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Synthetic Strategies Towards the Synthesis of Twistacenes, Oligoacenes, Polydibenzophoshole and Pentiptycene Rotor Derivatives

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Synthetic Strategies Towards the Synthesis of Twistacenes, Oligoacenes, Polydibenzophoshole and Pentiptycene Rotor Derivatives

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Chemistry

by

Miguel Angel Jimenez

2013

ABSTRACT OF THE DISSERTATION

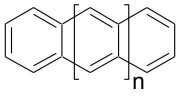
Synthetic Strategies Towards the Synthesis of
Twistacenes, Oligoacenes, Polydibenzophoshole
and Pentiptycene Rotor Derivatives

by

Miguel Angel Jimenez
Doctor of Philosophy in Chemistry
University of California, Los Angeles, 2013
Professor Fred Wudl, Co-Chair
Professor Miguel Garcia-Garibay, Co-Chair

Polycyclic aromatic hydrocarbons (PAHs) are a group of widely studied organic molecules due to their interesting electronic properties. Polyacene (**1**), has produced the most interest from this group, both because of the synthetic challenges it poses as well as its prediction to be highly conductive. Thus far a number of oligoacene precursors have been reported in the literature, but to date no system where n is greater than six (e.g. nonacene) has been reported. We have undertaken the synthetic challenge to synthesize heptacene as well as other extended oligoacenes, including polyacene. Additionally, we

have synthesized tetrabenzoheptacene (**2**), a twisted acene, which despite its twisted nature is quite stable and displays intereresting electronic properties.



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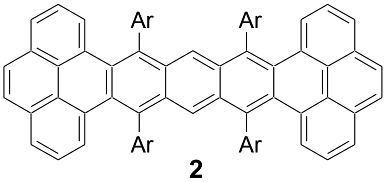

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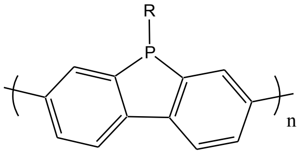
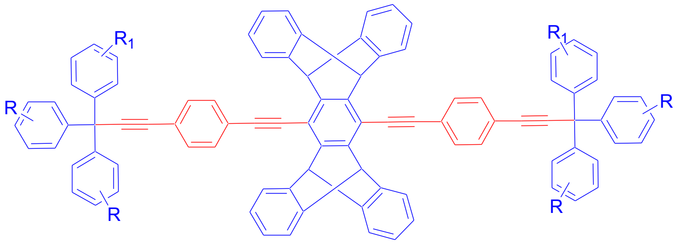
The development of full color red-green-blue (RGB) displays has been hindered by the lack of stable blue polymer light emitting diodes (PLEDs). We propose the synthesis of poly(dibenzophosphole) (**3**) as a potential candidate for a blue PLED.



3

Organic compounds possessing aromatic groups that are linearly conjugated through acetylene linkages have also received much attention. The cylindrical symmetry of the alkyne group maintains conjugation with the adjacent phenyl groups and results in low energy barriers in the ground state. However, rotation in the excited state displays a large energy difference as a function of the angle between the aromatic groups. The twisting and planarization of these aryl-alkynyl conjugated systems ultimately results in changes in both color and emission properties. We have synthesized several *p*-phenylene-ethynylene pentiptycene rotor derivatives (**4**) to probe the effects of chromophore rotation in the ground state and in the excited state both in solution and in the solid state. By incorporating pentipycene into the rotor it provides a protecting stator and a fixed central phenylene ring. The flanking ethynylphenylene rotators allow for free rotation to study the electronic properties as a function of angle. The crystal structure shows that pentiptycene rotor **4** (R=H, R_1 = OMe) packs in a way that the conjugated backbone of these rotors is aligned in a parallel manner, which is desirable for the development of novel functional materials.



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The dissertation of Miguel Angel Jimenez is approved.

Yang Yang

Fred Wudl, Committee Co-Chair

Miguel Garcia-Garibay, Committee Co-Chair

University of California, Los Angeles

2013

Esta obra es dedicada a mi Mama, Papa y a mi familia

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PUBLICATIONS AND PRESENTATIONS

Jimenez, Miguel A.; Duong, Hieu; and Wudl, Fred. **Synthesis of a Twistacene, A Building Block for Polyacenes.** Book of Abstracts, Society for Advancement of Chicanos and Native American Society for Native Americans in Science (SACNAS) National Conference, Austin, Texas, October 21-24 (2004).

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Hughs, Melissa; Jimenez, Miguel, Khan, Saeed, Garcia-Garibay, Miguel A. **Synthesis, Rotational Dynamics, and Photophysical Characterization of a Crystalline Linearly Conjugated Phenyleneethynylene Molecular Dirotor.** *J. Org. Chem.* **2013**, 78, 5293-5302.

CHAPTER 1

Twistacenes

1.1 Introduction

The initial interest for pyrene based-polycyclic aromatic hydrocarbons (PAHs) came from investigations in "Molecular Board" conducting ladder polymers. Pyrene-based ladder polymers and oligomers were proven to be conductive by Schluter and coworkers.[1] However, in contrast to other systems our synthetic target would consist of only 6-membered rings. We believed that this design feature would make our target molecule more conductive since the bond angle in 5-membered rings restricts maximum electron delocalization throughout the backbone.[2]

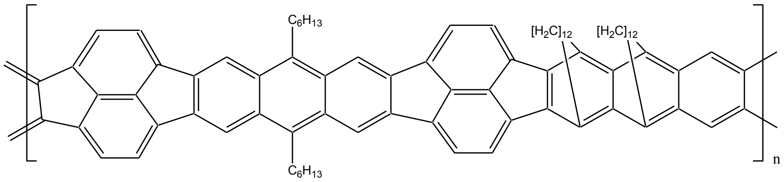
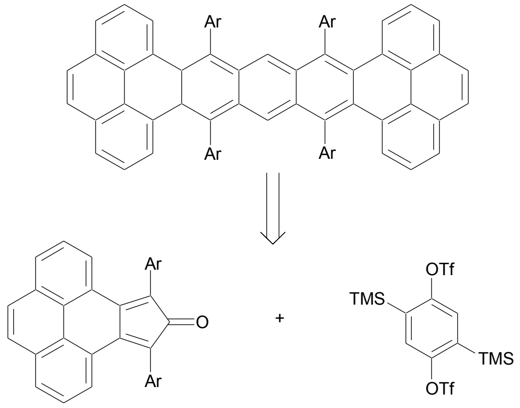


Figure 1.1 *Schluter's ladder polymer*

While the synthesis of a pyrene-based ladder polymer was never achieved by our group; we were able to synthesize a pyrene based acene derivative, tetrabenzoheptacene.[3] Our synthetic strategy involved the synthesis of cyclopentadienone and then utilizing benzyne trapping chemistry to build the molecule (Scheme 1.1). The synthesis and characterization of this acene molecule is described herein.



Scheme 1.1 *Retrosynthetic analysis of tetrabenzoheptacene*

1.2 Twisted Acene Systems

Generally when chemists think of “acenes” it brings to mind planar and rigid molecules. However, this is not always true of all acenes as the energy required to bend or twist most PAHs is actually quite modest, and a careful inspection of the crystal structures of most acenes and their derivatives show some deviation from planarity. The degree of “twisting” in acenes can be measured by comparing the torsion angles ABCD and BACD for the representative acene in question as shown in Figure 1.2.

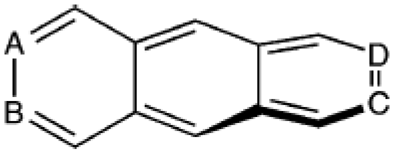
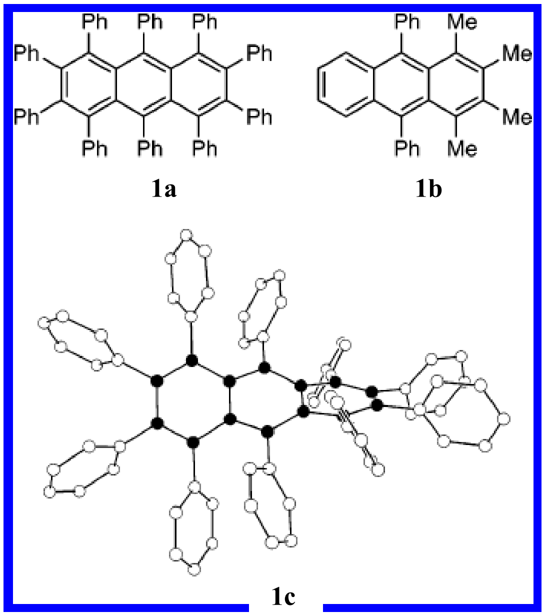


Figure 1.2 *A twisted acene*

Twisted PAHs are topologically interesting molecules which have been studied in detail, mostly by Pascal,[4] who has designed, synthesized and characterized several of these twisted molecules. Conceptually, the simplest way to deform an acene is to attach several bulky substituents to its periphery by single bonds. The resulting molecules will typically undergo some degree of twisting as a result of it being more energetically favorable to twist torsion angles (even in PAHs) than to distort bond angles or to compress or stretch C-C bonds. In the absence of benzannulation (which will be considered later), it is not uncommon for highly substituted acenes to retain most of the characteristic chemical or spectroscopic properties of the untwisted parent, although perturbed to varying degrees by the structural deformation and steric crowding.

When phenyl substituents were introduced to an anthracene core, the resulting sterically congested product, decaphenylanthracene **1a**, underwent a 63° end-to-end twist.[5] The crystal structure shown in Figure 1.3 shows this highly contorted molecule. The next most twisted "simple" anthracene compound is **1b**, which is less heavily substituted than **1a** yet still displays a modest 28° twist.[6] Despite its great distortion from planarity, decaphenylanthracene in many ways retains the characteristic properties of a "normal" anthracene. Its carbon NMR resonances are located in the aromatic region, its UV absorption while shifted 60 nm to the red of anthracene itself, it retains the characteristic vibrational fingerprint typical of anthracenes.[7] The anthracene core of compound **1a** is well protected by the surrounding phenyl rings leading to great stability despite the twisting. Decaphenylanthracene displays reversible electrochemistry and a very stable electrogenerated chemiluminescence.[8]



1a **1b**

1c

Figure 1.3 *Twisted anthracene molecules*

Another common strategy employed to induce twisting is to fuse benzo groups to the acene core. A number of benzannulated anthracene, tetracene, pentacene, hexacene and heptacene derivatives have been reported in the literature. [9] Tetrabenzotetracene (**1.0**) shown in Figure **1.4** is an example of this second group of twisted acenes displaying a 34° twist.[10] Because the benzo groups are intimately united with the acene cores many of these benzannulated derivatives display distinct electronic properties than the parent compound tetracene.

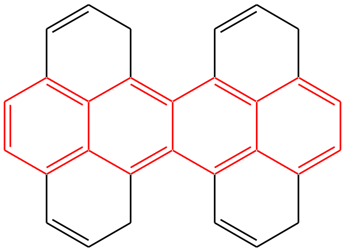


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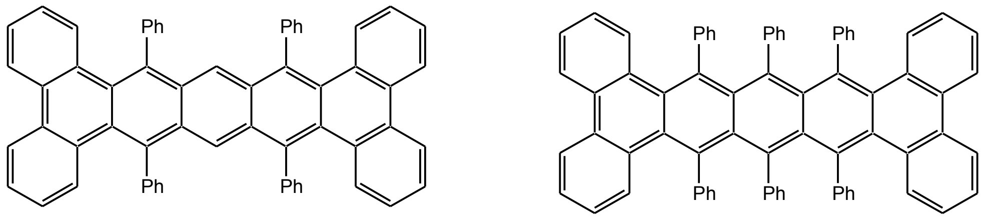
Figure 1.4 *A benzannulated tetracene derivative*

The greatest distortions of acene substructures are observed in molecules that possess some benzannulation in conjunction with bulky substituents. The first acene to possess and end to end twist of more than 90° was achieved using these two distorting features. Octaphenyl[*a,c*] napthacene, a tetracene derivative synthesized by the Pascal group displayed a twist of 105°.[11]

Interestingly, the incorporation of these two distorting agents can sometimes lead to some unexpected results. A case in point is the following two pentacene molecules. Pentacene **1c**, while not truly planar exhibits a net twist of 0°, which is contradictory to the 90° twist value predicted by their computational calculations.[12] Furthermore, since the molecule lacked steric protection on the central ring, it was highly sensitive to photooxidation in solution forming the endoperoxide quite readily. Two years later, a similar pentacene derivative **1d** was synthesized with increased steric hindrance around the central ring through the incorporation of phenyl groups. This resulted in a much more stable compound with a greater degree of twisting.[13] This pentacene derivative formed ruby red crystals and was reported to have a 144° end-to-end twist. The pitch of the helical core is almost 30° per ring, **1d** contains the most highly twisted naphthalene (60°), anthracene (86°) tetracene (116°) and pentacene substructures known. It is completely stable in the dark or in the solid state, but it decomposes in bright room light in solution with a half life of 36 hours.



1c **1d**

Figure 1.5 *Twisted pentacene derivatives*

In our own synthesis, we believed that we could utilize the structural rigidity present in these twisted systems to serve as a protective motif in our synthesis of stable acenes. By strategically placing the aryl substituents nearly perpendicular to the acene plane we believed they would effectively limit or prevent the dimerization observed with the larger oligoacenes such as heptacene, ultimately leading to a stable molecule that could be fully characterized in the solid state. Additionally, by incorporating terminal pyrene units we believed this would introduce a twist topology by its large sterics as well as providing additional stabilization to the conjugated system. Equally importantly, the electronic properties of the twisted molecule should be retained even under moderate twisting. By exploiting twisted acenes we believed we could synthesize acene analogs as potential surrogates for studying oligoacenes.

1.3 Benzyne and Bisbenzyne Systems

There have been a considerable number of different methods for producing benzyne **1.1** which have been reported in the literature.[14] The two most common methods for releasing benzyne are by thermally controlled release or chemically controlled release. Thermally controlled systems typically operate intermolecularly and involve the extrusion of inert gases or other stable by-products. The classic example of this type of system is the diazonium carboxylate system which extrudes nitrogen and carbon dioxide while producing benzyne.[15] Chemically initiated benzynes on the other hand offer more diverse triggering mechanisms for the formation of benzyne. In relatively harsh conditions, deprotonation of bromobenzene using a strong base such as lithium amide yields the benzyne.[16] By switching functional groups milder conditions can be employed to create other benzyne derivatives. Under oxidative conditions benzotriazole has been shown to work quite well with various dienes.[17] Kobayashi's benzyne derivative exploits the high affinity of fluoride ion for silicon to release the benzyne.[18]

While the number of benzyne precursors available in the literature is plentiful, the chemistry of 1,4-benzadiyenes (bisbenzyne) has not been studied to the same extent. Those that are reported in the literature are not always ideal. The oxidative benzyne precursor 1-aminobenzotriazole was modified by Hart et. al. to bistrizaole (**1.2**) in a lengthy seven step synthesis from 1,3 dichlorobenezene.[19] On the other hand there is p-dibromobenezene (**1.3**), which is a commercially available bisbenzyne precursor. However, the biggest drawback in **1.3** is the strong base that is required to reveals its benzadiyne.

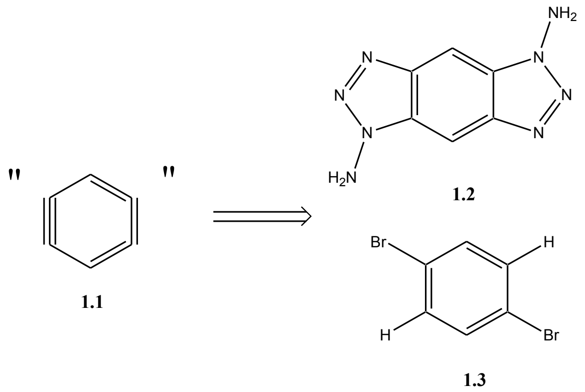
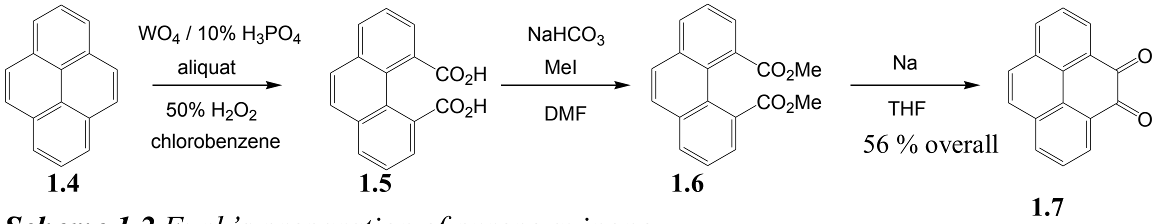


Figure 1.6 *Two examples of bisbenzyne precursors*

Bisbenzynes are of special interest, especially when it comes to assembling extended acenes. Their bi-directionality combined with high reactivity could with the right diene form large polycycles quite efficiently. Searching for a milder bisbenzyne our group developed a Kobayashi type bisbenzyne derivative.[20] The synthesis of this bisbenzyne derivative is explained in detail in the following pages.

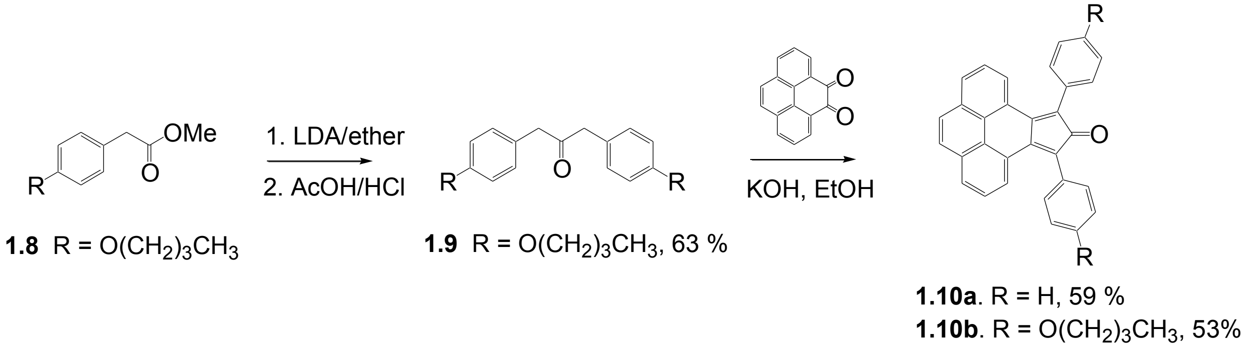
1.4 Synthesis of Cyclopentadienone

The synthesis of the pyrene quinone was achieved using a procedure developed by Funk *et al.* (Scheme 1.2). [21] This procedure was successfully repeated in our own group. In this procedure pyrene is oxidized to the dicarboxylic acid using hydrogen peroxide and tungstic acid to give the desired product in nearly quantitative yield. Esterification of the diacid to the diester was accomplished using sodium bicarbonate and methyl iodide. Lastly, acyloin condensation of the diester with sodium metal afforded the pyrene quinone after flash chromatography in a 56 % overall yield. As described in the paper this synthetic route could be run in large scale synthesis to give multigram quantities of the pyrene quinone.



Scheme 1.2 *Funk's preparation of pyrene quinone*

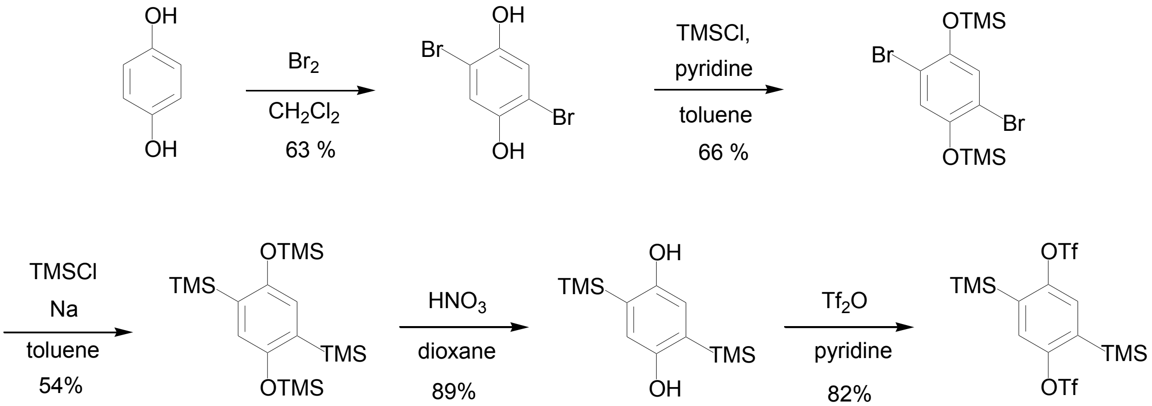
The preparation of cyclopentadienone **1.10a** involved the condensation of the pyrene quinone **1.7** by treating the it with ethanolic potassium hydroxide and commercially available 1,3-diphenyl acetone.[22] This seemingly straightforward procedure is quite temperamental. The addition of ethanolic potassium hydroxide solution needs to be added in a dropwise manner and at room temperature. The solution is then heated at reflux for a few minutes, cooled and filtered to cleanly afford the desired product in moderate 59 % yield. If there was any substantial deviation from this procedure no significant yield of product was recovered. A more soluble cyclopentadienone **1.10b** derivative was also prepared.



Scheme 1.3 *Preparation of cyclopentadienone derivatives*

1.5 Synthesis of Bisbenzyne

The bisbenzyne derivative, **1.13**, was synthesized in five steps starting from hydroquinone. Bromination of the hydroquinone gave the alcohol. Protection of the alcohol by treating it with trimethylsilyl chloride afforded the protected silyl ether. Deprotection of the trimethylsilyl ether with nitric acid followed by the addition of triflic anhydride afforded the bisbenzyne derivative.

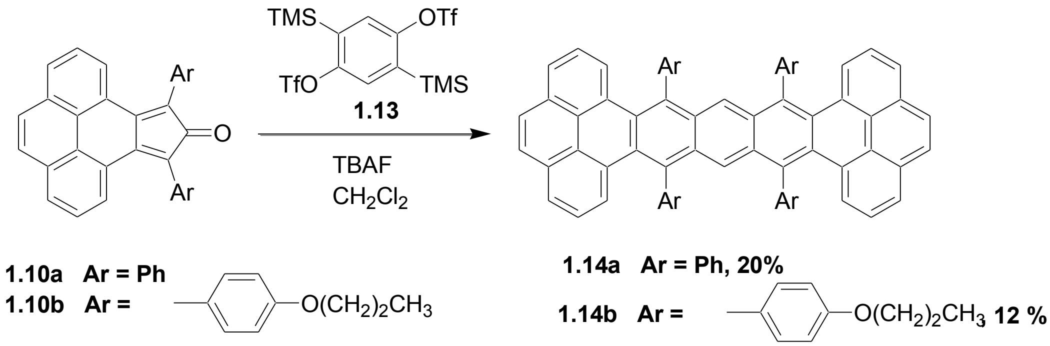


1.13

***Scheme 1.4** Synthesis of bisbenzyne*

1.6 Synthesis of Tetrabenzoheptacene

With the 2 key building blocks in hand, the synthesis of tetrabenzoheptacene was achieved by treating solution of bisbenzyne (**1.13**) and cyclopentadienone (**1.10a**) with TBAF to unmask the bisbenzyne, which subsequently undergoes a Diels Alder addition with two equivalents of cyclopentadienone . Heating the solution induces extrudes the carbon monoxide bridges to give tetrabenzoheptacene in 20 % yield. The resulting product was a bright orange solid which displayed low solubility in organic solvents.



1.10a Ar = Ph
1.10b Ar = —C_6H_4—$O(CH_2)_2CH_3$

1.14a Ar = Ph, 20%
1.14b Ar = —C_6H_4—$O(CH_2)_2CH_3$ **12 %**

Scheme 1.5 *Synthesis of a tetrabenzoheptacene derivative*

The low solubility of **1.14a** prompted us to prepare a tetrabenzoheptacene derivative with butyloxy sidechains. Tetrabenzoheptacene derivative **1.14b** was prepared by a similar fashion as described for **1.14a**. The only difference was in the synthesis of para-butyloxy cycloentadienone derivative **1.10b**, in which the 1,4 diarylacetone derivative was synthesized from an alkoxylated precursor **1.9** (Scheme 1.3). Methyl 4-methoxyphenylacetate is commercially available and the butyloxy derivative **1.8** was readily synthesized by the alkylation of commercially available methyl 4-hydroxyphenylacetate. The butyloxy substituted tetrabenzoheptacene derivative **1.14b** was indeed more soluble than the parent compound and as a result made it more difficult to isolate the product as it doesn't precipitate out of solution as readily as the parent therefore resulting in a lower yield, 12 %.

1.7 Properties of Tetrabenzoheptacene Compounds

The physical and electronic properties of both tetrabenzoheptacene derivatives were explored in more detail. **1.14b,** which contains the butyloxy groups, was found to be much more soluble than **1.14a** displaying solubility in nonpolar aryl solvent like toluene, benzene and ODCB. Whereas, the unsubstituted **1.14a** displayed slight solubility in these solvents. The X-ray structure of **1.14a** shows a twisted topology in which the terminal pyrene groups are coplanar while the central anthracene is twisted out of the plane.[23] The twist conformation is more dramatic than that reported for the parent **1.14c**. A comparison to the parent compound reveals longer C-C bonds and a more pronounced twisting about the C1-C2-C3-C4 and C14-C15-C17-C18. The more pronounced twist can be attributed to the increased amount of steric hindrance due to the phenyl substituents (at C1) and hydrogen atoms (at C4). Since the phenyl substituents are larger than hydrogen substituents the twist is more pronounced in **1.14a** than in the parent compound. A crystal structure of **1.14b** was not produced although we believe it to be similar to that of **1.14a** as most other experimental data correlated strongly with **1.14a.**

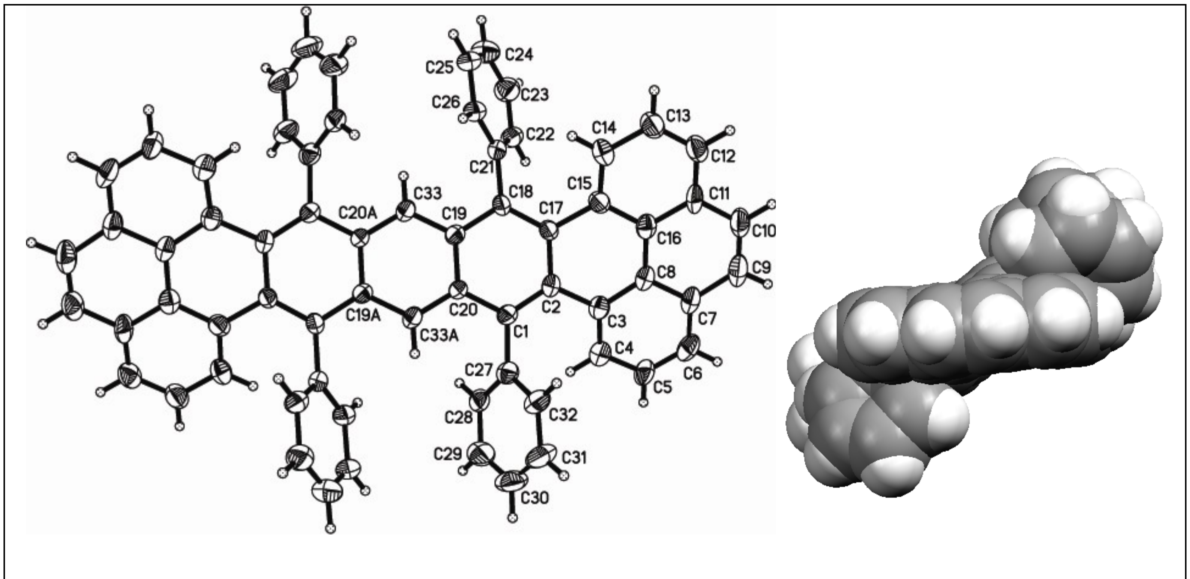


***Figure 1.**7 X-ray structure of **1.14a**: (left) Ortep, (right) spacing filling representation viewed from the longitudinal axis of the pyrenes*

The absorption spectra spectrum of both tetrabenzoheptacene compounds (**1.14a, 1.14b**) was measured. Figure **1.9** shows the absorption spectrum of both in toluene. Both tetrabenzoheptacene derivatives displayed nearly identical spectra. The aryl substituted tetrabenzoheptacene derivative **1.14b** was only slightly red shifted in comparison to **1.14a**. This indicates that the alkoxy sidechains have essentially little to no effect on the electronic structure of the acene backbone. The resonance contribution of the oxygen seems to cancels out its electron withdrawing effect, thus the overall perturbation is negligible.

The absorption spectra for both derivatives displayed a λ_{max} at around 530 nm. (528 nm for **1.14a**, 535 nm for **1.14b**) The absorption spectra is red shifted by 24 nm with respect to the parent compound, **1.14c** (λ_{max} = 506 nm). This red shift in the spectrum can either be attributed to the increased twist in both **1.14a** and **1.14b** or to the substituted aryl group. The λ_{max} falls between that of tetracene (475 nm) and pentacene (582 nm) and is considerably much longer wavelength than anthracene, the longest, non-crossconjugated moiety present in **1.14a** and **1.14b.**

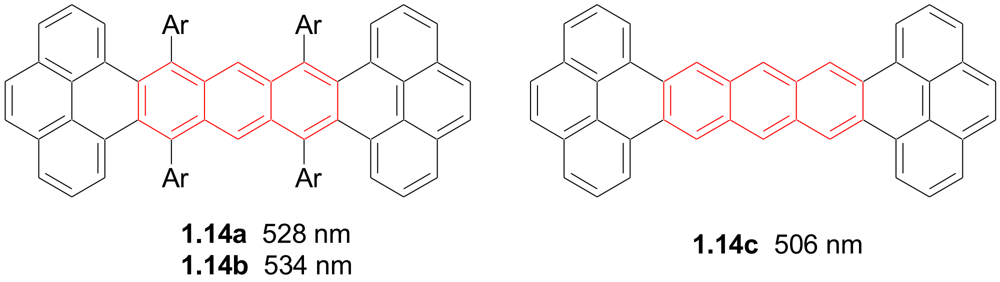


Figure 1.8** Tetraphenylbenzoheptacene derivatives **1.14a, 1.14b** and its parent **1.14c

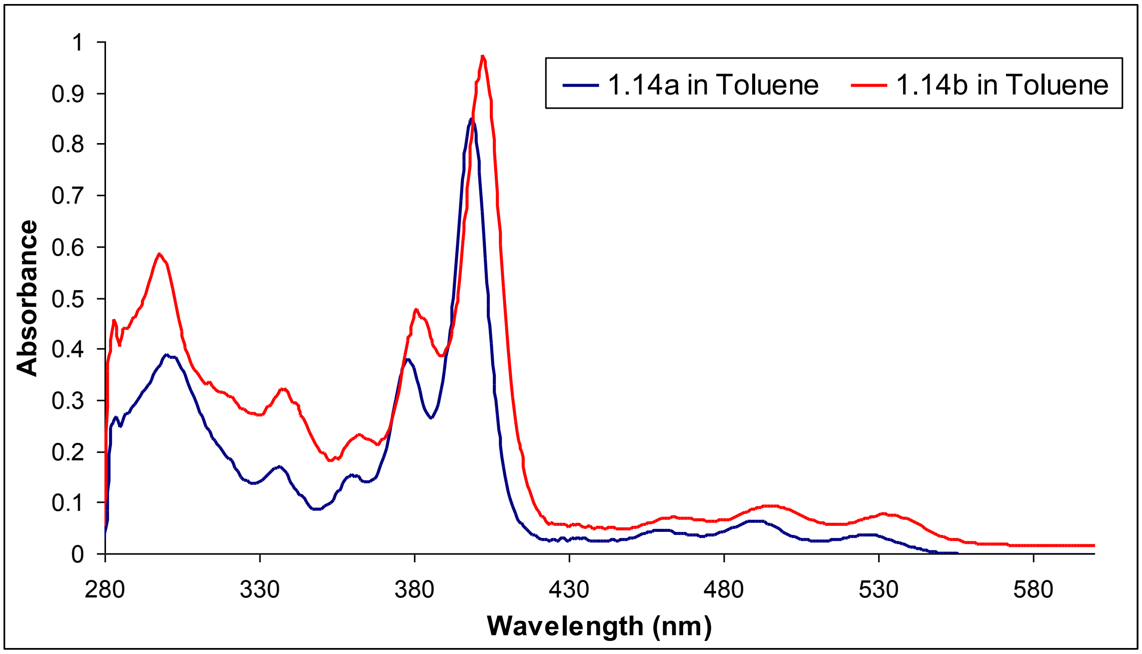


Figure 1.9** UV-Vis spectrum of tetrabenzoheptacene derivatives**1.14a**, **1.14b

From the UV-Vis data we can infer a HOMO-LUMO value of around 2.3 eV, which was further corroborated using cyclic voltametry. From cyclic voltametry the HOMO-LUMO gap of **1.14a** was determined to be 2.5 eV.[24] The experimental results placed the HOMO-LUMO gap of **1.14a** right in between tetracene (exp. 2.6 eV) and pentacene (exp. 2.1 eV). The electronic spectrum indicates that there are several advantages gained from the twisting of **1.14a** and **1.14b**. By attaching fusing pyrene units on the ends of an anthracene molecule it leads to a narrowing of the $\Delta E_{\text{HOMO-LUMO}}$ of the central acene π-system by approximately 130 nm, or by about 65 nm per pyrene unit. This is calculated using anthracene (375 nm), 1.14,4.5-dibenzopentacene (442 nm), and tetrabenzoheptacene **1.14c** (506) nm.[24] Additionally, the aryl substituents protect the central anthracene portion from degradation. This is evident by the fact that **5.9** showed no sign of decomposition after two years of storage in ambient laboratory conditions.

When **1.14a** was subjected to thermogravimetric analysis (under N_2) it displayed remarkable thermal stability. No weight loss was observed until the temperature exceed 410^o C. Additionally, Differential scanning calorimetry revealed no sign of decomposition or melting up to 400 °C.

The tetrabenzoheptacene molecules are highly conjugated and display unusual stability which makes them ideal candidates OLED devices. When **1.14a** was doped onto polyfluorene a bright, efficient and white light emitting diode was produced.[25]

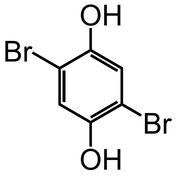
1.8 Conclusion

The synthesis of two tetrabenzoheptacene derivatives was achieved using a bisbenzyne strategy. The tetrabenzoheptacene derivatives were found to be quite stable and soluble in several organic solvents. The crystal structure shows some degree of twisting and distortion from planarity, but it doesn't seem to have a significant effect on the electronic properties. The electronic properties and stability bode well for electronic applications such as OLED devices.

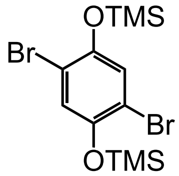
1.9 Experimental Results

Materials. Solvents and reagents were purchased from either Aldrich, Fisher or VWR. THF was distilled over sodium/benzophenone under nitrogen. Pyridine, toluene and methylene chloride were distilled from calcium hydride under nitrogen. 1,2-Dichloro ethane and ODCB were used as received. All experiments were carried out under argon or nitrogen unless specified. Other solvents and reagents were used as received.

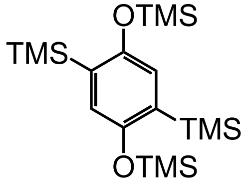
Measurements. Solution NMR spectra were taken on either a Avance 500, Bruker ARX 400, 500 or 600 spectrometers as noted. All chemical shifts (δ) are reported relative to tetramethylsilane (TMS) at 0.0 ppm. FT-IR spectra were recorded on a Mattson Infinity IIa spectrometer with a DRIFT accessory from PIKE Technologies, on a diamond frit. UV-Visible spectra were obtained with a Hewlett Packard 8453 spectrophotometer. EI-MS were taken using a VG Autospec EI/CI Magnetic Sector spectrometer.



2,5 -Dibromohydroquinone – Bromine (34 g, 0.21 mol) was added dropwise to a stirred suspension of hydroquinone (11.01 g, 0.100 mol) in dichloromethane (80 mL) at room temperature. As additional bromine was added the mixture became more and more viscous so additional dichloromethane was added. After a total time of 19 h, the suspension was filtered off. The white solid was washed with dichloromethane until the filtrate was almost colorless. The resulting white solid (18.53 g, 63 %) turned out to contain some minor unreacted hydroquinone impurities which were difficult to remove so the product was carried on to the next step with these impurities present. ^{1}H NMR (DMSO-$d_{6,}$ 500 MHz) δ 9.80 (2H, s, OH), 7.00 (2H, s, Ar); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 147.6, 119.7, 108.5 ppm.

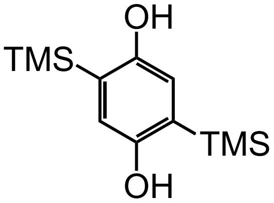


2,5-Dibromo-1,4-bis(trimethylsilyloxy) benzene – To a boiling solution of the 2,5-Dibromohydroquinone (19.3 g, 72 mmol) toluene (290 mL) was added a suspension of trimethylsilyl chloride (57.6 g, 0.53 mol) in pyridine (35 mL) over a 1 h period. The suspension was stirred at reflux for an additional 18 h. Then, the yellow suspension was cooled down to RT and filtered. After concentration of the product it was recrystallized from hexanes to afford colorless needles (20.9 g, 66%). ^{1}H NMR (CDCl$_{3,}$ 500 MHz) δ 7.08 (2H, s, Ar), 0.32 (18H, s, TMS); ^{13}C NMR (CDCl$_{3,}$ 125-MHz) δ 147.2, 124.0, 113.8, 0.1 ppm

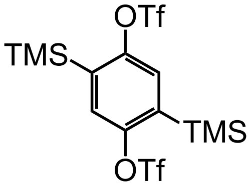


2,5-bis(trimethylsilyl)-1,4-bis(trimethylsilyloxy)benzene –To a suspension of 2,5-Dibromo-1,4-bis(trimethylsilyloxy) benzene (15.46 g, 37.5 mmol) and sodium (3.9 g, 0.17 mol) in toluene (130 mL) at 110^{0} C was added a solution of trimethylsilyl chloride

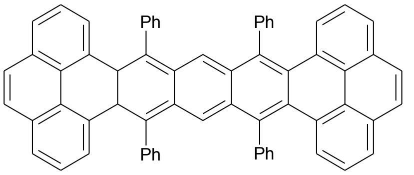
(8.663 g, 79.94 mmol) in toluene (20 mL) during a period of 35 minutes. The mixture turned a gray-bluish color. After the addition was finished, the mixture was refluxed for 18 h. The blue suspension was cooled down to RT and filtered under argon. The filtrate was evaporated and the resulting white solid was dried under vacuum. Recrystallization from methanol afforded white crystals (8.14 g, 54 %). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 6.76 (2H, s, Ar), 0.30 (18H, s, OTMS), 0.24 (18H, s, TMS); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 153.9, 131.6, 122.5, 0.7, -1.0 ppm



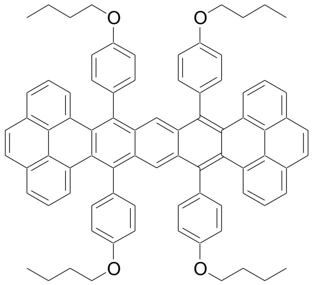
2,5-bis(trimethylsilyl)hydroquinone – To a colorless solution of 2,5-bis(trimethylsilyl)-1,4-bis(trimethylsilyloxy)benzene (6.525 g, 16.16 mmol) in dioxane (250 mL) was added dropwise at RT a 6M HNO$_3$ solution (16 mL). The solution was stirred at RT for 1h. Water (500 mL) was added and the resulting suspension was extracted with chloroform (3 x 700 mL). The combined organic layers were dried with Na$_2$SO$_4$ and concentrated in vacuum to yield a white solid, which was recrystallized form hexanes to yield the desired product (3.66 g, 89 %). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 6.69 (2H, s), 4.46 (2H, s, OH), 0.29 (18H, s, TMS); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 153.9, 128.0, 120.7, -1.1 ppm



2,5-bis(trimethylsilyl)-1,4-phenylenebis(trifluoromethanesulfonate)– To a solution of 2,5-bis(trimethylsilyl)hydroquinone (6.725 g, 26.42 mmol) in pyridine (120 mL) at 10^{o} C was added dropwise triflic anhydride (9.94 g, 35.23 mmol). After the addition was finished, the mixture was slowly warmed to RT and stirred overnight. After 16 h, the dark-red suspension was heated to 40^{0} C and stirred at this temperature for 3 h. The reaction was cooled to RT and the solvent was removed in vacuum. The resulting greasy, brown residue was intensively extracted with boiling hexanes. The solvent was evaporated and the resulting solid was recrystallized from hexanes to afford the desired product (6.44 g, 82 %). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.45 (2H, s, Ar), 0.38 (9H, s, TMS), 0.29 (6H, s, TMS); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.1, 137.4, 126.9, -1.2 ppm; EI-MS exact mass 518.01, calcd mass 518.01.



6,8,15,17-Tetraphenyl-1.18,4.5,9.10,13.14-tetrabenzoheptacene– To a solution of cyclopentadienone **1.10a** (500 mg, 1.23 mmol) and bisbenzyne **1.13** (314 mg. 0.61 mmol) in 50 mL CH_2Cl_2 was added TBAF (1.23 mL 1M THF solution, 1.23 mmol) dropwise. The solution was stirred at room temperature for 48 hours followed by reflux for 24 hours to give an orange solid collected by vacuum filtration. Successive washes using THF followed by centrifugations gave tetrabenzoheptacene **1.14a** (99 mg, 20%) as an orange solid; ^{1}H NMR (ODCB-d_4, T=400K, 500 MHz) δ 8.56 (s, 2H), 7.98 (d, 4H, J=7.93Hz), 7.71 (s, 4H), 7.68 (d, 4H, J=7.93Hz), 7.33-7.41 (m, 20H), 7.24 (t, 4H, J=7.93Hz); MALDI-TOF MS found 830.2940, calcd 830.2974; IR (DRIFT) 3050, 1947, 1808, 1599, 1491, 1443, 1384, 1308, 1075, 957, 905, 860, 770, 730, 539 cm^{-1}; UV-Vis (toluene) λ_{max} 301, 337, 379, 399, 460, 491, 528 nm; TLC using 1:1 hexanes:methylene chloride R_f 0.6 as a single yellow florescent spot.



6,8,15,17-Tetra-(4-butyloxy)phenyl-1.18,4.5,9.10,13.14-tetrabenzoheptacene – Butyloxytetrabenzoheptacene **1.14b** was prepared in the same manner as described for **1.14a**. ^{1}H NMR (ODCB-d_4, 500 MHz) δ 8.52 (s, 2H), 7.97 (d, 4H, J=7.92Hz), 7.68 (s, 4H), 7.66 (d, 4H, J=7.92 Hz), 7.30-7.41 (m, 20H), 7.25 (t, 4H, J=7.93Hz), 4.05 (t, 4H), 1.84 (m, 4H), 1.51 (m, 4H), 1.40 (t, 6H); MALDI-TOF MS found 1118.53, calcd 1118.53; IR (DRIFT) 3050, 1947, 1808, 1599, 1491, 1443, 1384, 1308, 1075, 957, 905, 860, 770, 730, 539 cm^{-1}; UV-Vis (toluene) λ_{max} 298, 339, 381, 402, 460, 497, 534 nm

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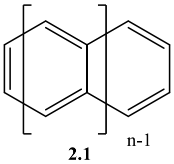
CHAPTER 2

Synthetic Strategies Towards the Synthesis of Oligoacenes

2.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are currently among the most widely studied group of organic π-functional materials.[1, 2] Of particular interest to our research group are linear polyacenes **2.1**. Linear polyacenes (or acenes), are linearly fused benzenoid hydrocarbons. Acenes have generated a significant amount of interest within the scientific community due to their importance as organic semiconducting materials. Applications of oligoacenes vary, but for the most part they are commonly used as organic field effect transistors (OFETs). Currently pentacene (n = 5) is the most widely studied organic semiconductor in OFETs and is widely regarded as the bench mark for other organic conductors.[3] Field effect mobility of thin film transistors (TFT) devices based on pentacene have improved to reach that of hydrogenated amorphous silicon (0.5 $cm^2/V\cdot s$) and supercede it by up to 3 $cm^2/V\cdot s$.[4] Most of this improvement is due to improvements in device fabrication and improved engineering techniques.[5] Therefore, in order to continue to improve the performance of organic electronics, the advent of novel materials needs to be realized. An effective and appropriate solution would be to synthesize longer acenes.

