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INCORPORATION OF INDENO[2,1-c]FLUORENES INTO POLYMERS VIA
NUCLEOPHILIC AROMATIC SUBSTITUTION

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

By

NATHANIEL BRACKETT
B.S. Wright State University 2015

2017
Wright State University

WRIGHT STATE UNIVERSITY

GRADUATE SCHOOL

August 17, 2017

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Nathaniel Brackett ENTITLED Incorporation of Indeno[2,1-c]fluorenes Into Polymers via Nucleophilic Aromatic Substitution. BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science

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ABSTRACT

Brackett, Nathaniel. M.S., Department of Chemistry, Wright State University, 2017.
Incorporation of Indeno[2,1-c]fluorenes into Polymers via Nucleophilic Aromatic Substitution.

A difluoro indeno[2,1-c]fluorene monomer was synthesized by a four-step process. The first compound synthesized by a two-step process was 2,5-bis(ethoxycarbonyl)-3,4-di(4-fluorophenyl)cyclopentadienone. The next two compounds synthesized were diethyl 2,3-bis(fluorophenyl)-5-hexylterephthalate and 2,3-bis(fluorophenyl)-5-hexylterephthalic acid. The final step involved an intramolecular Friedel-Crafts acylation of the terephthalic acid derivative to form 3,10-difluoro-5,8-dioxo-5,8-dihydro-6-hexylindeno[2,1-c]fluorene. The difluoro monomer was reacted in a series of nucleophilic aromatic substitution (NAS) polymerization reactions with bisphenol-A in N-methyl-pyrrolidone (NMP) in an attempt to form novel poly(ether ether ketone ketone)s containing the indeno[2,1-c]fluorene structure. Analysis of the product by NMR and TLC showed the reaction was unsuccessful and the difluoro monomer did not undergo significant fluorine displacement. A series of model reactions in NMP and dimethyl sulfoxide (DMSO) also confirmed that the monomer did not undergo fluorine displacement under polymerization conditions. In addition, the synthesis of diethyl 5,6-diphenyl-2,3-bis(2-thienyl)terephthalate and 2,8-dibromo-5,11-bis(4-bromophenyl)-indeno[1,2-b]fluorene-6,12-dione were carried out.

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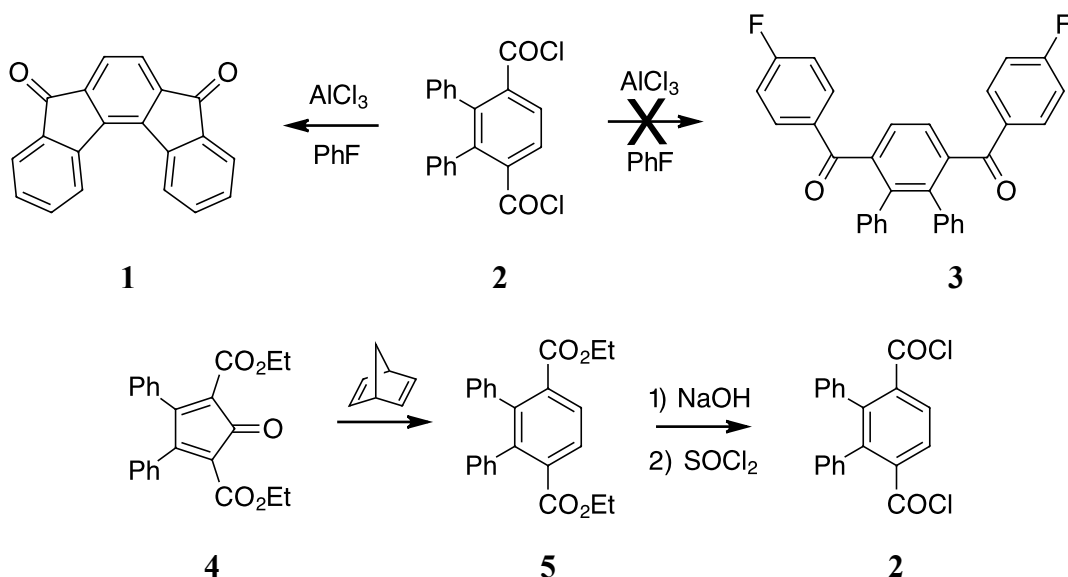
I would like to give a huge thank you to Kelly Burcham from the chemistry office for her wonderful demeanor and selflessness which is an inspiration to us all. The chemistry department could not function without her. I would also like to thank Dr. Eric Fossum and Dr. Ken Turnbull for being on my committee and not minding me pop in for a research question. I would also like to thank them for some of the most informative and convivial classroom settings I have ever experienced.

DEDICATION

I would like to dedicate this thesis to my mother Patty and my sister Shelly. These two women have never given up on me even when I had given up on myself. Their unconditional love and support has been a beacon guiding me to something better. I would also like to dedicate this to my stepfather John for his belief in me. To the rest of my friends and family, a big thank you, without all you I would not be the man I am today.

INTRODUCTION

In 1998,¹ a new method for synthesizing 5,8-dioxo-5,8-dihydroindeno-[2,1-c]fluorene **1** was discovered when the Friedel-Crafts acylation of fluorobenzene with 2,3-diphenylterephthaloyl dichloride **2** produced the **intramolecular** product **1** instead of the **intermolecular** product 1,4-bis(fluorobenzoyl)-2,3-diphenylbenzene **3**. This straight forward approach to the indeno[2,1-c]fluorene structure was aided by the facile



generation of the phenylated diacid halide **2** from 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone **4** (“Orange”) by way of the diester **5**. Although derivatives of **1** are readily generated by this process, no report of the incorporation of **1** or those derivatives into polymeric systems has been reported.

The objectives of this research were 1) to explore the functionalization of **1** to include polymerizable groups, 2) to assess the potential of appropriately substituted derivatives for polymerization and 3) to characterize the new materials produced.

HISTORICAL

Indenofluorenes are a class of compounds comprised of indene and fluorene that are fused together in a five-ring system.² Indenofluorenes exist as five distinct regioisomers that are named according to orientation of the indene structure with respect to the fluorene structure.

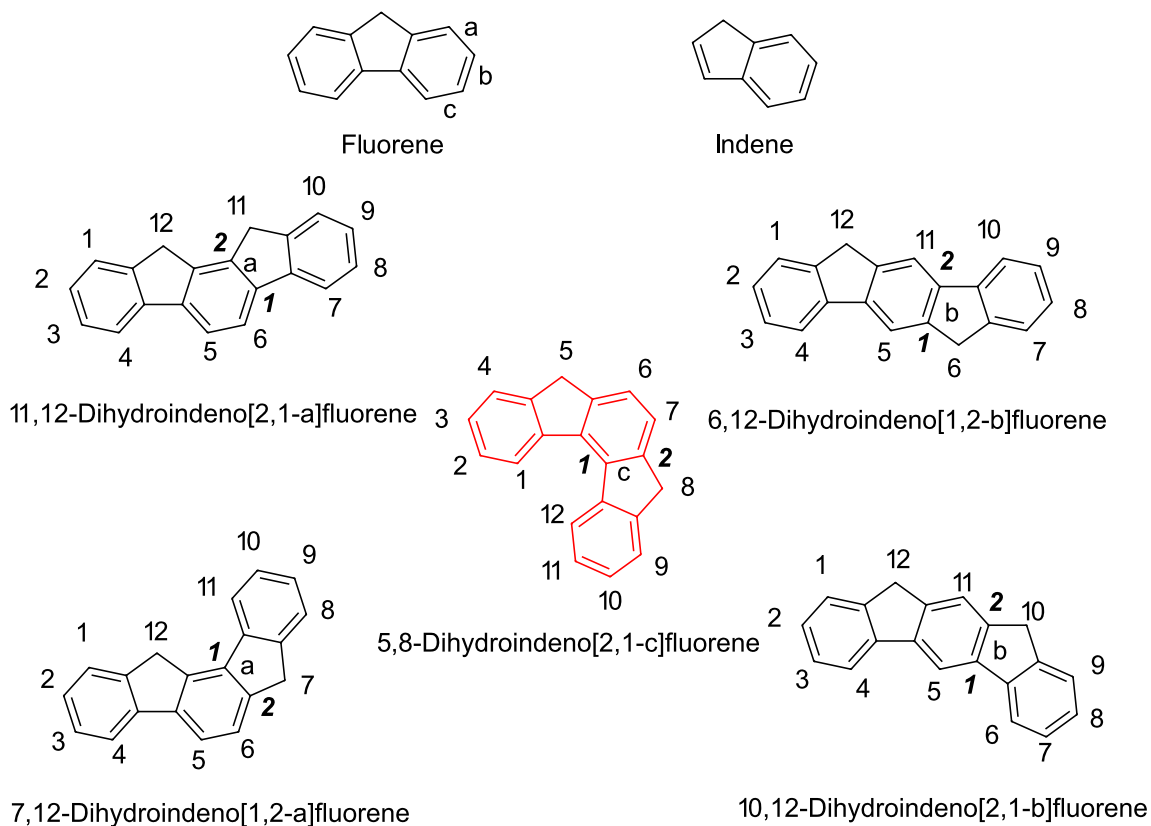


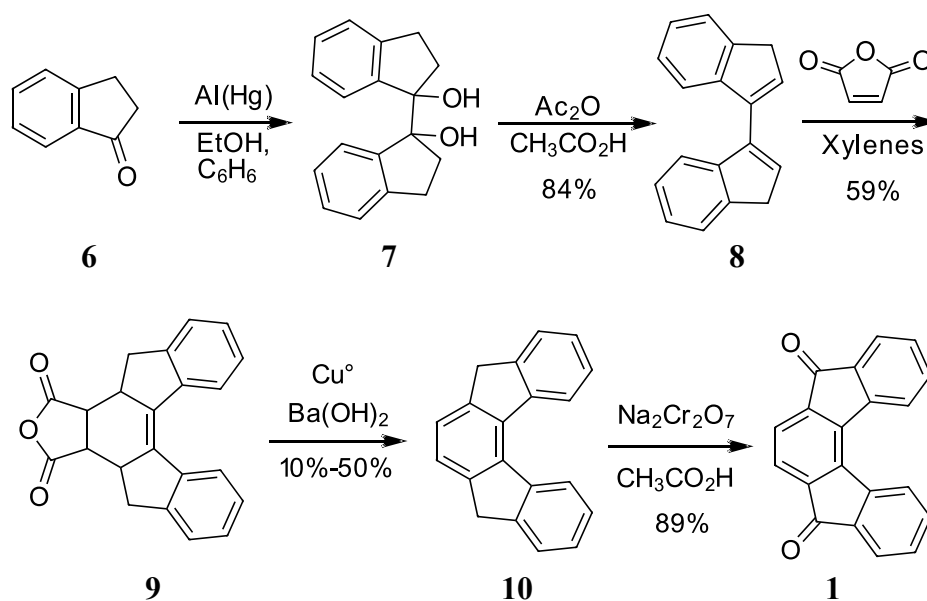
Figure 1. Structures of fluorene, indene and the five regioisomers of the dihydroindenofluorenes with number/letter designations and IUPAC names.

The bold numbers in italics (**Figure 1**) refer to the methylene bridge formed by each isomer. The [1,2] isomers have the five membered rings of the dihydroindenofluorene in an *anti*-conformation. The [2,1] isomers have the five membered rings in a

syn conformation. The lower case lettering (**Figure 1**) in the isomers pertain to the location of the indene/fluorene fusion. The [2,1] isomers all give rise to an *a*, *b* and *c* fusion structure. However, the [1,2] isomers only give rise to *a* and *b* fused structures due to the fact that the [1,2-*c*] structure is identical to the [1,2-*a*] structure. This work will be concerned with the indeno[2,1-*c*]fluorene isomer.

Initial Synthesis of 5,8-Dioxo-5,8-dihydroindeno[2,1-*c*]fluorene

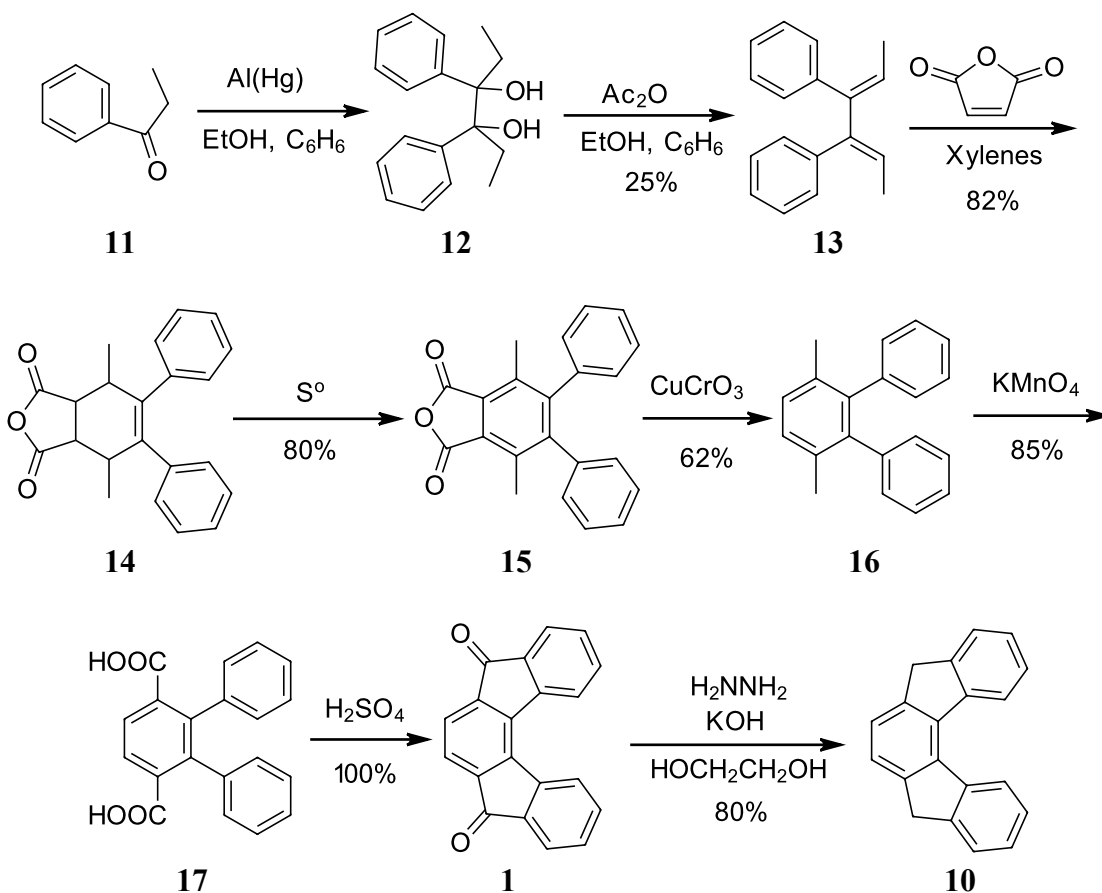
The first reported synthesis of 5,8-dioxo-5,8-dihydroindeno[2,1-*c*]fluorene **1** was completed in 1961.³ The initial reaction involved the Pinacol reaction of indanone **6** with aluminum amalgam to provide 1,1'-biindanyl-1,1'-diol **7**. Diol **7** was transformed into 3,3'-biindenyl **8** by the dehydration of the pinacol **7** using acetic anhydride/acetic acid. 3,3'-biindenyl **8** by the dehydration of the pinacol **7** using acetic anhydride/acetic acid.



Diene **8** underwent a standard Diels-Alder reaction with maleic anhydride as the dienophile in xylenes to yield 5,5a,6,7,7a,8-hexahydroindeno[2,1-*c*]fluoren-6,7-dicarboxylic anhydride **9**. A one-pot reaction using copper powder, barium hydroxide and soda-glass under an inert atmosphere was employed to first aromatize, then hydrolyze and finally decarboxylate **9** to form 5,8-dihydroindeno[2,1-*c*]fluorene **10**.

Compound **10** was oxidized at the 5 and 8 positions to provide 5,8-Dioxo-5,8-dihydroindeno[2,1-c]fluorene **1**. The synthesis resulted in an overall yield of 1.7-8.3%. This suggested the need for further investigation to identify a more efficient route to compound **1**.

In 1966,⁴ a second total synthesis of 5,8-dioxo-5,8-dihydroindeno[2,1-c]fluorene was reported which employed propiophenone **11** as the starting material. A Pinacol reaction of **11** using aluminum amalgam was used to provide 3,4-diphenyl-3,4-hexanediol **12**.

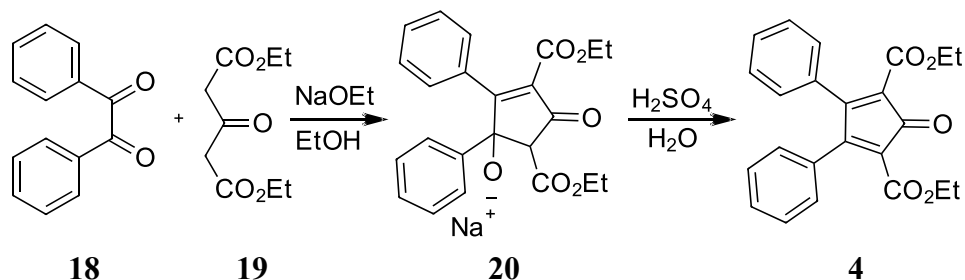


The diol **12** was dehydrated using acetic anhydride to afford 3,4-diphenyl-2,4-hexadiene **13**. A standard Diels-Alder reaction between **13** and maleic anhydride as the dienophile was carried out in benzene to yield 3,6-dimethyl-4,5-diphenyl-4-cyclohexene-1,2-

dicarboxylic anhydride **14**. Elemental sulfur was used to aromatize compound **14** to the anhydride **15**. The anhydride **15** underwent hydrolysis to afford 3,6-dimethyl-4,5-diphenylphthalic acid which was decarboxylated with copper chromite to 2,3-diphenyl-1,4-xylene **16**. The methyl groups in **16** were oxidized with potassium permanganate to create the terephthalic acid derivative **17**. The desired product **1** was then formed using sulfuric acid to catalyze an intramolecular Friedel-Crafts acylation of **17**. A Wolf-Kishner reduction was performed on the ketones of **1** at the 5 and 8 positions to yield compound **10**. The overall synthesis still only had around a 7% yield, thus a more direct approach to the synthesis of **1** was desired.

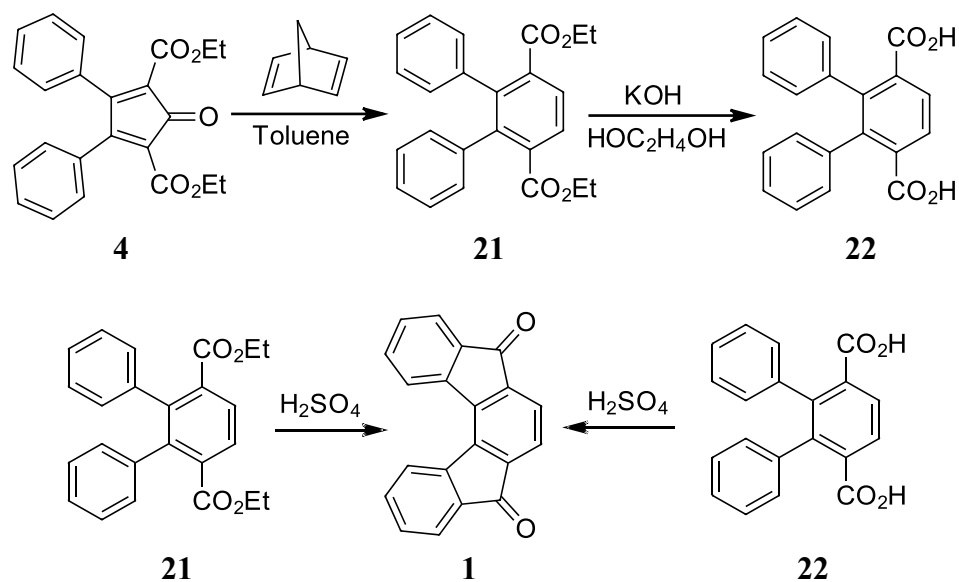
Synthesis of 2,5-Dicarboethoxy-3,4-diphenylcyclopentadienone

A novel two-step sequence was discovered in 1971 as an easy way to produce 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone **4** from benzil **18** and diethyl 1,3-acetonedicarboxylate **19**.⁵ The diene, 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone **4**, is a key precursor in the five-step synthesis of 5,8-dioxo-5,8-dihydroindeno[2,1-c]fluorene although this fact was not known for the succeeding 27 years. Benzil **18** and diethyl 1,3-diacetonedicarboxylate **19** were refluxed in ethanol using sodium ethoxide as base to provide a sodium salt **20** that was protonated and dehydrated with sulfuric acid and acetic anhydride to provide **4**.

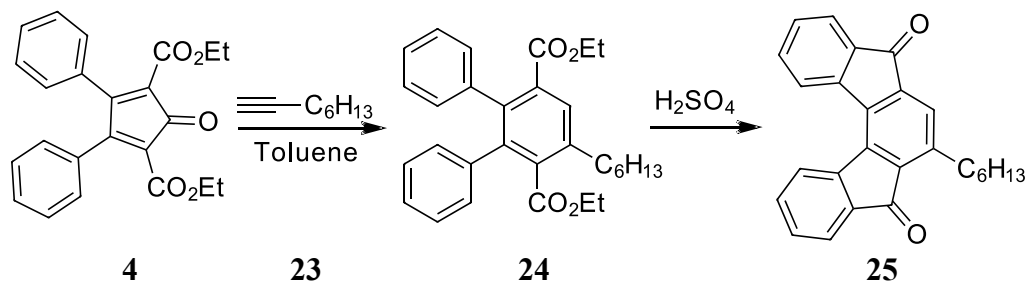


Cyclopentadienones as Precursors to Indenofluorenones

In 1998,¹ a new method for general indenofluorene synthesis was discovered after it was observed that the diacid halide **2** undergoes an intramolecular ring closure instead of the expected intermolecular reaction of fluorobenzene with **2** using aluminum chloride as catalyst. It was later shown that other acid derivatives behaved similarly. The initial step of the synthesis is an Inverse Electron Demand Diels-Alder (IEDDA) reaction between **4** and norbornadiene to form a terephthalic diester **21**. The diester **21** was hydrolyzed with KOH in ethylene glycol to form 2,3-diphenylterephthalic acid **22**. Both the terephthalic diester **21** and the terephthalic diacid **22** undergo intramolecular acylation in sulfuric acid to produce **1**.



Because of the limited solubility of **1**, an additional pendent on the indeno[2,1-c]fluorene skeleton was added. The only difference in the overall synthesis is the employment of 1-octyne **23** as the dienophile. The product, 5,8-dioxo-5,8-dihydro-5-hexylindenofluorene **25**, produced from the diester **24**, exhibited a melting point 170° lower than the unsubstituted indenofluorene **1**.

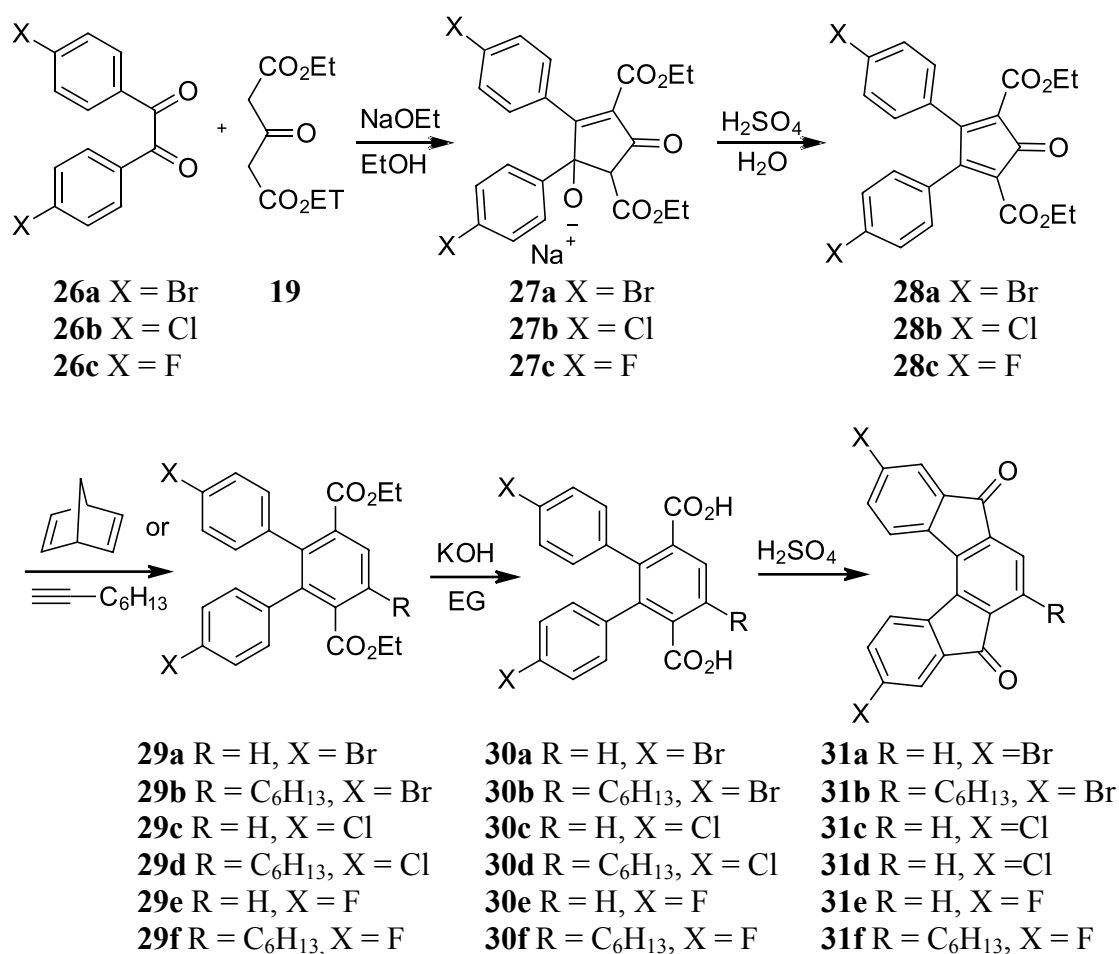


The added alkyl pendent in a 5,8-dioxoindeno[2,1-c]fluorene invariably leads to a lower melting point and increased solubility for a variety of indenofluorenes. This method proved to be a very efficient method for producing indenofluorenes from both functionalized benzils and alkynes.

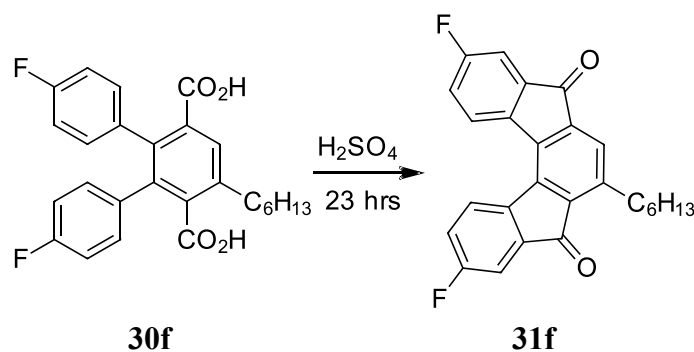
Halogenated Indeno[2,1-c]fluorenes

In 1999,⁶ a bromophenyl substituted indenofluorene was synthesized by using 4,4'-dibromobenzil **26a** and diethyl 1,3-acetonedicarboxylate **19** in the same synthesis described above to yield 2,5-bis(ethoxycarbonyl)-3,4-di(4-bromophenyl)cyclopentadienone **28a**. The brominated cyclopentadienone **28a** underwent an IEDDA reaction with norbornadiene in toluene at reflux to form diethyl 2,3-di(4-bromophenyl)-1,4-benzenedicarboxylate **29a**. The terephthalic acid derivative **29a** underwent base hydrolysis with potassium hydroxide in ethylene glycol to provide diacid **30a**. The brominated diester **29a** and diacid **30a** both underwent the intramolecular ring closure under the same conditions as the unsubstituted diacid and diester to form 3,10-dibromo-5,8-dioxo-5,8-dihydroindeno[2,1-c]fluorene **31a**. The substitution of 1-octyne for norbornadiene in the cycloaddition reaction of cyclopentadiene **28a** was employed to generate 3,10-dibromo-5,8-dioxo-5,8-dihydro-5-hexylindeno[2,1-c]fluorene **31b**. As expected, the melting point of **31b** was 204° lower than that of **31a** and the solubility increased dramatically.

