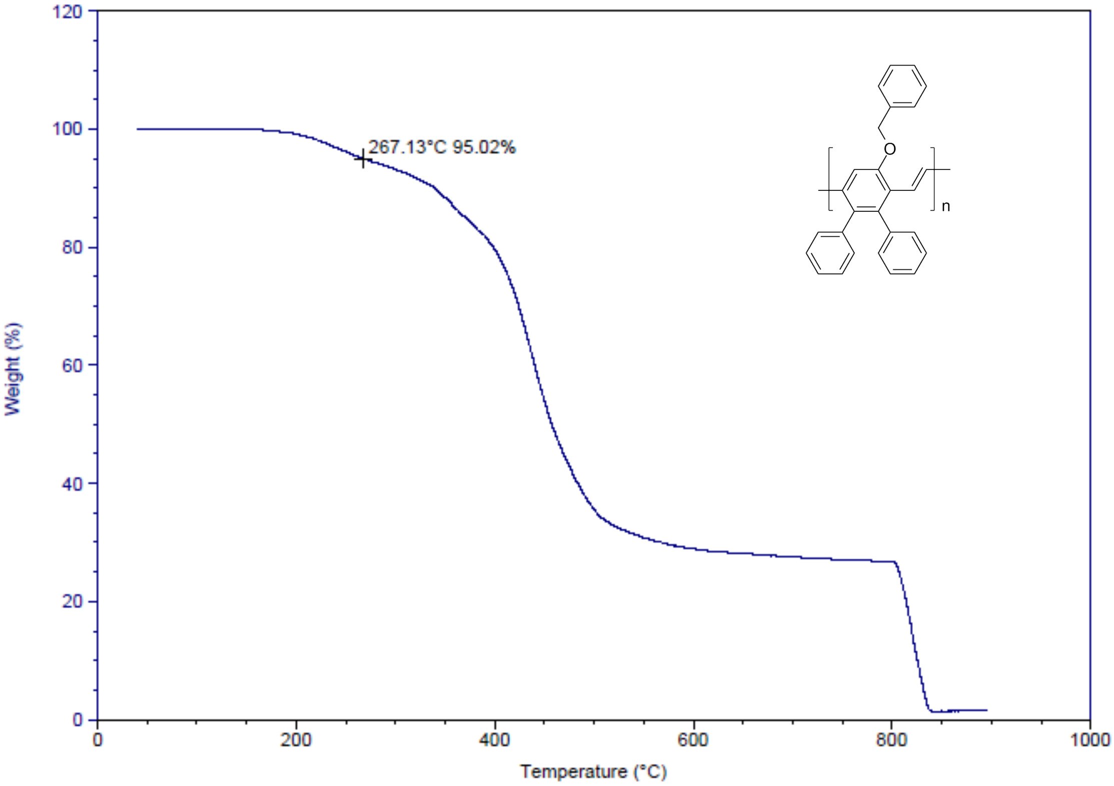


Figure 23. TGA trace of **80**.

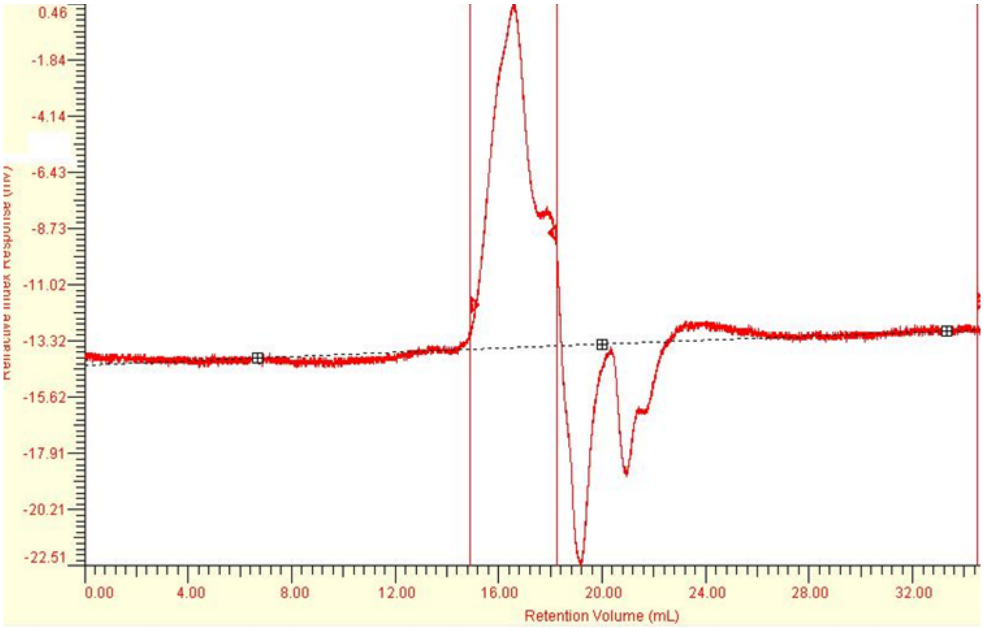


Figure 24. GPC trace of **80** relative to polystyrene in 5% acetic acid/ THF.