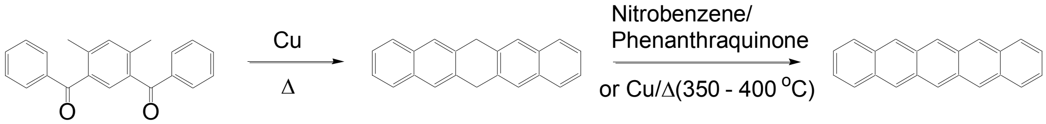


2.1

Oligoacenes are aromatic molecules.[6,7,8] Benzene, the smallest member of this group, was discovered in 1825 and is the most stable compound in the polyacene family.[9] However, as n increases the degree of aromaticity decreases, and therefore stability of oligoacenes, decreases drastically.[1] The lower homologues of the acene family from benzene to anthracene (n = 3) are readily available and can be extracted from coal, while higher homologues such as pentacene (n = 5), hexacene (n= 6), heptacene (n= 7), octacene (n = 8) and nonacene (n = 9) are only attainable via multistep synthesis. It is believed that longer acenes (n > 5), which are more conjugated than pentacene will exhibit more favorable electronic properties. However, as acenes are extended linearly they become synthetically challenging to make as they are plagued by facile photooxidation, insolubility, dimerization and polymerization.[10] Consequentially, there are only a few successful syntheses of these higher analogs (beyond pentacene) reported in the literature.[11]

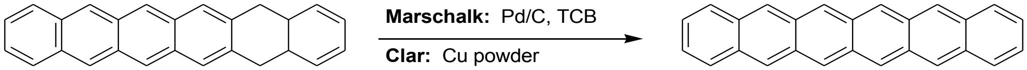
2.2 Oligoacenes Reported in the Literature

In the past few years much progress has been made in the synthesis and characterization of longer acenes since the discovery of benzene. As of 2004,[12] pentacene was the longest member of the acene family which could be readily prepared and stored in the absence of light and oxygen. Pentacene was first synthesized by Clar and John from 4,6-dibenzoyl-1,3-dimethylbenzene, as is shown below (Scheme 2.1).[13] Dehydrogenation to pentacene was achieved by boiling dihydropentacene in nitrobenzene with phenanthraquinone or by passing it through copper at high temperature.



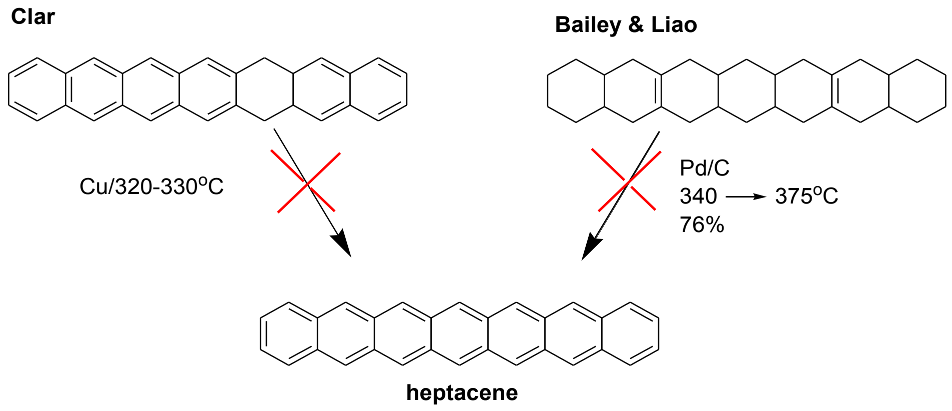
Scheme 2.1 *Synthesis of pentacene*

The first reported synthesis of hexacene was achieved individually by both Marschalk[14] and Clar in 1939.[15] Both synthetic pathways used a metal-catalyzed dehydrogenation step. Marschalk heated dihydrohexacene in trichlorobenzene while in the presence of palladium, while Clar sublimed hexacene directly from the precursor using copper powder (Scheme 2.2). Since the initial synthesis of hexacene by Clar and Marschalk, other syntheses of hexacene have been reported.[16]



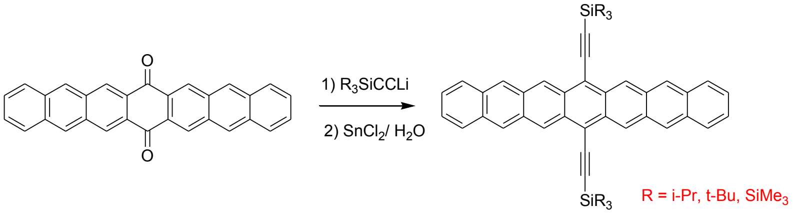
Scheme 2.2 *Synthesis of hexacene*

The synthesis of heptacene has also been reported, although it remained highly controversial until recently (Scheme 2.3). The first reported synthesis of heptacene came from Clar in 1942.[17,18] In that paper, Clar reportedly prepared heptacene by heating dihydroheptacene at 320-330°C in the presence of copper. Clar reported obtaining a greenish-black solid that decomposed at about 400°C. Clar's evidence for heptacene was substantiated by elemental analysis and UV-Vis spectroscopy. The second reported synthesis of heptacene was from Bailey and Liao in 1955.[19] In that paper Bailey and Liao heated a mixture of precursor and Pd/C at 375°C. Purification in both instances was achieved by sublimation.



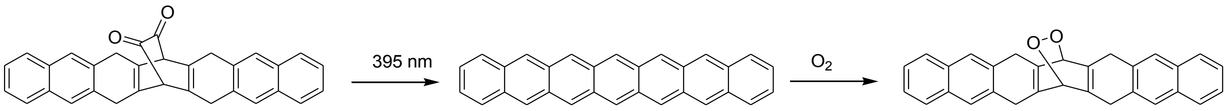
Scheme 2.3 *Reported synthesis of heptacene*

Marschalk, who was heavily involved in syntheses of large polyacenes, attempted to repeat Clar's work, but was unsuccessful in obtaining heptacene.[20] He noted that treating a pure sample of dihydroheptacene under the same conditions described by Clar failed to give heptacene. Other approaches with dihydroheptacene derivatives were also attempted, but none successfully produced heptacene. Additionally, when the entire synthesis was repeated using the exact method described by Clar, a "green solid" was observed. Marschalk concluded that the heptacene produced in Clar's experiment was not derived from dihydroheptacene, but rather from some impurity that was carried over from previous reactions. A few years later, Clar withdrew his claim of having produced heptacene.[21] The literature on heptacene remained highly controversial, although the general consensus is that heptacene has not been isolated in the pure state until recently. In 2005, Anthony successfully synthesized a group of heptacene derivatives (R = iPr, t-Bu, $SiMe_3$) from 7,16-heptacenequinone (Scheme 2.4).[11] Structural proof of heptacene was achieved through a crystal structure of heptacene (R = tris(trimethylsilyl)silyl). This heptacene compound's crystals were relatively stable when exposed to air and light, remaining unchanged for up to a week. This heptacene derivative was quite soluble in several solvents with a reported λ_{max} of 852 nm (in CH_2Cl_2).



Scheme 2.4 *Anthony's synthesis of heptacene*

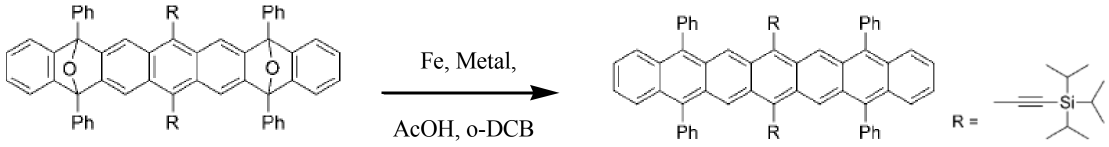
A year later (2006), the Neckers group reported the photogeneration of unsubstituted heptacene by photodecarbonylation of the dione precursor in a poly(methyl methacrylate) (PMMA) matrix (Scheme 2.5).[22] When irradiated with UV light an absorption band stretching from 600 to 825 nm with a λ_{max} centered at ~760 nm appears. Subsequent analysis by MALDI confirmed the formation of heptacene which is actually significantly blue shifted in comparison to Anthony's heptacene (λ_{max} = 810 nm). The unsubstituted heptacene was short lived surviving only 4 h in the PMMA matrix, thus confirming the high reactivity of this compound. Irradiation of the dione in solution failed to give heptacene. Irradiation of the dione in oxygenated toluene gave the endoperoxide presumably through a Diels-Alder reaction between O_2 and heptacene. The formation of thes oxygenated adducts was characterized by both MALDI and ^{1}H NMR.



Scheme 2.5 *Necker's synthesis of heptacene (in PMMA)*

The great contrast in stability between Anthony's substituted heptacene and unsubsituted heptacene illustrates the fact that stable heptacene derivatives can indeed be produced, but only if the acene core is protected by sterically hindering groups.

Since the first initial reported synthesis of heptacene by Anthony's group other research groups have successfully synthesized heptacene derivatives. Shortly afterwards, the Wudl group synthesized a highly stable heptacene compound. (Scheme 2.6) [23] This compound was found to be stable for over 21 days when coated with mineral oil and exposed to the atmosphere and light. Additionally, it was stable for 41 h in degassed toluene solution. In Wudl's heptacene the acene core was protected by several bulky substituents imparting enhanced stability on the acene core when compared to unsubstituted heptacene



Scheme 2.6 *Wudl's synthesis of heptacene*

A substituents effect on the acene core is important and was explored by the Miller group. They investigated the effect of several different types of subtituents by focusing on how they affected the acene core for a large series of pentacene derivatives. They concluded that steric effects, electronic effects and the location of substituents are all important factors in determining photooxidative resistances and HOMO-LUMO gaps of acenes.[24] The o-alkyl substituted phenyl groups were found to be more effective in providing photooxidative resistance than phenyl substituents. Additionally, thioalkyl and thioaryl substituents provided better photooxidative resistance than silylethynyl substituents. Using this knowledge, the Miller group successfully synthesized a persistent heptacene derivative that was soluble in a variety of organic solvents. This heptacene derivative was stable for weeks as a solid, for 1-2 days in solution if shielded from light and for several hours in solution when directly exposed to both light and air.[25]

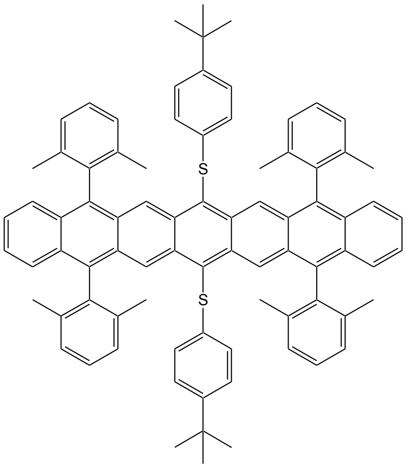


Figure 2.1 *Heptacene derivative synthesized by Miller group*

By incorporating sterically protecting groups both the Wudl and Miller groups protected the acene core and were able to produce relatively stable heptacene derivatives. In 2010, using 2,6-dimethylphenyl and thioaryl substituents the Miller group successfully synthesized a persistent nonacene derivative that is stable as a solid in the dark for at least 6 weeks and when protected from light it is stable in solution for 24 h. The reported HOMO-LUMO gap of this nonacene is 1.12 eV, which is the smallest experimentally measured HOMO-LUMO gap for any acene.[26]

In another recent publication (2010), the Bettinger group reported the synthesis of unsubstituted octacene and nonacene in a PMMA matrix. The approach used by the Bettinger group paralleled Necker's synthesis of heptacene in a PMMA matrix.[27]

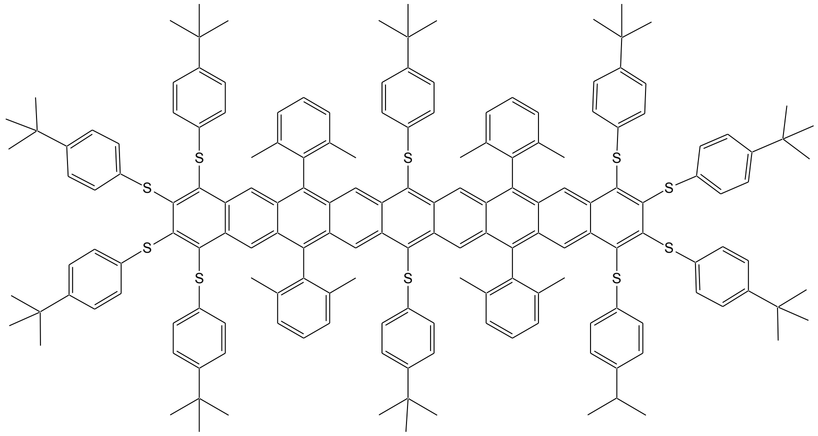
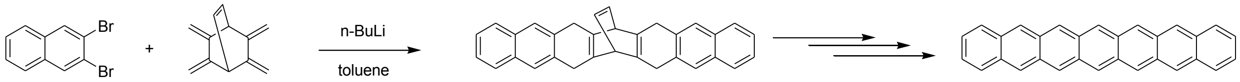


Figure 2.2 *Bettinger's nonacene derivative*

The significant progress achieved to date in the synthesis of acenes show that under the appropriate conditions the highly sought higher acenes are attainable. The synthesis of these new acenes will provide access to novel organic semiconductors.

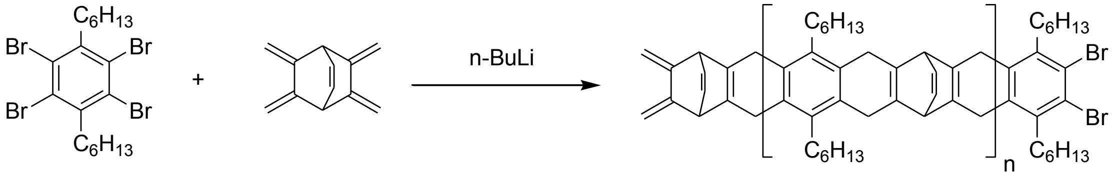
2.3 Reported Synthetic Strategies

The synthesis of higher acenes represents a major challenge in both preparative and polymer chemistry. There are several synthetic strategies reported in the literature for constructing the 6-membered rings of polycyclic aromatic hydrocarbons.[28] The earliest syntheses of these aromatic hydrocarbons were spearheaded by Clar and were heavily dependent on Friedel-Crafts reactions and metal oxidations and reductions as the tools for constructing acenes.[29] With the development and advent of new synthetic methods and shift to Diels-Alder chemistry was observed in the literature.[30] The Diels-Alder reaction has proven to be a powerful tool in acene synthesis and is often exploited in the synthesis of oligomers and polymers. The [4+2] type cycloaddition reactions have became the primary synthetic tool for assembling 6 membered rings and polycycles.[31] Diels-Alder reactions are effective in constructing large carbon skeletons of well-defined oligoacenes and polyacene precursors. In their synthesis of heptacene by Neckers *et al.* illustrate the effective use of Diels-Alder chemistry to build up the cyclic skeleton of heptacene.[32]



Scheme 2.7 *Necker's use of Diels Alder reaction to make heptacene*

Another great advantage of using Diels-Alder reactions over other methods is that they can be utilized in a sequential fashion to build up to extended systems and even polyacene precursor polymers as well as ladder polymers.[33] The Mullen group synthesized a poly[n]acene precursor polymer by using repetitive [4 + 2] cycloadditions.[34] By reacting a bisdiene with a bisdienophile they were able to successfully synthesize a defect free ladder type polymer in one step (Scheme 2.8).

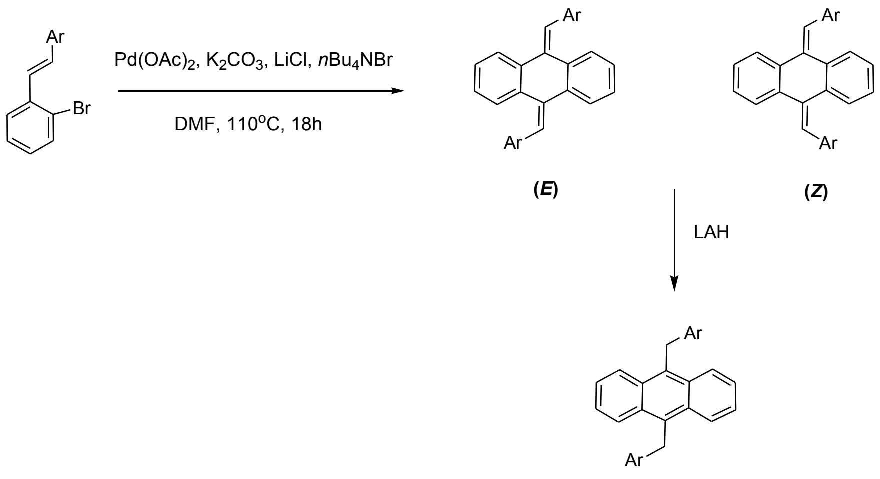


Scheme 2.8 *Mullen's polyacene precursor polymer*

Two precursor functionalities were successfully installed with each functionality being one chemical transformation away from aromatization. Unfortunately, these chemical transformations become more and more unlikely due huge volume of reactive sites and instability of products, which inevitably lead to defect areas being present that are hard to detect therefore leaving ambiguity in the synthesis. Aromatization of the polymer with chloranil leads to a polymer precursor that is one polymer analogous reaction away from a polyacene. Pyrolization of the ethylene bridge, which occurs through a retro Diels-Alder reaction, can be problematic if the molecule contains only ethylene bridges due to the fact that this type of bridge is much too stable to be thermally induced. Many other bridging precursors have been explored. One of the more commonly used bridging precursors is the oxa-bridged group due to its ease of removal.[35] However, there are also many examples of other heteroatoms being used as bridging groups.[36] Labile bridged systems such as lactams,[37] bicycle-ketones,[38] diazene[39] and other precursor derivatives are described in the literature.

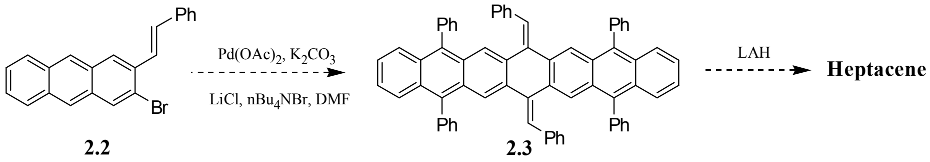
2.4 Our Synthetic Strategy

In 1998, De Meijere reported the synthesis of a series of 9,10-diaryl-9,10-dihydroanthracenes by palladium catalyzed cross coupling reaction of 2-bromostilbene (Scheme 2.9).[40] Subsequent reduction of the 9,10-diaryl-9,10-dihydroanthracenes with $LiAlH_4$ afforded anthracene. The De Meijere approach towards anthracene was intriguing since a new 6-membered ring in dihydroanthracene was produced using the Heck reaction by a [3+3] addition. The [3+3] addition approach shown by De Meijere could potentially lead to a more facile method for constructing 6-membered rings and might serve as a complement to the Diels Alder reaction. This new synthetic approach towards constructing rings could become a valuable tool in the synthesis of oligoacenes and polyacenes.



Scheme 2.9 *De Meijere Synthesis of 9,10-diaryl- 9,10-dihydroanthracenes*

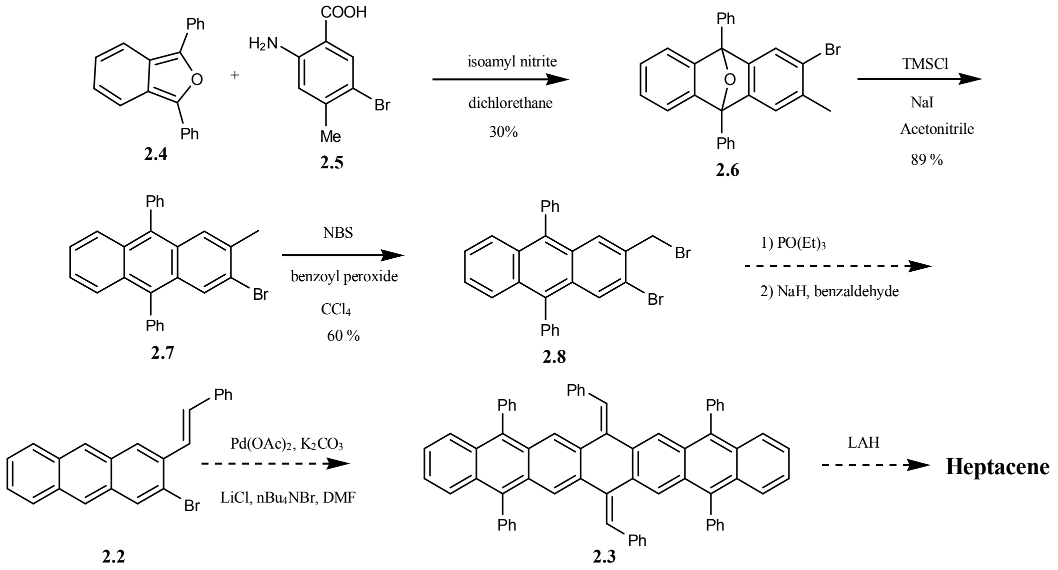
Relying on this strategy it was our goal to synthesize heptacene (which at the time had not been synthesized). The crucial steps in our proposed synthesis of heptacene involved the synthesis of stillbene **2.2**, which we planned on converting to **2.3** using De Meijere's [3+3] cycloaddition. Subsequent aromatization of **2.3** would provide the heptacene derivative. (Scheme 2.10)



Scheme 2.10 *[3+3] Cycloaddition step in heptacene synthesis*

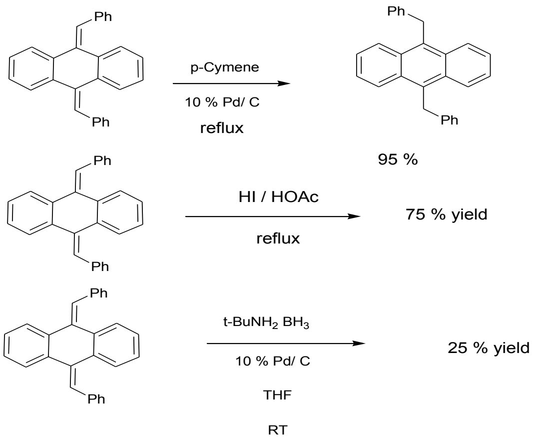
2.5 Results

The synthetic route towards heptacene begins with a benzyne reaction between 5-bromo-4-methyl anthranilic acid (**2.4**) and diphenylisobenzofuran (**2.5**) to give **2.6**. Care must be taken in this step to minimize the presence of oxygen in the reaction mixture because isobenzofuran reacts readily with oxygen to give unwanted side products. In spite of these precautions, we obtained only a 30 % yield for this reaction. The anthranilic acid derivative employed in this reaction was prepared from 4-bromo-3-methylaniline in three steps with an overall yield of 25 %.[41] The oxo-bridge of **2.6** was efficiently cleaved with TMSCl/NaI, to give the anthracene derivative (**2.7**) in 89 % yield. Radical bromination of the benzyl group with NBS afforded the dibromoanthracene derivative (**2.8**) in 60 % yield. With **2.8** in hand one could envision converting it to the phosphonate ester by treating **2.8** with triethyl phosphite followed via a Horner-Wadsworth-Emmons reaction with benzaldehyde to give the stilbene derivative (**2.2**). This stilbene derivative could then undergo a Pd catalyzed [3+3] cycloaddition to give the heptacene precursor (**2.3**) followed by reduction to give heptacene.



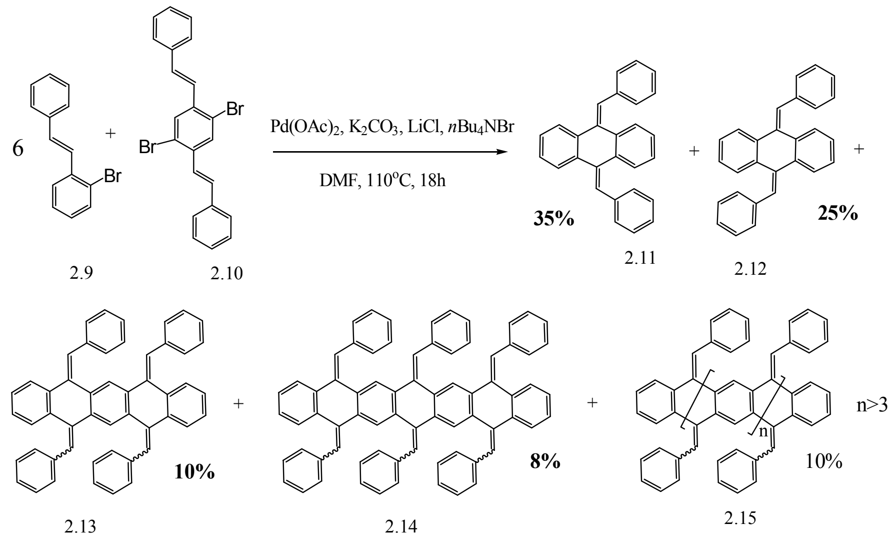
Scheme 2.11 *Proposed route towards heptacene*

While progress was being made towards heptacene using the synthetic route described above we decided to explore the reactivity of the 9,10-diaryl-9,10-dihydroanthracene systems as there was no reactivity studies done on these types of compounds that could be found in the literature besides their synthesis.[42] We were primarily interested in converting these compounds to their respective acene since this step would be a key component in our synthesis of heptacene. It was found that stillbene can be converted to dibenzyl anthracene quantitatively using strong reducing agents such as $LiAlH_4$ or Al/Hg. Other reagents that also accomplished this transformation were p-cymene and Pd/C (95 % yield) , HI/HOAc (75 % yield) and $t\text{-}BuNH_2{\cdot}BH_3$ (25 % yield). Weaker reducing agents like hydrazine and Zn/Hg weren't strong enough to reduce the stillbene to dibenzyl anthracene. Hydride reagents such as catecholborane and 9-BBN were also unsuccessful in forming anthracene.



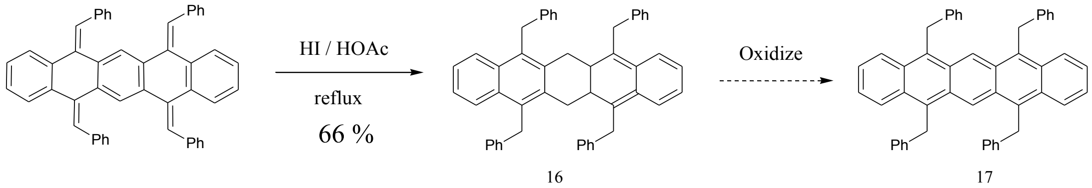
Scheme 2.12 *Aromatization of 9,10-diaryl-9,10-dihydroanthracene*

In our own research group a series of oligo(phenylmethylene-hydroacene)s were synthesized.[43] These hydroacene derivatives are potentially one reaction away from forming the respective acene. However, when reduction of **2.13** to pentacene was attempted, using the previous methods they failed to produce pentacene directly.



Scheme 2.13 Synthesis of oligo(phenylmethylene-hydroacene)s

While no method led directly to the pentacene, treating **2.13** with HI/HOAc did yield a reduced species **2.16**, which is an oxidation step away from pentacene **2.17** (Scheme 2.14). In the literature there are several methods in which a similar oxidation has been achieved by using Pd/C mixture,[44] choranil or DDQ.[45] Presumably **2.16** could be oxidized to pentacene using one of these methods.



Scheme 2.14 Synthesis of pentacene

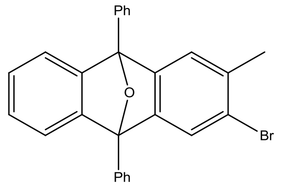
2.6 Conclusion

This chapter illustrates a unique approach towards synthesizing oligoacenes by utilizing a [3+3] addition reaction. Thus far we have been successful in making the anthracene derivative, but have been unsuccessful with the higher acene derivatives. Several alternative methods for aromatizing 9,10-diaryl-9,10-dihydroanthracenes to anthracene were discovered, but these methods were unsuccessful in obtaining the higher acene analogs. The synthesis of heptacene was started, but thus far we have only been able to make 2-bromo-3-(bromomethyl)-9,10-diphenylanthracene and have not had the opportunity to test our cyclization strategy.

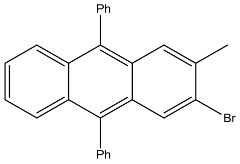
2.7 Experimental Results

Materials. Solvents and reagents were purchased from either Aldrich, Fisher or VWR. THF was distilled over sodium/benzophenone under nitrogen. Dichloroethane was distilled from calcium hydride under argon. All experiments were carried out under argon or nitrogen unless specified. Other solvents and reagents were used as received.

Measurements. Solution NMR spectra were taken on either a Bruker ARX 400, 500 or 600 spectrometers as noted. All chemical shifts (δ) are reported relative to tetramethylsilane (TMS) at 0.0 ppm. FT-IR spectra were recorded on a Mattson Infinity II a spectrometer with a DRIFT accessory from PIKE Technologies, on a diamond frit. EI-MS were taken using a VG Autospec EI/CI Magnetic Sector spectrometer.

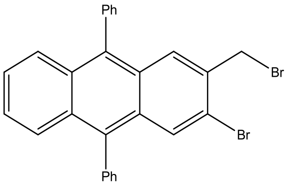


2-bromo-9,10-epoxy-9,10-dihydro-3-methyl-9,10-diphenylanthracene – To a 100 mL flame-dried 3-neck round bottom flask equipped with two addition funnels and a condenser was added 15.0 mL of distilled dichloroethane. Argon gas was bubbled through the solution for 10 min and aluminum foil covered the flask. 0.563 g (2.08 mmol) of isobenzofuran was added to the flask and argon gas bubbled for an additional 5 min. To one addition funnel 0.900 g (4.17 mmol) of 5-bromoanthranilic acid was added dissolved in 20 mL of dichloroethane. To the other addition funnel 1.1 mL (10 mmol) of isoamyl nitrite was added with 5 mL of dichloroethane. The reaction mixture was warmed to reflux, at which point both the anthranilic acid and isoamyl nitrite solutions were added dropwise. The reaction was heated at reflux for 4 h. The reaction was quenched by the addition of 5 % $Na_2S_2O_3$ solution and extracted with ether. The organic layer was washed sequentially with NaCl before drying with $MgSO_4$. The product was purified by column chromatography using hexanes as the eluant to give a solid product (0.27 g, 30 %). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.08 (t, 4H), 7.78 (t, 4H), 7.56 (m, 3H), 7.43 (m, 2H), 7.25 (s, 1H), 7.12 (m, 2H), 2.32 (s, 3H) ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.9, 149.9, 149.8, 149.7, 134.9, 134.6, 128.8, 128.7, 128.3, 128.3, 126.6, 126.5, 125.9, 125.4, 124.5, 122.8, 121.5, 120.3, 120.2, 90.3, 90.1, 22.9 ppm; EI-MS exact mass 438.05, calcd mass 438.05.

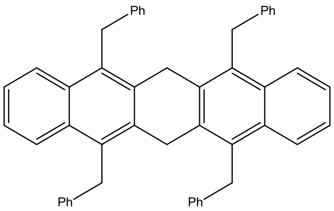


2-bromo-3-methyl-9,10-diphenylanthracene – A solution of 2-bromo-9,10-epoxy-9,10-dihydro-3-methyl-9,10-diphenylanthracene (0.500 g, 1.14 mmol) and anhydrous sodium iodide (0.052 g, 3.5 mmol) in 15 mL of dry acetonitrile was treated with trimethylsilyl chloride (0.49 mL, 3.5 mmol) at room temperature under nitrogen and stirred for 4 h. The reaction was quenched with the addition of 10 mL of aqueous $Na_2S_2O_3$. The resulting mixture was then extracted with diethyl ether. The organic layer was washed with 5 % aqueous $Na_2S_2O_3$ and brine and dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The residue thus obtained was purified by flash chromatography on silica gel with hexanes as the eluant to give a yellow solid in 89% yield (0.428 g). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.02 (s, 1H), 7.90 (m, 2H), 7.62 (s, 1H), 7.49 (m, 8H), 7.39

(m, 4H), 2.51 (s, 3H) ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.6, 137.5, 136.4, 135.6, 133.3, 132.9, 132.1, 131.0, 130.9, 129.4, 128.9, 128.1, 127.8, 127.1, 125.6, 125.7, 125.5, 120.4, 24.3 ppm; EI-MS exact mass 422.07, calcd mass 422.07.



2-bromo-3-(bromomethyl)-9,10-diphenylanthracene – 2-bromo-3-methyl-9,10-diphenylanthracene (760 mg, 1.8 mmol), benzoyl peroxide (5 mg, .02 mmol), and 10 mL of CCl_4 were added to a 25 mL three-necked flask equipped with a water-cooled reflux condenser. A solution of N-bromosuccinimide (0.32 g, (1.8 mmol) in CCl_4 was added dropwise, and the reaction mixture was heated at reflux until the reaction started (appearance of a white cloudy precipitate of succinimide), then it was left for 2h. The insoluble succinimide was filtered and the solution concentrated to afford the product as a white solid (0.569 g, 60 %). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.91 (m, 2H), 7.63 (s, 1H), 7.48 (m, 10 H), 7.37 (m, 2H), 4.69 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.5, 137.9, 136.4, 135.5, 133.6, 133.4, 132.1, 131.0, 130.9, 129.3, 129.1, 127.8, 127.5, 127.5, 125.7, 125.7, 125.7, 121.1, 34.2 ppm; EI-MS exact mass 499.98, calcd mass 499.98.



5,7,12,14-tetrabenzyl-6,13,-dihydropentacene – Phenylmethylene-hydropentacene derivative 1.12 (90 mg, 0.14 mmol), 3 ml of HI and 15 mL of acetic acid were added to a round bottom flask equipped with a condenser. The reaction mixture was refluxed for 3 h. The product was extracted with chloroform. The product was purified by flash chromatography using 5:1 hexanes:DCM as the eluant to give a solid product (59 mg, 66 %) . ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.99 (m, 4H), 7.37 (m, 4H), 7.22 (m, 12H), 7.06 (m, 8 H), 4.47 (s, 4H), 4.25 (s, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.7, 135.3, 131.8, 130.2, 128.4, 127.9, 125.8, 125.0, 124.8, 33.5, 29.6 ppm; EI-MS exact mass 640.31, calcd mass 640.31.

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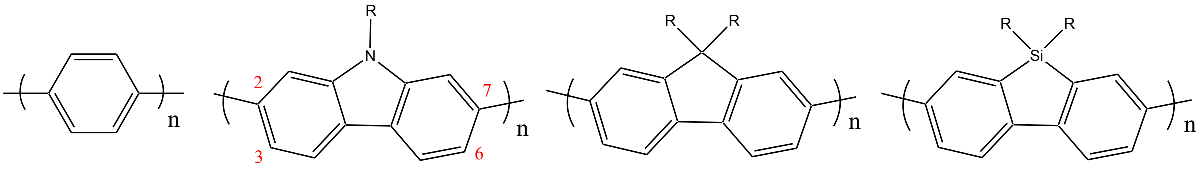
CHAPTER 3

Polydibenzophosphole

3.1 Introduction

Electroluminescence from conjugated polymers was first reported in 1990, when a green/yellow emission was observed from a poly(*p*-phenylene vinylene) PPV device produced at Cambridge University.[1] The discovery of electroluminescence in organic polymers stimulated a great deal of interest in PLEDs both academically and industrially. Since this discovery, a significant amount of progress has been made towards the development of materials for commercially viable devices.[2] The development of full color red-green-blue (RGB) displays based on organic materials is of particular interest to the scientific community because according to color theory all other colors can be made from these three additive primary colors.[3] Although these three colors have been demonstrated in PLEDs, only the red and green PLEDs have reached sufficiently high efficiencies and lifetimes for commercial applications.[4] The difficulty in finding a material that emits in the blue region (450-500 nm) is that it requires a high band gap polymer. Charge injection into high band gap polymers is difficult because of the high energy required to do this. Blue PLEDs have been plagued mainly by low device output efficiencies and short device lifetimes. A group of polymers which have been found to emit in the blue are shown below (Figure 3.1).



PPP

Poly(2,7-carbazole)

Poly(fluorene)

Poly(2,7-dibenzosilole)

Figure 3.1 *Blue fluorescent polymers*

The first simple conjugated polymer to emit blue light was PPP.[5] However, the polymerization proved to be difficult due to PPP's low solubility.[6] Typical degrees of polymerization (DPs) ranged from 5 to 15. During polymerization, as the growing chains increase, they precipitate out of solution, thus inhibiting further chain growth. Solubilizing side chains were added to PPP in attempts to improve the DP. While the side chains did solubilize PPP the problem of steric hindrance between neighboring phenylene groups caused the phenylenes to twist out of plane and thus effectively broke the polymer's conjugation and destroyed its blue emission. [7]

The most widely studied blue emitting polymer is poly(fluorene), which was first synthesized by Fukuda *et al.* via oxidative polymerization with ferric chloride in 1989.[8] Poly(fluorene) displays a band gap around 3 eV, which is ideal for blue emission. However, after operating poly(fluorene) devices for a short time the blue emission is slowly converted to green emission until eventually only green emission is observed.[9] The most widely accepted proposal is that the poly(fluorene) is oxidized to the keto form poly(fluorenone) leading to the observed green emission.[10] A number of theories have been proposed to explain the actual process that is taking place, but these theories are still under some debate.[11]

Poly(carbazoles) are neither plagued by insolubility or green emission. Oligomers of carbazoles emit in the blue region making poly(carbazole) polymers a viable option for blue LEDs. Unfortunately, in carbazoles the 3, 6 position is more reactive than the 2, 7 position.[12] In poly(3,6-carbazole) the conjugation does not go through the biphenyl system as in the case for PPP and poly(fluorene). The conjugated segments are best described as a substituted 1,4-diaminobiphenyl structures. Poly(2,7-carbazole) has been synthesized by Leclerc and others.[13] Unfortunately, this polymer was plagued by reactivity taking place in the 3,6 positions which effectively destroys the conjugation through the 2,7 position. In 2005, the Holmes group reported the synthesis of poly(2,7-dibenzosilole).[14] By replacing the vulnerable C-9 position in poly(fluorene) with a silicon atom they were able to achieve a polymer with high thermal and optical stability. More importantly, poly(2,7-dibenzosilole) displayed a strong blue electroluminescence. In fact, the optical properties in thin films were remarkably similar to the corresponding poly(fluorene) with an absorption maximum at 390 nm and a luminescence maximum at 425 nm and an optical band gap of 2.93 eV. However, in contrast with poly(fluorene) it was stable for 16 h at a temperature of 250^o C and in the presence of light whereas poly(fluorene) completely degraded after 4h at 200^o C. The literature on poly(2,7-dibenzolesilole) is limited, but it seems like a promising candidate for blue PLEDs. Several dibenzoborole derivatives have been reported as well. However, these dibenzoborole systems display different fluorescence properties than the C, N and Si analogs. The dibenzoborole derivatives emitted a green fluorescence and not a blue fluorescence. This difference is attributed to boron's empty p-orbital which allows for delocalization of electron density away from the biphenyl system and onto boron.[15]

3.2 Dibenzophospole, a candidate for blue emission

Recognizing the importance of polyheterofluorenes we focused on producing our own blue emitting polymer. Our proposed solution to the former problem involves a twofold answer. We wanted to develop a polymer that will emit in the blue region while at the same time maintaining a stable blue luminescence under the harsh conditions necessary to produce efficient PLEDs. Central to obtaining a solution will be to keep the *p*-phenylene structure intact as this structural feature leads to rigid polymers with a band gap suitable for blue emission. Equally important is to not disturb the conjugation of the biphenyl system as this shifts the emission. To maximize conjugation through the biphenyl groups both phenyl groups must be in plane. One way this is accomplished is by bridging the biphenyl group with a phosphorus atom as in dibenzophosphole (Fig. 3.2). Dibenzophospholes(4-phosphafluorenes) constitute an interesting class of compounds whose transition metal complexes have been known for year and have been used as catalysts in organic synthesis.[16] The crystal structures of dibenzophosphole show that both its phenyl groups are held in plane by the phosphorus atom.[17] Dibenzophosphole is a stable molecule whose electronic properties have not been fully explored, in fact, there are only a small number of publications on phosphorus-containing semiconducting polymers.[18]

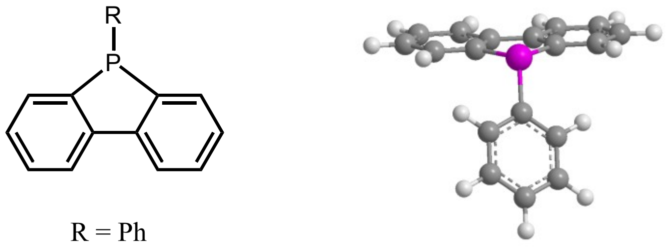
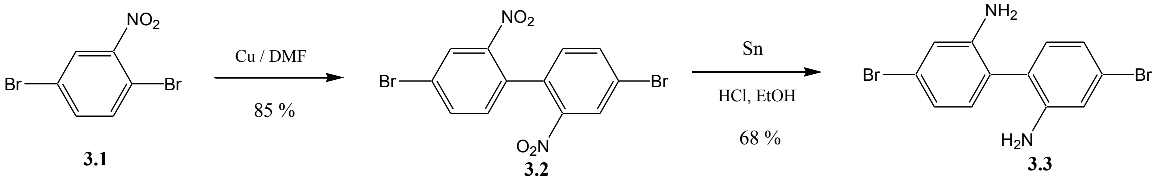


Figure 3.2 *Dibenzophosphole structure*

The most common semiconducting phosphorus-containing polymer is poly(phosphole); the phosphorous variant of thiophene, pyrrole and furan.[19] The aromaticity of phospholes, is one of the lowest among the 6π electron five-membered heterocycles. The weak aromatic character observed in phospholes is a consequence of their preference to adopt a pyramidal geometry and the high degree of s-character the lone pair exhibits. These features prevent an efficient interaction of the P-lone pair and the π-system.[20] Several studies have been reported in the literature, which compares phosphorus's lone pair contribution to aromaticity in phosphole and dibenzophosphole systems.[21] These studies show that the lone pair on the phosphole is more delocalized through the aromatic system than the lone pair of the dibenzophosphole system. In fact, the lone pair of dibenzophosphole correlates more closely to the lone pair of triphenylphosphine.[22] These studies provide strong indication that the lone pair of dibenzophosphole is not coupled to the aromatic system and therefore should not disrupt the conjugation through the biphenyl groups and should display electronic properties, which are similar to those of the other blue emitting polymers without the aforementioned undesirable problems that have plague the other blue emitting polymers.

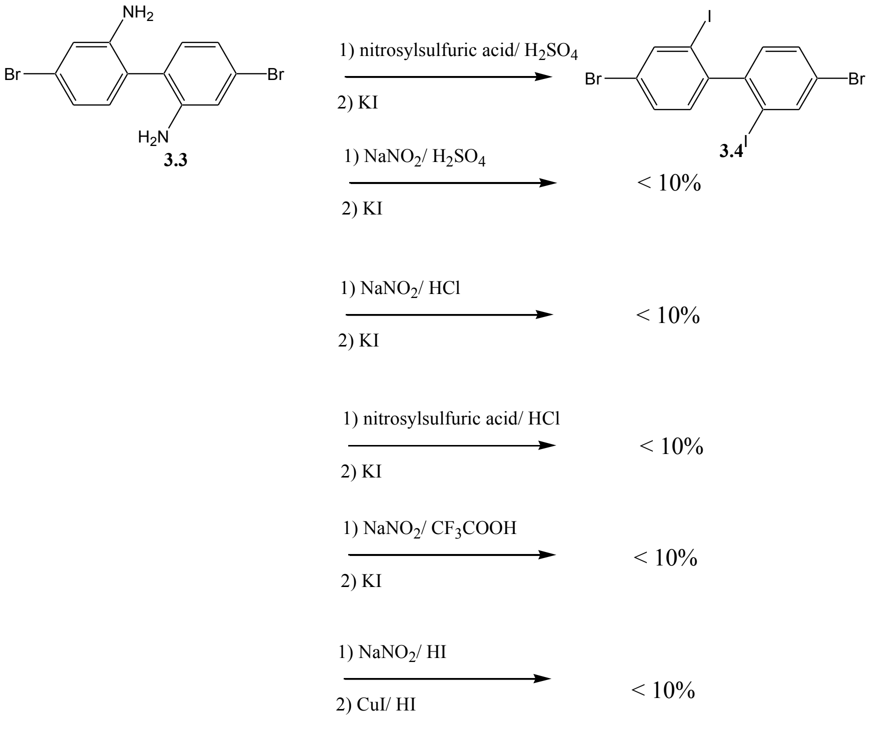
3.3 Results

The synthesis of 2,7-dibromodibenzophosphole (Scheme 3.1) begins with treatment of 1,4-dibromo-2-nitrobenzene (**3.1**) with Cu/DMF to give the Ullmann coupling product **3.2**. The dinitrobiphenyl compound (**3.2**) was reduced with Sn/HCl to give the corresponding diamine **3.3**.