The scope of these reactions were expanded in 2003 to include difluoro- and dichlorocyclopentadienones as shown in the reaction scheme below.⁷

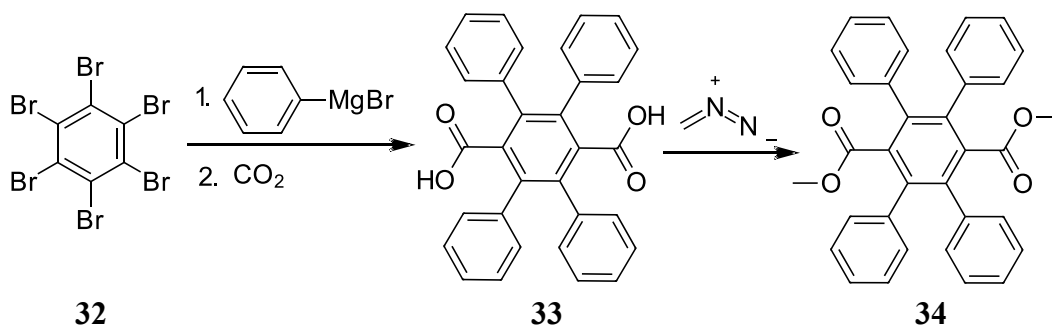


It should be noted that at the time, the difluoro substituted terephthalates **29e** and **29f** exhibited different behavior in ring closure reactions as compared to the dibromo and dichloro derivatives. Diester **29e** did not undergo ring closure in strong acid. Instead, the reaction resulted in a mixture of half-product and unreacted starting material. Diester **29f**, however, forms 3,10-difluoro-5,8-dihydro-5,8-dioxoindeno[2,1-c]fluorene **31f** on extended heating in strong acid.



Indeno[1,2-b]fluorenes

The first tetraphenylterephthalate was synthesized in 1939⁸ during an attempt to create hexaphenylbenzene. Hexabromobenzene **32** and phenylmagnesium bromide react to produce a symmetrical 2,3,5,6-tetraphenyl intermediate that could be carbonated with gaseous carbon dioxide at 0° to form 2,3,5,6-tetraphenylterephthalic acid **33**. The acid

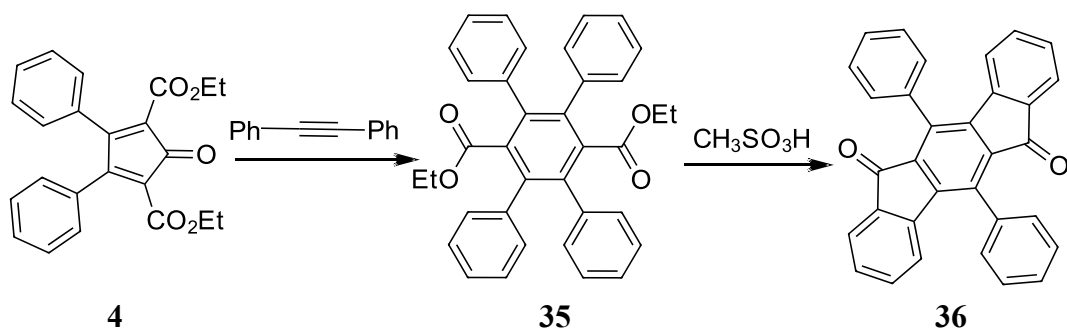


was esterified with diazomethane to form dimethyl 2,3,5,6-tetraphenylterephthalate **34**.

However, the overall yield was less than 1%.

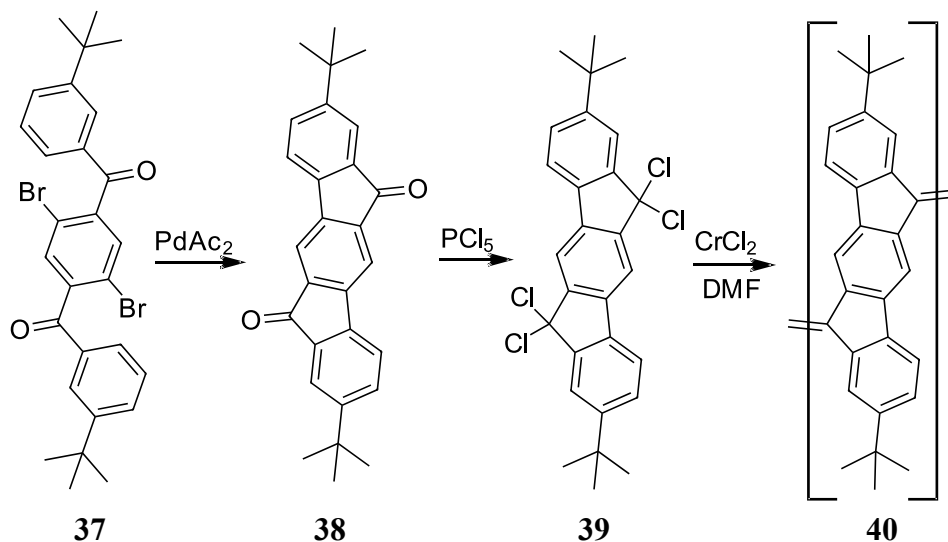
In 1998,⁹ a much more efficient, high-yield process involving cyclopentadienones was used to produce tetraphenylterephthalates. The reaction of 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone **4** with diphenylacetylene in a melt reaction yielded diethyl 2,3,5,6-tetraphenylterephthalate **35**. Terephthalate **35** underwent an **intramolecular** ring closure in methanesulfonic acid to form 5,11-diphenyl 6,12

dihydro-6,12-dioxoindeno[1,2-b]fluorene **36**. Tetraphenyl terephthalates only form the 1,2-b regioisomer of the indenofluorene structure.¹⁰



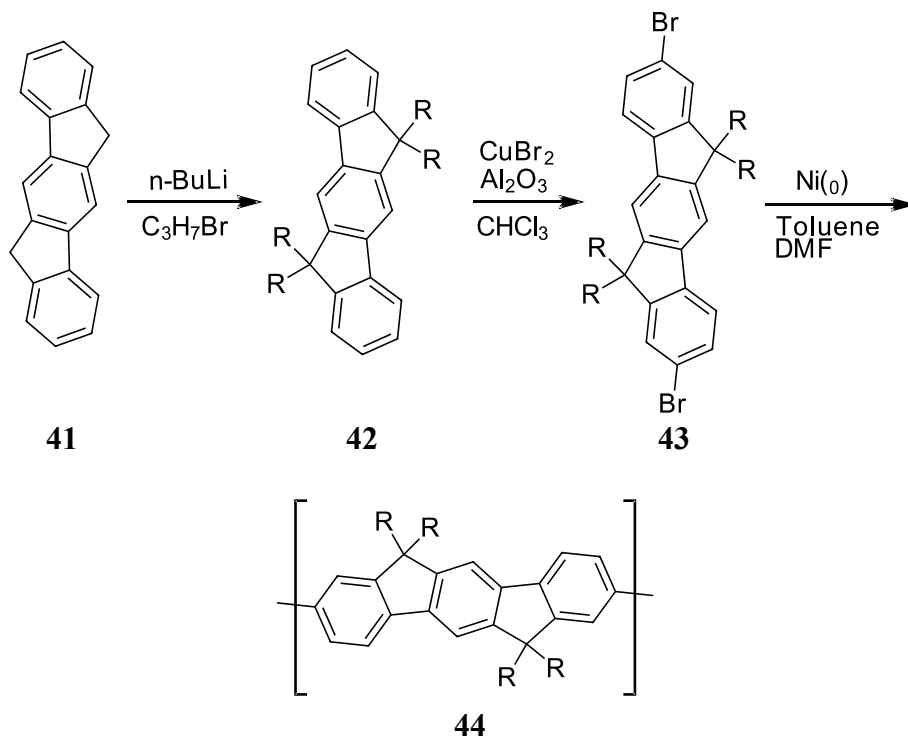
Indenofluorene Containing Polymers

Indenofluorenes were first incorporated into polymers in 1996.¹¹ Initially, 2,5-dibromo-1,4-bis-(4-tert-butylbenzoyl)benzene **37** underwent an intramolecular coupling using a Pd(0) catalyst to form 6,12-dioxo-6,12-dihydroindeno[1,2-b]fluorene **38**. The diketone **38** was converted into the monomer, 3,9-di-tert-butyl-6,6,12,12-tetrachloro-6,12-dihydroindeno[1,2-b]fluorene **39** by reaction with phosphorus pentachloride. The tetrachloro monomer **39** underwent a polycondensation reaction to form poly(3,9-di-tert-butylindeno[1,2-b]fluorene) **40** referred to as a “picket fence” polymer. Many different coupling methods were investigated in an attempt to increase the degree of



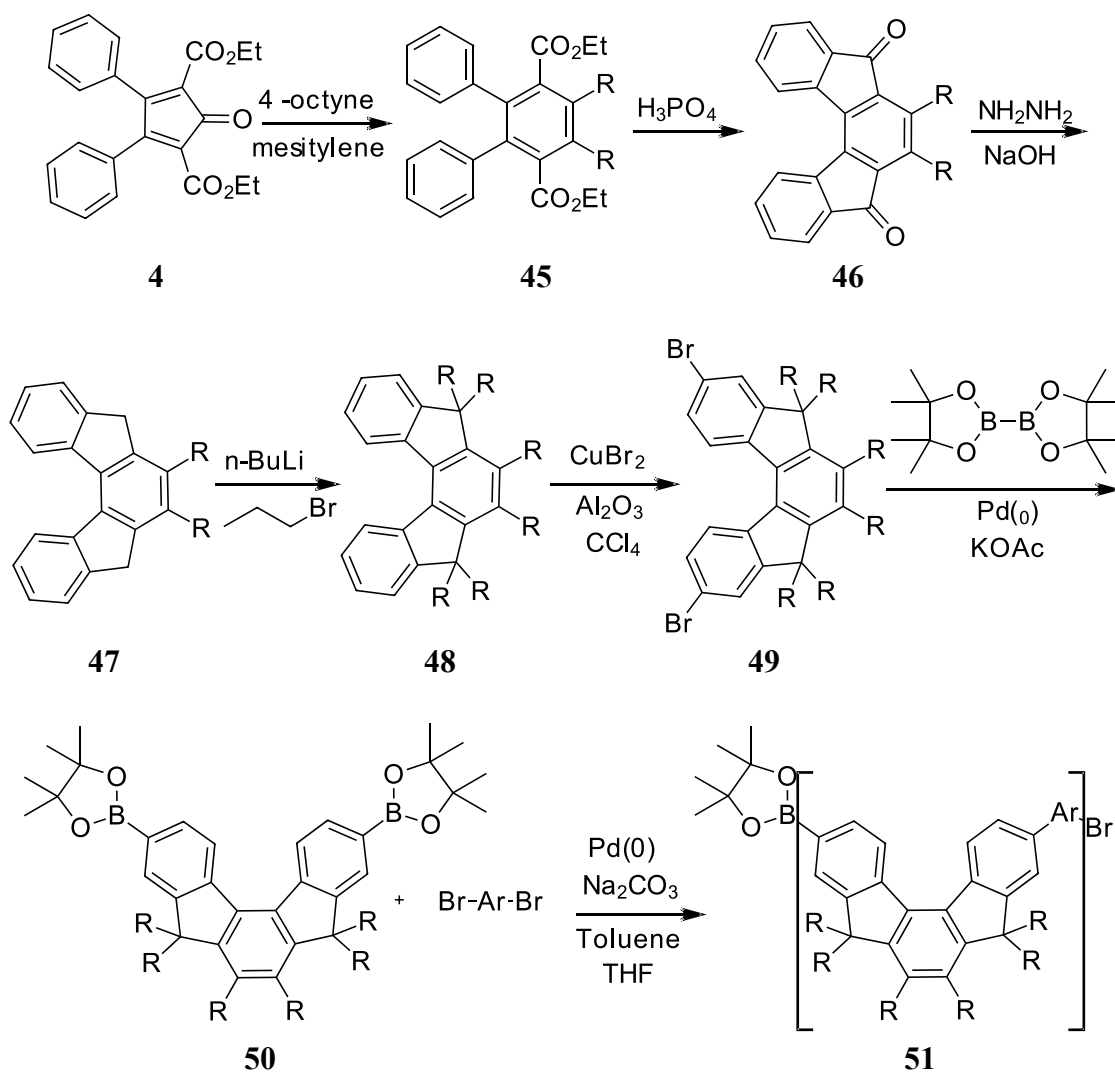
polymerization. The number average molecular weights (M_n , determined by GPC) ranged from 3,500-19,500 and the polydispersity index (PDI) range was 2.16-4.35.

Another example of indenofluorene incorporation into linear polymers was reported in 1999.¹² Initially, 6,12-dihydroindeno(1,2-b)fluorene **41** was tetraalkylated using *n*-butyl lithium and an alkylbromide to form 6,6',12,12'-tetraalkyl-6,12-dihydroindeno(1,2-b)fluorene **42**. The alkylated indenofluorene **42** was brominated at the 2 and 8 positions with copper(II) bromide on aluminum oxide in chloroform to provide 2,8-dibromo-6,6',12,12'-tetraalkyl-6,12-dihydroindeno(1,2-b)fluorene **43**. A Yamamoto coupling with a Ni(0) catalyst was used to form poly(6,6',12,12'-tetraalkyl-6,12-dihydroindeno(1,2-b)fluorene) **44**. Two polymerizations resulted in M_n values of 33,000 with a PDI of 5.2 for one and 39,000 with a PDI of 2.75 (determined by GPC) for the other. It was noted that rigid rod polymers in GPC can exhibit results that inflate the



molecular weights by as much as 25%. The high PDI indicates that a wide variety of chain lengths were produced by this polymerization technique. The polymers did exhibit excellent thermal properties with 5% weight loss occurring at 380° and decomposition at 450° by Thermal Gravimetric Analysis (TGA).

The first example of an indeno[2,1-c]fluorene being incorporated into a polymer occurred in 2013.¹³ A Diels-Alder reaction between “Orange” **4** and 4-octyne provided diethyl 2,3-diphenyl-5,6-dipropylterephthalate **45**. The tetrasubstituted terephthalate underwent an intramolecular ring closure in polyphosphoric acid to form 6,7-dipropyl-5,8-dihydro-5,8-dioxoindeno[2,1-c]fluorene **46**. The dioxoindenofluorene was reduced by a Wolf-Kishner reduction to yield 6,7-dipropyl-5,8-dihydroindeno[2,1-c]fluorene **47**. The 5 and 8 positions were alkylated using n-butyllithium and 1-bromopropane to form 5,5',6,7,8,8'-hexapropyl-5,8-dihydroindeno[2,1-c]fluorene **48**. The indenofluorene was brominated at the 3 and 10 positions using copper (II) bromide and aluminum oxide in carbon tetrachloride to form 3,10-dibromo-5,5',6,7,8,8'-hexapropyl-5,8-dihydroindeno[2,1-c]fluorene **49**. The alkylated dibromoindenofluorene derivative was converted to a bis(dioxaborolane) derivative **50** by a Pd(0) coupling reaction. A Suzuki polycondensation of **50** with a dibromo compound **49** gave rise to a polymer **51** that contains the indeno[2,1-c]fluorene subunit. Three polymers containing the indeno[2,1-c]fluorene subunit had a M_n range of 6,968-11,575 g/mol and the PDI were fairly consistent with a range from 1.57-1.92. The polymers showed desirable absorption and emission properties with maximum absorptions in the ranges of 416-432 nm.



It is clear that the indeno[2,1-c]fluorene and related indenofluorene substructures can be incorporated into polymeric systems. The substructures were, however, not the keto derivatives. From the previous discussion, the compound that appears to be a candidate for incorporating the 5,8-dioxo-5,8-dihydroindeno[2,1-c]fluorene substructure into a polymeric system is 3,10-difluoro-5,8-dioxo-5,8-dihydroindeno[2,1-c]fluorene **31f**. The resonance structures shown in **Figure 2** appear to indicate an electronic activation of the fluorine ipso carbon toward nucleophilic attack. Therefore, the main objectives of the current research were 1) the synthesis of reasonable quantities of **31f**, 2) the complete

characterization of **31f** and 3) the investigation of the behavior of **31f** in model Nucleophilic Aromatic Substitution (NAS) reactions with p-cresol as well as polymerizations with bisphenol-A.

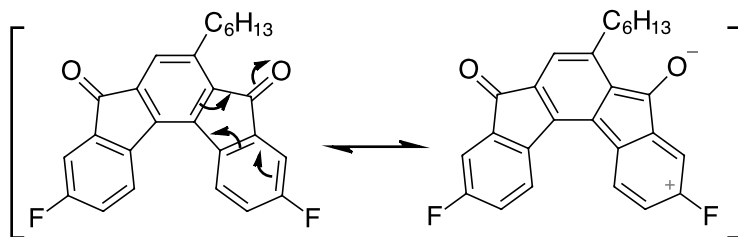
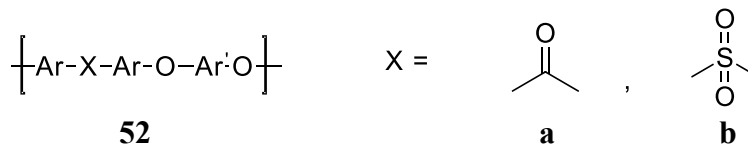


Figure 2. Resonance structures for nucleophilic fluorine displacement activation in 3,10-difluoro-5,8-dioxo-5,8-dihydroindeno[2,1-c]fluorene **31f**.

Poly(aryl ether)s

Poly(aryl ethers)s (PAE) **52a-b** are a class of high-performance, step-growth polymers which generally consist of phenylene units that are activated by electron withdrawing groups and connect by ether linkages. PAEs exhibit many desirable properties including excellent chemical resistance, high thermal stability, strong mechanical properties, and reasonable processability. PAEs are fairly inexpensive to manufacture which makes them very desirable.¹⁴



Nucleophilic aromatic substitution (NAS) is the most common synthetic technique used for creating the ether linkages in PAEs. PAEs are usually formed by step-growth polymerizations between a dihalo compound and a bisphenol (**Figure 3**). The halogens are activated by an electron-withdrawing group that increases the partial positive charge associated with the halogen ipso carbon.¹⁴ Ketones are a common

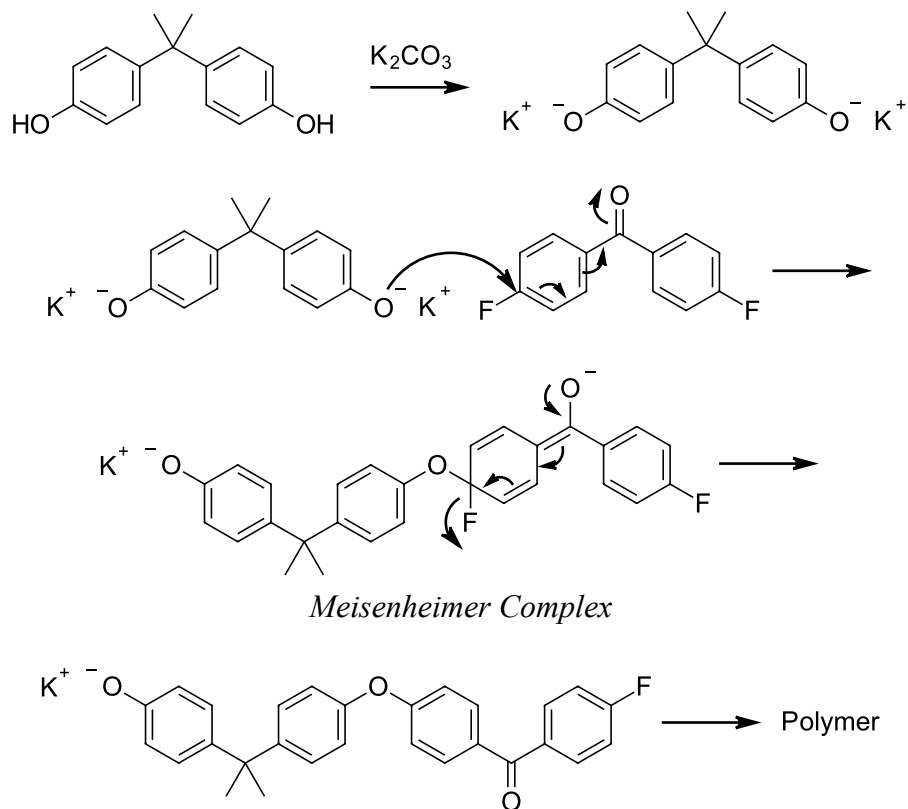


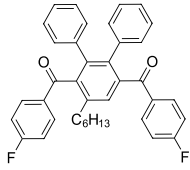
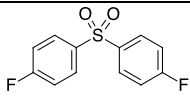
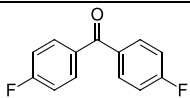
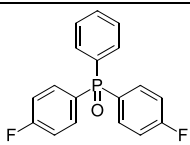
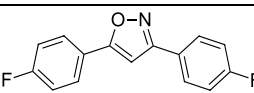
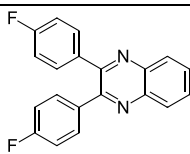

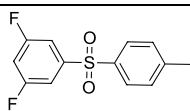
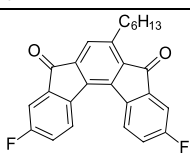
Figure 3. General mechanism for fluoro displacement via nucleophilic aromatic substitution (NAS).

withdrawing group used in the formation of PAEs. Nucleophilic attack by the phenoxide occurs at the halogen ipso carbon. A Meisenheimer complex is proposed as an intermediate in the reaction. The loss of fluoride completes the formation of the ether linkage. Repetition of these steps leads to polymers. Sulfones and imides are also commonly used as withdrawing groups in PAEs, all of which form a Meisenheimer complex in a similar fashion. This versatility allows for a wide variety of PAEs that have many desirable properties.

¹³C NMR Shifts and Fluorine Displacement

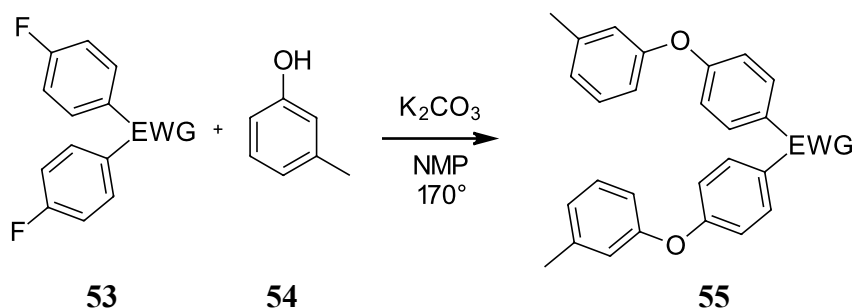
In 1995,¹⁵ an investigation was conducted to determine the fluorine displacement potential in PAE formation reactions by predicted by ¹³C NMR. The ¹³C NMR chemical

Table 1. List of fluorinated compounds that undergo fluoro displacement and the chemical shifts of the fluorine ipso carbon (from reference 14 unless otherwise noted).

<i>Fluoroaromatic Monomer</i>	<i>Fluorine ipso carbon ^{13}C chemical shift (ppm)</i>
	165.44 ¹⁶
	165.31
	165.27
	165.05
	164.50
	163.10
	162.82
	162.80 ¹⁷
	???

shifts of the ipso carbon for several fluoroaromatic PAE monomers (**Table 1**) were correlated with the reactivity of the compounds in model reactions with m-cresol. The investigation showed that ipso carbons of a C-F bond that have a chemical shift in the range of 162.80-165.31 ppm should undergo halogen displacement. Monomers with a chemical shift below 162.80 ppm are usually not able to form high molecular-weight

polymers due to the inability of the nucleophile to complete the S_NAr reaction or that high temperature degradations preclude the formation of high molecular weight polymers.



It appears that NAS could be a new way of incorporating indenofluorenes into polymeric systems. These systems could represent novel materials, some of which could be very useful for organic field effect transistors (OFET) and organic light emitting diodes (OLED) currently being developed.

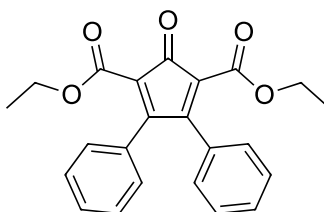
The objectives of this research were to 1) to further explore the functionalization of **1** to include polymerizable groups, 2) to assess the potential of appropriately substituted derivatives for polymerization and 3) to characterize the new materials produced.

Experimental

Instrumentation and Chemicals.

Carbon (^{13}C) and proton (^1H) Nuclear Magnetic Resonance (NMR) spectra were acquired using a Bruker Avance 300 NMR Spectrometer. Solvents used were deuterated chloroform (CDCl_3) and deuterated acetone (Acetone-d_6). Bruker Topspin 3.5p17 was used to process all NMR spectra. Splitting patterns are indicated as singlet – s, doublet – d, triplet – t, quartet – q, quintet – qn, sextet – sx. A Thermo Scientific Nicolet 6700 FT-IR was used to acquire the Infrared spectra (IR) employing thin films on a NaCl and KBr plates. Melting points were determined with a DigiMelt MPA-160 apparatus and a MEL-TEMP capillary MPA. Elemental analyses were performed by Midwest Micro Laboratories, Indianapolis, Indiana. Starting materials were acquired from Sigma-Aldrich and used without further purification unless otherwise stated.

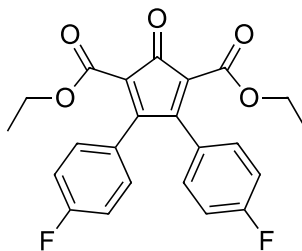
2,5-Bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone **4**



A solution of sodium metal (2.56 g, 0.11 mol) in ethanol (60 mL) was added to diethyl 1,3-acetonedicarboxylate (24.2 g, 0.12 mol) and benzil (21.0 g, 0.10 mol) dissolved in ethanol (100 mL) heated to reflux in a 250 mL round-bottomed flask. The solution initially turned orange and a yellow precipitate formed after 0.5 h. The solution

was heated at reflux for an additional 0.5 h and cooled to room temperature. After the precipitate was collected on a filter, washed with ethanol and air-dried, it was slurried in acetic anhydride (60 mL) in a 500 mL Erlenmeyer flask. Sulfuric acid was added dropwise until the solution was a translucent red and all solid had dissolved. Water was added dropwise, alternating with drops of sulfuric acid, until the temperature rose above 60°. The temperature was then maintained at 70° until the addition of water no longer raised the temperature. The orange precipitate was filtered and air-dried to yield (33.11 g, 0.088 mol, 88%) an orange product: mp 119-120° (lit.⁵ mp 120-121°); ¹H NMR (300 MHz, CDCl₃, δ) 1.17 (t, 6H, ³J_{HH} = 7.1 Hz, CH₃), 4.20 (q, 4H, ³J_{HH} = 7.1 Hz, CH₂), 7.00-7.07 (m, 4H, ArCH), 7.22-7.31 (m, 4H, ArCH), 7.32-7.41 (m, 2H, ArCH).

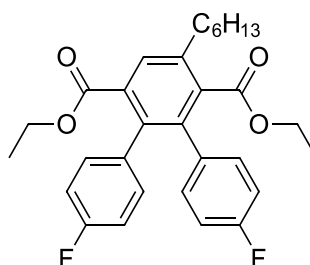
2,5-Bis(ethoxycarbonyl)-3,4-di(4-fluorophenyl)cyclopentadienone 28c



Sodium metal (0.47 g) was dissolved in ethanol (16 mL) to create a 12% sodium ethoxide solution. The solution was slowly added to a solution containing 4,4'-fluorobenzil (5.0 g, 0.021 mol, 1 equiv) and diethyl 1,3-acetonedicarboxylate (5.0 g, 0.025 mol, 1.2 equiv) in ethanol (50 mL) at reflux. The solution was held at reflux for 1 h during which a yellow precipitate formed. After the mixture was cooled to room temperature, the precipitate was collected by vacuum filtration, air dried overnight and slurried in acetic anhydride (30 mL). Sulfuric acid was added dropwise until the solution was a translucent red and all solid had dissolved. Water was added dropwise alternating with drops of sulfuric acid until the temperature was above 60°. The temperature was

maintained at 70° until the addition of water no longer raised the temperature. The crude product was filtered and recrystallized from hexanes to form orange crystals (7.541 g, 0.018 mol, 89%): mp 106-107°; IR (NaCl, cm⁻¹) 3074 (ArCH), 2986 (Aliphatic CH), 1735-1742 (C=O), ¹H NMR (300 MHz, CDCl₃, δ) 1.22 (t, 6H, ³J_{HH} = 7.1 Hz, CH₃), 4.22 (q, 4H, ³J_{HH} = 7.1 Hz, CH₂), 7.03 (m, 8H, ArCH); ¹³C NMR (75 MHz, CDCl₃, ppm) 190.58 (C=O), 163.72 (d, ¹J_{CF} = 252.5 Hz, ArCF), 161.91 (C=O), 160.90 (ArC), 131.38 (d, ³J_{HF} = 8.5 Hz, ArCH), 126.78 (d, ⁴J_{HF} = 3.5 Hz, ArC), 119.76 (ArC), 115.22 (d, ²J_{CF} = 22.0 Hz, ArC), 61.39 (CH₂), 13.97 (CH₃). Anal Calcd for C₂₃H₁₈F₂O₅: C, 66.99; H, 4.40. Found: C 66.95; H, 4.50.