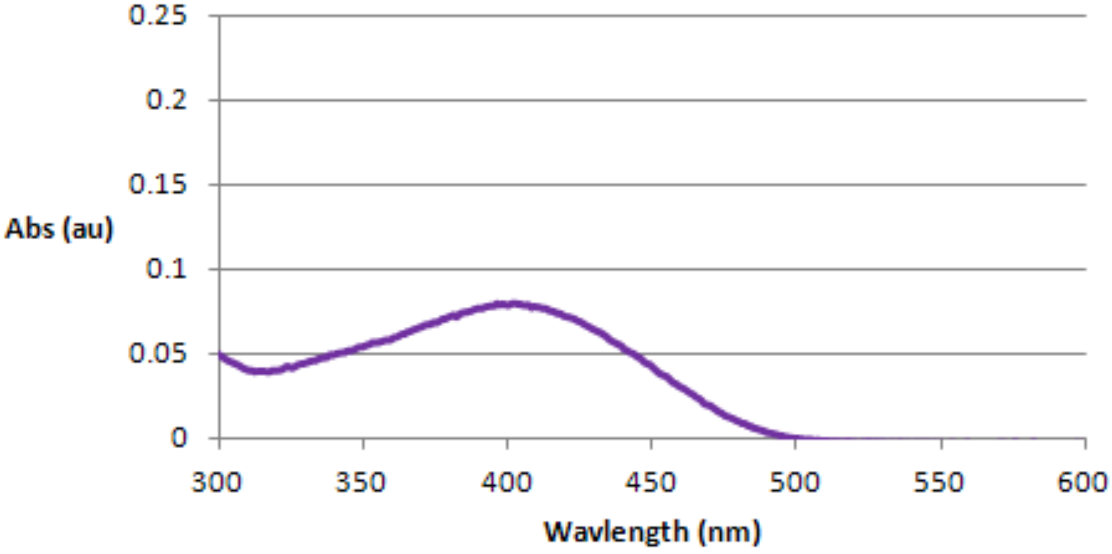


Figure 25. UV-VIS Spectrum of 10 ppm chloroform solution of **80** (Maximum Absorbance at 406 nm.).

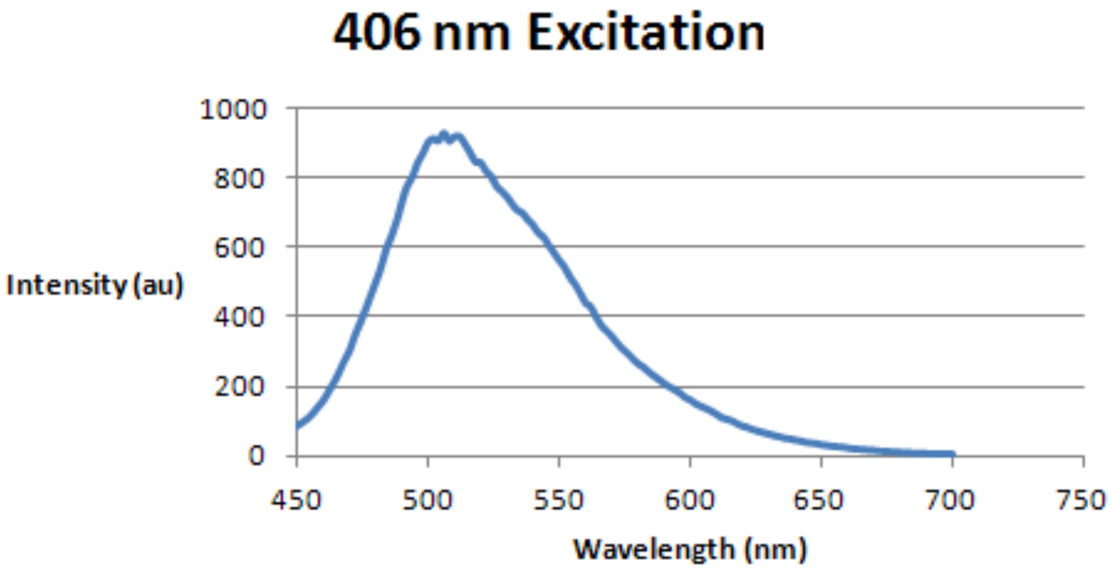


Figure 26. Fluorescence Spectrum of 10 ppm chloroform solution of **80** (Maximum Emission at 510 nm.)