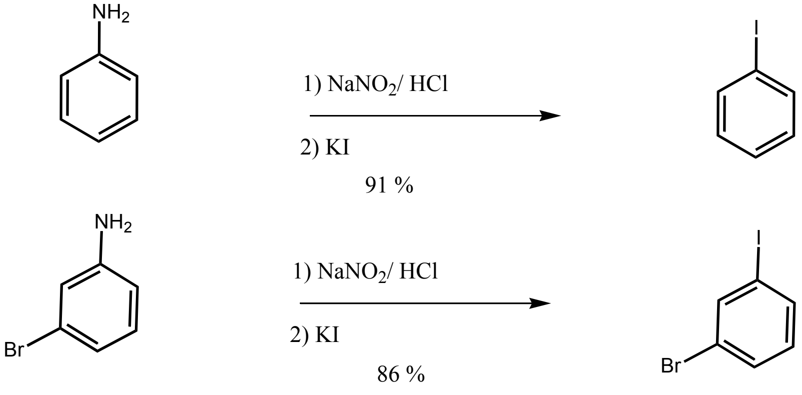
Scheme 3.1 *Synthesis of 4,4'-Dibromobiphenyl-2,2'-diamine*

One can envision halogenating the diamine via a Sandmeyer type reaction. Treatment of **3.3** with nitrosylsulfuric acid forms a diazonium species, which when treated with aqueous potassium iodide, gave the 4,4'-dibromo-2,2'-diiodobiphenyl (**3.4**).[23] However, this Sandmeyer reaction proved to be very problematic due to the extremely low yields of **3.4** (< 10 %). Additionally, the isolation of **3.4** was difficult due to the multiple sideproducts which were produced. When the reaction conditions such as the temperature, reagents, and amount of reagents were varied (Scheme 3.2) there was no noticeable improvement in the yield.



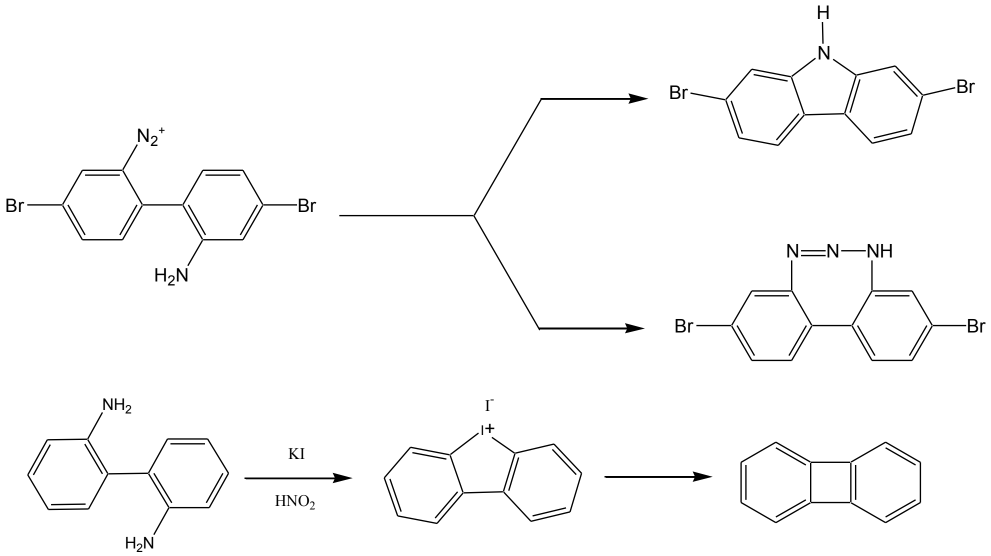
Scheme 3.2 *Sandmeyer reactions under various conditions*

When the Sandmeyer reaction was attempted on much simpler systems such as aniline and 3-bromoaniline the reaction proceeded to give the desired products in good yield.



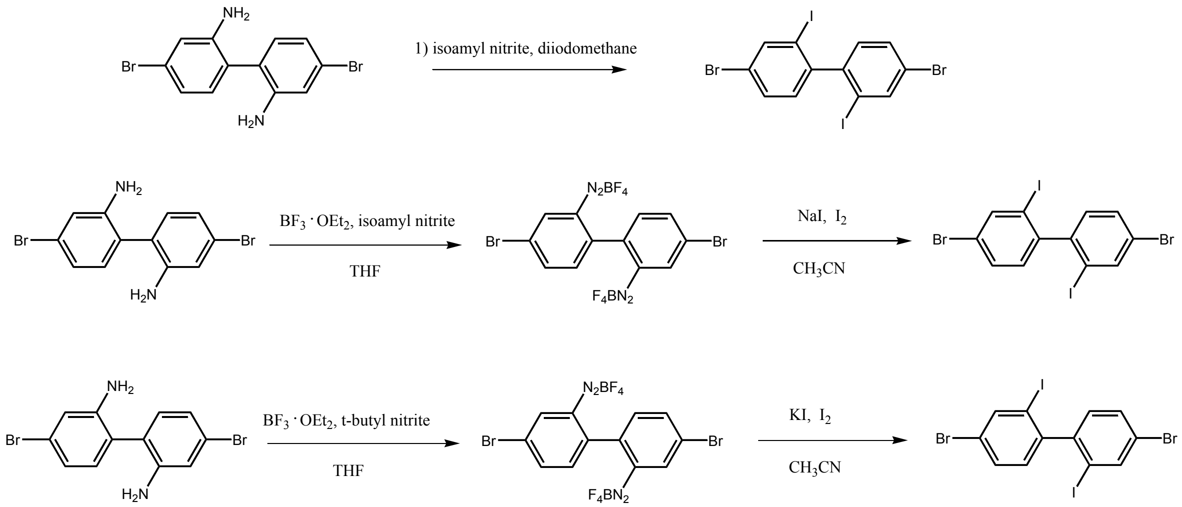
Scheme 3.3 *Sandmeyer reaction on simpler systems*

These results were disappointing due to the fact that the Sandmeyer reaction seems to be an efficient method for converting amines to halogens. Quite possibly the Sandmeyer reaction was inefficient in converting **3.3** to **3.4** due to the increased steric hindrance around the amine caused by substitution at the ortho and meta positions. Another possibility for the decreased yield could have been an intermolecular reaction where the amine attacks the diazonium species giving the carbazole product or the triazine product. This was ruled out due to the fact that there was no evidence by NMR either of these being the major products. The low yield may be attributed to an intermolecular cyclization of the first formed iodo substituent onto the neighboring 2'-position through the decomposition of the second diazonium iodide salt. [24] However, this side reaction may be minimized to some degree by using excess of iodide reagent, but in our case when this was attempted there was no significant improvement on the yield.



Scheme 3.4 *Possible unwanted side products from Sandmeyer reaction*

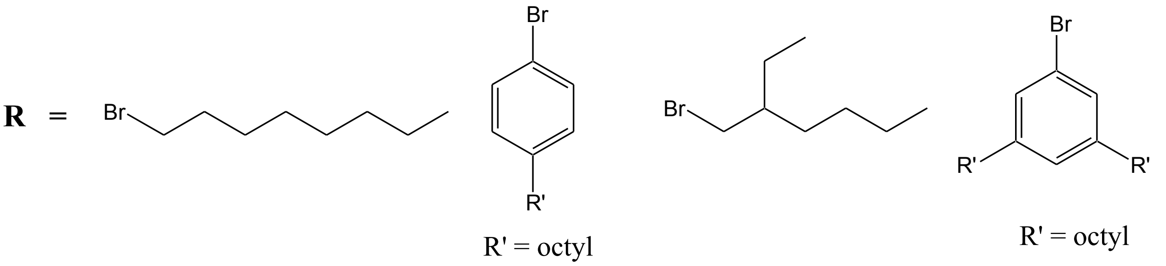
Since the Sandmeyer reaction route didn't seem promising different alternative routes to **3.4** were explored (Scheme 3.5). The first alternative route involved heating **3.3** in the presence of isoamyl nitrite and diiodomethane to 100°C forming the diazonium species which could then react with diiodomethane is situ giving **3.4**. Unfortunately, this reaction failed to give product yielding only side products and starting material. Another route which was explored was the diazotization of **3.3** to give the salt product which was then halogenated with I_2 and NaI (KI) to afford **3.4** in low yield. The only problem with this route was that an oil was collected and not a solid as had previously been reported for **3.4**, indicating that there was some type of impurities present.



Scheme 3.5 *Alternate routes to 4,4'-Dibromo-2,2'-diiodobiphenyl*

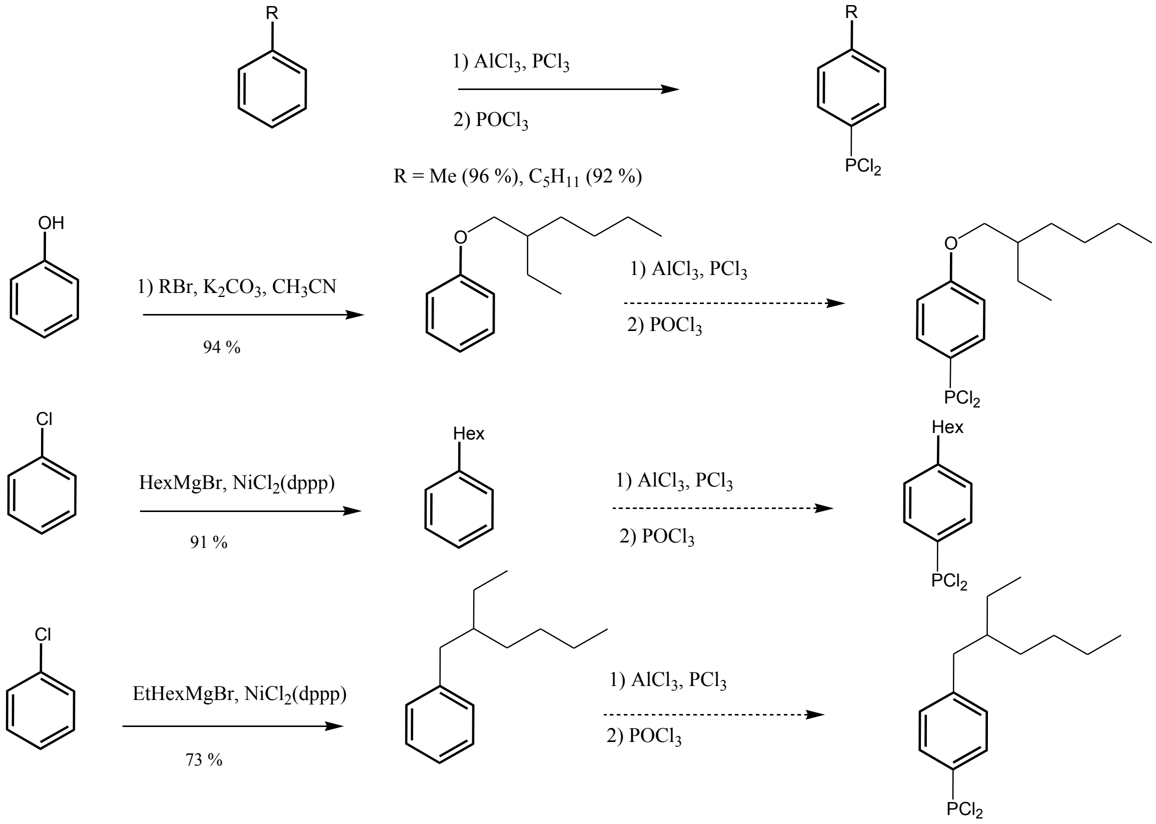
The alkyl(aryl)dichlorophosphine (R group) species is designed to impart solubility to the PDBP polymer (Scheme 3.6). The alkyl(aryl)dichlorophosphine groups can be synthesized by adding phosphorus trichloride to a Grignard reagent to afford the desired alkyl(aryl)dichlorophosphine.[25]

$$\mathrm{RMgBr} \xrightarrow{\mathrm{PCl_3}} \mathrm{RPCl_2}$$



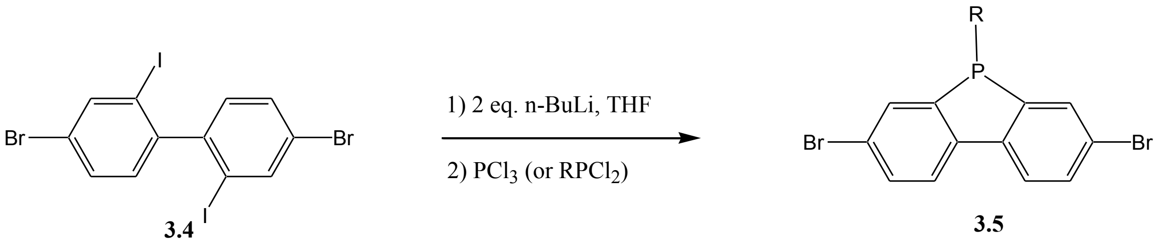
Scheme 3.6 *Synthesis of alkyl(aryl)dichlorophosphine*

Various aryldichlorophosphines have also been synthesized by Friedel-Crafts type reaction of phosphorous trichloride with aromatic hydrocarbons. This method was used for toluene and amylbenzene by Villemin *et. al.,* with phosphonation occurring highly regioselectively to give almost only the isomer in the para position with minimal traces of the ortho isomer.[26]



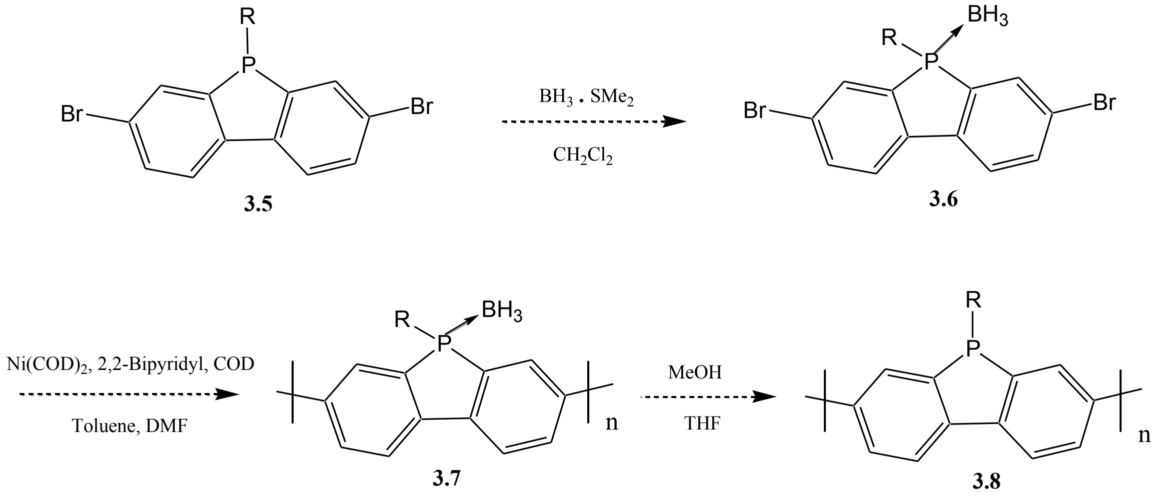
Scheme 3.7 *Synthesis of alkyl(aryl)dichlorophosphine*

The most direct route to the corresponding dibenzophosphole involves treating **3.4** with n-BuLi. The difference in reactivity between the bromo and iodo substituents towards n-BuLi makes it possible to selectively form the 2,2’-dithio-4,4’-dibromophenyl intermediate which can be trapped with an alky(aryl)dichlorophosphine to yield the desired dibenzophosphole derivative, **3.5**.[27] The reaction was attempted with phosphorous trichloride and the impure product **3.4** and it gave a mixture of products that was difficult to separate.



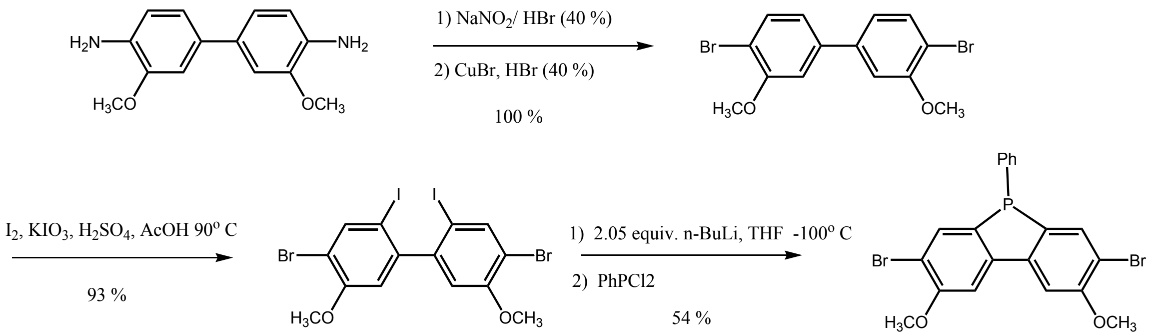
Scheme 3.8 *Synthesis of dibenzophosphole monomer*

In order to polymerize **3.5** to give PDBP it is necessary to protect the phosphorus atom. This is necessary because phosphorus has a lone pair which can bind to the metal catalyst forming a complex and terminating the polymerization. One method of protecting phosphorus is to treat it with borane, this forms the dibenzophospholeborane complex (**3.6**).[28] Polymerization can proceed using a Yamamoto type coupling to give the polymer **3.7**. Removal of the borane group can be accomplished by treating **3.7** with methanol and base in a polymer analogous reaction to give PDBP.[29]



Scheme 3.9 *Synthesis of PDBP polymer*

While this project was still underway Huang *et al.* reported the synthesis of a 2,7-dibromodibenzophosphole monomer.[30] Their reported synthesis is shown below (Scheme 3.10). They found that their dibenzophosphole monomer slightly oxidized to the phosphine oxide (~ 17%) form upon work up. No photophysical characterization of the dibenzophospholes monomer was reported and no polymer was reported by the group in this paper.



***Scheme 3.10**. Huang's synthesis of 2,7-Dibromodibenzophosphole monomer*

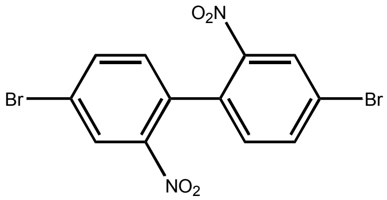
3.4 Conclusion

Dibenzophospholes are potentially interesting molecules who posses many similarities to other blue emitting monomers. The synthesis of PDBP was proposed and attempted. The synthesis has been plagued by the inability to efficiently synthesize 4,4'-Dibromo-2,2'-diiodobiphenyl via the Sandmeyer reaction. Once this step has been resolved the synthesis of the monomer may be achieved using the route described in this chapter. The photophysical properties of the polymer will be explored to determine its suitability in LED applications.

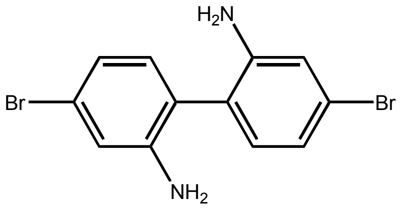
3.5 Experimental Results

Materials. Solvents and reagents were purchased from either Aldrich, Fisher or VWR. All experiments were carried out under argon or nitrogen unless specified. Other solvents and reagents were used as received.

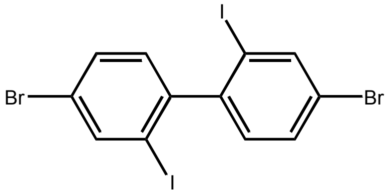
Measurements. Solution NMR spectra were taken on either a Avance 500, Bruker ARX 400, 500 or 600 spectrometers as noted. All chemical shifts (δ) are reported relative to tetramethylsilane (TMS) at 0.0 ppm. FT-IR spectra were recorded on a Mattson Infinity IIa spectrometer with a DRIFT accessory from PIKE Technologies, on a diamond frit.
UV-visible spectra were obtained with a Hewlett Packard 8453 spectrophotometer.
EI-MS were taken using a VG Autospec EI/CI Magnetic Sector spectrometer.



4,4'-Dibromobiphenyl-2,2'-dinitrobiphenyl -To a flask containing 10.0 g (35.8 mmol) of 2,5-dibromonitrobenzene in DMF (40 mL) was added copper powder (5.40 g, 84.8 mmol). The reaction mixture was heated to 125 °C. After 4 hours, the reaction mixture was cooled to room temperature. 40 ml of toluene was then added and the inorganic salts were removed by filtration through celite. The solvent was evaporated from the filtrate to yield the product as a yellow solid (6.08 g, 85.0 %) ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.39 (2H, d, J = 2.0, Ar), 7.84 (2H, dd, J = 8.2, 2.0, Ar), 7.18 (2H, d, J = 8.2, Ar); ^{13}C NMR ($CDCl_3$, 125-MHz) δ 147.4, 136.7, 132.1, 132.0, 128.1, 123.0 ppm, IR (DRIFT) 1527, 1343, 1103, 1005, 830, 729 cm^{-1}.



4,4’-Dibromobiphenyl-2,2’-diamine - To a 3 neck flask containing 10.0 g (24.8 mmol) of 4,4’-Dibromobiphenyl-2,2’-dinitrobiphenyl in 124 mL of absolute ethanol was added 82.6 mL of 30 % hydrochloric acid. To this stirring mixture 11.7 g (98.0 mmol) of tin powder was slowly added over 10 minutes and the reaction was refluxed for 3 hours. The reaction mixture was then cooled and poured into approximately 275 mL of ice water. The mixture was basified using 100 mL of 20 % NaOH solution. The product was extracted with diethyl ether and the organic layer was washed with brine and dried with anhydrous $MgSO_4$ and evaporated to dryness. The product was purified by crystallization in ethanol to afford 5.7 g (%) as light brown crystals. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.93 (6H, s, Ar), 3.74(4H, s, NH_2), ^{13}C NMR ($CDCl_3$, 125-MHz) δ 145.4, 132.3, 122.7, 122.1, 121.7, 118.2 ppm, IR (DRIFT) 3341, 3356, 3210, 1606, 1476, 1407, 994, 763 cm^{-1}.sh



4,4’-Dibromobiphenyl-2,2’-diiodobiphenyl - To a flask containing 0.24 mL of 40 % nitrosylsulfuric acid in concentrated sulfuric acid was added in 0.20 g (0.58 mmol) of 4,4’-Dibromobiphenyl-2,2’-diamine. The resulting mixture was stirred vigorously for an additional 3 hours forming a brown viscous solution. This mixture was added dropwise into an aqueous solution of potassium iodide (2.90 g in 300 mL) at 0 °C. The reaction mixture was left to stir overnight at room temperature. The reaction mixture was quenched with NaOH until it reached pH = 7. The product was extracted using diethyl ether and washed with brine. The product was dried using $MgSO_4$ and the solvent was evaporated. Purification by column chromatography using hexane as the eluant afforded the product (<10 % yield) as an light brown solid. ^1H NMR ($CDCl_{3,}$ 500 MHz) δ 8.09 (2H, d, J = 1.9, Ar), 7.55 (2H, dd, J = 8.2, 1.9, Ar), 7.03 (2H, d, J = 8.2, Ar); ^{13}C NMR ($CDCl_{3,}$ 125-MHz) δ 146.7, 141.0, 131.3, 130.7, 122.4, 99.8 ppm, IR (DRIFT) 1566, 1450, 1087, 992, 817, 711 cm^{-1}.

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CHAPTER 4

Pentiptycene Rotors

4.1 Introduction

There is a great deal of interest in organic compounds possessing aromatic groups that are linearly conjugated through acetylene linkages due to their interesting electronic properties and great potential in many electronic applications.[1] A great deal of interest in these π-conjugated systems is derived primarily from their ability to function in many roles such as when efficient charge transport, fast energy transfer and good luminescence properties are required.[2] Much theoretical research and experimental and research on the solid-state behavior of these types of systems has been reported. Poly(arylethynyl) systems are particularly appealing because of the cylindrical symmetry of the alkyne group, which allows it to maintain conjugation with the adjacent aryl groups regardless of the planar orientation of the aromatic groups.[3] The relatively low energy barrier of rotation about the alkyne-aryl bond (< 1 kcal/mol) leads to a coexistence of both the twisted and the coplanar forms.[4] These two forms rapidly equilibrate back and forth. While, the rapid equilibration in the ground state between the two forms bears no consequences, rotation about the alkyne-aryl bond in the excited state leads to a large energy difference as a function of the angle between the aromatic groups leading to different properties for the coplanar and twisted forms. The resulting energy differences between the coplanar and twisted forms can lead to entirely different emission and absorption spectra for the two forms.

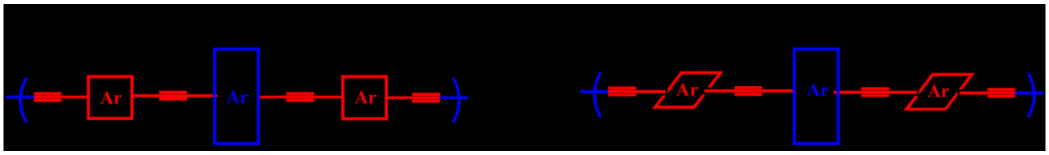
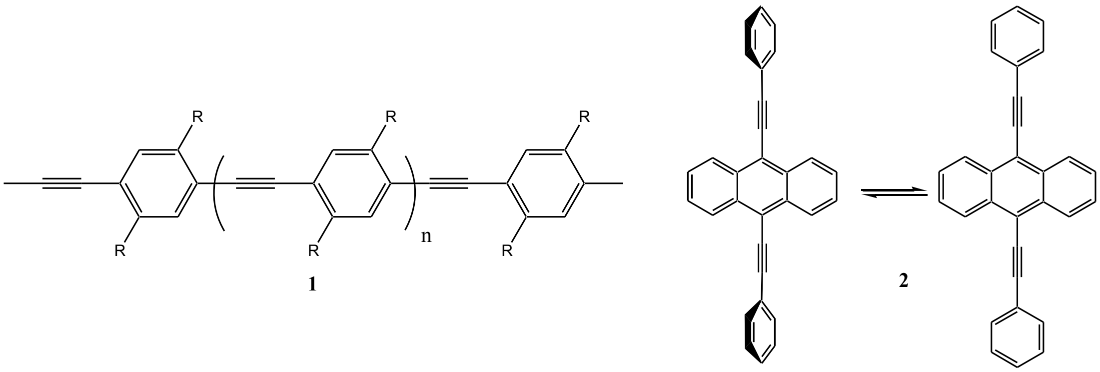


Figure 4.1 *Twisted and coplanar forms*

An explanation of this phenomenon was first reported by Bunz and coworkers while studying alkyl (R= $C_{10}H_{23}$) substituted arylethynyl polymers **1**.[5,6] They reported a change in the electronic properties of their polymer as it transitioned from the liquid crystalline phase to the isotropic phase, which they attributed to conformational changes along the polymer backbone which occur at the transition. A similar result was observed in Scherf's ladder polymer, in which case, the polymer bearing a poly(p-phenylene) backbone undergoes a dramatic bathochromic shift upon forced planarization.[7] Our own research group showed that planarization of 9,10-bis(phenylethynyl)anthracene (**2**) at low temperatures and in stretched polyethylene films resulted in significant changes to its UV absorption spectrum.[8] When the Uv-Vis spectra of **2** was obtained in polyethylene films it gave a well resolved UV-Vis spectrum. In contrast to measurements in solution where there was significant loss of vibrational resolution.

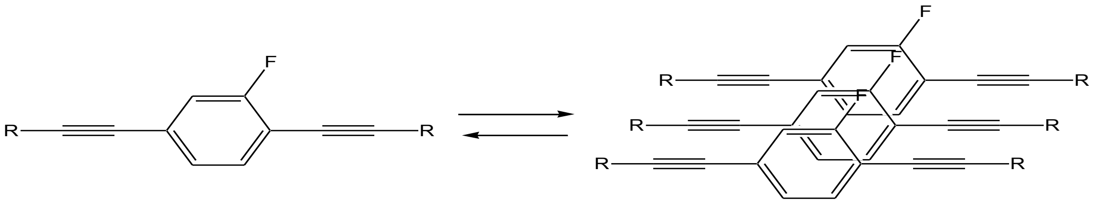


1

2

Figure 4.2 *Arylethynyl systems*

Research done by the Swager group demonstrated the effects of aggregation on the photophysics of poly(phenylenethylene) systems. They used self-assembled monolayers to facilitate cofacial interactions between neighboring polymer chains and observed an improvement in the photophysical properties as a function of distance between chains which was attributed to aggregation.[9] It is generally understood that the observed spectra shifts in poly(arylethynyl) systems can be attributed to both aggregation and planarization, however, the extent to the effect that each has on the electronic properties of arylethynylenes has been difficult to quantify. Our own research group studied the effects of aggregation of 1,4-diethynyl-2-fluorobenezene (R = H, **3**).[10] This molecule represents the simplest type of aryl-ethynyl system whose photophysical properties are independent of phenyl group rotation. In this manner the effects of aggregation could be studied while avoiding the complications from planarization that arise when multiple aryl groups are present. In the crystal form and at high concentrations a spectral broadening and a red shift of 60-80 nm was observed for **3,** which was attributed to aggregation.



3 **Aggregation**

Figure 4.3 *Aggregation of 1,4-diethynyl-2-fluorobenezene (3)*

At around the same time, our own research group studied 1,4-bis(phenylethynyl)benzene in an attempt to demarcate the effects of aggregation and planarization. This system was studied in solution, in low-temperature glasses and in stretched polyethylene films. The spectra in these different states were compared with the aggregates, which occur in the crystal state. It was found that planarization was responsible for modest shifts of around 20-30 nm, while still maintaining a high emission quantum yield. On the other hand it was proposed that aggregation resulted in larger shifts and loss of vibronic structure.[11] Other model systems have also been investigated in an effort to gain further insights into the effects of the intrachain conformation and interchain interactions on the fluorescence properties of poly(phenylenethylene)'s. Yang and coworkers synthesized a series of pentiptycene based oligo(p-phenylenethynylene) (n= 0, 1, 2).[12]

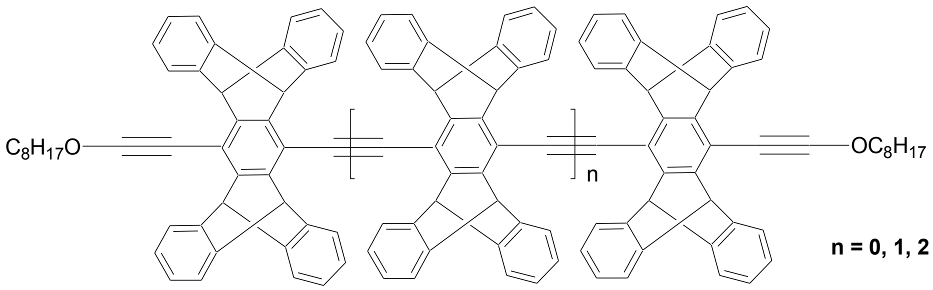


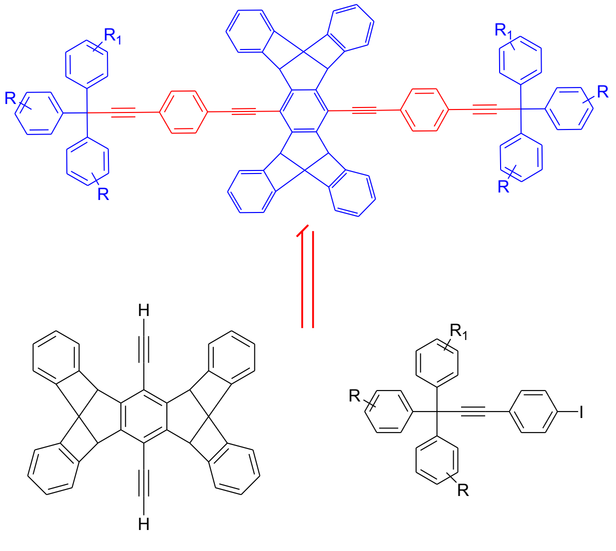
Figure 4.4 *Yang groups oligo(p-phenylenethynylene) pentiptycene derivatives*

They believed that by incorporating pentiptycene groups along the core it would allow the molecules to pack in a way that would limit or prevent interchain charge transfer interactions and in this way the solid-state fluorescence would be solely dependent on the interchain interactions and could more accurately be measured. They observed that twisting of the π-conjugated backbones resulted in blue-shifted absorption and fluorescence spectra and increased fluorescence quantum yields and lifetimes. They also observed a reduction in fluorescence quantum yields when they shifted from solution to films which they attributed to interchain energy transfer.

4.2 Our Pentiptycene Rotor Derivatives

While progress has been made in understanding the effects of conformation and aggregation on the electronic properties of phenylenethynylene systems much progress has been plagued by poor control of their conformations and thus poor knowledge of the effect of conformation. We wished to further explore effect of conformation as a function of angle between aromatic groups so we synthesized a bis(*p*-(2- (4-(3,3,3-triphenyl propynyl)-*p*-phenylene) ethynylene)pentiptycene molecule and several derivatives of this parent compound to probe the effects of chromophore rotation in the ground state and in the excited state both in solution and in the solid state.

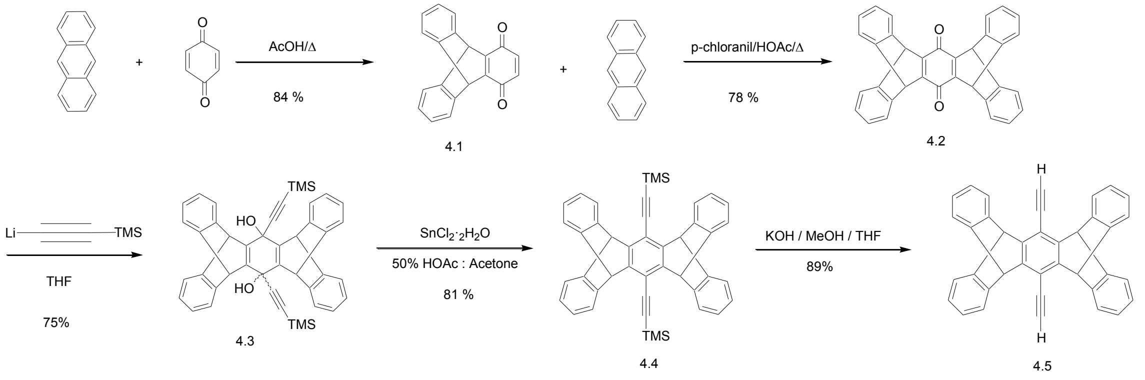
The synthetic strategy we used is shown below in scheme 4.1. It involved the synthesis of a pentiptycene molecule along with a trityl derivative. Coupling the three pieces together allowed us to create our pentiptycene rotor derivatives.



Scheme 4.1 *Retrosynthetic Strategy towards our pentiptycene rotor derivatives*

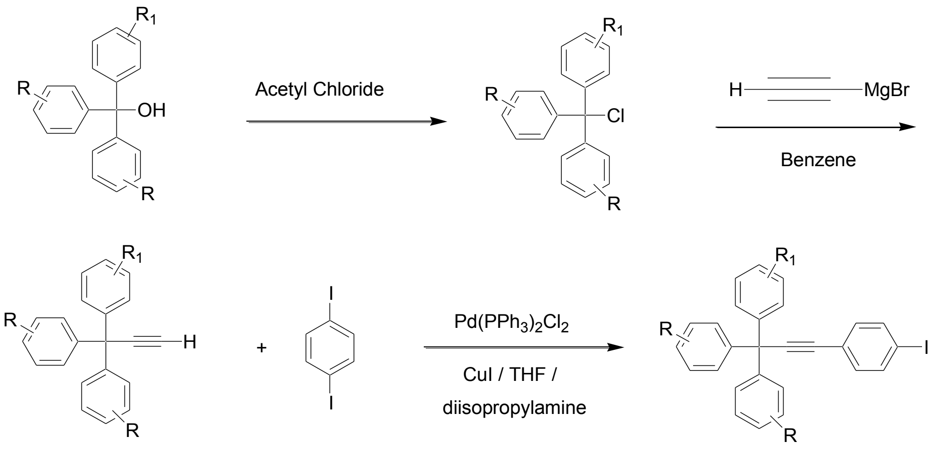
In the past, several groups have exploited the three dimensional rigid pentiptycene framework to construct molecules of both fundamental and practical importance.[13] The pentiptycene group has been employed because of its bulkiness and its unique ability to spatially isolate specific functional groups from their surroundings and create intra- or intermolecular free space so that desired properties (ex. light-emitting efficiency and ability of free rotation) can be studied.[14] Our newly synthesized pentiptycene derivative contains a “spatially isolated” central phenyl ring which forms a p-phenyleneethylene system with the alkynes in our molecule. We anticipate that by incorporating pentiptyl groups in our structure it will lead to interchain packing distances which are greater than 7 Å (in the solid state) as is commonly observed for other pentiptycene derivatives.[15] The phenylene rings will be capped on each end with trityl groups to prevent π-stacking interactions from occurring. While these interactions are unimportant for large systems like polymers their effects on smaller systems like ours would be significant. With these precautions in place it should greatly limit interchain interactions from occurring and allow us to isolated and study the intrachain interactions exclusively. The Swager group has demonstrated that by incorporating bulky pentiptycene groups in poly(phenylenes) it is sufficient to prevent excimer formation in thin films. [16]

Our synthesis of pentiptycene closely followed a procedure reported by Swager and coworkers (Scheme 4.2).[16] In the first step of this synthesis anthracene is reacted with bezoquinone in a Diels-Alder type reaction to produce a mixture of quinone product **4.1** (~80%) and pentiptyl quinone, **4.2** (~20 %). The mixture of products is not separated after this first step, but rather is refluxed in the acetic acid with additional anthracene and p-chloranil to undergo a second Diels-Alder reaction to yield the pentiptyl quinone **4.2**. Subsequent nucleophilic addition on both carbonyl groups by lithium trimethylsilylacteylide afforded the pentiptycene diol, **4.3**. Aromatization of the central phenylene ring with tin(II) chloride yielded the trimethylsilyl protected diethynylpentiptycene compound **4.4**. Deprotection of the TMS group with potassium hydroxide gave the desired diethynylpentiptycene product **4.5**. All synthetic steps in this synthesis were relatively high yielding (all steps > 74 %).



Scheme 4.2 *Synthesis of pentiptycene*

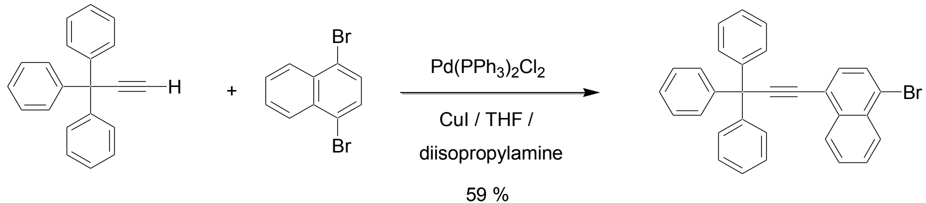
The synthesis of the trityl derivatives (**4.6-4.10**) was achieved using a sequence of steps commonly used within our research group in the synthesis of rotors. In the first step the triarylmethanols are chlorinated by treatment with acetyl chloride. The triarylchorides are reacted with ethynylmagnesium bromide to yield the triarylalkynyl product. Subsequent treatment with 1,4-diiodobenzene in a Sonagashira coupling reaction afforded the mono-addition trityl derivative product. Several different types of trityl derivatives with varying aryl substituents were synthesized in this fashion



4.6) R = H, R_1 = H
4.7) R = H, R_1 = m-OMe
4.8) R = H, R_1 = p-OMe
4.9) R = R_1 = m-OMe
4.10) R = R_1 = p-OMe

Scheme 4.3 *Synthesis of trityl derivatives*

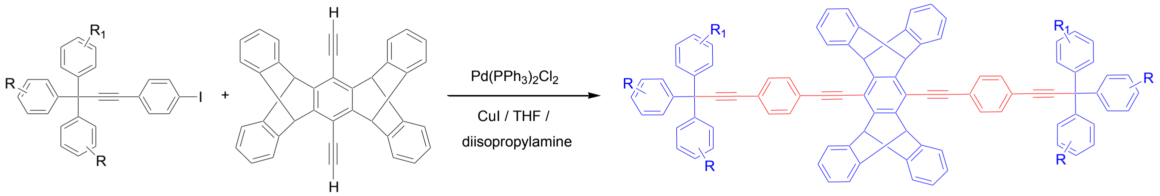
Other derivatives could be synthesized in a similar fashion to the synthesis outlined in scheme 4.3. A naphthalene trityl half rotor (**4.11**) was also synthesized in a similar fashion to the other trityl derivatives according to scheme 4.4 below.



4.11

Scheme 4.4 *Synthesis of naphthalene trityl derivative*

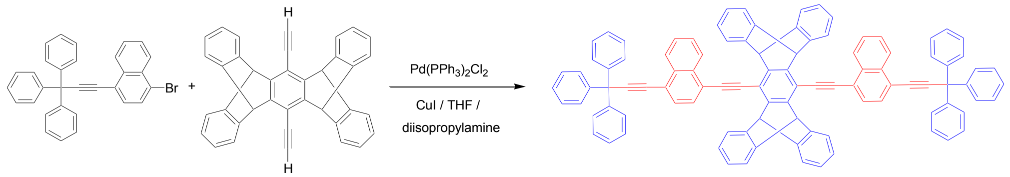
The trityl derivatives (**4.6-4.10)** were coupled to pentiptycene (**4.5**) in a two to one ratio via a palladium coupling reaction yielding the pentiptyl rotor derivatives (**4.12-4.16**) as shown in scheme 4.5.



4.12) R = H, R_1 = H
4.13) R = H, R_1 = m-OMe
4.14) R = H, R_1 = p-OMe
4.15) R = R_1 = m-OMe
4.16) R = R_1 = p-OMe

Scheme 4.5 *Synthesis of pentiptycene rotor derivatives*

Other pentiptycene rotor derivatives could be synthesized in a similar fashion to the synthesis outlined in scheme 4.6. A naphthalene pentiptycene rotor, **4.17**, was also synthesized in a similar fashion to the other pentiptycene rotor derivatives.



4.17

Scheme 4.6 *Synthesis of naphthalene pentiptycene derivative*

4.3 Properties of Pentiptycene Rotor Derivatives

The physical and electronic properties of these pentiptycene rotor derivatives were explored in more detail. In terms of solubility, the parent compound, **4.12**, was found to be nearly insoluble in all solvents that were attempted. Because of this methoxy groups were introduced on the trityl's outer phenyl rings to make pentiptycene derivatives (**4.13-4.16**). The amount of methoxy groups introduced varied (2 or 6) as well as the location of the methoxy groups (either meta or para). The more methoxy groups that were attached led to a more soluble pentiptycene derivative. Additionally, when equal amounts of methoxy groups were attached, the meta substituted methoxy derivatives were found to be more soluble than their para substituted counterparts.

Among the pentiptycene rotor derivatives only **4.13** was successfully crystallized by the slow evaporation of a toluene/dichloromethane solution. The X-ray crystal structure of **4.13** shows that the all the phenylenes in **4.13** are not coplanar. The two ethynylphenylenes are in the same plane, but the central phenylene (on pentiptycene) is not coplanar with them. Additionally, the alkynes present in the molecule were found to deviate from linearity leading **4.13** to develop a curved shape. The observed dihedral angle between the central pentiptycene phenyl ring and the outer rotator phenylenes was found to be 34.2°. All of the molecules in the crystal are aligned in the same direction. The interdigitated packing of our pentiptycene rotor derivative is similar to the observed packing of other pentiptycene derivatives.[17] The prevention of close intermolecular packing for **4.13** in the solid state due to the bulky groups is also evidenced by the presence of empty space in the crystal lattice, where several molecules of toluene are present in each unit cell. This packing arrangement where the pentiptycene rotor derivatives are widely spaced should be useful in limiting or preventing interchain electronic interactions. Also, it is important to note that the toluene molecules are found neighboring the phenylene rotators, which may allow for greater phenylene rotational freedom.

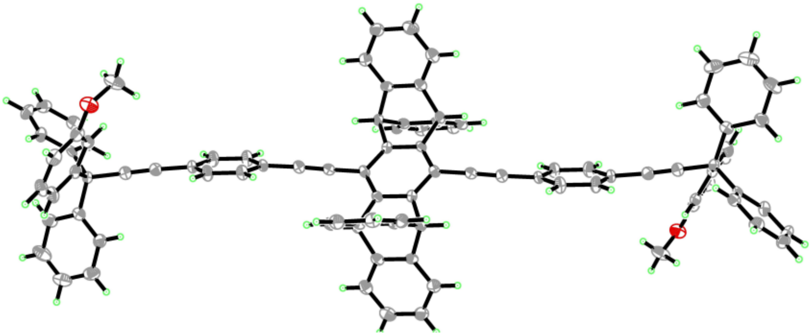


Figure 4.5 *Crystal structure of **4.13** at 100K with thermal ellipsoids at 50 % probability*

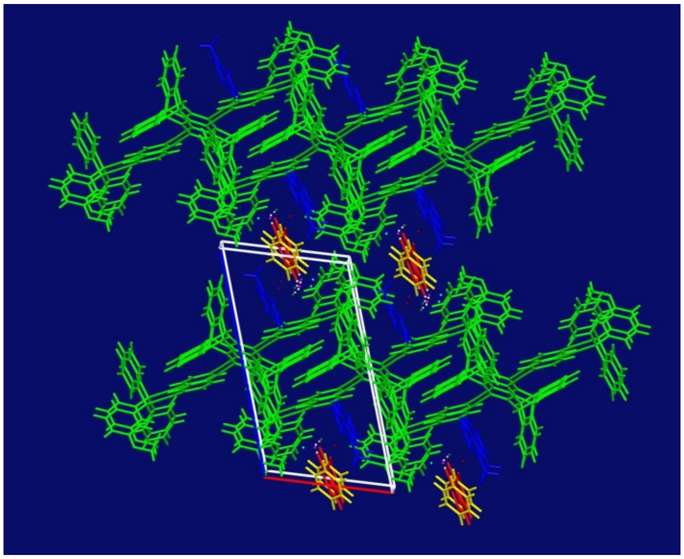


Figure 4.6 *Crystal packing of **4.13** illustrating the unit cell*

The thermal stability of the **4.13** was examined using thermogravimetric analysis (TGA). The TGA of the **4.13** shows that the molecule is stable up to 410 ^{o}C, at which point gradual loss of mass is observed. This gradual mass of mass can be possibly attributed to the loss of solvent from the crystal. While TGA analysis was not conducted on any other pentiptycene derivatives it is believed that they would display very similar TGA's as the one obtained for **4.13**.