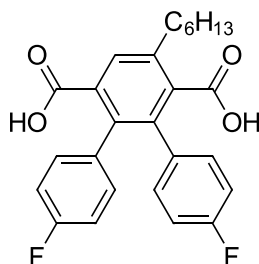
Diethyl 2,3-bis(4-fluorophenyl)-5-hexylterephthalate 29f



A mixture of 2,5-bis(ethoxycarbonyl)-3,4-di(4-fluorophenyl)cyclopentadienone (5.05 g, 20.5 mmol, 1 equiv) and 1-octyne (4.98 g, 24 mmol 1.2 equiv) were heated at reflux in toluene (60 mL) for 20 h. Toluene was removed under vacuum to form a light-brown oil. The oil was dried under vacuum and purified by column chromatography to yield a translucent oil (7.5 g, 15 mmol 75% yield): IR (NaCl, cm⁻¹) 2954-2859 (Aliphatic CH) 1728 (C=O); ¹H NMR (300 MHz, CDCl₃, δ) 0.91 (t, 3H, ³J_{HH} = 6.9 Hz, CH₃), 0.97 (t, 6H, ³J_{HH} = 7.1 Hz, CH₃), 1.37 (m, 6H, CH₂), 1.70 (qn, 2H, ³J_{HH} = 8.0 Hz, CH₂), 2.70 (t, 2H, ³J_{HH} = 8.1 Hz, CH₂), 3.99 (q, 2H, ³J_{HH} = 7.1, CH₂), 4.03 (q, 2H, ³J_{HH} = 7.1 Hz, CH₂), 6.90 (m, 8H, ArCH), 7.70 (s, 1H, ArCH); ¹³C NMR (75 MHz, CDCl₃, ppm) 168.59

(C=O), 168.19 (C=O), 161.79 (d, $^1J_{\text{CF}} = 246.7$ Hz, ArCH), 161.65 (d, $^1J_{\text{CF}} = 246.3$ Hz, ArC), 139.13 (ArC), 138.68 (ArC), 137.64 (ArC), 137.33 (ArC), 134.81 (d, $^4J_{\text{CF}} = 3.7$ Hz, ArC) 134.00 (d, $^4J_{\text{CF}} = 3.6$ Hz, ArCH) 133.4 (ArC), 131.79 (d, $^3J_{\text{CF}} = 8.1$ Hz, ArCH) 131.33 (d, $^3J_{\text{CF}} = 8.1$ Hz, ArCH), 129.35 (ArCH), 114.41 (d, $^2J_{\text{CF}} = 21.5$ Hz, ArCH), 114.37 (d, $^2J_{\text{CF}} = 21.4$ Hz, ArCH), 61.12 (CH₂), 61.09 (CH₂), 33.50 (CH₂), 31.58 (CH₂), 31.15 (CH₂), 29.26 (CH₂), 22.55 (CH₂), 14.05 (CH₃), 13.69 (CH₃), 13.64 (CH₃).

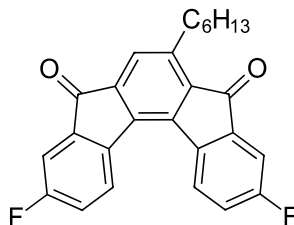
2,3-Bis(4-fluorophenyl)-5-hexylterephthalic acid 30f



A mixture of diethyl 2,3-bis(4-fluorophenyl)-5-hexylterephthalate (9.70 g, 19.6 mmol, 1 equiv) and potassium hydroxide (6.60 g, 118 mmol, 6 equiv) was heated to 160° in ethylene glycol (90 mL) for 20 h. The solution was cooled to room temperature, poured into water (400 mL) and stirred for 2 h. The solution was acidified with hydrochloric acid to a pH of 2. The milky white solution was filtered and the product was dried to yield a white solid (7.76 g, 17.7 mmol, 90% crude yield): IR (NaCl, cm⁻¹) 3300-2600 (OH), 2954-2860 (aliphatic CH), 1699 (C=O); ¹H NMR (300 MHz, CDCl₃, δ) 0.91 (t, 3H, $^3J_{\text{HH}} = 6.7$ Hz, CH₃), 1.37 (m, 6H, CH₂), 1.69 (qn, 2H, $^3J_{\text{HH}} = 7.5$ Hz, CH₂), 2.71 (t, 2H, $^3J_{\text{HH}} = 7.5$ Hz, CH₂), 6.87 (m, 8H, ArCH), 7.81 (s, 1H, ArCH), 8.76 (s, 2H, OH); ¹³C NMR (75 MHz, CDCl₃, ppm) 173.74 (C=O), 172.64 (C=O), 161.85 (d, $^1J_{\text{CF}} = 247.3$ Hz, ArCF), 161.72 (d, $^1J_{\text{CF}} = 246.5$ Hz, ArCF), 138.91 (ArC), 138.83 (ArC), 137.19 (ArC), 134.48 (d, $^4J_{\text{CF}} = 3.4$ Hz, ArC), 133.36 (d, $^4J_{\text{CF}} = 3.5$ Hz, ArC), 131.75 (d, $^3J_{\text{CF}} =$

8.2 Hz, ArCH) 131.56 (ArC) 131.20 (d, $^3J_{\text{CF}} = 8.0$ Hz) 130.26 (ArCH), 114.54 (d, $^2J_{\text{CF}} = 21.5$ Hz, ArCH), 114.47 (d, $^2J_{\text{CF}} = 21.5$ Hz, ArCH), 33.49 (CH₂), 31.51 (CH₂), 31.08 (CH₂), 29.17 (CH₂), 22.51 (CH₂), 14.05 (CH₃). Anal Calcd for C₂₆H₂₄F₂O₄: C, 71.22; H, 5.52. Found: C, 70.77; H, 5.32.

3,10-Difluoro-5,8-dioxo-5,8-dihydro-6-hexylindeno[2,1-c]fluorene 31f



A mixture of 2,3-bis(4-fluorophenyl)-5-hexylterephthalic acid (2.0 g, 4.6 mmol, 1 equiv) was dissolved in sulfuric acid (25 mL) and heated to 75° for 20 h. The solution was cooled to room temperature, poured in water (250 mL) and stirred for 1 h. The mixture was extracted with ethyl acetate and dried with magnesium sulfate. Ethyl acetate was removed by reduced pressure and crude product was purified by column chromatography (80:20, hexanes:ethyl acetate) to yield a yellow solid (1.55 g, 4.1 mmol, 90% yield): mp 156-157° (lit.⁷ mp 157°); IR (KBr, cm⁻¹) 3074 (ArCH), 2956-2858 (Aliphatic CH), 1707 (C=O); ¹H NMR (300 MHz, CDCl₃, δ) 0.90 (t, 3H, $^3J_{\text{HH}} = 6.5$ Hz, CH₃), 1.35 (m, 6H, CH₂), 1.54 (m, 2H, CH₂) 2.94 (t, 2H, $^3J_{\text{HH}} = 7.6$ Hz, CH₂), 7.21 (td, 2H, $^3J_{\text{HH}} = 8.4$, $^3J_{\text{HF}} = 8.4$ Hz, $^4J_{\text{HH}} = 2.5$ Hz, ArCH), 7.29 (s, 1H, ArCH) 7.32 (dd, 1H, $^3J = 7.1$ Hz, $^4J_{\text{HH}} = 2.6$ Hz, ArCH), 7.35 (dd, 1H, $^3J_{\text{HF}} = 7.1$, $^4J_{\text{HH}} = 2.6$ Hz, ArCH) 7.78 (dd, 2H, $^3J_{\text{HH}} = 8.4$ Hz, $^4J_{\text{HF}} = 4.3$ Hz, ArCH); ¹³C NMR (75 MHz, CDCl₃, ppm) 191.53 (d, $^4J_{\text{CF}} = 2.0$ Hz, C=O), 190.83 (d, $^4J_{\text{CF}} = 2.0$ Hz, C=O), 163.43 (d, $^1J_{\text{CF}} = 253.2$ Hz, ArCF), 163.13 (d, $^1J_{\text{CF}} = 253.3$ Hz, ArCF), 146.39 (ArC), 139.95 (d, $^5J_{\text{CF}} = 2.1$ Hz, ArC), 139.43 (d, $^4J_{\text{CF}} = 3.2$ Hz, ArC), 138.18 (ArC), 138.11 (d, $^4J_{\text{CF}} = 3.2$ Hz, ArC), 137.52 (d,

$^3J_{\text{CF}} = 7.2$ Hz, ArC), 137.37 (d, $^3J_{\text{CF}} = 7.2$ Hz, ArCH), 136.25 (d, $^5J_{\text{CF}} = 2.4$ Hz, ArC), 134.60 (ArC), 126.97 (ArCH), 124.94 (d, $^3J_{\text{CF}} = 7.2$ Hz, ArCH), 124.85 (d, $^3J_{\text{CF}} = 7.2$ Hz, ArCH), 121.22 (d, $^2J_{\text{CF}} = 23.9$ Hz, ArCH), 120.91 (d, $^2J_{\text{CF}} = 23.4$ Hz, ArCH), 112.35 (d, $^2J_{\text{CF}} = 23.2$ Hz, ArCH), 111.94 (d, $^2J_{\text{CF}} = 23.2$ Hz, ArCH), 31.61 (CH₂), 31.25 (CH₂), 30.05 (CH₂), 29.72 (CH₂), 22.58 (CH₂), 14.06 (CH₃); Anal Calcd for C₂₆H₂₀F₂O₂: C, 77.60; H, 5.01. Found: C, 77.79; H, 5.02.

Polymerization of 3,10-difluoro-5,8-dioxo-5,8-dihydro-6-hexylindeno[2,1-c]fluorene and Bisphenol-A

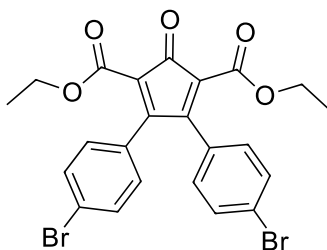
A solution of 3,10-difluoro-5,8-dioxo-5,8-dihydro-6-hexylindeno[2,1-c]fluorene (0.588 g, 1.47 mmol, 1 equiv), bisphenol A (0.334 g, 1.47 mmol, 1 equiv) and potassium carbonate (0.811 g, 5.87 mmol, 4 equiv) was heated in NMP (5 mL) for 24 h using Q-tube™ (30 mL) at 170°. The solution was cooled to room temperature. The solution was precipitated in a methanol/water solution (80:20, 100 mL) containing glacial acetic acid (2.5 mL), collected by vacuum filtration and reprecipitated two more times. The product was filtered and dried under vacuum overnight. A second polymerization was carried out at 150°. Proton NMR analysis is shown in **Figure 18**.

Model reaction of 3,10-difluoro-5,8-dioxo-5,8-dihydro-6-hexylindeno[2,1-c]fluorene and *p*-Cresol in NMP and DMSO

Monomer **31f** (0.2002 g, 0.497 mmol, 1 equiv) was weighed into a Q-Tube™ (30 mL) containing a magnetic stir bar. The transfer of *p*-cresol (0.1075 g, 0.994 mmol, 2 equiv) to the Q-Tube™ was aided by the use of NMP. Potassium carbonate (0.2805 g, 2.03 mmol, 4 equiv) was added to the reaction vessel. The remaining NMP (from 4 mL total) was used to insure all reactants were in the solvent. The mixture was slowly heated with stirring to 170° and held for 24 h. The solution was cooled to room temperature and

pipetted into a methanol-water solution (80:20, v:v) containing acetic acid (1.5 mL) and stirred for 1 h. The product was collected by vacuum filtration and reprecipitated twice from NMP into an acidified methanol-water solution. The product was a reddish solid (0.0847 g) that was collected by filtration and dried under vacuum. Proton and carbon NMR were used to analyze the product (**Figure 18 and 19**). Model reactions were conducted with DMSO as solvent under similar conditions and with similar results.

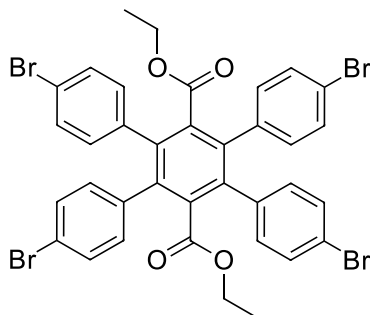
2,5-Bis(ethoxycarbonyl)-3,4-di(4-bromophenyl)cyclopentadienone 28a



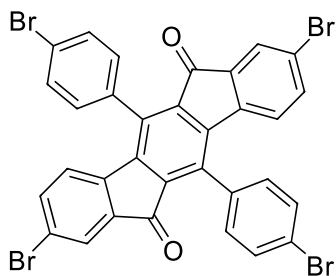
Sodium metal (0.76 g) was dissolved in ethanol (20 mL) to create a 12% sodium ethoxide solution. The solution was slowly added to a solution containing 4,4'-dibromobenzil (10.1 g, 0.027 mol, 1 equiv) and diethyl 1,3-acetonedicarboxylate (6.8 g, 0.032 mol, 1.2 equiv) in ethanol (70 mL) at reflux. The solution was held at reflux for 1 h during which a yellow precipitate formed. The mixture was cooled to room temperature. After the precipitate was collected by vacuum filtration and air-dried overnight, it was slurried in acetic anhydride (40 mL). Sulfuric acid was added dropwise until the solution was a translucent red and the solid had dissolved. Water was added dropwise alternating with drops of sulfuric acid until the temperature was above 60°. The temperature was maintained at 70° until the addition of water no longer raised the temperature. The orange precipitate was collected and recrystallized from ligroine (14.12 g, 0.026 mol, 98%): mp 155-156° (lit.⁶ mp 154-156°); ¹H NMR (300 MHz, CDCl₃, δ) 1.21 (t, 6H, ³J_{HH} = 7.1 Hz,

CH₃), 4.21 (q, 4H, $^3J_{\text{HH}} = 7.1$ Hz, CH₂), 6.93 (m, 4H, $^3J_{\text{HH}} = 8.6$ Hz, Ar, CH), 7.45 (m, 4H, $^3J_{\text{HH}} = 8.6$ Hz, Ar, CH); ^{13}C NMR (75 MHz, CDCl₃, ppm) 190.35 (C=O), 161.74 (ArC), 160.59 (ArC), 131.27 (ArCH), 130.51 (ArCH), 129.46 (ArC), 125.14 (ArC), 119.97 (ArC), 61.50 (CH₂), 13.99 (CH₃).

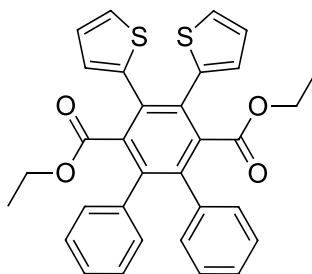
Diethyl 2,3,5,6-tetrakis(4-bromophenyl)terephthalate **61**



A solution of 2,5-bis(ethoxycarbonyl)-3,4-di(4-bromophenyl)cyclopentadienone (1.50 g, 2.9, mmol, 1 equiv.) and 1,2-bis(4-bromophenyl)ethyne¹⁹ (1.00 g, 3 mmol, 1.05 equiv.) was mixed and heated in a Q-Tube™ (30 mL) at reflux in dichlorobenzene (5 mL) for 24 h. The solution was cooled to room temperature and a small amount of hexanes (5 mL) was added to the Q-Tube™ and the mixture was stirred for 3 h in an ice bath to precipitate the reaction product. The solution was vacuum filtered and the precipitate was washed with hexanes. The product was heated in ligroine and hot filtered to remove unreacted starting material. The product was dried to yield a white solid (1.67 g, 1.9 mmol, 68%): mp 368-370°; IR (KBr, cm⁻¹) 2866-2969 (aliphatic CH), 1726 (C=O); ^1H NMR (300 MHz, CDCl₃, δ) 0.77 (t, 6H, $^3J_{\text{HH}} = 7.1$ Hz, CH₃), 3.71 (q, 4H, $^3J_{\text{HH}} = 7.1$ Hz, CH₂), 6.97 (d, 8H, $^3J_{\text{HH}} = 8.5$ Hz, ArCH), 7.35 (d, 8H, $^3J_{\text{HH}} = 8.5$ Hz, ArCH); ^{13}C NMR (75 MHz, CDCl₃, ppm) 167.50 (C=O), 137.21, (ArC), 136.56 (ArC), 136.19 (ArC), 131.52 (ArCH), 130.97 (ArCH), 121.92 (ArC), 61.23 (CH₂), 13.42 (CH₃). Anal Calcd for C₃₂H₁₄Br₄O₂: C, 51.34; H, 3.11. Found: C, 51.61; H, 3.25.

2,8-dibromo-5,11-bis(4-bromophenyl)indeno[1,2-b]fluorene-6,12-dione 62

A suspension of diethyl 2,3,5,6-tetrakis(4-bromophenyl)terephthalate (0.870 g, 1.19 mmol, 1 equiv) in sulfuric acid (15 mL) was heated at 130° for 3 h. The solid dissolved and the solution turned red after 1 h. The solution was cooled to room temperature and slowly poured into water (200 mL) and stirred for 2 h. The solution was filtered to yield a red solid. The red solid was washed with hot toluene to purify the product (0.712 g, 0.949 mmol, 80% yield): mp >400°; IR (KBr, cm⁻¹) 1716 (C=O), ¹H NMR (300 MHz, CDCl₃, δ) 6.22 (d, 2H, ⁴J_{HH} = 8.2 Hz, ArCH), 7.30 (m, 4H, ArCH), 7.37 (dd, 2H, ³J_{HH} = 8.2 Hz, ⁴J_{HH} = 1.9 Hz, ArCH), 7.63 (d, 2H, ⁴J_{HH} = 1.7 Hz, ArCH), 7.74 (d, 4H, ³J_{HH} = 8.4 Hz). Anal Calcd for C₃₂H₁₄Br₄O₂: C, 51.24; H, 1.88. Found: C, 51.07; H, 2.04.

Diethyl 5,6-diphenyl-2,3-bis(2-thienyl)terephthalate 64

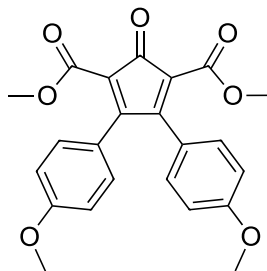
A mixture of 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone (1.98 g, 5.2 mmol, 1 equiv) and 1,2-bis(2-thienyl)ethyne²⁰ (1.0 g, 5.2 mmol, 1 equiv) was heated at reflux in dichlorobenzene (10 mL) for 18 h in a Q-Tube™ (30 mL). The solution was

cooled to room temperature, hexanes (8 mL) was added to the Q-Tube™ and solution was stirred for 2 h. The Q-Tube™ was placed in an ice bath for 2 h to precipitate the product. The solution was filtered by vacuum and the product was washed with hexanes. The crude product was recrystallized from benzene to yield a white solid (1.95 g, 3.6 mmol, 70%): mp 242-244; IR (NaCl, cm^{-1}) 3103 (ArCH), 2975-2896 (Aliph CH), 1725 (C=O); ^1H NMR (300 MHz, CDCl_3 , δ) 0.80 (t, 6H, $^3J_{\text{HH}} = 7.1$ Hz, CH₃), 3.77 (q, 4H, $^3J_{\text{HH}} = 7.1$ Hz, CH₃), 6.92 (dd, 2H, $^3J_{\text{HH}} = 5.1$ Hz, $^3J_{\text{HH}} = 3.5$ Hz, ArCH), 6.99 (dd, 2H, $^3J_{\text{HH}} = 3.5$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, ArCH), 7.15 (m, 10H, ArCH), 7.28 (dd, 2H, $^3J_{\text{HH}} = 5.1$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, ArCH); ^{13}C NMR (75 MHz, CDCl_3 , ppm) 167.73 (C=O), 139.11 (ArC), 138.06 (ArC), 137.66 (ArC), 137.45 (ArC), 132.05 (ArC), 130.01 (ArCH), 129.26 (ArCH), 127.45 (ArCH), 127.32 (ArCH), 127.24 (ArCH), 126.18 (ArCH), 61.00 (CH₂), 13.46 (CH₃); Anal Calcd for $\text{C}_{32}\text{H}_{26}\text{O}_4\text{S}_2$: C, 71.35; H, 4.87. Found: C, 71.33; H 4.79.

Intramolecular ring closure of diethyl 5,6-diphenyl-2,3-bis(2-thienyl)terephthalate

A solution of diethyl 5,6-diphenyl-2,3-bis(2-thienyl)terephthalate (0.50 g, .93 mmol, 1 equiv) was dissolved in a mixture of acetic acid (3.5 mL) and sulfuric acid (1.5 mL) and heated at 75° for 3 h. The solution was poured into water (150 mL) and stirred for 2 h. The black precipitate was collected by vacuum and dried. Analysis by NMR showed what appeared to be the degradation of the thiophene ring.

2,5-Bis(methoxycarbonyl)-3,4-di(4-methoxyphenyl)cyclopentadienone 66



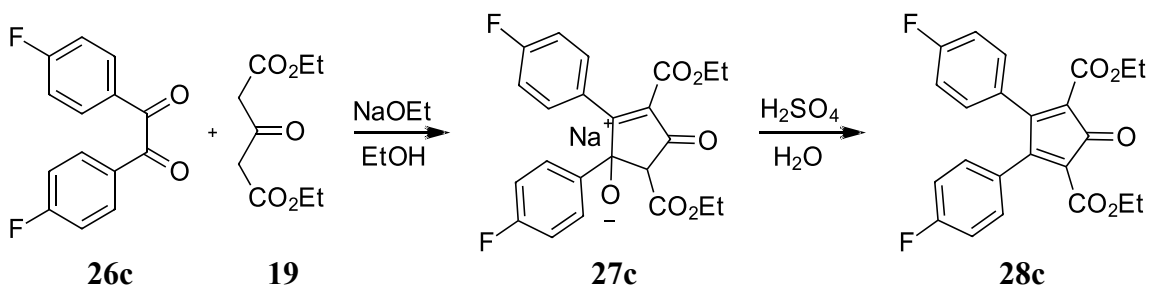
A solution of 4,4'-dimethoxybenzil (4.0 g, 14.8 mmol, 2.75 equiv), dimethyl 1,3-acetonedicarboxylate (2.73 g, 14.8 mmol, 2.75 equiv) and potassium hydroxide (0.34 g, 5.3 mmol, 1 equiv.) was refluxed in acetonitrile (40 mL) for 3.5 h. The solution was cooled and filtered to remove unreacted starting material. The filtrate was extracted with toluene and the solution was dried with magnesium sulfate. Toluene was removed by reduced pressure evaporation and the resulting oil was stirred in acetic anhydride (3 mL) containing 3 drops of sulfuric acid at room temperature for 1.5 h. The resulting solution was poured into water (200 mL) and stirred overnight. The precipitate was collected by vacuum filtration and purified by column chromatography (70:30, hexanes:ethyl acetate) to yield (0.81 g, 13%, 1.9 mmol) a red solid: mp 125-126° (lit¹⁸ mp 126-127°); IR (NaCl, cm⁻¹) 3085 (ArCH), 2980-2901 (Aliph CH), 1738 (C=O), 1712 (C=O); ¹H NMR (300 MHz, CDCl₃, δ) 3.78 (s, 6H, CH₃), 3.84 (s, 6H, CH₃), 6.82 (d, 4H, ³J_{HH} = 8.9 Hz, ArCH) 7.02 (d, 4H, ³J_{HH} = 8.9 Hz, ArCH); ¹³C NMR (75 MHz, CDCl₃, ppm) 191.0 (C=O), 163.1 (C=O), 162.3 (ArC) 161.4 (ArC), 131.6 (ArCH), 123.2 (ArC), 118.6 (ArC), 113.6 (ArCH), 55.3 (-OCH₃), 52.3 (COOCH₃).

RESULTS AND DISCUSSION

The major objective of this work was the generation of polymerizable derivatives of 5,8-dioxo-5,8-dihydroindeno[2,1-c]fluorene. The initial discussion will focus on the difluoro derivative, 3,10-difluoro-5,8-dioxo-5,8-dihydroindeno[2,1-c]fluorene **31f**, and its model compound and polymerization reactions. Subsequent discussions will focus on related syntheses.

Cyclopentadienone Synthesis

The reaction of the 4,4'-difluorobenzil **26c** with diethyl 1,3-acetonedicarboxylate **19** was carried out using the reported method⁵ for the synthesis of 2,5-dicarboethoxy-3,4-dihphenylcyclopentadienone **4**. Initially, a sodium ethoxide catalyzed reaction in absolute ethanol resulted in the formation of the sodium salt **27c**. The sodium salt was protonated and dehydrated in acetic anhydride by adding sulfuric acid dropwise. The dehydration reaction resulted in the formation of 2,5-bis(ethoxycarbonyl)-3,4-di(4-fluorophenyl)-cyclopentadienone **28c**. The difluoro substituted cyclopentadienone was characterized by IR, ¹H NMR and ¹³C NMR.



The IR absorption at 1742 cm⁻¹ (**Figure 27**) corresponds to the ester carbonyl and that at 1735 cm⁻¹ can be attributed to the ketone carbonyl. The ¹H NMR absorption

integrals are as expected (**Figure 28**). The ^1H NMR spectrum indicated the successful synthesis of the difluorocyclopentadienone **28c**. The absorptions in the aromatic region appear as a multiplet of peaks at δ 7.03 due to the similar chemical shifts of the protons and the fluoro-splitting that occurs in the molecule. The methylene absorption appears as a quartet at δ 4.22 labeled b in **Figure 4**, the methyl group absorption is present at δ 1.22 as a triplet labeled a.

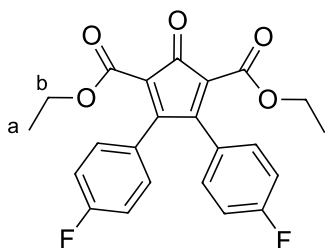


Figure 4. ^1H NMR assignments for 2,5-bis(ethoxycarbonyl)-3,4-di(4-fluorophenyl)cyclopentadienone **28c**

The ^{13}C NMR spectrum (**Figure 29**) displays ten distinct carbon absorptions. The comparison between the calculated ^{13}C NMR chemical shifts²¹⁻²³ and the experimental ^{13}C NMR chemical shifts are displayed in **Figure 5**.

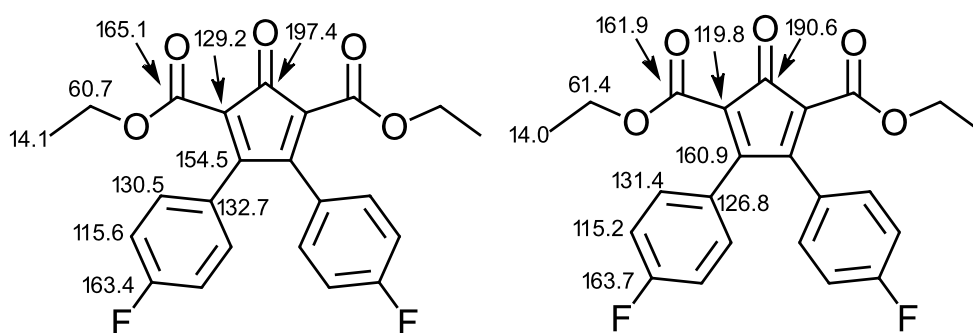


Figure 5. ^{13}C NMR absorptions for 2,5-dicarboethoxy-3,4-bis(fluorophenyl)-cyclopentadienone **28c** (predicted left and experimental right).

The ^{13}C NMR spectrum of difluorocyclopentadienone **28c** exhibits four aromatic carbon absorptions that appear as doublets due to C-F couplings (**Figure 6**); 1) 163.72 ppm with a $^1J_{\text{CF}} = 252.5$ Hz which is consistent with fluorine ipso carbon coupling, 2)

115.22 ppm with a $^2J_{\text{CF}} = 22.0$ Hz which occurs as a result of the *ortho* C-F coupling, 3) 131.38 ppm with a $^3J_{\text{CF}} = 8.5$ Hz which indicates *meta* C-F coupling and 4) 126.78 ppm with a $^4J = 3.5$ Hz which indicates *para* C-F coupling (**Figure 6 & Figure 29**).

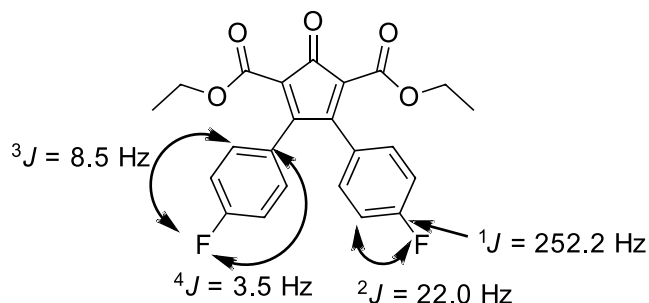
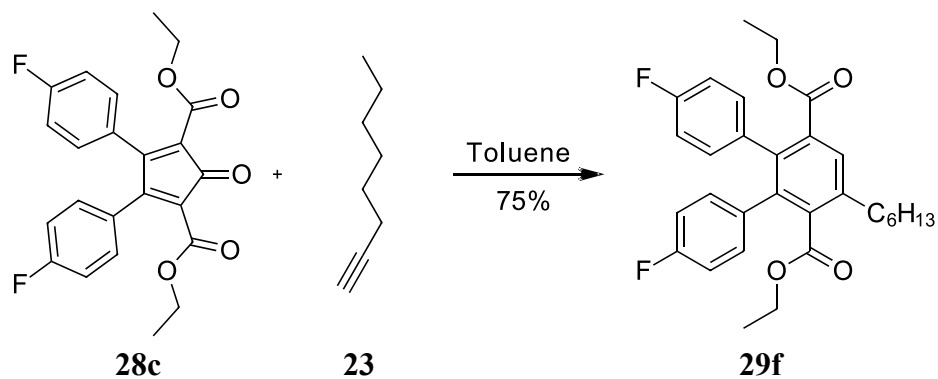


Figure 6. Carbon-fluorine couplings present in ^{13}C NMR spectrum of 2,5-bis(ethoxycarbonyl)-3,4-di(4-fluorophenyl)cyclopentadienone **28c**.