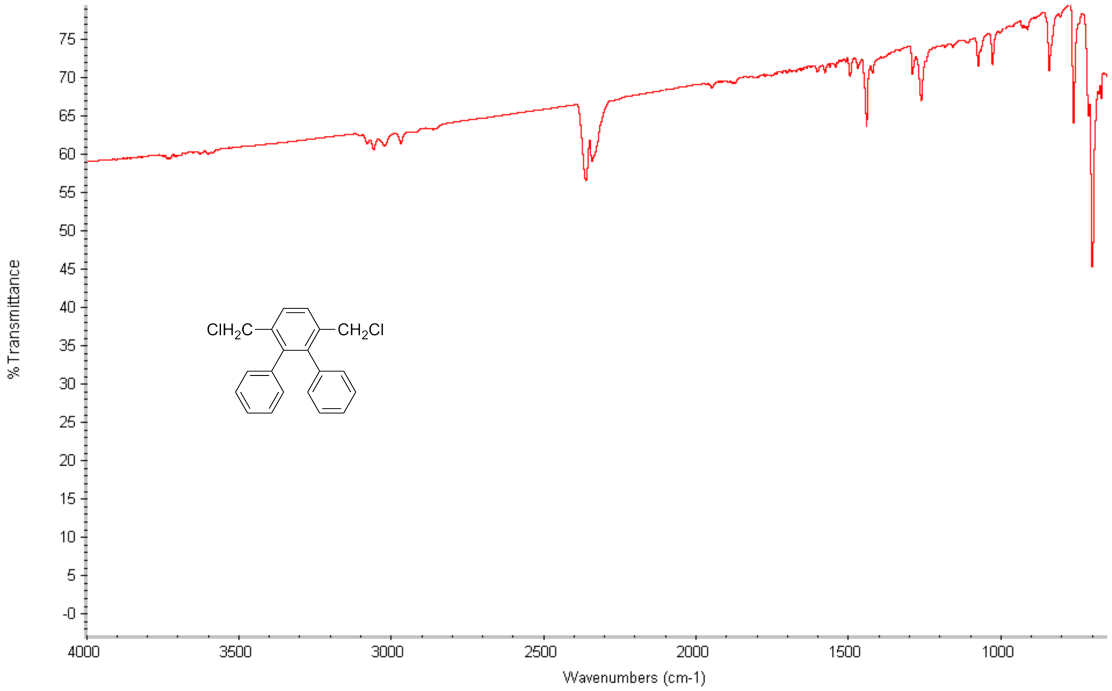


Figure 27. IR Spectrum (NaCl) of **27**.

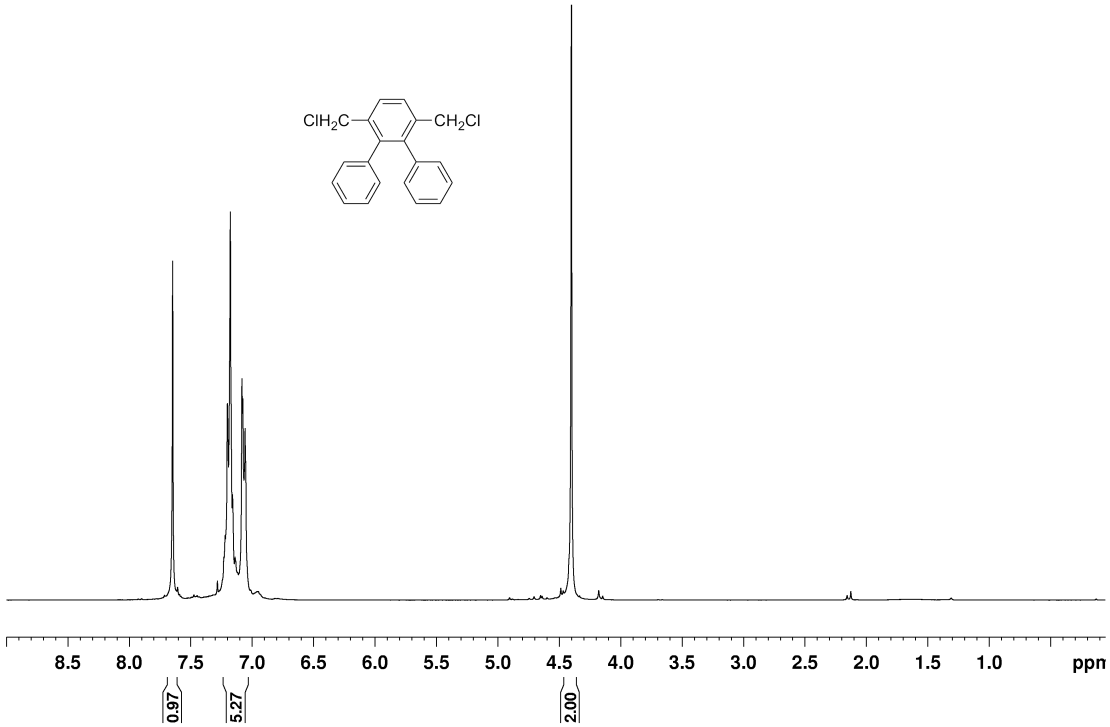


Figure 28. 300 MHz ^{1}H NMR Spectrum ($CDCl_3$) of **27**.