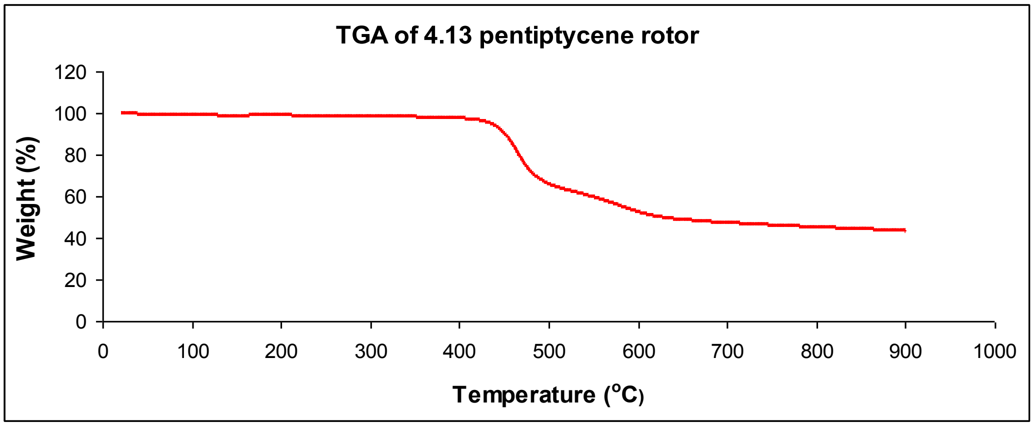


Figure 4.7** Thermogravimetric analysis of **4.13

The absorption spectrums of the four substituted pentiptycene derivatives (**4.13** – **4.16**) were measured at room temperature (in benzene) and are shown below in Figure 4.8. The spectrums of all four pentiptycene derivatives were nearly identical displaying a broad peak with a λ-max at 380 nm. The absorption spectra obtained shows some vibronic structure.

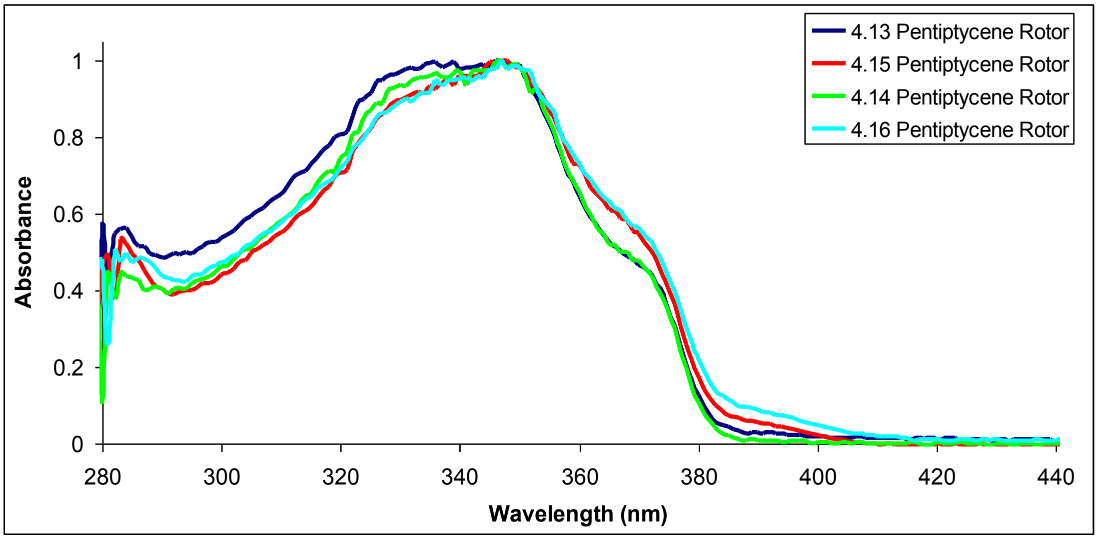


***Figure 4.8** UV-Vis spectrum of pentiptycene rotor derivatives (in benzene) at room temp.*

The fluorescence spectrum of the parent pentiptycene derivative (**4.12**) was obtained at room temperature (in benzene) and is shown below in Figure 4.9. The spectrums of all four pentiptycene derivatives were nearly identical displaying a broad peak with a λ-max at 380 nm. The fluorescence spectra obtained shows less vibronic structure.

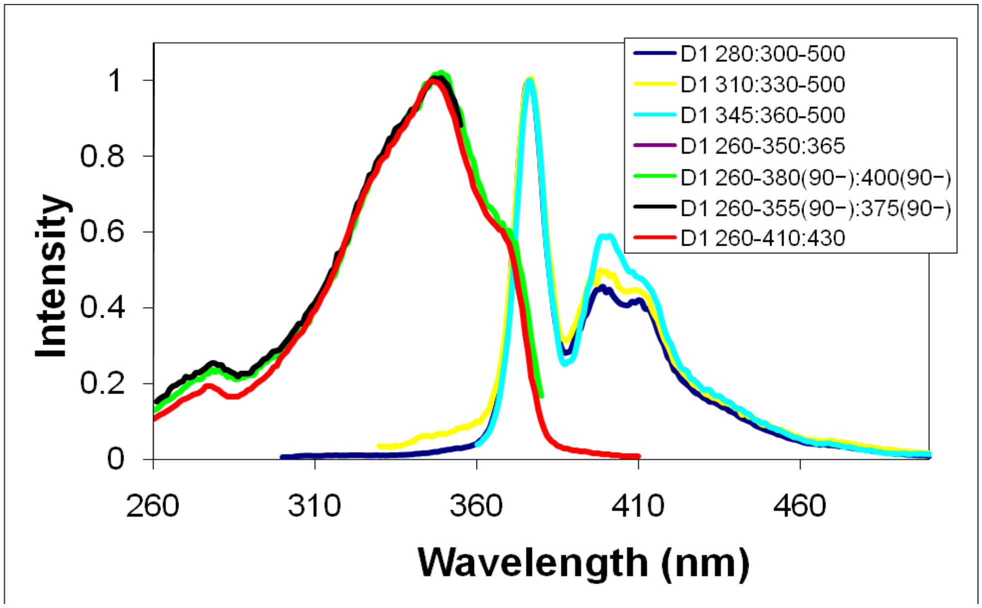
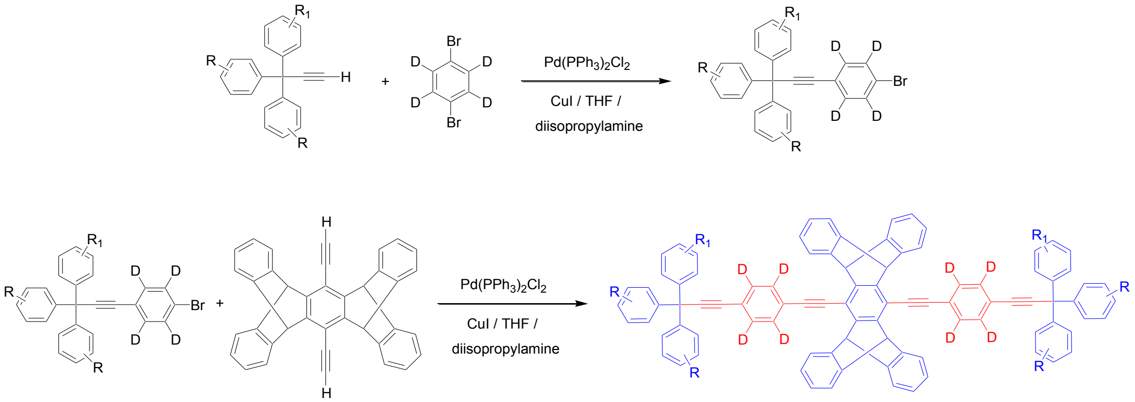


***Figure 4.9** Fluorescence spectra of **4.12** (in benzene)*

A lot of effort has been spent in our research group on designing dynamically interesting and rotational barrier free molecular rotors.[18] Increased interest in designing rotors with extra fast 2-fold exchange led us to explore the idea of increasing the stator frames as a means to decrease the rotational barrier. Our pentiptycene rotor derivatives with their bulky pentiptyl groups seemed like suitable candidates for this. In order to study the exchange rates in the solid state using cross polarization magic angle spinning(CPMAS) and dipolar dephasing (DD) spectra we synthesized a series of deuterated pentiptycene rotors (**4.18-4.22**) following the synthetic scheme previously used in the synthesis of nondeuterated pentiptycene rotors (**4.6-4.10**).



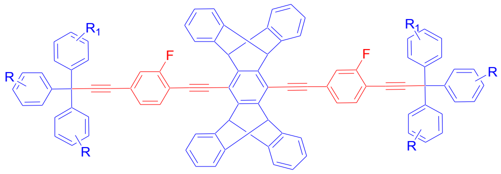
4.18) R = H, R_1 = H
4.19) R = H, R_1 = m-OMe
4.20) R = H, R_1 = p-OMe
4.21) R = R_1 = m-OMe
4.22) R = R_1 = p-OMe

Scheme 4.7 *Synthesis of deuterated pentiptycene rotor derivatives*

4.4 Conclusion

We have synthesized several pentiptycene rotor derivatives with the intent of studying the effects of planarization on the electronic properties of these phenyleneethynylene systems. By incorporating bulky pentiptycene groups it provides both a central shielding stator as well as a fixed central phenylene unit. The neighboring conjugated phenylene rotators will allow us to explore a variety of torsion angles and study their effects on the excitation and photophysical properties of our system. The X-ray crystal structure provides insight on how the molecule packs in the solid state. Some preliminary physical and electronic characterization of these derivatives has been achieved. Additionally, we have synthesized several deuterated pentiptycene rotor derivatives that will be studied using CPMAS and DD.

In the past, progress has been impeded by poor control of conformations and thus poor knowledge of the effect of planarization. We hope to address this problem in the future by introducing polar groups in the center rotating phenylenes (**4.23**) to help control the orientation of the linearly conjugated system.

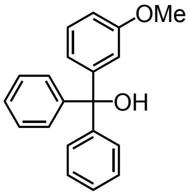


4.23

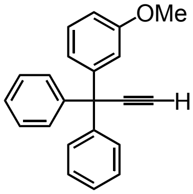
4.5 Experimental Results

Materials. Solvents and reagents were purchased from Aldrich, Fisher or VWR. THF was distilled over sodium/benzophenone under nitrogen. Dichloroethane was distilled from calcium hydride under argon. All experiments were carried out under argon or nitrogen unless specified. Other solvents and reagents were used as received.

Measurements. Solution NMR spectra were taken on either a Bruker ARX 400, 500 or an Avance 500 spectrometers as noted. All chemical shifts (δ) are reported relative to tetramethylsilane (TMS) at 0.0 ppm. FT-IR spectra were recorded on a Mattson Infinity II a spectrometer with a DRIFT accessory from PIKE Technologies, on a diamond frit. UV-visible spectra were obtained with a Hewlett Packard 8453 spectrophotometer. Mass spectra were obtained by matrix-assisted laser desorption/ionization (MALDI) on an Applied Biosystems Voyager-DE STR [matrix: dihydroxybenzoic acid (DHB] operated in reflector mode with internal calibration at an accelerating potential of 25 kV.

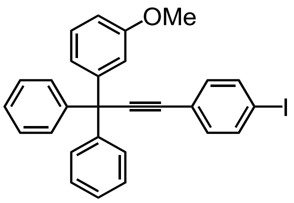


(3-methoxyphenyl)diphenylmethanol– A flame dried flask was charged with Mg turnings (2.16 g, 90 mmol). To this flask was added 150 mL of THF followed by the dropwise addition of 3-bromoanisole (7.2 mL, 60 mmol). The reaction mixture was left stirring for a period of 5 hours at RT. Afterwards, the newly prepared Grignard reagent was added to a flask containing benzophenone (9.11g, 50 mmol) dissolved in 40 mL of THF. The reaction mixture was left stirring overnight before being quenched with a saturated ammonium chloride solution and extracted with DCM. Silica gel chromatography starting with 10:1 hexanes: ether as the eluant and changing to a more polar eluant (5:1) afforded the alcohol product as a white solid (13.94 g, 96 %). ^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.34 - 7.28 (11 H, m, Ar), 6.98 – 6.88 (3H, m, Ar), 3.80 (3H, s), 2.98 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125-MHz) δ 159.2, 148.4, 146.7, 128.8, 127.8, 127.2, 120.5, 113.9, 112.,4, 81.9, 55.1 ppm.

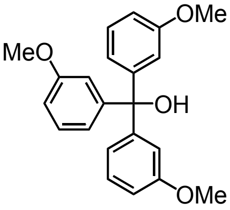


3-(3-methoxyphenyl)-3,3-diphenyl)propyne – To a flame dried flask was added 3-methoxyphenyl)diphenylmethanol (4.06 g, 14 mmol). The alcohol was dissolved using acetyl chloride (~ 8 mL). The solution was refluxed for a period of 2-3 hours. The excess acetyl chloride was evaporated. The resulting product was redissolved once again in acetyl chloride and stirred for a period of 12 hours. Removal of the excess acetyl chloride was followed by 3 washings with benzene. The resulting product was dissolved in benzene (~ 40 mL) and added to a flask containing benzene (~500 mL) and degassed with argon for 45 min. Under argon, ethynylmagnesium bromide (100 mL, 0.5 M THF, 50 mmol) was slowly added. The solution was refluxed for 6 – 12 hours. After cooling to room temperature the reaction was quenched with saturated ammonium chloride and the organic phase separated, the aqueous layer was extracted with DCM. The compound was purified by flash chromatography using 5:1 hexanes: DCM. The collected product (82 %) was a white solid. ^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.32- 7.28 (11H, m, Ar), 7.00- 6.88

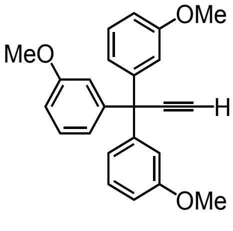
(3H, m, Ar), 3.81 ppm (3H, s), 2.79 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125-MHz) δ 159.2, 146.3, 144.6, 129.0, 128.8, 127.9, 126.9, 121.6, 115.4, 111.9, 89.6, 73.4, 55.4, 55.0 ppm;. MP 75.1 – 76.8° C; MS (MALDI): Calculated for $C_{22}H_{28}O$, 298.14 , found 298.13.



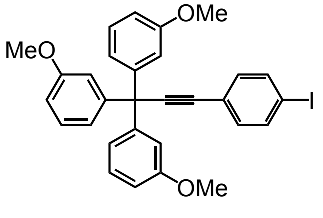
1-(4-iodophenyl)-3-(3-methoxyphenyl)-3,3-diphenylpropyne – To a 3-neck flask was added 150 ml of THF and 75 mL of diisopropylamine. The flask was purged with argon for 1 h. After 1h 3-(3-methoxyphenyl)-3,3-diphenyl)propyne (1.3 g, 4.4 mmol), 1,4-diiodobenzene (7.18 g, 21.8 mmol), bistriphenyl phosphine palladium dichloride (185 mg, 0.264 mmol), and copper iodide (50 mg, 0.528 mmol) were added quickly to the flask. The reaction mixture was refluxed overnight, cooled to room temperature, and quenched with saturated ammonium chloride. The aqueous layer was extracted with DCM and the solvent was evaporated. The resulting solid was purified by flash chromatography using hexanes to elute out the diiodobenzene and switching to a more polar hexanes: DCM mixture to elute out the product. The resulting product (61 %) was a white solid. ^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.72 (2H, m, Ar), 7.28-7.24 (13H, m, Ar), 6.94- 6.83 (3H, m, Ar), 3.76 (3H, s) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.2, 146.6, 144.9, 137.3, 133.1, 129.0, 128.9, 128.0, 126.9, 123.0, 121.7, 115.5, 111.8, 97.0, 93.7, 84.1, 56.1, 55.1 ppm; IR 2996, 2931, 2834, 1604, 1581, 1505, 1481, 1460, 1443, 1387, 1290, 1245, 1174, 1138, 1034, 1007, 827, 815, 778, 747, 695 cm^{-1}; MP 121.0 – 122.0° C; MS (MALDI): Calculated for $C_{28}H_{21}OI$, 500.06, found 500.01.



tri(3-methoxyphenyl)methanol– A flame dried flask was charged with Mg turnings (2.16 g, 90 mmol). To this flask was added 160 mL of THF followed by the dropwise addition of 3-bromoanisole (7.2 mL, 60 mmol). The reaction mixture was left stirring for a period of 5 hours at RT. Afterwards, the Grignard reagent was added to a flask containing diethyl carbonate (2.0 mL, 17 mmol) dissolved in 60 mL of THF. The reaction mixture was left stirring overnight before being quenched with a saturated ammonium chloride solution and extracted with DCM. Silica gel chromatography starting with 10:1 hexanes: ether as the eluant and changing to a more polar eluant afforded the alcohol product (4.49 g, 76 %). ^{1}H NMR (CDCl$_3$, 500-MHz) δ 7.20 (3H, m, Ar), 6.89- 6.88 (3H, m, Ar), 6.84- 6.80 (6H, m, Ar), 3.75 (9H, s) 2.82 (1H, s) ppm; ^{13}C NMR (CDCl$_3$, 125-MHz) δ 159.1, 148.1, 128.7, 120.4, 113.8, 112.4, 81.9, 55.1 ppm; IR 3457, 2936, 2833, 1604, 1582, 1481, 1448, 1433, 1316, 1290, 1234, 1163, 1146, 1046, 1033, 968, 952, 893, 874, 851, 720, 705 cm^{-1}; MP 118.0 – 119.0° C.

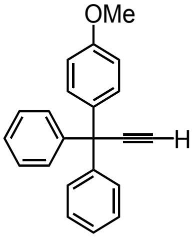


3,3,3-tri(3-methoxyphenyl)propyne – To a flame dried flask was added tri(3-methoxyphenyl)methanol (4.20 g, 12 mmol). The alcohol was dissolved using acetyl chloride (~ 14 mL). The solution was refluxed for a period of 2-3 hours. The excess acetyl chloride was evaporated. The resulting product was redissolved once again in acetyl chloride and stirred for a period of 12 hours. Removal of the excess acetyl chloride was followed by 3 washings with benzene. The resulting product was dissolved in benzene and added to a flask containing benzene (500 mL) and degassed with argon for 45 min. Under argon, ethynylmagnesium bromide (100 mL, 0.5 M THF, 50 mmol) was slowly added. The solution was refluxed for 6 – 12 hours. After cooling to room temperature the reaction was quenched with saturated ammonium chloride and the organic phase separated, the aqueous layer was extracted with DCM. The compound was purified by flash chromatography using 2: 1, hexanes : DCM. The product was recovered as an orange-yellow oil (3.41 g, 77 %). ^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.25 (3H, t, Ar), 6.90- 6.79 (9H, m, Ar), 3.74 (9H, s) 2.71 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125-MHz) δ 159.2, 145.9, 128.7, 121.6, 115.3, 111.9, 89.3, 73.4, 55.4, 55.1 ppm; IR : 3005, 2936, 2834, 1602, 1580, 1480, 1448, 1431, 1313, 1291, 1237, 1175, 1147, 1132, 1048, 1027, 1007, 875, 814, 773, 764, 697 cm^{-1}; MS (MALDI): Calculated for $C_{24}H_{22}O_3$, 358.16, found 358.15.

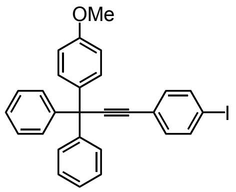


1-(4-iodophenyl)-3,3,3-tri(3-methoxyphenyl)propyne – To a 3-neck flask was added 250 ml of THF and 125 mL of diisopropylamine. The flask was purged with argon for 1 h. After 1h 3,3,3-tri(3-methoxyphenyl)propyne (3.26 g, 9.1 mmol), 1,4-diiodobenzene

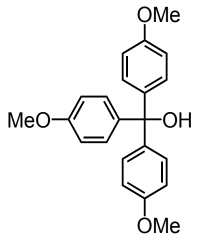
(14.8 g, 45 mmol), bistriphenyl phosphine palladium dichloride (383 mg,0.546 mmol), and copper iodide (210 mg, 1.092 mmol) were added quickly to the flask. The reaction mixture was refluxed overnight then it was cooled to room temperature and quenched with saturated ammonium chloride. The aqueous layer was extracted with DCM and the solvent was evaporated. The resulting solid was purified by flash chromatography using hexanes to elute out the diiodobenzene and switching to 2: 1 hexanes: DCM to elute out the product. The resulting product (3.21 g, 63 %) was a white solid. ^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.69 (2H, d, Ar), 7.31- 7.26 (5H, m, Ar), 6.97- 6.85 (9 H, m, Ar), 3.85 (9H, s) ppm; ^{13}C NMR ($CDCl_3$, 125-MHz) δ 159.2, 146.3, 137.3, 133.0, 128.8, 122.9, 121.6, 115.4, 111.9, 96.7, 93.7, 84.1, 56.0, 55.1 ppm; IR 3059, 3006, 2954, 2937, 2835, 1602, 1581, 1480, 1448, 1431, 1314, 1291, 1291, 1264, 1237, 1175, 1148, 1133, 1048, 1027, 1007, 875, 826, 814, 773, 764, 697 cm^{-1}; MP 142.0 – 143.0° C; MS (MALDI): Calculated for $C_{30}H_{25}OI$, 560.08, found 560.01.



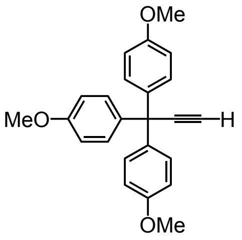
3-(4-methoxyphenyl)-3,3-diphenyl)propyne – (3-methoxyphenyl)diphenylmethanol (5.00 g, 16 mmol) was dissolved in benzene (500 mL) and degassed with argon for 45-60 min. Under argon ethynylmagnesium bromide (100 mL, 0.5 M THF, 50 mmol) was slowly added. The solution was refluxed for 6 hours. After cooling to room temperature the reaction was quenched with saturated ammonium chloride and the organic phase was separated, the aqueous layer was extracted with DCM. The combined organic phases were dried over sodium sulfate, evaporated to dryness under vacuum. The compound was purified by flash chromatography using 5: 1 hexanes: DCM. The product (3.35 g, 70 %) was a light yellow solid. ^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.35- 7.29 (12H, m, Ar), 6.95-6.92 (2H, m, Ar), 3.87 (3H, s), 2.80 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125-MHz) δ 158.4, 145.0, 136.8, 130.1, 129.0, 128.0, 126.9, 113.3, 89.9, 73.2, 55.2, 54.8 ppm; MS (MALDI): Calculated for $C_{22}H_{18}O$, 298.14, found 298.13.



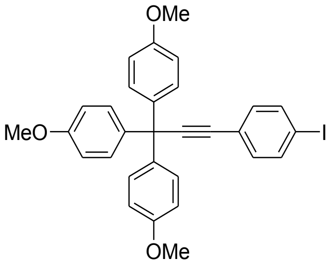
1-(4-iodophenyl)-3-(4-methoxyphenyl)-3,3-diphenyl)propyne – To a 3-neck flask was added 150 ml of THF and 75 mL of diisopropylamine. The flask was purged with argon for 1 h. After 1h 3-(4-methoxyphenyl)-3,3-diphenyl)propyne (1.2 g, 4.0 mmol), 1,4-diiodobenzene (6.46 g, 19.6 mmol), bistriphenyl phosphine palladium dichloride (166 mg, 0.237 mmol), and copper iodide (45 mg, 0.475 mmol) were added quickly to the flask. The reaction mixture was refluxed overnight then it was cooled to room temperature and quenched with saturated ammonium chloride. The aqueous layer was extracted with DCM and the solvent was evaporated. The resulting solid was purified by flash chromatography using hexanes to elute out the diiodobenzene and switching to 4: 1, hexanes: DCM to elute out the product. The resulting product (59 %) was a white solid. IR 3058, 3024, 2951, 2929, 2905, 2834, 1604, 1581, 1507, 1482, 1462, 1445, 1389, 1296, 1250, 1177, 1115, 1032, 1005, 816, 796, 756, 743, 696 cm^{-1}; MP 115.5 – 117.0° C.



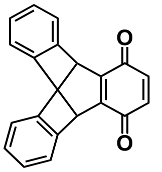
3,3,3-tri(4-methoxyphenyl)methanol – A flame dried flask was charged with Mg turnings (2.16 g, 90 mmol). To this flask was added 150 mL of THF followed by the drowse addition of 4-bromoanisole (7.2 mL, 60 mmol). The reaction mixture was left stirring for a period of 5 hours at RT. Afterwards, the Grignard reagent was added to a flask containing 4,4'-dimethoxybenzophenone (12.17g, 50 mmol) dissolved in 40 mL of THF. The reaction mixture was left stirring overnight before being quenched with a saturated ammonium chloride solution and extracted with DCM. Silica gel chromatography using 10:1 hexanes: ether as the eluant and changing to a more polar eluant afforded the alcohol product. ^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.24- 7.21 (6H, d, Ar), 6.89-6.86 (6H, d, Ar), 3.84 (9H, s), 2.86 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125-MHz) δ 185.4, 139.6, 129.0, 113.0, 81.0, 55.1 ppm.



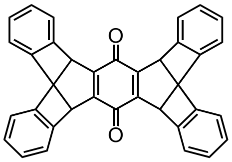
3,3,3-tri(4-methoxyphenyl)propyne - To a flame dried flask was added tri(4-methoxyphenyl)methanol (4.20 g, 12 mmol). The alcohol was dissolved using acetyl chloride (~ 16 mL). The solution was refluxed for a period of 2-3 hours. The excess acetyl chloride was evaporated. The resulting product was redissolved once again in acetyl chloride and stirred for a period of 12 hours. Removal of the excess acetyl chloride was followed by 3 washings with benzene. The resulting product was dissolved in benzene and added to a flask containing benzene (500 mL) and degassed with argon for 45 min. Under argon, ethynylmagnesium bromide (100 mL, 0.5 M THF, 50 mmol) was slowly added. The solution was refluxed for 6 – 12 hours. After cooling to room temperature the reaction was quenched with saturated ammonium chloride and the organic phase separated, the aqueous layer was extracted with DCM. The compound was purified by flash chromatography using, hexanes: DCM. The product was recovered as an orange- yellow oil (3.01 g, 68 %). ^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.25 (6H, d, Ar), 6.88 (6H, d, Ar), 3.85 (9H, s), 2.73 (1H, s) ppm; ^{13}C NMR ($CDCl_3$, 125-MHz) δ 158.2, 137.4, 129.9, 113.2, 90.2, 72.7, 55.1, 53.3 ppm; MS (MALDI): Calculated for $C_{24}H_{22}O_3$, 358.16, found 358.13.



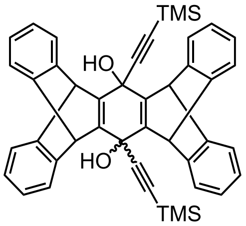
1-(4-iodophenyl)-3,3,3-tri(4-methoxyphenyl)propyne – To a 3-neck flask was added 250 ml of THF and 125 mL of diisopropylamine. The flask was purged with argon for 1 h. After 1h 3,3,3-tri(4-methoxyphenyl)propyne (3.26 g, 9.1 mmol), 1,4-diiodobenzene (14.8 g, 45 mmol), bistriphenyl phosphine palladium dichloride (383 mg,0.546 mmol), and copper iodide (210 mg, 1.092 mmol) were added quickly to the flask. The reaction mixture was refluxed overnight then it was cooled to room temperature and quenched with saturated ammonium chloride. The aqueous layer was extracted with DCM and the solvent was evaporated. The resulting solid was purified by flash chromatography using hexanes to elute out the diiodobenzene and switching to hexanes: DCM to elute out the product. The resulting product (3.09 g, 61 %) was a white solid. ^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.67 (2H, d, Ar), 7.26-7.24 (8H, m, Ar), 6.89 (6H, d, Ar), 3.82 (9H, s) ppm; ^{13}C NMR ($CDCl_3$, 125-MHz) δ 158.2, 137.7, 137.3, 133.1, 130.1, 123.1, 113.2, 97.7, 93.6, 83.5, 55.2, 54.0 ppm.



9,10-Dihydro-9,10-*o*-benzenoanthracene-1,4-dione A mixture of anthracene (4.0 g, 22.5 mmol) and benzoquinone (4.86 g, 45 mmol) were added to round bottom flask. Acetic acid (100 mL) was added to the flask and the reaction mixture was refluxed for 4 h. The reaction mixture was cooled to RT, poured into water, and the precipitate was filtered and collected. The crude product was dissolved in chloroform and extracted using a saturated $NaHCO_3$ solution. The resulting brown solid was purified by column chromatography using chloroform as the eluant to give a yellow solid the triptycene quinone (84 %). ^{1}H NMR ($CDCl_3$, 500-MHz) 5.80 (s, 2H), 6.60 (s, 2H), 7.04 (d, 4H, Ar), 7.43 (d, 4H, Ar) ppm; ^{13}C NMR ($CDCl_3$, 125-MHz) 47.4, 124.40, 125.6, 135.4, 143.6, 151.9, 183.5 ppm.

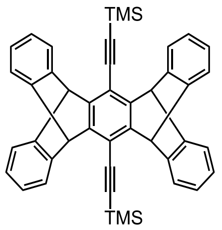


5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(*o*-benzeno)pentacene-6,13-dione - A mixture of 9,10-Dihydro-9,10-*o*-benzenoanthracene-1,4-dione (2.8 g, 10 mmol), anthracene (1.8 g, 1 mmol), and *p*-chloranil (2.5 g, 10 mmol) in AcOH (120 mL) was refluxed for 24 h. The resulting mixture was cooled to room temperature. The precipitate was filtered, washed with ether. Column chromatography using 4:1 Hexanes: DCM and switching to a more polar solvent mixture afforded the product. The product was dried in vacuo to give 4.56 g (82 %) as a yellow solid. ^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.37- 7.35 (8H, m, Ar), 6.99- 6.96 (8H, m, Ar), 6.60 (2H, s, Ar), 5.76 (4H, s) ppm; ^{13}C NMR ($CDCl_3$, 125-MHz) δ 179.9, 150.9, 143.5, 125.3, 124.1, 47.3 ppm.

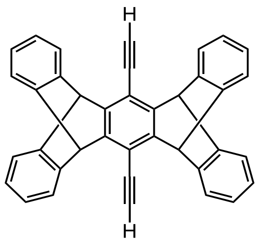


6,13-bis((trimethylsilyl)ethynyl)-5,6,7,12,13,14-hexahydro-5,14:7,12-bis([1,2]benzene)pentacene-6,13-diol - To a flask containing 60 mL of THF, trimethylsilyl acetylene (5 mL, 36 mmol) and at 0° C was added n-BuLi in hexane (30 mmol) dropwise. The TMSLi mixture was then kept at 0° C for another 1 h before it was added to a solution of 5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(*o*-benzeno)pentacene-6,13-dione (2.00 g, 4.35 mmol) in THF at 0°C. The mixture was left to warm to room temperature and stirred overnight. The reaction was quenched with saturated NH_4Cl and extracted with DCM. The solvent was evaporated and column chromatography using 3:1 Hexanes: DCM was used to elute the first impurities, followed by switching to 1:1 hexanes : DCM to elute out product. The resulting product was a white solid (75 %

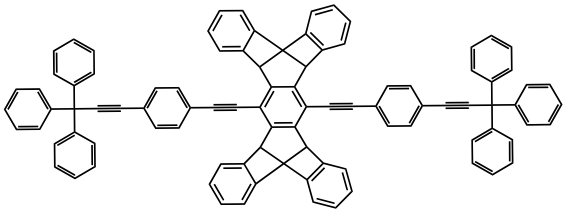
yield), which is a mixture of the trans and cis isomers. ^{1}H NMR ($CDCl_3$, 500-MHz) 7.36 (dd, *J* = 3.2 and 5.3 Hz, 8H, Ar), 6.96 (dd, *J* = 3.2 and 5.3 Hz, 8H, Ar), 5.80 (s, 4H), 0.51 (s, 18H) ppm; ^{13}C NMR $CDCl_3$, 125-MHz) 0.31, 52.2, 100.7, 102.5, 114.8, 123.8, 125.2, 144.1, 144.9 ppm.



6,13-bis((trimethylsilyl)ethynyl)-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzene)pentacene - This crude diol (3.464 g, 5.550 mmol) was dissolved in 60 mL of acetone and then a solution of tin(II) chloride dihydrate (3.235 g) in 50% of acetic acid (60 mL) was added dropwise. This mixture was stirred at room temperature for another 24 h and the resulting solid product was filtered to give a slightly yellow colored solid in 81 % yield. ^{1}H NMR ($CDCl_3$, 500-MHz) 7.34- 7.33 (8H, m, Ar), 6.96- 6.94 (8H, m, Ar), 5.78 (2H, s,), 0.49 (18H, s) ppm; ^{13}C NMR ($CDCl_3$, 125-MHz) δ 144.8, 143.9, 125.1, 123.6, 102.4, 100.5, 52.1, 0.2 ppm.

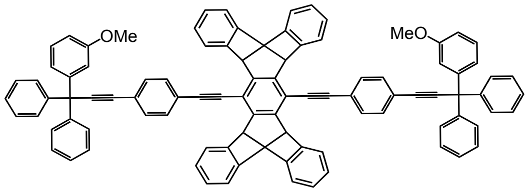


6,13-diethynyl-5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzene)pentacene-The deprotection of the trimethylsilyl group was carried out by dissolving compounds TMS protected (1.444 g, 2.369 mmol) in a mixture of KOH (two tablets in 1 mL of H_2O), THF, and MeOH and stirring at room temperature for 5 h. The resulting white solid product (89 %) was filtered and washed with water and then dried in vacuo. ^{1}H NMR ($CDCl_3$, 500-MHz) 3.79 (s, 2H), 5.85 (s, 2H), 6.07 (s, 2H), 6.91 (dd, *J* = 3.1 and 5.3 Hz, 4H), 7.32-7.36 (m. 8H), 7.67 (dd, *J* = 3.3 and 6.1 Hz, 4H), 7.82 (s, 4H) ppm; ^{13}C NMR ($CDCl_3$, 125-MHz) δ 51.24, 51.98, 78.96, 84.92, 114.13, 122.18, 123.83, 125.31, 125.75, 127.47, 131.90, 140.63, 143.12, 144.51, 145.35 ppm; MS (MALDI): Calculated for $C_{38}H_{22}$, 478.17, found 478.15.



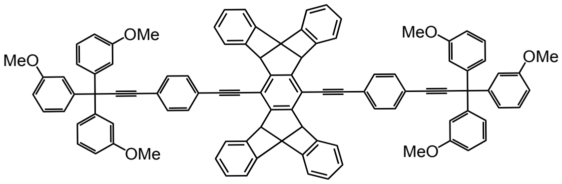
Bis(p-(2-(4-3,3,3-triphenylpropynyl)-p-phenylene)ethynylene pentiptycene- A flask containing THF (60 mL) and diisopropylamine (30 mL) was degassed with argon for a period of 1h. To this flask was added trityl derivative (0.220 g, 0.44 mmol), pentiptycene (0.96 g, 0.2 mmol), bis(triphenylphosphine) palladium dichloride (0.016 g, 0.026 mmol,), copper iodide (0.010 g, 0.0528 mmol). The flask was then sparged with argon for 10 min. The reaction mixture was heated to reflux for 48 h. The reaction was then cooled to room temperature, quenched with ammonium chloride solution and extracted with dichloromethane. The solvent was evaporated and the product was purified by column chromatography starting with CH_2Cl_2: hexanes 1: 4 and increasing the polarity of the solvent to elute the product. The product was obtained as a white solid (25 %).

MP decomposes 430° C; MS (MALDI): Calculated for $C_{92}H_{58}$, 1162.45 found 1162.66.

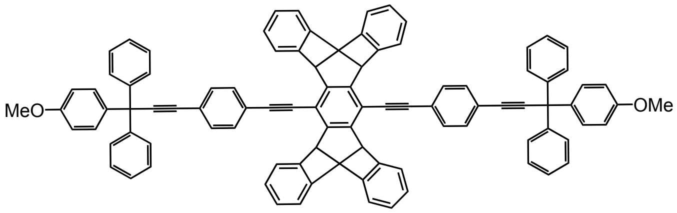


Bis(p-(2-(4-(3-(3-methoxyphenyl)-3,3-diphenyl)propynyl)-p-phenylene)ethynylene pentiptycene - A flask containing THF (60 mL) and diisopropylamine (30 mL) was degassed with argon for a period of 1h. To this flask was added 1-(4-iodophenyl)-3-(3-methoxyphenyl)-3,3-diphenylpropyne (0.220 g, 0.44 mmol), pentiptycene (0.96 g, 0.2 mmol), bis(triphenylphosphine) palladium dichloride (0.016 g, 0.026 mmol,), copper iodide (0.010 g, 0.0528 mmol). The flask was then sparged with argon for 10 min. The reaction mixture was heated to reflux for 48 h. The reaction was then cooled to room temperature, quenched with ammonium chloride solution and extracted with dichloromethane. The solvent was evaporated and the product was purified by column chromatography starting with CH_2Cl_2: hexanes 1: 4 and increasing the polarity of the solvent to elute the product. The product was obtained as a white solid (25 %).

^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.74 (4H, d, Ar), 7.67 ((4H, d, Ar), 7.39-6.85 (44H, m, Ar), 5.87 (4H, s), 3.79 (6H, s) ppm; IR 3021, 2962, 2925, 2852, 1725, 1597, 1582, 1508, 1487, 1458, 1446, 1433, 1290, 1249, 1179, 1149, 1102, 1034, 1026, 833, 749, 695 cm^{-1}; MP decomposes 430^o C; MS (MALDI): Calculated for $C_{94}H_{62}O_2$, 1222.47, found 1222.31.

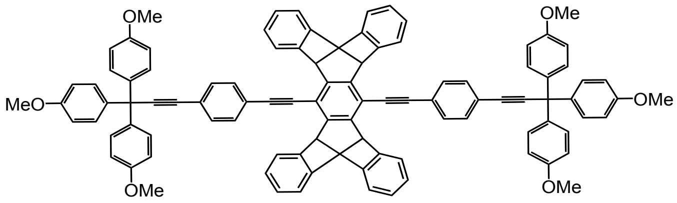


Bis(p-(2-(4-3,3,3-tri(3-methoxy)phenylpropynyl)-p-phenylene)ethynylene pentiptycene - A flask containing THF (95 mL) and diisopropylamine (45 mL) was degassed with argon for a period of 1h. To this flask was added 1-(4-iodophenyl)-3,3,3-tri(3-methoxyphenyl)propyne (0.700 g, 1.25 mmol), pentiptycene (0.239 g, 0.50 mmol), bis(triphenylphosphine) palladium dichloride (0.053 g, 0.075 mmol,), copper iodide (0.029 g, 0.15 mmol). The flask was then sparged with argon for 10 min. The reaction mixture was heated to reflux for 48 h. The reaction was then cooled to room temperature, quenched with ammonium chloride solution and extracted with dichloromethane. The solvent was evaporated and the product was purified by column chromatography starting with CH_2Cl_2: hexanes 1:1 and increasing the polarity of the solvent to elute the product. The product was obtained as a white solid (34 %). ^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.75 (4H,, d, Ar), 7.66 (4H, d, Ar), 7.39-7.27 (16H, m, Ar), 6.98 (20H, m, Ar), 6.85 (8H, m, Ar), 5.87 (4H, s), 3.79 (18H, s) ppm. IR 3001, 2934, 2832, 1597, 1582, 1508, 1483, 1458, 1432, 1379, 1312, 1290, 1240, 1177, 1150, 1048, 997, 875, 858, 835, 764, 754, 695 cm^{-1}; MP decomposes at 400^{o} C; MS (MALDI): Calculated for $C_{98}H_{70}O_6$, 1342.52, found 1342.38.

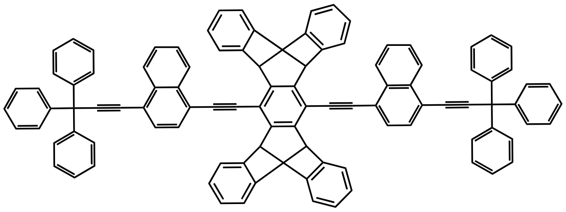


Bis(p-(2-(4-(3-(4-methoxyphenyl)-3,3-diphenyl)propynyl)-p-phenylene)ethynylene pentiptycene - A flask containing THF (60 mL) and diisopropylamine (30 mL) was degassed with argon for a period of 1h. To this flask was added 1-(4-iodophenyl)-3-(4-methoxyphenyl)-3,3-diphenyl)propyne (0.220 g, 0.44 mmol), pentiptycene (0.96 g, 0.2 mmol), bis(triphenylphosphine) palladium dichloride (0.016 g, 0.026 mmol,), copper iodide (0.010 g, 0.0528 mmol). The flask was then sparged with argon for 10 min. The reaction mixture was heated to reflux for 48 h. The reaction was then cooled to room temperature, quenched with ammonium chloride solution and extracted with dichloromethane. The solvent was evaporated and the product was purified by column chromatography starting with CH_2Cl_2: hexanes 1:4 and increasing the polarity of the solvent to elute the product. The product was obtained as a white solid (27 %).

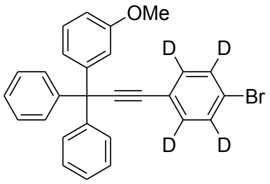
^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.81- 7.71 (9H, m, Ar), 7.44 – 7.31 (30H, m, Ar), 7.02-6.95 (13H, m, Ar), 5.94 (4H, s), 3.90 (6H, s) ppm; ^{13}C NMR ($CDCl_3$, 125-MHz) δ 158.3, 145.3, 144.6, 143.9, 137.2, 131.7, 131.5, 130.1, 129.0, 127.9, 126.8, 125.2, 123.9, 123.7, 122.7, 114.6, 113.3, 98.1, 96.5, 86.4, 84.5, 55.4, 55.1, 52.2 ppm; IR : 3061, 2925, 1603, 1582, 1507, 1489, 14457, 1446, 1381, 1293, 1251, 1178, 1033, 830, 794, 752, 699, 671 cm^{-1}; MP decomposes above 440° C; MS (MALDI): Calculated for $C_{94}H_{62}O_2$, 1222.49, found 1222.37.



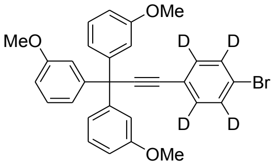
Bis(p-(2-(4-3,3,3-tri(4-methoxy)phenylpropynyl)-p-phenylene)ethynylene pentiptycene - A flask containing THF (90 mL) and diisopropylamine (45 mL) was degassed with argon for a period of 1h. To this flask was added 1-(4-iodophenyl)-3,3,3-tri(4-methoxyphenyl)propyne (0.560 g, 1 mmol), pentiptycene (0.191 g, 0.40 mmol), bis(triphenylphosphine) palladium dichloride (0.042 g, 0.06 mmol,), copper iodide (0.022 g, 0.12 mmol). The flask was then sparged with argon for 10 min. The reaction mixture was heated to reflux for 48 h. The reaction was then cooled to room temperature, quenched with ammonium chloride solution and extracted with dichloromethane. The solvent was evaporated and the product was purified by column chromatography starting with CH_2Cl_2: hexanes 1:1 and increasing the polarity of the solvent to elute the product. The product was obtained as a white solid (32 %). ^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.80-7.78 (4H, d, 8.0 Hz, Ar), 7.70-7.68 (4H, d, 8.0 Hz, Ar), 7.44 – 7.43 (9H, m, Ar), 7.34 – 7.31 (8 H, m, Ar), 7.01 – 6.93 (23 H, m, Ar) 5.96 (4 H, s) 3.89 ppm; (18 H, s) ppm; IR 3067, 3001, 2951, 2929, 2904, 1605, 1582, 1505, 1458, 1440, 1296, 1247, 1175, 1152, 1113, 1033, 904, 826, 754, 741, 672 cm^{-1}; MP decomposes above 370^o C;
MS (MALDI): Calculated for $C_{98}H_{70}O_6$, 1342.52, found 1342.17.