Terephthalate Synthesis



Diester derivatives of cyclopentadienones contain an electron-deficient diene that can rapidly undergo an inverse-electron-demand Diels-Alder (IEDDA) with acetylenes to form terephthalic acid derivatives. The reaction of 2,5-bis(ethoxycarbonyl)-3,4-di(4-fluorophenyl)cyclopentadienone **28c** and 1-octyne **23** in toluene at reflux results in the formation of the asymmetric aromatic compound, diethyl 2,3-bis(4-fluorophenyl)-5-hexylterephthalate **29f**, that was characterized by IR, ^1H NMR and ^{13}C NMR.

The IR spectrum (**Figure 31**) of **29f** contains an ester carbonyl absorption at 1728 cm^{-1} and aliphatic CH stretch absorptions from 2960-2859 cm^{-1} . The disappearance of the ketone absorption in the carbonyl range indicates successful synthesis of the pentasubstituted terephthalate **29f**.

The ^1H NMR spectrum clearly shows the addition of the hexyl tail as a result of the IEDDA reaction. The ^1H NMR spectrum of **29f** (**Figure 32**) exhibits: 1) overlapping triplet absorptions at δ 0.91 and δ 0.97 assigned to the CH_3 of the hexyl tail and the ethyl esters methyl groups, respectively (labeled a and a' in **Figure 7**), 2) a multiplet absorption at δ 1.37 accounting for six hydrogens located in the middle of the hexyl tail labeled b, 3) a multiplet absorption at δ 1.70 accounting for two protons of a CH_2 group on the hexyl tail labeled c, 4) a distorted triplet absorption at 2.70 assigned to the CH_2 group directly attached to the benzene ring labeled d, 5) a pair of overlapping quartet absorptions at δ 3.99 and δ 4.03 attributed to the methylene groups in the ethyl esters labeled e, 6) a multiplet absorption at δ 6.90 attributed to the eight aromatic protons located on the fluorine substituted rings labeled f, 7) a singlet absorption at δ 7.70 accounting for the aromatic CH labeled g which is shifted downfield due to its proximity to the ketone carbonyl.

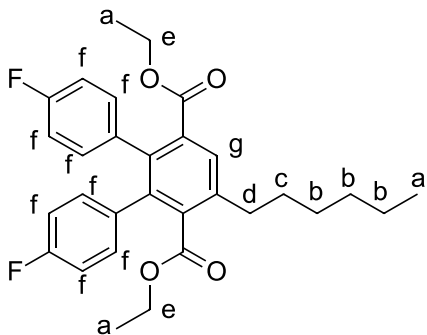


Figure 7. ^1H NMR assignments for diethyl 2,3-bis(4-fluorophenyl)-5-hexylterephthalate.

The asymmetric nature of the terephthalate results in a ^{13}C NMR spectrum (**Figure 33**) complicated by long-range C-F coupling. This both assists and obstructs assignments. For consistency, when absorptions are identified as belonging to similar carbons in related parts of the molecule, the downfield absorption will be assigned (in figures) to what is considered to be the carbon in the more sterically hindered position (this will be followed in subsequent ^{13}C NMR descriptions as well). The calculated²¹⁻²³ and observed ^{13}C NMR chemical shifts for diethyl 2,3-bis(4-fluorophenyl)-5-hexylterephthalate are shown in **Figure 8**.

The aliphatic region exhibits the anticipated absorptions. Absorptions at 13.64 and 13.69 ppm can be attributed to the methyls and two absorptions at 61.09 and 61.12 ppm can be assigned to the methylenes of the ethyl esters. A third methyl absorption at 14.05 ppm can be assigned to the methyl group at the end of the hexyl tail. The DEPT135 spectrum (**Figure 34**) spectrum confirms the presence of five methylene groups in the pendant hexyl chain.

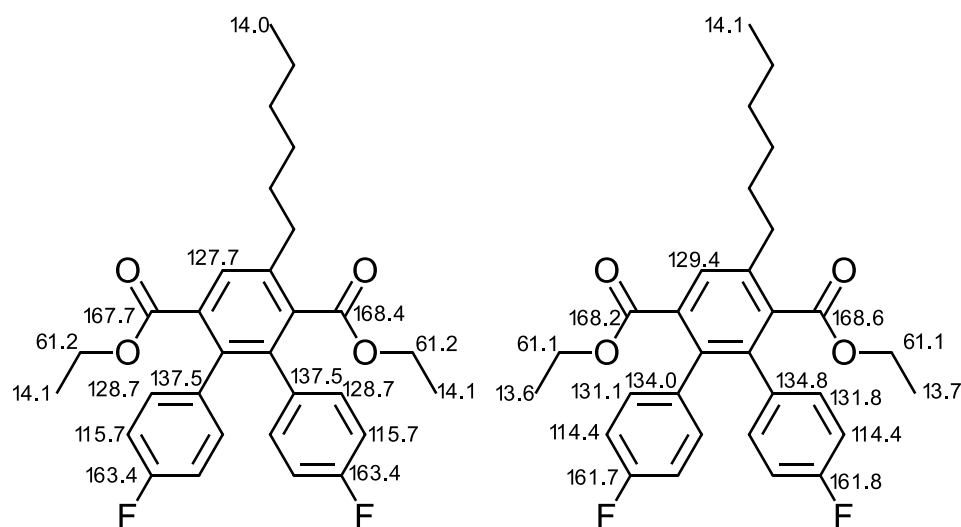


Figure 8. Calculated (left) and observed (right) ^{13}C NMR absorptions for diethyl 2,3-bis(4-fluorophenyl)-5-hexylterephthalate **29f**.

The aromatic region of the ^{13}C NMR spectrum displays eight doublets, four for each pendent fluorophenyl ring (**Figure 9**). Positional assignments for these absorptions can be made by a combination of coupling constant values and the DEPT135 spectrum. Thus, the doublet absorptions at 161.65 ppm, $^1J_{\text{CF}} = 246.3$ Hz and 161.79 ppm, $^1J_{\text{CF}} = 246.7$ Hz can be assigned to the *ipso* carbons. The doublet absorptions at 114.37 ppm, $^2J_{\text{CF}} = 21.4$ Hz, and 114.41 ppm, $^2J_{\text{CF}} = 21.5$ Hz, can be assigned to the *ortho* carbons. The doublet absorptions at 131.33 ppm, $^3J_{\text{CF}} = 8.1$ Hz, and 131.79 ppm, $^3J_{\text{CF}} = 8.1$ Hz can be assigned to the *meta* carbons. The doublet absorptions at 134.00 ppm, $^4J_{\text{CF}} = 3.6$ Hz, and 134.81 ppm, $^4J = 3.7$ Hz, can be assigned to the *para* carbons. The DEPT135 (**Figure 34**) spectrum clearly indicates that the absorption at 129.4 ppm can be assigned to the lone ArCH on the central pentasubstituted ring and the remaining quaternary carbon absorptions can be assigned to the remaining five carbons of that ring.

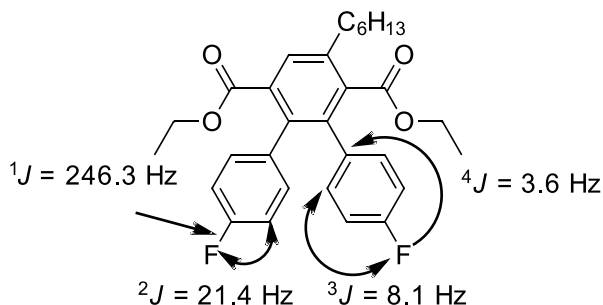
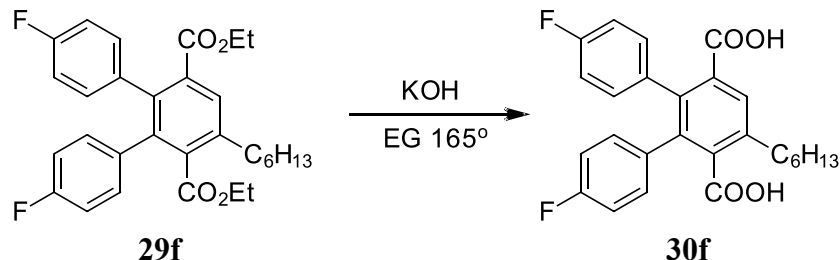


Figure 9. Carbon-fluorine couplings present in ^{13}C NMR spectrum of diethyl 2,3-bis(4-fluorophenyl)-5-hexylterephthalate **29f**.

Finally, two absorptions at 168.19 and 168.55 ppm can be attributed to the carbonyl carbons of the ester groups.

Terephthalic Acid Synthesis

The terephthalic ester **29f** was hydrolyzed in KOH/ethylene glycol to yield 2,3-bis(4-fluorophenyl)-5-hexylterephthalic acid **30f**.



The IR spectrum of 2,3-bis(4-fluorophenyl)-5-hexylterephthalic acid **30f** shows a broad absorption from 3300-2600 cm^{-1} which is assigned to the O-H stretch from the carboxylic acid functional group. The absorption at 1699 cm^{-1} (**Figure 35**) is attributed to the carboxylic acid carbonyl.

The ^1H NMR spectrum (**Figure 36**) integrations are as predicted for the terephthalic acid **30f**. The ^1H NMR spectrum displays 1) a singlet absorption at δ 7.81 which is attributed to the aromatic CH on the pentasubstituted benzene ring labeled a (**Figure 10**) and 2) a broad absorption at δ 8.76 which is assigned to the two hydrogens of the OH groups of the terephthalic acid labeled b. The integrations of the aliphatic region show the loss of ten hydrogens and that confirms that the hydrolysis of the ester was effective. Small peaks attributed to the diester **29f** and ethylene glycol remain in this region. The multiplet absorption in the aromatic region is due to the asymmetric nature of the diacid.

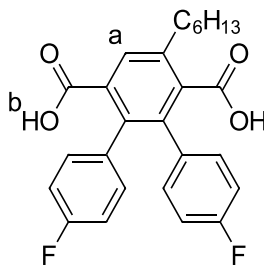


Figure 10. ^1H NMR proton assignments for 2,3-bis(4-fluorophenyl)-5-hexylterephthalic acid **30f**.

The ^{13}C NMR spectrum (**Figure 37**) shows small absorption peaks attributed to minute amounts of diester **29f** and ethylene glycol. The calculated²¹⁻²³ and observed peaks are shown in **Figure 11**. The DEPT135 spectrum (**Figure 38**) aided in the assignment of the nine absorptions of the aromatic CH groups. The singlet absorption at 130.27 ppm can be assigned to the lone CH group on the pentasubstituted aromatic ring. The two absorptions at 172.64 and 173.74 ppm are attributed to the carbonyl carbons of the ester groups. The two separate peaks for the carbonyls are due to asymmetry and proximity to the pendant hexyl tail.

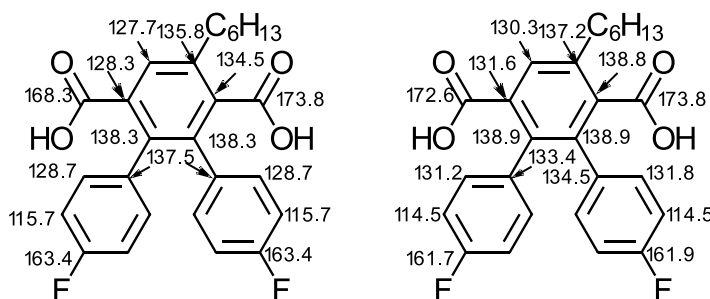


Figure 11. Predicted (left) and observed (right) ^{13}C NMR absorptions for 2,3-bis(4-fluorophenyl)-5-hexylterephthalic acid **30f**.

Among these peaks are eight distinct doublets that can clearly be seen in the aromatic region of the ^{13}C NMR spectrum of the terephthalic acid **30f** (**Figure 37**). The C-F couplings and J values can be seen in **Figure 12**.

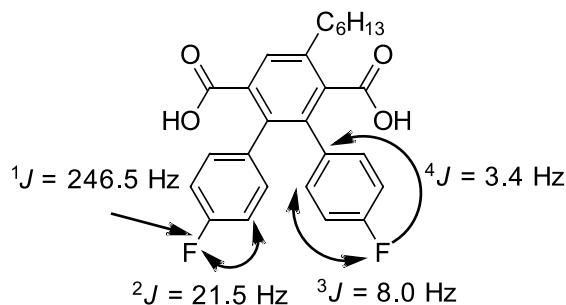
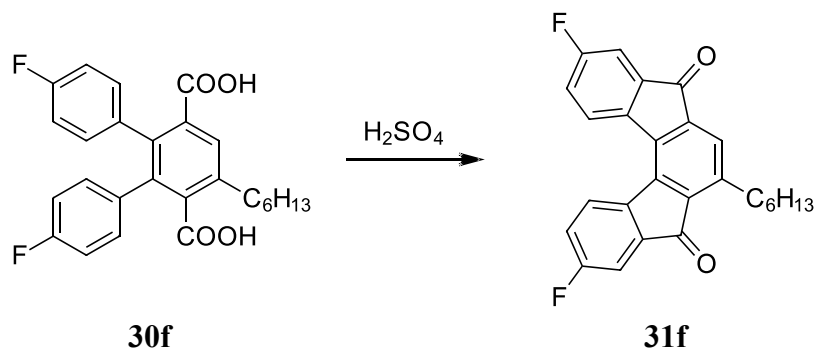


Figure 12. Carbon-fluorine couplings present in ^{13}C NMR spectrum of 2,3-bis(4-fluorophenyl)-5-hexylterephthalic acid **30f**.

The eight different doublets are present due asymmetry arising from the hexyl tail of the pentasubstituted benzene ring. The doublet absorptions at 161.72 ppm, $J_{CF} = 246.5$ Hz and 161.85 ppm, $J_{CF} = 247.3$ Hz can be assigned to the fluorine *ipso* carbons. The doublet absorptions at 114.47 ppm, $J_{CF} = 21.5$ Hz and 114.47 ppm, $J_{CF} = 21.5$ Hz can be assigned to the *ortho* carbons. The doublet absorptions at 131.20 ppm, $J_{CF} = 8.0$ Hz and 131.75 ppm, $J_{CF} = 8.2$ Hz can be assigned to the *meta* carbons. The doublet absorptions at 133.36 ppm, $J_{CF} = 3.5$ Hz and 134.48 ppm, $J_{CF} = 3.5$ Hz can be assigned to the *para* carbons. The other five quaternary carbon absorptions in the aromatic region can be assigned to the pentasubstituted ring.

Monomer Synthesis



The conversion of diacid **30f** to the monomer **31f** was accomplished by an intramolecular Friedel-Crafts reaction in sulfuric acid. The product was purified by column chromatography to yield 3,10-difluoro-5,8-dioxo-5,8-dihydro-6-hexylindeno[2,1-c]fluorene **31f** which was characterized by IR, ^1H NMR and ^{13}C NMR and exhibited acceptable elemental analysis.

The IR spectrum (**Figure 39**) of 3,10-difluoro-5,8-dioxo-5,8-dihydro-6-hexylindeno[2,1-c]fluorene exhibited absorption peaks from 2956-2858 cm^{-1} which are

indicative of the aliphatic CH stretches associated with the hexyl tail. The absorption at 1707 cm^{-1} can be attributed to the conjugated ketone carbonyl.

A combination of ^1H NMR, ^{13}C NMR, ^{13}C DEPT135 NMR and HSQC 2D NMR of 3,10-difluoro-5,8-dioxo-5,8-dihydro-6-hexylindeno[2,1-c]fluorene **31f** were used to confirm the structural features of **31f**.

Initially, a proton NMR spectrum of **31f** (**Figure 13**, spectrum a) revealed an aromatic region composed of three absorption areas integrating to 2H : 3H : 2H in accord with the structure and a singlet being the lone proton on the pentasubstituted ring. Whereas the downfield pattern was obviously a doublet of doublets, the other two patterns defied simple interpretation with respect to anticipated proton-proton and/or proton-fluorine couplings. Subsequently, a proton NMR spectrum at higher concentration (**Figure 13**, spectrum b, also see **Figure 40**) provided a clearer picture of the chemical shifts and coupling interactions. Two other ^1H NMR spectra at differing concentrations (**Figure 13**, spectrum c and d) show the concentration dependence of the proton chemical shifts and indicate significant intermolecular interactions in solution.

The aliphatic portion of the ^1H NMR spectrum for **31f** can be assigned similarly to that of **29f** and **30f**. The three aromatic hydrogens on each the fluorine substituted benzene rings all exhibit H-H and H-F coupling with the individual coupling constants shown in **Figure 14**. The assignments in **Figure 13** are; 1) a triplet of doublets absorption at δ 7.21 attributed to the aromatic hydrogens which are labeled e, 2) a singlet absorption at δ 7.29 attributed to the lone aromatic hydrogen on the pentasubstituted benzene ring labeled f, 3) a doublet of doublets absorption at δ 7.32 which is assigned to the aromatic hydrogen *ortho* to the fluorine and ketone groups labeled g and a second doublet of

doublets absorption at δ 7.35 attributed to the aromatic hydrogen between the fluorine and ketone groups on the hexyl substituted side labeled h (these fortuitously overlap to give the appearance of a triplet of doublets) and 4) a doublet of doublets absorption at δ 7.78 attributed to the two aromatic hydrogens labeled i in **Figure 13**. Further confirmation of these assignments came from ^{13}C NMR and an HSQC 2D NMR to be discussed later.

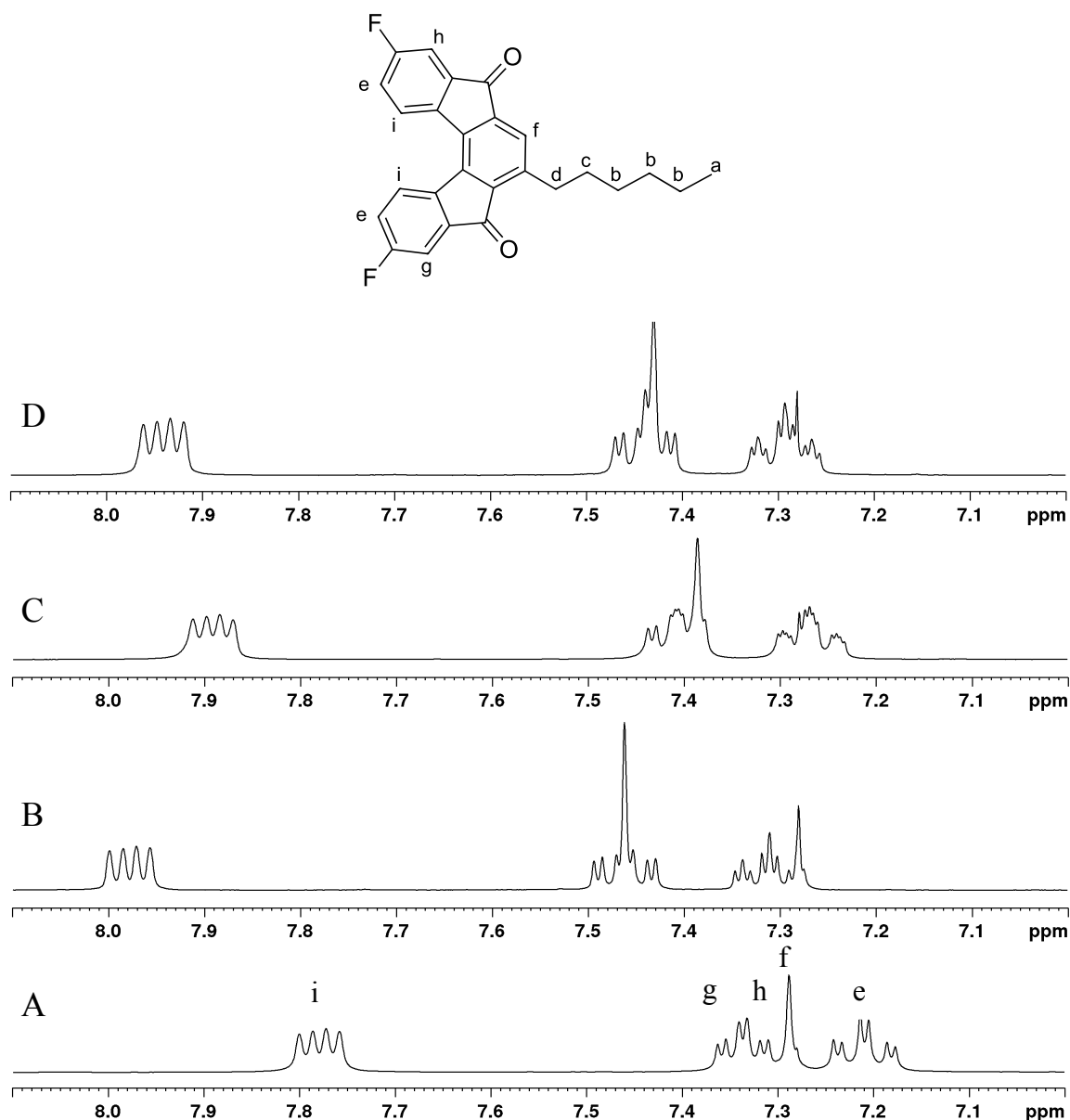


Figure 13. ^1H NMR spectra of 3,10-difluoro-5,8-dioxo-5,8-dihydro-6-hexylindeno[2,1-c]fluorene **31f** - A = 40 mg/mL, B = 30 mg/mL, C = 20 mg/mL, D = 14 mg/mL.

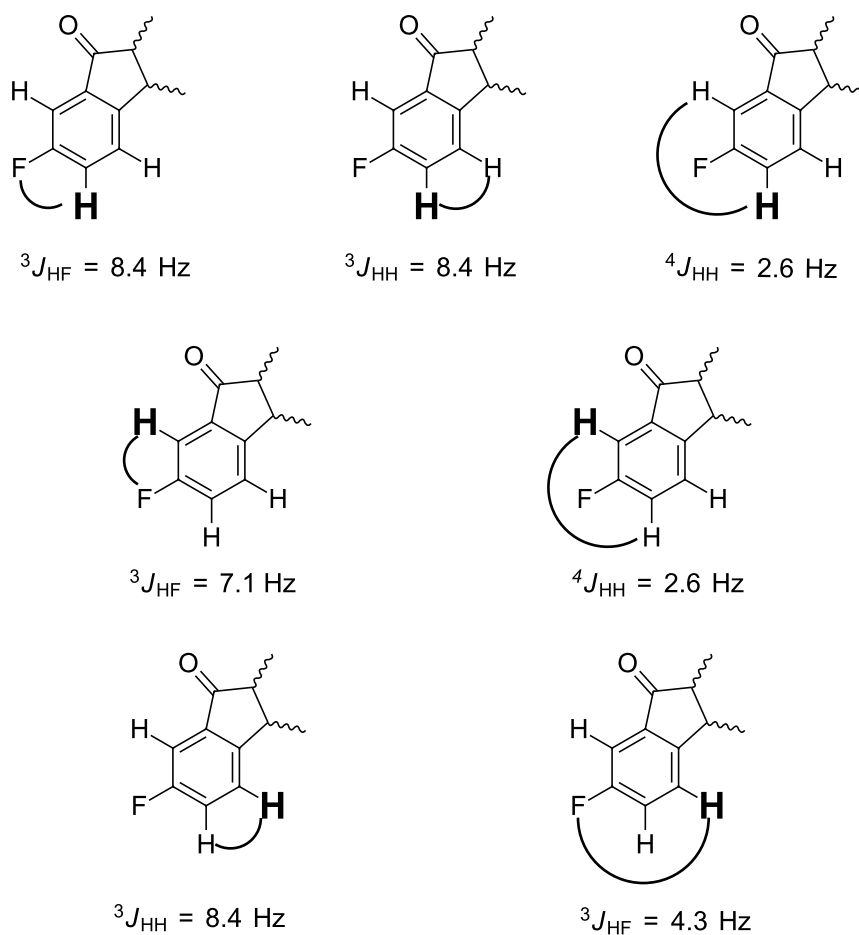


Figure 14. H-H and H-F coupling constants for the fluorine substituted benzene rings of 3,10-difluoro-5,8-dioxo-5,8-dihydro-6-hexylindeno[2,1-c]fluorene **31f**.

The ${}^{13}\text{C}$ NMR spectrum (**Figure 41**) for 3,10-difluoro-5,8-dioxo-5,8-dihydro-6-hexylindeno[2,1-c]fluorene exhibits numerous doublets due to the asymmetric nature of

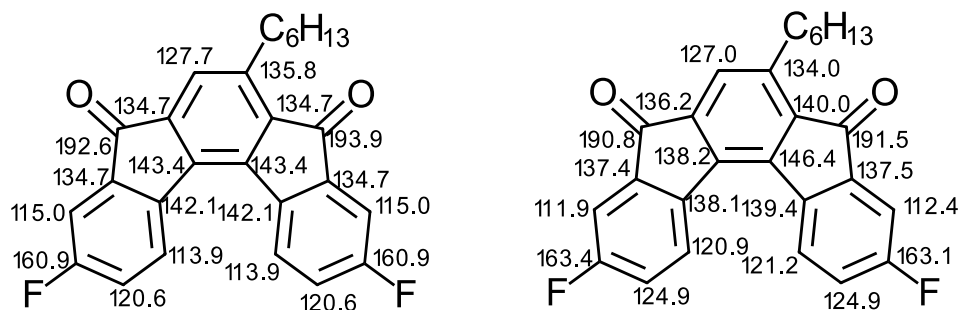


Figure 15. Predicted (left) and observed (right) ${}^{13}\text{C}$ NMR absorptions for 3,10-difluoro-5,8-dioxo-5,8-dihydro-6-hexylindeno[2,1-c]fluorene **31f**.

the molecule as well as some singlets for the remaining non-fluorine-coupled carbons.

The calculated²¹⁻²³ and observed chemical shifts can be seen in **Figure 15**.

The obvious ¹³C NMR assignments are: 1) the two absorptions at 191.52 and 191.55 ppm for the carbonyl carbons of the ketones exhibiting long range splitting of 2.0 Hz, 2) a singlet absorption at 127.0 ppm (**Figure 42**, DEPT135) attributed to the aromatic CH in the pentasubstituted ring and 3) two doublet absorptions at 163.1 and 163.4 ppm attributed to the fluorine ipso carbons. The DEPT135 NMR spectrum clearly identified the six doublets associated with the aromatic protonated carbons on the fluorinated rings. The use of an HSQC 2D NMR (**Figure 17**) correlated those carbons to the corresponding protons in the ¹H NMR.

The carbon-fluorine splittings and the associated *J* values are shown in **Figure 16**.

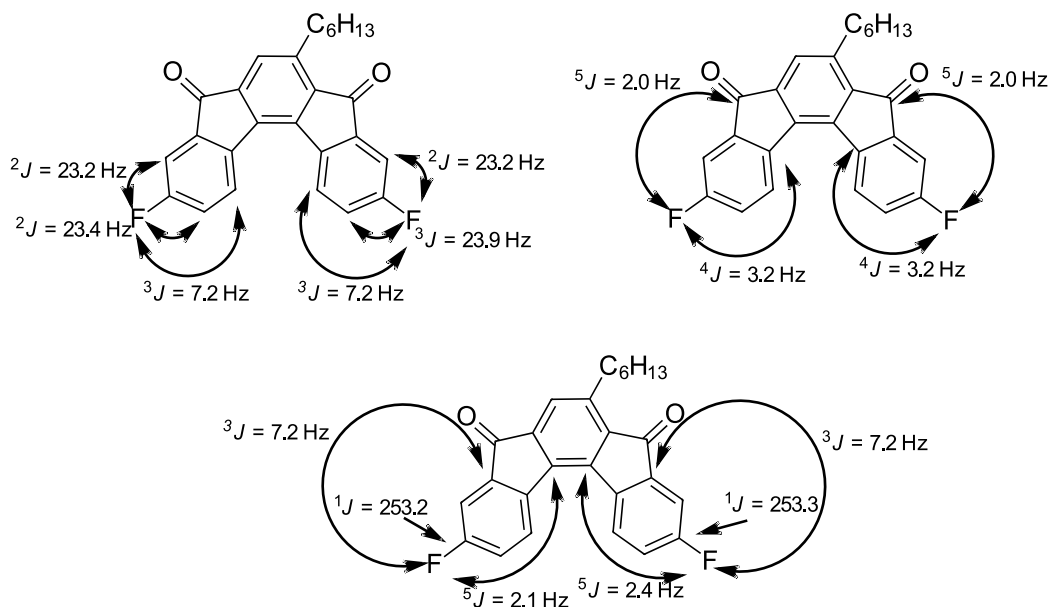


Figure 16. Carbon-fluorine couplings for 3,10-difluoro-5,8-dioxo-5,8-dihydro-6-hexylindeno[2,1-c]fluorene **31f**.