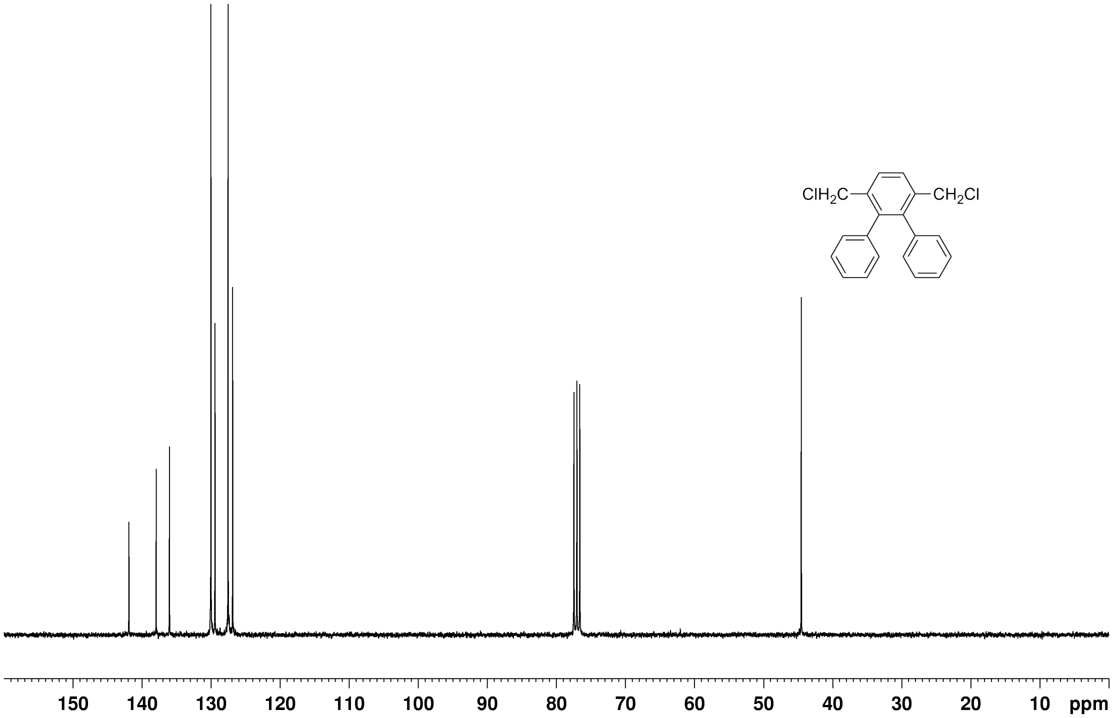


Figure 29. 75 MHz ^{13}C NMR Spectrum ($CDCl_3$) of **27**.

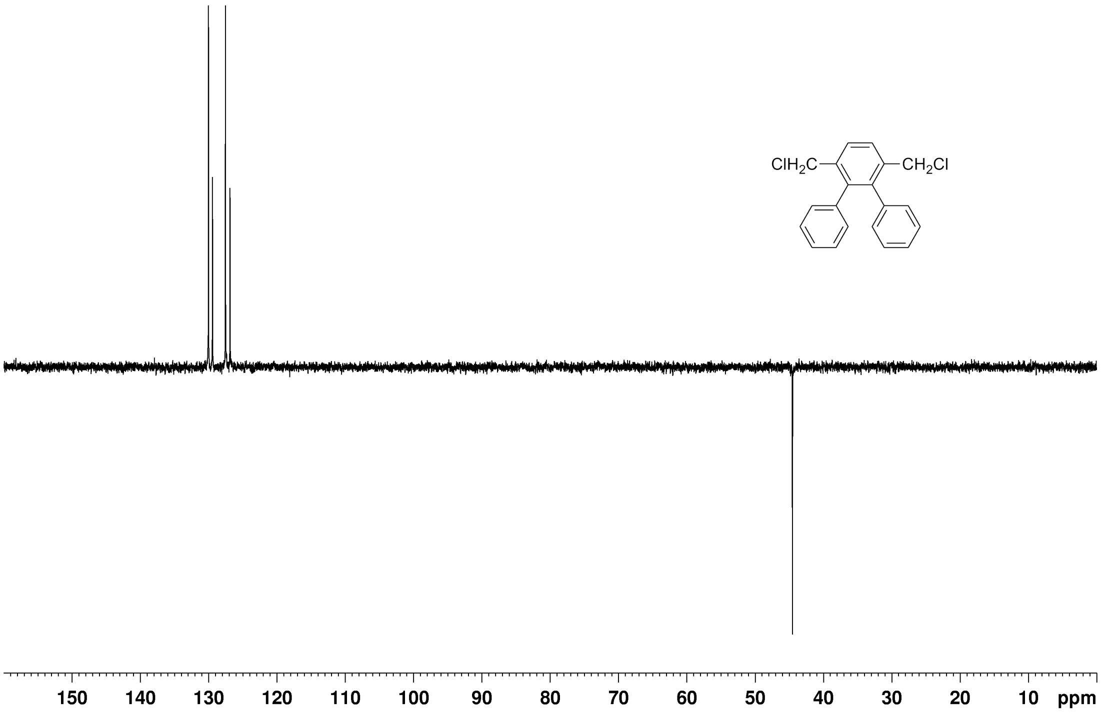


Figure 30. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) DEPT 135 of **27**.