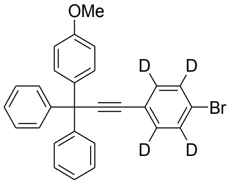
Bis(p-(2-(4-3,3,3-triphenylpropynyl)-p-naphthylene)ethynylene pentiptycene – To a 3-neck flask was added 60 ml of THF and 30 mL of diisopropylamine. The flask was purged with argon for 1 h. After 1h 1-(4-bromonaphthyl)-3,3,3-triphenylpropyne (208 mg, 0.44 mmol), pentiptycene (95.7 mg, 0.20 mmol), bistriphenyl phosphine palladium dichloride (19 mg, 0.026 mmol), and copper iodide (10 mg, 0.053 mmol) were added quickly to the flask. The reaction mixture was refluxed for 2-3 days then it was cooled to room temperature and quenched with saturated ammonium chloride. The aqueous layer was extracted with DCM and the solvent was evaporated. The resulting solid was purified by flash chromatography using 4: 1, hexanes : DCM and increasing the polarity of the solvent over time to elute out the product. The resulting product (0.064 g, 25 %) was a white solid. IR 3057, 3019, 2961, 2922, 1597, 1570, 1489, 1458, 1446, 1383, 1305, 1177, 1151, 1032, 1021, 890, 842, 762, 751, 742, 696, 673 cm^{-1}; MP decomposes 430^{o} C; MS (MALDI): Calculated for $C_{100}H_{62}$, 1262.49, found 1262.31.



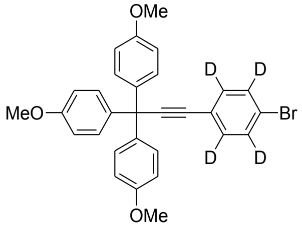
1-(d4-4-bromophenyl)-3-(3-methoxyphenyl)-3,3-diphenylpropyne – To a 3-neck flask was added 50 ml of THF and 25 mL of diisopropylamine. The flask was purged with argon for 1 h. After 1h 3-(3-methoxyphenyl)-3,3-diphenyl)propyne (0.80g, 2.67 mmol), 1,4-dibromobenzene-d4 (1.93 g, 8.04 mmol), bistriphenyl phosphine palladium dichloride (0.161 mmol, 113 mg), and copper iodide (0.322 mmol, 61 mg) were added quickly to the flask. The reaction mixture was refluxed overnight then it was cooled to room temperature and quenched with saturated ammonium chloride. The aqueous layer was extracted with DCM and the solvent was evaporated. The resulting solid was purified by flash chromatography using 10: 1 hexanes: DCM to elute out the d-dibromobenzene and switching to 4: 1 hexanes: DCM to elute out the product. The resulting product (0.77 g, 62 %) was a colorless solid. IR 3061, 3024, 2954, 2931, 2834, 1597, 1578, 1482, 1445, 1432, 1387, 1307, 1287, 1253, 1135, 1050, 1033, 1016, 1009, 875, 777, 764, 755, 736, 697 cm^{-1}; MP 117.5– 119.0^{o} C; MS (MALDI): Calculated for $C_{28}H_{17}D_4OBr$, 456.1, found 456.07.



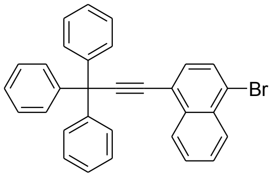
1-(d4-4-bromophenyl)-3,3,3-tri(3-methoxyphenyl)propyne - To a 3-neck flask was added 250 ml of THF and 125 mL of diisopropylamine. The flask was purged with argon for 1 h. After 1h 3,3,3-tri(3-methoxyphenyl)propyne (3.26 g, 9.1 mmol), 1,4-dibromobenzene-d4 (10.8 g, 45 mmol), bistriphenyl phosphine palladium dichloride (383 mg,0.546 mmol), and copper iodide (210 mg, 1.092 mmol) were added quickly to the flask. The reaction mixture was refluxed overnight then it was cooled to room temperature and quenched with saturated ammonium chloride. The aqueous layer was extracted with DCM and the solvent was evaporated. The resulting solid was purified by flash chromatography using hexanes to elute out the diiodobenzene and switching to 2: 1 hexanes: DCM to elute out the product. The resulting product (3.01 g, 59 %) was a white solid. ^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.33- 7.30 (3H, m, Ar), 7.06 – 7.05 (3H, m), 7.01-7.00 (3H, m, Ar), 6.91-6.89 (3H, m, Ar), 3.82 (3H, s) ppm; ^{13}C NMR ($CDCl_3$, 125-MHz) δ 159.3, 146.3, 132.8, 132.6, 132.4, 131.3, 131.1, 130.9, 128.9, 122.2, 121.9, 121.7, 115.5, 111.9, 96.5, 84.0, 56.1, 55.0 ppm;. IR 3052, 3001, 2956, 2937, 2834, 1596, 1582, 1482, 1432, 1290, 1240, 1148, 1050, 768, 734, 696 cm^{-1}; MS (MALDI): Calculated for $C_{30}H_{21}O_3D_4Br$, 516.12, found 516.10.



1-(4-d4-bromophenyl)-3-(4-methoxyphenyl)-3,3-diphenylpropyne (x) – To a 3-neck flask was added 50 ml of THF and 25 mL of diisopropylamine. The flask was purged with argon for 1 h. After 1h 3-(4-methoxyphenyl)-3,3-diphenyl)propyne (0.80g, 2.67 mmol), 1,4-dibromobenzene-d4 (1.93 g, 8.04 mmol), bistriphenyl phosphine palladium dichloride (0.161 mmol, 113 mg), and copper iodide (0.322 mmol, 61 mg) were added quickly to the flask. The reaction mixture was refluxed overnight then it was cooled to room temperature and quenched with saturated ammonium chloride. The aqueous layer was extracted with DCM and the solvent was evaporated. The resulting solid was purified by flash chromatography using 10 : 1, hexanes : DCM and increasing the polarity of the solvent over time to elute out the product. The resulting product (0.69 g, 56 %) was a colorless solid. IR 3031, 3004, 2928, 2832, 1607, 1598, 1583, 1507, 1490, 1457, 1446, 1389, 1300, 1248, 1178, 1152, 1116, 1020, 888, 823, 751, 739, 723, 696, 671 cm^{-1}; MP 115.5 – 117.0^{o} C; MS (MALDI): Calculated for $C_{28}H_{17}OD_4Br$, 456.10, found 456.07.

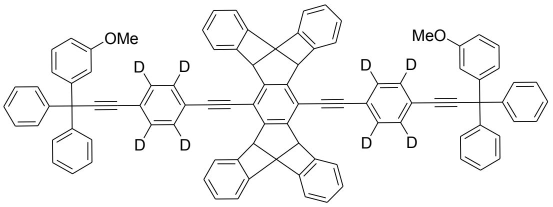


1-(d4-4-bromophenyl)-3,3,3-tri(4-methoxyphenyl)propyne – To a 3-neck flask was added 250 ml of THF and 125 mL of diisopropylamine. The flask was purged with argon for 1 h. After 1h 3,3,3-tri(4-methoxyphenyl)propyne (3.26 g, 9.1 mmol), 1,4-diiodobenzene (10.8 g, 45 mmol), bistriphenyl phosphine palladium dichloride (383 mg,0.546 mmol), and copper iodide (210 mg, 1.092 mmol) were added quickly to the flask. The reaction mixture was refluxed overnight then it was cooled to room temperature and quenched with saturated ammonium chloride. The aqueous layer was extracted with DCM and the solvent was evaporated. The resulting solid was purified by flash chromatography using hexanes to elute out the diiodobenzene and switching to hexanes: DCM to elute out the product. The resulting product (2.94g, 58 %) was a white solid. ^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.24- 7.23 (6H, m, Ar), 6.87 – 6.85 (3H, m) 3.82 (9H, s) ppm; ^{13}C NMR ($CDCl_3$, 125-MHz) δ 158.2, 137.7, 132.7, 132.5, 132.3, 131.1, 130.9, 130.7, 130.1, 129.9, 122.3, 121.7, 113.2, 97.4, 83.3, 55.1, 54.0 ppm; IR 2952, 2930, 2904, 2834, 1603, 1580, 1503, 1440, 1414, 1390, 1293, 1245, 1172, 1114, 1029, 1011, 823, 750, 704 cm^{-1}; MP 144.5 – 146.0^{o} C; MS (MALDI): Calculated for $C_{30}H_{21}O_3D_4Br$, 516.12, found 516.03.



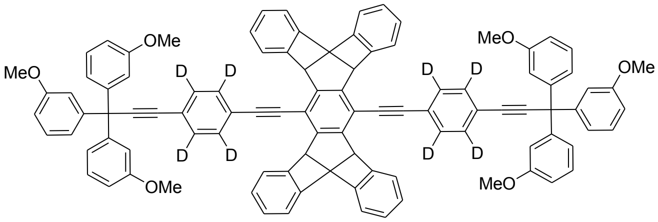
1-(4-bromonaphthyl)-3,3,3-triphenylpropyne – To a 3-neck flask was added 25 ml of THF and 12 mL of diisopropylamine. The flask was purged with argon for 1 h. After 1h trityl alkyne (0.201 g, 0.75 mmol), 1,4-dibromonapthalene (0.64 g, 2.25 mmol), bistriphenyl phosphine palladium dichloride (53 mg, 0.075 mmol), and copper iodide (61 mg, 0.315 mmol) were added quickly to the flask. The reaction mixture was refluxed overnight then it was cooled to room temperature and quenched with saturated ammonium chloride. The aqueous layer was extracted with DCM and the solvent was evaporated. The resulting solid was purified by flash chromatography first using hexanes to elute out the unreacted 1,4-dibromobnezne and then switching to a molar solvent using hexanes : DCM mixture . The resulting product (0.21 g, 59 %) was a white solid.

IR 3062, 3020, 1596, 1578, 1562, 1500, 1489, 1446, 1376, 1267, 1184, 1066, 1031, 897, 829, 757, 712, 697, 676 cm^{-1}; MS (MALDI): Calculated for $C_{31}H_{21}Br$, 472.08, found 472.00.

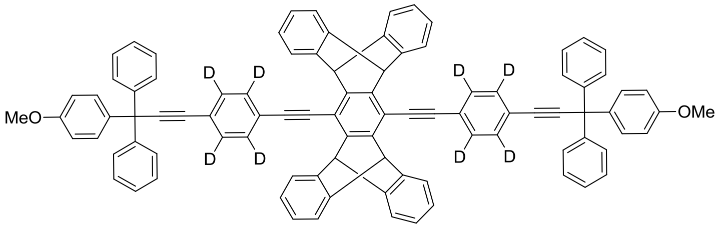


Bis(p-(2-(4-(3-(3-methoxyphenyl)-3,3-diphenyl)propynyl)-d8-p-phenylene)ethynylene pentiptycene – To a 3-neck flask was added 120 ml of THF and 60 mL of diisopropylamine. The flask was purged with argon for 1 h. After 1h 1-(d4-4-

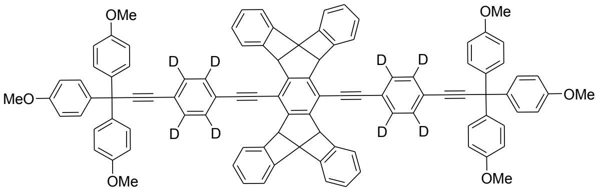
bromophenyl)-3-(3-methoxyphenyl)-3,3-diphenylpropyne (770 mg, 1.68 mmol), pentiptycene (323 mg, 0.675 mmol), bistriphenyl phosphine palladium dichloride (71 mg, 0.101 mmol), and copper iodide (38.6 mg, 0.203 mmol) were added quickly to the flask. The reaction mixture was refluxed for 2-3 days then it was cooled to room temperature and quenched with saturated ammonium chloride. The aqueous layer was extracted with DCM and the solvent was evaporated. The resulting solid was purified by flash chromatography using 4 : 1 , hexanes : DCM and increasing the polarity of the solvent over time to elute out the product. The resulting product (0.101 g, 15 %) was a white solid. IR 3061, 3021, 2969, 1597, 1487, 1458, 1447, 1431, 1416, 1311, 1290, 1249, 1180, 1153, 1050, 776, 745, 725, 715, 697 cm^{-1}; MP decomposes 430^{o} C; MS (MALDI): Calculated for $C_{94}H_{54}D_8O_2$, 1230.53, found 1230.46.



Bis(p-(2-(4-3,3,3-tri(3-methoxy)phenylpropynyl)-d8-p-phenylene)ethynylene pentiptycene – A flask containing THF (95 mL) and diisopropylamine (45 mL) was degassed with argon for a period of 1h. To this flask was added **1-(d4-4-bromophenyl)-3,3,3-tri(3-methoxyphenyl)propyne** (0.700 g, 1.25 mmol), pentiptycene (0.239 g, 0.50 mmol), bis(triphenylphosphine) palladium dichloride (0.053 g, 0.075 mmol,), copper iodide (0.029 g, 0.15 mmol). The flask was then sparged with argon for 10 min. The reaction mixture was heated to reflux for 48 h. The reaction was then cooled to room temperature, quenched with ammonium chloride solution and extracted with dichloromethane. The solvent was evaporated and the product was purified by column chromatography starting with CH_2Cl_2: hexanes 1:1 and increasing the polarity of the solvent to elute the product. The product was obtained as a white solid (34 %).



Bis(p-(2-(4-(3-(4-methoxyphenyl)-3,3-diphenyl)propynyl)-d8-p-phenylene)ethynylene pentiptycene – To a 3-neck flask was added 120 ml of THF and 60 mL of diisopropylamine. The flask was purged with argon for 1 h. After 1h 1-(4-d4-bromophenyl)-3-(4-methoxyphenyl)-3,3-diphenylpropyne (684 mg, 1.50 mmol), pentiptycene (287 mg, 0.6 mmol), bistriphenyl phosphine palladium dichloride (52.6 mg, 0.075 mmol), and copper iodide (28.6 mg, 0.15 mmol) were added quickly to the flask. The reaction mixture was refluxed for 2-3 days then it was cooled to room temperature and quenched with saturated ammonium chloride. The aqueous layer was extracted with DCM and the solvent was evaporated. The resulting solid was purified by flash chromatography using 4 : 1 , hexanes : DCM and increasing the polarity of the solvent over time to elute out the product. The resulting product (0.106 g, 15 %) was a white solid. ^{1}H NMR ($CDCl_3$, 500-MHz) δ 7.45- 7.31 (32H, m, Ar), 7.03 – 7.01 (8H, m, Ar), 6.96 -6.95 (4H, m, Ar), 5.93 (4H, s), 3.90 (6H, s); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 158.3, 145.3, 144.6, 143.9, 137.2, 130.1, 129.0, 127.9, 126.8, 125.2, 123.7, 122.5, 114.6, 113.3, 98.2, 96.4, 86.5, 84.4, 55.5, 55.1, 52.2 ppm; IR 3062, 3020, 2928, 2833, 1604, 1583, 1508, 1489, 1458, 1447, 1415, 1381, 1295, 1252, 1178, 1154, 1113, 1033, 968, 826, 794, 748, 724, 712, 698, 671 cm^{-1}; MP decomposes above 430^{o} C; MS (MALDI): Calculated for $C_{94}H_{54}D_8O_2$, 1230.53, found 1230.55.



Bis(p-(2-(4-3,3,3-tri(4-methoxy)phenylpropynyl)-d8-p-phenylene)ethynylene pentiptycene – To a 3-neck flask was added 80 ml of THF and 40 mL of diisopropylamine. The flask was purged with argon for 1 h. After 1-(d4-4-bromophenyl)-3,3,3-tri(4-methoxyphenyl)propyne (705 mg, 1.36 mmol), pentiptycene (261 mg, 0.545 mmol), bistriphenyl phosphine palladium dichloride (57 mg, 0.082 mmol), and copper iodide (31 mg, 0.16 mmol) were added quickly to the flask. The reaction mixture was refluxed for 2-3 days then it was cooled to room temperature and quenched with saturated ammonium chloride. The aqueous layer was extracted with DCM and the solvent was evaporated. The resulting solid was purified by flash chromatography using 1 : 1 , hexanes : DCM and increasing the polarity of the solvent over time to elute out the product. The resulting product (14 %) was a white solid. IR 3065, 2951, 2905, 2834, 1605, 1582, 1505, 1459, 1417, 1297, 1248, 1175, 1113, 1034, 825, 755, 725, 673 cm^{-1}; MP Decomposes at 450^{o} C.