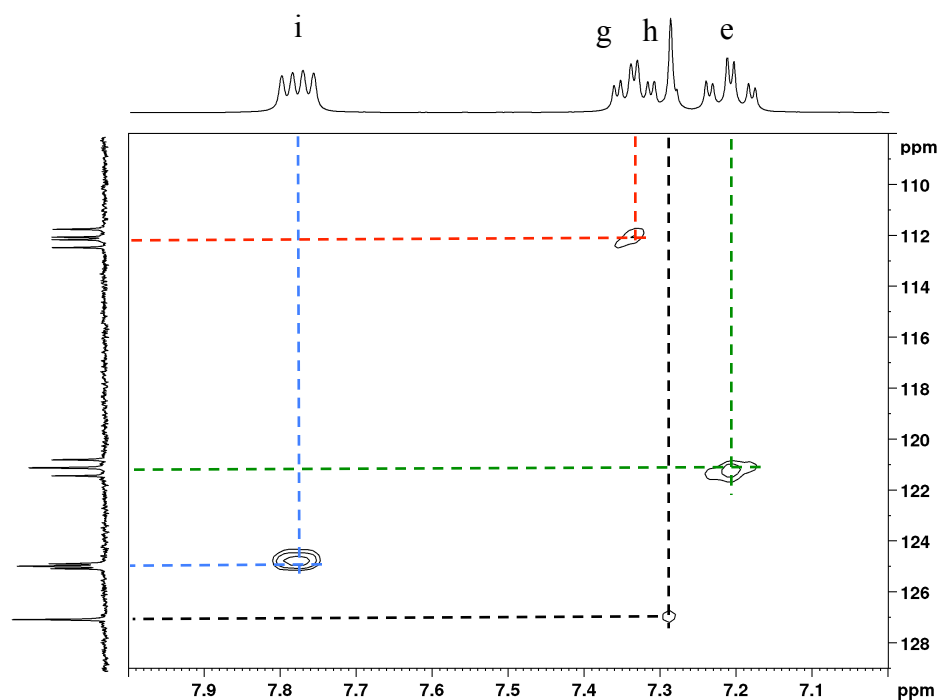
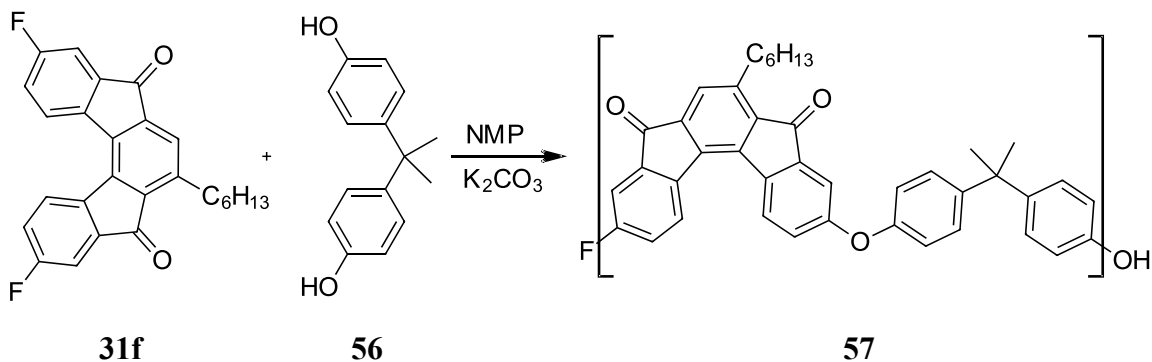


Figure 17. The HSQC 2D NMR spectrum for **31f**.

NAS Polymerization

After characterization of monomer **31f**, its polymerization was contemplated. The ^{13}C chemical shifts of the ipso carbons (163.1 and 163.4 ppm) in **31f** were compared to ipso carbon chemical shifts for compounds exhibiting displaceable fluorines (**Table 1**). Although those chemical shifts were at the low end of the series (see **Table 1, Entry 6 and 7**) polymerizations were attempted.



Difluoroindenofluorene **31f** and bisphenol-A **56** were polymerized in NMP employing potassium carbonate as base at 170° in a Q-tube™ as previously described. After a standard work-up, the ¹H NMR spectrum (**Figure 18**, middle) of the isolated material did not show that appreciable displacement of fluorine from **31f** had occurred. Polymer formation should be accompanied by the disappearance of the H-F coupling in the aromatic region (simplified ¹H spectrum) and the appearance of absorptions associated with bisphenol-A, particularly the gem-dimethyl singlet. Slight chemical shift changes in the aromatic region are probably due to the concentration effects referred to earlier. Subsequent polymerizations produced similar results - the isolation of starting monomer **31f**. A second polymerization at 150° gave similar results (**Figure 18**, top).

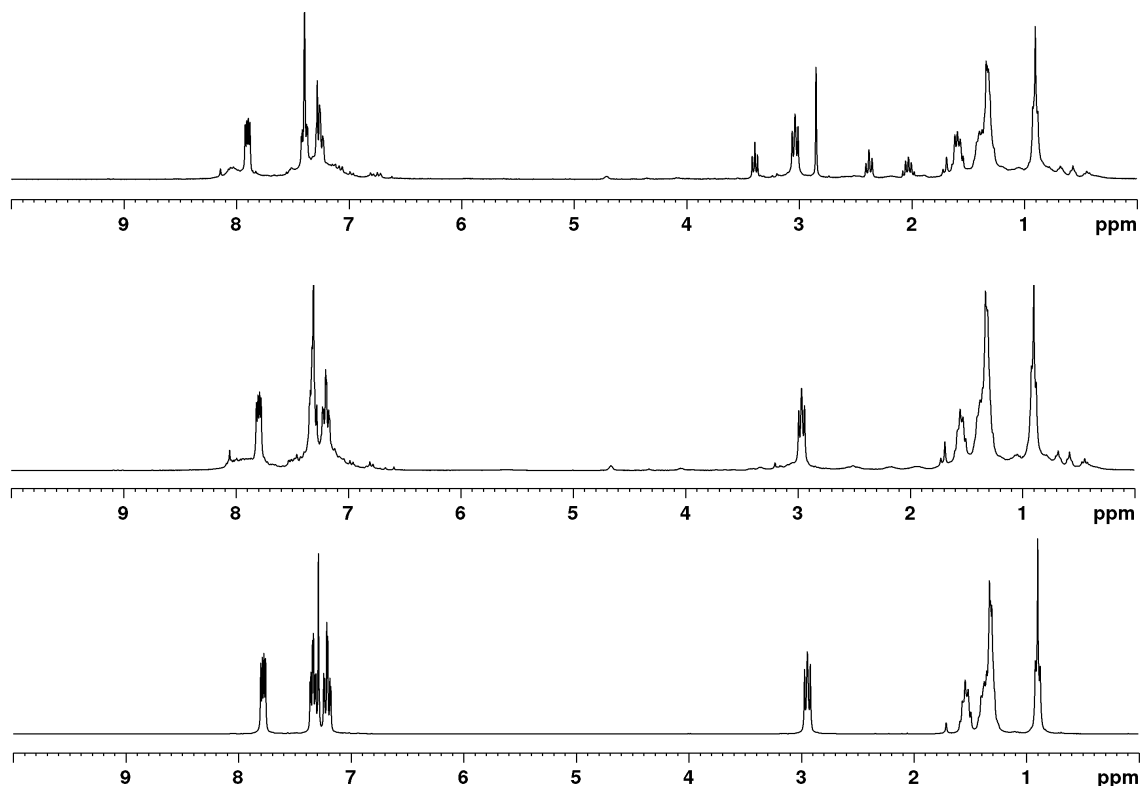


Figure 18. ¹H NMR spectra of the two polymerization attempts and monomer. The polymerization attempt at 150° (top), at 170° (middle) and indenofluorene monomer **31f** (bottom).

Corroborating results were obtained from the ^{13}C NMR spectra (**Figure 19**) obtained from the material isolated from two polymerizations. It was expected that polymerization would result in the disappearance of the fluorine *ipso* carbon doublet absorptions at 163.1 and 163.4 ppm and the appearance of oxygen *ipso* carbon singlets in

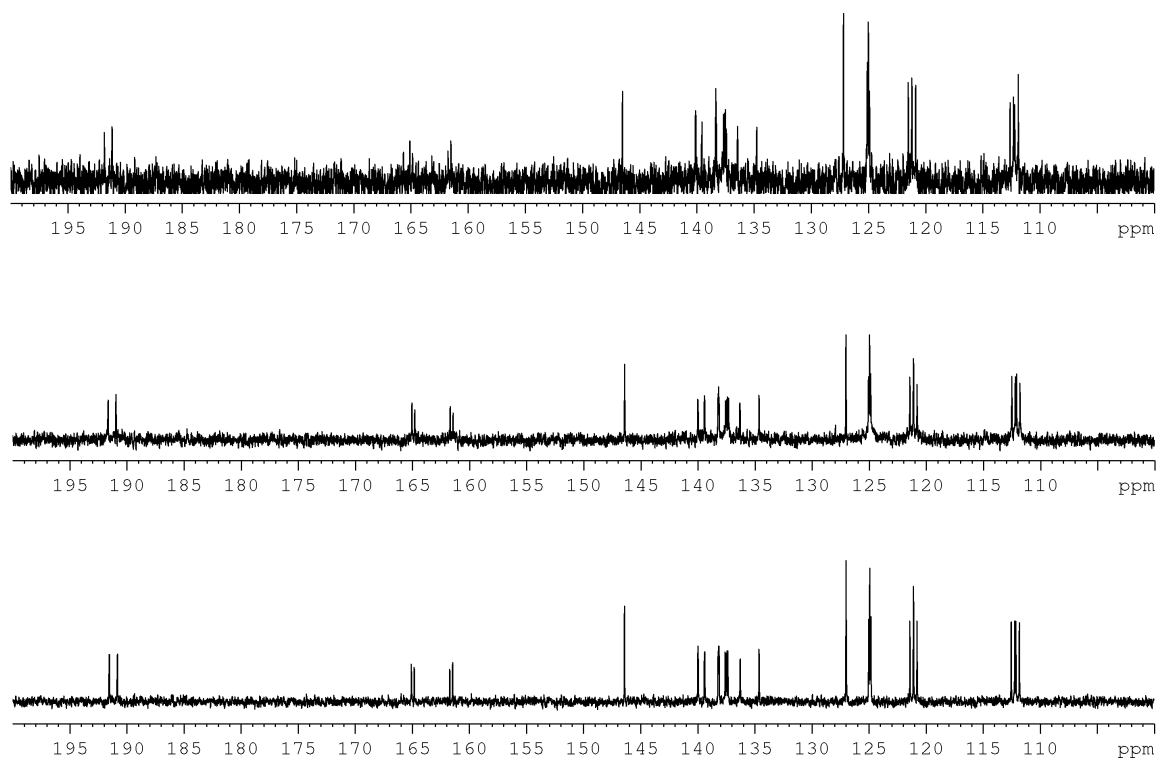


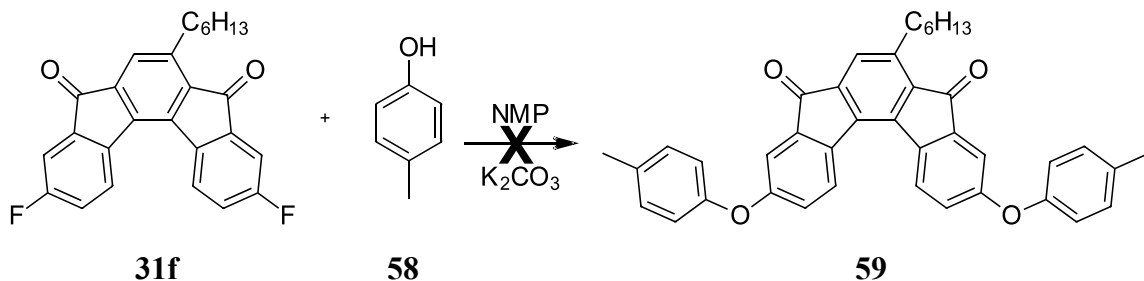
Figure 19. ^{13}C NMR spectra of the two polymerization attempts and monomer. The polymerization attempt at 150° (top), at 170° (middle) and indenofluorene monomer **31f** (bottom).

the same region as had been seen in other similar polymerizations involving fluorobenzoyl monomers. No singlet absorptions in the 163 ppm region were observed and the doublet absorptions remain suggesting no (or very minor) polymerization. In addition, no absorptions associated with bisphenol-A **56** in the aromatic or aliphatic region were observed. The gem-dimethyl singlet attributable to bisphenol-A is particularly diagnostic for its incorporation/presence.

After these two attempts, it was decided to investigate fluorine displacement in monomer **31f** through model reactions.

Model Reaction in NMP and DMSO

Monomer **31f** and p-cresol **58** were reacted in NMP at 170° employing potassium carbonate as base. After work-up, the crude reddish product was analyzed by TLC and



¹H NMR (**Figure 20**, middle). It was concluded that little if any fluorine substitution had occurred based on the similarity of the spectra of the product and **31f**. The reaction was

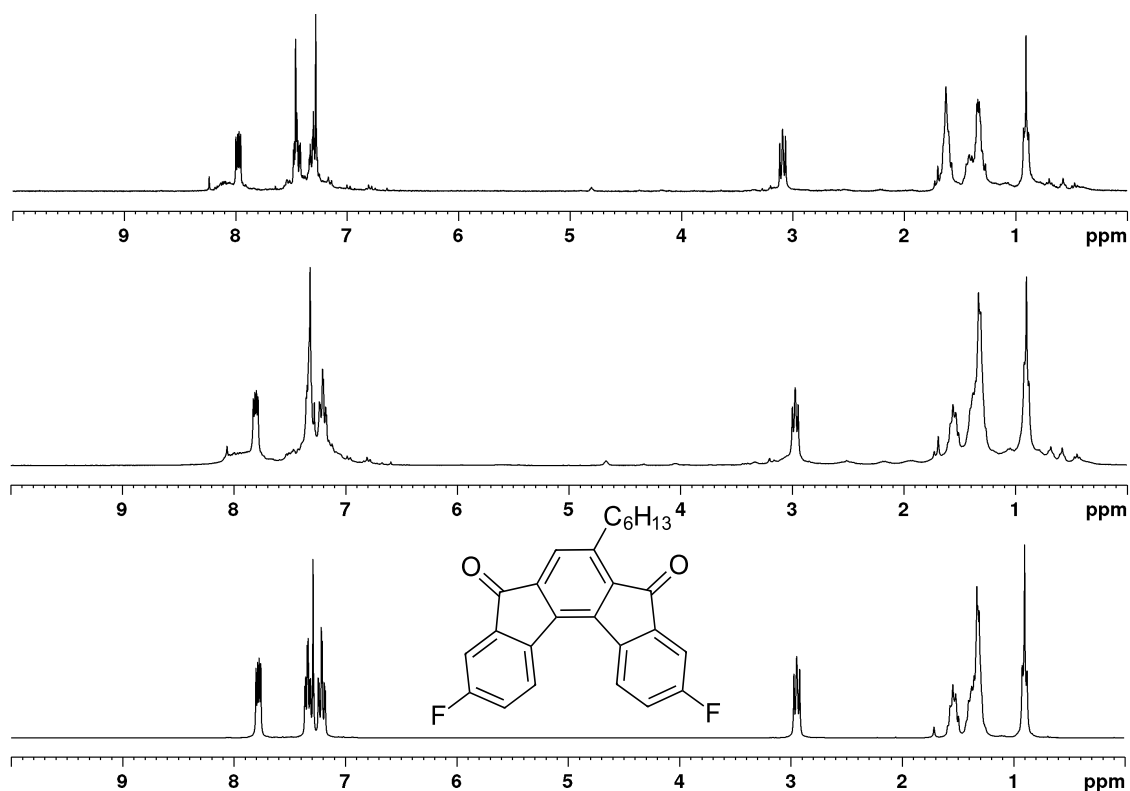


Figure 20. ¹H NMR spectra of 170° model reaction (top), 150° model reaction (middle) and monomer **31f** (bottom).

repeated at a lower temperature (150°) using the same procedure. Analysis of the product by ^1H NMR (**Figure 20**, top) again showed the lack of appreciable fluorine displacement. TLC analysis also indicated that only starting material was isolated. Model reactions in DMSO led to similar conclusions. The ^1H NMR spectra of the product obtained from two DMSO model reactions are shown in **Figure 21**.

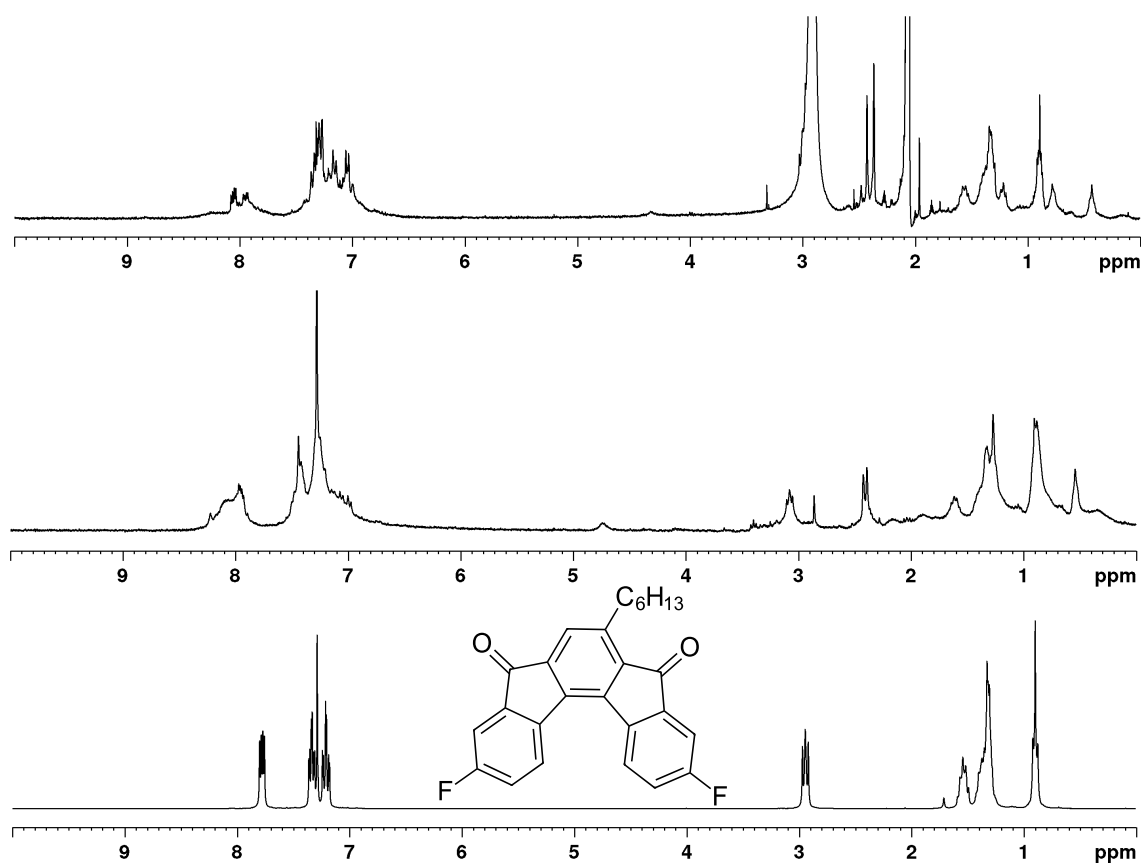
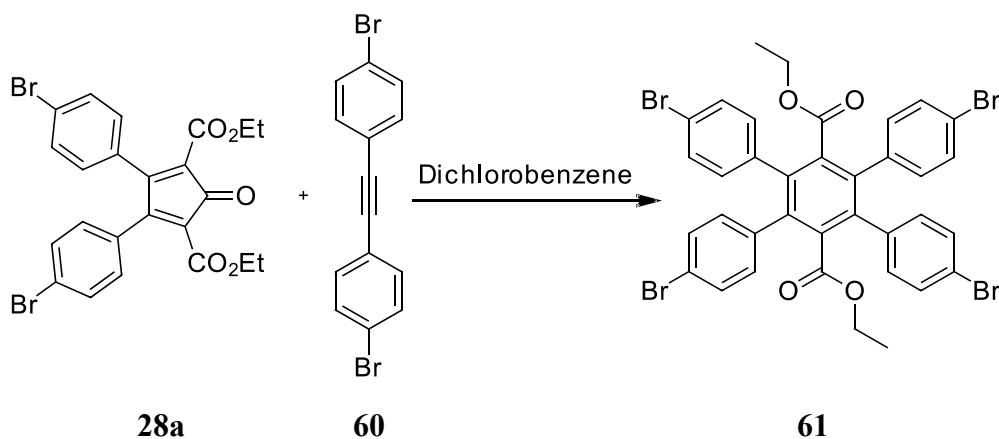


Figure 21. Spectra from DMSO model reaction at 175° (top), model reaction at 150° (middle) and monomer **31f** (bottom) starting material.

Related Syntheses

During the course of the polymerization study, a unique cyclopentadienone and two related terephthalates were synthesized as potential indenofluorenone precursors and monomers.

The Diels-Alder reaction of 2,5-bis(ethoxycarbonyl)-3,4-di(4-bromophenyl)cyclopentadienone **28a** and 1,2-bis(4-bromophenyl)ethyne **60**¹⁹ in *o*-dichlorobenzene yielded diethyl 2,3,5,6-tetrakis(4-bromophenyl)terephthalate **61** that was characterized by IR, ¹H NMR and ¹³C NMR.



The IR spectrum of **61** (**Figure 43**) exhibits an absorption at 1726 cm^{-1} attributed to the ester carbonyl.

The ¹H NMR spectrum (**Figure 44**) of diethyl 2,3,5,6-tetrakis(4-bromophenyl)terephthalate **61** exhibits 1) a triplet absorption at $\delta\ 0.77$ integrating to six hydrogens can be assigned to the methyl groups of the esters labeled a (**Figure 22**), 2) a quartet absorption at $\delta\ 3.71$ assigned to the methylene groups of the ethyl esters labeled b, 3) a doublet absorption at $\delta\ 6.97$ attributed to the eight hydrogens on the phenyl rings labeled c and 4) a doublet absorption at $\delta\ 7.35$ assigned to the eight hydrogens on the phenyl rings labeled d.

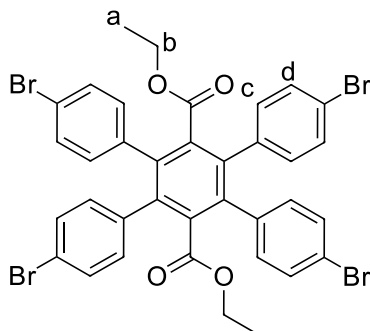


Figure 22. ^1H NMR assignments for diethyl 2,3,5,6-tetrakis(4-bromophenyl)terephthalate **61**

The ^{13}C NMR spectrum (**Figure 45**) for terephthalate **61** shows seven distinct absorptions in the aromatic region that would be expected from the symmetry associated with compound **61**. The absorptions at 61.23 and 13.41 ppm can be attributed to the methyl and methylene groups, respectively, in the ethyl ester. The aromatic CH absorptions at 130.97 and 131.52 ppm were identified by DEPT135 analysis (**Figure 46**). The calculated and observed ^{13}C NMR peaks are compared in **Figure 23**.

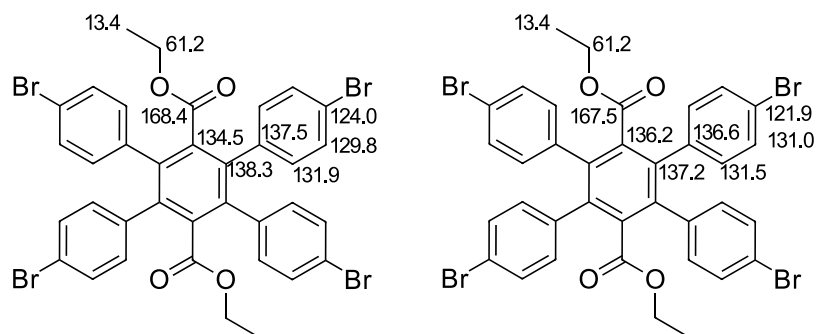
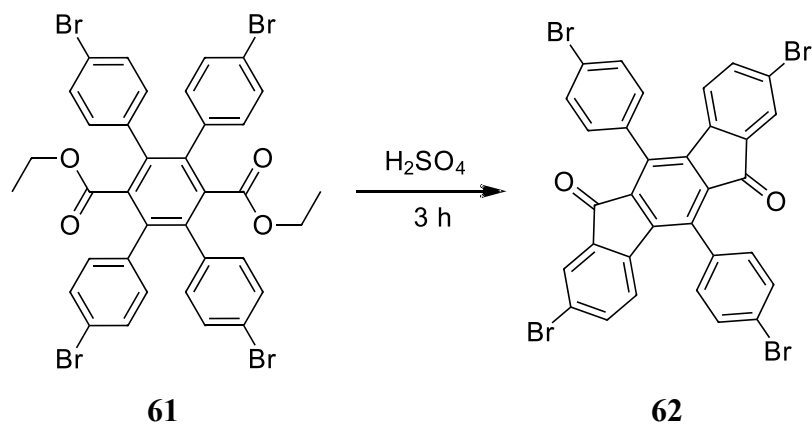


Figure 23. Predicted (left) and observed (right) ^{13}C NMR chemical shifts for diethyl 2,3,5,6-tetrakis(4-bromophenyl)terephthalate **61**.

Tetrabromophenyl terephthalate **61** was reacted in sulfuric acid to undergo an intramolecular Friedel-Crafts ring closure to produce 2,8-dibromo-5,11-bis(4-bromophenyl)indeno[1,2-b]fluorene-6,12-dione **62** as a red solid as had been indicated earlier for **36**.¹⁰

The IR spectrum (**Figure 47**) exhibited a conjugated ketone carbonyl absorption at 1716 cm^{-1} .



Although the product exhibited limited solubility in most deuterated solvents, the ^1H NMR spectrum of **62** in CDCl_3 (**Figure 24**) provides clear evidence of the ring closure. Doublet absorptions at δ 7.75 ($^3J_{\text{HH}} = 8.5\text{ Hz}$) and δ 7.30 ($^3J_{\text{HH}} = 8.5\text{ Hz}$) integrating to 4H each can be attributed to the p-bromophenyl pendent groups and the

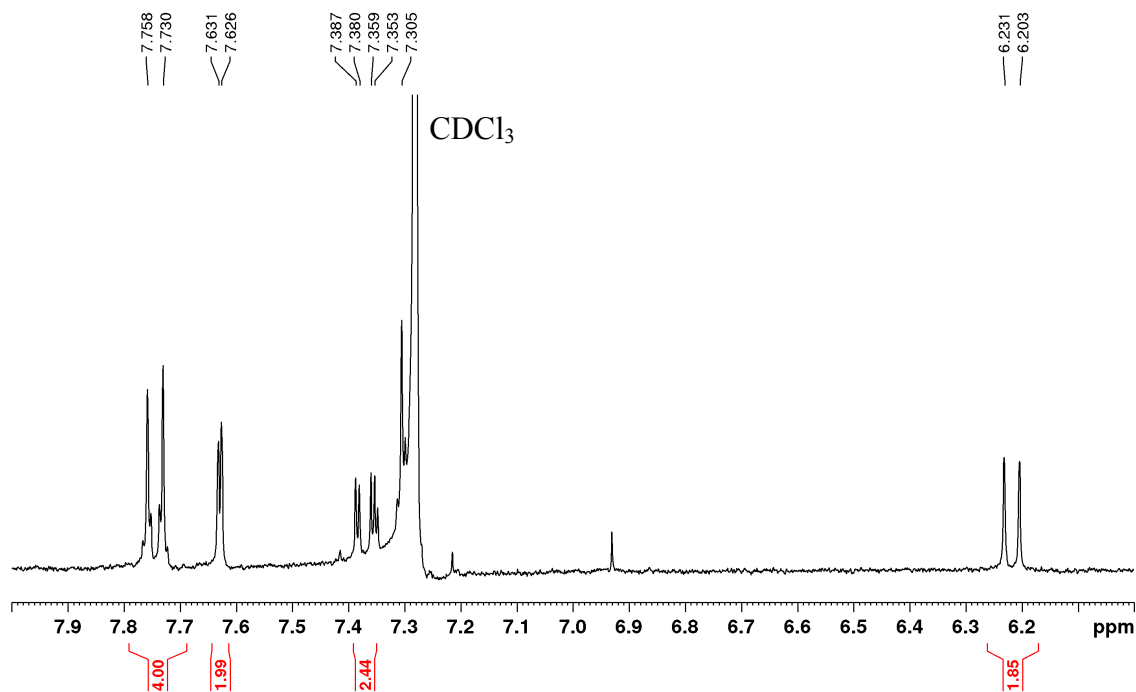
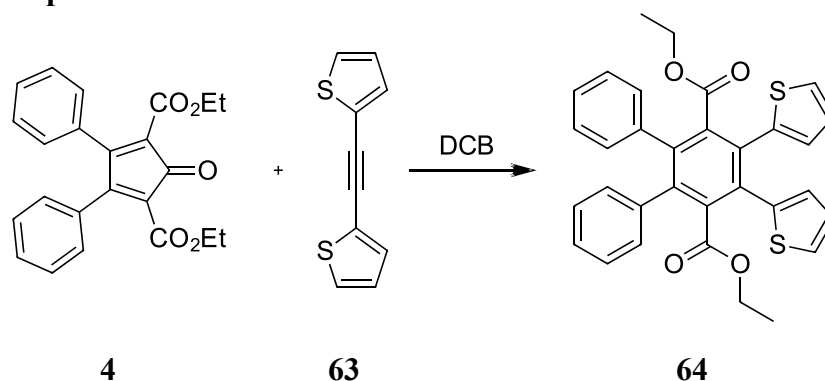


Figure 24. ^1H NMR spectra of 2,8-dibromo-5,11-bis(4-bromophenyl)indeno[1,2-b]fluorene-6,12-dione **62**.

absorptions at δ 7.63 ($^4J_{\text{HH}} = 1.7$ Hz), δ 7.63 ($^3J_{\text{HH}} = 8.2$ Hz, $^4J_{\text{HH}} = 1.9$ Hz) and δ 6.23 ($^3J_{\text{HH}} = 8.2$ Hz) are indicative of the 1,2,4 proton pattern associated with the fused brominated phenyl rings. An expansion of the aromatic portion of the ^1H NMR spectra of **62** is shown in **Figure 24**.