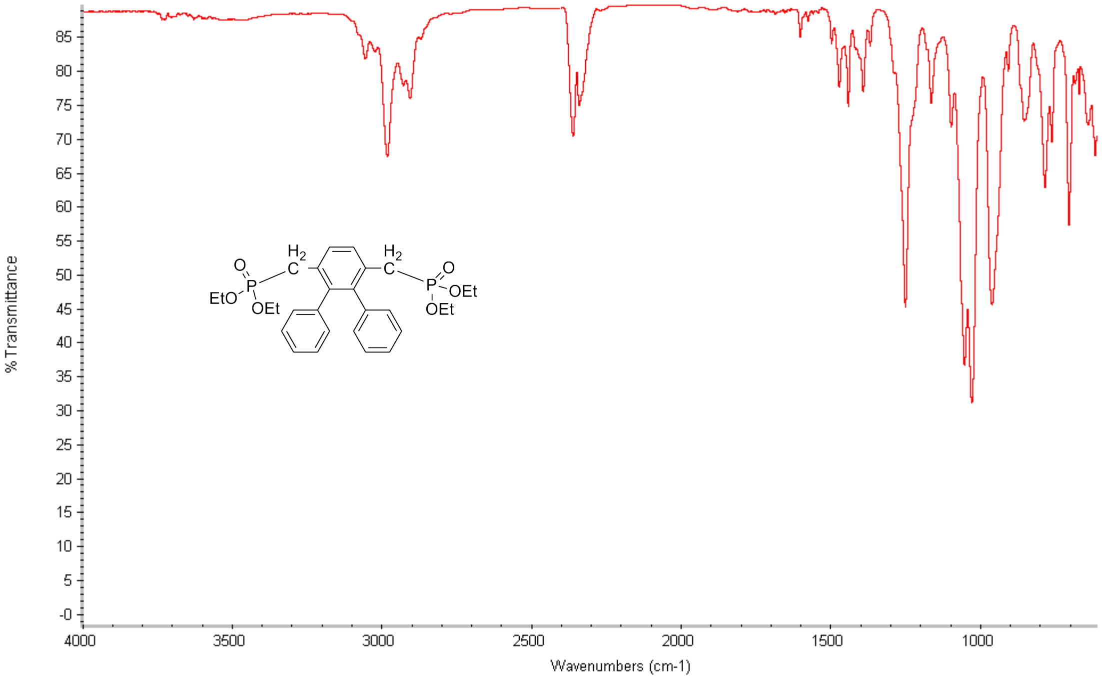


Figure 31. IR Spectrum (NaCl) of **79**.

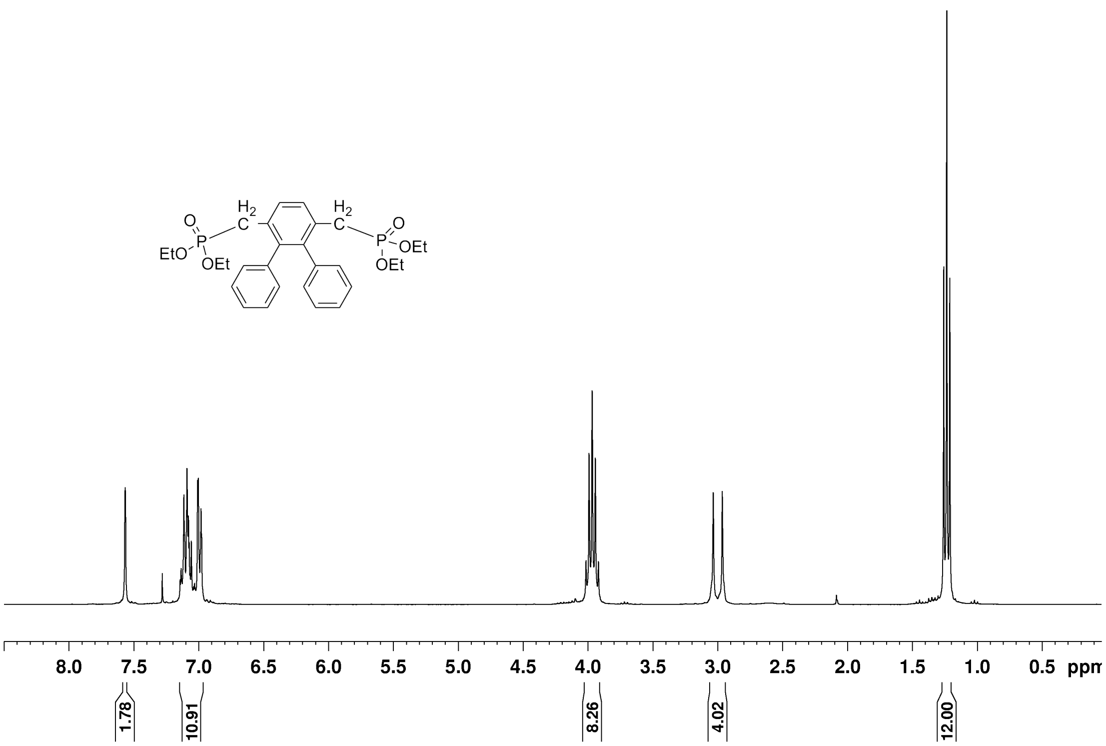


Figure 32. 300 MHz ^{1}H NMR Spectrum (CDCl$_3$) of **79**.