Figure 4.10 *3,3,3-tri(3-methoxyphenyl)propyne* ^{1}H *NMR*

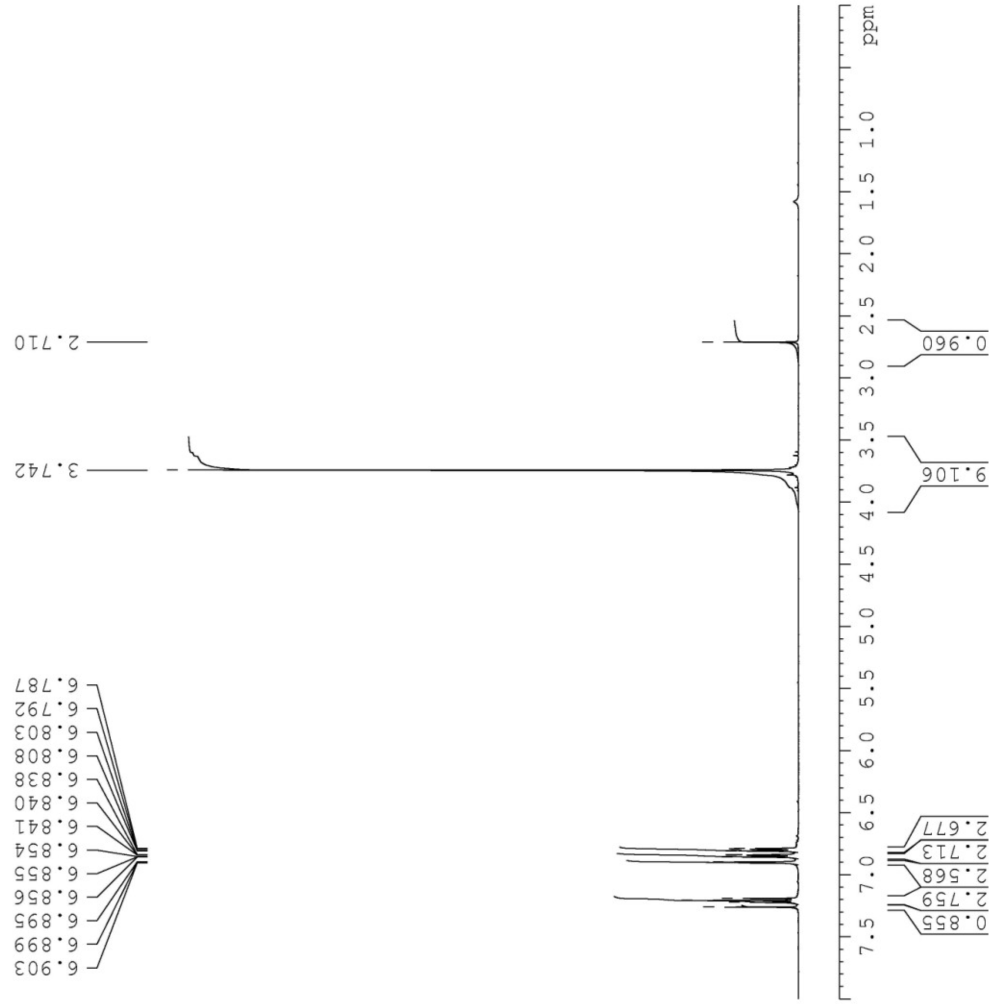


Figure 4.11 *3,3,3-tri(3-methoxyphenyl)propyne* ^{13}*C-NMR*

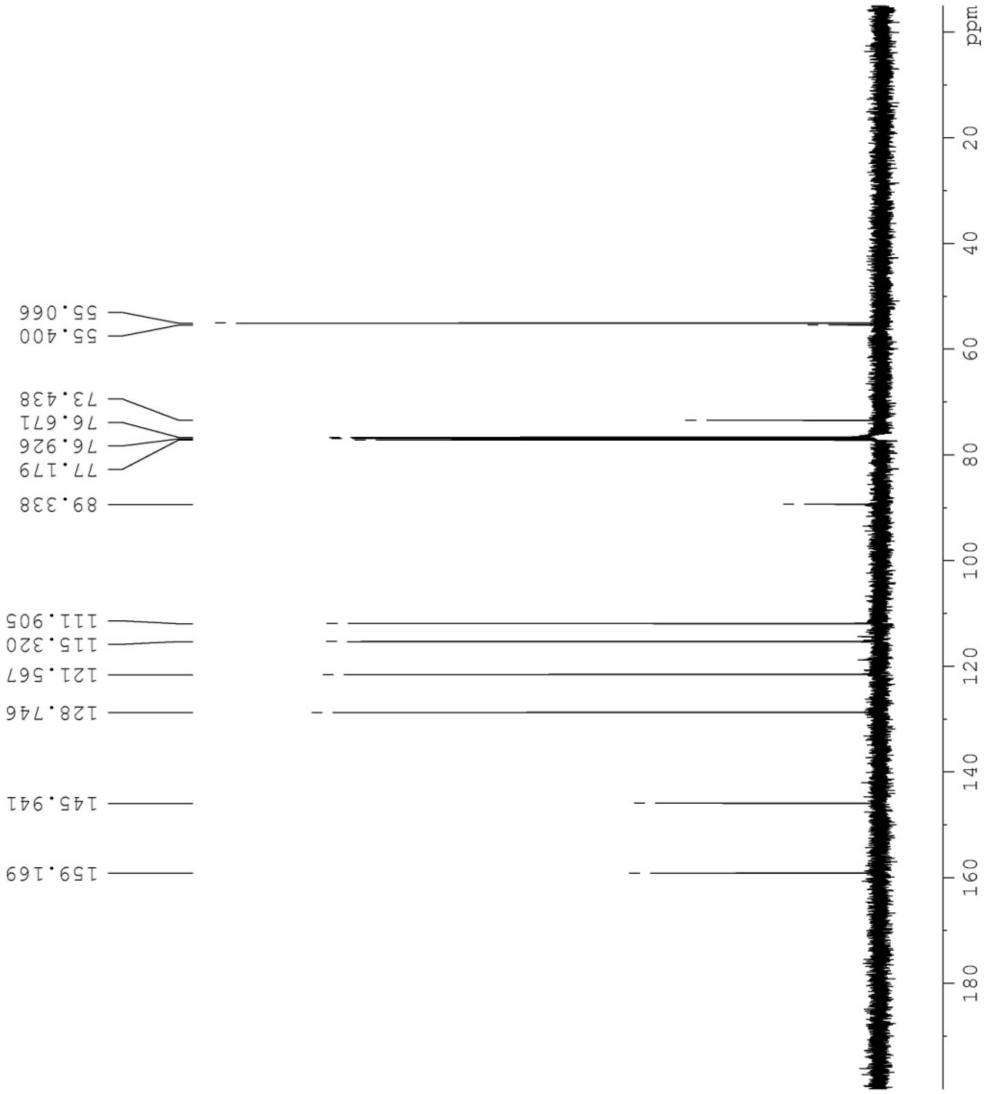


Figure 4.12 *(3-methoxyphenyl)diphenylmethanol* ^1H *NMR*

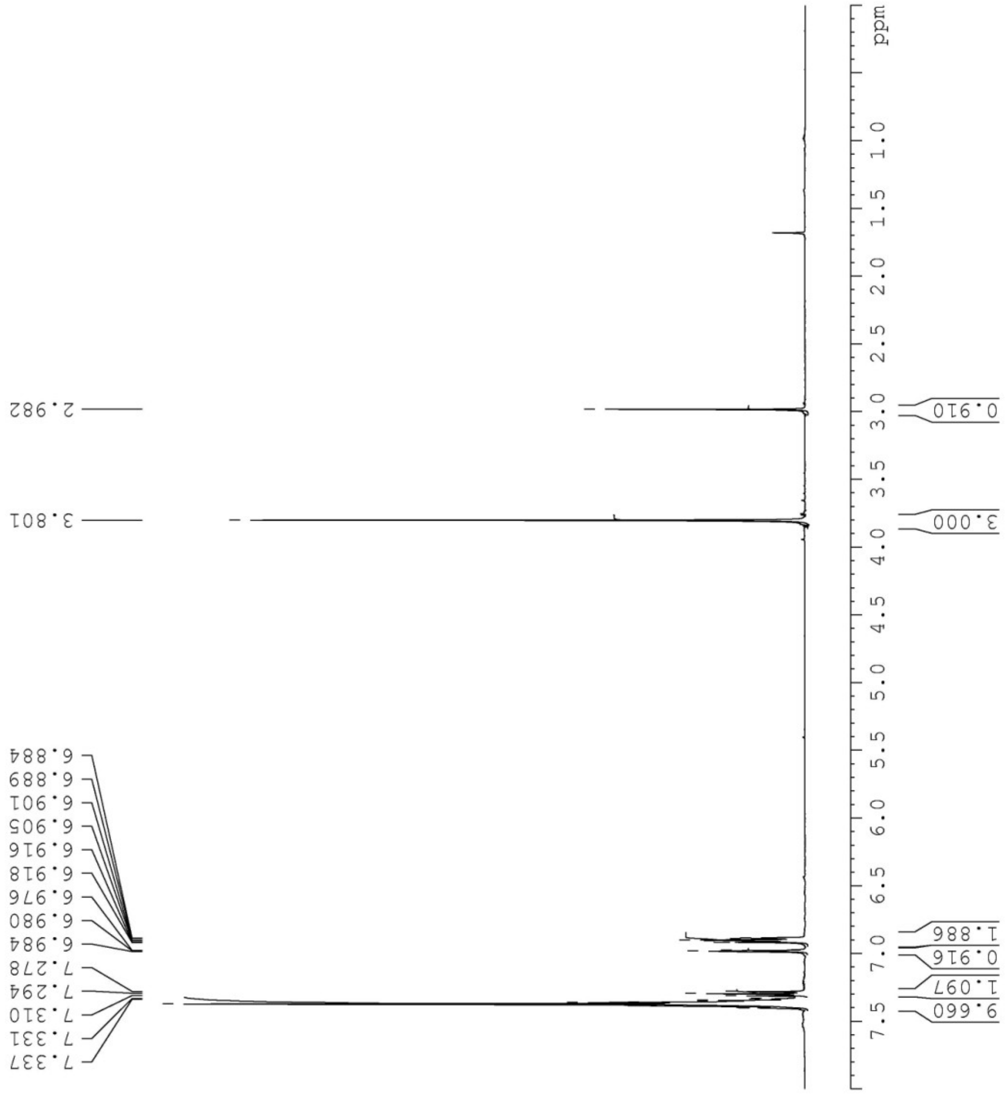


Figure 4.13 *(3-methoxyphenyl)diphenylmethanol* ^{13}*C-NMR*

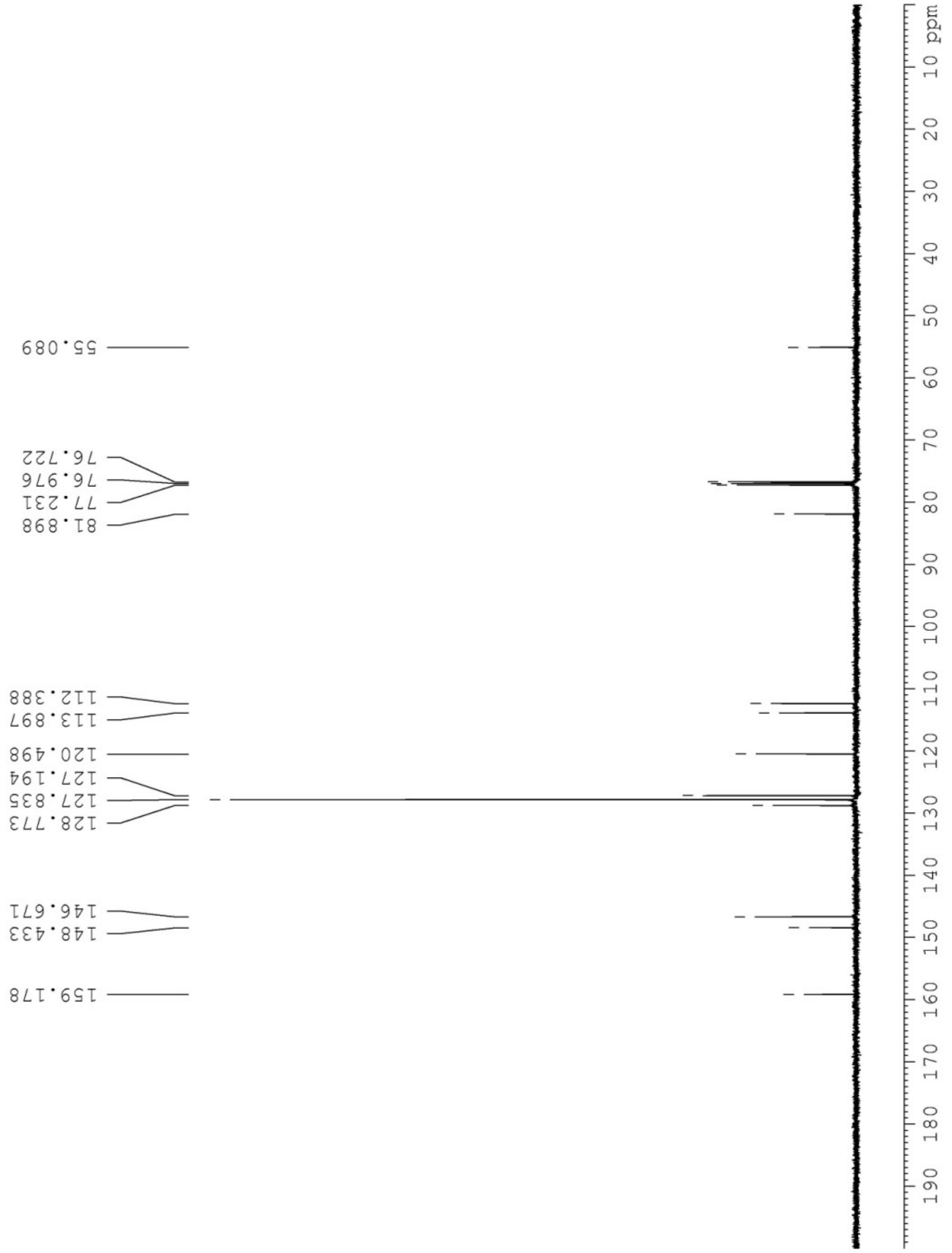


Figure 4.14 *3,3,3-tri(4-methoxyphenyl)propyne ^{1}H NMR*

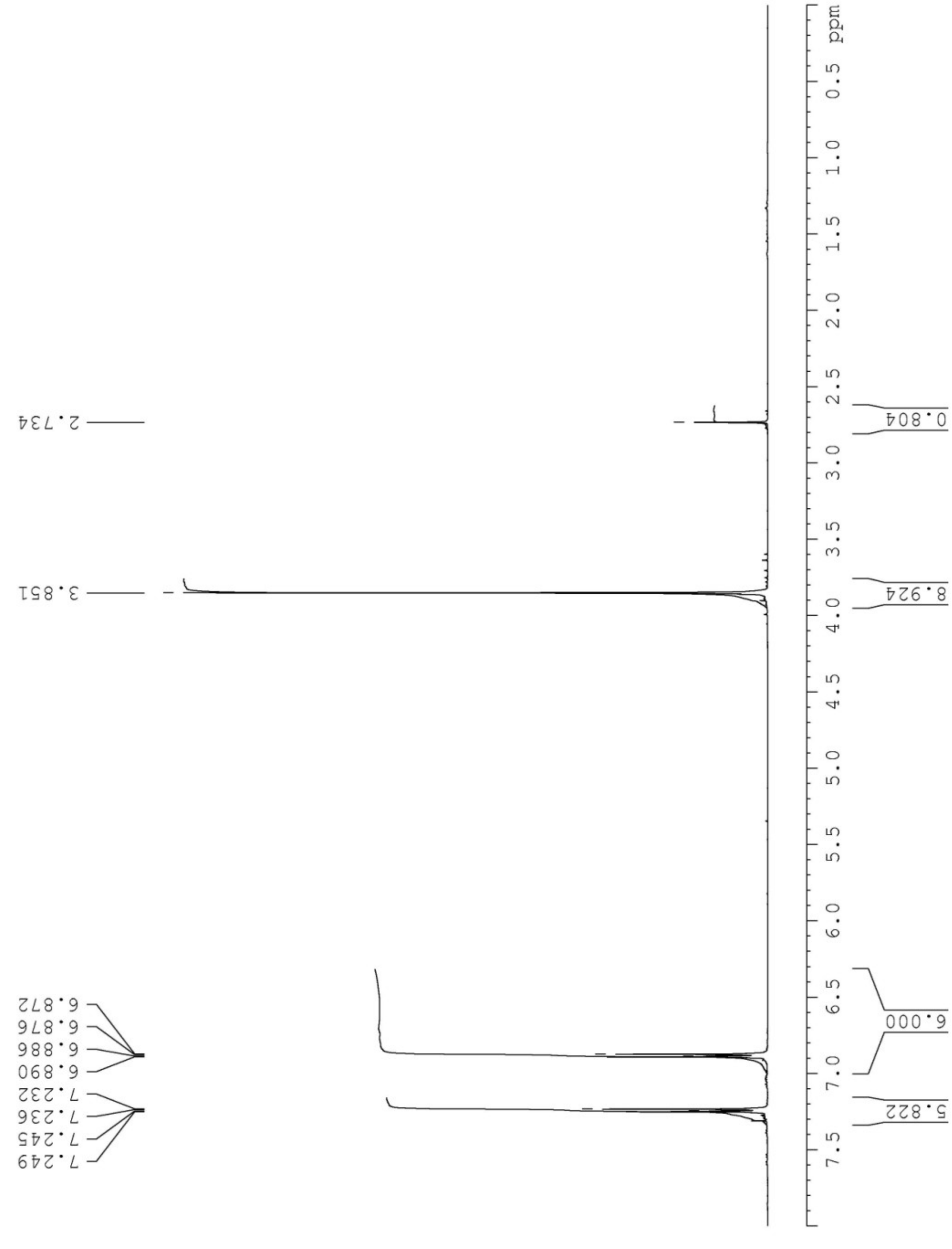


Figure 4.15 *3,3,3-tri(4-methoxyphenyl)propyne ^{13}C NMR*

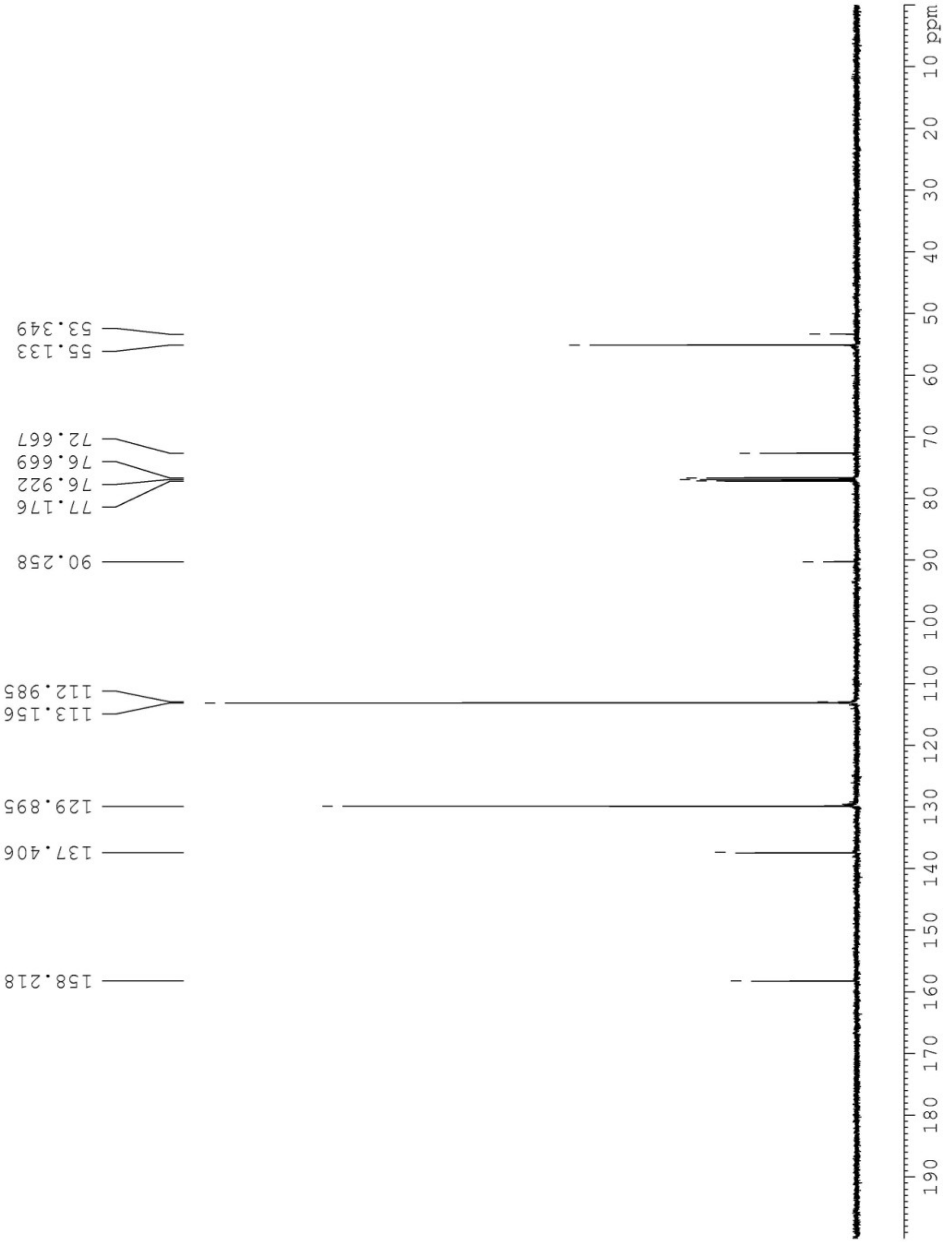


Figure 4.16 *3-(3-methoxyphenyl)-3,3-diphenyl)propyne ^{1}H NMR*

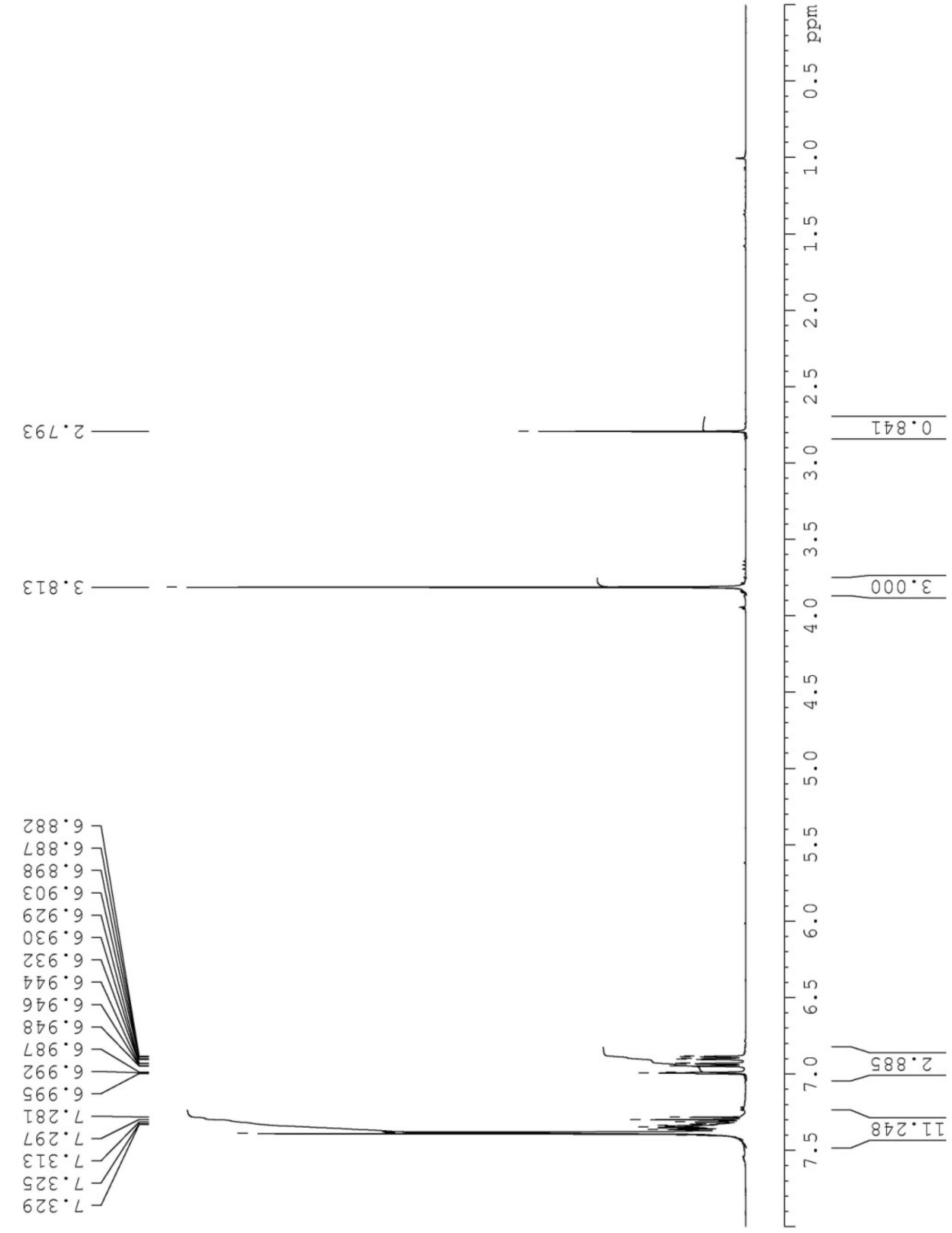


Figure 4.17 *3-(3-methoxyphenyl)-3,3-diphenyl)propyne* ^{13} *CNMR*

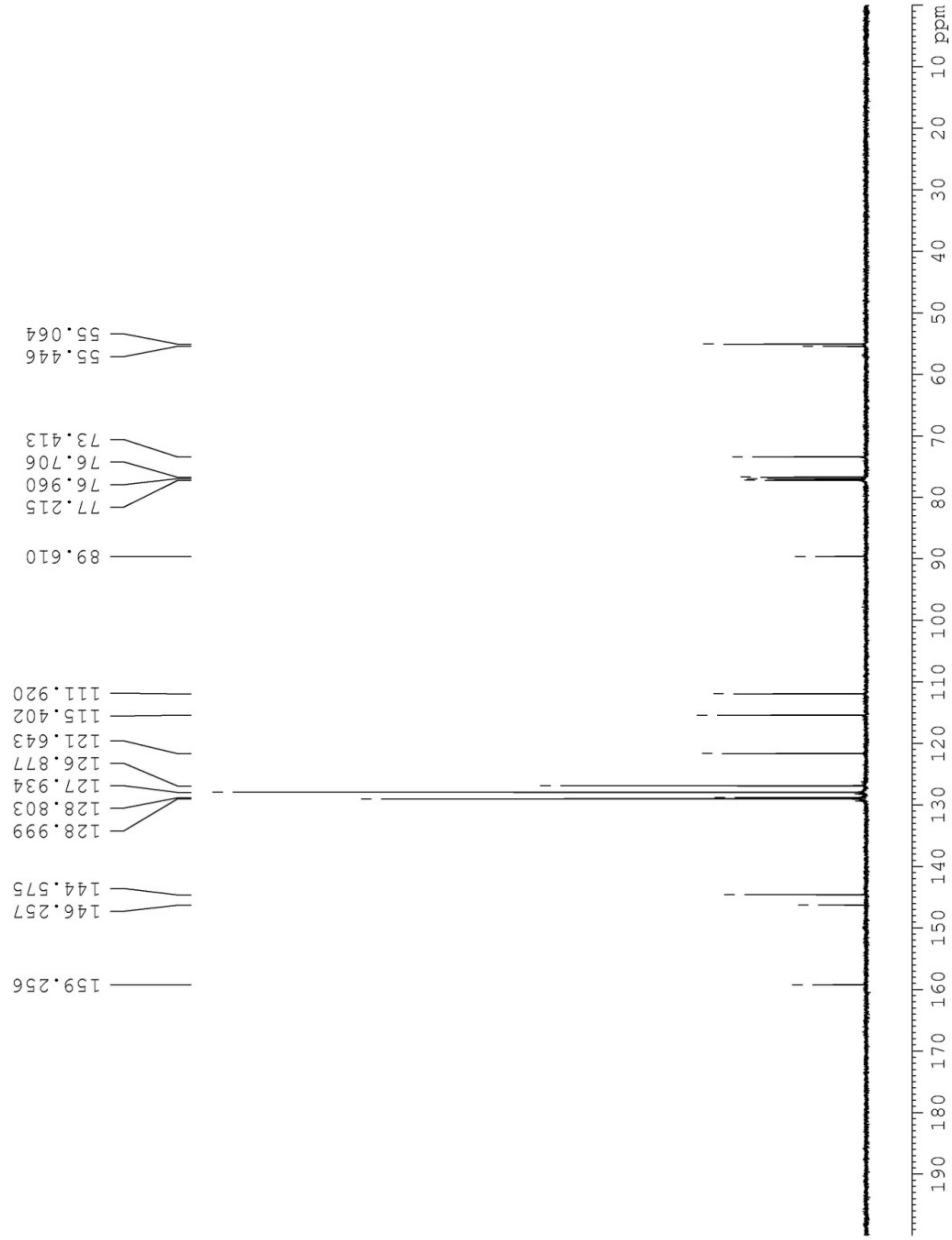


Figure 4.18 *1-(4-iodophenyl)-3,3,3-tri(3-methoxyphenyl)propyne* ^{1}H *NMR*

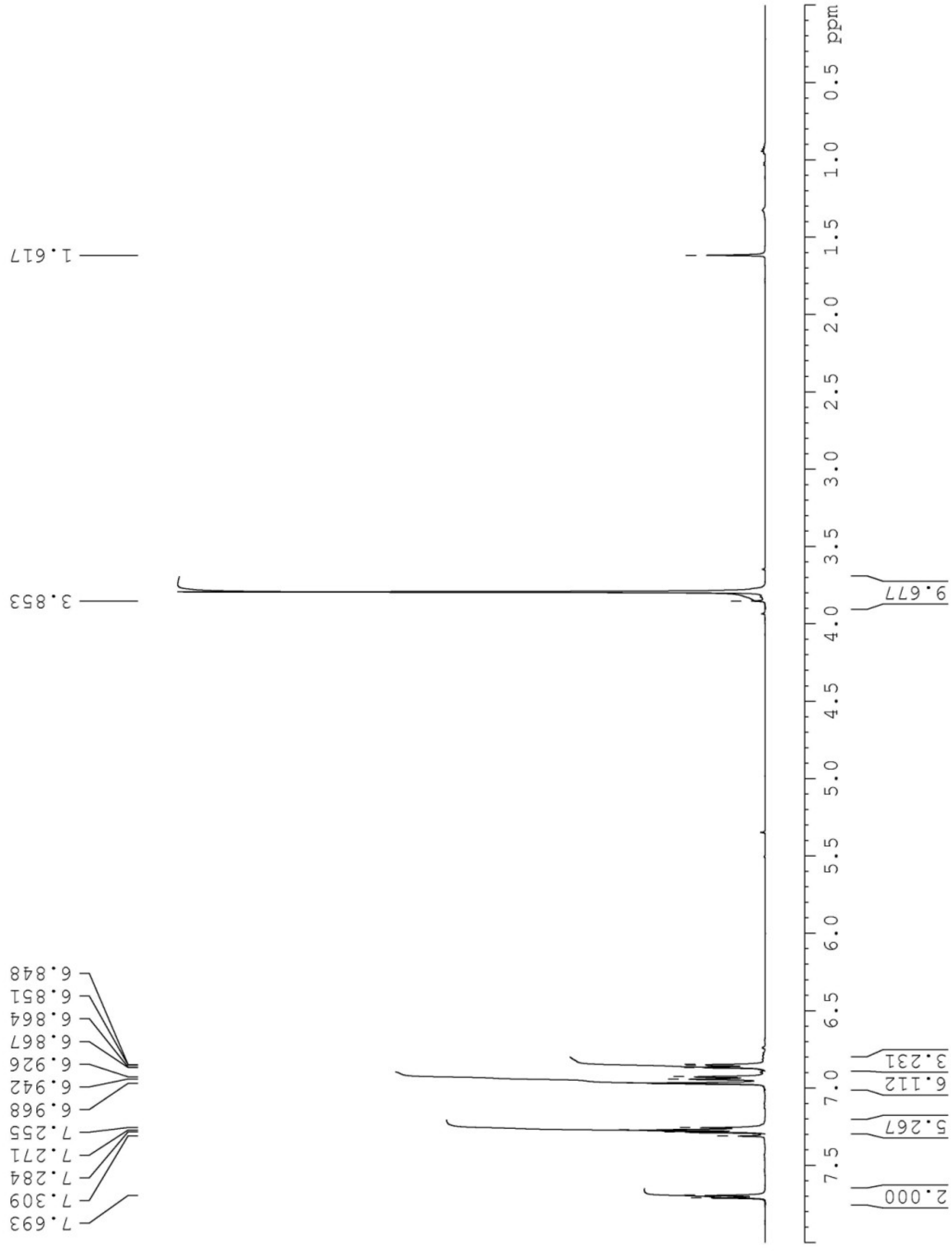


Figure 4.19 *1-(4-iodophenyl)-3,3,3-tri(3-methoxyphenyl)propyne ^{13}C NMR*

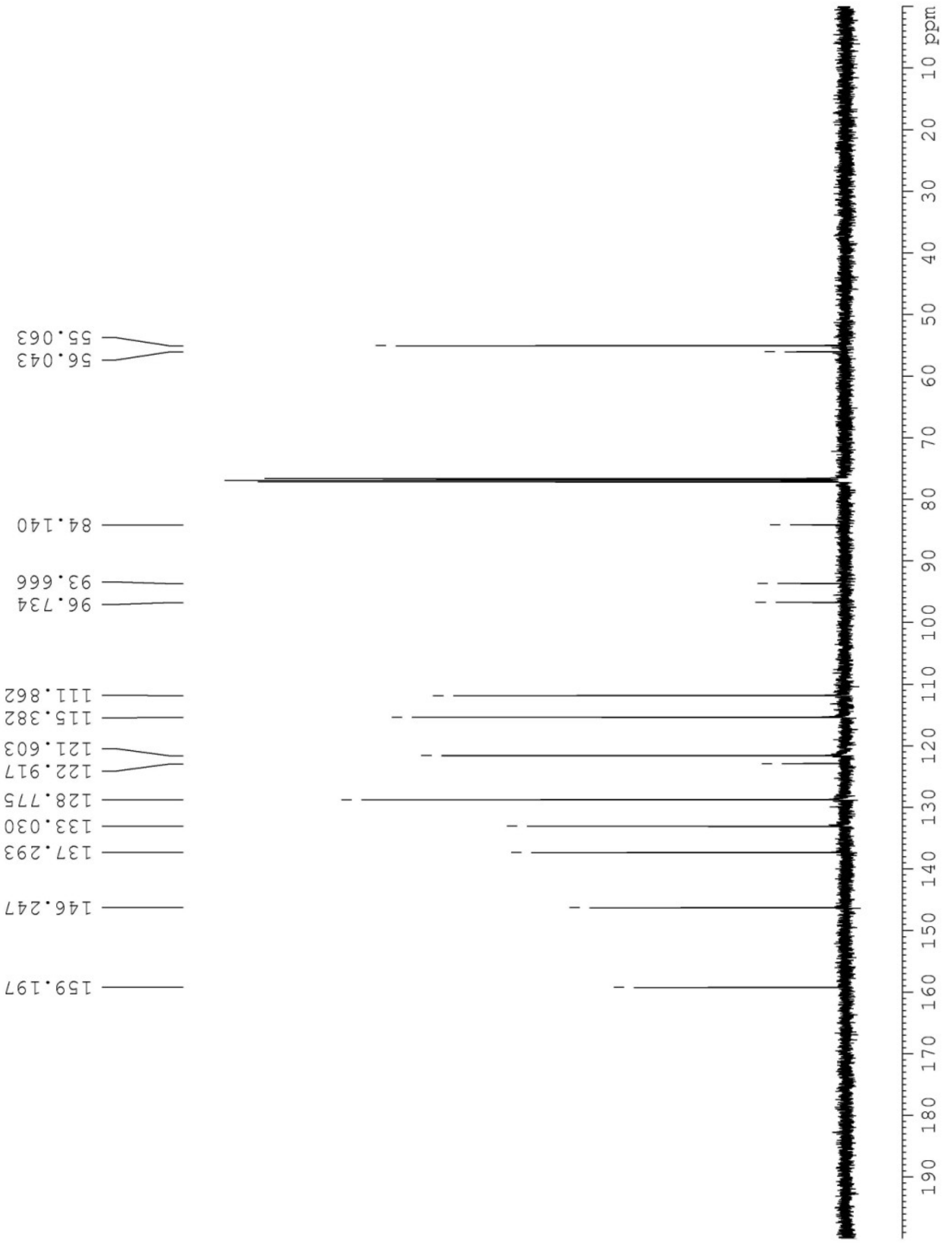


Figure 4.20 *3-(4-methoxyphenyl)-3,3-diphenyl)propyne* ^{1}*H NMR*

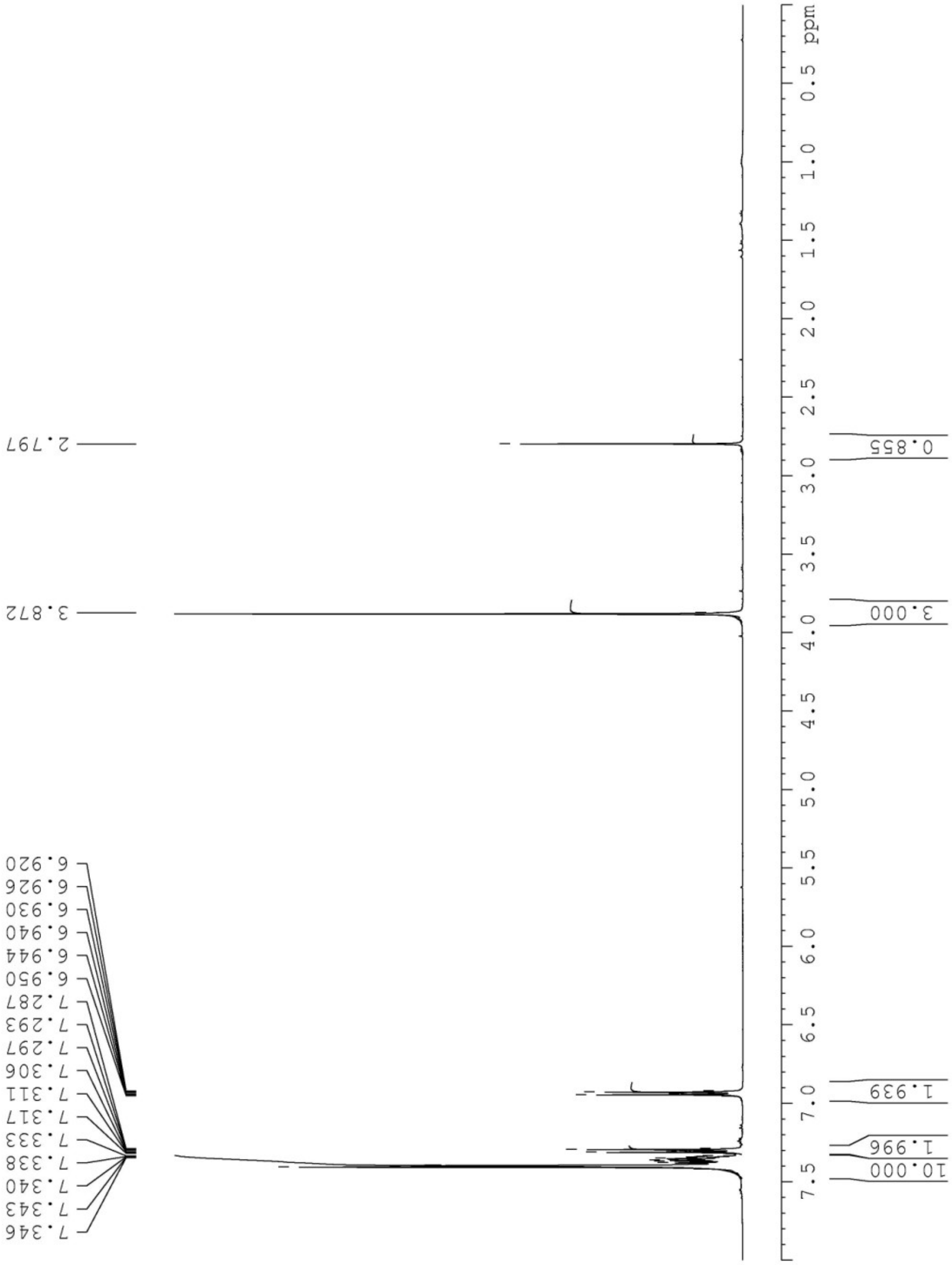


Figure 4.21 *3-(4-methoxyphenyl)-3,3-diphenyl)propyne* ^{13}C NMR

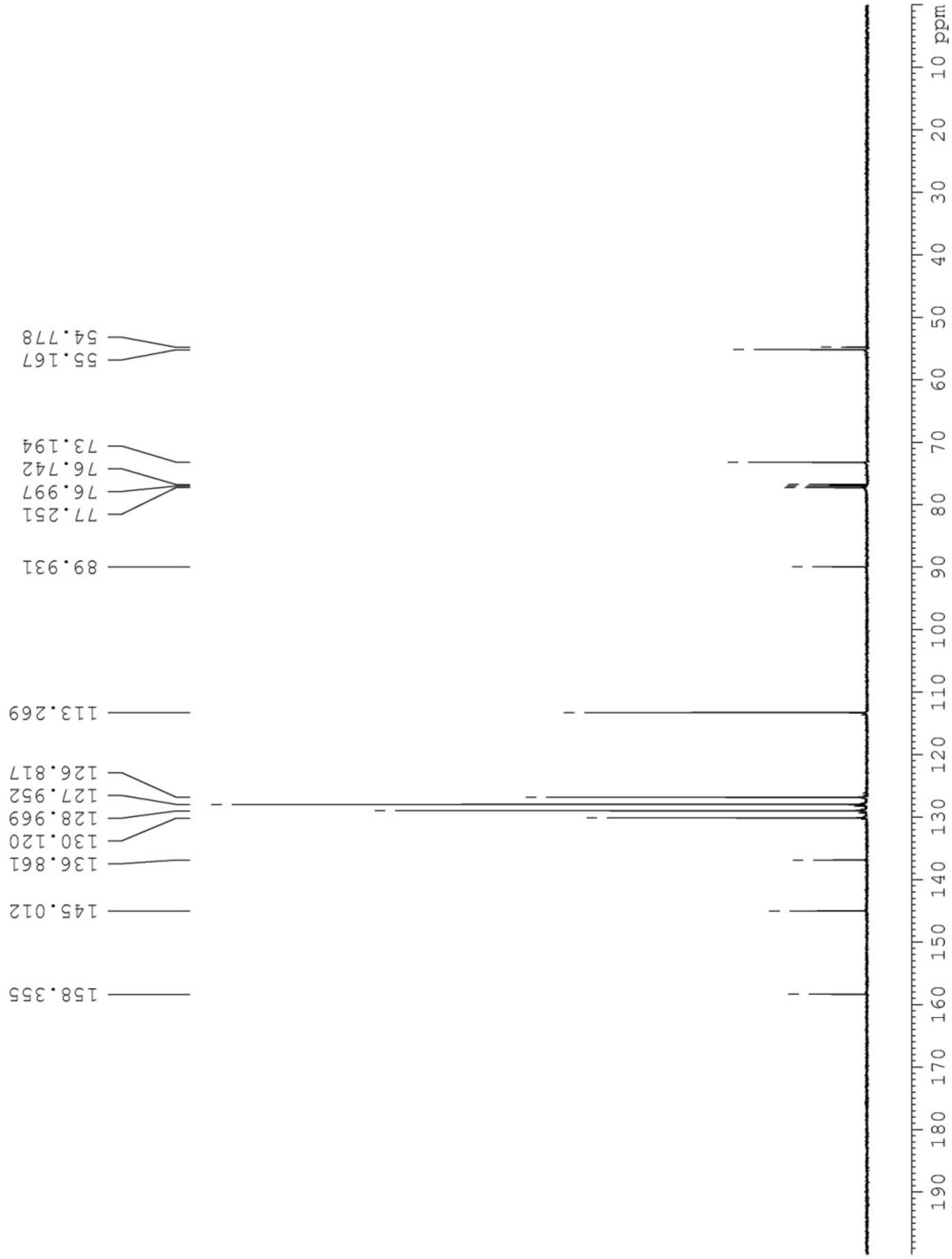


Figure 4.22 *3,3,3-tri(4-methoxyphenyl)methanol* ^{1}*H NMR*

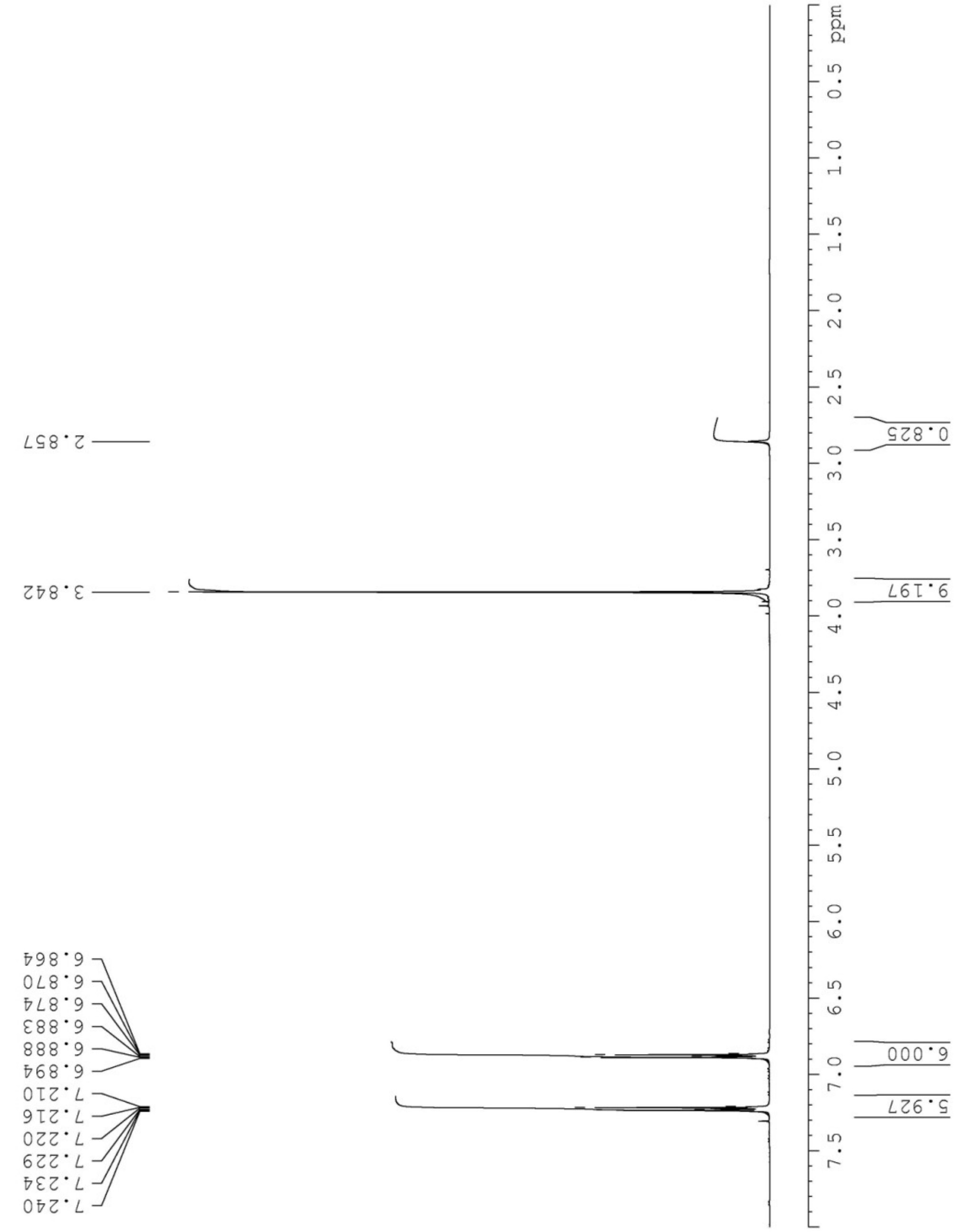


Figure 4.23 *3,3,3-tri(4-methoxyphenyl)methanol* ^{13}*C NMR*

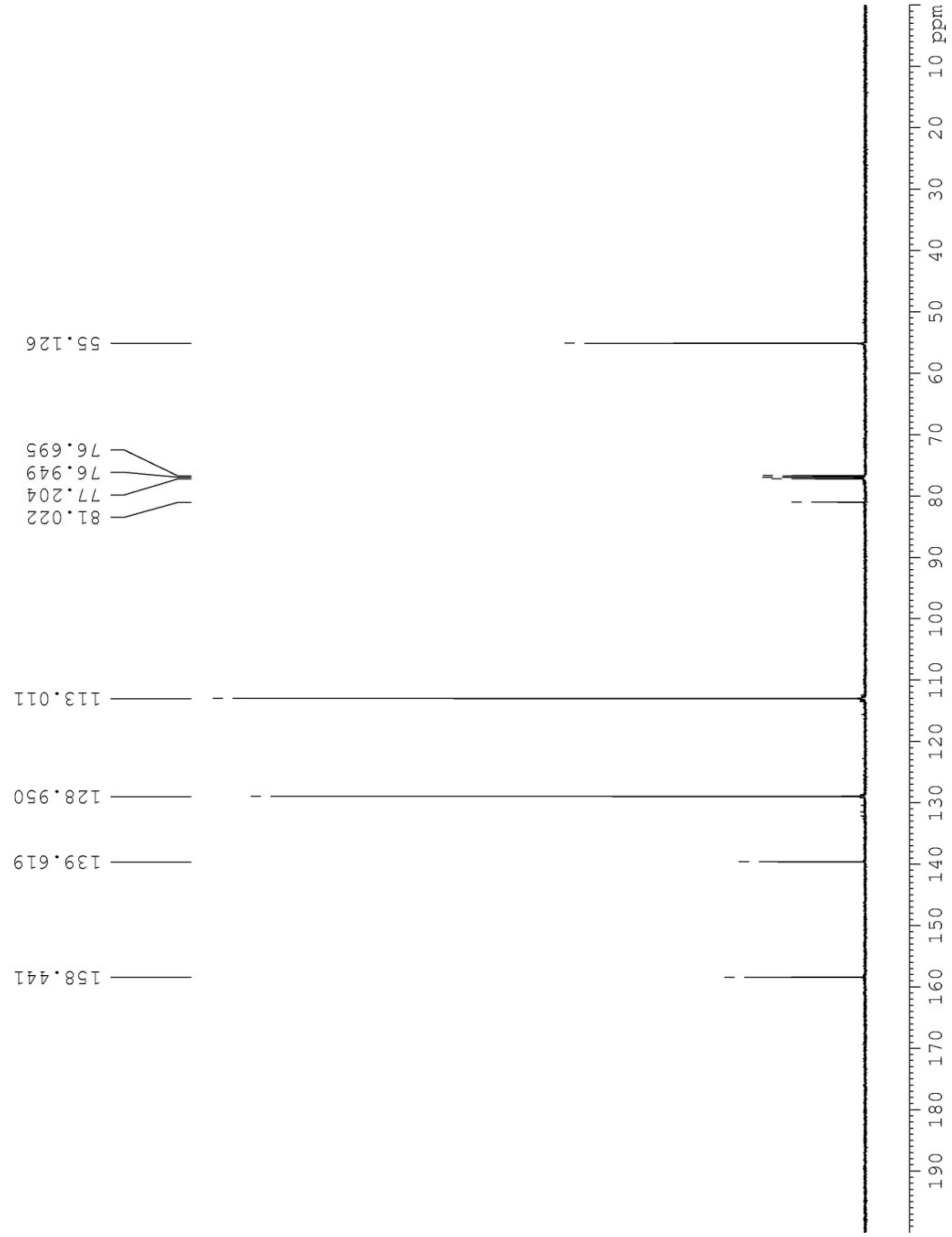


Figure 4.24 *Tri(3-methoxyphenyl)methanol* ^1H *NMR*

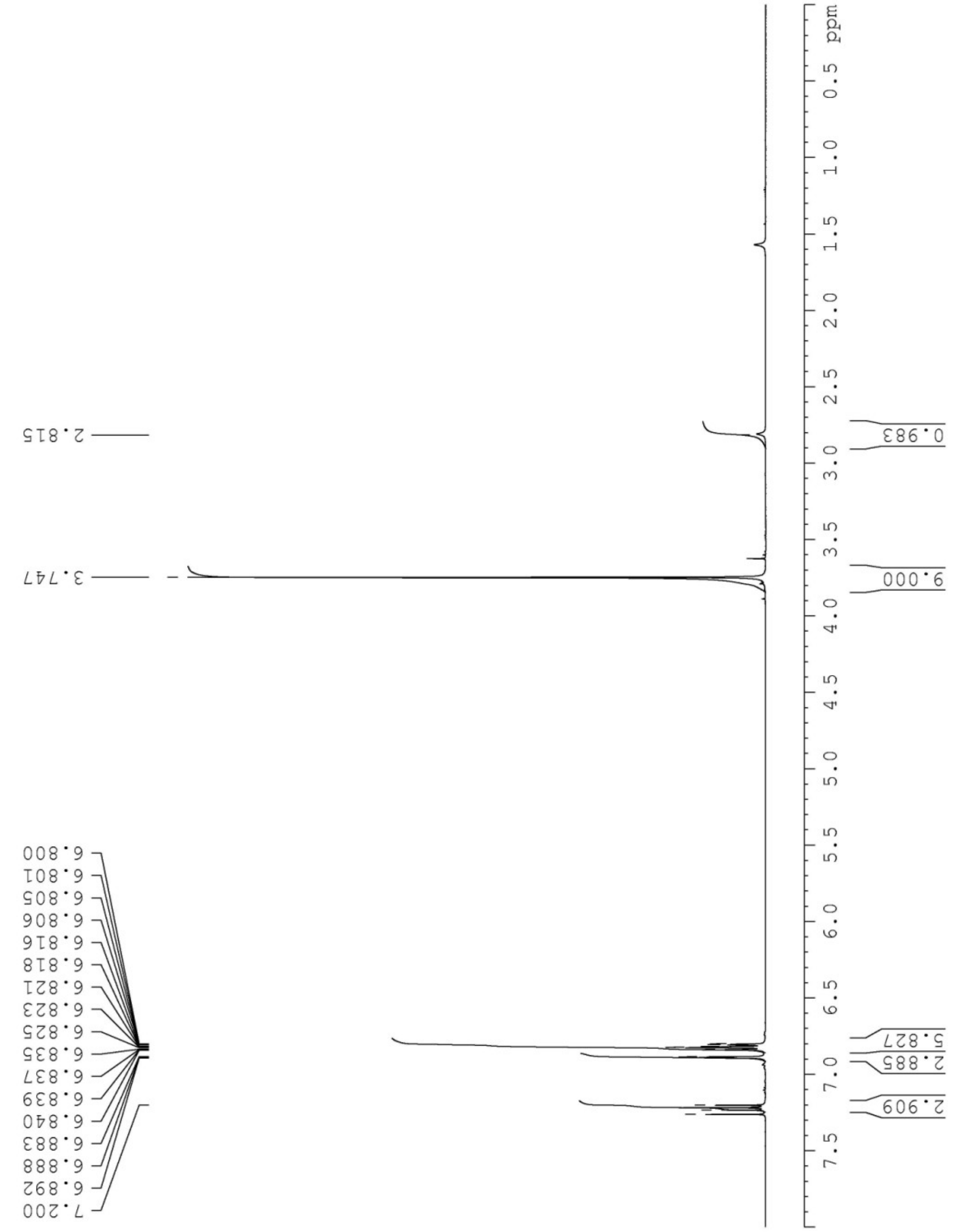


Figure 4.25 *Tri(3-methoxyphenyl)methanol* ^{13}*C NMR*

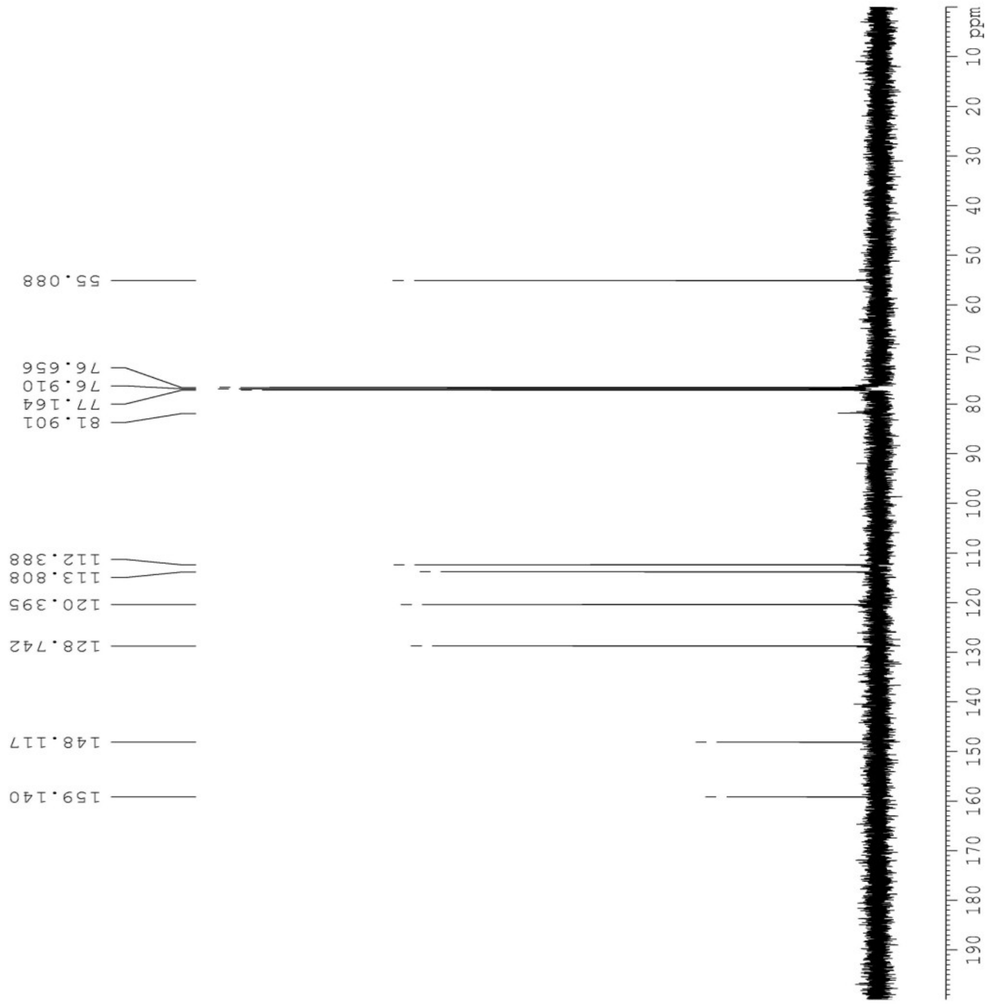


__Figure 4.26__ 1-(4-iodophenyl)-3-(3-methoxyphenyl)-3,3-diphenylpropyne ^{1} H NMR

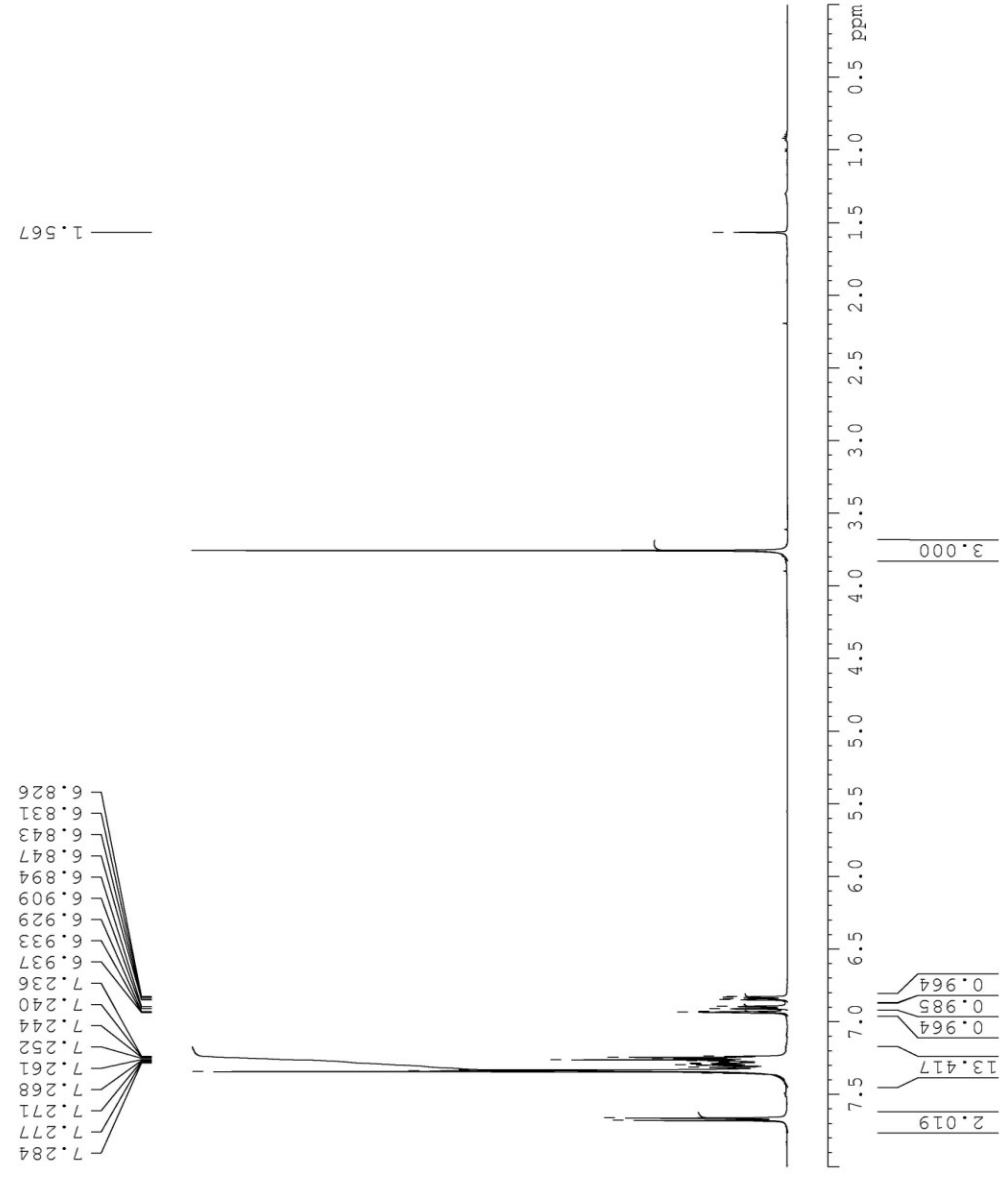


Figure 4.27 *1-(4-iodophenyl)-3-(3-methoxyphenyl)-3,3-diphenylpropyne* ^{13} *C NMR*

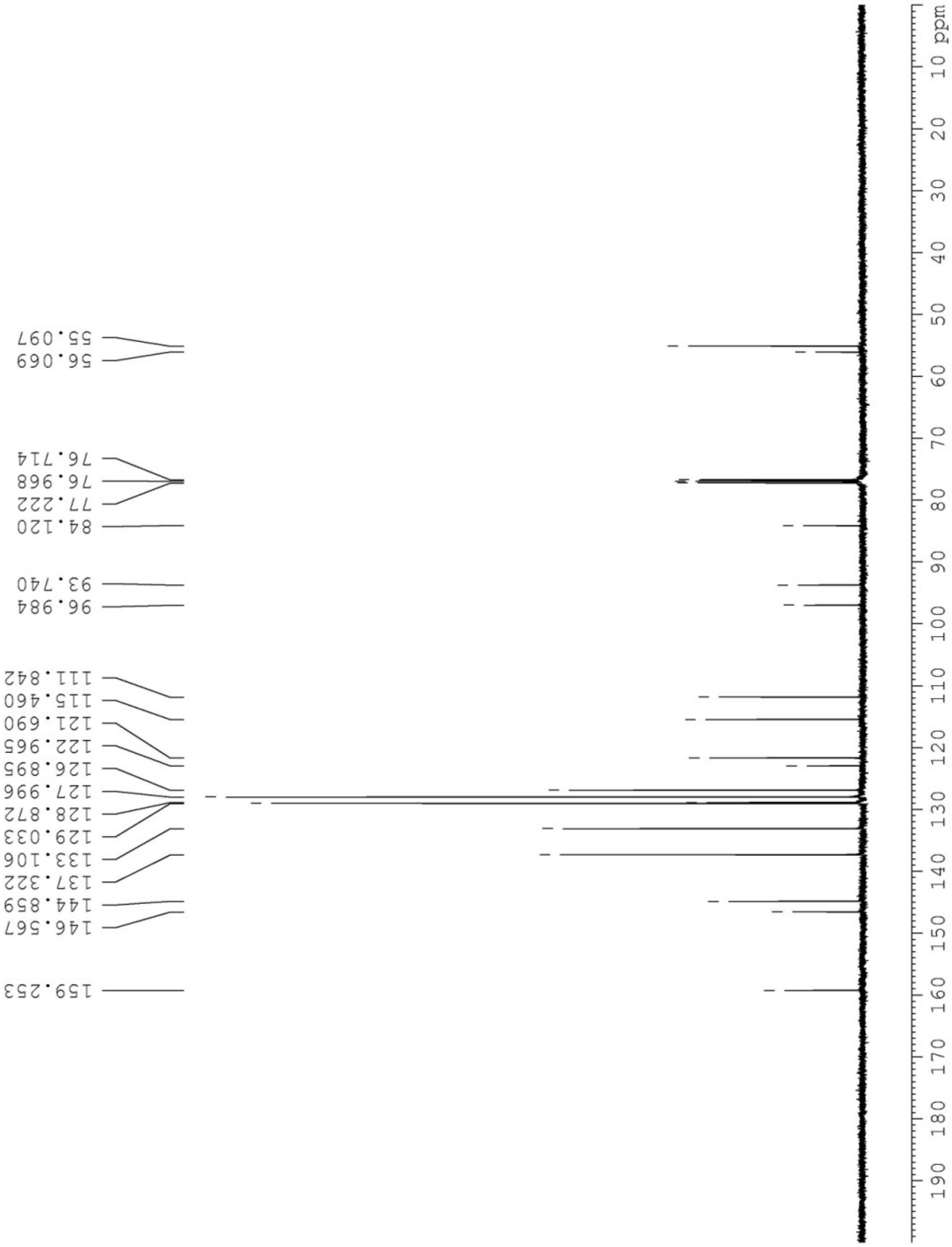


Figure 4.28 *1-(4-d4-broophenyl)-3,3,3-tri(3-methoxyphenyl)propyne ^{1}H NMR*

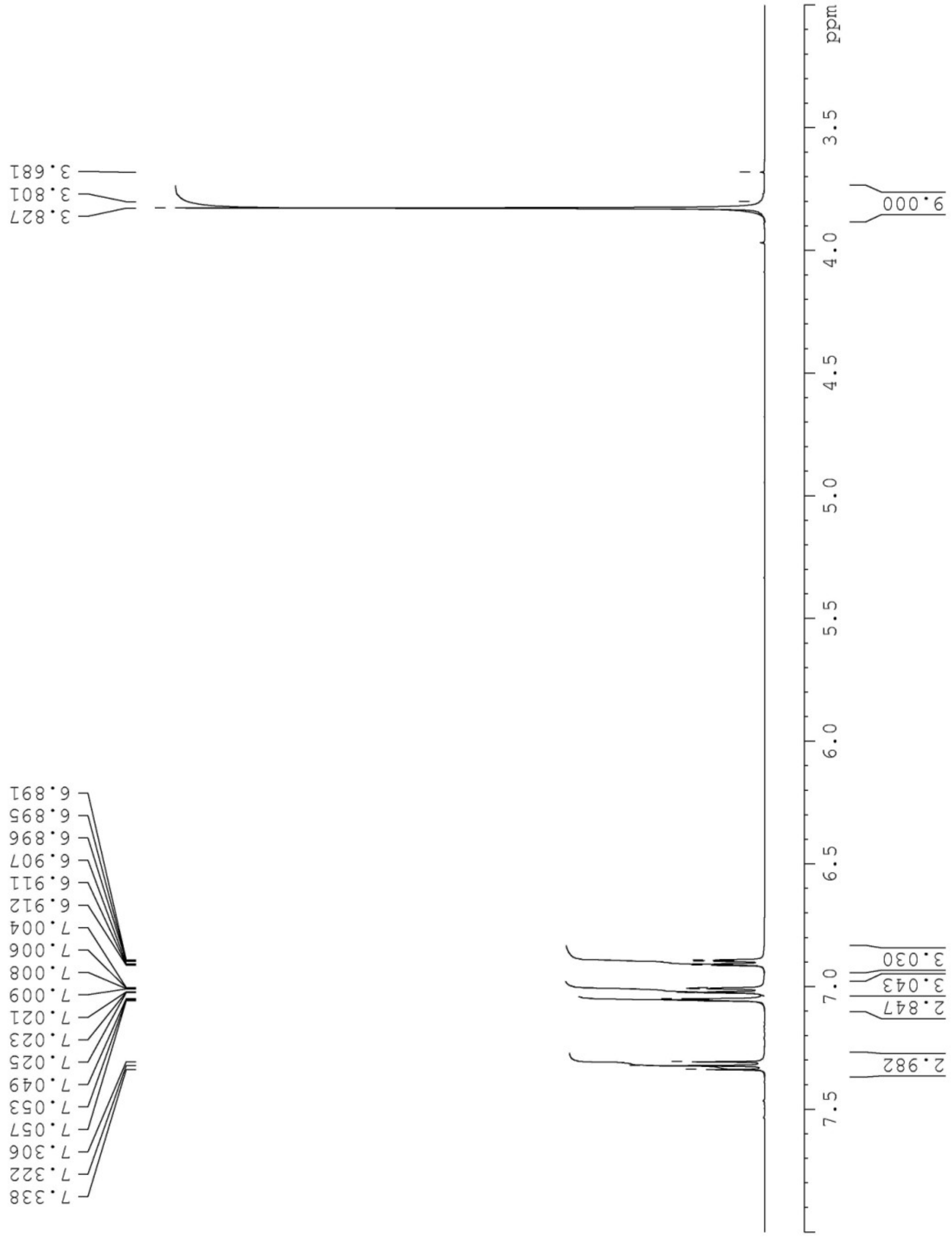


Figure 4.29 *1-(4-d4-broophenyl)-3,3,3-tri(3-methoxyphenyl)propyne* ^{13}*C NMR*

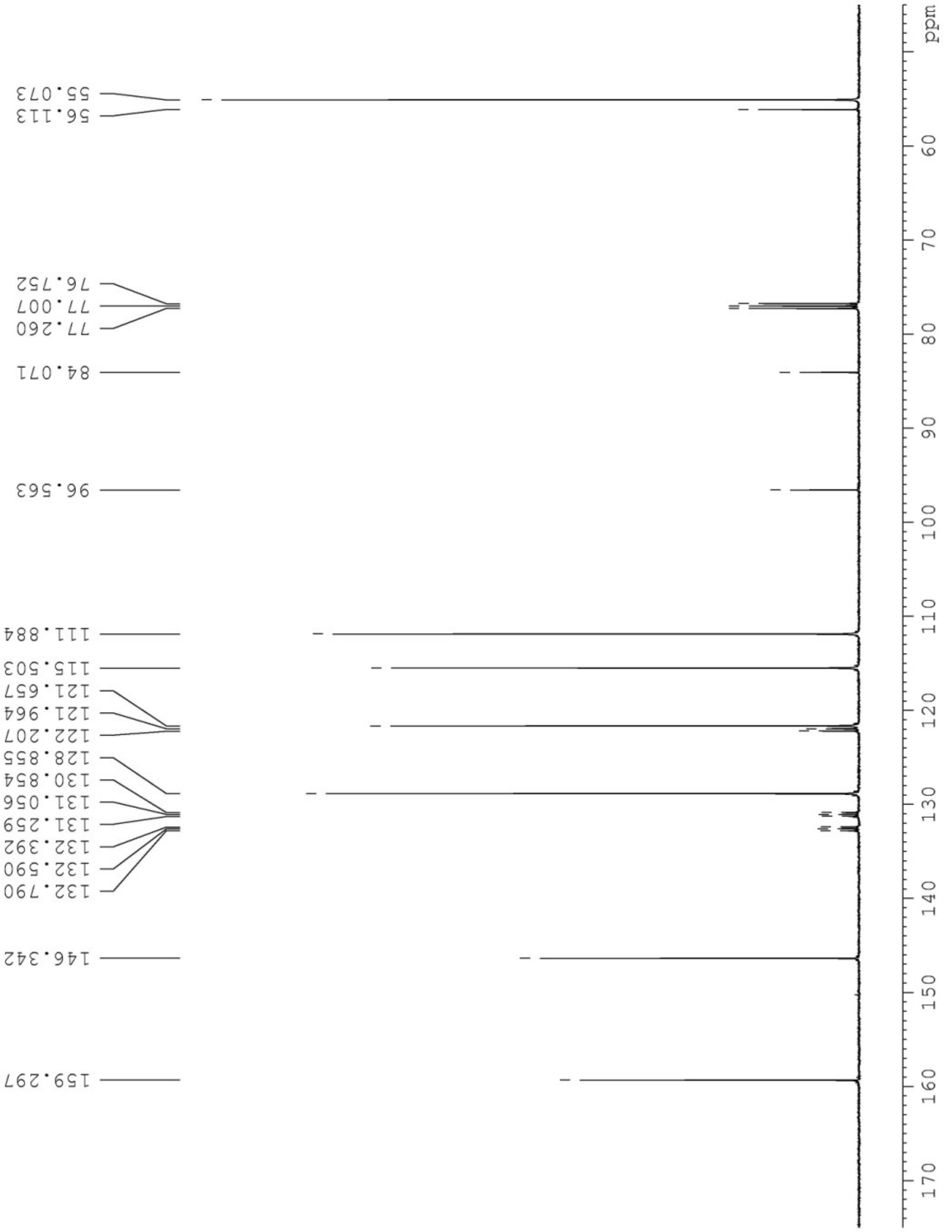


Figure 4.30 *1-(4-d4-bromophenyl)-3,3,3-tri(4-methoxyphenyl)propyne* ^{1}*H NMR*

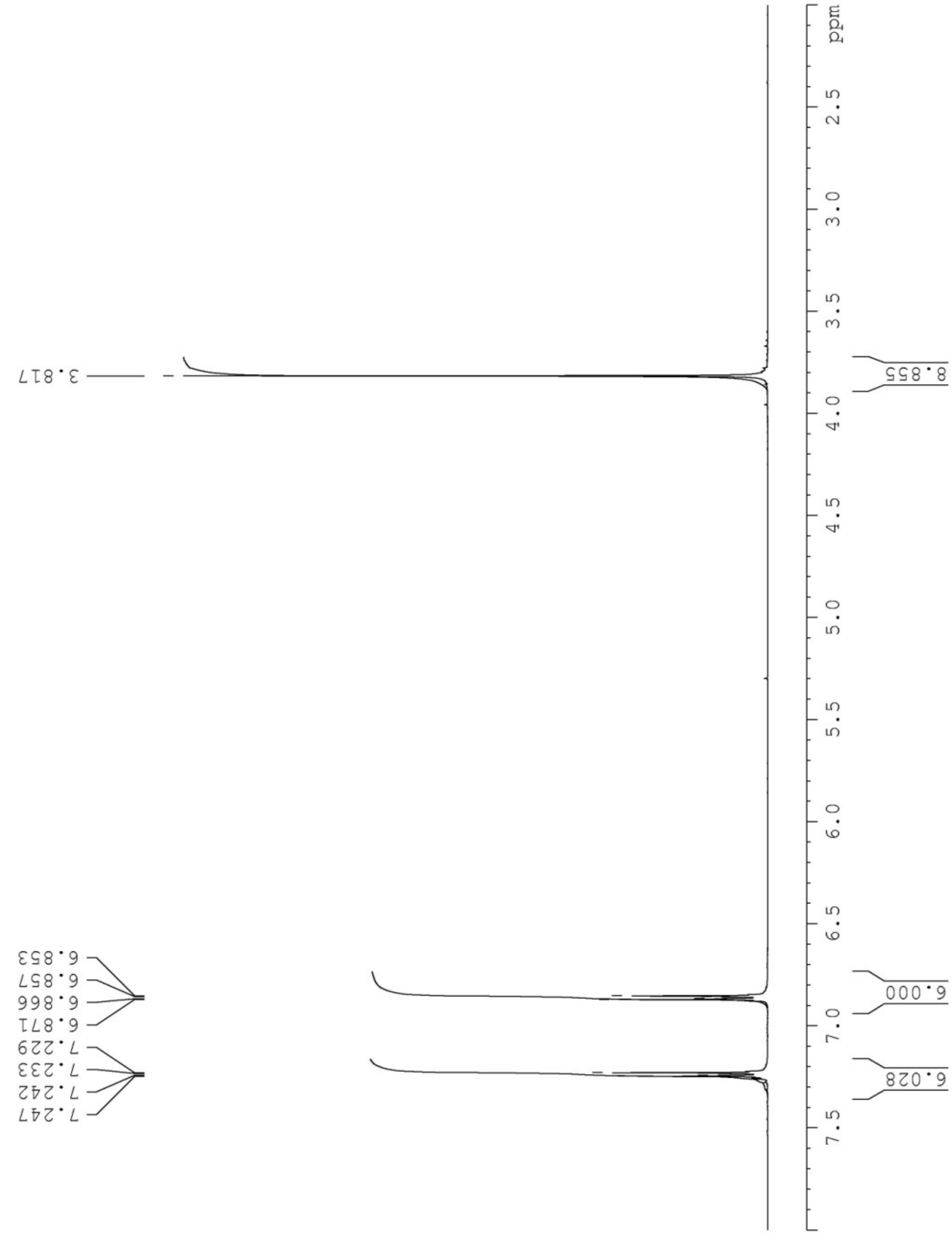


Figure 4.31 *1-(4-d4-bromophenyl)-3,3,3-tri(4-methoxyphenyl)propyne* ^{13}*C NMR*