The tetrabromo derivative **62** was envisioned as a component in boronate coupling reactions but solubility considerations may limit its usefulness.

Dithienyl Terephthalate



A solution of 2,5-bis(ethoxycarbonyl)-3,4-diphenylcyclopentadienone **4** and 1,2-bis(2-thienyl)ethyne **63**²⁰ was heated at reflux in dichlorobenzene to provide diethyl 5,6-diphenyl-2,3-bis(2-thienyl)terephthalate **64**.

The IR spectrum (**Figure 48**) displayed a strong absorption at 1727 cm^{-1} that can be attributed to the ester carbonyls and multiple absorption peaks from $2896\text{--}2982\text{ cm}^{-1}$ can be attributed to the aliphatic ethyl ester groups.

The ^1H NMR spectrum (**Figure 49**) of diethyl 5,6-diphenyl-2,3-bis(2-thienyl)terephthalate **64** displays; 1) a triplet absorption at δ 0.80 which is attributed to the methyls of the ethyl group labeled a (**Figure 25**), 2) a quartet absorption at δ 3.77 assigned to the methylene groups labeled b, 3) a doublet of doublets absorption at δ 6.92 representative of an aromatic hydrogen present on the thiophene ring labeled c, 4) a

doublet of doublets absorptions at δ 6.99 indicative of an aromatic proton on the thiophene labeled e, 5) a multiplet absorption at δ 7.15 assigned to the ten aromatic hydrogens on the unsubstituted phenyl rings labeled d, 6) a doublet of doublets absorptions at δ 7.28 indicative of an aromatic proton on the thiophene ring labeled f.

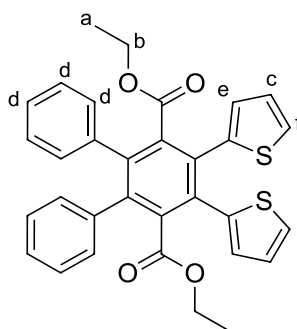


Figure 25. ^1H NMR assignments of diethyl 5,6-diphenyl-2,3-bis(2-thienyl)terephthalate **64**

The ^{13}C NMR spectrum (**Figure 50**) of diethyl 5,6-diphenyl-2,3-bis(2-thienyl)terephthalate **64** displays fourteen unique carbon absorptions. A comparison of the predicted and observed ^{13}C NMR chemical shifts for diethyl 5,6-diphenyl-2,3-bis(2-thienyl)terephthalate **64** can be seen in **Figure 25**. The DEPT135 spectrum (**Figure 51**) was used to aid in the carbon assignments.

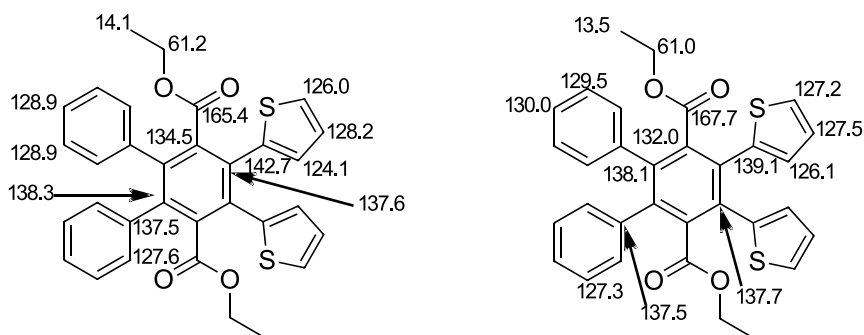
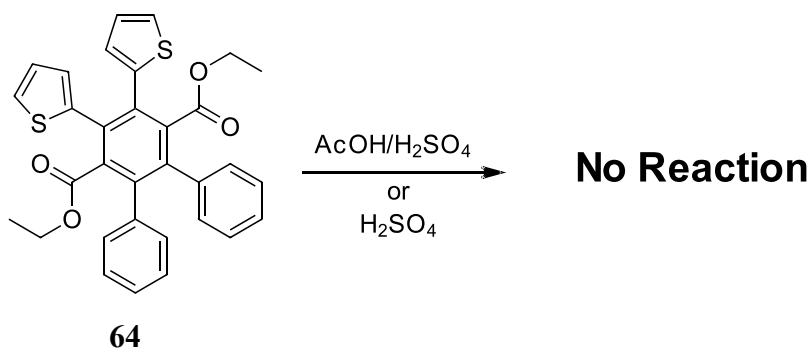


Figure 26. Predicted (left) and observed (right) ^{13}C NMR chemical shifts of diethyl 5,6-diphenyl-2,3-bis(2-thienyl)terephthalate **64**

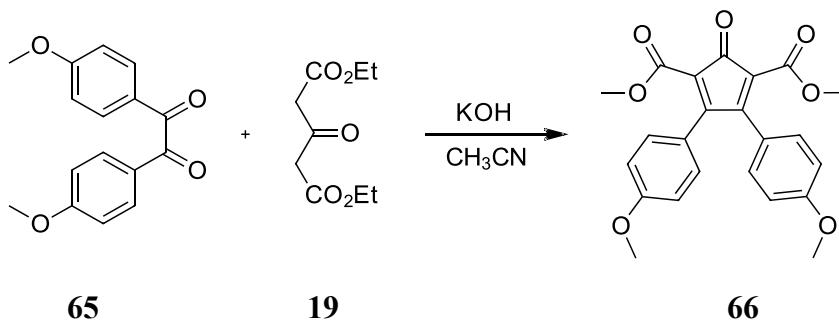
Unsubstituted tetraphenyl terephthalates are known to undergo intramolecular ring closures and form only 5,8-dioxo-5,8-dihydroindeno[1,2-b]fluorenes. The inclusion

of thiophenes in terephthalate **64** was anticipated to provide a competition in the intramolecular ring closure reaction by providing an electron-rich closure site that may influence the formation of the 1,2-c isomer in preference to the 1,2-b isomer.

Dithienyl terephthalate **64** was heated at reflux in an acetic acid/sulfuric acid mixture to undergo a Friedel-Crafts intramolecular ring closure. The reaction produced a black precipitate. The black solid was largely insoluble in deuterated chloroform. Extraction attempts of the solid were unsuccessful. The solid (minimal solubility) was analyzed by ^1H NMR (**Figure 52**). The spectrum showed no evidence of the intramolecular ring closure and seemed to show a decomposition of the thiophene rings due to extra absorption peaks in the aliphatic region of the ^1H NMR spectrum.



Originally, it was anticipated that a dihydroxy derivative **67** corresponding to the difluoro derivative **31f** could be prepared by a sequence starting with 2,5-bis(methoxycarbonyl)-3,4-di(4-methoxyphenyl)cyclopentadienone **66** that had been reported.¹⁸ Thus, the reaction of 4,4'-dimethoxybenzil **65** and diethyl

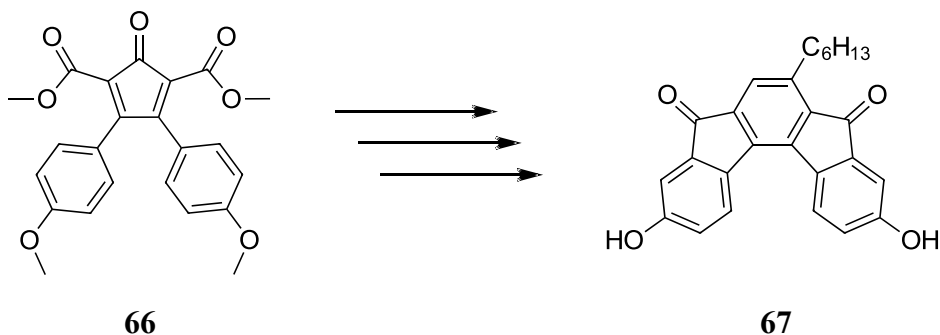


1,3-acetonedicarboxylate **19** yielded 2,5-bis(methoxycarbonyl)-3,4-di(4-methoxyphenyl)cyclopentadienone **66**¹⁸ that was characterized by IR, ¹H NMR and ¹³C NMR.

The IR spectrum of **66** (**Figure 53**) showed an absorption at 1738 cm⁻¹ attributed to the ketone carbonyl and an absorption at 1712 cm⁻¹ attributed to the ester carbonyl.

The ¹H NMR spectrum (**Figure 54**) of 2,5-bis(methoxycarbonyl)-3,4-di(4-methoxyphenyl)cyclopentadienone exhibits two singlet absorptions in the aliphatic region at δ 3.77 and δ 3.84 which are attributed the methoxy groups in cyclopentadienone **66**. The aromatic region exhibits two doublet absorptions at δ 6.82 and δ 7.02 which are attributed to the protons on the *para* substituted aromatic rings.

The ¹³C NMR spectrum (**Figure 55**) exhibits two singlet absorptions in the aliphatic region at 52.09 ppm and 55.31 ppm that are attributed to the methoxy groups. The DEPT135 spectrum (**Figure 56**) shows that the peaks at 113.22 ppm and 131.39 ppm can be assigned to the protonated carbons in the *para* substituted rings. The peak at 191.0 ppm is assigned to the ketone carbonyl on the cyclopentadiene ring. The highest yield for the reaction was 13% and after numerous attempts to increase the efficiency of the reaction, the synthesis was abandoned due to low yields with time consuming purification.



CONCLUSIONS

The monomer, 3,10-difluoro-5,8-dioxo-5,8-dihydro-6-hexylindeno[2,1-c]fluorene **31f** can be produced in a four-step process in 54% yield despite using column chromatography purification in the final step. The monomer exhibits a concentration dependent ^1H NMR spectrum that may suggest significant intermolecular interactions at high concentrations. The chemical shift of the fluorine ipso carbon (~ 163 ppm) casts doubt on the potential for polymerization as it is comparable to unactivated fluorine ipso carbon chemical shifts.

The polymerization of monomer **31f** under standard NAS PEEKK conditions was not successful. Only unreacted monomer was isolated from the polymer reactions under normal workup conditions. Likewise, model reactions of monomer **31f** with p-cresol gave similar results. Apparently the activation of the fluorine *ipso* carbon in **31f** and/or the stabilization of the predicted Meisenheimer complex is not sufficient for reaction.

The indeno[1,2-b]fluorene, 2,8-dibromo-5,11-bis(4-bromophenyl)indeno[1,2-b]fluorene-6,12-dione **62** and the thienyl derivative, diethyl 5,6-diphenyl-2,3-bis(2-thienyl)terephthalate **64** were synthesized as potential polymer components/precursors.

The synthesis of 2,5-bis(methoxycarbonyl)-3,4-di(4-methoxyphenyl)cyclopentadienone **66** proved to be a low yield reaction with a difficult purification that precluded an anticipated synthesis of 3,10-dihydroxy-5,8-dioxo-5,8-dihydro-6-hexylindeno[2,1-c]fluorene **67**.

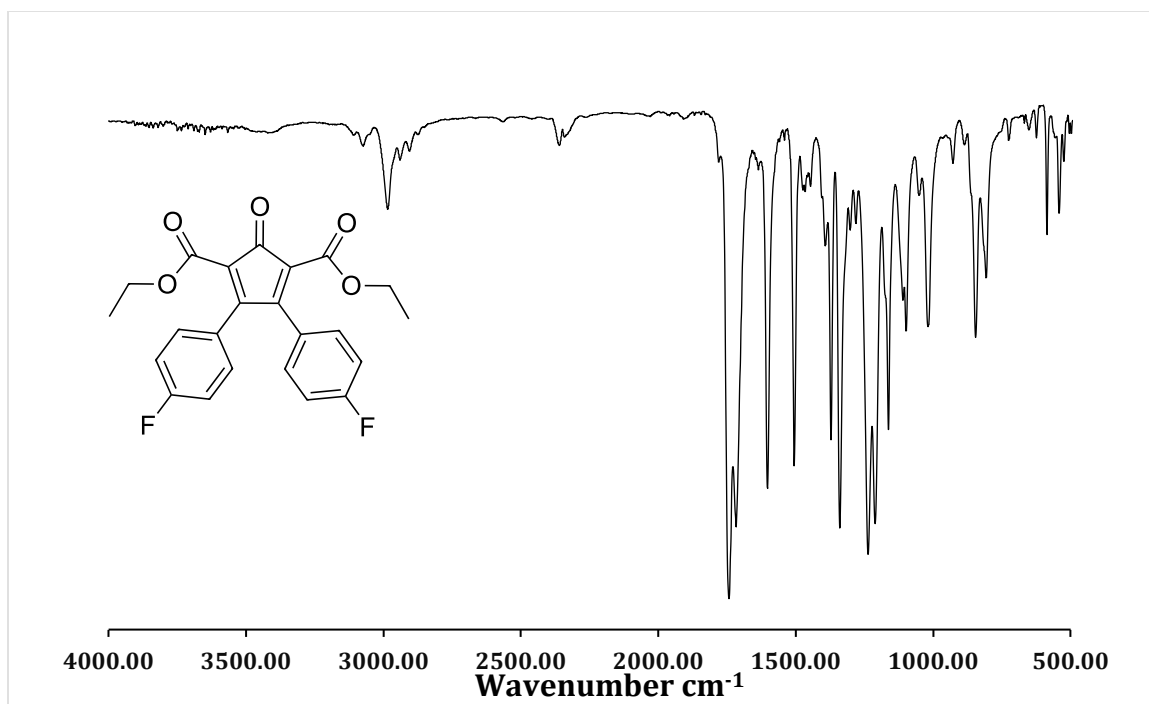


Figure 27. IR spectrum (NaCl) of cyclopentadienone **28c**.

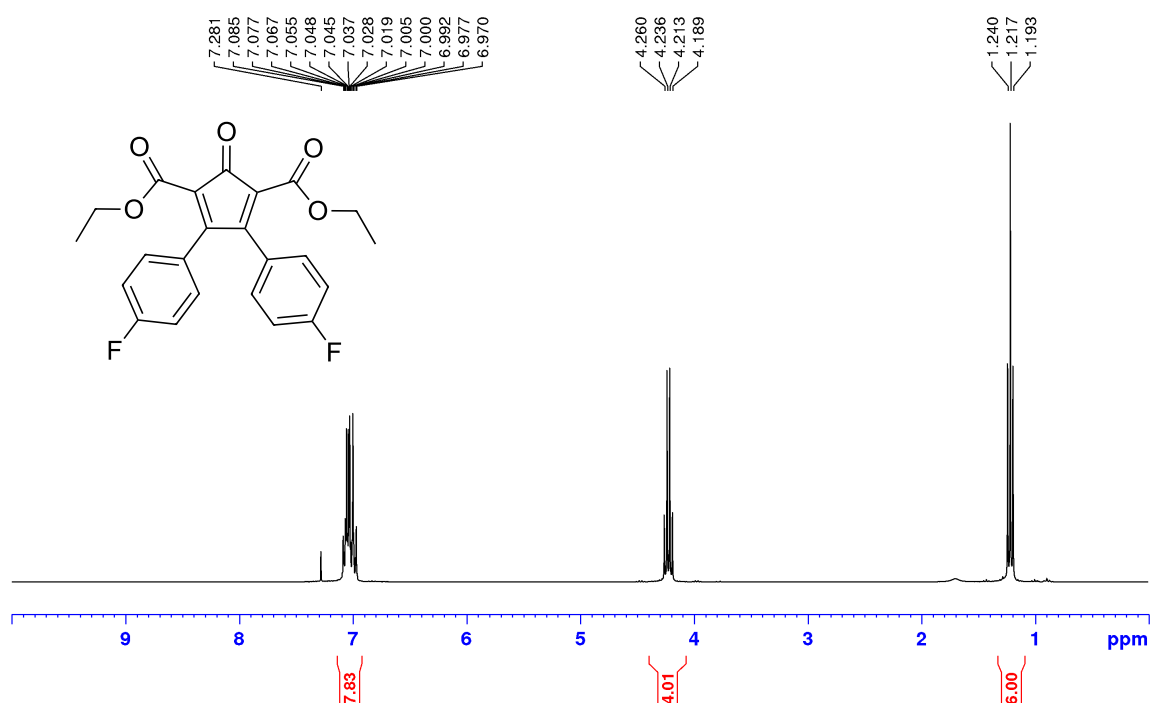


Figure 28. ¹H NMR spectrum (300 MHz, CDCl₃) of cyclopentadienone **28c**.

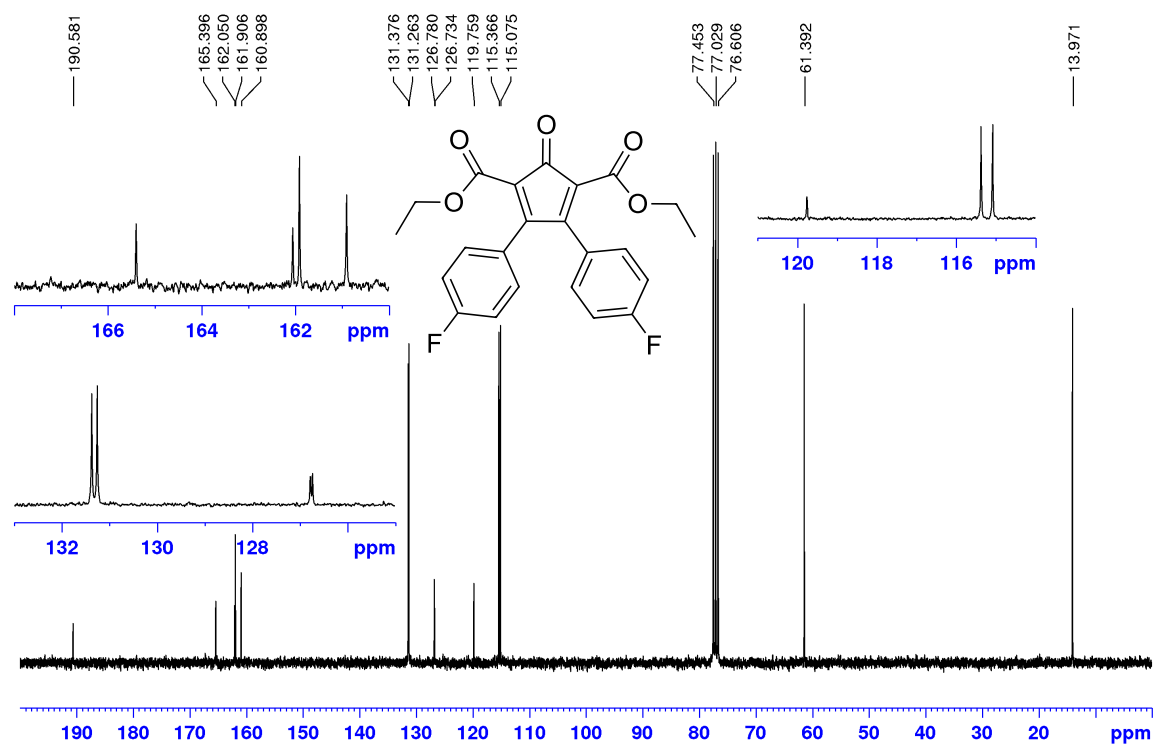


Figure 29. ^{13}C NMR spectrum (75 MHz, CDCl_3) of cyclopentadienone **28c** with insets of meta and para fluorine couplings.

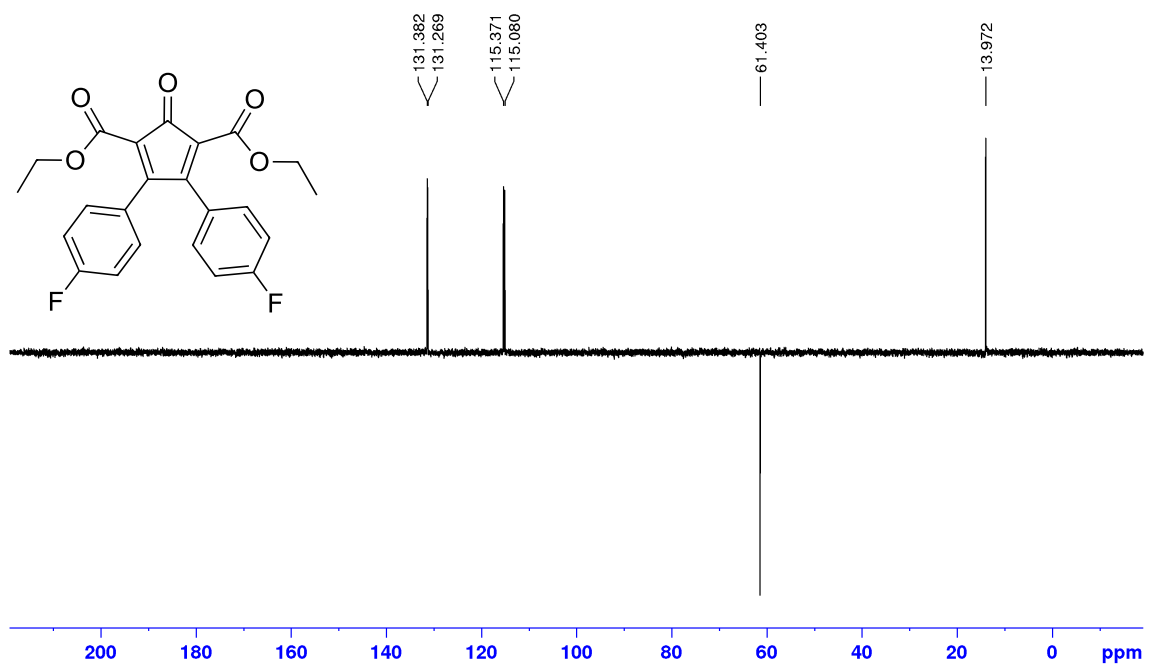


Figure 30. ^{13}C DEPT135 NMR spectrum (75 MHz, CDCl_3) of cyclopentadienone **28c**.

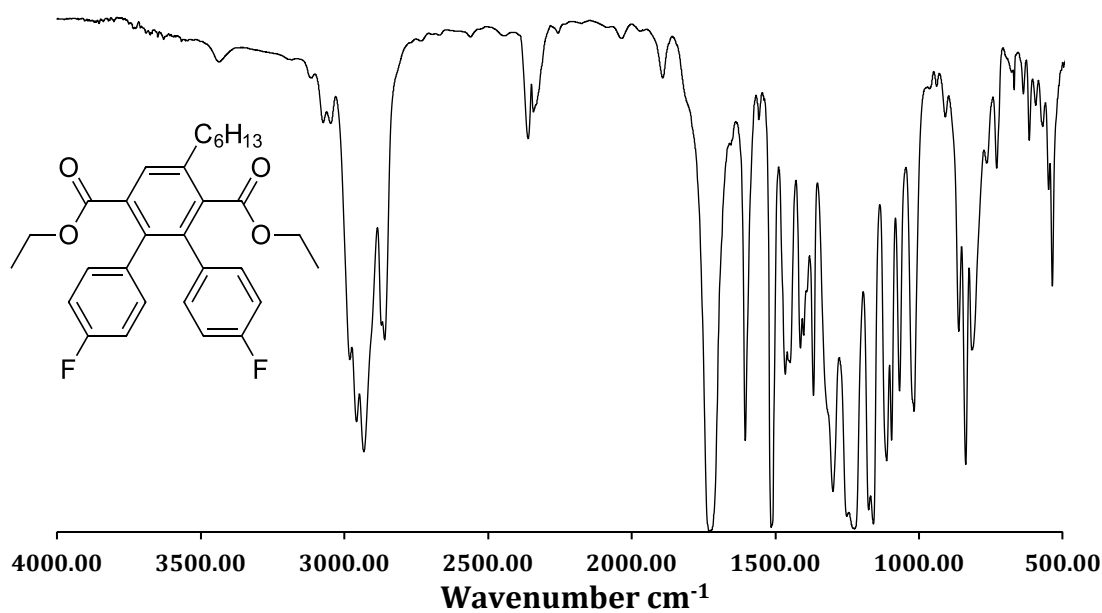


Figure 31. IR spectrum (NaCl) of diester **29f**.

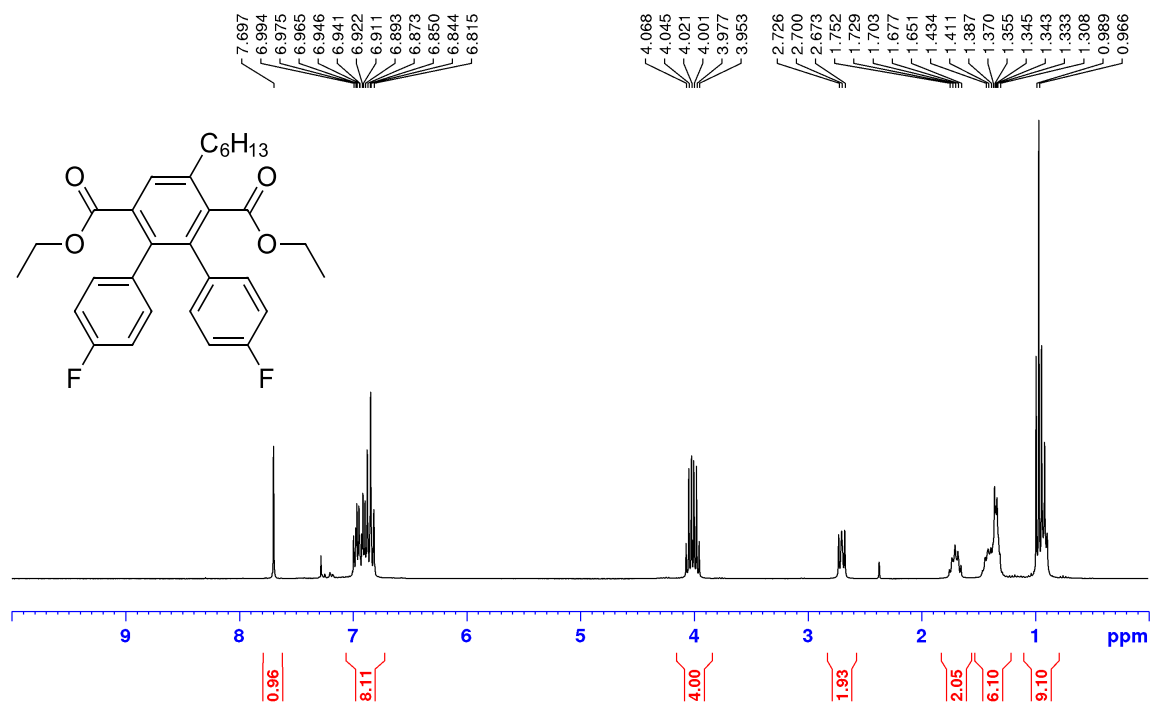


Figure 32. ^1H NMR spectrum (300 MHz, CDCl_3) of diester **29f**.