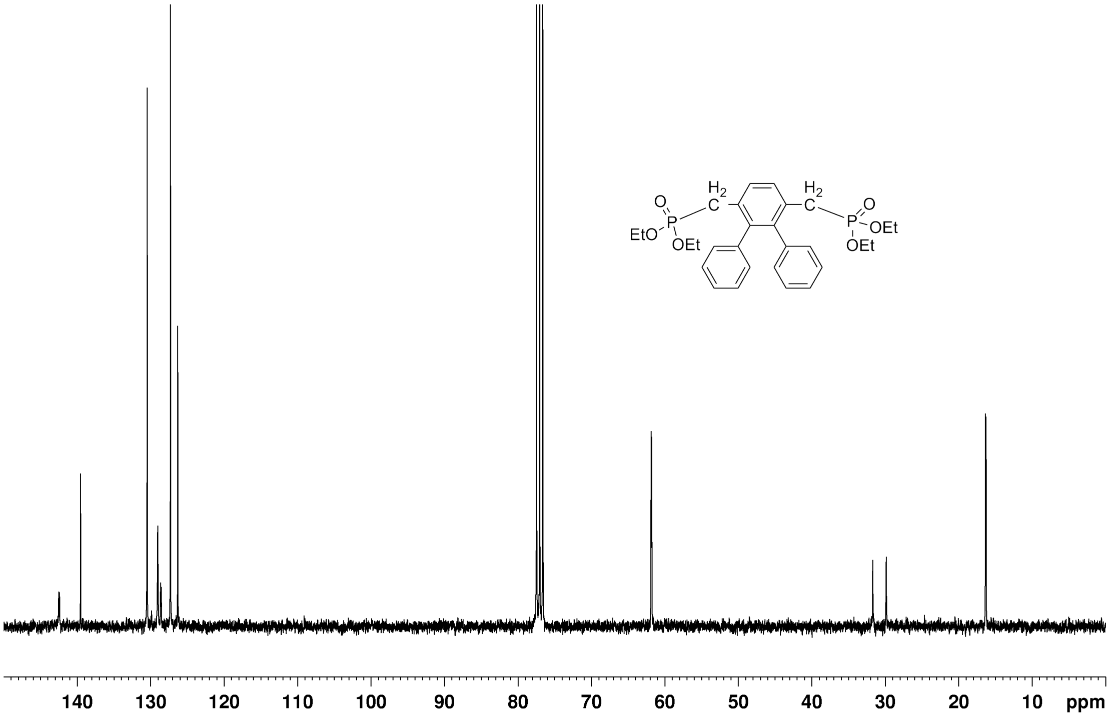


Figure 33. 75 MHz ^{13}C NMR Spectrum (CDCl$_3$) of **79**.

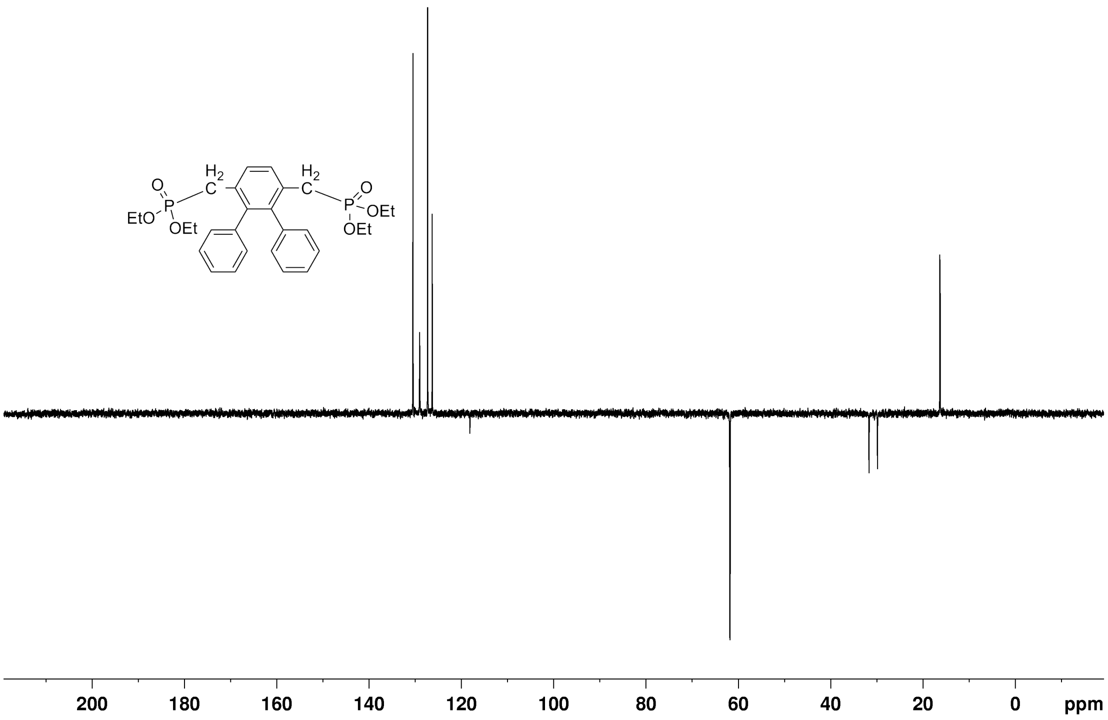


Figure 34. 75 MHz ^{13}C NMR Spectrum ($CDCl_3$) DEPT 135 of **79**.