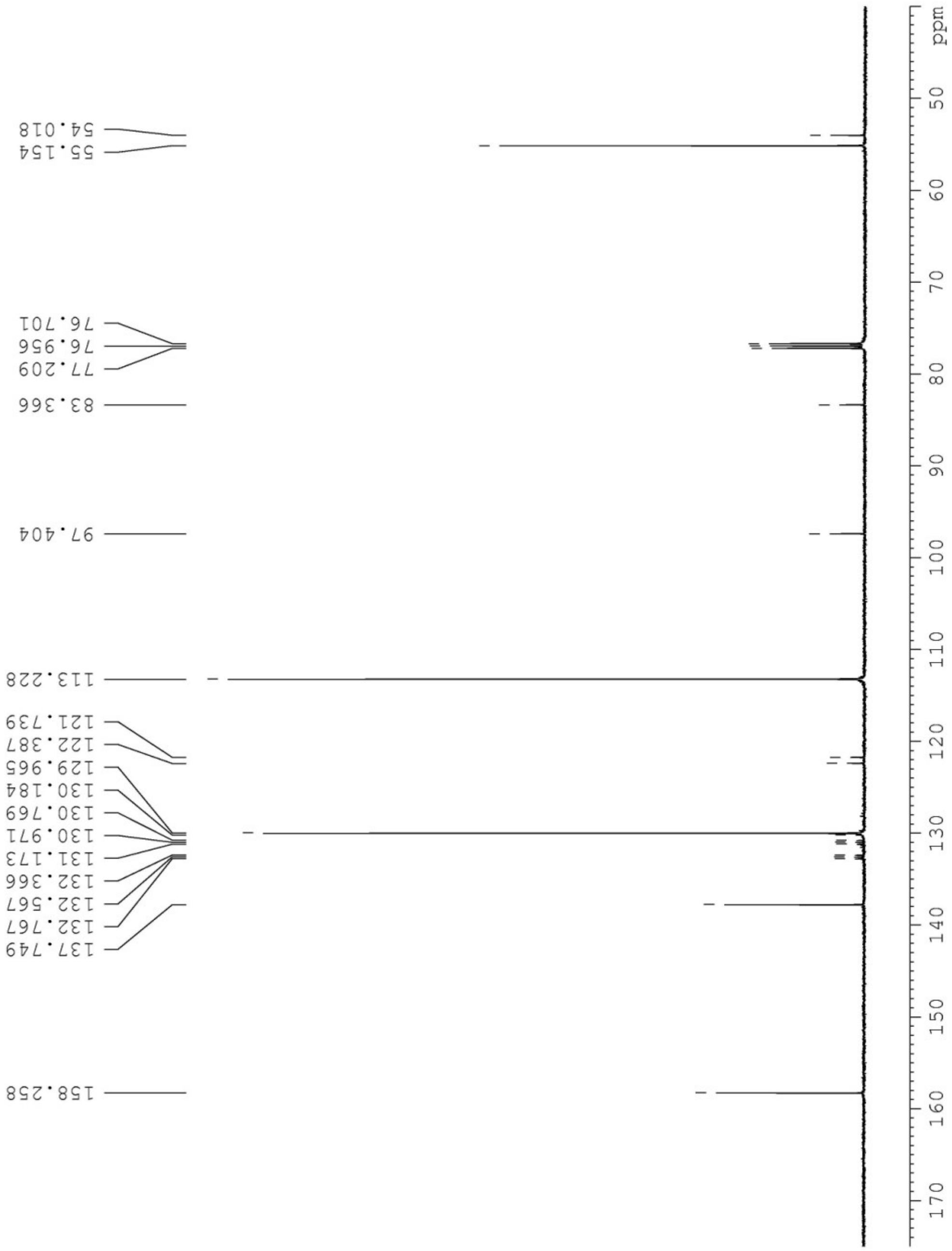


Figure 4.32 *1-(4-iodophenyl)-3,3,3-tri(4-methoxyphenyl)propyne ^{1}H NMR*

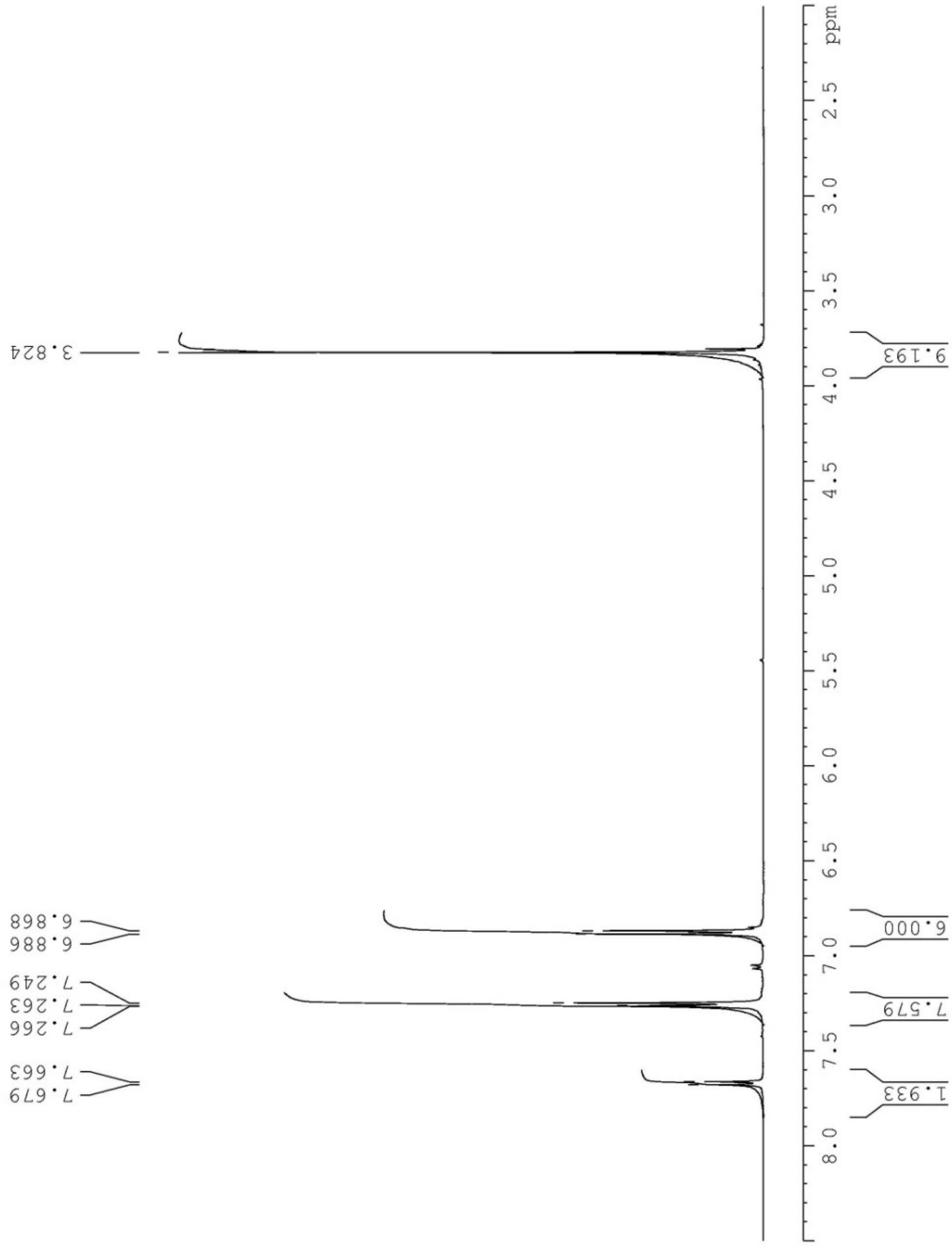


Figure 4.33 *1-(4-iodophenyl)-3,3,3-tri(4-methoxyphenyl)propyne* ^{13} *C NMR*

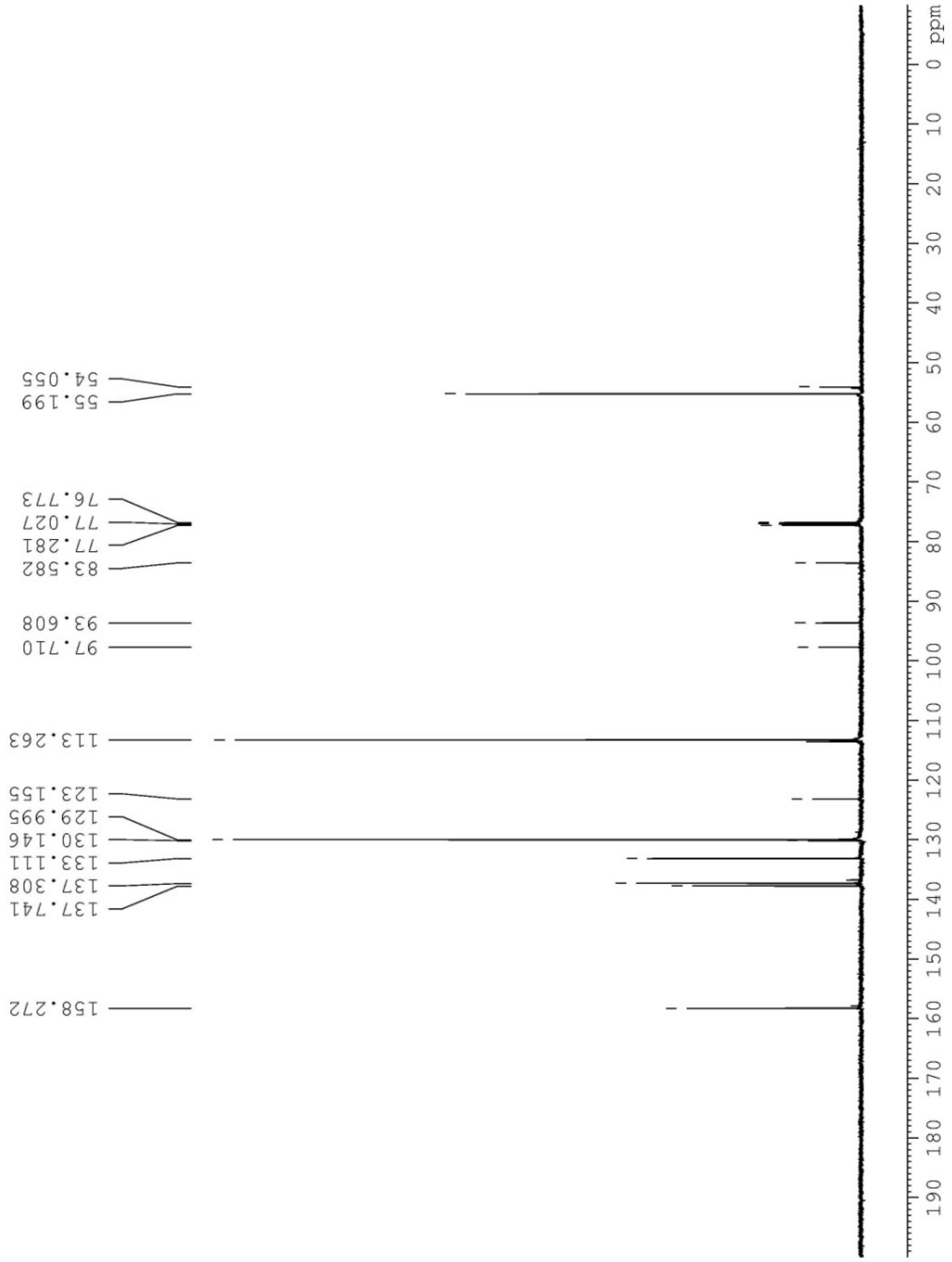


Figure 4.34 *Bis(p-(2-(4-(3-(3-methoxyphenyl)-3,3-diphenyl)propynyl)-p-phenylene)ethynylene pentiptycene* ^{1}*H NMR*

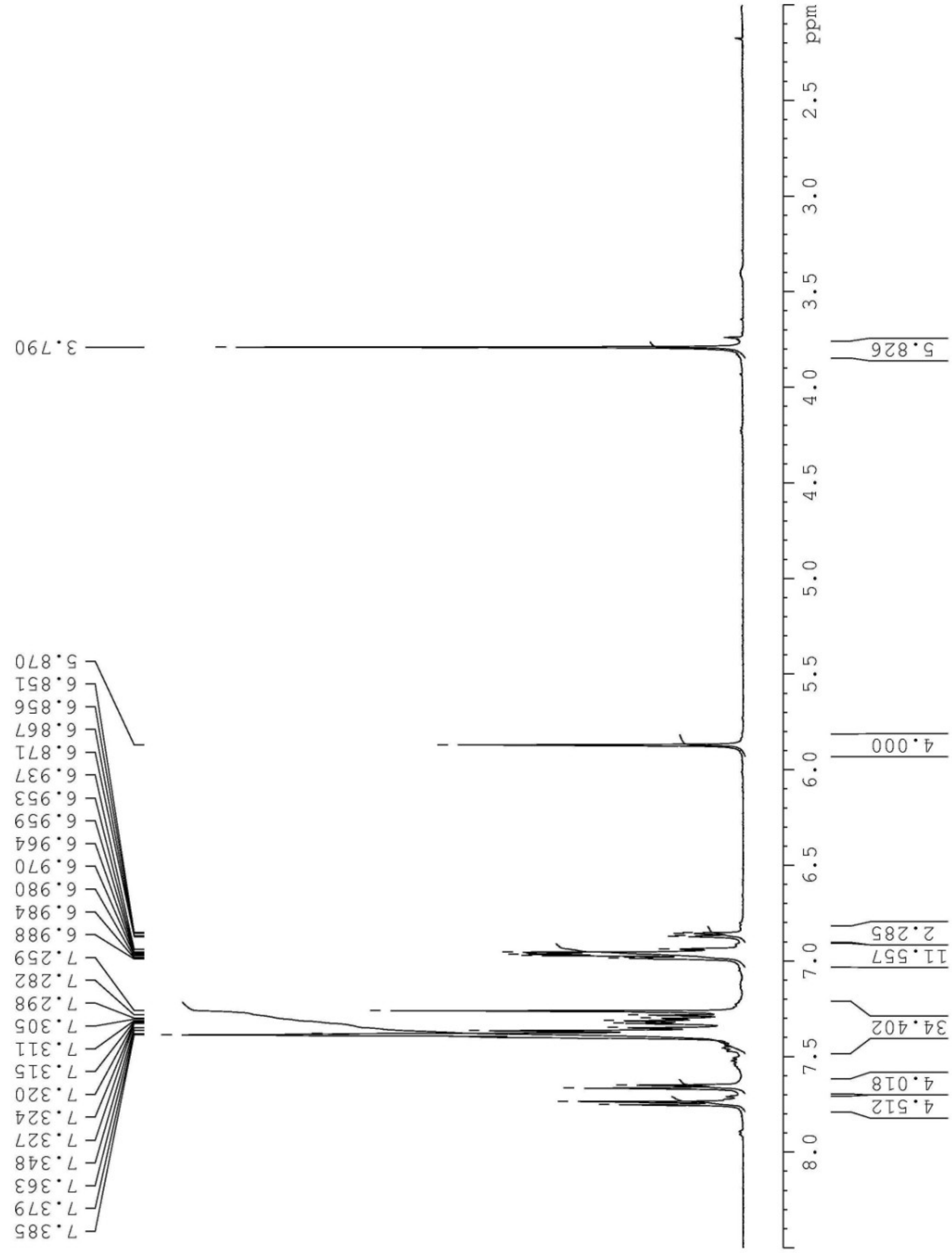


Figure 4.35 *Bis(p-(2-(4-3,3,3-tri(4-methoxy)phenylpropynyl)-p-phenylene)ethynylene pentiptycene* ^{1}*H NMR*

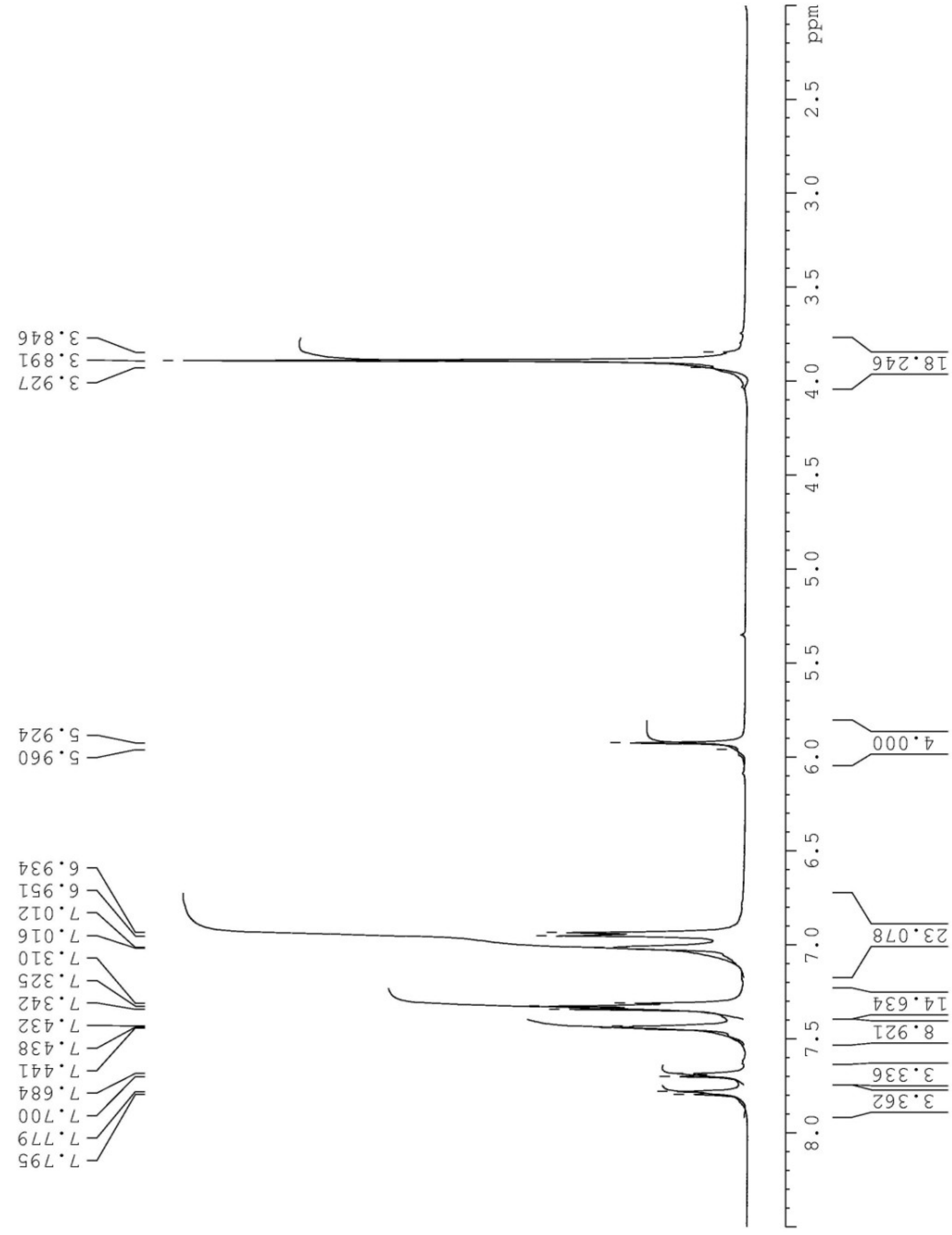


Figure 4.36 *Bis(p-(2-(4-(3-(4-methoxyphenyl)-3,3-diphenyl)propynyl)-d8-p-phenylene)ethynylene pentiptycene* ^1H *NMR*

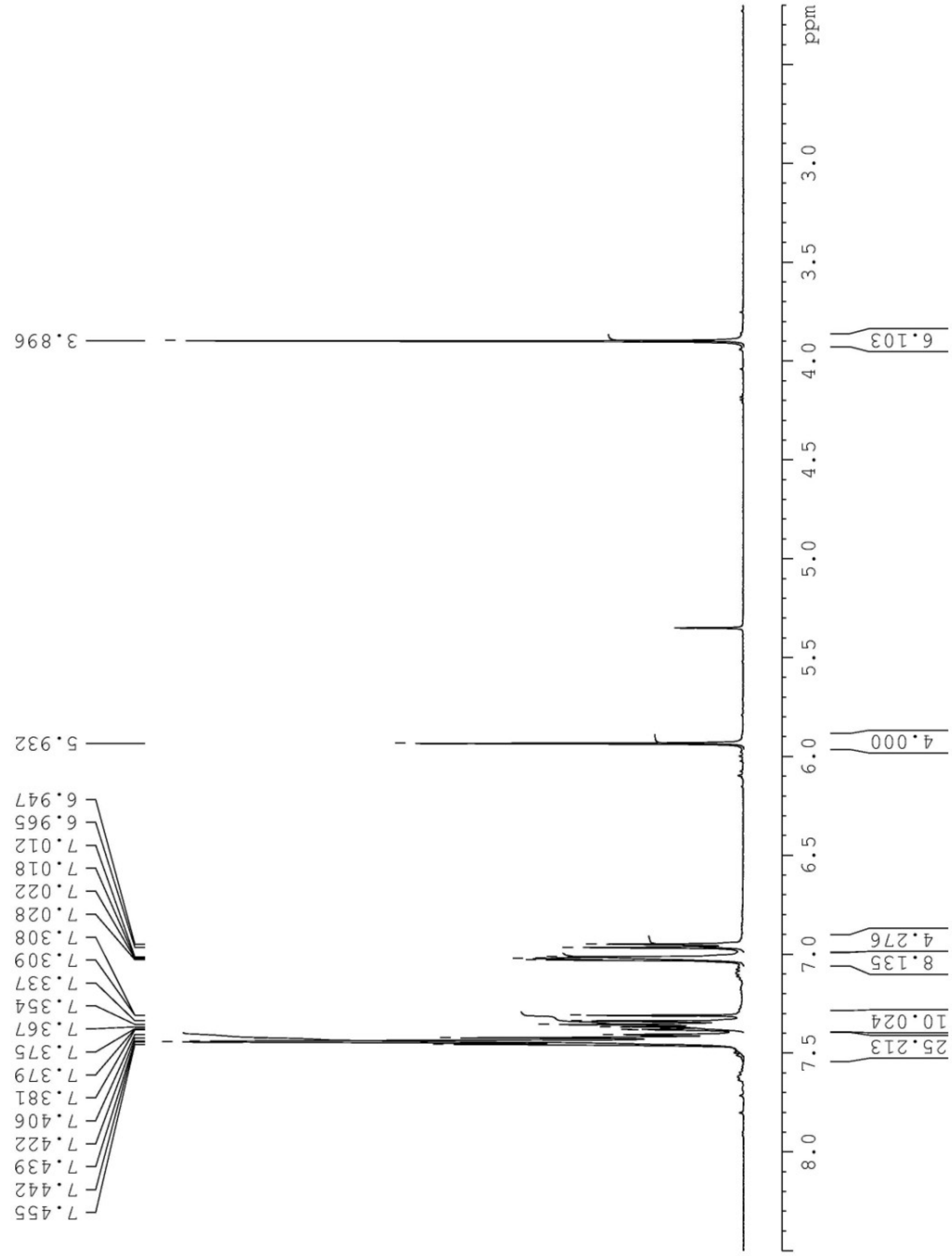


Figure 4.37 *Bis(p-(2-(4-(3-(4-methoxyphenyl)-3,3-diphenyl)propynyl)-d8-p-phenylene)ethynylene pentiptycene* ^{13}*C NMR*

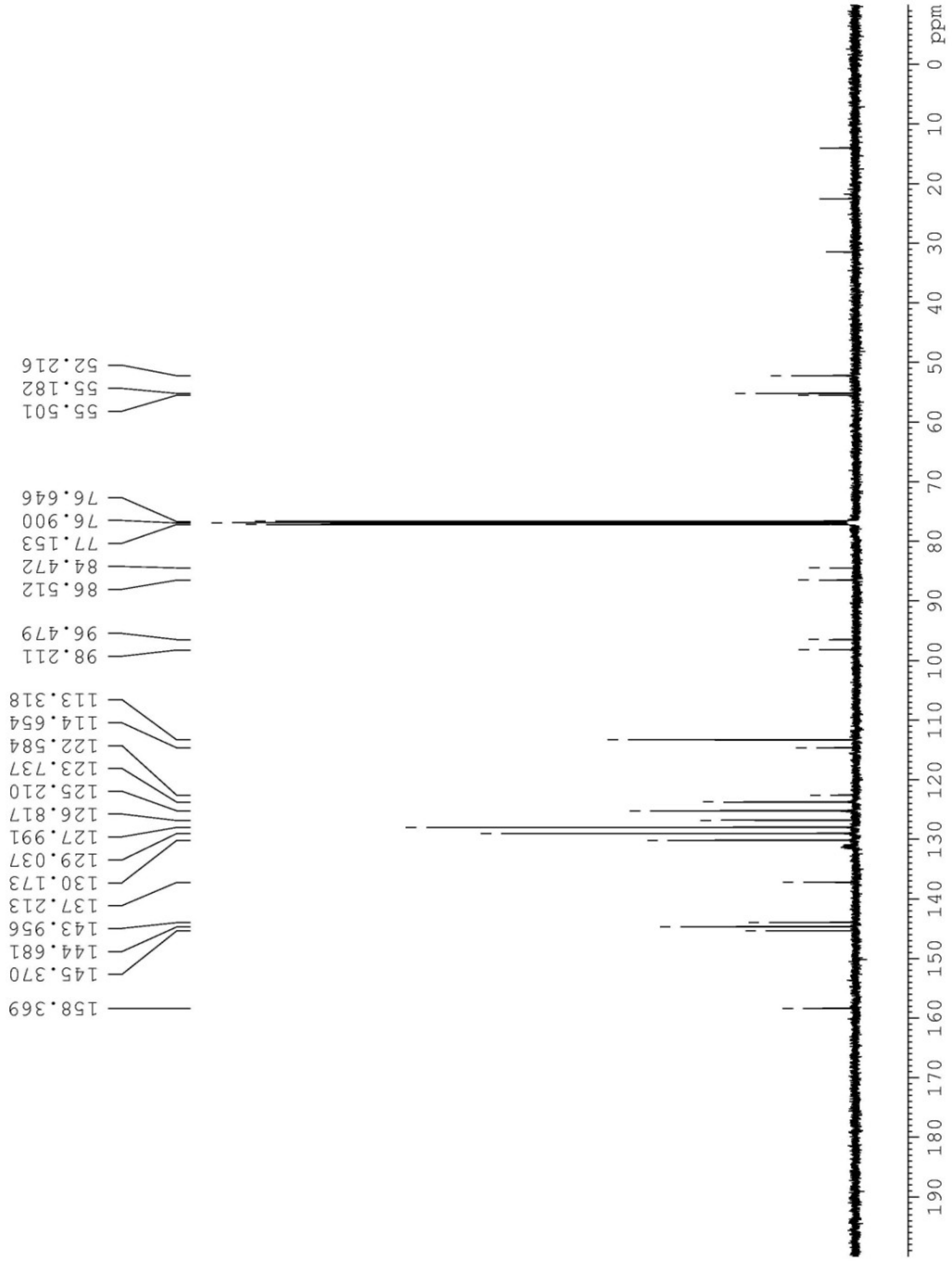


Figure 4.38 *Bis(p-(2-(4-(3-(4-methoxyphenyl)-3,3-diphenyl)propynyl)-p-phenylene)ethynylene pentiptycene* ^1H *NMR*

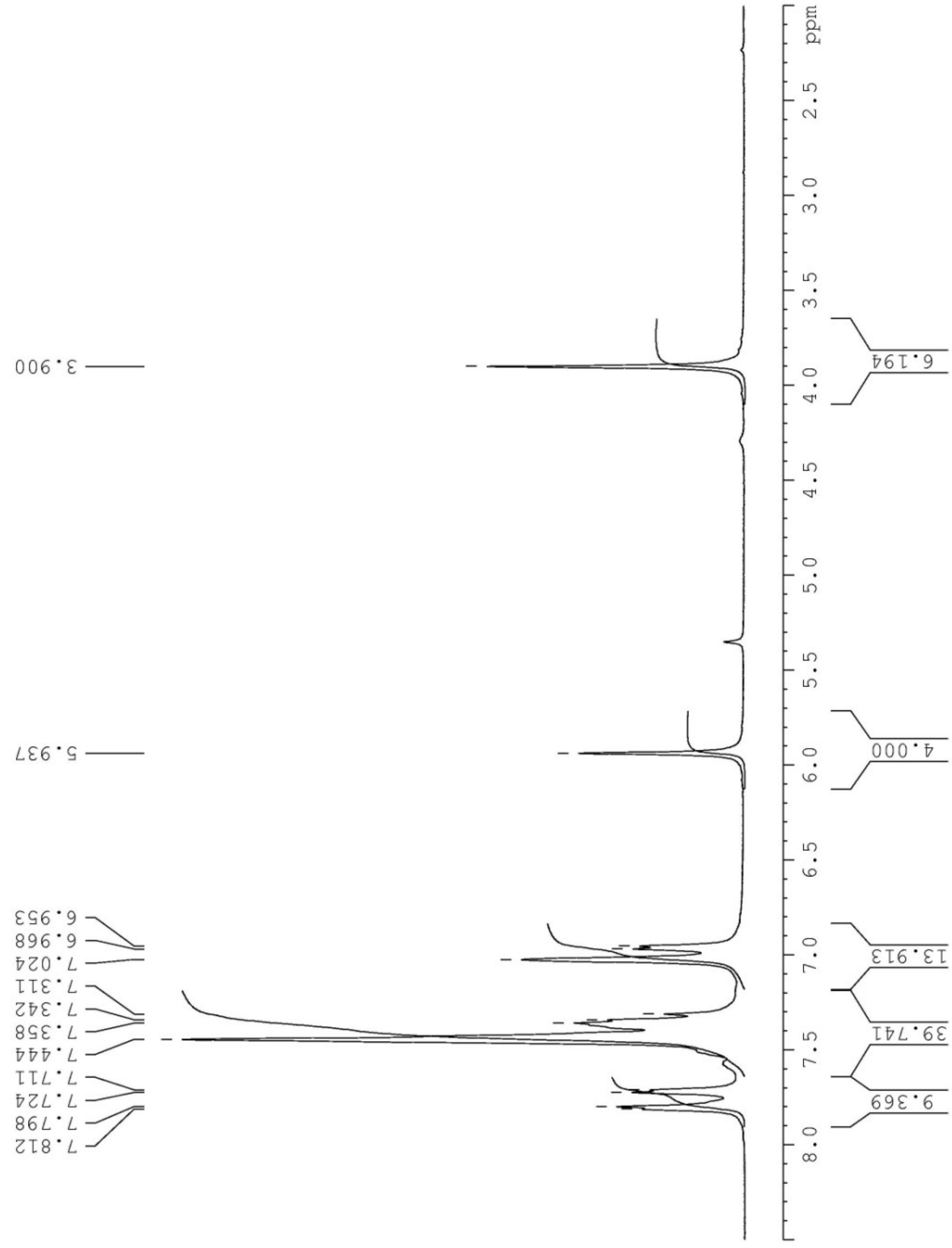


Figure 4.39 *Bis(p-(2-(4-(3-(4-methoxyphenyl)-3,3-diphenyl)propynyl)-p-phenylene)ethynylene pentiptycene* ^{13}*C NMR*

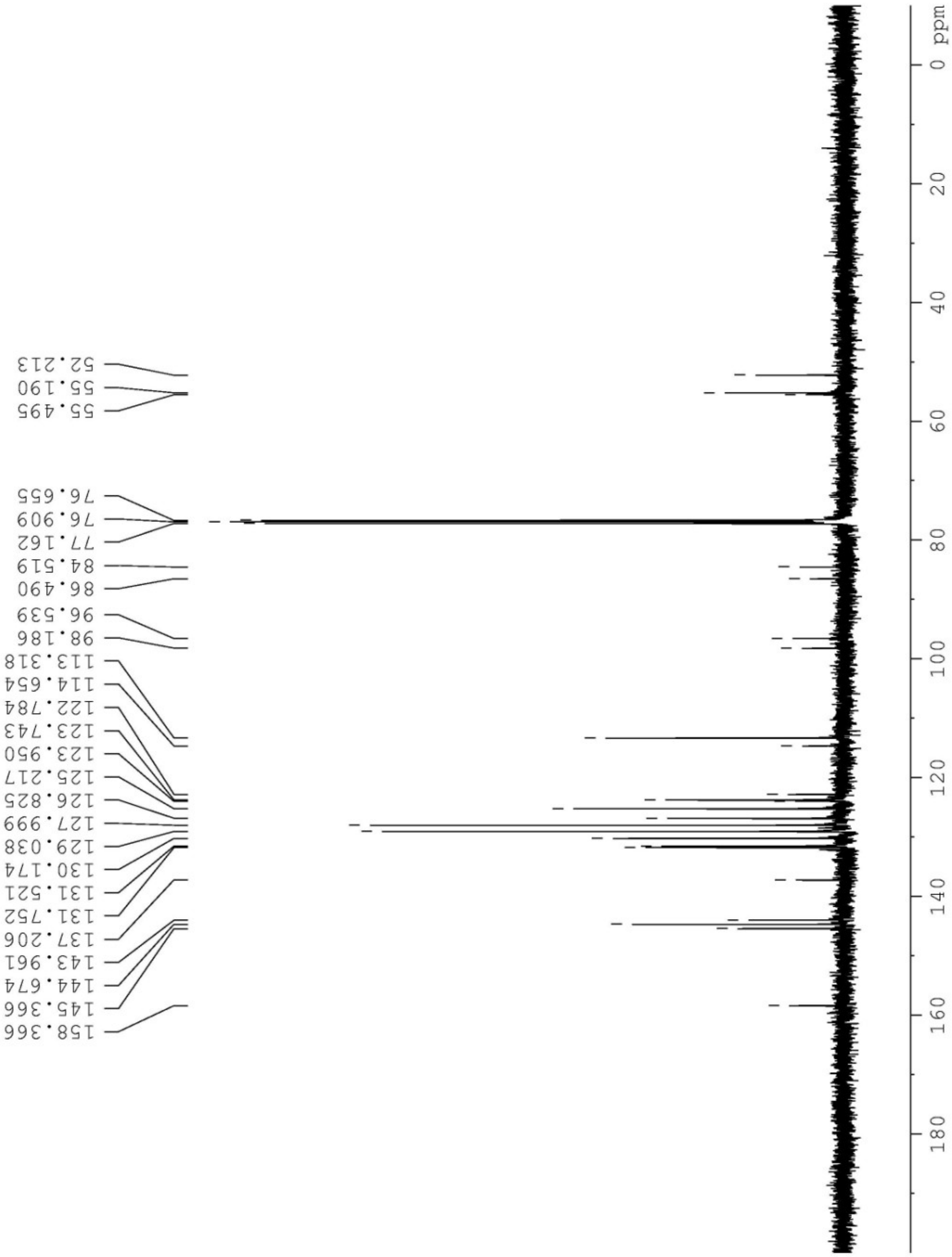


Figure 4.40 *Bis(p-(2-(4-3,3,3-triphenylpropynyl)-p-naphthylene)ethynylene pentiptycene* ^{1}*H NMR*

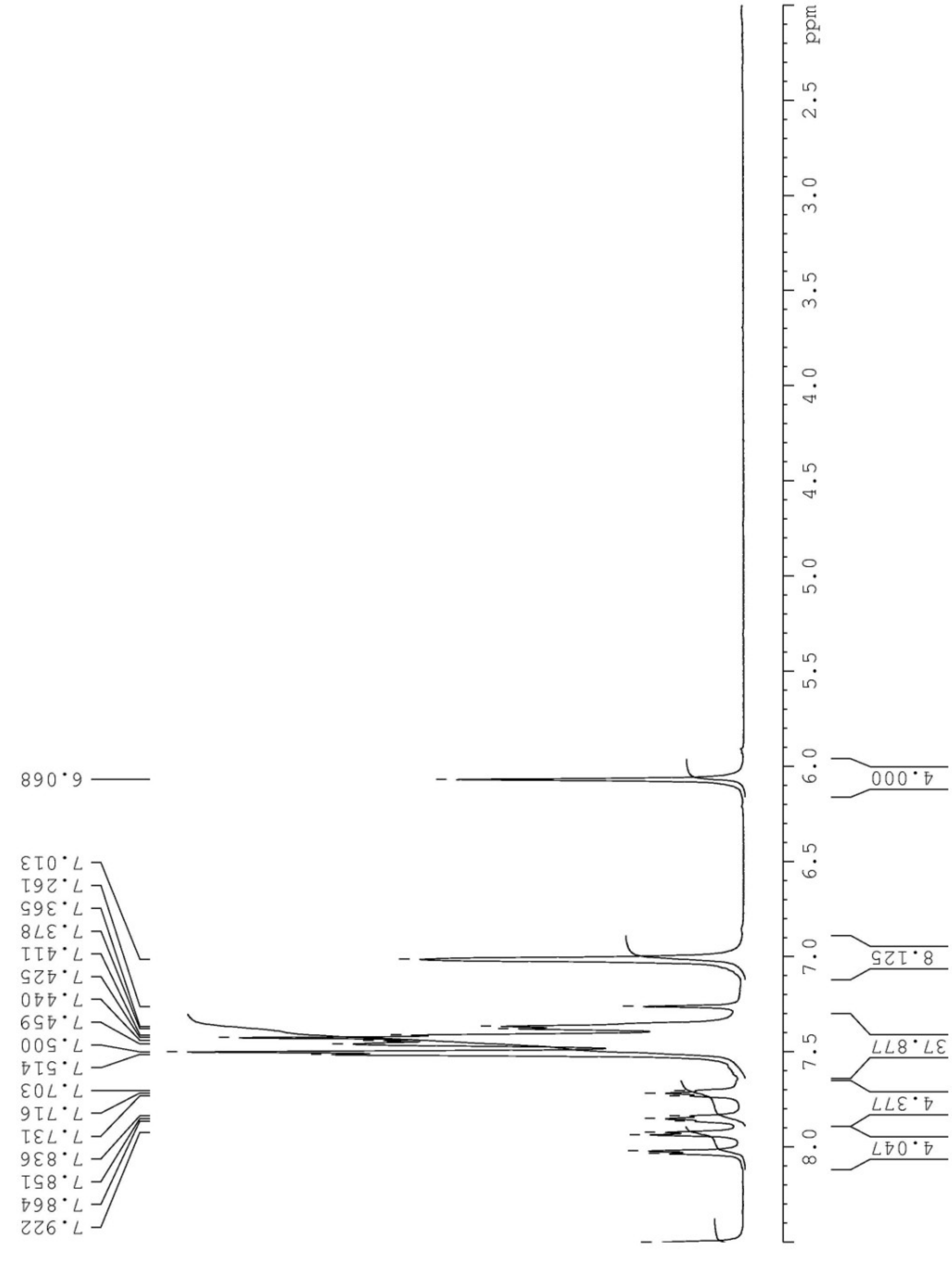


Figure 4.41 *Bis(p-(2-(4-3,3,3-tri(3-methoxy)phenylpropynyl)-p-phenylene)ethynylene pentiptycene* ^{1}*H NMR*