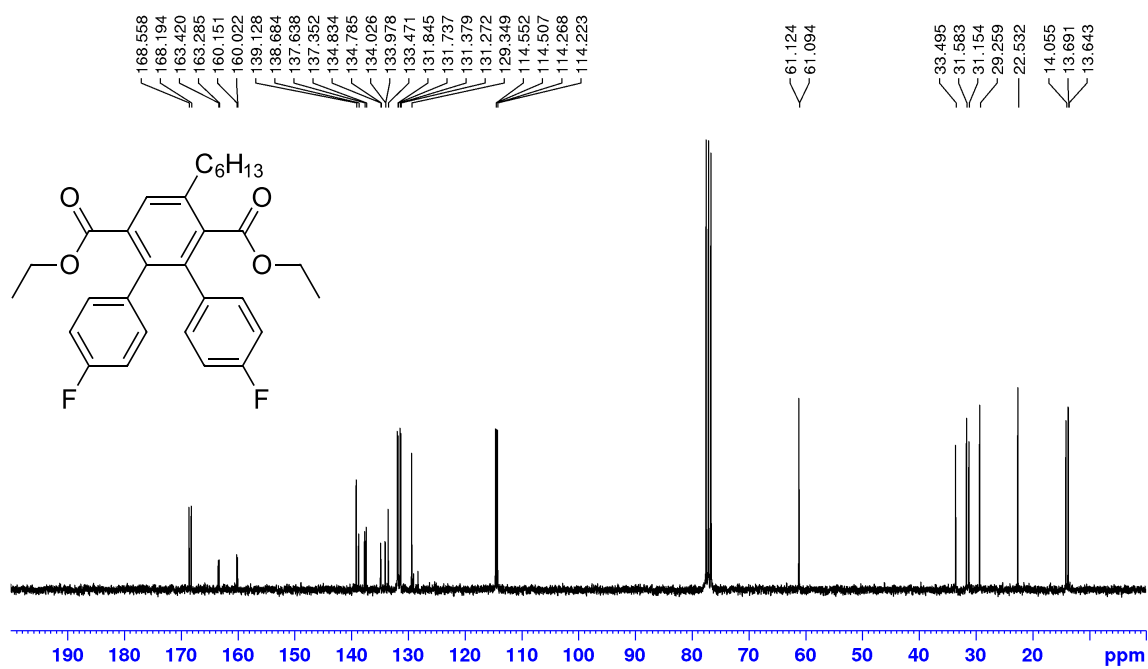


Figure 33. ^{13}C NMR spectrum (75 MHz, CDCl_3) of diester **29f**

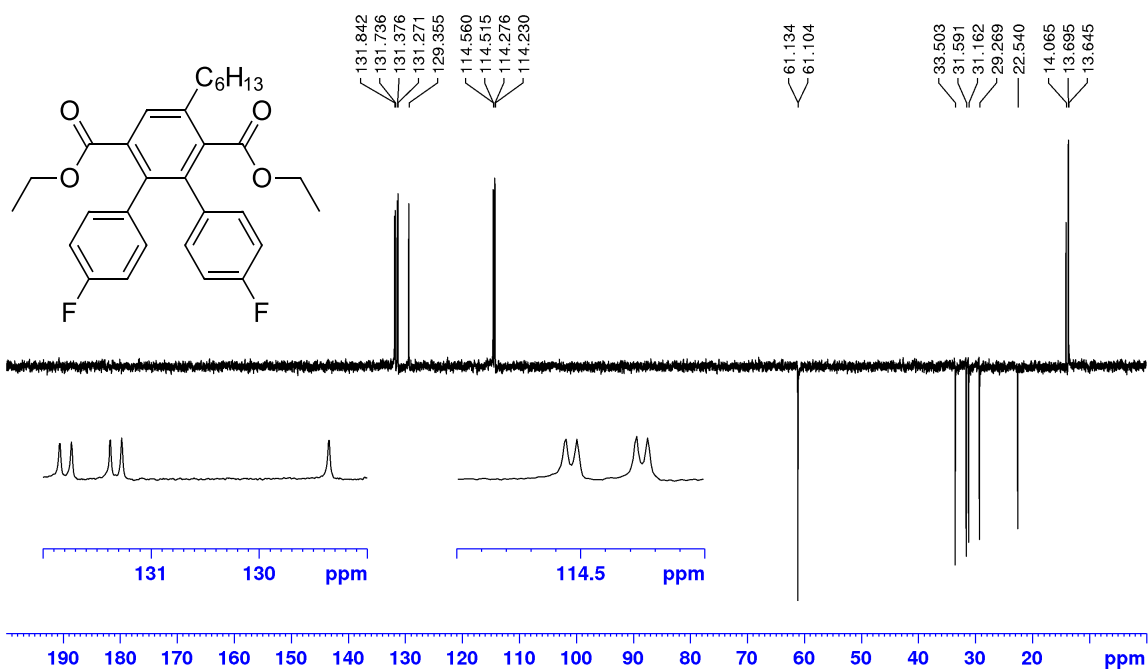


Figure 34. ^{13}C DEPT135 NMR spectrum (75 MHz, CDCl_3) of diester **29f**.

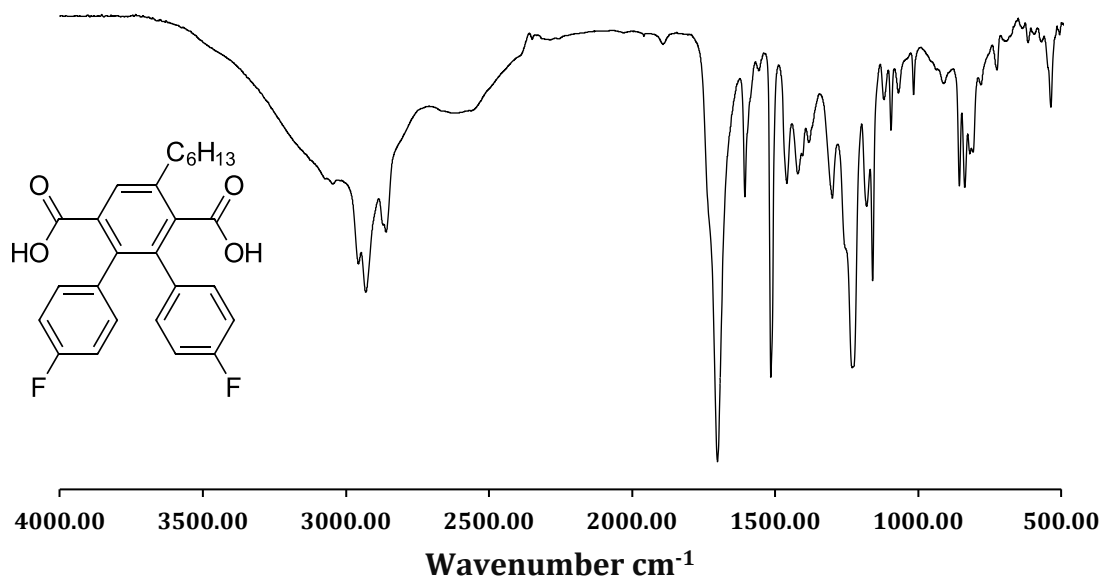


Figure 35. IR spectrum (NaCl) of diacid **30f**.

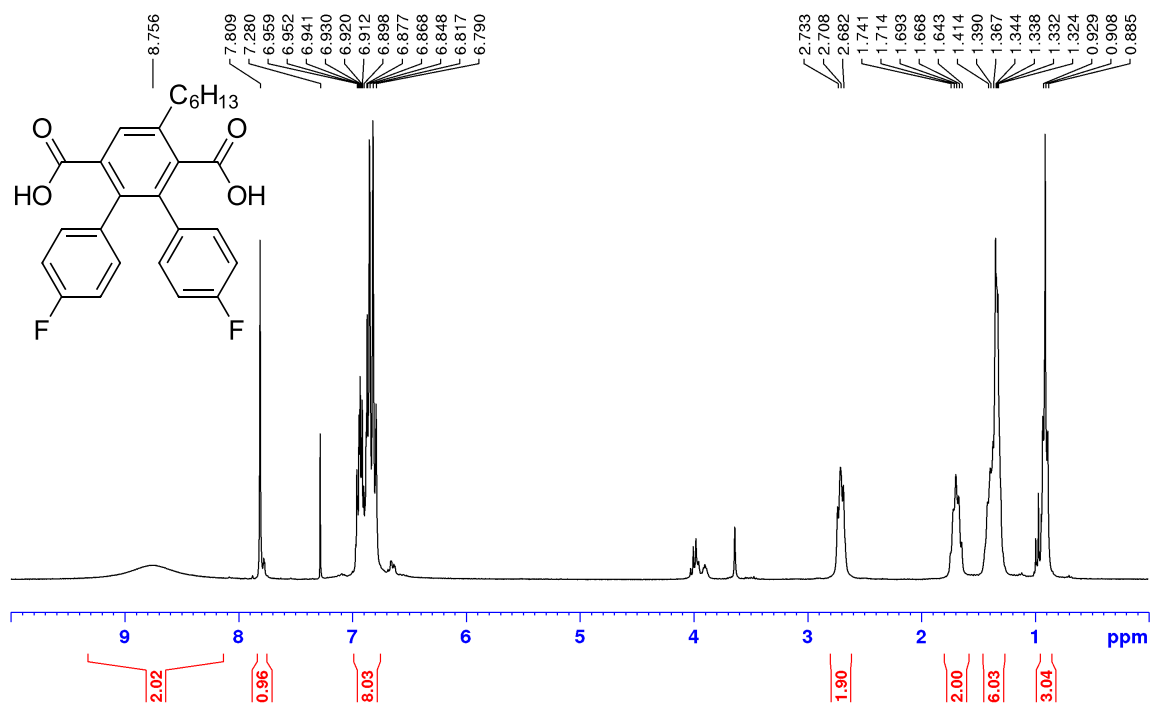


Figure 36. ^1H NMR spectrum (300 MHz, CDCl_3) of diacid **30f**.

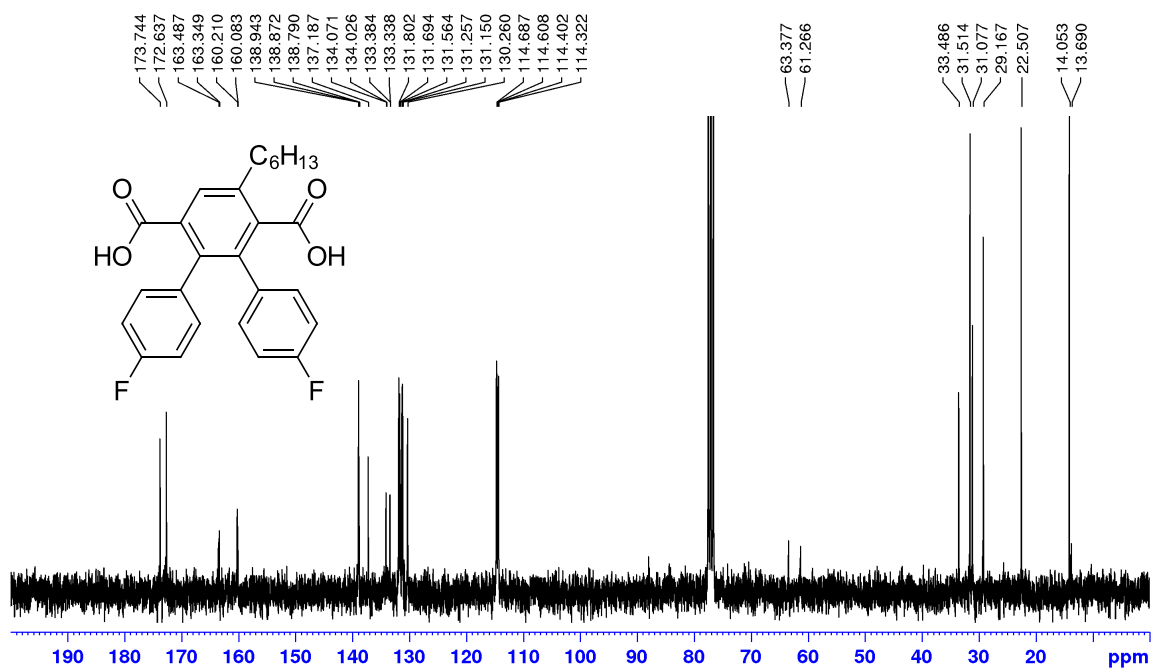


Figure 37. ^{13}C NMR spectrum (75 MHz, CDCl_3) of diacid **30f**.

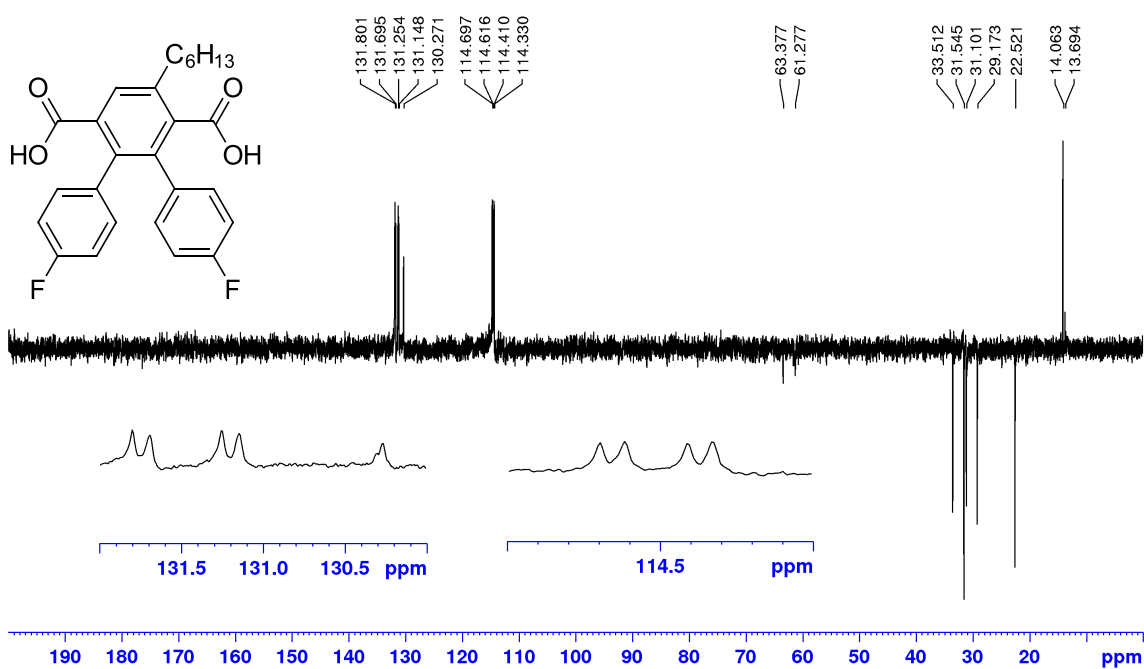


Figure 38. ^{13}C DEPT135 NMR spectrum (75MHz, CDCl_3) of diacid **30f**.

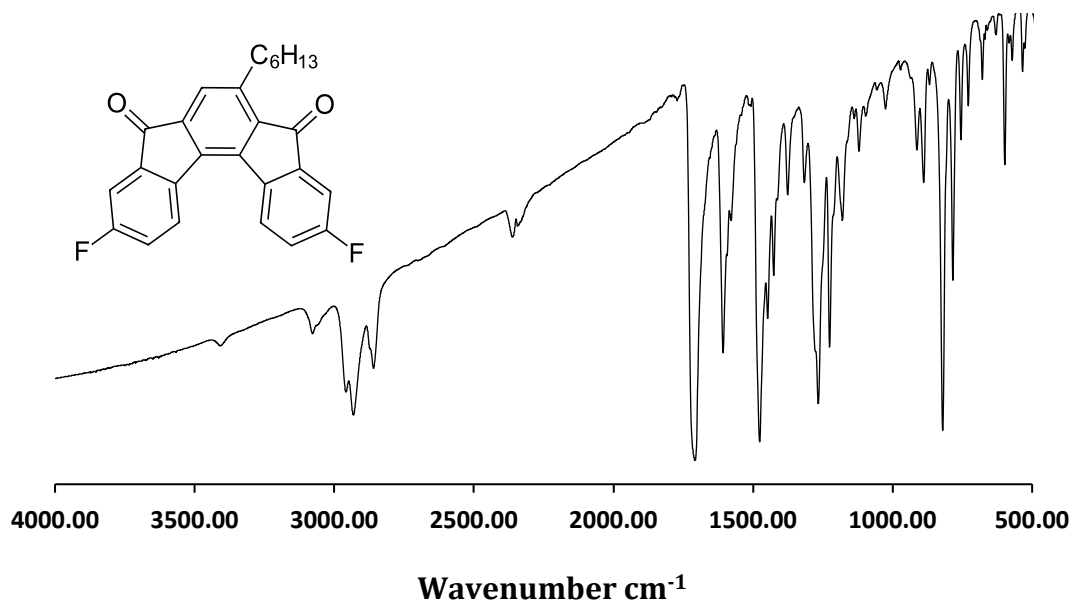


Figure 39. IR spectrum (KBr) of indenofluorene **31f**.

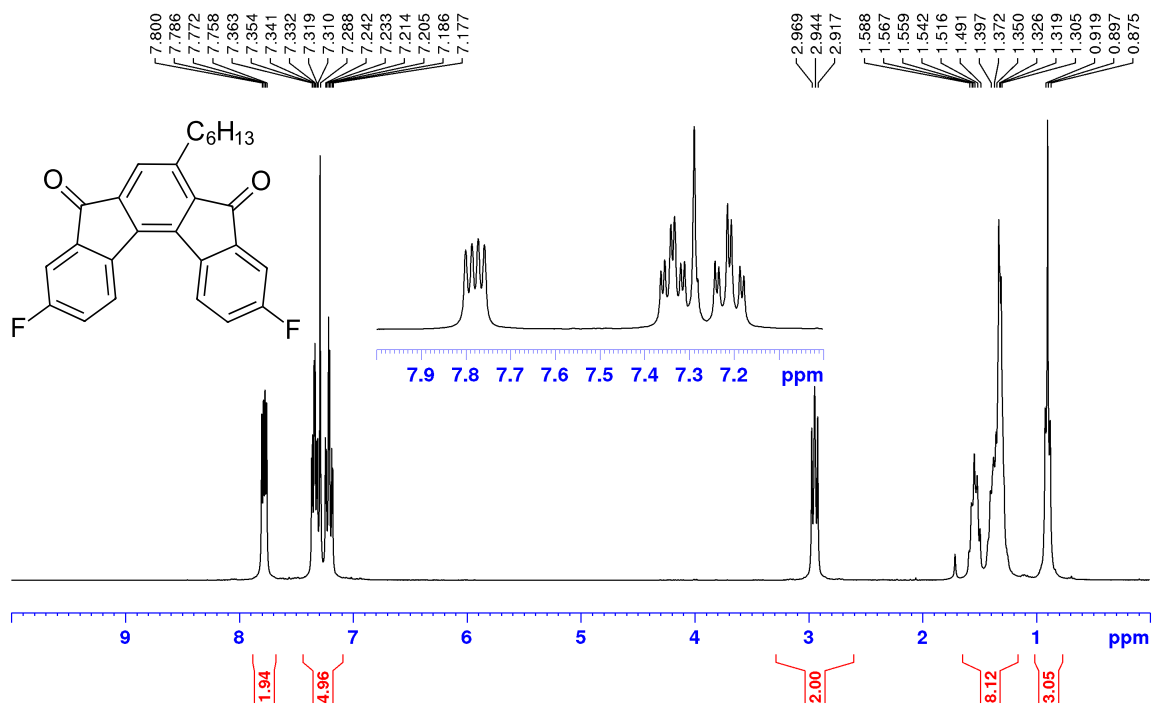


Figure 40. 1H NMR spectrum (300 MHz, $CDCl_3$) of indenofluorene **31f**.

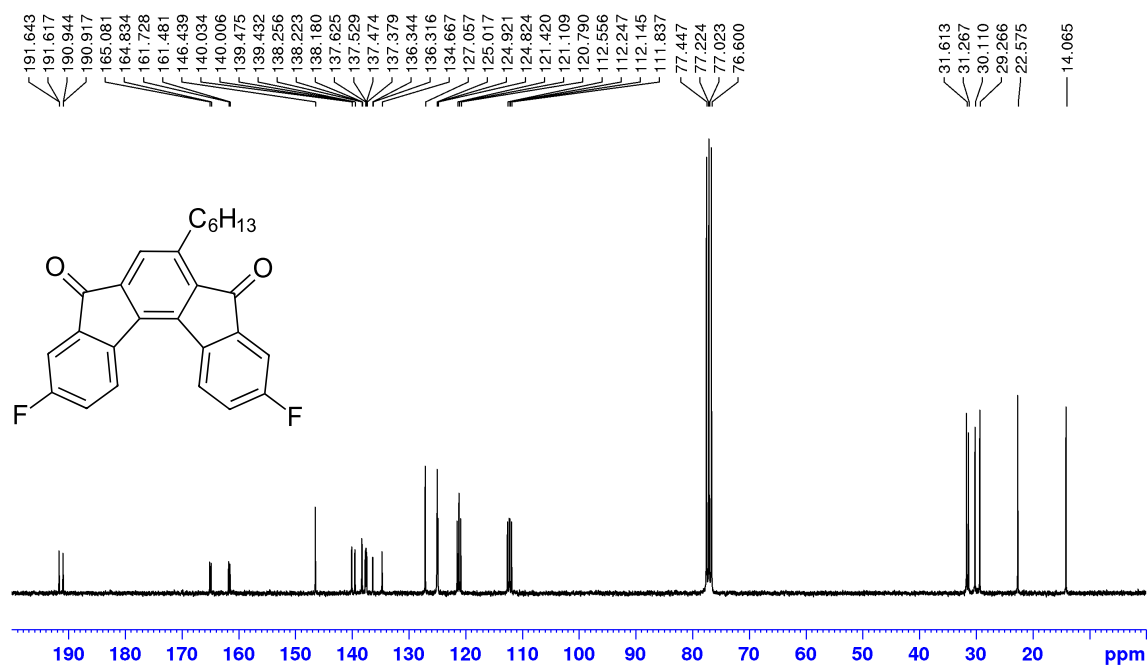


Figure 41. ^{13}C NMR spectrum (75 MHz, CDCl_3) of indenofluorene **31f**.

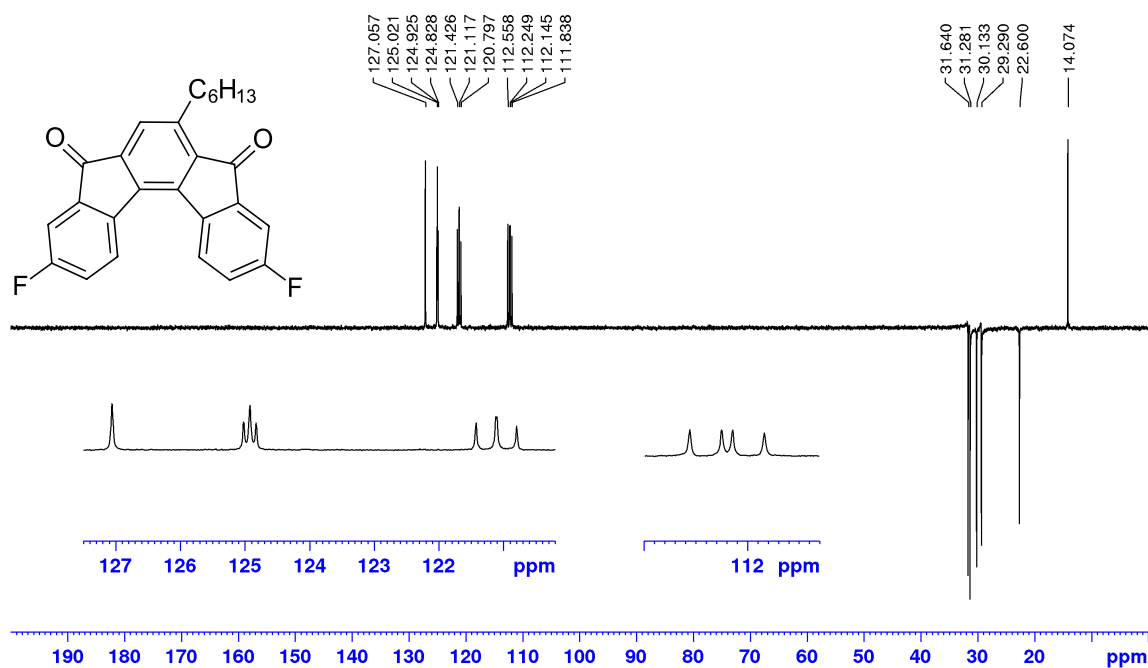


Figure 42. ^{13}C DEPT135 NMR spectrum (75MHz, CDCl_3) of indenofluorene **31f**.

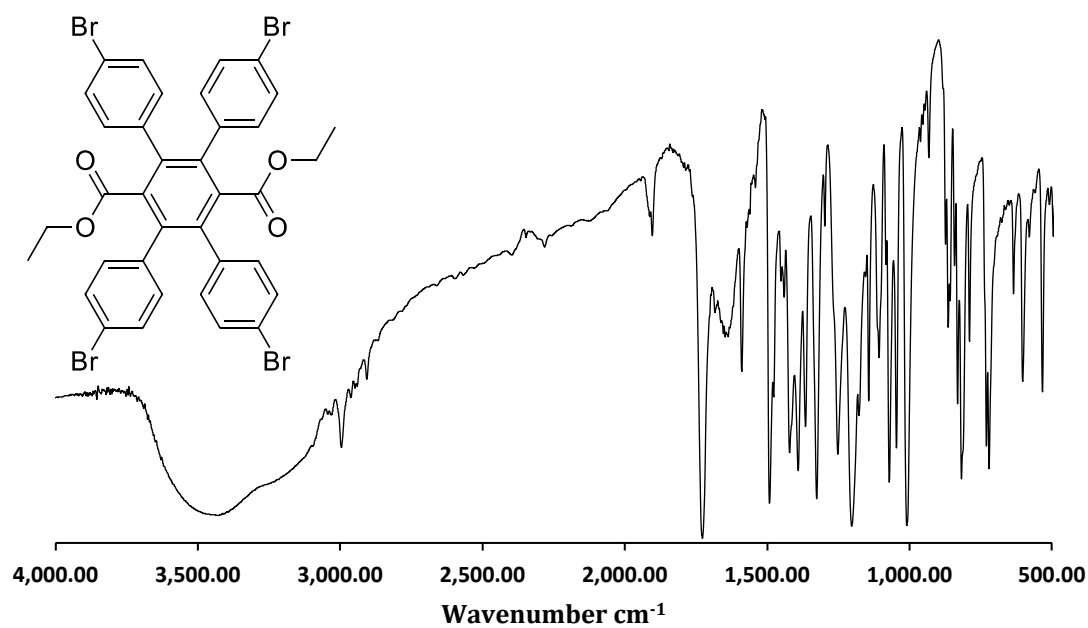


Figure 43. IR spectrum (KBr) of diester **61**.

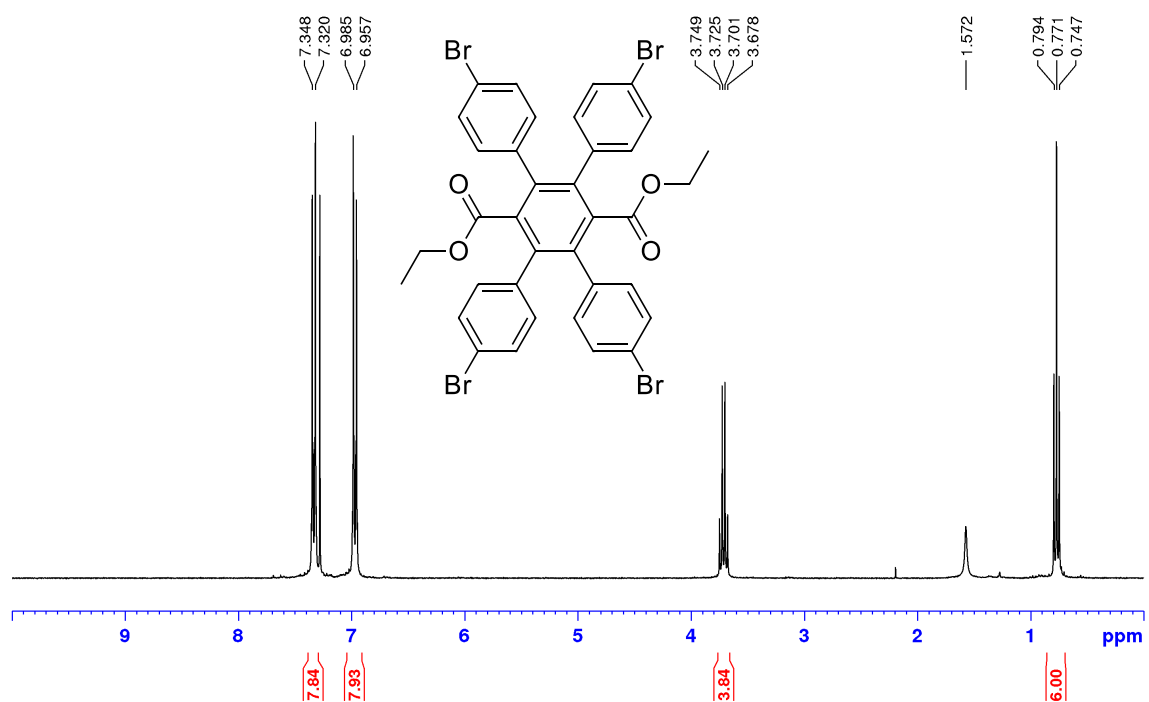


Figure 44. ^1H NMR spectrum (300 MHz, CDCl_3) of diester **61**.

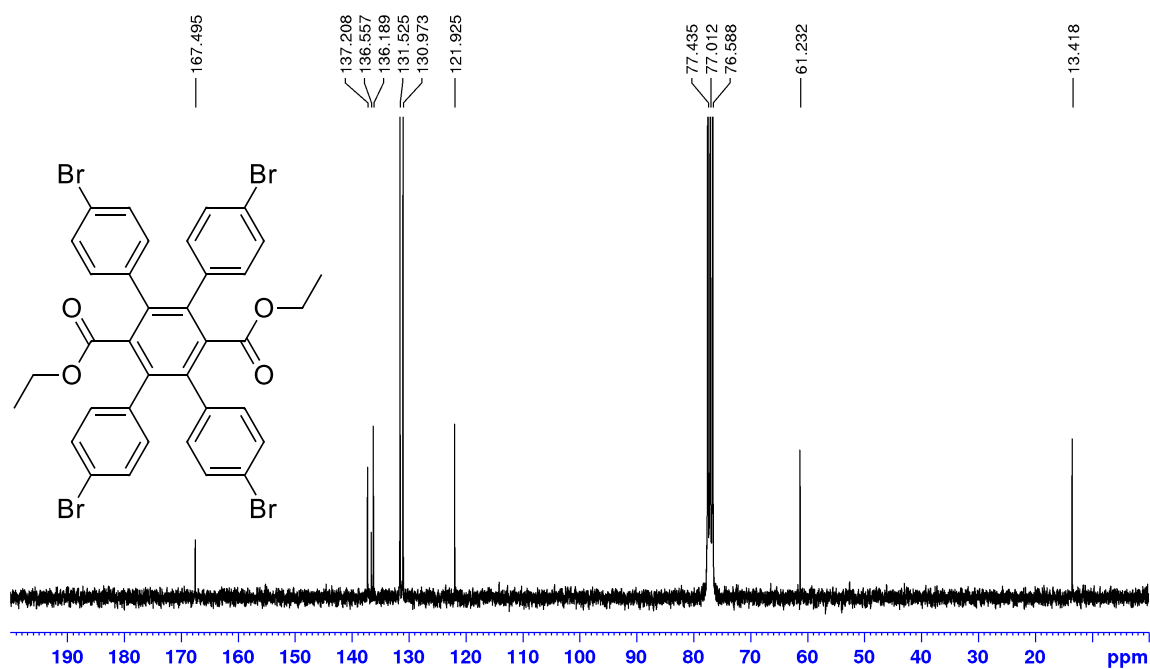


Figure 45. ^{13}C NMR spectrum (75 MHz, CDCl_3) of diester **61**.