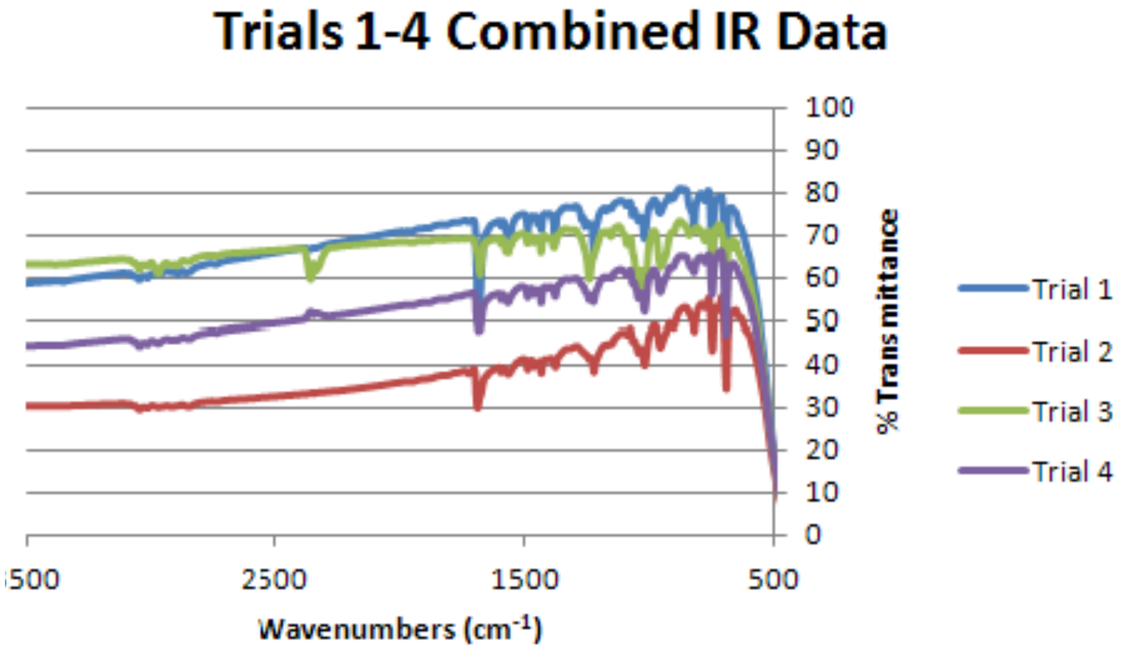


Figure 35. Combine IR Spectra (NaCl) of Trials 1-4 (**3a-3d**).

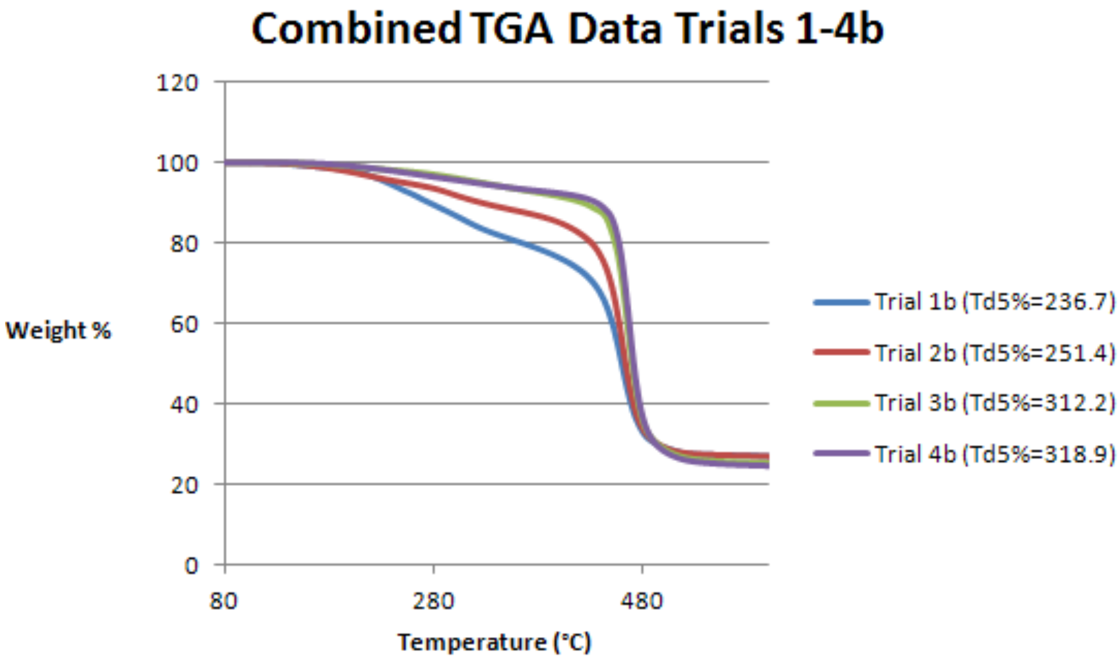


Figure 36. Combined TGA data of Trials 1-4 (**3a-3d**).

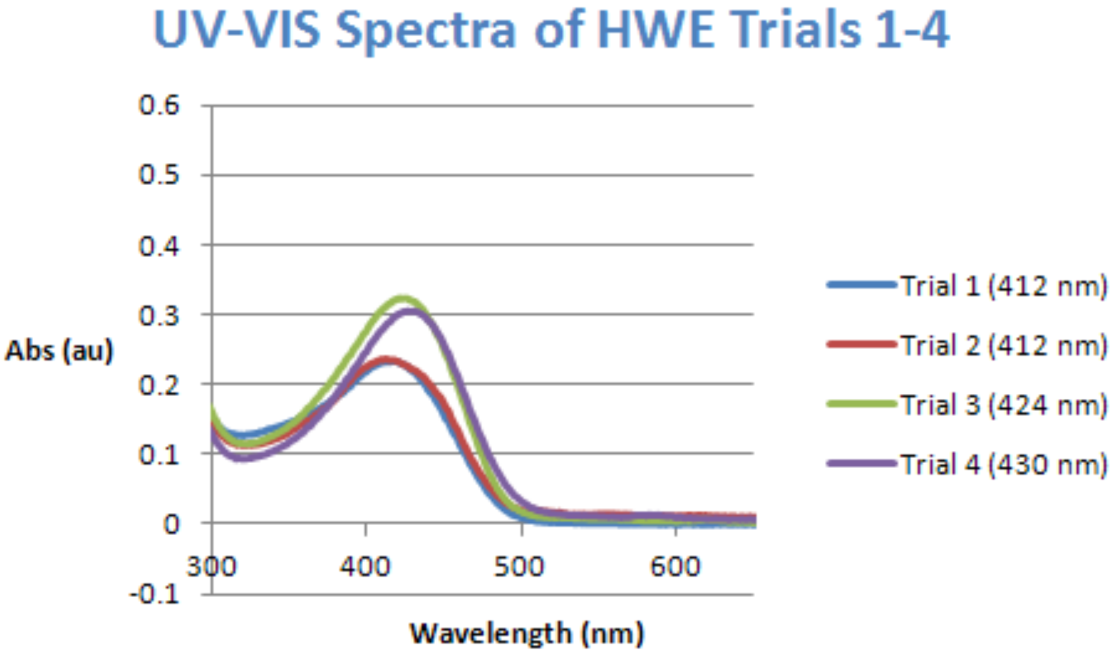


Figure 37. Combined UV-VIS data of Trials 1-4 (**3a-3d**).