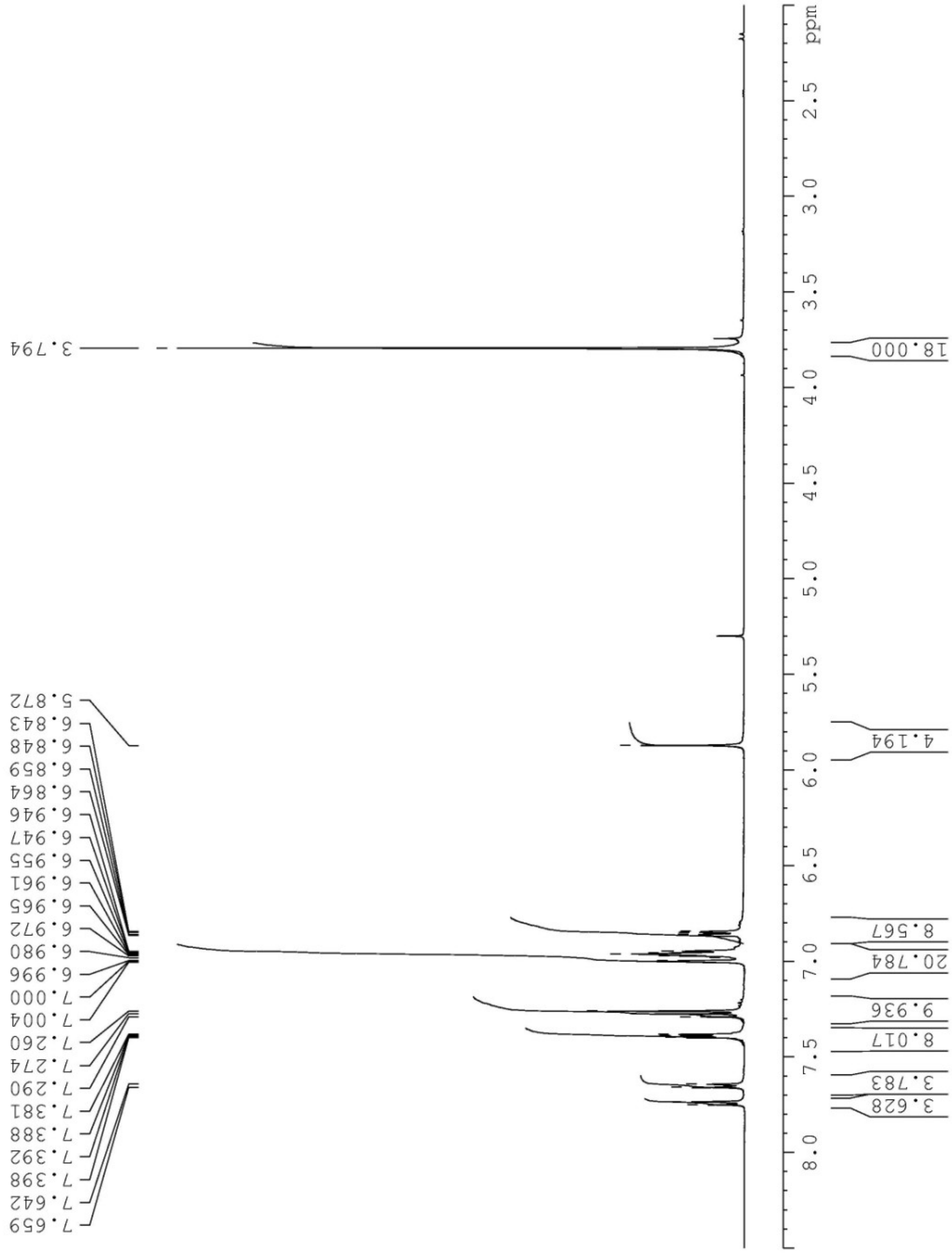


Figure 4.42 *1-(d4-4-bromophenyl)-3-(3-methoxyphenyl)-3,3-diphenylpropyne IR*

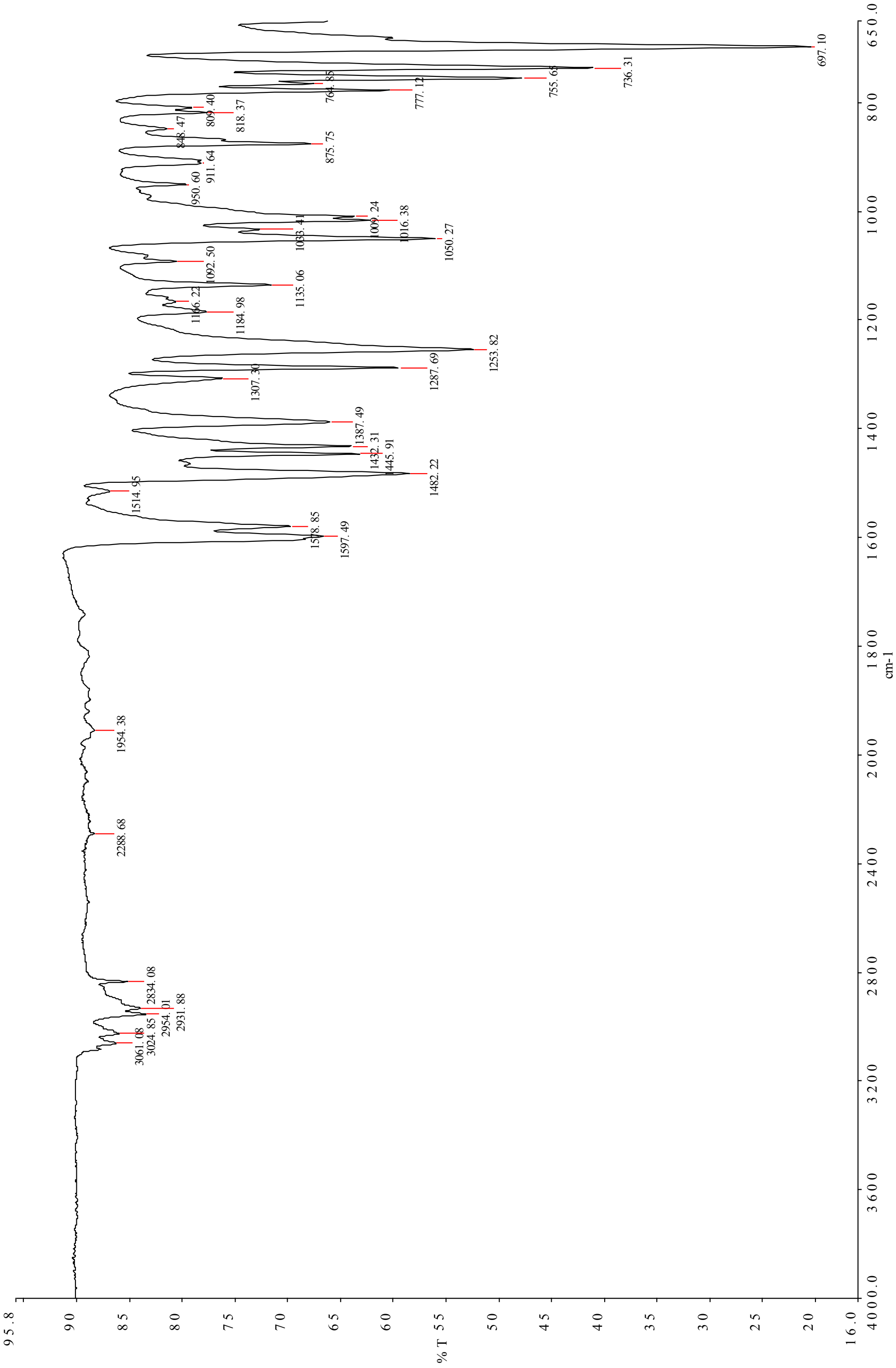


Figure 4.43 *Bis(p-(2-(4-(3-(3-methoxyphenyl)-3,3-diphenyl)propynyl)-d8-p-phenylene)ethynylene pentiptycene IR*

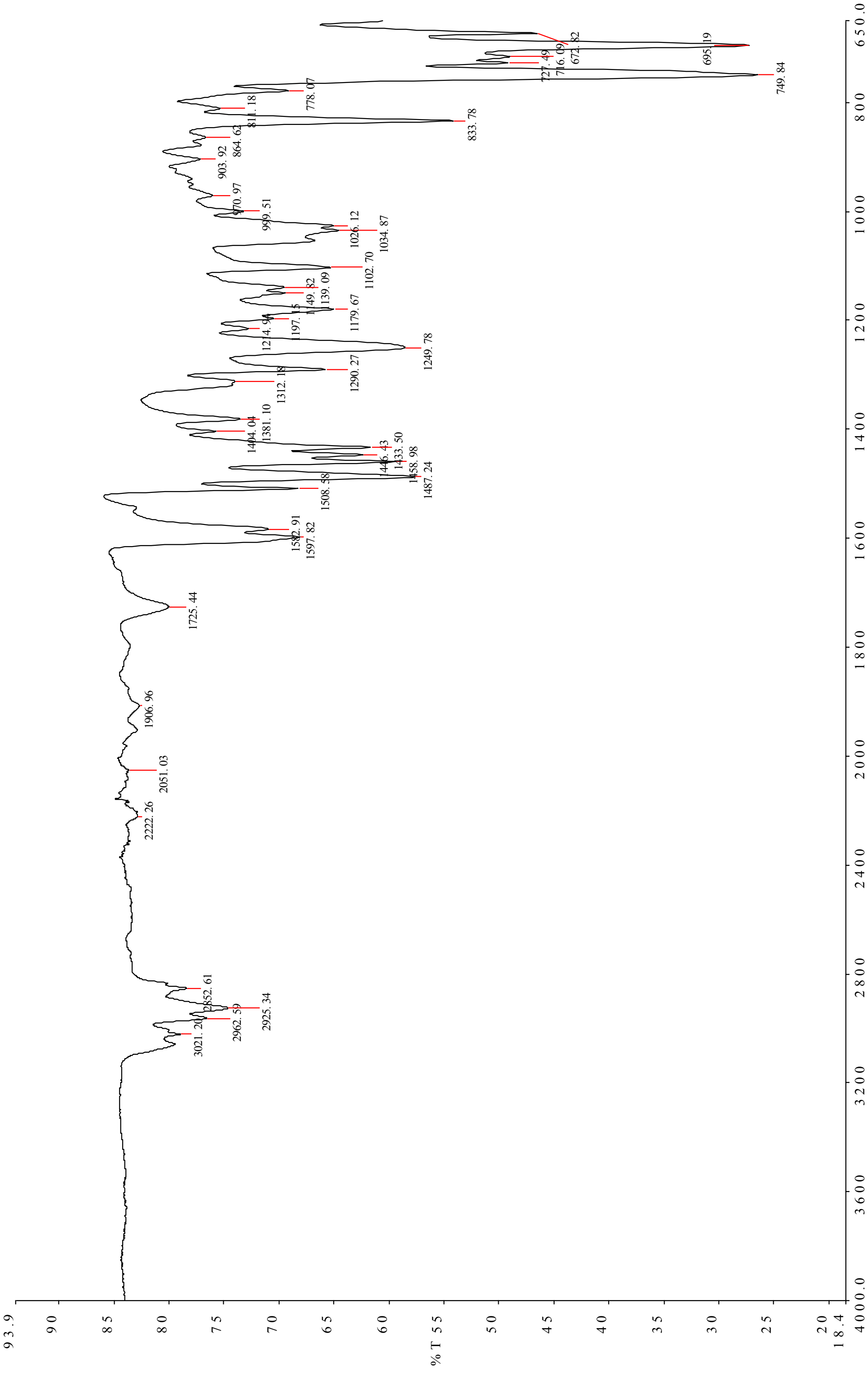


Figure 4.44 *Bis(p-(2-(4-(3-(3-methoxyphenyl)-3,3-diphenyl)propynyl)-d8-p-phenylene)ethynylene pentiptycene IR*

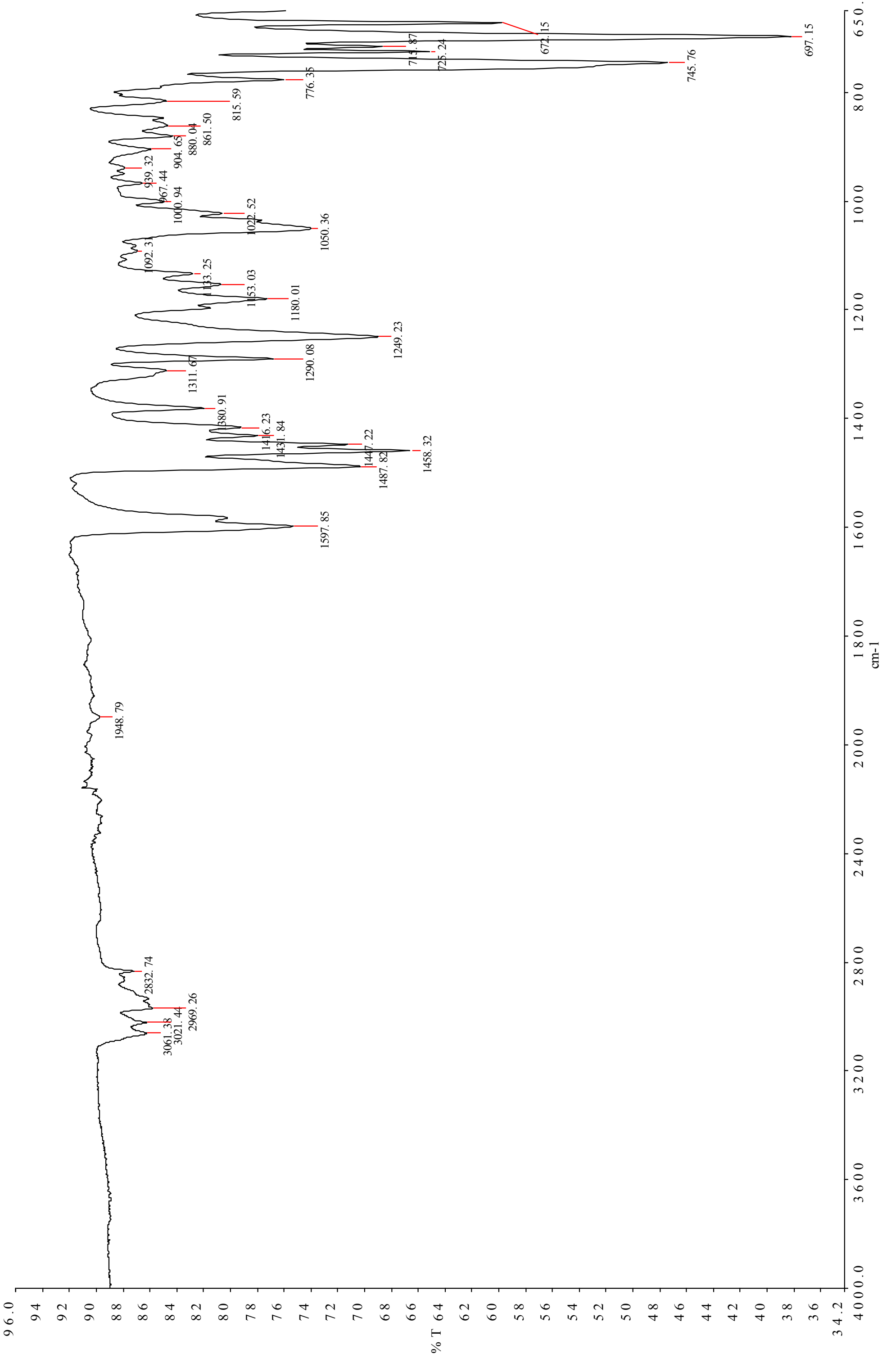


Figure 4.45 *1-(4-iodophenyl)-3-(4-methoxyphenyl)-3,3-diphenyl)propyne IR*

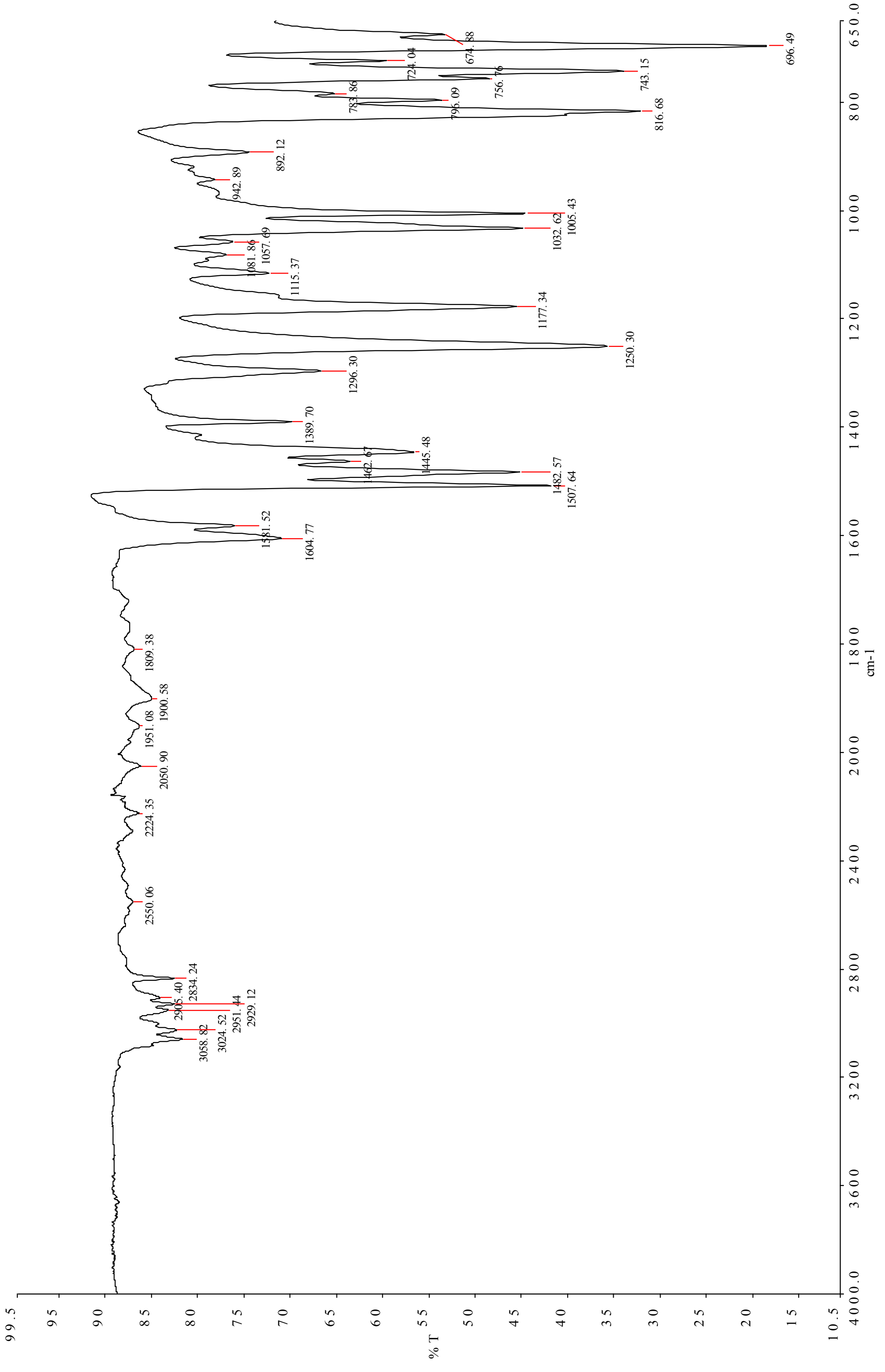


Figure 4.46 *Bis(p-(2-(4-(3-(4-methoxyphenyl)-3,3-diphenyl)propynyl)-p-phenylene)ethynylene pentiptycene IR*

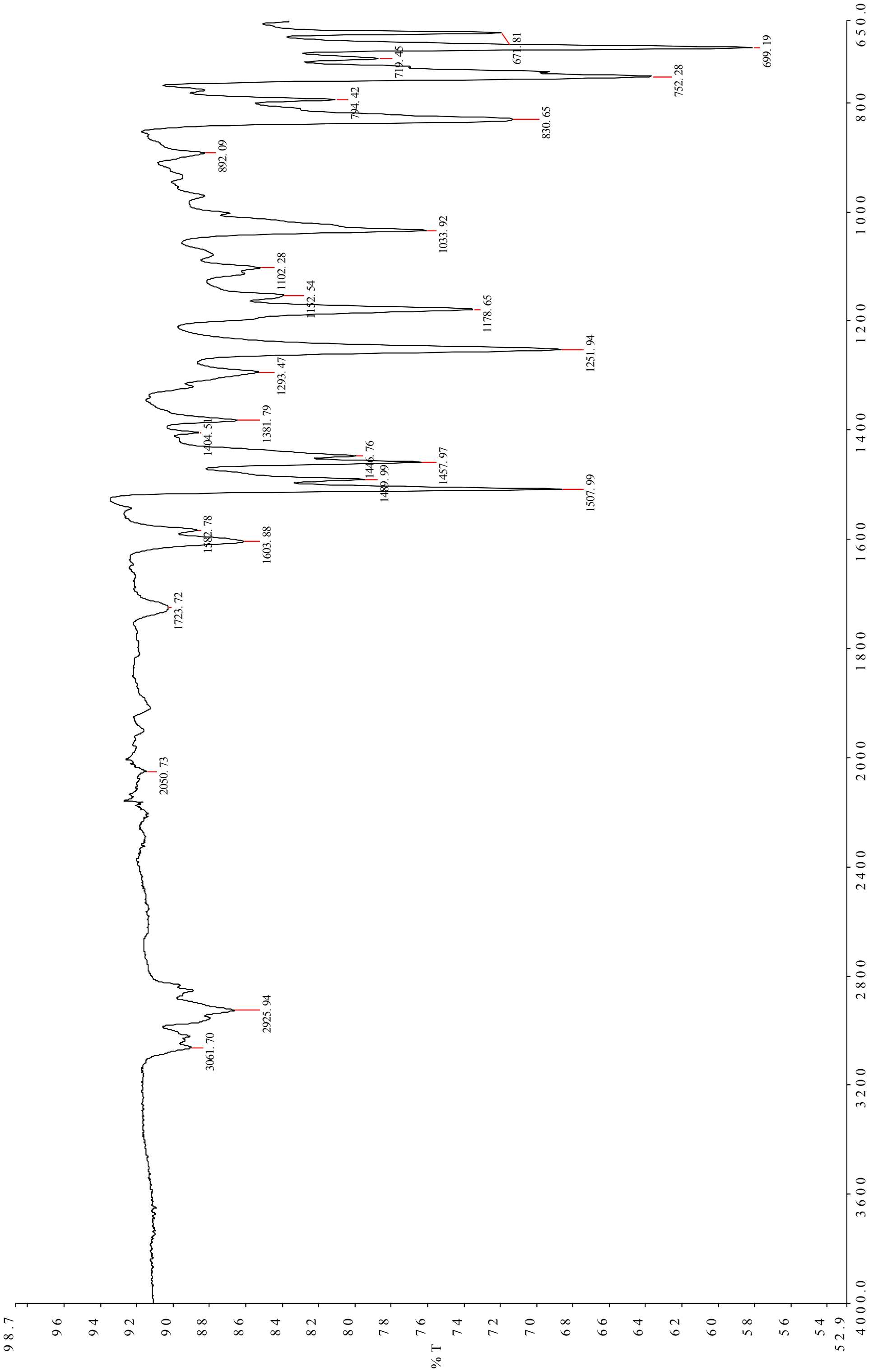


Figure 4.47 *Bis(p-(2-(4-(3-(4-methoxyphenyl)-3,3-diphenyl)propynyl)-d8-p-phenylene)ethynylene pentiptycene IR*

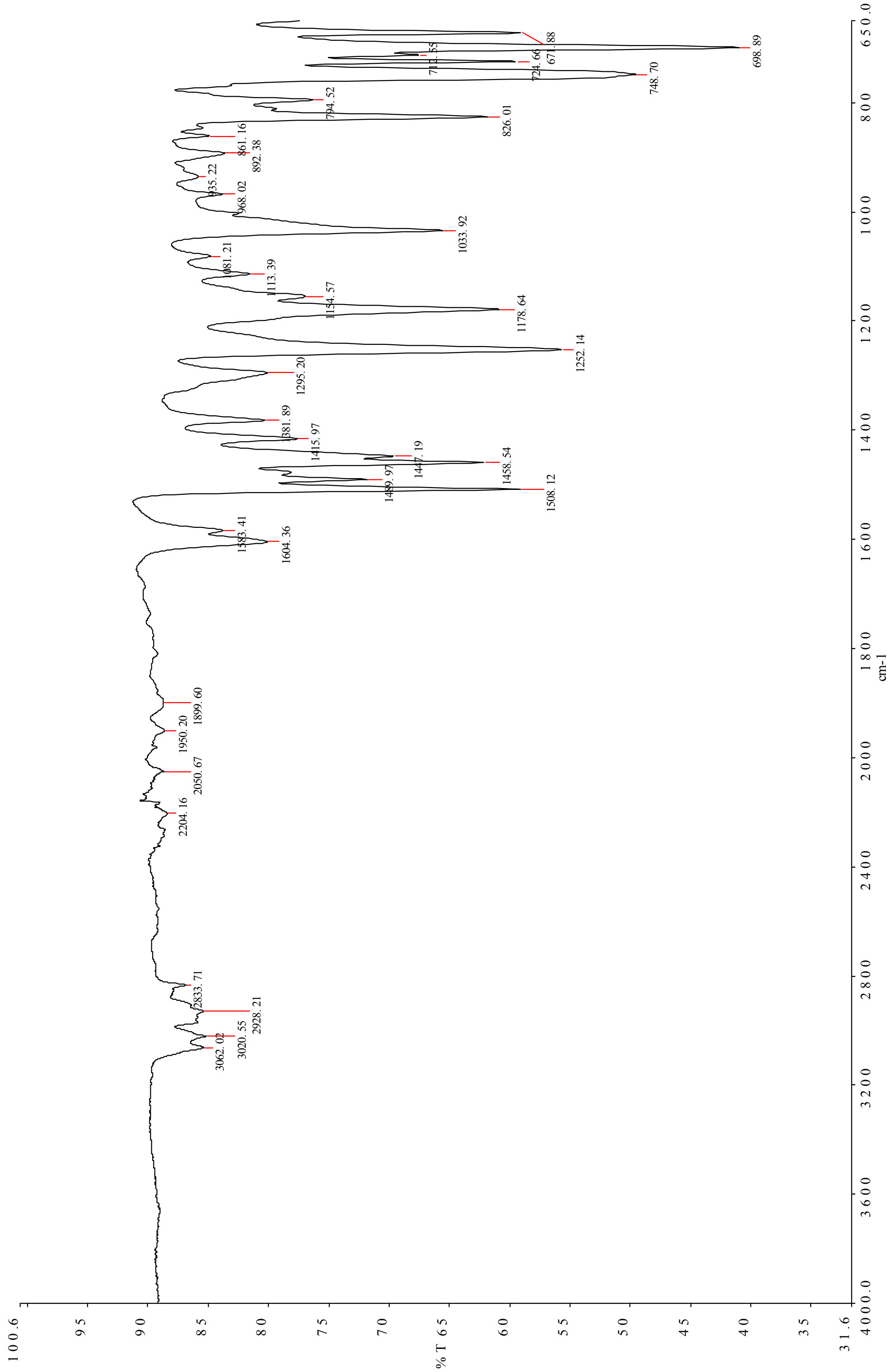


Figure 4.48 *1-(4-iodophenyl)-3,3,3-tri(3-methoxyphenyl)propyne IR*

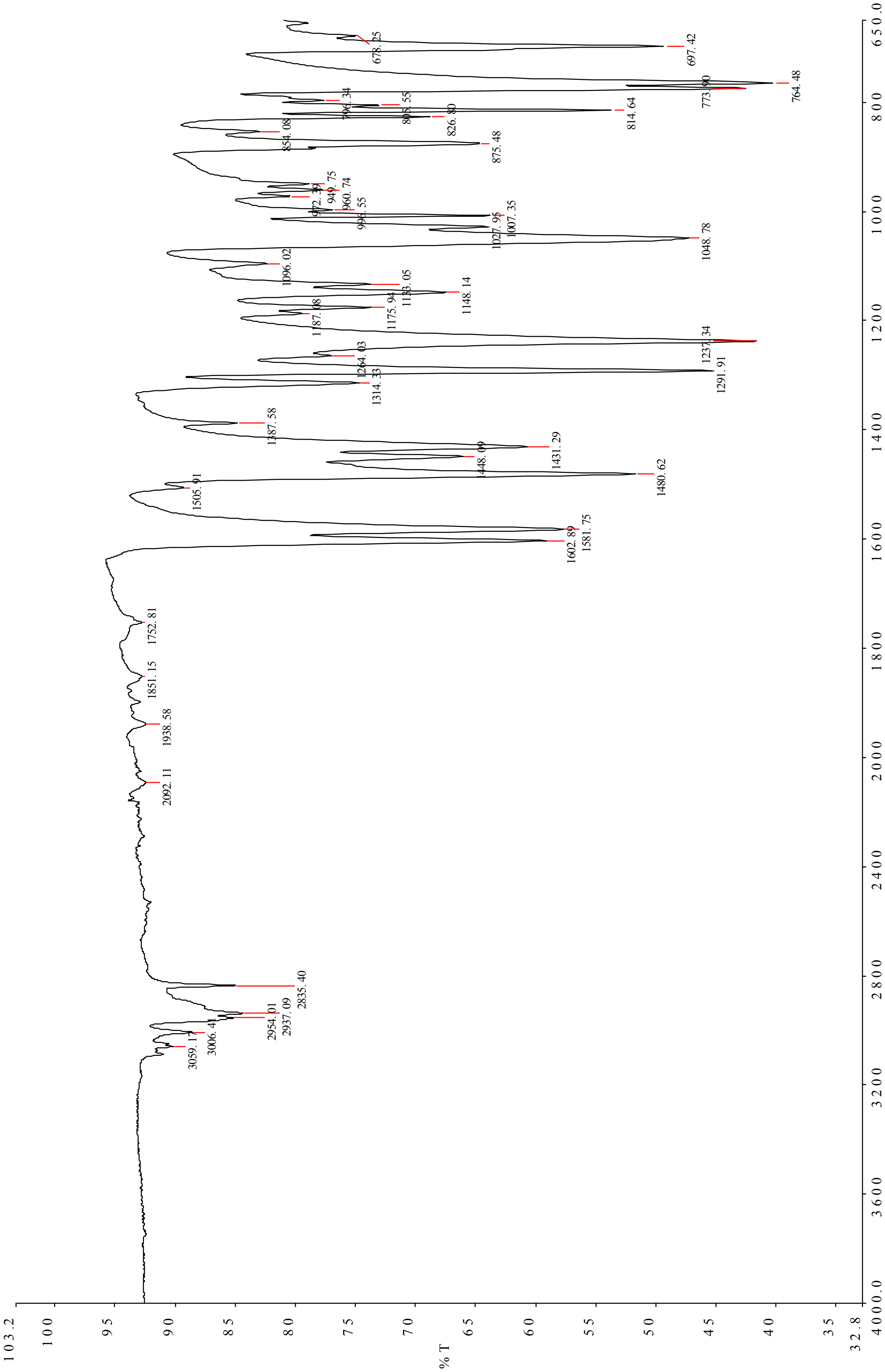


Figure 4.49 *Bis(p-(2-(4-3,3,3-triphenylpropynyl)-p-naphthylene)ethynylene pentiptycene IR*

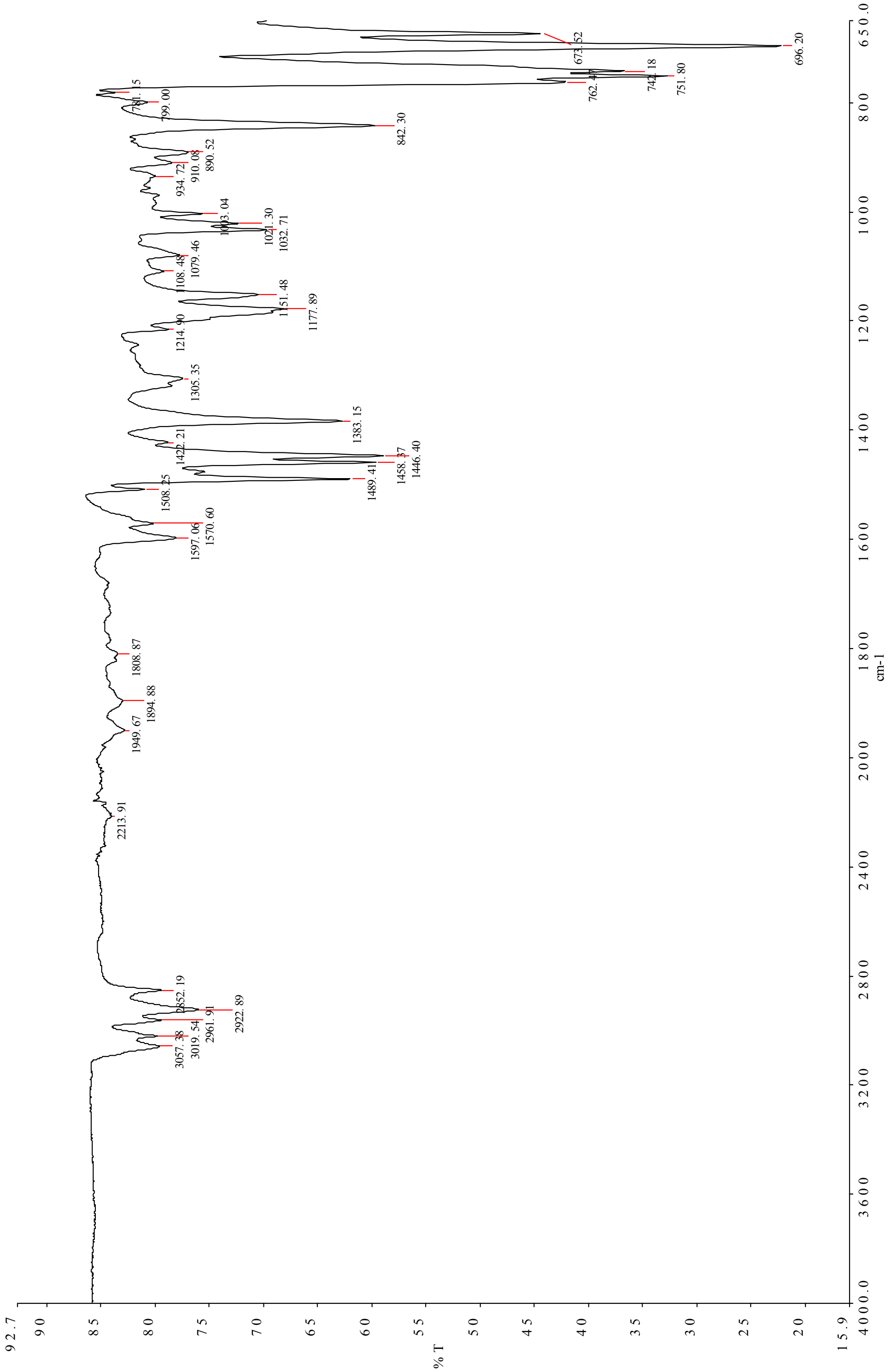


Figure 4.50 *6,13-bis((trimethylsilyl)ethynyl)-5,6,7,12,13,14-hexahydro-5,14:7,12-bis([1,2]benzene)pentacene-6,13-diol IR*

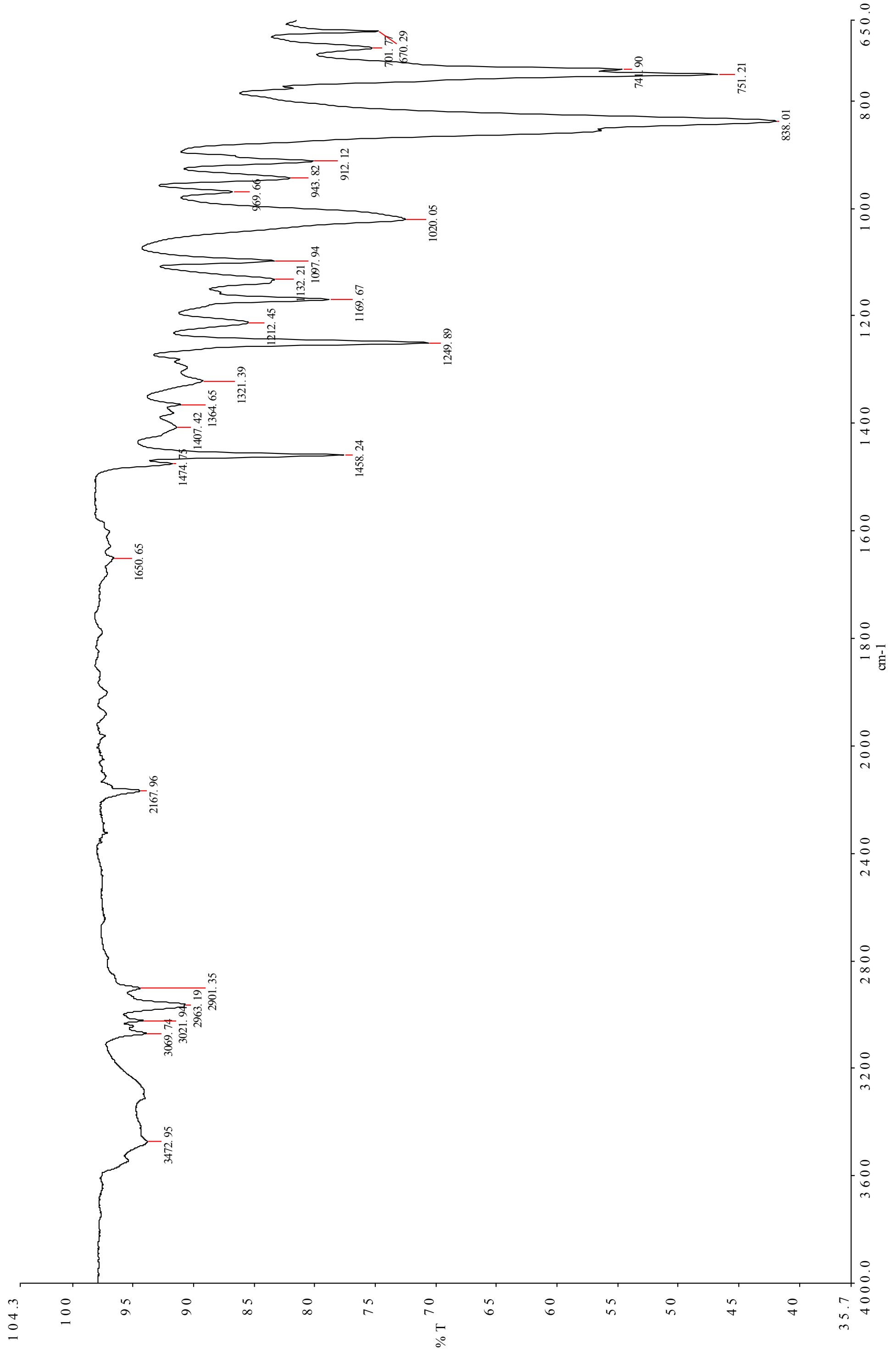


Figure 4.51 *5,6,7,12,13,14-Hexahydro-5,14:7,12-bis(o-benzeno)pentacene-6,13-dione IR*

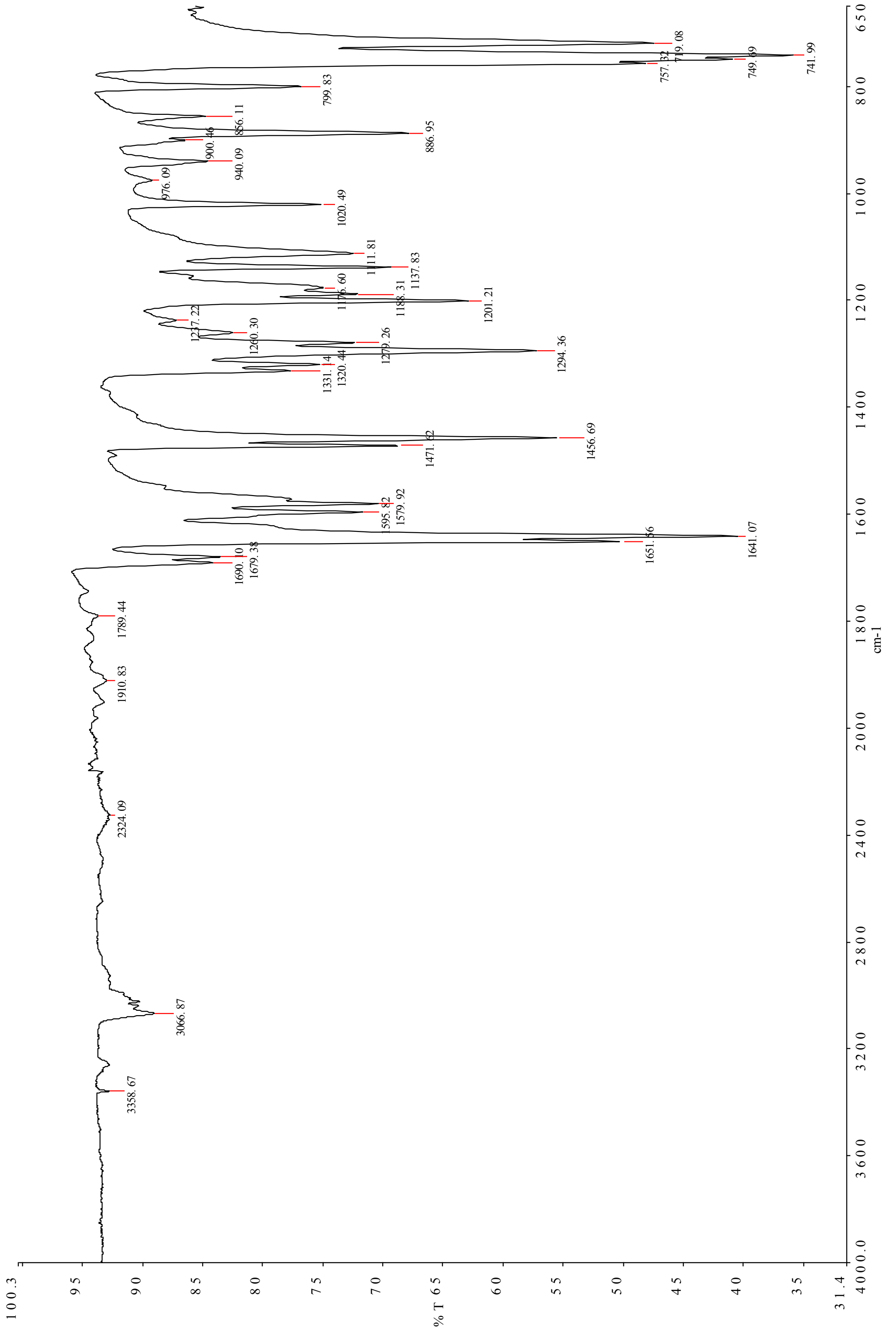
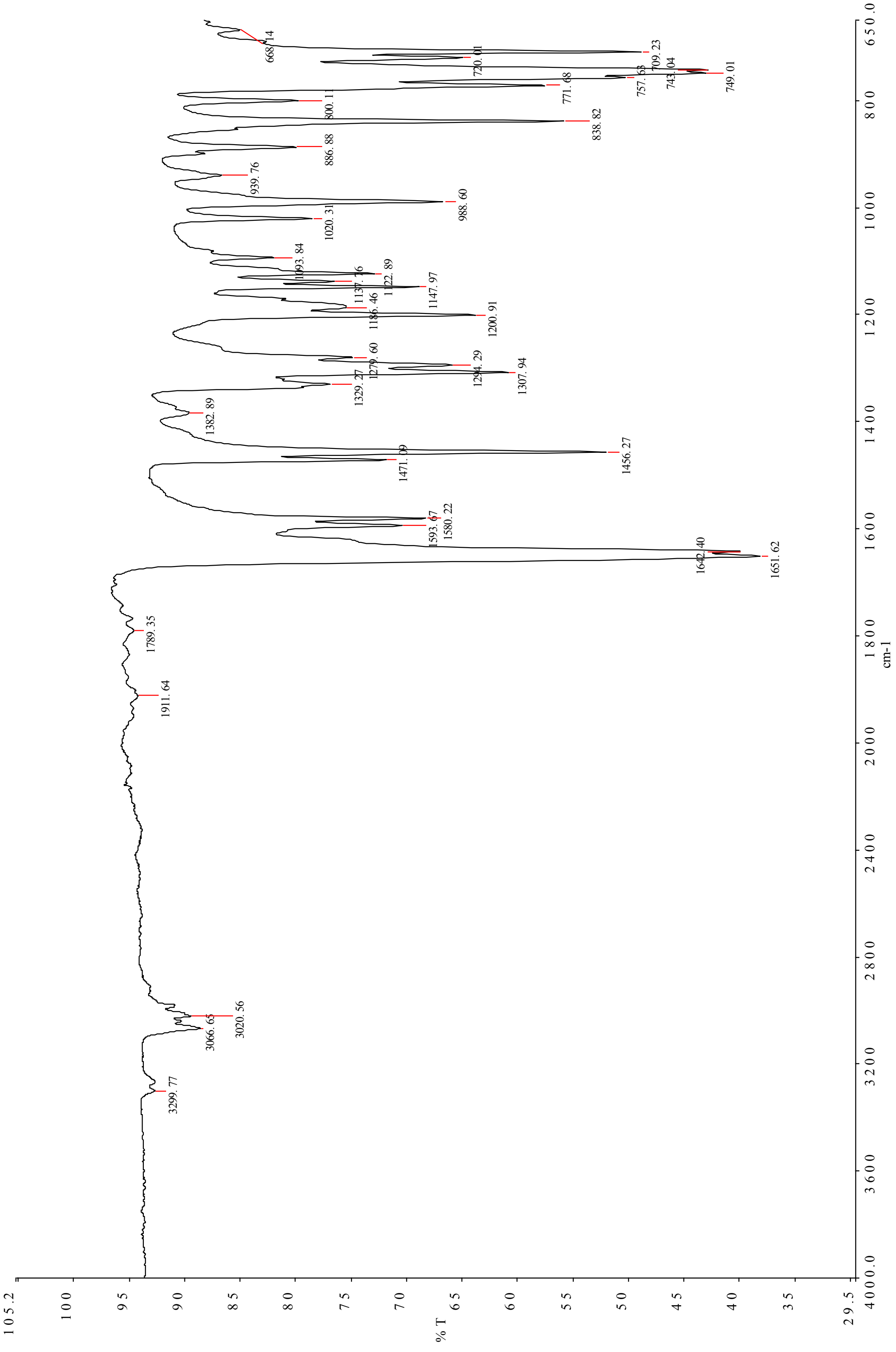


Figure 4.52 *9,10-Dihydro-9,10-o-benzenoanthracene-1,4-dione IR*



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