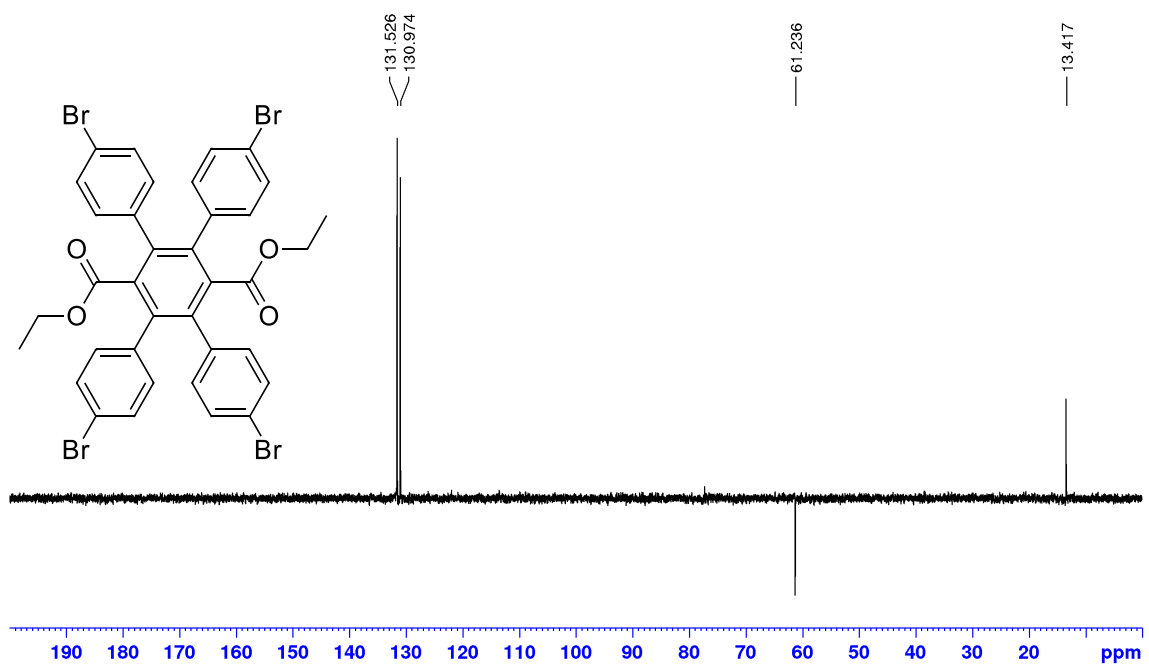


Figure 46. ^{13}C DEPT135 NMR spectrum (75MHz, CDCl_3) of diester **61**.

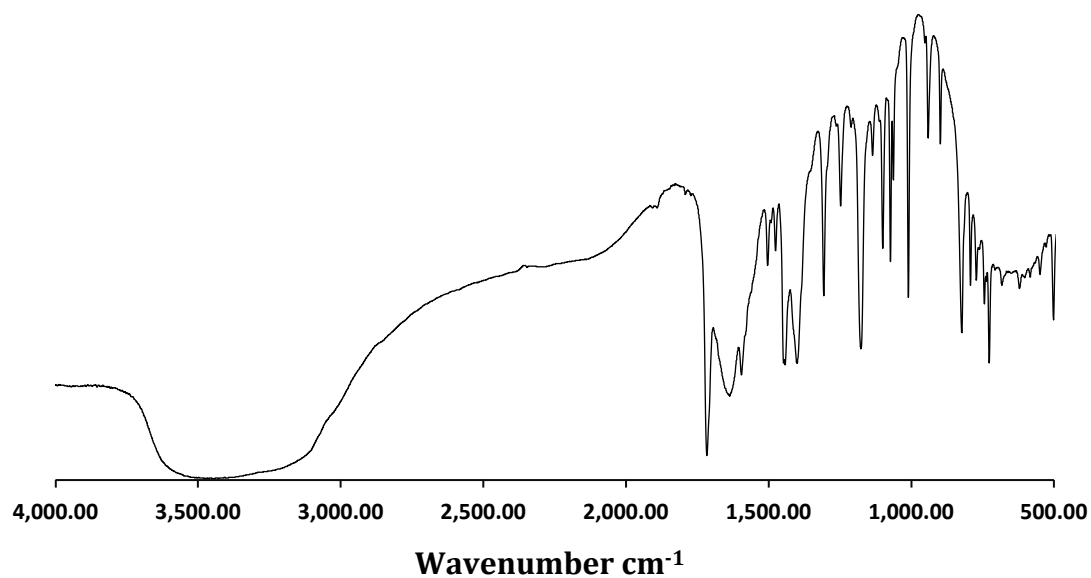


Figure 47. IR spectrum (KBr) of tetrabromo indenofluorene **62**.

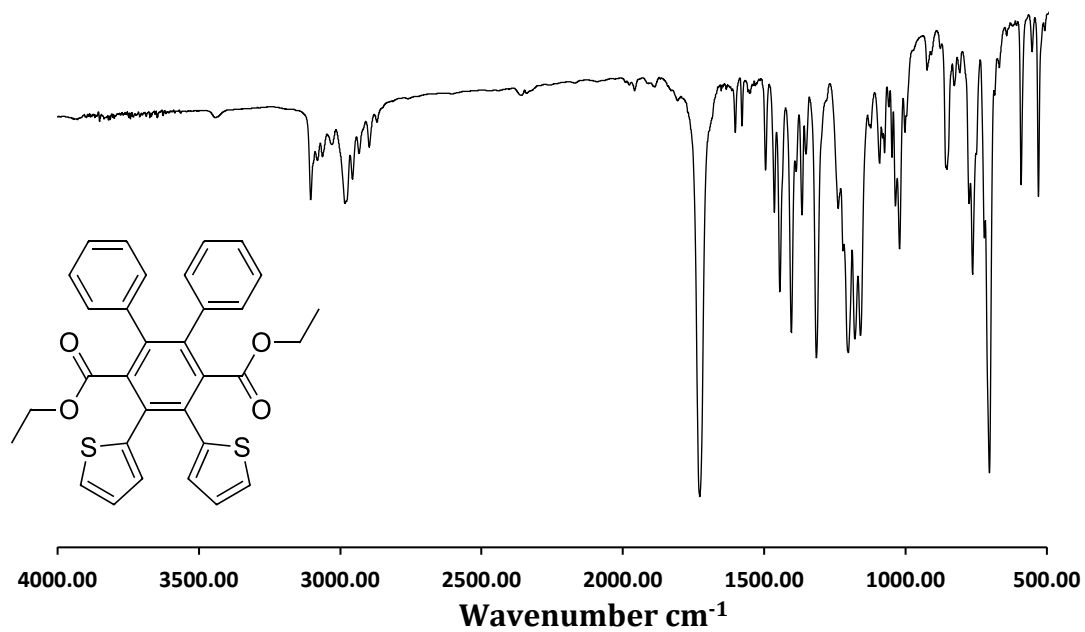


Figure 48. IR spectrum (NaCl) of diester **64**.

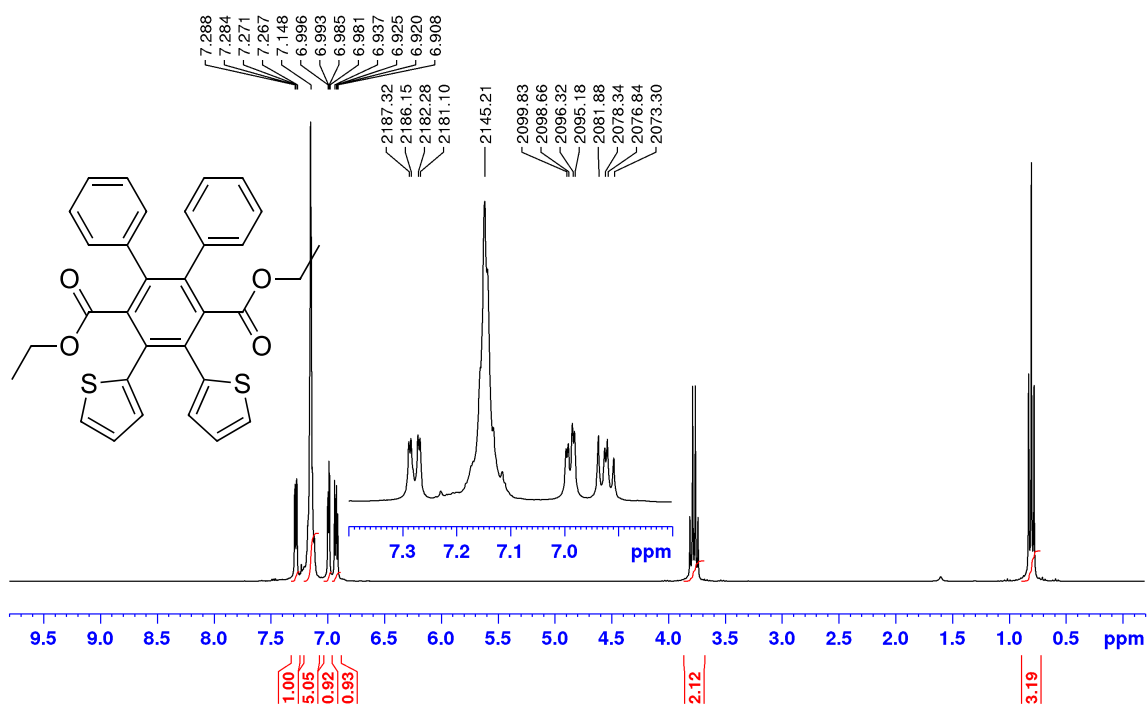


Figure 49. ¹H NMR spectrum (300 MHz, CDCl₃) of diester **64**.

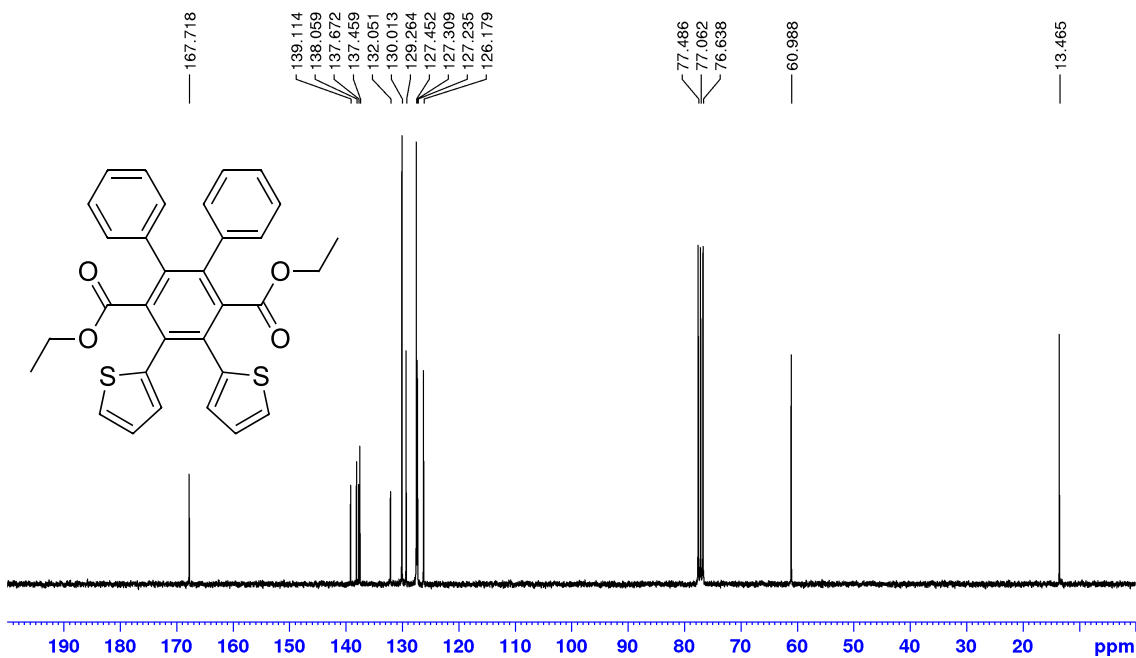


Figure 50. ¹³C NMR spectrum (75 MHz, CDCl₃) of diester **64**.

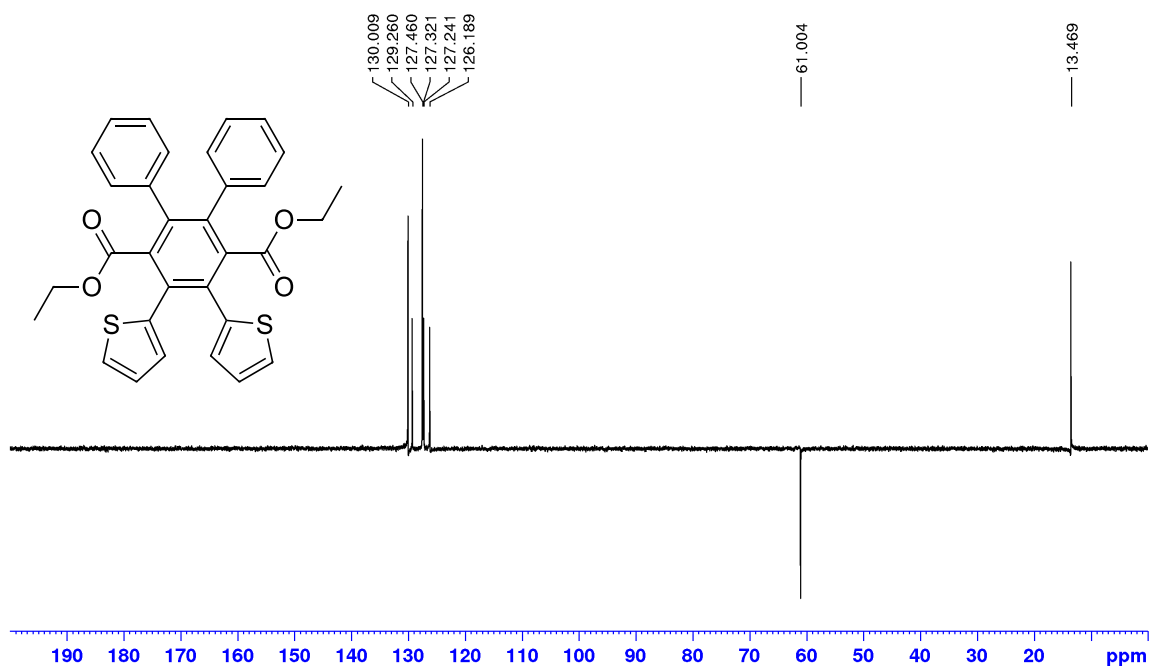


Figure 51. ^{13}C DEPT135 NMR spectrum (75MHz, CDCl_3) of diester **64**.

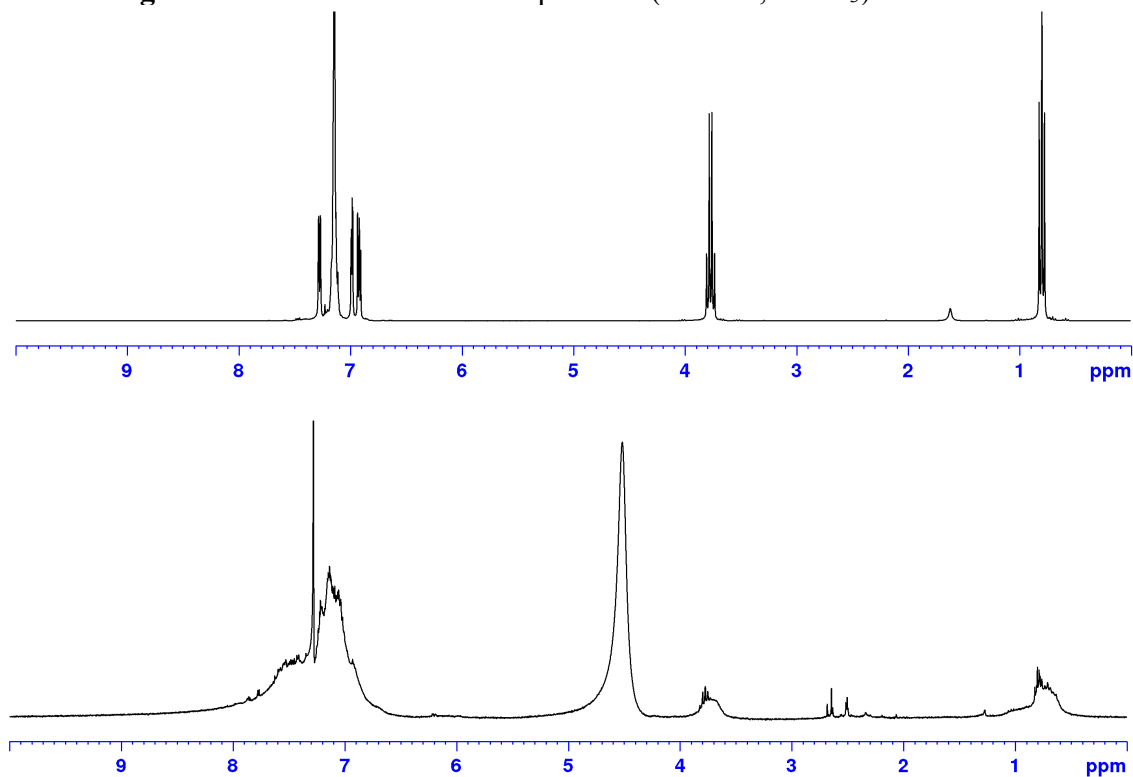


Figure 52. ^1H NMR of attempted ring closure of diester **64**.

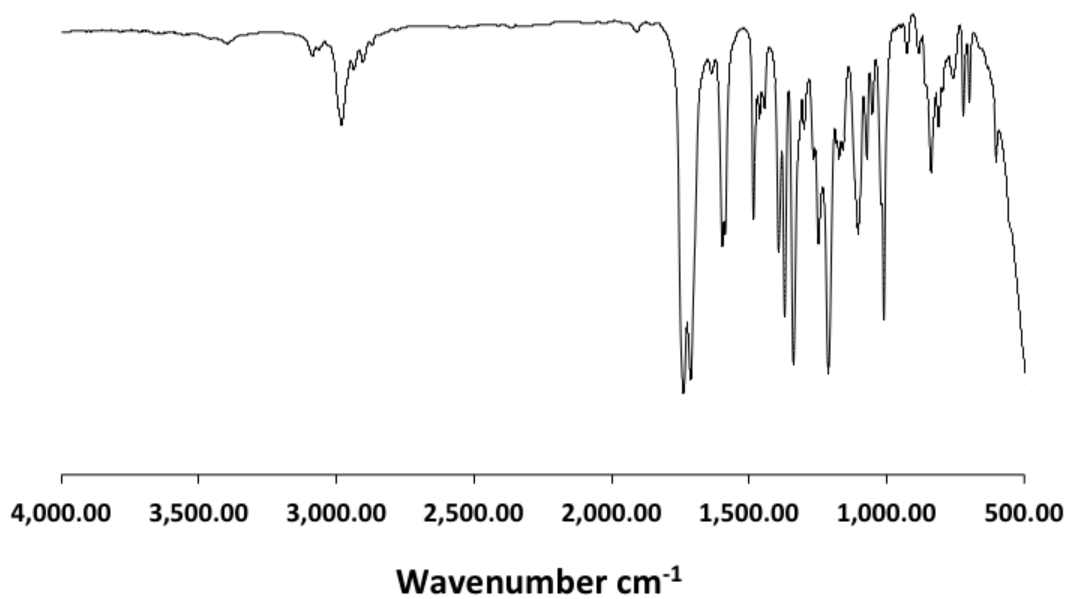


Figure 53. IR spectrum (300 MHz, CDCl_3) of dimethoxycyclopentadienone **66**.

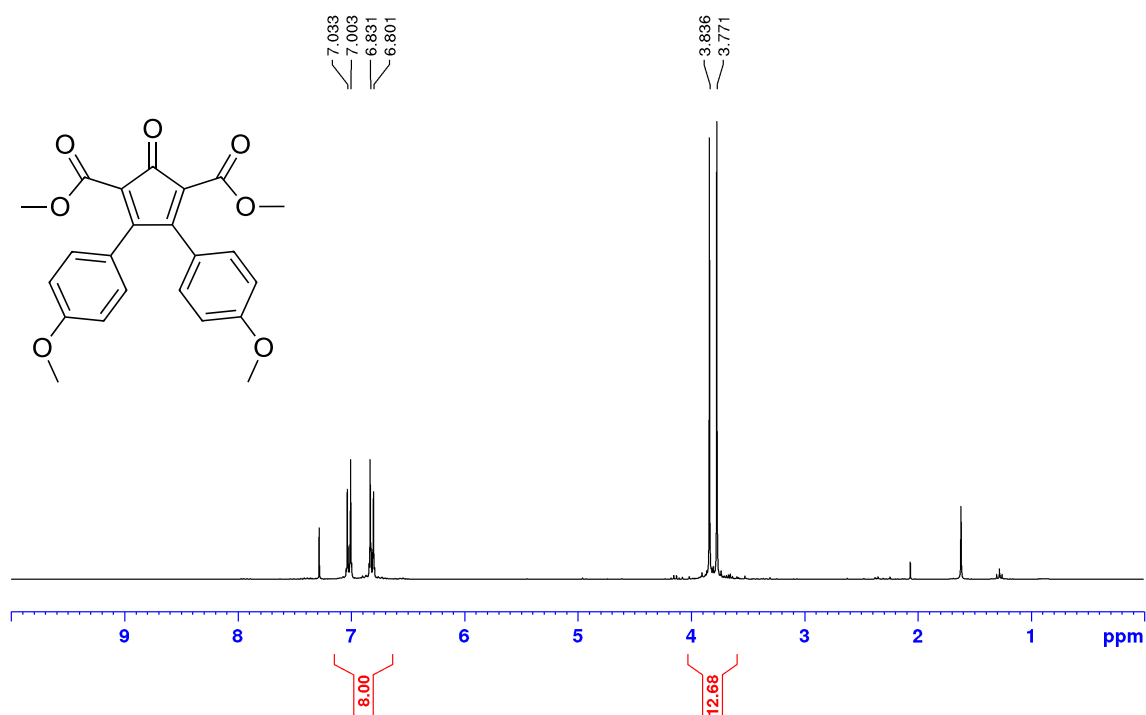


Figure 54. ^1H NMR spectrum (300 MHz, CDCl_3) of dimethoxycyclopentadienone **66**.

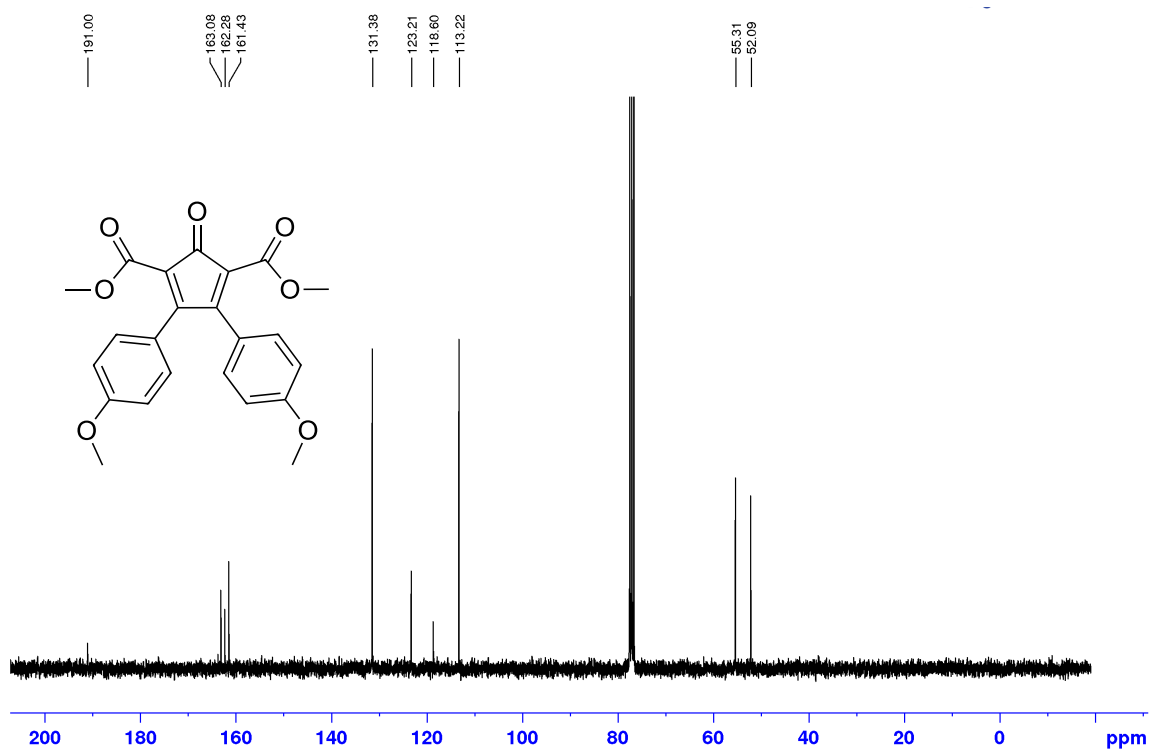


Figure 55. ¹³C NMR spectrum (75 MHz, CDCl₃) of dimethoxycyclopentadienone **66**.

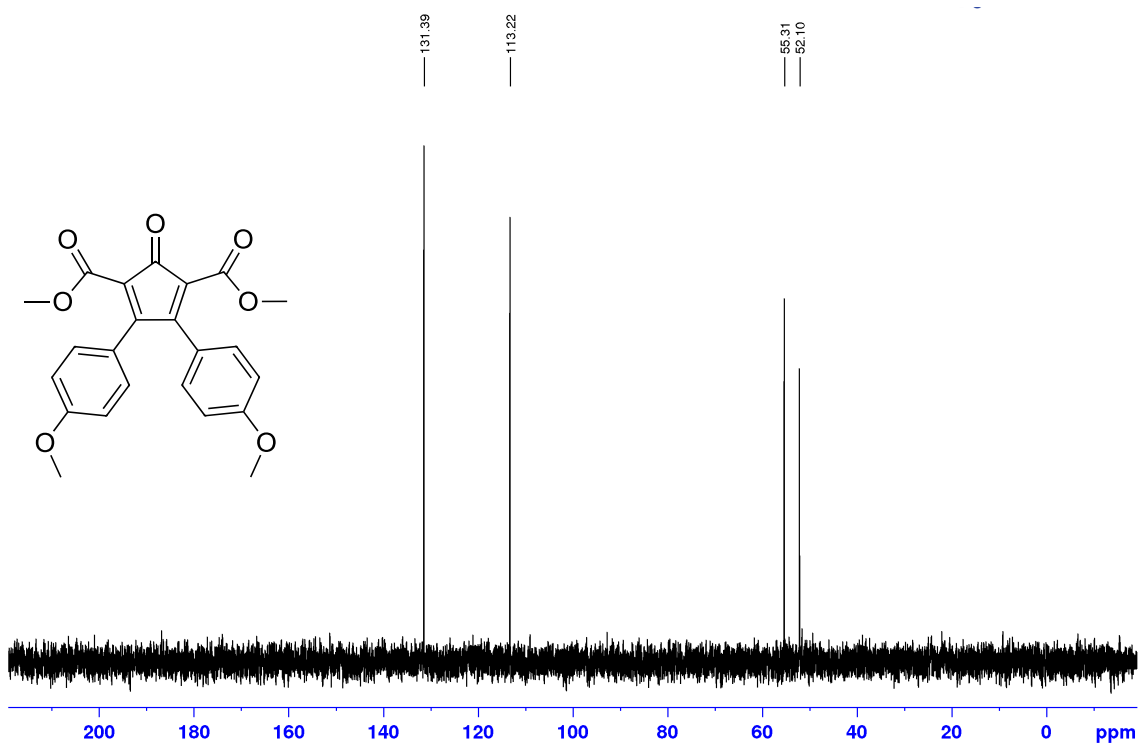


Figure 56. ¹³C DEPT135 NMR spectrum (75 MHz, CDCl₃) of dimethoxycyclopentadienone **66**.

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