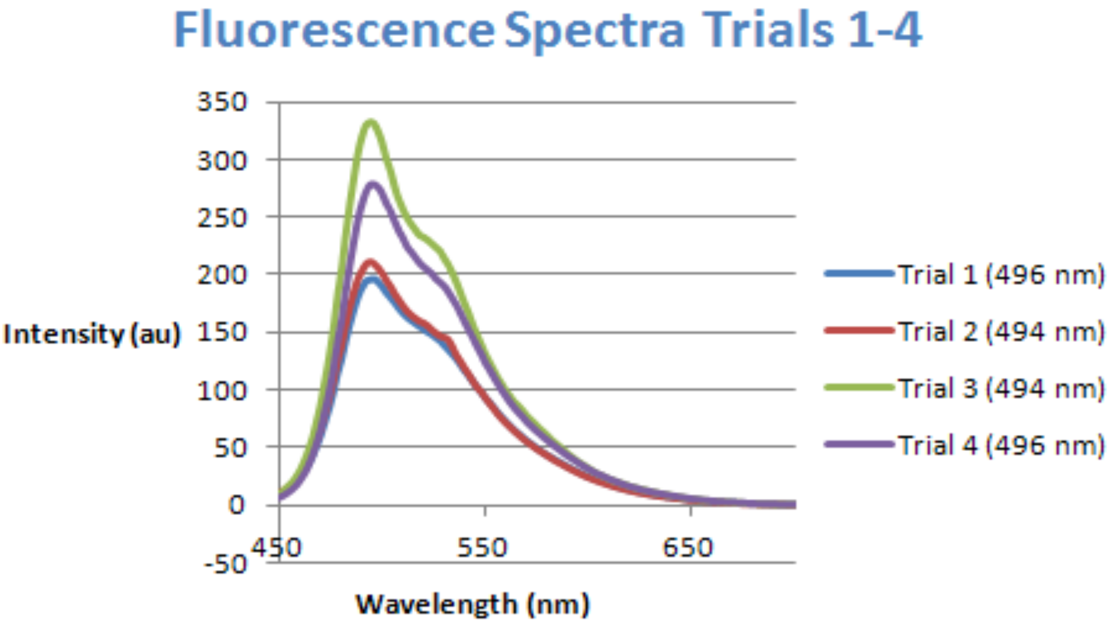


Figure 38. Combined Fluorescence data of Trials 1 - 4 (**3a-3d**) (416 nm Excitation).

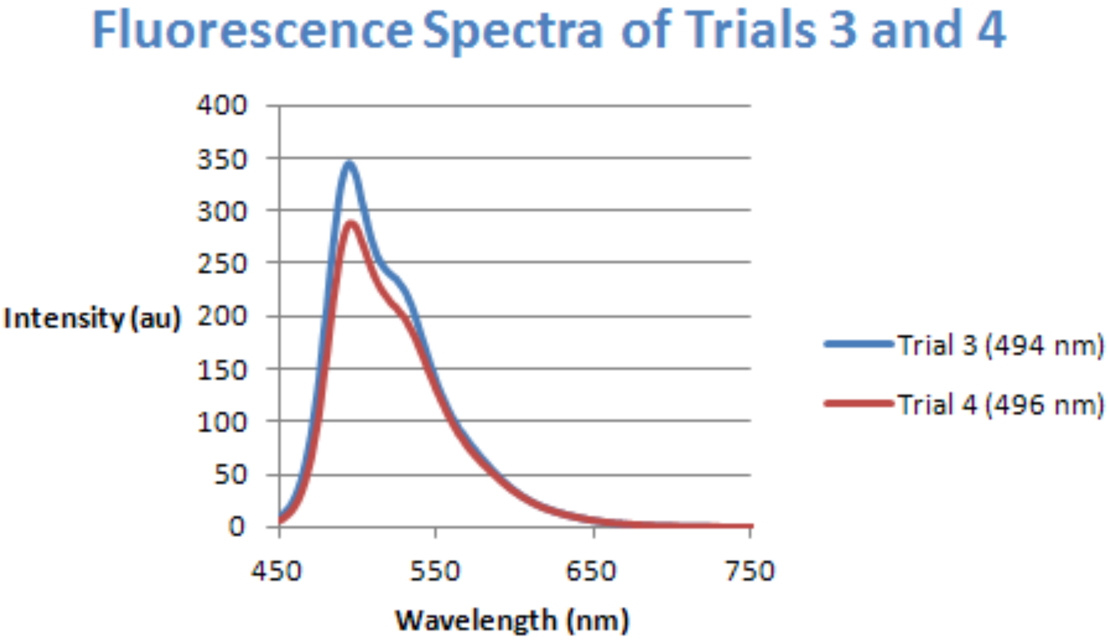


Figure 39. Combined Fluorescence data of Trials 3 - 4 (**3c-3d**) (424 nm Excitation).

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VITAE

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